博 士 学 位 論 文

アザローダサイクル中間体を経由する環化反応の開発

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序論

医薬品の開発のためには、候補化合物が優れた薬理活性を示すだけでなく、薬としてふさわしい性質、いわゆる drug-likeness を有することが求められる。すなわち、(i) 水溶性と膜透過性を両立し良好な bioavailability を示すこと、(ii) 化学的・代謝的に安定で良好な体内動態を示すこと、(iii) 毒性が薬効と比較して軽微で優れた忍容性を示すことは候補化合物に求められる極めて重要な性質である。

低分子化合物の drug-likeness に関する経験則として、rule of five が 1997 年に Lipinski らによって提唱された [1]。rule of five は分子量・水素結合受容体および供与体の数・脂溶性といった化合物の物理化学的性質を drug-likeness の指標として用いるものであり、その有用性と簡便さから現在の創薬研究において広く受け入れられている。この rule of five が提唱されて以降、化合物の物性パラメーターの重要性が広く認識され、polar surface area や rotatable bond 数など様々なパラメーターが相次いで報告されている [2]。

こうした中、近年着目されている指標の一つに、2009 年に Lovering らによって提唱された Fsp^3 がある [3]。Fsp^3 は化合物の全炭素数に占める sp^3 炭素数の割合として定義され、分子の三次元的な複雑さを表す。Fsp^3 が大きくなるにつれて水溶性が向上することや off-target の作用が減少すること、また上市品は研究段階の化合物に比べて高い Fsp^3 値を有することが報告されている。飽和結合に富んだ化合物は三次元的に広がった複雑な構造を有するため、平面的な分子に比べて広い chemical space を利用できる。その結果、分子量の大幅な増大を伴うことなく、標的分子とより特異的かつ強固に相互作用する可能性が示唆される [4]。

一方、近年の低分子創薬においては、平面的な構造である芳香環が多用されている [5]。鈴木-宮浦反応や Buchwald-Hartwig 反応などのカップリング反応が目覚しい発展を遂げ、多検体合成に広く用いられていることがその一因として挙げられる。医薬品開発の競争が激化し、新規合成手法を開発するための時間およびリソースが限られている現状では、汎用性が高く原料の入手が容易なカップリング反応は短期間で多数の化合物の合成を可能にするため、初期の探索段階では特に魅力的である。このことは、sp^3 炭素に富んだ化合物の利点が指摘されているにも関わらず、平面的な芳香環が創薬研究に広く用いられる要因となっている。

このような背景から、飽和結合に富んだ三次元的な化合物を効率的に合成する手法の開発が強く望まれている。平面的な骨格に立体的な側鎖を導入する手法では、骨格の平面性に由来するデメリットを克服できないことが多いため、骨格そのものを sp^3 炭素に富んだものにすることの重要性が特に指摘されている [3b]。そこで、筆者は博士後期課程において、比較的単純な構造の鎖状化合物から三次元的な骨格を一挙に構築する反応の開発に取り組むことにした。特に、創薬への応用という観点から、医薬品のリード化合物となりうる含窒素環状化合物の構築を指向して、新規環化反応の開発研究に着手した。

本論

第一章　Rh(I)触媒によるアルキン、アレンおよびイミン間での分子内[2+2+2]環化付加反応

第一節　研究の背景

[2+2+2]環化付加反応は三つの多重結合から六員環を含む多環式骨格を一挙に構築することが可能な原子効率の高い反応であることから、有機合成化学において重要な反応の一つである(Scheme 1)[6]。現在までに、分子間反応から分子内反応に至るまで様々な形式の[2+2+2]環化付加反応が報告されており、その有用性の高さから生物活性化合物の合成に広く利用されている(Figure 1)[7]。

Scheme 1

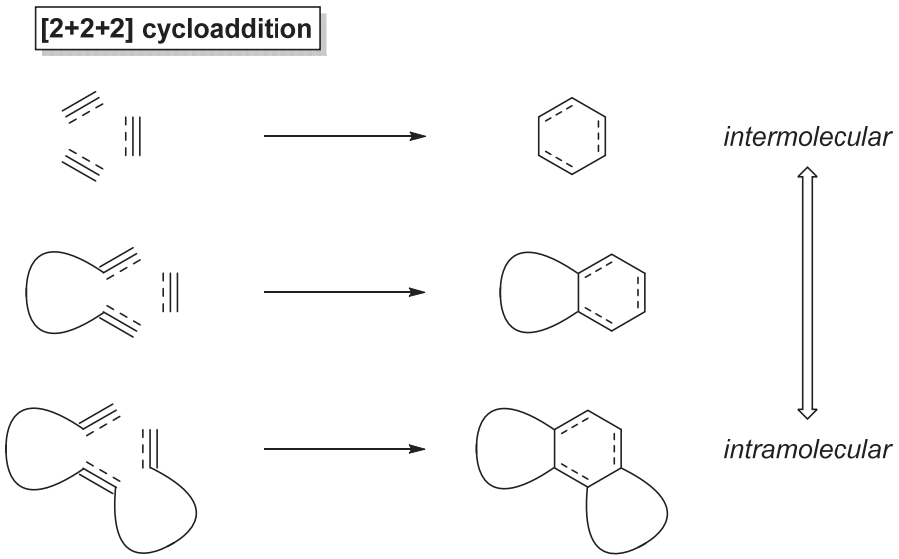


Figure 1

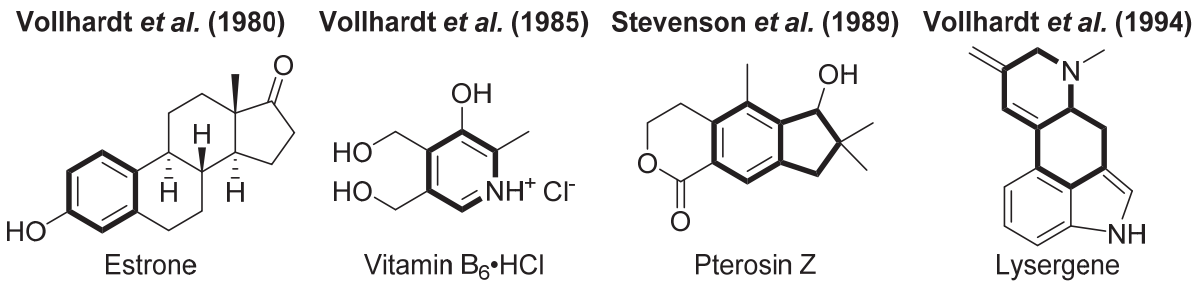
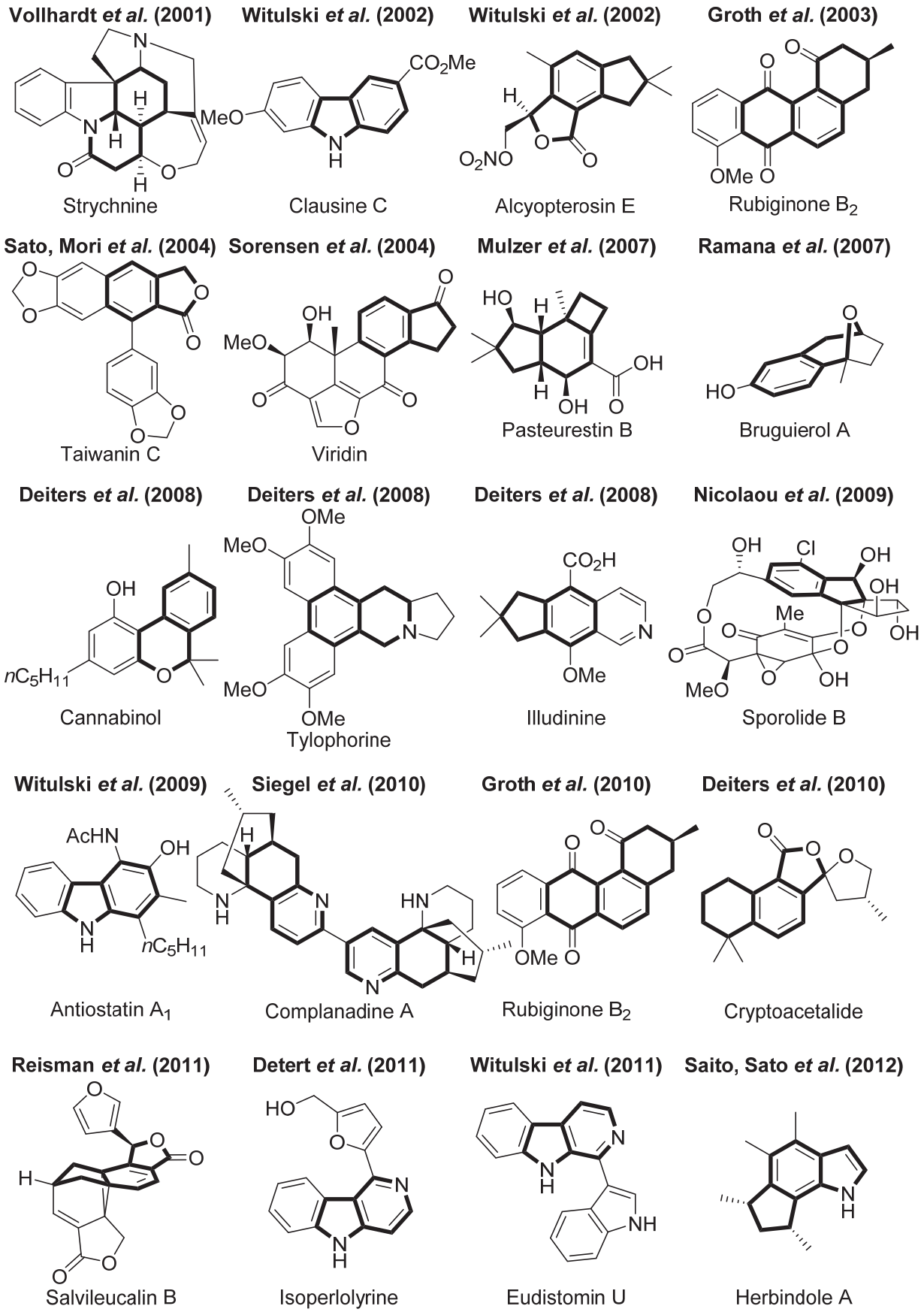


Figure 1 (continued)

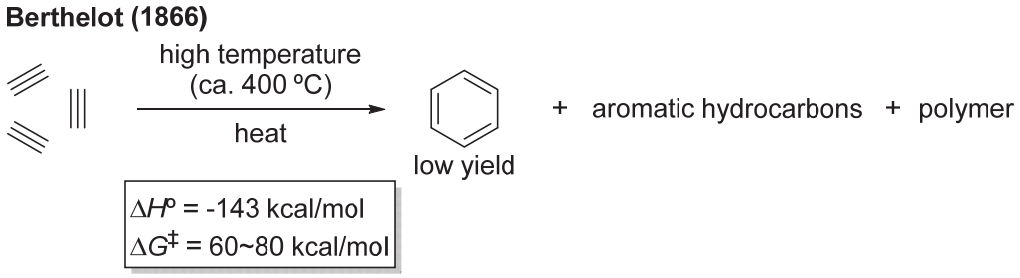


Selected Examples of Total Synthesis Utilizing [2+2+2] Cycloaddition

The rings constructed by [2+2+2] cycloaddition are highlighted.

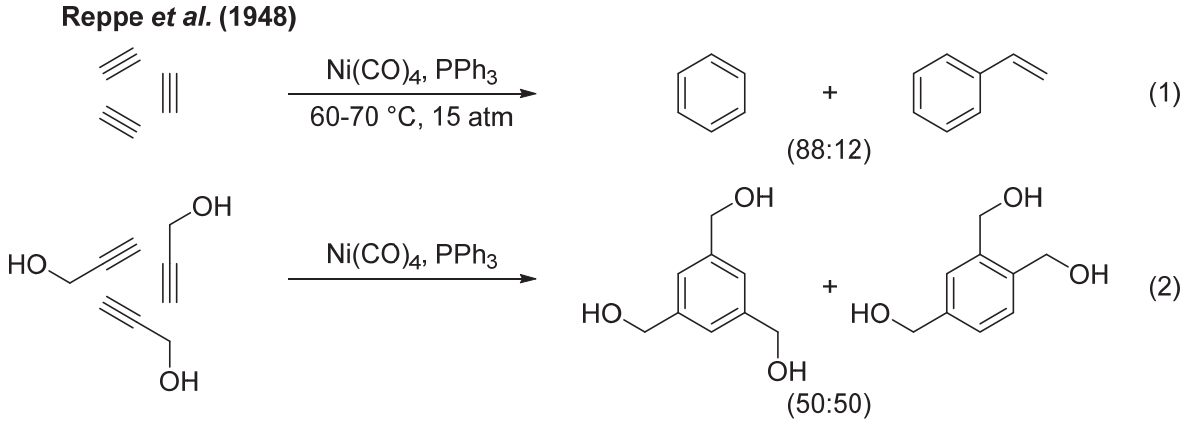
この[2+2+2]環化付加反応の初めての例として、1866 年に Berthelot は、アセチレンガスを加熱することでベンゼンが生成することを見出した (Scheme 2)[8]。アセチレンの 3 量化によりベンゼンが生成する過程は極めて発熱的であり[9,10]、Woodward-Hoffmann 則において熱的許容であるにも関わらず[11]、反応の進行には 400 °C を超える高温が必要であった。その結果、多くの副反応が進行することとなり、ベンゼンは様々な芳香族炭化水素やポリマーとのタール状混合物として低収率で得られるのみであった[12]。

Scheme 2



これに対して、Reppe らは 1948 年に、ニッケル錯体およびリン配位子を用いることでアセチレンの 3 量化反応が温和な条件下で進行し、ベンゼンがスチレンとともに生成することを見出した (Scheme 3, eq. 1)[13]。これは遷移金属錯体が[2+2+2]環化付加反応に有効であることを示した初めての報告である。また、彼らは一置換アルキンを同じくニッケル触媒と反応させることで、1,3,5-および 1,2,4-三置換ベンゼンの混合物が得られることも報告している (eq. 2)。この発見は Friedel-Crafts 反応などによりあらかじめ存在しているベンゼン環を誘導化する方法とは異なるアプローチで、多置換ベンゼンが合成可能であることを示すものであった。

Scheme 3



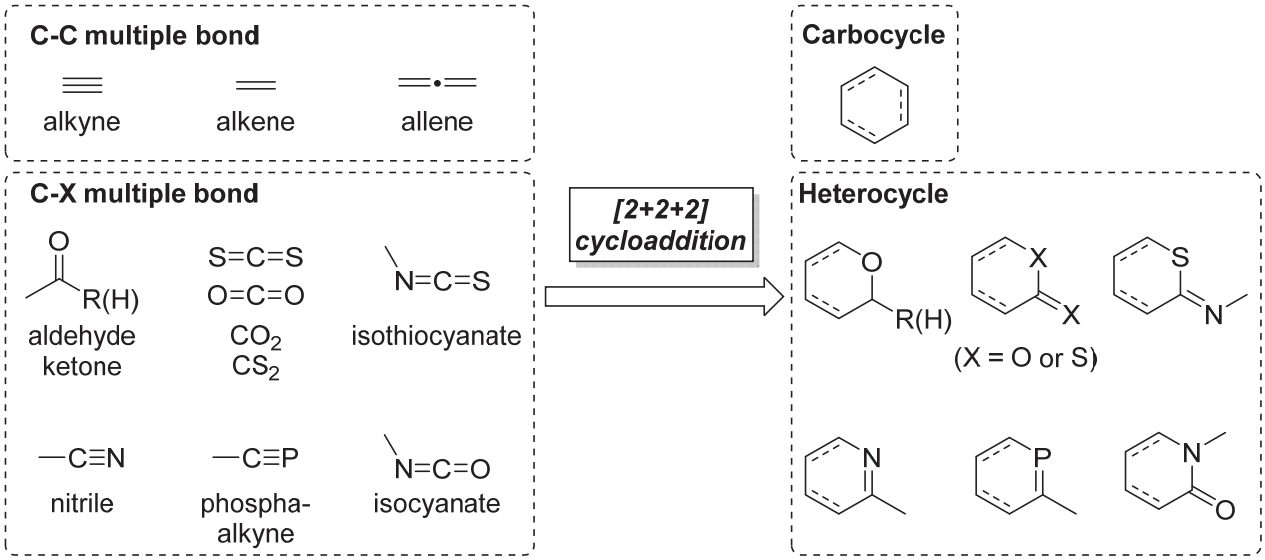
この報告を契機として、遷移金属錯体を用いる[2+2+2]環化付加反応が活発に研究され、Ru、Co、Rh、Ni、Pdなどの8~10族の金属を中心に多種多様な遷移金属錯体が有効であることが報告されてきた。

これと並行して、様々な多重結合を本反応に用いる試みも行われてきた (Scheme 4)。その結果、アルキンの他にもアルケンやアレンといった炭素-炭素多重結合が[2+2+2]環化付加反応に利用可能であることが示され、種々の炭素環化合物の合成が達成されてきた。

一方、炭素-ヘテロ原子不飽和結合を多重結合の一つとして用いることができれば、複素環化合物の合成が可能となる。これまでに、炭素-酸素、炭素-硫黄、炭素-窒素および炭素-リンなど様々な炭素-ヘテロ原子多重結合を用いる反応が報告されてきた。

なかでも、炭素-窒素多重結合を用いる[2+2+2]環化付加反応は、天然物や医薬品に広く存在し顕著な生物活性を示す含窒素複素環化合物の効率的な合成に資する可能性があるため、学術と応用の両面から極めて重要である。

Scheme 4

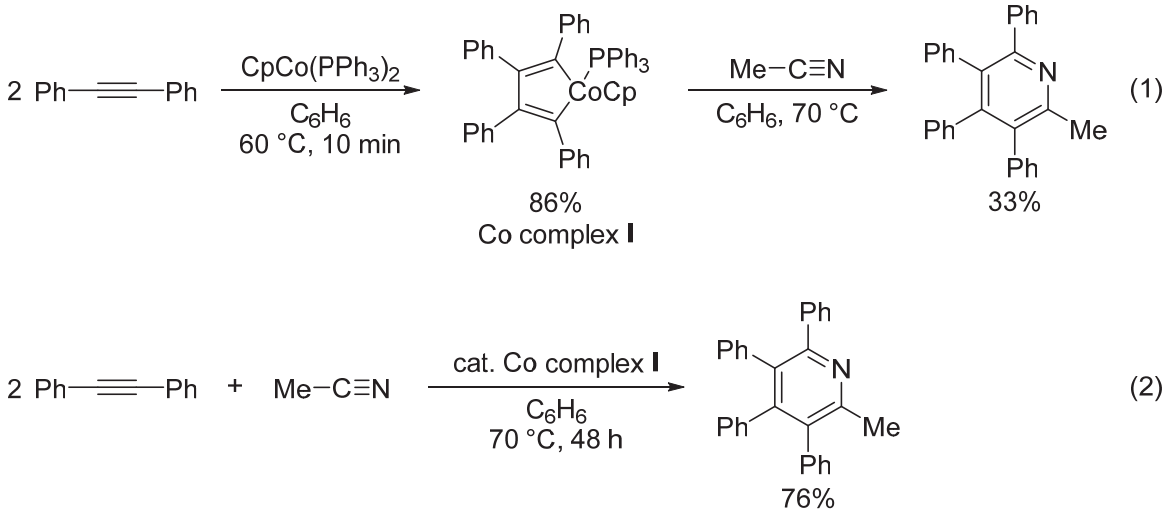


炭素-窒素多重結合を用いる初めての[2+2+2]環化付加反応として、1973 年に山崎らは、$CpCo(PPh_3)_2$錯体を用いることで2分子のアルキンと1分子のニトリルからピリジン誘導体が合成できることを報告した (Scheme 5, eq. 1)[14]。彼らはまた、コバルタシクロペンタジエン錯体 (Co complex **I**) を用いると反応が触媒的に進行することも見出した (eq. 2)。本反応は温和な条件下で進行し、様々なニトリル RCN (R = alkyl, aryl, vinyl) から比較的良好な収率でピリジン誘導体

を与える。

Scheme 5

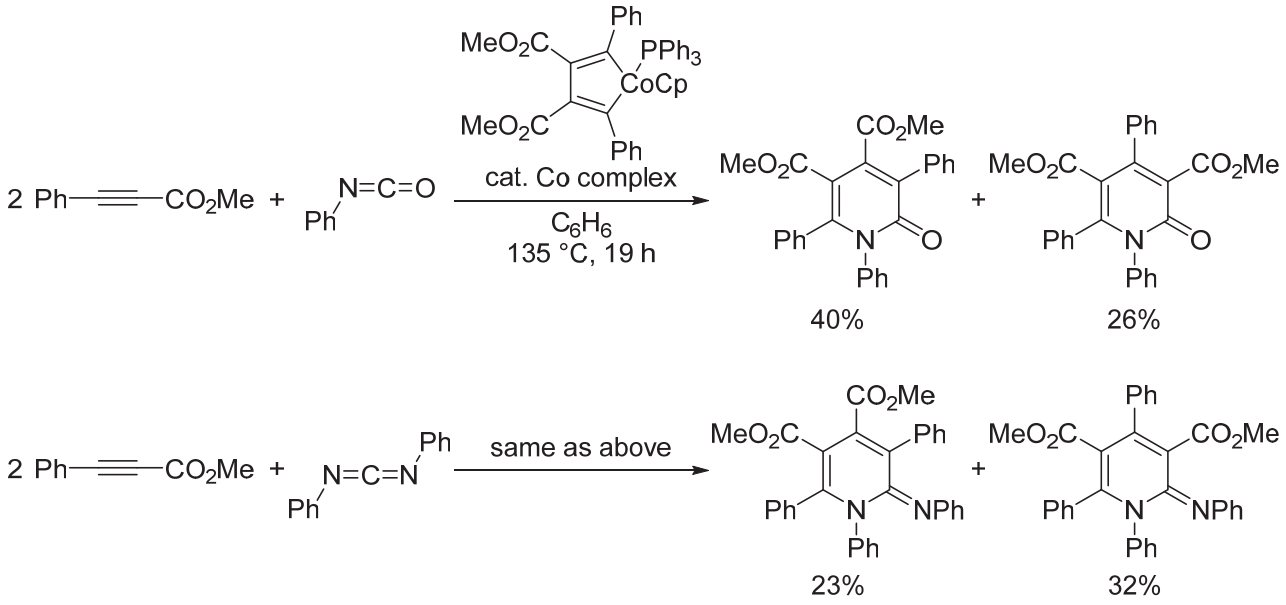
Yamazaki *et al.* (1973)



また、1977 年に同じく山崎らは、イソシアナートおよびカルボジイミドをそれぞれアルキンと反応させることにより、ピリドンおよびイミノピリジン誘導体が生成することを報告した (Scheme 6)[15]。これは、[2+2+2]環化付加反応に炭素-窒素二重結合が利用可能であることを示した初めての報告である。

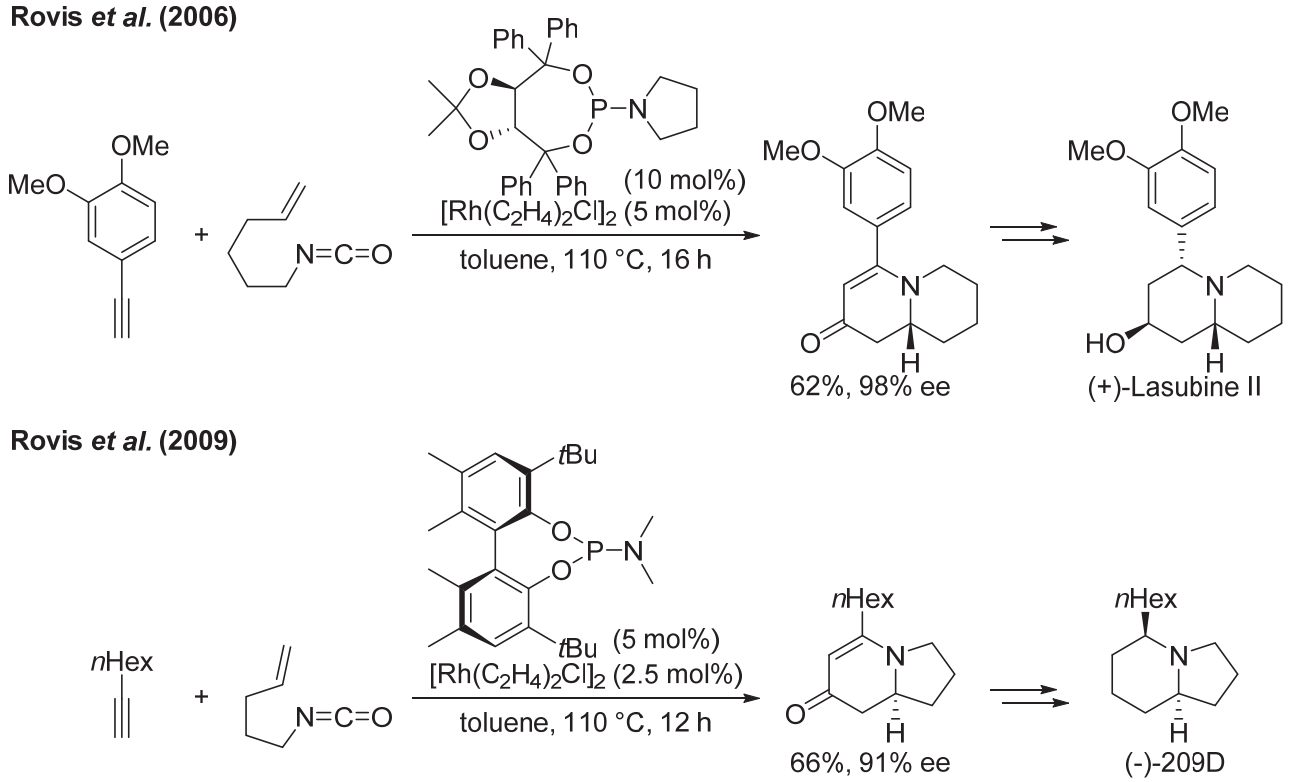
Scheme 6

Yamazaki *et al.* (1977)



これらの報告以降、ニトリルおよびイソシアナートを用いる環化付加反応が多数報告され、天然物の全合成においてもその威力を発揮してきた。例えば、最近 Rovis らは、イソシアナートとアルキンを光学活性な配位子および Rh(I)触媒存在下で反応させると、カルボニル基の転位を伴う[2+2+2]環化付加反応が進行し、キノリジノン骨格およびインドリジノン骨格が高エナンチオ選択的に構築できることを報告した (Scheme 7)[7ak,7al]。彼らは本反応を利用した(+)-Lasubine II および(-)-209D の効率的な全合成を相次いで達成している。

Scheme 7

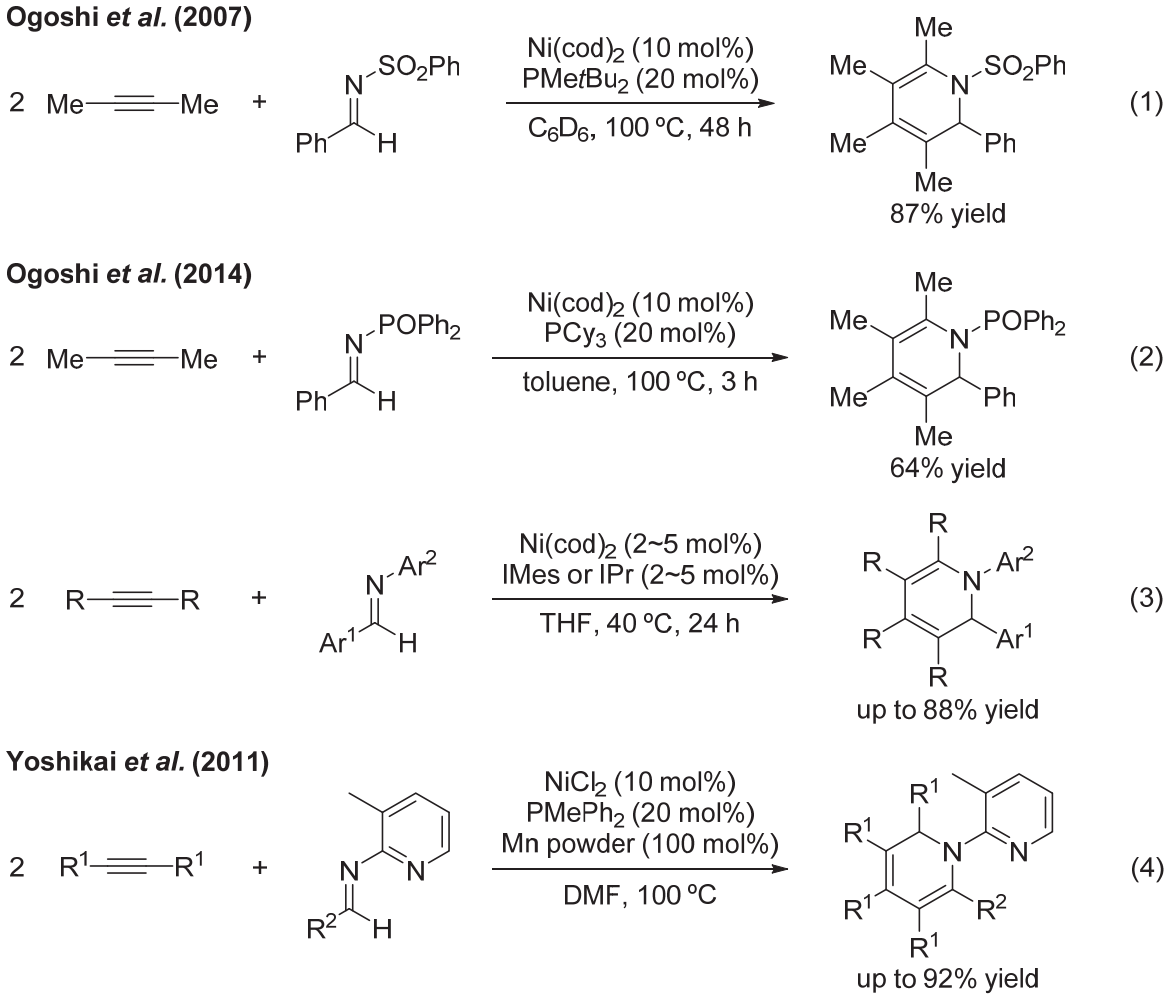


このように、炭素-窒素三重結合を有するニトリル、並びに活性化された炭素-窒素二重結合を有するイソシアナートやカルボジイミドを用いる[2+2+2]環化付加反応は古くから報告され、多くの研究が蓄積されてきた。しかしながら、炭素-窒素二重結合を有する最も基本的な化合物群であるイミンに関しては[2+2+2]環化付加反応への適用例が極めて少なく、これまでに分子間反応が数例報告されるのみである (Scheme 8)。

例えば、2007 年生越らは、Ni 触媒存在下、2 分子のアルキンとベンゼンスルホニルイミンとの反応により、ジヒドロピリジン誘導体が生成することを報告した (eq. 1)[16a,16b]。彼らはその後、PCy_3 や NHC 配位子を用いることにより、基質としてジフェニルホスフィノイルイミンおよびアリールイミンが

利用可能であることを見出した (eq. 2 and 3)[16c]。また、吉戒らは同じく Ni 触媒存在下、2-アミノ-3-ピコリンから合成されるイミンと 2 分子のアルキンとの[2+2+2]環化付加反応を報告している (eq. 4)[16d]。

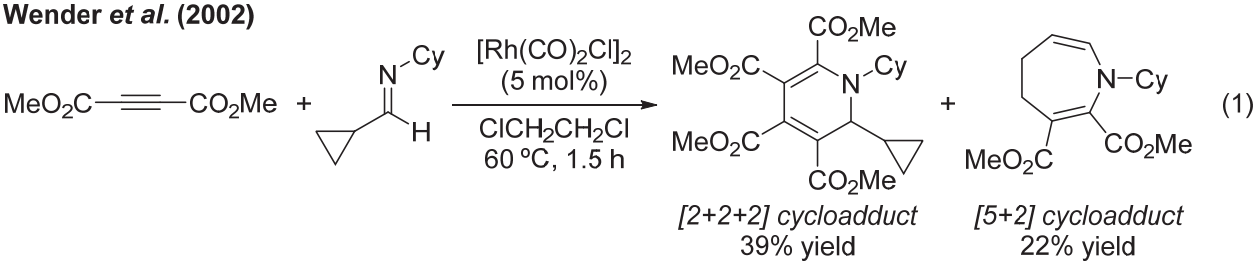
Scheme 8



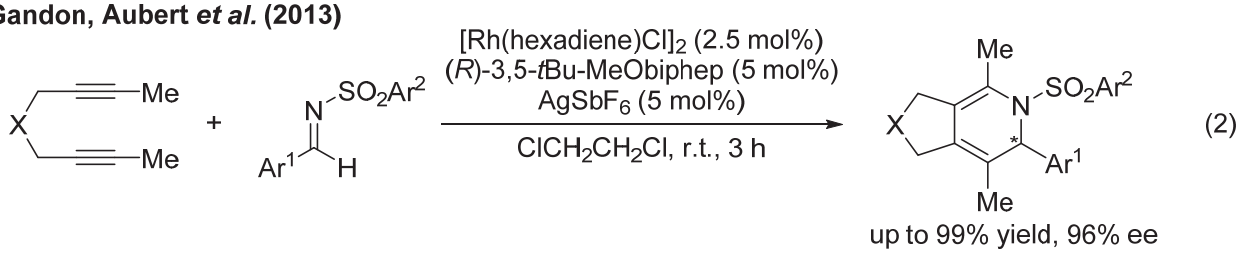
一方、Rh 触媒による反応例も少数ながら存在する (Scheme 9)。2002 年に Wender らは、Rh(I)触媒存在下、アセチレンジカルボン酸ジメチル (DMAD) とシクロプロピルイミンとを反応させると、2 分子の DMAD と 1 分子のイミンから生成する[2+2+2]環化付加体が[5+2]環化付加体とともに得られることを見出し報告した (eq. 1)[17a]。また、2013 年に Gandon、Aubert らは、光学活性な BIPHEP 配位子を用いることにより、ジインとスルホニルイミンとの[2+2+2]環化付加反応がエナンチオ選択的に進行することを見出した (eq. 2)[17b]。最近になって、Rh(III)触媒による末端アルキンと *N*-スルホニルケチミンとの[2+2+2]環化付加反応が報告された (eq. 3)[18]。

Scheme 9

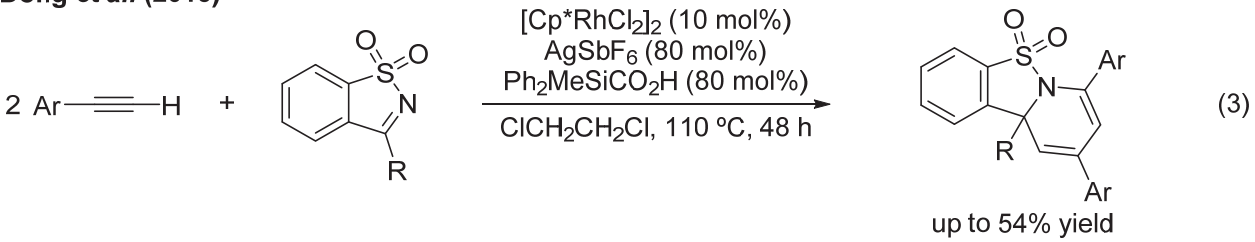
Wender *et al.* (2002)



Gandon, Aubert *et al.* (2013)



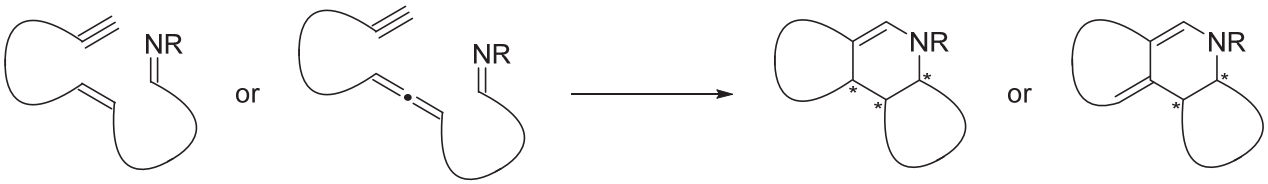
Dong *et al.* (2015)



現在のところ、イミンを多重結合の一つとして用いる[2+2+2]環化付加反応はこれら六例のみである。いずれもアルキンとの分子間反応であり、分子内反応は報告されていない。

このような背景から筆者は、立体的な含窒素環状化合物の合成を指向して、イミンを用いる分子内[2+2+2]環化付加反応の開発に取り組むことにした。この際、イミンと反応させる多重結合として、これまで用いられてきたアルキンの代わりにアルケンやアレンを利用することができれば、より sp^3 炭素に富んだ多環式骨格が構築可能になるものと考えられる (Scheme 10)。

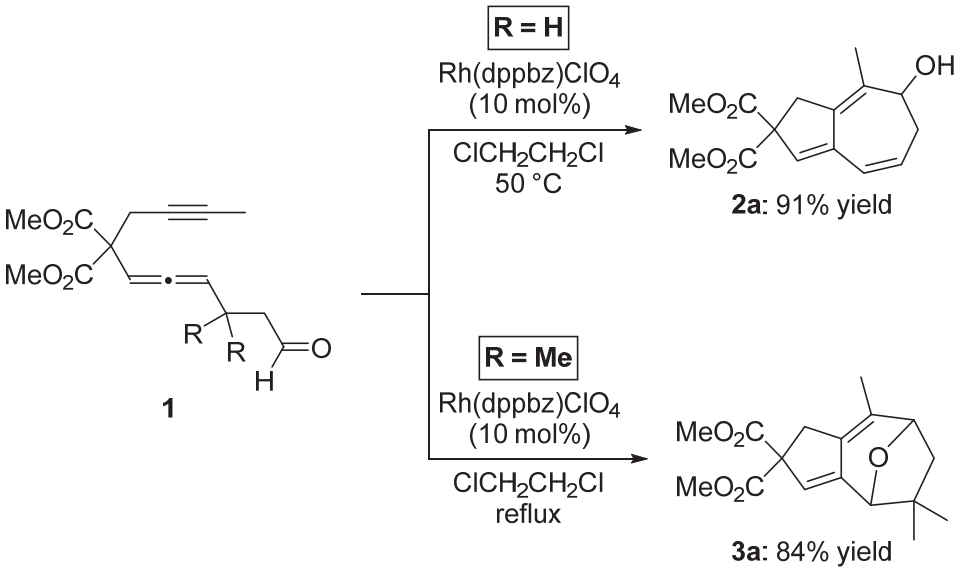
Scheme 10



Intramolecular [2+2+2] Cycloaddition using an imine and C-C double bonds

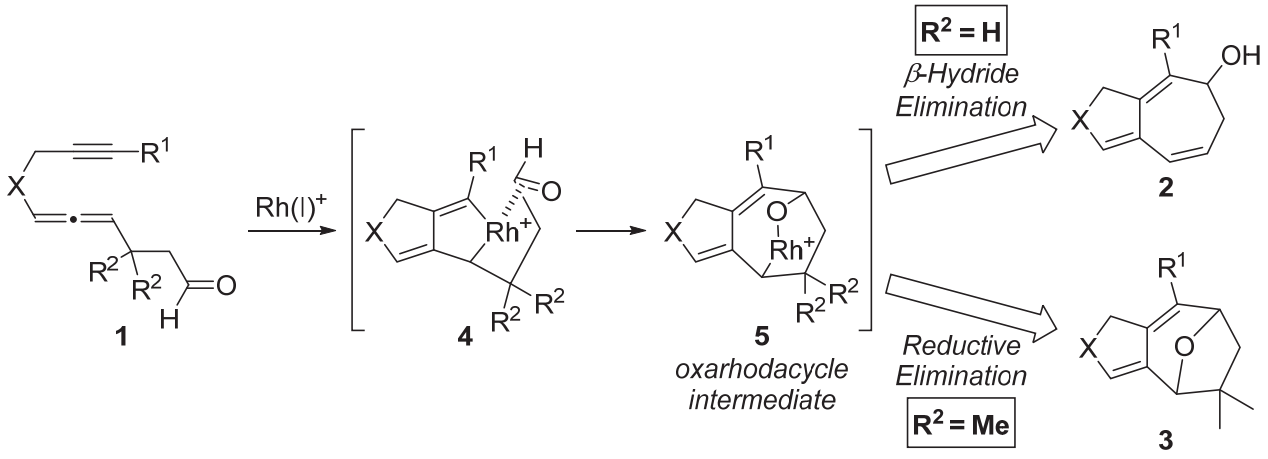
ところで、当研究室では、分子内にカルボニル基を有するアレン-イン **1** と Rh(I)錯体との分子内[2+2+2]環化付加反応により、bicyclo[5.3.0]decane 骨格を有する二環式アルコール **2a** および 8-oxabicyclo[3.2.1]octane 骨格を有する環化体 **3a** が得られることを見出し報告している (Scheme 11)[19]。

Scheme 11



これらの環化体は次のような反応機構で生成していると考えられる (Scheme 12)。基質 **1** のアルキンとアレンが Rh(I)錯体に酸化的環化付加し、ローダシクロペンテン中間体 **4** が生成する。続いて、この中間体 **4** の $C(sp^2)$-Rh 結合に側鎖のカルボニル基が挿入し、オキサローダサイクル中間体 **5** が形成される。この中間体 **5** の R^2 が水素原子の場合には β-水素脱離が進行し、還元的脱離を経て二環式アルコール **2** を与える。一方、R^2 がメチル基の場合は中間体 **5** から還元的脱離が進行し環化体 **3** を与える。

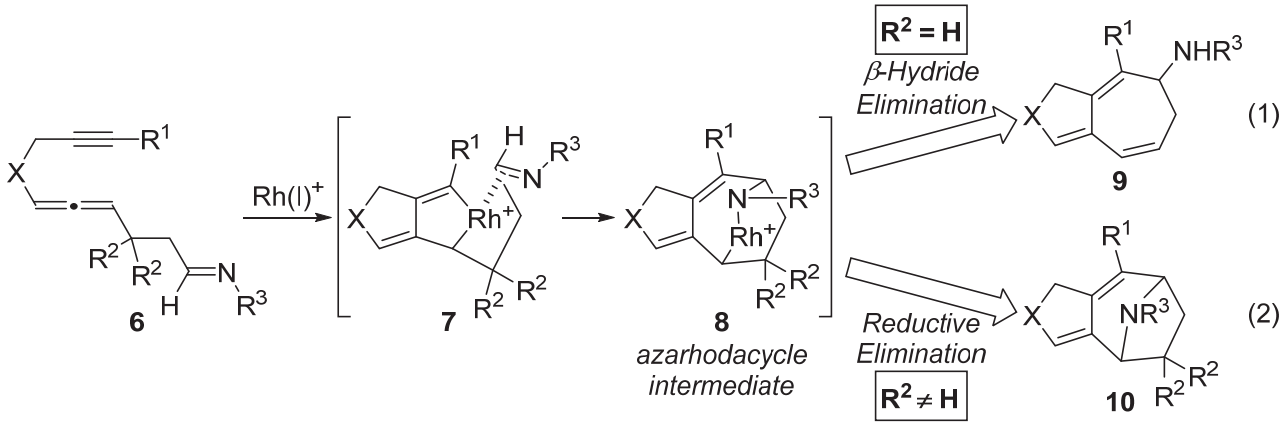
Scheme 12



すなわち、本反応では基質の構造によって反応経路が制御され、特徴的な二種類の環構造が構築される。また、ロータシクロペンテン中間体 **4** に側鎖のカルボニル基が挿入する際、非常にひずんだ構造となるにも関わらず C(sp^2)-Rh 結合で選択的に挿入反応が進行することから、反応機構の観点からも興味が持たれる*[1]。

そこで筆者は、カルボニル基の代わりにイミンを有する基質 **6** を用いて、同様の反応が進行する可能性を検討することにした (Scheme 13)。もし、本反応がイミン **6** を用いても進行するならば、アザローダサイクル中間体 **8** を経由して、bicyclo[5.3.0]decane 骨格を有する二環式アミン **9** および 8-azabicyclo[3.2.1]octane 骨格を有する環化体 **10** が生成するものと期待される。

Scheme 13

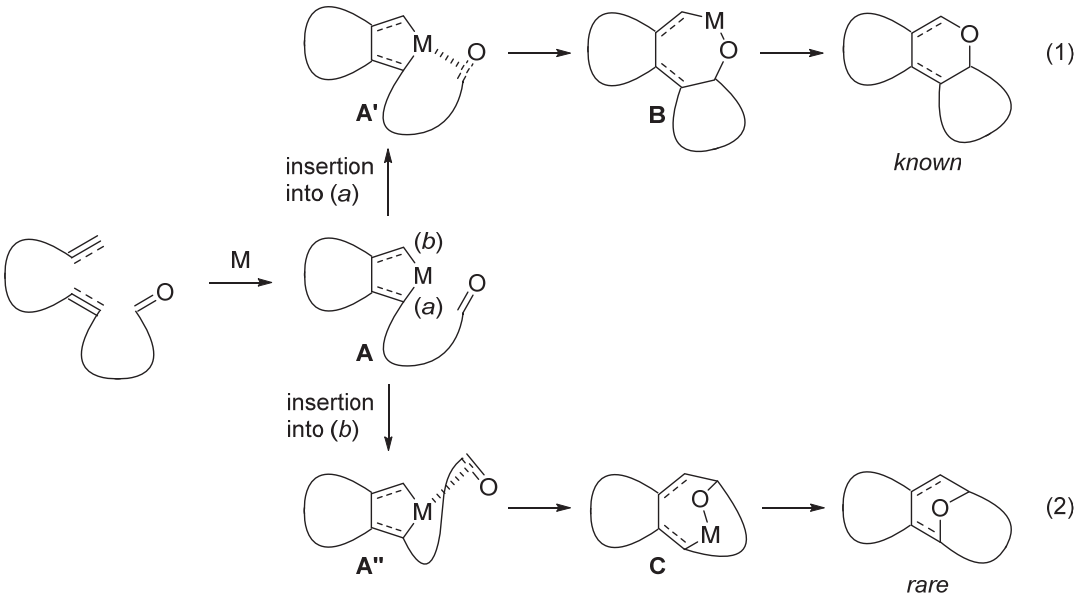


第二節で、アザローダサイクル中間体 **8** からの β-水素脱離を経由して二環式アミン **9** を与える反応について、続く第三節で、中間体 **8** からの還元的脱離により環化体 **10** を与える反応について詳細を報告する。

****

*[1] 一般に、二つの炭素-炭素多重結合と遷移金属錯体から形成される五員環メタラサイクル中間体 **A** に側鎖のカルボニル基が挿入する場合、C-M 結合 (*a*) と C-M 結合 (*b*) の二通りの挿入位置が考えられる (Scheme 14)。

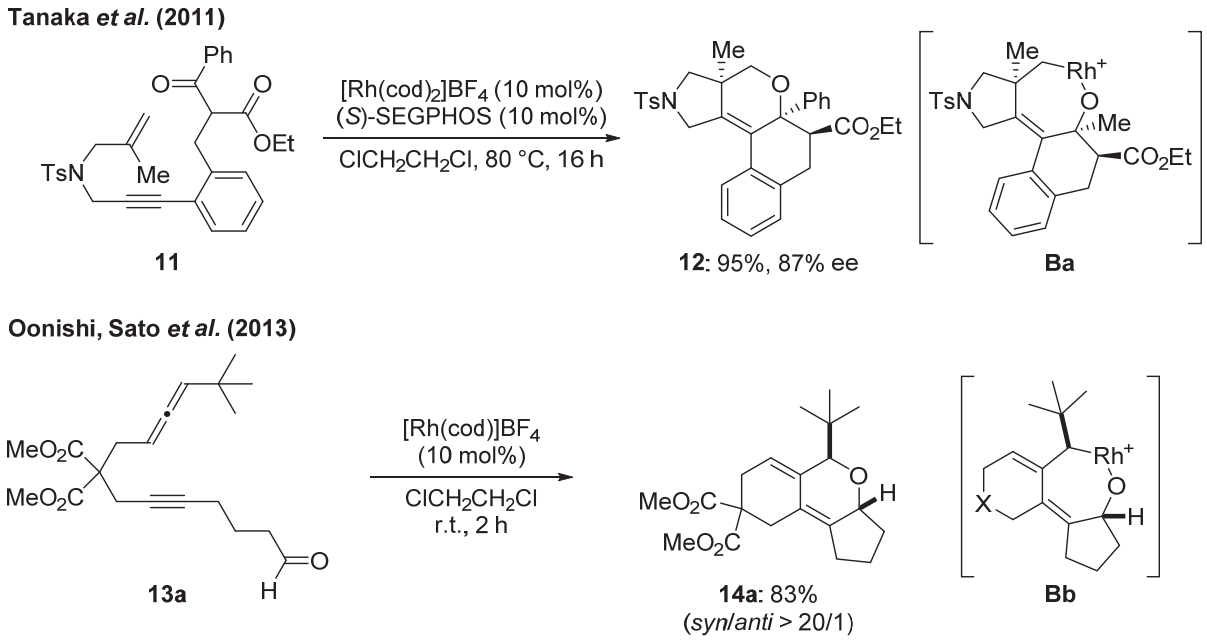
Scheme 14



C-M 結合 (*a*) で挿入反応が進行し、七員環オキサメタラサイクル中間体 **B** を経由する形式の反応は以下の二例が知られている (Scheme 15)。

2011 年に田中らは、カルボニル基を分子内に有する基質 **11** と光学活性な Rh(I)錯体との反応がオキサローダサイクル中間体 **Ba** を経由して進行し、ジヒドロピラン誘導体 **12** が良好な収率かつ高立体選択的に生成することを見出した [20a]。また、当研究室においても、アレン、アルキンおよびアルデヒド間での分子内[2+2+2]環化付加反応がオキサローダサイクル中間体 **Bb** を経由して進行し、三環式化合物 **14a** が良好な収率かつ高ジアステレオ選択的に生成することを報告している [20b]。

Scheme 15



一方、C-M 結合 (*b*) にカルボニル基が挿入する形式の反応は、遷移状態 **A"**およびオキサメタラサイクル中間体 **C** が非常にひずんだ構造になるためか、その報告例は極めて少ない (Scheme 14, eq. 2)。すなわち、本節で述べたアレン-イン **1** と Rh(I)錯体との分子内[2+2+2]環化付加反応が C-M 結合 (*b*) でのカルボニル基の挿入を経由する唯一の報告例である。

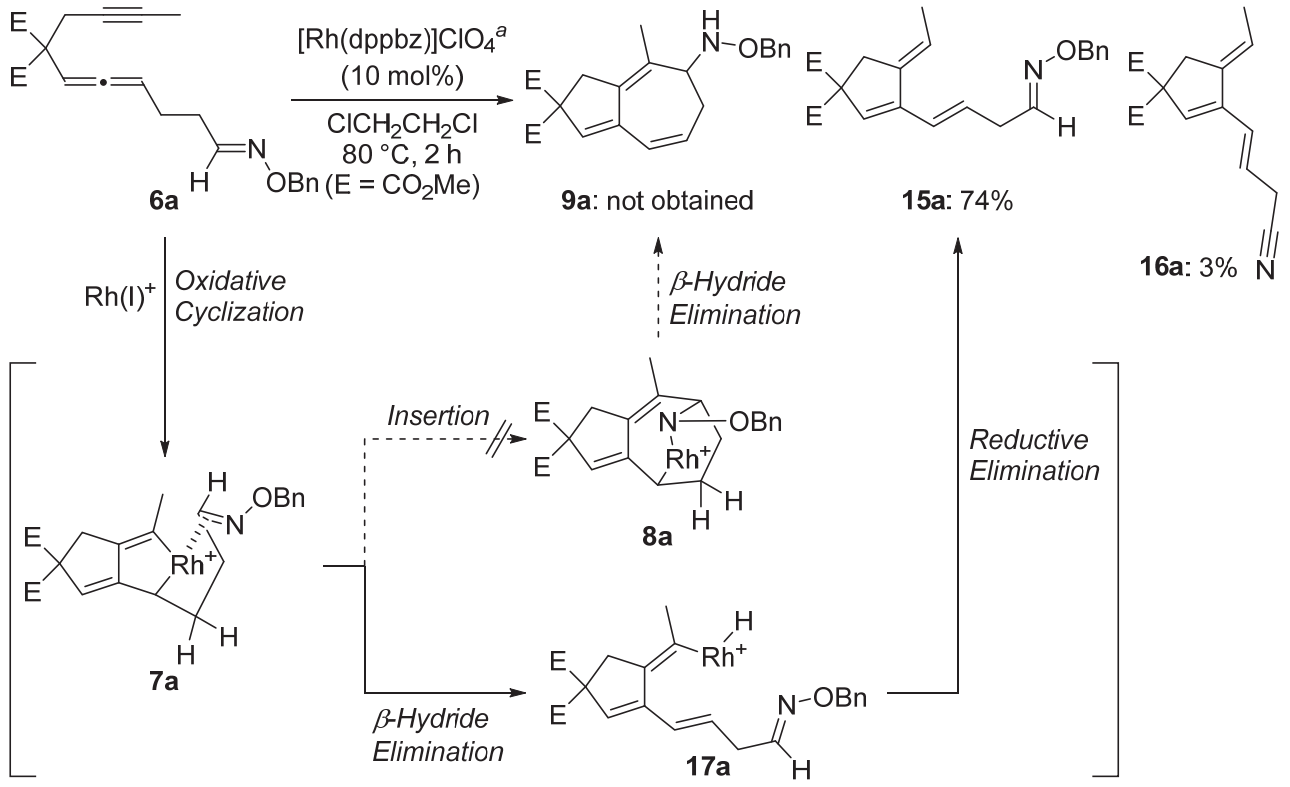
****

第二節　アザローダサイクル中間体からの β-水素脱離を経由する反応

初めに、イミン窒素原子上の置換基が本反応に及ぼす効果について検討を行った。先のカルボニル基の挿入反応[19] (Scheme 11, p. 11) で良好な結果を示した[Rh(dppbz)]ClO_4 錯体存在下、ベンジルオキシムを有するアレン-イン **6a** をジクロロエタン中、80 °C で反応させた (Scheme 16)*[2,*3]。しかしながら、目的とする二環式アミン **9a** は全く生成せず、五員環化合物 **15a** および **16a** がそれぞれ 74%、3%の収率で得られた。

これらの環化体は次のような反応機構で生成したものと考えられる。まず、基質 **6a** のアルキンとアレンが Rh(I)錯体に酸化的環化付加し、ローダシクロペンテン中間体 **7a** が生成する。この中間体 **7a** から β-水素脱離が進行しロジウムヒドリド中間体 **17a** が形成され、還元的脱離を経て五員環化合物 **15a** が生成する。また、この環化体 **15a** からベンジルアルコールが脱離するとニトリル体 **16a** が生成する*[4]。この結果は、ベンジルオキシムを有する基質 **6a** の場合、ローダシクロペンテン中間体 **7a** からの β-水素脱離が、炭素-窒素二重結合の挿入反応に優先して進行することを意味している*[5]。

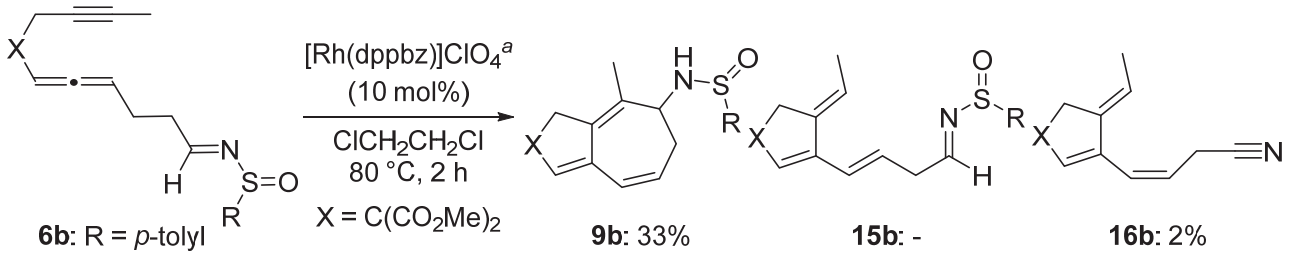
Scheme 16



[a][Rh(dppbz)]ClO_4 was generated from [Rh(dppbz)(nbd)]ClO_4 and H_2 in $ClCH_2CH_2Cl$.

次に、イミン窒素原子上に *p*-トルエンスルフィニル基が置換したアレン-イン **6b** を用いて反応を行った (Scheme 17)*[6]。その結果、五員環化合物 **15b** および **16b** の生成は顕著に抑制され、目的の二環式アミド **9b** が 33%の収率で得られた。さらに置換基の検討を行ったところ、*t*-ブタンスルフィニル基の場合に反応は選択的に進行し、二環式アミド **9c** が 69%の収率で得られた*[7,*8]。なお、基質 **6b** および **6c** はアレンと硫黄原子の 2 か所に立体中心を有するが、いずれも 1 対 1 のジアステレオマー混合物のまま反応に使用し、環化体 **9b** および **9c** はほぼ 1 対 1 のジアステレオ比で生成した。これ以降の検討においても、特に記載のある場合を除いて 1 対 1 のジアステレオマー混合物のアレン-イン **6** を反応に使用した*[9]。

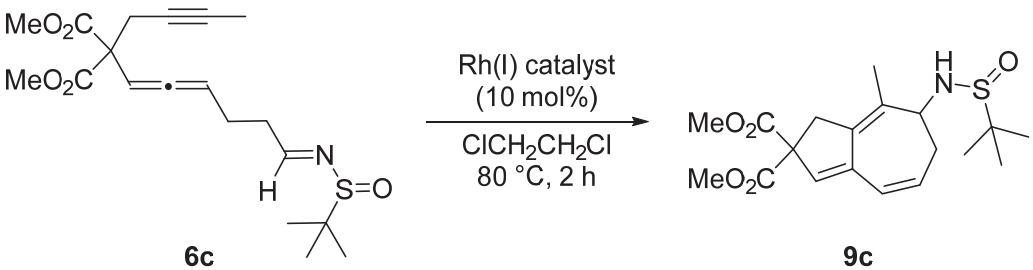
Scheme 17



[a][Rh(dppbz)]ClO_4 was generated from [Rh(dppbz)(nbd)]ClO_4 and H_2 in $ClCH_2CH_2Cl$.

続いて、イミン窒素原子上の置換基を最も良好な結果を示した *t*-ブタンスルフィニル基とし、配位子の検討を行った (Table 1)。[Rh(dppe)]ClO_4 および[Rh(dppp)]ClO_4 錯体を用いて反応を行ったところ、良好な収率で環化体 **9c** が生成した (Entries 2 and 3)。一方、[Rh(dppb)]ClO_4 および[Rh(*rac*-binap)]ClO_4 錯体を用いた場合は、原料は消失するものの複雑な混合物となり、環化体 **9c** はほとんど得られなかった (Entries 4 and 5)。次に、良好な結果を与えた[Rh(dppbz)]ClO_4 および[Rh(dppp)]ClO_4 錯体を用いて触媒量の検討を行った。5 mol%の[Rh(dppbz)]ClO_4 錯体を用いて反応を行った場合、反応時間を 8 時間まで延長してもほとんど反応が進行せず、環化体 **9c** は 7%の収率でしか得られなかった (Entry 6)。一方、[Rh(dppp)]ClO_4 錯体の場合は、触媒量を 5 mol%に低減しても反応は円滑に進行し、74%の収率で環化体 **9c** を与えた (Entry 7)。

Table 1



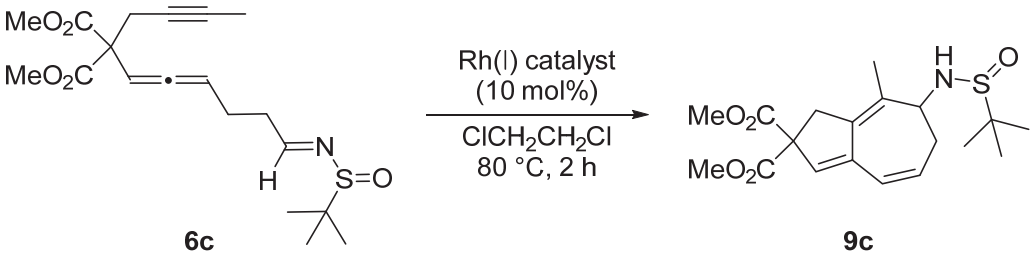
6c **9c**

Entry	Rh(I) catalyst[a]	Yield (%)[b]
1	[Rh(dppbz)]ClO_4	69
2	[Rh(dppe)]ClO_4	59
3	[Rh(dppp)]ClO_4	76
4	[Rh(dppb)]ClO_4	9
5	[Rh(*rac*-binap)]ClO_4	-[c]
6	[Rh(dppbz)]ClO_4[d]	7[e]
7	[Rh(dppp)]ClO_4[f]	74

[a][Rh(ligand)]ClO_4 was generated from [Rh(ligand)(nbd)]ClO_4 and H_2 in $ClCH_2CH_2Cl$. [b]Almost 1:1 diastereomixture of **9c** was obtained. [c]The complex mixture was obtained. [d]The reaction mixture was stirred at 80 °C for 8 h in the presence of 5 mol% of [Rh(dppbz)]ClO_4. [e]Allene-yne **6c** was recovered in 66% yield. [f]5 mol% of [Rh(dppp)]ClO_4 was used.

そこで、DPPP を配位子として対アニオンの検討を行った (Table 2)。弱配位性のトリフラート、テトラフルオロボラートなどを対アニオンとする Rh(I)錯体を用いて反応を行ったところ、いずれの場合も良好な収率で二環式アミド **9c** が生成した。この結果から、錯体の対アニオンは反応性にほとんど影響を及ぼさないことが明らかとなった。

Table 2



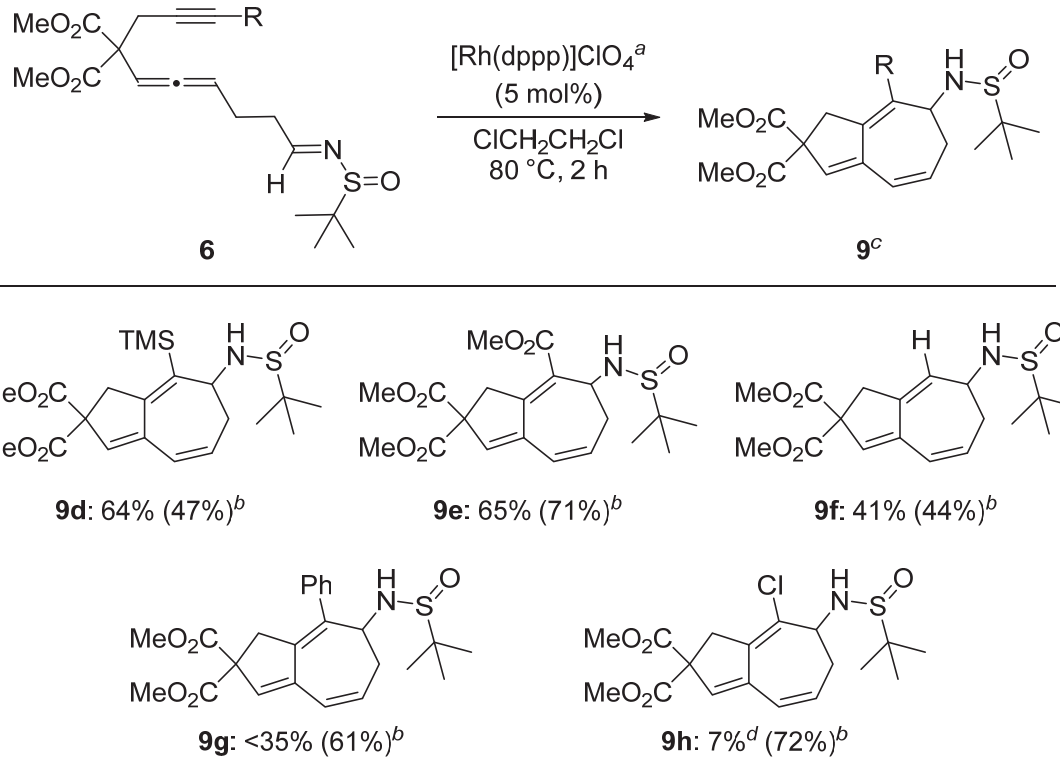
6c **9c**

Entry	Rh(I) catalyst[a]	Yield (%)[b]
1	[Rh(dppp)]ClO_4	65
2	[Rh(dppp)]OTf	69
3	[Rh(dppp)]BF_4	63
4	[Rh(dppp)]PF_6	70
5	[Rh(dppp)]SbF_6	64

[a][Rh(dppp)]X was generated from [Rh(nbd)$_2$]X, DPPP and H_2 in $ClCH_2CH_2Cl$. [b]Almost 1:1 diastereomixture of **9c** was obtained.

以上の結果から、5 mol%の[Rh(dppp)]ClO_4 錯体を最適な触媒とし、本反応における基質適用範囲の検討を行った (Table 3)*[7,*10]。アルキン上の置換基としてトリメチルシリル基やエステル基を有する基質 **6d** および **6e** を用いて反応を行ったところ、良好な収率で目的とする環化体 **9d** および **9e** を与えた。また、本反応には末端アルキンも利用可能であり、中程度の収率で環化体 **9f** が得られた。一方、アルキン上にフェニル基や塩素原子が置換した基質 **6g** および **6h** の場合、環化体の収率が大きく低下したが、10 mol%の[Rh(dppbz)]ClO_4 錯体を用いて反応を行うと収率が大幅に改善された。なお、アルキン上の置換基と反応性に関して、明確な傾向は明らかになっていない。

Table 3



[a][Rh(dppp)]ClO_4 was generated from [Rh(dppp)(nbd)]ClO_4 and H_2 in $ClCH_2CH_2Cl$. [b]The yields when using 10 mol% of [Rh(dppbz)]ClO_4 are shown in parentheses. [Rh(dppbz)]ClO_4 was generated from [Rh(dppbz)(nbd)]ClO_4 and H_2 in $ClCH_2CH_2Cl$. [c]The products were obtained as a diastereomixture. See the experimental section for the detail. [d]34% of allene-yne **6h** was recovered.

ここまでの研究により、イミン窒素原子上に *t*-ブタンスルフィニル基が置換したアレン-イン **6** と Rh(I)錯体との反応を検討した結果、アザローダサイクル中間体 **8** からの β-水素脱離を経由して、bicyclo[5.3.0]decane 骨格を有する二環式アミド **9** が良好な収率で生成することを見出した。

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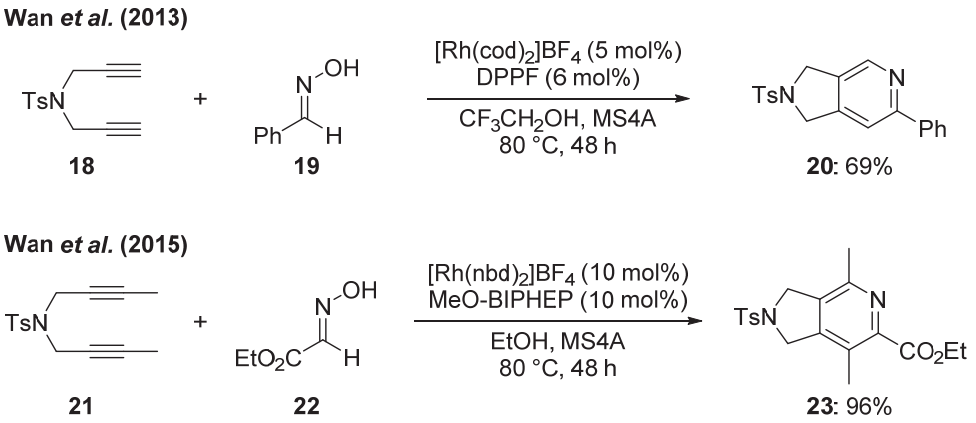
*[2] オキシムを多重結合の一つとして用いる[2+2+2]環化付加反応の報告例も極めて少なく、これまでにWanらによって以下の二例が報告されるのみである (Scheme 18)[21]。なお、これらの反応では[2+2+2]環化付加反応が進行した後に脱水反応が進行し、ピリジン誘導体が生成する。

Scheme 18



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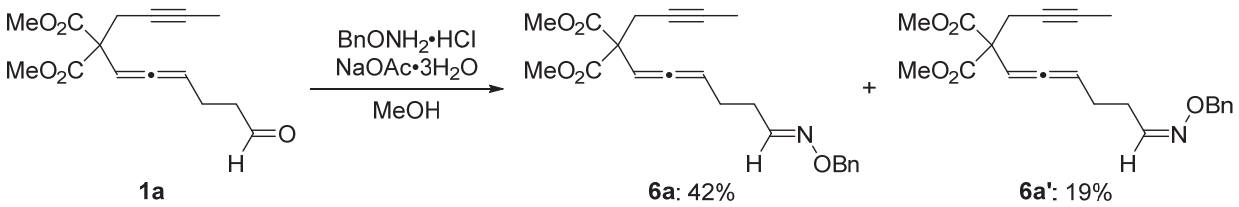
*[3] 基質 **6a** は文献既知のアルデヒド **1a**[19] と *O*-ベンジルヒドロキシルアミンから合成した (Scheme 19)。**6a** および **6a'**はシリカゲルカラムクロマトグラフィーにより分離可能であった。

Scheme 19



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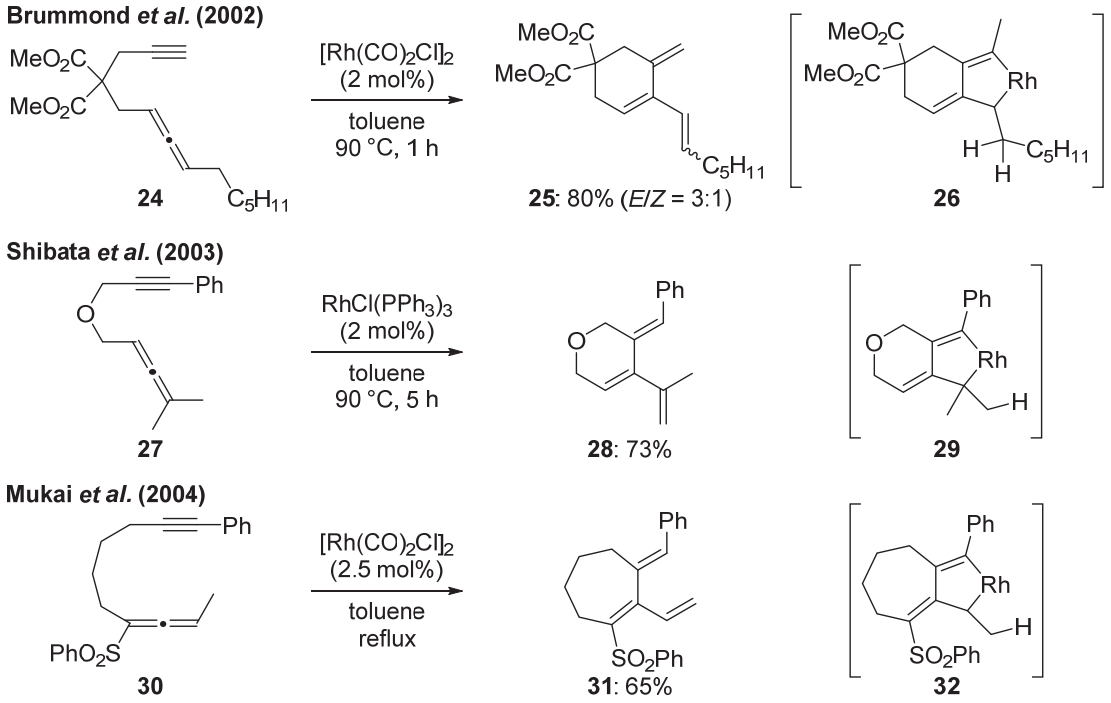
*[4] アレン-インとRh(I)錯体との反応に関連し、ローダシクロペンテン中間体からのβ-水素脱離を経由して**15**および**16**と同様の環化体を与える形式の反応は以下の三例が報告されている (Scheme 20)[22]。

Scheme 20



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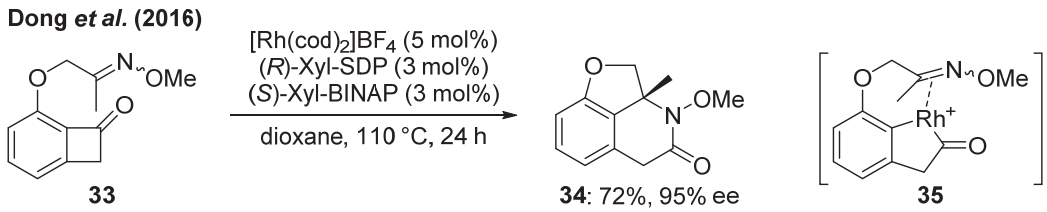
*[5] ごく最近、オキシムの炭素-窒素二重結合がオキソローダサイクル中間体**35**に挿入する形式の反応がDongらによって報告された (Scheme 21)[23]。

Scheme 21



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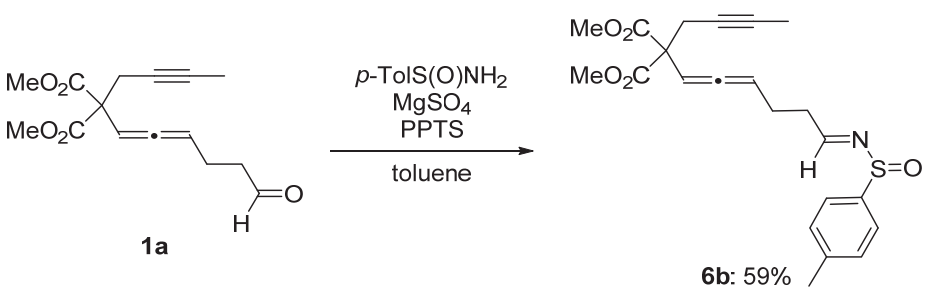
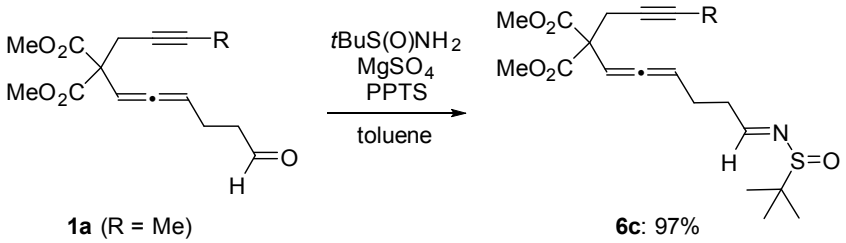
*[6] 基質 **6b** は文献既知のアルデヒド **1a**[19] と *p*-トルエンスルフィンアミドから合成した (Scheme 22)。

Scheme 22



*[7] 基質 **6c**,**6d**,**6e**,**6g**,**6h** は文献既知のアルデヒド **1a**,**1d**,**1e**,**1g**,**1h**[19] と *t*-ブタンスルフィンアミドから合成した (Scheme 23)。

Scheme 23

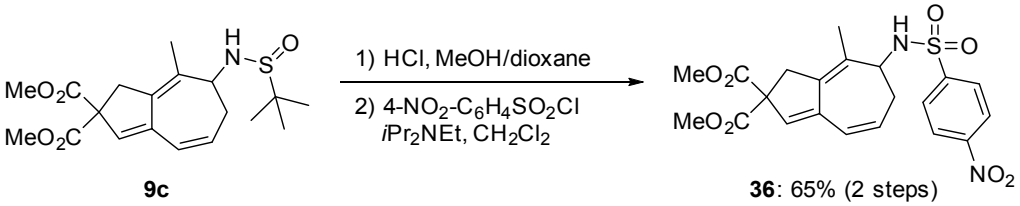


1a (R = Me)
1d (R = TMS)
1e (R = CO_2Me)
1g (R = Ph)
1h (R = Cl)

6c: 97%
6d: 90%
6e: 98%
6g: quant.
6h: 83%

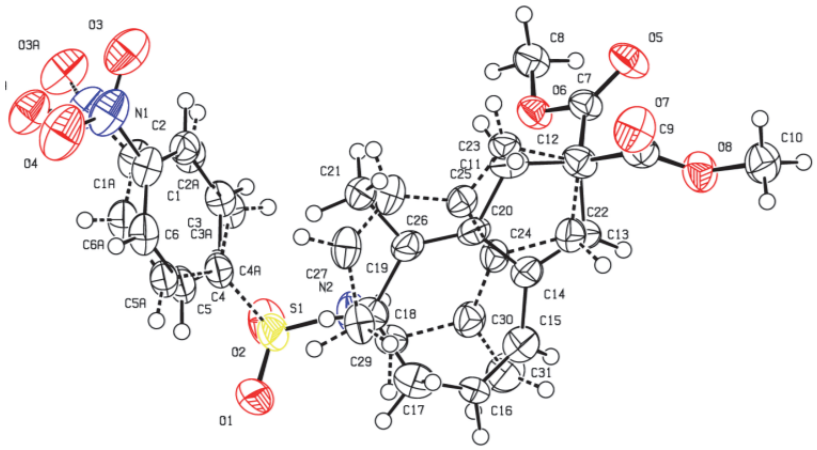
*[8] 二環式アミド **9c** の構造は *t*-ブタンスルフィニル基を脱保護した後、4-ニトロベンゼンスルホニルクロリドと反応させることで得られた **36** の単結晶 X 線結晶構造解析により確認した (Scheme 24)。

Scheme 24



9c

36: 65% (2 steps)



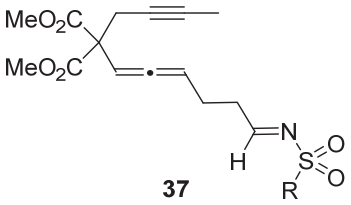
36

<Crystal Data>

Crystal System	triclinic
Space Group	P-1 (#2)
Lattice Parameters	a = 9.3707(3) Å
	b = 10.6221(4) Å
	c = 11.6440(5) Å
	α= 106.856(8)°
	β = 108.213(8)°
	γ = 90.485(6)°
	V = 1047.35(10) $Å^3$
R1 (I>2.00σ(I))	0.1056
R1 (All reflections)	0.1099
wR2	0.2376
GOF	1.146

*[9] 窒素原子上にスルホニル基を有するアルキルイミンは加水分解やエナミンへの異性化が起こりやすいため、一般に極めて不安定である[24]。そのため、*N*-スルホニルイミンを有するアレン-イン **37** を用いての検討はここでは行わなかった (Figure 2)。

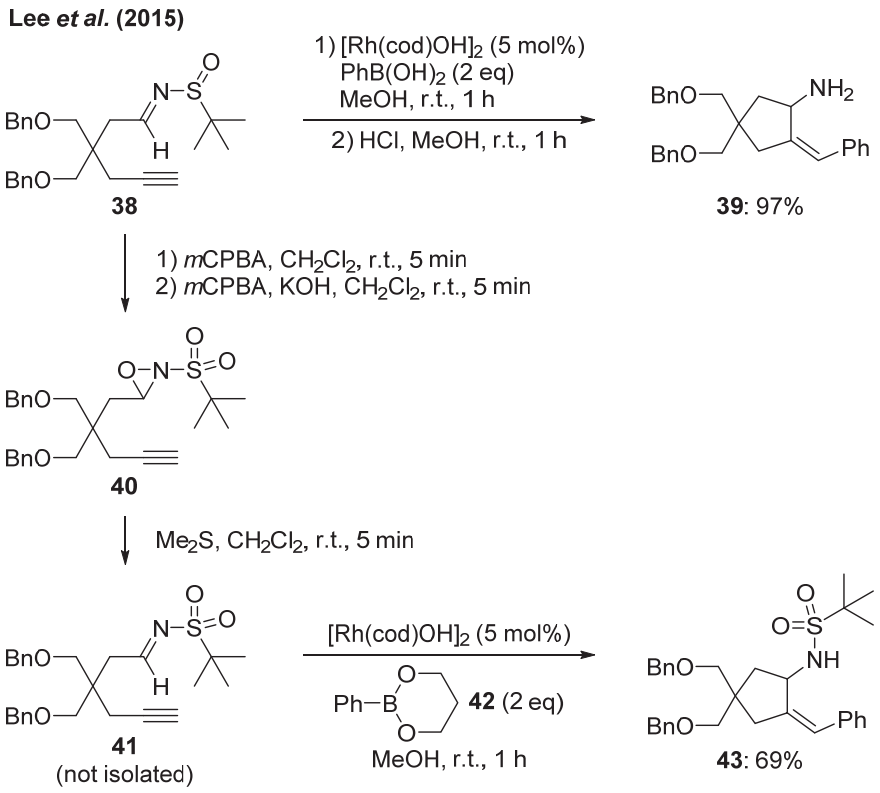
Figure 2



37

ごく最近 Lee らは、Rh(I)触媒存在下、そのような *N*-スルホニルイミンを有する基質 **41** に対するフェニルボロン酸エステル **42** の付加反応と続く分子内環化反応が連続して進行することを見出し報告した (Scheme 25)[25]。上述したとおり、*N*-スルホニルイミン **41** は不安定で取り扱いが困難である。そこで彼らは、スルフィニルイミン **38** を酸化することで一旦安定なオキサジリジン **40** へと導き、単離精製を行った。その後、このオキサジリジン **40** をジメチルスルフィドにより還元し、基質 **41** を合成した。この基質 **41** は単離することなく、溶媒と過剰量のジメチルスルフィドを除くことで、Rh(I)錯体によるフェニルボロン酸エステル **42** との反応に使用可能であった。オキサジリジン **40** の還元反応で生成するジメチルスルホキシドが系中に残存するが、Rh(I)触媒による反応を妨げることなく、目的の環化体 **43** が 69%の収率で生成した。

Scheme 25



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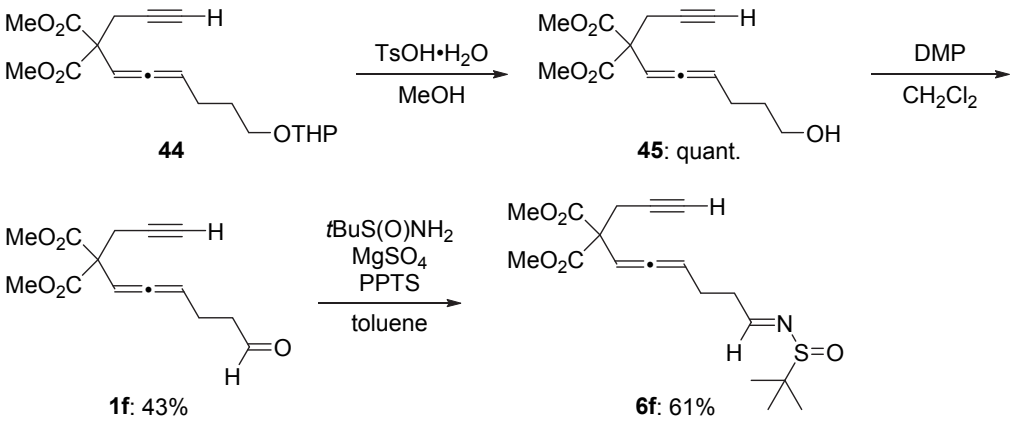
*[10] 基質 **6f** は以下に示す方法で合成した (Scheme 26)。文献既知の THP 体 **44**[19] を脱保護してアルコール体 **45** とした後に Dess-Martin 酸化、*t*-ブタンスルフィンアミドとの脱水反応を行い **6f** を得た。

Scheme 26



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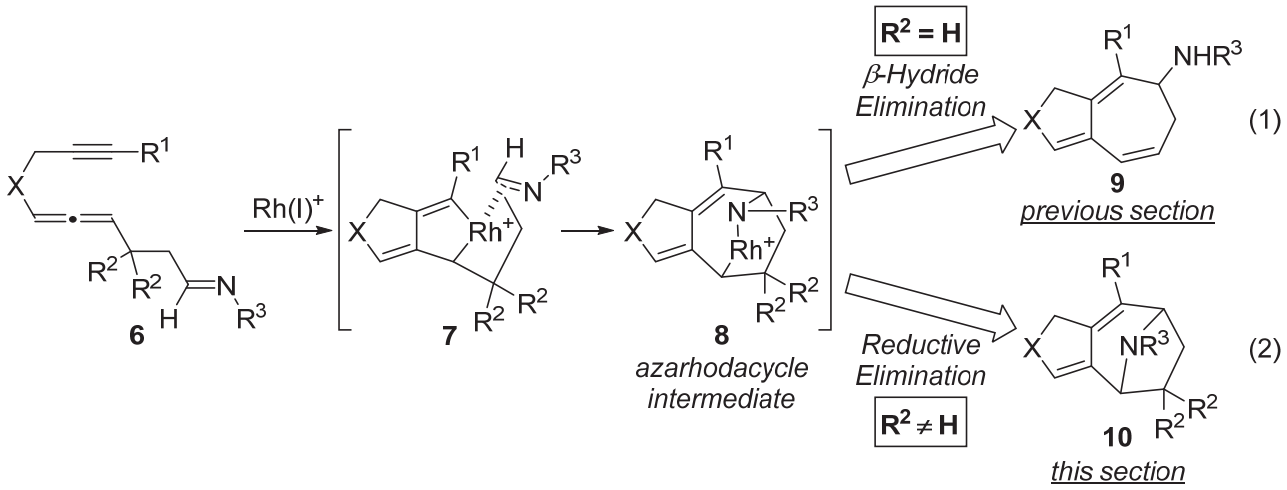
第三節　アザローダサイクル中間体からの還元的脱離を経由する反応

第一節で述べたように、イミンの β 位に水素原子をもたないアレン-イン **6** を基質に用いて Rh(I) 錯体との反応を行うならば、アザローダサイクル中間体 **8** から還元的脱離が進行し、8-azabicyclo[3.2.1]octane 骨格を有する環化体 **10** を与えるものと考えられる (Scheme 27, eq. 2)*[11]。

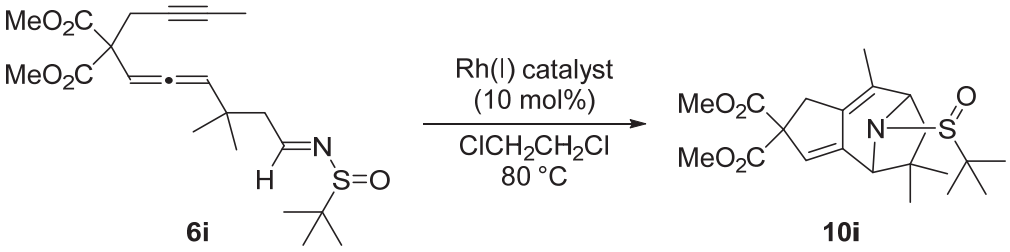
Scheme 27 (cf. Scheme 13, p. 12)



そこで、この形式の反応が進行する可能性を探るべく、イミンの β 位にジメチル基を導入したアレン-イン **6i** を基質とする環化反応について、配位子の検討を行うことにした (Table 4)*[12]。

前節で述べたアザローダサイクル中間体 **8** からの β-水素脱離を経由する環化反応で最適化した条件に従い、[Rh(dppp)]ClO_4 錯体との反応を行ったが環化体 **10i** は 33%の収率でしか得られなかった (Entry 1)*[13]。また、[Rh(dppe)]ClO_4 錯体の場合は収率が 24%に減少し (Entry 2)、[Rh(dppb)]ClO_4、[Rh(dppf)]ClO_4 および[Rh(dppbz)]ClO_4 錯体の場合は、いずれも収率は中程度であった (Entries 3-5)。さらに検討を行ったところ、[Rh(biphep)]ClO_4 および[Rh(*rac*-binap)]ClO_4 錯体の場合に良好な収率で環化体 **10i** が得られた (Entries 6 and 7)。なお、[Rh(dpephos)]ClO_4 や[Rh(pph_3)$_2$]ClO_4 錯体の場合は、環化体 **10i** は全く生成しなかった (Entries 8 and 9)。

Table 4



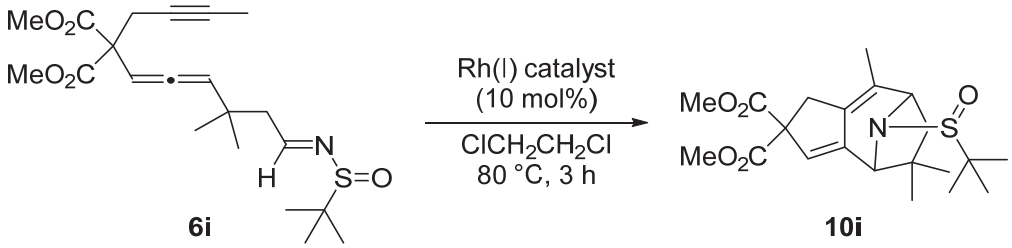
6i **10i**

Entry	Rh(I) catalyst[a]	Time (h)	Yield (%)	
			10i[b]	rec. **6i**
1	[Rh(dppp)]ClO_4	3	33	49
2	[Rh(dppe)]ClO_4	4	24	31
3	[Rh(dppb)]ClO_4	3	44	-
4	[Rh(dppf)]ClO_4	3	46	-
5	[Rh(dppbz)]ClO_4	2	55	-
6	[Rh(biphep)]ClO_4	3	75	-
7	[Rh(*rac*-binap)]ClO_4	3	74	-
8	[Rh(dpephos)]ClO_4	3	-	66
9	[Rh(PPh_3)$_2$]ClO_4	3	-	46

[a][Rh(ligand)]ClO_4 was generated from [Rh(nbd)$_2$]ClO_4, ligand and H_2 in $ClCH_2CH_2Cl$. [b]The product **10i** was obtained as a diastereomixture. See the experimental section for the detail.

次に、良好な結果を示したラセミ体の BINAP 配位子を用いて、対アニオンの検討を行った (Table 5)。弱配位性のトリフラート、テトラフルオロボラートなどを対アニオンとする Rh(I)錯体を用いて反応を行ったところ、いずれも良好な収率で環化体 **10i** が生成した。前節の β-水素脱離を経由する反応と同様、本反応においても対アニオンの影響はほとんど見られなかった。

Table 5



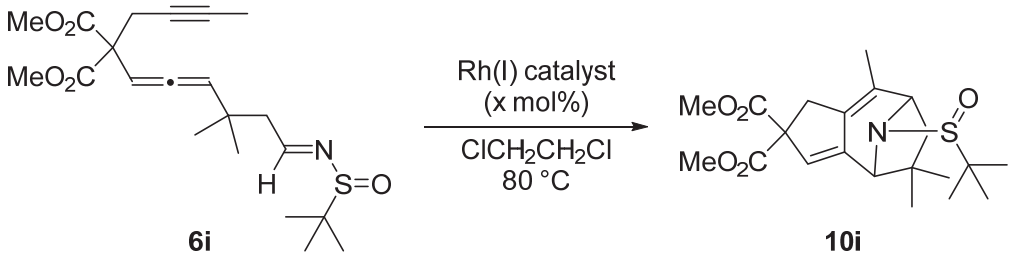
6i **10i**

Entry	Rh(I) catalyst[a]	Yield (%)[b]
1	[Rh(*rac*-binap)]ClO_4	74
2	[Rh(*rac*-binap)]OTf	70
3	[Rh(*rac*-binap)]BF_4	68
4	[Rh(*rac*-binap)]PF_6	67
5	[Rh(*rac*-binap)]SbF_6	80

[a][Rh(*rac*-binap)]X was generated from $[Rh(nbd)_2]X$, *rac*-BINAP and H_2 in $ClCH_2CH_2Cl$. [b]Almost 1:1 diastereomixture of **10i** was obtained.

続いて、[Rh(*rac*-binap)]ClO_4 錯体を用いて触媒量の検討を行った (Table 6)。触媒量を 10 mol%から 5 mol%に低減しても問題なく反応が進行し、84%の収率で環化体 **10i** を与えた (Entries 1 and 2)。一方、触媒量を 2 mol%にした場合は反応時間が延長し、環化体 **10i** の収率は若干低下した (Entry 3)。また、*rac*-BINAP とノルボルナジエンをともに配位子に有する [Rh(*rac*-binap)(nbd)]ClO_4 錯体を用いて反応を行った場合はほとんど反応が進行せず、環化体 **10i** の収率はわずか 9%であった (Entry 4)。[Rh(*rac*-binap)]ClO_4 錯体の場合と比較して反応性に顕著な差が見られたことから、より配位不飽和な Rh(I)錯体を使用することが本反応の進行に必須であることが明らかとなった (Entry 1 vs 4)。

Table 6



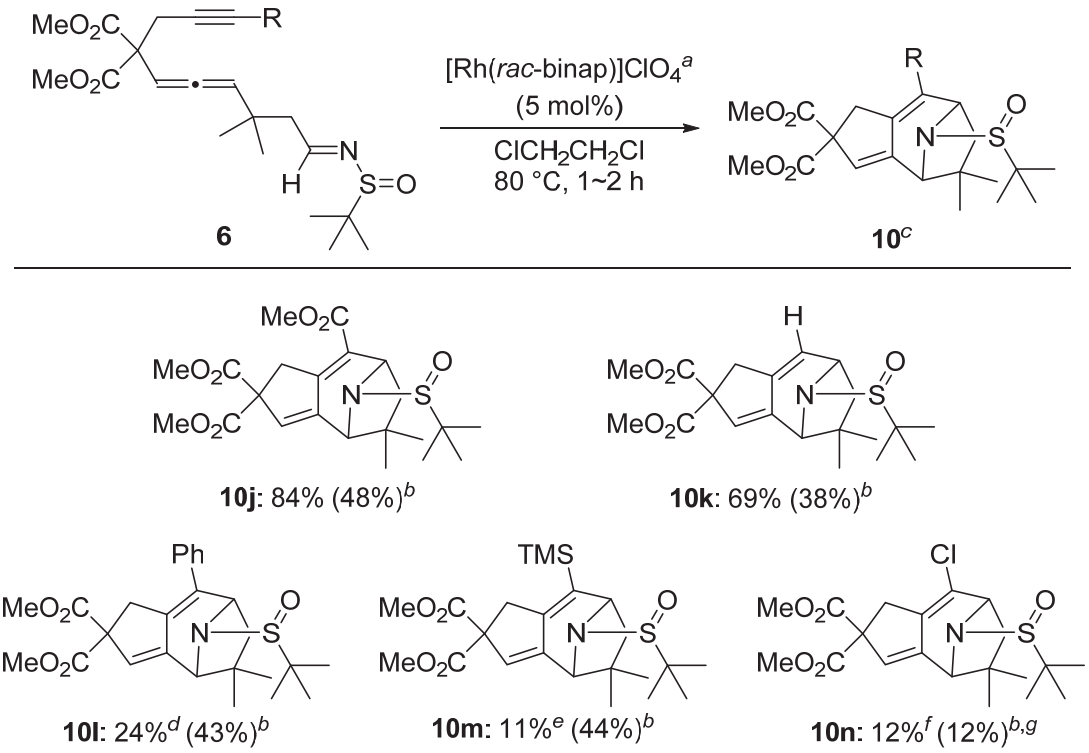
6i **10i**

Entry	Rh(I) catalyst	mol%	Time (h)	Yield (%)[b]	
				10i	rec. **6i**
1	[Rh(*rac*-binap)]ClO_4[a]	10	1	81	-
2	[Rh(*rac*-binap)]ClO_4[a]	5	1	84	-
3	[Rh(*rac*-binap)]ClO_4[a]	2	21	68	6
4	[Rh(*rac*-binap)(nbd)]ClO_4	10	1	9	85

[a][Rh(*rac*-binap)]ClO_4 was generated from [Rh(*rac*-binap)(nbd)] ClO_4 and H_2 in $ClCH_2CH_2Cl$.
[b]Almost 1:1 diastereomixture of **10i** was obtained.

以上の結果から、5 mol%の[Rh(*rac*-binap)]ClO_4 錯体を最適な触媒とし、本反応における基質適用範囲の検討を行った (Table 7)*[14]。アルキン上にエステル基を有する基質 **6j** および末端アルキンを有する基質 **6k** の場合は、良好な収率で目的の環化体 **10j** および **10k** を与えた。一方、アルキン上にフェニル基やトリメチルシリル基、塩素原子が置換した基質 **6l**、**6m** および **6n** の場合は、原料が残存し環化体の収率が大きく低下した。なお、基質 **6l** および **6m** に関しては 10 mol%の[Rh(dppbz)]ClO_4 錯体を用いて反応を行うと収率が改善されたが、その明確な理由は明らかとなっていない。

Table 7



[a][Rh(*rac*-binap)]ClO_4 was generated from [Rh(*rac*-binap)(nbd)]ClO_4 and H_2 in $ClCH_2CH_2Cl$. [b]The yields when using 10 mol% of [Rh(dppbz)]ClO_4 are shown in parentheses. [Rh(dppbz)]ClO_4 was generated from [Rh(dppbz)(nbd)]ClO_4 and H_2 in $ClCH_2CH_2Cl$. [c]The products were obtained as a diastereomixture. See the experimental section for the detail. [d]30% of allene-yne **6l** was recovered. [e]64% of allene-yne **6m** was recovered. [f]52% of allene-yne **6n** was recovered. [g]49% of allene-yne **6n** was recovered.

ここまでの研究により、イミンの β 位にジメチル基を有するアレン-イン **6** と Rh(I)錯体との反応を検討した結果、アザローダサイクル中間体 **8** からの還元的脱離を経由して、8-azabicyclo[3.2.1]octane 骨格を有する環化体 **10** が良好な収率で生成することを見出した。

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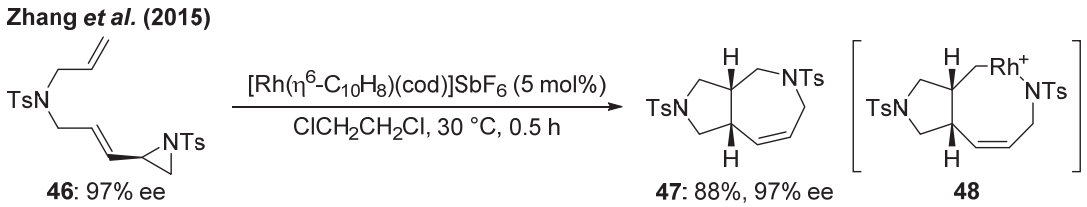
*[11] アザローダサイクル中間体からの還元的脱離により C(sp^3)-N(sp^3)結合が形成される反応はこれまで知られていなかったが、ごく最近 Zhang らによってそのような還元的脱離を経由する反応が報告された (Scheme 28)[26]。

Scheme 28



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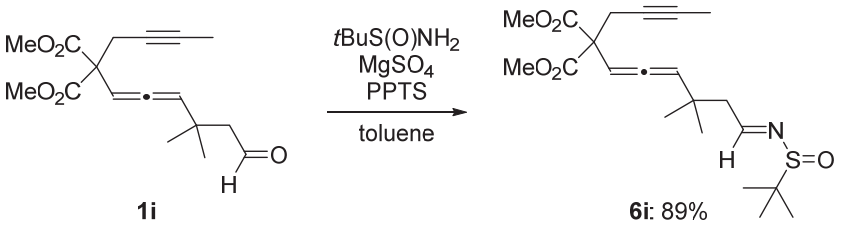
*[12] 基質 **6i** は文献既知のアルデヒド **1i**[19] と *t*-ブタンスルフィンアミドから合成した (Scheme 29)。

Scheme 29



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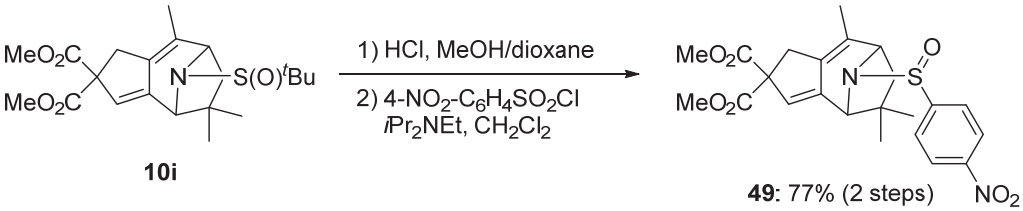
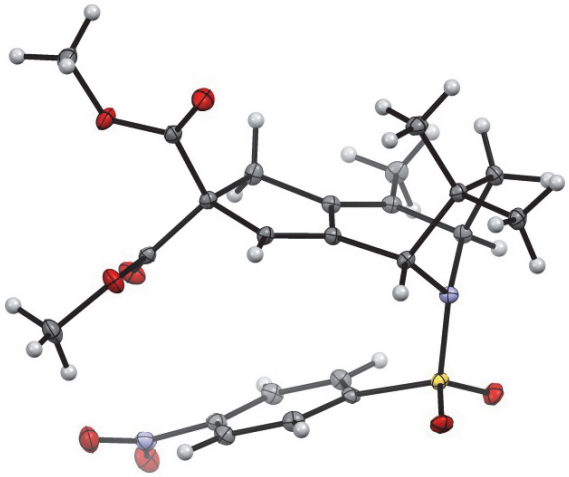
*[13] 環化体 **10i** の構造は *t*-ブタンスルフィニル基を脱保護した後、4-ニトロベンゼンスルホニルクロリドと反応させることで得られた **49** の単結晶 X 線結晶構造解析により確認した (Scheme 30)。

Scheme 30



10i

49: 77% (2 steps)



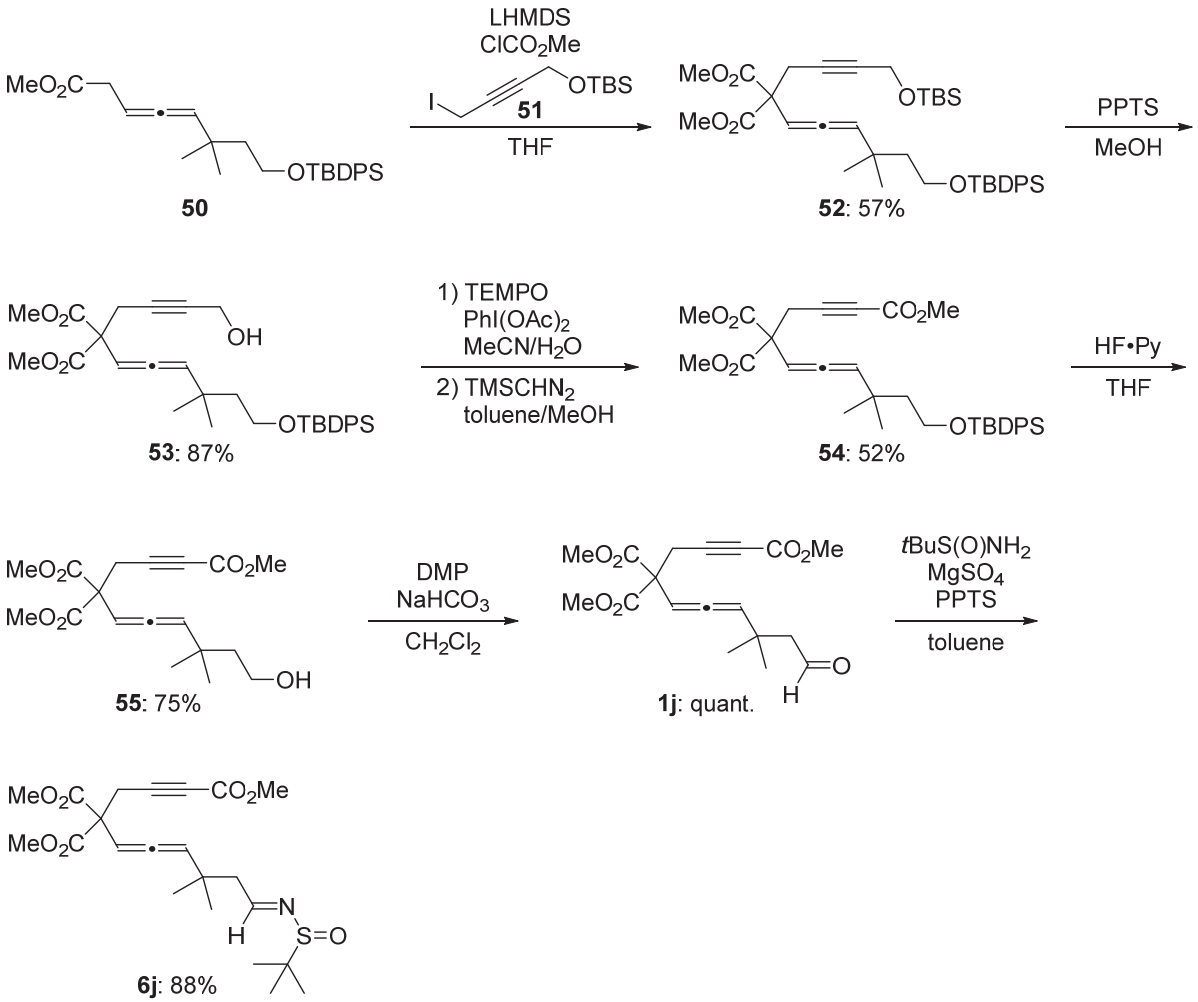
49

<Crystal Data>

Crystal System	monoclinic
Space Group	$P2_1/c$ (#14)
Lattice Parameters	a = 8.418(3) Å
	b = 21.178(4) Å
	c = 12.776(3) Å
	β = 101.44(2)°
	V = 2232.3(9) Å^3
R1 (I>2.00σ(I))	0.0351
R (All reflections)	0.0425
wR2	0.1523
GOF	1.039

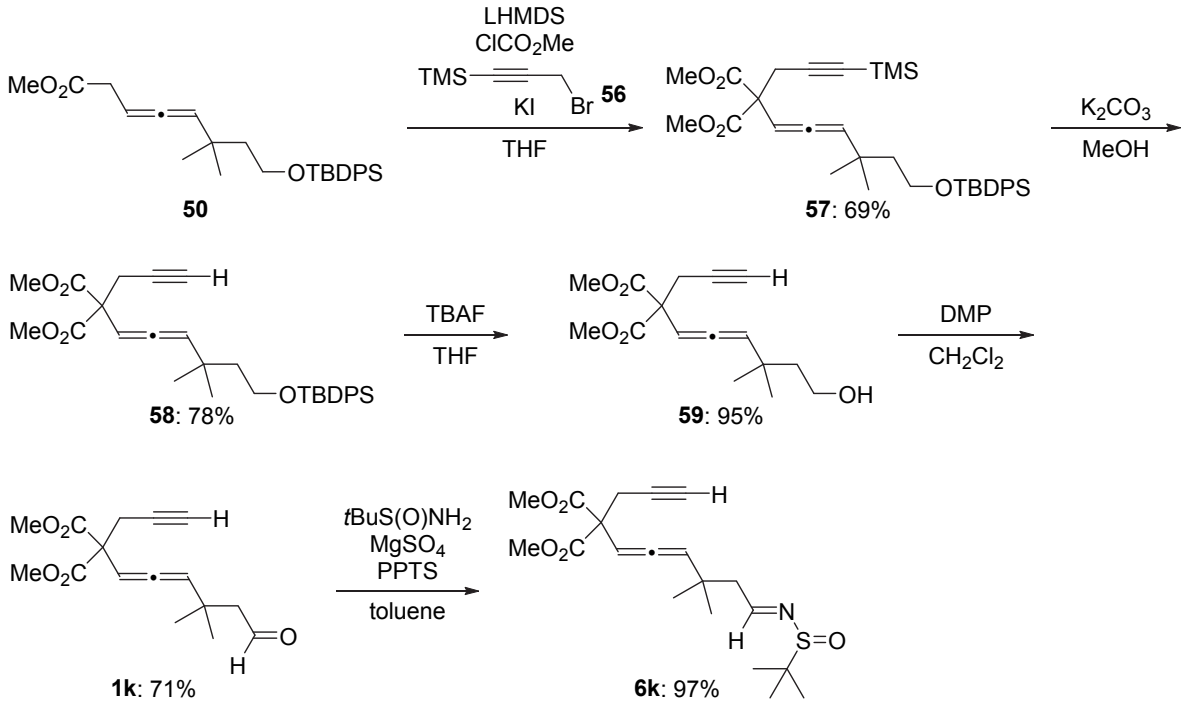
*[14] 基質 **6j** は以下に示す方法で合成した (Scheme 31)。文献既知のアレン **50**[27] を LHMDS で処理した後、クロロギ酸メチル、ヨウ素化物 **51**[28] と順次反応させアレン-イン **52** を得た。次に、TBS 基を選択的に脱保護し、生じたアルコール **53** を酸化してメチルエステル体 **54** へと変換した。その後、メチルエステル体 **54** の TBDPS 基を脱保護し、続く Dess-Martin 酸化、*t*-ブタンスルフィンアミドとの脱水反応により **6j** へと導いた。

Scheme 31



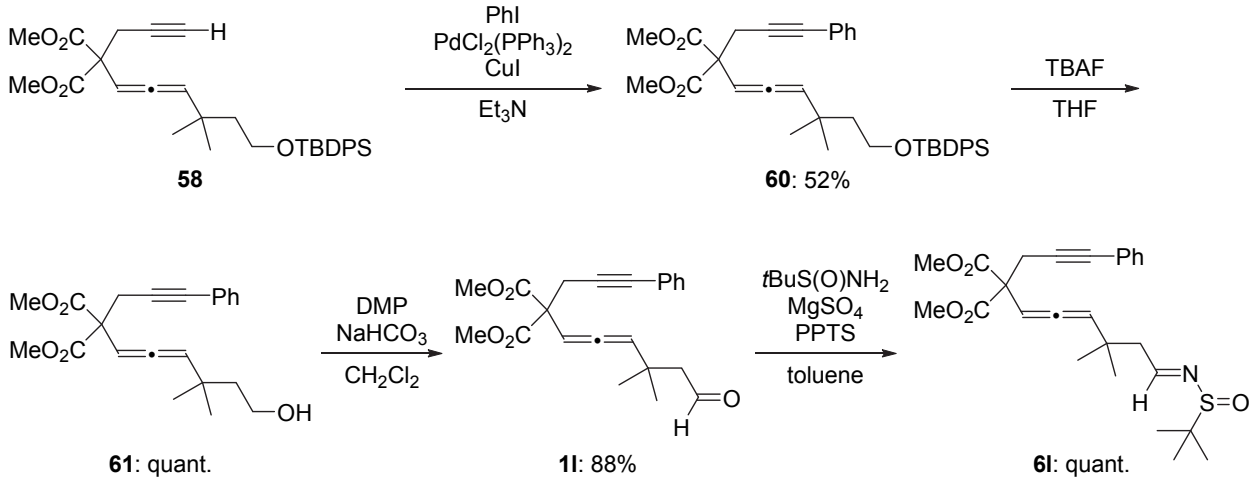
基質 **6k** は以下に示す方法で合成した (Scheme 32)。文献既知のアレン **50**[27] を LHMDS で処理した後、クロロギ酸メチル、市販の臭素化物 **56** と順次反応させアレン-イン **57** を得た。その後、**57** の TMS 基と TBDPS 基を順次脱保護し、Dess-Martin 酸化、*t*-ブタンスルフィンアミドとの脱水反応を行うことにより **6k** へと導いた。

Scheme 32



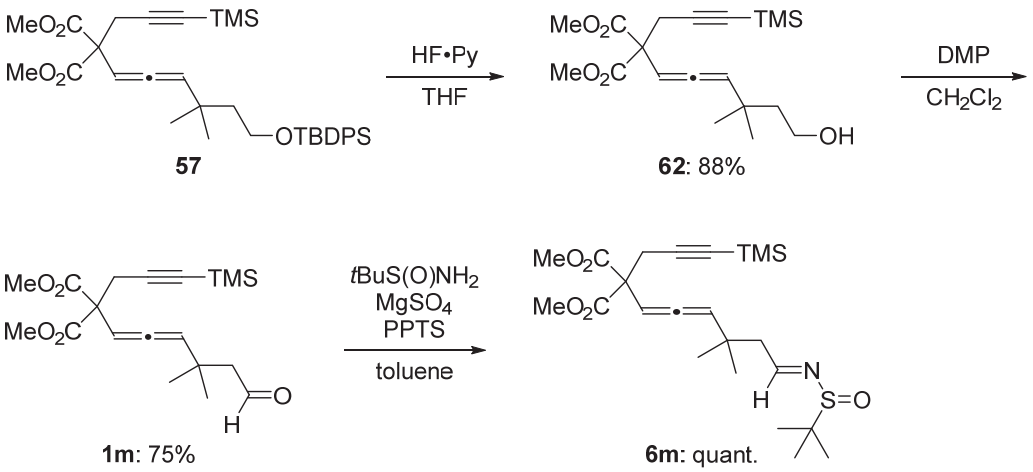
基質 **6l** は以下に示す方法で合成した (Scheme 33)。アレン **58** とヨードベンゼンとの薗頭カップリングにより、アルキン上にフェニル基を導入した。その後、TBDPS 基を脱保護し、Dess-Martin 酸化、*t*-ブタンスルフィンアミドとの脱水反応により **6l** へと導いた。

Scheme 33



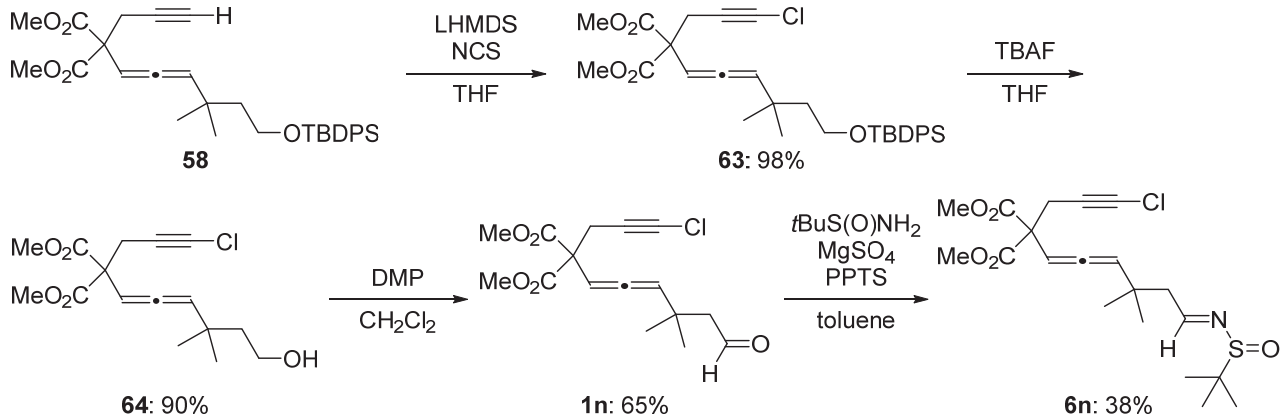
基質 **6m** はアレン **57** の TBDPS 基を脱保護した後、Dess-Martin 酸化、*t*-ブタンスルフィンアミドとの脱水反応を行うことにより合成した (Scheme 34)。

Scheme 34



基質 **6n** は以下に示す方法で合成した (Scheme 35)。アレン-イン **58** を LHMDS で処理した後 *N*-クロロスクシンイミドと反応させ、アルキン上に塩素原子を導入した。得られた **63** の TBDPS 基を脱保護した後、Dess-Martin 酸化、*t*-ブタンスルフィンアミドとの脱水反応を行うことにより **6n** へと導いた。

Scheme 35



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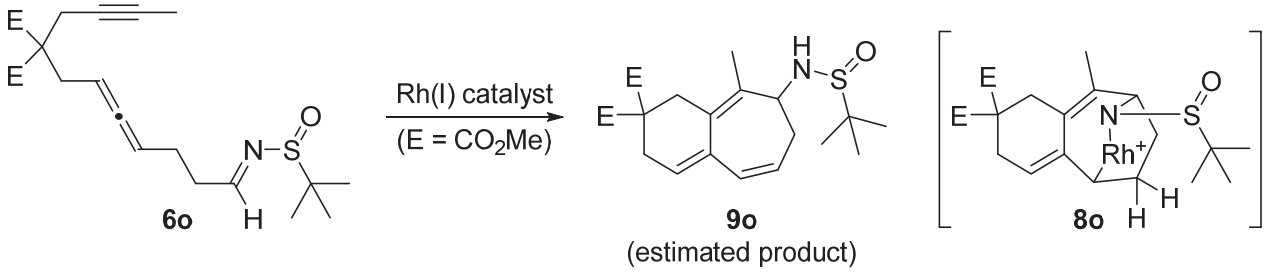
第四節　1,6-アレン-インを用いた検討および反応機構の考察

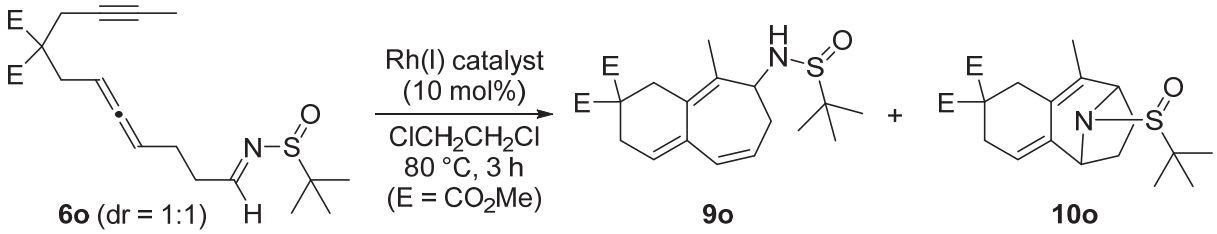
本反応の基質適用範囲をさらに精査するべく、アレンとアルキン間の炭素数が一つ多い 1,6-アレン-イン **6o** を基質とする反応を検討することにした (Scheme 36)*[15]。これまでの検討結果から、このアレン-イン **6o** を用いて反応を行うとアザローダサイクル中間体 **8o** からの β-水素脱離を経由して二環式アミド **9o** が生成するものと考えられる。

Scheme 36



まず、二環式アミド **9** を収率良く与えた[Rh(dppp)]ClO_4 錯体を用いてアレン-イン **6o** との反応を行ったが (Table 8, Entry 1)、反応は進行せずアレン-イン **6o** が回収された。そこで、[Rh(*rac*-binap)]ClO_4 錯体を用いて反応を行ったが、複雑な混合物を与えるのみであった (Entry 2)。一方、[Rh(dppbz)]ClO_4 錯体を用いて反応を行ったところ、予想された二環式アミド **9o** だけでなく環化体 **10o** も生成し、収率はそれぞれ 31%、29%であった (Entry 3)。さらに検討を行ったところ、[Rh(dppe)]ClO_4 錯体を用いた場合も二環式アミド **9o** と環化体 **10o** が生成し、収率はそれぞれ 51%、16%であった (Entry 4)*[16]。

Table 8



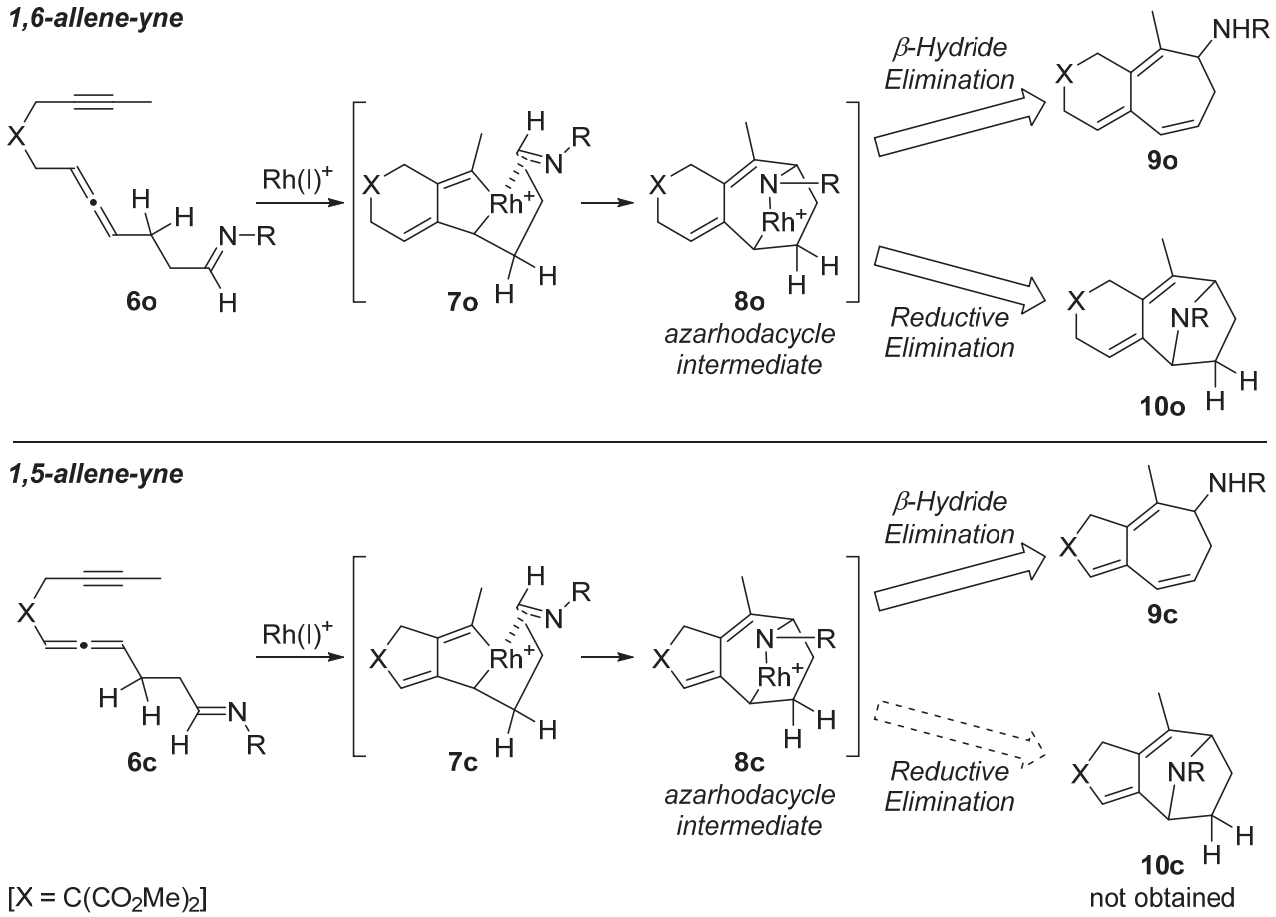
Entry	Rh(I) catalyst[a]	Yield (%) (dr)		
		9o	**10o**	rec. **6o**
1	$[Rh(dppp)]ClO_4$	-	-	67
2	[Rh(*rac*-binap)]ClO_4	-	-	-[b]
3	$[Rh(dppbz)]ClO_4$	31 (>20:1)	29 (>20:1)	-
4	$[Rh(dppe)]ClO_4$	51 (1.7:1)	16 (>20:1)	-

[a]$[Rh(ligand)]ClO_4$ was generated from $[Rh(ligand)(nbd)]\ ClO_4$ and H_2 in $ClCH_2CH_2Cl$. [b]The complex mixture was obtained.

本反応において二環式アミド **9o** と環化体 **10o** が同時に生成したことは、アザローダサイクル中間体 **8o** からの β-水素脱離と還元的脱離が競合して進行することを意味している (Scheme 37)。このことは、1,5-アレン-イン **6c** と Rh(I)錯体との反応で形成されるアザローダサイクル中間体 **8c** から選択的に β-水素脱離が進行することとは対照的である。

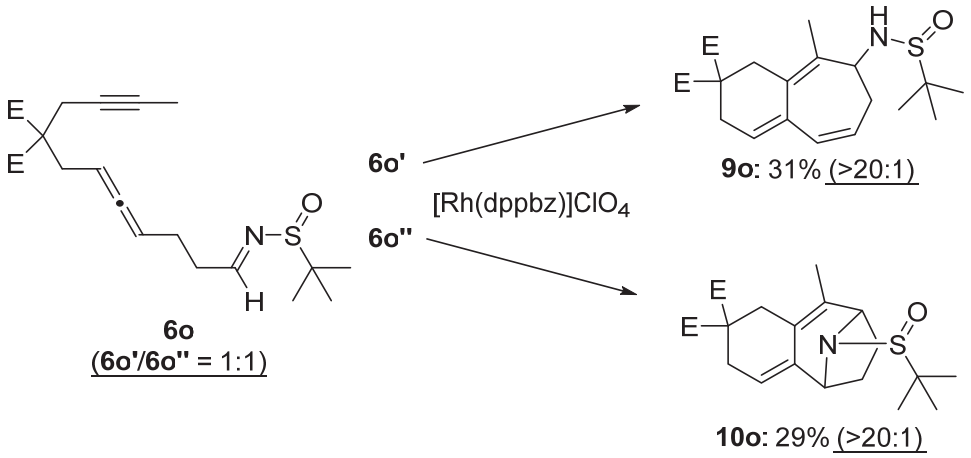
この反応性の違いは環化体 **10c** および **10o** の環骨格の炭素数が異なることに起因するものと考えられる。すなわち、環化体 **10o** は **10c** に比べて炭素数が一つ多くひずみが小さいために、アザローダサイクル中間体 **8o** からの還元的脱離が比較的起こりやすくなっているものと考えられる。その結果、本反応では中間体 **8o** からの還元的脱離が β-水素脱離と競合して進行し、二環式アミド **9o** と環化体 **10o** が生成した。

Scheme 37



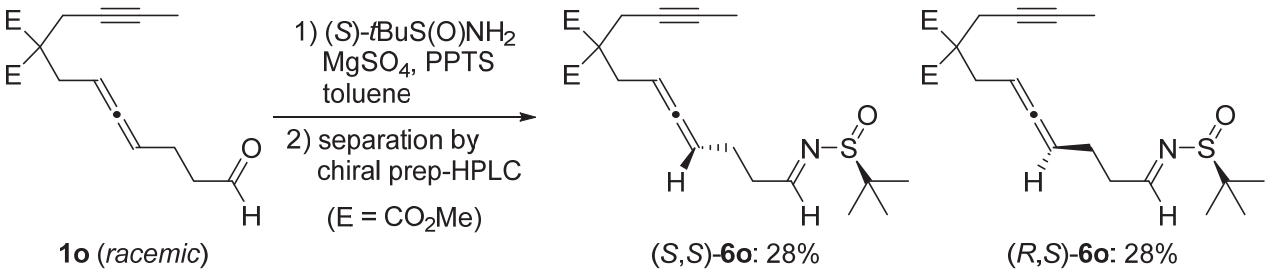
また、1,6-アレン-イン **6o** と Rh(I)-DPPBz 錯体との反応において、二環式アミド **9o** と環化体 **10o** は特徴的なジアステレオ比で生成した (Table 8, Entry 3)。すなわち、本反応では 1 対 1 のジアステレオマー混合物の 1,6-アレン-イン **6o** を基質として用いているにも関わらず、二環式アミド **9o** および環化体 **10o** はそれぞれ単一のジアステレオマーとして得られた。この結果から、これらの生成物は 1,6-アレン-イン **6o** の各ジアステレオマー (**6o'**および **6o"**と表記する) から選択的に生成している可能性が考えられた (Scheme 38)。

Scheme 38 (cf. Table 8, Entry 3, p. 36)



そこで、この仮説を検証するために、単一のジアステレオマーの 1,6-アレン-インを基質として用い Rh(I)錯体との反応を行うことにした。検討に必要な基質(*S*,*S*)-**6o** および(*R*,*S*)-**6o** はラセミ体のアルデヒド **1o**[29] と(*S*)-*t*-ブタンスルフィンアミドとの反応で生成したジアステレオマー混合物をキラル HPLC で分取することにより得た (Scheme 39)。なお、Table 9 にはこれらの基質(*S*,*S*)-**6o** および(*R*,*S*)-**6o** と Rh(I)錯体との反応で生成し得る四種類の環化体の構造を示している。

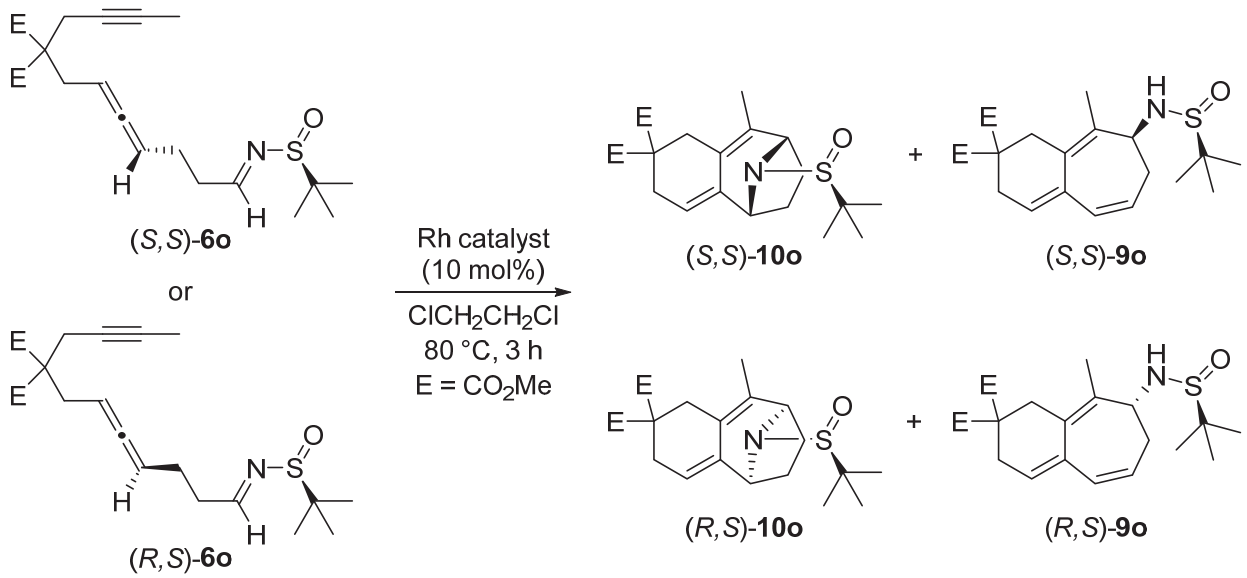
Scheme 39



まず、アレン-イン(*S*,*S*)-**6o** と[Rh(dppbz)]ClO_4 錯体との反応を行ったところ、環化体(*S*,*S*)-**10o** と二環式アミド(*R*,*S*)-**9o** がそれぞれ 19%、22%の収率で生成した (Table 9, Entry 1)*[17]。一方、アレン-イン(*R*,*S*)-**6o** と[Rh(dppbz)]ClO_4 錯体との反応を行った場合も環化体(*S*,*S*)-**10o** と二環式アミド(*R*,*S*)-**9o** が生成し、収率はそれぞれ 14%、24%であった (Entry 2)。当初は Scheme 38 に示したように、基質の一方のジアステレオマーからは二環式アミド ((*S*,*S*)-**9o** または(*R*,*S*)-**9o**) が、もう一方のジアステレオマーからは環化体 ((*S*,*S*)-**10o** または(*R*,*S*)-**10o**) が選択的に生成すると予想していた。しかしながら、実際には用いた基質のいずれのジアステレオマーからも環化体(*S*,*S*)-**10o** およ

び二環式アミド(*R*,*S*)-**9o** がそれぞれ同程度の収率 (ca. 20%) で生成し、環化体(*R*,*S*)-**10o** と二環式アミド(*S*,*S*)-**9o** は全く生成しなかった。

Table 9

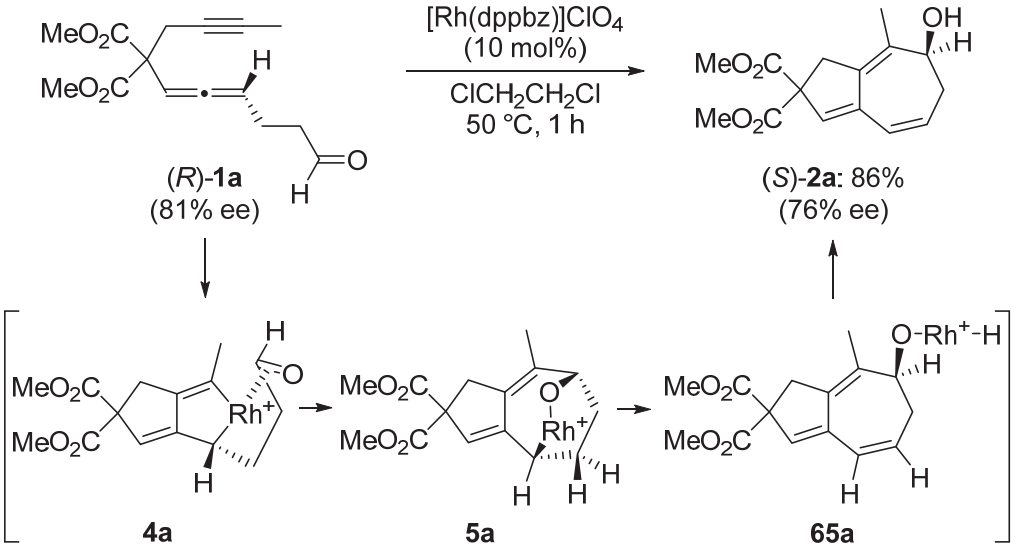


Entry	Substrate	Rh(I) catalyst[a]	Yield (%)			
			(*S*,*S*)-**10o**	(*R*,*S*)-**10o**	(*S*,*S*)-**9o**	(*R*,*S*)-**9o**
1	(*S*,*S*)-**6o**	[Rh(dppbz)]ClO_4	19	-	-	22
2	(*R*,*S*)-**6o**	[Rh(dppbz)]ClO_4	14	-	-	24
3	calcd. average from entries 1 & 2		(17)	-	-	(23)

[a][Rh(dppbz)]ClO_4 was generated from [Rh(dppbz)(nbd)] ClO_4 and H_2 in $ClCH_2CH_2Cl$.

上記の実験結果を基に、本反応の推定反応機構の考察を行った。当研究室ではこれまでに、分子内にカルボニル基を有する光学活性なアレン-イン(*R*)-**1a** (81% ee) と Rh(I)錯体との反応を行うとアレンの軸不斉が生成物に転写され、環化体(*S*)-**2a** が光学活性体として得られることを確認している (Scheme 40)[19]。この結果は、アレン-イン(*R*)-**1a** の Rh(I)錯体への酸化的環化付加、続く C(sp^2)-Rh 結合へのカルボニル基の挿入が立体特異的に進行したことを示唆するものである。

Scheme 40



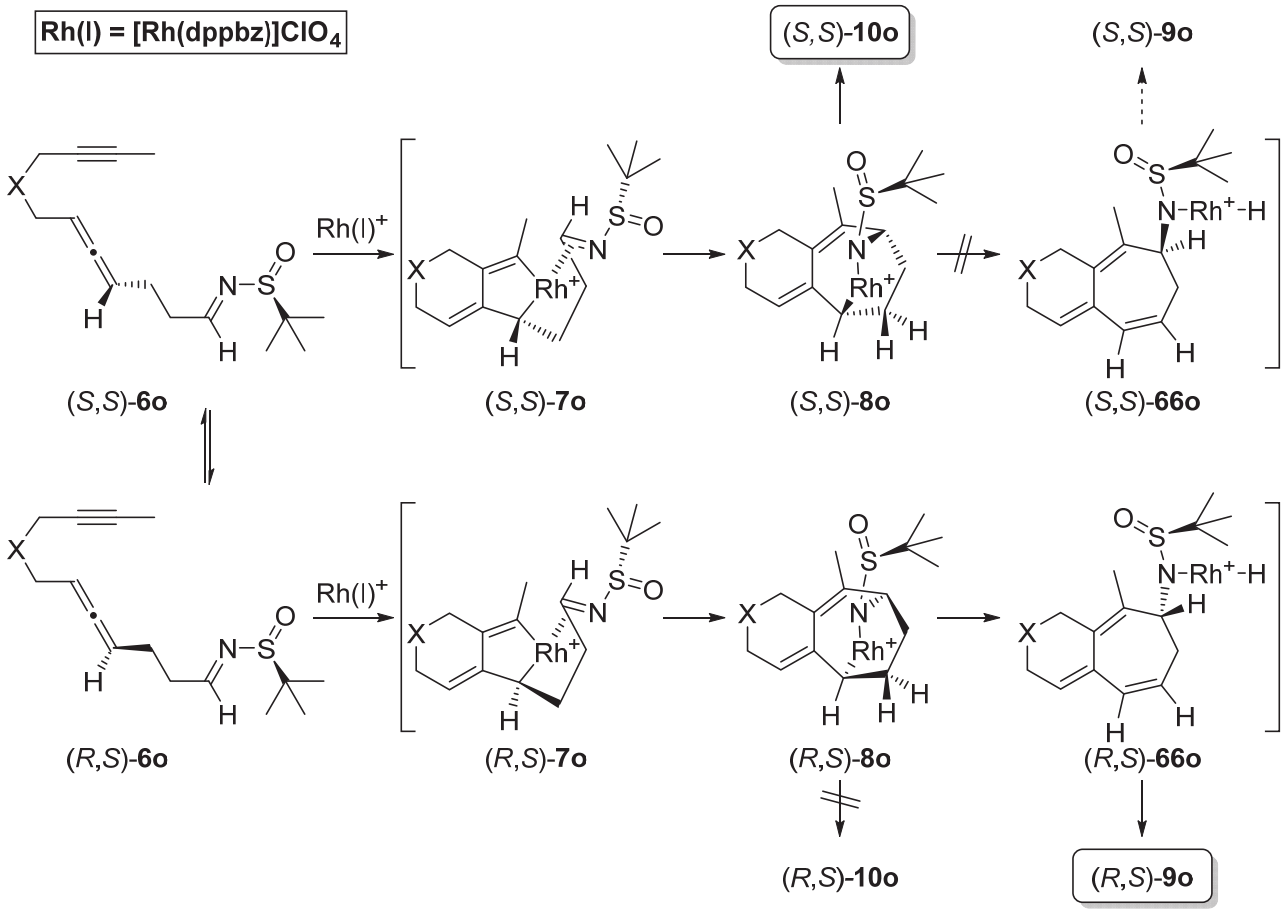
この知見に基づき、イミンを有する基質を用いた場合も同様に立体特異的に反応が進行すると考えると、アレン-イン(*S*,*S*)-**6o** からはアザローダサイクル中間体(*S*,*S*)-**8o** を経由して環化体(*S*,*S*)-**10o** と二環式アミド(*S*,*S*)-**9o** が生成する (Scheme 41)。一方、アレン-イン(*R*,*S*)-**6o** からはアザローダサイクル中間体(*R*,*S*)-**8o** を経由して環化体(*R*,*S*)-**10o** と二環式アミド(*R*,*S*)-**9o** が生成するものと考えられる。

ところが、実際にはいずれの立体化学の基質からも環化体(*S*,*S*)-**10o** および二環式アミド(*R*,*S*)-**9o** が生成したことから、反応条件下において基質のアレン部位のラセミ化が進行していることが示唆される*[18]。すなわち、本反応では光学活性な基質を用いた場合でもアレンのラセミ化が速やかに進行し、基質はジアステレオマーの混合物となる。続いて、Rh(I)錯体との立体特異的な環化反応により、アレン-イン(*S*,*S*)-**6o** からは環化体(*S*,*S*)-**10o** が、アレン-イン(*R*,*S*)-**6o** からは二環式アミド(*R*,*S*)-**9o** がそれぞれ生成する。その結果、いずれのジアステレオマーを基質に用いても、同一の立体化学を有する二つの生成物 (環化体(*S*,*S*)-**10o** および二環式アミド(*R*,*S*)-**9o**) を与えたと考えられる。

このように本反応では環化体(*S*,*S*)-**10o** と二環式アミド(*R*,*S*)-**9o** が生成したことから (Table 9, Entries 1 and 2)、(i) アザローダサイクル中間体(*S*,*S*)-**8o** からは選択的に還元的脱離が進行して環化体(*S*,*S*)-**10o** を与えること、一方、(ii) アザローダサイクル中間体(*R*,*S*)-**8o** からは選択的にβ-水素脱離が進行して(*R*,*S*)-**9o** を与えることが明らかとなった。このことは、ジアステレオマーの関係にあ

るアザローダサイクル中間体(*S*,*S*)-**8o** および(*R*,*S*)-**8o** が互いに異なる反応性を有することを意味しているが、一方からは還元的脱離が、もう一方からは β-水素脱離が選択的に進行することに関して明確な理由は明らかになっていない。

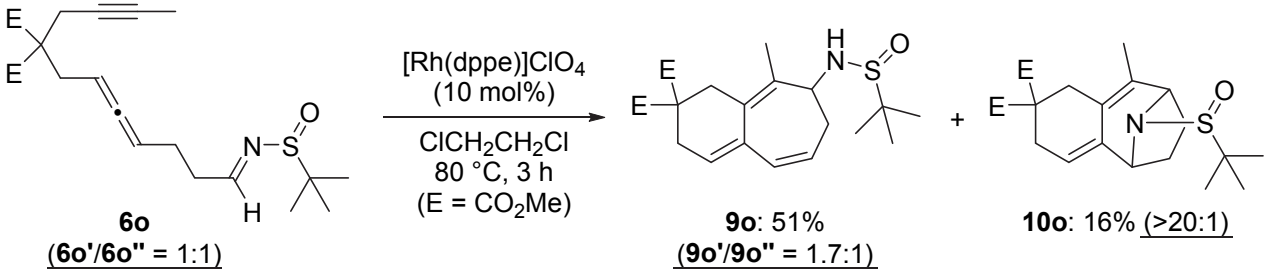
Scheme 41



ここまでの検討および考察は次のように要約される。ジアステレオマー混合物の 1,6-アレン-イン **6o** と Rh(I)-DPPBz 錯体との反応を行ったところ、二環式アミド **9o** および環化体 **10o** がいずれも単一のジアステレオマーとして生成した。そこで、この現象を詳しく調べるために単一のジアステレオマーの 1,6-アレン-イン(*S*,*S*)-**6o** および(*R*,*S*)-**6o** を用いて Rh(I)-DPPBz 錯体との反応を行った。その結果、本反応では (i) アレンのラセミ化が速やかに進行すること、(ii) アザローダサイクル中間体(*S*,*S*)-**8o** からは選択的に還元的脱離が進行して環化体(*S*,*S*)-**10o** を与えること、(iii) アザローダサイクル中間体(*R*,*S*)-**8o** からは選択的に β-水素脱離が進行して二環式アミド(*R*,*S*)-**9o** を与えることが明らかとなった。

続いて、1,6-アレン-イン **6o** とRh(I)-DPPE 錯体との反応に関しても同様に検討を行うことにした。先に述べたとおり、ジアステレオマー混合物の 1,6-アレン-イン **6o** とRh(I)-DPPE 錯体を反応させた場合、二環式アミド **9o** と環化体 **10o** がそれぞれ 51%、16%の収率で得られた (Scheme 42)。この際、二環式アミド **9o** は 1.7 対 1 のジアステレオ比で、環化体 **10o** はジアステレオ選択的に生成した。

Scheme 42 (cf. Table 8, Entry 4, p. 36)



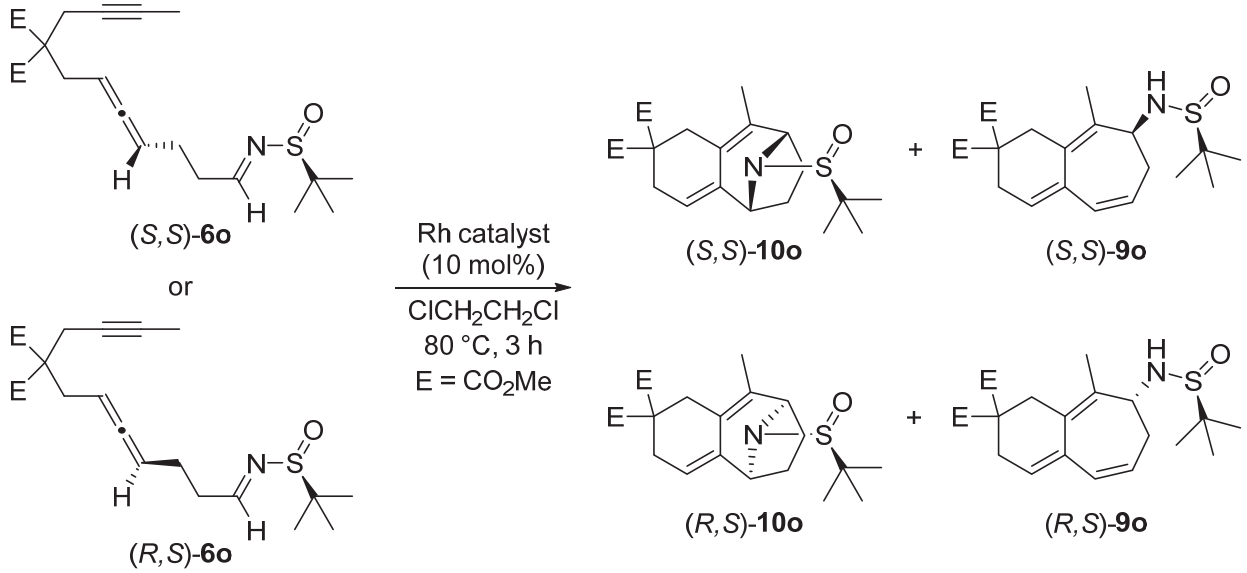
6o
(**6o'/6o"** = 1:1)

9o: 51%
(**9o'/9o"** = 1.7:1)

10o: 16% (>20:1)

本反応を詳細に検討するべく、単一のジアステレオマーの 1,6-アレン-インを基質とし、Rh(I)-DPPE 錯体との反応を行った。まず、アレン-イン(*S*,*S*)-**6o** と[Rh(dppe)]ClO_4 錯体との反応を行ったところ、環化体(*S*,*S*)-**10o**、二環式アミド(*S*,*S*)-**9o** および(*R*,*S*)-**9o** の三種類の生成物が得られ、収率はそれぞれ 24%、22%、14%であった (Table 10, Entry 1)*[19]。次に、アレン-イン(*R*,*S*)-**6o** と[Rh(dppe)]ClO_4 錯体との反応を行ったところ、同じ立体化学を有する三種類の生成物が得られ、収率はそれぞれ 7%、9%、55%であった (Entry 2)。

Table 10



Entry	Substrate	Rh(I) catalyst[a]	Yield (%)			
			(*S*,*S*)-**10o**	(*R*,*S*)-**10o**	(*S*,*S*)-**9o**	(*R*,*S*)-**9o**
1	(*S*,*S*)-**6o**	[Rh(dppe)]ClO_4	24	-	22	14
2	(*R*,*S*)-**6o**	[Rh(dppe)]ClO_4	7	-	9	55
3	calcd. average from entries 1 & 2		(16)	-	(16)	(35)

[a][Rh(dppe)]ClO_4 was generated from [Rh(dppe)(nbd)] ClO_4 and H_2 in $ClCH_2CH_2Cl$.

このように、いずれのジアステレオマーからも同じ三種類の環化体 (環化体(*S*,*S*)-**10o**、二環式アミド(*S*,*S*)-**9o** および(*R*,*S*)-**9o**) が生成したことから、Rh(I)-DPPE 錯体を用いた場合においても基質のアレン部位のラセミ化が進行していることが確認された (Scheme 43)。

しかしながら、本反応ではアレンのラセミ化よりも環化反応が速やかに進行するためか、用いる基質によって生成する三つの環化体の収率が異なることが分かった (Table 10, Entry 1 vs 2)。

すなわち、アレン-イン(*S*,*S*)-**6o** を基質に用いた場合は、その基質(*S*,*S*)-**6o** と Rh(I)錯体との環化反応が速やかに進行して環化体(*S*,*S*)-**10o** および二環式アミド(*S*,*S*)-**9o** が多く生成した。これに対し、(*S*,*S*)-**6o** から(*R*,*S*)-**6o** への異性化、続く環化反応により生成する二環式アミド(*R*,*S*)-**9o** は低収率であった (Table 10, Entry 1)。

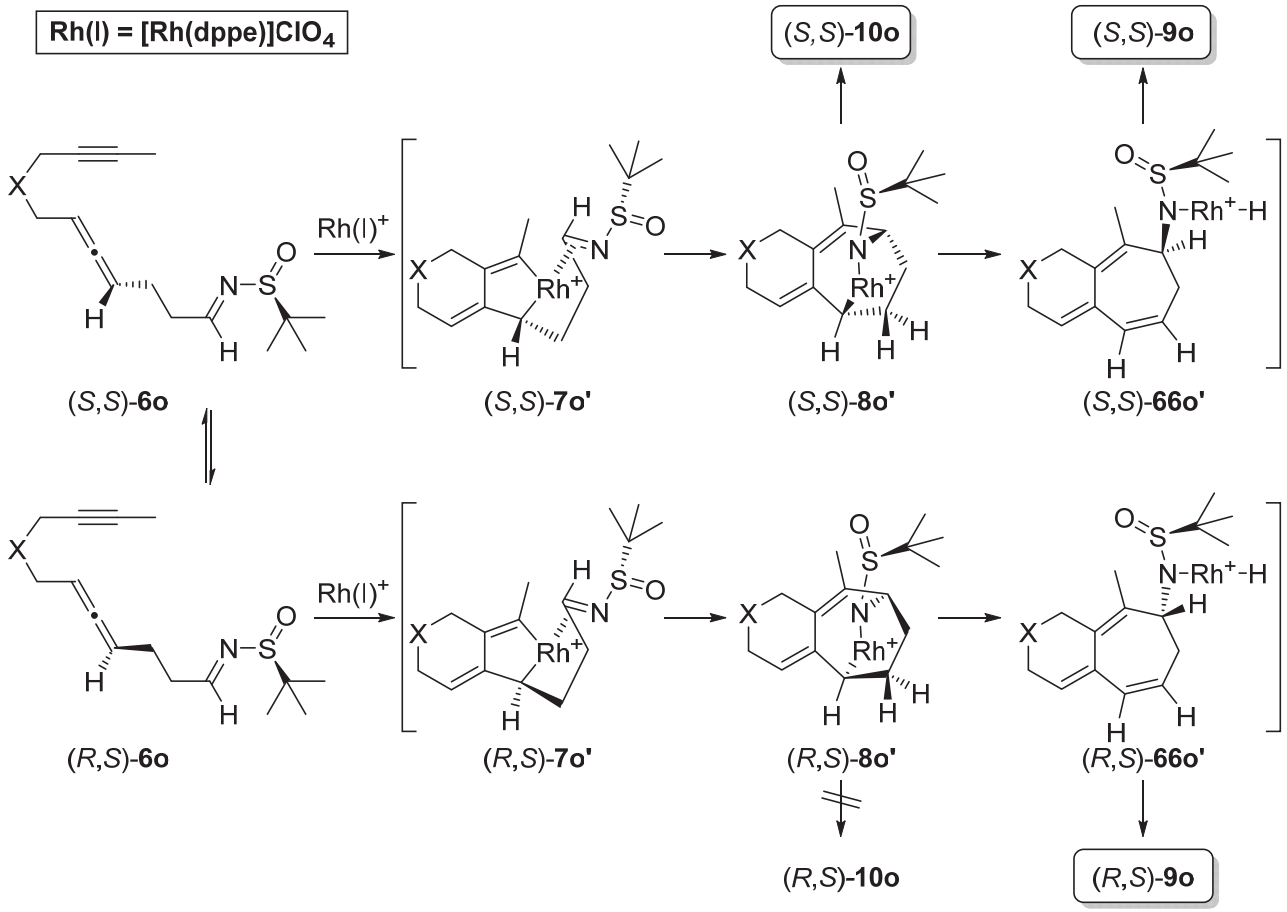
一方、アレン-イン(*R*,*S*)-**6o** を基質とした場合は、その基質(*R*,*S*)-**6o** と Rh(I)錯体との環化反応が速やかに進行して二環式アミド(*R*,*S*)-**9o** を主生成物として与えた。これに対し、(*R*,*S*)-**6o** から

(*S*,*S*)-**6o** への異性化、続く環化反応により生成する環化体(*S*,*S*)-**10o** および二環式アミド(*S*,*S*)-**9o** は低収率にとどまった (Table 10, Entry 2)。

また、Rh(I)-DPPE 錯体を用いた場合においても、ジアステレオマーの関係にあるアザローダサイクル中間体(*S*,*S*)-**8o'**および(*R*,*S*)-**8o'**は互いに異なる反応性を示した。すなわち、(i) アザローダサイクル中間体(*S*,*S*)-**8o'**からは β-水素脱離と還元的脱離がともに進行し、環化体(*S*,*S*)-**10o** および二環式アミド(*S*,*S*)-**9o** を与えた。一方、(ii) アザローダサイクル中間体(*R*,*S*)-**8o'**からは選択的に β-水素脱離が進行し、二環式アミド(*R*,*S*)-**9o** を与えた。

特に、アザローダサイクル中間体(*S*,*S*)-**8o'**から β-水素脱離と還元的脱離が進行したことは、Rh(I)-DPPBz 錯体との反応で形成されるアザローダサイクル中間体(*S*,*S*)-**8o** から選択的に還元的脱離が進行したことと異なるものであり (Scheme 41, p. 41)、配位子によってアザローダサイクル中間体の反応性が変化することを示唆している。

Scheme 43



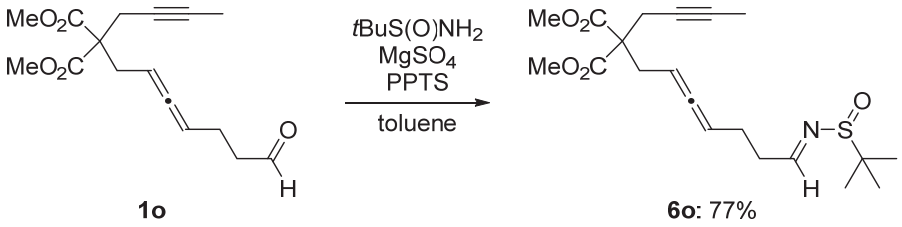
以上、単一のジアステレオマーの 1,6-アレン-イン **6o** と Rh(I)-DPPE 錯体との反応を検討した結果から、(i) 本反応においてもアレンのラセミ化が進行すること、(ii) アザローダサイクル中間体(*S*,*S*)-**8o'**からは β-水素脱離と還元的脱離が進行して二環式アミド(*S*,*S*)-**9o** および環化体(*S*,*S*)-**10o** を与えること、(iii) アザローダサイクル中間体(*R*,*S*)-**8o'**からは選択的に β-水素脱離が進行して二環式アミド(*R*,*S*)-**9o** を与えることが明らかとなった。

なお、単一のジアステレオマーである(*S*,*S*)-**6o** および(*R*,*S*)-**6o** を反応させた場合の収率を平均したものは、ジアステレオマー混合物の **6o** を用いた場合の収率およびジアステレオ比と良い一致を示している [(Table 8, Entry 3, p. 36) vs (Table 9, Entry 3, p. 39); (Table 8, Entry 4, p. 36) vs (Table 10, Entry 3, p. 43)]。

****

*[15] 基質 **6o** は文献既知のアルデヒド **1o**[29] と *t*-ブタンスルフィンアミドから合成した (Scheme 44)。

Scheme 44



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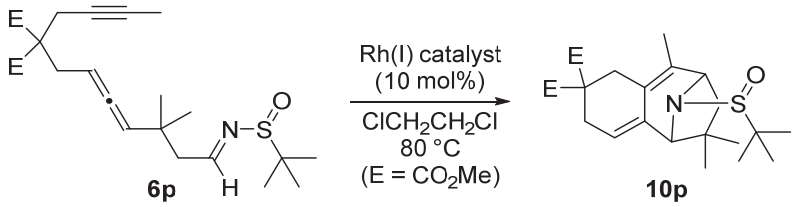
*[16] さらに基質の適用範囲を精査するべく、イミンの β 位にジメチル基を導入した 1,6-アレン-イン **6p** を基質として用い、Rh(I)錯体との反応を検討した (Table 11)*[20]。まず、[Rh(dppp)]ClO_4 錯体を用いて反応を行ったが、反応は進行せず環化体 **10p** は全く得られなかった (Entry 1)。そこで、[Rh(*rac*-binap)]ClO_4 錯体を用いて反応を行ったが複雑な混合物を与え、環化体 **10p** は全く得られなかった (Entry 2)。一方、[Rh(dppbz)]ClO_4 錯体および [Rh(dppe)]ClO_4 錯体を用いて反応を行ったところ、環化体 **10p** が中程度の収率で得られた (Entries 3 and 4)。

Table 11

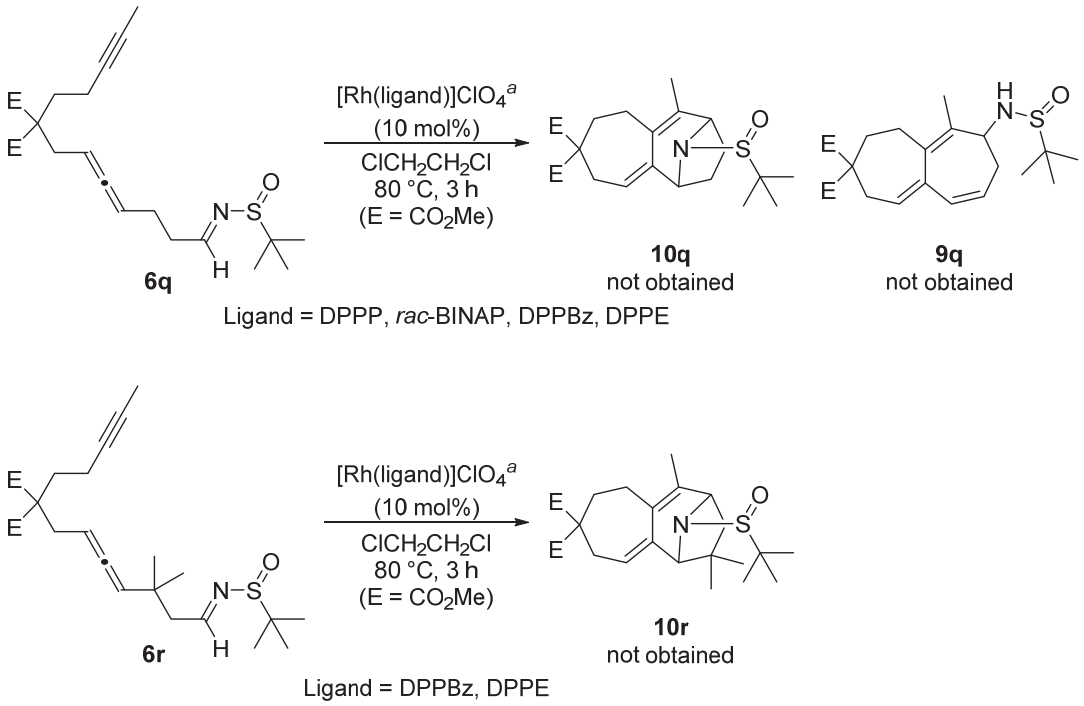


Entry	Rh(I) catalyst[a]	Time (h)	Yield (%)[b]	
			10p	rec. **6p**
1	[Rh(dppp)]ClO_4	3	-	66
2	[Rh(*rac*-binap)]ClO_4	1	-	-[c]
3	[Rh(dppbz)]ClO_4	3	38	-
4	[Rh(dppe)]ClO_4	3	41	-

[a][Rh(ligand)]ClO_4 was generated from [Rh(ligand)(nbd)] ClO_4 and H_2 in $ClCH_2CH_2Cl$. [b] The product **10p** was obtained as a diastereomixture. See the experimental section for the detail. [c]The complex mixture was obtained.

続いて、アレンとアルキン間の炭素数がもう一つ多い 1,7-アレン-イン **6q** および **6r** を基質として用い Rh(I)錯体との反応を検討したが、原料が回収されるか複雑な混合物を与えるのみで、環化体 **9q**、**10q** および **10r** は得られなかった (Scheme 45)*[21]。

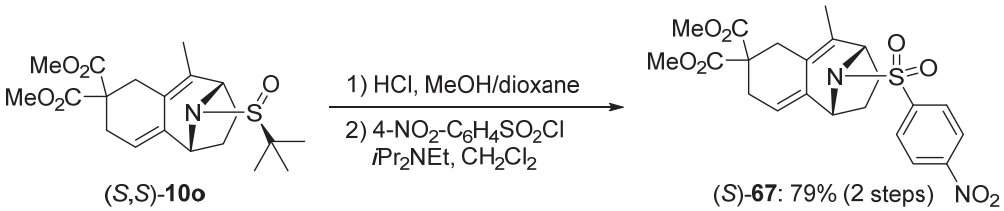
Scheme 45

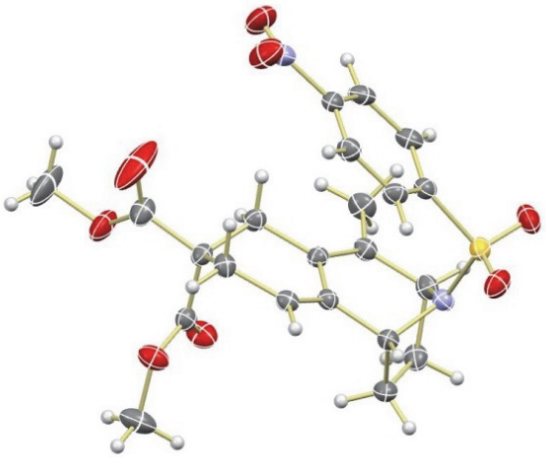


[a][Rh(ligand)]ClO_4 was generated from [Rh(ligand)(nbd)] ClO_4 and H_2 in $ClCH_2CH_2Cl$.

*[17] 環化体(*S*,*S*)-**10o** の絶対配置は *t*-ブタンスルフィニル基を脱保護した後、4-ニトロベンゼンスルホニルクロリドと反応させることで得られた(*S*)-**67** の単結晶 X 線結晶構造解析により決定した (Scheme 46)

Scheme 46





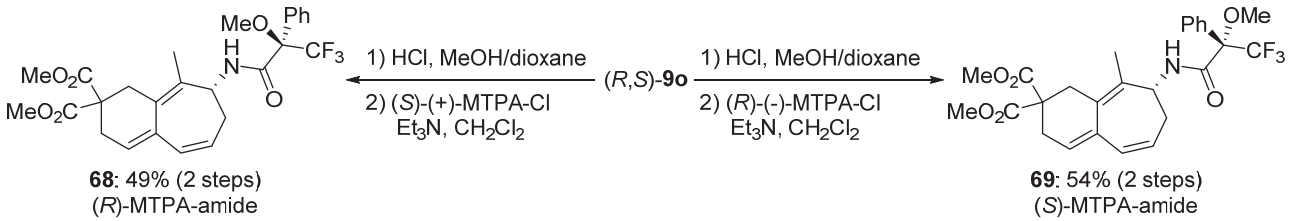
(*S*)-**67**

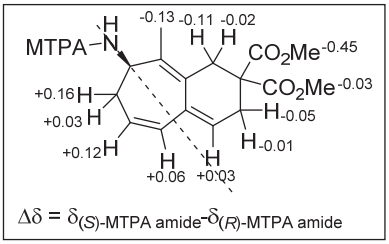
<Crystal Data>

Crystal System	orthorhombic
Space Group	$P2_12_12_1$ (#19)
Lattice Parameters	a = 8.1516(4) Å
	b = 8.9362(3) Å
	c = 29.836(1) Å
	V = 2173.4(2) Å^3
R1 (I>2.00σ(I))	0.0466
R1 (All reflections)	0.0523
wR2	0.1468
GOF	1.015
Flack Parameter	-0.02(9)

二環式アミド(*R*,*S*)-**9o** の絶対配置は、*t*-ブタンスルフィニル基を脱保護した後に(*S*)-MTPA-Cl および(*R*)-MTPA-Cl を用いて MTPA アミド **68** および **69** へと誘導化し、改良 Mosher 法を適用して決定した (Scheme 47)[30]。

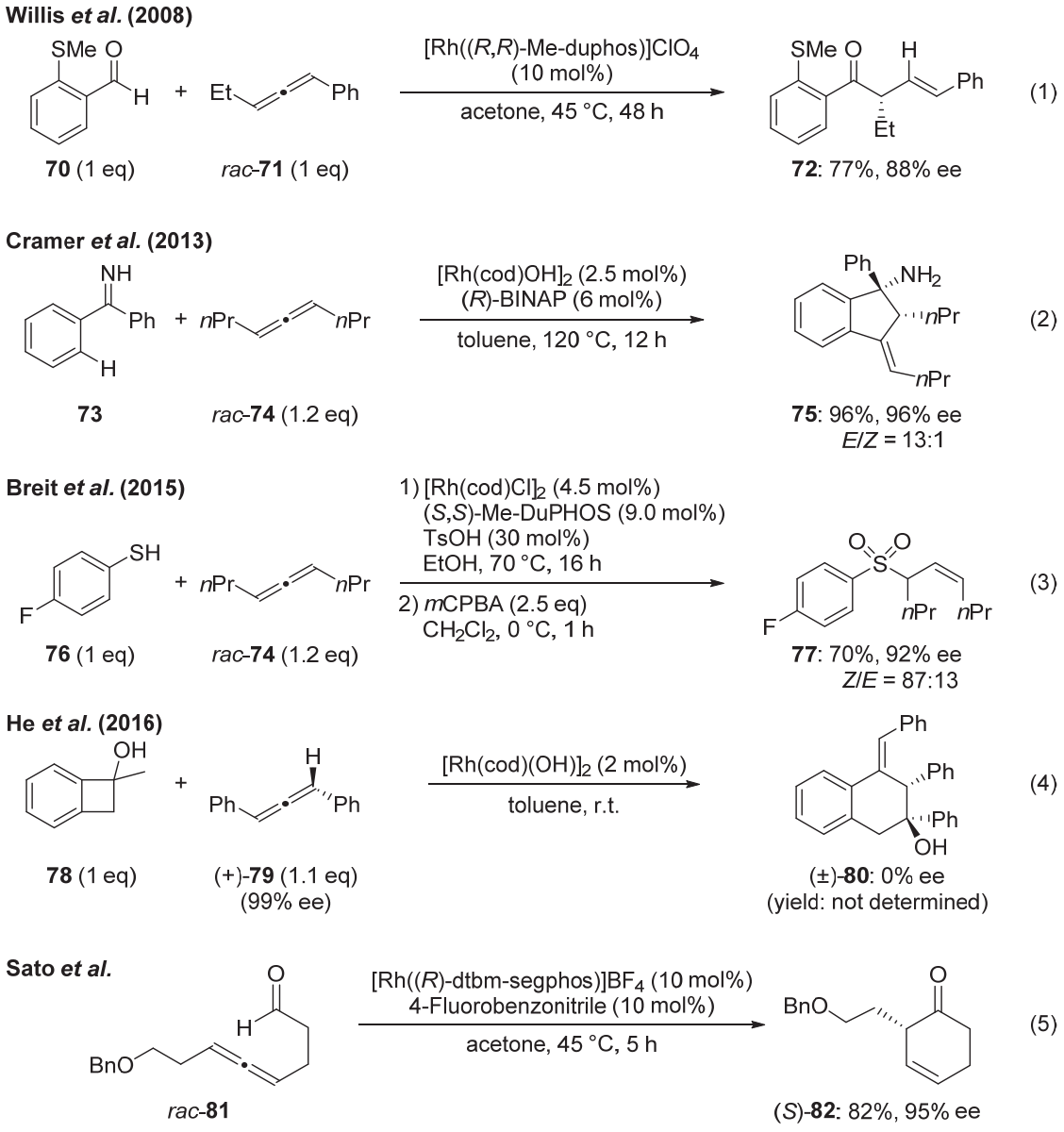
Scheme 47





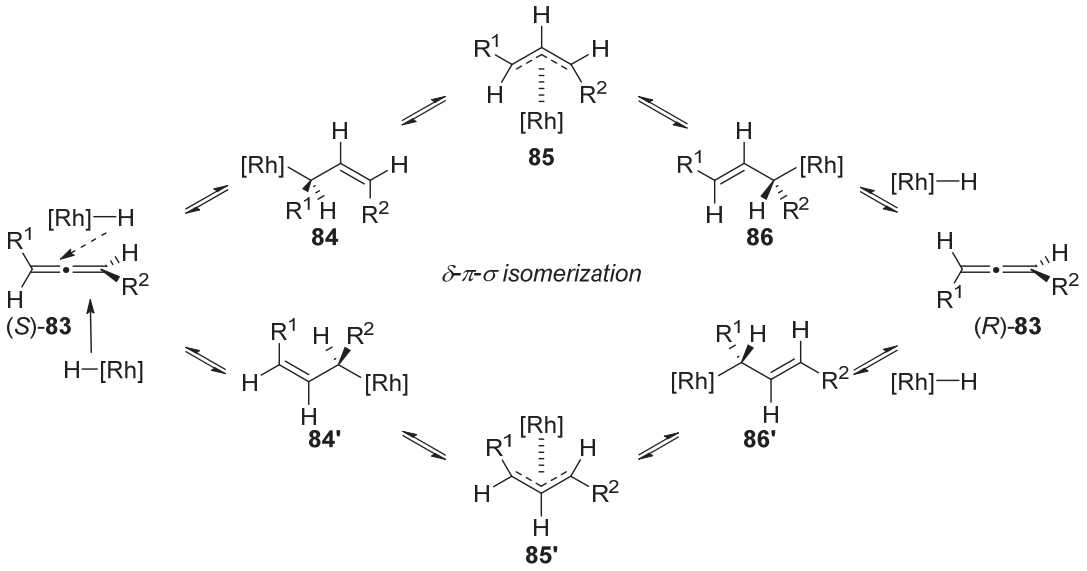
*[18]Rh 触媒を用いる反応でアレンのラセミ化を伴う例はいくつか知られている (Scheme 48)。例えば、2008 年に Willis らは、オルト位に硫黄原子を有するベンズアルデヒド **70** とアレン **71** とのエナンチオ選択的なヒドロアシル化反応を報告している (eq. 1)[31a]。2013 年に Cramer らは、Rh(I)触媒によるケチミン **73** とアレン **74** との不斉[3+2]環化付加反応を見出した (eq. 2)[31b]。2015 年に Breit らは、Rh(I)触媒存在下、アレン **74** へのチオール **76** の付加反応がエナンチオ選択的に進行することを報告した (eq. 3)[31c]。ごく最近 He らは、光学活性なアレン **79** とベンゾシクロブタノール **78** との反応において、テトラリン誘導体 **80** がラセミ体として得られることを報告した (eq. 4)[31d]。また、当研究室においても、Rh(I)触媒による 4-アレナール **81** の不斉ヒドロアシル化反応が見出されている (eq. 5)[31e]。反応機構に関する検討から、これらの反応はアレンのラセミ化を伴って進行しているものと考えられている。

Scheme 48



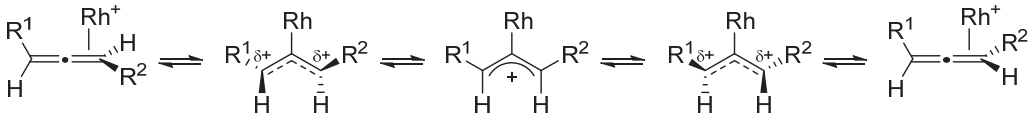
Cramer らは、アレンのラセミ化に Rh-ヒドリド種が関与していると提唱した[31b]。すなわち、Rh-ヒドリド錯体へのアレンの挿入、π-アリルロジウム中間体 **85** (または **85'**) を経由する異性化、続くβ-水素脱離によってアレンのラセミ化が進行すると報告されている (Scheme 49)。

Scheme 49



筆者が見出した反応においても水素ガス雰囲気下で錯体調製を行っていることから、Rh-ヒドリド種が系内に存在しており、Cramer らと同様の機構でアレンのラセミ化が進行している可能性が考えられる。また、アレンの二重結合が Rh(I)錯体によって活性化されカチオン性中間体 **88** を生じ、この中間体を経由してアレンのラセミ化が進行している可能性も考えられる (Scheme 50)[32]。

Scheme 50



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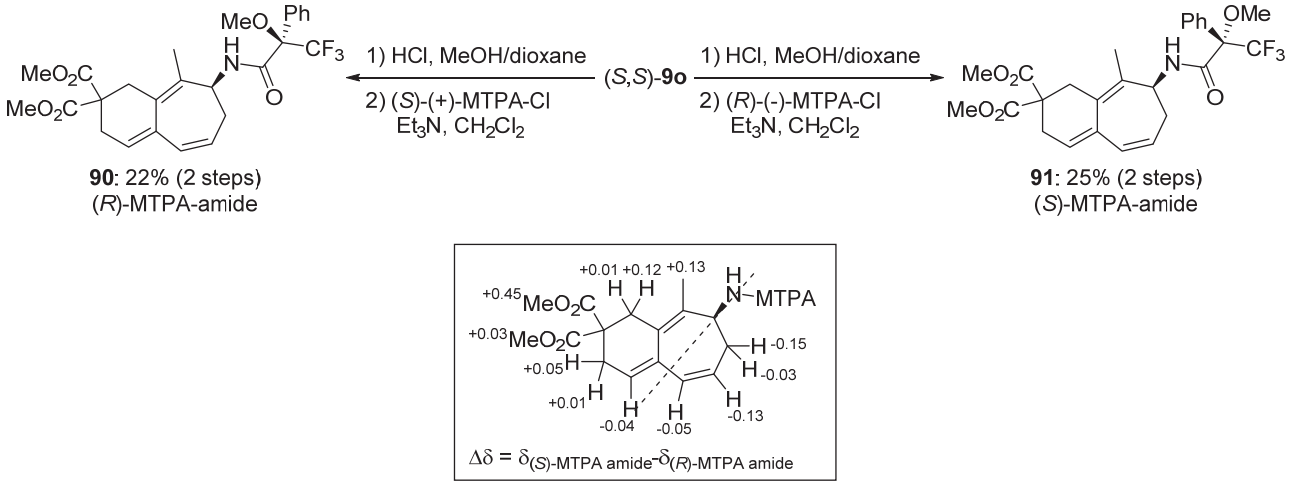
*[19] 二環式アミド(*S*,*S*)-**9o** の絶対配置は、*t*-ブタンスルフィニル基を脱保護した後に(*S*)-MTPA-Cl および(*R*)-MTPA-Cl を用いて MTPA アミド **90** および **91** へと誘導化し、改良 Mosher 法を適用して決定した (Scheme 51)[30]。

Scheme 51



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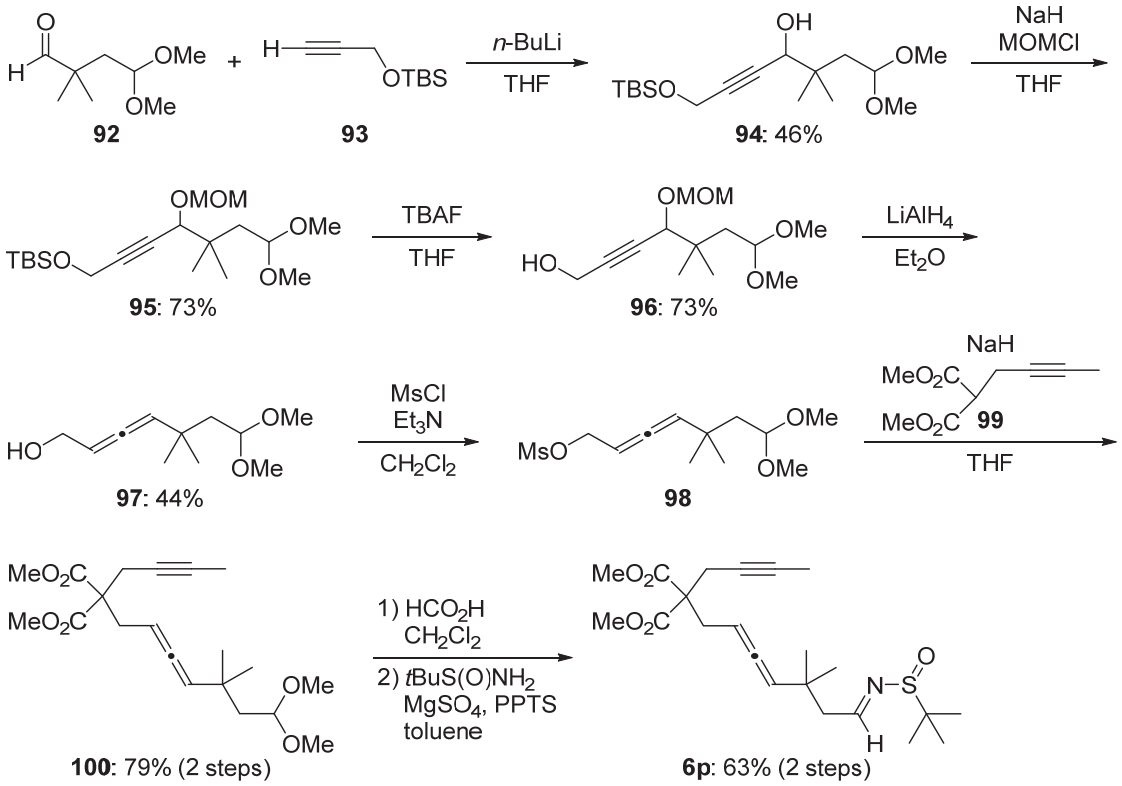
*[20] 基質 **6p** は以下に示す方法によって合成した (Scheme 52)。文献既知の末端アルキン **93**[33] と *n*-BuLi からアセチリドを発生させ、文献既知のアルデヒド **92**[34] と反応させた。生じたアルコールを MOM 基で保護した後に TBS 基を脱保護した。**96** を $LiAlH_4$ と反応させることによりアレン **97** へと変換した後、ヒドロキシ基をメシル化した。これを文献既知の **99**[35] とカップリングさせ、ジメチルアセタールの脱保護、続く *t*-ブタンスルフィンアミドとの脱水反応によって **6p** へと導いた。

Scheme 52



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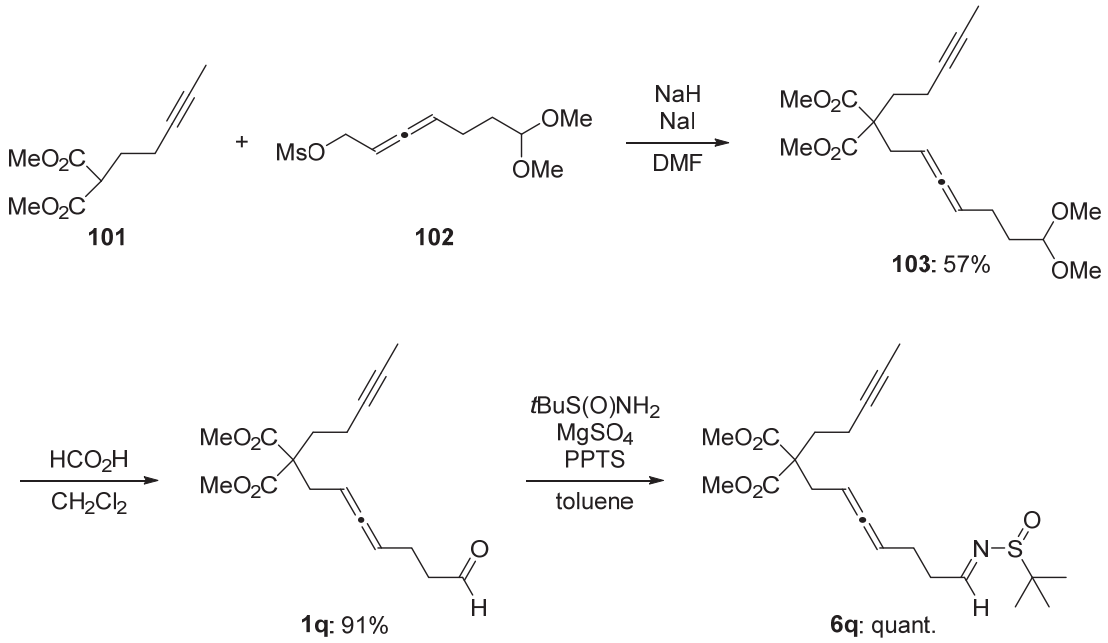
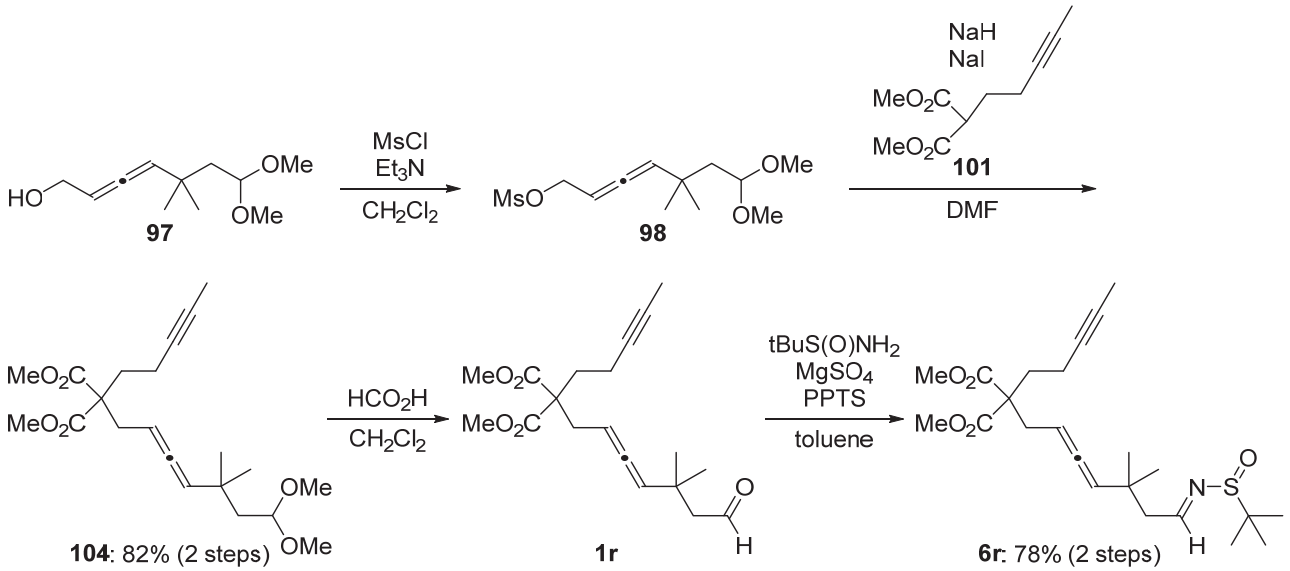
*[21] 基質 **6q** は以下に示す方法によって合成した (Scheme 53)。文献既知の **101**[36] とメシル体 **102**[29] をカップリングさせ **103** を得た。その後、ジメチルアセタールを脱保護し、*t*-ブタンスルフィンアミドとの脱水反応を行うことで **6q** へと導いた。

Scheme 53



基質 **6r** は以下に示す方法によって合成した (Scheme 54)。**97** をメシル化した後、文献既知の **101**[36] とカップリングさせた。その後、ジメチルアセタールを脱保護し、*t*-ブタンスルフィンアミドとの脱水反応を行うことで **6r** へと導いた。

Scheme 54



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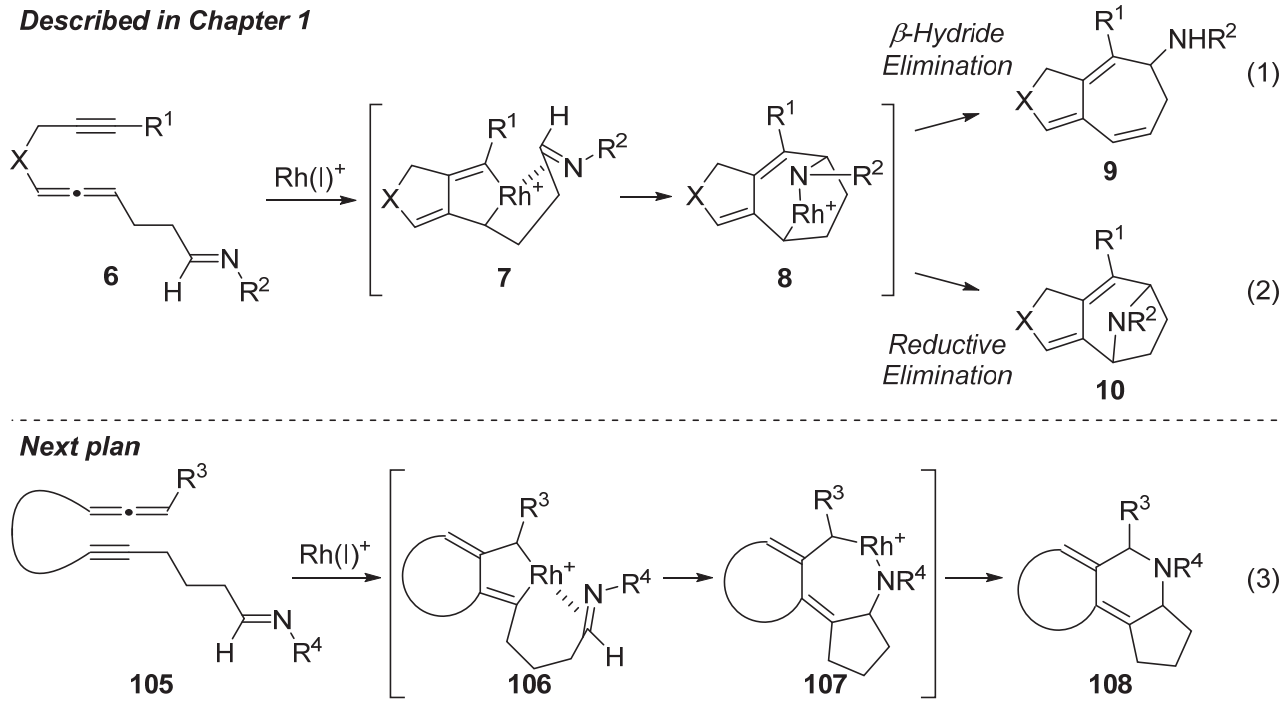
第二章　Rh(I)触媒によるアルキン、アルケンおよびイミン間でのジアステレオ選択的な分子内環化反応

第一節　新たな分子内[2+2+2]環化付加反応の開発を指向した初期検討

第一章で述べたとおり、分子内にイミンを有するアレン-イン **6** と Rh(I)錯体との反応を検討した結果、アザローダサイクル中間体 **8** からの β-水素脱離および還元的脱離を経由する反応を新たに見出した (Scheme 55, eq. 1 and 2)。本反応はイミンを多重結合の一つとして用いる分子内[2+2+2]環化付加反応の初めての例であり、含窒素環状化合物の効率的な合成を可能にすることから、本反応の更なる研究展開に興味が持たれる。

そこで筆者は、新たな含窒素複素環骨格の構築を指向し、**6** のアルキンとアレンの位置関係を反対にした基質 **105** を用いて[2+2+2]環化付加反応が進行する可能性を検討することとした (Scheme 55, eq. 3)。本反応では、まず基質 **105** のアルキンとアレンが Rh(I)錯体に酸化的環化付加し、ローダシクロペンテン中間体 **106** が生成する。続いて、この中間体 **106** に側鎖のイミンが挿入するならば、アザローダサイクル中間体 **107** が形成される。最後に、このものからの還元的脱離により三環式複素環化合物 **108** が生成すると考えた*[22]。

Scheme 55

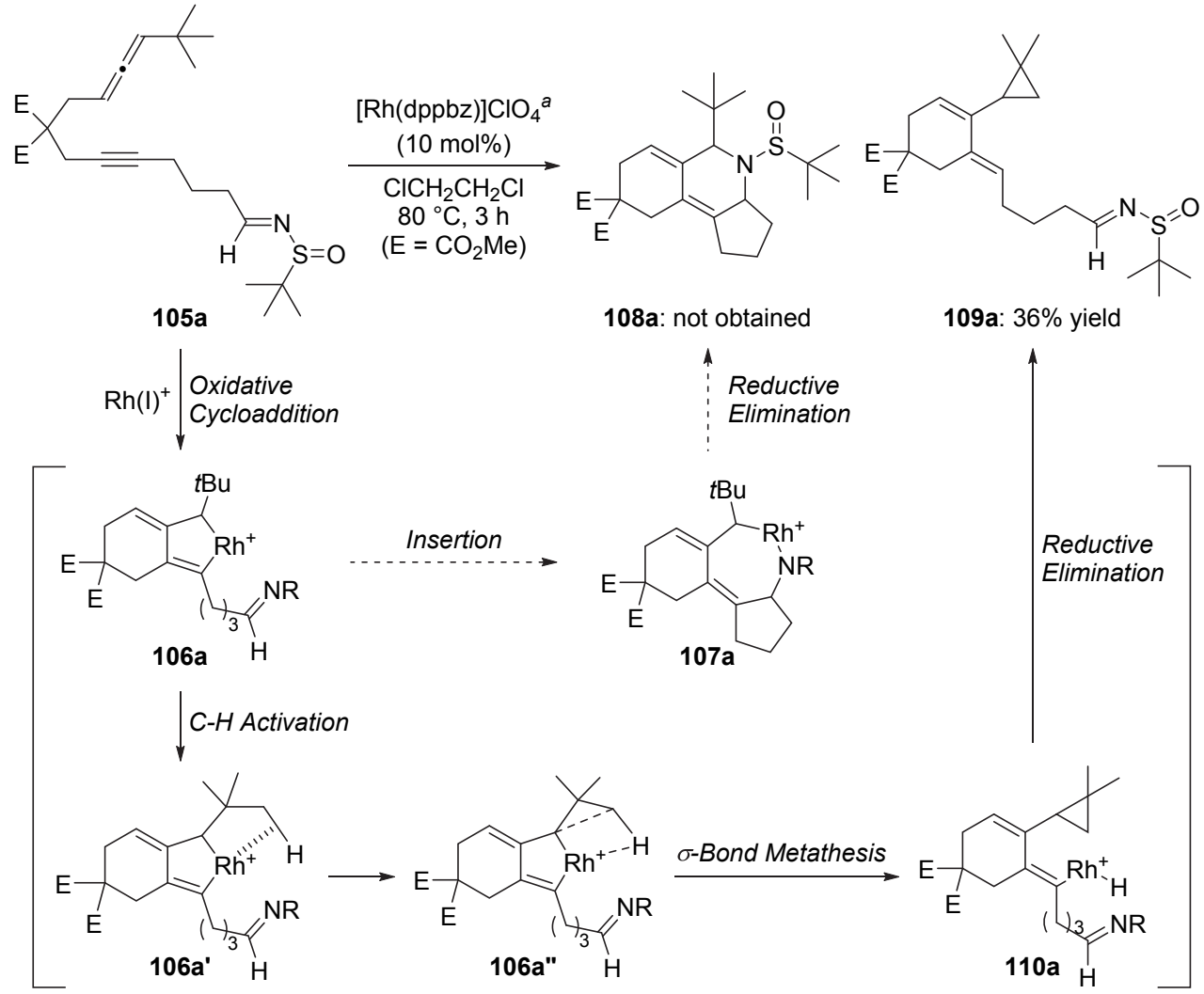


まず、アレン上に *t*-ブチル基が置換した基質 **105a** と Rh(I)錯体との反応を検討した (Scheme 56)*[23]。これまでの反応で良好な結果を示した[Rh(dppp)]ClO_4 および[Rh(*rac*-binap)]ClO_4 錯体を用いて反応を行ったが、複雑な混合物を与えるのみで目的の環化体 **108a** は全く得られなかった。一方、[Rh(dppbz)]ClO_4 錯体を用いて反応を行ったところ目的とする環化体 **108a** は得られなかったが、シクロプロパン構造を有する環化体 **109a** が 36%の収率で生成していることが確認された。

この環化体 **109a** は次のような反応機構で生成したものと考えられる。まず、基質 **105a** のアルキンとアレンが Rh(I)錯体に酸化的環化付加し、ロータシクロペンテン中間体 **106a** が生成する。次に、Rh 原子に近接した *t*-ブチル基の C(sp^3)-H 結合が活性化され、**106a"**のような遷移状態を経て σ 結合メタセシスが進行し、ロジウムヒドリド中間体 **110a** が形成される。最後に、この中間体 **110a** からの還元的脱離が進行して環化体 **109a** が生成する*[24]。

この結果から、*t*-ブチル基を有する基質の場合、ロータシクロペンテン中間体 **106a** への炭素-窒素二重結合の挿入反応と比べて、中間体 **106a** からの σ 結合メタセシスの方が有利であることが明らかとなった。

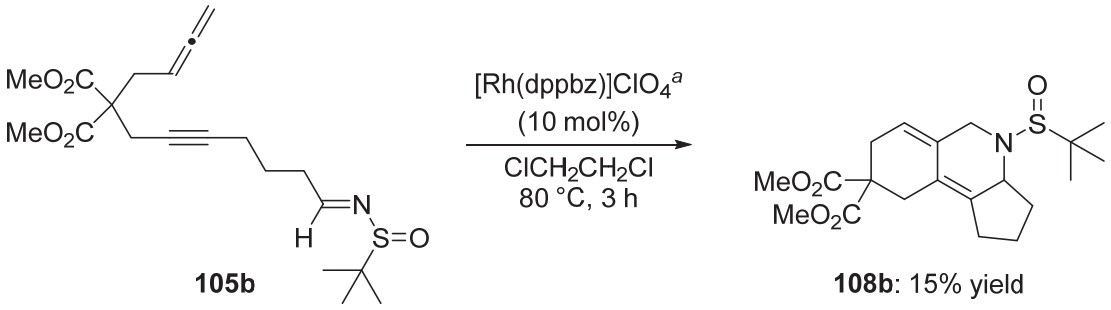
Scheme 56



[a][Rh(ligand)]ClO_4 was generated from [Rh(ligand)(nbd)]ClO_4 and H_2 in $ClCH_2CH_2Cl$.

この結果から筆者は、アレン上に *t*-ブチル基を持たない基質で反応を行うならばσ結合メタセシスを経由する副反応はおこらず、望みの[2+2+2]環化付加反応が進行するのではないかと考えた。実際に、末端アレン構造を有する基質 **105b** を合成し[Rh(dppbz)]ClO_4 錯体との反応を行ったところ、予想どおり目的の環化体 **108b** が低収率ではあるものの生成していることが確認された(Scheme 57)*[25]。そこで、この環化体 **108b** の収率の向上を目指して、[Rh(dppp)]ClO_4、[Rh(*rac*-binap)]ClO_4 など種々の Rh(I)錯体との反応を試みたが、多くの場合で反応系が複雑となり環化体 **108b** はいずれも低収率にとどまった。

Scheme 57



([Rh(dppp)]ClO_4,[a] [Rh(*rac*-binap)]ClO_4:[a] not effective)

[a][Rh(ligand)]ClO_4 was generated from [Rh(ligand)(nbd)]ClO_4 and H_2 in $ClCH_2CH_2Cl$.

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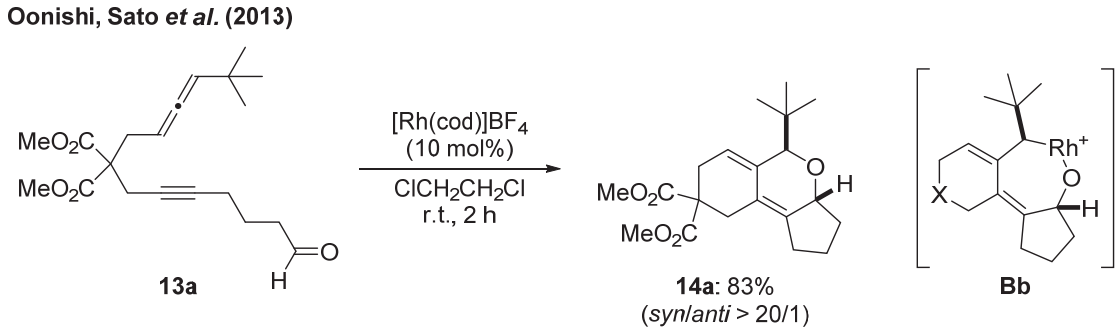
*[22] 当研究室では、イミンの代わりにアルデヒドを有する同様の基質 **13a** と Rh(I)触媒との[2+2+2]環化付加反応により、ジヒドロピランを含む三環式化合物 **14a** が良好な収率かつ高ジアステレオ選択的に生成することを報告している (Scheme 58)[20b]。

Scheme 58 (cf. Scheme 15, p. 14)



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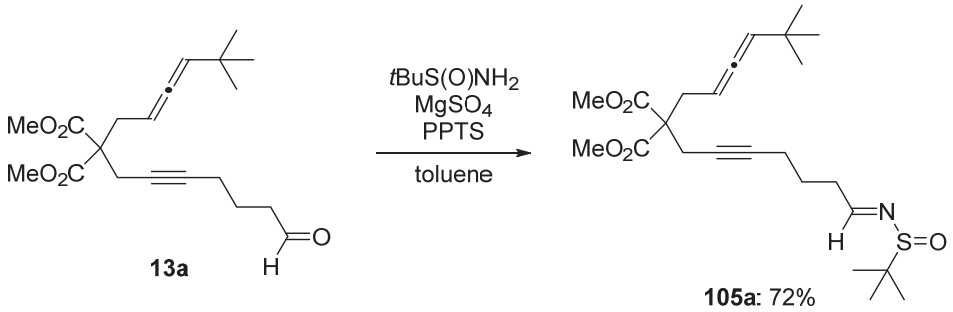
*[23] 基質 **105a** は文献既知のアルデヒド **13a**[20b] と *t*-ブタンスルフィンアミドとの脱水反応により合成した (Scheme 59)。

Scheme 59



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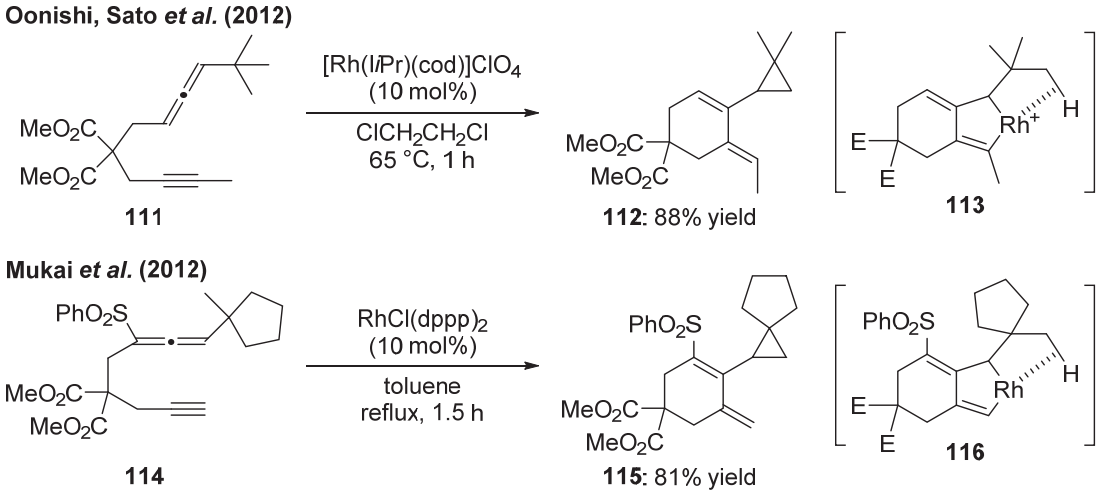
*[24] ローダサイクル中間体において同様の C-H 結合の活性化を経由する反応は、これまでに以下の二例が報告されている (Scheme 60)。2012 年に当研究室では、アレン上に *t*-ブチル基を有するアレン-イン **111** と NHC 配位子を有する Rh(I)錯体との反応により、シクロプロパン構造を有する環化体 **112** が良好な収率で生成することを報告した [37a]。また、ほぼ同時期に向らは、アレニルシクロペンタンおよびアルキンを分子内に有する基質 **114** と Rh(I)錯体とを反応させると、同じくシクロプロパン構造を有する環化体 **115** が得られることを報告した [37b]。これらの反応ではローダサイクル中間体が Directing Group としての役割を果たす。すなわち、ローダサイクル中間体を形成した際、Rh 原子に近接した位置に存在する C-H 結合が選択的に活性化され反応が進行する。

なお、これらの反応に関して DFT 計算により反応機構の解明を試みた研究が Huang によって報告されている[38]。

Scheme 60



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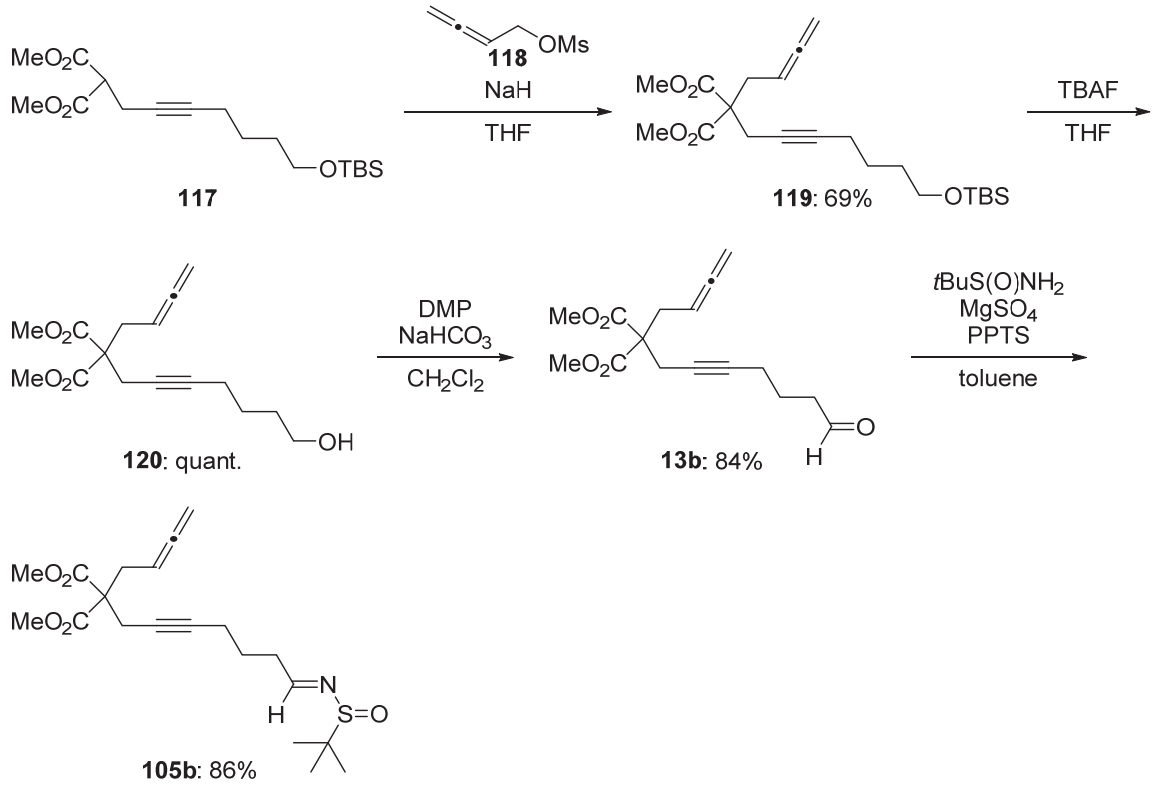
*[25] 基質 **105b** は以下に示す方法によって合成した (Scheme 61)。文献既知の **117**[20b] とメシル化体 **118**[39] をカップリングさせた後、TBS 基を脱保護した。続いて、Dess-Martin 酸化、*t*-ブタンスルフィンアミドとの脱水反応を行うことで **105b** へと導いた。

Scheme 61



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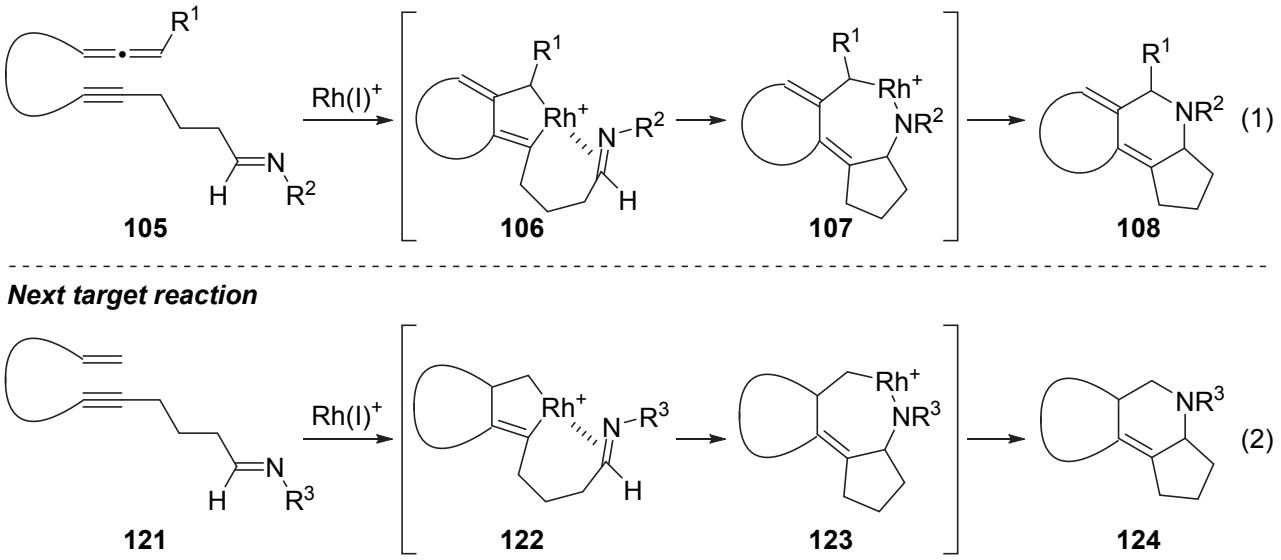
第二節　アルキン、アルケンおよびイミン間での分子内環化反応

前節で述べたように、アレン-イン **105** を基質として用いRh(I)錯体との反応を検討したが、多くの場合で複雑な混合物を与えるなど望みとする[2+2+2]環化付加反応が効率的に進行しなかった (Scheme 62, eq. 1)。筆者はアレンの反応性の高さがその原因であると考え、次にアレンを環化付加反応においてより反応性が低いとされるアルケンに代えた基質 **121** を用いてRh(I)錯体との反応を検討することとした (eq. 2)。なお、アルキン、アルケンおよびイミン間での[2+2+2]環化付加反応はこれまでのところ報告されていない。

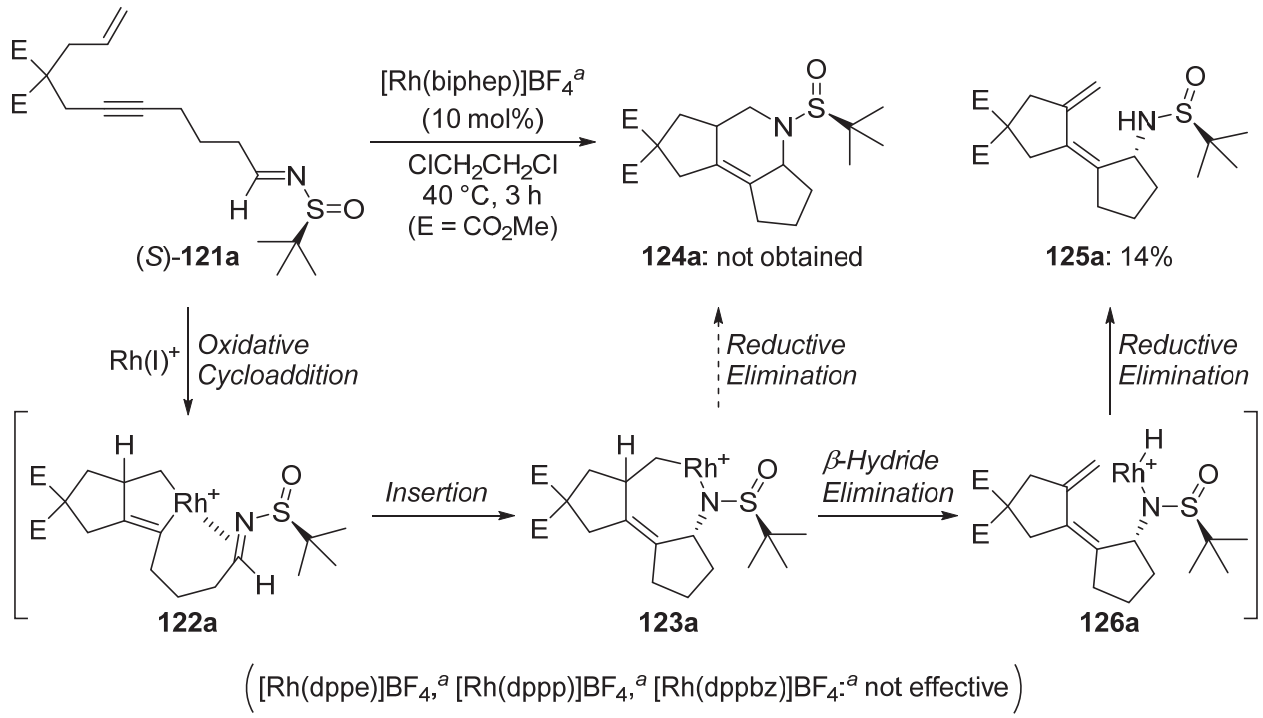
Scheme 62



まず、(*S*)-*t*-ブタンスルフィニル基を有するエン-イン(*S*)-**121a** を基質として用い、配位子の検討を行った (Scheme 63)*[26]。[Rh(dppe)]BF_4、[Rh(dppp)]BF_4および[Rh(dppbz)]BF_4錯体を用いて反応を行ったが、全く反応は進行せず原料が回収された。一方、[Rh(biphep)]BF_4 錯体を用いて反応を行ったところ、目的の環化体 **124a** は得られないものの、五員環化合物 **125a** が単一の立体異性体として生成していることが確認された*[27]。この五員環化合物 **125a** は次のような反応機構で生成していると考えられる。まず、基質(*S*)-**121a** のアルケンとアルキンがロジウム錯体に酸化的環化付加し、ローダサイクル中間体 **122a** が生成する。続いて、分子内のイミンの挿入が起こりアザローダサイクル中間体 **123a** が形成される。この中間体 **123a** から還元的脱離が起こると目的の環化体 **124a** を与えるが、本反応では中間体 **123a** からのβ-水素脱離が選択的に進行し、続く還元的脱離

を経て五員環化合物 **125a** が生成したものと考えられる*[28]。

Scheme 63



[a][Rh(ligand)]BF_4 was generated from [Rh(cod)$_2$]BF_4, ligand and H_2 in $ClCH_2CH_2Cl$.

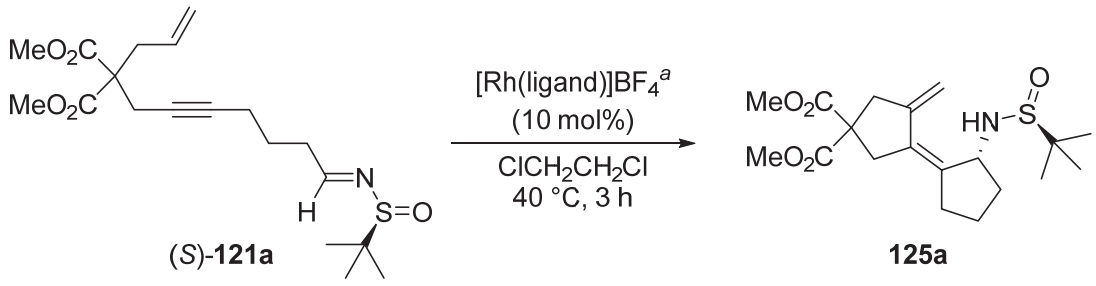
このように、エン-イン(*S*)-**121a** と[Rh(biphep)]BF_4 錯体との反応を検討した結果、当初想定していた環化付加体 **124a** は得られなかったものの、アザローダサイクル中間体を経由すると考えられる新たな反応を見出すことができた。本反応はジアステレオ選択的に進行し、五員環化合物 **125a** を単一の立体異性体として与えるといった特徴を有している。そこで、この五員環化合物 **125a** の収率の向上を目指して、さらに配位子の検討を行うことにした。

BIPHEP の場合に低収率ながらも環化体 **125a** が生成したことから、BIPHEP と同様にビアリール骨格を有する BINAP 系配位子を用いて検討を行った (Table 12)。*R* 体の絶対配置を有する BINAP 系配位子を用いて反応を行ったところ、ほとんど反応は進行せず原料が残存した (Entries 1-4)。一方、*S* 体の配位子を用いた場合にはすみやかに反応が進行し (Entries 5-8)、特に (*S*)-H_8-BINAP の場合には 88%と良好な収率で五員環化合物 **125a** を与えた (Entry 8)。

次に、テトラフルオロボラートの代わりにパークロラートを対アニオンとする [Rh((*S*)-H_8-binap)]ClO_4 錯体を用いて反応を行った (Entry 9)。その結果、環化体 **125a** が良好な収率で生成し、[Rh((*S*)-H_8-binap)]BF_4 錯体の場合と比較して反応性に大きな差は見られなかった

(Entry 8 vs 9)。

Table 12



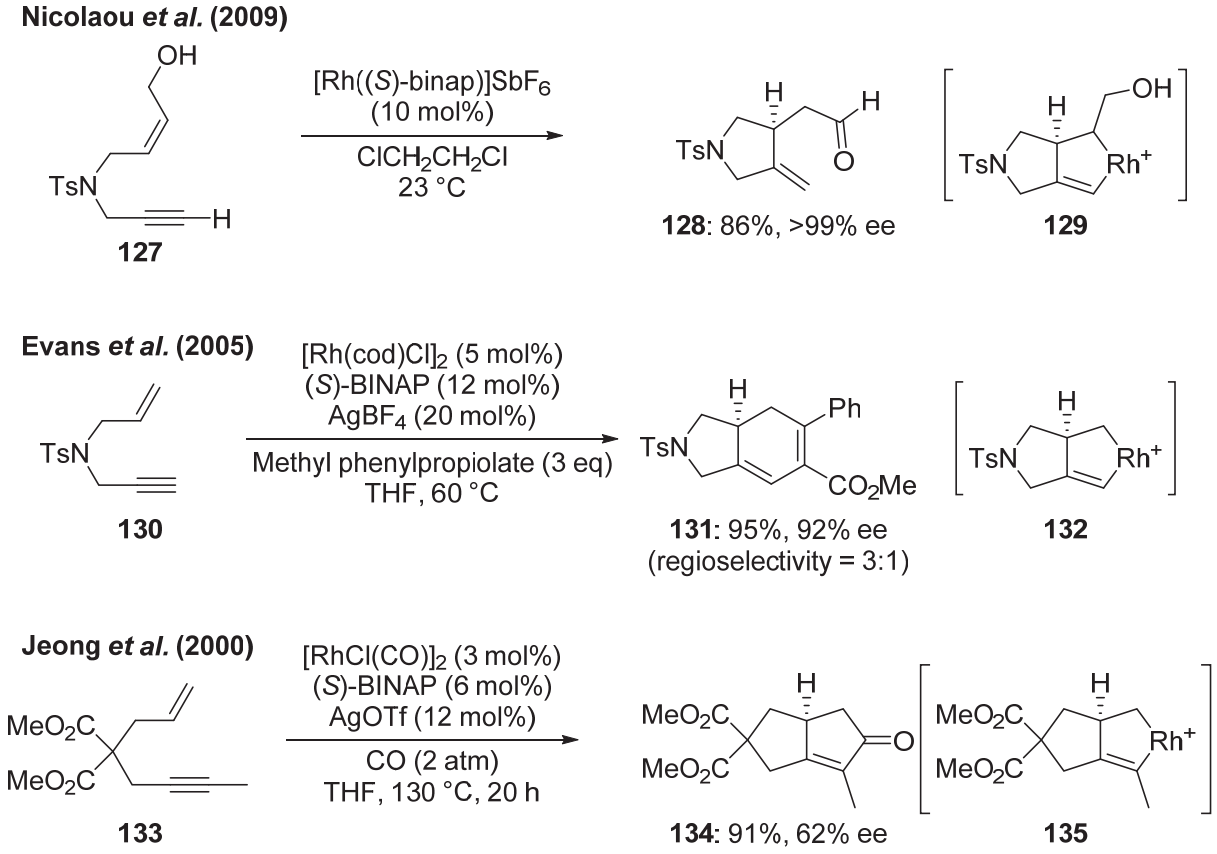
Entry	Ligand	Yield (%)		Entry	Ligand	Yield (%)	
		125a	rec. **121a**			**125a**	rec. **121a**
1	(*R*)-BINAP	-	97	5	(*S*)-BINAP	57	-
2	(*R*)-Tol-BINAP	2	97	6	(*S*)-Tol-BINAP	53	-
3	(*R*)-Xyl-BINAP	-	97	7	(*S*)-Xyl-BINAP	60	35
4	(*R*)-H_8-BINAP	2	93	8	(*S*)-H_8-BINAP	88	<5
				9[b]	(*S*)-H_8-BINAP	78	-

[a]$[Rh(ligand)]BF_4$ was generated from $[Rh(cod)_2]BF_4$, ligand and H_2 in $ClCH_2CH_2Cl$. [b]$[Rh((S)\text{-}H_8\text{-binap})]ClO_4$ was used. $[Rh((S)\text{-}H_8\text{-binap})]ClO_4$ was generated from $[Rh(cod)_2]ClO_4$, (*S*)-H_8-BINAP and H_2 in $ClCH_2CH_2Cl$.

ここまでの検討により、(i) エン-イン(*S*)-**121a** と Rh(I)錯体との反応がジアステレオ選択的に進行し環化体 **125a** を与えること、また、(ii) BINAP 系配位子を用いた場合、その絶対配置によって反応性が大きく変化することが明らかとなった。次に、これらの現象が起こる理由について考察を行った。

これまでに、光学活性な BINAP 系配位子を有する Rh(I)錯体による 1,6-エン-インの不斉環化反応はいくつか報告されている (Scheme 64)[40]。これらの反応では、基質のアルケンとアルキンが Rh(I)錯体に酸化的環化付加し、ローダシクロペンテン中間体が形成される。この際、*S* 体の BINAP 系配位子を用いた場合は、一貫して Scheme 64 に示した立体化学のローダシクロペンテン中間体 (**129**, **132** and **135**) を経由して反応が進行すると報告されている。

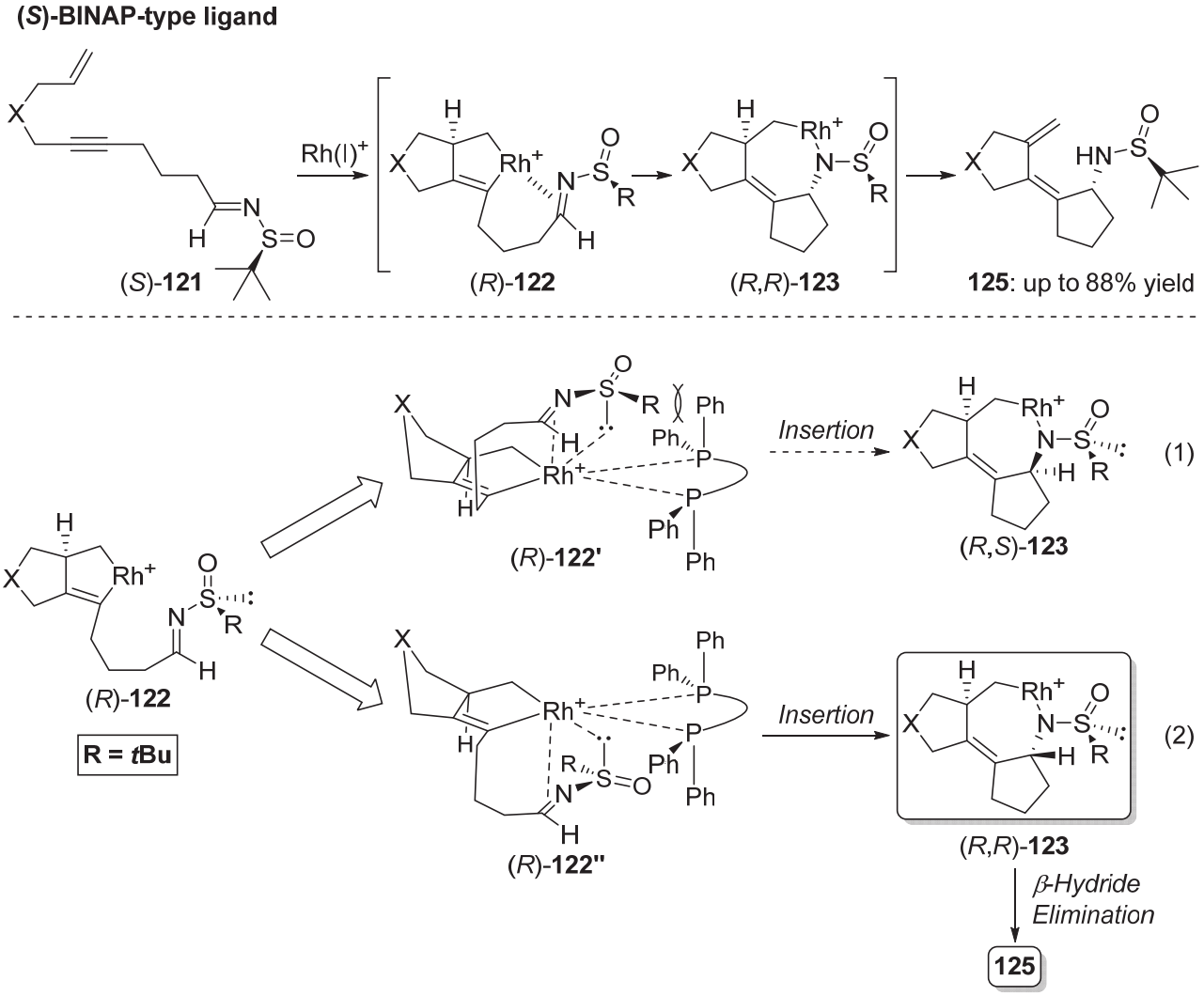
Scheme 64



したがって、エン-イン(*S*)-**121a**とRh(I)錯体との反応においても、*S*体のBINAP系配位子を用いた場合、同様の立体化学を有するローダシクロペンテン中間体(*R*)-**122** を経由して反応が進行するものと考えられる (Scheme 65)。

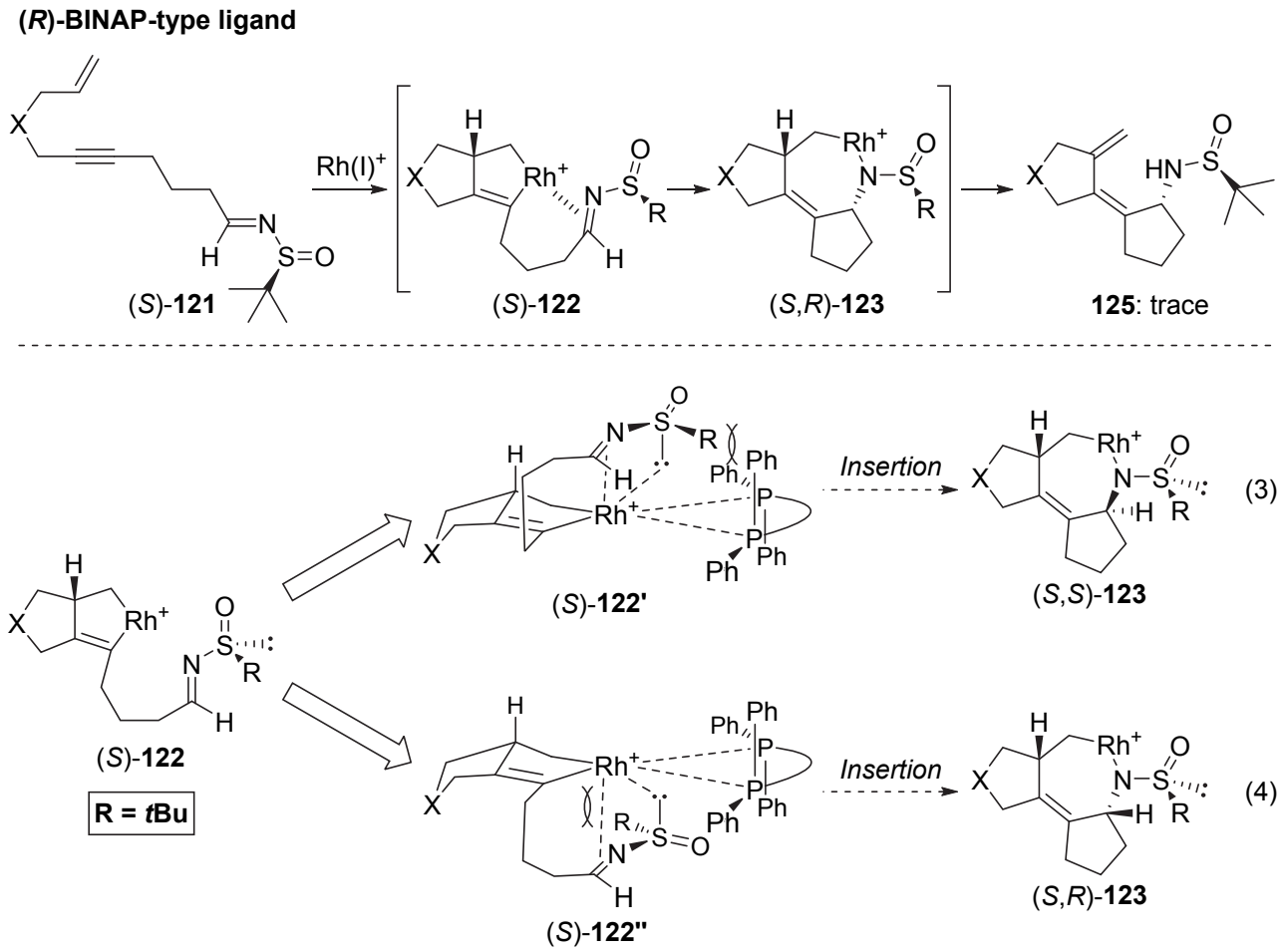
このRh(III)中間体(*R*)-**122**は平面四配位構造をとり、イミンの挿入はそのアピカル位で進行する。この際、電子的な要因から、イミンの二重結合の π 電子とスルフィニル基の硫黄原子上の非共有電子対がともに Rh 原子に接近するようにして挿入反応が進行するものと考えられる。すなわち、硫黄原子上の非共有電子対が Rh 原子に配位しつつイミンがアピカル位に接近すると、(*R*)-**122'** および(*R*)-**122"**の二通りの遷移状態を経由すると考えられる。このとき、(*R*)-**122'**においては、かさ高い *t*-ブチル基とBINAP配位子との間に立体障害が生じる (Scheme 65, eq. 1)。一方、(*R*)-**122"** の場合は *t*-ブチル基が配位子とは離れた位置に存在するため、立体障害は発生しない (Scheme 65, eq. 2)。その結果、この遷移状態(*R*)-**122"**を経由してイミンがローダサイクル中間体のコンベックス面から挿入し、アザローダサイクル中間体(*R*,*R*)-**123**が形成される。その後、β-水素脱離および還元的脱離を経て環化体 **125** が立体選択的に生成する。

Scheme 65



一方、*R* 体の BINAP 系配位子を用いた場合は、反応がほとんど進行しなかった (Table 12, Entries 1-4)。この結果についても先ほどと同様に考察した (Scheme 66)。まず、この場合には *S* 体の配位子を用いた場合とは逆の立体化学を有するロータシクロペンテン中間体(*S*)-**122** が形成される。続いて、硫黄原子上の非共有電子対が Rh 原子に配位しつつイミンがアピカル位に接近すると、(*S*)-**122'**および(*S*)-**122"**の二通りの遷移状態を経由すると考えられる。(*S*)-**122'**の場合は *t*-ブチル基とBINAP配位子との間に立体障害が発生する (Scheme 66, eq. 3)。一方、(*S*)-**122"**の場合、*t*-ブチル基は配位子とは離れた位置に存在するが、ロータシクロペンテン中間体のコンケーブ面に接近するため立体障害が生じる (Scheme 66, eq. 4)。したがって、*R* 体の配位子を用いた場合はいずれのアピカル位においてもイミンの挿入反応が進行せず、基質(*S*)-**121a** が回収される。

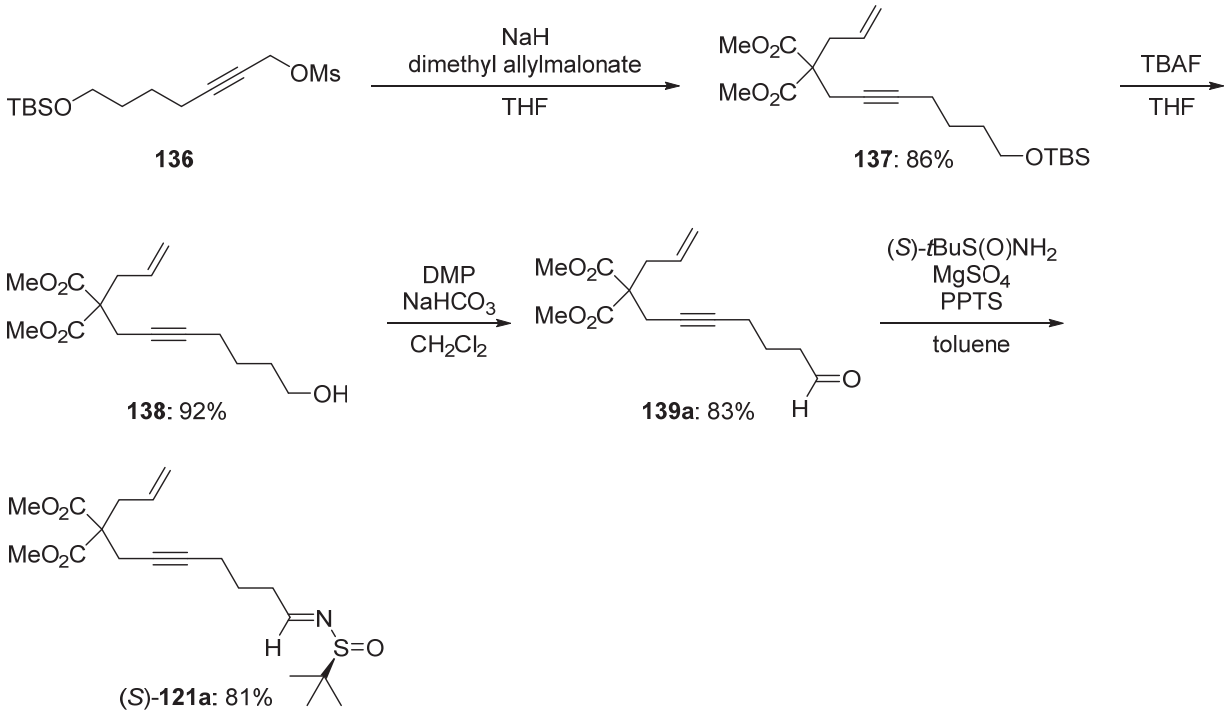
Scheme 66


(R)-BINAP-type ligand
Rh(I)+
(S)-121
(S)-122
(S,R)-123
125: trace
Insertion
(S)-122'
(S,S)-123
(3)
(S)-122
R = tBu
(S)-122''
(S,R)-123
(4)

****

*[26] 基質(*S*)-**121a** は以下に示す方法によって合成した (Scheme 67)。文献既知のメシル化体 **136**[20b] と市販のアリルマロン酸ジメチルをカップリングさせ **137** を得た。**137** の TBS 基を脱保護した後に Dess-Martin 酸化、(*S*)-*t*-ブタンスルフィンアミドとの脱水反応を行うことで(*S*)-**121a** へと導いた。

Scheme 67



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*[27] 環化体 **125a** の絶対配置は 4-ニトロフェニルマレイミドとの Diels-Alder 反応によって得られた化合物 **190ab** の単結晶 X 線結晶構造解析により決定した。その ORTEP 図は第二章第四節 Figure 3 (p. 79) に記載した。

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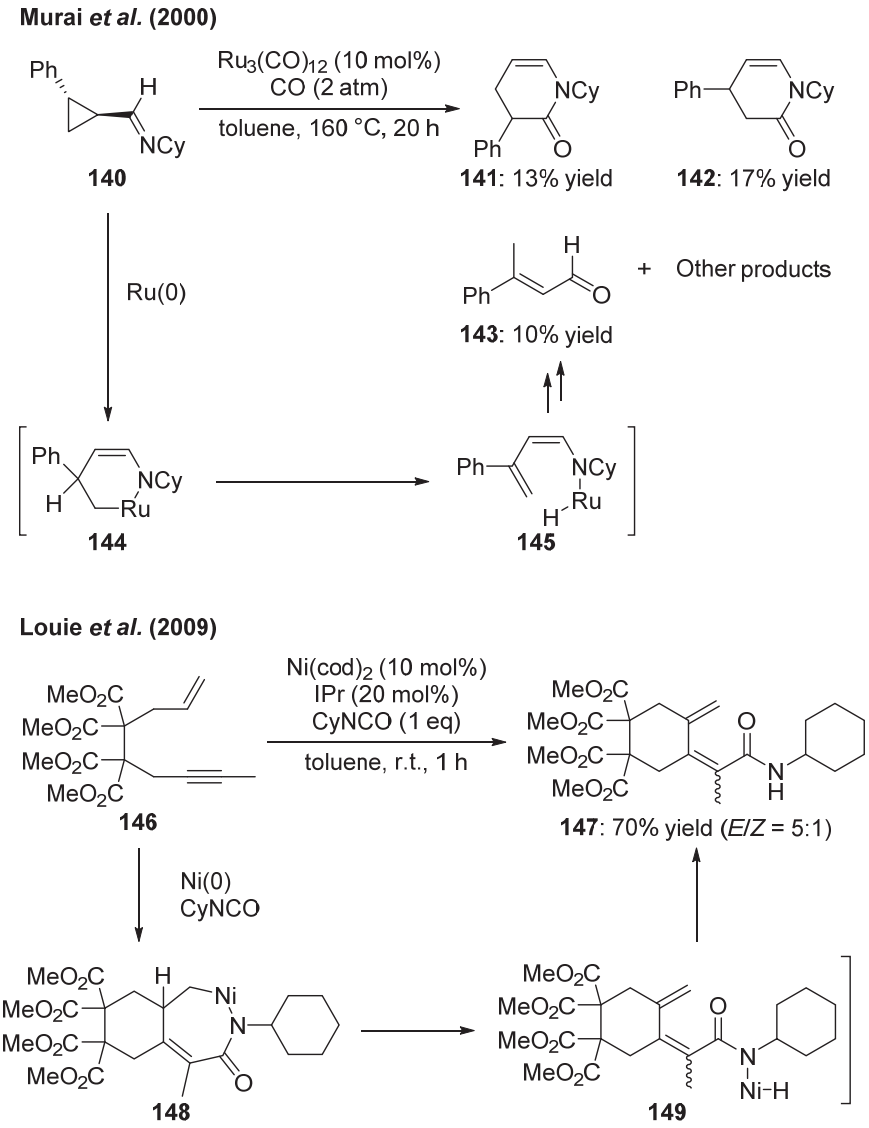
*[28] アザメタラサイクル中間体からの β-水素脱離を経由する形式の反応は以下の二例が報告されている (Scheme 68)。2000 年に村井らは、アザルテナシクロヘキセン中間体 **144** からの β-水素脱離を経由してアルデヒド **143** が得られることを報告している[41a]。また、2009 年に Louie らは、アザニッケラサイクル中間体 **148** からの β-水素脱離を経由してアミド **147** が得られることを報告している[41b]。

Scheme 68

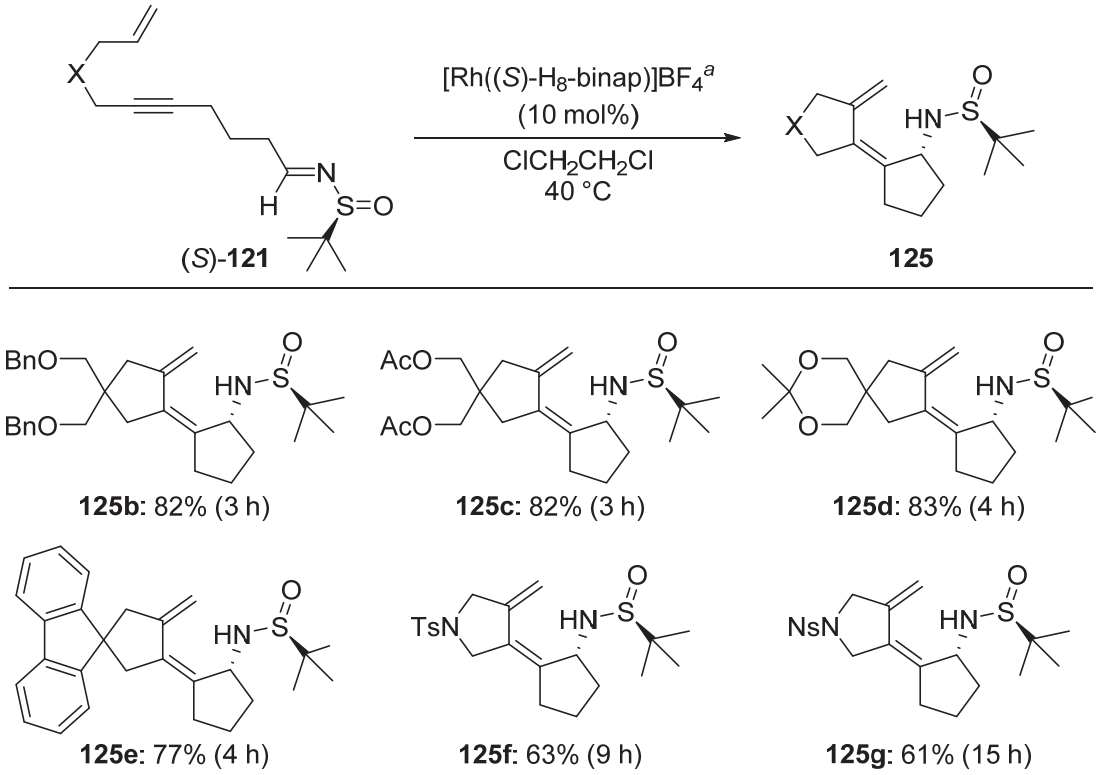

Murai et al. (2000)
Ph
H
NCy
140
Ru3(CO)12 (10 mol%)
CO (2 atm)
toluene, 160 °C, 20 h
NCy
Ph
O
141: 13% yield
Ph
NCy
O
142: 17% yield
Ru(0)
H
Ph
O
143: 10% yield
+ Other products
Ph
NCy
H
Ru
144
Ph
NCy
Ru
H
145
Louie et al. (2009)
MeO2C
MeO2C
MeO2C
MeO2C
146
Ni(cod)2 (10 mol%)
IPr (20 mol%)
CyNCO (1 eq)
toluene, r.t., 1 h
O
N
H
147: 70% yield (E/Z = 5:1)
Ni(0)
CyNCO
H
Ni
N
O
148
N
Ni-H
149

****

第三節　基質適用範囲の検討

前節で配位子の検討を行ったところ、(*S*)-H_8-BINAPを用いた場合に最も良好な結果を与えた。そこで、[Rh((*S*)-H_8-binap)]BF_4錯体を用いて基質適用範囲の検討を行った (Table 13)*[29]。ベンジルオキシ基およびアセトキシ基を有する基質(*S*)-**121b** および(*S*)-**121c** を用いて反応を行ったところ、いずれも良好な収率で対応する環化体 **125b** および **125c** が生成した。また、スピロ構造を有する基質(*S*)-**121d** および(*S*)-**121e** の場合も、環化体 **125d** および **125e** が良好な収率で得られた。スルホンアミド基を有する基質(*S*)-**121f** および(*S*)-**121g** の場合は、中程度の収率で環化体 **125f** および **125g** が生成した*[30,*31]。

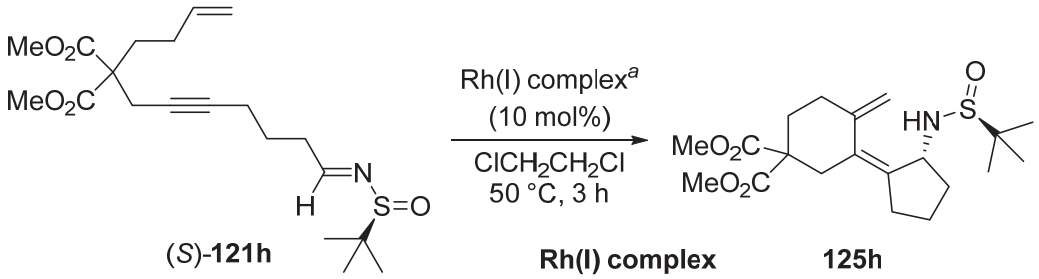
Table 13



[a][Rh((*S*)-H_8-binap)]BF_4 was generated from [Rh(cod)$_2$]BF_4, (*S*)-H_8-BINAP and H_2 in $ClCH_2CH_2Cl$.

次に、多重結合間のリンカーの長さを変えた基質を用いて反応を行った。アルケンとアルキン間の炭素数が一つ多い基質(*S*)-**121h** の場合は原料が残存し、環化体 **125h** の収率は 37%にとどまった (Scheme 69)*[32,*33]。この基質に関しては、(*S*)-Tol-BINAP を配位子として用いると収率が81%に向上したが、その明確な理由は明らかとなっていない。

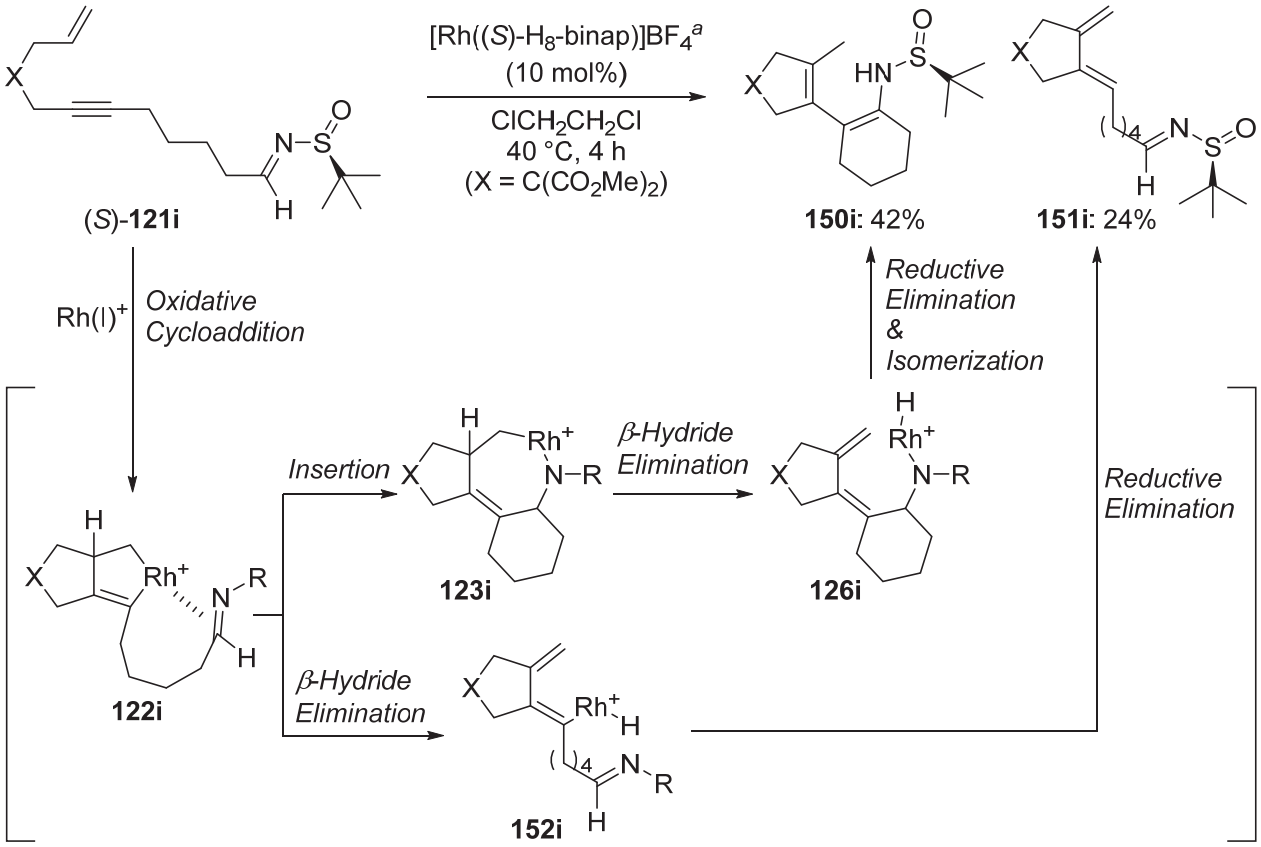
Scheme 69



[a][Rh(ligand)]BF_4 was generated from [Rh(cod)$_2$]BF_4, ligand and H_2 in $ClCH_2CH_2Cl$. [b]The substrate **121h** was recovered in 55% yield.

一方、アルキンとイミン間の炭素数が一つ多い基質(*S*)-**121i** の場合、環化反応が進行した後に二重結合が異性化したと考えられる六員環化合物 **150i** が 42%の収率で得られた (Scheme 70)*[34]。また、本反応ではイミン体 **151i** が 24%の収率で副生したことから、ローダシクロペンテン中間体 **122i** においてイミンの挿入とβ-水素脱離が競合していることが明らかとなった。おそらく、炭素鎖が長くなったことでイミンの挿入が進行しにくくなったためと考えられる*[35]。

Scheme 70



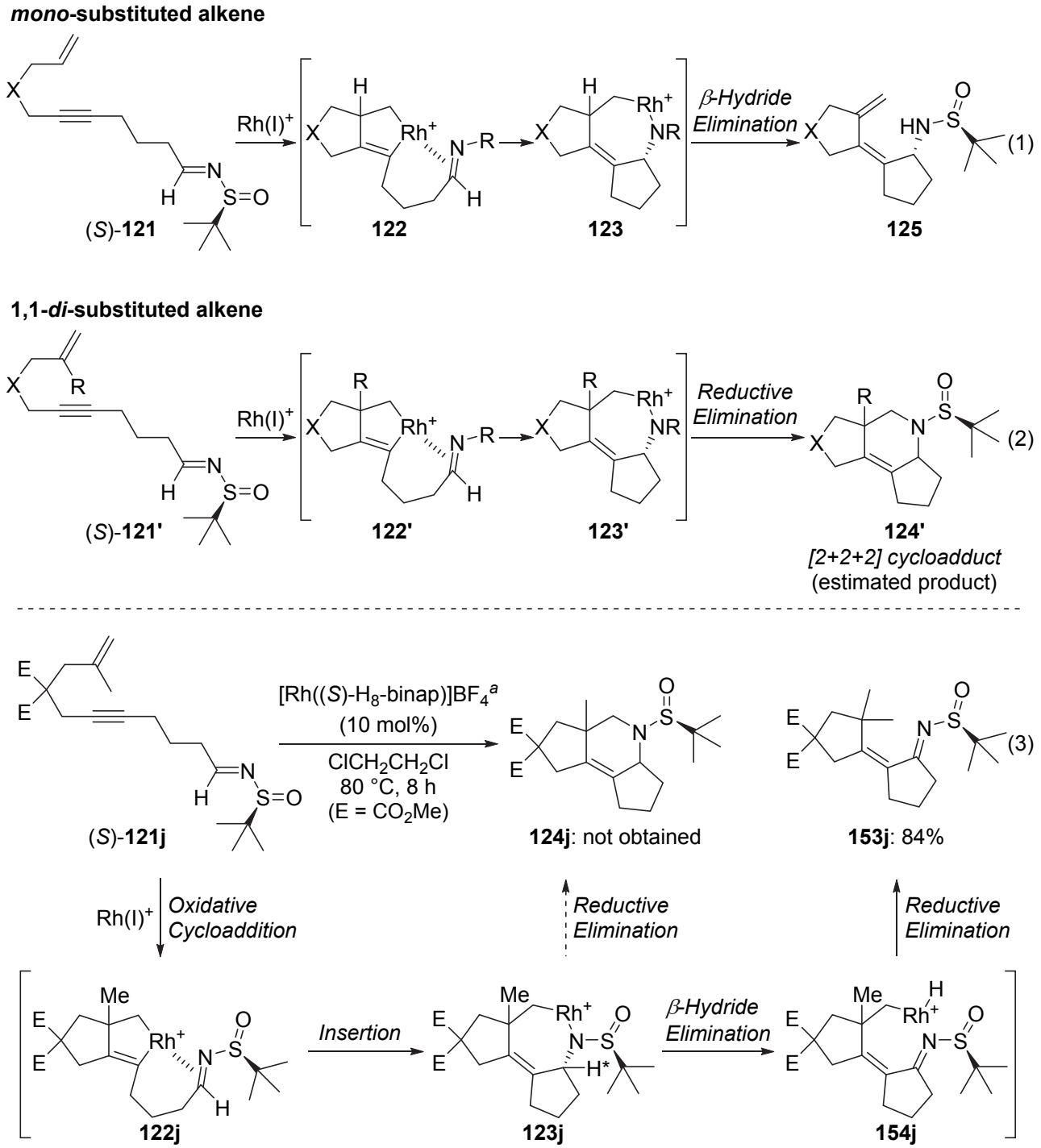
[a][Rh((*S*)-H_8-binap)]BF_4 was generated from [Rh(cod)$_2$]BF_4, (*S*)-H_8-BINAP and H_2 in $ClCH_2CH_2Cl$.

続いて、1,1-二置換アルケンを有する基質(*S*)-**121'**を用いて反応を行うことにした (Scheme 71, eq. 2)*[36]。これまでの一置換アルケン体(*S*)-**121** を用いた反応では、アザローダサイクル中間体 **123** からの β-水素脱離を経由してジエン体 **125** が生成した (eq. 1)。そこで、1,1-二置換アルケン体(*S*)-**121'**を用いて反応を行うならば、アザローダサイクル中間体 **123'**を形成した際、橋頭位に水素原子が存在しないため β-水素脱離はおこらず、還元的脱離が進行して[2+2+2]環化付加体 **124'** が生成すると予想した (eq. 2)。

実際に、基質(*S*)-**121j** と Rh(I)錯体との反応を行ったところ、予想に反して[2+2+2]環化付加体 **124j** は全く生成せず、イミン体 **153j** が 84%の収率で得られた (eq. 3)。おそらくこのイミン体 **153j** は、形成されたアザローダサイクル中間体 **123j** において窒素原子 α 位に水素原子 (H*) が存在するため、β-水素脱離が進行して生成したものと考えられる。

以上の結果から、本節で検討した反応は七員環アザローダサイクル中間体 **123** または **123'**を経由して進行していることが示唆される。

Scheme 71

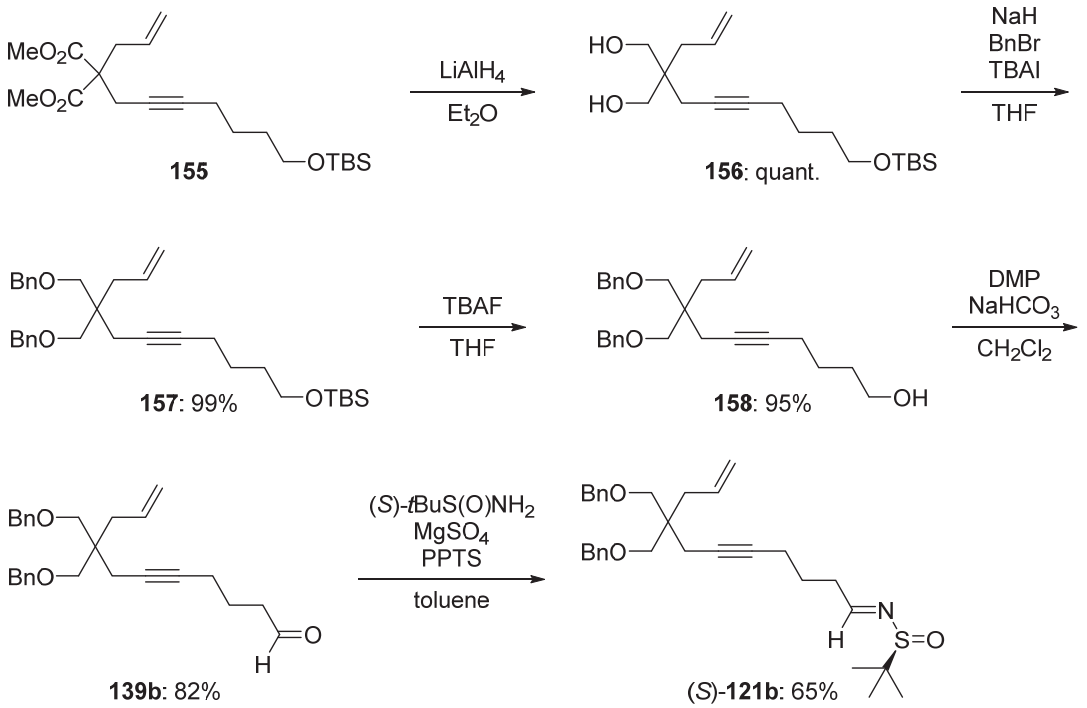


[a][Rh((*S*)-H_8-binap)]BF_4 was generated from [Rh(cod)$_2$]BF_4, (*S*)-H_8-BINAP and H_2 in $ClCH_2CH_2Cl$.

****

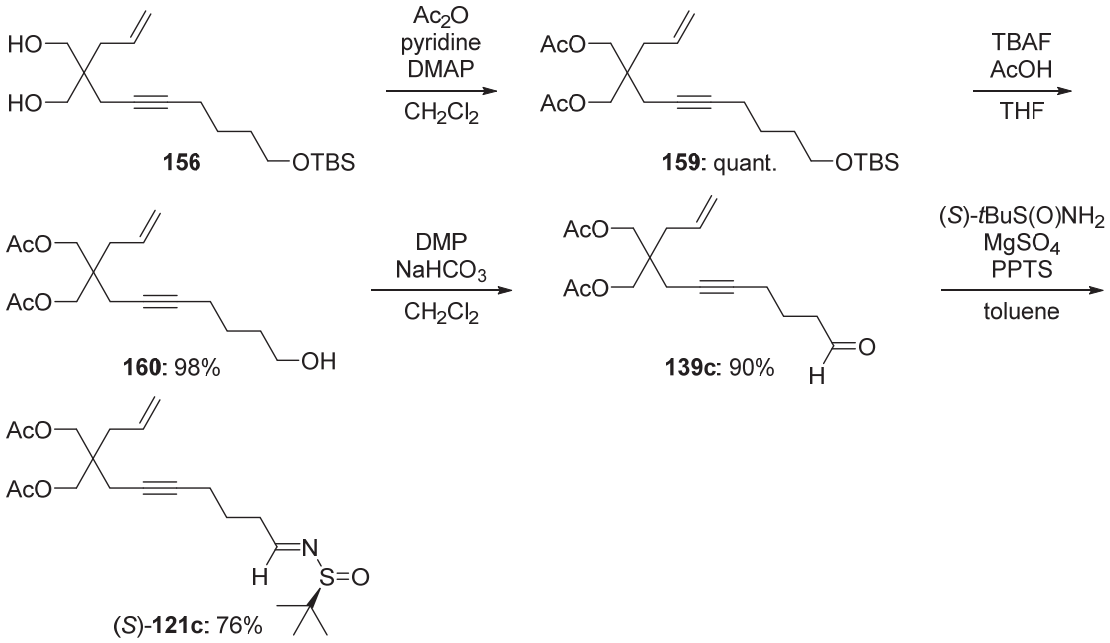
*[29] 基質(*S*)-**121b** は以下に示す方法によって合成した (Scheme 72)。**155** を $LiAlH_4$ で還元しジオール **156** を得た。**156** のアルコール部位をベンジル化し、TBS 基の脱保護、Dess-Martin 酸化、(*S*)-*t*-ブタンスルフィンアミドとの脱水反応を行うことで(*S*)-**121b** へと導いた。

Scheme 72



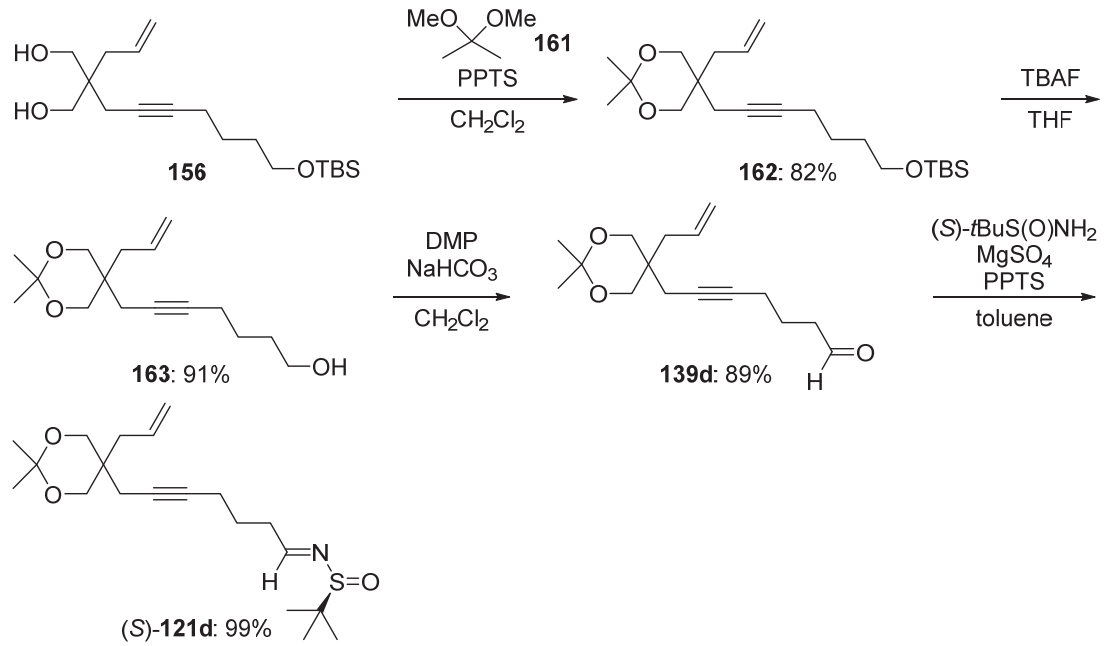
基質(*S*)-**121c** は以下に示す方法によって合成した (Scheme 73)。**156** のジオール部位をアセチル基で保護した後に TBS 基の脱保護、Dess-Martin 酸化、(*S*)-*t*-ブタンスルフィンアミドとの脱水反応を行うことで(*S*)-**121c** へと導いた。

Scheme 73



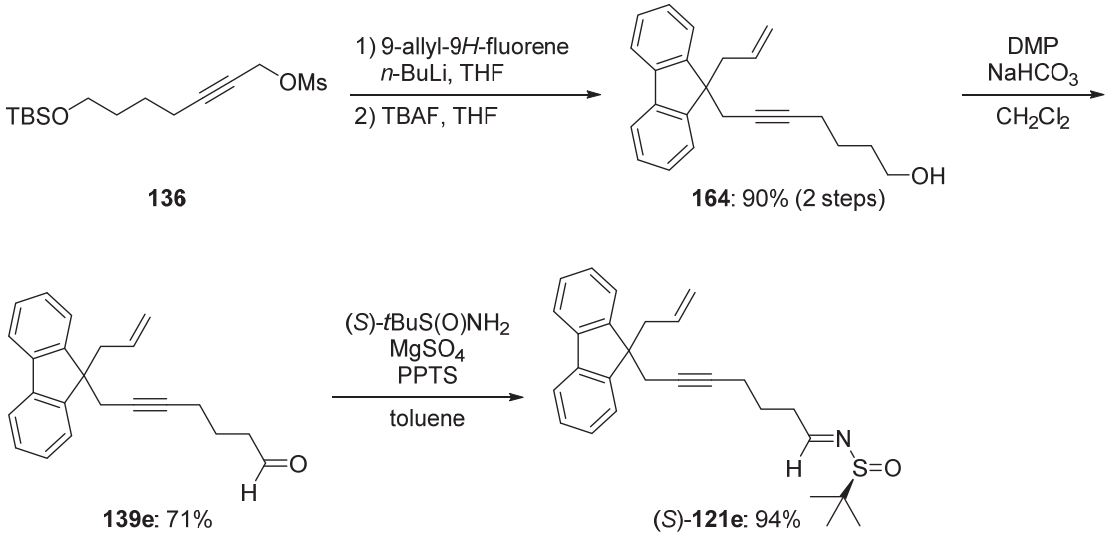
基質(*S*)-**121d** は以下に示す方法によって合成した (Scheme 74)。**156** のジオール部位をアセトニドで保護した後に TBS 基の脱保護、Dess-Martin 酸化、(*S*)-*t*-ブタンスルフィンアミドとの脱水反応を行うことで(*S*)-**121d** へと導いた。

Scheme 74



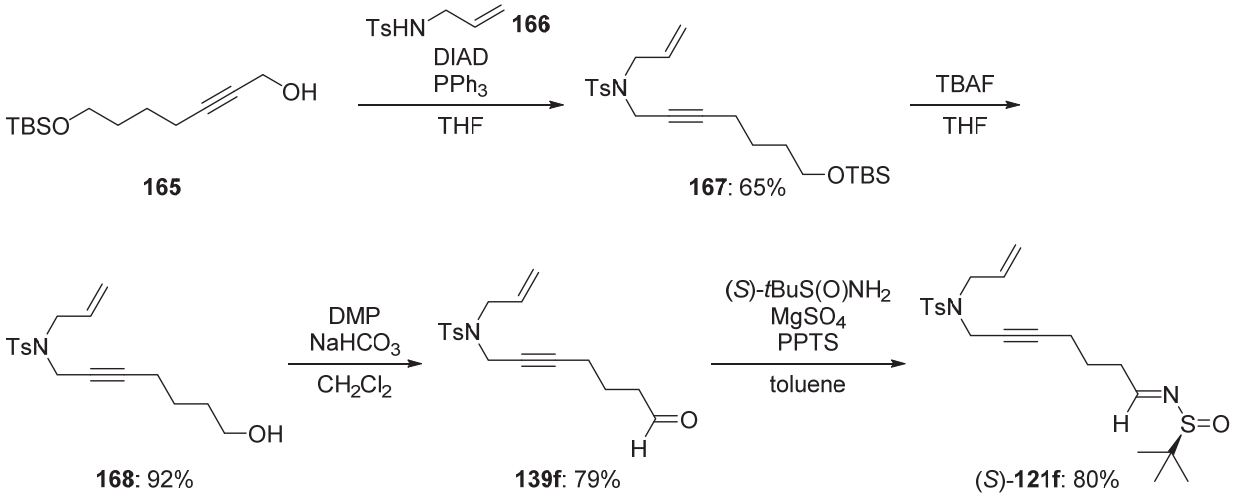
基質(*S*)-**121e** は以下に示す方法によって合成した (Scheme 75)。メシル体 **136**[20b] と文献既知のアリルフルオレン [42] をカップリングさせた後、TBS 基を脱保護してアルコール **164** を得た。その後、Dess-Martin 酸化、(*S*)-*t*-ブタンスルフィンアミドとの脱水反応を行うことで(*S*)-**121e** へと導いた。

Scheme 75



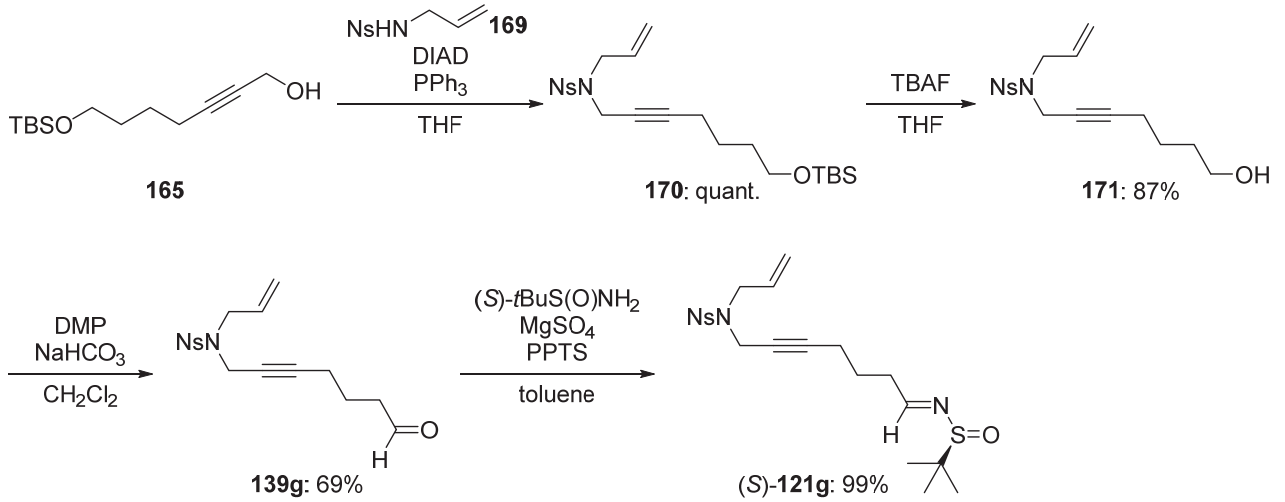
基質(*S*)-**121f** は以下に示す方法によって合成した (Scheme 76)。文献既知のアルコール体 **165**[43] と *N*-アリルトシルアミド **166**[44] をカップリングさせた後、TBS 基を脱保護してアルコール **168** を得た。その後、Dess-Martin 酸化、(*S*)-*t*-ブタンスルフィンアミドとの脱水反応を行うことで(*S*)-**121f** へと導いた。

Scheme 76



基質(*S*)-**121g** は以下に示す方法によって合成した (Scheme 77)。文献既知のアルコール体 **165**[43] と *N*-アリルノシルアミド **169**[45] をカップリングさせた後、TBS 基を脱保護してアルコール **171** を得た。その後、Dess-Martin 酸化、(*S*)-*t*-ブタンスルフィンアミドとの脱水反応を行うことで(*S*)-**121g** へと導いた。

Scheme 77



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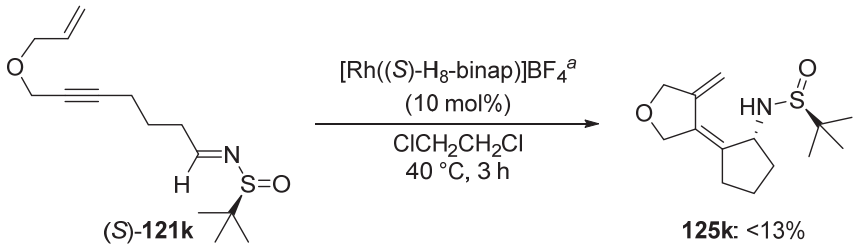
*[30] アルケンとアルキンの間に酸素原子を有する基質(*S*)-**121k** と Rh(I)錯体との反応の場合、反応系が複雑となり、環化体 **125k** はほとんど得られなかった (Scheme 78)*[37]。アルケンの異性化などの副反応が優先したためではないかと推測される[46]。

Scheme 78



[a][Rh((*S*)-H_8-binap)]BF_4 was generated from [Rh(cod)$_2$]BF_4, (*S*)-H_8-BINAP and H_2 in $ClCH_2CH_2Cl$.

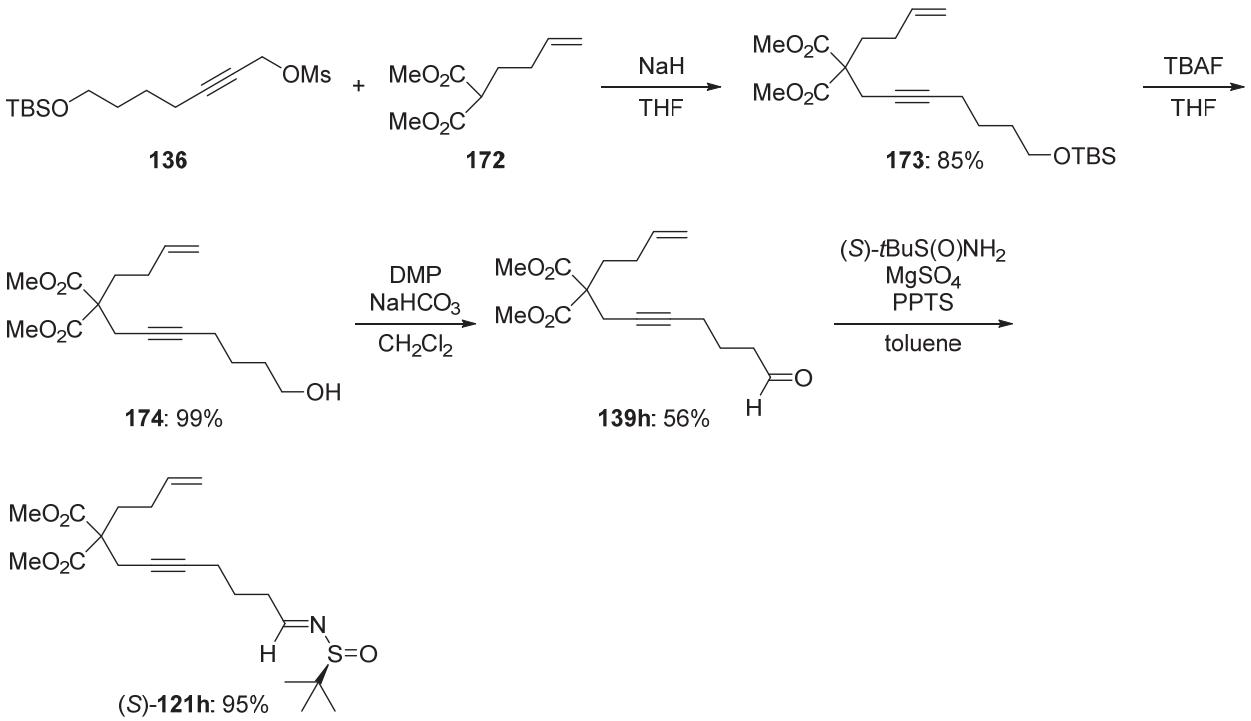
---

*[31] 環化体 **125b-g** はすべて単一の立体異性体として得られた。その絶対配置は反応機構に関する考察 (第二章、第二節) および **125a** の絶対配置 (脚注*[27], p. 65) からの類推に基づき、Table 13 に示したとおりに決定した。

---

*[32] 基質(*S*)-**121h** は以下に示す方法によって合成した (Scheme 79)。文献既知のメシル化体 **136**[20b] とホモアリルマロン酸ジメチル **172**[47] をカップリングさせ **173** を得た。**173** の TBS 基を脱保護した後に Dess-Martin 酸化、(*S*)-*t*-ブタンスルフィンアミドとの脱水反応を行うことで(*S*)-**121h** へと導いた。

Scheme 79



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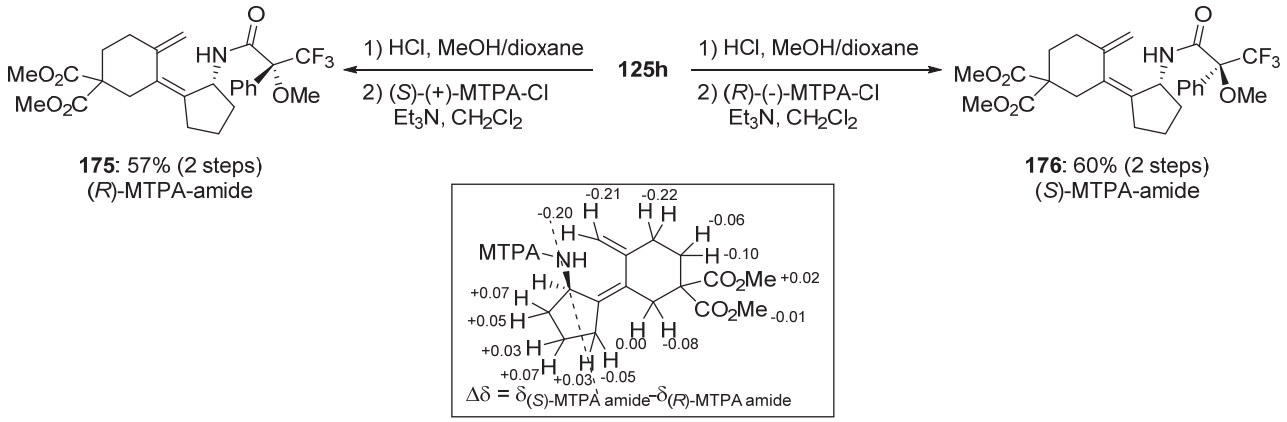
*[33] 環化体 **125h** の絶対配置は、*t*-ブタンスルフィニル基を脱保護した後に(*S*)-MTPA-Cl および(*R*)-MTPA-Cl を用いて MTPA アミド **175** および **176** へと誘導化し、改良 Mosher 法を適用して決定した (Scheme 80)[30]。

Scheme 80



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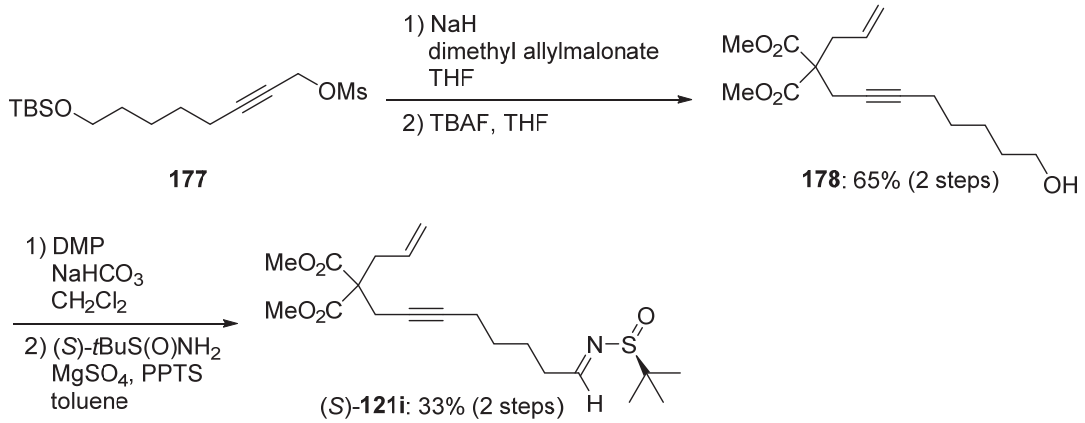
*[34] 基質(*S*)-**121i** は以下に示す方法によって合成した (Scheme 81)。文献既知のメシル化体 **177**[37a] と市販のアリルマロン酸ジメチルをカップリングさせた後、TBS 基を脱保護して **178** を得た。その後、Dess-Martin 酸化、(*S*)-*t*-ブタンスルフィンアミドとの脱水反応を行うことで(*S*)-**121i** へと導いた。

Scheme 81



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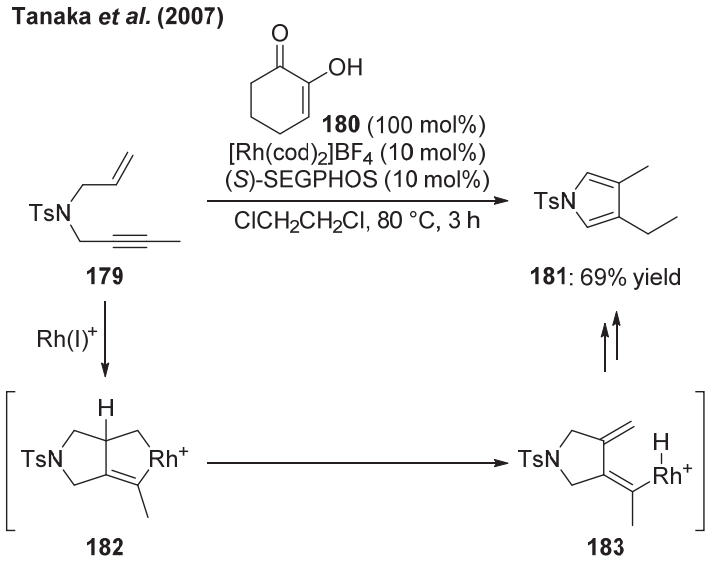
*[35] 1,6-エン-インと Rh(I)錯体との反応において、ローダシクロペンテン中間体からの β-水素脱離を経由する形式の反応は田中らによって報告されている (Scheme 82)[48]。

Scheme 82



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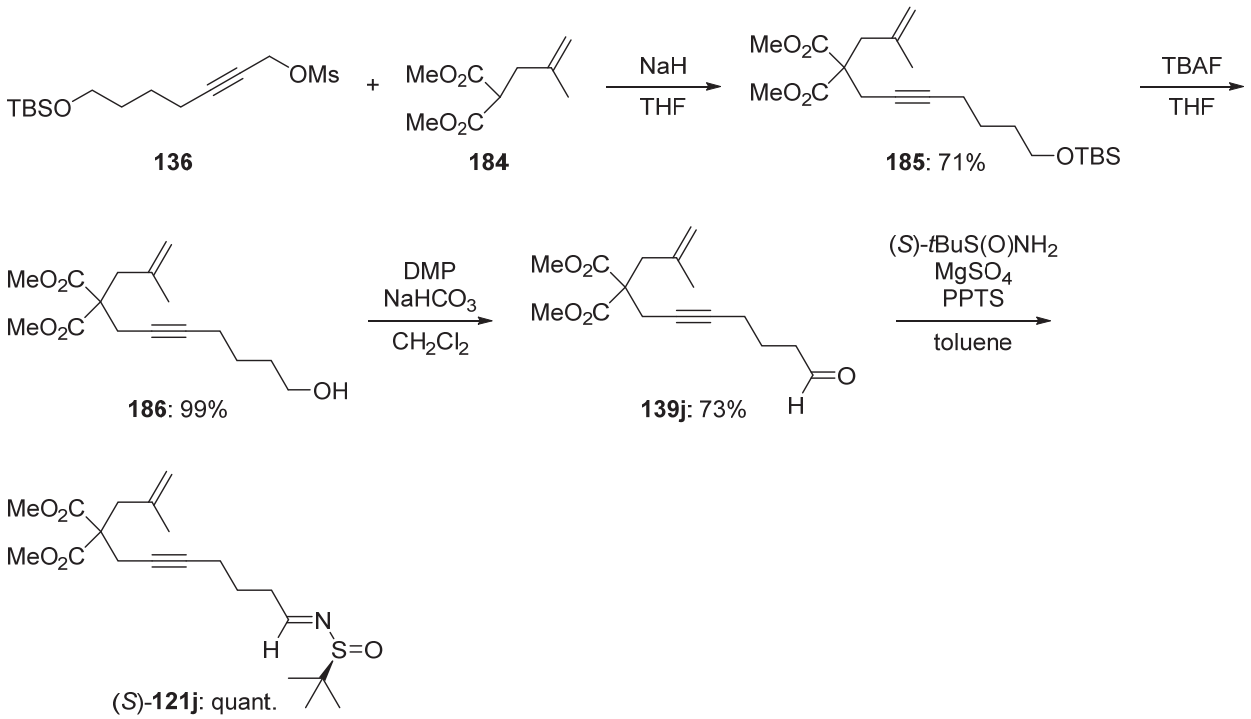
*[36] 基質(*S*)-**121j** は以下に示す方法によって合成した (Scheme 83)。文献既知のメシル化体 **136**[20b] と **184**[49] をカップリングさせた後、TBS 基を脱保護して **186** を得た。その後、Dess-Martin 酸化、(*S*)-*t*-ブタンスルフィンアミドとの脱水反応を行うことで(*S*)-**121j** へと導いた。

Scheme 83



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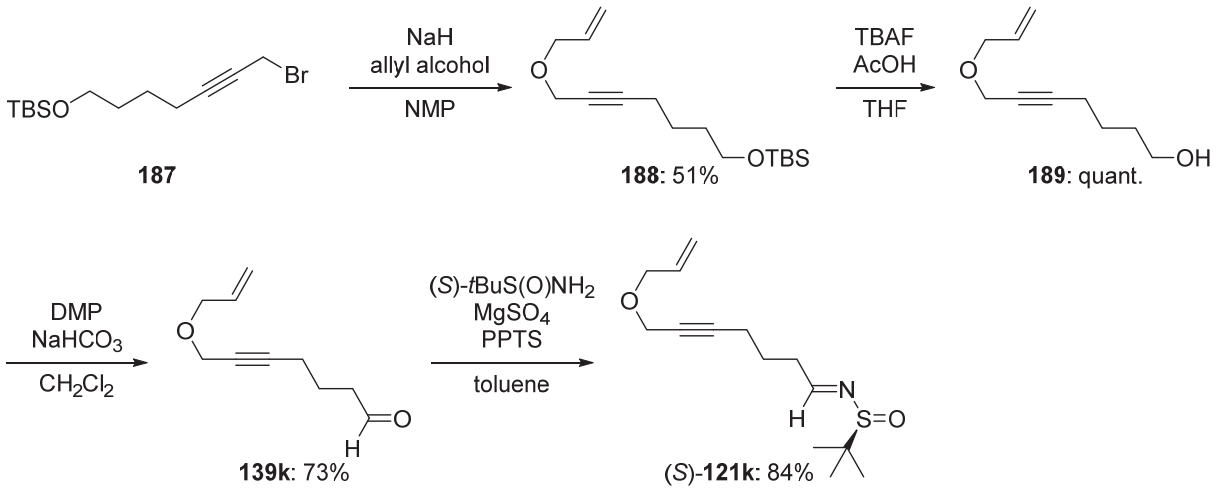
*[37] 基質(*S*)-**121k** は以下に示す方法によって合成した (Scheme 84)。文献既知の臭素化体 **187**[50] と市販のアリルアルコールをカップリングさせた後、TBS 基を脱保護して **189** を得た。その後、Dess-Martin 酸化、(*S*)-*t*-ブタンスルフィンアミドとの脱水反応を行うことで(*S*)-**121k** へと導いた。

Scheme 84



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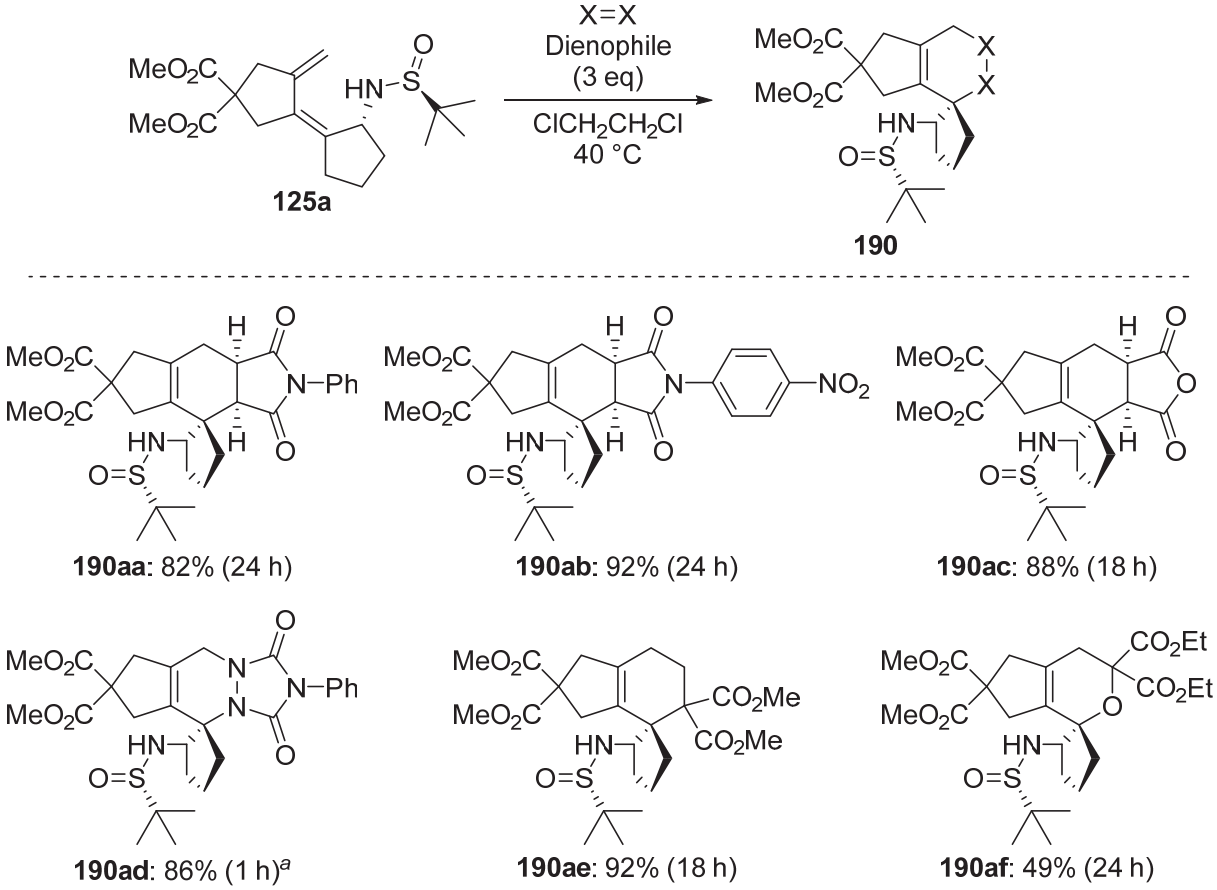
第四節　立体選択的な Diels-Alder 反応への応用

エン-イン **121** と Rh(I)錯体との反応で生成する環化体 **125** は 1,3-ジエン構造を有する。そこで、本環化体 **125** を Diels-Alder 反応に適用することにより、多環式骨格の構築が可能になると考え検討を行った (Table 14)*[38]。まず、ジエン **125a** とマレイミド誘導体および無水マレイン酸との反応をジクロロエタン中、40 °C で行ったところ、環化体 **190aa**、**190ab** および **190ac** が良好な収率かつ単一の立体異性体として生成した。また、4-フェニル-1,2,4-トリアゾリン-3,5-ジオンとの反応は室温で速やかに進行し、環化体 **190ad** が立体選択的に得られた。非環状のジエノフィルであるメチレンマロン酸エステルやケトマロン酸エステルとの反応は位置選択的かつ立体選択的に進行した。

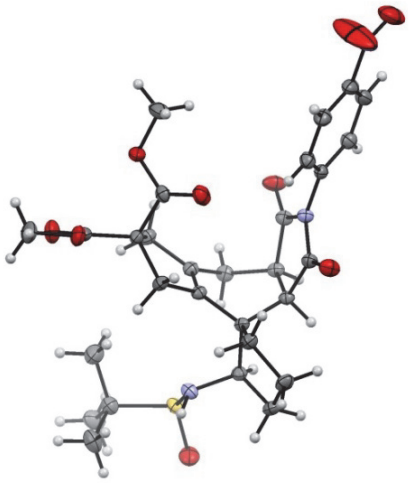
Table 14



[a]The reaction was carried out at r.t.

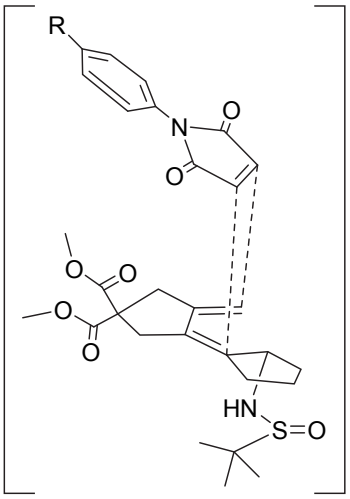
なお、Diels-Alder 付加体の立体化学は、4-ニトロフェニルマレイミドとの反応によって得られた環化体 **190ab** の単結晶 X 線結晶構造解析により決定した (Figure 3)。この結果から、Diels-Alder 反応はかさ高い *t*-ブタンスルフィンアミド基との立体反発を避けるように、このものとは反対の面からエンド選択的に進行していることが明らかとなった*[39]。

Figure 3



190ab

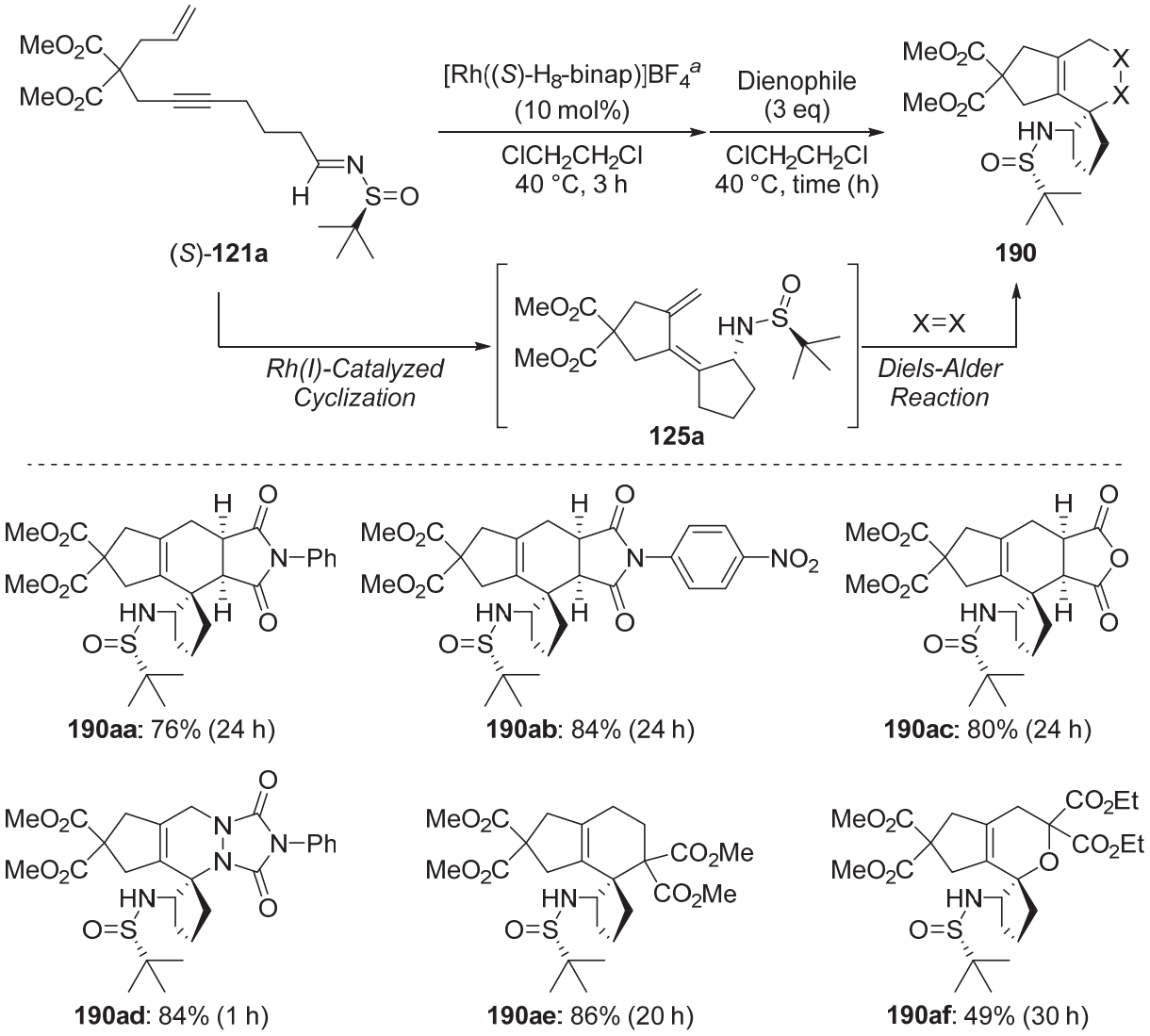
<Crystal Data>	
Crystal System	monoclinic
Space Group	$P2_1$ (#4)
Lattice Parameters	a = 6.8242(3) Å
	b = 14.9933(5) Å
	c = 14.3182(4) Å
	β = 93.6230(11)°
	V = 1462.07(8) Å^3
R1 (I>2.00σ(I))	0.0293
R1 (All reflections)	0.0306
wR2	0.0771
GOF	1.049
Flack Parameter	-0.006(15)



このように、環化体 **125** の Diels-Alder 反応が効率的に進行したので、次に Rh(I)触媒による環化反応と Diels-Alder 反応のワンポット反応を検討することとした (Table 15)。

まず、Rh(I)触媒とエン-イン(*S*)-**121a** との反応を 40 °C で 3 時間行い、系中にジエン **125a** を発生させた。続いて、この反応溶液にジエノフィルを加え、さらに撹拌した。その結果、先ほど用いた全てのジエノフィルとジエン **125a** との Diels-Alder 反応が Rh(I)錯体存在下においても問題なく進行し、良好な収率かつ立体選択的に対応する環化体 **190** が生成した。

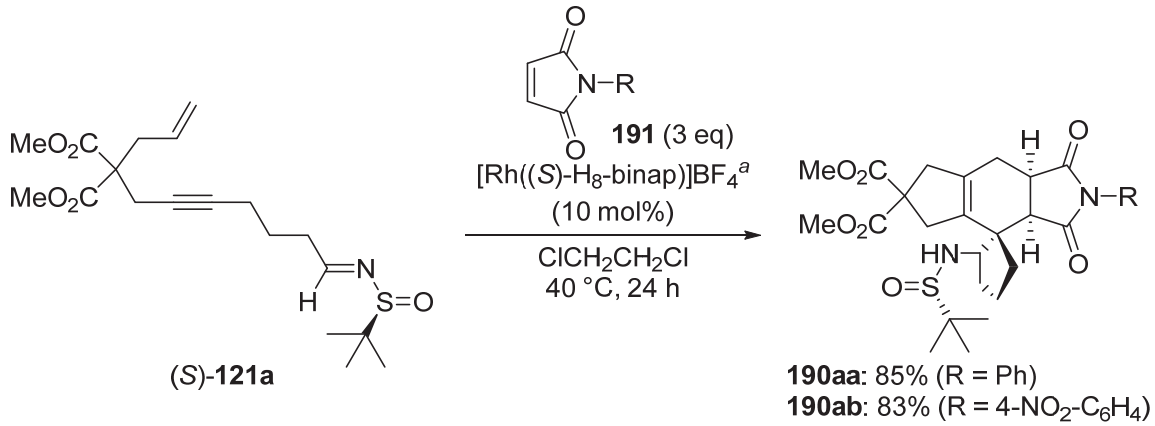
Table 15



[a][Rh((*S*)-H_8-binap)]BF_4 was generated from [Rh(cod)$_2$]BF_4, (*S*)-H_8-BINAP and H_2 in $ClCH_2CH_2Cl$.

このように、エン-イン(*S*)-**121a**を出発物質として用いるワンポット反応が円滑に進行することが明らかになったので、次にRh(I)触媒による環化反応とDiels-Alder反応のドミノ型連続反応[51]を検討した (Scheme 85)。すなわち、ジエノフィルであるマレイミド **191** が反応の開始時から系内に存在する状態で、Rh(I)触媒とエン-イン(*S*)-**121a**との反応を40 °Cで24時間行った。その結果、対応する環化体 **190aa** および **190ab** が良好な収率かつ立体選択的に生成した。このことから、マレイミド **191** 存在下においても Rh(I)触媒による環化反応が問題なく進行し、続いて生成したジエン **125a** とマレイミド **191** との Diels-Alder 反応が順次進行することが明らかとなった。

Scheme 85



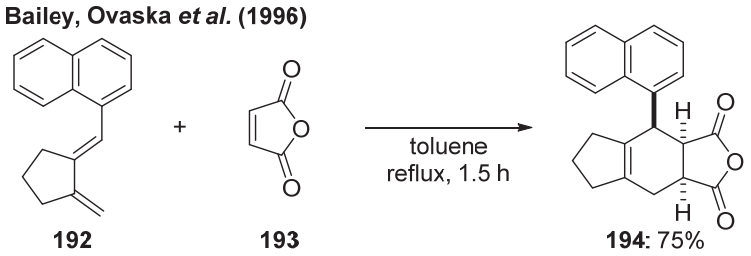
[a][Rh((*S*)-H_8-binap)]BF_4 was generated from [Rh(cod)$_2$]BF_4, (*S*)-H_8-BINAP and H_2 in $ClCH_2CH_2Cl$.

ここまでの研究により、分子内にイミンを有するエン-イン(*S*)-**121a** と Rh(I)錯体との反応を検討した結果、アルキン、アルケンおよびイミンの三つの多重結合と Rh(I)錯体から形成されるアザローダサイクル中間体 **123** を経由して、1,3-ジエン構造を有する環化体 **125** がジアステレオ選択的に生成することを見出した。また、得られた環化体 **125** とジエノフィルとの Diels-Alder 反応を検討した結果、スピロ構造を有する多環式化合物 **190** が良好な収率かつ立体選択的に生成することを見出した。

****

*[38] エキソサイクリック 1,3-ジエンを用いる Diels-Alder 反応の一例として、Bailey、Ovaska らによる報告を下記に示す (Scheme 86)[52]。本報告においても Diels-Alder 反応はエンド選択的に進行することが確認されている。

Scheme 86



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*[39] 環化体 **190** はすべて単一の立体異性体として得られた。NOESY を含む各種二次元 NMR の測定により、いずれも図式に記載したとおり **190ab** と同じ立体化学を有することを確認した。

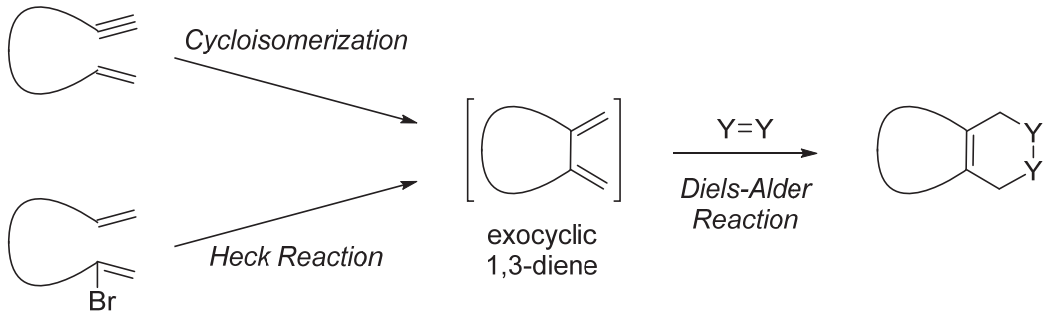
****

第三章　Rh(I)および Rh(II)触媒を用いた連続反応による三環式スピロ骨格の立体選択的な構築

第一節　研究の背景

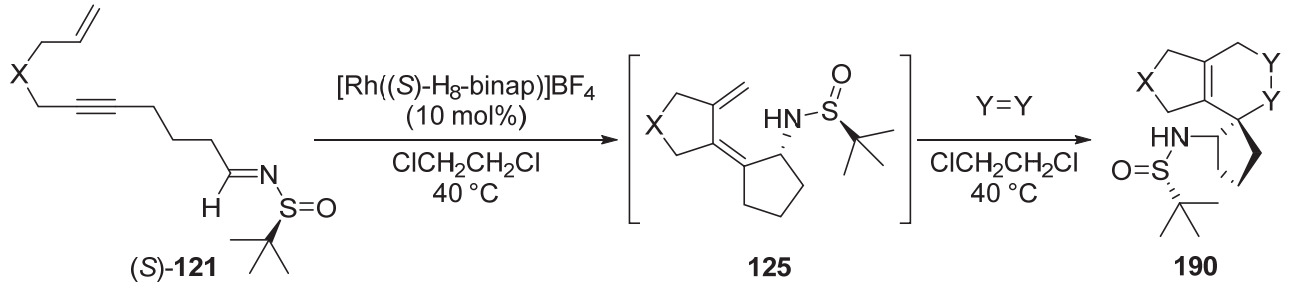
多環式骨格を立体選択的に構築する手法の開発は有機合成化学において重要な課題の一つである。ワンポット連続反応は複数の反応を一つの反応容器中で行う合成手法であり、複雑な化合物の効率的な合成を可能にすることから、この課題に対する有力な解決策となり得る[53]。特に、エキソサイクリック 1,3-ジエンは Diels-Alder 反応により多環式骨格へと変換することが可能であるため、これまでに、このようなジエンを中間体として経由する連続反応が盛んに研究されている。例えば、遷移金属触媒を用いるエン-インの環化異性化反応や分子内 Heck 反応によってエキソサイクリック1,3-ジエンを発生させ、これを直ちにワンポットでの Diels-Alder 反応に用いる手法が多環式骨格の効率的な合成法として報告されている (Scheme 87)[54]。

Scheme 87



第二章で述べたように、筆者は分子内にイミンを有するエン-イン(*S*)-**121** と Rh(I)錯体との反応を検討した結果、1,3-ジエン構造を有する環化体 **125** がジアステレオ選択的に生成することを見出した。さらに、この環化体 **125** をジエノフィルとワンポットで反応させることにより、スピロ構造を有する多環式化合物 **190** が立体選択的に構築できることも明らかにした (Scheme 88)。

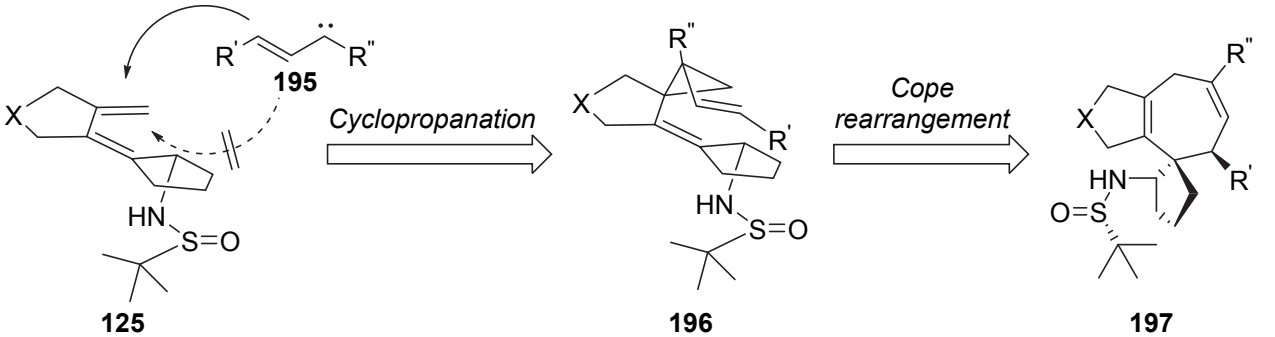
Scheme 88



しかしながら、これらの連続反応において、系内で発生したエキソサイクリック 1,3-ジエンを多環式骨格へと変換する際に用いられる反応は、これまでのところ、ほぼ Diels-Alder 反応に限られている。そのため、生成する多環式化合物は基本的に六員環を含むものに限定されている。そこで筆者は、従来の連続反応では合成困難な多環式骨格の構築を目指し、エキソサイクリック 1,3-ジエンの新たな利用法の開発に取り組むこととした。

環化体 **125** の Diels-Alder 反応が立体選択的に進行したことから、*t*-ブタンスルフィンアミド基はジエンの片面を効果的に遮蔽していると考えられる (Scheme 89)。そこで、このエキソサイクリック 1,3-ジエン **125** とビニルカルベノイド **195** との反応を行うならば、シクロプロパン化反応が面選択的に進行するものと予想した。続いて、生成したジビニルシクロプロパン **196** の Cope 転位が進行すると、七員環を有する多環式骨格 **197** が立体選択的に構築できるのではないかと考え、検討を開始した[55]。

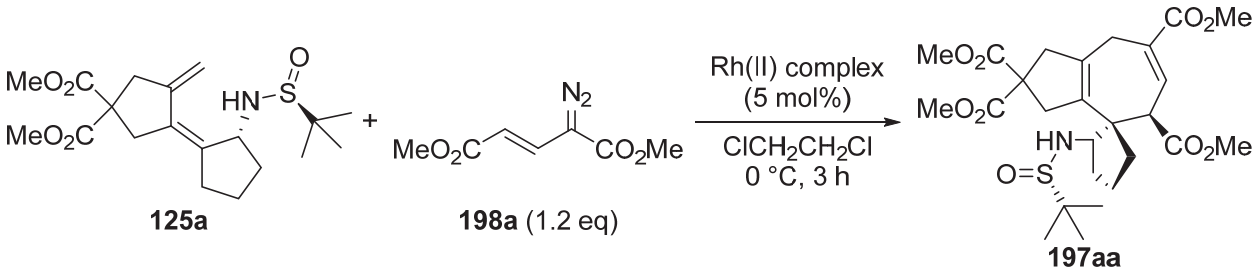
Scheme 89



第二節　反応条件および基質適用範囲の検討

初めに、ジエン **125a** とビニルジアゾアセテート **198a** をモデル基質として用い、種々の Rh(II)触媒存在下、シクロプロパン化反応と Cope 転位の連続反応が進行する可能性を検討した (Table 16)。Rh(II)触媒として $Rh_2(OAc)_4$ および $Rh_2(TFA)_4$ を用いた場合は反応が全く進行せず、ジエン **125a** が回収された (Entries 1 and 2)。一方、$Rh_2(oct)_4$ の場合はジエン **125a** が 50%程度残存するものの、目的の環化体 **197aa** が 36%の収率で生成した (Entry 3)。また、$Rh_2(TPA)_4$ を用いた場合はジエン **125a** がほぼ完全に消費され、環化体 **197aa** の収率は 60%に向上した (Entry 4)。さらに Rh(II)錯体の検討を行ったところ、$Rh_2(piv)_4$ および $Rh_2(esp)_2$ を用いた場合にそれぞれ 72%、79%と良好な収率で環化体 **197aa** が生成した (Entries 5 and 6)*[40]。なお、本検討において反応はいずれの場合も立体選択的に進行し、環化体 **197aa** は単一の立体異性体として得られた。

Table 16

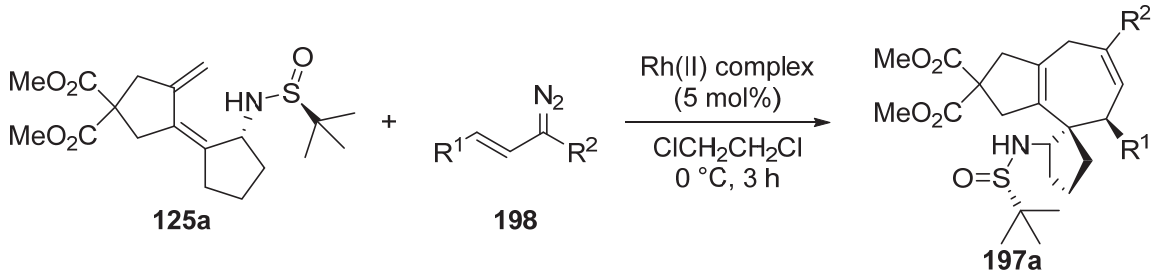


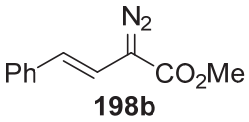
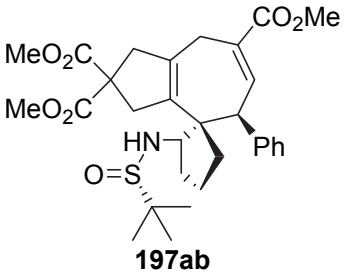
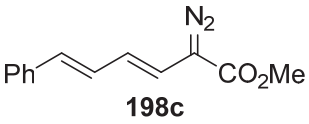
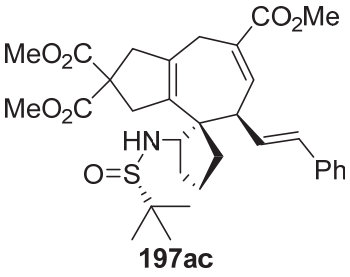
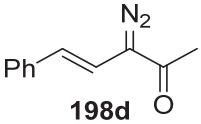
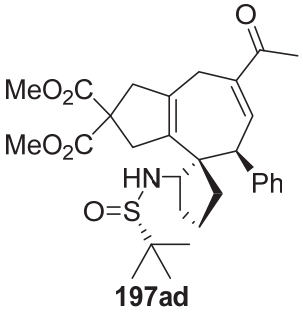
125a　　**198a** (1.2 eq)　　**197aa**

Entry	Rh(II) complex	Yield (%)	
		197aa	rec. **125a**
1	$Rh_2(OAc)_4$	-	96
2	$Rh_2(TFA)_4$	-	89
3	$Rh_2(oct)_4$	36	50
4	$Rh_2(TPA)_4$	60	trace
5	$Rh_2(piv)_4$	72	trace
6	$Rh_2(esp)_2$	79	trace

このように、$Rh_2(piv)_4$ および $Rh_2(esp)_2$ がシクロプロパン化反応と Cope 転位の連続反応に有効であることが明らかとなったので、次にこの二つの Rh(II)錯体を用いてジエン **125a** と種々のビニルジアゾ化合物 **198** との反応を検討した (Table 17)。R^1 にフェニル基やスチリル基を有するビニルジアゾ化合物 **198b** および **198c** との反応はいずれの Rh(II)錯体を用いた場合も円滑に進行し、良好な収率で対応する環化体 **197ab** および **197ac** が生成した (Entries 1-4)。また、R^2 にアセチル基を有するビニルジアゾ化合物 **198d** との反応の場合は、1.8 当量の **198d** を用いることで良好な収率で環化体 **197ad** が得られた (Entries 5 and 6)。

Table 17



Entry	Substrate **198**	**198** (equiv.)	Rh(II)	Product **197a**	Yield (%)
1	 **198b**	1.5	$Rh_2(piv)_4$	 **197ab**	94
2		1.5	$Rh_2(esp)_2$		95
3	 **198c**	1.2	$Rh_2(piv)_4$	 **197ac**	88
4		1.2	$Rh_2(esp)_2$		82
5	 **198d**	1.8	$Rh_2(piv)_4$	 **197ad**	78
6		1.8	$Rh_2(esp)_2$		65

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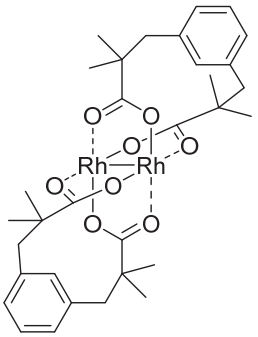
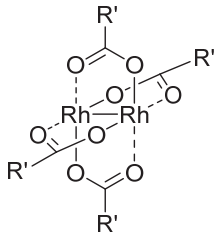
*[40] 検討に使用した Rh(II)錯体の構造を以下に示す (Figure 4)。これらの錯体の中で最も電子供与的でかつ立体的にかさ高い $Rh_2(piv)_4$ および $Rh_2(esp)_2$ 錯体を用いた場合に環化体 **197aa** が良好な収率で得られたことから (Table 16, Entries 5 and 6)、Rh(II)錯体とビニルジアゾ化合物 **198** から生成するロジウムカルベノイドがより安定であることが、収率の向上に寄与している可能性が示唆される。

Figure 4



$Rh_2(esp)_2$



R' = Me	**$Rh_2(OAc)_4$**
R' = CF_3	**$Rh_2(TFA)_4$**
R' = *n*-C_7H_{15}	**$Rh_2(oct)_4$**
R' = CPh_3	**$Rh_2(TPA)_4$**
R' = *t*Bu	**$Rh_2(piv)_4$**

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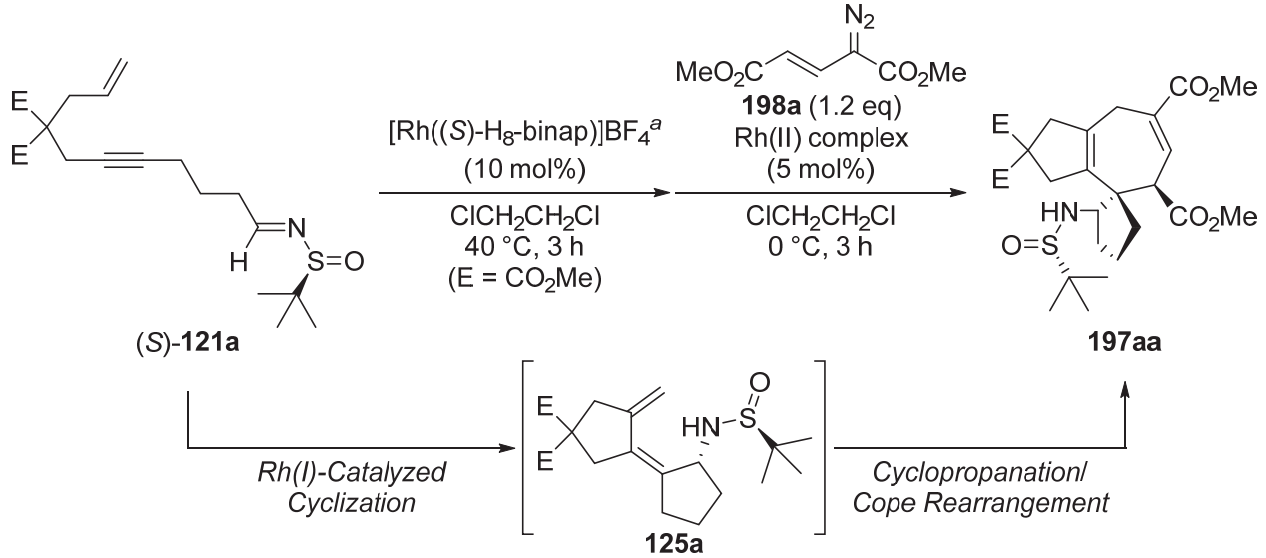
第三節　ワンポット連続反応への展開

前節の検討により、ジエン **125a** とビニルジアゾ化合物 **198** とのシクロプロパン化反応および Cope 転位から構成される連続反応が立体選択的に進行することが明らかとなった。そこで次に、より効率的な多段階反応の開発を指向して、エン-イン(*S*)-**121** を出発物質として用いるワンポット連続反応を検討することとした。

まず、エン-イン(*S*)-**121a** と[Rh((*S*)-H_8-binap)]BF_4 錯体との反応を 40 °C で 3 時間行い、系中にジエン **125a** を発生させた。この反応溶液を 0 °C に冷却した後に Rh(II)錯体とビニルジアゾ化合物 **198a** を加え、さらに 3 時間撹拌した (Table 18)。その結果、Rh(II)錯体として $Rh_2(piv)_4$ および $Rh_2(esp)_2$ を用いた場合に、それぞれ 53%、62%の収率で環化体 **197aa** が生成した。この結果から、カチオン性 Rh(I)錯体存在下においても、Rh(II)触媒によるシクロプロパン化反応と続く Cope 転位が問題なく進行することが明らかとなった。

Table 18

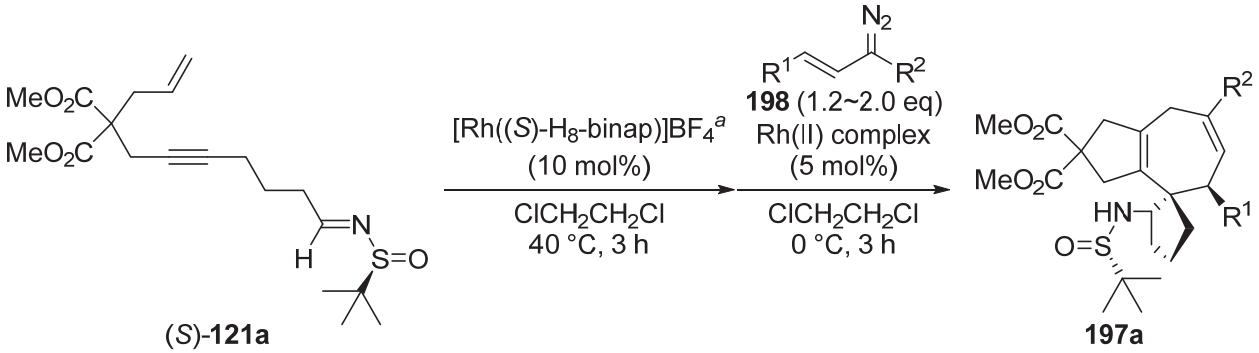


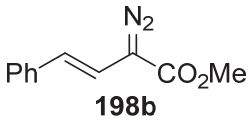
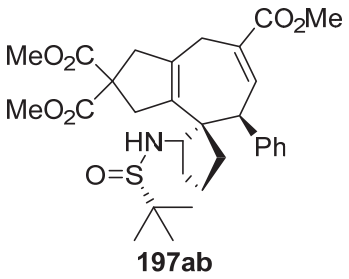
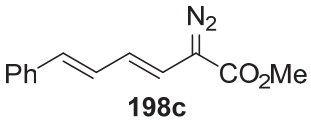
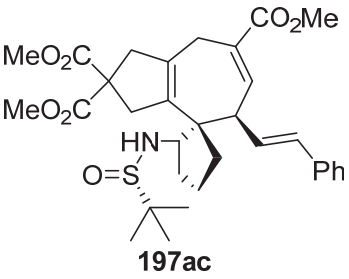
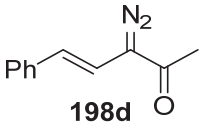
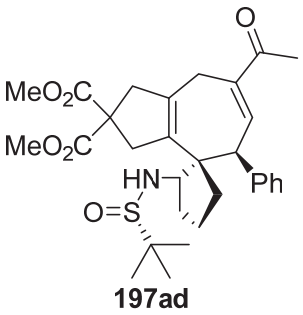
Entry	Rh(II) complex	Yield (%)	
		197aa	**125a**
1	$Rh_2(piv)_4$	53	<26
2	$Rh_2(esp)_2$	62	<11

[a][Rh((*S*)-H_8-binap)]BF_4 was generated from $[Rh(cod)_2]BF_4$, (*S*)-H_8-BINAP and H_2 in $ClCH_2CH_2Cl$.

本連続反応について、まずジアゾ化合物 **198** の適用範囲の検討を行った (Table 19)。R^1 にフェニル基やスチリル基を有するビニルジアゾ化合物 **198b** および **198c** との反応は良好な収率で対応する環化体 **197ab** および **197ac** を与えた (Entries 1-4)。R^2 にアセチル基を有するビニルジアゾ化合物 **198d** との反応は $Rh_2(piv)_4$ 錯体を用いた場合に収率の低下がみられたが、$Rh_2(esp)_2$ 錯体存在下で反応を行うと良好な収率で環化体 **197ad** が得られた (Entries 5-7)。

Table 19

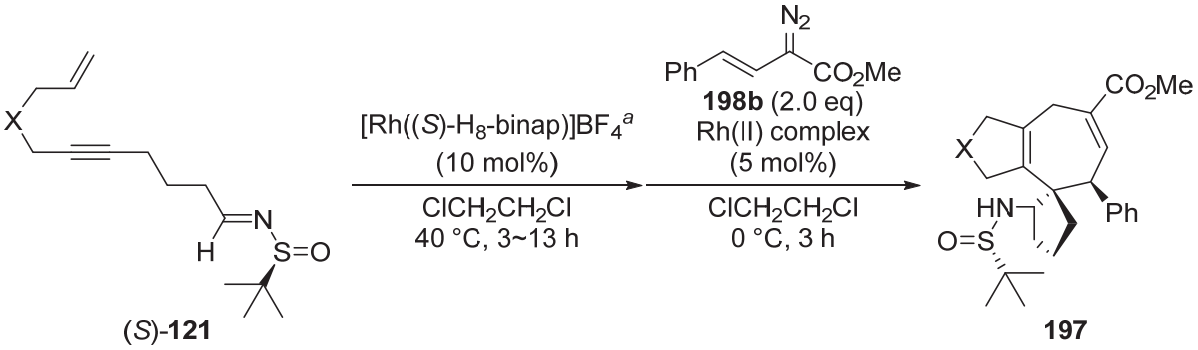


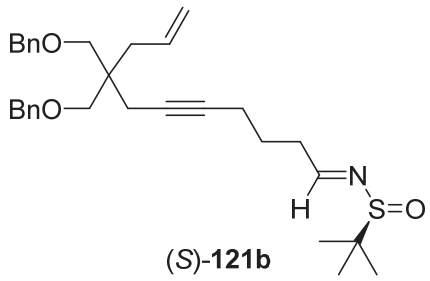
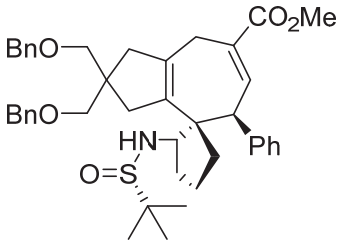
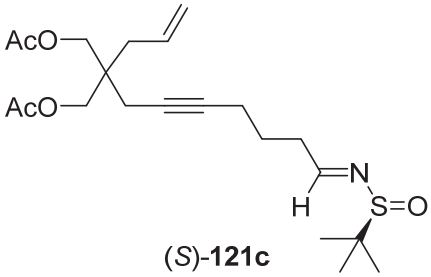
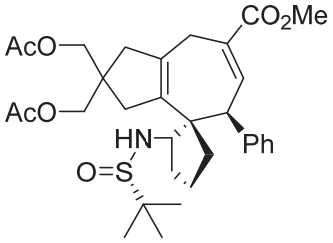
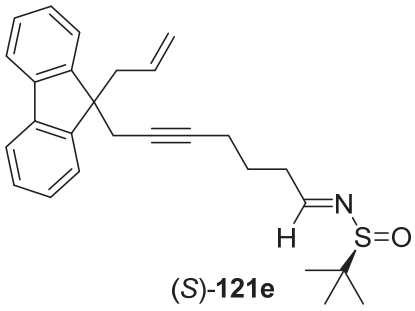
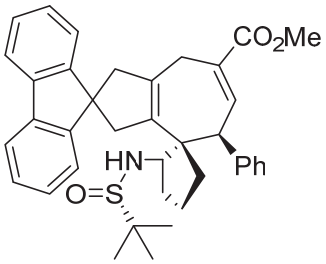
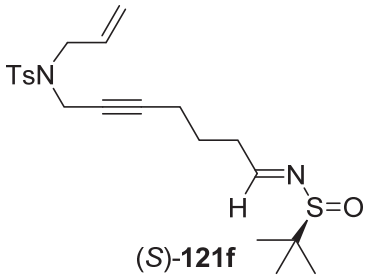
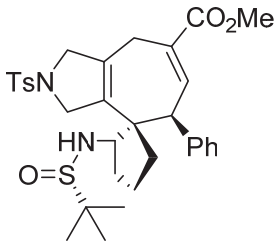
Entry	Substrate **198**	**198** (equiv.)	Rh(II)	Product **197a**	Yield (%)
1	 **198b**	1.8	$Rh_2(piv)_4$	 **197ab**	81
2		1.8	$Rh_2(esp)_2$		70
3	 **198c**	1.5	$Rh_2(piv)_4$	 **197ac**	81
4		1.8	$Rh_2(esp)_2$		77
5	 **198d**	1.2	$Rh_2(piv)_4$	 **197ad**	36[b]
6		1.2	$Rh_2(esp)_2$		60[c]
7		2.0	$Rh_2(esp)_2$[d]		72[e]

[a] $[Rh((S)\text{-}H_8\text{-binap})]BF_4$ was generated from $[Rh(cod)_2]BF_4$, (*S*)-H_8-BINAP and H_2 in $ClCH_2CH_2Cl$. [b] 38% of **125a** was obtained. [c] 28% of **125a** was obtained. [d] 10 mol% of $Rh_2(esp)_2$ was used. [e] 10% of **125a** was obtained.

続いて、エン-イン(*S*)-**121** に関して基質適用範囲の検討を行った (Table 20)。ベンジルオキシ基およびアセトキシ基を有するエン-イン(*S*)-**121b** および(*S*)-**121c** とジアゾ化合物 **198b** との反応を行ったところ、良好な収率で環化体 **197bb** および **197cb** が生成した (Entries 1-4)。また、スピロ骨格を有するエン-イン(*S*)-**121e** を用いて反応を行った場合も良好な結果を与えた (Entries 5 and 6)。一方、スルホンアミド基を有するエン-イン(*S*)-**121f** を用いて反応を行った場合は環化体 **197fb** の収率が若干低下した (Entries 7 and 8)。おそらく、エン-イン(*S*)-**121f** と Rh(I)錯体との反応によって生成するジエン **125f** の収率が中程度であることが、その原因として考えられる (Scheme 90)。

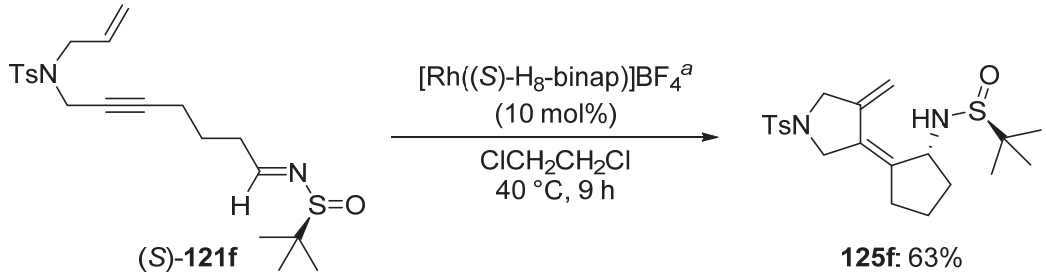
Table 20



Entry	Substrate (*S*)-**121**	Rh(II)	Product **197**	Yield (%)
1	 (*S*)-**121b**	$Rh_2(piv)_4$	 **197bb**	69
2		$Rh_2(esp)_2$		65
3	 (*S*)-**121c**	$Rh_2(piv)_4$	 **197cb**	88
4		$Rh_2(esp)_2$		80
5	 (*S*)-**121e**	$Rh_2(piv)_4$	 **197eb**	74
6		$Rh_2(esp)_2$		82
7	 (*S*)-**121f**	$Rh_2(piv)_4$	 **197fb**	45
8		$Rh_2(esp)_2$		42

[a] [Rh((*S*)-H_8-binap)]BF_4 was generated from [Rh(cod)$_2$]BF_4, (*S*)-H_8-BINAP and H_2 in $ClCH_2CH_2Cl$.

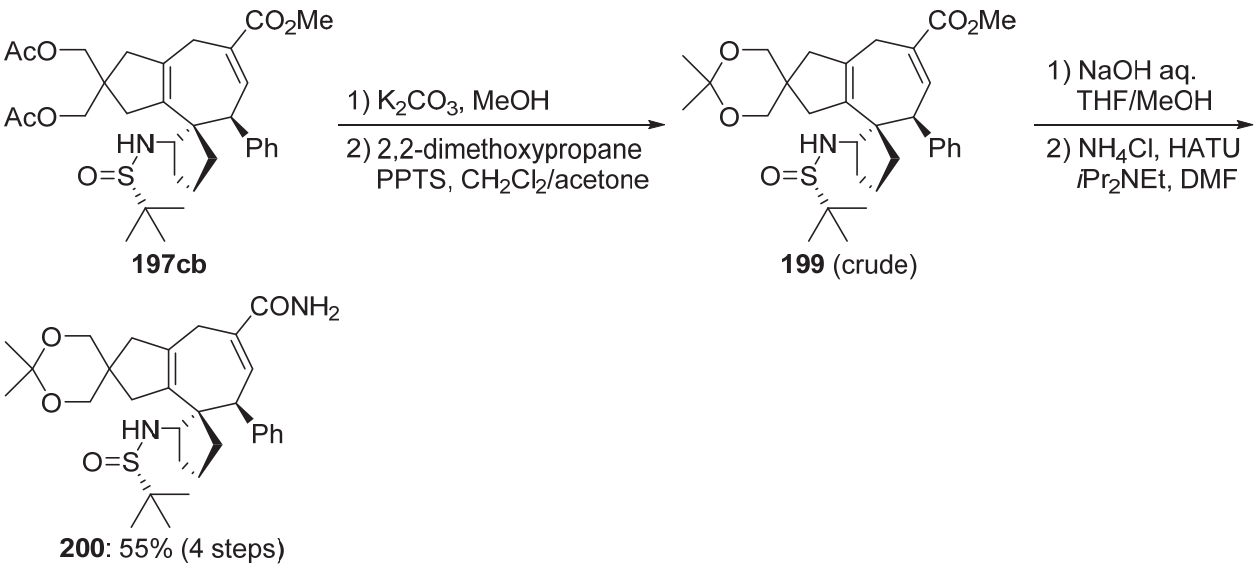
Scheme 90 (cf. Table 13, p. 67)

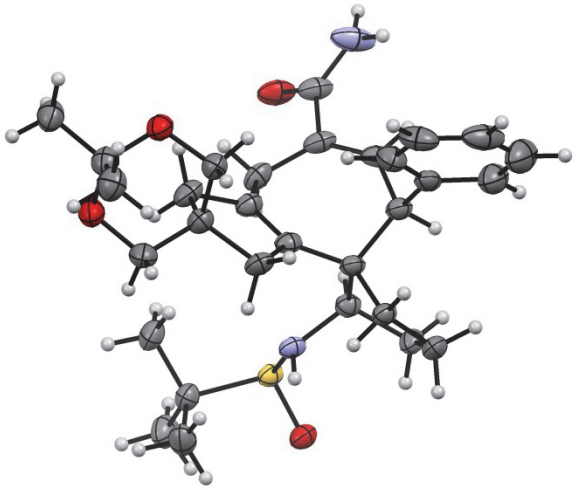


[a][Rh((*S*)-H_8-binap)]BF_4 was generated from [Rh(cod)$_2$]BF_4, (*S*)-H_8-BINAP and H_2 in $ClCH_2CH_2Cl$.

なお、基質適用範囲の検討で生成した環化体 **197** は全て単一の立体異性体として得られた。その絶対配置は **197cb** から四工程で合成されたアミド体 **200** の単結晶 X 線結晶構造解析により確認した (Scheme 91)。

Scheme 91





200

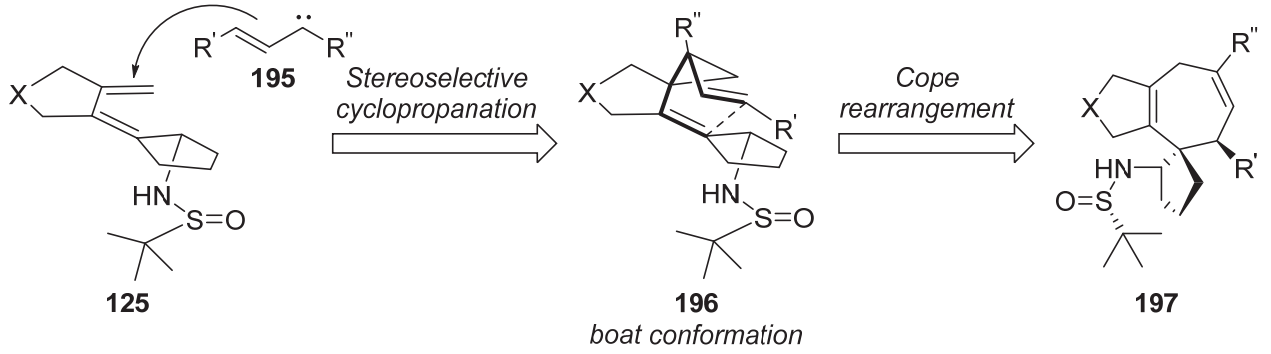
<Crystal Data>

Crystal System	monoclinic
Space Group	C2 (#5)
Lattice Parameters	a = 22.508(3) Å
	b = 15.8459(17) Å
	c = 26.254(4) Å
	β = 93.149(4)°
	V = 9349.6(19) Å^3
R1 (I>2.00σ(I))	0.0621
R1 (All reflections)	0.0771
wR2	0.1598
GOF	0.713
Flack Parameter	-0.009(13)

この結果から、本連続反応は当初予想したとおりの立体選択性で進行していることが確認された (Scheme 92)。すなわち、まずジエン **125** とビニルジアゾ化合物 **195** とのシクロプロパン化反応が面選択的に進行し、ジビニルシクロプロパン **196** が生成する。その後、**196** の Cope 転位が六員環舟型遷移状態を経由して進行し、環化体 **197** が立体選択的に生成した。

また、本反応で得られたすべての環化体 **197** に関して、NOESY を含む各種二次元 NMR の測定を行い、いずれも図式に記載したとおり **197cb** と同じ立体化学を有することを確認した。

Scheme 92



ここまでの研究により、鎖状の化合物であるエン-イン(*S*)-**121** から七員環を含む三環式骨格を立体選択的に合成する手法の開発に成功した。本連続反応では、Rh(I)触媒によるエン-イン(*S*)-**121** の環化反応、Rh(II)触媒によるビニルジアゾ化合物とのシクロプロパン化反応、続く Cope 転位という三つの反応が連続して進行し、環化体 **197** が単一の立体異性体として生成する*[41]。

****

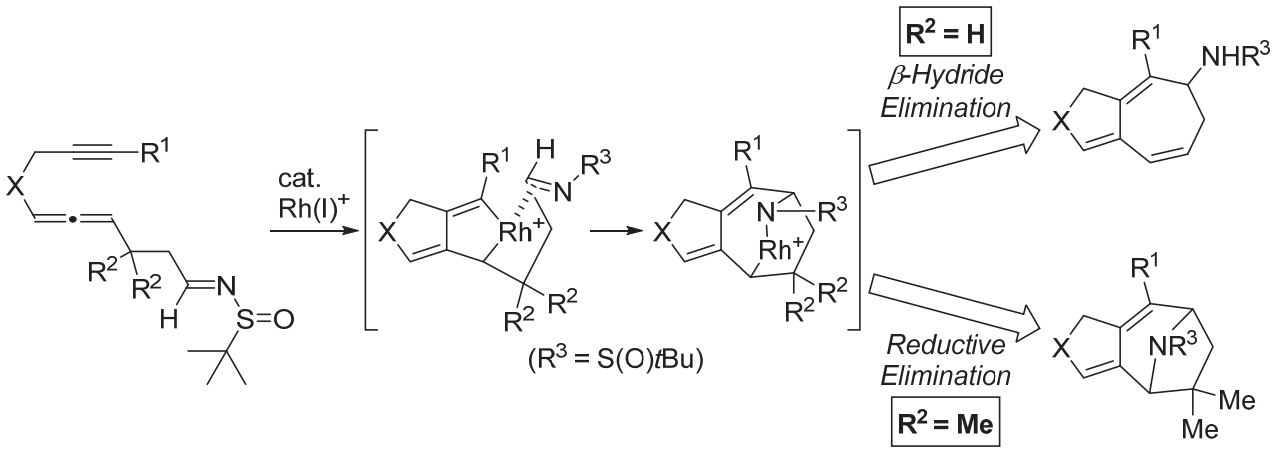
*[41] 本連続反応では、ジエン **125** とビニルカルベノイド **195** との反応によって生成するジビニルシクロプロパン **196** を捕捉することはできなかった。このことから、ジビニルシクロプロパン **196** の Cope 転位は速やかに進行しているものと考えられる。また、この Cope 転位は 0 °C と極めて温和な反応条件下で進行することも本反応の特徴の一つである。この理由として、(i) 五員環と三員環から構成されるスピロ構造によりジビニルシクロプロパン **196** が Cope 転位に有利なコンフォメーションに固定されていること、(ii) Cope 転位が進行することによってジビニルシクロプロパン **196** の有する歪みが解消されること、(iii) Rh 錯体がルイス酸として働き Cope 転位を促進させていることなどが考えられる [56]。なお、反応系中には I 価、II 価および III 価の Rh 錯体が存在する可能性が考えられるが、このいずれの価数の Rh 錯体もルイス酸として機能することが知られている [57]。

****

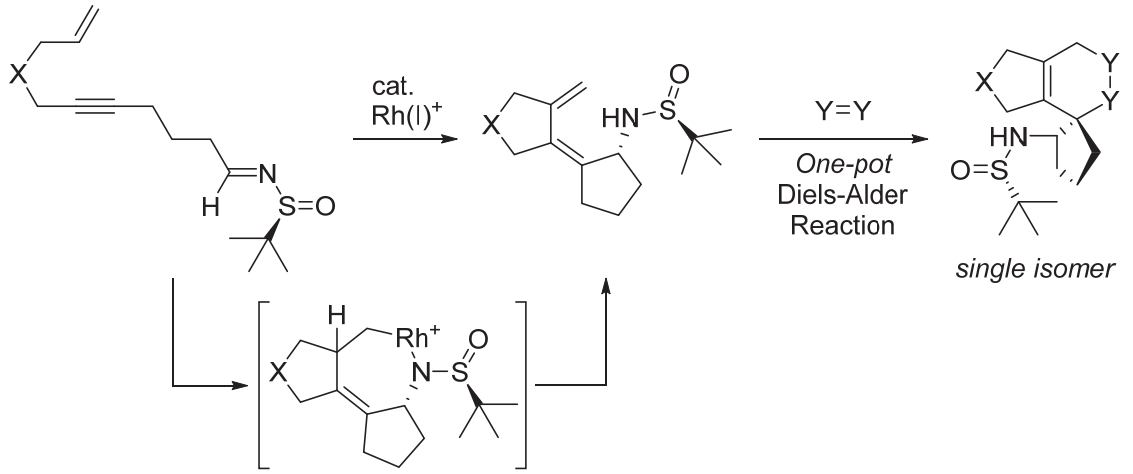
結語

筆者は、博士後期課程において、鎖状化合物から三次元的な骨格を一挙に構築する手法の開発を目指して検討を行い、以下の反応を見出した。

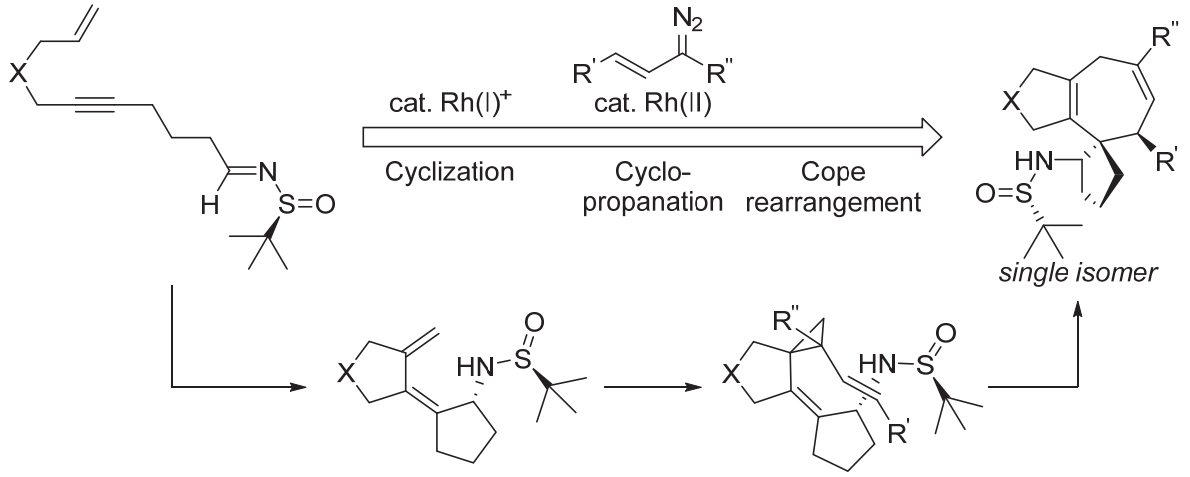
分子内に *t*-ブタンスルフィニルイミンを有するアレン-インと Rh(I)錯体との反応を検討した結果、アザローダサイクル中間体からの β-水素脱離または還元的脱離を経由して、bicyclo[5.3.0]decane 骨格を有する二環式アミドおよび 8-azabicyclo[3.2.1]octane 骨格を有する環化体が良好な収率で生成することを見出した。本反応は、イミンを多重結合の一つとして用いる分子内[2+2+2]環化付加反応の初めての例である。反応機構に関する検討から、本反応はアレンのラセミ化を伴って進行しており、アレンとスルフィニル基の立体化学および配位子が反応経路に大きな影響を及ぼすことを明らかにした [58]。



分子内に光学活性な(*S*)-*t*-ブタンスルフィニルイミンを有するエン-インと[Rh((*S*)-H_8-binap)]BF_4錯体との反応を検討した結果、アザローダサイクル中間体からの β-水素脱離を経由して、エキソサイクリック 1,3-ジエン構造を有する環化体がジアステレオ選択的に生成することを見出した。本反応の検討過程において、基質および配位子の絶対配置が反応性に大きな影響を及ぼすことを明らかにした。さらに、生成した環化体とジエノフィルとの Diels-Alder 反応をワンポットで行うことにより、多環式骨格が立体選択的に構築できることを見出した。



鎖状化合物であるエン-インから、七員環を含むスピロ骨格を一挙に構築する連続反応の開発に成功した。本連続反応では、Rh(I)触媒によるエン-インの環化反応、Rh(II)触媒によるビニルジアゾ化合物とのシクロプロパン化反応、続く Cope 転位という三つの反応が連続して進行し、スピロ化合物が単一の立体異性体として生成することを見出した。



Experimental Section

General Considerations

Reactions dealing with air- or moisture-sensitive compounds were performed in a dry vessel under an argon atmosphere. Solvents (THF, Et_2O, toluene, DMF, CH_3CN) were purified under an argon atmosphere using The Ultimate Solvent System (Glass Counter Inc.). Anhydrous grade solvents (THF, Et_2O, toluene, DMF, CH_2Cl_2) were purchased from Wako Pure Chemical Industries, Ltd. 1,2-Dichloroethane was distilled under an argon atmosphere from CaH_2. NMR spectra were recorded on JEOL ECA-500, ECX-400P, ECS-400, Agilent Unity INOVA 500 or INOVA 600 spectrometer at operating frequencies of 600/500/400 MHz (^{1}H) or 150/125/100 MHz (^{13}C). Chemical shifts (δ) were reported in ppm, relative to the solvent residual peak ($CDCl_3$; 7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C). Data for ^{1}H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad signal, m = multiplet, app = apparent), coupling constants (*J*) in Hz and integration. IR spectra were measured on JASCO FT/IR-460 Plus spectrometer and only significant absorptions were listed. TLC and PTLC were performed on Silica gel 60 $F_{254\alpha}$ (Merck). Column chromatography was performed on RediSep Rf Gold column (Teledyne Isco) using automated flash chromatography system W-prep 2XY (Yamazen Corporation). ESI and APCI mass spectra were measured on Thermo Scientific Exactive mass spectrometer. EI mass spectra were measured on JEOL JMS-T100GC$_V$. Optical rotations were measured on JASCO P-1030 digital polarimeter at the sodium D line (589 nm). Melting points were measured on Yanaco Micro Melting Point apparatus MP-J3.

General Procedure for Rh(I)-Catalyzed Cyclization

General Procedure (1) for Cyclization Using [Rh(ligand)]X

A solution of [Rh(ligand)(diene)]X[59] (0.0150 mmol, 10 mol% to a substrate) in $ClCH_2CH_2Cl$ (0.58 mL, 0.026 M to Rh, degassed by three freeze-pump up-thaw cycles) was stirred under H_2 atmosphere at room temperature for 1 h. Then the reaction mixture was degassed by three freeze-pump up-thaw cycles and the reaction flask was filled with an argon gas. To the mixture, was added a solution of a substrate (0.150 mmol) in $ClCH_2CH_2Cl$ (0.92 mL, 0.16 M to a substrate, degassed by three freeze-pump up-thaw cycles) by cannulation under an argon atmosphere and the reaction mixture was stirred at the indicated temperature for the indicated time. After removal of the solvent, the residue was purified by silica gel column chromatography to give a product.

General Procedure (2) for Cyclization Using [Rh(ligand)]X

A solution of $[Rh(diene)_2]X$[59] (0.0150 mmol, 10 mol% to a substrate) and ligand (0.0150 mmol, 10 mol% to a substrate) in $ClCH_2CH_2Cl$ (0.58 mL, 0.026 M to Rh, degassed by three freeze-pump up-thaw cycles) was stirred under H_2 atmosphere at room temperature for 1 h. Then the reaction mixture was degassed by three freeze-pump up-thaw cycles and the reaction flask was filled with an argon gas. To the mixture, was added a solution of a substrate (0.150 mmol) in $ClCH_2CH_2Cl$ (0.92 mL, 0.16 M to a substrate, degassed by three freeze-pump up-thaw cycles) by cannulation under an argon atmosphere and the reaction mixture was stirred at the indicated temperature for the indicated time. After removal of the solvent, the residue was purified by silica gel column chromatography to give a product.

Chapter 1

<Section 2>

<Scheme 16>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6a** (57.5 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~20:80) to give **15a** (42.5 mg, 74% yield) as a pale yellow oil and **16a** (1.4 mg, 3% yield) as a pale yellow oil.

Dimethyl (*E*)-3-((1*E*,4*E*)-4-((benzyloxy)imino)but-1-en-1-yl)-4-ethylidenecyclopent-2-ene-1,1-dicarboxylate (15a)

Spectral data of **15a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.44 (t, *J* = 6.1 Hz, 1H), 7.38-7.29 (m, 5H), 6.09 (t, *J* = 3.4 Hz, 2H), 6.01 (s, 1H), 5.58-5.52 (m, 1H), 5.07 (s, 2H), 3.75 (s, 6H), 3.17-3.15 (br m, 2H), 3.05-3.03 (m, 2H), 1.73 (d, *J* = 6.8 Hz, 3H) ppm; ^{1}H NMR (500 MHz, C_6D_6) δ: 7.33 (d, *J* = 7.8 Hz, 2H), 7.23 (t, *J* = 6.0 Hz, 1H), 7.14-7.00 (m, 3H), 6.23 (s, 1H), 5.90 (d, *J* = 16.6 Hz, 1H), 5.83-5.77 (m, 1H), 5.38-5.34 (m, 1H), 5.09 (s, 2H), 3.36-3.34 (br m, 2H), 3.32 (s, 6H), 2.62 (t, *J* = 6.2 Hz, 2H), 1.48 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.3 (2C), 148.7, 144.4, 141.5, 137.7, 129.0, 128.5 (2C), 128.4 (2C), 128.0, 127.2, 124.2, 116.1, 75.9, 63.5, 53.0, 53.0, 36.0, 33.3, 14.9 ppm; IR (neat) $\tilde{\nu}$: 2952, 1736 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{22}H_{25}NO_5$ [M^+] 383.1733, found 383.1731.

Dimethyl (*E*)-3-((*E*)-3-cyanoprop-1-en-1-yl)-4-ethylidenecyclopent-2-ene-1,1-dicarboxylate (16a)

Spectral data of **16a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.40 (dd, *J* = 16.0, 1.1 Hz, 1H), 6.07 (s, 1H), 5.98 (dt, *J* = 16.0, 5.4 Hz, 1H), 5.61-5.55 (m, 1H), 3.75 (s, 6H), 3.22 (dd, *J* = 5.7, 1.7 Hz, 2H), 3.17 (s, 2H), 1.74 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.1 (2C), 143.4, 141.2, 128.4, 126.3, 121.5, 117.0, 117.0, 63.5, 53.1 (2C), 35.9, 21.0, 14.9 ppm; IR (neat) ν̃: 2954, 2252, 1735 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{15}H_{17}NO_4$ [M^+] 275.1158, found 275.1156.

<Scheme 17>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6b** (62.3 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **9b** (20.7 mg, 33% yield, dr = 1.2:1) as a pale yellow oil and **16b** (1.0 mg, 2% yield) as a pale yellow oil.

Dimethyl 8-methyl-7-((*p*-toluenesulfinyl)amino)-6,7-dihydroazulene-2,2(1*H*)-dicarboxylate (9b)

Spectral data of **9b**: Diastereomixture (1.1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.58 (t, *J* = 6.8 Hz, 2H and 2H), 7.30 (dd, *J* = 10.9, 8.4 Hz, 2H and 2H), 6.34 (dd, *J* = 11.1, 2.3 Hz, 1H), 6.28 (dd, *J* = 11.1, 2.3 Hz, 1H), 5.95 (s, 1H), 5.93 (s, 1H), 5.86-5.82 (m, 1H), 5.74-5.69 (m, 1H), 4.45 (d, *J* = 9.5 Hz, 1H), 4.24 (d, *J* = 9.5 Hz, 1H), 3.93-3.88 (m, 1H), 3.75-3.70 (m, 7H and 6H), 3.22-3.07 (m, 2H and 2H), 2.85-2.79 (m, 1H), 2.62-2.57 (m, 2H), 2.42 (s, 3H), 2.40 (s, 3H), 2.39-2.35 (m, 1H), 1.94 (s, 3H), 1.53 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.1, 171.1, 171.0, 143.8, 142.2, 141.4, 141.4, 141.4, 137.3, 137.1, 133.6, 133.6, 131.9, 131.4, 129.6, 129.6, 129.5, 129.3, 126.8, 126.7, 126.4, 125.9, 62.8, 57.1, 55.8, 53.2, 38.7, 38.7, 35.8, 35.2, 21.5, 21.5, 21.4, 21.1 ppm; IR (neat) ν̃: 3308, 2953, 1734 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{22}H_{25}NO_5S$ [M^+] 415.1453, found 415.1468.

Dimethyl (*E*)-3-((*Z*)-3-cyanoprop-1-en-1-yl)-4-ethylidenecyclopent-2-ene-1,1-dicarboxylate (16b)

Spectral data of **16b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.21 (dd, *J* = 10.9, 1.2 Hz, 1H), 5.89 (s, 1H), 5.76 (dt, *J* = 10.9, 6.9 Hz, 1H), 5.42-5.37 (m, 1H), 3.77 (s, 6H), 3.23 (dd, *J* = 7.4, 1.7 Hz, 2H), 3.15 (s, 2H), 1.72 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.1 (2C), 142.3, 142.2, 130.8, 127.0, 122.9, 117.9, 117.7, 64.2, 53.3 (2C), 35.2, 17.5, 15.0 ppm; IR (neat) ν̃: 2955, 2252, 1735 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{15}H_{17}NNaO_4^+$ [$(M+Na)^+$] 298.1050, found 298.1049.

Dimethyl 7-((*tert*-butanesulfinyl)amino)-8-methyl-6,7-dihydroazulene-2,2(1*H*)-dicarboxylate (9c)

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6c** (57.2 mg, 0.150 mmol) and $[Rh(dppbz)(nbd)]ClO_4$ (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **9c** (39.3 mg, 69% yield, dr = 1.1:1) as a pale yellow oil.

Spectral data of **9c**: Diastereomixture (1.2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.33 (dd, *J* = 11.2, 2.6 Hz, 1H), 6.28 (dd, *J* = 11.5, 2.9 Hz, 1H), 5.96 (s, 1H), 5.95 (s, 1H), 5.81-5.77 (m, 1H), 5.73-5.69 (m, 1H), 3.90-3.80 (m, 1H and 1H), 3.76 (s, 3H and 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.44 (d, *J* = 10.9 Hz, 1H), 3.27-3.11 (m, 1H and 3H), 2.83-2.45 (m, 2H and 2H), 1.96 (s, 3H), 1.84 (s, 3H), 1.18 (s, 9H), 1.16 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.1, 171.0, 170.9, 170.8, 143.8, 143.7, 137.1, 136.8, 133.6, 133.2, 131.4, 131.2, 129.2, 128.8, 127.1, 126.4, 62.6, 60.2, 59.6, 56.2, 55.8, 53.1, 53.1, 38.6, 38.5, 35.0, 34.9, 22.7, 22.6, 21.8, 21.5 ppm; IR (neat) ν̃: 3296, 2954, 1736 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{19}H_{27}NO_5S$ [M^+] 381.1610, found 381.1608.

<Table 1>

<Entry 2>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6c** (57.2 mg, 0.150 mmol) and $[Rh(dppe)(nbd)]ClO_4$ (10.4 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50

mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **9c** (33.7 mg, 59% yield, dr = 1.5:1) as a pale yellow oil.

<Entry 3>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6c** (57.2 mg, 0.150 mmol) and [Rh(dppp)(nbd)]ClO_4 (10.6 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **9c** (43.7 mg, 76% yield, dr = 1:1.1) as a pale yellow oil.

<Entry 4>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6c** (57.2 mg, 0.150 mmol) and [Rh(dppb)(nbd)]ClO_4 (10.8 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **9c** (5.2 mg, 9% yield, dr = 1.8:1) as a pale yellow oil.

<Entry 5>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6c** (57.2 mg, 0.150 mmol) and [Rh(*rac*-binap)(nbd)]ClO_4 (13.8 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was obtained as a complex mixture.

<Entry 6>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6c** (57.2 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (5.56 mg, 0.00750 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 8 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **9c** (3.9 mg, 7% yield, dr = 1:1) as a pale yellow oil and **6c** (37.6 mg, 66% yield) as a pale yellow oil.

<Entry 7>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6c** (57.2 mg, 0.150 mmol) and [Rh(dppp)(nbd)]ClO_4 (5.30 mg, 0.00750 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **9c** (42.5 mg, 74% yield, dr = 1.2:1) as a pale yellow oil.

<Table 2>

<Entry 1>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6c** (57.2 mg, 0.150 mmol), [Rh(nbd)$_2$]ClO_4 (5.80 mg, 0.0150 mmol) and DPPP (6.19 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **9c** (37.4 mg, 65% yield, dr = 1.2:1) as a pale yellow oil.

<Entry 2>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6c** (57.2 mg, 0.150 mmol), [Rh(nbd)$_2$]OTf (6.54 mg, 0.0150 mmol) and DPPP (6.19 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **9c** (39.5 mg, 69% yield, dr = 1.2:1) as a pale yellow oil.

<Entry 3>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6c** (57.2 mg, 0.150 mmol), [Rh(nbd)$_2$]BF_4 (5.61 mg, 0.0150 mmol) and DPPP (6.19 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **9c** (36.3 mg, 63% yield, dr = 1.2:1) as a pale yellow oil.

<Entry 4>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6c** (57.2 mg, 0.150 mmol), $[Rh(nbd)_2]PF_6$ (6.48 mg, 0.0150 mmol) and DPPP (6.19 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **9c** (40.1 mg, 70% yield, dr = 1.2:1) as a pale yellow oil.

<Entry 5>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6c** (57.2 mg, 0.150 mmol), $[Rh(nbd)_2]SbF_6$ (7.84 mg, 0.0150 mmol) and DPPP (6.19 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **9c** (36.6 mg, 64% yield, dr = 1.2:1) as a pale yellow oil.

<Table 3>

Dimethyl

7-((*tert*-butanesulfinyl)amino)-8-(trimethylsilyl)-6,7-dihydroazulene-2,2(1*H*)-dicarboxylate

(9d)

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6d** (65.9 mg, 0.150 mmol) and $[Rh(dppp)(nbd)]ClO_4$ (5.30 mg, 0.00750 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~50:50) to give **9d** (less polar diastereomer: 35.2 mg, 53% yield, more polar diastereomer: 7.2 mg, 11% yield) as a pale yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6d** (65.9 mg, 0.150 mmol) and $[Rh(dppbz)(nbd)]ClO_4$ (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc =

90:10~40:60) to give **9d** (less polar diastereomer: 23.7 mg, 36% yield, more polar diastereomer: 7.3 mg, 11% yield) as a pale yellow oil.

The stereochemistries of these diastereomers were not determined.

Spectral data of **9d**: Less polar diastereomer; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.24 (dd, *J* = 11.5, 2.9 Hz, 1H), 6.13 (s, 1H), 5.70-5.65 (m, 1H), 4.30 (t, *J* = 5.2 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.31 (d, *J* = 16.0 Hz, 1H), 3.18 (d, *J* = 16.0 Hz, 1H), 3.08 (d, *J* = 5.2 Hz, 1H), 2.65 (ddd, *J* = 17.2, 8.0, 5.7 Hz, 1H), 2.54 (d, *J* = 17.2 Hz, 1H), 1.13 (s, 9H), 0.29 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.8, 170.4, 152.3, 146.4, 136.5, 136.0, 129.4, 125.3, 63.3, 55.7, 53.7, 53.1 (2C), 41.5, 35.3, 22.6 (3C), 0.1 (3C) ppm; IR (neat) ṽ: 3323, 2954, 1738, 1560 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{20}H_{30}NO_5SSi$ [(M-Me)$^+$] 424.1614, found 424.1612.

More polar diastereomer; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.33 (dd, *J* = 10.9, 2.9 Hz, 1H), 6.10 (s, 1H), 5.81-5.77 (m, 1H), 4.20 (dd, *J* = 10.3, 5.7 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.54 (d, *J* = 10.3 Hz, 1H), 3.33 (d, *J* = 16.6 Hz, 1H), 3.16 (d, *J* = 16.6 Hz, 1H), 2.89 (ddd, *J* = 16.2, 8.4, 5.9 Hz, 1H), 2.68 (d, *J* = 16.2 Hz, 1H), 1.16 (s, 9H), 0.22 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.9, 170.6, 151.1, 146.1, 135.9, 135.7, 130.5, 126.1, 63.3, 56.1, 55.5, 53.2, 53.1, 41.0, 36.2, 22.8 (3C), 0.1 (3C) ppm; IR (neat) ṽ: 3295, 2954, 1739, 1597 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{33}NNaO_5SSi^+$ [(M+Na)$^+$] 462.1741, found 462.1741.

Trimethyl 5-((*tert*-butanesulfinyl)amino)-5,6-dihydroazulene-2,2,4(3*H*)-tricarboxylate (9e)

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6e** (63.8 mg, 0.150 mmol) and [Rh(dppp)(nbd)]ClO_4 (5.30 mg, 0.00750 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~50:50) to give **9e** (41.7 mg, 65% yield, dr = 1:1.3) as a pale yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6e** (63.8 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **9e** (45.5 mg, 71% yield, dr = 1:1.1) as a pale yellow oil.

Spectral data of **9e**: Diastereomixture (1:1.3); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.41-6.38 (m, 1H and 2H), 6.34 (dd, *J* = 10.9, 2.3 Hz, 1H), 5.89-5.85 (m, 1H), 5.83-5.78 (m, 1H), 4.91-4.88 (m, 1H), 4.85-4.82 (m, 1H), 3.83-3.61 (m, 11H and 11H), 3.47 (d, *J* = 9.7 Hz, 1H), 3.39 (d, *J* = 7.4 Hz, 1H), 2.93-2.87 (m, 1H), 2.73-2.59 (m, 1H and 2H), 1.14 (s, 9H), 1.13 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.1, 170.0, 169.9, 167.8, 167.7, 154.5, 154.2, 144.2, 144.1, 142.3, 142.1, 130.2, 129.6, 127.4, 126.9, 126.0, 125.4, 63.4, 63.4, 56.1, 55.9, 53.5, 53.3, 53.2, 52.7, 52.1, 52.0, 41.5, 41.4, 35.0, 34.1, 22.7, 22.5 ppm; IR (neat) ν̃: 3291, 2953, 1738, 1709, 1611 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{27}NNaO_7S^+$ [$(M+Na)^+$] 448.1400, found 448.1399.

Dimethyl 7-((*tert*-butanesulfinyl)amino)-6,7-dihydroazulene-2,2(1*H*)-dicarboxylate (9f)

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6f** (55.1 mg, 0.150 mmol) and $[Rh(dppp)(nbd)]ClO_4$ (5.30 mg, 0.00750 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **9f** (22.3 mg, 41% yield, dr = 2.4:1) as a pale yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6f** (55.1 mg, 0.150 mmol) and $[Rh(dppbz)(nbd)]ClO_4$ (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **9f** (24.0 mg, 44% yield, dr = 1.1:1) as a pale yellow oil.

Spectral data of **9f**: Diastereomixture (1.3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.25 (dd, *J* = 11.4, 6.2 Hz, 1H and 1H), 6.04 (d, *J* = 4.9 Hz, 1H and 1H), 5.87-5.78 (m, 2H and 1 H), 5.71 (d, *J* = 2.4 Hz, 1H), 4.13-4.09 (m, 1H and 1H), 3.74 (s, 6H and 6H), 3.32-3.18 (m, 3H and 3H), 2.77-2.52 (m, 2H and 2H), 1.19 (s, 9H and 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.9, 170.8, 170.7, 170.7, 144.1, 144.0, 141.7, 141.2, 135.3, 135.0, 130.1, 129.8, 125.9, 125.8, 125.0, 124.9, 63.4, 63.4, 56.1, 55.9, 54.4, 53.7, 53.2, 53.1, 53.1, 39.5, 39.4, 37.3, 36.5, 22.7, 22.7 ppm; IR (neat) ν̃: 3216, 2954, 1735, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{18}H_{25}NNaO_5S^+$ [$(M+Na)^+$] 390.1346, found 390.1346.

Dimethyl 7-((*tert*-butanesulfinyl)amino)-8-phenyl-6,7-dihydroazulene-2,2(1*H*)-dicarboxylate (9g)

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6g** (65.5 mg, 0.150 mmol) and [Rh(dppp)(nbd)]ClO_4 (5.30 mg, 0.00750 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **9g** (<23.2 mg, <35% yield, dr = 1:>20) as a pale yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6g** (66.5 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **9g** (40.8 mg, 61% yield, dr = 1:2.5) as a pale yellow oil.

Spectral data of **9g**: Diastereomixture (1:2.9); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40-7.24 (m, 5H and 5H), 6.43 (dd, *J* = 11.2, 2.0 Hz, 1H), 6.36 (dd, *J* = 11.2, 2.4 Hz, 1H), 6.13 (s, 1H), 6.11 (s, 1H), 5.91-5.86 (m, 1H), 5.81-5.76 (m, 1H), 4.34 (app t, *J* = 5.1 Hz, 1H), 4.18-4.16 (m, 1H), 3.72 (s, 3H and 3H), 3.70 (s, 3H and 3H), 3.52 (d, *J* = 5.6 Hz, 1H), 3.16-2.93 (m, 2H and 5H), 2.80 (d, *J* = 15.9 Hz, 1H), 2.68 (ddd, *J* = 16.7, 7.9, 6.0 Hz, 1H), 1.15 (s, 9H), 1.13 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.7, 170.7, 170.6, 144.4, 144.2, 143.2, 142.4, 140.1, 139.4, 137.0, 136.8, 135.5, 135.3, 129.9, 129.1, 128.8, 128.7, 128.1, 127.8, 127.4, 127.2, 126.5, 125.8, 62.9, 62.8, 60.3, 58.4, 56.3, 56.1, 56.0, 53.1, 53.1, 53.1, 53.1, 40.4, 39.9, 36.1, 35.4, 22.7, 22.6 ppm; IR (neat) ν̃: 3304, 2954, 1732, 1599 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{24}H_{29}NNaO_5S^+$ [$(M+Na)^+$] 466.1659, found 466.1656.

Dimethyl 7-((*tert*-butanesulfinyl)amino)-8-chloro-6,7-dihydroazulene-2,2(1*H*)-dicarboxylate (9h)

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6h** (60.3 mg, 0.150 mmol) and [Rh(dppp)(nbd)]ClO_4 (5.30 mg, 0.00750 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **9h** (4.3 mg, 7% yield, dr = 1:1.3) as a pale yellow oil and **6h** (20.6 mg, 34%

yield) as a pale yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6h** (60.3 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **9h** (43.2 mg, 72% yield, dr = 1:1.1) as a pale yellow oil.

Spectral data of **9h**: Diastereomixture (1:1.1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.33 (d, *J* = 10.9 Hz, 1H), 6.29 (dd, *J* = 11.2, 2.6 Hz, 1H), 6.09 (s, 1H and 1H), 5.84-5.79 (m, 1H), 5.77-5.73 (m, 1H), 4.25 (t, *J* = 5.2 Hz, 1H), 4.17 (dt, *J* = 10.3, 4.0 Hz, 1H), 3.74 (s, 3H and 3H), 3.73 (s, 3H and 3H), 3.49 (d, *J* = 10.9 Hz, 1H), 3.47 (d, *J* = 6.9 Hz, 1H), 3.40-3.24 (m, 2H and 2H), 2.83-2.81 (m, 2H), 2.75 (dd, *J* = 15.8, 2.6 Hz, 1H), 2.61-2.55 (m, 1H), 1.18 (s, 9H), 1.15 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.4, 170.3, 170.1, 141.4, 141.3, 140.4, 139.8, 136.7, 136.4, 128.9, 128.5, 128.4, 128.1, 126.8, 126.2, 62.7, 62.5, 62.5, 61.2, 56.7, 56.2, 53.3, 53.3, 40.2, 34.8, 34.0, 22.6, 22.6 ppm; IR (neat) ν̃: 3293, 2954, 1738 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{18}H_{25}ClNO_5S^+$ $[(M+H)^+]$ 402.1137, found 402.1145.

<Scheme 19>

A suspension of **1a**[19] (417 mg, 1.50 mmol), *O*-benzylhydroxylamine hydrochloride (311 mg, 1.95 mmol) and $NaOAc{\cdot}3H_2O$ (306 mg, 2.25 mmol) in MeOH (7.5 mL) was stirred at r.t. for 2 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 90:10~80:20) to give **6a** (241 mg, 42% yield) and **6a'** (107 mg, 19% yield) as a yellow oil.

Dimethyl (*E*)-2-(6-((benzyloxy)imino)hexa-1,2-dien-1-yl)-2-(but-2-yn-1-yl)malonate (6a)

Spectral data of **6a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.47 (t, *J* = 5.7 Hz, 1H), 7.37-7.27 (m, 5H), 5.77-5.75 (m, 1H), 5.41 (q, *J* = 6.4 Hz, 1H), 5.05 (s, 2H), 3.75 (s, 3H), 3.74 (s, 3H), 2.85-2.83 (m, 2H), 2.35-2.31 (m, 2H), 2.26-2.20 (m, 2H), 1.72 (t, *J* = 2.6 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 203.5, 169.8, 169.7, 150.4, 137.8, 128.5 (2C), 128.4 (2C), 127.9, 94.7, 91.3, 78.7, 75.7,

73.8, 57.9, 53.1 (2C), 28.9, 25.6, 25.0, 3.6 ppm; IR (neat) ṽ: 2953, 1969, 1739 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}NNaO_5^+$ $[(M+Na)^+]$ 406.1625, found 406.1617.

Dimethyl (*Z*)-2-(6-((benzyloxy)imino)hexa-1,2-dien-1-yl)-2-(but-2-yn-1-yl)malonate (6a')

Spectral data of **6a'**: ^1H NMR (500 MHz, $CDCl_3$) δ: 7.35-7.27 (m, 5H), 6.72 (t, *J* = 5.3 Hz, 1H), 5.80-5.77 (m, 1H), 5.40 (q, *J* = 6.4 Hz, 1H), 5.10 (s, 2H), 3.74 (s, 3H), 3.72 (s, 3H), 2.85 (q, *J* = 2.4 Hz, 2H), 2.49 (td, *J* = 7.4, 5.4 Hz, 2H), 2.27-2.18 (m, 2H), 1.72 (t, *J* = 2.4 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 203.5, 169.8, 169.7, 151.3, 138.1, 128.5 (2C), 128.1 (2C), 127.9, 94.8, 91.4, 78.7, 75.9, 73.8, 57.9, 53.1, 53.0, 25.1 (2C), 25.1, 3.6 ppm; IR (neat) ṽ: 2953, 1969, 1739, 1632 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}NNaO_5^+$ $[(M+Na)^+]$ 406.1625, found 406.1615.

<Scheme 22>

Dimethyl 2-(but-2-yn-1-yl)-2-((*E*)-6-((*p*-toluenesulfinyl)imino)hexa-1,2-dien-1-yl)malonate (6b)

A suspension of **1a**[19] (500 mg, 1.80 mmol), *p*-toluenesulfinamide (335 mg, 2.16 mmol), PPTS (45.1 mg, 0.180 mmol) and $MgSO_4$ (1.08 g, 8.98 mmol) in toluene (3.5 mL) was stirred at 60 °C for 3 h. The reaction mixture was diluted with EtOAc and filtered. The filtrate was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **6b** (437 mg, 59% yield, dr = 1:1) as a pale yellow oil.

Spectral data of **6b**: Diastereomixture (1:1); ^1H NMR (500 MHz, $CDCl_3$) δ: 8.24 (t, *J* = 4.2 Hz, 1H and 1H), 7.55 (d, *J* = 8.1 Hz, 2H and 2H), 7.30 (d, *J* = 8.1 Hz, 2H and 2H), 5.75-5.70 (m, 1H and 1H), 5.43 (ddd, *J* = 12.6, 6.2, 1.2 Hz, 1H and 1H), 3.75-3.73 (m, 6H and 6H), 2.87-2.78 (m, 2H and 2H), 2.68-2.56 (m, 2H and 2H), 2.40 (s, 3H and 3H), 2.38-2.33 (m, 2H and 2H), 1.69-1.67 (br m, 3H and 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 203.5, 203.4, 169.6, 169.6, 166.0, 166.0, 141.8, 141.8, 141.7, 141.7, 129.8, 129.8, 124.6, 124.6, 94.5, 94.4, 91.5, 91.5, 78.6, 78.6, 73.7, 57.8, 57.8, 53.0, 34.8, 34.7, 24.9, 24.8, 23.9, 23.8, 21.5, 3.5 ppm; IR (neat) ṽ: 2953, 1969, 1739, 1621 cm^{-1}; HRMS (APCI) *m/z* calcd. for $C_{22}H_{26}NO_5S^+$ $[(M+H)^+]$ 416.1526, found 416.1526.

<Scheme 23>

Dimethyl (*E*)-2-(but-2-yn-1-yl)-2-(6-((*tert*-butanesulfinyl)imino)hexa-1,2-dien-1-yl)malonate (6c)

A suspension of **1a**[19] (404 mg, 1.45 mmol), *t*-butanesulfinamide (211 mg, 1.74 mmol), PPTS (36.5 mg, 0.145 mmol) and $MgSO_4$ (874 mg, 7.26 mmol) in toluene (7.3 mL) was stirred at 40 °C for 3 h. The reaction mixture was diluted with EtOAc and filtered. The filtrate was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 70:30~60:40) to give **6c** (539 mg, 97% yield, dr = 1:1) as a yellow oil.

Spectral data of **6c**: Diastereomixture (1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (t, *J* = 4.1 Hz, 1H and 1H), 5.80-5.76 (m, 1H and 1H), 5.51-5.45 (m, 1H and 1H), 3.76 (s, 3H and 3H), 3.75 (s, 3H and 3H), 2.86-2.84 (m, 2H and 2H), 2.69-2.64 (m, 2H and 2H), 2.40-2.35 (m, 2H and 2H), 1.73 (t, *J* = 2.5 Hz, 3H and 3H), 1.19 (s, 9H and 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 203.5, 203.4, 169.7, 169.6, 168.5, 168.5, 94.7, 94.6, 91.6, 91.5, 78.6, 73.7, 57.8, 56.7, 56.6, 53.1, 35.1, 35.0, 24.9, 24.1, 23.9, 22.4, 3.6 ppm; IR (neat) ν̃: 2954, 1969, 1739, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{19}H_{27}NNaO_5S^+$ $[(M+Na)^+]$ 404.1502, found 404.1500.

Dimethyl (*E*)-2-(6-((*tert*-butanesulfinyl)imino)hexa-1,2-dien-1-yl)-2-(3-(trimethylsilyl)prop-2-yn-1-yl)malonate (6d)

A suspension of **1d**[19] (603 mg, 1.79 mmol), *t*-butanesulfinamide (260 mg, 2.15 mmol), PPTS (45.0 mg, 0.179 mmol) and $MgSO_4$ (1.08 g, 8.95 mmol) in toluene (18 mL) was stirred at 40 °C for 2 h. The reaction mixture was diluted with EtOAc and filtered. The filtrate was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 6:1~3:1) to give **6d** (711 mg, 90% yield, dr = 1:1) as a pale yellow oil.

Spectral data of **6d**: Diastereomixture (1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (t, *J* = 3.6 Hz, 1H and 1H), 5.80-5.76 (m, 1H and 1H), 5.51-5.44 (m, 1H and 1H), 3.76 (s, 3H and 3H), 3.75 (s, 3H and 3H), 2.95 (d, *J* = 16.8 Hz, 1H and 1H), 2.90 (d, *J* = 16.8 Hz, 1H and 1H), 2.70-2.60(m, 2H and

2H), 2.42-2.37 (m, 2H and 2H), 1.19 (s, 9H and 9H), 0.11 (s, 9H and 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 203.4, 203.3, 169.4, 169.4, 168.4, 168.4, 101.5, 94.9, 94.8, 91.5, 91.4, 87.9, 87.9, 57.8, 57.8, 56.7, 53.1, 53.0, 35.2, 35.1, 26.0, 25.9, 24.1, 23.9, 22.4, 0.1 ppm; IR (neat) ν̃: 2956, 2180, 1970, 1741, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{33}NNaO_5SSi^+$ [$(M+Na)^+$] 462.1741, found 462.1741.

Trimethyl (*E*)-10-((*tert*-butanesulfinyl)imino)deca-5,6-dien-1-yne-1,4,4-tricarboxylate (6e)

A suspension of **1e**[19] (188 mg, 0.585 mmol), *t*-butanesulfinamide (85.0 mg, 0.701 mmol), PPTS (14.7 mg, 0.0585 mmol) and $MgSO_4$ (352 mg, 2.92 mmol) in toluene (5.8 mL) was stirred at 40 °C for 1 h. The reaction mixture was diluted with EtOAc and filtered. The filtrate was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 2:1~1:1) to give **6e** (244 mg, 98% yield, dr = 1:1) as a yellow oil.

Spectral data of **6e**: Diastereomixture (1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (t, *J* = 4.1 Hz, 1H and 1H), 5.80-5.75 (m, 1H and 1H), 5.58-5.51 (m, 1H and 1H), 3.79 (s, 3H and 3H), 3.78 (s, 3H and 3H), 3.73 (s, 3H and 3H), 3.08 (d, *J* = 17.2 Hz, 1H and 1H), 3.03 (d, *J* = 17.2 Hz, 1H and 1H), 2.68-2.64 (m, 2H and 2H), 2.45-2.38 (m, 2H and 2H), 1.19 (s, 9H and 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 203.6, 203.5, 168.9, 168.9, 168.4, 153.7, 95.7, 95.6, 91.0, 90.9, 84.0, 75.1, 56.9, 56.7, 53.5, 52.8, 35.1, 35.0, 24.4, 24.0, 23.9, 22.5 ppm; IR (neat) ν̃: 2956, 2242, 1968, 1740, 1717, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{27}NNaO_7S^+$ [$(M+Na)^+$] 448.1400, found 448.1399.

Dimethyl (*E*)-2-(6-((*tert*-butanesulfinyl)imino)hexa-1,2-dien-1-yl)-2-(3-phenylprop-2-yn-1-yl)malonate (6g)

A suspension of **1g**[19] (317 mg, 0.932 mmol), *t*-butanesulfinamide (136 mg, 1.12 mmol), PPTS (23.4 mg, 0.0932 mmol) and $MgSO_4$ (561 mg, 4.66 mmol) in toluene (5.0 mL) was stirred at 40 °C for 1 h. The reaction mixture was diluted with EtOAc and filtered. The filtrate was concentrated and

purified by silica gel column chromatography (Hexane/EtOAc = 3:1~2:1) to give **6g** (417 mg, quant., dr = 1:1) as a yellow oil.

Spectral data of **6g**: Diastereomixture (1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02 (d, *J* = 4.0 Hz, 1H and 1H), 7.35-7.24 (m, 5H and 5H), 5.86-5.82 (m, 1H and 1H), 5.55-5.48 (m, 1H and 1H), 3.79 (s, 3H and 3H), 3.78 (s, 3H and 3H), 3.15 (d, *J* = 16.8 Hz, 1H and 1H), 3.10 (d, *J* = 16.8 Hz, 1H and 1H), 2.67-2.62 (m, 2H and 2H), 2.43-2.35 (m, 2H and 2H), 1.16 (s, 9H and 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 203.6, 203.5, 169.6, 169.5, 168.4, 168.4, 131.7, 128.4, 128.1, 123.2, 95.0, 94.9, 91.6, 91.5, 84.7, 83.4, 57.9, 56.7, 53.2, 53.2, 35.1, 35.0, 25.5, 25.5, 24.1, 23.9, 22.4 ppm; IR (neat) ṽ: 2954, 1969, 1739, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{24}H_{29}NNaO_5S^+$ [$(M+Na)^+$] 466.1659, found 466.1655.

Dimethyl

(*E*)-2-(6-((*tert*-butanesulfinyl)imino)hexa-1,2-dien-1-yl)-2-(3-chloroprop-2-yn-1-yl)malonate

(6h)

A suspension of **1h**[19] (312 mg, 1.04 mmol), *t*-butanesulfinamide (152 mg, 1.25 mmol), PPTS (26.2 mg, 0.104 mmol) and $MgSO_4$ (628 mg, 5.22 mmol) in toluene (10 mL) was stirred at 40 °C for 2 h. The reaction mixture was diluted with EtOAc and filtered. The filtrate was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 3:1~2:1) to give **6h** (350 mg, 83% yield, dr = 1:1) as a yellow oil.

Spectral data of **6h**: Diastereomixture (1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (t, *J* = 4.0 Hz, 1H and 1H), 5.78-5.74 (m, 1H and 1H), 5.54-5.48 (m, 1H and 1H), 3.78 (s, 3H and 3H), 3.76 (s, 3H and 3H), 2.93 (d, *J* = 17.5 Hz, 1H and 1H), 2.88 (t, *J* = 9.9 Hz, 1H and 1H), 2.69-2.64 (m, 2H and 2H), 2.43-2.37 (m, 2H and 2H), 1.19 (s, 9H and 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 203.6, 203.5, 169.3, 169.3, 168.4, 168.4, 95.2, 95.1, 91.2, 91.1, 64.8, 60.3, 57.4, 56.7, 53.3, 35.1, 35.0, 24.6, 24.1, 24.0, 22.5 ppm; IR (neat) ṽ: 2955, 2247, 1969, 1740, 1623 cm^{-1}; HRMS (APCI) *m/z* calcd. for $C_{18}H_{25}ClNO_5S^+$ [$(M+H)^+$] 402.1137, found 402.1138.

<Scheme 24>

Dimethyl 8-methyl-7-((4-nitrophenyl)sulfonamido)-6,7-dihydroazulene-2,2(1*H*)-dicarboxylate (36)

To a solution of **9c** (140 mg, 0.367 mmol) in MeOH (1.8 mL), was added 4N HCl in dioxane (0.367 mL, 1.47 mmol). The reaction mixture was stirred at r.t. for 0.5 h. The mixture was concentrated and used in the next reaction without purification. To a solution of the crude amine in CH_2Cl_2 (1.8 mL), were added 4-nitrobenzenesulfonyl chloride (122 mg, 0.551 mmol) and DIPEA (0.256 mL, 1.47 mmol). The reaction mixture was stirred at r.t. for 0.5 h. The reaction was quenched with brine and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~50:50) to give **36** (111 mg, 65% yield, 2 steps) as a yellow solid. The structure of **36** was unambiguously determined by X-ray crystal structure analysis.

CCDC 1052420 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Spectral data of **36**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.36 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 2H), 6.32 (dd, *J* = 11.2, 2.4 Hz, 1H), 6.04 (s, 1H), 5.57-5.53 (m, 1H), 4.97 (d, *J* = 9.5 Hz, 1H), 4.01 (app t, *J* = 7.1 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.09 (d, *J* = 17.1 Hz, 1H), 3.03 (d, *J* = 17.1 Hz, 1H), 2.59 (d, *J* = 15.9 Hz, 1H), 2.48-2.42 (m, 1H), 1.59 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.7, 170.6, 150.1, 147.4, 143.1, 138.5, 135.3, 129.6, 128.3 (2C), 127.8, 127.1, 124.5 (2C), 62.7, 56.4, 53.3, 53.2, 38.7, 33.9, 21.7 ppm; IR (CH_2Cl_2) $\tilde{\nu}$: 3297, 2954, 1732, 1605, 1530 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{21}H_{22}N_2O_8S$ [M^+] 462.1097, found 462.1088; mp 144-146 °C (recrystallized from Hexane/$CHCl_3$ at -30 °C).

<Scheme 26>

Dimethyl 2-(6-hydroxyhexa-1,2-dien-1-yl)-2-(prop-2-yn-1-yl)malonate (45)

A solution of **44**[19] (606 mg, 1.73 mmol) and $TsOH \cdot H_2O$ (32.9 mg, 0.173 mmol) in MeOH (8.6 mL)

was stirred at r.t. for 1 h. The reaction was quenched with saturated $NaHCO_3$ aq. and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 70:30~40:60) to give **45** (467 mg, quant.) as a colorless oil.

Spectral data of **45**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.77-5.75 (m, 1H), 5.44 (q, *J* = 6.6 Hz, 1H), 3.77 (s, 3H), 3.77 (s, 3H), 3.68-3.67 (m, 2H), 2.91 (d, *J* = 2.7 Hz, 2H), 2.18-2.13 (m, 2H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.75-1.64 (m, 2H), 1.41 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 203.5, 169.6, 169.5, 95.8, 90.3, 79.2, 71.2, 62.0, 57.5, 53.2 (2C), 31.7, 24.6, 24.6 ppm; IR (neat) ν̃: 3290, 2954, 1968, 1739 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{14}H_{18}O_5$ [M^+] 266.1154, found 266.1159.

Dimethyl 2-(6-oxohexa-1,2-dien-1-yl)-2-(prop-2-yn-1-yl)malonate (1f)

A suspension of **45** (467 mg, 1.75 mmol) and DMP (1.12 g, 2.63 mmol) in CH_2Cl_2 (8.8 mL) was stirred at r.t. for 3 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with EtOAc. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified with silica gel column chromatography (Hexane/EtOAc = 80:20~60:40) to give **1f** (200 mg, 43% yield) as a colorless oil.

Spectral data of **1f**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.79 (s, 1H), 5.82-5.79 (m, 1H), 5.51 (app q, *J* = 6.1 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 2.94-2.86 (m, 2H), 2.62-2.59 (m, 2H), 2.40-2.35 (m, 2H), 1.99 (t, *J* = 2.6 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 203.4, 201.5, 169.4, 169.3, 94.9, 91.6, 79.2, 71.3, 57.5, 53.2, 53.2, 42.4, 24.5, 20.8 ppm; IR (neat) ν̃: 3286, 2955, 1969, 1739 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{14}H_{16}O_5$ [M^+] 264.0998, found 264.0990.

Dimethyl (*E*)-2-(6-((*tert*-butanesulfinyl)imino)hexa-1,2-dien-1-yl)-2-(prop-2-yn-1-yl)malonate (6f)

A suspension of **1f** (200 mg, 0.757 mmol), *t*-butanesulfinamide (110 mg, 0.908 mmol), PPTS (19.0 mg, 0.076 mmol) and $MgSO_4$ (455 mg, 3.78 mmol) in toluene (3.8 mL) was stirred at 40 °C for 2 h. The reaction mixture was diluted with EtOAc and filtered. The filtrate was concentrated and

purified by silica gel column chromatography (Hexane/EtOAc = 70:30~30:70) to give **6f** (170 mg, 61% yield, dr = 1:1) as a colorless oil.

Spectral data of **6f**: Diastereomixture (1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.09 (t, *J* = 4.2 Hz, 1H and 1H), 5.81-5.78 (m, 1H and 1H), 5.53-5.48 (m, 1H and 1H), 3.78 (s, 3H and 3H), 3.76 (s, 3H and 3H), 2.95-2.87 (m, 2H and 2H), 2.68-2.64 (m, 2H and 2H), 2.43-2.37 (m, 2H and 2H), 1.99 (app td, *J* = 2.6, 1.4 Hz, 1H and 1H), 1.19 (app d, *J* = 0.7 Hz, 9H and 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.0, 169.6, 169.5, 135.7 (4C), 134.1 (2C), 129.7 (2C), 127.8 (4C), 106.7, 101.7, 92.0, 87.9, 61.3, 58.0, 53.0, 52.9, 45.4, 34.4, 28.5, 27.7, 27.0 (3C), 26.3, 19.3, 0.1 (3C) ppm; IR (neat) ṽ: 3290, 2955, 2241, 1969, 1739, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{18}H_{25}NNaO_5S^+$ $[(M+Na)^+]$ 390.1346, found 390.1339.

<Section 3>

<Table 4>

Dimethyl 9-(*tert*-butanesulfinyl)-5,5,8-trimethyl-4,5,6,7-tetrahydro-4,7-epiminoazulene-2,2(1*H*)-dicarboxylate (10i)

Spectral data of **10i**: Diastereomixture (1.1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.63 (s, 1H), 5.57 (s, 1H), 3.90-3.87 (m, 1H and 1H), 3.76-3.75 (m, 1H and 1H), 3.73-3.71 (m, 6H and 6H), 3.12-2.97 (m, 2H and 2H), 1.85-1.78 (m, 1H and 1H), 1.75 (s, 3H), 1.73 (s, 3H), 1.51 (d, *J* = 12.0 Hz, 1H), 1.50 (d, *J* = 12.0 Hz, 1H), 1.27 (s, 3H), 1.25 (s, 3H), 1.14 (s, 9H), 1.10 (s, 9H), 0.93 (s, 3H), 0.90 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.4, 171.4, 171.3, 171.2 146.5, 144.9, 135.1, 135.0, 133.2, 132.2, 122.8, 121.8, 70.7, 68.2, 65.0, 64.9, 61.5, 59.9, 58.5, 58.1, 52.9, 47.3, 45.6, 42.8, 42.6, 33.7, 31.6, 30.9, 26.8, 26.5, 22.5, 17.4, 17.0 ppm; IR (neat) ν̃: 2955, 2867, 1737 cm^{-1}; HRMS (APCI) *m/z* calcd. for $C_{21}H_{32}NO_5S^+$ [$(M+H)^+$] 410.1996, found 410.1997.

<Entry 1>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol), $[Rh(nbd)_2]ClO_4$ (5.80 mg, 0.0150 mmol) and DPPP (6.19 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **10i** (20.5 mg, 33% yield, dr = 1:2.2) as a pale yellow oil and **6i** (30.1 mg, 49% yield) as a pale yellow oil.

<Entry 2>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol), $[Rh(nbd)_2]ClO_4$ (5.80 mg, 0.0150 mmol) and DPPE (5.98 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 4 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **10i** (14.8 mg, 24% yield, dr = 1:3.1) as a

pale yellow oil and **6i** (19.1 mg, 31% yield) as a pale yellow oil.

<Entry 3>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol), $[Rh(nbd)_2]ClO_4$ (5.80 mg, 0.0150 mmol) and DPPB (6.40 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **10i** (26.9 mg, 44% yield, dr = 1:2.1) as a pale yellow oil.

<Entry 4>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol), $[Rh(nbd)_2]ClO_4$ (5.80 mg, 0.0150 mmol) and DPPF (8.32 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **10i** (28.0 mg, 46% yield, dr = 1:4.0) as a pale yellow oil.

<Entry 5>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol), $[Rh(nbd)_2]ClO_4$ (5.80 mg, 0.0150 mmol) and DPPBz (6.70 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **10i** (33.8 mg, 55% yield, dr = 1:2.8) as a pale yellow oil.

<Entry 6>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol), $[Rh(nbd)_2]ClO_4$ (5.80 mg, 0.0150 mmol) and BIPHEP (7.83 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column

chromatography (Hexane/EtOAc = 90:10~20:80) to give **10i** (46.4 mg, 75% yield, dr = 1.1:1) as a pale yellow oil.

<Entry 7>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol), $[Rh(nbd)_2]ClO_4$ (5.80 mg, 0.0150 mmol) and *rac*-BINAP (9.34 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **10i** (45.3 mg, 74% yield, dr = 1.1:1) as a pale yellow oil.

<Entry 8>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol), $[Rh(nbd)_2]ClO_4$ (5.80 mg, 0.0150 mmol) and DPEphos (8.08 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **6i** (40.6 mg, 66% yield) as a pale yellow oil.

<Entry 9>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol), $[Rh(nbd)_2]ClO_4$ (5.80 mg, 0.0150 mmol) and PPh_3 (7.87 mg, 0.0300 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **6i** (28.0 mg, 46% yield) as a pale yellow oil.

<Table 5>

<Entry 1>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6i** 61.4 mg, 0.150 mmol), $[Rh(nbd)_2]ClO_4$ (5.80 mg, 0.0150 mmol) and *rac*-BINAP (9.34 mg, 0.0150

mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **10i** (45.3 mg, 74% yield, dr = 1.1:1) as a pale yellow oil.

<Entry 2>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol), $[Rh(nbd)_2]OTf$ (6.54 mg, 0.0150 mmol) and *rac*-BINAP (9.34 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **10i** (42.7 mg, 70% yield, dr = 1.1:1) as a pale yellow oil.

<Entry 3>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol), $[Rh(nbd)_2]BF_4$ (5.61 mg, 0.0150 mmol) and *rac*-BINAP (9.34 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **10i** (41.7 mg, 68% yield, dr = 1.1:1) as a pale yellow oil.

<Entry 4>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol), $[Rh(nbd)_2]PF_6$ (6.48 mg, 0.0150 mmol) and *rac*-BINAP (9.34 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **10i** (41.3 mg, 67% yield, dr = 1.1:1) as a pale yellow oil.

<Entry 5>

According to the general procedure (2) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol), $[Rh(nbd)_2]SbF_6$ (7.84 mg, 0.0150 mmol) and *rac*-BINAP (9.34 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **10i** (49.2 mg, 80% yield, dr = 1.1:1) as a pale yellow oil.

<Table 6>

<Entry 1>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol) and [Rh(*rac*-binap)(nbd)]ClO_4 (13.8 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 1 h, was purified by column chromatography on silica gel (Hexane/EtOAc = 90:10~60:40) to give **10i** (49.6 mg, 81% yield, dr = 1.1:1) as a pale yellow oil.

<Entry 2>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol) and [Rh(*rac*-binap)(nbd)]ClO_4 (6.88 mg, 0.00750 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 1 h, was purified by column chromatography on silica gel (Hexane/EtOAc = 90:10~60:40) to give **10i** (51.5 mg, 84% yield, dr = 1.1:1) as a pale yellow oil.

<Entry 3>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6i** (61.4 mg, 0.150 mmol) and [Rh(*rac*-binap)(nbd)]ClO_4 (2.75 mg, 0.00300 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 21 h, was purified by column chromatography on silica gel (Hexane/EtOAc = 90:10~60:40) to give **10i** (41.5 mg, 68% yield, dr = 1.1:1) as a pale yellow oil and **6i** (3.5 mg, 6% yield) as a pale yellow oil.

<Entry 4>

To a solution of [Rh(*rac*-binap)(nbd)]ClO_4 (13.8 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (0.58 mL, 0.026 M to Rh, degassed by three freeze-pump up-thaw cycles), was added a solution of **6i** (61.4 mg, 0.150 mmol) in $ClCH_2CH_2Cl$ (0.92 mL, 0.16 M to a substrate, degassed by three freeze-pump up-thaw cycles) by cannulation under an argon gas at room temperature. The reaction mixture was stirred at 80 °C for 1 h. After removal of the solvent, the residue was purified by silica gel column chromatography to give **10i** (5.7 mg, 9% yield, dr = 1.2:1) as a pale yellow oil and **6i** (52.5 mg, 85% yield) as a pale yellow oil.

<Table 7>

Trimethyl 9-(*tert*-butanesulfinyl)-5,5-dimethyl-4,5,6,7-tetrahydro-4,7-epiminoazulene-2,2,8(1*H*)-tricarboxylate (10j)

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6j** (68.0 mg, 0.150 mmol) and [Rh(*rac*-binap)(nbd)]ClO_4 (6.88 mg, 0.0075 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~0:100) to give **10j** (57.4 mg, 84% yield, dr = 1.4:1) as a pale yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6j** (68.0 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **10j** (32.3 mg, 48% yield, dr = 1:9.2) as a pale yellow oil.

Spectral data of **10j**: Diastereomixture (1.1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.16 (s, 1H), 6.11 (s, 1H), 4.63 (dd, *J* = 23.4, 7.0 Hz, 1H and 1H), 4.02 (s, 1H), 3.92 (s, 1H), 3.78-3.74 (m, 9H and 9H), 3.54-3.45 (m, 2H and 2H), 1.97-1.93 (m, 1H and 1H), 1.56-1.54 (m, 1H and 1H), 1.31 (s, 3H), 1.28 (s, 3H), 1.17 (s, 9H), 1.13 (s, 9H), 0.93 (s, 3H), 0.91 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.5, 170.4, 170.1, 170.0, 166.1, 166.0, 154.1, 151.2, 146.6, 145.2, 132.6, 132.0, 128.4, 127.4, 69.9, 68.2, 65.7, 65.5, 58.9, 58.4, 57.3, 56.3, 53.2, 51.8, 51.7, 48.4, 47.4, 43.0, 42.6, 37.8, 37.7, 31.4,

31.1, 26.7, 26.6, 23.0, 22.7 ppm; IR (neat) ν̃: 2956, 1739, 1705 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{31}NNaO_7S^+$ $[(M+Na)^+]$ 476.1713, found 476.1705.

Dimethyl 9-(*tert*-butanesulfinyl)-5,5-dimethyl-4,5,6,7-tetrahydro-4,7-epiminoazulene-2,2(1*H*)-dicarboxylate (10k)

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6k** (59.3 mg, 0.150 mmol) and [Rh(*rac*-binap)(nbd)]ClO_4 (6.88 mg, 0.0075 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 1 h, was purified by silica gel column chromatography (Hexane/EtOAc = 75:25~20:80) to give **10k** (41.0 mg, 69% yield, dr = 1.1:1) as a pale yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6k** (59.3 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 2 h, was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~30:70) to give **10k** (22.4 mg, 38% yield, dr = 1:11) as a pale yellow oil.

Spectral data of **10k**: Diastereomixture (1.1:1); ^1H NMR (500 MHz, $CDCl_3$) δ: 5.99-5.97 (m, 1H and 1H), 5.77 (d, *J* = 1.7 Hz, 1H), 5.71 (d, *J* = 1.7 Hz, 1H), 4.14 (t, *J* = 6.3 Hz, 1H), 4.07 (t, *J* = 6.1 Hz, 1H), 3.97 (s, 1H), 3.89 (s, 1H), 3.74-3.72 (m, 6H and 6H), 3.13-3.03 (m, 2H and 2H), 1.84 (dt, *J* = 12.8, 5.9 Hz, 1H and 1H), 1.60-1.58 (m, 1H and 1H), 1.29 (s, 3H), 1.26(s, 3H), 1.16 (s, 9H), 1.13 (s, 9H), 0.96 (s, 3H), 0.95 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.2, 171.1, 171.0, 170.9, 146.7, 145.3, 142.1, 139.4, 125.5, 125.5, 124.5, 124.1, 70.9, 68.0, 65.4, 65.2, 58.7, 58.3, 57.7, 55.7, 53.0, 48.5, 47.1, 42.9, 42.6, 35.1, 35.1, 31.5, 31.1, 26.9, 26.7, 22.9, 22.7 ppm; IR (neat) ν̃: 2955, 1737 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{29}NNaO_5S^+$ $[(M+Na)^+]$ 418.1659, found 418.1655.

Dimethyl 9-(*tert*-butanesulfinyl)-5,5-dimethyl-8-phenyl-4,5,6,7-tetrahydro-4,7-epiminoazulene-2,2(1*H*)-dicarboxylate (10l)

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6l** (70.7 mg, 0.150 mmol) and [Rh(*rac*-binap)(nbd)]ClO_4 (6.88 mg, 0.0075 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 1 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **10l** (less polar diastereomer: 10.0 mg, 14% yield, more polar diastereomer: 7.1 mg, 10% yield) as a pale yellow oil and **6l** (21.0 mg, 30% yield) as a pale yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6l** (70.7 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 1 h, was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~20:80) to give **10l** (less polar diastereomer: 1.3 mg, 2% yield, more polar diastereomer: 28.9 mg, 41% yield) as a pale yellow oil.

The stereochemistries of these diastereomers were not determined.

Spectral data of **10l**: Less polar distereomer; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39-7.23 (m, 5H), 5.84 (s, 1H), 4.35 (d, *J* = 6.9 Hz, 1H), 3.89 (s, 1H), 3.73 (d, *J* = 1.0 Hz, 6H), 3.38 (d, *J* = 17.6 Hz, 1H), 3.18 (d, *J* = 17.6 Hz, 1H), 1.97 (dd, *J* = 11.9, 6.9 Hz, 1H), 1.71 (d, *J* = 11.9 Hz, 1H), 1.31 (s, 3H), 1.18 (s, 9H), 1.00 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.1, 171.0, 145.5, 138.4, 138.4, 134.7, 128.6 (2C), 127.4, 127.4 (2C), 125.3, 68.1, 65.1, 61.7, 58.7, 53.0 (2C), 47.1, 42.9, 35.5, 31.6, 26.8, 22.6 (3C) ppm; IR (neat) $\tilde{\nu}$: 2954, 1736, 1598 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{26}H_{33}NNaO_5S^+$ $[(M+Na)^+]$ 494.1972, found 494.1963.

More Polar diastereomer; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39-7.24 (m, 5H), 5.79 (s, 1H), 4.48 (d, *J* = 7.2 Hz, 1H), 4.03 (s, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 3.43 (d, *J* = 17.5 Hz, 1H), 3.30 (d, *J* = 17.5 Hz, 1H), 2.04 (dd, *J* = 12.0, 7.2 Hz, 1H), 1.74 (d, *J* = 12.0 Hz, 1H), 1.35 (s, 3H), 1.13 (s, 9H), 1.01 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.1, 170.8, 147.2, 138.0, 137.6, 136.4, 128.6 (2C), 127.3, 126.6 (2C), 124.3, 70.4, 65.4, 59.4, 58.3, 53.0, 53.0, 48.7, 43.0, 36.2, 31.0, 26.8, 22.6 (3C)

ppm; IR (neat) $\tilde{\nu}$: 2955, 1739, 1598 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{26}H_{33}NNaO_5S^+$ $[(M+Na)^+]$ 494.1972, found 494.1970.

Dimethyl 9-(*tert*-butanesulfinyl)-5,5-dimethyl-8-(trimethylsilyl)-4,5,6,7-tetrahydro-4,7-epiminoazulene-2,2(1*H*)-dicarboxylate (10m)

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6m** (70.2 mg, 0.150 mmol) and $[Rh(rac\text{-binap})(nbd)]ClO_4$ (6.88 mg, 0.0075 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 1 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **10m** (less polar diastereomer: 5.2 mg, 7% yield, more polar diastereomer: 2.5 mg, 4% yield) as a pale yellow oil and **6m** (44.9 mg, 64% yield) as a pale yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6m** (70.2 mg, 0.150 mmol) and $[Rh(dppbz)(nbd)]ClO_4$ (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 1 h, was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~20:80) to give **10m** (30.9 mg, 44% yield, dr = 1:6.9) as a pale yellow oil.

The stereochemistries of these diastereomers were not determined.

Spectral data of **10m**: Less polar diastereomer; ^1H NMR (500 MHz, $CDCl_3$) δ: 5.76 (s, 1H), 4.06 (d, *J* = 7.1 Hz, 1H), 3.95 (s, 1H), 3.73 (d, *J* = 1.7 Hz, 6H), 3.13 (d, *J* = 17.2 Hz, 1H), 3.04 (d, *J* = 17.2 Hz, 1H), 1.83 (dd, *J* = 11.7, 7.1 Hz, 1H), 1.43 (d, *J* = 11.7 Hz, 1H), 1.24 (s, 3H), 1.12 (s, 9H), 0.92 (s, 3H), 0.16 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.2, 171.1, 147.0, 145.6, 138.1, 125.4, 66.4, 65.0, 61.2, 58.6, 53.0 (2C), 47.5, 42.8, 36.6, 31.1, 27.0, 22.8 (3C), -0.9 (3C) ppm; IR (neat) $\tilde{\nu}$: 2954, 1738, 1604 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{22}H_{34}NO_5SSi$ $[(M-Me)^+]$ 452.1927, found 452.1929.

More polar diastereomer; ^1H NMR (500 MHz, $CDCl_3$) δ: 5.73 (s, 1H), 4.22 (d, *J* = 7.1 Hz, 1H), 3.92 (s, 1H), 3.73 (s, 6H), 3.09 (s, 2H), 1.84 (dd, *J* = 11.9, 7.2 Hz, 1H), 1.43 (d, *J* = 11.9 Hz, 1H), 1.28 (s, 3H), 1.11 (s, 9H), 0.94 (s, 3H), 0.16 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.2, 170.9, 149.6, 147.0, 136.5, 124.8, 71.2, 65.2, 58.2, 57.6, 53.0 (2C), 48.8, 43.0, 36.6, 30.8, 27.1, 22.7

(3C), -0.8 (3C) ppm; IR (neat) ν̃: 2955, 1738, 1600 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{23}H_{37}NNaO_5SSi^+$ [$(M+Na)^+$] 490.2054, found 490.2052.

Dimethyl 9-(*tert*-butanesulfinyl)-8-chloro-5,5-dimethyl-4,5,6,7-tetrahydro-4,7-epiminoazulene-2,2(1*H*)-dicarboxylate (10n)

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6n** (64.5 mg, 0.150 mmol) and [Rh(*rac*-binap)(nbd)]ClO_4 (6.88 mg, 0.0075 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 1 h, was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~20:80) to give **10n** (7.7 mg, 12% yield, dr = 1.7:1) as a pale yellow oil and **6n** (33.4 mg, 52% yield) as a pale yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6n** (64.5 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 1 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~20:80) to give **10n** (8.0 mg, 12% yield, dr = 1:3.0) as a pale yellow oil and **6n** (31.7 mg, 49% yield) as a pale yellow oil.

Spectral data of **10n**: Diastereomixture (1:1); ^1H NMR (500 MHz, $CDCl_3$) δ: 5.80 (s, 1H), 5.73 (s, 1H), 4.03 (dd, *J* = 23.3, 6.7 Hz, 1H and 1H), 3.98 (s, 1H), 3.79 (s, 1H), 3.76-3.74 (m, 6H and 6H), 3.22-3.10 (m, 2H and 2H), 1.92-1.87 (m, 1H and 1H), 1.74 (dd, *J* = 12.2, 3.2 Hz, 1H and 1H), 1.30 (s, 3H), 1.27 (s, 3H), 1.18 (s, 9H), 1.15 (s, 9H), 0.97 (s, 3H), 0.95 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.8, 170.7, 170.5, 170.3, 145.7, 144.3, 137.8, 135.0, 130.0, 128.3, 126.0, 124.8, 69.8, 68.4, 65.0, 64.9, 62.9, 62.6, 58.9, 58.5, 53.1, 47.5, 45.9, 43.0, 42.9, 34.5, 34.4, 31.7, 31.1, 26.6, 26.4, 22.5, 22.5 ppm; IR (neat) ν̃: 2957, 1738 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{28}ClNNaO_5S^+$ [$(M+Na)^+$] 452.1269, found 452.1263.

<Scheme 29>

Dimethyl (*E*)-2-(but-2-yn-1-yl)-2-(6-((*tert*-butanesulfinyl)imino)-4,4-dimethylhexa-1,2-dien-1-yl)malonate (6i)

A suspension of **1i**[19] (950 mg, 3.10 mmol), *t*-butanesulfinamide (451 mg, 3.72 mmol), PPTS (77.9 mg, 0.310 mmol) and $MgSO_4$ (1.87 g, 15.5 mmol) in toluene (16 mL) was stirred at 50 °C for 4 h. The reaction mixture was diluted with EtOAc and filtered. The filtrate was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **6i** (1.12 g, 89% yield, dr = 1:1) as a pale yellow oil.

Spectral data of **6i**: Diastereomixture (1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.08 (t, *J* = 5.7 Hz, 1H), 8.07 (t, *J* = 5.7 Hz, 1H), 5.87 (d, *J* = 6.3 Hz, 1H), 5.86 (d, *J* = 6.9 Hz, 1H), 5.45 (d, *J* = 6.9 Hz, 1H), 5.44 (d, *J* = 6.3 Hz, 1H), 3.75 (s, 6H and 6H), 2.89-2.80 (m, 2H and 2H), 2.60-2.51 (m, 2H and 2H), 1.73 (m, 3H and 3H), 1.20, (s, 9H and 9H), 1.15-1.14 (m, 6H and 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.1, 201.1, 169.7, 169.6, 168.1, 168.1, 105.5, 105.4, 93.0, 78.9, 73.8, 73.8, 58.1, 56.8, 53.1, 53.0, 48.6, 48.5, 35.5, 35.4, 28.4, 27.6, 25.3, 22.6, 3.7 ppm; IR (neat) ν̃: 2959, 1968, 1740, 1619 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{31}NNaO_5S^+$ [$(M+Na)^+$] 432.1815, found 432.1807.

<Scheme 30>

Dimethyl 5,5,8-trimethyl-9-((4-nitrophenyl)sulfonyl)-4,5,6,7-tetrahydro-4,7-epiminoazulene-2,2(1*H*)-dicarboxylate (49)

A solution of **10i** (95.2 mg, 0.232 mmol), 4N HCl in dioxane (0.232 mL, 0.930 mmol) in MeOH (2.0 mL) was stirred at r.t. for 0.5 h. The reaction mixture was concentrated. A solution of the crude amine, 4-nitrobenzenesulfonyl chloride (77.1 mg, 0.348 mmol) and DIPEA (0.162 mL, 0.928 mmol) in CH_2Cl_2 (2.0 mL) was stirred at r.t. for 0.5 h. The reaction mixture was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **49** (87.3 mg, 77% yield, 2

steps) as a pale yellow solid. The structure of **49** was unambiguously determined by X-ray crystal structure analysis.

CCDC 1052421 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Spectral data of **49**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.15 (dt, *J* = 9.1, 2.2 Hz, 2H), 7.83 (dt, *J* = 9.1, 2.2 Hz, 2H), 5.62 (s, 1H), 4.24 (s, 1H), 4.16 (d, *J* = 7.1 Hz, 1H), 3.74 (s, 3H), 3.65 (s, 3H), 2.74 (d, *J* = 17.6 Hz, 1H), 2.05 (dd, *J* = 12.0, 7.1 Hz, 1H), 1.71 (d, *J* = 17.6 Hz, 1H), 1.56 (s, 3H), 1.50 (d, *J* = 12.0 Hz, 1H), 1.33 (s, 3H), 0.87 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.5, 169.8, 149.8, 145.1, 141.6, 134.0, 131.2, 128.9 (2C), 125.7, 123.5 (2C), 67.1, 64.6, 61.1, 53.2, 53.1, 47.3, 43.5, 32.6, 31.5, 25.6, 17.5 ppm; IR (CH_2Cl_2) ν̃: 2958, 1734, 1606, 1531, 1350 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{23}H_{26}N_2O_8S$ [M^+] 490.1410, found 490.1411; mp 194-195 °C (recrystallized from Hexane/$CHCl_3$ at 0 °C).

<Scheme 31>

Dimethyl 2-(4-((*tert*-butyldimethylsilyl)oxy)but-2-yn-1-yl)-2-(6-((*tert*-butyldiphenylsilyl)oxy)-4,4-dimethylhexa-1,2-dien-1-yl)malonate (52)

To a solution of **50**[27] (2.03 g, 4.66 mmol) in THF (9.3 mL), was added LHMDS (1.3 M in THF, 7.53 mL, 9.87 mmol) at -78 °C. The mixture was stirred at -78 °C for 0.5 h. To the mixture, was added $ClCO_2Me$ (0.372 mL, 4.85 mmol) at -78 °C. The mixture was stirred at -78 °C for 0.5 h. To the mixture, was added 4-(*tert*-butyldiphenylsiloxy)-1-iodo-2-butyne **51**[28] at -78 °C. The mixture was warmed to r.t. and stirred for 20 h. The reaction was quenched with saturated NH_4Cl aq. and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography. (Hexane/EtOAc = 100:0~85:15) to give **52** (1.78 g, 57% yield) as a pale brown oil.

Spectral data of **52**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.67-7.65 (m, 4H), 7.43-7.36 (m, 6H), 5.77 (d, *J*

= 6.4 Hz, 1H), 5.30 (d, *J* = 6.4 Hz, 1H), 4.22 (t, *J* = 2.1 Hz, 2H), 3.74-3.69 (m, 8H), 2.88 (s, 2H), 1.67-1.58 (m, 2H), 1.04 (s, 9H), 0.97 (s, 3H), 0.96 (s, 3H), 0.88 (s, 9H), 0.08 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.1, 169.6, 169.5, 135.7 (4C), 134.1, 134.1, 129.7 (2C), 127.8 (4C), 106.6, 92.0, 81.6, 79.9, 61.3, 57.8, 53.0, 53.0, 51.9, 45.3, 34.4, 28.5, 27.6, 27.0 (3C), 26.0 (3C), 25.5, 19.3, 18.4, -5.0, -5.1 ppm; IR (neat) ν̃: 2956, 2246, 1967, 1741 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{35}H_{47}O_6Si_2$ [(M-*t*Bu)$^+$] 619.2911, found 619.2888.

Dimethyl

2-(6-((*tert*-butyldiphenylsilyl)oxy)-4,4-dimethylhexa-1,2-dien-1-yl)-2-(4-hydroxybut-2-yn-1-yl) malonate (53)

A solution of **52** (1.78 g, 2.63 mmol) and PPTS (66.1 mg, 0.263 mmol) in MeOH (13 mL) was stirred at r.t. for 15 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **53** (1.29 g, 87% yield) as a colorless oil.

Spectral data of **53**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.68-7.66 (m, 4H), 7.44-7.37 (m, 6H), 5.76 (d, *J* = 6.4 Hz, 1H), 5.32 (d, *J* = 6.4 Hz, 1H), 4.15 (td, *J* = 4.2, 2.0 Hz, 2H), 3.73-3.70 (m, 8H), 2.88 (s, 2H), 1.70-1.61 (m, 2H), 1.53 (t, *J* = 6.2 Hz, 1H), 1.04 (s, 9H), 0.97 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.1, 169.6, 169.6, 135.7 (4C), 134.0, 134.0, 129.7 (2C), 127.8 (4C), 106.8, 91.9, 81.4, 81.1, 61.3, 57.7, 53.1, 53.1, 51.3, 45.1, 34.4, 28.3, 27.8, 27.0 (3C), 25.2, 19.2 ppm; IR (neat) ν̃: 3480, 2957, 1967, 1739 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{29}H_{33}O_6Si$ [(M-*t*Bu)$^+$] 505.2046, found 505.2039.

Trimethyl

10-((*tert*-butyldiphenylsilyl)oxy)-8,8-dimethyldeca-5,6-dien-1-yne-1,4,4-tricarboxylate (54)

A solution of **53** (1.29 g, 2.28 mmol), TEMPO (71.4 mg, 0.457 mmol) and $PhI(OAc)_2$ (1.62 g, 5.02 mmol) in $MeCN/H_2O$ (9.2 mL, 1:1) was stirred at r.t. for 42 h. The reaction mixture was diluted with EtOAc, dried over $MgSO_4$, filtered and concentrated. The residue was dissolved in toluene/MeOH (10 mL, 4:1). To this solution, was added $TMSCHN_2$ (0.6 M in hexane, 7.61 mL,

4.57 mmol) at r.t. The reaction mixture was stirred at r.t. for 0.5 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 95:5~70:30) to give **54** (704 mg, 52% yield, 2 steps) as a brown oil.

Spectral data of **54**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.66 (dd, *J* = 7.8, 1.5 Hz, 4H), 7.44-7.37 (m, 6H), 5.75 (d, *J* = 6.4 Hz, 1H), 5.37 (d, *J* = 6.1 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.71-3.69 (m, 5H), 2.97 (s, 2H), 1.68-1.59 (m, 2H), 1.04 (s, 9H), 0.98 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.2, 169.1, 169.0, 153.8, 135.7 (4C), 134.0, 134.0, 129.7 (2C), 127.8 (4C), 107.3, 91.5, 84.2, 75.0, 61.3, 57.1, 53.3, 53.3, 52.7, 45.2, 34.4, 28.3, 27.7, 27.0 (3C), 24.9, 19.2 ppm; IR (neat) ṽ: 2956, 2244, 1966, 1741, 1718 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{30}H_{33}O_7Si$ [(M-*t*Bu)$^+$] 533.1996, found 533.1975.

Trimethyl 10-hydroxy-8,8-dimethyldeca-5,6-dien-1-yne-1,4,4-tricarboxylate (55)

To a solution of **54** (680 mg, 1.15 mmol) in THF (12 mL), was added HF-pyridine (1.10 mL, 42.3 mmol) at r.t. The mixture was stirred at r.t. for 5 h. The reaction was quenched with saturated $NaHCO_3$ aq. and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~40:60) to give **55** (305 mg, 75% yield) as a colorless oil.

Spectral data of **55**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.82 (d, *J* = 6.4 Hz, 1H), 5.46 (d, *J* = 6.4 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 3.72-3.66 (m, 2H), 3.05 (s, 2H), 1.68-1.63 (m, 2H), 1.42 (t, *J* = 4.6 Hz, 1H), 1.05 (s, 3H), 1.05 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.2, 169.0, 168.9, 153.8, 107.2, 91.6, 84.1, 75.1, 59.9, 57.1, 53.4, 53.3, 52.7, 45.3, 34.4, 28.1, 28.0, 24.9 ppm; IR (neat) ṽ: 3416, 2958, 2244, 1966, 1839 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{18}H_{24}NaO_7^+$ [(M+Na)$^+$] 357.1414, found 357.1410.

Trimethyl 8,8-dimethyl-10-oxodeca-5,6-dien-1-yne-1,4,4-tricarboxylate (1j)

A suspension of **55** (300 mg, 0.851 mmol), $NaHCO_3$ (143 mg, 1.70 mmol) and DMP (542 mg, 1.28 mmol) in CH_2Cl_2 (4.3 mL) was stirred at r.t. for 2 h. The reaction was quenched with saturated

$Na_2S_2O_3$ aq. and extracted with EtOAc. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **1j** (298 mg, quant.) as a colorless oil.

Spectral data of **1j**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.78 (t, *J* = 2.7 Hz, 1H), 5.87 (d, *J* = 6.4 Hz, 1H), 5.56 (d, *J* = 6.4 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 3.05 (s, 2H), 2.44-2.35 (m, 2H), 1.19 (s, 3H), 1.18 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 202.3, 201.2, 168.8, 168.7, 153.6, 106.1, 92.5, 83.9, 75.2, 57.1, 54.8, 53.4, 53.4, 52.7, 34.5, 28.3, 28.1, 24.8 ppm; IR (neat) ν̃: 2958, 2242, 1968, 1739 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{17}H_{19}O_7$ [(M-Me)$^+$] 335.1131, found 335.1127.

Trimethyl

(*E*)-10-((*tert*-butanesulfinyl)imino)-8,8-dimethyldeca-5,6-dien-1-yne-1,4,4-tricarboxylate (6j)

A suspension of **1j** (340 mg, 0.970 mmol), *t*-butanesulfinamide (141 mg, 1.16 mmol), PPTS (24.4 mg, 0.0970 mmol) and $MgSO_4$ (584 mg, 4.85 mmol) in toluene (4.9 mL) was stirred at 50 °C for 1 h. The reaction mixture was diluted with EtOAc and filtered. The filtrate was concentrated and purified with silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **6j** (389 mg, 88% yield, dr = 1:1) as a colorless oil.

Spectral data of **6j**: Diastereomixture (1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.07 (t, *J* = 5.6 Hz, 1H and 1H), 5.86 (t, *J* = 6.8 Hz, 1H and 1H), 5.53 (t, *J* = 6.0 Hz, 1H and 1H), 3.79 (s, 3H and 3H), 3.78 (s, 3H and 3H), 3.73 (s, 3H and 3H), 3.05 (d, *J* = 2.0 Hz, 2H and 2H), 2.60-2.51 (m, 2H and 2H), 1.21 (s, 9H and 9H), 1.16-1.14 (m, 6H and 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.3, 201.3, 168.8, 168.7, 167.8, 167.7, 153.7, 106.3, 106.3, 92.4, 83.9, 75.1, 57.1, 57.1, 56.7, 53.4, 53.3, 52.7, 48.5, 48.4, 35.5, 35.4, 28.3, 28.3, 27.6, 27.6, 24.8, 22.5 ppm; IR (neat) ν̃: 2959, 2244, 1968, 1740, 1715, 1619 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{31}NNaO_7S^+$ [(M+Na)$^+$] 476.1713, found 476.1704.

<Scheme 32>

Dimethyl 2-(6-((*tert*-butyldiphenylsilyl)oxy)-4,4-dimethylhexa-1,2-dien-1-yl)-2-(3-(trimethylsilyl)prop-2-yn-1-yl)malonate (57)

To a solution of **50**[27] (15.5 g, 35.5 mmol) in THF (118 mL), was added LHMDS (1.3 M in THF, 60.1 mL, 78.1 mmol) at -78 °C. The mixture was stirred at -78 °C for 0.5 h. To the mixture, was added $ClCO_2Me$ (2.83 mL, 36.9 mmol) at -78 °C. The mixture was stirred at -78 °C for 0.5 h. To the mixture, were added 3-bromo-1-(trimethylsilyl)-1-propyne **56** (6.03 mL, 42.6 mmol) and KI (5.89 g, 35.5 mmol) at -78 °C. The mixture was warmed to r.t. and stirred for 12 h. The reaction was quenched with saturated NH_4Cl aq. and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 100:0~90:10) to give **57** (14.7 g, 69% yield) as a pale brown oil.

Spectral data of **57**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.67 (app d, *J* = 6.6 Hz, 4H), 7.44-7.37 (m, 6H), 5.76 (d, *J* = 6.4 Hz, 1H), 5.30 (d, *J* = 6.4 Hz, 1H), 3.73-3.70 (m, 8H), 2.89 (d, *J* = 16.9 Hz, 1H), 2.84 (d, *J* = 16.9 Hz, 1H), 1.68-1.59 (m, 2H), 1.04 (s, 9H), 0.99 (s, 3H), 0.98 (s, 3H), 0.10 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.0, 169.6, 169.5, 135.7 (4C), 134.1 (2C), 129.7 (2C), 127.8 (4C), 106.7, 101.7, 92.0, 87.9, 61.3, 58.0, 53.0, 52.9, 45.4, 34.4, 28.5, 27.7, 27.0 (3C), 26.3, 19.3, 0.1 (3C) ppm; IR (neat) ν̃: 2958, 2181, 1967, 1741 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{31}H_{39}O_5Si_2$ $[(M-tBu)^+]$ 547.2336, found 547.2318.

Dimethyl 2-(6-((*tert*-butyldiphenylsilyl)oxy)-4,4-dimethylhexa-1,2-dien-1-yl)-2-(prop-2-yn-1-yl)malonate (58)

A suspension of **57** (3.63 g, 6.00 mmol) and K_2CO_3 (1.24 g, 9.00 mmol) in MeOH (30 mL) was stirred at r.t. for 4 h. The reaction was quenched with brine and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 95:5~85:15) to give **58** (2.50 g, 78% yield) as a pale

yellow oil.

Spectral data of **58**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.67-7.66 (m, 4H), 7.44-7.37 (m, 6H), 5.77 (d, *J* = 6.4 Hz, 1H), 5.33 (d, *J* = 6.4 Hz, 1H), 3.77-3.70 (m, 8H), 2.84 (d, *J* = 2.4 Hz, 2H), 1.94 (t, *J* = 2.4 Hz, 1H), 1.68-1.60 (m, 2H), 1.04 (s, 9H), 0.98 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.1, 169.5, 169.4, 135.7 (4C), 134.0, 134.0, 129.7 (2C), 127.7 (4C), 106.8, 91.8, 79.3, 71.2, 61.3, 57.6, 53.0, 53.0, 45.2, 34.4, 28.3, 27.8, 27.0 (3C), 24.9, 19.2 ppm; IR (neat) ν̃: 3305, 2957, 1967, 1740 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{28}H_{31}O_5Si$ [(M-*t*Bu)$^{+}$] 475.1941, found 475.1936.

Dimethyl 2-(6-hydroxy-4,4-dimethylhexa-1,2-dien-1-yl)-2-(prop-2-yn-1-yl)malonate (59)

A solution of **58** (906 mg, 1.70 mmol) and TBAF (1.0 M in THF, 2.04 mL, 2.04 mmol) in THF (8.5 mL) was stirred at r.t. for 1 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 90:10~50:50) to give **59** (477 mg, 95 % yield) as a pale brown oil.

Spectral data of **59**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.84 (d, *J* = 6.4 Hz, 1H), 5.42 (d, *J* = 6.4 Hz, 1H), 3.77 (s, 3H), 3.77 (s, 3H), 3.71 (t, *J* = 6.2 Hz, 2H), 2.91 (d, *J* = 2.7 Hz, 2H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.69-1.60 (m, 2H), 1.37 (s, 1H), 1.05 (s, 3H), 1.05 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.2, 169.6, 169.5, 106.6, 92.0, 79.2, 71.4, 60.1, 57.6, 53.2, 53.2, 45.5, 34.5, 28.2, 28.1, 25.1 ppm; IR (neat) ν̃: 3292, 2958, 1967, 1738 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{15}H_{19}O_5$ [(M-Me)$^{+}$] 279.1233, found 279.1243.

Dimethyl 2-(4,4-dimethyl-6-oxohexa-1,2-dien-1-yl)-2-(prop-2-yn-1-yl)malonate (1k)

A suspension of **59** (470 mg, 1.56 mmol) and DMP (1.02 g, 2.40 mmol) in CH_2Cl_2 (8.0 mL) was stirred at r.t. for 1 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with EtOAc. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~65:35) to give **1k** (333 mg, 71% yield) as a colorless oil.

Spectral data of **1k**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.78 (t, *J* = 2.8 Hz, 1H), 5.90 (d, *J* = 6.4 Hz, 1H), 5.52 (d, *J* = 6.4 Hz, 1H), 3.77 (s, 3H), 3.77 (s, 3H), 2.94-2.91 (m, 1H), 2.90-2.87 (m, 1H), 2.42 (dd, *J* = 15.2, 2.7 Hz, 1H), 2.37 (dd, *J* = 15.2, 2.7 Hz, 1H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.19 (s, 3H), 1.17 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 202.6, 201.1, 169.3, 169.3, 105.6, 92.9, 79.1, 71.5, 57.7, 55.0, 53.2, 53.2, 34.5, 28.4, 28.2, 24.9 ppm; IR (neat) ṽ: 3287, 2958, 2123, 1968, 1738 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{16}H_{20}O_5$ [M^+] 292.1311, found 292.1307.

Dimethyl (*E*)-2-(6-((*tert*-butanesulfinyl)imino)-4,4-dimethylhexa-1,2-dien-1-yl)-2-(prop-2-yn-1-yl)malonate (6k)

A suspension of **1k** (320 mg, 1.10 mmol), *t*-butanesulfinamide (159 mg, 1.31 mmol), PPTS (27.5 mg, 0.109 mmol) and $MgSO_4$ (659 mg, 5.47 mmol) in toluene (5.5 mL) was stirred at 50 °C for 2 h. The reaction mixture was diluted with EtOAc and filtered. The filtrate was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 90:10~65:35) to give **6k** (420 mg, 97% yield, dr = 1:1) as a colorless oil.

Spectral data of **6k**: Diastereomixture (1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.08 (td, *J* = 5.7, 1.5 Hz, 1H and 1H), 5.88 (dd, *J* = 7.7, 6.5 Hz, 1H and 1H), 5.48 (dd, *J* = 7.1, 6.6 Hz, 1H and 1H), 3.77 (d, *J* = 2.7 Hz, 6H and 6H), 2.95-2.87 (m, 2H and 2H), 2.60-2.51 (m, 2H and 2H), 2.00-1.99 (m, 1H and 1H), 1.21 (s, 9H and 9H), 1.16-1.15 (m, 6H and 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.2, 201.2, 169.4, 169.3, 168.0, 167.9, 105.9, 105.8, 92.7, 92.7, 79.2, 79.2, 71.4, 57.6, 57.6, 56.8, 53.2, 53.1, 53.1, 48.6, 48.5, 35.5, 35.4, 28.4, 28.4, 27.7, 27.7, 24.9, 24.9, 22.6, 22.6 ppm; IR (neat) ṽ: 3290, 2960, 1969, 1739, 1619 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{29}NNaO_5S^+$ [$(M+Na)^+$] 418.1659, found 418.1658.

<Scheme 33>

Dimethyl 2-(6-((*tert*-butyldiphenylsilyl)oxy)-4,4-dimethylhexa-1,2-dien-1-yl)-2-(3-phenylprop-2-yn-1-yl) malonate (60)

A suspension of **58** (677 mg, 1.27 mmol), iodobenzene (0.171 mL, 1.53 mmol), $PdCl_2(PPh_3)_2$ (44.6 mg, 0.0636 mmol) and CuI (48.4 mg, 0.254 mmol) in Et_3N (6.4 mL) was stirred at 70 °C for 4 h. The reaction was quenched with brine and extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 99:1~85:15) to give **60** (400 mg, 52% yield) as a yellow oil.

Spectral data of **60**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.66 (d, *J* = 6.1 Hz, 4H), 7.42-7.36 (m, 6H), 7.32-7.24 (m, 5H), 5.83 (d, *J* = 6.4 Hz, 1H), 5.33 (d, *J* = 6.4 Hz, 1H), 3.75-3.70 (m, 8H), 3.06 (app dd, *J* = 18.9, 17.0 Hz, 2H), 1.67-1.61 (m, 2H), 1.03 (s, 9H), 0.99 (s, 3H), 0.98 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.1, 169.7, 169.6, 135.7 (4C), 134.1, 134.1, 131.8 (2C), 129.7 (2C), 128.3 (2C), 128.0, 127.8 (4C), 123.4, 106.7, 92.1, 84.9, 83.3, 61.3, 58.1, 53.1, 53.0, 45.3, 34.4, 28.4, 27.8, 27.0 (3C), 25.9, 19.2 ppm; IR (neat) ν̃: 2956, 1967, 1740 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{38}H_{44}O_5Si$ [M^+] 608.2958, found 608.2937.

Dimethyl 2-(6-hydroxy-4,4-dimethylhexa-1,2-dien-1-yl)-2-(3-phenylprop-2-yn-1-yl)malonate (61)

A solution of **60** (400 mg, 0.657 mmol) and TBAF (1.0 M in THF, 0.788 mL, 0.788 mmol) in THF (3.3 mL) was stirred at r.t. for 2 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 80:20~50:50) to give **61** (243 mg, quant.) as a colorless oil.

Spectral data of **61**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36-7.25 (m, 5H), 5.89 (d, *J* = 6.4 Hz, 1H), 5.42 (d, *J* = 6.4 Hz, 1H), 3.79 (s, 6H), 3.73-3.68 (m, 2H), 3.13 (dd, *J* = 19.2, 16.7 Hz, 2H), 1.65 (td, *J* = 7.1, 2.8 Hz, 2H), 1.53 (s, 1H), 1.06 (s, 3H), 1.06 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ:

201.1, 169.7, 169.6, 131.7 (2C), 128.3 (2C), 128.1, 123.3, 106.5, 92.2, 84.7, 83.4, 60.1, 58.1, 53.1, 53.1, 45.4, 34.4, 28.2, 28.1, 26.0 ppm; IR (neat) $\tilde{\nu}$: 3416, 2957, 2250, 1967, 1739 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{22}H_{26}O_5$ [M^+] 370.1780, found 370.1787.

Dimethyl 2-(4,4-dimethyl-6-oxohexa-1,2-dien-1-yl)-2-(3-phenylprop-2-yn-1-yl)malonate (1l)

A suspension of **61** (254 mg, 0.686 mmol), $NaHCO_3$ (115 mg, 1.37 mmol) and DMP (436 mg, 1.03 mmol) in CH_2Cl_2 (3.4 mL) was stirred at r.t. for 2 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with EtOAc. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 95:5~70:30) to give **1l** (222 mg, 88% yield) as a colorless oil.

Spectral data of **1l**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.76 (t, *J* = 2.8 Hz, 1H), 7.35-7.26 (m, 5H), 5.95 (d, *J* = 6.4 Hz, 1H), 5.52 (d, *J* = 6.4 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.12 (app dd, *J* = 22.1, 16.7 Hz, 2H), 2.40 (app ddd, *J* = 28.3, 15.2, 2.9 Hz, 2H), 1.19 (s, 3H), 1.18 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 202.7, 201.1, 169.5, 169.4, 131.8 (2C), 128.3 (2C), 128.2, 123.2, 105.5, 93.2, 84.7, 83.6, 58.1, 55.0, 53.2, 53.2, 34.5, 28.4, 28.2, 25.9 ppm; IR (neat) $\tilde{\nu}$: 2957, 1968, 1739 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{22}H_{24}O_5$ [M^+] 368.1624, found 368.1614.

Dimethyl

(*E*)-2-(6-((*tert*-butanesulfinyl)imino)-4,4-dimethylhexa-1,2-dien-1-yl)-2-(3-phenylprop-2-yn-1-yl)malonate (6l)

A suspension of **1l** (222 mg, 0.603 mmol), *t*-butanesulfinamide (87.6 mg, 0.723 mmol), PPTS (15.1 mg, 0.0603 mmol) and $MgSO_4$ (363 mg, 3.01 mmol) in toluene (3.0 mL) was stirred at 50 °C for 1 h. The reaction mixture was diluted with EtOAc and filtered. The filtrate was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **6l** (284 mg, quant., dr = 1:1) as a colorless oil.

Spectral data of **6l**: Diastereomixture (1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.07 (td, *J* = 5.6, 4.1 Hz, 1H and 1H), 7.35-7.33 (m, 2H and 2H), 7.29-7.24 (m, 3H and 3H), 5.94 (t, *J* = 6.8 Hz, 1H and 1H),

5.49 (t, *J* = 6.5 Hz, 1H and 1H), 3.78 (d, *J* = 0.7 Hz, 6H and 6H), 3.15 (dd, *J* = 16.7, 3.3 Hz, 1H and 1H), 3.10 (d, *J* = 16.9 Hz, 1H and 1H), 2.61-2.51 (m, 2H and 2H), 1.19 (d, *J* = 2.0 Hz, 9H and 9H), 1.16 (d, *J* = 5.9 Hz, 6H and 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.3, 201.2, 169.5, 169.5, 168.0, 167.9, 131.8, 128.3, 128.1, 123.3, 105.8, 105.7, 93.0, 84.8, 84.7, 83.5, 58.1, 58.1, 56.8, 53.2, 53.2, 53.1, 48.6, 48.5, 35.5, 35.4, 28.5, 28.5, 27.7, 27.7, 25.9, 25.9, 22.6, 22.6 ppm; IR (neat) ν̃: 2959, 1968, 1739, 1619 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{26}H_{33}NNaO_5S^+$ [(M+Na)$^+$] 494.1972, found 494.1965.

<Scheme 34>

Dimethyl

2-(6-hydroxy-4,4-dimethylhexa-1,2-dien-1-yl)-2-(3-(trimethylsilyl)prop-2-yn-1-yl)malonate (62)

To a solution of **57** (1.82 g, 3.00 mmol) in THF (30 mL), was added HF-pyridine (3.00 mL, 115 mmol) at 0 °C. The mixture was stirred at r.t. for 12 h. The reaction was quenched with saturated $NaHCO_3$ aq. and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~50:50) to give **62** (968 mg, 88% yield) as a colorless oil.

Spectral data of **62**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.82 (d, *J* = 6.4 Hz, 1H), 5.38 (d, *J* = 6.4 Hz, 1H), 3.75 (s, 6H), 3.71 (t, *J* = 6.1 Hz, 2H), 2.94 (d, *J* = 16.9 Hz, 1H), 2.90 (d, *J* = 16.9 Hz, 1H), 1.69-1.60 (m, 2H), 1.39 (s, 1H), 1.06 (s, 3H), 1.05 (s, 3H), 0.12 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.0, 169.6, 169.5, 106.5, 101.6, 92.2, 88.1, 60.2, 58.0, 53.1, 53.0, 45.5, 34.5, 28.2, 28.2, 26.4, 0.1 (3C) ppm; IR (neat) ν̃: 3407, 2959, 2181, 1967, 1740 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{18}H_{27}O_5Si$ [(M-Me)$^+$] 351.1628, found 351.1616.

Dimethyl

2-(4,4-dimethyl-6-oxohexa-1,2-dien-1-yl)-2-(3-(trimethylsilyl)prop-2-yn-1-yl)malonate (1m)

A suspension of **62** (967 mg, 2.64 mmol) and DMP (1.68 g, 3.96 mmol) in CH_2Cl_2 (13 mL) was

stirred at r.t. for 3 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with EtOAc. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **1m** (717 mg, 75% yield) as a colorless oil.

Spectral data of **1m**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.79 (t, *J* = 2.7 Hz, 1H), 5.88 (d, *J* = 6.4 Hz, 1H), 5.49 (d, *J* = 6.4 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 2.95 (d, *J* = 16.9 Hz, 1H), 2.89 (d, *J* = 16.9 Hz, 1H), 2.43 (dd, *J* = 15.2, 2.7 Hz, 1H), 2.37 (dd, *J* = 15.2, 2.7 Hz, 1H), 1.18 (d, *J* = 5.1 Hz, 6H), 0.12 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 202.7, 201.0, 169.3, 169.3, 105.5, 101.5, 93.1, 88.2, 58.0, 55.0, 53.1, 53.0, 34.5, 28.4, 28.3, 26.3, 0.1 (3C) ppm; IR (neat) ṽ: 2959, 2180, 1797, 1740 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{19}H_{28}NaO_5Si^+$ [$(M+Na)^+$] 387.1598, found 387.1603.

Dimethyl

(*E*)-2-(6-((*tert*-butanesulfinyl)imino)-4,4-dimethylhexa-1,2-dien-1-yl)-2-(3-(trimethylsilyl)prop-2-yn-1-yl)malonate (6m)

A suspension of **1m** (700 mg, 1.92 mmol), *t*-butanesulfinamide (279 mg, 2.03 mmol), PPTS (48.3 mg, 0.192 mmol) and $MgSO_4$ (1.12 g, 9.60 mmol) in toluene (9.6 mL) was stirred at 50 °C for 2 h. The reaction mixture was diluted with EtOAc and filtered. The filtrate was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **6m** (899 mg, quant., dr = 1:1) as a colorless oil.

Spectral data of **6m**: Diastereomixture (1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.08 (app t, *J* = 5.5 Hz, 1H and 1H), 5.87 (app t, *J* = 6.6 Hz, 1H and 1H), 5.45 (app t, *J* = 6.7 Hz, 1H and 1H), 3.75 (s, 6H and 6H), 2.95 (app dd, *J* = 17.0, 3.5 Hz, 1H and 1H), 2.89 (d, *J* = 17.1 Hz, 1H and 1H), 2.61-2.50 (m, 2H and 2H), 1.21 (s, 9H and 9H), 1.17-1.15 (m, 6H and 6H), 0.11 (s, 9H and 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.1, 201.1, 169.4, 169.4, 168.0, 168.0, 105.8, 105.7, 101.6, 101.6, 93.0, 88.1, 88.1, 58.0, 56.8, 53.1, 53.0, 48.7, 48.6, 35.5, 35.4, 28.6, 28.6, 27.7, 27.6, 26.3, 26.3, 22.6, 22.6, 0.1 ppm; IR (neat) ṽ: 2960, 2181, 1969, 1741, 1619 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{23}H_{37}NNaO_5SSi^+$ [$(M+Na)^+$] 490.2054, found 490.2046.

<Scheme 35>

Dimethyl 2-(6-((*tert*-butyldiphenylsilyl)oxy)-4,4-dimethylhexa-1,2-dien-1-yl)-2-(3-chloroprop-2-yn-1-yl) malonate (63)

To a solution of **58** (1.07 g, 2.00 mmol) and NCS (588 mg, 4.40 mmol) in THF (10 mL), was added LHMDS (0.5 M in THF, 4.80 mL, 2.40 mmol) at -78 °C. The mixture was stirred at -78 °C for 2 h. The reaction was quenched with saturated NH_4Cl aq. and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 100:0~90:10) to give **63** (1.11 g, 98% yield) as a colorless oil.

Spectral data of **63**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.69-7.67 (m, 4H), 7.44-7.37 (m, 6H), 5.75 (d, *J* = 6.4 Hz, 1H), 5.34 (d, *J* = 6.4 Hz, 1H), 3.74-3.71 (m, 8H), 2.84 (s, 2H), 1.65 (td, *J* = 7.2, 2.4 Hz, 2H), 1.05 (s, 9H), 0.98 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.2, 169.5, 169.4, 135.7 (4C), 134.1, 134.1, 129.7, 129.7, 127.8 (4C), 106.8, 91.7, 64.8, 61.3, 60.3, 57.5, 53.1, 53.1, 45.3, 34.4, 28.3, 27.8, 27.0 (3C), 25.1, 19.2 ppm; IR (neat) ν̃: 2957, 2248, 1966, 1740 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{28}H_{30}ClO_5Si$ [(M-*t*Bu)$^+$] 509.1551, found 509.1547.

Dimethyl 2-(3-chloroprop-2-yn-1-yl)-2-(6-hydroxy-4,4-dimethylhexa-1,2-dien-1-yl)malonate (64)

A solution of **63** (1.05 g, 1.86 mmol) and TBAF (1.0 M in THF, 2.23 mL, 2.23 mmol) was stirred at r.t. for 1 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 90:10~50:50) to give **64** (547 mg, 90% yield) as a yellow oil.

Spectral data of **64**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.81 (d, *J* = 6.4 Hz, 1H), 5.42 (d, *J* = 6.4 Hz, 1H), 3.77 (d, *J* = 2.2 Hz, 6H), 3.71 (t, *J* = 6.8 Hz, 2H), 2.90 (s, 2H), 1.65 (td, *J* = 7.1, 2.2 Hz, 2H), 1.37 (s, 1H), 1.05 (s, 3H), 1.05 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.2, 169.5, 169.4, 106.6, 91.9, 64.7, 60.5, 60.1, 57.6, 53.2, 53.2, 45.4, 34.4, 28.1, 28.1, 25.3 ppm; IR (neat) ν̃: 3437, 2958, 2248, 1967, 1739 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{21}ClNaO_5^+$ [(M+Na)$^+$] 351.0970, found 351.0971.

Dimethyl 2-(3-chloroprop-2-yn-1-yl)-2-(4,4-dimethyl-6-oxohexa-1,2-dien-1-yl)malonate (1n)

A suspension of **64** (546 mg, 1.66 mmol) and DMP (1.06 g, 2.49 mmol) in CH_2Cl_2 (8.3 mL) was stirred at r.t. for 3 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with EtOAc. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **1n** (350 mg, 65% yield) as a colorless oil.

Spectral data of **1n**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.78 (t, *J* = 2.7 Hz, 1H), 5.86 (d, *J* = 6.4 Hz, 1H), 5.52 (d, *J* = 6.4 Hz, 1H), 3.77 (s, 6H), 2.92 (d, *J* = 16.9 Hz, 1H), 2.88 (d, *J* = 16.9 Hz, 1H), 2.42 (dd, *J* = 15.1, 2.7 Hz, 1H), 2.37 (dd, *J* = 15.1, 2.7 Hz, 1H), 1.19 (s, 3H), 1.17 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 202.5, 201.2, 169.2, 169.2, 105.6, 92.8, 64.7, 60.6, 57.6, 54.9, 53.2, 53.2, 34.5, 28.3, 28.1, 25.1 ppm; IR (neat) ν̃: 2959, 2248, 1968, 1739 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{19}ClNaO_5^+$ [$(M+Na)^+$] 349.0813, found 349.0815.

Dimethyl (*E*)-2-(6-((*tert*-butanesulfinyl)imino)-4,4-dimethylhexa-1,2-dien-1-yl)-2-(3-chloroprop-2-yn-1-yl)malonate (6n)

A suspension of **1n** (350 mg, 1.07 mmol), *t*-butanesulfinamide (156 mg, 1.29 mmol), PPTS (26.9 mg, 0.107 mmol) and $MgSO_4$ (645 mg, 5.36 mmol) in toluene (5.4 mL) was stirred at 50 °C for 2 h. The reaction mixture was diluted with EtOAc and filtered. The filtrate was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **6n** (174 mg, 38% yield, dr = 1:1) as a colorless oil.

Spectral data of **6n**: Diastereomixture (1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.08 (t, *J* = 5.1 Hz, 1H and 1H), 5.85 (app t, *J* = 7.0 Hz, 1H and 1H), 5.48 (app t, *J* = 6.8 Hz, 1H and 1H), 3.77 (s, 6H and 6H), 2.94-2.87 (m, 2H and 2H), 2.60-2.51 (m, 2H and 2H), 1.21 (s, 9H and 9H), 1.16-1.15 (m, 6H and 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.3, 201.3, 169.3, 169.2, 167.9, 167.9, 105.9, 105.8, 92.7, 64.7, 60.5, 57.6, 57.6, 56.8, 53.2, 53.2, 48.6, 48.5, 35.5, 35.4, 28.4, 28.4, 27.7, 27.6, 25.1, 22.6, 22.6 ppm; IR (neat) ν̃: 2959, 2247, 1968, 1739, 1619 cm^{-1}; HRMS (ESI) *m/z* calcd. for

$C_{20}H_{28}ClNNaO_5S^+$ [$(M+Na)^+$] 452.1269, found 452.1267.

<Section 4>

<Table 8>

Dimethyl 8-((*tert*-butanesulfinyl)amino)-9-methyl-1,3,7,8-tetrahydro-2*H*-benzo[7]annulene-2,2-dicarboxylate (9o)

Spectral data of **9o**:

More polar diastereomer [racemic mixture of (*R*,*S*) and (*S*,*R*)-**9o**]

^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.03 (d, *J* = 12.0 Hz, 1H), 5.70 (t, *J* = 4.2 Hz, 1H), 5.49-5.45 (m, 1H), 3.87-3.77 (m, 2H), 3.72 (s, 3H), 3.68 (s, 3H), 3.10 (d, *J* = 13.7 Hz, 1H), 2.98 (dd, *J* = 19.4, 4.0 Hz, 1H), 2.66-2.64 (br m, 2H), 2.57-2.52 (m, 2H), 1.91 (s, 3H), 1.17 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.8, 170.6, 137.2, 136.2, 131.9, 131.1, 126.8, 123.7, 60.6, 56.2, 53.8, 52.9, 52.6, 34.2, 33.8, 32.5, 22.7 (3C), 21.5 ppm; IR (neat) $\tilde{\nu}$: 3313, 2954, 1736 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{20}H_{29}NO_5S$ [M^+] 395.1766, found 395.1768.

Less polar diastereomer [racemic mixture of (*S*,*S*) and (*R*,*R*)-**9o**]

^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.94 (dd, *J* = 12.0, 2.6 Hz, 1H), 5.69 (t, *J* = 3.8 Hz, 1H), 5.38-5.35 (m, 1H), 3.88 (t, *J* = 5.0 Hz, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.43 (d, *J* = 5.3 Hz, 1H), 3.12 (d, *J* = 12.9 Hz, 1H), 2.99 (dd, *J* = 19.3, 3.5 Hz, 1H), 2.55-2.43 (m, 4H), 1.95 (s, 3H), 1.17 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.9, 170.8, 138.4, 136.6, 131.1, 130.9, 127.8, 123.3, 59.6, 55.9, 54.0, 53.1, 52.9, 33.7, 33.5, 32.8, 22.8 (3C), 21.0 ppm; IR (neat) $\tilde{\nu}$: 3317, 2955, 1732 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{20}H_{29}NO_5S$ [M^+] 395.1766, found 395.1753.

Dimethyl 10-(*tert*-butanesulfinyl)-9-methyl-1,3,5,6,7,8-hexahydro-2*H*-5,8-epiminobenzo[7]annulene-2,2-dicarboxylate (10o)

Spectral data of **10o** [racemic mixture of (*S*,*S*) and (*R*,*R*)-**10o**]: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.32 (t, *J* = 4.2 Hz, 1H), 4.04-4.00 (m, 2H), 3.68 (s, 6H), 2.80-2.59 (m, 4H), 2.17-2.10 (m, 1H),

2.06-1.99 (m, 1H), 1.82 (s, 3H), 1.74-1.69 (m, 1H), 1.52-1.46 (m, 2H), 1.12 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.5, 171.5, 139.9, 137.2, 123.1, 114.3, 66.9, 59.7, 57.9, 54.3, 52.7, 52.7, 34.5, 31.6, 30.9 (2C), 22.6 (3C), 16.6 ppm; IR (neat) $\tilde{\nu}$: 2952, 1739 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{29}NNaO_5S^+$ [$(M+Na)^+$] 418.1659, found 418.1659.

<Entry 1>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6o** (59.3 mg, 0.150 mmol) and [Rh(dppp)(nbd)]ClO_4 (10.6 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 70:30~0:100) to give **6o** (39.5 mg, 67% yield) as a pale yellow oil.

<Entry 2>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6o** (59.3 mg, 0.150 mmol) and [Rh(*rac*-binap)(nbd)]ClO_4 (13.8 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was obtained as a complex mixture.

<Entry 3>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6o** (59.3 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 70:30~0:100) to give **9o** (18.4 mg, 31% yield, dr = >20/1, more polar diastereomer) and **10o** (17.1 mg, 29% yield, dr = >20:1) as a pale yellow oil.

<Entry 4>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6o** (59.3 mg, 0.150 mmol) and [Rh(dppe)(nbd)]ClO_4 (10.4 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc =

70:30~0:100) to give less polar **9o** (11.1 mg, 19% yield), more polar **9o** (19.0 mg, 32% yield) and **10o** (9.7 mg, 16% yield, dr = >20:1) as a pale yellow oil.

<Scheme 39>

Synthesis of (*S*,*S*)-**6o** and (*R*,*S*)-**6o**

A suspension of **1o**[29] (1.79 g, 6.13 mmol), (*S*)-*t*-butanesulfinamide (891 mg, 7.35 mmol), PPTS (154 mg, 0.613 mmol) and $MgSO_4$ (3.69 g, 30.6 mmol) in toluene (20 mL) was stirred at 40 °C for 1 h. The reaction mixture was filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~50:50) to give the mixture of (*S*,*S*)-**6o** and (*R*,*S*)-**6o** (1.73 g, 71% yield) as a colorless oil. The diastereomers were separated by preparative HPLC with DAICEL CHIRALPAK IE (TBME/Hexane/EtOH = 95:5:0.1, UV 220 nm) to give (*S*,*S*)-**6o** (679 mg, 28% yield, 98% *de*) and (*R*,*S*)-**6o** (677 mg, 28% yield, 97% *de*) as a colorless oil. The absolute configuration was determined by comparing the HPLC retention time of the authentic sample (*S*,*S*)-**6o** (94% *de*), which was synthesized from (*S*)-**1o**[29] (94% *ee*) and (*S*)-*t*-butanesulfinamide.

Spectral data of (*S*,*S*)-**6o**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.09 (t, *J* = 4.2 Hz, 1H), 5.19-5.16 (m, 1H), 5.01-4.95 (m, 1H), 3.73 (d, *J* = 1.7 Hz, 6H), 2.80 (q, *J* = 2.4 Hz, 2H), 2.75 (dd, *J* = 7.8, 2.2 Hz, 2H), 2.65-2.61 (m, 2H), 2.31 (ddd, *J* = 13.9, 7.1, 3.0 Hz, 2H), 1.75 (t, *J* = 2.6 Hz, 3H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 206.0, 170.5 (2C), 168.7, 89.8, 86.3, 79.1, 73.3, 57.5, 56.7, 52.9, 52.8, 35.4, 32.4, 24.5, 23.2, 22.5 (3C), 3.6 ppm; IR (neat) ν̃: 2954, 2240, 1964, 1738, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{29}NNaO_5S^+$ [$(M+H)^+$] 418.1659, found 418.1656; $[\alpha]_D^{26}$ +120.1 (*c* 0.60, $CHCl_3$).

Spectral data of (*R*,*S*)-**6o**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.09 (t, *J* = 4.3 Hz, 1H), 5.19-5.15 (m, 1H), 5.02-4.96 (m, 1H), 3.73 (d, *J* = 2.2 Hz, 6H), 2.79 (q, *J* = 2.4 Hz, 2H), 2.75 (dd, *J* = 7.8, 2.2 Hz, 2H), 2.63 (td, *J* = 7.4, 4.4 Hz, 2H), 2.31 (ddd, *J* = 14.2, 7.1, 2.8 Hz, 2H), 1.75 (t, *J* = 2.4 Hz, 3H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 206.0, 170.5 (2C), 168.7, 89.8, 86.2, 79.1, 73.3, 57.5, 56.7, 52.8, 52.8, 35.5, 32.5, 24.6, 23.2, 22.5 (3C), 3.6 ppm; IR (neat) ν̃: 2954, 2240, 1964,

1739, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{29}NNaO_5S^+$ $[(M+H)^+]$ 418.1659, found 418.1657; $[\alpha]_D^{26}$ +52.1 (*c* 0.55, $CHCl_3$).

<Table 9>

Compound (*R*,*S*)-9o

Specific optical rotation of (*R*,*S*)-**9o**: $[\alpha]_D^{24}$ -2.7 (*c* 1.00, $CHCl_3$).

Compound (*S*,*S*)-10o

Specific optical rotation of (*S*,*S*)-**10o**: $[\alpha]_D^{20}$ -5.1 (*c* 1.00, $CHCl_3$).

<Entry 1>

According to the general procedure (1) for cyclization, a crude product, which was prepared from (*S*,*S*)-**6o** (59.3 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 70:30~0:100) to give (*R*,*S*)-**9o** (13.0 mg, 22% yield, dr = >20:1) and (*S*,*S*)-**10o** (11.4 mg, 19% yield, dr = >20:1) as a pale yellow oil.

<Entry 2>

According to the general procedure (1) for cyclization, a crude product, which was prepared from (*R*,*S*)-**6o** (59.3 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 70:30~0:100) to give (*R*,*S*)-**9o** (14.5 mg, 24% yield, dr = >20:1) and (*S*,*S*)-**10o** (8.4 mg, 14% yield, dr = >20:1) as a pale yellow oil.

<Table 10>

Compound (*S*,*S*)-9o

Specific optical rotation of (*S*,*S*)-**9o**: $[\alpha]_D^{23}$ +110.9 (*c* 0.98, $CHCl_3$).

<Entry 1>

According to the general procedure (1) for cyclization, a crude product, which was prepared from (*S*,*S*)-**6o** (59.3 mg, 0.150 mmol) and [Rh(dppe)(nbd)]ClO_4 (10.4 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 70:30~0:100) to give (*R*,*S*)-**9o** (8.4 mg, 14% yield), (*S*,*S*)-**9o** (12.8 mg, 22% yield) and (*S*,*S*)-**10o** (14.4 mg, 24% yield, dr = >20:1) as a pale yellow oil.

<Entry 2>

According to the general procedure (1) for cyclization, a crude product, which was prepared from (*R*,*S*)-**6o** (59.3 mg, 0.150 mmol) and [Rh(dppe)(nbd)]ClO_4 (10.4 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 70:30~0:100) to give (*R*,*S*)-**9o** (32.4 mg, 55% yield), (*S*,*S*)-**9o** (5.4 mg, 9% yield) and (*S*,*S*)-**10o** (4.1 mg, 7% yield, dr = >20:1) as a pale yellow oil.

<Scheme 44>

Dimethyl (*E*)-2-(but-2-yn-1-yl)-2-(7-((*tert*-butanesulfinyl)imino)hepta-2,3-dien-1-yl)malonate (6o)

A suspension of **1o**[29] (1.84g, 6.29 mmol), *t*-butanesulfinamide (915 mg, 7.55 mmol), PPTS (158 mg, 0.629 mmol) and $MgSO_4$ (3.79 g, 31.5 mmol) in toluene (21 mL) was stirred at 40 °C for 1 h. The reaction mixture was filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **6o** (1.92 g, 77% yield, dr = 1:1) as a pale yellow oil.

Spectral data of **6o**: Diastereomixture (1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.09 (t, *J* = 4.3 Hz, 1H and 1H), 5.19-5.15 (m, 1H and 1H), 5.01-4.95 (m, 1H and 1H), 3.73 (s, 3H and 3H), 3.73 (s, 3H and 3H), 2.80-2.79 (m, 2H and 2H), 2.75 (dd, *J* = 7.8, 2.2 Hz, 2H and 2H), 2.65-2.61 (m, 2H and 2H), 2.34-2.29 (m, 2H and 2H), 1.75 (t, *J* = 2.6 Hz, 3H and 3H), 1.19 (s, 9H and 9H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ: 205.9, 205.9, 170.4, 168.6, 168.6, 89.7, 89.7, 86.2, 86.1, 79.0, 73.2,

57.4, 56.6, 52.7, 52.7, 35.4, 35.3, 32.4, 32.3, 24.5, 24.4, 23.1, 22.4, 3.5 ppm; IR (neat) ṽ: 2954, 2240, 1964, 1738, 1623 cm^{-1}; HRMS (APCI) *m/z* calcd. for $C_{20}H_{30}NO_5S^+$ $[(M+H)^+]$ 396.1839, found 396.1838.

<Table 11>

Dimethyl 10-(*tert*-butanesulfinyl)-6,6,9-trimethyl-1,3,5,6,7,8-hexahydro-2*H*-5,8-epiminobenzo[7]annulene-2,2-dicarboxylate (10p)

Spectral data of **10p**: Diastereomixture (1:2.6); ^1H NMR (500 MHz, $CDCl_3$) δ: 5.36 (t, *J* = 4.2 Hz, 1H*), 5.30 (t, *J* = 4.2 Hz, 1H), 3.90 (d, *J* = 6.6 Hz, 1H), 3.76-3.71 (m, 3H*+1H*), 3.68 (d, *J* = 3.2 Hz, 3H*+6H), 3.59 (s, 1H), 3.37 (s, 1H*), 2.89-2.67 (m, 4H+4H*), 1.78 (t, *J* = 9.0 Hz, 3H+3H*+1H+1H*), 1.48 (d, *J* = 11.7 Hz, 1H+1H*), 1.22 (d, *J* = 13.2 Hz, 3H+3H*), 1.13 (d, *J* = 22.7 Hz, 9H+9H*), 0.87 (d, *J* = 9.8 Hz, 3H+3H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.9, 171.8, 171.6, 171.5, 138.7, 136.9, 136.4, 134.5, 123.0, 120.6, 118.7, 117.4, 76.5, 74.4, 62.5, 61.2, 58.4, 58.1, 54.0, 53.9, 53.0, 52.8, 52.8, 52.8, 47.2, 45.3, 42.4, 41.9, 31.9, 31.1, 31.0, 30.9, 30.6, 30.5, 27.1, 26.6, 22.6, 22.6, 16.5, 16.1 ppm; IR (neat) ṽ: 2953, 1731 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{33}NNaO_5S^+$ $[(M+Na)^+]$ 446.1972, found 446.1971.

<Entry 1>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6p** (63.5 mg, 0.150 mmol) and $[Rh(dppp)(nbd)]ClO_4$ (10.6 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~30:70) to give **6p** (41.8 mg, 66% yield) as a pale yellow oil.

<Entry 2>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6p** (63.5 mg, 0.150 mmol) and [Rh(*rac*-binap)(nbd)]ClO_4 (13.8 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 1 h, was obtained as a complex mixture.

<Entry 3>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6p** (63.5 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 70:30~0:100) to give **10p** (24.3 mg, 38% yield, dr = 9.1:1) as a pale yellow oil.

<Entry 4>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6p** (63.5 mg, 0.150 mmol) and [Rh(dppe)(nbd)]ClO_4 (10.4 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 70:30~30:70) to give **10p** (26.2 mg, 41% yield, dr = 1.7:1) as a pale yellow oil.

<Scheme 45>

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6q** (61.4 mg, 0.150 mmol) and [Rh(dppp)(nbd)]ClO_4 (10.6 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~0:100) to give **6q** (47.9 mg, 78% yield) as a pale yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6q** (61.4 mg, 0.150 mmol) and [Rh(*rac*-binap)(nbd)]ClO_4 (13.8 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was obtained as a complex mixture.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6q** (61.4 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~0:100) to give **6q** (28.8 mg, 47% yield) as a pale yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6q** (61.4 mg, 0.150 mmol) and [Rh(dppe)(nbd)]ClO_4 (10.4 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~0:100) to give **6q** (37.9 mg, 62% yield) as a pale yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6r** (65.6 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~0:100) to give **6r** (41.2 mg, 63% yield) as a pale yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **6r** (65.6 mg, 0.150 mmol) and [Rh(dppe)(nbd)]ClO_4 (10.4 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~20:80) to give **6r** (44.6 mg, 68% yield) as a pale yellow oil.

<Scheme 46>

Dimethyl (5*S*)-9-methyl-10-((4-nitrophenyl)sulfonyl)-1,3,5,6,7,8-hexahydro-2*H*-5,8-epiminobenzo[7]annulene-2,2-dicarboxylate ((*S*)-67)

A solution of (*S*,*S*)-**10o** (32.3 mg, 0.0817 mmol), 4N HCl in dioxane (0.0817 mL, 0.327 mmol) in MeOH (0.82 mL) was stirred at r.t. for 1 h. The reaction mixture was concentrated. A solution of the crude amine, 4-nitrobenzenesulfonyl chloride (27.3 mg, 0.123 mmol) and DIPEA (0.0573 mL,

0.328 mmol) in CH_2Cl_2 (0.82 mL) was stirred at r.t. for 1 h. The reaction mixture was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give (*S*)-**67** (31.0 mg, 79% yield, 2 steps) as a yellow solid. The structure and the absolute configuration of (*S*)-**67** were unambiguously determined by X-ray crystal structure analysis.

CCDC 1052422 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Spectral data of (*S*)-**67**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.25 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 5.43 (dd, *J* = 5.9, 2.2 Hz, 1H), 4.48 (d, *J* = 7.3 Hz, 1H), 4.20 (d, *J* = 6.3 Hz, 1H), 3.67 (s, 3H), 3.59 (s, 3H), 2.72-2.67 (m, 2H), 2.37-2.30 (m, 1H), 2.22-2.10 (m, 2H), 1.81-1.76 (m, 1H), 1.67 (s, 3H), 1.41-1.36 (m, 1H), 1.15 (d, *J* = 15.4 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.4, 170.5, 149.9, 145.4, 135.9, 134.4, 129.1 (2C), 123.2 (2C), 122.7, 118.1, 61.7, 61.4, 53.5, 53.1, 52.7, 33.4, 32.0, 30.5, 30.3, 16.8 ppm; IR (CH_2Cl_2) $\tilde{\nu}$: 3100, 2952, 2876, 1731, 1605, 1529, 1352, 1164 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{24}N_2NaO_8S^+$ $[(M+Na)^+]$ 499.1146, found 499.1145; $[\alpha]_D^{17}$ -32.0 (*c* 1.01, $CHCl_3$); mp 221-222 °C (recrystallized from Hexane/$CHCl_3$ at 0 °C).

<Scheme 47>

Dimethyl (*R*)-9-methyl-8-((*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanamido)-1,3,7,8-tetrahydro-2*H*-benzo[7]annulene-2,2-dicarboxylate (68)

A solution of (*R*,*S*)-**9o** (30.6 mg, 0.0774 mmol), 4N HCl in dioxane (0.0774 mL, 0.309 mmol) in MeOH (0.77 mL) was stirred at r.t. for 1 h. The reaction mixture was concentrated. A solution of the crude amine hydrochloride, (*S*)-MTPA-Cl (0.0288 mL, 0.154 mmol) and Et_3N (0.0427 mL, 0.308 mmol) in CH_2Cl_2 (0.77 mL) was stirred at r.t. for 1 h. The reaction was quenched with H_2O and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **68** (19.2 mg, 49% yield, 2 steps) as a colorless oil.

Spectral data of **68**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.52-7.51 (m, 2H), 7.38-7.35 (m, 3H), 7.07 (d, *J* = 7.3 Hz, 1H), 5.93 (d, *J* = 12.0 Hz, 1H), 5.72 (t, *J* = 4.0 Hz, 1H), 5.35-5.30 (m, 1H), 4.47-4.44 (m, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.38 (d, *J* = 1.0 Hz, 3H), 3.18 (d, *J* = 13.2 Hz, 1H), 3.03 (dd, *J* = 19.4, 4.0 Hz, 1H), 2.54-2.51 (m, 3H), 2.47 (d, *J* = 13.4 Hz, 1H), 2.00 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.9, 170.5, 165.8, 137.3, 136.1, 133.2, 132.1, 131.6, 129.4, 128.5 (2C), 127.7, 127.7, 127.4, 123.9 ($J^{1}_{C\text{-}F}$ = 290.0 Hz), 123.3, 83.9 ($J^{2}_{C\text{-}F}$ = 26.1 Hz), 55.3, 53.9, 53.9, 53.0, 52.7, 33.7, 32.7, 31.2, 21.4 ppm; IR (neat) ν̃: 3410, 3021, 2954, 2847, 1732, 1694, 1588, 1505 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{26}H_{28}F_3NNaO_6^+$ [$(M+Na)^+$] 530.1761, found 530.1768; $[\alpha]_D^{22}$ -117.4 (*c* 1.09, $CHCl_3$).

Dimethyl

(*R*)-9-methyl-8-((*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanamido)-1,3,7,8-tetrahydro-2*H*-benzo[7]annulene-2,2-dicarboxylate (69)

A solution of (*R*,*S*)-**9o** (27.5 mg, 0.0695 mmol), 4N HCl in dioxane (0.0695 mL, 0.278 mmol) in MeOH (0.70 mL) was stirred at r.t. for 1 h. The reaction mixture was concentrated. A solution of the crude amine hydrochloride, (*R*)-MTPA-Cl (0.0262 mL, 0.140 mmol) and Et_3N (0.0388 mL, 0.280 mmol) in CH_2Cl_2 (0.70 mL) was stirred at r.t. for 1 h. The reaction was quenched with H_2O and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **69** (19.2 mg, 54% yield, 2 steps) as a colorless oil.

Spectral data of **69**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 7.3 Hz, 2H), 7.40-7.32 (m, 3H), 7.00 (d, *J* = 7.6 Hz, 1H), 5.99 (dd, *J* = 11.7, 2.4 Hz, 1H), 5.75 (t, *J* = 4.0 Hz, 1H), 5.45 (t, *J* = 8.7 Hz, 1H), 4.48 (t, *J* = 6.1 Hz, 1H), 3.70 (s, 3H), 3.42 (d, *J* = 1.0 Hz, 3H), 3.25 (s, 3H), 3.07 (d, *J* = 13.4 Hz, 1H), 2.98 (dd, *J* = 19.3, 3.9 Hz, 1H), 2.67 (dt, *J* = 17.9, 6.5 Hz, 1H), 2.55-2.49 (m, 2H), 2.45 (d, *J* = 13.4 Hz, 1H), 1.87 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.7, 170.6, 165.7, 136.5, 136.0, 133.1, 131.9, 131.3, 129.3, 128.5 (2C), 128.0, 127.9, 127.9, 123.9 ($J^{1}_{C\text{-}F}$ = 290.0 Hz), 123.8, 84.0 ($J^{2}_{C\text{-}F}$ = 26.1 Hz), 55.2, 53.9 (2C), 52.9, 52.3, 33.7, 32.7, 31.5, 21.4 ppm; IR (neat) ν̃: 3407,

3021, 2953, 2846, 1732, 1693, 1587, 1504 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{26}H_{28}F_3NNaO_6^+$ [$(M+Na)^+$] 530.1761, found 530.1770; $[\alpha]_D^{23}$ +11.0 (*c* 1.88, $CHCl_3$).

<Scheme 51>

Dimethyl (*S*)-9-methyl-8-((*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanamido)-1,3,7,8-tetrahydro-2*H*-benzo[7]annulene-2,2-dicarboxylate (90)

A solution of (*S*,*S*)-**9o** (8.0 mg, 0.0202 mmol), 4N HCl in dioxane (0.0202 mL, 0.0809 mmol) in MeOH (0.20 mL) was stirred at r.t. for 1 h. The reaction mixture was concentrated. A solution of the crude amine hydrochloride, (*S*)-MTPA-Cl (0.0075 mL, 0.040 mmol) and Et_3N (0.0111 mL, 0.0800 mmol) in CH_2Cl_2 (0.20 mL) was stirred at r.t. for 1 h. The reaction was quenched with H_2O and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **90** (2.2 mg, 22% yield, 2 steps) as a colorless oil.

Spectral data of **90**: ^1H NMR (500 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 7.3 Hz, 2H), 7.39-7.32 (m, 3H), 7.00 (d, *J* = 7.6 Hz, 1H), 5.99 (dd, *J* = 11.7, 2.4 Hz, 1H), 5.75 (t, *J* = 3.9 Hz, 1H), 5.45 (t, *J* = 8.7 Hz, 1H), 4.48 (t, *J* = 6.0 Hz, 1H), 3.70 (s, 3H), 3.42 (d, *J* = 1.0 Hz, 3H), 3.25 (s, 3H), 3.07 (d, *J* = 13.4 Hz, 1H), 2.98 (dd, *J* = 19.2, 3.8 Hz, 1H), 2.67 (dt, *J* = 17.9, 6.5 Hz, 1H), 2.55-2.49 (m, 2H), 2.45 (d, *J* = 13.7 Hz, 1H), 1.87 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.7, 170.6, 165.7, 136.5, 136.0, 133.1, 131.9, 131.3, 129.3, 128.5 (2C), 128.0, 127.9, 127.9, 123.8 ($J^1_{C\text{-}F}$ = 290.0 Hz), 123.8, 84.0 ($J^2_{C\text{-}F}$ = 26.1 Hz), 55.2, 53.9 (2C), 52.9, 52.3, 33.7, 32.7, 31.5, 21.4 ppm; IR (neat) ν̃: 3406, 3021, 2953, 2847, 1736, 1690, 1588, 1505 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{26}H_{28}F_3NNaO_6^+$ [$(M+Na)^+$] 530.1761, found 530.1771; $[\alpha]_D^{20}$ -12.0 (*c* 1.49, $CHCl_3$).

Dimethyl

(*S*)-9-methyl-8-((*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanamido)-1,3,7,8-tetrahydro-2*H*-benzo[7]annulene-2,2-dicarboxylate (91)

A solution of (*S*,*S*)-**9o** (7.0 mg, 0.0177 mmol), 4N HCl in dioxane (0.0177 mL, 0.0708 mmol) in MeOH (0.18 mL) was stirred at r.t. for 1 h. The reaction mixture was concentrated. A solution of the crude amine hydrochloride, (*R*)-MTPA-Cl (0.0067 mL, 0.036 mmol) and Et_3N (0.0100 mL, 0.0720 mmol) in CH_2Cl_2 (0.18 mL) was stirred at r.t. for 1 h. The reaction was quenched with H_2O and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **91** (2.3 mg, 25% yield, 2 steps) as a colorless oil.

Spectral data of **91**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.52-7.51 (m, 2H), 7.38-7.35 (m, 3H), 7.07 (d, *J* = 7.3 Hz, 1H), 5.94 (d, *J* = 12.0 Hz, 1H), 5.72 (t, *J* = 4.0 Hz, 1H), 5.35-5.30 (m, 1H), 4.47-4.44 (m, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.38 (d, *J* = 1.2 Hz, 3H), 3.18 (d, *J* = 13.4 Hz, 1H), 3.03 (dd, *J* = 19.4, 4.0 Hz, 1H), 2.54-2.51 (m, 3H), 2.47 (d, *J* = 13.9 Hz, 1H), 2.00 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.9, 170.5, 165.8, 137.3, 136.1, 133.2, 132.2, 131.6, 129.4, 128.5 (2C), 127.7, 127.7, 127.4, 123.9 ($J^1_{C\text{-}F}$ = 290.4 Hz), 123.3, 83.9 ($J^2_{C\text{-}F}$ = 26.1 Hz), 55.3, 53.9, 53.9, 53.0, 52.7, 33.7, 32.7, 31.2, 21.4 ppm; IR (neat) ν̃: 3410, 3021, 2954, 2847, 1739, 1693, 1587, 1504 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{26}H_{28}F_3NNaO_6^+$ [$(M+Na)^+$] 530.1761, found 530.1774; $[\alpha]_D^{22}$ +119.9 (*c* 0.90, $CHCl_3$).

<Scheme 52>

1-((*tert*-butyldimethylsilyl)oxy)-7,7-dimethoxy-5,5-dimethylhept-2-yn-4-ol (94)

To a solution of 3-((*tert*-butyldimethylsilyl)oxy)-1-propyne **93**[33] (23.6 g, 138 mmol) in THF (115 mL), was added *n*-BuLi (1.6 M in hexane, 79.1 mL, 127 mmol) at -78 °C. The mixture was stirred at -78 °C for 1 h. To the mixture, was added 4,4-dimethoxy-2,2-dimethylbutanal **92**[34] (18.5 g, 115 mmol) at -78 °C. The mixture was warmed to r.t. and stirred for 5 h. The reaction was quenched with saturated $NaHCO_3$ aq. and extracted with EtOAc. The organic layer was washed with saturated

$NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 100:0~75:25) to give **94** (17.5 g, 46% yield) as a brown oil.

Spectral data of **94**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.56 (dd, *J* = 6.8, 3.7 Hz, 1H), 4.37 (d, *J* = 1.7 Hz, 2H), 4.11 (dt, *J* = 7.3, 1.7 Hz, 1H), 3.34 (s, 3H), 3.31 (s, 3H), 1.93 (dd, *J* = 14.5, 7.0 Hz, 1H), 1.56-1.52 (m, 1H), 1.06 (s, 3H), 1.03 (s, 3H), 0.90 (s, 9H), 0.12 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 102.1, 84.5, 84.2, 70.3, 52.7, 52.3, 51.9, 40.9, 37.6, 25.9 (3C), 25.0, 24.4, 18.4, -5.0, -5.1 ppm; IR (neat) ν̃: 3437, 2956 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{17}H_{34}NaO_4Si^+$ $[(M+Na)^+]$ 353.2119, found 353.2121.

5-(4,4-Dimethoxy-2-methylbutan-2-yl)-10,10,11,11-tetramethyl-2,4,9-trioxa-10-siladodec-6-yne (95)

To a solution of **94** (1.00 g, 3.03 mmol) in THF (10 mL), was added NaH (60% dispersion in mineral oil, 218 mg, 5.45 mmol) at 0 °C. The mixture was stirred at r.t. for 0.5 h. To the mixture, was added MOMCl (0.368 mL, 4.84 mmol) at 0 °C. The mixture was stirred at 60 °C for 1 h. The reaction mixture was poured into saturated $NaHCO_3$ aq. at 0 °C and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 100:0~85:15) to give **95** (831 mg, 73% yield) as a colorless oil.

Spectral data of **95**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.96 (d, *J* = 6.8 Hz, 1H), 4.56 (d, *J* = 6.8 Hz, 1H), 4.53 (t, *J* = 5.4 Hz, 1H), 4.36 (d, *J* = 1.7 Hz, 2H), 4.09 (s, 1H), 3.38 (s, 3H), 3.30 (d, *J* = 1.7 Hz, 6H), 1.74 (d, *J* = 5.4 Hz, 2H), 1.05 (s, 6H), 0.90 (s, 9H), 0.11 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 102.6, 94.4, 85.6, 81.8, 74.1, 56.0, 52.5, 52.2, 51.8, 40.0, 36.8, 25.9 (3C), 23.8, 23.6, 18.4, -5.1 (2C) ppm; IR (neat) ν̃: 2930 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{19}H_{38}NaO_5Si^+$ $[(M+Na)^+]$ 397.2381, found 397.2380.

7,7-Dimethoxy-4-(methoxymethoxy)-5,5-dimethylhept-2-yn-1-ol (96)

A solution of **95** (1.00 g, 2.67 mmol) and TBAF (1.0 M in THF, 3.20 mL, 3.20 mmol) in THF (8.9 mL) was stirred at r.t. for 10 min. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 70:30~50:50) to give **96** (508 mg, 73% yield) as a pale yellow oil

Spectral data of **96**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.95 (d, *J* = 6.8 Hz, 1H), 4.57 (d, *J* = 7.8 Hz, 1H), 4.55 (t, *J* = 5.3 Hz, 1H), 4.31 (d, *J* = 4.7 Hz, 2H), 4.11 (s, 1H), 3.39 (s, 3H), 3.31 (d, *J* = 1.2 Hz, 6H), 1.74 (d, *J* = 5.3 Hz, 2H), 1.58-1.57 (m, 1H), 1.05 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 102.6, 94.4, 85.5, 82.6, 74.0, 55.9, 52.5, 52.3, 51.0, 40.0, 36.8, 23.8, 23.7 ppm; IR (neat) ν̃: 3435, 2937 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_{24}NaO_5^+$ [$(M+Na)^+$] 283.1516, found 283.1517.

7,7-Dimethoxy-5,5-dimethylhepta-2,3-dien-1-ol (97)

To a suspension of $LiAlH_4$ (583 mg, 15.4 mmol) in Et_2O (38 mL), was added **96** (1.00 g, 3.84 mmol) at r.t. The mixture was refluxed for 1 h. The mixture was quenched with H_2O (0.583 mL), 4N NaOH aq. (0.583 mL) and H_2O (1.75 mL) at 0 °C. The mixture was stirred at r.t. for 0.5 h, filtered through celite and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **97** (335 mg, 44% yield) as a colorless oil

Spectral data of **97**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.43 (q, *J* = 5.9 Hz, 1H), 5.30-5.28 (m, 1H), 4.51 (t, *J* = 5.0 Hz, 1H), 4.12-4.09 (m, 2H), 3.29 (s, 3H), 3.28 (s, 3H), 2.11 (t, *J* = 6.2 Hz, 1H), 1.71 (dd, *J* = 14.2, 4.6 Hz, 1H), 1.64 (dd, *J* = 14.2, 5.6 Hz, 1H), 1.07 (s, 3H), 1.06 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.1, 104.1, 102.6, 94.1, 60.8, 52.4, 51.7, 44.4, 33.4, 28.8, 28.6 ppm; IR (neat) ν̃: 3419, 2959, 1961 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{10}H_{17}O_3$ [$(M-Me)^+$] 185.1178, found 185.1177.

Dimethyl 2-(but-2-yn-1-yl)-2-(7,7-dimethoxy-5,5-dimethylhepta-2,3-dien-1-yl)malonate (100)

To a solution of **97** (501 mg, 2.50 mmol) and Et_3N (0.520 mL, 3.75 mmol) in CH_2Cl_2 (13 mL), was added MsCl (0.234 mL, 3.75 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 0.5 h. The

reaction was quenched with saturated $NaHCO_3$ aq. and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated to give a crude mesylate **98** as a pale brown oil. To a suspension of NaH (60% dispersion in mineral oil, 150 mg, 3.75 mmol) in THF (13 mL), was added **99**[35] (691 mg, 3.75 mmol) at 0 °C. The mixture was stirred at 0 °C for 10 min. To the mixture, was added the mesylate **98** at 0 °C. The reaction mixture was stirred at r.t. for 20 h. The reaction was quenched with saturated NH_4Cl aq. and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 95:5~75:25) to afford **100** (726 mg, 79% yield, 2 steps) as a colorless oil.

Spectral data of **100**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.11 (dt, *J* = 6.3, 2.4 Hz, 1H), 4.97 (td, *J* = 7.8, 6.3 Hz, 1H), 4.43 (t, *J* = 5.1 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.29 (s, 3H), 3.29 (s, 3H), 2.81-2.80 (m, 2H), 2.76 (dd, *J* = 7.8, 2.4 Hz, 2H), 1.75 (t, *J* = 2.4 Hz, 3H), 1.63 (d, *J* = 5.1 Hz, 2H), 1.04 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 203.8, 170.6, 170.6, 103.0, 101.6, 86.7, 79.1, 73.4, 57.5, 52.8, 52.8, 52.5, 52.4, 45.1, 33.3, 32.9, 28.5, 28.3, 23.2, 3.6 ppm; IR (neat) ν̃: 2956, 1962, 1739 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{30}NaO_6^+$ $[(M+Na)^+]$ 389.1935, found 389.1933.

Dimethyl (*E*)-2-(but-2-yn-1-yl)-2-(7-((*tert*-butanesulfinyl)imino)-5,5-dimethylhepta-2,3-dien-1-yl)malonate (6p)

A solution of **100** (700 mg, 1.91 mmol) and HCO_2H (2.20 mL, 57.3 mmol) in CH_2Cl_2 (19 mL) was stirred at r.t. for 12 h. The reaction was quenched with saturated $NaHCO_3$ aq. and extracted with EtOAc. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated to give a crude aldehyde as a pale brown oil. A suspension of the aldehyde, *t*-butanesulfinamide (278 mg, 2.29 mmol), PPTS (48.0 mg, 0.191 mmol) and $MgSO_4$ (1.15 g, 9.55 mmol) in toluene (6.4 mL) was stirred at 50 °C for 1 h. The reaction mixture was filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 95:5~70:30) to give **6p** (513 mg, 63% yield, dr = 1:1, 2 steps) as a colorless oil.

Spectral data of **6p**: Diastereomixture (1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.07 (t, *J* = 5.6 Hz, 1H and 1H), 5.17-5.14 (m, 1H and 1H), 5.06-5.00 (m, 1H and 1H), 3.73 (s, 3H and 3H), 3.73 (s, 3H and 3H), 2.80-2.76 (m, 4H and 4H), 2.58-2.48 (m, 2H and 2H), 1.74 (t, *J* = 2.6 Hz, 3H and 3H), 1.20 (d, *J* = 1.2 Hz, 9H and 9H), 1.13-1.12 (m, 6H and 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 203.8, 203.8, 170.5, 170.5, 168.4, 168.3, 100.9, 100.8, 87.7, 79.2, 79.2, 73.3, 73.3, 57.4, 57.4, 56.7, 56.7, 52.8, 52.8, 48.7, 48.7, 34.9, 34.8, 32.7, 32.7, 28.6, 28.6, 27.9, 27.9, 23.3, 22.6, 22.5, 3.6 ppm; IR (neat) ν̃: 2959, 1963, 1739, 1619 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{33}NNaO_5S^+$ [$(M+Na)^+$] 446.1972, found 446.1970.

<Scheme 53>

Dimethyl 2-(7,7-dimethoxyhepta-2,3-dien-1-yl)-2-(pent-3-yn-1-yl)malonate (103)

To a suspension of NaH (60% dispersion in mineral oil, 263 mg, 6.58 mmol) in DMF (18 mL), was added dimethyl 2-(pent-3-yn-1-yl)malonate **101**[36] (1.31 g, 6.58 mmol) at 0 °C. The mixture was stirred at 0 °C for 0.5 h. To the mixture, were added 7,7-dimethoxyhepta-2,3-dien-1-yl methanesulfonate **102**[29] (1.37 g, 5.49 mmol) and NaI (1.23 g, 8.23 mmol) at 0 °C. The reaction mixture was stirred at r.t. for 20 h. The reaction was quenched with H_2O and extracted with EtOAc. The organic layer was washed with H_2O, dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 95:5~70:30) to give **103** (1.11 g, 57% yield) as a pale brown oil.

Spectral data of **103**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.14-5.11 (m, 1H), 4.95-4.90 (m, 1H), 4.38 (t, *J* = 5.6 Hz, 1H), 3.72 (s, 3H), 3.72 (s, 3H), 3.32 (s, 6H), 2.61 (dd, *J* = 8.2, 2.3 Hz, 2H), 2.18-2.16 (m, 2H), 2.12-2.08 (m, 2H), 2.05-2.01 (m, 2H), 1.75 (t, *J* = 2.3 Hz, 3H), 1.71-1.68 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 205.8, 171.3 (2C), 104.1, 90.6, 85.4, 77.9, 76.3, 57.2, 53.0 (2C), 52.6, 52.6, 32.8, 32.0, 31.8, 23.9, 14.2, 3.6 ppm; IR (neat) ν̃: 2952, 1963, 1735 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{18}H_{25}O_6$ [$(M-Me)^+$] 337.1651, found 337.1655.

Dimethyl 2-(7-oxohepta-2,3-dien-1-yl)-2-(pent-3-yn-1-yl)malonate (1q)

A solution of **103** (1.11 g, 3.14 mmol) and HCO_2H (3.61 mL, 94.2 mmol) in CH_2Cl_2 (31 mL) was stirred at r.t. for 20 h. The reaction mixture was quenched with saturated $NaHCO_3$ aq. and extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 95:5~70:30) to give **1q** (875 mg, 91% yield) as a colorless oil.

Spectral data of **1q**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.78 (s, 1H), 5.20-5.17 (m, 1H), 5.00-4.96 (m, 1H), 3.72 (s, 6H), 2.61 (d, *J* = 7.6 Hz, 2H), 2.56 (t, *J* = 7.0 Hz, 2H), 2.33-2.29 (m, 2H), 2.18-2.15 (m, 2H), 2.10-2.09 (m, 2H), 1.75 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 205.8, 201.7, 171.2, 171.2, 89.8, 86.6, 77.8, 76.4, 57.1, 52.6, 52.6, 42.7, 32.6, 31.9, 21.2, 14.2, 3.6 ppm; IR (neat) ν̃: 2953, 1964, 1733 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{17}H_{22}NaO_5^+$ [(M+Na)$^+$] 329.1359, found 329.1360.

Dimethyl (*E*)-2-(7-((*tert*-butanesulfinyl)imino)hepta-2,3-dien-1-yl)-2-(pent-3-yn-1-yl)malonate (6q)

A suspension of **1q** (875 mg, 2.86 mmol), *t*-butanesulfinamide (415 mg, 3.43 mmol), PPTS (71.8 mg, 0.286 mmol) and $MgSO_4$ (1.72 g, 14.3 mmol) in toluene (9.0 mL) was stirred at 40 °C for 1 h. The reaction mixture was filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **6q** (1.17 g, quant., dr = 1:1) as a pale yellow oil.

Spectral data of **6q**: Diastereomixture (1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.09 (t, *J* = 4.3 Hz, 1H and 1H), 5.19-5.17 (m, 1H and 1H), 4.99-4.95 (m, 1H and 1H), 3.72 (s, 6H and 6H), 2.63-2.61 (m, 4H and 4H), 2.34-2.31 (m, 2H and 2H), 2.18-2.15 (m, 2H and 2H), 2.10-2.09 (m, 2H and 2H), 1.76-1.75 (m, 3H and 3H), 1.19 (s, 9H and 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 205.8, 205.8, 171.2, 168.7, 168.6, 89.9, 89.9, 86.3, 86.3, 77.7, 76.3, 57.1, 56.7, 52.6, 35.4, 35.4, 32.6, 31.9, 31.8, 24.5, 24.4, 22.4, 14.2, 3.6 ppm; IR (neat) ν̃: 2953, 1963, 1733, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{31}NNaO_5S^+$ [(M+Na)$^+$] 432.1815, found 432.1814.

<Scheme 54>

Dimethyl 2-(7,7-dimethoxy-5,5-dimethylhepta-2,3-dien-1-yl)-2-(pent-3-yn-1-yl)malonate (104)

To a solution of **97** (501 mg, 2.50 mmol) and Et_3N (0.520 mL, 3.75 mmol) in CH_2Cl_2 (13 mL), was added MsCl (0.234 mL, 3.75 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 0.5 h. The reaction was quenched with saturated $NaHCO_3$ aq. and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated to give a crude mesylate **98** as a pale brown oil. To a suspension of NaH (60% dispersion in mineral oil, 120 mg, 3.00 mmol) in DMF (13 mL), was added **101**[36] (595 mg, 3.00 mmol) at 0 °C. The mixture was stirred at 0 °C for 0.5 h. To the mixture, were added the mesylate **98** and NaI (562 mg, 3.75 mmol) at 0 °C. The reaction mixture was stirred at r.t. for 2 h. The reaction was quenched with saturated $NaHCO_3$ aq. and extracted with EtOAc. The organic layer was washed with H_2O, dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 95:5~80:20) to give **104** (782 mg, 82% yield, 2 steps) as a colorless oil.

Spectral data of **104**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.13-5.11 (m, 1H), 4.97 (dd, J = 14.0, 7.7 Hz, 1H), 4.42 (t, J = 5.1 Hz, 1H), 3.72 (s, 3H), 3.72 (s, 3H), 3.29 (s, 6H), 2.68-2.59 (m, 2H), 2.19-2.16 (m, 2H), 2.11-2.08 (m, 2H), 1.75 (t, J = 2.3 Hz, 3H), 1.62 (d, J = 5.1 Hz, 2H), 1.04 (s, 3H), 1.03 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 203.6, 171.3, 171.3, 103.0, 101.7, 86.8, 77.8, 76.3, 57.2, 52.6, 52.6, 52.5, 52.4, 45.1, 33.3, 33.1, 31.9, 28.5, 28.3, 14.2, 3.6 ppm; IR (neat) ν̃: 2955, 1961, 1733 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{32}NaO_6^+$ [$(M+Na)^+$] 403.2091, found 403.2090.

Dimethyl (*E*)-2-(7-((*tert*-butanesulfinyl)imino)-5,5-dimethylhepta-2,3-dien-1-yl)-2-(pent-3-yn-1-yl)malonate (6r)

A solution of **104** (720 mg, 1.89 mmol) and HCO_2H (2.18 mL, 56.8 mmol) in CH_2Cl_2 (19 mL) was stirred at r.t. for 20 h. The reaction was quenched with saturated $NaHCO_3$ aq. and extracted with EtOAc. The organic layer was washed with $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated to give a crude aldehyde **1r** as a pale brown oil. A suspension of the aldehyde **1r**,

t-butanesulfinamide (275 mg, 2.27 mmol), PPTS (47.5 mg, 0.189 mmol) and $MgSO_4$ (1.14 g, 9.46 mmol) in toluene (9.5 mL) was stirred at 50 °C for 1 h. The reaction mixture was filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **6r** (643 mg, 78% yield, dr = 1:1, 2 steps) as a colorless oil.

Spectral data of **6r**: Diastereomixture (1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.07 (t, *J* = 5.6 Hz, 1H), 5.18-5.15 (m, 1H), 5.06-5.00 (m, 1H), 3.72 (s, 6H), 2.68-2.59 (m, 2H), 2.56-2.47 (m, 2H), 2.18-2.15 (m, 2H), 2.11-2.09 (m, 2H), 1.75 (t, *J* = 2.2 Hz, 3H), 1.20 (s, 9H), 1.13-1.12 (m, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 203.5, 171.2, 171.1, 168.3, 168.3, 100.9, 100.9, 87.8, 77.7, 76.3, 57.1, 57.1, 56.7, 52.6, 52.6, 48.7, 48.6, 34.9, 34.9, 32.9, 32.9, 31.9, 28.6, 28.5, 28.0, 28.0, 22.5, 22.5, 14.2, 3.6 ppm; IR (neat) $\tilde{\nu}$: 2958, 1962, 1733, 1619 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{23}H_{35}NNaO_5S^+$ $[(M+Na)^+]$ 460.2128, found 460.2125.

Chapter 2

<Section 1>

<Scheme 56>

Dimethyl (*E*)-5-((*E*)-5-((*tert*-butanesulfinyl)imino)pentylidene)-4-(2,2-dimethylcyclopropyl)cyclohex-3-ene-1,1-dicarboxylate (109a)

Spectral data of **109a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.10 (t, *J* = 4.7 Hz, 1H), 5.63 (t, *J* = 7.6 Hz, 1H), 5.44 (s, 1H), 3.72 (s, 3H), 3.62 (s, 3H), 3.07 (d, *J* = 14.6 Hz, 1H), 2.80 (dd, *J* = 17.6, 4.7 Hz, 1H), 2.66 (d, *J* = 14.6 Hz, 1H), 2.61-2.55 (m, 3H), 2.33-2.21 (m, 2H), 1.79-1.75 (m, 2H), 1.20 (s, 10H), 1.15 (s, 3H), 0.69 (s, 3H), 0.51-0.46 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ: 172.1, 171.2, 169.4, 169.4, 136.7, 133.3, 126.2, 122.2, 56.6, 54.2, 52.8, 52.6, 35.9, 31.6, 31.4, 27.9, 27.2, 26.8, 25.6, 22.5 (3C), 19.2, 17.3, 16.9 ppm; IR (neat) $\tilde{\nu}$: 2952, 1737, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{24}H_{37}NNaO_5S^+$ $[(M+Na)^+]$ 474.2285, found 474.2281.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **105a** (67.7 mg, 0.150 mmol) and $[Rh(dppp)(nbd)]ClO_4$ (10.6 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~0:100) to give **105a** (17.9 mg, 26% yield) as a pale yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **105a** (67.7 mg, 0.150 mmol) and $[Rh(rac\text{-binap})(nbd)]ClO_4$ (13.8 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was obtained as a complex mixture.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **105a** (67.7 mg, 0.150 mmol) and $[Rh(dppbz)(nbd)]ClO_4$ (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$

(1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **109a** (24.1 mg, 36% yield) as a pale yellow oil.

<Scheme 57>

Dimethyl 4-(*tert*-butanesulfinyl)-1,2,3,3a,4,5,7,9-octahydro-8*H*-cyclopenta[*c*]isoquinoline-8,8-dicarboxylate (108b)

Spectral data of **108b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.44 (s, 1H), 4.21 (d, *J* = 14.4 Hz, 1H), 3.88-3.86 (m, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.56 (dd, *J* = 14.5, 1.8 Hz, 1H), 2.88 (d, *J* = 15.1 Hz, 1H), 2.76 (d, *J* = 17.8 Hz, 1H), 2.64-2.60 (m, 2H), 2.42 (d, *J* = 8.5 Hz, 2H), 2.20-2.16 (m, 1H), 1.95-1.88 (m, 1H), 1.78-1.60 (m, 2H), 1.20 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.8, 171.5, 139.7, 131.1, 122.0, 116.6, 62.7, 59.8, 53.9, 52.9, 52.8, 45.5, 32.1, 31.8, 30.8, 26.8, 23.6 (3C), 22.2 ppm; IR (neat) $\tilde{\nu}$: 2955, 1736, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{29}NNaO_5S^+$ $[(M+Na)^+]$ 418.1659, found 418.1659.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **105b** (59.3 mg, 0.150 mmol) and $[Rh(dppp)(nbd)]ClO_4$ (10.6 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **105b** (18.4 mg, 31% yield) as a pale yellow oil and **108b** (4.0 mg, 7% yield) as a yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **105b** (59.3 mg, 0.150 mmol) and [Rh(*rac*-binap)(nbd)]ClO_4 (13.8 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **108b** (1.4 mg, 2% yield) as a yellow oil.

According to the general procedure (1) for cyclization, a crude product, which was prepared from **105b** (59.3 mg, 0.150 mmol) and [Rh(dppbz)(nbd)]ClO_4 (11.1 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **108b** (9.1 mg, 15% yield) as a pale yellow oil.

<Scheme 59>

Dimethyl (*E*)-2-(7-((*tert*-butanesulfinyl)imino)hept-2-yn-1-yl)-2-(5,5-dimethylhexa-2,3-dien-1-yl)malonate (105a)

A suspension of **13a**[20b] (1.50 g, 4.30 mmol), *t*-butanesulfinamide (626 mg, 5.17 mmol), PPTS (108 mg, 0.430 mmol) and $MgSO_4$ (2.59 g, 21.5 mmol) in toluene (14 mL) was stirred at 50 °C for 6 h. The reaction mixture was filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **105a** (1.39 g, 72% yield, dr = 1:1) as a colorless oil.

Spectral data of **105a**: Diastereomixture (1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.08 (t, *J* = 4.4 Hz, 1H), 5.10-5.09 (m, 1H), 4.93 (q, *J* = 7.2 Hz, 1H), 3.73 (d, *J* = 2.3 Hz, 6H), 2.86-2.80 (m, 2H), 2.76-2.74 (m, 2H), 2.62-2.59 (m, 2H), 2.23 (t, *J* = 6.7 Hz, 2H), 1.82-1.77 (m, 2H), 1.19 (s, 9H), 1.02 (s, 9H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ: 203.3, 170.5 (2C), 168.9, 103.1, 86.3, 82.4, 75.7, 57.5, 56.7, 52.8, 52.8, 35.0, 32.9, 31.8, 30.2 (3C), 24.7, 23.2, 22.5 (3C), 18.3 ppm; IR (neat) ν̃: 2957, 2241, 1961, 1739, 1624 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{24}H_{37}NNaO_5S^+$ $[(M+Na)^+]$ 474.2285, found 474.2281.

<Scheme 61>

Dimethyl 2-(buta-2,3-dien-1-yl)-2-(7-((*tert*-butyldimethylsilyl)oxy)hept-2-yn-1-yl)malonate (119)

To a suspension of NaH (60% dispersion in mineral oil, 0.636 g, 26.5 mmol) in THF (84 mL), was added **117**[20b] (6.75 g, 18.9 mmol) at 0 °C. To the mixture, was added **118**[39] (3.74 g, 25.2 mmol) at 0

°C. The reaction mixture was stirred at r.t. for 14 h. The reaction was quenched with saturated NH_4Cl aq. and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 95:5~85:15) to give **119** (5.37 g, 69% yield) as a brown oil.

Spectral data of **119**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.98-4.93 (m, 1H), 4.67-4.65 (m, 2H), 3.73 (s, 6H), 3.61 (t, *J* = 6.2 Hz, 2H), 2.81 (t, *J* = 2.1 Hz, 2H), 2.75 (td, *J* = 5.3, 2.7 Hz, 2H), 2.15-2.13 (m, 2H), 1.60-1.48 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ: 210.2, 170.5 (2C), 84.1, 83.7, 74.7, 74.4, 62.8, 57.7, 52.8 (2C), 32.0, 31.9, 26.1 (3C), 25.4, 23.2, 18.6, 18.5, -5.2 (2C) ppm; IR (neat) ν̃: 2953, 1956, 1739 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{36}NaO_5Si^+$ [$(M+Na)^+$] 431.2224, found 431.2220.

Dimethyl 2-(buta-2,3-dien-1-yl)-2-(7-hydroxyhept-2-yn-1-yl)malonate (120)

A solution of **119** (5.37 g, 13.1 mmol) and TBAF (1.0 M in THF, 15.8 mL, 15.8 mmol) in THF (44 mL) was stirred at r.t. for 1 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 80:20~50:50) to give **120** (3.85 g, quant.) as a colorless oil.

Spectral data of **120**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.97-4.91 (m, 1H), 4.66-4.65 (m, 2H), 3.72 (d, *J* = 1.2 Hz, 6H), 3.63 (td, *J* = 6.4, 1.6 Hz, 2H), 2.79-2.79 (m, 2H), 2.74-2.72 (m, 2H), 2.17-2.14 (m, 2H), 1.66-1.60 (m, 3H), 1.55-1.50 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 210.2, 170.5 (2C), 84.0, 83.5, 74.8, 74.7, 62.5, 57.7, 52.8 (2C), 31.9, 31.8, 25.1, 23.2, 18.5 ppm; IR (neat) ν̃: 3410, 2952, 1955, 1737 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{22}NaO_5^+$ [$(M+Na)^+$] 317.1359, found 317.1357.

Dimethyl 2-(buta-2,3-dien-1-yl)-2-(7-oxohept-2-yn-1-yl)malonate (13b)

A suspension of **120** (3.85 g, 13.1 mmol), DMP (7.77 g, 18.3 mmol) and $NaHCO_3$ (1.65 g, 19.6 mmol) in CH_2Cl_2 (44 mL) was stirred at r.t. for 3 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with EtOAc. The organic layer was washed with saturated $NaHCO_3$ aq.,

dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **13b** (3.19 g, 84% yield) as a colorless oil.

Spectral data of **13b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.79 (t, *J* = 1.3 Hz, 1H), 4.97-4.92 (m, 1H), 4.68-4.66 (m, 2H), 3.73 (s, 6H), 2.81 (t, *J* = 2.3 Hz, 2H), 2.74 (dt, *J* = 8.0, 2.3 Hz, 2H), 2.55 (td, *J* = 7.3, 1.2 Hz, 2H), 2.23-2.19 (m, 2H), 1.81-1.75 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 210.3, 202.1, 170.4 (2C), 84.0, 82.5, 75.6, 74.8, 57.5, 52.8 (2C), 42.8, 31.9, 23.1, 21.4, 18.2 ppm; IR (neat) ṽ: 2953, 1955, 1738 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{21}O_5^+$ [$(M+H)^+$] 293.1384, found 293.1383.

Dimethyl (*E*)-2-(buta-2,3-dien-1-yl)-2-(7-((*tert*-butanesulfinyl)imino)hept-2-yn-1-yl)malonate (105b)

A suspension of **13b** (1.32 g, 4.50 mmol), *t*-butanesulfinamide (654 mg, 5.40 mmol), PPTS (113 mg, 0.450 mmol) and $MgSO_4$ (2.71 g, 22.5 mmol) in toluene (15 mL) was stirred at 50 °C for 1 h. The reaction mixture was filtered through a short silica gel pad and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **105b** (1.54 g, 86% yield) as a colorless oil.

Spectral data of **105b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.08 (t, *J* = 4.4 Hz, 1H), 4.98-4.92 (m, 1H), 4.68-4.66 (m, 2H), 3.73 (s, 6H), 2.82 (t, *J* = 2.3 Hz, 2H), 2.76-2.73 (m, 2H), 2.61 (td, *J* = 7.3, 4.4 Hz, 2H), 2.23 (t, *J* = 6.6 Hz, 2H), 1.82-1.77 (m, 2H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 210.3, 170.4 (2C), 168.9, 84.0, 82.5, 75.5, 74.8, 57.6, 56.7, 52.8 (2C), 35.0, 31.9, 24.6, 23.2 (3C), 22.5, 18.3 ppm; IR (neat) ṽ: 2953, 1955, 1738, 1624 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{29}NNaO_5S^+$ [$(M+Na)^+$] 418.1659, found 418.1655.

<Section 2>

<Scheme 63>

Dimethyl (*R*,*Z*)-2'-(((*S*)-*tert*-butanesulfinyl)amino)-5-methylene-(1,1'-bi(cyclopentylidene))-3,3-dicarboxylate (125a)

Spectral data of **125a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.36 (s, 1H), 5.11 (s, 1H), 4.49-4.47 (br m, 1H), 3.73 (d, *J* = 1.0 Hz, 6H), 3.19 (d, *J* = 8.3 Hz, 1H), 3.03 (s, 2H), 2.94 (s, 2H), 2.38-2.23 (m, 3H), 1.85-1.78 (m, 3H), 1.18 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.0, 171.9, 143.7, 139.6, 132.6, 110.7, 58.7, 57.4, 56.6, 53.0, 53.0, 43.1, 40.9, 36.3, 32.0, 22.9 (3C), 22.0 ppm; IR (neat) ν̃: 3222, 2954, 1738, 1622 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{19}H_{29}NNaO_5S^+$ [$(M+Na)^+$] 418.1659, found 418.1657; $[\alpha]_D^{23}$ -104.9 (*c* 1.59, $CHCl_3$).

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121a** (57.5 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and DPPE (5.98 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give (*S*)-**121a** (53.8 mg, 94% yield) as a pale yellow oil.

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121a** (57.5 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and DPPP (6.19 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give (*S*)-**121a** (56.6 mg, 98% yield) as a pale yellow oil.

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121a** (57.5 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and DPPBz (6.70 mg,

0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give (*S*)-**121a** (55.5 mg, 97% yield) as a pale yellow oil.

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121a** (57.5 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and BIPHEP (7.84 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **125a** (7.9 mg, 14% yield, dr = >20:1) as a pale yellow oil and (*S*)-**121a** (9.2 mg, 16% yield) as a pale yellow oil.

<Table 12>

<Entry 1>

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121a** (57.5 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*R*)-BINAP (9.34 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give (*S*)-**121a** (55.5 mg, 97% yield) as a pale yellow oil.

<Entry 2>

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121a** (57.5 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*R*)-Tol-BINAP (10.2 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **125a** (1.1 mg, 2% yield, dr = >20:1) as a pale yellow oil and (*S*)-**121a** (55.6 mg, 97% yield) as a pale yellow oil.

<Entry 3>

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121a** (57.5 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*R*)-Xyl-BINAP (11.0 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give (*S*)-**121a** (55.8 mg, 97% yield) as a pale yellow oil.

<Entry 4>

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121a** (57.5 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*R*)-H_8-BINAP (9.46 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **125a** (1.0 mg, 2% yield, dr = >20:1) as a pale yellow oil and (*S*)-**121a** (53.4 mg, 93% yield) as a pale yellow oil.

<Entry 5>

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121a** (57.5 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*S*)-BINAP (9.34 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **125a** (33.0 mg, 57% yield, dr = >20:1) as a pale yellow oil.

<Entry 6>

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121a** (57.5 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*S*)-Tol-BINAP (10.2 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **125a** (30.2 mg, 53% yield, dr = >20:1) as a pale yellow oil.

<Entry 7>

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121a** (57.5 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*S*)-Xyl-BINAP (11.0 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **125a** (34.5 mg, 60% yield, dr = >20:1) as a pale yellow oil and (*S*)-**121a** (20.3 mg, 35% yield) as a pale yellow oil.

<Entry 8>

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121a** (57.5 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **125a** (50.5 mg, 88% yield, dr = >20:1) as a pale yellow oil and (*S*)-**121a** (<2.6 mg, <5% yield) as a pale yellow oil.

<Entry 9>

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121a** (57.5 mg, 0.150 mmol), $[Rh(cod)_2]ClO_4$ (6.28 mg, 0.0150 mmol) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **125a** (44.9 mg, 78% yield, dr = >20:1) as a pale yellow oil.

<Scheme 67>

Dimethyl 2-allyl-2-(7-((*tert*-butyldimethylsilyl)oxy)hept-2-yn-1-yl)malonate (137)

To a suspension of NaH (60% dispersion in mineral oil, 119 mg, 2.99 mmol) in THF (11 mL), was added dimethyl allylmalonate (0.343 mL, 2.13 mmol) at 0 °C. To the mixture, was added **136**[20b] (684 mg, 2.13 mmol) at 0 °C. The reaction mixture was stirred at r.t. for 20 h. The reaction was quenched with saturated NH_4Cl aq. and extracted with EtOAc. The organic layer was dried over

$MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 95:5~85:15) to give **137** (727 mg, 86% yield) as a colorless oil.

Spectral data of **137**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.67-5.60 (m, 1H), 5.17-5.10 (m, 2H), 3.72 (s, 6H), 3.61 (t, *J* = 6.2 Hz, 2H), 2.79-2.75 (m, 4H), 2.16-2.13 (m, 2H), 1.60-1.48 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.6 (2C), 132.2, 119.7, 83.7, 74.5, 62.8, 57.5, 52.8 (2C), 36.8, 32.0, 26.1 (3C), 25.5, 23.2, 18.6, 18.5, -5.2 (2C) ppm; IR (neat) ν̃: 2953, 1740, 1642 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{36}NaO_5Si^+$ [$(M+Na)^+$] 419.2224, found 419.2220.

Dimethyl 2-allyl-2-(7-hydroxyhept-2-yn-1-yl)malonate (138)

A solution of **137** (710 mg, 1.79 mmol) and TBAF (1.0 M in THF, 2.15 mL, 2.15 mmol) in THF (6.0 mL) was stirred at r.t. for 0.5 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 80:20~60:40) to give **138** (465 mg, 92% yield) as a colorless oil.

Spectral data of **138**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.66-5.59 (m, 1H), 5.17-5.11 (m, 2H), 3.73 (s, 6H), 3.66 (t, *J* = 6.4 Hz, 2H), 2.79-2.76 (m, 4H), 2.19-2.16 (m, 2H), 1.68-1.63 (m, 2H), 1.57-1.54 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.7 (2C), 132.1, 119.8, 83.5, 74.8, 62.5, 57.4, 52.8 (2C), 36.8, 31.8, 25.2, 23.2, 18.5 ppm; IR (neat) ν̃: 3437, 2952, 1738, 1642 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{15}H_{22}NaO_5^+$ [$(M+Na)^+$] 305.1359, found 305.1361.

Dimethyl 2-allyl-2-(7-oxohept-2-yn-1-yl)malonate (139a)

A suspension of **138** (450 mg, 1.59 mmol), DMP (946 mg, 2.23 mmol) and $NaHCO_3$ (201 mg, 2.39 mmol) in CH_2Cl_2 (16 mL) was stirred at r.t. for 2 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~60:40) to give **139a** (372 mg, 83% yield) as a colorless oil.

Spectral data of **139a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.80 (s, 1H), 5.66-5.59 (m, 1H), 5.17-5.11 (m, 2H), 3.73 (s, 6H), 2.78-2.76 (m, 4H), 2.56 (td, *J* = 7.3, 1.2 Hz, 2H), 2.23-2.20 (m, 2H), 1.81-1.76 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 202.0, 170.5 (2C), 132.0, 119.8, 82.4, 75.7, 57.3, 52.8 (2C), 42.8, 36.8, 23.2, 21.4, 18.2 ppm; IR (neat) ν̃: 2954, 1737, 1642 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{15}H_{20}NaO_5^+$ [$(M+Na)^+$] 303.1203, found 303.1199.

Dimethyl (*S*,*E*)-2-allyl-2-(7-((*tert*-butanesulfinyl)imino)hept-2-yn-1-yl)malonate ((*S*)-121a)

A suspension of **139a** (981 mg, 3.50 mmol), (*S*)-*t*-butanesulfinamide (509 mg, 4.20 mmol), PPTS (88 mg, 0.350 mmol) and $MgSO_4$ (2.11 g, 17.5 mmol) in toluene (18 mL) was stirred at 40 °C for 2 h. The reaction mixture was filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give (*S*)-**121a** (1.09 g, 81% yield) as a colorless oil.

Spectral data of (*S*)-**121a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.08 (t, *J* = 4.4 Hz, 1H), 5.66-5.59 (m, 1H), 5.17-5.11 (m, 2H), 3.73 (s, 6H), 2.78-2.76 (m, 4H), 2.63-2.60 (m, 2H), 2.24 (td, *J* = 6.9, 2.1 Hz, 2H), 1.83-1.78 (m, 2H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.5 (2C), 168.9, 132.0, 119.8, 82.4, 75.6, 57.3, 56.7, 52.8 (2C), 36.8, 35.0, 24.7, 23.2, 22.5 (3C), 18.3 ppm; IR (neat) ν̃: 2953, 1739, 1641, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{19}H_{29}NNaO_5S^+$ [$(M+Na)^+$] 406.1659, found 406.1655; $[\alpha]_D^{24}$ +126.3 (*c* 1.04, $CHCl_3$).

<Section 3>

<Table 13>

(*S*)-*N*-((*R*,*Z*)-4',4'-Bis((benzyloxy)methyl)-2'-methylene-(1,1'-bi(cyclopentylidene))-2-yl)-2-methylpropane-2-sulfinamide (125b)

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121b** (76.2 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **125b** (62.1 mg, 82% yield, dr = >20:1) as a pale yellow oil.

Spectral data of **125b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.33-7.25 (m, 10H), 5.31 (s, 1H), 5.03 (s, 1H), 4.50 (s, 4H), 4.47-4.46 (m, 1H), 3.41-3.35 (m, 4H), 3.17 (d, *J* = 8.3 Hz, 1H), 2.40 (s, 2H), 2.31-2.15 (m, 5H), 1.83-1.73 (m, 3H), 1.18 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.5, 139.0, 138.9, 138.8, 135.1, 128.4 (4C), 127.5 (4C), 127.5 (2C), 110.2, 73.3, 73.3, 73.3, 73.0, 58.8, 56.5, 45.0, 41.7, 39.6, 36.3, 32.0, 22.9 (3C), 21.9 ppm; IR (neat) $\tilde{\nu}$: 3315, 2959, 2860, 1617 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{31}H_{41}NNaO_3S^+$ [$(M+Na)^+$] 530.2699, found 530.2698; $[\alpha]_D^{19}$ -102.4 (*c* 5.82, $CHCl_3$).

((*R*,*Z*)-2'-(((*S*)-*tert*-butanesulfinyl)amino)-5-methylene-(1,1'-bi(cyclopentylidene))-3,3-diyl)bis(methylene) diacetate (125c)

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121c** (61.7 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **125c** (50.7 mg, 82% yield, dr = >20:1) as a pale yellow oil and (*S*)-**121c** (5.2 mg, 8% yield) as a pale yellow oil.

Spectral data of **125c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.39 (s, 1H), 5.09 (s, 1H), 4.48 (d, *J* = 4.4 Hz, 1H), 3.98 (t, *J* = 12.5 Hz, 4H), 3.21 (d, *J* = 8.5 Hz, 1H), 2.43-2.15 (m, 7H), 2.07 (d, *J* = 2.7 Hz, 6H), 1.82 (tt, *J* = 13.9, 5.8 Hz, 3H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.2, 171.1,

144.8, 139.9, 133.6, 111.2, 66.6, 66.4, 58.8, 56.6, 42.9, 41.5, 39.3, 36.3, 32.0, 22.9 (3C), 21.8, 21.0, 21.0 ppm; IR (neat) $\tilde{\nu}$: 3278, 2957, 1741, 1621 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{33}NNaO_5S^+$ $[(M+Na)^+]$ 434.1972, found 434.1967; $[\alpha]_D^{20}$ -116.5 (*c* 5.81, $CHCl_3$).

(*S*)-*N*-((*R*,*Z*)-2-(8,8-Dimethyl-3-methylene-7,9-dioxaspiro[4.5]decan-2-ylidene)cyclopentyl)-2-methylpropane-2-sulfinamide (125d)

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121d** (55.1 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 4 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **125d** (45.6 mg, 83% yield, dr = >20:1) as a pale yellow oil.

Spectral data of **125d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.37 (s, 1H), 5.09 (s, 1H), 4.50-4.48 (m, 1H), 3.64 (d, *J* = 11.5 Hz, 2H), 3.60 (dd, *J* = 11.2, 3.2 Hz, 2H), 3.20 (d, *J* = 8.3 Hz, 1H), 2.41-2.19 (m, 7H), 1.85-1.77 (m, 3H), 1.43 (s, 6H), 1.18 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.4, 139.6, 134.1, 111.0, 98.1, 68.6, 68.3, 58.8, 56.6, 42.7, 40.7, 38.7, 36.3, 32.0, 24.2, 23.7, 22.9 (3C), 21.9 ppm; IR (neat) $\tilde{\nu}$: 3252, 2989, 2956, 2864, 1621 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{33}NNaO_3S^+$ $[(M+Na)^+]$ 390.2073, found 390.2075; $[\alpha]_D^{19}$ -147.8 (*c* 1.05, $CHCl_3$).

(*S*)-2-Methyl-*N*-((*R*,*Z*)-2-(3-methylenespiro(cyclopentane-1,9'-fluoren)-4-ylidene)cyclopentyl)propane-2-sulfinamide (125e)

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121e** (62.6 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 4 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **125e** (47.9 mg, 77% yield, dr = >20:1) as a pale yellow oil.

Spectral data of **125e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 7.3 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.36-7.32 (m, 2H), 7.30-7.21 (m, 2H), 5.62 (s, 1H), 5.23 (s, 1H), 4.73

(t, *J* = 6.6 Hz, 1H), 3.34 (d, *J* = 8.1 Hz, 1H), 3.00 (d, *J* = 15.1 Hz, 1H), 2.88 (d, *J* = 16.4 Hz, 1H), 2.81-2.73 (m, 2H), 2.36-2.28 (m, 2H), 2.24-2.17 (m, 1H), 1.96-1.75 (m, 3H), 1.28 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.9, 151.2, 146.8, 139.9, 139.8, 139.6, 135.3, 127.6, 127.4, 127.3, 127.3, 123.0, 122.7, 119.9, 119.9, 110.7, 58.7, 56.7, 53.9, 48.1, 46.1, 36.6, 32.2, 23.0 (3C), 21.9 ppm; IR (neat) ν̃: 3433, 3065, 2959, 2828, 1619 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{27}H_{31}NNaOS^+$ [$(M+Na)^+$] 440.2019, found 440.2013; $[\alpha]_D^{18}$ -85.9 (*c* 1.95, $CHCl_3$).

(*S*)-2-Methyl-*N*-((*R*,*E*)-2-(4-methylene-1-tosylpyrrolidin-3-ylidene)cyclopentyl)propane-2-sulfinamide (125f)

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121f** (63.4 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 9 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **125f** (39.7 mg, 63% yield, dr = >20:1) as a pale yellow oil.

Spectral data of **125f**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.41 (s, 1H), 5.11 (s, 1H), 4.41-4.39 (m, 1H), 3.96 (dd, *J* = 24.5, 13.1 Hz, 2H), 3.86 (dd, *J* = 24.9, 14.2 Hz, 2H), 3.14 (d, *J* = 8.5 Hz, 1H), 2.43 (s, 3H), 2.31-2.14 (m, 3H), 1.85-1.73 (m, 3H), 1.16 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.6, 140.1, 140.0, 132.8, 129.9 (2C), 129.5, 128.1 (2C), 110.6, 58.7, 56.7, 54.5, 53.2, 36.2, 31.7, 22.9 (3C), 21.9, 21.7 ppm; IR (neat) ν̃: 3286, 2963, 1625, 1598, 1346, 1163 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{30}N_2NaO_3S_2^+$ [$(M+Na)^+$] 445.1590, found 445.1601; $[\alpha]_D^{22}$ -103.4 (*c* 2.15, $CHCl_3$).

(*S*)-2-Methyl-*N*-((*R*,*E*)-2-(4-methylene-1-((2-nitrophenyl)sulfonyl)pyrrolidin-3-ylidene)cyclopentyl)propane-2-sulfinamide (125g)

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121g** (68.0 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 15 h, was purified by silica gel column

chromatography (Hexane/EtOAc = 90:10~0:100) to give **125g** (41.4 mg, 61% yield, dr = >20:1) as a pale yellow oil.

Spectral data of **125g**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02-8.00 (m, 1H), 7.73-7.62 (m, 3H), 5.50 (s, 1H), 5.18 (s, 1H), 4.49-4.47 (m, 1H), 4.20 (s, 2H), 4.12 (s, 2H), 3.20 (d, *J* = 8.3 Hz, 1H), 2.36-2.20 (m, 3H), 1.88-1.81 (m, 3H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 148.6, 140.5, 139.6, 133.9, 131.7, 131.3, 130.9, 129.2, 124.2, 111.0, 58.7, 56.7, 54.3, 53.0, 36.2, 31.7, 22.9 (3C), 21.9 ppm; IR (neat) ν̃: 3308, 2962, 2870, 1590, 1546, 1371, 1170 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{27}N_3NaO_5S_2^+$ [$(M+Na)^+$] 476.1284, found 476.1285; $[\alpha]_D^{20}$ -125.3 (*c* 2.17, $CHCl_3$).

<Scheme 69>

Dimethyl (*Z*)-3-((*R*)-2-(((*S*)-*tert*-butanesulfinyl)amino)cyclopentylidene)-4-methylenecyclohexane-1,1-dicarboxylate (125h)

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121h** (59.6 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 50 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **125h** (21.9 mg, 37% yield, dr = >20:1) as a pale yellow oil and (*S*)-**121h** (32.8 mg, 55% yield) as a pale yellow oil.

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121h** (59.6 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*S*)-Tol-BINAP (10.2 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 50 °C for 3 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **125h** (48.4 mg, 81% yield, dr = >20:1) as a pale yellow oil and (*S*)-**121h** (<8.2 mg, <14% yield) as a pale yellow oil.

Spectral data of **125h**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.91 (d, *J* = 10.5 Hz, 2H), 4.49 (s, 1H), 3.71 (s, 6H), 3.01 (d, *J* = 7.0 Hz, 1H), 2.89 (d, *J* = 13.5 Hz, 1H), 2.61 (d, *J* = 13.5 Hz, 1H), 2.47-2.28 (m, 5H), 2.08-1.98 (m, 2H), 1.88-1.73 (m, 3H), 1.16 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.8, 171.2, 146.7, 139.5, 132.1, 111.1, 57.9, 56.3, 55.8, 52.8, 52.6, 37.7, 35.6, 33.3, 32.6, 28.6, 22.7 (3C),

22.3 ppm; IR (neat) ṽ: 3291, 2954, 1734, 1637 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{31}NNaO_5S^+$ [$(M+Na)^+$] 420.1815, found 420.1815; $[\alpha]_D^{21}$ -18.9 (*c* 1.35, $CHCl_3$).

<Scheme 70>

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121i** (59.6 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 4 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **150i** (25.3 mg, 42% yield) as a pale yellow oil and **151i** (14.0 mg, 24% yield) as a pale yellow oil.

Dimethyl (*S*)-3-(2-((*tert*-butanesulfinyl)amino)cyclohex-1-en-1-yl)-4-methylcyclopent-3-ene-1,1-dicarboxylate (150i)

Spectral data of **150i**: ^1H NMR (500 MHz, $CDCl_3$) δ: 5.52 (s, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.05-2.88 (m, 4H), 2.51-2.45 (m, 1H), 2.16-2.10 (m, 1H), 1.97-1.96 (m, 2H), 1.76-1.59 (m, 7H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.9, 172.7, 132.6, 132.0, 131.9, 111.8, 57.7, 55.6, 53.0, 52.9, 45.5, 43.2, 27.2, 25.9, 22.8, 22.7 (3C), 22.6, 14.7 ppm; IR (neat) ṽ: 3285, 2952, 2929, 2861, 1735, 1621 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{31}NNaO_5S^+$ [$(M+Na)^+$] 420.1815, found 420.1819; $[\alpha]_D^{20}$ +7.1 (*c* 2.18, $CHCl_3$).

Dimethyl (*E*)-3-((*E*)-6-(((*S*)-*tert*-butanesulfinyl)imino)hexylidene)-4-methylenecyclopentane-1,1-dicarboxylate (151i)

Spectral data of **151i**: ^1H NMR (500 MHz, $CDCl_3$) δ: 8.06 (t, *J* = 4.6 Hz, 1H), 5.84 (tt, *J* = 7.4, 2.5 Hz, 1H), 5.24 (s, 1H), 4.83 (s, 1H), 3.72 (s, 6H), 3.01 (s, 2H), 2.96 (s, 2H), 2.52 (td, *J* = 7.4, 4.7 Hz, 2H), 2.12 (q, *J* = 7.4 Hz, 2H), 1.68-1.62 (m, 2H), 1.51-1.45 (m, 2H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.9 (2C), 169.6, 145.1, 136.6, 121.8, 103.2, 57.7, 56.7, 53.0 (2C), 41.5,

37.8, 36.1, 29.4, 28.9, 25.3, 22.5 (3C) ppm; IR (neat) $\tilde{\nu}$: 2952, 2862, 1739, 1622 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{31}NNaO_5S^+$ $[(M+Na)^+]$ 420.1815, found 420.1814; $[\alpha]_D^{21}$ +136.4 (*c* 1.22, $CHCl_3$).

<Scheme 71>

Dimethyl (1*Z*,2'*E*)-2'-(((*S*)-*tert*-butanesulfinyl)imino)-5,5-dimethyl-(1,1'-bi(cyclopentylidene))-3,3-dicarboxylate (153j)

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121j** (59.6 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 80 °C for 8 h, was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **153j** (49.8 mg, 84% yield) as a pale yellow oil.

Spectral data of **153j**: ^1H NMR (500 MHz, $CDCl_3$) δ: 3.74 (d, *J* = 0.7 Hz, 6H), 3.13-3.05 (m, 3H), 2.78 (ddd, *J* = 18.2, 8.4, 6.0 Hz, 1H), 2.49-2.45 (m, 2H), 2.43 (s, 2H), 1.93-1.76 (m, 2H), 1.39 (s, 3H), 1.35 (s, 3H), 1.28 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 185.5, 172.3, 172.1, 158.4, 131.8, 57.7, 56.5, 52.9, 52.9, 51.7, 44.6, 43.8, 36.5, 33.1, 26.1, 25.5, 22.6 (3C), 21.8 ppm; IR (neat) $\tilde{\nu}$: 2955, 1732, 1630, 1568 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{31}NNaO_5S^+$ $[(M+Na)^+]$ 420.1815, found 420.1817; $[\alpha]_D^{15}$ -50.0 (*c* 1.57, $CHCl_3$).

<Scheme 72>

2-Allyl-2-(7-((*tert*-butyldimethylsilyl)oxy)hept-2-yn-1-yl)propane-1,3-diol (156)

To a suspension of $LiAlH_4$ (4.08 g, 108 mmol) in Et_2O (120 mL), was added **155** (14.2 g, 35.9 mmol) at 0 °C. The reaction mixture was stirred at r.t. for 2 h. The reaction was quenched with H_2O (4.01 mL), 15% NaOH aq. (4.01 mL) and H_2O (12.0 mL). The mixture was filtered through celite and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 70:30~20:80) to give **156** (12.2 g, quant.) as a colorless oil.

Spectral data of **156**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.87-5.80 (m, 1H), 5.14-5.10 (m, 2H), 3.68-3.61 (m, 6H), 2.21-2.14 (m, 6H), 2.08-2.05 (m, 2H), 1.63-1.59 (m, 2H), 1.57-1.56 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 133.8, 118.5, 83.1, 76.5, 67.9 (2C), 62.8, 42.4, 36.6, 32.2, 26.1 (3C), 25.6, 22.1, 18.7, 18.5, -5.2 (2C) ppm; IR (neat) $\tilde{\nu}$: 3389, 2929, 2858, 2244, 1639 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{19}H_{36}NaO_3Si^+$ $[(M+Na)^+]$ 363.2326, found 363.2327.

((8,8-Bis((benzyloxy)methyl)undec-10-en-5-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane (157)

To a suspension of NaH (60% dispersion in mineral oil, 840 mg, 21.0 mmol) in THF (20 mL), was added **156** (2.04 g, 6.00 mmol) at 0 °C. The reaction mixture was stirred at r.t. for 0.5 h. To the mixture, were added BnBr (2.49 mL, 21.0 mmol) and TBAI (222 mg, 0.600 mmol) at 0 °C. The reaction mixture was stirred at r.t. for 14 h. The reaction mixture was poured into saturated NH_4Cl aq. and the mixture was extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 100:0~90:10) to give **157** (3.10 g, 99% yield) as a colorless oil.

Spectral data of **157**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.33-7.24 (m, 10H), 5.82-5.76 (m, 1H), 5.07 (d, *J* = 17.0 Hz, 1H), 5.03 (dd, *J* = 10.3, 2.1 Hz, 1H), 4.49 (s, 4H), 3.60 (t, *J* = 6.2 Hz, 2H), 3.38 (q, *J* = 8.6 Hz, 4H), 2.22-2.21 (m, 4H), 2.17-2.14 (m, 2H), 1.62-1.49 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ: 139.1 (2C), 134.3, 128.4 (4C), 127.5 (4C), 127.4 (2C), 118.0, 82.2, 76.9, 73.4 (2C), 72.2 (2C), 62.9, 42.4, 36.5, 32.2, 26.1 (3C), 25.8, 22.6, 18.8, 18.5, -5.1 (2C) ppm; IR (neat) $\tilde{\nu}$: 2928, 2857, 1638 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{33}H_{48}NaO_3Si^+$ $[(M+Na)^+]$ 543.3265, found 543.3261.

8,8-Bis((benzyloxy)methyl)undec-10-en-5-yn-1-ol (158)

A solution of **157** (3.10 g, 5.95 mmol) and TBAF (1.0 M in THF, 7.14 mL, 7.14 mmol) in THF (20 mL) was stirred at r.t. for 2 h. The reaction mixture was concentrated and purified by silica gel

column chromatography (Hexane/EtOAc = 80:20~60:40) to give **158** (2.30 g, 95% yield) as a colorless oil.

Spectral data of **158**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34-7.24 (m, 10H), 5.83-5.74 (m, 1H), 5.09-5.02 (m, 2H), 4.49 (s, 4H), 3.63 (t, *J* = 6.3 Hz, 2H), 3.38 (dd, *J* = 14.4, 8.8 Hz, 4H), 2.23-2.16 (m, 6H), 1.67-1.50 (m, 4H), 1.24 (br s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 139.0 (2C), 134.3, 128.4 (4C), 127.5 (4C), 127.5 (2C), 118.0, 81.9, 77.2, 73.4 (2C), 72.2 (2C), 62.6, 42.4, 36.5, 32.1, 25.5, 22.6, 18.7 ppm; IR (neat) ν̃: 3371, 2933, 2861, 1638 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{27}H_{34}NaO_3^+$ [$(M+Na)^+$] 429.2400, found 429.2400.

8,8-Bis((benzyloxy)methyl)undec-10-en-5-ynal (139b)

A suspension of **158** (2.30 g, 5.66 mmol), DMP (3.36 g, 7.92 mmol) and $NaHCO_3$ (713 mg, 8.49 mmol) in CH_2Cl_2 (19 mL) was stirred at r.t. for 2 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **139b** (1.87 g, 82% yield) as a colorless oil.

Spectral data of **139b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.75 (s, 1H), 7.33-7.26 (m, 10H), 5.82-5.75 (m, 1H), 5.08-5.03 (m, 2H), 4.49 (s, 4H), 3.37 (dd, *J* = 14.6, 8.8 Hz, 4H), 2.51 (t, *J* = 7.3 Hz, 2H), 2.23-2.20 (m, 6H), 1.79-1.75 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 202.1, 139.0 (2C), 134.2, 128.4 (4C), 127.5 (6C), 118.1, 80.9, 78.1, 73.4 (2C), 72.1 (2C), 43.0, 42.3, 36.5, 22.6, 21.7, 18.4 ppm; IR (neat) ν̃: 2860, 2720, 1724 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{27}H_{33}O_3^+$ [$(M+H)^+$] 405.2424, found 405.2426.

(*S*,*E*)-*N*-(8,8-Bis((benzyloxy)methyl)undec-10-en-5-yn-1-ylidene)-2-methylpropane-2-sulfinamide ((*S*)-121b)

A suspension of **139b** (1.87 g, 4.61 mmol), (*S*)-*t*-butanesulfinamide (671 mg, 5.53 mmol), PPTS (116 mg, 0.461 mmol) and $MgSO_4$ (2.77 g, 23.1 mmol) in toluene (15 mL) was stirred at 40 °C for

2 h. The reaction mixture was filtered through a short silica gel pad and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give (*S*)-**121b** (1.52 g, 65% yield) as a colorless oil.

Spectral data of (*S*)-**121b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.06 (t, *J* = 4.4 Hz, 1H), 7.33-7.26 (m, 10H), 5.81-5.74 (m, 1H), 5.08-5.02 (m, 2H), 4.49 (s, 4H), 3.37 (dd, *J* = 15.5, 9.1 Hz, 4H), 2.60 (td, *J* = 7.3, 4.5 Hz, 2H), 2.23-2.20 (m, 6H), 1.81-1.76 (m, 2H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 169.0, 139.0 (2C), 134.2, 128.4 (4C), 127.5 (6C), 118.1, 80.9, 78.0, 73.4 (2C), 72.1 (2C), 56.7, 42.3, 36.5, 35.2, 25.0, 22.6, 22.5 (3C), 18.5 ppm; IR (neat) ν̃: 2902, 2862, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{31}H_{41}NNaO_3S^+$ [$(M+Na)^+$] 530.2699, found 530.2697; $[\alpha]_D^{25}$ +91.6 (*c* 0.58, $CHCl_3$).

<Scheme 73>

2-Allyl-2-(7-((*tert*-butyldimethylsilyl)oxy)hept-2-yn-1-yl)propane-1,3-diyl diacetate (159)

A solution of **156** (2.04 g, 6.00 mmol), pyridine (2.42 mL, 30.0 mmol), Ac_2O (1.70 mL, 18.0 mmol) and DMAP (73.3 mg, 0.600 mmol) in CH_2Cl_2 (20 mL) was stirred at r.t. for 14 h. The reaction was quenched with saturated $NaHCO_3$ aq. and extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 100:0~75:25) to give **159** (2.55 g, quant.) as a colorless oil.

Spectral data of **159**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.79-5.72 (m, 1H), 5.13-5.10 (m, 2H), 3.99 (dd, *J* = 12.6, 11.4 Hz, 4H), 3.62 (t, *J* = 6.2 Hz, 2H), 2.21-2.16 (m, 6H), 2.06 (s, 6H), 1.61-1.51 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.9 (2C), 132.4, 119.4, 83.4, 75.0, 65.8 (2C), 62.8, 40.3, 36.2, 32.2, 26.1 (3C), 25.6, 22.5, 21.0 (2C), 18.7, 18.5, -5.2 (2C) ppm; IR (neat) ν̃: 2952, 2858, 1747, 1641 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{23}H_{40}NaO_5Si^+$ [$(M+Na)^+$] 447.2537, found 447.2540.

2-Allyl-2-(7-hydroxyhept-2-yn-1-yl)propane-1,3-diyl diacetate (160)

A solution of **159** (2.55 g, 6.00 mmol), AcOH (1.03 mL, 18.0 mmol) and TBAF (1.0 M in THF, 9.01 mL, 9.01 mmol) in THF (20 mL) was stirred at r.t. for 24 h. The reaction was quenched with saturated $NaHCO_3$ aq. and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~50:50) to give **160** (1.83 g, 98% yield) as a colorless oil.

Spectral data of **160**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.80-5.71 (m, 1H), 5.14-5.10 (m, 2H), 4.01 (dd, *J* = 15.1, 11.0 Hz, 4H), 3.67-3.65 (br m, 2H), 2.21-2.19 (m, 6H), 2.07 (s, 6H), 1.70-1.64 (m, 2H), 1.59-1.55 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.1 (2C), 132.4, 119.4, 83.2, 75.3, 65.8 (2C), 62.6, 40.3, 36.3, 32.1, 25.3, 22.5, 21.0 (2C), 18.7 ppm; IR (neat) $\tilde{\nu}$: 3460, 2939, 1743, 1640 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{17}H_{26}NaO_5^+$ [$(M+Na)^+$] 333.1673, found 333.1672.

2-Allyl-2-(7-oxohept-2-yn-1-yl)propane-1,3-diyl diacetate (139c)

A suspension of **160** (1.83 g, 5.90 mmol), DMP (3.50 g, 8.25 mmol) and $NaHCO_3$ (1.45 g, 17.7 mmol) in CH_2Cl_2 (20 mL) was stirred at r.t. for 2 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~30:70) to give **139c** (1.63 g, 90% yield) as a colorless oil.

Spectral data of **139c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.80 (s, 1H), 5.79-5.71 (m, 1H), 5.14-5.10 (m, 2H), 4.00 (dd, *J* = 13.4, 11.2 Hz, 4H), 2.56 (td, *J* = 7.2, 1.1 Hz, 2H), 2.25-2.19 (m, 6H), 2.07 (s, 6H), 1.85-1.79 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 202.0, 170.9 (2C), 132.3, 119.5, 82.2, 76.2, 65.7 (2C), 42.9, 40.2, 36.3, 22.5, 21.5, 21.0 (2C), 18.3 ppm; IR (neat) $\tilde{\nu}$: 2939, 2845, 2725, 1739, 1640 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{17}H_{24}NaO_5^+$ [$(M+Na)^+$] 331.1516, found 331.1519.

(*S*,*E*)-2-Allyl-2-(7-((*tert*-butanesulfinyl)imino)hept-2-yn-1-yl)propane-1,3-diyl diacetate ((*S*)-121c)

A suspension of **139c** (1.63 g, 5.29 mmol), (*S*)-*t*-butanesulfinamide (769 mg, 6.34 mmol), PPTS (133 mg, 0.529 mmol) and $MgSO_4$ (3.18 g, 26.4 mmol) in toluene (18 mL) was stirred at 40 °C for 2 h. The reaction mixture was filtered through a short silica gel pad and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~50:50) to give (*S*)-**121c** (1.65 g, 76% yield) as a colorless oil.

Spectral data of (*S*)-**121c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.09 (t, *J* = 4.4 Hz, 1H), 5.80-5.71 (m, 1H), 5.13-5.10 (m, 2H), 4.00 (dd, *J* = 12.6, 11.4 Hz, 4H), 2.62 (td, *J* = 7.3, 4.4 Hz, 2H), 2.26 (t, *J* = 6.7 Hz, 2H), 2.23-2.20 (m, 4H), 2.06 (s, 6H), 1.86-1.80 (m, 2H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ:170.9 (2C), 168.9, 132.3, 119.5, 82.2, 76.1, 65.7 (2C), 56.7, 40.3, 36.3, 35.2, 24.8, 22.5, 22.5 (3C), 21.0 (2C), 18.4 ppm; IR (neat) ν̃: 2956, 2869, 1744, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{33}NNaO_5S^+$ [(M+Na)$^+$] 434.1972, found 434.1963; $[\alpha]_D^{23}$ +135.9 (*c* 0.51, $CHCl_3$).

<Scheme 74>

((7-(5-Allyl-2,2-dimethyl-1,3-dioxan-5-yl)hept-5-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane (162)

A solution of **156** (2.04 g, 6.00 mmol), 2,2-dimethoxypropane **161** (3.68 mL, 30.0 mmol) and PPTS (151 mg, 0.600 mmol) in CH_2Cl_2 (20 mL) was stirred at r.t. for 3 h. The reaction mixture was concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 100:0~90:10) to give **162** (1.88 g, 82% yield) as a colorless oil.

Spectral data of **162**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.80-5.73 (m, 1H), 5.13-5.10 (m, 2H), 3.67-3.61 (m, 6H), 2.30 (t, *J* = 2.3 Hz, 2H), 2.20-2.16 (m, 4H), 1.63-1.52 (m, 4H), 1.41 (d, *J* = 5.9 Hz, 6H), 0.89 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 132.9, 118.8, 98.2, 83.0, 76.2, 66.9 (2C), 62.8, 37.2, 35.7, 32.2, 26.1 (3C), 25.7, 25.5, 22.9, 22.4, 18.7, 18.5, -5.2 (2C) ppm; IR (neat) ν̃: 2930, 2859, 1639 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{40}NaO_3Si^+$ [(M+Na)$^+$] 403.2639, found 403.2636.

7-(5-Allyl-2,2-dimethyl-1,3-dioxan-5-yl)hept-5-yn-1-ol (163)

A solution of **162** (1.88 g, 4.94 mmol) and TBAF (1.0 M in THF, 5.93 mL, 5.93 mmol) in THF (16 mL) was stirred at r.t. for 2 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 80:20~50:50) to give **163** (1.19 g, 91% yield) as a colorless oil.

Spectral data of **163**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.80-5.73 (m, 1H), 5.13-5.10 (m, 2H), 3.68-3.62 (m, 6H), 2.32 (s, 2H), 2.22 (t, *J* = 7.0 Hz, 2H), 2.16 (d, *J* = 7.6 Hz, 2H), 1.70-1.65 (m, 2H), 1.61-1.57 (m, 2H), 1.41 (d, *J* = 5.9 Hz, 6H), 1.26 (br s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 132.8, 118.8, 98.2, 82.7, 76.5, 66.9 (2C), 62.5, 37.2, 35.7, 32.1, 25.6, 25.5, 22.8, 22.2, 18.7 ppm; IR (neat) ṽ: 3419, 2939, 2864, 1639 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{26}NaO_3^+$ [(M+Na)$^+$] 289.1774, found 289.1774.

7-(5-Allyl-2,2-dimethyl-1,3-dioxan-5-yl)hept-5-ynal (139d)

A suspension of **163** (1.19 g, 4.47 mmol), DMP (2.65 g, 6.26 mmol) and $NaHCO_3$ (563 mg, 6.70 mmol) in CH_2Cl_2 (15 mL) was stirred at r.t. for 2 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **139d** (1.05 g, 89% yield) as a colorless oil.

Spectral data of **139d**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.80 (s, 1H), 5.79-5.72 (m, 1H), 5.13-5.10 (m, 2H), 3.64 (t, *J* = 12.6 Hz, 4H), 2.59-2.56 (m, 2H), 2.33-2.33 (m, 2H), 2.26-2.24 (m, 2H), 2.14 (d, *J* = 7.6 Hz, 2H), 1.85-1.80 (m, 2H), 1.41 (d, *J* = 7.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 202.0, 132.7, 118.9, 98.2, 81.7, 77.5, 66.9 (2C), 43.0, 37.2, 35.6, 25.8, 22.8, 22.0, 21.6, 18.4 ppm; IR (neat) ṽ: 2939, 2864, 1725 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{25}O_3^+$ [(M+H)$^+$] 265.1798, found 265.1801.

(*S*,*E*)-*N*-(7-(5-Allyl-2,2-dimethyl-1,3-dioxan-5-yl)hept-5-yn-1-ylidene)-2-methylpropane-2-sulfinamide ((*S*)-121d)

A suspension of **139d** (1.05 g, 3.96 mmol), (*S*)-*t*-butanesulfinamide (576 mg, 4.75 mmol), PPTS (99.4 mg, 0.396 mmol) and $MgSO_4$ (2.38 g, 19.8 mmol) in toluene (13 mL) was stirred at 40 °C for 2 h. The reaction mixture was filtered through a short silica gel pad and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~50:50) to give (*S*)-**121d** (1.44 g, 99% yield) as a colorless oil.

Spectral data of (*S*)-**121d**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.09 (t, *J* = 4.4 Hz, 1H), 5.79-5.72 (m, 1H), 5.13-5.10 (m, 2H), 3.64 (s, 4H), 2.64 (td, *J* = 7.3, 4.7 Hz, 2H), 2.33 (t, *J* = 2.1 Hz, 2H), 2.29-2.26 (m, 2H), 2.15 (d, *J* = 7.6 Hz, 2H), 1.86-1.81 (m, 2H), 1.41 (d, *J* = 7.0 Hz, 6H), 1.20 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 168.9, 132.7, 118.9, 98.2, 81.7, 77.4, 66.9 (2C), 56.7, 37.2, 35.7, 35.2, 25.8, 24.9, 22.8, 22.5 (3C), 22.1, 18.5 ppm; IR (neat) ν̃: 2951, 2866, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{33}NNaO_3S^+$ [$(M+Na)^+$] 390.2073, found 390.2075; $[\alpha]_D^{25}$ +127.9 (*c* 0.54, $CHCl_3$).

<Scheme 75>

7-(9-Allyl-9*H*-fluoren-9-yl)hept-5-yn-1-ol (164)

To a solution of 9-allyl-9*H*-fluorene[42] (928 mg, 4.50 mmol) in THF (15 mL), was added *n*-BuLi (2.65 M in THF, 1.87 mL, 4.95 mmol) at -78 °C. The reaction mixture was stirred at r.t. for 2 h. To the mixture, was added **136**[20b] at -78 °C. The reaction mixture was stirred at r.t. for 2 h. The reaction was quenched with saturated NH_4Cl aq. and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The oil was used in the next reaction without purification. A solution of the crude oil and TBAF (1.0 M in THF, 5.40 mL, 5.40 mmol) in THF (15 mL) was stirred at r.t. for 14 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 90:10~50:50) to give **164** (1.28 g, 90% yield, 2 steps) as a colorless oil.

Spectral data of **164**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 7.3 Hz, 2H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.35 (dd, *J* = 7.3, 6.6 Hz, 2H), 7.30 (dd, *J* = 7.3, 6.6 Hz, 2H), 5.31-5.23 (m, 1H), 4.87 (d, *J* = 16.8 Hz, 1H), 4.77 (d, *J* = 10.0 Hz, 1H), 3.60 (q, *J* = 5.1 Hz, 2H), 2.84 (d, *J* = 7.3 Hz, 2H), 2.64 (t, *J* = 2.3 Hz, 2H), 2.17-2.14 (m, 2H), 1.52-1.42 (m, 4H), 1.13 (t, *J* = 4.9 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 149.4 (2C), 140.6 (2C), 133.9, 127.5 (2C), 127.1 (2C), 123.8 (2C), 119.9 (2C), 117.9, 82.1, 77.5, 62.6, 52.8, 41.9, 31.8, 29.6, 25.2, 18.6 ppm; IR (neat) ν̃: 3357, 3068, 2936, 2864, 1639 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{23}H_{24}NaO^+$ [$(M+Na)^+$] 339.1719, found 339.1721.

7-(9-Allyl-9*H*-fluoren-9-yl)hept-5-ynal (139e)

A suspension of **164** (1.41 g, 4.46 mmol), DMP (2.65 g, 6.24 mmol) and $NaHCO_3$ (1.12 g, 13.4 mmol) in CH_2Cl_2 (15 mL) was stirred at r.t. for 3 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 95:5~70:30) to give **139e** (989 mg, 71% yield) as a pale brown oil.

Spectral data of **139e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.67 (s, 1H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.51 (d, *J* = 7.1 Hz, 2H), 7.35 (td, *J* = 7.4, 1.1 Hz, 2H), 7.31 (td, *J* = 7.4, 1.2 Hz, 2H), 5.32-5.23 (m, 1H), 4.87 (dd, *J* = 17.0, 1.8 Hz, 1H), 4.78 (dt, *J* = 10.2, 1.0 Hz, 1H), 2.80 (d, *J* = 7.3 Hz, 2H), 2.68 (t, *J* = 2.3 Hz, 2H), 2.27 (td, *J* = 7.3, 1.2 Hz, 2H), 2.11 (tt, *J* = 6.7, 2.4 Hz, 2H), 1.65-1.59 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 202.2, 149.3 (2C), 140.7 (2C), 133.7, 127.6 (2C), 127.2 (2C), 123.7 (2C), 119.9 (2C), 118.0, 80.9, 78.2, 53.0, 42.6, 42.2, 29.6, 21.3, 18.1 ppm; IR (neat) ν̃: 3067, 2901, 2834, 2721, 1722, 1639 cm^{-1}; HRMS (APCI) *m/z* calcd. for $C_{23}H_{23}O^+$ [$(M+H)^+$] 315.1743, found 315.1743.

(*S*,*E*)-*N*-(7-(9-Allyl-9*H*-fluoren-9-yl)hept-5-yn-1-ylidene)-2-methylpropane-2-sulfinamide ((*S*)-121e)

A suspension of **139e** (968 mg, 3.08 mmol), (*S*)-*t*-butanesulfinamide (448 mg, 3.69 mmol), PPTS (77.4 mg, 0.308 mmol) and $MgSO_4$ (1.85 g, 15.4 mmol) in toluene (10 mL) was stirred at 40 °C for 4 h. The reaction mixture was filtered through a short silica gel pad and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give (*S*)-**121e** (1.21 g, 94% yield) as a pale yellow oil.

Spectral data of (*S*)-**121e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02 (t, *J* = 4.3 Hz, 1H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.52 (dd, *J* = 7.2, 3.1 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 5.31-5.23 (m, 1H), 4.87 (d, *J* = 17.6 Hz, 1H), 4.77 (d, *J* = 10.3 Hz, 1H), 2.82 (d, *J* = 7.1 Hz, 2H), 2.67 (t, *J* = 2.3 Hz, 2H), 2.40-2.37 (m, 2H), 2.18 (t, *J* = 6.8 Hz, 2H), 1.71-1.65 (m, 2H), 1.20 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 169.1, 149.3 (2C), 140.7, 140.7, 133.8, 127.6 (2C), 127.2, 127.2, 123.8, 123.7, 119.9 (2C), 117.9, 81.1, 78.2, 56.7, 52.9, 42.0, 34.9, 29.6, 24.6, 22.5 (3C), 18.3 ppm; IR (neat) ν̃: 3068, 3005, 2979, 2959, 2925, 2901, 2867, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{27}H_{31}NNaOS^+$ $[(M+Na)^+]$ 440.2019, found 440.2015; $[\alpha]_D^{17}$ +114.0 (*c* 1.07, $CHCl_3$).

<Scheme 76>

***N*-Allyl-*N*-(7-((*tert*-butyldimethylsilyl)oxy)hept-2-yn-1-yl)-4-methylbenzenesulfonamide (167)**

To a solution of **165**[43] (1.58 g, 6.50 mmol), *N*-allyl-4-methyl-benzenesulfonamide **166**[44] (1.51 g, 7.15 mmol) and PPh_3 (3.41 g, 13.0 mmol) in THF (22 mL), was added DIAD (1.9 M in toluene, 6.84 mL, 13.0 mmol) at 0 °C. The reaction mixture was stirred at r.t. for 14 h. The reaction mixture was concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 95:5~85:15) to **167** (1.84 g, 65% yield) as a colorless oil.

Spectral data of **167**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.73 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 5.77-5.71 (m, 1H), 5.27 (d, *J* = 17.0 Hz, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 4.06 (s, 2H), 3.80 (d, *J* = 6.4 Hz, 2H), 3.55 (t, *J* = 6.2 Hz, 2H), 2.42 (s, 3H), 1.93 (t, *J* = 7.0 Hz, 2H), 1.46-1.41 (m, 2H), 1.36-1.31 (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.3, 136.4,

132.3, 129.5 (2C), 128.0 (2C), 119.7, 86.2, 72.7, 62.6, 49.1, 36.5, 32.0, 26.1 (3C), 25.0, 21.7, 18.5, 18.4, -5.2 (2C) ppm; IR (neat) $\tilde{\nu}$: 2952, 2929, 2857, 2223, 1644, 1599 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{23}H_{37}NNaO_3SSi^+$ $[(M+Na)^+]$ 458.2156, found 458.2156.

_N_-Allyl-_N_-(7-hydroxyhept-2-yn-1-yl)-4-methylbenzenesulfonamide (168)

A solution of **167** (1.84 g, 4.23 mmol) and TBAF (1.0 M in THF, 5.08 mL, 5.08 mmol) in THF (14 mL) was stirred at r.t. for 2 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 80:20~50:50) to give **168** (1.25 g, 92% yield) as a colorless oil.

Spectral data of **168**: ^1H NMR (600 MHz, $CDCl_3$) δ: 7.74 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 5.77-5.70 (m, 1H), 5.27 (d, *J* = 17.0 Hz, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 4.06 (t, *J* = 2.1 Hz, 2H), 3.81 (d, *J* = 6.4 Hz, 2H), 3.60 (q, *J* = 5.9 Hz, 2H), 2.43 (s, 3H), 1.99-1.96 (m, 2H), 1.52-1.48 (m, 2H), 1.40-1.35 (m, 2H), 1.19 (t, *J* = 5.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.4, 136.4, 132.3, 129.5 (2C), 128.0 (2C), 119.7, 85.9, 73.0, 62.4, 49.1, 36.4, 31.8, 24.8, 21.7, 18.4 ppm; IR (neat) $\tilde{\nu}$: 3410, 2938, 2224, 1598 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{17}H_{23}NNaO_3S^+$ $[(M+Na)^+]$ 344.1291, found 344.1290.

_N_-Allyl-4-methyl-_N_-(7-oxohept-2-yn-1-yl)benzenesulfonamide (139f)

A suspension of **168** (1.25 g, 3.89 mmol), DMP (2.31 g, 5.44 mmol) and $NaHCO_3$ (490 mg, 5.83 mmol) in CH_2Cl_2 (19 mL) was stirred at r.t. for 3 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **139f** (978 mg, 79% yield) as a colorless oil.

Spectral data of **139f**: ^1H NMR (600 MHz, $CDCl_3$) δ: 9.73 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.77-5.70 (m, 1H), 5.26 (d, *J* = 17.0 Hz, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 4.06 (s, 2H), 3.80 (d, *J* = 6.4 Hz, 2H), 2.42 (s, 3H), 2.39 (t, *J* = 7.0 Hz, 2H), 2.01 (tt, *J* = 6.7, 2.1 Hz, 2H),

1.63-1.59 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.5, 143.5, 136.4, 132.3, 129.5 (2C), 127.9 (2C), 119.7, 84.8, 73.8, 49.2, 42.7, 36.4, 21.6, 20.9, 18.0 ppm; IR (neat) ν̃: 2925, 2224, 1722, 1598 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{17}H_{21}NNaO_3S^+$ [$(M+Na)^+$] 342.1134, found 342.1144.

(*S*,*E*)-*N*-Allyl-*N*-(7-((*tert*-butanesulfinyl)imino)hept-2-yn-1-yl)-4-methylbenzenesulfonamide ((*S*)-121f)

A suspension of **139f** (978 mg, 3.06 mmol), (*S*)-*t*-butanesulfinamide (445 mg, 3.67 mmol), PPTS (76.8 mg, 0.306 mmol) and $MgSO_4$ (1.84 g, 15.3 mmol) in toluene (15 mL) was stirred at 40 °C for 2 h. The reaction mixture was filtered through a short silica gel pad and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~60:40) to give (*S*)-**121f** (1.04 g, 80% yield) as a colorless oil.

Spectral data of (*S*)-**121f**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.02 (t, *J* = 4.1 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 5.77-5.70 (m, 1H), 5.27 (d, *J* = 17.0 Hz, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 4.07 (s, 2H), 3.81 (d, *J* = 6.4 Hz, 2H), 2.46-2.42 (m, 5H), 2.04 (t, *J* = 7.0 Hz, 2H), 1.67-1.59 (m, 2H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 168.5, 143.5, 136.5, 132.3, 129.5 (2C), 127.9 (2C), 119.7, 84.8, 73.8, 56.7, 49.1, 36.4, 35.0, 24.2, 22.5 (3C), 21.7, 18.2 ppm; IR (neat) ν̃: 2959, 2926, 2224, 1623, 1598 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{30}N_2NaO_3S_2^+$ [$(M+Na)^+$] 445.1590, found 445.1586; $[\alpha]_D^{19}$ +123.1 (*c* 0.51, $CHCl_3$).

<Scheme 77>

***N*-Allyl-*N*-(7-((*tert*-butyldimethylsilyl)oxy)hept-2-yn-1-yl)-2-nitrobenzenesulfonamide (170)**

To a solution of **165**[43] (1.58 g, 6.50 mmol), *N*-allyl-2-nitrobenzenesulfonamide **169**[45] (1.73 g, 7.15 mmol) and PPh_3 (3.41 g, 13.0 mmol) in THF (22 mL), was added DIAD (1.9 M in toluene, 6.84 mL, 13.0 mmol) at 0 °C. The reaction mixture was stirred at r.t. for 14 h. The reaction was quenched with H_2O and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **170** (3.03 g, quant.) as a colorless oil.

Spectral data of **170**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.09-8.06 (m, 1H), 7.70-7.62 (m, 3H), 5.77-5.69 (m, 1H), 5.31 (dd, *J* = 17.1, 1.2 Hz, 1H), 5.25 (d, *J* = 10.3 Hz, 1H), 4.12 (s, 2H), 4.02 (d, *J* = 6.3 Hz, 2H), 3.57 (t, *J* = 6.1 Hz, 2H), 2.06-2.03 (m, 2H), 1.51-1.38 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 148.4, 133.6, 133.4, 132.0, 131.6, 131.2, 124.2, 120.1, 86.4, 72.9, 62.6, 49.5, 36.6, 32.0, 26.1 (3C), 25.1, 18.5 (2C), -5.2 (2C) ppm; IR (neat) ν̃: 2952, 2929, 2857, 2228, 1645, 1591, 1549, 1361, 1169 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{34}N_2NaO_5SSi^+$ [$(M+Na)^+$] 489.1850, found 489.1845.

_N_-Allyl-_N_-(7-hydroxyhept-2-yn-1-yl)-2-nitrobenzenesulfonamide (171)

A solution of **170** (3.03 g, 6.49 mmol) and TBAF (1.0 M in THF, 7.79 mL, 7.79 mmol) in THF (22 mL) was stirred at r.t. for 2 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 70:30~30:70) to give **171** (1.98 g, 87% yield) as a colorless oil.

Spectral data of **171**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.10-8.07 (m, 1H), 7.71-7.63 (m, 3H), 5.77-5.69 (m, 1H), 5.30 (dd, *J* = 17.1, 1.2 Hz, 1H), 5.25 (dd, *J* = 10.1, 1.1 Hz, 1H), 4.11 (s, 2H), 4.01 (d, *J* = 6.3 Hz, 2H), 3.62 (dd, *J* = 10.7, 6.1 Hz, 2H), 2.09-2.06 (m, 2H), 1.58-1.53 (m, 2H), 1.48-1.42 (m, 2H), 1.24 (br s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 148.4, 133.7, 133.3, 131.9, 131.7, 131.2, 124.3, 120.2, 86.1, 73.3, 62.4, 49.5, 36.6, 31.8, 24.9, 18.4 ppm; IR (neat) ν̃: 3389, 2939, 2867, 2228, 1644, 1590, 1546, 1359, 1167 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{20}N_2NaO_5S^+$ [$(M+Na)^+$] 375.0985, found 375.0982.

_N_-Allyl-2-nitro-_N_-(7-oxohept-2-yn-1-yl)benzenesulfonamide (139g)

A suspension of **171** (1.98 g, 5.62 mmol), DMP (3.34 g, 7.87 mmol) and $NaHCO_3$ (708 mg, 8.43 mmol) in CH_2Cl_2 (19 mL) was stirred at r.t. for 2 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 80:20~50:50) to give **139g** (1.36 g, 69% yield) as a colorless oil.

Spectral data of **139g**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.75 (s, 1H), 8.08-8.07 (m, 1H), 7.73-7.63 (m, 3H), 5.77-5.69 (m, 1H), 5.30 (dd, *J* = 17.0, 1.3 Hz, 1H), 5.26 (d, *J* = 10.3 Hz, 1H), 4.11 (t, *J* = 2.1 Hz, 2H), 4.01 (d, *J* = 6.3 Hz, 2H), 2.47 (td, *J* = 7.2, 1.0 Hz, 2H), 2.11 (tt, *J* = 7.0, 2.2 Hz, 2H), 1.70-1.65 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.6, 148.3, 133.8, 133.2, 131.9, 131.7, 131.2, 124.3, 120.2, 85.0, 74.1, 49.6, 42.6, 36.5, 21.0, 18.0 ppm; IR (neat) ν̃: 3093, 2938, 2838, 2728, 2227, 1722, 1644, 1549, 1360 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{18}N_2NaO_5S^+$ [$(M+Na)^+$] 373.0829, found 373.0833.

(*S*,*E*)-*N*-Allyl-*N*-(7-((*tert*-butanesulfinyl)imino)hept-2-yn-1-yl)-2-nitrobenzenesulfonamide ((*S*)-121g)

A suspension of **139g** (1.37 g, 3.90 mmol), (*S*)-*t*-butanesulfinamide (567 mg, 4.68 mmol), PPTS (97.9 mg, 0.390 mmol) and $MgSO_4$ (2.35 g, 19.5 mmol) in toluene (13 mL) was stirred at 40 °C for 2 h. The reaction mixture was filtered through a short silica gel pad and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 70:30~30:70) to give (*S*)-**121g** (1.75 g, 99% yield) as a colorless oil.

Spectral data of (*S*)-**121g**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.09-8.07 (m, 1H), 8.02 (t, *J* = 4.3 Hz, 1H), 7.72-7.63 (m, 3H), 5.77-5.69 (m, 1H), 5.30 (d, *J* = 17.1 Hz, 1H), 5.25 (d, *J* = 10.3 Hz, 1H), 4.12 (s, 2H), 4.01 (d, *J* = 6.3 Hz, 2H), 2.51 (td, *J* = 7.3, 4.4 Hz, 2H), 2.15 (t, *J* = 7.0 Hz, 2H), 1.75-1.66 (m, 2H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 168.5, 148.4, 133.7, 133.3, 131.9, 131.7, 131.3, 124.3, 120.2, 85.0, 74.0, 56.8, 49.5, 36.5, 34.9, 24.3, 22.5 (3C), 18.2 ppm; IR (neat) ν̃: 3090, 2960, 2927, 2869, 2229, 1623, 1590, 1549, 1361 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{27}N_3NaO_5S_2^+$ [$(M+Na)^+$] 476.1284, found 476.1283; $[\alpha]_D^{22}$ +109.4 (*c* 0.52, $CHCl_3$).

<Scheme 78>

According to the general procedure (2) for cyclization, a crude product, which was prepared from (*S*)-**121k** (40.4 mg, 0.150 mmol), $[Rh(cod)_2]BF_4$ (6.09 mg, 0.0150 mmol) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol) in $ClCH_2CH_2Cl$ (1.50 mL) at 40 °C for 3 h, was purified by silica gel column

chromatography (Hexane/EtOAc = 90:10~0:100) to give **125k** (not pure, <5.2 mg, <13% yield) as a pale yellow oil. **125k** was not obtained as a pure product and could not be separated from impurities by silica gel column chromatography.

<Scheme 79>

Dimethyl 2-(but-3-en-1-yl)-2-(7-((*tert*-butyldimethylsilyl)oxy)hept-2-yn-1-yl)malonate (173)

To a suspension of NaH (60% dispersion in mineral oil, 100 mg, 2.51 mmol) in THF (9.0 mL), was added dimethyl 2-(but-3-en-1-yl)malonate **172**[47] (333 mg, 1.79 mmol) at 0 °C. To the mixture, was added **136**[20b] (574 mg, 1.79 mmol) at 0 °C. The reaction mixture was stirred at r.t. for 20 h. The reaction was quenched with saturated NH_4Cl aq. and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 95:5~85:15) to give **173** (622 mg, 85% yield) as a colorless oil.

Spectral data of **173**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.82-5.75 (m, 1H), 5.06-4.96 (m, 2H), 3.72 (s, 6H), 3.60 (t, *J* = 6.2 Hz, 2H), 2.80 (t, *J* = 2.3 Hz, 2H), 2.15-2.12 (m, 4H), 1.98-1.94 (m, 2H), 1.59-1.47 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.1 (2C), 137.6, 115.3, 83.6, 74.5, 62.8, 57.1, 52.8 (2C), 32.0, 31.4, 28.5, 26.1 (3C), 25.5, 23.4, 18.6, 18.5, -5.2 (2C) ppm; IR (neat) ν̃: 2953, 1739, 1643 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{38}NaO_5Si^+$ [$(M+Na)^+$] 433.2381, found 433.2382.

Dimethyl 2-(but-3-en-1-yl)-2-(7-hydroxyhept-2-yn-1-yl)malonate (174)

A solution of **173** (600 mg, 1.46 mmol) and TBAF (1.0 M in THF, 1.75 mL, 1.75 mmol) in THF (4.9 mL) was stirred at r.t. for 2 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 80:20~50:50) to give **174** (428 mg, 99% yield) as a colorless oil.

Spectral data of **174**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.83-5.76 (m, 1H), 5.07-4.97 (m, 2H), 3.73 (s, 6H), 3.65 (t, *J* = 6.4 Hz, 2H), 2.80 (t, *J* = 2.3 Hz, 2H), 2.19-2.12 (m, 4H), 1.98-1.94 (m, 2H), 1.67-1.62 (m, 2H), 1.56-1.52 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.1 (2C), 137.5,

115.3, 83.4, 74.8, 62.5, 57.1, 52.8 (2C), 31.8, 31.4, 28.4, 25.1, 23.4, 18.5 ppm; IR (neat) ṽ: 3437, 2952, 1736, 1642 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{24}NaO_5^+$ $[(M+Na)^+]$ 319.1516, found 319.1515.

Dimethyl 2-(but-3-en-1-yl)-2-(7-oxohept-2-yn-1-yl)malonate (139h)

A suspension of **174** (400 mg, 1.35 mmol), DMP (801 mg, 1.89 mmol) and $NaHCO_3$ (170 mg, 2.03 mmol) in CH_2Cl_2 (14 mL) was stirred at r.t. for 1 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **139h** (220 mg, 56% yield) as a colorless oil.

Spectral data of **139h**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.79 (t, *J* = 1.3 Hz, 1H), 5.83-5.75 (m, 1H), 5.07-4.97 (m, 2H), 3.73 (s, 6H), 2.80 (t, *J* = 2.3 Hz, 2H), 2.55 (td, *J* = 7.2, 1.3 Hz, 2H), 2.21 (tt, *J* = 6.8, 2.4 Hz, 2H), 2.14-2.11 (m, 2H), 1.98-1.94 (m, 2H), 1.80-1.75 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 202.0, 171.0 (2C), 137.5, 115.3, 82.3, 75.6, 57.0, 52.8 (2C), 42.7, 31.4, 28.4, 23.4, 21.4, 18.2 ppm; IR (neat) ṽ: 2954, 1731, 1642 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{23}O_5^+$ $[(M+H)^+]$ 295.1540, found 295.1543.

Dimethyl (*S*,*E*)-2-(but-3-en-1-yl)-2-(7-((*tert*-butanesulfinyl)imino)hept-2-yn-1-yl)malonate ((*S*)-121h)

A suspension of **139h** (1.03 g, 3.50 mmol), (*S*)-*t*-butanesulfinamide (509 mg, 4.20 mmol), PPTS (88 mg, 0.350 mmol) and $MgSO_4$ (2.11 g, 17.5 mmol) in toluene (18 mL) was stirred at 40 °C for 2 h. The reaction mixture was filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give (*S*)-**121h** (1.32 g, 95% yield) as a colorless oil.

Spectral data of (*S*)-**121h**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.08 (t, *J* = 4.1 Hz, 1H), 5.82-5.75 (m, 1H), 5.04 (dd, *J* = 17.0, 1.8 Hz, 1H), 4.98 (dd, *J* = 10.5, 1.2 Hz, 1H), 3.72 (s, 6H), 2.81 (t, *J* = 2.3

Hz, 2H), 2.61 (td, *J* = 7.3, 4.7 Hz, 2H), 2.23 (td, *J* = 6.7, 1.8 Hz, 2H), 2.14-2.12 (m, 2H), 1.98-1.94 (m, 2H), 1.82-1.77 (m, 2H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.9 (2C), 168.9, 137.5, 115.3, 82.4, 75.5, 57.0, 57.0, 52.8 (2C), 35.0, 31.4, 28.4, 24.7, 23.4, 22.5 (3C), 18.3 ppm; IR (neat) ν̃: 2953, 1737, 1641, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{31}NNaO_5S^+$ [$(M+Na)^+$] 420.1815, found 420.1811; $[\alpha]_D^{25}$ +133.1 (*c* 1.06, $CHCl_3$).

<Scheme 80>

Dimethyl

(*Z*)-4-methylene-3-((*R*)-2-((*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanamido)cyclopentylidene)cyclohexane-1,1-dicarboxylate (175)

A solution of **125h** (36.8 mg, 0.0926 mmol), 4N HCl in dioxane (0.0926 mL, 0.370 mmol) in MeOH (0.30 mL) was stirred at r.t. for 1 h. The reaction mixture was concentrated. A solution of the crude amine hydrochloride, (*S*)-MTPA-Cl (0.0348 mL, 0.186 mmol) and Et_3N (0.0516 mL, 0.372 mmol) in CH_2Cl_2 (0.30 mL) was stirred at r.t. for 12 h. The reaction was quenched with H_2O and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **175** (27.0 mg, 57% yield, 2 steps) as a colorless oil.

Spectral data of **175**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49-7.47 (m, 2H), 7.41-7.38 (m, 3H), 6.58 (d, *J* = 6.1 Hz, 1H), 4.90-4.87 (m, 3H), 3.71 (s, 3H), 3.68 (s, 3H), 3.35 (s, 3H), 2.88 (d, *J* = 13.7 Hz, 1H), 2.61 (d, *J* = 13.7 Hz, 1H), 2.53-2.47 (m, 1H), 2.40-2.25 (m, 4H), 2.11-2.06 (m, 1H), 1.89-1.83 (m, 1H), 1.80-1.70 (m, 2H), 1.65-1.58 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.6, 171.4, 165.3, 145.3, 138.5, 132.8, 132.7, 129.5, 128.7 (2C), 127.8 (2C), 124.0 ($J^1_{C\text{-}F}$ = 289.9 Hz), 111.8, 83.9 ($J^2_{C\text{-}F}$ = 26.3 Hz), 56.4, 54.9, 52.8, 52.7, 52.5, 37.8, 34.3, 32.9, 32.4, 29.8, 23.2 ppm; IR (neat) ν̃: 3421, 2953, 1733, 1691, 1639 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{26}H_{30}F_3NNaO_6^+$ [$(M+Na)^+$] 532.1917, found 532.1924; $[\alpha]_D^{17}$ -34.0 (*c* 3.38, $CHCl_3$).

Dimethyl

(*Z*)-4-methylene-3-((*R*)-2-((*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanamido)cyclopentylidene)cyclohexane-1,1-dicarboxylate (176)

A solution of **125h** (39.1 mg, 0.0984 mmol), 4N HCl in dioxane (0.0984 mL, 0.393 mmol) in MeOH (0.30 mL) was stirred at r.t. for 1 h. The reaction mixture was concentrated. A solution of the crude amine hydrochloride, (*R*)-MTPA-Cl (0.0367 mL, 0.196 mmol) and Et_3N (0.0543 mL, 0.392 mmol) in CH_2Cl_2 (0.30 mL) was stirred at r.t. for 12 h. The reaction was quenched with H_2O and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~70:30) to give **176** (30.1 mg, 60% yield, 2 steps) as a colorless oil.

Spectral data of **176**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.51-7.50 (m, 2H), 7.38-7.35 (m, 3H), 6.49 (d, J = 6.1 Hz, 1H), 4.84-4.82 (br m, 1H), 4.68 (d, J = 9.0 Hz, 2H), 3.70 (s, 6H), 3.42 (s, 3H), 2.88 (d, J = 13.7 Hz, 1H), 2.53 (d, J = 13.7 Hz, 2H), 2.36-2.29 (m, 1H), 2.21-2.18 (m, 1H), 2.10-1.63 (m, 7H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.6, 171.3, 165.1, 145.6, 139.1, 132.8, 132.6, 129.5, 128.4 (2C), 127.9 (2C), 123.9 ($J^1_{C\text{-}F}$ = 289.7 Hz), 111.5, 84.0 ($J^2_{C\text{-}F}$ = 26.0 Hz), 56.3, 55.0, 52.8, 52.5, 52.5, 37.8, 34.7, 32.7, 32.4, 30.0, 23.3 ppm; IR (neat) ν̃: 3423, 2953, 1732, 1692, 1638 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{26}H_{30}F_3NNaO_6^+$ [(M+Na)$^+$] 532.1917, found 532.1925; $[\alpha]_D^{18}$ +45.7 (*c* 3.21, $CHCl_3$).

<Scheme 81>

Dimethyl 2-allyl-2-(8-hydroxyoct-2-yn-1-yl)malonate (178)

To a suspension of NaH (60% dispersion in mineral oil, 320 mg, 8.00 mmol) in THF (29 mL), was added dimethyl allylmalonate (0.919 mL, 5.72 mmol) at 0 °C. To the mixture, was added **177**[37a] (1.91 g, 5.72 mmol) at 0 °C. The reaction mixture was stirred at r.t. for 14 h. The reaction was quenched with saturated NH_4Cl aq. and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was used in the next reaction without purification. A solution of the crude oil and TBAF (1.0 M in THF, 6.86 mL, 6.86 mmol) in THF (19 mL) was

stirred at r.t. for 2 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 80:20~50:50) to give **178** (1.09 g, 65% yield, 2 steps) as a colorless oil.

Spectral data of **178**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.67-5.59 (m, 1H), 5.16 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.11 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.73 (s, 6H), 3.66 (q, *J* = 5.9 Hz, 2H), 2.79 (d, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 2.4 Hz, 2H), 2.17-2.13 (m, 2H), 1.60-1.42 (m, 7H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.7 (2C), 132.1, 119.7, 83.6, 74.6, 62.9, 57.4, 52.8 (2C), 36.7, 32.4, 28.6, 24.9, 23.2, 18.7 ppm; IR (neat) ṽ: 3389, 2937, 2862, 1739, 1642 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{24}NaO_5^+$ $[(M+Na)^+]$ 319.1516, found 319.1513.

Dimethyl (*S*,*E*)-2-allyl-2-(8-((*tert*-butanesulfinyl)imino)oct-2-yn-1-yl)malonate ((*S*)-121i)

A suspension of **178** (1.09 g, 3.52 mmol), DMP (2.19 g, 5.17 mmol) and $NaHCO_3$ (930 mg, 11.1 mmol) in CH_2Cl_2 (12 mL) was stirred at r.t. for 2 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was used in the next reaction without purification. A suspension of the crude oil, (*S*)-*t*-butanesulfinamide (537 mg, 4.43 mmol), PPTS (92.7 mg, 0.369 mmol) and $MgSO_4$ (2.22 g, 18.5 mmol) in toluene (12 mL) was stirred at 40 °C for 2 h. The reaction mixture was filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~50:50) to give (*S*)-**121i** (484 mg, 33% yield, 2 steps) as a colorless oil.

Spectral data of (*S*)-**121i**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.07 (t, *J* = 4.6 Hz, 1H), 5.67-5.58 (m, 1H), 5.15 (d, *J* = 16.8 Hz, 1H), 5.11 (d, *J* = 10.0 Hz, 1H), 3.72 (s, 6H), 2.78-2.75 (m, 4H), 2.53 (td, *J* = 7.3, 4.6 Hz, 2H), 2.17 (tt, *J* = 7.0, 2.3 Hz, 2H), 1.75-1.69 (m, 2H), 1.57-1.51 (m, 2H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.6 (2C), 169.4, 132.1, 119.8, 83.0, 74.9, 57.4, 56.7, 52.8 (2C), 36.8, 35.7, 28.5, 24.6, 23.2, 22.5 (3C), 18.6 ppm; IR (neat) ṽ: 2981, 2952, 2866, 1739, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{31}NNaO_5S^+$ $[(M+Na)^+]$ 420.1815, found 420.1819; $[\alpha]_D^{18}$ +101.2 (*c* 1.16, $CHCl_3$).

<Scheme 83>

Dimethyl 2-(7-((*tert*-butyldimethylsilyl)oxy)hept-2-yn-1-yl)-2-(2-methylallyl)malonate (185)

To a suspension of NaH (60% dispersion in mineral oil, 774 mg, 19.4 mmol) in THF (46 mL), was added **184**[49] (2.57 g, 13.8 mmol) at 0 °C. The mixture was stirred at r.t. for 0.5 h. To the mixture, was added **136**[20b] (4.43 g, 13.8 mmol) at 0 °C. The reaction mixture was stirred at r.t. for 20 h. The reaction was quenched with saturated NH_4Cl aq. and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 100:0~85:15) to give **185** (4.02 g, 71% yield) as a colorless oil.

Spectral data of **185**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.89 (s, 1H), 4.82 (s, 1H), 3.72 (s, 6H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.82 (s, 2H), 2.79 (t, *J* = 2.3 Hz, 2H), 2.16-2.13 (m, 2H), 1.66 (s, 3H), 1.60-1.49 (m, 4H), 0.88 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.0 (2C), 140.2, 116.2, 83.9, 74.9, 62.8, 57.0, 52.7 (2C), 39.7, 32.0, 26.1 (3C), 25.5, 23.4, 23.2, 18.6, 18.5, -5.2 (2C) ppm; IR (neat) ν̃: 2952, 1740, 1645 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{38}NaO_5Si^+$ [$(M+Na)^+$] 433.2381, found 433.2375.

Dimethyl 2-(7-hydroxyhept-2-yn-1-yl)-2-(2-methylallyl)malonate (186)

A solution of **185** (4.02 g, 9.79 mmol) and TBAF (1.0 M in THF, 11.8 mL, 11.8 mmol) in THF (20 mL) was stirred at r.t. for 2 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 80:20~50:50) to give **186** (2.86 g, 99% yield) as a colorless oil.

Spectral data of **186**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.90 (s, 1H), 4.82 (s, 1H), 3.73 (s, 6H), 3.66 (t, *J* = 6.4 Hz, 2H), 2.82 (s, 2H), 2.80 (t, *J* = 2.3 Hz, 2H), 2.20-2.17 (m, 2H), 1.68-1.63 (m, 5H), 1.58-1.53 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.0 (2C), 140.1, 116.2, 83.7, 75.2, 62.5, 57.0, 52.8 (2C), 39.7, 31.8, 25.2, 23.4, 23.2, 18.5 ppm; IR (neat) ν̃: 3399, 2951, 1737, 1645 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{24}NaO_5^+$ [$(M+Na)^+$] 319.1516, found 319.1517.

Dimethyl 2-(2-methylallyl)-2-(7-oxohept-2-yn-1-yl)malonate (139j)

A suspension of **186** (2.86 g, 9.65 mmol), DMP (5.73 g, 13.5 mmol) and $NaHCO_3$ (2.43 g, 29.0 mmol) in CH_2Cl_2 (32 mL) was stirred at r.t. for 6 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 95:5~70:30) to give **139j** (2.08 g, 73% yield) as a colorless oil.

Spectral data of **139j**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.80 (s, 1H), 4.90 (s, 1H), 4.81 (s, 1H), 3.73 (s, 6H), 2.81 (s, 2H), 2.80 (t, *J* = 2.3 Hz, 2H), 2.56 (td, *J* = 7.0, 1.2 Hz, 2H), 2.23-2.20 (m, 2H), 1.81-1.76 (m, 2H), 1.65 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 202.0, 170.9 (2C), 140.1, 116.3, 82.6, 76.0, 56.9, 52.8 (2C), 42.8, 39.7, 23.4, 23.2, 21.4, 18.2 ppm; IR (neat) ṽ: 2953, 2725, 1732, 1645 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{23}O_5^+$ [$(M+H)^+$] 295.1540, found 295.1541.

Dimethyl (*S*,*E*)-2-(7-((*tert*-butanesulfinyl)imino)hept-2-yn-1-yl)-2-(2-methylallyl)malonate ((*S*)-121j)

A suspension of **139j** (2.08 g, 7.08 mmol), (*S*)-*t*-butanesulfinamide (1.03 g, 8.50 mmol), PPTS (178 mg, 0.708 mmol) and $MgSO_4$ (4.26 g, 35.4 mmol) in toluene (24 mL) was stirred at 40 °C for 5 h. The reaction mixture was filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give (*S*)-**121j** (2.81 g, quant.) as a colorless oil.

Spectral data of (*S*)-**121j**: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.08 (t, *J* = 4.4 Hz, 1H), 4.90 (s, 1H), 4.81 (s, 1H), 3.72 (s, 6H), 2.81-2.80 (m, 4H), 2.62 (td, *J* = 7.3, 4.5 Hz, 2H), 2.24 (t, *J* = 5.9 Hz, 2H), 1.83-1.78 (m, 2H), 1.65 (s, 3H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.9 (2C), 168.9, 140.1, 116.2, 82.6, 76.0, 56.9, 56.7, 52.8 (2C), 39.7, 35.0, 24.7, 23.4, 23.1, 22.5 (3C), 18.3 ppm; IR (neat) ṽ: 2953, 1739, 1645, 1624 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{31}NNaO_5S^+$ [$(M+Na)^+$] 420.1815, found 420.1816; $[\alpha]_D^{24}$ +114.2 (*c* 0.59, $CHCl_3$).

<Scheme 84>

((7-(Allyloxy)hept-5-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane (188)

To a suspension of NaH (60% dispersion in mineral oil, 301 mg, 7.52 mmol) in NMP (17 mL), was added allyl alcohol (0.512 mL, 7.52 mmol) at 0 °C. The mixture was stirred at r.t. for 0.5 h. To the mixture, was added **187**[50] (1.53 g, 5.02 mmol) at 0 °C. The reaction mixture was stirred at r.t. for 14 h. The reaction was quenched with saturated NH_4Cl aq. and extracted with EtOAc. The organic layer was washed with H_2O, dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 100:0~80:20) to give **188** (0.72 g, 51% yield) as a colorless oil.

Spectral data of **188**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.95-5.87 (m, 1H), 5.30 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.20 (dd, *J* = 10.4, 1.1 Hz, 1H), 4.13 (t, *J* = 2.1 Hz, 2H), 4.05 (d, *J* = 5.6 Hz, 2H), 3.62 (t, *J* = 6.1 Hz, 2H), 2.26-2.24 (m, 2H), 1.65-1.56 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 134.4, 117.8, 87.0, 76.1, 70.6, 62.8, 57.9, 32.1, 26.1 (3C), 25.2, 18.7, 18.5, -5.2 (2C) ppm; IR (neat) ν̃: 2952, 2930, 2857, 2224, 1648 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{30}NaO_2Si^+$ [$(M+Na)^+$] 305.1907, found 305.1908.

7-(Allyloxy)hept-5-yn-1-ol (189)

A solution of **188** (0.72 g, 2.55 mmol) and TBAF (1.0 M in THF, 3.06 mL, 3.06 mmol) in THF (8.5 mL) was stirred at r.t. for 2 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 80:20~60:40) to give **189** (429 mg, quant.) as a colorless oil.

Spectral data of **189**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.95-5.87 (m, 1H), 5.30 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.21 (dd, *J* = 10.4, 1.1 Hz, 1H), 4.13 (t, *J* = 2.1 Hz, 2H), 4.05 (d, *J* = 5.9 Hz, 2H), 3.68 (t, *J* = 6.0 Hz, 2H), 2.28 (tt, *J* = 6.8, 2.1 Hz, 2H), 1.71-1.66 (m, 2H), 1.64-1.58 (m, 2H), 1.25 (br s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 134.3, 117.8, 86.7, 76.4, 70.6, 62.5, 57.8, 31.9, 25.0, 18.7 ppm; IR (neat) ν̃: 3399, 2940, 2863, 2224, 1647 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{10}H_{16}NaO_2^+$ [$(M+Na)^+$] 191.1043, found 191.1047.

7-(Allyloxy)hept-5-ynal (139k)

A suspension of **189** (664 mg, 3.95 mmol), DMP (2.34 g, 5.53 mmol) and $NaHCO_3$ (995 mg, 11.8 mmol) in CH_2Cl_2 (13 mL) was stirred at r.t. for 2 h. The reaction was quenched with saturated $Na_2S_2O_3$ aq. and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give **139k** (478 mg, 73% yield) as a colorless oil.

Spectral data of **139k**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.81 (s, 1H), 5.95-5.87 (m, 1H), 5.30 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.21 (dd, *J* = 10.5, 1.0 Hz, 1H), 4.13 (t, *J* = 2.1 Hz, 2H), 4.04 (d, *J* = 5.9 Hz, 2H), 2.59 (td, *J* = 7.3, 1.1 Hz, 2H), 2.31 (tt, *J* = 6.8, 2.1 Hz, 2H), 1.88-1.82 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.9, 134.2, 117.9, 85.6, 77.2, 70.7, 57.8, 42.8, 21.1, 18.3 ppm; IR (neat) ṽ: 2940, 2850, 2726, 2224, 1724, 1647 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{10}H_{15}O_2^+$ [$(M+H)^+$] 167.1067, found 167.1070.

(*S*,*E*)-*N*-(7-(Allyloxy)hept-5-yn-1-ylidene)-2-methylpropane-2-sulfinamide ((*S*)-121k)

A suspension of **139k** (478 mg, 2.88 mmol), (*S*)-*t*-butanesulfinamide (418 mg, 3.45 mmol), PPTS (72.3 mg, 0.288 mmol) and $MgSO_4$ (1.73 g, 14.4 mmol) in toluene (9.6 mL) was stirred at 40 °C for 2 h. The reaction mixture was filtered through a short silica gel pad and concentrated. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~60:40) to give (*S*)-**121k** (652 mg, 84% yield) as a colorless oil.

Spectral data of (*S*)-**121k**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.10 (t, *J* = 4.4 Hz, 1H), 5.95-5.87 (m, 1H), 5.30 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.21 (dd, *J* = 10.4, 1.1 Hz, 1H), 4.14 (t, *J* = 2.2 Hz, 2H), 4.04 (d, *J* = 5.6 Hz, 2H), 2.65 (td, *J* = 7.3, 4.4 Hz, 2H), 2.36-2.33 (m, 2H), 1.91-1.83 (m, 2H), 1.20 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 168.8, 134.3, 117.9, 85.7, 77.1, 70.7, 57.8, 56.7, 35.1, 24.4, 22.5 (3C), 18.5 ppm; IR (neat) ṽ: 2956, 2865, 2223, 1623 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{14}H_{23}NNaO_2S^+$ [$(M+Na)^+$] 292.1342, found 292.1342; $[\alpha]_D^{23}$ +171.3 (*c* 0.54, $CHCl_3$).

<Section 4>

<Table 14>

Dimethyl (1*S*,2*R*,3a'*R*,8a'*R*)-2-(((*S*)-*tert*-butanesulfinyl)amino)-1',3'-dioxo-2'-phenyl-1',2',3',3a',5',7',8',8a'-octahydro-6'*H*-spiro(cyclopentane-1,4'-cyclopenta[*f*]isoindole)-6',6'-dicarboxylate (190aa)

A solution of **125a** (50.4 mg, 0.131 mmol) and *N*-phenylmaleimide (68.3 mg, 0.394 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) was stirred at 40 °C for 24 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 70:30~0:100) to give **190aa** (60.3 mg, 82% yield) as a colorless oil.

Spectral data of **190aa**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.24-7.22 (m, 2H), 3.77-3.71 (m, 7H), 3.44-3.39 (m, 1H), 3.34 (d, *J* = 10.5 Hz, 1H), 3.11 (d, *J* = 8.5 Hz, 1H), 3.07 (d, *J* = 16.1 Hz, 3H), 2.88 (d, *J* = 16.4 Hz, 1H), 2.66-2.61 (m, 1H), 2.43 (d, *J* = 18.3 Hz, 1H), 2.36 (td, *J* = 13.6, 7.6 Hz, 1H), 2.18 (dt, *J* = 16.0, 7.1 Hz, 1H), 2.10-2.04 (m, 1H), 1.87-1.81 (m, 2H), 1.70-1.62 (m, 1H), 1.22 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 178.7, 176.3, 172.8, 171.7, 134.5, 133.9, 131.8, 129.2 (2C), 128.7, 126.5 (2C), 67.4, 57.9, 55.8, 53.2, 53.0, 49.0, 48.8, 43.6, 43.0, 39.2, 33.2, 31.7, 25.3, 22.8 (3C), 21.1 ppm; IR (neat) ν̃: 3275, 2955, 1731, 1712, 1598, 1499 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{29}H_{36}N_2NaO_7S^+$ $[(M+Na)^+]$ 579.2135, found 579.2137; $[\alpha]_D^{20}$ -62.0 (*c* 5.73, $CHCl_3$).

Dimethyl (1*S*,2*R*,3a'*R*,8a'*R*)-2-(((*S*)-*tert*-butanesulfinyl)amino)-2'-(4-nitrophenyl)-1',3'-dioxo-1',2',3',3a',5',7',8',8a'-octahydro-6'*H*-spir(cyclopentane-1,4'-cyclopenta[*f*]isoindole)-6',6'-dicarboxylate (190ab)

A solution of **125a** (50.9 mg, 0.133 mmol) and *N*-(4-nitrophenyl)maleimide (86.8 mg, 0.398 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) was stirred at 40 °C for 24 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **190ab** (73.1

mg, 92% yield) as a white solid. The structure and absolute configuration of **190ab** was unambiguously determined by X-ray crystal structure analysis.

CCDC 1412638 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Spectral data of **190ab**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.31 (dt, *J* = 9.5, 2.3 Hz, 2H), 7.55 (dt, *J* = 9.5, 2.4 Hz, 2H), 3.77-3.70 (m, 7H), 3.49-3.44 (m, 1H), 3.33 (d, *J* = 10.3 Hz, 1H), 3.15 (d, *J* = 8.5 Hz, 1H), 3.07-3.01 (m, 3H), 2.89 (d, *J* = 16.8 Hz, 1H), 2.66 (dd, *J* = 18.1, 10.0 Hz, 1H), 2.45 (d, *J* = 18.3 Hz, 1H), 2.40-2.34 (m, 1H), 2.20-2.13 (m, 1H), 2.11-2.04 (m, 1H), 1.89-1.82 (m, 2H), 1.71-1.65 (m, 1H), 1.22 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.9, 175.5, 172.6, 171.7, 147.0, 137.4, 134.6, 133.9, 127.0 (2C), 124.4 (2C), 67.0, 57.9, 55.8, 53.2, 53.0, 49.0 (2C), 43.6, 42.9, 39.3, 33.1, 31.7, 25.3, 22.8 (3C), 21.0 ppm; IR ($CHCl_3$) $\tilde{\nu}$: 3276, 2956, 1724, 1597, 1526, 1345 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{29}H_{35}N_3NaO_9S^+$ $[(M+Na)^+]$ 624.1986, found 624.1982; $[\alpha]_D^{21}$ -65.3 (*c* 7.07, $CHCl_3$); mp 193-195 °C (recrystallized from Hexane/EtOAc at 0 °C).

Dimethyl

(1*S*,2*R*,3a'*R*,8a'*R*)-2-(((*S*)-*tert*-butanesulfinyl)amino)-1',3'-dioxo-3',3a',5',7',8',8a'-hexahydrospiro(cyclopentane-1,4'-indeno[5,6-*c*]furan)-6',6'(1'*H*)-dicarboxylate (190ac)

A solution of **125a** (35.9 mg, 0.0936 mmol) and maleic anhydride (27.5 mg, 0.281 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) was stirred at 40 °C for 18 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **190ac** (39.5 mg, 88% yield) as a colorless oil.

Spectral data of **190ac**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.74 (s, 3H), 3.72 (s, 3H), 3.57-3.48 (m, 2H), 3.43 (d, *J* = 11.0 Hz, 1H), 3.20 (d, *J* = 8.5 Hz, 1H), 3.08 (d, *J* = 16.8 Hz, 1H), 3.01 (s, 2H), 2.80 (d, *J* = 16.8 Hz, 1H), 2.58 (dd, *J* = 18.7, 10.6 Hz, 1H), 2.39-2.30 (m, 2H), 2.20-2.14 (m, 1H), 1.98-1.92 (m, 1H), 1.87-1.77 (m, 2H), 1.66-1.57 (m, 1H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 173.3, 173.0, 171.3, 170.8, 133.6, 133.4, 68.2, 57.6, 55.9, 53.3, 53.1, 50.9, 47.3, 43.4, 42.7, 39.0,

33.4, 32.0, 24.7, 22.9 (3C), 20.9 ppm; IR (neat) ṽ: 3267, 2957, 1858, 1783, 1731 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{23}H_{31}NNaO_8S^+$ $[(M+Na)^+]$ 504.1663, found 504.1664; $[\alpha]_D^{22}$ -61.2 (*c* 1.81, $CHCl_3$).

Dimethyl (1*S*,2*R*)-2-(((*S*)-*tert*-butanesulfinyl)amino)-1',3'-dioxo-2'-phenyl-2',3',6',9'-tetrahydro-1'*H*-spiro(cyclopentane-1,5'-cyclopenta[*d*][1,2,4]triazolo[1,2-*a*]pyridazine)-7',7'(8'*H*)-dicarboxylate (190ad)

A solution of **125a** (40.0 mg, 0.104 mmol) and 4-phenyl-1,2,4-triazoline-3,5-dione (54.8 mg, 0.313 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) was stirred at room temperature for 1 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **190ad** (50.0 mg, 86% yield) as a colorless oil.

Spectral data of **190ad**: ^1H NMR (500 MHz, $CDCl_3$) δ: 7.49-7.45 (m, 4H), 7.40-7.36 (m, 1H), 4.50-4.44 (m, 1H), 4.15 (d, *J* = 16.4 Hz, 1H), 3.98 (d, *J* = 16.4 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.58 (d, *J* = 9.5 Hz, 1H), 3.35 (d, *J* = 16.9 Hz, 1H), 3.19 (d, *J* = 16.1 Hz, 1H), 3.07 (d, *J* = 16.1 Hz, 1H), 2.96 (d, *J* = 16.9 Hz, 1H), 2.83-2.78 (m, 1H), 2.43-2.38 (m, 1H), 2.16-2.02 (m, 2H), 1.86-1.73 (m, 2H), 1.14 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.3, 171.0, 151.6, 151.3, 132.5, 131.1, 129.3 (2C), 128.5, 128.4, 125.8 (2C), 71.3, 64.3, 58.2, 55.9, 53.5, 53.3, 43.3, 41.3, 41.1, 34.5, 31.8, 22.7 (3C), 20.4 ppm; IR (neat) ṽ: 3288, 2956, 1731, 1706, 1600, 1504 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{27}H_{34}N_4NaO_7S^+$ $[(M+Na)^+]$ 581.2040, found 581.2039; $[\alpha]_D^{18}$ -128.6 (*c* 5.00, $CHCl_3$).

Tetramethyl (1*R*,2*R*)-2-(((*S*)-*tert*-butanesulfinyl)amino)-1',3',6',7'-tetrahydrospiro(cyclopentane-1,4'-indene)-2',2',5',5'-tetracarboxylate (190ae)

A solution of **125a** (53.0 mg, 0.138 mmol) and dimethyl 2-methylenemalonate (59.8 mg, 0.415 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) was stirred at 40 °C for 18 h. The reaction mixture was

concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **190ae** (66.7 mg, 92% yield) as a colorless oil.

Spectral data of **190ae**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.77 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H), 3.62 (d, *J* = 12.9 Hz, 4H), 3.42 (td, *J* = 11.0, 7.2 Hz, 1H), 3.13 (d, *J* = 16.6 Hz, 1H), 3.00 (s, 2H), 2.73-2.67 (m, 1H), 2.65 (d, *J* = 16.8 Hz, 1H), 2.36-2.28 (m, 2H), 2.19 (dt, *J* = 16.9, 7.6 Hz, 1H), 2.11 (dd, *J* = 13.9, 5.9 Hz, 1H), 1.96 (dd, *J* = 18.6, 5.4 Hz, 1H), 1.75-1.59 (m, 3H), 1.43-1.31 (m, 1H), 1.19 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 173.6, 171.7, 171.6, 170.8, 133.6, 133.3, 65.1, 63.1, 57.5, 55.7, 53.2, 52.9, 52.7, 52.3, 50.3, 43.6, 43.1, 36.8, 31.3, 26.4, 23.2, 23.0 (3C), 21.7 ppm; IR (neat) ṽ: 3278, 2955, 2840, 1731 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{25}H_{37}NNaO_9S^+$ [$(M+Na)^+$] 550.2081, found 550.2081; $[\alpha]_D^{23}$ -129.2 (*c* 4.42, $CHCl_3$).

3',3'-Diethyl 6',6'-dimethyl (1*S*,2*R*)-2-(((*S*)-*tert*-butanesulfinyl)amino)-5',7'-dihydro-3'*H*-spiro(cyclopentane-1,4'-cyclopenta[*c*]pyran)-3',3',6',6'(1'*H*)-tetracarboxylate (190af)

A solution of **125a** (41.7 mg, 0.109 mmol) and diethyl ketomalonate (0.0497 mL, 0.326 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) was stirred at 40 °C for 24 h. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **190af** (29.9 mg, 49% yield) as a colorless oil.

Spectral data of **190af**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.30-4.08 (m, 4H), 3.90-3.81 (m, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.47 (d, *J* = 10.0 Hz, 1H), 3.21 (d, *J* = 16.4 Hz, 1H), 3.09 (d, *J* = 15.6 Hz, 1H), 2.94 (d, *J* = 16.8 Hz, 1H), 2.86 (dd, *J* = 15.9, 2.0 Hz, 1H), 2.74 (d, *J* = 16.1 Hz, 1H), 2.36-2.28 (m, 2H), 2.09-2.02 (m, 1H), 1.92-1.82 (m, 2H), 1.74-1.59 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 6H), 1.16 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.8, 171.4, 169.3, 168.5, 131.7, 131.5, 87.2, 79.6, 68.3, 62.1, 61.9, 57.9, 55.8, 53.3, 53.1, 43.3, 41.2, 33.6, 31.3, 30.1, 22.9 (3C), 19.5, 14.1, 14.1 ppm; IR (neat) ṽ: 3290, 2980, 2958, 1735 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{26}H_{39}NNaO_{10}S^+$ [$(M+Na)^+$] 580.2187, found 580.2182; $[\alpha]_D^{23}$ -1.65 (*c* 6.62, $CHCl_3$).

<Table 15>

General Procedure for One-pot Synthesis of 190 from (*S*)-121a

A solution of $[Rh(cod)_2]BF_4$[59] (6.09 mg, 0.0150 mmol, 10 mol% to a substrate) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol, 10 mol% to a substrate) in $ClCH_2CH_2Cl$ (0.58 mL, 0.026 M to Rh, degassed by three freeze-pump up-thaw cycles) was stirred under H_2 atmosphere at room temperature for 1 h. Then the reaction mixture was degassed by three freeze-pump up-thaw cycles and the reaction vessel was filled with an argon gas. To the mixture, was added a solution of (*S*)-**121a** (57.5 mg, 0.150 mmol, 1 equiv.) in $ClCH_2CH_2Cl$ (0.92 mL, 0.16 M to a substrate, degassed by three freeze-pump up-thaw cycles) by cannulation under an argon gas and the reaction mixture was stirred at 40 °C for 3 h. To the mixture, was added a dienophile (0.450 mmol, 3 equiv.) and the reaction mixture was stirred at 40 °C for the indicated time. After removal of the solvent, the residue was purified by silica gel column chromatography to give a product **190**.

According to the general procedure for one-pot synthesis of **190**, a crude product, which was prepared from (*S*)-**121a** and *N*-phenylmaleimide (77.9 mg, 0.450 mmol) at 40 °C for 3 h (the first step) and 24 h (the second step), was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **190aa** (63.3 mg, 76% yield) as a pale yellow oil and **125a** (12.0 mg, 21% yield) as a pale yellow oil.

According to the general procedure for one-pot synthesis of **190**, a crude product, which was prepared from (*S*)-**121a** and *N*-(4-nitrophenyl)maleimide (98.2 mg, 0.450 mmol) at 40 °C for 3 h (the first step) and 24 h (the second step), was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **190ab** (76.2 mg, 84% yield) as a white solid.

According to the general procedure for one-pot synthesis of **190**, a crude product, which was prepared from (*S*)-**121a** and maleic anhydride (44.1 mg, 0.450 mmol) at 40 °C for 3 h (the first step)

and 24 h (the second step), was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **190ac** (57.6 mg, 80% yield) as a colorless oil.

According to the general procedure for one-pot synthesis of **190**, a crude product, which was prepared from (*S*)-**121a** and 4-phenyl-1,2,4-triazoline-3,5-dione (78.8 mg, 0.450 mmol) at 40 °C for 3 h (the first step) and 1 h (the second step), was purified by silica gel column chromatography (Hexane/EtOAc = 60:40~0:100) to give **190ad** (70.0 mg, 84% yield) as a colorless oil.

According to the general procedure for one-pot synthesis of **190**, a crude product, which was prepared from (*S*)-**121a** and dimethyl 2-methylenemalonate (64.9 mg, 0.450 mmol) at 40 °C for 3 h (the first step) and 20 h (the second step), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **190ae** (68.1 mg, 86% yield) as a colorless oil.

According to the general procedure for one-pot synthesis of **190**, a crude product, which was prepared from (*S*)-**121a** and diethyl ketomalonate (0.0686, 0.450 mmol) at 40 °C for 3 h (the first step) and 30 h (the second step), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **190af** (40.7 mg, 49% yield) as a colorless oil.

<Scheme 85>

General Procedure for Domino Reaction of (*S*)-121a to Synthesize 190

A solution of $[Rh(cod)_2]BF_4$[59] (6.09 mg, 0.0150 mmol, 10 mol% to a substrate) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol, 10 mol% to a substrate) in $ClCH_2CH_2Cl$ (0.58 mL, 0.026 M to Rh, degassed by three freeze-pump up-thaw cycles) was stirred under H_2 atmosphere at room temperature for 1 h. Then the reaction mixture was degassed by three freeze-pump up-thaw cycles and the reaction vessel was filled with an argon gas. To the mixture, was added a solution of (*S*)-**121a** (57.5 mg, 0.150 mmol, 1 equiv.) and maleimide **191** (0.450 mmol, 3 equiv.) in $ClCH_2CH_2Cl$ (0.92 mL, 0.16 M to a substrate, degassed by three freeze-pump up-thaw cycles) by

cannulation under an argon gas and the reaction mixture was stirred at 40 °C for 24 h. After removal of the solvent, the residue was purified by silica gel column chromatography to give a product **190**.

According to the general procedure for domino reaction of (*S*)-**121a**, a crude product, which was prepared from (*S*)-**121a** and *N*-phenylmaleimide (77.9 mg, 0.450 mmol), was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **190aa** (71.1 mg, 85% yield) as a colorless oil.

According to the general procedure for domino reaction of (*S*)-**121a**, a crude product, which was prepared from (*S*)-**121a** and *N*-(4-nitrophenyl)maleimide (98.2 mg, 0.450 mmol), was purified by silica gel column chromatography (Hexane/EtOAc = 90:10~0:100) to give **190ab** (75.0 mg, 83% yield) as a white solid.

Chapter 3

<Section 2>

<Table 16>

Tetramethyl (2'*R*,4*S*,5*R*)-2'-(((*S*)-*tert*-butanesulfinyl)amino)-1,3,5,8-tetrahydro-2*H*-spiro(azulene-4,1'-cyclopentane)-2,2,5,7-tetracarboxylate (197aa)

Spectral data of **197aa**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.06 (d, *J* = 8.5 Hz, 1H), 3.73 (d, *J* = 1.0 Hz, 6H), 3.72 (s, 3H), 3.66 (s, 3H), 3.52-3.50 (m, 3H), 3.21 (d, *J* = 16.6 Hz, 1H), 3.15-2.98 (m, 4H), 2.86 (d, *J* = 16.8 Hz, 1H), 2.26-2.19 (m, 1H), 2.08-2.03 (m, 1H), 1.91-1.75 (m, 3H), 1.71-1.61 (m, 1H), 1.15 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.9, 171.8, 171.4, 167.0, 137.0, 133.9, 133.3, 131.2, 66.9, 56.5, 55.8, 53.0, 52.9, 52.8, 52.2, 52.1, 52.1, 46.7, 45.4, 34.5, 33.2, 29.4, 22.8 (3C), 20.8 ppm; IR (neat) ν̃: 3278, 2954, 1731, 1659 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{26}H_{37}NNaO_9S^+$ $[(M+Na)^+]$ 562.2081, found 562.2078; $[\alpha]_D^{23}$ -66.7 (*c* 4.04, $CHCl_3$).

<Entry 1>

To a solution of **125a** (40.8 mg, 0.106 mmol) and $Rh_2(OAc)_4$ (2.35 mg, 0.00532 mmol) in $ClCH_2CH_2Cl$ (0.41 mL, degassed by three freeze-pump up-thaw cycles), was added **198a**[60] (23.5 mg, 0.128 mmol) in $ClCH_2CH_2Cl$ (0.65 mL, degassed by three freeze-pump up-thaw cycles) at 0 °C by cannulation under an argon gas. The reaction mixture was stirred at 0 °C for 3 h under an argon gas. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 40:60~0:100) to give **125a** (39.0 mg, 96% yield) as a colorless oil.

<Entry 2>

To a solution of **125a** (16.7 mg, 0.435 mmol) and $Rh_2(TFA)_4$ (1.43 mg, 0.00218 mmol) in $ClCH_2CH_2Cl$ (0.17 mL, degassed by three freeze-pump up-thaw cycles), was added **198a**[60] (9.62

mg, 0.523 mmol) in $ClCH_2CH_2Cl$ (0.27 mL, degassed by three freeze-pump up-thaw cycles) at 0 °C by cannulation under an argon gas. The reaction mixture was stirred at 0 °C for 3 h under an argon gas. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 40:60~0:100) to give **125a** (14.8 mg, 89% yield) as a colorless oil.

<Entry 3>

To a solution of **125a** (37.4 mg, 0.0975 mmol) and $Rh_2(oct)_4$ (3.80 mg, 0.00488 mmol) in $ClCH_2CH_2Cl$ (0.38 mL, degassed by three freeze-pump up-thaw cycles), was added **198a**[60] (21.6 mg, 0.117 mmol) in $ClCH_2CH_2Cl$ (0.60 mL, degassed by three freeze-pump up-thaw cycles) at 0 °C by cannulation under an argon gas. The reaction mixture was stirred at 0 °C for 3 h under an argon gas. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 40:60~0:100) to give **197aa** (18.9 mg, 36% yield) as a colorless oil and **125a** (18.8 mg, 50% yield) as a colorless oil.

<Entry 4>

To a solution of **125a** (42.3 mg, 0.110 mmol) and $Rh_2(TPA)_4$ (7.47 mg, 0.00551 mmol) in $ClCH_2CH_2Cl$ (0.43 mL, degassed by three freeze-pump up-thaw cycles), was added **198a**[60] (24.4 mg, 0.132 mmol) in $ClCH_2CH_2Cl$ (0.68 mL, degassed by three freeze-pump up-thaw cycles) at 0 °C by cannulation under an argon gas. The reaction mixture was stirred at 0 °C for 3 h under an argon gas. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197aa** (35.9 mg, 60% yield) as a colorless oil and **125a** (<2.2 mg, <5% yield) as a colorless oil.

<Entry 5>

To a solution of **125a** (24.9 mg, 0.0649 mmol) and $Rh_2(piv)_4$ (1.98 mg, 0.00325 mmol) in $ClCH_2CH_2Cl$ (0.25 mL, degassed by three freeze-pump up-thaw cycles), was added **198a**[60] (14.4 mg, 0.0779 mmol) in $ClCH_2CH_2Cl$ (0.40 mL, degassed by three freeze-pump up-thaw cycles) at

0 °C by cannulation under an argon gas. The reaction mixture was stirred at 0 °C for 3 h under an argon gas. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197aa** (25.2 mg, 72% yield) as a colorless oil and **125a** (<4.5 mg, <18% yield) as a colorless oil.

<Entry 6>

To a solution of **125a** (25.9 mg, 0.0675 mmol) and $Rh_2(esp)_2$ (2.56 mg, 0.00338 mmol) in $ClCH_2CH_2Cl$ (0.26 mL, degassed by three freeze-pump up-thaw cycles), was added **198a**[60] (14.9 mg, 0.0810 mmol) in $ClCH_2CH_2Cl$ (0.41 mL, degassed by three freeze-pump up-thaw cycles) at 0 °C by cannulation under an argon gas. The reaction mixture was stirred at 0 °C for 3 h under an argon gas. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197aa** (28.9 mg, 79% yield) as a colorless oil and **125a** (<2.6 mg, <10% yield) as a colorless oil.

<Table 17>

<Entry 1>

Trimethyl (2'*R*,4*S*,5*S*)-2'-(((*S*)-*tert*-butanesulfinyl)amino)-5-phenyl-1,3,5,8-tetrahydro-2*H*-spiro(azulene-4,1'-cyclopentane)-2,2,7-tricarboxylate (197ab)

To a solution of **125a** (21.4 mg, 0.0558 mmol) and $Rh_2(piv)_4$ (1.70 mg, 0.00279 mmol) in $ClCH_2CH_2Cl$ (0.22 mL, degassed by three freeze-pump up-thaw cycles), was added **198b**[60,61] (16.9 mg, 0.0837 mmol) in $ClCH_2CH_2Cl$ (0.34 mL, degassed by three freeze-pump up-thaw cycles) at 0 °C by cannulation under an argon gas. The reaction mixture was stirred at 0 °C for 3 h under an argon gas. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197ab** (29.3 mg, 94% yield) as a colorless oil.

Spectral data of **197ab**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.25-7.20 (m, 3H), 7.11-7.08 (m, 3H), 3.99 (t, *J* = 6.6 Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.66 (s, 3H), 3.44 (d, *J* = 5.9 Hz, 1H), 3.37-3.28 (m,

2H), 3.21 (d, *J* = 20.8 Hz, 1H), 3.08 (d, *J* = 14.9 Hz, 2H), 2.93 (d, *J* = 16.6 Hz, 1H), 2.41 (d, *J* = 16.6 Hz, 1H), 2.32-2.25 (m, 1H), 2.02-1.96 (m, 1H), 1.85-1.59 (m, 4H), 1.16 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.6, 172.2, 168.2, 141.9, 139.0, 135.4, 131.6, 130.3 (2C), 128.3 (2C), 127.9, 127.3, 64.8, 56.7, 55.9, 55.4, 53.0, 52.9, 52.2, 50.1, 46.9, 46.0, 32.7, 31.8, 29.5, 22.7 (3C), 20.0 ppm; IR (neat) ν̃: 3281, 3025, 2953, 1732, 1650, 1599 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{30}H_{39}NNaO_7S^+$ [$(M+Na)^+$] 580.2339, found 580.2343; $[\alpha]_D^{22}$ -153.2 (*c* 4.19, $CHCl_3$).

<Entry 2>

To a solution of **125a** (20.9 mg, 0.0545 mmol) and $Rh_2(esp)_2$ (2.07 mg, 0.00272 mmol) in $ClCH_2CH_2Cl$ (0.21 mL, degassed by three freeze-pump up-thaw cycles), was added **198b**[60,61] (16.5 mg, 0.0817 mmol) in $ClCH_2CH_2Cl$ (0.33 mL, degassed by three freeze-pump up-thaw cycles) at 0 °C by cannulation under an argon gas. The reaction mixture was stirred at 0 °C for 3 h under an argon gas. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197ab** (28.8 mg, 95% yield) as a colorless oil.

<Entry 3>

Trimethyl (2'*R*,4*S*,5*R*)-2'-(((*S*)-*tert*-butanesulfinyl)amino)-5-((*E*)-styryl)-1,3,5,8-tetrahydro-2*H*-spiro(azulene-4,1'-cyclopentane)-2,2,7-tricarboxylate (197ac)

To a solution of **125a** (30.0 mg, 0.0782 mmol) and $Rh_2(piv)_4$ (2.39 mg, 0.00391 mmol) in $ClCH_2CH_2Cl$ (0.30 mL, degassed by three freeze-pump up-thaw cycles), was added **198c**[62] (21.4 mg, 0.0939 mmol) in $ClCH_2CH_2Cl$ (0.48 mL, degassed by three freeze-pump up-thaw cycles) at 0 °C by cannulation under an argon gas. The reaction mixture was stirred at 0 °C for 3 h under an argon gas. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197ac** (40.1 mg, 88% yield) as a colorless oil.

Spectral data of **197ac**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.1 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.02 (dd, *J* = 15.4,

9.0 Hz, 1H), 3.82-3.79 (m, 1H), 3.72 (s, 6H), 3.69 (s, 3H), 3.26-2.98 (m, 8H), 2.25-2.22 (m, 1H), 1.89-1.81 (m, 4H), 1.72-1.67 (m, 1H), 1.14 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.5, 172.3, 167.8, 141.2, 137.0, 134.8, 133.0, 131.2, 128.5 (2C), 127.8 (2C), 127.5, 126.4 (2C), 65.3, 56.9, 55.7, 54.5, 52.9, 52.9, 52.0, 50.1, 46.9, 46.2, 33.8, 32.7, 30.1, 22.7 (3C), 20.2 ppm; IR (neat) ν̃: 3280, 2953, 1731, 1714, 1652, 1599 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{32}H_{41}NNaO_7S^+$ $[(M+Na)^+]$ 606.2496, found 606.2488; $[\alpha]_D^{26}$ -161.4 (*c* 6.81, $CHCl_3$).

<Entry 4>

To a solution of **125a** (30.0 mg, 0.0782 mmol) and $Rh_2(esp)_2$ (2.97 mg, 0.00391 mmol) in $ClCH_2CH_2Cl$ (0.30 mL, degassed by three freeze-pump up-thaw cycles), was added **198c**[62] (21.4 mg, 0.0939 mmol) in $ClCH_2CH_2Cl$ (0.48 mL, degassed by three freeze-pump up-thaw cycles) at 0 °C by cannulation under an argon gas. The reaction mixture was stirred at 0 °C for 3 h under an argon gas. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197ac** (37.3 mg, 82% yield) as a colorless oil.

<Entry 5>

Dimethyl

(2'*R*,4*S*,5*S*)-7-acetyl-2'-(((*S*)-*tert*-butanesulfinyl)amino)-5-phenyl-1,3,5,8-tetrahydro-2*H*-spiro(azulene-4,1'-cyclopentane)-2,2-dicarboxylate (197ad)

To a solution of **125a** (36.1 mg, 0.0941 mmol) and $Rh_2(piv)_4$ (2.87 mg, 0.00471 mmol) in $ClCH_2CH_2Cl$ (0.36 mL, degassed by three freeze-pump up-thaw cycles), was added **198d**[61] (31.6 mg, 0.169 mmol) in $ClCH_2CH_2Cl$ (0.58 mL, degassed by three freeze-pump up-thaw cycles) at 0 °C by cannulation under an argon gas. The reaction mixture was stirred at 0 °C for 3 h under an argon gas. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197ad** (39.5 mg, 78% yield) as a colorless oil and **125a** (<6.0 mg, <17% yield) as a colorless oil.

Spectral data of **197ad**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.29-7.23 (m, 3H), 7.13 (d, *J* = 6.3 Hz, 2H), 6.94 (d, *J* = 6.3 Hz, 1H), 3.93 (s, 1H), 3.69 (s, 3H), 3.66 (s, 3H), 3.54-3.51 (m, 1H), 3.34 (s, 1H), 3.30 (d, *J* = 6.8 Hz, 1H), 3.16 (d, *J* = 9.0 Hz, 1H), 3.08 (d, *J* = 17.1 Hz, 2H), 2.92 (d, *J* = 17.6 Hz, 1H), 2.44 (d, *J* = 14.9 Hz, 1H), 2.29 (s, 4H), 2.05-1.97 (m, 1H), 1.86-1.81 (m, 1H), 1.72-1.62 (m, 3H), 1.15 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.4, 172.6, 172.1, 143.3, 139.0, 137.7, 135.0, 132.0, 130.2 (2C), 128.3 (2C), 127.3, 64.7, 56.6, 55.9, 55.2, 52.9, 52.8, 50.3, 46.8, 45.8, 32.8, 31.8, 27.6, 25.5, 22.7 (3C), 20.0 ppm; IR (neat) ν̃: 3283, 2955, 1732, 1666, 1599 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{30}H_{39}NNaO_6S^+$ $[(M+Na)^+]$ 564.2390, found 564.2397; $[\alpha]_D^{26}$ -153.0 (*c* 5.42, $CHCl_3$).

<Entry 6>

To a solution of **125a** (34.4 mg, 0.0897 mmol) and $Rh_2(esp)_2$ (3.40 mg, 0.00448 mmol) in $ClCH_2CH_2Cl$ (0.35 mL, degassed by three freeze-pump up-thaw cycles), was added **198d**[61] (30.1 mg, 0.161 mmol) in $ClCH_2CH_2Cl$ (0.55 mL, degassed by three freeze-pump up-thaw cycles) at 0 °C by cannulation under an argon gas. The reaction mixture was stirred at 0 °C for 3 h under an argon gas. The reaction mixture was concentrated and purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197ad** (31.8 mg, 65% yield) as a colorless oil and **125a** (<2.5 mg, <7% yield) as a colorless oil.

<Section 3>

<Table 18>

General Procedure for One-pot Synthesis of 197aa from (*S*)-121a

A solution of $[Rh(cod)_2]BF_4$[59] (6.09 mg, 0.0150 mmol, 10 mol% to a substrate) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol, 10 mol% to a substrate) in $ClCH_2CH_2Cl$ (0.58 mL, 0.026 M to Rh, degassed by three freeze-pump up-thaw cycles) was stirred under H_2 atmosphere at room temperature for 1 h. Then the reaction mixture was degassed by three freeze-pump up-thaw cycles and the reaction vessel was filled with an argon gas. To the mixture, was added a solution of (*S*)-**121a** (57.5 mg, 0.150 mmol, 1 equiv.) in $ClCH_2CH_2Cl$ (0.92 mL, 0.16 M to a substrate, degassed by three freeze-pump up-thaw cycles) by cannulation under an argon gas and the reaction mixture was stirred at 40 °C for 3 h. To the mixture, were added **198a**[60] (33.1 mg, 0.180 mmol, 1.2 equiv.) and Rh(II) complex (0.00750 mmol, 5 mol% to a substrate) at 0 °C and the reaction mixture was stirred at 0 °C for 3 h. After removal of the solvent, the residue was purified by silica gel column chromatography to give product **197aa**.

<Entry 1>

According to the general procedure for one-pot synthesis of **197aa**, a crude product, which was prepared from (*S*)-**121a**, **198a**[60] and $Rh_2(piv)_4$ (4.58 mg, 0.00750 mmol), was purified by silica gel column chromatography (Hexane/EtOAc = 40:60~0:100) to give **197aa** (43.2 mg, 53% yield) as a colorless oil and **125a** (<14.8 mg, <26% yield) as a pale yellow oil.

<Entry 2>

According to the general procedure for one-pot synthesis of **197aa**, a crude product, which was prepared from (*S*)-**121a**, **198a**[60] and $Rh_2(esp)_2$ (5.69 mg, 0.00750 mmol), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197aa** (49.8 mg, 62% yield) as a colorless oil and **125a** (<6.5 mg, <11% yield) as a pale yellow oil.

<Table 19>

General Procedure for One-pot Synthesis of 197a from (*S*)-121a

A solution of $[Rh(cod)_2]BF_4$[59] (6.09 mg, 0.0150 mmol, 10 mol% to a substrate) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol, 10 mol% to a substrate) in $ClCH_2CH_2Cl$ (0.58 mL, 0.026 M to Rh, degassed by three freeze-pump up-thaw cycles) was stirred under H_2 atmosphere at room temperature for 1 h. Then the reaction mixture was degassed by three freeze-pump up-thaw cycles and the reaction vessel was filled with an argon gas. To the mixture, was added a solution of (*S*)-**121a** (57.5 mg, 0.150 mmol, 1 equiv.) in $ClCH_2CH_2Cl$ (0.92 mL, 0.16 M to a substrate, degassed by three freeze-pump up-thaw cycles) by cannulation under an argon gas and the reaction mixture was stirred at 40 °C for 3 h. To the mixture, were added **198** and Rh(II) complex (0.00750 mmol, 5 mol% to a substrate) at 0 °C and the reaction mixture was stirred at 0 °C for 3 h. After removal of the solvent, the residue was purified by silica gel column chromatography to give a product **197a**.

<Entry 1>

According to the general procedure for one-pot synthesis of **197a**, a crude product, which was prepared from (*S*)-**121a**, **198b**[60,61] (54.6 mg, 0.270 mmol, 1.8 equiv.) and $Rh_2(piv)_4$ (4.58 mg, 0.00750 mmol), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197ab** (67.4 mg, 81% yield) as a colorless oil.

<Entry 2>

According to the general procedure for one-pot synthesis of **197a**, a crude product, which was prepared from (*S*)-**121a**, **198b**[60,61] (54.6 mg, 0.270 mmol, 1.8 equiv.) and $Rh_2(esp)_2$ (5.69 mg, 0.00750 mmol), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197ab** (58.6 mg, 70% yield) as a colorless oil.

<Entry 3>

According to the general procedure for one-pot synthesis of **197a**, a crude product, which was prepared from (*S*)-**121a**, **198c**[62] (51.4 mg, 0.225 mmol, 1.5 equiv.) and $Rh_2(piv)_4$ (4.58 mg, 0.00750 mmol), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197ac** (70.5 mg, 81% yield) as a colorless oil.

<Entry 4>

According to the general procedure for one-pot synthesis of **197a**, a crude product, which was prepared from (*S*)-**121a**, **198c**[62] (61.6 mg, 0.270 mmol, 1.8 equiv.) and $Rh_2(esp)_2$ (5.69 mg, 0.00750 mmol), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197ac** (67.7 mg, 77% yield) as a colorless oil.

<Entry 5>

According to the general procedure for one-pot synthesis of **197a**, a crude product, which was prepared from (*S*)-**121a**, **198d**[61] (33.5 mg, 0.180 mmol, 1.2 equiv.) and $Rh_2(piv)_4$ (4.58 mg, 0.00750 mmol), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197ad** (28.9 mg, 36% yield) as a colorless oil and **125a** (21.6 mg, 38% yield) as a pale yellow oil.

<Entry 6>

According to the general procedure for one-pot synthesis of **197a**, a crude product, which was prepared from (*S*)-**121a**, **198d**[61] (33.5 mg, 0.180 mmol, 1.2 equiv.) and $Rh_2(esp)_2$ (5.69 mg, 0.00750 mmol), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197ad** (49.0 mg, 60% yield) as a colorless oil and **125a** (16.1 mg, 28% yield) as a pale yellow oil.

<Entry 7>

According to the general procedure for one-pot synthesis of **197a**, a crude product, which was prepared from (*S*)-**121a**, **198d**[61] (55.9 mg, 0.300 mmol, 2.0 equiv.) and $Rh_2(esp)_2$ (11.4 mg, 0.0150

mmol), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197ad** (58.3 mg, 72% yield) as a colorless oil and **125a** (5.5 mg, 10% yield) as a pale yellow oil.

<Table 20>

General Procedure for One-pot Synthesis of 197 from (*S*)-121

A solution of $[Rh(cod)_2]BF_4$[59] (6.09 mg, 0.0150 mmol, 10 mol% to a substrate) and (*S*)-H_8-BINAP (9.46 mg, 0.0150 mmol, 10 mol% to a substrate) in $ClCH_2CH_2Cl$ (0.58 mL, 0.026 M to Rh, degassed by three freeze-pump up-thaw cycles) was stirred under H_2 atmosphere at room temperature for 1 h. Then the reaction mixture was degassed by three freeze-pump up-thaw cycles and the reaction vessel was filled with an argon gas. To the mixture, was added a solution of (*S*)-**121** (0.150 mmol, 1 equiv.) in $ClCH_2CH_2Cl$ (0.92 mL, 0.16 M to a substrate, degassed by three freeze-pump up-thaw cycles) by cannulation under an argon gas and the reaction mixture was stirred at 40 °C for the indicated time. To the mixture, were added **198b**[60,61] (60.7 mg, 0.300 mmol, 2.0 equiv.) and Rh(II) complex (0.00750 mmol, 5 mol% to a substrate) at 0 °C and the reaction mixture was stirred at 0 °C for 3 h. After removal of the solvent, the residue was purified by silica gel column chromatography to give a product **197**.

Methyl

(2'*R*,4*S*,5*S*)-2,2-bis((benzyloxy)methyl)-2'-(((*S*)-*tert*-butanesulfinyl)amino)-5-phenyl-2,3,5,8-tetrahydro-1*H*-spiro(azulene-4,1'-cyclopentane)-7-carboxylate (197bb)

Spectral data of **197bb**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.33-7.07 (m, 16H), 4.46 (s, 2H), 4.42 (dd, *J* = 16.6, 12.5 Hz, 2H), 3.98 (t, *J* = 6.7 Hz, 1H), 3.72 (s, 3H), 3.42 (d, *J* = 7.3 Hz, 1H), 3.37-3.15 (m, 6H), 2.97 (d, *J* = 9.1 Hz, 1H), 2.40 (dd, *J* = 25.9, 17.6 Hz, 2H), 2.27-2.21 (m, 1H), 2.15 (d, *J* = 16.9 Hz, 1H), 2.02-2.01 (m, 1H), 1.82-1.57 (m, 5H), 1.09 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 168.4, 141.7, 139.0, 138.8, 138.7, 135.8, 132.4, 130.5 (2C), 128.3 (2C), 128.3 (3C), 128.0 (2C), 127.6 (2C), 127.5 (3C), 127.5, 127.2, 74.1, 73.8, 73.2 (2C), 64.8, 55.7, 55.7, 52.1, 49.8, 46.3, 45.3, 44.3, 32.3, 31.7, 30.3, 22.6 (3C), 19.8 ppm; IR (neat) ν̃: 3417, 3027, 2952, 2886, 2853, 1711, 1650,

1600 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{42}H_{51}NNaO_5S^+$ $[(M+Na)^+]$ 704.3380, found 704.3377; $[\alpha]_D^{27}$ -88.6 (*c* 8.02, $CHCl_3$).

<Entry 1>

According to the general procedure for one-pot synthesis of **197**, a crude product, which was prepared from (*S*)-**121b** (76.2 mg, 0.150 mmol), **198b**,[60,61] and $Rh_2(piv)_4$ (4.58 mg, 0.00750 mmol) at 40 °C for 3 h (the first step) and at 0 °C for 3 h (the second step), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197bb** (70.2 mg, 69% yield) as a colorless oil.

<Entry 2>

According to the general procedure for one-pot synthesis of **197**, a crude product, which was prepared from (*S*)-**121b** (76.2 mg, 0.150 mmol), **198b**,[60,61] and $Rh_2(esp)_2$ (5.69 mg, 0.00750 mmol) at 40 °C for 3 h (the first step) and at 0 °C for 3 h (the second step), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197bb** (66.2 mg, 65% yield) as a colorless oil.

((2'*R*,4*S*,5*S*)-2'-(((*S*)-*tert*-butanesulfinyl)amino)-7-(methoxycarbonyl)-5-phenyl-2,3,5,8-tetrahydro-1*H*-spiro(azulene-4,1'-cyclopentane)-2,2-diyl)bis(methylene) diacetate (197cb)

Spectral data of **197cb**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31-7.23 (m, 3H), 7.12 (d, *J* = 7.0 Hz, 2H), 7.10 (d, *J* = 7.3 Hz, 1H), 4.06 (t, *J* = 7.3 Hz, 1H), 3.99 (d, *J* = 10.9 Hz, 1H), 3.96 (d, *J* = 10.9 Hz, 1H), 3.91 (d, *J* = 10.9 Hz, 1H), 3.76 (d, *J* = 10.9 Hz, 1H), 3.73 (s, 3H), 3.44 (d, *J* = 5.2 Hz, 1H), 3.29 (d, *J* = 21.0 Hz, 1H), 3.21 (d, *J* = 21.3 Hz, 1H), 2.98 (d, *J* = 9.1 Hz, 1H), 2.41-2.26 (m, 3H), 2.17 (d, *J* = 16.6 Hz, 1H), 2.06-2.01 (m, 7H), 1.88-1.81 (m, 2H), 1.74-1.70 (m, 1H), 1.64-1.57 (m, 2H), 1.18 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.0 (2C), 168.2, 141.5, 138.5, 136.1, 132.0, 130.3 (2C), 128.2 (2C), 128.0, 127.5, 67.1, 66.5, 64.5, 55.8, 55.8, 52.2, 49.2, 45.7, 44.7, 42.4, 32.0, 31.4, 30.0, 22.7 (3C), 20.9 (2C), 19.6 ppm; IR (neat) ῡ: 3275, 3024, 2955, 2893, 2844, 1740,

1650, 1599 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{32}H_{43}NNaO_7S^+$ $[(M+Na)^+]$ 608.2652, found 608.2659; $[\alpha]_D^{26}$ -91.0 (*c* 4.91, $CHCl_3$).

<Entry 3>

According to the general procedure for one-pot synthesis of **197**, a crude product, which was prepared from (*S*)-**121c** (61.7 mg, 0.150 mmol), **198b**,[60,61] and $Rh_2(piv)_4$ (4.58 mg, 0.00750 mmol) at 40 °C for 4 h (the first step) and at 0 °C for 3 h (the second step), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197cb** (77.4 mg, 88% yield) as a colorless oil.

<Entry 4>

According to the general procedure for one-pot synthesis of **197**, a crude product, which was prepared from (*S*)-**121c** (61.7 mg, 0.150 mmol), **198b**,[60,61] and $Rh_2(esp)_2$ (5.69 mg, 0.00750 mmol) at 40 °C for 4 h (the first step) and at 0 °C for 3 h (the second step), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197cb** (70.6 mg, 80% yield) as a colorless oil.

Methyl

(1*S*,2*R*,5'*S*)-2-(((*S*)-*tert*-butanesulfinyl)amino)-5'-phenyl-1',3',5',8'-tetrahydrodispiro(cyclopentane-1,4'-azulene-2',9''-fluorene)-7'-carboxylate (197eb)

Spectral data of **197eb**: ^1H NMR (500 MHz, $CDCl_3$) δ: 7.65-7.62 (m, 2H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.40-7.20 (m, 11H), 3.91 (dd, *J* = 16.2, 7.1 Hz, 1H), 3.74-3.71 (m, 4H), 3.42 (t, *J* = 23.6 Hz, 2H), 3.25 (d, *J* = 9.6 Hz, 1H), 3.08 (dd, *J* = 36.1, 16.9 Hz, 2H), 2.88 (d, *J* = 16.6 Hz, 1H), 2.62 (d, *J* = 16.6 Hz, 1H), 2.28-2.27 (m, 1H), 1.94-1.93 (m, 1H), 1.79-1.77 (m, 1H), 1.70-1.60 (m, 3H), 1.33 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 168.1, 154.1 (2C), 142.9, 139.8, 139.4, 139.3, 136.1, 134.3, 130.4 (2C), 129.3, 128.4 (2C), 127.7. 127.7, 127.5, 127.2, 127.1, 122.7, 122.3, 119.8, 119.7, 66.5, 56.0, 55.4, 53.2, 53.1, 52.2, 52.1, 51.9, 33.7, 33.2, 30.5, 22.7 (3C), 20.5 ppm; IR (neat) ν̃:

3299, 3063, 2956, 2839, 1710, 1659, 1600 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{38}H_{41}NNaO_3S^+$ [$(M+Na)^+$] 614.2699, found 614.2695; $[\alpha]_D^{27}$ -14.4 (*c* 5.91, $CHCl_3$).

<Entry 5>

According to the general procedure for one-pot synthesis of **197**, a crude product, which was prepared from (*S*)-**121e** (62.6 mg, 0.150 mmol), **198b**,[60,61] and $Rh_2(piv)_4$ (4.58 mg, 0.00750 mmol) at 40 °C for 4 h (the first step) and at 0 °C for 3 h (the second step), was purified by silica gel column chromatography (Hexane/EtOAc = 70:30~0:100) to give **197eb** (65.4 mg, 74% yield) as a colorless oil.

<Entry 6>

According to the general procedure for one-pot synthesis of **197**, a crude product, which was prepared from (*S*)-**121e** (62.6 mg, 0.150 mmol), **198b**,[60,61] and $Rh_2(esp)_2$ (5.69 mg, 0.00750 mmol) at 40 °C for 4 h (the first step) and at 0 °C for 3 h (the second step), was purified by silica gel column chromatography (Hexane/EtOAc = 70:30~0:100) to give **197eb** (72.4 mg, 82% yield) as a colorless oil.

Methyl

(2'*R*,4*S*,5*S*)-2'-(((*S*)-*tert*-butanesulfinyl)amino)-5-phenyl-2-tosyl-2,3,5,8-tetrahydro-1*H*-spiro(cyclohepta[*c*]pyrrole-4,1'-cyclopentane)-7-carboxylate (197fb)

Spectral data of **197fb**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.04-6.99 (m, 3H), 6.90 (d, *J* = 7.8 Hz, 2H), 4.12 (dd, *J* = 25.8, 14.7 Hz, 2H), 4.04 (t, *J* = 7.4 Hz, 1H), 3.92 (d, *J* = 13.5 Hz, 1H), 3.70 (s, 3H), 3.40 (d, *J* = 13.0 Hz, 1H), 3.34 (d, *J* = 7.5 Hz, 1H), 3.20 (s, 2H), 2.86 (d, *J* = 8.6 Hz, 1H), 2.47 (s, 3H), 2.33-2.26 (m, 1H), 1.91-1.75 (m, 3H), 1.61 (dd, *J* = 13.4, 7.9 Hz, 1H), 1.43 (dd, *J* = 23.5, 10.2 Hz, 1H), 1.02 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.9, 143.4, 141.3, 138.1, 134.3, 134.0, 130.0 (2C), 129.8 (2C), 128.7, 128.4 (2C), 127.7 (2C), 127.4, 127.0, 64.2, 59.1, 58.9, 55.8, 55.4, 52.3, 49.0, 32.4, 30.4,

27.6, 22.5 (3C), 21.7, 19.6 ppm; IR (neat) ṽ: 3276, 2954, 1711, 1650, 1598, 1344, 1162 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{32}H_{40}N_2NaO_5S_2^+$ [$(M+Na)^+$] 619.2271, found 619.2276; $[\alpha]_D^{26}$ -112.2 (*c* 2.61, $CHCl_3$).

<Entry 7>

According to the general procedure for one-pot synthesis of **197**, a crude product, which was prepared from (*S*)-**121f** (63.4 mg, 0.150 mmol), **198b**,[60,61] and $Rh_2(piv)_4$ (4.58 mg, 0.00750 mmol) at 40 °C for 13 h (the first step) and at 0 °C for 3 h (the second step), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197fb** (40.2 mg, 45% yield) as a colorless oil.

<Entry 8>

According to the general procedure for one-pot synthesis of **197**, a crude product, which was prepared from (*S*)-**121f** (63.4 mg, 0.150 mmol), **198b**,[60,61] and $Rh_2(esp)_2$ (5.69 mg, 0.00750 mmol) at 40 °C for 13 h (the first step) and at 0 °C for 3 h (the second step), was purified by silica gel column chromatography (Hexane/EtOAc = 50:50~0:100) to give **197fb** (37.6 mg, 42% yield) as a colorless oil.

<Scheme 91>

(1*S*,2*R*,5'*S*)-2-(((*S*)-*tert*-Butanesulfinyl)amino)-2'',2''-dimethyl-5'-phenyl-1',3',5',8'-tetrahydro dispiro(cyclopentane-1,4'-azulene-2',5''-[1,3]dioxane)-7'-carboxamide (200)

A suspension of **197cb** (250 mg, 0.427 mmol) and K_2CO_3 (177 mg, 1.28 mmol) in MeOH (4.3 mL) was stirred at r.t. for 0.5 h. The mixture was diluted with EtOAc. The organic layer was washed with H_2O, dried over $MgSO_4$, filtered and concentrated. The residue was used in the next reaction without purification. A solution of the crude diol, 2,2-dimethoxypropane (0.525 mL, 4.27 mmol) and PPTS (32.2 mg, 0.128 mmol) in acetone (2.2 mL) and CH_2Cl_2 (2.2 mL) was stirred at r.t. for 14 h. The reaction was quenched with saturated $NaHCO_3$ aq. and extracted with EtOAc. The organic

layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was used in the next reaction without purification. A solution of the crude acetonide **199** and 2N NaOH aq. (0.854 mL, 1.71 mmol) in THF (2.2 mL) and MeOH (2.2 mL) was stirred at r.t. for 14 h. The reaction was quenched with 2N HCl aq. (0.854 mL) and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was used in the next reaction without purification. A solution of the crude acid, HATU (487 mg, 1.28 mmol), NH_4Cl (68.5 mg, 1.28 mmol) and *i*Pr_2NEt (0.447 mL, 2.56 mmol) in DMF (4.3 mL) was stirred at r.t. for 14 h. The reaction was quenched with saturated $NaHCO_3$ aq. and extracted with EtOAc. The organic layer was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography ($CHCl_3$/MeOH = 100:0~95:5) to give **200** (124.3 mg, 55% yield in 4 steps) as a white solid. The structure and absolute configuration of **200** was unambiguously determined by X-ray crystal structure analysis.

Spectral data of **200**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.28-7.23 (m, 3H), 7.13 (d, *J* = 6.6 Hz, 2H), 6.54 (d, *J* = 7.6 Hz, 1H), 5.68 (br s, 2H), 4.10 (t, *J* = 7.2 Hz, 1H), 3.58-3.56 (m, 3H), 3.44 (d, *J* = 11.2 Hz, 1H), 3.39 (d, *J* = 7.1 Hz, 1H), 3.30-3.21 (m, 2H), 3.09 (d, *J* = 8.5 Hz, 1H), 2.52 (d, *J* = 16.8 Hz, 1H), 2.41 (d, *J* = 17.1 Hz, 1H), 2.32-2.25 (m, 1H), 2.15 (d, *J* = 16.8 Hz, 1H), 2.06-2.01 (m, 1H), 1.89-1.61 (m, 5H), 1.41 (s, 3H), 1.35 (s, 3H), 1.17 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.2, 139.1, 136.0, 134.9, 132.2, 131.6, 130.4 (2C), 127.9 (2C), 127.3, 97.6, 69.6, 69.4, 64.4, 56.0, 55.8, 48.6, 47.3, 45.8, 38.1, 31.9, 31.1, 30.4, 24.4, 23.1, 22.8 (3C), 19.6 ppm; IR ($CHCl_3$) $\tilde{\nu}$: 3373, 3182, 2958, 2856, 1652, 1599 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{30}H_{42}N_2NaO_4S^+$ $[(M+Na)^+]$ 549.2758, found 549.2758; $[\alpha]_D^{23}$ -176.6 (*c* 1.00, $CHCl_3$); mp 187-188 °C (recrystallized from Hexane/MeOAc at 0 °C).

CCDC 1442259 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-ray Structure Report

for

36

June 5, 2014

Experimental

Data Collection

A yellow block crystal of $C_{21}H_{22}N_2O_8S$ having approximate dimensions of 0.169 x 0.115 x 0.074 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using multi-layer mirror monochromated Cu-Kα radiation.

The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive triclinic cell with dimensions:

a	= 9.3707(3) Å	α	= 106.856(8)^o
b	= 10.6221(4) Å	β	= 108.213(8)^o
c	= 11.6440(5) Å	γ	= 90.485(6)^o
V	= 1047.35(10) Å^3		

For Z = 2 and F.W. = 462.47, the calculated density is 1.466 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P-1 (#2)

The data were collected at a temperature of -180 $\pm$ 1 ^{o}C to a maximum 2θ value of 136.3^o. A total of 90 oscillation images were collected. A sweep of data was done using ω scans from 80.0 to 260.0^o in 10.00^o step, at χ = 54.0^o and ϕ = 0.0^o. The exposure rate was 5.0 sec./^{o}. A second sweep was performed using ω scans from 80.0 to 260.0^o in 10.00^o step, at χ = 54.0^o and ϕ = 90.0^o. The exposure rate was 5.0 sec./^{o}. Another sweep was performed using ω scans from 80.0 to 260.0^o in 10.00^o step, at χ = 54.0^o and ϕ = 180.0^o. The exposure rate was 5.0 sec./^{o}. Another sweep was performed using ω scans from 80.0 to 260.0^o in 10.00^o step, at χ = 54.0^o and ϕ = 270.0^o. The exposure rate was 5.0 sec./^{o}. Another sweep was performed using ω scans from 80.0 to 260.0^o in 10.00^o step, at χ =0.0^o and ϕ = 0.0^o. The exposure rate was 5.0 sec./^{o}. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 12570 reflections were collected, where 3751 were unique (R_{int} = 0.0236); equivalent reflections were merged.

The linear absorption coefficient, μ, for Cu-Kα radiation is 18.446 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.693 to 0.872. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[2] on F^2 was based on 3751 observed reflections and 464 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma||Fo|-|Fc||/\Sigma|Fo| = 0.1056$$

$$wR2 = [\Sigma(w(Fo^2-Fc^2)^2)/\Sigma w(Fo^2)^2]^{1/2} = 0.2376$$

The goodness of fit[3] was 1.15. Unit weights were used. Plots of $\Sigma w(|Fo|-|Fc|)^2$ versus |Fo|, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.98 and -0.47 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4.[4] Anomalous dispersion effects were included in Fcalc;[5] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[6] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[7] All calculations were performed using the CrystalStructure[8] crystallographic software package except for refinement, which was performed using SHELXL2013.[9]

References

(1) SIR2011: Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Mallamo, M., Mazzone, A., Polidori, G. and Spagna, R. (2012). J. Appl. Cryst. 45, 357-361.

(2) Least Squares function minimized: (SHELXL2013)

$\Sigma w(F_o^2-F_c^2)^2$ where w = Least Squares weights.

(3) Goodness of fit is defined as:

$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$

where: N_o = number of observations
N_v = number of variables

(4) International Tables for Crystallography, Vol.C (1992). Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, Netherlands, Table 6.1.1.4, pp. 572.

(5) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(6) Creagh, D. C. & McAuley, W. J.; "International Tables for Crystallography", Vol C, (A. J. C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(7) Creagh, D. C. & Hubbell, J. H.; "International Tables for Crystallography", Vol C, (A. J. C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(8) CrystalStructure 4.1: Crystal Structure Analysis Package, Rigaku Corporation (2000-2014). Tokyo 196-8666, Japan.

(9) SHELXL2013: Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{21}H_{22}N_2O_8S$
Formula Weight	462.47
Crystal Color, Habit	yellow, block
Crystal Dimensions	0.169 X 0.115 X 0.074 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.3707(3) Å b = 10.6221(4) Å c = 11.6440(5) Å α = 106.856(8)° β = 108.213(8)° γ = 90.485(6)° V = 1047.35(10) Å^3
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.466 g/cm^3
F_{000}	484.00
μ(CuKα)	18.446 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	CuKα (λ = 1.54187 Å) multi-layer mirror monochromated
Voltage, Current	40 kV, 30 mA
Temperature	-180.0 °C
Detector Aperture	460.0 x 256.0 mm
Data Images	90 exposures
ω oscillation Range (χ = 54.0, ϕ = 0.0)	80.0 - 260.0°
Exposure Rate	5.0 sec./°
ω oscillation Range (χ = 54.0, ϕ = 90.0)	80.0 - 260.0°
Exposure Rate	5.0 sec./°
ω oscillation Range (χ = 54.0, ϕ = 180.0)	80.0 - 260.0°
Exposure Rate	5.0 sec./°
ω oscillation Range (χ = 54.0, ϕ = 270.0)	80.0 - 260.0°
Exposure Rate	5.0 sec./°
ω oscillation Range (χ = 0.0, ϕ = 0.0)	80.0 - 260.0°
Exposure Rate	5.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	136.3°
No. of Reflections Measured	Total: 12570 Unique: 3751 (R_{int} = 0.0236)

Corrections	Lorentz-polarization Absorption (trans. factors: 0.693 - 0.872) Decay (0.00% increase)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR2011)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w(Fo^2-Fc^2)^2$
Least Squares Weights	$w = 1/[\sigma^2(Fo^2)+(0.0424 \cdot P)^2 +5.4009 \cdot P]$ where $P = (Max(Fo^2,0)+2Fc^2)/3$
$2\theta_{max}$ cutoff	136.3^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	3751
No. Variables	464
Reflection/Parameter Ratio	8.08
Residuals: R1 ($I>2.00\sigma(I)$)	0.1056
Residuals: R (All reflections)	0.1099
Residuals: wR2 (All reflections)	0.2376
Goodness of Fit Indicator	1.146
Max Shift/Error in Final Cycle	0.003
Maximum peak in Final Diff. Map	0.98 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.47 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
S1	0.43663(17)	0.07149(16)	0.67763(19)	4.53(4)	1
O1	0.3523(5)	0.0602(5)	0.7574(6)	5.90(12)	1
O2	0.3604(5)	0.0642(5)	0.5474(5)	5.45(11)	1
O3	0.9510(8)	0.5916(6)	0.9101(6)	5.80(14)	0.812(5)
O3A	0.727(3)	0.640(3)	0.725(2)	6.0(4)	0.188(5)
O4	0.8220(9)	0.6503(6)	1.0401(7)	7.04(17)	0.812(5)
O4A	0.746(3)	0.698(2)	0.920(2)	5.1(3)	0.188(5)
O5	1.1999(5)	-0.2931(5)	0.5219(4)	4.16(9)	1
O6	0.9894(4)	-0.1917(4)	0.4953(4)	3.42(7)	1
O7	1.2840(6)	-0.3040(5)	0.8297(4)	4.96(10)	1
O8	1.1626(5)	-0.4767(4)	0.6616(4)	4.31(9)	1
N1	0.8449(10)	0.5748(7)	0.9465(7)	5.22(14)	0.812(5)
N2	0.5542(6)	-0.0365(5)	0.6772(6)	4.82(12)	1
N1a	0.741(2)	0.589(3)	0.812(2)	4.8(3)	0.188(5)
C1	0.7389(9)	0.4530(7)	0.8763(7)	3.84(12)	0.812(5)
C1A	0.694(3)	0.467(3)	0.805(3)	4.0(2)	0.188(5)
C2	0.7314(9)	0.3864(7)	0.7526(7)	3.24(12)	0.812(5)
C2A	0.688(4)	0.363(3)	0.697(3)	3.7(3)	0.188(5)
C3	0.6333(12)	0.2733(9)	0.6887(11)	3.43(16)	0.812(5)
C3A	0.617(5)	0.246(5)	0.679(5)	3.4(3)	0.188(5)
C4	0.5455(13)	0.2263(9)	0.7474(10)	3.19(15)	0.812(5)
C4A	0.551(5)	0.228(3)	0.765(5)	3.2(3)	0.188(5)
C5	0.5564(12)	0.2952(7)	0.8709(11)	3.55(14)	0.812(5)
C5A	0.553(5)	0.330(4)	0.878(5)	3.4(3)	0.188(5)
C6	0.6520(9)	0.4120(7)	0.9358(8)	3.93(13)	0.812(5)
C6A	0.628(3)	0.450(3)	0.892(3)	3.7(3)	0.188(5)
C7	1.0947(6)	-0.2559(6)	0.5537(5)	3.10(10)	1
C8	1.0097(7)	-0.1625(6)	0.3872(6)	3.67(11)	1
C9	1.1848(7)	-0.3504(7)	0.7318(6)	3.91(12)	1
C10	1.2740(7)	-0.5612(7)	0.7059(7)	4.49(13)	1
C11	1.045(2)	-0.146(2)	0.761(2)	3.4(3)	0.647(9)
C12	1.0618(6)	-0.2732(6)	0.6703(5)	3.43(10)	1
C13	0.905(3)	-0.3525(18)	0.6255(15)	3.2(3)	0.647(9)
C14	0.8127(12)	-0.2824(13)	0.6809(11)	3.44(17)	0.647(9)
C15	0.6506(15)	-0.3423(12)	0.6442(13)	4.5(2)	0.647(9)
C16	0.5660(10)	-0.2932(9)	0.7173(10)	3.56(17)	0.647(9)
C17	0.5911(12)	-0.1701(11)	0.8216(13)	5.4(2)	0.647(9)

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy (continued)

atom	x	y	z	B_{eq}	occ
C18	0.6594(13)	-0.0437(13)	0.8106(14)	4.3(2)	0.647(9)
C19	0.8235(10)	-0.0440(9)	0.8126(9)	3.33(16)	0.647(9)
C20	0.8830(14)	-0.1479(13)	0.7579(11)	3.15(18)	0.647(9)
C21	0.9143(14)	0.0890(11)	0.8788(12)	3.5(2)	0.647(9)
C22	0.910(5)	-0.325(3)	0.657(3)	3.3(5)	0.353(9)
C23	1.076(4)	-0.122(3)	0.765(4)	2.8(4)	0.353(9)
C24	0.835(2)	-0.209(3)	0.721(2)	2.9(3)	0.353(9)
C25	0.943(2)	-0.0978(19)	0.7844(17)	2.8(3)	0.353(9)
C26	0.929(3)	0.037(2)	0.859(2)	3.3(3)	0.353(9)
C27	0.816(2)	0.0699(16)	0.9030(15)	3.6(3)	0.353(9)
C28	0.679(2)	-0.0207(18)	0.8851(18)	3.5(3)	0.353(9)
C29	0.597(2)	-0.1099(19)	0.7553(17)	3.2(3)	0.353(9)
C30	0.6811(18)	-0.2270(16)	0.7032(16)	3.5(3)	0.353(9)
C31	0.573(3)	-0.344(2)	0.630(3)	4.8(4)	0.353(9)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Atomic coordinates and B_{iso} and occupancy involving hydrogen atoms

atom	x	y	z	B_{iso}	occ
H2	0.79249	0.41827	0.71338	3.886	0.812(5)
H2A	0.73307	0.37511	0.63800	4.448	0.188(5)
H3	0.62518	0.22652	0.60352	4.111	0.812(5)
H3A	0.61213	0.17439	0.60561	4.133	0.188(5)
H5	0.49779	0.26247	0.91159	4.263	0.812(5)
H5A	0.50784	0.31715	0.93663	4.101	0.188(5)
H6	0.65678	0.46178	1.01940	4.717	0.812(5)
H6A	0.63521	0.52374	0.96394	4.493	0.188(5)
H8A	1.01310	-0.24510	0.32342	4.401	1
H8B	1.10464	-0.10545	0.41479	4.401	1
H8C	0.92519	-0.11699	0.35016	4.401	1
H10A	1.27051	-0.63931	0.63471	5.390	1
H10B	1.25175	-0.58912	0.77221	5.390	1
H10C	1.37497	-0.51213	0.74064	5.390	1
H11A	1.07249	-0.07043	0.73560	4.139	0.647(9)
H11B	1.11352	-0.13696	0.84774	4.139	0.647(9)
H13	0.87810	-0.43921	0.56677	3.887	0.647(9)
H15	0.60914	-0.41481	0.56895	5.386	0.647(9)
H16	0.47519	-0.34720	0.69829	4.275	0.647(9)
H17A	0.65798	-0.18566	0.89975	6.476	0.647(9)
H17B	0.49269	-0.15218	0.83431	6.476	0.647(9)
H21A	0.85179	0.15294	0.91303	5.249	0.647(9)
H21B	1.00261	0.08243	0.94837	5.249	0.647(9)
H21C	0.94793	0.11831	0.81811	5.249	0.647(9)
H22A	0.91625	-0.39460	0.69887	4.012	0.353(9)
H22B	0.84922	-0.36326	0.56642	4.012	0.353(9)
H23	1.16507	-0.06132	0.80067	3.306	0.353(9)
H26	1.00571	0.10540	0.87540	3.930	0.353(9)
H27	0.82180	0.15980	0.95157	4.281	0.353(9)
H28A	0.71155	-0.07616	0.94175	4.163	0.353(9)
H28B	0.60568	0.03575	0.91469	4.163	0.353(9)
H31A	0.47320	-0.32522	0.63602	7.137	0.353(9)
H31B	0.56790	-0.36833	0.54055	7.137	0.353(9)
H31C	0.60581	-0.41753	0.66330	7.137	0.353(9)
H18	0.65055	0.03479	0.87953	5.142	0.647(9)
H29	0.50208	-0.14987	0.75917	3.809	0.353(9)
H2B	0.56021	-0.08985	0.60563	5.789	1

Table 2. Atomic coordinates and B_{iso} involving hydrogens/B_{eq} and occupancy (continued)

atom	x	y	z	B_{eq}	occ

Table 3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	0.0338(8)	0.0450(9)	0.0910(13)	0.0133(6)	0.0188(8)	0.0194(8)
O1	0.048(3)	0.070(3)	0.132(5)	0.025(2)	0.044(3)	0.052(3)
O2	0.035(2)	0.068(3)	0.072(3)	0.013(2)	-0.009(2)	0.003(2)
O3	0.082(4)	0.059(3)	0.066(4)	-0.007(3)	0.006(3)	0.020(3)
O3A	0.092(10)	0.061(9)	0.067(10)	-0.010(9)	0.014(9)	0.021(8)
O4	0.122(5)	0.057(4)	0.063(4)	-0.004(4)	0.016(4)	-0.004(3)
O4A	0.089(6)	0.046(6)	0.053(6)	-0.003(6)	0.018(6)	0.011(5)
O5	0.039(2)	0.076(3)	0.055(3)	0.018(2)	0.021(2)	0.031(2)
O6	0.038(2)	0.054(2)	0.047(2)	0.0124(17)	0.0173(17)	0.0230(19)
O7	0.069(3)	0.065(3)	0.049(3)	0.010(2)	0.005(2)	0.024(2)
O8	0.047(2)	0.054(3)	0.059(3)	0.014(2)	0.012(2)	0.018(2)
N1	0.085(4)	0.046(3)	0.056(3)	-0.001(3)	0.010(3)	0.012(3)
N2	0.045(3)	0.040(3)	0.094(4)	0.016(2)	0.020(3)	0.016(3)
N1a	0.079(5)	0.046(5)	0.054(5)	-0.001(5)	0.014(5)	0.017(4)
C1	0.060(3)	0.034(3)	0.050(3)	0.009(3)	0.015(3)	0.012(3)
C1A	0.062(5)	0.039(4)	0.049(4)	0.007(4)	0.018(4)	0.013(4)
C2	0.047(3)	0.037(3)	0.044(3)	0.010(3)	0.019(3)	0.017(3)
C2A	0.053(5)	0.041(5)	0.048(5)	0.010(5)	0.019(5)	0.013(5)
C3	0.046(3)	0.042(4)	0.045(3)	0.013(3)	0.018(3)	0.013(3)
C3A	0.047(5)	0.040(5)	0.047(5)	0.014(5)	0.018(5)	0.013(5)
C4	0.041(3)	0.039(3)	0.045(4)	0.017(3)	0.018(3)	0.015(3)
C4A	0.046(5)	0.039(5)	0.045(5)	0.016(5)	0.021(5)	0.016(5)
C5	0.053(3)	0.041(4)	0.049(3)	0.020(3)	0.026(3)	0.015(4)
C5A	0.052(5)	0.039(5)	0.046(5)	0.018(5)	0.024(5)	0.015(5)
C6	0.064(4)	0.041(3)	0.045(3)	0.018(3)	0.020(3)	0.012(3)
C6A	0.059(5)	0.039(5)	0.047(5)	0.015(5)	0.021(5)	0.013(5)
C7	0.032(3)	0.047(3)	0.041(3)	0.006(2)	0.012(2)	0.017(3)
C8	0.042(3)	0.057(4)	0.046(3)	0.011(3)	0.015(3)	0.024(3)
C9	0.051(4)	0.061(4)	0.051(4)	0.012(3)	0.025(3)	0.030(3)
C10	0.050(4)	0.057(4)	0.065(4)	0.016(3)	0.012(3)	0.028(3)
C11	0.039(8)	0.049(8)	0.046(6)	-0.006(5)	0.014(6)	0.017(5)
C12	0.041(3)	0.054(4)	0.040(3)	0.009(3)	0.016(3)	0.019(3)
C13	0.041(6)	0.043(7)	0.049(7)	0.006(6)	0.022(6)	0.020(5)
C14	0.043(5)	0.039(5)	0.057(5)	0.007(4)	0.020(4)	0.023(4)
C15	0.054(5)	0.048(5)	0.070(6)	0.004(5)	0.022(5)	0.019(4)
C16	0.041(4)	0.038(4)	0.066(5)	0.004(3)	0.034(4)	0.013(4)
C17	0.046(5)	0.069(6)	0.093(6)	0.004(4)	0.027(5)	0.025(5)

Table 3. Anisotropic displacement parameters (continued)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C18	0.043(5)	0.053(5)	0.075(6)	0.008(4)	0.024(5)	0.026(5)
C19	0.039(4)	0.040(4)	0.056(4)	0.006(3)	0.014(3)	0.028(4)
C20	0.036(5)	0.037(5)	0.051(5)	0.000(4)	0.014(4)	0.021(4)
C21	0.047(5)	0.041(6)	0.054(6)	0.012(5)	0.022(4)	0.024(5)
C22	0.043(10)	0.037(10)	0.048(11)	0.009(8)	0.015(9)	0.015(8)
C23	0.039(11)	0.037(10)	0.033(8)	0.001(8)	0.018(8)	0.011(8)
C24	0.040(7)	0.036(7)	0.042(7)	0.012(6)	0.015(5)	0.019(6)
C25	0.040(7)	0.036(7)	0.035(6)	0.007(6)	0.010(5)	0.019(5)
C26	0.051(8)	0.037(8)	0.033(7)	0.012(7)	0.002(6)	0.019(6)
C27	0.052(7)	0.038(7)	0.037(6)	0.013(6)	0.004(6)	0.010(5)
C28	0.046(7)	0.043(7)	0.037(7)	0.015(6)	0.009(6)	0.008(6)
C29	0.041(6)	0.042(7)	0.044(7)	0.006(6)	0.020(6)	0.017(6)
C30	0.042(6)	0.040(6)	0.052(7)	0.008(5)	0.010(5)	0.019(5)
C31	0.044(8)	0.054(9)	0.074(10)	0.003(8)	0.003(9)	0.025(8)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
S1	O1	1.423(7)	S1	O2	1.439(5)
S1	N2	1.597(6)	S1	C4	1.756(9)
S1	C4A	1.80(3)	O3	N1	1.226(13)
O3A	N1a	1.25(5)	O4	N1	1.232(11)
O4A	N1a	1.43(3)	O5	C7	1.189(8)
O6	C7	1.328(7)	O6	C8	1.447(9)
O7	C9	1.187(7)	O8	C9	1.328(7)
O8	C10	1.452(8)	N1	C1	1.479(10)
N2	C18	1.583(16)	N2	C29	1.34(2)
N1a	C1A	1.34(5)	C1	C2	1.387(11)
C1	C6	1.362(14)	C1A	C2A	1.40(4)
C1A	C6A	1.39(6)	C2	C3	1.370(11)
C2A	C3A	1.33(6)	C3	C4	1.391(19)
C3A	C4A	1.40(9)	C4	C5	1.382(16)
C4A	C5A	1.43(6)	C5	C6	1.388(10)
C5A	C6A	1.40(6)	C7	C12	1.542(10)
C9	C12	1.535(9)	C11	C12	1.49(2)
C11	C20	1.51(2)	C12	C13	1.54(2)
C12	C22	1.47(5)	C12	C23	1.64(3)
C13	C14	1.34(3)	C14	C15	1.521(17)
C14	C20	1.466(16)	C15	C16	1.34(2)
C16	C17	1.462(14)	C17	C18	1.54(2)
C18	C19	1.531(16)	C19	C20	1.326(16)
C19	C21	1.501(13)	C22	C24	1.53(5)
C23	C25	1.35(5)	C24	C25	1.41(3)
C24	C30	1.39(3)	C25	C26	1.48(3)
C26	C27	1.32(3)	C27	C28	1.53(3)
C28	C29	1.48(2)	C29	C30	1.55(3)
C30	C31	1.46(3)			

Table 5. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
N2	H2B	0.880	C2	H2	0.950
C2A	H2A	0.950	C3	H3	0.950
C3A	H3A	0.950	C5	H5	0.950
C5A	H5A	0.950	C6	H6	0.950
C6A	H6A	0.950	C8	H8A	0.980
C8	H8B	0.980	C8	H8C	0.980
C10	H10A	0.980	C10	H10B	0.980
C10	H10C	0.980	C11	H11A	0.990
C11	H11B	0.990	C13	H13	0.950
C15	H15	0.950	C16	H16	0.950
C17	H17A	0.990	C17	H17B	0.990
C18	H18	1.000	C21	H21A	0.980
C21	H21B	0.980	C21	H21C	0.980
C22	H22A	0.990	C22	H22B	0.990
C23	H23	0.950	C26	H26	0.950
C27	H27	0.950	C28	H28A	0.990
C28	H28B	0.990	C29	H29	1.000
C31	H31A	0.980	C31	H31B	0.980
C31	H31C	0.980			

Table 6. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
O1	S1	O2	120.4(3)	O1	S1	N2	109.5(4)
O1	S1	C4	107.4(5)	O1	S1	C4A	102.5(19)
O2	S1	N2	107.2(3)	O2	S1	C4	105.4(5)
O2	S1	C4A	111.3(16)	N2	S1	C4	106.1(4)
N2	S1	C4A	105.0(13)	C7	O6	C8	116.1(5)
C9	O8	C10	116.6(4)	O3	N1	O4	124.8(7)
O3	N1	C1	118.1(7)	O4	N1	C1	117.0(9)
S1	N2	C18	117.3(6)	S1	N2	C29	128.5(10)
O3A	N1a	O4A	105(3)	O3A	N1a	C1A	130(2)
O4A	N1a	C1A	119(3)	N1	C1	C2	118.6(8)
N1	C1	C6	118.4(7)	C2	C1	C6	123.0(7)
N1a	C1A	C2A	118(4)	N1a	C1A	C6A	119(3)
C2A	C1A	C6A	122(3)	C1	C2	C3	118.2(10)
C1A	C2A	C3A	119(4)	C2	C3	C4	120.6(10)
C2A	C3A	C4A	121(4)	S1	C4	C3	122.3(8)
S1	C4	C5	117.6(10)	C3	C4	C5	119.6(9)
S1	C4A	C3A	102(3)	S1	C4A	C5A	133(4)
C3A	C4A	C5A	123(4)	C4	C5	C6	120.6(11)
C4A	C5A	C6A	113(5)	C1	C6	C5	118.0(8)
C1A	C6A	C5A	122(4)	O5	C7	O6	125.1(6)
O5	C7	C12	125.0(6)	O6	C7	C12	109.8(5)
O7	C9	O8	124.9(7)	O7	C9	C12	124.6(6)
O8	C9	C12	110.4(4)	C12	C11	C20	108.4(12)
C7	C12	C9	107.4(5)	C7	C12	C11	113.7(12)
C7	C12	C13	108.9(8)	C7	C12	C22	119.9(14)
C7	C12	C23	104.7(18)	C9	C12	C11	113.6(9)
C9	C12	C13	110.0(9)	C9	C12	C22	112.3(16)
C9	C12	C23	110.5(13)	C11	C12	C13	103.1(11)
C22	C12	C23	101(2)	C12	C13	C14	110.8(12)
C13	C14	C15	118.5(12)	C13	C14	C20	111.6(13)
C15	C14	C20	129.4(11)	C14	C15	C16	120.4(10)
C15	C16	C17	130.4(10)	C16	C17	C18	118.8(13)
N2	C18	C17	103.3(8)	N2	C18	C19	109.3(12)
C17	C18	C19	115.3(10)	C18	C19	C20	125.2(9)
C18	C19	C21	113.6(9)	C20	C19	C21	121.2(10)
C11	C20	C14	105.4(12)	C11	C20	C19	124.4(12)
C14	C20	C19	130.1(11)	C12	C22	C24	108(2)

Table 6. Bond angles (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C12	C23	C25	110(2)	C22	C24	C25	109(2)
C22	C24	C30	119(2)	C25	C24	C30	132(2)
C23	C25	C24	111(2)	C23	C25	C26	118(2)
C24	C25	C26	130(2)	C25	C26	C27	124(2)
C26	C27	C28	127.3(16)	C27	C28	C29	118.0(19)
N2	C29	C28	108.5(15)	N2	C29	C30	112.2(16)
C28	C29	C30	115.8(15)	C24	C30	C29	121.2(16)
C24	C30	C31	129.1(19)	C29	C30	C31	109.5(16)

Table 7. Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom	angle
S1	N2	H2B	121.4	C18	N2	H2B	121.4
C29	N2	H2B	101.9	C1	C2	H2	120.9
C3	C2	H2	120.9	C1A	C2A	H2A	120.7
C3A	C2A	H2A	120.7	C2	C3	H3	119.7
C4	C3	H3	119.7	C2A	C3A	H3A	119.6
C4A	C3A	H3A	119.6	C4	C5	H5	119.7
C6	C5	H5	119.7	C4A	C5A	H5A	123.4
C6A	C5A	H5A	123.5	C1	C6	H6	121.0
C5	C6	H6	121.0	C1A	C6A	H6A	118.8
C5A	C6A	H6A	118.8	O6	C8	H8A	109.5
O6	C8	H8B	109.5	O6	C8	H8C	109.5
H8A	C8	H8B	109.5	H8A	C8	H8C	109.5
H8B	C8	H8C	109.5	O8	C10	H10A	109.5
O8	C10	H10B	109.5	O8	C10	H10C	109.5
H10A	C10	H10B	109.5	H10A	C10	H10C	109.5
H10B	C10	H10C	109.5	C12	C11	H11A	110.0
C12	C11	H11B	110.0	C20	C11	H11A	110.0
C20	C11	H11B	110.0	H11A	C11	H11B	108.4
C12	C13	H13	124.6	C14	C13	H13	124.6
C14	C15	H15	119.8	C16	C15	H15	119.8
C15	C16	H16	114.8	C17	C16	H16	114.8
C16	C17	H17A	107.6	C16	C17	H17B	107.6
C18	C17	H17A	107.6	C18	C17	H17B	107.6
H17A	C17	H17B	107.0	N2	C18	H18	109.6
C17	C18	H18	109.6	C19	C18	H18	109.6
C19	C21	H21A	109.5	C19	C21	H21B	109.5
C19	C21	H21C	109.5	H21A	C21	H21B	109.5
H21A	C21	H21C	109.5	H21B	C21	H21C	109.5
C12	C22	H22A	110.1	C12	C22	H22B	110.1
C24	C22	H22A	110.1	C24	C22	H22B	110.1
H22A	C22	H22B	108.4	C12	C23	H23	125.2
C25	C23	H23	125.2	C25	C26	H26	117.8
C27	C26	H26	117.8	C26	C27	H27	116.4
C28	C27	H27	116.4	C27	C28	H28A	107.8
C27	C28	H28B	107.8	C29	C28	H28A	107.8
C29	C28	H28B	107.8	H28A	C28	H28B	107.2
N2	C29	H29	106.6	C28	C29	H29	106.6

Table 7. Bond angles involving hydrogens (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C30	C29	H29	106.6	C30	C31	H31A	109.5
C30	C31	H31B	109.5	C30	C31	H31C	109.5
H31A	C31	H31B	109.5	H31A	C31	H31C	109.5
H31B	C31	H31C	109.5				

Table 8. Torsion Angles(°)
(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
O1	S1	N2	C18	-50.9(4)	O1	S1	N2	C29	-13.5(5)
O1	S1	C4	C3	-175.2(7)	O1	S1	C4	C5	12.4(8)
O1	S1	C4A	C3A	-172.3(17)	O1	S1	C4A	C5A	-7(4)
O2	S1	N2	C18	177.0(4)	O2	S1	N2	C29	-145.6(4)
O2	S1	C4	C3	-45.6(8)	O2	S1	C4	C5	141.9(6)
O2	S1	C4A	C3A	-42(2)	O2	S1	C4A	C5A	123(3)
N2	S1	C4	C3	67.9(8)	N2	S1	C4	C5	-104.6(7)
C4	S1	N2	C18	64.7(6)	C4	S1	N2	C29	102.1(6)
N2	S1	C4A	C3A	73(2)	N2	S1	C4A	C5A	-122(3)
C4A	S1	N2	C18	58.5(19)	C4A	S1	N2	C29	96.0(19)
C8	O6	C7	O5	-2.0(7)	C8	O6	C7	C12	177.1(3)
C10	O8	C9	O7	-3.7(11)	C10	O8	C9	C12	177.8(5)
O3	N1	C1	C2	-21.0(11)	O3	N1	C1	C6	159.6(7)
O4	N1	C1	C2	161.0(7)	O4	N1	C1	C6	-18.4(11)
S1	N2	C18	C17	105.8(7)	S1	N2	C18	C19	-131.0(6)
S1	N2	C29	C28	-65.3(16)	S1	N2	C29	C30	165.5(6)
C18	N2	C29	C28	16.2(11)	C18	N2	C29	C30	-113(2)
C29	N2	C18	C17	-13.7(17)	C29	N2	C18	C19	110(2)
O3A	N1a	C1A	C2A	31(4)	O3A	N1a	C1A	C6A	-137(3)
O4A	N1a	C1A	C2A	179(2)	O4A	N1a	C1A	C6A	11(4)
N1	C1	C2	C3	179.7(6)	N1	C1	C6	C5	-178.0(6)
C2	C1	C6	C5	2.7(12)	C6	C1	C2	C3	-0.9(12)
N1a	C1A	C2A	C3A	-168(2)	N1a	C1A	C6A	C5A	168(2)
C2A	C1A	C6A	C5A	0(5)	C6A	C1A	C2A	C3A	-0(4)
C1	C2	C3	C4	-0.8(13)	C1A	C2A	C3A	C4A	0(6)
C2	C3	C4	S1	-171.6(8)	C2	C3	C4	C5	0.7(15)
C2A	C3A	C4A	S1	167(3)	C2A	C3A	C4A	C5A	-0(6)
S1	C4	C5	C6	173.8(6)	C3	C4	C5	C6	1.1(15)
S1	C4A	C5A	C6A	-162(3)	C3A	C4A	C5A	C6A	0(6)
C4	C5	C6	C1	-2.7(13)	C4A	C5A	C6A	C1A	-0(5)
O5	C7	C12	C9	-2.1(7)	O5	C7	C12	C11	124.4(5)
O5	C7	C12	C13	-121.2(5)	O5	C7	C12	C22	-131.9(5)
O5	C7	C12	C23	115.4(5)	O6	C7	C12	C9	178.8(3)
O6	C7	C12	C11	-54.7(5)	O6	C7	C12	C13	59.7(5)
O6	C7	C12	C22	49.0(6)	O6	C7	C12	C23	-63.7(4)
O7	C9	C12	C7	108.0(8)	O7	C9	C12	C11	-18.6(11)
O7	C9	C12	C13	-133.6(7)	O7	C9	C12	C22	-118.1(8)

Table 8. Torsion angles (°) (continued)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
O7	C9	C12	C23	-5.6(10)	O8	C9	C12	C7	-73.5(7)
O8	C9	C12	C11	159.9(5)	O8	C9	C12	C13	44.9(8)
O8	C9	C12	C22	60.5(7)	O8	C9	C12	C23	172.9(5)
C12	C11	C20	C14	8(2)	C12	C11	C20	C19	-170.0(12)
C20	C11	C12	C7	112.6(16)	C20	C11	C12	C9	-124.2(14)
C20	C11	C12	C13	-5.2(19)	C20	C11	C12	C22	-10.0(16)
C7	C12	C13	C14	-120.9(11)	C7	C12	C22	C24	-106.6(17)
C7	C12	C23	C25	119(3)	C9	C12	C13	C14	121.7(11)
C9	C12	C22	C24	125.8(17)	C9	C12	C23	C25	-125(2)
C11	C12	C13	C14	0.2(18)	C11	C12	C22	C24	11(2)
C13	C12	C23	C25	-0(3)	C23	C12	C13	C14	-4(2)
C22	C12	C23	C25	-6(3)	C23	C12	C22	C24	8(3)
C12	C13	C14	C15	177.5(10)	C12	C13	C14	C20	5.1(17)
C13	C14	C15	C16	163.4(14)	C13	C14	C20	C11	-8.2(16)
C13	C14	C20	C19	169.7(14)	C15	C14	C20	C11	-179.5(13)
C15	C14	C20	C19	-2(2)	C20	C14	C15	C16	-26(2)
C14	C15	C16	C17	13(2)	C15	C16	C17	C18	39.0(18)
C16	C17	C18	N2	52.0(12)	C16	C17	C18	C19	-67.2(13)
N2	C18	C19	C20	-78.0(13)	N2	C18	C19	C21	99.3(9)
C17	C18	C19	C20	37.9(17)	C17	C18	C19	C21	-144.8(10)
C18	C19	C20	C11	179.9(11)	C18	C19	C20	C14	2(2)
C21	C19	C20	C11	2.8(19)	C21	C19	C20	C14	-174.8(12)
C12	C22	C24	C25	-8(3)	C12	C22	C24	C30	169.3(19)
C12	C23	C25	C24	2(3)	C12	C23	C25	C26	-174.8(17)
C22	C24	C25	C23	4(3)	C22	C24	C25	C26	179(2)
C22	C24	C30	C29	-174(2)	C22	C24	C30	C31	-0(4)
C25	C24	C30	C29	2(4)	C25	C24	C30	C31	176(2)
C30	C24	C25	C23	-173(2)	C30	C24	C25	C26	3(4)
C23	C25	C26	C27	-168(3)	C24	C25	C26	C27	16(4)
C25	C26	C27	C28	-2(3)	C26	C27	C28	C29	-47(3)
C27	C28	C29	N2	-57(2)	C27	C28	C29	C30	71(2)
N2	C29	C30	C24	83.1(18)	N2	C29	C30	C31	-92.3(17)
C28	C29	C30	C24	-42(3)	C28	C29	C30	C31	142.4(17)

Table 9. Possible hydrogen bonds

Donor	H	Acceptor	D...A	D-H	H...A	D-H...A	
N2	H2B	S1	1.597(6)	0.88	2.19	38.56	intramol.
N2	H2B	O2[1]	2.903(10)	0.88	2.22	134.78	

Symmetry Operators:

(1) -X+1,-Y,-Z+1

Table 10. Intramolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
S1	C17	3.540(14)	S1	C28	3.149(19)
O1	C5	2.840(9)	O1	C5A	3.11(4)
O1	C17	3.415(13)	O1	C18	3.036(13)
O1	C28	3.200(19)	O1	C29	2.93(2)
O2	C3	3.055(10)	O2	C3A	2.79(4)
O3	C2	2.756(9)	O3	C6	3.514(12)
O3A	C2A	2.88(5)	O3A	C6A	3.47(5)
O4	C2	3.539(9)	O4	C6	2.713(10)
O4A	C6A	2.73(4)	O5	O7	3.458(7)
O5	O8	2.960(8)	O5	C8	2.667(8)
O5	C9	2.728(10)	O5	C11	3.51(3)
O5	C13	3.46(3)	O5	C23	3.43(4)
O6	C11	2.86(3)	O6	C13	2.84(2)
O6	C14	3.429(15)	O6	C20	3.413(15)
O6	C22	2.92(4)	O6	C23	2.85(4)
O6	C24	3.42(3)	O6	C25	3.39(2)
O7	C7	3.338(8)	O7	C10	2.678(8)
O7	C11	2.86(2)	O7	C13	3.53(2)
O7	C22	3.42(4)	O7	C23	2.84(4)
O8	C7	2.953(8)	O8	C13	2.73(2)
O8	C22	2.87(4)	N2	C3	3.322(12)
N2	C3A	3.05(6)	N2	C5	3.587(9)
N2	C14	3.578(13)	N2	C15	3.325(14)
N2	C16	2.895(12)	N2	C20	3.268(14)
N2	C21	3.440(12)	N2	C24	3.21(2)
N2	C25	3.59(2)	N2	C26	3.43(2)
N2	C27	2.902(15)	N2	C31	3.17(3)
N1a	C3A	3.54(6)	C1	C4	2.732(11)
C1A	C4A	2.71(5)	C2	C5	2.771(16)
C2A	C5A	2.87(8)	C3	C6	2.776(14)
C3A	C6A	2.76(6)	C7	C14	3.455(15)
C7	C20	3.509(16)	C7	C24	3.52(3)
C7	C25	3.45(2)	C9	C14	3.469(13)
C9	C24	3.60(2)	C9	C25	3.57(2)
C11	C21	2.96(2)	C14	C17	3.075(19)
C14	C18	3.158(18)	C15	C18	3.187(17)
C15	C19	3.291(14)	C16	C19	3.251(13)

Table 10. Intramolecular contacts less than 3.60 Å (continued)

atom	atom	distance	atom	atom	distance
C16	C20	3.170(17)	C17	C20	3.07(2)
C22	C31	3.07(5)	C24	C27	3.15(3)
C24	C28	3.06(3)	C25	C28	3.08(3)
C25	C29	3.15(3)	C26	C29	3.17(3)
C26	C30	3.30(3)	C27	C30	3.29(2)

Table 11. Intramolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H3	2.882	S1	H3A	2.442
S1	H5	2.768	S1	H5A	3.240
S1	H17B	3.344	S1	H28B	2.856
S1	H18	2.701	S1	H29	2.786
O1	H5	2.425	O1	H5A	2.942
O1	H17B	2.847	O1	H28B	2.574
O1	H18	2.767	O1	H29	2.648
O1	H2B	3.168	O2	H3	2.796
O2	H3A	2.426	O2	H2B	2.558
O3	H2	2.495	O3A	H2A	2.709
O4	H6	2.429	O4A	H6A	2.366
O5	H8A	2.614	O5	H8B	2.664
O5	H11A	3.421	O5	H22B	3.587
O5	H23	3.570	O6	H11A	2.574
O6	H13	3.234	O6	H22B	2.692
O6	H23	3.274	O7	H10B	2.897
O7	H10C	2.437	O7	H11A	3.404
O7	H11B	2.406	O7	H22A	3.307
O7	H23	2.885	O8	H13	2.630
O8	H22A	2.592	O8	H22B	3.179
N1	H2	2.629	N1	H6	2.600
N2	H3	3.271	N2	H3A	2.712
N2	H16	3.470	N2	H17A	3.317
N2	H17B	2.672	N2	H21A	3.359
N2	H27	3.447	N2	H28A	3.125
N2	H28B	2.530	N2	H31A	3.015
N2	H31B	3.443	N1a	H2A	2.551
N1a	H6A	2.533	C1	H3	3.228
C1	H5	3.218	C1A	H3A	3.206
C1A	H5A	3.310	C2	H6	3.271
C2A	H6A	3.275	C3	H5	3.255
C3A	H5A	3.358	C3A	H2B	3.416
C4	H2	3.261	C4	H6	3.267
C4	H2B	3.310	C4A	H2A	3.232
C4A	H6A	3.236	C4A	H2B	3.362
C5	H3	3.253	C5A	H3A	3.340
C6	H2	3.268	C6A	H2A	3.286

Table 11. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C7	H8A	2.585	C7	H8B	2.602
C7	H8C	3.167	C7	H11A	2.505
C7	H11B	3.235	C7	H13	2.869
C7	H22A	3.316	C7	H22B	2.623
C7	H23	2.885	C9	H10A	3.152
C9	H10B	2.753	C9	H10C	2.485
C9	H11A	3.156	C9	H11B	2.495
C9	H13	2.880	C9	H22A	2.444
C9	H22B	3.110	C9	H23	2.963
C11	H13	3.297	C11	H21B	2.884
C11	H21C	2.918	C13	H11A	3.084
C13	H11B	3.013	C13	H15	2.674
C14	H11A	3.083	C14	H11B	2.978
C14	H16	3.311	C14	H17A	3.235
C14	H2B	3.221	C15	H13	2.668
C15	H17A	2.937	C15	H17B	3.267
C15	H2B	2.934	C16	H18	3.397
C16	H2B	2.819	C17	H15	3.365
C17	H2B	2.816	C18	H16	3.337
C18	H21A	2.487	C18	H21B	3.189
C18	H21C	3.157	C19	H11A	2.739
C19	H11B	2.849	C19	H17A	2.743
C19	H17B	3.404	C19	H2B	2.777
C20	H13	3.236	C20	H15	3.492
C20	H17A	3.144	C20	H21A	3.250
C20	H21B	2.723	C20	H21C	2.723
C20	H18	3.305	C20	H2B	3.161
C21	H11A	2.791	C21	H11B	3.061
C21	H18	2.536	C22	H23	3.319
C22	H31B	3.035	C22	H31C	3.034
C23	H22A	3.020	C23	H22B	3.134
C23	H26	2.589	C24	H23	3.191
C24	H26	3.405	C24	H28A	3.118
C24	H31A	3.333	C24	H31B	2.847
C24	H31C	2.847	C24	H29	3.325
C24	H2B	2.986	C25	H22A	3.001
C25	H22B	3.095	C25	H27	3.302

Table 11. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C25	H28A	3.217	C25	H2B	3.555
C26	H23	2.650	C26	H28A	2.898
C26	H28B	3.291	C27	H29	3.386
C27	H2B	3.458	C28	H26	3.381
C28	H2B	2.950	C29	H27	3.311
C29	H31A	2.369	C29	H31B	3.074
C29	H31C	3.141	C30	H22A	2.848
C30	H22B	2.718	C30	H28A	2.698
C30	H28B	3.389	C30	H2B	2.209
C31	H22A	3.152	C31	H22B	2.897
C31	H29	2.412	C31	H2B	2.795
H2	H3	2.329	H2A	H3A	2.280
H3	H2B	3.419	H3A	H2B	2.845
H5	H6	2.348	H5A	H6A	2.378
H11A	H21B	2.811	H11A	H21C	2.435
H11B	H21B	2.665	H11B	H21C	3.187
H13	H15	2.543	H15	H16	2.220
H15	H2B	3.406	H16	H17A	2.547
H16	H17B	2.181	H16	H2B	3.389
H17A	H18	2.420	H17B	H18	2.295
H17B	H2B	3.162	H21A	H18	2.121
H21B	H18	3.141	H21C	H18	3.261
H22A	H31B	3.269	H22A	H31C	2.805
H22B	H31B	2.556	H22B	H31C	2.962
H23	H26	2.467	H26	H27	2.183
H27	H28A	2.661	H27	H28B	2.259
H28A	H29	2.321	H28B	H29	2.215
H28B	H2B	3.341	H31A	H29	1.949
H31A	H2B	2.775	H31B	H29	3.135
H31B	H2B	2.840	H31C	H29	3.026
H18	H2B	2.913	H29	H2B	2.272

Table 12. Intermolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
O1	C23[1]	3.26(4)	O2	O2[2]	3.303(7)
O2	O6[2]	3.504(6)	O2	N2[2]	2.903(10)
O3	O3[3]	3.195(10)	O3	O4[3]	3.414(10)
O3	N1[3]	3.057(11)	O3	C1[3]	3.323(10)
O3	C6[3]	3.596(10)	O3A	C12[4]	3.56(3)
O4	O3[3]	3.414(10)	O5	C2[5]	3.328(10)
O5	C2A[5]	2.96(4)	O5	C3[5]	3.345(15)
O5	C3A[5]	3.43(6)	O5	C16[6]	3.475(10)
O5	C31[6]	3.43(2)	O6	O2[2]	3.504(6)
O6	O8[7]	3.511(5)	O6	C10[7]	3.344(7)
O7	C5[8]	3.310(13)	O7	C5A[8]	3.36(6)
O7	C6[8]	3.151(11)	O7	C16[6]	3.309(13)
O7	C17[6]	3.239(14)	O8	O6[7]	3.511(5)
O8	C7[7]	3.484(6)	O8	C13[7]	3.164(16)
O8	C22[7]	3.54(3)	N1	O3[3]	3.057(11)
N1	N1[3]	3.389(12)	N2	O2[2]	2.903(10)
C1	O3[3]	3.323(10)	C2	O5[5]	3.328(10)
C2A	O5[5]	2.96(4)	C3	O5[5]	3.345(15)
C3A	O5[5]	3.43(6)	C4	C10[9]	3.430(13)
C4A	C10[9]	3.48(4)	C5	O7[8]	3.310(13)
C5	C10[9]	3.407(12)	C5A	O7[8]	3.36(6)
C5A	C10[9]	3.21(5)	C6	O3[3]	3.596(10)
C6	O7[8]	3.151(11)	C6A	C10[9]	3.33(3)
C7	O8[7]	3.484(6)	C10	O6[7]	3.344(7)
C10	C4[10]	3.430(13)	C10	C4A[10]	3.48(4)
C10	C5[10]	3.407(12)	C10	C5A[10]	3.21(5)
C10	C6A[10]	3.33(3)	C10	C13[7]	3.525(17)
C12	O3A[11]	3.56(3)	C13	O8[7]	3.164(16)
C13	C10[7]	3.525(17)	C16	O5[1]	3.475(10)
C16	O7[1]	3.309(13)	C17	O7[1]	3.239(14)
C22	O8[7]	3.54(3)	C23	O1[6]	3.26(4)
C23	C27[8]	3.55(5)	C25	C27[8]	3.56(2)
C26	C26[8]	3.47(3)	C26	C27[8]	3.53(3)
C27	C23[8]	3.55(5)	C27	C25[8]	3.56(2)
C27	C26[8]	3.53(3)	C31	O5[1]	3.43(2)

Symmetry Operators:

(1) X-1,Y,Z	(2) -X+1,-Y,-Z+1
(3) -X+2,-Y+1,-Z+2	(4) X,Y+1,Z
(5) -X+2,-Y,-Z+1	(6) X+1,Y,Z
(7) -X+2,-Y-1,-Z+1	(8) -X+2,-Y,-Z+2
(9) X-1,Y+1,Z	(10) X+1,Y-1,Z
(11) X,Y-1,Z	

Table 13. Intermolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H3A[1]	3.457	S1	H8C[1]	3.357
S1	H10A[2]	3.549	S1	H2B[1]	3.369
O1	H8C[1]	2.669	O1	H11A[3]	2.860
O1	H23[3]	2.426	O2	H3[1]	3.106
O2	H3A[1]	2.709	O2	H8B[3]	2.716
O2	H8C[1]	3.246	O2	H10A[2]	3.223
O2	H2B[1]	2.216	O3	H6[4]	3.595
O4	H5[5]	3.310	O4	H8A[6]	3.078
O4	H8C[6]	3.561	O4	H10B[7]	2.728
O4A	H5A[5]	3.332	O5	H2[8]	2.700
O5	H2A[8]	2.102	O5	H3[8]	2.719
O5	H3A[8]	3.095	O5	H13[9]	2.735
O5	H16[10]	2.933	O5	H22A[9]	3.470
O5	H22B[9]	3.478	O5	H31A[10]	2.568
O5	H31B[10]	3.501	O5	H29[10]	3.251
O6	H8B[8]	3.247	O6	H8C[8]	3.204
O6	H10A[9]	2.737	O6	H10B[9]	3.396
O7	H5[7]	2.969	O7	H5A[7]	2.852
O7	H6[7]	2.705	O7	H16[10]	2.661
O7	H17A[10]	3.474	O7	H17B[10]	2.502
O7	H21A[7]	3.578	O7	H27[7]	3.027
O7	H28B[7]	3.340	O7	H31A[10]	3.239
O7	H29[10]	3.050	O8	H6[7]	3.522
O8	H8A[9]	3.445	O8	H13[9]	2.449
O8	H16[10]	3.077	O8	H22B[9]	2.674
O8	H31A[10]	3.448	N2	H3[1]	3.204
N2	H3A[1]	3.061	N1a	H10C[2]	3.354
C1	H10C[2]	3.355	C1A	H10C[2]	2.874
C2	H8A[8]	3.064	C2	H10C[2]	3.492
C2A	H8A[8]	3.126	C2A	H8B[8]	3.542
C2A	H10C[2]	3.351	C3	H8A[8]	3.372
C3	H8B[8]	3.367	C3	H10A[2]	3.446
C3	H10C[2]	3.411	C3	H2B[1]	3.318
C3A	H8A[8]	3.470	C3A	H8B[8]	3.331
C3A	H10A[2]	3.419	C3A	H10C[2]	3.510
C3A	H2B[1]	3.130	C4	H10A[2]	3.072
C4	H10B[2]	3.430	C4	H10C[2]	3.226

Table 13. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C4A	H10A[2]	3.163	C4A	H10B[2]	3.432
C4A	H10C[2]	3.267	C5	H6[5]	3.472
C5	H10A[2]	3.429	C5	H10B[2]	3.131
C5	H10C[2]	3.102	C5A	H6A[5]	3.056
C5A	H10A[2]	3.315	C5A	H10B[2]	2.950
C5A	H10C[2]	2.843	C6	H6[5]	3.324
C6	H10B[7]	3.202	C6	H10C[2]	3.157
C6A	H5A[5]	3.241	C6A	H6A[5]	3.367
C6A	H10B[2]	3.338	C6A	H10B[7]	3.551
C6A	H10C[2]	2.591	C7	H2[8]	3.569
C7	H2A[8]	3.136	C7	H10A[9]	3.405
C7	H13[9]	3.181	C7	H31A[10]	3.517
C8	H2[8]	3.433	C8	H2A[8]	3.339
C8	H3[8]	3.469	C8	H3A[8]	3.523
C8	H8B[8]	3.515	C8	H8C[8]	3.475
C8	H10A[9]	3.251	C8	H10B[9]	3.259
C8	H11A[8]	3.186	C8	H21C[8]	2.708
C8	H26[8]	3.246	C9	H6[7]	3.365
C9	H13[9]	3.408	C9	H16[10]	2.868
C9	H17B[10]	3.235	C9	H31A[10]	3.265
C9	H29[10]	3.519	C10	H5A[11]	3.474
C10	H6[7]	2.915	C10	H6A[7]	3.567
C10	H8A[9]	3.243	C10	H13[9]	3.048
C10	H16[10]	2.979	C10	H22B[9]	2.873
C10	H31A[10]	3.533	C10	H31B[9]	3.524
C11	H8C[8]	3.445	C11	H21B[7]	3.429
C13	H10A[9]	2.938	C14	H10A[9]	3.352
C15	H10A[9]	3.502	C15	H15[12]	3.338
C16	H10C[3]	3.047	C19	H21B[7]	2.899
C20	H21B[7]	3.106	C21	H8A[8]	3.464
C21	H8B[8]	3.423	C21	H8C[8]	3.523
C21	H11B[7]	3.170	C21	H21B[7]	3.023
C22	H10A[9]	3.195	C23	H8C[8]	3.197
C23	H27[7]	3.281	C23	H28A[7]	3.402
C25	H8B[8]	3.537	C25	H8C[8]	3.525
C25	H27[7]	3.422	C26	H8B[8]	3.387
C26	H8C[8]	3.428	C26	H28A[7]	3.386

Table 13. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C27	H23^{7}	3.429	C28	H23^{7}	3.328
C31	H10C^{3}	3.329	C31	H31B^{12}	3.129
C31	H31C^{12}	3.494	H2	O5^{8}	2.700
H2	C7^{8}	3.569	H2	C8^{8}	3.433
H2	H8A^{8}	2.641	H2	H8B^{8}	3.504
H2A	O5^{8}	2.102	H2A	C7^{8}	3.136
H2A	C8^{8}	3.339	H2A	H8A^{8}	2.741
H2A	H8B^{8}	3.245	H3	O2^{1}	3.106
H3	O5^{8}	2.719	H3	N2^{1}	3.204
H3	C8^{8}	3.469	H3	H8A^{8}	3.216
H3	H8B^{8}	2.888	H3	H2B^{1}	2.514
H3A	S1^{1}	3.457	H3A	O2^{1}	2.709
H3A	O5^{8}	3.095	H3A	N2^{1}	3.061
H3A	C8^{8}	3.523	H3A	H8A^{8}	3.371
H3A	H8B^{8}	2.822	H3A	H2B^{1}	2.382
H5	O4^{5}	3.310	H5	O7^{7}	2.969
H5	H6^{5}	3.280	H5	H10B^{2}	3.105
H5	H10C^{2}	3.521	H5A	O4A^{5}	3.332
H5A	O7^{7}	2.852	H5A	C6A^{5}	3.241
H5A	C10^{2}	3.474	H5A	H6A^{5}	2.422
H5A	H10B^{2}	2.948	H5A	H10C^{2}	3.272
H5A	H10C^{7}	3.533	H6	O3^{4}	3.595
H6	O7^{7}	2.705	H6	O8^{7}	3.522
H6	C5^{5}	3.472	H6	C6^{5}	3.324
H6	C9^{7}	3.365	H6	C10^{7}	2.915
H6	H5^{5}	3.280	H6	H6^{5}	2.987
H6	H10B^{7}	2.287	H6	H10C^{2}	3.572
H6	H10C^{7}	2.800	H6A	C5A^{5}	3.056
H6A	C6A^{5}	3.367	H6A	C10^{7}	3.567
H6A	H5A^{5}	2.422	H6A	H6A^{5}	2.989
H6A	H10B^{2}	3.563	H6A	H10B^{7}	2.786
H6A	H10C^{2}	2.881	H6A	H10C^{7}	3.508
H8A	O4^{13}	3.078	H8A	O8^{9}	3.445
H8A	C2^{8}	3.064	H8A	C2A^{8}	3.126
H8A	C3^{8}	3.372	H8A	C3A^{8}	3.470
H8A	C10^{9}	3.243	H8A	C21^{8}	3.464
H8A	H2^{8}	2.641	H8A	H2A^{8}	2.741

Table 13. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H8A	H3^{8}	3.216	H8A	H3A^{8}	3.371
H8A	H10A^{9}	3.148	H8A	H10B^{9}	2.750
H8A	H21C^{8}	2.514	H8A	H26^{8}	3.055
H8B	O2^{10}	2.716	H8B	O6^{8}	3.247
H8B	C2A^{8}	3.542	H8B	C3^{8}	3.367
H8B	C3A^{8}	3.331	H8B	C8^{8}	3.515
H8B	C21^{8}	3.423	H8B	C25^{8}	3.537
H8B	C26^{8}	3.387	H8B	H2^{8}	3.504
H8B	H2A^{8}	3.245	H8B	H3^{8}	2.888
H8B	H3A^{8}	2.822	H8B	H8B^{8}	3.568
H8B	H8C^{8}	3.145	H8B	H11A^{8}	3.073
H8B	H21C^{8}	2.562	H8B	H26^{8}	3.210
H8C	S1^{1}	3.357	H8C	O1^{1}	2.669
H8C	O2^{1}	3.246	H8C	O4^{13}	3.561
H8C	O6^{8}	3.204	H8C	C8^{8}	3.475
H8C	C11^{8}	3.445	H8C	C21^{8}	3.523
H8C	C23^{8}	3.197	H8C	C25^{8}	3.525
H8C	C26^{8}	3.428	H8C	H8B^{8}	3.145
H8C	H8C^{8}	3.489	H8C	H10A^{9}	3.237
H8C	H10B^{9}	3.222	H8C	H11A^{8}	2.475
H8C	H21C^{8}	2.587	H8C	H23^{8}	2.901
H8C	H26^{8}	2.929	H10A	S1^{11}	3.549
H10A	O2^{11}	3.223	H10A	O6^{9}	2.737
H10A	C3^{11}	3.446	H10A	C3A^{11}	3.419
H10A	C4^{11}	3.072	H10A	C4A^{11}	3.163
H10A	C5^{11}	3.429	H10A	C5A^{11}	3.315
H10A	C7^{9}	3.405	H10A	C8^{9}	3.251
H10A	C13^{9}	2.938	H10A	C14^{9}	3.352
H10A	C15^{9}	3.502	H10A	C22^{9}	3.195
H10A	H8A^{9}	3.148	H10A	H8C^{9}	3.237
H10A	H13^{9}	2.693	H10A	H15^{9}	3.111
H10A	H16^{10}	3.396	H10A	H22B^{9}	2.267
H10A	H31B^{9}	2.914	H10B	O4^{7}	2.728
H10B	O6^{9}	3.396	H10B	C4^{11}	3.430
H10B	C4A^{11}	3.432	H10B	C5^{11}	3.131
H10B	C5A^{11}	2.950	H10B	C6^{7}	3.202
H10B	C6A^{11}	3.338	H10B	C6A^{7}	3.551

Table 13. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H10B	C8[9]	3.259	H10B	H5[11]	3.105
H10B	H5A[11]	2.948	H10B	H6[7]	2.287
H10B	H6A[11]	3.563	H10B	H6A[7]	2.786
H10B	H8A[9]	2.750	H10B	H8C[9]	3.222
H10C	N1a[11]	3.354	H10C	C1[11]	3.355
H10C	C1A[11]	2.874	H10C	C2[11]	3.492
H10C	C2A[11]	3.351	H10C	C3[11]	3.411
H10C	C3A[11]	3.510	H10C	C4[11]	3.226
H10C	C4A[11]	3.267	H10C	C5[11]	3.102
H10C	C5A[11]	2.843	H10C	C6[11]	3.157
H10C	C6A[11]	2.591	H10C	C16[10]	3.047
H10C	C31[10]	3.329	H10C	H5[11]	3.521
H10C	H5A[11]	3.272	H10C	H5A[7]	3.533
H10C	H6[11]	3.572	H10C	H6[7]	2.800
H10C	H6A[11]	2.881	H10C	H6A[7]	3.508
H10C	H13[9]	3.508	H10C	H15[9]	3.512
H10C	H16[10]	2.226	H10C	H22B[9]	3.386
H10C	H31A[10]	2.889	H10C	H31B[9]	3.364
H10C	H31C[10]	2.865	H11A	O1[10]	2.860
H11A	C8[8]	3.186	H11A	H8B[8]	3.073
H11A	H8C[8]	2.475	H11B	C21[7]	3.170
H11B	H21A[7]	2.757	H11B	H21B[7]	2.826
H11B	H18[7]	3.118	H13	O5[9]	2.735
H13	O8[9]	2.449	H13	C7[9]	3.181
H13	C9[9]	3.408	H13	C10[9]	3.048
H13	H10A[9]	2.693	H13	H10C[9]	3.508
H13	H13[9]	3.227	H15	C15[12]	3.338
H15	H10A[9]	3.111	H15	H10C[9]	3.512
H15	H15[12]	2.497	H15	H16[12]	3.250
H16	O5[3]	2.933	H16	O7[3]	2.661
H16	O8[3]	3.077	H16	C9[3]	2.868
H16	C10[3]	2.979	H16	H10A[3]	3.396
H16	H10C[3]	2.226	H16	H15[12]	3.250
H17A	O7[3]	3.474	H17A	H21B[7]	3.122
H17B	O7[3]	2.502	H17B	C9[3]	3.235
H21A	O7[7]	3.578	H21A	H11B[7]	2.757
H21A	H21B[7]	3.426	H21B	C11[7]	3.429

Table 13. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H21B	C19[7]	2.899	H21B	C20[7]	3.106
H21B	C21[7]	3.023	H21B	H11B[7]	2.826
H21B	H17A[7]	3.122	H21B	H21A[7]	3.426
H21B	H21B[7]	2.402	H21C	C8[8]	2.708
H21C	H8A[8]	2.514	H21C	H8B[8]	2.562
H21C	H8C[8]	2.587	H22A	O5[9]	3.470
H22B	O5[9]	3.478	H22B	O8[9]	2.674
H22B	C10[9]	2.873	H22B	H10A[9]	2.267
H22B	H10C[9]	3.386	H23	O1[10]	2.426
H23	C27[7]	3.429	H23	C28[7]	3.328
H23	H8C[8]	2.901	H23	H27[7]	3.311
H23	H28A[7]	2.780	H23	H28B[7]	3.270
H23	H29[10]	3.440	H26	C8[8]	3.246
H26	H8A[8]	3.055	H26	H8B[8]	3.210
H26	H8C[8]	2.929	H26	H28A[7]	2.919
H27	O7[7]	3.027	H27	C23[7]	3.281
H27	C25[7]	3.422	H27	H23[7]	3.311
H28A	C23[7]	3.402	H28A	C26[7]	3.386
H28A	H23[7]	2.780	H28A	H26[7]	2.919
H28B	O7[7]	3.340	H28B	H23[7]	3.270
H28B	H28B[14]	3.429	H31A	O5[3]	2.568
H31A	O7[3]	3.239	H31A	O8[3]	3.448
H31A	C7[3]	3.517	H31A	C9[3]	3.265
H31A	C10[3]	3.533	H31A	H10C[3]	2.889
H31A	H31B[12]	3.252	H31B	O5[3]	3.501
H31B	C10[9]	3.524	H31B	C31[12]	3.129
H31B	H10A[9]	2.914	H31B	H10C[9]	3.364
H31B	H31A[12]	3.252	H31B	H31B[12]	2.827
H31B	H31C[12]	2.802	H31C	C31[12]	3.494
H31C	H10C[3]	2.865	H31C	H31B[12]	2.802
H31C	H31C[12]	3.582	H18	H11B[7]	3.118
H29	O5[3]	3.251	H29	O7[3]	3.050
H29	C9[3]	3.519	H29	H23[3]	3.440
H2B	S1[1]	3.369	H2B	O2[1]	2.216
H2B	C3[1]	3.318	H2B	C3A[1]	3.130
H2B	H3[1]	2.514	H2B	H3A[1]	2.382
H2B	H2B[1]	3.463			

Symmetry Operators:

(1)	-X+1,-Y,-Z+1	(2)	X-1,Y+1,Z
(3)	X-1,Y,Z	(4)	-X+2,-Y+1,-Z+2
(5)	-X+1,-Y+1,-Z+2	(6)	X,Y+1,Z+1
(7)	-X+2,-Y,-Z+2	(8)	-X+2,-Y,-Z+1
(9)	-X+2,-Y-1,-Z+1	(10)	X+1,Y,Z
(11)	X+1,Y-1,Z	(12)	-X+1,-Y-1,-Z+1
(13)	X,Y-1,Z-1	(14)	-X+1,-Y,-Z+2

X-ray Structure Report

for

49

August 26, 2013

Experimental

Data Collection

A colorless prismatic crystal of $C_{23}H_{26}N_2O_8S$ having approximate dimensions of 0.200 x 0.200 x 0.200 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer using graphite monochromated Mo-Kα radiation and a rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $29.72 < 2\theta < 29.98^o$ corresponded to a primitive monoclinic cell with dimensions:

a = 8.418(3) Å
b = 21.178(4) Å β = 101.44(2)^o
c = 12.776(3) Å
V = 2232.3(9) Å^3

For Z = 4 and F.W. = 490.53, the calculated density is 1.459 g/cm^3. The reflection conditions of:

h0l: l = 2n
0k0: k = 2n

uniquely determine the space group to be:

$P2_1/c$ (#14)

The data were collected at a temperature of 23 $\pm$ 1 ^{o}C using the ω-2θ scan technique to a maximum 2θ value of 55.0^o. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.26^o with a take-off angle of 6.0^o. Scans of (1.52 + 0.30 tan θ)^o were made at a speed of 4.0^o/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 7 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 235 mm. The computer-controlled slits were set to 3.0 mm (horizontal) and 3.0 mm (vertical).

Data Reduction

Of the 5442 reflections that were collected, 5105 were unique (R_{int} = 0.0570); equivalent reflections were merged. The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied.

The linear absorption coefficient, μ, for Mo-Kα radiation is 1.990 cm^{-1}. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction[1] was applied (coefficient = 42.923000).

Structure Solution and Refinement

The structure was solved by direct methods[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[3] on F^2 was based on 5105 observed reflections and 334 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma||Fo|-|Fc||/\Sigma|Fo| = 0.0351$$

$$wR2 = [\Sigma(w(Fo^2-Fc^2)^2)/\Sigma w(Fo^2)^2]^{1/2} = 0.1523$$

The standard deviation of an observation of unit weight[4] was 1.04. A Sheldrick weighting scheme was used. Plots of $\Sigma w(|Fo|-|Fc|)^2$ versus |Fo|, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.65 and -0.61 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[5] Anomalous dispersion effects were included in Fcalc;[6] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[7] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[8] All calculations were performed using the CrystalStructure[9,10] crystallographic software package.

References

(1) Larson, A. C. (1970), Crystallographic Computing, 291-294. F. R. Ahmed, ed. Munksgaard, Copenhagen (equation 22, with V replaced by the cell volume).

(2) SIR92: Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M., Polidori, G. and Camalli, M. (1994) J. Appl. Cryst., 27, 435.

(3) Least Squares function minimized:

$\Sigma w(F_o^2-F_c^2)^2$ where w = Least Squares weights.

(4) Standard deviation of an observation of unit weight:

$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$

where: N_o = number of observations
N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W. J.; "International Tables for Crystallography", Vol C, (A. J. C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J. H.; "International Tables for Crystallography", Vol C, (A. J. C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000-2010). Tokyo 196-8666, Japan.

(10) CRYSTALS Issue 11: Carruthers, J. R., Rollett, J. S., Betteridge, P. W., Kinna, D., Pearce, L., Larsen, A. and Gabe, E. Chemical Crystallography Laboratory, Oxford, UK. (1999)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{23}H_{26}N_2O_8S$
Formula Weight	490.53
Crystal Color, Habit	colorless, prismatic
Crystal Dimensions	0.200 X 0.200 X 0.200 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (29.7 - 30.0°)
Omega Scan Peak Width at Half-height	0.26°
Lattice Parameters	a = 8.418(3) Å b = 21.178(4) Å c = 12.776(3) Å β = 101.44(2)° V = 2232.3(9) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.459 g/cm^3
F_{000}	1032.00
μ(MoKα)	1.990 cm^{-1}

B. Intensity Measurements

Diffractometer	AFC7R
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factor = 7.21)
Take-off Angle	6.0°
Detector Aperture	3.0 mm horizontal 3.0 mm vertical
Crystal to Detector Distance	235 mm
Voltage, Current	50 kV, 100 mA
Temperature	23.0 °C
Scan Type	ω-2θ
Scan Rate	4.0 °/min (in ω) (up to 7 scans)
Scan Width	(1.52 + 0.30 tan θ)°
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 5442 Unique: 5105 (R_{int} = 0.0570)
Corrections	Lorentz-polarization Secondary Extinction (coefficient: 4.29230e+001)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w(Fo^2-Fc^2)^2$
Least Squares Weights	$1/[0.0047Fo^2+1.0000\sigma(Fo^2)]/(4Fo^2)$
$2\theta_{max}$ cutoff	55.0^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5105
No. Variables	334
Reflection/Parameter Ratio	15.28
Residuals: R1 (I>2.00σ(I))	0.0351
Residuals: R (All reflections)	0.0425
Residuals: wR2 (All reflections)	0.1523
Goodness of Fit Indicator	1.039
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.65 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.61 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
S1	0.40132(3)	0.04220(1)	0.20514(2)	0.787(8)
O1	0.8888(2)	0.30388(4)	0.38102(7)	1.50(2)
O2	0.8405(1)	0.36292(4)	0.23213(7)	1.24(2)
O3	0.5500(2)	0.29653(5)	0.05092(7)	1.45(2)
O4	0.4882(1)	0.33752(4)	0.20012(7)	1.20(2)
O5	0.4089(1)	-0.01579(4)	0.14775(7)	1.21(2)
O6	0.2890(1)	0.04886(4)	0.27546(7)	1.11(2)
O7	0.2069(2)	0.22203(5)	-0.22199(7)	1.62(2)
O8	0.1963(2)	0.29477(4)	-0.10370(8)	1.66(2)
N10	0.2229(2)	0.24054(5)	-0.12890(8)	1.17(2)
N11	0.5809(2)	0.05318(5)	0.27642(8)	0.78(2)
C1	0.7036(2)	0.26470(5)	0.22515(9)	0.80(2)
C2	0.7959(2)	0.21661(5)	0.16607(9)	0.98(2)
C3	0.7509(2)	0.15249(5)	0.20463(9)	0.82(2)
C4	0.7840(2)	0.09401(5)	0.17473(9)	0.82(2)
C5	0.7323(2)	0.03947(5)	0.2388(1)	0.87(2)
C6	0.8508(2)	0.03462(5)	0.34789(9)	0.96(2)
C7	0.7782(2)	0.07842(5)	0.42530(9)	0.85(2)
C8	0.6228(2)	0.10673(5)	0.35198(8)	0.73(2)
C9	0.6605(2)	0.16290(5)	0.29009(8)	0.78(2)
C10	0.6300(2)	0.22423(5)	0.30191(8)	0.80(2)
C11	0.8204(2)	0.31204(5)	0.29006(9)	0.88(2)
C12	0.5731(2)	0.30055(5)	0.14636(9)	0.85(2)
C13	0.8780(2)	0.07786(6)	0.0906(1)	1.17(2)
C14	0.8979(2)	0.12907(6)	0.47627(9)	1.19(3)
C15	0.7234(2)	0.03878(5)	0.5121(1)	1.07(3)
C16	0.9463(2)	0.41120(6)	0.2873(1)	1.36(3)
C17	0.3654(2)	0.37652(6)	0.1360(1)	1.52(3)
C18	0.3554(2)	0.10307(5)	0.10858(9)	0.83(2)
C19	0.2673(2)	0.15535(6)	0.13025(9)	1.02(2)
C20	0.2261(2)	0.20194(5)	0.0528(1)	1.06(3)
C21	0.2751(2)	0.19377(6)	-0.04373(9)	1.01(2)
C22	0.3673(2)	0.14308(6)	-0.06590(9)	1.11(3)
C23	0.4091(2)	0.09705(6)	0.01229(9)	1.04(2)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Atomic coordinates and B_{iso} involving hydrogen atoms

atom	x	y	z	B_{iso}
H1	0.9125	0.2222	0.1847	1.21
H2	0.7608	0.2190	0.0891	1.22
H3	0.7252	-0.0003	0.1990	1.06
H4	0.9578	0.0488	0.3410	1.17
H5	0.8567	-0.0087	0.3729	1.21
H6	0.5368	0.1156	0.3916	0.87
H7	0.5713	0.2401	0.3506	0.95
H8	0.9752	0.0558	0.1224	1.51
H9	0.8130	0.0515	0.0377	1.47
H10	0.9059	0.1159	0.0575	1.52
H11	0.8442	0.1584	0.5148	1.38
H12	0.9387	0.1511	0.4214	1.45
H13	0.9863	0.1096	0.5245	1.42
H14	0.6886	0.0662	0.5630	1.31
H15	0.8119	0.0132	0.5476	1.29
H16	0.6350	0.0121	0.4798	1.29
H17	0.9131	0.4220	0.3527	1.68
H18	0.9408	0.4480	0.2428	1.65
H19	1.0557	0.3957	0.3030	1.65
H20	0.2921	0.3504	0.0872	1.93
H21	0.3064	0.3987	0.1816	1.95
H22	0.4160	0.4064	0.0965	1.98
H23	0.2359	0.1589	0.1958	1.29
H24	0.1681	0.2376	0.0654	1.31
H25	0.3998	0.1399	-0.1311	1.39
H26	0.4716	0.0625	0.0006	1.30

Table 3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	0.0104(2)	0.0108(2)	0.0086(2)	-0.00187(8)	0.0016(2)	0.00055(8)
O1	0.0213(5)	0.0199(5)	0.0131(5)	-0.0039(4)	-0.0031(4)	0.0030(4)
O2	0.0202(5)	0.0127(5)	0.0131(5)	-0.0061(4)	0.0010(4)	0.0018(3)
O3	0.0171(5)	0.0266(6)	0.0103(4)	0.0036(4)	0.0006(4)	-0.0003(4)
O4	0.0169(5)	0.0171(5)	0.0118(4)	0.0067(4)	0.0029(4)	0.0015(4)
O5	0.0185(5)	0.0116(5)	0.0149(4)	-0.0026(3)	0.0011(3)	-0.0031(3)
O6	0.0113(5)	0.0193(5)	0.0127(4)	-0.0022(3)	0.0050(4)	0.0025(3)
O7	0.0238(5)	0.0266(6)	0.0118(4)	0.0042(4)	0.0050(4)	0.0046(4)
O8	0.0229(5)	0.0152(5)	0.0250(5)	0.0049(4)	0.0044(4)	0.0040(4)
N10	0.0109(5)	0.0187(6)	0.0152(5)	0.0006(4)	0.0032(4)	0.0040(4)
N11	0.0097(5)	0.0110(5)	0.0088(5)	-0.0003(4)	0.0019(4)	-0.0014(4)
C1	0.0106(5)	0.0108(5)	0.0093(5)	0.0000(4)	0.0032(4)	0.0004(4)
C2	0.0161(6)	0.0104(5)	0.0124(5)	0.0002(4)	0.0069(4)	-0.0009(4)
C3	0.0101(5)	0.0131(6)	0.0080(5)	-0.0000(4)	0.0020(4)	0.0006(4)
C4	0.0098(5)	0.0138(6)	0.0079(5)	-0.0000(4)	0.0026(4)	-0.0002(4)
C5	0.0111(6)	0.0115(6)	0.0114(6)	0.0012(4)	0.0041(4)	-0.0002(4)
C6	0.0121(6)	0.0126(6)	0.0122(6)	0.0027(4)	0.0031(4)	0.0013(4)
C7	0.0115(5)	0.0119(5)	0.0090(5)	-0.0007(4)	0.0021(4)	0.0012(4)
C8	0.0108(5)	0.0101(5)	0.0075(5)	-0.0015(4)	0.0027(4)	-0.0006(4)
C9	0.0100(5)	0.0125(6)	0.0072(5)	-0.0001(4)	0.0021(4)	0.0016(4)
C10	0.0109(5)	0.0116(6)	0.0086(5)	-0.0006(4)	0.0033(4)	0.0018(4)
C11	0.0112(5)	0.0113(5)	0.0116(5)	0.0006(4)	0.0035(4)	0.0013(4)
C12	0.0101(6)	0.0117(6)	0.0113(5)	-0.0012(4)	0.0037(4)	0.0016(4)
C13	0.0162(6)	0.0162(6)	0.0143(5)	-0.0000(5)	0.0086(5)	-0.0022(5)
C14	0.0139(6)	0.0168(6)	0.0134(6)	-0.0029(4)	0.0001(5)	0.0006(5)
C15	0.0161(6)	0.0139(6)	0.0105(6)	-0.0010(4)	0.0026(5)	0.0031(4)
C16	0.0186(6)	0.0135(6)	0.0186(6)	-0.0051(5)	0.0011(5)	0.0007(5)
C17	0.0186(6)	0.0191(6)	0.0200(6)	0.0075(5)	0.0034(5)	0.0062(5)
C18	0.0092(5)	0.0131(5)	0.0083(5)	-0.0004(4)	-0.0002(4)	0.0012(4)
C19	0.0134(6)	0.0157(6)	0.0103(5)	-0.0005(4)	0.0038(4)	-0.0017(4)
C20	0.0131(6)	0.0148(6)	0.0123(6)	0.0015(4)	0.0026(5)	-0.0005(4)
C21	0.0105(6)	0.0159(6)	0.0115(6)	-0.0010(4)	0.0011(4)	0.0018(4)
C22	0.0143(6)	0.0183(6)	0.0100(5)	0.0007(5)	0.0033(4)	0.0015(4)
C23	0.0132(6)	0.0150(6)	0.0114(5)	0.0018(4)	0.0029(4)	-0.0002(4)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
S1	O5	1.4383(10)	S1	O6	1.4346(11)
S1	N11	1.6192(11)	S1	C18	1.7731(12)
O1	C11	1.2027(14)	O2	C11	1.3368(15)
O2	C16	1.4446(15)	O3	C12	1.1991(15)
O4	C12	1.3380(16)	O4	C17	1.4443(16)
O7	N10	1.2339(14)	O8	N10	1.2253(14)
N10	C21	1.4726(16)	N11	C5	1.4774(18)
N11	C8	1.4857(15)	C1	C2	1.5629(17)
C1	C10	1.5238(17)	C1	C11	1.5284(15)
C1	C12	1.5358(15)	C2	C3	1.5179(16)
C3	C4	1.3416(16)	C3	C9	1.4660(18)
C4	C5	1.5283(17)	C4	C13	1.4949(19)
C5	C6	1.5477(16)	C6	C7	1.5659(17)
C7	C8	1.5691(16)	C7	C14	1.5266(17)
C7	C15	1.5325(18)	C8	C9	1.4969(16)
C9	C10	1.3384(16)	C18	C19	1.3906(18)
C18	C23	1.3977(18)	C19	C20	1.3921(17)
C20	C21	1.3863(19)	C21	C22	1.3860(18)
C22	C23	1.3902(17)			

Table 5. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
C2	H1	0.970	C2	H2	0.970
C5	H3	0.980	C6	H4	0.970
C6	H5	0.970	C8	H6	0.980
C10	H7	0.930	C13	H8	0.960
C13	H9	0.960	C13	H10	0.960
C14	H11	0.960	C14	H12	0.960
C14	H13	0.960	C15	H14	0.960
C15	H15	0.960	C15	H16	0.960
C16	H17	0.960	C16	H18	0.960
C16	H19	0.960	C17	H20	0.960
C17	H21	0.960	C17	H22	0.960
C19	H23	0.930	C20	H24	0.930
C22	H25	0.930	C23	H26	0.930

Table 6. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
O5	S1	O6	120.32(6)	O5	S1	N11	106.16(6)
O5	S1	C18	106.96(6)	O6	S1	N11	106.94(6)
O6	S1	C18	106.53(6)	N11	S1	C18	109.70(6)
C11	O2	C16	115.71(9)	C12	O4	C17	116.01(10)
O7	N10	O8	124.07(11)	O7	N10	C21	117.26(11)
O8	N10	C21	118.66(10)	S1	N11	C5	123.94(9)
S1	N11	C8	123.35(9)	C5	N11	C8	104.62(9)
C2	C1	C10	104.41(9)	C2	C1	C11	111.20(10)
C2	C1	C12	111.42(10)	C10	C1	C11	108.65(10)
C10	C1	C12	111.73(10)	C11	C1	C12	109.33(9)
C1	C2	C3	104.26(10)	C2	C3	C4	130.85(12)
C2	C3	C9	107.87(10)	C4	C3	C9	121.25(11)
C3	C4	C5	116.60(11)	C3	C4	C13	125.83(11)
C5	C4	C13	117.38(10)	N11	C5	C4	112.42(10)
N11	C5	C6	99.43(10)	C4	C5	C6	109.36(9)
C5	C6	C7	105.47(9)	C6	C7	C8	103.47(9)
C6	C7	C14	112.22(11)	C6	C7	C15	110.09(9)
C8	C7	C14	112.83(9)	C8	C7	C15	107.83(10)
C14	C7	C15	110.14(10)	N11	C8	C7	99.12(9)
N11	C8	C9	108.14(9)	C7	C8	C9	112.32(10)
C3	C9	C8	118.02(10)	C3	C9	C10	111.69(10)
C8	C9	C10	130.24(11)	C1	C10	C9	111.19(11)
O1	C11	O2	124.18(11)	O1	C11	C1	124.28(11)
O2	C11	C1	111.51(9)	O3	C12	O4	124.64(11)
O3	C12	C1	125.57(12)	O4	C12	C1	109.78(10)
S1	C18	C19	119.44(10)	S1	C18	C23	118.84(9)
C19	C18	C23	121.73(11)	C18	C19	C20	119.37(12)
C19	C20	C21	117.88(11)	N10	C21	C20	118.37(11)
N10	C21	C22	117.85(11)	C20	C21	C22	123.76(11)
C21	C22	C23	117.93(12)	C18	C23	C22	119.25(12)

Table 7. Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom	angle
C1	C2	H1	112.2	C1	C2	H2	112.0
C3	C2	H1	109.6	C3	C2	H2	109.2
H1	C2	H2	109.4	N11	C5	H3	111.7
C4	C5	H3	111.5	C6	C5	H3	111.8
C5	C6	H4	110.0	C5	C6	H5	110.0
C7	C6	H4	111.1	C7	C6	H5	110.7
H4	C6	H5	109.5	N11	C8	H6	112.2
C7	C8	H6	112.2	C9	C8	H6	112.1
C1	C10	H7	124.4	C9	C10	H7	124.4
C4	C13	H8	109.6	C4	C13	H9	109.3
C4	C13	H10	109.6	H8	C13	H9	109.4
H8	C13	H10	109.4	H9	C13	H10	109.4
C7	C14	H11	109.6	C7	C14	H12	109.4
C7	C14	H13	109.5	H11	C14	H12	109.4
H11	C14	H13	109.4	H12	C14	H13	109.4
C7	C15	H14	109.6	C7	C15	H15	109.6
C7	C15	H16	109.3	H14	C15	H15	109.4
H14	C15	H16	109.4	H15	C15	H16	109.4
O2	C16	H17	109.6	O2	C16	H18	109.4
O2	C16	H19	109.4	H17	C16	H18	109.4
H17	C16	H19	109.4	H18	C16	H19	109.4
O4	C17	H20	109.6	O4	C17	H21	109.5
O4	C17	H22	109.5	H20	C17	H21	109.4
H20	C17	H22	109.4	H21	C17	H22	109.4
C18	C19	H23	120.1	C20	C19	H23	120.5
C19	C20	H24	121.1	C21	C20	H24	121.0
C21	C22	H25	121.0	C23	C22	H25	121.1
C18	C23	H26	120.3	C22	C23	H26	120.4

Table 8. Torsion Angles(°)
(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
O5	S1	N11	C5	39.21(10)	O5	S1	N11	C8	-176.98(8)
O5	S1	C18	C19	149.45(8)	O5	S1	C18	C23	-30.48(10)
O6	S1	N11	C5	168.82(8)	O6	S1	N11	C8	-47.37(10)
O6	S1	C18	C19	19.59(9)	O6	S1	C18	C23	-160.35(7)
N11	S1	C18	C19	-95.82(9)	N11	S1	C18	C23	84.24(9)
C18	S1	N11	C5	-76.03(9)	C18	S1	N11	C8	67.78(10)
C16	O2	C11	O1	-3.02(17)	C16	O2	C11	C1	178.70(9)
C17	O4	C12	O3	-2.54(16)	C17	O4	C12	C1	177.22(9)
O7	N10	C21	C20	-150.99(10)	O7	N10	C21	C22	27.34(15)
O8	N10	C21	C20	28.16(15)	O8	N10	C21	C22	-153.51(10)
S1	N11	C5	C4	84.58(11)	S1	N11	C5	C6	-159.83(7)
S1	N11	C8	C7	158.70(8)	S1	N11	C8	C9	-84.08(11)
C5	N11	C8	C7	-51.71(10)	C5	N11	C8	C9	65.51(10)
C8	N11	C5	C4	-64.78(10)	C8	N11	C5	C6	50.81(9)
C2	C1	C10	C9	-3.01(11)	C10	C1	C2	C3	6.35(10)
C2	C1	C11	O1	-88.56(14)	C2	C1	C11	O2	89.72(11)
C11	C1	C2	C3	123.34(9)	C2	C1	C12	O3	-5.13(15)
C2	C1	C12	O4	175.11(8)	C12	C1	C2	C3	-114.41(9)
C10	C1	C11	O1	25.81(15)	C10	C1	C11	O2	-155.90(9)
C11	C1	C10	C9	-121.75(9)	C10	C1	C12	O3	-121.50(12)
C10	C1	C12	O4	58.75(11)	C12	C1	C10	C9	117.54(10)
C11	C1	C12	O3	118.19(12)	C11	C1	C12	O4	-61.57(12)
C12	C1	C11	O1	147.99(11)	C12	C1	C11	O2	-33.73(13)
C1	C2	C3	C4	174.11(10)	C1	C2	C3	C9	-7.59(10)
C2	C3	C4	C5	174.35(9)	C2	C3	C4	C13	-0.47(18)
C2	C3	C9	C8	-171.47(8)	C2	C3	C9	C10	6.21(11)
C4	C3	C9	C8	7.03(14)	C4	C3	C9	C10	-175.29(9)
C9	C3	C4	C5	-3.76(14)	C9	C3	C4	C13	-178.58(8)
C3	C4	C5	N11	33.87(13)	C3	C4	C5	C6	-75.57(12)
C13	C4	C5	N11	-150.85(9)	C13	C4	C5	C6	99.71(11)
N11	C5	C6	C7	-28.50(10)	C4	C5	C6	C7	89.41(11)
C5	C6	C7	C8	-1.36(11)	C5	C6	C7	C14	-123.28(9)
C5	C6	C7	C15	113.66(9)	C6	C7	C8	N11	30.49(10)
C6	C7	C8	C9	-83.51(10)	C14	C7	C8	N11	152.00(10)
C14	C7	C8	C9	38.01(13)	C15	C7	C8	N11	-86.13(10)
C15	C7	C8	C9	159.87(8)	N11	C8	C9	C3	-38.83(12)
N11	C8	C9	C10	144.00(10)	C7	C8	C9	C3	69.52(11)

Table 8. Torsion angles (°) (continued)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C7	C8	C9	C10	-107.65(12)	C3	C9	C10	C1	-1.89(12)
C8	C9	C10	C1	175.43(9)	S1	C18	C19	C20	-177.56(7)
S1	C18	C23	C22	177.02(7)	C19	C18	C23	C22	-2.91(17)
C23	C18	C19	C20	2.38(17)	C18	C19	C20	C21	0.18(16)
C19	C20	C21	N10	175.95(10)	C19	C20	C21	C22	-2.27(17)
N10	C21	C22	C23	-176.49(9)	C20	C21	C22	C23	1.74(17)
C21	C22	C23	C18	0.86(16)					

Table 9. Intramolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
S1	C4	3.4970(16)	S1	C9	3.3959(12)
O1	C2	3.2737(15)	O1	C10	2.7825(16)
O1	C12	3.5912(17)	O1	C16	2.6577(17)
O2	O3	3.3270(15)	O2	O4	2.9617(16)
O2	C2	3.2138(15)	O2	C12	2.6523(16)
O3	O8	3.2305(17)	O3	N10	3.4289(16)
O3	C2	2.8467(16)	O3	C10	3.4962(15)
O3	C11	3.4444(16)	O3	C17	2.6716(19)
O3	C20	3.3874(18)	O3	C21	3.2316(17)
O4	C10	2.8734(14)	O4	C11	2.8564(17)
O5	C5	2.9794(17)	O5	C23	2.9507(16)
O6	C8	3.0433(16)	O6	C19	2.9029(16)
O7	C20	3.5075(17)	O7	C22	2.7436(16)
O8	C17	3.5597(17)	O8	C20	2.7793(16)
O8	C22	3.5140(16)	N11	C3	2.7988(17)
N11	C15	3.0268(17)	N11	C23	3.5222(17)
C2	C13	3.2103(18)	C3	C6	3.1109(16)
C3	C7	3.1945(17)	C3	C11	3.5634(16)
C3	C12	3.4907(16)	C3	C14	3.4810(17)
C3	C18	3.4729(19)	C3	C23	3.5905(18)
C4	C7	3.2283(18)	C4	C8	2.8745(18)
C4	C10	3.5726(17)	C4	C18	3.543(2)
C4	C23	3.4169(19)	C5	C9	2.7900(16)
C5	C15	3.506(2)	C5	C18	3.5430(19)
C6	C9	3.1658(16)	C6	C13	3.4632(19)
C7	C10	3.5772(16)	C8	C18	3.4588(17)
C9	C11	3.4334(16)	C9	C12	3.4461(16)
C9	C14	2.8774(16)	C9	C18	3.3488(17)
C9	C19	3.5308(19)	C10	C14	3.4811(17)
C12	C20	3.5967(18)	C18	C21	2.7224(17)
C19	C22	2.8090(19)	C20	C23	2.8088(18)

Table 10. Intramolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H3	2.887	S1	H6	2.883
S1	H23	2.828	S1	H26	2.825
O1	H1	3.086	O1	H7	2.951
O1	H11	3.578	O1	H12	3.291
O1	H17	2.542	O1	H18	3.596
O1	H19	2.702	O2	H1	3.125
O2	H2	3.549	O3	H1	3.555
O3	H2	2.395	O3	H20	2.575
O3	H22	2.700	O3	H24	3.488
O4	H7	2.812	O4	H24	3.586
O5	H3	2.633	O5	H26	2.638
O6	H6	2.706	O6	H16	3.591
O6	H23	2.547	O7	H25	2.502
O8	H20	2.685	O8	H24	2.529
N10	H20	3.569	N10	H24	2.614
N10	H25	2.603	N11	H4	3.118
N11	H5	2.738	N11	H16	2.692
N11	H26	3.467	C2	H7	3.338
C2	H10	2.801	C2	H12	3.530
C3	H3	3.243	C3	H4	3.114
C3	H6	3.358	C3	H7	3.213
C3	H8	3.107	C3	H9	3.137
C3	H10	2.610	C3	H12	2.905
C4	H1	2.915	C4	H2	2.855
C4	H4	2.518	C4	H5	3.302
C4	H12	3.386	C4	H26	3.160
C5	H6	3.223	C5	H8	2.778
C5	H9	2.796	C5	H10	3.386
C5	H12	3.527	C5	H16	3.389
C5	H26	3.416	C6	H6	3.290
C6	H8	3.285	C6	H11	3.387
C6	H12	2.690	C6	H13	2.809
C6	H14	3.369	C6	H15	2.675
C6	H16	2.753	C7	H3	3.290
C8	H3	3.220	C8	H4	3.105
C8	H5	3.118	C8	H7	2.857
C8	H11	2.732	C8	H12	2.794

Table 10. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C8	H13	3.399	C8	H14	2.778
C8	H15	3.336	C8	H16	2.575
C9	H1	3.004	C9	H2	3.094
C9	H4	3.448	C9	H11	2.980
C9	H12	2.609	C9	H23	3.539
C10	H1	3.052	C10	H2	3.131
C10	H6	2.753	C10	H11	3.263
C10	H12	3.149	C11	H1	2.539
C11	H2	3.196	C11	H7	2.821
C11	H17	2.535	C11	H18	3.150
C11	H19	2.638	C12	H1	3.256
C12	H2	2.544	C12	H7	2.909
C12	H20	2.564	C12	H21	3.157
C12	H22	2.617	C13	H1	3.276
C13	H2	3.146	C13	H3	2.650
C13	H4	3.196	C13	H26	3.401
C14	H4	2.545	C14	H5	3.193
C14	H6	3.031	C14	H14	2.623
C14	H15	2.764	C14	H16	3.329
C15	H4	3.229	C15	H5	2.495
C15	H6	2.553	C15	H11	2.728
C15	H12	3.334	C15	H13	2.652
C17	H24	3.411	C18	H24	3.250
C18	H25	3.253	C19	H26	3.270
C20	H20	3.209	C20	H25	3.278
C21	H23	3.228	C21	H26	3.226
C22	H24	3.278	C23	H9	3.487
C23	H23	3.270	H1	H10	2.771
H1	H12	3.347	H2	H10	2.573
H3	H4	2.607	H3	H5	2.284
H3	H8	2.759	H3	H9	2.570
H3	H10	3.568	H3	H26	3.258
H4	H8	2.829	H4	H11	3.476
H4	H12	2.417	H4	H13	2.644
H4	H15	3.214	H5	H12	3.485
H5	H13	3.222	H5	H14	3.432
H5	H15	2.382	H5	H16	2.560

Table 10. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H6	H7	2.716	H6	H11	2.895
H6	H12	3.413	H6	H14	2.532
H6	H15	3.494	H6	H16	2.528
H6	H23	3.317	H7	H11	3.280
H7	H12	3.582	H7	H23	3.553
H9	H26	2.828	H11	H14	2.496
H11	H15	3.124	H11	H16	3.550
H12	H14	3.528	H12	H15	3.599
H13	H14	2.803	H13	H15	2.566
H13	H16	3.559	H20	H24	2.601
H23	H24	2.345	H25	H26	2.341

Table 11. Intermolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
O1	O7[1]	3.2552(18)	O1	O8[1]	3.3017(15)
O1	N10[1]	2.9917(17)	O1	C20[1]	3.2277(18)
O1	C21[1]	3.2032(19)	O2	O7[1]	3.5176(16)
O2	C14[2]	3.4020(17)	O2	C15[2]	3.4802(16)
O3	C8[2]	3.4130(16)	O3	C10[2]	3.4081(16)
O4	O7[3]	3.0205(16)	O4	C22[3]	3.3686(17)
O5	C22[4]	3.5624(17)	O5	C23[4]	3.2759(17)
O6	C15[5]	3.3072(16)	O6	C16[6]	3.5265(16)
O7	O1[7]	3.2552(18)	O7	O2[7]	3.5176(16)
O7	O4[2]	3.0205(16)	O7	C11[7]	3.3651(19)
O7	C16[7]	3.5899(18)	O7	C17[2]	3.2232(19)
O7	C19[2]	3.3087(17)	O7	C20[2]	3.3294(17)
O8	O1[7]	3.3017(15)	O8	C14[7]	3.3125(19)
N10	O1[7]	2.9917(17)	N10	C11[7]	3.5213(19)
C8	O3[3]	3.4130(16)	C10	O3[3]	3.4081(16)
C11	O7[1]	3.3651(19)	C11	N10[1]	3.5213(19)
C14	O2[3]	3.4020(17)	C14	O8[1]	3.3125(19)
C15	O2[3]	3.4802(16)	C15	O6[5]	3.3072(16)
C16	O6[8]	3.5265(16)	C16	O7[1]	3.5899(18)
C17	O7[3]	3.2232(19)	C19	O7[3]	3.3087(17)
C20	O1[7]	3.2277(18)	C20	O7[3]	3.3294(17)
C21	O1[7]	3.2032(19)	C22	O4[2]	3.3686(17)
C22	O5[4]	3.5624(17)	C23	O5[4]	3.2759(17)

Symmetry Operators:

(1)	X+1,-Y+1/2,Z+1/2	(2)	X,-Y+1/2,Z+1/2-1
(3)	X,-Y+1/2,Z+1/2	(4)	-X+1,-Y,-Z
(5)	-X+1,-Y,-Z+1	(6)	-X+1,Y+1/2-1,-Z+1/2
(7)	X-1,-Y+1/2,Z+1/2-1	(8)	-X+1,Y+1/2,-Z+1/2

Table 12. Intermolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H8[1]	3.545	O1	H2[2]	3.099
O1	H10[2]	2.804	O1	H24[3]	3.106
O2	H11[4]	2.819	O2	H13[4]	3.190
O2	H14[4]	2.732	O2	H15[4]	3.503
O3	H6[4]	2.744	O3	H7[4]	2.714
O3	H11[4]	2.776	O3	H14[4]	3.125
O4	H14[4]	3.354	O4	H25[2]	2.463
O5	H9[5]	2.814	O5	H17[6]	3.013
O5	H18[6]	3.584	O5	H21[6]	3.421
O5	H25[5]	3.112	O5	H26[5]	2.518
O6	H4[1]	3.066	O6	H8[1]	2.962
O6	H14[7]	3.175	O6	H15[7]	2.884
O6	H16[7]	3.325	O6	H17[6]	3.418
O6	H18[6]	2.860	O7	H1[8]	2.790
O7	H7[4]	3.128	O7	H19[8]	2.846
O7	H20[4]	3.083	O7	H21[4]	3.028
O7	H23[4]	2.761	O7	H24[4]	2.805
O8	H1[8]	3.254	O8	H6[4]	3.448
O8	H7[4]	3.403	O8	H12[8]	2.529
O8	H13[8]	3.325	O8	H23[4]	2.824
N10	H1[8]	3.264	N10	H7[4]	3.024
N10	H12[8]	3.466	N10	H19[8]	3.252
N10	H23[4]	3.108	N11	H21[6]	3.419
N11	H22[6]	3.504	C1	H11[4]	3.540
C2	H11[4]	3.349	C5	H18[9]	3.335
C5	H21[6]	3.187	C6	H15[10]	3.060
C6	H18[9]	2.931	C6	H21[6]	3.159
C12	H11[4]	3.211	C12	H14[4]	3.234
C13	H17[4]	3.112	C13	H23[11]	3.496
C14	H5[10]	3.591	C14	H20[3]	3.368
C15	H4[10]	3.487	C15	H16[7]	3.224
C15	H18[2]	3.159	C15	H22[6]	3.242
C15	H22[2]	3.212	C16	H3[12]	3.316
C16	H4[12]	3.514	C16	H5[12]	3.341
C16	H8[12]	3.292	C16	H10[2]	3.581
C16	H13[4]	3.468	C16	H14[4]	3.269
C16	H15[4]	3.442	C16	H21[11]	3.564

Table 12. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C17	H3[13]	3.530	C17	H5[13]	3.055
C17	H13[8]	3.240	C17	H14[4]	3.279
C17	H16[13]	3.229	C17	H25[2]	2.952
C18	H8[1]	3.392	C19	H1[1]	3.498
C19	H8[1]	3.227	C19	H10[1]	3.114
C20	H1[1]	3.429	C20	H10[1]	3.264
C21	H7[4]	3.367	C21	H19[8]	3.067
C22	H3[5]	3.480	C22	H7[4]	3.307
C22	H19[8]	2.936	C22	H21[4]	3.286
C23	H3[5]	3.399	C23	H19[8]	3.587
C23	H26[5]	3.539	H1	O7[3]	2.790
H1	O8[3]	3.254	H1	N10[3]	3.264
H1	C19[11]	3.498	H1	C20[11]	3.429
H1	H11[4]	3.307	H1	H23[11]	3.012
H1	H24[11]	2.891	H2	O1[4]	3.099
H2	H7[4]	3.264	H2	H11[4]	2.898
H2	H24[11]	3.524	H3	C16[9]	3.316
H3	C17[6]	3.530	H3	C22[5]	3.480
H3	C23[5]	3.399	H3	H18[9]	2.971
H3	H19[9]	2.876	H3	H21[6]	2.670
H3	H25[5]	3.200	H3	H26[5]	3.051
H4	O6[11]	3.066	H4	C15[10]	3.487
H4	C16[9]	3.514	H4	H15[10]	2.531
H4	H18[9]	2.606	H5	C14[10]	3.591
H5	C16[9]	3.341	H5	C17[6]	3.055
H5	H13[10]	2.709	H5	H15[10]	2.774
H5	H18[9]	2.632	H5	H19[9]	3.217
H5	H20[6]	3.314	H5	H21[6]	2.416
H5	H22[6]	3.001	H6	O3[2]	2.744
H6	O8[2]	3.448	H6	H22[2]	3.026
H7	O3[2]	2.714	H7	O7[2]	3.128
H7	O8[2]	3.403	H7	N10[2]	3.024
H7	C21[2]	3.367	H7	C22[2]	3.307
H7	H2[2]	3.264	H7	H25[2]	2.954
H8	S1[11]	3.545	H8	O6[11]	2.962
H8	C16[9]	3.292	H8	C18[11]	3.392
H8	C19[11]	3.227	H8	H17[9]	2.981

Table 12. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H8	H17[4]	3.414	H8	H18[9]	2.862
H8	H19[9]	3.544	H8	H23[11]	3.106
H9	O5[5]	2.814	H9	H17[4]	2.721
H9	H26[5]	3.368	H10	O1[4]	2.804
H10	C16[4]	3.581	H10	C19[11]	3.114
H10	C20[11]	3.264	H10	H17[4]	2.749
H10	H23[11]	3.118	H10	H24[11]	3.382
H11	O2[2]	2.819	H11	O3[2]	2.776
H11	C1[2]	3.540	H11	C2[2]	3.349
H11	C12[2]	3.211	H11	H1[2]	3.307
H11	H2[2]	2.898	H11	H24[3]	3.464
H12	O8[3]	2.529	H12	N10[3]	3.466
H12	H20[3]	3.292	H12	H24[3]	3.356
H13	O2[2]	3.190	H13	O8[3]	3.325
H13	C16[2]	3.468	H13	C17[3]	3.240
H13	H5[10]	2.709	H13	H15[10]	3.334
H13	H18[2]	3.136	H13	H19[2]	3.491
H13	H20[3]	2.677	H13	H21[3]	3.029
H13	H22[3]	3.567	H13	H24[3]	3.574
H14	O2[2]	2.732	H14	O3[2]	3.125
H14	O4[2]	3.354	H14	O6[7]	3.175
H14	C12[2]	3.234	H14	C16[2]	3.269
H14	C17[2]	3.279	H14	H16[7]	3.142
H14	H18[2]	2.818	H14	H22[2]	2.485
H15	O2[2]	3.503	H15	O6[7]	2.884
H15	C6[10]	3.060	H15	C16[2]	3.442
H15	H4[10]	2.531	H15	H5[10]	2.774
H15	H13[10]	3.334	H15	H18[2]	2.645
H15	H22[6]	3.284	H16	O6[7]	3.325
H16	C15[7]	3.224	H16	C17[6]	3.229
H16	H14[7]	3.142	H16	H16[7]	2.482
H16	H21[6]	3.265	H16	H22[6]	2.444
H16	H22[2]	3.114	H17	O5[13]	3.013
H17	O6[13]	3.418	H17	C13[2]	3.112
H17	H8[12]	2.981	H17	H8[2]	3.414
H17	H9[2]	2.721	H17	H10[2]	2.749
H18	O5[13]	3.584	H18	O6[13]	2.860

Table 12. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H18	C5[12]	3.335	H18	C6[12]	2.931
H18	C15[4]	3.159	H18	H3[12]	2.971
H18	H4[12]	2.606	H18	H5[12]	2.632
H18	H8[12]	2.862	H18	H13[4]	3.136
H18	H14[4]	2.818	H18	H15[4]	2.645
H18	H21[11]	3.482	H19	O7[3]	2.846
H19	N10[3]	3.252	H19	C21[3]	3.067
H19	C22[3]	2.936	H19	C23[3]	3.587
H19	H3[12]	2.876	H19	H5[12]	3.217
H19	H8[12]	3.544	H19	H13[4]	3.491
H19	H21[11]	2.857	H19	H25[3]	2.950
H20	O7[2]	3.083	H20	C14[8]	3.368
H20	H5[13]	3.314	H20	H12[8]	3.292
H20	H13[8]	2.677	H20	H25[2]	3.538
H21	O5[13]	3.421	H21	O7[2]	3.028
H21	N11[13]	3.419	H21	C5[13]	3.187
H21	C6[13]	3.159	H21	C16[1]	3.564
H21	C22[2]	3.286	H21	H3[13]	2.670
H21	H5[13]	2.416	H21	H13[8]	3.029
H21	H16[13]	3.265	H21	H18[1]	3.482
H21	H19[1]	2.857	H21	H25[2]	2.503
H22	N11[13]	3.504	H22	C15[13]	3.242
H22	C15[4]	3.212	H22	H5[13]	3.001
H22	H6[4]	3.026	H22	H13[8]	3.567
H22	H14[4]	2.485	H22	H15[13]	3.284
H22	H16[13]	2.444	H22	H16[4]	3.114
H23	O7[2]	2.761	H23	O8[2]	2.824
H23	N10[2]	3.108	H23	C13[1]	3.496
H23	H1[1]	3.012	H23	H8[1]	3.106
H23	H10[1]	3.118	H24	O1[8]	3.106
H24	O7[2]	2.805	H24	H1[1]	2.891
H24	H2[1]	3.524	H24	H10[1]	3.382
H24	H11[8]	3.464	H24	H12[8]	3.356
H24	H13[8]	3.574	H25	O4[4]	2.463
H25	O5[5]	3.112	H25	C17[4]	2.952
H25	H3[5]	3.200	H25	H7[4]	2.954
H25	H19[8]	2.950	H25	H20[4]	3.538

Table 12. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H25	H21[4]	2.503	H26	O5[5]	2.518
H26	C23[5]	3.539	H26	H3[5]	3.051
H26	H9[5]	3.368	H26	H26[5]	2.693

Symmetry Operators:

(1) X-1,Y,Z
(2) X,-Y+1/2,Z+1/2
(3) X+1,-Y+1/2,Z+1/2
(4) X,-Y+1/2,Z+1/2-1
(5) -X+1,-Y,-Z
(6) -X+1,Y+1/2-1,-Z+1/2
(7) -X+1,-Y,-Z+1
(8) X-1,-Y+1/2,Z+1/2-1
(9) -X+2,Y+1/2-1,-Z+1/2
(10) -X+2,-Y,-Z+1
(11) X+1,Y,Z
(12) -X+2,Y+1/2,-Z+1/2
(13) -X+1,Y+1/2,-Z+1/2

X-ray Structure Report

for

(*S*)-**67**

March 5, 2015

Experimental

Data Collection

A white block crystal of $C_{22}H_{24}N_2O_8S$ having approximate dimensions of 0.450 x 0.243 x 0.129 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Mo-Kα radiation.

The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell with dimensions:

a = 8.1516(4) Å
b = 8.9362(3) Å
c = 29.836(1) Å
V = 2173.4(2) Å^3

For Z = 4 and F.W. = 476.50, the calculated density is 1.456 g/cm^3. The reflection conditions of:

h00: h = 2n
0k0: k = 2n
00l: l = 2n

uniquely determine the space group to be:

$P2_12_12_1$ (#19)

The data were collected at a temperature of -150 $\pm$ 1 ^{o}C to a maximum 2θ value of 54.8^o. A total of 44 oscillation images were collected. A sweep of data was done using ω scans from 130.0 to 190.0^o in 5.0^o step, at χ = 45.0^o and ϕ = 0.0^o. The exposure rate was 90.0 sec./^{o}. A second sweep was performed using ω scans from 0.0 to 160.0^o in 5.0^o step, at χ = 45.0^o and ϕ = 180.0^o. The exposure rate was 90.0 sec./^{o}. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 20967 reflections that were collected, 4966 were unique (R_{int} = 0.0426); equivalent reflections were merged.

The linear absorption coefficient, μ, for Mo-Kα radiation is 2.021 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.698 to 0.974. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[2] on F^2 was based on 4966 observed reflections and 323 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma||Fo|-|Fc||/\Sigma|Fo| = 0.0466$$

$$wR2 = [\Sigma(w(Fo^2-Fc^2)^2)/\Sigma w(Fo^2)^2]^{1/2} = 0.1468$$

The standard deviation of an observation of unit weight[3] was 1.01. A Sheldrick weighting scheme was used. Plots of $\Sigma w(|Fo|-|Fc|)^2$ versus |Fo|, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.44 and -0.97 $e^-/Å^3$, respectively. The absolute structure was deduced based on Flack parameter, -0.02(9), refined using 2115 Friedel pairs.[4]

Neutral atom scattering factors were taken from Cromer and Waber.[5] Anomalous dispersion effects were included in Fcalc;[6] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[7] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[8] All calculations were performed using the CrystalStructure[9,10] crystallographic software package.

References

(1) SIR92: Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M., Polidori, G. and Camalli, M. (1994) J. Appl. Cryst., 27, 435.

(2) Least Squares function minimized:

$\Sigma w(F_o^2-F_c^2)^2$ where w = Least Squares weights.

(3) Standard deviation of an observation of unit weight:

$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$

where: N_o = number of observations
N_v = number of variables

(4) Flack, H. D. (1983), Acta Cryst. A39, 876-881.

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EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{22}H_{24}N_2O_8S$
Formula Weight	476.50
Crystal Color, Habit	white, block
Crystal Dimensions	0.450 X 0.243 X 0.129 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 8.1516(4) Å b = 8.9362(3) Å c = 29.836(1) Å V = 2173.4(2) Å^3
Space Group	$P2_12_12_1$ (#19)
Z value	4
D_{calc}	1.456 g/cm^3
F_{000}	1000.00
μ(MoKα)	2.021 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50 kV, 40 mA
Temperature	-150.0 ^{o}C
Detector Aperture	280 x 256 mm
Data Images	44 exposures
ω oscillation Range (χ = 45.0, ϕ = 0.0)	130.0 - 190.0^o
Exposure Rate	90.0 sec./^{o}
ω oscillation Range (χ = 45.0, ϕ = 180.0)	0.0 - 160.0^o
Exposure Rate	90.0 sec./^{o}
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	54.8^o
No. of Reflections Measured	Total: 20967 Unique: 4966 (R_{int} = 0.0426) Friedel pairs: 2115
Corrections	Lorentz-polarization Absorption (trans. factors: 0.698 - 0.974)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w(Fo^2-Fc^2)^2$
Least Squares Weights	$1/[0.0032Fo^2+1.0000\sigma(Fo^2)]/(4Fo^2)$
$2\theta_{max}$ cutoff	54.8^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	4966
No. Variables	323
Reflection/Parameter Ratio	15.37
Residuals: R1 (I>2.00σ(I))	0.0466
Residuals: R (All reflections)	0.0523
Residuals: wR2 (All reflections)	0.1468
Goodness of Fit Indicator	1.015
Flack Parameter (Friedel pairs = 2115)	-0.02(9)
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	1.44 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.97 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
S1	0.32307(8)	0.85475(6)	0.73557(2)	2.07(1)
O1	0.6009(3)	0.7295(2)	0.53104(7)	2.89(4)
O2	0.7236(3)	0.5112(2)	0.54729(6)	2.68(4)
O3	0.2683(6)	0.3286(4)	0.54661(8)	7.32(9)
O4	0.3948(3)	0.4569(3)	0.49385(6)	3.67(5)
O5	0.4280(3)	0.8008(2)	0.77073(5)	2.74(4)
O6	0.2095(3)	0.9741(2)	0.74399(7)	2.96(4)
O7	-0.1249(3)	0.3444(3)	0.63093(7)	3.87(5)
O8	0.0003(3)	0.2002(3)	0.67827(8)	3.89(5)
N1	0.4448(3)	0.9131(2)	0.69597(6)	1.86(4)
N3	-0.0293(3)	0.3233(3)	0.66197(7)	2.51(5)
C1	0.4434(3)	0.5334(3)	0.56830(8)	1.94(5)
C2	0.3165(3)	0.6548(3)	0.57917(7)	1.87(4)
C3	0.3805(3)	0.7628(3)	0.61445(7)	1.71(4)
C4	0.3198(3)	0.9025(3)	0.61996(7)	1.95(4)
C5	0.3883(4)	1.0012(3)	0.65677(8)	2.10(5)
C6	0.5558(4)	1.0652(3)	0.64183(9)	2.52(5)
C7	0.6791(4)	0.9383(3)	0.65216(9)	2.47(5)
C8	0.5778(3)	0.8176(3)	0.67747(7)	1.91(4)
C9	0.5062(3)	0.7049(3)	0.64518(7)	1.73(4)
C10	0.5515(3)	0.5618(3)	0.64549(7)	1.75(4)
C11	0.4922(4)	0.4506(3)	0.61171(7)	1.99(5)
C12	0.5951(3)	0.6044(3)	0.54650(7)	1.97(5)
C13	0.3641(4)	0.4238(3)	0.53556(8)	2.63(5)
C14	0.1866(4)	0.9723(3)	0.59206(9)	2.61(5)
C15	0.8752(4)	0.5677(4)	0.5292(1)	3.50(7)
C16	0.3195(7)	0.3636(5)	0.4599(1)	5.8(1)
C17	0.2099(3)	0.6982(3)	0.71629(8)	2.01(5)
C18	0.2653(3)	0.5545(3)	0.72683(8)	2.16(5)
C19	0.1852(3)	0.4306(3)	0.70951(8)	2.24(5)
C20	0.0541(3)	0.4544(3)	0.68118(8)	2.08(5)
C21	-0.0030(3)	0.5964(3)	0.66973(8)	2.30(5)
C22	0.0753(3)	0.7200(3)	0.68803(8)	2.28(5)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Atomic coordinates and B_{iso} involving hydrogen atoms

atom	x	y	z	B_{iso}
H1	0.2176	0.6088	0.5908	2.25
H2	0.2902	0.7113	0.5524	2.26
H3	0.3109	1.0801	0.6654	2.55
H4	0.5815	1.1550	0.6587	2.99
H5	0.5539	1.0883	0.6101	3.03
H6	0.7678	0.9740	0.6710	2.96
H7	0.7241	0.8965	0.6248	2.96
H8	0.6413	0.7694	0.7013	2.29
H9	0.6237	0.5295	0.6676	2.09
H10	0.5792	0.3792	0.6058	2.39
H11	0.3984	0.3988	0.6244	2.41
H12	0.2222	1.0690	0.5820	3.14
H13	0.0892	0.9830	0.6099	3.15
H14	0.1633	0.9103	0.5666	3.14
H15	0.9603	0.4947	0.5333	4.20
H16	0.9045	0.6584	0.5444	4.21
H17	0.8623	0.5878	0.4978	4.20
H18	0.3216	0.2610	0.4694	6.93
H19	0.3785	0.3734	0.4322	6.96
H20	0.2078	0.3947	0.4556	6.97
H21	0.3557	0.5423	0.7455	2.61
H22	0.2182	0.3342	0.7170	2.69
H23	-0.0917	0.6073	0.6504	2.75
H24	0.0384	0.8163	0.6817	2.74

Table 3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	0.0274(3)	0.0280(3)	0.0233(3)	-0.0026(3)	0.0040(3)	-0.0034(3)
O1	0.035(1)	0.0312(9)	0.044(1)	-0.0026(8)	0.0073(9)	0.0106(9)
O2	0.028(1)	0.037(1)	0.037(1)	0.0044(8)	0.0064(8)	0.0113(8)
O3	0.156(4)	0.082(2)	0.040(2)	-0.086(3)	-0.011(2)	0.006(2)
O4	0.059(2)	0.056(2)	0.0240(9)	-0.028(2)	-0.0008(9)	-0.0071(9)
O5	0.046(2)	0.0354(9)	0.0231(8)	-0.0107(9)	-0.0037(8)	0.0017(8)
O6	0.038(2)	0.035(1)	0.040(1)	0.0014(9)	0.0134(9)	-0.0069(9)
O7	0.040(2)	0.057(2)	0.050(2)	-0.004(1)	-0.018(1)	-0.012(1)
O8	0.046(2)	0.036(1)	0.066(2)	-0.007(1)	-0.013(2)	-0.003(1)
N1	0.022(1)	0.0243(9)	0.0239(9)	0.0008(8)	0.0022(8)	-0.0008(8)
N3	0.021(1)	0.039(2)	0.035(1)	-0.0021(9)	0.0025(9)	-0.006(1)
C1	0.027(2)	0.025(1)	0.022(1)	-0.0049(9)	-0.0009(9)	-0.0012(9)
C2	0.023(1)	0.026(1)	0.0221(9)	-0.001(1)	-0.0017(9)	-0.0007(9)
C3	0.022(1)	0.022(1)	0.022(1)	-0.0022(9)	-0.0001(9)	0.0002(9)
C4	0.024(1)	0.026(1)	0.024(1)	0.0016(9)	0.0022(9)	0.0034(9)
C5	0.028(2)	0.026(2)	0.026(1)	0.004(1)	0.002(1)	0.000(1)
C6	0.036(2)	0.027(2)	0.033(2)	-0.006(1)	0.007(1)	-0.000(1)
C7	0.027(2)	0.032(2)	0.034(2)	-0.005(1)	0.006(1)	-0.005(1)
C8	0.020(1)	0.028(1)	0.024(1)	0.0008(9)	0.0003(9)	-0.003(1)
C9	0.021(1)	0.026(1)	0.0186(9)	-0.0008(9)	0.0034(8)	0.0012(9)
C10	0.022(1)	0.025(1)	0.0193(9)	0.0010(9)	0.0019(8)	0.0053(9)
C11	0.030(2)	0.024(1)	0.022(1)	-0.0001(9)	0.0027(9)	0.0018(9)
C12	0.025(2)	0.028(2)	0.021(1)	0.0007(9)	-0.0015(9)	-0.000(1)
C13	0.043(2)	0.031(2)	0.026(1)	-0.010(2)	-0.001(1)	0.001(1)
C14	0.032(2)	0.035(2)	0.033(2)	0.010(1)	-0.003(1)	0.007(1)
C15	0.025(2)	0.061(2)	0.047(2)	0.005(2)	0.006(2)	0.015(2)
C16	0.107(4)	0.082(3)	0.030(2)	-0.053(3)	-0.012(2)	-0.010(2)
C17	0.022(2)	0.030(2)	0.024(1)	-0.0010(9)	0.0016(9)	-0.000(1)
C18	0.022(1)	0.033(2)	0.027(1)	0.0000(9)	-0.0031(9)	0.002(1)
C19	0.025(2)	0.030(2)	0.030(1)	0.004(1)	-0.002(1)	-0.001(1)
C20	0.021(2)	0.033(2)	0.025(1)	-0.003(1)	0.0020(9)	-0.003(1)
C21	0.018(2)	0.040(2)	0.029(2)	-0.001(1)	-0.0000(9)	0.004(1)
C22	0.021(1)	0.032(2)	0.034(2)	0.003(1)	0.004(1)	0.006(1)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
S1	O5	1.4366(19)	S1	O6	1.434(2)
S1	N1	1.628(2)	S1	C17	1.772(3)
O1	C12	1.210(3)	O2	C12	1.338(3)
O2	C15	1.441(4)	O3	C13	1.201(5)
O4	C13	1.304(3)	O4	C16	1.449(5)
O7	N3	1.225(3)	O8	N3	1.227(4)
N1	C5	1.483(3)	N1	C8	1.486(3)
N3	C20	1.471(4)	C1	C2	1.533(4)
C1	C11	1.544(4)	C1	C12	1.535(4)
C1	C13	1.527(4)	C2	C3	1.520(3)
C3	C4	1.353(4)	C3	C9	1.469(4)
C4	C5	1.516(4)	C4	C14	1.503(4)
C5	C6	1.546(4)	C6	C7	1.546(4)
C7	C8	1.554(4)	C8	C9	1.511(4)
C9	C10	1.331(4)	C10	C11	1.496(4)
C17	C18	1.397(4)	C17	C22	1.397(4)
C18	C19	1.385(4)	C19	C20	1.379(4)
C20	C21	1.394(4)	C21	C22	1.388(4)

Table 5. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
C2	H1	0.970	C2	H2	0.970
C5	H3	0.980	C6	H4	0.970
C6	H5	0.970	C7	H6	0.970
C7	H7	0.970	C8	H8	0.980
C10	H9	0.930	C11	H10	0.970
C11	H11	0.970	C14	H12	0.960
C14	H13	0.960	C14	H14	0.960
C15	H15	0.960	C15	H16	0.960
C15	H17	0.960	C16	H18	0.960
C16	H19	0.960	C16	H20	0.960
C18	H21	0.930	C19	H22	0.930
C21	H23	0.930	C22	H24	0.930

Table 6. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
O5	S1	O6	120.37(12)	O5	S1	N1	105.94(11)
O5	S1	C17	106.39(12)	O6	S1	N1	106.38(11)
O6	S1	C17	107.93(12)	N1	S1	C17	109.54(11)
C12	O2	C15	116.5(3)	C13	O4	C16	117.1(3)
S1	N1	C5	123.59(17)	S1	N1	C8	122.01(15)
C5	N1	C8	103.78(17)	O7	N3	O8	124.3(3)
O7	N3	C20	117.8(3)	O8	N3	C20	118.0(3)
C2	C1	C11	109.61(19)	C2	C1	C12	109.9(2)
C2	C1	C13	107.7(2)	C11	C1	C12	110.2(2)
C11	C1	C13	109.8(2)	C12	C1	C13	109.6(2)
C1	C2	C3	111.36(19)	C2	C3	C4	123.0(2)
C2	C3	C9	116.60(19)	C4	C3	C9	120.3(2)
C3	C4	C5	119.3(2)	C3	C4	C14	125.4(2)
C5	C4	C14	115.2(2)	N1	C5	C4	112.14(19)
N1	C5	C6	98.6(2)	C4	C5	C6	109.4(2)
C5	C6	C7	104.2(2)	C6	C7	C8	105.1(2)
N1	C8	C7	99.78(19)	N1	C8	C9	109.74(19)
C7	C8	C9	110.98(19)	C3	C9	C8	115.62(19)
C3	C9	C10	122.4(2)	C8	C9	C10	121.9(2)
C9	C10	C11	122.9(2)	C1	C11	C10	109.27(19)
O1	C12	O2	123.5(3)	O1	C12	C1	125.0(3)
O2	C12	C1	111.5(2)	O3	C13	O4	123.2(3)
O3	C13	C1	123.6(3)	O4	C13	C1	112.6(3)
S1	C17	C18	118.95(19)	S1	C17	C22	119.64(19)
C18	C17	C22	121.2(3)	C17	C18	C19	119.9(3)
C18	C19	C20	118.1(3)	N3	C20	C19	118.3(3)
N3	C20	C21	118.3(2)	C19	C20	C21	123.3(3)
C20	C21	C22	118.3(3)	C17	C22	C21	119.2(3)

Table 7. Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom	angle
C1	C2	H1	109.6	C1	C2	H2	110.1
C3	C2	H1	107.8	C3	C2	H2	108.5
H1	C2	H2	109.5	N1	C5	H3	112.0
C4	C5	H3	111.7	C6	C5	H3	112.3
C5	C6	H4	110.3	C5	C6	H5	110.3
C7	C6	H4	111.3	C7	C6	H5	111.2
H4	C6	H5	109.5	C6	C7	H6	111.1
C6	C7	H7	111.1	C8	C7	H6	110.0
C8	C7	H7	110.0	H6	C7	H7	109.5
N1	C8	H8	111.6	C7	C8	H8	112.2
C9	C8	H8	111.9	C9	C10	H9	118.6
C11	C10	H9	118.4	C1	C11	H10	110.6
C1	C11	H11	110.6	C10	C11	H10	108.8
C10	C11	H11	108.0	H10	C11	H11	109.4
C4	C14	H12	109.1	C4	C14	H13	109.4
C4	C14	H14	110.0	H12	C14	H13	109.4
H12	C14	H14	109.4	H13	C14	H14	109.4
O2	C15	H15	109.4	O2	C15	H16	109.3
O2	C15	H17	109.7	H15	C15	H16	109.4
H15	C15	H17	109.4	H16	C15	H17	109.4
O4	C16	H18	109.6	O4	C16	H19	109.7
O4	C16	H20	109.3	H18	C16	H19	109.4
H18	C16	H20	109.4	H19	C16	H20	109.4
C17	C18	H21	119.9	C19	C18	H21	120.2
C18	C19	H22	121.0	C20	C19	H22	120.9
C20	C21	H23	120.4	C22	C21	H23	121.2
C17	C22	H24	120.3	C21	C22	H24	120.5

Table 8. Torsion Angles(°)
(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
O5	S1	N1	C5	-169.13(14)	O5	S1	N1	C8	52.06(17)
O5	S1	C17	C18	-17.2(2)	O5	S1	C17	C22	167.86(16)
O6	S1	N1	C5	-39.93(18)	O6	S1	N1	C8	-178.74(14)
O6	S1	C17	C18	-147.70(16)	O6	S1	C17	C22	37.4(2)
N1	S1	C17	C18	96.87(18)	N1	S1	C17	C22	-78.05(19)
C17	S1	N1	C5	76.49(17)	C17	S1	N1	C8	-62.32(17)
C15	O2	C12	O1	1.1(4)	C15	O2	C12	C1	-177.81(18)
C16	O4	C13	O3	-5.8(5)	C16	O4	C13	C1	-177.4(3)
S1	N1	C5	C4	-83.0(2)	S1	N1	C5	C6	161.89(13)
S1	N1	C8	C7	-165.34(13)	S1	N1	C8	C9	78.1(2)
C5	N1	C8	C7	49.05(19)	C5	N1	C8	C9	-67.6(2)
C8	N1	C5	C4	61.9(3)	C8	N1	C5	C6	-53.21(18)
O7	N3	C20	C19	-167.0(2)	O7	N3	C20	C21	12.8(4)
O8	N3	C20	C19	13.5(4)	O8	N3	C20	C21	-166.7(2)
C2	C1	C11	C10	-55.4(3)	C11	C1	C2	C3	56.3(3)
C2	C1	C12	O1	-15.2(3)	C2	C1	C12	O2	163.65(17)
C12	C1	C2	C3	-65.0(3)	C2	C1	C13	O3	-78.0(3)
C2	C1	C13	O4	93.5(3)	C13	C1	C2	C3	175.63(17)
C11	C1	C12	O1	-136.2(2)	C11	C1	C12	O2	42.7(3)
C12	C1	C11	C10	65.8(3)	C11	C1	C13	O3	41.2(4)
C11	C1	C13	O4	-147.2(2)	C13	C1	C11	C10	-173.48(19)
C12	C1	C13	O3	162.4(3)	C12	C1	C13	O4	-26.1(3)
C13	C1	C12	O1	103.0(3)	C13	C1	C12	O2	-78.2(3)
C1	C2	C3	C4	158.52(19)	C1	C2	C3	C9	-25.6(3)
C2	C3	C4	C5	178.53(18)	C2	C3	C4	C14	-1.7(4)
C2	C3	C9	C8	175.23(17)	C2	C3	C9	C10	-6.4(3)
C4	C3	C9	C8	-8.8(3)	C4	C3	C9	C10	169.5(2)
C9	C3	C4	C5	2.9(4)	C9	C3	C4	C14	-177.41(18)
C3	C4	C5	N1	-31.0(3)	C3	C4	C5	C6	77.4(3)
C14	C4	C5	N1	149.3(2)	C14	C4	C5	C6	-102.4(3)
N1	C5	C6	C7	35.0(2)	C4	C5	C6	C7	-82.2(3)
C5	C6	C7	C8	-6.5(3)	C6	C7	C8	N1	-24.6(3)
C6	C7	C8	C9	91.1(2)	N1	C8	C9	C3	42.5(3)
N1	C8	C9	C10	-135.82(19)	C7	C8	C9	C3	-66.8(3)
C7	C8	C9	C10	114.9(3)	C3	C9	C10	C11	6.5(4)
C8	C9	C10	C11	-175.24(18)	C9	C10	C11	C1	25.1(3)
S1	C17	C18	C19	-175.54(15)	S1	C17	C22	C21	173.97(15)

Table 8. Torsion angles (°) (continued)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C18	C17	C22	C21	-0.8(4)	C22	C17	C18	C19	-0.7(4)
C17	C18	C19	C20	1.6(4)	C18	C19	C20	N3	178.8(2)
C18	C19	C20	C21	-1.0(4)	N3	C20	C21	C22	179.70(18)
C19	C20	C21	C22	-0.5(4)	C20	C21	C22	C17	1.4(4)

Table 9. Intramolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
S1	C4	3.476(3)	S1	C9	3.361(3)
O1	O4	3.160(3)	O1	C2	2.807(3)
O1	C3	3.084(3)	O1	C9	3.499(3)
O1	C11	3.576(3)	O1	C13	3.348(4)
O1	C15	2.664(4)	O2	O4	3.156(3)
O2	C10	3.279(3)	O2	C11	2.747(3)
O2	C13	3.052(4)	O3	C2	3.098(4)
O3	C11	2.880(5)	O3	C16	2.639(4)
O4	C2	3.165(3)	O4	C12	2.621(4)
O5	C8	3.043(3)	O5	C18	2.884(3)
O6	C5	2.993(4)	O6	C22	3.023(4)
O7	C19	3.533(4)	O7	C21	2.720(4)
O8	C19	2.717(4)	O8	C21	3.550(4)
N1	C3	2.827(3)	N1	C10	3.589(3)
N1	C22	3.479(4)	C1	C9	2.806(4)
C2	C10	2.877(4)	C2	C14	3.052(4)
C3	C6	3.164(4)	C3	C7	3.107(4)
C3	C11	2.936(4)	C3	C12	3.029(4)
C3	C17	3.391(4)	C3	C22	3.340(4)
C4	C7	3.100(4)	C4	C8	2.818(4)
C4	C17	3.521(4)	C4	C22	3.279(4)
C5	C9	2.838(4)	C5	C17	3.550(4)
C6	C9	3.246(4)	C6	C14	3.457(4)
C7	C10	3.527(4)	C8	C17	3.388(4)
C9	C12	3.162(3)	C9	C17	3.216(4)
C9	C18	3.405(4)	C10	C12	2.999(3)
C10	C18	3.367(4)	C17	C20	2.730(4)
C18	C21	2.798(4)	C19	C22	2.811(4)

Table 10. Intramolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H3	2.907	S1	H8	2.891
S1	H21	2.820	S1	H24	2.843
O1	H2	2.616	O1	H7	3.325
O1	H16	2.586	O1	H17	2.670
O2	H10	2.414	O3	H1	2.860
O3	H2	3.429	O3	H10	3.122
O3	H11	2.627	O3	H18	2.420
O3	H19	3.552	O3	H20	2.823
O4	H1	3.508	O4	H2	2.991
O5	H8	2.719	O5	H21	2.500
O6	H3	2.661	O6	H24	2.717
O7	H23	2.434	O8	H22	2.433
N1	H4	2.674	N1	H5	3.132
N1	H6	2.790	N1	H7	3.117
N1	H24	3.450	N3	H22	2.603
N3	H23	2.611	C1	H9	3.308
C2	H10	3.359	C2	H11	2.739
C2	H13	3.588	C2	H14	2.629
C3	H3	3.266	C3	H5	3.237
C3	H7	3.060	C3	H8	3.353
C3	H9	3.285	C3	H11	3.270
C3	H12	3.176	C3	H13	3.087
C3	H14	2.629	C3	H24	3.469
C4	H1	2.888	C4	H2	2.654
C4	H4	3.313	C4	H5	2.547
C4	H7	3.299	C4	H24	3.042
C5	H6	3.132	C5	H7	3.046
C5	H8	3.211	C5	H12	2.679
C5	H13	2.815	C5	H14	3.357
C5	H24	3.380	C6	H8	3.259
C6	H12	3.253	C7	H3	3.282
C8	H3	3.219	C8	H4	3.066
C8	H5	3.152	C8	H9	2.619
C9	H1	2.983	C9	H2	3.282
C9	H6	3.305	C9	H7	2.541
C9	H10	3.194	C9	H11	2.939
C9	H21	3.547	C10	H1	3.200

Table 10. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C10	H7	3.362	C10	H8	2.598
C10	H21	3.389	C11	H1	2.719
C11	H2	3.358	C12	H1	3.350
C12	H2	2.669	C12	H10	2.683
C12	H11	3.368	C12	H15	3.158
C12	H16	2.568	C12	H17	2.623
C13	H1	2.623	C13	H2	2.687
C13	H10	2.762	C13	H11	2.674
C13	H18	2.475	C13	H19	3.118
C13	H20	2.718	C14	H1	3.259
C14	H2	2.749	C14	H3	2.596
C14	H5	3.214	C14	H24	3.250
C17	H22	3.254	C17	H23	3.251
C18	H9	3.422	C18	H11	3.530
C18	H24	3.272	C19	H11	3.091
C19	H23	3.271	C20	H1	3.308
C20	H11	3.316	C20	H21	3.216
C20	H24	3.236	C21	H1	2.964
C21	H22	3.276	C22	H1	3.278
C22	H13	3.312	C22	H21	3.269
H1	H11	2.587	H1	H13	3.550
H1	H14	2.825	H1	H23	3.084
H1	H24	3.595	H2	H12	3.363
H2	H13	3.395	H2	H14	2.100
H3	H4	2.314	H3	H5	2.579
H3	H12	2.592	H3	H13	2.599
H3	H14	3.527	H3	H24	3.276
H4	H6	2.249	H4	H7	2.776
H5	H6	2.719	H5	H7	2.248
H5	H12	2.836	H6	H8	2.285
H7	H8	2.638	H7	H16	3.526
H8	H9	2.372	H8	H21	3.359
H9	H10	2.309	H9	H11	2.530
H9	H21	3.193	H11	H22	3.182
H13	H24	2.644	H21	H22	2.333
H23	H24	2.343			

Table 11. Intermolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
O1	C15[1]	3.145(4)	O2	O7[2]	3.158(3)
O2	C16[3]	3.446(5)	O3	C14[4]	3.525(4)
O4	C14[5]	3.553(4)	O5	C6[6]	3.355(3)
O5	C10[7]	3.423(3)	O5	C18[7]	3.376(4)
O5	C19[7]	3.411(4)	O6	O8[8]	3.292(3)
O6	N3[9]	3.442(3)	O6	C19[9]	3.526(4)
O6	C20[9]	3.104(4)	O6	C21[9]	3.264(4)
O7	O2[10]	3.158(3)	O7	C10[10]	3.304(4)
O7	C11[10]	3.312(4)	O7	C16[11]	3.318(4)
O8	O6[4]	3.292(3)	O8	C7[12]	3.597(4)
O8	C17[13]	3.582(4)	N1	C18[7]	3.534(3)
N3	O6[13]	3.442(3)	C6	O5[7]	3.355(3)
C6	C11[8]	3.597(4)	C7	O8[14]	3.597(4)
C10	O5[6]	3.423(3)	C10	O7[2]	3.304(4)
C11	O7[2]	3.312(4)	C11	C6[4]	3.597(4)
C14	O3[8]	3.525(4)	C14	O4[1]	3.553(4)
C15	O1[5]	3.145(4)	C16	O2[11]	3.446(5)
C16	O7[3]	3.318(4)	C17	O8[9]	3.582(4)
C18	O5[6]	3.376(4)	C18	N1[6]	3.534(3)
C19	O5[6]	3.411(4)	C19	O6[13]	3.526(4)
C20	O6[13]	3.104(4)	C21	O6[13]	3.264(4)

Symmetry Operators:

(1) X+1/2-1,-Y+1/2+1,-Z+1
(2) X+1,Y,Z
(3) X+1/2,-Y+1/2,-Z+1
(4) X,Y-1,Z
(5) X+1/2,-Y+1/2+1,-Z+1
(6) -X+1,Y+1/2-1,-Z+1/2+1
(7) -X+1,Y+1/2,-Z+1/2+1
(8) X,Y+1,Z
(9) -X,Y+1/2,-Z+1/2+1
(10) X-1,Y,Z
(11) X+1/2-1,-Y+1/2,-Z+1
(12) X-1,Y-1,Z
(13) -X,Y+1/2-1,-Z+1/2+1
(14) X+1,Y+1,Z

Table 12. Intermolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H9[1]	3.313	S1	H21[1]	3.160
O1	H2[2]	2.975	O1	H14[2]	3.209
O1	H15[3]	3.328	O1	H16[3]	2.939
O1	H17[3]	2.681	O1	H20[2]	3.493
O2	H14[2]	3.504	O2	H18[4]	2.609
O2	H23[5]	3.531	O3	H12[6]	2.577
O3	H15[7]	2.943	O4	H12[2]	3.507
O4	H13[2]	3.518	O4	H14[2]	3.074
O5	H3[8]	3.473	O5	H4[8]	2.478
O5	H9[1]	2.782	O5	H11[1]	3.545
O5	H21[1]	2.829	O5	H22[1]	2.923
O6	H8[1]	3.332	O6	H9[1]	3.008
O6	H22[9]	3.318	O6	H23[10]	3.503
O7	H4[11]	3.046	O7	H5[11]	3.533
O7	H9[7]	2.851	O7	H10[7]	2.544
O7	H15[7]	3.281	O7	H18[12]	3.170
O7	H19[12]	2.709	O8	H3[6]	2.777
O8	H4[11]	3.487	O8	H6[11]	2.779
O8	H12[6]	3.591	O8	H13[6]	2.908
O8	H19[12]	3.505	O8	H24[6]	3.446
N1	H21[1]	2.651	N3	H3[6]	3.525
N3	H4[11]	3.512	N3	H6[11]	3.543
N3	H9[7]	3.380	N3	H13[6]	3.549
N3	H19[12]	3.398	C2	H15[7]	3.514
C2	H16[7]	3.515	C2	H17[3]	3.271
C4	H17[3]	3.530	C6	H10[9]	3.011
C6	H11[9]	3.287	C6	H19[2]	3.478
C6	H20[2]	3.179	C6	H21[1]	3.444
C7	H13[5]	3.595	C7	H19[2]	3.436
C7	H20[2]	3.551	C7	H21[1]	3.204
C7	H23[5]	3.499	C7	H24[5]	3.247
C8	H21[1]	3.099	C8	H22[1]	3.564
C8	H23[5]	3.383	C9	H23[5]	3.395
C10	H23[5]	2.940	C11	H4[6]	3.078
C11	H5[6]	3.277	C12	H14[2]	3.422
C12	H17[3]	3.593	C13	H15[7]	3.353
C14	H17[3]	3.086	C14	H19[3]	2.955

Table 12. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C15	H1[5]	3.363	C15	H2[2]	3.209
C15	H14[2]	3.345	C15	H18[4]	2.971
C16	H5[3]	3.038	C16	H7[3]	3.403
C16	H10[12]	3.520	C16	H12[2]	3.565
C16	H13[2]	3.324	C16	H14[2]	3.544
C16	H15[12]	3.408	C18	H6[8]	3.143
C18	H8[8]	3.416	C19	H3[6]	3.549
C19	H8[8]	3.340	C20	H9[7]	3.595
C21	H8[7]	3.418	C21	H9[7]	3.101
C22	H6[7]	3.419	C22	H8[7]	3.587
H1	C15[7]	3.363	H1	H15[7]	2.895
H1	H16[7]	2.938	H2	O1[3]	2.975
H2	C15[3]	3.209	H2	H15[7]	3.362
H2	H16[7]	3.188	H2	H16[3]	3.250
H2	H17[3]	2.409	H3	O5[1]	3.473
H3	O8[9]	2.777	H3	N3[9]	3.525
H3	C19[9]	3.549	H3	H11[9]	3.181
H3	H22[9]	2.846	H4	O5[1]	2.478
H4	O7[13]	3.046	H4	O8[13]	3.487
H4	N3[13]	3.512	H4	C11[9]	3.078
H4	H9[9]	3.375	H4	H10[9]	2.550
H4	H11[9]	2.833	H4	H20[2]	3.588
H4	H21[1]	3.073	H5	O7[13]	3.533
H5	C11[9]	3.277	H5	C16[2]	3.038
H5	H10[9]	2.611	H5	H11[9]	3.080
H5	H18[2]	3.493	H5	H19[2]	2.951
H5	H20[2]	2.331	H6	O8[13]	2.779
H6	N3[13]	3.543	H6	C18[1]	3.143
H6	C22[5]	3.419	H6	H13[5]	3.193
H6	H19[2]	3.487	H6	H21[1]	2.755
H6	H22[1]	3.570	H6	H23[5]	3.526
H6	H24[5]	2.637	H7	C16[2]	3.403
H7	H13[5]	3.107	H7	H19[2]	2.950
H7	H20[2]	3.040	H7	H23[5]	3.086
H7	H24[5]	3.157	H8	O6[8]	3.332
H8	C18[1]	3.416	H8	C19[1]	3.340
H8	C21[5]	3.418	H8	C22[5]	3.587

Table 12. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H8	H21[1]	2.910	H8	H22[1]	2.755
H8	H23[5]	3.024	H8	H24[5]	3.316
H9	S1[8]	3.313	H9	O5[8]	2.782
H9	O6[8]	3.008	H9	O7[5]	2.851
H9	N3[5]	3.380	H9	C20[5]	3.595
H9	C21[5]	3.101	H9	H4[6]	3.375
H9	H23[5]	2.476	H10	O7[5]	2.544
H10	C6[6]	3.011	H10	C16[4]	3.520
H10	H4[6]	2.550	H10	H5[6]	2.611
H10	H18[4]	3.243	H10	H19[4]	3.512
H10	H20[4]	3.232	H11	O5[8]	3.545
H11	C6[6]	3.287	H11	H3[6]	3.181
H11	H4[6]	2.833	H11	H5[6]	3.080
H11	H12[6]	3.513	H12	O3[9]	2.577
H12	O4[3]	3.507	H12	O8[9]	3.591
H12	C16[3]	3.565	H12	H11[9]	3.513
H12	H17[3]	2.989	H12	H19[3]	2.880
H13	O4[3]	3.518	H13	O8[9]	2.908
H13	N3[9]	3.549	H13	C7[7]	3.595
H13	C16[3]	3.324	H13	H6[7]	3.193
H13	H7[7]	3.107	H13	H19[3]	2.485
H14	O1[3]	3.209	H14	O2[3]	3.504
H14	O4[3]	3.074	H14	C12[3]	3.422
H14	C15[3]	3.345	H14	C16[3]	3.544
H14	H16[7]	3.154	H14	H17[3]	2.514
H14	H19[3]	3.021	H15	O1[2]	3.328
H15	O3[5]	2.943	H15	O7[5]	3.281
H15	C2[5]	3.514	H15	C13[5]	3.353
H15	C16[4]	3.408	H15	H1[5]	2.895
H15	H2[5]	3.362	H15	H18[4]	2.551
H15	H19[4]	3.510	H15	H20[5]	3.203
H16	O1[2]	2.939	H16	C2[5]	3.515
H16	H1[5]	2.938	H16	H2[5]	3.188
H16	H2[2]	3.250	H16	H14[5]	3.154
H16	H23[5]	3.194	H17	O1[2]	2.681
H17	C2[2]	3.271	H17	C4[2]	3.530
H17	C12[2]	3.593	H17	C14[2]	3.086

Table 12. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H17	H2[2]	2.409	H17	H12[2]	2.989
H17	H14[2]	2.514	H17	H18[4]	3.284
H17	H20[5]	3.535	H18	O2[12]	2.609
H18	O7[4]	3.170	H18	C15[12]	2.971
H18	H5[3]	3.493	H18	H10[12]	3.243
H18	H15[12]	2.551	H18	H17[12]	3.284
H19	O7[4]	2.709	H19	O8[4]	3.505
H19	N3[4]	3.398	H19	C6[3]	3.478
H19	C7[3]	3.436	H19	C14[2]	2.955
H19	H5[3]	2.951	H19	H6[3]	3.487
H19	H7[3]	2.950	H19	H10[12]	3.512
H19	H12[2]	2.880	H19	H13[2]	2.485
H19	H14[2]	3.021	H19	H15[12]	3.510
H20	O1[3]	3.493	H20	C6[3]	3.179
H20	C7[3]	3.551	H20	H4[3]	3.588
H20	H5[3]	2.331	H20	H7[3]	3.040
H20	H10[12]	3.232	H20	H15[7]	3.203
H20	H17[7]	3.535	H21	S1[8]	3.160
H21	O5[8]	2.829	H21	N1[8]	2.651
H21	C6[8]	3.444	H21	C7[8]	3.204
H21	C8[8]	3.099	H21	H4[8]	3.073
H21	H6[8]	2.755	H21	H8[8]	2.910
H22	O5[8]	2.923	H22	O6[6]	3.318
H22	C8[8]	3.564	H22	H3[6]	2.846
H22	H6[8]	3.570	H22	H8[8]	2.755
H23	O2[7]	3.531	H23	O6[14]	3.503
H23	C7[7]	3.499	H23	C8[7]	3.383
H23	C9[7]	3.395	H23	C10[7]	2.940
H23	H6[7]	3.526	H23	H7[7]	3.086
H23	H8[7]	3.024	H23	H9[7]	2.476
H23	H16[7]	3.194	H24	O8[9]	3.446
H24	C7[7]	3.247	H24	H6[7]	2.637
H24	H7[7]	3.157	H24	H8[7]	3.316

Symmetry Operators:

(1)	-X+1,Y+1/2,-Z+1/2+1	(2)	X+1/2,-Y+1/2+1,-Z+1
(3)	X+1/2-1,-Y+1/2+1,-Z+1	(4)	X+1/2,-Y+1/2,-Z+1
(5)	X+1,Y,Z	(6)	X,Y-1,Z
(7)	X-1,Y,Z	(8)	-X+1,Y+1/2-1,-Z+1/2+1
(9)	X,Y+1,Z	(10)	-X,Y+1/2,-Z+1/2+1
(11)	X-1,Y-1,Z	(12)	X+1/2-1,-Y+1/2,-Z+1
(13)	X+1,Y+1,Z	(14)	-X,Y+1/2-1,-Z+1/2+1

X-ray Structure Report

for

190ab

March 5, 2015

Experimental

Data Collection

A colorless block crystal of $C_{29}H_{35}N_3O_9S$ having approximate dimensions of 0.242 x 0.211 x 0.100 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Mo-Kα radiation.

The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 6.8242(3) Å
b = 14.9933(5) Å β = 93.6230(11)^o
c = 14.3182(4) Å
V = 1462.07(8) Å^3

For Z = 2 and F.W. = 601.67, the calculated density is 1.367 g/cm^3. Based on the reflection conditions of:

0k0: k = 2n

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

$P2_1$ (#4)

The data were collected at a temperature of 23 $\pm$ 1 ^{o}C to a maximum 2θ value of 55.0^o. A total of 44 oscillation images were collected. A sweep of data was done using ω scans from 130.0 to 190.0^o in 5.00^o step, at χ = 45.0^o and ϕ = 0.0^o. The exposure rate was 60.0 sec./^{o}. A second sweep was performed using ω scans from 0.0 to 160.0^o in 5.00^o step, at χ = 45.0^o and ϕ = 180.0^o. The exposure rate was 60.0 sec./^{o}. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 14351 reflections were collected, where 6124 were unique (R_{int} = 0.0145); equivalent reflections were merged.

The linear absorption coefficient, μ, for Mo-Kα radiation is 1.693 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.892 to 0.983. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically and the rest were refined using the riding model.The final cycle of full-matrix least-squares refinement[2] on F^2 was based on 6124 observed reflections and 383 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma||Fo|-|Fc||/\Sigma|Fo| = 0.0293$$

$$wR2 = [\Sigma(w(Fo^2-Fc^2)^2)/\Sigma w(Fo^2)^2]^{1/2} = 0.0771$$

The goodness of fit[3] was 1.05. Unit weights were used. Plots of $\Sigma w(|Fo|-|Fc|)^2$ versus |Fo|, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.27 and -0.16 $e^-/Å^3$, respectively. The final Flack parameter[4] was -0.006(15), indicating that the present absolute structure is correct.[5]

Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4.[6] Anomalous dispersion effects were included in Fcalc;[7] the values for Δf' and Δf" were those of Creagh and McAuley.[8] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[9] All calculations were performed using the CrystalStructure[10] crystallographic software package except for refinement, which was performed using SHELXL2013.[11]

References

(1) SIR2008: Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G., Siliqi, D. and Spagna R. (2007). J. Appl. Cryst. 40, 609-613.

(2) Least Squares function minimized: (SHELXL2013)

$\Sigma w(F_o^2-F_c^2)^2$ where w = Least Squares weights.

(3) Goodness of fit is defined as:

$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$

where: N_o = number of observations
N_v = number of variables

(4) Parsons, S. and Flack, H. (2004), Acta Cryst. A60, s61.

(5) Flack, H. D. and Bernardinelli (2000), J. Appl. Cryst. 33, 114-1148.

(6) International Tables for Crystallography, Vol.C (1992). Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, Netherlands, Table 6.1.1.4, pp. 572.

(7) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(8) Creagh, D. C. & McAuley, W. J.; "International Tables for Crystallography", Vol C, (A. J. C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(9) Creagh, D. C. & Hubbell, J. H.; "International Tables for Crystallography", Vol C, (A. J. C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(10) CrystalStructure 4.1: Crystal Structure Analysis Package, Rigaku Corporation (2000-2014). Tokyo 196-8666, Japan.

(11) SHELXL2013: Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{29}H_{35}N_3O_9S$
Formula Weight	601.67
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.242 X 0.211 X 0.100 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 6.8242(3) Å b = 14.9933(5) Å c = 14.3182(4) Å β = 93.6230(11)^o V = 1462.07(8) Å^3
Space Group	$P2_1$ (#4)
Z value	2
D_{calc}	1.367 g/cm^3
F_{000}	636.00
μ(MoKα)	1.693 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50 kV, 40 mA
Temperature	23.0 ^{o}C
Detector Aperture	460.0 x 256.0 mm
Data Images	44 exposures
ω oscillation Range (χ = 45.0, ϕ = 0.0)	130.0 - 190.0^o
Exposure Rate	60.0 sec./^{o}
ω oscillation Range (χ = 45.0, ϕ = 180.0)	0.0 - 160.0^o
Exposure Rate	60.0 sec./^{o}
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	55.0^o
No. of Reflections Measured	Total: 14351 Unique: 6124 (R_{int} = 0.0145) Parsons quotients (Flack x parameter): 2494
Corrections	Lorentz-polarization Absorption (trans. factors: 0.892 - 0.983)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR2008)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w(Fo^2-Fc^2)^2$
Least Squares Weights	$w = 1/[\sigma^2(Fo^2)+(0.0498\cdot P)^2 +0.2213\cdot P]$ where $P = (Max(Fo^2,0)+2Fc^2)/3$
$2\theta_{max}$ cutoff	55.0^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	6124
No. Variables	383
Reflection/Parameter Ratio	15.99
Residuals: R1 (I>2.00σ(I))	0.0293
Residuals: R (All reflections)	0.0306
Residuals: wR2 (All reflections)	0.0771
Goodness of Fit Indicator	1.049
Flack parameter (Parsons' quotients = 2494)	-0.006(15)
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.27 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.16 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
S1	0.03416(7)	0.08731(3)	0.91813(3)	1.833(9)
O1	-0.6533(2)	0.35994(11)	0.65903(11)	2.47(3)
O2	-0.5996(3)	0.31786(11)	0.51284(11)	2.47(3)
O3	-0.7373(2)	0.13228(11)	0.56962(10)	2.36(3)
O4	-0.1217(2)	0.49131(12)	0.70838(11)	2.43(3)
O5	0.1109(2)	0.04833(12)	1.00853(12)	2.81(3)
O6	-0.4376(3)	0.10726(12)	0.51772(12)	2.96(3)
O7	-0.9700(4)	0.7656(2)	0.6188(3)	8.60(11)
O8	-0.7119(4)	0.84611(15)	0.62432(16)	4.42(5)
O9	-0.5744(2)	0.45837(11)	0.92662(10)	2.25(3)
N1	-0.1996(2)	0.11925(12)	0.92324(12)	1.71(3)
N2	-0.7962(4)	0.77631(16)	0.63737(17)	3.65(5)
N3	-0.3729(2)	0.49109(11)	0.80798(11)	1.44(2)
C1	-0.1940(3)	0.46248(14)	0.77708(13)	1.61(3)
C2	-0.3600(3)	0.27040(13)	0.89405(12)	1.32(3)
C3	-0.2794(3)	0.36824(13)	0.90593(12)	1.38(3)
C4	-0.2162(3)	0.26715(13)	0.73871(13)	1.50(3)
C5	-0.4806(3)	0.56374(13)	0.76515(12)	1.55(3)
C6	-0.4306(3)	0.44183(13)	0.88465(13)	1.55(3)
C7	-0.5269(3)	0.19907(14)	0.73650(12)	1.58(3)
C8	-0.2187(3)	0.21124(13)	0.95944(13)	1.57(3)
C9	-0.3635(3)	0.24673(13)	0.79167(12)	1.40(3)
C10	-0.2577(3)	0.24196(15)	0.63749(13)	1.75(3)
C11	-0.0386(3)	0.31454(14)	0.78063(13)	1.59(3)
C12	-0.1099(3)	0.39032(13)	0.84207(13)	1.46(3)
C13	-0.6789(3)	0.55316(15)	0.73951(14)	1.86(3)
C14	-0.5578(3)	0.25584(14)	0.93762(13)	1.66(3)
C15	-0.5440(3)	0.14723(14)	0.56625(13)	1.85(3)
C16	-0.4820(3)	0.22159(13)	0.63392(12)	1.52(3)
C17	-0.6833(4)	0.70215(16)	0.68131(15)	2.34(4)
C18	-0.3830(3)	0.64284(15)	0.74807(14)	1.96(3)
C19	-0.5094(3)	0.25847(16)	1.04328(14)	2.08(3)
C20	-0.4856(4)	0.71316(15)	0.70513(15)	2.32(4)
C21	-0.7818(3)	0.62356(16)	0.69755(14)	2.20(3)
C22	0.0032(3)	-0.00738(15)	0.83659(15)	2.27(3)
C23	0.2131(4)	-0.04213(18)	0.82970(18)	3.02(4)
C24	-0.3070(4)	0.21438(16)	1.05677(14)	2.29(4)

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
C25	-0.8195(4)	0.06440(18)	0.50660(17)	3.09(5)
C26	-0.6919(4)	0.39958(17)	0.47864(18)	3.09(4)
C27	-0.1297(4)	-0.07795(17)	0.87512(19)	2.93(4)
C28	-0.0745(4)	0.0295(2)	0.74184(17)	3.30(5)
C29	-0.5904(3)	0.30740(13)	0.60531(13)	1.60(3)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Atomic coordinates and B_{iso} involving hydrogen atoms

atom	x	y	z	B_{iso}
H1	-0.267(4)	0.079(2)	0.9494(19)	2.5(5)
H2	-0.22862	0.37536	0.97106	1.657
H3	-0.65443	0.22165	0.75137	1.897
H4	-0.52204	0.13529	0.74776	1.897
H5	-0.08845	0.23905	0.96447	1.882
H6	-0.18292	0.18986	0.62109	2.095
H7	-0.22881	0.29080	0.59612	2.095
H8	0.03793	0.33852	0.73161	1.912
H9	0.04343	0.27354	0.81809	1.912
H10	0.00177	0.41446	0.88039	1.754
H11	-0.74175	0.49946	0.75041	2.234
H12	-0.65008	0.30263	0.91864	1.993
H13	-0.61400	0.19869	0.91881	1.993
H14	-0.24990	0.64861	0.76529	2.351
H15	-0.60629	0.22558	1.07616	2.500
H16	-0.50507	0.31944	1.06598	2.500
H17	-0.42262	0.76647	0.69269	2.779
H18	-0.91509	0.61814	0.68054	2.640
H19	0.29296	0.00394	0.80520	3.623
H20	0.26635	-0.05917	0.89076	3.623
H21	0.21137	-0.09292	0.78884	3.623
H22	-0.31944	0.15453	1.08142	2.746
H23	-0.22267	0.24866	1.10044	2.746
H24	-0.95763	0.05882	0.51436	3.710
H25	-0.79922	0.08102	0.44318	3.710
H26	-0.75600	0.00839	0.52050	3.710
H27	-0.69184	0.40131	0.41162	3.707
H28	-0.82463	0.40173	0.49705	3.707
H29	-0.62027	0.44984	0.50458	3.707
H30	-0.07383	-0.09864	0.93443	3.520
H31	-0.25682	-0.05271	0.88310	3.520
H32	-0.14235	-0.12709	0.83217	3.520
H33	0.01492	0.07363	0.72101	3.961
H34	-0.08641	-0.01810	0.69705	3.961
H35	-0.20088	0.05627	0.74798	3.961

Table 3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	0.0193(2)	0.0199(2)	0.0302(2)	0.00067(17)	-0.00016(17)	0.0022(2)
O1	0.0347(8)	0.0252(8)	0.0351(8)	0.0060(6)	0.0106(6)	-0.0027(7)
O2	0.0480(10)	0.0213(8)	0.0232(7)	0.0081(7)	-0.0071(6)	0.0009(6)
O3	0.0350(8)	0.0290(9)	0.0250(7)	-0.0065(6)	-0.0039(6)	-0.0081(6)
O4	0.0273(8)	0.0353(9)	0.0310(8)	0.0075(6)	0.0113(6)	0.0134(7)
O5	0.0348(8)	0.0343(9)	0.0361(9)	0.0106(7)	-0.0100(7)	-0.0006(7)
O6	0.0478(10)	0.0298(10)	0.0354(8)	0.0046(7)	0.0061(7)	-0.0116(7)
O7	0.0648(17)	0.0630(18)	0.191(4)	0.0145(14)	-0.056(2)	0.048(2)
O8	0.0788(15)	0.0341(11)	0.0570(13)	0.0230(10)	0.0188(11)	0.0172(10)
O9	0.0260(7)	0.0299(8)	0.0311(8)	0.0081(6)	0.0122(6)	0.0066(7)
N1	0.0196(8)	0.0180(8)	0.0271(8)	-0.0004(6)	-0.0005(6)	0.0013(7)
N2	0.0635(15)	0.0311(13)	0.0436(12)	0.0199(11)	-0.0013(11)	0.0077(10)
N3	0.0171(7)	0.0190(8)	0.0188(7)	0.0004(6)	0.0016(6)	0.0024(6)
C1	0.0172(8)	0.0215(9)	0.0225(9)	0.0010(7)	0.0008(7)	0.0024(8)
C2	0.0157(8)	0.0182(9)	0.0160(8)	-0.0020(6)	-0.0004(6)	0.0025(7)
C3	0.0158(8)	0.0190(9)	0.0175(8)	0.0002(7)	-0.0000(6)	0.0017(7)
C4	0.0173(8)	0.0203(10)	0.0194(8)	0.0028(7)	0.0005(7)	0.0006(7)
C5	0.0244(9)	0.0187(10)	0.0157(8)	0.0042(7)	0.0018(7)	-0.0009(7)
C6	0.0204(9)	0.0188(9)	0.0197(8)	-0.0006(7)	0.0017(7)	0.0015(7)
C7	0.0192(8)	0.0250(10)	0.0156(8)	-0.0024(7)	-0.0004(6)	0.0002(7)
C8	0.0211(9)	0.0187(9)	0.0193(8)	0.0002(7)	-0.0024(7)	0.0020(7)
C9	0.0161(8)	0.0192(9)	0.0176(8)	0.0011(6)	-0.0003(6)	0.0006(7)
C10	0.0198(9)	0.0281(10)	0.0187(8)	0.0034(7)	0.0027(7)	0.0005(8)
C11	0.0137(8)	0.0230(10)	0.0239(9)	0.0008(7)	0.0020(7)	0.0011(8)
C12	0.0140(8)	0.0218(10)	0.0196(8)	-0.0013(6)	-0.0004(6)	0.0031(7)
C13	0.0237(9)	0.0233(10)	0.0236(9)	0.0041(7)	-0.0001(7)	-0.0025(8)
C14	0.0184(8)	0.0254(10)	0.0193(9)	-0.0042(7)	0.0015(7)	0.0007(7)
C15	0.0343(10)	0.0189(10)	0.0167(8)	0.0019(8)	-0.0030(7)	0.0015(7)
C16	0.0213(9)	0.0207(10)	0.0155(8)	0.0022(7)	0.0000(6)	-0.0014(7)
C17	0.0421(12)	0.0249(11)	0.0218(9)	0.0135(9)	0.0006(8)	0.0018(9)
C18	0.0269(10)	0.0242(11)	0.0237(9)	0.0004(8)	0.0041(7)	-0.0003(8)
C19	0.0285(10)	0.0327(12)	0.0185(9)	-0.0043(8)	0.0055(8)	0.0018(8)
C20	0.0434(12)	0.0201(10)	0.0252(10)	0.0028(9)	0.0077(8)	0.0033(8)
C21	0.0277(10)	0.0295(11)	0.0258(10)	0.0080(8)	-0.0032(8)	-0.0014(9)
C22	0.0352(11)	0.0233(11)	0.0278(10)	0.0033(8)	0.0027(8)	-0.0000(9)
C23	0.0437(13)	0.0331(13)	0.0396(12)	0.0122(10)	0.0160(10)	0.0058(11)
C24	0.0416(12)	0.0287(12)	0.0164(9)	0.0046(9)	-0.0003(8)	0.0045(8)

Table 3. Anisotropic displacement parameters (continued)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C25	0.0526(14)	0.0326(13)	0.0306(11)	-0.0109(10)	-0.0110(10)	-0.0086(10)
C26	0.0508(14)	0.0239(12)	0.0410(13)	0.0057(10)	-0.0099(11)	0.0075(10)
C27	0.0404(13)	0.0234(12)	0.0478(14)	-0.0042(9)	0.0034(10)	-0.0049(11)
C28	0.0570(16)	0.0389(14)	0.0287(11)	0.0095(12)	-0.0036(10)	-0.0033(11)
C29	0.0171(8)	0.0182(9)	0.0253(9)	-0.0020(7)	-0.0004(7)	-0.0023(8)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
S1	O5	1.4852(17)	S1	N1	1.6716(17)
S1	C22	1.842(2)	O1	C29	1.199(3)
O2	C26	1.449(3)	O2	C29	1.331(2)
O3	C15	1.341(3)	O3	C25	1.449(3)
O4	C1	1.208(3)	O6	C15	1.197(3)
O7	N2	1.210(4)	O8	N2	1.214(3)
O9	C6	1.208(2)	N1	C8	1.482(3)
N2	C17	1.471(3)	N3	C1	1.393(2)
N3	C5	1.430(2)	N3	C6	1.400(3)
C1	C12	1.516(3)	C2	C3	1.572(3)
C2	C8	1.575(3)	C2	C9	1.507(2)
C2	C14	1.538(3)	C3	C6	1.528(3)
C3	C12	1.555(3)	C4	C9	1.332(3)
C4	C10	1.507(3)	C4	C11	1.498(3)
C5	C13	1.389(3)	C5	C18	1.389(3)
C7	C9	1.506(3)	C7	C16	1.556(2)
C8	C24	1.554(3)	C10	C16	1.559(3)
C11	C12	1.535(3)	C13	C21	1.384(3)
C14	C19	1.528(3)	C15	C16	1.520(3)
C16	C29	1.527(3)	C17	C20	1.380(3)
C17	C21	1.384(3)	C18	C20	1.388(3)
C19	C24	1.532(3)	C22	C23	1.533(3)
C22	C27	1.520(3)	C22	C28	1.529(3)

Table 5. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
N1	H1	0.86(3)	C3	H2	0.980
C7	H3	0.970	C7	H4	0.970
C8	H5	0.980	C10	H6	0.970
C10	H7	0.970	C11	H8	0.970
C11	H9	0.970	C12	H10	0.980
C13	H11	0.930	C14	H12	0.970
C14	H13	0.970	C18	H14	0.930
C19	H15	0.970	C19	H16	0.970
C20	H17	0.930	C21	H18	0.930
C23	H19	0.960	C23	H20	0.960
C23	H21	0.960	C24	H22	0.970
C24	H23	0.970	C25	H24	0.960
C25	H25	0.960	C25	H26	0.960
C26	H27	0.960	C26	H28	0.960
C26	H29	0.960	C27	H30	0.960
C27	H31	0.960	C27	H32	0.960
C28	H33	0.960	C28	H34	0.960
C28	H35	0.960			

Table 6. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
O5	S1	N1	111.08(9)	O5	S1	C22	105.61(10)
N1	S1	C22	100.20(10)	C26	O2	C29	115.35(18)
C15	O3	C25	115.95(18)	S1	N1	C8	112.76(13)
O7	N2	O8	123.3(3)	O7	N2	C17	118.2(3)
O8	N2	C17	118.5(2)	C1	N3	C5	122.37(16)
C1	N3	C6	112.48(16)	C5	N3	C6	125.15(16)
O4	C1	N3	124.05(18)	O4	C1	C12	126.67(18)
N3	C1	C12	109.27(16)	C3	C2	C8	105.32(13)
C3	C2	C9	107.99(15)	C3	C2	C14	113.49(15)
C8	C2	C9	114.64(15)	C8	C2	C14	101.49(14)
C9	C2	C14	113.65(14)	C2	C3	C6	115.15(14)
C2	C3	C12	113.78(15)	C6	C3	C12	104.30(15)
C9	C4	C10	112.79(16)	C9	C4	C11	120.10(17)
C10	C4	C11	127.04(16)	N3	C5	C13	119.47(18)
N3	C5	C18	119.11(17)	C13	C5	C18	121.40(18)
O9	C6	N3	124.00(18)	O9	C6	C3	127.47(18)
N3	C6	C3	108.51(15)	C9	C7	C16	102.05(15)
N1	C8	C2	112.35(15)	N1	C8	C24	112.92(17)
C2	C8	C24	104.97(16)	C2	C9	C4	122.26(16)
C2	C9	C7	125.98(16)	C4	C9	C7	111.76(16)
C4	C10	C16	101.83(15)	C4	C11	C12	107.63(15)
C1	C12	C3	104.27(14)	C1	C12	C11	107.33(15)
C3	C12	C11	117.01(16)	C5	C13	C21	119.1(2)
C2	C14	C19	104.93(15)	O3	C15	O6	124.81(19)
O3	C15	C16	109.53(17)	O6	C15	C16	125.65(19)
C7	C16	C10	105.24(14)	C7	C16	C15	112.28(16)
C7	C16	C29	108.37(15)	C10	C16	C15	113.45(16)
C10	C16	C29	107.56(16)	C15	C16	C29	109.67(15)
N2	C17	C20	119.5(2)	N2	C17	C21	117.9(2)
C20	C17	C21	122.6(2)	C5	C18	C20	119.50(19)
C14	C19	C24	104.49(16)	C17	C20	C18	118.5(2)
C13	C21	C17	118.9(2)	S1	C22	C23	103.45(15)
S1	C22	C27	110.71(16)	S1	C22	C28	107.63(17)
C23	C22	C27	111.6(2)	C23	C22	C28	109.8(2)
C27	C22	C28	113.1(2)	C8	C24	C19	107.33(16)
O1	C29	O2	124.37(18)	O1	C29	C16	124.63(17)
O2	C29	C16	110.96(16)				

Table 7. Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom	angle
S1	N1	H1	111(2)	C8	N1	H1	116(2)
C2	C3	H2	107.8	C6	C3	H2	107.8
C12	C3	H2	107.8	C9	C7	H3	111.4
C9	C7	H4	111.4	C16	C7	H3	111.4
C16	C7	H4	111.4	H3	C7	H4	109.2
N1	C8	H5	108.8	C2	C8	H5	108.8
C24	C8	H5	108.8	C4	C10	H6	111.4
C4	C10	H7	111.4	C16	C10	H6	111.4
C16	C10	H7	111.4	H6	C10	H7	109.3
C4	C11	H8	110.2	C4	C11	H9	110.2
C12	C11	H8	110.2	C12	C11	H9	110.2
H8	C11	H9	108.5	C1	C12	H10	109.3
C3	C12	H10	109.3	C11	C12	H10	109.3
C5	C13	H11	120.4	C21	C13	H11	120.4
C2	C14	H12	110.8	C2	C14	H13	110.8
C19	C14	H12	110.8	C19	C14	H13	110.8
H12	C14	H13	108.8	C5	C18	H14	120.2
C20	C18	H14	120.3	C14	C19	H15	110.9
C14	C19	H16	110.9	C24	C19	H15	110.8
C24	C19	H16	110.9	H15	C19	H16	108.9
C17	C20	H17	120.8	C18	C20	H17	120.8
C13	C21	H18	120.5	C17	C21	H18	120.5
C22	C23	H19	109.5	C22	C23	H20	109.5
C22	C23	H21	109.5	H19	C23	H20	109.5
H19	C23	H21	109.5	H20	C23	H21	109.5
C8	C24	H22	110.3	C8	C24	H23	110.2
C19	C24	H22	110.3	C19	C24	H23	110.2
H22	C24	H23	108.5	O3	C25	H24	109.5
O3	C25	H25	109.5	O3	C25	H26	109.5
H24	C25	H25	109.5	H24	C25	H26	109.5
H25	C25	H26	109.5	O2	C26	H27	109.5
O2	C26	H28	109.5	O2	C26	H29	109.5
H27	C26	H28	109.5	H27	C26	H29	109.5
H28	C26	H29	109.5	C22	C27	H30	109.5
C22	C27	H31	109.5	C22	C27	H32	109.5
H30	C27	H31	109.5	H30	C27	H32	109.5
H31	C27	H32	109.5	C22	C28	H33	109.5

Table 7. Bond angles involving hydrogens (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C22	C28	H34	109.5	C22	C28	H35	109.5
H33	C28	H34	109.5	H33	C28	H35	109.5
H34	C28	H35	109.5				

Table 8. Torsion Angles(°)
(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
O5	S1	N1	C8	87.08(13)	O5	S1	C22	C23	-63.37(13)
O5	S1	C22	C27	56.31(15)	O5	S1	C22	C28	-179.60(12)
N1	S1	C22	C23	-178.82(11)	N1	S1	C22	C27	-59.14(14)
N1	S1	C22	C28	64.95(14)	C22	S1	N1	C8	-161.67(11)
C26	O2	C29	O1	0.4(3)	C26	O2	C29	C16	-177.27(16)
C25	O3	C15	O6	-2.2(3)	C25	O3	C15	C16	178.36(15)
S1	N1	C8	C2	129.17(12)	S1	N1	C8	C24	-112.34(13)
O7	N2	C17	C20	-178.6(3)	O7	N2	C17	C21	1.1(4)
O8	N2	C17	C20	-0.9(3)	O8	N2	C17	C21	178.7(2)
C1	N3	C5	C13	130.44(17)	C1	N3	C5	C18	-48.0(2)
C5	N3	C1	O4	-5.7(3)	C5	N3	C1	C12	175.01(14)
C1	N3	C6	O9	175.23(16)	C1	N3	C6	C3	-3.0(2)
C6	N3	C1	O4	175.06(16)	C6	N3	C1	C12	-4.3(2)
C5	N3	C6	O9	-4.0(3)	C5	N3	C6	C3	177.74(14)
C6	N3	C5	C13	-50.4(2)	C6	N3	C5	C18	131.13(17)
O4	C1	C12	C3	-169.88(18)	O4	C1	C12	C11	-45.1(2)
N3	C1	C12	C3	9.41(18)	N3	C1	C12	C11	134.18(14)
C3	C2	C8	N1	-149.42(13)	C3	C2	C8	C24	87.50(15)
C8	C2	C3	C6	-155.35(13)	C8	C2	C3	C12	84.31(15)
C3	C2	C9	C4	42.9(2)	C3	C2	C9	C7	-136.75(16)
C9	C2	C3	C6	81.72(16)	C9	C2	C3	C12	-38.61(17)
C3	C2	C14	C19	-71.17(17)	C14	C2	C3	C6	-45.21(19)
C14	C2	C3	C12	-165.55(12)	C8	C2	C9	C4	-74.1(2)
C8	C2	C9	C7	106.21(18)	C9	C2	C8	N1	-30.9(2)
C9	C2	C8	C24	-153.94(14)	C8	C2	C14	C19	41.32(17)
C14	C2	C8	N1	92.06(16)	C14	C2	C8	C24	-31.02(16)
C9	C2	C14	C19	164.92(14)	C14	C2	C9	C4	169.77(15)
C14	C2	C9	C7	-9.9(3)	C2	C3	C6	O9	65.1(2)
C2	C3	C6	N3	-116.74(15)	C2	C3	C12	C1	115.66(14)
C2	C3	C12	C11	-2.7(2)	C6	C3	C12	C1	-10.61(16)
C6	C3	C12	C11	-128.94(14)	C12	C3	C6	O9	-169.51(17)
C12	C3	C6	N3	8.66(18)	C9	C4	C10	C16	12.7(2)
C10	C4	C9	C2	-176.44(15)	C10	C4	C9	C7	3.3(2)
C9	C4	C11	C12	-44.7(2)	C11	C4	C9	C2	0.5(3)
C11	C4	C9	C7	-179.73(15)	C10	C4	C11	C12	131.81(18)
C11	C4	C10	C16	-164.03(17)	N3	C5	C13	C21	-179.58(15)
N3	C5	C18	C20	178.94(15)	C13	C5	C18	C20	0.5(3)

Table 8. Torsion angles (°) (continued)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C18	C5	C13	C21	-1.1(3)	C9	C7	C16	C10	24.51(17)
C9	C7	C16	C15	148.39(14)	C9	C7	C16	C29	-90.32(15)
C16	C7	C9	C2	161.95(15)	C16	C7	C9	C4	-17.76(19)
N1	C8	C24	C19	-112.72(17)	C2	C8	C24	C19	10.0(2)
C4	C10	C16	C7	-22.74(18)	C4	C10	C16	C15	-145.87(14)
C4	C10	C16	C29	92.66(15)	C4	C11	C12	C1	-73.21(17)
C4	C11	C12	C3	43.46(19)	C5	C13	C21	C17	0.8(3)
C2	C14	C19	C24	-35.74(19)	O3	C15	C16	C7	58.98(19)
O3	C15	C16	C10	178.15(13)	O3	C15	C16	C29	-61.57(19)
O6	C15	C16	C7	-120.4(2)	O6	C15	C16	C10	-1.3(3)
O6	C15	C16	C29	119.0(2)	C7	C16	C29	O1	18.2(2)
C7	C16	C29	O2	-164.05(14)	C10	C16	C29	O1	-95.1(2)
C10	C16	C29	O2	82.64(17)	C15	C16	C29	O1	141.13(17)
C15	C16	C29	O2	-41.2(2)	N2	C17	C20	C18	178.82(18)
N2	C17	C21	C13	-179.48(18)	C20	C17	C21	C13	0.2(3)
C21	C17	C20	C18	-0.8(3)	C5	C18	C20	C17	0.5(3)
C14	C19	C24	C8	15.4(2)					

Table 9. Possible hydrogen bonds

Donor	H	Acceptor	D...A	D-H	H...A	D-H...A	
N1	H1	S1	1.6716(17)	0.86(3)	2.13(3)	47.1(15)	intramol.

Table 10. Intramolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
O1	N3	3.400(2)	O1	C4	3.421(2)
O1	C5	3.579(2)	O1	C7	2.770(3)
O1	C9	3.150(2)	O1	C10	3.258(3)
O1	C13	3.127(3)	O1	C15	3.552(3)
O1	C26	2.647(3)	O2	O3	3.063(2)
O2	O6	3.345(2)	O2	C10	3.066(2)
O2	C15	2.690(3)	O3	C7	2.888(2)
O3	C29	2.845(3)	O4	C3	3.599(2)
O4	C4	3.455(3)	O4	C5	2.845(2)
O4	C6	3.470(3)	O4	C11	2.888(3)
O4	C18	2.965(3)	O5	C8	3.364(3)
O5	C23	3.018(3)	O5	C27	3.088(3)
O6	C7	3.510(3)	O6	C10	2.874(3)
O6	C25	2.679(3)	O6	C29	3.439(3)
O7	C20	3.543(4)	O7	C21	2.696(4)
O8	C20	2.733(3)	O8	C21	3.539(3)
O9	C1	3.469(2)	O9	C2	3.223(2)
O9	C5	2.905(2)	O9	C13	3.076(3)
O9	C14	3.042(3)	O9	C19	3.446(3)
N1	C4	3.446(3)	N1	C7	3.580(2)
N1	C9	2.861(2)	N1	C14	3.206(3)
N1	C19	3.499(3)	N1	C27	3.080(3)
N1	C28	3.093(3)	N3	C2	3.530(3)
N3	C11	3.533(3)	C1	C2	3.553(3)
C1	C4	2.982(3)	C1	C9	3.446(3)
C1	C13	3.587(3)	C1	C18	3.014(3)
C2	C11	2.887(3)	C3	C4	2.889(3)
C3	C19	3.071(3)	C3	C24	3.174(3)
C4	C8	3.271(3)	C4	C29	3.149(3)
C5	C17	2.730(3)	C6	C9	3.258(3)
C6	C13	3.087(3)	C6	C14	3.031(3)
C7	C14	3.023(3)	C8	C11	3.296(3)
C8	C12	3.277(3)	C9	C12	2.827(3)
C9	C29	3.134(2)	C13	C20	2.796(3)
C18	C21	2.787(3)			

Table 11. Intramolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H5	2.527	S1	H9	3.141
S1	H19	2.767	S1	H20	2.751
S1	H21	3.532	S1	H30	2.897
S1	H31	2.911	S1	H33	2.825
S1	H34	3.587	S1	H35	2.869
O1	H3	2.459	O1	H7	3.257
O1	H11	2.560	O1	H27	3.590
O1	H28	2.607	O1	H29	2.612
O2	H7	2.758	O3	H3	2.950
O3	H4	2.862	O4	H7	3.465
O4	H8	2.549	O4	H10	2.800
O4	H14	2.661	O5	H1	2.70(3)
O5	H5	3.212	O5	H19	3.304
O5	H20	2.606	O5	H22	3.555
O5	H30	2.721	O5	H31	3.354
O6	H4	3.405	O6	H6	2.534
O6	H7	3.265	O6	H25	2.655
O6	H26	2.633	O7	H18	2.401
O8	H17	2.457	O9	H2	2.708
O9	H11	2.772	O9	H12	2.393
O9	H16	2.903	N1	H4	3.242
N1	H9	3.269	N1	H13	3.065
N1	H22	2.512	N1	H23	3.206
N1	H30	3.379	N1	H31	2.665
N1	H33	3.396	N1	H35	2.681
N2	H17	2.625	N2	H18	2.594
N3	H2	3.024	N3	H10	2.932
N3	H11	2.601	N3	H14	2.593
C1	H2	3.092	C1	H8	2.552
C1	H9	3.298	C1	H14	2.820
C2	H1	3.03(3)	C2	H3	2.868
C2	H4	3.069	C2	H9	3.024
C2	H10	3.295	C2	H15	3.260
C2	H16	2.809	C2	H22	3.193
C2	H23	3.061	C3	H5	2.453
C3	H8	3.435	C3	H9	2.967
C3	H12	2.731	C3	H13	3.430

Table 11. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C3	H16	2.933	C3	H23	3.314
C4	H3	3.084	C4	H4	2.883
C4	H5	3.321	C4	H10	3.290
C4	H33	3.320	C4	H35	3.166
C5	H17	3.244	C5	H18	3.236
C6	H10	2.984	C6	H11	2.904
C6	H12	2.632	C6	H16	3.245
C7	H6	2.958	C7	H7	3.254
C7	H12	3.193	C7	H13	2.714
C7	H35	3.085	C8	H2	2.468
C8	H9	2.937	C8	H12	3.266
C8	H13	2.730	C8	H15	3.224
C8	H16	3.026	C9	H1	3.41(3)
C9	H2	3.296	C9	H5	3.012
C9	H6	2.931	C9	H7	3.073
C9	H8	3.230	C9	H9	2.807
C9	H12	2.878	C9	H13	2.674
C9	H35	3.141	C10	H3	3.262
C10	H4	2.944	C10	H8	2.764
C10	H9	3.235	C10	H33	3.314
C10	H35	3.214	C11	H2	3.224
C11	H5	2.905	C11	H6	3.066
C11	H7	2.891	C12	H5	2.864
C13	H14	3.259	C14	H1	3.31(3)
C14	H2	2.890	C14	H3	2.754
C14	H4	3.286	C14	H5	3.212
C14	H22	2.961	C14	H23	3.163
C15	H3	3.015	C15	H4	2.600
C15	H6	2.618	C15	H7	3.054
C15	H24	3.164	C15	H25	2.595
C15	H26	2.595	C16	H35	3.478
C17	H11	3.229	C17	H14	3.223
C18	H11	3.260	C19	H1	3.47(3)
C19	H2	2.840	C19	H5	3.166
C20	H18	3.258	C21	H17	3.260
C22	H1	2.84(3)	C23	H30	2.678
C23	H31	3.347	C23	H32	2.742

Table 11. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C23	H33	2.645	C23	H34	2.725
C23	H35	3.333	C24	H1	2.57(3)
C24	H2	2.775	C24	H12	3.249
C24	H13	2.797	C27	H1	2.77(3)
C27	H19	3.346	C27	H20	2.712
C27	H21	2.712	C27	H33	3.359
C27	H34	2.736	C27	H35	2.736
C28	H1	3.41(3)	C28	H4	3.447
C28	H6	3.025	C28	H19	2.640
C28	H20	3.332	C28	H21	2.732
C28	H30	3.361	C28	H31	2.734
C28	H32	2.735	C29	H3	2.517
C29	H4	3.304	C29	H6	3.288
C29	H7	2.492	C29	H27	3.148
C29	H28	2.578	C29	H29	2.578
H1	H4	3.382	H1	H5	2.691
H1	H13	2.981	H1	H22	2.251
H1	H23	3.339	H1	H30	2.987
H1	H31	2.196	H1	H35	2.966
H2	H5	2.261	H2	H9	3.330
H2	H10	2.181	H2	H12	3.123
H2	H16	2.536	H2	H23	2.652
H3	H12	2.684	H3	H13	2.420
H4	H6	3.138	H4	H13	2.737
H4	H35	2.491	H5	H9	2.389
H5	H10	2.973	H5	H16	3.489
H5	H22	2.689	H5	H23	2.208
H6	H8	3.073	H6	H9	3.371
H6	H33	2.581	H6	H34	3.354
H6	H35	2.712	H7	H8	2.673
H7	H9	3.588	H8	H10	2.442
H9	H10	2.318	H9	H33	3.304
H11	H18	2.327	H12	H15	2.535
H12	H16	2.287	H13	H15	2.286
H13	H16	2.841	H13	H22	3.051
H14	H17	2.332	H15	H22	2.226
H15	H23	2.642	H16	H22	2.781

Table 11. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H16	H23	2.228	H19	H30	3.555
H19	H33	2.420	H19	H34	2.950
H19	H35	3.506	H20	H30	2.513
H20	H31	3.566	H20	H32	3.037
H20	H33	3.506	H21	H30	2.942
H21	H31	3.597	H21	H32	2.581
H21	H33	2.968	H21	H34	2.603
H31	H33	3.600	H31	H34	3.018
H31	H35	2.579	H32	H33	3.600
H32	H34	2.579	H32	H35	3.018

Table 12. Intermolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
O1	C11[1]	3.315(2)	O2	O7[2]	3.478(4)
O2	O8[3]	3.013(3)	O2	C20[3]	3.574(3)
O4	C13[4]	3.165(3)	O4	C21[4]	3.063(3)
O4	C25[5]	3.268(3)	O5	O9[6]	3.509(2)
O5	N3[6]	3.200(2)	O5	C1[6]	3.344(3)
O5	C3[6]	3.152(3)	O5	C6[6]	3.038(3)
O5	C12[6]	3.192(3)	O6	C17[3]	3.335(3)
O6	C20[3]	3.573(3)	O6	C21[3]	3.519(3)
O6	C26[3]	3.236(3)	O7	O2[7]	3.478(4)
O7	C26[7]	3.302(4)	O8	O2[5]	3.013(3)
O8	C23[8]	3.451(4)	O8	C26[5]	3.304(4)
O9	O5[9]	3.509(2)	N3	O5[9]	3.200(2)
C1	O5[9]	3.344(3)	C3	O5[9]	3.152(3)
C6	O5[9]	3.038(3)	C11	O1[4]	3.315(2)
C12	O5[9]	3.192(3)	C13	O4[1]	3.165(3)
C17	O6[5]	3.335(3)	C18	C19[10]	3.570(3)
C19	C18[11]	3.570(3)	C20	O2[5]	3.574(3)
C20	O6[5]	3.573(3)	C21	O4[1]	3.063(3)
C21	O6[5]	3.519(3)	C23	O8[12]	3.451(4)
C25	O4[3]	3.268(3)	C26	O6[5]	3.236(3)
C26	O7[2]	3.302(4)	C26	O8[3]	3.304(4)

Symmetry Operators:

(1) X-1,Y,Z
(2) -X-2,Y+1/2-1,-Z+1
(3) -X-1,Y+1/2-1,-Z+1
(4) X+1,Y,Z
(5) -X-1,Y+1/2,-Z+1
(6) -X,Y+1/2-1,-Z+2
(7) -X-2,Y+1/2,-Z+1
(8) X-1,Y+1,Z
(9) -X,Y+1/2,-Z+2
(10) -X-1,Y+1/2,-Z+2
(11) -X-1,Y+1/2-1,-Z+2
(12) X+1,Y-1,Z

Table 13. Intermolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H13[1]	2.924	O1	H8[2]	2.429
O1	H9[2]	3.427	O2	H17[3]	3.055
O3	H6[2]	3.290	O3	H33[2]	2.966
O4	H11[1]	2.627	O4	H18[1]	2.415
O4	H24[4]	3.421	O4	H25[4]	2.581
O4	H26[4]	3.340	O5	H2[5]	2.725
O5	H10[5]	2.703	O5	H13[1]	3.250
O5	H15[1]	3.389	O6	H24[1]	3.358
O6	H27[3]	3.351	O6	H28[3]	3.577
O6	H29[3]	2.418	O7	H7[4]	3.462
O7	H14[2]	3.410	O7	H17[2]	3.327
O7	H21[6]	3.403	O7	H25[7]	3.278
O7	H27[7]	3.087	O7	H28[7]	2.931
O7	H34[6]	3.538	O8	H7[4]	3.264
O8	H19[6]	3.507	O8	H21[6]	2.611
O8	H26[8]	2.857	O8	H27[4]	2.953
O8	H29[4]	3.390	O8	H34[6]	3.478
O9	H1[9]	2.80(3)	O9	H10[2]	2.999
O9	H20[10]	3.260	O9	H22[9]	3.029
O9	H30[9]	3.325	O9	H31[9]	3.029
N2	H7[4]	3.365	N2	H21[6]	2.922
C1	H11[1]	3.182	C1	H18[1]	3.363
C3	H20[10]	3.104	C3	H30[10]	3.254
C5	H15[9]	3.351	C5	H22[9]	2.987
C6	H20[10]	3.338	C7	H9[2]	3.412
C7	H19[2]	3.345	C11	H3[1]	3.021
C11	H11[1]	3.477	C11	H12[1]	3.210
C12	H11[1]	3.336	C12	H12[1]	3.513
C12	H30[10]	3.367	C13	H22[9]	2.981
C14	H9[2]	3.133	C15	H29[3]	3.345
C17	H21[6]	3.531	C17	H22[9]	3.470
C17	H23[9]	3.304	C18	H15[9]	2.811
C18	H18[1]	3.414	C18	H22[9]	3.277
C18	H25[4]	3.215	C19	H20[10]	3.305
C19	H30[9]	3.591	C19	H31[9]	3.447
C19	H32[9]	3.508	C20	H15[9]	3.160
C20	H22[9]	3.521	C20	H23[9]	3.563

Table 13. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C20	H25[4]	3.568	C20	H27[4]	3.532
C21	H14[2]	3.417	C21	H22[9]	3.230
C21	H23[9]	3.446	C21	H24[7]	3.554
C21	H25[7]	3.451	C22	H2[5]	3.536
C23	H2[5]	3.105	C23	H4[1]	3.462
C23	H16[5]	3.183	C23	H23[5]	3.292
C24	H20[10]	3.485	C25	H6[2]	3.590
C25	H18[11]	3.240	C25	H28[11]	3.440
C25	H29[3]	3.470	C25	H33[2]	3.341
C25	H34[2]	3.593	C26	H17[3]	3.294
C26	H24[7]	3.386	C26	H26[4]	3.464
C26	H34[4]	3.108	C27	H2[5]	3.262
C27	H10[5]	3.556	C27	H15[12]	3.545
C27	H16[12]	3.091	C27	H23[5]	3.543
C28	H24[1]	3.430	C28	H27[3]	3.259
C29	H8[2]	3.240	H1	O9[12]	2.80(3)
H2	O5[10]	2.725	H2	C22[10]	3.536
H2	C23[10]	3.105	H2	C27[10]	3.262
H2	H20[10]	2.238	H2	H21[10]	3.465
H2	H30[10]	2.427	H3	C11[2]	3.021
H3	H8[2]	2.735	H3	H9[2]	2.453
H3	H19[2]	3.378	H3	H33[2]	3.175
H4	C23[2]	3.462	H4	H19[2]	2.506
H4	H33[2]	3.291	H5	H12[1]	3.246
H5	H13[1]	3.398	H5	H15[1]	3.572
H5	H30[10]	3.007	H6	O3[1]	3.290
H6	C25[1]	3.590	H6	H24[1]	2.976
H7	O7[3]	3.462	H7	O8[3]	3.264
H7	N2[3]	3.365	H7	H28[1]	3.589
H8	O1[1]	2.429	H8	C29[1]	3.240
H8	H3[1]	2.735	H8	H11[1]	2.847
H8	H12[1]	3.358	H9	O1[1]	3.427
H9	C7[1]	3.412	H9	C14[1]	3.133
H9	H3[1]	2.453	H9	H12[1]	2.501
H9	H13[1]	2.895	H10	O5[10]	2.703
H10	O9[1]	2.999	H10	C27[10]	3.556
H10	H11[1]	2.926	H10	H12[1]	2.931

Table 13. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H10	H30[10]	2.673	H11	O4[2]	2.627
H11	C1[2]	3.182	H11	C11[2]	3.477
H11	C12[2]	3.336	H11	H8[2]	2.847
H11	H10[2]	2.926	H11	H22[9]	3.354
H12	C11[2]	3.210	H12	C12[2]	3.513
H12	H5[2]	3.246	H12	H8[2]	3.358
H12	H9[2]	2.501	H12	H10[2]	2.931
H12	H30[9]	3.266	H13	S1[2]	2.924
H13	O5[2]	3.250	H13	H5[2]	3.398
H13	H9[2]	2.895	H13	H19[2]	3.383
H14	O7[1]	3.410	H14	C21[1]	3.417
H14	H15[9]	2.780	H14	H18[1]	2.693
H14	H25[4]	3.190	H14	H32[8]	3.560
H15	O5[2]	3.389	H15	C5[12]	3.351
H15	C18[12]	2.811	H15	C20[12]	3.160
H15	C27[9]	3.545	H15	H5[2]	3.572
H15	H14[12]	2.780	H15	H17[12]	3.359
H15	H30[9]	3.419	H15	H31[9]	3.512
H15	H32[9]	3.135	H16	C23[10]	3.183
H16	C27[9]	3.091	H16	H19[10]	3.579
H16	H20[10]	2.495	H16	H21[10]	3.088
H16	H30[9]	3.125	H16	H31[9]	2.645
H16	H32[9]	3.000	H17	O2[4]	3.055
H17	O7[1]	3.327	H17	C26[4]	3.294
H17	H15[9]	3.359	H17	H27[4]	2.660
H17	H32[8]	3.116	H18	O4[2]	2.415
H18	C1[2]	3.363	H18	C18[2]	3.414
H18	C25[7]	3.240	H18	H14[2]	2.693
H18	H24[7]	3.004	H18	H25[7]	2.610
H19	O8[13]	3.507	H19	C7[1]	3.345
H19	H3[1]	3.378	H19	H4[1]	2.506
H19	H13[1]	3.383	H19	H16[5]	3.579
H19	H31[1]	3.312	H20	O9[5]	3.260
H20	C3[5]	3.104	H20	C6[5]	3.338
H20	C19[5]	3.305	H20	C24[5]	3.485
H20	H2[5]	2.238	H20	H16[5]	2.495
H20	H23[5]	2.900	H20	H31[1]	3.264

Table 13. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H21	O7[13]	3.403	H21	O8[13]	2.611
H21	N2[13]	2.922	H21	C17[13]	3.531
H21	H2[5]	3.465	H21	H16[5]	3.088
H21	H23[5]	2.854	H22	O9[12]	3.029
H22	C5[12]	2.987	H22	C13[12]	2.981
H22	C17[12]	3.470	H22	C18[12]	3.277
H22	C20[12]	3.521	H22	C21[12]	3.230
H22	H11[12]	3.354	H23	C17[12]	3.304
H23	C20[12]	3.563	H23	C21[12]	3.446
H23	C23[10]	3.292	H23	C27[10]	3.543
H23	H20[10]	2.900	H23	H21[10]	2.854
H23	H30[10]	3.117	H23	H32[10]	3.210
H24	O4[3]	3.421	H24	O6[2]	3.358
H24	C21[11]	3.554	H24	C26[11]	3.386
H24	C28[2]	3.430	H24	H6[2]	2.976
H24	H18[11]	3.004	H24	H27[11]	3.570
H24	H28[11]	2.784	H24	H29[11]	3.308
H24	H33[2]	2.985	H24	H34[2]	3.039
H25	O4[3]	2.581	H25	O7[11]	3.278
H25	C18[3]	3.215	H25	C20[3]	3.568
H25	C21[11]	3.451	H25	H14[3]	3.190
H25	H18[11]	2.610	H25	H29[3]	3.515
H26	O4[3]	3.340	H26	O8[14]	2.857
H26	C26[3]	3.464	H26	H27[3]	3.534
H26	H28[11]	3.274	H26	H29[3]	2.759
H26	H33[2]	3.494	H26	H34[2]	3.515
H27	O6[4]	3.351	H27	O7[11]	3.087
H27	O8[3]	2.953	H27	C20[3]	3.532
H27	C28[4]	3.259	H27	H17[3]	2.660
H27	H24[7]	3.570	H27	H26[4]	3.534
H27	H34[4]	2.424	H27	H35[4]	3.308
H28	O6[4]	3.577	H28	O7[11]	2.931
H28	C25[7]	3.440	H28	H7[2]	3.589
H28	H24[7]	2.784	H28	H26[7]	3.274
H28	H34[4]	3.054	H29	O6[4]	2.418
H29	O8[3]	3.390	H29	C15[4]	3.345
H29	C25[4]	3.470	H29	H24[7]	3.308

Table 13. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H29	H25[4]	3.515	H29	H26[4]	2.759
H29	H34[4]	3.441	H30	O9[12]	3.325
H30	C3[5]	3.254	H30	C12[5]	3.367
H30	C19[12]	3.591	H30	H2[5]	2.427
H30	H5[5]	3.007	H30	H10[5]	2.673
H30	H12[12]	3.266	H30	H15[12]	3.419
H30	H16[12]	3.125	H30	H23[5]	3.117
H31	O9[12]	3.029	H31	C19[12]	3.447
H31	H15[12]	3.512	H31	H16[12]	2.645
H31	H19[2]	3.312	H31	H20[2]	3.264
H32	C19[12]	3.508	H32	H14[14]	3.560
H32	H15[12]	3.135	H32	H16[12]	3.000
H32	H17[14]	3.116	H32	H23[5]	3.210
H33	O3[1]	2.966	H33	C25[1]	3.341
H33	H3[1]	3.175	H33	H4[1]	3.291
H33	H24[1]	2.985	H33	H26[1]	3.494
H34	O7[13]	3.538	H34	O8[13]	3.478
H34	C25[1]	3.593	H34	C26[3]	3.108
H34	H24[1]	3.039	H34	H26[1]	3.515
H34	H27[3]	2.424	H34	H28[3]	3.054
H34	H29[3]	3.441	H35	H27[3]	3.308

Symmetry Operators:

(1) X+1,Y,Z	(2) X-1,Y,Z
(3) -X-1,Y+1/2-1,-Z+1	(4) -X-1,Y+1/2,-Z+1
(5) -X,Y+1/2-1,-Z+2	(6) X-1,Y+1,Z
(7) -X-2,Y+1/2,-Z+1	(8) X,Y+1,Z
(9) -X-1,Y+1/2,-Z+2	(10) -X,Y+1/2,-Z+2
(11) -X-2,Y+1/2-1,-Z+1	(12) -X-1,Y+1/2-1,-Z+2
(13) X+1,Y-1,Z	(14) X,Y-1,Z

X-ray Structure Report

for

200

November 25, 2015

Experimental

Data Collection

A colorless chip crystal of $C_{31}H_{42}N_2O_{4.67}S$ having approximate dimensions of 0.840 x 0.550 x 0.020 mm was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-Kα radiation.

The crystal-to-detector distance was 35.15 mm.

Cell constants and an orientation matrix for data collection corresponded to a C-centered monoclinic cell with dimensions:

a = 22.508(3) Å
b = 15.8459(17) Å β = 93.149(4)^o
c = 26.254(4) Å
V = 9349.6(19) Å^3

For Z = 12 and F.W. = 549.46, the calculated density is 1.171 g/cm^3. Based on the reflection conditions of:

hkl: h+k = 2n

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

C2 (#5)

The data were collected at a temperature of -173 $\pm$ 1 ^{o}C to a maximum 2θ value of 150.9^o. The crystal-to-detector distance was 35.15 mm. Readout was performed in the 0.172 mm pixel mode.

Data Reduction

Of the 64326 reflections were collected, where 18083 were unique (R_{int} = 0.0859); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku).[1]

The linear absorption coefficient, μ, for Cu-Kα radiation is 12.264 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.706 to 0.976. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[2] and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[3] on F^2 was based on 18083 observed reflections and 1127 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma||Fo|-|Fc||/\Sigma|Fo| = 0.0621$$

$$wR2 = [\Sigma(w(Fo^2-Fc^2)^2)/\Sigma w(Fo^2)^2]^{1/2} = 0.1598$$

The goodness of fit[4] was 0.71. A Sheldrick weighting scheme was used. Plots of $\Sigma w(|Fo|-|Fc|)^2$ versus |Fo|, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.60 and -1.05 e^-/A^3, respectively. The final Flack parameter[5] was -0.009(13), indicating that the present absolute structure is correct.[6]

Neutral atom scattering factors were taken from International Tables for X-ray Crystallography (IT), Vol. IV, Table 2.2B.[7] Anomalous dispersion effects were included in Fcalc;[8] the values for Δf' and Δf" were those of Creagh and McAuley.[9] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[10] All calculations were performed using the CrystalStructure[11,12] crystallographic software package.

References

(1) CrystalClear: Data Collection and Processing Software, Rigaku Corporation (1998-2014). Tokyo 196-8666, Japan.

(2) SIR2004: Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. and Spagna R. (2005). J. Appl. Cryst. 38, 381-388.

(3) Least Squares function minimized:

$\Sigma w(F_o^2-F_c^2)^2$ where w = Least Squares weights.

(4) Goodness of fit is defined as:

$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$

where: N_o = number of observations
N_v = number of variables

(5) Flack, H. D. (1983), Acta Cryst. A39, 876-881.

(6) Flack, H. D. and Bernardinelli (2000), J. Appl. Cryst. 33, 114-1148.

(7) International Tables for X-ray Crystallography, Vol. IV (1974). Ed. J. A. Ibers and W. C. Hamilton, The Kynoch Press, Birmingham, England, Table 2.2B, pp. 99.

(8) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

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EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{31}H_{42}N_2O_{4.67}S$
Formula Weight	549.46
Crystal Color, Habit	colorless, chip
Crystal Dimensions	0.840 X 0.550 X 0.020 mm
Crystal System	monoclinic
Lattice Type	C-centered
Lattice Parameters	a = 22.508(3) Å b = 15.8459(17) Å c = 26.254(4) Å β = 93.149(4)^o V = 9349.6(19) Å^3
Space Group	C2 (#5)
Z value	12
D_{calc}	1.171 g/cm^3
F_{000}	3544.32
μ(CuKα)	12.264 cm^{-1}

B. Intensity Measurements

Diffractometer	XtaLAB P200
Radiation	CuKα (λ = 1.54187 Å) multi-layer mirror monochromated
Voltage, Current	40 kV, 30 mA
Temperature	-173.0 ^{o}C
Detector Aperture	83.8 x 70.0 mm
Detector Position	35.15 mm
Pixel Size	0.172 mm
$2\theta_{max}$	150.9^o
No. of Reflections Measured	Total: 64326 Unique: 18083 (R_{int} = 0.0859) Friedel pairs: 8323
Corrections	Lorentz-polarization Absorption (trans. factors: 0.706 - 0.976)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR2004)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w(Fo^2-Fc^2)^2$
Least Squares Weights	$1/[0.0058Fo^2+1.0000\sigma(Fo^2)]/(4Fo^2)$
$2\theta_{max}$ cutoff	150.9^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	18083
No. Variables	1127
Reflection/Parameter Ratio	16.05
Residuals: R1 (I>2.00σ(I))	0.0621
Residuals: R (All reflections)	0.0771
Residuals: wR2 (All reflections)	0.1598
Goodness of Fit Indicator	0.713
Flack Parameter (Friedel pairs = 8323)	-0.009(13)
Max Shift/Error in Final Cycle	0.005
Maximum peak in Final Diff. Map	2.60 $e^-/Å^3$
Minimum peak in Final Diff. Map	-1.05 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
S1	0.38403(3)	0.89715(5)	0.89404(3)	2.211(15)	1
S2	0.78581(3)	0.95849(6)	0.76631(3)	2.499(16)	1
S3	0.35881(4)	1.15209(7)	0.56254(3)	3.48(2)	1
O1	0.43435(10)	0.86670(15)	0.92897(8)	2.66(5)	1
O2	0.32026(13)	1.08879(17)	0.70043(9)	3.65(6)	1
O3	0.07203(10)	1.05947(16)	0.89974(10)	3.24(6)	1
O4	0.08434(10)	1.19600(15)	0.86748(9)	2.84(5)	1
O5	0.81954(10)	0.90025(17)	0.73326(9)	3.09(5)	1
O6	0.64713(9)	0.98345(15)	0.96986(8)	2.53(5)	1
O7	0.58774(15)	1.33151(18)	0.75640(11)	4.47(7)	1
O8	0.50404(13)	1.27701(18)	0.79437(10)	4.12(6)	1
O9	0.34123(15)	1.22892(19)	0.59126(10)	4.45(7)	1
O10	0.30264(11)	0.95593(18)	0.37063(8)	3.33(5)	1
O11	0.52565(10)	0.76850(15)	0.59789(9)	2.93(5)	1
O12	0.45846(10)	0.66257(16)	0.57176(9)	3.02(5)	1
O13	0.03670	0.92468	0.56515	6.913	1/2
O14	-0.06850	0.94328	0.53361	5.987	1/2
O15	0.00000	0.83798	1.00000	16.928	1/2
O16	-0.06011	0.86565	1.04423	4.471	1/2
N1	0.35574(11)	0.98667(18)	0.91537(10)	2.32(5)	1
N2	0.3337(2)	1.2289(2)	0.70358(12)	4.59(9)	1
N3	0.71542(11)	0.96504(18)	0.74591(10)	2.38(5)	1
N4	0.56052(12)	0.91199(19)	0.96352(9)	2.61(6)	1
N5	0.33223(13)	1.0661(2)	0.58827(11)	3.11(6)	1
N6	0.22573(17)	0.8675(3)	0.37457(12)	4.70(9)	1
C1	0.32086(15)	0.8253(2)	0.90534(13)	2.83(7)	1
C2	0.34531(19)	0.7382(3)	0.89371(18)	3.98(9)	1
C3	0.30169(19)	0.8299(3)	0.96005(14)	3.74(9)	1
C4	0.27062(16)	0.8505(3)	0.86736(15)	3.55(8)	1
C5	0.38390(14)	1.0635(2)	0.89613(12)	2.35(7)	1
C6	0.44295(15)	1.0863(2)	0.92558(14)	2.78(7)	1
C7	0.42671(15)	1.1496(2)	0.96751(13)	2.82(7)	1
C8	0.35919(14)	1.1626(2)	0.96028(12)	2.38(6)	1
C9	0.34330(14)	1.1418(2)	0.90358(11)	2.27(6)	1
C10	0.27733(14)	1.1237(2)	0.89301(11)	2.27(6)	1
C11	0.23152(14)	1.1284(2)	0.93319(12)	2.66(7)	1
C12	0.17089(14)	1.1188(2)	0.90270(12)	2.54(7)	1

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy (continued)

atom	x	y	z	B_{eq}	occ
C13	0.18694(15)	1.0822(2)	0.85076(13)	2.95(7)	1
C14	0.25242(14)	1.0983(2)	0.84848(12)	2.45(7)	1
C15	0.28258(15)	1.0812(2)	0.79993(13)	2.94(7)	1
C16	0.32140(15)	1.1517(2)	0.78271(12)	2.74(7)	1
C17	0.35418(15)	1.2055(2)	0.81165(12)	2.59(7)	1
C18	0.36587(15)	1.2143(2)	0.86850(12)	2.44(7)	1
C19	0.32540(17)	1.1552(2)	0.72537(12)	3.08(8)	1
C20	0.34772(15)	1.3026(2)	0.88559(12)	2.52(7)	1
C21	0.28929(17)	1.3247(2)	0.89172(15)	3.36(8)	1
C22	0.2741(2)	1.4032(3)	0.91170(15)	3.99(9)	1
C23	0.3177(2)	1.4611(3)	0.92269(15)	4.62(11)	1
C24	0.3764(2)	1.4424(3)	0.91446(19)	5.06(12)	1
C25	0.3912(2)	1.3627(3)	0.89671(16)	3.98(9)	1
C26	0.12688(16)	1.0639(2)	0.92944(14)	3.10(8)	1
C27	0.14075(14)	1.2050(2)	0.89438(13)	2.61(7)	1
C28	0.04452(15)	1.1403(2)	0.89128(14)	2.98(7)	1
C29	0.02236(18)	1.1762(3)	0.94007(16)	3.90(9)	1
C30	-0.00600(16)	1.1252(3)	0.85252(16)	3.50(8)	1
C31	0.81055(16)	1.0649(2)	0.74819(14)	3.10(8)	1
C32	0.87670(19)	1.0651(3)	0.7654(2)	5.23(12)	1
C33	0.80218(19)	1.0785(3)	0.69115(16)	4.06(9)	1
C34	0.7755(2)	1.1273(3)	0.77805(19)	4.61(10)	1
C35	0.67492(13)	0.9050(2)	0.77059(12)	2.38(6)	1
C36	0.67220(17)	0.8180(2)	0.74362(14)	3.08(8)	1
C37	0.61997(16)	0.8237(2)	0.70340(13)	3.04(8)	1
C38	0.59418(15)	0.9124(2)	0.70863(11)	2.60(7)	1
C39	0.60965(14)	0.9388(2)	0.76489(11)	2.29(6)	1
C40	0.60494(14)	1.0324(2)	0.77465(12)	2.42(7)	1
C41	0.58580(18)	1.0947(2)	0.73327(13)	3.16(8)	1
C42	0.57780(17)	1.1797(3)	0.76153(13)	3.32(8)	1
C43	0.61263(17)	1.1668(2)	0.81318(13)	3.08(8)	1
C44	0.61852(14)	1.0730(2)	0.81805(12)	2.51(7)	1
C45	0.64082(16)	1.0349(2)	0.86772(12)	2.78(7)	1
C46	0.60472(13)	0.9615(2)	0.88595(11)	2.33(6)	1
C47	0.57724(13)	0.9018(2)	0.85759(11)	2.28(6)	1
C48	0.57072(13)	0.8864(2)	0.80082(11)	2.36(7)	1
C49	0.60517(13)	0.9527(2)	0.94336(11)	2.26(6)	1

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy (continued)

atom	x	y	z	B_{eq}	occ
C50	0.50456(14)	0.8886(2)	0.78437(11)	2.39(6)	1
C51	0.47460(16)	0.8148(3)	0.76957(13)	3.09(8)	1
C52	0.41538(17)	0.8187(3)	0.75117(15)	3.99(9)	1
C53	0.38609(15)	0.8957(3)	0.74774(12)	3.79(9)	1
C54	0.41497(17)	0.9670(3)	0.76311(14)	3.65(9)	1
C55	0.47309(15)	0.9632(3)	0.78231(14)	3.25(8)	1
C56	0.5987(2)	1.2533(3)	0.73156(15)	3.91(9)	1
C57	0.51175(19)	1.1958(3)	0.77126(15)	3.63(9)	1
C58	0.5266(2)	1.3433(3)	0.76547(16)	4.35(10)	1
C59	0.4884(3)	1.3594(3)	0.71623(19)	5.66(12)	1
C60	0.5267(3)	1.4210(3)	0.8000(2)	5.56(13)	1
C61	0.4378(2)	1.1390(3)	0.58077(16)	4.49(10)	1
C62	0.4668(3)	1.2181(6)	0.5609(3)	9.0(2)	1
C63	0.4484(2)	1.1306(3)	0.63779(17)	4.83(11)	1
C64	0.4581(2)	1.0604(5)	0.5544(2)	7.19(16)	1
C65	0.27730(15)	1.0303(3)	0.56289(13)	3.05(8)	1
C66	0.22038(17)	1.0660(3)	0.58530(16)	3.99(9)	1
C67	0.20720(18)	1.0085(3)	0.62886(16)	4.43(10)	1
C68	0.25292(16)	0.9364(3)	0.62861(13)	3.40(8)	1
C69	0.27405(14)	0.9350(2)	0.57314(12)	2.79(7)	1
C70	0.33303(14)	0.8901(2)	0.56686(11)	2.61(7)	1
C71	0.36862(16)	0.8510(3)	0.61145(13)	3.33(8)	1
C72	0.42011(16)	0.8042(3)	0.58777(13)	3.01(8)	1
C73	0.41988(15)	0.8355(2)	0.53232(12)	2.91(7)	1
C74	0.36145(15)	0.8815(2)	0.52426(12)	2.75(7)	1
C75	0.34446(15)	0.9160(3)	0.47205(12)	3.02(8)	1
C76	0.27977(15)	0.9050(3)	0.45326(12)	2.91(7)	1
C77	0.23248(15)	0.8973(3)	0.48072(12)	3.11(7)	1
C78	0.22407(15)	0.8947(3)	0.53741(12)	3.14(7)	1
C79	0.27063(16)	0.9111(3)	0.39572(12)	2.94(7)	1
C80	0.20812(16)	0.8051(3)	0.55301(12)	3.22(8)	1
C81	0.15452(19)	0.7902(3)	0.57720(15)	4.22(10)	1
C82	0.1405(2)	0.7107(4)	0.59428(16)	5.00(12)	1
C83	0.1784(3)	0.6450(3)	0.58790(15)	4.99(11)	1
C84	0.2299(2)	0.6575(3)	0.56266(16)	4.53(10)	1
C85	0.24450(18)	0.7371(3)	0.54452(14)	3.71(9)	1
C86	0.47972(15)	0.8196(2)	0.61684(13)	2.94(7)	1

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy (continued)

atom	x	y	z	B_{eq}	occ
C87	0.40931(15)	0.7087(3)	0.59000(14)	3.17(8)	1
C88	0.51355(15)	0.6804(2)	0.59871(14)	3.07(8)	1
C89	0.51469(18)	0.6460(3)	0.65294(15)	3.77(9)	1
C90	0.56172(17)	0.6391(3)	0.56838(16)	3.74(9)	1
C91	-0.00699	0.94220	0.52195	5.202	1
C92	-0.07349	0.94423	0.58574	5.870	1/2
C93	-0.02031	0.87853	1.01650	8.284	1/2
C94	0.00000	0.97188	1.00000	6.335	1/2
C95	-0.08062	0.80206	1.07435	5.606	1/2

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Atomic coordinates and B_{iso} involving hydrogen atoms

atom	x	y	z	B_{iso}	occ
H1	0.35411	0.98322	0.94767	2.752	1
H2	0.34656	1.22867	0.66891	5.477	1
H3	0.34226	1.27273	0.71723	5.469	1
H4	0.70903	0.95229	0.70987	2.848	1
H5	0.56780	0.89931	0.99936	3.112	1
H6	0.53652	0.90183	0.94966	3.109	1
H7	0.32573	1.06693	0.62318	3.689	1
H8	0.21993	0.87007	0.34292	5.572	1
H9	0.21981	0.82991	0.38579	5.582	1
H10	0.31518	0.69640	0.89806	4.731	1
H11	0.35732	0.73675	0.85918	4.733	1
H12	0.37915	0.72630	0.91656	4.737	1
H13	0.33437	0.81457	0.98303	4.481	1
H14	0.28908	0.88640	0.96743	4.481	1
H15	0.26914	0.79171	0.96396	4.473	1
H16	0.28430	0.84731	0.83339	4.214	1
H17	0.25784	0.90711	0.87395	4.203	1
H18	0.23790	0.81242	0.87049	4.215	1
H19	0.39061	1.05672	0.85987	2.800	1
H20	0.46091	1.03591	0.94066	3.290	1
H21	0.47010	1.11194	0.90271	3.291	1
H22	0.43701	1.12700	1.00120	3.329	1
H23	0.44682	1.20308	0.96344	3.343	1
H24	0.34892	1.22038	0.96813	2.805	1
H25	0.33898	1.12448	0.98245	2.823	1
H26	0.23807	1.08292	0.95768	3.169	1
H27	0.23412	1.18209	0.95066	3.169	1
H28	0.17967	1.02197	0.84908	3.498	1
H29	0.16537	1.10995	0.82255	3.512	1
H30	0.25216	1.07111	0.77293	3.483	1
H31	0.30715	1.03129	0.80463	3.491	1
H32	0.37414	1.24532	0.79294	3.110	1
H33	0.40929	1.21308	0.87402	2.916	1
H34	0.25942	1.28593	0.88288	4.020	1
H35	0.23453	1.41578	0.91730	4.797	1
H36	0.30782	1.51413	0.93458	5.481	1
H37	0.40587	1.48218	0.92228	5.962	1

Table 2. Atomic coordinates and B_{iso} involving hydrogens/B_{eq} and occupancy (continued)

atom	x	y	z	B_{eq}	occ
H38	0.43092	1.35009	0.89181	4.700	1
H39	0.11711	1.08695	0.96215	3.697	1
H40	0.14061	1.00620	0.93425	3.701	1
H41	0.16355	1.24272	0.87394	3.128	1
H42	0.13279	1.23291	0.92623	3.125	1
H43	-0.00434	1.13665	0.95472	4.685	1
H44	0.00181	1.22821	0.93304	4.666	1
H45	0.05556	1.18619	0.96393	4.677	1
H46	0.00935	1.10043	0.82264	4.160	1
H47	-0.03436	1.08763	0.86645	4.186	1
H48	-0.02495	1.17785	0.84379	4.168	1
H49	0.88056	1.05659	0.80163	6.195	1
H50	0.89701	1.02059	0.74861	6.195	1
H51	0.89410	1.11837	0.75711	6.185	1
H52	0.82180	1.03395	0.67367	4.843	1
H53	0.76048	1.07775	0.68131	4.842	1
H54	0.81889	1.13174	0.68216	4.848	1
H55	0.73374	1.12152	0.76872	5.535	1
H56	0.78237	1.11636	0.81370	5.534	1
H57	0.78790	1.18383	0.77055	5.527	1
H58	0.68717	0.89803	0.80674	2.805	1
H59	0.70896	0.80712	0.72720	3.709	1
H60	0.66501	0.77321	0.76764	3.718	1
H61	0.63378	0.81620	0.66940	3.649	1
H62	0.58995	0.78136	0.70967	3.660	1
H63	0.55147	0.91125	0.70181	3.111	1
H64	0.61196	0.95120	0.68519	3.103	1
H65	0.61590	1.09853	0.70833	3.725	1
H66	0.54870	1.07536	0.71672	3.777	1
H67	0.65158	1.19280	0.81328	3.651	1
H68	0.59107	1.18880	0.84127	3.688	1
H69	0.64060	1.07863	0.89347	3.275	1
H70	0.68123	1.01563	0.86399	3.286	1
H71	0.55863	0.86115	0.87673	2.707	1
H72	0.58274	0.82768	0.79608	2.824	1
H73	0.49397	0.76299	0.77202	3.707	1
H74	0.39548	0.76949	0.74109	4.771	1

Table 2. Atomic coordinates and B_{iso} involving hydrogens/B_{eq} and occupancy (continued)

atom	x	y	z	B_{eq}	occ
H75	0.34682	0.89803	0.73463	4.534	1
H76	0.39529	1.01857	0.76092	4.397	1
H77	0.49168	1.01240	0.79440	3.903	1
H78	0.57845	1.25741	0.69797	4.665	1
H79	0.64127	1.25195	0.72768	4.650	1
H80	0.48717	1.19595	0.73974	4.314	1
H81	0.49631	1.15443	0.79436	4.314	1
H82	0.44758	1.36657	0.72447	6.714	1
H83	0.50176	1.40937	0.69971	6.707	1
H84	0.49135	1.31199	0.69373	6.705	1
H85	0.54312	1.46847	0.78262	6.609	1
H86	0.48668	1.43293	0.80772	6.617	1
H87	0.55036	1.41062	0.83100	6.623	1
H88	0.45968	1.22127	0.52432	10.692	1
H89	0.50906	1.21524	0.56864	10.692	1
H90	0.45041	1.26570	0.57663	10.695	1
H91	0.49008	1.12268	0.64598	5.706	1
H92	0.43494	1.18065	0.65397	5.717	1
H93	0.42689	1.08256	0.65025	5.686	1
H94	0.43633	1.01231	0.56600	8.595	1
H95	0.45008	1.06665	0.51817	8.593	1
H96	0.49951	1.05244	0.56174	8.602	1
H97	0.27691	1.04082	0.52608	3.616	1
H98	0.22801	1.12330	0.59734	4.737	1
H99	0.18817	1.06669	0.55927	4.762	1
H100	0.21090	1.03848	0.66114	5.293	1
H101	0.16731	0.98581	0.62390	5.303	1
H102	0.23451	0.88305	0.63678	4.061	1
H103	0.28567	0.94775	0.65326	4.054	1
H104	0.38333	0.89482	0.63461	3.972	1
H105	0.34358	0.81245	0.62935	3.968	1
H106	0.45248	0.87387	0.52725	3.482	1
H107	0.42124	0.78909	0.50829	3.473	1
H108	0.36922	0.88858	0.44795	3.593	1
H109	0.35288	0.97613	0.47274	3.608	1
H110	0.19708	0.89370	0.46100	3.674	1
H111	0.18843	0.92836	0.54265	3.720	1

Table 2. Atomic coordinates and B_{iso} involving hydrogens/B_{eq} and occupancy (continued)

atom	x	y	z	B_{eq}	occ
H112	0.12886	0.83535	0.58191	5.059	1
H113	0.10541	0.70223	0.61065	6.000	1
H114	0.16891	0.59128	0.59941	5.915	1
H115	0.25563	0.61241	0.55808	5.312	1
H116	0.27858	0.74443	0.52660	4.387	1
H117	0.47818	0.80672	0.65284	3.491	1
H118	0.49272	0.87744	0.61295	3.468	1
H119	0.37485	0.69178	0.56854	3.775	1
H120	0.40455	0.68876	0.62444	3.747	1
H121	0.50651	0.58654	0.65199	4.465	1
H122	0.55319	0.65542	0.66965	4.454	1
H123	0.48498	0.67432	0.67141	4.460	1
H124	0.55530	0.57899	0.56768	4.443	1
H125	0.60018	0.65088	0.58413	4.455	1
H126	0.55945	0.66032	0.53408	4.454	1

Table 3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	0.0314(4)	0.0286(4)	0.0234(4)	0.0013(3)	-0.0041(3)	-0.0026(3)
S2	0.0336(4)	0.0331(5)	0.0270(4)	-0.0011(3)	-0.0092(3)	0.0000(3)
S3	0.0500(5)	0.0551(6)	0.0257(4)	0.0089(4)	-0.0092(3)	-0.0026(4)
O1	0.0342(11)	0.0343(13)	0.0317(12)	0.0035(10)	-0.0062(9)	-0.0021(9)
O2	0.0720(18)	0.0409(16)	0.0245(12)	0.0126(13)	-0.0074(11)	-0.0050(10)
O3	0.0359(12)	0.0330(14)	0.0534(15)	-0.0022(10)	-0.0060(11)	0.0025(11)
O4	0.0349(12)	0.0323(13)	0.0400(13)	0.0018(10)	-0.0055(10)	0.0004(10)
O5	0.0376(12)	0.0406(14)	0.0381(13)	0.0035(11)	-0.0083(10)	-0.0008(11)
O6	0.0350(11)	0.0364(13)	0.0241(11)	-0.0023(10)	-0.0059(9)	-0.0016(9)
O7	0.084(2)	0.0402(16)	0.0456(15)	0.0037(15)	-0.0024(14)	-0.0026(12)
O8	0.0613(17)	0.0439(17)	0.0501(16)	0.0101(13)	-0.0071(13)	-0.0071(13)
O9	0.085(2)	0.0477(17)	0.0350(14)	0.0140(15)	-0.0076(13)	0.0018(12)
O10	0.0443(13)	0.0602(17)	0.0211(11)	0.0022(13)	-0.0052(10)	-0.0040(11)
O11	0.0339(12)	0.0319(13)	0.0447(14)	0.0069(10)	-0.0059(10)	0.0010(10)
O12	0.0342(12)	0.0379(14)	0.0417(13)	0.0032(10)	-0.0075(10)	-0.0049(11)
N1	0.0332(13)	0.0335(15)	0.0207(12)	0.0019(12)	-0.0044(10)	-0.0002(11)
N2	0.111(3)	0.037(2)	0.0255(16)	0.0154(19)	-0.0032(17)	0.0007(13)
N3	0.0309(13)	0.0336(16)	0.0250(13)	-0.0015(12)	-0.0051(10)	-0.0001(11)
N4	0.0313(13)	0.0470(18)	0.0202(12)	-0.0022(12)	-0.0033(10)	-0.0010(12)
N5	0.0405(15)	0.053(2)	0.0241(14)	0.0135(14)	-0.0078(12)	-0.0103(13)
N6	0.082(2)	0.071(3)	0.0237(15)	-0.033(2)	-0.0134(15)	0.0030(15)
C1	0.0361(17)	0.036(2)	0.0347(18)	-0.0051(15)	-0.0064(14)	-0.0013(14)
C2	0.053(2)	0.034(2)	0.062(3)	-0.0047(17)	-0.0110(19)	-0.0065(18)
C3	0.056(2)	0.052(3)	0.0336(19)	-0.0190(19)	0.0017(16)	0.0006(17)
C4	0.0361(18)	0.049(2)	0.049(2)	-0.0067(17)	-0.0118(16)	-0.0022(18)
C5	0.0342(16)	0.0291(18)	0.0258(16)	0.0007(13)	-0.0004(13)	-0.0003(13)
C6	0.0325(16)	0.0287(19)	0.0429(19)	0.0008(14)	-0.0096(14)	0.0010(14)
C7	0.0378(16)	0.037(2)	0.0309(16)	-0.0061(15)	-0.0107(13)	0.0049(14)
C8	0.0360(16)	0.0272(18)	0.0262(15)	-0.0002(13)	-0.0080(12)	-0.0003(13)
C9	0.0368(16)	0.0262(17)	0.0223(14)	0.0007(13)	-0.0060(12)	0.0022(12)
C10	0.0349(16)	0.0240(17)	0.0267(16)	0.0060(13)	-0.0030(12)	0.0004(12)
C11	0.0356(16)	0.040(2)	0.0243(15)	0.0043(15)	-0.0057(13)	-0.0009(14)
C12	0.0318(16)	0.0346(19)	0.0296(17)	-0.0000(14)	-0.0015(13)	-0.0013(13)
C13	0.0345(17)	0.041(2)	0.0353(18)	0.0086(15)	-0.0110(14)	-0.0060(15)
C14	0.0355(16)	0.0296(18)	0.0272(16)	0.0042(13)	-0.0052(13)	-0.0030(13)
C15	0.0365(17)	0.043(2)	0.0306(17)	0.0017(15)	-0.0077(13)	-0.0094(15)
C16	0.0423(17)	0.0367(19)	0.0239(15)	0.0134(15)	-0.0077(13)	-0.0021(14)

Table 3. Anisotropic displacement parameters (continued)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C17	0.0434(18)	0.0259(18)	0.0289(17)	0.0095(14)	-0.0010(14)	0.0033(13)
C18	0.0351(16)	0.0318(18)	0.0253(16)	0.0022(14)	-0.0043(13)	0.0029(13)
C19	0.054(2)	0.035(2)	0.0261(16)	0.0146(17)	-0.0072(14)	-0.0020(15)
C20	0.0424(18)	0.0310(19)	0.0218(15)	-0.0013(14)	-0.0045(13)	0.0046(13)
C21	0.047(2)	0.031(2)	0.049(2)	0.0020(16)	-0.0002(16)	0.0076(16)
C22	0.061(2)	0.046(2)	0.045(2)	0.020(2)	0.0088(18)	0.0159(19)
C23	0.106(4)	0.031(2)	0.036(2)	0.016(2)	-0.013(2)	-0.0030(17)
C24	0.079(3)	0.037(2)	0.072(3)	-0.004(2)	-0.027(2)	-0.007(2)
C25	0.057(2)	0.038(2)	0.055(2)	-0.0012(18)	-0.0137(19)	-0.0010(18)
C26	0.0397(18)	0.033(2)	0.044(2)	0.0002(15)	-0.0054(15)	0.0078(15)
C27	0.0305(16)	0.0347(19)	0.0337(17)	-0.0013(14)	-0.0005(13)	0.0011(14)
C28	0.0322(16)	0.034(2)	0.047(2)	0.0039(15)	-0.0004(14)	-0.0027(15)
C29	0.0405(19)	0.053(3)	0.054(2)	-0.0009(18)	0.0010(17)	-0.0027(19)
C30	0.0362(17)	0.039(2)	0.057(2)	-0.0009(16)	-0.0050(16)	-0.0036(17)
C31	0.0376(18)	0.033(2)	0.046(2)	-0.0060(15)	-0.0076(15)	-0.0012(15)
C32	0.042(2)	0.058(3)	0.096(4)	-0.016(2)	-0.020(2)	0.012(3)
C33	0.054(2)	0.046(2)	0.054(2)	-0.0104(19)	-0.0040(18)	0.0148(19)
C34	0.061(3)	0.038(2)	0.076(3)	-0.011(2)	0.006(2)	-0.017(2)
C35	0.0323(15)	0.0303(18)	0.0271(15)	-0.0021(14)	-0.0037(12)	-0.0013(13)
C36	0.0452(19)	0.034(2)	0.0384(19)	0.0010(15)	0.0060(15)	-0.0040(15)
C37	0.0440(19)	0.039(2)	0.0328(18)	-0.0088(16)	0.0049(14)	-0.0104(14)
C38	0.0338(16)	0.044(2)	0.0208(15)	-0.0067(15)	-0.0032(12)	-0.0045(14)
C39	0.0341(16)	0.0316(18)	0.0209(15)	0.0003(13)	-0.0020(12)	-0.0039(12)
C40	0.0325(16)	0.0361(19)	0.0229(15)	0.0072(14)	-0.0038(12)	0.0001(13)
C41	0.059(2)	0.034(2)	0.0263(17)	0.0075(17)	-0.0077(15)	-0.0022(14)
C42	0.056(2)	0.041(2)	0.0278(17)	0.0105(17)	-0.0098(15)	-0.0032(14)
C43	0.052(2)	0.036(2)	0.0291(17)	0.0094(16)	-0.0050(15)	-0.0054(14)
C44	0.0312(16)	0.0370(19)	0.0268(16)	0.0012(14)	-0.0024(13)	-0.0012(13)
C45	0.0437(18)	0.037(2)	0.0241(16)	-0.0074(15)	-0.0101(14)	-0.0012(14)
C46	0.0287(14)	0.0366(19)	0.0226(15)	0.0034(14)	-0.0046(11)	-0.0010(13)
C47	0.0319(15)	0.0298(17)	0.0243(15)	0.0034(14)	-0.0029(12)	-0.0002(13)
C48	0.0325(15)	0.0300(19)	0.0270(16)	0.0004(14)	-0.0019(12)	-0.0038(13)
C49	0.0297(15)	0.0304(17)	0.0248(15)	0.0079(14)	-0.0064(12)	-0.0030(13)
C50	0.0335(15)	0.039(2)	0.0186(14)	-0.0006(14)	-0.0007(12)	-0.0020(13)
C51	0.0389(18)	0.043(2)	0.0351(18)	-0.0001(16)	0.0010(14)	-0.0042(15)
C52	0.0398(19)	0.073(3)	0.039(2)	-0.017(2)	0.0004(16)	-0.0129(19)
C53	0.0322(17)	0.088(3)	0.0228(16)	0.006(2)	-0.0019(13)	0.0000(19)

Table 3. Anisotropic displacement parameters (continued)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C54	0.0424(19)	0.061(3)	0.0360(19)	0.0138(19)	0.0084(15)	0.0120(18)
C55	0.0372(17)	0.048(2)	0.0387(19)	0.0019(17)	0.0046(14)	0.0028(16)
C56	0.071(3)	0.038(2)	0.039(2)	0.0052(19)	-0.0022(19)	0.0018(17)
C57	0.058(2)	0.039(2)	0.040(2)	0.0100(18)	-0.0084(17)	-0.0057(16)
C58	0.068(3)	0.047(3)	0.050(2)	0.012(2)	-0.010(2)	-0.0023(19)
C59	0.103(4)	0.046(3)	0.063(3)	0.014(3)	-0.022(3)	-0.001(2)
C60	0.093(4)	0.049(3)	0.067(3)	0.017(2)	-0.010(3)	-0.012(2)
C61	0.056(2)	0.067(3)	0.046(2)	-0.002(2)	-0.0131(18)	0.002(2)
C62	0.072(4)	0.151(7)	0.116(5)	-0.041(4)	-0.033(3)	0.071(5)
C63	0.053(2)	0.073(3)	0.055(2)	0.006(2)	-0.0234(19)	-0.005(2)
C64	0.048(3)	0.147(6)	0.077(4)	0.026(3)	-0.004(2)	-0.034(4)
C65	0.0374(18)	0.050(2)	0.0269(17)	0.0132(16)	-0.0097(14)	-0.0089(15)
C66	0.0395(19)	0.062(3)	0.049(2)	0.0203(19)	-0.0077(16)	-0.015(2)
C67	0.040(2)	0.087(3)	0.041(2)	0.019(2)	-0.0023(17)	-0.018(2)
C68	0.0384(18)	0.066(3)	0.0243(17)	0.0133(17)	-0.0023(14)	-0.0098(16)
C69	0.0310(16)	0.054(2)	0.0200(15)	0.0114(14)	-0.0063(12)	-0.0059(14)
C70	0.0349(16)	0.042(2)	0.0209(15)	0.0053(15)	-0.0056(12)	-0.0066(14)
C71	0.0411(18)	0.059(2)	0.0256(17)	0.0147(17)	-0.0040(14)	-0.0048(16)
C72	0.0390(18)	0.047(2)	0.0274(17)	0.0131(16)	-0.0072(14)	-0.0031(15)
C73	0.0382(17)	0.045(2)	0.0273(17)	0.0124(16)	-0.0031(13)	-0.0062(14)
C74	0.0361(16)	0.039(2)	0.0281(17)	0.0066(14)	-0.0070(13)	-0.0057(14)
C75	0.0369(17)	0.051(2)	0.0265(16)	0.0078(16)	-0.0032(13)	-0.0028(15)
C76	0.0411(17)	0.045(2)	0.0230(15)	0.0072(16)	-0.0066(13)	-0.0068(15)
C77	0.0401(18)	0.048(2)	0.0283(16)	0.0054(17)	-0.0122(14)	-0.0031(15)
C78	0.0333(16)	0.058(2)	0.0270(16)	0.0092(17)	-0.0068(13)	-0.0071(16)
C79	0.0404(17)	0.047(2)	0.0233(16)	0.0008(16)	-0.0052(14)	-0.0032(15)
C80	0.0398(18)	0.060(3)	0.0212(16)	0.0069(17)	-0.0090(14)	-0.0013(15)
C81	0.052(2)	0.074(3)	0.034(2)	0.001(2)	0.0003(17)	-0.001(2)
C82	0.072(3)	0.084(4)	0.035(2)	-0.012(3)	0.003(2)	0.001(2)
C83	0.095(4)	0.064(3)	0.028(2)	-0.018(3)	-0.018(2)	0.006(2)
C84	0.065(3)	0.058(3)	0.046(2)	0.008(2)	-0.031(2)	-0.006(2)
C85	0.045(2)	0.059(3)	0.035(2)	-0.0003(19)	-0.0151(16)	-0.0068(17)
C86	0.0384(17)	0.042(2)	0.0295(17)	0.0055(15)	-0.0086(14)	-0.0032(14)
C87	0.0323(17)	0.049(2)	0.0379(19)	0.0018(16)	-0.0087(14)	-0.0045(16)
C88	0.0345(17)	0.034(2)	0.047(2)	0.0023(15)	-0.0109(15)	0.0001(15)
C89	0.051(2)	0.036(2)	0.055(2)	0.0000(17)	-0.0179(17)	0.0040(17)
C90	0.0420(19)	0.038(2)	0.062(2)	0.0100(17)	-0.0050(17)	-0.0004(18)

Table 3. Anisotropic displacement parameters (continued)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 4. Fragment Analysis

fragment: 1

S(1)	O(1)	O(2)	O(3)	O(4)
N(1)	N(2)	C(1)	C(2)	C(3)
C(4)	C(5)	C(6)	C(7)	C(8)
C(9)	C(10)	C(11)	C(12)	C(13)
C(14)	C(15)	C(16)	C(17)	C(18)
C(19)	C(20)	C(21)	C(22)	C(23)
C(24)	C(25)	C(26)	C(27)	C(28)
C(29)	C(30)			

fragment: 2

S(2)	O(5)	O(6)	O(7)	O(8)
N(3)	N(4)	C(31)	C(32)	C(33)
C(34)	C(35)	C(36)	C(37)	C(38)
C(39)	C(40)	C(41)	C(42)	C(43)
C(44)	C(45)	C(46)	C(47)	C(48)
C(49)	C(50)	C(51)	C(52)	C(53)
C(54)	C(55)	C(56)	C(57)	C(58)
C(59)	C(60)			

fragment: 3

Table 4. Fragment Analysis (continued)

	O(11)	O(12)		S(3)	O(9)	O(10)
	N(5)	N(6)	C(61)	C(62)	C(63)	
	C(64)	C(65)	C(66)	C(67)	C(68)	
	C(69)	C(70)	C(71)	C(72)	C(73)	
	C(74)	C(75)	C(76)	C(77)	C(78)	
	C(79)	C(80)	C(81)	C(82)	C(83)	
	C(84)	C(85)	C(86)	C(87)	C(88)	
	C(89)	C(90)				
fragment: 4						
	O(13)	O(14)	C(91)	C(92)		
fragment: 5						
	O(15)	O(16)	C(93)	C(94)	C(95)	

Table 5. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
S1	O1	1.497(2)	S1	N1	1.664(3)
S1	C1	1.858(4)	S2	O5	1.501(3)
S2	N3	1.648(3)	S2	C31	1.846(4)
S3	O9	1.497(3)	S3	N5	1.647(3)
S3	C61	1.828(5)	O2	C19	1.242(4)
O3	C26	1.425(4)	O3	C28	1.434(4)
O4	C27	1.426(4)	O4	C28	1.427(4)
O6	C49	1.242(4)	O7	C56	1.428(5)
O7	C58	1.422(6)	O8	C57	1.438(5)
O8	C58	1.407(5)	O10	C79	1.229(4)
O11	C86	1.424(4)	O11	C88	1.422(4)
O12	C87	1.431(4)	O12	C88	1.422(4)
O13	C91	1.486	O14	C91	1.434
O14	C92	1.379	O15	C93	0.912
O15	C93[1]	0.912	O16	C93	1.202
O16	C95	1.376	N1	C5	1.475(4)
N2	C19	1.318(5)	N3	C35	1.490(4)
N4	C49	1.328(4)	N5	C65	1.485(4)
N6	C79	1.321(5)	C1	C2	1.523(5)
C1	C3	1.524(5)	C1	C4	1.520(5)
C5	C6	1.543(5)	C5	C9	1.559(5)
C6	C7	1.548(5)	C7	C8	1.535(5)
C8	C9	1.547(4)	C9	C10	1.523(4)
C9	C18	1.574(5)	C10	C11	1.517(4)
C10	C14	1.331(4)	C11	C12	1.551(4)
C12	C13	1.543(5)	C12	C26	1.519(5)
C12	C27	1.535(5)	C13	C14	1.500(5)
C14	C15	1.501(5)	C15	C16	1.502(5)
C16	C17	1.338(5)	C16	C19	1.514(4)
C17	C18	1.508(4)	C18	C20	1.532(5)
C20	C21	1.379(5)	C20	C25	1.384(5)
C21	C22	1.400(6)	C22	C23	1.363(7)
C23	C24	1.384(8)	C24	C25	1.393(6)
C28	C29	1.511(6)	C28	C30	1.503(5)
C31	C32	1.532(6)	C31	C33	1.514(6)
C31	C34	1.511(6)	C35	C36	1.550(5)
C35	C39	1.563(4)	C36	C37	1.539(5)

Table 5. Bond lengths (Å) (continued)

atom	atom	distance	atom	atom	distance
C37	C38	1.529(5)	C38	C39	1.556(4)
C39	C40	1.510(5)	C39	C48	1.561(4)
C40	C41	1.513(5)	C40	C44	1.329(5)
C41	C42	1.552(5)	C42	C43	1.542(5)
C42	C56	1.497(6)	C42	C57	1.543(6)
C43	C44	1.497(5)	C44	C45	1.498(5)
C45	C46	1.512(5)	C46	C47	1.334(4)
C46	C49	1.513(4)	C47	C48	1.510(4)
C48	C50	1.528(4)	C50	C51	1.394(5)
C50	C55	1.377(5)	C51	C52	1.394(5)
C52	C53	1.388(7)	C53	C54	1.353(6)
C54	C55	1.377(5)	C58	C59	1.534(7)
C58	C60	1.529(7)	C61	C62	1.518(10)
C61	C63	1.509(6)	C61	C64	1.508(9)
C65	C66	1.546(5)	C65	C69	1.536(5)
C66	C67	1.504(6)	C67	C68	1.538(6)
C68	C69	1.557(5)	C69	C70	1.523(5)
C69	C78	1.561(5)	C70	C71	1.514(5)
C70	C74	1.326(4)	C71	C72	1.536(5)
C72	C73	1.538(5)	C72	C86	1.526(5)
C72	C87	1.533(6)	C73	C74	1.508(5)
C74	C75	1.506(5)	C75	C76	1.522(5)
C76	C77	1.324(5)	C76	C79	1.516(4)
C77	C78	1.511(5)	C78	C80	1.526(6)
C80	C81	1.414(6)	C80	C85	1.379(6)
C81	C82	1.379(8)	C82	C83	1.362(8)
C83	C84	1.380(7)	C84	C85	1.395(6)
C88	C89	1.524(5)	C88	C90	1.528(5)
C91	C91[2]	1.211	C93	C93[1]	1.294
C93	C94	1.614			

Symmetry Operators:

(1) -X,Y,-Z+2 (2) -X,Y,-Z+1

Table 6. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
N1	H1	0.853	N2	H2	0.970
N2	H3	0.800	N3	H4	0.970
N4	H5	0.967	N4	H6	0.655
N5	H7	0.936	N6	H8	0.835
N6	H9	0.680	C2	H10	0.959
C2	H11	0.960	C2	H12	0.962
C3	H13	0.957	C3	H14	0.962
C3	H15	0.960	C4	H16	0.961
C4	H17	0.960	C4	H18	0.959
C5	H19	0.978	C6	H20	0.970
C6	H21	0.969	C7	H22	0.970
C7	H23	0.970	C8	H24	0.970
C8	H25	0.969	C11	H26	0.972
C11	H27	0.966	C13	H28	0.969
C13	H29	0.969	C15	H30	0.971
C15	H31	0.970	C17	H32	0.930
C18	H33	0.980	C21	H34	0.931
C22	H35	0.931	C23	H36	0.927
C24	H37	0.930	C25	H38	0.932
C26	H39	0.970	C26	H40	0.971
C27	H41	0.969	C27	H42	0.971
C29	H43	0.963	C29	H44	0.958
C29	H45	0.962	C30	H46	0.959
C30	H47	0.960	C30	H48	0.958
C32	H49	0.959	C32	H50	0.961
C32	H51	0.960	C33	H52	0.962
C33	H53	0.960	C33	H54	0.959
C34	H55	0.962	C34	H56	0.956
C34	H57	0.962	C35	H58	0.980
C36	H59	0.969	C36	H60	0.969
C37	H61	0.969	C37	H62	0.973
C38	H63	0.968	C38	H64	0.972
C41	H65	0.970	C41	H66	0.970
C43	H67	0.969	C43	H68	0.970
C45	H69	0.969	C45	H70	0.969
C47	H71	0.931	C48	H72	0.979
C51	H73	0.930	C52	H74	0.930

Table 6. Bond lengths involving hydrogens (Å) (continued)

atom	atom	distance	atom	atom	distance
C53	H75	0.931	C54	H76	0.930
C55	H77	0.932	C56	H78	0.973
C56	H79	0.969	C57	H80	0.970
C57	H81	0.970	C59	H82	0.961
C59	H83	0.960	C59	H84	0.960
C60	H85	0.963	C60	H86	0.953
C60	H87	0.962	C62	H88	0.966
C62	H89	0.963	C62	H90	0.945
C63	H91	0.958	C63	H92	0.957
C63	H93	0.969	C64	H94	0.964
C64	H95	0.964	C64	H96	0.950
C65	H97	0.980	C66	H98	0.973
C66	H99	0.969	C67	H100	0.971
C67	H101	0.969	C68	H102	0.970
C68	H103	0.971	C71	H104	0.969
C71	H105	0.970	C73	H106	0.967
C73	H107	0.971	C75	H108	0.969
C75	H109	0.971	C77	H110	0.928
C78	H111	0.979	C81	H112	0.932
C82	H113	0.929	C83	H114	0.932
C84	H115	0.932	C85	H116	0.929
C86	H117	0.969	C86	H118	0.970
C87	H119	0.971	C87	H120	0.970
C89	H121	0.960	C89	H122	0.961
C89	H123	0.959	C90	H124	0.963
C90	H125	0.957	C90	H126	0.960

Table 7. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
O1	S1	N1	111.04(13)	O1	S1	C1	105.33(14)
N1	S1	C1	99.11(15)	O5	S2	N3	111.02(14)
O5	S2	C31	104.08(16)	N3	S2	C31	99.03(15)
O9	S3	N5	110.73(17)	O9	S3	C61	103.9(2)
N5	S3	C61	99.72(19)	C26	O3	C28	113.3(3)
C27	O4	C28	114.1(3)	C56	O7	C58	112.6(3)
C57	O8	C58	112.7(3)	C86	O11	C88	114.2(3)
C87	O12	C88	113.6(3)	C91	O14	C92	110.1
C93	O15	C93[1]	90.4	C93	O16	C95	139.2
S1	N1	C5	114.1(2)	S2	N3	C35	114.8(2)
S3	N5	C65	116.4(2)	S1	C1	C2	103.6(2)
S1	C1	C3	112.3(3)	S1	C1	C4	106.4(2)
C2	C1	C3	110.9(3)	C2	C1	C4	111.8(3)
C3	C1	C4	111.5(3)	N1	C5	C6	113.3(3)
N1	C5	C9	110.4(3)	C6	C5	C9	104.2(3)
C5	C6	C7	106.1(3)	C6	C7	C8	105.6(3)
C7	C8	C9	105.4(3)	C5	C9	C8	100.6(2)
C5	C9	C10	113.6(3)	C5	C9	C18	107.3(3)
C8	C9	C10	112.8(3)	C8	C9	C18	110.1(3)
C10	C9	C18	111.9(2)	C9	C10	C11	123.9(3)
C9	C10	C14	125.2(3)	C11	C10	C14	110.9(3)
C10	C11	C12	104.4(2)	C11	C12	C13	104.5(3)
C11	C12	C26	113.3(3)	C11	C12	C27	110.8(3)
C13	C12	C26	112.5(3)	C13	C12	C27	109.4(3)
C26	C12	C27	106.3(3)	C12	C13	C14	104.4(3)
C10	C14	C13	112.6(3)	C10	C14	C15	127.7(3)
C13	C14	C15	119.6(3)	C14	C15	C16	114.8(3)
C15	C16	C17	128.0(3)	C15	C16	C19	113.2(3)
C17	C16	C19	118.7(3)	C16	C17	C18	133.0(3)
C9	C18	C17	117.9(3)	C9	C18	C20	113.3(3)
C17	C18	C20	109.8(3)	O2	C19	N2	122.2(3)
O2	C19	C16	118.9(3)	N2	C19	C16	118.8(3)
C18	C20	C21	122.5(3)	C18	C20	C25	119.5(3)
C21	C20	C25	117.9(3)	C20	C21	C22	121.6(4)
C21	C22	C23	119.3(4)	C22	C23	C24	120.4(4)
C23	C24	C25	119.7(4)	C20	C25	C24	121.0(4)
O3	C26	C12	110.0(3)	O4	C27	C12	110.8(3)

Table 7. Bond angles (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
O3	C28	O4	110.1(3)	O3	C28	C29	111.4(3)
O3	C28	C30	105.5(3)	O4	C28	C29	112.5(3)
O4	C28	C30	105.8(3)	C29	C28	C30	111.2(3)
S2	C31	C32	103.2(3)	S2	C31	C33	111.2(3)
S2	C31	C34	106.9(3)	C32	C31	C33	111.0(4)
C32	C31	C34	111.9(3)	C33	C31	C34	112.3(3)
N3	C35	C36	112.3(3)	N3	C35	C39	109.5(3)
C36	C35	C39	104.3(3)	C35	C36	C37	105.7(3)
C36	C37	C38	105.8(3)	C37	C38	C39	105.4(3)
C35	C39	C38	99.1(2)	C35	C39	C40	113.2(3)
C35	C39	C48	108.4(2)	C38	C39	C40	114.3(3)
C38	C39	C48	109.1(3)	C40	C39	C48	111.9(3)
C39	C40	C41	122.6(3)	C39	C40	C44	127.3(3)
C41	C40	C44	110.0(3)	C40	C41	C42	105.0(3)
C41	C42	C43	103.8(3)	C41	C42	C56	112.1(3)
C41	C42	C57	111.1(3)	C43	C42	C56	113.9(3)
C43	C42	C57	108.9(3)	C56	C42	C57	107.0(3)
C42	C43	C44	104.2(3)	C40	C44	C43	113.1(3)
C40	C44	C45	127.0(3)	C43	C44	C45	119.9(3)
C44	C45	C46	115.2(3)	C45	C46	C47	127.5(3)
C45	C46	C49	114.3(3)	C47	C46	C49	117.9(3)
C46	C47	C48	133.1(3)	C39	C48	C47	118.9(3)
C39	C48	C50	112.8(2)	C47	C48	C50	108.4(2)
O6	C49	N4	122.4(3)	O6	C49	C46	119.0(3)
N4	C49	C46	118.5(3)	C48	C50	C51	120.6(3)
C48	C50	C55	121.5(3)	C51	C50	C55	118.0(3)
C50	C51	C52	119.9(4)	C51	C52	C53	120.2(4)
C52	C53	C54	119.7(3)	C53	C54	C55	120.3(4)
C50	C55	C54	121.9(4)	O7	C56	C42	111.6(3)
O8	C57	C42	111.0(3)	O7	C58	O8	111.9(3)
O7	C58	C59	112.6(4)	O7	C58	C60	103.6(4)
O8	C58	C59	112.1(4)	O8	C58	C60	105.7(4)
C59	C58	C60	110.4(4)	S3	C61	C62	104.3(4)
S3	C61	C63	111.6(3)	S3	C61	C64	106.7(3)
C62	C61	C63	111.5(5)	C62	C61	C64	112.2(5)
C63	C61	C64	110.3(4)	N5	C65	C66	112.1(3)
N5	C65	C69	110.1(3)	C66	C65	C69	104.2(3)

Table 7. Bond angles (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C65	C66	C67	105.6(3)	C66	C67	C68	106.7(3)
C67	C68	C69	104.7(3)	C65	C69	C68	99.8(3)
C65	C69	C70	113.0(3)	C65	C69	C78	109.7(3)
C68	C69	C70	114.9(3)	C68	C69	C78	108.7(3)
C70	C69	C78	110.3(3)	C69	C70	C71	122.3(3)
C69	C70	C74	127.1(3)	C71	C70	C74	110.5(3)
C70	C71	C72	105.3(3)	C71	C72	C73	105.3(3)
C71	C72	C86	112.5(3)	C71	C72	C87	109.7(3)
C73	C72	C86	112.3(3)	C73	C72	C87	111.2(3)
C86	C72	C87	106.0(3)	C72	C73	C74	104.3(3)
C70	C74	C73	112.9(3)	C70	C74	C75	128.3(3)
C73	C74	C75	118.6(3)	C74	C75	C76	116.4(3)
C75	C76	C77	128.2(3)	C75	C76	C79	113.0(3)
C77	C76	C79	118.6(3)	C76	C77	C78	133.4(3)
C69	C78	C77	117.1(3)	C69	C78	C80	113.1(3)
C77	C78	C80	109.5(3)	O10	C79	N6	122.3(3)
O10	C79	C76	121.3(3)	N6	C79	C76	116.4(3)
C78	C80	C81	119.7(4)	C78	C80	C85	122.2(3)
C81	C80	C85	118.1(4)	C80	C81	C82	121.0(4)
C81	C82	C83	120.1(5)	C82	C83	C84	119.8(5)
C83	C84	C85	120.9(4)	C80	C85	C84	119.9(4)
O11	C86	C72	111.7(3)	O12	C87	C72	111.4(3)
O11	C88	O12	110.5(3)	O11	C88	C89	111.9(3)
O11	C88	C90	105.7(3)	O12	C88	C89	111.3(3)
O12	C88	C90	106.2(3)	C89	C88	C90	110.9(3)
O13	C91	O14	116.4	O13	C91	C91[2]	122.0
O14	C91	C91[2]	120.5	O15	C93	O16	125.3
O15	C93	C93[1]	44.8	O15	C93	C94	111.2
O16	C93	C93[1]	169.4	O16	C93	C94	123.3
C93[1]	C93	C94	66.4	C93	C94	C93[1]	47.2

Symmetry Operators:

(1) -X,Y,-Z+2

(2) -X,Y,-Z+1

Table 8. Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom	angle
S1	N1	H1	108.6	C5	N1	H1	115.9
C19	N2	H2	117.5	C19	N2	H3	127.7
H2	N2	H3	110.3	S2	N3	H4	113.1
C35	N3	H4	103.3	C49	N4	H5	113.4
C49	N4	H6	121.1	H5	N4	H6	125.5
S3	N5	H7	118.1	C65	N5	H7	105.9
C79	N6	H8	117.8	C79	N6	H9	116.0
H8	N6	H9	116.8	C1	C2	H10	109.6
C1	C2	H11	109.5	C1	C2	H12	109.6
H10	C2	H11	109.5	H10	C2	H12	109.3
H11	C2	H12	109.3	C1	C3	H13	109.5
C1	C3	H14	109.7	C1	C3	H15	109.1
H13	C3	H14	109.5	H13	C3	H15	109.7
H14	C3	H15	109.3	C1	C4	H16	109.3
C1	C4	H17	110.3	C1	C4	H18	109.0
H16	C4	H17	109.3	H16	C4	H18	109.4
H17	C4	H18	109.5	N1	C5	H19	109.5
C6	C5	H19	109.8	C9	C5	H19	109.4
C5	C6	H20	109.9	C5	C6	H21	110.0
C7	C6	H20	110.6	C7	C6	H21	110.5
H20	C6	H21	109.6	C6	C7	H22	110.8
C6	C7	H23	111.0	C8	C7	H22	110.3
C8	C7	H23	109.5	H22	C7	H23	109.5
C7	C8	H24	110.2	C7	C8	H25	109.7
C9	C8	H24	111.1	C9	C8	H25	110.8
H24	C8	H25	109.6	C10	C11	H26	109.8
C10	C11	H27	110.3	C12	C11	H26	111.5
C12	C11	H27	111.1	H26	C11	H27	109.6
C12	C13	H28	111.3	C12	C13	H29	111.9
C14	C13	H28	109.3	C14	C13	H29	110.1
H28	C13	H29	109.6	C14	C15	H30	108.4
C14	C15	H31	108.7	C16	C15	H30	107.5
C16	C15	H31	107.9	H30	C15	H31	109.4
C16	C17	H32	113.6	C18	C17	H32	113.4
C9	C18	H33	104.5	C17	C18	H33	105.2
C20	C18	H33	104.8	C20	C21	H34	119.0
C22	C21	H34	119.4	C21	C22	H35	120.3

Table 8. Bond angles involving hydrogens (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C23	C22	H35	120.4	C22	C23	H36	119.9
C24	C23	H36	119.7	C23	C24	H37	119.7
C25	C24	H37	120.6	C20	C25	H38	119.8
C24	C25	H38	119.2	O3	C26	H39	105.7
O3	C26	H40	106.6	C12	C26	H39	112.2
C12	C26	H40	112.9	H39	C26	H40	109.0
O4	C27	H41	105.8	O4	C27	H42	105.7
C12	C27	H41	112.6	C12	C27	H42	112.5
H41	C27	H42	109.0	C28	C29	H43	109.6
C28	C29	H44	109.8	C28	C29	H45	109.5
H43	C29	H44	109.4	H43	C29	H45	109.1
H44	C29	H45	109.5	C28	C30	H46	109.0
C28	C30	H47	109.5	C28	C30	H48	109.5
H46	C30	H47	109.5	H46	C30	H48	109.7
H47	C30	H48	109.5	C31	C32	H49	109.0
C31	C32	H50	110.0	C31	C32	H51	109.7
H49	C32	H50	109.4	H49	C32	H51	109.5
H50	C32	H51	109.3	C31	C33	H52	109.4
C31	C33	H53	109.3	C31	C33	H54	109.8
H52	C33	H53	109.3	H52	C33	H54	109.4
H53	C33	H54	109.6	C31	C34	H55	109.7
C31	C34	H56	109.2	C31	C34	H57	109.7
H55	C34	H56	109.6	H55	C34	H57	109.1
H56	C34	H57	109.6	N3	C35	H58	110.3
C36	C35	H58	110.1	C39	C35	H58	110.1
C35	C36	H59	110.4	C35	C36	H60	111.0
C37	C36	H59	110.1	C37	C36	H60	109.9
H59	C36	H60	109.7	C36	C37	H61	110.7
C36	C37	H62	110.8	C38	C37	H61	109.8
C38	C37	H62	110.4	H61	C37	H62	109.4
C37	C38	H63	110.1	C37	C38	H64	110.7
C39	C38	H63	110.4	C39	C38	H64	110.6
H63	C38	H64	109.5	C40	C41	H65	110.1
C40	C41	H66	108.6	C42	C41	H65	111.9
C42	C41	H66	111.7	H65	C41	H66	109.5
C42	C43	H67	111.2	C42	C43	H68	111.7
C44	C43	H67	110.3	C44	C43	H68	109.7

Table 8. Bond angles involving hydrogens (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
H67	C43	H68	109.6	C44	C45	H69	107.7
C44	C45	H70	108.1	C46	C45	H69	107.8
C46	C45	H70	108.3	H69	C45	H70	109.7
C46	C47	H71	113.4	C48	C47	H71	113.5
C39	C48	H72	105.1	C47	C48	H72	105.5
C50	C48	H72	104.9	C50	C51	H73	120.2
C52	C51	H73	119.9	C51	C52	H74	119.9
C53	C52	H74	119.9	C52	C53	H75	119.8
C54	C53	H75	120.5	C53	C54	H76	119.7
C55	C54	H76	120.0	C50	C55	H77	118.9
C54	C55	H77	119.2	O7	C56	H78	105.8
O7	C56	H79	105.3	C42	C56	H78	112.5
C42	C56	H79	112.3	H78	C56	H79	108.9
O8	C57	H80	106.3	O8	C57	H81	106.6
C42	C57	H80	111.6	C42	C57	H81	111.9
H80	C57	H81	109.2	C58	C59	H82	109.2
C58	C59	H83	110.0	C58	C59	H84	109.5
H82	C59	H83	109.4	H82	C59	H84	109.4
H83	C59	H84	109.5	C58	C60	H85	109.7
C58	C60	H86	108.3	C58	C60	H87	110.3
H85	C60	H86	109.8	H85	C60	H87	109.0
H86	C60	H87	109.8	C61	C62	H88	109.5
C61	C62	H89	109.1	C61	C62	H90	108.9
H88	C62	H89	108.6	H88	C62	H90	110.2
H89	C62	H90	110.4	C61	C63	H91	109.5
C61	C63	H92	109.3	C61	C63	H93	110.5
H91	C63	H92	109.8	H91	C63	H93	108.8
H92	C63	H93	108.9	C61	C64	H94	109.7
C61	C64	H95	108.8	C61	C64	H96	109.6
H94	C64	H95	108.8	H94	C64	H96	110.0
H95	C64	H96	110.0	N5	C65	H97	109.8
C66	C65	H97	110.5	C69	C65	H97	110.0
C65	C66	H98	109.3	C65	C66	H99	109.8
C67	C66	H98	110.9	C67	C66	H99	111.8
H98	C66	H99	109.3	C66	C67	H100	110.9
C66	C67	H101	110.0	C68	C67	H100	110.0
C68	C67	H101	109.8	H100	C67	H101	109.5

Table 8. Bond angles involving hydrogens (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C67	C68	H102	110.6	C67	C68	H103	110.0
C69	C68	H102	110.6	C69	C68	H103	111.5
H102	C68	H103	109.4	C70	C71	H104	109.9
C70	C71	H105	109.6	C72	C71	H104	111.1
C72	C71	H105	111.2	H104	C71	H105	109.6
C72	C73	H106	111.7	C72	C73	H107	111.8
C74	C73	H106	109.9	C74	C73	H107	109.5
H106	C73	H107	109.6	C74	C75	H108	107.8
C74	C75	H109	107.4	C76	C75	H108	108.1
C76	C75	H109	107.5	H108	C75	H109	109.5
C76	C77	H110	113.2	C78	C77	H110	113.4
C69	C78	H111	105.2	C77	C78	H111	105.8
C80	C78	H111	105.2	C80	C81	H112	118.8
C82	C81	H112	120.2	C81	C82	H113	119.9
C83	C82	H113	120.0	C82	C83	H114	120.1
C84	C83	H114	120.0	C83	C84	H115	119.8
C85	C84	H115	119.3	C80	C85	H116	119.9
C84	C85	H116	120.2	O11	C86	H117	106.7
O11	C86	H118	105.8	C72	C86	H117	112.1
C72	C86	H118	111.1	H117	C86	H118	109.2
O12	C87	H119	105.8	O12	C87	H120	105.8
C72	C87	H119	112.0	C72	C87	H120	112.6
H119	C87	H120	109.0	C88	C89	H121	109.5
C88	C89	H122	109.8	C88	C89	H123	109.2
H121	C89	H122	109.4	H121	C89	H123	109.6
H122	C89	H123	109.4	C88	C90	H124	108.9
C88	C90	H125	110.0	C88	C90	H126	109.6
H124	C90	H125	109.4	H124	C90	H126	109.2
H125	C90	H126	109.7				

Table 9. Torsion Angles(°)
(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
O1	S1	N1	C5	90.28(18)	O1	S1	C1	C2	-57.7(2)
O1	S1	C1	C3	62.0(2)	O1	S1	C1	C4	-175.67(17)
N1	S1	C1	C2	-172.60(17)	N1	S1	C1	C3	-52.9(2)
N1	S1	C1	C4	69.4(2)	C1	S1	N1	C5	-159.32(17)
O5	S2	N3	C35	93.4(2)	O5	S2	C31	C32	-65.1(2)
O5	S2	C31	C33	53.9(2)	O5	S2	C31	C34	176.82(17)
N3	S2	C31	C32	-179.58(18)	N3	S2	C31	C33	-60.6(2)
N3	S2	C31	C34	62.4(2)	C31	S2	N3	C35	-157.68(19)
O9	S3	N5	C65	99.8(2)	O9	S3	C61	C62	-63.0(3)
O9	S3	C61	C63	57.5(3)	O9	S3	C61	C64	178.1(2)
N5	S3	C61	C62	-177.4(2)	N5	S3	C61	C63	-56.9(3)
N5	S3	C61	C64	63.7(3)	C61	S3	N5	C65	-151.1(2)
C26	O3	C28	O4	56.8(3)	C26	O3	C28	C29	-68.8(3)
C26	O3	C28	C30	170.5(2)	C28	O3	C26	C12	-60.0(3)
C27	O4	C28	O3	-54.9(3)	C27	O4	C28	C29	70.1(3)
C27	O4	C28	C30	-168.4(2)	C28	O4	C27	C12	56.1(3)
C56	O7	C58	O8	56.8(4)	C56	O7	C58	C59	-70.4(4)
C56	O7	C58	C60	170.3(3)	C58	O7	C56	C42	-57.4(4)
C57	O8	C58	O7	-56.5(4)	C57	O8	C58	C59	71.1(4)
C57	O8	C58	C60	-168.6(3)	C58	O8	C57	C42	55.9(4)
C86	O11	C88	O12	55.3(3)	C86	O11	C88	C89	-69.3(3)
C86	O11	C88	C90	169.9(2)	C88	O11	C86	C72	-56.8(3)
C87	O12	C88	O11	-55.6(4)	C87	O12	C88	C89	69.3(3)
C87	O12	C88	C90	-169.8(2)	C88	O12	C87	C72	57.4(3)
C92	O14	C91	O13	12.1	C92	O14	C91	C91[1]	-179.2
C93	O15	C93[2]	O16[2]	175.0	C93	O15	C93[2]	C93	0.0
C93	O15	C93[2]	C94	0.0	C93[2]	O15	C93	O16	175.0
C93[2]	O15	C93	C93[2]	0.0	C93[2]	O15	C93	C94	0.0
C95	O16	C93	O15	24.0	C95	O16	C93	C94	-161.6
S1	N1	C5	C6	-81.1(3)	S1	N1	C5	C9	162.40(16)
S2	N3	C35	C36	-86.4(2)	S2	N3	C35	C39	158.22(17)
S3	N5	C65	C66	-90.9(3)	S3	N5	C65	C69	153.6(2)
N1	C5	C6	C7	-93.8(3)	N1	C5	C9	C8	81.4(3)
N1	C5	C9	C10	-39.3(3)	N1	C5	C9	C18	-163.5(2)
C6	C5	C9	C8	-40.5(3)	C6	C5	C9	C10	-161.3(2)
C6	C5	C9	C18	74.5(3)	C9	C5	C6	C7	26.2(3)
C5	C6	C7	C8	-1.0(3)	C6	C7	C8	C9	-24.8(3)

Table 9. Torsion angles (°) (continued)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C7	C8	C9	C5	40.3(3)	C7	C8	C9	C10	161.6(2)
C7	C8	C9	C18	-72.6(3)	C5	C9	C10	C11	115.6(3)
C5	C9	C10	C14	-61.3(4)	C5	C9	C18	C17	71.7(3)
C5	C9	C18	C20	-158.1(2)	C8	C9	C10	C11	2.0(4)
C8	C9	C10	C14	-174.9(3)	C8	C9	C18	C17	-179.7(2)
C8	C9	C18	C20	-49.5(3)	C10	C9	C18	C17	-53.5(3)
C10	C9	C18	C20	76.7(3)	C18	C9	C10	C11	-122.7(3)
C18	C9	C10	C14	60.3(4)	C9	C10	C11	C12	171.5(3)
C9	C10	C14	C13	177.5(3)	C9	C10	C14	C15	0.7(5)
C11	C10	C14	C13	0.2(4)	C11	C10	C14	C15	-176.6(3)
C14	C10	C11	C12	-11.2(4)	C10	C11	C12	C13	17.0(3)
C10	C11	C12	C26	139.9(3)	C10	C11	C12	C27	-100.7(3)
C11	C12	C13	C14	-16.9(3)	C11	C12	C26	O3	178.8(3)
C11	C12	C27	O4	-178.5(2)	C13	C12	C26	O3	-62.9(3)
C26	C12	C13	C14	-140.2(3)	C13	C12	C27	O4	66.7(3)
C27	C12	C13	C14	101.8(3)	C26	C12	C27	O4	-55.0(3)
C27	C12	C26	O3	56.8(3)	C12	C13	C14	C10	11.0(4)
C12	C13	C14	C15	-172.0(2)	C10	C14	C15	C16	-52.2(5)
C13	C14	C15	C16	131.3(3)	C14	C15	C16	C17	33.9(5)
C14	C15	C16	C19	-150.5(3)	C15	C16	C17	C18	2.3(6)
C15	C16	C19	O2	-29.4(5)	C15	C16	C19	N2	150.1(3)
C17	C16	C19	O2	146.6(3)	C17	C16	C19	N2	-33.9(5)
C19	C16	C17	C18	-173.0(3)	C16	C17	C18	C9	9.2(5)
C16	C17	C18	C20	-122.6(4)	C9	C18	C20	C21	-55.7(4)
C9	C18	C20	C25	122.6(3)	C17	C18	C20	C21	78.4(4)
C17	C18	C20	C25	-103.3(3)	C18	C20	C21	C22	174.2(3)
C18	C20	C25	C24	-177.2(3)	C21	C20	C25	C24	1.2(5)
C25	C20	C21	C22	-4.1(5)	C20	C21	C22	C23	3.8(6)
C21	C22	C23	C24	-0.4(6)	C22	C23	C24	C25	-2.5(6)
C23	C24	C25	C20	2.1(6)	N3	C35	C36	C37	-91.5(3)
N3	C35	C39	C38	78.6(3)	N3	C35	C39	C40	-42.9(3)
N3	C35	C39	C48	-167.7(2)	C36	C35	C39	C38	-41.8(3)
C36	C35	C39	C40	-163.3(2)	C36	C35	C39	C48	72.0(3)
C39	C35	C36	C37	27.0(3)	C35	C36	C37	C38	-0.5(3)
C36	C37	C38	C39	-26.5(3)	C37	C38	C39	C35	42.0(3)
C37	C38	C39	C40	162.7(2)	C37	C38	C39	C48	-71.3(3)
C35	C39	C40	C41	113.5(3)	C35	C39	C40	C44	-63.5(4)

Table 9. Torsion angles (°) (continued)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C35	C39	C48	C47	73.8(3)	C35	C39	C48	C50	-157.6(2)
C38	C39	C40	C41	1.0(4)	C38	C39	C40	C44	-176.1(3)
C38	C39	C48	C47	-179.2(2)	C38	C39	C48	C50	-50.6(3)
C40	C39	C48	C47	-51.8(3)	C40	C39	C48	C50	76.8(3)
C48	C39	C40	C41	-123.6(3)	C48	C39	C40	C44	59.4(4)
C39	C40	C41	C42	171.5(3)	C39	C40	C44	C43	175.8(3)
C39	C40	C44	C45	-1.0(5)	C41	C40	C44	C43	-1.5(4)
C41	C40	C44	C45	-178.4(3)	C44	C40	C41	C42	-11.1(4)
C40	C41	C42	C43	18.3(3)	C40	C41	C42	C56	141.8(3)
C40	C41	C42	C57	-98.6(3)	C41	C42	C43	C44	-18.9(3)
C41	C42	C56	O7	176.3(3)	C41	C42	C57	O8	-176.2(3)
C43	C42	C56	O7	-66.1(4)	C56	C42	C43	C44	-141.1(3)
C43	C42	C57	O8	70.1(4)	C57	C42	C43	C44	99.5(3)
C56	C42	C57	O8	-53.5(4)	C57	C42	C56	O7	54.3(4)
C42	C43	C44	C40	13.4(4)	C42	C43	C44	C45	-169.4(3)
C40	C44	C45	C46	-50.6(5)	C43	C44	C45	C46	132.7(3)
C44	C45	C46	C47	35.7(5)	C44	C45	C46	C49	-149.7(3)
C45	C46	C47	C48	-1.5(6)	C45	C46	C49	O6	-23.6(4)
C45	C46	C49	N4	156.6(3)	C47	C46	C49	O6	151.5(3)
C47	C46	C49	N4	-28.4(4)	C49	C46	C47	C48	-175.8(3)
C46	C47	C48	C39	11.1(5)	C46	C47	C48	C50	-119.4(4)
C39	C48	C50	C51	116.9(3)	C39	C48	C50	C55	-61.3(3)
C47	C48	C50	C51	-109.3(3)	C47	C48	C50	C55	72.5(3)
C48	C50	C51	C52	-175.4(2)	C48	C50	C55	C54	173.9(3)
C51	C50	C55	C54	-4.3(5)	C55	C50	C51	C52	2.9(5)
C50	C51	C52	C53	-0.3(5)	C51	C52	C53	C54	-1.1(5)
C52	C53	C54	C55	-0.3(5)	C53	C54	C55	C50	3.1(5)
N5	C65	C66	C67	-88.9(3)	N5	C65	C69	C68	77.9(3)
N5	C65	C69	C70	-44.6(3)	N5	C65	C69	C78	-168.1(2)
C66	C65	C69	C68	-42.5(3)	C66	C65	C69	C70	-164.9(2)
C66	C65	C69	C78	71.6(3)	C69	C65	C66	C67	30.1(3)
C65	C66	C67	C68	-4.6(4)	C66	C67	C68	C69	-22.1(4)
C67	C68	C69	C65	39.6(3)	C67	C68	C69	C70	160.7(3)
C67	C68	C69	C78	-75.2(3)	C65	C69	C70	C71	112.7(3)
C65	C69	C70	C74	-64.9(4)	C65	C69	C78	C77	64.4(4)
C65	C69	C78	C80	-166.9(2)	C68	C69	C70	C71	-0.9(5)
C68	C69	C70	C74	-178.5(3)	C68	C69	C78	C77	172.6(3)

Table 9. Torsion angles (°) (continued)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C68	C69	C78	C80	-58.7(4)	C70	C69	C78	C77	-60.6(4)
C70	C69	C78	C80	68.1(3)	C78	C69	C70	C71	-124.1(3)
C78	C69	C70	C74	58.2(4)	C69	C70	C71	C72	173.5(3)
C69	C70	C74	C73	178.2(3)	C69	C70	C74	C75	2.5(6)
C71	C70	C74	C73	0.4(4)	C71	C70	C74	C75	-175.3(3)
C74	C70	C71	C72	-8.5(4)	C70	C71	C72	C73	12.8(4)
C70	C71	C72	C86	135.3(3)	C70	C71	C72	C87	-107.0(3)
C71	C72	C73	C74	-12.4(3)	C71	C72	C86	O11	173.5(3)
C71	C72	C87	O12	-175.7(2)	C73	C72	C86	O11	-68.0(4)
C86	C72	C73	C74	-135.1(3)	C73	C72	C87	O12	68.3(3)
C87	C72	C73	C74	106.3(3)	C86	C72	C87	O12	-54.0(3)
C87	C72	C86	O11	53.7(3)	C72	C73	C74	C70	7.9(4)
C72	C73	C74	C75	-176.0(3)	C70	C74	C75	C76	-46.0(5)
C73	C74	C75	C76	138.5(3)	C74	C75	C76	C77	26.2(5)
C74	C75	C76	C79	-159.1(3)	C75	C76	C77	C78	-1.3(7)
C75	C76	C79	O10	-31.0(5)	C75	C76	C79	N6	150.7(3)
C77	C76	C79	O10	144.3(4)	C77	C76	C79	N6	-34.0(5)
C79	C76	C77	C78	-175.8(3)	C76	C77	C78	C69	22.4(7)
C76	C77	C78	C80	-108.0(5)	C69	C78	C80	C81	105.2(3)
C69	C78	C80	C85	-74.6(4)	C77	C78	C80	C81	-122.3(3)
C77	C78	C80	C85	57.9(4)	C78	C80	C81	C82	-176.4(3)
C78	C80	C85	C84	175.6(3)	C81	C80	C85	C84	-4.2(5)
C85	C80	C81	C82	3.4(5)	C80	C81	C82	C83	-0.1(6)
C81	C82	C83	C84	-2.3(6)	C82	C83	C84	C85	1.5(6)
C83	C84	C85	C80	1.8(6)	O13	C91	C91[1]	O13[1]	154.5
O13	C91	C91[1]	O14[1]	-13.5	O14	C91	C91[1]	O13[1]	-13.5
O14	C91	C91[1]	O14[1]	178.4	O15	C93	C93[2]	O15	0.0
O15	C93	C93[2]	C94	180.0	O15	C93	C94	C93[2]	0.0
O16	C93	C94	C93[2]	-175.1	C93[2]	C93	C94	C93[2]	0.0
C94	C93	C93[2]	O15	180.0	C94	C93	C93[2]	C94	0.0

Symmetry Operators:

(1) -X,Y,-Z+1 (2) -X,Y,-Z+2

Table 10. Possible hydrogen bonds

Donor	H	Acceptor	D...A	D-H	H...A	D-H...A	
N1	H1	S1	1.664(3)	0.85	2.10	48.79	intramol.
N1	H1	O6[1]	3.018(3)	0.85	2.17	175.85	
N2	H2	O9	2.963(4)	0.97	2.04	159.35	
N2	H3	O5[2]	2.848(4)	0.80	2.13	149.00	
N3	H4	S2	1.648(3)	0.97	2.22	43.15	intramol.
N3	H4	O10[3]	3.068(3)	0.97	2.12	166.33	
N4	H5	O1[1]	2.909(3)	0.97	1.95	168.41	
N4	H6	O1	3.020(3)	0.65	2.40	159.12	
N5	H7	S3	1.647(3)	0.94	2.25	40.36	intramol.
N5	H7	O2	2.993(4)	0.94	2.07	169.56	
N6	H8	O5[3]	3.001(4)	0.84	2.20	161.87	
N6	H9	O9[4]	2.836(5)	0.68	2.21	152.76	

Symmetry Operators:

(1) -X+1,Y,-Z+2 (2) X+1/2-1,Y+1/2,Z
(3) -X+1,Y,-Z+1 (4) -X+1/2,Y+1/2-1,-Z+1

Table 11. Intramolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
S1	C6	3.363(4)	S2	C36	3.418(4)
S3	C66	3.483(4)	O1	C2	2.969(5)
O1	C3	3.192(5)	O1	C5	3.414(4)
O1	C6	3.487(4)	O2	C15	2.793(4)
O2	C17	3.505(4)	O3	C13	2.973(4)
O3	C27	2.785(4)	O4	C13	2.982(4)
O4	C26	2.788(4)	O5	C32	3.012(6)
O5	C33	3.050(5)	O5	C35	3.451(4)
O5	C36	3.587(4)	O6	C45	2.799(4)
O6	C47	3.511(4)	O7	C43	3.043(5)
O7	C57	2.789(5)	O8	C43	3.022(5)
O8	C56	2.791(5)	O9	C62	2.983(8)
O9	C63	3.069(6)	O9	C65	3.523(5)
O10	C75	2.846(4)	O10	C77	3.495(4)
O11	C73	3.051(4)	O11	C87	2.781(4)
O12	C73	3.040(4)	O12	C86	2.785(4)
O13	O14[1]	2.743	O13	C92	2.586
O15	O16[2]	1.882	O15	C95	2.796
O15	C95[2]	2.796	N1	C3	3.030(5)
N1	C4	3.106(5)	N1	C7	3.294(4)
N1	C8	3.025(4)	N1	C10	2.839(4)
N1	C14	3.343(4)	N2	C17	2.873(4)
N3	C33	3.069(5)	N3	C34	3.004(5)
N3	C37	3.258(4)	N3	C38	2.968(4)
N3	C40	2.846(4)	N3	C41	3.569(5)
N3	C44	3.424(4)	N4	C47	2.831(4)
N5	C63	3.033(5)	N5	C64	3.016(6)
N5	C67	3.197(5)	N5	C68	2.957(5)
N5	C70	2.846(5)	N5	C71	3.550(5)
N5	C74	3.455(5)	N6	C77	2.822(4)
C5	C14	3.197(4)	C5	C15	3.320(5)
C5	C16	3.512(4)	C5	C17	3.204(5)
C6	C18	3.014(5)	C7	C18	3.048(5)
C8	C11	2.972(4)	C8	C20	2.964(5)
C8	C21	3.465(5)	C9	C15	3.128(4)
C9	C16	3.188(4)	C9	C21	3.151(5)
C10	C16	3.143(4)	C10	C17	3.105(5)

Table 11. Intramolecular contacts less than 3.60 Å (continued)

atom	atom	distance	atom	atom	distance
C10	C20	3.259(5)	C10	C21	3.196(5)
C10	C27	3.335(5)	C11	C21	3.564(5)
C12	C28	2.864(5)	C13	C28	3.554(5)
C14	C17	3.051(5)	C14	C18	3.166(5)
C14	C27	3.311(5)	C15	C18	3.291(5)
C17	C21	3.233(5)	C17	C25	3.417(5)
C20	C23	2.790(5)	C21	C24	2.747(6)
C22	C25	2.763(6)	C26	C29	2.975(6)
C27	C29	3.017(5)	C35	C44	3.228(5)
C35	C45	3.397(5)	C35	C47	3.257(4)
C36	C48	3.004(5)	C37	C48	3.011(5)
C37	C50	3.596(5)	C38	C41	2.969(5)
C38	C50	2.934(4)	C38	C51	3.559(5)
C38	C55	3.521(5)	C39	C45	3.145(4)
C39	C46	3.207(4)	C39	C55	3.156(5)
C40	C46	3.131(4)	C40	C47	3.092(5)
C40	C50	3.229(5)	C40	C55	3.180(5)
C40	C57	3.330(5)	C41	C55	3.577(5)
C42	C58	2.842(6)	C43	C58	3.589(6)
C44	C47	3.066(5)	C44	C48	3.170(5)
C44	C57	3.278(5)	C45	C48	3.287(5)
C46	C50	3.587(4)	C47	C51	3.463(5)
C47	C55	3.137(5)	C50	C53	2.787(5)
C51	C54	2.760(6)	C52	C55	2.736(6)
C56	C59	3.008(7)	C57	C59	3.000(6)
C65	C74	3.223(5)	C65	C75	3.413(5)
C65	C76	3.500(5)	C65	C77	3.143(5)
C66	C78	2.994(6)	C67	C78	3.043(6)
C68	C71	2.990(5)	C68	C80	3.010(5)
C68	C81	3.430(6)	C69	C75	3.179(5)
C69	C76	3.193(4)	C69	C81	3.542(6)
C69	C85	3.284(6)	C70	C76	3.161(4)
C70	C77	3.112(4)	C70	C80	3.121(5)
C70	C85	3.172(5)	C70	C87	3.386(5)
C72	C88	2.878(5)	C74	C77	3.071(5)
C74	C78	3.137(5)	C74	C85	3.549(5)
C74	C87	3.380(5)	C75	C78	3.303(5)

Table 11. Intramolecular contacts less than 3.60 Å (continued)

atom	atom	distance	atom	atom	distance
C76	C80	3.525(5)	C77	C81	3.586(6)
C77	C85	3.044(6)	C80	C83	2.792(7)
C81	C84	2.741(7)	C82	C85	2.775(6)
C86	C89	3.001(6)	C87	C89	2.986(5)
C91	C92[1]	3.441	C93	C95[2]	3.594

Symmetry Operators:

(1) -X,Y,-Z+1 (2) -X,Y,-Z+2

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H10	3.543	S1	H11	2.757
S1	H12	2.775	S1	H13	2.951
S1	H14	2.960	S1	H16	2.794
S1	H17	2.865	S1	H18	3.575
S1	H19	2.690	S1	H20	3.016
S1	H31	3.546	S2	H49	2.758
S2	H50	2.753	S2	H51	3.533
S2	H52	2.867	S2	H53	2.956
S2	H55	2.839	S2	H56	2.797
S2	H57	3.573	S2	H58	2.689
S2	H59	3.099	S3	H88	2.759
S3	H89	3.522	S3	H90	2.747
S3	H92	2.907	S3	H93	2.912
S3	H94	2.818	S3	H95	2.770
S3	H96	3.540	S3	H97	2.689
S3	H98	3.163	O1	H1	2.648
O1	H11	3.202	O1	H12	2.560
O1	H13	2.848	O1	H14	3.489
O1	H20	2.761	O2	H2	2.450
O2	H3	2.985	O2	H30	2.524
O2	H31	2.914	O3	H28	2.889
O3	H29	3.103	O3	H42	3.131
O3	H43	2.609	O3	H44	3.250
O3	H45	2.660	O3	H46	2.489
O3	H47	2.543	O3	H48	3.176
O4	H28	3.543	O4	H29	2.610
O4	H39	3.083	O4	H43	3.258
O4	H44	2.650	O4	H45	2.653
O4	H46	2.512	O4	H47	3.175
O4	H48	2.520	O5	H4	2.660
O5	H49	3.313	O5	H50	2.600
O5	H52	2.636	O5	H53	3.367
O5	H59	2.890	O6	H5	2.391
O6	H6	2.830	O6	H69	2.507
O6	H70	2.968	O7	H67	2.982
O7	H68	3.173	O7	H80	3.134
O7	H82	3.267	O7	H83	2.677

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
O7	H84	2.668	O7	H85	2.504
O7	H86	3.148	O7	H87	2.509
O8	H67	3.588	O8	H68	2.654
O8	H78	3.126	O8	H82	2.596
O8	H83	3.250	O8	H84	2.699
O8	H85	3.179	O8	H86	2.529
O8	H87	2.527	O9	H7	2.729
O9	H88	3.275	O9	H90	2.575
O9	H92	2.713	O9	H93	3.342
O9	H98	3.060	O10	H8	2.387
O10	H9	2.775	O10	H108	2.678
O10	H109	2.870	O10	H110	3.587
O11	H106	2.933	O11	H107	3.249
O11	H120	3.118	O11	H121	3.253
O11	H122	2.649	O11	H123	2.643
O11	H124	3.186	O11	H125	2.547
O11	H126	2.542	O12	H106	3.546
O12	H107	2.710	O12	H117	3.137
O12	H121	2.609	O12	H122	3.250
O12	H123	2.658	O12	H124	2.558
O12	H125	3.194	O12	H126	2.529
N1	H13	3.304	N1	H14	2.621
N1	H16	3.423	N1	H17	2.714
N1	H20	2.546	N1	H21	3.282
N1	H22	3.594	N1	H25	2.843
N1	H26	3.301	N1	H31	3.130
N2	H32	2.483	N3	H52	3.320
N3	H53	2.699	N3	H55	2.579
N3	H56	3.300	N3	H59	2.553
N3	H60	3.305	N3	H61	3.545
N3	H64	2.758	N3	H65	3.197
N3	H70	3.333	N4	H71	2.415
N5	H92	3.343	N5	H93	2.622
N5	H94	2.590	N5	H95	3.311
N5	H98	2.538	N5	H99	3.290
N5	H100	3.447	N5	H103	2.779
N5	H104	3.165	N5	H109	3.407

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
N6	H110	2.429	C1	H1	2.822
C2	H13	2.662	C2	H14	3.336
C2	H15	2.722	C2	H16	2.673
C2	H17	3.346	C2	H18	2.727
C3	H1	2.728	C3	H10	2.696
C3	H11	3.335	C3	H12	2.694
C3	H16	3.338	C3	H17	2.708
C3	H18	2.701	C4	H1	3.459
C4	H10	2.744	C4	H11	2.674
C4	H12	3.341	C4	H13	3.336
C4	H14	2.698	C4	H15	2.704
C4	H28	3.420	C4	H31	3.427
C5	H22	3.112	C5	H23	3.121
C5	H24	3.245	C5	H25	2.710
C5	H31	2.926	C5	H33	2.513
C6	H1	2.670	C6	H24	3.240
C6	H25	2.908	C6	H33	2.516
C7	H1	3.130	C7	H19	3.250
C7	H33	2.662	C8	H1	2.862
C8	H19	3.235	C8	H20	3.109
C8	H21	3.094	C8	H26	3.001
C8	H27	2.830	C8	H33	2.706
C8	H34	3.535	C9	H1	2.772
C9	H20	3.239	C9	H21	2.894
C9	H22	3.237	C9	H23	2.905
C9	H26	2.978	C9	H27	2.882
C9	H31	3.201	C9	H32	3.440
C9	H34	2.994	C10	H1	3.119
C10	H17	3.493	C10	H19	2.937
C10	H24	2.913	C10	H25	2.661
C10	H28	2.912	C10	H29	3.051
C10	H30	3.280	C10	H31	2.855
C10	H33	3.352	C10	H34	2.613
C10	H41	3.198	C11	H1	3.597
C11	H24	3.111	C11	H25	2.680
C11	H28	2.967	C11	H29	3.204
C11	H34	2.909	C11	H39	2.803

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C11	H40	2.819	C11	H41	2.789
C11	H42	2.769	C12	H34	3.372
C12	H45	3.305	C13	H17	3.241
C13	H26	2.975	C13	H27	3.195
C13	H30	2.587	C13	H31	3.130
C13	H39	3.396	C13	H40	2.756
C13	H41	2.675	C13	H42	3.374
C14	H17	3.104	C14	H19	3.178
C14	H26	2.913	C14	H27	3.041
C14	H34	3.108	C14	H41	3.135
C15	H17	3.438	C15	H19	2.849
C15	H28	2.871	C15	H29	2.773
C15	H32	3.329	C16	H2	3.305
C16	H3	2.635	C16	H19	2.906
C16	H33	3.176	C17	H3	2.698
C17	H19	2.779	C17	H30	3.254
C17	H31	2.959	C17	H34	3.179
C17	H38	3.501	C18	H19	2.571
C18	H21	2.951	C18	H23	3.011
C18	H24	2.666	C18	H25	3.397
C18	H31	3.567	C18	H34	2.696
C18	H38	2.655	C19	H30	2.506
C19	H31	2.907	C19	H32	2.485
C20	H23	3.338	C20	H24	2.528
C20	H32	2.693	C20	H35	3.261
C20	H37	3.255	C21	H24	2.874
C21	H27	3.042	C21	H32	3.535
C21	H33	3.283	C21	H36	3.225
C21	H38	3.213	C21	H41	3.126
C22	H37	3.218	C23	H34	3.220
C23	H38	3.237	C24	H35	3.226
C25	H23	3.285	C25	H24	3.114
C25	H32	3.303	C25	H33	2.483
C25	H34	3.207	C25	H36	3.236
C26	H26	2.588	C26	H27	3.082
C26	H28	2.565	C26	H29	3.070
C26	H41	3.312	C26	H42	2.683

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C26	H43	3.272	C26	H45	2.704
C27	H26	3.302	C27	H27	2.528
C27	H28	3.273	C27	H29	2.500
C27	H34	2.993	C27	H39	2.656
C27	H40	3.320	C27	H44	3.361
C27	H45	2.736	C28	H29	3.380
C28	H39	2.552	C28	H40	3.193
C28	H41	3.187	C28	H42	2.597
C29	H39	2.598	C29	H42	2.686
C29	H46	3.306	C29	H47	2.658
C29	H48	2.689	C30	H43	2.687
C30	H44	2.669	C30	H45	3.311
C31	H4	3.027	C32	H52	2.692
C32	H53	3.335	C32	H54	2.697
C32	H55	3.345	C32	H56	2.659
C32	H57	2.753	C33	H4	2.958
C33	H49	3.329	C33	H50	2.705
C33	H51	2.699	C33	H55	2.707
C33	H56	3.327	C33	H57	2.703
C34	H4	3.583	C34	H49	2.659
C34	H50	3.342	C34	H51	2.759
C34	H52	3.331	C34	H53	2.662
C34	H54	2.751	C34	H67	3.161
C35	H61	3.103	C35	H62	3.118
C35	H63	3.231	C35	H64	2.687
C35	H70	3.011	C35	H72	2.531
C36	H4	2.466	C36	H63	3.232
C36	H64	2.901	C36	H72	2.506
C37	H4	2.857	C37	H58	3.253
C37	H72	2.617	C37	H73	3.574
C38	H4	2.660	C38	H58	3.236
C38	H59	3.091	C38	H60	3.088
C38	H65	2.990	C38	H66	2.790
C38	H72	2.684	C39	H4	2.737
C39	H59	3.251	C39	H60	2.904
C39	H61	3.241	C39	H62	2.907
C39	H65	2.942	C39	H66	2.824

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C39	H70	3.223	C39	H71	3.439
C39	H77	3.039	C40	H4	3.230
C40	H55	3.236	C40	H58	2.915
C40	H63	2.922	C40	H64	2.690
C40	H67	2.911	C40	H68	3.059
C40	H69	3.261	C40	H70	2.842
C40	H72	3.335	C40	H77	2.648
C40	H81	3.182	C41	H55	3.434
C41	H63	3.109	C41	H64	2.682
C41	H67	2.946	C41	H68	3.200
C41	H77	3.023	C41	H78	2.741
C41	H79	2.794	C41	H80	2.751
C41	H81	2.807	C42	H77	3.422
C42	H84	3.312	C43	H55	3.108
C43	H65	2.962	C43	H66	3.191
C43	H69	2.578	C43	H70	3.110
C43	H78	3.398	C43	H79	2.727
C43	H80	3.363	C43	H81	2.645
C44	H55	3.060	C44	H58	3.196
C44	H65	2.906	C44	H66	3.015
C44	H77	3.043	C44	H81	3.071
C45	H58	2.922	C45	H67	2.899
C45	H68	2.757	C45	H71	3.332
C46	H5	3.286	C46	H6	2.516
C46	H58	3.034	C46	H72	3.190
C46	H77	3.497	C47	H6	2.632
C47	H58	2.876	C47	H69	3.259
C47	H70	2.952	C47	H73	3.597
C47	H77	3.030	C48	H58	2.624
C48	H60	2.947	C48	H62	2.966
C48	H63	2.641	C48	H64	3.383
C48	H70	3.561	C48	H73	2.690
C48	H77	2.673	C49	H69	2.540
C49	H70	2.943	C49	H71	2.462
C50	H62	3.293	C50	H63	2.489
C50	H71	2.688	C50	H74	3.252
C50	H76	3.241	C51	H62	3.153

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C51	H63	2.972	C51	H71	3.383
C51	H72	2.503	C51	H75	3.250
C51	H77	3.217	C52	H76	3.212
C53	H73	3.249	C53	H77	3.201
C54	H74	3.208	C54	H81	3.561
C55	H63	2.944	C55	H66	3.057
C55	H71	3.456	C55	H72	3.276
C55	H73	3.220	C55	H75	3.212
C55	H81	3.088	C56	H65	2.562
C56	H66	3.053	C56	H67	2.580
C56	H68	3.070	C56	H80	2.690
C56	H81	3.302	C56	H83	3.373
C56	H84	2.725	C57	H65	3.320
C57	H66	2.552	C57	H67	3.278
C57	H68	2.493	C57	H77	3.008
C57	H78	2.688	C57	H79	3.312
C57	H82	3.275	C57	H84	2.764
C58	H68	3.427	C58	H78	2.566
C58	H79	3.167	C58	H80	2.575
C58	H81	3.171	C59	H78	2.657
C59	H80	2.663	C59	H85	2.704
C59	H86	2.672	C59	H87	3.350
C60	H82	2.731	C60	H83	2.668
C60	H84	3.340	C61	H7	3.036
C62	H91	2.724	C62	H92	2.651
C62	H93	3.339	C62	H94	3.336
C62	H95	2.666	C62	H96	2.726
C63	H7	2.945	C63	H88	3.330
C63	H89	2.689	C63	H90	2.678
C63	H94	2.661	C63	H95	3.302
C63	H96	2.664	C64	H7	3.569
C64	H88	2.670	C64	H89	2.726
C64	H90	3.311	C64	H91	2.661
C64	H92	3.299	C64	H93	2.672
C64	H106	3.041	C64	H109	3.381
C64	H118	3.353	C65	H94	3.587
C65	H100	3.054	C65	H101	3.103

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C65	H102	3.216	C65	H103	2.707
C65	H109	3.110	C65	H111	2.603
C66	H7	2.520	C66	H102	3.207
C66	H103	2.927	C66	H111	2.538
C67	H7	2.836	C67	H97	3.236
C67	H111	2.609	C67	H112	3.452
C68	H7	2.648	C68	H97	3.231
C68	H98	3.116	C68	H99	3.068
C68	H104	3.004	C68	H105	2.831
C68	H111	2.618	C68	H112	3.389
C69	H7	2.698	C69	H98	3.233
C69	H99	2.854	C69	H100	3.226
C69	H101	2.924	C69	H104	2.937
C69	H105	2.854	C69	H109	3.322
C69	H110	3.397	C69	H116	3.262
C70	H7	3.176	C70	H94	3.027
C70	H97	2.880	C70	H102	2.957
C70	H103	2.717	C70	H106	2.947
C70	H107	3.034	C70	H108	3.269
C70	H109	2.878	C70	H111	3.337
C70	H116	2.794	C70	H119	3.280
C71	H7	3.572	C71	H94	3.237
C71	H102	3.167	C71	H103	2.695
C71	H106	3.006	C71	H107	3.171
C71	H116	3.381	C71	H117	2.731
C71	H118	2.823	C71	H119	2.770
C71	H120	2.712	C72	H94	3.370
C72	H123	3.292	C73	H94	2.955
C73	H104	3.002	C73	H105	3.171
C73	H108	2.576	C73	H109	3.070
C73	H116	3.488	C73	H117	3.389
C73	H118	2.689	C73	H119	2.688
C73	H120	3.387	C74	H94	2.852
C74	H95	3.556	C74	H97	3.163
C74	H104	2.920	C74	H105	3.015
C74	H116	2.866	C74	H119	3.231
C75	H94	3.483	C75	H95	3.535

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C75	H97	2.911	C75	H106	2.841
C75	H107	2.785	C75	H110	3.333
C75	H116	3.446	C76	H8	3.175
C76	H9	2.472	C76	H97	2.882
C76	H111	3.225	C76	H116	3.192
C77	H9	2.712	C77	H97	2.732
C77	H99	3.561	C77	H108	3.244
C77	H109	3.002	C77	H116	2.873
C78	H97	2.627	C78	H99	2.908
C78	H101	3.031	C78	H102	2.613
C78	H103	3.379	C78	H112	2.668
C78	H116	2.701	C79	H108	2.569
C79	H109	2.858	C79	H110	2.463
C80	H101	3.563	C80	H102	2.563
C80	H105	3.557	C80	H110	2.793
C80	H113	3.268	C80	H115	3.236
C81	H101	3.340	C81	H102	2.747
C81	H111	2.505	C81	H114	3.219
C81	H116	3.240	C82	H102	3.595
C82	H115	3.212	C83	H112	3.217
C83	H116	3.249	C84	H113	3.213
C84	H119	3.304	C85	H102	3.365
C85	H105	3.288	C85	H110	3.441
C85	H111	3.282	C85	H112	3.231
C85	H114	3.253	C85	H119	3.053
C86	H94	3.452	C86	H104	2.541
C86	H105	3.102	C86	H106	2.548
C86	H107	3.111	C86	H119	3.309
C86	H120	2.690	C86	H122	3.342
C86	H123	2.710	C87	H104	3.238
C87	H105	2.475	C87	H106	3.268
C87	H107	2.522	C87	H116	3.348
C87	H117	2.693	C87	H118	3.303
C87	H121	3.285	C87	H123	2.714
C88	H107	3.518	C88	H117	2.604
C88	H118	3.182	C88	H119	3.183
C88	H120	2.584	C89	H117	2.676

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C89	H120	2.638	C89	H124	2.683
C89	H125	2.712	C89	H126	3.339
C90	H121	2.712	C90	H122	2.689
C90	H123	3.335	H1	H13	2.872
H1	H14	2.202	H1	H17	3.072
H1	H19	2.748	H1	H20	2.561
H1	H21	3.565	H1	H22	3.219
H1	H25	2.448	H1	H26	3.076
H2	H32	3.292	H3	H32	2.121
H4	H52	3.047	H4	H53	2.439
H4	H55	3.129	H4	H58	2.754
H4	H59	2.345	H4	H60	3.391
H4	H61	2.907	H4	H64	2.245
H4	H65	3.123	H5	H71	3.271
H6	H71	2.106	H7	H92	3.118
H7	H93	2.361	H7	H94	3.100
H7	H97	2.751	H7	H98	2.436
H7	H99	3.440	H7	H100	2.856
H7	H102	3.594	H7	H103	2.254
H7	H104	3.028	H8	H110	3.192
H9	H110	2.301	H10	H13	2.926
H10	H14	3.584	H10	H15	2.558
H10	H16	2.992	H10	H18	2.606
H11	H13	3.542	H11	H15	3.587
H11	H16	2.471	H11	H17	3.542
H11	H18	2.973	H12	H13	2.492
H12	H14	3.553	H12	H15	3.015
H12	H16	3.534	H13	H17	3.574
H13	H18	3.569	H14	H16	3.569
H14	H17	2.537	H14	H18	2.976
H14	H26	3.324	H15	H16	3.574
H15	H17	2.988	H15	H18	2.537
H16	H31	3.062	H17	H26	3.591
H17	H28	2.590	H17	H31	2.939
H17	H40	3.520	H19	H20	2.597
H19	H21	2.238	H19	H31	2.344
H19	H32	3.476	H19	H33	2.537

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H20	H22	2.234	H20	H23	2.738
H20	H25	3.322	H20	H33	3.474
H21	H22	2.740	H21	H23	2.235
H21	H33	2.213	H22	H24	2.586
H22	H25	2.235	H23	H24	2.231
H23	H25	2.797	H23	H33	2.456
H23	H38	3.003	H24	H26	3.312
H24	H27	2.669	H24	H33	2.887
H24	H34	3.107	H24	H38	3.472
H25	H26	2.419	H25	H27	2.624
H26	H28	3.222	H26	H39	2.732
H26	H40	2.553	H26	H42	3.425
H27	H34	2.512	H27	H39	3.064
H27	H40	3.505	H27	H41	2.674
H27	H42	2.470	H28	H30	2.761
H28	H31	3.160	H28	H39	3.509
H28	H40	2.460	H28	H41	3.580
H29	H30	2.484	H29	H31	3.482
H29	H40	3.434	H29	H41	2.501
H29	H42	3.459	H29	H46	3.515
H32	H33	2.288	H32	H38	3.281
H33	H34	3.585	H33	H38	2.268
H34	H35	2.328	H34	H41	2.264
H34	H42	3.237	H35	H36	2.296
H35	H41	3.342	H36	H37	2.304
H37	H38	2.321	H39	H41	3.580
H39	H42	2.530	H39	H43	2.841
H39	H44	3.480	H39	H45	2.098
H40	H45	3.545	H41	H45	3.595
H42	H43	3.559	H42	H44	2.964
H42	H45	2.177	H43	H46	3.545
H43	H47	2.502	H43	H48	2.996
H44	H46	3.547	H44	H47	2.920
H44	H48	2.517	H45	H47	3.538
H45	H48	3.553	H49	H52	3.560
H49	H54	3.564	H49	H55	3.523
H49	H56	2.441	H49	H57	2.982

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H50	H52	2.533	H50	H53	3.576
H50	H54	2.983	H50	H56	3.516
H51	H52	2.974	H51	H53	3.572
H51	H54	2.533	H51	H56	2.991
H51	H57	2.647	H52	H55	3.553
H52	H57	3.592	H53	H55	2.502
H53	H56	3.537	H53	H57	2.922
H53	H65	3.385	H54	H55	3.057
H54	H57	2.594	H55	H65	3.036
H55	H67	2.510	H55	H70	3.285
H55	H79	3.085	H56	H67	3.183
H56	H70	3.131	H57	H67	3.327
H57	H79	3.594	H58	H59	2.606
H58	H60	2.271	H58	H70	2.402
H58	H71	3.560	H58	H72	2.603
H59	H61	2.215	H59	H62	2.724
H59	H64	3.306	H59	H72	3.466
H60	H61	2.722	H60	H62	2.215
H60	H72	2.210	H61	H63	2.569
H61	H64	2.239	H61	H72	3.582
H62	H63	2.238	H62	H64	2.817
H62	H72	2.398	H62	H73	2.796
H63	H65	3.303	H63	H66	2.631
H63	H72	2.861	H63	H73	3.295
H63	H77	3.263	H64	H65	2.413
H64	H66	2.591	H64	H72	3.599
H65	H67	3.198	H65	H78	2.664
H65	H79	2.542	H65	H80	3.424
H66	H77	2.663	H66	H78	3.008
H66	H79	3.491	H66	H80	2.455
H66	H81	2.716	H67	H69	2.797
H67	H70	3.163	H67	H78	3.518
H67	H79	2.434	H67	H81	3.555
H68	H69	2.450	H68	H70	3.445
H68	H79	3.397	H68	H80	3.450
H68	H81	2.465	H71	H72	2.277
H71	H73	3.414	H71	H77	3.511

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H72	H73	2.303	H72	H77	3.572
H73	H74	2.321	H74	H75	2.314
H75	H76	2.287	H76	H77	2.298
H76	H80	3.551	H76	H81	3.218
H77	H80	3.242	H77	H81	2.253
H78	H80	2.573	H78	H82	3.518
H78	H83	2.965	H78	H84	2.140
H79	H84	3.572	H80	H82	2.868
H80	H83	3.562	H80	H84	2.205
H82	H85	3.033	H82	H86	2.539
H82	H87	3.599	H83	H85	2.502
H83	H86	2.899	H83	H87	3.559
H84	H85	3.557	H84	H86	3.560
H88	H91	3.588	H88	H92	3.538
H88	H94	3.536	H88	H95	2.464
H88	H96	2.971	H89	H91	2.560
H89	H92	2.918	H89	H93	3.587
H89	H95	2.978	H89	H96	2.594
H90	H91	3.012	H90	H92	2.478
H90	H93	3.543	H90	H95	3.508
H90	H96	3.583	H91	H94	2.941
H91	H95	3.539	H91	H96	2.495
H92	H94	3.530	H92	H96	3.534
H93	H94	2.496	H93	H95	3.544
H93	H96	2.952	H93	H104	3.152
H94	H104	2.893	H94	H106	2.454
H94	H109	3.057	H94	H118	2.743
H95	H106	3.064	H95	H109	2.825
H96	H106	3.137	H96	H118	3.089
H97	H98	2.578	H97	H99	2.260
H97	H109	2.490	H97	H110	3.353
H97	H111	2.725	H98	H100	2.198
H98	H101	2.684	H98	H103	3.372
H98	H111	3.501	H99	H100	2.732
H99	H101	2.198	H99	H111	2.235
H100	H102	2.607	H100	H103	2.232
H100	H111	3.578	H101	H102	2.235

Table 12. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H101	H103	2.798	H101	H111	2.391
H101	H112	2.747	H102	H104	3.358
H102	H105	2.715	H102	H111	2.723
H102	H112	2.815	H103	H104	2.428
H103	H105	2.604	H103	H111	3.552
H104	H106	3.310	H104	H117	2.574
H104	H118	2.572	H104	H120	3.313
H105	H116	3.185	H105	H117	3.060
H105	H118	3.560	H105	H119	2.612
H105	H120	2.400	H106	H108	2.734
H106	H109	3.057	H106	H117	3.483
H106	H118	2.379	H106	H119	3.572
H107	H108	2.482	H107	H109	3.445
H107	H116	3.348	H107	H118	3.408
H107	H119	2.480	H107	H120	3.478
H110	H111	2.232	H110	H116	3.403
H111	H112	2.277	H111	H116	3.589
H112	H113	2.311	H113	H114	2.295
H114	H115	2.309	H115	H116	2.318
H115	H119	2.963	H116	H119	2.518
H117	H120	2.581	H117	H121	3.547
H117	H122	2.951	H117	H123	2.157
H118	H123	3.574	H119	H123	3.575
H120	H121	2.869	H120	H122	3.528
H120	H123	2.146	H121	H124	2.527
H121	H125	3.012	H121	H126	3.574
H122	H124	2.941	H122	H125	2.535
H122	H126	3.571	H123	H124	3.560
H123	H125	3.573			

Table 13. Intermolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
O1	N4	3.020(3)	O1	N4[1]	2.909(3)
O2	N5	2.993(4)	O2	C53	3.591(5)
O2	C54	3.255(5)	O2	C63	3.462(5)
O2	C67	3.332(5)	O2	C68	3.372(5)
O3	O16[2]	3.422(3)	O3	C60[3]	3.524(6)
O3	C94	3.457(3)	O4	C47[4]	3.275(4)
O4	C48[4]	3.493(4)	O5	N2[5]	2.848(4)
O5	N6[6]	3.001(4)	O6	N1[1]	3.018(3)
O6	C3[1]	3.225(5)	O6	C7[1]	3.563(4)
O6	C8[1]	3.386(4)	O6	C22[5]	3.548(5)
O9	N2	2.963(4)	O9	N6[7]	2.836(5)
O10	N3[6]	3.068(3)	O10	C33[6]	3.398(5)
O10	C37[6]	3.402(4)	O10	C38[6]	3.276(4)
O10	C83[7]	3.208(6)	O11	C37	3.507(4)
O12	C92[5]	3.557(3)	O13	C81	3.403(5)
O13	C90[4]	3.444(4)	O15	C7[3]	3.494(4)
O15	C7[8]	3.494(4)	O15	C25[3]	3.574(4)
O15	C25[8]	3.574(4)	O16	O3[2]	3.422(3)
O16	C26[2]	3.566(4)	N1	O6[1]	3.018(3)
N2	O5[4]	2.848(4)	N2	O9	2.963(4)
N2	N6[7]	3.244(5)	N2	C63	3.544(6)
N3	O10[6]	3.068(3)	N4	O1	3.020(3)
N4	O1[1]	2.909(3)	N4	N4[1]	3.415(4)
N5	O2	2.993(4)	N6	O5[6]	3.001(4)
N6	O9[9]	2.836(5)	N6	N2[9]	3.244(5)
C3	O6[1]	3.225(5)	C7	O6[1]	3.563(4)
C7	O15[10]	3.494(4)	C8	O6[1]	3.386(4)
C22	O6[4]	3.548(5)	C24	C93[10]	3.595(5)
C24	C94[10]	3.509(5)	C25	O15[10]	3.574(4)
C26	O16[2]	3.566(4)	C27	C47[4]	3.543(5)
C29	C29[2]	3.356(6)	C30	C32[11]	3.528(6)
C32	C30[12]	3.528(6)	C33	O10[6]	3.398(5)
C37	O10[6]	3.402(4)	C37	O11	3.507(4)
C38	O10[6]	3.276(4)	C47	O4[5]	3.275(4)
C47	C27[5]	3.543(5)	C48	O4[5]	3.493(4)
C53	O2	3.591(5)	C54	O2	3.255(5)
C60	O3[10]	3.524(6)	C63	O2	3.462(5)

Table 13. Intermolecular contacts less than 3.60 Å (continued)

atom	atom	distance	atom	atom	distance
C63	N2	3.544(6)	C64	C64[6]	3.510(8)
C67	O2	3.332(5)	C68	O2	3.372(5)
C81	O13	3.403(5)	C83	O10[9]	3.208(6)
C90	O13[5]	3.444(4)	C92	O12[4]	3.557(3)
C93	C24[3]	3.595(5)	C94	O3	3.457(3)
C94	O3[2]	3.457(3)	C94	C24[3]	3.509(5)
C94	C24[8]	3.509(5)			

Symmetry Operators:

(1) -X+1,Y,-Z+2	(2) -X,Y,-Z+2
(3) X+1/2-1,Y+1/2-1,Z	(4) X+1/2-1,Y+1/2,Z
(5) X+1/2,Y+1/2-1,Z	(6) -X+1,Y,-Z+1
(7) -X+1/2,Y+1/2,-Z+1	(8) -X+1/2,Y+1/2-1,-Z+2
(9) -X+1/2,Y+1/2-1,-Z+1	(10) X+1/2,Y+1/2,Z
(11) X-1,Y,Z	(12) X+1,Y,Z

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H5[1]	2.945	S2	H3[2]	3.481
S2	H8[3]	3.188	S3	H2	3.071
O1	H5	3.478	O1	H5[1]	1.954
O1	H6	2.399	O1	H6[1]	3.266
O1	H44[2]	2.667	O1	H71	3.184
O2	H7	2.068	O2	H75	3.200
O2	H76	2.513	O2	H92	3.258
O2	H93	2.802	O2	H98	3.364
O2	H100	2.735	O2	H103	2.651
O3	H85[4]	3.426	O3	H87[4]	2.994
O4	H60[5]	3.491	O4	H71[5]	2.694
O4	H72[5]	2.804	O4	H73[5]	3.314
O5	H2[2]	3.276	O5	H3[2]	2.132
O5	H8[3]	2.196	O5	H9[3]	3.390
O5	H32[2]	3.127	O5	H82[2]	2.952
O6	H1[1]	2.167	O6	H13[1]	2.968
O6	H14[1]	2.622	O6	H20[1]	3.571
O6	H22[1]	3.082	O6	H25[1]	2.572
O6	H26[1]	3.499	O6	H35[2]	2.687
O8	H32	2.965	O8	H33	3.231
O8	H38	3.325	O9	H2	2.036
O9	H3	3.378	O9	H8[6]	3.185
O9	H9[6]	2.214	O9	H110[6]	3.052
O10	H4[3]	2.116	O10	H52[3]	3.220
O10	H53[3]	2.719	O10	H59[3]	3.486
O10	H61[3]	2.867	O10	H64[3]	2.481
O10	H114[6]	2.361	O10	H115[6]	3.412
O11	H61	3.085	O11	H62	3.207
O11	H63	3.567	O11	H107[3]	3.110
O11	H108[3]	3.314	O12	H126[3]	2.786
O13	H89[4]	3.379	O13	H90[4]	3.205
O13	H101	3.385	O13	H111	3.498
O13	H112	2.530	O13	H121[5]	3.523
O13	H124[5]	2.481	O14	H88[4]	3.585
O14	H90[4]	3.053	O14	H110[7]	3.010
O14	H111[7]	3.280	O14	H124[5]	3.594
O14	H124[6]	3.445	O15	H23[4]	2.607

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
O15	H23[8]	2.607	O15	H38[4]	3.168
O15	H38[8]	3.168	O16	H23[4]	3.346
O16	H38[8]	3.286	O16	H40[9]	2.945
O16	H87[8]	3.348	N1	H5[1]	3.077
N2	H7	3.322	N2	H8[6]	2.792
N2	H9[6]	3.035	N2	H59[5]	3.163
N2	H80	3.569	N2	H82	3.387
N2	H92	2.792	N2	H93	3.472
N3	H8[3]	3.193	N4	H1[1]	3.148
N4	H5[1]	3.105	N4	H6[1]	3.246
N4	H13[1]	3.096	N4	H20	3.016
N4	H20[1]	3.248	N4	H22[1]	3.530
N4	H42[2]	3.440	N4	H44[2]	3.279
N4	H45[2]	3.580	N5	H2	3.338
N6	H2[10]	2.930	N6	H3[10]	3.162
N6	H4[3]	3.039	N6	H52[3]	3.092
N6	H59[3]	3.263	N6	H61[3]	3.520
C2	H48[2]	3.403	C2	H56[4]	3.134
C2	H57[4]	3.523	C3	H5[1]	3.260
C3	H27[8]	3.441	C6	H5[1]	3.574
C6	H22[1]	3.292	C7	H22[1]	3.152
C7	H23[1]	3.397	C15	H76	2.959
C16	H76	2.765	C17	H76	3.398
C17	H81	3.355	C19	H7	3.026
C19	H59[5]	3.561	C19	H76	2.806
C19	H92	3.204	C19	H93	3.306
C19	H100	3.526	C21	H58[5]	3.324
C22	H14[11]	3.557	C22	H58[5]	3.291
C22	H70[5]	2.970	C23	H70[5]	3.469
C24	H47[12]	3.347	C24	H49[5]	3.477
C25	H86	3.445	C27	H60[5]	3.569
C27	H71[5]	3.108	C27	H72[5]	3.431
C28	H71[5]	3.537	C29	H6[5]	3.597
C29	H12[5]	3.344	C29	H43[9]	2.883
C29	H44[9]	3.503	C29	H45[9]	3.153
C29	H71[5]	3.489	C30	H11[5]	3.560
C30	H12[5]	3.543	C30	H37[4]	3.582

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C30	H49[13]	3.019	C30	H51[13]	3.275
C30	H73[5]	3.038	C30	H85[4]	3.314
C30	H86[4]	3.267	C32	H46[14]	3.315
C32	H47[14]	3.254	C32	H48[14]	3.439
C32	H74[12]	3.332	C32	H86[2]	3.383
C33	H8[3]	3.451	C33	H120[12]	3.446
C34	H10[12]	3.408	C34	H11[12]	3.242
C36	H8[3]	3.513	C37	H117	3.399
C37	H122	3.164	C38	H117	3.368
C38	H118	3.347	C41	H91	3.090
C45	H35[2]	3.066	C46	H35[2]	3.078
C47	H41[2]	3.197	C47	H42[2]	3.424
C48	H41[2]	3.577	C49	H1[1]	2.995
C49	H13[1]	3.176	C49	H14[1]	3.412
C49	H20	3.502	C49	H22[1]	3.287
C49	H25[1]	3.538	C49	H35[2]	3.083
C49	H42[2]	3.570	C51	H48[2]	2.916
C51	H117	3.073	C51	H123	3.423
C52	H11	3.441	C52	H48[2]	3.512
C52	H51[4]	3.215	C52	H104	3.331
C52	H105	3.505	C52	H117	3.016
C52	H123	3.526	C53	H16	3.385
C53	H31	3.209	C53	H103	3.365
C53	H104	2.967	C53	H105	3.463
C54	H19	2.988	C54	H31	2.899
C54	H93	3.506	C54	H104	3.596
C55	H19	3.194	C56	H113[12]	3.287
C57	H32	3.275	C57	H91	3.496
C57	H92	3.456	C59	H3	3.565
C59	H50[5]	3.416	C59	H92	3.453
C60	H38	3.507	C60	H46[12]	2.935
C60	H47[12]	3.488	C60	H50[5]	3.521
C61	H2	3.481	C62	H88[3]	2.856
C62	H89[3]	3.474	C62	H113[12]	3.325
C63	H2	2.923	C63	H66	3.105
C63	H80	2.956	C63	H84	3.346
C64	H95[3]	2.889	C64	H96[3]	3.248

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C65	H115[6]	3.474	C66	H125[5]	3.020
C67	H125[5]	3.458	C68	H75	3.455
C71	H75	3.381	C73	H106[3]	3.400
C73	H126[3]	3.325	C75	H114[6]	3.356
C76	H114[6]	3.484	C76	H115[6]	3.391
C77	H115[6]	3.572	C79	H4[3]	2.909
C79	H52[3]	3.320	C79	H53[3]	3.376
C79	H61[3]	3.196	C79	H64[3]	3.538
C79	H114[6]	3.163	C79	H115[6]	3.475
C81	H89[4]	3.478	C82	H65[4]	3.552
C82	H78[4]	3.213	C82	H79[4]	3.562
C82	H89[4]	2.998	C83	H53[4]	3.173
C83	H109[10]	3.173	C84	H53[4]	3.397
C84	H97[10]	2.972	C84	H109[10]	3.521
C86	H62	3.435	C86	H63	3.049
C87	H54[4]	3.468	C87	H126[3]	3.456
C89	H62	3.068	C90	H99[2]	3.090
C90	H107[3]	3.152	C91	H88[4]	3.582
C91	H90[4]	3.310	C91	H124[5]	2.814
C91	H124[6]	3.337	C92	H83[4]	3.401
C92	H90[4]	2.892	C92	H110[7]	3.084
C92	H121[5]	3.318	C93	H23[4]	3.179
C93	H23[8]	3.263	C93	H37[4]	3.336
C93	H37[8]	3.385	C93	H38[4]	3.425
C93	H38[8]	3.084	C94	H37[4]	2.864
C94	H37[8]	2.864	C94	H39	3.398
C94	H39[9]	3.398	C94	H43	2.868
C94	H43[9]	2.868	C95	H22[4]	3.409
C95	H23[4]	3.394	C95	H23[8]	3.584
C95	H24[4]	3.388	C95	H38[8]	3.520
C95	H40[9]	3.508	C95	H68[8]	2.871
C95	H87[8]	3.068	H1	O6[1]	2.167
H1	N4[1]	3.148	H1	C49[1]	2.995
H1	H5[1]	2.554	H2	S3	3.071
H2	O5[5]	3.276	H2	O9	2.036
H2	N5	3.338	H2	N6[6]	2.930
H2	C61	3.481	H2	C63	2.923

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H2	H7	2.858	H2	H8[6]	2.703
H2	H9[6]	2.575	H2	H82	3.422
H2	H84	3.543	H2	H90	3.507
H2	H92	2.185	H2	H93	2.994
H2	H98	3.590	H3	S2[5]	3.481
H3	O5[5]	2.132	H3	O9	3.378
H3	N6[6]	3.162	H3	C59	3.565
H3	H8[6]	2.567	H3	H9[6]	3.110
H3	H59[5]	3.075	H3	H80	3.501
H3	H82	2.796	H3	H84	3.501
H3	H92	3.102	H4	O10[3]	2.116
H4	N6[3]	3.039	H4	C79[3]	2.909
H4	H8[3]	2.533	H5	S1[1]	2.945
H5	O1	3.478	H5	O1[1]	1.954
H5	N1[1]	3.077	H5	N4[1]	3.105
H5	C3[1]	3.260	H5	C6[1]	3.574
H5	H1[1]	2.554	H5	H5[1]	3.054
H5	H6[1]	2.766	H5	H13[1]	2.599
H5	H14[1]	3.297	H5	H20	3.527
H5	H20[1]	2.774	H5	H44[2]	3.508
H5	H45[2]	3.510	H6	O1	2.399
H6	O1[1]	3.266	H6	N4[1]	3.246
H6	C29[2]	3.597	H6	H5[1]	2.766
H6	H6[1]	3.189	H6	H13[1]	3.594
H6	H20	2.724	H6	H20[1]	3.576
H6	H42[2]	3.519	H6	H44[2]	2.887
H6	H45[2]	3.462	H7	O2	2.068
H7	N2	3.322	H7	C19	3.026
H7	H2	2.858	H8	S2[3]	3.188
H8	O5[3]	2.196	H8	O9[10]	3.185
H8	N2[10]	2.792	H8	N3[3]	3.193
H8	C33[3]	3.451	H8	C36[3]	3.513
H8	H2[10]	2.703	H8	H3[10]	2.567
H8	H4[3]	2.533	H8	H52[3]	2.788
H8	H53[3]	3.385	H8	H59[3]	2.696
H8	H61[3]	3.434	H9	O5[3]	3.390
H9	O9[10]	2.214	H9	N2[10]	3.035

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H9	H2[10]	2.575	H9	H3[10]	3.110
H9	H59[3]	3.467	H9	H98[10]	3.498
H10	C34[4]	3.408	H10	H36[15]	3.051
H10	H56[4]	2.623	H10	H57[4]	3.376
H11	C30[2]	3.560	H11	C34[4]	3.242
H11	C52	3.441	H11	H47[2]	3.393
H11	H48[2]	2.859	H11	H49[4]	3.285
H11	H51[4]	3.410	H11	H56[4]	2.773
H11	H57[4]	2.857	H11	H74	3.303
H12	C29[2]	3.344	H12	C30[2]	3.543
H12	H43[2]	3.100	H12	H44[2]	2.771
H12	H45[8]	3.450	H12	H47[2]	3.260
H12	H48[2]	3.058	H13	O6[1]	2.968
H13	N4[1]	3.096	H13	C49[1]	3.176
H13	H5[1]	2.599	H13	H6[1]	3.594
H13	H27[8]	3.179	H13	H35[8]	3.503
H13	H42[8]	2.775	H13	H45[8]	3.440
H14	O6[1]	2.622	H14	C22[8]	3.557
H14	C49[1]	3.412	H14	H5[1]	3.297
H14	H35[8]	3.136	H15	H24[8]	3.470
H15	H27[8]	2.840	H16	C53	3.385
H16	H57[4]	3.075	H16	H75	3.122
H18	H57[4]	3.553	H18	H67[4]	3.050
H19	C54	2.988	H19	C55	3.194
H19	H76	2.675	H19	H77	3.009
H19	H81	3.386	H20	O6[1]	3.571
H20	N4	3.016	H20	N4[1]	3.248
H20	C49	3.502	H20	H5	3.527
H20	H5[1]	2.774	H20	H6	2.724
H20	H6[1]	3.576	H20	H20[1]	3.493
H20	H22[1]	3.051	H21	H22[1]	3.196
H21	H68	3.461	H21	H77	3.311
H21	H81	3.013	H22	O6[1]	3.082
H22	N4[1]	3.530	H22	C6[1]	3.292
H22	C7[1]	3.152	H22	C49[1]	3.287
H22	C95[12]	3.409	H22	H20[1]	3.051
H22	H21[1]	3.196	H22	H22[1]	2.840

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H22	H23[1]	2.981	H22	H69[1]	3.438
H23	O15[12]	2.607	H23	O16[12]	3.346
H23	C7[1]	3.397	H23	C93[12]	3.179
H23	C93[11]	3.263	H23	C95[12]	3.394
H23	C95[11]	3.584	H23	H22[1]	2.981
H23	H23[1]	2.985	H24	C95[12]	3.388
H24	H15[11]	3.470	H25	O6[1]	2.572
H25	C49[1]	3.538	H25	H69[1]	3.345
H26	O6[1]	3.499	H26	H36[8]	3.252
H27	C3[11]	3.441	H27	H13[11]	3.179
H27	H15[11]	2.840	H28	H85[4]	3.552
H28	H87[4]	3.414	H29	H60[5]	2.961
H30	H76	3.359	H30	H100	3.073
H31	C53	3.209	H31	C54	2.899
H31	H75	2.969	H31	H76	2.354
H32	O5[5]	3.127	H32	O8	2.965
H32	C57	3.275	H32	H80	3.070
H32	H81	3.103	H32	H82	3.159
H33	O8	3.231	H33	H81	3.086
H34	H58[5]	3.072	H35	O6[5]	2.687
H35	C45[5]	3.066	H35	C46[5]	3.078
H35	C49[5]	3.083	H35	H13[11]	3.503
H35	H14[11]	3.136	H35	H58[5]	3.050
H35	H69[5]	3.373	H35	H70[5]	2.391
H36	H10[16]	3.051	H36	H26[11]	3.252
H36	H39[11]	3.322	H36	H40[11]	3.575
H36	H56[5]	3.581	H36	H70[5]	3.313
H37	C30[12]	3.582	H37	C93[12]	3.336
H37	C93[11]	3.385	H37	C94[12]	2.864
H37	H39[11]	3.522	H37	H43[12]	3.258
H37	H47[12]	2.640	H37	H49[5]	3.399
H38	O8	3.325	H38	O15[12]	3.168
H38	O16[11]	3.286	H38	C60	3.507
H38	C93[12]	3.425	H38	C93[11]	3.084
H38	C95[11]	3.520	H38	H86	2.911
H38	H87	3.342	H39	C94	3.398
H39	H36[8]	3.322	H39	H37[8]	3.522

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H39	H43[9]	3.526	H40	O16[9]	2.945
H40	C95[9]	3.508	H40	H36[8]	3.575
H41	C47[5]	3.197	H41	C48[5]	3.577
H41	H58[5]	3.091	H41	H60[5]	2.834
H41	H71[5]	3.020	H41	H72[5]	2.982
H42	N4[5]	3.440	H42	C47[5]	3.424
H42	C49[5]	3.570	H42	H6[5]	3.519
H42	H13[11]	2.775	H42	H71[5]	2.892
H43	C29[9]	2.883	H43	C94	2.868
H43	H12[5]	3.100	H43	H37[4]	3.258
H43	H39[9]	3.526	H43	H43[9]	2.375
H43	H44[9]	3.282	H43	H45[9]	2.603
H44	O1[5]	2.667	H44	N4[5]	3.279
H44	C29[9]	3.503	H44	H5[5]	3.508
H44	H6[5]	2.887	H44	H12[5]	2.771
H44	H43[9]	3.282	H44	H44[9]	3.521
H44	H45[9]	3.132	H44	H71[5]	2.910
H45	N4[5]	3.580	H45	C29[9]	3.153
H45	H5[5]	3.510	H45	H6[5]	3.462
H45	H12[11]	3.450	H45	H13[11]	3.440
H45	H43[9]	2.603	H45	H44[9]	3.132
H45	H45[9]	3.219	H45	H71[5]	3.599
H46	C32[13]	3.315	H46	C60[4]	2.935
H46	H49[13]	3.002	H46	H50[13]	3.351
H46	H51[13]	3.046	H46	H73[5]	2.910
H46	H85[4]	2.478	H46	H86[4]	2.727
H46	H87[4]	3.150	H47	C24[4]	3.347
H47	C32[13]	3.254	H47	C60[4]	3.488
H47	H11[5]	3.393	H47	H12[5]	3.260
H47	H37[4]	2.640	H47	H49[13]	2.539
H47	H50[13]	3.544	H47	H51[13]	3.250
H47	H85[4]	3.446	H47	H86[4]	2.948
H47	H87[4]	3.545	H48	C2[5]	3.403
H48	C32[13]	3.439	H48	C51[5]	2.916
H48	C52[5]	3.512	H48	H11[5]	2.859
H48	H12[5]	3.058	H48	H49[13]	3.030
H48	H51[13]	2.989	H48	H71[5]	3.542

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H48	H73[5]	2.375	H48	H74[5]	3.472
H49	C24[2]	3.477	H49	C30[14]	3.019
H49	H11[12]	3.285	H49	H37[2]	3.399
H49	H46[14]	3.002	H49	H47[14]	2.539
H49	H48[14]	3.030	H49	H86[2]	3.087
H50	C59[2]	3.416	H50	C60[2]	3.521
H50	H46[14]	3.351	H50	H47[14]	3.544
H50	H82[2]	2.781	H50	H83[2]	3.263
H50	H85[2]	3.460	H50	H86[2]	2.840
H51	C30[14]	3.275	H51	C52[12]	3.215
H51	H11[12]	3.410	H51	H46[14]	3.046
H51	H47[14]	3.250	H51	H48[14]	2.989
H51	H73[12]	3.219	H51	H74[12]	2.432
H51	H123[12]	3.246	H52	O10[3]	3.220
H52	N6[3]	3.092	H52	C79[3]	3.320
H52	H8[3]	2.788	H52	H115[12]	3.532
H52	H120[12]	3.380	H53	O10[3]	2.719
H53	C79[3]	3.376	H53	C83[12]	3.173
H53	C84[12]	3.397	H53	H8[3]	3.385
H53	H114[12]	2.904	H53	H115[12]	3.277
H54	C87[12]	3.468	H54	H74[12]	3.136
H54	H105[12]	3.243	H54	H115[12]	3.496
H54	H119[12]	3.435	H54	H120[12]	2.674
H56	C2[12]	3.134	H56	H10[12]	2.623
H56	H11[12]	2.773	H56	H36[2]	3.581
H57	C2[12]	3.523	H57	H10[12]	3.376
H57	H11[12]	2.857	H57	H16[12]	3.075
H57	H18[12]	3.553	H57	H74[12]	2.917
H58	C21[2]	3.324	H58	C22[2]	3.291
H58	H34[2]	3.072	H58	H35[2]	3.050
H58	H41[2]	3.091	H59	O10[3]	3.486
H59	N2[2]	3.163	H59	N6[3]	3.263
H59	C19[2]	3.561	H59	H3[2]	3.075
H59	H8[3]	2.696	H59	H9[3]	3.467
H60	O4[2]	3.491	H60	C27[2]	3.569
H60	H29[2]	2.961	H60	H41[2]	2.834
H61	O10[3]	2.867	H61	O11	3.085

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H61	N6[3]	3.520	H61	C79[3]	3.196
H61	H8[3]	3.434	H61	H108[3]	3.285
H61	H117	3.509	H61	H118	3.564
H61	H122	3.128	H61	H125	3.501
H62	O11	3.207	H62	C86	3.435
H62	C89	3.068	H62	H117	2.882
H62	H118	3.598	H62	H122	2.382
H62	H123	3.034	H63	O11	3.567
H63	C86	3.049	H63	H117	2.624
H63	H118	2.672	H64	O10[3]	2.481
H64	C79[3]	3.538	H64	H114[12]	3.458
H64	H118	3.407	H65	C82[12]	3.552
H65	H91	3.215	H65	H113[12]	3.044
H65	H114[12]	3.161	H66	C63	3.105
H66	H91	2.342	H66	H92	3.404
H66	H93	3.170	H67	H18[12]	3.050
H68	C95[11]	2.871	H68	H21	3.461
H69	H22[1]	3.438	H69	H25[1]	3.345
H69	H35[2]	3.373	H70	C22[2]	2.970
H70	C23[2]	3.469	H70	H35[2]	2.391
H70	H36[2]	3.313	H71	O1	3.184
H71	O4[2]	2.694	H71	C27[2]	3.108
H71	C28[2]	3.537	H71	C29[2]	3.489
H71	H41[2]	3.020	H71	H42[2]	2.892
H71	H44[2]	2.910	H71	H45[2]	3.599
H71	H48[2]	3.542	H72	O4[2]	2.804
H72	C27[2]	3.431	H72	H41[2]	2.982
H73	O4[2]	3.314	H73	C30[2]	3.038
H73	H46[2]	2.910	H73	H48[2]	2.375
H73	H51[4]	3.219	H73	H117	3.205
H73	H122	3.507	H73	H123	2.989
H74	C32[4]	3.332	H74	H11	3.303
H74	H48[2]	3.472	H74	H51[4]	2.432
H74	H54[4]	3.136	H74	H57[4]	2.917
H74	H104	3.428	H74	H105	3.171
H74	H117	3.107	H74	H120	3.336
H74	H123	3.176	H75	O2	3.200

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H75	C68	3.455	H75	C71	3.381
H75	H16	3.122	H75	H31	2.969
H75	H102	3.512	H75	H103	2.599
H75	H104	2.795	H75	H105	3.076
H76	O2	2.513	H76	C15	2.959
H76	C16	2.765	H76	C17	3.398
H76	C19	2.806	H76	H19	2.675
H76	H30	3.359	H76	H31	2.354
H76	H93	3.194	H77	H19	3.009
H77	H21	3.311	H78	C82[12]	3.213
H78	H91	3.175	H78	H92	3.583
H78	H112[12]	3.532	H78	H113[12]	2.558
H79	C82[12]	3.562	H79	H113[12]	3.231
H80	N2	3.569	H80	C63	2.956
H80	H3	3.501	H80	H32	3.070
H80	H91	2.726	H80	H92	2.494
H80	H93	3.200	H81	C17	3.355
H81	H19	3.386	H81	H21	3.013
H81	H32	3.103	H81	H33	3.086
H82	O5[5]	2.952	H82	N2	3.387
H82	H2	3.422	H82	H3	2.796
H82	H32	3.159	H82	H50[5]	2.781
H82	H92	3.483	H83	C92[12]	3.401
H83	H50[5]	3.263	H83	H121[16]	3.079
H84	C63	3.346	H84	H2	3.543
H84	H3	3.501	H84	H90	3.245
H84	H91	3.251	H84	H92	2.624
H85	O3[12]	3.426	H85	C30[12]	3.314
H85	H28[12]	3.552	H85	H46[12]	2.478
H85	H47[12]	3.446	H85	H50[5]	3.460
H86	C25	3.445	H86	C30[12]	3.267
H86	C32[5]	3.383	H86	H38	2.911
H86	H46[12]	2.727	H86	H47[12]	2.948
H86	H49[5]	3.087	H86	H50[5]	2.840
H87	O3[12]	2.994	H87	O16[11]	3.348
H87	C95[11]	3.068	H87	H28[12]	3.414
H87	H38	3.342	H87	H46[12]	3.150

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H87	H47[12]	3.545	H88	O14[12]	3.585
H88	C62[3]	2.856	H88	C91[12]	3.582
H88	H88[3]	2.276	H88	H89[3]	2.579
H88	H90[3]	3.494	H88	H95[3]	3.409
H89	O13[12]	3.379	H89	C62[3]	3.474
H89	C81[12]	3.478	H89	C82[12]	2.998
H89	H88[3]	2.579	H89	H95[3]	3.437
H89	H112[12]	3.303	H89	H113[12]	2.387
H90	O13[12]	3.205	H90	O14[12]	3.053
H90	C91[12]	3.310	H90	C92[12]	2.892
H90	H2	3.507	H90	H84	3.245
H90	H88[3]	3.494	H91	C41	3.090
H91	C57	3.496	H91	H65	3.215
H91	H66	2.342	H91	H78	3.175
H91	H80	2.726	H91	H84	3.251
H91	H113[12]	3.074	H92	O2	3.258
H92	N2	2.792	H92	C19	3.204
H92	C57	3.456	H92	C59	3.453
H92	H2	2.185	H92	H3	3.102
H92	H66	3.404	H92	H78	3.583
H92	H80	2.494	H92	H82	3.483
H92	H84	2.624	H93	O2	2.802
H93	N2	3.472	H93	C19	3.306
H93	C54	3.506	H93	H2	2.994
H93	H66	3.170	H93	H76	3.194
H93	H80	3.200	H94	H95[3]	3.575
H95	C64[3]	2.889	H95	H88[3]	3.409
H95	H89[3]	3.437	H95	H94[3]	3.575
H95	H95[3]	2.489	H95	H96[3]	2.450
H96	C64[3]	3.248	H96	H95[3]	2.450
H96	H96[3]	3.243	H96	H113[12]	3.554
H97	C84[6]	2.972	H97	H115[6]	2.555
H98	O2	3.364	H98	H2	3.590
H98	H9[6]	3.498	H98	H125[5]	2.912
H99	C90[5]	3.090	H99	H115[6]	3.471
H99	H124[5]	3.017	H99	H125[5]	2.504
H99	H126[5]	3.290	H100	O2	2.735

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H100	C19	3.526	H100	H30	3.073
H100	H125[5]	3.594	H101	O13	3.385
H101	H124[5]	3.210	H101	H125[5]	3.169
H102	H75	3.512	H103	O2	2.651
H103	C53	3.365	H103	H75	2.599
H104	C52	3.331	H104	C53	2.967
H104	C54	3.596	H104	H74	3.428
H104	H75	2.795	H105	C52	3.505
H105	C53	3.463	H105	H54[4]	3.243
H105	H74	3.171	H105	H75	3.076
H106	C73[3]	3.400	H106	H106[3]	2.638
H106	H107[3]	3.323	H107	O11[3]	3.110
H107	C90[3]	3.152	H107	H106[3]	3.323
H107	H107[3]	3.596	H107	H125[3]	3.284
H107	H126[3]	2.375	H108	O11[3]	3.314
H108	H61[3]	3.285	H108	H114[6]	3.533
H108	H118[3]	3.576	H109	C83[6]	3.173
H109	C84[6]	3.521	H109	H114[6]	2.656
H109	H115[6]	3.327	H110	O9[10]	3.052
H110	O14[7]	3.010	H110	C92[7]	3.084
H111	O13	3.498	H111	O14[7]	3.280
H112	O13	2.530	H112	H78[4]	3.532
H112	H89[4]	3.303	H113	C56[4]	3.287
H113	C62[4]	3.325	H113	H65[4]	3.044
H113	H78[4]	2.558	H113	H79[4]	3.231
H113	H89[4]	2.387	H113	H91[4]	3.074
H113	H96[4]	3.554	H114	O10[10]	2.361
H114	C75[10]	3.356	H114	C76[10]	3.484
H114	C79[10]	3.163	H114	H53[4]	2.904
H114	H64[4]	3.458	H114	H65[4]	3.161
H114	H108[10]	3.533	H114	H109[10]	2.656
H115	O10[10]	3.412	H115	C65[10]	3.474
H115	C76[10]	3.391	H115	C77[10]	3.572
H115	C79[10]	3.475	H115	H52[4]	3.532
H115	H53[4]	3.277	H115	H54[4]	3.496
H115	H97[10]	2.555	H115	H99[10]	3.471
H115	H109[10]	3.327	H117	C37	3.399

Table 14. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H117	C38	3.368	H117	C51	3.073
H117	C52	3.016	H117	H61	3.509
H117	H62	2.882	H117	H63	2.624
H117	H73	3.205	H117	H74	3.107
H118	C38	3.347	H118	H61	3.564
H118	H62	3.598	H118	H63	2.672
H118	H64	3.407	H118	H108[3]	3.576
H119	H54[4]	3.435	H119	H126[3]	3.183
H120	C33[4]	3.446	H120	H52[4]	3.380
H120	H54[4]	2.674	H120	H74	3.336
H121	O13[2]	3.523	H121	C92[2]	3.318
H121	H83[15]	3.079	H122	C37	3.164
H122	H61	3.128	H122	H62	2.382
H122	H73	3.507	H123	C51	3.423
H123	C52	3.526	H123	H51[4]	3.246
H123	H62	3.034	H123	H73	2.989
H123	H74	3.176	H124	O13[2]	2.481
H124	O14[2]	3.594	H124	O14[10]	3.445
H124	C91[2]	2.814	H124	C91[10]	3.337
H124	H99[2]	3.017	H124	H101[2]	3.210
H125	C66[2]	3.020	H125	C67[2]	3.458
H125	H61	3.501	H125	H98[2]	2.912
H125	H99[2]	2.504	H125	H100[2]	3.594
H125	H101[2]	3.169	H125	H107[3]	3.284
H126	O12[3]	2.786	H126	C73[3]	3.325
H126	C87[3]	3.456	H126	H99[2]	3.290
H126	H107[3]	2.375	H126	H119[3]	3.183
H126	H126[3]	3.137			

Symmetry Operators:

(1) -X+1,Y,-Z+2
(2) X+1/2,Y+1/2-1,Z
(3) -X+1,Y,-Z+1
(4) X+1/2-1,Y+1/2-1,Z
(5) X+1/2-1,Y+1/2,Z
(6) -X+1/2,Y+1/2,-Z+1
(7) -X,Y,-Z+1
(8) -X+1/2,Y+1/2-1,-Z+2
(9) -X,Y,-Z+2
(10) -X+1/2,Y+1/2-1,-Z+1
(11) -X+1/2,Y+1/2,-Z+2
(12) X+1/2,Y+1/2,Z
(13) X-1,Y,Z
(14) X+1,Y,Z
(15) X,Y-1,Z
(16) X,Y+1,Z

List of Abbreviations

Ac : acetyl

APCI : atmospheric pressure chemical ionization

aq. : aqueous

Ar : aryl

atm : atmosphere (1 atmosphere = 10^5 Pa (pressure) = 0.1 MPa)

BINAP : 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl

BIPHEP : 2,2'-bis(diphenylphosphino)-1,1'-biphenyl

Bn : benzyl

Bu : butyl

ºC : degrees Celsius

ca. : circa

calcd. : calculated

cat. : catalyst

cm^{-1} : wave number

CO : carbon monoxide

cod : 1,5-cyclooctadiene

Cp : cyclopentadienyl

Cp* : 1,2,3,4,5-pentamethylcyclopentadienyl

Cy : cyclohexyl

DIPEA : *N*,*N*-diisopropylethylamine

DMAD : dimethyl acetylenedicarboxylate

DMF : *N*,*N*-dimethylformamide

DMP : Dess-Martin periodinane

DPPB : 1,4-bis(diphenylphosphino)butane

DPEphos : 2,2'-bis(diphenylphosphino)diphenyl ether

DPPBz : 1,2-bis(diphenylphosphino)benzene

DPPE : 1,2-bis(diphenylphosphino)ethane

DPPF : 1,1'-bis(diphenylphosphino)ferrocene

DPPP : 1,3-bis(diphenylphosphino)propane

dr : diastereomeric ratio

ee : enantiomeric excess

EI : electron ionization

eq. : equation or equivalent(s) (depending on the context)

equiv. : equivalent(s)

ESI : electrospray ionization

Et : ethyl

h : hour(s)

H_8-BINAP : 2,2’-bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl

HPLC : high performance liquid chromatography

HRMS : high-resolution mass spectroscopy

i : iso

IMes : 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene

I*i*Pr : 1,3-diisopropylimidazol-2-ylidene

IPr : 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene

IR : infrared spectroscopy

LHMDS : lithium hexamethyldisilazide

M : metal or molar (depending on the context)

*m*CPBA : *meta*-chloroperoxybenzoic acid

Me : methyl

min : minute(s)

MOM : methoxymethyl

mp : melting point

Ms : methanesulfonyl

MS4A : molecular sieves 4A

MTPA : α-methoxy-α-(trifluoromethyl)phenylacetic acid

n : normal

N : normality (equivalent concentration)

nbd : 2,5-norbornadiene

NCS : *N*-chlorosuccinimide

NHC : *N*-heterocyclic carbene

NMP : *N*-methyl-2-pyrrolidone

NMR : nuclear magnetic resonance

NOESY : nuclear Overhauser effect spectroscopy

Ns : 2-nitrobenzenesulfonyl

p : para

Ph : phenyl

PPTS : pyridinium *p*-toluenesulfonate

Pr : propyl

PTLC : preparative thin-layer chromatography

Py : pyridine

quant. : quantitative yield

R : any substituent

rac : racemic

rec. : recovered

r.t. : room temperature

Me-DuPHOS : 1,2-bis(2,5-dimethylphospholano)benzene

SEGPHOS : 5,5′-bis(diphenylphosphino)-4,4′-bi-1,3-benzodioxole

t : tertiary

tert : tertiary

TBAF : tetra-*n*-butylammonium fluoride

TBAI : tetra-*n*-butylammonium iodide

TBDPS : *t*-butyldiphenylsilyl

TBS : *t*-butyldimethylsilyl

TEMPO : 2,2,6,6-tetramethylpiperidine 1-oxyl

Tf : trifluoromethanesulfonyl

THF : tetrahydrofuran

TLC : thin-layer chromatography

TMS : trimethylsilyl

Tol-BINAP : 2,2’-bis(di-*p*-tolylphosphino)-1,1'-binaphthyl

Ts : *p*-toluenesulfonyl

X : any atom or substituent

Xyl-BINAP : 2,2'-bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl

Xyl-SDP : 7,7’-bis[di(3,5-dimethylphenyl)phosphino]-2,2’,3,3’-tetrahydro-1,1’-spirobiindane

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