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博士学位論文

外輪型二核遷移金属錯体の構造解析と全合成研究への応用

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略語表

本論文において下記の略語を使用した。化合物の位置番号は 18*E*-lyngbyaloside C の位置番号に準じた。

Ac	acetyl
aq.	aqueous
Ar	aryl
	argon
Bn	benzyl
BPTPI	3-benzene-fused-phthalimidopiperidinonate
brsm	based on recovered starting material
Bu	normal butyl
^{t}Bu	*tert*-butyl
Bz	benzoyl
calcd	calculated
cat.	catalyst
cap	caprolactamate
Cy	cyclohexyl
CSA	10-camphorsulfonic acid
DBU	1,8-diazabicyclo[5,4,0]undec-7-ene
DCC	*N*,*N*'-dicyclohexylcarbodiimide
DCE	dichloroethane
DDQ	2,3-dichloro-5,6-dicyano-*p*-benzoquinone
DET	diethyl tartrate
DFT	density functional theory
DIBAL	diisobutylaluminium hydride
DIPA	diisopropanolamine
DIPT	diisopropyl tartrate
DMAD	dimethyl acetylenedicarboxylate
DMAP	*N*,*N*-dimethyl-4-aminopyridine
DME	1,2-dimethoxyethane
DMF	*N*,*N*-dimethylformamide
DMP	Dess–Martin periodinane
DMSO	dimethyl sulfoxide
dr	diastereomeric ratio
EDCI	1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride
ee	enantiomeric excess
ent	enantiomer of
EPR	electron paramagnetic resonance
equiv.	equivalent
ESI	electrospray ionization

Et	ethyl
FAB	fast atom bombardment
GPC	gel permeation chromatography
HDA	hetero-Diels–Alder
HMPA	hexamethylphosphoramide
hp	2-hydroxypyridinate
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectrometry
IC_{50}	half maximal inhibitory concentration
imp.	impure
IR	infrared
Ipc	isopinocampheyl
KHMDS	potassium hexamethyldisilazane
LC	liquid chromatography
LDA	lithium diisopropylamide
LiHMDS	lithium hexamethyldisilazane
LRMS	low resolution mass spectrometry
Me	methyl
MEM	2-methoxyethoxymethyl
mer	meridional
Mes	mesyl
MOM	methoxymethyl
MPM	*p*-methoxyphenylmethyl
MS	mass spectrometry
	molecular sieves
NaHMDS	sodium hexamethyldisilazane
NBS	*N*-bromosuccinimide
NBSH	nitrobenzenesulfonylhydrazide
NMO	4-methylmorpholine *N*-oxide
NMP	*N*-methylpyrrolidone
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
NOESY	NOE correlated spectroscopy
PCC	pyridinium chlorochromate
Ph	phenyl
PMB	*p*-methoxybenzyl
PMP	*p*-methoxyphenyl
PPTS	pyridinium *p*-toluenesulfonate
^{i}Pr	isopropyl
^{n}Pr	normal propyl
prep.	preparative
PTPI	3-phthalimidopiperidinonate
PTTL	*N*-phthaloyl-*tert*-leicinate

Py	pyridyl
quant.	quantitative yield
Red-Al$^{®}$	sodium bis(2-methoxyethoxy)alminum hydride
R_f	retention factor (in chromatography)
r.t.	room temperature
SM	starting material
(*S*,*S*)-[Ti]	cyclopentadienyl[(4*R*,*trans*)-2,2-dimethyl-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethano-*O*,*O*']titanium chloride
TBAF	tetrabutylammonium fluoride
TBDPS	*tert*-butyldiphenylsilyl
TBHP	*tert*-butyl hydroperoxide
TBS	*tert*-butyldimethylsilyl
TBSP	*tert*-butylsulfonylprolinate
TC	thiophene-2-carboxylate
TES	triethylsilyl
temp.	temperature
TEMPO	2,2,6,6-tetramethylpiperidine 1-oxyl
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid
TFAA	trifluoroacetic anhydride
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin-layer chromatography
TM	target material
TMS	trimethylsilyl
Tr	trityl (triphenylmethyl)
${}_t$R	retention time
Ts	*p*-toluenesulfonyl
UV	ultraviolet
Vis	visible
wt	weight

目次

序論

長きに渡る日本の鎖国体制は、マシュー・カルブレイス・ペリー率いるアメリカ合衆国海軍東インド艦隊が江戸湾浦賀へ入港した、いわゆる「黒船来航」を機に終焉を迎えた。そして、幕末と呼ばれる激動の時代が始まり、日本は明治維新という大きな転換点を迎えることとなった。当時来航した船はその見た目から“黒船”と呼ばれ、現代の教科書でその詳細が語られることは少ないが、ペリーの搭乗した黒船、旗艦サスケハナは著名な外輪船の一つである。外輪船は、船体の両側面もしくは後方に水車型の装置（外輪：paddlewheel）を備え、動力によってこれを回転させることで推進力を得る。初期の動力船こそ外輪船が主体であったが、後に開発されたスクリュー船よりも効率が悪いことからその主役を取って代われ、現代では一部の観光船、湖に浮かぶスワンボートを除いてそのほとんどがスクリュー船となっている。

この“外輪：paddlewheel”という単語は分野を超えて化学の領域でも用いられている。隣接する 2 つの中心金属原子に対して通常 4 つの配位子がこれらを架橋した骨格をもつ金属錯体を“外輪型二核金属錯体：paddlewheel complex”と呼び*、現在までに様々な金属原子を含んだ外輪型錯体が合成されている 1)。数多くある外輪型二核金属錯体の中でも、そのバリエーションの豊富さと有機化学反応への適用を考慮すると、外輪型二核ロジウム(II)錯体は名実ともに優れた錯体である 2)。

外輪型骨格を有する二核ロジウム(II)錯体は α-ジアゾカルボニル化合物と速やかに反応し、窒素分子の放出を経てロジウム(II)カルベン中間体を生成することが知られている(Figure 1, eq. 1)。本中間体の炭素カルベンは非常に高い求電子性を示し、炭素–炭素多重結合への付加、X–H 挿入反応(X = C, O, N, S…)、イリド形成を引き金とする転位・付加環化反応を引き起こす。また、イミノヨージナン等を前駆体としたナイトレン種の生成、続くアジリジン化反応、C–H アミノ化反応、スルフイミド化反応にも本錯体は用いられる(Figure 1, eq. 2)。さらに、二核ロジウム(II)錯体はアキシアル位に Lewis 塩基性分子が配位する Lewis 酸としての性質も示し、光学活性化合物のシフト試薬、ヘテロ Diels–Alder 反応および[2+2]付加環化反応における触媒としても用いられている(Figure 1, eq. 3)。

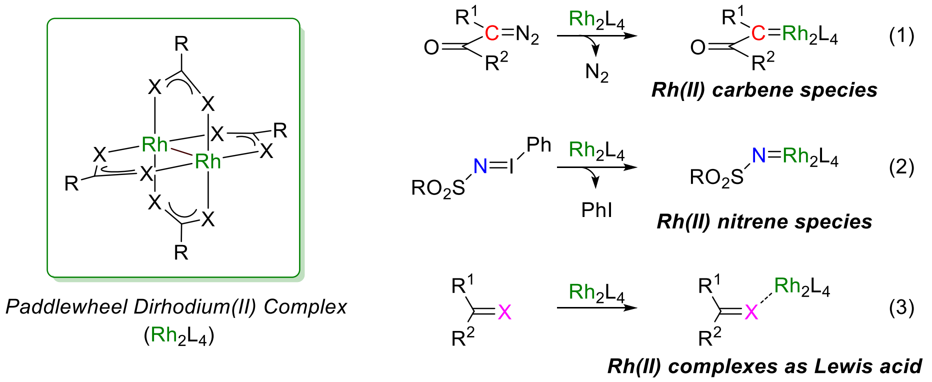

Figure 1. Schematic representation of paddlewheel dirhodium(II) complex and key intermediate of its catalyses

母型錯体である酢酸ロジウム(II)に含まれる 4 つの酢酸配位子は、配位子交換反応によって容易に他の配位子へと交換可能である。光学活性な配位子を用いることによってキラル二核

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*研究者によっては同様の二核金属錯体の形を lanthanum もしくは Chinese-lanthanum と表現することもある。

ロジウム(II)錯体を合成することも可能であり、これまでに多種多様なキラル錯体が報告されている。上記の各有機反応に関してもキラルな錯体を用いた触媒的不斉反応の研究が 20 年以上にわたって盛んに行なわれ、高収率かつ高立体選択的な反応が達成されている 2)。

著者の所属する研究室でもこれまでに数種のキラル二核ロジウム(II)錯体を開発し、多くの触媒的不斉反応の開発を行なってきた。その中の一例として、キラル二核ロジウム(II)アミダート錯体 Rh$_2$(*S*-BPTPI)$_4$(**1**)を開発し、Danishefsky ジエン(**2**)とアルデヒドとのヘテロ Diels–Alder 反応において不斉 Lewis 酸触媒として機能することを見出している 3a) (Figure 2, eq. 1)。本反応では、完璧な *endo* 選択性かつ高いエナンチオ選択性でジヒドロピラノン誘導体を得ることが可能である。最近では、これまでに Lewis 酸触媒の適用例がない Rawal ジエン(**3**)とアルデヒドとのヘテロ Diels–Alder 反応においても Rh$_2$(*S*-BPTPI)$_4$ (**1**)が優れた Lewis 酸触媒として機能することを報告している(Figure 2, eq. 2)3b,3c)。本法では特に Danishefsky ジエンを用いた場合には満足のいく結果が得られなかった分岐した脂肪族アルデヒドとのヘテロ Diels–Alder 反応において良好な結果を得ることができ、これら 2 つのジエンを使い分けることによって幅広い基質適用範囲を実現することが可能となっている。

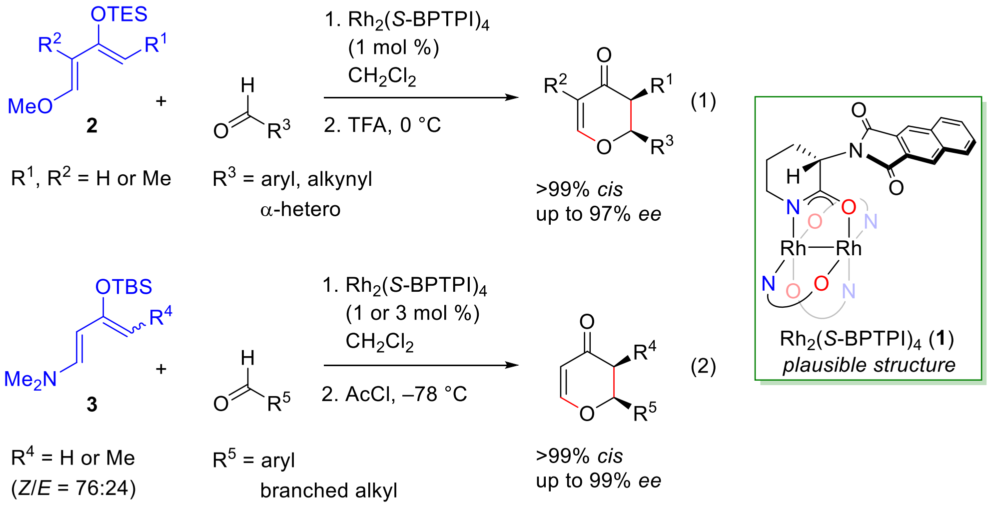


Figure 2. Chiral dirhodium(II) carboxamidate complex catalyzed asymmetric hetero-Diels–Alder reactions

今回著者は、所属研究室で開発されたキラル二核ロジウム(II)触媒を用いた不斉ヘテロ Diels–Alder 反応のさらなる有用性を示すべく、応用研究の一環として海洋産抗腫瘍活性天然物である 18*E*-リングビアロシド C の触媒的不斉合成について検討を行なった。また、長年研究されてきたこの二核ロジウム(II)触媒に関して一度見直し、本触媒が抱える問題点を解決すべく新たな遷移金属触媒の開発について検討を行なった。本論文ではこれら 2 項目について報告する。

本論

第 1 部　18*E*-リングビアロシド C の触媒的不斉全合成

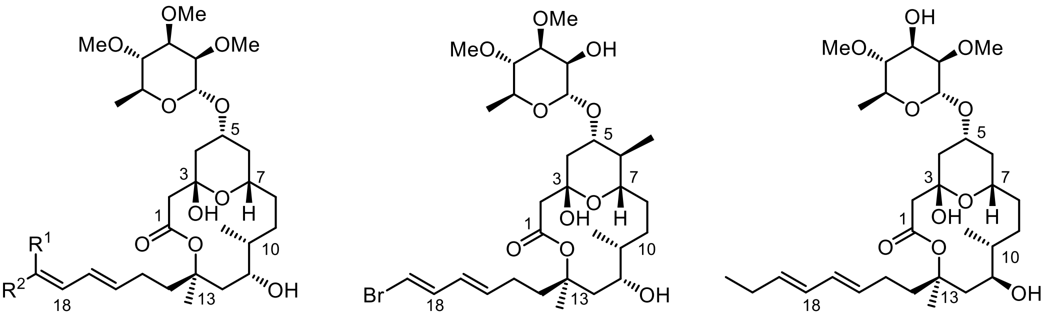
第 1 章　リングビアロシド類の合成研究および全合成

第 1 節　背景

18*E*-リングビアロシド C(**4**)は、2010 年にグアムのアプラ港に位置するフィンガー・リーフおよびウェスタンショールズにおいて採取された藍藻類 *Lyngbya bouillonii* より単離、構造決定されたグリコシドマクロライドである4)。本化合物の構造上の特徴として、6 員環ヘミアセタール構造とブロモジエン側鎖をもつ 14 員環マクロラクトンからなるアグリコン部分に 6 つの立体中心を有し、さらにそのマクロラクトンを構築するエステル結合が他のマクロライドには類を見ない第三級アルコールに由来する点があげられる。本化合物の相対立体配置は、ビシナルプロトン間のカップリング定数および NOESY スペクトルによって決定されている。主な生物活性として、HeLa 細胞に対して IC_{50} = 9.3 μM、HT29 細胞に対して IC_{50} = 13 μM の細胞毒性を示すことが同時に報告されているが、未だ作用機序については明らかとされていない。

また、18*E*-リングビアロシド C(**4**)と構造が類似している化合物として、18*Z*-リングビアロシド C(**5**)4)、リングビアロシド B(**6**)5)、リングボウイロシド(**7**)6)が同じように *Lyngbya sp.*より単離、構造決定されている。18*E*-リングビアロシド C を含めたこれらリングビアロシド類に特徴的である第三級アルコール由来のマクロラクトンを如何様にして構築するかという点で合成上関心がもたれており、これまでにいくつかの研究グループによってこれらの合成研究が為されている7-14)。以降の節では、それぞれの化合物に関する合成研究について紹介する。

Figure 3. Lyngbyalosides containing tertiary methyl carbinol at C13



R^1 = H, R^2 = Br;
18*E*–Lyngbyaloside C (**4**) 4)
(Proposed structure)
R^1 = Br, R^2 = H;
18*Z*–Lyngbyaloside C (**5**) 4)
(Proposed structure)

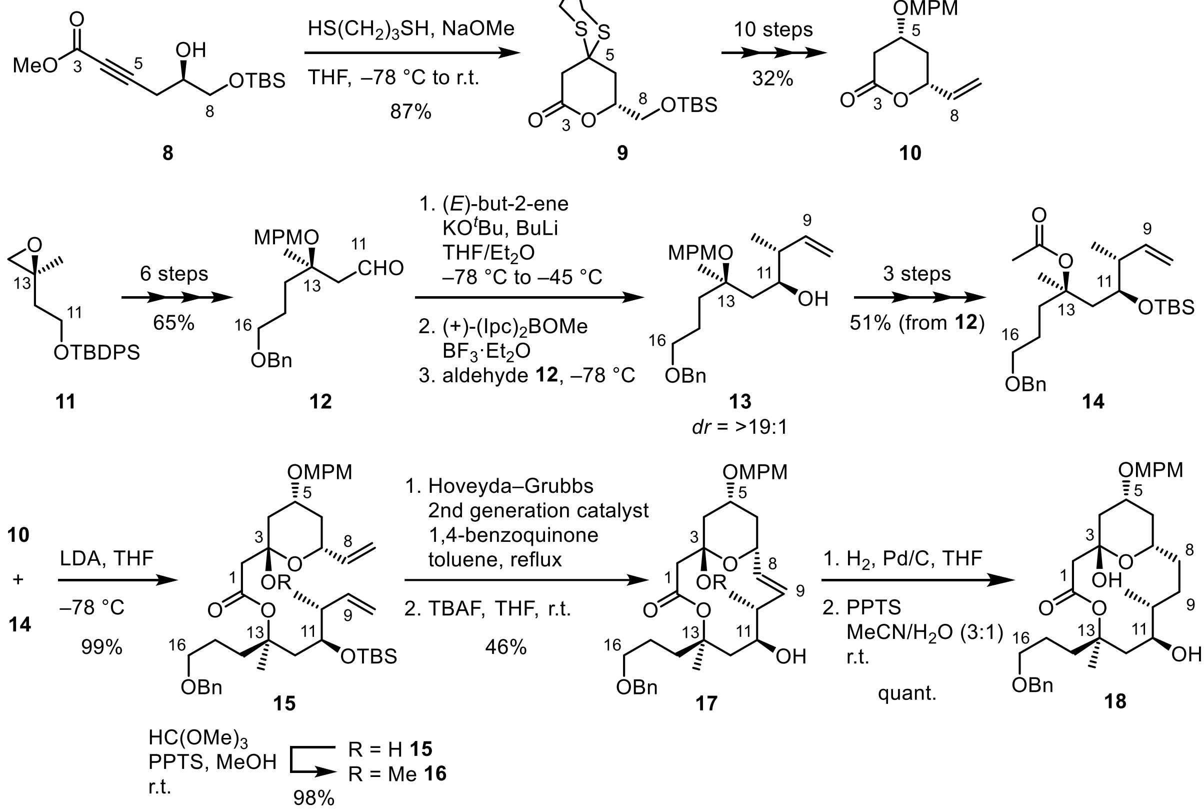
Lyngbyaloside B (**6**) 5)
(Proposed structure)

Lyngbouilloside (**7**) 6)
(Proposed structure)

第2節　リングボウイロシドの合成研究

(1) Ley らによる合成研究(Scheme 1)7)

Ley らは立体的な障害の大きい C13 位の第三級アルコールのマクロラクトン化は非常に困難であると予測し、これを避けるためにマクロサイクルを C2–C3 位および C8–C9 位間で切断することを選択した。エステル **8** に対して 1,3-プロパンジチオールの環化を伴う連続的共役付加によりラクトン骨格を構築することで **9** を得、10 工程の変換を経てラクトン **10** を合成した。また、光学活性なエポキシド **11** から 6 工程の変換を経てアルデヒド **12** としたのちに、不斉補助基を有するクロチルボラン試薬を作用させることにより C10 位と C11 位の立体化学を構築し、3 工程の変換を経てエステル **14** を合成している。合成した **10** と **14** をクライゼン反応によってカップリングし、続く閉環メタセシスによってコア構造であるマクロラクトンの構築を行なっている。Ley らはその後、接触水素化とシリル基の除去によって **18** を得、天然物との ^{1}H NMR および ^{13}C NMR の比較を行なっているが、どちらも一致しないことが明らかとなり、提案されている構造が誤っているのではないかと結論付けている

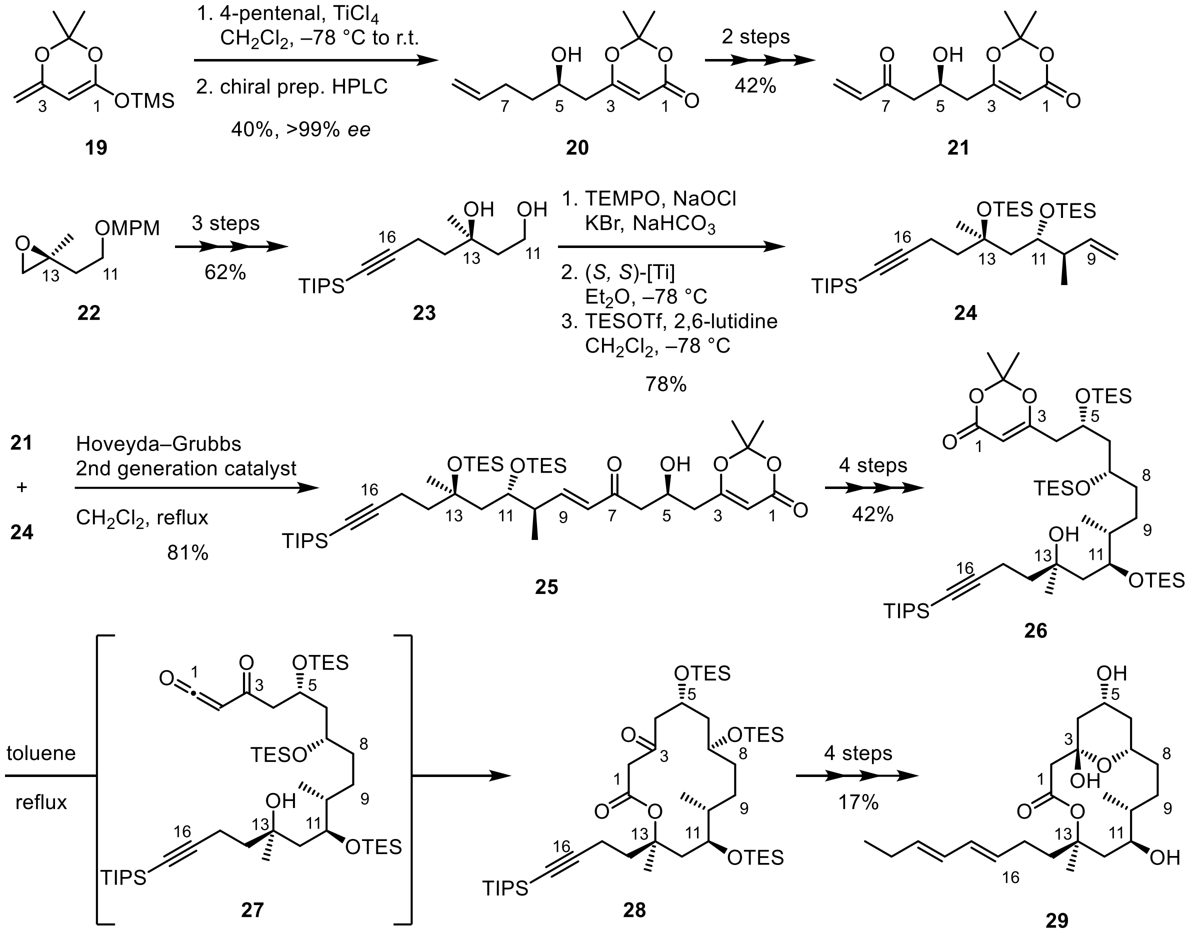


Scheme 1. Synthetic studies of lyngbouilloide by Ley group

(2) Cossy らによる合成研究(Scheme 2)8)

Cossy らは第三級アルコールの一般的なマクロラクトン化は困難であると考え、分子内でアシルケテンを捕捉することによりマクロサイクルを構築し 9)、その前駆体は C1–C8 フラグメントと C9–C13 フラグメントのクロスメタセシスで合成することとした。**19** と 4-ペンテナールとのアルドール反応を行なったのちにキラル HPLC によって望みとするエナンチオマー**20** を単離し、2 工程の変換を経て C1–C8 フラグメント **21** を合成している。続いて、光学活性なエポキシド **22** から 3 工程の変換を経てジオール **23** とした後、TEMPO 酸化に続く不斉クロチ

ルチタン化によってC9–C13フラグメント**24**を調製した。これら2つのフラグメントをクロスメタセシスによってカップリングしたのち、4工程の変換を経てアルコール**26**を調製し、このものをトルエン中加熱することによって生成するアシルケテン**27**を中間体とする環化、続くテトラヒドロピラン環の構築によってアグリコン**29**を合成した。Cossyらも同様に^{1}H NMRおよび^{13}C NMRの合成品と天然物との比較を行なっており、どちらも大きく異なっていることが明らかとなった。また、リングボウイロシドと18*E*-リングビアロシドCの^{13}C NMRに類似性がみられることから、リングボウイロシドの提示された構造は誤りであり、C11位の水酸基の立体化学は18*E*-リングビアロシドCと同様のものではないかと結論づけている*。



Scheme 2. Synthetic studies of lyngbouilloide by Cossy group

(3) Sabithaらによる合成研究(Scheme 3)[10)]

Sabithaらは LeyおよびCossyらの報告をもとに、リングボウイロシドの推定される訂正構造(**30**)の合成研究について報告している。コア構造であるマクトラクトンの構築まで至っていないため詳細な合成スキームは省略するが、逆合成解析をScheme 3に示した。問題となるマクロラクトンはC8–C9位間での結合切断とラクトン部分で結合切断することによって、C1–C8フラグメント**31**およびC9–C16フラグメント**32**の2つのフラグメントに分けて合成することとしている。本文献では両フラグメントの合成まで完了しているが、これらのカップリングについては一切述べられていなかった。

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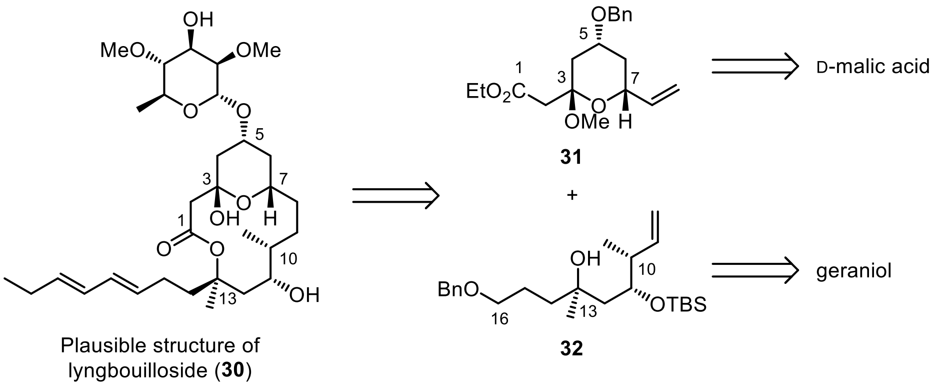
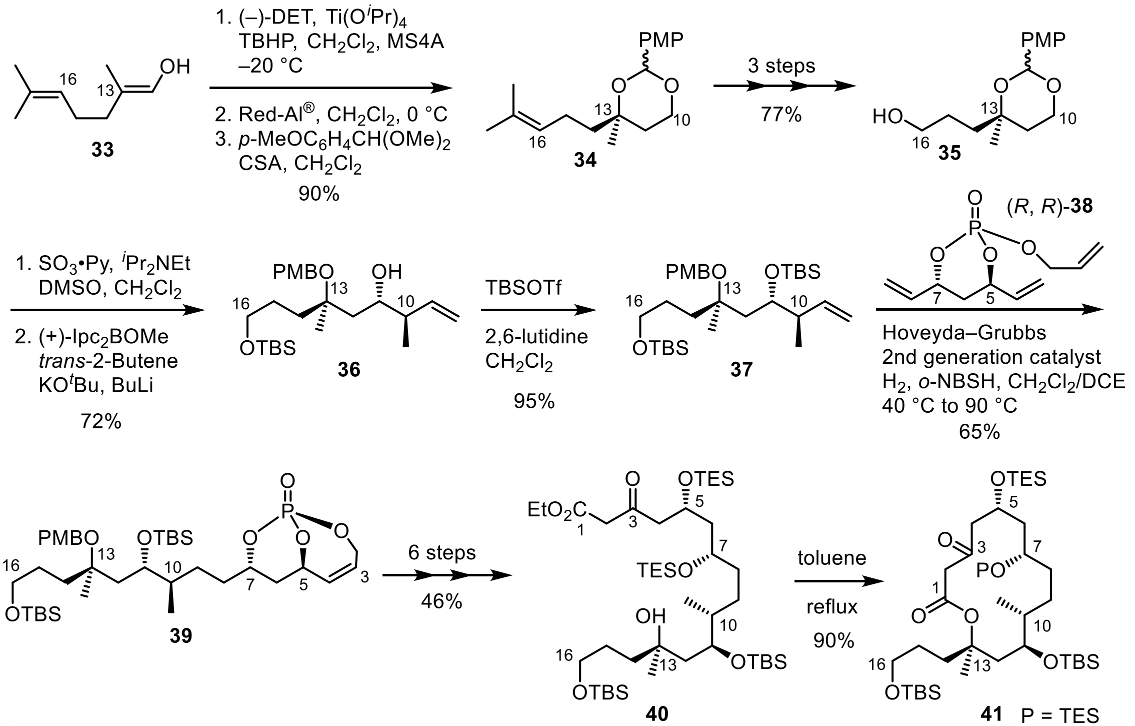
*Leyらは合成したマクロラクトン**18**の化合物データを文献に記載しておらず、Cossyらの合成したアグリコン**29**との比較を行なうことはできなかった。



Scheme 3. Retrosynthetic analysis of revised structure of lyngbouilloside by Sabitha group

(4) Hanson らによる合成研究(Scheme 4)11)

Hanson らは Cossy らと同様アシルケテンを中間体とするマクロラクトン化によってコア構造を構築することを試みている。ゲラニオール **33** に対して Sharpless 不斉エポキシ化を行なった後に、Red-Al®を用いて位置選択的にエポキシドの開環を行ない、ジオールをアセタールとして保護することで **34** を得ている。3 工程の変換によってアルコール **35** とした後に、Parikh–Doering 酸化、続く Brown クロチル化によって **36** へと変換し、第二級水酸基を保護することで C8–C16 フラグメント **37** を調製した。このものに対してトリエン **38** を用いた閉環メタセシス/クロスメタセシス/選択的水素化の連続的な反応を行なうことで **39** へと変換し、6 工程の変換を経て **40** を得ている。その後、トルエン中加熱することによってマクロラクトン **41** を構築している。Hanson らは Ley、Cossy らが述べていた C11 位に関する立体化学の検証については行なっていなかった。

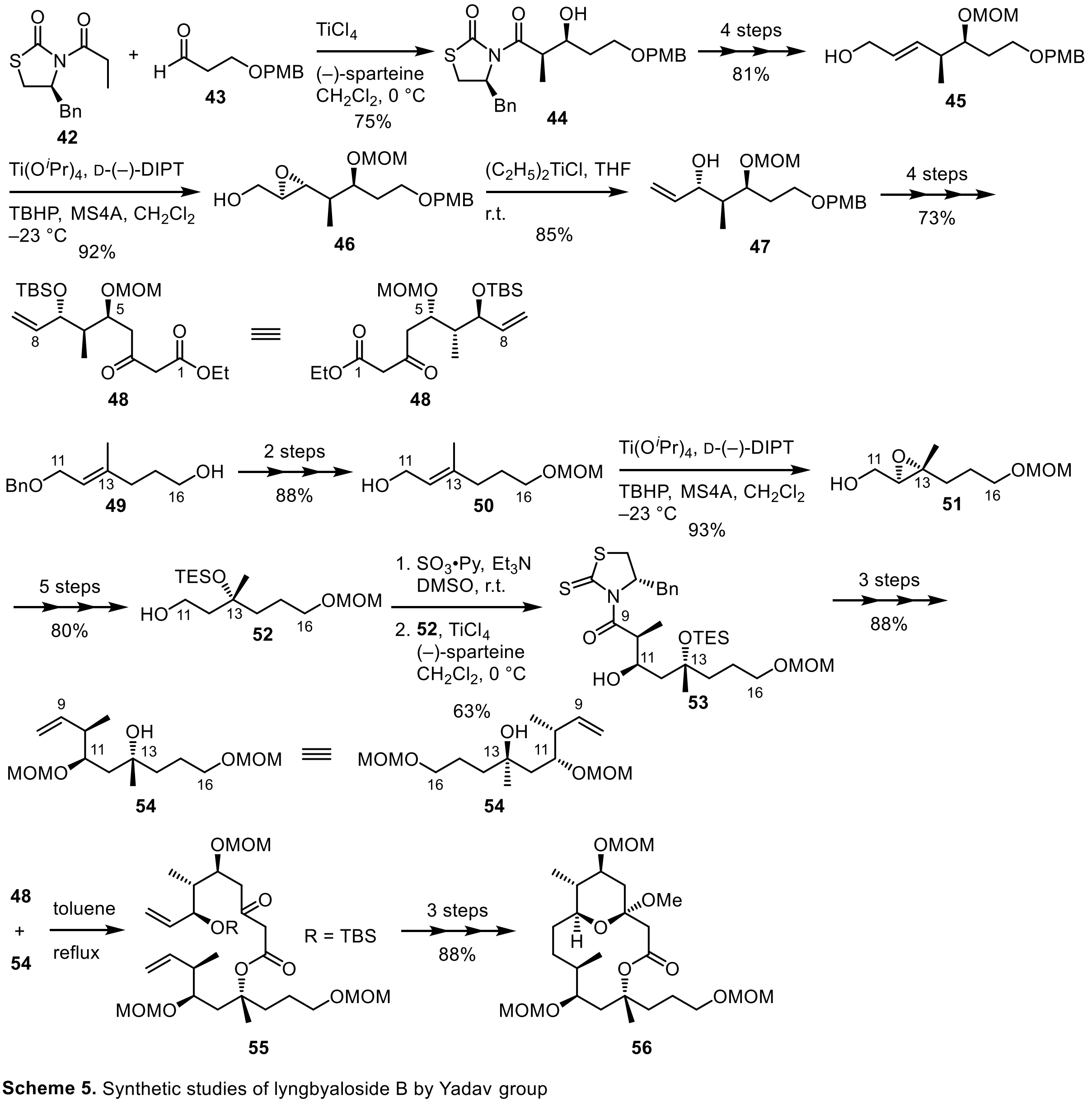


Scheme 4. Synthetic studies of lyngbouilloside by Hanson group

第 3 節　リングビアロシド B の合成研究

(1) Yadav らによる合成研究(Scheme 5)[12)]

Yadav らは Cossy、Hanson らが用いているアシルケテンを捕捉する手法をマクロラクトン化ではなく分子間のエステル化に用いている。アルデヒド **43** に対して Evans アルドール反応を行なって **44** とした後に 4 工程の変換によって **45** とし、香月–Sharpless 不斉エポキシ化を行なって **46** を得ている。位置選択的な脱酸素化を行ない **47** としたのちに 4 工程の変換を経て C1–C8 フラグメント **48** を合成した。また、アルコール **49** を 2 工程の変換で **50** とした後、香月–Sharples 不斉エポキシ化によってエポキシドを導入し、5 工程の変換を経てアルコール **52** を得ている。その後、酸化したのちに Evans アルドール反応を行ない **53** とし、3 工程の変換によって C9–C16 フラグメント **54** を合成した。これら 2 つのフラグメントをトルエン中加熱することによってカップリングし、続く 3 工程の変換によってコア構造であるマクロラクトン **56** を構築している。

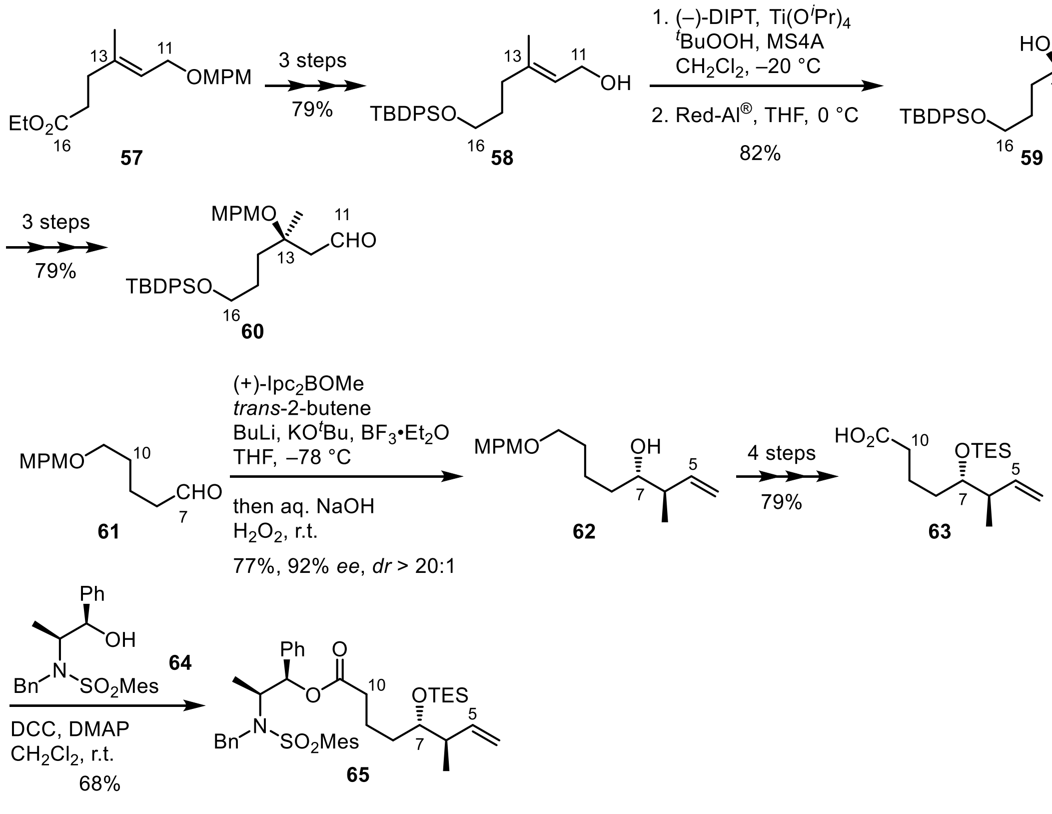


Scheme 5. Synthetic studies of lyngbyaloside B by Yadav group

(2) 不破らによる全合成および構造訂正(Scheme 6–8)13)

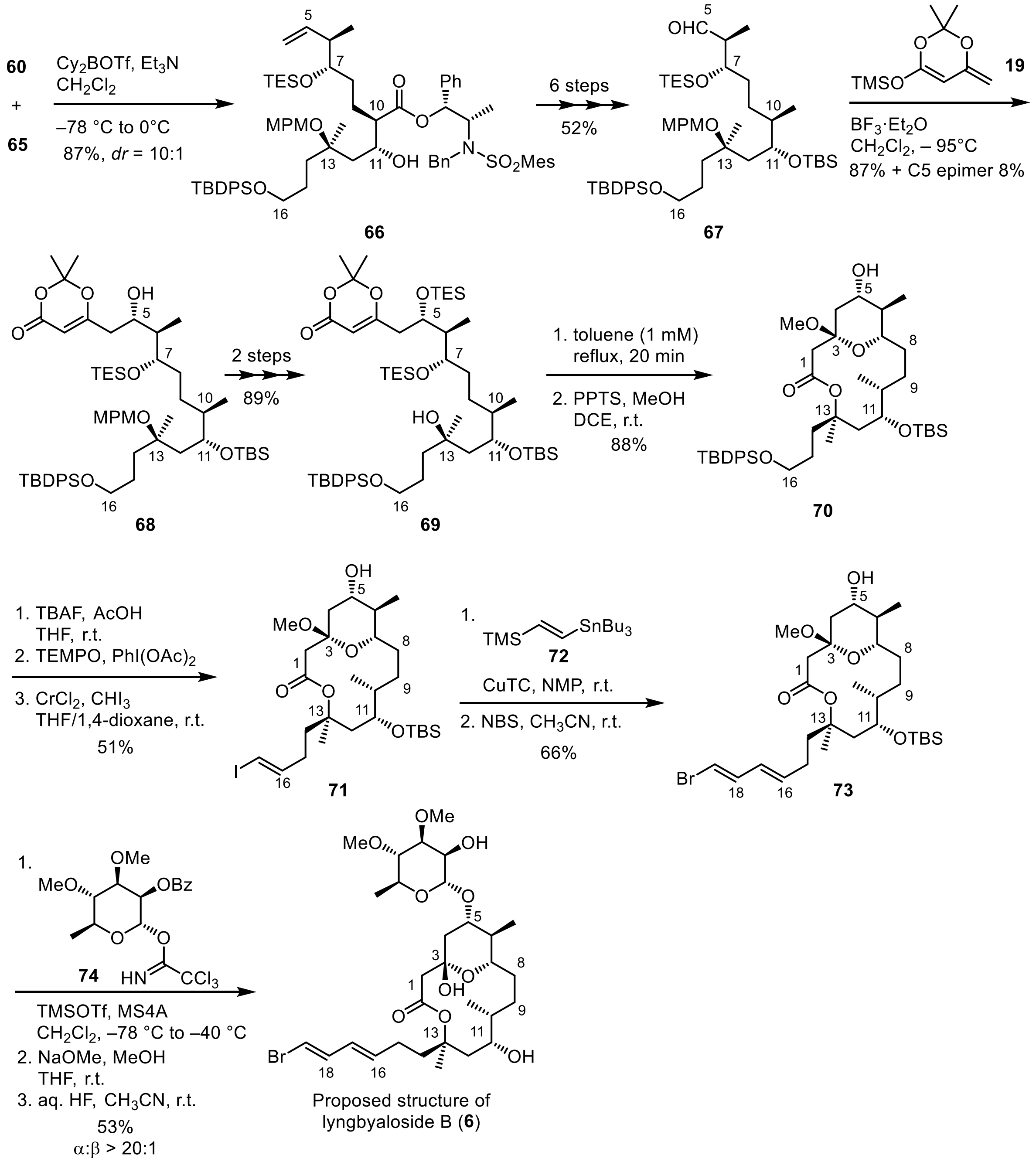
最近、不破らによってリングビアロシド B(**6**)の全合成が達成された。彼らは Cossy らと同様に分子内でアシルケテンを捕捉することによってマクロサイクルの構築を行なうこととし、その前駆体を 3 つのビルディングブロックから合成している。文献既知のエステル **57** から 3 工程の変換によってアルコール **58** としたのち、香月–Sharpless 不斉エポキシ化に続く Red-Al® を用いたエポキシアルコールの位置選択的な開環によって C13 位の立体中心を構築した。その後、3 工程の変換を経て 1 つ目のビルディングブロック **60** を合成した。

続いて文献既知のアルデヒド **61** に対して Brown 不斉クロチル化を行なうことで C6 位および C7 位の立体中心を構築し、続く 4 工程の変換によってカルボン酸 **63** としたのちにアルコール **64** と縮合させることで 2 つ目のビルディングブロック **65** を合成した。



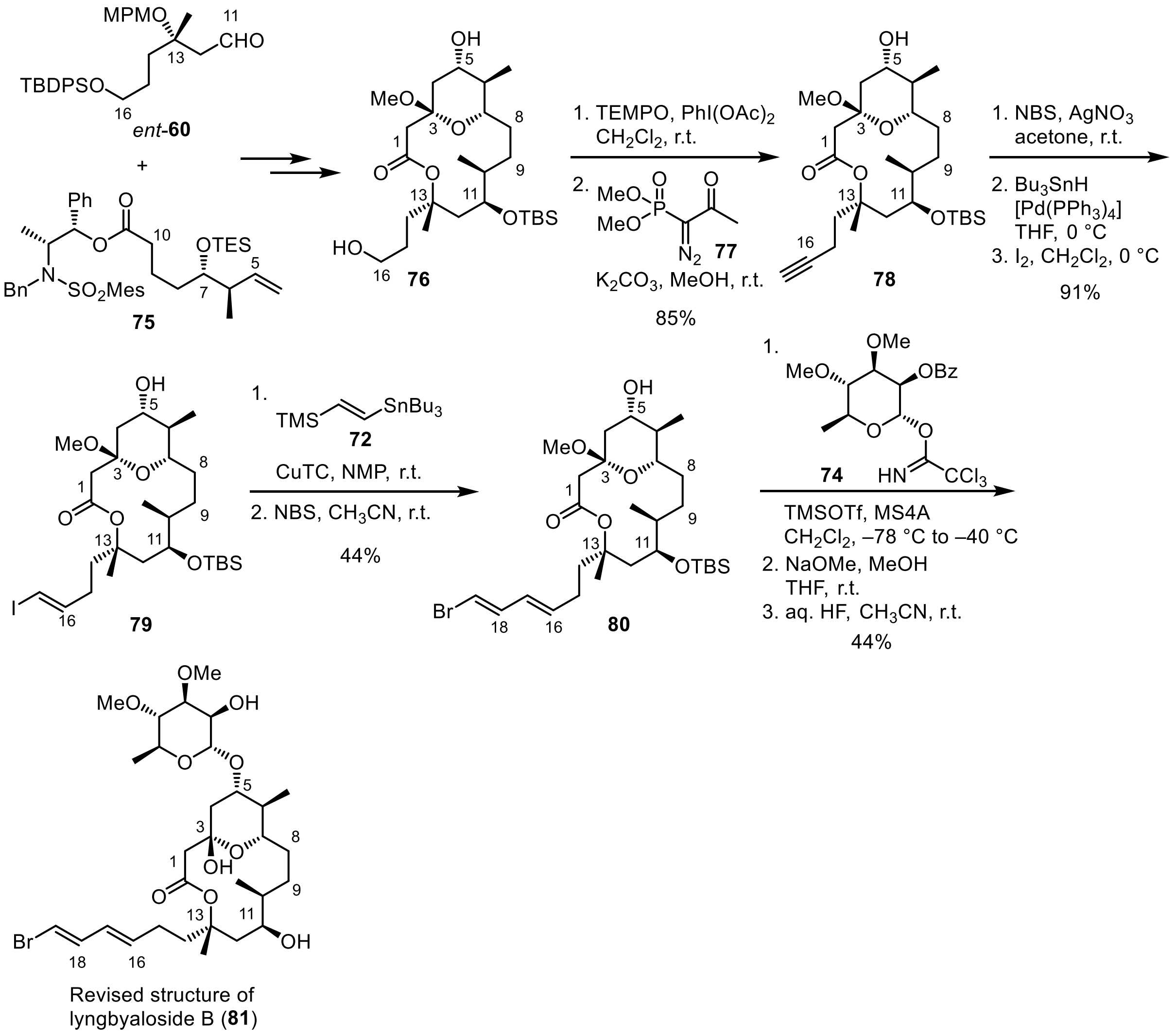
Scheme 6. Total synthesis of proposed structure of lyngbyaloside B by Fuwa group

合成したこれら 2 つのビルディングブロックを安孫子–正宗アンチアルドール反応によって縮合することで C10 位および C11 位の立体中心を含む **66** を合成した。6 工程の変換を経たのちに、3 つ目のビルディングブロックである文献既知のシリルジエノールエーテル **19** とのビニロガス向山アルドール反応によって C5 位の水酸基を立体選択的に導入し、続く 2 工程の変換によって前駆体 **69** を合成した。このものをトルエン中加熱することによってマクロラクトンを形成したのち、酸性条件下テトラヒドロピラン環の構築を行なうことでコア構造 **70** を合成した。その後、第一級水酸基を保護している TBDPS 基を選択的に除去した後に、TEMPO 酸化、続く高井オレフィン化によって **71** へと変換した。このものと **72** との Stille カップリングによってシリルジエン側鎖を構築し、NBS を用いて TMS 基を臭素原子に置換することによってブロモジエン側鎖の導入を完了している。その後、TMSOTf をプロモーターとする **74** を用いた Schmidt グリコシル化によってラムノース誘導体を導入したのちに、すべての保護基を除去することでリングビアロシド B(**6**)の全合成を達成した。



Scheme 7. Total synthesis of proposed structure of lyngbyaloside B by Fuwa group

ところが、合成品と天然物との ^{1}H NMR および ^{13}C NMR を比較したところ、大きな差異が見られることがわかり、考察の結果、彼らは C10 位、C11 位および C13 位の立体化学が誤っているのではないかと結論づけた。そこで新たにビルディングブロック *ent*-**60** および **75** を調製し、同様にアシルケテンを中間体とするマクロラクトン化*によってコア構造 **76** を構築した。先ほどとは異なり、大平–Bestmann 変法によってアルキン **78** としたのちに、ヨウ化ビニル **79** へと変換している。その後、先ほどと同様の変換を経て推定される正しい構造である **81** を合成した。^{1}H NMR および ^{13}C NMR を比較したところ天然物との良い一致が見られ、リングビアロシド B(**6**)の構造が **81** へと訂正される次第となった。



Revised structure of
lyngbyaloside B (**81**)

Scheme 8. Synthesis of revised structure of lyngbyaloside B by Fuwa group

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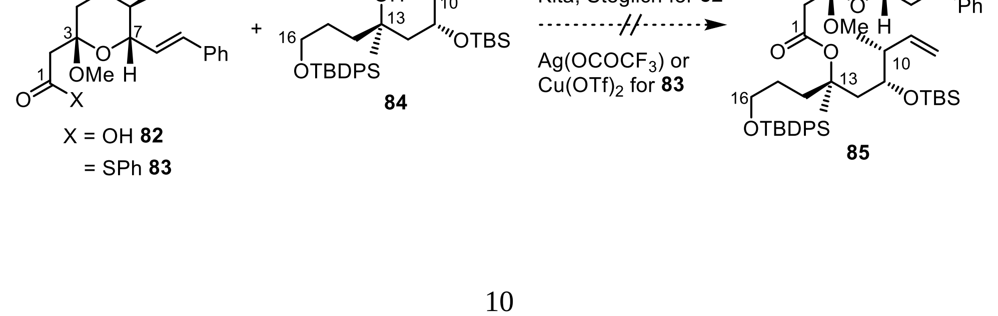
*当初提案されていた構造ではあるが、彼らは先に第三級アルコール由来のエステル結合を先に構築する手法も検討していた。しかし、望みとするエステルを得ることはできていなかった 13c)。

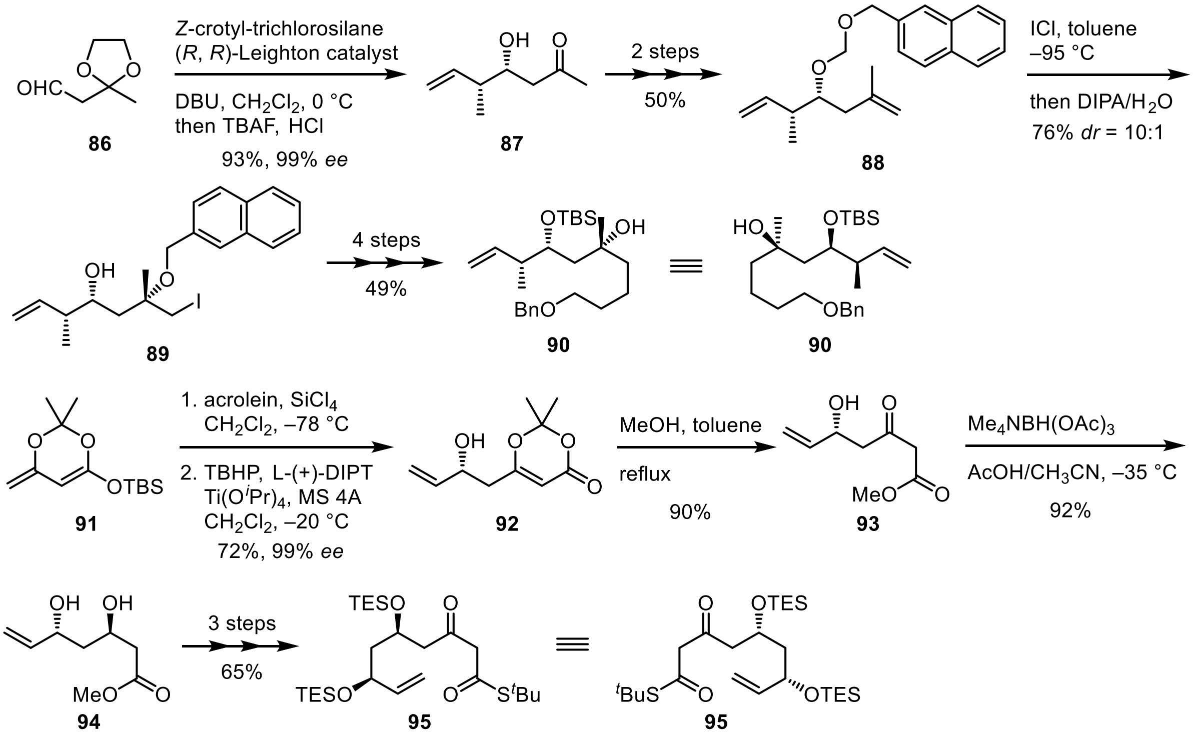


第4節　リングビアロシドCの合成研究

Taylorらによる全合成および構造訂正(Scheme 9–11)[14]

最近、TaylorらによってリングビアロシドCの全合成が達成された。彼らはこれまでの報告とは異なり、チオエステルと銀塩から生成するケテンを利用する手法[15]を選択し、エステル化に続く閉環メタセシスによってコア構造の構築を行なうこととした。既知のアルデヒド**86**に対してLeightonクロチル化を行なうことで2つの立体中心を構築し、2工程の変換を経て**88**を得たのちにナフチルメチルエーテルを転移させることでC13位の立体中心を含む**89**を合成した。このものから4工程の変換を経てアルコール**90**を調製した。

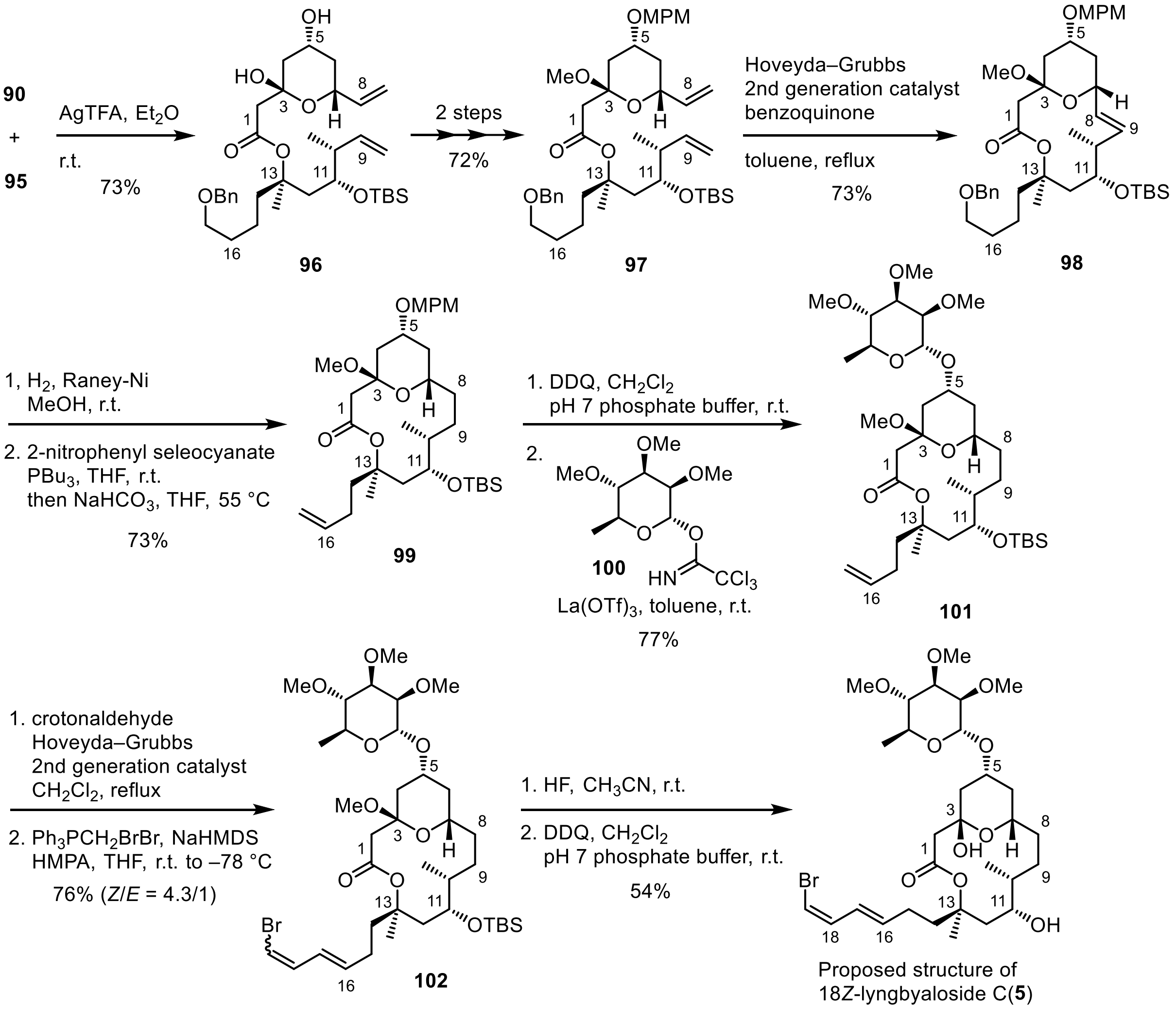
続いて、既知のシリルジエノールエーテル**91**とアクロレインとのビニロガス向山アルドール反応ののちにSharpless速度論的光学分割によってキラルなアリルアルコール**92**を得た。**93**へと変換したのちに$Me_4NBH(OAc)_3$を用いたβ-ヒドロキシケトンの立体選択的な還元によって*anti*-1,3ジオール**94**を得たのちに3工程の変換を経てチオエステル**95**を調製した。



Scheme 9. Total synthesis of proposed structure of 18*Z*-lyngbyaloside C by Taylor group

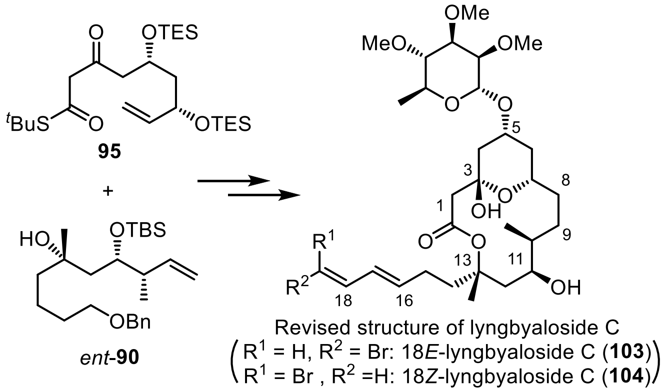
合成した**90**と**95**をカップリングさせ2つの水酸基を保護して**97**としたのちに、閉環メタセシスに続く二重結合の還元と末端オレフィンの構築によってコア構造**99**を合成した。C5位の水酸基の保護基を除去し、**100**を用いたSchmidtグリコシル化によってラムノース誘導体を導入して**101**を得ている。クロトンアルデヒドとのクロスメタセシス反応の後にWittig反応によってブロモジエン側鎖の導入を完了しているが、選択的に導入することができず*E*体と*Z*体の混合物**102**として得ている。すべての保護基の除去し、ブロモジエンの末端をすべて*Z*体に異性化させることよって18*Z*-リングビアロシドC(**5**)の全合成を達成した。

不破らによるリングビアロシドB(**6** and **81**)の全合成からも推測されるように、構造が近似している18*Z*-リングビアロシドC(**5**)に関しても提案されている立体化学が誤っていることが



Scheme 10. Total synthesis of proposed structure of 18*Z*-lyngbyaloside C by Taylor group

予測されており、実際、Taylor らが合成品と天然物との ^{1}H NMR および ^{13}C NMR の比較を行なったところ一致しないことが明らかとなった。リングビアロシド B(**6**)と同様に C10 位、C11 位および C13 位の立体化学が誤っているとの推測のもと、アルコール *ent*-**90** を新たに調製し、先ほどと同じ合成ルートで推定される正しい構造の合成を行なったところ NMR データの良い一致が見られ、リングビアロシド C の構造の訂正に至った*。



Scheme 11. Total synthesis of revised structure of lyngbyaloside C by Taylor group

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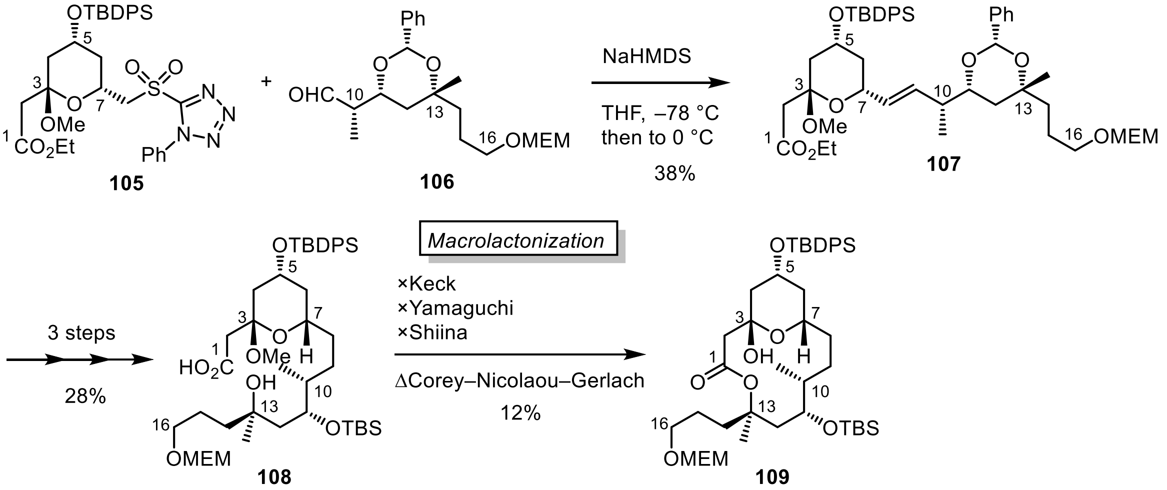
*訂正された構造においては、カラムクロマトグラフィーで C18 位の幾何異性体を分離している。18*E*-リングビアロシド C に関しては NMR の比較を行なっておらず言及はされていないが、単離報告と合成品の NMR を比較するとこちらも同様に誤っていたと考えられる。

第5節　合成計画

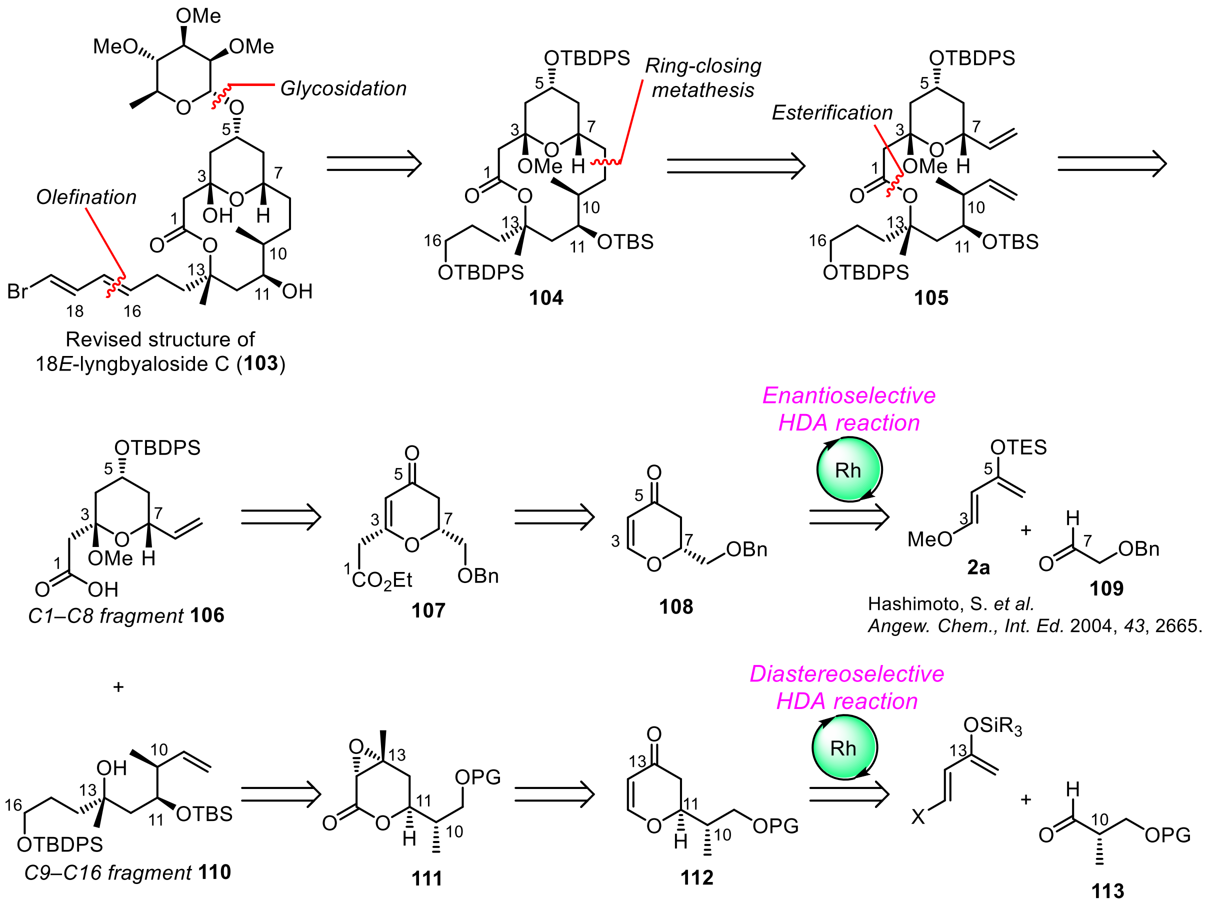
立体化学が訂正される前のものではあるが、これまで所属研究室ではマクロラクトン化によるコア構造の構築を試みていた(Scheme 12)16)。2つのフラグメント**105**および**106**をそれぞれ合成し、これらをJulia–Kocienskiオレフィン化によってカップリングした後に3工程の変換によってセコ酸**108**の合成を完了していた。しかし、続くマクロラクトン化においては、代表的なKeck法、山口法、椎名法では望みとするマクロラクトンが得られなかった。一方で、Corey–Nicolaou–Gerlach法を用いた際にはC3位メトキシ基がヒドロキシル基に変換されたマクロラクトン**109**を得ることができたが、極めて低収率であった。



Scheme 12. Synthetic studies of 18*E*-lyngbyaloside C (proposed structure) in our group

上記の合成ルートにおいて、Julia–Kocienskiオレフィン化によるカップリングは低収率であり、また、マクロラクトン化によるコア構造の構築は困難であったことから、今回著者はこれらの点を踏まえて新たな合成ルートのもと、18*E*-リングビアロシドC(**103**)の合成研究に取り組むこととした。

逆合成解析をScheme 13に示した。ラムノース誘導体およびブロモジエン側鎖の導入は合成の終盤にそれぞれグリコシル化反応、オレフィン化反応によって行なうこととした。コア構造である**105**は、上記の研究結果を踏まえ、先に困難が予想される第三級アルコール由来のエステル結合を形成し、続く閉環メタセシスと接触水素化によってコア構造を構築することとした。鍵反応となるエステル化は2つのフラグメント、C1–C8フラグメント**106**およびC9–C16フラグメント**110**を用いて行なうこととした。それぞれのフラグメントは所属研究室で開発したキラル二核ロジウム(II)触媒を用いた不斉ヘテロDiels–Alder反応3)を機軸として各種変換することによって合成可能であると考えた。



Hashimoto, S. *et al.*
Angew. Chem., Int. Ed. 2004, *43*, 2665.

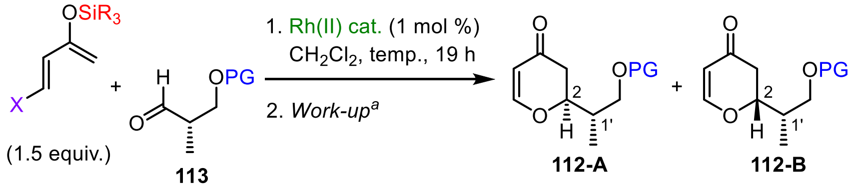
Scheme 13. Retrosynthetic analysis

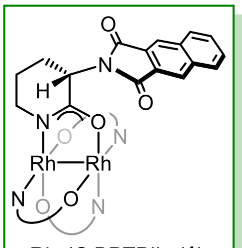
第 2 章　二核ロジウム(II)アミダート錯体触媒を用いるジアステレオ選択的ヘテロ Diels–Alder 反応の開発

第 1 節　2 位置換および 2,3 位置換ジヒドロピラン-4-オンの触媒的不斉合成

C9–C16 フラグメント合成に用いるジアステレオ選択的なヘテロ Diels–Alder 反応に関しては未報告であったため、全合成研究に先立ち本反応について検討を行なった(Table 1)。水酸基を TBS 基で保護した分岐アルデヒド **113a**[17)]に対し、ロジウム(II)触媒存在下、Danishefsky ジエン(**2a**)[3,18)]とのヘテロ Diels–Alder 反応を行なうと、*R* 体のロジウム(II)触媒を用いた際に高いジアステレオ選択性が発現したが(entry 1)、*S* 体の錯体ではジアステレオ選択性がほとんど発現しなかった(entry 2)。また、どちらの場合も収率は低収率にとどまった。そこで、Danishefsky ジエンよりも反応性の高いことで知られる Rawal ジエン(**3a**)[19)]を用いて反応を行なったところ、収率と選択性を大幅に改善することができた(entries 3, 4)。ここで、アルデヒドの水酸基の保護基を TBS 基から MPM 基[20)]に変更したところ、収率と選択性がさらに向上することが明らかとなった(entries 5, 6)*。全合成研究に必要とするジアステレオマーは **112-A**[20d)]であり、それを最も結果よく与えた entry 6 の条件を C9–C16 フラグメント合成に採用することとした。

Table 1. Dirhodium(II) carboxamidate complexes catalyzed diastereoselective hetero-Diels–Alder reactions

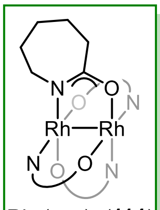




Rh$_2$(*S*-BPTPI)$_4$ (**1**)

entry	X	SiR$_3$		PG		Rh(II) cat.	temp. [°C]	yield^b [%]	dr^c (**112-A**:**112-B**)
1	OMe	TES	**2a**	TBS	**113a**	Rh$_2$(*R*-BPTPI)$_4$	r.t.	17	4:96
2	OMe	TES	**2a**	TBS	**113a**	Rh$_2$(*S*-BPTPI)$_4$	r.t.	15	40:60
3	NMe$_2$	TBS	**3a**	TBS	**113a**	Rh$_2$(*R*-BPTPI)$_4$	–20	81	2:>98
4	NMe$_2$	TBS	**3a**	TBS	**113a**	Rh$_2$(*S*-BPTPI)$_4$	–20	68	92:8
5	NMe$_2$	TBS	**3a**	MPM	**113b**	Rh$_2$(*R*-BPTPI)$_4$	–20	97	2:>98
6	NMe$_2$	TBS	**3a**	MPM	**113b**	Rh$_2$(*S*-BPTPI)$_4$	–20	88	96:4
7	NMe$_2$	TBS	**3a**	MPM	**113b**	Rh$_2$(cap)$_4$	–20	18	43:57

^{a}Entries 1, 2: TFA, r.t., 1.5 h; Entries 3–6: DMAD, 0 °C, 1.5 h then AcCl, –78 °C, 1.5 h.
^{b}Isolated combined yield. ^{c}Determined by ^{1}H NMR analysis.



Rh$_2$(cap)$_4$ (**114**)

また、ジアステレオ選択的な反応を他の基質でも行なうことが可能か調査を行なった。乳酸由来のアルデヒド **115** との反応を行なうと、良好な収率かつ高いジアステレオ選択性でジヒドロピラノン **116** を得ることができた(eq. 3)。また、メチル基が置換した Rawal ジエン(**3b**)[3c)]を用いたアルデヒド **113b** とのヘテロ Diels–Alder 反応においては、完璧な *endo* 選択性かつ高

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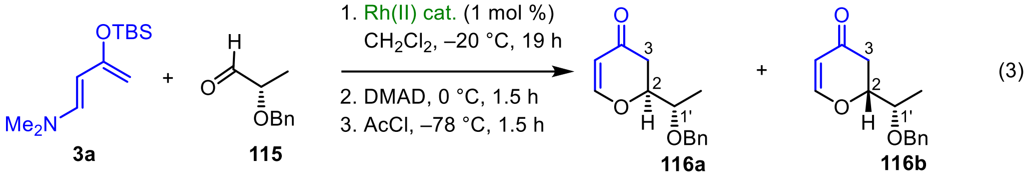
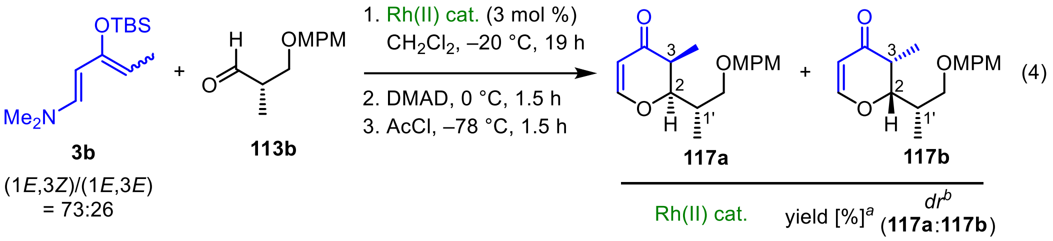
*Rh$_2$(*S*-BPTPI)$_4$(**1**)とアルデヒド **113** の複合体を分子模型で作成したところ､TBS 基と MPM 基では MPM 基の方が自由回転を促すメチレン鎖が存在するためロジウム触媒に含まれるベンゾフタルイミド基との立体反発をより小さくすることができると考えられた。その結果、ロジウム(II)触媒へ配位しやすくなり、収率と選択性が向上したと考えられる。

いジアステレオ選択性でジヒドロピラノン **117** を得ることができ、連続する 3 つの立体中心を一挙に構築することに成功した(eq. 4)。また、アザジエン **118**21)と乳酸由来のアルデヒド **115** との反応では、収率は中程度にとどまるものの良好な選択性でシス配置の含窒素ヘテロ環 **119** の構築に成功した(eq. 5)。



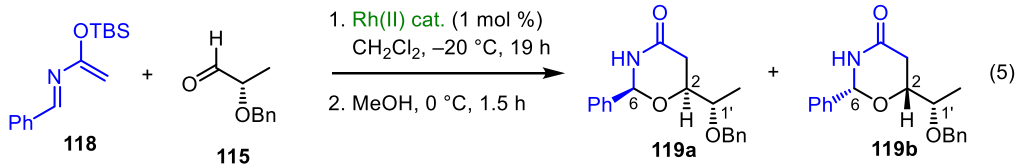
Rh(II) cat.	yield [%]^a	dr^b (**116a**:**116b**)
Rh_2(*R*-BPTPI)$_4$	76	11:89
Rh_2(*S*-BPTPI)$_4$	80	97:3

^{a}Isolated yield. ^{b}Determined by ^{1}H NMR analysis.



Rh(II) cat.	yield [%]^a	dr^b (**117a**:**117b**)
Rh_2(*R*-BPTPI)$_4$	92	5:95
Rh_2(*S*-BPTPI)$_4$	74	90:10

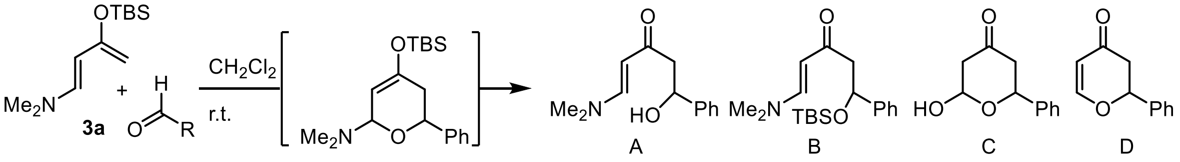
^{a}Isolated yield. ^{b}Determined by ^{1}H NMR analysis.



Rh(II) cat.	yield [%]^a	dr^b (**119a**:**119b**)
Rh_2(*R*-BPTPI)$_4$	50	25:75
Rh_2(*S*-BPTPI)$_4$	63	98:2

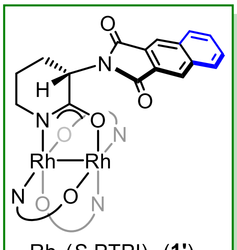
^{a}Isolated yield. ^{b}Determined by ^{1}H NMR analysis.

**Rawal ジエンを用いたヘテロ Diels–Alder 反応の後処理ではアセチルクロライドを用いることによって望みとするジヒドロピラノンが得られることが明らかとなっている 19a)。



entry	hydrolysis conditions	time, h	A	B	C	D
1	silica gel or alumina		78%			
2	TFA-THF	24		72%		
3	HF-CH_3CN	20			42%	17%
4	AcCl, –78 °C	0.5				86%

第 2 節 立体反応経路の考察

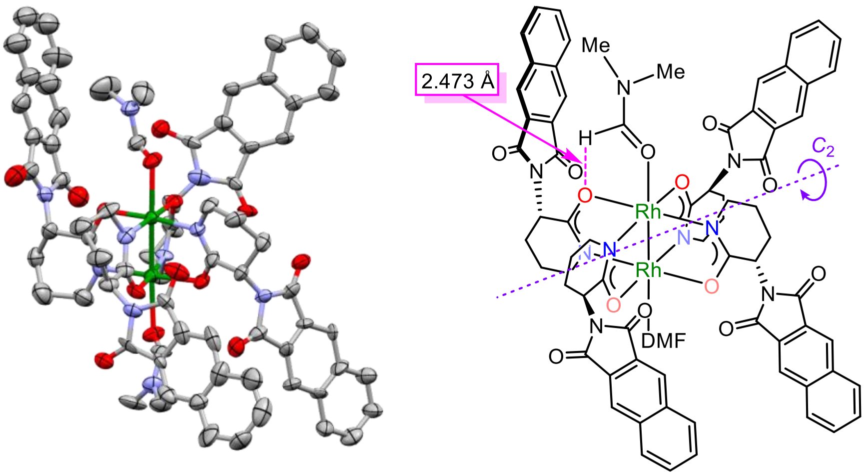


Rh_2(*S*-PTPI)$_4$ (**1'**)
Rh_2(*S*-BPTPI)$_4$ (**1**)

これまで Rh_2(*S*-BPTPI)$_4$(**1**)の構造は、^{1}H NMR 解析の結果と類似の配位子である *S*-PTPI 配位子を有した Rh_2(*S*-PTPI)$_4$(**1'**)の X 線結晶構造解析の結果から推察しており*、その結晶構造は明らかとなっていなかった。今回著者は、アルデヒドのモデルとして DMF が付加した Rh_2(*S*-BPTPI)$_4$ の X 線結晶構造解析に成功した(Figure 4)。

各ロジウム原子に対して、アミダート配位子の 2 つの酸素原子および窒素原子がそれぞれ *cis* で配位しており、4 つのベンゾフタルイミド基は”down-down-up-up”の配列で各ロジウム原子のアキシアル方向に大きく張り出した C_2 対称型構造をとっていることが明らかとなった。また、DMF のホルミル水素原子とアミダート配位子の酸素原子間の距離が、それらの Van der Waals 半径の和(2.72 Å)よりも短くなっていることから水素結合の存在が示唆され、本錯体においても Corey らの提唱しているホルミル C–H···O 水素結合コンセプト [22]が適用可能であると考えられる。

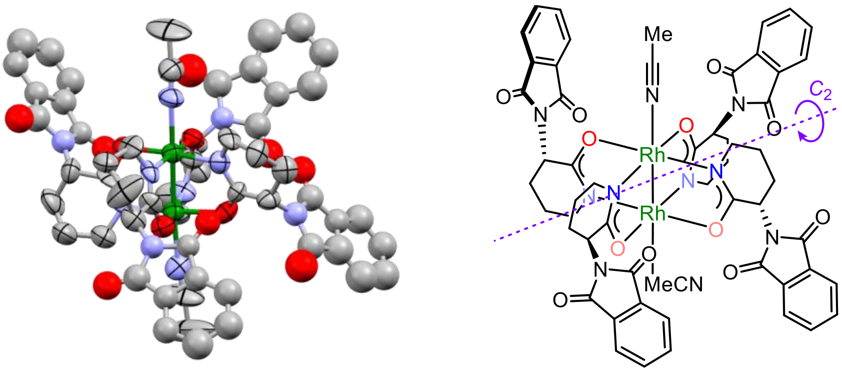
Figure 4. Left: thermal-elipsoid representation of bis(dimethylformamide) adduct of Rh_2(*S*-BPTPI)$_4$ (**1**), (50% probability elipsoids). Right: chemical structure of Rh_2(*S*-BPTPI)$_4$·2DMF. Two molecules, hydrogen atoms, and free solvents were omitted for clarity.



Rh_2(*S*-BPTPI)$_4$·2DMF

---

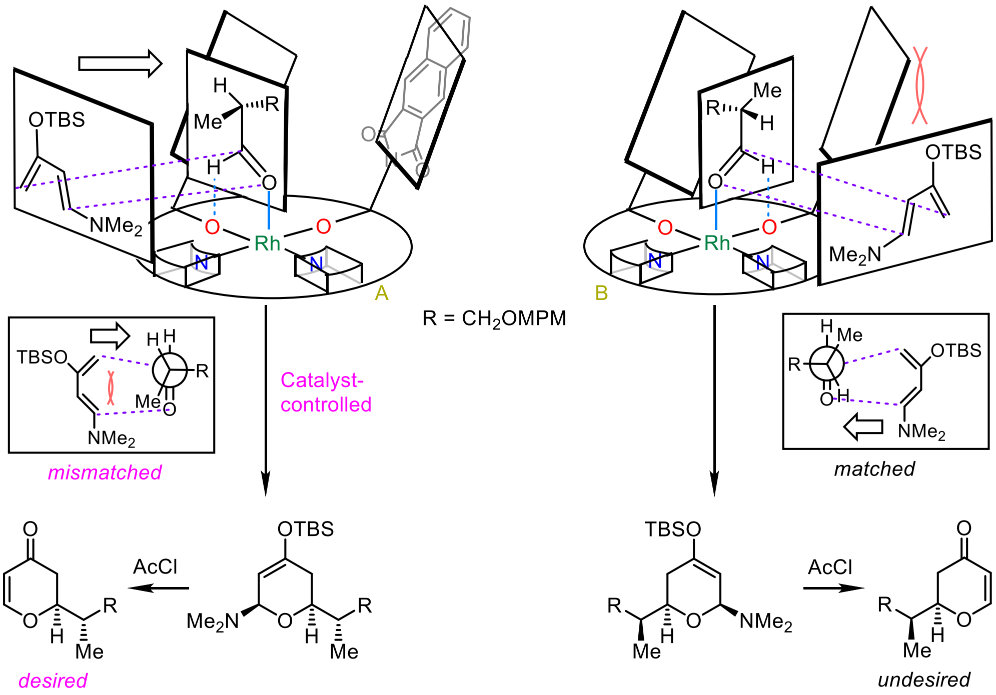
*Rh_2(*S*-PTPI)$_4$·2MeCN の X 線結晶構造を下図に示す [3a)]。本錯体はアミダート配位子がそれぞれ *cis* に配位した C_2 対称型の構造を有している。加えて、Rh_2(*S*-BPTPI)$_4$ の ^{1}H NMR 測定では非等価な二組の配位子のスペクトルが観測されており、これらの結果から Rh_2(*S*-BPTPI)$_4$ も同様に配位子が *cis* に配置していると推定していた。



Rh_2(*S*-PTPI)$_4$·2MeCN

以上の結果をもとに、ヘテロ Diels–Alder 反応の立体反応経路を以下のように考察した (Figure 5)。アルデヒドの酸素原子がロジウム原子のアキシアル位に配位し、ホルミル水素原子がアミダート配位子の酸素原子と水素結合した中間体 A または B の中間体が想定される。中間体 B ではアルデヒドの置換基と 2 つのベンゾフタルイミド基との間に立体反発を生じ、中間体 A では B よりも空いた位置に置換基が収まるため、中間体 A が優先的に生成すると考えられる。さらに、中間体 B に対するジエンの接近は、張り出したベンゾフタルイミド基との立体反発から不利となる。したがって、中間体 A に対し、ロジウム(II)錯体との立体反発を避けるようにシロキシ基を外側に向けてジエンが接近すれば、実験結果に合致する優先絶対配置をもつ *endo* 付加体が得られることになる。

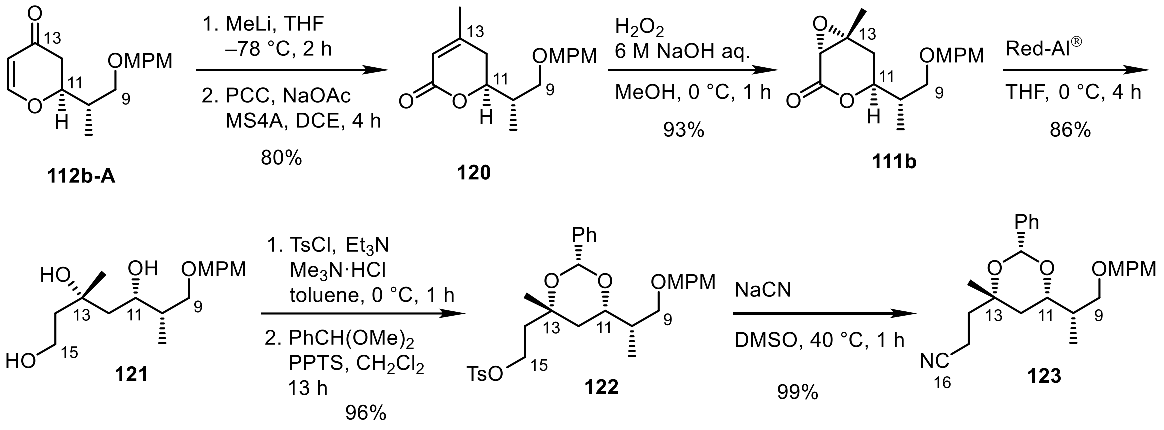
Figure 5. Plausible stereochemical cource of diastereoselective hetero-Diels–Alder reaction catalyzed by Rh_2(*S*-BPTPI)$_4$



第 3 章　コア構造フラグメントの合成

第 1 節　C9–C16 フラグメントの全合成

第 2 章第 1 節において最適条件下得られたジヒドロピラノン **112b-A** の C13 位にメチル基を導入したのち、酸化的転位反応によって α,β-不飽和ラクトン **120** へと変換した(Scheme 14)。立体選択的にエポキシドを導入したのちに、還元的開環反応23)によってトリオール **121** へと導いた。第一級水酸基をトシラートへ変換したのちに24)、残る二つの水酸基をベンジリデンアセタールとして保護して **122** を得た*。その後 NaCN を用いて増炭反応を行ない、ニトリル **123** へと変換した。



Scheme 14. Synthesis of nitrile **123**

123 の第一級水酸基を保護している MPM 基を DDQ20c)を用いて除去したのちに、Dess–Martin 酸化によってアルデヒド **126** へと変換した(Scheme 15)。その後、LiHMDS と $Ph_3P^+MeBr^-$ を用いた Wittig 反応**によって末端アルケン **127** を調製した。

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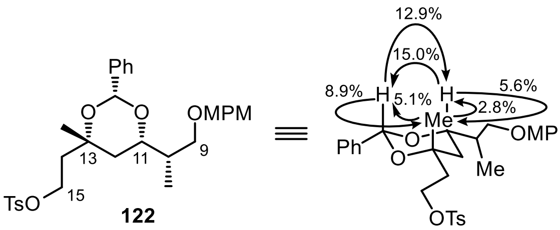
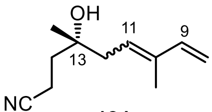
*エポキシド **111b** の C13 位メチル基および C14 位水素原子を標的とした NOE 相関を観測することは困難であった。そこでアセタール **122** での NOE 測定を行ない、C11 位水素原子とベンジリデンアセタール部の水素原子間、C11 位水素原子と C13 メチル基間、C13 位メチル基とベンジリデンアセタール部の水素原子間で NOE 相関が観測されたことから、アセタール **122** およびエポキシド **111b** の相対立体配置を上記のように決定した。

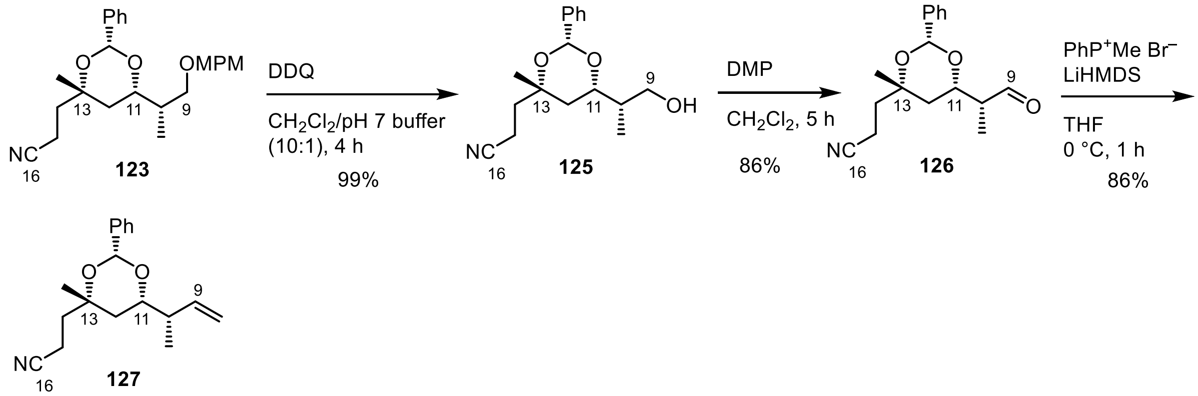


また第一級水酸基をトシラートへ変換したジオールは不安定であったため、単離することなくジオールをアセタールとして保護した。

NaHMDS や KHMDS を塩基として用いた場合には、アルデヒドの β 位酸素原子が脱離したジエン **124 が副生成物として得られ、望みとするアルケン **127** の収率は 50%程度にとどまった。

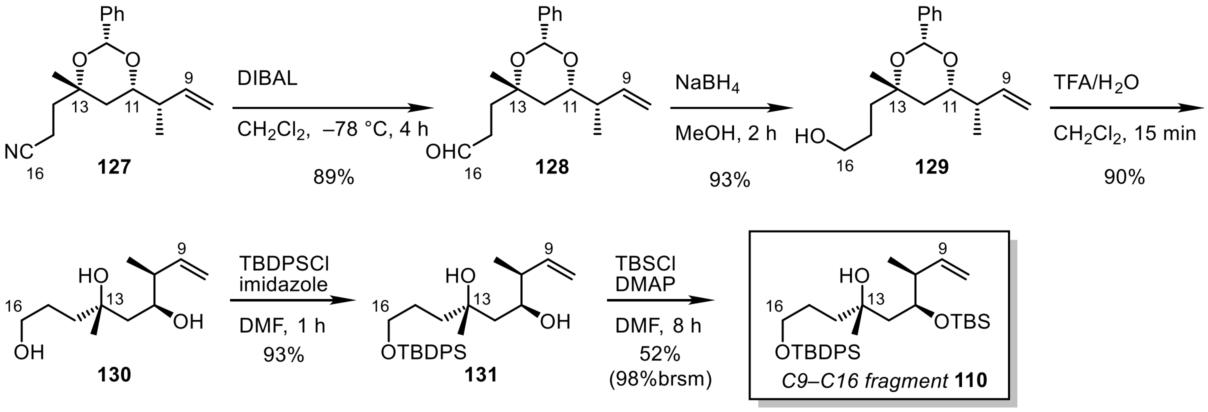


124



Scheme 15. Synthesis of alkene **127**

アルケン **127** のシアノ基を段階的に還元することによってアルコール **129** へと変換したのちに、ベンジリデンアセタールの除去を行ないトリオール **130** へと導いた(Scheme 16)。その後、第一級水酸基を TBDPS 基で、第二級水酸基を TBS 基で保護することで*C9–C16 フラグメント **110** の合成を完了した。



Scheme 16. Synthesis of C9–C16 fragment **110**

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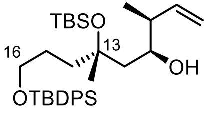
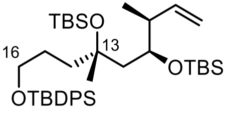
*第二級水酸基を TBS 基で選択的に保護することは困難を要し、過剰量の TBSCl および DMAP を用いている。この時、第三級アルコールへシリル基が転移した化合物 **132** やこのものに対してさらに TBS 保護が起こった **133** が時間とともに得られてしまうため反応を完結させずに原料回収することで望みとする C9–C16 フラグメント **110** のみを得ている。



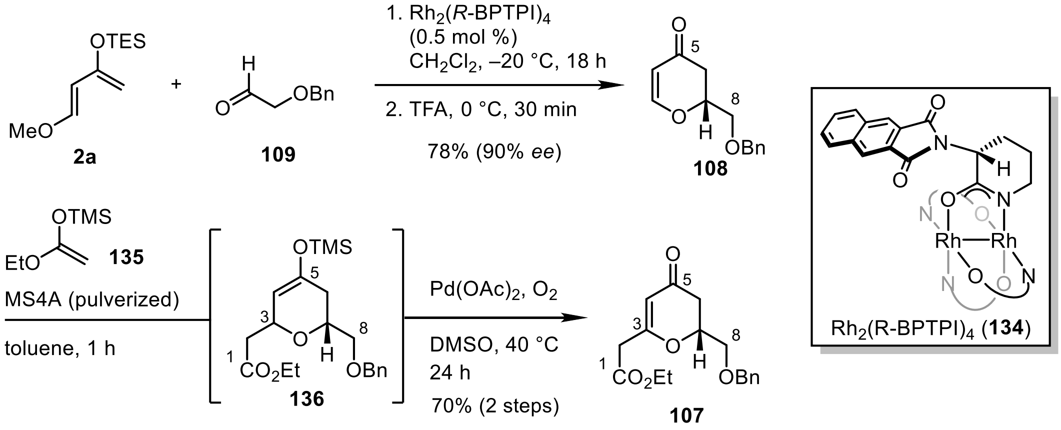
132



133

第 2 節　C1–C8 フラグメントの合成

Danishefsky ジエン(**2a**)と文献既知のアルデヒド **109**[25]との Rh_2(*R*-BPTPI)$_4$(**134**)を用いたヘテロ Diels–Alder 反応[3a]によって望みとするジヒドロピラノン **108** を収率 78%、90% *ee* で得た*。MS4A を用いたシリルケテンアセタール **135** との向山–Michael 反応[26]によってシリルエノールエーテル **136** としたのちに、このものを精製することなく伊藤–三枝酸化[27]を行なうことによって C1–C8 フラグメントのすべての炭素骨格を含む **107** へと変換した(Scheme 17)。



Scheme 17. Synthesis of dihydropyranone **107**

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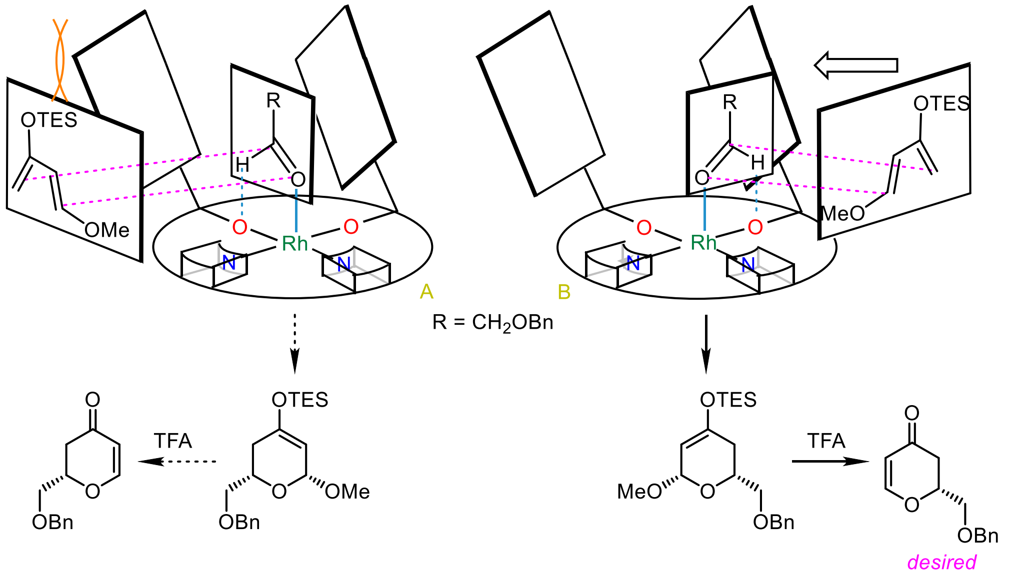
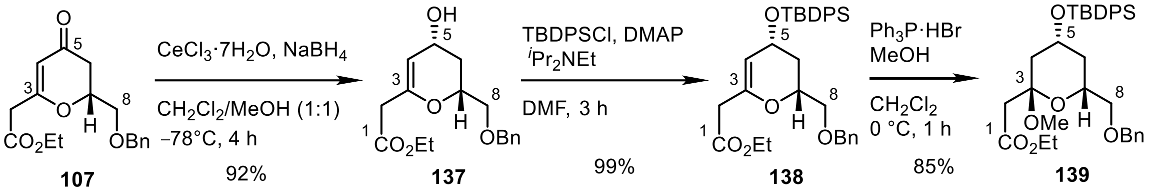
*Rh_2(*S*-BPTPI)$_4$ の X 線結晶構造解析の結果より、*R* 体のロジウム(II)触媒を用いた本反応の立体反応経路も第 2 章第 2 節と同様に議論することができる。アルデヒドのカルボニル酸素原子がロジウム原子のアキシアル位に配位し、ホルミル水素原子がアミダート配位子の酸素原子と水素結合した中間体 A または B を想定することができる。アルデヒドの置換基と 2 つのベンゾフタルイミド基との立体反発から中間体 B の方が A よりも有利になると考えられる。また、中間体 A に対するジエンの接近は張り出したベンゾフタルイミド基との立体反発から不利となる。したがって、中間体 B を経て反応が進行することで実験結果に合致する優先絶対配置をもつ *endo* 付加体が得られたと推定される。

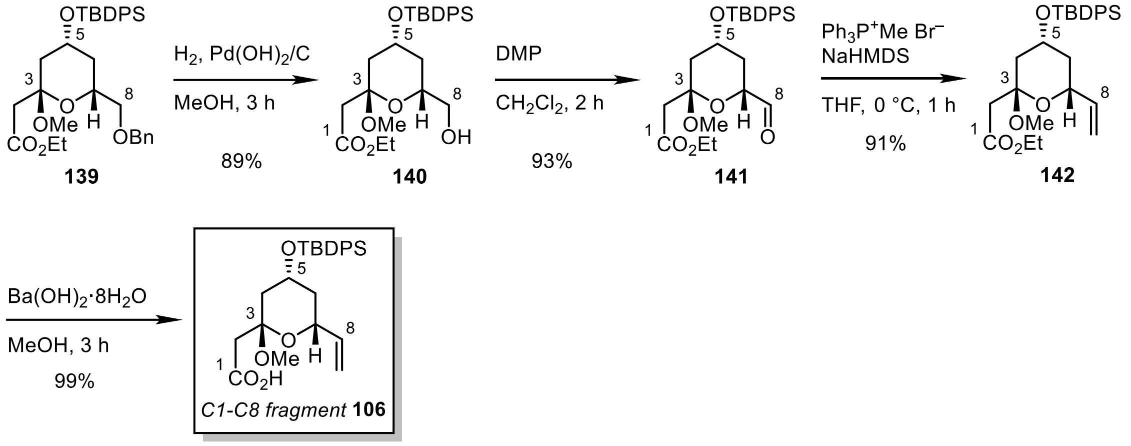


Luche 還元の条件下ケトンの立体選択的な還元を行ないアルコール **137** としたのちに*、生じた水酸基を TBDPS 基で保護し、PPh_3·HBr を酸触媒として28)メトキシ基を立体選択的に導入して **139** を得た**(Scheme 18)。



Scheme 18. Synthesis of tetrahydropyran **139**

ベンジル基の除去を行ないアルコール **140** としたのちに、生じた水酸基を Dess–Martin 酸化に続く Wittig 反応によってビニル基へと変換した(Scheme 19)。その後、エステルの加水分解を行ない C1–C8 フラグメント **106** の合成を完了した。



Scheme 19. Synthesis of C1–C8 fragment **106**

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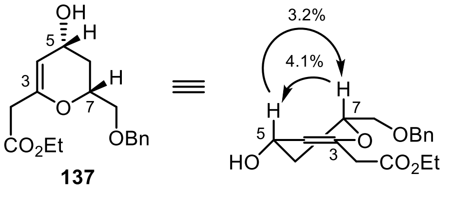
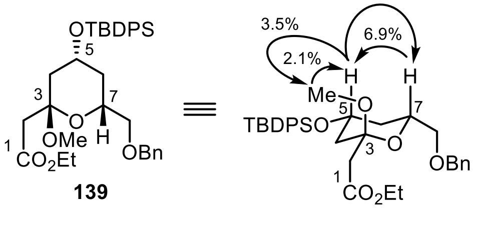
*アルコール **137** の相対立体配置は、C5 位水素原子と C7 位水素原子の間で NOE 相関が観測されたことにより決定した。



テトラヒドロピラン **139 の相対立体配置は、C3 位メトキシ基と C5 位水素原子間および C5 位水素原子と C7 位水素原子間で NOE 相関が観測されたことにより決定した。

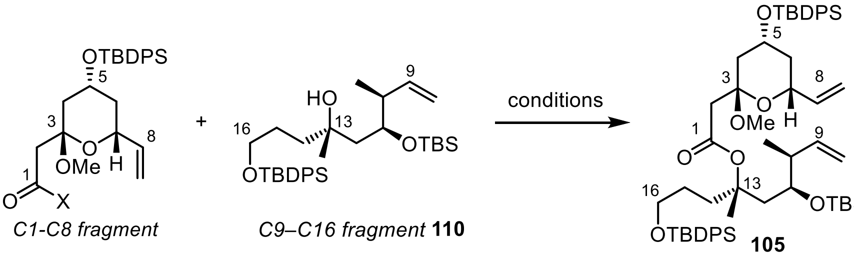


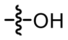
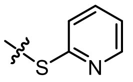
第4章 18*E*-リングビアロシドCの全合成

第1節 マクロラクトンコア構造の構築と変換

まず、C1–C8 フラグメント **106** と C9–C16 フラグメント **110** とのカップリング反応を検討した(Table 2)。Steglich エステル化29) (entry 1)や EDCI30) (entry 2)を用いた反応では望みとするエステル **105** は低収率に留まった。DMAP 塩酸塩を添加する Keck 法31) (entry 3)および改良 Keck 法32) (entry 4)を用いてエステル化を行なったが収率は改善されなかった。また、山口法33) (entry 5)および椎名法34) (entry 6)を用いた場合にもエステル **105** を得ることができたが、その収率は満足のいくものではなかった*。

Table 2. Esterification between carboxylic acid **106** or thioester **143** and alcohol **110**



entry	X	conditions	yield (%)
1	 **106**	DCC, DMAP, CH_2Cl_2, r.t., 1 h	12
2		EDCI, DMAP, CH_2Cl_2, r.t., 1 h	7
3		DCC, DMAP, DMAP•HCl, CH_2Cl_2, r.t., 1 h	trace
4		EDCI, DMAP, DMAP•HCl, CH_2Cl_2, r.t., 1 h	trace
5		2,4,6-trichlorobenzoyl chloride Et_3N, toluene, r.t., 0.5 h then DMAP, r.t., 1 h	8
6		2-methyl-6-nitrobenzoic anhydride DMAP, Et_3N, CH_2Cl_2, r.t., 1 h	2
7	 **143**	AgOTf, 2,6-*di*-*tert*-butyl-4-methylpyridine toluene, r.t., 1 h	77

一方で、Corey35a,35b)、Gerlach の論文35c)を参考にチオエステル **143****を用いてカップリング反応を行なったところ、良好な収率でエステル **105** を得ることに成功した(entry 7)。また、本反応では未反応のアルコール **110** および活性化されたチオエステル **143** が系中に微量に存在

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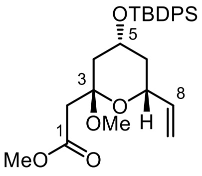
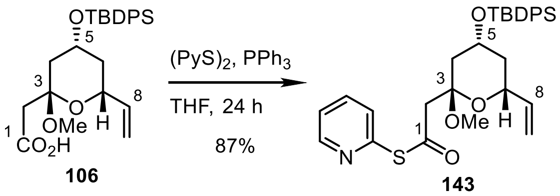
*満足のいく結果が得られなかったエステル化について、副生成物としておもにカルボン酸 **106** がメチルエステルとなった **144** が確認されたことから、これらの条件下ではカルボン酸 **106** が不安定であることが示唆された。



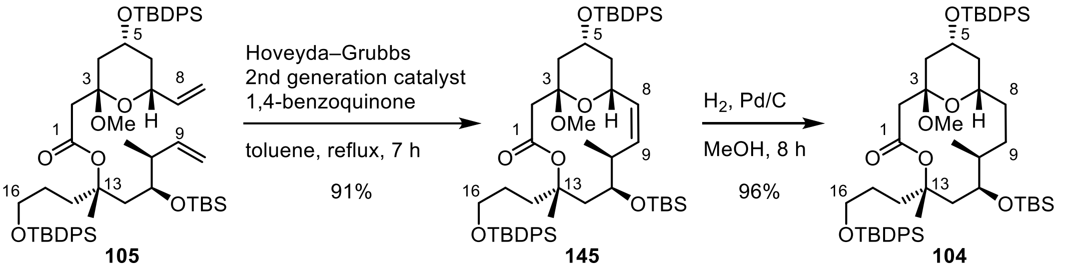
144

チオエステル **143 は向山らの報告を参考に調製した36)。



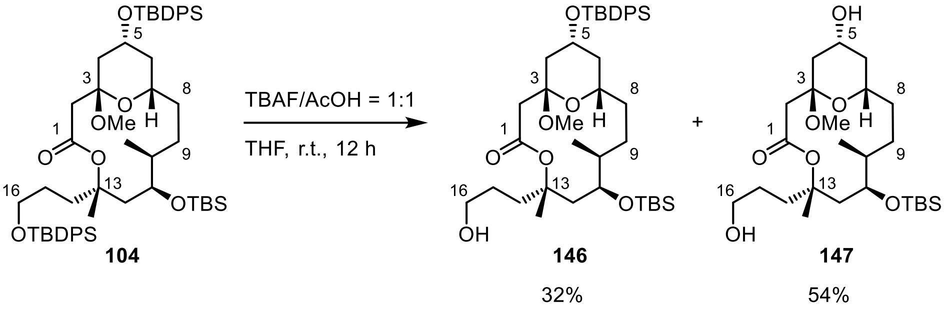
する水と反応したことで生成するカルボン酸**106**を回収することが可能であった。

エステル**105**に対して第2世代Hoveyda–Grubbs触媒を用いた閉環メタセシスを行なった後に、続く接触水素化によってコア構造であるマクロラクトン **104** の構築を完了した(Scheme 20)。



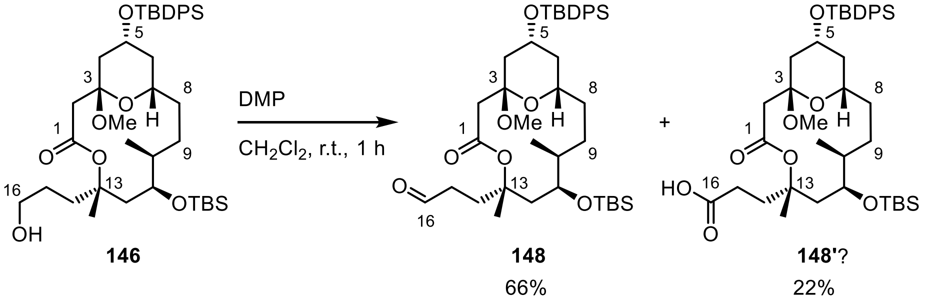
Scheme 20. Synthesis of core structure **104**

まず先にブロモジエン側鎖を導入する合成ルートを検討することとした。得られたラクトン**104**に対し、C16位の水酸基を保護しているTBDPS基の選択的除去を試みたが[37)]、アルコール**146**のみならずC5位の水酸基を保護しているTBDPS基も除去されたジオール**147**が同時に得られた(Scheme 21)。本反応において用いたTBAFの当量数は1.2当量であり、使用した物質量に対して過剰にアルコール**146**およびジオール**147**が生成してしまっていることがわかった。



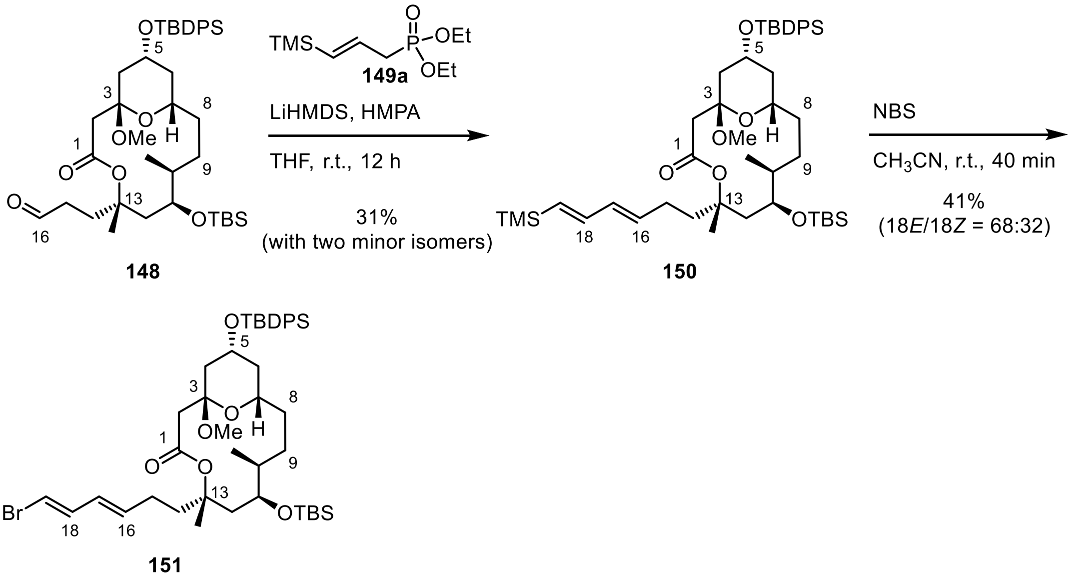
Scheme 21. Selective removal of 1°-TBDPS protecting group

十分な選択性が得られていないが、今後の変換が可能かどうか調査するため合成を進めることとした。アルコール**146**に対してDess–Martin酸化を行なったところ、望みとするアルデヒド**148**は中程度の収率にとどまり、過剰に酸化されたカルボン酸**148'**と思われる化合物が副生した(Scheme 22)。



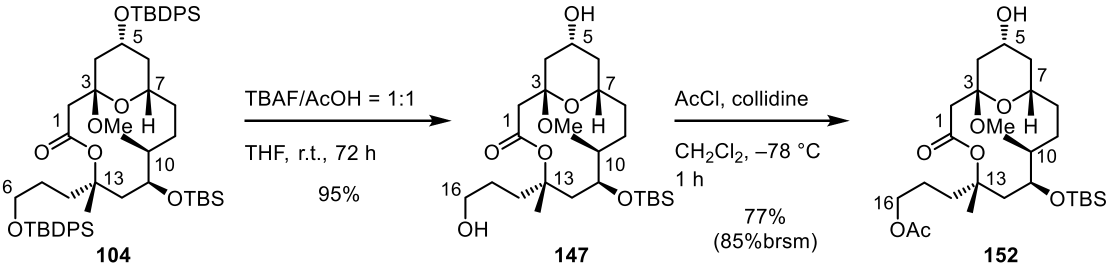
Scheme 22. Dess–Martin oxidation of alcohol **146**

アルデヒド **148** に対してシリルアリルホスホナート **149a**38)を用いた Horner–Wadsworth–Emmons 反応を行なうことで、低収率ながらもジエン **150** を得ることができた(Scheme 23)。本化合物は ^{1}H NMR 上において主生成物のほかに 2 つの異性体が ^{1}H NMR 上で微量確認されたが、シリカゲルカラムで分離することができなかった。その後、NBS を用いて TMS 基を臭素原子に置換することを試みたが、先行研究の結果13)とは異なり末端異性体が多く生成し、18*E*/18*Z* = 68:32 の比で保護されたアグリコン **151** を得た。



Scheme 23. Toward synthesis of aglycon

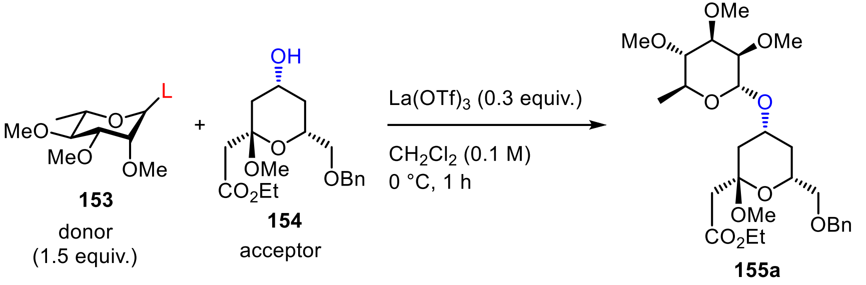
各工程に条件検討の必要性はあるが、アグリコン **151** の合成まで到達することができた。しかし、第一級水酸基を保護している TBDPS 基の選択的脱保護は困難であったため、ジオール **147** を主生成物として得るようにし、先にラムノース誘導体を導入する合成ルートを確立することとした。TBDPS 基の脱保護については TBAF を過剰に用い、長時間を要するものの良好な収率でジオール **147** を得ることができた(Scheme 24)。得られたジオール **147** の第一級水酸基をアセチル基で選択的に保護し、糖受容体 **152** を合成した。

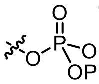
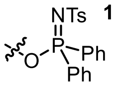
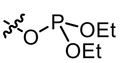
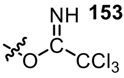


Scheme 24. Synthesis of glycosyl acceptor **152**

第2節　グリコシル化反応の検討

Table 3. Screening of leaving groups



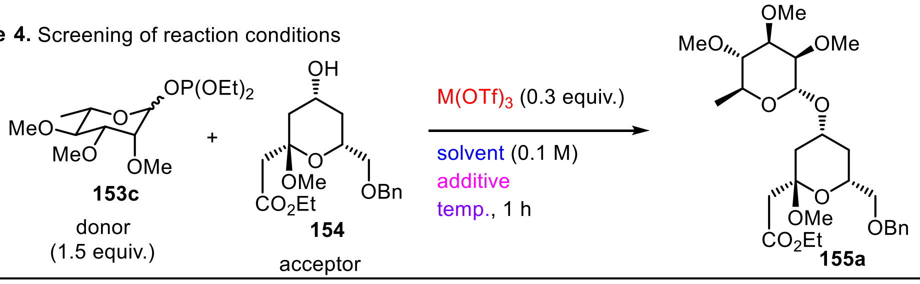
L	**153a** 	**153b** 	**153c** 	**153d** 
yield(α)[%][a]	3	29	56	54
α:β[a]	–	73:27	74:26	75:25

[a]Determined by ^{1}H NMR analysis of crude product using benzyl benzoate as an internal standard.

ラムノース誘導体を導入するにあたり、モデル基質を用いてグリコシル化反応の検討を行なった。まず、脱離基について検討を行なった(Table 3)。所属研究室では、種々の元素で修飾容易なリン原子に着目して数種の含リン脱離基を開発し、含リン脱離基の特性を活かすことで、様々な結合様式をもつグリコシドの高収率かつ高立体選択的な合成を達成してきた $^{39)}$。18*E*-リングビアロシド C の合成においても本法を用いることで良好な結果で望みとするグリコシドが得られることを期待し、含リン脱離基について検討を行なうこととした。なお、本検討ではプロモーターとして La(OTf)$_3$ を用いているが、先行研究の報告において TMSOTf や TBSOTf を用いた Schmidt 法では、全合成の基質を分解してしまうことが報告されていた $^{14b)}$。加えて、著者も初期検討としてグリコシル化反応に広く用いられる BF$_3$·Et$_2$O をプロモーターとして用いたが、モデル基質 **154** の分解が確認された。したがって、先行研究に倣い La(OTf)$_3$ をまず用いている。ホスファート **153a** を脱離基とした際には、糖供与体そのものの安定性に問題もあり、望みとするグリコシドをほとんど得ることができなかった。ホスフィンイミダート **153b** の場合には良好な選択性が得られたが、収率は低収率にとどまった。一方で、ホスファイト **153c** を脱離基とした場合には中程度の収率でグリコシドを得ることができ、この結果は Schmidt 法 $^{40)}$であるトリクロロアセトイミダート **153d**$^{14b)}$を用いた時の結果と同等であった。これらの結果より、ジエチルホスファイト **153c** を脱離基としたグリコシル化反応についてさらに条件検討を行なった。

初めにプロモーターについて検討を行なった(Table 4, entries 1–10)。希土類トリフラートが良い結果を示すと考え数種検討を行なったところ、顕著な差は見られなかったが、Eu(OTf)$_3$ を用いた際に良い収率と選択性を与えることが明らかとなった(entry 6)。続いてプロモーターを Eu(OTf)$_3$ に固定し、各種溶媒を検討した(entries 11–15)。極性溶媒を使用した際には収率が大きく低下する結果となったが(entries 13–15)、toluene を用いた際に若干収率が低下するものの選択性が向上することが明らかとなった(entry 11)。そこで、良好な収率を与えた CH$_2$Cl$_2$ と良好な選択性を与えた toluene を 1:1 の混合溶媒として用いたところ、両方の良さを兼ね備えた結果を得ることができた(entry 12)。温度について検討を行なったが、低温下では予想外に選択性が低下する結果となった(entries 17–19)。また、室温条件下では選択性は維持したが収率が若干低下した(entry 16)。系中に微量に存在する水分を取り除くために MS4A を添加したところ、大きな変化は見られず(entry 20)、収率の向上を指向して糖供与体の当量数を 3.0 当量に増加させたが、収率の向上にはつながらなかった(entry 21)。しかし、これらの条件を組み合わせたところ最も良い結果が得られ(entry 22)、本条件を全合成のグリコシル化反応に適用することとした。

Table 4. Screening of reaction conditions



entry	$M(OTf)_3$	solvent	additive	temp. [°C]	yield(α) [%][a]	α:β[a]
1	$Sc(OTf)_3$	CH_2Cl_2	none	0	39	78:22
2	$Y(OTf)_3$	CH_2Cl_2	none	0	46	74:26
3	$La(OTf)_3$	CH_2Cl_2	none	0	56	74:26
4	$Pr(OTf)_3$	CH_2Cl_2	none	0	42	76:24
5	$Sm(OTf)_3$	CH_2Cl_2	none	0	43	75:25
6	$Eu(OTf)_3$	CH_2Cl_2	none	0	62	74:26
7	$Gd(OTf)_3$	CH_2Cl_2	none	0	53	75:25
8	$Er(OTf)_3$	CH_2Cl_2	none	0	54	76:24
9	$Tm(OTf)_3$	CH_2Cl_2	none	0	47	74:26
10	$Yb(OTf)_3$	CH_2Cl_2	none	0	55	74:26
11	$Eu(OTf)_3$	toluene	none	0	50	81:19
12	$Eu(OTf)_3$	CH_2Cl_2/toluene =1:1	none	0	57	81:19
13	$Eu(OTf)_3$	THF	none	0	29	70:30
14	$Eu(OTf)_3$	Et_2O	none	0	29	74:26
15	$Eu(OTf)_3$	dioxane	none	0	25	71:29
16	$Eu(OTf)_3$	CH_2Cl_2/toluene =1:1	none	23	50	81:19
17	$Eu(OTf)_3$	CH_2Cl_2/toluene =1:1	none	–20	38	79:21
18	$Eu(OTf)_3$	CH_2Cl_2/toluene =1:1	none	–40	37	75:25
19	$Eu(OTf)_3$	CH_2Cl_2/toluene =1:1	none	–78	4	75:25
20	$Eu(OTf)_3$	CH_2Cl_2/toluene =1:1	MS4A (100 wt %)	0	46	87:13
21[b]	$Eu(OTf)_3$	CH_2Cl_2/toluene =1:1	none	0	58	79:21
22[b]	$Eu(OTf)_3$	CH_2Cl_2/toluene =1:1	MS4A (100 wt %)	0	71	82:18

[a]Determined by ^1H NMR analysis of crude product using benzyl benzoate as an internal standard. [b]Donor (3.0 equiv.)

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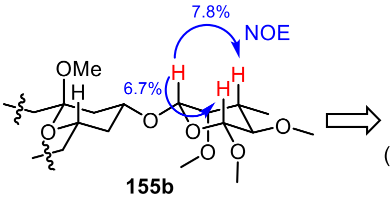
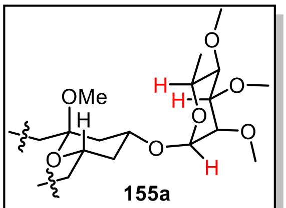
*α 体と β 体の同定は、単離精製して得られた 2 つの化合物について一方に β 体に由来する NOE 相関がみられたため、そちらを β 体、もう一方を α 体とした。



155b

β anomer
(minor isomer)

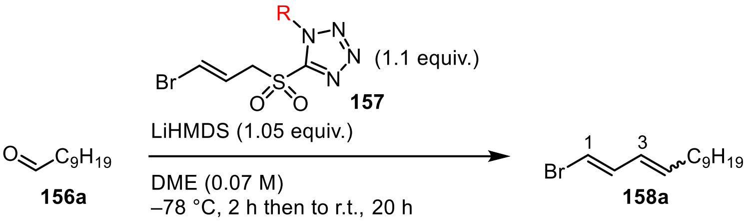


155a
α anomer
(major isomer)

第 3 節　ブロモジエン側鎖導入の検討41)

18*E*-リングビアロシド C に含まれるブロモジエン骨格は、リングビアロシド類4,5,42)に限らず他の海洋産天然物にもみられる構造である43)。加えて、末端臭素原子からカップリング反応を用いることによってポリエン骨格を構築する足掛かりともなる有用な骨格である44)。リングビアロシド B13b,13c)およびリングビアロシド C14b)の全合成研究において、先行研究ではこのブロモジエン骨格を 2 段階の炭素鎖伸長を経て構築しており、工程数の削減が見込まれた。著者はこれら 3 点に着目し、調製が容易なアルデヒドから 1 工程でブロモジエン骨格を構築する新たな手法を開発することとした。

Table 5. Screening of sulfones **157**



entry	R	yield [%]^a	(1*E*,3*E*)/(1*E*,3*Z*)^b
1	Ph **157a**	72	52:48
2	p-MeO-C_6H_4 **157b**	78	58:42
3	p-CF_3-C_6H_4 **157c**	71	54:46
4	Me **157d**	59	11:89
5	^{i}Pr **157e**	65	6:94
6	^{t}Bu **157f**	18	2:>98
7	1-adamantyl **157g**	25	2:>98

^{a}Isolated yield. ^{b}Determined by ^{1}H NMR analysis.

Julia オレフィン化を機軸として開発を行なうこととし*、デカナール **156a** を基質としてブロモアリル骨格を有するスルホン **157** に関してテトラゾール上の置換基を種々検討した(Table **5**)。一般にフェニル基が置換したテトラゾールを用いる Julia–Kocienski オレフィン化45)では、*E* 体のオレフィンを優先的に与えるが、本反応系ではほとんど選択性が発現しない結果となった(entry 1)。フェニル基のパラ位に芳香環状の電子密度を変化させるメトキシ基、トリフルオロメチル基を導入したスルホン **157b**, **157c** を用いても選択性にほとんど影響を与えないことが明らかとなった(entries 2, 3)。そこで、アリール基の代わりにアルキル基を導入したスルホン **157d–157g** を調製し再度検討を行なったが、この場合はアルキル基のかさ高さによらず全合成研究には望みとしない *Z* 体のオレフィンを優先する結果となった(entries 4–7)。アルキル基がかさ高くなるにつれて *Z* 選択性は向上したが、収率は低下する傾向となった。

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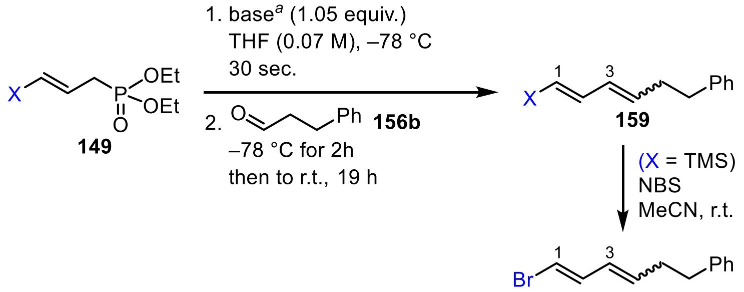
*当初、Scheme **23** に示したように Hornor–Wadsworth–Emmons オレフィン化による構築を試みていたが、モデル基質を用いた検討では高い *E* 選択性で目的物が得られるものの低収率にとどまった (下図)。加えて、その後の臭素化の際に異性化が起こることが問題となっていた。これを解決すべく、TMS 基の代わりに Bu_3Sn 基が置換したホスホナート **149b** を検討したが良好な結果が得られず、Br 基が置換したホスホナート **149c** の場合には複雑な混合物を与える結果となったため、Hornor–Wadsworth–Emmons オレフィン化での検討を断念した。



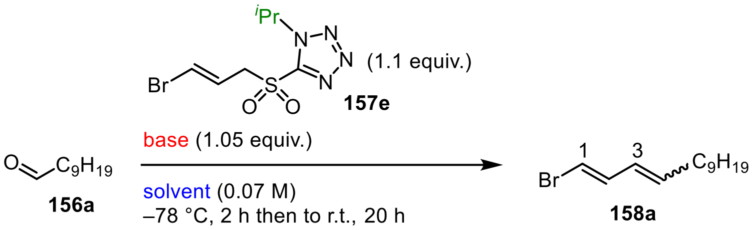
158b
42% (78:5:17^c)

The best result was shown.

X		yield^b [%]	(1*E*,3*E*)/(1*E*,3*Z*)^b
TMS	**149a**	48	95:5
Bu_3Sn	**149b**	25	60:3:37^c
Br	**149c**	complex mixture	–

^{a}LiHMDS, NaHMDS, or KHMDS was used.
^{b}Determined by ^{1}H NMR analysis of crude product using benzyl benzoate as an internal standard.
^{c}(1*E*,3*E*)/(1*E*,3*Z*)/(1*Z*,3*E*) ratio.

Table 6. Screening of reaction conditions

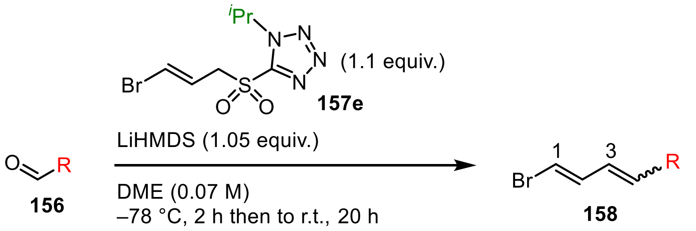


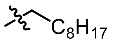
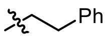
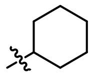
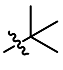
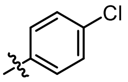
entry	base	solvent	yield [%]^a	(1*E*,3*E*)/(1*E*,3*Z*)^b
1	LiHMDS	DME	65	6:94
2	NaHMDS	DME	39	17:83
3	KHMDS	DME	5	38:62
4	LiHMDS	DMF	31	7:45:28:20^c
5	LiHMDS	DMF/HMPA	47	8:74:5:13^c

^{a}Isolated yield. ^{b}Determined by ^{1}H NMR analysis. ^{c}(1*E*,3*E*)/(1*E*,3*Z*)/(1*Z*,3*E*)/(1*Z*,3*Z*) ratio.

全合成研究に必要とする(*E*,*E*)配置のブロモジエンを選択的に得ることはできなかったが、最も良い結果を与えた entry 2 の条件を 18*E*-リングビアロシド C の全合成研究に採用することとした。一方で、良好な収率かつ高い *Z* 選択性を与えた entry 5 の条件については、(*E*,Z)配置のブロモジエン骨格を有する天然物が存在し43a,43d)、加えて多様なポリエン構築において有用で応用する価値があると考え、より反応条件の精査を行なった(Table 6)。塩基のカウンターカチオンを検討したが収率と選択性がともに低下し(entries 1–3)、溶媒を他の極性溶媒に変更すると収率の低下とともにすべての異性体が生成する結果となり(entries 4, 5)、entry 1 の結果を上回ることはできなかった。最後に、最適条件下基質一般性について調査を行なった(Table 7)。アルデヒドの α 位が第一級、第二級炭素の場合では(**156a–156c**)中程度から良好な収率かつ高い *Z* 選択性で望みとするブロモジエンを得ることができた。一方で、α 位が第三級および芳香族アルデヒドの場合では高い選択性は発現するものの低収率にとどまる結果となった(**156d, 156e**)*。

Table 7. Scope and limitations



R =					
	156a, 158a	**156b, 158b**	**156c, 158c**	**156d, 158d**	**156e, 158e**
yield [%]^a (1*E*,3*E*)/(1*E*,3*Z*)^b	65 6:94	57 6:94	77 16:84	39 21:79	25 7:93

^{a}Isolated yield. ^{b}Determined by ^{1}H NMR analysis.

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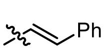
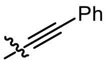
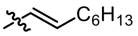
*以下の α,β-不飽和アルデヒドを基質とした際には劣悪な結果となった。

R =			
	156f, 158f	**156g, 158g**	**156h, 158h**
yield [%]^a (1*E*,3*E*)/(1*E*,3*Z*)^b	6 (imp.) 4:96	3 (imp.) 5:95	15 (imp.) 11:89

^{a}Isolated yield. ^{b}Determined by ^{1}H NMR analysis.

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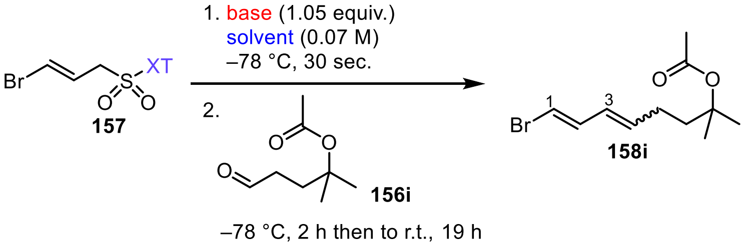
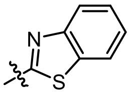
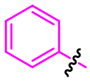
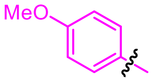
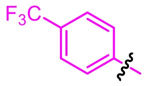
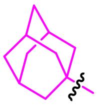
*より高度化したモデル基質での結果を下図に示す。本検討においてもパラ位にメトキシ基が置換したスルホン **157b** を用いる条件が (1*E*,3*E*)配置の化合物に関して最も良い結果を与えた。

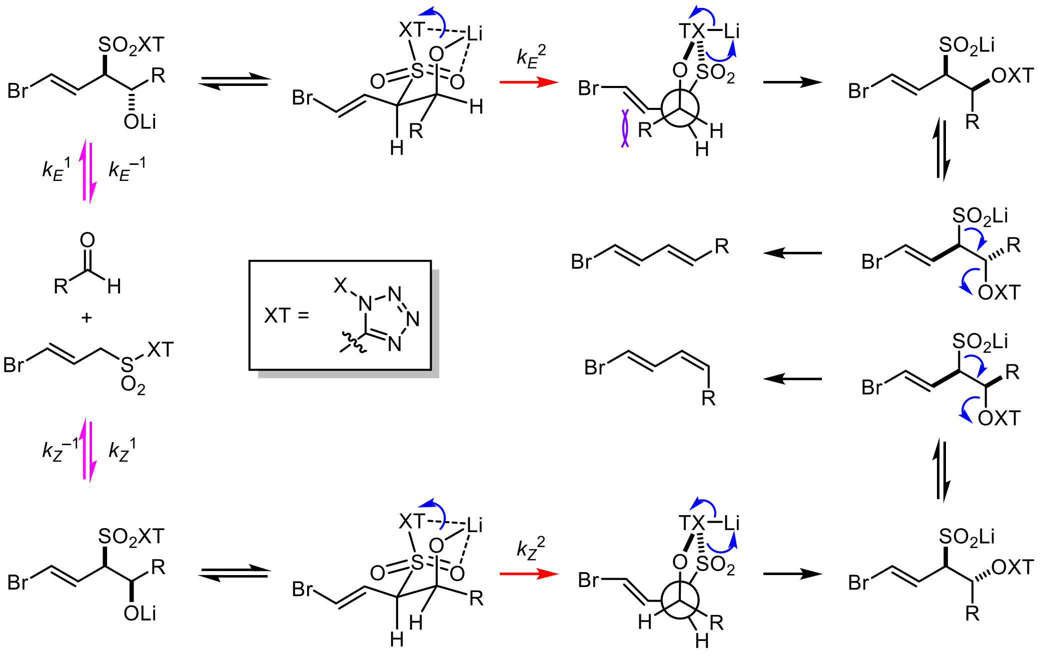


XT =	 , R =					
						
	157a	**157b**	**157c**	**157d**	**157g**	**157h**
yield[a][%]	63%	71%	53%	49%	32%	66%
(1*E*,3*E*)/(1*E*,3*Z*)[a]	54:46	50:50	49:51	8:92	2:>98	32:68

[base: LiHMDS, NaHMDS, KHMDS; solvent: DME, THF, toluene] All conbinations were tried.
The best results were shown in table.

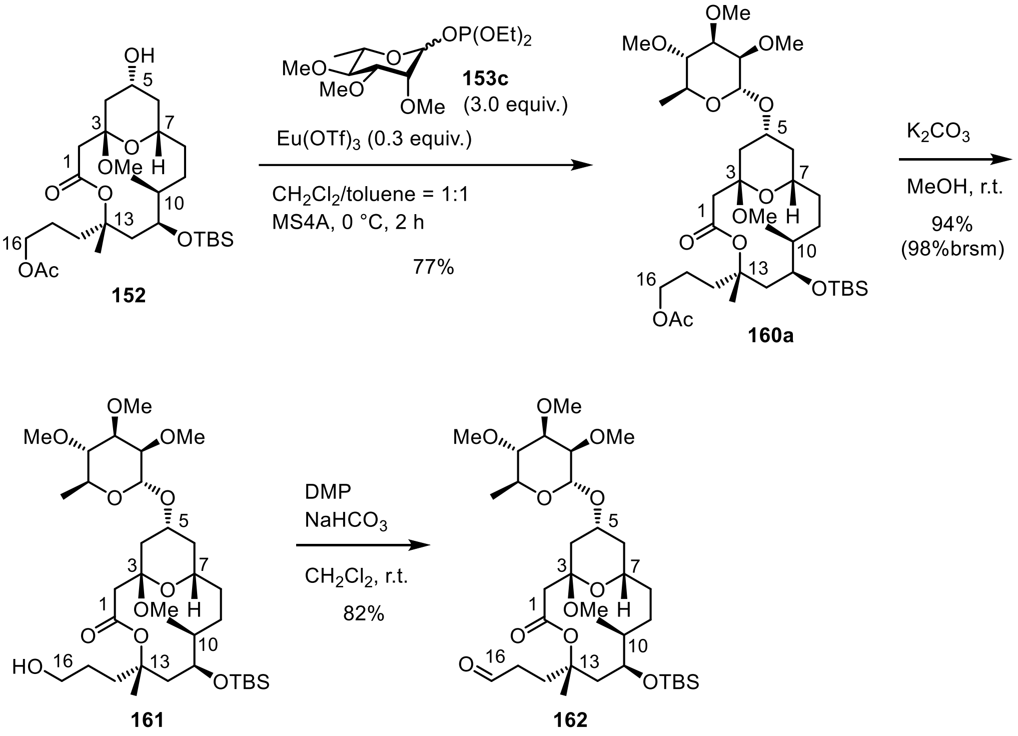
[a] Determined by ^{1}H NMR analysis of crude product using benzyl benzoate as an internal standard.

**本反応の立体選択性を含めた反応機構は以下のように考えられている(下図)[46]。アリル骨格を有するスルホンを用いた場合にはアルデヒドへの付加が可逆的となり、以降の Smiles 転位によって立体が左右される([k_E^1, k_E^{-1}, k_Z^1, k_Z^{-1}] >> [k_E^2, k_Z^2])。Smiles 転位の速度はアルキル基同士の立体反発から k_Z^2 の方が速いと想定され、従って *Z* 体のオレフィンが優先したと考えられる。アリール基が置換したスルホンを用いた際には、アリル基とアリール基との間で相互作用が起こり、*E* 体を与える遷移状態が安定化さることでこちらの経路で進行する割合が増え、選択性がほとんど発現しない(= *Z* 選択性が低下した)結果となったと考えられる。



第 4 節　18*E*-リングビアロシド C の合成

ラムノース誘導体およびブロモジエン側鎖導入に関してモデル基質で最適条件を見出したためそれらを全合成研究に適用した。糖受容体 **152** に対して **153c** を用いたグリコシル化反応を行なうことにより、粗生成物において α:β=80:20 の選択性でグリコシド **160** を得た。グリコシドの α 体と β 体はシリカゲルカラムクロマトグラフィーで分離可能であり、単離収率 77%で望みとする α 体のグリコシド **160a** を得ることができた(Scheme 25)*。その後、炭酸カリウムによってアセチル基を除去したのちに、Dess–Martin 酸化によってアルデヒド **162** へと変換した。

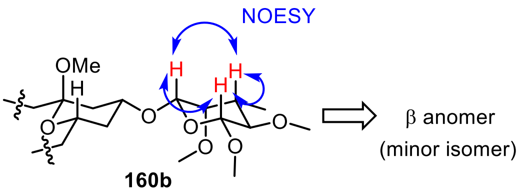


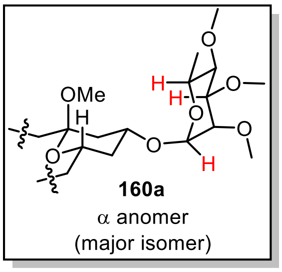
Scheme 25. Synthesis of aldehyde **162**

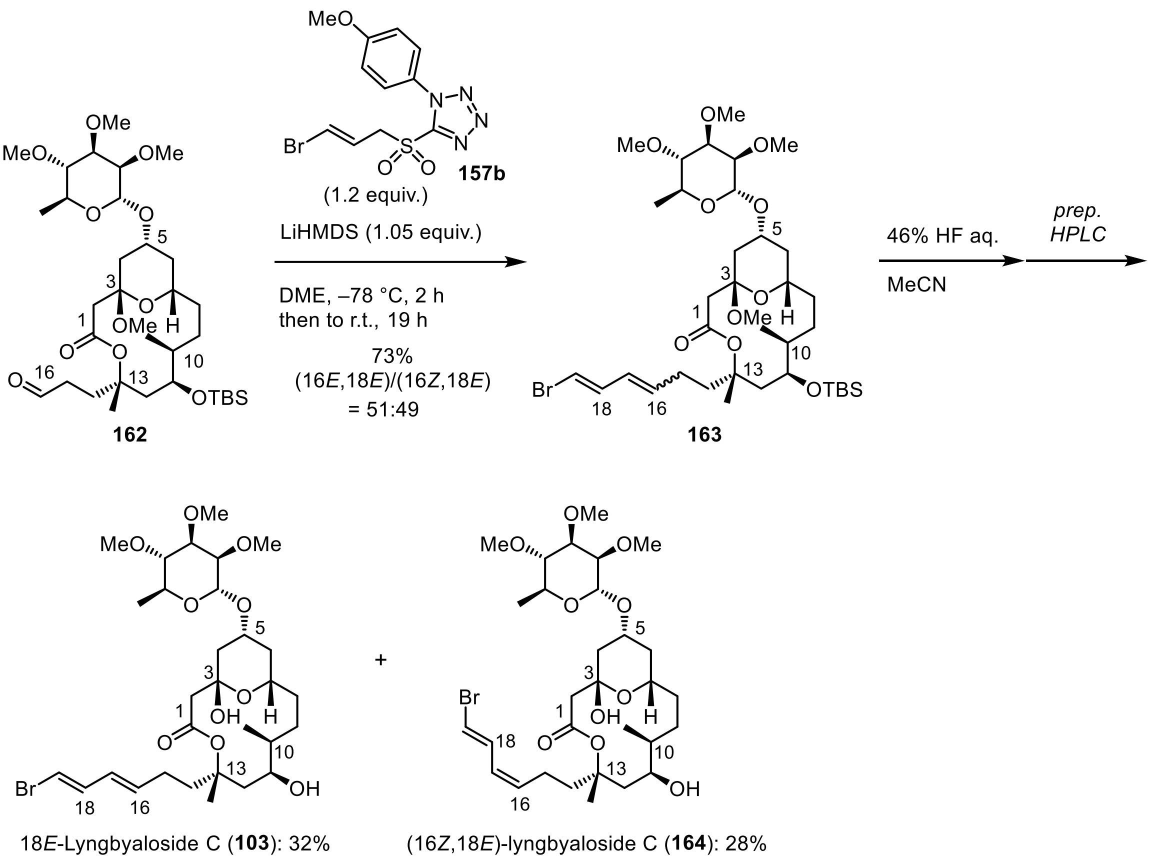
アルデヒド **162** に対し、スルホン **157b** を用いた Julia オレフィン化によって、モデル基質同様選択性は発現しなかったが、良好な収率でブロモジエン側鎖の構築に成功した(Scheme 26)。最後に、フッ化水素酸によってすべての保護基を除去したのちに、分取 HPLC によってジエンの異性体を分離することによって、18*E*-リングビアロシド C (**103**)および非天然型の(16*Z*,18*E*)-リングビアロシド C(**164**)の全合成を達成した。

---

*α 体と β 体の同定については、一方のグリコシドに β 体特有の NOESY 相関がみられたことから同定した。また、β 体の単離収率は 19%であった。







Scheme 26. Completion of total synthesis

^{1}H NMR および ^{13}C NMR は Luesch らによる単離の報告4)および Taylor らの全合成研究の報告14b)とよく一致していることがうかがえる(Figure 6, 7)。

以上、光学活性なアルデヒド **113b** およびアルデヒド **109** から総工程数 37 工程、最長直線工程において 26 工程および総収率 2.1%で 18*E*-リングビアロシド C の全合成を達成した。

Figure 6. Comparison of ^{1}H NMR of 18*E*-lyngbyaloside C (my synthetic product (up), Taylor's synthetic product (middle), Luesch's isolated report (down)

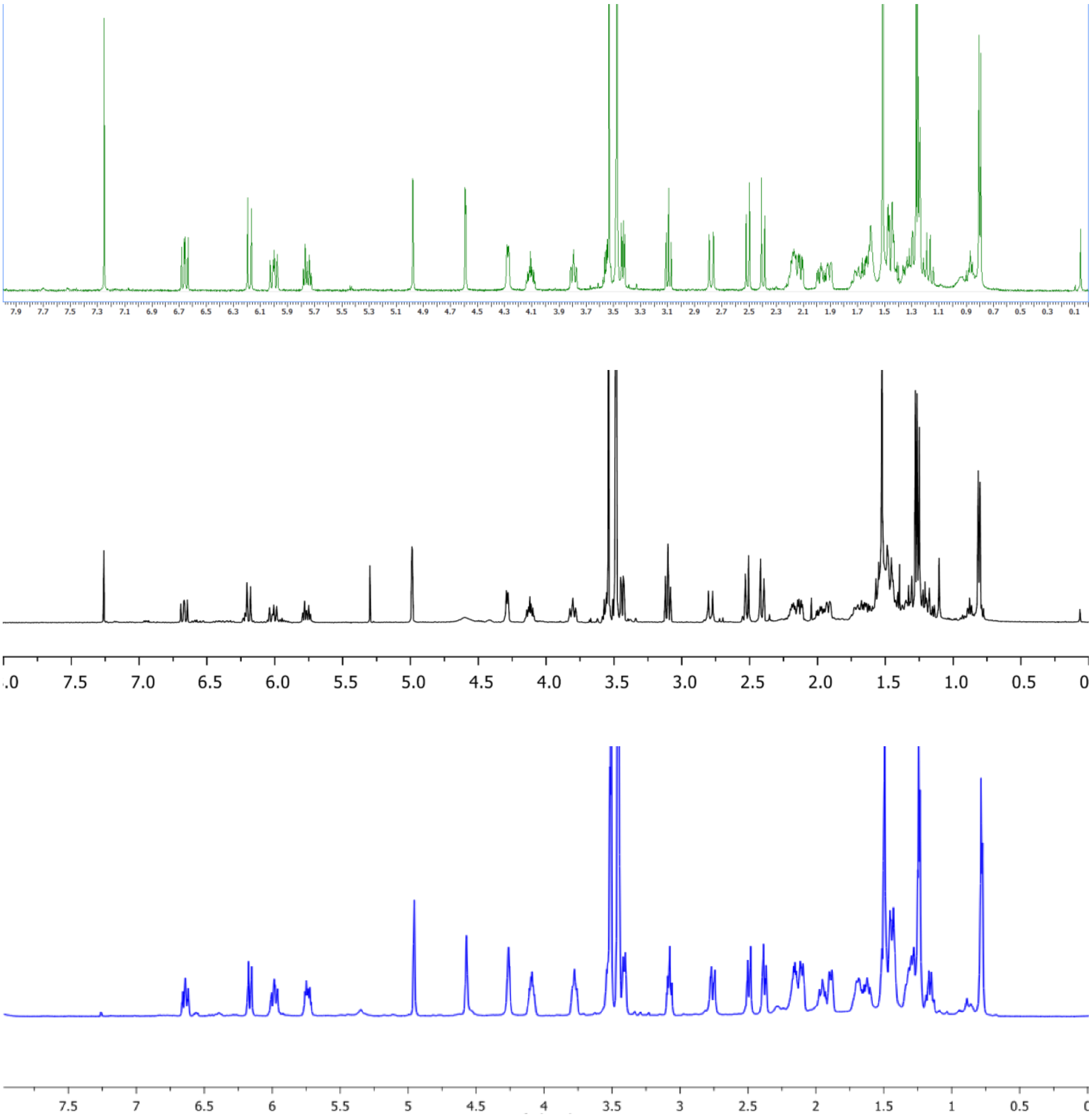
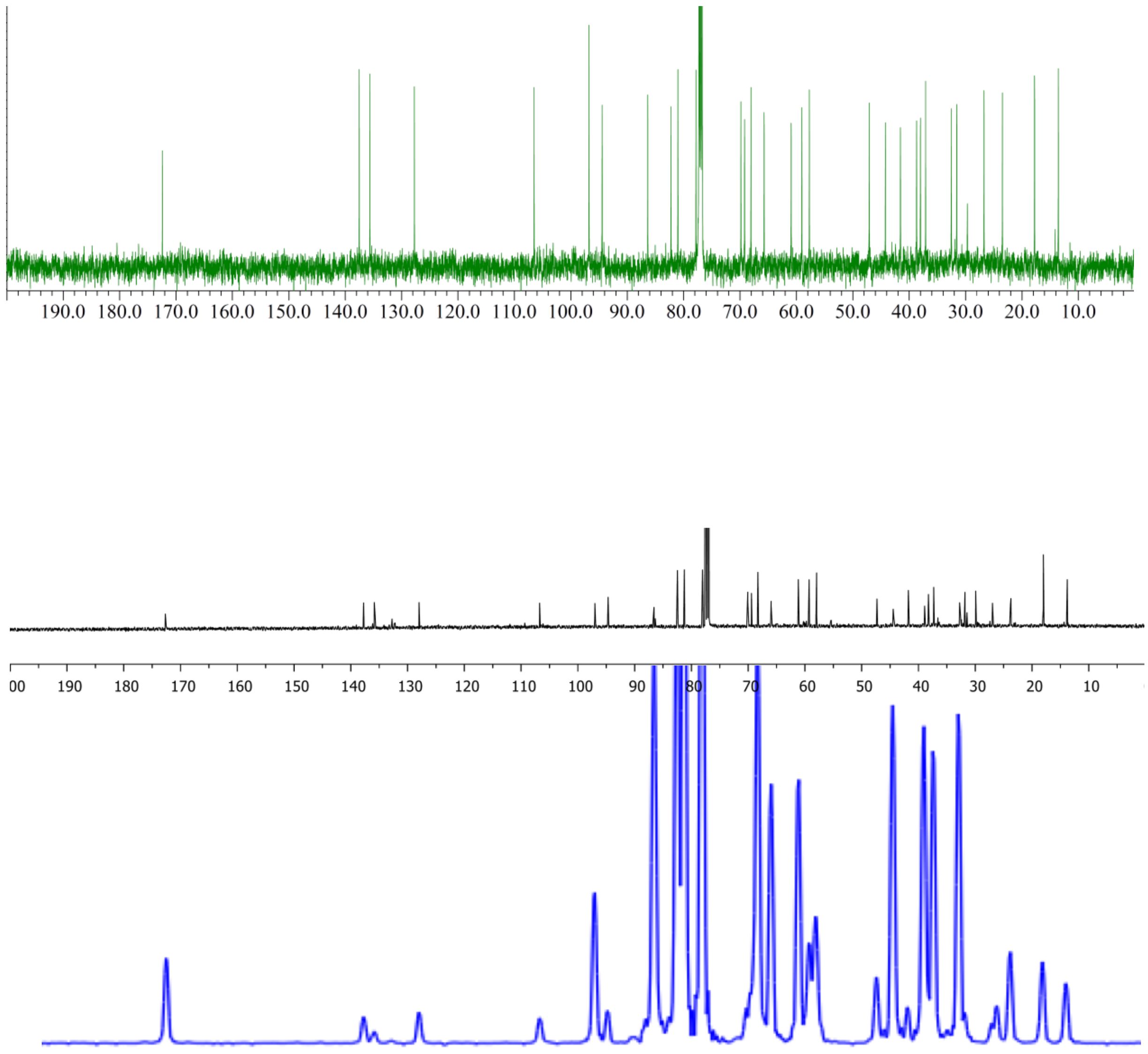


Figure 7. Comparison of ^{13}C NMR of 18*E*-lyngbyaloside C (my synthetic product (up), Taylor's synthetic product (middle), Luesch's isolated report (down)



本論

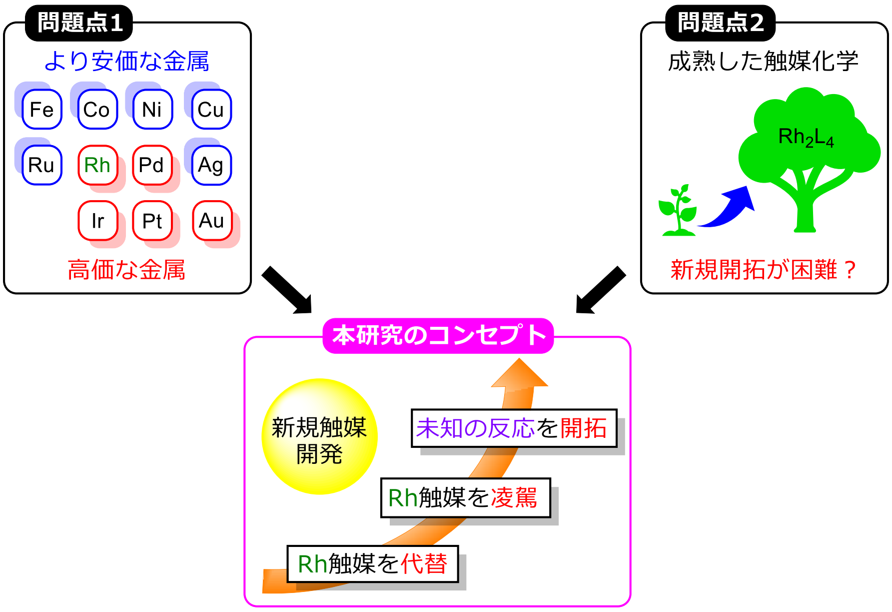
第 2 部　新規外輪型二核遷移金属錯体の創製とその応用

第 1 章　キラル外輪型二核ルテニウム(II,III)錯体の創製と全合成研究への応用

第 1 節　背景

二核ロジウム(II)触媒はカルベン・ナイトレンの化学や Lewis 酸の化学において優れた触媒として機能してきた。しかしこの優れた触媒性能の一方で、ロジウム金属そのものが希少な資源で高価であることがしばしば問題として取り上げられる。近年では、元素戦略の観点から高価な遷移金属に代わってより安価な遷移金属を用いて触媒反応を達成する研究も盛んに行われており 47)、このことは看過できない問題となりつつある(Figure 8, 問題点 1)。また、二核ロジウム(II)触媒の歴史は長く、キラル触媒のみに限定をしても過去 20 年以上にわたって研究がなされ、成熟した触媒化学となっている。今後もこの二核ロジウム(II)触媒の化学を追求することは研究戦略の 1 つとなる一方で、長年研究されてきたという背景から近い将来新規反応系開拓が困難になることが予想される(Figure 8, 問題点 2)。

Figure 8. Problems about dirhodium(II) catalyses and research concept

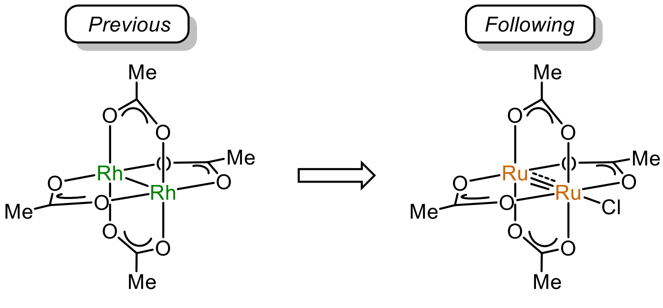


著者は、これら 2 つの問題を同時に解決することを目指し、**1)** 二核ロジウム(II)触媒を代替するもの、**2)** 代替するのみならず二核ロジウム(II)触媒を触媒性能として凌駕するもの、**3)** 新たな反応系探索を可能とするもの、この 3 点を達成する新たな遷移金属触媒を開発することとした。開発する遷移金属触媒としては、二核ロジウム(II)触媒で培った知見を有効に活用するため外輪型二核遷移金属触媒を開発候補とした。

酢酸ルテニウム塩素錯体[$Ru_2(OAc)_4Cl$](**166**)は、1966 年に Stephenson、Wilkinson らによってはじめて合成され 48)、酢酸ロジウム(**165**)と同様に外輪型二核構造を有していることが知られている (Figure 9)。特徴として、ロジウム錯体とは異なり一方のルテニウム原子に塩素原子が結合し、中心金属原子価が二価、三価となっていることがあげられる*。また、金属原子間結

合がロジウム錯体では単結合であると考えられているのに対し、ルテニウム錯体では二重結合と三重結合の間であると考えられている**。著者はこの二核ルテニウム(II,III)錯体***に関して、中心金属原子がより安価な金属に替わることによって元素戦略的に優位となる、中心金属原子価が二価、三価であることがこれまでの二核ロジウム触媒では見られなかった新たな反応性を引き起こすと考え、本錯体を対象として研究を進めることとした。

Figure 9. Research target, paddlewheel diruthenium(II,III) complex



$Rh_2(OAc)_4$ (**165**)

$Ru_2(OAc)_4Cl$ (**166**)

- · *Development candidate: bimetallic paddlewheel complex*
- · *Element strategy: cheaper metal, ruthenium*
- · *New reactivity: mixed-valence Ru(II,III)*

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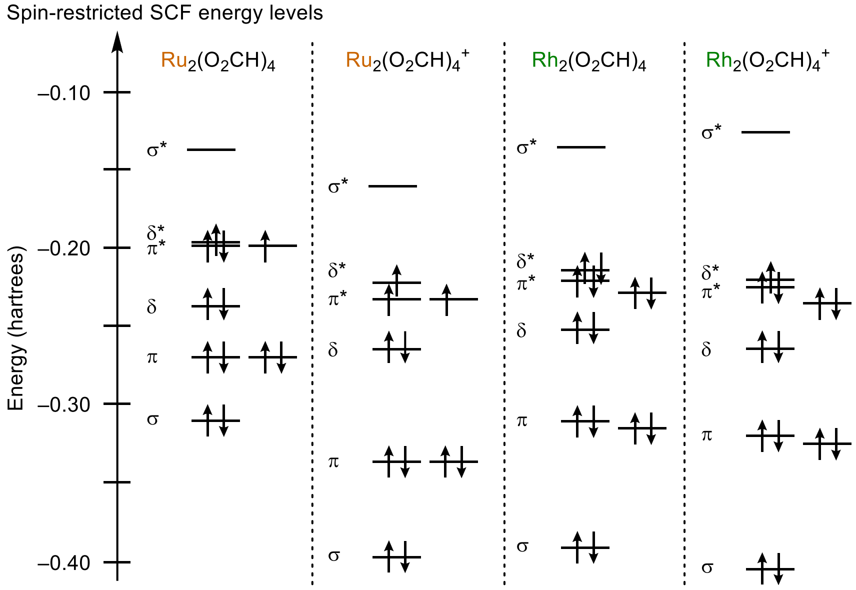
*二核ルテニウム(II,III)錯体の中心金属原子価については、塩素錯体のX線結晶構造解析の結果から錯体が塩素原子をブリッジとして連なっており disorder も観測されなかったことから、二価と三価が2つの金属原子に局在化しておらず均一になっている、Ru(2.5)–Ru(2.5)という考えをもつ研究者もいる 49)。1975年に Cotton らによって EPR スペクトルの測定が行なわれ、断定まではできないがこれを支持するような結果が得られている 50)。その後、1984年に Drago らによって Cotton らの実験の追試が行なわれ、確かに完全に局在化していると仮定した場合の結果とは大きく異なり、均一に近い実験結果が得られたと報告している 51)。しかし、原子価数が均一ではないとした場合に観測できるその差は小さく、同位体として純粋なルテニウム錯体を測定対象としないとこれを観測することができないため、現段階では明確に判断できないと彼らは結論付けている。

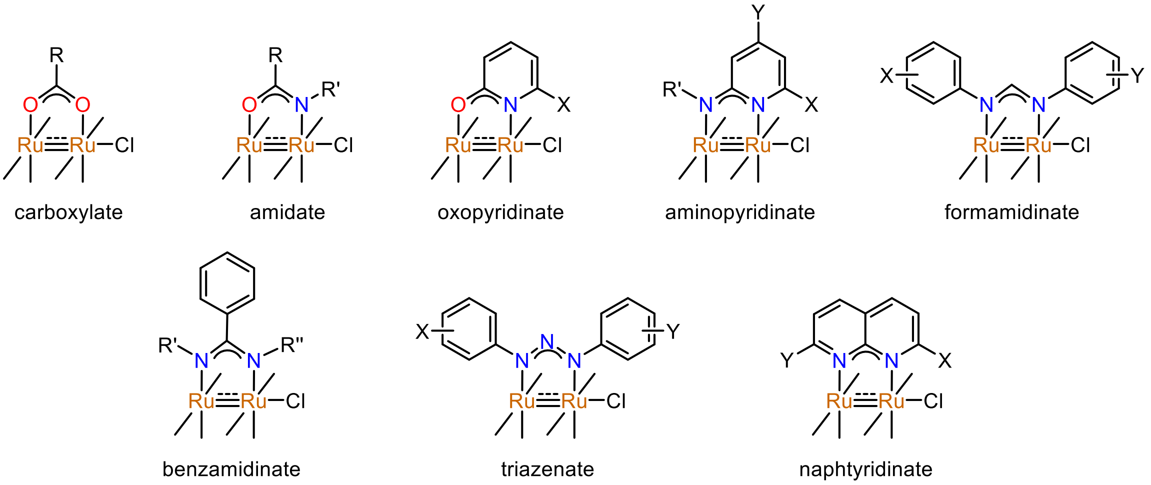
**1979年に Norman Jr.らによって $Ru_2(O_2CH)_4^+$に関して SCF-Xα-SW 法を用いた分子軌道計算が行なわれている(下図)52)。その結果、Ru^{II}–Ru^{III}結合は縮退した3つの半占軌道を有した $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$ の電子配置をもち(注:この電子配置は配位子に依存して変化するが 53)、x*軌道を占める総電子数に変化はない)、このことから二重結合と三重結合の間であると結論づけられている。また、この分子軌道計算とは別に二核ルテニウム(II,III)錯体に関して共鳴ラマンスペクトル 54)や磁化率の測定 48,50,55)が行なわれており、計算結果はこれらの結果とも合致している。



***外輪型二核ルテニウム錯体は Ru(II,III)の状態が最安定となる。これは3つの縮退した半占軌道が安定性に寄与していることに加え、Ru(II,II)錯体では Jahn–Teller 効果によって熱力学的には安定になるが外輪型構造を維持することが困難になるためと考えられている 52)。

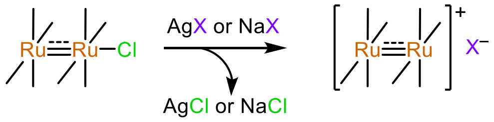
酢酸ルテニウム塩素錯体に含まれる 4 つの酢酸配位子はロジウム錯体同様交換可能であり、これまでに多種多様な架橋配位子を組み込んだ二核ルテニウム(II,III)錯体が合成されている[1)]*。架橋配位子のドナー原子に応じて *O,O* 型、*N,O* 型、*N,N* 型の 3 種が存在し、Figure 10 には一般的に利用される配位子について示している**。

Figure 10. General examples of bridging ligands coordinating to paddlewheel diruthenium(II,III) core

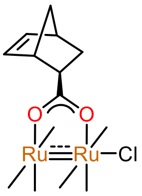


また、軸配位子の塩素原子は銀塩、ナトリウム塩で処理することによって容易に交換することが可能であり、かさ高いカウンターアニオンを組み込むことによってカチオン性錯体の合成も可能となっている (Figure 11)。

Figure 11. Exchange of axial chloride ligand



しかし、アキラルな錯体に関しては数多くの合成報告例があるのに対し、キラルな錯体に関しては 1997 年に McCann らが報告した $Ru_2[(–)\text{-}endo\text{-}\mu\text{-}O_2CC_7H_9]_4Cl$ (**167**)のみとなっている[56)]***。



$Ru_2[(–)\text{-}endo\text{-}\mu\text{-}O_2CC_7H_9]_4Cl$ (**167**)

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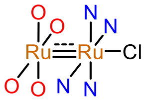
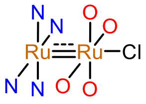
*外輪型二核ルテニウム錯体は中心金属原子価の異なる 4 つのパターン、Ru(I,I)、Ru(II,II)、Ru(II,III)、Ru(III,III)の錯体もこれまで合成されており、配位子の種類、配位子交換数も含めると非常に多様性に富んでいる[1)]。本研究では最安定である Ru(II,III)錯体かつ 4 つ配位子が等しく交換されたものを研究対象としたが、他の錯体に関してもその反応性等は大変興味深いものである。

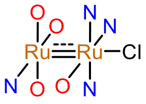
**4 つすべての配位子が交換されたものについて、amidate、oxopyridinate、aminopyridinate に関しては配位方向に応じて *N*-(4,0)、*O*-(4,0)、*N*-(3,1)、*O*-(3,1)、*trans*-(2,2)、*cis*-(2,2)の 6 種類を想定することができる。これらのうち、amidate は配位子の種類に応じて *N*-(4,0)、*cis*-(2,2)、*trans*-(2,2)、oxopyridinate は *N*-(4,0)もしくは *O*-(4,0)、aminopyridinate は *N*-(4,0)か *N*-(3,1)が報告されている。



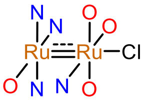
N-(4,0)



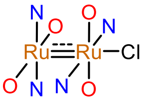
O-(4,0)



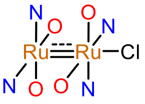
N-(3,1)



O-(3,1)



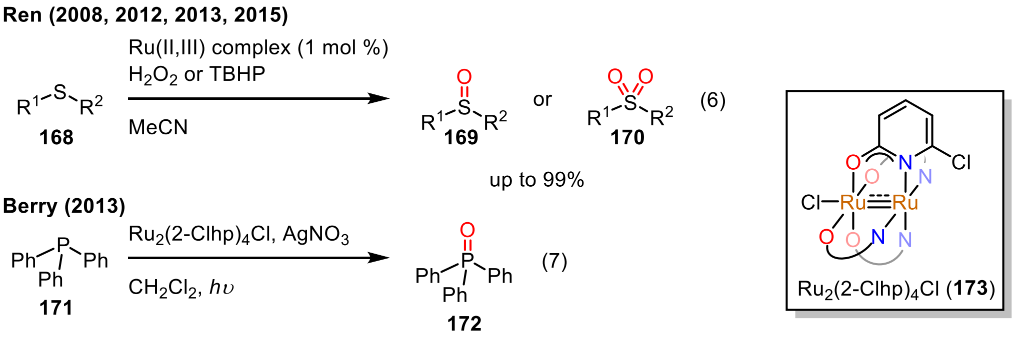
trans-(2,2)



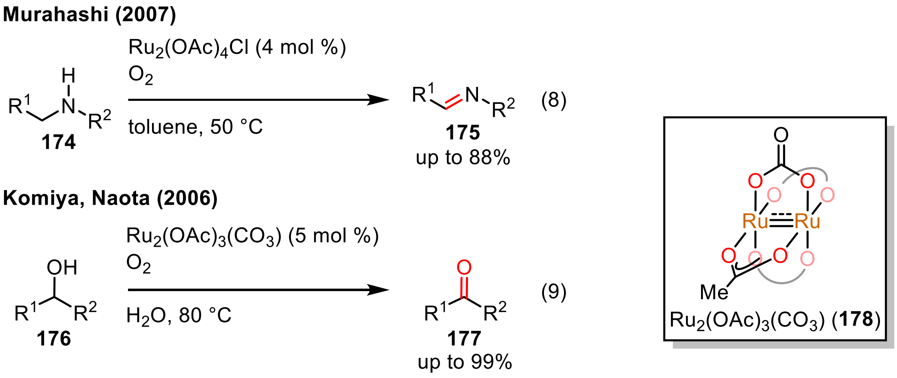
cis-(2,2)

***McCann らは同論文内で、同じ配位子を有する Cu(II,II)錯体に関して X 線結晶構造解析を行ない構造決定しているが、Ru(II,III)錯体に関しては元素分析、磁化率、IR、UV-Vis、モル導電率、FAB-MS の測定によって同定を行なっており、結晶構造は明らかとしていない。

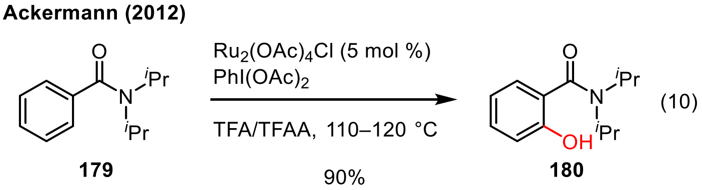
二核ルテニウム(II,III)錯体を用いた反応開発は酸化反応を中心に報告がなされている。Ren らは、種々の二核ルテニウム(II,III)錯体を用いたスルフィドの酸化について精力的に研究を行なっており、本錯体存在下過酸を作用させることによってスルホキシドもしくはスルホンの合成を報告している(eq. 6)57)。Berry らは、反応開発という観点ではないが現象として、2-クロロヒドロキシピリジン塩素錯体(**173**)と硝酸銀存在下光照射によってホスフィン **171** の酸化が起こることを見出している(eq. 7)58)*。



村橋らは酸素雰囲気下、酢酸塩素錯体を用いたアミンの酸化によるイミンの合成を報告し(eq. 8)59)、特にベンジルアミンを基質とした際にはベンゾニトリルが得られることを見出している。小宮・直田らは一つの酢酸配位子と塩素原子の代わりに炭酸配位子を架橋させたルテニウム錯体 $Ru_2(OAc)_3(CO_3)$ (**178**)を合成し、これを酸素雰囲気下アルコールに作用させることにより、アルデヒドおよびケトンへの酸化を報告している(eq. 9)60)。



また、上記の反応とは異なり、近年盛んに研究が行なわれている C–H 結合官能基化にも二核ルテニウム錯体は用いられている。2012 年に Ackermann らは二核ルテニウム錯体を主体とした論文ではないが反応条件検討の中で酢酸ルテニウム塩素錯体を用いている(eq. 10)61)。こ



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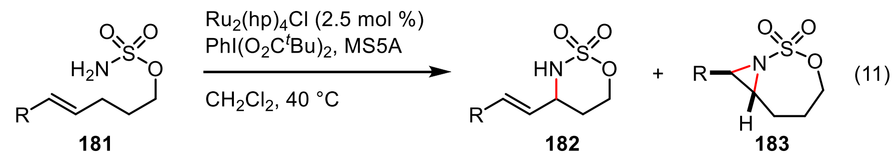
*本反応系では系中で Ru(II,II)錯体が生成していると考えられている。また、Berry らは 2013 年に Ru_2(2-Clhp)$_4$Cl (**173**)とアジ化ナトリウムを組み合わせて PPh_3 への窒素原子移動を行なうことにより $[H_2NPPh_3]Cl$ が得られることも報告している 62)。

れにより、C(sp^2)–H 結合のヒドロキシル化が 90%の収率で進行することを見出している。

2011 年に Du Bois らはヒドロキシピリジン塩素錯体(**184**)を用いた C–H アミノ化反応において、挿入反応とアジリジン化が競合する基質においても挿入体 **182** が良好な収率かつ高い選択性で得られることを報告している(eq. 11)[63)]。この C–H アミノ化反応は、二核ロジウム(II)触媒でも触媒的不斉反応含め深く研究されている領域であり [2c,2d)]、それを二核ルテニウム(II,III)錯体で代替した先駆的な例となっている。

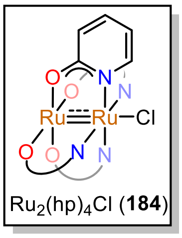
Du Bois (2011)



181 **182** **183**

up to 73%, **182**/**183**=20:1

(11)

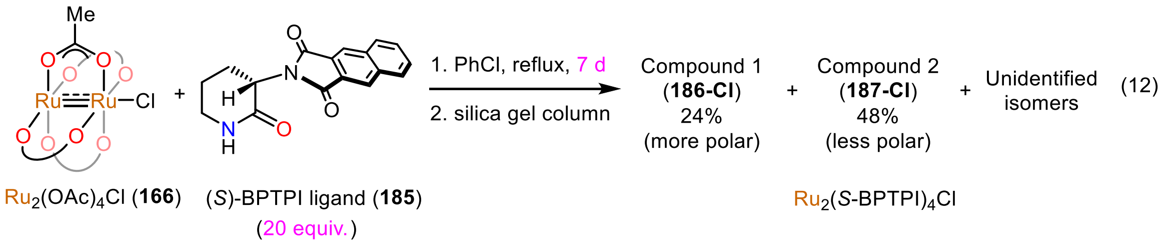


$Ru_2(hp)_4Cl$ (**184**)

このように、二核ルテニウム(II,III)錯体を用いた反応開発はなされてはいるものの、キラルな錯体の合成例が McCann らの $Ru_2[(–)\text{-}endo\text{-}\mu\text{-}O_2CC_7H_9]_4Cl$ (**167**)のみであることに加えて本錯体は触媒反応に用いられていないことから、触媒的不斉反応に関しては一切の報告例がない。著者は、二核ルテニウム(II,III)錯体が Ru^{III} 原子の存在によってロジウム(II)触媒よりも高い Lewis 酸性を示すと仮定し、本錯体を不斉 Lewis 酸触媒として利用することを念頭に、新規キラル錯体の創製に着手した。

第 2 節　キラル外輪型二核ルテニウム(II,III)錯体の創製

母型錯体である酢酸ルテニウム(II,III)塩素錯体(**166**)に対し、所属研究室が開発した(*S*)-BPTPI 配位子(**185**)[3a)]を用いて配位子交換を行なったところ、長時間を要するものの 4 つの酢酸配位子が完全に置換されることが LC-MS 解析により確認された。得られた粗生成物をシリカゲルカラムクロマトグラフィーにて精製したところ、主に 2 種類の錯体 Compound 1(**186-Cl**)および Compound 2(**187-Cl**)が得られた*(eq. 12)。また、得られた 2 種類の錯体をビス(トリフルオロメタンスルホニル)イミド銀もしくは過塩素酸銀で処理することにより、対応するカチオン性錯体の調製も行なった(eq. 13)。



$$\begin{array}{c}\mathrm{Ru_2}(S\text{-BPTPI})_4\mathrm{Cl}\\ (\textbf{186-Cl}\text{ or }\textbf{187-Cl})\end{array} \xrightarrow[\mathrm{CH_2Cl_2}\qquad >95\%]{\mathrm{AgNTf_2}\text{ or }\mathrm{AgClO_4}} \begin{array}{c}\mathrm{Ru_2}(S\text{-BPTPI})_4\mathrm{NTf_2}\\ (\textbf{186-NTf}_\mathbf{2}\text{ or }\textbf{187-NTf}_\mathbf{2})\\ \mathrm{Ru_2}(S\text{-BPTPI})_4\mathrm{ClO_4}\\ (\textbf{186-ClO}_\mathbf{4}\text{ or }\textbf{187-ClO}_\mathbf{4})\end{array} \qquad (13)$$

得られた 2 種類の錯体に関しては X 線結晶構造解析により構造を明らかとした。高極性側に現れた Compound 1(**186-Cl**)については塩素錯体のままでは十分な解析結果を得ることができなかったため、過塩素酸錯体(**186-ClO$_4$**)へと変換したものを用いた。その結果、アミダート配位子の 2 つの酸素原子および窒素原子が各ルテニウム原子にそれぞれ *cis* で配位しており、ベンゾフタルイミド基部分がルテニウム原子のアキシアル位に張り出した C_2 対称型の骨格を有することが明らかとなった(Figure 12)。本錯体の骨格は同じ配位子を有する $\mathrm{Rh_2}$(*S*-BPTPI)$_4$ (**1**)と同じ骨格である。以降、本骨格を *cis*-$\mathrm{Ru_2}$(*S*-BPTPI)$_4$X [X: 軸配位子もしくはカウンターアニオン]と表記する(*e.g.* *cis*-$\mathrm{Ru_2}$(*S*-BPTPI)$_4$Cl (**186-Cl**), *cis*-$\mathrm{Ru_2}$(*S*-BPTPI)$_4$NTf$_2$ (**186-NTf$_2$**), *cis*-$\mathrm{Ru_2}$(*S*-BPTPI)$_4$ClO$_4$ (**186-ClO$_4$**))。

低極性側に現れた Compound 2 (**187-Cl**)に関しては塩素錯体で十分な解析結果が得られ、これによりアミダート配位子の 3 つの酸素原子および 1 つの窒素原子が二価のルテニウム原子側に配位した C_1 対称の *meridional* 型配向を持つことが明らかとなった**(Figure 13)。以降、

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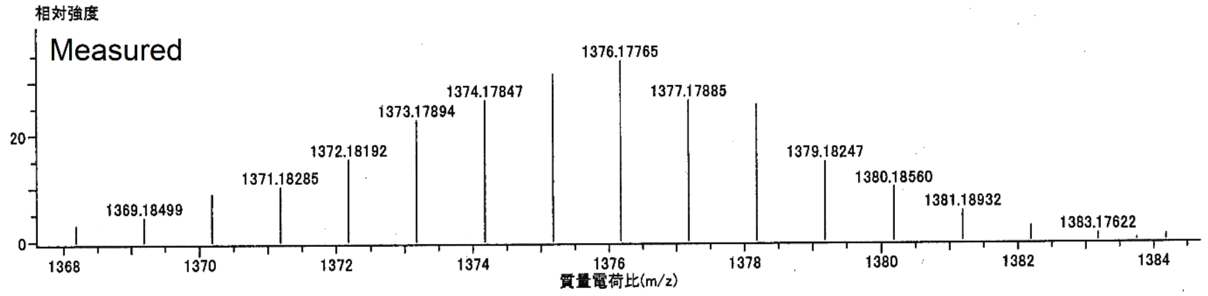
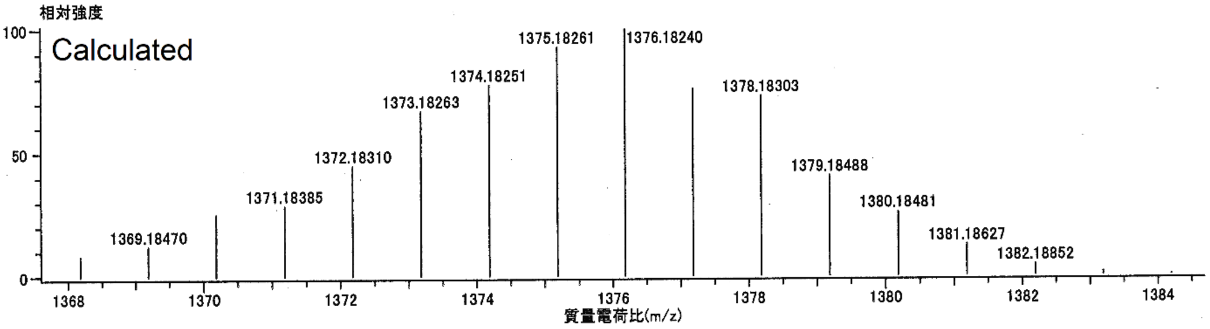
*配位子交換後、回収した(*S*)-BPTPI 配位子のエナンチオ過剰率を測定したところ 98% *ee* であり、わずかにラセミ化していることが明らかとなった。単離精製したそれぞれの錯体は LC-MS 上ではシングルピークであったが、立体化学の反転した配位子が錯体に組み込まれた可能性を考慮し、キラル HPLC、GPC による確認を試みたが大きくブロードしたため判断することができなかった。現段階では *S* 体の配位子のみが組み込まれた錯体であると想定している。また、2 種類の錯体とは別に得られた化合物は不溶性固体であり同定を行なうことができていないが、その不溶性から精製の段階で錯体が多量化したものであると推定している。なお、酢酸ロジウム(II)に対して同配位子を用いた配位子交換を行なった際には、今回のような 2 種類の化合物は確認できず単一のロジウム錯体が得られていた。

**二核ルテニウム(II,III)錯体において同様の配向をもつ報告例はないが、二核ロジウム(II)錯体に関しては Doyle らによって報告されている[64)]。しかし、不斉触媒としては満足に機能していない。

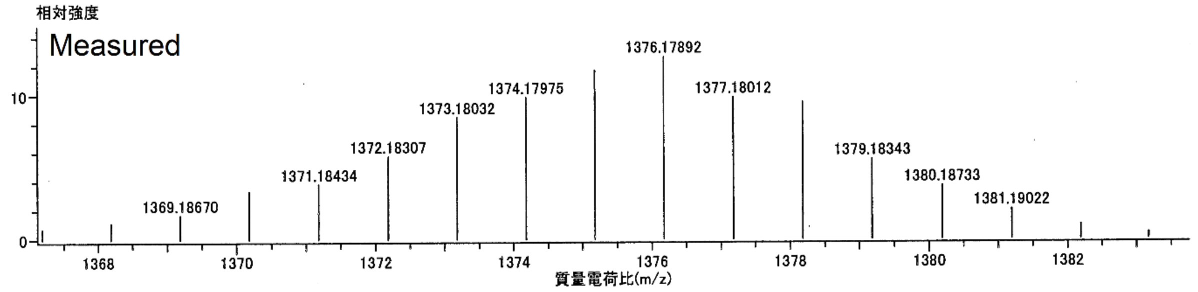
***質量分析における同位体ピークパターンを下図に示した。測定結果は計算結果と合致しており、X 線結晶構造解析の結果と合わせてルテニウム二核構造が保たれていることが示唆されている。

cis-Ru$_2$(*S*-BPTPI)$_4$Cl (Compound 1); Detected as [M–Cl]$^+$





mer-Ru$_2$(*S*-BPTPI)$_4$Cl (Compound 2) ; Detected as [M–Cl]$^+$



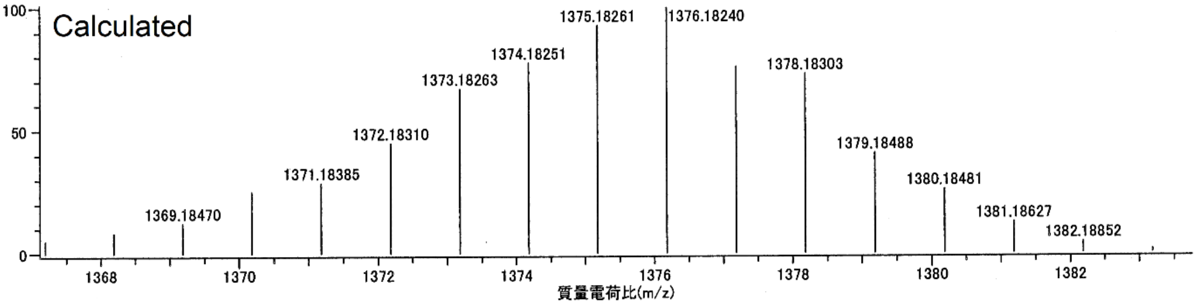
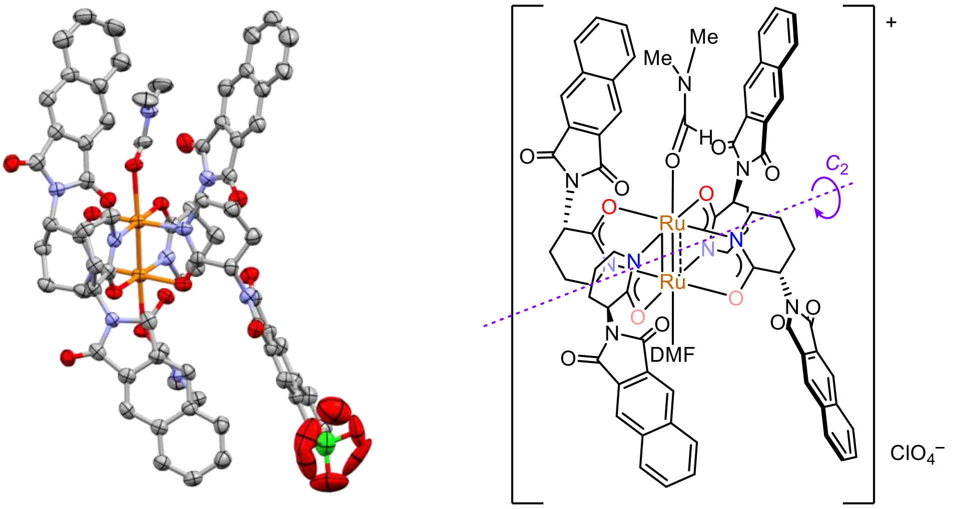
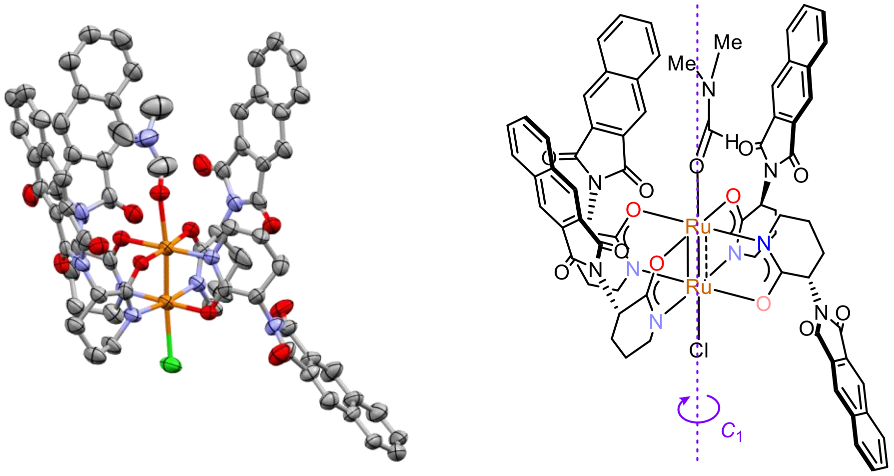


Figure 12. Left: thermal-ellipsoid representation of bis(dimethylformamide) adduct of *cis*-Ru_2(*S*-BPTPI)$_4$$ClO_4$ (**186-ClO$_4$**), (50% probability elipsoids). Right: chemical structure of *cis*-Ru_2(*S*-BPTPI)$_4$$ClO_4$·2DMF. Hydrogen atoms and free solvents were omitted for clarity.



cis-Ru_2(*S*-BPTPI)$_4$$ClO_4$·2DMF

Figure 13. Left: thermal-ellipsoid representation of dimethylformamide adduct of *mer*-Ru_2(*S*-BPTPI)$_4$Cl (**187-Cl**), (50% probability elipsoids). Right: chemical structure of *mer*-Ru_2(*S*-BPTPI)$_4$$ClO_4$·DMF. (*R*)-complex, hydrogen atoms, and free solvents were omitted for clarity.



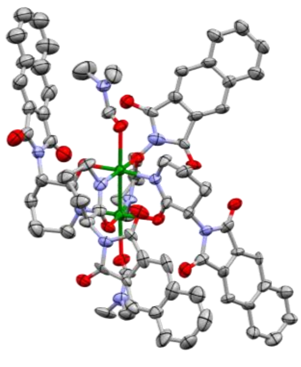
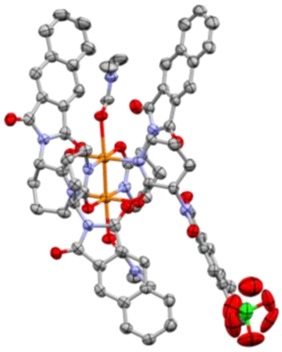
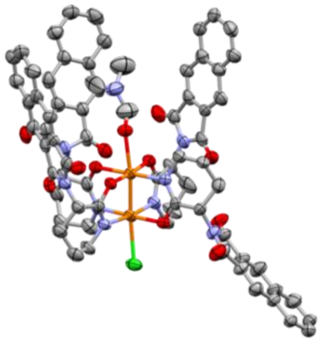
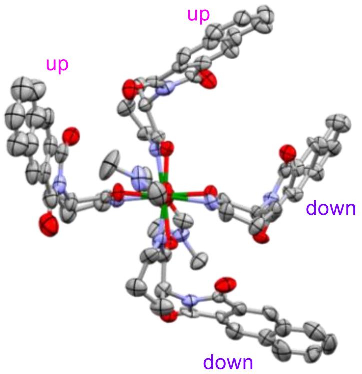
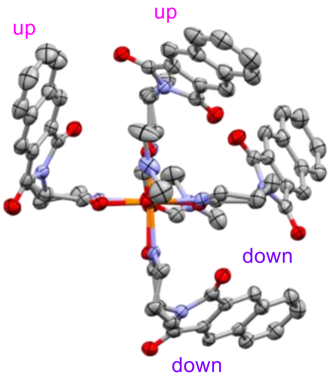
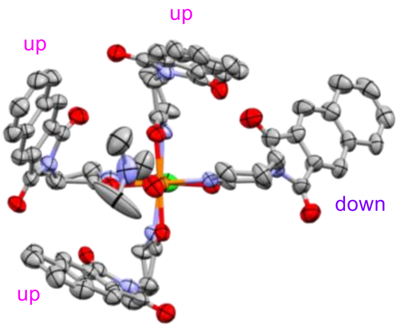
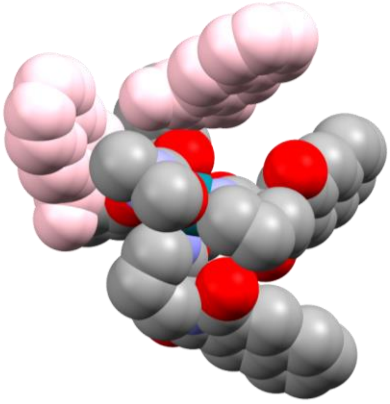
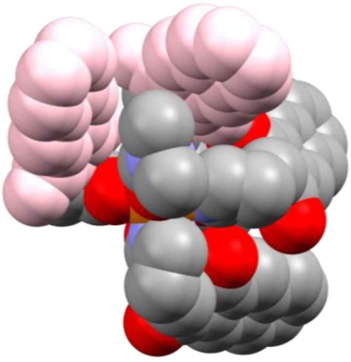
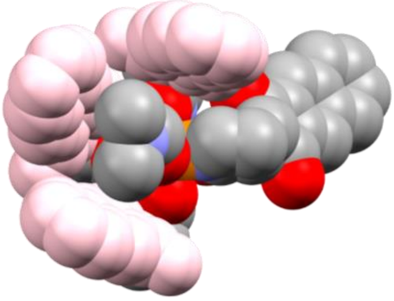
mer-Ru_2(*S*-BPTPI)$_4$Cl·DMF

本骨格を *mer*-Ru_2(*S*-BPTPI)$_4$X [X: 軸配位子もしくはカウンターアニオン]と表記する(*e.g.* *mer*-Ru_2(*S*-BPTPI)$_4$Cl (**187-Cl**), *mer*-Ru_2(*S*-BPTPI)$_4$$NTf_2$ (**187-NTf$_2$**), *mer*-Ru_2(*S*-BPTPI)$_4$$ClO_4$ (**187-ClO$_4$**))。

第 1 部にて結晶構造を明らかにした Rh_2(*S*-BPTPI)$_4$ (**1**)、および今回創製し構造を明らかにした *cis*-Ru_2(*S*-BPTPI)$_4$$ClO_4$ (**186-Cl**)、*mer*-Ru_2(*S*-BPTPI)$_4$Cl (**187-Cl**)の結晶構造を比較として示した(Figure 14)。中心金属原子間の結合距離は、ロジウム錯体が約 2.40 Å であるのに対し、ルテニウム錯体ではそれぞれ約 2.27 Å、2.28 Å となりルテニウム原子間の方が短い。このことは、ロジウム原子間が単結合であると考えられているのに対し、ルテニウム原子間は二重結合と三重結合の間であると考えられていることと一致している。また、不斉反応において重要となる不斉空間の構築は、両金属種で異なっていることがうかがえる。金属原子のアキシアル位に張り出しているベンゾフタルイミド基が、ロジウム錯体では 45 度程度傾いているのに対し、ルテニウム錯体では比較的垂直よりに張り出していることがうかがえる。図最下段

に示した空間充填モデルにおいてはその違いが見て取れ(桜色部分が紙面手前に出ているベンゾフタルイミド基を示す)、傾きの小さなルテニウム錯体の方が構築する不斉空間がより狭いと考えられる。

Figure 14. Comparison of crystal structures [Rh$_2$(*S*-BPTPI)$_4$ (**1**), *cis*-Ru$_2$(*S*-BPTPI)$_4$ClO$_4$ (**186-Cl**), *mer*-Ru$_2$(*S*-BPTPI)$_4$Cl (**187-Cl**)] up: bird's eye view; middle: top view (ball and stick model); down: top view (spacefill model)

Rh$_2$(*S*-BPTPI)$_4$(**1**)	*cis*-Ru$_2$(*S*-BPTPI)$_4$ClO$_4$ (**186-Cl**)	*mer*-Ru$_2$(*S*-BPTPI)$_4$Cl (**187-Cl**)
 Rh–Rh: 2.3988(10) Å	 Ru–Ru: 2.2714(6) Å	 Ru–Ru: 2.2824(8) Å
		
		

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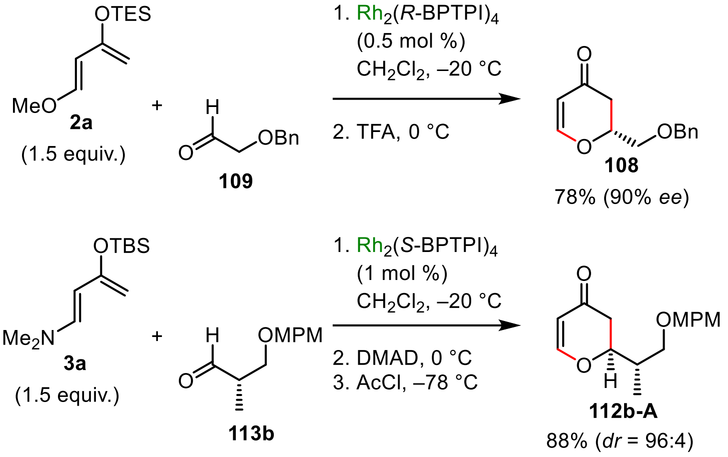
*_meridional_型錯体が形成した原因は定かではない。_N,O_配位型の二核ルテニウム(II,III)錯体は、配位子の種類に応じて_N_-(4,0)、_O_-(4,0)もしくは_cis_-(2,2)の3種類が報告されている(p.37脚注参照)。$\mathrm{Ru^{III}}$の方がより電子不足であり2-クロロヒドロキシピリジンのような塩素原子との立体反発を生じる置換基も存在しないため電子供与性のより高い窒素原子が$\mathrm{Ru^{III}}$側に配位した_N_-(4,0)が_O_-(4,0)よりもかなり優先すると考えられる。しかし、かさ高いベンゾフタルイミド基同士の立体反発があるため_N_-(4,0)が生成することができず、_meridional_型の_N_-(3,1)が生成し、それでもなおベンゾフタルイミド基との立体反発から_cis_型錯体が生成したと推定できる。一方で、立体反発を避けるように_cis_型錯体が先に形成、電子的な安定化を図るため_N_-(4,0)錯体に変化しようとする過程で_meridional_型錯体が生成したという逆の経路も想定できる。なお、LC-MSでは両錯体のピークは${}_{t}R$が近く、混合物として存在している間はどちらが先に生成しているか判別が困難であった。また、_cis_型錯体と_meridional_型錯体の生成比が反応条件によってどのように変化するかについては、現段階では検討を行なっておらず明らかとなっていない。

第 3 節　全合成研究に用いたヘテロ Diels–Alder 反応への適用

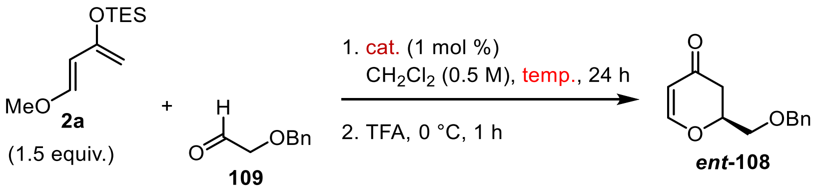
Figure 15 には第 1 部で述べた 18*E*-リングビアロシド C の触媒的不斉全合成において鍵反応として用いたヘテロ Diels–Alder 反応を示したが、両反応ともに収率・選択性に改善の余地を残していた。そこで著者は、創製した新規キラル二核ルテニウム(II,III)錯体に関して、**1)**Ru^{III} の存在に起因した高い Lewis 酸性によって収率が向上する、**2)** 狭い不斉空間によって選択性が向上する、と考え、これらの反応に創製した新規錯体を適用し種々検討を行なうこととした。

Figure 15. Stereoselective hetero-Diels–Alder reactions used in catalytic asymmetric total synthesis of 18*E*-lyngbyaloside C in chapter 1



初めに、エナンチオ選択的なヘテロ Diels–Alder 反応について検討を行なった(Table 8)*。まず、ロジウム触媒の時と同条件に付したところ、*cis* 型塩素錯体において選択性の向上はみられなかったものの、高収率で目的物を得ることができた(entry 4)。一方で、*meridional* 型塩素錯体ではほぼラセミ体を与える結果となった(entry 6)。収率と選択性の向上を指向し温度について検討を行なったが、改善の傾向はみられなかった(entries 3, 6)。また、–20 °C においてカチオン性錯体である *cis* 型トリフリミド錯体を用いた際には収率が低下する結果となった(entry 8)。本反応では–20 °C において *cis* 型塩素錯体を用いる条件を最適条件とし、ロジウム触媒の時と同等の選択性を得るとともに収率の向上を達成することができた(entries 4, 5)。

Table 8. Optimization of reaction conditions [Enantioselective heter-Diels–Alder reaction]



entry	cat.	temp. [°C]	yield^{a,*} [%]	*ee*^{b,*} [%]
1^{c}	Rh$_2$(*S*-BPTPI)$_4$	–20	(83)	(91)
2^{d}	Rh$_2$(*R*-BPTPI)$_4$	–20	(78)	(–90)
3	*cis*-Ru$_2$(*S*-BPTPI)$_4$Cl	0	91	89
4	*cis*-Ru$_2$(*S*-BPTPI)$_4$Cl	–20	90 (90)	90 (91)
5	*cis*-Ru$_2$(*R*-BPTPI)$_4$Cl	–20	(86)	(–91)
6	*cis*-Ru$_2$(*S*-BPTPI)$_4$Cl	–40	81	91
7	*cis*-Ru$_2$(*S*-BPTPI)$_4$NTf$_2$	0	92	87
8	*cis*-Ru$_2$(*S*-BPTPI)$_4$NTf$_2$	–20	80	89
9	*cis*-Ru$_2$(*S*-BPTPI)$_4$NTf$_2$	–40	79	90
10	*mer*-Ru$_2$(*S*-BPTPI)$_4$Cl	–20	79	–13

^{a}Determined by ^{1}H NMR analysis of crude product using 1,1,2,2-tetrachloroethane as an internal standard. ^{b}Determined by chiral HPLC analysis. ^{c}Reported result, reaction time is 18 h$^{3a)}$. ^{d}0.5 mol % cat. data (>3 mmol scale). *(): Isolated scale.

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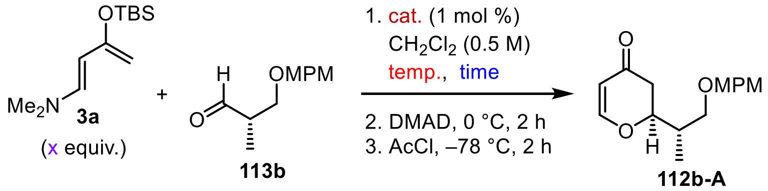
*全合成研究には *R* 体の錯体を用いたが、本検討では *S* 体の錯体を用いて条件検討を行なった。

続いて、ジアステレオ選択的なヘテロ Diels–Alder 反応について検討を行なった(Table 9)。まず、先と同様にロジウム触媒の時と同条件下で反応を行なったところ、*cis* 型塩素錯体、*meridional* 型塩素錯体どちらを用いた場合でも収率は中程度に留まるが選択性の向上がみられた(entries 3, 4)。原料のアルデヒド **113b** はほとんど消失していることから、低温下長時間攪拌したことによりヘテロ Diels–Alder 反応の付加環化中間体が分解していることが示唆された。また、本条件では収率の向上を指向して Rawal ジエン(**3a**)を過剰に用い、余剰分を DMAD(**188**)で処理する工程を含んでいるが*、Lewis 酸の種類によっては本工程が悪影響を及ぼし予期せぬ副生成物を与えることが知見としてあった 65)。加えて、DMAD の添加は生成物 **112b** の単離精製の際に負荷をかけることも第 1 部の全合成研究の際に経験として持ち合わせていた。そこで、反応時間を短縮し、Rawal ジエン(**3a**)の当量を制限することで DMAD の添加工程を省き、これらの問題を解決できないか検討を行なうこととした。*cis* 型塩素錯体、*meridional* 型塩素錯体ともに温度について検討を行なった結果(entries 5, 7, 8, 10, 12, 13)、*meridional* 型塩素錯体かつ 0 °C の条件の際に最も良い結果を与え(entry 10)、ロジウム触媒最適条件の entry 1 の結果と同程度の収率・選択性で目的物を得ること成功した。entry 9 および entry 14 では 0 °C

Table 9. Optimization of reaction conditions [Diastereoselective hetero-Diels–Alder reactions]



entry	cat.	x	temp.[°C]	time [h]	yield^{a,*} [%]	*dr*^{a,*}
1	Rh_2(*S*-BPTPI)$_4$	1.5	–20	19	(88)	(96:4)
2	Rh_2(*R*-BPTPI)$_4$	1.5	–20	19	(97)	(2:>98)
3	*cis*-Ru_2(*S*-BPTPI)$_4$Cl	1.5	–20	19	64	>98:2
4	*mer*-Ru_2(*S*-BPTPI)$_4$Cl	1.5	–20	19	40	98:2
5^b	*cis*-Ru_2(*S*-BPTPI)$_4$Cl	1.03	0	2	75	98:2
6^b	*cis*-Ru_2(*R*-BPTPI)$_4$Cl	1.03	0	2	(78)	(2:>98)
7^b	*cis*-Ru_2(*S*-BPTPI)$_4$Cl	1.03	–20	2	60	98:2
8^b	*cis*-Ru_2(*S*-BPTPI)$_4$Cl	1.03	–40	2	47	>98:2
9^b	*cis*-Ru_2(*S*-BPTPI)$_4$NTf$_2$	1.03	0	2	67	97:3
10^b	*mer*-Ru_2(*S*-BPTPI)$_4$Cl	1.03	0	2	82 (82)	98:2 (98:2)
11^b	*mer*-Ru_2(*R*-BPTPI)$_4$Cl	1.03	0	2	(83)	(2:>98)
12^b	*mer*-Ru_2(*S*-BPTPI)$_4$Cl	1.03	–20	2	73	98:2
13^b	*mer*-Ru_2(*S*-BPTPI)$_4$Cl	1.03	–40	2	64	98:2
14^b	*mer*-Ru_2(*S*-BPTPI)$_4$NTf$_2$	1.03	0	2	69	97:3
15^b	Rh_2(*S*-BPTPI)$_4$	1.03	0	2	52	95:5

^{a}Determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. ^{b}Without 2nd step. *(): Isolated scale.

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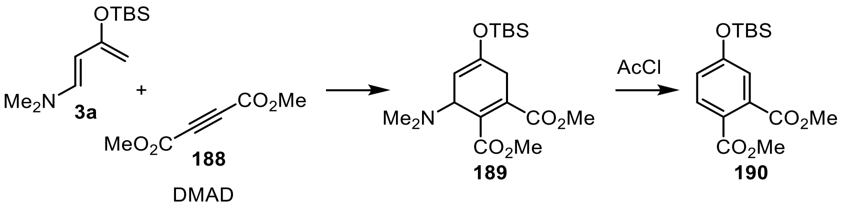
*DMAD(**188**)による Rawal ジエンの処理は以下のように進行する。



の条件下カチオン性のトリフリミド錯体を用いたが、選択性はほぼ維持されるものの収率が低下する結果となった。entry 15 ではルテニウム触媒最適条件下、代わりにロジウム触媒を用いたところ、収率が中程度にとどまった。また、entry 11 では *R* 体の錯体を用いる matched pair での条件になるが、entry 2 のロジウム触媒最適条件下の収率を 10 ポイント程度下回る結果となった。またこの際、*R* 体の *cis* 型塩素錯体も検討したが、同様に収率が低下する結果となった(entry 6)*。以上より、全合成研究に必要とする基質(mismatched pair でのケース)においては Rawal ジエン(**3a**)の当量、反応時間を削減し、DMAD の添加工程を省いても *meridional* 型塩素錯体を用いることで同等の収率と選択性を得ることができた。Matched pair のケースでは 10 ポイント程度収率が低下する結果となったが、選択性を維持したまま同様に当量・反応時間・工程数の削減を行なうことが可能であった。

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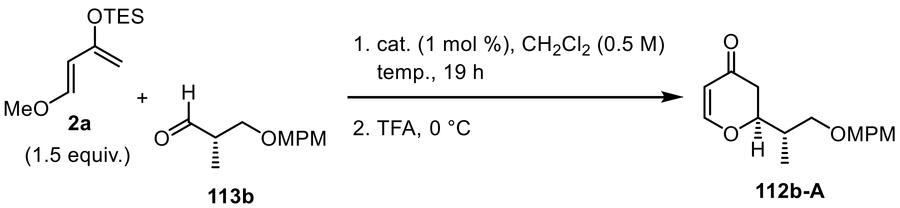
*良好な結果が得られなかった原因は定かではないが、反応性の高い Rawal ジエンと Lewis 酸性が高いと想定されるルテニウム錯体の組み合わせでは、*meridional* 型錯体よりも不斉反応場が開けている *cis* 型錯体では望みとしない副反応が進行したと推定している。

Danishefsky ジエン(2a**)を用いてジアステレオ選択的なヘテロ Diels–Alder 反応を行なった結果を以下に示す。この場合も *meridional* 型錯体が良い結果を与えたが、Rawal ジエン(**3a**)を用いた際の結果を上回ることはできなかった。



entry	cat.	temp. [°C]	yield^a [%]	*dr*^{a} [%]
1	*cis*-Ru_2(*S*-BPTPI)$_4$Cl	r.t.	3	87:13
2	*mer*-Ru_2(*S*-BPTPI)$_4$Cl	r.t.	14	89:11
3	*cis*-Ru_2(*S*-BPTPI)$_4$Cl	0	2	–
4	*mer*-Ru_2(*S*-BPTPI)$_4$Cl	0	13	91:9
5	*cis*-Ru_2(*S*-BPTPI)$_4$NTf$_2$	0	2	87:13
6	*mer*-Ru_2(*S*-BPTPI)$_4$NTf$_2$	0	42	87:13

^{a}Determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

***中性錯体とカチオン性錯体では後者の方がより電子不足になるために Lewis 酸性が高いと推定される。しかしながら、現段階ではそれを定量的に評価することができておらず、今後の大きな課題となっている。また、ベンジルオキシアセトアルデヒド(**109**)や Rawal ジエン(**3a**)とカチオン性錯体の組み合わせで収率が中性錯体よりも低下した原因については、反応性の高い者同士の組み合わせになることで望みとしない反応が中性錯体よりも優先したためと考えられる。

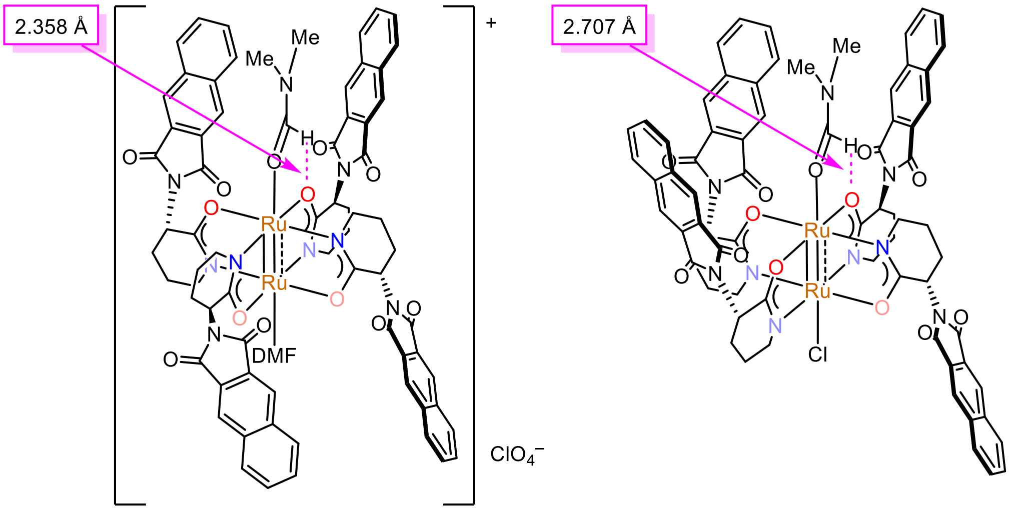
****カチオン性錯体においてカウンターイオンがアルデヒドの配位を阻害しないと仮定する場合、カチオン性錯体は中性錯体と異なり 2 つのルテニウム原子が反応に関与することができる。したがって、触媒回転数が中性錯体よりも高くなると考えられるが、本反応系ではカチオン性錯体が反応条件の最適化において良好な結果を与えなかったため検討は行なっていない。

******cis* 型錯体と *meridional* 型錯体を使い分ける明確な基準は明らかとなっていないが、ヘテロ Diels–Alder 反応の予備検討において、α 位が分岐したアルデヒドに関しては *meridional* 型錯体の方が良い結果を与える傾向にあった。

第 4 節　立体反応経路の考察

創製したキラル二核ルテニウム錯体の X 線結晶構造解析の結果から、DMF のホルミル水素原子とアミダート配位子の酸素原子間の距離がそれらの Van deer Waals 半径の和(2.72 Å)よりも短くなっていることから水素結合の存在が示唆され、両錯体ともにロジウム錯体同様 Corey らの提唱しているホルミル C–H…O 水素結合コンセプト [35]が適用できると考えられる(Figure 16)。

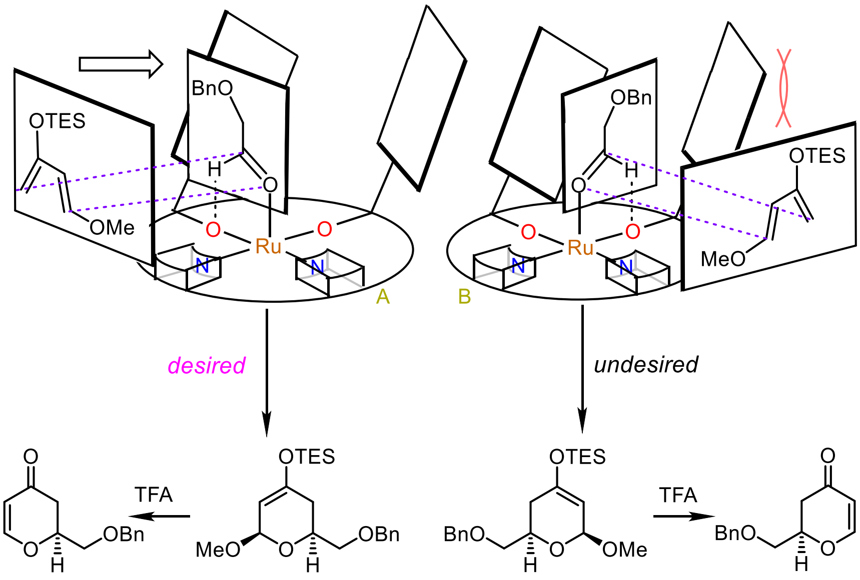
Figure 16. Chemical structure of *cis*-Ru_2(*S*-BPTPI)$_4$$ClO_4$·2DMF (left) and *mer*-$Ru_2$(*S*-BPTPI)$_4$Cl·DMF (right)



cis-Ru_2(*S*-BPTPI)$_4$$ClO_4$·2DMF　　*mer*-$Ru_2$(*S*-BPTPI)$_4$Cl·DMF

エナンチオ選択的なヘテロ Diels–Alder 反応においては、用いた *cis* 型錯体は同じ配位子を有する Rh_2(*S*-BPTPI)$_4$ と類似の骨格を有しており、発現した選択性も傾向が同じであることから、ロジウム触媒と同様の立体反応経路で進行すると考えられる(Figure 17)。

Figure 17. Plausible stereochemical cource of enantioselective hetero-Diels–Alder reaction catalyzed by *cis*-Ru_2(*S*-BPTPI)$_4$Cl



続いて、ジアステレオ選択的なヘテロ Diels–Alder 反応については、*meridional* 型錯体は 2 つのルテニウム原子を挟んで対称性を持たない構造をしているため、まずどちらの面で進行

するかについて立体反応経路を考察する必要がある。しかし、塩素錯体は配位子が1つだけ張り出している側のルテニウム原子に塩素原子が結合しているため、アルデヒドはこちら側に配位することができず、3つの配位子が張り出したより混み入った側の二価のルテニウム原子に配位すると考えられる(Figure 18)。したがって、中間体はアルデヒドの配位方向に応じてA、B、Cの3種類が想定される(Figure 19)*。Figure 19にて桃色で示したベンゾフタルイミド基は、アルデヒドの面に対するジエンの接近を妨げる。中間体Bではアルデヒドのどちらの面もベンゾフタルイミド基によってふさがれてしまっているためジエンは接近することができず、Diels–Alder反応は起こらないと考えられる。以上より、本反応の立体反応経路は中間体AまたはCを想定できる。

Figure 18. Coordination site of *mer*-Ru_2(*S*-BPTPI)$_4$Cl

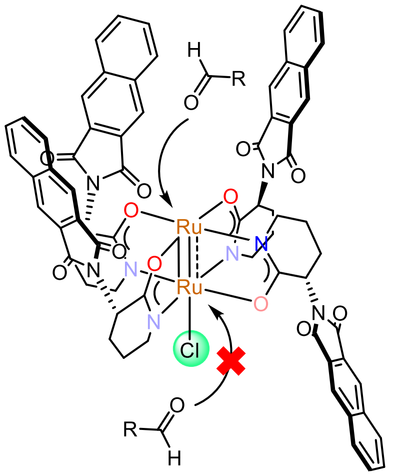
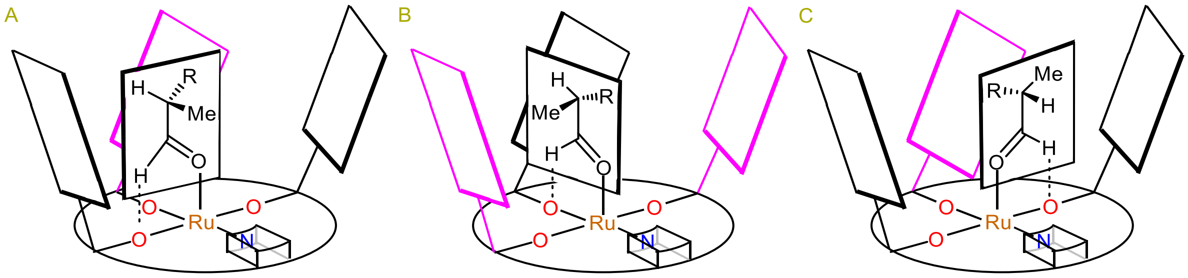


Figure 18. Plausible intermediate complexes between *mer*-Ru_2(*S*-BPTPI)$_4$Cl and chiral aldehyde **113b** (R = CH_2OMPM)



アルデヒドの置換基と3つのベンゾフタルイミド基との立体反発を考慮すると、より空いた位置に置換基が収まる中間体Aが優先して生成すると考えられる(Figure 19)。また、中間体Cに対するジエンの接近は張り出したベンゾフタルイミド基との立体反発から不利となる。したがって、中間体Aに対してルテニウム錯体との立体反発を避けるようにシロキシ基を外側に向けてジエンが接近することで、実験結果に合致する優先絶対配置をもつ*endo*付加環化体が得られたと考えられる**,***。

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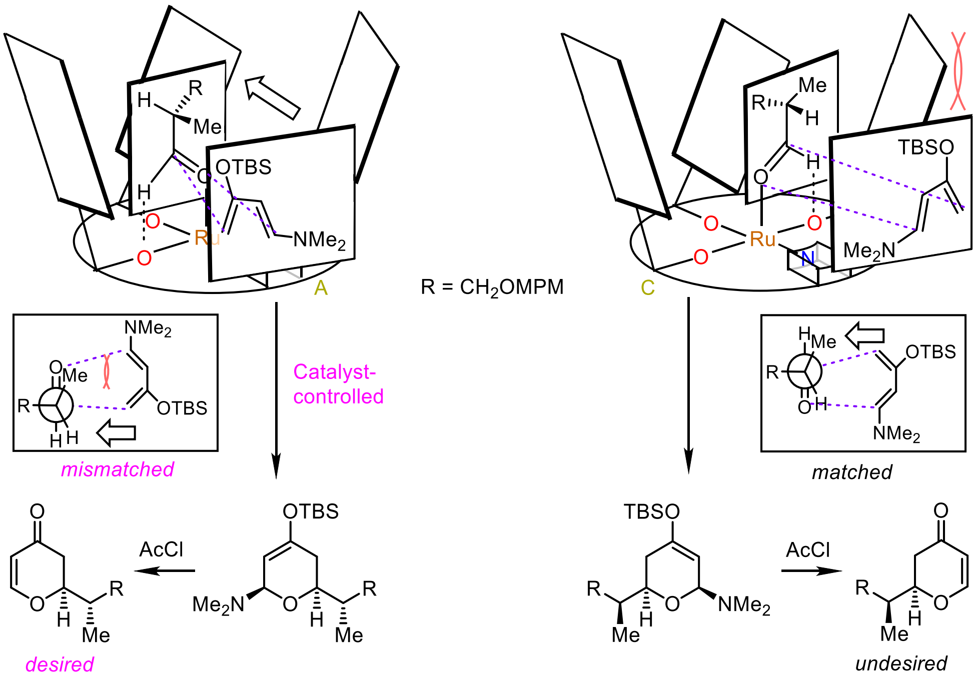
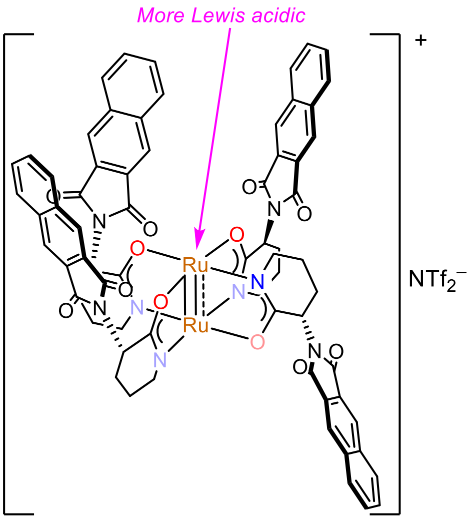
*エナンチオ選択的なヘテロDiels–Alder反応において*meridional*型塩素錯体はほぼラセミ体を与える結果だった。本反応は触媒非存在下ではほとんど進行しないので(収率<2%)、触媒関与で反応が進行していると考えられる。ベンジルオキシアセトアルデヒドはアルデヒドα位に分岐がないことに加え、おそらくフェニル基がベンゾフタルイミド基と相互作用することにより、望みとしない反応が進行する中間体Cが中間体Aと同等以上に生成したため、先の実験結果が得られたと考えられる。

Figure 19. Plausible stereochemical cource of diastereoselective hetero-Diels–Alder reaction catalyzed by *mer*-Ru_2(*S*-BPTPI)$_4$Cl

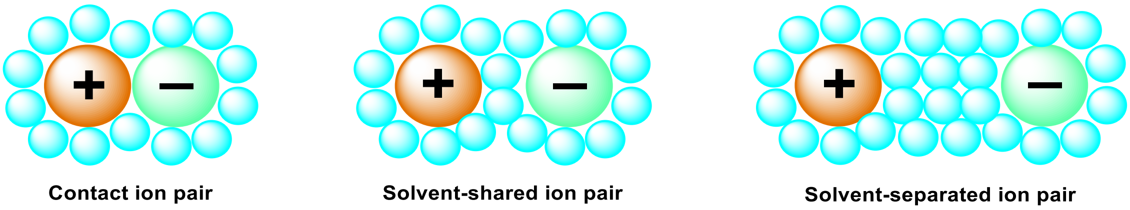


** 配位場が 2 つ考えられるカチオン性の *meridional* 型トリフリミド錯体を用いた場合でも非常に高いジアステレオ選択性が発現したことについて主に以下の理由が考えられる。

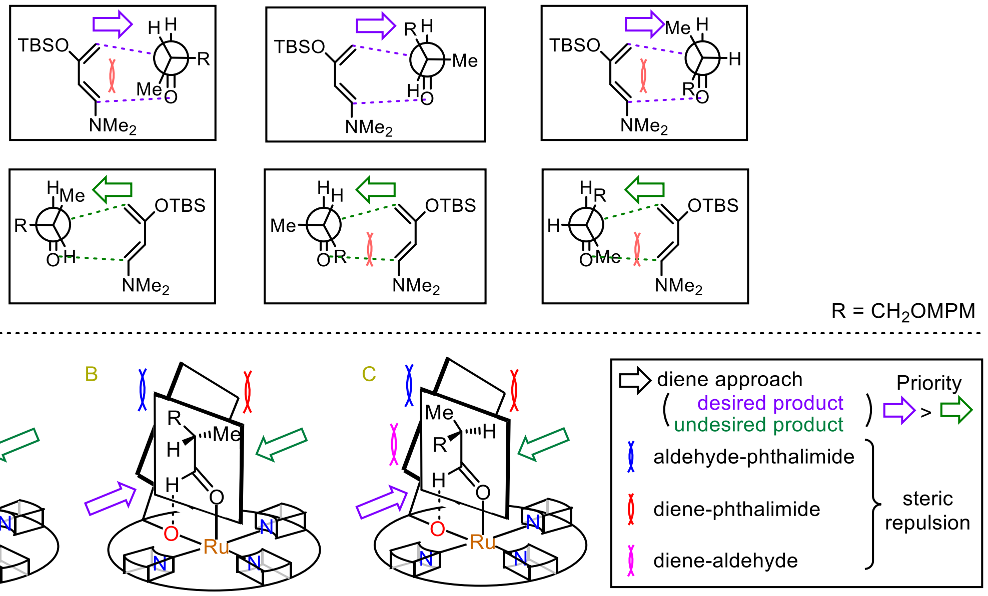
1. カチオン性 *meridional* 型錯体の結晶構造はまだ明らかとなっていないため、塩素錯体時の構造をカチオン性錯体にしても維持しているかは定かではない。しかし、溶液中でも保持していると仮定した場合、より電子求引性の酸素原子が 3 つ置換したルテニウム原子の方がより Lewis 酸性が高いと考えられ(右図)、塩素錯体同様混み入った側でヘテロ Diels–Alder 反応が進行したと推定できる。



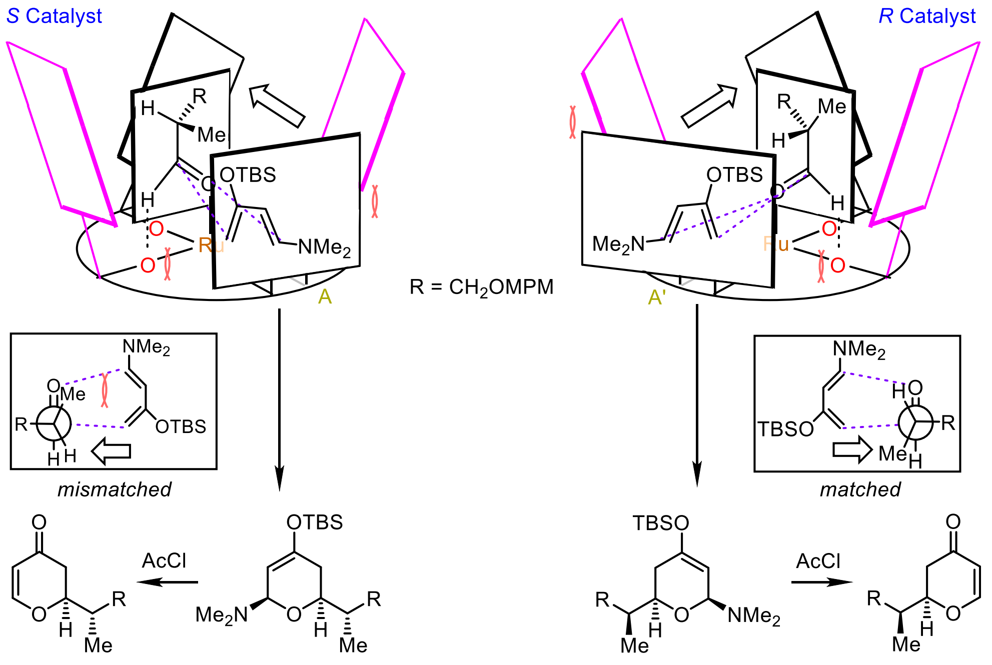
2. 溶液中においてイオンペアーは下図の 3 種類が考えられる。本反応ではジクロロメタンを溶媒としているため、contact ion pair もしくは solvent-shared ion pair の 2 パターンを想定することができる。*meridional* 型トリフリミド錯体の場合、立体的により空いた側にカウンターアニオンが局在化することでアルデヒドの配位を妨げ、より混み入った側での反応を促したと考えることができる。



3. 上記2つに当てはまらずより空いた側でヘテロ Diels–Alder 反応が進行することも十分想定可能であり、立体反応経路は数種の立体反発に基づいて説明できる(下図)。なお、紫色で示した矢印の方からジエンが接近して Diels–Alder 反応が進行したときに全合成研究に望みとするジアステレオマー(**112b-A**)を与える。 *cis* 型錯体とは異なりベンゾフタルイミド基の壁は1つしかなく、アルデヒドのどちらの面もふさいでいないため、両面で反応が進行する可能性が考えられる(下図上段)。緑色矢印の接近は張り出したベンゾフタルイミド基との立体反発から不利になると考えられるため(下図下段、赤色立体反発)、ジエンの接近は紫色矢印が優先すると想定でき、中間体は A、B、C の 3 種類が想定できる。このとき、置換基とベンゾフタルイミド基との立体反発(青色立体反発マーク)を考慮すると、中間体 A が最も生成しやすい。したがって、アルデヒドの置換基とジエンとの間に立体反発(桃色立体反発マーク)が生じる mismatched pair にはなるが中間体 A を経て反応が進行することで実験結果に合致する付加環化体が得られたと考えられる。



*** *R* 体の錯体を用いる matched pair の場合ではロジウム触媒最適条件の収率を 10 ポイント程度下回る結果になったが、*meridional* 型塩素錯体を用いる場合では優先する中間体においても張り出したベンゾフタルイミド基とジエンとの間に立体反発が少ないながらも生じていると考えられ、その結果、収率が低下したと考えられる。



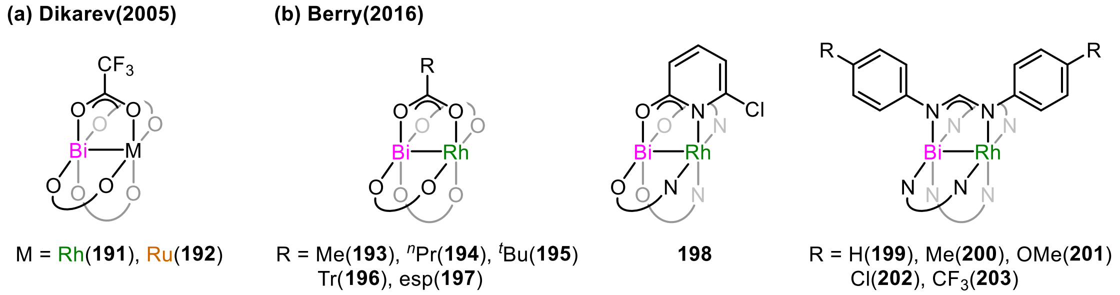
第 2 章　外輪型ヘテロ二核遷移金属錯体の創製

第 1 節　背景

外輪型二核構造を有する金属錯体は、既に紹介したロジウム(II)錯体やルテニウム(II,III)錯体のようなホモ二核錯体だけではなく、異なる金属原子を 2 つ組み込んだヘテロ二核錯体も合成されている66)。

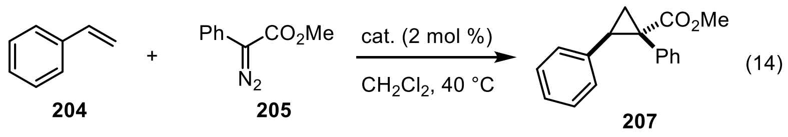
2005 年に Dikarev らは金属原子の 1 つとして典型元素であるビスマスを組み込んだビスマス/ロジウム、ビスマス/ルテニウムヘテロ二核錯体の合成を報告した(Figure 20, (a))66a)*。良好に錯体を調製することができたビスマス/ロジウム錯体に関しては引き続き研究が行なわれ66b–66d)、2016 年には Berry らによって数種の新たなビスマス/ロジウム錯体の合成が報告された(Figure 20, (b))66e–66g)。

Figure 20. Reported bismuth-based heterobimetallic paddlewheel complexes

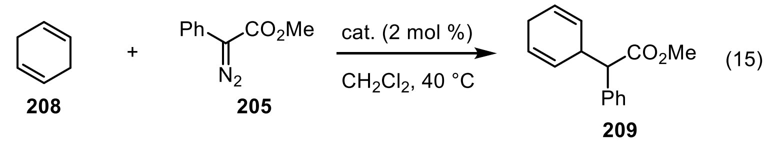


本錯体を用いた触媒反応の報告は、2009 年に Davies らによって報告されたシクロプロパン化反応、C–H 挿入反応が第一報となる(Figure 21)66h)。シクロプロパン化反応(eq. 14)、C–H 挿入反応(eq. 15)ともに同じ配位子を有する二核ロジウム(II)触媒と同等の収率と選択性を示し、両反応が競合する基質 **210** においても、二核ロジウム(II)触媒と大きな差は見られない結果が得られている(eq. 16)。

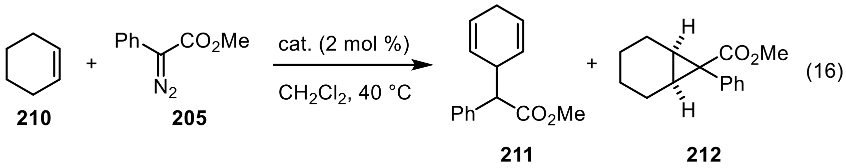
Figure 21. Bismuth-rhodium paddlewheel carboxylates as catalyst for metal carbenoid transformations



cat.	yield [%]	*de* [%]
BiRh(TFA)$_4$	94	>95
Rh$_2$(TFA)$_4$	96	>95



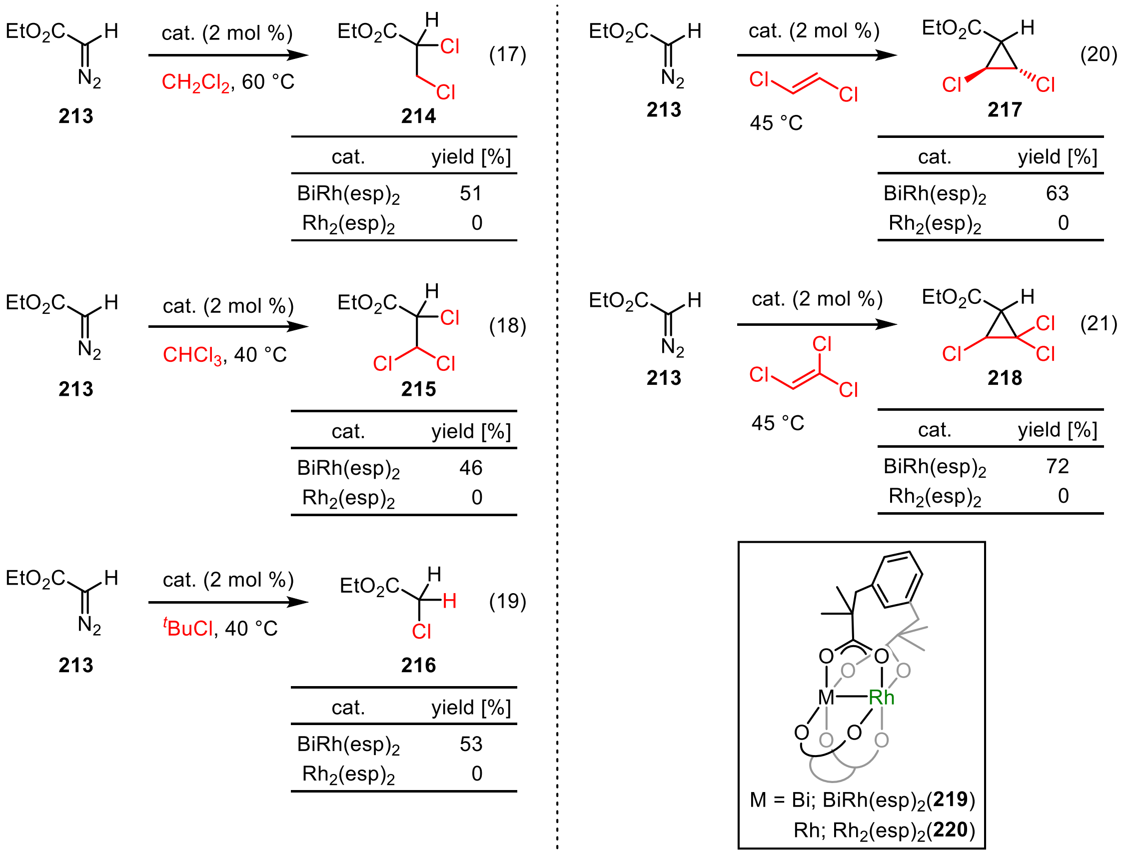
cat.	yield [%]
BiRh(TFA)$_4$	84
Rh$_2$(TFA)$_4$	74



cat.	yield [%]	**211 / 212**
BiRh(TFA)$_4$	94	79:21
Rh$_2$(TFA)$_4$	96	84:16

2018 年 Fürstner らは、$\mathrm{BiRh(esp)_2}$(**219**)存在下において、ジアゾ化合物 **213** から生じたアクセプター型カルベン種がハロアルカン溶媒と反応し、C–Cl 挿入反応を引き起こすことを見出した(Figure 22, eq. 17, 18)[66i]。^{t}BuCl を溶媒とした際には、H–Cl 脱離[67]が起こり **216** を与え(Figure 22, eq. 19)、電子不足なハロアルケンを用いた場合ではシクロプロパン化反応が進行することが明らかとなった(Figure 22, eq. 20, 21)。これらの反応は同じ配位子をもつ $\mathrm{Rh_2(esp)_2}$(**220**)を用いても望みとする化合物が一切得られないことが確認されており、ビスマス/ロジウム錯体の優位性を示す結果となっている。

Figure 22. Bismuth-rhodium paddlewheel carboxylates catalyses with haloalkane solvents



eq. 17

cat.	yield [%]
$\mathrm{BiRh(esp)_2}$	51
$\mathrm{Rh_2(esp)_2}$	0

eq. 18

cat.	yield [%]
$\mathrm{BiRh(esp)_2}$	46
$\mathrm{Rh_2(esp)_2}$	0

eq. 19

cat.	yield [%]
$\mathrm{BiRh(esp)_2}$	53
$\mathrm{Rh_2(esp)_2}$	0

eq. 20

cat.	yield [%]
$\mathrm{BiRh(esp)_2}$	63
$\mathrm{Rh_2(esp)_2}$	0

eq. 21

cat.	yield [%]
$\mathrm{BiRh(esp)_2}$	72
$\mathrm{Rh_2(esp)_2}$	0

これと同時に Davies らはキラルなビスマス/ロジウム錯体 $\mathrm{BiRh(\mathit{S}\text{-}TBSP)_4}$(**226**)を新たに開発し、本錯体を用いた不斉シクロプロパン化反応、不斉 C–H 挿入反応を報告した(Figure 23)[66j]。シクロプロパン化反応では、全体的に収率は同じ配位子を有するロジウム(II)錯体(**227**)よりも劣る結果となったが、エナンチオ選択性は上回る結果を示した(eq. 22)**。1,4-シクロヘキサジエン(**208**)を基質とした C–H 挿入反応の際には、$\mathrm{BiRh(\mathit{S}\text{-}TBSP)_4}$(**226**)は $\mathrm{Rh_2(\mathit{S}\text{-}TBSP)_4}$(**227**)よりも非常に反応速度が遅く、同程度の結果を得るために 720 倍もの時間を要している(eq. 23)。これはシクロヘキサン(**224**)を基質とした際にも同様であり、ロジウム触媒を上回る結果は得られていない(eq. 24)

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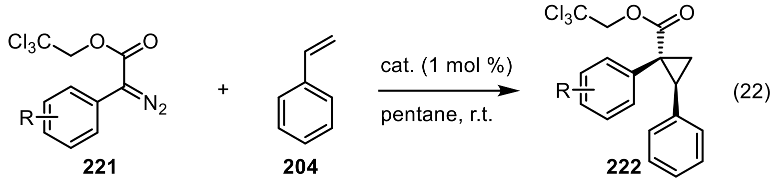
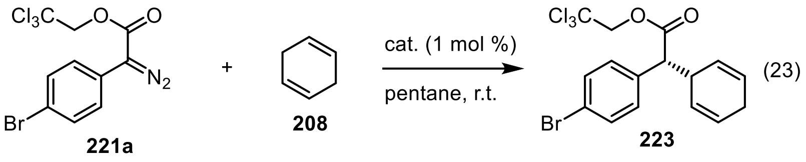
*Dikarev らの計算結果より、Mayer 結合次数に関して Bi–Rh 結合は 1.0、Bi–Ru 結合は 1.2 であることが明らかとなっている[66a]。

**ごくごく最近、Fürstner らによってキラルなビスマス/ロジウム錯体 $\mathrm{BiRh(\mathit{S}\text{-}PTTL)_4}$ を用いた不斉シクロプロパン化反応が報告され、同配位子を有するロジウム錯体 $\mathrm{Rh_2(\mathit{S}\text{-}PTTL)_4}$ よりも高いエナンチオ選択性で目的物が得られている[66k]。

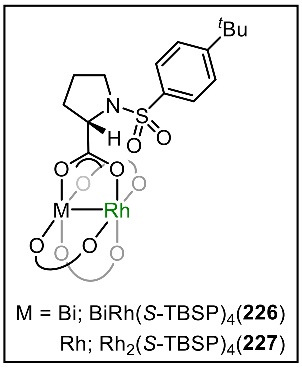
Figure 23. Chiral bismuth-rhodium paddlewheel carboxylates as catalyst for carbenoid transformations

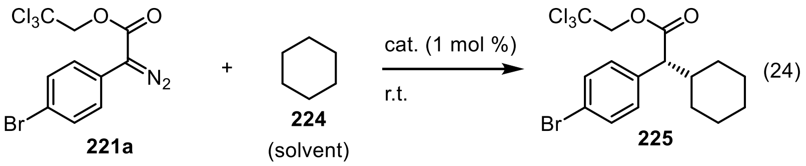


$\mathrm{BiRh}(S\text{-TBSP})_4$: up to 88% yield, 93% *ee*
$\mathrm{Rh}_2(S\text{-TBSP})_4$; up to 96% yield, 84% *ee*



cat.	time	yield [%]	*ee* [%]
$\mathrm{BiRh}(S\text{-TBSP})_4$	12 h	75	71
$\mathrm{Rh}_2(S\text{-TBSP})_4$	1 min	82	84

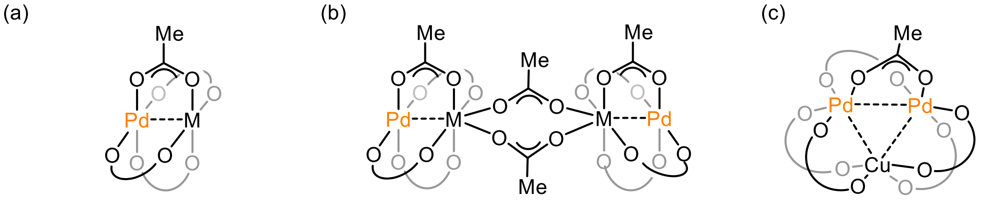




cat.	time	yield [%]	*ee* [%]
$\mathrm{BiRh}(S\text{-TBSP})_4$	15 h	78	86
$\mathrm{Rh}_2(S\text{-TBSP})_4$	15 min	97	90

さて、第 1 章の冒頭でも述べた「ロジウム触媒からの脱却」という観点も重要である。ロジウム原子を含まない外輪型ヘテロ二核錯体に関しては、パラジウムを基盤とした錯体が 1968 年に Claridge らによってはじめて合成された 66l)。対金属原子としてタリウム 66m)およびカドミウム 66n)を組み込んだものはそれぞれ別のグループによって合成され、X 線結晶構造解析により分子構造が明らかとなっている。その後、Vargaftik らによってほとんどの錯体に関して X 線結晶構造解析が行なわれ、同様に分子構造が明らかとなった 66o–66t)。パラジウムの対金属原子は多様性に富んでおり、コバルトやニッケル、銅といった第 4 周期の遷移金属 66l,66p,66r)のみならず、アルカリ金属 66l,66q)やランタノイド 66n,66p,66s,66u)を含んだ錯体の合成も行なわれている*。どの錯体も外輪型構造を有しているが、対金属原子によって 3 種類の異なる構

Figure 24. Known molecular structures of palladium-based heterobimetallic paddlewheel acetate complexes



M = Ca(**228**), Sr(**229**), Ba(**230**)
Mn(**231**), Co(**232**), Ni(**233**)
Zn(**234**), Tl(**235**)

M = Nd(**236**), Sm(**237**), Eu(**238**)
Tm(**239**), Yb(**240**), Ce(**241**)
Cd(**242**),

243

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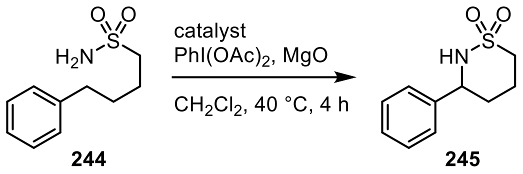
*以降対金属原子を指定しない場合は、パラジウム/M 錯体と表記する。

造をもち、(a)これまでに紹介したような一般的な外輪型二核構造をもつもの以外にも、(b)対金属原子同士がさらに架橋され二量体のような構造をもつもの、(c)3 つの金属原子を含み三つ葉型に架橋されたものが存在していることが分かっている(Figure 24)。

これらの錯体すべてに共通する事項として、中心金属原子間距離がそれらの Van deer Waals 半径の和よりも短くなっているが、直接的な結合が存在するかどうか詳細には明らかとなっていない点があげられ、先述の二核ロジウム錯体、二核ルテニウム錯体、ビスマス/ロジウム錯体とは大きく異なっている**。

このパラジウム/M 錯体を用いた反応例は、Chuang らによるパラジウム/コバルト酢酸錯体(**232**)を用いた C–H アミノ化反応のみに限られている68)。本反応では、酢酸コバルトもしくは酢酸パラジウム単体だけでは反応が進行せず、あらかじめ調製したパラジウム/コバルト酢酸錯体(**232**)を添加するか、酢酸コバルトと酢酸パラジウムを同時に添加する必要がある(eq. 25)。この結果から、パラジウム–コバルト原子間の協働作用が重要であることがうかがえるが、別々に添加を行なっても同等の結果が得られることから、外輪型二核構造が必要でない可能性も示唆されている。Chuang らは種々の基質に関して C–H アミノ化反応を検討しているが、そのほとんどが中程度の収率にとどまっている。



(25)

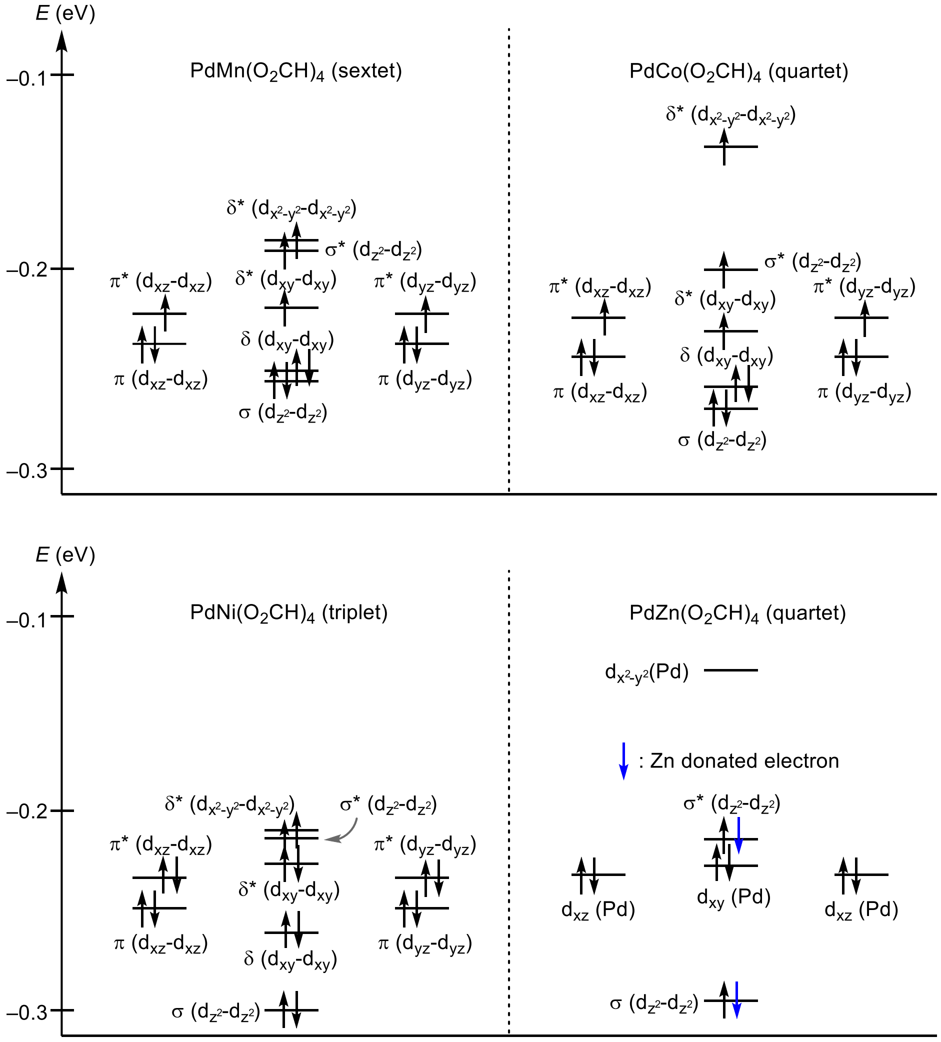
catalyst	mol %	TM/SM ratio
$PdCo(OAc)_4$	5	53:47
$Co(OAc)_2$	10	0:100
$Pd(OAc)_2$	10	0:100
$Pd(OAc)_2/Co(OAc)_2$	10/10	49:51

上記以外にも、白金を基盤とした錯体66w–66δ)や、モリブデンを基盤とした錯体66ε–66θ)も報告されており、多様な金属種に関して外輪型ヘテロ二核錯体の研究がなされている。

このような中、著者はパラジウム/M 錯体に関して、本錯体を用いた反応開発がほとんど未開拓であることに加え、従来の外輪型二核遷移金属錯体とは異なる中心金属原子間の協働作用があることによって新たな反応系を開拓できると期待し、本錯体に関する研究に取り組んだ。

**Zhao らによってパラジウム/M (M = マンガン、コバルト、ニッケル、亜鉛)ギ酸錯体アセトニトリル付加物に対して、金属原子間結合に関する DFT 計算が行なわれている(下図)69)。この結果からマンガンでは単結合と二重結合の間の結合を形成すると推定できるのに対し、コバルト・ニッケル・亜鉛では結合を形成しないと推定できる。

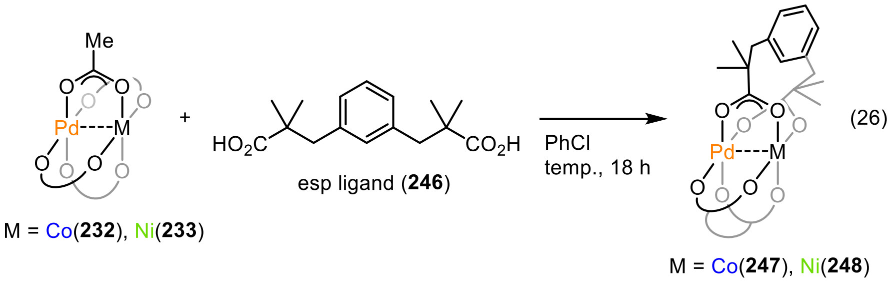
Electron configulations of metal–metal bonding in each stable Pd–M-MeCN complex



第 2 節　架橋型パラジウム/コバルト，パラジウム/ニッケル外輪型二核錯体の創製

Chuang らの結果[68]からパラジウム/コバルト酢酸錯体は反応系中で外輪型構造を維持していない可能性も考えられた。そこで、外輪型構造をより剛直にするためにテザー型架橋配位子を組み込んだパラジウム/M 錯体の合成を行なうこととし、対金属原子としてコバルトおよびニッケルを設定、テザー型架橋配位子として Du Bois らが報告した esp 配位子(**246**)[70]を用いることとした。

ロジウム錯体やルテニウム錯体同様に配位子交換をクロロベンゼン中加熱還流条件下で行なうと、反応液が黒変し望みとする錯体を得ることができなかった(eq. 26)。ここで、反応温度を 70 °C にして再度配位子交換を行なったところ、TLC 上で原料および配位子とは異なる新たな単一のスポットが確認された。粗生成物はシリカゲルカラムクロマトグラフィーで精製可能であり、精製した化合物について質量分析を行なった結果、同位体ピークパターンから望みとするパラジウム/コバルト、もしくはパラジウム/ニッケルの両金属原子を含んだ esp 錯体、PdCo(esp)$_2$(**247**)および PdNi(esp)$_2$(**248**)が得られていることが分かった*。また X 線結晶構造解析により、両錯体ともに外輪型二核構造を有していることを明らかにした(Figure 25, 26)。続けて、創製した両錯体を種々の触媒反応に適用したが、現段階では有用な結果が得られておらず、今後の発展を期待したい。



temp. [°C]	yield [%]
140	decomp.
70	>99

Figure 25. Left: thermal-ellipsoid representation of H_2O adduct of PdCo(esp)$_2$ (**247**), (50% probability elipsoids). Right: chemical structure of PdCo(esp)$_2$·2H_2O. hydrogen atoms were omitted for clarity.

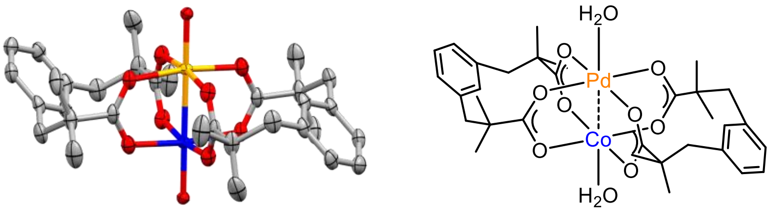
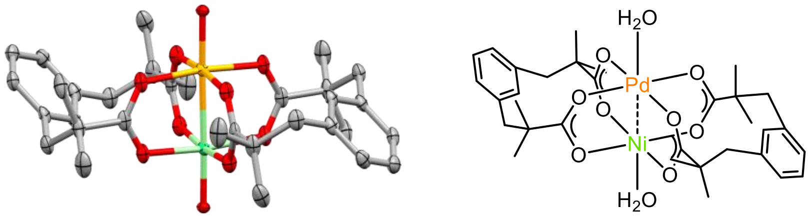


Figure 26. Left: thermal-ellipsoid representation of H_2O adduct of PdCo(esp)$_2$ (**248**), (50% probability elipsoids). Right: chemical structure of PdCo(esp)$_2$·2H_2O. hydrogen atoms were omitted for clarity.



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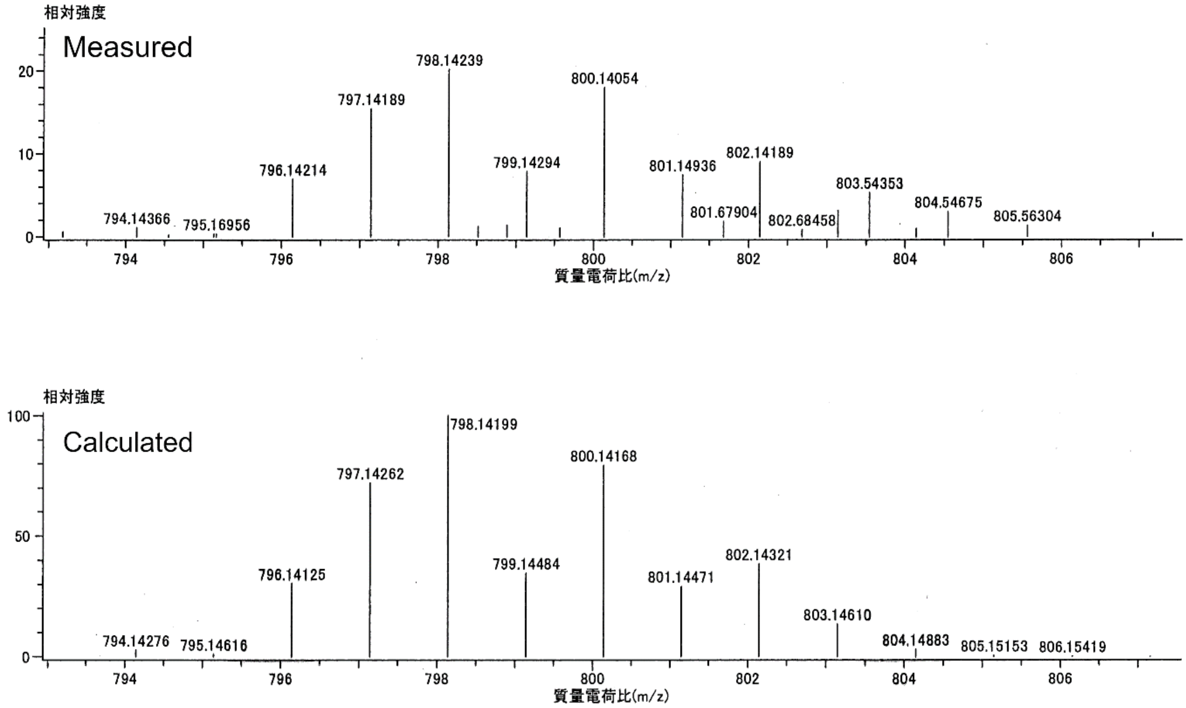
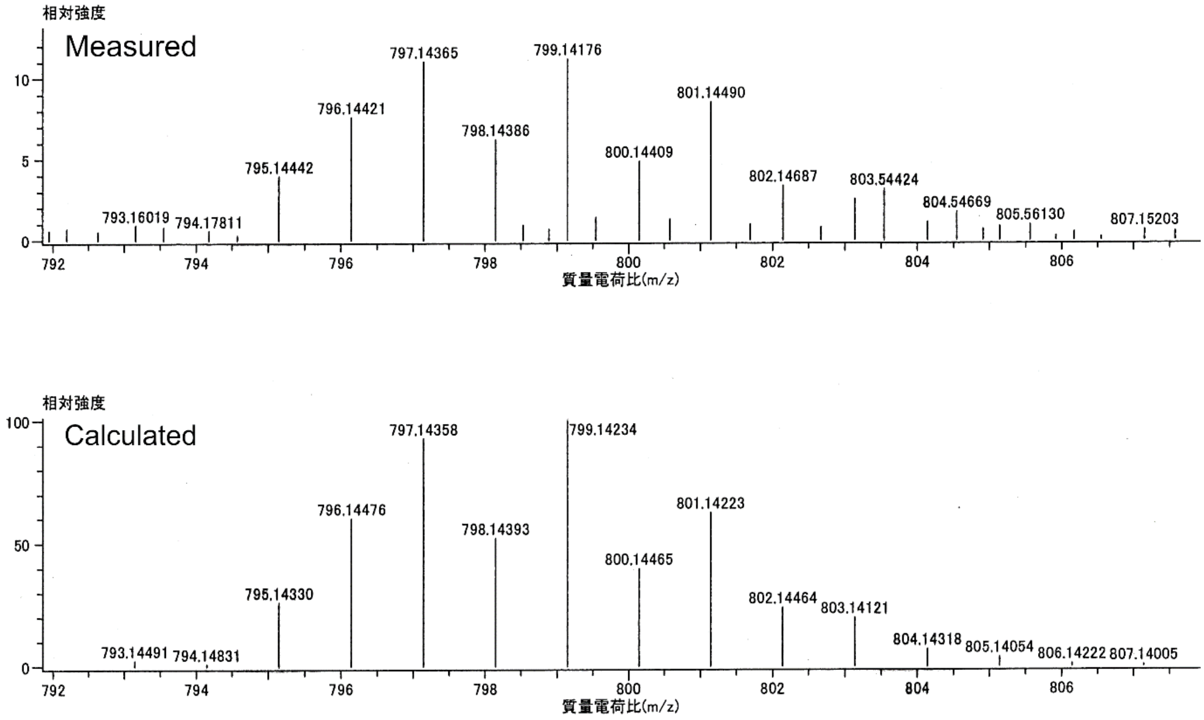
*質量分析によって得られた同位体ピークパターンを下図に示す。

PdCo(esp)$_2$; Detected as [M+acetone+Na]$^+$



PdNi(esp)$_2$; Detected as [M+acetone+Na]$^+$



結語

以上著者は、外輪型二核遷移金属錯体を機軸に種々の研究に取り組んだ。本研究の成果を総括すると次のようになる。

1. 所属研究室が開発したキラル二核ロジウム(II)アミダート錯体 $Rh_2(S\text{-BPTPI})_4$ を不斉 Lewis 酸触媒として用いたヘテロ Diels–Alder 反応について、キラルなアルデヒドを用いたジアステレオ選択的なヘテロ Diels–Alder 反応へ適用系を拡張した。また、これまで推定構造であった本錯体に関して X 線結晶構造解析によりその構造を明らかとした。

2. $Rh_2(S\text{-BPTPI})_4$ を用いた不斉ヘテロ Diels–Alder 反応の応用研究として海洋産抗腫瘍活性天然物 18*E*-リングビアロシド C の触媒的不斉全合成に取り組んだ。不斉ヘテロ Diels–Alder 反応を第 1 工程としたそれぞれ 10 工程および 16 工程の変換によって、標的化合物のコア構造であるマクロラクトンを構築するための 2 つのフラグメントを合成した。これらのカップリングはピリジルチオエステルと銀塩を組み合わせた手法によって達成することができ、続く 2 工程の変換でコア構造の構築に成功した。その後、所属研究室が開発した含リン脱離法によるグリコシル化反応によって糖部を、新規に開発したスルホンを用いた Julia オレフィン化によってジエン側鎖部を導入し、総工程数 37 工程、最長直線工程において総収率 2.1%で 18*E*-リングビアロシド C の全合成を達成した。

3. 外輪型二核ロジウム(II)触媒からの脱却と凌駕、新規反応系開拓を指向して、新規キラル外輪型二核ルテニウム(II,III)錯体 *cis*-$Ru_2(S\text{-BPTPI})_4Cl$ および *mer*-$Ru_2(S\text{-BPTPI})_4Cl$ を開発した。X 線結晶構造解析により両錯体の構造を明らかにし、本錯体を上記の全合成研究に用いたヘテロ Diels–Alder 反応に適用することによって、創製した二核ルテニウム(II,III)触媒が二核ロジウム(II)触媒を代替し、触媒性能として凌駕することを示すことができた。

4. 金属原子間の協働作用に着目し、異種金属原子を含んだ外輪型二核遷移金属錯体において剛直なテザー型架橋配位子を組み込むことで、新規外輪型パラジウム/コバルト、パラジウム/ニッケルヘテロ二核錯体を合成した。

以上の結果は、現在も広く利用されている二核ロジウム(II)錯体、その二核ロジウム(II)錯体を代替する選択肢としての二核ルテニウム(II,III)錯体、両者の有用性を示すものである。本研究が外輪型二核遷移金属錯体に関する研究の一助となること、全合成研究を通じて医薬品リード化合物の創出に貢献することを期待する。

Experimental Section

General

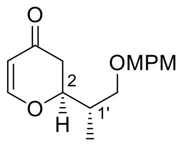
Melting points were determined on a Yamato melting point apparatus model MP-21 and were uncorrected. Optical rotations were recorded on JASCO P-1030 digital polarimeter. IR spectra were recorded on JASCO FT/IR-5300 spectrophotometer and absorbance bands are reported in wavenumber (cm^{-1}). ^{1}H NMR spectra were recorded on JEOL JNM-ECS 400 (400 MHz), JEOL JNM-ECX 400P (400 MHz), JEOL JNM-ECA 500 (500 MHz) spectrometers with tetramethylsilane (δ_H 0.00), chloroform-d_1 (δ_H 7.26) or benzene-d_6 (δ_H 7.16) as an internal standard. Coupling constants (*J*) are reported in hertz (Hz). Abbreviations of multiplicity are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Data are presented as follows: chemical shift, multiplicity, coupling constants, integration and assignment. 18*E*-lyngbyaloside C numbering is used for proton assignments of all intermediates. ^{13}C NMR spectra were recorded on JEOL JNM-ECS 400 (400 MHz), JEOL JNM-ECX 400P (400 MHz), JEOL JNM-ECA 500 (500 MHz) spectrometers with chloroform-d_1 (δ_C 77.0) as an internal standard. ESI-HRMS was measured with Thermo Scientific Exactive spectrometer and ESI-LRMS was measured with ACQUITY QDa spectrometer.

Column chromatography was carried out on Kanto silica gel 60 N (40–50 mesh). Analytical thin layer chromatography was carried out on Merck Kieselgel 60 F_{254} plates. Visualization was accomplished with ultraviolet light and anisaldehyde or phosphomolybdic acid stain, followed by heating.

Reagents and solvents were purified by standard means or used as received unless otherwise noted. Acetyl chloride (AcCl) was refluxed with PCl_5 then distilled from dimethylaniline prior to use. DMF was dried with MS4A or distilled from calcium hydride prior to use. Diisopropylethylamine (^{i}Pr$_2$NEt) and MeOH were distilled from calcium hydride prior to use. 1,4-Benzoquinone was sublimated prior to use. All reactions were conducted under an argon atmosphere. Dehydrated stabilizer-free THF, dichloromethane (CH_2Cl_2) and toluene were purchased from Kanto Chemical Co., Inc.

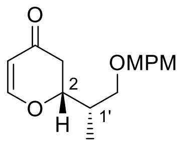
Part 1 Chapter 2 Section 1

Typical procedure for diastereoselective hetero-Diels–Alder reactions with Rawal's diene: (*S*)-2-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-2,3-dihydro-4*H*-pyran-4-one (112b-A)[20d)](TS10003)



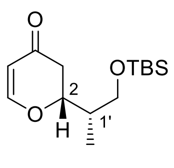
Rawal's diene (**3a**) (102 mg, 0.45 mmol) was added via syringe to a solution of aldehyde **113b** (62.5 mg, 0.30 mmol) and Rh_2(*S*-BPTPI)$_4$(**1**) (4.30 mg, 0.003 mmol, 1 mol %) in CH_2Cl_2 (0.6 mL) at –20 °C. After stirring for 19 h at this temperature, DMAD (85.3 mg, 0.60 mmol) in CH_2Cl_2 (0.6 mL) was added and stirred for 1.5 h at 0 °C. After that, the whole mixture was cooled to –78 °C, and treated dropwise with 1 M solution of AcCl in CH_2Cl_2 (0.60 mL, 0.60 mmol). After stirring for 1.5 h, the reaction was quenched with saturated aqueous $NaHCO_3$ (3 mL) and extracted with AcOEt (2×5 mL). The combined organic extracts were washed with water (3 mL) and brine (3 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product, which was purified by flash column chromatography (silica gel, 4:1 *n*-hexane/AcOEt) to give **112b-A** (73.2 g, 88%) as a pale-yellow oil: R_f 0.19 (2:1 *n*-hexane/AcOEt); $[\alpha]_D^{19}$ +64.4 (*c* 1.09, $CHCl_3$) for 96:4 2*R*-epimeric mixture; IR (NaCl) 1678, 1594, 1513, 1462, 1405, 1276, 1248, 1227, 1089, 1037 cm^{-1}; ^{1}H NMR (396 MHz, C_6D_6) δ 0.78 (d, *J* = 6.8 Hz, 3H, C1'-C*H*$_3$), 1.58–1.68 (m, 1H, C1'-*H*), 2.09 (ddd, *J* =16.6, 3.7, 1.4 Hz, 1H, C3-*H*), 2.23 (dd, *J* =16.6, 14.8 Hz, 1H, C3-*H*), 3.07 (dd, *J* = 9.3, 5.9 Hz, C2'-*H*), 3.18 (dd, *J* = 9.3, 6.8 Hz, 1H, C2'-*H*), 3.31 (s, 3H, ArOC*H*$_3$), 4.16 (ddd, *J* = 14.8. 4.1, 3.7 Hz, 1H, C2-*H*), 4.21 (s, 2H, OC*H*$_2$Ar), 5.21 (dd, *J* = 5.9, 1.3 Hz, 1H, C5-*H*), 6.60 (d, *J* = 5.9 Hz, 1H, C6-*H*), 6.79–6.82 (m, 2H, Ar*H*), 7.13–7.16 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6 (CH_3), 37.3 (CH), 39.6 (CH_2), 55.2 (CH_3), 70.8 (CH_2), 72.8 (CH_2), 79.8 (CH), 106.9 (CH), 113.7 (CH), 129.2 (CH), 130.1 (C), 159.2 (C), 163.4 (CH), 193.0 (C); ESI-HRMS *m/z* calcd for $C_{16}H_{20}O_4Na$ $(M+Na)^+$ 299.12538, found 299.12514. The diastereomeric ratio of **112b-A** was determined to be (2*S*,1'*S*)/(2*R*,1'*S*) = 96:4 by ^{1}H NMR analysis.

(*R*)-2-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-2,3-dihydro-4*H*-pyran-4-one (112b-B)[20d)](TS10008)



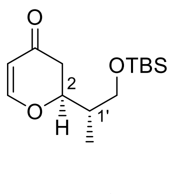
The product was prepared following the procedure for the preparation of **112b-A** using diene **3a** (102 mg, 0.45 mmol), aldehyde **113b** (62.5 mg, 0.30 mmol) and Rh_2(*R*-BPTPI)$_4$(**134**) (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by flash column chromatography (silica gel, 4:1 *n*-hexane/AcOEt) to give **112b-B** (80.7 g, 97%) as a pale-yellow oil: R_f 0.19 (2:1 *n*-hexane/AcOEt); $[\alpha]_D^{19}$ –59.0 (*c* 1.10, $CHCl_3$); IR (NaCl) 1375, 1595, 1513, 1463, 1406, 1363, 1174, 1098, 1036 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 0.69 (d, *J* = 6.9 Hz, 3H, C1'-C*H*$_3$), 1.85–1.92 (m, 1H, C10-*H*), 2.17 (ddd, *J* = 16.6, 4.9, 1.6 Hz, 2H, C3-*H*), 2.23 (dd, *J* = 16.6, 13.5 Hz, 1H, C3-*H*), 3.11 (d, *J* = 5.7 Hz, C9-*H*), 3.30 (s, 3H, ArOC*H*$_3$), 4.08 (ddd, *J* = 13.2. 5.7, 4.9 Hz, 1H, C2-*H*), 4.18 (d, *J* = 11.8 Hz, 1H, OC*H*$_2$Ar), 4.21 (d, *J* = 11.8 Hz, 1H, OC*H*$_2$Ar), 5.22 (dd, *J* = 6.0, 1.2 Hz, 1H, C5-*H*), 6.60 (d, *J* = 6.0 Hz, 1H, C6-*H*), 6.79–6.82 (m, 2H, Ar*H*), 7.13–7.14 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.5 (CH_2), 37.1 (CH), 38.4 (CH_2), 55.2 (CH_3), 70.5 (CH_2), 72.8 (CH_2), 80.6 (CH), 106.9 (CH), 113.7 (CH), 129.2 (CH), 130.1 (C), 159.1 (C), 163.5 (CH), 193.0 (C); ESI-HRMS *m/z* calcd for $C_{16}H_{20}O_4Na$ $(M+Na)^+$ 299.12538, found 299.12543. The diastereomeric ratio of **112b-B** was determined to be (2*R*,1'*S*)/(2*S*,1'*S*) = >98:2 by ^{1}H NMR analysis.

(*R*)-2-((*S*)-1-((tert-butyldimethylsilyl)oxy)propan-2-yl)-2,3-dihydro-4*H*-pyran-4-one (112a-B) (TS10050a)



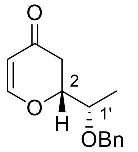
The product was prepared following the procedure for the preparation of **112b-A** using diene **3a** (102 mg, 0.45 mmol), aldehyde **113a** (60.7 mg, 0.30 mmol) and Rh_2(*R*-BPTPI)$_4$(**134**) (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by flash column chromatography (silica gel, 10:1 toluene/Et_2O) to give **112a-B** (65.9 g, 81%) as a colorless oil: R_f 0.37 (10:1 toluene/Et_2O); $[\alpha]_D^{18}$ –69.2 (*c* 1.13, $CHCl_3$); IR (NaCl) 1683, 1596, 1274. 1103, 837 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ -0.016 (s, 6H, Si(C*H*$_3$)$_2$), 0.65 (d, *J* = 6.9 Hz, 3H, C1'-C*H*$_3$), 0.91 (s, 9H, SiC(C*H*$_3$)$_3$), 1.69–1.76 (m, 1H, C1'-*H*), 2.17–2.25 (m, 2H, C3-*H*), 3.36 (dd, *J* = 10.3, 5.7 Hz, 1H, C2'-*H*), 3.40 (dd, *J* = 10.3, 5.7 Hz, 1H, C2'-H), 4.05 (ddd, *J* = 13.2, 6.9, 6.9 Hz, 1H, C2-*H*), 5.24 (d, *J* = 6.0 Hz, 1H, C5-*H*), 6.62 (d, *J* = 6.0 Hz, 1H, C6-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.57 (CH_3), 12.2 (CH_3), 18.2 (C), 25.8 (CH_3), 38.7 (CH_2), 39.2 (CH), 63.6 (CH_2), 80.4 (CH), 106.9 (CH), 163.4 (CH), 193.0 (C); ESI-HRMS *m/z* calcd for $C_{14}H_{26}O_3NaSi$ $(M+Na)^+$ 293.15434, found 293.15438. The diastereomeric ratio of **112a-B** was determined to be (2*R*,1'*S*)/(2*S*,1'*S*) = >98:2 by ^{1}H NMR analysis.

(*S*)-2-((*S*)-1-((tert-butyldimethylsilyl)oxy)propan-2-yl)-2,3-dihydro-4*H*-pyran-4-one (112a-A) (TS10050b)



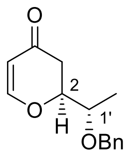
The product was prepared following the procedure for the preparation of **112b-A** using diene **3a** (102 mg, 0.45 mmol), aldehyde **113a** (60.7 mg, 0.30 mmol) and Rh_2(*S*-BPTPI)$_4$(**1**) (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by flash column chromatography (silica gel, 10:1 toluene/Et_2O) to give **112a-A** (55.4 mg, 68%) as a colorless oil: R_f 0.37 (10:1 toluene/Et_2O); $[\alpha]_D^{19}$ +77.1 (*c* 1.15, $CHCl_3$) for 92:8 2*R*-epimeric mixture; IR (NaCl) 1684, 1596, 1405, 1277, 1258, 1226, 1103, 1038, 838 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ –0.015 (s, 6H, SiC(C*H*$_3$)$_2$), 0.72 (d, *J* = 6.9 Hz, 3H, C1'-C*H*$_3$), 0.92 (s, 9H, SiC(C*H*$_3$)$_3$), 1.47–1.54 (m, 1H, C1'-*H*), 2.09 (ddd, *J* = 16.6, 3.2, 1.2 Hz, 1H, C3-*H*), 2.30 (dd, *J* = 16.6, 14.9 Hz, 1H, C3-*H*), 3.31 (dd, *J* = 10.3, 5.7 Hz, C2'-*H*), 3.39 (dd, *J* = 10.3, 6.9 Hz, 1H, C2'-*H*), 4.21 (ddd, *J*= 14.9, 3.4, 3.2 Hz, 1H, C2-*H*), 5.24 (dd, *J* = 5.7, 1.2 Hz, 1H, C5-*H*), 6.62 (d, *J* = 5.7 Hz, 1H, C6-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.57 (CH_3), 11.1 (CH_3), 18.2 (C), 25.8 (CH_3), 39.3 (CH), 39.6 (CH_2), 63.8 (CH_2), 79.4 (CH), 106.9 (CH), 163.4 (CH), 193.2 (C); ESI-HRMS *m/z* calcd for $C_{14}H_{26}O_3NaSi$ $(M+Na)^+$ 293.15434, found 293.15440. The diastereomeric ratio of **112a-A** was determined to be (2*S*,1'*S*)/(2*R*,1'*S*) = 92:8 by ^{1}H NMR analysis.

(*R*)-2-((*S*)-1-(benzyloxy)ethyl)-2,3-dihydro-4*H*-pyran-4-one (116b) (TS10043)



The product was prepared following the procedure for the preparation of **112b-A** using diene **3a** (102 mg, 0.45 mmol), aldehyde **115** (49.3 mg, 0.30 mmol) and Rh$_2$(*R*-BPTPI)$_4$(**134**) (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by flash column chromatography (silica gel, 3:1 *n*-hexane/AcOEt) to give **116b** (52.7 mg, 76%) as a pale-yellow oil: R_f 0.26 (3:1 *n*-hexane/AcOEt); $[\alpha]_D^{18}$ −113 (*c* 1.05, $CHCl_3$) for 89:11 2*S*-epimeric mixture; IR (NaCl) 1681, 1596, 1406, 1275, 1226 cm^{-1}; ^{1}H NMR (392 MHz, C_6D_6) δ 0.78 (d, *J* = 6.5 Hz, 3H, C1'-CH_3), 2.31 (ddd, *J* = 16.9, 3.8, 1.5 Hz, 1H, C3-*H*), 2.48 (dd, *J* = 16.9, 14.2 Hz, 1H, C3-*H*), 3.29 (qd, *J* = 6.5, 4.0 Hz, 1H, C1'-*H*), 3.77 (ddd, *J* = 14.2, 4.0, 3.8 Hz, 1H, C2-*H*), 4.20 (d, *J* = 12.1 Hz, 1H, OCH_2Ph), 4.27 (d, *J* = 12.1 Hz, 1H, OCH_2Ph), 5.22 (dd, *J* = 6.0, 1.5 Hz, 1H, C5-*H*), 6.56 (d, *J* = 6.0 Hz, 1H, C6-*H*), 7.07–7.11 (m, 1H, Ar*H*), 7.14–7.22 (m, 4H, Ar*H*); ^{13}C NMR (99 MHz, $CDCl_3$) δ 15.5 (CH_3), 37.0 (CH_2), 71.3 (CH_2), 74.7 (CH), 81.9 (CH), 107.1 (CH), 127.5 (CH), 127.7 (CH), 128.3 (CH), 137.8 (C), 162.9 (CH), 192.5 (C); ESI-HRMS *m/z* calcd for $C_{14}H_{16}O_3Na$ $(M+Na)^+$ 255.09917, found 255.09922. The diastereomeric ratio of **116b** was determined to be (2*R*,1'*S*)/(2*S*,1'*S*) = 89:11 by ^{1}H NMR analysis.

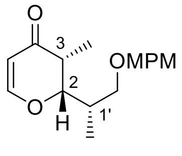
(*S*)-2-((*S*)-1-(benzyloxy)ethyl)-2,3-dihydro-4*H*-pyran-4-one (116a) (TS10042)



The product was prepared following the procedure for the preparation of **112b-A** using diene **3a** (102 mg, 0.45 mmol), aldehyde **115** (49.3 mg, 0.30 mmol) and Rh$_2$(*S*-BPTPI)$_4$(**1**) (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by flash column chromatography (silica gel, 3:1 *n*-hexane/AcOEt) to give **116a** (55.7 mg, 80%) as a pale-yellow oil: R_f 0.24 (3:1 *n*-hexane/AcOEt); $[\alpha]_D^{19}$ +140 (*c* 1.03, $CHCl_3$) for 97:3 2*R*-epimeric mixture; IR (NaCl) 1677, 1594, 1405, 1277, 1226 cm^{-1}; ^{1}H NMR (392 MHz, C_6D_6) δ 0.87 (d, *J* = 6.3 Hz, 3H, C1'-CH_3), 2.12 (ddd, *J* = 16.6, 3.6, 1.4 Hz, 1H, C3-*H*), 2.48 (dd, *J* = 16.6, 14.4 Hz, 1H, C3-*H*), 3.10 (qd, *J* = 6.3, 3.8 Hz, 1H, C1'-*H*), 3.80 (ddd, *J* = 14.4, 3.8, 3.6 Hz, 1H, C2-*H*), 4.11 (d, *J* = 12.1 Hz, 1H, OCH_2Ph), 4.28 (d, *J* = 12.1 Hz, 1H, OCH_2Ph), 5.22 (dd, *J* = 6.3, 1.4 Hz, 1H, C5-*H*), 6.59 (d, *J* = 6.3 Hz, 1H, C6-*H*), 7.07–7.11 (m, 1H, Ar*H*), 7.13–7.21 (m, 4H, Ar*H*); ^{13}C NMR (99 MHz, $CDCl_3$) δ 15.0 (CH_3), 37.9 (CH_2), 71.3 (CH_2), 74.0 (CH), 81.3 (CH), 107.0 (CH), 127.8 (CH), 127.8 (CH), 128.4 (CH), 137.6 (C), 163.0 (CH), 192.6 (C); ESI-HRMS *m/z* calcd for $C_{14}H_{16}O_3Na$ $(M+Na)^+$ 255.09917, found 255.09933. The diastereomeric ratio of **116a** was determined to be (2*S*,1'*S*)/(2*R*,1'*S*) = 97:3 by ^{1}H NMR analysis.

Typical procedure for diastereoselective hetero-Diels–Alder reactions with 4-methyl substituted Rawal's diene:

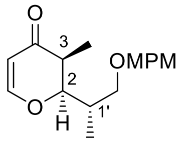
(2*S*,3*R*)-2-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-3-methyl-2,3-dihydro-4*H*-pyran-4-one (117b) (TS10092a)



4-methyl substituted Rawal's diene (**3b**) (147 mg, 0.45 mmol, (1*E*,3*Z*)/(1*E*,3*E*) = 74:26) in CH_2Cl_2 (0.3 mL) was added to a solution of aldehyde

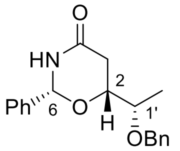
113b (62.5 mg, 0.30 mmol) and Rh_2(*R*-BPTPI)$_4$ (**134**) (4.30 mg, 0.003 mmol, 1 mol %) in CH_2Cl_2 (0.3 mL) at –20 °C. After stirring for 19 h at this temperature, DMAD (85.3 g, 0.60 mmol) in CH_2Cl_2 (0.6 mL) was added and stirred for 1.5 h at 0 °C. After that, the whole mixture was cooled to –78 °C, and treated dropwise with 1M solution of AcCl in CH_2Cl_2 (0.60 mL, 0.60 mmol). After stirring for 1.5 h, the reaction was quenched with saturated aqueous $NaHCO_3$ (3 mL) and extracted with AcOEt (2×5 mL). The combined organic extracts were washed with water (3 mL) and brine (3 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product, which was purified by flash column chromatography (silica gel, 5:1 *n*-hexane/AcOEt) to give **117b** (80.1 mg, 92%) as a pale-yellow oil: R_f 0.16 (5:1 *n*-hexane/AcOEt); $[\alpha]_D^{20}$ –56.1 (*c* 1.07, $CHCl_3$) for 95:5 2*R*- and 3*S*-diastereomeric mixture; IR (NaCl) 1674, 1597, 1514, 1272, 1247 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 0.66 (d, *J* = 6.9 Hz, 3H, C1'-C*H*$_3$), 0.87 (d, *J* = 7.5 Hz, 3H, C3-C*H*$_3$), 1.82–1.92 (1H, m, C1'-*H*), 2.26 (qdd, *J* = 7.5, 2.6, 1.2 Hz, 1H, C3-*H*), 3.31 (s, 3H, ArOC*H*$_3$), 3.33 (dd, *J* = 8.9, 5.7 Hz, 1H, C2'-*H*), 3.37 (dd, *J* = 8.9, 3.4 Hz, 1H, C2'-*H*), 3.92 (dd, *J* = 10.3, 2.6 Hz, 1H, C2-*H*), 4.28 (d, *J* = 11.8 Hz, OC*H*$_2$Ar), 4.31 (d, *J* = 11.8 Hz, OC*H*$_2$Ar), 5.18 (dd, *J* = 6.3, 1.2 Hz, 1H, C5-*H*), 6.57 (d, *J* = 6.3 Hz, 1H, C6-*H*), 6.79–6.82 (m, 2H, Ar*H*), 7.16–7.17 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.23 (CH_3), 12.8 (CH_3), 34.2 (CH), 41.4 (CH), 55.1 (CH_3), 70.5 (CH_2), 72.7 (CH_2), 82.1 (CH), 105.3 (CH), 113.6 (CH), 129.0 (CH), 130.4 (C), 159.0 (C), 162.7 (CH), 197.6 (C); ESI-HRMS *m/z* calcd for $C_{17}H_{22}O_4Na$ $(M+Na)^+$ 313.14103, found 313.14111. The diastereomeric ratio of **117b** was determined to be (2*S*,3*R*,1'*S*)/(2*R*,3*S*,1'*S*) = 95:5 by ^{1}H NMR analysis and the relative configuration at C3 was determined by NOE correlation between C2 and C3.

(2*R*,3*S*)-2-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-3-methyl-2,3-dihydro-4*H*-pyran-4-one (117a) (TS10092b)



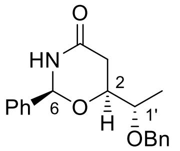
The product was prepared following the procedure for the preparation of **117b** using diene **3a** (147 mg, 0.40 mmol, (1*E*,3*Z*)/(1*E*,3*E*) = 74:26), aldehyde **113b** (62.5 mg, 0.30 mmol) and Rh_2(*S*-BPTPI)$_4$(**1**) (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by flash column chromatography (silica gel, 5:1 *n*-hexane/AcOEt) to give **117a** (64.3 mg, 74%) as a pale-yellow oil: R_f 0.19 (5:1 *n*-hexane/AcOEt); $[\alpha]_D^{21}$ +75.8 (*c* 1.13, $CHCl_3$) for 90:10 2*S*- and 3*R*-diastereomeric mixture; IR (NaCl) 1673, 1596, 1514, 1272, 1248, 1224 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 0.98 (δ, *J* = 7.5 Hz, 3H, C3-C*H*$_3$), 1.05 (d, *J* = 6.9 Hz, 3H, C1'-C*H*$_3$), 1.87–1.95 (m, 1H, C1'-*H*), 2.48 (qdd, *J* = 7.5, 2.9, 1.2 Hz, 1H, C3-*H*), 2.91 (dd, *J* = 9.5, 4.6 Hz, 1H, C2'-*H*), 2.95 (dd, *J* = 9.5, 4.6 Hz, 1H, C2'-*H*), 3.30 (s, 3H, ArOC*H*$_3$), 3.97 (dd, *J* = 9.7, 2.9 Hz, 1H, C2-*H*), 4.10 (d, *J* = 11.8 Hz, OC*H*$_2$Ar), 4.14 (d, *J* = 11.8 Hz, OC*H*$_2$Ar), 5.19 (dd, *J* = 5.5, 1.2 Hz, 1H, C5-*H*), 6.62 (d, *J* = 5.5 Hz, 1H, C6-*H*), 6.79–6.82 (m, 2H, Ar*H*), 7.11–7.14 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.0 (CH_3), 14.3 (CH_3), 34.2 (CH), 42.3 (CH), 55.2 (CH_3), 71.0 (CH_2), 72.9 (CH_2), 84.2 (CH), 105.3 (CH), 113.7 (CH), 129.1 (CH), 129.9 (C), 159.1 (C), 163.0 (CH), 197.8 (C); ESI-HRMS *m/z* calcd for $C_{17}H_{22}O_4Na$ $(M+Na)^+$ 313.14103, found 313.1417. The diastereomeric ratio of **117a** was determined to be (2*R*,3*S*,1'*S*)/(2*S*,3*R*,1'*S*) = 90:10 by ^{1}H NMR analysis and the relative configuration at C3 was determined by NOE correlation between C2 and C3.

Typical procedure for diastereoselective hetero-Diels–Alder reactions with 2-aza-3-silyloxy-1,3-butadiene: (2*R*,6*R*)-6-((*S*)-1-(benzyloxy)ethyl)-2-phenyl-1,3-oxazinan-4-one (119b) (TS10100a)



A solution of Ghosez's diene (**118**) (52.3 mg, 0.20 mmol) in CH_2Cl_2 (0.20 mL) was added to a solution of aldehyde **115** (49.3 mg, 0.30 mmol) and $Rh_2(R\text{-BPTPI})_4$(**134**) (2.86 mg, 0.002 mmol, 1 mol %) in CH_2Cl_2 (0.2 mL) at 0 °C. After stirring for 19 h at this temperature, the reaction mixture was treated dropwise with MeOH (0.1 mL). After stirring for 1.5 h, the reaction was concentrated *in vacuo* and afforded the crude product, which was purified by flash column chromatography (silica gel, 1:1 $CHCl_3$/AcOEt) to give **119b** (30.9 mg, 50%) as a colorless amorphous: R_f 0.35 (1:1 $CHCl_3$/AcOEt); $[\alpha]_D^{25}$ +16.6 (*c* 1.53, $CHCl_3$) for 75:25 2*S*- and 6*S*-diastereomeric mixture; IR (NaCl) 3392, 3270, 1660 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.19 (d, *J* = 6.3 Hz, 3H, C1'-C*H*$_3$), 2.55 (d, *J* = 7.3 Hz, 2H, C3-*H*), 3.57–3.64 (m, 1H, C1'-*H*), 3.84 (ddd, *J* = 7.3, 7.3, 5.0 Hz, 1H, C2-*H*), 4.50 (d, *J* = 11.8 Hz, 1H, OC*H*$_2$Ph), 4.58 (d, *J* = 11.8 Hz, 1H, OC*H*$_2$Ph), 5.65 (s, 1H, C6-*H*), 6.45 (br, 1H, N*H*), 7.19–7.27 (m, 5H, Ar*H*), 7.32–7.40 (m, 5H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.1 (CH_3), 33.2 (CH_2), 71.4 (CH_2), 76.0 (CH), 78.1 (CH), 85.3 (CH), 126.6 (CH), 127.6 (CH), 127.7 (CH), 128.3 (CH), 128.7 (CH), 129.7 (CH), 137.8 (C), 138.2 (C), 169.5 (C); ESI-HRMS *m/z* calcd for $C_{20}H_{20}O_3NNa$ $(M+Na)^+$ 334.14136, found 334.14151. The diastereomeric ratio of **119b** was determined to be (2*R*,6*R*,1'*S*)/(2*S*,6*S*,1'*S*) = 75:25 by ^{1}H NMR analysis and the relative configuration at C6 was determined by NOE correlation between C2 and C6.

(2*S*,6*S*)-6-((*S*)-1-(benzyloxy)ethyl)-2-phenyl-1,3-oxazinan-4-one (119a) (TS10100b)



The product was prepared following the procedure for the preparation of **119b** using diene **118** (52.3 mg, 0.20 mmol), aldehyde **115** (49.3 mg, 0.30 mmol) and $Rh_2(S\text{-BPTPI})_4$(**1**) (2.86 mg, 0.002 mmol, 1 mol %). The crude product was purified by flash column chromatography (silica gel, 1:1 $CHCl_3$/AcOEt) to give **119a** (39.3 mg, 63%) as a colorless amorphous: R_f 0.27 (1:1 $CHCl_3$/AcOEt); $[\alpha]_D^{24}$ –17.0 (*c* 1.91, $CHCl_3$) for 98:2 2*R*- and 6*R*-diastereomeric mixture; IR (NaCl) 3384, 3225, 1666 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.18 (d, *J* = 6.2 Hz, 3H, C1'-C*H*$_3$), 2.34 (dd, *J* = 17.2, 3.9 Hz, 1H, C3-*H*), 2.51 (dd, *J* = 17.2, 10.4 Hz, 1H, C3-*H*), 3.63 (quin, *J* = 6.2 Hz, 1H, C1'-*H*), 3.97 (ddd, *J* = 10.4, 6.2, 3.9 Hz, 1H, C2-*H*), 4.52 (d, *J* = 12.0 Hz, 1H, OC*H*$_2$Ph), 4.61 (d, *J* = 12.0 Hz, 1H, OC*H*$_2$Ph), 5.69 (s, 1H, C6-*H*), 6.69 (br, 1H, N*H*), 7.20–7.30 (m, 5H, Ar*H*), 7.36–7.42 (m, 5H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9 (CH_3), 32.9 (CH_2), 71.6 (CH_2), 75.4 (CH), 77.7 (CH), 85.3 (CH), 126.7 (CH), 127.5 (CH), 127.6 (CH), 128.3 (CH), 128.7 (CH), 129.7 (CH), 137.7 (C), 138.3 (C), 169.2 (C); ESI-HRMS *m/z* calcd for $C_{20}H_{20}O_3NNa$ $(M+Na)^+$ 334.14136, found 334.14151. The diastereomeric ratio of **119a** was determined to be (2*S*,6*S*,1'*S*)/(2*R*,6*R*,1'*S*) = 98:2 by ^{1}H NMR analysis and the relative configuration at C6 was determined by NOE correlation between C2 and C6.

Part 1 Chapter 2 Section 2

[Preparation of single crystal of Rh_2(*S*-BPTPI)$_4$]

Rh_2(*S*-BPTPI)$_4$ was put into a micro test tube and dissolved in toluene. Then, small amount of *N*,*N*-dimethylformamide was added to this mixture.* The test tube was equipped with cap having a hole and stored in screw cap vial quarterly filled with *n*-pentane. *n*-Pentane was diffused to the solution slowly and it afforded single crystal of Rh_2(*S*-BPTPI)$_4$ as platelet.

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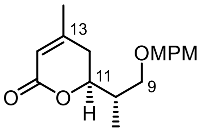
* If *N*,*N*-dimethylformamide was added to much, it resulted in two-layer of toluene-pentane mixture and *N*,*N*-dimethylformamide. It does not afford single crystal.

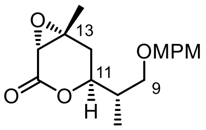
Part 1 Chapter 3 Section 1

(*S*)-6-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-4-methyl-5,6-dihydro-2*H*-pyran-2-one (120) (TS05071)



MeLi (1.07 M in THF, 32.5 mL, 34.8 mmol) was added to a stirred solution of dihydropyranone **112b-A** (8.74 g, 31.6 mmol) in THF (158 mL) at –78 °C. After stirring for 2 h at this temperature, the reaction was quenched with pH 7.0 phosphorous buffer (80 mL). The whole was extracted with AcOEt (300 mL) and washed with water (150 mL) and brine (150 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (9.80 g), which was used without further purification. To a stirred solution of crude alcohol (9.80 g), MS4Å (8.74 g, 100 wt %) and NaOAc (7.77 g, 94.8 mmol) in DCE (316 mL) were added PCC (13.6 g, 63.2 mmol) at 0 °C. After stirring for 4 h at room temperature, the reaction mixture was filtered through a layered-pad of Celite, silica gel, florisil, Celite washed with AcOEt. The filtrate was evaporated *in vacuo* furnished the crude product (12.0 g), which was purified by column chromatography (silica gel 180 g, 5:1 *n*-hexane/AcOEt then 2:1 *n*-hexane/AcOEt) to give **120** (7.39 g, 80%) as a colorless oil: R_f 0.42 (2:1 *n*-hexane/AcOEt); $[\alpha]_D^{20}$ –53.6 (*c* 1.01, $CHCl_3$); IR (NaCl) 2936, 2908, 1717, 1513, 1249, 1032 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.04 (d, *J* = 6.8 Hz, 3H, C10-CH_3), 1.96 (s, 3H, C13-CH_3), 1.98–2.08 (m, 2H, C12-*H*), 2.43–2.51 (m, 1H, C10-*H*), 3.42 (dd, *J* = 9.5, 5.0 Hz, C9-*H*), 3.52 (dd, *J* = 9.5, 7.7 Hz, C9-*H*), 3.81 (s, 3H, ArOCH_3), 4.40 (d, *J* = 11.3 Hz, 1H, OCH_2Ar), 4.46 (d, *J* = 11.3 Hz, 1H, OCH_2Ar), 4.52 (dt, *J* = 13.0, 3.9 Hz, 1H, C11-*H*), 5.79 (s, 1H, C14-*H*), 6.86–6.90 (m 2H, Ar*H*), 7.22–7.26 (m, 2H, Ar*H*); ^{13}C NMR (99 MHz, $CDCl_3$) δ 11.7 (CH_3), 23.0 (CH_3), 32.4 (CH_2), 37.4 (CH), 55.2 (CH_3), 71.1 (CH_2), 72.9 (CH_2), 77.5 (CH), 113.7 (CH), 116.2 (CH), 129.3 (CH), 130.2 (C), 157.7 (C), 159.1 (C), 165.5 (C); ESI-HRMS *m/z* calcd for $C_{17}H_{22}O_4Na$ $(M+Na)^+$ 313.14103, found 313.14093..

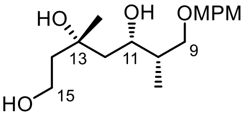
(1R,4S,6R)-4-((S)-1-((4-methoxybenzyl)oxy)propan-2-yl)-6-methyl-3,7-dioxabicyclo[4.1.0]heptan-2-one (111b) (TS05027)



6 M aqueous NaOH (0.53 mL) was added to a stirred solution of lactone **120** (1.55 g, 5.34 mmol) and 30% H_2O_2 (2.12 mL) in MeOH (76.3 mL) at 0 °C. After stirring for 1 h at room temperature, the reaction mixture was poured into a two-layer mixture of Et_2O (120 mL) and water (120 mL), then acidified until pH 3. The Et_2O layer was separated, and the aqueous layer was extracted with Et_2O (300 mL). The combined organic extracts were washed with brine (100 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (1.67 g), which was purified by column chromatography (silica gel 50 g, 19:1 toluene/AcOEt) to give **111b** (1.53 g, 93%) as a colorless oil: R_f 0.46 (2:1 toluene/AcOEt); $[\alpha]_D^{19}$ +42.7 (*c* 1.02, $CHCl_3$); IR (NaCl) 2968, 2934, 1738, 1612, 1514, 1248, 1103, 1033 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 0.96 (d, *J* = 7.3 Hz, 3H, C10-CH_3), 1.50 (s, 3H, C13-CH_3), 1.86–1.93 (m, 1H, C10-*H*), 2.05–2.07 (m, 1H, C12-*H*), 3.36 (dd, *J* = 9.3, 5.4 Hz, 1H,

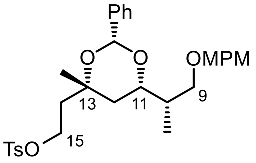
C9-*H*), 3.38 (s, 1H, C14-*H*), 3.42 (dd, *J* = 9.3, 7.3 Hz, 1H, C9-*H*), 3.82 (s, 3H, ArOC*H*$_3$), 4.39 (d, *J* = 11.3 Hz, 1H, OC*H*$_2$Ar), 4.44 (d, *J* = 11.3 Hz, 1H, OC*H*$_2$Ar), 4.66 (ddd, *J* = 10.0, 9.1, 4.1 Hz, 1H, C11-*H*), 6.86–6.90 (m, 2H, Ar*H*), 7.22–7.25 (m, 2H, Ar*H*); ^{13}C NMR (126 MHz, CDCl$_3$) δ 11.4 (CH$_3$), 20.2 (CH$_3$), 31.9 (CH$_2$), 37.0 (CH), 55.2 (CH), 55.4 (CH$_3$), 59.3 (C), 71.0 (CH$_2$), 72.8 (CH$_2$), 75.1 (CH), 113.7 (CH), 129.3 (CH), 130.2 (C), 159.2 (C), 168.3 (C); ESI-HRMS *m/z* calcd for C$_{17}$H$_{22}$O$_5$Na (M+Na)$^+$ 329.13594, found 329.13584..

(3S,5S,6S)-7-((4-methoxybenzyl)oxy)-3,6-dimethylheptane-1,3,5-triol (121) (TS05079)



Red-Al® (65% in toluene, 36.8 mL, 118 mmol) was added to a stirred solution of epoxide **111b** (7.20 g, 23.5 mmol) in THF (235 mL) at 0 °C. After stirring for 4 h at this temperature, saturated aqueous Rochelle salt (100 mL) was added dropwise, then diluted AcOEt (200 mL). The AcOEt layer was separated, and the aqueous layer was extracted with AcOEt (3 × 200 mL). The combined organic extracts were washed with brine (200 mL), and dried over anhydrous Na$_2$SO$_4$. Filtration and evaporation *in vacuo* furnished crude product (9.56 g), which was purified b column chromatography (silica gel, 150 g, 1:4 *n*-hexane/AcOEt) to give **121** (6.27 g, 86%) as a colorless oil: R_f 0.16 (1:2 *n*-hexane/AcOEt); $[\alpha]_D^{21}$ –6.16 (*c* 1.00, MeOH); IR (NaCl) 3375, 2937, 1613, 1514, 1248 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.93 (d, *J* = 7.2 Hz, 3H, C10-C*H*$_3$), 1.26 (dd, *J* = 13.8, 1.7 Hz, 1H, C12-*H*), 1.33 (s. 3H, C13-C*H*$_3$), 1.66–1.76 (m, 2H, C14-*H*), 1.87–1.92 (m, 2H, C10-*H* and C12-*H*), 3.50 (br, 2H, C9-*H* and O*H*), 3.56 (dd, *J* = 9.4, 4.5 Hz, 1H, C9-*H*), 3.70 (br, 1H, O*H*), 3.81 (s, 3H, ArOC*H*$_3$), 3.87 (br, 1H, C15-*H*), 4.22–4.24 (m, 1H, C11-*H*), 4.42 (d, *J* = 11.7 Hz, 1H, OC*H*$_2$Ar), 4.48 (d, *J* = 11.7 Hz, 1H, OC*H*$_2$Ar), 4.62 (br, 1H, OH), 6.89–6.91 (m, 2H, Ar*H*), 7.24–7.26 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, CDCl$_3$) δ 11.5 (CH$_3$), 26.3 (CH$_3$), 38.3 (CH), 41.9 (CH$_2$), 43.9 (CH$_2$), 55.3 (CH$_3$), 59.5 (CH$_2$), 72.3 (CH), 73.2 (CH$_2$), 74.0 (CH$_2$), 74.1 (C), 113.9 (CH), 129.4 (CH), 129.7 (C), 159.3 (C); ESI-HRMS *m/z* calcd for C$_{17}$H$_{28}$O$_5$Na (M+Na)$^+$ 335.18290, found 225.18285.

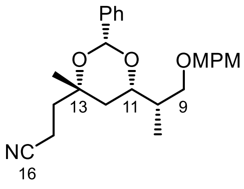
2-((2R,4S,6S)-6-((S)-1-((4-methoxybenzyl)oxy)propan-2-yl)-4-methyl-2-phenyl-1,3-dioxan-4-yl)ethyl 4-methylbenzenesulfonate (122) (TS05031)



TsCl (1.18 g, 6.20 mmol) was added to a stirred solution of triol **121** (1.29 g, 4.13 mmol), Et$_3$N (1.04 g, 6.20 mmol) and Me$_3$N·HCl (244 mg, 4.13 mmol) in toluene (8.26 mL) at 0 °C. After stirring for 1 h at this temperature, the reaction was quenched a bit of ice. The whole was extracted with AcOEt (20 mL), and the organic extract was washed with water (8 mL) and brine (8 mL), and dried over anhydrous Na$_2$SO$_4$. Filtration and evaporation *in vacuo* (until 4 mL) furnished the crude product (6.30 g), which was used without further purification. To a stirred solution of crude diol (6.30 g) and benzaldehyde dimethyl acetal (1.89 g, 12.4 mmol) in CH$_2$Cl$_2$ (41.3 mL) was added PPTS (104 mg, 0.413 mmol) at room temperature. After stirring for 12 h at this temperature, the reaction was quenched with Et$_3$N (1 mL). The whole was extracted with AcOEt (60 mL). The organic extract was washed with saturated aqueous NaHCO$_3$ (30 mL) and brine (30 mL), and dried over anhydrous

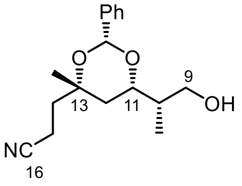
Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (3.37 g), which was purified by column chromatography (silica gel 90 g, 9:1 *n*-hexane/AcOEt) to give **122** (2.20 g, 96%) as a colorless oil: R_f 0.52 (2:1 *n*-hexane/AcOEt); $[\alpha]_D^{21}$ +22.6 (*c* 1.14, $CHCl_3$); IR (NaCl) 2971, 2909, 1612, 1513, 1362, 1176 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 0.99 (d, J = 6.8 Hz, 3H, C10-CH_3), 1.31 (dd, J = 13.1, 2.2 Hz, 1H, C12-*H*), 1.39 (s, 3H, C13-CH_3), 1.65 (dd, J = 13.1, 12.2 Hz, 1H, C12-*H*), 1.78–1.83 (m, 1H, C10-*H*), 1.96–1.99 (m, 2H, C14-*H*), 2.43 (s, 3H, SArCH_3), 3.34 (dd, J = 9.4, 5.4 Hz, 1H, C9-*H*), 3.47 (dd, J = 9.4, 6.7 Hz, 1H, C9-*H*), 3.79 (s, 3H, ArOCH_3), 4.02 (ddd, J =12.2, 4.9, 2.2 Hz, 1H, C11-*H*), 4.24–4.28 (m, 2H, C15-*H*), 4.23 (s, 2H, OCH_2Ar), 5.63 (s, 1H, OC*H*Ph), 6.84–6.88 (m, 2H, Ar*H*), 7.23–7.32 (m, 9H, Ar*H*), 7.77–7.79 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.3 (CH_3), 21.0 (CH_3), 21.6 (CH_3), 37.1 (CH_2), 38.4 (CH), 42.7 (CH_2), 55.2 (CH_3), 6.4 (CH_2), 71.4 (CH_2), 72.7 (CH_2), 72.8 (C), 72.9 (CH), 94.4 (CH), 113.7 (CH), 126.0 (CH), 127.8 (CH), 128.0 (CH), 128.4 (CH), 129.2 (CH), 129.8 (CH), 130.5 (C), 133.0 (C), 139.1 (C), 14.7 (C), 159.1 (C); ESI-HRMS *m/z* calcd for $C_{31}H_{387}SNa$ $(M+Na)^+$ 577.22305, found 577.22242.

3-((2R,4S,6S)-6-((S)-1-((4-methoxybenzyl)oxy)propan-2-yl)-4-methyl-2-phenyl-1,3-dioxan-4-yl)propanenitrile (123) (TS05086)



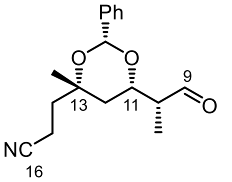
NaCN (4.04 g, 82.5 mmol) was added to a stirred solution of acetal **122** (9.14 g, 16.5 mmol) in DMF (41.3 mL) at room temperature. After stirring for 16 h at 40 °C, the reaction mixture was poured into a two-layer mixture of AcOEt (80 mL) and water (40 mL). The AcOEt layer was separated, and the aqueous layer was extracted with AcOEt (120 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (50 mL), water (50 mL) and brine (50 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (6.91 g), which was purified by column chromatography (silica gel 120 g, 19:1 toluene/AcOEt) to give **123** (6.69 g, 99%) as a colorless oil: R_f 0.63 (9:1 toluene/AcOEt); $[\alpha]_D^{21}$ +34.5 (*c* 1.04, $CHCl_3$); IR (NaCl) 2934, 2248, 1612, 1512, 1247 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.02 (d, J = 6.8 Hz, 3H, C10-CH_3), 1.33 (dd, J = 12.7, 2.3 Hz, 1H, C12-*H*), 1.43 (s, 3H, C13-CH_3), 1.67 (dd, J = 12.7, 12.3 Hz, 1H, C12-*H*), 1.82–1.89 (m, 1H, C10-*H*), 1.91–1.99 (m, 2H, C14-*H*), 2.49–2.53 (m, 2H, C15-*H*), 3.37 (dd, J = 9.1, 5.0 Hz, 1H, C9-*H*), 3.48 (dd, J = 9.1, 6.8 Hz, 1H, C9-*H*), 3.79 (s, 3H, ArOCH_3), 4.07 (ddd, J = 12.3, 5.0, 2.3 Hz, 1H, C11-*H*), 4.44 (s, 2H, OCH_2Ar), 5.67 (s, 1H, OC*H*Ph), 6.85–6.88 (m, 2H, Ar*H*), 7.24–7.26 (m, 2H, Ar*H*), 7.32–7.38 (m, 3H, Ar*H*), 7.39–7.43 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.0 (CH_2), 12.3 (CH_3), 20.6 (CH_3), 36.5 (CH_2), 38.3 (CH), 39.4 (CH_2), 55.2 (CH_3), 71.3 (CH_2), 72.6 (C), 72.7 (CH_3), 73.0 (CH), 94.7 (CH), 113.7 (CH), 120.3 (C), 126.0 (CH), 128.1 (CH), 128.5 (CH), 129.2 (CH), 130. (C), 159.1 (C); ESI-HRMS *m/z* calcd for $C_{25}H_{31}O_4NNa$ $(M+Na)^+$ 432.21453, found 432.21412.

3-((2R,4S,6S)-6-((S)-1-hydroxypropan-2-yl)-4-methyl-2-phenyl-1,3-dioxan-4-yl)propanenitrile (125) (TS06035)



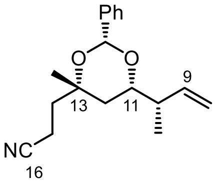
DDQ (1.25 g, 5.50 mmol) was added to a stirred solution of cyanide **123** (2.05 g, 5.00 mmol) in CH_2Cl_2 (90.9 mL) and pH 7 phosphorous buffer (9.09 mL) at 0 °C. After stirring for 4 h at room temperature, the reaction mixture was poured into a mixture of EtOH (90 mL) and saturated aqueous $NaHCO_3$ (45 mL) and 10% aqueous $Na_2S_2O_3$ (45 mL). The whole was extracted with CH_2Cl_2 (200 mL), and the organic extract was washed with saturated aqueous $NaHCO_3$ (50 mL), water (50 mL) and brine (50 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (2.07 g), which was purified by column chromatography (silica gel 60 g, 1:1 *n*-hexane/AcOEt) to give **125** (1.43 g, 99%) as a colorless oil: R_f 0.24 (1:1 *n*-hexane/AcOEt); $[\alpha]_D^{22}$ 28.2 (*c* 1.06, $CHCl_3$); IR (NaCl) 3467, 2973, 2932, 2249, 1026 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.00 (d, J = 7.5 Hz, 3H, C10-CH_3), 1.39 (dd, J = 12.6, 2.3 Hz, 1H, C12-H), 1.47 (s, 3H, C13-CH_3), 1.79 (dd, J = 12.6, 12.1 Hz, 1H, C12-H), 1.90–1.99 (m, 4H, C10-H and C14-H and OH), 2.49–2.60 (m, 2H, C15-H), 3.63–3.67 (m, 1H, C9-H), 3.71–3.76 (m, 1H, C9-H), 4.19 (ddd, J = 12.1, 4.0, 2.3 Hz, 1H, C11-H), 5.72 (s, 1H, OCHPh), 7.34–7.38 (m, 3H, ArH), 7.42–7.44 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.0 (CH_2), 11.6 (CH_3), 20.5 (CH_3), 35.5 (CH_2), 39.3 (CH_2), 39.5 (CH), 65.1 (CH_2) 72.7 (C), 74. (CH), 94.9 (CH), 120.2 (C), 126.0 (CH), 128.2 (CH), 128.8 (CH), 138.6 (C); ESI-HRMS *m/z* calcd for $C_{17}H_{23}O_3NNa$ $(M+Na)^+$ 312.15701, found 312.15700.

3-((2R,4S,6S)-4-methyl-6-((R)-1-oxopropan-2-yl)-2-phenyl-1,3-dioxan-4-yl)propanenitrile (126) (TS06041)



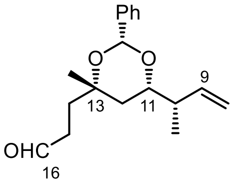
Dess–Martion periodinane (4.20 g, 9.90 mmol) was added to a solution of alcohol **125** (1.91 g, 6.60 mmol) in CH_2Cl_2 (33 mL) at 0 °C. After stirring for 5 h at room temperature, the reaction mixture was diluted with AcOEt (40 mL) and poured into a mixture of pH 7.4 phosphorous buffer (20 mL) and 10% aqueous $Na_2S_2O_3$ (20 mL). The layers were separated, the organic layer was washed with pH 7.4 phosphorous buffer (3 × 20 mL) and brine (20 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (3.05 g), which was purified by column chromatography (silica gel 60 g, 2:1 *n*-hexane/AcOEt) to give **126** (1.63 g, 86%) as a colorless oil: R_f 0.55 (1:1 *n*-hexane/AcOEt); $[\alpha]_D^{24}$ +12.1 (*c* 1.00, $CHCl_3$); IR (NaCl) 2979, 2248, 1724, 1390, 1087 cm^{-1}; ^1H NMR (392 MHz, $CDCl_3$) δ 1.23 (d, J = 7.2 Hz, 3H, C10-CH_3), 1.50–1.55 (m, 4H, C12-H and C13-CH_3), 1.69 (dd, J = 13.0, 12.4 Hz, 1H, C12-H), 1.97 (td, J = 8.1, 1.8 Hz, 2H, C14-H), 2.46–2.62 (m, 3H, C10-H and C15-H), 4.40 (ddd, J = 12.4, 5.4, 2.2 Hz, 1H, C11-H), 5.76 (s, 1H, OCHPh), 7.34–7.39 (m, 3H, ArH), 7.42–7.44 (m, 2H, ArH), 9.79 (s, 1H, C9-H); ^{13}C NMR (99 MHz, $CDCl_3$) δ 8.89 (CH_3), 11.0 (CH_2), 20.3 (CH_3), 36.5 (CH_2), 39.2 (CH_2), 50.7 (CH), 72.0 (CH), 72.7 (C), 94.9 (CH), 120.1 (C), 126.0 (CH), 128.2 (CH), 128.8 (CH), 138.3 (C), 203.2 (CH); ESI-HRMS *m/z* calcd for $C_{17}H_{22}O_3N$ $(M+H)^+$ 288.15942, found 288.15949.

3-((2R,4S,6S)-6-((S)-but-3-en-2-yl)-4-methyl-2-phenyl-1,3-dioxan-4-yl)propanenitrile (127) (TS06043)



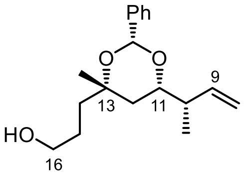
LiHMDS (1.0 M in THF, 8.51 mL, 8.51 mmol) was added to a stirred solution of PPh_3CH_3Br (4.04 g, 11.3 mmol) in THF (50 mL) at 0 °C. After stirring for 15 min at this temperature, a solution of aldehyde **126** (1.63 g, 5.67 mmol) in THF (30 mL) was added dropwise at 0 °C. After stirring for 1 h at this temperature, the reaction was quenched with saturated aqueous NH_4Cl (20 mL). The whole was extracted with EtOAc (150 mL), and the organic extract was washed with brine (40 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (3.26 g), which was purified by column chromatography (silica gel 90 g, 9:1 *n*-hexane/AcOEt) to give **127** (1.39 g, 86%) as a colorless oil: R_f 0.62 (2:1 *n*-hexane/AcOEt); $[\alpha]_D^{25}$ +4.38 (*c* 1.03, $CHCl_3$); IR (NaCl) 2976, 2248, 1200, 1028, 756 cm^{-1}; ^{1}H NMR (392 MHz, $CDCl_3$) δ 1.13 (d, *J* = 6.3 Hz, C10-CH_3), 1.43–1.53 (m, 5H, C12-*H*, C13-CH_3), 1.90–1.99 (m, 2H, C14-*H*), 2.29–2.38 (m, 1H, C10-*H*), 2.53 (t, *J* = 7.6 Hz, 2H, C15-*H*), 3.37 (ddd, *J* = 10.8, 7.6, 2.7 Hz, 1H, C11-*H*), 5.05–5.12 (m, 2H, =CH_2), 5.68–5.77 (m, 2H, C9-*H* and OC*H*Ph), 7.33–7.39 (m, 3H, Ar*H*), 7.45–7.48 (m, 2H, Ar*H*); ^{13}C NMR (99 MHz, $CDCl_3$) δ 11.1 (CH_2), 16.0 (CH_3), 20.7 (CH_3), 37.1 (CH_2), 39.3 (CH_2), 43.4 (CH), 72.7 (C), 75.9 (CH), 94.7 (CH), 115.7 (CH_2), 120.3 (C), 126.0 (CH), 128.1 (CH), 128.6 (CH), 128.8 (C), 129.5 (CH); ESI-HRMS *m/z* calcd for $C_{18}H_{23}O_2NNa$ $(M+Na)^+$ 308.16210, found 208.16201.

3-((2R,4S,6S)-6-((S)-but-3-en-2-yl)-4-methyl-2-phenyl-1,3-dioxan-4-yl)propanal (128) (TS06045)



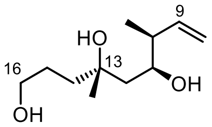
DIBAL (1.0 M in toluene, 9.12 mL, 9.12 mmol) was added to a solution of alkene **127** (2.17 g, 7.60 mmol) in CH_2Cl_2 (76 mL) at –78 °C. After stirring for 4 h at this temperature, the reaction was quenched with a mixture of AcOH and H_2O (1:1, 6.0 mL) and then stirred for 30 min at 0 °C. The mixture was poured into a two-layer of AcOEt (100 mL) and water (40 mL). The AcOEt layer was separated, and the organic layer was washed with saturated aqueous $NaHCO_3$ (40 mL) and brine (40 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (2.33 g), which was purified by column chromatography (silica gel 60 g, 15:1 toluene/ether) to give **128** (1.94 g, 89%) as a colorless oil: R_f 0.35 (15:1 toluene/ether); $[\alpha]_D^{24}$ +3.13 (*c* 1.02, MeOH); IR (NaCl) 2976, 1724, 1094, 1027, 755 cm^{-1}; ^{1}H NMR (392 MHz, $CDCl_3$) δ 1.14 (d, *J* = 6.7 Hz, 3H, C10-CH_3), 1.39–1.61 (m, 5H, C12-*H* and C13-CH_3), 1.92 (t, *J* = 7.4 Hz, 2H, C14-*H*), 2.29–2.38 (m, 1H, C10-*H*), 2.63 (t, *J* = 7.4 Hz, 2H, C15-*H*), 3.74 (ddd, *J* = 10.8, 7.6, 2.7 Hz, 1H, C11-*H*), 5.04–5.11 (m, 2H, =CH_2), 5.70–5.77 (m, 2H, C9-*H* and OC*H*Ph), 7.32–7.38 (m, 3H, Ar*H*), 7.45–7.48 (m, 2H, Ar*H*), 9.79 (s, 1H, C9-*H*); ^{13}C NMR (99 MHz, $CDCl_3$) δ 16.0 (CH_3), 20.8 (CH_3), 36.2 (CH_2), 37.6 (CH_2), 38.0 (CH_2), 3.5 (CH), 73.3 (C), 76.0 (CH), 94.6 (CH), 115.5 (CH_2), 126.0 (CH), 128.1 (CH), 128.5 (CH), 139.1 (C), 129.7 (CH), 202.6 (CH); ESI-HRMS *m/z* calcd for $C_{18}H_{24}O_3Na$ $(M+Na)^+$ 311.16177, found 311.16164.

3-((2R,4S,6S)-6-((S)-but-3-en-2-yl)-4-methyl-2-phenyl-1,3-dioxan-4-yl)propan-1-ol (129) (TS06047)



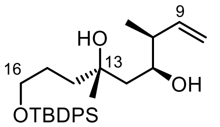
$NaBH_4$ (290 mg, 7.40 mmol) was added to a stirred solution of aldehyde **128** (1.94 g, 6.73 mmol) in MeOH (34 mL) at 0 °C. After stirring for 2 h at room temperature, the reaction was quenched with saturated aqueous NH_4Cl (20 mL). The whole was extracted with AcOEt (2 × 100 mL), and the organic extracts were washed with brine (30 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (2.00 g), which was purified by column chromatography (silica gel 60 g, 2:1 *n*-hexane/AcOEt) to give **129** (1.81 g, 93%) as a colorless oil: R_f 0.32 (2:1 *n*-hexane/AcOEt); $[\alpha]_D^{25}$ +5.80 (*c* 1.21, $CHCl_3$); IR (NaCl) 3403, 2953, 1093, 756 cm^{-1}; ^{1}H NMR (392 MHz, $CDCl_3$) δ 1.13 (d, *J* = 6.9 Hz, 3H, C10-CH_3), 1.41 (s, 3H, C13-CH_3), 1.45 (dd, *J* = 12.9, 2.3 Hz, 1H, C12-*H*), 1.59 (dd, *J* = 12.9, 11.8 Hz, 1H, C12-*H*), 1.65 (t, *J* = 7.5 Hz, 2H, C14-*H*), 1.71–1.81 (m, 2H, C15-*H*), 2.30–2.37 (m, 1H, C10-*H*), 3.65 (q, *J* = 6.3 Hz, 2H, C16-*H*), 3.74 (ddd, *J* = 11.8, 7.5, 2.3 Hz, 1H, C11-*H*), 5.04–5.10 (m, 2H, =CH_2), 5.72–5.79 (m, 2H, C9-*H* and OC*H*Ph), 7.31–7.37 (m, 3H, Ar*H*), 7.48–7.49 (m, 2H, Ar*H*); ^{13}C NMR (99 MHz, $CDCl_3$) δ 16.0 (CH_3), 20.5 (CH_3), 37.9 (CH_2), 40.9 (CH_2), 43.5 (CH), 63.2 (CH_2), 74.2 (C), 76.2 (CH), 94.7 (CH), 115.3 (CH_2), 126.1 (CH), 128.1 (CH), 128.5 (CH), 139.2 (C), 139.9 (CH); ESI-HRMS *m/z* calcd for $C_{18}H_{26}O_3Na$ (M+Na)$^+$ 313.17742, found 313.17715.

(4S,6S,7S)-4,7-dimethylnon-8-ene-1,4,6-triol (130) (TS06073)



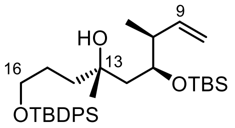
A mixture of TFA in H_2O (4:1, 62.3 mL) was added to a solution of alcohol **129** (1.81 g, 6.23 mmol) in CH_2Cl_2 (125 mL) at 0 °C. After stirring for 15 min at this temperature, the reaction mixture was poured into a two-layer of AcOEt (200 mL) and saturated aqueous $NaHCO_3$ (200 mL). The AcOEt layer was separated, the organic layer was washed with saturated aqueous $NaHCO_3$ (3 × 60 mL). The combined water layers were neutralized and extracted with AcOEt (6 × 200 mL). The combined organic layers were washed with brine (150 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (3.19 g), which was purified by column chromatography (silica gel 90 g, AcOEt only) to give **130** (1.13 g, 90%) as a colorless oil: R_f 0.23 (AcOEt only); $[\alpha]_D^{26}$ –23.2 (*c* 1.02, MeOH); IR (NaCl) 3388, 2948, 1640, 756 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (d, *J* = 6.9 Hz. C9-CH_3), 1.27 (s, 3H, C13-CH_3), 1.47 (dd, *J* = 14.3, 1.7 Hz, 1H, C12-*H*), 1.58–1.63 (m, 3H, C12-*H* and C14-*H*), 1.66–1.71 (m, 2H, C15-*H*), 2.20–2.27 (m, 1H, C10-*H*), 2.86 (br, 1H, O*H*), 3.65 (t, *J* = 5.7 Hz, 2H, C16-*H*), 3.90 (ddd, *J* = 10.9, 5.7, 1.7 Hz, 1H, C11-*H*), 5.05–5.09 (m, 2H, =CH_2), 5.72–5.79 (m, 1H, C9-*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.9 (CH_3), 25.8 (CH_3), 26.6 (CH_2), 41.5 (CH_2), 42.9 (CH_2), 44.4 (CH), 63.2 (CH_2), 72.5 (CH), 72.7 (C), 115.5 (CH_2), 140.5 (CH); ESI-HRMS *m/z* calcd for $C_{11}H_{22}O_3Na$ (M+Na)$^+$ 225.14612, found 225.14594.

(3S,4S,6S)-9-((tert-butyldiphenylsilyl)oxy)-3,6-dimethylnon-1-ene-4,6-diol (131) (TS06074)



TBDPSCl (1.87 g, 6.71 mmol) was added to a solution of triol **130** (1.13 g, 5.59 mmol) and imidazole (695 mg, 11.2 mmol) in DMF (11.2 mL) at 0 °C. After stirring for 1 h at room temperature, the reaction was quenched with a bit of ice. The whole was extracted with AcOEt (100 mL), and the organic extract was washed with water (2 × 20 mL) and brine (20 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (5.00 g), which was purified by column chromatography (silica gel 100 g, 4:1 *n*-hexane/AcOEt) to give **131** (2.29 g, 93%) as a colorless oil: R_f 0.34 (3:1 *n*-hexane/AcOEt); $[\alpha]_D^{26}$ –11.9 (*c* 1.06, $CHCl_3$); IR (NaCl) 3352, 2958, 1111, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05–1.07 (m, 13H, C9-CH_3 and SiC(CH_3)$_3$), 1.28 (s, 3H, C13-CH_3), 1.48 (d, *J* = 12.6 Hz, 1H, C12-*H*), 1.57–1.70 (m, 5H, C12-*H*, C14-*H* and C15-*H*), 2.20–2.27 (m, 1H, C10-*H*), 3.64–3.71 (m, 3H, C16-*H* and O*H*), 3.90 (dd, *J* = 12.6, 6.3 Hz, 1H, C11-*H*), 5.06–5.12 (m, 2H, =CH_2), 5.80 (ddd, *J* = 17.8, 10.3, 7.5 Hz, 1H, C9-*H*), 7.37–7.45 (m, 6H, Ar*H*), 7.66–7.68 (m, 4H, Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 15.0 (CH_3), 19.1 (C), 25.6 (CH_3), 26.6 (CH_2), 26.8 (CH_3), 41.6 (CH_2), 43.3 (CH_2), 44.3 (CH), 64.7 (CH_2), 72.3 (CH), 73.0 (C), 115.1 (CH_2), 127.7 (CH), 129.7 (CH), 133.4 (C), 135.6 (CH), 140.9 (CH); ESI-HRMS *m/z* calcd for $C_{27}H_{40}O_3SiNa$ $(M+Na)^+$ 463.26389, found 463.26352.

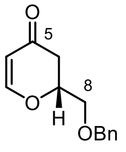
(5S,7S)-5-((S)-but-3-en-2-yl)-2,2,3,3,7,13,13-heptamethyl-12,12-diphenyl-4,11-dioxa-3,12-disilatetradecan-7-ol (110) (TS06075)



TBSCl (4.58 g, 30.4 mmol) was added to a solution of diol **131** (670 mg, 1.52 mmol) and DMAP (5.60 g, 45.6 mmol) in DMF (51 mL) at room temperature. After stirring for 8 h at this temperature, the reaction was quenched with a bit of ice. The whole was extracted with AcOEt (100 mL), and the organic extract was washed with water (2 × 30 mL) and brine (30 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (7.30 g), which was purified by column chromatography (silica gel 150 g, 30:1 *n*-hexane/AcOEt) to give **110** (437 mg, 52%; BRSM 98%) as a colorless oil and recovered starting material (317 mg, 47% recovered): R_f 0.48 (5:1 *n*-hexane/AcOEt); $[\alpha]_D^{25}$ –42.1 (*c* 1.01, $CHCl_3$); IR (NaCl) 3521, 2957, 2930, 2858, 1111, 702 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 0.17 (s, 3H, SiCH_3), 0.18 (s, 3H, SiCH_3), 0.93 (s, 9H, SiC(CH_3)$_3$), 0.96 (d, *J* = 7.3 Hz, 3H C10-CH_3), 1.05 (s, 9H, SiC(CH_3)$_3$), 1.20 (s, 3H, C13-CH_3), 1.35 (dd, *J* = 15.0, 2.5　Hz, 1H, C12-*H*), 1,46 (1.50 (m, 2H, C14-*H*), 1.56–1.67 (m, 3H, C12-*H* and C15-*H*), 2.54–2.55 (m, 1H, C10-*H*), 3.66 (t, *J* = 6.3 Hz, 2H, C16-*H*), 3.81 (s, 1H, O*H*), 4.09 (ddd, *J* = 10.4, 2.7, 2.5 Hz, 1H, C11-*H*), 5.04 (d, *J* = 16.8 Hz, 1H, =CH*H*), 5.14 (d, *J* = 10.7, 1H, =CH*H*), 6.06 (ddd, *J* = 16.8, 10.7, 5.0 Hz, 1H, C9-*H*), 7.35–7.44 (m, 6H, Ar*H*), 7.66–7.68 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ –4.60 (CH_3), –3.26 (CH_3), 14.8 (CH_3), 18.0 (C), 19.2 (C), 25.8 (CH_3), 25.9 (CH_3), 26.8 (CH_3), 26.9 (CH_2), 29.8 (CH_2), 40.4 (CH_2), 42.1 (CH), 64.5 (CH_2), 71.8 (C), 75.1 (CH), 114.9 (CH_2), 127.6 (CH), 129.5 (CH), 129.5 (CH), 134.0 (C), 135.6 (C), 128.3 (CH); ESI-HRMS *m/z* calcd for $C_{33}H_{54}O_3Si_2Na$ $(M+Na)^+$ 577.35037, found 577.35044.

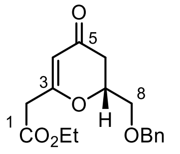
Part 1 Chapter 3 Section 2

(*R*)-2-((benzyloxy)methyl)-2,3-dihydro4*H*-pyran-4-one (108) (TS03013)71)



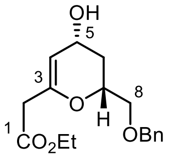
To a solution of benzyloxyacetoaldehyde (**109**) (593 mg, 3.94 mmol) in CH_2Cl_2 (3.94 mL) was added Rh_2(*R*-BPTPI)$_4$ (**134**) (28.2 mg, 0.0197 mmol, 0.5 mol %). The color of solution was changed from colorless to red and the mixture was stirred for 5 min at room temperature. A solution of *trans*-1-methoxy-3-(triethylsilyloxy)-1,3-butadiene (**2a**) (1.27 g, 5.92 mmol) in CH_2Cl_2 (3.94 mL) was added to the mixture dropwise at –20 °C. After stirring for 24 h at this temperature, a 10% solution of trifluoroacetic acid in CH_2Cl_2 (ca. 1.4 mL) was added and the mixture was stirred for an additional 2 h. The reaction was quenched with saturated $NaHCO_3$ (6 mL), and then the whole was extracted with AcOEt (2 ×15 mL). The organic extracts were washed with water (10 mL) and brine (10 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (2.00 g), which was purified by column chromatography (silica gel 60 g, 5:1 *n*-hexane/AcOEt) to give **08** (673 mg, 78%) as a colorless oil: R_f 0.09 (5:1 *n*-hexane/AcOEt); $[\alpha]_D^{19}$ –133.0 (*c* 1.16, $CDCl_3$) for 90% *ee* [*lit.*71), $[\alpha]_D^{24}$ +75.8 (*c* 0.455, $CHCl_3$) for (*S*)-enantiomer]; ^{1}H NMR (392 MHz, $CDCl_3$) δ 2.34 (dd, *J* = 2.4, 16.8 Hz, 1H, C6-*H*), 2.67 (dd, *J* = 14.4, 16.8 Hz, 1H, C6-*H*), 3.61 (dd, *J* = 5.1, 10.8 Hz, 1H, C8-*H*), 3.65 (dd, *J* = 3.8, 10.8 Hz, 1H, C8-*H*), 4.50–4.58 (m, 3H, OC*H*$_2$Ph and C7-*H*), 5.35 (d, *J* = 6.0 Hz, 1H, C4-*H*), 7.16–7.32 (m, 6H, Ar*H* and C4-*H*). The enantiomer excess of **124** was determined to be 90% by HPLC with a Chiralcel OD-H column (9:1 *n*-hecane/^{i}PrOH, 1.0 mL/min): t_R (major) = 17.0 min for (*R*)-enantiomer; t_R (minor) = 14.7 min for (*S*)-enantiomer.

Ethyl (*R*)-2-(2-((bensyloxy)methyl)-4-oxo-3,4-dihydro-2*H*-pyran-6-yl)acetate (107) (TS03007)



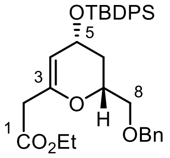
To a suspension of dihdropyranone **108** (794 mg, 3.64 mmol) and pulverized MS4A (1.99 g, 250 wt % of **108**) in toluene (3.64 mL) was added a solution of silyl ketene acetal **135** (701 mg, 4.37 mmol) in toluene (3.64 mL) at room temperature. After 1 h of stirring at this temperature, the reaction mixture was then filtered through a plug of Celite washed with toluene. Evaporation *in vacuo* furnished the crude product (1.56 g), which was used without further purification. To a solution of crude silyl enol ether (1.56 g) in DMSO (36.4 mL) was added $Pd(OAc)_2$ (81.7 mg, 0.364 mmol, 10 mol %), and the mixture was stirred for 24 h under 1 atm of oxygen atmosphere at 40 °C. The reaction was quenched with water (20 mL) and extracted with AcOEt (3 × 60 mL). The combined organic extracts were washed with brine (60 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished crude product (4.64 g), which was purified by column chromatography (silica gel 80 g, 2:1 *n*-hexane/AcOEt) to give **107** (787 mg, 70%) as a yellow oil: R_f 0.21 (2:1 *n*-hexane/AcOEt); $[\alpha]_D^{22}$ –87.8 (*c* 1.10, $CHCl_3$); IR (NaCl) 2922, 1734, 1669, 1616, 1398, 1338, 1255, 1027 cm^{-1}; ^{1}H NMR (392 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 2.41 (dd, *J* = 3.6, 16.6 Hz, 1H, C6-*H*), 2.71 (dd, *J* = 13.5, 16.6 Hz, 1H, C6-*H*), 3.29 (d, *J* = 4.0 H, 2H, C2-*H*), 3.69 (dd, *J* = 4.9, 10.8 Hz, 1H, C8-*H*), 3.74 (dd, 1H, *J* = 4.9, 10.8 Hz, C8-*H*), 4.18 (q, *J* = 7.2 Hz, 2H, OC*H*$_2$CH$_3$), 4.56–4.64 (m, 3H, OC*H*$_2$Ph and C7-*H*), 5.44 (s, 1H, C4-*H*), 7.28–7.36 (m, 5H, Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.2 (CH_3), 37.6 (CH_2), 40.8 (CH_2), 61.6 (CH_2), 70.5 (CH_2), 73.6 (CH_2), 78.8 (CH), 106.7 (CH), 127.8 (CH), 128,0 (CH), 128.6 (CH), 137.7 (C), 167.8 (C), 169.0 (C), 192.4 (C); ESI-HRMS *m/z* calcd for $C_{17}H_{20}O_5Na$ $(M+Na)^+$ 327.1208, found 327.1203.

Ethyl 2-((2*R*,4*R*)-2-((benzyloxy)methyl)-4-hydroxy-3,4-dihydro-2*H*-pyran-6-yl)acetate (137) (TS03010)



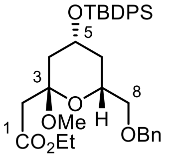
To a solution of dihydropyranone **107** (785 mg, 2.58 mmol) and CeCl·$7H_2O$ (961 mg, 2.58 mmol) in CH_2Cl_2 (6.45 mL) and MeOH (6.45 mL) was added $NaBH_4$ at –78 °C. After stirring for 5 h at this temperature, the reaction was quenched with saturated aqueous NH_4Cl (5 mL). The whole was extracted with AcOEt (20 mL), and the organic extract was washed with brine (10 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished crude product (840 mg), which was purified by column chromatography (silica gel 25 g, 2:1 *n*-hexane/AcOEt) to give **137** (725 mg, 92%) as a colorless oil: R_f 0.30 (1:1 *n*-hexane/AcOEt); $[\alpha]_D^{21}$ –16.1 (*c* 1.08, $CHCl_3$); IR (NaCl) 2923, 1722, 1612, 1512, 1461, 1450, 1371, 1299, 1243, 1081, 1027 cm^{-1}; ^{1}H NMR (392 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 1.75 (ddd, *J* = 3.1, 6.3 13.5 Hz, 1H, C6-*H*), 1.83 (br, 1H, OH), 2.21 (ddd, *J* = 3.1, 6.3, 13.5 Hz, 1H, C6-*H*), 3.06 (s, 2H, C2-*H*), 3.62 (dd, *J* = 4.5, 11.3 Hz, 1H, C8-*H*), 3.67 (dd, *J* = 4.5, 11.3 Hz, 1H, C8-*H*), 4.15 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 4.23 (ddd, *J* = 3.2, 4.5, 9.0 Hz, 1H, C7-*H*), 4.41 (m, 1H, C5-*H*), 4.58 (d, *J* = 2.2 Hz, 2H, OCH_2Ph), 4.80 (d, *J* = 2.2 Hz, 1H, C4-*H*), 7.26–7.35 (m, 5H, Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.3 (CH_3), 34.0 (CH_2), 40.2 (CH_2), 61.1 (CH_2), 62.6 (CH), 72.1 (CH_2), 73.6 (CH_2), 74.3 (CH), 103.9 (CH), 127.8 (CH), 127.9 (CH), 128.6 (CH), 138.0 (C), 149.5 (C), 170.0 (C); ESI-HRMS *m/z* calcd for $C_{17}H_{22}O_5Na$ $(M+Na)^+$ 329.1365, found 329.1359.

Ethyl 2-((2*R*,4*R*)-2-((benzyloxy)methyl)-4-((*tert*-butyldiphenylsilyl)oxy)-3,4-dihydro-2*H*-pyran-6-yl)acetate (138) (TS03023)



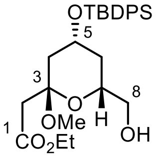
TBDPSCl (1.51 g, 5.49 mmol) was added to a stirred solution of alcohol **137** (1.12 g, 3.66 mmol) and DMAP (1.35 g, 11 mmol) and $^i Pr_2NEt$ (94.6 mg, 0.732 mmol) in DMF (3.66 mL) at 0 °C. After stirring for 5 h at this temperature, the reaction was quenched by addition of a bit of ice. The whole was extracted with AcOEt (25 mL), and the organic extract was washed with water (10 mL) and brine (10 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished crude product (3.82 g) which was purified by column chromatography (silica gel 100 g, 40:1 toluene/AcOEt) to give **138** (2.45 g,) as a colorless oil: R_f 0.31 (20:1 toluene/AcOEt); $[\alpha]_D^{22}$ –4.63 (*c* 1.49, $CHCl_3$); IR (NaCl) 2926, 2853, 1740, 1679, 1424, 1108, 1068 cm^{-1}; ^{1}H NMR (392 MHz, $CDCl_3$) δ 1.04 (s, 9H, $SiC(CH_3)_3$), 1.23 (t, *J* = 6.9 Hz, 3H, OCH_2CH_3);, 1.82 (ddd, *J* = 7.5, 9.2, 13.2 Hz, 1H, C6-*H*), 1.89 (ddd, *J* = 2.5, 5.8, 13.2 Hz, 1H, C6-*H*), 3.01 (d, *J* = 9.7 Hz, 2H, C2-*H*), 3.54 (dd, *J* =4.0, 10.3 Hz, 1H, C8-*H*), 3.72 (dd, *J* = 6.3, 10.5 Hz, 1H, C8-*H*), 4.09–4.14 (m, 3H, C7-*H* and OCH_2CH$_3$), 4.40 (ddd, *J* = 2.8, 6.3, 6.3 Hz, 1H, C5-*H*), 4.55 (s, 2H, OCH_2Ph), 4.65 (d, *J* = 2.3 Hz, 1H, C4-*H*), 7.28–7.43 (m, 11H, Ar*H*), 7.64–7.67 (m, 4H, Ar*H*); ^{13}C NMR (126 MHz, CDCl$_3$) δ 14.3 (CH$_3$), 19.3 (C), 27.1 (CH$_3$), 33.6 (CH$_2$), 40.3 (CH$_2$), 60.9 (CH$_2$), 63.9 (CH), 71.8 (CH$_2$), 73.4 (CH$_2$), 74.5 (CH), 104.3 (CH), 127.7 (CH), 127.8 (CH), 128.5 (CH), 129.8 (CH), 134.1 (C), 135.9 (CH), 138.4 (C), 148.4 (C), 170.1 (C); ESI-HRMS *m/z* calcd for $C_{33}H_{40}O_5SiNa$ (M+Na)$^+$ 567.2543, found 567.2537.

Ethyl 2-((2*S*, 4*R*, 6*R*)-6-((benzyloxymethyl)-4-((*tert*-butyldiphenylsilyl)oxy)-2-methoxytetrahydro-2*H*-pyran-2-yl)acetate (139) (TS03026)



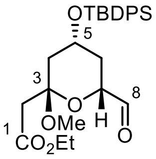
PPh$_3$·HBr (77.2 mg, 0.225 mmol, 5 mol %) was added to a stirred solution of dihydropyran **138** (2.45 g, 4.50 mmol) in CH$_2$Cl$_2$ (20.5 mL) and MeOH (2.05 mL) at room temperature. After stirring for 3 h at this temperature, the reaction was quenched with saturated aqueous NH$_4$Cl (5 mL). The whole was extracted with AcOEt (40 mL), and the organic extract was washed with brine (20 mL), and dried over anhydrous Na$_2$SO$_4$. Filtration and evaporation *in vacuo* furnished crude product (3.00 g) which was purified by column chromatography (silica gel 90 g, 30:1 toluene/AcOEt) to give **139** (2.20 g, 85%) as a colorless oil: R_f 0.29 (20:1 toluene/AcOEt); $[\alpha]_D^{21}$ –33.8 (*c* 1.25, CHCl$_3$); IR (NaCl) 3070, 2931,v2857, 1737, 1472, 1428, 1368, 1310, 1230 cm^{-1}; ^{1}H NMR (392 MHz, CDCl$_3$) δ 1.04 (s, 9H, SiC(CH_3)$_3$), 1.23 (t, *J* = 6.9 Hz, 3H, OCH$_2$CH_3), 1.34 (dd, *J* = 10.9, 12.9 Hz, 1H, C6-*H*), 1.67 (m, 1H, C6-*H*), 1.69 (dd, *J* = 7.4, 13.2 Hz, 1H, C4-*H*), 2.23 (ddd, *J* = 1.7, 5.2, 13.2 Hz, C4-*H*), 2.55 (d, *J* = 13.7 Hz, 1H, C2-*H*), 2.76 (d, *J* = 13.7 Hz, C2-*H*), 3.12 (s, 3H, OCH_3), 3.36 (dd, *J* = 4.0, 10.3 Hz, 1H, C8-*H*), 3.44 (dd, *J* = 6.3, 10.3 Hz, 1H, C8-*H*), 3.55 (m, 1H, C5-*H*), 4.10-4.14 (m, 3H, C7-*H* and OCH_2CH$_3$), 4.52 (s, 2H, OCH_2Ph), 7.27–7.42 (m, 11H, Ar*H*), 7.64–7.67 (m, 4H, Ar*H*); ^{13}C NMR (126 MHz, CDCl$_3$) δ 14.5 (CH$_3$), 19.3 (C), 27.1 (CH$_3$), 37.1 (CH$_2$), 42.3 (CH$_2$), 42.9 (CH$_2$), 48.0 (CH$_3$), 60.6 (CH$_2$), 66.2 (CH), 68.8 (CH), 73.0 (CH$_2$), 73.4 (CH$_2$), 99.9 (C), 127.5 (CH), 127.6 (CH), 127.7 (CH), 128.5 (CH), 129.7 (CH), 134.6 (C), 135.9 (CH), 138.5 (C), 169.5 (C); ESI-HRMS *m/z* calcd for $C_{33}H_{44}O_6SiNa$ (M+Na)$^+$ 599.2805, found 599. 2800.

Ethyl 2-((2*S*, 4*R*, 6*R*)-4-((*tert*-butyldiphenylsilyl)oxy)-6-(hydroxymethyl)-2-methoxytetrahydro-2*H*-pyran-2-yl)acetate (140) (TS03018)



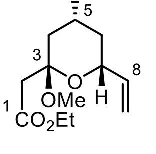
To a stirred solution of tetrahydropyran **139** (41.5 mg, 0.0719 mmol) in MeOH (1.44 mL) was added 20% Pd(OH)$_2$ on carbon (12.5 mg, 30 wt %) at 0 °C. The mixture was stirred for 8 h under 1 atm of hydrogen atmosphere. The catalyst was filtered through a Celite pad, and the filtrate was evaporated *in vacuo* to furnish the crude product (41.7 mg), which was purified by column chromatography (silica gel 5 g, 2:1 *n*-hexane/AcOEt) to give **140** (31.0 mg, 89%) as a colorless oil: R_f 0.29 (2:1 *n*-hexane/AcOEt); $[\alpha]_D^{23}$ –31.2 (*c* 1.27, CHCl$_3$); IR (NaCl) 3461, 3071, 2932, 2857, 1738, 1472, 1428, 1383, 1311, 1233, 1151, 1112 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) 1.04 (s, 9H, SiC(C*H*$_3$)$_3$), 1.25 (t, *J* = 6.9 Hz, 3H, OCH_2C*H*$_3$), 1.37 (m, 1H, C6-*H*), 1.57 (m, 1H, C6-*H*), 1.69 (dd, *J* = 10.9, 13.2 Hz, 1H, C4-*H*), 2.22 (ddd, *J* = 1.7, 5.7, 13.2 Hz, C4-*H*), 2.59 (d, *J* = 13.7 Hz, C2-*H*), 2.69 (d, *J* = 13.7 Hz, 1H, C2-*H*), 3.10 (s, 3H, OC*H*$_3$), 3.43–3.54 (m, 3H, C5-*H* and C8-*H*), 4.10–4.17 (m, 3H, C7-*H* and OC*H*$_2$CH$_3$), 7.35–7.43 (m, 6H, Ar*H*), 7.46–7.66 (m, 4H, Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.3 (CH_3), 19.2 (C), 27.0 (CH_3), 36.1 (CH_2), 42.2 (CH_2), 42.8 (CH_2), 48.0 (CH_3), 60.6 (CH_2), 65.7 (CH_2), 66.0 (CH), 69.9 (CH), 99.6 (C), 127.7 (CH), 129.7 (CH), 134.5 (C), 135.9 (CH), 169.3 (C); ESI-HRMS *m/z* calcd for $C_{27}H_{38}O_6SiNa$ (M+Na)$^+$ 509.2335, found 509.2330.

Ethyl 2-((2*S*, 4*R*, 6*R*)-4-((*tert*-butyldiphenylsilyl)oxy)-6-formyl-2-methoxytetrahydro-2*H*-pyran-2-yl)acetate (141) (TS03024)



Dess–Martin periodinane (1.81 g, 4.26 mmol) was added to a stirred solution of alcohol **140** (690 mg, 1.42 mmol) in CH_2Cl_2 (14.2 mL) at 0 °C. After stirring for 6 h at room temperature, the mixture was diluted with AcOEt (120 mL) and poured into the solution of saturated aqueous $NaHCO_3$ (18 mL) and 10% aqueous $Na_2S_2O_3$ (18 mL). The layers were separated and the organic layer was washed with brine (30 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (733 mg), which was purified column chromatography (silica gel 25 g, 4:1 *n*-hexane/AcOEt) to give **141** (638 mg, 93%) as a colorless oil: R_f 0.41 (1:1 *n*-hexane/AcOEt); $[\alpha]_D^{20}$ –32.4 (*c* 0.63, $CHCl_3$); IR (NaCl) 2931, 2857, 1737, 1472, 1428, 1230, 1112, 1042, 703 cm^{-1}; ^{1}H NMR (392 MHz, $CDCl_3$) 1.04 (s, 9H, SiC(C*H*$_3$)$_3$), 1.25 (t, *J* = 7.2 Hz, 3H, OCH_2C*H*$_3$), 1.38 (q, *J* = 12.6 Hz, C6-*H*), 1.73 (dd, *J* = 12.8, 10.8 Hz, C4-*H*), 1.92–1.96 (m, 1H, C6-*H*), 2.24 (ddd, *J* = 12.8, 4.9, 1.4 Hz, 1H, C4-*H*), 2.63 (d, *J* = 13.7 Hz, 1H, C2-*H*), 2.80 (d, *J* = 13.7 Hz, 1H, C2-*H*), 3.12 (s, 3H, OC*H*$_3$), 3.79 (dd, *J* = 12.6, 2.7 Hz, 1H, C7-*H*), 4.11–4.17 (m, 3H, C5-*H* and OC*H*$_2$CH$_3$), 7.35–7.44 (m, 6H, Ar*H*), 7.64–7.65 (m, 4H, Ar*H*), 9.54 (s, 1H, C8-*H*); ^{13}C NMR (99 MHz, $CDCl_3$) δ 14.2 (CH_3), 19.1 (C), 26.8 (CH_2), 34.6 (CH_2), 41.7 (CH_2), 42.5 (CH_2), 60.7 (CH_2), 65.3 (CH), 74.0 (CH), 100.1 (C), 127.6 (CH), 129.7 (CH), 133.9 (C), 135.7 (CH), 168.7 (C), 200.4 (CH); ESI-HRMS *m/z* calcd for $C_{27}H_{36}O_6SiNa$ (M+Na)$^+$ 507.21734, found 507.21790.

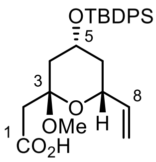
Ethyl 2-((2*S*, 4*R*, 6*R*)-4-((*tert*-butyldiphenylsilyl)oxy)-2-methoxy-6-vinyltetrahydro-2*H*-pyran-2-yl)acetate (142) (TS03032)



NaHMDS (1.0 M solution in THF, 3.05 mL, 3.05 mmol) was added to a stirred solution of Ph_3PCH_3Br (1.58 g, 4.42 mmol) in THF (18.4 mL) at 0 °C. After stirring for 30 min at this temperature, a solution of aldehyde **141** (1.07 g, 2.21 mmol) in THF (18.4 mL) was added dropwise at 0 °C. After stirring for 1 h at this temperature, the reaction was quenched with saturated aqueous NH_4Cl (20 mL). The whole was extracted with

AcOEt (50 mL), and the organic extract was washed with brine (20 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (1.94 g), which was purified b column chromatography (silica gel 60 g, 19:1 *n*-hexane/AcOEt) to give **142** (969 mg, 91%) as a colorless oil: R_f 0.20 (19:1 *n*-hexane/AcOEt); $[\alpha]_D^{20}$ –39.9 (*c* 1.42, $CHCl_3$); IR (NaCl) 2932, 2857, 1738, 1472, 1428, 1378, 1309, 1230, 1112, 1041 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.03 (s, 9H, $SiC(CH_3)_3$), 1.25 (t, *J* = 7.4 Hz, 3H, OCH_2CH_3), 1.36 (dd, *J* = 12.6, 12.6 Hz, C6-*H*), 1.70 (dd, *J* = 10.3, 12.6 Hz, C6-*H*), 1.76 (ddd, *J* = 2.3, 2.3, 12.6 Hz, C4-*H*), 2.23 (ddd, *J* = 2.3, 4.5, 12.6 Hz, C4-*H*), 2.58 (d, *J* = 9.2 Hz, C2-*H*), 2.76 (d, *J* = 9.2 Hz, C2-*H*), 3.11 (s, 3H, OCH_3), 3.80 (d, *J* = 5.7, 10.2 Hz, C5-*H*), 4.12 (m, 3H, C7-*H* and OCH_2CH_3), 5.04 (dt, *J* = 10.3, 1.6 Hz, =CH*H*), 5.14 (dt, *J* = 16.9, 1.6 Hz, =CH*H*), 5.73 (ddd, *J* = 16.9, 10.3, 5.8 Hz, 1H, C8-*H*), 7.35–7.43 (m, 6H, Ar*H*), 7.64–7.69 (m, 4H, Ar*H*); ^{13}C NMR (98.5 MHz, $CDCl_3$) δ 19.2 (C), 27.1 (CH_3), 40.4 (CH_2), 42.3 (CH_2), 42.7 (CH_2), 47.9 (CH_3), 60.6 (CH_2), 66.1 (CH_2), 69.9 (CH_2), 99.7 (C), 115.3 (CH_2), 127.7 (CH), 129.7 (CH), 134.4 (C), 135.9 (CH), 138.0 (CH), 169.2 (C); ESI-HRMS *m/z* calcd for $C_{28}H_{38}O_5SiNa$ $(M+Na)^+$ 505.23807, found 505.23838.

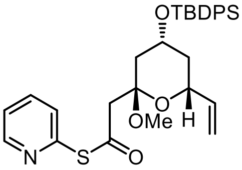
Ethyl 2-((2*S*, 4*R*, 6*R*)-4-((*tert*-butyldiphenylsilyl)oxy)-2-methoxy-6-vinyltetrahydro-2*H*-pyran-2-yl)acetic acid (106) (TS03036)



$Ba(OH)_2·8H_2O$ (3.18 g, 10.1 mmol) was added to a stirred solution of alkene **142** (969 mg, 2.01 mmol) in MeOH (67 mL) at 0 °C. After stirring for 24 h at room temperature, 1 M aqueous HCl was added until pH 3. The whole was extracted with AcOEt (3 × 100 mL), and the organic extracts were washed with brine (20 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (1.16 g), which was purified by column chromatography (silica gel 30 g, 2:1 *n*-hexane/AcOEt) to give **106** as a colorless oil: R_f 0.51 (1:1 *n*-hexane/AcOEt); $[\alpha]_D^{23}$ –43.3 (*c* 1.26, $CHCl_3$); IR (NaCl) 2931, 2857, 1713, 1472, 1428, 1379, 1310, 1255, 1148, 1112, 1047, 1007 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 1.04 (s, 9H, $SiC(CH_3)_3$), 1.40 (m, 1H, C6-*H*), 1.61 (dd, *J* = 11.1, 13.1 Hz, C6-*H*), 1.81 (dd, *J* = 2.3, 13.1 Hz, C4-*H*), 2.14 (m, 1H, C6-*H*), 2.66 (d, *J* = 15.7 Hz, C2-*H*), 2.77 (d, *J* = 15.7 Hz, 1H, C2-*H*), 3.08 (s, 3H, OCH_3), 3.95 (, 1H, C5-*H*), 4.10 (m, 1H, C7-*H*), 5.15 (dt, *J* = 10.4, 1.4 Hz, 1H, =CH*H*), 5.18 (dt, *J* = 16.8, 1.4 Hz, 1H, =CH*H*), 5.76 (ddd, *J* = 16.8, 10.4, 5.7 Hz, 1H, C8-*H*), 7.33–7.46 (m, 6H, Ar*H*), 7.61–7.69 (m, 4H, Ar*H*); ^{13}C NMR (99 MHz, $CDCl_3$) δ 19.7 (C), 27.5 (CH_3), 40.7 (CH_2), 42.5 (CH_2), 42.8 (CH_2), 48.7 (CH_3), 66.3 (CH), 70.9 (CH), 100.0 (C), 116.3 (CH_2), 128.2 (CH), 128.9 (CH), 130.2 (CH), 130.3 (CH), 134.6 (C), 134.9 (C), 136.3 (CH), 137.8 (CH), 173.6 (C); ESI-HRMS *m/z* calcd for $C_{26}H_{34}O_5Na$ $(M+Na)^+$ 477.2073, found 477.2061.

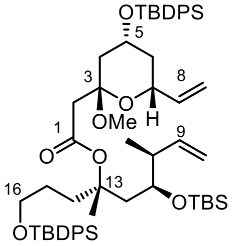
Part 1 Chapter 4 Section 1

S-(pyridin-2-yl) 2-((2*S*, 4*R*, 6*R*)-4-((*tert*-butyldiphenylsilyl)oxy)-2-methoxy-6-vinyltetrahydro-2*H*-pyran-2-yl)ethanethioate (143) (TS03038)



PPh$_3$ (1.38 g, 5.97 mmol) and 2,2-dipyridyl disulfide (1.32 g, 5.97 mmol) were added to a stirred solution of carboxylic acid **106** (903 mg, 1.99 mmol) in THF (9.95 mL) at 0 °C. After stirring for 24 h at room temperature, evaporation *in vacuo* furnished the crude product (3.30 g), which was purified by column chromatography (silica gel 90 g, 20:1 toluene/AcOEt) to give **143** (947 mg, 87%) as a yellow oil: R_f 0.56 (5:1 toluene/AcOEt); $[\alpha]_D^{20}$ –39.3 (*c* 1.37, CHCl$_3$); IR (NaCl) 2931, 2857, 1706, 1574, 1450, 1421, 1113, 704 cm^{-1}; ^{1}H NMR (396 MHz, CDCl$_3$) δ 0.96 (s, 9H, SiC(C*H*$_3$)$_3$), 1.30 (q, *J* = 11.1 Hz, 1H, C6-*H*), 1.63–1.69 (m, 2H, C4-*H* and C6-*H*), 2.18 (ddd, *J* = 13.1, 4.8, 1.4 Hz, 1H, C4-*H*), 2.91 (d, *J* = 14.2 Hz, C2-*H*), 2.98 (d, *J* = 14.2 Hz, C2-*H*), 3.06 (s, 3H, OC*H*$_3$), 3.76 (dd, *J* = 11.1, 5.5 Hz, C7-*H*), 4.08 (h, *J* = 4.5 Hz, 1H, C5-*H*), 4.99 (d, *J* = 10.4 Hz, 1H, =CH*H*), 5.13 (d, *J* = 17.2, 1H, =CH*H*), 5.68 (ddd, *J* = 16.8, 10.4, 5.5 Hz, 1H, C8-*H*), 7.20–7.35 (m, 7H, Ar*H* and Py*H*), 7.51–7.59 (m, 5H, Ar*H* and Py*H*), 7.67 (td, *J* = 7.7, 1.8 Hz, 1H, Py*H*), 8.56 (d, *J* = 3.2 Hz, 1H, Py*H*); ^{13}C NMR (99 MHz, CDCl$_3$) δ 19.1 (C), 26.9 (CH$_3$), 40.2 (CH$_2$), 42.4 (CH$_2$), 48.0 (CH$_3$), 50.1 (CH$_2$), 65.9 (CH), 69.9 (CH), 99.4 (C), 115.2 (CH$_2$), 123.5 (CH), 127.5 (CH), 129.5 (CH), 130.0 (CH), 134.1 (C), 134.3 (C), 135.7 (CH), 137.0 (CH), 137.6 (CH), 150.3 (CH), 151.6 (C), 191.8 (C); ESI-HRMS *m/z* calcd for $C_{31}H_{37}O_4NSSiNa$ (M+Na)$^+$ 570.21048, found 570.21077.

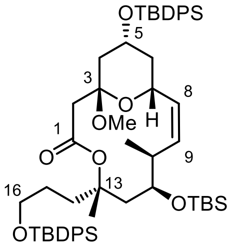
(5S,7S)-5-((S)-but-3-en-2-yl)-2,2,3,3,7,13,13-heptamethyl-12,12-diphenyl-4,11-dioxa-3,12-disilatetradecan-7-yl 2-((2S,4R,6R)-4-((tert-butyldiphenylsilyl)oxy)-2-methoxy-6-vinyltetrahydro-2H-pyran-2-yl)acetate (105) (TS06087)



Dehydrated stabilizer-free toluene was refluxed with Dean–Stark apparatus for 24 h and then bubbled argon gas for 30 min.

AgOTf in toluene (100 mg/mL, 4.04 mL) was added in one portion to a vigorously stirred solution of ester **143** (517 mg, 0.944 mmol), alcohol **110** (437 mg, 0.787 mmol) and 2,6-*di*-*tert*-butyl-4-methylpyridine (418 mg, 2.36 mmol) in toluene (7.87 mL) at room temperature. After stirring for 1 h, the reaction was quenched with saturated aqueous NaHCO$_3$ (15 mL) and then diluted with AcOEt (20 mL). The mixture was then filtered through a pad of Celite washed with AcOEt and the filtrate was washed with brine (10 mL), and dried over anhydrous Na$_2$SO$_4$. Filtration and evaporation *in vacuo* furnished the crude product (1.32 g), which was purified by column chromatography (silica gel 30 g, 30:1 *n*-hexane/AcOEt) to give **105** (598 mg, 77%) as a colorless oil and recovered alcohol **110** (101 mg, 23%) and carboxylic acid **106** (55.9 mg, 13%): R_f 0.43 (9:1 *n*-hexane/AcOEt); $[\alpha]_D^{26}$ –30.0 (*c* 1.07, CHCl$_3$); IR (NaCl) 2957, 2858, 1728, 1428, 1112, 759, 702 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.06 (s, 3H, SiCH_3), 0.07 (s, 3H, SiCH_3), 0.90 (s, 9H, SiC(CH_3)$_3$), 0.97 (d, *J* = 6.9 Hz, 3H, C9-CH_3), 1.03 (s, 9H, SiC(CH_3)$_3$), 1.07 (s, 9H, SiC(CH_3)$_3$), 1.34 (ddd, *J* = 12.6, 12.6, 12.6 Hz, 1H, C6-*H*), 1.49 (s, 3H, C13-CH_3), 1.57–1.66 (m, 2H, C15-*H*), 1.71–1.77 (m, 4H, C4-*H*, C6-*H*, C12-*H* and C14-*H*), 1.93–1.99 (m, 1H, C14-*H*), 2.11 (dd, *J* = 14.6, 4.3 Hz, 1H, C12-*H*), 2.24 (ddd, *J* = 12.6, 5.5, 2.0 Hz, 1H, C4-*H*), 2.38–2.45 (m, 1H, C10-*H*), 2.50 (d, *J* = 13.5 Hz, 1H, C2-*H*), 2.62 (d, *J* = 13.5 Hz, 1H, C2-*H*), 3.09 (s, 3H, OCH_3), 3.66 (t, *J* = 6.6 Hz, 2H, C16-*H*), 3.76–3.84 (m, 2H, C7-*H* and C11-*H*), 4.10–4.19 (m, 1H, C5-*H*), 4.98–5.06 (m, 3H, =CH_2 and =CH*H*), 5.14 (ddd, *J* = 16.6, 1.4, 1.4 Hz, 1H, =C*H*), 5.74 (ddd, *J* = 16.6, 10.0, 5.5 Hz, 1H, C8-*H*), 5.99 (ddd, *J* = 17.0, 10.0, 5.5 Hz, 1H, C9-*H*), 7.33–7.43 (m, 12H, Ar*H*), 7.64–7.69 (m, 8H, Ar*H*); ^{13}C NMR (126 MHz, CDCl$_3$) δ –4.07 (CH$_3$), –3.83 (CH$_3$), 12.8 (CH$_3$), 18.1 (C), 19.1 (C), 19.2 (C), 25.0 (CH$_3$), 26.0 (CH$_3$), 26.9 (CH$_3$), 27.0 (CH$_2$), 35.1 (CH$_2$), 40.2 (CH$_2$), 41.1 (CH$_2$), 42.5 (CH$_2$), 42.9 (CH), 43.1 (CH$_3$), 47.7 (CH$_3$), 64.1 (CH$_2$), 66.1 (CH), 69.7 (CH), 72.8 (CH), 84.9 (C), 99.7 (C), 114.2 (CH$_2$), 115.1 (CH$_2$), 127.5 (CH), 127.5 (CH), 127.6 (CH), 129.5 (CH), 129.6 (CH), 133.9 (C), 134.1 (C), 134.6 (C), 135.5 (CH), 135.7 (CH), 138.0 (CH), 140.4 (CH), 168.2 (C); ESI-HRMS *m/z* calcd for $C_{59}H_{86}O_7Si_3Na$ (M+Na)$^+$ 1013.55736, found 1013.55805.

(1S,5S,7S,8S,11R,13R,Z)-7-((tert-butyldimethylsilyl)oxy)-13-((tert-butyldiphenylsilyl)oxy)-5-(3-((tert-butyldiphenylsilyl)oxy)propyl)-1-methoxy-5,8-dimethyl-4,15-dioxabicyclo[9.3.1]pentadec-9-en-3-one (145) (TS06088)

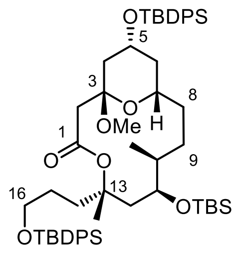


Dehydrated stabilizer-free toluene was refluxed for 24 h with Dean–Stark apparatus and then bubbled argon gas for 30 min.

A solution of ester **105** (597 mg, 0.602 mmol), Hoveyda–Grubbs 2nd generation catalyst (41.5 mg, 11 mol %), and 1,4-benzoquinone 104 mg, 0.963 mmol) in toluene (200 mL) was refluxed. After stirring for 7 h, the reaction mixture was absorbed on silica gel (415 mg, 10 equiv. wt, relative to Hoveyda-Grubbs 2nd generation catalyst) and passed through a pad of silica gel washed toluene. The filtrate was stirred for 12 h with activated charcoal (2.08 g, 50 equiv. wt of **105**). After the carbon was filtered, the filtrate was evaporated *in vacuo*, which was purified by column chromatography (silica gel 25 g, toluene only) to give **145** (530 mg, 91%) as a white amorphous: *R*$_f$ 0.28 (toluene only); $[\alpha]_D^{25}$ –43.6 (*c* 1.00, CHCl$_3$); IR (NaCl) 2956, 2931, 2857, 1724, 1111, 759, 703 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.06 (s. 3H, SiCH_3), 0.08 (s, 3H, SiCH_3), 0.90 (s, 9H, SiC(CH_3)$_3$), 0.92 (d, *J* = 6.9 Hz, 3H, C9-CH_3), 1.02 (s, 9H, SiC(CH_3)$_3$), 1.06 (s, 9H, SiC(CH_3)$_3$), 1.39–1.46 (m, 4H, C6-*H* and C13-CH_3), 1.57–1.67 (m, 3H, C4-*H* and C15-*H*), 1.73 (dd, *J* = 14.9, 2.9 Hz, 1H, C12-*H*), 1.77–1.84 (m, 2H, C6-*H* and C14-*H*), 1.99 (dd, *J* = 12.6, 2.9 Hz, 1H, C4-*H*), 2.08–2.18 (m, 2H, C12-*H* and C14-*H*), 2.31 (dd, *J* = 13.2 Hz, 1H, C2-*H*), 2.66 (d, *J* = 13.2 Hz, 1H, C2-*H*), 2.96 (s, 3H, OCH_3), 3.10–3.16 (m, 1H, C9-*H*), 3.65–3.74 (m, 2H, C16-*H*), 4.00–4.06 (m, 1H, C5-*H*), 4.08–4.10 (m, 1H, C11-*H*), 4.13–4.17 (m, 1H, C7-*H*), 5.04 (dd, *J* = 11.8, 2.9 Hz, 1H, C8-*H*), 5.37 (ddd, 11.8, 9.2, 1.7 Hz, 1H, C9-*H*), 7.35–7.43 (m, 12H, Ar*H*), 7.64–7.68 (m, 8H, Ar*H*); ^{13}C NMR (126 MHz, CDCl$_3$) δ –3.99 (CH$_3$), –3.95 (CH$_3$), 12.5 (CH$_3$), 18.3 (C), 19.0 (C), 19.2 (C), 25.1 (CH$_3$), 26.0 (CH$_3$), 26.9 (CH$_3$), 27.4 (CH$_2$), 36.2 (CH$_2$), 36.7

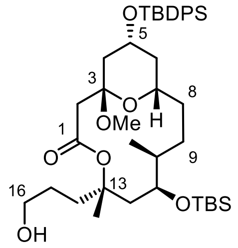
(CH), 41.1 (CH$_2$), 42.1 (CH$_2$), 44.4 (CH$_2$), 45.5 (CH$_2$), 38.9 (CH$_3$), 64.1 (CCH$_2$), 65.9 (CH), 68.3 (CH), 73.8 (CH), 83.3 (C), 100.3 (C), 126.3 (CH), 127.6 (CH), 129.5 (CH), 129.6 (CH), 133.9 (C), 134.0 (C), 134.2 (C), 134.4 (C), 135.5 (CH), 135.7 (CH), 138.7 (CH), 168.7 (C); ESI-HRMS *m/z* calcd for $C_{57}H_{82}O_7Si_3Na$ (M+Na)$^+$ 985.52606, found 985.52551.

(1S,5S,7S,8S,11S,13R)-7-((tert-butyldimethylsilyl)oxy)-13-((tert-butyldiphenylsilyl)oxy)-5-(3-((tert-butyldiphenylsilyl)oxy)propyl)-1-methoxy-5,8-dimethyl-4,15-dioxabicyclo[9.3.1]pentadecan-3-one (104) (TS06097)



A solution of alkene **145** (100 mg, 0.104 mmol) and 10% Pd/C (250 mg, 250 wt %) in MeOH (34.7 mL) was stirred under 1 atm hydrogen atmosphere. After stirring for 8 h, the mixture was filtered through a pad of Celite washed with AcOEt. Evaporating filtrate *in vacuo* furnished the crude product (113 mg), which was purified by column chromatography (silica gel 10 g, toluene only) to give **104** (96.8 mg, 96%) as a colorless oil: R_f 0.28 (toluene only); $[\alpha]_D^{26}$ –26.8 (*c* 1.65, CHCl$_3$); IR (NaCl) 2956, 2931, 2857, 1724, 1112, 760, 703 cm^{-1}; ^{1}H NMR (500 MHz, CDCL$_3$) δ 0.11 (s, 6H, SiCH_3 and SiCH_3), 0.81 (d, *J* = 6.9 Hz, 3H, C10-CH_3), 0.89 (s, 9H, SiC(CH_3)$_3$), 1.05 (s, 9H, SiC(CH_3)$_3$), 1.08 (s, 9H, SiC(CH_3)$_3$), 1.14–1.20 (m, 1H, C9-*H*), 1.36–1.46 (m, 5H, C6-*H*, C9-*H*, and C13-CH_3), 1.51–1.65 (m, 6H, C4-*H*, C6-*H*, C8-*H* and C15-*H*), 1.74 (td, *J* = 11.5, 5.2 Hz, 1H, C14-*H*), 1.87 (dd, *J* = 14.9, 2.9 Hz, 1H, C12-*H*), 1.99 (dd, *J* = 13.2, 3.4 Hz, 1H, C4-*H*), 2.03–2.16 (m, 3H, C10-*H*, C12-*H* and C14-*H*), 2.27 (d, *J* = 12.6 Hz, 1H, C2-*H*), 2.58 (d, *J* = 12.6 Hz, 1H, C2-*H*), 2.98 (s, 3H, OCH_3), 3.46–3.50 (m, 1H, C7-*H*), 3.65–3.73 (m, 2H, C16-*H*), 4.00–4.07 (m, 1H, C5-*H*), 4.19 (dd, *J* = 8.0, 2.9 Hz, 1H, C11-*H*), 7.35–7.45 (m, 12H, Ar*H*), 7.66–7.70 (m, 8H, Ar*H*); ^{13}C NMR (126 MHz, CDCl$_3$) δ –4.08 (CH$_3$), –3.35 (CH$_3$), 12.7 (CH$_3$), 18.4 (C), 19.1 (C), 19.2 (C), 25.1 (CH$_3$), 26.0 (CH$_3$), 26.9 (CH$_3$), 27.4 (CH$_2$), 32.1 (CH$_2$), 32.2 (CH$_2$), 35.7 (CH), 36.7 (CH$_2$), 38.7 (CH$_3$), 40.5 (CH$_2$), 42.7 (CH$_2$), 44.9 (CH$_2$), 45.4 (CH$_2$), 49.1 (CH$_3$), 64.1 (CH$_2$), 66.0 (CH), 69.3 (CH), 70.9 (C), 83.2 (C), 99.8 (C), 127.4 (CH), 127.5 (CH), 127.6 (CH), 129.5 (CH), 129.6 (CH), 133.9 (C), 134.0 (C), 134.3 (C), 134.4 (C), 135.6 (CH), 135.7 (CH), 168.9 (C); ESI-HRMS *m/z* calcd for $C_{57}H_{84}O_7Si_3Na$ (M+Na)$^+$ 987.54171, found 987.54076.

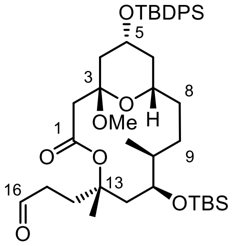
(1S,5S,7S,8S,11S,13R)-7-((tert-butyldimethylsilyl)oxy)-13-((tert-butyldiphenylsilyl)oxy)-5-(3-hydroxypropyl)-1-methoxy-5,8-dimethyl-4,15-dioxabicyclo[9.3.1]pentadecan-3-one (146) (TS06098)



A solution of AcOH (5.7 μL) in TBAF (1.0 M in THF, 0.10 mL) was added to a solution of lactone **104** (96.8 mg, 0.100 mmol) in THF (2 mL) at room temperature. After stirring for 12 h, the whole was extracted AcOEt (15 mL) and successively washed with saturated aqueous NaHCO$_3$ (4 mL), water (4 mL), and brine (4 mL), and dried over anhydrous Na$_2$SO$_4$. Filtration and evaporation *in vacuo* furnished the crude product (113 mg), which was purified by column chromatography (silica gel 10 g, 4:1 *n*-hexane/AcOEt then AcOEt only) to give **146** (23.2

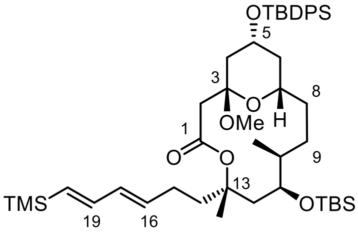
mg, 32%) and **147** (26.3 mg, 54%) as a colorless oils: R_f 0.16 (4:1 *n*-hexane/AcOEt); ^{1}H NMR (500 MHz, CDCL$_3$) δ 0.10 (s, 6H, SiC*H*$_3$ and SiC*H*$_3$), 0.80 (d, *J* = 6.9 Hz, 3H, C10-C*H*$_3$), 0.87 (s, 9H, SiC(C*H*$_3$)$_3$), 1.04 (s, 9H, SiC(C*H*$_3$)$_3$), 1.25–1.27 (m, 1H, C9-*H*), 1.38–1.50 (m, 5H, C6-*H*, C9-*H*, and C13-C*H*$_3$), 1.53–1.71 (m, 7H, C4-*H*, C6-*H*, C8-*H*, C9-*H* and C15-*H*), 1.83 (dd, *J* = 14.3, 3.4 Hz, 1H, C12-*H*), 1.97–2.00 (m, 2H, C4-*H* and C10-*H*), 2.07–2.17 (m, 2H, C12-*H* and C14-*H*), 2.30 (d, *J* = 12.6 Hz, 1H, C2-*H*), 2.60 (d, *J* = 12.6 Hz, 1H, C2-*H*), 2.96 (s, 3H, OC*H*$_3$), 3.47–3.51 (m, 1H, C7-*H*), 3.63–3.71 (m, 2H, C16-*H*), 3.99–4.05 (m, 1H, C5-*H*), 4.17 (dd, *J* = 8.0, 3.4 Hz, 1H, C11-*H*), 7.35–7.43 (m, 6H, Ar*H*), 7.65–7.67 (m, 4H, Ar*H*); ^{13}C NMR (126 MHz, CDCl$_3$) δ –4.03 (CH$_3$), –3.42 (CH$_3$), 14.7 (CH$_3$), 18.4 (C), 19.1 (C), 25.1 (CH$_3$), 26.0 (CH$_3$), 26.9 (CH$_3$), 27.2 (CH$_2$), 32.1 (CH$_2$), 32.2 (CH$_2$), 35.8 (CH), 36.6 (CH$_2$), 40.4 (CH$_2$), 42.4 (CH$_2$), 44.8 (CH$_2$), 45.5 (CH$_2$), 49.2 (CH$_3$), 63.1 (CH$_2$), 66.0 (CH), 69.4 (CH), 70.8 (CH), 83.1 (C), 99.9 (C), 127.5 (CH), 127.6 (CH), 129.5 (CH), 129.6 (CH), 134.3 (C), 134.4 (C), 135.7 (CH), 169.0 (C); ESI-HRMS *m/z* calcd for $C_{41}H_{66}O_7Si_2Na$ (M+Na)$^+$ 749.42393, found 749.42490.

3-((1S,5S,7S,8S,11S,13R)-7-((tert-butyldimethylsilyl)oxy)-13-((tert-butyldiphenylsilyl)oxy)-1-methoxy-5,8-dimethyl-3-oxo-4,15-dioxabicyclo[9.3.1]pentadecan-5-yl)propanal (148) (TS06099)



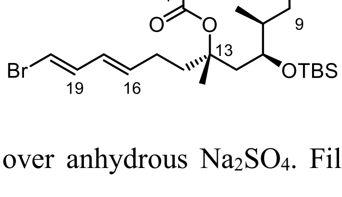
Dess–Martion periodinane (20.3 mg, 47.9 μmol) was added to a solution of alcohol **146** (23.2 mg, 31.9 μmol) in CH$_2$Cl$_2$ (0.160 mL) at 0 °C. After stirring for 1 h at room temperature, the reaction mixture was diluted with AcOEt (5 mL) and poured into a mixture of saturated aqueous NaHCO$_3$ (1.5 mL) and 10% aqueous Na$_2$S$_2$O$_3$ (1.5 mL). The layers were separated, the organic layer was washed with brine (2 mL), and dried over anhydrous Na$_2$SO$_4$. Filtration and evaporation *in vacuo* furnished the crude product (23.6 mg), which was purified by column chromatography (silica gel 10 g, 7:1 *n*-hexane/AcOEt) to give **148** (15.2 mg, 66%) as a colorless oil: R_f 0.33 (6:1 *n*-hexane/AcOEt); ^{1}H NMR (500 MHz, CDCL$_3$) δ 0.10 (s, 3H, SiC*H*$_3$), 0.12 (s, 3H, SiC*H*$_3$), 0.79 (d, *J* = 6.9 Hz, 3H, C10-C*H*$_3$), 0.87 (s, 9H, SiC(C*H*$_3$)$_3$), 1.04 (s, 9H, SiC(C*H*$_3$)$_3$), 1.12–1.18 (m, 1H, C9-*H*), 1.36–1.45 (m, 5H, C6-*H*, C8-*H*, and C13-C*H*$_3$), 1.49 (dd, *J* = 12.6, 10.9 Hz, 1H, C6-*H*), 1.55–1.68 (m, 4H, C4-*H*, C8-*H*, C9-*H* and C15-*H*), 1.79 (dd, *J* = 14.9, 3.4 Hz, 1H, C12-*H*), 1.84–1.93 (m, 2H, C10-*H* and C14-*H*), 1.99 (dd, *J* = 12.6, 4.6 Hz, 1H, C4-*H*), 2.24–2.32 (m, 2H, C2-*H* and C12-*H*), 2.42–2.57 (m, 3H, C2-*H* and C15-*H*), 2.95 (s, 3H, OC*H*$_3$), 3.47–3.51 (m, 1H, C7-*H*), 3.97–4.03 (m, 1H, C5-*H*), 4.17–4.19 (m, 1H, C11-*H*), 7.35–7.44 (m, 6H, Ar*H*), 7.65–7.67 (m, 4H, Ar*H*), 9.79 (s, 1H, C16-*H*); ^{13}C NMR (126 MHz, CDCl$_3$) δ –3.83 (CH$_3$), –3.44 (CH$_3$), 14.6 (CH$_3$), 18.4 (C), 19.1 (C), 24.8 (CH$_3$), 26.0 (CH$_3$), 26.9 (CH$_3$), 32.0 (CH$_2$), 32.3 (CH$_2$), 32.7 (CH$_2$), 36.3 (CH), 39.0 (CH$_2$), 40.7 (CH$_2$), 42.7 (CH$_2$), 44.8 (CH$_2$), 45.7 (CH$_2$), 49.4 (CH$_3$), 65.9 (CH), 68.8 (CH), 71.0 (CH), 82.2 (C), 99.9 (C), 127.5 (CH), 127.6 (CH), 129.6 (CH), 134.2 (C), 134.3 (C), 135.7 (CH), 168.9 (C), 201.7 (CH); ESI-HRMS *m/z* calcd for $C_{41}H_{63}O_7Si_2$ (M–H)$^-$ 723.41178, found 723.41226.

(1S,5S,7S,8S,11S,13R)-7-((tert-butyldimethylsilyl)oxy)-13-((tert-butyldiphenylsilyl)oxy)-1-methoxy-5,8-dimethyl-5-((3E,5E)-6-(trimethylsilyl)hexa-3,5-dien-1-yl)-4,15-dioxabicyclo[9.3.1]pentadecan-3-one (150) (TS07001)



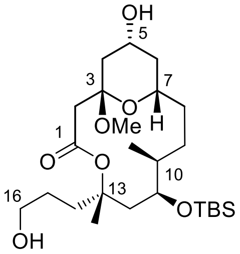
LiHMDS (1.0 M in THF, 54.6 μL, 54.6 μmol) was added to a stirred solution of silylallylphosphonate **149** (19.5 mg, 77.7 μmol) in THF (0.250 mL) at 0 °C. After stirring for 15 min at this temperature, a solution of aldehyde **152** (1.63 g, 5.67 mmol) and HMPA (20.8 mg, 116 μmol) in THF (0.300 mL) was added dropwise at 0 °C. After stirring for 2 h at room temperature, the reaction was quenched with saturated aqueous NH_4Cl (1 mL). The whole was extracted with EtOAc (6 mL), and the organic extract was washed with water (3 mL) and brine (3 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (30.9 mg), which was purified by column chromatography (silica gel 10 g, 30:1 *n*-hexane/AcOEt) to give **150** (5.3 mg, 31%) as a colorless oil: R_f 0.58 (9:1 *n*-hexane/AcOEt); ^{1}H NMR (500 MHz, $CDCL_3$) δ 0.07 (s, 9H, $Si(CH_3)_3$), 0.10 (s, 6H, $SiCH_3$ and $SiCH_3$), 0.79 (d, *J* = 6.9 Hz, 3H, C10-CH_3), 0.87 (s, 9H, $SiC(CH_3)_3$), 1.04 (s, 9H, $SiC(CH_3)_3$), 1.12–1.17 (m, 1H, C9-*H*), 1.39–1.46 (m, 5H, C6-*H*, C8-*H*, and C13-CH_3), 1.54–1.64 (m, 4H, C4-*H*, C6-*H*, C8-*H* and C9-*H*), 1.67–1.76 (m, 1H, C14-*H*), 1.87 (dd, *J* = 14.9, 3.4 Hz, 1H, C12-*H*), 1.96–2.06 (m, 3H, C4-*H*, C10-*H* and C12-*H*), 2.10–2.22 (m, 3H, C14-*H* and C15-*H*), 2.27 (d, *J* = 12.6 Hz, 1H, C2-*H*), 2.60 (d, *J* = 12.6 Hz, 1H, C2-*H*), 2.96 (s, 3H, OCH_3), 3.46–3.50 (m, 1H, C7-*H*), 3.99–4.05 (m, 1H, C5-*H*), 4.15–4.17 (m, 1H, C11-*H*), 5.68–5.75 (m, 2H, C16-*H* and C19-*H*), 6.09 (dd, *J* = 14.9, 10.3 Hz, 1H, C17-*H*), 6.48 (dd, *J* = 18.3, 10.3 Hz, 1H, C18-*H*), 7.35–7.43 (m, 6H, Ar*H*), 7.65–7.66 (m, 4H, Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ –4.09 (CH_3), –3.40 (CH_3), −1.27 (CH_3), 14.7 (CH_3), 18.4 (C), 19.1 (C), 26.0 (CH_3), 26.9 (CH_3), 27.1 (CH_2), 29.7 (CH_2), 32.1 (CH_2), 35.7 (CH), 38.7 (CH_3), 39.5 (CH_2), 40.3 (CH_2), 42.5 (CH_2), 44.8 (CH_2), 45.3 (CH_2), 49.1 (CH_3), 66.0 (CH), 69.5 (CH), 70.7 (CH), 82.9 (C), 99.8 (C), 127.5 (CH), 127.6 (CH), 129.6 (CH), 131.6 (CH), 133.5 (CH), 134.2 (C), 134.3 (C), 134.4 (CH), 134.8 (CH), 135.7 (CH), 144.2 (CH), 168.9 (C); ESI-HRMS *m/z* calcd for $C_{47}H_{76}O_6Si_2Na$ $(M+Na)^+$ 843.48419, found 843.48596.

(1S,5S,7S,8S,11S,13R)-5-((3E,5E)-6-bromohexa-3,5-dien-1-yl)-7-((tert-butyldimethylsilyl)oxy)-13-((tert-butyldiphenylsilyl)oxy)-1-methoxy-5,8-dimethyl-4,15-dioxabicyclo[9.3.1]pentadecan-3-one (151) (TS07005)



NBS (1.38 mg, 7.74 μmol) was added to a solution of diene **150** (5.3 mg, 6.45 μmol) in CH_3CN (0.650 mL) at room temperature. After stirring for 40 min at this temperature in the dark, the mixture was diluted with AcOEt (2 mL) and added water (1 mL). The layers were separated and the organic layer was washed with water (2 mL), 5% aqueous Na_2SO_3 (2 mL), water (2 mL) and brine (2 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product (5.6 mg), which was purified by preparative TLC (10:1 *n*-hexane/AcOEt) to give **151** (2.2 mg, 44%) as a colorless oil: R_f 0.53 (9:1 *n*-hexane/AcOEt); ^{1}H NMR (500 MHz, CDCL$_3$) δ 0.10 (s, 6H, SiCH_3 and SiCH_3), 0.79 (d, *J* = 6.3 Hz, 3H, C10-CH_3), 0.87 (s, 9H, SiC(CH_3)$_3$), 1.04 (s, 9H, SiC(CH_3)$_3$), 1.12–1.17 (m, 1H, C9-*H*), 1.39–1.47 (m, 5H, C6-*H*, C9-*H*, and C13-CH_3), 1.58–1.73 (m, 6H, C4-*H*, C6-*H*, C8-*H* and C14-*H*), 1.82–1.87 (m, 1H, C12-*H*), 1.97–2.04 (m, 2H, C6-*H* and C6-*H*), 2.05–2.13 (m, 2H, C12-*H*, C15-*H*), 2.27–2.37 (m, 2H, C2-*H* and C15-*H*), 2.59 (d, *J* = 12.6 Hz, 1H, C2-*H*), 2.95 (s, 3H, OCH_3), 3.47–3.51 (m, 1H, C7-*H*), 3.99–4.07 (m, 1H, C5-*H*), 4.13–4.18 (m, 1H, C11-*H*), 5.74 (dt, *J* = 14.7, 6.9 Hz, 1H, C16-*H*), 5.99 (dd, *J* = 14.7, 10.9 Hz, 1H, C17-*H*), 6.19 (dd, *J* = 13.5 Hz, 1H, C19-*H*), 6.67 (dd, *J* = 13.5, 10.9 Hz, 1H, C18-*H*), 7.35–7.44 (m, 6H, Ar*H*), 7.65–7.67 (m, 4H, Ar*H*); ESI-HRMS *m/z* calcd for $C_{44}H_{67}O_6BrSi_2Na$ (M+Na)$^+$ 849.35518, found 849.35559.

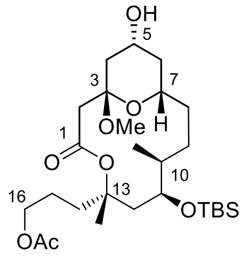
(1*S*,5*S*,7*S*,8*S*,11*S*,13*R*)-7-((tert-butyldimethylsilyl)oxy)-13-hydroxy-5-(3-hydroxypropyl)-1-methoxy-5,8-dimethyl-4,15-dioxabicyclo[9.3.1]pentadecan-3-one (147)



TBAF/AcOH =1:1 solution was prepared by mixing AcOH (17.2 μL) and TBAF (1.0 M in THF, 0.30 mL) and used immediately.

A solution of TBAF/AcOH (0.211 mL) was added to a solution of lactone **104** (96.6 mg, 0.100 mmol) in THF (2 mL) at room temperature. After stirring for 48 h, additional TBAF/AcOH (0.106 mL) was added and stirred for 24 h. The whole mixture was extracted AcOEt (15 mL) and successively washed with saturated aqueous $NaHCO_3$ (4 mL), water (4 mL), and brine (4 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product, which was purified by flash column chromatography (silica gel, 1:4 *n*-hexane/AcOEt) to give **147** (46.3 mg, 95%) as a white amorphous; R_f 0.22 (1:4 *n*-hexane/AcOEt); $[\alpha]_D^{26}$ –56.3 (*c* 0.40, CHCl$_3$); IR (NaCl) 3368, 2952, 2930, 1721, 1250, 1043, 835 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.062 (s, 6H, Si(CH_3)$_2$), 0.069 (s, 6H, Si(CH_3)$_2$), 0.82 (d, *J* = 6.4 Hz, 3H, C10-CH_3), 0.86 (s, 9H, SiC(CH_3)$_3$), 1.23–1.31 (m, 1H, C9-*H*), 1.44 (s, 3H, C13-CH_3), 1.49 (dd, *J* = 12.1, 11.5 Hz, 1H, C4-*H*), 1.57–1.69 (m, 6H, C8-*H*, C9-*H*, C12-*H* and C15-*H*), 1.76 (dd, *J* = 14.3, 2.9 Hz, 1H, C12-*H*), 1.83 (ddd, *J* = 12.0, 2.3, 2.3 Hz, 1H, C6-*H*), 2.11 (m, 1H, C14-*H*), 2.17–2.22 (m, 3H, C11-*H* and C14-*H*), 2.35 (d, *J* = 12.6 Hz, 1H, C2-*H*), 2.74 (d, *J* =12.6 Hz, 1H, C2-*H*), 3.22 (s, 3H, C3-OCH_3), 3.62–3.69 (m, 3H, C7-*H* and C16-*H*), 3.99–4.05 (m, 1H, C5-*H*), 4.14 (d, *J* = 6.9 Hz, 1H, C11-*H*); ^{13}C NMR (126 MHz, CDCl$_3$) δ –4.14 (CH$_3$), –3.52 (CH$_3$), 14.2 (CH$_3$), 18.3 (C), 25.2 (CH$_3$), 25.9 (CH$_3$), 27.2 (CH$_2$), 31.2 (CH$_2$), 32.3 (CH$_2$), 35.6 (CH), 36.0 (CH$_2$), 39.9 (CH$_2$), 43.0 (CH$_2$), 45.1 (CH$_2$), 45.5 (CH$_2$), 49.0 (CH$_3$), 62.9 (CH$_2$), 64.5 (CH), 69.8 (CH), 71.2 (CH), 83.7 (C), 99.6 (C), 169.0 (C); ESI-HRMS *m/z* calcd for $C_{30}H_{48}O_7SiNa$ (M+Na)$^+$ 511.30615, found 511.30659.

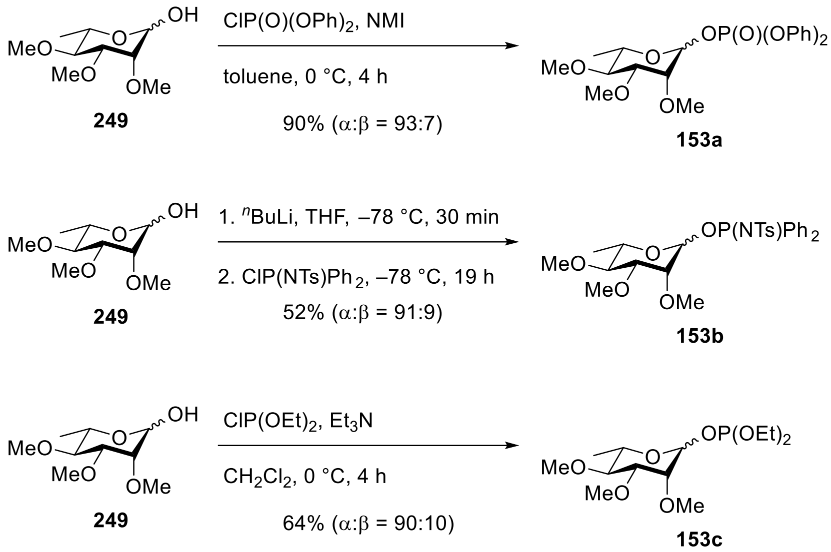
3-((1*S*,5*S*,7*S*,8*S*,11*S*,13*R*)-7-((tert-butyldimethylsilyl)oxy)-13-hydroxy-1-methoxy-5,8-dimethyl-3-oxo-4,15-dioxabicyclo[9.3.1]pentadecan-5-yl)propyl acetate (152) (TS10023)



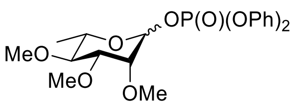
1.0 M AcCl in CH_2Cl_2 (0.0982 mL, 98.2 μmol) was added to a solution of diol **147** (45.7 mg, 93.5 μmol) and collidine (23.8 mg, 0.196 mmol) in CH_2Cl (0.935 mL) at –78 °C. After stirring for 1 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (2 mL) and whole mixture was extracted with AcOEt (2×5 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 mL), saturated aqueous $CuSO_4$ (2 mL), water (2 mL), brine (2 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished crude product, which was purified by flash column chromatography (silica gel, 1:1 to 1:5 hexane/AcOEt) to give **152** (38.2 mg, 77%, 85%brsm) as a colorless oil and recovered diol **147** (4.3 mg, 9%): R_f 0.55 (1:4 hexane/AcOEt); $[\alpha]_D^{26}$ –56.3 (*c* 0.40, $CHCl_3$); IR (NaCl) 3368, 2952, 2930, 1721, 1250, 1043, 835 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 0.059 (s, 3H, $\mathrm{Si(C}H_3)_2$), 0.064 (s, 3H, $\mathrm{Si(C}H_3)_2$), 0.82 (d, *J* = 6.8 Hz, 3H, $\mathrm{C10\text{-}C}H_3$), 0.86 (s, 9H, $\mathrm{SiC(C}H_3)_3$), 1.20–1.29 (m, 2H, C6-*H* and C9-*H*), 1.39–1.47 (m, 4H, C4-*H* and $\mathrm{C13\text{-}C}H_3$), 1.53–1.63 (m, 3H, C8-*H*, C9-*H* and C14-*H*), 1.64–1.70 (m, 3H, C8-*H* and C15-*H*), 1.74 (dd, *J* = 15.0, 3.2 Hz, 1H, C12-*H*), 1.82–1.86 (m, 1H, C6-*H*), 2.05 (s, 3H, $\mathrm{C}H_3\mathrm{CO}$), 2.11–2.17 (m, 3H, C4-*H*, C10-*H* and C14-*H*), 2.21 (dd, *J* = 15.0, 8.2 Hz, 1H, C12-*H*), 2.37 (d, *J* = 12.7 Hz, 1H, C2-*H*), 2.71 (d, *J* = 12.7 Hz, 1H, C2-*H*), 3.23 (s, 3H, $\mathrm{C3\text{-}OC}H_3$), 3.64–3.69 (m, 1H, C7-*H*), 3.98–4.16 (m, 4H, C5-*H*, C11-*H* and C16-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ –4.05 (CH_3), –3.53 (CH_3), 14.4 (CH_3), 18.3 (C), 21.0 (CH_3), 23.4 (CH_2), 25.0 (CH_3), 25.9 (CH_3), 31.8 (CH_2), 32.4 (CH_2), 35.9 (CH), 36.2 (CH_2), 40.3 (CH_2), 43.2 (CH_2), 45.2 (CH_2), 45.6 (CH_2), 49.2 (CH_3), 64.4 (CH), 64.5 (CH_2), 69.2 (CH), 71.3 (CH), 83.2 (C), 99.6 (C), 169.0 (C), 171.2 (C); ESI-HRMS *m/z* calcd for $C_{27}H_{50}O_8SiNa$ $(M+Na)^+$ 553.31672, found 553.31683.

Part 1 Chapter 4 Section 2

[Synthesis of phosphorous-containing glycosyl donors 153]*



diphenyl ((3*R*,4*R*,5*S*,6*S*)-3,4,5-trimethoxy-6-methyltetrahydro-2*H*-pyran-2-yl) phosphate (153a) (TS06051)



Diphenyl chlorophosphate (0.36 mL, 1.74 mmol) was added to a solution of lactol **249**$^{72)}$ (300 mg, 1.45 mmol), NMI (143 mg, 1.74 mmol), and Et_3N (176 mg, 1.74 mmol) in toluene (11.2 mL) at 0 °C. After stirring for 4 h at this temperature, the reaction mixture was quenched with ice and whole mixture was poured into a two-layered mixture of AcOEt (10 mL) and saturated aqueous $NaHCO_3$ (10 mL), and the whole mixture was extracted with AcOEt (30 mL). The organic extract was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product, which was purified by flash column chromatography (silica gel, 5% Et_3N in 1:2 hexane/AcOEt) to give **153a** (560 mg, 90%, α:β = 92:8) as a colorless oil: R_f 0.62 (1:2 hexane/AcOEt); ^{1}H NMR (392 MHz, $CDCl_3$) δ 1.18 (d, J = 6.3 Hz, 2.67H, α-C5-CH_3), 1.31 (d, J = 6.3 Hz, 0.23 H, β-C5-CH_3), 3.13 (dd, J = 9.6, 9.4 Hz, 1H, α-C4-*H*), 3.37–3.41 (m, 4H, α-OCH_3 and α-C3-*H*), 3.47 (s, 3H, α-OCH_3), 3.53–3.54 (m, 4H, α-OCH_3, α-C2-*H*), 3.63 (dq, J = 9.6, 6.3 Hz, 1H, α-C5-*H*), 5.35 (d, J = 7.2 Hz, 0.08H, β-C1-*H*), 5.91 (dd, J = 6.3, 2.2 Hz, 0.92H, α-C1-*H*), 7.19–7.28 (m, 6H, Ar*H*), 7.34–7.38 (m, 4H, Ar*H*); ESI-LRMS *m/z* calcd for $C_{21}H_{27}O_8PNa$ (M+Na)$^+$ 461.13, found 460.93. The diastereomeric ratio was determined by ^{1}H NMR analysis. Residual β-anomer peaks were difficult to assign.

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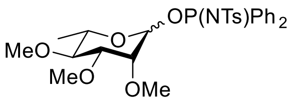
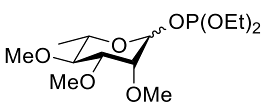
*Trichloroacetoimidate **153d** was synthesized according to reported procedure$^{73)}$.

(3*R*,4*R*,5*S*,6*S*)-3,4,5-trimethoxy-6-methyltetrahydro-2*H*-pyran-2-yl *P*,*P*-diphenyl-N-tosylphosphinimidate (153b) (TS06030)



^{n}BuLi (1.6 M in hexane, 0.95 mL, 1.52 mmol) was added to a stirred solution of lactol **249**$^{71)}$ (300 mg, 1.45 mmol) in THF (4.39 mL) at −78 °C. After stirring for 30 min, *P*,*P*-diphenyl-*N*-(*p*-toluenesulfonyl)phosphinimidic chloride$^{74)}$ (850 mg, 2.18 mmol) in THF (1.0 M, 2.2 mL, 2.18 mmol) was added, After stirring at this temperature for 19 h, the reaction was quenched by crushed ice. The mixture was poured into a two-layered mixture of AcOEt (10 mL) and saturated aqueous $NaHCO_3$ (10 mL), and the whole mixture was extracted with AcOEt (30 mL). The organic extract was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product, which was purified by flash column chromatography (silica gel, 10% Et_3N in 1:1 toluene/AcOEt) to give **153b** (560 mg, 52%, α:β = 91:9) as a colorless oil: R_f 0.52 (1:1 toluene/AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96 (d, *J* = 6.0 Hz, 2.67H, α-C5-C*H*$_3$), 2.32 (s, 3H, $SO_2C_6H_4$C*H*$_3$), 3.14 (dd, *J* = 9.7, 9.6 Hz, 1H, α-C4-*H*), 3.51 (dd, *J* = 9.6, 6.0 Hz, 1H, α-C5-*H*), 3.53 (s, 3H, α-OC*H*$_3$), 3.54 (s, 3H, α-OC*H*$_3$), 3.55 (s, 3H, α-OC*H*$_3$), 3.62 (dd, *J* = 9.7, 3.4 Hz, 1H, α-C3-*H*), 4.09–4.10 (m, 1H, α-C2-*H*), 4.69 (dd, *J* = 9.2, 2.9 Hz, 1H, β-C1-*H*), 6.13 (dd, *J* = 9.2, 1.7 Hz, α-C1-*H*), 7.07 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.37–7.46 (m, 5H, Ar*H*), 7.53–7.63 (m, 5H, Ar*H*), 7.80 (dd, *J* = 14.3, 8.6 Hz, 2H, Ar*H*); ESI-LRMS *m/z* calcd for $C_{28}H_{34}NO_7PSNa$ $(M+Na)^+$ 582.17, found 581.94. The diastereomeric ratio was determined by ^{1}H NMR analysis. Residual β-anomer peaks were difficult to assign.

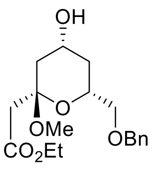
diethyl ((3*R*,4*R*,5*S*,6*S*)-3,4,5-trimethoxy-6-methyltetrahydro-2*H*-pyran-2-yl) phosphite (153c) (TS10024)



90% Chlorodiethylphosphite (0.65 mL, 4.04 mmol) was added to a solution of lactol **249**$^{71)}$ (555 mg, 2.69 mmol) and Et_3N (681 mg, 6.73 mmol) in CH_2Cl_2 (26.9 mL) at 0 °C. After stirring for 6 h at this temperature, the reaction mixture was quenched with ice and whole mixture was extracted with CH_2Cl_2 (30 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (15 mL), water (15 mL), brine (15 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product, which was purified by flash column chromatography (silica gel, 10% Et_3N in 4:1 hexane/AcOEt) to give **153c** (560 mg, 64%, α:β = 90:10) as a colorless oil: R_f 0.63 (1:2 hexane/AcOEt); $[\alpha]_D^{17}$ −33.9 (*c* 1.20, $CHCl_3$) for α:β = 90:10 anomeric mixture; IR (NaCl) 1445, 1388 cm^{-1}; ^{1}H NMR (392 MHz, $CDCl_3$) δ 1.25–1.30 (m, 8.7H, α,β-P(OCH_2C*H*$_3$)$_2$ and α-C5-C*H*$_3$), 1.33 (d, *J* = 5.8 Hz, 0.3 H, β-C5-C*H*$_3$), 3.14 (dd, *J* = 9.0, 9.0 Hz, 1H, α,β-C4-*H*), 3.50 (s, 3H, α,β-OC*H*$_3$), 3.51–3.53 (m, 3.7H, α-OCH_3 and α,β-C3-*H*), 3.55–3.57 (m, 4H, α,β-OC*H*$_3$ and α,β-C2-*H*), 3.64–3.69 (m, 0.4H, β-C5-*H* and β-OC*H*$_3$), 3.72–3.74 (m, 0.9H, α-C5-*H*), 3.86–3.95 (m, 4H, α,β-P(OC*H*$_2$$CH_3$)$_2$), 4.97 (d, *J* = 8.5 Hz, 0.1H, β-C1-*H*), 5.53 (dd, *J* = 7.6, 0.9 Hz, 0.9H, α-C1-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.8 (α,β-CH_3), 16.8 (α,β-CH_3), 17.6 (α,β-CH_3), 57.5 (β-CH_3), 57.7 (α-CH_3), 58.3 (α,β-CH_2), 58.5

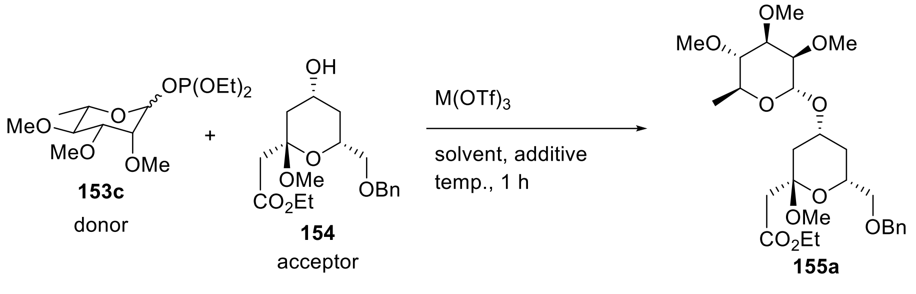
(α,β-CH$_2$), 58.9 (α-CH$_3$), 59.0 (β-CH$_3$), 60.9 (α-CH$_3$), 61.7 (β-CH$_3$), 68.7 (α-CH), 68.9 (d, $J_{\text{C–P}}$ = 9.5 Hz, β-CH), 72.1 (β-CH), 78.1 (d, $J_{\text{C–P}}$ = 3.8 Hz, α-CH), 80.5 (α-CH), 81.4 (β-CH), 81.9 (α-CH), 83.7 (β-CH), 91.0 (d, $J_{\text{C–P}}$ = 13.4 Hz, α-CH), 94.4 (d, $J_{\text{C–P}}$ = 13.4 Hz, β-CH); ^{31}P NMR (160 MHz, CDCl$_3$) δ 139.6 (β-anomer), 140.5 (α-anomer); ESI-HRMS *m/z* calcd for $C_{13}H_{27}O_7PNa$ (M+Na)$^+$ 349.13866, found 349.13842. The diastereomeric ratio was determined by ^{1}H NMR analysis.

[Preparation of model alcohol 154]



1 M solution of TBAF in THF (2.45 mL, 2.45 mmol) was added to a stirred solution of tetrahydropyran **139** (706 mg, 1.22 mmol) in THF (12.2 mL) at room temperature for 15 h. The whole was extracted with EtOAc (50 mL), and the organic extract was washed with brine (20 mL), and dried over anhydrous Na$_2$SO$_4$. Filtration and evapolation *in vacuo* furnished crude product (743 mg) which was purified by column chromatography (silica gel, 1:1 hexane/EtOAc) to give alcohol **154** (367 mg, 89%) as a colorless oil: R_f 0.14 (1:1 hexane/EtOAc); ^{1}H NMR (392 MHz, CDCl$_3$) δ 1.25–1.27 (m, 4H, OCH$_2$C*H*$_3$, C6-*H*), 1.54 (dd, *J* = 11.2, 12.6 Hz, 1H, C4-*H*), 1.94–1.99 (m, 1H, C6-*H*), 2.34 (ddd, *J* = 2.2, 4.9, 12.6 Hz, C4-*H*), 2.58 (d, *J* = 14.2 Hz, 1H, C2-*H*), 2.85 (d, *J* = 14.2 Hz, C2-*H*), 3.25 (s, 3H, OC*H*$_3$), 3.48 (dd, *J* = 4.5, 10.3 Hz, 1H, C8-*H*), 3.55 (dd, *J* = 5.8, 10.3 Hz, 1H, C8-*H*), 3.78–3.80 (m, 1H, C7-*H*), 4.08–4.18 (m, 3H, C5-*H* and OC*H*$_2$CH$_3$), 4.58 (s, 2H, OC*H*$_2$Ph), 7.29–7.33 (m, 5H, Ar-*H*); ^{13}C NMR (126 MHz, CDCl$_3$) δ 14.1 (CH$_3$), 36.6 (CH$_2$), 42.0 (CH$_2$), 42.7 (CH$_2$), 48.0 (CH$_3$), 60.6 (CH$_2$), 64.4 (CH), 68.9 (CH), 72.8 (CH$_2$), 68.8 (CH), 72.8 (CH$_2$), 73.3 (CH$_2$), 99.4 (C), 127.5 (CH), 127.6 (CH), 128.3 (CH), 138.2 (C), 169.1 (C); ESI-LRMS *m/z* calcd for $C_{18}H_{26}O_6Na$ (M+Na)$^+$ 361.16, found 361.15.

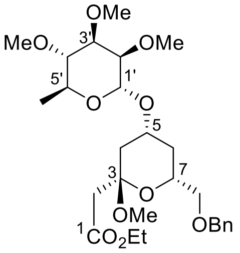
[Optimization of Reaction Conditions]



General Procedure for the Glycosidation (TS07051–TS07060, TS07062–TS07065, TS07068, TS07068, TS07076–TS07078, TS07087, TS07088)

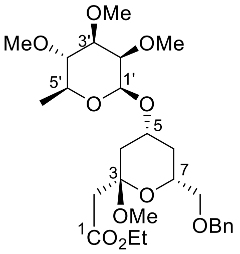
Promotor (0.3 equiv.) was added to a solution of acceptor alcohol **154**, glycosyl donor **153c** (1.5 equiv. or 3.0 equiv.), and MS4A (100 wt %, if added) in solvent (0.1 M) at set temperature. After stirring for 2 h at this temperature, the reaction mixture was quenched with Et$_3$N (0.1 mL) and extracted with AcOEt (5 mL). The organic layer was washed with saturated aqueous NaHCO$_3$ (2 mL), water (2 mL), brine (2 mL), and dried over anhydrous Na$_2$SO$_4$. Filtration and evaporation was furnished crude product, which was analyzed by ^{1}H NMR using benzyl benzoate as an internal standard in $\mathrm{CDCl_3}$.

Data for ethyl 2-((2S,4R,6R)-6-((benzyloxy)methyl)-2-methoxy-4-(((2R,3R,4R,5S,6S)-3,4,5-trimethoxy-6-methyltetrahydro-2H-pyran-2-yl)oxy)tetrahydro-2H-pyran-2-yl)acetate (155a)



Colorless oil: R_f 0.59 (1:2 hexane/AcOEt); ^{1}H NMR (396 MHz, $\mathrm{CDCl_3}$) δ 1.17–1.27 (m, 7H, $\mathrm{CO_2CH_2C}H_3$, C6-*H* and C5'-CH_3), 1.61 (dd, *J* = 12.7, 11.3 Hz, 1H, C6-*H*), 1.99–2.04 (m, 1H, C4-*H*), 2.30 (ddd, *J* = 12.7, 5.3, 1.4 Hz, 1H, C4-*H*), 2.57 (d, *J* = 13.8 Hz, 1H, C2-*H*), 2.81 (d, *J* = 13.8, 1 h, C2-*H*), 3.09 (dd, *J* = 9.5, 9.5 Hz, 1H, C4'-*H*), 3.24 (s, 3H, C3-OCH_3), 3.43–3.61 (m, 13H, C8-*H*, C2'-*H*, C3'-*H*, C5'-*H*, C2'-OCH_3, C3'-OCH_3 and C4'-OCH_3), 4.03–4.19 (m, 3H, C5-*H* and OCH_2CH$_3$), 4.57 (s, 2H, OCH_2Ph), 4.97 (d, *J* = 1.4 Hz, C1'-*H*), 7.28–7.35 (m, 5H, Ar*H*); ESI-LRMS *m/z* calcd for $\mathrm{C_{27}H_{42}O_{10}Na}$ (M+Na)$^+$ 549.27, found 548.99. The relative configuration at C1' was determined by NOE correlation from C1' to C3' and C5' of isolated minor isomer, β-anomer product (see below).

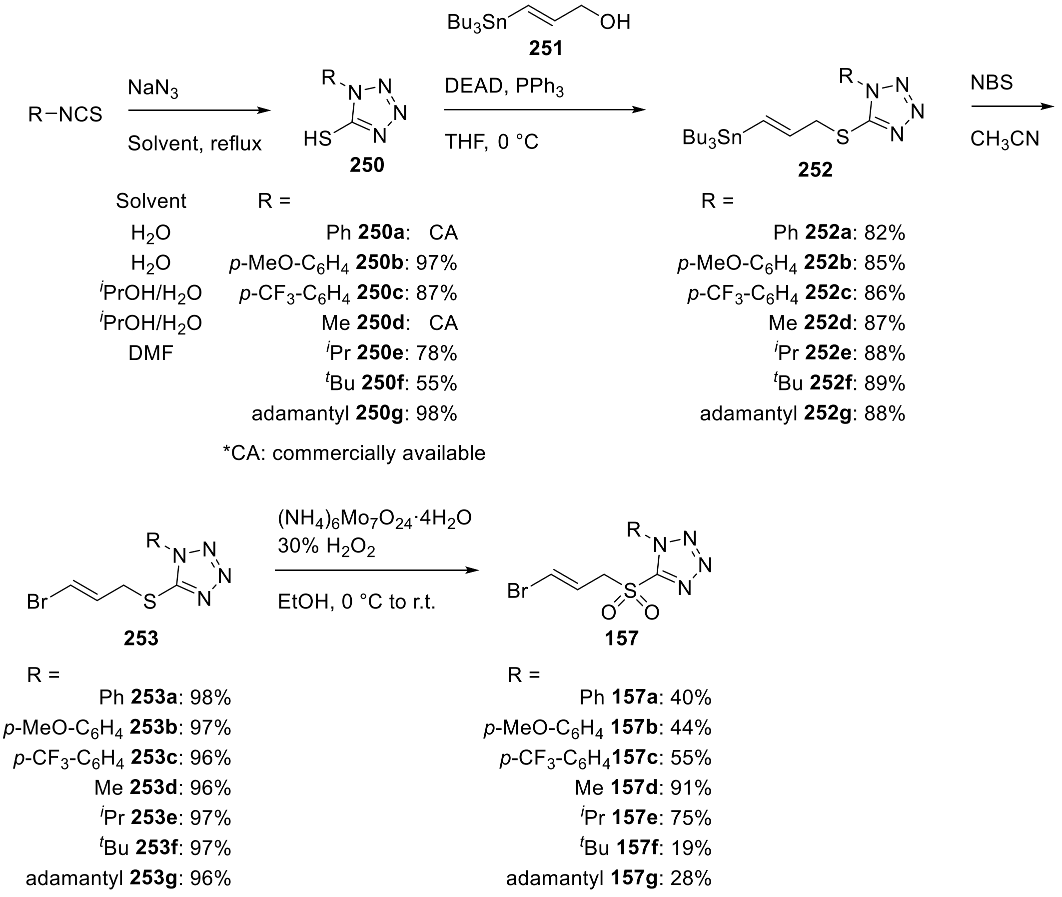
Data for ethyl 2-((2S,4R,6R)-6-((benzyloxy)methyl)-2-methoxy-4-(((2S,3R,4R,5S,6S)-3,4,5-trimethoxy-6-methyltetrahydro-2H-pyran-2-yl)oxy)tetrahydro-2H-pyran-2-yl)acetate (155b)



Colorless oil: R_f 0.53 (1:2 hexane/AcOEt); ^{1}H NMR (396 MHz, $\mathrm{CDCl_3}$) δ 1.26 (t, *J* = 6.8 Hz, 3H, $\mathrm{CO_2CH_2C}H_3$), 1.31 (d, *J* = 5.9 HZ, 3H, C5'-CH_3), 1.39 (dd, *J* = 12.2, 12.2 Hz, 1H, C6-*H*), 2.12–2.20 (m, 1H, C4-*H*), 2.38 (ddd, *J* = 12.7, 5.0, 1.8 Hz, 1H, C4-*H*), 2.57 (d, *J* = 14.0 Hz, 1H, C2-*H*), 2.86 (d, *J* = 14.0 Hz, 1H, C2-*H*), 3.07–3.08 (m, 1H, C3'-*H*), 3.14–3.18 (m, 1H, C5'-*H*), 3.25 (s, 3H, C3-OCH_3), 3.44–3.48 (m, 5H, C8-*H*, C4'-*H* and OCH_3), 3.51–3.55 (m, 4H, C8-*H* and OCH_3), 3.59–3.60 (m, 4H, C2'-*H* and OCH_3), 3.76–3.82 (m, 1H, C7-*H*), 4.03–4.16 (m, 3H, C5-*H* and $\mathrm{CO_2C}H_2\mathrm{CH_3}$), 4.47 (s, 1H, C1'-*H*), 4.56 (s, 2H, OCH_2Ph), 7.28–7.32 (m, 5H, Ar*H*); ESI-LRMS *m/z* calcd for $\mathrm{C_{27}H_{42}O_{10}Na}$ (M+Na)$^+$ 549.27, found 549.02. The relative configuration at C1' was determined by NOESY correlation from C1' to C3' and C5' in $\mathrm{C_6D_6}$.

Part 1 Chapter 4 Section 3

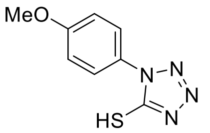
[Synthesis of bromosulfones 157]



General Procedure for the Preparation of Mercaptotetrazole 250

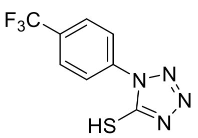
A mixture of Isothiocyanate (1.0 equiv.) and sodium azide (1.5 equiv.) in appropriate solvent (0.63 M) was refluxed for 6 h. When cool, this mixture was extracted with Et_2O (2 times). The aqueous phase was carefully acidified with *c* HCl until pH < 2 with ice cooling, and then extracted with Et_2O (2 times). The combined organic phase was washed with H_2O and brine, and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product, which was used in next step without further purification.

1-(4-methoxyphenyl)-1*H*-tetrazole-5-thiol (250b)$^{75)}$ (TS10010)



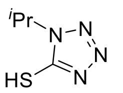
Refluxed in H_2O. 95% yield. White solid: m.p. 138–141 °C; R_f 0.19 (10:1 $CHCl_3$/MeOH); IR (KBr) 3057, 2931, 2910, 2761, 1516, 1490, 1357, 1260, 1050, 830 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.83 (s, 3H, CH_3OPh), 7.13 (d, J = 9.0 Hz, 2H,ArH), 7.74 (d, J = 9.0 Hz, 2H, ArH); ^{13}C NMR (101 MHz, DMSO-d_6) δ 55.6 (CH_3), 114.4 (CH), 126.3 (CH), 126.7 (C), 159.9 (C), 164.0 (C); ESI-HRMS *m/z* calcd for $C_8H_7ON_4S$ $(M–H)^-$ 207.03470, found 207.03470.

1-(4-(trifluoromethyl)phenyl)-1*H*-tetrazole-5-thiol (250c) (TS11078)



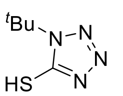
Refluxed in H_2O. 87% yield. Pale yellow solid: m.p. 123–126 °C; R_f 0.36 (10:1 $CHCl_3$/MeOH); IR (KBr) 3083, 2949, 2833, 2755, 1484, 1400, 1356, 1277, 1221, 1149, 847 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2H, ArH), 8.22 (d, J = 8.4 Hz, 2H, ArH); ^{13}C NMR (99 MHz, $CDCl_3$) δ 123.3 (q, $J_{C–F}$ = 282.5 Hz, C), 123.6 (CH), 126.7 (q, $J_{C–F}$ = 3.8 Hz, CH), 131.8 (q, $J_{C–F}$ = 33.8 Hz, C), 136.0 (C), 163.6 (C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –66.0 (s, ArCF_3); ESI-HRMS *m/z* calcd for $C_8H_4N_4F_3S$ $(M–H)^-$ 245.01142, found 245.01141.

1-isopropyl-1*H*-tetrazole-5-thiol (250e)[76] (TS11097)



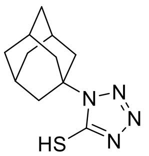
Refluxed in ^{i}PrOH/H_2O = 3:1. 78% yield. White solid: m.p. 74–79 °C; R_f 0.45 (10:1 $CHCl_3$/MeOH); IR (KBr) 3058, 2926, 2771, 1510, 1353, 1207, 1048, 785 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56 (d, J = 6.7 Hz, 6H, CHCH_3), 5.00 (sept, J = 6.7 Hz, 1H, CH(CH_3)$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.0 (CH), 50.6 (CH), 162.8 (C); ESI-HRMS *m/z* calcd for $C_4H_7N_4S$ $(M–H)^-$ 143.03969, found 143.03968.

1-(*tert*-butyl)-1*H*-tetrazole-5-thiol (250f)[77] (TS11098)



Refluxed in ^{i}PrOH/H_2O = 3:1. 55% yield. White solid: m.p. 81–86 °C; R_f 0.54 (10:1 $CHCl_3$/MeOH); IR (KBr) 3055, 2983, 2913, 2745, 2781, 1513, 1369, 1335, 1305, 1214, 1029, 805 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.85 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.6 (CH_3), 63.5 (C), 162.9 (C); ESI-HRMS *m/z* calcd for $C_5H_9N_4S$ $(M–H)^-$ 157.05534, found 157.05559.

1-(1-Adamantyl)-1*H*-tetrazole-5-thiol (250g)[78] (TS11076)

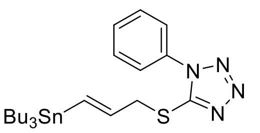


Refluxed in DMF, then diluted with H_2O. 98% yield. White solid: m.p. 166–169 °C; R_f 0.54 (10:1 $CHCl_3$/MeOH); IR (KBr) 3064, 2909, 1503, 1335, 1032, 790 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78 (m, 6H, 3 × CHCH_2CH), 2.27 (brs, 3H, 3 × CH_2C$H$$CH_2$), 2.59 (brd, 6H, 3 × CC$H_2$CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.5 (CH), 35.6 (CH_2), 39.2 (CH_2), 64.4 (C), 162.4 (C); ESI-HRMS *m/z* calcd for $C_{11}H_{15}N_4S$ $(M–H)^-$ 235.10229, found 235.10244.

General Procedure for the Preparation of Tributylstannylsulfide 252

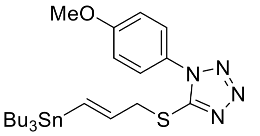
To a stirred mixture of alcohol **251**[78] (1.0 equiv.), mercaptotetrazole (1.06 equiv.), PPh_3 (1.10 equiv.) in THF (0.17 M) at 0 °C was added DEAD (1.10 equiv.). The consumption of starting alcohol **2** was checked by TLC analysis. Then the solvent was evaporated *in vacuo* furnished crude product, which was purified by flash column chromatography (silica gel, eluent: hexane/EtOAc) to afford the title compound.

(*E*)-1-phenyl-5-((3-(tributylstannyl)allyl)thio)-1*H*-tetrazole (252a)[79) (TS11082)



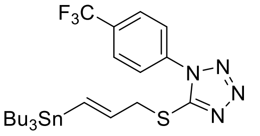
82% yield. colorless oil; R_f 0.54 (9:1 hexane/EtOAc); IR (neat) 2955, 2925, 1499, 760, 693 cm^{-1}; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ 0.79–0.96 (m, 15H, 3 × $\mathrm{SnC}H_2\mathrm{CH_2}$ and 3 × $\mathrm{CH_2C}H_3$), 1.27 (tq, J = 8.1, 8.1 Hz, 6H, 3 × $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.35–1.55 (m, 6H, 3 × $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 4.08 (m; the 4 highest peaks presumably interpretable as dd, J = 6.4, 1.3 Hz, flanking peaks probably due to $^{4}J_{\mathrm{Sn,H}}$, 2H, $\mathrm{CHC}H_2\mathrm{S}$), 6.07 (dt, J = 18.7, 6.4 Hz, each peak flanked by Sn isotope satellites as 2 interlocked d, $^{3}J_{^{119}\mathrm{Sn,H}}$ = 57.5 Hz, $^{3}J_{^{117}\mathrm{Sn,H}}$ = 55.3 Hz, 1H, $\mathrm{CHC}H\mathrm{CH_2}$), 6.34 (dt, J = 18.7, 1.3 Hz, each peak flanked by Sn isotope satellites as 2 interlocked d, $^{2}J_{^{119}\mathrm{Sn,H}}$ = 66.6 Hz, $^{2}J_{^{117}\mathrm{Sn,H}}$ = 63.7 Hz, 1H, $\mathrm{SnC}H\mathrm{CH}$), 7.51–7.60 (m, 5H, ArH); ^{13}C NMR (101 MHz, $\mathrm{CDCl_3}$) δ 9.45 ($\mathrm{CH_2}$, flanked by Sn isotope satellites as 2 d, $J_{^{119}\mathrm{Sn,C}}$ = 346.7 Hz, $^{1}J_{^{117}\mathrm{Sn,C}}$ = 331.3 Hz), 13.7 ($\mathrm{CH_3}$), 27.2 ($\mathrm{CH_2}$, flanked by Sn isotope satellites as 1 d, $^{3}J_{^{119}\mathrm{Sn,C}}$ = 54.6 Hz, $^{3}J_{^{117}\mathrm{Sn,C}}$ = 54.6 Hz), 29.0 ($\mathrm{CH_2}$, flanked by Sn isotope satellites as 1 d, $^{2}J_{^{119}\mathrm{Sn,C}}$ = 20.8 Hz, $^{2}J_{^{117}\mathrm{Sn,C}}$ = 20.8 Hz), 39.0 ($\mathrm{CH_2}$), 123.9 (CH), 129.7 (CH), 130.1 (CH), 133.7 (C), 136.1 (CH), 139.9 (CH), 153.9 (C); ESI-HRMS m/z calcd for $\mathrm{C_{22}H_{36}N_4SSnNa}$ $(\mathrm{M+Na})^+$ 531.15803, found 531.15826.

(*E*)-1-(4-methoxyphenyl)-5-((3-(tributylstannyl)allyl)thio)-1*H*-tetrazole (252b) (TS09058)



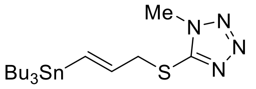
85% yield. White solid: m.p. 44–46 °C; R_f 0.67 (3:1 hexane/AcOEt); IR (KBr) 1608, 1589, 1513, 1462, 1440, 1408, 1387, 1316, 1258, 1171, 1082, 1040, 1021, 991, 835 cm^{-1}; ^{1}H NMR (392 MHz, $\mathrm{CDCl_3}$) δ 0.78–0.95 (m, 15H, 3 × $\mathrm{SnC}H_2\mathrm{CH_2}$), 1.27 (tq, J = 7.2, 7.2 Hz, 6H, 3 × $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.34–1.55 (m, 6H, 3 × $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 3.88 (s, 3H, $\mathrm{OC}H_3$), 4.05 (m; the 4 highest peaks presumably interpretable as dd, J = 6.7, 1.3 Hz, flanking peaks probably due to $^{4}J_{\mathrm{Sn,H}}$, 2H, $\mathrm{CHC}H_2\mathrm{S}$), 6.06 (dt, J = 18.4, 6.7 Hz, each peak flanked by Sn isotope satellites as 2 interlocked d, $^{3}J_{^{119}\mathrm{Sn,H}}$ = 57.9 Hz, $^{3}J_{^{117}\mathrm{Sn,H}}$ = 55.2 Hz, 1H, $\mathrm{CHC}H\mathrm{CH_2}$), 6.33 (dt, J = 18.4, 1.3 Hz, each peak flanked by Sn isotope satellites as 2 interlocked d, $^{2}J_{^{119}\mathrm{Sn,H}}$ = 66.4 Hz, $^{2}J_{^{117}\mathrm{Sn,H}}$ = 63.7 Hz, 1H, $\mathrm{SnC}H\mathrm{CH}$), 7.01–7.06 (m, 2H, ArH), 7.43–7.48 (m, 2H, ArH); ^{13}C NMR (99 MHz, $\mathrm{CDCl_3}$) δ 9.45 ($\mathrm{CH_3}$, flanked by Sn isotope satellites as 2 d, $^{1}J_{^{119}\mathrm{Sn,C}}$ = 346.7 Hz, $^{1}J_{^{117}\mathrm{Sn,C}}$ = 330.7 Hz), 13.7 ($\mathrm{CH_3}$), 27.2 ($\mathrm{CH_2}$, flanked by Sn isotope satellites as 1 d, $^{3}J_{^{119}\mathrm{Sn,C}}$ = 54.5 Hz, $^{3}J_{^{117}\mathrm{Sn,C}}$ = 54.5 Hz), 29.0 ($\mathrm{CH_2}$, flanked by Sn isotope satellites as 1 d, $^{2}J_{^{119}\mathrm{Sn,C}}$ = 21.6 Hz, $^{2}J_{^{117}\mathrm{Sn,C}}$ = 21.6 Hz), 38.9 ($\mathrm{CH_2}$), 55.6 ($\mathrm{CH_3}$), 114.8 (CH), 125.5 (CH), 126.3 (C), 135.9 (CH), 140.0 (CH), 154.0 (C), 160.7 (C); ESI-HRMS m/z calcd for $\mathrm{C_{23}H_{38}ON_4SSnNa}$ $(\mathrm{M+Na})^+$ 561.16860, found 561.16886.

(*E*)-5-((3-(tributylstannyl)allyl)thio)-1-(4-(trifluoromethyl)phenyl)-1*H*-tetrazole (252c) (TS11081)



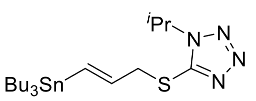
86% yield. Pale yellow oil; R_f 0.66 (3:1 hexane/EtOAc); IR (neat) 2925, 1325, 1135, 1070, 845 cm^{-1}; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ 0.78–0.96 (m, 15H, 3 × $\mathrm{SnC}H_2\mathrm{CH_2}$), 1.27 (tq, J = 8.1, 8.1 Hz, 6H, 3 × $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.35–1.55 (m, 6H, 3 × $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 4.11 (m; the 4 highest peaks presumably interpretable as dd, J = 6.4, 1.1 Hz, flanking peaks probably due to $^{4}J_{\mathrm{Sn,H}}$, 2H, $\mathrm{CHC}H_2\mathrm{S}$), 6.07 (dt, J = 18.7, 6.4 Hz, each peak flanked by Sn isotope satellites as 2 interlocked d, $^{3}J_{^{119}\mathrm{Sn,H}}$ = 57.9 Hz, $^{3}J_{^{117}\mathrm{Sn,H}}$ = 54.9 Hz, 1H, CHC*H*CH$_2$), 6.38 (dt, *J* = 18.7, 1.1 Hz, each peak flanked by Sn isotope satellites as 2 interlocked d, $^{2}J_{^{119}\mathrm{Sn,H}}$ = 65.9 Hz, $^{2}J_{^{117}\mathrm{Sn,H}}$ = 63.0 Hz, 1H, SnC*H*CH), 7.78 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.85 (d, *J* = 8.4 Hz, 2H, Ar*H*); ^{13}C NMR (101 MHz, CDCl$_3$) δ 9.49 (CH$_2$, flanked by Sn isotope satellites as 2 d, $^{1}J_{^{119}\mathrm{Sn,C}}$ = 346.7 Hz, $^{1}J_{^{117}\mathrm{Sn,C}}$ = 331.3 Hz), 13.7 (CH$_3$), 27.2 (CH$_2$, flanked by Sn isotope satellites as 1 d, $^{3}J_{^{119}\mathrm{Sn,C}}$ = 55.4 Hz, $^{3}J_{^{117}\mathrm{Sn,C}}$ = 55.4 Hz), 29.0 (CH$_2$, flanked by Sn isotope satellites as 1 d, $^{2}J_{^{119}\mathrm{Sn,C}}$ = 20.8 Hz, $^{2}J_{^{117}\mathrm{Sn,C}}$ = 20.8 Hz), 39.1 (CH), 123.2 (q, $J_{\mathrm{C-F}}$ = 272.9 Hz, CH), 123.9 (CH), 127.0 (q, $J_{\mathrm{C-F}}$ = 3.8 Hz, CH), 132.0 (q, $J_{\mathrm{C-F}}$ = 33.1 Hz), 136.5 (C), 136.7 (CH), 139.5 (CH), 154.1 (C); ^{19}F NMR (376 MHz, CDCl$_3$) δ –66.0 (C*F*$_3$); ESI-HRMS *m/z* calcd for $C_{23}H_{35}F_3N_4SSnNa$ (M+Na)$^+$ 599.14542, found 599.14567.

(*E*)-1-methyl-5-((3-(tributylstannyl)allyl)thio)-1*H*-tetrazole (252d) (TS11079)



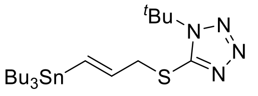
87% yield. Colorless oil; R_f 0.49 (3:1 hexane/EtOAc); IR (neat) 2955, 2925, 1593, 1463, 1171, 986, 734 cm^{-1}; ^{1}H NMR (396 MHz, CDCl$_3$) δ 0.76–0.95 (m, 15H, 3 × SnC*H*$_2$CH$_2$), 1.27 (tq, *J* = 7.7, 7.7 Hz, 6H, 3 × CH$_2$C*H*$_2$CH$_3$), 1.34–1.55 (m, 6H, 3 × CH$_2$C*H*$_2$CH$_2$), 3.91 (s, 3H, NC*H*$_3$), 4.00 (m; the 4 highest peaks presumably interpretable as dd, *J* = 6.8, 1.3 Hz, flanking peaks probably due to $^{4}J_{\mathrm{Sn,H}}$, 2H, CHC*H*$_2$S), 6.03 (dt, *J* = 18.6, 6.8 Hz, each peak flanked by Sn isotope satellites as 2 interlocked d, $^{3}J_{^{119}\mathrm{Sn,H}}$ = 57.1 Hz, $^{3}J_{^{117}\mathrm{Sn,H}}$ = 55.3 Hz, 1H, CHC*H*CH$_2$), 6.29 (dt, *J* = 18.6, 1.3 Hz, each peak flanked by Sn isotope satellites as 2 interlocked d, $^{2}J_{^{119}\mathrm{Sn,H}}$ = 66.2 Hz, $^{2}J_{^{117}\mathrm{Sn,H}}$ = 63.4 Hz, 1H, SnC*H*CH); ^{13}C NMR (99 MHz, CDCl$_3$) δ 9.44 (CH$_2$, flanked by Sn isotope satellites as 2 d, $^{1}J_{^{119}\mathrm{Sn,C}}$ = 347.1 Hz, $^{1}J_{^{117}\mathrm{Sn,C}}$ = 331.2 Hz), 13.6 (CH$_3$), 27.2 (CH$_2$, flanked by Sn isotope satellites as 1 d, $^{3}J_{^{119}\mathrm{Sn,C}}$ = 54.4 Hz, $^{3}J_{^{117}\mathrm{Sn,C}}$ = 54.4 Hz), 28.9 (CH$_2$, flanked by Sn isotope satellites as 1 d, $^{2}J_{^{119}\mathrm{Sn,C}}$ = 21.0 Hz, $^{2}J_{^{117}\mathrm{Sn,C}}$ = 21.0 Hz), 33.4 (CH$_3$), 39.1 (CH$_2$), 135.9 (CH), 140.1 (CH), 153.4 (C); ESI-HRMS *m/z* calcd for $C_{17}H_{34}N_4SSnNa$ (M+Na)$^+$ 469.14238, found 469.14251.

(*E*)-1-isopropyl-5-((3-(tributylstannyl)allyl)thio)-1*H*-tetrazole (252e) (TS12001)



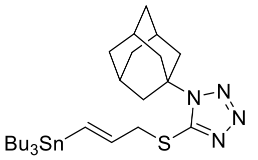
88% yield. Colorless oil; R_f 0.50 (5:1 hexane/EtOAc); IR (neat) 2955, 2925, 1593, 1427, 1384, 1107, 984 cm^{-1}; ^{1}H NMR (396 MHz, CDCl$_3$) δ 0.78–0.95 (m, 15H, 3 × SnC*H*$_2$CH$_2$), 1.27 (tq, *J* = 7.3, 7.3 Hz, 6H, 3 × CH$_2$C*H*$_2$CH$_3$), 1.34–1.53 (m, 6H, 3 × CH$_2$C*H*$_2$CH$_2$), 1.57 (d, *J* = 6.8 Hz, 6H, NCH(C*H*$_3$)$_2$), 4.02 (m; the 4 highest peaks presumably interpretable as dd, *J* = 6.3, 0.9 Hz, flanking peaks probably due to $^{4}J_{\mathrm{Sn,H}}$, 2H, CHC*H*$_2$S), 4.59 (sept, *J* = 6.8 Hz, 1H, NC*H*(CH$_3$)$_2$), 6.04 (dt, *J* = 19.0, 6.3 Hz, each peak flanked by Sn isotope satellites as 2 interlocked d, $^{3}J_{^{119}\mathrm{Sn,H}}$ = 57.5 Hz, $^{3}J_{^{117}\mathrm{Sn,H}}$ = 55.3 Hz, 1H, CHC*H*CH$_2$), 6.30 (dt, *J* = 19.0, 1.1 Hz, each peak flanked by Sn isotope satellites as 2 interlocked d, $^{2}J_{^{119}\mathrm{Sn,H}}$ = 66.6 Hz, $^{2}J_{^{117}\mathrm{Sn,H}}$ = 63.9 Hz, 1H, SnC*H*CH); ^{13}C NMR (100 MHz, CDCl$_3$) δ 9.45 (CH$_2$, flanked by Sn isotope satellites as 2 d, $^{1}J_{^{119}\mathrm{Sn,C}}$ = 346.2 Hz, $^{1}J_{^{117}\mathrm{Sn,C}}$ = 330.1 Hz), 13.6 (CH$_3$), 21.8 (CH$_3$), 27.2 (CH$_2$, flanked by Sn isotope satellites as 1 d, $^{3}J_{^{119}\mathrm{Sn,C}}$ = 54.4 Hz, $^{3}J_{^{117}\mathrm{Sn,C}}$ = 54.4 Hz), 28.9 (CH$_2$, flanked by Sn isotope satellites as 1 d, $^{2}J_{^{119}\mathrm{Sn,C}}$ = 21.0 Hz, $^{2}J_{^{117}\mathrm{Sn,C}}$ = 21.0 Hz), 38.9 ($\mathrm{CH_2}$), 51.1 (CH), 135.7 (CH), 140.3 (CH), 152.2 (C); ESI-HRMS *m/z* calcd for $\mathrm{C_{19}H_{38}N_4SSnNa}$ $(\mathrm{M+Na})^+$ 497.17368, found 497.17385.

(*E*)-1-(*tert*-butyl)-5-((3-(tributylstannyl)allyl)thio)-1*H*-tetrazole (252f) (TS12002)



89% yield. Colorless oil; R_f 0.58 (5:1 hexane/EtOAc); IR (neat) 2955, 2925, 1593, 1391, 1363, 1226, 987 cm^{-1}; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ 0.79–0.95 (m, 15H, 3 × $\mathrm{SnC}H_2\mathrm{CH_2}$), 1.27 (tq, J = 7.3, 7.3 Hz, 6H, 3 × $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.35–1.56 (m, 6H, 3 × $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 1.72 (s, 9H, $\mathrm{NC(C}H_3)_3$), 4.07 (m; the 4 highest peaks presumably interpretable as d, J = 6.6 Hz, flanking peaks probably due to $^{4}J_{\mathrm{Sn,H}}$, 2H, $\mathrm{CHC}H_2\mathrm{S}$), 6.07 (dt, J = 18.7, 6.6 Hz, each peak flanked by Sn isotope satellites as 2 interlocked d, $^{3}J_{^{119}\mathrm{Sn,H}}$ = 56.8 Hz, $^{3}J_{^{117}\mathrm{Sn,H}}$ = 56.8 Hz, 1H, $\mathrm{CHC}H\mathrm{CH_2}$, 1H, $\mathrm{CHC}H\mathrm{CH_2}$), 6.33 (dd, J = 18.7, 1.1 Hz, each peak flanked by Sn isotope satellites as 2 interlocked d, $^{2}J_{^{119}\mathrm{Sn,H}}$ = 66.3 Hz, $^{2}J_{^{117}\mathrm{Sn,H}}$ = 66.3 Hz, 1H, $\mathrm{SnC}H\mathrm{CH}$); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$) δ 9.47 ($\mathrm{CH_2}$, flanked by Sn isotope satellites as 2 d, $^{1}J_{^{119}\mathrm{Sn,C}}$ = 345.9 Hz, $^{1}J_{^{117}\mathrm{Sn,C}}$ = 330.5 Hz), 13.7 ($\mathrm{CH_3}$), 27.2 ($\mathrm{CH_2}$, flanked by Sn isotope satellites as 1 d, $^{3}J_{^{119}\mathrm{Sn,C}}$ = 54.6 Hz, $^{3}J_{^{117}\mathrm{Sn,C}}$ = 54.6 Hz), 29.0 ($\mathrm{CH_2}$, flanked by Sn isotope satellites as 1 d, $^{2}J_{^{119}\mathrm{Sn,C}}$ = 20.8 Hz, $^{2}J_{^{117}\mathrm{Sn,C}}$ = 20.8 Hz), 39.7 ($\mathrm{CH_2}$), 60.9 (C), 135.6 (CH), 140.4 (CH), 152.3 (C); ESI-HRMS *m/z* calcd for $\mathrm{C_{20}H_{40}N_4SSnNa}$ $(\mathrm{M+Na})^+$ 511.18933, found 511.18952.

1-(1-Adamantyl)-5-(((*E*)-3-(tributylstannyl)allyl)thio)-1*H*-tetrazole (252g) (TS11080)

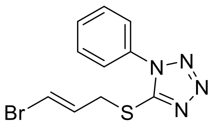


88% yield. Colorless oil; R_f 0.71 (3:1 hexane/EtOAc); IR (neat) 2956, 2916, 2854, 1594, 1359, 11035, 733 cm^{-1}; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ 0.78–0.96 (m, 15H, 3 × $\mathrm{SnC}H_2\mathrm{CH_2}$), 1.27 (tq, J = 7.7, 7.7 Hz, 6H, 3 × $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.35–1.56 (m, 6H, 3 × $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 1.76–1.78 (m, 6H, 3 × $\mathrm{CHC}H_2\mathrm{CH}$), 2.25 (brs, 3H, 3 × $\mathrm{CH_2C}H\mathrm{CH_2}$), 2.35 (brd, 6H, 3 × $\mathrm{CC}H_2\mathrm{CH}$), 4.07 (m; the 4 highest peaks presumably interpretable as dd, J = 6.3, 1.0 Hz, flanking peaks probably due to $^{4}J_{\mathrm{Sn,H}}$, 2H, $\mathrm{CHC}H_2\mathrm{S}$), 6.07 (dt, J = 18.8, 6.3 Hz, each peak flanked by Sn isotope satellites as 2 interlocked d, $^{3}J_{^{119}\mathrm{Sn,H}}$ = 58.4 Hz, $^{3}J_{^{117}\mathrm{Sn,H}}$ = 55.7 Hz, 1H, $\mathrm{CHC}H\mathrm{CH_2}$), 6.31 (dd, J = 18.8, 1.0 Hz, each peak flanked by Sn isotope satellites as 2 interlocked d, $^{2}J_{^{119}\mathrm{Sn,H}}$ = 68.0 Hz, $^{2}J_{^{117}\mathrm{Sn,H}}$ = 65.2 Hz, 1H, $\mathrm{SnC}H\mathrm{CH}$); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$) δ 9.46 ($\mathrm{CH_2}$, flanked by Sn isotope satellites as 2 d, $^{1}J_{^{119}\mathrm{Sn,C}}$ = 346.2 Hz, $^{1}J_{^{117}\mathrm{Sn,C}}$ = 330.9 Hz), 13.7 ($\mathrm{CH_3}$), 27.2 ($\mathrm{CH_2}$, flanked by Sn isotope satellites as 1 d, $J_{^{119}\mathrm{Sn,C}}$ = 54.4 Hz, $^{3}J_{^{117}\mathrm{Sn,C}}$ = 54.4 Hz), 29.0 ($\mathrm{CH_2}$, flanked by Sn isotope satellites as 1 d, $^{2}J_{^{119}\mathrm{Sn,C}}$ = 21.0 Hz, $^{2}J_{^{117}\mathrm{Sn,C}}$ = 21.0 Hz), 35.6 ($\mathrm{CH_2}$), 39.7 ($\mathrm{CH_2}$), 40.9 ($\mathrm{CH_2}$), 61.7 (C), 135.5 (CH), 140.5 (CH), 151.8 (C); ESI-HRMS *m/z* calcd for $\mathrm{C_{26}H_{46}N_4SSnNa}$ $(\mathrm{M+Na})^+$ 589.23628, found 589.23661.

General Procedure for the Preparation of Bromosulfide 253

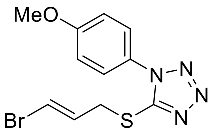
A mixture of tributylstannylsulfide (1.0 equiv.) and NBS (1.2 equiv.) in $\mathrm{CH_3CN}$ (0.1 M) was stirred for 1 h. Then, the mixture was diluted with $\mathrm{H_2O}$ and whole mixture was extracted with EtOAc. The organic phase was washed with $\mathrm{H_2O}$ and brine, and dried over anhydrous $\mathrm{Na_2SO_4}$. Filtration and evaporation *in vacuo* furnished crude product, which was purified by flash column chromatography (10% w/w K$_2$CO$_3$ in silica gel, eluent: hexane/EtOAc) to afford the title compoundss

(*E*)-5-((3-bromoallyl)thio)-1-phenyl-1*H*-tetrazole (253a) (TS11089)



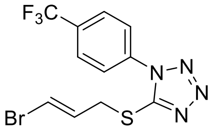
98% yield. White solid: 42–44 °C; R_f 0.33 (5:1 hexane/EtOAc); IR (KBr) 1406, 1498, 1381, 948, 759 cm^{-1}; ^{1}H NMR (396 MHz, CDCl$_3$) δ 4.00 (dd, J = 7.7, 0.9 Hz, 2H, CHC*H*$_2$S), 6.36 (dt, J = 13.6, 7.7 Hz, 1H, CHC*H*CH$_2$), 6.54 (dt, J = 13.6, 0.9 Hz, 1H, BrC*H*CH), 7.52–7.60 (m, 5H, Ar*H*); ^{13}C NMR (101 MHz, CDCl$_3$) δ 34.6 (CH$_2$), 111.4 (CH), 123.8 (CH), 129.8 (CH), 130.3 (CH), 130.6 (CH), 133.4 (C), 153.1 (C); ESI-HRMS *m/z* calcd for C$_{10}$H$_9$N$_4$BrSNa (M+Na)$^+$ 318.96235, found 318.96244.

(*E*)-5-((3-bromoallyl)thio)-1-(4-methoxyphenyl)-1*H*-tetrazole (253b) (TS09062)



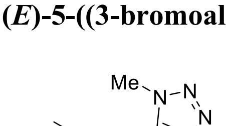
97% yield. White solid: m.p. 102–103 °C; R_f 0.34 (3:1 hexane/AcOEt); IR (KBr) 1621, 1609, 1519, 1438, 1391, 1307, 1266, 1207, 1173, 1089, 1024, 942, 835 cm^{-1}; ^{1}H NMR (396 MHz, CDCl$_3$) δ 3.89 (s, 3H, OC*H*$_3$), 3.98 (dd, J = 7.7, 0.9 Hz, 2H, CHC*H*$_2$S), 6.35 (dt, J =13.6, 7.7 Hz, 1H, CHC*H*CH$_2$), 6.54 (dt, J = 13.6, 0.9 Hz, 1H, BrC*H*CH), 7.03–7.07 (m, 2H, Ar*H*), 7.42–7.46 (m, 2H, Ar*H*); ^{13}C NMR (99 MHz, CDCl$_3$) δ 34.5 (CH$_2$), 55.7 (CH$_3$), 111.3 (CH), 114.9 (CH), 125.5 (CH), 126.0 (C), 130.6 (CH), 153.2 (C), 160.8 (C); ESI-HRMS *m/z* calcd for C$_{11}$H$_{11}$ON$_4$BrSNa (M+Na)$^+$ 348.97292, found 348.97293.

(*E*)-5-((3-bromoallyl)thio)-1-(4-(trifluoromethyl)phenyl)-1*H*-tetrazole (253c) (TS11088)



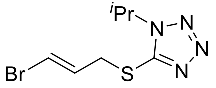
96% yield. White solid: m.p. 73–76 °C; R_f 0.52 (3:1 hexane/EtOAc); IR (KBr) 3058, 1614, 1383, 1321, 1170, 1061, 933, 849 cm^{-1}; ^{1}H NMR (396 MHz, CDCl$_3$) δ 4.04 (dd, J = 8.2, 1.2 Hz, 2H, CHC*H*$_2$S), 6.36 (dt, J =13.4, 8.2 Hz, 1H, CHC*H*CH$_2$), 6.58 (dt, J = 13.4, 1.2 Hz, 1H, BrC*H*CH), 7.76 (d, J = 8.2 Hz, 2H, Ar*H*), 7.86 (d, J = 8.2 Hz, 2H, Ar*H*); ^{13}C NMR (100 MHz, CDCl$_3$) δ 34.8 (CH$_2$), 55.7 (CH$_3$), 111.8 (CH), 114.9 (CH), 123.2 (q, $J_{\text{C–F}}$ = 273 Hz, CH), 126.0 (C), 127.1 (q, $J_{\text{C–F}}$ = 3.8 Hz, CH), 130.3 (CH), 132.2 (q, $J_{\text{C–F}}$ = 33.4 Hz, CH), 136.3 (C), 153.2 (C); ^{19}F NMR (373 MHz, CDCl$_3$) δ –66.1 (C*F*$_3$); ESI-HRMS *m/z* calcd for C$_{11}$H$_9$N$_4$BrF$_3$S (M)$^+$ 364.96779, found 364.96822.

(*E*)-5-((3-bromoallyl)thio)-1-methyl-1*H*-tetrazole (253d) (TS11087)



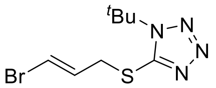
96% yield. Colorless oil; R_f 0.21 (3:1 hexane/EtOAc); IR (neat) 3066, 2948, 1618, 146+, 1389, 1281, 1172, 1226, 909, 699 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.92 (s, 3H, NC*H*$_3$), 3.94 (dd, J = 8.0, 1.2 Hz, 2H, CHC*H*$_2$S), 6.32 (dt, J =13.5, 8.0 Hz, 1H, CHC*H*CH$_2$), 6.48 (dt, J = 13.5, 1.2 Hz, 1H, BrC*H*CH); ^{13}C NMR (100 MHz, CDCl$_3$) δ 33.4 (CH$_3$), 34.7 (CH$_2$), 111.3 (CH), 130.6 (CH), 153.0 (C); ESI-HRMS *m/z* calcd for C$_5$H$_7$N$_4$BrSNa (M+Na)$^+$ 256.94670, found 256.94676.

(*E*)-5-((3-bromoallyl)thio)-1-isopropyl-1*H*-tetrazole (253e) (TS12003)



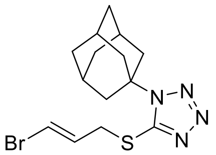
97% yield. Colorless oil; R_f 0.37 (3:1 hexane/EtOAc); IR (neat) 2984, 1618, 1428, 1385, 1218, 1108, 938, 888 cm^{-1}; ^{1}H NMR (396 MHz, CDCl$_3$) δ 1.57 (d, *J* = 6.6 Hz, 6H, NCH(C*H*$_3$)$_2$), 3.94 (dd, *J* = 8.0, 1.1 Hz, 2H, CHC*H*$_2$S), 4.55 (sept, *J* = 6.6 Hz, 1H, NC*H*(CH$_3$)$_2$), 6.32 (dt, *J* =13.4, 7.7 Hz, 1H, CHC*H*CH$_2$), 6.46 (dt, *J* = 13.4, 1.1 Hz, 1H, BrC*H*CH); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.8 (CH$_3$), 34.6 (CH$_2$), 51.3 (CH), 111.1 (CH), 130.8 (CH), 151.4 (C); ESI-HRMS *m/z* calcd for $C_7H_{11}NJ_4BrSNa$ (M+Na)$^+$ 284.97800, found 284.97820.

(*E*)-5-((3-bromoallyl)thio)-1-(*tert*-butyl)-1*H*-tetrazole (253f) (TS12004)



97% yield. White solid: m.p. 61–63 °C; R_f 0.48 (3:1 hexane/EtOAc); IR (KBr) 2980, 1617, 1389, 1334, 1103, 949 cm^{-1}; ^{1}H NMR (396 MHz, CDCl$_3$) δ 1.71 (s, 9H, NC(C*H*$_3$)$_3$), 3.99 (dd, *J* = 7.7, 0.9 Hz, 2H, CHC*H*$_2$S) 6.34 (dt, *J* =13.6, 7.3 Hz, 1H, CHC*H*CH$_2$), 6.50 (dt, *J* = 13.6, 0.9 Hz, 1H, BrC*H*CH); ^{13}C NMR (100 MHz, CDCl$_3$) δ 28.7 (CH$_3$), 35.3 (CH$_2$), 61.1 (C), 111.0 (CH), 130.9 (CH), 151.3 (C); ESI-HRMS *m/z* calcd for $C_8H_{13}N_4BrSNa$ (M+Na)$^+$ 298.99365, found 2968.99384.

1-(1-Adamantyl)-5-(((*E*)-3-bromoallyl)thio)-1*H*-tetrazole (253g) (TS11086)

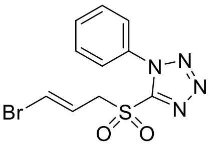


96% yield. White solid: m.p. 118–121 °C; R_f 0.52 (3:1 hexane/EtOAc); IR (KBr) 3052, 2930, 2855, 1619, 139, 1358, 1033, 953, 833, 715 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.74–1.80 (m, 6H, 3 × CHC*H*$_2$CH), 2.26 (brs, 3H, 3 × CH$_2$C*H*CH$_2$), 2.33 (brd, 6H, 3 × CC*H*$_2$CH), 4.00 (dd, *J* = 7.5, 1.2 Hz, 2H, CHC*H*$_2$S), 6.37 (dt, *J* =13.8, 7.5 Hz, 1H, CHC*H*CH$_2$), 6.49 (dt, *J* = 13.8, 1.2 Hz, 1H, BrC*H*CH); ^{13}C NMR (128 MHz, CDCl$_3$) δ 29.8 (CH), 35.2 (CH$_2$), 35.6 (CH$_2$), 40.9 (CH$_2$), 61.9 (C), 110.9 (CH), 131.0 (CH), 151.0 (C); ESI-HRMS *m/z* calcd for $C_{14}H_{19}N_4BrSNa$ (M+Na)$^+$ 377.04060, found 377.04080.

General Procedure for the Preparation of Bromosulfone 157

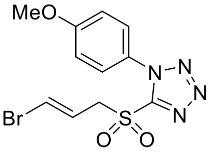
$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.20 equiv.) was added to a stirred solution of bromosulfide (1.0 equiv.) in EtOH (0.20 M) at room temperature. The mixture was cooled to 0 °C and 30% H_2O_2 (10 equiv.) was added. After stirring for 1 h at this temperature, the reaction mixture was additionally stirred at room temperature until consumption of starting sulfide and intermediate sulfoxide (checked by TLC monitoring). The reaction mixture was quenched by saturated aqueous $Na_2S_2O_3$ solution at 0 °C and extracted with EtOAc (2 times). The combined organic phase was washed with H_2O and brine, and dried over anhydrous Na_2SO_4. Filtration and evaporation *n vacuo* furnished crude product, which was purified by flash column chromatography (silica gel, eluent; hexane/EtOAc) to afford the title compound.

(*E*)-5-((3-bromoallyl)sulfonyl)-1-phenyl-1*H*-tetrazole (157a) (TS10005)



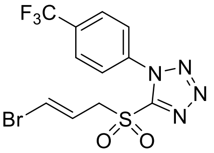
40% yield. White solid: m.p. 86–89 °C; *R*$_f$ 0.61 (2:1 hexane/EtOAc); IR (KBr) 3075, 2980, 2901, 1497, 1352, 1155, 949, 890, 763 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.43 (dd, *J* = 6.9, 1.2 Hz, 2H, CHC*H*$_2$S), 6.30 (dt, *J* = 13.8, 8.0 Hz, 1H, CHC*H*CH$_2$), 6.71 (dt, *J* = 13.8, 1.2 Hz, 1H, BrC*H*CH), 7.59–7.69 (m, 5H, Ar*H*); ^{13}C NMR (126 MHz, CDCl$_3$) δ 59.1(CH$_2$), 118.2 (CH), 121.2 (CH), 125.0 (CH), 129.7 (CH), 136.1 (CH), 132.8 (C), 152.7 (C); ESI- HRMS *m/z* calcd for C$_{10}$H$_9$O$_2$N$_4$BrSNa (M+Na)$^+$ 350.95218, found 350.95248.

(*E*)-5-((3-bromoallyl)sulfonyl)-1-(4-methoxyphenyl)-1*H*-tetrazole (157b) (TS09065)



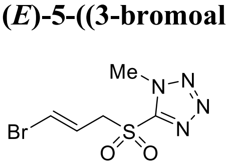
44% yield. White solid: m.p. 83–88 °C; *R*$_f$ 0.55 (3:1 hexane/AcOEt); IR (KBr) 1621, 1605, 1588, 1508, 1456, 1389, 1338, 1312, 1303, 1252, 1175, 1139, 1100, 1041 cm^{-1}; ^{1}H NMR (392 MHz, CDCl$_3$) δ 3.90 (s, 3H, OC*H*$_3$), 4.41 (dd, *J* = 7.6, 0.9 Hz, 2H, CHC*H*$_2$S), 6.27 (dt, *J* = 14.8, 7.6 Hz, 1H, CHC*H*CH$_2$), 6.69 (dt, *J* = 14.8, 0.9 Hz, 1H, BrC*H*CH), 7.03–7.07 (m, 2H, Ar*H*), 7.53–7.54 (m, 2H, Ar*H*); ^{13}C NMR (126 MHz, CDCl$_3$) δ 55.7 (CH$_3$), 59.0(CH$_2$), 114.8 (CH), 118.1 (CH), 121.2 (CH), 125.3 (C), 126.5 (CH), 152.7 (C), 161.8 (C); ESI-HRMS *m/z* calcd for C$_{11}$H$_{11}$O$_3$N$_4$BrSNa (M+Na)$^+$ 380.96274, found 380.96299.

(*E*)-5-((3-bromoallyl)sulfonyl)-1-(4-(trifluoromethyl)phenyl)-1*H*-tetrazole (157c) (TS09070)



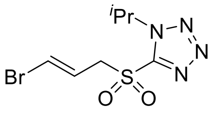
65% yield. White solid: m.p. 117–120 °C; *R*$_f$ 0.23 (3:1 hexane/EtOAc); IR (KBr) 3083, 2919, 1617, 1330, 1173, 1128, 1070, 943, 851, 732 cm^{-1}; H NMR (500 MHz, CDCl$_3$) δ 4.47 (dd, *J* = 7.5, 1.2 Hz, 2H, CHC*H*$_2$S), 6.30 (dt, *J* = 13.8, 8.0 Hz, 1H, CHC*H*CH$_2$), 6.75 (d, *J* = 13.8 Hz, 1H, BrC*H*CH), 7.86 (d, *J* = 8.6 Hz, 2H, Ar*H*), 7.90 (d, *J* = 8.6 Hz, 2H, Ar*H*); ^{13}C NMR (100MHz, CDCl$_3$) δ 59.2(CH$_2$), 118.5 (CH), 121.0 (CH), 123.1 (q, $J_{C\text{–}F}$ = 273 Hz, CH), 125.6 (CH), 127.1 (q, $J_{C\text{–}F}$ = 3.8 Hz, CH), 133.6 (q, $J_{C\text{–}F}$ = 33.4 Hz, CH), 135.4 (C), 152.8 (C); ^{19}F NMR (373 MHz, CDCl$_3$) δ –66.2 (C*F*$_3$); ESI-HRMS *m/z* calcd for C$_{11}$H$_7$O$_2$N$_4$BrF$_3$S (M)$^+$ 394.94307, found 394.94352.

(*E*)-5-((3-bromoallyl)sulfonyl)-1-methyl-1*H*-tetrazole (157d) (TS09067)



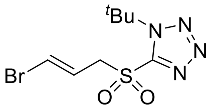
91% yield. White solid: m.p. 77–79 °C; *R*$_f$ 0.28 (3:1 hexane/EtOAc); IR (KBr) 3072, 2969, 2907, 1621, 1337, 1140 944, 891, 739 cm^{-1}; ^{1}H NMR (396 MHz, CDCl$_3$) δ 4.34–4.36 (m, 5H, NC*H*$_3$ and CHC*H*$_2$S), 6.26(dt, *J* = 13.8, 8.2 Hz, 1H, CHC*H*CH$_2$), 6.63 (dt, *J* = 13.8, 1.1 Hz, 1H, BrC*H*CH); ^{13}C NMR (126 MHz, CDCl$_3$) δ 36.1 (CH$_3$), 58.9 (CH$_2$), 118.3 (CH), 120.9 (CH), 152.4 (C); ESI-HRMS *m/z* calcd for C$_5$H$_6$O$_2$N$_4$BrS (M)$^+$ 264.94003, found 264.94052.

(*E*)-5-((3-bromoallyl)sulfonyl)-1-isopropyl-1*H*-tetrazole (157e) (TS12005)



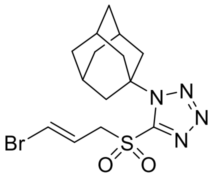
75% yield. White solid: m.p. 36–41 °C; R_f 0.64 (3:1 hexane/EtOAc); IR (neat) 3070, 2986, 2923, 1621, 1342, 1157, 942, 892, 741 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.68 (d, *J* = 6.8 Hz, 6H, NCH(C*H*$_3$)$_2$), 4.38 (dd, *J* = 8.2, 1.3 Hz, 2H, CHC*H*$_2$S), 5.28 (sept, *J* = 6.3 Hz, 1H, NC*H*(CH$_3$)$_2$), 6.27 (dt, *J* = 13.6, 8.2 Hz, 1H, CHC*H*CH$_2$), 6.64 (dt, *J* = 13.6, 1.3 Hz, 1H, BrC*H*CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6 (CH_3), 54.4 (CH), 59.0 (CH_2), 118.2 (CH), 121.2 (CH), 151.7 (C); ESI-HRMS *m/z* calcd for $C_7H_{11}O_2N_4BrSNa$ (M+Na)$^+$ 316.96783, found 316.96770.

(*E*)-5-((3-bromoallyl)sulfonyl)-1-(*tert*-butyl)-1*H*-tetrazole (157f) (TS12006)



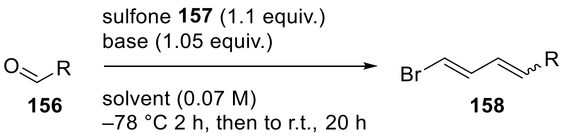
19% yield. White solid: m.p. 61–64 °C; R_f 0.57 (3:1 hexane/EtOAc); IR (KBr) 2990, 2923, 1626, 1378, 1346, 1163, 939, 884, 719 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.85 (s, 9H, NC(C*H*$_3$)$_3$), 4.51 (dd, *J* = 8.1, 1.1 Hz, 2H, CHC*H*$_2$S), 6.35 (dt, *J* = 13.9, 7.7 Hz, 1H, CHC*H*CH$_2$), 6.73 (dt, *J* = 13.9, 1.1 Hz, 1H, BrC*H*CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 29.6 (CH_3), 59.7 (CH_2), 65.6 (C), 117.8 (CH), 121.8 (CH), 153.4 (C); ESI-HRMS *m/z* calcd for $C_8H_{13}O_2N_4BaSNa$ (M+Na)$^+$ 330.98348, found 330.98343.

1-(1-Adamantyl)-5-(((*E*)-3-bromoallyl)sulfonyl)-1*H*-tetrazole (157g) (TS09066)



28% yield. White solid: m.p. 128–131 °C; R_f 0.58 (3:1 hexane/EtOAc); IR (KBr) 2912, 2560, 1624, 1351, 1342, 1139, 934, 737 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.76–1.83 (m, 6H, 3 × CHC*H*$_2$CH), 2.31 (brs, 3H, 3 × CH$_2$C*H*CH$_2$), 2.45 (brd, 6H, 3 × CC*H*$_2$CH), 4.51 (dd, *J* = 7.8 1.2 Hz, 2H, CHC*H*$_2$S), 6.35 (dt, *J* =13.8, 7.8 Hz, 1H, CHC*H*CH$_2$), 6.72 (dt, *J* = 13.8, 1.2 Hz, 1H, BrC*H*CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.7 (CH), 35.4 (CH_2), 41.8 (CH_2), 59.8 (CH_2), 66.3 (C), 117.7 (CH), 121.9 (CH), 153.5 (C); ESI-HRMS *m/z* calcd for $C_{14}H_{19}O_2N_4BrSNa$ (M+Na)$^+$ 409.03043, found 409.03065.

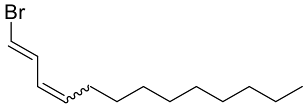
[Julia Olefination]



General Procedure for the Julia Olefination

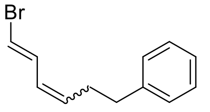
To a stirred solution of sulfone **157** (0.33 mmol) in solvent (1.3 mL) was added base (0.315 mL, 0.315 mmol, 1.0 M THF solution) at –78 °C (dry ice/acetone bath). After stirring for 5 min, aldehyde **156** (0.30 mmol) in solvent (1.5 mL) was added to the solution dropwisely and rinsed 2 times with DME (1.0 mL, 0.5 mL). The whole mixture was stirred at this temperature for 2 h, and then warmed to room temperature gradually by removing dry ice and stirred for 20 h. The reaction mixture was quenched with H_2O (2 mL) and the whole mixture was extracted with EtOAc. The organic layer was washed with H_2O and brine, and dried over anhydrous Na_2SO_4. Filtration and evaporation *in* *vacuo* furnished crude product, which was purified by flash column chromatography (silica gel, eluent: hexane only) to afford bromodiene **158**.

(1*E*,3*Z*)-1-bromotrideca-1,3-diene (158a) (TS11095, TS12013, TS12017, TS12018, TS12066, TS12067)



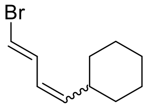
18–78% yield ((1*E*,3*E*)/(1*E*/3*Z*) = 52:48–2:>98). Colorless oil; R_f 0.77 (hexane only); IR (neat) 2925, 1574, 1465, 929, 799 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.88 (t, *J* = 6.8 Hz, 3H, CH$_2$CH$_2$C*H*$_3$), 1.27 (m, 14H, CHCH$_2$(C*H*$_2$)$_7$CH$_3$), 1.35–1.41 (m, 2H, CHC*H*$_2$(CH$_2$)$_7$), 2.13 (td, *J* = 7.5, 1.2 Hz, 2H, CHC*H*$_2$CH$_2$), 5.49 (dt, *J* = 10.9, 7.5 Hz, 1H, CHC*H*CH$_2$), 5.90 (dd, *J* = 11.2, 10.9 Hz, 1H, CHC*H*CHCH$_2$), 6.27 (d, *J* = 13.8 Hz, 1H, BrC*H*CH), 6.99 (ddd, *J* = 13.8, 11.2, 1.2 Hz, 1H, BrCHC*H*CH); ^{13}C NMR (100 MHz, CDCl$_3$) δ 14.1 (CH$_3$), 22.7 (CH$_2$), 27.9 (CH$_2$), 29.2 (CH$_2$), 29.3 (CH$_2$), 29.4 (CH$_2$), 29.5 (CH$_2$), 29.6 (CH$_2$), 31.9 (CH$_2$), 108.6 (CH), 125.6 (CH), 133.2 (CH), 133.9 (CH); EI-HRMS *m/z* calcd for $C_{13}H_{23}Br$ (M)$^+$ 258.09831, found 258.09938. ^{1}H NMR and ^{13}C NMR spectra of pure (1*E*,3*Z*)-isomer obtained from the reaction with adamantyl sulfone **5g** are provided in Supporting Information.

((1*E*,3*Z*)-1-bromohexa-1,3-dien-6-yl)benzene (158b) (TS12030)



57% yield ((1*E*,3*E*)/(1*E*/3*Z*) = 6:94). Colorless oil; R_f 0.38 (hexane only); IR (neat) 3062, 3042, 2925, 2856, 1573, 1496, 1453, 929, 800, 745, 698 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.48 (dtd, *J* = 7.6, 7.4, 1.2 Hz, 2H, CHC*H*$_2$CH$_2$Ar), 2.72 (t, *J* = 7.4 Hz, 2H, CH$_2$C*H*$_2$Ar), 5.53 (dt, *J* = 10.8, 7.6 Hz, 0.94H, CHC*H*CH$_2$ of (1*E*,3*Z*)-isomer), 5.77 (dt, *J* = 15.1, 7.0 Hz, 0.06H, CHC*H*CH$_2$ of (1*E*,3*E*)-isomer), 5.90–6.03 (m, 1H, CHC*H*CHCH$_2$), 6.20 (d, *J* = 13.4 Hz, 0.06H, BrCHC*H*CH of (1*E*,3*E*)-isomer), 6.23 (d, *J* = 13.4 Hz, 0.94H, BrCHC*H*CH of (1*E*,3*Z*)-isomer), 6.68 (dd, *J* = 13.4, 10.6 Hz, 0.06H, BrCHC*H*CH), 6.95 (ddd, *J* = 13.4, 11.6, 1.2 Hz, 0.79H, BrCHC*H*CH of (1*E*,3*Z*)-isomer); ^{13}C NMR (126 MHz, CDCl$_3$) δ 29.6 (CH$_2$ of (1*E*,3*Z*)-isomer), 34.3 (CH$_2$ of (1*E*,3*E*)-isomer), 35.3 (CH$_2$ of (1*E*,3*E*)-isomer), 35.5 (CH$_2$ of (1*E*,3*Z*)-isomer), 106.6 (CH of (1*E*,3*E*)-isomer), 109.2 (CH of (1*E*,3*Z*)-isomer), 125.9 (CH of (1*E*,3*E*)-isomer), 126.0 (CH of (1*E*,3*E*)-isomer), 126.3 (CH of (1*E*,3*Z*)-isomer), 128.1 (CH of (1*E*,3*E*)-isomer), 128.3 (CH of (1*E*,3*Z*)-isomer), 128.4 (CH of (1*E*,3*Z*)-isomer), 128.6 (CH of (1*E*,3*E*)-isomer), 132.2 (CH of (1*E*,3Z)-isomer), 132.9 (CH of (1*E*,3*Z*)-isomer), 135.1 (CH of (1*E*,3*E*)-isomer), 137.5 (CH of (1*E*,3E)-isomer), 141.2 (C of (1*E*,3*Z*)-isomer), 141.3 (C of (1*E*,3*E*)-isomer); EI-HRMS *m/z* calcd for $C_{12}H_{13}Br$ (M)$^+$ 236.02006, found 236.01997.

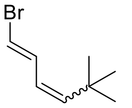
((1*E*,3*Z*)-1-bromobuta-1,3-dien-4-yl)cyclohexane (158c) (TS12021a)



77% yield ((1*E*,3*E*)/(1*E*/3*Z*) = 16:84). Colorless oil; R_f 0.76 (hexane only); IR (neat) 2925, 2849, 1574, 1447, ,930, 801, 755 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.05–1.13 (m, 2H, one of C2'-C*H*$_2$ and one of C6'-C*H*$_2$), 1.15–1.22 (m, 1H, one of

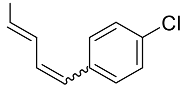
C4'-CH_2), 1.27–1.35 (m, 3H, one of C3'-CH_2, one of C4'-CH_2 and one of C5'-CH_2), 1.62–1.75 (m, 4H, one of C2'-CH_2, one of C3'-CH_2, one of C5'-CH_2 and one of C6'-CH_2), 1.95–2.01 (m, 0.16H, C1'-C*H* of (1*E*,3*E*)-isomer), 2.34–2.42 (m, 0.84H, C1'-C*H* of (1*E*,3*Z*)-isomer), 5.34 (dd, *J* = 10.9, 10.3 Hz, 0.84H, CHC*H*Cy of (1*E*,3*Z*)-isomer), 5.68 (dd, *J* = 15.5, 6.9 Hz, 0.16H, CHC*H*Cy of (1*E*,3*E*)-isomer), 5.80 (dd, *J* = 11.8, 10.9 Hz, 0.84H, CHC*H*CHCy of (1*E*,3*Z*)-isomer), 5.92 (dd, *J* = 15.5, 10.9 Hz, 0.16H, CHC*H*CHCy of (1*E*,3*E*)-isomer), 6.18 (d, *J* = 13.5 Hz, 0.16H, BrC*H*CH of (1*E*,3*E*)-isomer), 6.27 (d, *J* = 12.6 Hz, 0.84H, BrC*H*CH of (1*E*,3*Z*)-isomer), 6.66 (dd, *J* = 13.5, 10.9 Hz, BrCHC*H*CH of (1*E*,3*E*)-isomer), 7.00 (dd, *J* = 12.6, 11.8 Hz, 0.88H, BrCHC*H*CH of (1*E*,3*Z*)-isomer); ^{13}C NMR (126 MHz, CDCl$_3$) δ 25.7 (CH$_2$), 25.8 (CH$_2$), 26.0 (CH$_2$ of (1*E*,3*E*)-isomer), 32.5 (CH$_2$ of (1*E*,3*E*)-isomer), 33.0 (CH$_2$ of (1*E*,3*Z*)-isomer), 37.0 (CH of (1*E*,3*Z*)-isomer), 40.7 (CH of (1*E*,3*E*)-isomer), 106.0 (CH of (1*E*,3*E*)-isomer), 108.5 (CH of (1*E*,3*Z*)-isomer), 123.8 (CH of (1*E*,3*Z*)-isomer), 125.0 (CH of (1*E*,3*E*)-isomer), 133.4 (CH of (1*E*,3*Z*)-isomer), 137.7 (CH of (1*E*,3*E*)-isomer), 139.5 (CH of (1*E*,3*Z*)-isomer), 142.1 (CH of (1*E*,3*E*)-isomer); EI-HRMS *m/z* calcd for C$_{10}$H$_{15}$Br (M)$^+$ 214.03571, found 214.03490.

(1*E*,3*Z*)-1-bromo-5,5-dimethylhexa-1,3-diene (158d) (TS12021b)



39% yield ((1*E*,3*E*)/(1*E*/3*Z*) = 21:79). Colorless oil; *R*$_f$ 0.74 (hexane only); IR (neat) 2959, 2927, 1363, 1211, 980, 929, 770 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.07 (s, 2.2H, C(CH_3)$_3$ of (1*E*,3E)-isomer), 1.21 (s, 6.8H, C(CH_3)$_3$ of (1*E*,3*Z*)-isomer), 5.48 (d, *J* = 12.0 Hz, 0.79H, CHC*H*C of (1*E*,3*Z*)-isomer), 5.75–5.81 (m, 1H, CHC*H*CHC of (1*E*,3*Z*)-isomer and CHC*H*C of (1*E*,3*E*)-isomer), 5.93 (dd, *J* = 15.5, 10.3 Hz, 0.21H, CHC*H*CHC of (1*E*,3*E*-isomer), 6.23–6.28 (m, 1H, BrC*H*CH), 6.71 (dd, *J* = 13.2, 10.3 Hz, 0.21H, BrCHC*H*CH of (1*E*,3*E*)-isomer), 7.27 (ddd, *J* = 13.2, 12.0, 1.2 Hz, 0.79H, BrCHC*H*CH of (1*E*,3*Z*)-isomer); ^{13}C NMR (126 MHz, CDCl$_3$) δ 29.2 (CH$_3$ of (1*E*,3*E*)-isomer), 31.3 (CH$_3$ of (1*E*,3*Z*)-isomer), 106.0 (CH of (1*E*,3*E*)-isomer), 109.2 (CH of (1*E*,3*Z*)-isomer), 122.6 (CH of (1*E*,3*E*)-isomer), 123.8 (CH of (1*E*,3*Z*)-isomer), 133.4 (CH of (1*E*,3*Z*)-isomer), 138.0 (CH of (1*E*,3*E*)-isomer), 142.9 (CH of (1*E*,3*Z*)-isomer), 147.2 (CH of (1*E*,3*E*)-isomer); EI-HRMS *m/z* calcd for C$_8$H$_{13}$Br (M)$^+$ 188.02006, found 188.01924.

1-((1*E*,3*Z*)-1-bromobuta-1,3-dien-4-yl)-4-chlorobenzene (158e) (TS12021c)

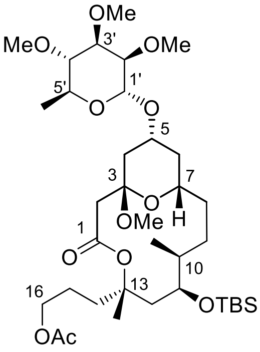


25% yield ((1*E*,3*E*)/(1*E*/3*Z*) = 7:93). Colorless oil; *R*$_f$ 0.53 (hexane only); IR (neat) 1490, 1093, 934, 848, 798 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.17 (dd, *J* = 11.5, 11.5 Hz, 1H, CHC*H*CHAr of (1*E*,3*Z*)-isomer), 6.25–6.47 (m, 1H, CHC*H*Ar), 6.51–6.54 (m, 1H, BrC*H*CH), 6.64 (dd, *J* = 15.5, 10.9 Hz, 0.70H, CHC*H*CHAr of (1*E*,3*E*)-isomer), 6.86 (dd, *J* = 13.2, 10.9 Hz, 0.70H, BrCHC*H*CH of (1*E*,3*E*)-isomer), 7.14 (ddd, *J* = 13.7, 12.0, 1.2 Hz, 0.93H, BrCHC*H*CH), 7.21–7.24 (m, 2H, Ar*H*), 7.90–7.35 (m, 2H, Ar*H*); ^{13}C NMR (126 MHz, CDCl$_3$) δ 109.6 (CH of (1*E*,3*E*)-isomer), 112.4 (CH of (1*E*,3*Z*)-isomer), 126.6 (CH of (1*E*,3E)-isomer), 127.5 (CH of (1*E*,3*Z*)-isomer), 127.6 (CH of (1*E*,3*E*)-isomer), 128.6 (CH of (1*E*,3*Z*)-isomer), 128.9 (CH of (1*E*,3*E*)-isomer), 129.5 (CH of (1*E*,3*Z*)-isomer), 130.1 (CH of (1*E*,3*Z*)-isomer), 131.9 (CH of (1*E*,3*Z*)-isomer), 133.3 (C of (1*E*,3*Z*)-isomer) 133.5 (CH of (1*E*,3*Z*)-isomer), 135.1 (CH of

(1*E*,3*Z*)-isomer), 137.4 (C of (1*E*,3*E*)-isomer); EI-HRMS *m/z* calcd for $C_{10}H_8BrCl$ $(M)^+$ 241.94979, found 241.94923.

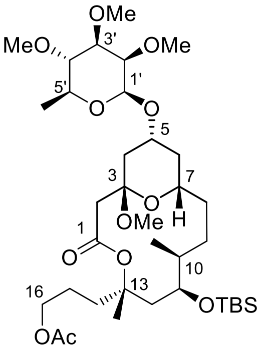
Part 1 Chapter 4 Section 4

3-((1*S*,5*S*,7*S*,8*S*,11*S*,13*R*)-7-((tert-butyldimethylsilyl)oxy)-1-methoxy-5,8-dimethyl-3-oxo-13-(((2*R*,3*R*,4*R*,5*S*,6*S*)-3,4,5-trimethoxy-6-methyltetrahydro-2*H*-pyran-2-yl)oxy)-4,15-dioxabicyclo[9.3.1]pentadecan-5-yl)propyl acetate (160a)



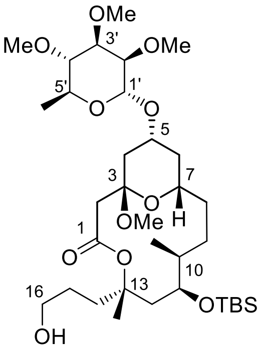
Eu(OTf)$_3$ (12.6 mg, 21 μmol) was added to a solution of alcohol **152** (37.2 mg, 70.1 μmol), phosphite donor **153c** (68.5 mg, 210 μmol) and MS4A (37.2 mg, 100 wt %) in CH$_2$Cl$_2$/toluene = 1:1 (0.70 mL) at 0 °C. After stirring for 2 h at this temperature, the reaction mixture was quenched with Et$_3$N (0.2 mL) and extracted with AcOEt (15 mL). The organic layer was washed with saturated aqueous NaHCO$_3$ (5 mL), water (5 mL), brine (5 mL), and dried over anhydrous Na$_2$SO$_4$. Filtration and evaporation was furnished crude product, which was purified by flash column chromatography (silica gel, 3:1 then 2:1 hexane/AcOEt) to give **160a** (38.6 mg, 77%) as a colorless oil and anomeric isomer **160b** (9.8 mg, 19%) as a colorless oil: R_f 0.61 (1:1 hexane/AcOEt); $[\alpha]_D^{18}$ –66.5 (*c* 1.17, CHCl$_3$); IR (NaCl) 1741, 1727, 1239, 1119, 1104, 1044 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.067 (s, 3H, SiC(C*H*$_3$)$_2$), 0.069 (s, 3H, SiC(C*H*$_3$)$_2$), 0.82 (d, *J* = 6.9 Hz, 3H, C10-C*H*$_3$), 0.86 (s, 9H, SiC(C*H*$_3$)$_3$), 1.19–1.27 (m, 5H, C6-*H*, C9-*H* and C5'-C*H*$_3$), 1.43 (s, 3H, C13-C*H*$_3$), 1.51–1.71 (m, 7H, C4-*H*, C8-*H*, C9-*H*, C14-*H* and C15-*H*), 1.82 (dd, *J* = 14.9, 2.9 Hz, 1H, C12-*H*), 1.87–1.90 (m, 1H, C6-*H*), 2.05–2.19 (m, 7H, C4-*H*, C10-*H*, C12-*H*, C14-*H* and COC*H*$_3$), 2.35 (d, *J* = 12.6 Hz, 1H, C2-*H*), 2.70 (d, *J* = 12.6 Hz, 1H, C2-*H*), 3.09 (dd, *J* = 9.7, 9.5 Hz, 1H, C4'-*H*), 3.22 (s, 3H, C3-OC*H*$_3$), 3.44 (dd, *J* = 9.5, 3.4 Hz, 1H, C3'-*H*), 3.47–3.50 (m, 7H, OC*H*$_3$, OC*H*$_3$ and C2'-*H*), 3.53 (s, 3H, OC*H*$_3$), 3.54–3.59 (m, 1H, C5'-*H*), 3.63–3.67 (m, 1H, C7-*H*), 3.79–4.12 (m, 3H, C5-*H* and C16-*H*), 4.16 (dd, *J* = 7.5, 2.9 Hz, 1H, C11-*H*), 4.96 (d, *J* = 1.4 Hz, 1H, C1'-*H*); ^{13}C NMR (126 MHz, CDCl$_3$) δ –4.08 (CH$_3$), –3.44 (CH$_3$), 14.6 (CH$_3$), 17.8 (CH$_3$), 18.4 (C), 21.0 (CH$_3$), 23.3 (CH$_2$), 25.0 (CH$_3$), 26.0 (CH$_3$), 32.1 (CH$_2$), 32.2 (CH$_2$), 36.1 (CH), 36.4 (CH$_2$), 36.5 (CH$_2$), 40.9 (CH$_2$), 45.0 (CH$_2$), 45.5 (CH$_2$), 49.2 (CH$_3$), 57.7 (CH$_3$), 59.0 (CH$_3$), 60.9 (CH$_3$), 64.6 (CH$_2$), 68.0 (CH), 69.0 (CH), 69.1 (CH), 70.8 (CH), 77.8 (CH), 81.0 (CH), 82.2 (CH), 83.0 (C), 94.3 (CH), 99.6 (C), 168.9 (C), 171.1 (C); ESI-HRMS *m/z* calcd for $C_{36}H_{66}O_{12}SiNa$ $(M+Na)^+$ 741.42157, found 741.42194. The relative configuration at C1' was determined by NOESY correlation between C1', C3' and C5' of isolated minor isomer, β-anomer product (see below).

Data for 3-((1S,5S,7S,8S,11S,13R)-7-((tert-butyldimethylsilyl)oxy)-1-methoxy-5,8-dimethyl-3-oxo-13-(((2S,3R,4R,5S,6S)-3,4,5-trimethoxy-6-methyltetrahydro-2H-pyran-2-yl)oxy)-4,15-dioxabicyclo[9.3.1]pentadecan-5-yl)propyl acetate (160b)



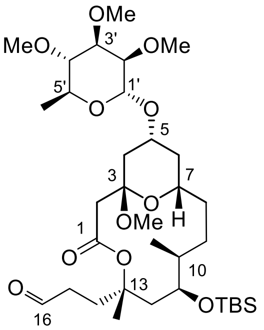
Colorless oil: R_f 0.42 (1:1 hexane/AcOEt); $[\alpha]_D^{18}$ –66.5 (*c* 1.17, CHCl$_3$); IR (NaCl) 1741, 1727, 1239, 1119, 1104, 1044 cm^{-1}; ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 0.321 (s, 3H, SiC(CH_3)$_2$), 0.23 (s, 3H, SiC(CH_3)$_2$), 1.03 (s, 12H, C10-CH_3 and SiC(CH_3)$_3$), 1.19–1.24 (m, 1H, C9-*H*), 1.34–1.36 (m, 3H, C13-CH_3 and C5'-CH_3), 1.39–1.69 (m, 7H, C4-*H*, C6-*H*, C8-*H*, C14-*H* and C15-*H*), 1.74–1.80 (m, 4H, C9-*H* and COCH_3), 1.97–2.04 (m, 2H, C6-*H* and C12-*H*), 2.15–2.22 (m, 2H, C4-*H* and C12-*H*), 2.26–2.32 (m, 2H, C2-*H* and C10-*H*), 2.69 (d, *J* = 12.6 Hz, 1H, C2-*H*), 2.95 (dd, *J* = 9.5, 3.4 Hz, 1H, C3'-*H*), 3.01 (s, 3H, C3-OCH_3), 3.13 (dd, *J* = 9.2, 5.7 Hz, 1H, C5'-*H*), 3.23 (s, 3H, OCH_3), 3.33 (dd, iJi = 9.5, 9.2 Hz, 1H, C4'-*H*), 3.41–3.44 (m, 4H, C2'-*H* and OCH_3), 3.47–3.51 (m, 1H, C7-*H*), 3.61 (s, 3H, OCH_3), 3.96 (t, *J* = 6.3 Hz, C16-*H*), 4.19–4.25 (m, 2H, C5-*H* and C1'-*H*), 4.34 (dd, *J* = 8.6, 2.3 Hz, 1H, C11-*H*); ^{13}C NMR (126 MHz, CDCl$_3$) δ –4.13 (CH$_3$), –3.55 (CH$_3$), 14.6 (CH$_2$), 17.7 (CH$_2$), 18.3 (C), 20.9 (CH$_3$), 23.3 (CH$_2$), 25.1 (CH$_3$), 25.9 (CH$_3$), 31.9 (CH$_2$), 32.0 (CH$_2$), 36.1 (CH$_3$), 36.2 (CH), 38.3 (CH$_3$), 40.2 (CH$_2$), 45.2 (CH$_2$), 45.4 (CH$_2$), 48.9 (CH$_3$), 57.3 (CH$_3$), 61.0 (CH$_3$), 61.7 (CH$_3$), 64.5 (CH$_2$), 69.4 (CH), 71.2 (CH), 71.3 (CH), 71.7 (CH), 81.7 (CH), 83.2 (C), 83.8 (CH), 91.6 (CH), 99.2 (CH), 99.5 (C), 169.0 (C), 171.0 (C); ESI-HRMS *m/z* calcd for C$_{36}$H$_{66}$O$_{12}$SiNa (M+Na)$^+$ 741.42157, found 741.42186. The relative configuration at C1' was determined by NOESY correlation between C1', C3' and C5'.

(1*S*,5*S*,7*S*,8*S*,11*S*,13*R*)-7-((tert-butyldimethylsilyl)oxy)-5-(3-hydroxypropyl)-1-methoxy-5,8-dimethyl-13-(((2*R*,3*R*,4*R*,5*S*,6*S*)-3,4,5-trimethoxy-6-methyltetrahydro-2*H*-pyran-2-yl)oxy)-4,15-dioxabicyclo[9.3.1]pentadecan-3-one (161)



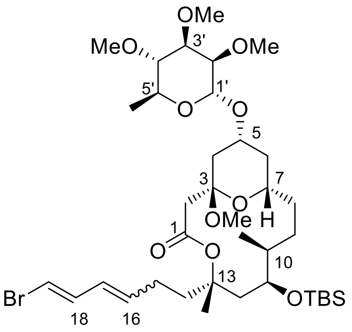
A solution of glycoside **160a** (38.6 mg, 53.7 μmol) and K$_2$CO$_3$ (5.04 mg, 36.5 μmol) in MeOH (0.537 mL) was stirred for 3 h at room temperature. The mixture was quenched with saturated aqueous NH$_4$Cl (2 mL), water (1 mL) and whole mixture was extracted with AcOEt (8 mL). Organic layer was washed with brine (3 mL) and dried over anhydrous Na$_2$SO$_4$. Filtration and evaporation *in vacuo* furnished the crude product, which was purified by flash column chromatography (silica gel, 1:1 hexane/AcOEt) to give **161** (36.0 mg, 99%) as a colorless oil: R_f 0.34 (1:1 hexane/AcOEt); $[\alpha]_D^{19}$ –66.3 (*c* 1.03, CHCl$_3$); IR (NaCl) 3488, 1723, 1119, 1104, 1046, 835 cm^{-1}; ^{1}H NMR (396 MHz, CDCl$_3$) δ 0.068 (s, 3H, SiC(CH_3)$_2$), 0.071 (s, 3H, SiC(CH_3)$_2$), 0.82 (d, *J* = 6.8 Hz, 3H, C10-CH_3), 0.85 (s, 9H, SiC(CH_3)$_3$), 1.21–1.30 (m, 6H, C6-*H*, C9-*H*, C14-*H* and C5'-CH_3), 1.43 (s, 3H, C13-CH_3), 1.56–1.66 (m, 6H, C4-*H*, C8-*H*, C9-*H*, C14-*H* and C15-*H*), 1.77–1.85 (m, 2H, C6-*H* and C12-*H*), 2.04–2.22 (m, 4H, C4-*H*, C8-*H*, C10-*H* and C12-*H*), 2.31 (d, *J* = 12.7 Hz, 1H, C2-*H*), 2.71 (d, *J* = 12.7 Hz, 1H, C2-*H*), 3.10 (dd, *J* = 9.3, 9.1 Hz, 1H, C4'-*H*), 3.20 (s, 3H, C3-OCH_3), 3.41–3.46 (m, 8H, OCH_3, OCH_3, C2'-*H* and C3'-*H*), 3.53 (s, 3H, OCH_3), 3.57 (dd, *J* = 9.3, 6.3 Hz, 1H, C5'-*H*), 3.60–3.68 (m, 3H, C7-*H* and C16-*H*), 3.97–4.05 (m, 1H, C5-*H*), 4.13 (dd, *J* = 7.7, 1.8 Hz, 1H, C11-*H*), 4.96 (d, *J* = 1.4 Hz, 1H, C1'-*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ –4.17 (CH_3), –3.47 (CH_3), 14.5 (CH_3), 17.7 (CH_3), 18.3 (C), 25.1 (CH_3), 25.9 (CH_3), 37.2 (CH_2), 31.8 (CH_2), 32.1 (CH_2), 36.0 (CH and CH_2), 36.3 (CH_2), 10.7 (CH_2), 44.8 (CH_2), 45.4 (CH_2), 48.8 (CH_3), 57.6 (CH_3), 58.9 (CH_3), 60.9 (CH_3), 62.8 (CH_2), 67.9 (CH), 69.8 (CH), 70.0 (CH), 70.6 (CH), 77.8 (CH), 81.0 (CH), 82.2 (CH), 83.4 (C), 94.7 (CH), 99.5 (C), 168.8 (C); ESI-HRMS *m/z* calcd for $C_{34}H_{64}O_{11}SiNa$ $(M+Na)^+$ 699.41101, found 699.41143.

3-((1*S*,5*S*,7*S*,8*S*,11*S*,13*R*)-7-((tert-butyldimethylsilyl)oxy)-1-methoxy-5,8-dimethyl-3-oxo-13-(((2*R*,3*R*,4*R*,5*S*,6*S*)-3,4,5-trimethoxy-6-methyltetrahydro-2*H*-pyran-2-yl)oxy)-4,15-dioxabicyclo[9.3.1]pentadecan-5-yl)propanal (162)



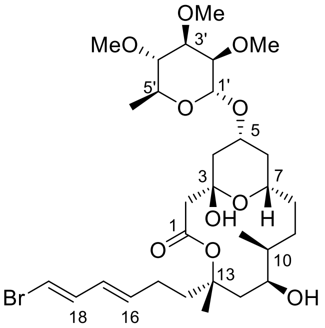
Dess–Martin periodinane (67.7 mg, 160 μmol) was added to a solution of alcohol **161** (36.0 mg, 53.2 μmol) and $NaHCO_3$ (179 mg, 2.13 mmol) in CH_2Cl_2 (1.06 mL) at 0 °C. After stirring for 1 h at room temperature, additional Dess–Martin periodinane (67.7 mg, 160 μmol) was added at 0 °C. The reaction mixture was stirred for 1 h at room temperature and diluted with AcOEt (10 mL), then quenched with saturated aqueous $NaHCO_3$ (5 mL) and aqueous 10% $Na_2S_2O_3$ (5 mL). The aqueous layer was extracted with AcOEt (30 mL) and combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL), water (10 mL) brine (10 mL) and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product, which was purified by flash column chromatography (silica gel, 2:1 hexane/AcOEt) to give **162** (29.4 mg, 82%) as a colorless oil: R_f 0.52 (1:1 hexane/AcOEt); $[\alpha]_D^{20}$ –61.7 (*c* 1.47, C_6H_6); IR (NaCl) 1727, 1119, 1103, 1045, 835 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 0.25 (s, 6H, SiC(CH_3)$_2$), 1.02–1.04 (m, 12H, C10-CH_3 and SiC(CH_3)$_3$), 1.19–1.26 (m, 5H, C6-*H*, C9-*H* and C13-CH_3), 1.35–1.41 (m, 4H, C8-*H* and C5'-CH_3), 1.56 (dd, *J* = 12.0, 12.0, 1H, C4-*H*), 1.62–1.77 (m, 4H, C6-*H*, C8-*H*, C9-*H* and C15-*H*), 1.87 (dd, *J* = 14.6, 3.4 Hz, 1H, C12-*H*), 1.91–1.97 (m, 1H, C15-*H*), 2.05–2.11 (m, 1H, C15-*H*), 2.17–2.22 (m, 3H, C2-*H*, C4-*H* and C10-*H*), 2.37 (dd, *J* = 14.9, 8.0 Hz, 1H, C12-*H*), 2.43–2.49 (m, 1H, C14-*H*), 2.52 (d, *J* = 12.6 Hz, 1H, C2-*H*), 3.10 (s, 3H, C3-OCH_3), 3.32 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.42–3.50 (m, 5H, C7-*H*, C4'-*H* and OCH_3), 3.57 (dd, *J* = 2.9, 2.0 Hz, 1H, C2'-*H*), 3.72 (dd, *J* = 9.2, 2.9 Hz, 1H, C3'-*H*), 3.85–3.91 (m, 1H, C5'-*H*), 4.09–4.15 (m, 1H, C5-*H*), 4.26 (dd, *J* = 7.5, 2.9 Hz, 1H, C11-*H*), 5.09 (d, *J* = 2.0 Hz, 1H, C1'-*H*), 9.35 (s, 1H, C16-*H*); ^{13}C NMR (126 MHz, C_6D_6) δ –3.69 (CH_3), –3.03 (CH_3), 15.1 (CH_3), 18.2 (CH_3), 18.8 (C), 24.9 (CH_3), 26.4 (CH_3), 32.6 (CH_2), 32.8 (CH_2), 36.8 (CH), 37.0 (CH_2), 39.0 (CH_2), 41.7 (CH_2), 45.3 (CH_2), 46.0 (CH_2), 49.3 (CH_3), 57.4 (CH_3), 59.2 (CH_3), 60.9 (CH_3), 69.0 (CH), 69.3 (CH), 69.6 (CH), 71.1 (CH), 78.4 (CH), 82.2 (CH), 82.5 (CH), 82.9 (C), 95.8 (CH), 100.0 (C), 168.6 (C), 199.9 (CH); ESI-HRMS *m/z* calcd for $C_{34}H_{62}O_{11}SiNa$ $(M+Na)^+$ 697.39536, found 697.39734.

(1*S*,5*S*,7*S*,8*S*,11*S*,13*R*)-5-((5*E*)-6-bromohexa-3,5-dien-1-yl)-7-((tert-butyldimethylsilyl)oxy)-1-methoxy-5,8-dimethyl-13-(((2*R*,3*R*,4*R*,5*S*,6*S*)-3,4,5-trimethoxy-6-methyltetrahydro-2*H*-pyran-2-yl)oxy)-4,15-dioxabicyclo[9.3.1]pentadecan-3-one (163)



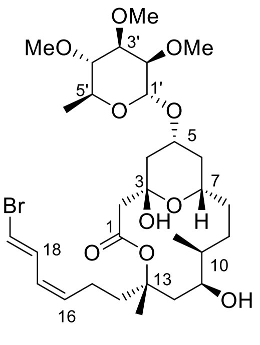
LiHMDS (45.5 µL, 45.5 µmol) was added to a solution of bromosulfone **157b** (18.7 mg, 52.0 µmol) in DME (0.58 mL) at –78 °C with dry ice-acetone bath. After stirring for 5 min at this temperature, aldehyde **162** (29.2 mg, 43.3 µmol) in DME (0.58 mL, rinsed 2×0.29 mL) was added and stirred for 2 h at –78 °C. The reaction mixture was warmed to room temperature by removing dry ice and stirred for 19 h. Water (2 mL) was added at 0 °C and whole mixture was extracted with AcOEt (10 mL). Organic layer was washed with brine, and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished crude product, which was purified by flash column chromatography (silica gel, 3:1 hexane/AcOEt) to give **163** (24.6 mg, 73%, (16*E*,18*E*)/(16*Z*,18*E*) = 51:49) as a colorless oil: R_f 0.69 (1:1 hexane/AcOEt); ^{1}H NMR (500 MHz, C_6D_6) δ 0.23 (s, 1.5H, SiC(CH_3)$_2$), 0.24 (s, 1.5H, SiC(CH_3)$_2$), 0.26 (s, 1.5H, SiC(CH_3)$_2$), 0.26 (s, 1.5H, SiC(CH_3)$_2$), 1.04–1.07 (m, 12H, C10-CH_3 and SiC(CH_3)$_3$), 1.23–1.30 (m, 2H, C6-*H* and C9-*H*), 1.34 (s, 1.5H, C13-CH_3), 1.40–1.47 (m, 5.5H, C8-*H*, C13-CH_3 and C5'-CH_3), 1.61–1.75 (m, 4H, C4-*H*, C8-*H* and C14-*H*), 1.78–1.85 (m, 1H, C9-*H*), 1.94–2.00 (m, 1H, C15-*H*), 2.03–2.09 (m, 1.5H, C12-*H* and C15-*H*), 2.16–2.38 (m, 6H, C2-*H*, C4-*H*, C6-*H*, C10-*H*, C12-*H* and C15-*H*), 2.57 (d, *J* = 12.6 Hz, 0.5H, C2-*H*), 2.60 (d, *J* = 12.6 Hz, 0.5H, C2-*H*), 3.06 (s, 1.5H, C3-OCH_3), 3.09 (s, 1.5H, C3-OCH_3), 3.32 (s, 1.5H, OCH_3), 3.33 (s, 1.5H, OCH_3), 3.38 (m, 1.5H, OCH_3), 3.39 (s, 1.5H, OCH_3), 3.47–3.52 (m, 5H, C7-*H*, C4'-*H* and OCH_3), 3.57–3.59 (m, 1H, C2'-*H*), 3.71–3.75 (m, 1H, C3'-*H*), 3.86–3.93 (m, 1H, C5'-*H*), 4.11–4.17 (m, 1H, C5-*H*), 4.39–4.41 (m, 1H, C11-*H*), 5.10 (m, 1H, C1'-*H*), 5.31 (dt, *J* = 10.9, 7.5Hz, 0.5H, C16-*H*), 5.38 (dt, *J* = 15.5, 6.9 Hz, 0.5H, C16-*H*), 5.62 (dd, *J* = 11.2, 10.9 Hz, 0.5H, C15-*H*), 5.70 (dd, *J* = 15.5, 10.9 Hz, 0.5H, C15-*H*), 5.87 (d, *J* = 13.5 Hz, 0.5H, C19-*H*), 5.93 (d, *J* = 13.2 Hz 0.5H, C19-*H*), 6.55 (dd, *J* = 13.5, 10.9 Hz, 0.5H, C18-*H*), 7.07 (dd, *J* = 13.2, 11.2 Hz, 0.5H, C18-*H*); ^{13}C NMR (126 MHz, C_6D_6) δ –3.91 (CH_3), –3.84 (CH_3), –3.03 (CH_3), –2.98 (CH_3), 15.2 (CH_3), 15.2 (CH_3), 18.2 (CH_3), 18.7 (C), 22.7 (CH_2), 25.2 (CH_3), 25.4 (CH_3), 26.3 (CH_3), 26.3 (CH_3), 27.5 (CH_2), 32.3 (CH_2), 32.4 (CH_2), 32.7 (CH_2), 32.8 (CH_2), 36.3 (CH), 36.3 (CH), 36.6 (CH_2), 36.7 (CH_2), 40.3 (CH_2), 41.1 (CH_2), 41.3 (CH_2), 44.9 (CH_2), 45.1 (CH_2), 45.6 (CH_2), 45.7 (CH_2), 48.9 (CH_3), 49.1 (CH_3), 57.3 (CH_3), 59.1 (CH_3), 60.8 (CH_3), 68.9 (CH), 69.5 (CH), 69.5 (CH), 70.2 (CH), 70.8 (CH), 70.9 (CH), 78.4 (CH), 82.5 (CH), 82.5 (C), 82.6 (C), 82.8 (CH), 95.8 (CH), 95.8 (CH), 99.9 (C), 100.0 (C), 107.1 (CH), 109.9 (CH), 126.5 (CH), 132.5 (CH), 133.1 (CH), 135.3 (CH), 137.8 (CH), 168.6 (C), 168.6 (C); ESI-HRMS *m/z* calcd for $C_{37}H_{65}O_{10}BrSiNa$ $(M+Na)^+$ 799.34226, found 799.34332. The regioisomeric ratio of @ was determined to be (16*E*,18*E*)/(16*Z*,18*E*) = 51:49 by ^{1}H NMR analysis.

(1*S*,5*S*,7*S*,8*S*,11*S*,13*R*)-5-((3*E*,5*E*)-6-bromohexa-3,5-dien-1-yl)-1,7-dihydroxy-5,8-dimethyl-13-(((2*R*,3*R*,4*R*,5*S*,6*S*)-3,4,5-trimethoxy-6-methyltetrahydro-2*H*-pyran-2-yl)oxy)-4,15-dioxabicyclo[9.3.1]pentadecan-3-one, 18*E*-lyngbyaloside C (103)



46% aqueous HF (0.10 mL) was added to a solution of protected macrolide **163** (5.6 mg, 7.20 μmol) in CH_3CN (1.8 mL, 4 mM) at 0 °C. After stirring for 5.5 h at room temperature, the reaction mixture was cooled to 0 °C and quenched with saturated aqueous $NaHCO_3$ (3 mL, dropwise) with vigorous stirring. The whole mixture was extracted with AcOEt (15 mL) and organic layer was washed with brine (3 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product, which was purified by flash column chromatography (silica gel, 2:1 hexane/AcOEt). Further purification by preparative HPLC (column: COSMOSIL 5SL-II packed column (10 mm I.D. × 250 mm); eluent: hexane/IPA/MeOH = 88:1:1; flow rate: 4.7 mL/min; temperature: room temperature; UV detection: 254 nm) afforded **103** (1.5 mg, 32%, $t_R = 20.0$ min) as a white amorphous and **164** (1.3 mg, 28%, $t_R =$ 24.0 min) as a white amorphous together with unidentified minor isomers (0.4 mg, 9%, $t_R = 21.4$ min; 0.5 mg, 11%, $t_R = 26.0$ min): R_f 0.49 (1:1 hexane/AcOEt); $[\alpha]_D^{21}$ −18.3 (*c* 0.43, MeOH) [*lit.*[@], $[\alpha]_D^{20}$ −13 (*c* 0.13, MeOH)]; ^1H NMR (500 MHz, $CDCl_3$) δ 0.81 (d, *J* = 6.9 Hz, 3H, C10-C*H*$_3$), 1.19 (ddd, *J* = 11.6, 12.0 ,12.0 Hz, 1H, C6-*H*), 1.27 (d, *J* = 6.3 Hz, 3H, C5'-C*H*$_3$), 1.30–1.38 (m, 2H, C4-*H* and C9-*H*), 1.41–1.49 (m, 3H, C8-*H*, C9-*H*, C10-*H* and C12-*H*), 1.52 (s, 3H, C13-C*H*$_3$), 1.61–1.75 (m, 2H, C8-*H* and C14-*H*), 1.92 (dt, *J* = 12.0, 1.9 Hz, 1H, C6-*H*), 1.95–2.00 (m, 1H, C14-*H*), 2.13 (dd, *J* = 12.0, 4.6 Hz, 1H, C4-*H*), 2.16–2.23 (m, 2H, C15-*H*), 2.41 (d, *J* = 12.0 Hz, 1H, C2-*H*), 2.52 (d, *J* = 12.0 Hz, 1H, C2-*H*), 2.79 (d, *J* = 15.5 Hz, 1H, C12-*H*), 3.10 (dd, *J* = 9.5, 9.4 Hz, 1H, C4'-*H*), 3.44 (dd, *J* = 9.4, 2.9 Hz, 1H, C3'-*H*), 3.48–3.49 (m, 7H, C2'-*H*, C2'-OC*H*$_3$ and C3'-OC*H*$_3$), 3.54–3.57 (m, 4H, C5'-*H* and C4'-OC*H*$_3$), 3.80 (ddd, *J* = 11.6, 8.6, 1.9 Hz, 1H, C7-*H*), 4.09–4.14 (m, 1H, C5-*H*), 4.29 (d, *J* = 5.7 Hz, 1H, C11-*H*), 4.60 (d, *J* = 2.3 Hz, 1H, C3-O*H*), 4.99 (d, *J* = 1.2 Hz 1H, C1'-*H*), 5.76 (dt, *J* = 15.5, 6.9 Hz, 1H, C16-*H*), 6.01 (dd, *J* = 15.5, 10.9 Hz, 1H, C17-*H*), 6.19 (d, *J* = 13.8 Hz, 1H, C18-*H*), 6.67 (dd, *J* = 13.8, 10.9 Hz, 1H, C19-*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.6 (CH_3), 17.8 (CH_3), 23.5 (CH_3), 26.7 (CH_2), 31.6 (CH_2), 32.5 (CH_2), 37.1 (CH), 38.0 (CH_2), 38.7 (CH_2), 41.5 (CH_2), 44.2 (CH_2), 47.1 (CH_2), 57.7 (CH_3), 59.0 (CH_3), 60.9 (CH_3), 65.7 (CH), 68.1 (CH), 69.2 (CH), 69.8 (CH), 77.8 (CH), 81.0 (CH), 82.2 (CH), 86.4 (C), 94.4 (CH), 96.8 (C), 106.5 (CH), 127.7 (CH), 135.6 (CH), 137.5 (CH), 172.4 (C); ESI-HRMS *m/z* calcd for $C_{30}H_{49}O_{10}BrNa$ $(M+Na)^+$ 671.24013, found 671.24164.

Data for (1S,5S,7S,8S,11S,13R)-5-((3Z,5E)-6-bromohexa-3,5-dien-1-yl)-1,7-dihydroxy-5,8-dimethyl-13-(((2R,3R,4R,5S,6S)-3,4,5-trimethoxy-6-methyltetrahydro-2H-pyran-2-yl)oxy)-4,15-dioxabicyclo[9.3.1]pentadecan-3-one, (16Z,18E)-lyngbyaloside C (164)



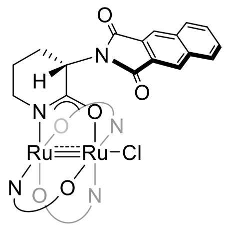
White amorphous: R_f 0.43 (1:1 hexane/AcOEt)); $[\alpha]_D^{22}$ –36.1 (*c* 0.33, MeOH); IR (NaCl) 3478, 1698, 1203, 1140, 1120, 1102, 1054, 1043, 1010 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82 (d, *J* = 6.9 Hz, 3H, C10-C*H*$_3$), 1.18–1.23 (m, 1H, C6-*H*), 1.27 (d, *J* = 6.3 Hz, 3H, C5'-C*H*$_3$), 1.29–1.38 (m, 2H, C4-*H* and C9-*H*), 1.41–1.50 (m, 4H, C8-*H*, C9-*H*, C10-*H* and C12-*H*), 1.56 (s, 3H, C13-C*H*$_3$), 1.60–1.74 (m, 2H, C8-*H* and C14-*H*), 1.91–1.97 (m, 2H, C6-*H* and C14-*H*), 2.13 (dd, *J* = 12.0, 3.4 Hz, 1H, C4-*H*), 2.19–2.31 (m, 2H, C15-*H*), 2.42 (d, *J* = 12.3 Hz, 1H, C2-*H*), 2.54 (d, *J* = 12.3 Hz, 1H, C2-*H*), 2.80 (d, *J* = 15.5 Hz, 1H, C12-*H*), 3.10 (dd, *J* = 9.6, 9.5 Hz, 1H, C4'-*H*), 3.44 (dd, *J* = 9.6, 3.4 Hz, 1H, C3'-*H*), 3.47–3.49 (m, 7H, C2'-*H*, OC*H*$_3$ and OC*H*$_3$), 3.54–3.58 (m, 4H, C5'-*H* and OC*H*$_3$), 3.80 (ddd, *J* = 11.7, 8.6, 1.7 Hz, 1H, C7-*H*), 4.09–4.15 (m, 1H, C5-*H*), 4.29 (d, *J* = 5.7 Hz, 1H, C11-*H*), 4.61 (d, *J* = 1.7 Hz, 1H, C3-O*H*), 4.99 (d, *J* = 1.7 Hz, 1H, C1'-*H*), 5.52 (dt, *J* = 10.9, 7.5 Hz, 1H, C16-*H*), 5.92 (dd, *J* = 11.5, 10.9 Hz, 1H, C17-*H*), 6.30 (d, *J* = 12.6 Hz, 1H, C18-*H*), 7.04 (dd, *J* = 12.6, 11.5 Hz, 1H, C19-*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.6 (CH_3), 17.8 (CH_3), 22.3 (CH_2), 23.5 (CH_3), 31.6 (CH_2), 32.5 (CH_2), 37.1 (CH), 38.0 (CH_2), 39.2 (CH_2), 41.5 (CH_2), 44.2 (CH_2), 47.1 (CH_2), 57.7 (CH_3), 59.0 (CH_3), 60.9 (CH_3), 65.7 (CH), 68.1 (CH), 69.2 (CH), 69.8 (CH), 77.8 (CH), 81.0 (CH), 82.2 (CH), 86.4 (C), 94.4 (CH), 96.8(C), 109.1 (CH), 126.1 (CH), 132.8 (CH), 133.1 (CH), 172.5 (C); ESI-HRMS *m/z* calcd for $C_{30}H_{49}O_{10}BrNa$ $(M+Na)^+$ 671.24013, found 671.24127.

Part 2 Chapter 1 Section 2

Tetrakis[(*S*)-3-(1,3-dioxobenzo[f]isoindol-2-yl)-2-piperidonate]diruthenium(II,III) chloride, Ru_2(*S*-BPTPI)$_4$Cl (TS14009)

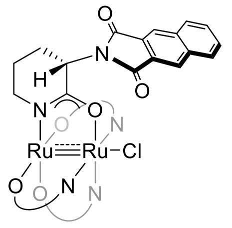
A mixture of $Ru_2(OAc)_4Cl$ (**166**)[48,63)] (237 mg, 0.50 mmol) and (*S*)-BPTPI ligand (**185**)[3a)] (2.94 g, 10 mmol) in 100 mL of chlorobenzene, contained in a round-bottom flask fitted with a Soxlet extraction apparatus was heated at reflux (set temperature: 165 °C) with vigorous stirring under Ar. The thimble in the Soxlet extraction apparatus was charged with an oven-dried mixture of one-part sodium carbonate and one-part sea sand. After completion of the reaction (monitored by LC-MS), the mixture was cooled to room temperature and then filtered through Hirsch funnel washed with CH_2Cl_2. The filtrate was absorbed in silica gel (9 g) and evaporated *in vacuo*. Chromatography (silica gel, CH_3CN only followed by 20:1 $CHCl_3$/MeOH, then 5:1 $CHCl_3$/MeOH) afforded *cis*-Ru_2(*S*-BPTPI)$_4$Cl (**186-Cl**) (164 mg, 24%, more polar) and *mer*-Ru_2(*S*-BPTPI)$_4$Cl (**187-Cl**) (342 mg, 48%, less polar) as a brown solid. *cis*-Ru_2(*R*-BPTPI)$_4$Cl (**254-Cl**) and *mer*-Ru_2(*R*-BPTPI)$_4$Cl (**255-Cl**) were synthesized by same procedure.

Data for cis-tetrakis[(S)-3-(1,3-dioxobenzo[f]isoindol-2-yl)-2-piperidonate]diruthenium(II,III) chloride, cis-Ru₂(S-BPTPI)₄Cl (186-Cl)



R_f = 0.07 (20:1 $CHCl_3$/MeOH); t_R = 12.706 (LC-MS; column: InertSustainSwift™ C18 column (3 µm, 3.0 × 100 mm); CH_3CN/H_2O (CH_3CN: 15% to 80% linear gradient for 8 min, then CH_3CN: 80% constant for 7 min, then CH_3CN: 15% constant for 5 min); IR (KBr) 2358, 2343, 1768, 1710, 1378, 1348, 768, 619 cm^{-1}; ESI-HRMS *m/z* calcd for $C_{68}H_{52}O_{12}Ru_2$ $(M–Cl)^+$ 1376.18240, found 1376.17765. Isotopic peaks indicate bimetallic ruthenium-ruthenium core.

Data for meridional-tetrakis[(S)-3-(1,3-dioxobenzo[f]isoindol-2-yl)-2-piperidonate] diruthenium(II,III) chloride, mer-Ru₂(S-BPTPI)₄Cl (187-Cl)



R_f = 0.29 (20:1 $CHCl_3$/MeOH); t_R = 12.563 (LC-MS; column: InertSustainSwift™ C18 column (3 µm, 3.0 × 100 mm); CH_3CN/H_2O (CH_3CN: 15% to 80% linear gradient for 8 min, then CH_3CN: 80% constant for 7 min, then CH_3CN: 15% constant for 5 min); IR (KBr) 2939, 2860, 1768, 1711, 1378, 1348, 765, 622 cm^{-1}; ESI-HRMS *m/z* calcd for $C_{68}H_{52}O_{12}Ru_2$ $(M–Cl)^+$ 1376.18240, found 1376.17892. Isotopic peaks indicate bimetallic ruthenium-ruthenium core. Single crystal suitable for X-ray crystallography was obtained by bellow procedure: *mer*-Ru_2(*S*-BPTPI)$_4$Cl and *mer*-Ru_2(*R*-BPTPI)$_4$Cl were put into a micro test tube and dissolved in $CHCl_3$. Then, small amount of *N*,*N*-dimethylformamide was added to this mixture.* The test tube was equipped with cap having a hole and stored in screw cap vial quarterly filled with *n*-pentane. *n*-Pentane was diffused to the solution slowly and it afforded single crystal of *mer*-Ru_2(BPTPI)$_4$Cl as platelet.

General procedure for the preparation of cationic complexes, Ru_2(*S*-BPTPI)$_4$NTf$_2$ (186-NTf$_2$, 187-NTf$_2$) (TS14026)

Ru_2(*S*-BPTPI)$_4$Cl (**186-Cl** or **187-Cl**) (1.0 equiv.) and AgNTf$_2$ (1.1 equiv.) in CH_2Cl_2 (0.04 M) was stirred at 35 °C for 24 h in dark. A precipitate was removed by passing through silica gel short column (eluent: 1:1 CH_2Cl_2/AcOEt) and the filtrate was evaporated. Desired complexes were obtained in >95% yield as a brown solid.

General procedure for the preparation of cationic complexes, Ru_2(*S*-BPTPI)$_4$ClO$_4$ (186-ClO$_4$, 187-ClO$_4$) (TS12071, TS12088)

Ru_2(*S*-BPTPI)$_4$Cl (**186-Cl** or **187-Cl**) (1.0 equiv.) and $AgClO_4$ (1.1 equiv.) in CH_2Cl_2 (0.04 M) was stirred at 35 °C for 24 h in dark. A precipitate was removed by passing through silica gel short column (eluent: 1:1 CH_2Cl_2/AcOEt) and the filtrate was evaporated. Desired complexes were obtained in >95% yield as a brown solid. Single crystal of *cis*-Ru_2(BPTPI)$_4$ClO$_4$ suitable for X-ray crystallography was obtained by bellow procedure: *cis*-Ru_2(*S*-BPTPI)$_4$ClO$_4$ and *cis*-Ru_2(*R*-BPTPI)$_4$ClO$_4$ was put into a micro test tube and dissolved in $CHCl_3$. Then, small amount of *N*,*N*-dimethylformamide was added to this mixture.* The test tube was equipped with cap having a hole and stored in screw cap vial quarterly filled with *n*-pentane. *n*-Pentane was diffused to the solution slowly and it afforded single crystal of *cis*-Ru_2(BPTPI)$_4$ClO$_4$ as platelet.

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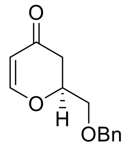
* If *N*,*N*-dimethylformamide was added to much, it resulted in two-layer of toluene-pentane mixture and *N*,*N*-dimethylformamide. It does not afford single crystal.

Part 2 Chapter 1 Section 3

General procedure for optimization of reaction conditions of enantioselective hetero-Diels–Alder reactions with Danishefsky's diene: (*S*)-2-((benzyloxy)methyl)-2,3-dihydro4*H*-pyran-4-one (*ent*-108)

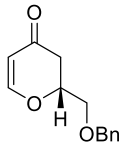
To a solution of benzyloxyacetoaldehyde (**109**) (15.1 mg, 0.10 mmol) in CH_2Cl_2 (0.1 mL) was added *cis*-Ru_2(*S*-BPTPI)$_4$Cl (**186-Cl**) (1.41 mg, 0.001 mmol, 1 mol %). A solution of Danishefsky's diene (**2a**) (32.2 mg, 0.15 mmol) in CH_2Cl_2 (0.1 mL) was added to the mixture dropwise at –20 °C. After stirring for 24 h at this temperature, a 10% solution of trifluoroacetic acid in CH_2Cl_2 (ca. 0.1 mL) was added and the mixture was stirred for an additional 2 h. The reaction was quenched with saturated $NaHCO_3$, and then the whole was extracted with AcOEt. The organic extracts were washed with water and brine, and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product, which was passed through silica gel short column (eluent: 1:4 hexane/Et_2O) and evaporated. The product was analyzed by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. The enantiomer excess was determined by HPLC with a CHIRALPACK IB column (96:4 *n*-hecane/^{i}PrOH, 1.0 mL/min) after preparative TLC purification (eluent: 1:2 hexane/Et_2O).

Typical procedure for isolated scale of enantioselective hetero-Diels–Alder reactions with Danishefsky's diene: (*S*)-2-((benzyloxy)methyl)-2,3-dihydro4*H*-pyran-4-one (*ent*-108) (TS14071a)[71)]



To a solution of benzyloxyacetoaldehyde (**109**) (45.2 mg, 0.30 mmol) in CH_2Cl_2 (0.3 mL) was added *cis*-Ru_2(*S*-BPTPI)$_4$Cl (**186-Cl**) (4.23 mg, 0.003 mmol, 1 mol %). A solution of Danishefsky's diene (**2a**) (96.5 mg, 0.45 mmol) in CH_2Cl_2 (0.3 mL) was added to the mixture dropwise at –20 °C. After stirring for 24 h at this temperature, a 10% solution of trifluoroacetic acid in CH_2Cl_2 (ca. 0.1 mL) was added and the mixture was stirred for an additional 2 h. The reaction was quenched with saturated $NaHCO_3$ (3 mL), and then the whole was extracted with AcOEt (2 ×10 mL). The organic extracts were washed with water (3 mL) and brine (3 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product, which was passed through silica gel short column (eluent: 1:4 hexane/Et_2O) and evaporated. The product was purified by flash column chromatography (silica gel, 5:1 *n*-hexane/AcOEc) to give ***ent*-108** (58.9 mg, 90%) as a colorless oil: Analytical data was corresponded with reported data.[@)] The enantiomer excess of ***ent*-108** was determined to be 91% by HPLC with a CHIRALPACK IB column (96:4 *n*-hecane/^{i}PrOH, 1.0 mL/min): t_R (major) = 14.3 min for (*S*)-enantiomer; t_R (minor) = 15.6 min for (*R*)-enantiomer.

(*S*)-2-((benzyloxy)methyl)-2,3-dihydro4*H*-pyran-4-one (108) (TS14071b)[71)]

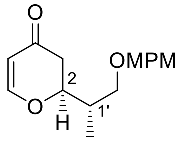


According to the typical procedure for isolated scale of enantioselective hetero-Diels–Alder reaction, **108** was prepared from diene **2a** (96.5 mg, 0.45 mmol), aldehyde **109** (45.2 mg, 0.30 mmol) and *cis*-Ru_2(*R*-BPTPI)$_4$Cl (**203-Cl**) (4.23 mg, 0.003 mmol, 1 mol %). The crude product was passed through silica gel short column (eluent: 1:4 hexane/Et_2O) and evaporated. Purifying by flash column chromatography (silica gel, 5:1 *n*-hexane/AcOEt) afforded **108** (56.6 mg, 86%) as a pale-yellow oil: Analytical data was corresponded with Part 1 Chapter 3 Section 2 data. The enantiomer excess of **108** was determined to be 91% by HPLC with a CHIRALPACK IB column (96:4 *n*-hecane/^{i}PrOH, 1.0 mL/min): t_R (major) = 16.0 min for (*S*)-enantiomer; t_R (minor) = 14.8 min for (*R*)-enantiomer.

General procedure for optimization of reaction conditions of diastereoselective hetero-Diels–Alder reactions with Rawal's diene: (*S*)-2-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-2,3-dihydro-4*H*-pyran-4-one (112b-A)[20d]

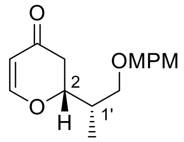
Rawal’s diene (**3a**) (23.4. mg, 0.103 mmol) was added via syringe to a solution of aldehyde **113b** (20.8 mg, 0.10 mmol) and *mer*-Ru_2(*S*-BPTPI)$_4$Cl (**187-Cl**) (1.41 mg, 0.001 mmol, 1 mol %) in CH_2Cl_2 (0.2 mL) at 0 °C. After stirring for 2 h at this temperature, the whole mixture was cooled to –78 °C, and treated dropwise with 1 M solution of AcCl in CH_2Cl_2 (0.20 mL, 0.20 mmol). After stirring for 2 h, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with AcOEt . The combined organic extracts were washed with water and brine, and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product, which was passed through silica gel short column (eluent: 1:4 hexane/Et_2O) and evaporated. The product was analyzed by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. The diastereomeric ratio of **112b-A** was finely determined by ^{1}H NMR analysis after preparative TLC purification.

Typical procedure for isolated scale of diastereoselective hetero-Diels–Alder reactions with Rawal's diene: (*S*)-2-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-2,3-dihydro-4*H*-pyran-4-one (112b-A)[20d)] (TS14074a)



Rawal’s diene (**3a**) (70.3 mg, 0.309 mmol) was added via syringe to a solution of aldehyde **113b** (62.5 mg, 0.30 mmol) and *mer*-Ru_2(*S*-BPTPI)$_4$Cl (**187-Cl**) (4.23 mg, 0.003 mmol, 1 mol %) in CH_2Cl_2 (0.6 mL) at 0 °C. After stirring for 2 h at this temperature, the whole mixture was cooled to –78 °C, and treated dropwise with 1 M solution of AcCl in CH_2Cl_2 (0.60 mL, 0.60 mmol). After stirring for 2 h, the reaction was quenched with saturated aqueous $NaHCO_3$ (3 mL) and extracted with AcOEt (2×10 mL). The combined organic extracts were washed with water (3 mL) and brine (3 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product, which was passed through silica gel short column (eluent: 1:4 hexane/Et_2O) and evaporated. The product was purified by flash column chromatography (silica gel, 4:1 *n*-hexane/AcOEt) to give **112b-A** (67.6 mg, 82%) as a pale-yellow oil: Analytical data was corresponded with Part 1 Chapter 2 Section 1 data. The diastereomeric ratio of **112b-A** was determined to be (2*S*,1'*S*)/(2*R*,1'*S*) = 98:2 by ^{1}H NMR analysis.

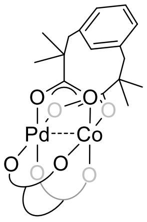
(*R*)-2-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-2,3-dihydro-4*H*-pyran-4-one (112b-B)$^{20d)}$ (TS10008)



According to the typical procedure for isolated scale of diastereoselective hetero-Diels–Alder reaction, **112b-B** was prepared from diene **3a** (70.3 mg, 0.309 mmol), aldehyde **113b** (62.5 mg, 0.30 mmol) and *mer*-Ru_2(*R*-BPTPI)$_4$Cl (**204-Cl**) (4.23 mg, 0.003 mmol, 1 mol %). The crude product was passed through silica gel short column (eluent: 1:4 hexane/Et_2O) and evaporated. Purifying by flash column chromatography (silica gel, 4:1 *n*-hexane/AcOEt) afforded **112b-B** (68.5 mg, 83%) as a pale-yellow oil: Analytical data was corresponded with Part 1 Chapter 2 Section 1 data. The diastereomeric ratio of **112b-B** was determined to be (2*R*,1'*S*)/(2*S*,1'*S*) = >98:2 by ^{1}H NMR analysis.

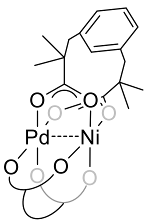
Part 2 Chapter 2 Section 2

Bis[(α,α,α',α'-tetramethyl-1,3-benzenedipropionic acid)] (cobalt) palladium (247) (TS10068)



A mixture of PdCo(OAc)$_4$(**232**)66k,66o) (177 mg, 0.40 mmol) and α,α,α',α'-tetramethyl-1,3-benzenedipropionic aci70) (111.5 mg, 0.40 mmol) in 20 mL of chlorobenzene was heated at 70 °C with vigorous stirring under Ar for 1 h. A second portion of α,α,α',α'-tetramethyl-1,3-benzenedipropionic acid (111.5 mg, 0.40 mmol) was added. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and evaporated *in vacuo*. Chromatography (silica gel, 1:1 hexane/AcOEt) afforded PdCo(esp)$_2$(**247**) (335 mg, >99%) as a dark brown solid: $R_f = 0.58$ (1:1 hexane/AcOEt); IR (KBr) 2985, 2970, 2952, 2939, 2919, 2867, 1594, 1472, 1400, 1374, 359, 1261, 1242, 708, 634 cm^{-1}; ESI-HRMS *m/z* calcd for $C_{35}H_{46}O_9RCoPdNa$ (M+acetone+Na)$^+$ 798.14199, found 798.14239. Isotopic peaks indicate bimetallic palladium-cobalt core. Single crystal suitable for X-ray crystallography was obtained by bellow procedure: PdCo(esp)$_2$ was put into a micro test tube and dissolved in acetone. Then, the test tube was equipped with cap having a hole and stored in screw cap vial quarterly filled with *n*-pentane. *n*-Pentane was diffused to the solution slowly and it afforded single crystal of PdCo(esp)$_2$ as block.

Bis[(α,α,α',α'-tetramethyl-1,3-benzenedipropionic acid)] (nickel) palladium (248) (TS07061)



A mixture of PdNi(OAc)$_4$(**233**)66k,66o) (162 mg, 0.366 mmol) and α,α,α',α'-tetramethyl-1,3-benzenedipropionic acid70) (102 mg, 0.366 mmol) in 18 mL of chlorobenzene was heated at 70 °C with vigorous stirring under Ar for 1 h. A second portion of α,α,α',α'-tetramethyl-1,3-benzenedipropionic acid (102 mg, 0.366 mmol) was added. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and evaporated *in vacuo*. Chromatography (silica gel, 4:1 hexane/AcOEt) afforded PdNi(esp)$_2$(**248**) (264 mg, >99%) as a yellowish brown solid: $R_f = 0.74$ (1:1 hexane/AcOEt); IR (KBr) 2983, 2970, 2952, 2939, 2920, 2867, 1594, 1473, 1402, 1375, 1359, 1262, 1243, 708, 634 cm^{-1}; ESI-HRMS *m/z* calcd for $C_{35}H_{46}O_9RNiPdNa$ (M+acetone+Na)$^+$ 799.14234, found 799.14176. Isotopic peaks indicate bimetallic palladium-nickel core. Single crystal suitable for X-ray crystallography was obtained by bellow procedure: PdNi(esp)$_2$ was put into a micro test tube and dissolved in acetone. Then, the test tube was equipped with cap having a hole and stored in screw cap vial quarterly filled with *n*-pentane. *n*-Pentane was diffused to the solution slowly and it afforded single crystal of PdNi(esp)$_2$ as block.

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X 線結晶構造解析データ

Rh_2(*S*-BPTPI)$_4$·2DMF

Figure 27. Full ortep plot (up) and stereoview of one dirhodium(II) molecule (down).

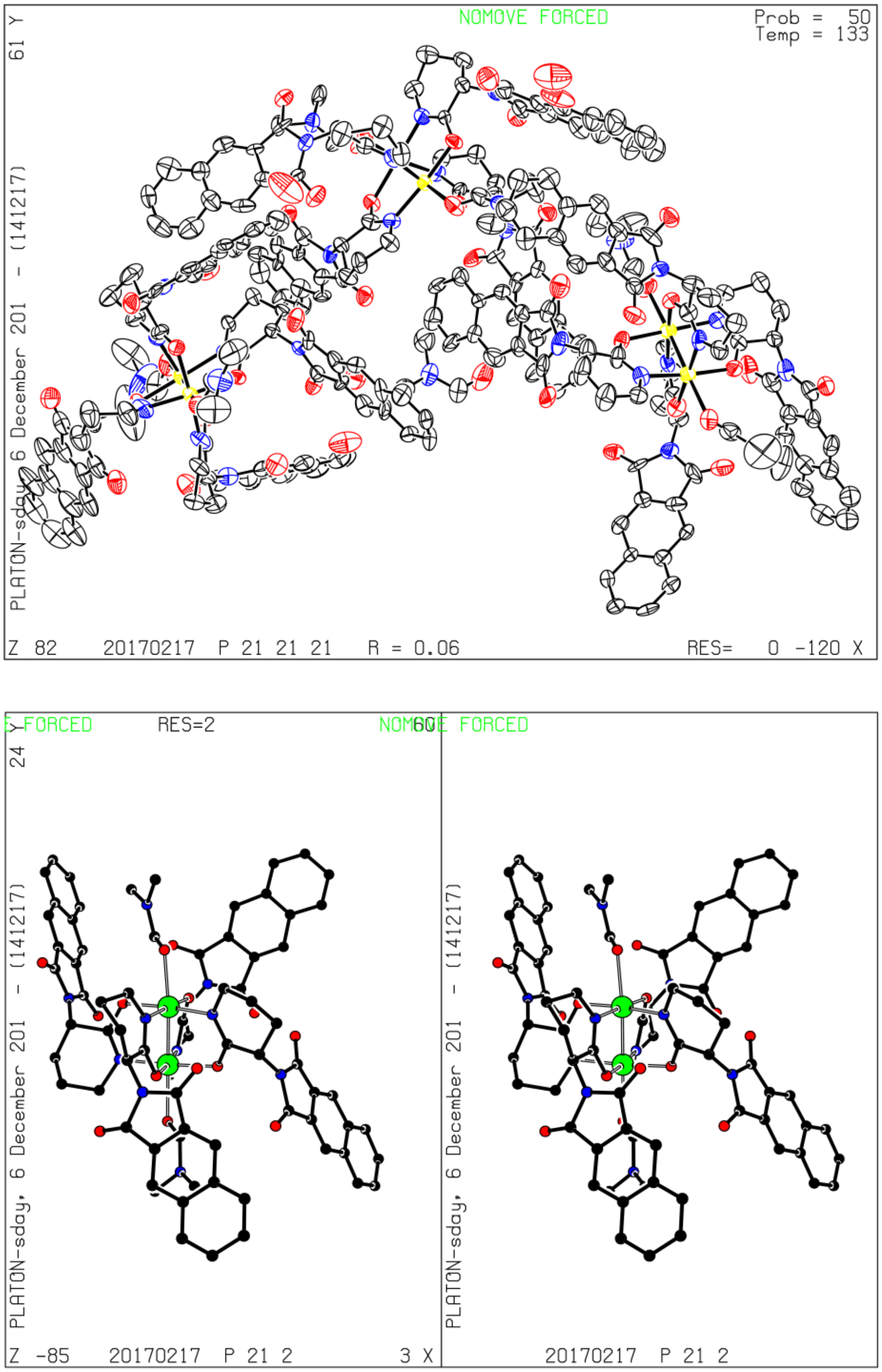

Table 1. Crystal data and structure refinement for Rh2(S-BPTPI)4.

Identification code	20170217	
Empirical formula	C224.50 H203.50 N31 O47 Rh6	
Formula weight	4705.13	
Temperature	133.15(2) K	
Wavelength	1.54187 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 15.0273(3) Å	α= 90°.
	b = 33.1425(6) Å	β= 90°.
	c = 55.0922(10) Å	γ = 90°.
Volume	27438.2(9) Å^3	
Z	4	
Density (calculated)	1.139 Mg/m^3	
Absorption coefficient	3.408 mm^{-1}	
F(000)	9654	
Crystal size	0.158 x 0.142 x 0.065 mm^3	
Theta range for data collection	3.048 to 68.214°.	
Index ranges	-18<=h<=18, -39<=k<=39, -65<=l<=66	
Reflections collected	310404	
Independent reflections	50012 [R(int) = 0.0589]	
Completeness to theta = 67.687°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.6692	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	50012 / 2059 / 2662	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0624, wR2 = 0.1504	
R indices (all data)	R1 = 0.0828, wR2 = 0.1597	
Absolute structure parameter	0.083(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.797 and -0.456 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Rh2(S-BPTPI)4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	1747(1)	5689(1)	6111(1)	39(1)
Rh(2)	-1406(1)	5282(1)	3980(1)	36(1)
Rh(3)	-2868(1)	5434(1)	4129(1)	36(1)
Rh(4)	3300(1)	5760(1)	6031(1)	38(1)
Rh(5)	3154(1)	2102(1)	3097(1)	45(1)
Rh(6)	1745(1)	2438(1)	3092(1)	45(1)
O(18)	-1792(5)	4398(2)	4922(1)	56(2)
O(19)	-2697(5)	5706(2)	5015(1)	53(2)
O(34)	2363(4)	4710(2)	5347(1)	50(2)
O(35)	3639(5)	5849(2)	5028(1)	64(2)
O(57)	1293(6)	4318(3)	6656(1)	81(2)
O(58)	2737(4)	4191(2)	5931(1)	63(2)
O(59)	1975(4)	5085(2)	6172(1)	44(2)
O(62)	-2484(4)	5231(2)	4464(1)	41(2)
O(64)	3097(4)	5543(2)	5688(1)	39(1)
O(72)	2642(4)	1717(2)	3363(1)	54(2)
O(73)	1746(4)	1510(2)	4018(1)	55(2)
O(74)	2730(5)	709(2)	3400(2)	72(2)
O(98)	2881(5)	847(2)	2385(1)	70(2)
O(99)	632(6)	1140(3)	2912(2)	89(3)
O(100)	2640(5)	1702(2)	2841(1)	53(2)
O(114)	2092(6)	3846(3)	3462(2)	78(2)
O(122)	2159(5)	3781(2)	2483(1)	69(2)
O(130)	2314(5)	2875(2)	2884(1)	55(2)
O(142)	-2851(5)	3748(2)	4181(1)	66(2)
O(143)	-1556(5)	3971(2)	3436(1)	64(2)
O(146)	-1835(4)	4690(2)	3923(1)	40(1)
O(158)	2936(5)	2890(3)	4029(2)	87(3)
O(170)	-406(5)	6190(2)	4593(2)	71(2)
O(171)	-2763(4)	7016(2)	4458(1)	52(2)
O(176)	-2347(4)	5997(2)	4234(1)	49(2)

O(191)	-1261(7)	5984(3)	3081(2)	96(3)
O(192)	-3101(6)	4937(2)	3241(1)	72(2)
O(193)	-1854(4)	5415(2)	3637(1)	46(2)
O(200)	2001(5)	5792(2)	6476(1)	48(2)
O(206)	1169(7)	6339(3)	7011(2)	91(3)
O(207)	3083(6)	5306(3)	6911(1)	74(2)
O(223)	1816(6)	6677(2)	5417(2)	71(2)
O(224)	3884(6)	7361(2)	5863(1)	70(2)
O(227)	3027(5)	6330(2)	5894(1)	52(2)
O(231)	4399(5)	3445(3)	3009(1)	74(2)
O(247)	2150(4)	2776(2)	3378(1)	45(2)
O(271)	4758(5)	5888(2)	5927(1)	57(2)
O(276)	275(5)	5613(3)	6228(2)	70(2)
O(279)	4479(5)	1727(3)	3102(1)	61(2)
O(288)	-4230(4)	5619(2)	4307(1)	59(2)
O(291)	475(5)	2800(3)	3096(2)	69(2)
O(292)	-50(4)	5090(2)	3824(1)	59(2)
O(305)	-1977(8)	2554(3)	4670(2)	122(4)
O(306)	-3043(6)	3296(3)	5476(2)	83(2)
O(307)	2562(6)	3869(3)	5443(2)	108(3)
O(308)	1260(16)	5782(16)	2585(4)	122(16)
O(309)	1325(6)	6891(4)	4591(2)	142(5)
N(7)	-2026(5)	5080(2)	4926(1)	40(2)
N(33)	2861(5)	5344(2)	5211(1)	41(2)
N(56)	2200(5)	4320(3)	6313(2)	50(2)
N(60)	3479(5)	5218(3)	6190(1)	51(2)
N(61)	1582(5)	5616(2)	5742(1)	40(2)
N(63)	1647(6)	6289(2)	6062(1)	48(2)
N(65)	-1028(5)	5192(2)	4331(1)	42(2)
N(71)	1290(5)	1977(2)	3298(1)	44(2)
N(75)	2048(5)	1156(3)	3669(2)	52(2)
N(97)	1742(6)	1090(3)	2620(2)	57(2)
N(101)	1451(6)	2111(3)	2786(1)	52(2)
N(115)	2685(6)	3339(3)	3707(2)	66(3)
N(126)	3346(5)	3533(3)	2707(1)	50(2)
N(129)	3539(5)	2483(3)	2828(1)	52(2)

N(141)	-2365(6)	3937(3)	3811(2)	60(2)
N(145)	-3276(4)	4881(2)	4001(1)	39(2)
N(172)	-1518(5)	6624(2)	4463(1)	43(2)
N(175)	-1119(5)	5861(2)	4016(1)	45(2)
N(182)	-3161(5)	5655(2)	3791(1)	47(2)
N(183)	-2331(6)	5526(3)	3185(1)	55(2)
N(198)	3418(6)	5996(3)	6366(1)	63(2)
N(199)	2298(7)	5897(3)	6944(2)	65(2)
N(211)	2672(7)	7028(3)	5688(2)	58(2)
N(246)	3562(5)	2534(3)	3342(1)	46(2)
N(272)	5557(7)	6180(3)	5620(2)	80(3)
N(277)	-608(15)	5378(5)	6538(3)	209(11)
N(278)	4750(6)	1101(3)	2955(2)	75(3)
N(287)	-4648(6)	6115(3)	4563(2)	54(2)
N(290)	663(6)	4896(3)	3492(2)	74(3)
N(294)	47(7)	3448(4)	3040(2)	85(3)
N(304)	-1625(6)	3062(3)	4936(2)	62(2)
C(8)	-2666(6)	5351(4)	5038(2)	48(3)
C(9)	-2221(7)	4681(3)	4993(2)	48(3)
C(10)	-2947(6)	4695(3)	5159(2)	43(2)
C(11)	-4141(3)	4471(2)	5428(1)	53(3)
C(15)	-4456(4)	4864(2)	5447(1)	38(2)
C(14)	-5220(4)	4944(2)	5580(1)	53(3)
C(13)	-5670(3)	4632(2)	5695(1)	63(3)
C(41)	-5356(4)	4239(2)	5676(1)	61(3)
C(12)	-4592(4)	4158(2)	5543(1)	59(3)
C(16)	-3974(6)	5174(3)	5330(2)	39(2)
C(17)	-3243(7)	5074(3)	5192(1)	43(2)
C(20)	-1363(6)	5240(3)	4768(1)	38(2)
C(21)	-1639(6)	5207(3)	4502(2)	47(2)
C(22)	4753(5)	5124(3)	4824(2)	42(2)
C(23)	-80(6)	5175(4)	4379(2)	52(2)
C(24)	192(7)	5244(4)	4634(2)	58(3)
C(26)	3997(7)	4442(4)	5040(2)	60(3)
C(27)	5110(4)	4022(2)	4843(1)	48(3)
C(25)	4771(3)	4406(2)	4884(1)	58(3)

C(43)	5170(3)	4739(2)	4777(1)	46(3)
C(28)	5909(4)	4689(2)	4628(1)	71(4)
C(42)	6248(3)	4305(2)	4587(1)	49(3)
C(210)	5848(3)	3971(2)	4694(1)	61(3)
C(29)	3653(6)	4796(2)	5082(2)	33(2)
C(30)	4023(6)	5154(4)	4980(2)	59(3)
C(31)	3516(5)	5496(3)	5066(2)	37(2)
C(32)	2871(6)	4916(3)	5231(2)	46(2)
C(36)	1250(6)	5512(3)	5239(2)	48(2)
C(37)	2185(6)	5593(3)	5325(1)	36(2)
C(38)	2275(6)	5591(3)	5608(1)	35(2)
C(39)	669(6)	5682(3)	5654(1)	43(2)
C(40)	635(6)	5781(3)	5378(2)	48(2)
C(44)	2753(7)	5000(3)	6233(2)	49(2)
C(45)	2824(7)	4606(3)	6391(2)	53(2)
C(46)	4365(6)	5117(3)	6265(2)	51(2)
C(47)	4404(7)	4776(3)	6468(2)	55(3)
C(48)	2168(6)	4129(3)	6077(2)	48(2)
C(49)	1417(8)	4178(4)	6449(2)	64(3)
C(50)	977(7)	3884(3)	6300(2)	53(2)
C(51)	1395(6)	3876(3)	6073(2)	49(2)
C(52)	1067(7)	3636(3)	5899(2)	54(2)
C(53)	289(4)	3393(2)	5942(1)	56(2)
C(228)	-135(4)	3419(2)	6166(1)	63(3)
C(249)	-919(4)	3207(2)	6206(1)	61(3)
C(150)	-1280(4)	2969(2)	6023(2)	77(3)
C(149)	-856(5)	2944(2)	5799(1)	76(3)
C(54)	-72(5)	3156(2)	5759(1)	68(3)
C(55)	248(7)	3667(3)	6348(2)	57(3)
C(66)	232(6)	1931(3)	3314(2)	55(3)
C(67)	-99(7)	1552(4)	3426(2)	62(3)
C(68)	485(7)	1386(4)	3612(2)	59(3)
C(69)	1482(6)	1319(3)	3499(2)	53(2)
C(70)	1810(6)	1693(3)	3381(2)	43(2)
C(76)	2660(9)	853(4)	3600(2)	70(4)
C(77)	3231(7)	769(3)	3812(2)	60(3)

C(78)	2940(6)	1013(3)	4000(2)	46(2)
C(79)	2162(7)	1264(3)	3914(2)	53(3)
C(80)	4008(6)	546(3)	3835(2)	39(2)
C(81)	3325(6)	990(3)	4229(2)	51(2)
C(84)	4077(3)	739(2)	4263(1)	50(3)
C(83)	4464(4)	542(2)	4067(1)	49(3)
C(82)	5280(4)	350(2)	4094(1)	50(3)
C(240)	5709(3)	355(2)	4318(1)	55(3)
C(86)	5321(4)	553(2)	4514(1)	51(3)
C(85)	4505(4)	745(1)	4486(1)	54(3)
C(87)	-3370(6)	4386(3)	5284(1)	42(2)
C(88)	1940(7)	1799(3)	2737(2)	50(2)
C(89)	1689(7)	1510(3)	2533(2)	56(2)
C(90)	781(9)	1581(4)	2425(2)	83(3)
C(91)	2178(7)	440(4)	2677(2)	56(2)
C(92)	2539(7)	68(3)	2681(2)	63(3)
C(95)	2321(6)	799(4)	2544(2)	52(3)
C(96)	1200(7)	944(4)	2805(2)	59(3)
C(102)	640(9)	2181(4)	2661(2)	71(3)
C(104)	2078(7)	3659(3)	3657(2)	54(3)
C(105)	1516(6)	3708(3)	3858(2)	51(2)
C(106)	1745(7)	3420(3)	4031(2)	66(3)
C(107)	1329(8)	3392(4)	4255(2)	79(3)
C(108)	578(4)	3647(2)	4307(1)	63(3)
C(109)	345(4)	3931(2)	4132(1)	47(2)
C(111)	-380(5)	4183(2)	4170(1)	58(3)
C(112)	-872(4)	4153(2)	4383(1)	64(3)
C(113)	-640(5)	3869(2)	4557(1)	87(3)
C(156)	86(6)	3617(2)	4519(1)	76(3)
C(110)	837(6)	3955(3)	3917(2)	51(2)
C(120)	2864(5)	4837(2)	2960(1)	62(3)
C(103)	3525(5)	4735(2)	3126(1)	59(2)
C(117)	3859(5)	5026(3)	3284(1)	77(3)
C(116)	3533(5)	5418(2)	3275(1)	79(3)
C(118)	2873(5)	5520(2)	3109(2)	74(3)
C(119)	2538(4)	5229(2)	2952(1)	74(3)

C(121)	2476(7)	4541(3)	2796(2)	56(2)
C(123)	2697(7)	3821(4)	2645(2)	59(3)
C(124)	3592(7)	4081(4)	2960(2)	58(3)
C(127)	3090(7)	2779(3)	2784(2)	50(2)
C(128)	3380(7)	3112(4)	2596(2)	65(3)
C(131)	-435(6)	5040(3)	4816(2)	50(2)
C(132)	-2702(5)	4649(3)	3914(2)	38(2)
C(133)	-2960(7)	4281(3)	3756(2)	50(2)
C(134)	-2370(6)	3704(3)	4016(2)	42(2)
C(135)	-1621(6)	3415(3)	3976(2)	50(2)
C(136)	-1219(7)	3486(3)	3754(2)	46(2)
C(137)	-1717(6)	3811(3)	3644(2)	44(2)
C(138)	-533(6)	3255(3)	3682(2)	49(2)
C(139)	-210(4)	2938(2)	3832(1)	56(2)
C(151)	-600(4)	2864(2)	4056(1)	58(2)
C(268)	-244(5)	2571(2)	4209(1)	79(3)
C(152)	503(5)	2354(2)	4137(1)	71(3)
C(235)	893(4)	2429(2)	3913(1)	67(3)
C(140)	537(4)	2721(2)	3760(1)	66(3)
C(144)	-1317(7)	3111(3)	4130(2)	61(3)
C(147)	-4224(5)	4803(3)	3976(2)	48(2)
C(148)	-4448(6)	4536(3)	3771(2)	56(2)
C(153)	1198(8)	240(3)	3002(2)	68(3)
C(154)	1565(5)	-157(2)	3003(2)	69(3)
C(264)	1249(5)	-455(3)	3158(1)	78(3)
C(254)	1604(6)	-842(2)	3148(2)	89(3)
C(238)	2276(6)	-930(2)	2983(2)	96(4)
C(302)	2592(5)	-632(3)	2828(1)	84(3)
C(93)	2236(5)	-245(2)	2838(1)	71(3)
C(155)	-555(17)	5184(8)	6760(4)	260(20)
C(157)	2530(7)	3192(4)	3927(2)	71(3)
C(159)	4345(7)	2390(4)	2703(2)	62(3)
C(160)	4451(8)	2584(4)	2464(2)	69(3)
C(161)	-2186(7)	6847(3)	4565(2)	51(3)
C(162)	-1023(6)	6430(3)	4641(2)	41(2)
C(163)	-1327(7)	6573(3)	4868(2)	57(3)

C(164)	-1019(8)	6512(3)	5103(2)	67(3)
C(165)	-1467(5)	6719(2)	5292(1)	72(4)
C(166)	-2190(5)	6975(2)	5260(1)	55(3)
C(168)	-2599(4)	7151(2)	5460(1)	85(4)
C(236)	-2286(6)	7071(2)	5692(1)	69(3)
C(169)	-1563(6)	6815(2)	5725(1)	83(4)
C(258)	-1154(5)	6639(2)	5525(2)	88(4)
C(167)	-2508(7)	7015(3)	5017(2)	58(3)
C(173)	-1383(6)	6544(3)	4200(2)	49(2)
C(174)	-1631(6)	6106(3)	4149(2)	42(2)
C(177)	-2768(7)	5778(4)	3371(2)	55(2)
C(178)	-2617(6)	5588(3)	3628(2)	41(2)
C(179)	-4035(8)	5830(3)	3767(2)	68(3)
C(180)	-4177(9)	6079(4)	3525(2)	84(3)
C(181)	-3785(7)	5827(4)	3321(2)	60(3)
C(184)	-2515(7)	5123(4)	3143(2)	56(2)
C(185)	-1881(5)	4990(2)	2962(1)	67(3)
C(186)	-1286(5)	5302(2)	2917(1)	61(2)
C(187)	-1605(9)	5656(4)	3067(2)	69(3)
C(188)	-608(5)	5250(2)	2748(2)	82(3)
C(190)	179(4)	4827(2)	2464(1)	102(4)
C(256)	-514(4)	4883(2)	2628(1)	89(3)
C(189)	-1079(4)	4564(2)	2684(1)	93(3)
C(255)	-951(5)	4189(2)	2576(1)	108(4)
C(125)	-258(6)	4134(2)	2412(1)	108(4)
C(94)	307(5)	4453(2)	2356(1)	103(4)
C(194)	2750(8)	5961(3)	6513(2)	54(3)
C(195)	4155(9)	6220(4)	6420(2)	80(3)
C(196)	4160(10)	6506(4)	6641(2)	88(3)
C(197)	3776(9)	6230(4)	6845(2)	85(3)
C(201)	2476(9)	5506(4)	6994(2)	65(3)
C(202)	1452(10)	6036(5)	7052(2)	73(3)
C(203)	1220(7)	5675(4)	7202(2)	70(3)
C(204)	504(8)	5648(4)	7365(2)	87(3)
C(205)	1683(9)	4992(4)	7281(2)	78(3)
C(208)	381(5)	5277(2)	7486(1)	86(3)

C(209)	960(4)	4957(3)	7446(1)	88(3)
C(301)	851(5)	4597(2)	7572(1)	91(4)
C(239)	162(5)	4557(3)	7739(1)	113(4)
C(266)	-417(4)	4878(3)	7779(1)	105(4)
C(265)	-308(5)	5237(3)	7653(1)	100(4)
C(212)	3498(9)	7229(3)	5693(2)	61(3)
C(213)	3763(4)	7257(2)	5423(1)	48(3)
C(214)	4480(4)	7429(2)	5302(1)	63(3)
C(219)	3904(3)	7182(2)	4922(1)	51(3)
C(215)	4534(3)	7403(1)	5050(1)	54(3)
C(216)	5240(3)	7582(2)	4928(1)	55(3)
C(217)	5315(4)	7540(2)	4678(1)	55(3)
C(300)	4685(4)	7319(1)	4550(1)	82(4)
C(218)	3979(4)	7140(2)	4672(1)	52(3)
C(220)	3196(4)	7003(2)	5044(1)	46(2)
C(221)	3137(4)	7033(2)	5295(1)	49(2)
C(222)	2466(7)	6879(3)	5469(2)	45(2)
C(225)	2258(8)	6941(3)	5911(2)	66(3)
C(226)	2288(8)	6472(3)	5965(2)	52(2)
C(229)	3893(8)	4350(3)	3121(2)	66(3)
C(230)	3835(7)	3646(4)	2904(2)	54(3)
C(232)	2868(7)	4170(4)	2798(2)	60(3)
C(233)	623(10)	2019(4)	2407(2)	89(4)
C(234)	1489(7)	516(4)	2845(2)	60(3)
C(237)	1806(8)	5363(4)	7162(2)	67(3)
C(241)	3005(7)	2805(3)	3422(2)	56(3)
C(242)	4837(8)	2853(4)	3552(3)	93(4)
C(243)	4297(8)	3208(4)	3593(3)	91(4)
C(244)	3348(7)	3174(4)	3540(2)	74(3)
C(245)	4563(7)	2561(4)	3378(2)	61(3)
C(248)	4295(8)	3044(4)	2501(2)	72(3)
C(250)	1227(10)	7103(4)	5919(3)	87(3)
C(251)	808(8)	6491(3)	6149(2)	62(3)
C(252)	899(9)	6955(3)	6172(2)	78(3)
C(253)	-1315(18)	5660(15)	6523(6)	190(30)
C(257)	-1776(5)	4620(2)	2846(2)	77(3)

C(259)	-2074(6)	6819(3)	4830(2)	38(2)
C(260)	-322(8)	6468(4)	3857(2)	70(3)
C(261)	-439(8)	6673(4)	4131(2)	77(3)
C(262)	-339(6)	6014(3)	3887(2)	56(3)
C(263)	3782(8)	4453(4)	6404(2)	68(3)
C(267)	2824(10)	6127(4)	6760(2)	81(3)
C(269)	-3989(6)	4165(3)	3767(2)	57(3)
C(270)	4814(8)	6039(4)	5724(2)	64(3)
C(273)	5639(12)	6410(5)	5395(3)	129(6)
C(274)	6441(9)	6097(6)	5735(3)	129(6)
C(275)	194(10)	5436(5)	6409(3)	95(5)
C(280)	4228(8)	1374(5)	3062(2)	71(3)
C(281)	5619(8)	1206(7)	2871(4)	166(9)
C(282)	4478(11)	683(5)	2907(3)	128(7)
C(283)	-4045(6)	5852(3)	4481(2)	51(3)
C(284)	-4438(7)	6390(3)	4756(2)	60(3)
C(285)	-5502(7)	6172(4)	4453(2)	77(4)
C(286)	-2529(9)	3286(4)	4859(2)	88(4)
C(289)	655(9)	3151(5)	3071(3)	85(3)
C(293)	-106(8)	4968(4)	3629(2)	70(3)
C(295)	-876(10)	3331(6)	2980(4)	160(7)
C(296)	261(11)	3854(5)	3065(3)	114(5)
C(297)	1529(8)	4949(5)	3586(3)	96(4)
C(298)	556(11)	4807(6)	3231(2)	128(6)
C(299)	-1064(8)	3215(4)	5111(2)	76(4)
C(303)	-1440(8)	2703(4)	4836(2)	71(4)
O(3)	1467(17)	6098(17)	2493(10)	150(20)

Table 3. Bond lengths [Å] and angles [°] for Rh2(S-BPTPI)4.

Rh(1)-Rh(4)	2.3852(10)
Rh(1)-O(59)	2.057(6)
Rh(1)-O(200)	2.075(6)
Rh(1)-O(276)	2.319(7)
Rh(1)-N(61)	2.060(7)
Rh(1)-N(63)	2.014(8)
Rh(2)-Rh(3)	2.3988(9)
Rh(2)-O(146)	2.089(6)
Rh(2)-O(193)	2.058(5)
Rh(2)-O(292)	2.303(6)
Rh(2)-N(65)	2.036(7)
Rh(2)-N(175)	1.976(8)
Rh(3)-O(62)	2.049(6)
Rh(3)-O(176)	2.103(7)
Rh(3)-O(288)	2.350(6)
Rh(3)-N(145)	2.059(7)
Rh(3)-N(182)	2.048(7)
Rh(4)-O(64)	2.044(6)
Rh(4)-O(227)	2.077(6)
Rh(4)-O(271)	2.304(7)
Rh(4)-N(60)	2.016(8)
Rh(4)-N(198)	2.012(9)
Rh(5)-Rh(6)	2.3926(10)
Rh(5)-O(72)	2.088(7)
Rh(5)-O(100)	2.086(7)
Rh(5)-O(279)	2.349(8)
Rh(5)-N(129)	2.035(9)
Rh(5)-N(246)	2.059(8)
Rh(6)-O(130)	2.036(7)
Rh(6)-O(247)	2.027(6)
Rh(6)-O(291)	2.254(7)
Rh(6)-N(71)	2.024(8)
Rh(6)-N(101)	2.051(8)
O(18)-C(9)	1.204(11)
O(19)-C(8)	1.184(11)
O(34)-C(32)	1.205(11)
O(35)-C(31)	1.203(10)
O(57)-C(49)	1.240(13)
O(58)-C(48)	1.192(10)
O(59)-C(44)	1.248(11)
O(62)-C(21)	1.289(11)
O(64)-C(38)	1.322(10)
O(72)-C(70)	1.257(11)
O(73)-C(79)	1.176(11)
O(74)-C(76)	1.202(12)
O(98)-C(95)	1.222(11)
O(99)-C(96)	1.224(13)
O(100)-C(88)	1.239(11)
O(114)-C(104)	1.243(13)
O(122)-C(123)	1.212(11)
O(130)-C(127)	1.327(11)
O(142)-C(134)	1.173(11)
O(143)-C(137)	1.287(11)
O(146)-C(132)	1.310(10)
O(158)-C(157)	1.301(14)
O(170)-C(162)	1.249(11)
O(171)-C(161)	1.191(11)
O(176)-C(174)	1.228(10)
O(191)-C(187)	1.206(13)
O(192)-C(184)	1.202(12)
O(193)-C(178)	1.283(11)
O(200)-C(194)	1.275(12)
O(206)-C(202)	1.116(15)
O(207)-C(201)	1.218(14)
O(223)-C(222)	1.218(11)
O(224)-C(212)	1.189(12)
O(227)-C(226)	1.267(12)

O(231)-C(230)	1.225(12)	N(97)-C(96)	1.391(13)
O(247)-C(241)	1.311(12)	N(101)-C(88)	1.298(12)
O(271)-C(270)	1.232(11)	N(101)-C(102)	1.419(13)
O(276)-C(275)	1.164(16)	N(115)-C(104)	1.422(14)
O(279)-C(280)	1.248(14)	N(115)-C(157)	1.328(15)
O(288)-C(283)	1.260(12)	N(115)-C(244)	1.465(13)
O(291)-C(289)	1.203(15)	N(126)-C(123)	1.406(13)
O(292)-C(293)	1.148(12)	N(126)-C(128)	1.523(14)
O(305)-C(303)	1.319(15)	N(126)-C(230)	1.365(12)
N(7)-C(8)	1.455(12)	N(129)-C(127)	1.214(12)
N(7)-C(9)	1.401(12)	N(129)-C(159)	1.428(12)
N(7)-C(20)	1.425(10)	N(141)-C(133)	1.480(12)
N(33)-C(31)	1.365(11)	N(141)-C(134)	1.366(12)
N(33)-C(32)	1.423(12)	N(141)-C(137)	1.402(12)
N(33)-C(37)	1.452(11)	N(145)-C(132)	1.251(10)
N(56)-C(45)	1.400(12)	N(145)-C(147)	1.454(11)
N(56)-C(48)	1.444(12)	N(172)-C(161)	1.368(11)
N(56)-C(49)	1.474(12)	N(172)-C(162)	1.388(11)
N(60)-C(44)	1.330(12)	N(172)-C(173)	1.488(12)
N(60)-C(46)	1.434(12)	N(175)-C(174)	1.338(11)
N(61)-C(38)	1.281(11)	N(175)-C(262)	1.462(11)
N(61)-C(39)	1.472(11)	N(182)-C(178)	1.236(11)
N(63)-C(226)	1.259(13)	N(182)-C(179)	1.443(13)
N(63)-C(251)	1.505(13)	N(183)-C(177)	1.476(12)
N(65)-C(21)	1.318(11)	N(183)-C(184)	1.382(14)
N(65)-C(23)	1.450(11)	N(183)-C(187)	1.340(14)
N(71)-C(66)	1.599(12)	N(198)-C(194)	1.293(13)
N(71)-C(70)	1.305(11)	N(198)-C(195)	1.366(14)
N(75)-C(69)	1.373(12)	N(199)-C(201)	1.351(16)
N(75)-C(76)	1.414(15)	N(199)-C(202)	1.478(17)
N(75)-C(79)	1.408(13)	N(199)-C(267)	1.493(15)
N(97)-C(89)	1.474(13)	N(211)-C(212)	1.409(15)
N(97)-C(95)	1.366(14)	N(211)-C(222)	1.340(12)

N(211)-C(225)	1.406(12)	C(14)-H(14)	0.9500
N(246)-C(241)	1.303(12)	C(14)-C(13)	1.3900
N(246)-C(245)	1.521(12)	C(13)-H(13)	0.9500
N(272)-C(270)	1.338(13)	C(13)-C(41)	1.3900
N(272)-C(273)	1.460(14)	C(41)-H(41)	0.9500
N(272)-C(274)	1.496(15)	C(41)-C(12)	1.3900
N(277)-C(155)	1.39(2)	C(12)-H(12)	0.9500
N(277)-C(253)	1.42(2)	C(16)-H(16)	0.9500
N(277)-C(275)	1.41(2)	C(16)-C(17)	1.376(11)
N(278)-C(280)	1.334(14)	C(20)-H(20)	1.0000
N(278)-C(281)	1.428(14)	C(20)-C(21)	1.527(12)
N(278)-C(282)	1.469(14)	C(20)-C(131)	1.566(13)
N(287)-C(283)	1.336(11)	C(22)-H(22)	0.9500
N(287)-C(284)	1.435(11)	C(22)-C(43)	1.444(10)
N(287)-C(285)	1.431(12)	C(22)-C(30)	1.398(11)
N(290)-C(293)	1.401(13)	C(23)-H(23A)	0.9900
N(290)-C(297)	1.411(14)	C(23)-H(23B)	0.9900
N(290)-C(298)	1.480(13)	C(23)-C(24)	1.483(12)
N(294)-C(289)	1.352(16)	C(24)-H(24A)	0.9900
N(294)-C(295)	1.479(16)	C(24)-H(24B)	0.9900
N(294)-C(296)	1.393(15)	C(24)-C(131)	1.533(13)
N(304)-C(286)	1.604(15)	C(26)-H(26)	0.9500
N(304)-C(299)	1.381(13)	C(26)-C(25)	1.450(10)
N(304)-C(303)	1.337(13)	C(26)-C(29)	1.304(12)
C(8)-C(17)	1.520(13)	C(27)-H(27)	0.9500
C(9)-C(10)	1.425(11)	C(27)-C(25)	1.3900
C(10)-C(17)	1.345(11)	C(27)-C(210)	1.3900
C(10)-C(87)	1.388(11)	C(25)-C(43)	1.3900
C(11)-C(15)	1.3900	C(43)-C(28)	1.3900
C(11)-C(12)	1.3900	C(28)-H(28)	0.9500
C(11)-C(87)	1.434(9)	C(28)-C(42)	1.3900
C(15)-C(14)	1.3900	C(42)-H(42)	0.9500
C(15)-C(16)	1.413(10)	C(42)-C(210)	1.3900

C(210)-H(210)	0.9500	C(228)-C(249)	1.3900
C(29)-C(30)	1.427(12)	C(228)-C(55)	1.419(11)
C(29)-C(32)	1.487(12)	C(249)-H(249)	0.9500
C(30)-C(31)	1.445(13)	C(249)-C(150)	1.3900
C(36)-H(36A)	0.9900	C(150)-H(150)	0.9500
C(36)-H(36B)	0.9900	C(150)-C(149)	1.3900
C(36)-C(37)	1.506(12)	C(149)-H(149)	0.9500
C(36)-C(40)	1.495(13)	C(149)-C(54)	1.3900
C(37)-H(37)	1.0000	C(54)-H(54)	0.9500
C(37)-C(38)	1.563(11)	C(55)-H(55)	0.9500
C(39)-H(39A)	0.9900	C(66)-H(66A)	0.9900
C(39)-H(39B)	0.9900	C(66)-H(66B)	0.9900
C(39)-C(40)	1.557(11)	C(66)-C(67)	1.487(15)
C(40)-H(40A)	0.9900	C(67)-H(67A)	0.9900
C(40)-H(40B)	0.9900	C(67)-H(67B)	0.9900
C(44)-C(45)	1.573(13)	C(67)-C(68)	1.455(14)
C(45)-H(45)	1.0000	C(68)-H(68A)	0.9900
C(45)-C(263)	1.527(15)	C(68)-H(68B)	0.9900
C(46)-H(46A)	0.9900	C(68)-C(69)	1.637(14)
C(46)-H(46B)	0.9900	C(69)-H(69)	1.0000
C(46)-C(47)	1.591(13)	C(69)-C(70)	1.485(14)
C(47)-H(47A)	0.9900	C(76)-C(77)	1.474(14)
C(47)-H(47B)	0.9900	C(77)-C(78)	1.387(13)
C(47)-C(263)	1.463(15)	C(77)-C(80)	1.389(12)
C(48)-C(51)	1.432(14)	C(78)-C(79)	1.512(12)
C(49)-C(50)	1.437(15)	C(78)-C(81)	1.388(12)
C(50)-C(51)	1.398(12)	C(80)-H(80)	0.9500
C(50)-C(55)	1.339(13)	C(80)-C(83)	1.451(9)
C(51)-C(52)	1.340(13)	C(81)-H(81)	0.9500
C(52)-H(52)	0.9500	C(81)-C(84)	1.414(10)
C(52)-C(53)	1.439(10)	C(84)-C(83)	1.3900
C(53)-C(228)	1.3900	C(84)-C(85)	1.3900
C(53)-C(54)	1.3900	C(83)-C(82)	1.3900

C(82)-H(82)	0.9500	C(109)-C(110)	1.398(10)
C(82)-C(240)	1.3900	C(111)-H(111)	0.9500
C(240)-H(240)	0.9500	C(111)-C(112)	1.3900
C(240)-C(86)	1.3900	C(112)-H(112)	0.9500
C(86)-H(86)	0.9500	C(112)-C(113)	1.3900
C(86)-C(85)	1.3900	C(113)-H(113)	0.9500
C(85)-H(85)	0.9500	C(113)-C(156)	1.3900
C(87)-H(87)	0.9500	C(156)-H(156)	0.9500
C(88)-C(89)	1.525(13)	C(110)-H(110)	0.9500
C(89)-H(89)	1.0000	C(120)-C(103)	1.3900
C(89)-C(90)	1.508(15)	C(120)-C(119)	1.3900
C(90)-H(90A)	0.9900	C(120)-C(121)	1.457(11)
C(90)-H(90B)	0.9900	C(103)-C(117)	1.3900
C(90)-C(233)	1.474(17)	C(103)-C(229)	1.391(12)
C(91)-C(92)	1.347(13)	C(117)-H(117)	0.9500
C(91)-C(95)	1.415(15)	C(117)-C(116)	1.3900
C(91)-C(234)	1.412(13)	C(116)-H(116)	0.9500
C(92)-H(92)	0.9500	C(116)-C(118)	1.3900
C(92)-C(93)	1.425(12)	C(118)-H(118)	0.9500
C(96)-C(234)	1.500(16)	C(118)-C(119)	1.3900
C(102)-H(10A)	0.9900	C(119)-H(119)	0.9500
C(102)-H(10B)	0.9900	C(121)-H(121)	0.9500
C(102)-C(233)	1.500(15)	C(121)-C(232)	1.363(13)
C(104)-C(105)	1.403(14)	C(123)-C(232)	1.455(15)
C(105)-C(106)	1.391(13)	C(124)-C(229)	1.335(13)
C(105)-C(110)	1.349(12)	C(124)-C(230)	1.519(15)
C(106)-C(107)	1.386(13)	C(124)-C(232)	1.438(13)
C(106)-C(157)	1.513(14)	C(127)-C(128)	1.574(14)
C(107)-H(107)	0.9500	C(128)-H(128)	1.0000
C(107)-C(108)	1.438(11)	C(128)-C(248)	1.489(15)
C(108)-C(109)	1.3900	C(131)-H(13A)	0.9900
C(108)-C(156)	1.3900	C(131)-H(13B)	0.9900
C(109)-C(111)	1.3900	C(132)-C(133)	1.547(12)

C(133)-H(133)	1.0000	C(264)-C(254)	1.3900
C(133)-C(269)	1.595(14)	C(254)-H(254)	0.9500
C(134)-C(135)	1.494(12)	C(254)-C(238)	1.3900
C(135)-C(136)	1.385(11)	C(238)-H(238)	0.9500
C(135)-C(144)	1.396(12)	C(238)-C(302)	1.3900
C(136)-C(137)	1.443(13)	C(302)-H(302)	0.9500
C(136)-C(138)	1.343(11)	C(302)-C(93)	1.3900
C(138)-H(138)	0.9500	C(155)-H(15A)	0.9800
C(138)-C(139)	1.421(10)	C(155)-H(15B)	0.9800
C(139)-C(151)	1.3900	C(155)-H(15C)	0.9800
C(139)-C(140)	1.3900	C(159)-H(15D)	0.9900
C(151)-C(268)	1.3900	C(159)-H(15E)	0.9900
C(151)-C(144)	1.413(10)	C(159)-C(160)	1.472(14)
C(268)-H(268)	0.9500	C(160)-H(16A)	0.9900
C(268)-C(152)	1.3900	C(160)-H(16B)	0.9900
C(152)-H(152)	0.9500	C(160)-C(248)	1.557(17)
C(152)-C(235)	1.3900	C(161)-C(259)	1.471(14)
C(235)-H(235)	0.9500	C(162)-C(163)	1.416(14)
C(235)-C(140)	1.3900	C(163)-C(164)	1.390(12)
C(140)-H(140)	0.9500	C(163)-C(259)	1.404(12)
C(144)-H(144)	0.9500	C(164)-H(164)	0.9500
C(147)-H(14A)	0.9900	C(164)-C(165)	1.418(13)
C(147)-H(14B)	0.9900	C(165)-C(166)	1.3900
C(147)-C(148)	1.476(13)	C(165)-C(258)	1.3900
C(148)-H(14C)	0.9900	C(166)-C(168)	1.3900
C(148)-H(14D)	0.9900	C(166)-C(167)	1.427(12)
C(148)-C(269)	1.412(14)	C(168)-H(168)	0.9500
C(153)-H(153)	0.9500	C(168)-C(236)	1.3900
C(153)-C(154)	1.425(12)	C(236)-H(236)	0.9500
C(153)-C(234)	1.334(13)	C(236)-C(169)	1.3900
C(154)-C(264)	1.3900	C(169)-H(169)	0.9500
C(154)-C(93)	1.3900	C(169)-C(258)	1.3900
C(264)-H(264)	0.9500	C(258)-H(258)	0.9500

C(167)-H(167)	0.9500	C(94)-H(94)	0.9500
C(167)-C(259)	1.381(12)	C(194)-C(267)	1.475(14)
C(173)-H(173)	1.0000	C(195)-H(19A)	0.9900
C(173)-C(174)	1.524(13)	C(195)-H(19B)	0.9900
C(173)-C(261)	1.529(14)	C(195)-C(196)	1.541(16)
C(177)-H(177)	1.0000	C(196)-H(19C)	0.9900
C(177)-C(178)	1.565(12)	C(196)-H(19D)	0.9900
C(177)-C(181)	1.560(14)	C(196)-C(197)	1.561(16)
C(179)-H(17A)	0.9900	C(197)-H(19E)	0.9900
C(179)-H(17B)	0.9900	C(197)-H(19F)	0.9900
C(179)-C(180)	1.587(15)	C(197)-C(267)	1.544(18)
C(180)-H(18A)	0.9900	C(201)-C(237)	1.448(14)
C(180)-H(18B)	0.9900	C(202)-C(203)	1.494(17)
C(180)-C(181)	1.518(16)	C(203)-C(204)	1.405(13)
C(181)-H(18C)	0.9900	C(203)-C(237)	1.378(14)
C(181)-H(18D)	0.9900	C(204)-H(204)	0.9500
C(184)-C(185)	1.447(11)	C(204)-C(208)	1.411(14)
C(185)-C(186)	1.3908(12)	C(205)-H(205)	0.9500
C(185)-C(257)	1.3906(11)	C(205)-C(209)	1.419(12)
C(186)-C(187)	1.514(12)	C(205)-C(237)	1.404(14)
C(186)-C(188)	1.3910(12)	C(208)-C(209)	1.3900
C(188)-H(188)	0.9500	C(208)-C(265)	1.3900
C(188)-C(256)	1.3918(11)	C(209)-C(301)	1.3900
C(190)-H(190)	0.9500	C(301)-H(301)	0.9500
C(190)-C(256)	1.3900	C(301)-C(239)	1.3900
C(190)-C(94)	1.3900	C(239)-H(239)	0.9500
C(256)-C(189)	1.3900	C(239)-C(266)	1.3900
C(189)-C(255)	1.3900	C(266)-H(266)	0.9500
C(189)-C(257)	1.3910(11)	C(266)-C(265)	1.3900
C(255)-H(255)	0.9500	C(265)-H(265)	0.9500
C(255)-C(125)	1.3900	C(212)-C(213)	1.541(10)
C(125)-H(125)	0.9500	C(213)-C(214)	1.3905(12)
C(125)-C(94)	1.3900	C(213)-C(221)	1.3913(12)

C(214)-H(214)	0.9500	C(248)-H(24I)	0.9900
C(214)-C(215)	1.3921(11)	C(248)-H(24J)	0.9900
C(219)-C(215)	1.3900	C(250)-H(25A)	0.9900
C(219)-C(218)	1.3900	C(250)-H(25B)	0.9900
C(219)-C(220)	1.3903(11)	C(250)-C(252)	1.563(16)
C(215)-C(216)	1.3900	C(251)-H(25C)	0.9900
C(216)-H(216)	0.9500	C(251)-H(25D)	0.9900
C(216)-C(217)	1.3900	C(251)-C(252)	1.546(15)
C(217)-H(217)	0.9500	C(252)-H(25E)	0.9900
C(217)-C(300)	1.3900	C(252)-H(25F)	0.9900
C(300)-H(300)	0.9500	C(253)-H(25G)	0.9800
C(300)-C(218)	1.3900	C(253)-H(25H)	0.9800
C(218)-H(218)	0.9500	C(253)-H(25I)	0.9800
C(220)-H(220)	0.9500	C(257)-H(257)	0.9500
C(220)-C(221)	1.3910(11)	C(260)-H(26C)	0.9900
C(221)-C(222)	1.481(10)	C(260)-H(26D)	0.9900
C(225)-H(225)	1.0000	C(260)-C(261)	1.664(16)
C(225)-C(226)	1.583(14)	C(260)-C(262)	1.515(16)
C(225)-C(250)	1.639(17)	C(261)-H(26E)	0.9900
C(229)-H(229)	0.9500	C(261)-H(26F)	0.9900
C(233)-H(23C)	0.9900	C(262)-H(26G)	0.9900
C(233)-H(23D)	0.9900	C(262)-H(26H)	0.9900
C(241)-C(244)	1.478(15)	C(263)-H(26A)	0.9900
C(242)-H(24C)	0.9900	C(263)-H(26B)	0.9900
C(242)-H(24D)	0.9900	C(267)-H(267)	1.0000
C(242)-C(243)	1.449(13)	C(269)-H(26I)	0.9900
C(242)-C(245)	1.424(12)	C(269)-H(26J)	0.9900
C(243)-H(24E)	0.9900	C(270)-H(270)	0.9500
C(243)-H(24F)	0.9900	C(273)-H(27A)	0.9800
C(243)-C(244)	1.460(14)	C(273)-H(27B)	0.9800
C(244)-H(244)	1.0000	C(273)-H(27C)	0.9800
C(245)-H(24G)	0.9900	C(274)-H(27D)	0.9800
C(245)-H(24H)	0.9900	C(274)-H(27E)	0.9800

C(274)-H(27F)	0.9800
C(275)-H(275)	0.9500
C(280)-H(280)	0.9500
C(281)-H(28G)	0.9800
C(281)-H(28H)	0.9800
C(281)-H(28I)	0.9800
C(282)-H(28J)	0.9800
C(282)-H(28K)	0.9800
C(282)-H(28L)	0.9800
C(283)-H(283)	0.9500
C(284)-H(28A)	0.9800
C(284)-H(28B)	0.9800
C(284)-H(28C)	0.9800
C(285)-H(28D)	0.9800
C(285)-H(28E)	0.9800
C(285)-H(28F)	0.9800
C(286)-H(28M)	0.9800
C(286)-H(28N)	0.9800
C(286)-H(28O)	0.9800
C(289)-H(289)	0.9500
C(293)-H(293)	0.9500
C(295)-H(29G)	0.9800
C(295)-H(29H)	0.9800
C(295)-H(29I)	0.9800
C(296)-H(29J)	0.9800
C(296)-H(29K)	0.9800
C(296)-H(29L)	0.9800
C(297)-H(29A)	0.9800
C(297)-H(29B)	0.9800
C(297)-H(29C)	0.9800
C(298)-H(29D)	0.9800
C(298)-H(29E)	0.9800
C(298)-H(29F)	0.9800
C(299)-H(29M)	0.9800
C(299)-H(29N)	0.9800
C(299)-H(29O)	0.9800
C(303)-H(303)	0.9500

O(59)-Rh(1)-Rh(4)	87.90(16)
O(59)-Rh(1)-O(200)	88.3(2)
O(59)-Rh(1)-O(276)	90.4(3)
O(59)-Rh(1)-N(61)	93.9(3)
O(200)-Rh(1)-Rh(4)	88.96(19)
O(200)-Rh(1)-O(276)	85.6(3)
O(276)-Rh(1)-Rh(4)	174.3(2)
N(61)-Rh(1)-Rh(4)	87.1(2)
N(61)-Rh(1)-O(200)	175.4(3)
N(61)-Rh(1)-O(276)	98.4(3)
N(63)-Rh(1)-Rh(4)	87.2(3)
N(63)-Rh(1)-O(59)	174.4(3)
N(63)-Rh(1)-O(200)	88.8(3)
N(63)-Rh(1)-O(276)	94.1(3)
N(63)-Rh(1)-N(61)	88.6(3)
O(146)-Rh(2)-Rh(3)	88.11(15)
O(146)-Rh(2)-O(292)	87.5(2)
O(193)-Rh(2)-Rh(3)	88.28(17)
O(193)-Rh(2)-O(146)	87.7(2)
O(193)-Rh(2)-O(292)	90.2(2)
O(292)-Rh(2)-Rh(3)	175.4(2)
N(65)-Rh(2)-Rh(3)	87.9(2)
N(65)-Rh(2)-O(146)	95.3(3)
N(65)-Rh(2)-O(193)	175.0(3)
N(65)-Rh(2)-O(292)	93.9(3)
N(175)-Rh(2)-Rh(3)	87.8(2)
N(175)-Rh(2)-O(146)	173.7(3)
N(175)-Rh(2)-O(193)	87.4(3)

N(175)-Rh(2)-O(292)	96.4(3)	O(72)-Rh(5)-O(279)	88.9(3)
N(175)-Rh(2)-N(65)	89.3(3)	O(100)-Rh(5)-Rh(6)	87.67(19)
O(62)-Rh(3)-Rh(2)	88.89(16)	O(100)-Rh(5)-O(72)	87.2(3)
O(62)-Rh(3)-O(176)	86.5(3)	O(100)-Rh(5)-O(279)	89.2(3)
O(62)-Rh(3)-O(288)	87.4(2)	O(279)-Rh(5)-Rh(6)	175.8(2)
O(62)-Rh(3)-N(145)	95.8(3)	N(129)-Rh(5)-Rh(6)	87.3(2)
O(176)-Rh(3)-Rh(2)	86.50(17)	N(129)-Rh(5)-O(72)	174.9(3)
O(176)-Rh(3)-O(288)	88.8(3)	N(129)-Rh(5)-O(100)	90.3(3)
O(288)-Rh(3)-Rh(2)	174.19(17)	N(129)-Rh(5)-O(279)	95.5(3)
N(145)-Rh(3)-Rh(2)	88.16(19)	N(129)-Rh(5)-N(246)	87.7(3)
N(145)-Rh(3)-O(176)	174.2(3)	N(246)-Rh(5)-Rh(6)	87.0(2)
N(145)-Rh(3)-O(288)	96.7(3)	N(246)-Rh(5)-O(72)	94.4(3)
N(182)-Rh(3)-Rh(2)	87.7(2)	N(246)-Rh(5)-O(100)	174.4(3)
N(182)-Rh(3)-O(62)	175.8(3)	N(246)-Rh(5)-O(279)	96.2(3)
N(182)-Rh(3)-O(176)	90.7(3)	O(130)-Rh(6)-Rh(5)	88.09(19)
N(182)-Rh(3)-O(288)	95.7(3)	O(130)-Rh(6)-O(291)	89.0(3)
N(182)-Rh(3)-N(145)	86.7(3)	O(130)-Rh(6)-N(101)	90.1(3)
O(64)-Rh(4)-Rh(1)	89.35(16)	O(247)-Rh(6)-Rh(5)	88.97(18)
O(64)-Rh(4)-O(227)	87.4(2)	O(247)-Rh(6)-O(130)	85.5(3)
O(64)-Rh(4)-O(271)	88.7(2)	O(247)-Rh(6)-O(291)	87.3(3)
O(227)-Rh(4)-Rh(1)	87.9(2)	O(247)-Rh(6)-N(101)	174.4(3)
O(227)-Rh(4)-O(271)	86.0(3)	O(291)-Rh(6)-Rh(5)	175.5(2)
O(271)-Rh(4)-Rh(1)	173.66(18)	N(71)-Rh(6)-Rh(5)	86.6(2)
N(60)-Rh(4)-Rh(1)	87.9(2)	N(71)-Rh(6)-O(130)	174.7(3)
N(60)-Rh(4)-O(64)	96.2(3)	N(71)-Rh(6)-O(247)	94.7(3)
N(60)-Rh(4)-O(227)	174.5(3)	N(71)-Rh(6)-O(291)	96.3(3)
N(60)-Rh(4)-O(271)	98.3(3)	N(71)-Rh(6)-N(101)	89.4(3)
N(198)-Rh(4)-Rh(1)	87.5(3)	N(101)-Rh(6)-Rh(5)	87.4(2)
N(198)-Rh(4)-O(64)	175.9(3)	N(101)-Rh(6)-O(291)	96.1(3)
N(198)-Rh(4)-O(227)	89.9(3)	C(44)-O(59)-Rh(1)	114.9(7)
N(198)-Rh(4)-O(271)	94.2(3)	C(21)-O(62)-Rh(3)	116.4(5)
N(198)-Rh(4)-N(60)	86.4(3)	C(38)-O(64)-Rh(4)	114.1(5)
O(72)-Rh(5)-Rh(6)	88.12(18)	C(70)-O(72)-Rh(5)	117.5(7)

C(88)-O(100)-Rh(5)	117.6(7)	C(21)-N(65)-C(23)	123.8(8)
C(127)-O(130)-Rh(6)	115.6(6)	C(23)-N(65)-Rh(2)	117.0(5)
C(132)-O(146)-Rh(2)	114.2(5)	C(66)-N(71)-Rh(6)	115.9(6)
C(174)-O(176)-Rh(3)	118.9(6)	C(70)-N(71)-Rh(6)	122.6(6)
C(178)-O(193)-Rh(2)	115.1(5)	C(70)-N(71)-C(66)	120.6(8)
C(194)-O(200)-Rh(1)	113.0(6)	C(69)-N(75)-C(76)	119.9(9)
C(226)-O(227)-Rh(4)	113.5(6)	C(69)-N(75)-C(79)	128.9(9)
C(241)-O(247)-Rh(6)	118.4(6)	C(79)-N(75)-C(76)	111.1(8)
C(270)-O(271)-Rh(4)	111.5(7)	C(95)-N(97)-C(89)	126.8(9)
C(275)-O(276)-Rh(1)	113.2(10)	C(95)-N(97)-C(96)	110.8(10)
C(280)-O(279)-Rh(5)	103.7(7)	C(96)-N(97)-C(89)	122.4(9)
C(283)-O(288)-Rh(3)	106.5(6)	C(88)-N(101)-Rh(6)	118.1(7)
C(289)-O(291)-Rh(6)	108.9(8)	C(88)-N(101)-C(102)	120.9(9)
C(293)-O(292)-Rh(2)	112.4(7)	C(102)-N(101)-Rh(6)	120.0(7)
C(9)-N(7)-C(8)	109.5(8)	C(104)-N(115)-C(244)	126.5(11)
C(9)-N(7)-C(20)	131.0(8)	C(157)-N(115)-C(104)	109.6(9)
C(20)-N(7)-C(8)	119.4(8)	C(157)-N(115)-C(244)	123.8(11)
C(31)-N(33)-C(32)	114.0(8)	C(123)-N(126)-C(128)	123.3(9)
C(31)-N(33)-C(37)	123.3(8)	C(230)-N(126)-C(123)	112.3(9)
C(32)-N(33)-C(37)	122.7(7)	C(230)-N(126)-C(128)	123.5(9)
C(45)-N(56)-C(48)	126.5(8)	C(127)-N(129)-Rh(5)	119.2(7)
C(45)-N(56)-C(49)	126.4(9)	C(127)-N(129)-C(159)	123.5(10)
C(48)-N(56)-C(49)	107.0(8)	C(159)-N(129)-Rh(5)	117.3(7)
C(44)-N(60)-Rh(4)	116.8(7)	C(134)-N(141)-C(133)	126.8(9)
C(44)-N(60)-C(46)	125.7(9)	C(134)-N(141)-C(137)	112.1(9)
C(46)-N(60)-Rh(4)	117.2(6)	C(137)-N(141)-C(133)	121.1(9)
C(38)-N(61)-Rh(1)	118.7(6)	C(132)-N(145)-Rh(3)	118.2(6)
C(38)-N(61)-C(39)	125.2(7)	C(132)-N(145)-C(147)	122.1(8)
C(39)-N(61)-Rh(1)	114.8(5)	C(147)-N(145)-Rh(3)	118.8(6)
C(226)-N(63)-Rh(1)	118.4(7)	C(161)-N(172)-C(162)	110.7(8)
C(226)-N(63)-C(251)	124.2(9)	C(161)-N(172)-C(173)	126.7(8)
C(251)-N(63)-Rh(1)	117.5(6)	C(162)-N(172)-C(173)	122.1(8)
C(21)-N(65)-Rh(2)	118.6(6)	C(174)-N(175)-Rh(2)	121.3(6)

C(174)-N(175)-C(262)	121.1(8)
C(262)-N(175)-Rh(2)	117.6(7)
C(178)-N(182)-Rh(3)	117.3(7)
C(178)-N(182)-C(179)	127.4(8)
C(179)-N(182)-Rh(3)	114.9(6)
C(184)-N(183)-C(177)	125.0(9)
C(187)-N(183)-C(177)	121.1(10)
C(187)-N(183)-C(184)	113.1(10)
C(194)-N(198)-Rh(4)	118.1(8)
C(194)-N(198)-C(195)	122.8(10)
C(195)-N(198)-Rh(4)	118.8(7)
C(201)-N(199)-C(202)	112.8(11)
C(201)-N(199)-C(267)	121.6(11)
C(202)-N(199)-C(267)	124.6(11)
C(222)-N(211)-C(212)	113.2(9)
C(222)-N(211)-C(225)	127.6(11)
C(225)-N(211)-C(212)	118.1(10)
C(241)-N(246)-Rh(5)	120.6(7)
C(241)-N(246)-C(245)	123.4(9)
C(245)-N(246)-Rh(5)	114.9(6)
C(270)-N(272)-C(273)	127.9(12)
C(270)-N(272)-C(274)	119.8(10)
C(273)-N(272)-C(274)	112.3(12)
C(155)-N(277)-C(253)	114(2)
C(155)-N(277)-C(275)	117(2)
C(275)-N(277)-C(253)	122(2)
C(280)-N(278)-C(281)	121.2(14)
C(280)-N(278)-C(282)	123.7(12)
C(281)-N(278)-C(282)	115.1(13)
C(283)-N(287)-C(284)	121.1(9)
C(283)-N(287)-C(285)	123.3(9)
C(285)-N(287)-C(284)	115.3(8)
C(293)-N(290)-C(297)	122.9(10)
C(293)-N(290)-C(298)	118.0(11)
C(297)-N(290)-C(298)	118.8(10)
C(289)-N(294)-C(295)	118.1(13)
C(289)-N(294)-C(296)	122.4(13)
C(296)-N(294)-C(295)	119.5(13)
C(299)-N(304)-C(286)	122.0(9)
C(303)-N(304)-C(286)	118.7(10)
C(303)-N(304)-C(299)	119.2(11)
O(19)-C(8)-N(7)	126.5(9)
O(19)-C(8)-C(17)	129.7(9)
N(7)-C(8)-C(17)	103.9(9)
O(18)-C(9)-N(7)	122.7(8)
O(18)-C(9)-C(10)	129.9(10)
N(7)-C(9)-C(10)	107.4(9)
C(17)-C(10)-C(9)	111.7(9)
C(17)-C(10)-C(87)	118.1(8)
C(87)-C(10)-C(9)	130.2(9)
C(15)-C(11)-C(12)	120.0
C(15)-C(11)-C(87)	120.0(5)
C(12)-C(11)-C(87)	120.0(5)
C(11)-C(15)-C(16)	118.3(5)
C(14)-C(15)-C(11)	120.0
C(14)-C(15)-C(16)	121.7(5)
C(15)-C(14)-H(14)	120.0
C(15)-C(14)-C(13)	120.0
C(13)-C(14)-H(14)	120.0
C(14)-C(13)-H(13)	120.0
C(41)-C(13)-C(14)	120.0
C(41)-C(13)-H(13)	120.0
C(13)-C(41)-H(41)	120.0
C(13)-C(41)-C(12)	120.0
C(12)-C(41)-H(41)	120.0
C(11)-C(12)-H(12)	120.0

C(41)-C(12)-C(11)	120.0
C(41)-C(12)-H(12)	120.0
C(15)-C(16)-H(16)	120.5
C(17)-C(16)-C(15)	119.0(8)
C(17)-C(16)-H(16)	120.5
C(10)-C(17)-C(8)	107.5(8)
C(10)-C(17)-C(16)	124.3(9)
C(16)-C(17)-C(8)	128.0(8)
N(7)-C(20)-H(20)	107.2
N(7)-C(20)-C(21)	111.7(7)
N(7)-C(20)-C(131)	111.2(7)
C(21)-C(20)-H(20)	107.2
C(21)-C(20)-C(131)	111.9(8)
C(131)-C(20)-H(20)	107.2
O(62)-C(21)-N(65)	125.0(8)
O(62)-C(21)-C(20)	114.7(7)
N(65)-C(21)-C(20)	120.0(8)
C(43)-C(22)-H(22)	119.6
C(30)-C(22)-H(22)	119.6
C(30)-C(22)-C(43)	120.9(9)
N(65)-C(23)-H(23A)	108.3
N(65)-C(23)-H(23B)	108.3
N(65)-C(23)-C(24)	116.0(8)
H(23A)-C(23)-H(23B)	107.4
C(24)-C(23)-H(23A)	108.3
C(24)-C(23)-H(23B)	108.3
C(23)-C(24)-H(24A)	109.1
C(23)-C(24)-H(24B)	109.1
C(23)-C(24)-C(131)	112.5(8)
H(24A)-C(24)-H(24B)	107.8
C(131)-C(24)-H(24A)	109.1
C(131)-C(24)-H(24B)	109.1
C(25)-C(26)-H(26)	120.1
C(29)-C(26)-H(26)	120.1
C(29)-C(26)-C(25)	119.9(9)
C(25)-C(27)-H(27)	120.0
C(25)-C(27)-C(210)	120.0
C(210)-C(27)-H(27)	120.0
C(27)-C(25)-C(26)	117.8(6)
C(27)-C(25)-C(43)	120.0
C(43)-C(25)-C(26)	122.2(5)
C(25)-C(43)-C(22)	116.0(4)
C(28)-C(43)-C(22)	123.9(4)
C(28)-C(43)-C(25)	120.0
C(43)-C(28)-H(28)	120.0
C(43)-C(28)-C(42)	120.0
C(42)-C(28)-H(28)	120.0
C(28)-C(42)-H(42)	120.0
C(210)-C(42)-C(28)	120.0
C(210)-C(42)-H(42)	120.0
C(27)-C(210)-H(210)	120.0
C(42)-C(210)-C(27)	120.0
C(42)-C(210)-H(210)	120.0
C(26)-C(29)-C(30)	121.6(9)
C(26)-C(29)-C(32)	130.8(9)
C(30)-C(29)-C(32)	107.6(8)
C(22)-C(30)-C(29)	119.4(10)
C(22)-C(30)-C(31)	132.1(10)
C(29)-C(30)-C(31)	108.5(7)
O(35)-C(31)-N(33)	124.8(8)
O(35)-C(31)-C(30)	128.7(8)
N(33)-C(31)-C(30)	106.4(8)
O(34)-C(32)-N(33)	126.8(9)
O(34)-C(32)-C(29)	129.8(10)
N(33)-C(32)-C(29)	103.4(8)
H(36A)-C(36)-H(36B)	108.4

C(37)-C(36)-H(36A)	110.1
C(37)-C(36)-H(36B)	110.1
C(40)-C(36)-H(36A)	110.1
C(40)-C(36)-H(36B)	110.1
C(40)-C(36)-C(37)	108.0(8)
N(33)-C(37)-C(36)	114.5(7)
N(33)-C(37)-H(37)	105.5
N(33)-C(37)-C(38)	111.6(7)
C(36)-C(37)-H(37)	105.5
C(36)-C(37)-C(38)	113.2(7)
C(38)-C(37)-H(37)	105.5
O(64)-C(38)-C(37)	114.6(7)
N(61)-C(38)-O(64)	124.9(7)
N(61)-C(38)-C(37)	120.4(7)
N(61)-C(39)-H(39A)	109.1
N(61)-C(39)-H(39B)	109.1
N(61)-C(39)-C(40)	112.6(7)
H(39A)-C(39)-H(39B)	107.8
C(40)-C(39)-H(39A)	109.1
C(40)-C(39)-H(39B)	109.1
C(36)-C(40)-C(39)	110.7(8)
C(36)-C(40)-H(40A)	109.5
C(36)-C(40)-H(40B)	109.5
C(39)-C(40)-H(40A)	109.5
C(39)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	108.1
O(59)-C(44)-N(60)	126.7(10)
O(59)-C(44)-C(45)	113.6(8)
N(60)-C(44)-C(45)	119.5(9)
N(56)-C(45)-C(44)	110.3(8)
N(56)-C(45)-H(45)	106.6
N(56)-C(45)-C(263)	114.9(9)
C(44)-C(45)-H(45)	106.6
C(263)-C(45)-C(44)	111.5(8)
C(263)-C(45)-H(45)	106.6
N(60)-C(46)-H(46A)	108.8
N(60)-C(46)-H(46B)	108.8
N(60)-C(46)-C(47)	113.8(8)
H(46A)-C(46)-H(46B)	107.7
C(47)-C(46)-H(46A)	108.8
C(47)-C(46)-H(46B)	108.8
C(46)-C(47)-H(47A)	109.9
C(46)-C(47)-H(47B)	109.9
H(47A)-C(47)-H(47B)	108.3
C(263)-C(47)-C(46)	109.0(8)
C(263)-C(47)-H(47A)	109.9
C(263)-C(47)-H(47B)	109.9
O(58)-C(48)-N(56)	120.4(10)
O(58)-C(48)-C(51)	132.2(10)
C(51)-C(48)-N(56)	107.4(8)
O(57)-C(49)-N(56)	118.0(10)
O(57)-C(49)-C(50)	135.1(10)
C(50)-C(49)-N(56)	106.9(9)
C(51)-C(50)-C(49)	108.6(9)
C(55)-C(50)-C(49)	128.9(10)
C(55)-C(50)-C(51)	122.3(10)
C(50)-C(51)-C(48)	109.7(9)
C(52)-C(51)-C(48)	131.1(9)
C(52)-C(51)-C(50)	119.1(9)
C(51)-C(52)-H(52)	119.6
C(51)-C(52)-C(53)	120.9(9)
C(53)-C(52)-H(52)	119.6
C(228)-C(53)-C(52)	118.9(7)
C(228)-C(53)-C(54)	120.0
C(54)-C(53)-C(52)	121.0(7)
C(53)-C(228)-C(249)	120.0

C(53)-C(228)-C(55)	118.5(6)	C(69)-C(68)-H(68A)	109.7
C(249)-C(228)-C(55)	121.5(6)	C(69)-C(68)-H(68B)	109.7
C(228)-C(249)-H(249)	120.0	N(75)-C(69)-C(68)	111.3(9)
C(150)-C(249)-C(228)	120.0	N(75)-C(69)-H(69)	106.4
C(150)-C(249)-H(249)	120.0	N(75)-C(69)-C(70)	114.9(8)
C(249)-C(150)-H(150)	120.0	C(68)-C(69)-H(69)	106.4
C(249)-C(150)-C(149)	120.0	C(70)-C(69)-C(68)	110.8(9)
C(149)-C(150)-H(150)	120.0	C(70)-C(69)-H(69)	106.4
C(150)-C(149)-H(149)	120.0	O(72)-C(70)-N(71)	121.5(9)
C(54)-C(149)-C(150)	120.0	O(72)-C(70)-C(69)	114.7(9)
C(54)-C(149)-H(149)	120.0	N(71)-C(70)-C(69)	123.8(8)
C(53)-C(54)-H(54)	120.0	O(74)-C(76)-N(75)	125.8(10)
C(149)-C(54)-C(53)	120.0	O(74)-C(76)-C(77)	126.7(13)
C(149)-C(54)-H(54)	120.0	N(75)-C(76)-C(77)	107.4(9)
C(50)-C(55)-C(228)	120.2(9)	C(78)-C(77)-C(76)	107.5(9)
C(50)-C(55)-H(55)	119.9	C(78)-C(77)-C(80)	120.4(9)
C(228)-C(55)-H(55)	119.9	C(80)-C(77)-C(76)	131.5(11)
N(71)-C(66)-H(66A)	108.3	C(77)-C(78)-C(79)	109.2(8)
N(71)-C(66)-H(66B)	108.3	C(81)-C(78)-C(77)	121.1(9)
H(66A)-C(66)-H(66B)	107.4	C(81)-C(78)-C(79)	129.7(9)
C(67)-C(66)-N(71)	115.7(8)	O(73)-C(79)-N(75)	125.4(9)
C(67)-C(66)-H(66A)	108.3	O(73)-C(79)-C(78)	129.8(10)
C(67)-C(66)-H(66B)	108.3	N(75)-C(79)-C(78)	104.8(8)
C(66)-C(67)-H(67A)	108.7	C(77)-C(80)-H(80)	120.5
C(66)-C(67)-H(67B)	108.7	C(77)-C(80)-C(83)	118.9(8)
H(67A)-C(67)-H(67B)	107.6	C(83)-C(80)-H(80)	120.5
C(68)-C(67)-C(66)	114.1(9)	C(78)-C(81)-H(81)	120.5
C(68)-C(67)-H(67A)	108.7	C(78)-C(81)-C(84)	119.1(8)
C(68)-C(67)-H(67B)	108.7	C(84)-C(81)-H(81)	120.5
C(67)-C(68)-H(68A)	109.7	C(83)-C(84)-C(81)	120.5(6)
C(67)-C(68)-H(68B)	109.7	C(83)-C(84)-C(85)	120.0
C(67)-C(68)-C(69)	109.7(9)	C(85)-C(84)-C(81)	118.7(6)
H(68A)-C(68)-H(68B)	108.2	C(84)-C(83)-C(80)	118.8(5)

C(84)-C(83)-C(82)	120.0	C(92)-C(91)-C(234)	116.6(11)
C(82)-C(83)-C(80)	121.2(5)	C(234)-C(91)-C(95)	107.5(10)
C(83)-C(82)-H(82)	120.0	C(91)-C(92)-H(92)	118.4
C(240)-C(82)-C(83)	120.0	C(91)-C(92)-C(93)	123.2(10)
C(240)-C(82)-H(82)	120.0	C(93)-C(92)-H(92)	118.4
C(82)-C(240)-H(240)	120.0	O(98)-C(95)-N(97)	124.5(11)
C(86)-C(240)-C(82)	120.0	O(98)-C(95)-C(91)	125.8(11)
C(86)-C(240)-H(240)	120.0	N(97)-C(95)-C(91)	109.7(9)
C(240)-C(86)-H(86)	120.0	O(99)-C(96)-N(97)	125.3(12)
C(240)-C(86)-C(85)	120.0	O(99)-C(96)-C(234)	129.3(11)
C(85)-C(86)-H(86)	120.0	N(97)-C(96)-C(234)	105.4(10)
C(84)-C(85)-H(85)	120.0	N(101)-C(102)-H(10A)	108.7
C(86)-C(85)-C(84)	120.0	N(101)-C(102)-H(10B)	108.7
C(86)-C(85)-H(85)	120.0	N(101)-C(102)-C(233)	114.3(10)
C(10)-C(87)-C(11)	120.0(7)	H(10A)-C(102)-H(10B)	107.6
C(10)-C(87)-H(87)	120.0	C(233)-C(102)-H(10A)	108.7
C(11)-C(87)-H(87)	120.0	C(233)-C(102)-H(10B)	108.7
O(100)-C(88)-N(101)	126.2(9)	O(114)-C(104)-N(115)	121.8(10)
O(100)-C(88)-C(89)	112.7(9)	O(114)-C(104)-C(105)	129.5(11)
N(101)-C(88)-C(89)	121.1(9)	C(105)-C(104)-N(115)	108.7(10)
N(97)-C(89)-C(88)	109.8(8)	C(106)-C(105)-C(104)	108.2(9)
N(97)-C(89)-H(89)	107.7	C(110)-C(105)-C(104)	135.6(11)
N(97)-C(89)-C(90)	109.1(10)	C(110)-C(105)-C(106)	116.2(10)
C(88)-C(89)-H(89)	107.7	C(105)-C(106)-C(157)	105.9(10)
C(90)-C(89)-C(88)	114.6(9)	C(107)-C(106)-C(105)	122.8(10)
C(90)-C(89)-H(89)	107.7	C(107)-C(106)-C(157)	131.1(11)
C(89)-C(90)-H(90A)	109.9	C(106)-C(107)-H(107)	120.3
C(89)-C(90)-H(90B)	109.9	C(106)-C(107)-C(108)	119.4(10)
H(90A)-C(90)-H(90B)	108.3	C(108)-C(107)-H(107)	120.3
C(233)-C(90)-C(89)	109.1(12)	C(109)-C(108)-C(107)	117.3(7)
C(233)-C(90)-H(90A)	109.9	C(109)-C(108)-C(156)	120.0
C(233)-C(90)-H(90B)	109.9	C(156)-C(108)-C(107)	122.7(7)
C(92)-C(91)-C(95)	135.9(11)	C(108)-C(109)-C(111)	120.0

C(108)-C(109)-C(110)	119.5(6)	C(118)-C(119)-C(120)	120.0
C(111)-C(109)-C(110)	120.5(6)	C(118)-C(119)-H(119)	120.0
C(109)-C(111)-H(111)	120.0	C(120)-C(121)-H(121)	122.3
C(109)-C(111)-C(112)	120.0	C(232)-C(121)-C(120)	115.3(10)
C(112)-C(111)-H(111)	120.0	C(232)-C(121)-H(121)	122.3
C(111)-C(112)-H(112)	120.0	O(122)-C(123)-N(126)	124.6(11)
C(111)-C(112)-C(113)	120.0	O(122)-C(123)-C(232)	129.1(12)
C(113)-C(112)-H(112)	120.0	N(126)-C(123)-C(232)	106.1(9)
C(112)-C(113)-H(113)	120.0	C(229)-C(124)-C(230)	133.4(10)
C(156)-C(113)-C(112)	120.0	C(229)-C(124)-C(232)	122.0(11)
C(156)-C(113)-H(113)	120.0	C(232)-C(124)-C(230)	104.5(9)
C(108)-C(156)-H(156)	120.0	O(130)-C(127)-C(128)	110.3(9)
C(113)-C(156)-C(108)	120.0	N(129)-C(127)-O(130)	126.9(10)
C(113)-C(156)-H(156)	120.0	N(129)-C(127)-C(128)	122.8(9)
C(105)-C(110)-C(109)	124.5(9)	N(126)-C(128)-C(127)	111.6(8)
C(105)-C(110)-H(110)	117.7	N(126)-C(128)-H(128)	108.1
C(109)-C(110)-H(110)	117.7	C(127)-C(128)-H(128)	108.1
C(103)-C(120)-C(119)	120.0	C(248)-C(128)-N(126)	108.1(10)
C(103)-C(120)-C(121)	122.1(7)	C(248)-C(128)-C(127)	112.5(9)
C(119)-C(120)-C(121)	117.9(7)	C(248)-C(128)-H(128)	108.1
C(120)-C(103)-C(117)	120.0	C(20)-C(131)-H(13A)	110.8
C(120)-C(103)-C(229)	119.5(7)	C(20)-C(131)-H(13B)	110.8
C(117)-C(103)-C(229)	120.3(7)	C(24)-C(131)-C(20)	104.6(8)
C(103)-C(117)-H(117)	120.0	C(24)-C(131)-H(13A)	110.8
C(116)-C(117)-C(103)	120.0	C(24)-C(131)-H(13B)	110.8
C(116)-C(117)-H(117)	120.0	H(13A)-C(131)-H(13B)	108.9
C(117)-C(116)-H(116)	120.0	O(146)-C(132)-C(133)	110.6(7)
C(118)-C(116)-C(117)	120.0	N(145)-C(132)-O(146)	127.4(8)
C(118)-C(116)-H(116)	120.0	N(145)-C(132)-C(133)	121.8(8)
C(116)-C(118)-H(118)	120.0	N(141)-C(133)-C(132)	110.1(7)
C(116)-C(118)-C(119)	120.0	N(141)-C(133)-H(133)	106.2
C(119)-C(118)-H(118)	120.0	N(141)-C(133)-C(269)	113.1(8)
C(120)-C(119)-H(119)	120.0	C(132)-C(133)-H(133)	106.2

C(132)-C(133)-C(269)	114.5(8)
C(269)-C(133)-H(133)	106.2
O(142)-C(134)-N(141)	125.1(9)
O(142)-C(134)-C(135)	131.1(9)
N(141)-C(134)-C(135)	103.7(8)
C(136)-C(135)-C(134)	110.4(9)
C(136)-C(135)-C(144)	121.1(9)
C(144)-C(135)-C(134)	128.4(8)
C(135)-C(136)-C(137)	105.6(8)
C(138)-C(136)-C(135)	119.9(9)
C(138)-C(136)-C(137)	134.4(9)
O(143)-C(137)-N(141)	126.2(9)
O(143)-C(137)-C(136)	125.7(8)
N(141)-C(137)-C(136)	108.0(9)
C(136)-C(138)-H(138)	119.6
C(136)-C(138)-C(139)	120.8(8)
C(139)-C(138)-H(138)	119.6
C(151)-C(139)-C(138)	120.3(5)
C(151)-C(139)-C(140)	120.0
C(140)-C(139)-C(138)	119.6(5)
C(139)-C(151)-C(144)	118.3(5)
C(268)-C(151)-C(139)	120.0
C(268)-C(151)-C(144)	121.6(5)
C(151)-C(268)-H(268)	120.0
C(151)-C(268)-C(152)	120.0
C(152)-C(268)-H(268)	120.0
C(268)-C(152)-H(152)	120.0
C(235)-C(152)-C(268)	120.0
C(235)-C(152)-H(152)	120.0
C(152)-C(235)-H(235)	120.0
C(140)-C(235)-C(152)	120.0
C(140)-C(235)-H(235)	120.0
C(139)-C(140)-H(140)	120.0
C(235)-C(140)-C(139)	120.0
C(235)-C(140)-H(140)	120.0
C(135)-C(144)-C(151)	119.6(8)
C(135)-C(144)-H(144)	120.2
C(151)-C(144)-H(144)	120.2
N(145)-C(147)-H(14A)	108.8
N(145)-C(147)-H(14B)	108.8
N(145)-C(147)-C(148)	113.7(8)
H(14A)-C(147)-H(14B)	107.7
C(148)-C(147)-H(14A)	108.8
C(148)-C(147)-H(14B)	108.8
C(147)-C(148)-H(14C)	108.5
C(147)-C(148)-H(14D)	108.5
H(14C)-C(148)-H(14D)	107.5
C(269)-C(148)-C(147)	115.0(9)
C(269)-C(148)-H(14C)	108.5
C(269)-C(148)-H(14D)	108.5
C(154)-C(153)-H(153)	119.8
C(234)-C(153)-H(153)	119.8
C(234)-C(153)-C(154)	120.4(11)
C(264)-C(154)-C(153)	121.7(7)
C(264)-C(154)-C(93)	120.0
C(93)-C(154)-C(153)	118.3(7)
C(154)-C(264)-H(264)	120.0
C(254)-C(264)-C(154)	120.0
C(254)-C(264)-H(264)	120.0
C(264)-C(254)-H(254)	120.0
C(264)-C(254)-C(238)	120.0
C(238)-C(254)-H(254)	120.0
C(254)-C(238)-H(238)	120.0
C(302)-C(238)-C(254)	120.0
C(302)-C(238)-H(238)	120.0
C(238)-C(302)-H(302)	120.0

C(93)-C(302)-C(238)	120.0
C(93)-C(302)-H(302)	120.0
C(154)-C(93)-C(92)	118.4(7)
C(302)-C(93)-C(92)	121.6(7)
C(302)-C(93)-C(154)	120.0
N(277)-C(155)-H(15A)	109.5
N(277)-C(155)-H(15B)	109.5
N(277)-C(155)-H(15C)	109.5
H(15A)-C(155)-H(15B)	109.5
H(15A)-C(155)-H(15C)	109.5
H(15B)-C(155)-H(15C)	109.5
O(158)-C(157)-N(115)	126.5(11)
O(158)-C(157)-C(106)	125.8(12)
N(115)-C(157)-C(106)	107.5(10)
N(129)-C(159)-H(15D)	108.4
N(129)-C(159)-H(15E)	108.4
N(129)-C(159)-C(160)	115.4(10)
H(15D)-C(159)-H(15E)	107.5
C(160)-C(159)-H(15D)	108.4
C(160)-C(159)-H(15E)	108.4
C(159)-C(160)-H(16A)	110.3
C(159)-C(160)-H(16B)	110.3
C(159)-C(160)-C(248)	107.2(9)
H(16A)-C(160)-H(16B)	108.5
C(248)-C(160)-H(16A)	110.3
C(248)-C(160)-H(16B)	110.3
O(171)-C(161)-N(172)	125.7(11)
O(171)-C(161)-C(259)	127.3(9)
N(172)-C(161)-C(259)	106.8(8)
O(170)-C(162)-N(172)	122.9(9)
O(170)-C(162)-C(163)	129.8(9)
N(172)-C(162)-C(163)	107.2(8)
C(164)-C(163)-C(162)	132.0(10)
C(164)-C(163)-C(259)	119.3(10)
C(259)-C(163)-C(162)	108.6(8)
C(163)-C(164)-H(164)	121.4
C(163)-C(164)-C(165)	117.2(10)
C(165)-C(164)-H(164)	121.4
C(166)-C(165)-C(164)	124.9(7)
C(166)-C(165)-C(258)	120.0
C(258)-C(165)-C(164)	115.1(6)
C(165)-C(166)-C(167)	116.0(6)
C(168)-C(166)-C(165)	120.0
C(168)-C(166)-C(167)	123.8(6)
C(166)-C(168)-H(168)	120.0
C(166)-C(168)-C(236)	120.0
C(236)-C(168)-H(168)	120.0
C(168)-C(236)-H(236)	120.0
C(169)-C(236)-C(168)	120.0
C(169)-C(236)-H(236)	120.0
C(236)-C(169)-H(169)	120.0
C(258)-C(169)-C(236)	120.0
C(258)-C(169)-H(169)	120.0
C(165)-C(258)-H(258)	120.0
C(169)-C(258)-C(165)	120.0
C(169)-C(258)-H(258)	120.0
C(166)-C(167)-H(167)	120.1
C(259)-C(167)-C(166)	119.9(9)
C(259)-C(167)-H(167)	120.1
N(172)-C(173)-H(173)	107.7
N(172)-C(173)-C(174)	108.3(8)
N(172)-C(173)-C(261)	108.6(8)
C(174)-C(173)-H(173)	107.7
C(174)-C(173)-C(261)	116.6(9)
C(261)-C(173)-H(173)	107.7
O(176)-C(174)-N(175)	122.2(9)

O(176)-C(174)-C(173)	115.2(8)
N(175)-C(174)-C(173)	122.6(8)
N(183)-C(177)-H(177)	108.4
N(183)-C(177)-C(178)	109.5(8)
N(183)-C(177)-C(181)	111.9(8)
C(178)-C(177)-H(177)	108.4
C(181)-C(177)-H(177)	108.4
C(181)-C(177)-C(178)	110.0(8)
O(193)-C(178)-C(177)	110.2(8)
N(182)-C(178)-O(193)	129.9(8)
N(182)-C(178)-C(177)	119.4(8)
N(182)-C(179)-H(17A)	108.7
N(182)-C(179)-H(17B)	108.7
N(182)-C(179)-C(180)	114.1(10)
H(17A)-C(179)-H(17B)	107.6
C(180)-C(179)-H(17A)	108.7
C(180)-C(179)-H(17B)	108.7
C(179)-C(180)-H(18A)	110.4
C(179)-C(180)-H(18B)	110.4
H(18A)-C(180)-H(18B)	108.6
C(181)-C(180)-C(179)	106.5(10)
C(181)-C(180)-H(18A)	110.4
C(181)-C(180)-H(18B)	110.4
C(177)-C(181)-H(18C)	110.1
C(177)-C(181)-H(18D)	110.1
C(180)-C(181)-C(177)	107.9(9)
C(180)-C(181)-H(18C)	110.1
C(180)-C(181)-H(18D)	110.1
H(18C)-C(181)-H(18D)	108.4
O(192)-C(184)-N(183)	124.5(10)
O(192)-C(184)-C(185)	129.3(11)
N(183)-C(184)-C(185)	106.2(8)
C(186)-C(185)-C(184)	108.7(6)
C(257)-C(185)-C(184)	131.3(6)
C(257)-C(185)-C(186)	119.98(8)
C(185)-C(186)-C(187)	105.9(5)
C(185)-C(186)-C(188)	119.99(8)
C(188)-C(186)-C(187)	134.0(5)
O(191)-C(187)-N(183)	127.4(11)
O(191)-C(187)-C(186)	126.6(11)
N(183)-C(187)-C(186)	105.9(9)
C(186)-C(188)-H(188)	120.0
C(186)-C(188)-C(256)	119.96(7)
C(256)-C(188)-H(188)	120.0
C(256)-C(190)-H(190)	120.0
C(256)-C(190)-C(94)	120.0
C(94)-C(190)-H(190)	120.0
C(190)-C(256)-C(188)	119.94(8)
C(190)-C(256)-C(189)	120.0
C(189)-C(256)-C(188)	119.94(7)
C(256)-C(189)-C(257)	120.00(8)
C(255)-C(189)-C(256)	120.0
C(255)-C(189)-C(257)	120.00(7)
C(189)-C(255)-H(255)	120.0
C(125)-C(255)-C(189)	120.0
C(125)-C(255)-H(255)	120.0
C(255)-C(125)-H(125)	120.0
C(255)-C(125)-C(94)	120.0
C(94)-C(125)-H(125)	120.0
C(190)-C(94)-H(94)	120.0
C(125)-C(94)-C(190)	120.0
C(125)-C(94)-H(94)	120.0
O(200)-C(194)-N(198)	128.6(10)
O(200)-C(194)-C(267)	112.3(10)
N(198)-C(194)-C(267)	119.1(11)
N(198)-C(195)-H(19A)	107.2

N(198)-C(195)-H(19B)	107.2	C(209)-C(208)-C(265)	120.0
N(198)-C(195)-C(196)	120.7(11)	C(265)-C(208)-C(204)	119.5(7)
H(19A)-C(195)-H(19B)	106.8	C(208)-C(209)-C(205)	121.3(8)
C(196)-C(195)-H(19A)	107.2	C(301)-C(209)-C(205)	118.7(8)
C(196)-C(195)-H(19B)	107.2	C(301)-C(209)-C(208)	120.0
C(195)-C(196)-H(19C)	111.4	C(209)-C(301)-H(301)	120.0
C(195)-C(196)-H(19D)	111.4	C(209)-C(301)-C(239)	120.0
C(195)-C(196)-C(197)	102.0(10)	C(239)-C(301)-H(301)	120.0
H(19C)-C(196)-H(19D)	109.2	C(301)-C(239)-H(239)	120.0
C(197)-C(196)-H(19C)	111.4	C(301)-C(239)-C(266)	120.0
C(197)-C(196)-H(19D)	111.4	C(266)-C(239)-H(239)	120.0
C(196)-C(197)-H(19E)	110.8	C(239)-C(266)-H(266)	120.0
C(196)-C(197)-H(19F)	110.8	C(265)-C(266)-C(239)	120.0
H(19E)-C(197)-H(19F)	108.9	C(265)-C(266)-H(266)	120.0
C(267)-C(197)-C(196)	104.7(11)	C(208)-C(265)-H(265)	120.0
C(267)-C(197)-H(19E)	110.8	C(266)-C(265)-C(208)	120.0
C(267)-C(197)-H(19F)	110.8	C(266)-C(265)-H(265)	120.0
O(207)-C(201)-N(199)	126.3(11)	O(224)-C(212)-N(211)	128.2(10)
O(207)-C(201)-C(237)	125.8(13)	O(224)-C(212)-C(213)	127.9(12)
N(199)-C(201)-C(237)	107.9(12)	N(211)-C(212)-C(213)	103.9(8)
O(206)-C(202)-N(199)	121.8(13)	C(214)-C(213)-C(212)	133.5(6)
O(206)-C(202)-C(203)	138.2(15)	C(214)-C(213)-C(221)	119.97(8)
N(199)-C(202)-C(203)	100.0(12)	C(221)-C(213)-C(212)	106.4(5)
C(204)-C(203)-C(202)	125.7(13)	C(213)-C(214)-H(214)	120.0
C(237)-C(203)-C(202)	111.4(10)	C(213)-C(214)-C(215)	119.94(8)
C(237)-C(203)-C(204)	122.9(12)	C(215)-C(214)-H(214)	120.0
C(203)-C(204)-H(204)	121.4	C(215)-C(219)-C(218)	120.0
C(203)-C(204)-C(208)	117.3(12)	C(215)-C(219)-C(220)	120.08(7)
C(208)-C(204)-H(204)	121.4	C(218)-C(219)-C(220)	119.92(7)
C(209)-C(205)-H(205)	121.0	C(219)-C(215)-C(214)	119.91(7)
C(237)-C(205)-H(205)	121.0	C(219)-C(215)-C(216)	120.0
C(237)-C(205)-C(209)	118.1(12)	C(216)-C(215)-C(214)	120.03(8)
C(209)-C(208)-C(204)	120.5(7)	C(215)-C(216)-H(216)	120.0

C(215)-C(216)-C(217)	120.0
C(217)-C(216)-H(216)	120.0
C(216)-C(217)-H(217)	120.0
C(300)-C(217)-C(216)	120.0
C(300)-C(217)-H(217)	120.0
C(217)-C(300)-H(300)	120.0
C(218)-C(300)-C(217)	120.0
C(218)-C(300)-H(300)	120.0
C(219)-C(218)-H(218)	120.0
C(300)-C(218)-C(219)	120.0
C(300)-C(218)-H(218)	120.0
C(219)-C(220)-H(220)	120.0
C(219)-C(220)-C(221)	119.95(8)
C(221)-C(220)-H(220)	120.0
C(213)-C(221)-C(222)	108.4(4)
C(220)-C(221)-C(213)	119.95(8)
C(220)-C(221)-C(222)	131.6(4)
O(223)-C(222)-N(211)	126.8(10)
O(223)-C(222)-C(221)	125.6(9)
N(211)-C(222)-C(221)	107.4(8)
N(211)-C(225)-H(225)	108.1
N(211)-C(225)-C(226)	110.5(8)
N(211)-C(225)-C(250)	111.9(10)
C(226)-C(225)-H(225)	108.1
C(226)-C(225)-C(250)	110.0(9)
C(250)-C(225)-H(225)	108.1
O(227)-C(226)-C(225)	109.4(9)
N(63)-C(226)-O(227)	128.5(10)
N(63)-C(226)-C(225)	122.1(10)
C(103)-C(229)-H(229)	120.3
C(124)-C(229)-C(103)	119.5(10)
C(124)-C(229)-H(229)	120.3
O(231)-C(230)-N(126)	126.8(11)
O(231)-C(230)-C(124)	126.0(10)
N(126)-C(230)-C(124)	107.1(9)
C(121)-C(232)-C(123)	129.5(10)
C(121)-C(232)-C(124)	121.2(11)
C(124)-C(232)-C(123)	109.3(10)
C(90)-C(233)-C(102)	106.6(11)
C(90)-C(233)-H(23C)	110.4
C(90)-C(233)-H(23D)	110.4
C(102)-C(233)-H(23C)	110.4
C(102)-C(233)-H(23D)	110.4
H(23C)-C(233)-H(23D)	108.6
C(91)-C(234)-C(96)	106.7(10)
C(153)-C(234)-C(91)	123.0(11)
C(153)-C(234)-C(96)	130.4(11)
C(203)-C(237)-C(201)	107.4(11)
C(203)-C(237)-C(205)	120.0(11)
C(205)-C(237)-C(201)	132.6(13)
O(247)-C(241)-C(244)	118.9(9)
N(246)-C(241)-O(247)	121.2(9)
N(246)-C(241)-C(244)	119.6(9)
H(24C)-C(242)-H(24D)	106.9
C(243)-C(242)-H(24C)	107.4
C(243)-C(242)-H(24D)	107.4
C(245)-C(242)-H(24C)	107.4
C(245)-C(242)-H(24D)	107.4
C(245)-C(242)-C(243)	119.7(11)
C(242)-C(243)-H(24E)	108.1
C(242)-C(243)-H(24F)	108.1
C(242)-C(243)-C(244)	116.8(11)
H(24E)-C(243)-H(24F)	107.3
C(244)-C(243)-H(24E)	108.1
C(244)-C(243)-H(24F)	108.1
N(115)-C(244)-C(241)	110.4(9)

N(115)-C(244)-H(244)	100.3
C(241)-C(244)-H(244)	100.3
C(243)-C(244)-N(115)	120.5(10)
C(243)-C(244)-C(241)	119.7(11)
C(243)-C(244)-H(244)	100.3
N(246)-C(245)-H(24G)	108.6
N(246)-C(245)-H(24H)	108.6
C(242)-C(245)-N(246)	114.5(9)
C(242)-C(245)-H(24G)	108.6
C(242)-C(245)-H(24H)	108.6
H(24G)-C(245)-H(24H)	107.6
C(128)-C(248)-C(160)	109.4(10)
C(128)-C(248)-H(24I)	109.8
C(128)-C(248)-H(24J)	109.8
C(160)-C(248)-H(24I)	109.8
C(160)-C(248)-H(24J)	109.8
H(24I)-C(248)-H(24J)	108.2
C(225)-C(250)-H(25A)	111.2
C(225)-C(250)-H(25B)	111.2
H(25A)-C(250)-H(25B)	109.2
C(252)-C(250)-C(225)	102.6(10)
C(252)-C(250)-H(25A)	111.2
C(252)-C(250)-H(25B)	111.2
N(63)-C(251)-H(25C)	108.9
N(63)-C(251)-H(25D)	108.9
N(63)-C(251)-C(252)	113.3(10)
H(25C)-C(251)-H(25D)	107.7
C(252)-C(251)-H(25C)	108.9
C(252)-C(251)-H(25D)	108.9
C(250)-C(252)-H(25E)	110.7
C(250)-C(252)-H(25F)	110.7
C(251)-C(252)-C(250)	105.3(10)
C(251)-C(252)-H(25E)	110.7
C(251)-C(252)-H(25F)	110.7
H(25E)-C(252)-H(25F)	108.8
N(277)-C(253)-H(25G)	109.5
N(277)-C(253)-H(25H)	109.5
N(277)-C(253)-H(25I)	109.5
H(25G)-C(253)-H(25H)	109.5
H(25G)-C(253)-H(25I)	109.5
H(25H)-C(253)-H(25I)	109.5
C(185)-C(257)-C(189)	119.97(7)
C(185)-C(257)-H(257)	120.0
C(189)-C(257)-H(257)	120.0
C(163)-C(259)-C(161)	106.1(8)
C(167)-C(259)-C(161)	130.9(8)
C(167)-C(259)-C(163)	122.6(9)
H(26C)-C(260)-H(26D)	108.5
C(261)-C(260)-H(26C)	110.1
C(261)-C(260)-H(26D)	110.1
C(262)-C(260)-H(26C)	110.1
C(262)-C(260)-H(26D)	110.1
C(262)-C(260)-C(261)	107.8(9)
C(173)-C(261)-C(260)	102.1(9)
C(173)-C(261)-H(26E)	111.4
C(173)-C(261)-H(26F)	111.4
C(260)-C(261)-H(26E)	111.4
C(260)-C(261)-H(26F)	111.4
H(26E)-C(261)-H(26F)	109.2
N(175)-C(262)-C(260)	114.2(9)
N(175)-C(262)-H(26G)	108.7
N(175)-C(262)-H(26H)	108.7
C(260)-C(262)-H(26G)	108.7
C(260)-C(262)-H(26H)	108.7
H(26G)-C(262)-H(26H)	107.6
C(45)-C(263)-H(26A)	109.3

C(45)-C(263)-H(26B)	109.3	O(276)-C(275)-H(275)	117.0
C(47)-C(263)-C(45)	111.8(9)	N(277)-C(275)-H(275)	117.0
C(47)-C(263)-H(26A)	109.3	O(279)-C(280)-N(278)	122.3(12)
C(47)-C(263)-H(26B)	109.3	O(279)-C(280)-H(280)	118.9
H(26A)-C(263)-H(26B)	107.9	N(278)-C(280)-H(280)	118.9
N(199)-C(267)-C(197)	113.5(10)	N(278)-C(281)-H(28G)	109.5
N(199)-C(267)-H(267)	104.2	N(278)-C(281)-H(28H)	109.5
C(194)-C(267)-N(199)	113.4(10)	N(278)-C(281)-H(28I)	109.5
C(194)-C(267)-C(197)	115.6(11)	H(28G)-C(281)-H(28H)	109.5
C(194)-C(267)-H(267)	104.2	H(28G)-C(281)-H(28I)	109.5
C(197)-C(267)-H(267)	104.2	H(28H)-C(281)-H(28I)	109.5
C(133)-C(269)-H(26I)	110.7	N(278)-C(282)-H(28J)	109.5
C(133)-C(269)-H(26J)	110.7	N(278)-C(282)-H(28K)	109.5
C(148)-C(269)-C(133)	105.3(9)	N(278)-C(282)-H(28L)	109.5
C(148)-C(269)-H(26I)	110.7	H(28J)-C(282)-H(28K)	109.5
C(148)-C(269)-H(26J)	110.7	H(28J)-C(282)-H(28L)	109.5
H(26I)-C(269)-H(26J)	108.8	H(28K)-C(282)-H(28L)	109.5
O(271)-C(270)-N(272)	126.0(11)	O(288)-C(283)-N(287)	120.6(10)
O(271)-C(270)-H(270)	117.0	O(288)-C(283)-H(283)	119.7
N(272)-C(270)-H(270)	117.0	N(287)-C(283)-H(283)	119.7
N(272)-C(273)-H(27A)	109.5	N(287)-C(284)-H(28A)	109.5
N(272)-C(273)-H(27B)	109.5	N(287)-C(284)-H(28B)	109.5
N(272)-C(273)-H(27C)	109.5	N(287)-C(284)-H(28C)	109.5
H(27A)-C(273)-H(27B)	109.5	H(28A)-C(284)-H(28B)	109.5
H(27A)-C(273)-H(27C)	109.5	H(28A)-C(284)-H(28C)	109.5
H(27B)-C(273)-H(27C)	109.5	H(28B)-C(284)-H(28C)	109.5
N(272)-C(274)-H(27D)	109.5	N(287)-C(285)-H(28D)	109.5
N(272)-C(274)-H(27E)	109.5	N(287)-C(285)-H(28E)	109.5
N(272)-C(274)-H(27F)	109.5	N(287)-C(285)-H(28F)	109.5
H(27D)-C(274)-H(27E)	109.5	H(28D)-C(285)-H(28E)	109.5
H(27D)-C(274)-H(27F)	109.5	H(28D)-C(285)-H(28F)	109.5
H(27E)-C(274)-H(27F)	109.5	H(28E)-C(285)-H(28F)	109.5
O(276)-C(275)-N(277)	126.0(18)	N(304)-C(286)-H(28M)	109.5

N(304)-C(286)-H(28N)	109.5
N(304)-C(286)-H(28O)	109.5
H(28M)-C(286)-H(28N)	109.5
H(28M)-C(286)-H(28O)	109.5
H(28N)-C(286)-H(28O)	109.5
O(291)-C(289)-N(294)	124.5(13)
O(291)-C(289)-H(289)	117.7
N(294)-C(289)-H(289)	117.7
O(292)-C(293)-N(290)	120.1(12)
O(292)-C(293)-H(293)	120.0
N(290)-C(293)-H(293)	120.0
N(294)-C(295)-H(29G)	109.5
N(294)-C(295)-H(29H)	109.5
N(294)-C(295)-H(29I)	109.5
H(29G)-C(295)-H(29H)	109.5
H(29G)-C(295)-H(29I)	109.5
H(29H)-C(295)-H(29I)	109.5
N(294)-C(296)-H(29J)	109.5
N(294)-C(296)-H(29K)	109.5
N(294)-C(296)-H(29L)	109.5
H(29J)-C(296)-H(29K)	109.5
H(29J)-C(296)-H(29L)	109.5
H(29K)-C(296)-H(29L)	109.5
N(290)-C(297)-H(29A)	109.5
N(290)-C(297)-H(29B)	109.5
N(290)-C(297)-H(29C)	109.5
H(29A)-C(297)-H(29B)	109.5
H(29A)-C(297)-H(29C)	109.5
H(29B)-C(297)-H(29C)	109.5
N(290)-C(298)-H(29D)	109.5
N(290)-C(298)-H(29E)	109.5
N(290)-C(298)-H(29F)	109.5
H(29D)-C(298)-H(29E)	109.5
H(29D)-C(298)-H(29F)	109.5
H(29E)-C(298)-H(29F)	109.5
N(304)-C(299)-H(29M)	109.5
N(304)-C(299)-H(29N)	109.5
N(304)-C(299)-H(29O)	109.5
H(29M)-C(299)-H(29N)	109.5
H(29M)-C(299)-H(29O)	109.5
H(29N)-C(299)-H(29O)	109.5
O(305)-C(303)-N(304)	119.4(12)
O(305)-C(303)-H(303)	120.3
N(304)-C(303)-H(303)	120.3

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for Rh2(S-BPTPI)4. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh(1)	39(1)	45(1)	32(1)	3(1)	6(1)	2(1)
Rh(2)	30(1)	47(1)	31(1)	0(1)	2(1)	2(1)
Rh(3)	29(1)	42(1)	37(1)	-2(1)	3(1)	1(1)
Rh(4)	40(1)	45(1)	31(1)	5(1)	2(1)	-4(1)
Rh(5)	39(1)	51(1)	44(1)	-4(1)	-1(1)	5(1)
Rh(6)	39(1)	51(1)	45(1)	-2(1)	-3(1)	4(1)
O(18)	63(4)	58(5)	48(4)	-3(3)	19(4)	1(4)
O(19)	73(5)	31(4)	54(4)	3(3)	7(3)	-12(4)
O(34)	46(4)	45(4)	60(4)	-6(3)	18(3)	-5(3)
O(35)	64(5)	58(5)	70(5)	-15(4)	32(4)	-8(4)
O(57)	82(6)	109(7)	52(4)	18(4)	16(4)	-23(5)
O(58)	47(4)	70(5)	72(5)	7(4)	19(4)	-16(4)
O(59)	28(3)	52(4)	51(4)	17(3)	6(3)	4(3)
O(62)	30(3)	58(4)	35(3)	3(3)	5(3)	-4(3)
O(64)	31(3)	50(4)	36(3)	4(3)	-2(3)	3(3)
O(72)	39(4)	54(5)	71(5)	-8(4)	2(3)	-3(3)
O(73)	41(4)	66(5)	57(4)	14(4)	2(3)	9(4)
O(74)	67(5)	51(5)	98(6)	10(5)	-28(5)	4(4)
O(98)	77(5)	80(6)	52(4)	-15(4)	-12(4)	21(5)
O(99)	70(6)	129(8)	67(5)	-34(5)	10(4)	-8(6)
O(100)	54(4)	49(5)	58(4)	-6(3)	-16(3)	7(4)
O(114)	82(6)	72(6)	79(5)	-8(4)	20(5)	-8(5)
O(122)	60(5)	87(6)	59(5)	-7(4)	-12(4)	5(4)
O(130)	59(5)	52(5)	54(4)	-4(3)	-3(3)	20(4)
O(142)	57(4)	58(5)	83(5)	11(4)	36(4)	29(4)
O(143)	66(5)	80(5)	45(4)	1(4)	2(4)	16(4)
O(146)	25(3)	54(4)	40(3)	-2(3)	0(2)	3(3)

O(158)	70(5)	108(7)	82(5)	-44(5)	-14(4)	63(5)
O(170)	56(5)	55(5)	101(6)	-22(4)	-7(4)	9(4)
O(171)	46(4)	44(4)	67(4)	-2(3)	3(3)	6(3)
O(176)	43(4)	36(4)	69(4)	-2(3)	4(3)	11(3)
O(191)	120(8)	101(7)	66(5)	8(5)	27(5)	14(6)
O(192)	78(6)	74(6)	65(5)	-6(4)	-9(4)	7(5)
O(193)	43(4)	66(5)	29(3)	9(3)	4(3)	11(4)
O(200)	68(5)	38(4)	38(3)	-2(3)	0(3)	-18(4)
O(206)	116(8)	97(7)	60(5)	-4(5)	15(5)	38(6)
O(207)	89(6)	80(6)	52(4)	0(4)	20(4)	-21(5)
O(223)	73(5)	42(5)	97(6)	11(4)	11(5)	6(4)
O(224)	105(6)	46(5)	58(5)	-10(4)	-7(4)	-12(4)
O(227)	79(5)	40(4)	38(3)	8(3)	7(3)	7(4)
O(231)	69(5)	98(7)	54(4)	14(4)	-12(4)	10(5)
O(247)	34(3)	48(4)	54(4)	-11(3)	7(3)	0(3)
O(271)	54(4)	63(5)	55(4)	11(3)	6(3)	-4(4)
O(276)	56(5)	87(6)	67(5)	-5(5)	38(4)	-4(4)
O(279)	62(5)	62(5)	60(4)	-8(4)	6(4)	-4(4)
O(288)	43(4)	91(6)	42(4)	-18(4)	5(3)	2(4)
O(291)	51(4)	58(5)	98(5)	-17(5)	-17(4)	20(4)
O(292)	34(3)	105(6)	38(3)	2(4)	4(3)	9(4)
O(305)	142(10)	107(8)	117(8)	-32(7)	25(8)	36(8)
O(306)	76(6)	77(6)	96(6)	-18(5)	2(5)	-8(5)
O(307)	72(6)	104(8)	147(9)	56(7)	24(6)	5(6)
O(308)	61(13)	190(40)	116(17)	53(17)	-44(11)	8(17)
O(309)	57(6)	246(14)	125(8)	29(9)	-35(6)	-60(8)
N(7)	45(5)	37(5)	39(4)	-6(3)	14(3)	-1(4)
N(33)	61(5)	42(5)	20(3)	3(3)	1(3)	10(4)
N(56)	37(4)	54(5)	59(4)	14(4)	9(4)	-9(4)
N(60)	40(4)	76(6)	38(4)	13(4)	-4(3)	-10(4)
N(61)	50(4)	33(4)	39(4)	8(3)	6(3)	12(3)
N(63)	74(5)	41(4)	28(3)	14(3)	9(4)	3(4)
N(65)	35(4)	52(5)	39(4)	9(3)	10(3)	5(4)

N(71)	40(4)	60(5)	30(3)	-7(3)	2(3)	1(4)
N(75)	37(5)	56(6)	62(5)	-5(4)	-13(4)	11(4)
N(97)	37(4)	80(7)	54(5)	-18(5)	2(4)	-13(5)
N(101)	60(5)	48(5)	47(4)	-5(4)	-11(4)	7(4)
N(115)	46(6)	74(7)	78(7)	-26(6)	23(5)	7(5)
N(126)	46(5)	57(6)	48(5)	-1(4)	-3(4)	20(4)
N(129)	47(4)	63(5)	46(4)	-16(4)	9(4)	2(4)
N(141)	53(5)	58(6)	70(6)	-20(5)	0(5)	6(5)
N(145)	20(3)	47(4)	51(4)	-3(3)	5(3)	7(3)
N(172)	42(5)	33(5)	55(5)	-10(4)	2(4)	4(4)
N(175)	31(4)	61(5)	42(4)	0(4)	-2(3)	-11(4)
N(182)	46(4)	52(5)	43(4)	-4(3)	-9(3)	4(4)
N(183)	58(5)	72(6)	35(4)	2(4)	-2(4)	28(4)
N(198)	80(6)	68(6)	40(4)	27(4)	12(4)	-18(5)
N(199)	81(6)	76(6)	37(4)	-7(4)	6(4)	-19(5)
N(211)	83(7)	37(6)	54(5)	6(4)	8(5)	18(5)
N(246)	38(4)	59(5)	42(4)	-2(4)	9(3)	-12(4)
N(272)	70(6)	85(7)	87(6)	20(5)	12(5)	-20(5)
N(277)	310(30)	121(14)	199(18)	13(12)	200(20)	1(15)
N(278)	55(6)	89(8)	81(7)	-30(6)	16(5)	-2(6)
N(287)	59(6)	48(6)	55(5)	-16(4)	0(4)	-1(4)
N(290)	57(5)	116(7)	48(5)	16(5)	14(4)	41(5)
N(294)	68(6)	78(7)	108(7)	32(6)	-8(6)	7(6)
N(304)	64(6)	52(6)	69(6)	-12(5)	19(5)	-8(5)
C(8)	34(5)	68(8)	41(5)	-4(5)	8(4)	-4(5)
C(9)	57(6)	59(7)	29(4)	-6(5)	8(4)	-4(6)
C(10)	35(5)	55(7)	40(5)	1(4)	18(4)	14(5)
C(11)	36(5)	75(8)	48(6)	11(5)	19(4)	-3(5)
C(15)	43(5)	31(5)	40(5)	-14(4)	12(4)	8(4)
C(14)	40(6)	60(7)	57(6)	12(5)	4(5)	7(5)
C(13)	45(6)	79(9)	65(7)	-4(6)	12(5)	-16(6)
C(41)	52(6)	60(8)	71(7)	0(6)	20(5)	15(6)
C(12)	56(7)	54(8)	68(7)	-8(6)	17(5)	1(6)

C(16)	34(5)	46(6)	38(5)	-9(4)	13(4)	-1(4)
C(17)	69(6)	30(5)	29(4)	0(4)	9(5)	6(5)
C(20)	39(4)	45(5)	30(4)	5(4)	5(3)	-8(4)
C(21)	43(5)	57(6)	40(4)	16(4)	9(4)	-6(4)
C(22)	21(4)	54(7)	50(5)	8(5)	6(4)	-1(4)
C(23)	31(4)	84(7)	40(5)	6(5)	10(4)	-4(5)
C(24)	49(5)	82(7)	44(5)	-16(5)	5(4)	0(5)
C(26)	47(6)	88(9)	45(6)	-4(6)	14(5)	-15(6)
C(27)	47(6)	50(7)	48(5)	10(5)	17(5)	11(5)
C(25)	52(6)	69(8)	53(6)	-33(6)	-1(5)	20(6)
C(43)	31(5)	70(8)	36(5)	-22(5)	12(4)	-27(5)
C(28)	94(9)	63(8)	56(6)	12(6)	39(6)	-5(7)
C(42)	47(6)	63(7)	38(5)	-12(5)	13(4)	-1(5)
C(210)	73(8)	57(8)	54(6)	-23(5)	15(6)	-13(6)
C(29)	38(5)	16(5)	45(5)	3(4)	12(4)	0(4)
C(30)	39(5)	108(10)	30(5)	-7(5)	12(4)	-6(6)
C(31)	31(5)	41(6)	38(5)	-17(4)	10(4)	-9(4)
C(32)	36(5)	66(8)	35(5)	-7(5)	-1(4)	12(5)
C(36)	40(5)	69(6)	33(4)	2(4)	-10(4)	3(5)
C(37)	33(4)	44(5)	32(4)	4(4)	4(3)	0(4)
C(38)	46(5)	36(5)	24(4)	5(3)	-6(3)	6(4)
C(39)	43(5)	54(6)	31(4)	-5(4)	-2(4)	2(4)
C(40)	48(5)	56(6)	39(4)	-4(4)	-3(4)	-7(5)
C(44)	48(5)	62(6)	36(4)	1(4)	7(4)	-8(5)
C(45)	64(6)	49(6)	45(5)	19(4)	0(4)	-9(5)
C(46)	43(5)	75(7)	37(4)	13(4)	-9(4)	-18(5)
C(47)	47(5)	62(6)	56(5)	15(5)	-6(4)	-1(5)
C(48)	42(4)	51(6)	51(5)	11(4)	18(4)	12(4)
C(49)	72(6)	60(6)	60(5)	11(5)	25(5)	-14(5)
C(50)	50(5)	50(6)	58(5)	8(4)	3(4)	-5(4)
C(51)	42(4)	43(5)	63(5)	13(4)	10(4)	0(4)
C(52)	57(5)	42(6)	62(5)	24(4)	21(5)	3(4)
C(53)	46(5)	45(5)	78(6)	11(5)	12(4)	17(4)

C(228)	54(5)	47(6)	88(6)	9(5)	15(5)	5(5)
C(249)	36(5)	40(6)	108(7)	13(5)	18(5)	0(4)
C(150)	63(6)	54(6)	115(8)	19(6)	13(6)	-6(5)
C(149)	54(6)	52(6)	123(8)	12(6)	15(6)	18(5)
C(54)	50(6)	51(6)	103(7)	2(6)	-3(5)	3(5)
C(55)	62(6)	47(6)	62(6)	8(5)	16(5)	2(5)
C(66)	35(5)	77(7)	53(5)	0(5)	-7(4)	12(5)
C(67)	39(5)	68(7)	79(6)	-7(5)	-6(5)	1(5)
C(68)	42(5)	79(7)	57(5)	4(5)	-11(4)	-23(5)
C(69)	34(5)	50(6)	76(6)	-1(5)	-16(4)	-3(4)
C(70)	25(4)	49(6)	57(5)	-4(4)	-7(4)	-3(4)
C(76)	85(9)	81(9)	43(6)	-11(6)	-29(6)	-13(7)
C(77)	62(7)	39(6)	79(7)	13(5)	-30(6)	-6(6)
C(78)	27(4)	61(7)	50(5)	-2(5)	-5(4)	7(4)
C(79)	51(6)	21(5)	87(8)	4(5)	-8(6)	18(5)
C(80)	45(5)	22(5)	50(5)	-3(4)	3(4)	-3(4)
C(81)	40(5)	39(6)	72(7)	-10(5)	2(5)	-3(5)
C(84)	65(7)	40(6)	46(5)	-9(5)	-13(5)	22(5)
C(83)	35(5)	48(7)	63(6)	-5(5)	-12(4)	0(5)
C(82)	38(5)	37(6)	75(7)	-5(5)	-4(5)	-4(4)
C(240)	50(6)	25(6)	90(8)	24(5)	-1(6)	6(5)
C(86)	65(7)	30(6)	58(6)	10(5)	-1(5)	-2(5)
C(85)	68(7)	49(7)	45(5)	-12(5)	-10(5)	3(6)
C(87)	55(6)	33(5)	39(5)	20(4)	8(4)	9(5)
C(88)	55(6)	55(6)	40(4)	0(4)	-8(4)	6(5)
C(89)	55(5)	69(6)	43(5)	-8(5)	-7(4)	22(5)
C(90)	90(7)	95(8)	65(6)	-25(6)	-20(6)	20(7)
C(91)	46(5)	68(6)	53(5)	-18(5)	-15(4)	0(5)
C(92)	49(5)	70(7)	68(6)	-26(5)	1(5)	9(5)
C(95)	37(6)	82(9)	37(5)	-4(5)	-3(4)	-14(6)
C(96)	32(5)	91(10)	52(6)	-6(6)	-9(5)	1(6)
C(102)	93(7)	71(7)	47(5)	-1(5)	-19(5)	26(6)
C(104)	36(5)	52(6)	76(6)	-26(5)	3(5)	-8(5)

C(105)	42(5)	59(6)	53(5)	-17(4)	-18(4)	2(4)
C(106)	47(5)	95(7)	55(5)	-35(5)	-22(4)	24(5)
C(107)	65(6)	114(8)	59(6)	3(6)	-2(5)	29(6)
C(108)	83(6)	57(6)	48(5)	-14(4)	2(5)	26(5)
C(109)	62(5)	38(5)	41(4)	-6(4)	-16(4)	9(4)
C(111)	55(6)	65(6)	54(5)	-14(5)	-12(4)	3(5)
C(112)	76(6)	49(6)	67(6)	0(5)	6(5)	34(5)
C(113)	102(8)	84(8)	76(7)	-18(6)	16(6)	18(7)
C(156)	110(8)	54(6)	63(6)	0(5)	27(6)	40(6)
C(110)	40(5)	57(6)	55(5)	-10(4)	-18(4)	17(4)
C(120)	60(5)	69(6)	56(5)	-4(5)	9(4)	-2(5)
C(103)	71(6)	58(6)	50(5)	14(4)	-3(4)	-6(5)
C(117)	75(7)	83(7)	72(6)	-12(6)	4(6)	-3(6)
C(116)	82(7)	90(7)	66(6)	1(6)	10(5)	-1(6)
C(118)	64(6)	79(7)	78(7)	-6(6)	17(5)	-2(6)
C(119)	71(6)	72(7)	80(7)	15(6)	19(6)	-12(6)
C(121)	53(5)	71(6)	45(5)	10(5)	10(4)	-11(5)
C(123)	50(6)	99(10)	28(5)	26(5)	2(5)	-26(6)
C(124)	58(6)	81(7)	33(4)	5(4)	7(4)	-5(5)
C(127)	36(5)	62(6)	51(5)	1(5)	11(4)	-5(5)
C(128)	57(6)	77(7)	62(6)	19(5)	3(5)	0(6)
C(131)	39(5)	69(6)	42(5)	9(4)	-6(4)	-6(5)
C(132)	32(4)	35(5)	47(5)	-8(4)	-6(4)	5(4)
C(133)	52(5)	41(5)	57(5)	-7(4)	-19(4)	9(5)
C(134)	35(5)	26(5)	64(6)	6(5)	7(5)	8(4)
C(135)	54(5)	49(5)	47(5)	-15(4)	23(4)	2(4)
C(136)	55(5)	35(5)	48(5)	-10(4)	0(4)	2(4)
C(137)	29(5)	27(5)	77(7)	-7(5)	7(5)	6(4)
C(138)	50(5)	61(6)	36(4)	-12(4)	2(4)	14(5)
C(139)	57(5)	64(6)	46(5)	-15(4)	12(4)	17(5)
C(151)	68(6)	60(6)	45(5)	4(4)	17(4)	14(5)
C(268)	96(7)	56(7)	86(7)	3(5)	33(6)	26(6)
C(152)	99(7)	51(6)	63(6)	5(5)	2(6)	33(6)

C(235)	83(7)	53(6)	67(6)	-8(5)	-16(5)	12(5)
C(140)	68(6)	53(6)	78(6)	-14(5)	-8(5)	23(5)
C(144)	73(6)	57(6)	51(5)	2(5)	35(5)	24(5)
C(147)	25(4)	53(6)	65(5)	-12(5)	1(4)	-4(4)
C(148)	28(4)	69(6)	71(6)	-15(5)	-7(4)	8(5)
C(153)	70(6)	77(7)	57(6)	-1(5)	7(5)	6(6)
C(154)	74(6)	76(6)	57(5)	-3(5)	-11(5)	2(5)
C(264)	80(7)	85(7)	70(6)	7(6)	-21(6)	1(6)
C(254)	91(8)	102(8)	74(7)	12(6)	-16(6)	-3(7)
C(238)	90(8)	106(9)	91(8)	-11(7)	-19(6)	28(7)
C(302)	77(7)	93(8)	82(7)	-14(6)	-14(6)	23(6)
C(93)	65(6)	76(6)	71(6)	-13(5)	-15(5)	12(5)
C(155)	320(40)	320(40)	140(20)	-60(20)	130(20)	-240(30)
C(157)	52(6)	80(8)	83(7)	-55(6)	-29(6)	23(6)
C(159)	64(6)	77(7)	47(5)	-4(5)	9(5)	14(6)
C(160)	57(6)	88(7)	63(6)	7(6)	14(5)	13(6)
C(161)	43(6)	16(5)	95(8)	0(5)	-1(6)	15(4)
C(162)	39(5)	30(6)	54(6)	-6(4)	-14(4)	9(4)
C(163)	63(7)	45(7)	64(7)	11(5)	-22(6)	-9(6)
C(164)	63(7)	46(7)	93(9)	29(6)	-31(7)	-5(6)
C(165)	85(9)	77(9)	55(7)	6(6)	-5(6)	-17(8)
C(166)	48(6)	62(8)	56(6)	0(5)	10(5)	3(6)
C(168)	80(9)	101(11)	74(8)	29(8)	29(7)	-21(8)
C(236)	82(9)	79(9)	45(6)	-18(6)	9(6)	-5(7)
C(169)	72(9)	115(12)	62(7)	21(7)	-25(7)	-40(8)
C(258)	90(10)	66(9)	109(11)	23(8)	27(9)	-2(8)
C(167)	34(5)	56(7)	86(8)	8(6)	-7(5)	4(5)
C(173)	30(4)	62(6)	56(5)	-6(5)	1(4)	1(4)
C(174)	24(4)	52(6)	51(5)	-3(4)	-5(4)	-2(4)
C(177)	65(6)	66(6)	35(4)	-4(4)	-4(4)	20(5)
C(178)	50(5)	39(5)	33(4)	-10(4)	-12(4)	9(4)
C(179)	67(6)	67(7)	69(6)	-6(5)	-5(5)	21(6)
C(180)	81(7)	93(8)	78(7)	4(6)	-19(6)	24(6)

C(181)	63(6)	74(7)	43(5)	7(5)	-9(5)	10(5)
C(184)	51(5)	84(7)	33(5)	-4(5)	-1(4)	7(5)
C(185)	67(6)	95(7)	41(5)	5(5)	-6(5)	22(5)
C(186)	55(5)	95(7)	34(4)	1(5)	-8(4)	17(5)
C(187)	76(7)	83(7)	46(5)	4(5)	11(5)	19(6)
C(188)	86(7)	117(8)	42(5)	5(6)	5(5)	23(7)
C(190)	95(8)	128(9)	83(7)	-18(7)	17(6)	20(8)
C(256)	87(7)	112(8)	68(6)	-9(6)	19(6)	17(6)
C(189)	97(7)	105(8)	78(6)	-16(6)	13(6)	13(7)
C(255)	105(8)	104(9)	114(8)	-31(7)	16(7)	16(8)
C(125)	107(9)	122(10)	95(8)	-11(8)	12(7)	31(8)
C(94)	96(8)	138(10)	74(7)	-10(7)	10(7)	35(8)
C(194)	95(7)	31(5)	36(5)	9(4)	13(5)	-12(5)
C(195)	94(8)	99(8)	45(5)	3(6)	5(6)	-27(7)
C(196)	119(8)	85(8)	61(6)	-7(6)	21(6)	-37(7)
C(197)	100(8)	96(8)	57(6)	0(6)	16(6)	-24(7)
C(201)	73(6)	86(7)	36(5)	0(5)	4(5)	-33(6)
C(202)	90(7)	85(7)	43(5)	-11(5)	-4(5)	-22(6)
C(203)	64(6)	114(7)	31(4)	-4(5)	5(4)	-32(6)
C(204)	78(7)	141(9)	42(5)	-14(6)	9(5)	-28(7)
C(205)	82(7)	120(8)	33(5)	-5(5)	9(5)	-50(6)
C(208)	65(6)	161(9)	34(5)	-3(6)	2(5)	-44(6)
C(209)	79(6)	139(8)	46(5)	15(6)	2(5)	-52(6)
C(301)	88(7)	136(9)	50(6)	11(6)	-1(5)	-65(7)
C(239)	86(8)	163(10)	91(7)	29(8)	-7(7)	-57(8)
C(266)	78(8)	173(11)	63(7)	-1(7)	5(6)	-55(7)
C(265)	68(6)	188(10)	44(5)	6(7)	-9(5)	-56(7)
C(212)	109(11)	18(6)	57(6)	2(5)	11(7)	21(6)
C(213)	51(6)	31(6)	63(6)	1(5)	22(5)	11(5)
C(214)	67(7)	36(7)	84(8)	-4(6)	-32(6)	29(6)
C(219)	60(7)	55(7)	38(5)	3(5)	6(5)	22(6)
C(215)	70(7)	48(7)	45(6)	7(5)	-3(5)	13(6)
C(216)	69(7)	54(7)	41(5)	8(5)	-1(5)	38(6)

C(217)	63(7)	39(6)	64(7)	22(5)	25(6)	9(5)
C(300)	68(8)	121(12)	57(7)	7(8)	11(6)	30(8)
C(218)	61(7)	45(7)	51(6)	-3(5)	-2(5)	-1(5)
C(220)	55(6)	25(5)	59(6)	-5(4)	-1(5)	-3(5)
C(221)	62(7)	26(5)	59(6)	14(4)	-5(5)	2(5)
C(222)	62(6)	21(5)	51(6)	4(4)	-2(5)	-7(5)
C(225)	94(7)	37(6)	67(6)	12(5)	43(5)	11(5)
C(226)	68(6)	39(5)	50(5)	8(4)	8(5)	12(5)
C(229)	70(6)	77(7)	49(5)	9(5)	5(5)	5(6)
C(230)	54(7)	66(8)	42(6)	0(5)	2(5)	9(6)
C(232)	53(5)	80(7)	48(5)	1(5)	-7(4)	-2(5)
C(233)	107(8)	107(8)	53(6)	-15(6)	-16(6)	34(7)
C(234)	56(6)	64(7)	59(6)	-7(5)	-8(5)	-5(5)
C(237)	78(6)	93(7)	30(4)	-6(4)	11(4)	-39(6)
C(241)	44(5)	65(7)	58(5)	-21(5)	16(4)	0(5)
C(242)	60(6)	98(8)	120(8)	-44(7)	-9(6)	-9(6)
C(243)	63(6)	101(8)	108(8)	-56(7)	16(6)	4(6)
C(244)	50(6)	89(7)	82(6)	-37(6)	0(5)	-12(6)
C(245)	54(5)	66(7)	62(6)	-8(5)	-17(5)	13(5)
C(248)	66(6)	93(7)	56(6)	31(6)	24(5)	4(6)
C(250)	111(8)	48(6)	102(7)	13(6)	37(7)	17(6)
C(251)	76(6)	47(6)	64(6)	12(5)	12(5)	15(5)
C(252)	87(7)	54(6)	94(7)	6(6)	32(6)	14(6)
C(253)	45(17)	420(80)	110(30)	30(40)	35(17)	80(30)
C(257)	81(7)	103(8)	47(5)	4(5)	0(5)	-8(7)
C(259)	32(5)	31(5)	50(5)	10(4)	-5(4)	9(4)
C(260)	60(6)	72(7)	77(6)	0(6)	27(5)	-11(6)
C(261)	63(6)	72(7)	95(7)	-12(6)	25(6)	-11(6)
C(262)	40(5)	74(6)	54(5)	-11(5)	20(4)	-22(5)
C(263)	74(7)	54(7)	78(6)	12(5)	4(6)	-1(5)
C(267)	109(8)	88(7)	47(5)	-14(5)	-7(6)	-15(7)
C(269)	43(5)	62(6)	66(6)	-14(5)	-17(5)	14(5)
C(270)	67(6)	77(7)	49(5)	14(5)	5(5)	-25(6)

C(273)	149(13)	127(13)	110(11)	40(9)	93(10)	43(11)
C(274)	74(9)	154(14)	158(14)	46(12)	30(9)	-15(10)
C(275)	86(10)	96(12)	103(11)	-21(10)	33(9)	-34(9)
C(280)	50(7)	99(10)	63(7)	4(7)	-5(6)	24(7)
C(281)	25(7)	220(20)	260(30)	-9(19)	4(11)	-20(10)
C(282)	118(14)	96(13)	170(17)	-62(12)	31(12)	-30(11)
C(283)	28(5)	45(7)	80(7)	-3(6)	23(5)	7(5)
C(284)	61(7)	66(8)	53(6)	-25(5)	0(5)	11(6)
C(285)	55(7)	93(10)	83(8)	-51(7)	-18(6)	42(7)
C(286)	86(9)	75(10)	103(10)	-24(8)	-20(8)	-11(8)
C(289)	67(7)	80(8)	108(8)	-17(7)	9(6)	12(7)
C(293)	58(6)	113(8)	40(5)	8(5)	12(5)	28(6)
C(295)	84(11)	158(16)	239(19)	15(15)	-9(13)	48(12)
C(296)	108(12)	114(13)	121(12)	-24(11)	16(10)	17(11)
C(297)	62(8)	120(11)	106(10)	29(9)	-6(7)	7(8)
C(298)	119(12)	206(16)	60(8)	-50(10)	-26(8)	25(12)
C(299)	52(7)	88(10)	88(9)	-14(7)	-14(7)	18(7)
C(303)	53(7)	79(10)	81(8)	-25(7)	8(6)	-9(7)
O(3)	60(15)	180(40)	210(40)	40(30)	-48(18)	-12(18)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{3}) for Rh2(S-BPTPI)4.

	x	y	z	U(eq)
H(14)	-5435	5213	5593	63
H(13)	-6192	4687	5786	75
H(41)	-5664	4025	5755	74
H(12)	-4377	3889	5530	71
H(16)	-4151	5448	5346	47
H(20)	-1304	5534	4806	46
H(22)	4977	5360	4747	50
H(23A)	218	5379	4276	62
H(23B)	142	4907	4328	62
H(24A)	205	5538	4667	70
H(24B)	802	5138	4658	70
H(26)	3740	4207	5110	72
H(27)	4837	3794	4916	58
H(28)	6182	4917	4555	85
H(42)	6753	4270	4485	59
H(210)	6080	3709	4665	73
H(36A)	1202	5568	5063	57
H(36B)	1093	5226	5267	57
H(37)	2320	5876	5274	44
H(39A)	399	5908	5746	51
H(39B)	310	5437	5686	51
H(40A)	20	5745	5317	57
H(40B)	808	6066	5352	57
H(45)	2652	4683	6560	63
H(46A)	4659	5363	6328	62
H(46B)	4706	5024	6122	62
H(47A)	5015	4666	6480	66

H(47B)	4241	4892	6628	66
H(52)	1351	3627	5745	64
H(249)	-1209	3225	6359	73
H(150)	-1816	2825	6051	92
H(149)	-1102	2781	5674	91
H(54)	218	3138	5606	82
H(55)	-14	3678	6505	68
H(66A)	-7	2162	3408	66
H(66B)	-13	1950	3147	66
H(67A)	-690	1604	3499	75
H(67B)	-179	1347	3297	75
H(68A)	244	1126	3670	71
H(68B)	515	1574	3751	71
H(69)	1420	1113	3368	64
H(80)	4237	398	3701	47
H(81)	3086	1140	4361	61
H(82)	5545	215	3960	60
H(240)	6267	224	4337	66
H(86)	5614	556	4667	61
H(85)	4240	879	4620	65
H(87)	-3148	4118	5274	51
H(89)	2138	1542	2400	67
H(90A)	748	1457	2261	100
H(90B)	320	1455	2528	100
H(92)	3020	12	2574	75
H(10A)	528	2475	2655	85
H(10B)	149	2055	2754	85
H(107)	1537	3207	4373	95
H(111)	-539	4377	4050	70
H(112)	-1368	4325	4409	77
H(113)	-976	3848	4703	105
H(156)	245	3423	4639	91
H(110)	683	4161	3804	61

H(117)	4310	4956	3397	92
H(116)	3762	5617	3383	95
H(118)	2650	5788	3104	88
H(119)	2087	5299	2839	89
H(121)	1984	4602	2694	68
H(128)	2956	3104	2457	78
H(13A)	-238	5090	4985	60
H(13B)	-461	4745	4788	60
H(133)	-2834	4359	3585	60
H(138)	-261	3304	3529	59
H(268)	-510	2520	4362	95
H(152)	746	2154	4242	85
H(235)	1403	2280	3864	81
H(140)	803	2772	3607	80
H(144)	-1590	3070	4284	73
H(14A)	-4538	5064	3955	57
H(14B)	-4445	4679	4128	57
H(14C)	-5095	4481	3775	67
H(14D)	-4321	4682	3617	67
H(153)	743	308	3115	82
H(264)	790	-394	3271	94
H(254)	1388	-1045	3254	106
H(238)	2519	-1195	2976	115
H(302)	3051	-692	2715	101
H(15A)	-1153	5108	6814	396
H(15B)	-286	5366	6880	396
H(15C)	-187	4941	6744	396
H(15D)	4378	2094	2680	75
H(15E)	4853	2470	2807	75
H(16A)	4014	2474	2347	83
H(16B)	5057	2535	2400	83
H(164)	-529	6339	5136	81
H(168)	-3093	7326	5438	102

H(236)	-2566	7192	5829	82
H(169)	-1349	6760	5884	99
H(258)	-660	6464	5547	106
H(167)	-3017	7175	4984	70
H(173)	-1807	6719	4108	59
H(177)	-2488	6052	3368	66
H(17A)	-4142	6011	3908	81
H(17B)	-4484	5612	3774	81
H(18A)	-4819	6127	3496	101
H(18B)	-3871	6343	3535	101
H(18C)	-3881	5962	3163	72
H(18D)	-4075	5559	3316	72
H(188)	-209	5465	2714	98
H(190)	565	5045	2426	122
H(255)	-1337	3971	2614	129
H(125)	-170	3878	2338	129
H(94)	781	4415	2244	123
H(19A)	4291	6385	6275	95
H(19B)	4656	6029	6441	95
H(19C)	3777	6744	6613	106
H(19D)	4771	6597	6680	106
H(19E)	4138	5982	6864	102
H(19F)	3764	6375	7003	102
H(204)	118	5870	7393	104
H(205)	2071	4771	7252	94
H(301)	1246	4378	7544	109
H(239)	87	4312	7825	136
H(266)	-888	4850	7893	126
H(265)	-703	5456	7681	120
H(214)	4931	7565	5390	75
H(216)	5671	7733	5015	66
H(217)	5798	7663	4594	67
H(300)	4736	7291	4378	98

H(218)	3548	6989	4584	63
H(220)	2754	6860	4955	55
H(225)	2597	7083	6042	79
H(229)	4356	4280	3230	79
H(23C)	39	2073	2330	107
H(23D)	1093	2148	2307	107
H(24C)	5438	2946	3505	111
H(24D)	4899	2712	3710	111
H(24E)	4542	3431	3494	109
H(24F)	4360	3287	3766	109
H(244)	3296	3370	3402	89
H(24G)	4786	2293	3429	73
H(24H)	4844	2626	3220	73
H(24I)	4738	3153	2616	86
H(24J)	4367	3187	2344	86
H(25A)	1200	7401	5906	104
H(25B)	870	6983	5786	104
H(25C)	641	6378	6308	75
H(25D)	321	6430	6033	75
H(25E)	1335	7025	6300	94
H(25F)	318	7078	6214	94
H(25G)	-1849	5545	6598	287
H(25H)	-1437	5722	6353	287
H(25I)	-1148	5908	6609	287
H(257)	-2180	4406	2878	92
H(26C)	-813	6556	3749	84
H(26D)	249	6554	3784	84
H(26E)	5	6565	4247	92
H(26F)	-385	6971	4124	92
H(26G)	-318	5888	3724	67
H(26H)	203	5929	3975	67
H(26A)	3821	4236	6527	82
H(26B)	3953	4338	6245	82

H(267)	2518	6394	6751	98
H(26I)	-4160	4005	3622	69
H(26J)	-4122	4006	3914	69
H(270)	4281	6056	5631	77
H(27A)	5970	6251	5276	193
H(27B)	5957	6663	5427	193
H(27C)	5044	6471	5332	193
H(27D)	6353	6005	5902	193
H(27E)	6798	6345	5735	193
H(27F)	6752	5888	5642	193
H(275)	716	5319	6476	114
H(280)	3645	1297	3110	85
H(28G)	5892	1398	2984	249
H(28H)	5575	1329	2710	249
H(28I)	5987	962	2861	249
H(28J)	4021	603	3025	192
H(28K)	4995	505	2922	192
H(28L)	4235	663	2742	192
H(283)	-3472	5841	4553	61
H(28A)	-3953	6278	4854	90
H(28B)	-4964	6429	4858	90
H(28C)	-4252	6649	4688	90
H(28D)	-5428	6220	4279	116
H(28E)	-5798	6404	4528	116
H(28F)	-5865	5930	4478	116
H(28M)	-2391	3557	4799	132
H(28N)	-2921	3306	5001	132
H(28O)	-2828	3131	4732	132
H(289)	1265	3225	3072	102
H(293)	-675	4914	3562	85
H(29G)	-1279	3555	3017	240
H(29H)	-1047	3094	3076	240
H(29I)	-916	3265	2807	240

H(29J)	80	3948	3227	171
H(29K)	-51	4011	2941	171
H(29L)	905	3890	3046	171
H(29A)	1780	5202	3524	144
H(29B)	1906	4723	3536	144
H(29C)	1503	4959	3764	144
H(29D)	-74	4758	3195	193
H(29E)	903	4566	3189	193
H(29F)	768	5036	3135	193
H(29M)	-894	3492	5068	114
H(29N)	-530	3047	5122	114
H(29O)	-1371	3216	5268	114
H(303)	-927	2557	4886	85

Table 6. Torsion angles [°] for Rh2(S-BPTPI)4.

Rh(1)-O(59)-C(44)-N(60)	-22.4(13)
Rh(1)-O(59)-C(44)-C(45)	153.0(6)
Rh(1)-O(200)-C(194)-N(198)	-16.0(14)
Rh(1)-O(200)-C(194)-C(267)	165.2(8)
Rh(1)-O(276)-C(275)-N(277)	173.1(14)
Rh(1)-N(61)-C(38)-O(64)	11.4(12)
Rh(1)-N(61)-C(38)-C(37)	-171.9(6)
Rh(1)-N(61)-C(39)-C(40)	158.8(6)
Rh(1)-N(63)-C(226)-O(227)	-1.7(15)
Rh(1)-N(63)-C(226)-C(225)	177.9(8)
Rh(1)-N(63)-C(251)-C(252)	163.3(8)
Rh(2)-O(146)-C(132)-N(145)	-22.1(12)
Rh(2)-O(146)-C(132)-C(133)	152.9(6)
Rh(2)-O(193)-C(178)-N(182)	-7.3(14)
Rh(2)-O(193)-C(178)-C(177)	164.6(6)
Rh(2)-O(292)-C(293)-N(290)	170.0(9)
Rh(2)-N(65)-C(21)-O(62)	7.9(14)
Rh(2)-N(65)-C(21)-C(20)	-165.6(7)
Rh(2)-N(65)-C(23)-C(24)	160.7(8)
Rh(2)-N(175)-C(174)-O(176)	-7.9(12)
Rh(2)-N(175)-C(174)-C(173)	174.1(7)
Rh(2)-N(175)-C(262)-C(260)	161.8(7)
Rh(3)-O(62)-C(21)-N(65)	-19.7(13)
Rh(3)-O(62)-C(21)-C(20)	154.1(6)
Rh(3)-O(176)-C(174)-N(175)	-8.2(12)
Rh(3)-O(176)-C(174)-C(173)	169.9(6)
Rh(3)-O(288)-C(283)-N(287)	156.6(8)
Rh(3)-N(145)-C(132)-O(146)	10.2(13)
Rh(3)-N(145)-C(132)-C(133)	-164.3(7)
Rh(3)-N(145)-C(147)-C(148)	146.8(7)
Rh(3)-N(182)-C(178)-O(193)	-3.9(15)

Rh(3)-N(182)-C(178)-C(177)	-175.2(7)
Rh(3)-N(182)-C(179)-C(180)	167.8(8)
Rh(4)-O(64)-C(38)-N(61)	-26.4(11)
Rh(4)-O(64)-C(38)-C(37)	156.7(6)
Rh(4)-O(227)-C(226)-N(63)	-15.4(14)
Rh(4)-O(227)-C(226)-C(225)	164.9(7)
Rh(4)-O(271)-C(270)-N(272)	173.7(11)
Rh(4)-N(60)-C(44)-O(59)	4.5(13)
Rh(4)-N(60)-C(44)-C(45)	-170.7(7)
Rh(4)-N(60)-C(46)-C(47)	158.7(7)
Rh(4)-N(198)-C(194)-O(200)	0.4(15)
Rh(4)-N(198)-C(194)-C(267)	179.2(8)
Rh(4)-N(198)-C(195)-C(196)	162.0(9)
Rh(5)-O(72)-C(70)-N(71)	-21.3(12)
Rh(5)-O(72)-C(70)-C(69)	157.9(6)
Rh(5)-O(100)-C(88)-N(101)	-6.1(14)
Rh(5)-O(100)-C(88)-C(89)	173.2(7)
Rh(5)-O(279)-C(280)-N(278)	152.0(10)
Rh(5)-N(129)-C(127)-O(130)	-5.3(15)
Rh(5)-N(129)-C(127)-C(128)	174.2(8)
Rh(5)-N(129)-C(159)-C(160)	160.7(8)
Rh(5)-N(246)-C(241)-O(247)	10.3(14)
Rh(5)-N(246)-C(241)-C(244)	-162.9(8)
Rh(5)-N(246)-C(245)-C(242)	-178.4(9)
Rh(6)-O(130)-C(127)-N(129)	-9.4(14)
Rh(6)-O(130)-C(127)-C(128)	171.0(6)
Rh(6)-O(247)-C(241)-N(246)	-22.3(13)
Rh(6)-O(247)-C(241)-C(244)	151.0(8)
Rh(6)-O(291)-C(289)-N(294)	173.0(12)
Rh(6)-N(71)-C(66)-C(67)	169.0(7)
Rh(6)-N(71)-C(70)-O(72)	9.1(12)
Rh(6)-N(71)-C(70)-C(69)	-170.0(7)
Rh(6)-N(101)-C(88)-O(100)	-9.0(15)

Rh(6)-N(101)-C(88)-C(89)	171.8(7)
Rh(6)-N(101)-C(102)-C(233)	162.7(9)
O(18)-C(9)-C(10)-C(17)	179.5(10)
O(18)-C(9)-C(10)-C(87)	-0.8(18)
O(19)-C(8)-C(17)-C(10)	-179.7(10)
O(19)-C(8)-C(17)-C(16)	4.0(17)
O(57)-C(49)-C(50)-C(51)	175.5(14)
O(57)-C(49)-C(50)-C(55)	1(2)
O(58)-C(48)-C(51)-C(50)	175.1(11)
O(58)-C(48)-C(51)-C(52)	-1.5(19)
O(59)-C(44)-C(45)-N(56)	36.2(12)
O(59)-C(44)-C(45)-C(263)	165.1(9)
O(74)-C(76)-C(77)-C(78)	177.3(12)
O(74)-C(76)-C(77)-C(80)	6(2)
O(99)-C(96)-C(234)-C(91)	-178.8(11)
O(99)-C(96)-C(234)-C(153)	1(2)
O(100)-C(88)-C(89)-N(97)	48.8(12)
O(100)-C(88)-C(89)-C(90)	171.9(10)
O(114)-C(104)-C(105)-C(106)	178.5(11)
O(114)-C(104)-C(105)-C(110)	-1(2)
O(122)-C(123)-C(232)-C(121)	-0.8(19)
O(122)-C(123)-C(232)-C(124)	-178.0(10)
O(130)-C(127)-C(128)-N(126)	51.6(11)
O(130)-C(127)-C(128)-C(248)	173.4(10)
O(142)-C(134)-C(135)-C(136)	-177.7(11)
O(142)-C(134)-C(135)-C(144)	1.8(19)
O(146)-C(132)-C(133)-N(141)	42.5(11)
O(146)-C(132)-C(133)-C(269)	171.2(8)
O(170)-C(162)-C(163)-C(164)	4(2)
O(170)-C(162)-C(163)-C(259)	-176.5(10)
O(171)-C(161)-C(259)-C(163)	177.0(10)
O(171)-C(161)-C(259)-C(167)	-9.9(18)
O(192)-C(184)-C(185)-C(186)	-175.5(11)

O(192)-C(184)-C(185)-C(257)	2(2)
O(200)-C(194)-C(267)-N(199)	30.3(15)
O(200)-C(194)-C(267)-C(197)	163.8(11)
O(206)-C(202)-C(203)-C(204)	-6(2)
O(206)-C(202)-C(203)-C(237)	174.2(16)
O(207)-C(201)-C(237)-C(203)	-177.1(11)
O(207)-C(201)-C(237)-C(205)	4(2)
O(224)-C(212)-C(213)-C(214)	-0.1(18)
O(224)-C(212)-C(213)-C(221)	175.7(10)
O(247)-C(241)-C(244)-N(115)	32.2(15)
O(247)-C(241)-C(244)-C(243)	178.8(12)
N(7)-C(8)-C(17)-C(10)	-1.2(10)
N(7)-C(8)-C(17)-C(16)	-177.6(9)
N(7)-C(9)-C(10)-C(17)	2.8(11)
N(7)-C(9)-C(10)-C(87)	-177.5(9)
N(7)-C(20)-C(21)-O(62)	31.4(12)
N(7)-C(20)-C(21)-N(65)	-154.4(9)
N(7)-C(20)-C(131)-C(24)	-179.9(8)
N(33)-C(37)-C(38)-O(64)	30.4(11)
N(33)-C(37)-C(38)-N(61)	-146.7(8)
N(56)-C(45)-C(263)-C(47)	175.6(9)
N(56)-C(48)-C(51)-C(50)	-3.4(11)
N(56)-C(48)-C(51)-C(52)	180.0(10)
N(56)-C(49)-C(50)-C(51)	-6.4(12)
N(56)-C(49)-C(50)-C(55)	178.6(11)
N(60)-C(44)-C(45)-N(56)	-148.0(9)
N(60)-C(44)-C(45)-C(263)	-19.1(13)
N(60)-C(46)-C(47)-C(263)	43.9(13)
N(61)-C(39)-C(40)-C(36)	42.9(11)
N(63)-C(251)-C(252)-C(250)	54.7(14)
N(65)-C(23)-C(24)-C(131)	40.0(14)
N(71)-C(66)-C(67)-C(68)	31.0(13)
N(75)-C(69)-C(70)-O(72)	30.2(13)

N(75)-C(69)-C(70)-N(71)	-150.6(9)
N(75)-C(76)-C(77)-C(78)	1.3(13)
N(75)-C(76)-C(77)-C(80)	-169.6(10)
N(97)-C(89)-C(90)-C(233)	162.7(10)
N(97)-C(96)-C(234)-C(91)	-0.9(10)
N(97)-C(96)-C(234)-C(153)	179.1(11)
N(101)-C(88)-C(89)-N(97)	-131.9(10)
N(101)-C(88)-C(89)-C(90)	-8.8(15)
N(101)-C(102)-C(233)-C(90)	59.1(16)
N(115)-C(104)-C(105)-C(106)	-1.3(11)
N(115)-C(104)-C(105)-C(110)	179.4(11)
N(126)-C(123)-C(232)-C(121)	174.1(11)
N(126)-C(123)-C(232)-C(124)	-3.1(11)
N(126)-C(128)-C(248)-C(160)	161.7(9)
N(129)-C(127)-C(128)-N(126)	-128.0(11)
N(129)-C(127)-C(128)-C(248)	-6.2(16)
N(129)-C(159)-C(160)-C(248)	52.1(14)
N(141)-C(133)-C(269)-C(148)	166.0(9)
N(141)-C(134)-C(135)-C(136)	-0.4(11)
N(141)-C(134)-C(135)-C(144)	179.1(11)
N(145)-C(132)-C(133)-N(141)	-142.2(9)
N(145)-C(132)-C(133)-C(269)	-13.5(13)
N(145)-C(147)-C(148)-C(269)	53.6(13)
N(172)-C(161)-C(259)-C(163)	-0.1(10)
N(172)-C(161)-C(259)-C(167)	173.0(10)
N(172)-C(162)-C(163)-C(164)	-173.0(11)
N(172)-C(162)-C(163)-C(259)	6.7(11)
N(172)-C(173)-C(174)-O(176)	48.3(11)
N(172)-C(173)-C(174)-N(175)	-133.5(9)
N(172)-C(173)-C(261)-C(260)	167.2(9)
N(182)-C(179)-C(180)-C(181)	44.4(14)
N(183)-C(177)-C(178)-O(193)	33.4(12)
N(183)-C(177)-C(178)-N(182)	-153.8(9)

N(183)-C(177)-C(181)-C(180)	178.4(9)
N(183)-C(184)-C(185)-C(186)	5.2(11)
N(183)-C(184)-C(185)-C(257)	-177.4(11)
N(198)-C(194)-C(267)-N(199)	-148.7(11)
N(198)-C(194)-C(267)-C(197)	-15.2(17)
N(198)-C(195)-C(196)-C(197)	47.5(17)
N(199)-C(201)-C(237)-C(203)	2.1(12)
N(199)-C(201)-C(237)-C(205)	-177.2(11)
N(199)-C(202)-C(203)-C(204)	174.0(10)
N(199)-C(202)-C(203)-C(237)	-5.7(11)
N(211)-C(212)-C(213)-C(214)	177.4(9)
N(211)-C(212)-C(213)-C(221)	-6.7(10)
N(211)-C(225)-C(226)-O(227)	38.0(14)
N(211)-C(225)-C(226)-N(63)	-141.7(11)
N(211)-C(225)-C(250)-C(252)	177.1(10)
N(246)-C(241)-C(244)-N(115)	-154.5(10)
N(246)-C(241)-C(244)-C(243)	-7.8(18)
C(8)-N(7)-C(9)-O(18)	179.4(9)
C(8)-N(7)-C(9)-C(10)	-3.6(10)
C(8)-N(7)-C(20)-C(21)	-96.4(10)
C(8)-N(7)-C(20)-C(131)	137.7(8)
C(9)-N(7)-C(8)-O(19)	-178.5(10)
C(9)-N(7)-C(8)-C(17)	3.0(9)
C(9)-N(7)-C(20)-C(21)	80.4(12)
C(9)-N(7)-C(20)-C(131)	-45.4(13)
C(9)-C(10)-C(17)-C(8)	-0.9(11)
C(9)-C(10)-C(17)-C(16)	175.6(9)
C(9)-C(10)-C(87)-C(11)	-174.9(9)
C(11)-C(15)-C(14)-C(13)	0.0
C(11)-C(15)-C(16)-C(17)	3.5(10)
C(15)-C(11)-C(12)-C(41)	0.0
C(15)-C(11)-C(87)-C(10)	-1.3(11)
C(15)-C(14)-C(13)-C(41)	0.0

C(15)-C(16)-C(17)-C(8)	175.7(8)
C(15)-C(16)-C(17)-C(10)	0.0(14)
C(14)-C(15)-C(16)-C(17)	-177.3(6)
C(14)-C(13)-C(41)-C(12)	0.0
C(13)-C(41)-C(12)-C(11)	0.0
C(12)-C(11)-C(15)-C(14)	0.0
C(12)-C(11)-C(15)-C(16)	179.2(6)
C(12)-C(11)-C(87)-C(10)	176.7(6)
C(16)-C(15)-C(14)-C(13)	-179.2(6)
C(17)-C(10)-C(87)-C(11)	4.7(13)
C(20)-N(7)-C(8)-O(19)	-1.0(14)
C(20)-N(7)-C(8)-C(17)	-179.6(7)
C(20)-N(7)-C(9)-O(18)	2.4(15)
C(20)-N(7)-C(9)-C(10)	179.4(8)
C(21)-N(65)-C(23)-C(24)	-9.9(16)
C(21)-C(20)-C(131)-C(24)	54.4(10)
C(22)-C(43)-C(28)-C(42)	-177.7(7)
C(22)-C(30)-C(31)-O(35)	-3.8(18)
C(22)-C(30)-C(31)-N(33)	178.5(10)
C(23)-N(65)-C(21)-O(62)	178.3(10)
C(23)-N(65)-C(21)-C(20)	4.8(15)
C(23)-C(24)-C(131)-C(20)	-60.7(11)
C(26)-C(25)-C(43)-C(22)	-1.8(8)
C(26)-C(25)-C(43)-C(28)	-179.7(7)
C(26)-C(29)-C(30)-C(22)	2.1(14)
C(26)-C(29)-C(30)-C(31)	-178.4(9)
C(26)-C(29)-C(32)-O(34)	-0.6(17)
C(26)-C(29)-C(32)-N(33)	178.2(10)
C(27)-C(25)-C(43)-C(22)	177.9(7)
C(27)-C(25)-C(43)-C(28)	0.0
C(25)-C(26)-C(29)-C(30)	-0.2(14)
C(25)-C(26)-C(29)-C(32)	179.6(8)
C(25)-C(27)-C(210)-C(42)	0.0

C(25)-C(43)-C(28)-C(42)	0.0
C(43)-C(22)-C(30)-C(29)	-3.9(13)
C(43)-C(22)-C(30)-C(31)	176.8(9)
C(43)-C(28)-C(42)-C(210)	0.0
C(28)-C(42)-C(210)-C(27)	0.0
C(210)-C(27)-C(25)-C(26)	179.7(7)
C(210)-C(27)-C(25)-C(43)	0.0
C(29)-C(26)-C(25)-C(27)	-179.6(7)
C(29)-C(26)-C(25)-C(43)	0.1(12)
C(29)-C(30)-C(31)-O(35)	176.9(10)
C(29)-C(30)-C(31)-N(33)	-0.8(10)
C(30)-C(22)-C(43)-C(25)	3.7(10)
C(30)-C(22)-C(43)-C(28)	-178.5(7)
C(30)-C(29)-C(32)-O(34)	179.2(10)
C(30)-C(29)-C(32)-N(33)	-2.0(9)
C(31)-N(33)-C(32)-O(34)	-179.6(9)
C(31)-N(33)-C(32)-C(29)	1.6(9)
C(31)-N(33)-C(37)-C(36)	115.3(9)
C(31)-N(33)-C(37)-C(38)	-114.4(9)
C(32)-N(33)-C(31)-O(35)	-178.3(9)
C(32)-N(33)-C(31)-C(30)	-0.5(10)
C(32)-N(33)-C(37)-C(36)	-61.4(10)
C(32)-N(33)-C(37)-C(38)	68.8(10)
C(32)-C(29)-C(30)-C(22)	-177.7(8)
C(32)-C(29)-C(30)-C(31)	1.7(10)
C(36)-C(37)-C(38)-O(64)	161.3(8)
C(36)-C(37)-C(38)-N(61)	-15.7(12)
C(37)-N(33)-C(31)-O(35)	4.7(14)
C(37)-N(33)-C(31)-C(30)	-177.6(7)
C(37)-N(33)-C(32)-O(34)	-2.5(14)
C(37)-N(33)-C(32)-C(29)	178.6(7)
C(37)-C(36)-C(40)-C(39)	-62.6(10)
C(38)-N(61)-C(39)-C(40)	-8.1(13)

C(39)-N(61)-C(38)-O(64)	177.8(9)
C(39)-N(61)-C(38)-C(37)	-5.5(14)
C(40)-C(36)-C(37)-N(33)	178.4(7)
C(40)-C(36)-C(37)-C(38)	48.9(11)
C(44)-N(60)-C(46)-C(47)	-15.7(14)
C(44)-C(45)-C(263)-C(47)	49.2(13)
C(45)-N(56)-C(48)-O(58)	4.5(15)
C(45)-N(56)-C(48)-C(51)	-176.8(9)
C(45)-N(56)-C(49)-O(57)	-1.1(16)
C(45)-N(56)-C(49)-C(50)	-179.5(9)
C(46)-N(60)-C(44)-O(59)	178.8(10)
C(46)-N(60)-C(44)-C(45)	3.6(15)
C(46)-C(47)-C(263)-C(45)	-61.1(12)
C(48)-N(56)-C(45)-C(44)	63.1(12)
C(48)-N(56)-C(45)-C(263)	-63.9(12)
C(48)-N(56)-C(49)-O(57)	-177.3(10)
C(48)-N(56)-C(49)-C(50)	4.3(11)
C(48)-C(51)-C(52)-C(53)	177.1(9)
C(49)-N(56)-C(45)-C(44)	-112.4(10)
C(49)-N(56)-C(45)-C(263)	120.6(11)
C(49)-N(56)-C(48)-O(58)	-179.3(10)
C(49)-N(56)-C(48)-C(51)	-0.6(10)
C(49)-C(50)-C(51)-C(48)	6.2(12)
C(49)-C(50)-C(51)-C(52)	-176.7(10)
C(49)-C(50)-C(55)-C(228)	173.8(10)
C(50)-C(51)-C(52)-C(53)	0.7(15)
C(51)-C(50)-C(55)-C(228)	-0.7(16)
C(51)-C(52)-C(53)-C(228)	1.8(12)
C(51)-C(52)-C(53)-C(54)	177.7(7)
C(52)-C(53)-C(228)-C(249)	175.9(7)
C(52)-C(53)-C(228)-C(55)	-3.7(8)
C(52)-C(53)-C(54)-C(149)	-175.8(7)
C(53)-C(228)-C(249)-C(150)	0.0

C(53)-C(228)-C(55)-C(50)	3.2(13)
C(228)-C(53)-C(54)-C(149)	0.0
C(228)-C(249)-C(150)-C(149)	0.0
C(249)-C(228)-C(55)-C(50)	-176.4(8)
C(249)-C(150)-C(149)-C(54)	0.0
C(150)-C(149)-C(54)-C(53)	0.0
C(54)-C(53)-C(228)-C(249)	0.0
C(54)-C(53)-C(228)-C(55)	-179.6(7)
C(55)-C(50)-C(51)-C(48)	-178.4(10)
C(55)-C(50)-C(51)-C(52)	-1.3(16)
C(55)-C(228)-C(249)-C(150)	179.6(8)
C(66)-N(71)-C(70)-O(72)	177.4(8)
C(66)-N(71)-C(70)-C(69)	-1.7(13)
C(66)-C(67)-C(68)-C(69)	-55.6(13)
C(67)-C(68)-C(69)-N(75)	-178.9(9)
C(67)-C(68)-C(69)-C(70)	52.0(12)
C(68)-C(69)-C(70)-O(72)	157.4(8)
C(68)-C(69)-C(70)-N(71)	-23.4(13)
C(69)-N(75)-C(76)-O(74)	-1.8(18)
C(69)-N(75)-C(76)-C(77)	174.3(9)
C(69)-N(75)-C(79)-O(73)	3.6(18)
C(69)-N(75)-C(79)-C(78)	-174.0(9)
C(70)-N(71)-C(66)-C(67)	0.0(13)
C(76)-N(75)-C(69)-C(68)	139.5(10)
C(76)-N(75)-C(69)-C(70)	-93.6(12)
C(76)-N(75)-C(79)-O(73)	179.5(11)
C(76)-N(75)-C(79)-C(78)	1.9(12)
C(76)-C(77)-C(78)-C(79)	-0.1(12)
C(76)-C(77)-C(78)-C(81)	177.2(10)
C(76)-C(77)-C(80)-C(83)	175.4(10)
C(77)-C(78)-C(79)-O(73)	-178.5(11)
C(77)-C(78)-C(79)-N(75)	-1.1(11)
C(77)-C(78)-C(81)-C(84)	5.7(15)

C(77)-C(80)-C(83)-C(84)	4.4(10)
C(77)-C(80)-C(83)-C(82)	-174.8(7)
C(78)-C(77)-C(80)-C(83)	5.6(14)
C(78)-C(81)-C(84)-C(83)	4.6(10)
C(78)-C(81)-C(84)-C(85)	174.5(7)
C(79)-N(75)-C(69)-C(68)	-44.9(14)
C(79)-N(75)-C(69)-C(70)	82.1(13)
C(79)-N(75)-C(76)-O(74)	-178.1(12)
C(79)-N(75)-C(76)-C(77)	-2.1(13)
C(79)-C(78)-C(81)-C(84)	-177.7(9)
C(80)-C(77)-C(78)-C(79)	171.9(9)
C(80)-C(77)-C(78)-C(81)	-10.8(16)
C(80)-C(83)-C(82)-C(240)	179.2(7)
C(81)-C(78)-C(79)-O(73)	4.5(19)
C(81)-C(78)-C(79)-N(75)	-178.1(10)
C(81)-C(84)-C(83)-C(80)	-9.5(6)
C(81)-C(84)-C(83)-C(82)	169.7(6)
C(81)-C(84)-C(85)-C(86)	-169.9(6)
C(84)-C(83)-C(82)-C(240)	0.0
C(83)-C(84)-C(85)-C(86)	0.0
C(83)-C(82)-C(240)-C(86)	0.0
C(82)-C(240)-C(86)-C(85)	0.0
C(240)-C(86)-C(85)-C(84)	0.0
C(85)-C(84)-C(83)-C(80)	-179.2(7)
C(85)-C(84)-C(83)-C(82)	0.0
C(87)-C(10)-C(17)-C(8)	179.4(8)
C(87)-C(10)-C(17)-C(16)	-4.1(15)
C(87)-C(11)-C(15)-C(14)	178.0(7)
C(87)-C(11)-C(15)-C(16)	-2.8(8)
C(87)-C(11)-C(12)-C(41)	-178.0(7)
C(88)-N(101)-C(102)-C(233)	-29.3(16)
C(88)-C(89)-C(90)-C(233)	39.1(14)
C(89)-N(97)-C(95)-O(98)	-0.9(15)

C(89)-N(97)-C(95)-C(91)	178.3(8)
C(89)-N(97)-C(96)-O(99)	0.3(15)
C(89)-N(97)-C(96)-C(234)	-177.8(8)
C(89)-C(90)-C(233)-C(102)	-62.2(15)
C(91)-C(92)-C(93)-C(154)	-3.3(13)
C(91)-C(92)-C(93)-C(302)	176.3(8)
C(92)-C(91)-C(95)-O(98)	-0.3(19)
C(92)-C(91)-C(95)-N(97)	-179.5(11)
C(92)-C(91)-C(234)-C(96)	180.0(9)
C(92)-C(91)-C(234)-C(153)	0.0(16)
C(95)-N(97)-C(89)-C(88)	-114.5(10)
C(95)-N(97)-C(89)-C(90)	119.1(11)
C(95)-N(97)-C(96)-O(99)	178.4(10)
C(95)-N(97)-C(96)-C(234)	0.3(10)
C(95)-C(91)-C(92)-C(93)	-179.0(10)
C(95)-C(91)-C(234)-C(96)	1.0(11)
C(95)-C(91)-C(234)-C(153)	-178.9(10)
C(96)-N(97)-C(89)-C(88)	63.3(12)
C(96)-N(97)-C(89)-C(90)	-63.1(11)
C(96)-N(97)-C(95)-O(98)	-178.9(9)
C(96)-N(97)-C(95)-C(91)	0.3(11)
C(102)-N(101)-C(88)-O(100)	-177.3(10)
C(102)-N(101)-C(88)-C(89)	3.5(15)
C(104)-N(115)-C(157)-O(158)	177.5(10)
C(104)-N(115)-C(157)-C(106)	1.8(12)
C(104)-N(115)-C(244)-C(241)	-97.6(13)
C(104)-N(115)-C(244)-C(243)	116.0(15)
C(104)-C(105)-C(106)-C(107)	178.4(11)
C(104)-C(105)-C(106)-C(157)	2.2(11)
C(104)-C(105)-C(110)-C(109)	177.0(10)
C(105)-C(106)-C(107)-C(108)	5.3(18)
C(105)-C(106)-C(157)-O(158)	-178.3(10)
C(105)-C(106)-C(157)-N(115)	-2.5(12)

C(106)-C(105)-C(110)-C(109)	-2.2(14)
C(106)-C(107)-C(108)-C(109)	-4.2(15)
C(106)-C(107)-C(108)-C(156)	175.1(9)
C(107)-C(106)-C(157)-O(158)	5.9(19)
C(107)-C(106)-C(157)-N(115)	-178.3(12)
C(107)-C(108)-C(109)-C(111)	179.3(9)
C(107)-C(108)-C(109)-C(110)	0.2(10)
C(107)-C(108)-C(156)-C(113)	-179.3(9)
C(108)-C(109)-C(111)-C(112)	0.0
C(108)-C(109)-C(110)-C(105)	3.1(12)
C(109)-C(108)-C(156)-C(113)	0.0
C(109)-C(111)-C(112)-C(113)	0.0
C(111)-C(109)-C(110)-C(105)	-176.0(8)
C(111)-C(112)-C(113)-C(156)	0.0
C(112)-C(113)-C(156)-C(108)	0.0
C(156)-C(108)-C(109)-C(111)	0.0
C(156)-C(108)-C(109)-C(110)	-179.1(8)
C(110)-C(105)-C(106)-C(107)	-2.1(16)
C(110)-C(105)-C(106)-C(157)	-178.3(9)
C(110)-C(109)-C(111)-C(112)	179.1(8)
C(120)-C(103)-C(117)-C(116)	0.0
C(120)-C(103)-C(229)-C(124)	-1.6(13)
C(120)-C(121)-C(232)-C(123)	-174.6(9)
C(120)-C(121)-C(232)-C(124)	2.2(14)
C(103)-C(120)-C(119)-C(118)	0.0
C(103)-C(120)-C(121)-C(232)	-6.5(11)
C(103)-C(117)-C(116)-C(118)	0.0
C(117)-C(103)-C(229)-C(124)	-176.8(8)
C(117)-C(116)-C(118)-C(119)	0.0
C(116)-C(118)-C(119)-C(120)	0.0
C(119)-C(120)-C(103)-C(117)	0.0
C(119)-C(120)-C(103)-C(229)	-175.2(8)
C(119)-C(120)-C(121)-C(232)	175.0(7)

C(121)-C(120)-C(103)-C(117)	-178.4(8)
C(121)-C(120)-C(103)-C(229)	6.4(9)
C(121)-C(120)-C(119)-C(118)	178.5(7)
C(123)-N(126)-C(128)-C(127)	-108.0(10)
C(123)-N(126)-C(128)-C(248)	127.7(10)
C(123)-N(126)-C(230)-O(231)	174.3(10)
C(123)-N(126)-C(230)-C(124)	-9.1(11)
C(127)-N(129)-C(159)-C(160)	-20.9(16)
C(127)-C(128)-C(248)-C(160)	37.9(13)
C(128)-N(126)-C(123)-O(122)	-7.6(14)
C(128)-N(126)-C(123)-C(232)	177.2(8)
C(128)-N(126)-C(230)-O(231)	5.0(17)
C(128)-N(126)-C(230)-C(124)	-178.5(8)
C(131)-C(20)-C(21)-O(62)	156.9(8)
C(131)-C(20)-C(21)-N(65)	-29.0(13)
C(132)-N(145)-C(147)-C(148)	-22.2(13)
C(132)-C(133)-C(269)-C(148)	38.8(12)
C(133)-N(141)-C(134)-O(142)	-0.9(17)
C(133)-N(141)-C(134)-C(135)	-178.3(9)
C(133)-N(141)-C(137)-O(143)	0.9(15)
C(133)-N(141)-C(137)-C(136)	177.1(8)
C(134)-N(141)-C(133)-C(132)	72.9(12)
C(134)-N(141)-C(133)-C(269)	-56.6(13)
C(134)-N(141)-C(137)-O(143)	-180.0(9)
C(134)-N(141)-C(137)-C(136)	-3.8(11)
C(134)-C(135)-C(136)-C(137)	-1.8(11)
C(134)-C(135)-C(136)-C(138)	-179.4(9)
C(134)-C(135)-C(144)-C(151)	179.0(9)
C(135)-C(136)-C(137)-O(143)	179.5(9)
C(135)-C(136)-C(137)-N(141)	3.3(11)
C(135)-C(136)-C(138)-C(139)	-0.3(15)
C(136)-C(135)-C(144)-C(151)	-1.5(16)
C(136)-C(138)-C(139)-C(151)	-0.1(12)

C(136)-C(138)-C(139)-C(140)	-175.9(8)
C(137)-N(141)-C(133)-C(132)	-108.2(10)
C(137)-N(141)-C(133)-C(269)	122.4(10)
C(137)-N(141)-C(134)-O(142)	-179.9(10)
C(137)-N(141)-C(134)-C(135)	2.6(11)
C(137)-C(136)-C(138)-C(139)	-177.0(10)
C(138)-C(136)-C(137)-O(143)	-3.5(18)
C(138)-C(136)-C(137)-N(141)	-179.6(11)
C(138)-C(139)-C(151)-C(268)	-175.7(8)
C(138)-C(139)-C(151)-C(144)	-0.3(9)
C(138)-C(139)-C(140)-C(235)	175.8(8)
C(139)-C(151)-C(268)-C(152)	0.0
C(139)-C(151)-C(144)-C(135)	1.1(13)
C(151)-C(139)-C(140)-C(235)	0.0
C(151)-C(268)-C(152)-C(235)	0.0
C(268)-C(151)-C(144)-C(135)	176.5(8)
C(268)-C(152)-C(235)-C(140)	0.0
C(152)-C(235)-C(140)-C(139)	0.0
C(140)-C(139)-C(151)-C(268)	0.0
C(140)-C(139)-C(151)-C(144)	175.4(8)
C(144)-C(135)-C(136)-C(137)	178.7(10)
C(144)-C(135)-C(136)-C(138)	1.1(15)
C(144)-C(151)-C(268)-C(152)	-175.3(9)
C(147)-N(145)-C(132)-O(146)	179.2(9)
C(147)-N(145)-C(132)-C(133)	4.8(14)
C(147)-C(148)-C(269)-C(133)	-59.0(12)
C(153)-C(154)-C(264)-C(254)	178.0(9)
C(153)-C(154)-C(93)-C(92)	1.6(9)
C(153)-C(154)-C(93)-C(302)	-178.0(9)
C(154)-C(153)-C(234)-C(91)	-1.6(17)
C(154)-C(153)-C(234)-C(96)	178.5(10)
C(154)-C(264)-C(254)-C(238)	0.0
C(264)-C(154)-C(93)-C(92)	179.6(8)

C(264)-C(154)-C(93)-C(302)	0.0
C(264)-C(254)-C(238)-C(302)	0.0
C(254)-C(238)-C(302)-C(93)	0.0
C(238)-C(302)-C(93)-C(92)	-179.6(8)
C(238)-C(302)-C(93)-C(154)	0.0
C(93)-C(154)-C(264)-C(254)	0.0
C(155)-N(277)-C(275)-O(276)	-175.1(17)
C(157)-N(115)-C(104)-O(114)	179.8(10)
C(157)-N(115)-C(104)-C(105)	-0.4(12)
C(157)-N(115)-C(244)-C(241)	78.3(14)
C(157)-N(115)-C(244)-C(243)	-68.1(17)
C(157)-C(106)-C(107)-C(108)	-179.5(10)
C(159)-N(129)-C(127)-O(130)	176.2(10)
C(159)-N(129)-C(127)-C(128)	-4.2(16)
C(159)-C(160)-C(248)-C(128)	-60.1(13)
C(161)-N(172)-C(162)-O(170)	176.0(9)
C(161)-N(172)-C(162)-C(163)	-6.8(11)
C(161)-N(172)-C(173)-C(174)	-107.1(10)
C(161)-N(172)-C(173)-C(261)	125.4(10)
C(162)-N(172)-C(161)-O(171)	-172.8(9)
C(162)-N(172)-C(161)-C(259)	4.3(10)
C(162)-N(172)-C(173)-C(174)	64.4(10)
C(162)-N(172)-C(173)-C(261)	-63.1(12)
C(162)-C(163)-C(164)-C(165)	177.3(10)
C(162)-C(163)-C(259)-C(161)	-4.1(11)
C(162)-C(163)-C(259)-C(167)	-177.9(9)
C(163)-C(164)-C(165)-C(166)	0.3(13)
C(163)-C(164)-C(165)-C(258)	178.0(7)
C(164)-C(163)-C(259)-C(161)	175.7(9)
C(164)-C(163)-C(259)-C(167)	1.9(15)
C(164)-C(165)-C(166)-C(168)	177.6(9)
C(164)-C(165)-C(166)-C(167)	2.4(9)
C(164)-C(165)-C(258)-C(169)	-177.9(8)

C(165)-C(166)-C(168)-C(236)	0.0
C(165)-C(166)-C(167)-C(259)	-2.9(11)
C(166)-C(165)-C(258)-C(169)	0.0
C(166)-C(168)-C(236)-C(169)	0.0
C(166)-C(167)-C(259)-C(161)	-171.2(9)
C(166)-C(167)-C(259)-C(163)	0.9(15)
C(168)-C(166)-C(167)-C(259)	-178.0(7)
C(168)-C(236)-C(169)-C(258)	0.0
C(236)-C(169)-C(258)-C(165)	0.0
C(258)-C(165)-C(166)-C(168)	0.0
C(258)-C(165)-C(166)-C(167)	-175.3(6)
C(167)-C(166)-C(168)-C(236)	174.9(6)
C(173)-N(172)-C(161)-O(171)	-0.5(16)
C(173)-N(172)-C(161)-C(259)	176.6(8)
C(173)-N(172)-C(162)-O(170)	3.3(14)
C(173)-N(172)-C(162)-C(163)	-179.5(8)
C(174)-N(175)-C(262)-C(260)	-16.7(13)
C(174)-C(173)-C(261)-C(260)	44.6(13)
C(177)-N(183)-C(184)-O(192)	5.7(16)
C(177)-N(183)-C(184)-C(185)	-174.9(8)
C(177)-N(183)-C(187)-O(191)	-5.2(18)
C(177)-N(183)-C(187)-C(186)	173.3(8)
C(178)-N(182)-C(179)-C(180)	-19.9(16)
C(178)-C(177)-C(181)-C(180)	56.4(12)
C(179)-N(182)-C(178)-O(193)	-176.1(10)
C(179)-N(182)-C(178)-C(177)	12.7(16)
C(179)-C(180)-C(181)-C(177)	-62.5(13)
C(181)-C(177)-C(178)-O(193)	156.8(9)
C(181)-C(177)-C(178)-N(182)	-30.4(13)
C(184)-N(183)-C(177)-C(178)	58.8(12)
C(184)-N(183)-C(177)-C(181)	-63.4(12)
C(184)-N(183)-C(187)-O(191)	-175.3(12)
C(184)-N(183)-C(187)-C(186)	3.2(11)

C(184)-C(185)-C(186)-C(187)	-3.4(11)
C(184)-C(185)-C(186)-C(188)	-179.7(9)
C(184)-C(185)-C(257)-C(189)	-177.5(10)
C(185)-C(186)-C(187)-O(191)	178.8(12)
C(185)-C(186)-C(187)-N(183)	0.3(11)
C(185)-C(186)-C(188)-C(256)	-1.3(15)
C(186)-C(185)-C(257)-C(189)	-0.4(15)
C(186)-C(188)-C(256)-C(190)	-178.2(7)
C(186)-C(188)-C(256)-C(189)	-2.3(12)
C(187)-N(183)-C(177)-C(178)	-110.0(11)
C(187)-N(183)-C(177)-C(181)	127.7(11)
C(187)-N(183)-C(184)-O(192)	175.4(10)
C(187)-N(183)-C(184)-C(185)	-5.3(11)
C(187)-C(186)-C(188)-C(256)	-176.4(10)
C(188)-C(186)-C(187)-O(191)	-6(2)
C(188)-C(186)-C(187)-N(183)	175.8(10)
C(188)-C(256)-C(189)-C(255)	-175.9(7)
C(188)-C(256)-C(189)-C(257)	4.5(8)
C(190)-C(256)-C(189)-C(255)	0.0
C(190)-C(256)-C(189)-C(257)	-179.6(7)
C(256)-C(190)-C(94)-C(125)	0.0
C(256)-C(189)-C(255)-C(125)	0.0
C(256)-C(189)-C(257)-C(185)	-3.1(12)
C(189)-C(255)-C(125)-C(94)	0.0
C(255)-C(189)-C(257)-C(185)	177.2(7)
C(255)-C(125)-C(94)-C(190)	0.0
C(94)-C(190)-C(256)-C(188)	175.9(7)
C(94)-C(190)-C(256)-C(189)	0.0
C(194)-N(198)-C(195)-C(196)	-10.7(19)
C(195)-N(198)-C(194)-O(200)	173.3(11)
C(195)-N(198)-C(194)-C(267)	-7.9(17)
C(195)-C(196)-C(197)-C(267)	-62.8(14)
C(196)-C(197)-C(267)-N(199)	-174.1(10)

C(196)-C(197)-C(267)-C(194)	52.4(15)
C(201)-N(199)-C(202)-O(206)	-172.8(12)
C(201)-N(199)-C(202)-C(203)	7.2(11)
C(201)-N(199)-C(267)-C(194)	62.4(15)
C(201)-N(199)-C(267)-C(197)	-72.1(14)
C(202)-N(199)-C(201)-O(207)	173.1(11)
C(202)-N(199)-C(201)-C(237)	-6.1(12)
C(202)-N(199)-C(267)-C(194)	-105.2(13)
C(202)-N(199)-C(267)-C(197)	120.2(13)
C(202)-C(203)-C(204)-C(208)	178.6(10)
C(202)-C(203)-C(237)-C(201)	2.5(13)
C(202)-C(203)-C(237)-C(205)	-178.0(9)
C(203)-C(204)-C(208)-C(209)	0.9(13)
C(203)-C(204)-C(208)-C(265)	178.8(7)
C(204)-C(203)-C(237)-C(201)	-177.1(10)
C(204)-C(203)-C(237)-C(205)	2.4(17)
C(204)-C(208)-C(209)-C(205)	-0.6(9)
C(204)-C(208)-C(209)-C(301)	177.9(8)
C(204)-C(208)-C(265)-C(266)	-177.9(8)
C(205)-C(209)-C(301)-C(239)	178.5(5)
C(208)-C(209)-C(301)-C(239)	0.0
C(209)-C(205)-C(237)-C(201)	177.4(10)
C(209)-C(205)-C(237)-C(203)	-1.9(15)
C(209)-C(208)-C(265)-C(266)	0.0
C(209)-C(301)-C(239)-C(266)	0.0
C(301)-C(239)-C(266)-C(265)	0.0
C(239)-C(266)-C(265)-C(208)	0.0
C(265)-C(208)-C(209)-C(205)	-178.5(5)
C(265)-C(208)-C(209)-C(301)	0.0
C(212)-N(211)-C(222)-O(223)	176.4(10)
C(212)-N(211)-C(222)-C(221)	-8.0(11)
C(212)-N(211)-C(225)-C(226)	-109.2(11)
C(212)-N(211)-C(225)-C(250)	127.8(11)

C(212)-C(213)-C(214)-C(215)	-180.0(9)
C(212)-C(213)-C(221)-C(220)	179.5(8)
C(212)-C(213)-C(221)-C(222)	2.4(10)
C(213)-C(214)-C(215)-C(219)	-4.1(10)
C(213)-C(214)-C(215)-C(216)	178.7(6)
C(213)-C(221)-C(222)-O(223)	178.8(9)
C(213)-C(221)-C(222)-N(211)	3.1(11)
C(214)-C(213)-C(221)-C(220)	-4.0(13)
C(214)-C(213)-C(221)-C(222)	178.9(8)
C(214)-C(215)-C(216)-C(217)	177.1(5)
C(219)-C(215)-C(216)-C(217)	0.0
C(219)-C(220)-C(221)-C(213)	2.8(13)
C(219)-C(220)-C(221)-C(222)	179.1(9)
C(215)-C(219)-C(218)-C(300)	0.0
C(215)-C(219)-C(220)-C(221)	-2.3(11)
C(215)-C(216)-C(217)-C(300)	0.0
C(216)-C(217)-C(300)-C(218)	0.0
C(217)-C(300)-C(218)-C(219)	0.0
C(218)-C(219)-C(215)-C(214)	-177.2(5)
C(218)-C(219)-C(215)-C(216)	0.0
C(218)-C(219)-C(220)-C(221)	177.8(6)
C(220)-C(219)-C(215)-C(214)	2.9(7)
C(220)-C(219)-C(215)-C(216)	-179.9(7)
C(220)-C(219)-C(218)-C(300)	179.9(7)
C(220)-C(221)-C(222)-O(223)	2.2(17)
C(220)-C(221)-C(222)-N(211)	-173.5(10)
C(221)-C(213)-C(214)-C(215)	4.7(13)
C(222)-N(211)-C(212)-O(224)	-173.3(10)
C(222)-N(211)-C(212)-C(213)	9.2(10)
C(222)-N(211)-C(225)-C(226)	57.4(15)
C(222)-N(211)-C(225)-C(250)	-65.6(14)
C(225)-N(211)-C(212)-O(224)	-4.7(16)
C(225)-N(211)-C(212)-C(213)	177.7(8)

C(225)-N(211)-C(222)-O(223)	9.2(17)
C(225)-N(211)-C(222)-C(221)	-175.2(9)
C(225)-C(250)-C(252)-C(251)	-71.4(13)
C(226)-N(63)-C(251)-C(252)	-15.8(15)
C(226)-C(225)-C(250)-C(252)	53.8(13)
C(229)-C(103)-C(117)-C(116)	175.1(8)
C(229)-C(124)-C(230)-O(231)	1.2(19)
C(229)-C(124)-C(230)-N(126)	-175.4(11)
C(229)-C(124)-C(232)-C(121)	2.2(16)
C(229)-C(124)-C(232)-C(123)	179.7(10)
C(230)-N(126)-C(123)-O(122)	-177.0(10)
C(230)-N(126)-C(123)-C(232)	7.8(11)
C(230)-N(126)-C(128)-C(127)	60.2(13)
C(230)-N(126)-C(128)-C(248)	-64.1(12)
C(230)-C(124)-C(229)-C(103)	179.7(10)
C(230)-C(124)-C(232)-C(121)	-179.5(10)
C(230)-C(124)-C(232)-C(123)	-2.1(11)
C(232)-C(124)-C(229)-C(103)	-2.6(16)
C(232)-C(124)-C(230)-O(231)	-176.7(11)
C(232)-C(124)-C(230)-N(126)	6.7(11)
C(234)-C(91)-C(92)-C(93)	2.5(15)
C(234)-C(91)-C(95)-O(98)	178.4(10)
C(234)-C(91)-C(95)-N(97)	-0.9(11)
C(234)-C(153)-C(154)-C(264)	-177.3(8)
C(234)-C(153)-C(154)-C(93)	0.7(14)
C(237)-C(203)-C(204)-C(208)	-1.8(16)
C(237)-C(205)-C(209)-C(208)	1.1(11)
C(237)-C(205)-C(209)-C(301)	-177.4(7)
C(241)-N(246)-C(245)-C(242)	13.7(16)
C(242)-C(243)-C(244)-N(115)	136.3(14)
C(242)-C(243)-C(244)-C(241)	-7(2)
C(243)-C(242)-C(245)-N(246)	-28.9(19)
C(244)-N(115)-C(104)-O(114)	-3.8(16)

C(244)-N(115)-C(104)-C(105)	176.0(9)
C(244)-N(115)-C(157)-O(158)	1.0(18)
C(244)-N(115)-C(157)-C(106)	-174.7(9)
C(245)-N(246)-C(241)-O(247)	177.5(9)
C(245)-N(246)-C(241)-C(244)	4.4(16)
C(245)-C(242)-C(243)-C(244)	26(2)
C(250)-C(225)-C(226)-O(227)	162.1(9)
C(250)-C(225)-C(226)-N(63)	-17.6(15)
C(251)-N(63)-C(226)-O(227)	177.4(10)
C(251)-N(63)-C(226)-C(225)	-2.9(16)
C(253)-N(277)-C(275)-O(276)	-28(4)
C(257)-C(185)-C(186)-C(187)	179.0(9)
C(257)-C(185)-C(186)-C(188)	2.6(15)
C(257)-C(189)-C(255)-C(125)	179.6(6)
C(259)-C(163)-C(164)-C(165)	-2.4(15)
C(261)-C(173)-C(174)-O(176)	171.1(9)
C(261)-C(173)-C(174)-N(175)	-10.7(14)
C(261)-C(260)-C(262)-N(175)	54.0(12)
C(262)-N(175)-C(174)-O(176)	170.6(9)
C(262)-N(175)-C(174)-C(173)	-7.5(13)
C(262)-C(260)-C(261)-C(173)	-65.6(12)
C(267)-N(199)-C(201)-O(207)	4.1(18)
C(267)-N(199)-C(201)-C(237)	-175.1(9)
C(267)-N(199)-C(202)-O(206)	-4.2(18)
C(267)-N(199)-C(202)-C(203)	175.7(9)
C(273)-N(272)-C(270)-O(271)	-170.9(13)
C(274)-N(272)-C(270)-O(271)	11(2)
C(281)-N(278)-C(280)-O(279)	-3(2)
C(282)-N(278)-C(280)-O(279)	179.5(13)
C(284)-N(287)-C(283)-O(288)	-178.3(10)
C(285)-N(287)-C(283)-O(288)	-4.6(16)
C(286)-N(304)-C(303)-O(305)	3.7(17)
C(295)-N(294)-C(289)-O(291)	-14(2)

C(296)-N(294)-C(289)-O(291)	165.3(15)
C(297)-N(290)-C(293)-O(292)	3(2)
C(298)-N(290)-C(293)-O(292)	-169.6(13)
C(299)-N(304)-C(303)-O(305)	179.5(12)

Symmetry transformations used to generate equivalent atoms:

cis-Ru_2(*S*-BPTPI)$_4$$ClO_4$·2DMF

Figure 28. Full ortep plot (up) and stereoview of diruthenium core (down)

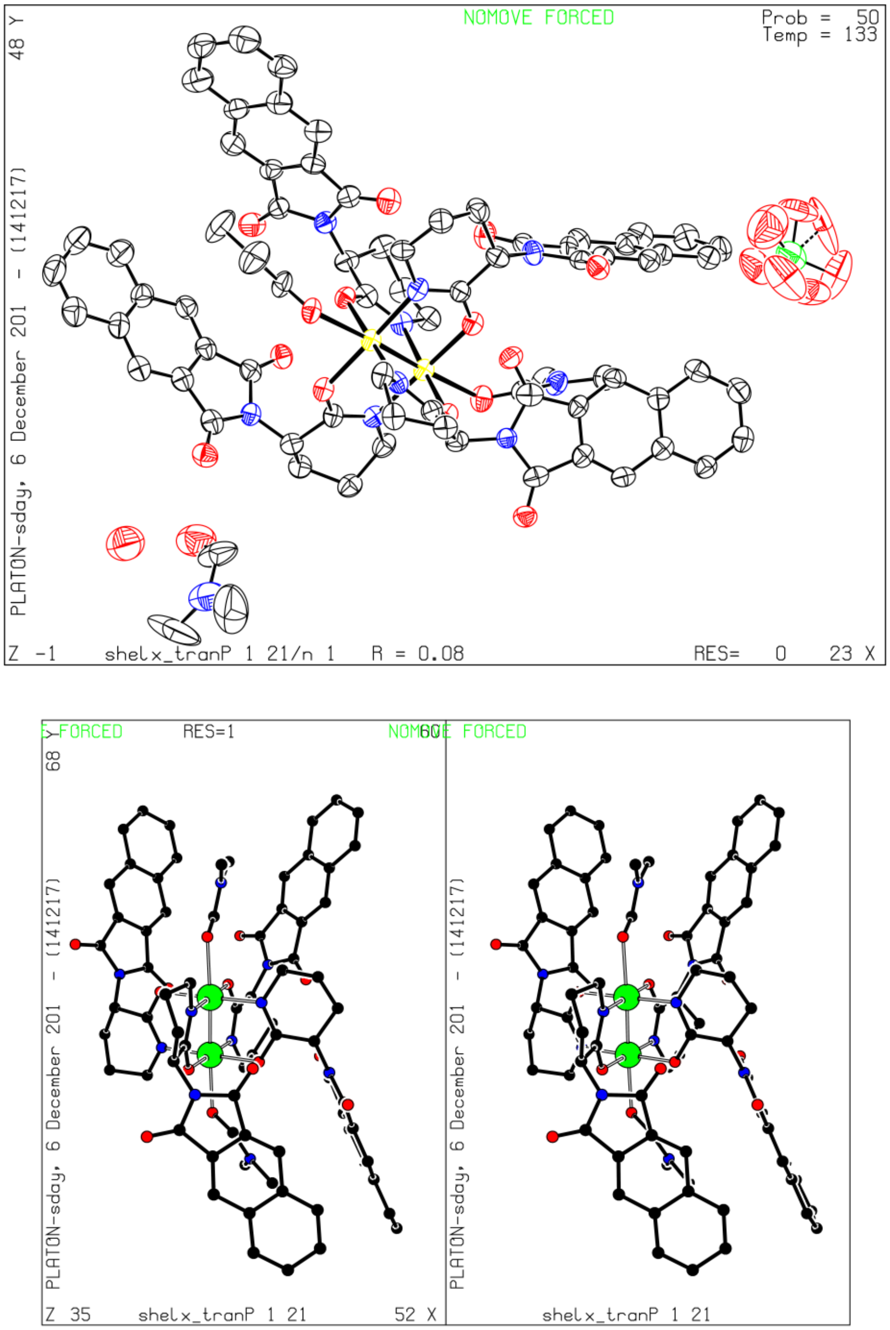

Table 1. Crystal data and structure refinement for cis-Ru2(RS-BPTPI)4ClO4.

Identification code	shelx_trans	
Empirical formula	C77 H72 Cl N11 O20 Ru2	
Formula weight	1709.04	
Temperature	133.15(2) K	
Wavelength	1.5418 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 11.3245(2) Å	α= 90°.
	b = 37.6524(7) Å	β= 96.594(7)°.
	c = 18.9138(3) Å	γ = 90°.
Volume	8011.4(3) Å^3	
Z	4	
Density (calculated)	1.417 Mg/m^3	
Absorption coefficient	4.004 mm^{-1}	
F(000)	3504	
Crystal size	0.1 x 0.089 x 0.04 mm^3	
Theta range for data collection	3.323 to 68.211°.	
Index ranges	-13<=h<=13, -45<=k<=45, -22<=l<=22	
Reflections collected	90600	
Independent reflections	14606 [R(int) = 0.0729]	
Completeness to theta = 67.680°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.7329	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14606 / 36 / 1034	
Goodness-of-fit on F^2	1.257	
Final R indices [I>2sigma(I)]	R1 = 0.0762, wR2 = 0.1941	
R indices (all data)	R1 = 0.1018, wR2 = 0.2064	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.083 and -0.747 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for cis-Ru2(RS-BPTPI)4ClO4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(01)	7227(1)	5719(1)	6666(1)	34(1)
Ru(02)	7535(1)	5717(1)	7874(1)	33(1)
Cl(03)	14244(2)	7152(1)	4090(1)	75(1)
O(004)	6160(3)	6063(1)	7914(2)	36(1)
O(005)	8537(3)	5351(1)	6631(2)	37(1)
O(006)	10884(3)	4669(1)	5826(2)	44(1)
O(007)	6358(3)	5310(1)	7908(2)	37(1)
O(008)	8483(3)	6102(1)	6630(2)	39(1)
O(009)	11507(3)	6654(1)	6129(2)	44(1)
O(00A)	6834(3)	6845(1)	7964(2)	51(1)
O(00B)	3742(3)	5650(1)	7611(2)	44(1)
O(00C)	10970(3)	5752(1)	6928(2)	45(1)
O(00D)	7636(3)	6865(1)	6486(2)	52(1)
O(00E)	4514(3)	4597(1)	8781(2)	50(1)
N(00F)	10806(4)	5175(1)	6513(2)	35(1)
N(00G)	5959(4)	5331(1)	6708(2)	36(1)
O(00H)	3132(3)	6552(1)	8520(2)	54(1)
N(00I)	9602(4)	6714(1)	6462(3)	42(1)
N(00J)	4930(4)	6653(1)	8085(3)	40(1)
N(00K)	4174(4)	5084(1)	8046(2)	36(1)
N(00L)	5951(4)	6098(1)	6711(2)	37(1)
O(00M)	7108(4)	5727(1)	5463(2)	46(1)
O(00N)	7633(3)	5709(1)	9102(2)	44(1)
N(00O)	8916(3)	5372(1)	7830(2)	36(1)
N(00P)	8675(4)	6135(1)	7843(2)	39(1)
N(00Q)	7798(4)	6035(1)	4559(3)	44(1)
C(00R)	10488(5)	6747(1)	5998(3)	41(1)
N(00S)	7021(5)	5946(1)	10093(3)	55(1)
C(00T)	12278(5)	5850(2)	4760(3)	40(1)
C(00U)	11522(4)	5248(2)	5430(3)	39(1)
C(00V)	11886(5)	5881(1)	5449(3)	41(1)

C(00W)	9712(5)	5293(2)	8490(3)	44(1)
C(00X)	11535(4)	5583(2)	5768(3)	37(1)
C(00Y)	3408(5)	5471(2)	8812(3)	40(1)
C(00Z)	11098(5)	5539(2)	6471(3)	44(2)
C(010)	9875(5)	6910(1)	5344(3)	40(1)
C(011)	5655(5)	6198(1)	7330(3)	40(1)
C(012)	11037(4)	4980(2)	5915(3)	40(1)
C(013)	10258(5)	5032(1)	7107(3)	40(1)
C(014)	11850(4)	5206(1)	4771(3)	39(1)
C(015)	3771(4)	5434(2)	8087(3)	39(1)
C(016)	4694(5)	6472(1)	7405(3)	41(1)
C(017)	4739(5)	4961(1)	7439(3)	40(1)
C(018)	6035(5)	6815(1)	8313(3)	42(1)
C(019)	5741(4)	5214(1)	7327(3)	36(1)
C(01A)	9109(5)	6321(1)	8507(3)	40(1)
C(01B)	8311(5)	7233(2)	4296(3)	45(2)
C(01C)	4167(5)	4894(2)	8673(3)	43(1)
C(01D)	10458(5)	4967(2)	8423(3)	44(2)
C(01E)	5282(6)	7121(2)	10363(3)	48(2)
C(01F)	9181(5)	5264(1)	7210(3)	40(1)
O(01G)	13029(4)	7073(1)	4090(3)	102(2)
C(01H)	8928(5)	6246(1)	7215(3)	39(1)
C(01I)	9827(5)	6539(1)	7155(3)	41(1)
C(01J)	12231(4)	5514(2)	4411(3)	39(1)
C(01K)	3643(5)	5147(2)	9170(3)	42(1)
C(01L)	8671(5)	6970(1)	5444(3)	39(1)
C(01M)	10123(5)	6570(2)	8454(3)	53(2)
O(01N)	2558(6)	4143(2)	7606(3)	115(2)
C(01O)	8518(5)	6848(1)	6172(3)	40(1)
C(01P)	10303(5)	7000(1)	4729(3)	41(1)
C(01Q)	9506(5)	7165(2)	4183(3)	44(1)
C(01R)	5925(5)	6935(1)	9049(3)	41(1)
C(01S)	5201(5)	5231(2)	6044(3)	45(2)
C(01T)	2588(5)	5353(2)	10903(4)	62(2)
C(01U)	4790(5)	6855(1)	9222(3)	41(1)
C(01V)	11141(4)	5003(1)	7785(3)	40(1)

C(01W)	4517(5)	4889(2)	6117(3)	45(2)
C(01X)	3840(5)	4915(2)	6771(3)	42(1)
C(01Y)	4142(5)	6670(1)	8606(3)	40(1)
C(01Z)	3375(5)	5098(2)	9848(3)	43(1)
C(020)	7922(5)	5850(2)	5158(3)	44(1)
C(021)	12977(5)	6123(2)	3728(4)	56(2)
C(022)	6427(6)	7207(2)	10178(3)	51(2)
C(023)	9919(5)	6792(2)	7775(3)	52(2)
C(024)	12922(5)	5795(2)	3386(3)	50(2)
C(025)	12649(5)	6153(2)	4397(3)	50(2)
C(026)	2619(5)	5706(2)	9826(4)	49(2)
C(027)	6751(5)	7106(1)	9509(3)	50(2)
C(028)	7554(5)	7415(2)	3762(3)	51(2)
C(029)	2893(5)	5749(2)	9122(3)	46(2)
C(02A)	12553(5)	5500(2)	3717(3)	43(1)
C(02B)	5463(5)	6275(2)	6045(3)	46(2)
C(02C)	6888(6)	5867(2)	9409(3)	47(2)
C(02D)	2068(7)	5629(2)	11225(4)	74(2)
C(02E)	2870(5)	5384(2)	10190(3)	47(2)
C(02F)	7879(5)	7129(1)	4946(3)	46(2)
C(02G)	4348(5)	6497(2)	6110(3)	52(2)
C(02H)	4507(5)	6722(2)	6771(3)	50(2)
C(02I)	5758(7)	7405(2)	11509(4)	62(2)
C(02J)	7984(6)	7522(2)	3154(4)	55(2)
C(02K)	9149(6)	7448(2)	3034(3)	54(2)
C(02L)	4439(6)	6941(2)	9864(3)	51(2)
C(02M)	4951(7)	7226(2)	11035(4)	70(2)
O(02N)	64(5)	4112(2)	7680(3)	118(2)
N(02O)	3752(9)	3664(2)	7665(3)	116(3)
C(02P)	9886(5)	7272(2)	3527(3)	49(2)
C(02Q)	8828(6)	6147(2)	4219(3)	59(2)
C(02R)	2080(6)	5985(2)	10177(4)	68(2)
C(02S)	1812(7)	5950(2)	10861(4)	78(2)
C(02T)	6621(6)	6108(2)	4208(4)	71(2)
C(02U)	6896(8)	7491(2)	11316(4)	75(2)
C(02V)	7233(6)	7398(2)	10677(4)	60(2)

C(02W)	3659(12)	4013(2)	7662(4)	118(4)
C(02X)	6091(8)	6142(2)	10412(4)	99(3)
C(02Y)	8054(6)	5848(2)	10554(4)	79(2)
C(02Z)	5038(11)	3533(3)	7781(6)	175(6)
C(031)	2677(11)	3409(3)	7577(5)	191(7)
O(2)	14980(20)	6903(6)	4419(14)	123(12)
O(4)	14531(14)	7477(4)	4339(16)	111(9)
O(9)	14409(16)	7154(9)	3297(9)	162(10)
O(6)	14729(16)	7233(9)	4869(12)	160(11)
O(8)	14920(20)	6892(6)	3920(20)	144(14)
O(0AA)	14418(17)	7466(7)	3763(18)	154(15)

Table 3. Bond lengths [Å] and angles [°] for cis-Ru2(RS-BPTPI)4ClO4.

Ru(01)-Ru(02)	2.2702(6)
Ru(01)-O(005)	2.037(3)
Ru(01)-O(008)	2.030(4)
Ru(01)-N(00G)	2.056(4)
Ru(01)-N(00L)	2.039(4)
Ru(01)-O(00M)	2.264(4)
Ru(02)-O(004)	2.038(3)
Ru(02)-O(007)	2.038(3)
Ru(02)-O(00N)	2.312(4)
Ru(02)-N(00O)	2.042(4)
Ru(02)-N(00P)	2.040(5)
Cl(03)-O(01G)	1.407(4)
Cl(03)-O(2)	1.357(16)
Cl(03)-O(4)	1.336(12)
Cl(03)-O(9)	1.534(15)
Cl(03)-O(6)	1.54(2)
Cl(03)-O(8)	1.302(19)
Cl(03)-O(0AA)	1.360(15)
O(004)-C(011)	1.289(6)
O(005)-C(01F)	1.288(6)
O(006)-C(012)	1.193(6)
O(007)-C(019)	1.284(6)
O(008)-C(01H)	1.283(6)
O(009)-C(00R)	1.203(6)
O(00A)-C(018)	1.186(6)
O(00B)-C(015)	1.209(6)
O(00C)-C(00Z)	1.200(6)
O(00D)-C(01O)	1.221(6)
O(00E)-C(01C)	1.193(6)
N(00F)-C(00Z)	1.415(7)
N(00F)-C(012)	1.400(6)
N(00F)-C(013)	1.449(6)
N(00G)-C(019)	1.302(6)
N(00G)-C(01S)	1.486(6)
O(00H)-C(01Y)	1.221(6)
N(00I)-C(00R)	1.413(7)
N(00I)-C(01I)	1.464(7)
N(00I)-C(01O)	1.382(6)
N(00J)-C(016)	1.452(6)
N(00J)-C(018)	1.414(7)
N(00J)-C(01Y)	1.406(7)
N(00K)-C(015)	1.399(6)
N(00K)-C(017)	1.453(7)
N(00K)-C(01C)	1.387(7)
N(00L)-C(011)	1.310(7)
N(00L)-C(02B)	1.476(6)
O(00M)-C(020)	1.233(6)
O(00N)-C(02C)	1.233(6)
N(00O)-C(00W)	1.484(6)
N(00O)-C(01F)	1.309(7)
N(00P)-C(01A)	1.472(6)
N(00P)-C(01H)	1.321(7)
N(00Q)-C(020)	1.324(7)
N(00Q)-C(02Q)	1.457(7)
N(00Q)-C(02T)	1.445(7)
C(00R)-C(010)	1.481(8)
N(00S)-C(02C)	1.318(7)
N(00S)-C(02X)	1.472(8)
N(00S)-C(02Y)	1.425(8)
C(00T)-C(00V)	1.428(7)
C(00T)-C(01J)	1.426(7)
C(00T)-C(025)	1.422(7)
C(00U)-C(00X)	1.416(7)
C(00U)-C(012)	1.508(7)
C(00U)-C(014)	1.350(7)
C(00V)-H(00V)	0.9300
C(00V)-C(00X)	1.354(7)

C(00W)-H(00A)	0.9700
C(00W)-H(00B)	0.9700
C(00W)-C(01D)	1.504(7)
C(00X)-C(00Z)	1.481(8)
C(00Y)-C(015)	1.482(8)
C(00Y)-C(01K)	1.406(7)
C(00Y)-C(029)	1.363(7)
C(010)-C(01L)	1.416(7)
C(010)-C(01P)	1.354(7)
C(011)-C(016)	1.518(7)
C(013)-H(013)	0.9800
C(013)-C(01F)	1.529(7)
C(013)-C(01V)	1.536(7)
C(014)-H(014)	0.9300
C(014)-C(01J)	1.433(7)
C(016)-H(016)	0.9800
C(016)-C(02H)	1.519(7)
C(017)-H(017)	0.9800
C(017)-C(019)	1.513(7)
C(017)-C(01X)	1.538(7)
C(018)-C(01R)	1.481(8)
C(01A)-H(01A)	0.9700
C(01A)-H(01B)	0.9700
C(01A)-C(01M)	1.495(7)
C(01B)-C(01Q)	1.418(7)
C(01B)-C(028)	1.423(8)
C(01B)-C(02F)	1.429(8)
C(01C)-C(01K)	1.508(8)
C(01D)-H(01C)	0.9700
C(01D)-H(01D)	0.9700
C(01D)-C(01V)	1.513(7)
C(01E)-C(022)	1.418(8)
C(01E)-C(02L)	1.433(8)
C(01E)-C(02M)	1.420(8)
C(01H)-C(01I)	1.515(7)
C(01I)-H(01I)	0.9800
C(01I)-C(023)	1.503(7)
C(01J)-C(02A)	1.403(7)
C(01K)-C(01Z)	1.363(7)
C(01L)-C(01O)	1.478(7)
C(01L)-C(02F)	1.363(7)
C(01M)-H(01E)	0.9700
C(01M)-H(01F)	0.9700
C(01M)-C(023)	1.527(8)
O(01N)-C(02W)	1.331(12)
C(01P)-H(01P)	0.9300
C(01P)-C(01Q)	1.433(7)
C(01Q)-C(02P)	1.417(8)
C(01R)-C(01U)	1.395(7)
C(01R)-C(027)	1.364(7)
C(01S)-H(01G)	0.9700
C(01S)-H(01H)	0.9700
C(01S)-C(01W)	1.520(7)
C(01T)-H(01T)	0.9300
C(01T)-C(02D)	1.370(9)
C(01T)-C(02E)	1.427(8)
C(01U)-C(01Y)	1.478(7)
C(01U)-C(02L)	1.360(8)
C(01V)-H(01J)	0.9700
C(01V)-H(01K)	0.9700
C(01W)-H(01L)	0.9700
C(01W)-H(01M)	0.9700
C(01W)-C(01X)	1.531(7)
C(01X)-H(01N)	0.9700
C(01X)-H(01O)	0.9700
C(01Z)-H(01Z)	0.9300

C(01Z)-C(02E)	1.410(8)	C(02I)-C(02M)	1.381(9)
C(020)-H(020)	0.9300	C(02I)-C(02U)	1.418(9)
C(021)-H(021)	0.9300	C(02J)-H(02N)	0.9300
C(021)-C(024)	1.393(8)	C(02J)-C(02K)	1.392(8)
C(021)-C(025)	1.363(8)	C(02K)-H(02O)	0.9300
C(022)-C(027)	1.410(8)	C(02K)-C(02P)	1.353(8)
C(022)-C(02V)	1.430(8)	C(02L)-H(02P)	0.9300
C(023)-H(02A)	0.9700	C(02M)-H(02Q)	0.9300
C(023)-H(02B)	0.9700	N(02O)-C(02W)	1.319(9)
C(024)-H(024)	0.9300	N(02O)-C(02Z)	1.529(12)
C(024)-C(02A)	1.363(7)	N(02O)-C(031)	1.544(12)
C(025)-H(025)	0.9300	C(02P)-H(02R)	0.9300
C(026)-C(029)	1.411(8)	C(02Q)-H(02S)	0.9600
C(026)-C(02E)	1.406(8)	C(02Q)-H(02T)	0.9600
C(026)-C(02R)	1.419(8)	C(02Q)-H(02U)	0.9600
C(027)-H(027)	0.9300	C(02R)-H(02V)	0.9300
C(028)-H(028)	0.9300	C(02R)-C(02S)	1.368(9)
C(028)-C(02J)	1.362(8)	C(02S)-H(02W)	0.9300
C(029)-H(029)	0.9300	C(02T)-H(02X)	0.9600
C(02A)-H(02C)	0.9300	C(02T)-H(02Y)	0.9600
C(02B)-H(02D)	0.9700	C(02T)-H	0.9600
C(02B)-H(02E)	0.9700	C(02U)-H(02Z)	0.9300
C(02B)-C(02G)	1.532(7)	C(02U)-C(02V)	1.355(9)
C(02C)-H(02F)	0.9300	C(02V)-H(02)	0.9300
C(02D)-H(02G)	0.9300	C(02X)-H(0AA)	0.9600
C(02D)-C(02S)	1.407(10)	C(02X)-HA	0.9600
C(02F)-H(02H)	0.9300	C(02X)-HB	0.9600
C(02G)-H(02I)	0.9700	C(02Y)-H(1AA)	0.9600
C(02G)-H(02J)	0.9700	C(02Y)-HC	0.9600
C(02G)-C(02H)	1.504(7)	C(02Y)-HD	0.9600
C(02H)-H(02K)	0.9700	C(02Z)-H(2AA)	0.9600
C(02H)-H(02L)	0.9700	C(02Z)-HE	0.9600
C(02I)-H(02M)	0.9300	C(02Z)-HF	0.9600

C(031)-H(03A)	0.9600
C(031)-H(03B)	0.9600
C(031)-H(03C)	0.9600

O(005)-Ru(01)-Ru(02)	90.15(10)
O(005)-Ru(01)-N(00G)	91.83(15)
O(005)-Ru(01)-N(00L)	178.42(15)
O(005)-Ru(01)-O(00M)	86.29(14)
O(008)-Ru(01)-Ru(02)	90.53(11)
O(008)-Ru(01)-O(005)	88.07(14)
O(008)-Ru(01)-N(00G)	179.73(17)
O(008)-Ru(01)-N(00L)	90.44(16)
O(008)-Ru(01)-O(00M)	85.30(14)
N(00G)-Ru(01)-Ru(02)	89.22(13)
N(00G)-Ru(01)-O(00M)	94.94(16)
N(00L)-Ru(01)-Ru(02)	89.34(13)
N(00L)-Ru(01)-N(00G)	89.65(17)
N(00L)-Ru(01)-O(00M)	94.12(16)
O(00M)-Ru(01)-Ru(02)	174.60(10)
Ru(01)-Ru(02)-O(00N)	173.93(10)
O(004)-Ru(02)-Ru(01)	90.33(10)
O(004)-Ru(02)-O(007)	88.58(14)
O(004)-Ru(02)-O(00N)	85.42(14)
O(004)-Ru(02)-N(00O)	179.70(17)
O(004)-Ru(02)-N(00P)	89.84(15)
O(007)-Ru(02)-Ru(01)	90.50(10)
O(007)-Ru(02)-O(00N)	85.07(13)
O(007)-Ru(02)-N(00O)	91.67(15)
O(007)-Ru(02)-N(00P)	178.42(15)
N(00O)-Ru(02)-Ru(01)	89.50(13)
N(00O)-Ru(02)-O(00N)	94.77(16)
N(00P)-Ru(02)-Ru(01)	89.59(13)
N(00P)-Ru(02)-O(00N)	94.72(16)
N(00P)-Ru(02)-N(00O)	89.91(17)
O(01G)-Cl(03)-O(9)	103.3(8)
O(01G)-Cl(03)-O(6)	106.5(8)
O(2)-Cl(03)-O(01G)	113.7(11)
O(2)-Cl(03)-O(9)	108.3(12)
O(4)-Cl(03)-O(01G)	113.1(7)
O(4)-Cl(03)-O(2)	111.0(13)
O(4)-Cl(03)-O(9)	106.8(11)
O(8)-Cl(03)-O(01G)	116.1(11)
O(8)-Cl(03)-O(6)	102.9(14)
O(8)-Cl(03)-O(0AA)	115.2(15)
O(0AA)-Cl(03)-O(01G)	112.2(9)
O(0AA)-Cl(03)-O(6)	102.1(14)
C(011)-O(004)-Ru(02)	119.1(4)
C(01F)-O(005)-Ru(01)	119.3(3)
C(019)-O(007)-Ru(02)	118.6(3)
C(01H)-O(008)-Ru(01)	118.6(4)
C(00Z)-N(00F)-C(013)	121.9(5)
C(012)-N(00F)-C(00Z)	113.4(5)
C(012)-N(00F)-C(013)	124.6(5)
C(019)-N(00G)-Ru(01)	118.8(4)
C(019)-N(00G)-C(01S)	121.6(5)
C(01S)-N(00G)-Ru(01)	119.1(4)
C(00R)-N(00I)-C(01I)	122.2(5)
C(01O)-N(00I)-C(00R)	112.6(5)
C(01O)-N(00I)-C(01I)	125.2(5)
C(018)-N(00J)-C(016)	122.6(5)
C(01Y)-N(00J)-C(016)	125.1(5)
C(01Y)-N(00J)-C(018)	112.1(5)
C(015)-N(00K)-C(017)	121.3(5)
C(01C)-N(00K)-C(015)	113.9(5)
C(01C)-N(00K)-C(017)	123.9(5)
C(011)-N(00L)-Ru(01)	119.6(4)

C(011)-N(00L)-C(02B)	121.6(5)	C(01D)-C(00W)-H(00B)	109.0
C(02B)-N(00L)-Ru(01)	118.6(4)	C(00U)-C(00X)-C(00Z)	108.6(5)
C(020)-O(00M)-Ru(01)	120.9(4)	C(00V)-C(00X)-C(00U)	121.7(5)
C(02C)-O(00N)-Ru(02)	120.7(4)	C(00V)-C(00X)-C(00Z)	129.7(5)
C(00W)-N(00O)-Ru(02)	119.2(4)	C(01K)-C(00Y)-C(015)	107.9(5)
C(01F)-N(00O)-Ru(02)	119.4(4)	C(029)-C(00Y)-C(015)	130.4(5)
C(01F)-N(00O)-C(00W)	120.7(5)	C(029)-C(00Y)-C(01K)	121.7(6)
C(01A)-N(00P)-Ru(02)	119.5(4)	O(00C)-C(00Z)-N(00F)	124.0(6)
C(01H)-N(00P)-Ru(02)	118.3(4)	O(00C)-C(00Z)-C(00X)	130.7(6)
C(01H)-N(00P)-C(01A)	122.0(5)	N(00F)-C(00Z)-C(00X)	105.2(5)
C(020)-N(00Q)-C(02Q)	121.2(5)	C(01L)-C(010)-C(00R)	108.6(5)
C(020)-N(00Q)-C(02T)	119.6(5)	C(01P)-C(010)-C(00R)	130.0(5)
C(02T)-N(00Q)-C(02Q)	119.1(5)	C(01P)-C(010)-C(01L)	121.4(5)
O(009)-C(00R)-N(00I)	125.4(6)	O(004)-C(011)-N(00L)	121.2(5)
O(009)-C(00R)-C(010)	129.7(6)	O(004)-C(011)-C(016)	116.2(5)
N(00I)-C(00R)-C(010)	104.9(5)	N(00L)-C(011)-C(016)	122.6(5)
C(02C)-N(00S)-C(02X)	120.6(6)	O(006)-C(012)-N(00F)	126.3(6)
C(02C)-N(00S)-C(02Y)	122.4(6)	O(006)-C(012)-C(00U)	128.9(5)
C(02Y)-N(00S)-C(02X)	117.0(6)	N(00F)-C(012)-C(00U)	104.8(5)
C(01J)-C(00T)-C(00V)	119.7(5)	N(00F)-C(013)-H(013)	108.0
C(025)-C(00T)-C(00V)	121.1(5)	N(00F)-C(013)-C(01F)	107.7(4)
C(025)-C(00T)-C(01J)	119.1(6)	N(00F)-C(013)-C(01V)	112.2(4)
C(00X)-C(00U)-C(012)	107.9(5)	C(01F)-C(013)-H(013)	108.0
C(014)-C(00U)-C(00X)	122.0(5)	C(01F)-C(013)-C(01V)	112.7(5)
C(014)-C(00U)-C(012)	130.0(5)	C(01V)-C(013)-H(013)	108.0
C(00T)-C(00V)-H(00V)	120.7	C(00U)-C(014)-H(014)	120.8
C(00X)-C(00V)-C(00T)	118.5(5)	C(00U)-C(014)-C(01J)	118.4(5)
C(00X)-C(00V)-H(00V)	120.7	C(01J)-C(014)-H(014)	120.8
N(00O)-C(00W)-H(00A)	109.0	O(00B)-C(015)-N(00K)	124.8(6)
N(00O)-C(00W)-H(00B)	109.0	O(00B)-C(015)-C(00Y)	129.7(5)
N(00O)-C(00W)-C(01D)	112.7(5)	N(00K)-C(015)-C(00Y)	105.4(5)
H(00A)-C(00W)-H(00B)	107.8	N(00J)-C(016)-C(011)	109.8(4)
C(01D)-C(00W)-H(00A)	109.0	N(00J)-C(016)-H(016)	106.7

N(00J)-C(016)-C(02H)	113.8(5)
C(011)-C(016)-H(016)	106.7
C(011)-C(016)-C(02H)	112.6(5)
C(02H)-C(016)-H(016)	106.7
N(00K)-C(017)-H(017)	107.7
N(00K)-C(017)-C(019)	108.4(4)
N(00K)-C(017)-C(01X)	112.0(4)
C(019)-C(017)-H(017)	107.7
C(019)-C(017)-C(01X)	113.1(5)
C(01X)-C(017)-H(017)	107.7
O(00A)-C(018)-N(00J)	125.1(6)
O(00A)-C(018)-C(01R)	130.3(6)
N(00J)-C(018)-C(01R)	104.6(5)
O(007)-C(019)-N(00G)	122.2(5)
O(007)-C(019)-C(017)	113.6(5)
N(00G)-C(019)-C(017)	124.2(5)
N(00P)-C(01A)-H(01A)	108.5
N(00P)-C(01A)-H(01B)	108.5
N(00P)-C(01A)-C(01M)	115.1(5)
H(01A)-C(01A)-H(01B)	107.5
C(01M)-C(01A)-H(01A)	108.5
C(01M)-C(01A)-H(01B)	108.5
C(01Q)-C(01B)-C(028)	119.1(6)
C(01Q)-C(01B)-C(02F)	120.5(5)
C(028)-C(01B)-C(02F)	120.4(6)
O(00E)-C(01C)-N(00K)	126.6(6)
O(00E)-C(01C)-C(01K)	129.1(6)
N(00K)-C(01C)-C(01K)	104.3(5)
C(00W)-C(01D)-H(01C)	109.7
C(00W)-C(01D)-H(01D)	109.7
C(00W)-C(01D)-C(01V)	109.7(5)
H(01C)-C(01D)-H(01D)	108.2
C(01V)-C(01D)-H(01C)	109.7
C(01V)-C(01D)-H(01D)	109.7
C(022)-C(01E)-C(02L)	120.2(6)
C(022)-C(01E)-C(02M)	120.0(6)
C(02M)-C(01E)-C(02L)	119.7(6)
O(005)-C(01F)-N(00O)	121.1(5)
O(005)-C(01F)-C(013)	114.8(5)
N(00O)-C(01F)-C(013)	124.1(5)
O(008)-C(01H)-N(00P)	122.4(5)
O(008)-C(01H)-C(01I)	116.4(5)
N(00P)-C(01H)-C(01I)	121.0(5)
N(00I)-C(01I)-C(01H)	110.2(4)
N(00I)-C(01I)-H(01I)	106.4
N(00I)-C(01I)-C(023)	113.8(4)
C(01H)-C(01I)-H(01I)	106.4
C(023)-C(01I)-C(01H)	112.9(5)
C(023)-C(01I)-H(01I)	106.4
C(00T)-C(01J)-C(014)	119.6(5)
C(02A)-C(01J)-C(00T)	117.7(5)
C(02A)-C(01J)-C(014)	122.7(5)
C(00Y)-C(01K)-C(01C)	108.3(5)
C(01Z)-C(01K)-C(00Y)	121.4(6)
C(01Z)-C(01K)-C(01C)	130.3(5)
C(010)-C(01L)-C(01O)	107.1(5)
C(02F)-C(01L)-C(010)	123.0(5)
C(02F)-C(01L)-C(01O)	129.9(5)
C(01A)-C(01M)-H(01E)	109.5
C(01A)-C(01M)-H(01F)	109.5
C(01A)-C(01M)-C(023)	110.9(5)
H(01E)-C(01M)-H(01F)	108.1
C(023)-C(01M)-H(01E)	109.5
C(023)-C(01M)-H(01F)	109.5
O(00D)-C(01O)-N(00I)	124.3(5)
O(00D)-C(01O)-C(01L)	128.9(5)

N(00I)-C(01O)-C(01L)	106.8(5)	C(01X)-C(01W)-H(01M)	109.9
C(010)-C(01P)-H(01P)	121.0	C(017)-C(01X)-H(01N)	109.9
C(010)-C(01P)-C(01Q)	118.1(5)	C(017)-C(01X)-H(01O)	109.9
C(01Q)-C(01P)-H(01P)	121.0	C(01W)-C(01X)-C(017)	109.0(4)
C(01B)-C(01Q)-C(01P)	120.1(5)	C(01W)-C(01X)-H(01N)	109.9
C(02P)-C(01Q)-C(01B)	118.3(6)	C(01W)-C(01X)-H(01O)	109.9
C(02P)-C(01Q)-C(01P)	121.6(6)	H(01N)-C(01X)-H(01O)	108.3
C(01U)-C(01R)-C(018)	109.5(5)	O(00H)-C(01Y)-N(00J)	123.4(6)
C(027)-C(01R)-C(018)	128.1(6)	O(00H)-C(01Y)-C(01U)	130.6(6)
C(027)-C(01R)-C(01U)	122.4(6)	N(00J)-C(01Y)-C(01U)	106.0(5)
N(00G)-C(01S)-H(01G)	109.0	C(01K)-C(01Z)-H(01Z)	120.8
N(00G)-C(01S)-H(01H)	109.0	C(01K)-C(01Z)-C(02E)	118.3(6)
N(00G)-C(01S)-C(01W)	112.9(5)	C(02E)-C(01Z)-H(01Z)	120.8
H(01G)-C(01S)-H(01H)	107.8	O(00M)-C(020)-N(00Q)	126.0(6)
C(01W)-C(01S)-H(01G)	109.0	O(00M)-C(020)-H(020)	117.0
C(01W)-C(01S)-H(01H)	109.0	N(00Q)-C(020)-H(020)	117.0
C(02D)-C(01T)-H(01T)	119.6	C(024)-C(021)-H(021)	119.9
C(02D)-C(01T)-C(02E)	120.7(7)	C(025)-C(021)-H(021)	119.9
C(02E)-C(01T)-H(01T)	119.6	C(025)-C(021)-C(024)	120.2(6)
C(01R)-C(01U)-C(01Y)	107.7(5)	C(01E)-C(022)-C(02V)	119.0(6)
C(02L)-C(01U)-C(01R)	121.9(6)	C(027)-C(022)-C(01E)	120.0(6)
C(02L)-C(01U)-C(01Y)	130.3(6)	C(027)-C(022)-C(02V)	121.0(6)
C(013)-C(01V)-H(01J)	109.8	C(01I)-C(023)-C(01M)	107.4(5)
C(013)-C(01V)-H(01K)	109.8	C(01I)-C(023)-H(02A)	110.2
C(01D)-C(01V)-C(013)	109.2(4)	C(01I)-C(023)-H(02B)	110.2
C(01D)-C(01V)-H(01J)	109.8	C(01M)-C(023)-H(02A)	110.2
C(01D)-C(01V)-H(01K)	109.8	C(01M)-C(023)-H(02B)	110.2
H(01J)-C(01V)-H(01K)	108.3	H(02A)-C(023)-H(02B)	108.5
C(01S)-C(01W)-H(01L)	109.9	C(021)-C(024)-H(024)	119.8
C(01S)-C(01W)-H(01M)	109.9	C(02A)-C(024)-C(021)	120.5(6)
C(01S)-C(01W)-C(01X)	109.0(4)	C(02A)-C(024)-H(024)	119.8
H(01L)-C(01W)-H(01M)	108.3	C(00T)-C(025)-H(025)	119.7
C(01X)-C(01W)-H(01L)	109.9	C(021)-C(025)-C(00T)	120.6(6)

C(021)-C(025)-H(025)	119.7
C(029)-C(026)-C(02R)	120.6(6)
C(02E)-C(026)-C(029)	120.5(6)
C(02E)-C(026)-C(02R)	118.8(6)
C(01R)-C(027)-C(022)	118.0(6)
C(01R)-C(027)-H(027)	121.0
C(022)-C(027)-H(027)	121.0
C(01B)-C(028)-H(028)	120.0
C(02J)-C(028)-C(01B)	119.9(6)
C(02J)-C(028)-H(028)	120.0
C(00Y)-C(029)-C(026)	117.9(6)
C(00Y)-C(029)-H(029)	121.0
C(026)-C(029)-H(029)	121.0
C(01J)-C(02A)-H(02C)	119.1
C(024)-C(02A)-C(01J)	121.9(6)
C(024)-C(02A)-H(02C)	119.1
N(00L)-C(02B)-H(02D)	108.7
N(00L)-C(02B)-H(02E)	108.7
N(00L)-C(02B)-C(02G)	114.2(5)
H(02D)-C(02B)-H(02E)	107.6
C(02G)-C(02B)-H(02D)	108.7
C(02G)-C(02B)-H(02E)	108.7
O(00N)-C(02C)-N(00S)	124.4(6)
O(00N)-C(02C)-H(02F)	117.8
N(00S)-C(02C)-H(02F)	117.8
C(01T)-C(02D)-H(02G)	119.7
C(01T)-C(02D)-C(02S)	120.7(7)
C(02S)-C(02D)-H(02G)	119.7
C(01Z)-C(02E)-C(01T)	121.2(6)
C(026)-C(02E)-C(01T)	118.7(6)
C(026)-C(02E)-C(01Z)	120.2(6)
C(01B)-C(02F)-H(02H)	121.5
C(01L)-C(02F)-C(01B)	116.9(5)
C(01L)-C(02F)-H(02H)	121.5
C(02B)-C(02G)-H(02I)	109.5
C(02B)-C(02G)-H(02J)	109.5
H(02I)-C(02G)-H(02J)	108.1
C(02H)-C(02G)-C(02B)	110.7(5)
C(02H)-C(02G)-H(02I)	109.5
C(02H)-C(02G)-H(02J)	109.5
C(016)-C(02H)-H(02K)	110.2
C(016)-C(02H)-H(02L)	110.2
C(02G)-C(02H)-C(016)	107.4(5)
C(02G)-C(02H)-H(02K)	110.2
C(02G)-C(02H)-H(02L)	110.2
H(02K)-C(02H)-H(02L)	108.5
C(02M)-C(02I)-H(02M)	120.1
C(02M)-C(02I)-C(02U)	119.9(7)
C(02U)-C(02I)-H(02M)	120.1
C(028)-C(02J)-H(02N)	119.5
C(028)-C(02J)-C(02K)	121.0(6)
C(02K)-C(02J)-H(02N)	119.5
C(02J)-C(02K)-H(02O)	119.7
C(02P)-C(02K)-C(02J)	120.6(6)
C(02P)-C(02K)-H(02O)	119.7
C(01E)-C(02L)-H(02P)	121.3
C(01U)-C(02L)-C(01E)	117.4(6)
C(01U)-C(02L)-H(02P)	121.3
C(01E)-C(02M)-H(02Q)	120.2
C(02I)-C(02M)-C(01E)	119.6(7)
C(02I)-C(02M)-H(02Q)	120.2
C(02W)-N(02O)-C(02Z)	113.3(10)
C(02W)-N(02O)-C(031)	123.9(10)
C(02Z)-N(02O)-C(031)	122.8(8)
C(01Q)-C(02P)-H(02R)	119.5
C(02K)-C(02P)-C(01Q)	121.1(6)

C(02K)-C(02P)-H(02R)	119.5
N(00Q)-C(02Q)-H(02S)	109.5
N(00Q)-C(02Q)-H(02T)	109.5
N(00Q)-C(02Q)-H(02U)	109.5
H(02S)-C(02Q)-H(02T)	109.5
H(02S)-C(02Q)-H(02U)	109.5
H(02T)-C(02Q)-H(02U)	109.5
C(026)-C(02R)-H(02V)	119.1
C(02S)-C(02R)-C(026)	121.7(7)
C(02S)-C(02R)-H(02V)	119.1
C(02D)-C(02S)-H(02W)	120.3
C(02R)-C(02S)-C(02D)	119.3(7)
C(02R)-C(02S)-H(02W)	120.3
N(00Q)-C(02T)-H(02X)	109.5
N(00Q)-C(02T)-H(02Y)	109.5
N(00Q)-C(02T)-H	109.5
H(02X)-C(02T)-H(02Y)	109.5
H(02X)-C(02T)-H	109.5
H(02Y)-C(02T)-H	109.5
C(02I)-C(02U)-H(02Z)	119.1
C(02V)-C(02U)-C(02I)	121.9(7)
C(02V)-C(02U)-H(02Z)	119.1
C(022)-C(02V)-H(02)	120.2
C(02U)-C(02V)-C(022)	119.6(7)
C(02U)-C(02V)-H(02)	120.2
N(02O)-C(02W)-O(01N)	116.0(11)
N(00S)-C(02X)-H(0AA)	109.5
N(00S)-C(02X)-HA	109.5
N(00S)-C(02X)-HB	109.5
H(0AA)-C(02X)-HA	109.5
H(0AA)-C(02X)-HB	109.5
HA-C(02X)-HB	109.5
N(00S)-C(02Y)-H(1AA)	109.5
N(00S)-C(02Y)-HC	109.5
N(00S)-C(02Y)-HD	109.5
H(1AA)-C(02Y)-HC	109.5
H(1AA)-C(02Y)-HD	109.5
HC-C(02Y)-HD	109.5
N(02O)-C(02Z)-H(2AA)	109.5
N(02O)-C(02Z)-HE	109.5
N(02O)-C(02Z)-HF	109.5
H(2AA)-C(02Z)-HE	109.5
H(2AA)-C(02Z)-HF	109.5
HE-C(02Z)-HF	109.5
N(02O)-C(031)-H(03A)	109.5
N(02O)-C(031)-H(03B)	109.5
N(02O)-C(031)-H(03C)	109.5
H(03A)-C(031)-H(03B)	109.5
H(03A)-C(031)-H(03C)	109.5
H(03B)-C(031)-H(03C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for cis-Ru2(RS-BPTPI)4ClO4. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(01)	29(1)	41(1)	32(1)	-1(1)	1(1)	2(1)
Ru(02)	27(1)	41(1)	31(1)	0(1)	1(1)	1(1)
Cl(03)	53(1)	63(1)	110(2)	5(1)	15(1)	2(1)
O(004)	31(2)	43(2)	34(2)	-3(2)	4(2)	2(2)
O(005)	31(2)	47(2)	31(2)	-1(2)	-3(2)	2(2)
O(006)	44(2)	38(2)	51(3)	-3(2)	7(2)	3(2)
O(007)	30(2)	49(2)	32(2)	2(2)	1(2)	2(2)
O(008)	33(2)	49(2)	35(2)	-2(2)	3(2)	1(2)
O(009)	32(2)	43(2)	57(3)	5(2)	7(2)	3(2)
O(00A)	38(2)	60(3)	53(3)	1(2)	3(2)	1(2)
O(00B)	39(2)	48(2)	46(3)	5(2)	6(2)	-1(2)
O(00C)	43(2)	49(2)	45(3)	-11(2)	8(2)	0(2)
O(00D)	42(2)	63(3)	52(3)	8(2)	11(2)	4(2)
O(00E)	56(3)	43(2)	50(3)	8(2)	1(2)	4(2)
N(00F)	29(2)	35(2)	41(3)	-4(2)	6(2)	-2(2)
N(00G)	26(2)	44(3)	35(3)	-6(2)	-4(2)	4(2)
O(00H)	38(2)	52(2)	73(3)	-11(2)	7(2)	-1(2)
N(00I)	36(3)	48(3)	43(3)	6(2)	4(2)	-1(2)
N(00J)	31(2)	44(3)	43(3)	-5(2)	4(2)	0(2)
N(00K)	28(2)	43(3)	36(3)	1(2)	3(2)	2(2)
N(00L)	27(2)	46(3)	36(3)	5(2)	-5(2)	2(2)
O(00M)	45(2)	60(3)	33(2)	5(2)	0(2)	1(2)
O(00N)	42(2)	58(3)	33(2)	1(2)	9(2)	-2(2)
N(00O)	25(2)	41(3)	40(3)	2(2)	-2(2)	-6(2)
N(00P)	38(3)	46(3)	33(3)	0(2)	6(2)	6(2)
N(00Q)	53(3)	50(3)	32(3)	2(2)	8(2)	7(2)
C(00R)	41(3)	35(3)	48(4)	-9(3)	8(3)	-5(3)

N(00S)	86(4)	49(3)	30(3)	2(2)	11(3)	8(3)
C(00T)	38(3)	46(3)	36(4)	0(3)	0(3)	-2(3)
C(00U)	24(3)	50(3)	44(4)	-3(3)	3(3)	5(2)
C(00V)	38(3)	36(3)	48(4)	-7(3)	3(3)	-4(3)
C(00W)	29(3)	63(4)	39(4)	3(3)	1(3)	3(3)
C(00X)	24(3)	48(3)	38(4)	-4(3)	5(2)	3(2)
C(00Y)	33(3)	45(3)	41(4)	1(3)	1(3)	-8(3)
C(00Z)	31(3)	45(4)	54(4)	-3(3)	-9(3)	8(3)
C(010)	39(3)	39(3)	43(4)	-2(3)	2(3)	-5(3)
C(011)	34(3)	45(3)	40(4)	4(3)	-4(3)	0(3)
C(012)	28(3)	43(3)	46(4)	-9(3)	-5(3)	9(2)
C(013)	33(3)	41(3)	47(4)	-7(3)	5(3)	4(2)
C(014)	22(3)	41(3)	52(4)	-13(3)	-1(3)	0(2)
C(015)	24(3)	43(3)	51(4)	2(3)	3(3)	-3(2)
C(016)	27(3)	46(3)	48(4)	-12(3)	-2(3)	-1(2)
C(017)	39(3)	42(3)	37(4)	-2(3)	-1(3)	1(3)
C(018)	39(3)	41(3)	44(4)	0(3)	2(3)	6(3)
C(019)	27(3)	47(3)	34(3)	2(3)	2(2)	2(2)
C(01A)	41(3)	39(3)	39(4)	-6(3)	-3(3)	-2(2)
C(01B)	46(3)	46(3)	41(4)	-4(3)	-2(3)	-6(3)
C(01C)	28(3)	53(4)	46(4)	2(3)	-4(3)	-10(3)
C(01D)	36(3)	56(4)	40(4)	12(3)	-3(3)	6(3)
C(01E)	69(4)	37(3)	39(4)	-3(3)	4(3)	4(3)
C(01F)	28(3)	44(3)	50(4)	-9(3)	8(3)	-6(2)
O(01G)	42(3)	89(4)	179(6)	13(4)	27(3)	-8(3)
C(01H)	33(3)	38(3)	47(4)	-1(3)	10(3)	2(2)
C(01I)	37(3)	38(3)	47(4)	1(3)	-1(3)	-3(2)
C(01J)	27(3)	48(3)	42(4)	-2(3)	0(3)	4(2)
C(01K)	30(3)	49(3)	44(4)	3(3)	-3(3)	-5(3)
C(01L)	37(3)	40(3)	42(4)	2(3)	13(3)	-1(2)
C(01M)	54(4)	56(4)	47(4)	-5(3)	5(3)	-9(3)
O(01N)	168(7)	82(4)	94(5)	1(4)	6(5)	13(4)
C(01O)	35(3)	40(3)	44(4)	0(3)	4(3)	-3(3)

C(01P)	34(3)	42(3)	46(4)	1(3)	4(3)	0(2)
C(01Q)	50(4)	42(3)	41(4)	-4(3)	8(3)	-10(3)
C(01R)	42(3)	36(3)	43(4)	-1(3)	-4(3)	0(3)
C(01S)	37(3)	60(4)	38(4)	-10(3)	2(3)	1(3)
C(01T)	50(4)	82(5)	53(5)	0(4)	1(3)	-16(4)
C(01U)	50(4)	38(3)	32(4)	-2(3)	0(3)	2(3)
C(01V)	30(3)	44(3)	45(4)	1(3)	-4(3)	7(2)
C(01W)	39(3)	54(4)	40(4)	-10(3)	-2(3)	-1(3)
C(01X)	35(3)	52(4)	37(4)	-5(3)	-4(3)	-7(3)
C(01Y)	38(3)	37(3)	48(4)	3(3)	11(3)	6(3)
C(01Z)	35(3)	51(4)	42(4)	6(3)	-4(3)	-2(3)
C(020)	45(4)	46(3)	41(4)	-4(3)	4(3)	3(3)
C(021)	57(4)	53(4)	56(5)	4(3)	7(3)	-11(3)
C(022)	58(4)	46(4)	47(4)	1(3)	-1(3)	1(3)
C(023)	50(4)	56(4)	49(4)	0(3)	5(3)	-15(3)
C(024)	51(4)	60(4)	39(4)	3(3)	9(3)	0(3)
C(025)	52(4)	43(3)	53(4)	0(3)	-1(3)	-7(3)
C(026)	42(4)	53(4)	54(4)	-7(3)	12(3)	-3(3)
C(027)	53(4)	44(3)	50(4)	-2(3)	-4(3)	3(3)
C(028)	40(3)	55(4)	56(4)	1(3)	-3(3)	0(3)
C(029)	42(3)	44(3)	54(4)	3(3)	9(3)	-4(3)
C(02A)	36(3)	50(4)	43(4)	-7(3)	5(3)	-1(3)
C(02B)	44(3)	46(3)	45(4)	5(3)	-1(3)	3(3)
C(02C)	56(4)	58(4)	31(4)	6(3)	14(3)	11(3)
C(02D)	76(5)	99(6)	51(5)	-10(5)	24(4)	-14(5)
C(02E)	39(3)	65(4)	36(4)	-2(3)	2(3)	-13(3)
C(02F)	35(3)	48(3)	53(4)	4(3)	1(3)	-5(3)
C(02G)	48(4)	55(4)	50(4)	1(3)	-10(3)	11(3)
C(02H)	46(4)	51(4)	50(4)	-5(3)	-2(3)	13(3)
C(02I)	97(6)	54(4)	36(4)	2(3)	5(4)	11(4)
C(02J)	54(4)	65(4)	45(4)	-1(3)	-5(3)	-10(3)
C(02K)	70(5)	52(4)	42(4)	5(3)	11(3)	-11(3)
C(02L)	56(4)	45(4)	52(4)	6(3)	6(3)	4(3)

C(02M)	112(6)	50(4)	46(5)	5(3)	0(4)	13(4)
O(02N)	121(5)	113(5)	122(6)	-19(4)	18(4)	-3(4)
N(02O)	229(10)	64(5)	58(5)	7(4)	25(6)	17(6)
C(02P)	50(4)	48(4)	49(4)	-3(3)	8(3)	-5(3)
C(02Q)	83(5)	55(4)	43(4)	2(3)	17(4)	-4(4)
C(02R)	71(5)	72(5)	63(5)	-10(4)	14(4)	-3(4)
C(02S)	83(6)	84(6)	71(6)	-20(5)	32(5)	2(5)
C(02T)	73(5)	86(5)	52(5)	16(4)	-4(4)	19(4)
C(02U)	102(7)	63(5)	57(5)	1(4)	-6(5)	-2(4)
C(02V)	76(5)	50(4)	50(5)	-4(3)	-6(4)	-7(3)
C(02W)	257(14)	54(5)	45(5)	4(4)	25(7)	40(7)
C(02X)	168(9)	81(5)	60(5)	15(4)	59(6)	61(6)
C(02Y)	86(6)	111(6)	35(4)	-14(4)	-6(4)	2(5)
C(02Z)	201(13)	131(9)	213(14)	91(9)	110(11)	75(9)
C(031)	370(20)	64(6)	123(10)	13(6)	-36(11)	-94(9)
O(2)	63(10)	102(17)	190(20)	78(18)	-29(14)	16(9)
O(4)	80(9)	44(9)	220(30)	-37(11)	41(15)	-16(7)
O(9)	162(15)	240(30)	94(13)	-7(14)	68(11)	31(16)
O(6)	124(14)	200(30)	160(20)	-41(18)	35(13)	-11(15)
O(8)	75(14)	67(14)	300(40)	-60(20)	70(20)	3(10)
O(0AA)	76(10)	170(20)	220(30)	150(20)	38(17)	-8(12)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cis-Ru2(RS-BPTPI)4ClO4.

	x	y	z	U(eq)
H(00V)	11872	6100	5673	49
H(00A)	9234	5259	8879	53
H(00B)	10232	5494	8607	53
H(013)	9970	4792	6978	48
H(014)	11829	4984	4555	47
H(016)	3949	6341	7416	49
H(017)	5091	4728	7560	48
H(01A)	9353	6145	8869	48
H(01B)	8454	6454	8665	48
H(01C)	9951	4758	8368	53
H(01D)	11008	4937	8851	53
H(01I)	10604	6423	7167	49
H(01E)	10853	6435	8454	63
H(01F)	10209	6726	8864	63
H(01P)	11091	6956	4663	49
H(01G)	5699	5205	5663	54
H(01H)	4641	5422	5913	54
H(01T)	2758	5143	11153	74
H(01J)	11651	4798	7753	48
H(01K)	11637	5214	7835	48
H(01L)	5063	4689	6170	54
H(01M)	3963	4850	5694	54
H(01N)	3375	4702	6814	51
H(01O)	3302	5117	6722	51
H(01Z)	3521	4882	10079	52
H(020)	8693	5809	5368	53
H(021)	13239	6322	3500	67

H(02A)	9192	6929	7770	62
H(02B)	10575	6955	7749	62
H(024)	13139	5777	2927	60
H(025)	12669	6374	4617	60
H(027)	7505	7156	9384	60
H(028)	6767	7460	3829	61
H(029)	2728	5961	8877	56
H(02C)	12513	5285	3476	52
H(02D)	5273	6095	5682	55
H(02E)	6071	6427	5887	55
H(02F)	6185	5936	9141	57
H(02G)	1882	5603	11689	89
H(02H)	7094	7167	5025	55
H(02I)	4191	6649	5695	63
H(02J)	3670	6341	6127	63
H(02K)	3809	6868	6801	60
H(02L)	5190	6877	6764	60
H(02M)	5554	7469	11955	75
H(02N)	7492	7648	2813	66
H(02O)	9422	7521	2612	65
H(02P)	3682	6885	9975	61
H(02Q)	4196	7173	11154	84
H(02R)	10656	7219	3433	58
H(02S)	8808	6400	4155	89
H(02T)	8812	6033	3764	89
H(02U)	9542	6081	4513	89
H(02V)	1905	6197	9937	82
H(02W)	1465	6137	11083	93
H(02X)	6500	5977	3769	107
H(02Y)	6542	6357	4111	107
H	6039	6036	4511	107
H(02Z)	7427	7615	11637	90
H(02)	7985	7459	10562	72

H(0AA)	5405	6168	10067	149
HA	6385	6373	10559	149
HB	5878	6014	10817	149
H(1AA)	8493	5672	10325	118
HC	7821	5752	10987	118
HD	8543	6054	10661	118
H(2AA)	5567	3733	7806	262
HE	5191	3383	7392	262
HF	5163	3402	8218	262
H(03A)	2650	3276	8008	286
H(03B)	2756	3249	7190	286
H(03C)	1958	3544	7477	286

mer-Ru_2(*S*-BPTPI)$_4$Cl·DMF

Figure 29. Full ortep plot (up) and stereoview of *S*-isomer of diruthenium molecule (down)

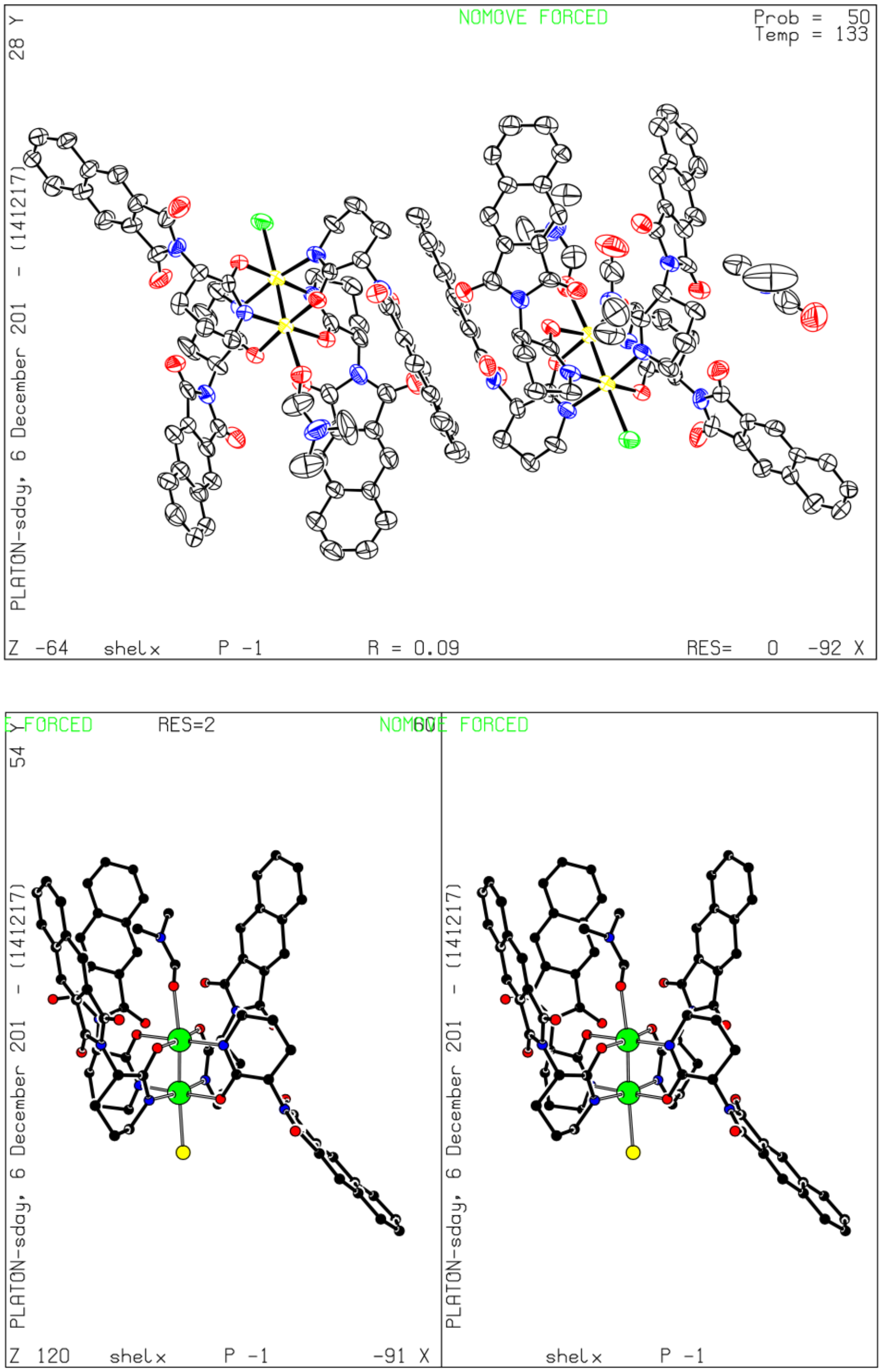

Table 1. Crystal data and structure refinement for mer-Ru2(RS-BPTPI)4Cl.

Identification code	shelx	
Empirical formula	C148 H132 Cl2 N20 O28 Ru4	
Formula weight	3113.91	
Temperature	133(2) K	
Wavelength	1.5418 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.4802(2) Å	α= 93.000(7)°.
	b = 23.3087(4) Å	β= 96.973(7)°.
	c = 26.3994(5) Å	γ = 92.289(7)°.
Volume	8213.2(3) Å^3	
Z	2	
Density (calculated)	1.259 Mg/m^3	
Absorption coefficient	3.795 mm^{-1}	
F(000)	3188	
Crystal size	0.287 x 0.098 x 0.060 mm^3	
Theta range for data collection	3.306 to 68.244°.	
Index ranges	-16<=h<=16, -27<=k<=28, -31<=l<=31	
Reflections collected	91778	
Independent reflections	29391 [R(int) = 0.0858]	
Completeness to theta = 67.680°	98.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.4065	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	29391 / 0 / 1827	
Goodness-of-fit on F^2	1.198	
Final R indices [I>2sigma(I)]	R1 = 0.0907, wR2 = 0.2199	
R indices (all data)	R1 = 0.1326, wR2 = 0.2379	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.352 and -0.851 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for mer-Ru2(RS-BPTPI)4Cl. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(01)	682(1)	3214(1)	528(1)	48(1)
Ru(02)	4148(1)	1984(1)	4699(1)	50(1)
Ru(03)	3798(1)	2743(1)	5224(1)	50(1)
Ru(04)	1070(1)	2382(1)	117(1)	51(1)
Cl(05)	3345(1)	3532(1)	5872(1)	66(1)
Cl(06)	1579(1)	1507(1)	-412(1)	70(1)
O(007)	1370(3)	2842(2)	-496(2)	51(1)
O(008)	2128(3)	3402(2)	782(2)	49(1)
O(009)	6394(3)	3177(2)	4206(2)	65(2)
O(00A)	5633(3)	2102(2)	4902(2)	58(1)
O(00B)	542(3)	2788(2)	1172(2)	54(1)
O(00C)	2267(3)	2633(2)	3515(2)	59(1)
O(00D)	5280(4)	2023(2)	6658(2)	69(2)
O(00E)	4188(4)	4334(2)	1507(2)	66(2)
O(00F)	-1625(4)	2240(2)	1146(2)	71(2)
O(00G)	-789(3)	3067(2)	316(2)	59(1)
O(00H)	498(4)	992(2)	3774(2)	64(1)
O(00I)	2533(3)	2669(2)	1801(2)	56(1)
O(00J)	2695(3)	1834(2)	4451(2)	52(1)
O(00K)	8416(3)	2232(2)	4664(2)	64(2)
O(00L)	4258(3)	2522(2)	4122(2)	57(1)
O(00M)	445(4)	2487(2)	2661(2)	72(2)
N(00N)	2302(4)	2642(3)	4872(2)	57(2)
O(00O)	3547(3)	2169(2)	5766(2)	53(1)
O(00P)	2732(4)	3612(3)	-1686(2)	77(2)
O(00Q)	4237(4)	2898(2)	2713(2)	68(2)
N(00R)	805(4)	3637(2)	-117(2)	44(1)
N(00S)	3501(4)	3424(3)	1575(2)	54(2)
O(00T)	4486(4)	1286(2)	4102(2)	73(2)
O(00U)	-1873(4)	3525(2)	-714(2)	72(2)
N(00V)	5172(4)	3135(3)	3501(2)	59(2)

O(00W)	2272(4)	1139(3)	6848(2)	83(2)
N(00X)	2536(4)	2523(2)	494(2)	54(2)
N(00Y)	1227(4)	1890(3)	3713(2)	49(2)
O(00Z)	-3574(4)	2948(2)	589(2)	71(2)
O(010)	-348(4)	2861(3)	-1444(2)	79(2)
N(011)	-2658(4)	3099(3)	-84(2)	59(2)
N(012)	7499(4)	1993(3)	5308(2)	54(2)
N(013)	-431(4)	2274(3)	1853(2)	64(2)
N(014)	4076(4)	1442(3)	5273(2)	57(2)
N(015)	5344(4)	2811(3)	5495(2)	55(2)
O(016)	6722(4)	1475(2)	5897(2)	77(2)
N(017)	-447(4)	2296(3)	-174(2)	60(2)
N(018)	3731(4)	1557(3)	6627(2)	57(2)
N(019)	4045(4)	3287(3)	4653(2)	56(2)
N(01A)	749(4)	1937(3)	736(2)	58(2)
C(01B)	2743(5)	1722(4)	2661(3)	61(2)
C(01C)	-3868(5)	4835(4)	404(3)	57(2)
C(01D)	2080(5)	2221(4)	4536(3)	56(2)
C(01E)	-3342(5)	5036(4)	5(3)	59(2)
O(01F)	328(4)	4001(2)	1031(2)	72(2)
C(01G)	1040(5)	1320(4)	3570(3)	57(2)
N(01H)	1228(4)	3290(3)	-1442(2)	54(2)
C(01I)	3400(5)	1765(3)	7448(3)	56(2)
C(01J)	8227(5)	64(4)	5062(3)	62(2)
C(01K)	-3897(5)	4251(3)	523(3)	56(2)
C(01L)	-4229(6)	5838(4)	604(3)	72(3)
C(01M)	595(5)	2748(3)	-2181(3)	57(2)
C(01N)	-3291(5)	5610(4)	-108(3)	65(2)
C(01O)	5942(5)	2484(4)	5265(3)	63(2)
C(01P)	2108(5)	1699(4)	3046(3)	58(2)
N(01Q)	5485(6)	847(3)	3587(3)	83(2)
C(01R)	-255(6)	2536(4)	2346(3)	63(2)
C(01S)	4219(5)	3060(4)	4221(3)	53(2)
C(01T)	7617(5)	1920(3)	3089(3)	55(2)
C(01U)	1115(5)	3365(4)	-519(3)	60(2)
C(01V)	1055(5)	2137(3)	4210(3)	58(2)

C(01W)	3688(5)	4006(4)	1722(3)	61(2)
C(01X)	6085(5)	2998(3)	3772(3)	57(2)
C(01Y)	2610(5)	3609(4)	2260(3)	55(2)
C(01Z)	3133(5)	4118(4)	2174(3)	60(2)
C(020)	2742(5)	2998(3)	771(3)	50(2)
C(021)	6529(5)	2593(3)	3413(3)	54(2)
C(022)	383(6)	2364(4)	-3044(3)	67(2)
C(023)	-2271(5)	3568(3)	2733(3)	56(2)
C(024)	8232(6)	-528(4)	5137(3)	67(2)
C(025)	-2877(5)	4069(4)	-157(3)	52(2)
C(026)	4384(5)	3401(4)	3760(3)	61(2)
C(027)	3739(5)	3156(3)	1114(3)	53(2)
C(028)	8730(5)	312(4)	4677(3)	57(2)
C(029)	2827(5)	3164(4)	1875(3)	49(2)
C(02A)	2790(6)	1202(4)	2348(3)	66(2)
C(02B)	-2409(6)	3549(4)	-371(3)	66(2)
C(02C)	5866(5)	2506(3)	2962(3)	57(2)
C(02D)	4530(6)	1891(4)	6856(3)	64(2)
C(02E)	-2919(5)	3465(3)	2254(3)	60(2)
C(02F)	1544(5)	2983(3)	-2251(3)	54(2)
C(02G)	4969(6)	2852(3)	3017(3)	57(2)
C(02H)	7732(5)	446(4)	5395(3)	63(2)
C(02I)	1299(5)	4093(4)	3346(3)	64(2)
C(02J)	-1150(5)	2905(4)	2397(3)	60(2)
C(02K)	8743(5)	903(4)	4605(3)	60(2)
C(02L)	8630(6)	-886(4)	4784(3)	75(3)
C(02M)	6941(5)	1825(3)	2627(3)	59(2)
C(02N)	-1318(5)	2423(4)	1586(3)	61(2)
C(02O)	3007(7)	1440(4)	6958(3)	63(2)
C(02P)	1917(5)	2138(4)	3414(3)	58(2)
C(02Q)	4387(5)	2627(3)	1196(3)	65(2)
C(02R)	8101(5)	1871(4)	4917(3)	57(2)
C(02S)	1258(5)	3673(3)	-985(3)	58(2)
C(02T)	3556(6)	2113(4)	8306(3)	68(2)
C(02U)	3798(5)	1646(4)	5698(3)	57(2)
C(02V)	7080(5)	2552(3)	5389(3)	53(2)

C(02W)	7400(5)	2305(3)	3486(3)	58(2)
C(02X)	1934(5)	4077(4)	2950(3)	61(2)
C(02Y)	7263(5)	1497(3)	5561(3)	58(2)
N(02Z)	8024(6)	4624(4)	4716(3)	86(2)
C(030)	-3385(5)	3888(3)	239(3)	54(2)
C(031)	1345(6)	2594(3)	-3108(3)	58(2)
C(032)	1612(5)	3132(3)	4929(3)	62(2)
C(033)	4318(5)	2036(3)	7396(3)	57(2)
C(034)	6058(5)	2144(4)	2577(3)	68(2)
C(035)	4601(6)	4052(4)	3887(3)	72(3)
C(036)	-3266(5)	3254(4)	296(3)	59(2)
C(037)	1713(6)	2514(3)	-3593(3)	56(2)
C(038)	-2662(5)	3118(3)	1847(3)	58(2)
C(039)	420(6)	4227(3)	-138(3)	71(2)
N(03A)	-583(7)	4409(3)	1596(3)	98(3)
C(03B)	-1366(5)	3249(4)	2780(3)	67(2)
C(03C)	46(6)	1310(4)	1563(3)	82(3)
C(03D)	-2201(5)	2543(3)	-105(3)	63(2)
C(03E)	1568(5)	1188(4)	3111(3)	57(2)
C(03F)	458(5)	2682(4)	4188(3)	66(2)
C(03G)	4872(6)	2346(4)	7787(3)	76(3)
C(03H)	-3727(6)	6000(4)	198(3)	75(2)
C(03I)	1951(6)	2902(3)	-2701(3)	59(2)
C(03J)	391(6)	2948(4)	-1648(3)	63(2)
C(03K)	-2849(5)	4607(4)	-299(3)	66(2)
C(03L)	8267(5)	1241(3)	4919(3)	54(2)
C(03M)	6830(6)	3364(3)	5983(3)	77(3)
C(03N)	523(6)	4151(3)	-1069(3)	65(2)
C(03O)	3226(5)	2057(3)	549(3)	64(2)
C(03P)	-3377(6)	4216(4)	3048(3)	73(2)
C(03Q)	635(6)	4539(3)	-585(3)	64(2)
C(03R)	2033(5)	3587(4)	2641(3)	59(2)
C(03S)	1962(6)	3329(4)	-1774(3)	62(2)
C(03T)	3683(5)	1259(3)	6130(3)	58(2)
C(03U)	-1075(5)	2636(3)	7(3)	54(2)
C(03V)	7398(5)	2827(3)	5933(3)	70(2)

C(03W)	-1795(6)	2825(3)	1928(3)	59(2)
C(03X)	-4300(6)	5259(4)	711(3)	68(2)
C(03Y)	169(7)	2034(4)	-3926(3)	81(3)
C(03Z)	4675(7)	2698(4)	9165(3)	75(3)
C(040)	3008(5)	1808(3)	7898(3)	62(2)
C(041)	3914(6)	4246(4)	4272(3)	71(2)
C(042)	4283(6)	468(3)	5617(3)	68(2)
C(043)	8482(5)	1598(3)	3154(3)	65(2)
C(044)	-228(6)	2068(4)	-3464(3)	81(3)
C(045)	3434(6)	1209(4)	1952(3)	78(3)
C(046)	9167(5)	-77(4)	4335(3)	66(2)
C(047)	6(6)	2441(4)	-2563(3)	78(3)
C(048)	-3807(5)	3792(4)	2197(3)	71(2)
C(049)	7751(5)	1015(4)	5300(3)	58(2)
O(04A)	10493(7)	4201(4)	7527(3)	151(3)
C(04B)	548(5)	2241(4)	1150(3)	59(2)
C(04C)	4438(6)	790(3)	6135(3)	65(2)
C(04D)	4470(6)	876(3)	5202(3)	63(2)
N(04E)	10658(7)	4126(4)	6671(4)	109(3)
C(04F)	1627(6)	705(4)	2832(3)	70(2)
C(04G)	4502(6)	2373(4)	8268(3)	64(2)
C(04H)	328(5)	1960(4)	1627(3)	62(2)
C(04I)	2359(6)	5095(4)	3187(3)	74(3)
C(04J)	9113(6)	-663(4)	4385(3)	71(2)
C(04K)	-4021(6)	4150(4)	2591(4)	83(3)
C(04L)	5055(6)	2655(4)	8708(3)	74(3)
C(04M)	2460(6)	4588(4)	2872(3)	69(3)
C(04N)	7151(5)	1428(3)	2243(3)	61(2)
C(04O)	4315(5)	2255(3)	707(3)	64(2)
C(04P)	5714(5)	3206(3)	5933(3)	67(2)
C(04Q)	-797(5)	1827(3)	-563(3)	72(3)
C(04R)	755(5)	1037(4)	1217(3)	71(2)
O(04S)	9320(5)	4289(4)	4349(3)	142(3)
C(04T)	1093(7)	2243(4)	-3990(3)	73(3)
C(04U)	3082(5)	4603(4)	2460(3)	61(2)
C(04V)	1218(6)	4584(4)	3641(3)	78(3)

C(04W)	2255(6)	713(4)	2427(3)	71(3)
C(04X)	8651(6)	1204(4)	2774(3)	72(2)
C(04Y)	660(6)	1310(3)	691(3)	70(2)
C(050)	3191(6)	2181(4)	8802(3)	90(3)
C(051)	-2501(6)	3936(3)	3123(3)	68(2)
C(052)	-2545(6)	2171(4)	-586(4)	92(3)
C(053)	535(5)	2966(4)	4708(3)	71(2)
C(054)	7985(6)	1116(4)	2305(3)	85(3)
C(055)	2962(7)	221(5)	1726(4)	94(3)
C(056)	5329(9)	1184(4)	4007(4)	106(4)
C(057)	2353(7)	207(5)	2107(3)	95(3)
C(058)	4122(5)	3917(3)	4752(3)	63(2)
C(059)	3752(7)	2465(4)	9202(3)	86(3)
C(05A)	8514(8)	4215(5)	4519(4)	101(3)
C(05B)	1725(7)	5070(5)	3559(3)	80(3)
C(05C)	6510(7)	707(4)	3515(4)	104(3)
C(05D)	-1883(6)	1640(3)	-571(4)	93(3)
C(05E)	3499(7)	714(5)	1658(4)	88(3)
C(05H)	156(11)	4592(6)	1977(5)	252(11)
C(05I)	8404(7)	5211(5)	4806(4)	122(4)
C(05J)	10382(7)	3850(5)	6167(4)	121(4)
C(05K)	-457(9)	4113(4)	1178(4)	109(4)
C(05M)	10275(9)	3972(5)	7065(5)	110(4)
C(05P)	7024(7)	4532(4)	4881(4)	118(4)
C(05Q)	-1615(8)	4560(5)	1679(4)	129(4)
C(05U)	4736(9)	648(5)	3230(4)	163(6)
C(067)	11322(10)	4630(6)	6669(7)	232(10)

Table 3. Bond lengths [Å] and angles [°] for mer-Ru2(RS-BPTPI)4Cl.

Ru(01)-Ru(04)	2.2827(7)
Ru(01)-O(008)	2.005(4)
Ru(01)-O(00B)	2.039(5)
Ru(01)-O(00G)	2.006(5)
Ru(01)-N(00R)	2.032(5)
Ru(01)-O(01F)	2.307(5)
Ru(02)-Ru(03)	2.2890(7)
Ru(02)-O(00A)	2.013(4)
Ru(02)-O(00J)	1.998(4)
Ru(02)-O(00L)	2.038(5)
Ru(02)-O(00T)	2.302(5)
Ru(02)-N(014)	2.033(6)
Ru(03)-Cl(05)	2.5887(18)
Ru(03)-N(00N)	2.115(6)
Ru(03)-O(00O)	2.057(5)
Ru(03)-N(015)	2.116(5)
Ru(03)-N(019)	2.068(6)
Ru(04)-Cl(06)	2.5741(18)
Ru(04)-O(007)	2.059(5)
Ru(04)-N(00X)	2.107(6)
Ru(04)-N(017)	2.093(6)
Ru(04)-N(01A)	2.061(6)
O(007)-C(01U)	1.281(8)
O(008)-C(020)	1.280(7)
O(009)-C(01X)	1.217(8)
O(00A)-C(01O)	1.293(8)
O(00B)-C(04B)	1.273(9)
O(00C)-C(02P)	1.232(9)
O(00D)-C(02D)	1.229(8)
O(00E)-C(01W)	1.208(8)
O(00F)-C(02N)	1.233(8)
O(00G)-C(03U)	1.275(8)
O(00H)-C(01G)	1.227(8)
O(00I)-C(029)	1.202(8)
O(00J)-C(01D)	1.278(8)
O(00K)-C(02R)	1.196(9)
O(00L)-C(01S)	1.270(8)
O(00M)-C(01R)	1.192(8)
N(00N)-C(01D)	1.290(9)
N(00N)-C(032)	1.514(8)
O(00O)-C(02U)	1.288(8)
O(00P)-C(03S)	1.198(8)
O(00Q)-C(02G)	1.206(8)
N(00R)-C(01U)	1.325(8)
N(00R)-C(039)	1.491(8)
N(00S)-C(01W)	1.397(10)
N(00S)-C(027)	1.416(8)
N(00S)-C(029)	1.413(9)
O(00T)-C(056)	1.225(10)
O(00U)-C(02B)	1.225(9)
N(00V)-C(01X)	1.404(8)
N(00V)-C(026)	1.471(8)
N(00V)-C(02G)	1.398(9)
O(00W)-C(02O)	1.188(9)
N(00X)-C(020)	1.296(8)
N(00X)-C(03O)	1.460(8)
N(00Y)-C(01G)	1.367(9)
N(00Y)-C(01V)	1.453(8)
N(00Y)-C(02P)	1.417(9)
O(00Z)-C(036)	1.179(9)
O(010)-C(03J)	1.204(8)
N(011)-C(02B)	1.379(10)
N(011)-C(036)	1.412(9)
N(011)-C(03D)	1.458(9)
N(012)-C(02R)	1.413(8)
N(012)-C(02V)	1.457(8)
N(012)-C(02Y)	1.409(9)

N(013)-C(01R)	1.398(9)	C(01I)-C(040)	1.359(9)
N(013)-C(02N)	1.378(8)	C(01J)-C(024)	1.403(10)
N(013)-C(04H)	1.449(9)	C(01J)-C(028)	1.422(10)
N(014)-C(02U)	1.297(8)	C(01J)-C(02H)	1.456(10)
N(014)-C(04D)	1.454(8)	C(01K)-H(01K)	0.9500
N(015)-C(01O)	1.311(8)	C(01K)-C(030)	1.364(9)
N(015)-C(04P)	1.464(8)	C(01L)-H(01L)	0.9500
O(016)-C(02Y)	1.216(8)	C(01L)-C(03H)	1.396(10)
N(017)-C(03U)	1.299(8)	C(01L)-C(03X)	1.394(11)
N(017)-C(04Q)	1.481(8)	C(01M)-C(02F)	1.408(9)
N(018)-C(02D)	1.362(9)	C(01M)-C(03J)	1.518(9)
N(018)-C(02O)	1.414(9)	C(01M)-C(047)	1.358(9)
N(018)-C(03T)	1.446(8)	C(01N)-H(01N)	0.9500
N(019)-C(01S)	1.283(9)	C(01N)-C(03H)	1.381(10)
N(019)-C(058)	1.476(8)	C(01O)-C(02V)	1.530(9)
N(01A)-C(04B)	1.333(9)	C(01P)-C(02P)	1.426(10)
N(01A)-C(04Y)	1.459(9)	C(01P)-C(03E)	1.399(10)
C(01B)-H(01B)	0.9500	N(01Q)-C(056)	1.365(10)
C(01B)-C(01P)	1.409(10)	N(01Q)-C(05C)	1.464(10)
C(01B)-C(02A)	1.438(11)	N(01Q)-C(05U)	1.346(11)
C(01C)-C(01E)	1.426(10)	C(01R)-C(02J)	1.525(10)
C(01C)-C(01K)	1.413(10)	C(01S)-C(026)	1.524(10)
C(01C)-C(03X)	1.431(10)	C(01T)-C(02M)	1.432(9)
C(01D)-C(01V)	1.536(9)	C(01T)-C(02W)	1.410(9)
C(01E)-C(01N)	1.387(10)	C(01T)-C(043)	1.409(9)
C(01E)-C(03K)	1.478(10)	C(01U)-C(02S)	1.486(10)
O(01F)-C(05K)	1.204(10)	C(01V)-H(01V)	1.0000
C(01G)-C(03E)	1.502(10)	C(01V)-C(03F)	1.531(10)
N(01H)-C(02S)	1.460(8)	C(01W)-C(01Z)	1.499(10)
N(01H)-C(03J)	1.392(9)	C(01X)-C(021)	1.495(10)
N(01H)-C(03S)	1.401(8)	C(01Y)-C(01Z)	1.399(10)
C(01I)-C(02O)	1.492(10)	C(01Y)-C(029)	1.477(10)
C(01I)-C(033)	1.392(9)	C(01Y)-C(03R)	1.346(9)

C(01Z)-C(04U)	1.335(10)	C(02I)-C(02X)	1.429(10)
C(020)-C(027)	1.547(9)	C(02I)-C(04V)	1.365(10)
C(021)-C(02C)	1.399(9)	C(02J)-C(03B)	1.325(10)
C(021)-C(02W)	1.375(9)	C(02J)-C(03W)	1.424(10)
C(022)-C(031)	1.416(10)	C(02K)-H(02K)	0.9500
C(022)-C(044)	1.426(10)	C(02K)-C(03L)	1.348(9)
C(022)-C(047)	1.430(9)	C(02L)-H(02L)	0.9500
C(023)-C(02E)	1.451(9)	C(02L)-C(04J)	1.413(11)
C(023)-C(03B)	1.450(9)	C(02M)-C(034)	1.426(9)
C(023)-C(051)	1.378(10)	C(02M)-C(04N)	1.398(9)
C(024)-H(024)	0.9500	C(02N)-C(03W)	1.486(10)
C(024)-C(02L)	1.390(10)	C(02Q)-H(02A)	0.9900
C(025)-C(02B)	1.505(10)	C(02Q)-H(02B)	0.9900
C(025)-C(030)	1.390(9)	C(02Q)-C(04O)	1.509(9)
C(025)-C(03K)	1.328(10)	C(02R)-C(03L)	1.496(11)
C(026)-H(026)	1.0000	C(02S)-H(02S)	1.0000
C(026)-C(035)	1.546(10)	C(02S)-C(03N)	1.526(9)
C(027)-H(027)	1.0000	C(02T)-C(040)	1.377(10)
C(027)-C(02Q)	1.550(9)	C(02T)-C(04G)	1.406(10)
C(028)-C(02K)	1.402(10)	C(02T)-C(050)	1.455(10)
C(028)-C(046)	1.438(9)	C(02U)-C(03T)	1.509(10)
C(02A)-C(045)	1.437(10)	C(02V)-H(02V)	1.0000
C(02A)-C(04W)	1.363(11)	C(02V)-C(03V)	1.545(9)
C(02C)-C(02G)	1.498(9)	C(02W)-H(02W)	0.9500
C(02C)-C(034)	1.342(10)	C(02X)-C(03R)	1.389(10)
C(02D)-C(033)	1.512(9)	C(02X)-C(04M)	1.399(11)
C(02E)-C(038)	1.395(9)	C(02Y)-C(049)	1.503(10)
C(02E)-C(048)	1.442(9)	N(02Z)-C(05A)	1.303(11)
C(02F)-C(03I)	1.376(9)	N(02Z)-C(05I)	1.439(11)
C(02F)-C(03S)	1.498(9)	N(02Z)-C(05P)	1.476(10)
C(02H)-H(02H)	0.9500	C(030)-C(036)	1.507(11)
C(02H)-C(049)	1.362(10)	C(031)-C(037)	1.434(9)
C(02I)-H(02I)	0.9500	C(031)-C(03I)	1.412(9)

C(032)-H(03Q)	0.9900	C(03I)-H(03I)	0.9500
C(032)-H(03S)	0.9900	C(03K)-H(03K)	0.9500
C(032)-C(053)	1.524(9)	C(03L)-C(049)	1.403(10)
C(033)-C(03G)	1.356(9)	C(03M)-H(03)	0.9900
C(034)-H(034)	0.9500	C(03M)-H	0.9900
C(035)-H(03T)	0.9900	C(03M)-C(03V)	1.501(9)
C(035)-H(03U)	0.9900	C(03M)-C(04P)	1.522(9)
C(035)-C(041)	1.520(9)	C(03N)-H(03G)	0.9900
C(037)-H(037)	0.9500	C(03N)-H(03J)	0.9900
C(037)-C(04T)	1.369(10)	C(03N)-C(03Q)	1.516(9)
C(038)-H(038)	0.9500	C(03O)-H(03L)	0.9900
C(038)-C(03W)	1.377(9)	C(03O)-H(03M)	0.9900
C(039)-H(03A)	0.9900	C(03O)-C(04O)	1.523(8)
C(039)-H(03B)	0.9900	C(03P)-H(03P)	0.9500
C(039)-C(03Q)	1.471(10)	C(03P)-C(04K)	1.396(10)
N(03A)-C(05H)	1.365(12)	C(03P)-C(051)	1.369(9)
N(03A)-C(05K)	1.303(11)	C(03Q)-H(03N)	0.9900
N(03A)-C(05Q)	1.486(11)	C(03Q)-H(03O)	0.9900
C(03B)-H(03C)	0.9500	C(03R)-H(03R)	0.9500
C(03C)-H(03D)	0.9900	C(03T)-H(0AA)	1.0000
C(03C)-H(03E)	0.9900	C(03T)-C(04C)	1.522(9)
C(03C)-C(04H)	1.543(11)	C(03V)-H(1AA)	0.9900
C(03C)-C(04R)	1.536(10)	C(03V)-HA	0.9900
C(03D)-H(03F)	1.0000	C(03X)-H(03X)	0.9500
C(03D)-C(03U)	1.515(9)	C(03Y)-H(03Y)	0.9500
C(03D)-C(052)	1.513(10)	C(03Y)-C(044)	1.391(10)
C(03E)-C(04F)	1.325(10)	C(03Y)-C(04T)	1.352(10)
C(03F)-H(03V)	0.9900	C(03Z)-H(2AA)	0.9500
C(03F)-H(03W)	0.9900	C(03Z)-C(04L)	1.368(10)
C(03F)-C(053)	1.483(9)	C(03Z)-C(059)	1.354(11)
C(03G)-H(03Z)	0.9500	C(040)-H(040)	0.9500
C(03G)-C(04G)	1.418(10)	C(041)-H(04L)	0.9900
C(03H)-H(03H)	0.9500	C(041)-H(04M)	0.9900

C(041)-C(058)	1.518(10)	C(04L)-H(04Y)	0.9500
C(042)-H(04N)	0.9900	C(04M)-C(04U)	1.454(9)
C(042)-H(04O)	0.9900	C(04N)-H(04Z)	0.9500
C(042)-C(04C)	1.512(9)	C(04N)-C(054)	1.361(10)
C(042)-C(04D)	1.523(10)	C(04O)-H(04A)	0.9900
C(043)-H(043)	0.9500	C(04O)-H(04B)	0.9900
C(043)-C(04X)	1.370(10)	C(04P)-H(04)	0.9900
C(044)-H(044)	0.9500	C(04P)-HB	0.9900
C(045)-H(045)	0.9500	C(04Q)-H(04C)	0.9900
C(045)-C(05E)	1.369(12)	C(04Q)-H(04D)	0.9900
C(046)-H(046)	0.9500	C(04Q)-C(05D)	1.509(10)
C(046)-C(04J)	1.379(10)	C(04R)-H(04E)	0.9900
C(047)-H(047)	0.9500	C(04R)-H(04F)	0.9900
C(048)-H(048)	0.9500	C(04R)-C(04Y)	1.550(10)
C(048)-C(04K)	1.365(11)	O(04S)-C(05A)	1.233(11)
O(04A)-C(05M)	1.301(12)	C(04T)-H(04T)	0.9500
C(04B)-C(04H)	1.505(10)	C(04U)-H(04U)	0.9500
C(04C)-H(04P)	0.9900	C(04V)-H(04V)	0.9500
C(04C)-H(04Q)	0.9900	C(04V)-C(05B)	1.341(11)
C(04D)-H(04R)	0.9900	C(04W)-C(057)	1.434(12)
C(04D)-H(04S)	0.9900	C(04X)-H(3AA)	0.9500
N(04E)-C(05J)	1.447(12)	C(04X)-C(054)	1.438(10)
N(04E)-C(05M)	1.279(13)	C(04Y)-H(04G)	0.9900
N(04E)-C(067)	1.449(13)	C(04Y)-H(04J)	0.9900
C(04F)-H(04W)	0.9500	C(050)-H(050)	0.9500
C(04F)-C(04W)	1.442(10)	C(050)-C(059)	1.348(10)
C(04G)-C(04L)	1.417(10)	C(051)-H(051)	0.9500
C(04H)-H(04H)	1.0000	C(052)-H(05A)	0.9900
C(04I)-H(04I)	0.9500	C(052)-H(05B)	0.9900
C(04I)-C(04M)	1.431(11)	C(052)-C(05D)	1.554(10)
C(04I)-C(05B)	1.381(10)	C(053)-H(05M)	0.9900
C(04J)-H(04X)	0.9500	C(053)-H(05N)	0.9900
C(04K)-H(04K)	0.9500	C(054)-H(054)	0.9500

C(055)-H(055)	0.9500
C(055)-C(057)	1.376(11)
C(055)-C(05E)	1.365(12)
C(056)-H(056)	0.9500
C(057)-H(057)	0.9500
C(058)-H(05O)	0.9900
C(058)-H(05P)	0.9900
C(059)-H(059)	0.9500
C(05A)-H(05X)	0.9500
C(05B)-H(05C)	0.9500
C(05C)-H(05Q)	0.9800
C(05C)-H(05R)	0.9800
C(05C)-H(05S)	0.9800
C(05D)-H(05D)	0.9900
C(05D)-H(05E)	0.9900
C(05E)-H(05T)	0.9500
C(05H)-H(05F)	0.9800
C(05H)-H(05G)	0.9800
C(05H)-H(05H)	0.9800
C(05I)-H(05Y)	0.9800
C(05I)-HC	0.9800
C(05I)-HD	0.9800
C(05J)-H(05)	0.9800
C(05J)-HE	0.9800
C(05J)-HF	0.9800
C(05K)-H(05K)	0.9500
C(05M)-H(4AA)	0.9500
C(05P)-H(05Z)	0.9800
C(05P)-HG	0.9800
C(05P)-HH	0.9800
C(05Q)-H(05I)	0.9800
C(05Q)-H(05J)	0.9800
C(05Q)-H(05L)	0.9800

C(05U)-H(05U)	0.9800
C(05U)-H(05V)	0.9800
C(05U)-H(05W)	0.9800
C(067)-H(06A)	0.9800
C(067)-H(06B)	0.9800
C(067)-H(06C)	0.9800

Ru(04)-Ru(01)-O(01F)	173.32(13)
O(008)-Ru(01)-Ru(04)	91.37(12)
O(008)-Ru(01)-O(00B)	89.63(17)
O(008)-Ru(01)-O(00G)	175.75(18)
O(008)-Ru(01)-N(00R)	91.05(19)
O(008)-Ru(01)-O(01F)	86.82(18)
O(00B)-Ru(01)-Ru(04)	90.34(14)
O(00B)-Ru(01)-O(01F)	83.23(19)
O(00G)-Ru(01)-Ru(04)	92.60(14)
O(00G)-Ru(01)-O(00B)	88.84(18)
O(00G)-Ru(01)-N(00R)	90.5(2)
O(00G)-Ru(01)-O(01F)	89.1(2)
N(00R)-Ru(01)-Ru(04)	89.59(15)
N(00R)-Ru(01)-O(00B)	179.3(2)
N(00R)-Ru(01)-O(01F)	96.9(2)
Ru(03)-Ru(02)-O(00T)	173.97(14)
O(00A)-Ru(02)-Ru(03)	92.83(13)
O(00A)-Ru(02)-O(00L)	89.03(19)
O(00A)-Ru(02)-O(00T)	87.91(19)
O(00A)-Ru(02)-N(014)	89.6(2)
O(00J)-Ru(02)-Ru(03)	91.18(13)
O(00J)-Ru(02)-O(00A)	175.75(17)
O(00J)-Ru(02)-O(00L)	89.54(18)
O(00J)-Ru(02)-O(00T)	87.96(19)
O(00J)-Ru(02)-N(014)	91.8(2)
O(00L)-Ru(02)-Ru(03)	90.13(14)

O(00L)-Ru(02)-O(00T)	83.90(19)	N(01A)-Ru(04)-N(017)	88.8(2)
N(014)-Ru(02)-Ru(03)	90.58(16)	C(01U)-O(007)-Ru(04)	119.5(4)
N(014)-Ru(02)-O(00L)	178.51(19)	C(020)-O(008)-Ru(01)	118.2(5)
N(014)-Ru(02)-O(00T)	95.4(2)	C(01O)-O(00A)-Ru(02)	117.9(4)
Ru(02)-Ru(03)-Cl(05)	174.72(5)	C(04B)-O(00B)-Ru(01)	119.1(5)
N(00N)-Ru(03)-Ru(02)	87.34(17)	C(03U)-O(00G)-Ru(01)	118.4(4)
N(00N)-Ru(03)-Cl(05)	91.92(17)	C(01D)-O(00J)-Ru(02)	119.1(5)
N(00N)-Ru(03)-N(015)	173.5(2)	C(01S)-O(00L)-Ru(02)	118.3(5)
O(00O)-Ru(03)-Ru(02)	88.56(13)	C(01D)-N(00N)-Ru(03)	117.7(5)
O(00O)-Ru(03)-Cl(05)	86.25(13)	C(01D)-N(00N)-C(032)	122.0(6)
O(00O)-Ru(03)-N(00N)	92.35(19)	C(032)-N(00N)-Ru(03)	118.8(5)
O(00O)-Ru(03)-N(015)	90.98(19)	C(02U)-O(00O)-Ru(03)	118.7(4)
O(00O)-Ru(03)-N(019)	177.2(2)	C(01U)-N(00R)-Ru(01)	120.0(5)
N(015)-Ru(03)-Ru(02)	87.19(16)	C(01U)-N(00R)-C(039)	122.3(6)
N(015)-Ru(03)-Cl(05)	93.84(17)	C(039)-N(00R)-Ru(01)	117.3(4)
N(019)-Ru(03)-Ru(02)	88.81(16)	C(01W)-N(00S)-C(027)	124.7(7)
N(019)-Ru(03)-Cl(05)	96.38(17)	C(01W)-N(00S)-C(029)	111.3(7)
N(019)-Ru(03)-N(00N)	86.7(2)	C(029)-N(00S)-C(027)	122.3(7)
N(019)-Ru(03)-N(015)	89.7(2)	C(056)-O(00T)-Ru(02)	123.9(7)
Ru(01)-Ru(04)-Cl(06)	174.25(5)	C(01X)-N(00V)-C(026)	121.6(6)
O(007)-Ru(04)-Ru(01)	89.40(12)	C(02G)-N(00V)-C(01X)	113.8(6)
O(007)-Ru(04)-Cl(06)	84.97(13)	C(02G)-N(00V)-C(026)	122.0(6)
O(007)-Ru(04)-N(00X)	93.1(2)	C(020)-N(00X)-Ru(04)	117.7(4)
O(007)-Ru(04)-N(017)	90.7(2)	C(020)-N(00X)-C(03O)	119.2(6)
O(007)-Ru(04)-N(01A)	178.7(2)	C(03O)-N(00X)-Ru(04)	121.5(5)
N(00X)-Ru(04)-Ru(01)	87.38(15)	C(01G)-N(00Y)-C(01V)	122.9(6)
N(00X)-Ru(04)-Cl(06)	91.75(15)	C(01G)-N(00Y)-C(02P)	110.3(7)
N(017)-Ru(04)-Ru(01)	86.33(16)	C(02P)-N(00Y)-C(01V)	123.0(7)
N(017)-Ru(04)-Cl(06)	94.90(17)	C(02B)-N(011)-C(036)	113.7(7)
N(017)-Ru(04)-N(00X)	172.6(2)	C(02B)-N(011)-C(03D)	123.5(7)
N(01A)-Ru(04)-Ru(01)	89.38(18)	C(036)-N(011)-C(03D)	122.0(7)
N(01A)-Ru(04)-Cl(06)	96.25(19)	C(02R)-N(012)-C(02V)	122.8(7)
N(01A)-Ru(04)-N(00X)	87.3(2)	C(02Y)-N(012)-C(02R)	112.0(7)

C(02Y)-N(012)-C(02V)	124.8(6)
C(01R)-N(013)-C(04H)	122.0(6)
C(02N)-N(013)-C(01R)	113.1(7)
C(02N)-N(013)-C(04H)	124.1(7)
C(02U)-N(014)-Ru(02)	118.0(5)
C(02U)-N(014)-C(04D)	124.4(7)
C(04D)-N(014)-Ru(02)	117.0(5)
C(01O)-N(015)-Ru(03)	117.9(5)
C(01O)-N(015)-C(04P)	122.0(6)
C(04P)-N(015)-Ru(03)	120.1(4)
C(03U)-N(017)-Ru(04)	119.5(5)
C(03U)-N(017)-C(04Q)	120.9(6)
C(04Q)-N(017)-Ru(04)	119.6(4)
C(02D)-N(018)-C(02O)	113.4(6)
C(02D)-N(018)-C(03T)	124.6(6)
C(02O)-N(018)-C(03T)	121.1(6)
C(01S)-N(019)-Ru(03)	118.0(5)
C(01S)-N(019)-C(058)	120.5(7)
C(058)-N(019)-Ru(03)	121.3(5)
C(04B)-N(01A)-Ru(04)	117.7(6)
C(04B)-N(01A)-C(04Y)	122.5(7)
C(04Y)-N(01A)-Ru(04)	119.6(5)
C(01P)-C(01B)-H(01B)	121.8
C(01P)-C(01B)-C(02A)	116.4(8)
C(02A)-C(01B)-H(01B)	121.8
C(01E)-C(01C)-C(03X)	117.1(8)
C(01K)-C(01C)-C(01E)	122.0(7)
C(01K)-C(01C)-C(03X)	120.6(8)
O(00J)-C(01D)-N(00N)	122.5(7)
O(00J)-C(01D)-C(01V)	114.5(7)
N(00N)-C(01D)-C(01V)	123.0(7)
C(01C)-C(01E)-C(03K)	117.8(8)
C(01N)-C(01E)-C(01C)	122.5(7)
C(01N)-C(01E)-C(03K)	119.6(8)
C(05K)-O(01F)-Ru(01)	128.3(7)
O(00H)-C(01G)-N(00Y)	124.7(7)
O(00H)-C(01G)-C(03E)	127.4(9)
N(00Y)-C(01G)-C(03E)	107.8(7)
C(03J)-N(01H)-C(02S)	123.7(6)
C(03J)-N(01H)-C(03S)	113.2(6)
C(03S)-N(01H)-C(02S)	121.7(6)
C(033)-C(01I)-C(02O)	109.2(7)
C(040)-C(01I)-C(02O)	129.9(8)
C(040)-C(01I)-C(033)	120.9(7)
C(024)-C(01J)-C(028)	121.8(8)
C(024)-C(01J)-C(02H)	120.2(8)
C(028)-C(01J)-C(02H)	118.0(8)
C(01C)-C(01K)-H(01K)	121.8
C(030)-C(01K)-C(01C)	116.4(7)
C(030)-C(01K)-H(01K)	121.8
C(03H)-C(01L)-H(01L)	120.3
C(03X)-C(01L)-H(01L)	120.3
C(03X)-C(01L)-C(03H)	119.4(8)
C(02F)-C(01M)-C(03J)	107.3(7)
C(047)-C(01M)-C(02F)	121.8(7)
C(047)-C(01M)-C(03J)	130.8(7)
C(01E)-C(01N)-H(01N)	121.1
C(03H)-C(01N)-C(01E)	117.8(8)
C(03H)-C(01N)-H(01N)	121.1
O(00A)-C(01O)-N(015)	123.7(7)
O(00A)-C(01O)-C(02V)	114.5(6)
N(015)-C(01O)-C(02V)	121.8(7)
C(01B)-C(01P)-C(02P)	129.2(8)
C(03E)-C(01P)-C(01B)	120.2(8)
C(03E)-C(01P)-C(02P)	110.7(7)
C(056)-N(01Q)-C(05C)	118.9(9)

C(05U)-N(01Q)-C(056)	122.6(10)	O(008)-C(020)-C(027)	111.8(6)
C(05U)-N(01Q)-C(05C)	118.4(8)	N(00X)-C(020)-C(027)	125.5(6)
O(00M)-C(01R)-N(013)	127.8(8)	C(02C)-C(021)-C(01X)	108.7(6)
O(00M)-C(01R)-C(02J)	127.0(8)	C(02W)-C(021)-C(01X)	129.6(7)
N(013)-C(01R)-C(02J)	105.2(7)	C(02W)-C(021)-C(02C)	121.6(7)
O(00L)-C(01S)-N(019)	124.3(7)	C(031)-C(022)-C(044)	120.2(7)
O(00L)-C(01S)-C(026)	111.6(7)	C(031)-C(022)-C(047)	120.2(7)
N(019)-C(01S)-C(026)	124.1(8)	C(044)-C(022)-C(047)	119.6(8)
C(02W)-C(01T)-C(02M)	121.0(7)	C(03B)-C(023)-C(02E)	115.5(7)
C(043)-C(01T)-C(02M)	118.9(7)	C(051)-C(023)-C(02E)	122.7(7)
C(043)-C(01T)-C(02W)	120.0(7)	C(051)-C(023)-C(03B)	121.8(7)
O(007)-C(01U)-N(00R)	120.3(7)	C(01J)-C(024)-H(024)	120.8
O(007)-C(01U)-C(02S)	118.7(6)	C(02L)-C(024)-C(01J)	118.4(8)
N(00R)-C(01U)-C(02S)	120.8(7)	C(02L)-C(024)-H(024)	120.8
N(00Y)-C(01V)-C(01D)	107.1(6)	C(030)-C(025)-C(02B)	106.9(7)
N(00Y)-C(01V)-H(01V)	107.2	C(03K)-C(025)-C(02B)	129.5(8)
N(00Y)-C(01V)-C(03F)	114.3(6)	C(03K)-C(025)-C(030)	123.7(7)
C(01D)-C(01V)-H(01V)	107.2	N(00V)-C(026)-C(01S)	108.5(6)
C(03F)-C(01V)-C(01D)	113.6(7)	N(00V)-C(026)-H(026)	107.2
C(03F)-C(01V)-H(01V)	107.2	N(00V)-C(026)-C(035)	112.5(6)
O(00E)-C(01W)-N(00S)	124.4(8)	C(01S)-C(026)-H(026)	107.2
O(00E)-C(01W)-C(01Z)	129.7(9)	C(01S)-C(026)-C(035)	114.0(7)
N(00S)-C(01W)-C(01Z)	105.9(8)	C(035)-C(026)-H(026)	107.2
O(009)-C(01X)-N(00V)	125.0(7)	N(00S)-C(027)-C(020)	107.5(5)
O(009)-C(01X)-C(021)	130.6(7)	N(00S)-C(027)-H(027)	108.0
N(00V)-C(01X)-C(021)	104.5(7)	N(00S)-C(027)-C(02Q)	113.5(6)
C(01Z)-C(01Y)-C(029)	107.8(7)	C(020)-C(027)-H(027)	108.0
C(03R)-C(01Y)-C(01Z)	121.1(8)	C(020)-C(027)-C(02Q)	111.9(6)
C(03R)-C(01Y)-C(029)	131.1(8)	C(02Q)-C(027)-H(027)	108.0
C(01Y)-C(01Z)-C(01W)	108.2(8)	C(01J)-C(028)-C(046)	117.1(8)
C(04U)-C(01Z)-C(01W)	129.7(9)	C(02K)-C(028)-C(01J)	122.2(7)
C(04U)-C(01Z)-C(01Y)	122.1(8)	C(02K)-C(028)-C(046)	120.6(8)
O(008)-C(020)-N(00X)	122.7(6)	O(00I)-C(029)-N(00S)	122.4(7)

O(00I)-C(029)-C(01Y)	130.9(8)
N(00S)-C(029)-C(01Y)	106.7(7)
C(045)-C(02A)-C(01B)	117.9(9)
C(04W)-C(02A)-C(01B)	121.4(8)
C(04W)-C(02A)-C(045)	120.7(9)
O(00U)-C(02B)-N(011)	125.9(8)
O(00U)-C(02B)-C(025)	127.8(9)
N(011)-C(02B)-C(025)	106.1(7)
C(021)-C(02C)-C(02G)	108.2(7)
C(034)-C(02C)-C(021)	121.7(7)
C(034)-C(02C)-C(02G)	130.0(7)
O(00D)-C(02D)-N(018)	125.6(7)
O(00D)-C(02D)-C(033)	128.1(8)
N(018)-C(02D)-C(033)	106.3(7)
C(038)-C(02E)-C(023)	122.9(7)
C(038)-C(02E)-C(048)	120.9(7)
C(048)-C(02E)-C(023)	116.0(7)
C(01M)-C(02F)-C(03S)	108.4(6)
C(03I)-C(02F)-C(01M)	122.7(7)
C(03I)-C(02F)-C(03S)	128.9(7)
O(00Q)-C(02G)-N(00V)	126.4(7)
O(00Q)-C(02G)-C(02C)	128.8(8)
N(00V)-C(02G)-C(02C)	104.8(6)
C(01J)-C(02H)-H(02H)	121.4
C(049)-C(02H)-C(01J)	117.3(8)
C(049)-C(02H)-H(02H)	121.4
C(02X)-C(02I)-H(02I)	119.3
C(04V)-C(02I)-H(02I)	119.3
C(04V)-C(02I)-C(02X)	121.5(8)
C(03B)-C(02J)-C(01R)	131.1(8)
C(03B)-C(02J)-C(03W)	122.0(7)
C(03W)-C(02J)-C(01R)	106.9(7)
C(028)-C(02K)-H(02K)	121.1
C(03L)-C(02K)-C(028)	117.8(8)
C(03L)-C(02K)-H(02K)	121.1
C(024)-C(02L)-H(02L)	119.2
C(024)-C(02L)-C(04J)	121.6(9)
C(04J)-C(02L)-H(02L)	119.2
C(034)-C(02M)-C(01T)	117.9(7)
C(04N)-C(02M)-C(01T)	120.3(7)
C(04N)-C(02M)-C(034)	121.8(7)
O(00F)-C(02N)-N(013)	124.1(8)
O(00F)-C(02N)-C(03W)	128.7(7)
N(013)-C(02N)-C(03W)	107.2(7)
O(00W)-C(02O)-N(018)	125.1(7)
O(00W)-C(02O)-C(01I)	130.6(8)
N(018)-C(02O)-C(01I)	104.3(7)
O(00C)-C(02P)-N(00Y)	120.9(7)
O(00C)-C(02P)-C(01P)	132.6(8)
N(00Y)-C(02P)-C(01P)	106.3(7)
C(027)-C(02Q)-H(02A)	109.7
C(027)-C(02Q)-H(02B)	109.7
H(02A)-C(02Q)-H(02B)	108.2
C(04O)-C(02Q)-C(027)	109.9(6)
C(04O)-C(02Q)-H(02A)	109.7
C(04O)-C(02Q)-H(02B)	109.7
O(00K)-C(02R)-N(012)	123.4(8)
O(00K)-C(02R)-C(03L)	130.4(7)
N(012)-C(02R)-C(03L)	106.2(8)
N(01H)-C(02S)-C(01U)	113.2(7)
N(01H)-C(02S)-H(02S)	106.7
N(01H)-C(02S)-C(03N)	111.2(6)
C(01U)-C(02S)-H(02S)	106.7
C(01U)-C(02S)-C(03N)	111.8(6)
C(03N)-C(02S)-H(02S)	106.7
C(040)-C(02T)-C(04G)	121.8(8)

C(040)-C(02T)-C(050)	121.8(8)
C(04G)-C(02T)-C(050)	116.4(8)
O(00O)-C(02U)-N(014)	123.1(7)
O(00O)-C(02U)-C(03T)	116.2(6)
N(014)-C(02U)-C(03T)	120.6(7)
N(012)-C(02V)-C(01O)	108.4(6)
N(012)-C(02V)-H(02V)	107.8
N(012)-C(02V)-C(03V)	112.9(6)
C(01O)-C(02V)-H(02V)	107.8
C(01O)-C(02V)-C(03V)	111.9(6)
C(03V)-C(02V)-H(02V)	107.8
C(01T)-C(02W)-H(02W)	121.1
C(021)-C(02W)-C(01T)	117.9(7)
C(021)-C(02W)-H(02W)	121.1
C(03R)-C(02X)-C(02I)	123.2(8)
C(03R)-C(02X)-C(04M)	119.6(8)
C(04M)-C(02X)-C(02I)	117.2(8)
N(012)-C(02Y)-C(049)	105.4(7)
O(016)-C(02Y)-N(012)	125.6(7)
O(016)-C(02Y)-C(049)	128.8(8)
C(05A)-N(02Z)-C(05I)	123.7(10)
C(05A)-N(02Z)-C(05P)	123.6(9)
C(05I)-N(02Z)-C(05P)	112.7(8)
C(01K)-C(030)-C(025)	122.9(8)
C(01K)-C(030)-C(036)	127.3(7)
C(025)-C(030)-C(036)	109.8(7)
C(022)-C(031)-C(037)	119.6(7)
C(03I)-C(031)-C(022)	121.1(7)
C(03I)-C(031)-C(037)	119.2(7)
N(00N)-C(032)-H(03Q)	109.2
N(00N)-C(032)-H(03S)	109.2
N(00N)-C(032)-C(053)	112.1(6)
H(03Q)-C(032)-H(03S)	107.9
C(053)-C(032)-H(03Q)	109.2
C(053)-C(032)-H(03S)	109.2
C(01I)-C(033)-C(02D)	106.8(7)
C(03G)-C(033)-C(01I)	122.5(7)
C(03G)-C(033)-C(02D)	130.7(8)
C(02C)-C(034)-C(02M)	120.0(7)
C(02C)-C(034)-H(034)	120.0
C(02M)-C(034)-H(034)	120.0
C(026)-C(035)-H(03T)	110.1
C(026)-C(035)-H(03U)	110.1
H(03T)-C(035)-H(03U)	108.4
C(041)-C(035)-C(026)	107.9(7)
C(041)-C(035)-H(03T)	110.1
C(041)-C(035)-H(03U)	110.1
O(00Z)-C(036)-N(011)	126.6(8)
O(00Z)-C(036)-C(030)	129.9(8)
N(011)-C(036)-C(030)	103.4(7)
C(031)-C(037)-H(037)	120.8
C(04T)-C(037)-C(031)	118.4(8)
C(04T)-C(037)-H(037)	120.8
C(02E)-C(038)-H(038)	121.2
C(03W)-C(038)-C(02E)	117.6(7)
C(03W)-C(038)-H(038)	121.2
N(00R)-C(039)-H(03A)	108.5
N(00R)-C(039)-H(03B)	108.5
H(03A)-C(039)-H(03B)	107.5
C(03Q)-C(039)-N(00R)	115.1(6)
C(03Q)-C(039)-H(03A)	108.5
C(03Q)-C(039)-H(03B)	108.5
C(05H)-N(03A)-C(05Q)	115.9(9)
C(05K)-N(03A)-C(05H)	125.6(11)
C(05K)-N(03A)-C(05Q)	118.5(10)
C(023)-C(03B)-H(03C)	119.6

C(02J)-C(03B)-C(023)	120.9(7)
C(02J)-C(03B)-H(03C)	119.6
H(03D)-C(03C)-H(03E)	108.5
C(04H)-C(03C)-H(03D)	110.3
C(04H)-C(03C)-H(03E)	110.3
C(04R)-C(03C)-H(03D)	110.3
C(04R)-C(03C)-H(03E)	110.3
C(04R)-C(03C)-C(04H)	107.3(7)
N(011)-C(03D)-H(03F)	106.3
N(011)-C(03D)-C(03U)	109.0(6)
N(011)-C(03D)-C(052)	114.2(6)
C(03U)-C(03D)-H(03F)	106.3
C(052)-C(03D)-H(03F)	106.3
C(052)-C(03D)-C(03U)	114.0(6)
C(01P)-C(03E)-C(01G)	104.6(8)
C(04F)-C(03E)-C(01G)	131.6(9)
C(04F)-C(03E)-C(01P)	123.6(8)
C(01V)-C(03F)-H(03V)	109.9
C(01V)-C(03F)-H(03W)	109.9
H(03V)-C(03F)-H(03W)	108.3
C(053)-C(03F)-C(01V)	109.0(6)
C(053)-C(03F)-H(03V)	109.9
C(053)-C(03F)-H(03W)	109.9
C(033)-C(03G)-H(03Z)	121.2
C(033)-C(03G)-C(04G)	117.6(8)
C(04G)-C(03G)-H(03Z)	121.2
C(01L)-C(03H)-H(03H)	118.6
C(01N)-C(03H)-C(01L)	122.8(8)
C(01N)-C(03H)-H(03H)	118.6
C(02F)-C(03I)-C(031)	116.6(7)
C(02F)-C(03I)-H(03I)	121.7
C(031)-C(03I)-H(03I)	121.7
O(010)-C(03J)-N(01H)	125.6(7)
O(010)-C(03J)-C(01M)	128.7(7)
N(01H)-C(03J)-C(01M)	105.5(6)
C(01E)-C(03K)-H(03K)	121.5
C(025)-C(03K)-C(01E)	117.1(8)
C(025)-C(03K)-H(03K)	121.5
C(02K)-C(03L)-C(02R)	130.0(8)
C(02K)-C(03L)-C(049)	122.0(8)
C(049)-C(03L)-C(02R)	107.7(7)
H(03)-C(03M)-H	108.2
C(03V)-C(03M)-H(03)	109.8
C(03V)-C(03M)-H	109.8
C(03V)-C(03M)-C(04P)	109.5(7)
C(04P)-C(03M)-H(03)	109.8
C(04P)-C(03M)-H	109.8
C(02S)-C(03N)-H(03G)	110.2
C(02S)-C(03N)-H(03J)	110.2
H(03G)-C(03N)-H(03J)	108.5
C(03Q)-C(03N)-C(02S)	107.5(6)
C(03Q)-C(03N)-H(03G)	110.2
C(03Q)-C(03N)-H(03J)	110.2
N(00X)-C(03O)-H(03L)	108.7
N(00X)-C(03O)-H(03M)	108.7
N(00X)-C(03O)-C(04O)	114.4(6)
H(03L)-C(03O)-H(03M)	107.6
C(04O)-C(03O)-H(03L)	108.7
C(04O)-C(03O)-H(03M)	108.7
C(04K)-C(03P)-H(03P)	118.8
C(051)-C(03P)-H(03P)	118.8
C(051)-C(03P)-C(04K)	122.4(8)
C(039)-C(03Q)-C(03N)	112.0(7)
C(039)-C(03Q)-H(03N)	109.2
C(039)-C(03Q)-H(03O)	109.2
C(03N)-C(03Q)-H(03N)	109.2

C(03N)-C(03Q)-H(03O)	109.2
H(03N)-C(03Q)-H(03O)	107.9
C(01Y)-C(03R)-C(02X)	120.1(8)
C(01Y)-C(03R)-H(03R)	120.0
C(02X)-C(03R)-H(03R)	120.0
O(00P)-C(03S)-N(01H)	125.1(7)
O(00P)-C(03S)-C(02F)	129.2(7)
N(01H)-C(03S)-C(02F)	105.6(6)
N(018)-C(03T)-C(02U)	114.5(7)
N(018)-C(03T)-H(0AA)	106.9
N(018)-C(03T)-C(04C)	111.0(6)
C(02U)-C(03T)-H(0AA)	106.9
C(02U)-C(03T)-C(04C)	110.3(6)
C(04C)-C(03T)-H(0AA)	106.9
O(00G)-C(03U)-N(017)	122.3(7)
O(00G)-C(03U)-C(03D)	114.1(6)
N(017)-C(03U)-C(03D)	123.5(7)
C(02V)-C(03V)-H(1AA)	110.3
C(02V)-C(03V)-HA	110.3
C(03M)-C(03V)-C(02V)	107.3(6)
C(03M)-C(03V)-H(1AA)	110.3
C(03M)-C(03V)-HA	110.3
H(1AA)-C(03V)-HA	108.5
C(02J)-C(03W)-C(02N)	107.6(7)
C(038)-C(03W)-C(02J)	121.0(7)
C(038)-C(03W)-C(02N)	131.4(7)
C(01C)-C(03X)-H(03X)	119.9
C(01L)-C(03X)-C(01C)	120.2(8)
C(01L)-C(03X)-H(03X)	119.9
C(044)-C(03Y)-H(03Y)	117.9
C(04T)-C(03Y)-H(03Y)	117.9
C(04T)-C(03Y)-C(044)	124.1(8)
C(04L)-C(03Z)-H(2AA)	120.2
C(059)-C(03Z)-H(2AA)	120.2
C(059)-C(03Z)-C(04L)	119.6(8)
C(01I)-C(040)-C(02T)	118.2(8)
C(01I)-C(040)-H(040)	120.9
C(02T)-C(040)-H(040)	120.9
C(035)-C(041)-H(04L)	109.8
C(035)-C(041)-H(04M)	109.8
H(04L)-C(041)-H(04M)	108.2
C(058)-C(041)-C(035)	109.4(6)
C(058)-C(041)-H(04L)	109.8
C(058)-C(041)-H(04M)	109.8
H(04N)-C(042)-H(04O)	108.2
C(04C)-C(042)-H(04N)	109.7
C(04C)-C(042)-H(04O)	109.7
C(04C)-C(042)-C(04D)	109.9(6)
C(04D)-C(042)-H(04N)	109.7
C(04D)-C(042)-H(04O)	109.7
C(01T)-C(043)-H(043)	120.4
C(04X)-C(043)-C(01T)	119.2(7)
C(04X)-C(043)-H(043)	120.4
C(022)-C(044)-H(044)	121.8
C(03Y)-C(044)-C(022)	116.3(8)
C(03Y)-C(044)-H(044)	121.8
C(02A)-C(045)-H(045)	120.8
C(05E)-C(045)-C(02A)	118.5(9)
C(05E)-C(045)-H(045)	120.8
C(028)-C(046)-H(046)	119.4
C(04J)-C(046)-C(028)	121.2(8)
C(04J)-C(046)-H(046)	119.4
C(01M)-C(047)-C(022)	117.5(8)
C(01M)-C(047)-H(047)	121.2
C(022)-C(047)-H(047)	121.2
C(02E)-C(048)-H(048)	120.0

C(04K)-C(048)-C(02E)	120.0(8)
C(04K)-C(048)-H(048)	120.0
C(02H)-C(049)-C(02Y)	128.7(8)
C(02H)-C(049)-C(03L)	122.6(7)
C(03L)-C(049)-C(02Y)	108.7(7)
O(00B)-C(04B)-N(01A)	122.5(7)
O(00B)-C(04B)-C(04H)	115.3(7)
N(01A)-C(04B)-C(04H)	122.1(8)
C(03T)-C(04C)-H(04P)	110.1
C(03T)-C(04C)-H(04Q)	110.1
C(042)-C(04C)-C(03T)	107.8(6)
C(042)-C(04C)-H(04P)	110.1
C(042)-C(04C)-H(04Q)	110.1
H(04P)-C(04C)-H(04Q)	108.5
N(014)-C(04D)-C(042)	114.3(6)
N(014)-C(04D)-H(04R)	108.7
N(014)-C(04D)-H(04S)	108.7
C(042)-C(04D)-H(04R)	108.7
C(042)-C(04D)-H(04S)	108.7
H(04R)-C(04D)-H(04S)	107.6
C(05J)-N(04E)-C(067)	112.9(12)
C(05M)-N(04E)-C(05J)	123.0(12)
C(05M)-N(04E)-C(067)	123.8(13)
C(03E)-C(04F)-H(04W)	121.1
C(03E)-C(04F)-C(04W)	117.9(9)
C(04W)-C(04F)-H(04W)	121.1
C(02T)-C(04G)-C(03G)	118.8(8)
C(02T)-C(04G)-C(04L)	119.3(8)
C(04L)-C(04G)-C(03G)	121.8(8)
N(013)-C(04H)-C(03C)	111.3(7)
N(013)-C(04H)-C(04B)	109.0(6)
N(013)-C(04H)-H(04H)	106.8
C(03C)-C(04H)-H(04H)	106.8
C(04B)-C(04H)-C(03C)	115.8(7)
C(04B)-C(04H)-H(04H)	106.8
C(04M)-C(04I)-H(04I)	120.7
C(05B)-C(04I)-H(04I)	120.7
C(05B)-C(04I)-C(04M)	118.6(9)
C(02L)-C(04J)-H(04X)	120.3
C(046)-C(04J)-C(02L)	119.4(8)
C(046)-C(04J)-H(04X)	120.3
C(03P)-C(04K)-H(04K)	119.5
C(048)-C(04K)-C(03P)	120.9(8)
C(048)-C(04K)-H(04K)	119.5
C(03Z)-C(04L)-C(04G)	121.4(9)
C(03Z)-C(04L)-H(04Y)	119.3
C(04G)-C(04L)-H(04Y)	119.3
C(02X)-C(04M)-C(04I)	120.0(8)
C(02X)-C(04M)-C(04U)	119.6(8)
C(04I)-C(04M)-C(04U)	120.4(9)
C(02M)-C(04N)-H(04Z)	119.6
C(054)-C(04N)-C(02M)	120.9(7)
C(054)-C(04N)-H(04Z)	119.6
C(02Q)-C(04O)-C(03O)	108.9(6)
C(02Q)-C(04O)-H(04A)	109.9
C(02Q)-C(04O)-H(04B)	109.9
C(03O)-C(04O)-H(04A)	109.9
C(03O)-C(04O)-H(04B)	109.9
H(04A)-C(04O)-H(04B)	108.3
N(015)-C(04P)-C(03M)	114.7(6)
N(015)-C(04P)-H(04)	108.6
N(015)-C(04P)-HB	108.6
C(03M)-C(04P)-H(04)	108.6
C(03M)-C(04P)-HB	108.6
H(04)-C(04P)-HB	107.6
N(017)-C(04Q)-H(04C)	108.8

N(017)-C(04Q)-H(04D)	108.8
N(017)-C(04Q)-C(05D)	114.0(6)
H(04C)-C(04Q)-H(04D)	107.6
C(05D)-C(04Q)-H(04C)	108.8
C(05D)-C(04Q)-H(04D)	108.8
C(03C)-C(04R)-H(04E)	109.5
C(03C)-C(04R)-H(04F)	109.5
C(03C)-C(04R)-C(04Y)	110.8(6)
H(04E)-C(04R)-H(04F)	108.1
C(04Y)-C(04R)-H(04E)	109.5
C(04Y)-C(04R)-H(04F)	109.5
C(037)-C(04T)-H(04T)	119.4
C(03Y)-C(04T)-C(037)	121.2(8)
C(03Y)-C(04T)-H(04T)	119.4
C(01Z)-C(04U)-C(04M)	117.6(8)
C(01Z)-C(04U)-H(04U)	121.2
C(04M)-C(04U)-H(04U)	121.2
C(02I)-C(04V)-H(04V)	119.8
C(05B)-C(04V)-C(02I)	120.5(9)
C(05B)-C(04V)-H(04V)	119.8
C(02A)-C(04W)-C(04F)	120.5(9)
C(02A)-C(04W)-C(057)	118.4(9)
C(057)-C(04W)-C(04F)	121.1(9)
C(043)-C(04X)-H(3AA)	119.0
C(043)-C(04X)-C(054)	122.1(8)
C(054)-C(04X)-H(3AA)	119.0
N(01A)-C(04Y)-C(04R)	112.9(7)
N(01A)-C(04Y)-H(04G)	109.0
N(01A)-C(04Y)-H(04J)	109.0
C(04R)-C(04Y)-H(04G)	109.0
C(04R)-C(04Y)-H(04J)	109.0
H(04G)-C(04Y)-H(04J)	107.8
C(02T)-C(050)-H(050)	119.5
C(059)-C(050)-C(02T)	121.0(9)
C(059)-C(050)-H(050)	119.5
C(023)-C(051)-H(051)	121.0
C(03P)-C(051)-C(023)	118.0(8)
C(03P)-C(051)-H(051)	121.0
C(03D)-C(052)-H(05A)	110.4
C(03D)-C(052)-H(05B)	110.4
C(03D)-C(052)-C(05D)	106.7(6)
H(05A)-C(052)-H(05B)	108.6
C(05D)-C(052)-H(05A)	110.4
C(05D)-C(052)-H(05B)	110.4
C(032)-C(053)-H(05M)	109.1
C(032)-C(053)-H(05N)	109.1
C(03F)-C(053)-C(032)	112.7(6)
C(03F)-C(053)-H(05M)	109.1
C(03F)-C(053)-H(05N)	109.1
H(05M)-C(053)-H(05N)	107.8
C(04N)-C(054)-C(04X)	118.7(8)
C(04N)-C(054)-H(054)	120.7
C(04X)-C(054)-H(054)	120.7
C(057)-C(055)-H(055)	120.0
C(05E)-C(055)-H(055)	120.0
C(05E)-C(055)-C(057)	120.0(11)
O(00T)-C(056)-N(01Q)	121.7(10)
O(00T)-C(056)-H(056)	119.2
N(01Q)-C(056)-H(056)	119.2
C(04W)-C(057)-H(057)	119.8
C(055)-C(057)-C(04W)	120.4(11)
C(055)-C(057)-H(057)	119.8
N(019)-C(058)-C(041)	113.4(7)
N(019)-C(058)-H(05O)	108.9
N(019)-C(058)-H(05P)	108.9
C(041)-C(058)-H(05O)	108.9

C(041)-C(058)-H(05P)	108.9
H(05O)-C(058)-H(05P)	107.7
C(03Z)-C(059)-H(059)	118.9
C(050)-C(059)-C(03Z)	122.2(8)
C(050)-C(059)-H(059)	118.9
N(02Z)-C(05A)-H(05X)	117.7
O(04S)-C(05A)-N(02Z)	124.6(12)
O(04S)-C(05A)-H(05X)	117.7
C(04I)-C(05B)-H(05C)	118.9
C(04V)-C(05B)-C(04I)	122.2(9)
C(04V)-C(05B)-H(05C)	118.9
N(01Q)-C(05C)-H(05Q)	109.5
N(01Q)-C(05C)-H(05R)	109.5
N(01Q)-C(05C)-H(05S)	109.5
H(05Q)-C(05C)-H(05R)	109.5
H(05Q)-C(05C)-H(05S)	109.5
H(05R)-C(05C)-H(05S)	109.5
C(04Q)-C(05D)-C(052)	110.3(7)
C(04Q)-C(05D)-H(05D)	109.6
C(04Q)-C(05D)-H(05E)	109.6
C(052)-C(05D)-H(05D)	109.6
C(052)-C(05D)-H(05E)	109.6
H(05D)-C(05D)-H(05E)	108.1
C(045)-C(05E)-H(05T)	119.0
C(055)-C(05E)-C(045)	122.0(10)
C(055)-C(05E)-H(05T)	119.0
N(03A)-C(05H)-H(05F)	109.5
N(03A)-C(05H)-H(05G)	109.5
N(03A)-C(05H)-H(05H)	109.5
H(05F)-C(05H)-H(05G)	109.5
H(05F)-C(05H)-H(05H)	109.5
H(05G)-C(05H)-H(05H)	109.5
N(02Z)-C(05I)-H(05Y)	109.5
N(02Z)-C(05I)-HC	109.5
N(02Z)-C(05I)-HD	109.5
H(05Y)-C(05I)-HC	109.5
H(05Y)-C(05I)-HD	109.5
HC-C(05I)-HD	109.5
N(04E)-C(05J)-H(05)	109.5
N(04E)-C(05J)-HE	109.5
N(04E)-C(05J)-HF	109.5
H(05)-C(05J)-HE	109.5
H(05)-C(05J)-HF	109.5
HE-C(05J)-HF	109.5
O(01F)-C(05K)-N(03A)	126.8(12)
O(01F)-C(05K)-H(05K)	116.6
N(03A)-C(05K)-H(05K)	116.6
O(04A)-C(05M)-H(4AA)	117.1
N(04E)-C(05M)-O(04A)	125.8(14)
N(04E)-C(05M)-H(4AA)	117.1
N(02Z)-C(05P)-H(05Z)	109.5
N(02Z)-C(05P)-HG	109.5
N(02Z)-C(05P)-HH	109.5
H(05Z)-C(05P)-HG	109.5
H(05Z)-C(05P)-HH	109.5
HG-C(05P)-HH	109.5
N(03A)-C(05Q)-H(05I)	109.5
N(03A)-C(05Q)-H(05J)	109.5
N(03A)-C(05Q)-H(05L)	109.5
H(05I)-C(05Q)-H(05J)	109.5
H(05I)-C(05Q)-H(05L)	109.5
H(05J)-C(05Q)-H(05L)	109.5
N(01Q)-C(05U)-H(05U)	109.5
N(01Q)-C(05U)-H(05V)	109.5
N(01Q)-C(05U)-H(05W)	109.5
H(05U)-C(05U)-H(05V)	109.5

H(05U)-C(05U)-H(05W)	109.5
H(05V)-C(05U)-H(05W)	109.5
N(04E)-C(067)-H(06A)	109.5
N(04E)-C(067)-H(06B)	109.5
N(04E)-C(067)-H(06C)	109.5
H(06A)-C(067)-H(06B)	109.5
H(06A)-C(067)-H(06C)	109.5
H(06B)-C(067)-H(06C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for mer-Ru2(RS-BPTPI)4Cl. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(01)	46(1)	59(1)	41(1)	4(1)	4(1)	21(1)
Ru(02)	43(1)	64(1)	45(1)	4(1)	2(1)	16(1)
Ru(03)	41(1)	62(1)	49(1)	2(1)	4(1)	14(1)
Ru(04)	45(1)	57(1)	51(1)	2(1)	3(1)	20(1)
Cl(05)	55(1)	75(1)	69(1)	-7(1)	12(1)	16(1)
Cl(06)	60(1)	67(1)	81(1)	-11(1)	7(1)	22(1)
O(007)	53(3)	57(3)	45(3)	-3(2)	8(2)	20(2)
O(008)	51(3)	49(3)	50(3)	10(2)	10(2)	16(2)
O(009)	36(3)	96(4)	62(3)	-11(3)	5(2)	8(3)
O(00A)	46(3)	78(4)	48(3)	-17(3)	1(2)	24(3)
O(00B)	47(3)	68(4)	51(3)	6(3)	12(2)	17(3)
O(00C)	46(3)	80(4)	51(3)	17(3)	0(2)	3(3)
O(00D)	60(3)	85(4)	63(4)	-2(3)	16(3)	-1(3)
O(00E)	64(4)	77(4)	61(4)	-1(3)	16(3)	11(3)
O(00F)	50(3)	95(4)	70(4)	13(3)	6(3)	23(3)
O(00G)	46(3)	81(4)	52(3)	3(3)	6(2)	24(3)
O(00H)	62(3)	78(4)	53(3)	12(3)	7(3)	11(3)
O(00I)	58(3)	56(3)	52(3)	16(3)	-2(2)	5(3)
O(00J)	49(3)	63(3)	44(3)	-1(2)	4(2)	17(2)
O(00K)	47(3)	70(4)	74(4)	5(3)	5(3)	4(3)
O(00L)	43(3)	63(4)	65(3)	4(3)	0(2)	19(3)
O(00M)	50(3)	102(5)	64(4)	27(3)	-4(3)	16(3)
N(00N)	47(4)	71(5)	58(4)	22(4)	15(3)	22(3)
O(00O)	43(3)	63(3)	54(3)	1(3)	4(2)	17(2)
O(00P)	66(4)	106(5)	59(4)	-5(3)	18(3)	-9(3)
O(00Q)	52(3)	94(4)	60(3)	15(3)	-3(3)	21(3)
N(00R)	44(3)	47(4)	42(3)	1(3)	6(3)	10(3)

N(00S)	47(4)	50(4)	64(4)	-1(3)	-5(3)	16(3)
O(00T)	82(4)	73(4)	64(4)	1(3)	0(3)	27(3)
O(00U)	72(4)	96(4)	56(3)	19(3)	28(3)	34(3)
N(00V)	40(3)	84(5)	56(4)	14(4)	7(3)	12(3)
O(00W)	73(4)	126(6)	48(3)	11(3)	5(3)	-17(4)
N(00X)	53(4)	49(4)	59(4)	-5(3)	3(3)	19(3)
N(00Y)	47(4)	68(5)	33(3)	12(3)	4(3)	6(3)
O(00Z)	51(3)	81(4)	82(4)	28(3)	6(3)	11(3)
O(010)	68(4)	111(5)	56(3)	-30(3)	19(3)	-6(3)
N(011)	55(4)	66(5)	58(4)	17(4)	2(3)	22(3)
N(012)	39(3)	67(5)	59(4)	9(3)	10(3)	13(3)
N(013)	43(4)	91(5)	63(4)	32(4)	4(3)	17(3)
N(014)	52(4)	63(4)	55(4)	-5(3)	6(3)	22(3)
N(015)	43(3)	68(4)	57(4)	14(3)	11(3)	21(3)
O(016)	62(4)	105(5)	71(4)	15(3)	23(3)	29(3)
N(017)	55(4)	68(4)	55(4)	-3(3)	-2(3)	25(3)
N(018)	47(4)	73(5)	46(4)	-5(3)	-10(3)	-3(3)
N(019)	47(4)	49(4)	71(4)	-1(3)	8(3)	16(3)
N(01A)	45(4)	66(5)	64(4)	14(4)	10(3)	15(3)
C(01B)	35(4)	79(6)	68(5)	20(5)	-10(4)	11(4)
C(01C)	34(4)	71(6)	63(5)	-1(4)	-5(3)	4(4)
C(01D)	56(5)	65(6)	49(5)	14(4)	6(4)	10(4)
C(01E)	53(5)	58(6)	62(5)	-6(4)	-3(4)	10(4)
O(01F)	83(4)	78(4)	59(4)	-6(3)	13(3)	36(3)
C(01G)	47(5)	90(7)	35(4)	19(4)	3(3)	12(4)
N(01H)	50(4)	67(4)	43(4)	-7(3)	4(3)	-5(3)
C(01I)	50(5)	63(5)	55(5)	12(4)	0(4)	13(4)
C(01J)	43(4)	82(6)	57(5)	7(5)	-9(4)	14(4)
C(01K)	45(4)	63(6)	60(5)	6(4)	5(4)	11(4)
C(01L)	74(6)	96(7)	44(5)	-3(5)	0(4)	27(5)
C(01M)	52(5)	64(5)	57(5)	-4(4)	21(4)	7(4)
C(01N)	55(5)	71(6)	74(6)	14(5)	15(4)	22(4)
C(01O)	50(5)	80(6)	60(5)	5(5)	11(4)	21(4)

C(01P)	44(4)	76(6)	59(5)	27(5)	5(4)	20(4)
N(01Q)	108(6)	85(6)	56(5)	-4(4)	15(4)	13(5)
C(01R)	43(5)	87(7)	63(6)	31(5)	14(4)	10(4)
C(01S)	32(4)	70(6)	62(5)	23(5)	11(3)	15(4)
C(01T)	45(4)	68(6)	54(5)	2(4)	9(4)	6(4)
C(01U)	56(5)	87(6)	36(4)	-1(4)	-8(3)	29(4)
C(01V)	45(4)	82(6)	46(4)	17(4)	-2(3)	7(4)
C(01W)	33(4)	95(7)	51(5)	11(5)	-4(3)	6(4)
C(01X)	36(4)	69(6)	71(6)	9(5)	22(4)	8(4)
C(01Y)	48(5)	62(6)	50(5)	10(4)	-15(4)	13(4)
C(01Z)	53(5)	69(6)	58(5)	6(4)	0(4)	26(4)
C(020)	47(4)	67(5)	39(4)	17(4)	9(3)	16(4)
C(021)	47(4)	69(5)	46(4)	8(4)	2(3)	5(4)
C(022)	57(5)	90(7)	56(5)	-7(5)	18(4)	15(5)
C(023)	39(4)	74(6)	56(5)	14(4)	6(4)	4(4)
C(024)	79(6)	57(6)	64(5)	14(4)	-3(4)	17(5)
C(025)	46(4)	70(6)	40(4)	4(4)	4(3)	20(4)
C(026)	34(4)	79(6)	73(6)	22(5)	8(4)	15(4)
C(027)	45(4)	57(5)	56(5)	2(4)	3(3)	12(4)
C(028)	51(5)	70(6)	52(5)	0(4)	5(4)	26(4)
C(029)	43(4)	64(6)	40(4)	21(4)	-3(3)	15(4)
C(02A)	59(5)	80(7)	60(5)	17(5)	4(4)	23(5)
C(02B)	48(5)	80(7)	64(6)	-7(5)	-22(4)	27(4)
C(02C)	42(4)	79(6)	53(5)	26(4)	12(4)	15(4)
C(02D)	63(5)	85(6)	45(5)	0(4)	5(4)	31(5)
C(02E)	43(4)	81(6)	59(5)	14(4)	9(4)	17(4)
C(02F)	57(5)	53(5)	49(5)	-10(4)	11(4)	-9(4)
C(02G)	53(5)	62(5)	62(5)	28(4)	14(4)	13(4)
C(02H)	46(5)	71(6)	78(6)	25(5)	15(4)	11(4)
C(02I)	57(5)	69(6)	67(6)	15(5)	12(4)	9(4)
C(02J)	46(5)	78(6)	61(5)	16(5)	10(4)	12(4)
C(02K)	51(5)	76(6)	52(5)	7(4)	-2(4)	28(4)
C(02L)	61(5)	77(7)	86(7)	14(6)	-1(5)	18(5)

C(02M)	52(5)	67(6)	59(5)	8(4)	11(4)	20(4)
C(02N)	43(5)	84(6)	60(5)	29(5)	5(4)	8(4)
C(02O)	69(6)	83(7)	37(4)	5(4)	0(4)	11(5)
C(02P)	31(4)	84(7)	55(5)	7(5)	-7(3)	11(4)
C(02Q)	46(4)	75(6)	74(6)	-5(5)	1(4)	19(4)
C(02R)	34(4)	91(7)	45(5)	-8(4)	0(3)	10(4)
C(02S)	57(5)	77(6)	41(4)	-3(4)	7(3)	18(4)
C(02T)	71(6)	83(6)	49(5)	5(5)	0(4)	34(5)
C(02U)	48(4)	79(6)	44(5)	7(4)	7(3)	15(4)
C(02V)	36(4)	54(5)	70(5)	6(4)	2(4)	6(3)
C(02W)	48(4)	63(5)	60(5)	13(4)	-5(4)	3(4)
C(02X)	42(4)	89(7)	53(5)	20(5)	0(4)	9(4)
C(02Y)	37(4)	56(5)	78(6)	1(5)	-2(4)	19(4)
N(02Z)	90(6)	71(6)	95(6)	-7(5)	0(5)	22(5)
C(030)	34(4)	70(6)	60(5)	23(4)	1(3)	6(4)
C(031)	78(6)	59(5)	42(4)	2(4)	17(4)	14(4)
C(032)	35(4)	65(5)	86(6)	0(4)	7(4)	13(4)
C(033)	51(5)	78(6)	42(4)	-6(4)	-1(4)	21(4)
C(034)	51(5)	97(7)	56(5)	3(5)	2(4)	10(5)
C(035)	61(5)	86(7)	81(6)	36(5)	34(4)	27(5)
C(036)	41(4)	81(7)	54(5)	9(5)	-4(4)	14(4)
C(037)	74(5)	54(5)	47(5)	9(4)	27(4)	16(4)
C(038)	41(4)	73(6)	58(5)	12(4)	0(4)	2(4)
C(039)	81(6)	74(6)	56(5)	-7(5)	-4(4)	37(5)
N(03A)	136(8)	91(6)	75(6)	-6(5)	39(5)	34(5)
C(03B)	50(5)	90(7)	63(5)	22(5)	4(4)	3(4)
C(03C)	57(5)	114(8)	78(6)	27(6)	6(4)	35(5)
C(03D)	41(4)	71(6)	79(6)	10(5)	1(4)	17(4)
C(03E)	50(5)	67(6)	57(5)	14(4)	8(4)	15(4)
C(03F)	49(5)	99(7)	52(5)	12(5)	9(4)	16(4)
C(03G)	47(5)	113(8)	66(6)	-22(5)	0(4)	27(5)
C(03H)	78(6)	67(6)	83(7)	24(5)	3(5)	15(5)
C(03I)	64(5)	61(5)	54(5)	8(4)	21(4)	0(4)

C(03J)	59(5)	84(6)	48(5)	-10(4)	18(4)	7(5)
C(03K)	52(5)	80(6)	67(6)	16(5)	2(4)	24(4)
C(03L)	41(4)	65(6)	53(5)	-1(4)	-7(3)	12(4)
C(03M)	63(5)	73(6)	90(7)	-20(5)	-8(5)	14(5)
C(03N)	72(5)	69(6)	49(5)	5(4)	-3(4)	1(4)
C(03O)	37(4)	68(5)	83(6)	1(4)	-7(4)	20(4)
C(03P)	67(6)	87(7)	68(6)	4(5)	23(5)	14(5)
C(03Q)	85(6)	55(5)	52(5)	-3(4)	1(4)	30(4)
C(03R)	54(5)	80(6)	44(5)	9(4)	3(4)	9(4)
C(03S)	54(5)	83(6)	45(5)	-3(4)	6(4)	-14(4)
C(03T)	59(5)	62(5)	48(5)	-4(4)	-14(4)	14(4)
C(03U)	45(4)	63(5)	55(5)	4(4)	1(4)	11(4)
C(03V)	47(5)	83(6)	78(6)	0(5)	-1(4)	21(4)
C(03W)	52(5)	72(6)	55(5)	15(4)	5(4)	10(4)
C(03X)	63(5)	96(7)	48(5)	9(5)	9(4)	24(5)
C(03Y)	75(6)	116(8)	47(5)	-25(5)	-7(4)	45(6)
C(03Z)	79(6)	92(7)	52(5)	-15(5)	-4(4)	47(5)
C(040)	54(5)	85(6)	51(5)	10(4)	18(4)	6(4)
C(041)	61(5)	82(6)	80(6)	23(5)	28(4)	27(4)
C(042)	73(6)	57(5)	70(6)	-5(5)	-6(4)	12(4)
C(043)	46(5)	82(6)	67(5)	-2(5)	2(4)	11(4)
C(044)	74(6)	96(7)	67(6)	-26(5)	-4(5)	14(5)
C(045)	56(5)	121(9)	65(6)	34(6)	9(4)	30(5)
C(046)	65(5)	72(6)	60(5)	3(5)	6(4)	17(4)
C(047)	49(5)	129(8)	55(5)	-20(5)	6(4)	1(5)
C(048)	47(5)	96(7)	71(6)	7(5)	3(4)	15(4)
C(049)	43(4)	68(6)	62(5)	5(4)	0(4)	8(4)
O(04A)	208(9)	134(7)	107(6)	-22(6)	-7(6)	71(6)
C(04B)	41(4)	82(7)	55(5)	27(5)	1(4)	14(4)
C(04C)	85(6)	67(6)	42(5)	9(4)	1(4)	4(5)
C(04D)	79(6)	53(5)	53(5)	-2(4)	-6(4)	29(4)
N(04E)	113(8)	110(8)	107(8)	-3(7)	24(6)	23(6)
C(04F)	63(5)	82(7)	65(6)	14(5)	2(4)	22(5)

C(04G)	50(5)	89(6)	54(5)	-4(5)	3(4)	36(4)
C(04H)	48(5)	74(6)	67(5)	31(5)	-1(4)	21(4)
C(04I)	63(5)	69(6)	85(7)	-17(5)	-3(5)	14(4)
C(04J)	67(6)	69(6)	76(6)	-9(5)	4(5)	15(5)
C(04K)	50(5)	100(8)	105(8)	19(6)	15(5)	18(5)
C(04L)	65(5)	100(7)	56(5)	-8(5)	0(4)	33(5)
C(04M)	46(5)	109(8)	58(5)	24(5)	12(4)	29(5)
C(04N)	49(5)	86(6)	46(5)	4(4)	4(4)	6(4)
C(04O)	34(4)	69(6)	87(6)	-3(5)	6(4)	8(4)
C(04P)	46(5)	71(6)	77(6)	-16(5)	-10(4)	12(4)
C(04Q)	52(5)	74(6)	84(6)	-14(5)	-16(4)	23(4)
C(04R)	53(5)	73(6)	90(7)	18(5)	10(4)	22(4)
O(04S)	89(5)	164(8)	187(8)	38(6)	56(5)	46(5)
C(04T)	84(6)	86(7)	53(5)	9(5)	17(5)	38(5)
C(04U)	52(5)	75(6)	56(5)	1(4)	9(4)	12(4)
C(04V)	64(6)	99(8)	72(6)	0(6)	6(5)	26(5)
C(04W)	64(6)	90(7)	64(6)	19(5)	13(4)	38(5)
C(04X)	57(5)	77(6)	84(7)	-3(5)	19(5)	9(4)
C(04Y)	62(5)	62(6)	87(7)	17(5)	8(4)	13(4)
C(050)	79(6)	140(9)	52(5)	-6(6)	16(5)	21(6)
C(051)	59(5)	79(6)	69(6)	5(5)	20(4)	6(4)
C(052)	44(5)	96(7)	125(8)	-5(6)	-31(5)	22(5)
C(053)	43(4)	107(7)	65(5)	15(5)	3(4)	21(4)
C(054)	65(6)	104(8)	85(7)	-19(6)	10(5)	9(5)
C(055)	85(7)	118(9)	86(7)	20(7)	16(6)	62(7)
C(056)	118(9)	107(9)	94(8)	-6(7)	11(7)	34(7)
C(057)	83(7)	136(9)	72(7)	23(6)	18(5)	54(6)
C(058)	53(5)	54(5)	86(6)	11(5)	27(4)	9(4)
C(059)	96(7)	120(9)	43(5)	-16(5)	9(5)	33(6)
C(05A)	98(8)	98(8)	105(9)	4(7)	-3(7)	34(7)
C(05B)	79(7)	106(8)	63(6)	13(6)	23(5)	34(6)
C(05C)	97(8)	90(8)	133(9)	8(6)	43(7)	12(6)
C(05D)	76(6)	56(6)	135(9)	-25(6)	-33(6)	21(5)

C(05E)	70(6)	122(9)	81(7)	23(7)	28(5)	45(6)
C(05H)	315(19)	259(18)	138(11)	-128(12)	-154(13)	218(16)
C(05I)	125(9)	109(10)	132(10)	24(8)	5(7)	21(8)
C(05J)	127(9)	124(10)	121(10)	1(8)	32(8)	62(7)
C(05K)	147(11)	73(7)	121(10)	2(7)	66(8)	2(7)
C(05M)	128(10)	73(8)	129(12)	15(8)	0(9)	41(7)
C(05P)	85(8)	109(9)	156(11)	-38(8)	16(7)	15(6)
C(05Q)	132(10)	110(9)	156(11)	1(8)	64(8)	-4(8)
C(05U)	185(12)	150(11)	130(10)	-37(9)	-90(9)	91(9)
C(067)	159(13)	133(13)	420(30)	-64(15)	159(15)	-54(11)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for mer-Ru2(RS-BPTPI)4Cl.

	x	y	z	U(eq)
H(01B)	3119	2063	2610	74
H(01K)	-4253	4119	786	67
H(01L)	-4519	6119	806	86
H(01N)	-2968	5731	-388	78
H(01V)	657	1842	4372	69
H(024)	7969	-680	5423	80
H(026)	3752	3358	3517	73
H(027)	4124	3445	939	63
H(02H)	7409	305	5667	76
H(02I)	925	3754	3406	76
H(02K)	9077	1062	4344	72
H(02L)	8578	-1290	4811	90
H(02A)	5093	2756	1304	78
H(02B)	4153	2401	1470	78
H(02S)	1943	3864	-925	69
H(02V)	7332	2815	5141	64
H(02W)	7842	2363	3796	69
H(03Q)	1853	3466	4753	74
H(03S)	1633	3251	5296	74
H(034)	5605	2101	2271	82
H(03T)	5309	4127	4033	87
H(03U)	4476	4266	3574	87
H(037)	2370	2647	-3637	68
H(038)	-3070	3086	1527	69
H(03A)	-313	4199	-135	85
H(03B)	714	4455	175	85
H(03C)	-922	3288	3089	81

H(03D)	120	1139	1900	98
H(03E)	-658	1245	1406	98
H(03F)	-2419	2330	185	76
H(03V)	726	2947	3952	79
H(03W)	-253	2581	4061	79
H(03Z)	5487	2539	7741	92
H(03H)	-3683	6396	130	91
H(03I)	2606	3047	-2737	70
H(03K)	-2526	4711	-583	79
H(03)	6969	3624	5713	93
H	7046	3567	6319	93
H(03G)	672	4372	-1363	77
H(03J)	-171	3985	-1142	77
H(03L)	3177	1828	219	76
H(03M)	3013	1800	807	76
H(03P)	-3552	4464	3317	87
H(03N)	1327	4709	-523	77
H(03O)	174	4857	-632	77
H(03R)	1692	3236	2698	71
H(0AA)	3004	1063	6056	70
H(1AA)	7240	2557	6192	84
HA	8127	2922	5984	84
H(03X)	-4637	5146	988	82
H(03Y)	-235	1853	-4215	97
H(2AA)	5057	2891	9455	90
H(040)	2373	1632	7931	75
H(04L)	4029	4664	4358	86
H(04M)	3207	4174	4123	86
H(04N)	3591	300	5550	82
H(04O)	4748	151	5612	82
H(043)	8941	1653	3457	78
H(044)	-871	1904	-3429	97
H(045)	3805	1550	1896	94

H(046)	9499	74	4070	79
H(047)	-633	2283	-2512	94
H(048)	-4244	3758	1885	85
H(04P)	5127	963	6203	78
H(04Q)	4335	524	6406	78
H(04R)	5201	922	5191	75
H(04S)	4165	699	4868	75
H(04W)	1266	363	2896	84
H(04H)	952	2008	1875	74
H(04I)	2721	5443	3141	89
H(04X)	9397	-914	4153	85
H(04K)	-4616	4356	2554	100
H(04Y)	5704	2818	8684	89
H(04Z)	6705	1376	1935	73
H(04A)	4731	1917	759	76
H(04B)	4565	2476	435	76
H(04)	5565	3029	6250	80
HB	5344	3563	5905	80
H(04C)	-383	1492	-498	86
H(04D)	-692	1957	-904	86
H(04E)	592	618	1166	85
H(04F)	1453	1093	1383	85
H(04T)	1316	2200	-4317	87
H(04U)	3439	4946	2396	73
H(04V)	799	4581	3905	94
H(3AA)	9227	981	2822	86
H(04G)	1187	1165	494	84
H(04J)	3	1187	498	84
H(050)	2547	2023	8844	107
H(051)	-2066	3994	3434	81
H(05A)	-2463	2387	-893	110
H(05B)	-3259	2049	-597	110
H(05M)	241	2702	4938	85

H(05N)	142	3316	4696	85
H(054)	8124	846	2044	103
H(055)	3008	-113	1509	113
H(056)	5890	1342	4230	127
H(057)	1995	-140	2159	113
H(05O)	4804	4030	4920	75
H(05P)	3642	4027	4992	75
H(059)	3492	2502	9520	104
H(05X)	8232	3834	4504	121
H(05C)	1645	5408	3764	96
H(05Q)	6980	918	3779	156
H(05R)	6650	817	3177	156
H(05S)	6584	293	3541	156
H(05D)	-1970	1429	-262	112
H(05E)	-2096	1377	-875	112
H(05T)	3932	713	1400	105
H(05F)	782	4417	1915	377
H(05G)	-31	4480	2307	377
H(05H)	248	5012	1983	377
H(05Y)	9114	5234	4759	182
HC	8326	5346	5156	182
HD	8031	5452	4563	182
H(05)	10984	3723	6029	182
HE	10049	4124	5941	182
HF	9926	3517	6189	182
H(05K)	-1046	3970	968	131
H(4AA)	9788	3661	7017	132
H(05Z)	6558	4791	4706	177
HG	7067	4613	5251	177
HH	6784	4132	4796	177
H(05I)	-1735	4470	2025	194
H(05J)	-2098	4339	1429	194
H(05L)	-1690	4972	1636	194

H(05U)	4462	280	3328	245
H(05V)	4992	592	2900	245
H(05W)	4208	926	3202	245
H(06A)	12010	4533	6784	349
H(06B)	11120	4935	6900	349
H(06C)	11284	4764	6322	349

$PdCo(esp)_2 \cdot 2H_2O$

Figure 30. Full Ortep plot (up) and stereoview (down)

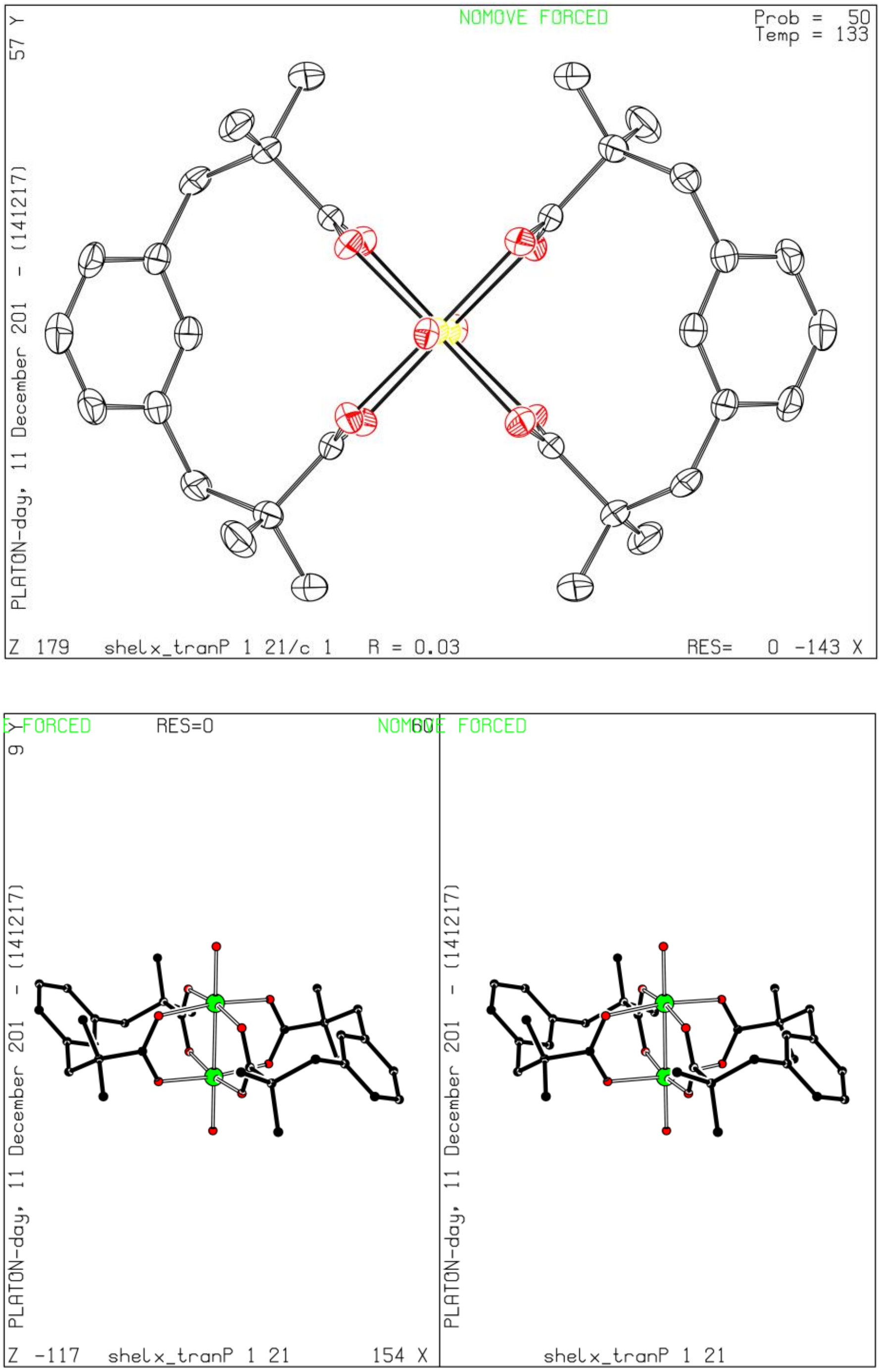

Table 1. Crystal data and structure refinement for PdCo(esp)2.

Identification code	shelx_trans	
Empirical formula	C32 H42 Co O9 Pd	
Formula weight	735.98	
Temperature	133(2) K	
Wavelength	1.5418 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 6.58100(10) Å	α= 90°.
	b = 19.1863(4) Å	β= 93.737(7)°.
	c = 12.6742(2) Å	γ = 90°.
Volume	1596.91(5) Å^3	
Z	2	
Density (calculated)	1.531 Mg/m^3	
Absorption coefficient	9.048 mm^{-1}	
F(000)	758	
Crystal size	0.280 x 0.200 x 0.130 mm^3	
Theta range for data collection	4.187 to 68.226°.	
Index ranges	-7<=h<=7, -22<=k<=23, -15<=l<=15	
Reflections collected	17455	
Independent reflections	2916 [R(int) = 0.0371]	
Completeness to theta = 67.680°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.5645	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2916 / 0 / 204	
Goodness-of-fit on F^2	0.899	
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.1000	
R indices (all data)	R1 = 0.0354, wR2 = 0.1031	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.407 and -0.934 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for PdCo(esp)2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(01)	8342(1)	4803(1)	5381(1)	19(1)
O(002)	10391(3)	6165(1)	4577(1)	30(1)
O(003)	10269(3)	4916(1)	3185(1)	31(1)
O(004)	7332(3)	4611(1)	3859(1)	31(1)
O(005)	7455(3)	5811(1)	5198(1)	30(1)
C(006)	7595(4)	6258(1)	2411(2)	29(1)
C(007)	8614(4)	6272(1)	4865(2)	28(1)
C(008)	8444(5)	4696(1)	3106(2)	29(1)
C(009)	7836(5)	7031(1)	4809(2)	35(1)
C(00A)	3524(4)	6500(2)	1871(2)	37(1)
C(00B)	6638(4)	6824(1)	2858(2)	30(1)
C(00C)	7581(5)	4514(2)	1981(2)	38(1)
C(00D)	4588(4)	6941(1)	2579(2)	34(1)
C(00E)	4494(4)	5929(2)	1444(2)	35(1)
C(00F)	7852(4)	7282(1)	3640(2)	33(1)
C(00G)	5732(5)	7089(2)	5202(2)	48(1)
C(00H)	7638(6)	5177(1)	1287(2)	37(1)
C(00I)	6546(4)	5798(1)	1708(2)	31(1)
C(00J)	9363(6)	7478(2)	5491(2)	50(1)
C(00K)	5422(5)	4233(2)	2002(2)	49(1)
O(00L)	5836(5)	4525(2)	5991(2)	21(1)
C(00M)	8941(6)	3949(2)	1538(2)	59(1)
Co(1)	8342(1)	4803(1)	5381(1)	19(1)

Table 3. Bond lengths [Å] and angles [°] for PdCo(esp)2.

Pd(01)-Pd(01)#1	2.5576(4)
Pd(01)-O(002)#1	2.0358(17)
Pd(01)-O(003)#1	2.0519(19)
Pd(01)-O(004)	2.0321(17)
Pd(01)-O(005)	2.0276(18)
Pd(01)-O(00L)	1.942(3)
O(002)-C(007)	1.265(3)
O(003)-C(008)	1.271(4)
O(004)-C(008)	1.251(4)
O(004)-Co(1)	2.0321(17)
O(005)-C(007)	1.259(3)
O(005)-Co(1)	2.0276(18)
C(006)-H(006)	0.9300
C(006)-C(00B)	1.395(4)
C(006)-C(00I)	1.403(4)
C(007)-C(009)	1.542(4)
C(008)-C(00C)	1.540(4)
C(009)-C(00F)	1.558(3)
C(009)-C(00G)	1.507(4)
C(009)-C(00J)	1.543(4)
C(00A)-H(00A)	0.9300
C(00A)-C(00D)	1.389(4)
C(00A)-C(00E)	1.394(4)
C(00B)-C(00D)	1.390(4)
C(00B)-C(00F)	1.512(3)
C(00C)-C(00H)	1.548(4)
C(00C)-C(00K)	1.522(5)
C(00C)-C(00M)	1.536(4)
C(00D)-H(00D)	0.9300
C(00E)-H(00E)	0.9300
C(00E)-C(00I)	1.393(4)
C(00F)-H(00B)	0.9700
C(00F)-H(00C)	0.9700
C(00G)-H(00F)	0.9600
C(00G)-H(00G)	0.9600
C(00G)-H(00H)	0.9600
C(00H)-H(00I)	0.9700
C(00H)-H(00J)	0.9700
C(00H)-C(00I)	1.506(4)
C(00J)-H(00K)	0.9600
C(00J)-H(00L)	0.9600
C(00J)-H(00M)	0.9600
C(00K)-H(00N)	0.9600
C(00K)-H(00O)	0.9600
C(00K)-H(00P)	0.9600
O(00L)-H(00Q)	0.8808
O(00L)-H(00R)	0.8799
C(00M)-H(00S)	0.9600
C(00M)-H(00T)	0.9600
C(00M)-H(00U)	0.9600
O(002)#1-Pd(01)-Pd(01)#1	85.46(5)
O(002)#1-Pd(01)-O(003)#1	93.33(7)
O(003)#1-Pd(01)-Pd(01)#1	85.12(6)
O(004)-Pd(01)-Pd(01)#1	85.95(6)
O(004)-Pd(01)-O(002)#1	88.13(7)
O(004)-Pd(01)-O(003)#1	170.82(8)
O(005)-Pd(01)-Pd(01)#1	85.52(6)
O(005)-Pd(01)-O(002)#1	170.80(7)
O(005)-Pd(01)-O(003)#1	87.68(7)
O(005)-Pd(01)-O(004)	89.46(7)
O(00L)-Pd(01)-Pd(01)#1	178.34(10)
O(00L)-Pd(01)-O(002)#1	95.49(11)
O(00L)-Pd(01)-O(003)#1	93.46(11)
O(00L)-Pd(01)-O(004)	95.43(11)
O(00L)-Pd(01)-O(005)	93.57(12)
C(007)-O(002)-Pd(01)#1	121.75(16)

C(008)-O(003)-Pd(01)#1	121.44(17)	C(00A)-C(00D)-H(00D)	119.8
C(008)-O(004)-Pd(01)	121.98(18)	C(00B)-C(00D)-H(00D)	119.8
C(008)-O(004)-Co(1)	121.98(18)	C(00A)-C(00E)-H(00E)	119.7
C(007)-O(005)-Pd(01)	122.21(16)	C(00I)-C(00E)-C(00A)	120.7(2)
C(007)-O(005)-Co(1)	122.21(16)	C(00I)-C(00E)-H(00E)	119.7
C(00B)-C(006)-H(006)	118.9	C(009)-C(00F)-H(00B)	108.7
C(00B)-C(006)-C(00I)	122.1(2)	C(009)-C(00F)-H(00C)	108.7
C(00I)-C(006)-H(006)	118.9	C(00B)-C(00F)-C(009)	114.0(2)
O(002)-C(007)-C(009)	116.8(2)	C(00B)-C(00F)-H(00B)	108.7
O(005)-C(007)-O(002)	125.0(2)	C(00B)-C(00F)-H(00C)	108.7
O(005)-C(007)-C(009)	118.2(2)	H(00B)-C(00F)-H(00C)	107.6
O(003)-C(008)-C(00C)	116.0(3)	C(009)-C(00G)-H(00F)	109.5
O(004)-C(008)-O(003)	125.4(2)	C(009)-C(00G)-H(00G)	109.5
O(004)-C(008)-C(00C)	118.6(3)	C(009)-C(00G)-H(00H)	109.5
C(007)-C(009)-C(00F)	108.2(2)	H(00F)-C(00G)-H(00G)	109.5
C(007)-C(009)-C(00J)	107.3(2)	H(00F)-C(00G)-H(00H)	109.5
C(00G)-C(009)-C(007)	111.4(2)	H(00G)-C(00G)-H(00H)	109.5
C(00G)-C(009)-C(00F)	110.8(2)	C(00C)-C(00H)-H(00I)	108.6
C(00G)-C(009)-C(00J)	110.6(2)	C(00C)-C(00H)-H(00J)	108.6
C(00J)-C(009)-C(00F)	108.4(2)	H(00I)-C(00H)-H(00J)	107.6
C(00D)-C(00A)-H(00A)	119.9	C(00I)-C(00H)-C(00C)	114.7(3)
C(00D)-C(00A)-C(00E)	120.3(2)	C(00I)-C(00H)-H(00I)	108.6
C(00E)-C(00A)-H(00A)	119.9	C(00I)-C(00H)-H(00J)	108.6
C(006)-C(00B)-C(00F)	119.0(2)	C(006)-C(00I)-C(00H)	119.7(3)
C(00D)-C(00B)-C(006)	118.6(2)	C(00E)-C(00I)-C(006)	117.9(3)
C(00D)-C(00B)-C(00F)	122.4(2)	C(00E)-C(00I)-C(00H)	122.4(3)
C(008)-C(00C)-C(00H)	108.6(2)	C(009)-C(00J)-H(00K)	109.5
C(00K)-C(00C)-C(008)	110.6(2)	C(009)-C(00J)-H(00L)	109.5
C(00K)-C(00C)-C(00H)	111.0(2)	C(009)-C(00J)-H(00M)	109.5
C(00K)-C(00C)-C(00M)	108.8(3)	H(00K)-C(00J)-H(00L)	109.5
C(00M)-C(00C)-C(008)	108.0(2)	H(00K)-C(00J)-H(00M)	109.5
C(00M)-C(00C)-C(00H)	109.7(3)	H(00L)-C(00J)-H(00M)	109.5
C(00A)-C(00D)-C(00B)	120.4(3)	C(00C)-C(00K)-H(00N)	109.5

C(00C)-C(00K)-H(00O)	109.5
C(00C)-C(00K)-H(00P)	109.5
H(00N)-C(00K)-H(00O)	109.5
H(00N)-C(00K)-H(00P)	109.5
H(00O)-C(00K)-H(00P)	109.5
Pd(01)-O(00L)-H(00Q)	111.8
Pd(01)-O(00L)-H(00R)	111.3
H(00Q)-O(00L)-H(00R)	102.5
C(00C)-C(00M)-H(00S)	109.5
C(00C)-C(00M)-H(00T)	109.5
C(00C)-C(00M)-H(00U)	109.5
H(00S)-C(00M)-H(00T)	109.5
H(00S)-C(00M)-H(00U)	109.5
H(00T)-C(00M)-H(00U)	109.5
O(002)#1-Co(1)-O(003)#1	93.33(7)
O(004)-Co(1)-O(002)#1	88.13(7)
O(004)-Co(1)-O(003)#1	170.82(8)
O(005)-Co(1)-O(002)#1	170.80(7)
O(005)-Co(1)-O(003)#1	87.68(7)
O(005)-Co(1)-O(004)	89.46(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for PdCo(esp)2. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(01)	16(1)	21(1)	20(1)	0(1)	3(1)	-2(1)
O(002)	39(1)	22(1)	26(1)	-2(1)	-3(1)	3(1)
O(003)	40(1)	32(1)	22(1)	-3(1)	-1(1)	8(1)
O(004)	41(1)	29(1)	21(1)	-3(1)	-9(1)	2(1)
O(005)	39(1)	24(1)	26(1)	1(1)	-2(1)	8(1)
C(006)	39(1)	28(1)	20(1)	8(1)	0(1)	1(1)
C(007)	40(2)	24(1)	17(1)	-1(1)	-6(1)	7(1)
C(008)	44(2)	21(1)	23(1)	-3(1)	-6(1)	11(1)
C(009)	57(2)	24(1)	23(1)	-2(1)	-3(1)	11(1)
C(00A)	37(1)	39(2)	33(2)	11(1)	-5(1)	4(1)
C(00B)	43(2)	23(1)	23(1)	8(1)	-1(1)	1(1)
C(00C)	59(2)	29(2)	22(1)	-8(1)	-13(1)	10(1)
C(00D)	45(2)	28(1)	30(1)	9(1)	1(1)	9(1)
C(00E)	47(2)	33(2)	23(1)	6(1)	-11(1)	-1(1)
C(00F)	50(2)	20(1)	29(1)	3(1)	-2(1)	4(1)
C(00G)	77(2)	36(2)	32(2)	4(1)	12(1)	28(2)
C(00H)	58(2)	36(2)	16(1)	-6(1)	-7(1)	4(1)
C(00I)	48(2)	28(1)	17(1)	4(1)	-3(1)	4(1)
C(00J)	84(2)	29(2)	35(2)	-10(1)	-14(2)	11(2)
C(00K)	80(2)	31(2)	34(2)	-2(1)	-24(2)	-9(2)
O(00L)	19(2)	24(2)	21(2)	4(1)	-1(1)	-2(1)
C(00M)	95(3)	45(2)	34(2)	-19(1)	-16(2)	32(2)
Co(1)	16(1)	21(1)	20(1)	0(1)	3(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for PdCo(esp)2.

	x	y	z	U(eq)
H(006)	8972	6182	2585	35
H(00A)	2158	6586	1681	44
H(00D)	3925	7316	2868	41
H(00E)	3763	5633	979	42
H(00B)	7309	7751	3592	40
H(00C)	9251	7299	3442	40
H(00F)	4793	6824	4752	72
H(00G)	5320	7570	5195	72
H(00H)	5741	6912	5911	72
H(00I)	9049	5304	1214	45
H(00J)	7038	5069	587	45
H(00K)	9346	7337	6217	75
H(00L)	8986	7960	5427	75
H(00M)	10706	7415	5253	75
H(00N)	5443	3798	2376	74
H(00O)	4866	4162	1291	74
H(00P)	4595	4562	2351	74
H(00Q)	5072	4263	5554	32
H(00R)	5045	4886	6086	32
H(00S)	10288	4131	1480	89
H(00T)	8384	3807	852	89
H(00U)	9001	3554	2005	89

PdNi(esp)$_2$·2H$_2$O

Figure 31. Full ortep plot (up) and stereoview (down)

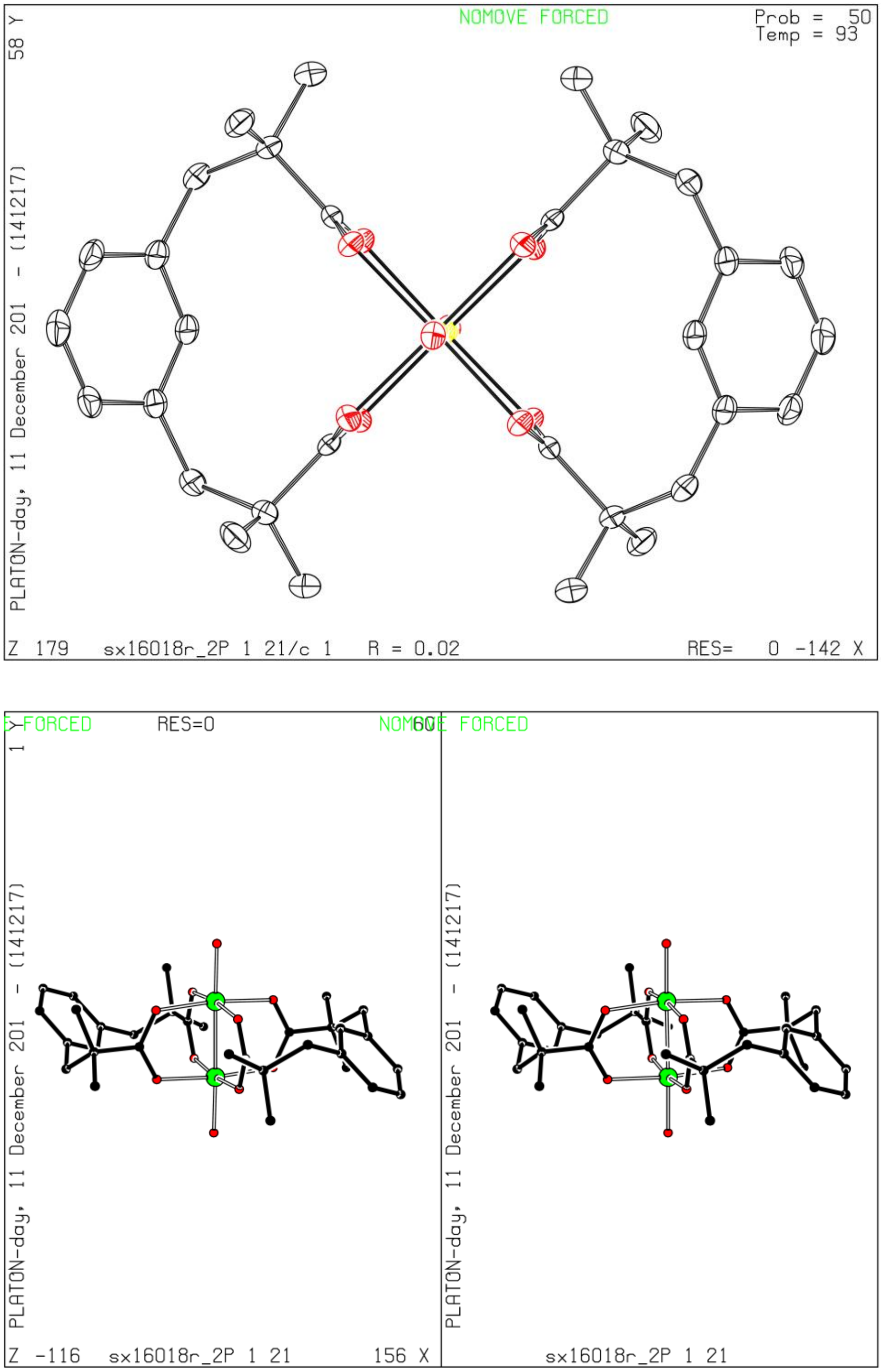

Table 1. Crystal data and structure refinement for PdNi(esp)2.

Identification code	sx16018r_2	
Empirical formula	C32 H42 Ni O9 Pd	
Formula weight	735.76	
Temperature	93.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 6.4807(2) Å	α= 90°.
	b = 19.2908(7) Å	β= 93.202(3)°.
	c = 12.6415(5) Å	γ = 90°.
Volume	1577.95(10) Å^3	
Z	2	
Density (calculated)	1.549 Mg/m^3	
Absorption coefficient	1.219 mm^{-1}	
F(000)	760	
Crystal size	0.027 x 0.02 x 0.018 mm^3	
Theta range for data collection	2.658 to 27.485°.	
Index ranges	-8<=h<=6, -19<=k<=25, -16<=l<=16	
Reflections collected	12038	
Independent reflections	3622 [R(int) = 0.0247]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.904 and 0.823	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3622 / 7 / 211	
Goodness-of-fit on F^2	1.007	
Final R indices [I>2sigma(I)]	R1 = 0.0244, wR2 = 0.0535	
R indices (all data)	R1 = 0.0327, wR2 = 0.0558	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.693 and -0.497 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for PdNi(esp)2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	8341(1)	4810(1)	5371(1)	16(1)
Ni(1)	8341(1)	4810(1)	5371(1)	16(1)
O(2)	10414(2)	6152(1)	4563(1)	24(1)
O(3)	7416(2)	5806(1)	5202(1)	25(1)
O(4)	10323(2)	4929(1)	3191(1)	25(1)
O(5)	7319(2)	4615(1)	3862(1)	25(1)
O(16)	5900(3)	4525(1)	5997(2)	17(1)
C(6)	8487(3)	4703(1)	3104(1)	22(1)
C(7)	8611(3)	6263(1)	4858(1)	22(1)
C(8)	7825(3)	7015(1)	4800(2)	27(1)
C(9)	7653(3)	6252(1)	2398(1)	22(1)
C(10)	7632(3)	4518(1)	1978(2)	28(1)
C(11)	3547(3)	6499(1)	1840(2)	28(1)
C(12)	4533(3)	5933(1)	1417(2)	27(1)
C(13)	7887(3)	7270(1)	3637(2)	25(1)
C(14)	7736(3)	5176(1)	1277(2)	27(1)
C(15)	4603(3)	6937(1)	2552(2)	26(1)
C(17)	5654(4)	7074(1)	5191(2)	35(1)
C(18)	6683(3)	6817(1)	2844(1)	22(1)
C(19)	6613(3)	5800(1)	1694(1)	24(1)
C(20)	5420(4)	4243(1)	1989(2)	35(1)
C(21)	9347(4)	7458(1)	5495(2)	37(1)
C(22)	9048(4)	3959(1)	1541(2)	44(1)

Table 3. Bond lengths [Å] and angles [°] for PdNi(esp)2.

Pd(1)-Pd(1)#1	2.5028(3)
Pd(1)-O(2)#1	2.0236(12)
Pd(1)-O(3)	2.0205(13)
Pd(1)-O(4)#1	2.0331(12)
Pd(1)-O(5)	2.0186(12)
Pd(1)-O(16)	1.890(2)
Ni(1)-O(2)#1	2.0236(12)
Ni(1)-O(3)	2.0205(13)
Ni(1)-O(4)#1	2.0331(12)
Ni(1)-O(5)	2.0186(12)
O(2)-C(7)	1.265(2)
O(3)-C(7)	1.266(2)
O(4)-C(6)	1.266(2)
O(5)-C(6)	1.266(2)
O(16)-H(16A)	0.964(10)
O(16)-H(16B)	0.958(10)
C(6)-C(10)	1.540(2)
C(7)-C(8)	1.537(2)
C(8)-C(13)	1.554(3)
C(8)-C(17)	1.522(3)
C(8)-C(21)	1.542(3)
C(9)-H(9)	0.9500
C(9)-C(18)	1.393(3)
C(9)-C(19)	1.393(3)
C(10)-C(14)	1.553(3)
C(10)-C(20)	1.529(3)
C(10)-C(22)	1.539(3)
C(11)-H(11)	0.9500
C(11)-C(12)	1.387(3)
C(11)-C(15)	1.387(3)
C(12)-H(12)	0.9500
C(12)-C(19)	1.398(3)
C(13)-H(13B)	0.9900
C(13)-H(13A)	0.9900
C(13)-C(18)	1.513(3)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(14)-C(19)	1.516(3)
C(15)-H(15)	0.9500
C(15)-C(18)	1.397(3)
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(17)-H(17A)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22C)	0.9800
C(22)-H(22B)	0.9800

O(2)#1-Pd(1)-Pd(1)#1	86.33(4)
O(2)#1-Pd(1)-O(4)#1	92.38(5)
O(3)-Pd(1)-Pd(1)#1	86.41(4)
O(3)-Pd(1)-O(2)#1	172.66(6)
O(3)-Pd(1)-O(4)#1	88.16(5)
O(4)#1-Pd(1)-Pd(1)#1	86.02(4)
O(5)-Pd(1)-Pd(1)#1	86.82(4)
O(5)-Pd(1)-O(2)#1	88.70(5)
O(5)-Pd(1)-O(3)	89.86(5)
O(5)-Pd(1)-O(4)#1	172.68(6)
O(16)-Pd(1)-Pd(1)#1	177.23(7)
O(16)-Pd(1)-O(2)#1	93.29(8)
O(16)-Pd(1)-O(3)	94.01(8)
O(16)-Pd(1)-O(4)#1	91.26(8)

O(16)-Pd(1)-O(5)	95.91(8)
O(2)#1-Ni(1)-O(4)#1	92.38(5)
O(3)-Ni(1)-O(2)#1	172.66(6)
O(3)-Ni(1)-O(4)#1	88.16(5)
O(5)-Ni(1)-O(2)#1	88.70(5)
O(5)-Ni(1)-O(3)	89.86(5)
O(5)-Ni(1)-O(4)#1	172.68(6)
C(7)-O(2)-Pd(1)#1	121.02(12)
C(7)-O(3)-Pd(1)	121.01(12)
C(7)-O(3)-Ni(1)	121.01(12)
C(6)-O(4)-Pd(1)#1	120.95(12)
C(6)-O(5)-Pd(1)	120.77(12)
C(6)-O(5)-Ni(1)	120.77(12)
Pd(1)-O(16)-H(16A)	97.3(17)
Pd(1)-O(16)-H(16B)	124(4)
H(16A)-O(16)-H(16B)	102.5(14)
O(4)-C(6)-O(5)	125.39(17)
O(4)-C(6)-C(10)	116.64(17)
O(5)-C(6)-C(10)	117.97(17)
O(2)-C(7)-O(3)	125.19(17)
O(2)-C(7)-C(8)	117.00(17)
O(3)-C(7)-C(8)	117.80(17)
C(7)-C(8)-C(13)	108.54(15)
C(7)-C(8)-C(21)	107.24(16)
C(17)-C(8)-C(7)	111.44(17)
C(17)-C(8)-C(13)	110.88(16)
C(17)-C(8)-C(21)	110.28(17)
C(21)-C(8)-C(13)	108.33(17)
C(18)-C(9)-H(9)	118.8
C(19)-C(9)-H(9)	118.8
C(19)-C(9)-C(18)	122.34(17)
C(6)-C(10)-C(14)	108.24(15)
C(20)-C(10)-C(6)	111.22(17)
C(20)-C(10)-C(14)	111.02(16)
C(20)-C(10)-C(22)	109.77(18)
C(22)-C(10)-C(6)	107.66(16)
C(22)-C(10)-C(14)	108.83(18)
C(12)-C(11)-H(11)	119.7
C(15)-C(11)-H(11)	119.7
C(15)-C(11)-C(12)	120.53(18)
C(11)-C(12)-H(12)	119.8
C(11)-C(12)-C(19)	120.46(18)
C(19)-C(12)-H(12)	119.8
C(8)-C(13)-H(13B)	108.8
C(8)-C(13)-H(13A)	108.8
H(13B)-C(13)-H(13A)	107.7
C(18)-C(13)-C(8)	113.87(16)
C(18)-C(13)-H(13B)	108.8
C(18)-C(13)-H(13A)	108.8
C(10)-C(14)-H(14A)	108.6
C(10)-C(14)-H(14B)	108.6
H(14A)-C(14)-H(14B)	107.6
C(19)-C(14)-C(10)	114.44(16)
C(19)-C(14)-H(14A)	108.6
C(19)-C(14)-H(14B)	108.6
C(11)-C(15)-H(15)	119.8
C(11)-C(15)-C(18)	120.30(18)
C(18)-C(15)-H(15)	119.8
C(8)-C(17)-H(17B)	109.5
C(8)-C(17)-H(17C)	109.5
C(8)-C(17)-H(17A)	109.5
H(17B)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17A)	109.5
H(17C)-C(17)-H(17A)	109.5
C(9)-C(18)-C(13)	119.46(17)
C(9)-C(18)-C(15)	118.28(17)

C(15)-C(18)-C(13)	122.25(17)
C(9)-C(19)-C(12)	118.07(18)
C(9)-C(19)-C(14)	119.64(17)
C(12)-C(19)-C(14)	122.26(17)
C(10)-C(20)-H(20A)	109.5
C(10)-C(20)-H(20B)	109.5
C(10)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(8)-C(21)-H(21A)	109.5
C(8)-C(21)-H(21B)	109.5
C(8)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(10)-C(22)-H(22A)	109.5
C(10)-C(22)-H(22C)	109.5
C(10)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22B)	109.5
H(22C)-C(22)-H(22B)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for PdNi(esp)2. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	19(1)	15(1)	13(1)	0(1)	1(1)	0(1)
Ni(1)	19(1)	15(1)	13(1)	0(1)	1(1)	0(1)
O(2)	34(1)	17(1)	19(1)	-1(1)	-3(1)	5(1)
O(3)	36(1)	19(1)	19(1)	0(1)	-2(1)	7(1)
O(4)	36(1)	23(1)	14(1)	-2(1)	-4(1)	5(1)
O(5)	36(1)	22(1)	16(1)	-3(1)	-7(1)	3(1)
O(16)	14(1)	18(1)	18(1)	3(1)	1(1)	-3(1)
C(6)	35(1)	14(1)	17(1)	-1(1)	-6(1)	8(1)
C(7)	36(1)	19(1)	10(1)	-3(1)	-6(1)	5(1)
C(8)	42(1)	18(1)	20(1)	-2(1)	-3(1)	8(1)
C(9)	28(1)	22(1)	15(1)	6(1)	-1(1)	1(1)
C(10)	45(1)	21(1)	17(1)	-6(1)	-9(1)	7(1)
C(11)	29(1)	30(1)	26(1)	10(1)	-5(1)	1(1)
C(12)	36(1)	26(1)	18(1)	5(1)	-8(1)	-3(1)
C(13)	34(1)	16(1)	23(1)	2(1)	-2(1)	2(1)
C(14)	40(1)	28(1)	14(1)	-3(1)	-5(1)	4(1)
C(15)	34(1)	21(1)	23(1)	7(1)	0(1)	6(1)
C(17)	56(1)	24(1)	25(1)	2(1)	7(1)	18(1)
C(18)	32(1)	18(1)	16(1)	6(1)	-1(1)	0(1)
C(19)	36(1)	22(1)	13(1)	5(1)	-1(1)	1(1)
C(20)	57(1)	24(1)	23(1)	-1(1)	-16(1)	-5(1)
C(21)	60(2)	23(1)	28(1)	-9(1)	-11(1)	9(1)
C(22)	70(2)	33(1)	26(1)	-14(1)	-13(1)	20(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for PdNi(esp)2.

	x	y	z	U(eq)
H(16A)	5350(40)	4981(7)	6112(11)	80(20)
H(16B)	4770(40)	4296(9)	5620(40)	67(18)
H(9)	9075	6172	2582	26
H(11)	2136	6587	1641	34
H(12)	3789	5634	936	32
H(13B)	7324	7746	3590	30
H(13A)	9345	7289	3443	30
H(14A)	9205	5301	1210	33
H(14B)	7139	5066	559	33
H(15)	3909	7320	2842	31
H(17B)	4698	6798	4734	42
H(17C)	5219	7561	5170	42
H(17A)	5646	6902	5920	42
H(20A)	4528	4599	2276	42
H(20B)	5396	3827	2432	42
H(20C)	4918	4128	1264	42
H(21A)	8947	7947	5437	45
H(21B)	10748	7399	5255	45
H(21C)	9311	7309	6235	45
H(22A)	8552	3836	819	52
H(22C)	9030	3546	1993	52
H(22B)	10462	4138	1533	52

Table 6. Torsion angles [°] for PdNi(esp)2.

Pd(1)#1-O(2)-C(7)-O(3)	-0.9(2)
Pd(1)#1-O(2)-C(7)-C(8)	178.65(11)
Pd(1)-O(3)-C(7)-O(2)	2.2(2)
Pd(1)-O(3)-C(7)-C(8)	-177.29(11)
Pd(1)#1-O(4)-C(6)-O(5)	-0.2(2)
Pd(1)#1-O(4)-C(6)-C(10)	-179.74(11)
Pd(1)-O(5)-C(6)-O(4)	-1.8(2)
Pd(1)-O(5)-C(6)-C(10)	177.74(11)
Ni(1)-O(3)-C(7)-O(2)	2.2(2)
Ni(1)-O(3)-C(7)-C(8)	-177.29(11)
Ni(1)-O(5)-C(6)-O(4)	-1.8(2)
Ni(1)-O(5)-C(6)-C(10)	177.74(11)
O(2)-C(7)-C(8)-C(13)	58.4(2)
O(2)-C(7)-C(8)-C(17)	-179.26(15)
O(2)-C(7)-C(8)-C(21)	-58.5(2)
O(3)-C(7)-C(8)-C(13)	-122.09(18)
O(3)-C(7)-C(8)-C(17)	0.3(2)
O(3)-C(7)-C(8)-C(21)	121.08(19)
O(4)-C(6)-C(10)-C(14)	-58.5(2)
O(4)-C(6)-C(10)-C(20)	179.23(16)
O(4)-C(6)-C(10)-C(22)	58.9(2)
O(5)-C(6)-C(10)-C(14)	121.85(18)
O(5)-C(6)-C(10)-C(20)	-0.4(2)
O(5)-C(6)-C(10)-C(22)	-120.7(2)
C(6)-C(10)-C(14)-C(19)	-56.3(2)
C(7)-C(8)-C(13)-C(18)	56.0(2)
C(8)-C(13)-C(18)-C(9)	-88.0(2)
C(8)-C(13)-C(18)-C(15)	90.8(2)
C(10)-C(14)-C(19)-C(9)	88.3(2)
C(10)-C(14)-C(19)-C(12)	-90.0(2)
C(11)-C(12)-C(19)-C(9)	-0.3(3)

C(11)-C(12)-C(19)-C(14)	178.12(18)
C(11)-C(15)-C(18)-C(9)	0.3(3)
C(11)-C(15)-C(18)-C(13)	-178.50(17)
C(12)-C(11)-C(15)-C(18)	0.6(3)
C(15)-C(11)-C(12)-C(19)	-0.6(3)
C(17)-C(8)-C(13)-C(18)	-66.7(2)
C(18)-C(9)-C(19)-C(12)	1.2(3)
C(18)-C(9)-C(19)-C(14)	-177.21(17)
C(19)-C(9)-C(18)-C(13)	177.60(17)
C(19)-C(9)-C(18)-C(15)	-1.3(3)
C(20)-C(10)-C(14)-C(19)	66.1(2)
C(21)-C(8)-C(13)-C(18)	172.14(16)
C(22)-C(10)-C(14)-C(19)	-173.02(17)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1