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Selectivity Control of C–H Functionalization
under Group 9 Metal Catalysis

(第9族遷移金属触媒を用いた C–H 官能基化における選択性制御)

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Abbreviations

Ac	acetyl
Ar	aryl
aq.	aqueous
BINOL	1,1'-bi-2,2'-naphthol
Bn	benzyl
Boc	<i>tertiary</i> -butoxycarbonyl
Bu	butyl
<i>n</i> Bu	<i>normal</i> -butyl
<i>t</i> Bu	<i>tertiary</i> -butyl
cat.	catalyst
CCA	chiral carboxylic acid
conv.	conversion
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
DCE	1,2-dichloroethane
DCM	dichloromethane
DFT	density functional theory
DG	directing group
DMF	<i>N, N</i> -dimethylformamide
dr	diastereomeric ratio
equiv.	equivalent
er	enantiomeric ratio
ESI	electrospray ionization
Et	ethyl
Fig.	figure
h	hour
HFIP	1,1,1,3,3,3-hexafluoro-2-propanol
HMPA	hexamethylphosphoramide
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectrum
IR	infrared ray
KIE	kinetic isotope effect
Me	methyl
min	minute

MS	molecular sieves or mass spectrometry
NCI	non-covalent interaction
NCS	<i>N</i> -chlorosuccinimide
NMR	nuclear magnetic resonance
Ph	phenyl
Piv	pivaloyl
ppm	parts per million
<i>i</i> Pr	isopropyl
R_f	retention factor
rt	room temperature
Tf	trifluoromethanesulfonyl
TFE	2,2,2-trifluoroethanol
THF	tetrahydrofuran
TLC	thin-layer chromatography
TMS	trimethylsilyl or tetramethylsilane
t_R	retention time
UV	ultraviolet

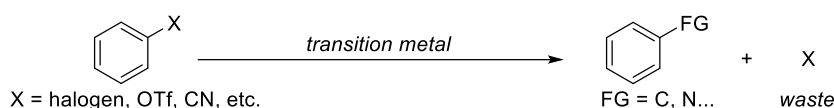
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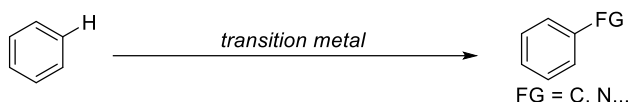
General Introduction

Conventional transition-metal-catalyzed cross-coupling reactions are widely employed for the formation of C–C and C–heteroatom (e.g., N, O, or halogen) bonds owing to their broad applicability and reliability (**Figure 1A**). However, these reactions generally require prefunctionalized substrates bearing suitable leaving groups, which inevitably generate stoichiometric amounts of waste and compromise atom- and step-economy.¹ In contrast, catalytic direct C–H functionalization has emerged as an efficient and sustainable strategy for the synthesis of a wide range of organic molecules (**Figure 1B**).² By directly converting inert C–H bonds into C–C or C–heteroatom bonds, this approach reduces the number of reaction steps and minimizes waste generation, thereby giving significant advantages in terms of both step- and atom-economy.

A: Traditional cross coupling with transition metal



B: C–H functionalization with transition metal



☺ Requirement for prefunctionalization

☺ Less waste

Figure 1. Coupling reactions by transition metals

The origins of this research field can be traced back to the catalytic synthesis of phthalimidines from imines using a catalytic amount of $\text{Co}_2(\text{CO})_8$, as reported by Murahashi (**Figure 2**, top).³ Although a detailed mechanistic investigation was not presented, the observed *ortho*-selectivity was presumably governed by coordination of the imine group, which acted as a directing group. However, most of these early transformations required harsh reaction conditions and control over regioselectivity was limited.

A significant progress of regioselective catalytic C–H activation was reported in 1971, when Fahey demonstrated that palladium catalysts could determine *ortho*-selectivity in the C–H halogenation of azobenzene (**Figure 2**, middle).⁴ Subsequently, Tremont and co-workers reported *ortho*-C–H alkylation of acetanilides using $\text{Pd}(\text{OAc})_2$, proposing a Pd(II)/Pd(IV) catalytic cycle based on mechanistic considerations (**Figure 2**, bottom).⁵ These catalytic C–H functionalization of compounds with a directing group demonstrated that the strategy using a directing group are feasible for high regio-selectivity although substrate generality was not satisfactory, affording the key knowledge to development of this chemistry in the future.

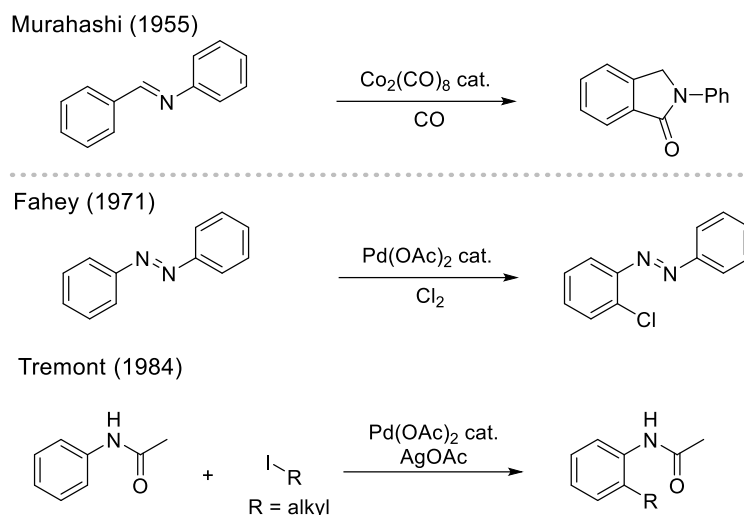


Figure 2. Early works of catalytic directed C–H functionalization

This concept of directing group-assisted C–H functionalization was dramatically advanced by the ruthenium-catalyzed C–H alkylation reported by Murai and co-workers in 1993.⁶ In this transformation, oxidative addition of a C–H bond to a low-valent ruthenium complex was identified as the key elementary step, enabling highly regioselective C–H activation under the control of a coordinating directing group under mild conditions. (**Figure 3**). This discovery represented a breakthrough in the field, as it significantly expanded both substrate diversity and catalytic efficiency in C–H functionalization.

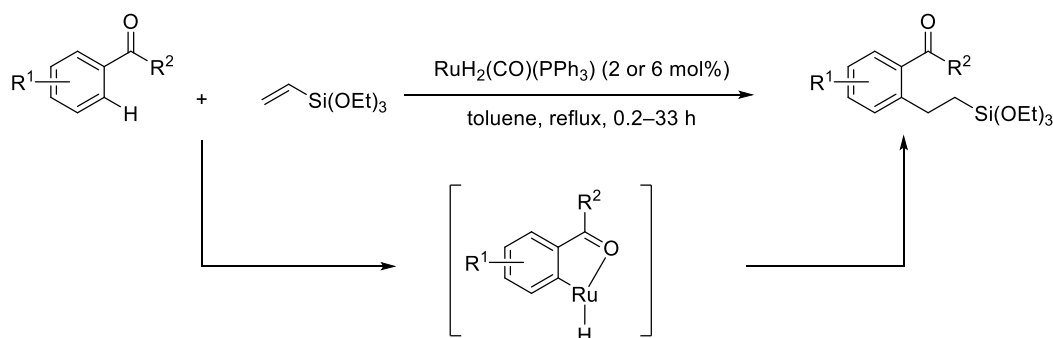


Figure 3. Murai reaction as a breakthrough in directed C–H functionalization

Following this pioneering work, a wide range of transition-metal catalysts have been developed for C–H functionalization. In low-valent metal catalysis, iridium-catalyzed C–H borylation and silylation have become among the most widely recognized and reliable transformations.⁷ In contrast, high-valent metal catalysis, particularly based on Pd(II), has been extensively explored for C–H functionalization, enabling mainly C–C and C–O bond formation from both C(sp²)–H and C(sp³)–H bonds.⁸ High-valent group 9 transition metals bearing cyclopentadienyl (Cp) ligands have also attracted considerable attention owing to their excellent functional-group tolerance and high catalytic activity (**Figure 4**). High valent transition metal catalysts enable C–H functionalization for C–O and C–N bond formation because transformation from C–H to C–heteroatom bond is intrinsically oxidative reaction and a catalyst with high valent transition metal is

suitable for oxidation of C–H bond. Sato, Miura, and co-workers first reported Cp^{*}Rh(III)-catalyzed C–H alkenylation of phenyl moiety with carboxylic acids,⁹ which was subsequently extended to Cp^{*}Ir(III)-¹⁰ and Cp^{*}Co(III)-catalyzed systems.^{11,12}

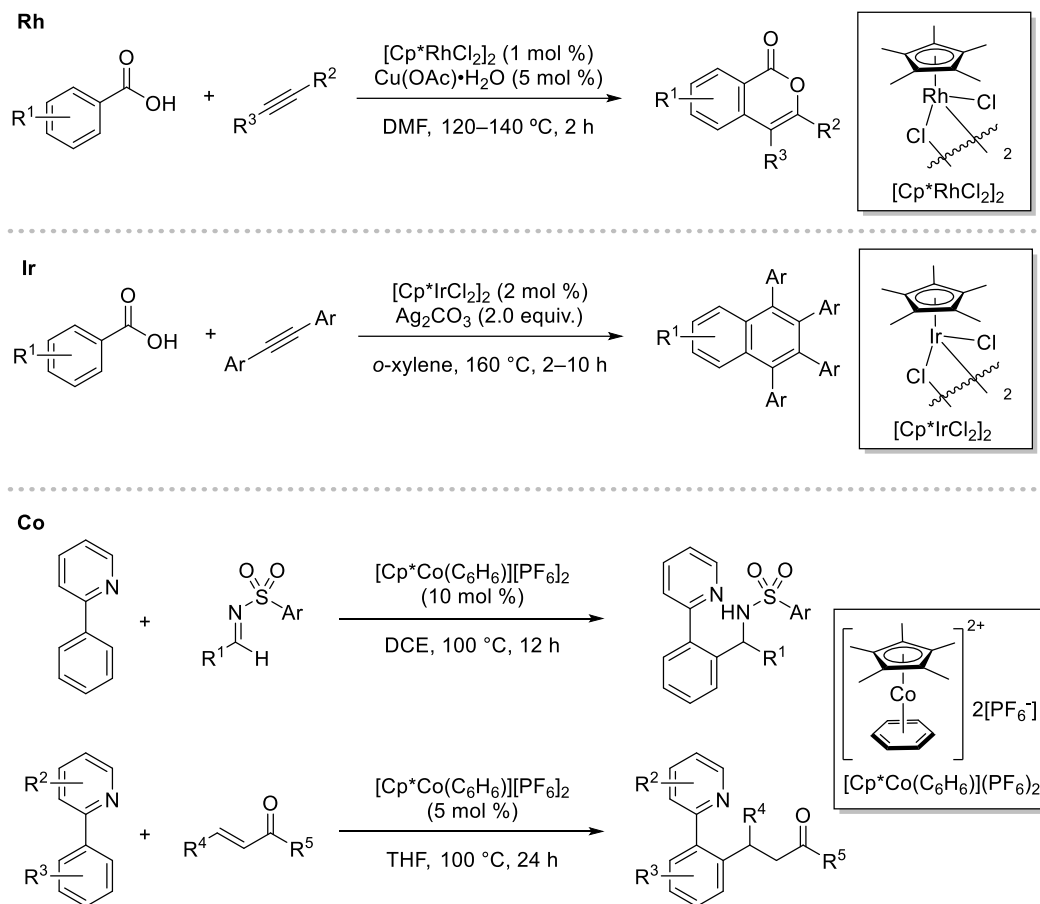


Figure 4. Initial works in directed C–H functionalization by Cp^{*}M(III)

Introduction

Directed C–H activation mediated by $\text{Cp}^*\text{M(III)}$ catalysts is generally proposed to proceed via a concerted metallation–deprotonation (CMD) mechanism (**Figure 5**).¹³ In this process, the $\text{Cp}^*\text{M(III)}$ center is coordinated by a directing group in the substrate together with a weak base, typically a carboxylate ligand. The C–H bond at the *ortho* position is cleaved simultaneously through metal–carbon bond formation, as the acidity of the C–H bond is enhanced by an agostic interaction between the metal center and the C–H bond. On the basis of this mechanism, $\text{Cp}^*\text{M(III)}$ -catalyzed C–H functionalization has been further developed into fine control of selectivity, including enantioselectivity, primarily using chiral cyclopentadienyl ligands¹⁴ and chiral carboxylic acids.¹⁵

Concerted Metallation-Deprotonation (CMD)

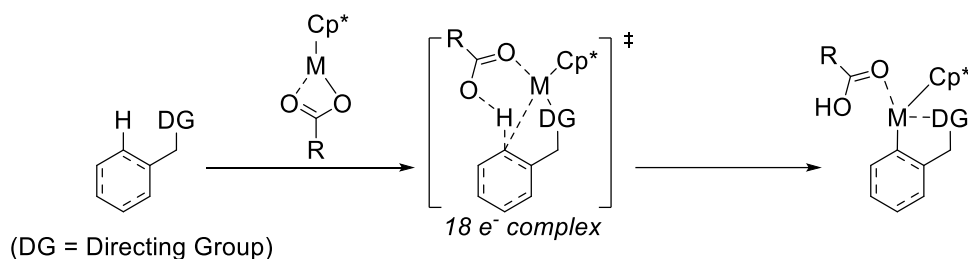


Figure 5. CMD mechanism

Although C–H functionalization has been developed into a wide variety of transformations, several important issues remain unresolved. One such issue is the limited substrate generality in enantioselective C–H functionalization, and other fundamental challenges lie in controlling selectivity, particularly site-selectivity.

In this thesis, control of enantioselectivity and site-selectivity in C–H functionalization is addressed through the development of several strategies. Special attention is paid to mechanistic and conformational factors that have often been overlooked or treated ambiguously, such as rotation of the *E/Z* configuration during C–H functionalization of oxime derivatives.

In addition, it is proposed that fine three-dimensional design of catalysts can unlock unprecedented reactivity and selectivity in C–H functionalization. An overview of the strategies investigated in this thesis is summarized in **Figure 6**.

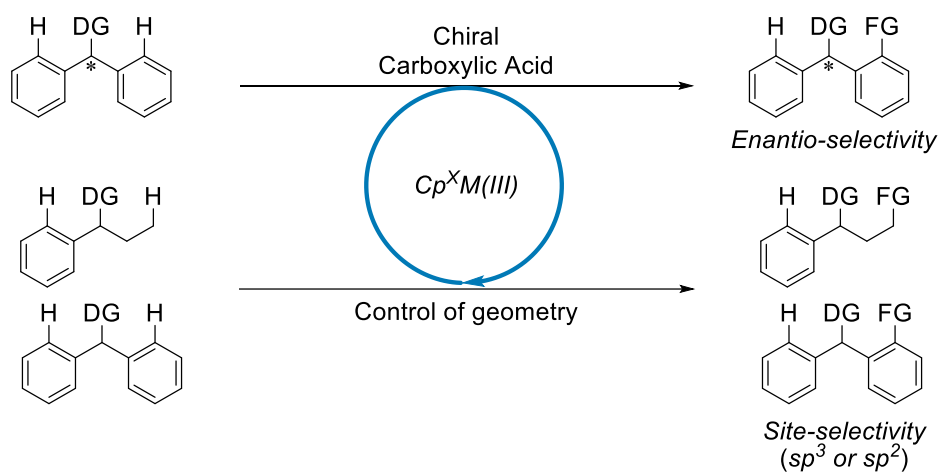
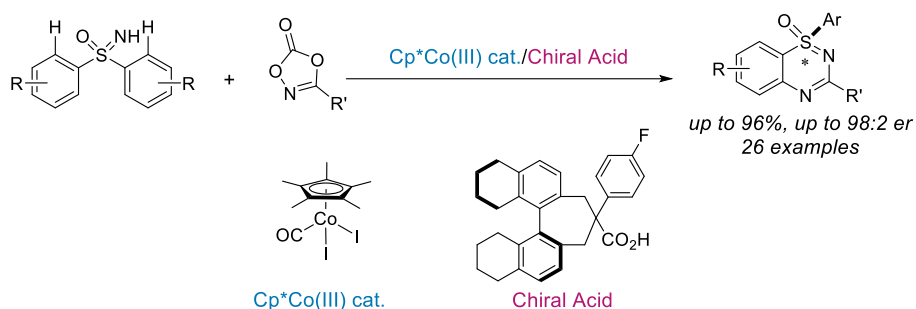


Figure 6. Main contents: selectivity control in C–H functionalization

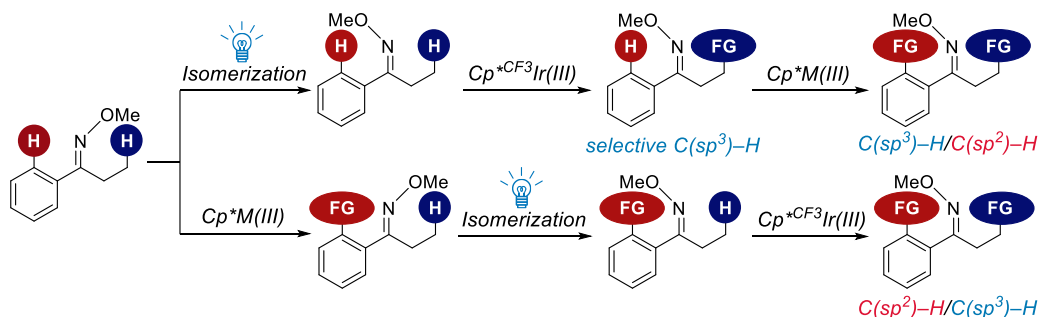
Chapter 1 (control of enantioselectivity): Asymmetric synthesis of benzothiadiazine-1-oxide by combination of Cp*Co(III) and chiral carboxylic acid

The combination of Cp*Co(III) and a chiral carboxylic acid enabled the asymmetric C–H amidation of sulfoximines, and subsequent dehydration afforded benzothiadiazine-1-oxide derivatives, which are interesting as pharmaceutical candidates. Detailed transition state analysis of the C–H activation step provided mechanistic insight into the origin of enantioselectivity and demonstrated that the newly developed chiral carboxylic acid can be applied to other substrate classes.



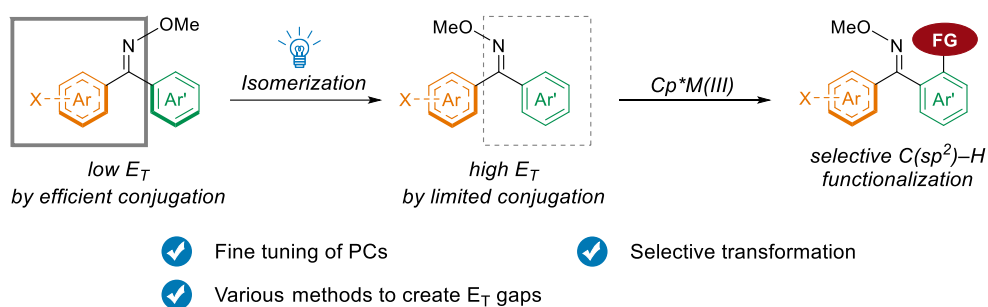
Chapter 2 (control of site-selectivity): Site-selective C(sp³)–H functionalization and successive C(sp³)–H/C(sp²)–H functionalization by geometry control in directing group

Control of the geometry of a directing group enabled site-selective C(sp³)–H functionalization through photoinduced *E/Z* isomerization. Furthermore, successive C(sp³)–H/C(sp²)–H and C(sp²)–H/C(sp³)–H functionalization was achieved by switching the orientation of the directing group under thermal or photochemical conditions.



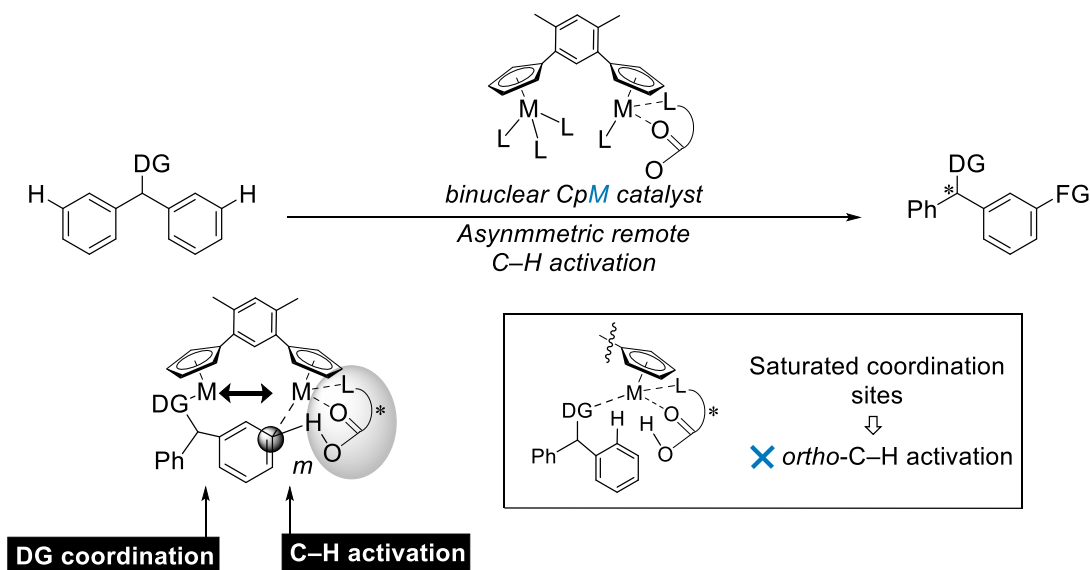
Chapter 3 (control of site-selectivity): Selective *E/Z* isomerization of diaryl oxime derivatives and selective transformation

Fine tuning and rational design of substrates enabled selective *E/Z* isomerization of diaryl oxime ethers bearing structurally and electronically similar aryl groups. Moreover, the resulting *E/Z* geometry was demonstrated to govern site-selectivity in C(sp²)-H functionalization.



Chapter 4 (control of site-selectivity): Synthesis of binuclear $CpRh(III)$ catalyst for remote C-H functionalization

A binuclear $CpRh(III)$ catalyst was three-dimensionally designed to overcome intrinsic limitations of conventional $Cp^*M(III)$ -catalyzed C-H functionalization, such as the difficulty of achieving remote C-H activation. The combination of the newly designed binuclear $CpRh(III)$ catalyst and a bidentate CMD ligand was hypothesized to enable remote C-H activation by suppressing conventional proximal C-H activation.



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1. Asymmetric synthesis of benzothiazine-1-oxide by combination of Cp*Co(III) and chiral carboxylic acid

Section 1: Introduction

As discussed in the General Introduction, Cp*M(III) catalysts featuring high-valent transition metals have emerged as powerful tools for the direct conversion of inert C–H bonds into C–X bonds (X = C, N, etc.). Their application has been extended to enantioselective C–H functionalization. In the development of enantioselective C–H functionalization using Cp*M(III) catalysts, a primary challenge has been the limited availability of the coordination sites on the metal center (**Figure 1**). C–H activation by CpM(III) complexes is generally proposed to proceed via a concerted metallation–deprotonation (CMD) mechanism.¹ In the C–H activation step, the hydrogen atom of the C–H bond is abstracted by a coordinating weak base, such as a carboxylate, while the high-valent metal center weakens the C–H bond through an agostic interaction. Since only three coordination sites remain available around the Cp*M(III) center, these must be fully utilized for C–H activation. Consequently, external chiral ligands such as chiral diphosphines cannot be employed. Therefore, the introduction of chirality into either the Cp ligand or the carboxylate is essential to achieve asymmetric C–H functionalization with CpM(III) catalysts.

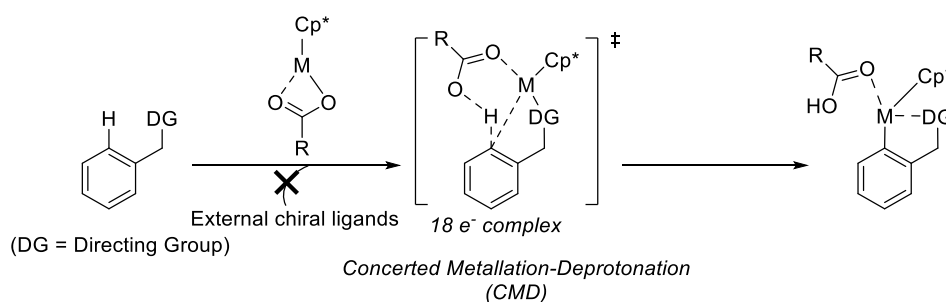


Figure 1. CMD mechanism

Chiral Cp method

One powerful approach to asymmetric C–H functionalization is the use of chiral Cp ligands.² In 2012, Cramer and co-workers reported that an in situ generated chiral CpRh(III) catalyst enabled asymmetric C–H alkylation with excellent enantioselectivity (**Figure 2**).³ Since this pioneering work, various chiral Cp ligands and their corresponding metal complexes have been developed and successfully applied to asymmetric C–H functionalization, achieving high enantioselectivity across a range of reactions (**Figure 3**).⁴ Although the chiral Cp strategy often affords outstanding enantioselectivity owing to the rigid and well-defined chiral environment around the metal center, the substrate generality of these systems remains relatively limited. For example, while chiral CpCo(III) catalysts show excellent selectivity in C–H functionalization, there are a few reports using limited substrates.⁵

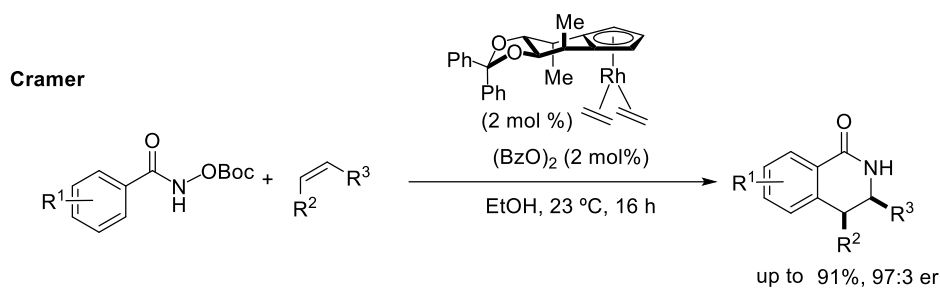


Figure 2. Application of chiral Cp ligands for asymmetric C–H functionalization

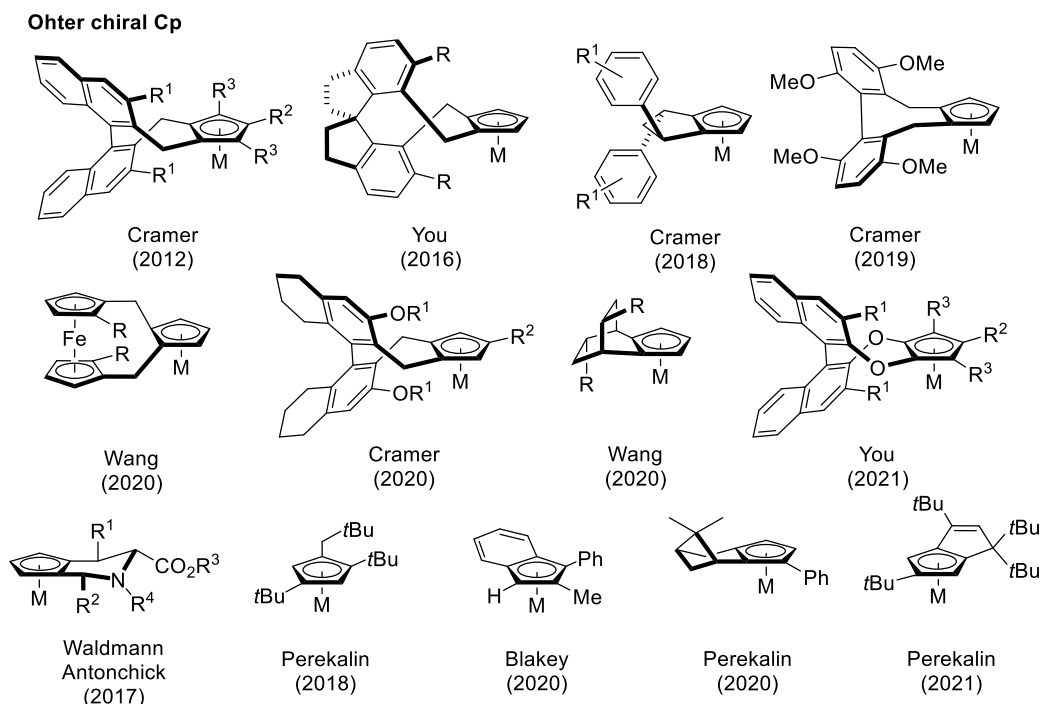
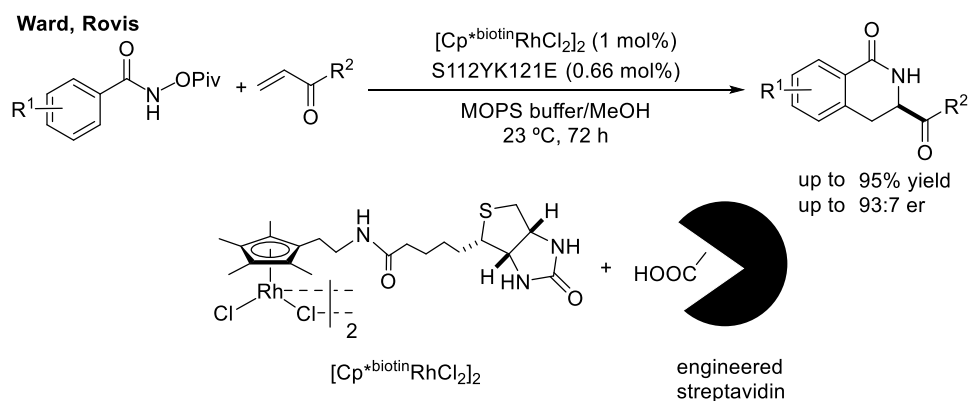


Figure 3. Examples of chiral Cps

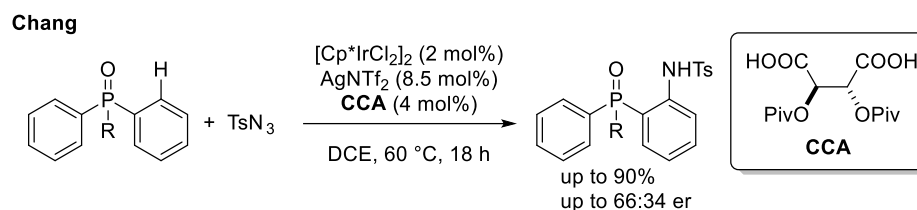
In connection with the chiral Cp strategy, Rovis, Ward, and co-workers reported that a CpRh(III) complex tethered to biotin, in combination with streptavidin, enabled asymmetric C–H alkylation (**Scheme 1**).⁶ This work represents the first example of enantioselective C–H functionalization achieved using a chiral environment within a protein scaffold.



Scheme 1. Asymmetric C–H functionalization using metalloenzyme

Chiral carboxylic acid method

Another approach to asymmetric C–H functionalization is the use of a chiral carboxylic acid additive.⁷ In 2015, Chang and co-workers reported that a Cp*Ir(III) catalyst with a chiral carboxylic acid derived from tartaric acid enabled asymmetric C–H amidation, although the enantioselectivity achieved was relatively low (**Scheme 2**).⁸



Scheme 2. Asymmetric C–H amidation with chiral carboxylic acid

A proposed mechanism for the enantioselective C–H functionalization using a chiral carboxylic acid is shown in **Figure 4**. As mentioned above, C–H activation using Cp*M(III) proceeds via a CMD mechanism, in which a hydrogen is abstracted by a carboxylate as a proton.¹ A chiral carboxylic acid recognizes one of the enantiotopic C–H bonds on a substrate and activates it, leading to the formation of a chiral metallacycle. This pioneering example demonstrated that a carboxylate could participate in the enantioselective step, inspiring the further development of more effective chiral carboxylate ligands.

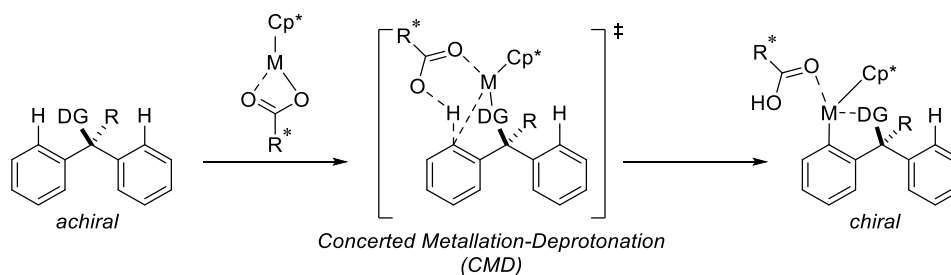


Figure 4. Desymmetrization with chiral carboxylic acid

Following the Chang's report, several research groups, including our own, have developed a variety of chiral carboxylic acids featuring binaphthyl,⁹ amino acid,¹⁰ and ferrocene frameworks,¹¹ and have applied them to asymmetric C–H functionalization (**Figure 5**).^{12–15} Despite these advances, this methodology still has considerable room for further development, particularly in terms of improving enantioselectivity and expanding substrate generality.

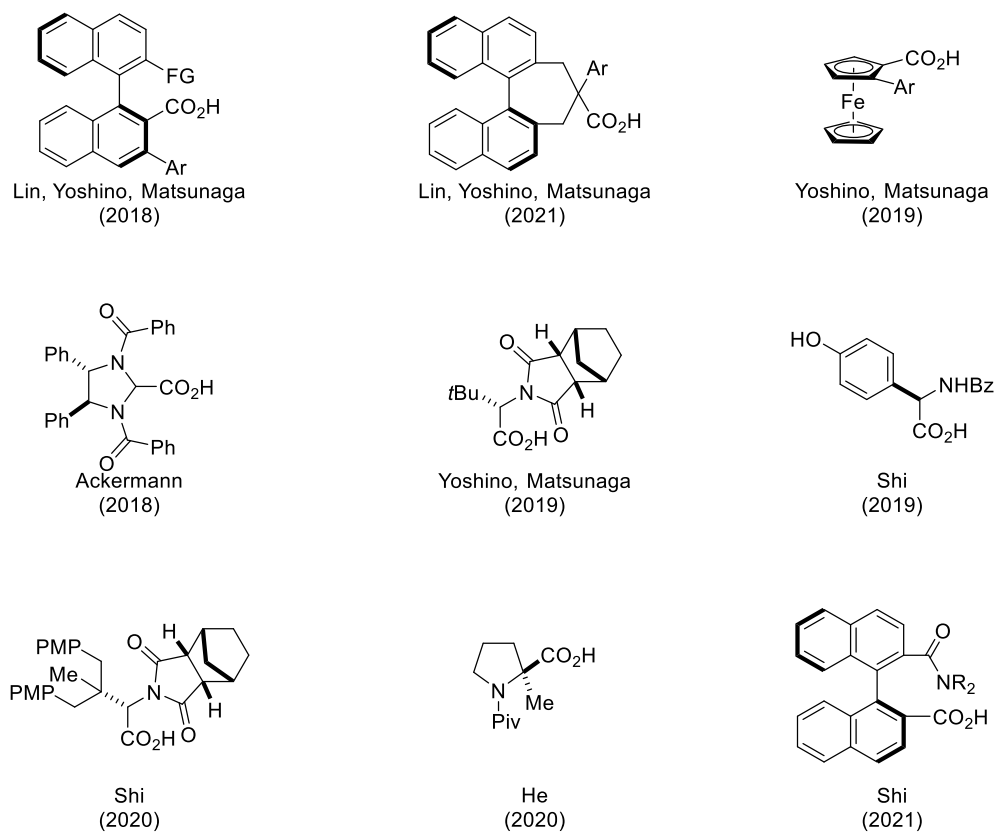


Figure 5. Examples of chiral carboxylic acids

Benzothiazine-1-oxide and benzothiadiazine-1-oxide as target molecules in C–H functionalization

Benzothiazine-1-oxide and benzothiadiazine-1-oxide derivatives bearing a chiral center at sulfur are known as pharmaceutical candidates, including analogs of Prazosin and partial agonists for benzodiazepine receptors (**Figure 6**).¹⁶ These structures can be synthesized through the C–H functionalization of sulfoximines mediated by transition-metal catalysts.

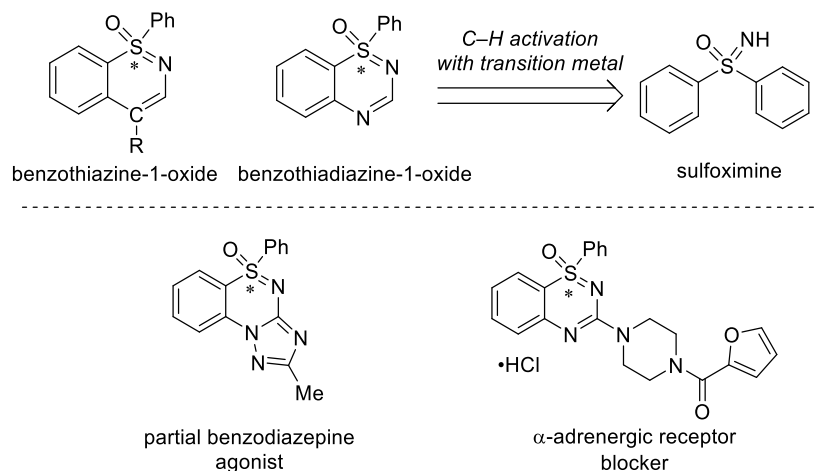
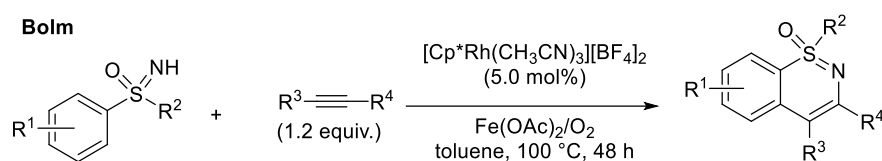


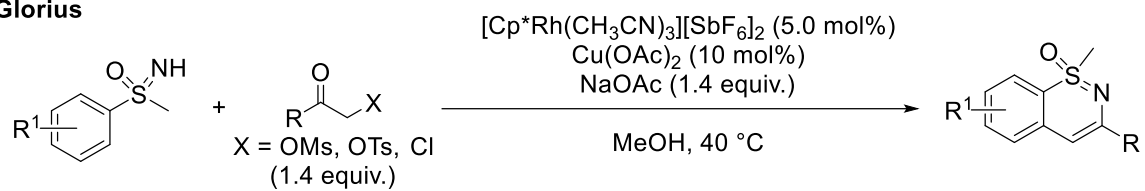
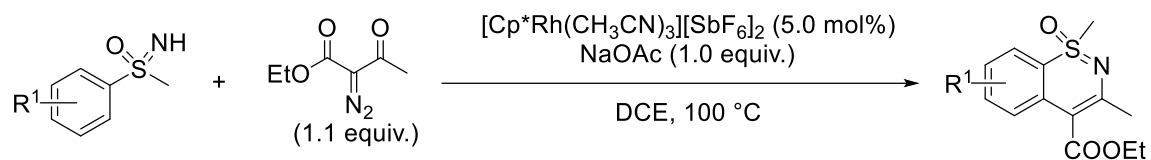
Figure 6. Utility of benzothiazine-1-oxides and benzothiadiazine-1-oxides in medicinal chemistry

In 2013, Bolm and co-workers reported that C–C bond formation via C–H activation using a $\text{Cp}^*\text{Rh(III)}$ catalyst followed by an intramolecular cyclization afforded benzothiazine-1-oxides from sulfoximines (**Scheme 3**).¹⁷ This example demonstrated that C–H functionalization followed by cyclization and dehydration enables access to such valuable compounds and stimulated further exploration toward asymmetric synthesis.

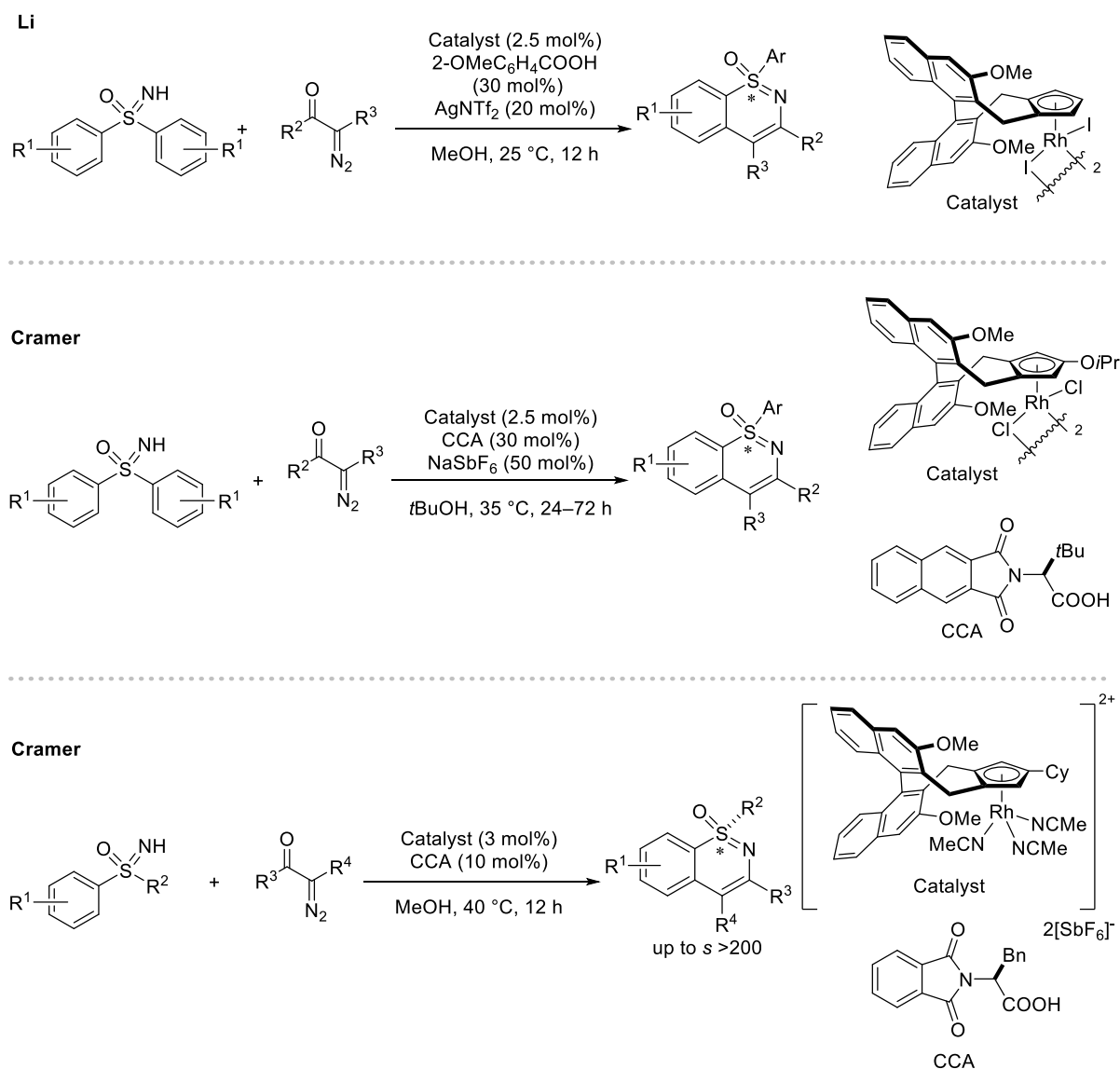


Scheme 3. First report of benzothiazine-1-oxide synthesis via C–H activation of sulfoximines

Following this work, several groups have achieved racemic synthesis of benzothiazine-1-oxides using various catalysts and reagents (**Scheme 4**).¹⁸ Glorius and co-workers demonstrated that $\text{Cp}^*\text{Rh(III)}$ enabled synthesis of benzothiazine-1-oxide via C–H alkylation of sulfoximines using acyloin derivatives (**Scheme 4**, top).¹⁹ Bolm and co-workers reported that C–H alkylation of sulfoximines using α -diazo dicarbonyl compounds gave benzothiazine-1-oxide with high yield (**Scheme 4**, bottom).²⁰

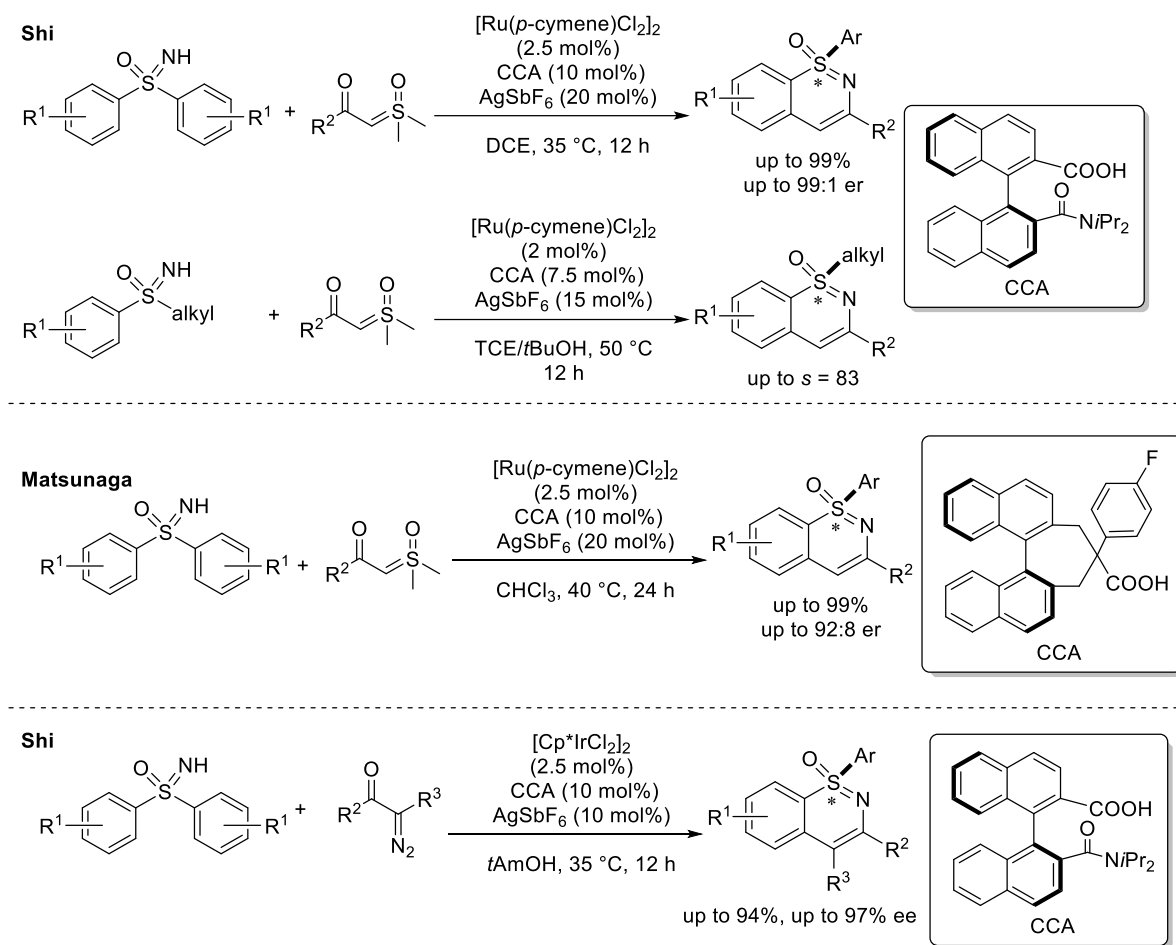
Glorius**Bolm****Scheme 4.** Examples of synthesis of benzothiazine-1-oxide via C–H activation

The first examples of the asymmetric variant were reported by Li's group and Cramer's group independently, who employed chiral CpRh(III) catalysts (**Scheme 5**). Desymmetrization of diaryl sulfoximines using these chiral CpRh catalysts followed by intramolecular cyclization afforded benzothiazine-1-oxides with excellent enantioselectivity.^{21,22} Notably, a chiral carboxylic acid was used as auxiliary of asymmetric reaction in Cramer's report. In 2019, Cramer and co-workers further applied chiral CpRh catalyst with assistance of a chiral carboxylic acid to kinetic resolution, providing enantio-enriched benzothiazine-1-oxide derivatives bearing alkyl and aryl substituents with high *s* values.²³



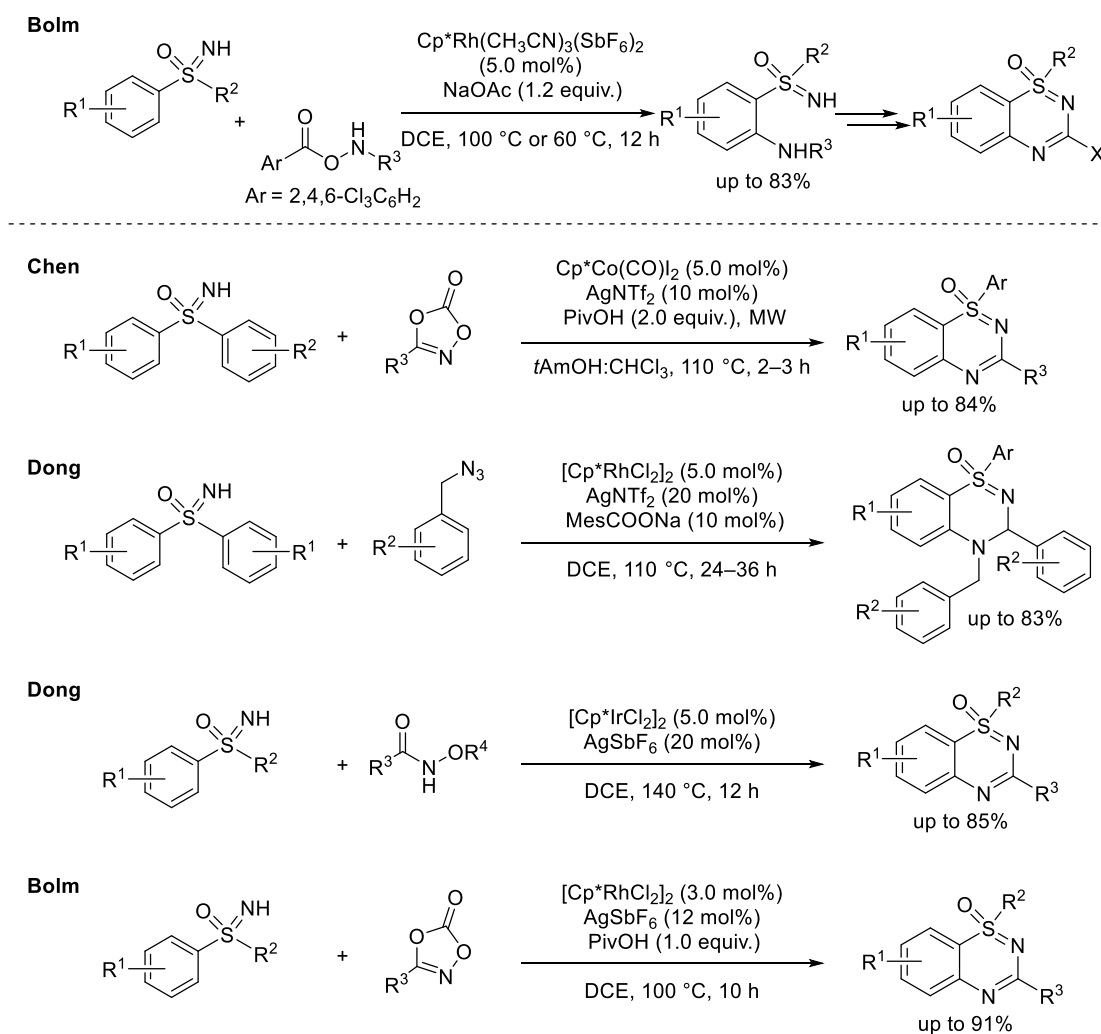
Scheme 5. Asymmetric synthesis of benzothiazine-1-oxides using chiral CpRh(III)

As additional examples, Shi and co-workers demonstrated that the combination of $[(p\text{-cymene})\text{RuCl}_2]_2$ and chiral carboxylic acids bearing amide moieties enabled the asymmetric synthesis of benzothiazine-1-oxides via both desymmetrization of diaryl sulfoximines and kinetic resolution of aryl-alkyl sulfoximines (**Scheme 6**, above).¹⁴ Shortly after the publication of Shi's work, our group discovered that a pseudo- C_2 -symmetric chiral carboxylic acid was also effective for the asymmetric synthesis of benzothiazine-1-oxides (**Scheme 6**, middle).²⁴ Asymmetric synthesis of benzothiazine-1-oxides was also enabled by the combination of $\text{Cp}^*\text{Ir(III)}$ and a chiral carboxylic acid reported by Shi and co-workers (**Scheme 6**, bottom).²⁵



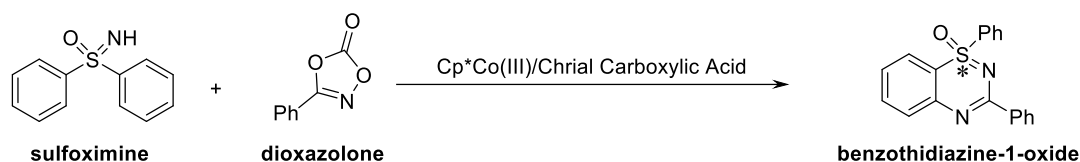
Scheme 6. Asymmetric synthesis of benzothiazine-1-oxides using chiral carboxylic acids

On the other hand, benzothiadiazine-1-oxides, which bear two nitrogen atoms within the heterocycle, can also be synthesized via C–H amination of sulfoximines under high-valent transition-metal catalysis. Bolm and co-workers reported that a Cp*Rh(III) catalyst enabled the C–H amination of aryl sulfoximines followed by additional transformations to afford benzothiadiazine-1-oxides (**Scheme 7**).²⁶ One-step construction of benzothiadiazine-1-oxides via C–H amidation was pioneered by Chen and co-workers using a Cp*Co(III) catalyst and dioxazolones as amidating agents.²⁷ Dong and co-workers subsequently reported the synthesis of benzodihydrothiadiazine-1-oxides via Cp*Rh(III)-catalyzed C–H amidation, as well as the synthesis of benzothiadiazine-1-oxides using a Cp*Ir(III) catalyst.²⁸ In the latter report, C–H amidation of alkyl–aryl sulfoximines was achieved, although the yield remained low.²⁹ However, these Cp*Co(III) and Cp*Ir(III) catalytic systems were applicable mainly to diaryl sulfoximines because hydrolysis of alkyl–aryl sulfoximines to sulfones easily proceeded, which would be due to the high Lewis acidity of the Co and Ir centers. In 2020, Bolm and co-workers reported that a Cp*Rh(III) catalyst, featuring a lower Lewis acidity, enabled the C–H amidation of alkyl–aryl sulfoximines using dioxazolones as amidating agents.³⁰



Scheme 7. Racemic synthesis of benzothiadiazine-1-oxides using CpM(III) catalysts

While CpM(III)-catalyzed synthesis of benzothiadiazine-1-oxides has been reported as discussed above, catalytic asymmetric synthesis of benzothiadiazine-1-oxides with controlling the stereogenic sulfur center has not yet been realized. Therefore, the author sought to apply a chiral carboxylic acid (CCA)/CpM(III) hybrid catalytic system to the enantioselective synthesis of benzothiadiazine-1-oxides (**Scheme 8**). Herein, the author reports the first catalytic enantioselective synthesis of benzothiadiazine-1-oxide derivatives via Cp*Co(III)-catalyzed C–H amidation enabled by a chiral carboxylic acid. After my report, Shi and co-workers achieved similar asymmetric synthesis of benzothiadiazine-1-oxide.³¹

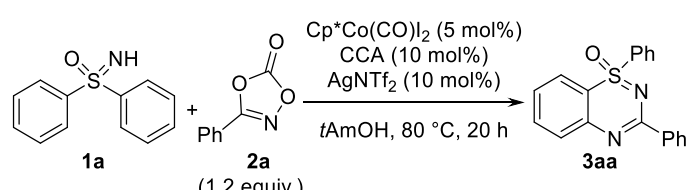


Scheme 8. My work: Asymmetric synthesis of benzothiadiazine-1-oxides using Cp*Co(III)/CCA

Section 2: Synthesis of H₈-BINOL-based chiral carboxylic acid and asymmetric synthesis of benzothiadiazine-1-oxide

Based on the reaction conditions for the racemic synthesis of benzothiadiazine-1-oxides reported by Chen and co-workers,²⁷ the initial trial was conducted using a Cp*Co(III) catalyst, diphenyl sulfoximine **1a**, dioxazolone **2a**, and a chiral carboxylic acid (CCA; **Table 1**). Among the carboxylic acids examined, CCA **4** derived from an amino acid,⁹ CCA **5** bearing a ferrocene framework,¹⁰ and the C₁-symmetric CCA **6**¹¹ exhibited moderate enantioselectivity (entries 1-3). In contrast, the use of pseudo-C₂-symmetric CCA **7a**¹² provided benzothiadiazine-1-oxide **3aa** with relatively high enantioselectivity (entry 4, 86:14 er).

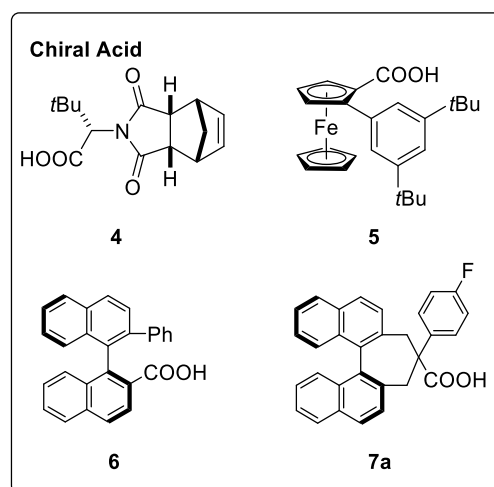
Table 1. Screening of CCAs with different frameworks



entry	CCA	% 3aa ^a	er ^b
1	4	73	34:66
2	5	80	71:29
3	6	39	59:41
4	7a	68	86:14

^aYields were determined by ¹H NMR of the crude mixture using 1,1,2,2-tetrachloroethane as the internal standard.

^bDetermined by chiral HPLC.



With the results of the initial screening of CCA in hand, structural modification of the chiral carboxylic acid was conducted (**Table 2**). CCA **7b**, bearing a phenyl group (entry 1), CCA **7c** with a *p*-chlorophenyl group (entry 2), and CCA **7d** with a *p*-methoxyphenyl group (entry 3) did not improve the enantioselectivity, although the yield of **3aa** increased. When CCA **7e** containing a 3,4,5-trifluorophenyl substituent was employed, the yield deteriorated compared with that obtained using CCA **7a** (entry 4). These results indicate that the electronic effects on the aryl substituent of the CCA do not significantly influence the enantioselectivity. In addition, the introduction of *tert*-butoxy groups at the 3,3'-positions of the binaphthyl backbone to modify the steric environment around the metal center also failed to improve the enantioselectivity (entry 5). Therefore, CCA **7a** bearing a *p*-fluorophenyl group was selected for further optimization of the reaction conditions.

Table 2. Tuning of pseudo- C_2 -symmetric CCA

entry	Chiral Acid	R ¹	R ²	% 3aa ^a	er ^b
0	7a	F	H	68	86:14
1	7b	H	H	77	83:17
2	7c	Cl	H	74	84:16
3	7d	OMe	H	83	84:16
4	7e	3,4,5-F ₃	H	31	86:14
5	7f	H	OtBu	75	84:16

CCA 7

^aYields were determined by ¹H NMR of the crude mixture using 1,1,2,2-tetrachloroethane as the internal standard.

^bDetermined by chiral HPLC.

The effects of solvents were examined using **CCA 7a** (Table 3). When the solvent was changed from *t*-AmOH to DCE, a halogenated solvent, almost racemic **3aa** was obtained in inferior yield (entry 1). The use of 1,4-dioxane also failed to improve the enantioselectivity, although the yield increased (entry 2). Since these screenings indicated that alcohols were more suitable solvents, MeOH, EtOH, *i*PrOH, and HFIP were subsequently evaluated (entries 3-6). As a result, the enantioselectivity was slightly improved; however, the yield decreased as the steric bulk of the alcohol decreased. This trend may be attributed to nucleophilic attack by a smaller alcohol on the dioxazolone, leading to its decomposition.

Table 3. Screening of solvents

entry	solvent	% 3aa ^a	er ^b
0	<i>t</i> AmOH	68	86:14
1	DCE	39	56:44
2	1,4-dioxane	83	83:17
3	MeOH	7	89:11
4	EtOH	39	88:12
5	<i>i</i> PrOH	62	86:14
6	HFIP	49	78:22

CCA 7a

^aYields were determined by ¹H NMR of the crude mixture using 1,1,2,2-tetrachloroethane as the internal standard.

^bDetermined by chiral HPLC.

With the optimal solvent identified, I next investigated the effect of reaction temperature (**Table 4**). When the reaction was conducted at 40 °C, the corresponding uncyclized product **8aa** was detected, and the enantioselectivities of the cyclized and uncyclized products were 90:10 er (19% yield) and 89:11 er (61% yield), respectively (entry 2). At 20 °C, only the uncyclized product was obtained, and its enantioselectivity was slightly improved (91:9 er), albeit that the yield decreased dramatically to 23% (entry 3).

Table 4. Screening of temperature

entry	temp. (°C)	% 3aa ^a	er ^b	% 8aa ^a	er ^b
0	80	68	86:14	N.D.	-
1	60	52	86:14	13	84:16
2	40	19	90:10	61	89:11
3	20	trace	-	23	91:9

^aYields were determined by ¹H NMR of the crude mixture using 1,1,2,2-tetrachloroethane as the internal standard.

^bDetermined by chiral HPLC.

CCA **7a**

On the basis of these results, I next examined the effects of silver salts (**Table 5**). Changing the additive from AgNTf₂ to AgSbF₆, AgOTf, AgBF₄, AgPF₆, or Ag₂CO₃ improved the enantioselectivity, with AgOTf providing a notable improvement in the yield (entries 1-5). When AgOTf was employed at 30 °C, the enantioselectivity increased slightly, although the product was obtained in a somewhat lower yield (entry 6).

Table 5. Screening of silver salts

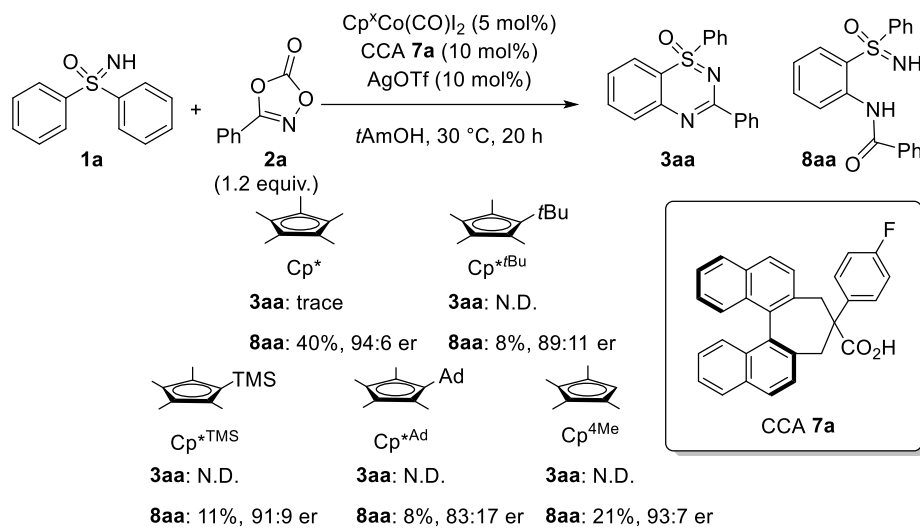
entry	Ag salts	% 3aa ^a	er	% 8aa ^b	er
0	AgNTf ₂	19	90:10	61	89:11
1	AgSbF ₆	3	90:10	49	90:10
2	AgOTf	15	93:7	50	93:7
3	AgBF ₄	10	93:7	50	93:7
4	AgPF ₆	trace	92:8	21	92:8
5 ^c	Ag ₂ CO ₃	N.D.	-	1	-
6 ^d	AgOTf	trace	-	40%	94:6

^aYields were determined by ¹H NMR of the crude mixture using 1,1,2,2-tetrachloroethane as the internal standard.

^bDetermined by chiral HPLC. ^c5.0 mol% ^dTemperature was 30 °C.

CCA **7a**

Substituents on the Cp ligand of the cobalt catalyst had an impact on both the enantioselectivity and the yield; however, despite screening a variety of substituted Cp ligands, the Cp* ligand used in the initial studies proved to be the most effective (**Scheme 9**).



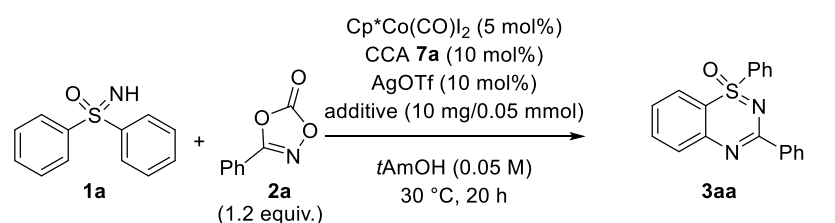
^aYields were determined by ¹H NMR of the crude mixture using 1,1,2,2-tetrachloroethane as the internal standard.

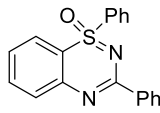
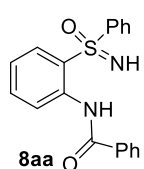
^bDetermined by chiral HPLC.

Scheme 9. Screening of Cp ligands^{a,b}

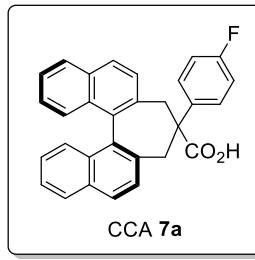
Despite extensive optimization of the reaction conditions, the desired product could not be obtained in a satisfactory yield. The uncyclized product (**8aa**), which was formed as the major product, contains both an imine and an amide functional groups, allowing for the bidentate coordination to the Cp*Co(III) center. This coordination mode was presumed to inhibit the catalytic turnover. Therefore, promotion of the cyclization of **8aa** to **3aa** was expected to improve the product yield, since the cyclized product **3aa** lacks a moiety capable of bidentate coordination. In this reaction, **3aa** is generated through nucleophilic attack of the imino nitrogen to the carbonyl group of the introduced amide, followed by dehydration to afford the cyclized product **3aa**. To facilitate this cyclization step, molecular sieves were examined as desiccants to promote dehydration (**Table 6**). The addition of molecular sieves proved effective in enhancing the product yield, with MS 5Å showing the best performance (entry 2). However, varying the amount of MS (entries 3,4) or extending the reaction time did not significantly affect the combined yield of **3aa** and **8aa** (entry 5).

Table 6. Screening of additives



entry	additive	% 3aa ^a	er ^b	% 8aa ^a	er ^b
0	-	trace	-	40	94:6
1	MS 4A	trace	-	53	93:7
2	MS 5A	8	93:7	68	93:7
3 ^c	MS 5A	6	93:7	62	93:7
4 ^d	MS 5A	8	93:7	63	93:7
5 ^e	MS 5A	25	92:8	51	91:9

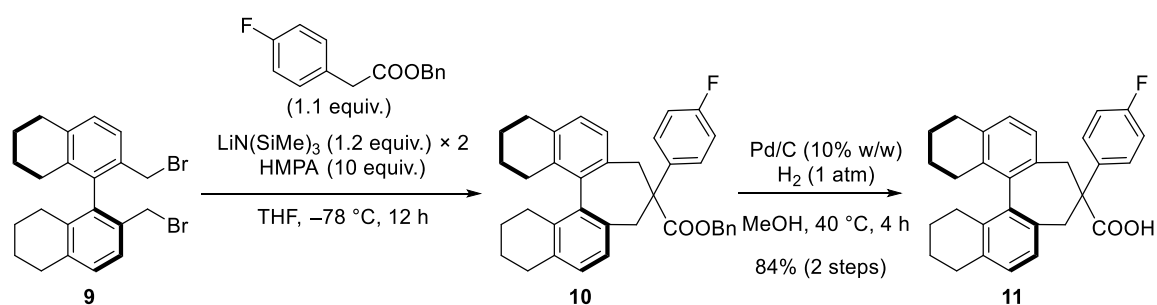


CCA 7a

^aYields were determined by ¹H NMR of the crude mixture using 1,1,2,2-tetrachloroethane as the internal standard.

^bDetermined by chiral HPLC. ^cMS (5 mg/0.05 mmol) was added. ^dMS (20 mg/0.05 mmol) was added. ^eReaction time was 72 h.

As further fine-tuning of the chiral carboxylic acids was required to improve the enantioselectivity, an H8-BINOL-type pseudo-*C*₂-symmetric CCA designed to adjust the dihedral angle of the biaryl framework was prepared (**Scheme 10**). Based on the synthetic route for **CCA 7a**, the target **CCA 11** was successfully synthesized from the reported dibromide **9**³² in 84% yield over two steps.



Scheme 10. Synthetic route of a new H₈-BINOL CCA **11**

Using **CCA 11** for the asymmetric synthesis of **3aa** and **8aa** resulted in a slight improvement in the enantioselectivity (96:4 er and 95:5 er, respectively), while the yields were maintained (**Table 7**, entry 1). Increasing the catalyst loading of Cp*Co(III) to 10 mol% improved the combined yield of **3aa** and **8aa** to 72% (entry 2). Furthermore, examinations of equivalent of sulfoximine and dioxazolone (entries 2,3) revealed that reversing the equivalents of sulfoximine and dioxazolone provided the products with the highest yield (75%, entry 4). The detail reason for higher selectivity using **CCA 11** is unclear, but the change of dihedral angle in biaryl moiety would be related.

Table 7. Asymmetric reaction with newly synthesized **CCA 11**

entry	Chiral Acid	X	Y	Z	% 3aa ^a	er ^b	% 8aa ^a	er ^b
0	7a	1.0	1.2	5.0	8	93:7	68	93:7
1	11	1.0	1.2	5.0	3	96:4	63	95:5
2	11	1.0	1.2	10	19	96:4	53	95:5
3	11	1.0	1.0	10	17	96:4	49	94:6
4	11	1.2	1.0	10	17	96:4	58	95:5

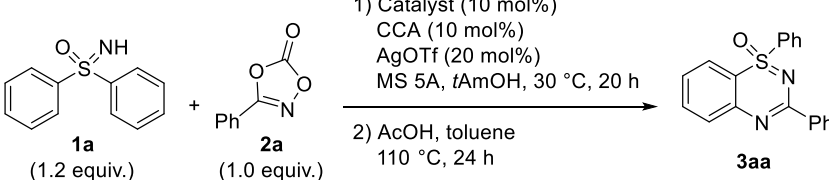
7a

11

^aYields were determined by ¹H NMR of the crude mixture using 1,1,2,2-tetrachloroethane as the internal standard. ^bDetermined by chiral HPLC.

To examine the effects of the chiral carboxylic acids and transition metal catalysts, several control experiments were performed (**Table 8**). Prior to these studies, it was confirmed that the cyclization of the uncyclized intermediate **8aa** was facilitated under acidic conditions at 110 °C following the asymmetric C–H amidation. The enantioselectivity of the cyclized product **3aa** is summarized in **Table 8** and the best condition are shown in entry 1. **CCA 4'**, **CCA 5**, **CCA 6**, and **CCA 7** bearing different structural motifs, showed lower selectivity and reactivity, even under the optimized conditions (entries 2–5). When $[\text{Cp}^*\text{Co}(\text{CH}_3\text{CN})_3][\text{SbF}_6]_2$ was used without any silver salt, the yield decreased dramatically (entry 6). The reaction temperature also had a significant impact on both yield and enantioselectivity: a lower temperature (10 °C) resulted in a poor yield, whereas a higher temperature (60 °C) led to a decrease in enantioselectivity (entries 7 and 8). Other metal catalysts, including $[\text{Cp}^*\text{RhCl}_2]_2$, $[\text{Cp}^*\text{IrCl}_2]_2$, and $[(p\text{-cymene})\text{RuCl}_2]_2$ were found to be less effective than $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ (entries 9–11).

Table 8. Control experiments in catalysts

				
entry	Catalyst	Chiral Acid	% 3aa ^a	er ^b
1	$\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$	11	94	96:4
2		4'	27	60:40
3		5	63	78:22
4		6	21	71:29
5		7a	94	94:6
6	$\text{Cp}^*\text{Co}(\text{CH}_3\text{CN})_3[\text{SbF}_6]_2$		20	95:5
7 ^c	$\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$		36	97:3
8 ^d			93	94:6
9 ^e	$[\text{Cp}^*\text{RhCl}_2]_2$		5	63:37
10 ^e	$[\text{Cp}^*\text{IrCl}_2]_2$		4	91:9
11 ^e	$[p\text{-cymene-RuCl}_2]_2$		6	88:12

^aYields were determined by ^1H NMR of the crude mixture using 1,1,2,2-tetrachloroethane as the internal standard.

^bDetermined by chiral HPLC. ^cReaction temp. was 10 °C. ^dReaction temp. was 60 °C. ^eCatalyst (5.0 mol%).

Determination of absolute configuration of **3aa**

X-ray single-crystal analysis of **3aa**, recrystallized from EtOAc/hexane, revealed that the absolute configuration of the major enantiomer is (*R*) (**Figure 7**). HPLC analysis of the XRD-authenticated sample of **3aa** further confirmed that this enantiomer corresponds to the major product of the asymmetric C–H amidation.

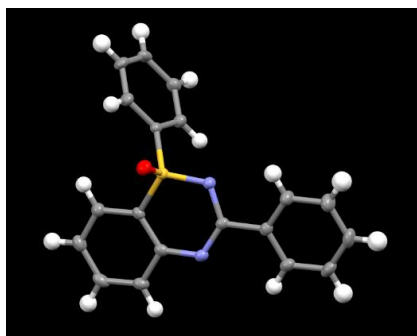
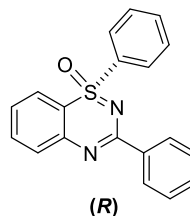


Figure 7. Crystal structure of **3aa**

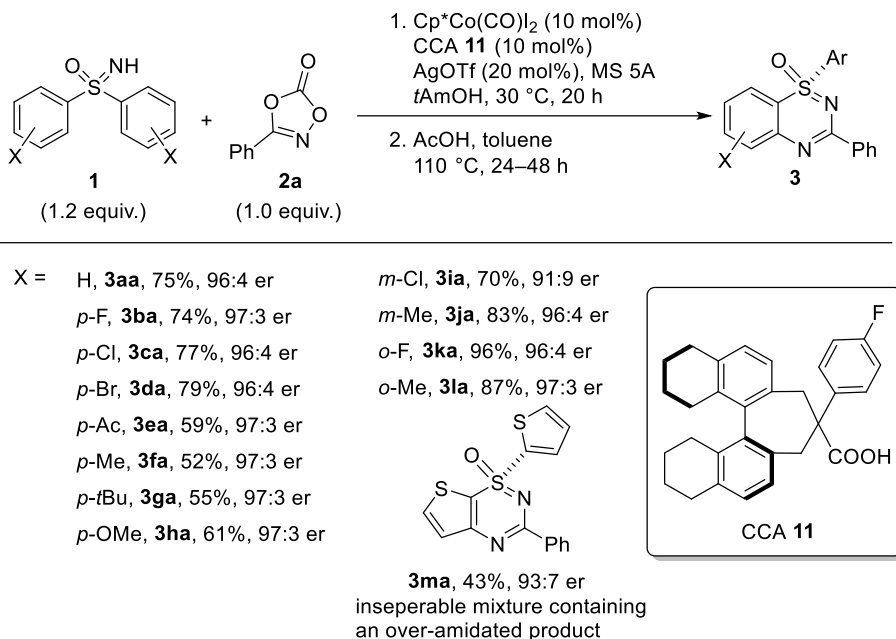


$R_1 = 0.0262$, $wR_2 = 0.0714$

Flack parameter 0.033(4)

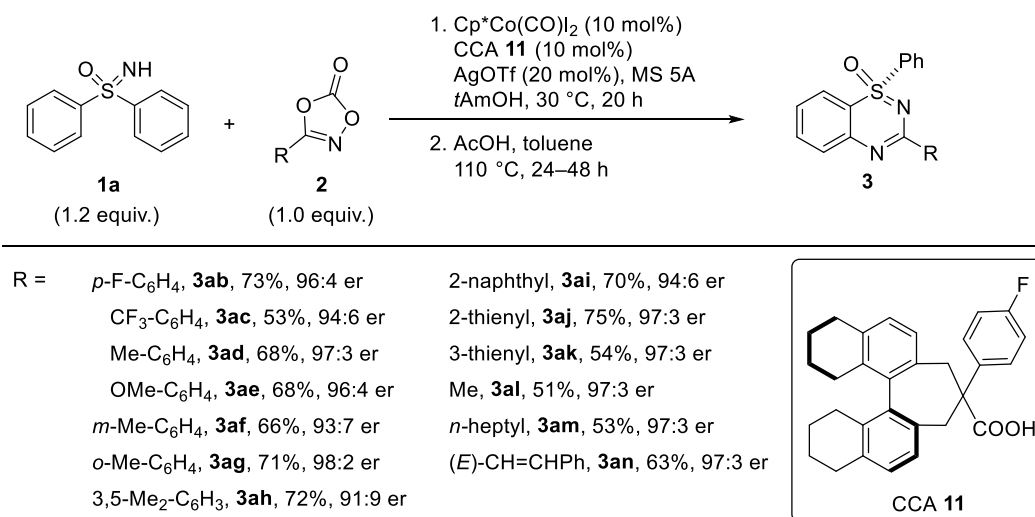
Substrate scope

The substrate scope of sulfoximines is shown in **Scheme 11**. Sulfoximine **1a** bearing phenyl groups afforded the desired product **3aa** in good yield and enantioselectivity (75%, 96:4 er). Substrates containing a *para*-fluoro (**1b**), *para*-chloro (**1c**), or *para*-bromo (**1d**) substituent on aryl groups were also compatible, providing the corresponding products **3ba**, **3ca**, and **3da** in satisfactory yields and enantioselectivities. The substrate with electro-withdrawing *para*-acetyl groups **1e** was tolerated, although the reactivity was slightly decreased (**3ea**). Sulfoximines with alkyl substituents such as Me and *t*-Bu at *para*-position (**1f** and **1g**) furnished the desired products in moderate yields and high enantioselectivities (**3fa** and **3ga**). The introduction of an electron-donating group was likewise unproblematic, delivering **3ha** in good selectivity. While a substrate bearing *meta*-chloro substituents exhibited reduced enantioselectivity (**3ia**), *meta*-methyl groups were well tolerated (**3ja**). *Ortho*-substituted substrates containing fluoro or methyl groups were also applicable and afforded the corresponding products with high selectivity (**3ka** and **3la**). A heteroaryl substrate bearing 2-thienyl groups provided **3ma** in 43% yield and 93:7 er, along with a small amount of an inseparable over-amidated byproduct.



Scheme 11. Substrate scope of sulfoximines

Next, the scope of dioxazolones was examined (Scheme 12). Various substituents on the aryl group were well tolerated, providing the desired products in good yields and high enantioselectivities (53–73%, 91:9–98:2 er), with the *ortho*-methyl-substituted dioxazolone giving particularly high selectivity (**3ag**, 98:2 er). Dioxazolones bearing alkyl groups such as methyl or heptyl also participated smoothly in the asymmetric C–H amidation, affording **3al** and **3am**, respectively. In addition, a cinnamyl-substituted dioxazolone was applicable, furnishing **3an**.



Scheme 12. Substrate scope of dioxazolones

Section 3: Mechanistic study

To investigate the origin of enantioselectivity, several mechanistic studies and DFT calculations were performed. The proposed reaction mechanism, based on the racemic reaction reported by Chen and co-workers in 2017,²⁶ is shown in **Figure 8**. The reaction is initiated by coordination of sulfoximine **1** to the Cp*Co(III)/CCA complex to form intermediate **A**. Enantioselective C–H bond cleavage then proceeds via a CMD pathway, in which the Cp*Co(III) catalyst and the chiral carboxylate cooperatively deprotonate the ortho C–H bond, generating cobaltacycle **B**. The protonated CCA is subsequently replaced by dioxazolone **2** to give intermediate **C**. Upon decomposition of **2** with release of CO₂, a nitrenoid species is formed, which undergoes C–N bond formation to produce intermediate **D**. After protonation of the amide moiety and replacement of the product with sulfoximine **1**, the Co catalyst is regenerated. The imine moiety of the directing group in the amidated sulfoximine attacks the intramolecular carbonyl group of the newly introduced amide, followed by dehydration to afford the cyclized product **3**.

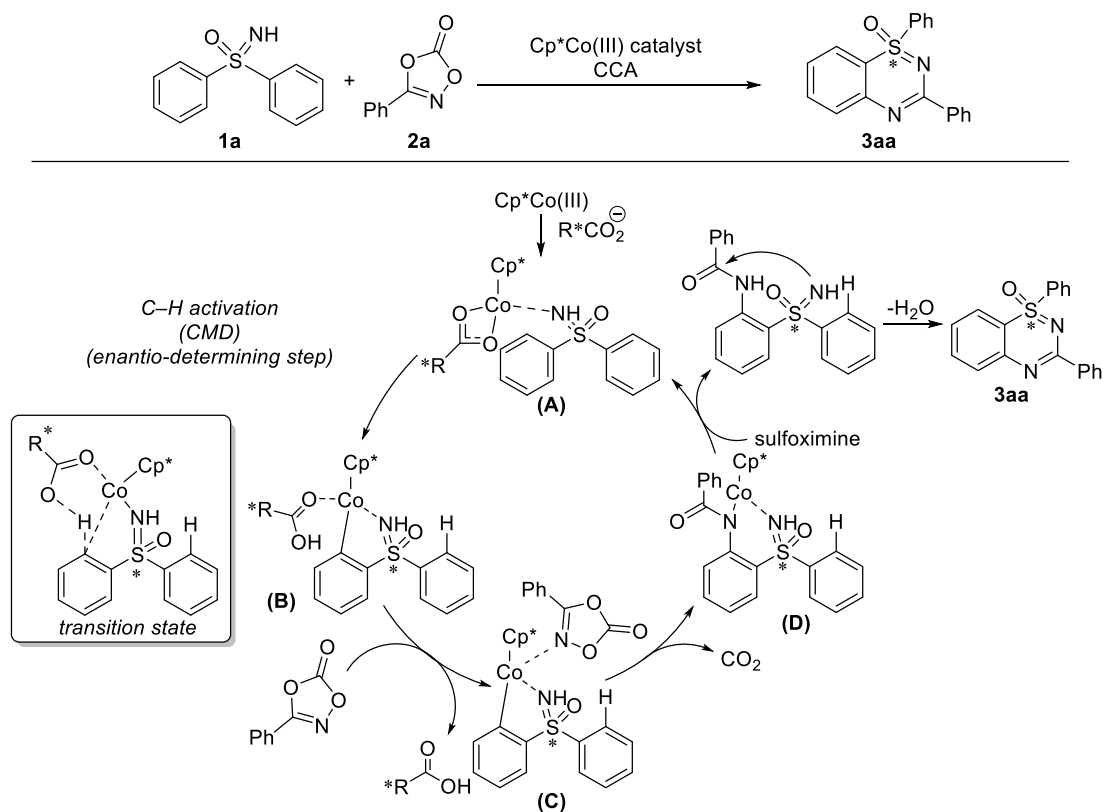
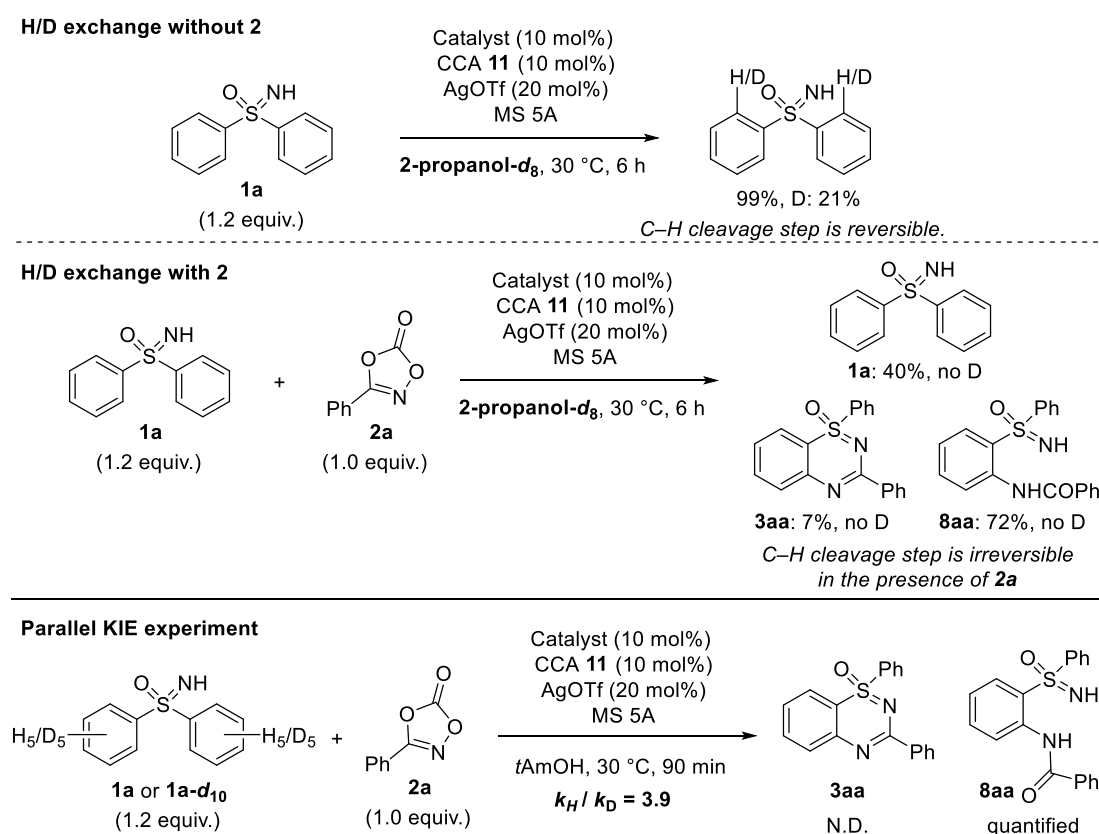


Figure 8. Proposed mechanism

To determine which steps are enantio-determining and rate-determining, H/D exchange experiments were first conducted (**Scheme 13**). For accessibility, 2-propanol- d_8 was used as both the solvent and deuterium source. In the absence of dioxazolone **2a** under the otherwise standard reaction conditions, 21% deuterium incorporation at the ortho-position of sulfoximine **1a** was observed, indicating that the C–H cleavage step is reversible. In contrast, when dioxazolone **2a** was present, sulfoximine **1a** (40%), cyclized product **3aa** (7%), and uncyclized intermediate **8aa** (72%) were obtained without any detectable deuteration. These results suggest that although the C–H activation step itself is reversible, the addition of **2a** renders this step virtually irreversible due to the much faster reaction between the cobaltacycle intermediate and **2a** than C–H activation.

To gain further insight into the reaction mechanism, a parallel KIE experiment was performed using **1a** and deuterated **1a- d_{10}** . A significant kinetic isotope effect ($k_H/k_D = 3.9$) was observed, indicating that the C–H cleavage step is the rate-determining step (**Figure 9, Table 9**). These findings indicate that results of H/D exchange and KIE experiments are consistent with the proposed mechanism which the enantio- and rate-determining step is C–H bond cleavage and CCA is involved in enantioselective C–H bond cleavage.



Scheme 13. H/D exchange experiments and KIE experiments

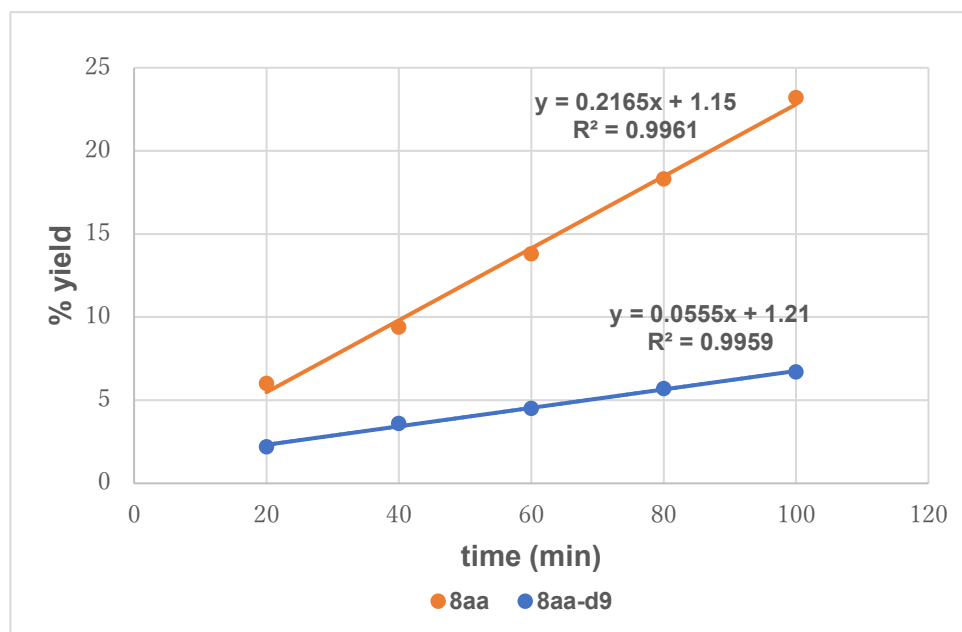


Figure 9. Plots of KIE experiments

Table 9. Summary of KIE experiments

	20 min	40 min	60 min	80 min	100 min
% 8aa	6.0	9.4	13.8	18.3	23.2
% 8aa-d9	2.2	3.6	4.5	5.7	6.7

DFT calculation of transition states

To clarify the origin of the high enantioselectivity observed with **CCA 11**, DFT calculations of the transition states were performed (for details of the computational procedures used to obtain the transition-state structures, see Experimental section). Considering mechanistic studies, C–H bond cleavage would be practically irreversible and enantio-determining step. Thus, free energies of transition states in C–H bond cleavage will be discussed. After conformational sampling using GFN1-xTB/CREST,^{33,34} the geometries of the transition states and their single-point energies were calculated at the M06/def2-TZVPP+SMD(*t*-BuOH)//M06L/def2-SVP³⁵⁻³⁸ level of theory. These calculations afforded one stable conformer corresponding to the major enantiomer (TS_{major}–(*R*)) and two stable conformers corresponding to the minor enantiomer (TS_{minor1}–(*S*) and TS_{minor2}–(*S*)) (**Figure 10**). Among these, TS_{major}–(*R*) was the most stable structure, while TS_{minor1}–(*S*) and TS_{minor2}–(*S*) were higher in energy by 2.3 kcal/mol and 2.2 kcal/mol, respectively. These results are consistent with experimental results. Visualization by non-covalent interaction (NCI) plots³⁹ indicated that a CH– π interaction between the aryl group of **CCA 11** and the phenyl substituent of the sulfoximine would play a key role in the high enantioselectivity. Furthermore, in subsequent investigations by our group, **CCA 11** was also found to be applicable to sulfondiimines, which are sulfoximine analogues bearing two imine groups.⁴⁰

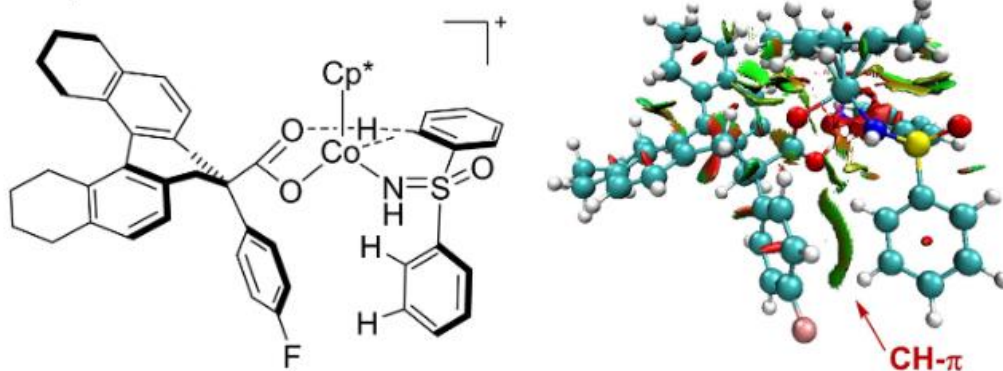
Short summary

I achieved asymmetric synthesis of benzothiadiazine-1-oxide by combination of Cp*Co(III) and newly synthesized chiral carboxylic acid with high enantioselectivity. The detailed mechanistic study demonstrated that C–H bond cleavage would be enantio- and rate-determining steps, and non-covalent interaction between CCA and the substrate would be important for high enantioselectivity.

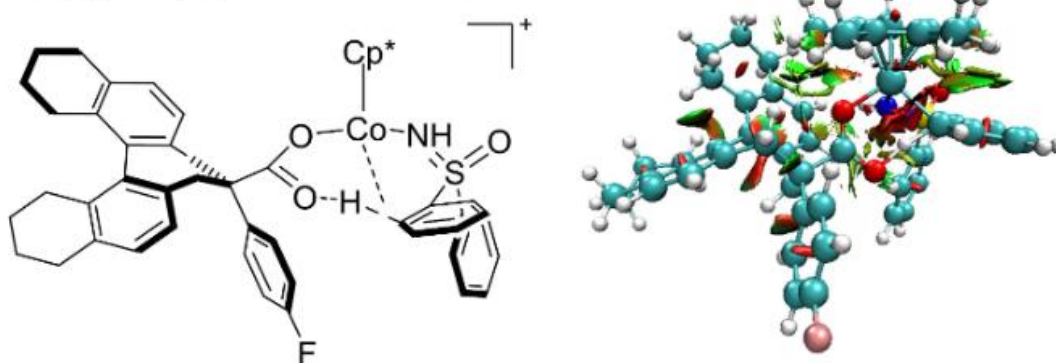
Publication

Hirata, Y.; Sekine, D.; Kato, Y.; Lin, L.; Yoshino, T.; Matsunaga, S. *Angew. Chem. Int. Ed.* **2022**, *61*, e202205341.

TS_{major} for (*R*)-enantiomer: $\Delta\Delta G^\ddagger = +0.0$ kcal/mol



TS_{minor1} for (*S*)-enantiomer: $\Delta\Delta G^\ddagger = +2.3$ kcal/mol



TS_{minor2} for (*S*)-enantiomer: $\Delta\Delta G^\ddagger = +2.2$ kcal/mol

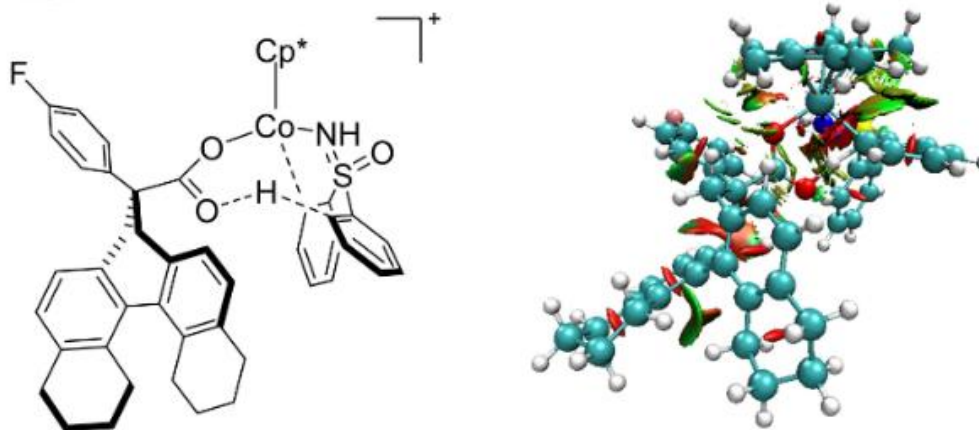


Figure 10. Structures and energies of TSs

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Experimental Section

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1. General

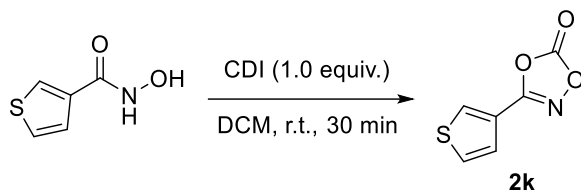
All non-aqueous reactions were carried out in a flame-dried glassware under argon atmosphere unless otherwise noted or in an argon-filled glove box. Enantioselectivities were determined by high performance liquid chromatography (HPLC) analysis using 4.6 mm × 25 cm Daicel Chiralpak columns. NMR spectra were recorded on JEOL JNM-ECS400 spectrometers operating at 391.78 MHz for ^1H NMR, 98.52 MHz for ^{13}C NMR and 368.59 Hz for ^{19}F NMR, JOEL JNM-ECX400 spectrometers operating at 395.88 MHz for ^1H NMR, 99.55 MHz for ^{13}C NMR and 372.48 MHz for ^{19}F NMR, JNM-ECA500 spectrometers operating at 500.16 MHz for ^1H NMR and 125.77 MHz for ^{13}C NMR, JOEL JNM-ECZ400 spectrometers operating at 399.78 MHz for ^1H NMR, 100.53 MHz for ^{13}C NMR and 368.61 MHz for ^{19}F NMR. Chemical shifts were reported in the scale relative to TMS (0.00 ppm for ^1H NMR in CDCl_3), CHCl_3 (7.26 ppm for ^1H NMR in CDCl_3), CDCl_3 (77.00 ppm for ^{13}C NMR in CDCl_3) and PhCF_3 (−63.72 ppm for ^{19}F NMR) as an internal reference, respectively. ESI mass spectra were measured on Thermo Scientific Exactive spectrometer. Optical rotations were measured on a JASCO P-1010 polarimeter. Column chromatography was performed with silica gel Kanto Silica gel 60 N (40-50 mesh), Yamazen YFLC AI-580 using Universal Column SiOH.

Materials: Dichloromethane (DCM) and toluene were purified by Glass Contour solvent purification system before use. Sulfoximines **1**,^[S1] dioxazolones **2**,^[S2] chiral carboxylic acids (**4–7**)^[S3a,S3b,S3c,S3d] and $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$ ^[S4] were synthesized according to the previously described methods. MS5A was preactivated by flame-drying under vacuum. All other reagents were commercially available and used as received unless otherwise noted.

2. Experimental procedures

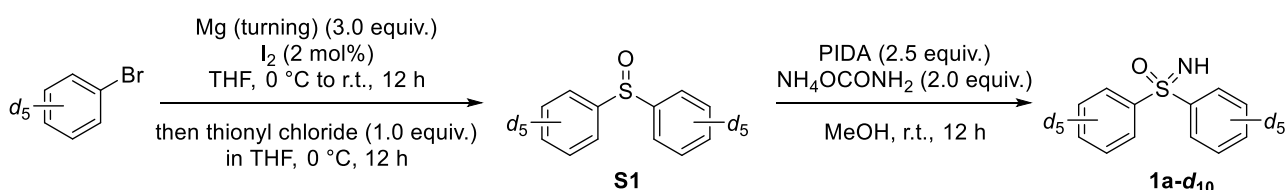
2-1. Preparation of substrates

Preparation of 3-(thiophen-3-yl)-1,4,2-dioxazol-5-one **2k**



To a solution of *N*-hydroxythiophene-3-carboxamide^[S2] (2.01 g, 14.0 mmol, 1.0 equiv.) in DCM (14 mL) was added 1,1'-carbonyldiimidazole (2.53 g, 14.0 mmol, 1.0 equiv.) at room temperature. After the mixture was stirred for 30 min, the reaction was quenched by adding aq. HCl and extracted with DCM (x 2). The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under vacuum. The residue was purified by recrystallization with hot hexane to give 3-(thiophen-3-yl)-1,4,2-dioxazol-5-one **2k** (405 mg, 2.4 mmol, 17%). **MP** 85.1-87.0 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.04 (1H, dd, *J* = 2.7, 1.1 Hz), 7.58-7.48 (2H, m). ¹³C NMR (CDCl₃, 100 MHz) δ 160.3, 153.6, 130.4, 128.6, 124.6, 121.0. **Rf** 0.19 (AcOEt/DCM = 2/1). We could not obtain high resolution MS peak due to the instability of **2k** under the most ionization conditions.

Preparation of deuterated sulfoximine **1a-d₁₀**^[S1]

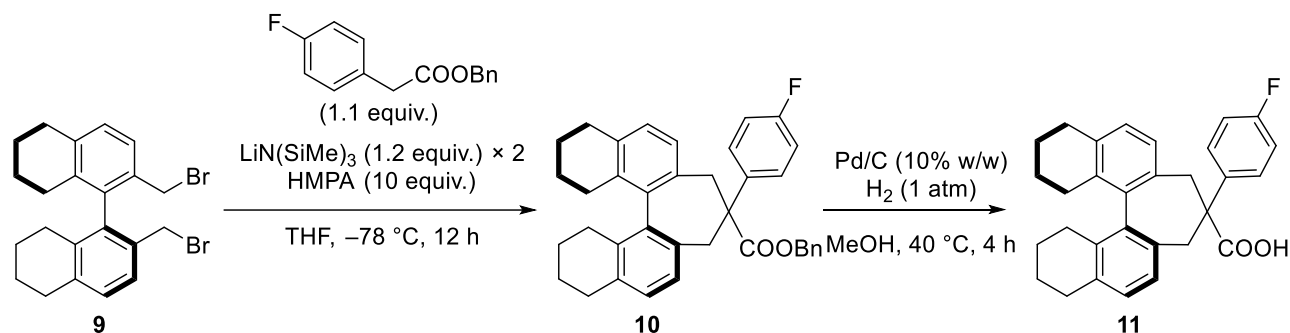


To a suspension of Mg turning (693 mg, 28.5 mmol, 3.0 equiv.) and I₂ (24 mg, 0.19 mmol, 2 mol%) in THF (38 mL) was added bromobenzene-*d*₅ (2 mL, 19.0 mmol, 2.0 equiv.) dropwise at 0 °C. The mixture was stirred at room temperature for 12 h. To the mixture was added thionyl chloride (665 μL, 9.5 mmol, 1.0 equiv.) in THF (19.0 mL) dropwise at 0 °C, and the mixture was further stirred for 12 h at room temperature. The mixture was quenched with brine and extracted with AcOEt three times. The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under vacuum. The residue was purified by silica gel column chromatography (DCM/AcOEt = 5/2) to give **S1** (1.13 g, 5.31 mmol, 56%) as a colorless solid. **MP** 64.0-65.2 °C. ¹³C NMR (CDCl₃, 100 MHz) δ 145.4, 130.4 (t, *J* = 24.6 Hz), 128.7 (t, *J* = 24.6 Hz), 124.3 (*J* = 25.0 Hz). **HRMS** (ESI): *m/z* calculated for C₁₂D₁₀O₄NaS⁺ [*M*+Na]⁺: 235.0972, found: 235.0965. **Rf** 0.58 (DCM/AcOEt = 5/2).

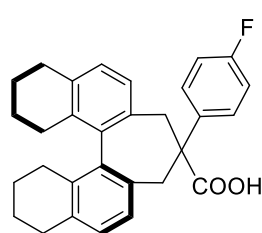
To a round bottom flask charged with **S1** (500 mg, 2.35 mmol, 1.0 equiv.), PIDA (1.90 g, 5.89 mmol, 2.5 equiv.), and ammonium carbamate (368 mg, 4.71 mmol, 2.0 equiv.) was added MeOH (11.8 mL) at room temperature. After the mixture was stirred at the same temperature for 12 h, the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (DCM/AcOEt = 5/2) to give **1a-d₁₀** (482 mg, 2.12 mmol, 90%) as a colorless solid. **MP** 94.2-96.1 °C. ¹³C NMR (CDCl₃, 100 MHz) δ 143.2, 132.0 (t, *J* = 25.0 Hz), 128.6 (t, *J* = 25.0 Hz), 127.5 (t, *J* = 25.0 Hz). **HRMS** (ESI): *m/z* calculated for C₁₂HD₁₀ONNaS⁺ [*M*+Na]⁺: 250.1081,

found: 250.1075. **Rf** 0.48 (DCM/AcOEt = 5/2).

2-2. Preparation of CCA **11**^[S3]



4-(4-fluorophenyl)-4,5,8,9,10,11,12,13,14,15-decahydro-3H-cyclohepta[2,1-a:3,4-a']dinaphthalene-4-carboxylic acid (**11**)



To a solution of benzyl 2-(4-fluorophenyl)acetate^[S5] (179.8 mg, 0.74 mmol, 1.1 equiv.) and HMPA (1.16 mL, 6.69 mmol, 10 equiv.) in THF (21.3 mL) was added $\text{LiN}(\text{SiMe}_3)_2$ (1 M in THF, 804 μL , 0.80 mmol, 1.2 equiv.) dropwise at -78°C . After the mixture was stirred for 1.5 hours at the same temperature, the solution was warmed up to 0°C and stirred for further 1.5 hours. The reaction mixture was cooled to -78°C and stirred for 1 h. To the reaction mixture was added **9** (300 mg, 0.67 mmol, 1.0 equiv.) in THF (6 mL)

dropwise at -78°C . After 1.5 hours with stirring, the solution was warmed up to 0°C and stirred for 1.5 hours. The reaction mixture was again cooled to -78°C and stirred for 1 h. To the reaction mixture was added $\text{LiN}(\text{SiMe}_3)_2$ (1 M in THF, 804 μL , 0.80 mmol, 1.2 equiv.) dropwise at -78°C . The reaction mixture was stirred for 12 h at -78°C . The reaction was quenched by adding water at 0°C , and extracted with AcOEt three times. The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and evaporated under vacuum. The residue was purified by silica gel column chromatography (hexane/AcOEt = 9/1) to give **10** as a colorless solid (331 mg, ca. 0.62 mmol) with contaminated some impurities, which was used for the next step without further purification.

A mixture of **S3** (331 mg, 0.62 mmol) and Pd/C (10% w/w, 33.1 mg) in MeOH (6.2 mL) was stirred under H_2 (1 atm) at 40°C for 4 hours. The reaction mixture was cooled to room temperature, filtered through a Celite® pad, and evaporated under vacuum. The residue was treated with KOH aq. and MeOH until the solution became transparent, and purified by reversed phase column chromatography (C18, $\text{H}_2\text{O}/\text{MeOH}$). After evaporation, the residue was treated with Et_2O and aq. HCl (1 M) and extracted with AcOEt three times. The combined organic layers were evaporated under reduced pressure. Further azeotropic dehydration with anhydrous toluene afforded **11** as a colorless solid (248 mg, 0.56 mmol, 84% in 2 steps). **MP** $195.0\text{--}198.8^\circ\text{C}$. **^1H NMR** (CDCl_3 , 400 MHz) δ 7.35–7.31 (2H, m), 7.01 (1H, d, $J = 7.7$ Hz), 7.01–6.94 (3H, m), 6.79 (1H, d, $J = 7.7$ Hz), 6.54 (1H, d, $J = 7.5$ Hz), 3.36 (1H, d, $J = 12.8$ Hz), 2.98 (1H, d, $J = 13.7$ Hz), 2.89–2.61 (7H, m), 2.56 (1H, d, $J = 12.7$ Hz), 2.24–2.16 (2H, m), 1.83–1.72 (6H, m), 1.65–1.50 (2H, m). **^{13}C {**1H**, **19F**} NMR** (CDCl_3 , 100 MHz) δ 180.9, 161.8, 137.9, 137.9, 136.6, 136.5, 136.2, 135.6, 135.5, 133.3, 132.4, 128.6, 128.0, 127.5, 126.4, 126.0, 115.1, 59.3, 40.0, 38.3, 29.5, 29.4, 27.7, 22.9, 22.8. **^{19}F NMR** (CDCl_3 , 369 MHz) [$\text{C}_6\text{H}_5\text{CF}_3$ (–63.70 ppm) as an internal standard] δ –116.54––116.61 (m). **HRMS** (ESI): m/z calculated for $\text{C}_{30}\text{H}_{29}\text{FO}_2^-$ [$\text{M}-\text{H}$] $^-$: 439.2079, found: 439.2074. **$[\alpha]_D^{23.4}$** = –161.5 ($c = 0.27$, CHCl_3). **Rf** 0.19 (hexane/AcOEt = 1/1).

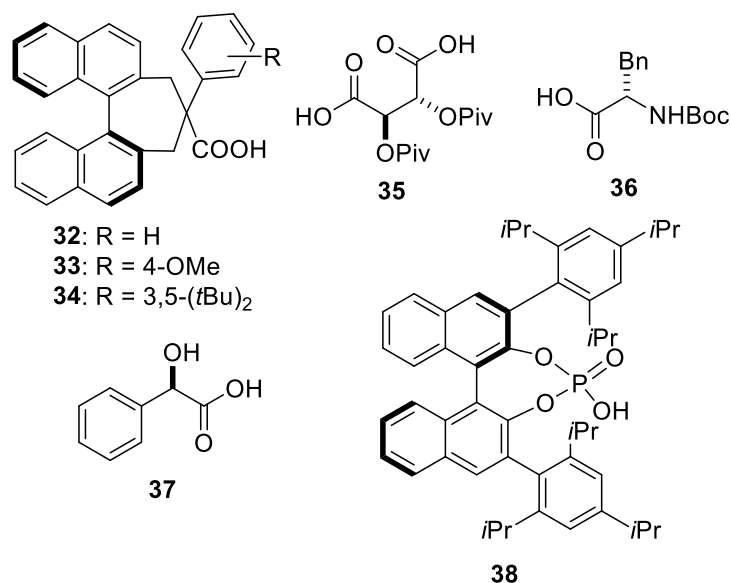
2-3. Investigation of other chiral acids and reaction conditions

Table S1. Effects of other chiral acids and reaction conditions.

(1) $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$ (10 mol %)
CCA (10 mol %)
MS5A, solvent
30 °C, 20 h

(2) AcOH, toluene
110 °C, 24 h

Entry	CCA	Solvent	% 3aa ^a	er ^b
1	32	<i>t</i> AmOH	47	93:7
2	33	<i>t</i> AmOH	62	92:8
3	34	<i>t</i> AmOH	18	76:24
4	35	<i>t</i> AmOH	25	71:29
5	36	<i>t</i> AmOH	27	40:60
6	37	<i>t</i> AmOH	N.D.	-
7	38	<i>t</i> AmOH	N.D.	-
8	11	<i>t</i> AmOH/ CHCl_3 = 1/1	78	92:8
9	11	CHCl_3	24	68:32
10	11	<i>i</i> PrOH	49	89:11
11	11	EtOH	27	88:12
12 ^c	11	<i>t</i> AmOH	49	92:8



^aDetermined by ¹H NMR analysis of the crude mixture using 1,1,2,2-tetrachloroethane as the internal standard. ^bDetermined by chiral HPLC analysis. ^cWithout MS5A.

2-4. Cobalt(III)/chiral carboxylic acid-catalyzed enantioselective C(sp²)-H amidation of sulfoximines

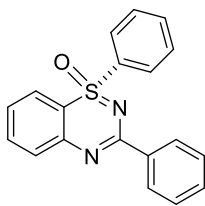
General Procedure A1

In an argon-filled glovebox, a screw-cap test tube was charged with Cp*Co(CO)I₂ (9.5 mg, 0.02 mmol, 10 mol %), AgOTf (10.3 mg, 0.04 mmol, 20 mol %), chiral acid **CCA 11** (8.8 mg, 0.02 mmol, 10 mol %) and *t*AmOH (4 mL). After the mixture was stirred for 10 min, MS5A (40 mg), sulfoximine **1** (0.24 mmol, 1.2 equiv.), and dioxazolone **2** (0.20 mmol, 1.0 equiv.) were successively added. The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 20 h at 30 °C. The reaction mixture was quenched by adding K₂CO₃ (27.6 mg, 0.20 mmol, 1.0 equiv.) and MeOH (500 µL) to decompose the remaining dioxazolone **2**. After stirred for 30 min, sat. EDTA aq. was added, and the mixture was extracted with AcOEt twice. The organic layers were combined, dried over Na₂SO₄, and evaporated under reduced pressure. A screw-cap test tube was charged with the crude mixture, AcOH (114 µL, 2 mmol, 10 equiv.), and toluene (4 mL). The mixture was stirred at 110 °C until the amidated intermediate **8** was consumed (checked by TLC analysis; 24–48 h). The reaction mixture was filtered through a short pad of silica gel, eluted with AcOEt, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (DCM/acetone) to afford **3**.

General Procedure A2

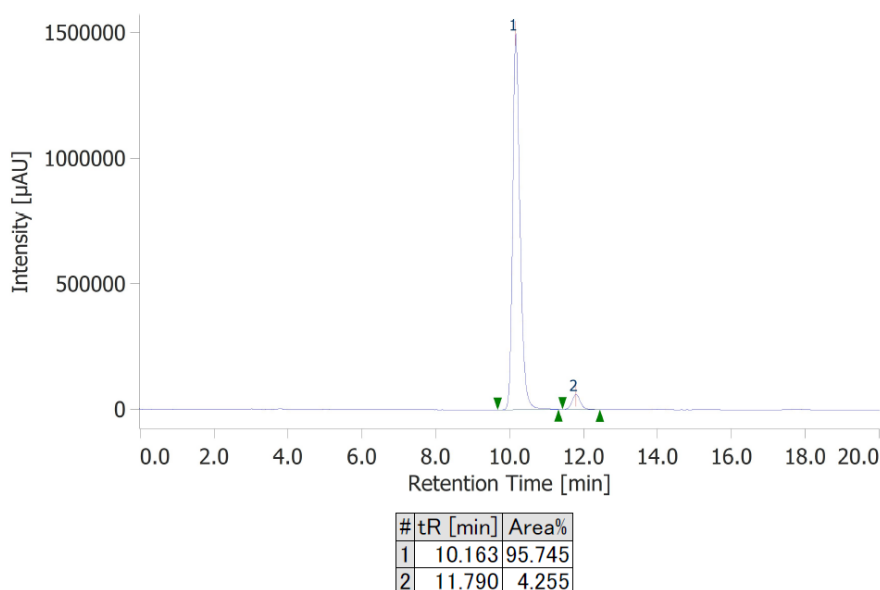
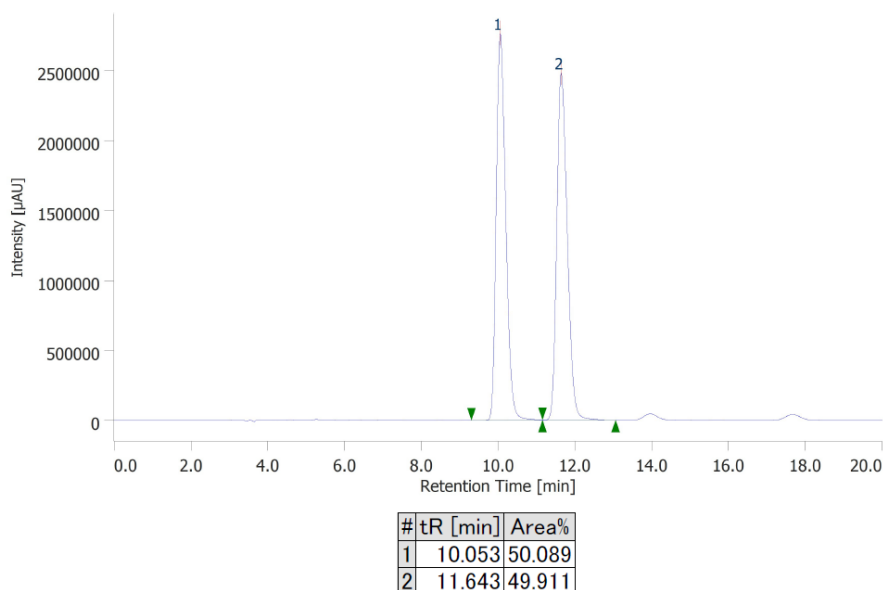
In an argon-filled glovebox, a screw-cap test tube was charged with Cp*Co(CO)I₂ (9.5 mg, 0.02 mmol, 10 mol %), AgOTf (10.3 mg, 0.04 mmol, 20 mol %), chiral acid **CCA 11** (8.8 mg, 0.02 mmol, 10 mol %) and *t*AmOH (2 mL). After the mixture was stirred for 10 min, MS5A (40 mg), sulfoximine **1** (0.24 mmol, 1.2 equiv.), and dioxazolone **2** (0.20 mmol, 1.0 equiv.) in *t*AmOH (2 mL) were successively added. The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 20 h at 30 °C. The reaction mixture was quenched by adding K₂CO₃ (1.0 equiv) and MeOH (500 µL) to decompose the remaining dioxazolone **2**. After stirred for 30 min, sat. EDTA aq. was added, and the mixture was extracted with AcOEt twice. The organic layers were combined, dried over Na₂SO₄, and evaporated under reduced pressure. A screw-cap test tube was charged with the crude mixture, AcOH (114 µL, 2 mmol, 10 equiv.), and toluene (4 mL). The mixture was stirred at 110 °C until the amidated intermediate **8** was consumed (checked by TLC analysis; 24–48 h). The reaction mixture was filtered through a short pad of silica gel, eluted with AcOEt, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (DCM/acetone) to afford **3**.

1,3-diphenylbenzo[e][1,2,4]thiadiazine 1-oxide (3aa)

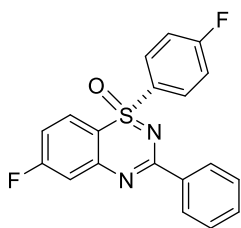


General Procedure A1 using iminodiphenyl- λ^6 -sulfanone **1a** (52.1 mg, 0.24 mmol) and 3-phenyl-1,4,2-dioxazol-5-one **2a** (32.2 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 40/1) afforded **3aa** as a colorless solid (47.8 mg, 75%). **¹H NMR** (CDCl₃, 400 MHz) δ 8.46-8.40 (2H, m), 7.92-7.86 (2H, m), 7.70-7.60 (3H, m), 7.60-7.53 (2H, m), 7.48-7.42 (4H, m), 7.29-7.23 (1H, m). **¹³C NMR** (CDCl₃, 100 MHz) δ 158.0, 147.2, 140.6, 137.5, 134.3, 133.8, 130.9, 129.2, 128.6, 128.6, 128.6, 128.1, 126.2, 124.7, 113.7. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 10.2 (major) and 11.8 (minor) min. $[\alpha]_D^{22.8}$ = +191.7 (c = 1.08, CHCl₃). **Rf** 0.52 (DCM/acetone = 39/1).

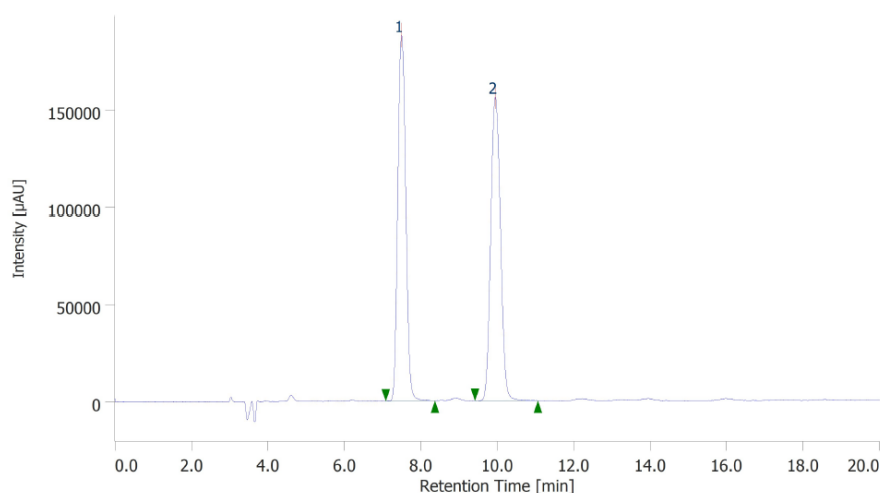
Reported compound. [S5]



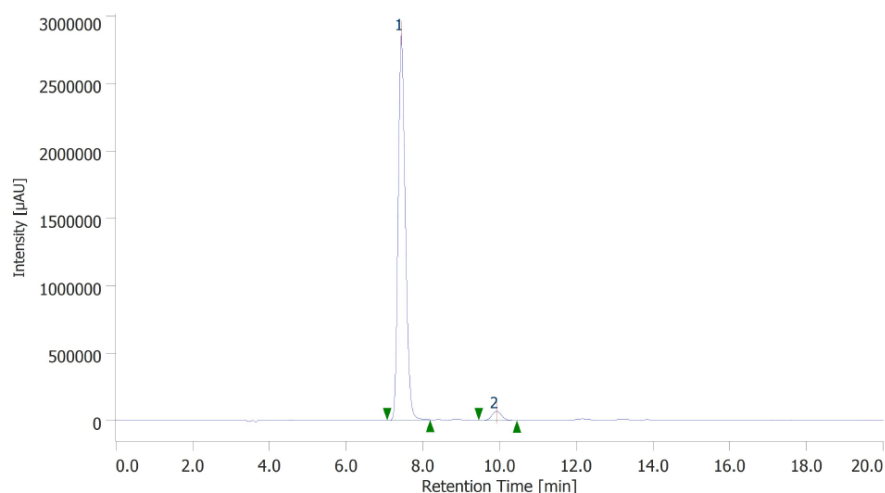
6-fluoro-1-(4-fluorophenyl)-3-phenylbenzo[e][1,2,4]thiadiazine 1-oxide (3ba)



General Procedure A1 using bis(4-fluorophenyl)(imino)- λ^6 -sulfanone **1b** (60.8 mg, 0.24 mmol) and 3-phenyl-1,4,2-dioxazol-5-one **2a** (32.2 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) twice afforded **3ba** as a colorless solid (52.5 mg, 74%). **¹H NMR** (CDCl₃, 400 MHz) δ 8.45-8.38 (2H, m), 7.89 (2H, m), 7.53-7.43 (4H, m), 7.33 (1H, dd, J = 10.3, 2.5 Hz), 7.30-7.23 (3H, m), 7.02 (1H, ddd, J = 9.7, 7.1, 1.7 Hz). **¹³C {¹H, ¹⁹F} NMR** (CDCl₃, 100 MHz) δ 166.0, 165.9, 159.0, 150.1, 137.0, 136.7, 131.4, 128.7, 128.2, 127.3, 116.8, 115.2, 113.9, 110.1. **¹⁹F NMR** (CDCl₃, 369 MHz) [C₆H₅CF₃ (−63.7 as an internal standard)] δ −102.96–103.03 (m), −103.66–103.73 (m). **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 300 nm): t_R = 7.4 (major) and 9.9 (minor) min. **[α]_D^{23.0}** = +176.6 (c = 0.57, CHCl₃). **Rf** 0.50 (DCM/acetone = 39/1). Reported compound.^[S6]

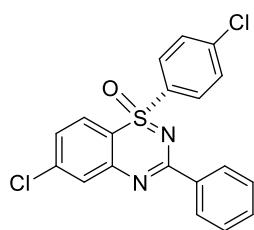


#	tR [min]	Area%
1	7.497	49.963
2	9.950	50.037



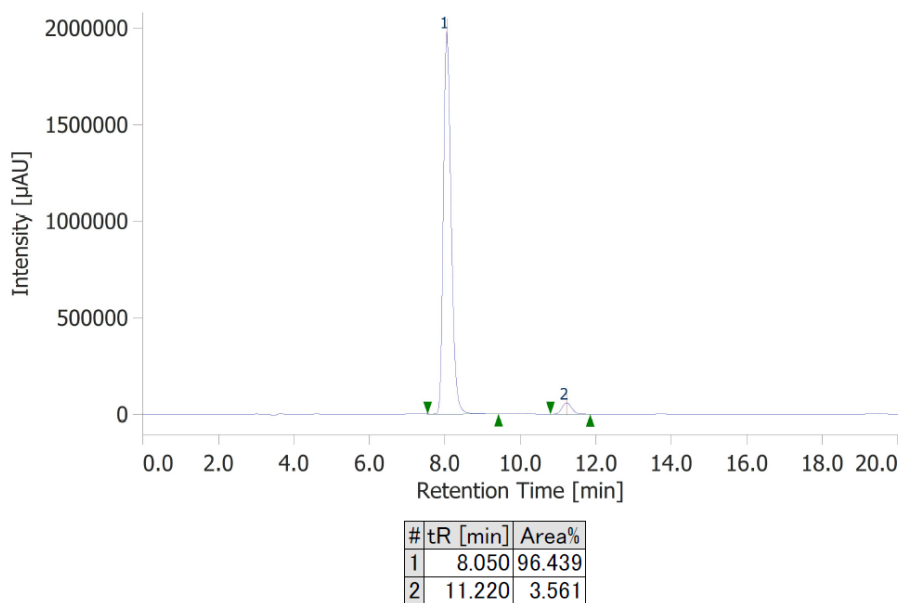
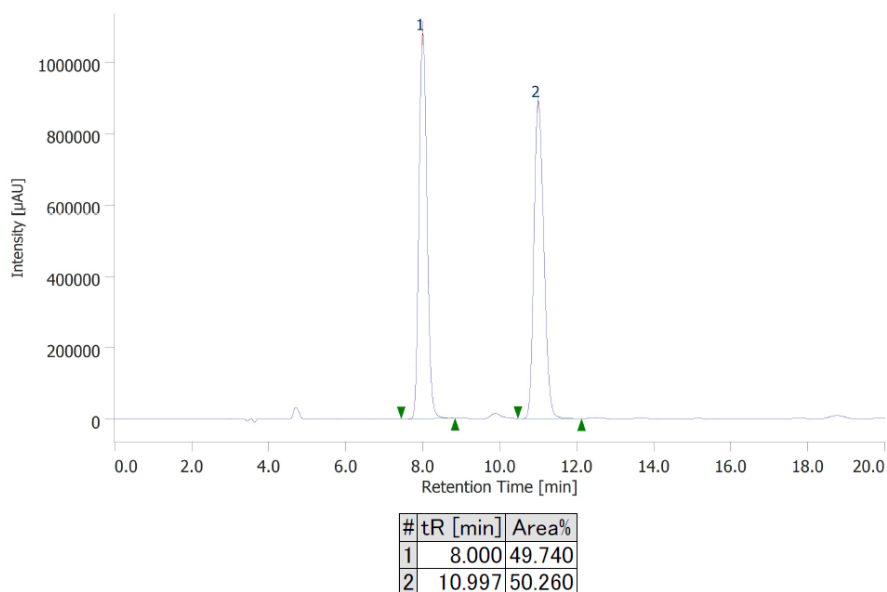
#	tR [min]	Area%
1	7.440	97.025
2	9.920	2.975

6-chloro-1-(4-chlorophenyl)-3-phenylbenzo[e][1,2,4]thiadiazine 1-oxide (**3ca**)

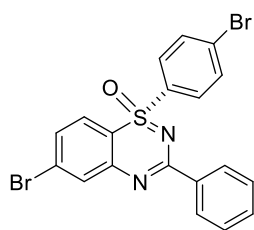


General Procedure A1 using bis(4-chlorophenyl)(imino)- λ^6 -sulfanone **1c** (68.7 mg, 0.24 mmol) and 3-phenyl-1,4,2-dioxazol-5-one **2a** (32.2 mg, 0.2 mmol) and purification by silica gel column chromatography (hexane/DCM = 1/4) afforded **3ca** as a colorless solid (60.0 mg, 77%). $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.44-8.34 (2H, m), 7.82-7.75 (2H, m), 7.67 (1H, d, $J = 1.9$ Hz), 7.58-7.40 (5H, m), 7.36 (1H, d, $J = 8.6$ Hz), 7.22 (1H, dd, $J = 8.6, 2.0$ Hz). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 158.9, 148.6, 141.0, 140.7, 138.9, 136.9, 131.4, 129.9,

129.7, 128.7, 128.2, 128.1, 126.8, 126.0, 111.7. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 310 nm): $t_R = 8.1$ (major) and 11.2 (minor) min. $[\alpha]_D^{23.1} = +188.2$ ($c = 1.08$, CHCl_3). **Rf** 0.55 (DCM/acetone = 39/1). Reported compound.^[S5]

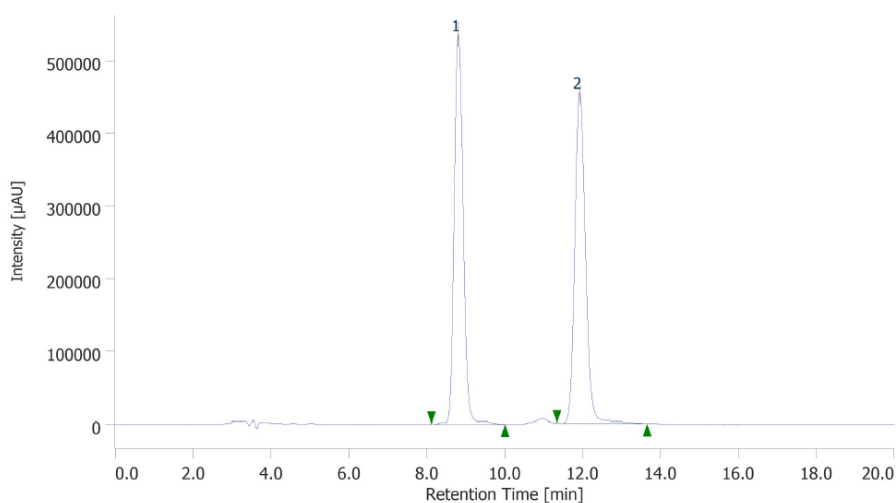


6-bromo-1-(4-bromophenyl)-3-phenylbenzo[e][1,2,4]thiadiazine 1-oxide (3da)

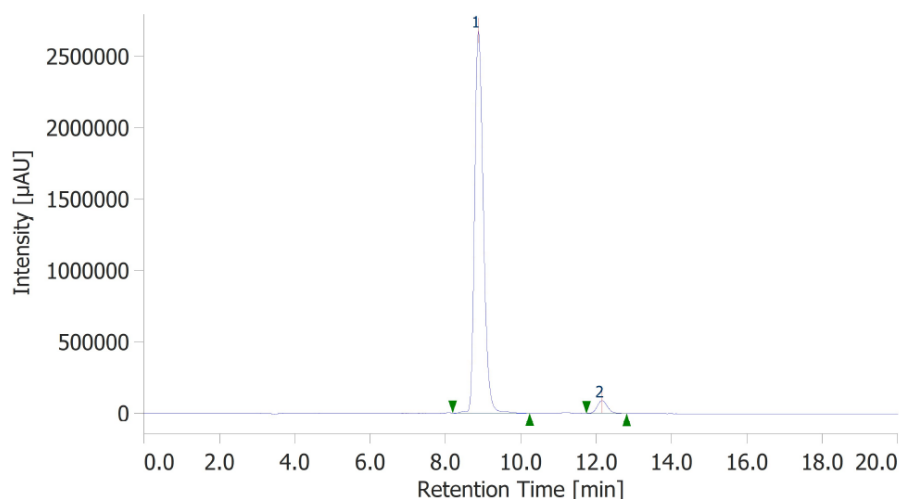


General Procedure A1 using bis(4-bromophenyl)(imino)- λ^6 -sulfanone **1d** (90.0 mg, 0.24 mmol) and 3-phenyl-1,4,2-dioxazol-5-one **2a** (32.2 mg, 0.2 mmol) and purification by silica gel column chromatography (hexane/DCM = 1/4) afforded **3da** as a colorless solid (75.2 mg, 79%). ¹H NMR (CDCl₃, 400 MHz) δ 8.44-8.36 (2H, m), 7.86 (1H, d, J = 1.8 Hz), 7.71 (4H, s), 7.53-7.41 (3H, m), 7.38 (1H, dd, J = 8.5, 1.6 Hz), 7.28 (1H, d, J = 8.6 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 158.9, 148.5, 139.4, 136.9, 132.7, 131.5, 131.3, 130.0,

129.7, 129.5, 129.2, 128.7, 128.2, 125.9, 112.1. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 310 nm): t_R = 8.9 (major) and 12.2 (minor) min. $[\alpha]_D^{23.1} = +139.9$ (c = 1.04, CHCl₃). **Rf** 0.57 (DCM/acetone = 39/1). Reported compound.^[S6]

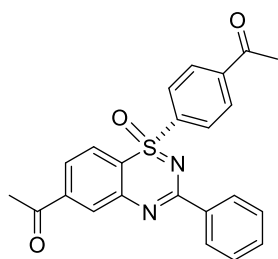


#	tR [min]	Area%
1	8.810	49.702
2	11.920	50.298

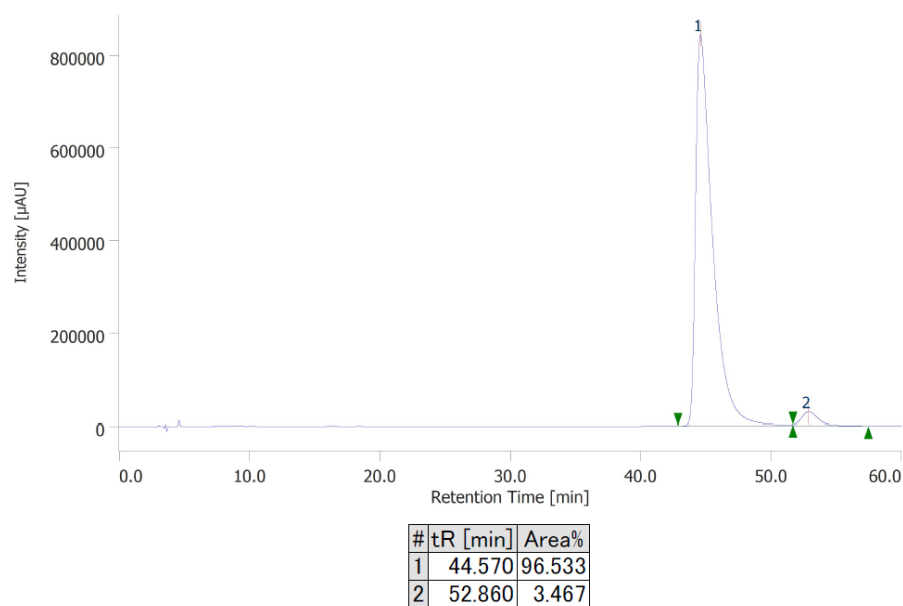
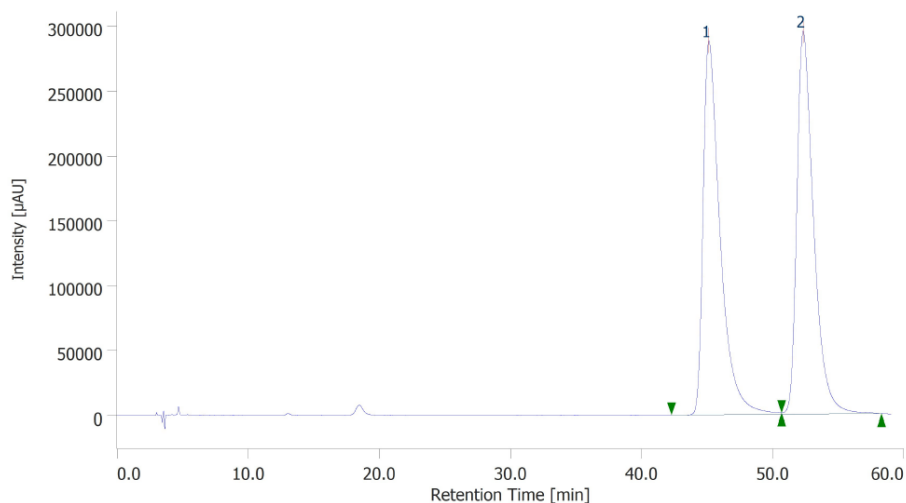


#	tR [min]	Area%
1	8.870	96.207
2	12.150	3.793

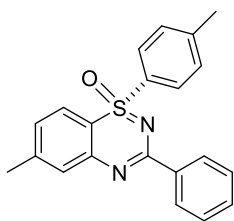
1-(4-(6-acetyl-1-oxido-3-phenyl-1 λ^4 -benzo[e][1,2,4]thiadiazin-1-yl)phenyl)ethan-1-one (3ea)



General Procedure A1 using 1,1'-(sulfonimidobis(4,1-phenylene))bis(ethan-1-one) **1e** (72.3 mg, 0.24 mmol) and 3-phenyl-1,4,2-dioxazol-5-one **2a** (32.2 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) twice afforded **3ea** as a pale yellow solid (47.4 mg, 59%). **MP** 155.1-156.8 °C. **¹H NMR** (CDCl₃, 400 MHz) δ 8.47-8.41 (2H, m), 8.22 (1H, d, J = 1.3 Hz), 8.14 (2H, m), 8.00 (2H, m), 7.82 (1H, dd, 8.4, 1.7 Hz), 7.53-7.44 (4H, m), 2.69 (3H, s), 2.66 (3H, s). **¹³C NMR** (CDCl₃, 100 MHz) δ 196.9, 196.4, 158.6, 147.8, 143.5, 141.7, 141.0, 136.8, 131.5, 129.8, 129.1, 128.7, 128.3, 125.1, 124.5, 115.8, 26.9, 26.9; one aromatic signal was missing probably due to overlapping. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 44.6 (major) and 52.9 (minor) min. **HRMS** (ESI): m/z calculated for C₂₃H₁₉O₃N₂S⁺ [M+H]⁺: 403.1111, found: 403.1100. **[α]_D^{23.2}** = +186.0 (c = 1.03, CHCl₃). **R_f** 0.30 (DCM/acetone = 39/1).



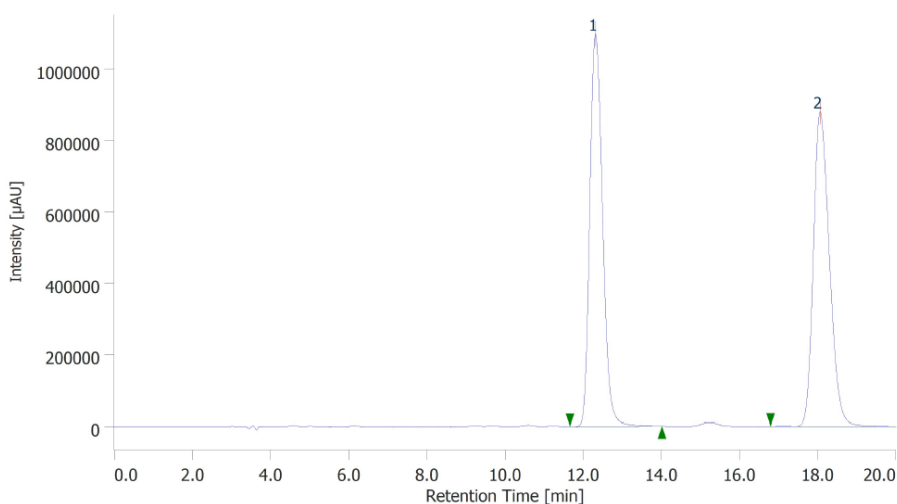
6-methyl-3-phenyl-1-(p-tolyl)benzo[e][1,2,4]thiadiazine 1-oxide (3fa)



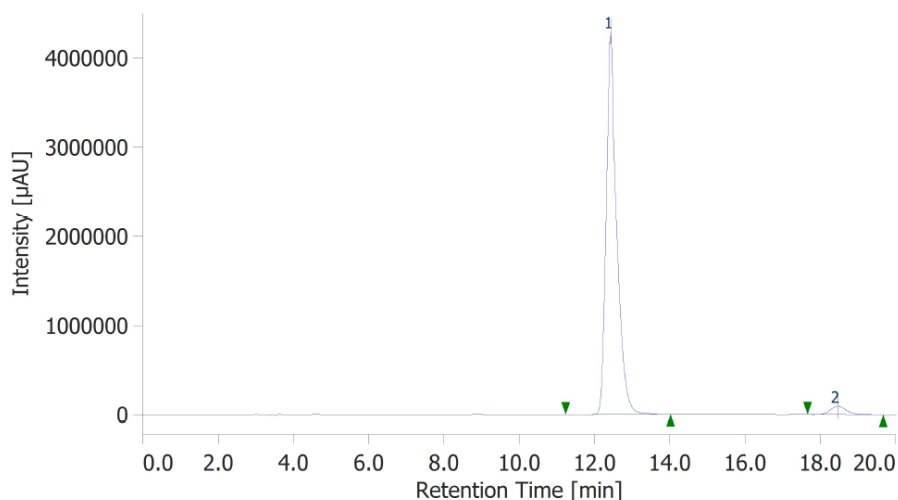
General Procedure A1 using iminodi-p-tolyl- λ^6 -sulfanone **1f** (58.9 mg, 0.24 mmol) and 3-phenyl-1,4,2-dioxazol-5-one **2a** (32.2 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) afforded **3fa** as a pale yellow solid (36.0 mg, 52%).

¹H NMR (CDCl₃, 400 MHz) δ 8.46-8.38 (2H, m), 7.74 (2H, m), 7.48-7.40 (4H, m), 7.37-7.30 (3H, m), 7.10-7.05 (1H, m), 2.43 (6H, s). **¹³C NMR** (CDCl₃, 100 MHz) δ 158.1, 147.3, 145.2, 144.8, 138.1, 137.7, 130.8, 129.8, 128.6, 128.5, 128.2, 128.1, 127.6, 124.5, 111.4,

21.8, 21.6. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 12.4 (major) and 18.4 (minor) min. $[\alpha]_D^{22.8}$ = +153.4 (c = 0.70, CHCl₃). **Rf** 0.50 (DCM/acetone = 39/1). Reported compound.^[S5]

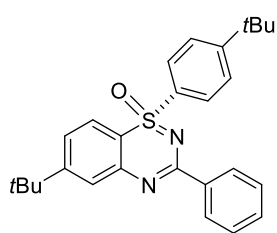


#	tR [min]	Area%
1	12.310	49.772
2	18.053	50.228

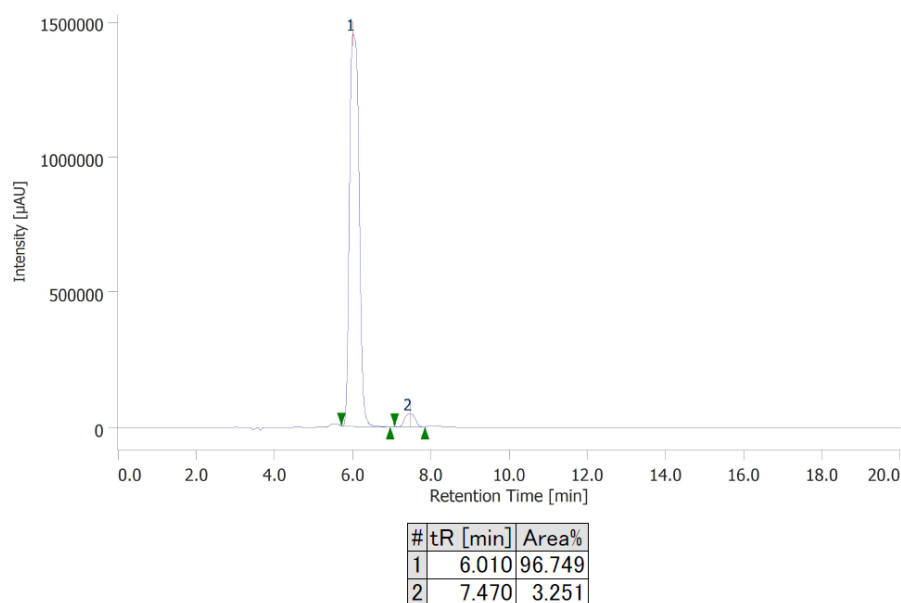
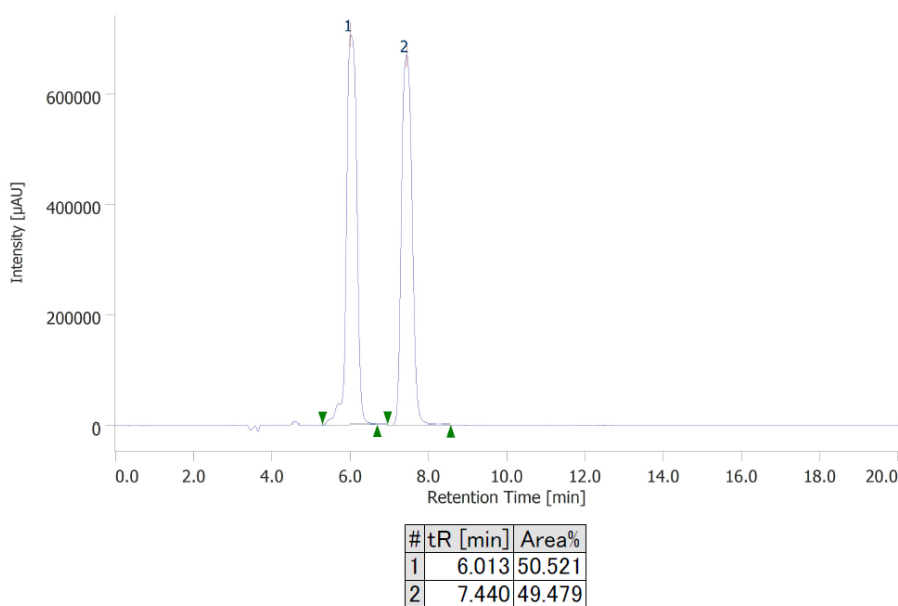


#	tR [min]	Area%
1	12.430	96.827
2	18.447	3.173

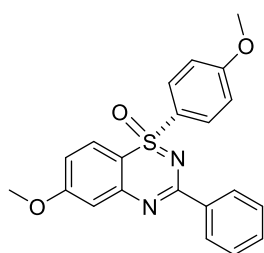
6-(*tert*-butyl)-1-(4-(*tert*-butyl)phenyl)-3-phenylbenzo[*e*][1,2,4]thiadiazine 1-oxide (3ga)



General Procedure A1 using bis(4-(*tert*-butyl)phenyl)(imino)- λ^6 -sulfanone **1g** (79.1 mg, 0.24 mmol) and 3-phenyl-1,4,2-dioxazol-5-one **2a** (32.2 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) afforded **3ga** as a colorless solid (47.0 mg, 55%). **MP** >200 °C. **¹H NMR** (CDCl₃, 400 MHz) δ 8.48-8.36 (2H, m), 7.80 (2H, m), 7.67 (1H, d, J = 1.8 Hz), 7.60-7.54 (2H, m), 7.48-7.39 (4H, m), 7.33 (1H, dd, J = 8.5, 1.9 Hz), 1.36 (9H, s), 1.33 (9H, s). **¹³C NMR** (CDCl₃, 100 MHz) δ 158.2, 158.1, 157.7, 147.1, 137.8, 137.8, 130.8, 128.5, 128.4, 128.1, 126.3, 124.8, 124.4, 124.3, 111.2, 35.3, 35.3, 31.0, 30.9. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 330 nm): t_R = 6.0 (major) and 7.5 (minor) min. **HRMS** (ESI): m/z calculated for C₂₇H₃₁ON₂S⁺ [M+H]⁺: 431.2152, found: 431.2142. **[α]_D^{23.2}** = +98.4 (c = 0.96, CHCl₃). **Rf** 0.57 (DCM/acetone = 39/1).



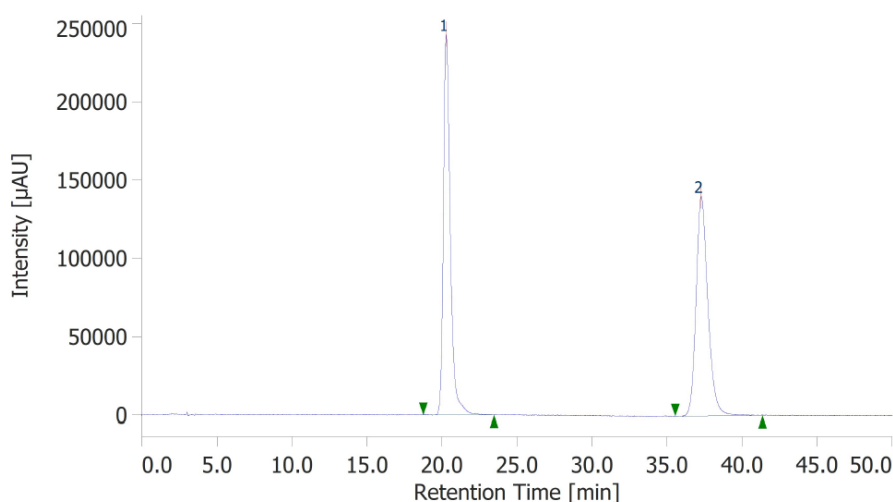
6-methoxy-1-(4-methoxyphenyl)-3-phenylbenzo[e][1,2,4]thiadiazine 1-oxide (3ha)



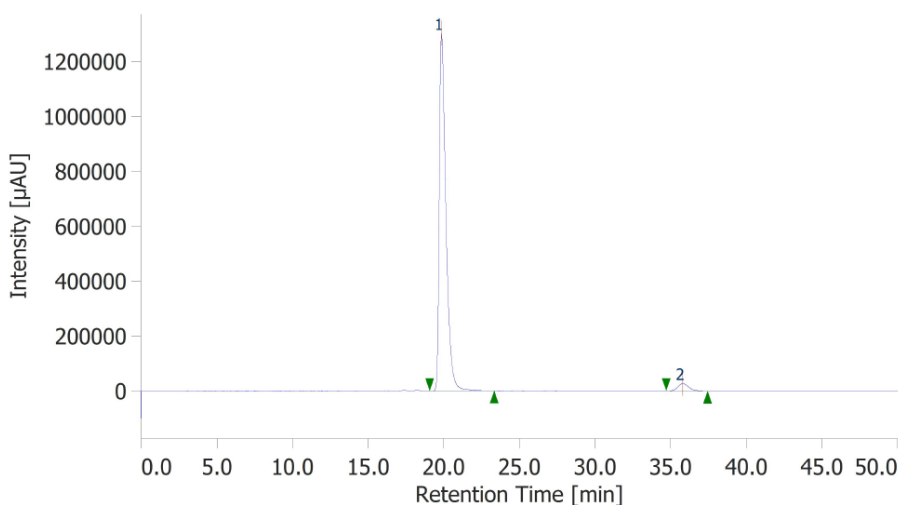
General Procedure A1 using iminobis(4-methoxyphenyl)- λ^6 -sulfanone **1h** (66.6 mg, 0.24 mmol) and 3-phenyl-1,4,2-dioxazol-5-one **2a** (32.2 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) afforded **3ha** as a pale yellow solid (45.6 mg, 61%). ¹H NMR (CDCl₃, 400 MHz) δ 8.46-8.38 (2H, m), 7.80-7.73 (2H, m), 7.50-7.40 (3H, m), 7.34 (1H, d, J = 8.8 Hz), 7.06 (1H, d, J = 2.5 Hz), 7.03-6.96 (2H, m), 6.83 (1H, dd, J = 8.8, 2.5 Hz), 3.90 (3H, s), 3.85 (3H, s). ¹³C NMR (CDCl₃, 100 MHz)

δ 164.0, 163.7, 158.7, 149.7, 137.7, 132.6, 130.8, 130.5, 128.5, 128.1, 126.1, 116.5, 114.4, 108.8, 106.8, 55.7, 55.7.

HPLC (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 300 nm): t_R = 19.8 (major) and 35.8 (minor) min. $[\alpha]_D^{22.7}$ = +156.4 (c = 1.17, CHCl₃). **Rf** 0.26 (DCM/acetone = 39/1). Reported compound.^[S5]

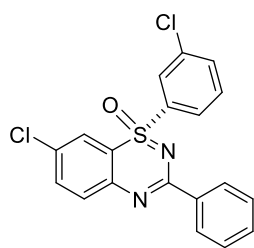


#	tR [min]	Area%
1	20.277	50.254
2	37.250	49.746



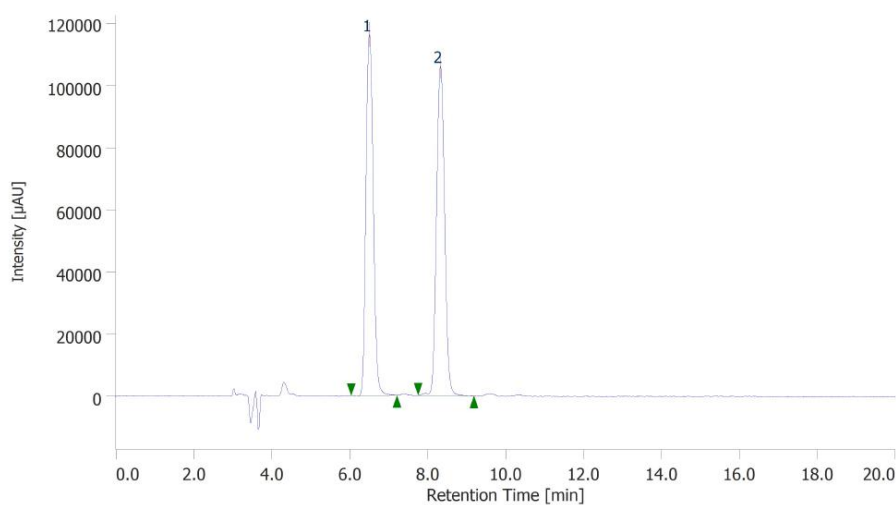
#	tR [min]	Area%
1	19.843	96.820
2	35.770	3.180

7-chloro-1-(3-chlorophenyl)-3-phenylbenzo[e][1,2,4]thiadiazine 1-oxide (3ia)

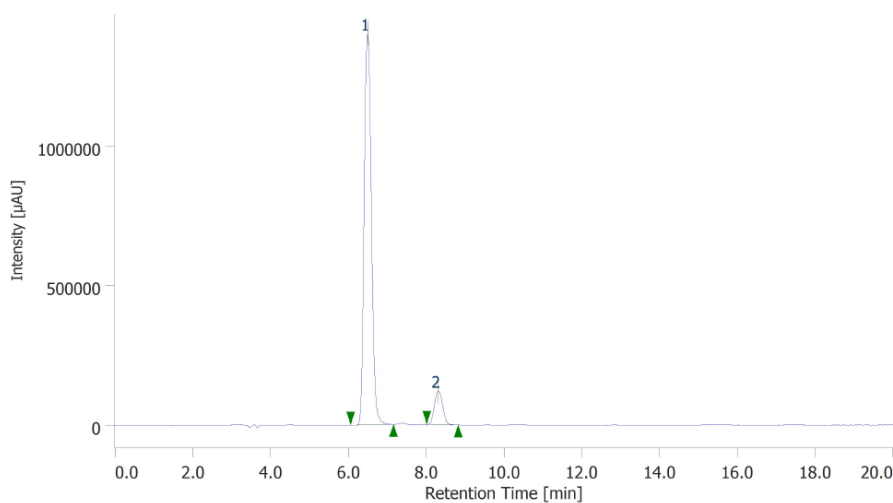


General Procedure A1 using bis(3-chlorophenyl)(imino)- λ^6 -sulfanone **1i** (68.7 mg, 0.24 mmol) and 3-phenyl-1,4,2-dioxazol-5-one **2a** (32.2 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) afforded **3ia** as a colorless solid (54.2 mg, 70%). $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.41 (2H, d, $J = 7.0$ Hz), 7.85 (1H, s), 7.77 (1H, d, $J = 7.9$ Hz), 7.67-7.43 (7H, m), 7.40 (1H, d, $J = 1.6$ Hz). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 158.0, 145.8, 141.8, 136.9, 135.8, 135.2, 134.3, 131.4, 131.1, 130.7, 130.5,

128.6, 128.2, 126.8, 123.8, 113.8; one aromatic signal was missing probably due to overlapping. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 300 nm): $t_R = 6.5$ (major) and 8.3 (minor) min. $[\alpha]_D^{23.2} = +101.8$ ($c = 1.15$, CHCl_3). **Rf** 0.48 (DCM/acetone = 39/1). Reported compound.^[S6]

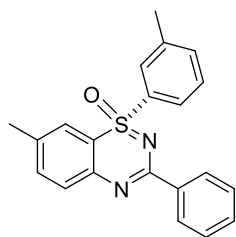


#	tR [min]	Area%
1	6.507	49.997
2	8.327	50.003



#	tR [min]	Area%
1	6.493	91.453
2	8.313	8.547

7-methyl-3-phenyl-1-(m-tolyl)benzo[e][1,2,4]thiadiazine 1-oxide (3ja)

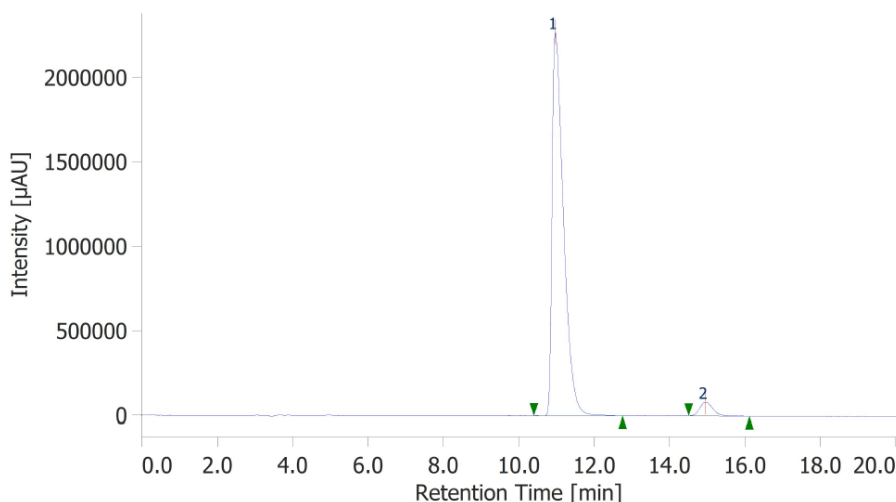
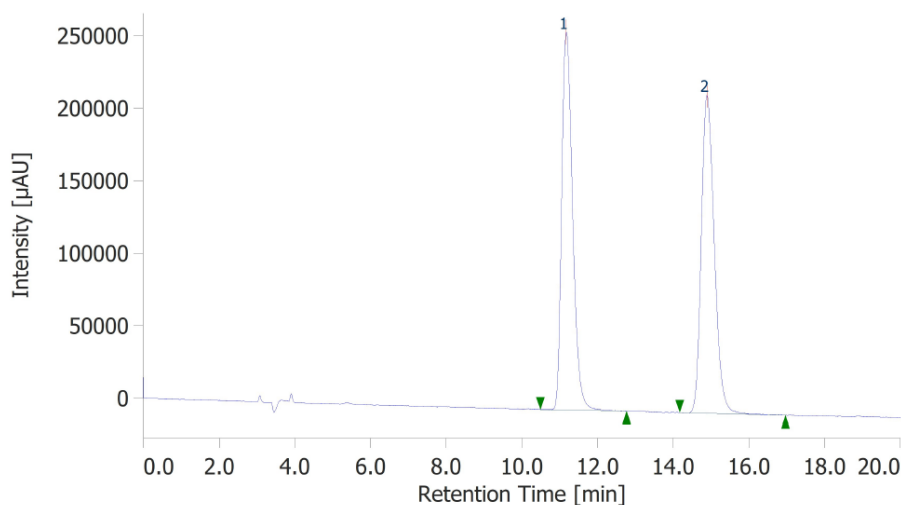


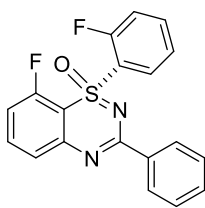
General Procedure A1 using iminodi-m-tolyl- λ^6 -sulfanone **1j** (58.9 mg, 0.24 mmol) and 3-phenyl-1,4,2-dioxazol-5-one **2a** (32.2 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) afforded **3ja** as a colorless solid (57.5 mg, 83%).

¹H NMR (CDCl₃, 400 MHz) δ 8.45-8.37 (2H, m), 7.72-7.68 (1H, m), 7.67-7.64 (1H, m), 7.57 (1H, d, J = 8.4 Hz), 7.49-7.39 (6H, m), 7.23-7.20 (1H, m), 2.41 (3H, s), 2.31 (3H, s).

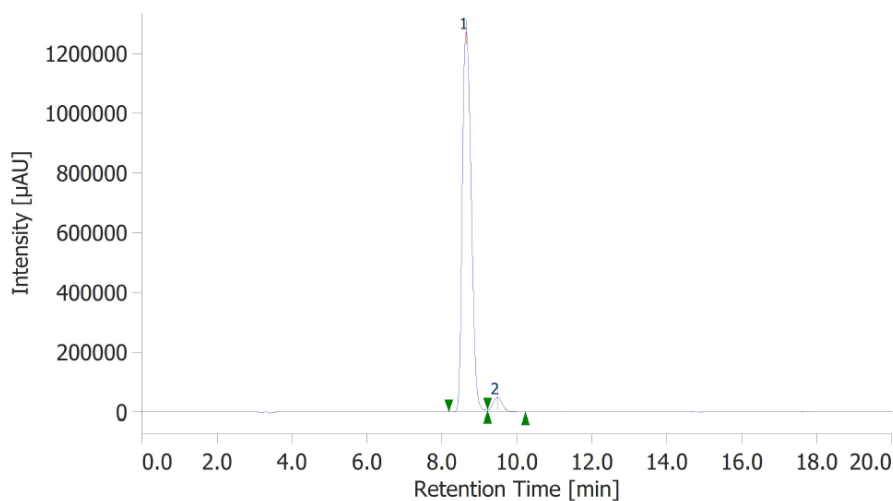
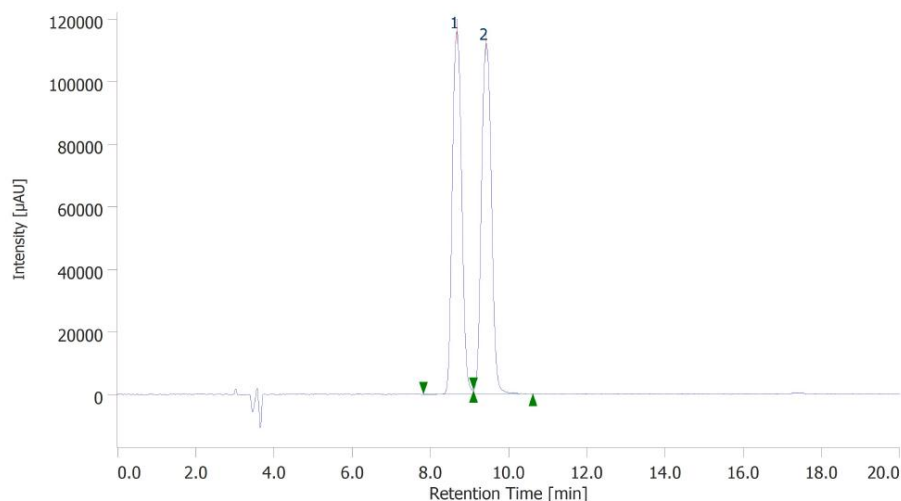
¹³C NMR (CDCl₃, 100 MHz) δ 157.2, 145.1, 140.6, 139.6, 137.7, 136.5, 135.8, 134.5, 130.7,

129.0, 128.8, 128.5, 128.4, 128.1, 125.8, 123.9, 113.3, 21.3, 21.1. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 15/1; flow rate: 1.0 mL/min; detection: at 310 nm): t_R = 11.0 (major) and 15.0 (minor) min. $[\alpha]_D^{23.1} = +126.2$ (c = 0.94, CHCl₃). **Rf** 0.39 (DCM/acetone = 39/1). Reported compound.^[S6]

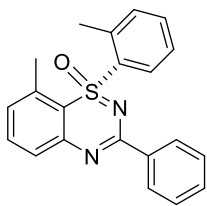


8-fluoro-1-(2-fluorophenyl)-3-phenylbenzo[e][1,2,4]thiadiazine 1-oxide (3ka)

General Procedure A1 using bis(2-fluorophenyl)(imino)- λ^6 -sulfanone **1k** (60.8 mg, 0.24 mmol) and 3-phenyl-1,4,2-dioxazol-5-one **2a** (32.2 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) twice afforded **3ka** as a colorless solid (68.2 mg, 96%). **MP** 132.0-133.8 °C. **¹H NMR** (CDCl₃, 400 MHz) δ 8.42-8.36 (2H, m), 8.23 (1H, td, J = 7.7, 1.7 Hz), 7.70-7.61 (2H, m), 7.53-7.40 (5H, m), 7.13-7.05 (1H, m), 6.96-6.88 (1H, m). **¹³C {¹H, ¹⁹F} NMR** (CDCl₃, 100 MHz) δ 160.1, 158.3, 158.0, 150.0, 137.1, 135.4, 131.3, 129.8, 128.9, 128.7, 128.2, 124.5, 124.4, 117.6, 111.6, 102.6; one aromatic signal was missing probably due to overlapping. **¹⁹F NMR** (CDCl₃, 369 MHz) [C₆H₅CF₃ (−63.7 as an internal standard)] δ −109.83–−109.87 (m), −111.09–−111.13 (m). **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 370 nm): t_R = 8.6 (major) and 9.5 (minor) min. **HRMS** (ESI): m/z calculated for C₁₉H₁₃ON₂F₂S⁺ [M+H]⁺: 355.0711, found: 355.0703. **[α]_D^{22.9}** = −37.6 (c = 0.20, CHCl₃). **R_f** 0.38 (DCM/acetone = 39/1).



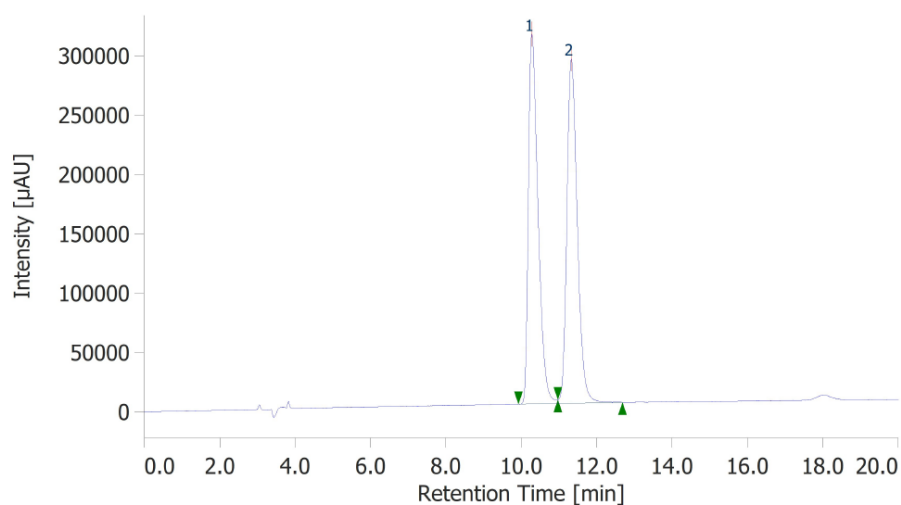
8-methyl-3-phenyl-1-(o-tolyl)benzo[e][1,2,4]thiadiazine 1-oxide (3la)



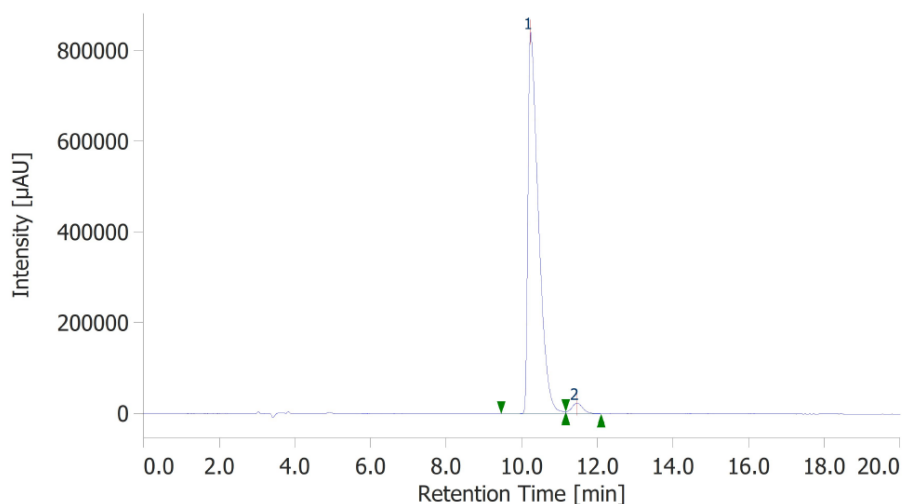
General Procedure A1 using iminodi-o-tolyl- λ^6 -sulfanone **11** (58.9 mg, 0.24 mmol) and 3-phenyl-1,4,2-dioxazol-5-one **2a** (32.2 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) twice afforded **3la** as a colorless solid (60.3 mg, 87%).

¹H NMR (CDCl₃, 400 MHz) δ 8.42-8.33 (3H, m), 7.59-7.54 (2H, m), 7.54-7.49 (2H, m), 7.47-7.38 (3H, m), 7.24-7.20 (1H, m), 7.08-7.03 (1H, m), 2.15 (3H, s), 1.76 (3H, s). **¹³C NMR**

(CDCl₃, 100 MHz) δ 157.0, 149.1, 139.4, 139.2, 137.3, 135.5, 134.3, 134.1, 133.2, 130.8, 129.1, 128.8, 128.4, 128.1, 126.8, 126.5, 111.2, 19.8, 18.9. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 15/1; flow rate: 1.0 mL/min; detection: at 310 nm): t_R = 10.2 (major) and 11.5 (minor) min. **[α]_D^{23.4}** = -69.5 (c = 0.88, CHCl₃). **Rf** 0.38 (DCM/acetone = 39/1). Reported compound.^[S6]

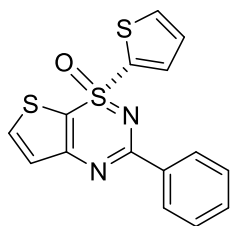


#	tR [min]	Area%
1	10.277	49.776
2	11.323	50.224

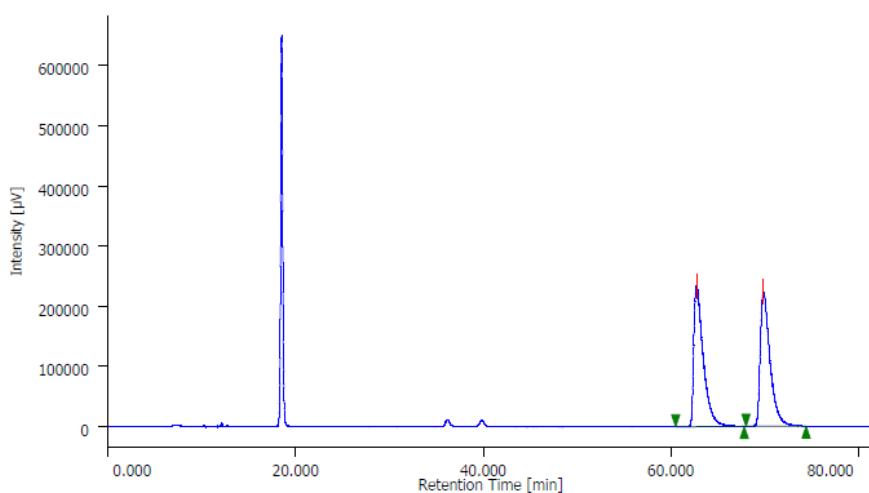


#	tR [min]	Area%
1	10.233	97.019
2	11.457	2.981

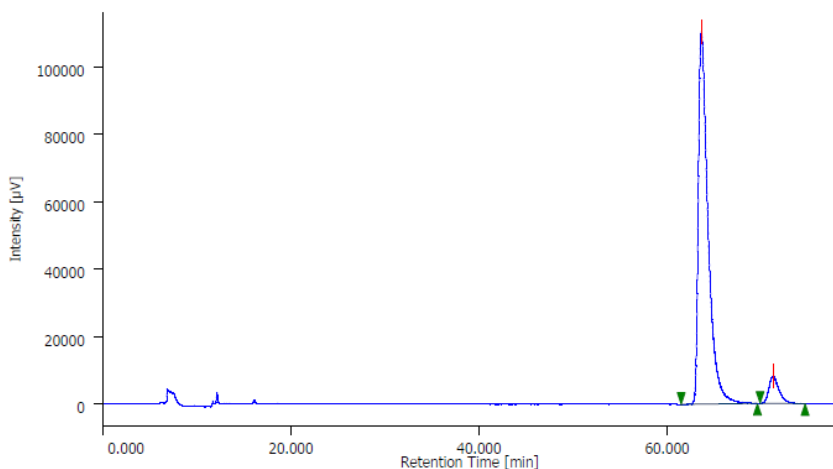
3-phenyl-1-(thiophen-2-yl)thieno[3,2-e][1,2,4]thiadiazine 1-oxide (3ma)



General Procedure A1 using iminodi(thiophen-2-yl)- λ^6 -sulfanone **1m** (60.8 mg, 0.24 mmol) and 3-phenyl-1,4,2-dioxazol-5-one **2a** (32.2 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) twice afforded **3ma** as a pale yellow amorphous (30.8 mg), in which a small amount of an inseparable over-amidated product was contaminated. The purity-corrected yield of **3ma** was 28.7 mg (43%). **¹H NMR** (CDCl₃, 400 MHz) δ 8.46-8.36 (2H, m), 7.81-7.72 (2H, m), 7.59 (1H, dd, J = 3.9, 1.4 Hz), 7.50-7.42 (3H, m), 7.28-7.24 (1H, m), 7.14 (1H, dd, J = 5.0, 3.9 Hz). **¹³C NMR** (CDCl₃, 100 MHz) δ 158.9, 158.1, 143.9, 136.7, 136.0, 134.3, 132.7, 131.1, 128.6, 128.2, 126.1, 107.0; one aromatic signal was missing probably due to overlapping. **HPLC** (chiral column: DAICEL CHIRALPAK IA-3 x 2; solvent: hexane/2-propanol = 98/2; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 63.6 (major) and 71.2 (minor) min. **HRMS** (ESI): m/z calculated for C₁₅H₁₁N₂OS₃⁺ [M+H]⁺: 331.00280, found: 331.00207. [α]_D^{24.6} = +191.6 (c = 0.11, CHCl₃). **Rf** 0.44 (DCM/acetone = 39/1).

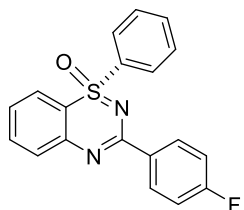


#	tR [min]	Area%
1	62.706	50.268
2	69.831	49.702

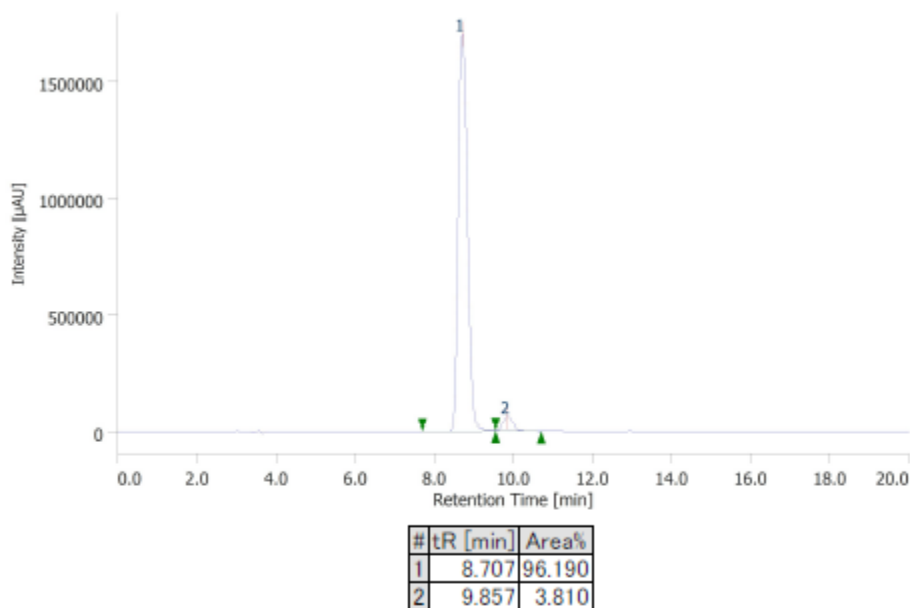
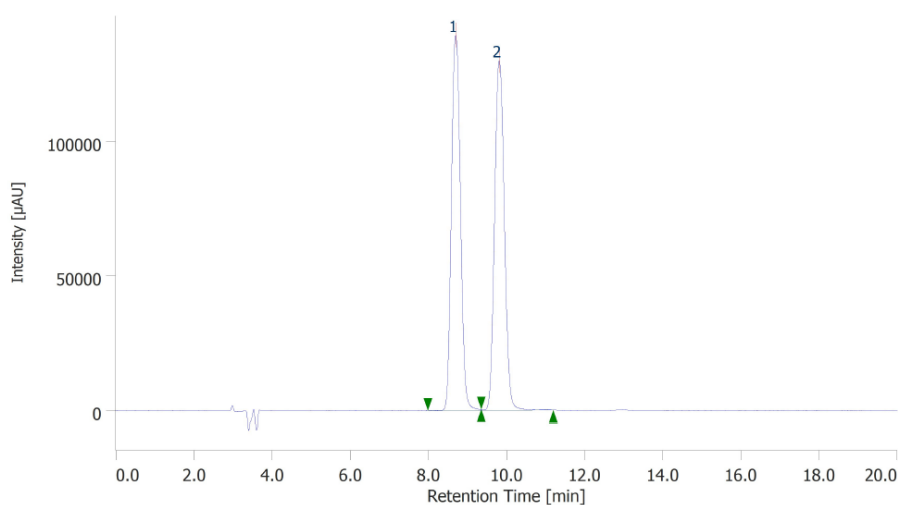


#	tR [min]	Area%
1	63.550	83.846
2	71.154	1.154

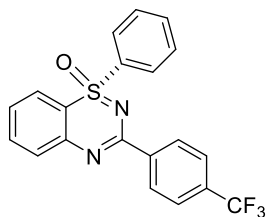
3-(4-fluorophenyl)-1-phenylbenzo[*e*][1,2,4]thiadiazine 1-oxide (**3ab**)



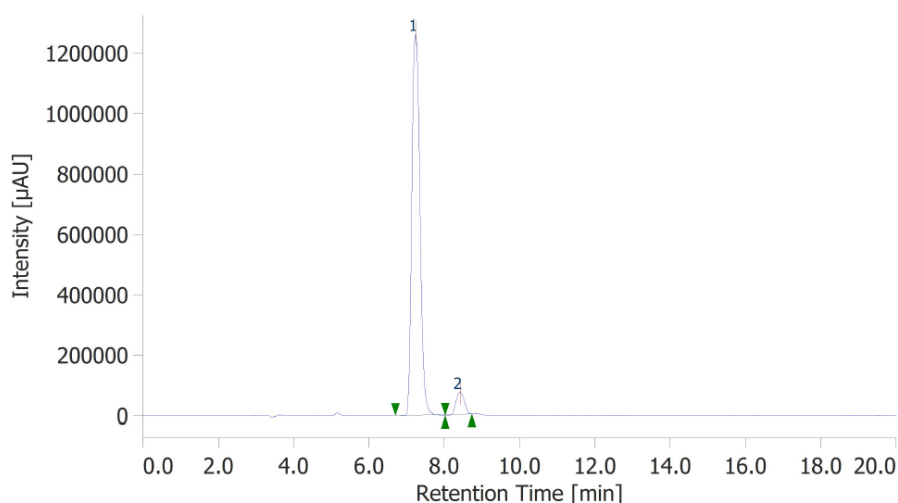
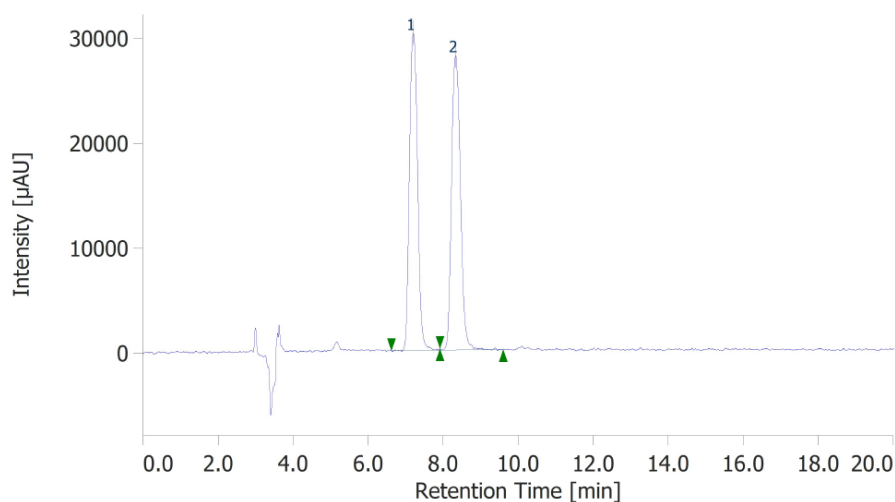
General Procedure A1 using iminodiphenyl- λ^6 -sulfanone **1a** (52.1 mg, 0.24 mmol) and 3-(4-fluorophenyl)-1,4,2-dioxazol-5-one **2b** (36.2 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) afforded **3ab** as a colorless solid (51.3 mg, 73%). ^1H NMR (CDCl_3 , 400 MHz) δ 8.47-8.42 (2H, m), 7.92-7.86 (2H, m), 7.70-7.56 (5H, m), 7.45 (1H, m), 7.30-7.25 (1H, m), 7.16-7.08 (2H, m). ^{13}C {**1H**, **19F**} NMR (CDCl_3 , 100 MHz) δ 164.8, 157.0, 147.2, 140.6, 134.4, 133.9, 133.7, 130.8, 129.3, 128.6, 128.6, 126.2, 124.8, 115.1, 113.6. ^{19}F NMR (CDCl_3 , 369 MHz) [$\text{C}_6\text{H}_5\text{CF}_3$ (−63.7 as an internal standard)] δ −110.72—110.79 (m). HPLC (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 350 nm): t_R = 8.7 (major) and 9.9 (minor) min. $[\alpha]_D^{23.1} = +200.6$ ($c = 0.15$, CHCl_3). **Rf** 0.50 (DCM/acetone = 39/1). Reported compound.^[S5]



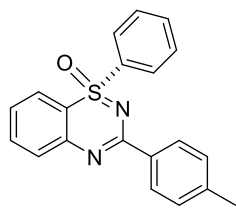
1-phenyl-3-(4-(trifluoromethyl)phenyl)benzo[*e*][1,2,4]thiadiazine 1-oxide (**3ac**)



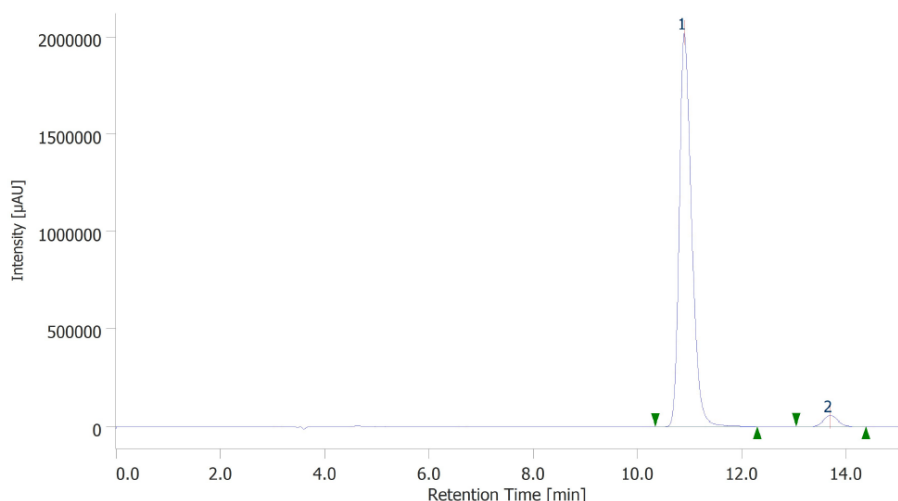
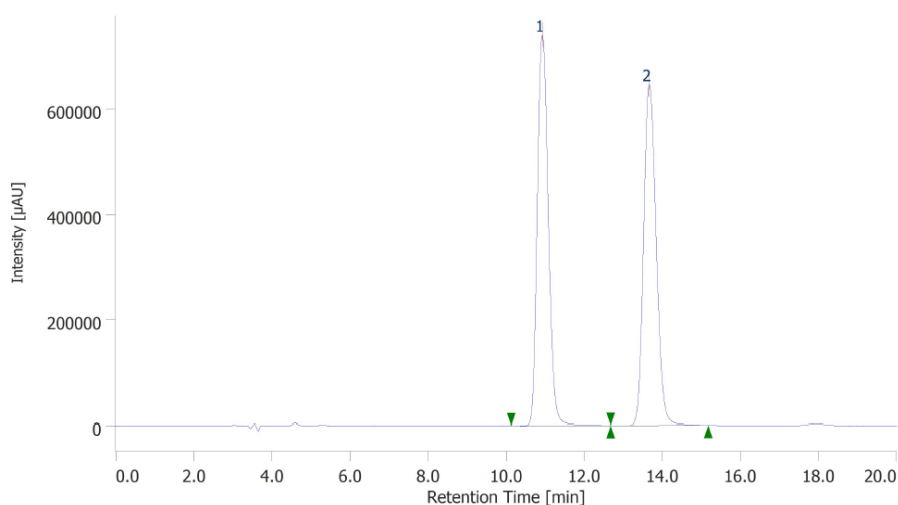
General Procedure A1 using iminodiphenyl- λ^6 -sulfanone **1a** (52.1 mg, 0.24 mmol) and 3-(4-(trifluoromethyl)phenyl)-1,4,2-dioxazol-5-one **2c** (46.2 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) twice afforded **3ac** as a pale yellow solid (41.0 mg, 53%). ^1H NMR (CDCl_3 , 400 MHz) δ 8.55 (2H, d, J = 8.0 Hz), 7.92-7.87 (2H, m), 7.73-7.63 (5H, m), 7.63-7.57 (2H, m), 7.47 (1H, m), 7.35-7.29 (1H, m). ^{13}C {**1H**, **19F**} NMR (CDCl_3 , 100 MHz) δ 156.5, 146.9, 140.9, 140.4, 134.5, 134.0, 129.4, 128.9, 128.8, 128.7, 126.8, 125.0, 124.8, 113.9; two aromatic signals were missing probably due to overlapping. ^{19}F NMR (CDCl_3 , 369 MHz) [$\text{C}_6\text{H}_5\text{CF}_3$ (−63.7 as an internal standard)] δ −63.64. HPLC (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 7.2 (major) and 8.4 (minor) min. $[\alpha]_D^{23.1}$ = +127.4 (c = 0.77, CHCl_3). **Rf** 0.60 (DCM/acetone = 39/1). Reported compound.^[S5]



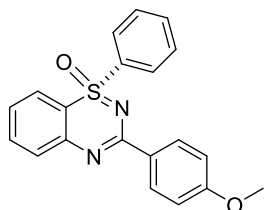
1-phenyl-3-(p-tolyl)benzo[e][1,2,4]thiadiazine 1-oxide (3ad)



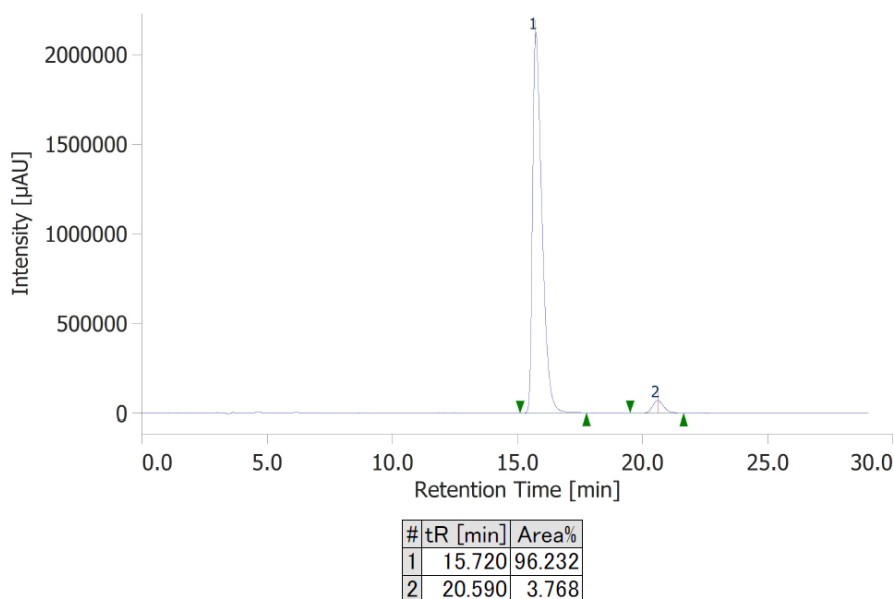
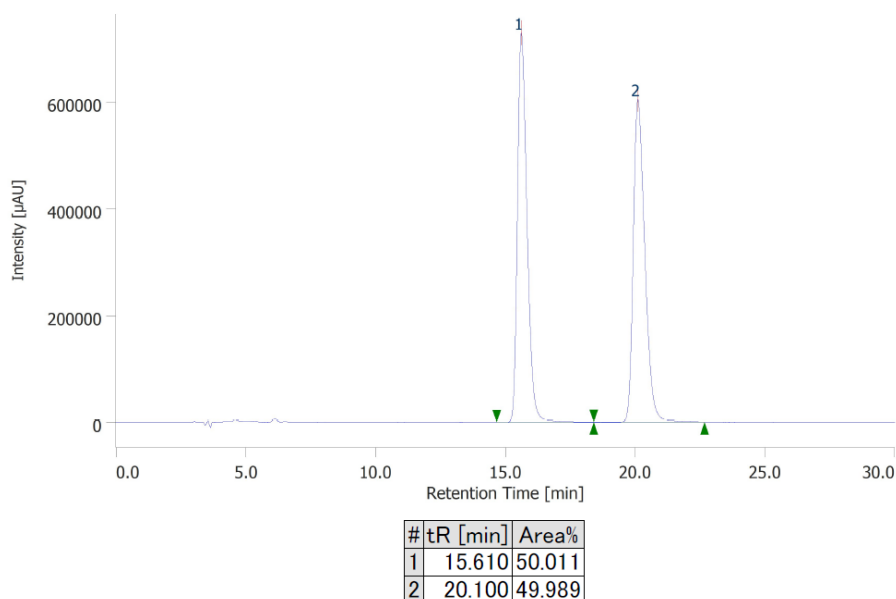
General Procedure A1 using iminodiphenyl- λ^6 -sulfanone **1a** (52.1 mg, 0.24 mmol) and 3-(p-tolyl)-1,4,2-dioxazol-5-one **2d** (35.4 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) twice afforded **3ad** as a pale yellow solid (45.3 mg, 68%). **¹H NMR** (CDCl₃, 400 MHz) δ 8.35-8.30 (2H, m), 7.90-7.85 (2H, m), 7.68-7.52 (5H, m), 7.46-7.40 (1H, m), 7.27-7.20 (3H, m), 2.41 (3H, s). **¹³C NMR** (CDCl₃, 100 MHz) δ 158.1, 147.4, 141.3, 140.8, 134.8, 134.3, 133.7, 129.2, 128.9, 128.6, 128.6, 126.0, 124.7, 113.7, 21.5; one aromatic signal was missing probably due to overlapping. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 10.9 (major) and 13.7 (minor) min. **$[\alpha]_D^{22.7}$** = +225.4 (c = 0.57, CHCl₃). **Rf** 0.45 (DCM/acetone = 39/1). Reported compound.^[S5]



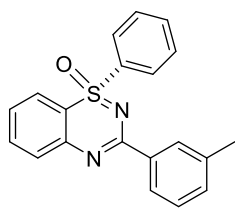
3-(4-methoxyphenyl)-1-phenylbenzo[e][1,2,4]thiadiazine 1-oxide (3ae)



General Procedure A1 using iminodiphenyl- λ^6 -sulfanone **1a** (52.1 mg, 0.24 mmol) and 3-(4-methoxyphenyl)-1,4,2-dioxazol-5-one **2e** (38.6 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) afforded **3ae** as a pale yellow solid (47.4 mg, 68%). $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.43-8.37 (2H, m), 7.92-7.86 (2H, m), 7.67-7.53 (5H, m), 7.46-7.41 (1H, m), 7.26-7.19 (1H, m), 6.99-6.93 (2H, m), 3.86 (3H, s). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 162.1, 157.7, 147.4, 140.7, 134.3, 133.7, 130.4, 130.0, 129.2, 128.6, 128.4, 125.7, 124.7, 113.4, 55.3; one aromatic signal was missing probably due to overlapping. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 15.7 (major) and 20.6 (minor) min. $[\alpha]_D^{23.5} = +237.6$ ($c = 0.68$, CHCl_3). **Rf** 0.23 (DCM/acetone = 39/1). Reported compound.^[S5]



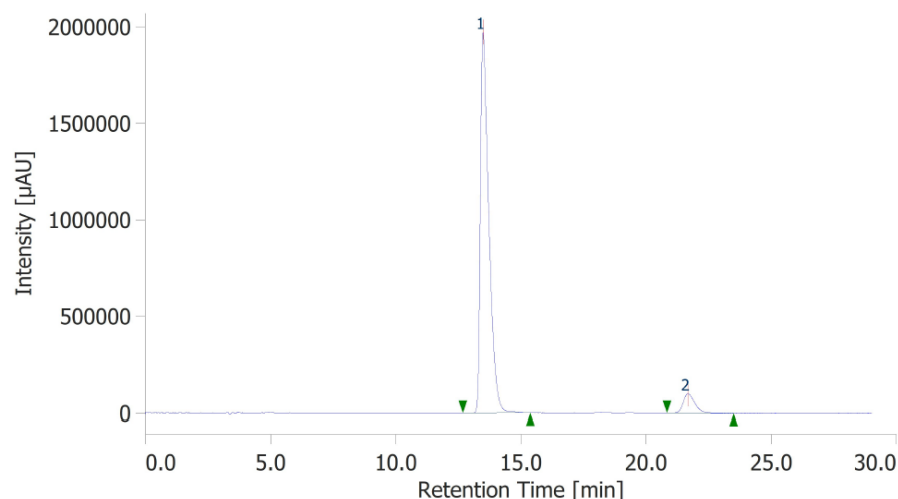
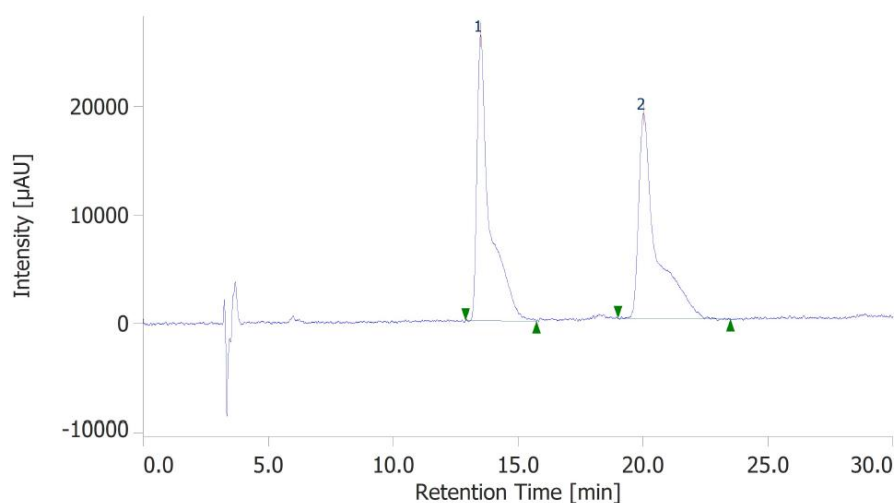
1-phenyl-3-(m-tolyl)benzo[e][1,2,4]thiadiazine 1-oxide (3af)



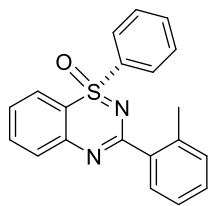
General Procedure A1 using iminodiphenyl- λ^6 -sulfanone **1a** (52.1 mg, 0.24 mmol) and 3-(m-tolyl)-1,4,2-dioxazol-5-one **2f** (35.4 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) afforded **3af** as a colorless solid (43.9 mg, 66%).

^1H NMR (CDCl_3 , 400 MHz) δ 8.27-8.20 (2H, m), 7.91-7.85 (2H, m), 7.69-7.60 (3H, m), 7.60-7.53 (2H, m), 7.44-7.41 (1H, m), 7.37-7.21 (3H, m), 2.42 (3H, s). **^{13}C NMR** (CDCl_3 , 100

MHz) δ 158.2, 147.3, 140.7, 137.7, 137.5, 134.3, 133.8, 131.8, 129.2, 129.1, 128.6, 128.1, 126.1, 125.8, 124.7, 113.7, 21.4; one aromatic signal was missing probably due to overlapping. **HPLC** (chiral column: DAICEL CHIRALPAK IE; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 300 nm): t_R = 13.5 (major) and 21.7 (minor) min. **$[\alpha]_D^{23.3}$** = +182.7 (c = 1.01, CHCl_3). **Rf** 0.47 (DCM/acetone = 39/1). Reported compound.^[S5]



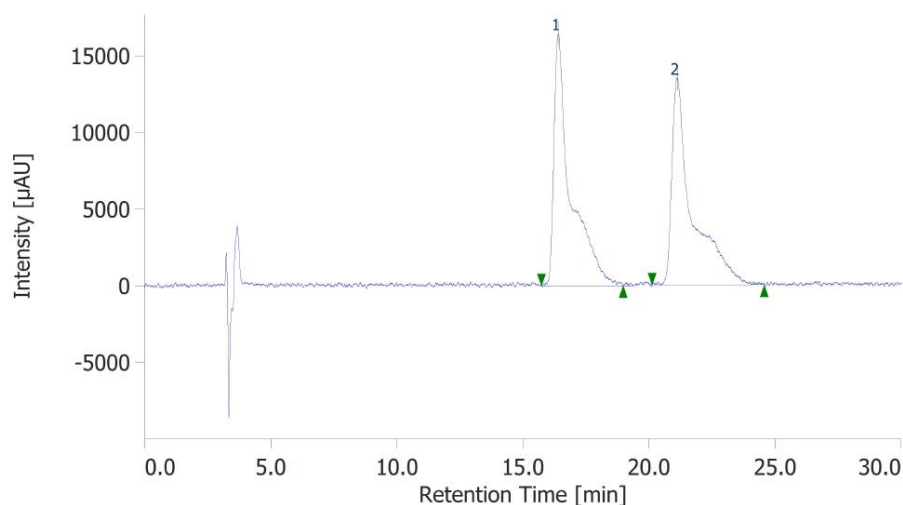
1-phenyl-3-(o-tolyl)benzo[e][1,2,4]thiadiazine 1-oxide (**3ag**)



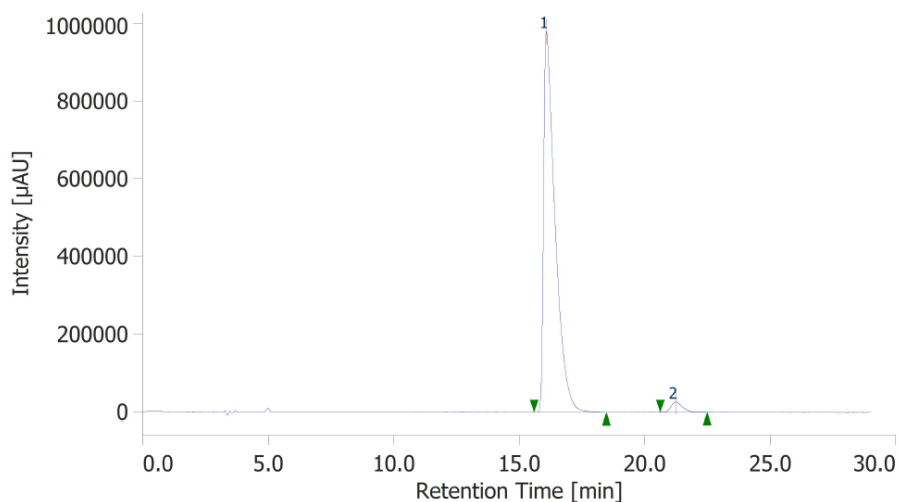
General Procedure A1 using iminodiphenyl- λ^6 -sulfanone **1a** (52.1 mg, 0.24 mmol) and 3-(o-tolyl)-1,4,2-dioxazol-5-one **2g** (35.4 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) twice afforded **3ag** as a colorless solid (47.4 mg, 71%).

¹H NMR (CDCl₃, 400 MHz) δ 7.93-7.87 (2H, m), 7.84 (1H, dd, J = 7.4, 1.6 Hz), 7.65-7.61 (3H, m), 7.61-7.55 (2H, m), 7.46-7.41 (1H, m), 7.33-7.22 (4H, m), 2.64 (3H, s). **¹³C NMR**

(CDCl₃, 100 MHz) δ 160.8, 146.9, 140.2, 138.4, 137.1, 134.3, 133.9, 131.1, 129.5, 129.4, 129.2, 128.6, 128.5, 126.4, 125.7, 124.6, 113.0, 21.0. **HPLC** (chiral column: DAICEL CHIRALPAK IE; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 300 nm): t_R = 16.1 (major) and 21.2 (minor) min. $[\alpha]_D^{22.6}$ = +125.9 (c = 0.27, CHCl₃). **Rf** 0.47 (DCM/acetone = 39/1). Reported compound.^[85]

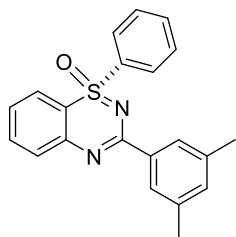


#	tR [min]	Area%
1	16.397	50.163
2	21.113	49.837

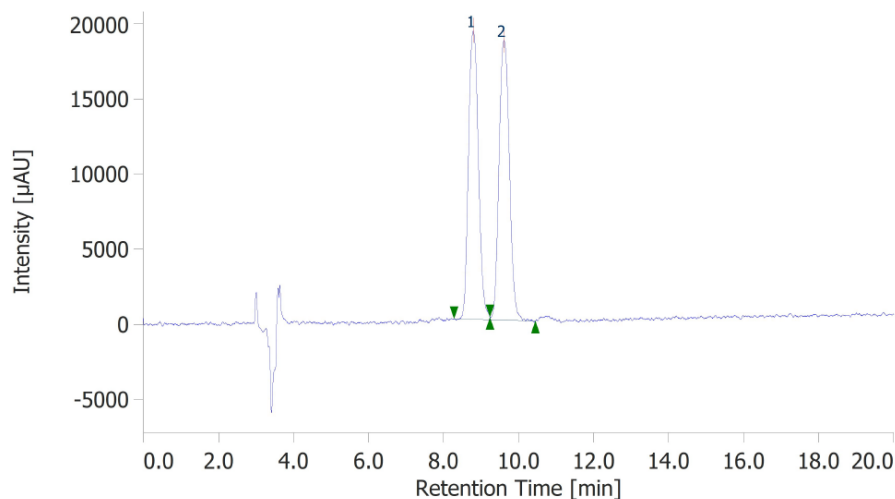


#	tR [min]	Area%
1	16.073	97.508
2	21.213	2.492

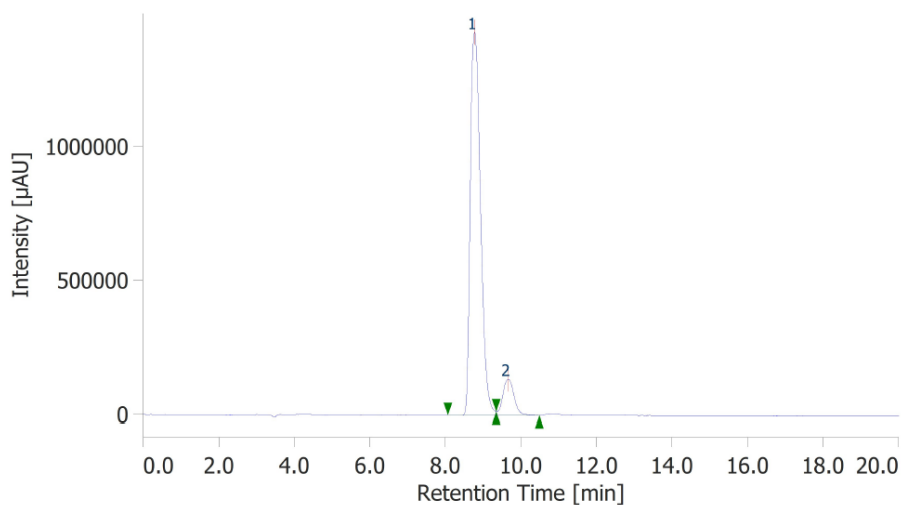
3-(3,5-dimethylphenyl)-1-phenylbenzo[e][1,2,4]thiadiazine 1-oxide (3ah)



General Procedure A1 using iminodiphenyl- λ^6 -sulfanone **1a** (52.1 mg, 0.24 mmol) and 3-(3,5-dimethylphenyl)-1,4,2-dioxazol-5-one **2h** (38.2 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) afforded **3ah** as a pale yellow solid (49.6 mg, 72%). **MP** 131.8-136.8 °C. **¹H NMR** (CDCl₃, 400 MHz) δ 8.05 (2H, d, J = 0.5 Hz), 7.90-7.86 (2H, m), 7.69-7.59 (3H, m), 7.59-7.53 (2H, m), 7.44 (1H, dt, J = 8.0, 0.7 Hz), 7.28-7.22 (1H, m), 7.12 (1H, d, J = 0.6 Hz), 2.39 (6H, s). **¹³C NMR** (CDCl₃, 100 MHz) δ 158.4, 147.3, 140.8, 137.7, 137.4, 134.3, 133.7, 132.8, 129.2, 128.6, 126.4, 126.1, 124.8, 113.7, 21.3; one aromatic signal was missing probably due to overlapping. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 350 nm): t_R = 8.8 (major) and 9.7 (minor) min. **HRMS** (ESI): m/z calculated for C₂₁H₁₉ON₂S⁺ [M+H]⁺: 347.1213, found: 347.1204. **[α]_D^{22.6}** = +181.43 (c = 0.78, CHCl₃). **Rf** 0.50 (DCM/acetone = 39/1).

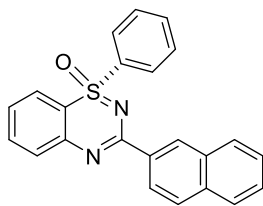


#	tR [min]	Area%
1	8.790	49.695
2	9.603	50.305

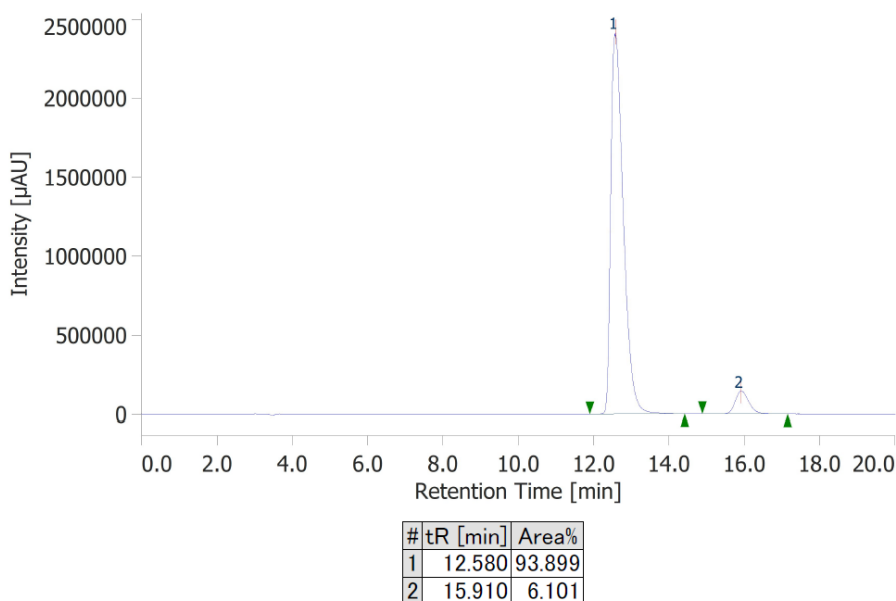
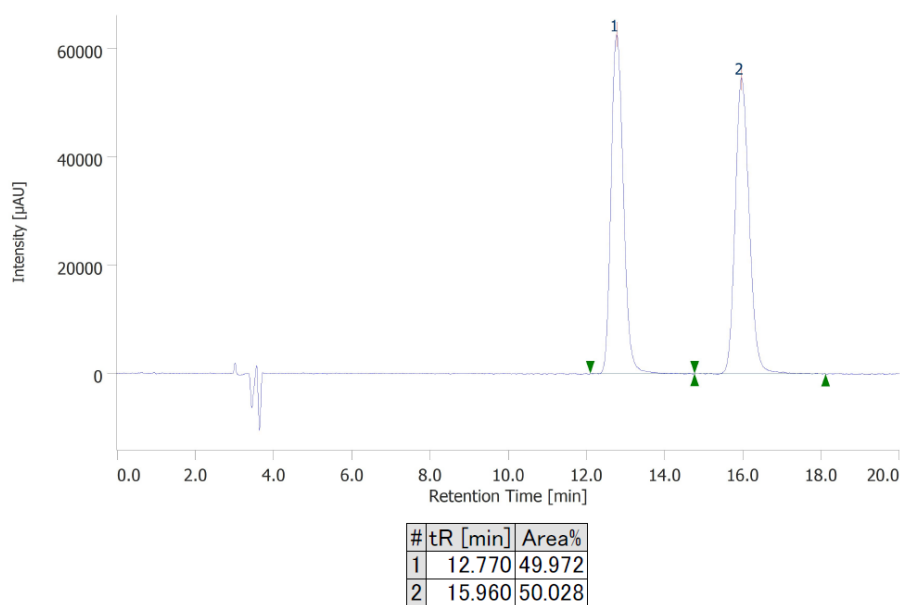


#	tR [min]	Area%
1	8.773	90.761
2	9.660	9.239

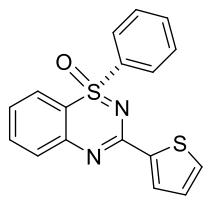
3-(naphthalen-2-yl)-1-phenylbenzo[e][1,2,4]thiadiazine 1-oxide (3ai)



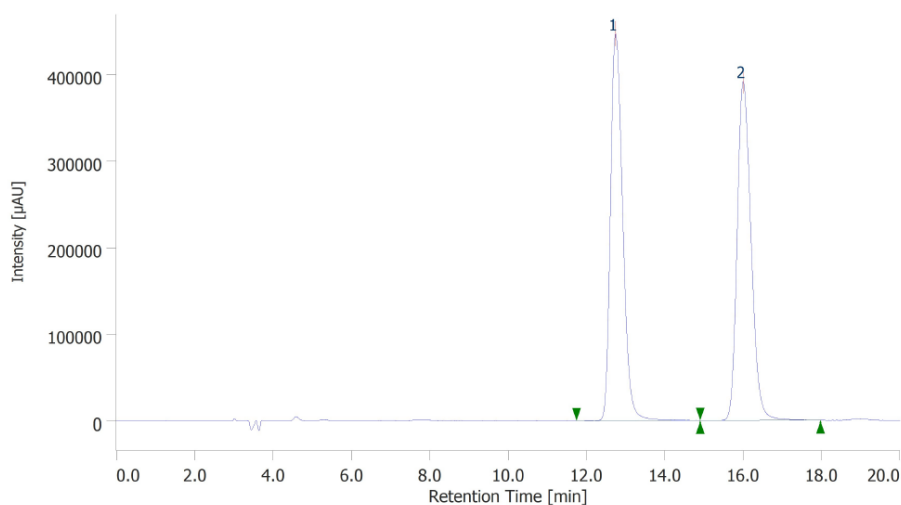
General Procedure A1 using iminodiphenyl- λ^6 -sulfanone **1a** (52.1 mg, 0.24 mmol) and 3-(naphthalen-2-yl)-1,4,2-dioxazol-5-one **2i** (42.6 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) afforded **3ai** as a pale yellow solid (51.7 mg, 70%). **¹H NMR** (CDCl₃, 400 MHz) δ 8.96 (1H, s), 8.61-8.53 (1H, m), 7.99-7.83 (5H, m), 7.75-7.69 (1H, m), 7.68-7.60 (2H, m), 7.60-7.43 (5H, m), 7.29-7.23 (1H, m). **¹³C NMR** (CDCl₃, 100 MHz) δ 157.9, 147.2, 140.6, 134.9, 134.8, 134.4, 133.8, 132.9, 129.3, 129.2, 128, 6, 127.7, 127.6, 127.1, 126.3, 126.1, 125.3, 124.8, 113.8; two aromatic signals were missing probably due to overlapping. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 370 nm): t_R = 12.6 (major) and 15.9 (minor) min. $[\alpha]_D^{23.3}$ = +233.0 (c = 0.75, CHCl₃). **Rf** 0.55 (DCM/acetone = 39/1). Reported compound.^[S5]



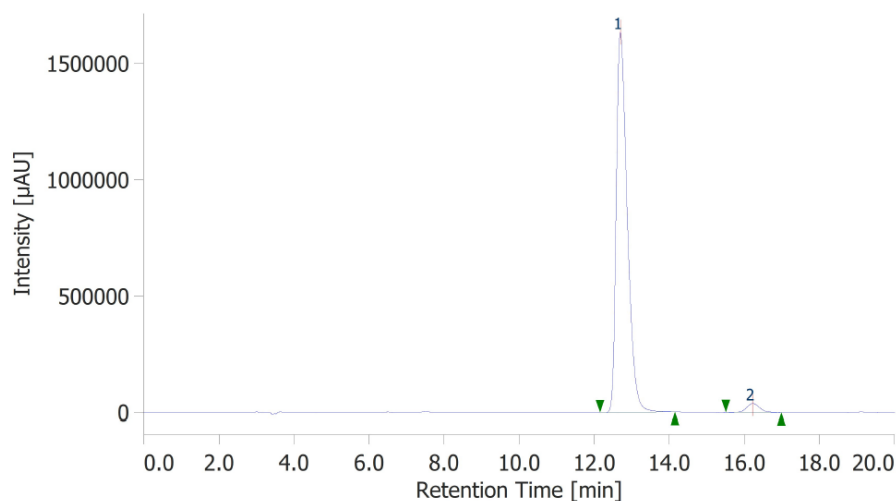
1-phenyl-3-(thiophen-2-yl)benzo[e][1,2,4]thiadiazine 1-oxide (3aj)



General Procedure A1 using iminodiphenyl- λ^6 -sulfanone **1a** (52.1 mg, 0.24 mmol) and 3-(thiophen-2-yl)-1,4,2-dioxazol-5-one **2j** (33.8 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) afforded **3aj** as a colorless solid (48.8 mg, 75%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.97 (1H, d, J = 3.6 Hz), 7.92 (2H, d, J = 7.6 Hz), 7.71-7.57 (5H, m), 7.50 (1H, d, J = 4.9 Hz), 7.44 (1H, d, J = 8.1 Hz), 7.31-7.22 (1H, m), 7.13 (1H, t, J = 4.3 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 154.3, 147.1, 143.5, 140.4, 134.4, 133.9, 130.3, 130.0, 129.3, 128.6, 128.2, 127.8, 125.9, 124.8, 113.8. HPLC (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 300 nm): t_R = 12.7 (major) and 16.2 (minor) min. $[\alpha]_D^{23.2} = +257.6$ (c = 1.22, CHCl_3). R_f 0.42 (DCM/acetone = 39/1). Reported compound.^[S5]

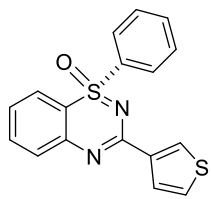


#	tR [min]	Area%
1	12.740	50.052
2	15.997	49.948

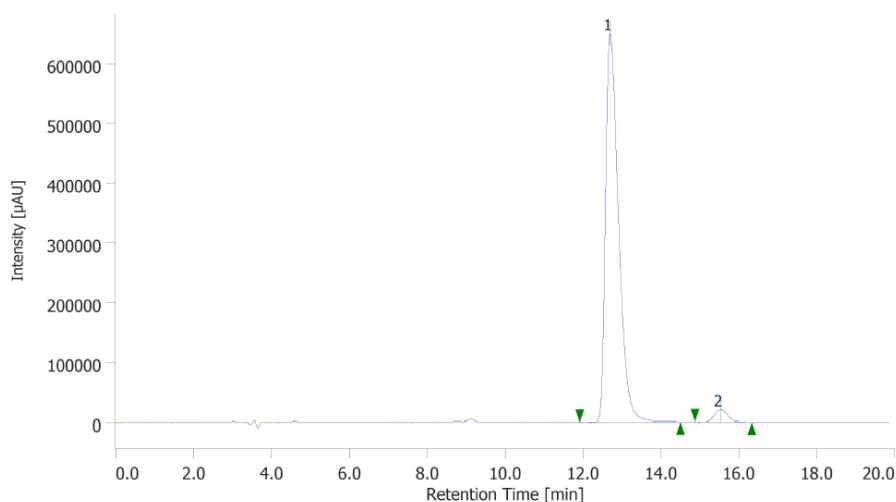
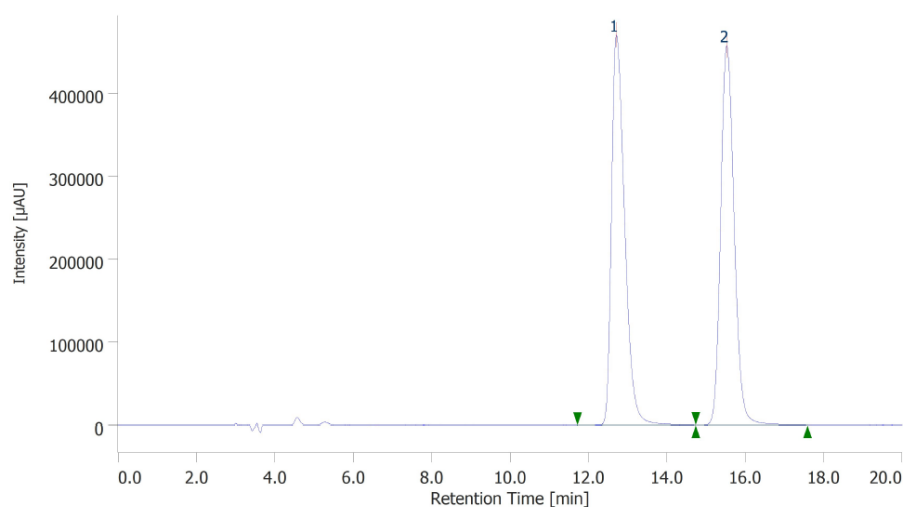


#	tR [min]	Area%
1	12.690	97.408
2	16.213	2.592

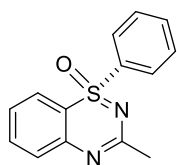
1-phenyl-3-(thiophen-3-yl)benzo[e][1,2,4]thiadiazine 1-oxide (**3ak**)



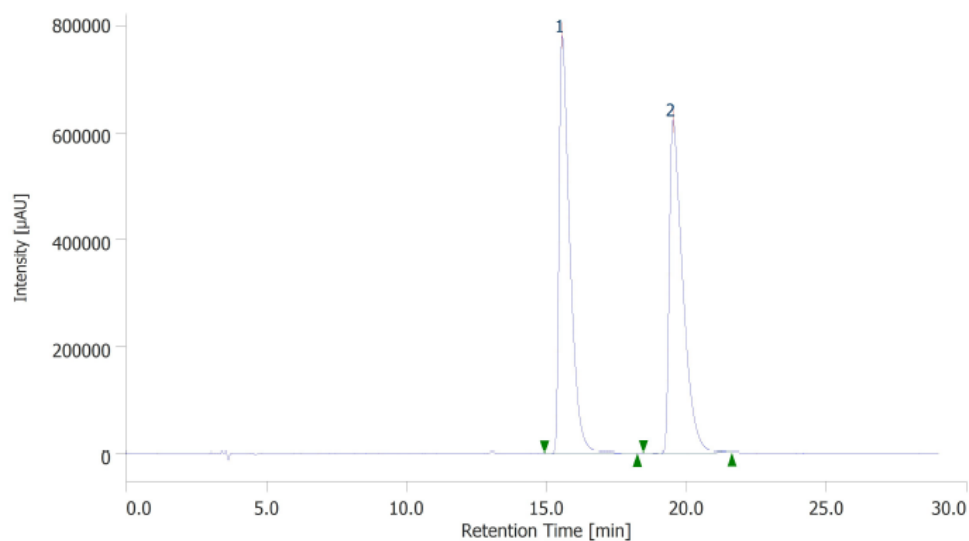
General Procedure A1 using iminodiphenyl- λ^6 -sulfanone **1a** (52.1 mg, 0.24 mmol) and 3-(thiophen-3-yl)-1,4,2-dioxazol-5-one **2k** (33.8 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) afforded **3ak** as a colorless solid (35.0 mg, 54%). **MP** 188.5-190.8 °C. **¹H NMR** (CDCl₃, 400 MHz) δ 8.24 (1H, dd, J = 3.1, 1.2 Hz), 7.92-7.85 (3H, m), 7.67-7.54 (5H, m), 7.42 (1H, dt, J = 8.0, 1.0 Hz), 7.32 (1H, dd, J = 5.1, 3.1 Hz), 7.27-7.20 (1H, m). **¹³C NMR** (CDCl₃, 100 MHz) δ 154.7, 147.4, 141.7, 140.7, 134.4, 133.8, 129.3, 129.1, 128.6, 128.4, 127.7, 126.0, 125.4, 124.8, 113.8. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 12.7 (major) and 15.5 (minor) min. **HRMS** (ESI): m/z calculated for C₁₇H₁₂ON₂NaS₂⁺ [M+Na]⁺: 347.0283, found: 347.0274. **[α]_D^{23.3}** = +226.7 (c = 0.81, CHCl₃). **R_f** 0.45 (DCM/acetone = 39/1).



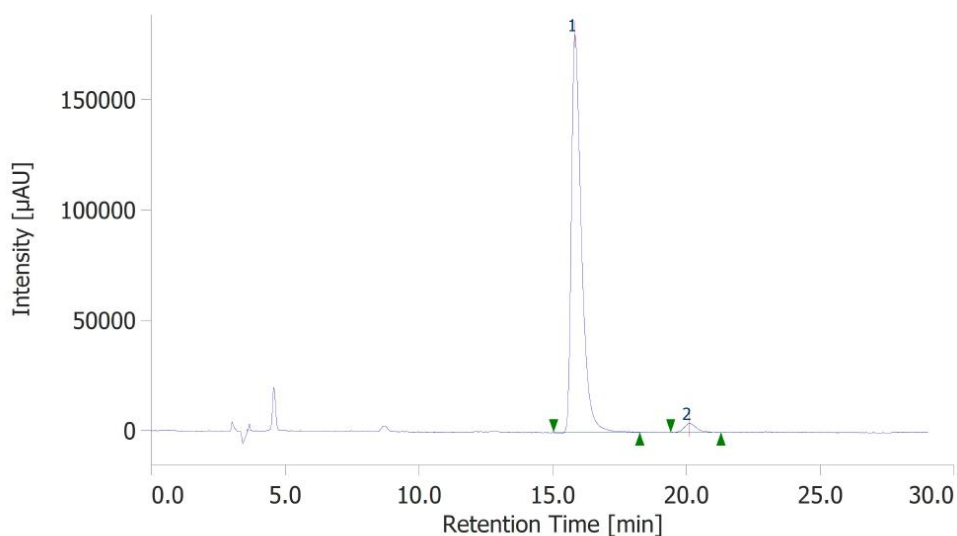
3-methyl-1-phenylbenzo[e][1,2,4]thiadiazine 1-oxide (3a)



General Procedure A2 using iminodiphenyl- λ^6 -sulfanone **1a** (52.1 mg, 0.24 mmol) and 3-methyl-1,4,2-dioxazol-5-one **2l** (20.2 μ L, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 20/1 twice and 20/1 to 10/1) afforded **3a** as a pale yellow oil (25.9 mg, 51%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.84 (2H, d, J = 7.7 Hz), 7.69-7.55 (4H, m), 7.52 (1H, d, J = 8.2 Hz), 7.39 (1H, d, J = 8.0 Hz), 7.25 (1H, t, J = 8.0 Hz), 2.52 (3H, s). ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.0, 146.7, 140.2, 134.5, 133.9, 129.3, 128.5, 127.5, 126.1, 124.7, 112.8, 27.8. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 15.8 (major) and 20.1 (minor) min. **HRMS** (ESI): m/z calculated for $\text{C}_{14}\text{H}_{13}\text{ON}_2\text{S}^+ [\text{M}+\text{H}]^+$: 257.0743, found: 257.0735. $[\alpha]_D^{23.0} = -30.3$ (c = 0.65, CHCl_3). **Rf** 0.13 (DCM/acetone = 39/1).

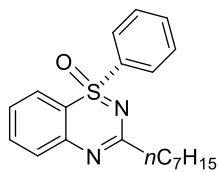


#	tR [min]	Area%
1	15.563	50.117
2	19.520	49.883

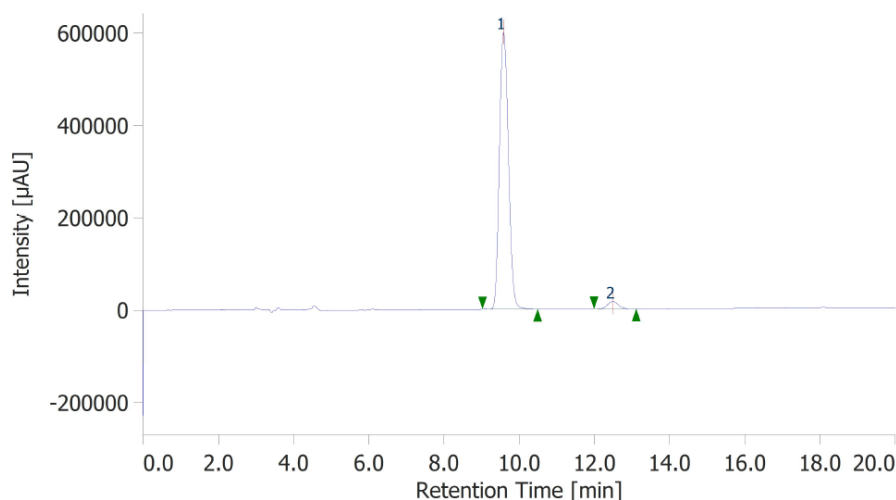
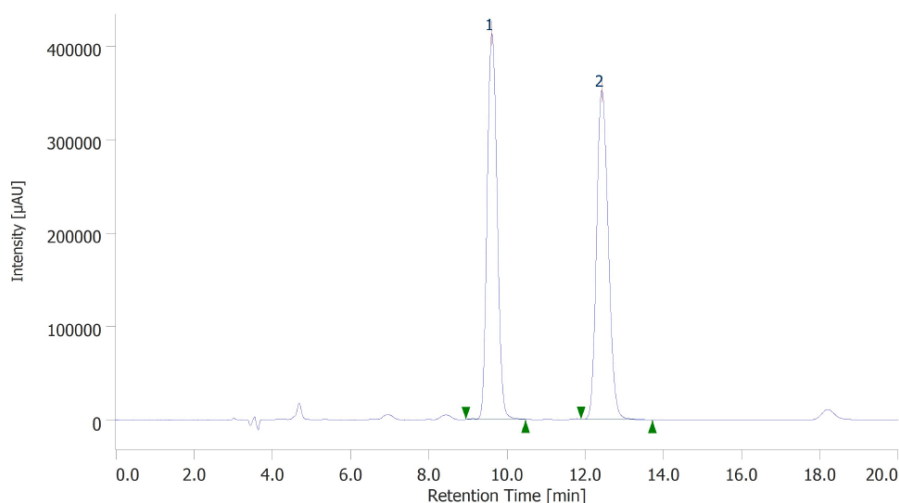


#	tR [min]	Area%
1	15.823	97.347
2	20.100	2.653

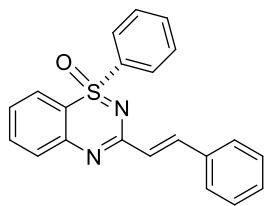
3-heptyl-1-phenylbenzo[*e*][1,2,4]thiadiazine 1-oxide (**3am**)



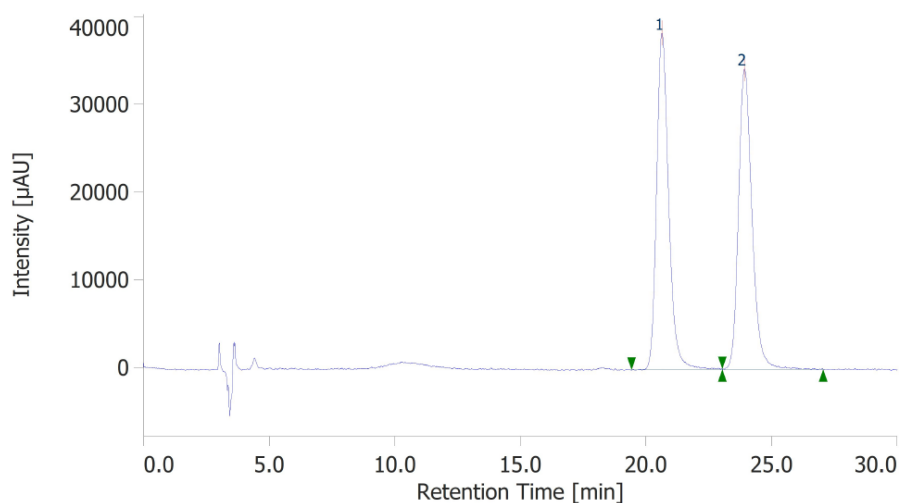
General Procedure A2 using iminodiphenyl- λ^6 -sulfanone **1a** (52.1 mg, 0.24 mmol) and 3-heptyl-1,4,2-dioxazol-5-one **2m** (37.0 μ L, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1 twice, 39/1 to 20/1, and 20/1) afforded **3am** as a yellow oil (35.8 mg, 53%). ¹H NMR (CDCl₃, 400 MHz) δ 7.84 (1H, *J* = 8.1 Hz), 7.68-7.54 (4H, m), 7.53 (1H, d, *J* = 8.3 Hz), 7.39 (1H, d, *J* = 8.0 Hz), 7.25 (1H, m), 2.71 (2H, t, *J* = 7.8 Hz), 1.91-1.80 (2H, m), 1.47-1.26 (8H, m), 0.87 (3H, t, *J* = 6.6 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 165.4, 146.9, 140.4, 134.4, 133.8, 129.2, 128.5, 127.8, 125.9, 124.7, 113.1, 41.3, 31.7, 29.4, 29.1, 27.8, 22.6, 14.0. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): *t_R* = 9.6 (major) and 12.5 (minor) min. [α]_D^{22.7} = +17.9 (*c* = 0.31, CHCl₃). **R_f** 0.33 (DCM/acetone = 39/1). Reported compound.^[S5]



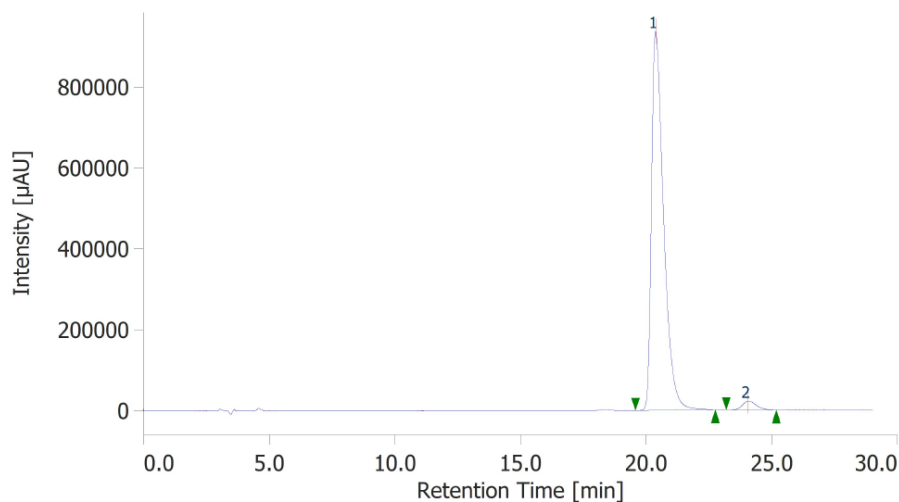
(*E*)-1-phenyl-3-styrylbenzo[*e*][1,2,4]thiadiazine 1-oxide (3an)



General Procedure A1 using iminodiphenyl- λ^6 -sulfanone **1a** (52.1 mg, 0.24 mmol) and (*E*)-3-styryl-1,4,2-dioxazol-5-one **2n** (37.8 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/acetone = 39/1) twice afforded **3an** a pale yellow solid (43.4 mg, 63%). **¹H NMR** (CDCl₃, 400 MHz) δ 7.92-7.82 (3H, m), 7.68-7.55 (7H, m), 7.46-7.40 (1H, m), 7.39-7.28 (3H, m), 7.28-7.21 (1H, m), 7.05 (1H, d, *J* = 15.7 Hz). **¹³C NMR** (CDCl₃, 100 MHz) δ 158.4, 147.1, 140.6, 139.6, 135.8, 134.4, 133.8, 129.3, 129.1, 128.7, 128.6, 128.1, 127.8, 127.7, 126.2, 124.9, 114.3. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): *t_R* = 20.4 (major) and 24.1 (minor) min. [α]_D^{22.5} = +315.0 (*c* = 0.47, CHCl₃). **R_f** 0.43 (DCM/acetone = 39/1). Reported compound.^[S5]



#	tR [min]	Area%
1	20.627	50.095
2	23.907	49.905



#	tR [min]	Area%
1	20.367	97.386
2	24.053	2.614

2-4. Mechanistic studies

H/D exchange experiment with dioxazolone **1a** (Scheme 3a)

In an argon-filled glovebox, a screw-cap test tube was charged with Cp*Co(CO)I₂ (4.8 mg, 0.01 mmol, 10 mol %), AgOTf (5.1 mg, 0.02 mmol, 20 mol %), chiral acid **CCA 11** (4.4 mg, 0.01 mmol, 10 mol %) and 2-propanol-*d*₆ (2 mL). After the mixture was stirred for 10 min, MS5A (20 mg), sulfoximine **1a** (26.1 mg, 0.12 mmol, 1.2 equiv.), and dioxazolone **2a** (16.3mg, 0.1 mmol, 1.0 equiv.) were successively added. The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 20 h at 30 °C. The reaction mixture was quenched by adding sat. EDTA aq., and the mixture was extracted with AcOEt twice. The organic layers were combined, dried over Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (DCM/acetone = 40/1 to 25/1 to 10/1) to afford **1a** (8.7 mg, 40%), **3aa** (2.2 mg, 7%) and **8aa** (24.3 mg, 72%), which were further purified by preparative TLC and analyzed by ¹H NMR to evaluate deuterium incorporation. The NMR spectra were shown in Figure S1, S2, and S3.

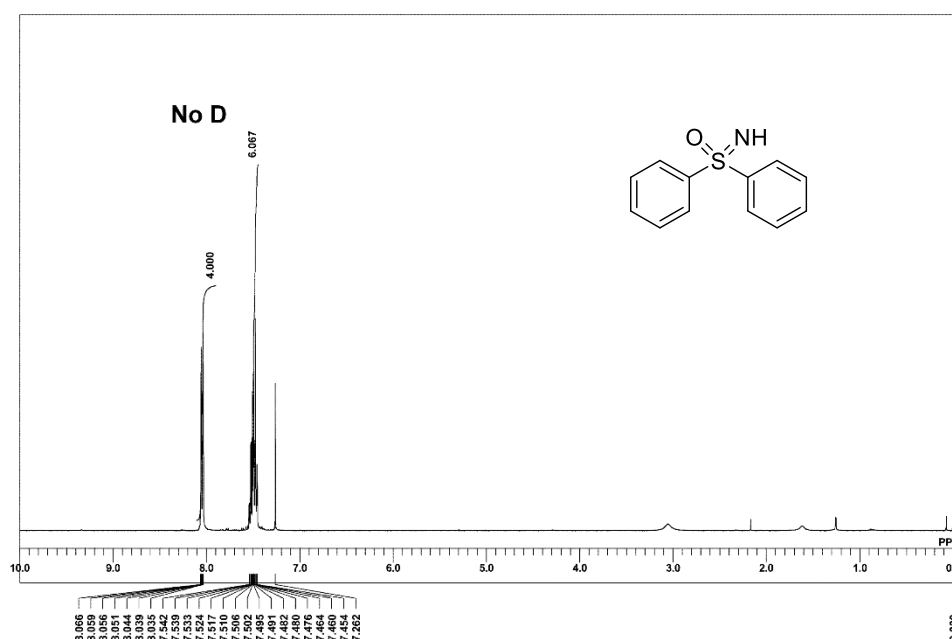


Figure S1. ¹H NMR spectrum of **1a** in CDCl₃ (H/D exchange with **2a**).

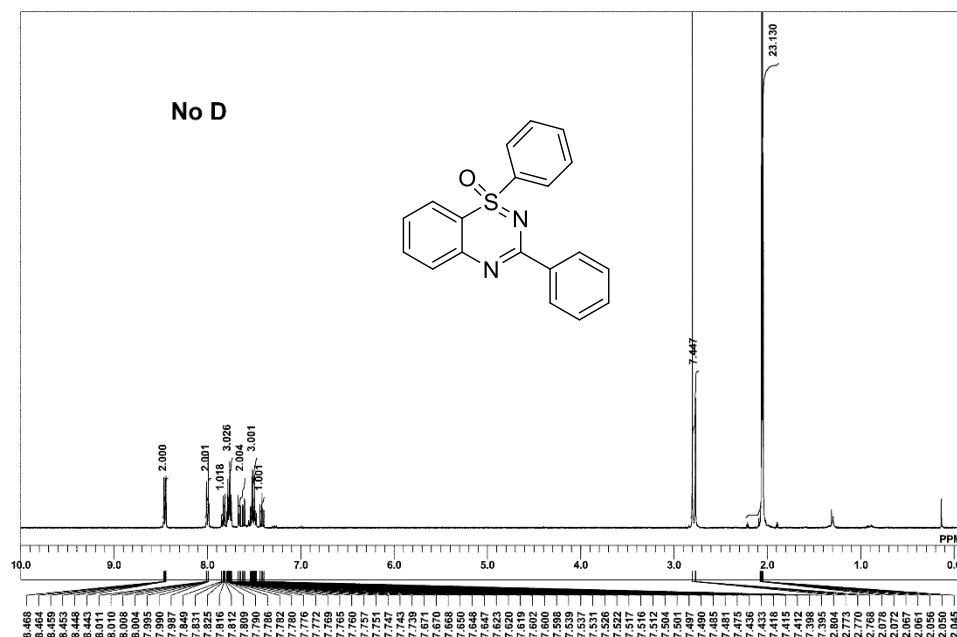


Figure S2. ^1H NMR spectrum of **3aa** in acetone- d_6 (H/D exchange with **2a**).

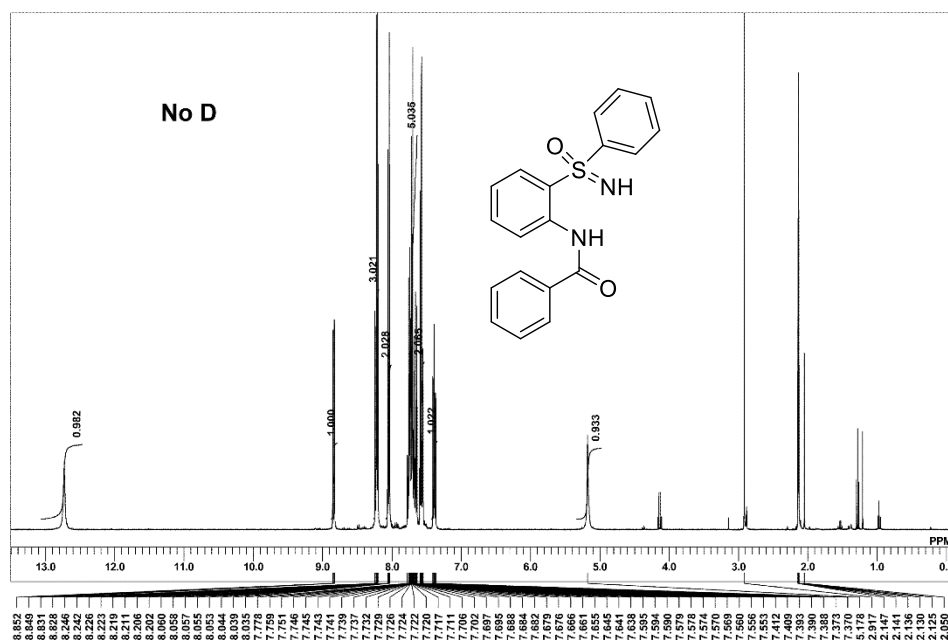


Figure S3. ^1H NMR spectrum of **4aa** in acetone- d_6 (H/D exchange with **2a**).

H/D exchange experiment without dioxazolone **1a** (Scheme 3b)

In an argon-filled glovebox, a screw-cap test tube was charged with $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$ (2.4 mg, 0.005 mmol, 10 mol %), AgOTf (2.6 mg, 0.01 mmol, 20 mol %), chiral acid **CCA 11** (2.2 mg, 0.005 mmol, 10 mol %) and 2-propanol- d_6 (1 mL). After the mixture was stirred for 10 min, MS5A (10 mg) and sulfoximine **1a** (13.0 mg, 0.06 mmol, 1.2 equiv.)

were successively added. The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 20 h at 30 °C. The reaction mixture was quenched by adding sat. EDTA aq., and the mixture was extracted with AcOEt twice. The organic layers were combined, dried over Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (DCM/acetone = 20/1) to recover **1a** (12.9 mg, 99%), which was analyzed by ¹H NMR to evaluate deuterium incorporation. The ¹H NMR spectrum is shown in Figure S4.

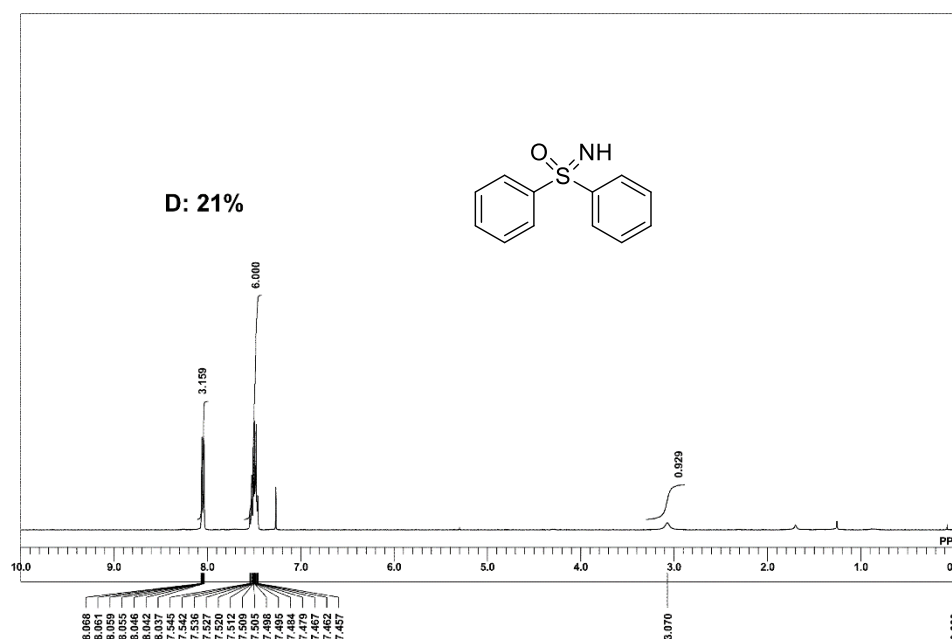


Figure S4. ¹H NMR spectrum of **1a** in CDCl₃ (H/D exchange without **2a**).

KIE experiments (Scheme 3c)

In an argon-filled glovebox, to a screw-cap vial was added Cp*Co(CO)I₂ (28.6 mg, 0.06 mmol), AgOTf (30.8 mg, 0.12 mmol), and *t*AmOH (2.4 mL). The mixture was stirred at room temperature to give a catalyst solution. A solution of dioxazolone was similarly prepared with dioxazolone **2a** (81.6 mg, 0.5 mmol) and *t*AmOH (2.0 mL).

To a test tube was charged with sulfoximine **1a** or **1a-d₁₀** (0.24 mmol, 1.2 equiv.) and *t*AmOH (3.4 mL). The mixture was stirred for 30 min until the sulfoximine was dissolved completely. To the mixture was successively added chiral acid **CCA 11** (8.8 mg, 0.02 mmol, 10 mol %), MS5A (40 mg), and the above-prepared catalyst solution (800 μL, 10 mol % catalyst). The test tube was brought out of the glovebox. To the mixture was added the above-prepared solution of dioxazolone **2a** in *t*AmOH (800 μL, 0.2 mmol of **2a**, 1.0 equiv.) at 30 °C. The reaction mixture was stirred at 30 °C, during which an aliquot of the mixture (800 μL) was taken via syringe at each reaction time and quenched by adding sat. EDTA aq. The quenched aliquot mixture was extracted with AcOEt twice, and the organic layers were combined, dried over Na₂SO₄, and evaporated under reduced pressure. The crude mixture was analyzed by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard to calculate the amount of product **8aa** or **8aa-d₉**. The area of NH (ca. 12.31 ppm in CDCl₃) was used to calculate the amount of **8aa** and **8aa-d₉**. The results are summarized in Figure S5 and Table S2.

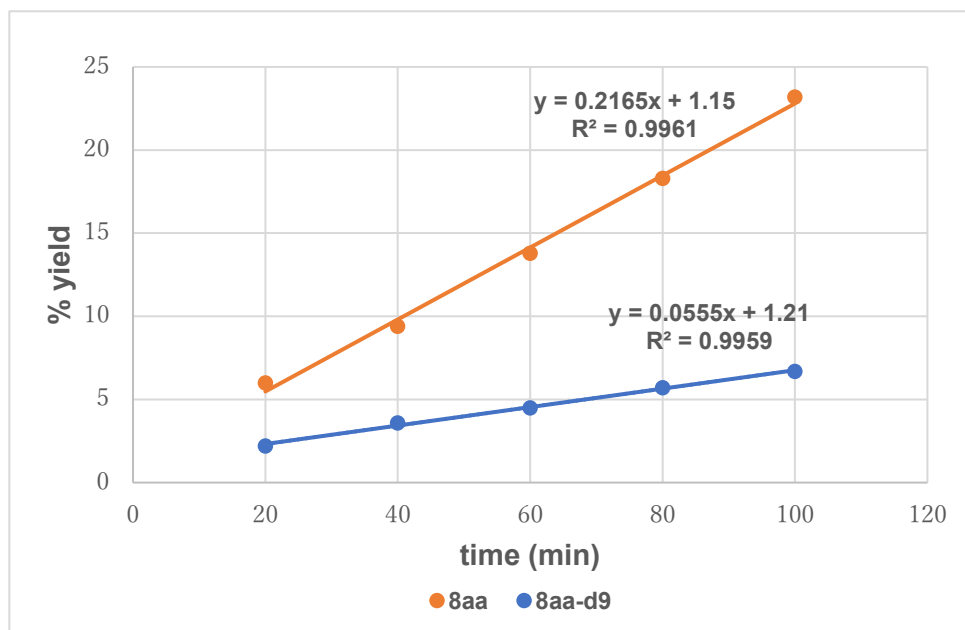


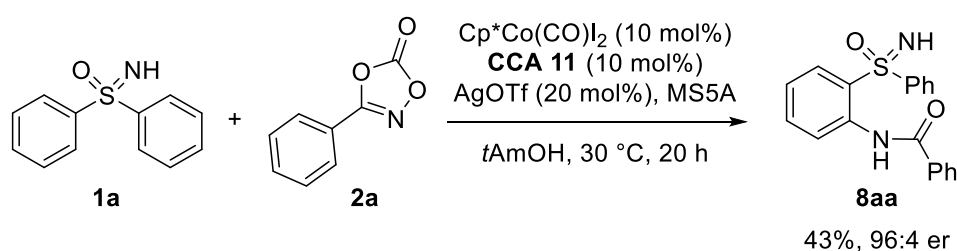
Figure S5. Results of KIE experiments.

Table S2. Yields (%) of **4aa** and **4aa-d₉** in KIE experiments.

	20 min	40 min	60 min	80 min	100 min
% 8aa	6.0	9.4	13.8	18.3	23.2
% 8aa-d₉	2.2	3.6	4.5	5.7	6.7

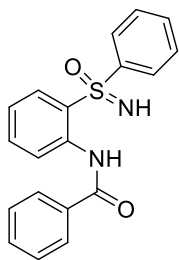
Cyclization experiment

Synthesis of **4aa**



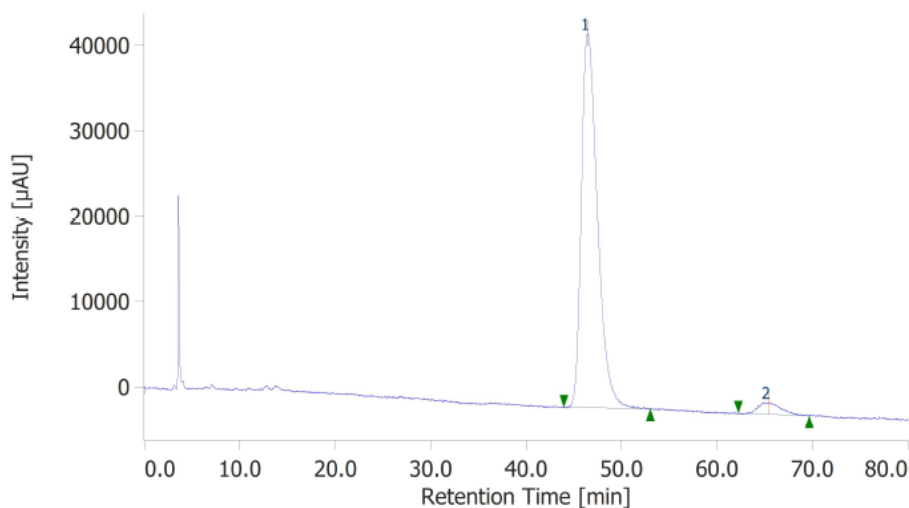
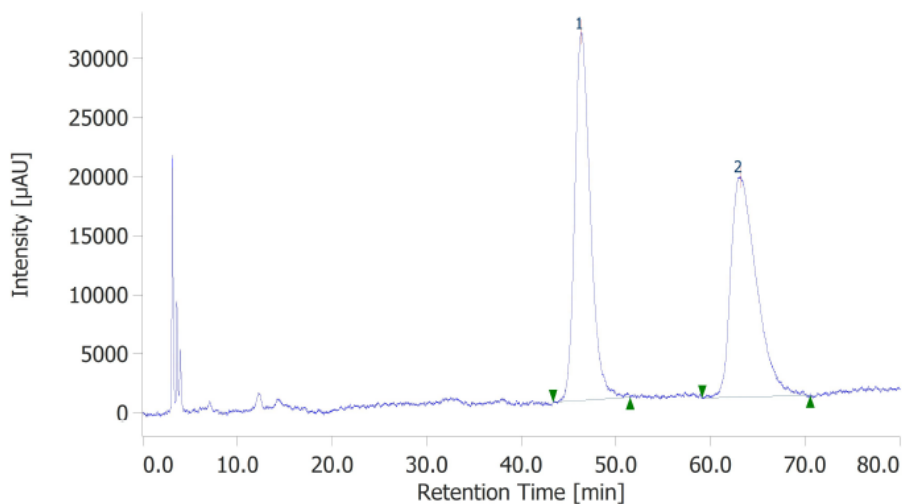
In an argon-filled glovebox, a screw-cap test tube was charged with $\text{Cp}^*\text{Co(CO)I}_2$ (4.8 mg, 0.01 mmol, 10 mol %), AgOTf (5.1 mg, 0.02 mmol, 20 mol %), chiral acid **CCA 11** (4.4 mg, 0.01 mmol, 10 mol %) and *t*AmOH (2 mL). After the mixture was stirred for 10 min, MS5A (20 mg), sulfoximine **1a** (26.1 mg, 0.12 mmol, 1.2 equiv.), and dioxazolone **2a** (16.3 mg, 0.10 mmol, 1.0 equiv.) were successively added. The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 20 h at 30 °C. The reaction mixture was quenched by adding K_2CO_3 (13.8 mg, 0.10 mmol, 1.0 equiv.) and MeOH (250 μL) to decompose the remaining dioxazolone **2a**. After stirred for 30 min, sat. EDTA aq. was added, and the mixture was extracted with AcOEt twice. The organic layers were combined, dried over Na_2SO_4 , and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography twice (DCM/acetone = 39/1 and 80/1) to afford **8aa** (14.3 mg, 0.043 mmol, 43%). The low yield would be due to the difficulty in the purification.

N-(2-(phenylsulfonimidoyl)phenyl)benzamide (8aa)

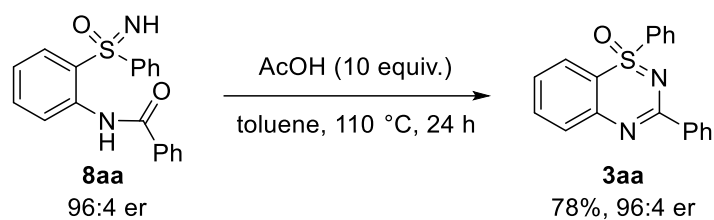


¹H NMR (CDCl₃, 400 MHz) δ 12.12 (1H, s), 8.75-8.64 (1H, m), 8.13-8.05 (3H, m), 7.88-7.83 (2H, m), 7.63-7.52 (4H, m), 7.52-7.46 (1H, m), 7.41-7.35 (2H, m), 7.25-7.20 (1H, m), 3.49 (1H, s). **¹³C NMR** (CDCl₃, 100 MHz) δ 165.1, 143.3, 137.7, 134.7, 134.3, 133.1, 132.2, 129.6, 129.3, 128.9, 127.9, 127.4, 127.0, 123.7, 122.3. **HPLC** (chiral column: DAICEL CHIRALPAK OD-H; solvent: hexane/2-propanol = 19/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 46.4 (major) and 65.4 (minor) min. [α]_D^{24.7} = +163.8 (c = 0.37, CHCl₃). **R_f** 0.18 (DCM/acetone = 80/1).

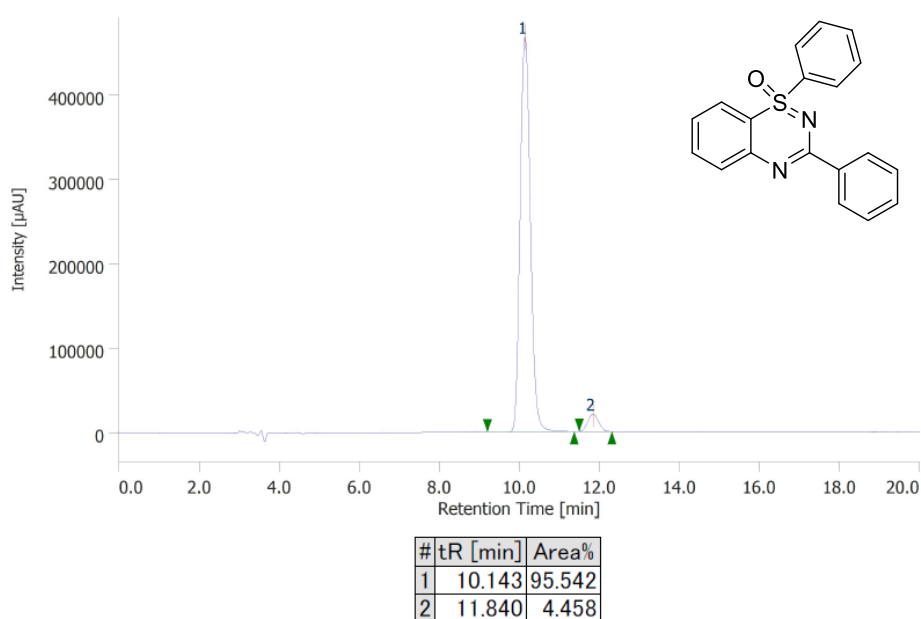
Reported compound.^[85]



Cyclization experiment of 4aa



A screw-cap test tube was charged with **8aa** (5 mg, 0.015 mmol, 1.0 equiv.), AcOH (8.5 μ L, 0.15 mmol, 10 equiv.), and toluene (300 μ L). The mixture was stirred at 110 °C for 24 h. The crude product was purified by silica gel column chromatography (DCM/acetone = 39/1) to afford **3aa** (3.7 mg, 0.012 mmol, 78%). The enantiomeric ratio of **3aa** was determined to be 96:4. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm).



2-5. Determination of the absolute configuration of **3aa**

Single crystal X-ray crystallography of **3aa**

A single crystal of **3aa** suitable for X-ray diffraction analysis (XRD) was obtained by recrystallization from AcOEt/hexane. Single crystal X-ray analysis was performed on a Rigaku R-Axis RAPID/S equipped with an imaging plate area detector and a graphite-monochromated Cu-K α radiation source ($\lambda = 1.5418 \text{ \AA}$). The detailed crystallographic data are available as a crystallographic information file (CIF), which is available from CCDC (2153931). The structure and crystal data are shown in **Figure S6** and **Table S3**.

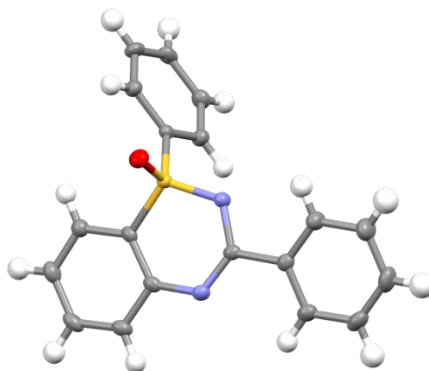


Figure S6. The structure of **3aa**

Table S3. Crystal data and structure refinement for **3aa**.

Identification code	shelx_trans	
Empirical formula	C ₁₉ H ₁₄ N ₂ O S	
Formula weight	318.38	
Temperature	133(2) K	
Wavelength	1.54187 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 9.7934(2) Å	$\alpha = 90^\circ$.
	b = 9.8034(2) Å	$\beta = 90^\circ$.
	c = 16.2101(3) Å	$\gamma = 90^\circ$.
Volume	1556.31(5) Å ³	
Z	4	
Density (calculated)	1.359 Mg/m ³	
Absorption coefficient	1.886 mm ⁻¹	
F(000)	664	
Crystal size	0.430 x 0.390 x 0.360 mm ³	
Theta range for data collection	5.273 to 68.220°.	
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -19 ≤ l ≤ 19	

Reflections collected	17703
Independent reflections	2818 [R(int) = 0.0252]
Completeness to theta = 67.687°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8012
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2818 / 0 / 209
Goodness-of-fit on F ²	1.094
Final R indices [I>2sigma(I)]	R1 = 0.0262, wR2 = 0.0714
R indices (all data)	R1 = 0.0264, wR2 = 0.0715
Absolute structure parameter	0.033(4)
Extinction coefficient	0.0084(6)
Largest diff. peak and hole	0.229 and -0.275 e.Å ⁻³

3. DFT Calculations and non-covalent interaction plots.

All DFT calculations and structure optimizations were performed using Gaussian 16 Rev C.01 program package^[S7] and GRRM17^[S8] unless otherwise noted.

We first prepared four initial structures (R1_init, R2_init, S1_init, S2_init, shown in Figure S7) that possess a common key core structure near to the transition state for the C–H bond cleavage (optimized near to the first-order saddle point at the M06L/LANL2DZ level of theory,^[S9,S10] but not completely converged).

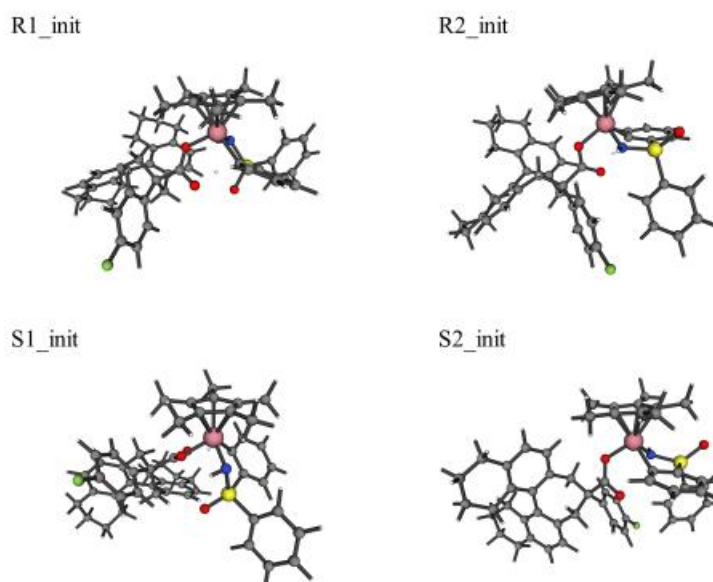


Figure S7. initial TS conformers

With these initial structures, we performed conformational searches using Grimme's crest 2.10.2^[S11] and xtb 6.3.3^[S12] programs. To keep the structures near to the desired transition state rather than local minima, key 7 atoms (Co, N of the sulfoximine, C and H to be cleaved, carbonyl C and two O of the carboxylate) were fixed with a force constant = 0.5. The conformation searches were run at GFN2-xTB level with iMTD-GC algorithm, and the energy threshold was set to 10 kcal/mol for each search. Total 445 conformers (R1_init: 107; R2_init 118; S1_init: 103; S2_init: 117) were generated. All the conformers obtained from R1_init are 5.0 kcal/mol higher in energy than the most stable conformer obtained from R2_init, and thus these conformers were omitted at this point. To further reduce the calculation cost, the similar conformers were summarized using cregen tool implemented in crest (R2_init: ewin 6, rthr 1, ethr 2; S1_init: ewin 6, rthr 1, ethr 2; S2_init: ewin 6, rthr 1.1, ethr 2;). Total 82 conformers remained (R2_init 29; S1_init: 23; S2_init: 30). These structures were partially optimized with fixing key 6 atoms (Co, N of the sulfoximine, C and H to be cleaved, two O of the carboxylate) at the M06L/LANL2DZ level of theory (opt = loose, maxcycle = 20). The obtained conformers were further summarized using cregen (ewin = 10, rthr = 0.5, ethr = 1.2) to give 5 conformers for the major *R*-enantiomer and 9 conformers for the minor *S*-enantiomer. These structures were fully optimized to transition state structures (first-order saddle points) at the M06L/def2-SVP^[S13] level of theory. The vibrational calculations were performed at the optimized geometry to confirm that the obtained structures were the desired transition state structures and to calculate the correction terms for Gibbs free energies. To obtain more accurate electronic energies, single point energies with the optimized geometries were

calculated at the M06/def2-TZVPP^[S14] level of theory with SMD implicit solvation (solvent = 2-methyl-2-propanol).^[S15] The calculated free energies of the final 14 transition state structures are summarized in Table S4–S6. The cartesian coordinates of these structures and the initial 4 structures used for the conformation searches are shown below.

Based on the calculated free energies, R_TS_1 was the most plausible transition state structure to give the major *R*-enantiomer (TS_{major}). Although R_TS_2 and R_TS_3 have non-negligible contribution, these structures are very similar to R_TS_1 and thus we provided the discussion based on R_TS_1 (TS_{major}). S2_TS_1 and S2_TS_2 were the most plausible transition states structures to give the minor *S*-enantiomer (S2_TS_1 = TS_{minor2}, S2_TS_2 = TS_{minor1}). For these three structures, IRC calculation were performed at the M06L/def2-SVP level of theory to confirm that they are the desired transition states for C–H bond cleavage. NCI plots were calculated by Multiwfn 3.7^[S16] using the wavefunction files (wfx files) generated at the single point energy calculations (M06/def2-TZVPP+SMD(*t*BuOH)), and visualized by VMD 1.9.4 (Figure 1).^[S17]

Table S4. Parameters of TS structures to afford major *R*-product

	EE (M06/def2-TZVPP+SMD(<i>t</i> BuOH)) (Hartrees)	Imaginary Frequency (cm ⁻¹)	G correction term (Hartrees)	G (Hartrees)	Relative G to R_TS_1 (kcal/mol)
R_TS_1	-4174.33525387	-1455.62	0.846687461933	-4173.48856640807	0
R_TS_2	-4174.33479953	-1459.10	0.847169939349	-4173.48762959065	0.59
R_TS_3	-4174.33475705	-1452.50	0.847603141571	-4173.48715390843	0.89
R_TS_4	-4174.33298844	-1446.53	0.848466648403	-4173.48452179160	2.54
R_TS_5	-4174.33141627	-1448.53	0.849744482671	-4173.48167178733	4.33

Table S5. Parameters of TS structures to afford minor *S*-product

	EE (M06/def2-TZVPP+SMD(<i>t</i> BuOH)) (Hartrees)	Imaginary Frequency (cm ⁻¹)	G correction term (Hartrees)	G (Hartrees)	Relative G to R_TS_1 (kcal/mol)
S1_TS_1	-4174.32760520	-1469.09	0.846905124179	-4173.48070007582	4.94
S1_TS_2	-4174.32717746	-1453.22	0.846666363288	-4173.48051109671	5.05
S1_TS_3	-4174.32594697	-1483.56	0.846823317299	-4173.47912365270	5.93
S1_TS_4	-4174.32634247	-1504.35	0.850245132001	-4173.47609733800	7.82

Table S6. Parameters of TS structures to give minor *S*-product

	EE (M06/def2-TZVPP+SMD(<i>t</i> BuOH)) (Hartrees)	Imaginary Frequency (cm ⁻¹)	G correction term (Hartrees)	G (Hartrees)	Relative G to R_TS_1 (kcal/mol)
S2_TS_1	-4174.32968908	-1460.16	0.844665797843	-4173.48502328216	2.22
S2_TS_2	-4174.33118332	-1493.41	0.846213031299	-4173.48497028870	2.26
S2_TS_3	-4174.32772051	-1461.41	0.848322812160	-4173.47939769783	5.75
S2_TS_4	-4174.32914174	-1499.26	0.851362736813	-4173.47777900319	6.77
S2_TS_5	-4174.32369419	-1493.21	0.851390462763	-4173.47230372724	10.20

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C	5.064555791464	-3.066187936218	-1.111681575481	S	2.876546299411	0.951177001179	-1.542038048911
C	5.634762264748	-2.084869640102	-1.938379909436	N	2.394880598590	1.150682149369	0.139879376709
C	5.010938430606	-0.831784034948	-2.070138480399	H	3.433177330149	-3.593886067225	0.189191322682

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H -4.948857889588 1.717777400186 1.388050434298
C -3.615228344867 4.421764492717 -1.115807777725
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H -1.447135175977 -3.595683071203 -1.683213584937
C 0.584649366836 -5.237305141657 0.462394955431
H 1.439729668927 -4.459355387066 2.274068730923
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R_TS_2

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C 4.892035274475 -1.204340968520 2.139360752880
C 3.901722769555 -0.870233405822 1.221430727838
C 2.575605505656 -1.339791925342 1.277425031845
S 4.365483985554 0.130540436503 -0.171841490034
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Chapter 2: Site-selective C(sp³)-H functionalization and successive C(sp³)-H/C(sp²)-H functionalization by geometry control in directing group

Section 1: Introduction

C-H functionalization is an attractive tool to modify organic molecules; however, challenges remain in manipulating selectivity in C-H activation. One major issue concerns the differentiation between C(sp³)-H and C(sp²)-H functionalization. C-H activation by high-valent transition-metal catalysts typically proceeds via a concerted metallation-deprotonation (CMD) mechanism, in which the hydrogen atom is abstracted as a proton by a weak base.¹ Consequently, the acidity of the C-H bond significantly influences the activation energy. Because C(sp³)-H bonds are less acidic than C(sp²)-H bonds, C(sp²)-H activation generally preferentially proceeds. When a substrate contains both C(sp³)-H and C(sp²)-H bonds in accessible positions, either exclusive C(sp²)-H functionalization or a mixture of C(sp²)-H and C(sp³)-H functionalized products is typically observed (**Figure 1**, above).² In C(sp³)-H amidation reported by Chang and co-workers, a substrate with both C(sp³)-H and C(sp²)-H bonds gave a mixture of C(sp²)-H and C(sp³)-H functionalized products. (**Figure 1**, bottom).³

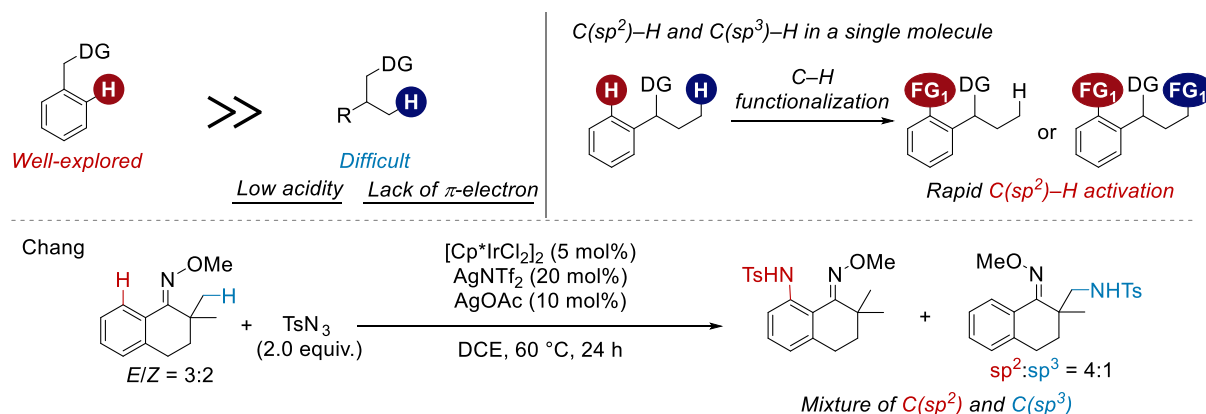


Figure 1. Difficulty of site-selective C(sp³)-H functionalization in a single molecule

As mentioned above, site-selective C(sp³)-H functionalization in molecules containing both C(sp³)-H and C(sp²)-H bonds are inherently challenging. Nevertheless, several research groups have reported strategies for achieving such selectivity using transition-metal catalysts. Huang and co-workers demonstrated that a low-valent Ir(I) complex bearing a bulky pincer-type ligand enabled site-selective intramolecular C(sp³)-H silylation (**Figure 2**).⁴ In contrast, the use of a less bulky ligand such as phenanthroline predominantly afforded the corresponding C(sp²)-H silylated product.

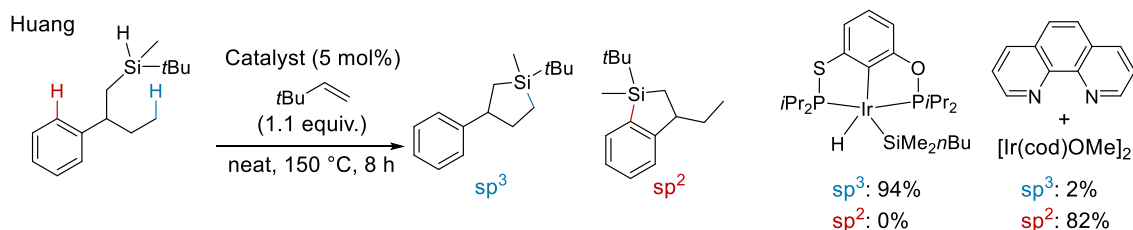


Figure 2. Site-selective C(sp³)-H silylation by Ir(I)

In high-valent transition-metal catalysis, Yu and co-workers reported C(sp³)-H iodination of oxime ethers prepared from hydroxyl amines with a carboxylic acid and ketones bearing aryl and bulky alkyl substituents using a palladium catalyst (**Figure 3**).⁵ Bidentate directing group facilitated C-H activation and bulky alkyl group promoted the site-selective C(sp³)-H iodination.

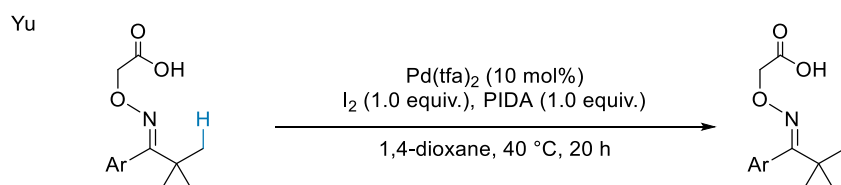


Figure 3. Site-selective C(sp³)-H iodination by Pd(II)

Another strategy involves the use of substrates in which C(sp²)-H activation forms a six-membered metallacycle, whereas C(sp³)-H activation generates a five-membered metallacycle.⁶ Because five-membered metallacycles generally form more rapidly than six-membered ones, C(sp³)-H functionalization becomes kinetically favored (**Figure 4**). These examples represent pioneering works in site-selective C(sp³)-H functionalization under high-valent metal catalysis. However, they often require designer's directing groups, and achieving successive C-H functionalization within a single molecule remains challenging.

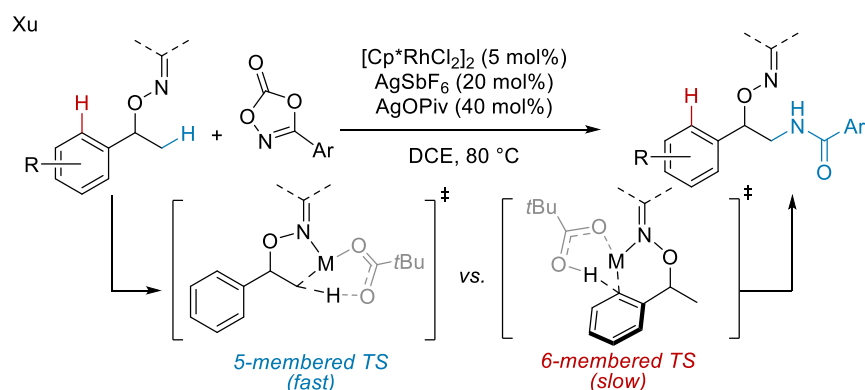
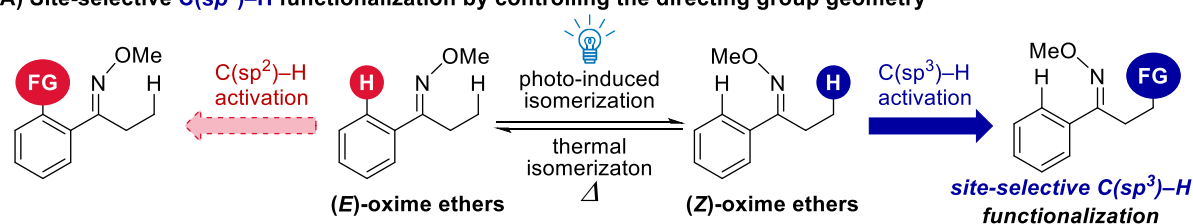


Figure 4. Site-selective C(sp³)-H amidation depending on characteristics of substrates

To achieve site-selective $C(sp^3)$ -H functionalization and sequential C-H functionalization, the author focused on the geometry of the directing group in oxime ethers (**Figure 5A**). Oxime ethers are commonly used as substrates in C-H functionalization and contain an imine moiety that serves as a directing group. This imine has two geometric configurations, the *E* and *Z* isomers, in which the lone pair on nitrogen is oriented toward opposite directions. In C-H activation by transition metal catalysts, catalysts are coordinated by a lone pair in directing group and cleavage the proximal C-H bond to a transition metal center. Therefore, controlling the geometry of a lone pair in oxime ether, which *E/Z* configurations can be switched under hash thermal or photo-induced condition while they are sufficiently stable under moderate temperature, would lead to emergence of site-selectivity in C-H activation. In oxime ethers bearing ethyl and phenyl substituents, the *E*-isomer is thermodynamically favored, and its lone pair is oriented toward the adjacent $C(sp^2)$ -H bond (**Figure 5B**). In contrast, in the *Z*-isomer, the lone pair is directed toward the opposite $C(sp^3)$ -H bond. In directed C-H functionalization, the lone pair coordinates to a transition-metal catalyst, enabling activation of the proximal C-H bond. Therefore, controlling the geometric orientation of the lone pair in oxime ethers should enable site-selective C-H functionalization. Moreover, switching the geometry of the directing group offers the potential to realize successive C-H functionalizations in a controlled manner.

(A) Site-selective $C(sp^3)$ -H functionalization by controlling the directing group geometry



(B) Successive $C(sp^3)$ -H/ $C(sp^2)$ -H or $C(sp^2)$ -H/ $C(sp^3)$ -H functionalization

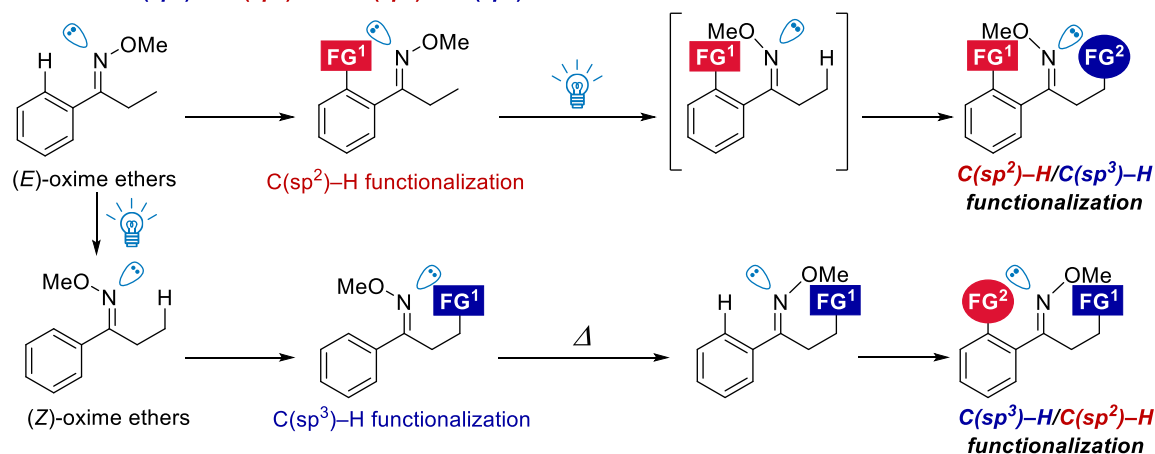
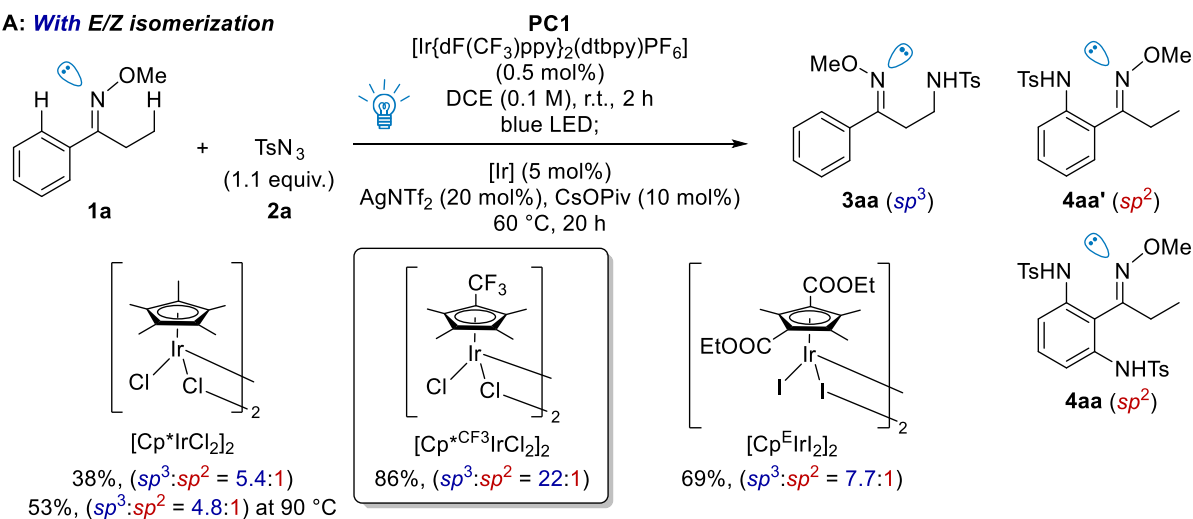


Figure 5. Strategy for site-selective $C(sp^3)$ -H functionalization and switchable C-H functionalization

Section 2: Site-selective C(sp³)-H functionalization using geometry of directing group

To demonstrate this concept, C(sp³)-H amidation by Cp*Ir(III), as reported by Chang and co-workers,³ was selected as a model reaction, and photo-induced *E/Z* isomerization of oxime ethers, developed by Rovis and co-workers,⁷ was adopted as a method for switching the directing group geometry. As an initial trial, C-H amidation of *O*-methyl ethyl phenyl oxime ether, which predominantly exists in the (*E*)-configuration (*Z:E* = 1:>25), was performed using a Cp*Ir(III) catalyst following *E/Z* isomerization (**Figure 6A**). The isomerization was carried out in one pot under blue-light irradiation with [Ir{dF(CF₃)ppy}₂(dtbpy)][PF₆] as a photocatalyst (*Z:E* = 1:>25 to 19:1). Consequently, the C(sp³)-H functionalized product **3aa** was obtained in 38% yield, whereas the corresponding C(sp²)-H functionalized product **4aa** was formed only in 7% yield. To improve the yield of the C(sp³)-H functionalized product **3aa**, electron-deficient CpIr(III) catalysts were examined, motivated by previous reports showing that CpIr(III) complexes bearing electron-withdrawing substituents on the Cp ring can accelerate C-H functionalization.⁸ When Cp^{CF₃}Ir(III)⁹ was employed, **3aa** was obtained in 86% yield with excellent site-selectivity. Although Cp^EIr(III) also accelerated C-H functionalization,^{8f} its yield and selectivity were inferior to one with Cp^{CF₃}Ir(III). A detailed examination of catalyst effects is presented later. In the absence of *E/Z* isomerization, the reaction afforded only the diamidated C(sp²)-H functionalized product **4aa** in 99% yield, with no formation of the C(sp³)-H amidated product **3aa** (**Figure 6B**). These results clearly demonstrate that the geometry of the directing group in oxime ethers enables control and switching of site-selectivity in C-H functionalization.

A: With *E/Z* isomerization



B: No *E/Z* isomerization

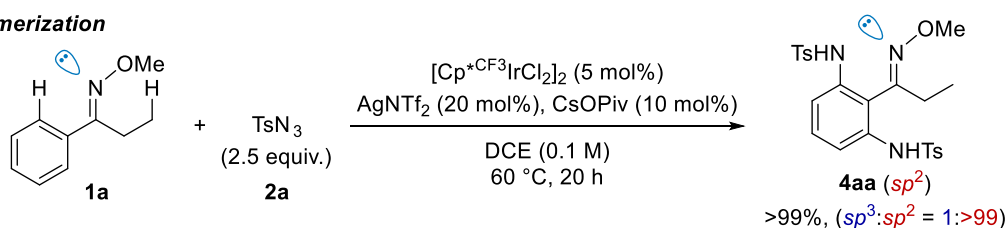


Figure 6. Initial trials and control experiment

DFT calculations were carried out to compare the activation energies of C(sp³)-H activation from the (*Z*)-oxime ether and C(sp²)-H activation from the (*E*)-oxime ether at the B3LYP-D3/6-311++G(d,p), Ir = SDD, CPCM(DCE)//B3LYP-D3/6-31G(d,p), Ir = LanL2DZ, CPCM(DCE) level of theory (**Figure 7**). As expected, C(sp³)-H activation of the (*Z*)-oxime ether requires an activation barrier 12.8 kcal/mol higher than that for C(sp²)-H activation of the (*E*)-oxime ether. These computational results suggest that although C(sp²)-H activation is intrinsically more rapid than C(sp³)-H activation, the *E/Z* configurations of oxime ethers are sufficiently stable under the reaction conditions and that site-selective C(sp³)-H functionalization might be governed by the geometry of the directing group.

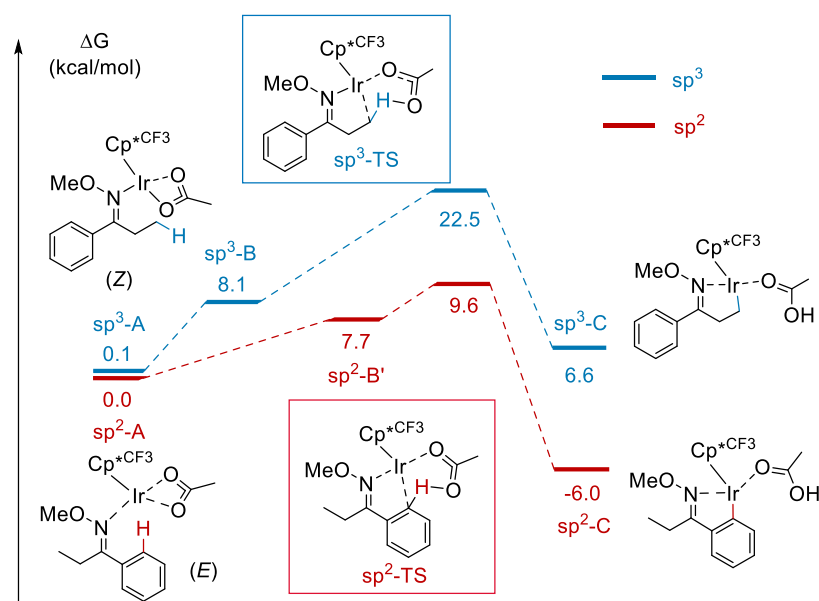


Figure 7. DFT calculation in C(sp³)-H or C(sp²)-H functionalization

To verify that the configurations of the oxime ether are sufficiently stable under the reaction condition, time-course experiments were conducted (**Figure 8**). Under the reaction conditions, no (*E*)-oxime ether was detected, and the C(sp²)-H functionalized product **4aa** was formed in approximately 4% yield. After photo-induced isomerization, the *Z/E* ratio of the starting material changed from 1:>25 to 19:1. The 4% yield of **4aa** corresponds to the amount of (*E*)-oxime ether **1a** present in the starting material after *E/Z* isomerization. Considering the observation that (*E*)-oxime ether **1a** was not detected at any point during the time-course experiment, these results indicate that rotation of the iminyl group does not occur under the reaction conditions.

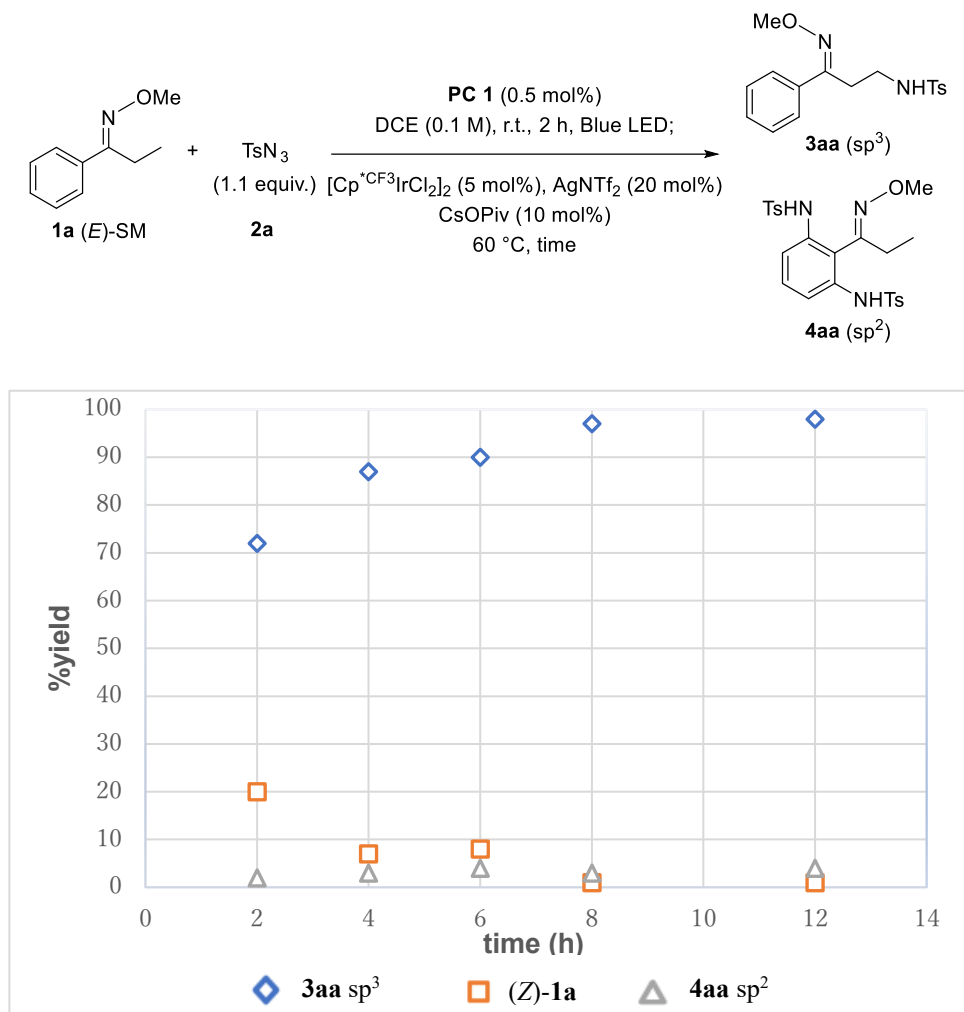


Figure 8. Time course experiments

The effect of the electron-deficient $\text{Cp}^{\text{CF}_3}\text{Ir(III)}$ catalyst was examined in detail. C–H functionalization via the CMD mechanism is known to be accelerated by electron-deficient Cp ligands because stronger agostic interaction between the transition metal and the C–H bond stabilizes the intermediate.⁸ In this $\text{C(sp}^3\text{)}\text{–H}$ activation, as shown in **Figure 9**, the electron-rich $\text{Cp}^*\text{Ir(III)}$ catalyst exhibited low reactivity even at elevated temperatures. The electron-deficient $\text{Cp}^{\text{F}}\text{Ir(III)}$ catalyst, although similar in character to $\text{Cp}^{\text{CF}_3}\text{Ir(III)}$, provided inferior yield and site-selectivity compared with $\text{Cp}^{\text{CF}_3}\text{Ir(III)}$. To elucidate the origin of these differences in reactivity, the electron deficiency of the catalysts was quantified by evaluating the CO stretching frequencies of their corresponding carbonyl complexes. Higher stretching frequencies indicate a more electron-deficient metal center due to weaker π -backdonation from the metal center to the π^* orbital of CO. The complex $[\text{Cp}^*\text{Ir(CO)I}_2]$ was synthesized in two steps (see experimental section for experimental details), and IR analysis was performed. Comparing the reported vibrational frequencies of $[\text{Cp}^*\text{Ir(CO)I}_2]$ (2016 cm^{-1})¹⁰ and $[\text{Cp}^{\text{F}}\text{Ir(CO)I}_2]$ (2051 cm^{-1}),^{8f} $[\text{Cp}^{\text{CF}_3}\text{Ir(CO)I}_2]$ exhibited a moderate stretching frequency of 2035 cm^{-1} , indicating an intermediate electron deficiency. These findings suggest that the electron-rich $\text{Cp}^*\text{Ir(III)}$ catalyst is insufficiently reactive for C–H functionalization, whereas the highly electron-deficient $\text{Cp}^{\text{F}}\text{Ir(III)}$ catalyst may undergo decomposition due to excessive electron deficiency, resulting in a reduced yield of the desired product.

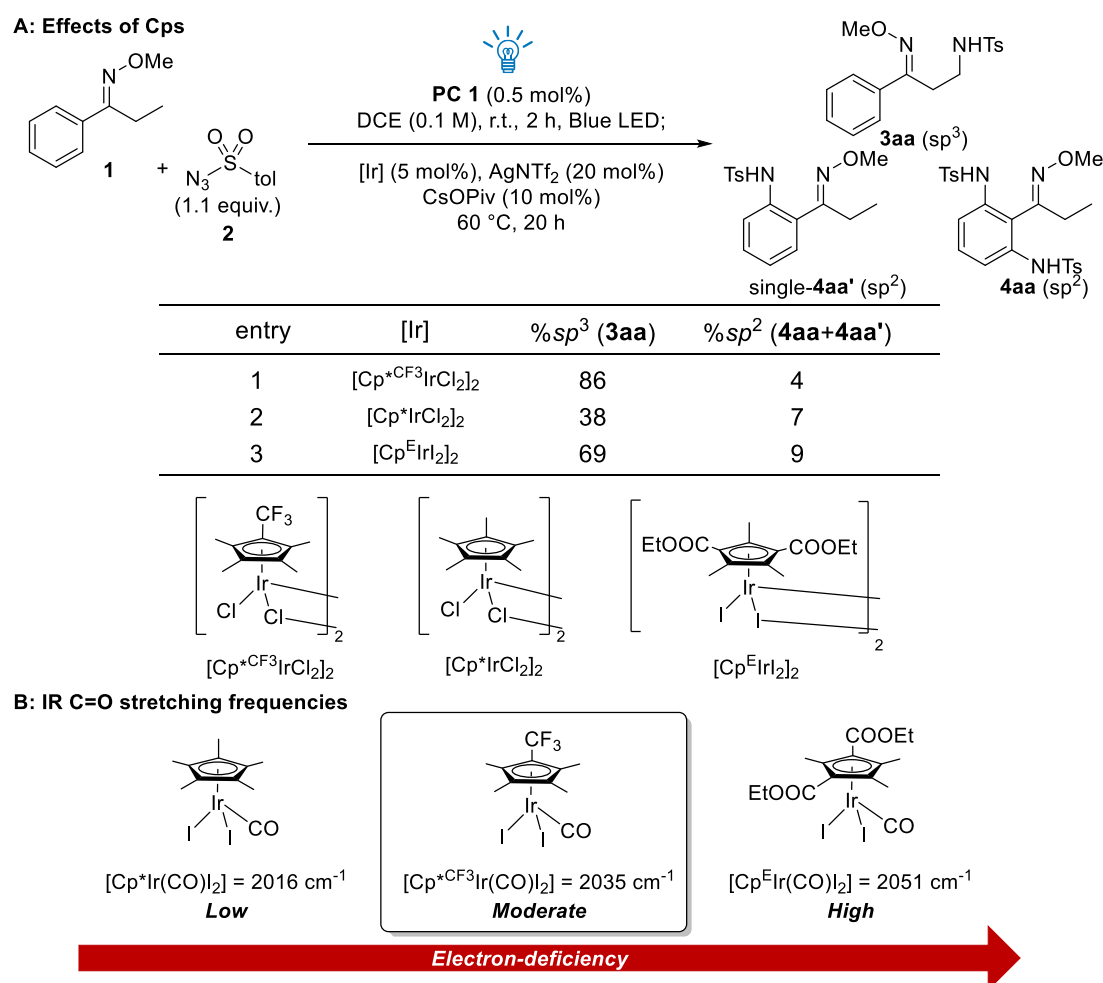


Figure 9. Control experiments and quantification of electron-deficiency on metal center

To clarify the effect of the electron-deficient $\text{Cp}^*\text{CF}_3\text{Ir(III)}$ catalyst, DFT calculations were performed to determine which step of the reaction is accelerated (**Figure 10**). The C–H amidation pathway can be divided into three elementary steps: (1) C–H activation, (2) nitrenoid formation from the sulfonyl azide, and (3) insertion to form the C–N bond. Computational analysis of the full reaction pathway revealed that, with $\text{Cp}^*\text{CF}_3\text{Ir(III)}$, the activation barriers for these steps were **22.4 kcal/mol (C–H activation)**, 17.9 kcal/mol (nitrenoid formation), and 17.1 kcal/mol (C–N bond formation). In comparison, the corresponding barriers using $\text{Cp}^*\text{Ir(III)}$ were **23.3 kcal/mol**, 20.5 kcal/mol, and 12.3 kcal/mol, respectively. In both catalytic systems, the C–H activation step is predicted to be rate-determining. The pathway involving a concerted nitrenoid formation and insertion process is not discussed here, as Nudged Elastic Band calculations indicated that this process requires an activation barrier exceeding 30 kcal/mol. Overall, the DFT results demonstrate that $\text{Cp}^*\text{CF}_3\text{Ir(III)}$ slightly lowers the barrier for the C–H activation step, consistent with the experimental observations.

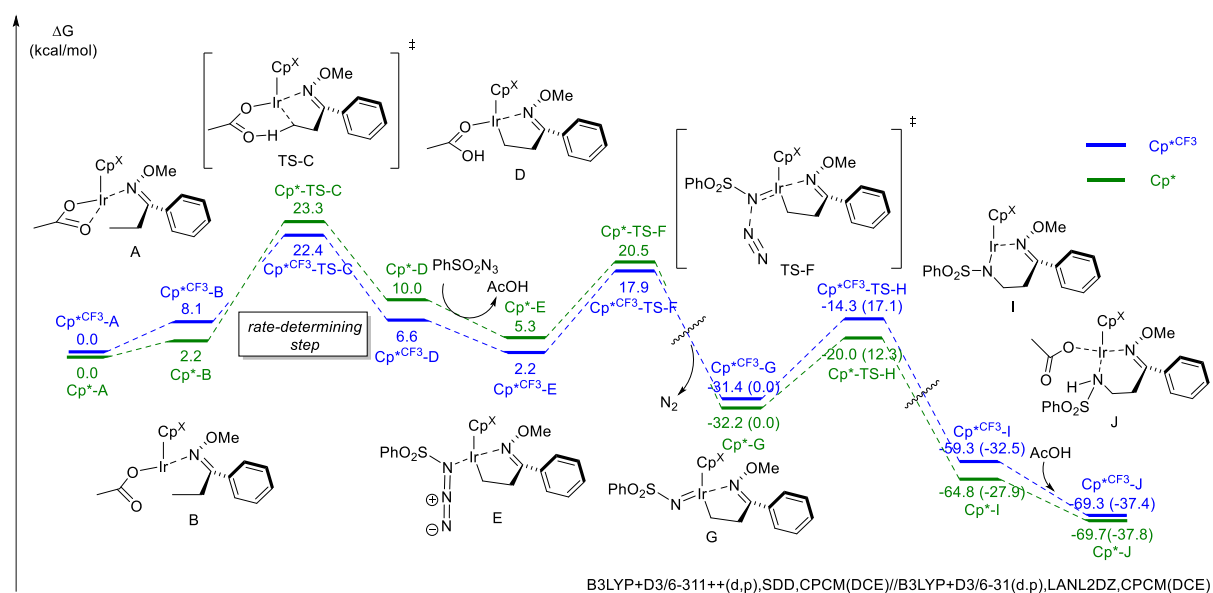


Figure 10. DFT calculation of full reaction pathway (ΔG based on intermediate G are in parenthesis.)

The substrate scope of the site-selective C(sp³)-H amidation is shown in **Figure 11**. A variety of oxime ethers were subjected to the optimized conditions. Substrates bearing *para* substituents were well tolerated regardless of their electronic properties (**3aa-3ha**). *Meta*-substituted substrates also afforded the desired products in good yields and with high site-selectivity (**3ia-3ka**). Oxime ethers bearing *ortho*-methyl or *ortho*-fluoro substituents similarly produced the corresponding products in good yield and selectivity (**3la, 3ma**). In the case of the *ortho*-trifluoromethyl derivative, site-selective C-H amidation proceeded successfully when a larger amount of photocatalyst and a longer irradiation time were employed (**3na**). α -Disubstituted substrates also provided the desired products in moderate yield (**3oa-3qa**). An oxime ether with 2-thienyl groups afforded the desired product with high selectivity using [Ru(bpy)₃][PF₆]₂ as a photocatalyst (**3ra**). Various aryl azides were also applicable to this site-selective C(sp³)-H amidation, furnishing the desired products with high yield and selectivity (**3ab-3ad**).

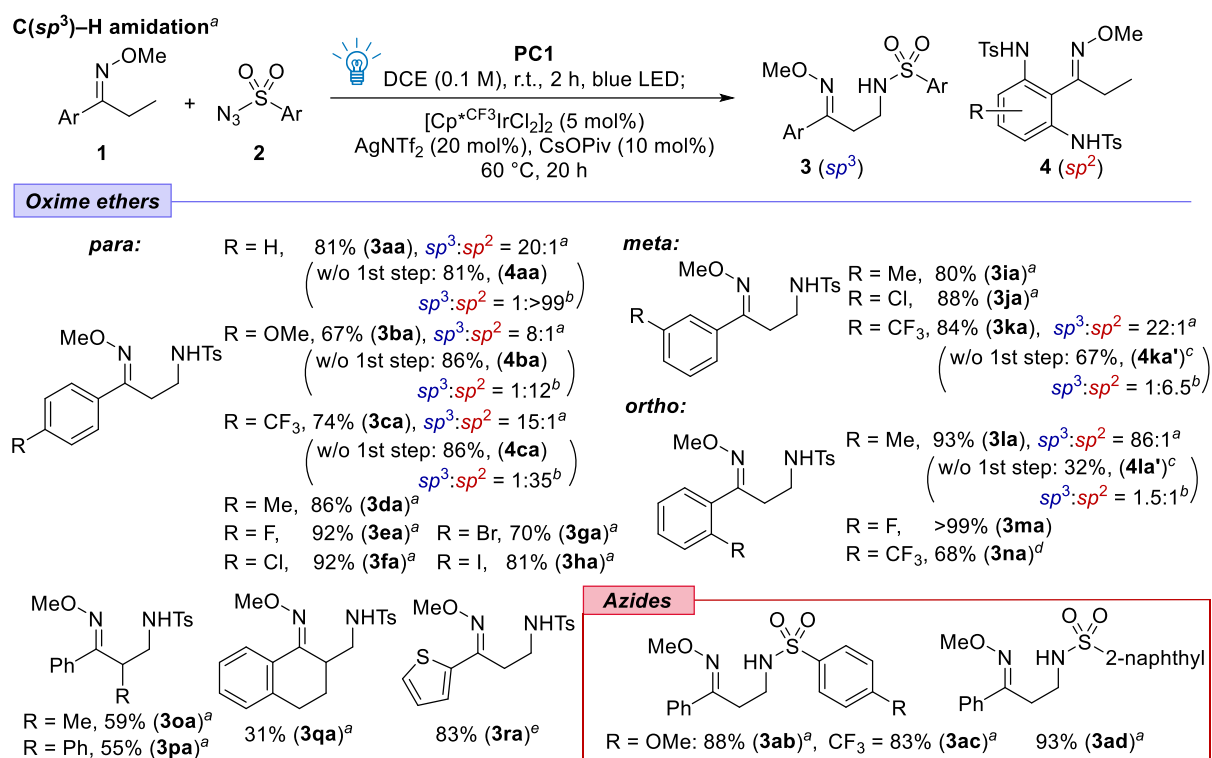
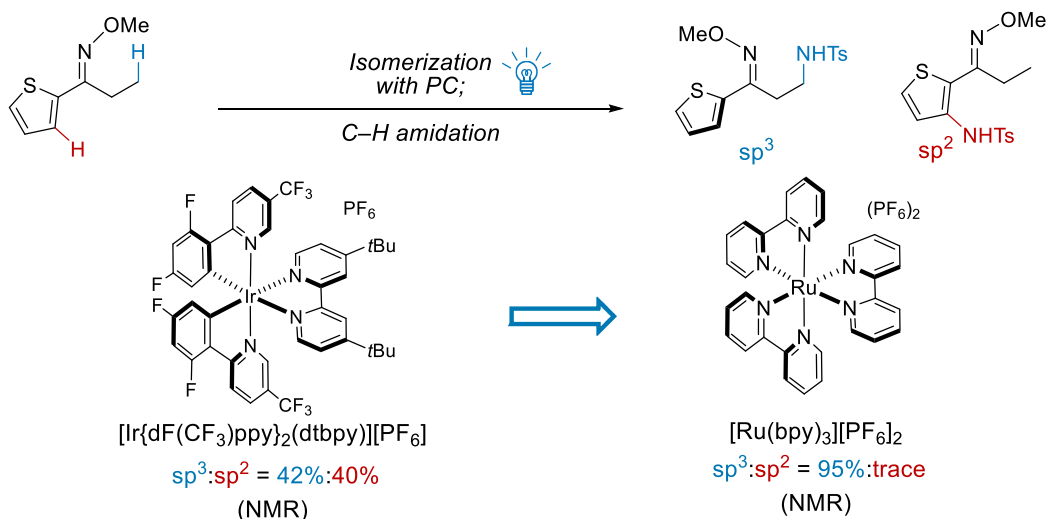


Figure 11. Substrate scope in C-H amidation

^aReaction conditions: **1** (0.20 mmol), **PC1** (1.0 μ mol, 0.50 mol%), DCE (2.0 mL), blue LED, r.t., 2 h; then [Cp*CF₃IrCl₂]₂ (0.010 mmol, 5 mol%), AgNTf₂ (0.040 mmol, 20 mol%), CsOPiv (0.020 mmol, 10 mol%), and **2** (0.22 mmol, 1.1 equiv.), 60°C, 2 h. The ratio of sp³ and sp² was determined by ¹H NMR analysis of the crude mixture. ^bWithout **PC1** and the isomerization step; 2.5 equiv. of **2** were used. ^c**4ka'** and **4la'** were obtained as mono-amidated products. ^d**PC1** (3.0 μ mol, 1.5 mol%) was used and the reaction time was 4 h for the isomerization step. ^e[Ru(bpy)₃][PF₆]₂ (**PC2**) (2.0 μ mol, 1.0 mol%) was used instead of **PC1**.

A 2-thienyl oxime ether (**2r**) required the use of $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ as the photocatalyst during the isomerization step in order to achieve high site-selectivity. When $[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbpy})][\text{PF}_6]$ was used, selectivity of $\text{C}(\text{sp}^3)\text{--H}$ amidation was not observed ($\text{sp}^3:\text{sp}^2 = 42\%:40\%$), while when $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ was used, selectivity of $\text{C}(\text{sp}^3)\text{--H}$ amidation was improved. The key factor governing site-selective $\text{C}(\text{sp}^3)\text{--H}$ amidation was found to be the *E/Z* ratio of the oxime ether (**Figure 12**).^{11,12} When $[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbpy})][\text{PF}_6]$, a photocatalyst with a high triplet energy ($E_T = 61.8$ kcal/mol), was used, both *E* and *Z* isomers were isomerized, resulting in nearly 1:1 of *E/Z* ratios after irradiation. This is likely the reason why site-selectivity was not observed under these conditions. By contrast, when $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$, a photocatalyst with a relatively lower triplet energy ($E_T = 46.4$ kcal/mol), was employed, $\text{C}(\text{sp}^3)\text{--H}$ amidation proceeded selectively. This outcome can be attributed to selective isomerization of only the (*E*)-isomer by the Ru photocatalyst, and it allows accumulation of the (*Z*)-isomer, which subsequently underwent site-selective $\text{C}(\text{sp}^3)\text{--H}$ amidation.

A: Selectivity depended on PC



B: Difference of triplet energies

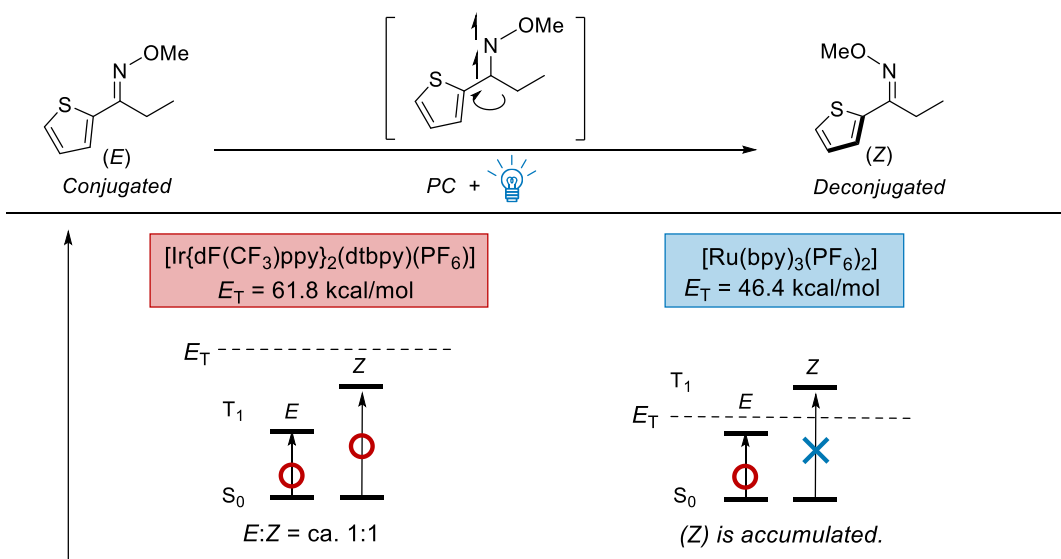


Figure 12. Dependency on triplet energy of PC with 2-thienyl oxime ether

To demonstrate the generality of this geometry-controlled strategy, site-selective C(sp³)-H alkylation¹³ was investigated (**Table 1**). This approach was successfully applied to C-H alkylation, affording the desired alkynylated product **6a** in 98% yield.

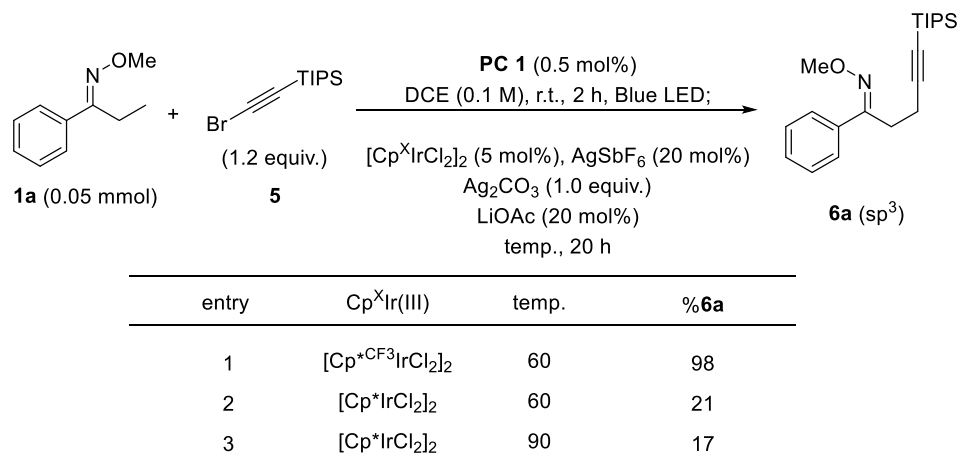


Table 1. Initial results of site-selective C(sp³)-H alkylation

The Cp^{CF3}Ir(III) catalyst exhibited high reactivity in the C-H alkylation like the previously discussed C-H amidation, whereas the Cp^{*}Ir(III) catalyst did not promote the reaction efficiently even at elevated temperatures. The substrate scope is shown in **Figure 13**. A variety of oxime ethers were compatible with the site-selective C(sp³)-H alkylation. For the 2-thienyl oxime ether, [Ru(bpy)₃][PF₆]₂ served as the optimal photocatalyst, consistent with the results observed in the C-H amidation reaction.

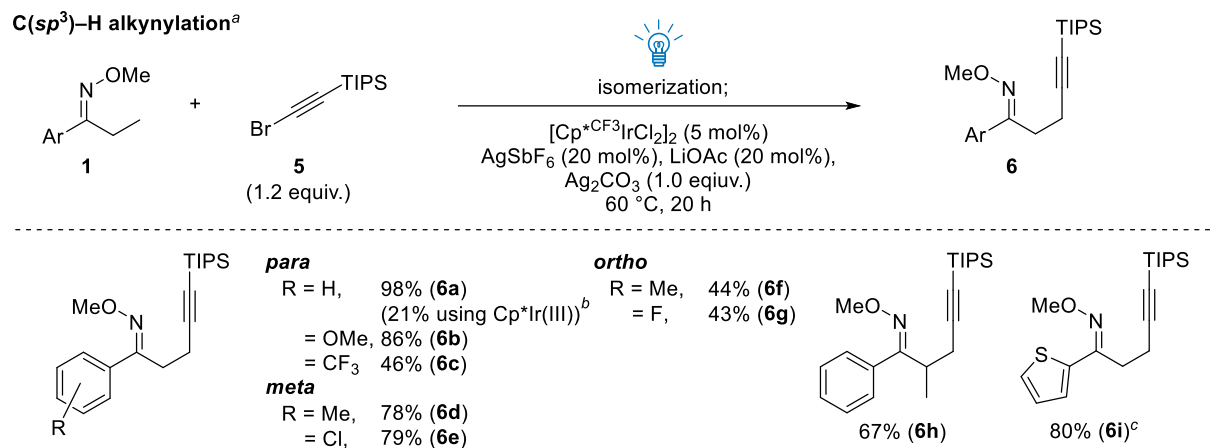


Figure 13. Substrate scope of the site-selective C(sp³)-H alkylation.

^aReaction conditions: **1** (0.20 mmol), **PC1** (1.0 μmol, 0.5 mol%), DCE (2.0 ml), r.t., blue LED, 2 h; then [Cp^{CF3}IrCl₂]₂ (0.010 mmol, 5.0 mol%), AgSbF₆ (0.040 mmol, 20 mol%), LiOAc (0.040 mmol, 20 mol%), Ag₂CO₃ (0.20 mmol, 1.0 equiv.), **5** (0.24 mmol, 1.2 equiv.), 60 °C, 20 h. ^bThe reaction was performed in 0.05 mmol scale with [Cp^{*}IrCl₂]₂, and the yield was determined by ¹H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. ^c**PC2** (2.0 μmol, 1.0 mol%) was used instead of **PC1**.

Section 3: Successive C(sp³)-H/C(sp²)-H functionalization

Successive C(sp³)-H/C(sp²)-H functionalization enabled by switching the geometry of the directing group was investigated (**Figure 14**). The (*Z*)-amidated oxime ether **3aa**, obtained via site-selective C(sp³)-H amidation, was re-isomerized under thermal conditions using *O*-methylhydroxylamine hydrochloride and pyridine to give the corresponding (*E*)-oxime ether **3aa** (*Z*/*E* = 11:1–14:1). Successive C(sp²)-H alkylation of (*E*)-**3aa** using a Cp*Rh(III) catalyst and a diazomalonate as the alkylating agent¹⁴ afforded the sequentially functionalized product in 77% yield (**10**). Other C(sp²)-H transformations including cyanation (**11**),¹⁵ alkynylation (**12**),¹³ and isoquinoline synthesis via alkenylation (**13**),¹⁶ also provided the desired sequentially functionalized products in good yields. These results demonstrate that controlling the geometry of the directing group allows manipulation of site-selectivity in C–H functionalization.

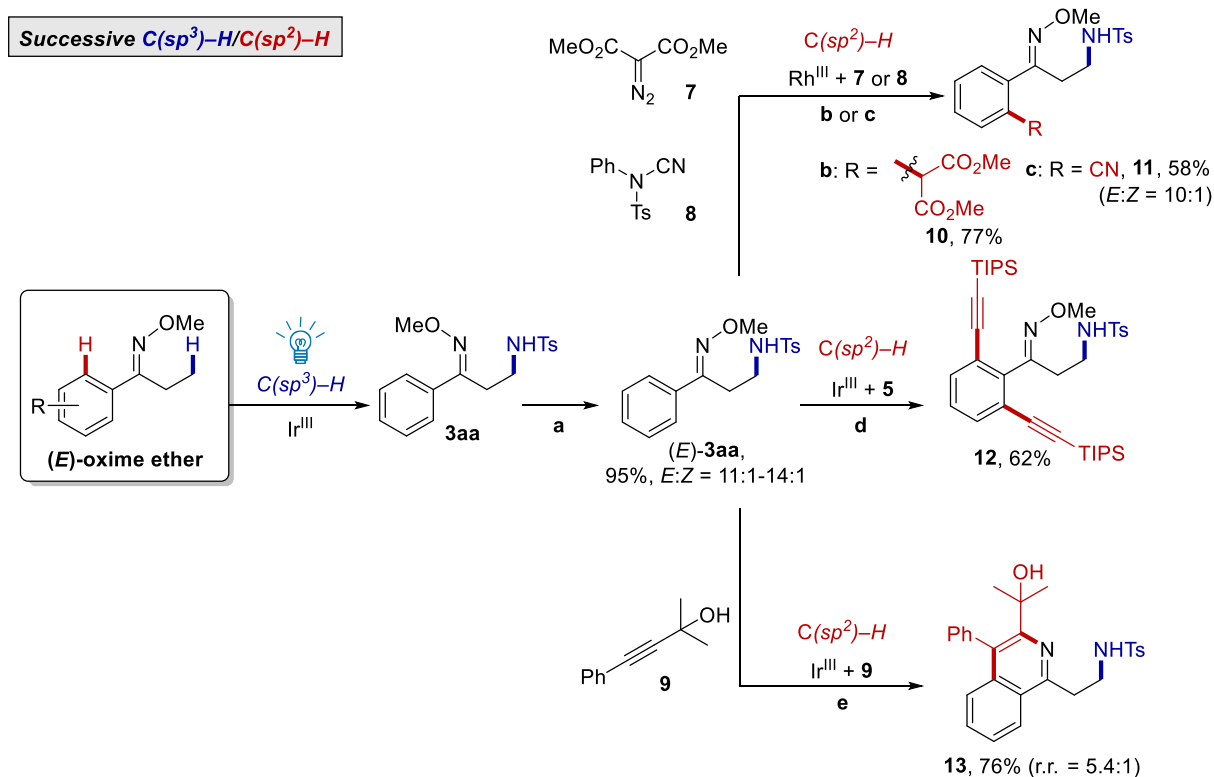


Figure 14. Successive C(sp³)-H/C(sp²)-H functionalization reactions.

Reaction conditions: (a) *O*-methylhydroxylamine hydrochloride (1.5 equiv.), pyridine (4.0 equiv.), EtOH, 100 °C, 25 h; 95% (*E*)-**3aa**. (b) (*E*)-**3aa** (*E*:*Z*=11:1, 0.050 mmol), [Cp*RhCl₂]₂ (1.25 mol%), AgOAc (7.5 mol%), **7** (1.0 equiv.), MeOH, 70 °C, 20 h; 77% **10**. (c) (*E*)-**3aa** (*E*:*Z*=14:1, 0.20 mmol), [Cp*RhCl₂]₂ (10 mol%), Ag₂CO₃ (40 mol%), **8** (2.0 equiv.), 1,4-dioxane, 120 °C, 20 h; 58% **11** (*E*:*Z*=10:1). (d) (*E*)-**3aa** (*E*:*Z*=11:1, 0.050 mmol), [Cp*CF₃IrCl₂]₂ (5.0 mol%), AgSbF₆ (20 mol%), LiOAc (20 mol%), Ag₂CO₃ (1.5 equiv.), **5** (2.2 equiv.), DCE, 60 °C, 20 h; 62% **12**. (e) (*E*)-**3aa** (0.2 mmol, *E*:*Z*=14:1), [Cp*IrCl₂]₂ (10 mol%), AgOAc (1.0 equiv.), **9** (1.1 equiv.), MeOH, 40 °C, 48 h; 76% **13** (r.r.=5.4:1).

Finally, successive C(sp²)-H/C(sp³)-H functionalization was examined. Initial Cp^{*}Rh(III)-catalyzed C(sp²)-H alkylation¹⁴ of oxime ether **1a** afforded the alkylated product **14**. After isolation, site-selective C(sp³)-H amidation via photo-induced *E/Z* isomerization proceeded to give **15** in moderate yield. In another example, Cp^{CF3}Ir(III)-catalyzed C-H amidation of *m*-CF₃ oxime ether with tosyl azide furnished the mono-amidated C(sp²)-H product (**4ka'**), which subsequently underwent site-selective C(sp³)-H amidation with *p*-methoxyphenylsulfonyl azide to afford diamidated products bearing two different sulfonyl groups (**16**).

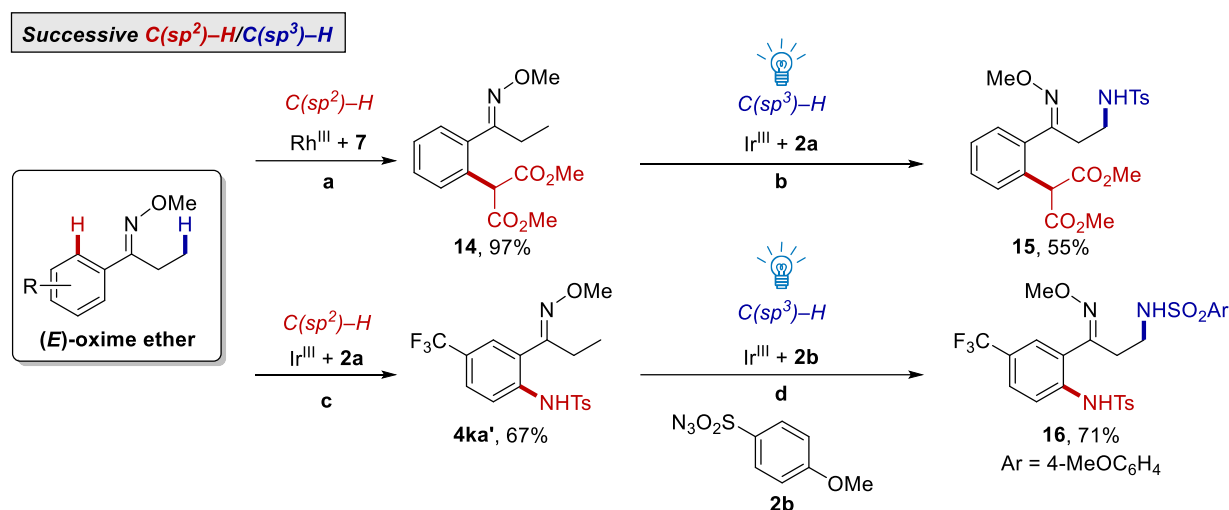


Figure 15. Successive C(sp²)-H/C(sp³)-H functionalization reactions.

Reaction conditions: (a) **1a** (0.20 mmol), [Cp^{*}RhCl₂]₂ (1.25 mol%), AgOAc (7.5 mol%), **7** (1.0 equiv.), MeOH, 70 °C, 20 h; 97% **14**. (b) **14** (0.20 mmol), **PC1** (0.50 mol%), DCE (2.0 mL), r.t., 2 h, blue LED; [Cp^{*}CF₃IrCl₂]₂ (5.0 mol%), AgNTf₂ (20 mol%), CsOPiv (10 mol%), **2a** (1.1 equiv.); 55% **15**. (c) **1k** (0.20 mmol), [Cp^{*}CF₃IrCl₂]₂ (5.0 mol%), AgNTf₂ (20 mol%), CsOPiv (10 mol%), **2a** (1.1 equiv.), DCE, 60 °C, 20 h; 67% **4ka'**. (d) **4ka'** (0.050 mmol), **PC1** (1.0 mol%), DCE (0.50 mL), r.t., 2 h, blue LED; [Cp^{*}CF₃IrCl₂]₂ (5.0 mol%), AgNTf₂ (20 mol%), CsOPiv (10 mol%), **2b** (1.5 equiv.); 71% **16**.

Short summary

These studies establish site-selective and switchable C-H functionalization by photo- and thermally induced-control of geometry in the directing group. In addition, Cp^{*}CF₃Ir(III), electron-deficient catalyst, was found to be effective for C(sp³)-H functionalization.

Publication

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Experimental Section

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1. General

All non-aqueous reactions were carried out in a flame-dried glassware under argon atmosphere unless otherwise noted or in an argon-filled glove box. NMR spectra were recorded on JEOL JNM-ECA600 spectrometers operating at 600.17 MHz for ^1H NMR, 150.92 MHz for ^{13}C NMR and 564.69 MHz for ^{19}F NMR. Chemical shifts were reported in the scale relative to TMS (0.00 ppm for ^1H NMR in CDCl_3), CHCl_3 (7.26 ppm for ^1H NMR in CDCl_3), CDCl_3 (77.00 ppm for ^{13}C NMR in CDCl_3), and PhCF_3 (−63.72 ppm for ^{19}F NMR in CDCl_3) as an internal reference, respectively. APCI mass spectra were measured on Thermo Scientific Exactive spectrometer. Column chromatography was performed with silica gel Kanto Silica gel 60 N (40-50 mesh), Yamazen YFLC AI-580 using Universal Column SiOH. High resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF II-KR spectrometer in Atmospheric Pressure Chemical Ionization (APCI) method using “LC/MS tuning mix, for APCI, low concentration” as the internal standard. Reverse phase column chromatography was performed with Universal column ODS using Yamazen YFLC AI-580. Infrared (IR) spectra were recorded on an Agilent Technologies Cary 630 FTIR spectrophotometer.

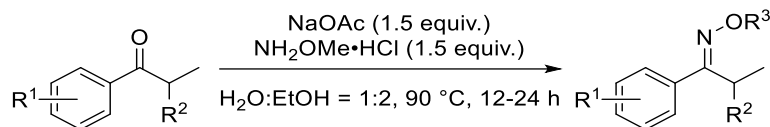
Materials: Dichloromethane (DCM) was purified by Glass Contour solvent purification system before use. Dichloroethane (DCE) was purchased from Kanto Chemical Co., Inc. (Super Dehydrated: 10357-05). MeOH (Super Dehydrated: 133-16771), EtOH (Super Dehydrated: 050-08425), and 1,4-dioxane (Super Dehydrated: 040-31651) was purchased from Fujifilm Wako Pure Chemical Co.. Oxime ethers **1a**, **1b**, and **1d**^[S1] sulfonyl azide **2**,^[S2] TIPS acetylene bromide **5**,^[S3] $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$,^[S4] $[\text{Cp}^*\text{CF}_3\text{IrCl}_2]_2$,^[S5] ketone **1h**,^[S6] **1l**, **1m**,^[S7] **1p**,^[S8] were synthesized according to the previously described methods. All other reagents were commercially available and used as received unless otherwise noted. Photo-irradiation was performed with a blue LED light (ISLM-150X150-BB447, 447 nm) purchased from CCS Inc..

Oxime ether derivatives are generally obtained as *E/Z* mixtures. Several NMR signals of minor isomers were difficult to assign in some cases, and the assignment is reported as is.

2. Experimental procedures

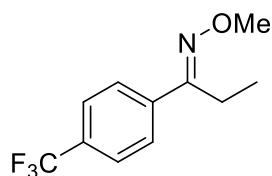
2-1. Preparation of substrates

General procedure A: preparation of oxime ethers^[S1]



A screw-cap test tube was charged with the corresponding ketone (1.0 equiv.), NaOAc (1.5 equiv.), *O*-alkyl hydroxyl amine (1.5 equiv.), H₂O, and EtOH (0.67 M, H₂O/EtOH = 1:2). Then the reaction mixture was stirred at 90 °C for 12-24 h, and the solvent was evaporated. Water was added and the mixture was extracted with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under vacuum. The residue was purified by silica gel column chromatography to afford oxime ether **1** as a *E/Z* mixture.

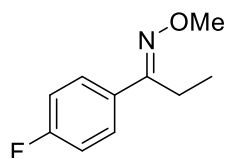
(*E*)-1-(4-(trifluoromethyl)phenyl)propan-1-one *O*-methyl oxime (**1c**)



General Procedure A using the corresponding ketone (404.4 mg, 2.0 mmol) afforded **1c** as a colorless liquid (377.7 mg, 82%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.75 (d, *J* = 8.1 Hz, 2H, major), 7.65 (d, *J* = 8.0 Hz, 2H, minor), 7.62 (d, *J* = 8.2 Hz, 2H, major), 7.45 (d, *J* = 8.0 Hz, 2H, minor), 4.00 (s, 3H, major), 3.83 (s, 3H, minor), 2.76 (q, *J* = 7.6 Hz, 2H, major), 2.55 (q, *J* = 7.5 Hz, 2H, minor), 1.13 (t, *J* = 7.6 Hz, 3H, major), 1.07 (t, *J* = 7.5

Hz, 3H, minor). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 158.3, 139.0, 130.7 (q, ²*J*_{C-F} = 32.3 Hz), 128.1, 126.4, 125.3 (q, ³*J*_{C-F} = 4.3 Hz), 125.1, 124.1 (q, ²*J*_{C-F} = 272.6 Hz), 62.1, 61.7, 28.7, 19.8, 11.3, 10.9. Some aromatic signals probably those of the minor isomer were missing. ¹⁹F NMR (CDCl₃, 564.69 MHz) δ -63.73 (s), -63.83 (s). HRMS (APCI): *m/z* calculated for C₁₁H₁₃F₃NO⁺ [M+H]⁺: 232.0944, found: 232.0941.

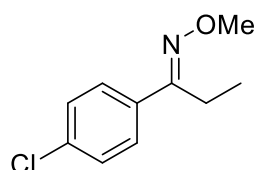
(*E*)-1-(4-fluorophenyl)propan-1-one *O*-methyl oxime (**1e**)



General Procedure A using the corresponding ketone (230.3 mg, 1.5 mmol) afforded **1e** as a colorless liquid (234.3 mg, 86%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.64-7.59 (m, 2H, major), 7.40-7.36 (m, 2H, minor), 7.10-7.02 (m, 2H), 3.97 (s, 3H, major), 3.83 (s, 3H, minor), 2.72 (q, *J* = 7.7 Hz, 2H, major), 2.53 (q, *J* = 7.4 Hz, 2H, minor), 1.12 (t, *J* = 7.7 Hz, 3H, major), 1.05 (t, *J* = 7.2 Hz, 3H, minor). Some aromatic signals probably those of the minor isomer were overlapped.

¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 163.3 (d, ¹*J*_{C-F} = 248.5 Hz), 158.7, 131.7 (d, ³*J*_{C-F} = 4.3 Hz), 129.9 (d, ³*J*_{C-F} = 7.2 Hz), 128.0 (d, ³*J*_{C-F} = 7.2 Hz), 115.4 (d, ²*J*_{C-F} = 21.7 Hz), 115.2 (d, ²*J*_{C-F} = 21.7 Hz), 61.9, 61.6, 28.8, 20.0, 11.5, 11.0. ¹⁹F NMR (CDCl₃, 564.69 MHz) δ -113.11-113.16 (m, minor), -113.61-113.66 (m, major). HRMS (APCI): *m/z* calculated for C₁₀H₁₃FNO⁺ [M+H]⁺: 182.0976, found: 182.0970.

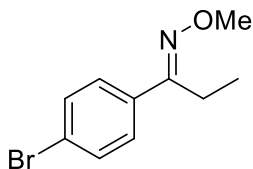
(*E*)-1-(4-chlorophenyl)propan-1-one *O*-methyl oxime (**1f**)



General Procedure A using the corresponding ketone (253.0 mg, 1.5 mmol) afforded **1f** as a colorless liquid (230.7 mg, 78%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.60-7.55 (m, 2H, major), 7.38-7.30 (m, 2H), 3.98 (s, 3H, major), 3.83 (s, 3H, minor), 2.72 (q, *J* = 7.6 Hz, 2H, major), 2.52 (q, *J* = 7.4 Hz, 2H, minor), 1.11 (t, *J* = 7.7 Hz, 3H, major), 1.05 (t, *J* = 7.6

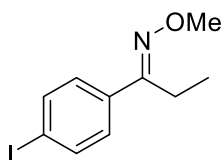
Hz, 3H, minor). Some aromatic signals probably those of the minor isomer were overlapped. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 158.6, 134.9, 134.0, 128.6, 127.5, 62.0, 19.8, 11.1. **HRMS** (APCI): m/z calculated for $\text{C}_{10}\text{H}_{13}\text{ClNO}^+$ $[\text{M}+\text{H}]^+$: 198.0680, found: 198.0671.

(E)-1-(4-bromophenyl)propan-1-one O-methyl oxime (1g)



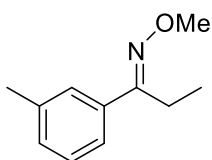
General Procedure A using the corresponding ketone (426.1 mg, 2.0 mmol) afforded **1g** as a pale yellow liquid (344.0 mg, 71%). ^1H NMR (CDCl_3 , 600.17 MHz) δ 7.53-7.47 (m, 4H), 7.26-7.23 (m, 2H, minor), 3.97 (s, 3H, major), 3.82 (s, 3H, minor), 2.71 (q, J = 7.7 Hz, 2H, major), 2.52 (q, J = 7.6 Hz, 2H, minor), 1.11 (t, J = 7.6 Hz, 3H, major), 1.05 (t, J = 7.6 Hz, 3H, minor). Some aromatic signals probably those of the minor isomer were overlapped. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 158.6, 134.4, 131.6, 127.8, 123.2, 62.0, 19.8, 11.1. **HRMS** (APCI): m/z calculated for $\text{C}_{10}\text{H}_{13}\text{BrNO}^+$ $[\text{M}+\text{H}]^+$: 242.0175, found: 242.0180.

(E)-1-(4-iodophenyl)propan-1-one O-methyl oxime (1h)



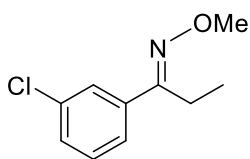
General Procedure A using the corresponding ketone^[S6] (300.0 mg, 1.15 mmol) afforded **1h** as a colorless oil (326.5 mg, 98%). ^1H NMR (CDCl_3 , 600.17 MHz) δ 7.74-7.71 (m, 2H, minor), 7.71-7.67 (m, 2H, major), 7.40-7.35 (m, 2H, major), 7.12-7.09 (m, 2H, minor), 3.97 (s, 3H, major), 3.82 (s, 3H, minor), 2.70 (q, J = 7.6 Hz, 2H, major), 2.51 (q, J = 7.5 Hz, 2H, minor), 1.10 (t, J = 7.6 Hz, 3H, major), 1.05 (t, J = 7.5 Hz, 3H, minor). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 158.7, 137.5, 135.0, 127.9, 95.0, 62.0, 19.7, 11.1. **HRMS** (APCI): m/z calculated for $\text{C}_{10}\text{H}_{13}\text{INO}^+$ $[\text{M}+\text{H}]^+$: 290.0036, found: 290.0039.

(E)-1-(m-tolyl)propan-1-one O-methyl oxime (1i)



General Procedure A using the corresponding ketone (296.4 mg, 2.0 mmol) afforded **1i** as a colorless liquid (266.0 mg, 75%). ^1H NMR (CDCl_3 , 600.17 MHz) δ 7.45 (s, 1H, major), 7.42-7.38 (m, 1H, major), 7.30-7.23 (m, 1H), 7.19-7.15 (m, 1H, major), 7.15-7.12 (m, 1H, minor), 3.98 (s, 3H, major), 3.82 (s, 3H, minor), 2.73 (q, J = 7.6 Hz, 2H, major), 2.52 (q, J = 7.4 Hz, 2H, minor), 2.37 (s, 3H), 1.12 (t, J = 7.6 Hz, 3H, major), 1.05 (t, J = 7.4 Hz, 3H, minor). Some aromatic signals probably those of the minor isomer were overlapped. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 160.0, 138.1, 135.5, 129.8, 128.3, 126.8, 123.4, 61.8, 21.5, 20.2, 11.2. **HRMS** (APCI): m/z calculated for $\text{C}_{11}\text{H}_{16}\text{NO}^+$ $[\text{M}+\text{H}]^+$: 178.1226, found: 178.1233.

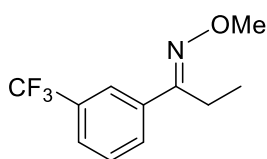
(E)-1-(3-chlorophenyl)propan-1-one O-methyl oxime (1j)



General Procedure A using the corresponding ketone (350. mg, 2.1 mmol) afforded **1j** as a colorless liquid (315.0 mg, 77%). ^1H NMR (CDCl_3 , 600.17 MHz) δ 7.65-7.62 (m, 1H, major), 7.52-7.48 (m, 1H, major), 7.36-7.27 (m, 2H), 7.24-7.21 (m, 1H), 3.98 (s, 3H, major), 3.83 (s, 3H, minor), 2.71 (q, J = 7.7 Hz, 2H, major), 2.52 (q, J = 7.4 Hz, 2H, minor), 1.12 (t, J = 7.6 Hz, 3H, major), 1.06 (t, J = 7.4 Hz, 3H, minor). Some aromatic signals probably those of the minor isomer were overlapped. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 158.4, 137.4, 134.5, 129.7, 128.9, 126.3, 124.3, 62.1, 19.9,

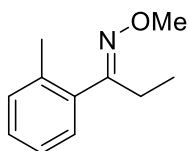
11.0. **HRMS** (APCI): m/z calculated for $C_{10}H_{13}ClNO^+$ $[M+H]^+$: 198.0680, found: 198.0680.

(E)-1-(3-(trifluoromethyl)phenyl)propan-1-one O-methyl oxime (1k)



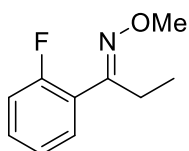
General Procedure A using the corresponding ketone (1.0 g, 5.0 mmol) afforded **1k** as a colorless liquid (804.3 mg, 70%). ^1H NMR ($CDCl_3$, 600.17 MHz) δ 7.92-7.89 (m, 1H, major), 7.83-7.79 (m, 1H, major), 7.63-7.59 (m, 1H), 7.51-7.46 (m, 1H), 4.00 (s, 3H, major), 3.84 (s, 3H, minor), 2.76 (q, J = 7.6 Hz, 2H, major), 2.56 (q, J = 7.5 Hz, 2H, minor), 1.13 (t, J = 7.6 Hz, 3H, major), 1.07 (t, J = 7.5 Hz, 3H, minor). Some aromatic signals probably those of the minor isomer were overlapped. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.92 MHz) δ 158.2, 157.3, 136.4, 134.6, 131.2, 130.9 (q, $^2J_{C-F}$ = 32.3 Hz), 130.7, 130.5, 129.4, 128.9, 128.6, 125.5 (q, $^3J_{C-F}$ = 3.9 Hz), 125.3 (q, $^3J_{C-F}$ = 4.3 Hz), 124.8, 124.6 (q, $^3J_{C-F}$ = 3.9 Hz), 124.0 (q, $^1J_{C-F}$ = 272.1 Hz), 123.0 ($^3J_{C-F}$ = 4.3 Hz), 62.1, 61.7, 28.6, 19.8, 11.4, 11.0. ^{19}F NMR ($CDCl_3$, 564.69 MHz) δ -63.67 (s), -63.69 (s). **HRMS** (APCI): m/z calculated for $C_{11}H_{13}F_3NO^+$ $[M+H]^+$: 232.0944, found: 232.0942.

(E)-1-(o-tolyl)propan-1-one O-methyl oxime (1l)



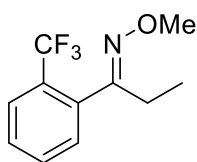
General Procedure A using the corresponding ketone^[S7] (296.4 mg, 2.0 mmol) afforded **1l** as a colorless liquid (278.3 mg, 79%). ^1H NMR ($CDCl_3$, 600.17 MHz) δ 7.27-7.14 (m, 4H, major), 7.02 (d, J = 7.2 Hz, 1H, major), 3.94 (s, 3H, minor), 3.81 (s, 3H, major), 2.66 (q, J = 7.6 Hz, 2H, minor), 2.48 (q, J = 7.3 Hz, 2H, major), 2.33 (s, 3H, minor), 2.22 (s, 3H, major), 1.07 (t, J = 7.6 Hz, 3H, major), 1.00 (t, J = 7.6 Hz, 3H, minor). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.92 MHz) δ 159.7, 145.6, 136.1, 136.0, 135.2, 135.1, 130.5, 129.8, 128.5, 128.3, 128.2, 126.1, 125.6, 125.5, 61.6, 61.6, 29.3, 23.0, 19.9, 19.6, 10.9, 10.1. **HRMS** (APCI): m/z calculated for $C_{11}H_{16}NO^+$ $[M+H]^+$: 178.1226, found: 178.1230.

(E)-1-(2-fluorophenyl)propan-1-one O-methyl oxime (1m)



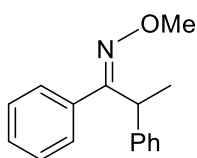
General Procedure A using the corresponding ketone^[S7] (300.0 mg, 2.0 mmol) afforded **1m** as a colorless liquid (318.5 mg, 89%). ^1H NMR ($CDCl_3$, 600.17 MHz) δ 7.41 (td, J = 7.6, 1.7 Hz, 1H, major), 7.36-7.31 (m), 7.19-7.12 (m), 7.12-7.04 (m), 3.97 (s, 3H, major), 3.83 (s, 3H, minor), 2.73 (q, J = 7.6 Hz, 2H, major), 2.53 (q, J = 7.6 Hz, 2H, minor), 1.09-1.04 (m, 3H). Some aromatic signals probably those of the minor isomer were overlapped. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.92 MHz) δ 160.4 (d, $^1J_{C-F}$ = 250.0 Hz), 158.5 (d, $^1J_{C-F}$ = 250.0 Hz), 158.5, 154.9, 130.5 (d, $^3J_{C-F}$ = 7.2 Hz), 130.2 (d, $^3J_{C-F}$ = 2.9 Hz), 130.2 (d, $^3J_{C-F}$ = 8.7 Hz), 128.8 (d, $^3J_{C-F}$ = 4.3 Hz), 124.3 (d, $^2J_{C-F}$ = 14.4 Hz), 124.2, 123.8, 122.3 (d, $^2J_{C-F}$ = 17.3 Hz), 115.9 (d, $^2J_{C-F}$ = 21.7 Hz), 115.6 (d, $^2J_{C-F}$ = 21.7 Hz), 61.9, 61.7, 28.6, 22.3, 11.0, 10.2. ^{19}F NMR ($CDCl_3$, 564.69 MHz) δ -114.29--114.31 (m, minor), -115.93--115.96 (m, major). **HRMS** (APCI): m/z calculated for $C_{10}H_{13}FNO^+$ $[M+H]^+$: 182.0976, found: 182.0975.

(E)-1-(2-(trifluoromethyl)phenyl)propan-1-one O-methyl oxime (1n)



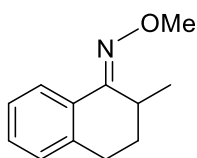
General Procedure A using the corresponding ketone (404.4 mg, 2.0 mmol) afforded **1n** as a colorless liquid (411.0 mg, 89%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.73-7.67 (m, 1H), 7.59-7.52 (m, 1H), 7.51-7.44 (m, 1H), 7.35-7.31 (m, 1H, major), 7.14 (dd, *J* = 7.7, 0.5 Hz, 1H, minor), 3.94 (s, major, 3H), 3.77 (s, minor, 3H), 2.70 (q, *J* = 7.7 Hz, 2H, major), 2.57 (td, *J* = 15.4, 7.7 Hz, 1H, minor), 2.46 (td, *J* = 15.3, 7.4 Hz, 1H, minor), 1.12 (t, *J* = 7.6 Hz, 3H, minor), 0.98 (t, 7.6 Hz, 3H, major). Some aromatic signals probably those of the minor isomer were overlapped. ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 160.1, 158.0, 135.1, 134.0, 131.6, 131.5, 130.4, 128.7 (q, ²*J*_{C-F} = 30.3 Hz), 128.6, 128.3, 128.2, 126.6 (q, ³*J*_{C-F} = 4.8 Hz), 126.4 (q, ³*J*_{C-F} = 4.3 Hz), 123.9 (q, ¹*J*_{C-F} = 277.4 Hz), 61.8, 61.5, 29.1, 23.2, 10.7, 9.9. ¹⁹F NMR (CDCl₃, 564.69 MHz) δ -59.02 (s), -61.62 (s). HRMS (APCI): *m/z* calculated for C₁₁H₁₃F₃NO⁺ [M+H]⁺: 232.0944, found: 232.0940.

(E)-1,2-diphenylpropan-1-one O-methyl oxime (1p)



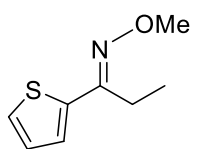
General Procedure A using the corresponding ketone^[S8] (50.0 mg, 0.238 mmol) afforded **1p** as a pale yellow oil (60.8 mg, >99%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.30 (m, 3H, major), 7.28-7.16 (m, 5H, major), 6.94-6.90 (m, 2H, major), 5.03 (q, *J* = 7.3 Hz, 1H, minor), 4.00 (s, 3H, minor), 3.96 (q, *J* = 7.1 Hz, 1H, major), 3.86 (s, 3H, major), 1.50 (d, *J* = 7.1 Hz, 3H, major), 1.46 (d, *J* = 7.3 Hz, 3H, minor). Some aromatic signals probably those of the minor isomer were overlapped. ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 169.3, 160.2, 128.5, 128.3, 128.3, 128.1, 127.9, 127.9, 127.8, 127.7, 127.6, 127.3, 126.6, 126.3, 61.9, 45.6, 36.2, 29.3, 18.8, 16.2. Some signals were overlapped and missing. HRMS (APCI): *m/z* calculated for C₁₆H₁₈NO⁺ [M+H]⁺: 240.1383, found: 240.1384.

(E)-2-methyl-3,4-dihydronaphthalen-1(2H)-one O-methyl oxime (1q)



General Procedure A using the corresponding ketone (320.4 mg, 2.0 mmol) afforded **1q** as a pale colorless oil (295.6 mg, 78%). ¹H NMR (CDCl₃, 600.17 MHz) δ 8.01-7.97 (m, 1H), 7.24 (td, 1H, *J* = 7.4, 1.4 Hz), 7.20-7.16 (m, 1H), 7.12 (d, 1H, *J* = 7.6 Hz), 3.98 (s, 3H), 3.57-3.49 (m, 1H), 3.00-2.90 (m, 1H), 2.65 (dt, 1H, *J* = 16.5, 4.2 Hz), 2.00-1.91 (m, 1H), 1.75-1.68 (m, 1H), 1.16 (d, 3H, *J* = 7.1 Hz). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 157.8, 138.6, 129.9, 128.9, 128.7, 126.2, 124.6, 61.9, 28.4, 27.2, 25.0, 15.4. HRMS (APCI): *m/z* calculated for C₁₂H₁₅NO⁺ [M+H]⁺: 190.1226, found: 190.1227.

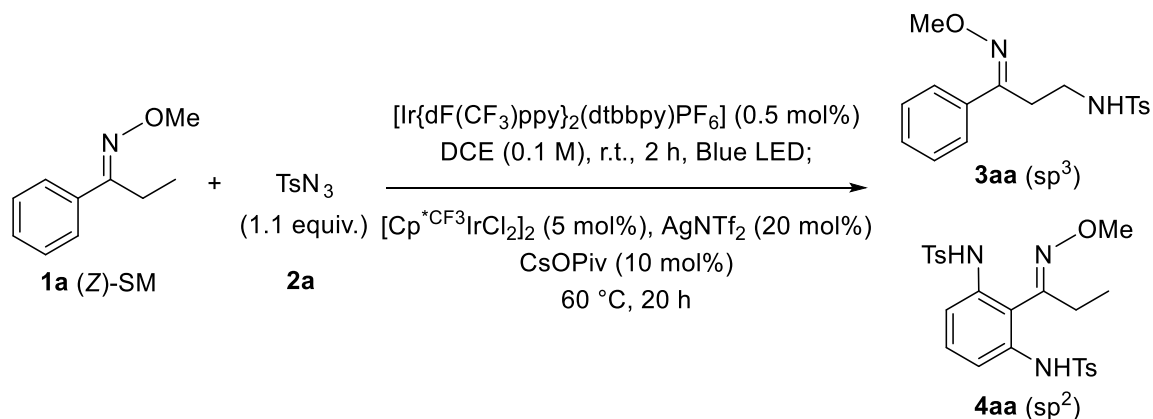
(E)-1-(thiophen-2-yl)propan-1-one O-methyl oxime (1r)



General Procedure A using the corresponding ketone (350.0 mg, 2.5 mmol) afforded **1r** as a colorless oil (343.6 mg, 81%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.51 (dd, *J* = 5.2, 1.0 Hz, 1H, minor), 7.47 (dd, *J* = 3.9, 1.0 Hz, 1H, minor), 7.27 (dd, *J* = 5.2, 1.1 Hz, 1H, major), 7.22 (dd, *J* = 3.7, 1.0 Hz, 1H, major), 7.10 (dd, *J* = 5.0, 3.9 Hz, 1H, minor), 7.02 (dd, *J* = 5.0, 3.7 Hz, 1H, major), 4.04 (s, 3H, minor), 3.96 (s, 3H, major), 2.76-2.69 (m, 2H), 1.28 (t, *J* = 7.5 Hz, 3H, minor), 1.18 (t, *J* = 7.6 Hz, 3H, major). Some aromatic signals probably those of the minor isomer were overlapped. ¹³C{¹H} NMR (CDCl₃,

150.92 MHz) δ 155.7, 150.7, 139.5, 131.8, 130.2, 129.1, 127.0, 126.7, 125.9, 125.5, 62.0, 61.7, 27.1, 20.7, 12.9, 11.4. **HRMS** (APCI): m/z calculated for $C_8H_{12}NOS^+ [M+H]^+$: 170.0634, found: 170.0632.

2-2. Time course experiments



In an argon-filled glovebox, a screw-cap test tube was charged with Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (0.28 mg, 0.00025 mmol, 0.50 mol %), oxime **1a** (0.050 mmol, 1.0 equiv.), and DCE (0.50 mL). The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 2 h at room temperature under blue light irradiation. The reaction mixture was taken into the glovebox and [Cp^{*CF₃}IrCl₂]₂ (2.27 mg, 0.0025 mmol, 5.0 mol%), AgNTf₂ (3.88 mg, 0.010 mmol, 20 mol%), CsOPiv (1.18 mg, 0.0050 mmol, 10 mol%), and tosyl azide **2a** (8.43 μL, 0.060 mmol, 1.1 equiv.) were added. After stirred for the corresponding time at 60 °C, the reaction mixture was filtered through a short pad of silica gel, eluted with AcOEt, and evaporated under reduced pressure. The yields were determined by ¹H NMR analysis with 1,1,2,2-tetrachloroethane as an internal standard.

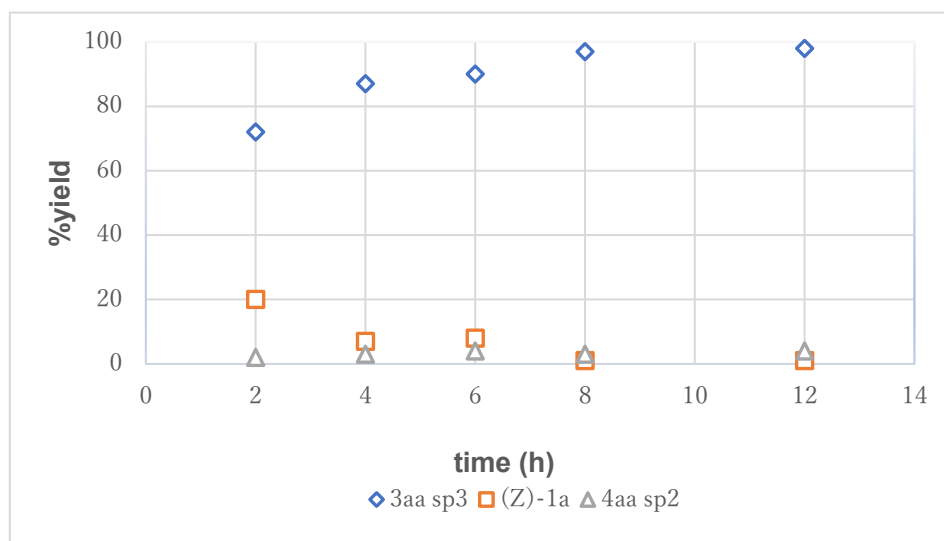


Figure S1. Plot of time course experiments

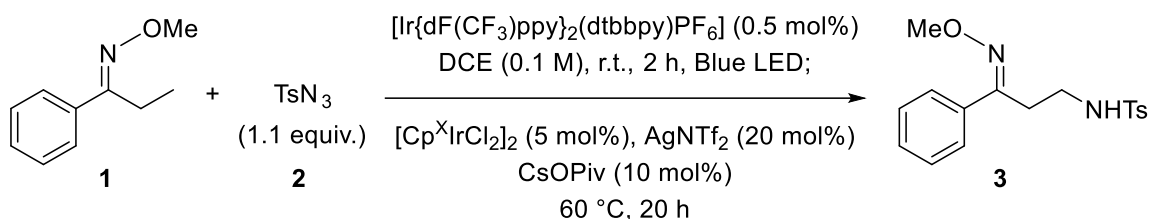
Table S1. Yields in time course experiments

Time (h)	% 3aa sp ³	% 4aa sp ²	%(Z)- 1a
2	72	2	20
4	87	3	7
6	90	4	8
8	97	3	1
12	98	4	1

C(sp³)-H amidation nearly completed within 8 hours and (*E*)-**1a** was not detected at any points, indicating that C(sp³)-H amidation catalyzed by Cp^{*CF₃}Ir(III) would proceed much more rapidly than the thermal re-isomerization of (Z)-**1a**.

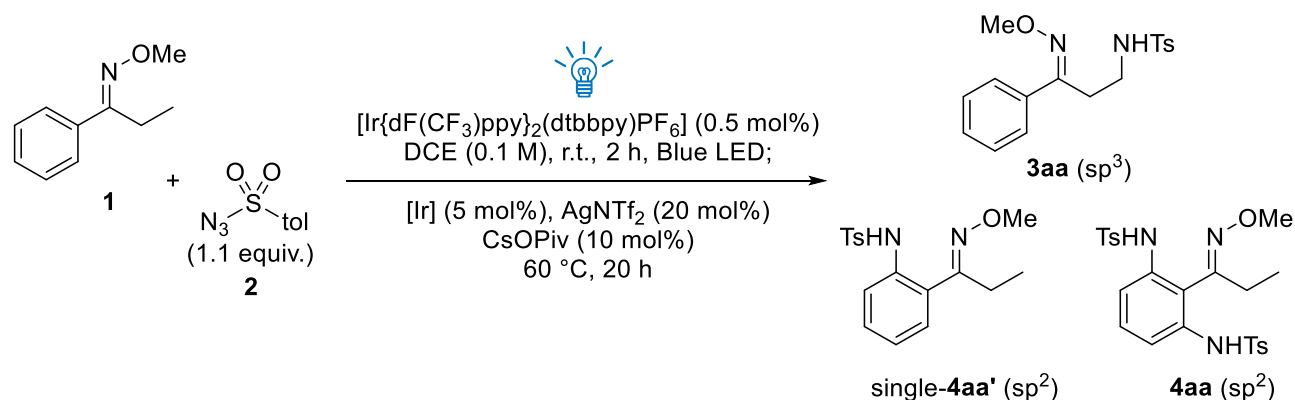
2-3. Iridium(III)-catalyzed selective C(sp³)-H amidation of oxime ethers

Control experiments: catalyst screening

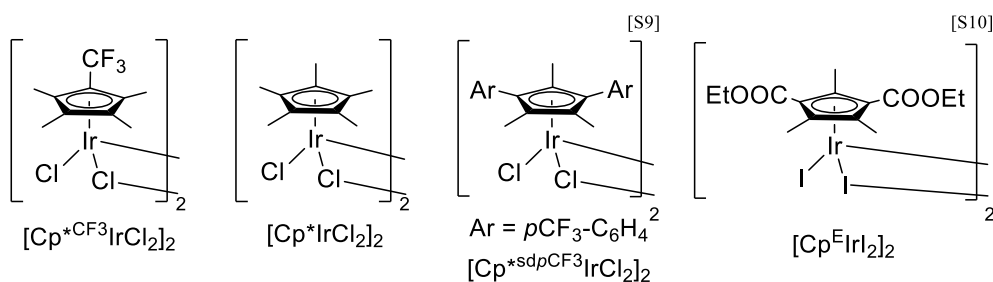


In an argon-filled glovebox, a screw-cap test tube was charged with Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (0.28 mg, 0.00025 mmol, 0.50 mol %), oxime **1a** (0.050 mmol, 1.0 equiv.), and DCE (0.50 mL). The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 2 h at room temperature under blue light irradiation. The reaction mixture was taken into the glovebox and [Cp^XIrCl₂]₂ (0.0025 mmol, 5.0 mol%), AgNTf₂ (3.88 mg, 0.010 mmol, 20 mol%), CsOPiv (1.18 mg, 0.0050 mmol, 10 mol%), and tosyl azide **2a** (8.43 μL, 0.060 mmol, 1.1 equiv.) were added. After stirred for 20 h at 60 °C, the reaction mixture was filtered through a short pad of silica gel, eluted with AcOEt, and evaporated under reduced pressure. The yields were determined by ¹H NMR analysis with 1,1,2,2-tetrachloroethane as an internal standard.

Table S2. Screening of catalysts

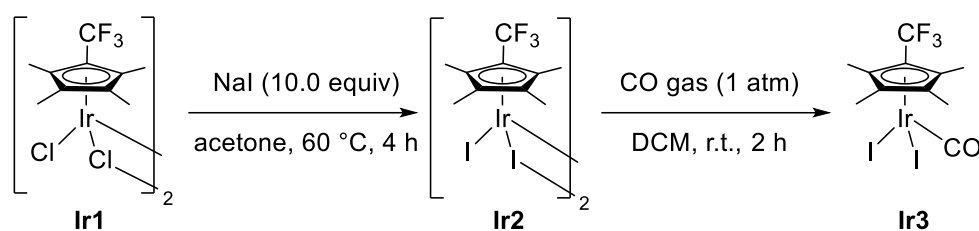


entry	[Ir]	%sp ³ (3aa)	%sp ² (4aa+4aa')
1	[Cp ^{*CF₃} IrCl ₂] ₂	86	4
2	[Cp [*] IrCl ₂] ₂	38	7
3	[Cp ^{*sdpCF₃} IrCl ₂] ₂	76	14
4	[Cp ^E IrI ₂] ₂	69	9



[Cp^{*sdpCF₃}IrCl₂]₂ and [Cp^EIrI₂]₂ were prepared according to the reported methods.

Synthesis of $[\text{Cp}^*\text{CF}_3\text{IrI}_2]_2$ and $[\text{Cp}^*\text{CF}_3\text{IrI}_2(\text{CO})]$



A screw-capped vial was charged with NaI (16.6 mg, 0.111 mmol, 10.0 equiv.), $[\text{Cp}^*\text{CF}_3\text{IrCl}_2]_2$ (10 mg, 0.011 mmol, 1.0 equiv.), and acetone (1.1 mL, 0.01 M). After stirred for 4 h at 60 °C, the mixture was washed with water three times, and organic layer was evaporated to afford $[\text{Cp}^*\text{CF}_3\text{IrI}_2]_2$ (**Ir2**) as a deep orange solid (15.0 mg, >99%). ^1H NMR (CDCl_3 , 600.17 MHz) δ 2.19 (s, 6H), 1.98 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 125.1 (q, $^1J_{\text{C-F}} = 271.7$ Hz), 94.4, 92.0, 70.9 (q, $^2J_{\text{C-F}} = 37.6$ Hz), 12.5, 10.2. ^{19}F NMR (CDCl_3 , 564.69 MHz) δ -55.51 (s). HRMS (APCI): m/z calculated for $\text{C}_{10}\text{H}_{12}\text{F}_3\text{Ir}^+ [1/2\text{M-I}^+]$: 508.9560, found: 508.9561.

A test tube was charged with $[\text{Cp}^*\text{CF}_3\text{IrI}_2]_2$ (**Ir2**) (15.0 mg, 0.011 mmol) and DCM (1.0 mL, 0.0011 M). The solution was bubbled with CO gas for 10 min and stirred for 2 h at room temperature under CO atmosphere (balloon). The removal of solvent afforded $[\text{Cp}^*\text{CF}_3\text{IrI}_2(\text{CO})]$ (**Ir3**) as a red solid (15.4 mg, >99%). IR (ATR, v/cm^{-1}) 2035. ^1H NMR (CDCl_3 , 600.17 MHz) δ 2.45 (s, 6H), 2.29 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 159.7, 122.7 (q, $J = 273.1$ Hz), 104.1, 103.0, 81.1 ($J = 37.6$ Hz), 11.3, 10.6. ^{19}F NMR (CDCl_3 , 564.69 MHz) δ -56.09 (s). HRMS (APCI): m/z calculated for $\text{C}_{11}\text{H}_{12}\text{F}_3\text{OIr}^+ [\text{M-I}^+]$: 536.9509, found: 536.9505.

Comparison of C=O stretching frequencies

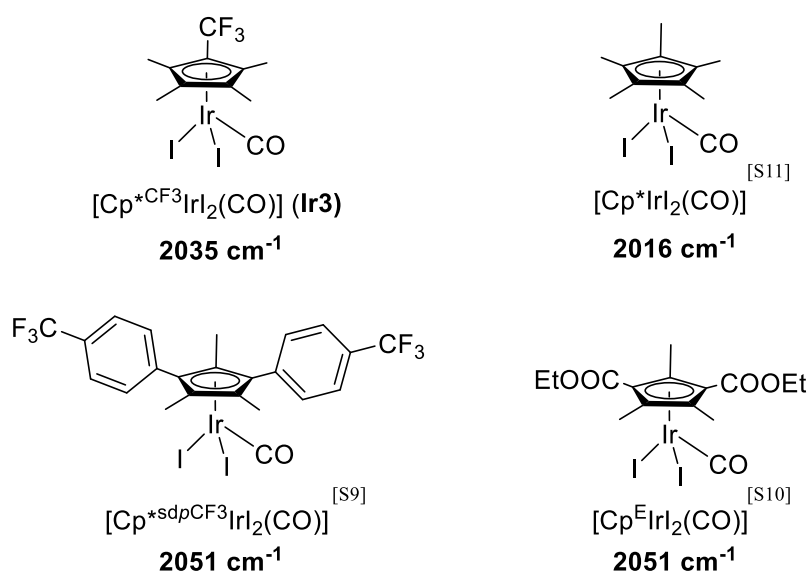
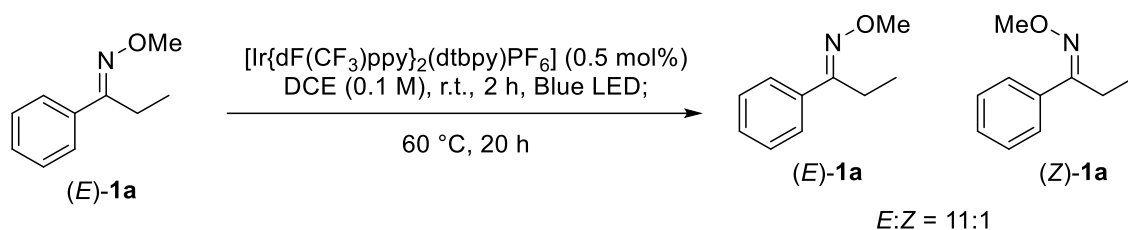


Figure S2. C=O stretching frequencies of $\text{Cp}^{\text{X}}\text{Ir}$ catalysts

To examine characteristics of $[\text{Cp}^*\text{CF}_3\text{IrCl}_2]_2$ (**Ir1**), $[\text{Cp}^*\text{CF}_3\text{IrI}_2(\text{CO})]$ (**Ir3**) was synthesized and C=O stretching frequencies in $[\text{Cp}^*\text{CF}_3\text{IrI}_2(\text{CO})]$ was compared with other iridium catalysts. Considering the value of C=O stretching frequencies of **Ir3**, Iridium center in **Ir3** would have moderate electron deficiency. Electron deficiency of $\text{Cp}^*\text{CF}_3\text{Ir}$

catalyst would be higher than Cp*Ir catalyst, but less than Cp*^{sdp}CF₃Ir catalyst and Cp^EIr catalyst.

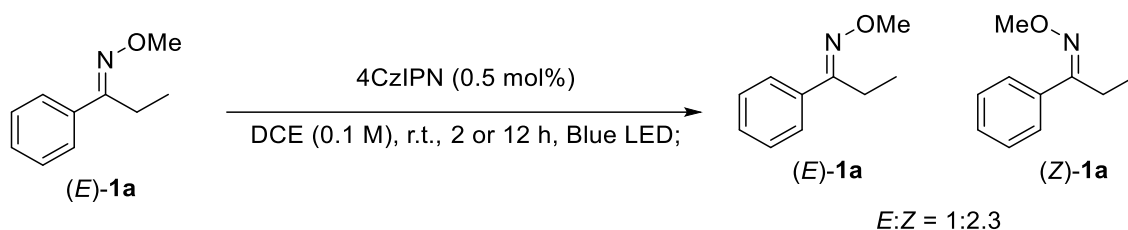
Thermodynamical isomerization of (Z)-oxime to (E)-oxime



Scheme S1. Thermodynamical isomerization

After photo-induced isomerization of (*E*)-oxime ether to (*Z*)-oxime ether, the reaction mixture was heated to 60 °C for 20 h without reagents for C–H amidation. The ¹H NMR analysis of the resulting mixture indicated that a thermodynamically stable (*E*)-isomer was a major product (*E:Z* = 11:1).

E/Z isomerization using organic photo-catalyst

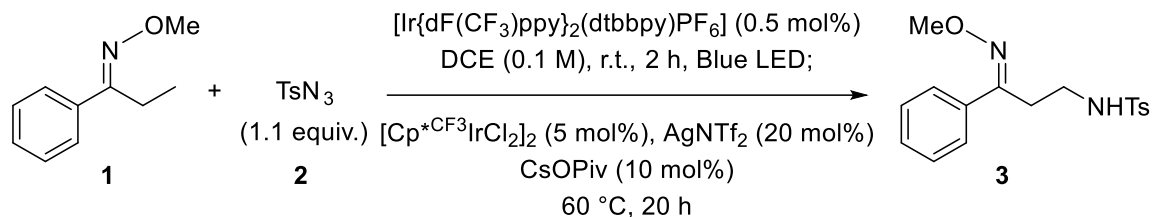


Scheme S2. Photo-isomerization using organic PC

In an argon-filled glovebox, a screw-cap test tube was charged with 4CzIPN (0.20 mg, 0.00025 mmol, 0.50 mol %), oxime **1a** (0.050 mmol, 1.0 equiv.), and DCE (0.50 mL). The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 2 or 12 h at room temperature under blue light irradiation. After evaporation, the ratio of *E/Z* isomer was determined by ¹H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. When 4CzIPN as an organic photo sensitizer was used instead of Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (**PC1**), *E/Z* isomerization of **1a** proceeded but the *E/Z* ratio was much lower than when **PC1** was used (*E:Z* = 1:2.3 (2 h), *E:Z* = 1:2.5 (12 h)).

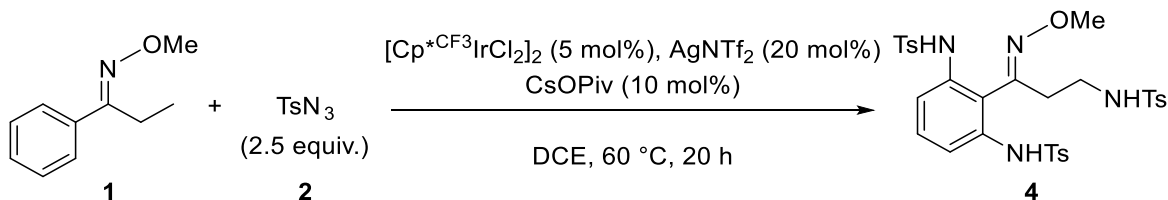
When the same experiment using **PC1** (2 h) was performed, we observed a high *E/Z* ratio (*E:Z* = 1:19).

General Procedure B: C(sp³)-H amidation after isomerization



In an argon-filled glovebox, a screw-cap test tube was charged with Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (1.12 mg, 0.0010 mmol, 0.50 mol %), oxime **1** (0.20 mmol, 1.0 equiv.), and DCE (2 mL). The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 2 h at room temperature under blue light irradiation. The reaction mixture was taken into the glovebox and [Cp^{*CF3}IrCl₂]₂ (9.06 mg, 0.010 mmol, 5.0 mol%), AgNTf₂ (15.52 mg, 0.040 mmol, 20 mol%), CsOPiv (4.72 mg, 0.020 mmol, 10 mol%), and sulfonyl azide **2** (0.22 mmol, 1.1 equiv.) were added. After stirred for 20 h at 60 °C, the reaction mixture was filtered through a short pad of silica gel, eluted with AcOEt, and evaporated under reduced pressure. The ratio of **3** and **4** was determined by ¹H NMR analysis of the crude mixture at this point. The crude product was purified by silica gel column chromatography to afford **3**.

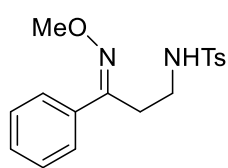
General Procedure C: C(sp²)-H amidation (control experiments)



In an argon-filled glovebox, a screw-cap test tube charged with oxime **1** (0.20 mmol, 1.0 equiv.), [Cp^{*CF3}IrCl₂]₂ (9.06 mg, 0.010 mmol, 5.0 mol%), AgNTf₂ (15.52 mg, 0.040 mmol, 20 mol%), CsOPiv (4.72 mg, 0.020 mmol, 10 mol%), sulfonyl azide **2** (0.22 mmol, 1.1 equiv.), and DCE (2.0 mL) were added. The test tube was capped, and then brought out of the glovebox. After stirred for 20 h at 60 °C, the reaction mixture was filtered through a short pad of silica gel, eluted with AcOEt, and evaporated under reduced pressure. The ratio of **3** and **4** was determined by ¹H NMR analysis of the crude mixture at this point. The crude product was purified by silica gel column chromatography to afford **4**.

Note: When (*E*)-isomer of **1a** was used without isomerization using 1.1 equiv. of TsN₃ **2a**, a mixture of mono-adduct **4aa'** and di-adduct **4aa** was obtained under highly reactive Cp^{*CF3}Ir(III) catalysis. On the other hand, *meta*-substituted (*E*)-**1k** gave mono-adduct **4ka'**.

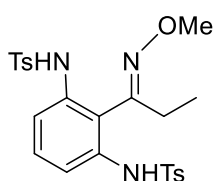
(*Z*)-*N*-(3-(methoxyimino)-3-phenylpropyl)-4-methylbenzenesulfonamide (**3aa**)



General Procedure B using **1a** (32.6 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol, 1.1 equiv.), and purification by silica gel column chromatography (hexane/EtOAc = 4/1 to 1:1) afforded **3aa** as a pale yellow solid (54.0 mg, 81%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.38-7.32 (m, 3H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.28-7.24 (m, 2H), 5.33 (t,

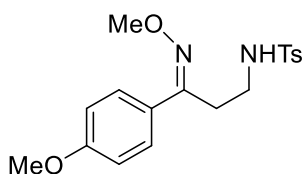
$J = 5.9$ Hz, 1H), 3.80 (s, 3H), 3.21 (q, $J = 6.2$ Hz, 2H), 2.65 (t, $J = 6.1$ Hz, 2H), 2.42 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 154.4, 143.3, 136.9, 133.1, 129.6, 129.1, 128.1, 127.5, 127.0, 62.0, 39.8, 34.7, 21.4. **HRMS** (APCI): m/z calculated for $\text{C}_{17}\text{H}_{21}\text{N}_2\text{O}_3\text{S}^+ [\text{M}+\text{H}]^+$: 333.1267, found: 333.1269.

(*E*)-*N,N'*-(2-(1-(methoxyimino)propyl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (4aa)



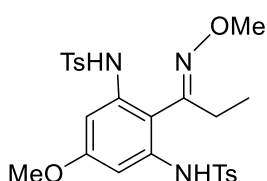
General Procedure C using **1a** (32.6 mg, 0.20 mmol) and **2a** (98.6 mg, 0.50 mmol), and purification by silica gel column chromatography (hexane/EtOAc = 2/1 to 1/1) afforded **4aa** as a pale yellow solid (81.4 mg, 81%). ^1H NMR (CDCl_3 , 600.17 MHz) δ 7.68-7.63 (m, 4H), 7.24 (d, $J = 8.0$ Hz, 4H), 7.19-7.11 (m, 3H), 7.02 (s, 2H), 3.96 (s, 3H), 2.39 (s, 6H), 2.31 (q, $J = 7.6$ Hz, 2H), 0.52 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 157.1, 144.2, 136.4, 135.5, 130.0, 129.7, 127.1, 119.3, 116.8, 62.4, 23.0, 21.5, 9.3. **HRMS** (APCI): m/z calculated for $\text{C}_{24}\text{H}_{28}\text{N}_3\text{O}_5\text{S}_2^+ [\text{M}+\text{H}]^+$: 502.1465, found: 502.1469.

(*Z*)-*N*-(3-(methoxyimino)-3-(4-methoxyphenyl)propyl)-4-methylbenzenesulfonamide (3ba)



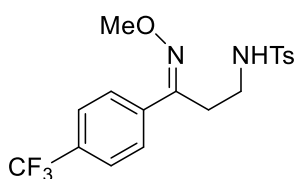
General Procedure B using **1b** (38.7 mg, 0.20 mmol), **2a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/Et₂O = 1/1) and GPC afforded **3ba** as a colorless oil (48.4 mg, 67%). ^1H NMR (CDCl_3 , 600.17 MHz) δ 7.77-7.73 (m, 2H), 7.34-7.28 (m, 4H), 6.90-6.84 (m, 2H), 5.30 (brs, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.20 (q, $J = 6.1$ Hz, 2H), 2.65 (t, $J = 6.0$ Hz, 2H), 2.42 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 159.9, 153.5, 143.3, 136.9, 129.6, 129.5, 127.0, 125.0, 113.4, 62.0, 55.2, 39.9, 34.5, 21.5. **HRMS** (APCI): m/z calculated for $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_4\text{S}^+ [\text{M}+\text{H}]^+$: 363.1373, found: 363.1375. **0**

(*E*)-*N,N'*-(5-methoxy-2-(1-(methoxyimino)propyl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (4ba)



General Procedure C using **1b** (38.7 mg, 0.20 mmol) and **2a** (98.6 mg, 0.50 mmol), and purification by silica gel column chromatography (hexane/EtOAc = 2/1 to 1/1) afforded **4ba** as a colorless solid (91.4 mg, 86%). ^1H NMR (CDCl_3 , 600.17 MHz) δ 7.69-7.66 (4H, m), 7.26-7.23 (m, 4H), 7.13 (s, 2H), 6.73 (s, 2H), 3.95 (s, 3H), 3.66 (s, 3H), 2.38 (s, 6H), 2.28 (q, $J = 7.7$ Hz, 2H), 0.49 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 160.4, 157.3, 144.2, 136.5, 136.3, 129.7, 127.2, 111.5, 102.5, 62.2, 55.3, 23.2, 21.5, 9.3. **HRMS** (APCI): m/z calculated for $\text{C}_{25}\text{H}_{30}\text{N}_3\text{O}_6\text{S}_2^+ [\text{M}+\text{H}]^+$: 532.1571, found: 532.1566.

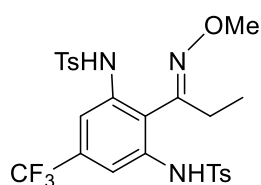
(*Z*)-*N*-(3-(methoxyimino)-3-(4-(trifluoromethyl)phenyl)propyl)-4-methylbenzenesulfonamide (3ca)



General Procedure B using **1c** (46.2 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/EtOAc = 3/1 to 2/1) afforded **3ca** as a colorless solid (58.2 mg, 73%). ^1H NMR (CDCl_3 , 600.17 MHz) δ 7.76-7.74 (m, 2H), 7.62-7.58 (m, 2H), 7.38-7.35 (m, 2H), 7.33-7.27 (m, 2H), 5.28 (t, $J = 6.4$ Hz, 1H), 3.82 (s, 3H), 3.22 (q, $J = 6.2$ Hz, 1H), 2.67 (t, $J = 6.1$ Hz, 1H), 2.43 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 153.2, 143.5, 136.9, 136.7, 130.9 (q, $^2J_{\text{C-F}} = 32.3$ Hz), 129.7, 128.0,

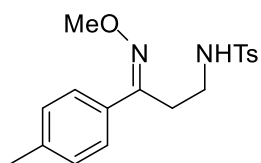
127.0, 125.2, 123.7 (q, $^1J_{\text{C-F}} = 270.9$ Hz), 62.2, 39.6, 34.8, 21.4. **^{19}F NMR** (CDCl_3 , 564.69 MHz) δ -63.94 (s). **HRMS** (APCI): m/z calculated for $\text{C}_{18}\text{H}_{20}\text{F}_3\text{N}_2\text{O}_3\text{S}^+ [\text{M}+\text{H}]^+$: 401.1141, found: 401.1141.

(*E*)-*N,N'*-(2-(1-(methoxyimino)propyl)-5-(trifluoromethyl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (4ca)



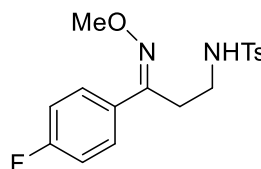
General Procedure C using **1c** (46.2 mg, 0.20 mmol), **2a** (98.6 mg, 0.50 mmol), and purification by silica gel column chromatography (hexane/EtOAc = 2/1 to 1/1) afforded **4ca** as a colorless solid (97.5 mg, 86%). **^1H NMR** (CDCl_3 , 600.17 MHz) δ 7.68 (d, $J = 8.1$ Hz, 4H), 7.45 (s, 2H), 7.26 (d, $J = 8.5$ Hz, 4H), 7.14 (s, 2H), 3.97 (s, 3H), 2.39 (s, 6H), 2.34 (q, $J = 7.6$ Hz, 2H), 0.51 (t, $J = 7.6$ Hz, 3H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (CDCl_3 , 150.92 MHz) δ 156.0, 144.8, 136.4, 135.8, 132.1 (q, $^2J_{\text{C-F}} = 32.6$ Hz), 129.9, 127.2, 122.9 (q, $^1J_{\text{C-F}} = 283.9$ Hz), 121.3, 112.6, 62.6, 22.8, 21.5, 9.3. **^{19}F NMR** (CDCl_3 , 564.69 MHz) δ -64.43 (s). **HRMS** (APCI): m/z calculated for $\text{C}_{25}\text{H}_{27}\text{F}_3\text{N}_3\text{O}_5\text{S}_2^+ [\text{M}+\text{H}]^+$: 570.1339, found: 570.1337.

(*Z*)-*N*-(3-(methoxyimino)-3-(*p*-tolyl)propyl)-4-methylbenzenesulfonamide (3da)



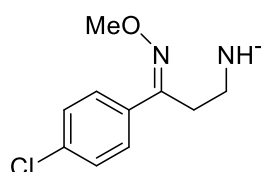
General Procedure B using **1d** (35.5 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol, 1.1 equiv.), and purification by silica gel column chromatography (hexane/EtOAc = 4/1 to 3/1 to 2/1 and hexane/Et₂O = 1/1) afforded **3da** as a colorless solid (59.4 mg, 86%). **^1H NMR** (CDCl_3 , 600.17 MHz) δ 7.75 (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.3$ Hz, 2H), 7.15 (d, $J = 8.1$ Hz, 2H), 5.30 (t, $J = 6.2$ Hz, 1H), 3.80 (s, 3H), 3.20 (q, $J = 6.1$ Hz, 2H), 2.64 (t, $J = 6.0$ Hz, 2H), 2.43 (s, 3H), 2.34 (s, 3H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (CDCl_3 , 150.92 MHz) δ 154.3, 143.3, 139.2, 136.9, 130.0, 129.6, 128.8, 127.5, 127.0, 62.0, 39.9, 34.6, 21.5, 21.3. **HRMS** (APCI): m/z calculated for $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_3\text{S}^+ [\text{M}+\text{H}]^+$: 347.1424, found: 347.1424.

(*Z*)-*N*-(3-(4-fluorophenyl)-3-(methoxyimino)propyl)-4-methylbenzenesulfonamide (3ea)



General Procedure B using **1e** (36.2 mg, 0.20 mmol) and **1a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/EtOAc = 4/1 to 3/1 and hexane/Et₂O = 1/1) afforded **3ea** as a colorless oil (64.6 mg, 92%). **^1H NMR** (CDCl_3 , 600.17 MHz) δ 7.77-7.74 (m, 2H), 7.34-7.29 (m, 4H), 7.05-7.00 (m, 2H), 5.31 (t, $J = 6.5$ Hz, 1H), 3.81 (s, 3H), 3.20 (q, $J = 6.2$ Hz, 2H), 2.65 (t, $J = 6.1$ Hz, 2H), 2.43 (s, 3H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (CDCl_3 , 150.92 MHz) δ 162.6 (d, $^1J_{\text{C-F}} = 250.0$ Hz), 153.1, 143.4, 136.9, 129.8 (d, $^3J_{\text{C-F}} = 8.7$ Hz), 129.7, 128.8, 127.0, 115.2 (d, $^2J_{\text{C-F}} = 21.7$ Hz), 62.1, 39.7, 34.7, 21.5. **^{19}F NMR** (CDCl_3 , 564.69 MHz) δ -111.84—111.89 (m). **HRMS** (APCI): m/z calculated for $\text{C}_{17}\text{H}_{20}\text{FN}_2\text{O}_3\text{S}^+ [\text{M}+\text{H}]^+$: 351.1173, found: 351.1176.

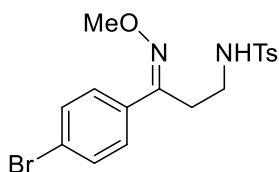
(*Z*)-*N*-(3-(4-chlorophenyl)-3-(methoxyimino)propyl)-4-methylbenzenesulfonamide (3fa)



General Procedure B using **1f** (39.5 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/Et₂O = 2/1) afforded **3fa** as a pale yellow solid (67.5 mg, 92%). **^1H NMR** (CDCl_3 , 600.17 MHz) δ 7.75 (d, $J = 8.3$ Hz, 2H), 7.34-7.28 (m, 4H), 7.23 (d, $J = 8.3$ Hz, 2H), 5.30 (t, $J = 6.3$ Hz, 1H), 3.81 (s, 3H),

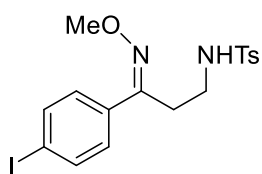
3.20 (q, $J = 6.2$ Hz, 2H), 2.64 (t, $J = 6.1$ Hz, 2H), 2.43 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 153.1, 143.4, 136.8, 135.0, 131.2, 129.7, 129.1, 128.4, 127.0, 62.1, 39.7, 34.6, 21.5. HRMS (APCI): m/z calculated for $\text{C}_{17}\text{H}_{20}\text{ClN}_2\text{O}_3\text{S}^+ [\text{M}+\text{H}]^+$: 367.0878, found: 367.0879.

(Z)-N-(3-(4-bromophenyl)-3-(methoxyimino)propyl)-4-methylbenzenesulfonamide (3ga)



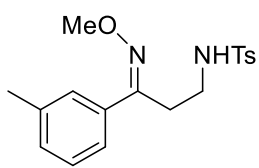
General Procedure B using **1g** (48.4 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/EtOAc = 4/1 to 1/1 and hexane/Et₂O = 2/1) afforded **3ga** as a colorless solid (57.2 mg, 70%). ^1H NMR (CDCl_3 , 600.17 MHz) δ 7.76-7.73 (m, 2H), 7.49-7.46 (m, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.18-7.15 (m, 2H), 5.24 (t, $J = 6.3$ Hz, 1H), 3.81 (s, 3H), 3.20 (q, $J = 6.2$ Hz, 2H), 2.64 (t, $J = 6.1$ Hz, 2H), 2.43 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 153.2, 143.4, 136.9, 131.7, 131.4, 129.7, 129.3, 127.0, 123.3, 62.2, 39.7, 34.6, 21.5. HRMS (APCI): m/z calculated for $\text{C}_{17}\text{H}_{20}\text{BrN}_2\text{O}_3\text{S}^+ [\text{M}+\text{H}]^+$: 413.0353, found: 413.0348.

(Z)-N-(3-(4-iodophenyl)-3-(methoxyimino)propyl)-4-methylbenzenesulfonamide (3ha)



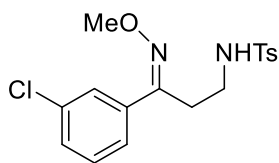
General Procedure B using **1h** (57.8 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/Et₂O = 2/1) and GPC afforded **3ha** as a colorless solid (74.3 mg, 81%). ^1H NMR (CDCl_3 , 600.17 MHz) δ 7.74 (d, $J = 8.1$ Hz, 2H), 7.69-7.66 (m, 2H), 7.30 (d, $J = 7.9$ Hz, 2H), 7.04-7.00 (m, 2H), 5.29 (t, $J = 6.3$ Hz, 1H), 3.80 (s, 3H), 3.19 (q, $J = 6.2$ Hz, 2H), 2.63 (t, $J = 6.1$ Hz, 2H), 2.43 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 153.3, 143.4, 137.3, 136.8, 132.3, 129.7, 129.3, 127.0, 95.3, 62.1, 39.6, 34.5, 21.5. HRMS (APCI): m/z calculated for $\text{C}_{17}\text{H}_{20}\text{IN}_2\text{O}_3\text{S}^+ [\text{M}+\text{H}]^+$: 459.0234, found: 459.0232.

(Z)-N-(3-(methoxyimino)-3-(*m*-tolyl)propyl)-4-methylbenzenesulfonamide (3ia)



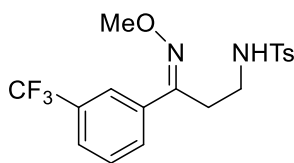
General Procedure B using **1i** (35.5 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/Et₂O = 2/1) afforded **3ia** as a pale yellow solid (55.3 mg, 80%). ^1H NMR (CDCl_3 , 600.17 MHz) δ 7.78-7.74 (m, 2H), 7.33-7.29 (m, 2H), 7.25-7.21 (m, 1H), 7.17-7.13 (m, 1H), 7.06-7.02 (m, 2H), 5.22 (brs, 1H), 3.81 (s, 3H), 3.22 (q, $J = 6.1$ Hz, 2H), 2.62 (t, $J = 6.0$ Hz, 2H), 2.43 (s, 3H), 2.34 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 154.8, 143.3, 137.9, 136.9, 133.1, 129.9, 129.7, 128.1, 127.8, 127.0, 124.5, 62.0, 39.8, 34.8, 21.5, 21.4. HRMS (APCI): m/z calculated for $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_3\text{S}^+ [\text{M}+\text{H}]^+$: 347.1424, found: 347.1427.

(Z)-N-(3-(3-chlorophenyl)-3-(methoxyimino)propyl)-4-methylbenzenesulfonamide (3ja)



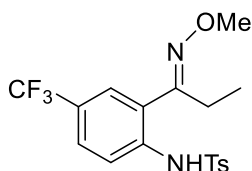
General Procedure B using **1j** (39.5 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/Et₂O = 2/1) afforded **3ja** as a pale yellow solid (64.5 mg, 88%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.78-7.74 (m, 2H), 7.33-7.26 (m, 4H), 7.24-7.21 (m, 1H), 7.16-7.13 (m, 1H), 5.31 (t, *J* = 6.4 Hz, 1H), 3.82 (s, 3H), 3.22 (q, *J* = 6.1 Hz, 2H), 2.61 (t, *J* = 6.0 Hz, 2H), 2.43 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 152.9, 143.4, 136.9, 134.7, 134.1, 129.7, 129.5, 129.2, 127.7, 127.0, 125.7, 62.2, 39.6, 34.7, 21.5. HRMS (APCI): *m/z* calculated for C₁₇H₂₀ClN₂O₃S⁺ [M+H]⁺: 367.0878, found: 367.0876.

(Z)-N-(3-(methoxyimino)-3-(3-(trifluoromethyl)phenyl)propyl)-4-methylbenzenesulfonamide (3ka)



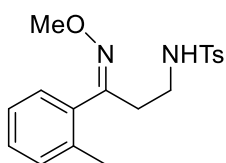
General Procedure B using **1k** (46.2 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/Et₂O = 2/1) afforded **3ka** as a pale yellow oil (67.1 mg, 84%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.78-7.75 (m, 2H), 7.62-7.58 (m, 1H), 7.53-7.45 (m, 3H), 7.34-7.30 (m, 2H), 5.34 (t, *J* = 6.4 Hz, 1H), 3.83 (s, 3H), 3.25 (q, *J* = 6.2 Hz, 2H), 2.66 (t, *J* = 6.1 Hz, 2H), 2.42 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 152.8, 143.5, 136.9, 133.8, 131.0, 130.6 (q, ²*J*_{C-F} = 33.7 Hz), 129.7, 128.8, 127.0, 126.4, 125.8 (q, ³*J*_{C-F} = 4.3 Hz), 124.4 (q, ³*J*_{C-F} = 3.9 Hz), 123.7 (q, ¹*J*_{C-F} = 274.1 Hz), 62.2, 39.6, 34.7, 21.4. ¹⁹F NMR (CDCl₃, 564.69 MHz) δ -63.74 (s). HRMS (APCI): *m/z* calculated for C₁₈H₂₀F₃N₂O₃S⁺ [M+H]⁺: 401.1141, found: 401.1146.

(E)-N-(2-(1-(methoxyimino)propyl)-4-(trifluoromethyl)phenyl)-4-methylbenzenesulfonamide (4ka')



General Procedure C using **1k** (46.2 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane:EtOAc = 4/1 to 1/1 and hexane/Et₂O = 4/1) afforded **4ka'** as a colorless solid (56.9 mg, 67%). ¹H NMR (CDCl₃, 600.17 MHz) δ 11.39 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.60-7.58 (m, 1H), 7.50-7.47 (m, 1H), 7.25-7.23 (m, 2H), 4.10 (s, 3H), 2.70 (q, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 1.01 (t, *J* = 7.6 Hz, 2H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 160.5, 144.1, 139.8, 136.4, 129.7, 127.1, 126.5, 125.3 (q, ²*J*_{C-F} = 33.2 Hz), 125.2, 123.8 (q, ¹*J*_{C-F} = 271.3 Hz), 121.5, 119.9, 62.9, 21.5, 20.0, 10.9. ¹⁹F NMR (CDCl₃, 564.69 MHz) δ -64.19 (s). HRMS (APCI): *m/z* calculated for C₁₈H₂₀F₃N₂O₃S⁺ [M+H]⁺: 401.1141, found: 401.1138.

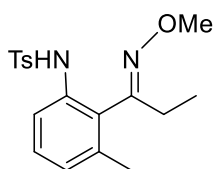
(Z)-N-(3-(methoxyimino)-3-(*o*-tolyl)propyl)-4-methylbenzenesulfonamide (3la)



General Procedure B using **1l** (35.5 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/Et₂O = 2/1) afforded **3la** as a pale yellow solid (64.2 mg, 93%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.79-7.76 (m, 2H), 7.35-7.30 (m, 2H), 7.26-7.21 (m, 1H), 7.20-7.13 (m, 2H), 6.85 (d, *J* = 7.5 Hz, 1H), 5.35 (t, *J* = 6.5 Hz, 1H), 3.78 (s, 3H), 3.24 (q, *J* = 6.1 Hz, 2H), 2.54 (t, *J* = 6.1 Hz, 2H), 2.44 (s, 3H), 2.13 (s, 3H). ¹³C{¹H} NMR

(CDCl₃, 150.92 MHz) δ 156.0, 143.4, 136.9, 134.6, 134.5, 129.9, 129.7, 128.6, 127.0, 125.8, 125.7, 62.0, 39.6, 35.3, 21.5, 19.3. **HRMS** (APCI): m/z calculated for C₁₈H₂₃N₂O₃S⁺ [M+H]⁺: 347.1424, found: 374.1419.

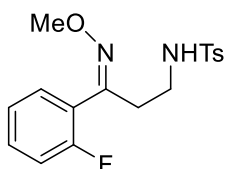
(E)-N-(2-(1-(methoxyimino)propyl)-3-methylphenyl)-4-methylbenzenesulfonamide (4la')



General Procedure C using **1l** (35.5 mg, 0.20 mmol) and **2a** (98.6 mg, 0.50 mmol), and purification by silica gel column chromatography (hexane/EtOAc = 2/1 to 1/1) afforded **4la'** as a colorless oil (22.4 mg, 32%). **¹H NMR** (CDCl₃, 600.17 MHz) δ 7.76-7.71 (m, 2H), 7.39- (d, J = 8.3 Hz, 1H), 7.26-7.21 (m, 3H), 7.14 (t, J = 8.0 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 3.97 (s, 3H), 2.45 (q, J = 7.6 Hz, 2H), 2.38 (s, 3H), 2.17 (s, 3H), 0.67 (t, J = 7.6 Hz, 3H). **¹³C{¹H}**

NMR (CDCl₃, 150.92 MHz) δ 159.5, 143.9, 137.4, 136.8, 134.7, 129.7, 129.0, 127.2, 126.4, 126.3, 117.3, 62.1, 23.2, 21.5, 20.0, 9.3. **HRMS** (APCI): m/z calculated for C₁₈H₂₃N₂O₃S⁺ [M+H]⁺: 347.1424, found: 347.1424.

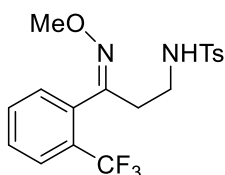
(Z)-N-(3-(2-fluorophenyl)-3-(methoxyimino)propyl)-4-methylbenzenesulfonamide (3ma)



General Procedure B using **1m** (36.2 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/Et₂O = 2/1) afforded **3ma** as a colorless oil (71.2 mg, >99%). **¹H NMR** (CDCl₃, 600.17 MHz) δ 7.78-7.74 (m, 2H), 7.35-7.30 (m, 3H), 7.15-7.10 (m, 1H), 7.08-7.03 (m, 2H), 5.25 (t, J = 6.3 Hz, 1H), 3.81 (s, 3H), 3.22 (q, J = 6.2 Hz, 2H), 2.63 (t, J = 6.1 Hz, 2H), 2.43 (s, 3H). **¹³C{¹H}**

NMR (CDCl₃, 150.92 MHz) δ 158.3 (d, $^1J_{C-F}$ = 248.5 Hz), 150.8, 143.4, 136.8, 130.7 (d, J = 7.2 Hz), 129.7, 128.7 (d, J = 4.3 Hz), 127.0, 124.0 (d, J = 2.9 Hz), 121.5 (d, $^2J_{C-F}$ = 17.3 Hz), 115.7 (d, $^2J_{C-F}$ = 21.7 Hz), 62.1, 39.6, 34.7, 21.5. **¹⁹F NMR** (CDCl₃, 564.69 MHz) δ -113.96—113.99 (m). **HRMS** (APCI): m/z calculated for C₁₇H₂₀FN₂O₃S⁺ [M+H]⁺: 351.1173, found: 351.1176.

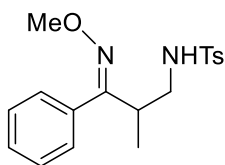
(Z)-N-(3-(methoxyimino)-3-(2-(trifluoromethyl)phenyl)propyl)-4-methylbenzenesulfonamide (3na)



General Procedure B using **PC1** (0.84 mg, 1.5 mol%), **1n** (46.2 mg, 0.20 mmol), and **2a** (43.4 mg, 0.22 mmol) [The reaction time for the isomerization was 4 h], and purification by silica gel column chromatography (hexane/Et₂O = 2/1) afforded **3na** as a colorless solid (54.5 mg, 68%). **¹H NMR** (CDCl₃, 600.17 MHz) δ 7.81-7.77 (m, 2H), 7.66 (d, J = 7.6 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.36-7.31 (m, 2H), 7.02 (d, J = 7.7 Hz, 1H), 5.43-5.29 (m, 1H), 3.74 (s, 3H), 3.28 (q, J = 6.1 Hz, 2H), 2.66-2.54 (m, 2H), 2.44 (s, 3H). **¹³C{¹H}**

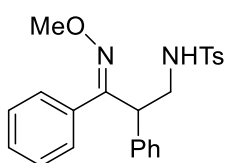
NMR (CDCl₃, 150.92 MHz) δ 154.3, 143.4, 136.9, 133.3, 132.0, 129.7, 128.7, 127.8, 127.0 (q, $^2J_{C-F}$ = 30.3 Hz), 127.0, 126.4 (q, $^3J_{C-F}$ = 5.3 Hz), 123.5 (q, $^1J_{C-F}$ = 304.9 Hz), 62.0, 39.4, 35.5, 21.5. **¹⁹F NMR** (CDCl₃, 564.69 MHz) δ -65.67 (s). **HRMS** (APCI): m/z calculated for C₁₈H₂₀F₃N₂O₃S⁺ [M+H]⁺: 401.1141, found: 401.1145.

(Z)-N-(3-(methoxyimino)-2-methyl-3-phenylpropyl)-4-methylbenzenesulfonamide (3oa)



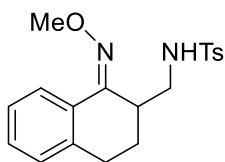
General Procedure B using **1p** (35.5 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/EtOAc = 4/1 to 1/1) afforded **3pa** as a pale yellow oil (40.8 mg, 59%). The corresponding C(sp³)-H di-functionalized products were not detected under the optimized conditions. ¹H NMR (CDCl₃, 600.17 MHz) δ 7.79-7.76 (m, 2H), 7.37-7.31 (m, 5H), 7.15-7.12 (m, 2H), 5.29 (t, *J* = 6.5 Hz, 1H), 3.78 (s, 3H), 3.20-3.10 (m, 2H), 2.87-2.80 (m, 1H), 2.44 (s, 3H), 0.97 (d, *J* = 7.1 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 159.2, 143.3, 137.1, 133.0, 129.7, 128.8, 128.2, 127.4, 127.0, 62.0, 45.8, 39.4, 21.5, 16.5. HRMS (APCI): *m/z* calculated for C₁₈H₂₃N₂O₃S⁺ [M+H]⁺: 347.1424, found: 347.1421.

(Z)-N-(3-(methoxyimino)-2,3-diphenylpropyl)-4-methylbenzenesulfonamide (3pa)



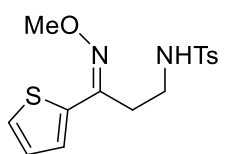
General Procedure B using **1p** (47.9 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/EtOAc = 4/1 to 1/1) afforded **3pa** as a yellow oil (44.6 mg, 55%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.31-7.27 (m, 2H), 7.24-7.16 (m, 6H), 7.13-7.09 (m, 2H), 7.04-7.00 (m, 2H), 5.20 (dd, *J* = 8.4, 5.0 Hz, 1H), 3.95 (dd, *J* = 9.3, 5.4 Hz, 1H), 3.88 (s, 3H), 3.55-3.49 (m, 1H), 3.37-3.31 (m, 1H), 2.42 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 156.1, 143.3, 137.5, 137.3, 133.3, 129.7, 128.8, 128.7, 128.3, 127.9, 127.6, 127.5, 127.0, 62.3, 51.7, 46.2, 21.5. HRMS (APCI): *m/z* calculated for C₂₃H₂₅N₂O₃S⁺ [M+H]⁺: 409.1580, found: 409.1581.

(Z)-N-((1-(methoxyimino)-1,2,3,4-tetrahydronaphthalen-2-yl)methyl)-4-methylbenzenesulfonamide (3qa)



General Procedure B using **1q** (37.9 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/EtOAc = 4/1 to 1/1) afforded **3pa** as a brown solid (22.2 mg, 31%). ¹H NMR (CDCl₃, 600.17 MHz) δ 8.30-8.24 (m, 1H), 7.75-7.68 (m, 2H), 7.33-7.25 (m, 3H), 7.22-7.16 (m, 1H), 7.16-7.13 (m, 1H), 3.90 (s, 3H), 3.20-3.15 (m, 1H), 3.08-3.00 (m, 1H), 2.90-2.86 (m, 2H), 2.68-2.63 (m, 1H), 2.42 (s, 3H), 2.04-1.96 (m, 1H), 1.78-1.70 (m, 1H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 152.4, 143.2, 139.4, 136.9, 131.0, 130.0, 129.6, 128.8, 127.5, 127.0, 125.5, 62.4, 45.1, 40.7, 28.4, 27.1, 21.5. HRMS (APCI): *m/z* calculated for C₁₉H₂₂N₂O₃S⁺ [M+H]⁺: 359.1424, found: 359.1425.

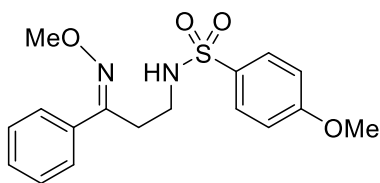
(Z)-N-(3-(methoxyimino)-3-(thiophen-2-yl)propyl)-4-methylbenzenesulfonamide (3ra)



General Procedure B using **1r** (33.9 mg, 0.20 mmol) and **2a** (43.4 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/Et₂O = 2/1) afforded **3ra** as a pale yellow solid (55.9 mg, 83%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.77-7.73 (m, 2H), 7.50 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.32 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.28-7.25 (m, 2H), 7.04 (dd, *J* = 5.2, 3.9 Hz, 1H), 5.32 (t, *J* = 6.2 Hz, 1H), 4.01 (s, 3H), 3.32 (q, *J* = 6.3 Hz, 2H), 2.87 (t, *J* = 6.2 Hz, 2H), 2.39 (s, 3H).

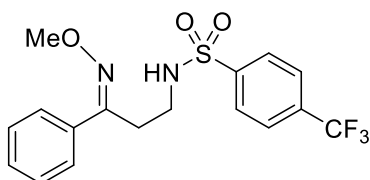
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 146.4, 143.2, 136.9, 131.4, 130.8, 129.6, 129.0, 126.9, 125.6, 62.2, 40.2, 32.8, 21.4. **HRMS** (APCI): m/z calculated for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_3\text{S}_2^+ [\text{M}+\text{H}]^+$: 339.0832, found: 339.0830.

(Z)-4-methoxy-N-(3-(methoxyimino)-3-phenylpropyl)benzenesulfonamide (3ab)



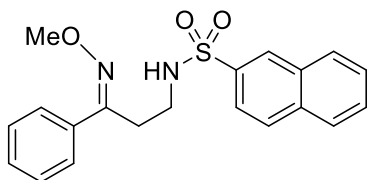
General Procedure B using **1a** (32.6 mg, 0.20 mmol) and *p*-OMe- C_6H_4 -sulfonyl azide **2b** (46.9 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/ Et_2O = 4/1 to 2/1) afforded **3ab** as a pale yellow oil (61.6 mg, 88%). ^1H NMR (CDCl_3 , 600.17 MHz) δ 7.83-7.78 (m, 2H), 7.37-7.33 (m, 3H), 7.28-7.25 (m, 2H), 7.00-6.94 (m, 2H), 5.28 (t, J = 6.3 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.20 (q, J = 6.1 Hz, 2H), 2.66 (t, J = 6.1 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 162.7, 154.4, 133.1, 131.4, 129.1, 129.1, 128.2, 127.5, 114.2, 62.0, 55.5, 39.8, 34.7. **HRMS** (APCI): m/z calculated for $\text{C}_{17}\text{H}_{21}\text{N}_2\text{O}_4\text{S}^+ [\text{M}+\text{H}]^+$: 349.1217, found: 349.1217.

(Z)-N-(3-(methoxyimino)-3-phenylpropyl)-4-(trifluoromethyl)benzenesulfonamide (3ac)



General Procedure B using **1a** (32.6 mg, 0.20 mmol) and *p*- CF_3 - C_6H_4 -sulfonyl azide **2c** (55.3 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/ Et_2O = 1/1) and GPC afforded **3ac** as a colorless solid (63.9 mg, 71%). ^1H NMR (CDCl_3 , 600.17 MHz) δ 8.03-7.99 (m, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.38-7.33 (m, 3H), 7.29-7.24 (m, 2H), 5.49 (brs, 1H), 3.81 (s, 3H), 3.28 (q, J = 6.1 Hz, 2H), 2.68 (t, J = 5.9 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 154.3, 143.6, 134.2 (q, $^2J_{\text{C-F}}$ = 33.2 Hz), 132.9, 129.3, 128.3, 127.5, 126.3 (q, $^3J_{\text{C-F}}$ = 3.4 Hz), 123.2 (q, $^1J_{\text{C-F}}$ = 271.7 Hz), 62.1, 39.9, 34.8. ^{19}F NMR (CDCl_3 , 564.66 MHz) δ -64.09 (s). **HRMS** (APCI): m/z calculated for $\text{C}_{17}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_3\text{S}^+ [\text{M}+\text{H}]^+$: 387.0985, found: 387.0989.

(Z)-N-(3-(methoxyimino)-3-phenylpropyl)naphthalene-2-sulfonamide (3ad)



General Procedure B using **1a** (32.6 mg, 0.20 mmol) and **2d** (51.3 mg, 0.22 mmol), and purification by silica gel column chromatography (hexane/ Et_2O = 1/1) afforded **3ad** as a pale yellow solid (68.2 mg, 93%). ^1H NMR (CDCl_3 , 600.17 MHz) δ 8.46-8.42 (m, 1H), 7.96 (d, J = 9.0 Hz, 1H), 7.94 (d, J = 9.0 Hz, 1H), 7.91 (d, J = 8.3 Hz, 1H), 7.86 (dd, J = 8.4, 1.8 Hz, 1H), 7.68-7.62 (m, 1H), 7.62-7.58 (m, 1H), 7.30-7.23 (m, 3H), 7.22-7.16 (m, 2H), 5.48 (t, J = 6.0 Hz, 1H), 3.79 (s, 3H), 3.26 (q, J = 6.2 Hz, 2H), 2.65 (t, J = 6.0 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 154.4, 136.6, 134.7, 132.9, 132.0, 129.5, 129.1, 129.0, 128.7, 128.3, 128.1, 127.8, 127.5, 127.4, 122.2, 62.0, 39.9, 34.8. **HRMS** (APCI): m/z calculated for $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}_3\text{S}^+ [\text{M}+\text{H}]^+$: 369.1267, found: 369.1265.

Determination of *E/Z* configuration of the C(sp³)–H amidation product

Single crystal X-ray crystallography of **3ad**

A single crystal of **3ad** suitable for X-ray diffraction analysis (XRD) was obtained by recrystallization from Et₂O/hexane. A suitable crystal of **3ad** was mounted with liquid paraffin on a Dual Thickness MicroLoops LD and transferred to the goniometer in a nitrogen stream at 159.2 K. Measurement was performed on a RIGAKU XtaLAB Synergy-R/Cu system with 1.2 kW PhotonJet-R/Cu microfocus rotating anode using graphite monochromated Cu-K α radiation source ($\lambda = 1.5418$ Å) and HyPix-6000HE detector. Cell parameters were determined and refined, and raw frame data were integrated using CrysAlisPro (Agilent Technologies, 2010). The structures were solved by direct methods with SHELXT 2018/2^[S12] and refined by full-matrix least-squares techniques against F^2 with SHELXL-2019/3^[S13] by using Olex2 software package.^[S14] The non-hydrogen atoms were anisotropically refined, and hydrogen atoms were placed using AFIX instructions. The detailed crystallographic data are available as a crystallographic information file (CIF), which is available from CCDC 2362952. The ORTEP-3 program was used to draw the molecule structures. The structure is drawn as thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. The structure and crystal data are shown in **Figure S2** and **Table S2**.

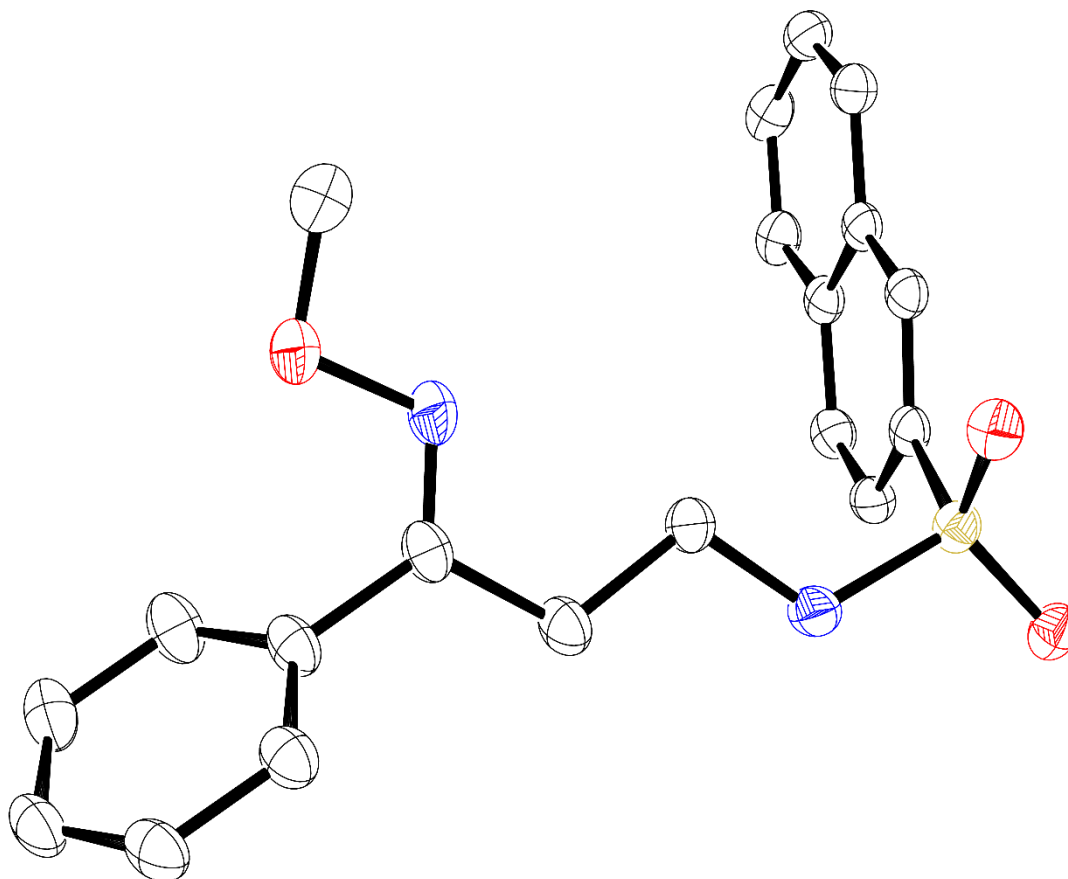


Figure S3. Single crystal X-ray crystallography of **3ad**

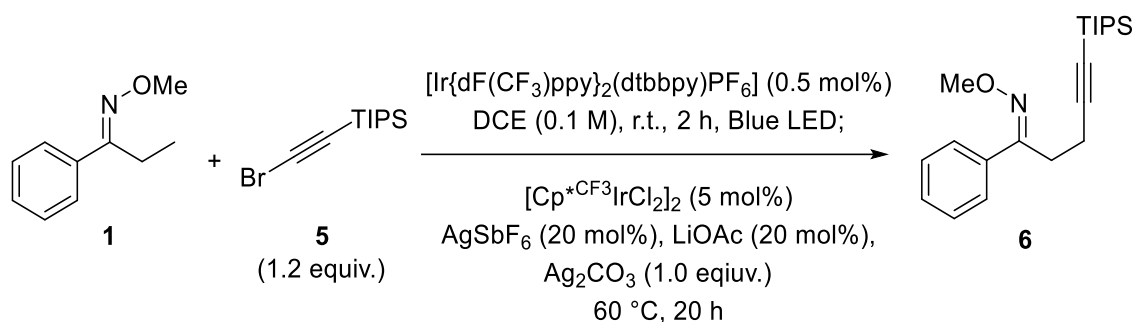
Table S3. Crystal data and structure refinement for YH2naphazide_auto.

Identification code	YH2naphazide_auto
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Empirical formula	C ₂₀ H ₂₀ N ₂ O ₃ S
Formula weight	368.44
Temperature/K	150.92
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	11.4667(2)
b/Å	5.78690(10)
c/Å	26.8837(5)
α /°	90
β /°	89.985(2)
γ /°	90
Volume/Å ³	1783.91(5)
Z	4
ρ calcg/cm ³	1.372
μ /mm ⁻¹	1.803
F(000)	776.0
Crystal size/mm ³	0.07 × 0.07 × 0.02
Radiation	Cu K α (λ = 1.54184)
2 Θ range for data collection/°	6.576 to 157.554
Index ranges	-14 ≤ h ≤ 14, -7 ≤ k ≤ 5, -34 ≤ l ≤ 34
Reflections collected	17113
Independent reflections	3715 [R _{int} = 0.0372, R _{sigma} = 0.0283]
Data/restraints/parameters	3715/0/236
Goodness-of-fit on F ²	1.062
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0494, wR ₂ = 0.1407
Final R indexes [all data]	R ₁ = 0.0568, wR ₂ = 0.1481
Largest diff. peak/hole / e Å ⁻³	0.64/-0.55

2-4. Iridium(III)-catalyzed selective C(sp³)-H alkynylation of oxime ethers

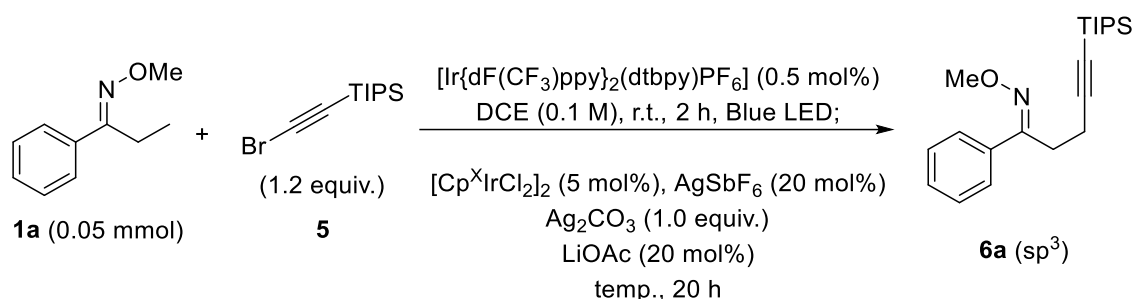
General procedure D: C(sp³)-H alkynylation



In an argon-filled glovebox, a screw-cap test tube was charged with Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (1.12 mg, 0.0010 mmol, 0.50 mol%), oxime **1** (0.20 mmol, 1.0 equiv.), and DCE (2.0 mL). The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 2 h at room temperature under blue light irradiation. The reaction mixture was taken into the glove box, and [Cp^{CF3}IrCl₂]₂ (9.04 mg, 0.010 mmol, 5.0 mol%), AgSbF₆ (13.8 mg, 0.040 mmol, 20 mol%), LiOAc (2.64 mg, 0.040 mmol, 20 mol%), Ag₂CO₃ (55.2 mg, 0.20 mmol, 1.0 equiv.), and TIPS acetylene bromide **5** (57.5 μL, 0.24 mmol, 1.2 equiv.) were added. After stirred for 20 h, the reaction mixture was filtered through a short pad of silica gel, eluted with AcOEt, and evaporated under reduced pressure. The crude product was purified by reversed phase column chromatography with Universal column ODS (CH₃CN/H₂O = 1/1 to 1/0) to afford **6**.

Control experiments using [Cp^{*}IrCl₂]₂ instead of [Cp^{CF3}IrCl₂]₂

Table S4. Control experiments using [Cp^{*}IrCl₂]₂

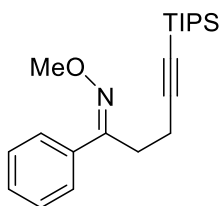


entry	Cp ^X Ir(III)	temp.	% 6a
0 ^a	[Cp ^{CF3} IrCl ₂] ₂	60	98
1	[Cp [*] IrCl ₂] ₂	60	21
2	[Cp [*] IrCl ₂] ₂	90	17

^a0.2 mmol scale and isolated yield.

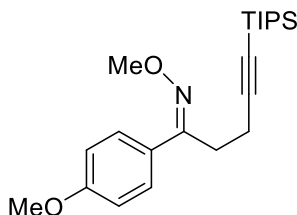
Control experiments (entries 1 and 2) were performed using [Cp^{*}IrCl₂]₂ (1.99 mg, 0.0025 mmol, 5.0 mol%) in 0.05 mmol scale, and the yields were determined by ¹H NMR analysis of the crude mixture using 1,1,2,2-tetrachloroethane as the internal standard. Much lower yields were observed compared with that obtained by using [Cp^{CF3}IrCl₂]₂ catalyst both at 60 °C and 90 °C.

(Z)-1-phenyl-5-(triisopropylsilyl)pent-4-yn-1-one O-methyl oxime (6a)



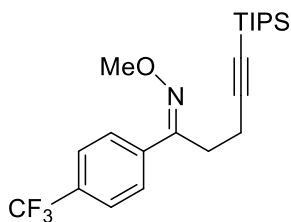
General Procedure D using **1a** (32.6 mg, 0.20 mmol) afforded **6a** as a colorless oil (67.5 mg, 98%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.43-7.30 (m, 5H), 3.82 (s, 3H), 2.75 (t, *J* = 7.3 Hz, 2H), 2.40 (t, *J* = 7.3 Hz, 2H), 1.09-0.98 (m, 21H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 155.7, 133.3, 128.8, 128.2, 127.7, 107.1, 81.3, 61.7, 34.8, 18.6, 17.6, 11.2. HRMS (APCI): *m/z* calculated for C₂₁H₃₄NOSi⁺ [M+H]⁺: 344.2404, found: 344.2406.

(Z)-1-(4-methoxyphenyl)-5-(triisopropylsilyl)pent-4-yn-1-one O-methyl oxime (6b)



General Procedure D using **1b** (38.7 mg, 0.20 mmol) afforded **6b** as a colorless oil (64.2 mg, 86%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.42-7.37 (m, 2H), 6.93-6.89 (m, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 2.75 (t, *J* = 7.4 Hz, 2H), 2.40 (t, *J* = 7.4 Hz, 2H), 1.10-0.97 (m, 21H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 159.7, 155.0, 129.5, 125.1, 113.5, 107.2, 81.2, 61.7, 55.2, 34.6, 18.6, 17.8, 11.2. HRMS (APCI): *m/z* calculated for C₂₂H₃₆NO₂Si⁺ [M+H]⁺: 374.2510, found: 374.2518.

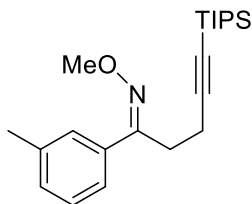
(Z)-1-(4-(trifluoromethyl)phenyl)-5-(triisopropylsilyl)pent-4-yn-1-one O-methyl oxime (6c)



General Procedure D using **1c** (46.2 mg, 0.20 mmol) afforded **6c** as a colorless oil (37.9 mg, 46%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 2.76 (t, *J* = 7.2 Hz, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 1.11-0.97 (m, 21H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 154.5, 137.0, 130.7 (q, ²*J*_{C-F} = 32.3 Hz), 128.1, 125.2 (q, ³*J*_{C-F} = 2.9 Hz), 123.9 (q, ¹*J*_{C-F} = 272.1 Hz), 106.6, 81.8, 61.9, 34.5, 18.6, 17.5, 11.2. ¹⁹F NMR (CDCl₃, 564.66 MHz) δ -63.59 (s). HRMS (APCI):

m/z calculated for C₂₂H₃₃F₃NOSi⁺ [M+H]⁺: 412.2278, found: 412.2275.

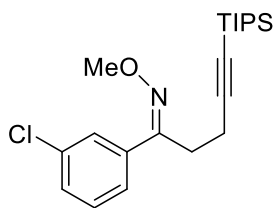
(Z)-1-(m-tolyl)-5-(triisopropylsilyl)pent-4-yn-1-one O-methyl oxime (6d)



General Procedure D using **1i**^[S6] (35.5 mg, 0.20 mmol) afforded **6d** as a colorless oil (55.5 mg, 78%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.29-7.25 (m, 1H), 7.17-7.12 (m, 3H), 3.82 (s, 3H), 2.73 (t, *J* = 7.3 Hz, 2H), 2.39 (t, *J* = 7.4 Hz, 2H), 2.36 (s, 3H), 1.10-0.98 (m, 21H). ¹³C NMR (CDCl₃, 150.92 MHz) δ 156.0, 137.8, 133.3, 129.5, 128.1, 124.7, 107.1, 81.2, 61.7, 34.9, 21.4, 18.6, 17.6, 11.2. HRMS (APCI): *m/z* calculated for C₂₂H₃₆NOSi⁺

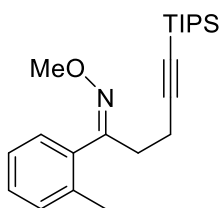
[M+H]⁺: 358.2561, found: 358.2565.

(Z)-1-(3-chlorophenyl)-5-(triisopropylsilyl)pent-4-yn-1-one O-methyl oxime (6e)



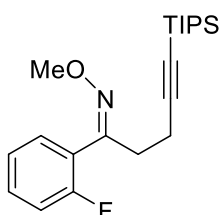
General Procedure D using **1j** (39.5 mg, 0.20 mmol) afforded **6e** as a colorless oil (59.7 mg, 79%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.37 (d, *J* = 1.4 Hz, 1H), 7.35-7.31 (m, 2H), 7.25-7.21 (m, 1H), 3.83 (s, 3H), 2.72 (t, *J* = 7.3 Hz, 2H), 2.40 (t, *J* = 7.3 Hz, 2H), 1.12-0.99 (m, 21H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 154.3, 134.9, 134.2, 129.5, 128.9, 127.9, 125.8, 106.7, 81.7, 61.9, 34.5, 18.6, 17.5, 11.2. **HRMS** (APCI): *m/z* calculated for C₂₁H₃₃ClNOSi⁺ [M+H]⁺: 378.2014, found: 378.2014.

(Z)-1-(o-tolyl)-5-(triisopropylsilyl)pent-4-yn-1-one O-methyl oxime (6f)



General Procedure D using **1l**^[S7] (35.4 mg, 0.20 mmol) afforded **6f** as a colorless oil (31.7 mg, 44%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.28-7.17 (m, 3H), 7.06 (d, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 2.68 (t, *J* = 7.4 Hz, 2H), 2.45 (t, *J* = 7.4 Hz, 2H), 2.24 (s, 3H), 1.10-0.98 (m, 21H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 156.5, 135.2, 134.5, 129.9, 128.4, 126.3, 125.6, 107.4, 81.2, 61.7, 35.4, 19.6, 18.6, 17.1, 11.2. **HRMS** (APCI): *m/z* calculated for C₂₂H₃₆NOSi⁺ [M+H]⁺: 358.2561, found: 358.2569.

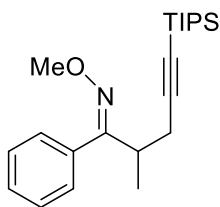
(Z)-1-(2-fluorophenyl)-5-(triisopropylsilyl)pent-4-yn-1-one O-methyl oxime (6g)



General Procedure D using **1m** (36.2 mg, 0.20 mmol) afforded **6g** as a colorless oil (31.4 mg, 43%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.37-7.31 (m, 1H), 7.27-7.22 (m, 1H), 7.16 (td, *J* = 7.5, 1.0 Hz, 1H), 7.12-7.07 (m, 1H), 3.83 (s, 3H), 2.75 (t, *J* = 7.5 Hz, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 1.15-0.92 (m, 21H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 158.6 (d, ¹*J*_{C-F} = 251.4 Hz), 151.8, 130.4 (d, ³*J*_{C-F} = 7.2 Hz), 129.3 (d, ³*J*_{C-F} = 4.3 Hz), 123.9 (d, ⁴*J*_{C-F} = 2.9 Hz), 121.6 (d, ²*J*_{C-F} = 17.3 Hz), 115.7 (d, ²*J*_{C-F} = 21.7 Hz), 81.3, 61.9, 34.5, 18.6, 17.4, 11.2. ¹⁹F

NMR (CDCl₃, 564.66 MHz) δ -114.01—114.05 (m) **HRMS** (APCI): *m/z* calculated for C₂₁H₃₃FN OSi⁺ [M+H]⁺: 362.2310, found: 362.2313.

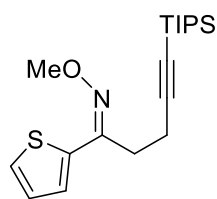
(Z)-2-methyl-1-phenyl-5-(triisopropylsilyl)pent-4-yn-1-one O-methyl oxime (6h)



General Procedure D using **1o** (36.9 mg, 0.20 mmol) afforded **6h** as a colorless oil (48.2 mg, 67%). The corresponding C(*sp*³)-H di-functionalized products were not detected under the optimized conditions. ¹H NMR (CDCl₃, 600.17 MHz) δ 7.41-7.36 (m, 2H), 7.36-7.32 (m, 1H), 7.27-7.24 (m, 2H), 3.79 (s, 3H), 2.93-2.85 (m, 1H), 2.47 (dd, *J* = 16.8, 6.3 Hz, 1H), 2.30 (dd, *J* = 16.9, 7.4 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.11-0.99 (m, 21H). ¹³C{¹H} NMR

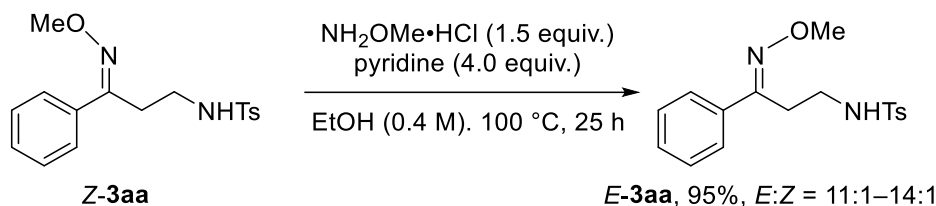
(CDCl₃, 150.92 MHz) δ 159.8, 133.7, 128.3, 128.1, 127.5, 106.6, 82.0, 61.7, 39.4, 25.0, 18.6, 17.7, 11.3. **HRMS** (APCI): *m/z* calculated for C₂₂H₃₆NOSi⁺ [M+H]⁺: 358.2561, found: 358.2563.

(Z)-1-(thiophen-2-yl)-5-(triisopropylsilyl)pent-4-yn-1-one O-methyl oxime (6i)



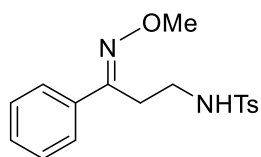
General Procedure D using **1q** (33.9 mg, 0.20 mmol) afforded **6i** as a colorless oil (55.9 mg, 80%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.51 (dd, *J* = 5.2, 0.9 Hz, 1H), 7.47 (dd, *J* = 3.8, 0.9 Hz, 1H), 7.08 (dd, *J* = 5.0, 4.0 Hz, 1H), 4.03 (s, 3H), 2.95 (t, *J* = 7.8 Hz, 2H), 2.64 (t, *J* = 7.9 Hz, 2H), 1.12-0.96 (m, 21H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 147.7, 131.7, 130.4, 129.0, 125.6, 107.5, 81.2, 61.9, 33.2, 18.8, 18.6, 11.2. **HRMS** (APCI): *m/z* calculated for C₁₉H₃₂NOSSi⁺ [M+H]⁺: 350.1968, found: 350.1960.

2-5. Re-isomerization of amidated product from Z to E (E-3aa)



A screw-capped vial was charged with **Z-3aa** (136.3 mg, 0.42 mmol, 1.0 equiv.) and *O*-methylhydroxylamine hydrochloride (53.0 mg, 0.64 mmol, 1.5 equiv.), followed by pyridine (136 μl, 1.69 mmol, 4.0 equiv.) and EtOH (1 mL, 0.4 M). The reaction mixture was stirred for 25 h at 100 °C. The reaction mixture was diluted with EtOAc and washed with 1 M HCl. The organic layer was dried with Na₂SO₄ and evaporated to afford **E-3aa** as a colorless solid (129.8 mg, 0.40 mmol, 95%), including **Z-3aa** (*E/Z* = 11:1). We repeated the same experiment and obtained the desired isomer in 95% yield and 14:1 ratio.

(E)-N-(3-(methoxyimino)-3-phenylpropyl)-4-methylbenzenesulfonamide (E-3aa)

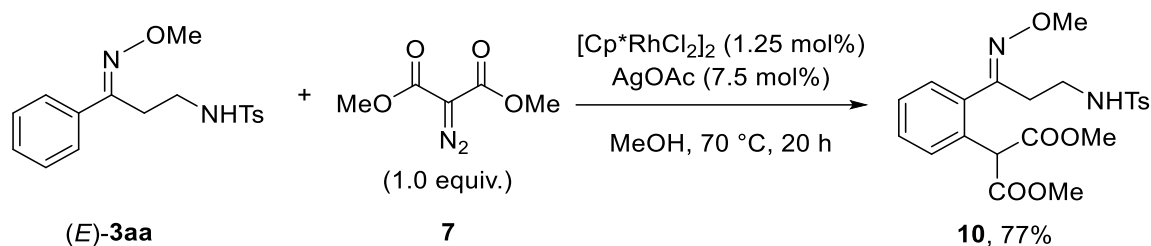


¹H NMR (CDCl₃, 600.17 MHz) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.38-7.27 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.83 (t, *J* = 5.8 Hz, 1H), 3.96 (s, 3H), 3.19 (q, *J* = 6.4 Hz, 2H), 2.92 (t, *J* = 7.0 Hz, 2H), 2.40 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 155.0, 143.3, 136.6, 134.5, 129.6, 129.3, 128.5, 127.0, 126.0, 62.0, 40.1, 27.0, 21.4.

HRMS (APCI): *m/z* calculated for C₁₇H₂₀N₂O₃S⁺ [M+H]⁺: 333.1267, found: 333.1267.

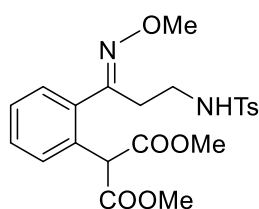
2-6. Switchable C–H functionalization: from C(sp³)–H to C(sp²)–H

C(sp²)–H alkylation with diazomalonate after C(sp³)–H amidation (10)^[S16]



In an argon-filled glovebox, a screw-cap tube was charged with *E*-3aa (13.0 mg, 0.04 mmol, *E*:*Z* = 11:1), [Cp*RhCl₂]₂ (0.62 mg, 0.001 mmol, 1.25 mol%), AgOAc (1.0 mg, 0.006 mmol, 7.5 mol%), diazomalonate (4.92 μl, 0.04 mmol, 1.0 equiv.), and MeOH (300 μL, 0.1 M). After stirred for 20 h at 70 °C, the reaction mixture was filtered through a silica gel short pad, and the organic layer was evaporated. Purification by preparative thin layered chromatography (EtOAc/hexane = 1:1) afforded **10** (14.2 mg, 77%) as a colorless oil.

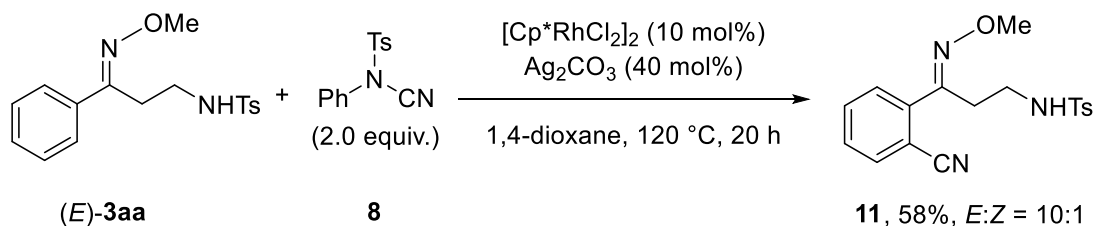
dimethyl (*E*)-2-(2-(1-(methoxyimino)-3-((4-methylphenyl)sulfonamido)propyl)phenyl)malonate (**10**)



¹H NMR (CDCl₃, 600.17 MHz) δ 7.68–7.66 (m, 2H), 7.48 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.39 (td, *J* = 7.9, 1.3 Hz, 1H), 7.33 (td, *J* = 7.6, 1.3 Hz, 1H), 7.31–7.24 (m, 2H), 7.17 (dd, *J* = 7.7, 1.2 Hz, 1H), 5.19 (s, 1H), 4.90 (t, *J* = 6.1 Hz, 1H), 3.90 (s, 3H), 3.76 (s, 6H), 3.16 (q, *J* = 6.6 Hz, 2H), 2.89 (t, *J* = 6.7 Hz, 2H), 2.42 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 169.0, 155.4, 143.3, 137.0, 135.2, 131.2, 130.1, 129.7, 129.1, 128.3, 128.2, 127.0,

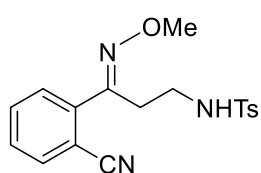
62.1, 54.6, 52.9, 39.7, 29.9, 21.5. HRMS (APCI): *m/z* calculated for C₂₂H₂₇N₂O₇S⁺ [M+H]⁺: 463.1533, found: 463.1528.

C(sp²)–H cyanation after C(sp³)–H amidation (**11**)^[S17]



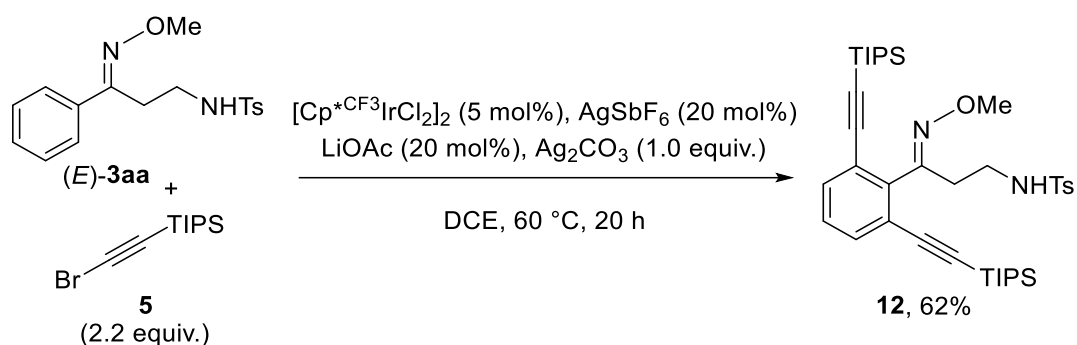
In an argon-filled glovebox, a screw-cap test tube was charged with *E*-3aa (65.0 mg, 0.20 mmol, *E*:*Z* = 14:1), [Cp*RhCl₂]₂ (16.7 mg, 0.020 mmol, 10 mol%), *N*-cyano-4-methyl-*N*-phenylbenzenesulfonamide (109 mg, 0.40 mmol, 2.0 equiv.), Ag₂CO₃ (22.1 mg, 0.080 mmol, 40 mol%), and 1,4-dioxane (2.0 mL, 0.20 M). After stirred for 20 h at 120 °C, the reaction mixture was filtered through a silica gel short pad, and the organic layer was evaporated. Purification by silica gel column chromatography (EtOAc/hexane = 4/1 to 1/1 and DCM only) afforded **11** (41.8 mg, 58%, *E*:*Z* = 10:1) as a colorless solid.

(*E*)-*N*-(3-(2-cyanophenyl)-3-(methoxyimino)propyl)-4-methylbenzenesulfonamide (**11**)



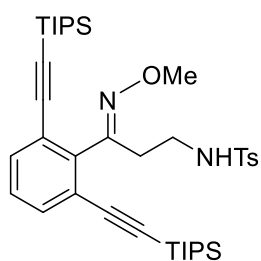
¹H NMR (CDCl₃, 600.17 MHz) δ 7.81 (d, *J* = 8.1 Hz, 1H, minor), 7.77 (d, *J* = 8.1 Hz, 2H, minor), 7.72-7.66 (m, 3H, major), 7.64-7.56 (m, 1H), 7.49-7.43 (m, 2H, major), 7.34-7.27 (m, 3H, minor), 7.27-7.25 (m, 2H, major), 7.19 (d, *J* = 8.5 Hz, 1H), 5.26 (t, *J* = 6.7 Hz, 1H, minor), 4.91 (t, *J* = 6.0 Hz, 1H, major), 4.01 (s, 3H, major), 3.84 (s, 3H, minor), 3.27 (q, *J* = 6.2 Hz, 2H, minor), 3.20 (q, *J* = 6.8 Hz, 2H, major), 2.96 (t, *J* = 7.0 Hz, 2H, major), 2.69 (t, *J* = 5.9 Hz, 2H, minor), 2.44 (s, 3H, minor), 2.42 (s, 3H, major). **¹³C{¹H} NMR** (CDCl₃, 150.92 MHz) δ 153.6, 143.5, 138.8, 136.7, 134.1, 132.8, 129.7, 129.1, 128.9, 127.0, 118.1, 110.9, 62.5, 39.6, 29.3, 21.5. **HRMS** (APCI): *m/z* calculated for C₁₈H₂₀N₃O₃S⁺ [M+H]⁺: 358.1220, found: 358.1211.

C(sp²)-H dialkynylation after C(sp³)-H amidation (**12**)



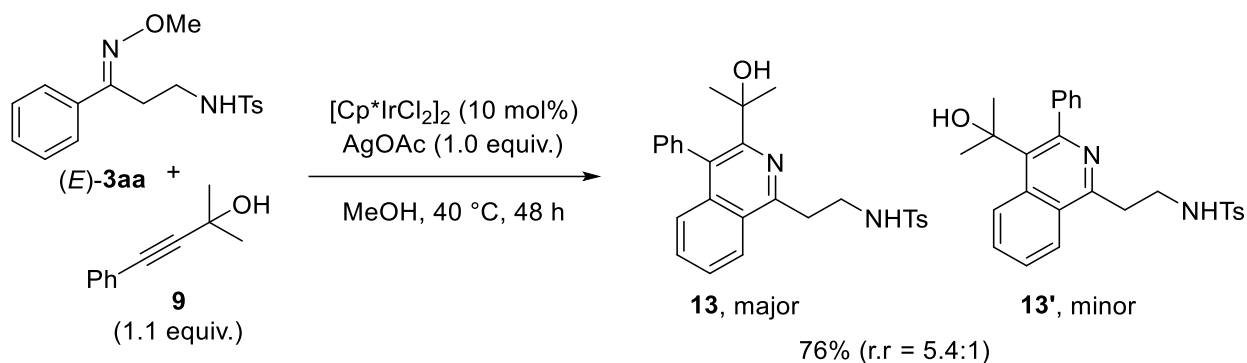
In an argon-filled glovebox, a screw-cap tube was charged with *E*-**3aa** (13.0 mg, 0.04 mmol, *E*:*Z* = 11:1), [Cp*CF₃IrCl₂]₂ (1.81 mg, 0.002 mmol, 5 mol%), LiOAc (0.008 mg, 0.53 mmol, 20 mol%), Ag₂CO₃ (16.6 mg, 0.06 mmol, 1.5 equiv.), AgSbF₆ (2.75 mg, 0.008 mmol, 20 mol%), TIPS acetylene bromide **5** (21.1 μL, 0.088 mmol, 2.2 equiv.), and DCE (400 μL, 0.10 M). After stirred for 20 h at 60 °C, the reaction mixture was filtered through a silica gel short pad, and the organic layer was evaporated. Purification by preparative thin layered chromatography (EtOAc/hexane = 9/1) afforded **12** (17.3 mg, 62%) as a colorless solid.

(*E*)-*N*-(3-(2,6-bis((triisopropylsilyl)ethynyl)phenyl)-3-(methoxyimino)propyl)-4-methylbenzenesulfonamide (**12**)



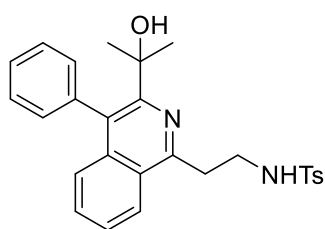
¹H NMR (CDCl₃, 600.17 MHz) δ 7.51 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.15-7.12 (m, 2H), 4.89 (t, *J* = 6.2 Hz, 1H), 3.88 (s, 3H), 3.27 (q, *J* = 6.6 Hz, 2H), 2.73 (t, *J* = 6.6 Hz, 2H), 2.38 (s, 3H), 1.10-1.06 (m, 42H). **¹³C{¹H} NMR** (CDCl₃, 150.92 MHz) δ 155.4, 142.8, 140.9, 137.5, 133.0, 129.5, 128.2, 126.6, 123.1, 103.9, 96.4, 61.8, 39.6, 30.7, 21.5, 18.6, 11.2. **HRMS** (APCI): *m/z* calculated for C₃₉H₆₁N₂O₃SSi₂⁺ [M+H]⁺: 693.3936, found: 693.3927.

C(sp²)-H alkenylation with propargyl alcohol after C(sp³)-H amidation (13)^[S18]



In an argon-filled glovebox, a screw-cap tube was charged with *E*-3aa (65.0 mg, 0.20 mmol, *E*:*Z* = 14:1), propargyl alcohol (35.2 mg, 0.22 mmol, 1.1 equiv.), [Cp*IrCl₂]₂ (15.9 mg, 0.020 mmol, 10 mol%), AgOAc (33.4 mg, 0.20 mmol, 1.0 equiv.), and MeOH (2.0 mL, 0.10 M). After stirred for 48 h at 40 °C, the reaction mixture was filtered through a silica gel short pad, and the organic layer was evaporated. Purification by preparative thin layered chromatography (DCM then DCM/EtOAc = 1/0 to 4/1) afforded **13** (69.6 mg, 76%) including regio-isomer **13'** (**13**:**13'** = 5.4:1) determined by ¹H NMR analysis. Recrystallization from DCM/hexane afforded **13** (47.7 mg, 52%) as a colorless solid.

***N*-(2-(3-(2-hydroxypropan-2-yl)-4-phenylisoquinolin-1-yl)ethyl)-4-methylbenzenesulfonamide (13)**

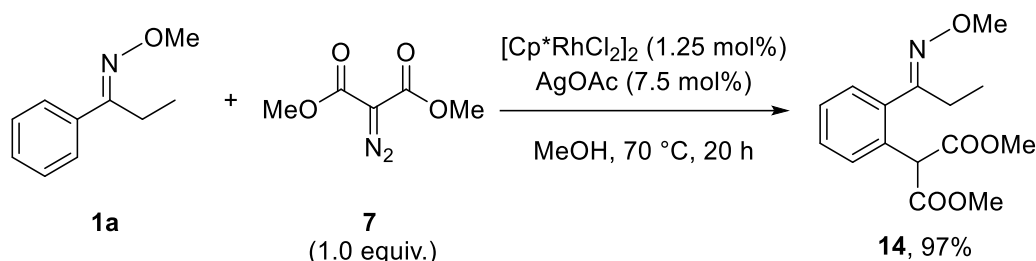


¹H NMR (CDCl₃, 600.17 MHz) δ 8.11-8.07 (m, 1H), 7.79-7.75 (m, 2H), 7.59-7.47 (m, 5H), 7.31-7.25 (m, 4H), 7.23-7.19 (m, 1H), 5.62 (s, 1H), 5.19 (t, *J* = 6.2 Hz, 1H), 3.66 (m, 2H), 3.59 (t, *J* = 6.2 Hz, 2H), 2.40 (s, 3H), 1.31 (s, 6H). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 155.2, 153.4, 143.4, 137.8, 137.4, 137.0, 130.9, 130.2, 129.7, 128.1, 128.1, 127.9, 127.0, 127.0, 126.5, 125.7, 124.3, 73.0, 41.2, 34.1, 31.2, 21.5. HRMS (APCI): *m/z* calculated for C₂₇H₂₉N₂O₃S⁺ [M+H]⁺: 461.1893, found:

461.1895.

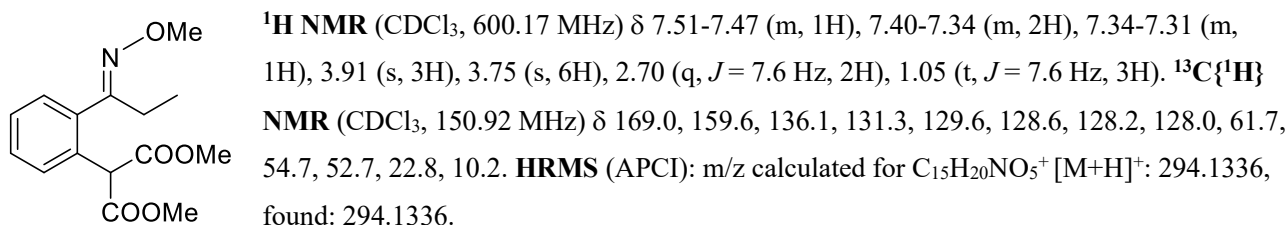
2-7. Switchable C–H functionalization: from C(sp²)–H to C(sp³)–H

C(sp²)–H alkylation with diazomalonate (**14**)^[S16]

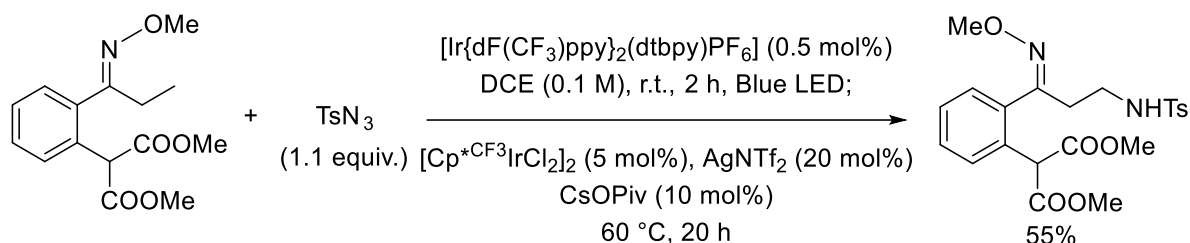


Following the previous report,^[S16] in an argon-filled glovebox, a screw-cap tube was charged with **1aa** (32.6 mg, 0.20 mmol), [Cp^{*}RhCl₂]₂ (3.09 mg, 0.0050 mmol, 1.25 mol%), AgOAc (5.00 mg, 0.030 mmol, 7.5 mol%), diazomalonate **7** (24.6 μl, 0.20 mmol, 1.0 equiv.), and MeOH (1.5 mL, 0.10 M). After stirred for 20 h at 70 °C, the reaction mixture was filtered through a silica gel short pad, and the organic layer was evaporated. Purification by preparative thin layered chromatography (EtOAc/hexane = 9:1) afforded **14** (56.9 mg, 97%) as a colorless oil.

dimethyl (E)-2-(2-(1-(methoxyimino)propyl)phenyl)malonate (**14**)

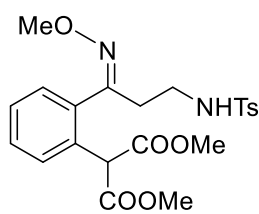


C(sp³)–H amidation after C(sp²)–H alkylation (**15**)



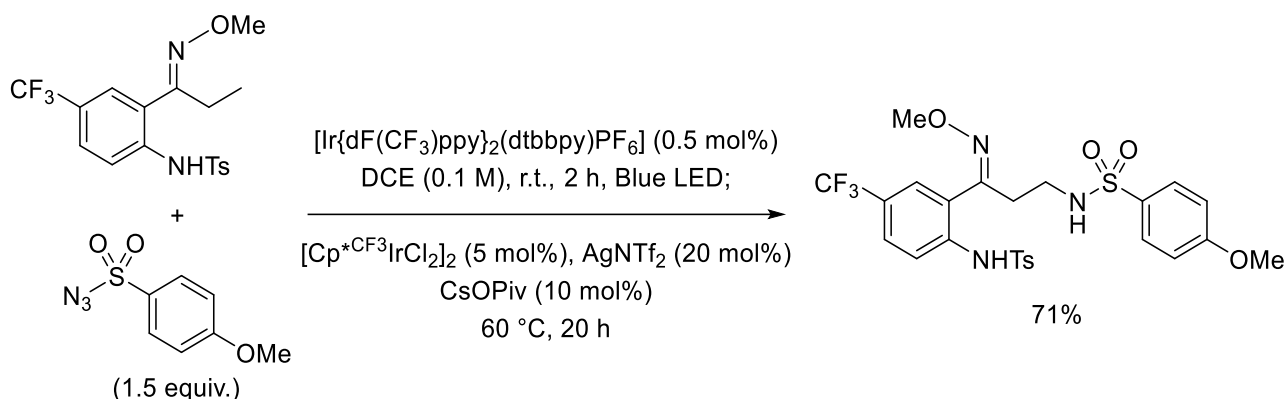
In an argon-filled glovebox, a screw-cap test tube was charged with Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (1.12 mg, 0.0010 mmol, 0.50 mol %), **14** (58.7 mg, 0.20 mmol), and DCE (2.0 mL). The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 2 h at room temperature under blue light irradiation. The reaction mixture was taken into the glove box, and Cp^{*}CF₃IrCl₂ (9.06 mg, 0.010 mmol, 5.0 mol%), AgNTf₂ (15.52 mg, 0.040 mmol, 20 mol%), CsOPiv (4.72 mg, 0.020 mmol, 10 mol%), and sulfonyl azide **2a** (0.220 mmol, 1.1 equiv.) were added. After stirred for 20 h at 60 °C, the reaction mixture was filtered through a short pad of silica gel, eluted with EtOAc, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 4/1 to 1/1) to afford **15** (50.7 mg, 55%) as a pale yellow oil.

dimethyl (Z)-2-(2-(1-(methoxyimino)-3-((4-methylphenyl)sulfonamido)propyl)phenyl)malonate (15)



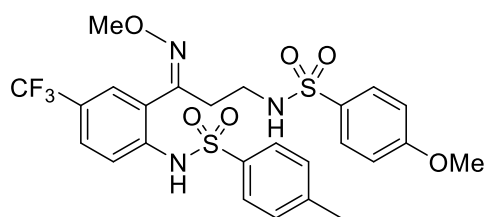
^1H NMR (CDCl_3 , 600.17 MHz) δ 7.78-7.74 (m, 2H), 7.60 (dd, J = 7.8, 1.3 Hz, 1H), 7.40 (td, J = 7.7, 1.4 Hz, 1H), 7.35 (td, J = 7.5, 1.3 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 6.98 (dd, J = 7.6, 1.3 Hz, 1H), 5.48 (t, J = 6.4 Hz, 1H), 4.44 (s, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 3.68 (s, 3H), 3.29-3.21 (m, 1H), 3.18-3.10 (m, 1H), 2.79-2.70 (m, 1H), 2.64-2.55 (m, 1H), 2.43 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 169.1, 167.8, 154.6, 143.3, 137.2, 134.3, 130.3, 129.7, 129.4, 129.2, 128.5, 127.0, 126.0, 61.7, 54.3, 53.2, 52.7, 39.6, 36.0, 21.5. HRMS (APCI): m/z calculated for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_7\text{S}^+ [\text{M}+\text{H}]^+$: 463.1533, found: 463.1538.

C(sp³)-H amidation after C(sp²)-H amidation (16)



In an argon-filled glovebox, a screw-cap test tube was charged with $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (0.56 mg, 0.0020 mmol, 1.0 mol %), **4ka'** (20.0 mg, 0.050 mmol), and DCE (500 μL). The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 2 h at room temperature under blue light irradiation. The reaction mixture was taken into the glove box, and $\text{Cp}^*\text{CF}_3\text{IrCl}_2)_2$ (2.26 mg, 0.0025 mmol, 5.0 mol%), AgNTf_2 (3.88 mg, 0.010 mmol, 20 mol%), CsOPiv (1.18 mg, 0.0050 mmol, 10 mol%), and sulfonyl azide **2b** (16.0 mg, 0.075 mmol, 1.5 equiv.) were added. After stirred for 20 h at 60 $^\circ\text{C}$, the reaction mixture was filtered through a short pad of silica gel, eluted with EtOAc, and evaporated under reduced pressure. The crude product was purified by preparative thin layered chromatography (DCM/MeOH = 9/1) afforded **16** (16.6 mg, 71%) as a pale yellow amorphous.

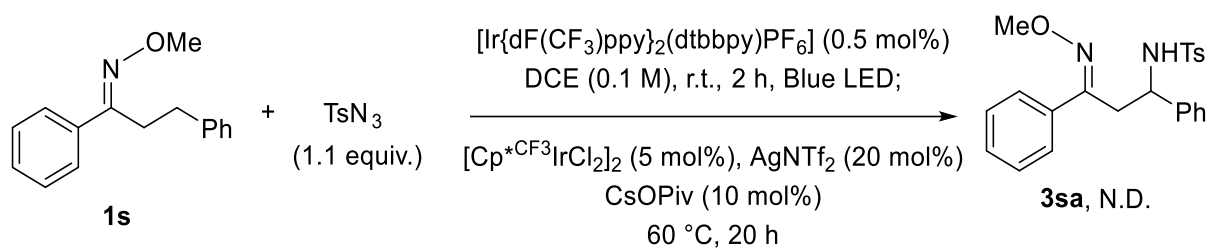
(Z)-4-methoxy-N-(3-(methoxyimino)-3-(2-((4-methylphenyl)sulfonamido)-5-(trifluoromethyl)phenyl)propyl)benzenesulfonamide (16)



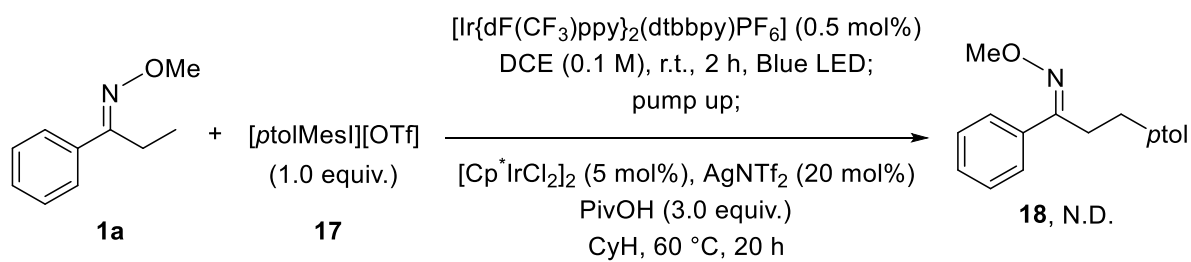
^1H NMR (CDCl_3 , 600.17 MHz, 60 $^\circ\text{C}$) δ 7.83-7.78 (m, 2H), 7.66-7.62 (m, 1H), 7.62-7.59 (m, 2H), 7.57 (dd, J = 8.5, 1.8 Hz, 1H), 7.28-7.23 (m, 2H), 7.15-7.12 (m, 1H), 7.02-6.98 (m, 2H), 6.96 (brs, 1H), 4.96 (t, J = 6.5 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.08 (q, J = 6.2 Hz, 2H), 2.40 (s, 3H), 2.12 (brs, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.92 MHz) δ 163.0, 152.9, 144.5, 136.6, 136.3, 131.5, 130.0, 129.1, 128.2, 127.7 (q, $^2J_{\text{C-F}}$ = 32.5 Hz), 127.2 (q, $^3J_{\text{C-F}}$ = 3.4 Hz), 127.1, 124.3, 124.1, 123.4 (q, $^1J_{\text{C-F}}$ = 269.5 Hz), 114.3, 62.8, 55.6, 39.2, 35.4, 21.6. ^{19}F NMR (CDCl_3 ,

564.66 MHz) δ -64.04 (s). **HRMS** (APCI): m/z calculated for $C_{25}H_{27}F_3N_3O_6S_2^+$ $[M+H]^+$: 586.1288, found: 586.1292.

Unsuccessful secondary C(sp³)-H amidation



Unsuccessful functionalization^[S19]



DFT calculations

All DFT calculations were performed using Gaussian 16 Rev C.01 program package^[S20] unless otherwise noted. Geometry optimization and the vibrational calculations at the optimized geometry to calculate the thermal correction terms for Gibbs free energies were performed using B3LYP functional with Grimme's D3ZERO correction; ^[S21] LANL2DZ^[S22] basis set for Ir and the 6-31G** basis set for all other atoms; CPCM solvation model^[S23] (solvent = 1,2-dichloroethane). To obtain more accurate electronic energies, single point energies with the optimized geometries were calculated with B3LYP functional with Grimme D3 correction; SDD basis set for Ir and the 6-311++G** basis set for all other atoms; CPCM solvation model (solvent = 1,2-dichloroethane).

We prepared two initial structures before the C(sp²)-H activation and C(sp³)-H activation steps that possess the corresponding oxime and μ^2 -acetate on the iridium center. With these initial structures, we performed conformation searches using Grimme's crest 2.10.2^[S24] and xtb 6.6.1^[S25] programs. The conformation searches were run at GFN2-xTB^[S25] level with iMTD-GC algorithm. To reduce the calculation cost, the similar conformers were summarized using cregen tool implemented in crest [--ewin 10 --rthr 1 --ethr 2]. Conformers with 5.0 kcal/mol higher in energy than the most stable conformer were omitted at this point. These structures were fully optimized at the DFT level (*vide supra*) bearing μ^2 -acetate and the oxime ether on the iridium center. From the thus-obtained representative stable conformers (*sp*²-B, *sp*²-B₂, *sp*³-B), transition state structures for C-H activation were obtained. Then we again performed constrained conformational searches for the transition states using Grimme's crest 2.10.2 and xtb 6.6.1 programs. To reduce the calculation cost, the similar conformers were summarized using cregen tool implemented in crest [--ewin 10 --rthr 1 --ethr 2]. The obtained structures were fully optimized to transition state structures for C-H activation at the DFT level, giving the most stable transition state structures (*sp*²-TS-C, *sp*³-TS-C). For these two structures, IRC calculations were performed to confirm that they are the desired transition states for C-H bond cleavage.

The calculated energy diagrams were summarized in Figure S3. Complexes B bearing μ^2 -acetate and the oxime ether on the iridium center were the resting states in the energy diagram for C-H activation steps. In the diagram for C(sp³)-H activation, *sp*³-B' bearing μ^1 -acetate and the oxime ether on the iridium center was found as an intermediate before a transition state during the IRC calculation. On the other hand, in the diagram for C(sp²)-H activation, intermediate *sp*²-B'' was located, which had a C-H bond directed to the iridium center via agostic interaction. The transition state for C(sp³)-H activation has much higher energy than that for C(sp²)-H activation (22.5 kcal/mol vs 9.6 kcal/mol). The metallacycle generated through C(sp³)-H activation had 12.6 kcal/mol higher energy than that generated from C(sp²)-H activation. These calculations indicated that C(sp²)-H activation is intrinsically much more feasible than C(sp³)-H activation. Considering these results along with the experimentally observed selectivity, the isomerization between (*E*)- and (*Z*)-oxime ethers would require a high activation energy and thus C(sp²)-H activation would be effectively suppressed after the photo-induced isomerization.

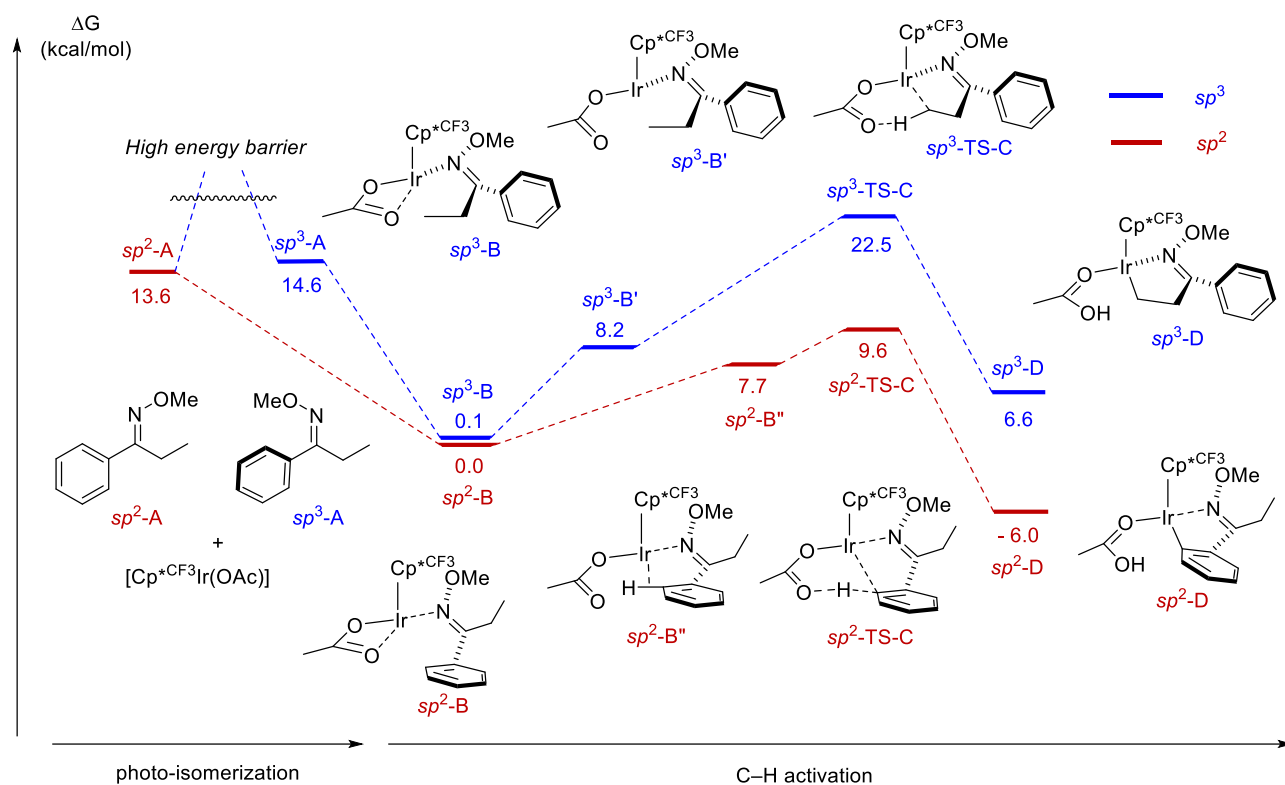


Figure S4. Calculated energy diagram

Table S5. Summary of DFT calculations

	EE (B3LYP-D3/M = SDD,6-311++G**+CPCM (DCE)) (Hartrees)	Imaginary Frequency (cm ⁻¹)	G correction term (Hartrees)	G (Hartrees)	Relative G to sp^2-B (kcal/mol)
$[Cp^*CF_3Ir(OAc)]$	-1020.87629858	-	0.200568	-1020.87629858	-
(<i>E</i>)-oxime	-518.9768228	-	0.172913	-518.8039098	-
(<i>E</i>)-oxime + $[Cp^*CF_3Ir(OAc)]$	-	-	-	-1539.479640	13.6
(sp^2-A)	-	-	-	-1539.479640	13.6
sp^2-B	-1539.900757	-	0.399375	-1539.501382	0
sp^2-B''	-1539.890074	-	0.400981	-1539.489093	7.7
sp^2-TS-C	-1539.883053	-475.7879	0.396963	-1539.48609	9.6
sp^2-D	-1539.912462	-	0.401593	-1539.510869	-6.0
(<i>Z</i>)-oxime	-518.9744004	-	0.171961	-518.8024394	-
(<i>Z</i>)-oxime + $[Cp^*CF_3Ir(OAc)]$	-	-	-	-1539.478170	14.6
(sp^3-A)	-	-	-	-1539.478170	14.6
sp^3-B	-1539.898619	-	0.397334	-1539.501285	0.1
sp^3-B'	-1539.889195	-	0.400843	-1539.488352	8.2
sp^3-TS-C	-1539.861278	-1207.4305	0.395736	-1539.465542	22.5
sp^3-D	-1539.893119	-	0.402288	-1539.490831	6.6

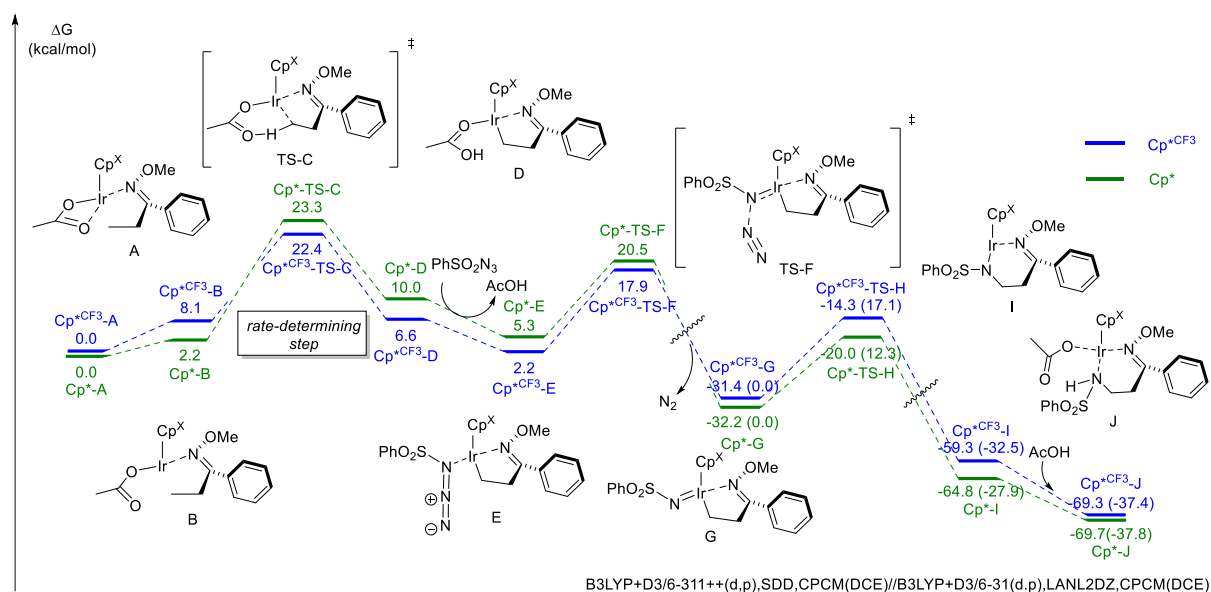


Figure S5. Comparison of Cp* and Cp*CF₃

Table S6. Summary of DFT calculations in comparison of Cp*CF₃ and Cp*

	EE (B3LYP-D3/M = SDD,6- 311++G**+CPCM (DCE)) (Hartrees)	Imaginary Frequency (cm ⁻¹)	G correction term (Hartrees)	G (Hartrees)	Relative G to Cp ^X -A (kcal/mol)
(Z)-oxime	-518.9744004	-	0.171961	-518.8024394	-
Cp*CF ₃ -A	-1539.898619	-	0.397334	-1539.501285	0.0
Cp*CF ₃ -B	-1539.889195	-	0.400843	-1539.488352	8.1
Cp*CF ₃ -TS-C	-1539.861278	-1207.4305	0.395736	-1539.465542	22.4
Cp*CF ₃ -D	-1539.893119	-	0.402288	-1539.490831	6.6
Cp*CF ₃ -E	-2255.327963	-	0.444459	-2254.883504	2.2
Cp*CF ₃ -TS-F	-2255.300669	-662.3011	0.442067	-2254.858602	17.9
Cp*CF ₃ -G	-2145.802112	-	0.437685	-2145.364427	-31.4
Cp*CF ₃ -TS-H	-2145.773706	-343.7629	0.436604	-2145.337102	-14.3
Cp*CF ₃ -I	-2145.850685	-	0.441802	-2145.408883	-59.3
Cp*CF ₃ -J	-2375.066229	-	0.501404	-2374.564825	-69.3
Cp*-A	-1242.08772	-	0.425305	-1241.662415	-
Cp*-B	-1242.082669	-	0.423712	-1241.658957	2.2
Cp*-TS-C	-1242.045579	-1240.3519	0.420219	-1241.62536	23.3
Cp*-D	-1242.074611	-	0.42817	-1241.646441	10.0
Cp*-E	-1957.509956	-	0.470281	-1957.039675	5.3
Cp*-TS-F	-1957.485081	-667.6102	0.469591	-1957.01549	20.5
Cp*-G	-1847.990263	-	0.463407	-1847.526856	-32.2
Cp*-TS-H	-1847.971478	-337.7165	0.464223	-1847.507255	-20.0
Cp*-I	-1848.04774	-	0.469036	-1847.578704	-64.8

Cp*-J	-2077.255699	-	0.529059	-2076.72664	-69.7
AcOH	-229.1747713	-	0.034656	-229.1401153	-
N ₂	-109.5598803	-	-0.012848	-109.5727283	-
PhN ₃	-944.6014059	-	0.075515	-944.5258909	-

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5. Cartesian coordinates

33				C	1.63767400	1.29161200	0.57154600
[Cp*CF ₃ IrOAc]				C	1.10064600	2.63309200	0.96738900
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H	4.74403600	-1.42460500	0.56536100	C	3.05107100	-2.16156400	1.11180200
O	2.56703300	-0.02329000	-0.80149800	H	3.08226800	-2.88711000	0.29691500
O	1.84247200	-1.67799900	0.41162100	H	4.06726600	-2.05333500	1.50715900
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C	0.81544000	-0.03049300	-0.12842000	H	-1.14713900	-3.82105600	0.41052000
H	3.10915400	-2.55602000	-0.00266000	H	0.55962600	-3.33075200	0.20945000
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H	3.73672400	1.69053700	0.27012500	C	-3.12900400	-1.74431500	1.80338800
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N	-1.40038500	-0.80528900	0.05573400	C	-3.09086700	-1.13531600	3.22131300
O	-2.76166100	-0.50979500	-0.09316800	H	-3.78528100	-1.67287600	3.87183600
C	-3.52591200	-1.66614600	0.24829500	H	-2.08514200	-1.21339600	3.64168900
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H	-3.35836900	-1.95839000	1.29099100	58			
C	-1.19214700	1.53794700	-0.69257800	sp ² -B"			
H	-2.04799900	1.35993200	-1.34954000	Ir	-0.23160900	-0.30590700	-0.09603100
H	-0.43877100	2.07067500	-1.27819200	C	-0.16594400	0.72759900	-2.07488300
C	-1.64427500	2.39130700	0.50698200	C	-0.70383200	-0.62145400	-2.18178700
H	-2.42111400	1.86761200	1.06959400	C	-1.93571700	-0.69425900	-1.40377900
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H	-2.04914100	3.34867900	0.16558000	C	-2.07926600	0.57999300	-0.74695800
H	0.67575200	-2.17573500	-0.25068500	C	-3.20284200	1.01852800	0.13998900
58				F	-2.73769300	1.65534500	1.24154600
sp ² -B				F	-4.01396700	1.88309100	-0.50468700
Ir	0.63969200	-0.37187200	-0.32449400	F	-3.95005600	-0.01901700	0.55774500
C	2.55956700	-0.83244700	0.63618100	C	-0.22246000	-2.17299300	2.31851500
C	2.83341400	-0.25464000	-0.68050800	C	-0.99171300	-3.25888200	3.04719600
C	2.28323900	1.05789800	-0.72222200	H	-1.08373800	-4.13270100	2.39416200
C	1.87601200	0.15186600	1.43004900	H	-0.47048400	-3.54048100	3.96236300

H	-2.00299700	-2.91492600	3.27935200	C	-0.38259000	-2.49417500	-2.54023900
O	-0.87840300	-1.70506500	1.28193000	H	-0.61340900	-2.52886900	-3.61027700
O	0.89825700	-1.80428900	2.67455500	H	0.70125600	-2.56758500	-2.42254700
C	-0.88649000	2.92087400	-0.88058100	H	-0.83607200	-3.36246600	-2.06160600
H	-1.35487500	3.16229900	0.07114400	C	-2.91492400	-2.09465800	-0.55669200
H	0.15944000	3.22698200	-0.84575400	H	-3.96028200	-1.83606300	-0.74418900
H	-1.38427700	3.49529200	-1.67054200	H	-2.70428700	-3.05843100	-1.01985900
C	1.04285000	1.24213100	-2.78889900	H	-2.77568200	-2.18411800	0.52350800
H	1.78540200	0.45409400	-2.92558600	C	3.11287200	2.35564600	0.41071400
H	0.75808300	1.61385100	-3.77891500	C	2.57587200	3.62220200	0.66402700
H	1.50961300	2.06033800	-2.23824500	C	1.24367900	3.76571900	1.06450200
C	-0.11879100	-1.70661300	-3.02334300	C	0.43211500	2.64020800	1.20283000
H	-0.35126700	-1.51369300	-4.07645600	C	0.93551700	1.35383800	0.93560200
H	0.96662800	-1.73858000	-2.90845100	C	2.30283800	1.22663300	0.54251100
H	-0.51848600	-2.68431300	-2.75357100	H	3.20507300	4.49952200	0.55391400
C	-2.82834800	-1.88345800	-1.25942300	H	0.84385500	4.75312400	1.27209000
H	-3.83599500	-1.62671200	-1.59719000	H	-0.59464200	2.74167300	1.53614200
H	-2.46272700	-2.72195500	-1.85117100	H	0.58682200	0.57805100	1.84737600
H	-2.88298400	-2.18508200	-0.21143000	C	2.76789000	-0.12806000	0.23163400
C	2.77204100	2.45140300	0.56803000	N	1.79839400	-0.97854900	0.04530800
C	2.19325900	3.60976600	1.09384300	O	2.19865500	-2.24496200	-0.35557200
C	1.06616600	3.53521400	1.92146100	C	1.52537800	-3.28871000	0.37732000
C	0.51718500	2.29365500	2.23976400	H	1.92010500	-4.21091400	-0.04875500
C	1.08883500	1.12345100	1.72410000	H	1.76690000	-3.22240100	1.44162200
C	2.21594600	1.20351900	0.86990700	H	0.44423800	-3.23456600	0.23788800
H	2.62266000	4.57664200	0.85208600	C	4.21080000	-0.49880300	0.06171000
H	0.62886700	4.44379400	2.32214300	H	4.35869100	-1.50816700	0.45191700
H	-0.33895300	2.22165100	2.90196800	H	4.82615300	0.18350600	0.65218100
H	0.81971700	0.14861400	2.14386200	C	4.62180900	-0.45212000	-1.42496700
C	2.73099000	-0.04376600	0.27093000	H	4.03680900	-1.17021900	-2.00520000
N	1.80935900	-0.89651500	-0.05350000	H	4.46476400	0.54410700	-1.84858600
O	2.27818400	-2.04178400	-0.68450300	H	5.68027300	-0.70513000	-1.52506900
C	1.65029200	-3.24284300	-0.19004700	H	4.14581400	2.26546700	0.09245000
H	2.08940700	-4.03867000	-0.79121300	58			
H	1.87938200	-3.37912800	0.86828200	sp ² -D			
H	0.56829300	-3.21072100	-0.33960100	Ir	-0.09810900	-0.29521500	-0.02640600
C	4.19075700	-0.27870100	0.00860900	C	-0.54791700	-1.58168300	-1.71618700
H	4.42462500	-1.30829600	0.29348700	C	-1.18167400	-2.31113900	-0.60988900
H	4.77167700	0.39065600	0.64703000	C	-2.14160600	-1.47030700	-0.02568100
C	4.55491600	-0.06298000	-1.47542700	C	-1.24079400	-0.32495200	-1.89535600
H	3.99593500	-0.75256100	-2.11221300	C	-2.12465700	-0.19317100	-0.76106300
H	4.33894900	0.95953200	-1.79782200	C	-3.09329400	0.90558700	-0.48080400
H	5.62250600	-0.24568600	-1.62129400	F	-2.74828100	2.07110300	-1.07505000
H	3.63513900	2.52597300	-0.08451700	F	-4.34032800	0.59440600	-0.89936800
58				F	-3.17854800	1.15361500	0.85098200
sp ² -TS-C				C	-0.51455100	1.35454400	2.62795800
Ir	-0.18607600	-0.28298100	-0.05207900	C	-1.05002100	1.45950100	4.02030800
C	-0.29906900	0.10029500	-2.23137000	H	-0.93491400	0.50743500	4.53590700
C	-0.88721100	-1.21185700	-1.95814700	H	-0.54769400	2.26313600	4.56162000
C	-2.02134600	-1.02774600	-1.10620200	H	-2.11502400	1.70831900	3.95620200
C	-1.08722300	1.09348200	-1.57009500	O	-0.30456000	0.24794500	2.10042400
C	-2.09275400	0.39198900	-0.78506700	O	-0.31514900	2.50606100	2.03005400
C	-3.18986700	1.02757700	0.00462500	C	-1.07705900	0.57350800	-3.08135600
F	-2.78225800	2.16598200	0.61615600	H	-1.52053800	1.55229800	-2.91929800
F	-4.23977100	1.35289200	-0.78042900	H	-0.02243900	0.70198500	-3.33076200
F	-3.64670700	0.20093000	0.96824400	H	-1.57559000	0.10697700	-3.93814900
C	-0.28738700	-1.13712700	2.82798800	C	0.45926200	-2.17170400	-2.65361500
C	-0.75754700	-2.06092300	3.92561500	H	1.19431000	-2.76551000	-2.10566600
H	-0.42856600	-3.08007000	3.70650000	H	-0.03950900	-2.82745600	-3.37628800
H	-0.36915000	-1.73887300	4.89112000	H	0.99017700	-1.39380900	-3.20471300
H	-1.85115300	-2.06306700	3.94571400	C	-0.79402300	-3.69825100	-0.20400300
O	-0.63896100	-1.47026500	1.63588200	H	-1.12892400	-4.41613100	-0.96065600
O	0.39568900	-0.11958300	3.09783600	H	0.29267900	-3.78183200	-0.12185000
C	-0.91824800	2.56926400	-1.73592700	H	-1.23257200	-3.98021200	0.75411300
H	-1.39142600	3.12748100	-0.93232000	C	-2.97817500	-1.73631700	1.18675500
H	0.13631200	2.84399300	-1.78401500	H	-4.03271600	-1.54908400	0.96340300
H	-1.38827800	2.85880100	-2.68270200	H	-2.87029200	-2.76755300	1.52333000
C	0.85402900	0.35605700	-3.14968700	H	-2.68906800	-1.06903000	2.00303000
H	1.55673800	-0.47915800	-3.13835900	C	3.34717800	2.21289000	-0.48878000
H	0.49200300	0.48087000	-4.17617400	C	2.88636100	3.42209400	-1.01077800
H	1.39401700	1.26072700	-2.86486300	C	1.52244200	3.59715300	-1.24886600

C	0.61011300	2.56606600	-0.97878100	H	1.46806600	-0.80473000	3.24700600
C	1.04625200	1.33804500	-0.46140500	C	-0.00229700	-2.73709000	1.62470000
C	2.43905400	1.18310300	-0.21114200	H	-0.08433500	-2.28758000	2.61503400
H	3.58737500	4.22172000	-1.22608200	H	-0.99868000	-2.77860300	1.18056800
H	1.15914700	4.53822500	-1.65165400	H	0.35682700	-3.76500400	1.74519700
H	-0.44478800	2.72809000	-1.17219700	C	0.08535900	-2.84213300	-1.56392400
H	0.04976000	2.37254300	1.12539000	H	-0.88086800	-2.99390800	-1.08203900
C	2.82988800	-0.11562500	0.33202800	H	-0.09550300	-2.34808500	-2.51869500
N	1.81349100	-0.91499000	0.49483000	H	0.53581100	-3.82275500	-1.75197400
O	2.11094100	-2.22059500	0.88357400	C	2.51375000	-1.02743800	-2.56713500
C	1.54170600	-2.51916300	2.17433700	H	3.43328200	-1.58972800	-2.76190400
H	1.84963900	-3.54453100	2.38055700	H	1.74137300	-1.38115300	-3.24974800
H	1.94032500	-1.83942700	2.93331100	H	2.71472800	0.02470000	-2.76812300
H	0.45037200	-2.45391300	2.15142200	C	-3.80229100	0.09750400	0.15238900
C	4.24386700	-0.53587900	0.59683700	C	-4.23078600	-1.11802500	-0.40559800
H	4.25379400	-1.27482900	1.39961000	C	-5.57953600	-1.31541000	-0.69221500
H	4.81709800	0.33151700	0.93315500	C	-6.50780100	-0.29971600	-0.44438800
C	4.88010100	-1.13592700	-0.67413000	C	-6.08562900	0.91171200	0.10747700
H	4.32902600	-2.02437500	-0.99459600	C	-4.74052400	1.10631500	0.42149000
H	4.87721100	-0.41279100	-1.49479600	H	-3.50936400	-1.90184400	-0.60267900
H	5.91512500	-1.42364400	-0.47234100	H	-5.90569400	-2.26163200	-1.11245500
H	4.40781800	2.07872800	-0.30235500	H	-7.55678300	-0.45392800	-0.67793900
25				H	-6.80201400	1.70380400	0.30074800
Z-oxime				H	-4.42038900	2.04800500	0.85543500
C	-0.48073500	0.05360300	-0.12522100	C	-2.38254700	0.29875500	0.54062300
C	-0.75184500	-0.98154200	0.78623900	N	-1.40330900	0.11724300	-0.29067000
C	-2.03201400	-1.52431100	0.88135900	O	-1.78513900	-0.31348200	-1.58243600
C	-3.06119300	-1.05252800	0.06219100	C	-1.94266800	0.80471200	-2.48037000
C	-2.80345100	-0.02500800	-0.84729200	H	-2.76219400	1.44959200	-2.14596200
C	-1.52675300	0.53065700	-0.93274300	H	-1.01403000	1.37273700	-2.55523400
H	0.04529200	-1.35530700	1.41668700	H	-2.19610400	0.34934600	-3.43860200
H	-2.22623000	-2.31840700	1.59625600	C	-2.10171900	0.69716500	1.96604900
H	-4.05638000	-1.48101100	1.13419300	H	-2.54976700	1.68677400	2.11887100
H	-3.59649400	0.34889000	-1.48789900	H	-1.03229000	0.81112600	2.12931800
H	-1.34263000	1.33205100	-1.64094200	C	-2.70487400	-0.29549600	2.97591600
C	0.86537500	0.68697600	-0.20285800	H	-2.29897100	-1.29997800	2.83033800
N	2.00350300	0.08247000	-0.19581500	H	-3.79211800	-0.35008600	2.88463100
O	1.89935500	-1.31856000	-0.16203300	H	-2.45929400	0.02742100	3.99076800
C	3.21370600	-1.87334000	-0.18026800	58			
H	3.79028300	-1.56398700	0.69911500	sp ³ -B'			
H	3.07558200	-2.95650700	-0.16548900	H	-0.69872900	0.73921300	2.52841000
H	3.75612700	-1.58358400	-1.08770200	Ir	0.96243200	0.21070100	-0.29926500
C	0.95531900	2.19813300	-0.26255900	C	2.97651600	-0.60613200	0.23390200
H	0.44846900	2.55678200	-1.16715100	C	2.57263400	-1.10053100	-1.05046900
H	2.01036000	2.46785600	-0.36319000	C	1.34381000	-1.88036000	-0.90829900
C	0.34076500	2.88076700	0.96945500	C	1.96844400	-1.00262000	1.18717900
H	0.43348100	3.96793400	0.89023900	C	0.96970200	-1.79238900	0.46747500
H	0.84853100	2.55996700	1.88469500	C	-0.19138900	-2.46475600	1.14272300
H	-0.72080700	2.63608000	1.06834200	C	0.24433100	-3.47199000	1.92222500
58				F	-1.07966900	-2.97045800	0.26652300
sp ³ -B				F	-0.86902500	-1.60277500	1.93862600
Ir	0.69297600	0.05320800	-0.05875500	C	2.03556900	2.89874000	0.27878900
C	0.94637200	-1.97467500	0.75678700	C	2.28173700	4.27613100	-0.29623500
C	0.99598400	-2.03382900	-0.69675400	H	1.33580600	4.82065200	-0.36777700
C	2.10449100	-1.23613000	-1.14492500	H	2.68190900	4.18395000	-1.31053900
C	2.03190100	-1.14529500	1.20947000	H	2.98245500	4.82755500	0.33057300
C	2.71883800	-0.64612200	0.03567900	O	2.56595600	2.48715500	1.30198400
C	3.95713600	0.19442600	0.09194500	O	1.14409300	2.20515700	-0.42794200
F	4.32426100	0.64403000	-1.12263200	C	2.00517400	-0.69049600	2.64502300
F	3.78311500	1.27671900	0.88726100	H	2.23212500	0.36983200	2.77935800
F	4.99142200	-0.50888900	0.60028100	H	2.80084800	-1.27923900	3.11561000
C	0.61798100	2.63131000	-0.12872700	H	1.06213400	-0.92551900	3.13507200
C	0.56287100	4.12443400	-0.17094900	C	4.25641700	0.10111100	0.54191700
H	-0.00992300	4.45041400	-1.04128500	H	4.18479700	0.65701500	1.47395700
H	0.12389200	4.51547900	0.74725300	H	4.52229200	0.80454800	-0.24899000
H	1.58234200	4.51178500	-0.27028200	H	5.05845200	-0.64109700	0.62489900
O	0.74208800	1.93542900	-1.19309100	C	3.30162900	-0.89717700	-2.33447800
O	0.56062500	1.98280400	0.96965300	H	3.97671800	-0.04306400	-2.27686600
C	2.36865000	-0.83824800	2.63165900	H	2.60840600	-0.74196900	-3.16363900
H	3.02006500	-1.62887700	3.02059600	H	3.89456800	-1.79345400	-2.55238200
H	2.89018500	0.11387800	2.71760400	C	0.68594000	-2.65487100	-2.00447400

H	1.01280600	-3.69888700	-1.94574200
H	0.97424900	-2.26523100	-2.98121800
H	-0.39654900	-2.62170000	-1.91510000
C	-3.46770300	0.70653500	-0.04335200
C	-3.88906700	-0.62660800	0.10460700
C	-5.24698000	-0.93257800	0.07216400
C	-6.19205800	0.07793800	-0.13231500
C	-5.77701900	1.40248600	-0.28610400
C	-4.42068600	1.72121700	-0.22328900
H	-3.15490400	-1.40850600	0.25781700
H	-5.56828300	-1.96124900	0.20193900
H	-7.24913300	-0.16705500	-0.16851900
H	-6.50692200	2.18929100	-0.44771600
H	-4.10386400	2.75250300	-0.34179000
C	-2.03144800	1.05550900	0.06637300
N	-1.11617800	0.45835000	-0.63702200
O	-1.60841800	-0.49539200	-1.55445700
C	-1.43697500	-0.01313100	-2.89939600
H	-0.37888100	0.15694200	-3.12888600
H	-2.00913000	0.90717700	-3.05287400
H	-1.82905000	-0.81075900	-3.53134100
C	-1.62491400	2.08260200	1.08940900
H	-0.68163600	2.54130100	0.79986100
H	-2.39263600	2.86127700	1.09677000
C	-1.51483200	1.46288600	2.49570400
H	-1.31258000	2.25027300	3.22599400
H	-2.44008300	0.95440200	2.78150500

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sp³-TS-C

H	-0.44301500	1.52692800	-1.55892800
Ir	-0.76032100	0.29721500	-0.02210000
C	-2.96409000	0.41810800	0.15315800
C	-2.44396800	0.01841700	1.45958500
C	-1.76000700	-1.22409000	1.31664000
C	-2.63185200	-0.60076600	-0.79528600
C	-1.79362200	-1.57096100	-0.10482700
C	-1.27954200	-2.85538700	-0.67091200
F	-2.19738700	-3.84033800	-0.58147700
F	-0.17296400	-3.27334100	-0.02061600
F	-0.94629900	-2.73316200	-1.97933700
C	-0.41411600	3.19858000	-0.28029900
C	-0.35050900	4.63145600	0.17698000
H	0.09901000	4.70361500	1.16721500
H	-1.37233900	5.02289800	0.22168800
H	0.20737000	5.22863800	-0.54637300
O	-0.59399800	2.93195500	-1.50034400
O	-0.30188800	2.28751500	0.61635800
C	-3.07075800	-0.62504400	-2.22560200
H	-3.14553700	0.38657100	-2.62806500
H	-4.06454600	-1.08383300	-2.27686400
H	-2.39540900	-1.20652200	-2.84905700
C	-3.79890200	1.63414700	-0.10234700
H	-3.71320800	1.96380500	-1.13875100
H	-3.49036700	2.45900400	0.54299100
H	-4.85246200	1.41728400	0.10518500
C	-2.61768300	0.82287600	2.70744900
H	-2.34065300	1.86480700	2.52631500
H	-2.00158700	0.44367800	3.52313000
H	-3.66608500	0.79893600	3.02308200
C	-1.12132100	-2.03212100	2.40112400
H	-1.63521000	-2.99546800	2.48109200
H	-1.19071600	-1.52310700	3.36226800
H	-0.07155200	-2.21959200	2.17856800
C	3.64612900	-0.10113400	-0.26124300
C	4.10945500	-1.23312300	0.43565200
C	5.47749700	-1.45096400	0.58095300
C	6.39830700	-0.54139200	0.05385600
C	5.94675500	0.58342100	-0.64104300
C	4.58096400	0.79548300	-0.81322900
H	3.40224300	-1.94267500	0.84326700
H	5.82465400	-2.33387700	1.10829700

H	7.46322000	-0.71169700	0.17901300
H	6.65664100	1.29232700	-1.05495900
H	4.24356000	1.66998100	-1.35898300
C	2.21228700	0.15466600	-0.49051800
N	1.26110700	-0.06169700	0.36573300
O	1.62526900	-0.60627800	1.59942200
C	1.65696600	0.42231600	2.61140600
H	0.70496900	0.95730800	2.65291000
H	2.47200800	1.12407600	2.40829500
H	1.83792300	-0.11169600	3.54426000
C	1.75427400	0.74067400	-1.80401400
H	1.93436100	1.82313400	-1.76874300
H	2.38046300	0.34556600	-2.60939400
C	0.27276300	0.47464100	-2.07002600
H	-0.04279100	0.98283000	-2.98992400
H	0.07665600	-0.57938800	-2.26131400

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sp³-D

H	-1.59152600	2.41326500	-1.20939900
Ir	-0.71724300	0.28092000	-0.07537600
C	-2.96954700	0.36962600	0.10457600
C	-2.55251400	-0.09038200	1.43643300
C	-1.84116600	-1.28887700	1.29184700
C	-2.57199200	-0.59833300	-0.86865800
C	-1.72888900	-1.55277100	-0.15598200
C	-1.16969400	-2.81907000	-0.71580600
F	-2.03156700	-3.85049400	-0.56046100
F	-0.01834400	-3.16748700	-0.09751200
F	-0.89531600	-2.71786100	-2.03630000
C	-0.45533500	3.35727600	-0.06504800
C	0.01018100	4.71351500	0.35046000
H	0.76475900	4.62580600	1.12978800
H	-0.84453400	5.29253300	0.71154900
H	0.41975100	5.23529200	-0.51910600
O	-1.38058300	3.35111200	-1.00650800
O	-0.00451700	2.31473400	0.43546000
C	-2.98790900	-0.64706700	-2.30707300
H	-3.31862100	0.33187800	-2.65699700
H	-3.82574000	-1.34539000	-2.41264900
H	-2.17958600	-0.99270400	-2.94901800
C	-3.90186300	1.52463800	-0.11160800
H	-3.95880300	1.81807800	-1.16138400
H	-3.60304700	2.39654000	0.47438800
H	-4.91085000	1.24023200	0.20797600
C	-2.86351300	0.64824100	2.70074000
H	-2.61323100	1.70845300	2.60230000
H	-2.31046300	0.24720900	3.55137600
H	-3.93379600	0.58188700	2.92653300
C	-1.24529200	-2.14789800	2.36159300
H	-1.71394300	-3.13755600	2.33821500
H	-1.40007700	-1.71687400	3.35112200
H	-0.17569300	-2.28167800	2.19455400
C	3.66001100	-0.07189900	-0.25198500
C	4.15718800	-1.22002600	0.39436100
C	5.53123400	-1.40763100	0.52648300
C	6.42636600	-0.45298200	0.03631300
C	5.94250800	0.68767700	-0.60946500
C	4.57101600	0.87057700	-0.76803400
H	3.47137800	-1.96522900	0.77323600
H	5.90335500	-2.30256600	1.01530300
H	7.49586900	-0.60016100	0.15174600
H	6.63204400	1.43172500	-0.99538000
H	4.20811600	1.75782100	-1.27555100
C	2.22274400	0.17079000	-0.45827500
N	1.26667900	-0.13152400	0.36780100
O	1.62066100	-0.79677300	1.54279800
C	1.47658500	0.06928700	2.68486200
H	0.43764400	0.39001300	2.80630100
H	2.13175800	0.94015100	2.58797600
H	1.78012700	-0.54244300	3.53467100
C	1.71711500	0.86709400	-1.69764400

67
Cp*CF3-E

Ir	0.18676300	-1.02805800	-0.17738800
C	-0.01803600	-2.66068900	1.56556600
C	0.57638600	-3.10512400	0.29293000
C	-0.45015500	-3.04135200	-0.72971200
C	-1.31623900	-2.20127300	1.31710700
C	-1.54697600	-2.32495000	-0.13228500
C	-2.86063300	-2.00846800	-0.76472600
F	-3.79469100	-2.93975800	-0.46865800
F	-2.78356900	-1.92025800	-2.10875200
F	-3.34357100	-0.81692400	-0.31993500
C	-2.31847200	-1.69126100	2.30485500
H	-1.92823600	-1.74149700	3.32176300
H	-3.22691200	-2.30038800	2.25141500
H	-2.59352700	-0.65769300	2.09794600
C	0.70780900	-2.70745400	2.87201500
H	0.80032000	-3.74528300	3.21133800
H	0.19243900	-2.13667100	3.64558800
H	1.71692100	-2.30344600	2.76101000
C	1.90410900	-3.79003400	0.18022900
H	2.26780100	-3.78802500	-0.84869400
H	1.82642700	-4.83066200	0.51526300
H	2.64737800	-3.28593800	0.80197800
C	-0.36952400	-3.63174800	-2.10293700
H	0.66727700	-3.78983200	-2.40171500
H	-0.85842700	-3.00109700	-2.84345600
H	-0.86989500	-4.60652800	-2.09739000
C	3.97270200	1.20102800	-0.48439900
C	4.21195000	2.38739000	-1.20600200
C	5.43180600	3.04958900	-1.09326800
C	6.44255000	2.52171500	-0.28574200
C	6.22441600	1.33120600	0.41262300
C	4.99808800	0.67584500	0.32557900
H	3.43670100	2.80495400	-1.83953300
H	5.59482300	3.97262400	-1.64048900
H	7.39734700	3.03239700	-0.20572700
H	7.01202000	0.90974500	1.02942200
H	4.83888400	-0.24664500	0.86624000
C	2.66580100	0.54645000	-0.65628600
N	1.99551600	-0.09573600	0.25371600
O	2.61850200	-0.28035300	1.48967600
C	1.98337400	0.51218900	2.51228100
H	2.04722400	1.57555300	2.26401300
H	2.54851600	0.29619400	3.41934900
H	0.93875800	0.21986100	2.63449900
C	1.94003300	0.58518100	-1.98001200
H	1.39288400	1.53510100	-2.03380800
H	2.66915000	0.60781400	-2.79657400
C	0.98602000	-0.61743200	-2.08074500
H	0.20254400	-0.44352800	-2.82582300
H	1.54669100	-1.50106800	-2.39744600
C	-2.38695600	4.30481600	0.06644000
C	-3.57114800	4.94129000	-0.30398700
C	-4.79120700	4.26795400	-0.20014400
C	-4.84579700	2.95312800	0.27631200
C	-3.67783000	2.29855200	0.65819100
C	-2.46803400	2.99463500	0.54637400
H	-1.42819600	4.80464900	-0.00765600
H	-3.53775000	5.96027800	-0.67401600
H	-5.70755600	4.76966600	-0.49388800
H	-5.79732500	2.43815300	0.35227800
H	-3.70597100	1.27901200	1.02433000
S	-0.97241800	2.16479300	1.00983100
O	-1.17461800	1.30179800	2.16759400
O	0.18034000	3.05653100	0.91505900
N	-0.78860900	0.94055200	-0.33035700
N	-1.21013500	1.32711000	-1.44246700
N	-1.59018900	1.60201600	-2.47413900

67
Cp*CF3-TS-F

Ir	-0.08814	-0.98597	-0.10967
C	-0.59735	-2.29528	1.77444
C	0.05812	-3.06515	0.71119
C	-0.81488	-3.0973	-0.42991
C	-1.81812	-1.79437	1.27122
C	-1.91625	-2.20884	-0.1272
C	-3.11969	-1.96091	-0.97907
F	-4.18713	-2.65904	-0.53252
F	-2.91628	-2.30469	-2.26659
F	-3.47727	-0.65144	-0.97216
C	-2.8126	-0.95306	2.00713
H	-2.32224	-0.34914	2.77111
H	-3.55285	-1.60055	2.49015
H	-3.33847	-0.28611	1.32489
C	-0.05618	-2.12175	3.15727
H	-0.30847	-2.99496	3.76966
H	-0.47043	-1.23477	3.6391
H	1.03059	-2.02821	3.13672
C	1.3382	-3.82229	0.8882
H	1.78353	-4.08658	-0.07196
H	1.15439	-4.74488	1.44981
H	2.06043	-3.21961	1.44238
C	-0.60734	-3.8951	-1.68013
H	0.40778	-4.28973	-1.72652
H	-0.79723	-3.30287	-2.57452
H	-1.30216	-4.74151	-1.68332
C	3.98995	0.57896	-0.58233
C	4.38843	1.70756	-1.32539
C	5.70389	2.16082	-1.2685
C	6.64658	1.4768	-0.49662
C	6.26575	0.3411	0.22345
C	4.94627	-0.10434	0.19333
H	3.66404	2.24412	-1.92885
H	5.99331	3.04278	-1.83087
H	7.67455	1.82422	-0.46019
H	6.99856	-0.20046	0.81334
H	4.65752	-0.98341	0.75276
C	2.58619	0.15586	-0.68981
N	1.85363	-0.34665	0.25792
O	2.47696	-0.66299	1.4659
C	2.36088	0.40107	2.43818
H	2.76493	1.33156	2.03184
H	2.96317	0.05991	3.28083
H	1.32158	0.53825	2.73508
C	1.81509	0.29477	-1.97886
H	1.35672	1.29136	-1.98772
H	2.49939	0.25132	-2.83163
C	0.74586	-0.80932	-2.02811
H	-0.03722	-0.60114	-2.76521
H	1.20368	-1.76796	-2.28965
C	-1.29457	4.51795	-0.28329
C	-2.27729	5.46951	-0.55694
C	-3.57372	5.29948	-0.06372
C	-3.90218	4.18177	0.71203
C	-2.93434	3.22232	0.99958
C	-1.64444	3.40935	0.49136
H	-0.2818	4.62758	-0.65382
H	-2.02903	6.34089	-1.15356
H	-4.33374	6.04283	-0.28241
H	-4.90994	4.05975	1.09474
H	-3.16771	2.3536	1.60492
S	-0.41236	2.17205	0.83563
O	-0.6157	1.62404	2.18321
O	0.90887	2.65149	0.4117
N	-0.95567	0.81159	-0.14396
N	-1.27445	1.47266	-1.55195
N	-1.77935	1.30373	-2.53813

65
Cp*CF3-G

Ir	-0.32371	-0.72218	0.08058
C	-0.73022	-2.59658	1.30971

C	-0.24865	-3.11651	0.03765
C	-1.15931	-2.73182	-0.9683
C	-2.00435	-1.93184	1.08634
C	-2.19008	-1.91164	-0.3318
C	-3.37233	-1.36241	-1.07444
F	-4.17354	-2.36264	-1.49497
F	-2.98167	-0.67345	-2.17364
F	-4.10467	-0.53019	-0.31482
C	-2.89993	-1.33663	2.12657
H	-2.49182	-1.49579	3.12444
H	-3.88772	-1.8018	2.07334
H	-3.01808	-0.26335	1.96213
C	-0.09561	-2.87503	2.63396
H	-0.38153	-3.87747	2.97297
H	-0.40718	-2.15319	3.38959
H	0.99159	-2.83953	2.55135
C	1.00401	-3.91842	-0.12684
H	1.3148	-3.9672	-1.1711
H	0.84405	-4.94036	0.2329
H	1.81867	-3.47984	0.45455
C	-1.14178	-3.1269	-2.40715
H	-0.14316	-3.41852	-2.73512
H	-1.51438	-2.32892	-3.05005
H	-1.80393	-3.99084	-2.53561
C	3.87813	0.25555	-0.68141
C	4.40824	1.40406	-1.30246
C	5.78237	1.62522	-1.31414
C	6.6466	0.69038	-0.73758
C	6.13048	-0.46429	-0.14289
C	4.75566	-0.68172	-0.10261
H	3.74624	2.1353	-1.75297
H	6.17814	2.52298	-1.77776
H	7.71894	0.85869	-0.7562
H	6.80043	-1.19837	0.29317
H	4.36299	-1.57848	0.3568
C	2.42222	0.07849	-0.70362
N	1.70543	-0.46145	0.23763
O	2.3465	-0.97947	1.35539
C	2.26745	-0.06372	2.47484
H	2.73848	0.88668	2.2162
H	2.81129	-0.56679	3.27382
H	1.22688	0.10042	2.76731
C	1.57722	0.58722	-1.83584
H	1.40743	1.65055	-1.64281
H	2.1214	0.50229	-2.78169
C	0.25427	-0.17509	-1.901
H	-0.56111	0.40684	-2.32899
H	0.37889	-1.09915	-2.46229
C	-0.82555	4.05452	-0.81855
C	-1.73584	4.90292	-1.4492
C	-3.00321	5.1065	-0.89568
C	-3.37025	4.46973	0.29539
C	-2.47252	3.62032	0.93805
C	-1.208	3.42601	0.3697
H	0.1658	3.89055	-1.22505
H	-1.45479	5.40519	-2.36912
H	-3.70821	5.76567	-1.39255
H	-4.35407	4.63591	0.72196
H	-2.73775	3.12092	1.86324
S	-0.07036	2.30851	1.169
O	-0.15784	2.44788	2.63702
O	1.25942	2.46995	0.54352
N	-0.90124	0.86273	0.8352

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Cp*CF3-TS-H

Ir	-0.40243	-0.69257	0.08646
C	-1.15697	-1.63595	1.93752
C	-0.53335	-2.71275	1.20188
C	-1.19394	-2.8333	-0.04981
C	-2.30376	-1.14716	1.17131
C	-2.27155	-1.8344	-0.08068

C	-3.23515	-1.72204	-1.22407
F	-4.02466	-2.81383	-1.28565
F	-2.5756	-1.64207	-2.4078
F	-4.02701	-0.64002	-1.1384
C	-3.25977	-0.10455	1.65522
H	-2.74111	0.63059	2.2731
H	-4.02564	-0.58709	2.27319
H	-3.7485	0.41058	0.83276
C	-0.80842	-1.24007	3.33635
H	-1.31447	-1.90736	4.04335
H	-1.11771	-0.21695	3.55421
H	0.26689	-1.31961	3.50264
C	0.63984	-3.50655	1.68278
H	1.11316	-4.05673	0.86869
H	0.31346	-4.22689	2.44055
H	1.38533	-2.84875	2.13533
C	-0.90672	-3.85217	-1.10654
H	0.15826	-4.08492	-1.15245
H	-1.2408	-3.52416	-2.0899
H	-1.44513	-4.77427	-0.86001
C	3.91203	-0.13729	-0.42078
C	4.60281	0.88342	-1.09514
C	5.98388	1.00323	-0.94875
C	6.68599	0.09526	-0.15243
C	6.00268	-0.92876	0.51013
C	4.61992	-1.04299	0.38701
H	4.0594	1.60176	-1.69905
H	6.50975	1.80472	-1.45765
H	7.7628	0.18531	-0.04734
H	6.54671	-1.63792	1.12596
H	4.08781	-1.83386	0.90191
C	2.4551	-0.26352	-0.61147
N	1.60081	-0.37801	0.35507
O	2.11705	-0.43911	1.6505
C	1.9126	0.81667	2.33696
H	2.45686	1.61595	1.83083
H	2.30409	0.64498	3.33958
H	0.84693	1.05862	2.38145
C	1.89099	-0.2477	-2.00608
H	2.18269	0.69931	-2.4697
H	2.39887	-1.03852	-2.57517
C	0.38857	-0.45142	-2.13634
H	-0.0925	0.22196	-2.83721
H	0.06132	-1.46945	-2.32651
C	-2.17576	3.7641	-0.73763
C	-3.09124	4.51513	-0.00293
C	-2.81697	4.84826	1.32817
C	-1.62292	4.44123	1.93184
C	-0.69512	3.69144	1.20955
C	-0.98674	3.36558	-0.11794
H	-2.36826	3.49476	-1.77015
H	-4.0173	4.83901	-0.46658
H	-3.5363	5.42981	1.89628
H	-1.41271	4.70965	2.96206
H	0.24089	3.37313	1.6535
S	0.17325	2.36401	-1.03652
O	1.48962	2.43764	-0.36556
O	0.13382	2.70297	-2.47377
N	-0.73142	0.94639	-0.83055

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Cp*CF3-I

Ir	-0.11415	-0.5991	0.10372
C	-0.73815	-2.16854	1.60983
C	-0.00841	-2.79782	0.57485
C	-0.67169	-2.48901	-0.69202
C	-1.92592	-1.51493	1.02772
C	-1.89432	-1.75712	-0.3725
C	-2.93037	-1.45241	-1.41492
F	-3.38017	-2.61383	-1.94276
F	-2.42483	-0.7253	-2.43456
F	-3.99204	-0.79277	-0.92339

C	-2.95493	-0.78658	1.82508
H	-2.4867	-0.24342	2.64742
H	-3.651	-1.51634	2.2556
H	-3.51655	-0.0831	1.21652
C	-0.40243	-2.15974	3.06464
H	-1.00093	-2.91658	3.58426
H	-0.62453	-1.19022	3.51523
H	0.65203	-2.38352	3.22847
C	1.24641	-3.59643	0.70944
H	1.88484	-3.47545	-0.16768
H	0.99198	-4.65807	0.80103
H	1.81659	-3.29244	1.58646
C	-0.29404	-3.01834	-2.03479
H	0.78904	-3.10763	-2.12914
H	-0.66864	-2.37268	-2.82913
H	-0.7344	-4.01423	-2.16168
C	4.13529	0.60793	-0.37371
C	4.80019	1.8444	-0.42681
C	6.18706	1.89812	-0.29291
C	6.92256	0.721	-0.13976
C	6.26688	-0.51365	-0.10839
C	4.8799	-0.57402	-0.21273
H	4.23826	2.7645	-0.54539
H	6.69065	2.85922	-0.31375
H	8.00335	0.76413	-0.04691
H	6.83642	-1.43108	0.00127
H	4.37164	-1.53017	-0.18304
C	2.66741	0.55436	-0.57241
N	1.88592	-0.1217	0.21544
O	2.51965	-0.75542	1.30786
C	2.45789	0.10655	2.46444
H	3.05594	1.00807	2.30017
H	2.88117	-0.48749	3.27484
H	1.42291	0.38131	2.68673
C	2.11933	1.35561	-1.72714
H	2.22753	2.407	-1.42743
H	2.80001	1.21998	-2.57379
C	0.6717	1.12731	-2.1863
H	0.41713	1.92964	-2.88567
H	0.59014	0.18267	-2.7303
C	-3.19368	2.13371	-0.67239
C	-4.52919	2.16918	-0.27245
C	-4.85992	2.5051	1.04436
C	-3.8564	2.80467	1.96981
C	-2.51573	2.77117	1.58307
C	-2.2026	2.43355	0.26477
H	-2.91835	1.84255	-1.67919
H	-5.30914	1.92108	-0.98483
H	-5.90127	2.52724	1.35031
H	-4.11489	3.05859	2.99283
H	-1.72111	2.99044	2.28685
S	-0.48709	2.47933	-0.24883
O	0.33318	2.45648	0.99251
O	-0.27334	3.62415	-1.16095
N	-0.33771	1.07428	-1.11787
73			
Cp*CF3-J			
Ir	0.28519	-0.9726	0.29307
C	-0.14132	-3.08734	-0.35277
C	0.7458	-3.11859	0.77486
C	1.95	-2.38362	0.46226
C	0.53066	-2.37212	-1.4298
C	1.79204	-1.92754	-0.91602
C	2.79639	-1.18993	-1.75799
F	3.27499	-1.99519	-2.72636
F	3.84307	-0.73591	-1.04467
F	2.23718	-0.11506	-2.3704
C	0.04036	-2.24683	-2.83627
H	0.23628	-3.19173	-3.35592
H	0.55543	-1.45064	-3.37236
H	-1.03204	-2.05672	-2.85932

C	-1.44152	-3.81851	-0.468
H	-2.04539	-3.42123	-1.28265
H	-2.02376	-3.73294	0.44992
H	-1.24328	-4.87821	-0.66393
C	0.45965	-3.72772	2.10825
H	-0.53078	-4.18203	2.13388
H	0.50878	-2.96376	2.88961
H	1.20564	-4.49748	2.32902
C	3.16332	-2.31255	1.33618
H	3.69728	-1.37659	1.19532
H	3.8371	-3.14182	1.09359
H	2.87893	-2.40272	2.38617
C	2.14824	3.09867	-0.16955
C	3.46444	2.83863	-0.58704
C	4.38954	3.87786	-0.648
C	4.019	5.17447	-0.27808
C	2.71202	5.43514	0.13915
C	1.77194	4.40541	0.17824
H	3.74914	1.83269	-0.87036
H	5.40232	3.67445	-0.98143
H	4.74678	5.97912	-0.31779
H	2.42029	6.43948	0.42928
H	0.75712	4.6164	0.4997
C	1.12684	2.02223	-0.18575
N	1.2927	0.89119	0.42213
O	2.53226	0.78122	1.08513
C	2.36371	0.87997	2.51326
H	1.89539	1.83349	2.77686
H	3.37967	0.83981	2.90707
H	1.77267	0.04469	2.89352
C	-0.15275	2.34023	-0.92423
H	-0.74855	2.96688	-0.24627
H	0.10687	2.97715	-1.77319
C	-1.01992	1.19869	-1.4441
H	-1.91124	1.64558	-1.89411
H	-0.50563	0.61553	-2.20818
C	-4.71159	1.15242	-1.79472
C	-5.62594	2.20643	-1.80785
C	-5.91142	2.90022	-0.6292
C	-5.28945	2.54792	0.57357
C	-4.37765	1.49485	0.61028
C	-4.10462	0.81508	-0.58237
H	-4.47675	0.59733	-2.69566
H	-6.11262	2.48271	-2.73729
H	-6.62208	3.7205	-0.6466
H	-5.51609	3.0918	1.48461
H	-3.87699	1.22108	1.53204
S	-2.93258	-0.52851	-0.54986
O	-2.88453	-1.16197	-1.87171
O	-3.11884	-1.31834	0.66752
N	-1.39867	0.29452	-0.32545
C	-1.06957	0.32369	2.75818
O	-0.40581	-0.67402	2.27585
O	-1.49838	1.29466	2.09397
C	-1.33619	0.23511	4.2445
H	-0.44246	-0.10143	4.77434
H	-1.66816	1.20066	4.62679
H	-2.12385	-0.50652	4.41413
H	-1.51353	0.84017	0.58839

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Cp*-A			
Ir	-1.06232400	0.11215000	-0.04610600
C	-1.95565100	-1.67623500	-0.87452400
C	-1.30997500	-2.02170600	0.37328700
C	-1.91660800	-1.24608000	1.42273200
C	-3.03547000	-0.74053300	-0.56847200
C	-3.00429000	-0.46165200	0.83223100
C	-3.92868300	0.43070900	1.59746600
C	-0.68814400	2.65886200	-0.33847500
C	-0.35452200	4.10671400	-0.52008100
H	-0.63298500	4.67446700	0.36888900

H	0.72756500	4.19893300	-0.66466700
H	-0.85549500	4.50474900	-1.40364800
O	-0.67689300	2.11074100	0.81440300
O	-0.95149000	1.90359000	-1.33288600
C	-3.97559700	-0.16534900	-1.57656100
H	-4.77875900	-0.88396400	-1.77538100
H	-4.42555300	0.76307400	-1.22283100
H	-3.46360500	0.03601600	-2.52002700
C	-1.67692100	-2.30164700	-2.20472900
H	-1.98341100	-1.64735300	-3.02303000
H	-0.61239500	-2.51559100	-2.31777400
H	-2.22898800	-3.24358600	-2.29838700
C	-0.17366000	-2.98376000	0.51332400
H	0.39048200	-2.80813600	1.43040700
H	-0.56395800	-4.00669700	-0.54016400
H	0.51093100	-2.89850000	-0.33301500
C	-1.59195800	-1.30120300	2.88127400
H	-0.57044600	-1.64423000	3.05199100
H	-1.70688500	-0.32029400	3.34782500
H	-2.27451400	-1.99591100	3.38372600
C	3.40952000	-0.21051500	0.19762100
C	4.03701700	0.45857500	-0.86593900
C	5.38467000	0.23414900	-1.13484700
C	6.11514300	-0.67176300	-0.35902700
C	5.49499700	-1.34262200	0.69645400
C	4.15049700	-1.10367600	0.98512800
H	3.47363000	1.16551500	-1.46476700
H	5.86502400	0.76506200	-1.95079200
H	7.16398000	-0.85009300	-0.57539300
H	6.05632500	-2.04821800	1.30083100
H	3.67571800	-1.62982900	1.80715100
C	1.99235500	0.07354500	0.53906800
N	1.03334500	-0.04141600	-0.32710000
O	1.44092700	-0.66234900	-1.52307300
C	1.04278200	0.06521300	-2.69742400
H	1.38779800	1.10130300	-2.65191700
H	1.53336000	-0.46411900	-3.51521200
H	-0.04067600	0.04652600	-2.83227200
C	1.69142500	0.52567400	1.94240300
H	2.13933600	-0.20839500	2.62230800
H	0.61731100	0.52476100	2.12228900
C	2.27963000	1.91817900	2.22977200
H	3.35982400	1.93673200	2.06204100
H	2.08738400	2.18982300	3.27093600
H	1.80773800	2.66458500	1.58689300
H	-4.71739200	-0.16883600	2.06565900
H	-4.40051400	1.16939400	0.94788600
H	-3.39504300	0.96205700	2.38836500

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Cp*-B

H	1.04129500	0.24213700	2.79907800
Ir	-0.92508600	-0.00065000	-0.03724000
C	-2.85607100	-0.66408300	0.81376600
C	-2.80581500	-1.02522800	-0.56243400
C	-1.65016100	-1.91517500	-0.75353900
C	-1.73790700	-1.32850400	1.48337200
C	-1.03315300	-2.13835500	0.52321600
C	0.14873500	-3.01535500	0.79470400
C	-1.94534700	2.75851600	-0.55582400
C	-1.56869100	4.22260800	-0.65758100
H	-1.02562700	4.52666000	0.24233900
H	-0.89644700	4.37108800	-1.50795000
H	-2.46087900	4.83702500	-0.77920000
O	-3.09884900	2.35774100	-0.62329100
O	-0.87528000	1.98168400	-0.40075900
C	-1.45821000	-1.23728000	2.94589600
H	-0.45645100	-1.59128000	3.19016100
H	-1.56802100	-0.21159300	3.30503500
H	-2.18109100	-1.86063100	3.48572500
C	-3.89490400	0.16523500	1.49505900
H	-3.46715400	0.71595200	2.33581000

H	-4.33183300	0.88385600	0.80423600
H	-4.68271200	-0.48911900	1.88610000
C	-3.76775300	-0.61911300	-1.62671100
H	-3.29089000	-0.61524400	-2.60883200
H	-4.59583800	-1.33737500	-1.65546600
H	-4.15929100	0.37710100	-1.42671000
C	-1.26298700	-2.56547400	-2.03980700
H	-1.49271600	-1.92576700	-2.89369700
H	-0.19764600	-2.79691800	-2.05461500
H	-1.82327200	-3.50059600	-2.15546100
C	3.55636600	0.32621100	0.07007000
C	4.47819500	1.35547500	-0.17818300
C	5.83139300	1.05874700	-0.34105800
C	6.27827300	-0.25896400	-0.22201500
C	5.36676000	-1.28440300	0.04821400
C	4.01022500	-0.99893100	0.18207700
H	4.13758800	2.38196500	-0.27016300
H	6.53467500	1.85766300	-0.55349500
H	7.33360600	-0.48691400	-0.33633000
H	5.71236700	-2.30834600	0.15039200
H	3.30188000	-1.79356000	0.38461200
C	2.12586600	0.66087000	0.27734600
N	1.16541500	0.06067600	-0.35440900
O	1.58470600	-0.92358400	-1.28003800
C	1.48704100	-0.40759800	-2.61985400
H	2.16480700	0.44168800	-2.75324000
H	1.79121800	-1.23568400	-3.26111200
H	0.45847200	-0.11212400	-2.85252500
C	1.77720800	1.67528500	1.33467800
H	0.80141900	2.11546200	1.13016100
H	2.52074800	2.47629300	1.29485000
C	1.80343000	1.02225400	2.73009500
H	1.59651700	1.77530800	3.49475700
H	2.77839300	0.57375500	2.94129900
H	-0.18452500	-4.03770500	1.00230700
H	0.82110300	-3.03521000	-0.06390400
H	0.71446400	-2.65975500	1.65800700

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Cp*-TS-C

H	0.62503	1.65275	-1.18942
Ir	0.86059	-0.02541	-0.12134
C	3.04931	-0.09523	-0.06933
C	2.55353	-0.79006	1.11657
C	1.7701	-1.90463	0.68522
C	2.60014	-0.82702	-1.22264
C	1.74745	-1.90922	-0.77528
C	1.12951	-2.97427	-1.62743
C	0.71142	2.84097	0.53171
C	0.74869	4.08062	1.3865
H	0.33393	3.88446	2.37506
H	1.79235	4.39454	1.49329
H	0.20517	4.88877	0.89328
O	0.88134	2.93972	-0.71806
O	0.52526	1.71808	1.11608
C	2.94017	-0.50899	-2.64368
H	2.15886	-0.83936	-3.33002
H	3.09733	0.56167	-2.78633
H	3.8668	-1.02763	-2.91399
C	3.974	1.08286	-0.05835
H	3.85967	1.68366	-0.96222
H	3.77529	1.7256	0.80202
H	5.01544	0.74772	0.00321
C	2.83316	-0.36065	2.5213
H	2.20891	-0.89501	3.23874
H	3.88295	-0.55246	2.76828
H	2.64643	0.7103	2.6358
C	1.10124	-2.92994	1.54285
H	1.05525	-2.61714	2.58661
H	0.08316	-3.12003	1.19927
H	1.66558	-3.86751	1.49053
C	-3.57762	-0.00508	-0.29675

C	-4.43052	1.10113	-0.47332	N	-1.20469100	-0.38492200	0.21363400
C	-5.80775	0.9622	-0.31709	O	-1.59704200	-1.30676600	1.19193300
C	-6.3555	-0.2872	-0.01576	C	-1.43978900	-0.73330100	2.50320800
C	-5.51853	-1.39619	0.13412	H	-2.10874700	0.12445400	2.62553500
C	-4.13804	-1.26048	0.00451	H	-1.71567300	-1.53077600	3.19372000
H	-4.01838	2.07569	-0.71186	H	-0.40202700	-0.42992600	2.67254900
H	-6.45185	1.82748	-0.43703	C	-1.59694600	1.15695600	-1.49766400
H	-7.4298	-0.39731	0.09611	H	-1.63069000	2.15570000	-1.04344200
H	-5.94107	-2.37163	0.35388	H	-2.26324800	1.18667400	-2.36663000
H	-3.49679	-2.12389	0.11922	C	-0.14898500	0.78942500	-1.86612700
C	-2.12871	0.19344	-0.49334	H	0.35926500	1.66287900	-2.28717400
N	-1.18598	-0.3666	0.20063	H	-0.15229100	0.01615800	-2.64077300
O	-1.589	-1.26856	1.19125	H	1.42590800	-4.01225900	-1.25061000
C	-1.40581	-0.69627	2.50011	H	-0.08048400	-3.33437000	-0.60867500
H	-2.05011	0.17946	2.62557	H	0.49052600	-2.85293800	-2.21109700
H	-1.69905	-1.48655	3.19146	67			
H	-0.36094	-0.41754	2.66374	Cp*-E			
C	-1.64257	1.13704	-1.5678	Ir	-0.45708100	-1.18217100	-0.25788200
H	-1.72289	2.16102	-1.17974	C	0.75722900	-3.03956600	-0.10018400
H	-2.31815	1.07646	-2.4266	C	0.34482900	-2.80508100	1.28718100
C	-0.19456	0.85306	-1.9694	C	-1.06375300	-2.79039300	1.31619100
H	0.14115	1.58942	-2.7101	C	-0.40885900	-3.27489900	-0.89613700
H	-0.10158	-0.10611	-2.47958	C	-1.56434200	-3.00427400	-0.04865000
H	1.81908	-3.81867	-1.73934	C	-3.00059900	-3.23708700	-0.40633500
H	0.20713	-3.34645	-1.17634	C	-0.44612400	-3.73994700	-2.31849200
H	0.89169	-2.59963	-2.6252	H	-0.47941400	-4.83500500	-2.34791000
58				H	-1.32923500	-3.36334300	-2.83806700
Cp*-D				H	0.43761300	-3.41236800	-2.86968300
H	1.86607000	2.18032800	-0.73100800	C	2.18238600	-3.16043000	-0.54533400
Ir	0.81328000	-0.02493800	-0.16870300	H	2.80867500	-2.41156300	-0.05430300
C	3.03165400	-0.19109100	-0.26622100	H	2.57637800	-4.14980600	-0.28586400
C	2.70333100	-0.75325100	1.05056800	H	2.27601600	-3.02936400	-1.62498000
C	1.84875200	-1.85399900	0.86623900	C	1.28858700	-2.65172000	2.43928200
C	2.41954100	-1.02187100	-1.26627200	H	2.13439100	-2.01475200	2.17571200
C	1.58424100	-1.98469100	-0.57575300	H	0.79706700	-2.20548100	3.30567800
C	0.81047100	-3.10669200	-1.19863100	H	1.67986300	-3.63147600	2.73814400
C	0.83234400	2.96539900	0.60862900	C	-1.96158600	-2.59708500	2.49717500
C	0.50840400	4.23732200	1.32230300	H	-1.40344800	-2.33034800	3.39540800
H	-0.25093900	4.05666400	2.08082900	H	-2.69383600	-1.80996100	2.29911200
H	1.41737400	4.63595500	1.78151400	H	-2.51066600	-3.52382700	2.69747200
H	0.15265600	4.97575200	0.59806400	C	-2.80566000	2.53245300	-0.33997300
O	1.75691000	3.07368300	-0.32803300	C	-3.94794000	2.79683700	-1.11143800
O	0.27479900	1.88845200	0.87120600	C	-4.70495500	3.94343200	-0.86976200
C	2.63308300	-0.92949800	-2.74437900	C	-4.31136800	4.84645900	0.12048100
H	1.78213600	-1.33026700	-3.29769000	C	-3.15968400	4.59883700	0.87422200
H	2.79016700	0.10354000	-3.06160800	C	-2.41196300	3.44463200	0.65329700
H	3.51974000	-1.51078200	-3.02180600	H	-4.25664500	2.09775900	-1.88251200
C	4.09616700	0.84194400	-0.49988100	H	-5.59676000	4.13304800	-1.45889500
H	4.01859100	1.28536400	-1.49547100	H	-4.89539800	5.74397300	0.30010700
H	4.04933300	1.64495000	0.23938400	H	-2.84289200	5.30669400	1.63394500
H	5.08612600	0.37752800	-0.42180600	H	-1.50410700	3.26275200	1.21618000
C	3.20967900	-0.19305900	2.34289800	C	-1.99324400	1.33264200	-0.61786900
H	2.65314500	-0.57971100	3.19825700	N	-1.62325700	0.47179400	0.27904700
H	4.26663600	-0.45026300	2.47843600	O	-2.24540200	0.60523100	1.52581800
C	3.13488600	0.89798000	2.35195200	C	-1.30648300	0.71076200	2.60800000
C	1.27388800	-2.76327600	1.90575700	H	-1.92120100	0.66274000	3.50731100
H	1.39497000	-2.35882200	2.91211300	H	-0.58944800	-0.11214200	2.59476900
H	0.20947500	-2.92904600	1.72633200	H	-0.76818000	1.66060700	2.56450200
H	1.77691100	-3.73637500	1.86787000	C	-1.47951100	1.03740800	-1.99901500
C	-3.59420400	0.01164900	-0.29433500	H	-0.61476000	1.69730600	-2.15591500
C	-4.43441300	1.11891700	-0.52291000	H	-2.22030600	1.35773900	-2.74082500
C	-5.81517600	1.00000800	-0.38367800	C	-1.09784000	-0.44668300	-2.12768800
C	-6.38095200	-0.23187400	-0.04539400	H	-0.34144900	-0.59298900	-2.90705800
C	-5.55781800	-1.34280800	0.15744100	H	-1.97816800	-1.02641200	-2.42138500
C	-4.17414900	-1.22635500	0.04351800	H	-3.18272400	-3.03635400	-1.46431900
H	-4.00778100	2.07943900	-0.79096000	H	-3.28148100	-4.27795500	-0.20590900
H	-6.44827300	1.86664100	-0.54572000	H	-3.65730900	-2.58990800	0.17967800
H	-7.45796200	-0.32706900	0.05386500	N	2.14011400	0.55077400	-2.62817300
H	-5.99401200	-2.30526400	0.40618800	N	1.73971000	0.43490300	-1.57359100
H	-3.54453600	-2.09149900	0.19949600	N	1.26288000	0.21265700	-0.43868400
C	-2.14316900	0.19366300	-0.47228400	S	1.82748400	1.35663100	0.85842900

O	0.95585300	2.52782400	0.76972300	C	3.11807	2.15643	0.32035
O	1.82831600	0.49782900	2.03598100	C	3.16198	3.37515	-0.36078
C	3.47647600	1.75240200	0.34553900	C	4.27002	1.4235	0.62415
C	3.69482500	2.93570300	-0.36706800	C	4.40612	3.87108	-0.75127
C	4.49962600	0.84563700	0.64503700	H	2.24602	3.91493	-0.57218
C	4.99372800	3.21627000	-0.78900100	C	5.50279	1.93338	0.22292
H	2.87422000	3.61303100	-0.57448900	H	4.20007	0.48512	1.16301
C	5.78861800	1.14699000	0.21207800	C	5.56887	3.15169	-0.46276
H	4.29127000	-0.05786200	1.20692100	H	4.46515	4.81714	-1.27901
C	6.03207900	2.32548400	-0.50199700	H	6.41072	1.38349	0.44736
H	5.19237200	4.12929700	-1.33977400	H	6.53336	3.54247	-0.7713
H	6.60217600	0.46513000	0.43497000	65			
H	7.03983700	2.55123100	-0.83555500	Cp*-G			
67				Ir	0.31649	-0.97898	-0.09676
Cp*-TS-F				C	1.61839	-2.65023	0.75287
Ir	-0.21319	-1.1661	-0.23957	C	0.22224	-2.86385	1.11359
C	0.79526	-2.71832	1.25407	C	-0.51292	-3.18935	-0.09947
C	-0.61135	-2.84795	1.34339	C	1.70953	-2.73682	-0.66883
C	-1.13743	-3.1485	0.01208	C	0.39689	-3.13328	-1.18049
C	1.17242	-2.93009	-0.14045	C	0.12998	-3.4878	-2.60389
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C	-0.04829	-3.75541	-2.30298	H	3.71548	-2.0389	-0.97893
C	2.58197	-2.90541	-0.64206	H	3.36913	-3.64145	-1.64957
H	3.10293	-2.01758	-0.27275	H	2.76114	-2.19375	-2.46343
H	3.12477	-3.78834	-0.2869	C	2.75152	-2.3729	1.68707
H	2.61964	-2.89656	-1.7325	H	2.39129	-2.06059	2.66789
C	1.76299	-2.43588	2.35973	H	3.35649	-3.27743	1.81061
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H	2.28925	-3.35644	2.63807	C	-0.33175	-2.97754	2.49706
H	2.50584	-1.69804	2.0518	H	-0.32341	-4.03111	2.80047
C	-1.46886	-2.74874	2.56379	H	0.25901	-2.41218	3.21871
H	-1.87277	-3.73828	2.80503	H	-1.36337	-2.62459	2.53433
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H	-2.31211	-2.07642	2.38862	H	-2.12207	-4.56622	0.19508
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H	-2.74028	-4.56822	-0.04057	H	-2.37523	-3.44148	-1.1495
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H	-1.99013	3.0692	1.19188	H	-6.83426	3.08921	-0.08589
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H	-0.56394	-0.07143	2.67392	H	-2.22799	-0.03991	3.4437
H	-1.03536	1.64048	2.56315	C	-1.28519	0.83432	-1.8671
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C	-1.56932	0.83553	-1.98756	H	-1.94312	0.93737	-2.73686
H	-0.78709	1.59221	-2.13341	C	-0.31348	-0.33073	-2.03604
H	-2.33161	1.04973	-2.74435	H	0.58146	-0.06891	-2.60144
C	-1.00637	-0.58828	-2.09219	H	-0.81852	-1.16628	-2.51542
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O	0.49711	2.51464	0.6126	C	3.75531	2.59083	0.60229
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H	1.13249	3.61661	-1.33856
C	4.79575	3.20478	-0.09207
H	3.94618	2.00613	1.49539
C	4.52413	3.96059	-1.23818
H	3.00577	4.70496	-2.57903
H	5.81654	3.09574	0.25988
H	5.33922	4.43513	-1.77575
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Cp*-TS-H			
Ir	0.3543	-1.00717	-0.03907
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C	1.84981	-2.36942	0.93907
C	0.49167	-2.80812	1.24743
C	0.78327	-2.9649	-1.04176
C	-0.13635	-3.2293	0.02267
C	-1.51735	-3.7951	-0.09462
C	0.57415	-3.27038	-2.48937
H	1.11301	-2.56896	-3.12961
H	0.96328	-4.2738	-2.69706
H	-0.48282	-3.25838	-2.7614
C	3.27165	-2.15074	-1.25407
H	3.80032	-3.08994	-1.45178
H	3.04125	-1.6789	-2.21161
H	3.9286	-1.47975	-0.70275
C	2.87272	-1.97446	1.95014
H	2.40848	-1.49562	2.81469
H	3.38845	-2.87658	2.30102
H	3.60129	-1.28736	1.52497
C	-0.08784	-2.97049	2.61665
H	-1.16726	-2.81383	2.60245
H	0.10703	-3.98638	2.97865
H	0.35493	-2.26909	3.32545
C	-3.65488	0.92547	-0.32026
C	-4.01283	2.23804	-0.6815
C	-5.32764	2.67407	-0.53441
C	-6.30645	1.79921	-0.05675
C	-5.964	0.48657	0.27923
C	-4.6471	0.04953	0.15859
H	-3.26403	2.92758	-1.05565
H	-5.58728	3.69428	-0.79809
H	-7.3328	2.13716	0.0484
H	-6.72427	-0.20033	0.63736
H	-4.38884	-0.96874	0.41713
C	-2.25887	0.49242	-0.51963
N	-1.58687	-0.27503	0.28245
O	-2.25418	-0.73763	1.42158
C	-1.84201	0.02291	2.57727
H	-2.3698	-0.43518	3.41383
H	-0.75995	-0.05176	2.72446
H	-2.13932	1.07005	2.4661
C	-1.50197	0.97518	-1.73127
H	-1.26166	2.03117	-1.57815
H	-2.16616	0.91688	-2.60364
C	-0.24275	0.19436	-2.01647
H	0.53094	0.72918	-2.55296
H	-0.42121	-0.78218	-2.46333
H	-2.19997	-3.28913	0.5916
H	-1.90812	-3.68721	-1.10772
H	-1.50807	-4.8616	0.15564
N	0.78897	0.84904	-0.25101
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O	3.36872	0.70221	0.33226
O	2.62826	1.38837	-1.98972
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C	1.56958	3.9955	-0.77395
C	2.71891	3.41152	1.3
C	1.42421	5.30421	-0.31756
H	1.19992	3.70068	-1.7503
C	2.56526	4.7264	1.74499
H	3.22334	2.66676	1.90514
C	1.91886	5.6676	0.94024

H	0.92841	6.04044	-0.9422
H	2.9524	5.01336	2.71749
H	1.80181	6.68832	1.291
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Cp*-I			
Ir	0.01566	-1.08474	-0.00568
C	1.31278	-2.82948	-0.43262
C	1.0911	-2.7836	0.97302
C	-0.34684	-2.9477	1.22026
C	0.00247	-2.9492	-1.06846
C	-0.99828	-3.10706	-0.03147
C	-2.44025	-3.41162	-0.28012
C	-0.23195	-3.07736	-2.5371
H	0.50475	-2.50358	-3.10274
H	-0.1421	-4.13048	-2.83055
H	-1.23073	-2.73203	-2.81047
C	2.61537	-2.86674	-1.16628
H	2.78272	-3.88333	-1.53979
H	2.61003	-2.18508	-2.01942
H	3.44248	-2.58096	-0.52026
C	2.10953	-2.71704	2.0613
H	1.80695	-2.00492	2.83316
H	2.1901	-3.7049	2.5306
H	3.08262	-2.41712	1.68147
C	-0.94169	-3.09135	2.58385
H	-2.02988	-3.03605	2.56221
H	-0.66173	-4.06838	2.99508
H	-0.56358	-2.32627	3.26612
C	-3.20603	2.06948	-0.27351
C	-3.3036	3.33586	0.33076
C	-4.52794	4.00016	0.37257
C	-5.65597	3.42707	-0.21946
C	-5.55805	1.8202	-0.8473
C	-4.34528	1.49739	-0.86722
H	-2.43205	3.79251	0.78804
H	-4.59768	4.96655	0.86146
H	-6.60683	3.95045	-0.19601
H	-6.42934	1.74022	-1.32033
H	-4.27374	0.53057	-1.3487
C	-1.88317	1.40522	-0.3284
N	-1.69216	0.14866	-0.05618
O	-2.85696	-0.55725	0.32479
C	-3.09456	-0.40086	1.73668
H	-3.89973	-1.0999	1.96595
H	-2.1964	-0.65578	2.30505
H	-3.41016	0.62069	1.9691
C	-0.69585	2.26787	-0.67739
H	-0.33183	2.72163	0.25529
H	-1.0483	3.08323	-1.31316
C	0.45698	1.56174	-1.36892
H	1.19042	2.32692	-1.63744
H	0.1266	1.09748	-2.30481
H	-3.05422	-3.21026	0.5967
H	-2.83345	-2.82051	-1.10835
H	-2.53792	-4.47261	-0.53687
N	1.06775	0.55032	-0.47977
S	2.74338	0.5874	-0.50235
O	3.2243	-0.35772	0.51819
O	3.26708	0.46772	-1.87899
C	3.09096	2.25023	0.08016
C	3.83764	3.11896	-0.71518
C	2.61754	2.62737	1.34144
C	4.11628	4.40042	-0.23301
H	4.18581	2.79335	-1.68897
C	2.90016	3.90948	1.80863
H	2.03615	1.9322	1.9378
C	3.64834	4.79358	1.02259
H	4.69545	5.08875	-0.84016
H	2.5384	4.21909	2.78398
H	3.86478	5.79138	1.39152
73			

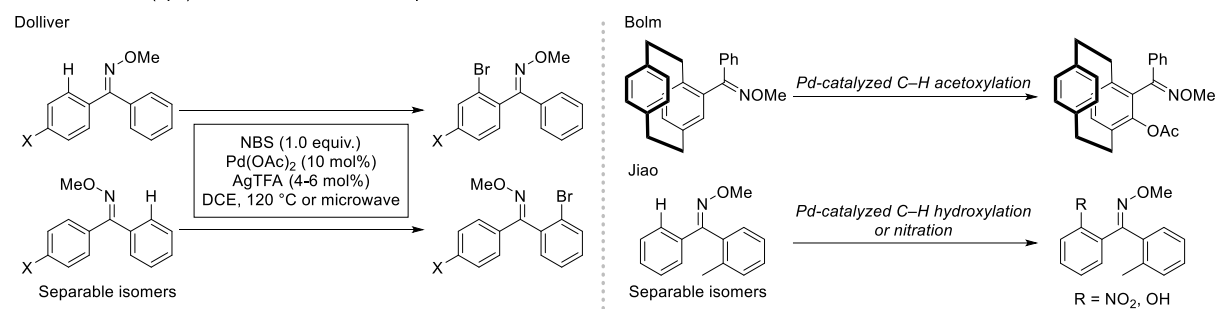
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C	0.72778	-3.1157	0.79421	8			
C	1.94219	-2.40813	0.47008	AcOH			
C	0.49829	-2.37106	-1.40788	C	-0.09255700	0.12272500	-0.00000900
C	1.76922	-1.93469	-0.89647	O	-0.77779200	-1.04350100	-0.00000200
C	2.77553	-1.21055	-1.74931	O	-0.64238400	1.20574100	0.00000100
F	3.22782	-2.02494	-2.72268	H	-1.72483200	-0.82074200	0.00002300
F	3.83875	-0.77483	-1.04969	C	1.39486700	-0.11167200	-0.00000200
F	2.2264	-0.12728	-2.35431	H	1.67758500	-0.69344400	0.88195300
C	0.00905	-2.24418	-2.81407	H	1.67755700	-0.69387700	-0.88167600
H	0.20489	-3.18954	-3.33306	H	1.91723500	0.84382700	-0.00023000
H	0.52646	-1.44889	-3.34919	17			
H	-1.06248	-2.05011	-2.83408	PhN3			
C	-1.46754	-3.81685	-0.43876	C	-1.11965200	-0.87442500	0.86193500
H	-2.07268	-3.42215	-1.25345	C	-2.44072900	-1.28712300	0.69196900
H	-2.04888	-3.72557	0.47909	C	-3.28858800	-0.58803700	-0.17125000
H	-1.26768	-4.87749	-0.62824	C	-2.82708500	0.53151400	-0.87032600
C	0.43858	-3.72649	2.12593	C	-1.51011700	0.95958700	-0.71453600
H	-0.60829	-4.01804	2.21003	C	-0.67901700	0.24582000	0.15294600
H	0.66708	-3.02345	2.9307	H	-0.44975600	-1.39623900	1.53540500
H	1.06157	-4.61705	2.26077	H	-2.80657400	-2.15084200	1.23688200
C	3.16602	-2.3469	1.33014	H	-3.49223800	1.07349600	-1.53413800
H	3.70042	-1.41095	1.19054	H	-1.13554500	1.82929300	-1.24201700
H	3.83548	-3.17473	1.07125	S	1.01315600	0.76902700	0.33983800
H	2.89743	-2.44684	2.38321	O	1.56756800	0.19730900	1.57008600
C	2.16988	3.0796	-0.17995	O	1.13085600	2.19102100	0.03166400
C	3.48209	2.80652	-0.60186	N	1.81950000	0.00692600	-1.03747800
C	4.41489	3.83815	-0.67454	N	2.16809500	-1.16682900	-0.80537700
C	4.0565	5.13998	-0.31123	N	2.52570000	-2.23664300	-0.67919200
C	2.75348	5.41378	0.1102	H	-4.31571600	-0.91496000	-0.29764000
C	1.80548	4.39192	0.16001	2			
H	3.75782	1.79686	-0.88038	N2			
H	5.42428	3.62459	-1.01192	N	0.00000000	0.00000000	0.55264300
H	4.79044	5.93854	-0.35967	N	0.00000000	0.00000000	-0.55264300
H	2.47106	6.4224	0.3947				
H	0.79328	4.6129	0.48312				
C	1.13798	2.01349	-0.18327				
N	1.29855	0.88205	0.4267				
O	2.54706	0.75678	1.07211				
C	2.40523	0.86146	2.50116				
H	1.95204	1.82054	2.77185				
H	3.42725	0.81253	2.87799				
H	1.81602	0.03204	2.89777				
C	-0.1447	2.33139	-0.91438				
H	-0.73898	2.95827	-0.23505				
H	0.11411	2.96952	-1.76313				
C	-1.00727	1.18043	-1.42292				
H	-1.89243	1.63108	-1.88235				
H	-0.48451	0.6123	-2.19682				
C	-4.59806	1.21104	-1.82814				
C	-5.52537	2.25403	-1.85776				
C	-5.91412	2.87906	-0.67044				
C	-5.38397	2.46407	0.55574				
C	-4.4579	1.42337	0.6033				
C	-4.07395	0.81361	-0.5956				
H	-4.29129	0.70508	-2.73651				
H	-5.9436	2.57379	-2.80663				
H	-6.63543	3.68982	-0.69879				
H	-5.69466	2.94798	1.47607				
H	-4.03995	1.09296	1.54651				
S	-2.87345	-0.51545	-0.54374				
O	-2.88553	-1.18096	-1.85917				
O	-3.09886	-1.30232	0.67726				
N	-1.39369	0.29344	-0.30148				
C	-1.07684	0.36722	2.75226				
O	-0.41521	-0.61633	2.31982				
O	-1.57539	1.28171	1.99506				
C	-1.31036	0.49892	4.22755				
H	-0.74463	-0.25196	4.7771				

Chapter 3. Selective *E/Z* isomerization of diaryl oxime derivatives and selective transformation

Section 1: Introduction

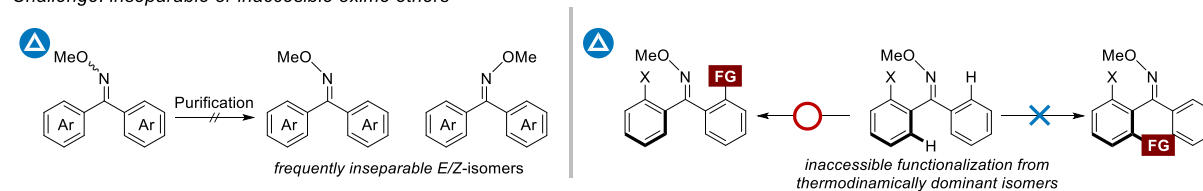
The author has achieved site-selective C(sp³)-H functionalization and successive C(sp³)-H/C(sp²)-H functionalization of oxime ethers by focusing on geometry control of the directing group in the previous Chapter. As a next target of site-selective C-H functionalization, I focused on site-selective C(sp²)-H functionalization of asymmetric diaryl oxime ethers. A fundamental challenge in the C(sp²)-H functionalization of asymmetric diaryl oxime ethers lies in controlling which aryl group is selectively functionalized. In cases of separable isomers of diaryl oxime ethers, several reports have shown that separable *E/Z* isomers undergo C(sp²)-H functionalization at positions proximal to the lone pair of the imine group (**Figure 1**).¹⁻⁴ For example, Dolliver and co-workers achieved site-selective C(sp²)-H halogenation of separable oxime ethers using a palladium catalyst (**Figure 1**, left).¹ Separable oxime ethers bearing an *ortho*-methyl substituent on the aryl group have also been applied to C(sp²)-H functionalization (**Figure 1**, right).²⁻

4

Site-selective C(sp²)-H functionalization of separable oxime ethers**Figure 1.** Previous reports of site-selective C(sp²)-H functionalization

However, in many cases, there is little difference in thermodynamic stability between the (*E*)- and (*Z*)-isomers of oxime ethers, and it is frequently difficult or impossible to separate them (**Figure 2**).³ These characteristics often lead to diminished yields of the desired site-selectively functionalized products and may render certain target structures inaccessible. Therefore, establishing a general method for site-selective C(sp²)-H functionalization would enhance atom economy and expand the range of synthetically accessible compounds.

Challenge: inseparable or inaccessible oxime ethers

**Figure 2.** Issues of inseparable and inaccessible oxime ethers

To accomplish site-selective C(sp²)-H functionalization using geometry-controlled strategy, the ratio of *E/Z* isomers in substrates is crucial for dictating site-selectivity in C-H functionalization like site-selective C(sp³)-H functionalization as discussed in Chapter 2.^{5,6} Thus, photo-induced selective *E/Z* isomerization of oxime ethers before C-H functionalization has a significant impact on selectivity. During photo-induced *E/Z* isomerization of oxime ethers bearing alkyl-aryl groups, the (*E*)-isomer is excited to its triplet state by energy transfer from the excited photocatalyst after intersystem crossing (**Figure 3A**).^{7,8} In contrast, the (*Z*)-isomer, which possesses a higher triplet energy due to its twisted structure arising from steric repulsion of the *O*-Me group, does not undergo isomerization (**Figure 3B**). As a result, selective *E/Z* isomerization can be achieved by accumulation of the non-isomerizing (*Z*)-isomer. The difference in triplet energy between the two isomers generally originates from the extent of conjugation that stabilizes the biradical triplet intermediate.⁹ Based on this mechanism, a diaryl oxime ether in which one aryl group bears a substituent capable of modifying the conjugation efficiency between the aryl group and the iminyl moiety is expected to undergo selective *E/Z* isomerization, thereby enabling site-selective C(sp²)-H functionalization (**Figure 3C**).

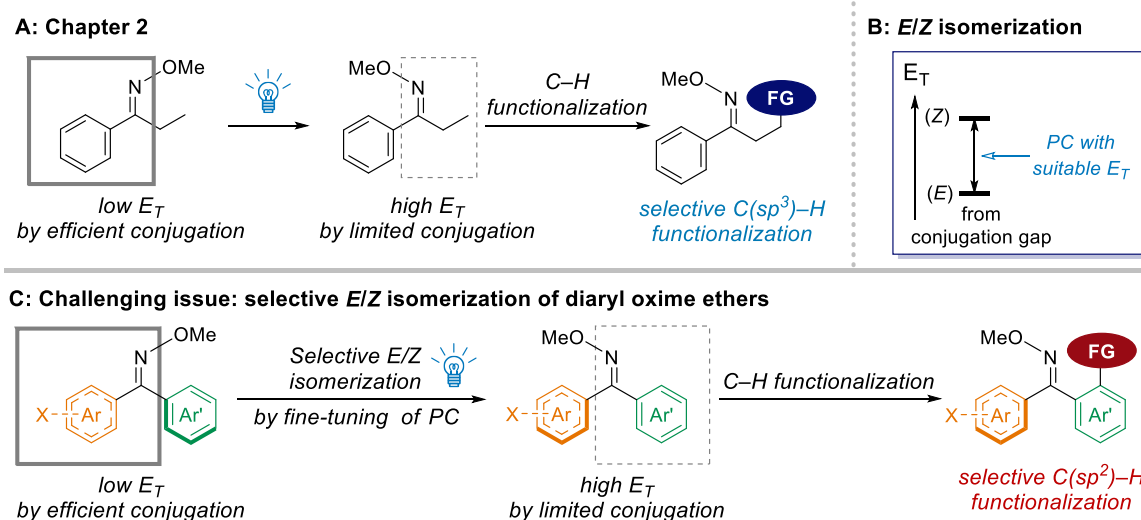


Figure 3. Site-selective C(sp²)-H functionalization as an application of *E/Z* isomerization of diaryl oximes

However, such isomerization of diaryl oxime ethers bearing two aryl groups on the same carbon atom has not yet been explored. Even in the field of alkene chemistry, where *E/Z* isomerization has been extensively investigated, selective isomerization of compounds possessing two aryl substituents on a single carbon atom remains limited. Visible light-induced *E/Z* isomerization of alkenes was pioneered by Radda and co-workers¹⁰ and Stephenson and co-workers.¹¹ Following these seminal studies, a wide variety of substrates have been successfully applied to photocatalytic *E/Z* isomerization.¹² Notably, most reported substrates are 1,1-alkyl-aryl alkenes, whose geometries undergo substantial structural changes upon isomerization (**Figure 4A**, left). In contrast, selective *E/Z* isomerization of 1,1-diaryl alkenes has been less explored (**Figure 4A**, right). This limitation primarily arises because the two isomers typically possess similar electronic and steric structures, resulting in only small differences in their triplet state energies.

In 2018, Cavallo, Rueping, and co-workers reported *in situ* *E/Z* isomerization of 1,1-diaryl alkenes generated through Ni-catalyzed reactions, in which one aryl group contained a substituent to extend a conjugation while the other did not (**Figure 4B**).¹³ Two additional examples of 1,1-diaryl alkene isomerization were later reported by Rueping and co-workers (**Figure 4C, D**).^{14,15}

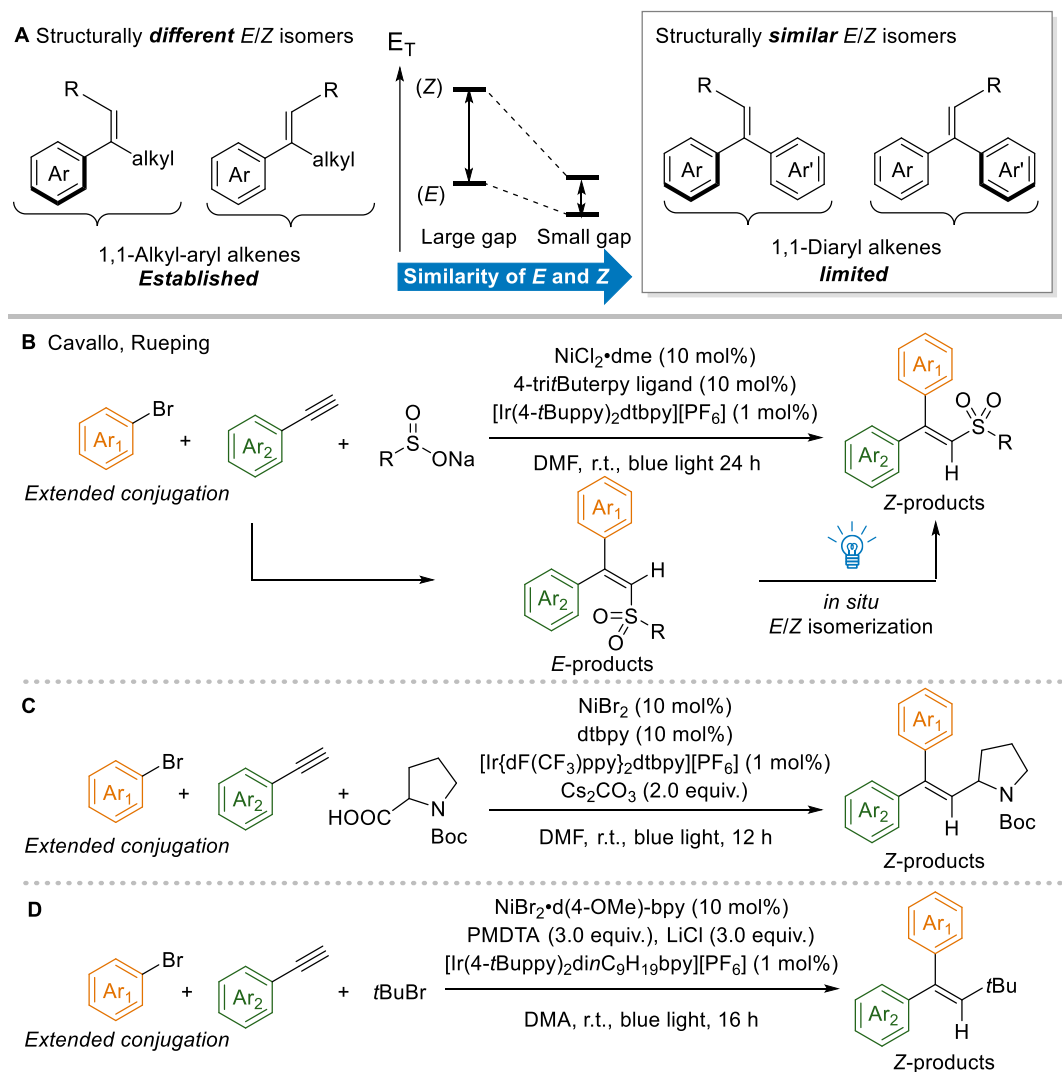


Figure 4. Issue and examples in *E/Z* isomerization of 1,1-diaryl alkenes

Although these studies illustrate the feasibility of selective isomerization in structurally similar 1,1-diaryl systems, investigation of analogous transformations in diaryl oxime ethers, containing a C=N double bond, remains undeveloped (**Figure 5**). Considering the previous reports on alkene isomerization reactions and isomerization of oxime ethers bearing alkyl-aryl substituents in Chapter 2, appropriate modification of substrates and fine-tuning of photocatalysts would be required to achieve selective *E/Z* isomerization of diaryl oxime ethers.

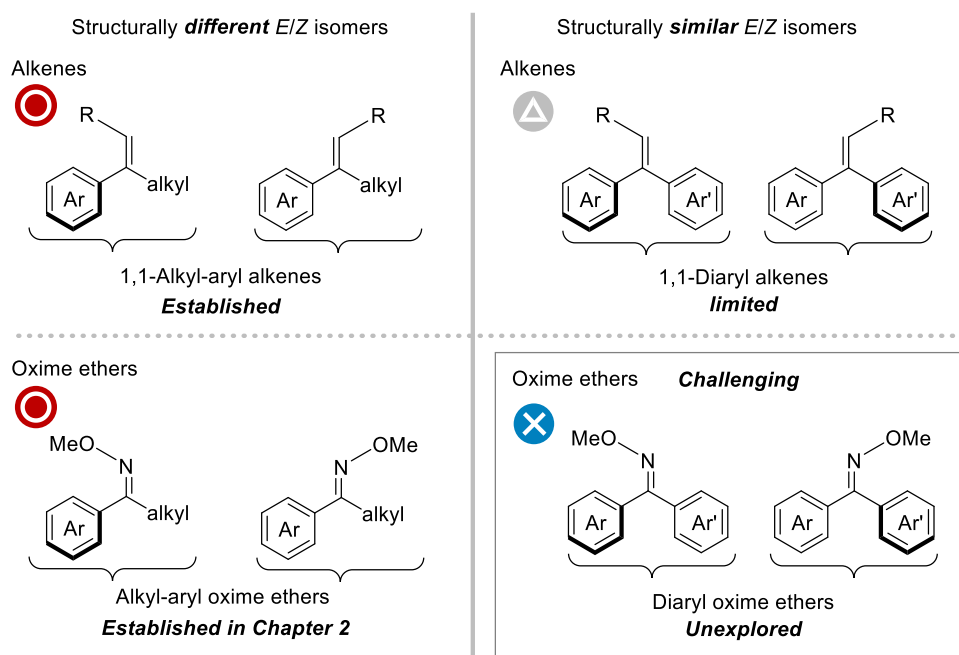


Figure 5. Challenging substrate of *E/Z* isomerization: diaryl oxime ethers

Substrates in which the triplet energies of the two *E/Z* isomers would have a significant difference are classified into four types and shown in **Figure 6**. The first class consists of diaryl oxime ethers bearing *ortho* substituent on one aryl group (**Figure 6.1**). In such systems, one isomer with a twisted conformation reduces conjugation between the *ortho*-substituted aryl ring and the imine moiety, resulting in a higher triplet energy compared with the isomer that maintains a planar, fully conjugated framework. The second class includes oxime ethers bearing π -extended substituent, such as a naphthyl group (**Figure 6.2**). Enhanced conjugation between the π -extended aryl unit and the imine group can stabilize the corresponding triplet state, thereby decreasing the triplet energy of one isomer relative to the other bearing twisted dihedral angle between aryl group and imine. If π -extension effectively modulates the triplet energies, substituents that extend conjugation at the *meta* or *para* positions may also serve as alternatives (**Figure 6.3**). The final class comprises substrates containing a five-membered aromatic ring (**Figure 6.4**). Compared with six-membered aromatic rings such as phenyl groups, five-membered systems can alter the degree of conjugation with the imine group and lead to different triplet energies between the *E* and *Z* isomers.

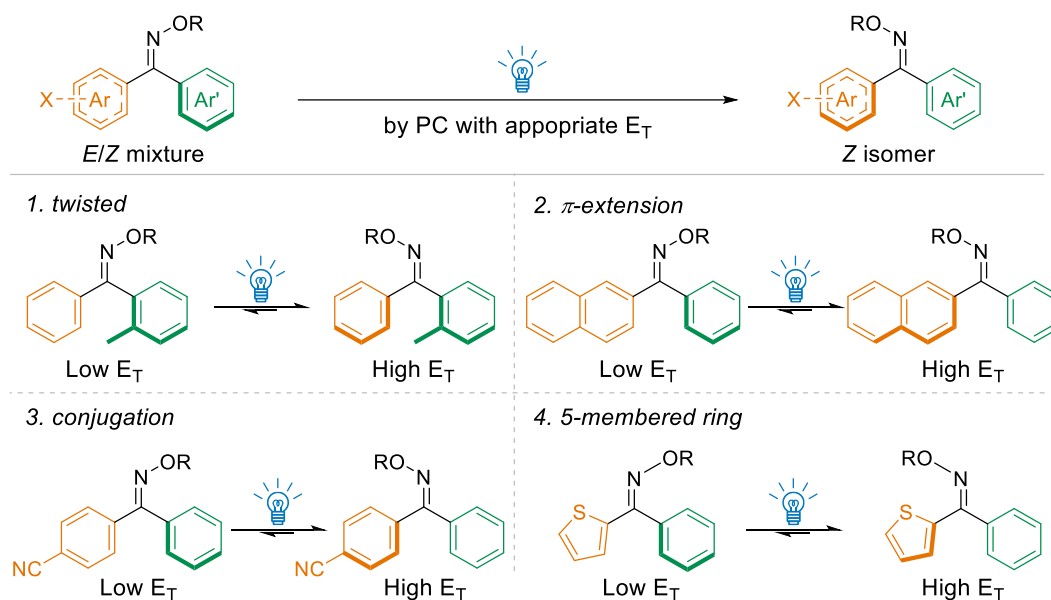


Figure 6. Classification of substrate candidates for *E/Z* isomerization

Section 2: *E/Z* isomerization of diaryl oxime ethers

First, photocatalysts were screened using a mono-*ortho*-chloro diaryl oxime ether, which possesses a twisted structure (*Z/E* = 1:5.0) (Table 1). Evaluation of various metal-based and organic photocatalysts with different triplet energies revealed that 3DPAFIPN was the most effective, affording predominantly the (*Z*)-isomer (*Z/E* = 14.0:1). This result demonstrates that tuning the efficiency of conjugation in the substrate can effectively modulate the triplet-energy difference between the *E* and *Z* isomers, thereby enabling selective *E/Z* isomerization by selection of appropriate photocatalysts.

Table 1. Screening of photocatalysts in *o*-substituted substrate

Reaction scheme: *E*-1a (*Z/E* = 1/5.0) $\xrightarrow[\text{DCE, 5 h, r.t., blue light}]{\text{PC (X mol\%)}}$ *Z*-1a (twisted)

entry	PC	X	<i>Z</i> : <i>E</i>	<i>E</i> _T
1	[Ru(bpy) ₃][PF ₆] ₂	1.0	1:4.4	46.4
2	3DPAFIPN	5.0	14.0:1	54.1
3	4CzPN	5.0	1:1.2	56.5
4	2CzTPN	5.0	5.6:1	57.2
5	4CzIPN	5.0	7.2:1	58.3
6	[Ir{dF(CF ₃)ppy} ₂ dtbpy][PF ₆]	1.0	4.3:1	61.8

[Ru(bpy)₃][PF₆]₂

3DPAFIPN

4CzPN

2CzTPN

4CzIPN

[Ir{dF(CF₃)ppy}₂(dtbbpy)][PF₆]

The substrate scope of oxime ethers bearing *ortho* substituents on the aryl group is shown in **Figure 7**. For all substrates examined, the *Z/E* ratio was successfully reversed using 3DPAFIPN as the photocatalyst (**1a**–**1e**). The major component of the *o*-methyl-substituted oxime ether **1a** prior to isomerization was isolated, and its structure was confirmed by single-crystal X-ray diffraction analysis. *o*-Amino- (**1f**) and *o*-hydroxyl- (**1g**) substituted oxime ethers did not undergo selective isomerization. Although the detailed reason remains unclear, it is plausible that intramolecular hydrogen bonding between the amino or hydroxyl group and the imine nitrogen alters a dihedral angle in the desired (*Z*) isomer to planar one and stabilizes triplet state, thereby decreasing triplet energy difference.

Controlled by a twist

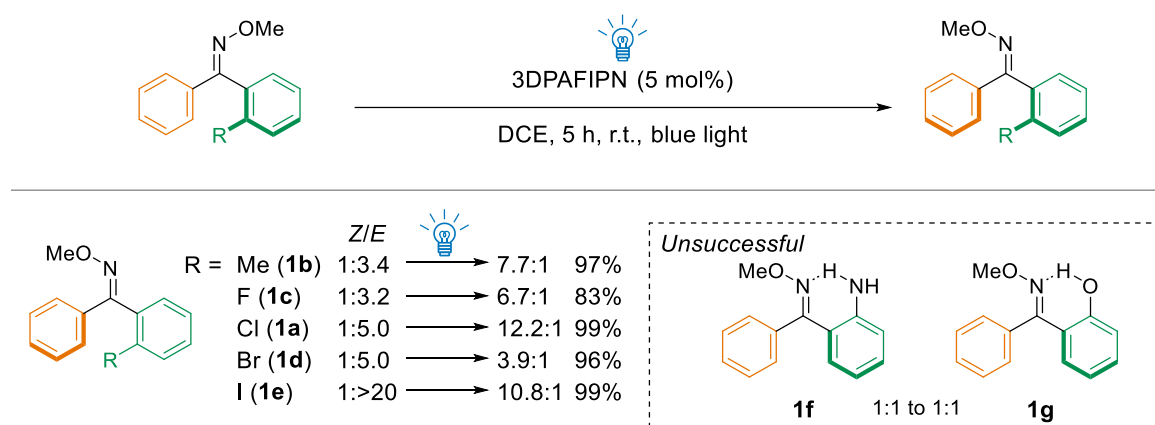


Figure 7. Substrate scope of *o*-substituted substrates

For substrates containing π -extended aryl groups, screening of photocatalysts in a 2-naphthyl phenyl oxime ether **1h** is shown in **Table 2**. As a result, 4CzPN exhibited efficient *E/Z* isomerization with good selectivity (*Z/E* = 1/1 to 12.9/1).

Table 2. Screening of photocatalysts using 2-naphthylphenyl oxime ether

entry	PC	X	<i>Z:E</i>	E_T
1	[Ru(bpy) ₃][PF ₆] ₂	1.0	1:1	46.4
2	3DPAFIPN	5.0	8.5:1	54.1
3	4CzPN	5.0	12.9:1	56.5
4	4CzIPN	5.0	5.2:1	58.3
5	[Ir{dF(CF ₃)ppy} ₂ dtbpy][PF ₆]	1.0	1:1	61.8

Substrate scope of substrates containing π -extended aryl groups was examined (**Figure 8**). In addition to **1h**, 2-quinolinyl phenyl oxime ether **1i** underwent selective isomerization under the same conditions with a little inferior selectivity ($Z/E = 1/1$ to 2.6/1).

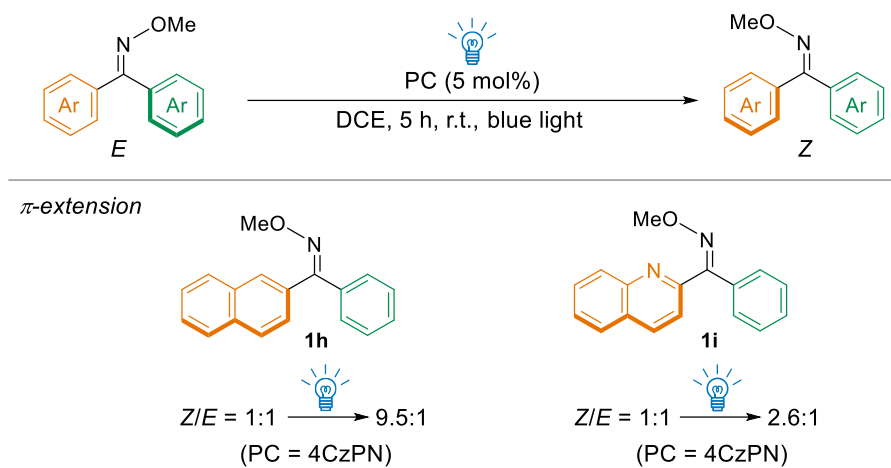


Figure 8. Substrate scope of π -extended substrates

Because π -extension proved effective, *para*-substituted diaryl oxime ethers were further investigated (**Table 3**). For the *p*-cyano derivative **1j** ($Z/E = 1.2/1$), photocatalyst screening identified 4CzPN as the best catalyst ($Z/E = 7.5/1$).

Table 3. Screening of photocatalysts in *p*-substituted substrates

1j
conjugated
E ($Z/E = 1.2:1$)

PC (X mol%)
DCE, 5 h, r.t., blue light

Z-1j

entry	PC	X	Z:E	E_T
1	[Ru(bpy) ₃][PF ₆] ₂	1.0	2.6:1	46.4
2	3DPAFIPN	5.0	4.3:1	54.1
3	4CzPN	5.0	7.5:1	56.5
4	2CzTPN	5.0	4.7:1	57.2
5	4CzIPN	5.0	2.3:1	58.3
6	[Ir{dF(CF ₃)ppy} ₂ dtbpy][PF ₆]	1.0	1.5:1	61.8

4CzPN

Substrate scope of *m*- and *p*-substituted oxime ethers is shown in **Figure 9**. In almost all substrates before isomerization, the ratio of *E/Z* isomers was approximately 1:1. Optimization of photocatalysts has been performed on each substrate because the most appropriate photocatalyst depended on a substituent of substrates. Electron-withdrawing substituents such as NO₂ (**1k**), COOH (**1l**), and COOMe (**1m**) were well tolerated (NO₂ (**1k**): $Z/E = 1/1$ to 10.0/1, COOH (**1l**): $Z/E = 1/1$ to 4.8/1, COOMe (**1m**): $Z/E = 1/1$ to 3.5/1). X-ray crystallography confirmed that the *p*-NO₂ oxime ether **1k** after isomerization adopted the (*Z*)-configuration as expected. The *m*-NO₂ derivative (**1s**) afforded a lower ratio of the (*Z*)-isomer using a photocatalyst with higher triplet energy (4CzIPN, $E_T = 58.3$ kcal/mol) than *p*-NO₂ (**1k**) ([Ru(bpy)₃][PF₆]₂, $E_T = 46.4$ kcal/mol), likely because *meta* substitution does not provide sufficient conjugation to stabilize the triplet radical intermediate due to cross-conjugation ($Z/E = 2.0/1$). Electron-donating substituents such as NMe₂ (**1n**) and OMe (**1o**) also enabled selective isomerization with moderate efficiency (NMe₂ (**1n**): $Z/E = 1/1$ to 4.9/1, OMe (**1o**): $Z/E = 1/1$ to 2.5/1), although the *m*-NMe₂ group resulted in slightly reduced selectivity (*m*-NMe₂ (**1t**): $Z/E = 1:1$ to 3.9:1). Phenyl substitution, serving as an electronically neutral group (**1p**), was compatible as well ($Z/E = 1/1$ to 5.9/1). Finally, halogen substituents such as F (**1q**) and Cl (**1r**), which provide only weak conjugation, yielded modest *E/Z* isomerization (F: $Z/E = 1/1$ to 1.7/1; Cl: $Z/E = 1/1$ to 1.3/1).

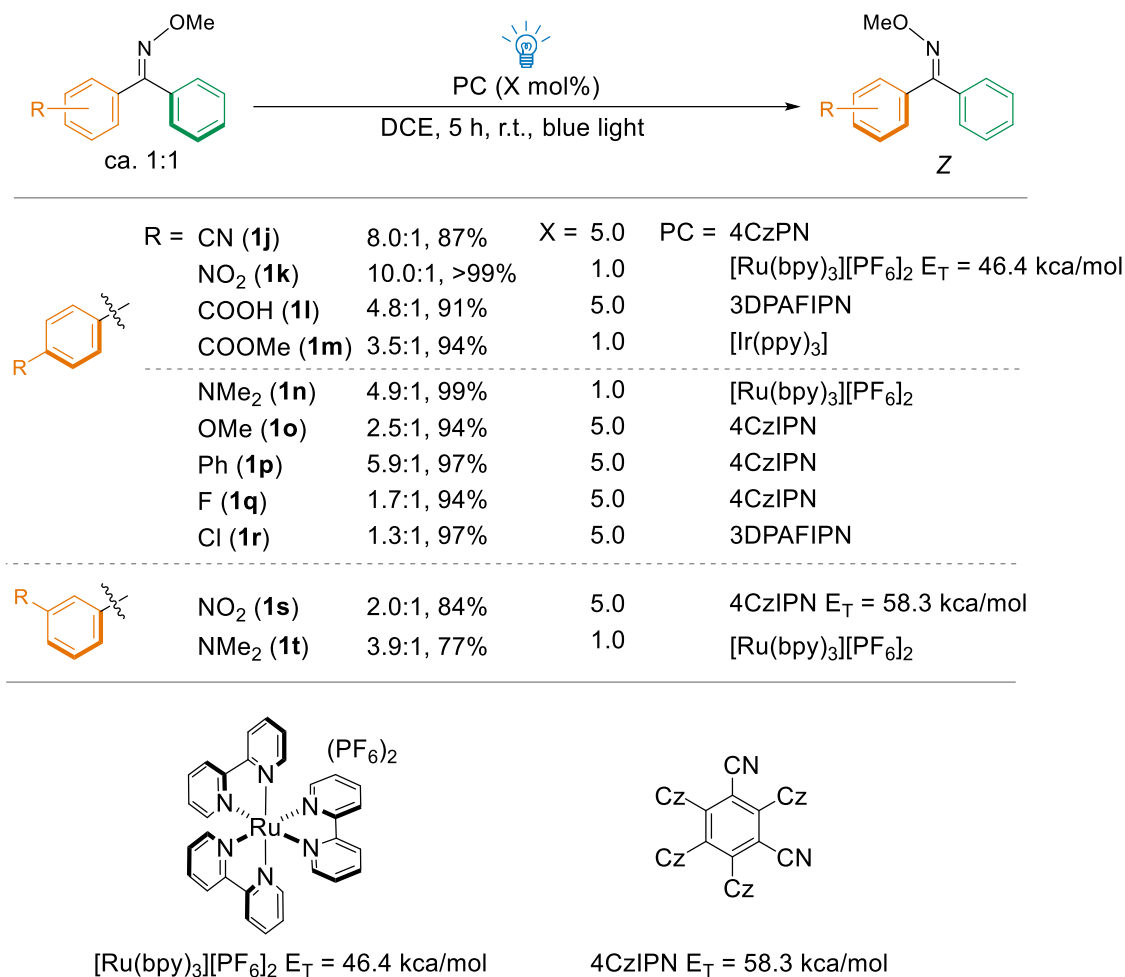


Figure 9. Substrate scope of *m*- or *p*-substituted oxime ethers

Oxime ethers containing five-membered aromatic rings were also examined (**Figure 10**). The substrate bearing a 2-thienyl group **1u** underwent highly selective *E/Z* isomerization using [Ru(bpy)₃][PF₆]₂ as the photocatalyst (*Z/E* = 2.0/1 to 17.5/1). 2-Furyl substituent **1v** was likewise effective, affording the (*Z*)-isomer as the major product (*Z/E* = 1/1.3 to 4.3/1).

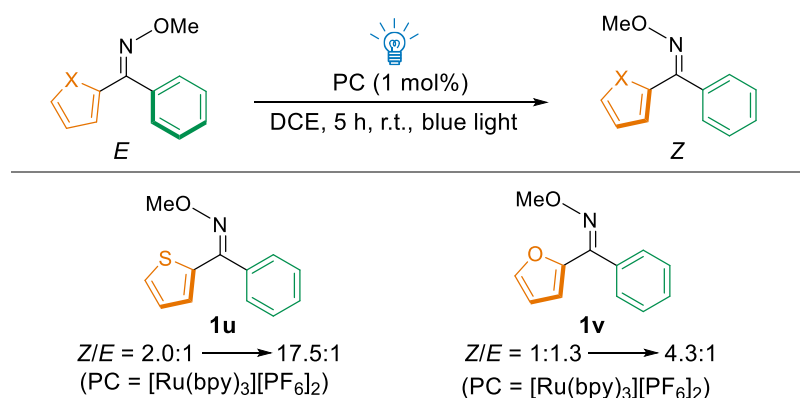


Figure 10. Substrate scope of oxime ethers with 5-membered ring

Section 3: Site-selective C(sp²)-H functionalization of diaryl oxime ethers via *E/Z* isomerization

As discussed in Chapter 2, the geometry of the directing group can govern site-selectivity in C-H functionalization. Accordingly, site-selective C(sp²)-H functionalization of diaryl oxime ethers was investigated via photoinduced *E/Z* isomerization like the previously explored C(sp³)-H functionalization.

Using an oxime ether derived from *o*-chlorobenzophenone **1a**, C-H alkynylation¹⁶ mediated by Cp*Ir(III) was conducted following *E/Z* isomerization with 3DPAFIPN as the photocatalyst (**Figure 11**). Under these conditions, alkynylation occurred predominantly at the C-H bond of the *o*-chloro-substituted aryl ring, affording the product in 93% yield (**2**), whereas functionalization at the opposite phenyl ring proceeded only in 7% (**3**). In the absence of photo-induced isomerization, however, alkynylation occurred mainly on the unsubstituted phenyl ring (**3**).

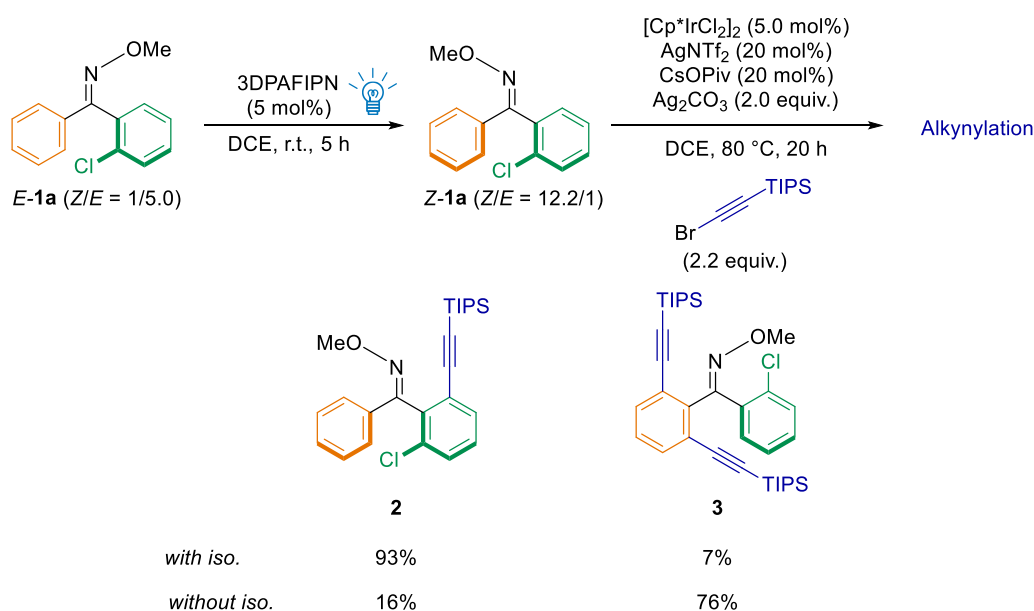


Figure 11. Site-selective C(sp²)-H alkynylation

A similar trend was observed in C–H amidation¹⁷ using a Cp*Ir(III) catalyst and a tosyl azide as the amidating agent (**Figure 12**). With *E/Z* isomerization, amidation occurred primarily on the *o*-chloro aryl ring (**4**), whereas without isomerization, the product arising from functionalization of the unsubstituted phenyl ring was obtained preferentially (**5**).

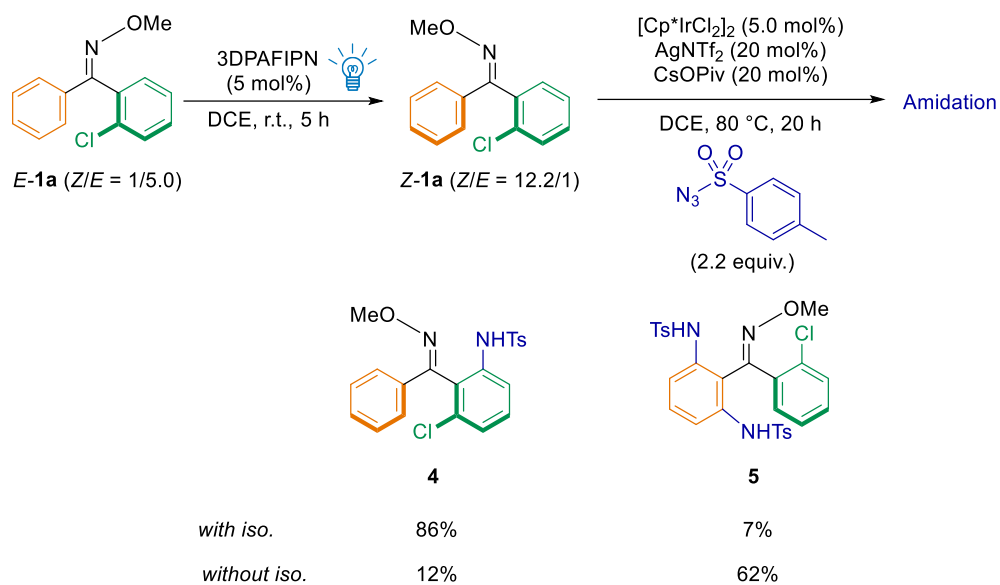


Figure 12. Site-selective C(sp²)–H amidation

Short summary

These results clearly demonstrate that fine tuning of substrates and careful selection of photocatalysts enables selective *E/Z* isomerization of diaryl oxime ethers. In addition, photo-induced control of *E/Z* geometry facilitates site-selectivity in C(sp²)-H functionalization of diaryl oxime ethers. Further applications of selective *E/Z* isomerization are currently under investigation.

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Experimental Section

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1. General

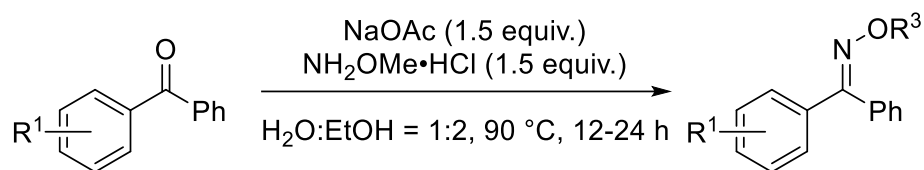
All non-aqueous reactions were carried out in a flame-dried glassware under argon atmosphere unless otherwise noted or in an argon-filled glove box. NMR spectra were recorded on JEOL JNM-ECZ400 spectrometer for ^1H NMR (399.78 MHz) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100.53 MHz). Chemical shifts were reported in the scale relative to TMS (0.00 ppm for ^1H NMR in CDCl_3), CHCl_3 (7.26 ppm for ^1H NMR in CDCl_3), and CDCl_3 (77.00 ppm for ^{13}C NMR in CDCl_3) as an internal reference, respectively. Column chromatography was performed with silica gel Kanto Silica gel 60 N (40-50 mesh), Yamazen YFLC AI-580 using Universal Column SiOH.

Materials: Dichloromethane (DCM) was purified by Glass Contour solvent purification system before use. Dichloroethane (DCE) was purchased from Kanto Chemical Co., Inc. (Super Dehydrated: 10357-05). MeOH (Super Dehydrated: 133-16771), EtOH (Super Dehydrated: 050-08425), and 1,4-dioxane (Super Dehydrated: 040-31651) was purchased from Fujifilm Wako Pure Chemical Co.. All other reagents were commercially available and used as received unless otherwise noted. Photo-irradiation was performed with a blue LED light (ISLM-150X150-BB447, 447 nm) purchased from CCS Inc..

2. Experimental procedures

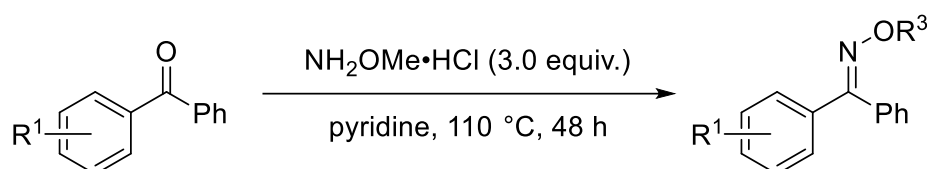
2-1. Preparation of substrates

General procedure A: preparation of oxime ethers^[S1]



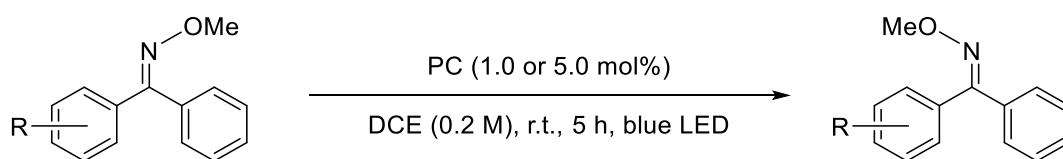
A screw-cap test tube was charged with the corresponding ketone (1.0 equiv.), NaOAc (1.5 equiv.), *O*-alkyl hydroxyl amine (1.5 equiv.), H₂O, and EtOH (0.67 M, H₂O/EtOH = 1:2). Then the reaction mixture was stirred at 90 °C for 12-24 h, and the solvent was evaporated. Water was added and the mixture was extracted with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under vacuum. The residue was purified by silica gel column chromatography to afford oxime ether **1** as a *E/Z* mixture.

General procedure B: preparation of oxime ethers^[S2]



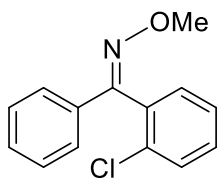
A screw-cap test tube was charged with the corresponding ketone (1.0 equiv.), *O*-alkyl hydroxyl amine (3.0 equiv.), H₂O, and pyridine (2 M). Then the reaction mixture was stirred at 110 °C for 48 h. Water, 1M HCl aq., and EtOAc were added, and the mixture was extracted with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under vacuum. The residue was purified by silica gel column chromatography to afford oxime ether **1** as a *E/Z* mixture.

2-2. *E/Z* isomerization of diaryl oximes (Procedure C)



In an argon-filled glovebox, a screw-cap test tube was charged with photo sensitizers (PC with transition metals: 0.0020 mmol, 1.0 mol%; organic PC: 0.010 mmol, 5.0 mol%), oxime **1** (0.20 mmol, 1.0 equiv.), and DCE (1 mL). The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 5 h at room temperature under blue light irradiation. The solvent was removed under reduced pressure. The crude mixture was purified by silica gel column chromatography to afford isomerized oximes.

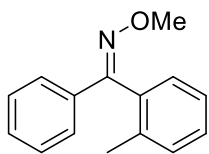
(2-chlorophenyl)(phenyl)methanone *O*-methyl oxime (**1a**)



General Procedure B using the corresponding ketone (500 mg, 2.31 mmol) afforded **1a** as a colorless oil (579.2 mg, >99%). ¹H NMR (CDCl₃, 399.78 MHz) δ 7.54-7.51 (m), 7.51-7.45 (m), 7.41-7.28 (m), 7.22-7.18 (1H, m, *Z*), 4.02 (3H, s, *E*), 3.97 (3H, s, *Z*). ¹³C{¹H} NMR (CDCl₃, 100.53 MHz) δ 155.5, 154.2, 134.7, 133.4, 132.4, 131.7, 130.1, 129.8, 129.8, 129.6, 129.5, 129.4, 128.4, 127.9, 126.8, 126.7, 62.7, 62.6.

Procedure C using the corresponding oxime ether **1a** (49.14 mg, 0.20 mmol) for isomerization by 3DPAFIPN afforded isomerized **1a** (48.8 mg, 0.199 mmol, 99%, *Z*:*E* = 1:5.0 to 12.2:1).

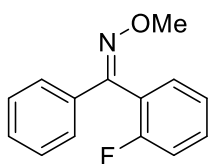
phenyl(*o*-tolyl)methanone *O*-methyl oxime (**1b**)



General Procedure B using the corresponding ketone (500 mg, 2.55 mmol) afforded **1b** as a colorless solid (603.7 mg, >99%). ¹H NMR (CDCl₃, 399.78 MHz) δ 7.47-7.41 (2H, m, *E*), 7.41-7.37 (2H, m, *Z*), 7.31-7.07 (m), 7.02-6.98 (1H, *E*), 3.93 (3H, s, *E*), 3.88 (3H, s, *Z*), 2.09 (3H, *Z*), 2.06 (3H, s, *E*). ¹³C{¹H} NMR (CDCl₃, 100.53 MHz) δ 156.6, 137.1, 136.5, 135.6, 133.9, 133.4, 130.7, 130.1, 129.9, 129.8, 129.2, 128.8, 128.6, 128.4, 128.0, 127.9, 126.9, 125.7, 125.6, 62.5, 62.3.

Procedure C using the corresponding oxime ether **1b** (45.06 mg, 0.20 mmol) for isomerization by 3DPAFIPN afforded isomerized **1b** (43.5 mg, 0.193 mmol, 97%, *Z*:*E* = 1:3.4 to 7.7:1).

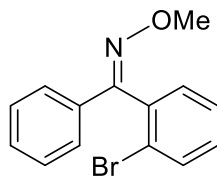
(2-fluorophenyl)(phenyl)methanone *O*-methyl oxime (**1c**)



General Procedure A using the corresponding ketone (750 mg, 3.75 mmol) afforded **1c** as a colorless liquid (774.4 mg, 90%). ¹H NMR (CDCl₃, 399.78 MHz) δ 7.56-7.46 (m), 7.44-7.32 (m), 7.25-7.15 (m), 7.06 (1H, ddd, *J* = 10.3, 8.3, 1.0 Hz, *E*), 4.04 (3H, s, *E*), 4.02 (3H, s, *Z*).

Procedure C using the corresponding oxime ether **1c** (45.85 mg, 0.20 mmol) for isomerization by 3DPAFIPN afforded isomerized **1c** (38.2 mg, mmol, 83%, *Z*:*E* = 1:3.2 to 6.7:1).

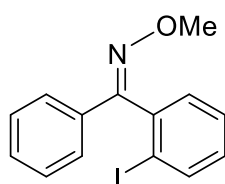
(2-bromophenyl)(phenyl)methanone *O*-methyl oxime (**1d**)



General Procedure B using the corresponding ketone (750 mg, 2.59 mmol) afforded **1d** as a colorless solid (717.7 mg, 96%). ¹H NMR (CDCl₃, 399.78 MHz) δ 7.70-7.67 (1H, m, *Z*), 7.60 (1H, dd, *J* = 8.0, 1.3 Hz), 7.58-7.54 (1H, m, *Z*), 7.52-7.46 (m), 7.42-7.31 (m), 7.30-7.24 (m), 7.19 (1H, dd, *J* = 7.6, 1.8 Hz, *Z*), 4.06 (3H, s, *E*), 4.01 (3H, s, *Z*).

Procedure C using the corresponding oxime ether **1d** (58.03 mg, 0.20 mmol) for isomerization by 3DPAFIPN afforded isomerized **1d** (55.9 mg, 0.193 mmol, 96%, *Z*:*E* = 1:5.0 to 3.9:1).

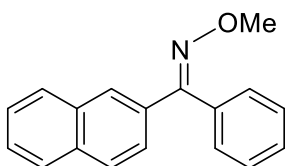
(2-iodophenyl)(phenyl)methanone *O*-methyl oxime (**1e**)



General Procedure A using the corresponding ketone (500 mg, 1.62 mmol) afforded **1e** as a colorless solid (526.1 mg, 97%). ¹H NMR (CDCl₃, 399.78 MHz) δ 7.84 (1H, d, *J* = 7.9 Hz, *Z*), 7.79 (1H, dt, *J* = 7.9, 0.8 Hz, *E*), 7.51-7.44 (m), 7.42-7.37 (m), 7.37-7.22 (m), 7.05-7.02 (1H, m, *Z*), 7.02-6.96 (1H, m, *E*), 3.97 (3H, s, *E*), 3.91 (3H, s, *Z*).

Procedure C using the corresponding oxime ether **1e** (67.43 mg, 0.20 mmol) for isomerization by 3DPAFIPN afforded isomerized **1e** (66.7 mg, 0.198 mmol, 99%, *Z:E* = 1:>20 to 10.8:1).

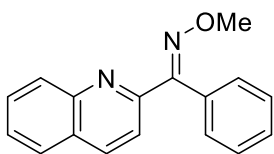
naphthalen-2-yl(phenyl)methanone *O*-methyl oxime (**1h**)



General Procedure A using the corresponding ketone (750 mg, 3.23 mmol) afforded **1h** as a pale yellow solid (751.0 mg, 89%). ¹H NMR (CDCl₃, 399.78 MHz) δ 7.98-7.81 (m), 7.79-7.75 (1H, m, *E*), 7.74 (1H, d, *J* = 1.3 Hz), 7.61-7.46 (m), 7.46-7.33 (m), 4.07 (3H, s, *E*), 4.05 (3H, s, *Z*).

Procedure C using the corresponding oxime ether **1h** (52.26 mg, 0.20 mmol) for isomerization by 4CzPN afforded isomerized **1h** (50.4 mg, 0.193 mmol, 96%, *Z:E* = 1:1 to 9.5:1).

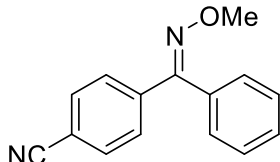
phenyl(quinolin-2-yl)methanone *O*-methyl oxime (**1i**)



General Procedure A using the corresponding ketone (250 mg, 1.07 mmol) afforded **1i** as a colorless oil (241.1 mg, 85%). ¹H NMR (CDCl₃, 399.78 MHz) δ 8.23 (1H, dd, *J* = 8.5, 0.6 Hz, *Z*), 8.19-8.15 (1H, m, *Z*), 8.13 (1H, dd, *J* = 8.7, 0.6 Hz, *E*), 8.04-8.00 (m, *E*), 7.93 (1H, d, *J* = 8.6 Hz), 7.86 (1H, dd, *J* = 8.1, 1.4 Hz, *Z*), 7.79 (1H, dd, *J* = 8.1, 1.3 Hz, *E*), 7.75-7.70 (1H, m, *Z*), 7.67-7.62 (1H, m, *E*), 7.61-7.56 (1H, m, *Z*), 7.56-7.41 (m), 7.38-7.27 (m), 4.09 (3H, s, *E*), 3.98 (3H, s, *Z*). ¹³C{¹H} NMR (CDCl₃, 100.53 MHz) δ 156.5, 155.9, 154.5, 153.6, 147.9, 147.6, 136.1, 136.0, 134.6, 132.0, 130.1, 129.8, 129.7, 129.6, 129.5, 129.4, 128.9, 128.3, 127.7, 127.7, 127.6, 127.4, 127.3, 127.3, 127.1, 126.9, 122.2, 120.1, 62.9, 62.7.

Procedure C using the corresponding oxime ether **1i** (52.46 mg, 0.20 mmol) for isomerization by 4CzPN afforded isomerized **1i** (48.6 mg, 0.185 mmol, 93%, *Z:E* = 1:1 to 2.6:1).

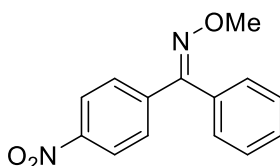
4-((methoxyimino)(phenyl)methyl)benzonitrile (**1j**)



General Procedure A using the corresponding ketone (300 mg, 1.45 mmol) afforded **1j** as a colorless oil (308.6 mg, 90%). ¹H NMR (CDCl₃, 399.78 MHz) δ 7.75-7.69 (2H, m, *Z*), 7.59 (4H, s, *E*), 7.48-7.27 (7H, m, *Z*; 5H, m, *E*), 3.99 (3H, s, *E*), 3.97 (3H, s, *Z*). ¹³C{¹H} NMR (CDCl₃, 100.53 MHz) δ 154.9, 154.9, 140.6, 137.8, 135.1, 132.0, 131.9, 131.9, 129.9, 129.7, 129.2, 128.9, 128.4, 128.3, 128.1, 127.5, 118.6, 118.4, 112.5, 62.8, 62.6.

Procedure C using the corresponding oxime ether **1j** (47.25 mg, 0.20 mmol) for isomerization by 4CzPN afforded isomerized **1j** (41.2 mg, 0.174 mmol, 87%, *Z:E* = 1.3:1 to 8.0).

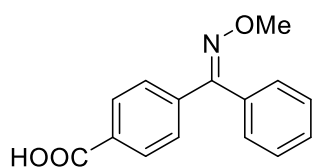
(4-nitrophenyl)(phenyl)methanone *O*-methyl oxime (**1k**)



General Procedure A using the corresponding ketone (500 mg, 2.20 mmol) afforded **1k** as a pale pink solid (580.7 mg, >99%). ¹H NMR (CDCl₃, 399.78 MHz) δ 8.33-8.27 (2H, m, *Z*), 8.20-8.15 (2H, m, *E*), 7.69-7.64 (2H, m, *E*), 7.55 (2H, m, *Z*), 7.49-7.31 (5H, m, *Z*; 5H, m, *E*), 4.03 (3H, s, *E*), 3.99 (3H, s, *Z*). ¹³C{¹H} NMR (CDCl₃, 100.53 MHz) δ 154.8, 148.1, 147.8, 142.5, 139.9, 135.0, 132.0, 130.3, 129.8, 129.4, 129.0, 128.5, 128.5, 128.4, 127.5, 123.4, 63.0, 62.7.

Procedure C using the corresponding oxime ether **1k** (51.25 mg, 0.20 mmol) for isomerization by [Ru(bpy)₃][PF₆]₂ afforded isomerized **1k** (52.0 mg, 0.20 mmol, >99%, *Z:E* = 1:1.1 to 10.0:1).

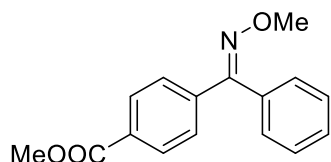
4-((methoxyimino)(phenyl)methyl)benzoic acid (**1l**)



General Procedure A using the corresponding ketone (750 mg, 3.32 mmol) afforded **1l** as a colorless solid (733.7 mg, 87%). ¹H NMR (CDCl₃, 399.78 MHz) δ 8.22-8.17 (2H, m, *Z*), 8.09-8.05 (2H, m, *E*), 7.63-7.58 (2H, m, *E*), 7.50-7.41 (m), 7.41-7.29 (m), 4.01 (3H, s, *E*), 3.99 (3H, s, *Z*). ¹³C{¹H} NMR (CDCl₃, 100.53 MHz) δ 172.0, 171.9, 155.8, 155.7, 141.5, 138.9, 135.5, 132.5, 130.1, 129.6, 129.4, 129.3, 129.1, 129.1, 128.5, 128.4, 128.3, 127.8, 127.6, 62.7, 62.6.

Procedure C using the corresponding oxime ether **1l** (51.05 mg, 0.20 mmol) for isomerization by 3DPAFIPN afforded isomerized **1l** (46.3 mg, 0.181 mmol, 91%, *Z:E* = 1:1 to 4.8:1).

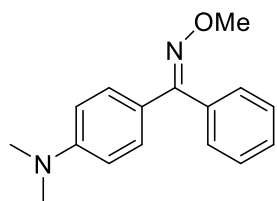
Methyl-4-((methoxyimino)(phenyl)methyl)benzoate (**1m**)



General Procedure A using the corresponding ketone (250 mg, 1.04 mmol) afforded **1m** as a colorless liquid (269.3 mg, 96%). ¹H NMR (CDCl₃, 399.78 MHz) δ 8.08-7.98 (2H, m, *Z*), 7.93-7.88 (2H, m, *E*), 7.51-7.44 (2H, m, *E*), 7.40-7.20 (7H, m, *Z*; 5H, m, *E*), 3.92 (3H, s, *E*), 3.89 (3H, s, *Z*), 3.85 (3H, s, *Z*), 3.83 (3H, s, *E*). ¹³C{¹H} NMR (CDCl₃, 100.53 MHz) δ 166.7, 166.6, 155.8, 155.8, 140.6, 137.9, 135.6, 132.6, 130.5, 130.3, 129.5, 129.4, 129.4, 129.2, 129.1, 128.3, 128.2, 127.6, 127.6, 62.6, 62.5, 52.2, 52.1.

Procedure C using the corresponding oxime ether **1m** (53.86 mg, 0.20 mmol) for isomerization by [Ir(ppy)₃] afforded isomerized **1m** (50.4 mg, 0.187 mmol, 94%, *Z:E* = 1.1:1 to 3.5:1).

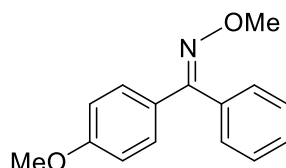
(*E*)-1-(*m*-tolyl)propan-1-one *O*-methyl oxime (**1n**)



General Procedure A using the corresponding ketone (500.0 mg, 2.22 mmol) afforded **1n** as a colorless solid (450.5 mg, 80%). ¹H NMR (CDCl₃, 399.78 MHz) δ 7.46-7.37 (2H, m, *Z*), 7.36-7.20 (5H, m, *Z*; 7H, m, *E*), 6.65-6.57 (2H, m, *Z*), 6.57-6.51 (2H, m, *E*), 3.91 (3H, s, *Z*), 3.85 (3H, s, *E*), 2.91 (6H, s, *Z*), 2.88 (6H, s, *E*). ¹³C{¹H} NMR (CDCl₃, 100.53 MHz) δ 157.0, 156.9, 151.0, 150.5, 137.4, 134.0, 131.2, 129.0, 128.9, 128.7, 128.5, 128.4, 128.0, 127.9, 123.9, 120.2, 111.5, 110.9, 62.2, 62.0, 40.2, 40.1.

Procedure C using the corresponding oxime ether **1n** (50.87 mg, 0.20 mmol) for isomerization by [Ru(bpy)₃][PF₆]₂ afforded isomerized **1n** (50.2 mg, 0.197 mmol, 99%, *Z:E* = 1:1 to 4.9:1).

(*E*)-1-(3-chlorophenyl)propan-1-one *O*-methyl oxime (**1o**)

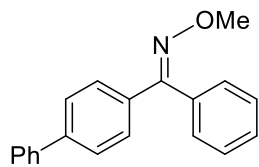


General Procedure B using the corresponding ketone (750 mg, 3.53 mmol) afforded **1o** as a colorless liquid (814.3 mg, 95%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.44-7.38 (2H, m, *Z*), 7.38-7.21 (5H, m, *Z*; 7H, m, *E*), 6.90-6.82 (2H, m, *Z*), 6.79-6.73 (2H, m, *E*), 3.91 (3H, s, *Z*), 3.87 (3H, s, *E*), 3.75 (3H, m, *Z*), 3.72 (3H, s, *E*). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 160.5, 159.8, 156.4, 136.8, 133.5, 131.1, 129.2, 128.9, 128.1, 125.3,

113.6, 113.4, 62.3, 62.3, 55.2, 55.2.

Procedure C using the corresponding oxime ether **1o** (48.26 mg, 0.20 mmol) for isomerization by 4CzIPN afforded isomerized **1o** (45.4 mg, 0.188 mmol, 94%, *Z:E* = 1:1 to 2.5:1).

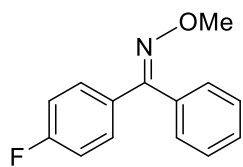
(*E*)-[1,1'-biphenyl]-4-yl(phenyl)methanone *O*-methyl oxime (1p**)**



General Procedure A using the corresponding ketone (250 mg, 0.978 mmol) afforded **1p** as a colorless solid (281.1 mg, >99%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.72-7.52 (m), 7.52-7.43 (m), 7.43-7.33 (m), 4.04 (3H, s, *Z*), 4.02 (3H, s, *E*). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 156.4, 156.4, 142.0, 141.6, 140.5, 140.4, 136.4, 135.3, 133.2, 132.0, 129.8, 129.3, 129.1, 128.8, 128.8, 128.2, 128.2, 128.1, 127.9, 127.6, 127.1, 127.0, 126.9, 126.8, 62.5.

Procedure C using the corresponding oxime ether **1p** (57.47 mg, 0.20 mmol) for isomerization by 4CzIPN afforded isomerized **1p** (55.9 mg, 0.195 mmol, 97%, *Z:E* = 1:1 to 5.9:1).

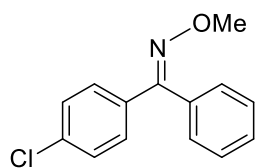
(4-fluorophenyl)(phenyl)methanone *O*-methyl oxime (1q**)**



General Procedure A using the corresponding ketone (750 mg, 3.75 mmol) afforded **1q** as a colorless oil (727.9 mg, 85%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.52-7.30 (m), 7.15-7.08 (m), 7.05-6.97 (m), 3.98 (s, 3H, *E*), 3.97 (s, 3H, *Z*). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 163.5 (d, *J* = 249.9 Hz), 162.7 (d, *J* = 248.9 Hz), 155.7, 136.3, 133.0, 132.5 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 8.0 Hz), 129.7, 129.6, 129.4, 129.1, 129.0, 128.3, 128.2, 127.8, 115.2 (d, *J* = 21.0 Hz), 115.2 (d, *J* = 21.0 Hz).

Procedure C using the corresponding oxime ether **1q** (45.85 mg, 0.20 mmol) for isomerization by 4CzIPN afforded isomerized **1q** (42.9 mg, 0.187 mmol, 94%, *Z:E* = 1:1 to 1.7:1).

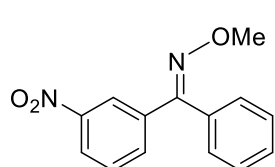
(4-chlorophenyl)(phenyl)methanone *O*-methyl oxime (1r**)**



General Procedure A using the corresponding ketone (750 mg, 3.46 mmol) afforded **1r** as a colorless liquid (702.71 mg, 83%). ¹H NMR (CDCl₃, 600.17 MHz) δ 7.44-7.17 (m), 3.90 (s, 3H, *Z*), 3.89 (s, 3H, *E*). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 155.6, 136.0, 135.3, 134.8, 134.8, 132.8, 131.5, 130.7, 129.1, 129.0, 129.9, 128.4, 128.3, 128.2, 127.8, 62.5, 62.5.

Procedure C using the corresponding oxime ether **1r** (49.14 mg, 0.20 mmol) for isomerization by 3DPAFIPN afforded isomerized **1r** (47.6 mg, 0.194 mmol, 97%, *Z:E* = 1:1 to 1.3:1).

(*E*)-(3-nitrophenyl)(phenyl)methanone *O*-methyl oxime (1s**)**

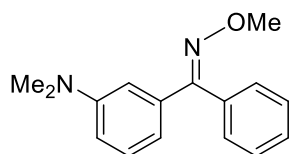


General Procedure A using the corresponding ketone (500 mg, 2.2 mmol) afforded **1s** as a pale orange oil (504.5 mg, 89%). ¹H NMR (CDCl₃, 600.17 MHz) δ 8.41-8.38 (1H, m, *E*), 8.28 (1H, ddd, *J* = 8.0, 2.3, 1.4 Hz, *Z*), 8.26-8.24 (1H, m, *Z*), 8.21 (1H, ddd, *J* = 8.4, 2.4, 1.2 Hz), 7.80 (1H, ddd, *J* = 7.8, 1.6, 1.1 Hz, *E*), 7.70-7.66 (1H, m, *Z*), 7.66-7.60 (1H, m, *Z*), 7.53-7.32 (m), 4.03 (3H, s, *E*), 4.00 (3H, s, *E*). ¹³C{¹H} NMR (CDCl₃, 150.92 MHz) δ 154.5, 154.3,

148.3, 148.0, 138.2, 135.4, 135.1, 134.7, 133.5, 131.8, 129.8, 129.5, 129.2, 129.0, 128.5, 128.5, 127.6, 124.4, 123.8, 123.7, 122.5, 62.8, 62.7.

Procedure C using the corresponding oxime ether **1s** (51.25 mg, 0.20 mmol) for isomerization by $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ afforded isomerized **1s** (43.1 mg, 0.168 mmol, 84%, *Z:E* = 1:1.2 to 2.0:1).

(*E*)-(3-(dimethylamino)phenyl)(phenyl)methanone *O*-methyl oxime (1t**)**



General Procedure A using the corresponding ketone (200 mg, 0.888 mmol) afforded

1t as a pale orange oil (196.53 mg, 87%). **¹H NMR** (CDCl_3 , 600.17 MHz) δ 7.49-7.41

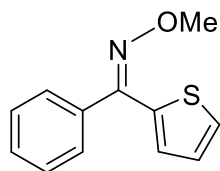
(2H, m, *Z*), 7.36-7.19 (m), 7.09 (1H, t, *J* = 8.0 Hz, *E*), 6.85 (1H, dd, *J* = 2.0, 2.0 Hz, *E*)

6.69 (1H, d, *J* = 8.4 Hz, *Z*), 6.69-6.62 (2H, m, *E*), 6.60-6.55 (2H, m, *Z*). **¹³C{¹H} NMR**

(CDCl_3 , 150.92 MHz) δ 157.4, 157.4, 150.4, 150.2, 137.0, 136.4, 134.1, 133.6, 129.2, 129.1, 128.8, 128.6, 128.1, 127.9, 127.7, 117.0, 116.9, 113.7, 112.7, 112.7, 111.6, 62.4, 62.3, 40.6, 40.5.

Procedure C using the corresponding oxime ether **1t** (50.87 mg, 0.20 mmol) for isomerization by 3DPAFIPN afforded isomerized **1t** (39.4 mg, 0.155 mmol, 77%, *Z:E* = 1:1.1 to 3.9:1).

phenyl(thiophen-2-yl)methanone *O*-methyl oxime (1u**)**



General Procedure B using the corresponding ketone (250 mg, 1.33 mmol) afforded **1u** as

a colorless oil (257.3 mg, 89%). **¹H NMR** (CDCl_3 , 399.78 MHz) δ 7.58 (1H, dd, *J* = 5.1, 1.1

Hz, *Z*), 7.56-7.50 (2H, m, *Z*), 7.49-7.38 (3H, m, *Z*; 5H, m, *E*), 7.32 (1H, dd, *J* = 5.1, 1.1 Hz,

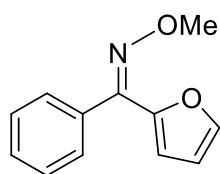
E), 7.18 (1H, dd, *J* = 3.9, 1.1 Hz, *Z*), 7.04 (1H, dd, *J* = 5.1, 4.0 Hz, *Z*), 6.96 (1H, dd, *J* = 5.0,

3.7 Hz, *E*), 6.83 (1H, dd, *J* = 3.6, 1.1 Hz, *E*). **¹³C{¹H} NMR** (CDCl_3 , 100.53 MHz) δ 152.7, 151.1, 140.1, 136.1,

132.6, 132.6, 130.7, 129.3, 129.2, 129.1, 129.1, 128.7, 128.3, 128.1, 127.2, 126.9, 125.5, 62.5, 62.4.

Procedure C using the corresponding oxime ether **1u** (43.46 mg, 0.20 mmol) for isomerization by $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ afforded isomerized **1u** (40.3 mg, 0.185 mmol, 93%, *Z:E* = 2.0:1 to 17.5:1).

furan-2-yl(phenyl)methanone *O*-methyl oxime (1v**)**



General Procedure A using the corresponding ketone (250 mg, 1.45 mmol) afforded **1v** as

a pale orange liquid (265.5 mg, 91%). **¹H NMR** (CDCl_3 , 399.78 MHz) δ 7.60-7.54 (m), 7.53

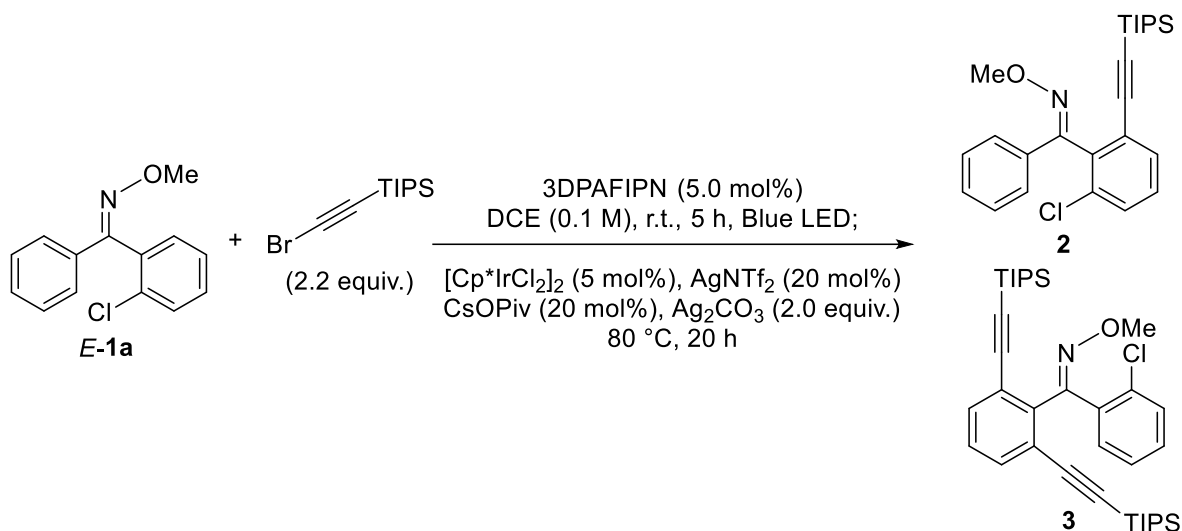
(1H, m, *E*), 7.48-7.40 (m), 7.40-7.35 (1H, m, *E*), 6.57 (1H, dd, *J* = 3.5, 1.8 Hz, *Z*), 6.41 (1H,

dd, *J* = 3.4, 1.8 Hz, *E*), 6.27-6.23 (1H, m, *E*), 4.13 (3H, s, *Z*), 3.99 (3H, s, *E*).

Procedure C using the corresponding oxime ether **1v** (40.25 mg, 0.20 mmol) for isomerization by $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ afforded isomerized **1v** (37.8 mg, 0.188 mmol, 94%, *Z:E* = 1:1.3 to 4.3:1).

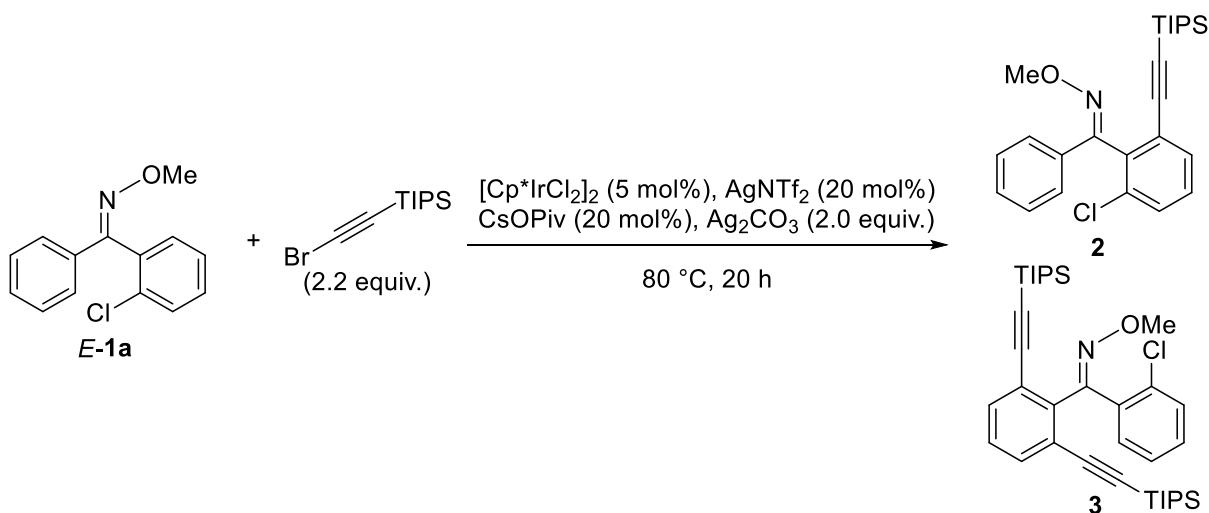
2-3. Selective C(sp²)-H functionalization of oxime ethers

C(sp²)-H alkylation with isomerization^[S3]



In an argon-filled glovebox, a screw-cap test tube was charged with 3DPAFIPN (6.48 mg, 0.010 mmol, 5.0 mol %), oxime **1a** (0.20 mmol, 1.0 equiv.), and DCE (2 mL). The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 5 h at room temperature under blue light irradiation. The reaction mixture was taken into the glovebox and [Cp*IrCl₂]₂ (7.97 mg, 0.010 mmol, 5.0 mol%), AgNTf₂ (15.52 mg, 0.040 mmol, 20 mol%), CsOPiv (9.44 mg, 0.040 mmol, 20 mol%), Ag₂CO₃ (110.30 mg, 0.4 mmol, 2.0 equiv.), and triisopropylsilyl acetylene bromide (0.44 mmol, 2.2 equiv.) were added. After stirred for 20 h at 80 °C, the reaction mixture was filtered through a short pad of silica gel, eluted with AcOEt, and evaporated under reduced pressure. The ratio of **2** and **3** was determined by ¹H NMR analysis of the crude mixture at this point (**2**:**3** = 93%:7%).

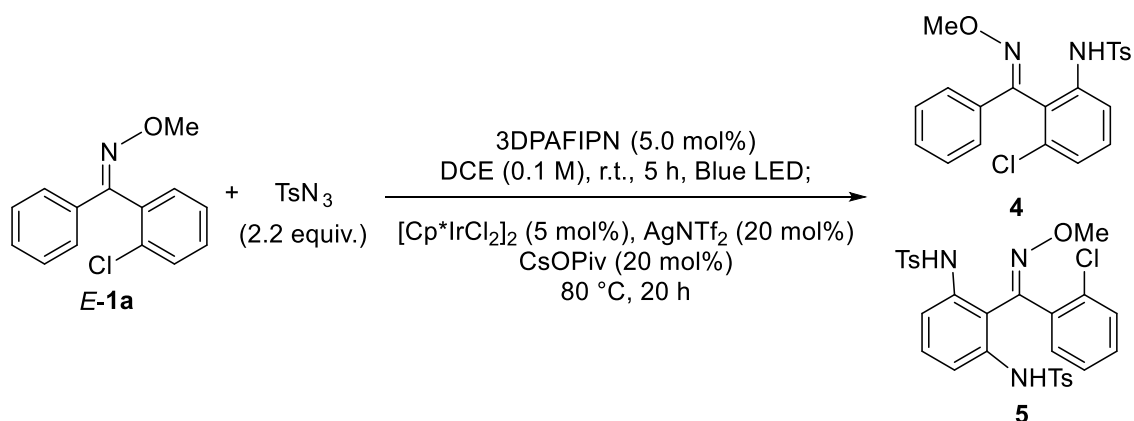
C(sp²)-H alkylation without isomerization



In an argon-filled glovebox, a screw-cap test tube was charged with oxime **1a** (0.20 mmol, 1.0 equiv.), [Cp*IrCl₂]₂ (7.97 mg, 0.010 mmol, 5.0 mol%), AgNTf₂ (15.52 mg, 0.040 mmol, 20 mol%), CsOPiv (9.44 mg, 0.040 mmol, 20 mol%), Ag₂CO₃ (110.30 mg, 0.4 mmol, 2.0 equiv.), triisopropylsilyl acetylene bromide (0.44 mmol, 2.2 equiv.),

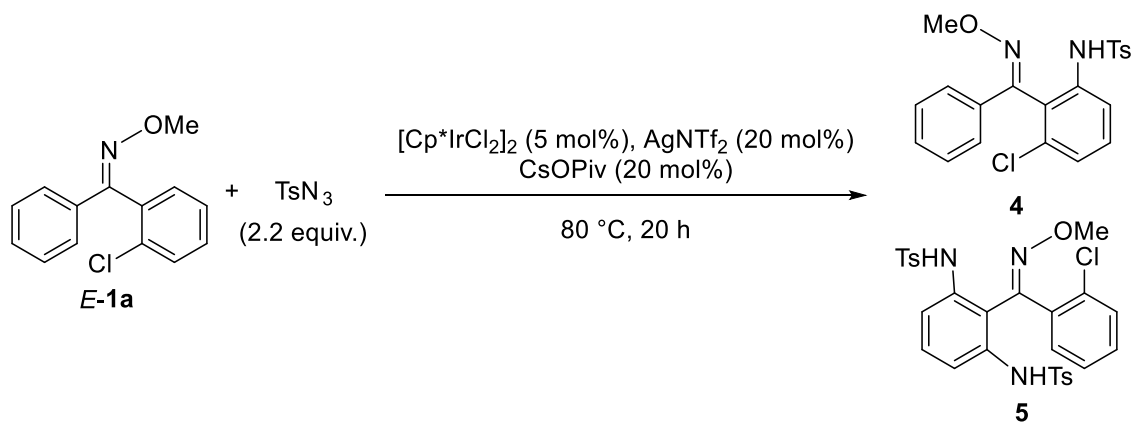
and DCE (2 mL) were added. After stirred for 20 h at 80 °C, the reaction mixture was filtered through a short pad of silica gel, eluted with AcOEt, and evaporated under reduced pressure. The ratio of **2** and **3** was determined by ¹H NMR analysis of the crude mixture at this point (**2:3** = 16%:76%).

C(sp²)-H amidation with isomerization^[S4]



In an argon-filled glovebox, a screw-cap test tube was charged with 3DPAFIPN (6.48 mg, 0.010 mmol, 5.0 mol %), oxime **1a** (0.20 mmol, 1.0 equiv.), and DCE (2 mL). The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 5 h at room temperature under blue light irradiation. The reaction mixture was taken into the glovebox and [Cp*IrCl₂]₂ (7.97 mg, 0.010 mmol, 5.0 mol%), AgNTf₂ (15.52 mg, 0.040 mmol, 20 mol%), CsOPiv (9.44 mg, 0.040 mmol, 20 mol%), and sulfonyl azide **2** (0.44 mmol, 2.2 equiv.) were added. After stirred for 20 h at 80 °C, the reaction mixture was filtered through a short pad of silica gel, eluted with AcOEt, and evaporated under reduced pressure. The ratio of **3** and **4** was determined by ¹H NMR analysis of the crude mixture at this point (**4**:**5** = 86%:7%).

C(sp²)-H amidation without isomerization



In an argon-filled glovebox, a screw-cap test tube was charged with oxime **1a** (0.20 mmol, 1.0 equiv.), [Cp*IrCl₂]₂ (7.97 mg, 0.010 mmol, 5.0 mol%), AgNTf₂ (15.52 mg, 0.040 mmol, 20 mol%), CsOPiv (9.44 mg, 0.040 mmol, 20 mol%), sulfonyl azide **2** (0.44 mmol, 2.2 equiv.), and DCE (2 mL) were added. After stirred for 20 h at 80 °C, the reaction mixture was filtered through a short pad of silica gel, eluted with AcOEt, and evaporated under reduced pressure. The ratio of **3** and **4** was determined by ¹H NMR analysis of the crude mixture at this point (**4**:**5** = 12%:62%).

Determination of *E/Z* configuration of the C(sp³)–H amidation product

Single crystal X-ray crystallography of **1b** before isomerization

A single crystal of **1b** before isomerization suitable for X-ray diffraction analysis (XRD) was obtained by recrystallization from hexane. A suitable crystal of **1b** was mounted with liquid paraffin on a Dual Thickness MicroLoops LD and transferred to the goniometer in a nitrogen stream at 159.2 K. Measurement was performed on a RIGAKU XtaLAB Synergy-R/Cu system with 1.2 kW PhotonJet-R/Cu microfocus rotating anode using graphite monochromated Cu-K α radiation source ($\lambda = 1.5418 \text{ \AA}$) and HyPix-6000HE detector. Cell parameters were determined and refined, and raw frame data were integrated using CrysAlisPro (Agilent Technologies, 2010). The structures were solved by direct methods with SHELXT 2018/2^[S12] and refined by full-matrix least-squares techniques against F^2 with SHELXL-2019/3^[S13] by using Olex2 software package.^[S14] The non-hydrogen atoms were anisotropically refined, and hydrogen atoms were placed using AFIX instructions. The detailed crystallographic data are available as a crystallographic information file (CIF), which is available from CCDC 2362952. The ORTEP-3 program was used to draw the molecule structures. The structure is drawn as thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. The structure and crystal data are shown in **Figure S1** and **Table S1**.

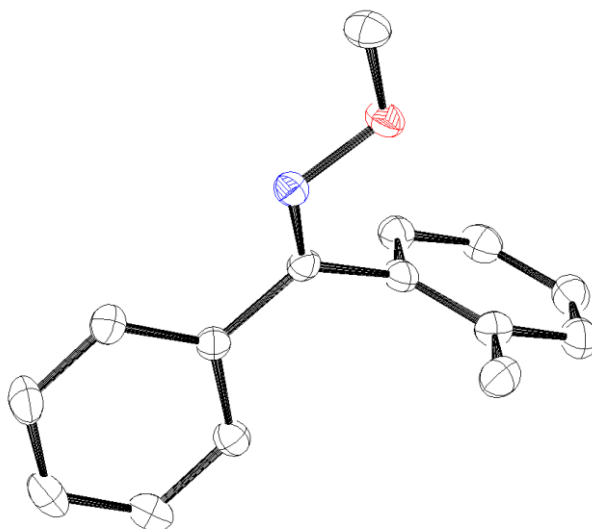


Figure S1. Single crystal X-ray crystallography of **1b** before isomerization

Table S1. Crystal data and structure refinement for YH09oMe_auto

Identification code	YH09oMe_auto
Empirical formula	C ₁₅ H ₁₅ NO
Formula weight	225.28
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	P21/c
a/ $\text{\AA}$	12.80331(13)

b/Å	7.57902(8)
c/Å	12.63440(13)
α /°	90
β /°	94.8865(9)
γ /°	90
Volume/Å ³	1221.54(2)
Z	4
ρ calcg/cm ³	1.225
μ /mm ⁻¹	0.601
F(000)	480.0
Crystal size/mm ³	0.2 × 0.2 × 0.2
Radiation	Cu K α (λ = 1.54184)
2 Θ range for data collection/°	6.93 to 156.726
Index ranges	-16 ≤ h ≤ 15, -8 ≤ k ≤ 9, -15 ≤ l ≤ 16
Reflections collected	13012
Independent reflections	2570 [R _{int} = 0.0308, R _{sigma} = 0.0169]
Data/restraints/parameters	2570/0/157
Goodness-of-fit on F ²	1.040
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0483, wR ₂ = 0.1203
Final R indexes [all data]	R ₁ = 0.0502, wR ₂ = 0.1218
Largest diff. peak/hole / e Å ⁻³	0.62/-0.30

Single crystal X-ray crystallography of **1k** after isomerization

A single crystal of **1k** after isomerization suitable for X-ray diffraction analysis (XRD) was obtained by recrystallization from hexane. A suitable crystal of **1k** was mounted with liquid paraffin on a Dual Thickness MicroLoops LD and transferred to the goniometer in a nitrogen stream at 159.2 K. Measurement was performed on a RIGAKU XtaLAB Synergy-R/Cu system with 1.2 kW PhotonJet-R/Cu microfocus rotating anode using graphite monochromated Cu-K α radiation source (λ = 1.5418 Å) and HyPix-6000HE detector. Cell parameters were determined and refined, and raw frame data were integrated using CrysAlisPro (Agilent Technologies, 2010). The structures were solved by direct methods with SHELXT 2018/2^[S12] and refined by full-matrix least-squares techniques against F^2 with SHELXL-2019/3^[S13] by using Olex2 software package.^[S14] The non-hydrogen atoms were anisotropically refined, and hydrogen atoms were placed using AFIX instructions. The detailed crystallographic data are available as a crystallographic information file (CIF), which is available from CCDC

2362952. The ORTEP-3 program was used to draw the molecule structures. The structure is drawn as thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. The structure and crystal data are shown in **Figure S2** and **Table S2**.

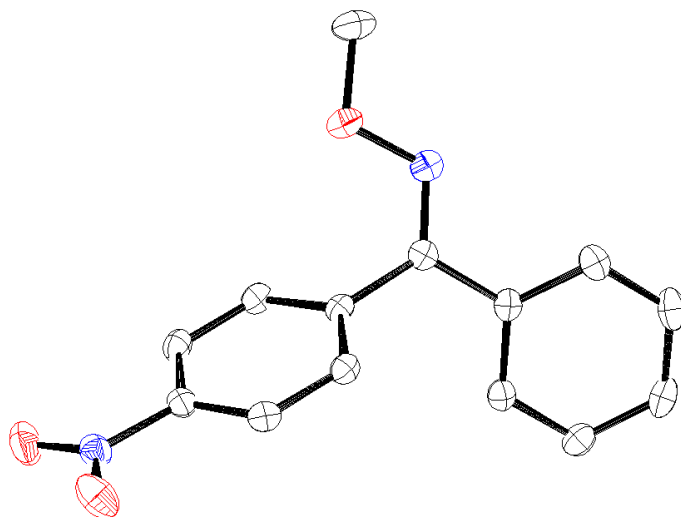


Figure S2. Single crystal X-ray crystallography of **1k** after isomerization

Table S2 Crystal data and structure refinement for YH09pNO2_2_auto

Identification code	YH09pNO2_2_auto
Empirical formula	C ₁₄ H ₁₂ N ₂ O ₃
Formula weight	256.26
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	P21/n
a/Å	8.82309(14)
b/Å	9.19527(16)
c/Å	16.0299(2)
α /°	90
β /°	102.8616(16)
γ /°	90
Volume/Å ³	1267.89(4)
Z	4
ρ calcg/cm ³	1.342

μ /mm ⁻¹	0.796
F(000)	536.0
Crystal size/mm ³	0.2 × 0.15 × 0.05
Radiation	Cu K α (λ = 1.54184)
2 Θ range for data collection/°	10.578 to 156.804
Index ranges	-10 ≤ h ≤ 11, -9 ≤ k ≤ 11, -20 ≤ l ≤ 20
Reflections collected	13657
Independent reflections	2677 [R _{int} = 0.0481, R _{sigma} = 0.0312]
Data/restraints/parameters	2677/0/174
Goodness-of-fit on F ²	1.062
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0387, wR ₂ = 0.1032
Final R indexes [all data]	R ₁ = 0.0418, wR ₂ = 0.1059
Largest diff. peak/hole / e Å ⁻³	0.31/-0.27

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Chapter 4. Synthesis of binuclear CpRh(III) catalyst for remote C-H functionalization

Section 1: Introduction

Cp*M(III)-catalyzed C-H functionalization has emerged as a step- and atom-economical strategy for accessing diverse organic molecules. Despite its utility, several inherent limitations remain (**Figure 1**). First, external ligands including chiral bidentate ligands to construct rigid chiral environment cannot generally be introduced for inducing enantioselectivity due to the mechanism of C-H activation via concerted metallation-deprotonation (CMD)¹ (**Figure 1**, left). In the CMD process, the three accessible coordination sites of the Cp*M(III) complex are fully occupied, preventing other ligands from participating in the C-H activation step. Chiral CpM(III) catalysts² and monodentate chiral carboxylic acids³ as a CMD ligand represent effective approaches for asymmetric C-H functionalization (**Figure 1**, right). However, achieving high enantioselectivity often requires elaborate catalyst structures that create a rigid chiral environment through additional noncovalent interactions, which in turn complicates the synthesis and modification of chiral ligands. Therefore, the development of more accessible methods for asymmetric C-H activation using simple chiral ligands such as chiral bidentate CMD ligand to construct rigid chiral environment is highly desirable.

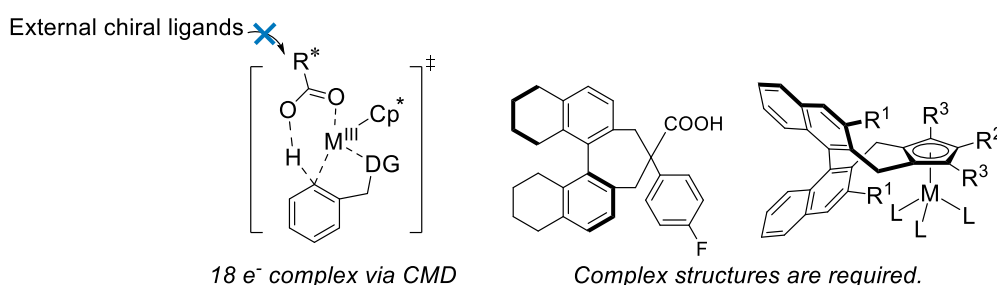


Figure 1. Issue in enantioselective C-H functionalization

Second, C-H activation typically occurs at positions proximal to a directing group, and *o*-C-H functionalization predominates in C(sp²)-H activation (**Figure 2**, left). Consequently, remote C-H functionalization remains challenging. This limitation arises because the coordination sites on the metal center are positioned adjacent to one another, and a metallacycle upon *meta*-C-H activation is formed with ring strain (**Figure 2**, right). As a result, the transition state for remote C-H activation is energetically unfavorable.

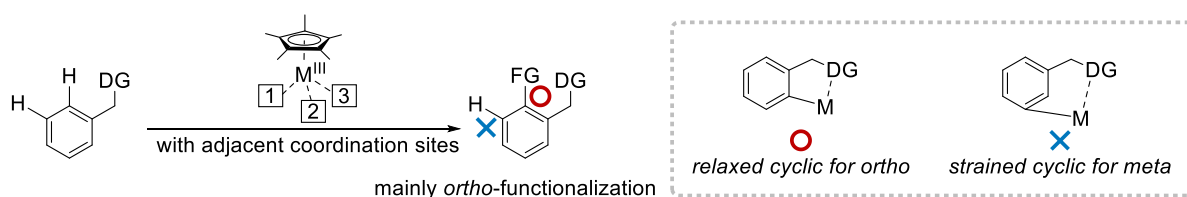


Figure 2. Issues in site-selectivity of C-H functionalization with Cp*M(III)

m-Selective C–H activation as remote C–H functionalization has been achieved primarily with low-valent iridium catalyst (**Figure 3**). Kuninobu, Kanai, and co-workers reported that designed ligand bearing urea group to attract carbonyl group enables *m*-selective C–H borylation of benzamides.⁴ Following this work, several groups have achieved *m*-selective C–H borylation by unique strategies.^{5–7}

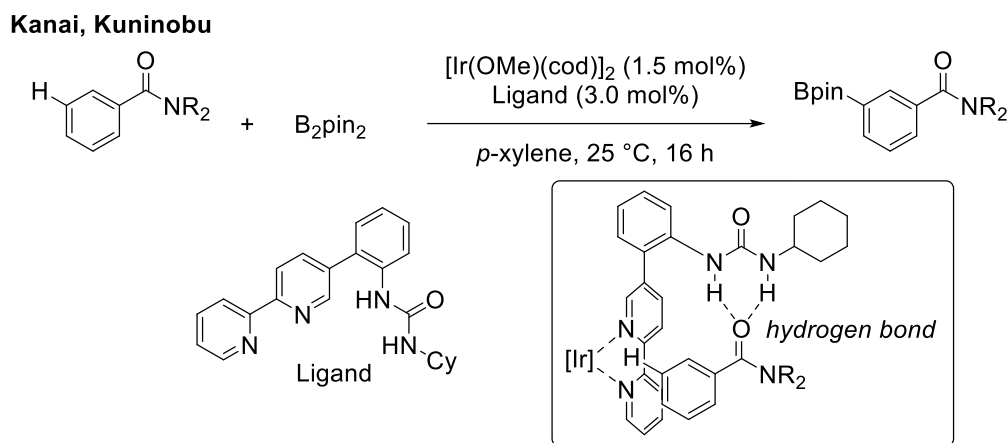


Figure 3. *m*-C–H borylation assisted by urea-ligand

In high-valent metal catalysis, reports of *m*-selective C–H functionalization have been achieved by limited strategies. Frost and co-workers demonstrated that *m*-C–H sulfonation of 2-phenyl pyridine could be achieved by Ru(II) catalyst (**Figure 4**).⁸ Ruthenacycle is proposed to facilitate outer-sphere type functionalization on opposite position of Ru–C bond, leading to *m*-functionalized products.⁹

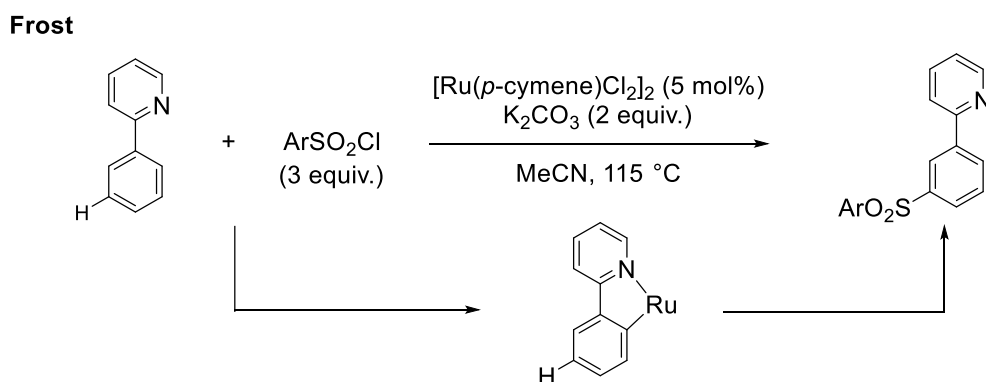


Figure 4. Indirect *m*-C–H sulfonation by ruthenium

Palladium catalysis enabled direct *m*-selective C–H functionalization through strategies such as template-assisted directing groups that induces a cyclophane-like transition state to avoid the strain associated with conventional cyclic transition states via *o*-C–H activation (**Figure 5**, top)¹⁰ and Catellani-type reaction (**Figure 5**, bottom).^{11,12}

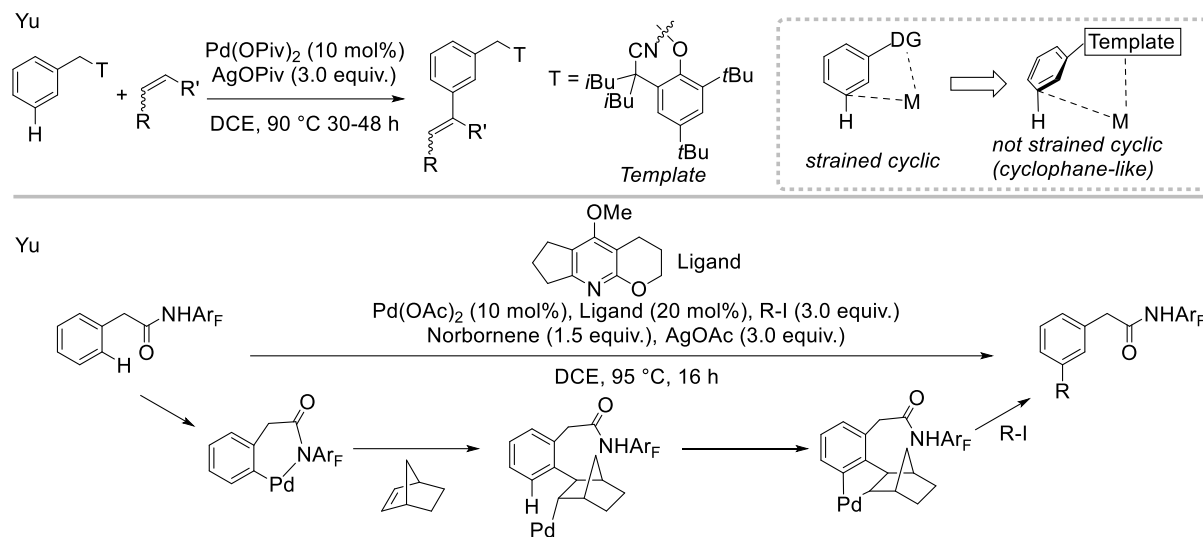


Figure 5. Pd-catalyzed *m*-C–H functionalization by designed directing group and Catellani-type reaction

In 2017, Yu and co-workers reported Cp*Rh(III)-catalyzed *m*-C–H functionalization using a template directing group (**Figure 6**).¹³ Although this study demonstrated the feasibility of *m*-selectivity under high-valent metal catalysis, the substrate scope was limited by the structural requirements of the template directing group.^{14–21} Consequently, the development of broadly applicable methods for *m*-selective C–H functionalization remains a significant challenge.

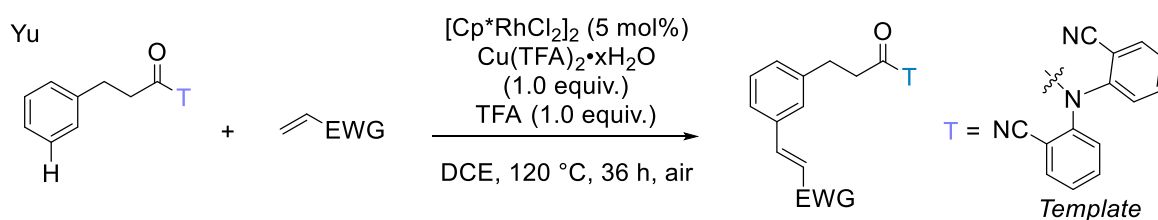


Figure 6. Rh-catalyzed *m*-C–H functionalization by designed directing group

To enable remote C–H activation and asymmetric catalysis using external chiral ligands under high-valent group 9 metal catalysis, a binuclear CpM(III) catalyst was designed (**Figure 7**). The advantages of this catalyst are as follows:

1. Remote C–H activation.

A binuclear CpM(III) complex features two spatially separated metal centers, allowing the directing group to coordinate to one metal center while the other metal center engages in C–H activation (**Figure 7**, left). Because the activation step would not require a strained metallacycle, remote C–H activation becomes feasible by the distance between the two metal sites.

2. Availability of bidentate chiral ligands.

The binuclear catalyst has six coordination sites. The use of chiral bidentate CMD ligands enables construction of a more rigid chiral environment, increasing the accessibility and generality of asymmetric C–H functionalization (**Figure 7**, right).

To achieve remote C–H activation, proximal *ortho*-C–H activation at a single metal center must be suppressed, as it competes with the desired remote activation involving both metal centers. The introduction of a bidentate CMD ligand provides a solution to this issue (**Figure 7**, right). When coordinated to one metal center of the binuclear complex, the bidentate ligand occupies 2 coordination sites, preventing directed proximal C–H activation as a major limitation of mononuclear Cp*M(III) catalysis (the detailed mechanism; see **Figure 1**, left). By inhibiting the proximal pathway, selective remote C–H activation is expected to proceed through cooperation of the two metal centers.

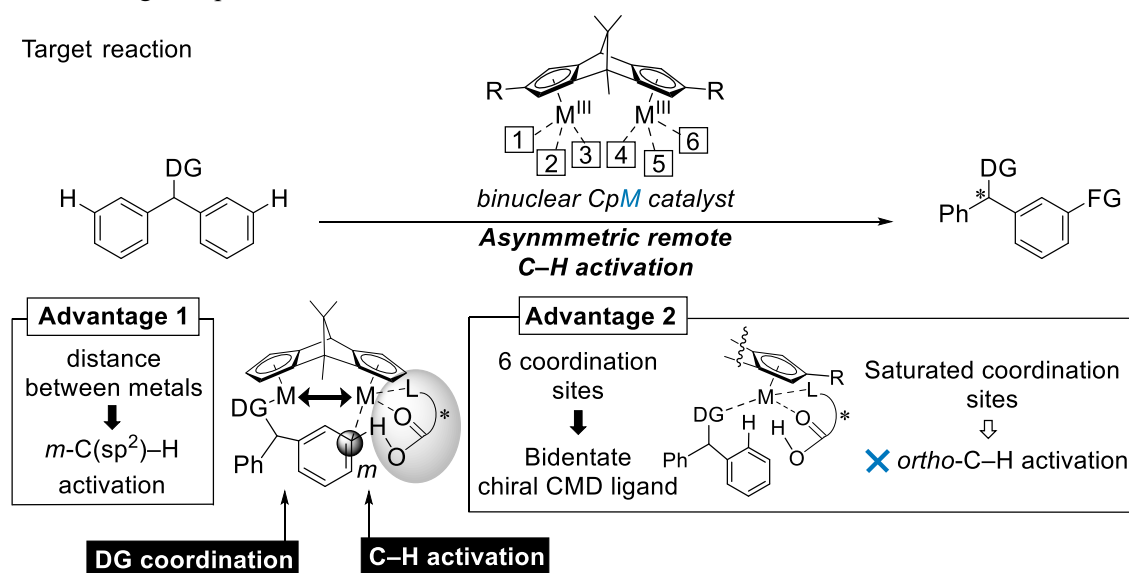


Figure 7. Design of binuclear CpM(III) catalysts

Section 2: Synthesis and single crystal X-ray diffraction analysis of binuclear CpRh complex

On the basis of these considerations, the synthesis of the corresponding binuclear CpM(III) complexes was conducted. Ligands incorporating a rigid framework and steric repulsion on one side, derived from borneol (**1**), were initially targeted (**Figure 8**, top). This ligand has rigid structure to fix the conformation in transition state for remote C–H functionalization. It also has steric repulsion on one side to prevent complexation with undesired *trans*-configuration. Although the synthesis was initially started from borneol, synthesis of a key intermediate involves a potentially explosive reaction (C–H oxidation by CrO_3), preventing further investigation of this ligand (**1**). Consequently, I next investigated the synthesis of a simpler rigid ligand lacking large steric repulsion to avoid explosive reaction (**2**), but the desired ligand could not be obtained after several trials (**Figure 8**, top right). Considering the accessibility, an *m*-phenylene-tethered Cp ligand **3** was then designed (**Figure 8**, bottom left). Methyl groups on the phenylene linker would prevent undesired *trans*-complexation because of steric repulsion between methyl groups and rhodium centers (**Figure 8**, bottom right).

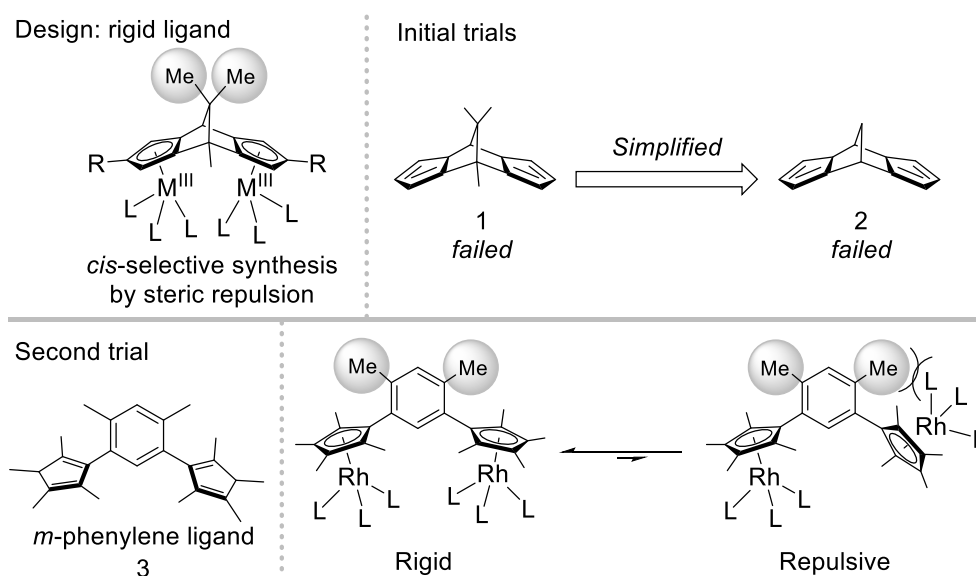
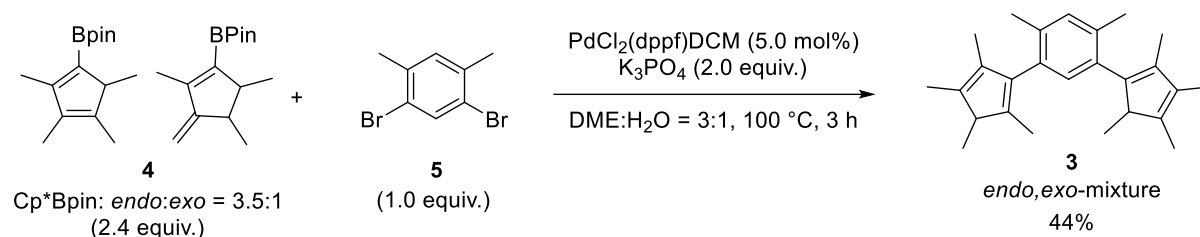


Figure 8. Design of rigid Cp ligands with steric repulsion on one side

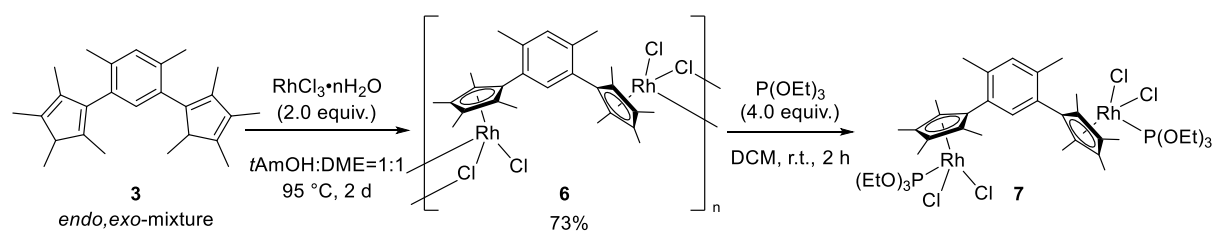
The corresponding ligand was synthesized via Suzuki–Miyaura coupling between Cp*Bpin²² and 1,5-dibromo-2,4-dimethylbenzene, affording the desired ligand **3** as an isomeric mixture (**Scheme 1**).



Scheme 1. Synthesis of *m*-phenylene ligand

Formation of the binuclear complex was carried out by heating ligand **3** with rhodium chloride in a mixture of *tert*-amyl alcohol (*t*AmOH) and DME. After stirring for two days, an insoluble orange solid was obtained, which was presumed to be a bridged polymeric compound. Addition of P(OEt)₃ afforded the monomeric binuclear rhodium complex. Recrystallization from DCM/Et₂O provided single crystals suitable for X-ray diffraction analysis.

However, single-crystal X-ray diffraction analysis of complex **7** revealed that the rhodium complex possesses an unintentional trans-configuration (**Figure 8**).



Scheme 2. Complexation of *m*-phenylene-tethered CpRh(III)

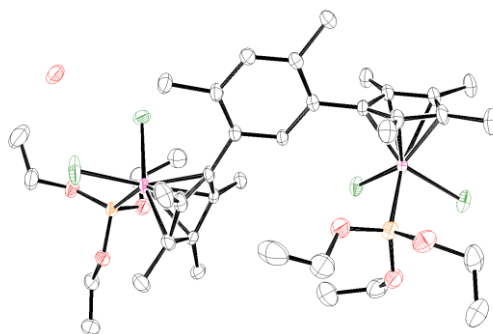
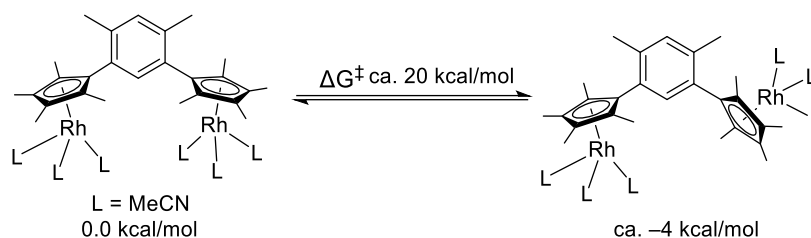


Figure 8. Xray single crystal analysis of Rh complex **7**

P2₁/c, monoclinic R₁=0.0354, wR₂=0.0894, GOF=1.061

Semiempirical calculations at the GFN2-xTB level suggested that the *trans*-isomer could undergo rotational interconversion even at room temperature ($\Delta G^\ddagger = 20$ kcal/mol, **Scheme 3**), and that the thermodynamic stabilities of the individual isomers were comparable. These results indicate that complex **5** with a *trans*-configuration could lead to the desired *cis*-configuration and then to the desired transition state required for remote C–H functionalization.



Scheme 3. Calculation of rotation energy

On the basis of these working hypotheses, a wide range of substrates and reagents was screened for *m*-C–H functionalization using the *m*-phenylene-tethered CpRh catalyst **6** (**Figure 9**). However, no products resulting from remote C–H functionalization were detected while *ortho*-C C–H functionalization proceeded in the use of ethyl-phenyl oxime ether as a substrate even in using *N*-Ac leucine as a bidentate CMD ligand. One possible reason for the lack of reactivity is that the *trans*-configured complex **6** may not undergo the required rotational interconversion under the reaction conditions in the presence of substrates and reagents. Accordingly, further refinement of the catalyst structure is necessary to achieve remote functionalization, and some strategies are required to suppress proximal functionalization (e.g. using strong coordinating bidentate CMD ligands)

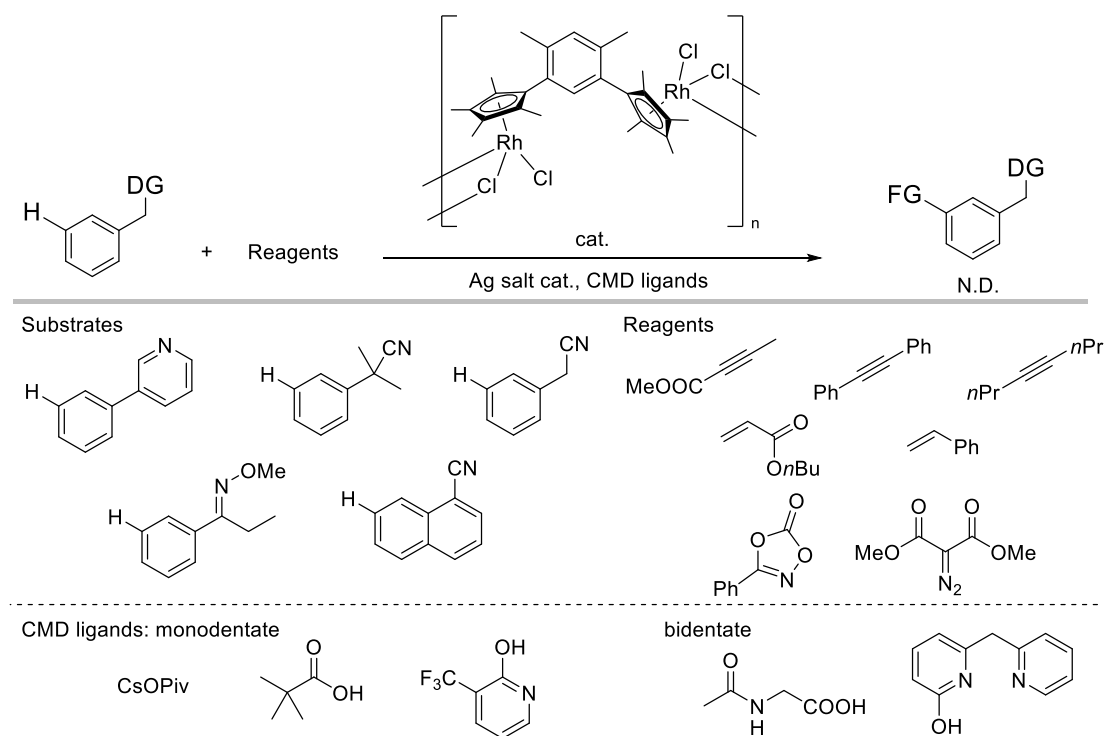


Figure 9. Unsuccessful substrates and reagents for *m*-C–H functionalization

To suppress rotational interconversion of the catalyst, a ligand incorporating bulkier substituents, trifluoromethyl groups, was designed (**Figure 10**). The trifluoromethyl group was expected to serve a dual role: inhibiting formation of the *trans*-isomer through increased steric hindrance and accelerating C–H activation via its electron-withdrawing effect.²³

Synthesis of the ligand was attempted via a Suzuki–Miyaura coupling between Cp*BPin and 1,5-dibromo-2,4-bis(trifluoromethyl)benzene, following the same strategy used for ligand **3** (**Figure 11**). However, the desired ligand was not obtained, most likely due to steric repulsion arising from the trifluoromethyl substituents.

Next design

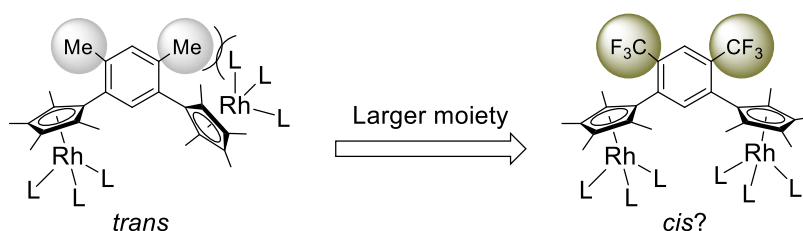


Figure 10. refined catalyst with bulkier trifluoromethyl groups

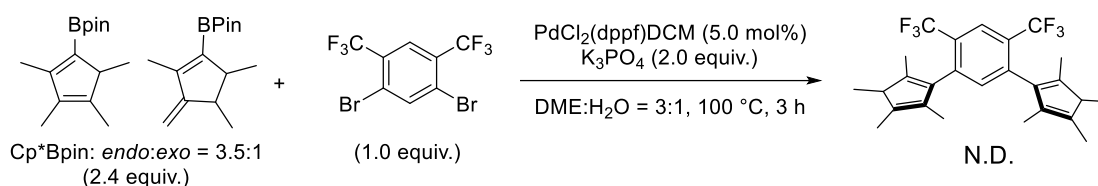


Figure 11. Synthesis of refined ligand with trifluoromethyl groups

As a next ligand candidate, Cp ligand bearing only two methyl substituents on each Cp ring was designed. This less hindered structure is expected to facilitate rotational flexibility of CpRh(III) moieties, thereby enabling access to the desired *cis*-type transition state. The synthesis of this ligand is currently under investigation.

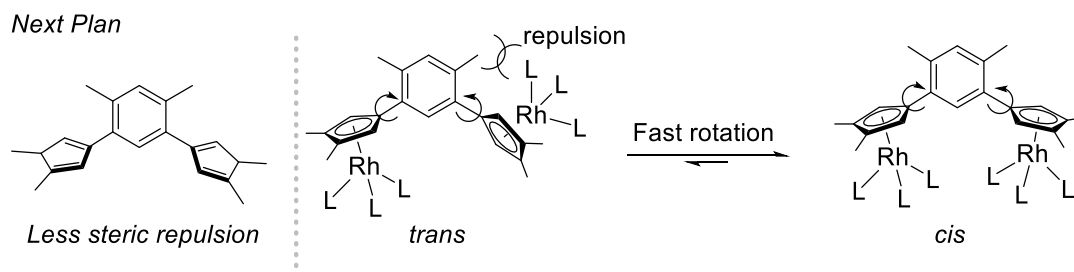


Figure 12. Next plan: Sterically less hindered Cp for fast *cis/trans* rotation

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Experimental Section

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1. General

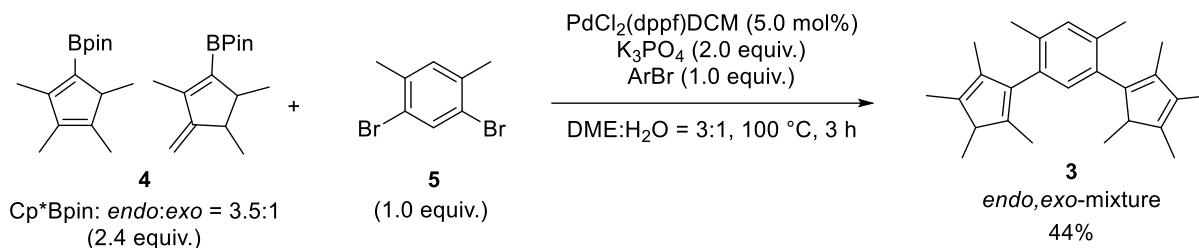
All non-aqueous reactions were carried out in a flame-dried glassware under argon atmosphere unless otherwise noted or in an argon-filled glove box. NMR spectra were recorded on JEOL JNM-ECA600 spectrometers operating at 600.17 MHz for ^1H NMR, 150.92 MHz for ^{13}C NMR and 564.69 MHz for ^{19}F NMR. Chemical shifts were reported in the scale relative to TMS (0.00 ppm for ^1H NMR in CDCl_3), CHCl_3 (7.26 ppm for ^1H NMR in CDCl_3), CDCl_3 (77.00 ppm for ^{13}C NMR in CDCl_3) as an internal reference, respectively. Column chromatography was performed with silica gel Kanto Silica gel 60 N (40-50 mesh)

Materials: Dichloromethane (DCM) and toluene were purified by Glass Contour solvent purification system before use. All other reagents were commercially available and used as received unless otherwise noted.

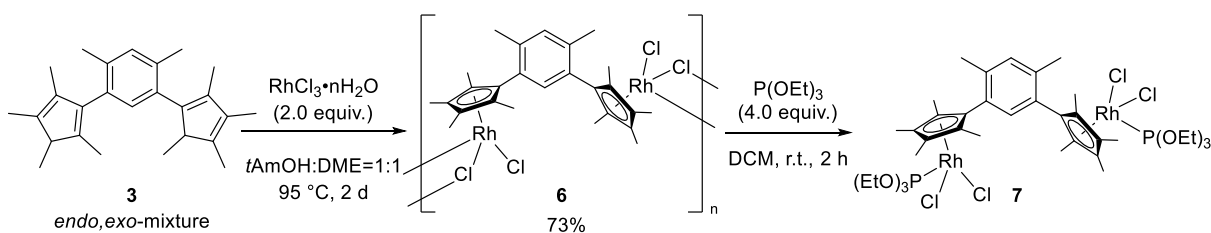
2. Experimental procedures

2-1. Synthesis of ligand and binuclear complex

Synthesis of **5**



A round bottom flask was charged with the corresponding isomeric mixture of Cp*Bpin **4** (*endo:exo* 3.5:1)^{S1} and DME/H₂O (3:1). Then, PdCl₂(dppf)DCM (5.0 mol%), K₃PO₄ (2.0 equiv.), and 1,4-dibromo-2,4-dimethylbenzene **5** (1.0 equiv.) were added to the solution of Cp*Bpin. Ar gas was bubbled through the mixture for 5 min. The reaction mixture was stirred for 3 h at 100 °C. The reaction mixture was quenched by adding H₂O and Et₂O and extracted with Et₂O twice. The organic layers were combined, dried over Na₂SO₄, and evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane) to afford **3** as an isomeric mixture, used for next reaction without further purification.



A screw-cap test tube was charged with **3** (1.0 equiv.) and *t*AmOH/DME (1:1). Then, RhCl₃·*n*H₂O (2.0 equiv., 40% w/w) was added to the mixture, and the reaction mixture was stirred for 2 d at 95 °C. After cooled to room temperature, the mixture was filtered and washed with EtOH and Et₂O. The residue was collected and dried *in vacuo* to afford **6** as a light orange solid (73%).

A test tube was charged with **6** (1.0 equiv.) and DCM (0.2 M), then P(OEt)₃ (4.0 equiv.) was added to the suspension of **6**. After the mixture was stirred for 2 h at room temperature, the solvent was evaporated and washed with Et₂O. The residue was recrystallized from DCM/Et₂O, and the single crystal of **7** was used for single-crystal X-ray diffraction analysis.

3. Determination of the structure of 7

Single crystal X-ray crystallography of 7

A single crystal of 7 suitable for X-ray diffraction analysis (XRD) was obtained by recrystallization from Et₂O/hexane. A suitable crystal of 7 was mounted with liquid paraffin on a Dual Thickness MicroLoops LD and transferred to the goniometer in a nitrogen stream at 159.2 K. Measurement was performed on a RIGAKU XtaLAB Synergy-R/Cu system with 1.2 kW PhotonJet-R/Cu microfocus rotating anode using graphite monochromated Cu-K α radiation source ($\lambda = 1.5418 \text{ \AA}$) and HyPix-6000HE detector. Cell parameters were determined and refined, and raw frame data were integrated using CrysAlisPro (Agilent Technologies, 2010). The structures were solved by direct methods with SHELXT 2018/2 and refined by full-matrix least-squares techniques against F^2 with SHELXL-2019/3 by using Olex2 software package. The non-hydrogen atoms were anisotropically refined, and hydrogen atoms were placed using AFIX instructions. The detailed crystallographic data are available as a crystallographic information file (CIF). The ORTEP-3 program was used to draw the molecule structures. The structure is drawn as thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. The structure and crystal data are shown in **Figure S1** and **Table S1**.

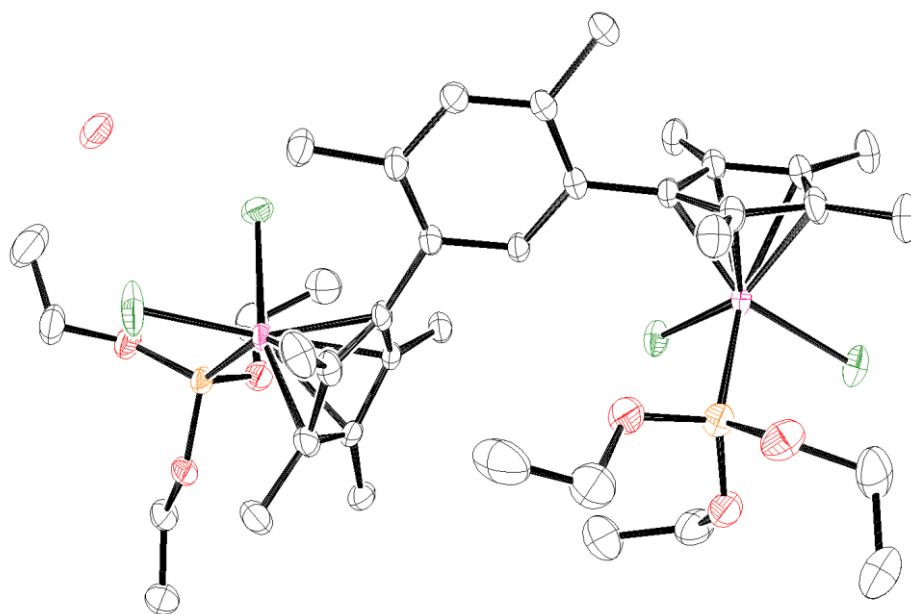


Figure S1. The structure of 7

Table 1 Crystal data and structure refinement for 7

Identification code	YH08156_auto
Empirical formula	C ₃₈ H _{62.67} Cl ₄ O _{6.33} P ₂ Rh ₂
Formula weight	1030.43
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	P21/c
a/ $\text{\AA}$	9.63030(10)

b/Å	30.5165(3)
c/Å	15.65300(10)
α /°	90
β /°	104.3930(10)
γ /°	90
Volume/Å ³	4455.77(7)
Z	4
ρ calcg/cm ³	1.536
μ /mm ⁻¹	9.220
F(000)	2117.0
Crystal size/mm ³	0.2 × 0.2 × 0.03
Radiation	Cu K α (λ = 1.54184)
2 Θ range for data collection/°	5.792 to 156.854
Index ranges	-12 ≤ h ≤ 11, -36 ≤ k ≤ 38, -14 ≤ l ≤ 19
Reflections collected	47560
Independent reflections	9312 [R _{int} = 0.0385, R _{sigma} = 0.0228]
Data/restraints/parameters	9312/0/497
Goodness-of-fit on F ²	1.061
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0354, wR ₂ = 0.0894
Final R indexes [all data]	R ₁ = 0.0369, wR ₂ = 0.0905
Largest diff. peak/hole / e Å ⁻³	1.20/-1.30

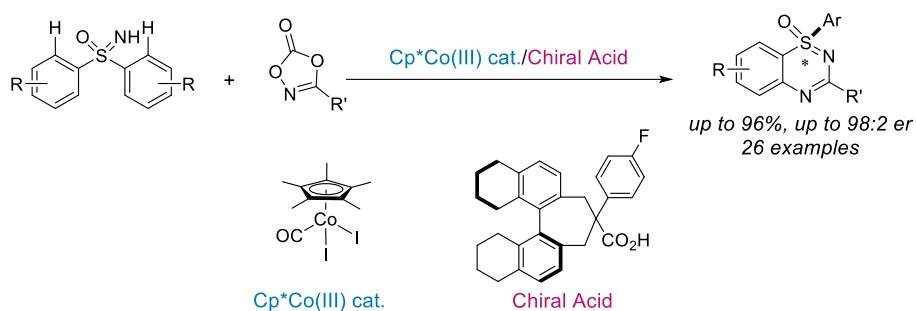
4. Reference

[S1] Yasui, T.; Tanabe, S.; Masueda, T.; Yamamoto, Y. *Synthesis* **2023**, *55*, 1207–1212.

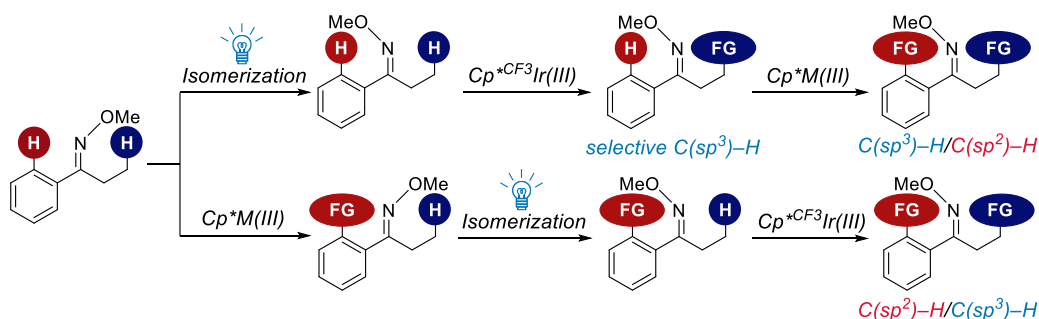
Conclusion

I engaged selectivity control of C–H functionalization under group 9 metal catalysis. The summary is shown below:

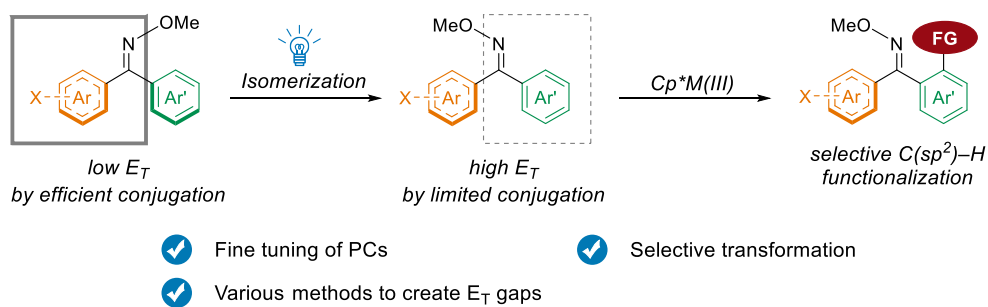
1. Asymmetric synthesis of benzothiadiazine-1-oxide has been achieved by combination of Cp*Co(III) and newly synthesized chiral carboxylic acid with high enantioselectivity and yield.



2. The geometry in a directing group enabled site-selective C(sp³)–H functionalization and switchable C(sp³)–H/C(sp²)–H functionalization of oxime ethers



3. Fine tuning of substrates and photocatalysts enabled selective *E/Z* isomerization and site-selective C(sp²)–H functionalization of diaryl oxime ethers



Publications

1. Hirata, Y.; Sekine, D.; Kato, Y.; Lin, L.; Kojima, M.; Yoshino, T.; Matsunaga, S. *Angew. Chem. Int. Ed.* **2022**, *61*, e202205341.
2. Hirata, Y.; Kimura, S.; Higashida, K.; Yoshino, T.; Matsunaga, S. *Angew. Chem., Int. Ed.* **2025**, *64*, e202421026.