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# Iron-catalyzed asymmetric intramolecular cyclopropanation reactions using chiral tetramethyl-1,1′-spirobiindane-based bisoxazoline (TMSI-BOX) ligands†

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The versatile application of chiral bisoxazoline (BOX) ligands in diverse metal-catalyzed asymmetric reactions results in growing demand for novel BOX ligands containing different motifs. Herein, the successful development of a chiral spiro bisoxazoline ligand (TMSI-BOX) on the basis of the tetramethyl-1,1′-spirobiindane motif and bisoxazoline chelating units is described. The corresponding Fe complexes of TMSI-BOX proved to be excellent catalysts in the asymmetric intramolecular cyclopropanation reaction of diazo derivatives, providing synthetically versatile [3.1.0]bicycloalkane derivatives bearing two contiguous quaternary chiral centers with high enantiomeric purity.

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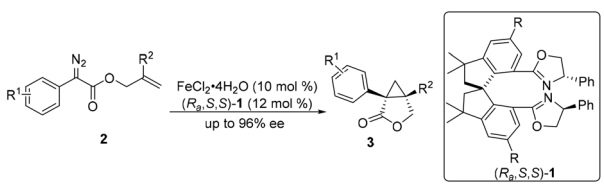
## Introduction

Iron is the most abundant transition metal in the Earth's crust. Also, iron is cheap, readily available and environmentally benign. Due to the above reasons, iron catalysis has attracted significant attention in organic synthesis. More and more iron-catalyzed organic transformations have been developed over the past decades,[1] such as substitutions, additions, reductions, oxidations, cycloadditions and so on. Chiral iron catalysis is quite challenging, and extensive research effort has been devoted to the development of highly enantioselective Fe-catalyzed reactions.[2] Although there has been significant progress in the chiral iron catalysis, the development of a sustainable chiral iron catalyst remains at the forefront and desirable.

The cyclopropanation of alkene bonds by α-diazo reagents is one of the most important transformations in organic synthesis since substituted cyclopropane molecules have been demonstrated to be versatile intermediates for syntheses of pharmaceuticals, peptidomimetics, and natural products.[3] In this context, transition metal-catalyzed asymmetric intramolecular cyclopropanation of diazo derivatives provides synthetically versatile bicyclic molecules.[4] Although a number of transition metals were used and showed excellent results for such asymmetric transformation,[5] including iridium, rhodium, ruthenium, palladium, copper and cobalt, only a few examples for the Fe-catalyzed asymmetric cyclopropanation reaction have been reported.[6] Despite these elegant contributions, the development of new methods is still important. We developed a series of chiral hexamethyl-1,1′-spirobiindane-derived bisoxazoline ligands and successfully applied in iron-catalyzed enantioselective Si–H bond insertions.[7] In this communication, we wish to report our discovery of the chiral spiro bisoxazoline ligand (TMSI-BOX) on the basis of the tetramethyl-1,1′-spirobiindane motif and bisoxazoline chelating units, and its successful application in asymmetric intramolecular cyclopropanation reactions of diazo derivatives to give synthetically versatile [3.1.0]bicycloalkane derivatives bearing two contiguous quaternary chiral centers with high enantiomeric purity (Scheme 1). Herein, we report the preliminary results of this study.

## Results and discussion

The enantiopure TMSI-BOX was synthesized from the spiro dialdehyde **4** (Scheme 2). The spiro dialdehyde **4** was obtained




**Scheme 1** Fe/TMSI-BOX-catalyzed asymmetric intramolecular cyclopropanation.

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† Electronic supplementary information (ESI) available: NMR and HPLC spectra. CCDC 1879959 for [($R_a$,*S*,*S*)-**1d**]. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8ob03065k

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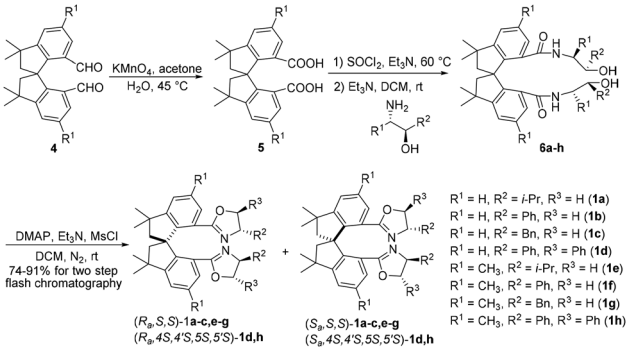



**Scheme 2** Synthesis of TMSI-BOX.

from industrially available bisphenol A or C according to the literature published by our group.[8] The spiro diacid **5** was prepared in 97% yield by oxidation of **4** with potassium permanganate solution in acetone. The spiro diacid **5** was further transformed to the corresponding hydroxyl amides **6a–h** as a diastereomer mixture in quantitative yield by reacting with thionyl chloride first and then a variety of enantiopure amino alcohols. The final cyclization with methanesulfonyl chloride[9] and trimethylamine in the presence of *N*,*N*-dimethylaminopyridine (DMAP) completed the synthesis of chiral spiro-bisoxazolines **1a–h** as a diastereomer mixture. The two diastereomers could be easily separated by flash chromatography to give the target TMSI-BOX ligands in good yields. The absolute configuration of ($R_a$,*S*,*S*)-**1d** was determined by X-ray crystallographic analysis of a single crystal (Fig. 1).

With the chiral TMSI-BOX ligands in hand, we first chose the intramolecular cyclopropanation of 2-methylallyl-2-diazoacetate **2a** into 3-oxabicyclo-[3.1.0]hexan-2-one **3a** as a bench mark enantioselective reaction for our chiral TMSI-BOX ligands. In initial investigation, the reaction was performed in chloroform at 60 °C in the presence of an iron-bisoxazoline complex catalyst, which was generated *in situ* from 10 mol% Fe$(ClO_4)_2$, 12 mol% of the chiral ligand ($R_a$,*S*,*S*)-**1a**, and 12 mol% $NaBAr_F$. However, we obtained the *cis* product **3a** in low yield (7%) and very low ee (6%) without the formation of the *trans* isomer (Table 1, entry 1). We screened the chiral TMSI-BOX ligands with different substituents on the oxazoline rings and found remarkable results for cyclopropanation reactions (Table 1, entries 2–8). To our delight, the aryl substituents on

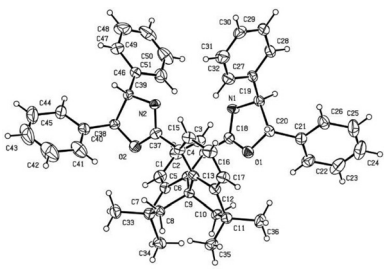
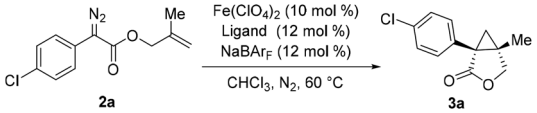


**Fig. 1** X-ray crystal structure of ($R_a$,*S*,*S*)-**1d**.

**Table 1** Reaction optimization: ligands[a]




| Entry | Ligand | [Fe] | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|---|
| 1 | ($R_a$,*S*,*S*)-**1a** | $Fe(ClO_4)_2$ | 7 | 6 |
| 2 | ($R_a$,*S*,*S*)-**1b** | $Fe(ClO_4)_2$ | 20 | 59 |
| 3 | ($R_a$,*S*,*S*)-**1c** | $Fe(ClO_4)_2$ | 8 | 27 |
| 4 | ($R_a$,4*S*,4*S*′,5*S*,5*S*′)-**1d** | $Fe(ClO_4)_2$ | 45 | 83 |
| 5 | ($R_a$,*S*,*S*)-**1e** | $Fe(ClO_4)_2$ | 47 | 3 |
| 6 | ($R_a$,*S*,*S*)-**1f** | $Fe(ClO_4)_2$ | 86 | 88 |
| 7 | ($R_a$,*S*,*S*)-**1g** | $Fe(ClO_4)_2$ | 62 | 58 |
| 8 | ($R_a$,4*S*,4*S*′,5*S*,5*S*′)-**1h** | $Fe(ClO_4)_2$ | 84 | 68 |
| 9 | ($S_a$,*S*,*S*)-**1a** | $Fe(ClO_4)_2$ | 5 | 9 |
| 10 | ($S_a$,*S*,*S*)-**1b** | $Fe(ClO_4)_2$ | 23 | 37 |
| 11 | ($S_a$,*S*,*S*)-**1c** | $Fe(ClO_4)_2$ | 10 | 19 |
| 12 | ($S_a$,4*S*,4*S*′,5*S*,5*S*′)-**1d** | $Fe(ClO_4)_2$ | 27 | 30 |
| 13 | ($S_a$,*S*,*S*)-**1e** | $Fe(ClO_4)_2$ | 35 | 2 |
| 14 | ($S_a$,*S*,*S*)-**1f** | $Fe(ClO_4)_2$ | 64 | 66 |
| 15 | ($S_a$,*S*,*S*)-**1g** | $Fe(ClO_4)_2$ | 60 | 37 |
| 16 | ($S_a$,4*S*,4*S*′,5*S*,5*S*′)-**1h** | $Fe(ClO_4)_2$ | 72 | 51 |

[a] Reaction conditions: **2a** (0.1 mmol), 10 mol% $Fe(ClO_4)_2$, 12 mol% ligand, and 12 mol% $NaBAr_F$ in 2 mL $CHCl_3$ at 60 °C for 24 h under an $N_2$ atmosphere. [b] Isolated yields. [c] Determined by chiral HPLC analysis. $NaBAr_F$: sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate.

the oxazoline ring of the chiral TMSI-BOX ligand gave good yield and significant enantioselectivity, and the ligand ($R_a$,*S*,*S*)-**1f** gave the desired product in 86% yield and 88% ee. The opposite diastereomers of the ligands **1a–h** were also tested under the same reaction conditions (Table 1, entries 9–16) which accordingly lowered the yields and ees.

Then, a series of other iron precursors were evaluated and all gave the desired products in moderate to high yields (Table 2, entries 1–8). The reactions catalyzed by iron precursors, such as $FeCl_2{\cdot}4H_2O$, $Fe(BF_4)_2{\cdot}6H_2O$, $FeCl_3$ and $FeCl_3{\cdot}6H_2O$, resulted in the corresponding products with more than 80% ee, and $FeCl_2{\cdot}4H_2O$ proved to be the best catalyst precursor with the highest ee (92%) and the best yield (93%) (Table 2, entry 2). Besides chiral TMSI-BOX ligands and iron precursors, we also screened solvents, temperature, and additives. The reaction was carried out in a variety of solvents, including dichloromethane, 1,2-dichloroethane, tetrahydrofuran (THF), acetonitrile, 1,4-dioxane, and toluene (Table 2, entries 9–14). The oxygen-containing solvents, such as THF and 1,4-dioxane, showed low activity and only moderate enantioselectivity. Other solvents all afforded the corresponding products with high ees (87–93% ee). Chloroform still is the best solvent in overall consideration, including the yields. Furthermore, at room temperature, the activity of the reaction sharply dropped although the enantioselectivity was improved a little (Table 2, entry 15). When $NaBAr_F$ was not used as the additive, the yield and ee were all reduced remarkably (Table 2, entry 16). We suggested that $NaBAr_F$ could provide the larger and noncoordinating ion $BAr_F^-$ to give the reactive catalyst $FeCl(BAr_F)[(R_a,S,S)\text{-}\mathbf{1f}]$.[7] When the catalyst

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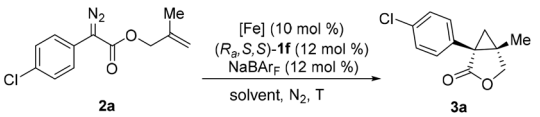
**Table 2** Optimization of reaction: iron precursors, solvents and temperature[a]

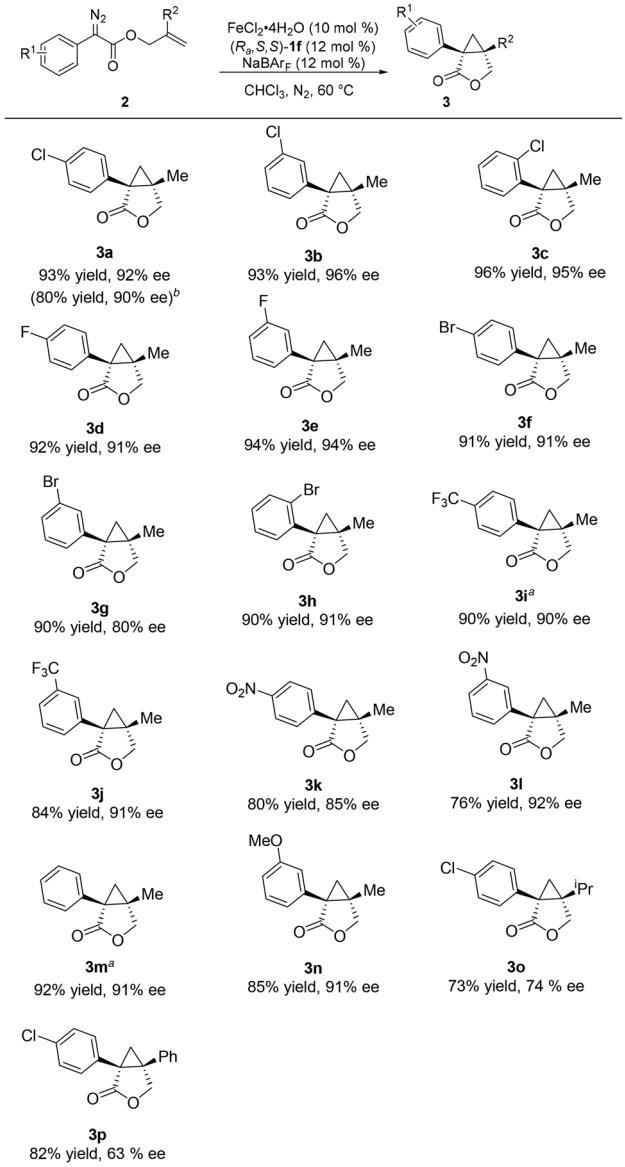



| Entry | [Fe] | Solvent | $T$ (°C) | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|---|---|
| 1 | $Fe(ClO_4)_2$ | $CHCl_3$ | 60 | 86 | 88 |
| 2 | $FeCl_2{\cdot}4H_2O$ | $CHCl_3$ | 60 | 93 | 92 |
| 3 | $Fe(OTf)_2$ | $CHCl_3$ | 60 | 68 | 72 |
| 4 | $Fe(BF_4)_2{\cdot}6H_2O$ | $CHCl_3$ | 60 | 71 | 89 |
| 5 | $Fe(acac)_2$ | $CHCl_3$ | 60 | 53 | 10 |
| 6 | $FeCl_3$ | $CHCl_3$ | 60 | 85 | 89 |
| 7 | $FeCl_3{\cdot}6H_2O$ | $CHCl_3$ | 60 | 88 | 84 |
| 8 | $Fe(OAc)_2$ | $CHCl_3$ | 60 | 45 | 75 |
| 9[d] | $FeCl_2{\cdot}4H_2O$ | $CH_2Cl_2$ | Reflux | 77 | 88 |
| 10 | $FeCl_2{\cdot}4H_2O$ | $ClCH_2CH_2Cl$ | 60 | 80 | 92 |
| 11 | $FeCl_2{\cdot}4H_2O$ | THF | 60 | 5 | 58 |
| 12 | $FeCl_2{\cdot}4H_2O$ | MeCN | 60 | 64 | 87 |
| 13 | $FeCl_2{\cdot}4H_2O$ | 1,4-Dioxane | 60 | 7 | 80 |
| 14 | $FeCl_2{\cdot}4H_2O$ | Toluene | 60 | 42 | 93 |
| 15 | $FeCl_2{\cdot}4H_2O$ | $CHCl_3$ | 25 | 33 | 93 |
| 16[d] | $FeCl_2{\cdot}4H_2O$ | $CHCl_3$ | 60 | 57 | 10 |
| 17[e] | $FeCl_2{\cdot}4H_2O$ | $CHCl_3$ | 60 | 10 | 91 |

[a] Reaction conditions: **2a** (0.1 mmol), 10 mol% [Fe], 12 mol% ($R_a$,*S*,*S*)-**1f**, and 12 mol% $NaBAr_F$ in 2 mL solvent for 24 h under an $N_2$ atmosphere. [b] Isolated yields. [c] Determined by chiral HPLC analysis. [d] No $NaBAr_F$. [e] With 5 mol% [Fe], 6 mol% ($R_a$,*S*,*S*)-**1f** and 6 mol% $NaBAr_F$.

loading was decreased from 10% to 5%, there was a significant drop in the yield of **3a**, although the enantioselectivity was not compromised (Table 2, entry 17, 10% yield, 91% ee).

With the optimized reaction conditions in hand (Table 2, entry 2), we next explored the substrate scope. The results are summarized in Scheme 3. There are various substituents on the phenyl ring of the α-diazoester substrates **2** which have a little impact on this reaction. All the tested substrates successfully participated in the asymmetric reaction to provide the corresponding products in good yields (73%–96%). Diazoesters with an electron-withdrawing group on the phenyl ring, for example, chlorine (**3a–c**), fluorine (**3d** and **3e**), bromine (**3f–h**), trifluoromethyl (**3i** and **3j**), and nitro (**3k** and **3l**), demonstrated excellent enantioselectivity. 2-(3-Chlorophenyl)-2-diazoacetate **2b** showed the highest enantioselectivity (96% ee, **2b**). α-Diazoester with no substituent group on the phenyl ring also carried out the reaction smoothly in 92% yield and 91% ee with ($R_a$,4*S*,4′*S*,5*S*,5′*S*)-**1h** instead of ($R_a$,*S*,*S*)-**1f** (**3m**). Surprisingly, the enantioselectivity of the cyclopropanation still maintained a high standard when we tested the substrates with an electron-donating group, such as 2-methoxyl on the phenyl ring (91% ee, **3n**). We also investigated the effect of the allyl moiety in the substrate, and found that the reaction proceeded in reasonable yield and good ee in which the isopropyl took the place of the methyl (73% yield, 74% ee, **3o**). We have carried out the reaction of **2a** at a 2 mmol scale, and **3a** was obtained in 80% yield and 90% ee. Moreover, we tested phenyl substituted alkenes in the asymmetric intramolecular cyclopropanation reaction, and the




**Scheme 3** Substrate scope. Reactions were performed with **2** (0.1 mmol), 10 mol% $FeCl_2{\cdot}4H_2O$, 12 mol% ($R_a$,*S*,*S*)-**1f**, and 12 mol% $NaBAr_F$ in 2 mL $CHCl_3$ at 60 °C for 24 h under an $N_2$ atmosphere. Yields are of the isolated products. Enantioselectivity was determined by chiral HPLC. [a]With ($R_a$,4*S*,4′*S*,5*S*,5′*S*)-**1h** as the catalyst. [b]On a 2.0 mmol scale, 24 hours, yield of **3a** = 80%, ee of **3a** = 90%.

product was obtained in good yield and moderate ee (82% yield, 63% ee, **3p**). The absolute configuration of the product **3** can be determined according to the literature.[6b]

## Conclusion

In summary, we have developed a series of chiral bisoxazoline (TMSI-BOX, **1**) ligands based on the tetramethyl-1,1′-spirobiindane scaffold from simple transformations of commercially available bisphenol. Meanwhile, the cationic Fe-complex of TMSI-BOX was successfully applied in asymmetric intra-

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molecular cyclopropanation reactions of α-diazoesters. Notably, excellent enantioselectivity could be achieved in most cases, and the corresponding optically active [3.1.0]bicycloalkane products with two contiguous quaternary carbon centers were obtained with ee values of up to 96%. The excellent performance of chiral TMSI-BOX ligands in sustainable iron catalysis will motivate us to further expand the new applications to other synthetically useful enantioselective reactions.

# Experimental

### General information

NMR spectra were recorded on a Bruker DPX 400 NMR spectrometer at 400 MHz for $^{1}$H NMR, 100 MHz for $^{13}$C NMR, and 376 MHz for $^{19}$F. The chemical shifts were reported in $CDCl_3$ or DMSO-$d_6$ with tetramethylsilane (TMS) as an internal standard. The following abbreviations were used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants were reported in hertz (Hz). Infrared spectra were recorded on an ATR-FTIR spectrometer. HRMS were obtained using EI ionization. Optical rotations were determined using a PerkinElmer Model 341 polarimeter at 25 °C. Enantiomeric excesses (ee) were determined by chiral high-performance liquid chromatography. HPLC analysis was performed using Chiralcel columns (Chiralcel OJ-H, AS-H).

### General procedure for synthesis of spiro diacid 5

A portion of the aldehyde **4** (2.5 mmol) was dissolved in acetone (80 mL) and stirred at room temperature. A solution of potassium permanganate (2.37 g, 15 mmol) in a mixture of water (20 mL) and acetone (80 mL) was added dropwise over a period of 10 min. The mixture was heated to 45 °C and stirred overnight. After cooling to room temperature, 4 M NaOH was added to the system until the pH was 10–11. Then, the solution was filtered and all the volatiles were removed under vacuum. The aqueous phase was washed with petroleum ether three times. Finally, the aqueous layer was acidified using 4 M HCl until the pH was around 2 and extracted with ethyl acetate. The combined organic phase was dried over anhydrous $Na_2SO_4$ and concentrated under vacuum to give the pure product **5** as a white solid without purification.

**5a**: 0.87 g, 95% yield; white solid, m.p. >320 °C; $^{1}$H NMR (400 MHz, DMSO) $\delta$ 12.12 (s, 2H), 7.48 (dd, $J$ = 7.5, 0.8 Hz, 2H), 7.34 (dd, $J$ = 7.5, 0.9 Hz, 2H), 7.22 (t, $J$ = 7.6 Hz, 2H), 2.76 (d, $J$ = 12.0 Hz, 2H), 2.22 (d, $J$ = 12.1 Hz, 2H), 1.39 (s, 6H), 1.36 (s, 6H); $^{13}$C NMR (100 MHz, DMSO) $\delta$ 167.82, 154.20, 149.02, 128.39, 126.88, 126.39, 125.23, 59.06, 56.23, 42.47, 32.36, 29.07; IR (film): $\gamma$ = 2954, 1703, 1608, 1463, 1410, 1359, 1307, 1085, 880, 715 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{23}H_{24}O_4$ 364.1675, found 364.1653.

**5b**: 0.95 g, 97% yield; white solid, m.p. 318–319 °C; $^{1}$H NMR (400 MHz, DMSO) $\delta$ 12.06 (s, 2H), 7.26 (s, 2H), 7.12 (s, 2H), 2.74 (d, $J$ = 12.1 Hz, 2H), 2.29 (s, 6H), 2.18 (d, $J$ = 12.1 Hz, 2H), 1.36 (s, 6H), 1.33 (s, 6H); $^{13}$C NMR (100 MHz, DMSO) $\delta$ 167.91, 154.38, 146.39, 135.27, 128.88, 126.68, 125.78, 58.28, 56.46, 42.28, 32.37, 29.05, 20.65; IR (film): $\gamma$ = 3432, 2952, 2865, 1701, 1610, 1576, 1461, 1408, 1361, 1310, 1260, 1085, 872, 711 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{25}H_{28}O_4$ 392.1988, found 392.1990.

### General procedure for synthesis of optically pure TMSI-BOX ligand 1

A solution of diacid **5** (5 mmol) and trimethylamine (2.78 mL, 20 mmol) in freshly distilled thionyl chloride (60 mL) was stirred at 60 °C for 3 hours, and then the volatiles were removed under vacuum to give the crude diacyl chloride. Under nitrogen, the diacylchloride was dissolved in dichloromethane (50 mL) at 0 °C, and then trimethylamine (2.78 mL, 20 mmol) and a solution of amino alcohol (20 mmol) in dichloromethane (10 mL) was injected into the solution successively. Then, the mixture was stirred overnight. The reaction solution was quenched with water and extracted with dichloromethane three times. The organic layers were mixed and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure to obtain the crude product **6** in quantitative yield for the next step without further purification. The crude amide **6** (5 mmol) was dissolved in dichloromethane (75 mL) under nitrogen, and to this was added 4-dimethylaminopyridine (DMAP, 122 mg, 1 mmol). Then the solution was cooled to 0 °C, and trimethylamine (5.7 mL, 40 mmol) and methanesulfonyl chloride (MsCl, 1.6 mL, 20 mmol) were successively added slowly. The system was stirred overnight allowing it to warm up to room temperature naturally. The reaction was quenched with water and the aqueous layer was extracted with dichloromethane three times. The combined organic layers were washed with brine, dried over anhydrous $NaSO_4$, and then concentrated under vacuum. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/15–1/4) to afford a pair of diastereomers **1** as a white solid.

($R_a$,$S$,$S$)-**1a**: 1.02 g, 82% yield (two steps); white solid, m.p. 24–26 °C; $[\alpha]_D^{20}$ = +58 ($c$ 0.09, $CH_2Cl_2$); $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.50 (dd, $J$ = 7.5, 1.3 Hz, 2H), 7.24 (dd, $J$ = 7.6, 1.4 Hz, 2H), 7.18 (t, $J$ = 7.5 Hz, 2H), 3.73 (dd, $J$ = 9.6, 8.1 Hz, 2H), 3.40 (td, $J$ = 9.4, 7.0 Hz, 2H), 3.04–2.94 (m, 2H), 2.89 (d, $J$ = 12.2 Hz, 2H), 2.30 (d, $J$ = 12.1 Hz, 2H), 1.47 (dq, $J$ = 13.6, 6.8 Hz, 2H), 1.39 (s, 6H), 1.39 (s, 6H), 0.86 (s, 3H), 0.84 (s, 3H), 0.67 (s, 3H), 0.65 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.12, 153.95, 148.25, 129.32, 126.45, 124.61, 123.98, 70.59, 68.90, 59.68, 57.11, 42.84, 32.52, 31.94, 29.64, 18.83, 17.24; IR (film): $\gamma$ = 2954, 2866, 2359, 2341, 1660, 1644, 1353, 1315, 1098, 979, 807, 752 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{33}H_{42}N_2O_2$ 498.3246, found 498.3238.

($S_a$,$S$,$S$)-**1a**: 0.97 g, 78% yield (two steps); colorless oil; $[\alpha]_D^{20}$ = −200 ($c$ 0.11, $CH_2Cl_2$); $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.69 (dd, $J$ = 7.5, 1.3 Hz, 2H), 7.29 (dd, $J$ = 7.5, 1.3 Hz, 2H), 7.21 (t, $J$ = 7.5 Hz, 2H), 3.68–3.56 (m, 4H), 2.90 (dd, $J$ = 9.3, 7.8 Hz, 2H), 2.73 (d, $J$ = 12.2 Hz, 2H), 2.33 (d, $J$ = 12.2 Hz, 2H), 1.64 (dq, $J$ = 13.4, 6.8 Hz, 2H), 1.41 (s, 6H), 1.38 (s, 6H), 0.82 (s, 3H), 0.80 (s, 3H), 0.73 (s, 3H), 0.71 (s, 3H); $^{13}$C NMR (100 MHz,

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$CDCl_3$) δ 164.13, 153.94, 148.24, 129.32, 126.46, 124.62, 123.96, 70.56, 68.89, 59.67, 57.10, 42.85, 32.52, 31.93, 29.64, 18.82, 17.23; IR (film): γ = 2955, 2868, 2359, 2341, 1651, 1465, 1357, 1316, 1101, 1071, 973, 811, 752 $cm^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{33}H_{42}N_2O_2$ 498.3246, found 498.3249.

($R_a$,*S*,*S*)-**1b**: 1.28 g, 90% yield (two steps); white solid, m.p. 53–54 °C; $[\alpha]_D^{20}$ = −24 (*c* 0.10, $CH_2Cl_2$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.29–7.13 (m, 14H), 4.66 (t, *J* = 10.1 Hz, 2H), 4.19 (dd, *J* = 10.0, 8.2 Hz, 2H), 3.09 (dd, *J* = 10.3, 8.2 Hz, 2H), 3.02 (d, *J* = 12.1 Hz, 2H), 2.35 (d, *J* = 12.1 Hz, 2H), 1.40 (s, 6H), 1.34 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 164.87, 154.57, 148.81, 141.93, 129.14, 128.32, 127.19, 127.10, 126.51, 124.59, 123.83, 74.29, 69.83, 59.52, 56.99, 43.17, 32.68, 29.05; IR (film): γ = 3062, 2950, 2863, 2359, 2341, 1659, 1634, 1454, 1357, 1274, 1098, 1071, 979, 805, 755, 698 $cm^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{39}H_{38}N_2O_2$ 566.2933, found 566.2936.

($S_a$,*S*,*S*)-**1b**: 1.25 g, 88% yield (two steps); white solid, m.p. 40–41 °C; $[\alpha]_D^{20}$ = −140 (*c* 0.10, $CH_2Cl_2$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.2, 1.7 Hz, 2H), 7.28–7.08 (m, 10H), 7.05–6.91 (m, 4H), 4.81 (dd, *J* = 10.2, 6.3 Hz, 2H), 3.70 (dd, *J* = 8.1, 6.3 Hz, 2H), 3.19 (dd, *J* = 10.2, 8.2 Hz, 2H), 2.72 (d, *J* = 12.3 Hz, 2H), 2.31 (d, *J* = 12.2 Hz, 2H), 1.37 (s, 6H), 1.25 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 164.39, 153.10, 147.25, 141.54, 128.45, 127.45, 126.18, 125.59 (d, *J* = 3.7 Hz), 124.06, 122.53, 73.19, 67.48, 58.83, 56.03, 41.82, 31.39, 28.67; IR (film): γ = 3065, 2951, 2862, 2358, 2340, 1651, 1644, 1454, 1316, 1158, 1104, 979, 752, 698 $cm^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{39}H_{38}N_2O_2$ 566.2933, found 566.2936.

($R_a$,*S*,*S*)-**1c**: 1.29 g, 87% yield (two steps); white solid, m.p. 30–31 °C; $[\alpha]_D^{20}$ = +28 (*c* 0.10, $CH_2Cl_2$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 5.9, 3.0 Hz, 2H), 7.33–7.28 (m, 4H), 7.26–7.13 (m, 6H), 7.08 (d, *J* = 7.0 Hz, 4H), 4.05–3.90 (m, 2H), 3.82–3.69 (m, 2H), 3.03 (dd, *J* = 13.7, 5.0 Hz, 2H), 2.86 (dd, *J* = 13.6, 4.9 Hz, 4H), 2.33 (d, *J* = 12.2 Hz, 2H), 2.27 (dd, *J* = 13.7, 9.7 Hz, 2H), 1.42 (s, 6H), 1.35 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 164.01, 154.41, 148.40, 138.65, 129.11, 128.84, 128.37, 126.43, 126.17, 124.55, 124.33, 71.54, 67.56, 59.56, 56.98, 43.00, 41.45, 32.54, 29.38; IR (film): γ = 3062, 3026, 2950, 2862, 2361, 2343, 1651, 1645, 1454, 1359, 1259, 1094, 977, 808, 753, 698 $cm^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{41}H_{42}N_2O_2$ 594.3246, found 594.3245.

($S_a$,*S*,*S*)-**1c**: 1.25 g, 84% yield (two steps); white solid, m.p. 49–50 °C; $[\alpha]_D^{20}$ = −105 (*c* 0.11, $CH_2Cl_2$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.26–7.14 (m, 10H), 7.08 (d, *J* = 7.0 Hz, 4H), 4.24–3.94 (m, 2H), 3.57 (dd, *J* = 8.3, 6.2 Hz, 2H), 3.04 (t, *J* = 8.8 Hz, 2H), 2.86 (dd, *J* = 13.8, 4.1 Hz, 2H), 2.79 (d, *J* = 12.2 Hz, 2H), 2.32 (d, *J* = 12.2 Hz, 2H), 2.14–2.02 (m, 2H), 1.41 (s, 6H), 1.37 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 164.17, 154.18, 148.17, 138.31, 129.15, 128.90, 128.44, 126.51, 126.26, 124.77, 124.01, 70.82, 66.74, 59.70, 56.80, 42.86, 40.84, 32.46, 29.59; IR (film): γ = 3065, 3026, 2950, 2862, 2359, 2341, 1657, 1651, 1454, 1358, 1317, 1271, 1092, 977, 808, 753, 702 $cm^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{41}H_{42}N_2O_2$ 594.3246, found 594.3251.

($R_a$,4*S*,4′*S*,5*S*,5′*S*)-**1d**: 1.35 g, 75% yield (two steps); white solid, m.p. 204–205 °C; $[\alpha]_D^{20}$ = −64 (*c* 0.09, $CH_2Cl_2$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 6.4, 2.3 Hz, 2H), 7.30–7.23 (m, 6H), 7.22–7.08 (m, 18H), 4.59 (d, *J* = 10.5 Hz, 2H), 4.12 (d, *J* = 10.5 Hz, 2H), 2.99 (d, *J* = 12.0 Hz, 2H), 2.31 (d, *J* = 12.0 Hz, 2H), 1.33 (s, 6H), 0.91 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 163.09, 153.90, 148.31, 140.00, 138.28, 128.88, 127.35, 127.09, 126.25, 126.07, 125.67, 125.39, 123.85, 122.27, 88.72, 77.96, 58.67, 55.49, 42.00, 31.81, 28.67, 27.25; IR (film): γ = 3062, 3030, 2949, 2862, 2355, 2340, 1651, 1644, 1454, 1331, 1268, 1099, 973, 808, 752, 698 $cm^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{51}H_{46}N_2O_2$ 718.3559, found 718.3553.

($S_a$,4*S*,4′*S*,5*S*,5′*S*)-**1d**: 1.33 g, 74% yield (two steps); white solid, m.p. 42–43 °C; $[\alpha]_D^{20}$ = +4 (*c* 0.10, $CH_2Cl_2$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.82–7.61 (m, 2H), 7.32–7.26 (m, 6H), 7.21 (dd, *J* = 6.5, 3.8 Hz, 6H), 7.07 (dd, *J* = 6.5, 3.0 Hz, 4H), 7.00 (d, *J* = 4.5 Hz, 4H), 6.82 (dd, *J* = 6.6, 2.9 Hz, 4H), 4.91 (d, *J* = 9.1 Hz, 2H), 4.78 (d, *J* = 9.1 Hz, 2H), 2.71 (d, *J* = 12.5 Hz, 2H), 2.29 (d, *J* = 12.5 Hz, 2H), 1.32 (s, 6H), 1.16 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 163.95, 153.68, 148.81, 141.31, 139.95, 129.36, 128.53, 128.39, 128.03, 127.16, 127.02, 126.58, 126.16, 125.20, 123.57, 87.86, 78.78, 60.83, 56.48, 42.35, 32.68, 29.43; IR (film): γ = 3062, 3030, 2951, 2860, 2358, 2337, 1651, 1644, 1454, 1316, 1267, 1091, 1074, 978, 751, 698 $cm^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{51}H_{46}N_2O_2$ 718.3559, found 718.3560.

($R_a$,*S*,*S*)-**1e**: 1.10 g, 84% yield (two steps); white solid, m.p. 67–68 °C; $[\alpha]_D^{20}$ = +93 (*c* 0.12, $CH_2Cl_2$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 2H), 7.03 (d, *J* = 0.9 Hz, 2H), 3.76 (dd, *J* = 9.6, 8.1 Hz, 2H), 3.44 (td, *J* = 9.4, 7.2 Hz, 2H), 2.95–2.88 (m, 2H), 2.84 (d, *J* = 12.2 Hz, 2H), 2.32 (s, 6H), 2.27 (d, *J* = 12.2 Hz, 2H), 1.45 (dq, *J* = 13.6, 6.8 Hz, 2H), 1.36 (s, 12H), 0.88 (s, 3H), 0.86 (s, 3H), 0.67 (s, 3H), 0.65 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 163.78, 154.29, 145.71, 135.69, 129.51, 124.78, 124.26, 72.19, 69.49, 58.58, 57.29, 42.81, 32.64, 32.50, 29.20, 20.86, 19.64, 18.07; IR (film): γ = 3453, 2955, 2868, 1652, 1463, 1383, 1356, 1265, 1172, 1100, 1075, 982, 938, 868, 803, 733 $cm^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{35}H_{46}N_2O_2$ 526.3559, found 526.3563.

($S_a$,*S*,*S*)-**1e**: 1.06 g, 81% yield (two steps); colorless oil; $[\alpha]_D^{20}$ = −173 (*c* 0.15, $CH_2Cl_2$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 2H), 7.07 (d, *J* = 0.8 Hz, 2H), 3.67 (dt, *J* = 9.7, 5.7 Hz, 2H), 3.60 (dd, *J* = 7.9, 6.2 Hz, 2H), 2.89 (dd, *J* = 9.6, 8.1 Hz, 2H), 2.67 (d, *J* = 12.2 Hz, 2H), 2.35 (s, 6H), 2.29 (d, *J* = 12.2 Hz, 2H), 1.65 (dq, *J* = 13.4, 6.7 Hz, 2H), 1.39 (s, 6H), 1.35 (s, 6H), 0.82 (s, 3H), 0.80 (s, 3H), 0.74 (s, 3H), 0.72 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 164.38, 154.11, 145.74, 135.93, 129.61, 125.43, 123.45, 70.51, 68.82, 59.08, 57.42, 42.58, 32.48, 31.92, 29.75, 20.96, 18.81, 17.19; IR (film): γ = 3447, 2955, 2868, 1652, 1462, 1383, 1357, 1269, 1177, 1096, 1074, 980, 934, 869, 803, 669 $cm^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{35}H_{46}N_2O_2$ 526.3559, found 526.3559.

($R_a$,*S*,*S*)-**1f**: 1.35 g, 91% yield (two steps); white solid, m.p. 171–172 °C; $[\alpha]_D^{20}$ = −47 (*c* 0.12, $CH_2Cl_2$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 0.7 Hz, 2H), 7.26 (dd, *J* = 8.3, 6.0 Hz, 4H), 7.23–7.13 (m, 6H), 7.01 (d, *J* = 0.8 Hz, 2H), 4.72 (t, *J* = 10.2 Hz, 2H), 4.21 (dd, *J* = 10.0, 8.2 Hz, 2H), 3.06 (dd, *J* = 10.3, 8.2 Hz, 2H), 2.99 (d, *J* = 12.1 Hz, 2H), 2.32 (d, *J* = 12.1 Hz, 2H), 2.21 (s, 6H), 1.38 (s, 6H), 1.32 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.19, 154.71, 146.21, 142.06, 135.97, 129.86, 128.27,

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127.07 (d, $J$ = 7.4 Hz), 125.16, 123.61, 77.37, 77.05, 76.74, 74.27, 69.74, 58.61, 57.33, 43.05, 32.72, 28.92, 20.88; IR (film): $\gamma$ = 2950, 2895, 1640, 1493, 1454, 1382, 1357, 1268, 1173, 1105, 981, 910, 870, 733, 700 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{41}H_{42}N_2O_2$ 594.3246, found 594.3241.

($S_a$,$S$,$S$)-**1f**: 1.29 g, 87% yield (two steps); white solid, m.p. 101–102 °C; $[\alpha]_D^{20}$ = −94 ($c$ 0.13, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.58 (s, 2H), 7.16 (dt, $J$ = 14.3, 7.8 Hz, 6H), 7.02 (d, $J$ = 8.7 Hz, 6H), 4.82 (dd, $J$ = 10.1, 6.1 Hz, 2H), 3.71 (dd, $J$ = 7.9, 6.3 Hz, 2H), 3.18 (dd, $J$ = 10.0, 8.3 Hz, 2H), 2.67 (d, $J$ = 12.3 Hz, 2H), 2.32 (s, 6H), 2.28 (d, $J$ = 12.3 Hz, 2H), 1.35 (s, 6H), 1.23 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.67, 154.33, 145.81, 142.68, 136.16, 129.84, 128.47, 127.23, 126.66, 125.87, 123.15, 74.25, 68.54, 59.21, 57.43, 42.64, 32.42, 29.78, 21.01; IR (film): $\gamma$ = 2950, 2863, 1644, 1493, 1454, 1382, 1357, 1269, 1163, 1106, 981, 910, 870, 733, 699 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{41}H_{42}N_2O_2$ 594.3246, found 594.3242.

($R_a$,$S$,$S$)-**1g**: 1.31 g, 84% yield (two steps); white solid, m.p. 57–58 °C; $[\alpha]_D^{20}$ = +51 ($c$ 0.15, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.50 (s, 2H), 7.25 (dd, $J$ = 9.0, 5.5 Hz, 4H), 7.18 (t, $J$ = 7.3 Hz, 2H), 7.08 (dd, $J$ = 10.7, 4.0 Hz, 6H), 4.04 (qd, $J$ = 9.2, 4.8 Hz, 2H), 3.76 (t, $J$ = 8.7 Hz, 2H), 3.10 (dd, $J$ = 13.6, 4.7 Hz, 2H), 2.79 (dd, $J$ = 14.2, 5.5 Hz, 4H), 2.42 (s, 6H), 2.28 (dd, $J$ = 14.3, 11.1 Hz, 4H), 1.40 (s, 6H), 1.32 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.40, 154.58, 145.95, 138.67, 135.87, 129.36, 129.11, 128.37, 126.16, 125.41, 123.81, 71.59, 67.47, 58.93, 57.33, 42.76, 41.59, 32.53, 29.50, 21.05; IR (film): $\gamma$ = 3026, 2950, 2863, 1645, 1605, 1454, 1359, 1266, 1176, 980, 910, 869, 733, 702 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{43}H_{46}N_2O_2$ 622.3559, found 622.3567.

($S_a$,$S$,$S$)-**1g**: 1.26 g, 81% yield (two steps); white solid, m.p. 43–44 °C; $[\alpha]_D^{20}$ = −24 ($c$ 0.19, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.43 (s, 2H), 7.29–7.22 (m, 6H), 7.18 (t, $J$ = 7.3 Hz, 2H), 7.09 (d, $J$ = 7.0 Hz, 4H), 7.03 (d, $J$ = 0.9 Hz, 2H), 4.28–3.96 (m, 2H), 3.57 (dd, $J$ = 8.2, 6.2 Hz, 2H), 3.02 (t, $J$ = 8.8 Hz, 2H), 2.91 (dd, $J$ = 13.8, 4.0 Hz, 2H), 2.75 (d, $J$ = 12.2 Hz, 2H), 2.33 (s, 6H), 2.29 (d, $J$ = 12.2 Hz, 2H), 2.08 (dd, $J$ = 13.7, 10.5 Hz, 2H), 1.38 (s, 6H), 1.34 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.55, 154.73, 146.11, 138.83, 136.02, 129.52, 129.27, 128.53, 126.32, 125.57, 123.96, 71.75, 67.63, 59.08, 57.48, 42.91, 41.76, 32.68, 29.66, 21.21; IR (film): $\gamma$ = 3026, 2949, 2863, 1645, 1605, 1454, 1358, 1266, 1175, 980, 910, 869, 733, 702 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{43}H_{46}N_2O_2$ 622.3559, found 622.3564.

($R_a$,4$S$,4′$S$,5$S$,5′$S$)-**1h**: 1.42 g, 76% yield (two steps); white solid, m.p. 196–197 °C; $[\alpha]_D^{20}$ = −97 ($c$ 0.10, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.69 (s, 2H), 7.30 (dd, $J$ = 10.8, 5.1 Hz, 6H), 7.24–7.08 (m, 14H), 6.95 (s, 2H), 4.64 (d, $J$ = 10.3 Hz, 2H), 4.08 (d, $J$ = 10.3 Hz, 2H), 2.97 (d, $J$ = 12.0 Hz, 2H), 2.27 (d, $J$ = 12.0 Hz, 2H), 2.18 (s, 6H), 1.30 (s, 6H), 0.91 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.51, 155.14, 146.77, 141.30, 139.62, 135.88, 130.69, 128.44, 128.15, 128.08, 127.17, 127.06, 126.56, 125.40, 123.22, 89.70, 78.87, 58.73, 56.99, 42.99, 32.90, 28.17, 20.82; IR (film): $\gamma$ = 3030, 2949, 2863, 1644, 1605, 1495, 1454, 1341, 1265, 1197, 1073, 976, 909, 871, 761, 733, 699 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{53}H_{50}N_2O_2$ 746.3872, found 746.3875.

($S_a$,4$S$,4′$S$,5$S$,5′$S$)-**1h**: 1.38 g, 74% yield (two steps); white solid, m.p. 52–53 °C; $[\alpha]_D^{20}$ = +8 ($c$ 0.12, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.51 (d, $J$ = 1.0 Hz, 2H), 7.31–7.27 (m, 6H), 7.25–7.19 (m, 6H), 7.10–6.99 (m, 4H), 6.94–6.87 (m, 4H), 6.80 (d, $J$ = 1.1 Hz, 2H), 4.90 (d, $J$ = 9.0 Hz, 2H), 4.75 (d, $J$ = 9.0 Hz, 2H), 2.64 (d, $J$ = 12.6 Hz, 2H), 2.29 (d, $J$ = 12.5 Hz, 2H), 2.15 (s, 6H), 1.31 (s, 6H), 1.17 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.45, 153.77, 146.62, 141.55, 139.94, 135.77, 130.23, 128.45, 128.33, 128.01, 127.18, 126.94, 126.11, 126.02, 123.07, 88.24, 78.67, 60.22, 57.02, 42.13, 32.73, 29.57, 21.08; IR (film): $\gamma$ = 3030, 2951, 2861, 1647, 1605, 1495, 1454, 1344, 1260, 1177, 1070, 978, 910, 869, 759, 733, 698 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{53}H_{50}N_2O_2$ 746.3872, found 746.3865.

### General procedure for Fe-catalyzed asymmetric intramolecular cyclopropanation

Under a nitrogen atmosphere, $FeCl_2{\cdot}4H_2O$ (2.0 mg, 0.01 mmol), ($R_a$,$S$,$S$)-**1f** (7.1 mg, 0.012 mmol) and $NaBAr_F$ (10.6 mg, 0.012 mmol) were dissolved in $CHCl_3$ (1.5 mL) in a dry Schlenk tube (10 mL). The mixture was stirred at room temperature for 4 hours. Then, the solution of α-diazoester **2** (0.1 mmol) in $CHCl_3$ (0.5 mL) was injected into the reaction mixture. Then, the reaction mixture was stirred at 60 °C for 24 hours. The mixture was cooled to room temperature and concentrated under reduced pressure, and then it was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1/10) to afford the product **3**.

### Characterization of compounds

**(1$S$,5$S$)-1-(4-Chlorophenyl)-5-methyl-3-oxabicyclo[3.1.0]hexan-2-one (3a).** 21 mg, 93% yield; white solid; m.p. 122–123 °C; 92% ee; HPLC analysis: Chiralpak OJ-H (hexane/i-PrOH = 80/20, 1.0 mL min$^{-1}$, 210 nm), $t_R$ (major) 18.115 min, $t_R$ (minor) 21.659 min; $[\alpha]_D^{20}$ = +49 ($c$ 0.04, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.39–7.32 (m, 2H), 7.23–7.16 (m, 2H), 4.36 (d, $J$ = 9.2 Hz, 1H), 4.19 (d, $J$ = 9.2 Hz, 1H), 1.58 (d, $J$ = 5.0 Hz, 1H), 1.41 (d, $J$ = 5.0 Hz, 1H), 1.17 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 176.91, 134.11, 131.05 (d, $J$ = 91.0 Hz), 130.60, 128.96, 73.14, 36.38, 31.38, 22.77, 15.14; IR (film): $\gamma$ = 2963, 2900, 1771, 1497, 1449, 1384, 1328, 1211, 1162, 1093, 1079, 1011, 868, 821, 734, 563 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{12}H_{11}O_2Cl$ 222.0448, found 222.0452.

**(1$S$,5$S$)-1-(3-Chlorophenyl)-5-methyl-3-oxabicyclo[3.1.0]hexan-2-one (3b).** 21 mg, 93% yield; white solid; m.p. 67–68 °C; 96% ee; HPLC analysis: Chiralpak AS-H (hexane/i-PrOH = 80/20, 1.0 mL min$^{-1}$, 210 nm), $t_R$ (major) 12.981 min, $t_R$ (minor) 19.715 min; $[\alpha]_D^{20}$ = +75 ($c$ 0.07, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.24 (dd, $J$ = 3.9, 1.3 Hz, 2H), 7.19 (dd, $J$ = 3.3, 1.8 Hz, 1H), 7.13–7.03 (m, 1H), 4.29 (d, $J$ = 9.2 Hz, 1H), 4.12 (d, $J$ = 9.2 Hz, 1H), 1.54 (d, $J$ = 5.0 Hz, 1H), 1.35 (d, $J$ = 5.0 Hz, 1H), 1.11 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 175.65, 133.51, 133.04, 129.22, 128.94, 127.38, 127.30, 72.08, 35.55, 30.51, 21.65, 14.09; IR (film): $\gamma$ = 2964, 2900, 1770, 1599, 1569, 1479, 1448, 1383, 1328, 1261, 1163, 1077, 1019, 808, 754, 692 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{12}H_{11}O_2Cl$ 222.0448, found 222.0450.

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**(1*R*,5*S*)-1-(2-Chlorophenyl)-5-methyl-3-oxabicyclo[3.1.0]hexan-2-one (3c).** 22 mg, 96% yield; white solid; m.p. 120–121 °C; 95% ee; HPLC analysis: Chiralpak AS-H (hexane/i-PrOH = 80/20, 1.0 mL min$^{-1}$, 210 nm), $t_R$ (major) 13.977 min, $t_R$ (minor) 16.589 min; $[\alpha]_D^{20}$ = +3 (*c* 0.05, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.42–7.31 (m, 1H), 7.28–7.18 (m, 3H), 4.31 (dd, *J* = 27.4, 9.0 Hz, 2H), 1.45 (d, *J* = 5.0 Hz, 1H), 1.36 (d, *J* = 5.0 Hz, 1H), 1.08 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 174.87, 135.18, 131.53, 130.14, 128.84, 128.51, 126.19, 72.09, 35.74, 29.81, 20.38, 13.55; IR (film): $\gamma$ = 2965, 2898, 1770, 1483, 1442, 1383, 1327, 1165, 1130, 1068, 1015, 808, 757, 710, 657 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{12}H_{11}O_2Cl$ 222.0448, found 222.0450.

**(1*S*,5*S*)-1-(4-Fluorophenyl)-5-methyl-3-oxabicyclo[3.1.0]hexan-2-one (3d).** 19 mg, 92% yield; white solid; m.p. 110–111 °C; 91% ee; HPLC analysis: Chiralpak AS-H (hexane/i-PrOH = 80/20, 1.0 mL min$^{-1}$, 210 nm), $t_R$ (major) 11.978 min, $t_R$ (minor) 15.280 min; $[\alpha]_D^{20}$ = +63 (*c* 0.05, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.24 (ddd, *J* = 7.5, 6.7, 4.1 Hz, 2H), 7.14–7.00 (m, 2H), 4.36 (d, *J* = 9.2 Hz, 1H), 4.19 (d, *J* = 9.2 Hz, 1H), 1.57 (d, *J* = 4.9 Hz, 1H), 1.41 (d, *J* = 4.9 Hz, 1H), 1.17 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 177.19, 162.53 (d, *J* = 247.2 Hz), 131.95 (d, *J* = 8.2 Hz), 127.90 (d, *J* = 3.4 Hz), 115.76 (d, *J* = 21.5 Hz), 73.16, 36.29, 31.09, 22.93, 15.19; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ −113.87; IR (film): $\gamma$ = 2968, 2901, 1766, 1516, 1452, 1384, 1329, 1224, 1164, 1079, 1029, 1012, 869, 828, 812, 571 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{12}H_{11}O_2F$ 206.0743, found 206.0741.

**(1*S*,5*S*)-1-(3-Fluorophenyl)-5-methyl-3-oxabicyclo[3.1.0]hexan-2-one (3e).** 19 mg, 94% yield; white solid; m.p. 57–58 °C; 94% ee; HPLC analysis: Chiralpak AS-H (hexane/i-PrOH = 80/20, 1.0 mL min$^{-1}$, 210 nm), $t_R$ (major) 11.952 min, $t_R$ (minor) 17.355 min; $[\alpha]_D^{20}$ = +58 (*c* 0.04, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.35 (td, *J* = 8.0, 6.1 Hz, 1H), 7.10–6.90 (m, 3H), 4.37 (d, *J* = 9.2 Hz, 1H), 4.19 (d, *J* = 9.2 Hz, 1H), 1.61 (d, *J* = 5.0 Hz, 1H), 1.42 (d, *J* = 5.0 Hz, 1H), 1.18 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 176.75, 162.80 (d, *J* = 246.9 Hz), 134.47 (d, *J* = 8.0 Hz), 130.27 (d, *J* = 8.3 Hz), 125.85 (d, *J* = 2.8 Hz), 117.14 (d, *J* = 22.1 Hz), 115.13 (d, *J* = 21.0 Hz), 73.12, 36.62 (d, *J* = 1.8 Hz), 31.64, 22.76, 15.07; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ −112.59; IR (film): $\gamma$ = 2967, 2902, 1771, 1616, 1588, 1492, 1444, 1383, 1329, 1205, 1088, 1018, 829, 784, 693 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{12}H_{11}O_2F$ 206.0743, found 206.0746.

**(1*S*,5*S*)-1-(4-Bromophenyl)-5-methyl-3-oxabicyclo[3.1.0]hexan-2-one (3f).** 24 mg, 91% yield; white solid; m.p. 109–110 °C; 91% ee; HPLC analysis: Chiralpak AS-H (hexane/i-PrOH = 80/20, 1.0 mL min$^{-1}$, 210 nm), $t_R$ (major) 12.398 min, $t_R$ (minor) 15.673 min; $[\alpha]_D^{20}$ = +61 (*c* 0.04, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.63–7.45 (m, 2H), 7.20–7.00 (m, 2H), 4.36 (d, *J* = 9.2 Hz, 1H), 4.19 (d, *J* = 9.2 Hz, 1H), 1.58 (d, *J* = 5.0 Hz, 1H), 1.41 (d, *J* = 5.0 Hz, 1H), 1.17 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 176.81, 131.91, 131.82, 131.13, 122.30, 73.14, 36.46, 31.40, 22.73, 15.14; IR (film): $\gamma$ = 2964, 2899, 1770, 1492, 1448, 1382, 1328, 1210, 1162, 1072, 1008, 867, 818, 717, 561 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{12}H_{11}O_2Br$ 265.9942, found 265.9939.

**(1*S*,5*S*)-1-(3-Bromophenyl)-5-methyl-3-oxabicyclo[3.1.0]hexan-2-one (3g).** 24 mg, 90% yield; white solid; m.p. 61–62 °C; 80% ee; HPLC analysis: Chiralpak AS-H (hexane/i-PrOH = 80/20, 1.0 mL min$^{-1}$, 210 nm), $t_R$ (major) 13.796 min, $t_R$ (minor) 20.390 min; $[\alpha]_D^{20}$ = +69 (*c* 0.01, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.56–7.35 (m, 2H), 7.32–7.14 (m, 2H), 4.36 (d, *J* = 9.2 Hz, 1H), 4.19 (d, *J* = 9.2 Hz, 1H), 1.61 (d, *J* = 5.0 Hz, 1H), 1.41 (d, *J* = 5.0 Hz, 1H), 1.19 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 176.68, 134.37, 133.16, 131.26, 130.25, 128.91, 122.71, 73.13, 36.56, 31.57, 22.71, 15.14; IR (film): $\gamma$ = 2965, 2899, 1770, 1596, 1564, 1478, 1449, 1382, 1328, 1163, 1074, 1016, 781, 732, 692 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{12}H_{11}O_2Br$ 265.9942, found 265.9938.

**(1*R*,5*S*)-1-(2-Bromophenyl)-5-methyl-3-oxabicyclo[3.1.0]hexan-2-one (3h).** 24 mg, 90% yield; white solid; m.p. 86–87 °C; 91% ee; HPLC analysis: Chiralpak AS-H (hexane/i-PrOH = 90/10, 0.8 mL min$^{-1}$, 210 nm), $t_R$ (major) 39.312 min, $t_R$ (minor) 42.360 min; $[\alpha]_D^{20}$ = −2 (*c* 0.05, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.62 (d, *J* = 7.9 Hz, 1H), 7.41–7.16 (m, 3H), 4.46–4.35 (m, 2H), 1.51 (d, *J* = 5.0 Hz, 1H), 1.44 (d, *J* = 5.0 Hz, 1H), 1.18 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 175.71, 133.12, 132.93, 132.87, 130.09, 127.81, 126.67, 73.13, 38.70, 31.00, 21.47, 14.59; IR (film): $\gamma$ = 2959, 2926, 1770, 1471, 1436, 1382, 1325, 1275, 1210, 1159, 1125, 1079, 1013, 754, 727, 648 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{12}H_{11}O_2Br$ 265.9942, found 265.9945.

**(1*S*,5*S*)-5-Methyl-1-(4-(trifluoromethyl)phenyl)-3-oxabicyclo[3.1.0]hexan-2-one (3i).** 23 mg, 90% yield; white solid; m.p. 58–59 °C; 90% ee; HPLC analysis: Chiralpak AS-H (hexane/i-PrOH = 80/20, 1.0 mL min$^{-1}$, 210 nm), $t_R$ (major) 7.970 min, $t_R$ (minor) 9.760 min; $[\alpha]_D^{20}$ = +26 (*c* 0.02, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.64 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 4.39 (d, *J* = 9.2 Hz, 1H), 4.22 (d, *J* = 9.2 Hz, 1H), 1.67 (d, *J* = 5.1 Hz, 1H), 1.47 (d, *J* = 5.1 Hz, 1H), 1.19 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 176.56, 136.16, 130.48, 130.22 (d, *J* = 32.7 Hz), 125.69 (q, *J* = 3.8 Hz), 123.99 (d, *J* = 271.8 Hz), 73.13, 36.68, 31.88, 22.72, 15.08; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ −62.67; IR (film): $\gamma$ = 2968, 2904, 1770, 1620, 1452, 1411, 1385, 1327, 1164, 1123, 1068, 1015, 873, 829, 610 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{13}H_{11}O_2F_3$256.0711, found 256.0711.

**(1*S*,5*S*)-5-Methyl-1-(3-(trifluoromethyl)phenyl)-3-oxabicyclo[3.1.0]hexan-2-one (3j).** 21 mg, 84% yield; white solid; m.p. 55–56 °C; 91% ee; HPLC analysis: Chiralpak AS-H (hexane/i-PrOH = 80/20, 1.0 mL min$^{-1}$, 210 nm), $t_R$ (major) 8.111 min, $t_R$ (minor) 10.910 min; $[\alpha]_D^{20}$ = +66 (*c* 0.02, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.61 (d, *J* = 7.7 Hz, 1H), 7.57–7.41 (m, 3H), 4.39 (d, *J* = 9.2 Hz, 1H), 4.23 (d, *J* = 9.2 Hz, 1H), 1.66 (d, *J* = 4.9 Hz, 1H), 1.47 (d, *J* = 5.1 Hz, 1H), 1.19 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 176.58, 133.72, 133.19, 131.15 (d, *J* = 32.6 Hz), 129.30, 126.77 (q, *J* = 3.7 Hz), 125.00 (q, *J* = 3.8 Hz), 123.89 (d, *J* = 271 Hz), 73.13, 36.70, 31.62, 22.75, 15.12; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ −62.61; IR (film): $\gamma$ = 2969, 2904, 1770, 1452, 1385, 1366, 1325, 1254, 1162, 1127, 1075, 1018, 961, 813, 797, 703 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{13}H_{11}O_2F_3$ 256.0711, found 256.0712.

**(1*S*,5*S*)-5-Methyl-1-(4-nitrophenyl)-3-oxabicyclo[3.1.0]hexan-2-one (3k).** 19 mg, 80% yield; yellow solid; m.p. 128–129 °C; 85% ee; HPLC analysis: Chiralpak OJ-H (hexane/i-PrOH = 70/30, 1.0 mL min$^{-1}$, 210 nm), $t_R$ (major) 35.710 min, $t_R$

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(minor) 93.335 min; $[\alpha]_D^{20}$ = +3 (*c* 0.01, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.25–8.11 (m, 2H), 7.44–7.30 (m, 2H), 4.34 (d, *J* = 9.3 Hz, 1H), 4.16 (d, *J* = 9.3 Hz, 1H), 1.66 (d, *J* = 5.2 Hz, 1H), 1.47 (d, *J* = 5.2 Hz, 1H), 1.13 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.95, 147.54, 139.60, 130.90, 123.86, 73.07, 36.67, 32.70, 23.03, 14.99; IR (film): γ = 2965, 2895, 1770, 1603, 1520, 1450, 1385, 1350, 1164, 1081, 1031, 1012, 852, 751, 695 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{12}H_{11}NO_4$ 233.0688, found 233.0685.

**(1*S*,5*S*)-5-Methyl-1-(3-nitrophenyl)-3-oxabicyclo[3.1.0]hexan-2-one (3l).** 18 mg, 76% yield; white solid; m.p. 133–134 °C; 92% ee; HPLC analysis: Chiralpak OJ-H (hexane/i-PrOH = 70/30, 1.0 mL min$^{-1}$, 210 nm), $t_R$ (major) 26.890 min, $t_R$ (minor) 33.628 min; $[\alpha]_D^{20}$ = +55 (*c* 0.01, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.22 (ddd, *J* = 8.0, 2.1, 1.2 Hz, 1H), 8.14 (t, *J* = 1.9 Hz, 1H), 7.79–7.47 (m, 2H), 4.42 (d, *J* = 9.3 Hz, 1H), 4.26 (d, *J* = 9.3 Hz, 1H), 1.72 (d, *J* = 5.2 Hz, 1H), 1.53 (d, *J* = 5.2 Hz, 1H), 1.22 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.17, 148.41, 136.46, 134.38, 129.83, 124.90, 123.15, 73.13, 36.55, 32.08, 22.91, 15.08; IR (film): γ = 2966, 2902, 1770, 1531, 1451, 1384, 1351, 1164, 1090, 1035, 1016, 810, 739, 686 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{12}H_{11}NO_4$ 233.0688, found 233.0684.

**(1*S*,5*S*)-5-Methyl-1-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (3m).** 17 mg, 92% yield; white solid; m.p. 58–59 °C; 91% ee; HPLC analysis: Chiralpak AS-H (hexane/i-PrOH = 80/20, 1.0 mL min$^{-1}$, 210 nm), $t_R$ (major) 12.708 min, $t_R$ (minor) 19.252 min; $[\alpha]_D^{20}$ = −5 (*c* 0.03, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42–7.30 (m, 3H), 7.29–7.23 (m, 2H), 4.36 (d, *J* = 9.1 Hz, 1H), 4.19 (d, *J* = 9.1 Hz, 1H), 1.62 (d, *J* = 4.9 Hz, 1H), 1.39 (d, *J* = 4.9 Hz, 1H), 1.16 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 177.40, 131.99, 130.18, 128.72, 128.04, 73.20, 36.92, 31.21, 22.62, 15.19; IR (film): γ = 2963, 2929, 2895, 1767, 1503, 1447, 1383, 1328, 1210, 1162, 1086, 1013, 808, 755, 699, 669 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0833.

**(1*S*,5*S*)-1-(3-Methoxyphenyl)-5-methyl-3-oxabicyclo[3.1.0]hexan-2-one (3n).** 18 mg, 85% yield; colorless oil; 91% ee; HPLC analysis: Chiralpak AS-H (hexane/i-PrOH = 90/10, 0.8 mL min$^{-1}$, 210 nm), $t_R$ (major) 44.522 min, $t_R$ (minor) 59.034 min; $[\alpha]_D^{20}$ = +93 (*c* 0.03, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 12.5, 4.6 Hz, 1H), 6.91–6.76 (m, 3H), 4.36 (d, *J* = 9.1 Hz, 1H), 4.19 (d, *J* = 9.1 Hz, 1H), 3.81 (s, 3H), 1.61 (d, *J* = 4.9 Hz, 1H), 1.38 (d, *J* = 4.9 Hz, 1H), 1.18 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 177.46, 159.73, 133.40, 129.74, 122.48, 116.08, 113.43, 73.27, 55.29, 36.98, 31.33, 22.73, 15.16; IR (film): γ = 2963, 2895, 1766, 1603, 1583, 1493, 1452, 1383, 1328, 1288, 1226, 1155, 1079, 1018, 818, 781, 697 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0942.

**(1*S*,5*R*)-1-(4-Chlorophenyl)-5-isopropyl-3-oxabicyclo[3.1.0]hexan-2-one (3o).** 18 mg, 73% yield; white solid; m.p. 104–105 °C; 75% ee; HPLC analysis: Chiralpak AS-H (hexane/i-PrOH = 80/20, 1.0 mL min$^{-1}$, 210 nm), $t_R$ (major) 10.823 min, $t_R$ (minor) 13.117 min; $[\alpha]_D^{20}$ = +20 (*c* 0.03, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39–7.31 (m, 2H), 7.25–7.18 (m, 2H), 4.40 (d, *J* = 9.2 Hz, 1H), 4.24 (d, *J* = 9.2 Hz, 1H), 1.74 (d, *J* = 5.1 Hz, 1H), 1.35 (d, *J* = 5.1 Hz, 1H), 1.29 (dd, *J* = 13.9, 7.0 Hz, 1H), 1.00 (d, *J* = 7.1 Hz, 3H), 0.86 (d, *J* = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 177.19, 133.88, 131.28, 130.39, 128.76, 68.63, 41.44, 37.26, 28.66, 21.44, 20.33, 18.32; IR (film): γ = 2965, 2905, 1770, 1498, 1466, 1370, 1345, 1242, 1142, 1094, 1083, 1031, 1010, 821, 737 cm$^{-1}$; HRMS (EI, GC-TOF): calcd for $C_{14}H_{15}O_2Cl$ 250.0761, found 250.0764.

**(1*S*,5*R*)-1-(4-Chlorophenyl)-5-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (3p).** 23 mg, 82% yield; white solid; m.p. 140–141 °C; 63% ee; HPLC analysis: Chiralpak AS-H (hexane/i-PrOH = 80/20, 1.0 mL min$^{-1}$, 210 nm), $t_R$ (major) 13.977 min, $t_R$ (minor) 17.221 min; $[\alpha]_D^{20}$ = +78 (*c* 0.05, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.30–7.23 (m, 3H), 7.18 (t, *J* = 6.4 Hz, 4H), 7.09 (d, *J* = 8.5 Hz, 2H), 4.57 (dd, *J* = 21.8, 9.5 Hz, 2H), 2.33 (d, *J* = 5.3 Hz, 1H), 1.75 (d, *J* = 5.3 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.82, 133.71, 133.60, 130.65, 129.93, 129.31, 128.90, 128.65, 128.37, 73.47, 41.28, 38.06, 21.56; IR (film): γ = 2903, 2360, 1766, 1497, 1349, 1091, 1021, 823, 699 cm$^{-1}$; HRMS (ESI): calcd for $C_{17}H_{13}O_2ClNa$ ([M + Na]$^+$) 307.0502, found 307.0495.

**For Fe-catalyzed asymmetric intramolecular cyclopropanation on a scale of 2.0 mmol.** Under a nitrogen atmosphere, $FeCl_2{\cdot}4H_2O$ (40.0 mg, 0.2 mmol), (*R*$_a$,*S*,*S*)-**1f** (142 mg, 0.24 mmol) and $NaBAr_F$ (212 mg, 0.24 mmol) were dissolved in $CHCl_3$ (30 mL) in a dry three-neck flask (100 mL). The mixture was stirred at room temperature for 4 hours. Then, the solution of α-diazoester **2a** (2 mmol) in $CHCl_3$ (10 mL) was injected into the reaction mixture. Then, the reaction mixture was stirred at 60 °C for 24 hours. The mixture was cooled to room temperature and concentrated under reduced pressure, and then it was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1/10) to afford the product **3a** (355 mg) in 80% yield with 90% ee.

## Conflicts of interest

There are no conflicts to declare.

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