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Iridium-catalyzed asymmetric ring-opening of azabicyclic alkenes with alcohols†

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A novel asymmetric ring-opening reaction of *N*-substituted azabenzonorbornadienes with a wide variety of substituted benzyl alcohols and the addition reaction of *N*-substituted azabenzonorbornadienes with thiols are reported, affording the corresponding 1,2-*trans*-alkoxyamino products in moderate yields with excellent enantioselectivities (up to 94% ee) and the corresponding thiol addition products in high yields with lower enantiomeric excesses (ee) in the presence of iridium catalyst, respectively. The effects of ligands, catalyst loading, solvents and additives, and temperature were also investigated. The *anti*-configuration of the product **3c** was confirmed by X-ray crystal structure analysis. A possible mechanism for the present catalytic reaction is proposed.

Introduction

It has been an attractive topic in organic synthesis to develop carbon–carbon bond and carbon–heteroatom bonds *via* transition metal asymmetric catalysis. These synthetic methods are important due to their potential to offer practical methods for the synthesis of compounds with biological interest.[1] For example, transition-metal-catalyzed asymmetric ring-opening reactions of oxa- and azabicyclic alkenes have been extensively investigated.[2] Many parameters had been investigated to optimize the ring-opening reactions, including the use of a variety of metal catalysts, such as Pd,[3] Rh,[4] Cu,[5] Ni,[6] Fe,[7] Ru[8] *etc.*, and nucleophiles, such as dialkylzincs,[3d–f,4b,c,5a,9] organoboronic acids,[3b,c,10] alkynyl compounds,[4d,5,11] organozinc halides,[12] amines,[4b,c,f,13] Grignard reagents,[5,7,14] carboxylates,[15] sulfur,[16] phenols,[4a] methanol[4b] and others.[5f,17] In recent years, our group has demonstrated that iridium-catalyzed asymmetric ring-opening of strained bicyclic alkenes is a highly efficient and enantioselective process for generating a functionalized dihydronaphthalene core. Chiral iridium(I) complexes catalyzed the ring-opening reaction of oxa- and azabicyclic alkenes with amines in high yield and enantioselectivity.[18] Very recently, we have reported an analogous asymmetric ring-opening reaction of oxa- and azabicyclic alkenes with oxygen-based nucleophiles such as phenols.[19] However, limited success has been achieved using methanol as nucleophile,[4b] probably due to its poor nucleophilicity.[20,21] To the best of our knowledge, the use of substituted benzyl alcohols as the nucleophile in asymmetric ring-opening has not been demonstrated, and the stereochemical outcome (*trans*/*cis*) of the alkoxyamino ring-opened product is unknown. Herein we report the full details of the catalytic asymmetric ring-opening of *N*-substituted azabenzonorbornadienes **1a–1d** with a wide variety of substituted benzyl alcohols in the presence of an iridium catalyst. The reactions afford the corresponding 1,2-*trans*-alkoxyamino products in moderate yields with excellent enantioselectivities (up to 94% ee). We subsequently investigated the effects of ligand, catalyst loading, the effects of solvents and additives, and reaction temperature on the yield and enantioselectivity. Furthermore, we investigated the ring-opening of *N*-substituted azabenzonorbornadienes **1a–1d** with thiols. However, we did not obtain any desired ring-opened product, while the corresponding thiol addition products were obtained in high yields with lower enantiomeric excesses (ee), demonstrating the impact of nucleophiles on the reaction types.

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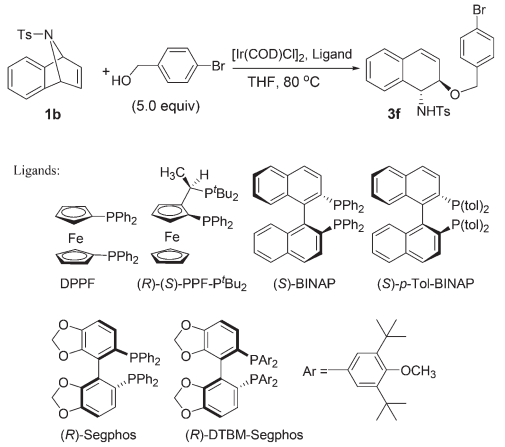
Results and discussion

The substrates **1a–1d** were readily prepared by the Diels–Alder reactions of benzynes with *N*-substituted pyrroles according to the literature procedures.[18] In order to explore the ring opening reactions, an achiral ligand 1,1′-bis(diphenylphosphino)ferrocene (DPPF) was first chosen to validate the

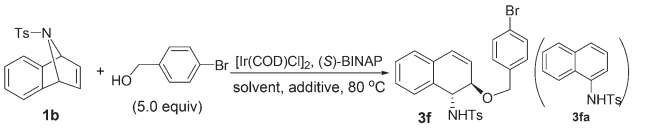
Table 1 Effect of ligand on the iridium-catalyzed asymmetric ring-opening of *N*-Ts-azabenzonorbornadiene **1b** with 4-bromophenylmethanol[a]



Entry	$[Ir(COD)Cl]_2$ [mol%]	Ligand [mol%]	Time [h]	Yield[b] [%]	ee[c] [%]
1	2.5	5.0 DPPF	13	52	0
2	2.5	5.0 (*R*,*S*)-PPFP^{t}Bu$_2$	13	Trace	
3	1.0	2.0 (*S*)-BINAP	12	27	10
4	1.5	3.0 (*S*)-BINAP	12	45	84
5	2.5	5.0 (*S*)-BINAP	12	55	92
6	3.5	7.0 (*S*)-BINAP	12	34	52
7	2.5	5.0 (*S*)-*p*-Tol-BINAP	13	11	16
8	2.5	5.0 (*R*)-Segphos	13	34	1
9	2.5	5.0 (*R*)-DTBM-Segphos	13	32	4
10[d]	2.5	5.0 (*S*)-BINAP	24	—	—

[a] The reaction was carried out with **1b** (0.2 mmol) and 5.0 equiv. of 4-bromophenylmethanol (1.0 mmol) in THF (2.0 mL) at 80 °C (oil bath temperature). [b] Isolated yield after silica gel column chromatography. [c] Determined by HPLC with a Chiralcel OD-H column. [d] The reaction was carried out at room temperature.

Table 2 The optimization of solvents and additives for the iridium-catalyzed asymmetric ring-opening of *N*-Ts-azabenzonorbornadiene **1b** with 4-bromophenylmethanol[a]



Entry	Solvent	Additive[b]	Time [h]	Yield[c] [%]	ee[d] [%]
1	THF		13	55	92
2	THP		13	25	79
3	Toluene		15	27	80
4	DCE		15	42	91
5	Dioxane		9	22	8
6	CH_2Cl_2		9	37	92
7	CH_3CN		40	nr	
8	THF	NaH	24	nr	
9	THF	DMAP[f]	24	nr	
10	THF	NH_4Br	18	Trace	
11	THF	NH_4I	36	Trace	
12	THF	Bu_4NI	15	56	5
13[e]	THF	AgOTf/Bu_4NI	12	38	19

[a] The reaction was carried out with **1b** (0.2 mmol) and 5.0 equiv. of 4-bromophenylmethanol (1.0 mmol) in THF (2.0 mL) at 80 °C (oil bath temperature) in the presence of $[Ir(COD)Cl]_2$ (2.5 mol%) and (*S*)-BINAP (5.0 mol%). [b] 1.0 equiv. of additive. [c] Isolated yield after silica gel column chromatography (0.2 mmol). [d] Determined by HPLC with a Chiralcel OD-H column. [e] AgOTf (10.0 mol%) and Bu_4NI (20.0 mol%) as additives. [f] 4-Dimethylaminopyridine (DMAP).

catalytic activity of the iridium complex in the ring-opening reactions of *N*-Ts-azabenzonorbornadiene **1b** with 4-bromophenylmethanol. The results were summarized in Table 1. The use of ferrocenyl bisphosphine ligand, (*R*,*S*)-PPF-P^{t}Bu$_2$, was thus attempted. Unfortunately, we did not obtain any desired ring-opening product **3f** (Table 1, entry 2). However, the use of (*S*)-BINAP[18a,c,e,22] as ligand was observed to give moderate yield and reasonable enantioselectivity (84% ee) (Table 1, entry 4). Encouraged by this result, we carried out an asymmetric version of the same reaction using different kinds of chiral ligands commercially available. Among the chiral ligands tested, (*S*)-BINAP was observed to give the best yield and excellent enantioselectivity (up to 92% ee) (Table 1, entry 5). Other chiral ligands, such as (*S*)-*p*-Tol-BINAP, (*R*)-Segphos, (*R*,*S*)-PPFP^{t}Bu$_2$, and (*R*)-DTBM-Segphos, gave unsatisfactory results (Table 1, entries 7–9). Therefore, (*S*)-BINAP was chosen as the best ligand for further optimization of reaction conditions. On the other hand, when the amount of catalyst loading was lowered to 1.0 mol% of $[Ir(COD)Cl]_2$ and 2.0 mol% of (*S*)-BINAP, the ring-opening products were obtained in a 27% yield only with low ee (10%) (Table 1, entry 3). Better results were observed when the molar ratio of $[Ir(cod)Cl]_2$ to (*S*)-BINAP was 2.5 : 5 (Table 1, entry 5). However, further increase of the catalyst loading improved neither the yield nor the enantioselectivity (Table 1, entries 6–10). By examining the effect of temperature, we observed that the enantioselectivity changed a lot at different temperatures. Unexpectedly, room temperature resulted in no reaction even after a prolonged reaction time (Table 1, entry 10); when the reaction was carried out at 80 °C (oil bath temperature), the product **3f** was obtained in 55% yield with 92% ee. Therefore, the optimum reaction temperature was identified as 80 °C in THF giving the desired product **3f** in moderate yield (55%) with excellent enantioselectivity (92% ee) in the presence of 2.5 mol% of $[Ir(COD)Cl]_2$ and 5.0 mol% of (*S*)-BINAP (Table 1, entry 5).

We next investigated the effects of the solvents and additives on the reactivity and enantioselectivity (Table 2). Some common solvents were initially tested without additives (Table 2, entries 1–7). It was observed that the reaction in tetrahydrofuran (THF) afforded the corresponding ring-opening product **3f** in moderate yield with high ee value (92% ee) (Table 2, entry 1). Other solvents, such as toluene, 1,2-dichloroethane (DCE), tetrahydropyran (THP), and CH_2Cl_2 offered high ee values with lower yields (Table 2, entries 2–4 and 6). The same reaction in 1,4-dioxane afforded the expected product **3f** in low yield with low ee (Table 2, entry 5). Therefore, the solvent effect study showed that THF was the best one among the solvents tested. It was also particularly noteworthy that a byproduct of 4-methyl-*N*-naphthalen-1-yl-benzenesulfonamide **3fa** was obtained in a 50% yield in THP.

It was formed by ring-opening and dehydroalkoxylation from substrate **1b**.

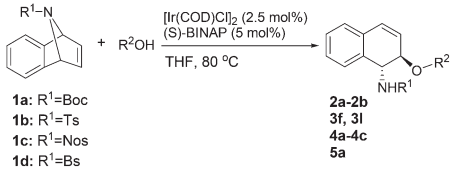
Additives such as NaH and 4-dimethylaminopyridine (DMAP) did not improve the yield and ee value (Table 2, entries 8 and 9), presumably due to the poisoning of catalysts by these additives. Lautens and co-workers[23] previously reported that the halide ions played an important role in Rh transition-metal catalyzed ring-opening and improved the reactivity and enantioselectivity of the desired products. Inspired by their work, we further investigated ammonium halides (NH_4Br, NH_4I and Bu_4NI) as additives[13a,16] (Table 2, entries 10–12). The results indicated that the halide ions and ammonium ions were not playing any significant role or might not be necessary. In some cases, the reaction obtained better results without the addition of halide ions and ammonium ions. We next investigated the impact of silver(I) salts on the reaction. It was observed that silver salts, such as silver triflate (AgOTf), might facilitate the reaction,[4f,9c,24] but the use of AgOTf and Bu_4NI as additives did not improve the yield and ee value (Table 2, entry 13). On the basis of these studies, the optimal reaction conditions are 2.5 mol% of $[Ir(COD)Cl]_2$ and 5 mol% of (*S*)-BINAP in THF at 80 °C.

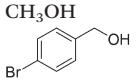
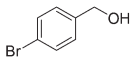
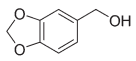
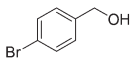
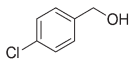
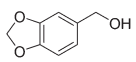
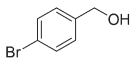
With the optimized reaction conditions in hand (2.5 mol% of $[Ir(COD)Cl]_2$ and 5 mol% of (*S*)-BINAP in THF at 80 °C), we attempted to expand the scope of this reaction to other *N*-protected (R^1) azabenzonorbornadienes. All reactions of *N*-protected (R^1) series (**1a–1d**) with alcohols proceeded smoothly to give the expected products in moderate yields. These results are summarized in Table 3, from which it can be seen that the enantioselectivities of these reactions were largely dependent on the *N*-protected (R^1) groups. For example, the reaction of *N*-Boc-azabenzonorbornadiene **1a** with 4-bromophenylmethanol afforded the corresponding ring-opened product **2b** in 32% yield with 75% ee (Table 3, entry 2). Excellent enantiomeric excesses of up to 92% were observed for *N*-Ts-azabenzonorbornadiene **1b** (Table 3, entry 3). However, *N*-Nos-azabenzonorbornadiene **1c** and *N*-Bs-azabenzonorbornadiene **1d** showed good reactivity with very poor enantioselectivities (Table 3, entries 5–8). The experimental results indicated that the *N*-protected group on the nitrogen atom of the azabicyclic alkenes has a remarkable impact on both the reactivity and enantioselectivity. It is noteworthy that *N*-Ts-azabenzonorbornadiene **1b** not only showed a remarkable reactivity, but also gave excellent enantioselectivities (Table 3, entries 3 and 4).

Having the optimized reaction conditions in hand, we then examined the ring-opening with different alcohols as the nucleophile. The results are summarized in Table 4. It was found that the structure of the alcohol had a significant impact on the yield and enantioselectivity for the catalytic ring-opening reaction. The results demonstrated that aliphatic alcohols offered high yields with poor enantioselectivities (Table 4, entries 1–4), while substituted benzyl alcohols gave moderate yields with satisfactory enantioselectivities (Table 4, entries 6–10 and 12). For example, the reaction of *N*-Ts-azabenzonorbornadiene **1b** with 4-bromophenylmethanol offered a high enantioselectivity (92% ee) (Table 4, entry 6). Despite the variety of steric and electronic properties of the aromatic rings of the alcohols, the enantioselectivities of the reactions were found to be more than 70% ee with moderate yields (Table 4, entries 5–9 and 12). The reaction of **1b** with *o*-bromophenylmethanol resulted in product **3k** with very poor enantioselectivity, presumably due to the steric hindrance of the *ortho*-bromo group (Table 4, entry 11). Due to the steric bulkiness of triphenylmethanol as nucleophile, the substrate **1b** did not afford any desired ring-opened product **3m** (Table 4, entry 13).

The impact of substituents on the aromatic ring on the asymmetric ring-opening reactions of **1b** were also investigated. Nucleophiles bearing electron-rich groups on the phenyl ring such as *p*-methoxyphenylmethanol offered moderate yield with excellent enantioselectivity (up to 82% ee) (Table 4, entry 9). When 4-chlorophenylmethanol bearing an electron-withdrawing Cl group was present, the yield and enantioselectivity was increased (Table 4, entry 8). On the other hand, 4-nitrophenylmethanol bearing a strong electron-withdrawing group ($-NO_2$) as nucleophile was found not to be favorable to enantioselectivity (Table 4, entry 10), and the ee was decreased to 60%.

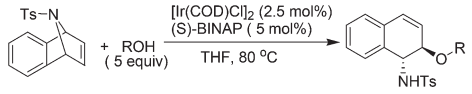
Table 3 Ir-catalyzed asymmetric ring-opening of *N*-protected azabenzonorbornadienes **1a–1d** with alcohols[a]



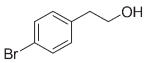
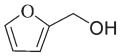
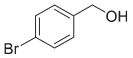
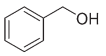
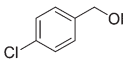
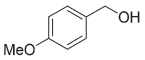
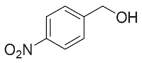
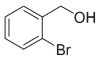
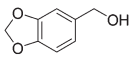
Entry	R^1 [b]	R^2OH	Time [h]	Product	Yield[c] [%]	ee[d] [%]
1	Boc	CH_3OH	12	**2a**	50	63
2	Boc		48	**2b**	32	75
3	Ts		15	**3f**	55	92
4	Ts		36	**3l**	45	88
5	Nos		48	**4a**	75	10
6	Nos		24	**4b**	65	16
7	Nos		48	**4c**	55	18
8	Bs		17	**5a**	68	4

[a] The reaction was carried out with **1a–1d** (0.2 mmol) and 5.0 equiv. of alcohols (1.0 mmol) in THF (2.0 mL) at 80 °C (oil bath temperature) in the presence of $[Ir(COD)Cl]_2$ (2.5 mol%) and (*S*)-BINAP (5.0 mol%). [b] R^1: Boc = *tert*-butoxycarbonyl ($COOC(CH_3)_3$), Ts = 4-methylbenzenesulfonyl, Nos = 4-nitro-benzenesulfonyl, Bs = 4-bromobenzenesulfonyl. [c] Isolated yield after silica gel column chromatography. [d] Determined by HPLC with a Chiralcel OD-H column.

Table 4 The scope of asymmetric ring-opening of *N*-Ts-azabenzonorbornadiene **1b** with various alcohols[a]

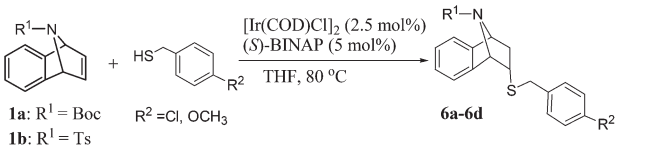


1b 3a-3l

Entry	ROH	Time [h]	Product	Yield[b] [%]	ee[c] [%]
1	CH_3OH	15	**3a**	85	4
2	CH_3CH_2OH	22	**3b**	90	1
3	$^{i}PrOH$	15	**3c**	75	12
4		24	**3d**	75	30
5		13	**3e**	51	94
6		15	**3f**	55	92
7		17	**3g**	45	78
8		36	**3h**	65	73
9		36	**3i**	32	82
10		36	**3j**	60	60
11		18	**3k**	75	12
12		48	**3l**	45	88
13	Ph_3COH	36	**3m**	Trace	

[a] The reaction was carried out with **1b** (0.2 mmol) and 5.0 equiv. of alcohol (1.0 mmol) in THF (2.0 mL) at 80 °C (oil bath temperature) in the presence of $[Ir(COD)Cl]_2$ (2.5 mol%) and (*S*)-BINAP (5.0 mol%). [b] Isolated yield after silica gel column chromatography. [c] Determined by HPLC with a Chiralcel OD-H column.

Table 5 The scope of the iridium-catalyzed addition reaction of *N*-substituted azabenzonorbornadienes **1a–1b** with thiols[a]



1a: R^1 = Boc
1b: R^1 = Ts
R^2 =Cl, OCH_3
6a-6d

Entry	R^1	R^2	Product	Yield[b] [%]	ee[c] [%]
1	Boc	Cl	**6a**	80	9
2	Boc	OCH_3	**6b**	82	8
3	Ts	Cl	**6c**	85	1
4	Ts	OCH_3	**6d**	88	5
5[d]	Boc	Cl	**6a**	6	0
6[d]	Boc	OCH_3	**6b**	48	0
7[d]	Ts	Cl	**6c**	29	0
8[d]	Ts	OCH_3	**6d**	46	0

[a] The reaction was carried out with **1a**, **1b** (0.2 mmol) and 5.0 equiv. of thiol (1.0 mmol) in THF (2.0 mL) at 80 °C (oil bath temperature) in the presence of $[Ir(COD)Cl]_2$ (2.5 mol%) and (*S*)-BINAP (5.0 mol%). [b] Isolated yield after silica gel column chromatography. [c] Determined by HPLC with a Chiralcel OD-H column. [d] The reaction was carried out with **1a**, **1b** (0.2 mmol) and 5.0 equiv. of thiol (1.0 mmol) in THF (2.0 mL) at 80 °C (oil bath temperature) in the absence of iridium catalyst.

Although the iridium catalyst system offered high enantioselectivity when substituted benzyl alcohols were used as nucleophiles, the standard condition was not suitable for thiols. While substituted benzyl alcohols offered ring-opening products, thiols, on the contrary, gave addition products. Reactions of **1a** and **1b** with aliphatic thiols, respectively, were found to give the corresponding thiol addition products **6a–6d** in high yields with lower ee without giving any ring-opening products. The results are summarized in Table 5. In light of the very low enantioselectivities obtained, and the known reactivity of strained azabicyclic alkenes with thiols, it is clear that the iridium catalyst plays a role in the addition reaction, the results indicate higher yields obtained in its presence than in its absence (Table 5, entries 1–8). It may be that the iridium catalyst as a Lewis acid promoted the addition reaction, but low ee values were obtained. It is interesting that the extent of the uncatalyzed reaction varies between substrates **1a** and **1b**. **1a** and **1b** reacted with (4-methoxy-phenyl)-methanethiol to afford higher yields than that of (4-chloro-phenyl)-methanethiol in the absence of iridium catalyst, respectively (Table 5, entries 5–8). Thiols containing an electron-donating group are beneficial for the addition reaction (Table 5, entries 6 and 8). It was proposed that hydrothiolations of strained alkenes can be rapid processes *via* radical addition mechanisms.[25] But further study needs to be carried out to clarify the ring-addition mechanism.

A single crystal of the ring-opened product **3c** was obtained by solvent evaporation from a solution consisting of dichloromethane, petroleum ether and chloroform. Its configuration was assigned as (1*R*,2*R*) and confirmed as 1,2-*trans*-configuration by X-ray crystal structure analysis as shown in Fig. 1.

Based on our findings and observations, a plausible mechanism has been proposed for the formation of the ring-opened products **3** as shown in Scheme 1. When $[Ir(COD)Cl]_2$ is used as the iridium source, the chiral dimeric iridium complex **A** is first formed. The nitrogen atom and the double bond of *N*-Ts-azabenzonorbornadiene **1b** are then reversibly coordinated to the iridium center of the catalyst to give the intermediate **B**. In this step, the intermediate **B** containing a smaller group (–Ts) is more stable than the counterpart containing a relatively larger group (–Boc). Oxidation insertion of the iridium into the C–N bond of **B** forms **C**. Then, nucleophilic attack by the alcohol with configuration inversion is proposed to occur in an S_N2' nucleophilic displacement of the iridium catalyst. The *trans*-1,2-alkoxyamino product **3** is subsequently released, and the iridium complex **A** is regenerated.

Conclusions

In summary, we have successfully developed the first enantioselective iridium-catalyzed ring-opening of *N*-protected

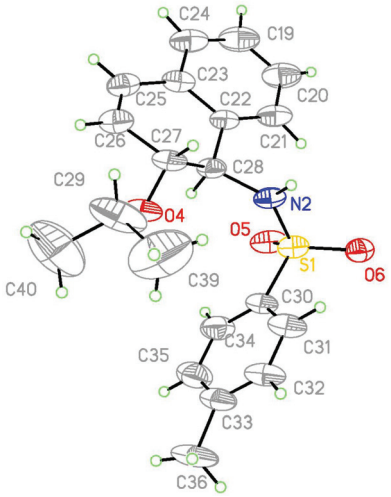
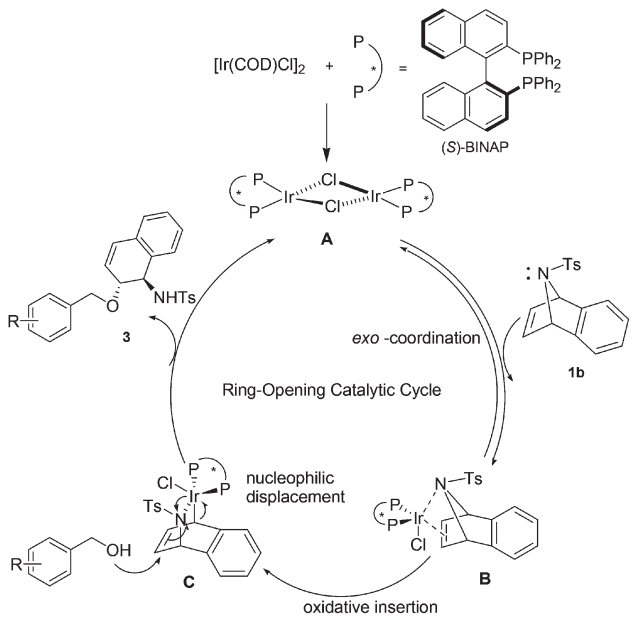


Fig. 1 ORTEP plot for **3c**[a]. [a]Crystal data. $C_{20}H_{25}NO_3S$, M = 359.47. Monoclinic, a = 9.807(5), b = 13.026(6), c = 14.561(7), α = 90, β = 96.029(8), γ = 90, T = 293 K, space group $P21/c$, Z = 4. wR_2 (reflections) = 0.1580 (3223). CCDC 918458.



Scheme 1 The proposed reaction mechanism for the asymmetric ring-opening of *N*-Ts-azabenzonorbornadiene **1b** with substituted benzyl alcohols.

azabicyclic alkenes with substituted benzyl alcohols. It may provide an efficient and practical access to optically pure *trans*-1,2-alkoxyamino derivatives in moderate yields with excellent enantioselectivities. However, when thiols were used as the nucleophiles, diastereoselective addition reactions of azabicyclic alkenes with thiols were observed, and we obtained the sulfide addition derivatives of *N*-protected azabenzonorbornadienes in good to excellent yield. Application of the iridium catalyst to generate chiral compounds with high enantiomeric excesses and further elaboration to asymmetric addition products are currently in progress.

Experimental

General procedures

All flasks were flame-dried under a stream of nitrogen and cooled before use. Solvents and solutions were transferred with syringes and cannulae using standard inert atmosphere techniques. NMR spectra were recorded at 400 MHz using a Varian INOVA NMR spectrometer with $CDCl_3$ as reference standard (δ 7.27 ppm) for ^{1}H NMR and (δ 77.23 ppm) for ^{13}C NMR. Spectral features are tabulated in the following order: chemical shift (δ, ppm); number of protons; multiplicity (s, singlet, d, doublet, t, triplet, m, complex multiplet, br, broad); coupling constants (J, Hz). IR spectra were obtained using a Nicolet DX FT-IR spectrometer as a KBr pellet or using a Perkin-Elmer Spectrum 1000 FT-IR spectrometer as a neat film on a NaCl plate. MS spectra were recorded on a Bruker esquire 6000 mass spectrometer (ESI). Optical rotations were measured on a Perkin-Elmer Model 243 Polarimeter using the sodium D line with spectra-grade $CHCl_3$ in a 1 dm cell. Melting points were taken on an XT_4 binocular micromelting point apparatus. HPLC analysis was performed on an Agilent 1100 Series HPLC with a Chiralcel AD column. Elemental analysis was conducted on a Thermo. Flash EA. TM. 1112. Crystal structure determination was carried out on a Bruker SMART-1000 X-ray diffraction apparatus.

Materials

DME was distilled from sodium benzophenone ketyl and stored. THP, dioxane, toluene, and THF were distilled from sodium benzophenone ketyl immediately prior to use. CH_3CN was distilled from calcium hydride. DMF was dried over $MgSO_4$ and stored over activated molecular sieves. The *N*-protected azabenzonorbornadienes **1a**, **1b**, **1c**, **1d** and $[Ir(COD)Cl]_2$ were prepared according to the reported procedure.[26]

General procedure I for the asymmetric ring-opening of azabicyclic alkenes with various alcohols

A 5.0 mL round-bottomed flask fitted with a reflux condenser was flame-dried under a stream of nitrogen and cooled to room temperature. $[Ir(COD)Cl]_2$ (3.5 mg, 2.5 mol%) and (*S*)-BINAP (6.5 mg, 5.0 mol%) were simultaneously added and followed by the addition of anhydrous tetrahydrofuran (2.0 mL). After the mixture was stirred for about 20 min, azabicyclic alkene **1b** (59.4 mg, 0.20 mmol) was added and the resulting mixture was heated to reflux. On the first sign of reflux, alcohol (5 equiv. to **1b**) was added. Then the oil bath temperature was continuously increased to 80 °C and kept at reflux until the reaction was completed as judged by thin layer chromatography. The solvent was removed *in vacuo* and the crude mixture was purified by column chromatography on silica gel (ethyl acetate–petroleum ether = 1 : 10, v/v) to give the target product.

(1*R*,2*R*)-[2-Methoxy-1,2-dihydro-naphthalen-1-yl]-carbamic acid *tert*-butyl ester (2a). Following the general procedure **I**, **2a** was obtained as a white solid (25.0 mg, 50%). R_f = 0.31 on silica gel (ethyl acetate–petroleum ether = 1 : 6, v/v). Mp 69–70 °C. The

ee was determined to be 63% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 95 : 5, 0.5 mL min^{-1}, λ = 254 nm); retention times were 18.4 min (minor) and 20.7 min (major). $[\alpha]_D^{20}$ = −100.5 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3448(w), 2973(w), 2928(w), 1703(s), 1489(m), 1366(m), 1274(w), 1160(w), 910(w), 750(w), 577(w). ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 2.4 Hz, 1H), 7.24–7.22 (m, 2H), 7.10 (d, *J* = 2.4 Hz, 1H), 6.59 (dd, *J* = 9.6 Hz, 2.8 Hz, 1H), 6.08 (dd, *J* = 9.6 Hz, 4.4 Hz, 1H), 4.98 (dd, *J* = 7.6 Hz, 4.8 Hz, 1H), 4.62 (d, *J* = 8.0 Hz, 1H), 3.99 (t, *J* = 4.8 Hz, 1H), 3.46 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 133.9, 131.9, 130.1, 129.0, 128.3, 127.1, 126.3, 125.8, 79.7, 76.6, 56.4, 51.1, 28.4. MS (ESI) calcd for $C_{16}H_{21}NO_3$ (M^+): 275.15; Found: 298.30 $(M + Na)^+$. Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.78; H, 7.71; N, 5.07.

(1*R*,2*R*)-[2-(4-Bromobenzyloxy)-1,2-dihydro-naphthalen-1-yl]-carbamic acid *tert*-butyl ester (2b). Following the general procedure (**I**), **2b** was obtained as a white solid (27.5 mg, 32%). R_f = 0.31 on silica gel (ethyl acetate–petroleum ether = 1 : 6, v/v). Mp 96–98 °C. The ee was determined to be 75% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 95 : 5, 0.5 mL min^{-1}, λ = 254 nm); retention times were 20.2 min (major) and 21.9 min (minor). $[\alpha]_D^{20}$ = −143.5 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3339(w), 2962(w), 2926(w), 1714(s), 1488(m), 1366(w), 1248(w), 1170(s), 1081(w), 1012(w), 802(w), 747(w), 647(w). ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 5.6 Hz, 1H), 7.30–7.24 (m, 4H), 7.15 (d, *J* = 6.4 Hz, 1H), 6.62 (d, *J* = 9.6 Hz, 1H), 6.05 (d, *J* = 9.6, 1H), 5.09 (t, *J* = 5.6 Hz, 1H), 4.70–4.65 (m, 3H), 4.20 (s, 1H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 137.5, 133.8, 132.0, 131.4, 130.2, 129.6, 128.4, 128.3, 127.1, 126.3, 125.9, 121.5, 79.8, 75.3, 69.7, 51.7, 28.4. MS (ESI) calcd for $C_{22}H_{24}BrNO_3$ (M^+): 429.09; Found: 452.37 $(M + Na)^+$. Anal. Calcd for $C_{22}H_{24}BrNO_3$: C, 61.40; H, 5.62; N, 3.25. Found: C, 61.36; H, 5.60; N, 3.25.

(1*R*,2*R*)-*N*-(2-Methoxy-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3a). Following the general procedure (**I**), **3a** was obtained as a white solid (73.0 mg, 85%). R_f = 0.25 on silica gel (ethyl acetate–petroleum ether = 1 : 6, v/v). Mp 71–72 °C. The ee was determined to be 4% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 90 : 10, 0.5 mL min^{-1}, λ = 254 nm); retention times were 52.9 min (major) and 58.0 min (minor). $[\alpha]_D^{20}$ = 10.6 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3273(w), 3038(w), 2926(w), 2853(w), 1721(s), 1598(m), 1493(m), 1454(w), 1329(m), 1159(s), 1093(m), 970(m), 916(w), 813(m), 666(m), 571(m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.22–7.18 (m, 1H), 7.07–7.04 (m, 2H), 6.60 (d, *J* = 8 Hz, 1H), 6.57 (d, *J* = 9.6 Hz, 1H), 6.03 (dd, *J* = 9.6 Hz, 4.8 Hz, 1H), 4.68 (d, *J* = 7.6 Hz, 1H), 4.49 (dd, *J* = 4.8 Hz, 7.6 Hz, 1H), 3.96 (t, *J* = 4.4 Hz, 1H), 3.25 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 137.7, 132.5, 131.7, 130.3, 129.6, 128.8, 128.3, 127.3, 125.0, 76.7, 56.5, 54.2, 21.6. MS (ESI) calcd for $C_{18}H_{19}NO_3S$ (M^+): 329.11; Found: 347.10 $(M + Na)^+$. Anal. Calcd for $C_{18}H_{19}NO_3S$: C, 65.63; H, 5.81; N, 4.25; S, 9.73. Found: C, 65.66; H, 5.78; N, 4.23; S, 9.69.

(1*R*,2*R*)-*N*-(2-Ethoxy-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3b). Following the general procedure (**I**), **3b** was obtained as a white solid (61.7 mg, 90%). R_f = 0.20 on silica gel (ethyl acetate–petroleum ether = 1 : 5, v/v). Mp 146–148 °C. The ee was determined to be 1% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 90 : 10, 0.5 mL min^{-1}, λ = 254 nm); retention times were 27.9 min (major) and 39.4 min (minor). $[\alpha]_D^{20}$ = −10.2 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3273(w), 3040(w), 2967(w), 2924(m), 2853(w), 1921(w), 1598(m), 1454(m), 1329(w), 1159(s), 1093(s), 968(m), 923(w), 813(m), 780(m), 737(m), 666(m), 547(m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.21–7.15 (m, 1H), 7.08–7.03 (m, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 9.6 Hz, 1H), 6.00 (dd, *J* = 9.6 Hz, 4.8 Hz, 1H), 4.74 (d, *J* = 7.6 Hz, 1H), 4.49 (dd, *J* = 4.8 Hz, 7.6 Hz, 1H), 4.04 (t, *J* = 4.8 Hz, 1H), 3.49 (q, *J* = 7.2 Hz, 14 Hz, 2H), 2.44 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 137.8, 132.7, 131.8, 129.8, 129.6, 128.7, 128.3, 128.2, 127.3, 127.2, 125.8, 75.3, 64.5, 54.7, 21.6, 15.4. MS (ESI) calcd for $C_{19}H_{21}NO_3S$ (M^+): 343.12; Found: 366.40 $(M + Na)^+$. Anal. Calcd for $C_{19}H_{21}NO_3S$: C, 66.45; H, 6.16; N, 4.08; S, 9.34. Found: C, 66.49; H, 6.14; N, 4.05; S, 9.30.

(1*R*,2*R*)-*N*-(2-Isopropoxy-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3c). Following the general procedure (**I**), **3c** was obtained as a white solid (53.6 mg, 75%). R_f = 0.16 on silica gel (ethyl acetate–petroleum ether = 1 : 5, v/v). Mp 121–123 °C. The ee was determined to be 12% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 90 : 10, 0.5 mL min^{-1}, λ = 254 nm); retention times were 22.6 min (minor) and 28.3 min (major). $[\alpha]_D^{20}$ = −23.5 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3255(w), 3040(w), 2957(w), 2923(m), 2852(w), 1727(w), 1598(w), 1495(m), 1462(w), 1288(w), 1185(w), 1161(s), 968(m), 776(m), 666(m), 568(w). ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8 Hz, 2H), 7.20–7.16 (m, 1H), 7.05–7.02 (m, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 9.6 Hz, 1H), 5.96 (dd, *J* = 9.6 Hz, 4.8 Hz, 1H), 4.68 (d, *J* = 7.6 Hz, 1H), 4.43 (dd, *J* = 4.8 Hz, 7.6 Hz, 1H), 4.09 (t, *J* = 4.8 Hz, 1H), 3.75–3.72 (m, 1H), 2.44 (s, 3H), 1.02 (dd, *J* = 2.4 Hz, 8.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 137.8, 132.7, 131.9, 129.7, 129.5, 128.6, 128.4, 128.2, 127.3, 127.2, 126.4, 72.8, 70.3, 55.3, 22.5, 21.6. MS (ESI) calcd for $C_{20}H_{23}NO_3S$ (M^+): 357.14; Found: 380.46 $(M + Na)^+$. Anal. Calcd for $C_{20}H_{23}NO_3S$: C, 67.20; H, 6.49; N, 3.92; S, 8.97. Found: C, 67.18; H, 6.50; N, 3.93; S, 8.95.

(1*R*,2*R*)-*N*-(2-(4-Bromophenethoxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3d). Following the general procedure (**I**), **3d** was obtained as a white solid (74.5 mg, 75%). R_f = 0.27 on silica gel (ethyl acetate–petroleum ether = 1 : 4, v/v). Mp 163–164 °C. The ee was determined to be 30% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 85 : 15, 0.5 mL min^{-1}, λ = 254 nm); retention times were 24.4 min (minor) and 36.3 min (major). $[\alpha]_D^{20}$ = −62.7 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3273(w), 3033(w), 2957(s), 2279(w), 1727(m), 1598(w), 1488(m), 1455(w), 1331(m), 1160(s), 1093(s), 962(w), 813(m), 666(m), 547(m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 4H), 7.21 (t, *J* =

7.6 Hz, 1H), 7.06 (d, J = 7.2 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 6.61 (d, J = 7.6 Hz, 1H), 6.56 (d, J = 9.6 Hz, 1H), 5.96 (dd, J = 4.8 Hz, 9.6 Hz, 1H), 4.58 (d, J = 7.6 Hz, 1H), 4.31 (dd, J = 4.0 Hz, 7.6 Hz, 1H), 4.07 (t, J = 4.4 Hz, 1H), 3.73–3.61 (m, 2H), 2.66 (t, J = 7.2 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 137.9, 137.6, 132.3, 131.7, 131.3, 130.7, 130.3, 129.7, 128.8, 128.5, 128.3, 172.3, 127.2, 125.1, 120.0, 75.3, 69.5, 54.2, 35.7, 21.6. MS (ESI) calcd for $C_{25}H_{24}BrNO_3S$ (M^+): 497.07; Found: 520.16 $(M + Na)^+$. Anal. Calcd for $C_{25}H_{24}BrNO_3S$: C, 60.24; H, 4.85; N, 2.81; S, 6.43. Found: C, 60.21; H, 4.87; N, 2.82; S, 6.40.

(1*R*,2*R*)-*N*-(2-(Furan-2-ylmethoxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3e). Following the general procedure (**I**), **3e** was obtained as a white solid (40.5 mg, 51%). R_f = 0.30 on silica gel (ethyl acetate–petroleum ether = 1 : 3, v/v). Mp 123–124 °C. The ee was determined to be 94% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 85 : 15, 0.5 mL min^{-1}, λ = 254 nm); retention times were 29.1 min (minor) and 33.3 min (major). $[\alpha]_D^{20}$ = −165 (c 1.00, $CHCl_3$). IR (film, cm^{-1}): 3269(w), 2926(w), 2854(w), 1715(m), 1598(w), 1503(w), 1454(m), 1331(m), 1159(s), 1069(m), 918(w), 815(m), 749(m), 665(m), 569(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.0 Hz, 2H), 7.37 (s, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.07 (d, J = 7.2 Hz, 2H), 6.84 (d, J = 7.6 Hz, 1H), 6.56 (d, J = 9.6 Hz, 1H), 6.32 (s, 1H), 6.27 (s, 1H), 5.92 (dd, J = 4.8 Hz, 9.6 Hz, 1H), 4.51–4.46 (m, 2H), 4.43 (s, J = 8.0 Hz, 2H), 4.18 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 143.5, 142.9, 137.5, 132.5, 131.7, 130.2, 129.6 128.7, 128.4, 128.3, 127.4, 125.2, 110.3, 109.8, 74.4, 62.8, 54.7, 21.6. MS (ESI) calcd for $C_{22}H_{21}NO_4S$ (M^+): 395.12; Found: 518.51 $(M + Na)^+$. Anal. Calcd for $C_{22}H_{21}NO_4S$: C, 66.82; H, 5.35; N, 3.54; S, 8.11. Found: C, 66.80; H, 5.34; N, 3.55; S, 8.08.

(1*R*,2*R*)-*N*-(2-(4-Bromobenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3f). Following the general procedure (**I**), **3f** was obtained as a white solid (53.5 mg, 55%). R_f = 0.24 on silica gel (ethyl acetate–petroleum ether = 1 : 4, v/v). Mp 132–134 °C. The ee was determined to be 92% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 85 : 15, 0.5 mL min^{-1}, λ = 254 nm); retention times were 27.6 min (minor) and 38.6 min (major). $[\alpha]_D^{20}$ = −175 (c 1.00, $CHCl_3$). IR (film, cm^{-1}): 3275(w), 3034(w), 2925(w), 1721(m), 1597(w), 1487(m), 1454(w), 1330(m), 1159(s), 1093(s), 1070(s), 1011(m), 912(w), 811(m), 666(m), 570(m), 547(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 8.0 Hz, 3H), 7.09–7.06 (m, 1H), 6.73 (d, J = 7.6 Hz, 1H), 6.63 (d, J = 9.6 Hz, 1H), 6.00 (dd, J = 4.8 Hz, 9.6 Hz, 1H), 4.56–4.51 (m, 3H), 4.46 (t, J = 8.0 Hz, 1H), 4.17 (t, J = 4.8 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 137.6, 137.2, 132.3, 131.7, 131.4, 130.5, 129.7 129.4, 129.0, 128.9, 128.5, 172.3, 127.2, 124.9, 121.6, 74.7, 70.1, 54.4, 21.6. MS (ESI) calcd for $C_{24}H_{22}BrNO_3S$ (M^+): 483.05; Found: 508.43 $(M + Na)^+$. Anal. Calcd for $C_{24}H_{22}BrNO_3S$: C, 59.51; H, 4.58; N, 2.89; S, 6.62. Found: C, 59.53; H, 4.59; N, 2.89; S, 6.60.

1-Naphthyltosylamine (3fa). 3fa was obtained as a light-brown solid and was purified by column chromatography (R_f = 0.22, ethyl acetate–petroleum ether = 1 : 4, v/v). Mp 145–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.84 (m, 1H), 7.81–7.79 (m, 1H), 7.70 (dd, J = 2.4, 7.2 Hz, 1H), 7.65 (s, 1H), 7.63 (s, 1H), 7.46–7.40 (m, 2H), 7.38–7.33 (m, 2H), 7.16 (s, 1H), 7.13 (s, 1H), 7.11 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 136.4, 134.3, 131.6, 129.7, 129.0, 128.5, 127.5, 127.3, 126.7, 126.4, 125.5, 122.8, 121.6, 21.6.

(1*R*,2*R*)-*N*-(2-Benzyloxy-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3g). Following the general procedure (**I**), **3g** was obtained as a white solid (36.5 mg, 45%). R_f = 0.25 on silica gel (ethyl acetate–petroleum ether = 1 : 4, v/v). Mp 113–114 °C. The ee was determined to be 78% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 85 : 15, 0.5 mL min^{-1}, λ = 254 nm); retention times were 26.4 min (minor) and 29.2 min (major). $[\alpha]_D^{20}$ = −135 (c 1.00, $CHCl_3$). IR (film, cm^{-1}): 3280(w), 3061(w), 2920(w), 1723(m), 1598(w), 1495(m), 1454(w), 1330(s), 1160(s), 1093(s), 966(w), 918(w), 813(m), 750(w), 698(w), 666(m), 569(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.4 Hz, 2H), 7.33–1.21 (m, 8H), 7.10 (d, J = 7.6 Hz, 2H), 6.79 (d, J = 7.2 Hz, 1H), 6.62 (d, J = 9.6 Hz, 1H), 6.00 (dd, J = 4.8 Hz, 9.6 Hz, 1H), 4.59–4.55 (m, 3H), 4.50 (t, J = 7.6 Hz, 1H), 4.18 (t, J = 4.8 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 138.1, 137.6, 132.5, 131.8, 130.3, 129.6, 128.8, 128.5, 128.4, 127.8, 127.7, 127.3, 127.2, 125.3, 74.5, 70.9, 54.5, 21.6. MS (ESI) calcd for $C_{24}H_{23}NO_3S$ (M^+): 405.14; Found: 428.64 $(M + Na)^+$. Anal. Calcd for $C_{24}H_{23}NO_3S$: C, 71.09; H, 5.72; N, 3.45; S, 7.91. Found: C, 71.12; H, 5.74; N, 3.48; S, 7.89.

(1*R*,2*R*)-*N*-(2-(4-Chlorobenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3h). Following the general procedure (**I**), **3h** was obtained as a white solid (36.5 mg, 65%). R_f = 0.22 on silica gel (ethyl acetate–petroleum ether = 1 : 4, v/v). Mp 133–134 °C. The ee was determined to be 73% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 85 : 15, 0.5 mL min^{-1}, λ = 254 nm); retention times were 25.4 min (minor) and 33.9 min (major). $[\alpha]_D^{20}$ = −135 (c 1.00, $CHCl_3$). IR (film, cm^{-1}): 3281(w), 2925(w), 1492(w), 1455(w), 1328(m), 1454(w), 1330(s), 1159(s), 1093(s), 1014(w), 812(m), 667(w), 666(m), 569(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.2 Hz, 2H), 7.30–7.27 (m, 4H), 7.24 (t, J = 7.2 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.12–7.08 (m, 2H), 6.73 (d, J = 7.6 Hz, 1H), 6.62 (d, J = 9.6 Hz, 1H), 6.00 (dd, J = 4.8 Hz, 9.6 Hz, 1H), 4.53 (d, J = 7.6 Hz, 2H), 4.49 (t, J = 7.6 Hz, 1H), 4.17 (t, J = 7.6 Hz, 1H), 2.46 (s, 3H), 2.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 137.6, 136.7, 133.4, 132.3, 131.7, 130.5, 129.7, 129.1, 128.9, 128.4, 128.5, 127.3, 127.2, 124.9, 74.7, 70.1, 54.4, 21.6. MS (ESI) calcd for $C_{24}H_{22}NO_3ClS$ (M^+): 439.10; Found: 462.58 $(M + Na)^+$. Anal. Calcd for $C_{24}H_{22}NO_3ClS$: C, 65.52; H, 5.04; N, 3.18; S, 7.29. Found: C, 65.53; H, 5.02; N, 3.19; S, 7.26.

(1*R*,2*R*)-*N*-(2-(4-Methoxybenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3i). Following the general procedure (**I**), **3i** was obtained as a white solid (27.9 mg, 32%). R_f = 0.15 on silica gel (ethyl acetate–petroleum ether = 1 : 5, v/v). Mp 83–84 °C. The ee was determined to be 82% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 85 : 15, 0.5 mL min^{-1}, λ = 254 nm); retention times were

37.6 min (minor) and 40.8 min (major). $[\alpha]_D^{20}$ = −143 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3276(w), 3035(w), 2925(w), 1724(w), 1612(w), 1514(w), 1454(w), 1329(m), 1248(m), 1159(s), 1094(m), 1034(m), 914(w), 8125(m), 664(m), 566(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 9.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 9.6 Hz, 1H), 5.96 (dd, *J* = 4.4 Hz, 9.6 Hz, 1H), 4.55–4.51 (m, 1H), 4.50–4.47 (m, 3H), 4.16 (s, 1H), 3.82 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 143.5, 137.7, 132.5, 131.8, 130.2, 130.1, 129.7, 129.5, 128.8, 128.5, 128.3, 127.3, 125.4, 113.7, 74.0, 70.6, 55.3, 54.4, 21.6. MS (ESI) calcd for $C_{25}H_{25}NO_4S$ (M^+): 435.15; Found: 458.45 $(M + Na)^+$. Anal. Calcd for $C_{25}H_{25}NO_4S$: C, 68.94; H, 5.79; N, 3.22; S, 7.36. Found: C, 68.93; H, 5.77; N, 3.19; S, 7.34.

(1*R*,2*R*)-*N*-(2-(4-Nitrobenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3j). Following the general procedure (**I**), **3j** was obtained as a white solid (54.1 mg, 60%). R_f = 0.12 on silica gel (ethyl acetate–petroleum ether = 1 : 4, v/v). Mp 190–191 °C. The ee was determined to be 60% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 90 : 10, 1.0 mL min^{-1}, λ = 254 nm); retention times were 47.3 min (minor) and 54.6 min (major). $[\alpha]_D^{20}$ = −121 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3282(w), 3045(w), 2925(w), 2854(w), 1958(w), 1519(w), 1397(w), 1344(s), 1161(s), 1092(m), 961(w), 814(m), 775(m), 667(m), 569(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.30–7.27 (m, 3H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 3H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 9.6 Hz, 1H), 5.98 (dd, *J* = 4.8 Hz, 9.6 Hz, 1H), 4.55–4.52 (m, 3H), 4.45 (t, *J* = 8.0 Hz, 1H), 4.16 (t, *J* = 4.8 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 137.6, 136.7, 133.4, 132.3, 131.7, 130.5, 129.7, 129.1, 128.9, 128.4, 128.5, 127.3, 127.2, 124.9, 79.2, 71.9, 54.4, 24.3. MS (ESI) calcd for $C_{24}H_{22}N_2O_5S$ (M^+): 450.13; Found: 473.52 $(M + Na)^+$. Anal. Calcd for $C_{24}H_{22}N_2O_5S$: C, 63.98; H, 4.92; N, 6.22; S, 7.12. Found: C, 63.95; H, 4.94; N, 6.19; S, 7.08.

(1*R*,2*R*)-*N*-(2-(2-Bromobenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3k). Following the general procedure (**I**), **3k** was obtained as a white solid (40.5 mg, 75%). R_f = 0.10 on silica gel (ethyl acetate–petroleum ether = 1 : 8, v/v). Mp 134–135 °C. The ee was determined to be 12% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 85 : 15, 0.5 mL min^{-1}, λ = 254 nm); retention times were 46.7 min (minor) and 50.3 min (major). $[\alpha]_D^{20}$ = −23 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3284(w), 3059(w), 2924(w), 1597(w), 1491(w), 1444(m), 1332(m), 1159(s), 1094(m), 928(w), 812(w), 664(m), 547(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 4.8 Hz, 1H), 7.26–7.21 (m, 4H), 7.16–7.09 (m, 3H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 9.6 Hz, 1H), 6.05 (dd, *J* = 4.8 Hz, 9.6 Hz, 1H), 4.62 (s, 1H), 4.56 (s, 2H), 4.23 (t, *J* = 4.0 Hz, 1H), 2.40 (s, 3H), 2.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 137.5, 137.3, 132.7, 132.4, 131.8, 130.4, 129.6, 129.4, 129.0, 128.7, 128.4, 128.3, 127.3, 127.2, 125.0, 122.8, 121.4, 75.5, 70.2, 54.7, 21.6. MS (ESI) calcd for $C_{24}H_{22}BrNO_3S$ (M^+): 485.05; Found: 506.33 $(M + Na)^+$. Anal. Calcd for $C_{24}H_{22}NBrO_3S$: C, 59.51; H, 4.58; N, 2.89; S, 6.62. Found: C, 59.54; H, 4.55; N, 2.88; S, 6.58.

(1*R*,2*R*)-*N*-(2-(Benzo[*d*][1,3]dioxol-5-ylmethoxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3l). Following the general procedure (**I**), **3l** was obtained as a white solid (72.6 mg, 45%). R_f = 0.15 on silica gel (ethyl acetate–petroleum ether = 1 : 5, v/v). Mp 63–64 °C. The ee was determined to be 88% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 85 : 15, 0.5 mL min^{-1}, λ = 254 nm); retention times were 26.1 min (minor) and 35.5 min (major). $[\alpha]_D^{20}$ = −128 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3268(w), 3059(w), 2957(w), 2924(w), 1597(w), 1454(w), 1329(m), 1161(s), 1093(s), 967(w), 916(w), 813(m), 752(m), 665(m), 548(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 2H), 6.77–6.73 (m, 4H), 6.59 (d, *J* = 9.6 Hz, 1H), 5.98 (d, *J* = 4.4 Hz, 1H), 5.95 (s, 2H), 4.52 (s, 2H), 4.43 (s, 2H), 4.14 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 143.2, 139.6, 133.7, 128.5, 127.9, 127.8, 126.4, 125.7, 124.9, 124.5, 124.4, 123.4, 123.3, 121.3, 117.6, 104.7, 104.1, 97.0, 70.1, 66.8, 50.5, 17.7. MS (ESI) calcd for $C_{25}H_{23}NO_5S$ (M^+): 449.13; Found: 472.33 $(M + Na)^+$. Anal. Calcd for $C_{25}H_{23}NO_5S$: C, 66.80; H, 5.16; N, 3.12; S, 7.13. Found: C, 66.81; H, 5.15; N, 3.12; S, 7.16.

(1*R*,2*R*)-*N*-(2-(4-Bromobenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-nitrobenzenesulfonamide (4a). Following the general procedure (**I**), **4a** was obtained as a white solid (77.3 mg, 75%). R_f = 0.18 on silica gel (ethyl acetate–petroleum ether = 1 : 4, v/v). Mp 166–167 °C. The ee was determined to be 10% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 80 : 20, 1.0 mL min^{-1}, λ = 254 nm); retention times were 33.5 min (minor) and 50.1 min (major). $[\alpha]_D^{20}$ = −19 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3274(w), 3059(w), 2925(w), 2854(m), 1724(m), 1605(w), 1530(s), 1487(w), 1455(w), 1348(s), 1288(m), 1164(m), 1092(m), 1073(m), 853(w), 811(w), 736(m), 615(m), 503(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.26 (s, 1H), 7.15–7.11 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 9.6 Hz, 1H), 5.99 (dd, *J* = 4.0 Hz, 3.6 Hz, 1H), 4.96 (d, *J* = 7.6 Hz, 1H), 4.65 (t, *J* = 7.2 Hz, 1H), 4.52 (d, *J* = 8.0 Hz, 1H), 4.36 (d, *J* = 9.6 Hz, 1H), 4.14 (t, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 146.5, 136.7, 132.1, 131.9, 131.5, 130.3, 129.3, 129.1, 128.5, 128.2, 127.7, 127.4, 125.1, 124.1, 121.9, 75.5, 70.2, 55.8. MS (ESI) calcd for $C_{23}H_{19}N_2O_5BrS$ (M^+): 514.02; Found: 538.34 $(M + Na)^+$. Anal. Calcd for $C_{23}H_{19}N_2O_5BrS$: C, 53.60; H, 3.72; N, 5.44; S, 6.22. Found: C, 53.62; H, 3.71; N, 5.44; S, 6.19.

(1*R*,2*R*)-*N*-(2-(4-Chlorobenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-nitrobenzenesulfonamide (4b). Following the general procedure (**I**), **4b** was obtained as a white solid (61.1 mg, 65%). R_f = 0.18 on silica gel (ethyl acetate–petroleum ether = 1 : 4, v/v). Mp 173–174 °C. The ee was determined to be 16% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 80 : 20, 1.0 mL min^{-1}, λ = 254 nm); retention times were 31.0 min (minor) and 42.7 min (major). $[\alpha]_D^{20}$ = −32 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}) 3283(w), 3104(w), 2919(w), 2852(w), 1728(w), 1605(w), 1530(s), 1492(w), 1454(w), 1348(s), 1164(s),

1091(m), 1014(w), 853(m), 813(m), 736(m), 558(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 4.8 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H), 7.36–7.24 (m, 4H), 7.14–1.10 (m, 3H), 6.97 (d, J = 7.6 Hz, 1H), 6.60 (d, J = 9.6 Hz, 1H), 6.00 (dd, J = 9.6 Hz, 4.0 Hz, 1H), 4.85 (d, J = 8.4 Hz, 1H), 4.66 (t, J = 6.0 Hz, 1H), 4.53 (d, J = 12.0 Hz, 1H), 4.38 (d, J = 9.6 Hz, 1H), 4.15 (t, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 136.1, 133.8, 132.1, 131.9, 130.3, 129.1, 128.9, 128.6, 128.5, 128.2, 127.7, 127.4, 125.1, 124.8, 124.1, 75.4, 70.1, 55.8. MS (ESI) calcd for $C_{23}H_{19}N_2O_5ClS$ (M^+): 470.07; Found: 493.43 (M + Na)$^+$. Anal. Calcd for $C_{23}H_{19}N_2O_5ClS$: C, 58.66; H, 4.07; N, 5.95; S, 6.81. Found: C, 58.67; H, 4.06; N, 5.94; S, 6.77.

(1*R*,2*R*)-*N*-(2-(Benzo[*d*][1,3]dioxol-5-ylmethoxy)-1,2-dihydronaphthalen-1-yl)-4-nitrobenzenesulfonamide (4c). Following the general procedure (**I**), **4c** was obtained as a white solid (52.8 mg, 55%). R_f = 0.15 on silica gel (ethyl acetate–petroleum ether = 1 : 5, v/v). Mp 173–175 °C. The ee was determined to be 18% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 75 : 25, 1.0 mL min^{-1}, λ = 254 nm); retention times were 38.6 min (major) and 53.7 min (minor). $[\alpha]_D^{20}$ = −28 (c 1.00, $CHCl_3$). IR (film, cm^{-1}): 3735(w), 3294(w), 2921(s), 1729(w), 1529(m), 1444(m), 1348(s), 1254(m), 1163(s), 1094(m), 1039(m), 929(w), 737(w), 615(w), 503(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 7.21–7.10 (m, 4H), 6.72 (d, J = 8.0 Hz, 1H), 6.63–6.56 (m, 3H), 6.00 (d, J = 3.6 Hz, 1H), 5.98 (d, J = 4.0 Hz, 2H), 4.75–4.68 (m, 2H), 4.46 (d, J = 12.0 Hz, 1H), 4.27 (d, J = 12.0 Hz, 1H), 4.10 (t, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 147.7, 147.3, 146.5, 132.6, 132.0, 131.2, 130.9, 129.9, 128.9, 128.5, 128.3, 127.5, 127.2, 125.6, 124.0, 121.3, 108.2, 101.2, 75.1, 70.6, 55.3. MS (ESI) calcd for $C_{24}H_{20}N_2O_7S$ (M^+): 480.10; Found: 503.76 (M + Na)$^+$. Anal. Calcd for $C_{24}H_{20}N_2O_7S$: C, 59.99; H, 4.20; N, 5.83; S, 6.67. Found: C, 59.95; H, 4.19; N, 5.80; S, 6.63.

(1*R*,2*R*)-*N*-(2-(4-Bromobenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-bromobenzenesulfonamide (5a). Following the general procedure (**I**), **5a** was obtained as a white solid (74.6 mg, 68%). R_f = 0.15 on silica gel (ethyl acetate–petroleum ether = 1 : 5, v/v). Mp 136–137 °C. The ee was determined to be 4% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 85 : 15, 1.0 mL min^{-1}, λ = 254 nm); retention times were 16.7 min (minor) and 27.1 min (major). $[\alpha]_D^{20}$ = −17 (c 1.00, $CHCl_3$). IR (film, cm^{-1}): 3565(w), 3270(w), 2924(s), 2028(w), 1575(w), 1487(w), 1390(s), 1333(m), 1275(w), 1162(s), 1069(m), 1011(m), 819(m), 739(m), 610(m), 558(w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.28–7.25 (m, 2H), 7.12–7.07 (m, 3H), 6.84 (d, J = 8.0 Hz, 1H), 6.60 (d, J = 9.6 Hz, 1H), 5.98 (dd, J = 9.6 Hz, 4.4 Hz, 1H), 4.63 (d, J = 8.0 Hz, 1H), 4.56–4.51 (m, 2H), 4.43 (d, J = 9.6 Hz, 1H), 4.13 (d, J = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7, 136.9, 132.3, 132.2, 131.7, 131.5, 130.5, 129.4, 129.0, 128.6, 128.5, 128.2, 127.7, 127.4, 124.9, 121.7, 74.9, 70.2, 54.9. MS (ESI) calcd for $C_{23}H_{19}NO_3Br_2S$ (M^+): 546.95; Found: 569.93 (M + Na)$^+$. Anal. Calcd for $C_{23}H_{19}NO_3Br_2S$: C, 50.29; H, 3.49; N, 2.55; S, 5.84. Found: C, 50.32; H, 3.48; N, 2.51; S, 5.80.

2-(4-Chloro-benzylsulfanyl)-1,2,3,4-tetrahydro-1,4-epiazano-naphthalene-9-carboxylic acid *tert*-butyl ester (6a). Following the general procedure (**I**), **6a** was obtained as a white solid (64.2 mg, 80%). R_f = 0.25 on silica gel (ethyl acetate–petroleum ether = 1 : 15, v/v). Mp 91–93 °C. The ee was determined to be 9% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 90 : 10, 0.5 mL min^{-1}, λ = 254 nm); retention times were 12.2 min (minor) and 16.2 min (major). $[\alpha]_D^{20}$ = 9 (c 1.00, $CHCl_3$). IR (film, cm^{-1}): 3339(w), 2962(w), 2926(w), 1714(m), 1488(w), 1366(m), 1248(s), 1170(m), 1081(w), 802(s), 747(m), 693(w), 526(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.26 (m, 4H), 7.20–7.12 (m, 4H), 5.14 (s, 1H), 4.76 (s, 1H), 3.88–3.78 (m, 2H), 2.60 (s, 1H), 1.87–1.84 (m, 1H), 1.78–1.75 (m, 1H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 145.0, 132.9, 130.9, 130.2, 128.8, 126.9, 126.7, 80.3, 65.6, 45.3, 36.4, 30.6, 29.7, 28.3. MS (ESI) calcd for $C_{22}H_{24}ClNO_2S$ (M^+): 401.12; Found: 424.23 (M + Na)$^+$. Anal. Calcd for $C_{22}H_{24}ClNO_2S$: C, 65.74; H, 6.02; N, 3.48; S, 7.98 Found: C, 65.75; H, 5.99; N, 3.44; S, 7.90.

2-(4-Methoxy-benzylsulfanyl)-1,2,3,4-tetrahydro-1,4-epiazano-naphthalene-9-carboxylic acid *tert*-butyl ester (6b). Following the general procedure (**I**), **6b** was obtained as a white solid (65.1 mg, 82%). R_f = 0.25 on silica gel (ethyl acetate–petroleum ether = 1 : 15, v/v). Mp 85–87 °C. The ee was determined to be 8% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 90 : 10, 0.5 mL min^{-1}, λ = 254 nm); retention times were 13.4 min (minor) and 15.2 min (major). $[\alpha]_D^{20}$ = 8 (c 1.00, $CHCl_3$). IR (film, cm^{-1}): 3339(w), 2962(w), 2926(w), 1714(m), 1488(w), 1366(m), 1248(s), 1170(m), 1081(w), 802(s), 747(m), 693(w), 526(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.12 (m, 6H), 6.89–6.87 (m, 2H), 5.15–4.99 (m, 1H), 4.77 (s, 1H), 3.87–3.79 (m, 5H), 2.63 (s, 1H), 1.90–1.84 (m, 1H), 1.80–1.73 (m, 1H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 145.1, 145.0, 130.0, 129.9, 126.8, 126.6, 114.0, 80.2, 65.2, 60.0, 55.3, 45.2, 36.5, 35.9, 28.3. MS (ESI) calcd for $C_{23}H_{27}NO_3S$ (M^+): 397.17; Found: 420.25 (M + Na)$^+$. Anal. Calcd for $C_{23}H_{27}NO_3S$: C, 69.49; H, 6.85; N, 3.52; S, 8.07. Found: C, 69.45; H, 6.83; N, 3.50; S, 8.17.

2-(4-Chloro-benzylsulfanyl)-9-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-1,4-epiazano-naphthalene (6c). Following the general procedure (**I**), **6c** was obtained as a white solid (77.3 mg, 85%). R_f = 0.25 on silica gel (ethyl acetate–petroleum ether = 1 : 15, v/v). Mp 94–96 °C. The ee was determined to be 1% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 85 : 15, 0.5 mL min^{-1}, λ = 254 nm); retention times were 35.4 min (major) and 41.9 min (minor). $[\alpha]_D^{20}$ = 1 (c 1.00, $CHCl_3$). IR (film, cm^{-1}): 2934(w), 2925(w), 1596(w), 1511(m), 1489(w), 1342(m), 1161(s), 1090(m), 1014(w), 971(s), 812(m), 693(w), 679(m), 604(m), 526(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.26 (m, 6H), 6.91 (d, J = 4.0 Hz, 2H), 6.86 (s, 3H), 6.73 (d, J = 4.4 Hz, 1H), 5.00 (d, J = 4.4 Hz, 1H), 4.52 (s, 1H), 3.84 (d, J = 4.8 Hz, 2H), 2.51 (dd, J = 3.6 Hz, 8.0 Hz, 1H), 2.25 (s, 3H), 2.01–1.98 (m, 1H), 1.78–1.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 142.9, 141.7, 136.9, 134.9, 132.9, 130.3, 128.9, 128.8, 127.9, 126.9, 126.7, 120.2, 120.1, 68.3, 63.1, 44.6, 36.7, 36.3, 21.4. MS (ESI) calcd for $C_{24}H_{22}ClNO_2S_2$ (M^+): 455.08; Found: 478.43 (M + Na)$^+$. Anal. Calcd for $C_{24}H_{22}ClNO_2S_2$: C,

63.21; H, 4.86; N, 3.07; S, 14.06. Found: C, 63.23; H, 4.83; N, 3.08; S, 14.12.

2-(4-Methoxy-benzylsulfanyl)-9-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-1,4-epiazano-naphthalene (6d). Following the general procedure (**I**), **6d** was obtained as a white solid (79.3 mg, 88%). R_f = 0.20 on silica gel (ethyl acetate–petroleum ether = 1 : 15, v/v). Mp 102–103 °C. The ee was determined to be 5% using HPLC analysis on a Chiralcel OD-H column (hexane–2-propanol = 85 : 15, 0.5 mL min^{-1}, λ = 254 nm); retention times were 39.0 min (minor) and 48.1 min (major). $[\alpha]_D^{20}$ = 5 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 2933(w), 2925(w), 1669(w), 1511(m), 1460(w), 1342(m), 1161(s), 1089(m), 1031(w), 971(s), 813(m), 604(w), 558(m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.87–6.85 (m, 5H), 6.75 (d, *J* = 4.0 Hz, 1H), 4. 98 (d, *J* = 3.6 Hz, 1H), 4.50 (s, 1H), 3.83 (d, *J* = 4.8 Hz, 2H), 3.80 (s, 3H), 2.55–2.52 (m, 1H), 2.25 (s, 3H), 2.00–1.96 (m, 1H), 1.78–1.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 139.1, 138.9, 137.9, 131.0, 126.3, 126.1, 124.9, 123.9, 122.9, 122.7, 116.3, 116.2, 110.1, 64.4, 59.2, 51.4, 40.6, 32.7, 32.5, 17.5. MS (ESI) calcd for $C_{25}H_{25}NO_3S_2$ (M^+): 451.13; Found: 474.41 $(M + Na)^+$. Anal. Calcd for $C_{25}H_{25}NO_3S_2$: C, 66.49; H, 5.58; N, 3.10; 14.20. Found: C, 66.55; H, 5.54; N, 3.12; 14.11.

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