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CHIRAL PHOSPHINE OXIDE-CATALYZED ENANTIOSELECTIVE RING OPENING OF OXETANES

Shunsuke Kotani,* Yuka Tashima, Hiroki Tanaka, Shohei Aoki, and Makoto Nakajima*

Graduate School of Pharmaceutical Sciences, Kumamoto University, 5-1 Oe-honmachi, Chuo-ku, Kumamoto 862-0973, Japan. e-mail: skotani@kumamoto-u.ac.jp, nakajima@gpo.kumamoto-u.ac.jp

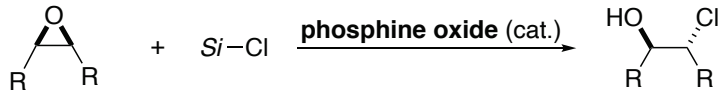
Abstract – Chiral phosphine oxide as a Lewis base could effectively catalyze the enantioselective ring opening of 3-substituted oxetanes with silicon tetrachloride in the presence of *N*,*N*-diisopropylethylamine, affording the corresponding 2-substituted 1,3-chlorohydrins in high yields and good enantioselectivities.

Desymmetrization of prochiral compounds is one of the most useful and reliable strategies to obtain enantiomerically enriched products in organic synthesis.[1] In particular, the asymmetric ring opening of three-membered heterocyclic compounds such as epoxides and aziridines has attracted significant attention for accessing enantiomerically enriched building blocks with two contiguous stereogenic centers. On the other hand, only a few examples of the asymmetric ring opening of four-membered heterocyclic compounds such as oxetanes and azetidines have been explored in synthetic chemistry. Among these, significant attention has been paid to oxetanes because of their structural relevance in medicinal chemistry.[2,3] In 1996, Tomioka and coworkers reported the asymmetric addition of phenyllithium to oxetanes with a moderate enantioselectivity.[4] Jacobsen and coworkers applied a chiral Co(salen) complex to the opening of 3-(*o*-hydroxyphenyl)oxetanes through an intramolecular rearrangement of the hydroxy group to access an enantiomerically enriched tetrahydrofuran derivative with high enantioselectivity.[5] Sun and coworkers reported that a chiral phosphoric acid catalyst successfully promoted the aminative oxetane opening sequence for the enantioselective synthesis of tetrahydroisoquinolines[6] and extended it to the enantioselective chlorinative oxetane opening using trimethoxysilyl chloride as the chloride source.[7] Recently, Jacobsen has demonstrated that chiral squaric acid could mediate the asymmetric oxetane opening in a highly enantioselective manner.[8] Thus, the development of asymmetric oxetane opening has particularly received considerable attention from synthetic chemists. In this study, we have developed

This paper is dedicated to Professor Yasuyuki Kita on the occasion of his 77th birthday.

the chiral phosphine oxide-catalyzed asymmetric oxetane opening with silicon tetrachloride. The silicon complex mediated the ring opening of epoxides to the desired product in high yield and high enantioselectivity (Figure 1-a).[9] The high Lewis acidity and nucleophilicity of the hypervalent silicon complex formed from silicon tetrachloride and phosphine oxide catalyst are speculated to facilitate the asymmetric opening of oxetanes (Figure 1-b).

(a) Previous Work: Epoxide opening catalyzed by chiral phosphine oxide



(b) **This Work**: Oxetane opening catalyzed by chiral phosphine oxide

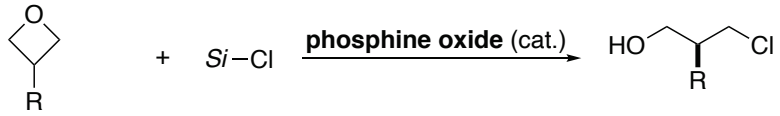
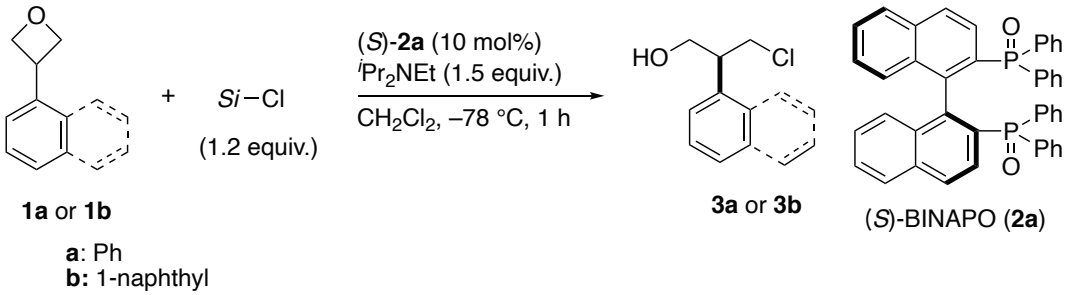


Figure 1. Phosphine oxide-catalyzed asymmetric ring openings

We initially examined the ring opening of 3-phenyloxetane (**1a**) with silicon tetrachloride in the presence of chiral phosphine oxide, (*S*)-BINAPO (**2a**, 10 mol%), and *N*,*N*-diisopropylethylamine in dichloromethane at –78 °C (Table 1, entry 1). Gratifyingly, the ring opening reaction of **1a** was complete in 1 hour and 2-phenyl-3-chloropropan-1-ol (**3a**) was obtained in 90% yield with moderate enantioselectivity (40% ee). To investigate the reactivity and selectivity, various chlorosilanes were employed for the oxetane opening (entries 2–5). Trichlorosilane and hexachlorodisilane could efficiently mediate the oxetane opening, although the yields and selectivities were poorer than those obtained with silicon tetrachloride (entries 2 and 3). Phenyltrichlorosilane and trichlorosilyl triflate were ineffective in this reaction (entries 4 and 5). Thus, silicon tetrachloride was concluded to be the optimal reagent for oxetane ring opening. We conducted an enantioselective ring opening of **1b** giving the corresponding alcohol **3b** in 90% yield and 60% ee (entry 6).

Table 1. Chiral phosphine oxide-catalyzed enantioselective oxetane opening[a]



1a or **1b**

a: Ph
b: 1-naphthyl

3a or **3b**

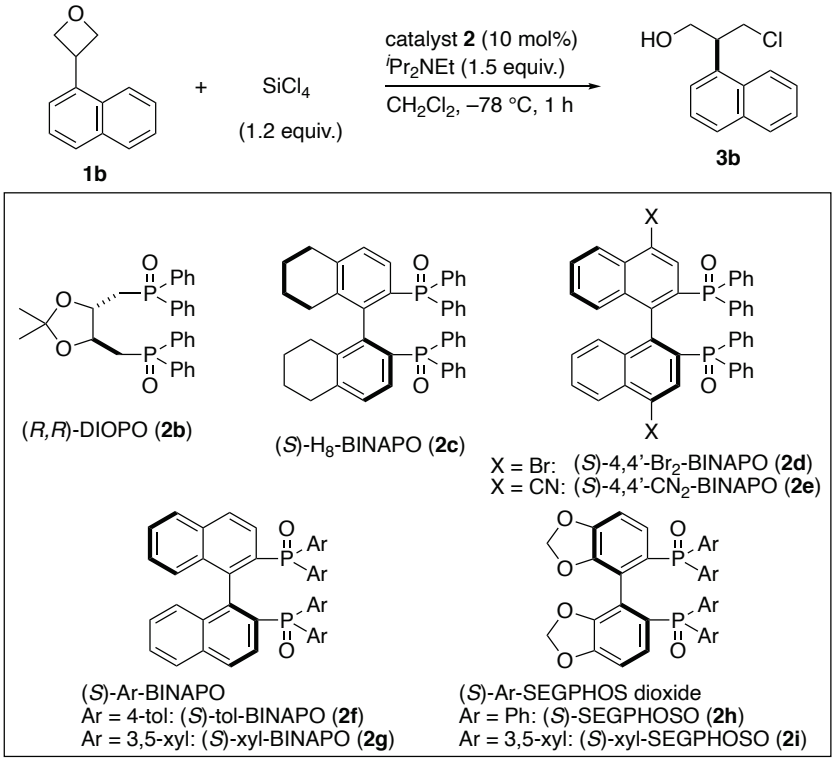
(*S*)-BINAPO (**2a**)

entry	**1**	*Si*-Cl	yield (%)[b]	ee (%)[c]
1	**1a**	$SiCl_4$	90	40
2	**1a**	$HSiCl_3$	26	5
3	**1a**	$Cl_3SiSiCl_3$	34	5
4	**1a**	$PhSiCl_3$	0	–[d]
5	**1a**	$SiCl_3OTf$	0	–[d]
6	**1b**	$SiCl_4$	90	60

[a]Reaction was conducted by treating oxetane **1** (0.5 mmol) with chlorosilane (1.2 equiv.) in the presence of catalyst (*S*)-**2a** (10 mol%) and $^{i}Pr_2NEt$ (1.5 equiv.) in CH_2Cl_2 at –78 °C. [b]Isolated yield. [c]Determined by HPLC. [d]Not determined.

To improve the enantioselectivity, we next screened a variety of chiral phosphine oxides in the reaction of oxetane **1b** (Table 2). Although the enantioselectivity decreased with (*R*,*R*)-DIOP dioxide (DIOPO, **2b**), the enantioselectivity with (*S*)-H_8-BINAPO (**2c**) was similar to that obtained with **2a** (entry 3). The introduction of 4,4'-substituents on the binaphthyl skeletons of **2a** increased the enantioselectivities slightly (entries 4 and 5). Replacing the phenyl groups of **2a** with 4-tolyl moieties ((*S*)-tol-BINAPO, **2f**) or 3,5-xylyl moieties ((*S*)-xyl-BINAPO, **2g**) increased the enantioselectivities (entries 6 and 7). The highest enantioselectivity was obtained with (*S*)-xyl-BINAPO (**2g**). A trend similar to that observed for the aryl substituents was observed with catalysts **2h** and **2i**, which bore the SEGPHOS skeleton (entries 8 and 9).

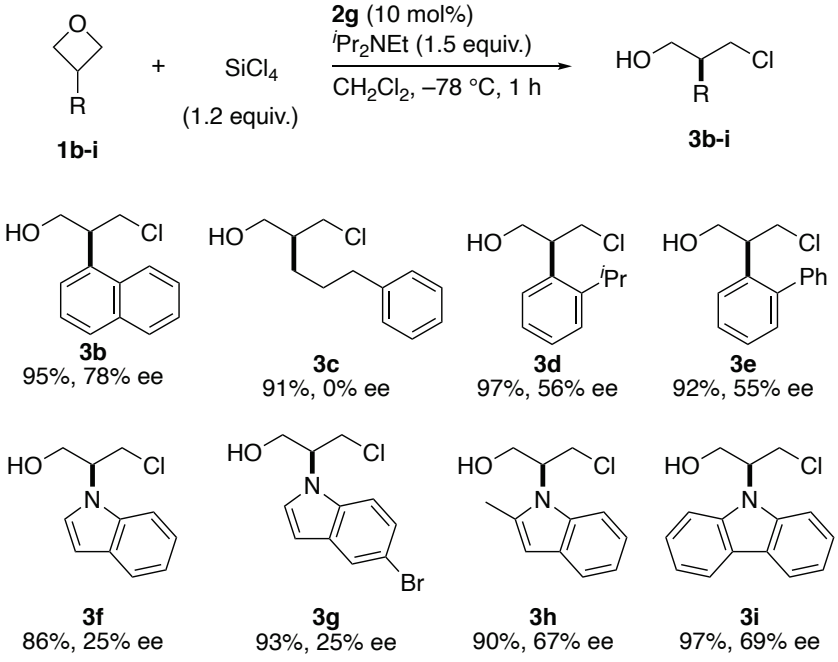
Table 2. Screening of chiral phosphine oxides[a]



entry	catalyst	yield (%)[b]	ee (%)[c]
1	**2a**	90	60
2	**2b**	57	25
3	**2c**	94	57
4	**2d**	97	64
5	**2e**	48	64
6	**2f**	80	65
7	**2g**	95	78
8	**2h**	97	71
9	**2i**	79	74

[a]Reaction was conducted by treating oxetane **1b** (0.5 mmol) with silicon tetrachloride (1.2 equiv.) in the presence of catalyst **2** (10 mol%) and $^{i}Pr_2NEt$ (1.5 equiv.) in CH_2Cl_2 at –78 °C. [b]Isolated yield. [c]Determined by HPLC.

With phosphine oxide **2g** as a catalyst, we conducted the enantioselective opening of various oxetane **1** (Scheme 1). There was a complete loss in enantioselectivity in the ring opening of oxetane **1c**, which bore a flexible propylene chain. *o*-Isopropylphenyloxetane (**1d**) and (1-biphenyl)-3-oxetane (**1e**), which are sterically rigid in the vicinity of the oxetane rings, gave products **3d** and **3e** with moderate enantioselectivities. The ring opening reaction of oxetanes **1f-i** bearing indole and carbazole moieties proceeded smoothly to give products **3f-i** in good yields, although there was some variation in the enantioselectivities.



Scheme 1. Enantioselective oxetane opening catalyzed by phosphine oxide **2g**.

In conclusion, we have demonstrated the phosphine oxide-catalyzed enantioselective oxetane opening reaction for the first time. The hypervalent silicon complex formed from phosphine oxide catalyst and silicon tetrachloride facilitated the oxetane opening to give optically enriched 3-chloropropan-1-ols with good enantioselectivities. Catalyst screening revealed that the substituent effect of the aryl groups affected the enantioselectivities. In future, we shall design and synthesize other novel phosphine oxide catalysts to further improve the stereoselectivity.

EXPERIMENTAL

Optical rotations were recorded on a JASCO P-1010 polarimeter. Infrared spectra were recorded on Perkin Elmer Frontier spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-ECX400 spectrometer. Tetramethylsilane (TMS) (δ = 0 ppm) and $CDCl_3$ (δ = 77.0 ppm) were used as the internal standards for ^{1}H and ^{13}C NMR spectroscopy, respectively. Mass spectrometry was performed on a Brüker Daltonics Impact II KUP spectrometer. High-performance liquid chromatography (HPLC) was performed on a JASCO P-2080 chromatograph equipped with a UV-2075 UV detector, and chiral separations were performed on Daicel CHIRALPAK or CHRALCEL columns (φ 0.46 x 25 cm). Thin-layer chromatography (TLC) was conducted on Merck Kieselgel 60 F_{254} plates. The plates were visualized under UV light (λ = 254 nm) and with phosphomolybdic acid and anisaldehyde. Column chromatography was performed using Kanto Chemical Silica Gel 60N (spherical, neutral, 63–210 μm). All the reactions were performed under argon atmosphere using oven-dried glassware equipped with a rubber septum and a magnetic stirring bar. Dry CH_2Cl_2(dehydrated) was purchased from Kanto Chemical. (*S*)-BINAP dioxide (BINAPO) was prepared by oxidizing (*S*)-BINAP with hydrogen peroxide in CH_2Cl_2.[10] (*S*)-4,4'-Disubstituted BINAPO derivatives were synthesized according to a literature method.[11] The 3-substituted oxetanes **1a-i** were prepared using literature methods.[7,12–14] All other solvents and chemicals were purified using standard procedures.

General experimental procedure: To a solution of oxetane **1a** (0.50 mmol), (*S*)-**2a** (32.3 mg, 10 mol%) in CH_2Cl_2, *N*,*N*-diisopropylethylamine (0.13 mL, 1.5 eq.) was added at –78 °C. To the mixture, silicon tetrachloride (0.60 mL, 1.2 eq., 1.0 M in CH_2Cl_2) was added dropwise, and the reaction mixture was stirred for 1 h at the same temperature. The reaction was quenched with 1.5 M KF/HCO_2H (3.0 mL), and the slurry was stirred for 1 h. The two-layer mixture was extracted with EtOAc (20 mL × 3). The combined organic layer was washed with brine (20 mL) and dried over Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography (SiO_2: 4.0 g, hexane/EtOAc = 12/1) to yield **3a** as a colorless liquid.

(*S*)-3-Chloro-2-phenylpropan-1-ol (3a):[7] Colorless liquid. TLC: R_f = 0.33 (hexane/EtOAc = 4/1, stained black with phosphomolybdic acid). $[\alpha]_D^{20}$ +3.8 (*c* 0.50, $CHCl_3$) for 40% ee,: lit. $[\alpha]_D^{25}$ −29.9 (*c* 1.0, $CHCl_3$) for 94% ee (*R*)-isomer).[7] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.16–3.22 (m, 1H), 3.79 (dd, 1H, *J* = 4.8, 6.4 Hz), 3.88 (dd, 1H, *J* = 4.8, 8.0 Hz), 3.97 (q, 2H, *J* = 2.8 Hz), 7.25–7.38 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.2, 128.8, 127.9, 127.6, 64.2, 49.9, 45.5. The enantiomeric excess was determined to be 40% ee by chiral HPLC with Daicel Chiralcel OD-3 column [eluent: hexane/IPA = 19/1; flow rate: 1.0 mL/min; detection: 254 nm; t_R: 14.7 min (minor), 15.8 min (major)]. The absolute configuration was determined by comparison to reported retention time of HPLC analysis and optical rotation.[7]

(+)-3-Chloro-2-(1-naphthyl)propan-1-ol (3b): Colorless liquid. TLC: R_f = 0.38 (hexane/EtOAc = 4/1, stained black with phosphomolybdic acid); $[\alpha]_D^{20}$ +14.3 (*c* 1.03, $CHCl_3$) for 78% ee. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.95 (q, 1H, *J* = 5.2 Hz), 4.02–4.19 (m, 4H), 7.41–7.59 (m, 4H), 7.80 (d, 1H, *J* = 8.4 Hz), 7.91 (d, 1H, *J* = 8.4 Hz), 8.07 (d, 1H, *J* = 8.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.9, 134.0, 131.6, 129.1, 128.0, 126.5, 125.7, 125.2, 124.0, 122.4, 63.4, 45.4, 43.8. IR (ATR, cm^{-1}): 3343. HRMS (ESI): Calcd for $C_{13}H_{13}ClNaO$ 243.0547, found 243.0542. The enantiomeric excess was determined to be 78% ee by chiral HPLC with Daicel Chiralcel IE-3 column [eluent: hexane/IPA = 19/1; flow rate: 1.0 mL/min; detection: 254 nm; t_R: 10.9 min (major), 16.2 min (minor)].

(±)-3-Chloro-2-(3-phenylpropyl)propan-1-ol (3c): Colorless liquid. TLC: R_f = 0.43 (hexane/EtOAc = 4/1, stained black with phosphomolybdic acid). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.38–1.48 (m, 2H), 1.59–1.74 (m, 2H), 1.88–1.92 (m, 1H), 2.63 (t, 2H, *J* = 7.6 Hz), 3.59–3.72 (m, 4H), 7.17–7.21 (m, 2H), 7.26–7.31 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.0, 128.3, 125.8, 62.6, 45.8, 42.3, 35.9, 28.6, 27.9. IR (ATR, cm^{-1}): 3341, 2932. HRMS (ESI): Calcd for $C_{12}H_{17}ClNaO$ 235.0860, found 235.0853. The enantiomeric excess was determined to be 0% ee by chiral HPLC with Daicel Chiralpak AS-H column [eluent: hexane/IPA = 19/1; flow rate: 1.0 mL/min; detection: 254 nm; t_R: 10.7 min, 11.7 min].

(+)-3-Chloro-2-(2-isopropylphenyl)propan-1-ol (3d): Colorless liquid. TLC: R_f = 0.37 (hexane/EtOAc = 4/1, stained black with phosphomolybdic acid); $[\alpha]_D^{20}$ +13.0 (*c* 1.1, $CHCl_3$) for 56% ee. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.25 (d, 6H, *J* = 6.8 Hz), 3.21–3.28 (m, 1H), 3.60–3.67 (m, 1H), 3.74 (dd, 1H, *J* = 4.8, 6.0 Hz), 3.89 (dd, 1H, *J* = 2.8, 8.0 Hz), 3.92–4.03 (m, 2H), 7.20 (d, 2H, *J* = 4.0 Hz), 7.27–7.29 (m, 1H), 7.33 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.4, 135.8, 127.6, 126.0, 125.8, 64.5, 45.9, 43.9, 28.4, 24.0, 23.9. IR (ATR, cm^{-1}): 3423, 2962. HRMS (ESI): Calcd for $C_{12}H_{17}ClNaO$ 235.0860, found 235.0860. The enantiomeric excess was determined to be 56% ee by chiral HPLC with Daicel Chiralcel OD-3 column [eluent: hexane/IPA = 19/1; flow rate: 1.0 mL/min; detection: 254 nm; t_R: 8.5 min (major), 10.9 min (minor)].

(–)-2-([1,1'-Biphenyl]-2-yl)-3-chloropropan-1-ol (3e): Colorless liquid. TLC: R_f = (hexane/EtOAc = 4/1, stained black with phosphomolybdic acid); $[\alpha]_D^{20}$ –1.3 (*c* 0.55, $CHCl_3$) for 55% ee. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.44–3.49 (m, 1H), 3.72 (dd, 1H, *J* = 6.8, 11.2 Hz), 3.81 (dd, 1H, *J* = 7.6, 11.2 Hz), 3.84–3.93 (m, 2H), 7.26–7.45 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.4, 136.5, 133.3, 130.6, 129.3, 128.2, 127.7, 127.1, 126.9, 126.4, 64.3, 45.8, 44.8. IR (ATR, cm^{-1}): 3338, 2878. HRMS (ESI): Calcd for $C_{15}H_{15}ClNaO$ 269.0704, found 269.0700. The enantiomeric excess was determined to be 55% ee by chiral HPLC with Daicel Chiralcel OD-3 column [eluent: hexane/IPA = 19/1; flow rate: 1.0 mL/min; detection: 254 nm; t_R: 9.7 min (major), 13.4 min (minor)].

(*S*)-3-Chloro-2-(1*H*-indol-1-yl)propan-1-ol (3f):[7] Colorless liquid. TLC: R_f = 0.21 (hexane/EtOAc = 4/1, stained black with phosphomolybdic acid); $[\alpha]_D^{20}$ –1.83 (*c* 1.11, $CHCl_3$) for 25% ee. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.91 (dd, 1H, *J* = 6.4, 11.6 Hz), 4.00 (dd, 1H, *J* = 6.9, 11.4 Hz), 4.12–4.21 (br, 2H), 4.73–4.79 (m, 1H), 6.60 (d, 1H, *J* = 3.7 Hz), 7.15 (t, 1H, *J* = 7.6 Hz), 7.22–7.27 (m, 1H), 7.30 (d, 1H, *J* = 3.2 Hz), 7.37 (d, 1H, *J* = 8.2 Hz), 7.66 (d, 1H, *J* = 7.6 Hz). The enantiomeric excess was determined to be 25% ee by chiral HPLC with Daicel Chiralpak AS-H column [eluent: hexane/IPA = 9/1; flow rate: 1.0 mL/min; detection: 254 nm; t_R: 9.97 min (major), 11.0 min (minor)]. The absolute configuration was determined by comparison to reported retention time of HPLC analysis.[7]

(*S*)-2-(5-Bromo-1*H*-indol-1-yl)-3-chloropropan-1-ol (3g):[7] Colorless liquid. TLC: R_f = 0.13 (hexane/EtOAc = 4/1, stained red with anisaldehyde). $[\alpha]_D^{29}$ –1.85 (*c* 1.04, $CHCl_3$) for 25% ee. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.88 (dd, 1H, *J* = 6.4, 11.6 Hz), 3.98 (dd, 1H, *J* = 6.4, 11.2 Hz), 4.08–4.18 (m, 2H), 4.66–4.72 (m, 1H), 6.52 (d, 1H, *J* = 3.2 Hz), 7.25 (d, 1H, *J* = 3.7 Hz), 7.30–7.32 (m, 1H), 7.76 (d, 1H, *J* = 2.1 Hz). The enantiomeric excess was determined to be 25% ee by chiral HPLC with Daicel Chiralcel IE-3 column [eluent: hexane/IPA = 19/1; flow rate: 1.0 mL/min; detection: 254 nm; t_R: 11.0 min (major), 12.0 min (minor)]. The absolute configuration was determined by comparison to reported retention time of HPLC analysis.[7]

(*S*)-2-(2-Methyl-1*H*-indol-1-yl)-3-chloropropan-1-ol (3h):[7] Colorless liquid. TLC: R_f = 0.25 (hexane/EtOAc = 4/1, stained black with phosphomolybdic acid). $[\alpha]_D^{30}$ +20.5 (*c* 1.07, $CHCl_3$) for 67% ee. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.47 (s, 3H), 4.06 (d, 2H, *J* = 7.2 Hz), 4.16 (d, 1H, *J* = 11.4 Hz), 4.29–4.34 (m, 1H), 4.68 (t, 1H, *J* = 4.8 Hz), 6.28 (s, 1H), 7.31 (dd, 1H, *J* = 2.5, 3.7 Hz), 7.53 (dd, *J* = 2.5, 6.2 Hz). The enantiomeric excess was determined to be 67% ee by chiral HPLC with Daicel Chiralcel IC-3 column [eluent: hexane/IPA = 19/1; flow rate: 1.0 mL/min; detection: 254 nm; t_R: 9.61 min (major), 11.4 min (minor)]. The absolute configuration was determined by comparison to reported retention time of HPLC analysis.[7]

(*S*)-2-(9*H*-Carbazol-9-yl)-3-chloropropan-1-ol (3i):[7] Colorless liquid. TLC: R_f = 0.23 (hexane/EtOAc = 4/1, stained black with phosphomolybdic acid). $[\alpha]_D^{20}$ –0.67 (*c* 1.10, $CHCl_3$) for 69% ee. ^1H NMR ($CDCl_3$, 400 MHz): δ 4.10–4.15 (m, 1H), 4.22 (dd, 1H, *J* = 6.8, 11.6 Hz), 4.32 (dd, *J* = 5.6, 12.0 Hz), 5.03–5.10 (m, 1H), 7.26–7.30 (m, 3H), 7.45–7.52 (m, 3H), 8.12 (d, 2H, *J* = 7.8 Hz). The enantiomeric excess was determined to be 69% ee by chiral HPLC with Daicel Chiralpak AS-H column [eluent: hexane/IPA = 9/1; flow rate: 1.0 mL/min; detection: 254 nm; t_R: 12.6 min (major), 14.1 min (minor)]. The absolute configuration was determined by comparison to reported retention time of HPLC analysis.[7]

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