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Aryl Bromides as Inexpensive Starting Materials in the Catalytic Enantioselective Arylation of Aryl Aldehydes: The Additive TMEDA Enhances the Enantioselectivity

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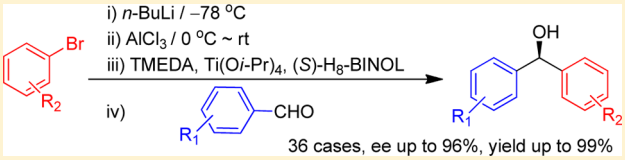
Supporting Information

ABSTRACT: We used aryl bromides as inexpensive starting materials to enantioselectively arylate aldehydes in one pot. Aryl bromides readily transfer aryls to aryllithiums with *n*-butyllithium, successively to triarylaluminums with aluminum chloride, and then to aryltitaniums with titanium isopropoxide. Finally aryltitaniums arylate aldehydes catalyzed by (*S*)-H_8-BINOL−Ti(O*i*-Pr)$_2$ in excellent yields and enantioselectivities. The additive TMEDA evidently suppresses the racemic background reaction promoted by LiCl generated from salt metathesis. This procedure represents a cost-effective and operationally convenient method for enantioenriched diarylmethanols.



Enantioenriched diarylmethanols are actively pursued because of the great importance of these compounds as key motifs and synthetic intermediates in a considerable number of bioactive compounds and pharmaceuticals.[1] The catalytic enantioselective arylation of aromatic aldehydes with arylmetal reagents has emerged as a powerful and versatile method for the synthesis of enantioenriched diarlymethanols by C−C bond formation.[2] Arylzincs and arylboronic acids have been widely explored for enantioselective arylation of aromatic aldehydes.[3,4] While these two methods are very successful for the preparation of enantioenriched diarylmethanols, their practicability and economic efficiency are greatly hampered by the high expense of arylzinc reagents, including diarylzincs and arylethylzincs derived from the corresponding arylboronic acids and easy-to-ignite diethylzinc,[3] and the expense of arylboronic acids themselves, which are commonly prepared from inexpensive aryl-Grignard reagents or aryllithiums.[5] The utilization of aryltitaniums in the enantioselective arylation of aldehydes, seminally demonstrated by Weber and Seebach,[6] is currently becoming popular because aryltitaniums can be formed from inexpensive starting materials. The successfully disclosed aryltitaniums have mainly been obtained from salt-free arylaluminums,[7] aryl-Grignard reagents,[8] and aryllithiums.[6,9] Aryllithiums can be readily prepared from aryl bromides and *n*-butyllithium.[10] This indicates that aryl bromides can be inexpensive starting materials for enantioenriched diarylmethanols, and the procedure cost can be largely reduced.

Because of the high reactivity, an alternative strategy to the use of aryllithiums is to transfer aryls from aryllithiums to less reactive arylmetals by transmetalation. Seebach,[6] Harada,[9] and Yus[11] transferred aryllithiums to aryltitaniums for enantioselective arylation of aldehydes. However, the method only with less reactive aryltitaniums cannot contribute to high enantioselectivity because the in situ-generated achiral Lewis acid highly introduces racemic background reactions.[11] Therefore, the adverse influence of achiral Lewis acids on the enantioselectivity is a central problem. In this regard, only the groups of Seebach[6] and Harada[9] demonstrated successful methods to address this problem. While they are very successful in affording high enantioselectivity, the practicality of their works suffers from the cost and inconvenience of preparing salt-free aryltitaniums, the slow introduction of reactive aryltitaniums to aldehydes over a long period of time with a syringe pump, or the change of the solvent during the reaction process. Therefore, the highly enantioselective catalytic arylation of aldehydes with aryltitanium intermediates starting from aryl bromides remains a challenge in its economy, practicality, operational convenience, and method diversity. Herein we report a different method for the catalytic enantioselective indirect arylation of aromatic aldehydes with aryllithiums with excellent enantioselectivity in high yield in one pot by using readily available TMEDA as an optimal additive. Aryllithiums are readily prepared in situ from the authentic aryl bromide starting materials, and the reaction conditions are milder. This method represents a conveniently performed, cost-effective, and practicable process.

The use of some appropriate additives to exclude the adverse effect of achiral Lewis acids is the current method, pioneered by

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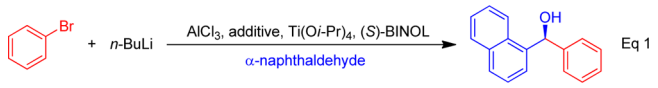
Table 1. Optimization of the Reaction Conditions for the Asymmetric Arylation of Aldehydes[a]



entry	mmol of PhLi[b]	mmol of $AlCl_3$	mmol of $Ti(Oi\text{-}Pr)_4$	ligand[c] (mmol)	additive[d] (mmol)	solvent	temp (time)	conv. (%)[e]	ee (%)[f]
1	1.2	0.4	0.425	L_1 (0.025)	none	THF/Hex	rt (24 h)	99	82
2	1.2	0.4	0.425	L_1 (0.025)	BDMAEE (1.2)	THF/Hex	rt (24 h)	98	88
3	1.2	0.4	0.425	L_1 (0.025)	BDMAEE (1.2)	THF/Hex	rt (24 h)	89	89
4	1.2	0.4	0.425	L_1 (0.025)	BDMAEE (1.2)	THF/Hex	rt (24 h)	93	73
5	1.6	0.4	0.425	L_1 (0.025)	BDMAEE (1.6)	THF/Hex	rt (24 h)	97	90
6	2.0	0.4	0.425	L_1 (0.025)	BDMAEE (2.0)	THF/Hex	rt (24 h)	93	85
7	1.6	0.4	0.425	L_2 (0.025)	BDMAEE (1.6)	THF/Hex	rt (24 h)	98	92
8	1.6	0.4	0.425	L_2 (0.025)	TMEDA (1.6)	THF/Hex	rt (24 h)	99	93
9	1.6	0.4	0.425	L_2 (0.025)	TMPDA (1.6)	THF/Hex	rt (24 h)	98	88
10	1.6	0.4	0.425	L_2 (0.025)	TEEDA (1.6)	THF/Hex	rt (24 h)	99	91
11	1.6	0.4	0.425	L_2 (0.0125)	TMEDA (1.6)	THF/Hex	rt (24 h)	99	85
12	1.6	0.4	0.425	L_2 (0.0325)	TMEDA (1.6)	THF/Hex	rt (24 h)	99	93
13	1.6	0.4	0.345	L_2 (0.025)	TMEDA (1.6)	THF/Hex	rt (24 h)	99	91
14	1.6	0.4	0.505	L_2 (0.025)	TMEDA (1.6)	THF/Hex	rt (24 h)	99	93
15	1.6	0.4	0.425	L_2 (0.025)	TMEDA (0.8)	THF/Hex	rt (24 h)	99	92
16	1.6	0.4	0.425	L_2 (0.025)	TMEDA (1.2)	THF/Hex	rt (24 h)	99	94
17	1.6	0.4	0.425	L_2 (0.025)	TMEDA (1.2)	THF/Hex	0 °C (60 h)	77	90
18	1.6	0.4	0.425	L_2 (0.025)	TMEDA (1.2)	THF/Hex	30 °C (12 h)	99	91
19	1.6	0.4	0.425	L_2 (0.025)	TMEDA (1.2)	THF/Hex	40 °C (6 h)	99 (91[g])	96
20	1.6	0.4	0.425	L_2 (0.025)	TMEDA (1.2)	THF/Hex	50 °C (3 h)	91	90
21	1.6	0.4	0.425	L_2 (0.025)	TMEDA (1.2)	THF	40 °C (3 h)	99	96
22	1.6	0.4	0.425	L_2 (0.025)	TMEDA (1.2)	Et_2O	40 °C (3 h)	99	78
23	1.6	0.4	0.425	L_2(0.025)	TMEDA (1.2)	toluene	40 °C (3 h)	97	79
24	1.6	0.4	0.425	L_2(0.025)	TMEDA (1.2)	MeCN	40 °C (3 h)	61	88
25	2.0	0.5	0.525	L_2(0.025)	TMEDA (1.5)	THF/Hex	40 °C (6 h)	96[g]	96
26	3.0	0.75	0.775	L_2(0.025)	TMEDA (2.25)	THF/Hex	40 °C (6 h)	96[g]	93

[a]0.25 mmol of aldehyde was used. [b]PhLi in entries 1 and 2 was prepared in situ using a PhBr:*n*-BuLi ratio of 1:1, in entries 3 and 5−26 using a PhBr:*n*-BuLi ratio of 1:1.2, and in entry 4 using a PhBr:*n*-BuLi ratio of 1:1.4. [c]$\mathbf{L_1}$ is (*S*)-BINOL; $\mathbf{L_2}$ is (*S*)-H_8-BINOL. [d]The coordinative additive. TMPDA = tetramethylpropanediamine, TEEDA = *N*,*N*,*N*′,*N*′-tetraethylethylenediamine. [e]The conversion was determined by HPLC using diphenyl as an internal standard. [f]Determined by chiral HPLC. The configurations were determined by comparison of the retention times of the major isomers in HPLC with the reported data.[8] [g]Isolated yield.

the groups of Bolm,[12] Chan,[13] and Walsh[14] in studies of catalytic enantioselective addition of arylzinc intermediates to aldehydes. We have also used bis[2-(*N*,*N*-dimethylamino)-ethyl] ether (BDMAEE) to successfully suppress the background reaction in the indirect addition of Grignard reagents to aldehydes.[8c−e] The introduction of additives excludes the need to use salt-free aryltitaniums and low reaction temperatures, to slowly add aryltitaniums to aldehydes over a long period, and to change one solvent to another during the reaction process. We recently explored the catalytic enantioselective arylation of enals with aryltitanium intermediates in excellent yield and enantioselectivity using TMEDA as the additive to exclude the negative catalytic activity of the achiral Lewis acid.[15] On the basis of these results, we determined to explore the operationally convenient and economical preparation of enantioenriched diarylmethanols starting from aryl bromides by searching for a proper additive to inhibit the undesired racemic background reaction promoted by the achiral Lewis acid formed from salt metathesis in this study.

Initially, we used a model reaction (eq 1 in Table 1) to optimize the reaction conditions with our familiar BDMAEE as the additive. PhLi was readily prepared in situ from PhBr and *n*-BuLi, initially in a ratio of 1:1. $AlCl_3$ and $Ti(Oi\text{-}Pr)_4$ were successively introduced to PhLi for the production of first Ph_3Al and then $PhTi(Oi\text{-}Pr)_3$ by salt metathesis. At first, the ratio of PhLi (1.2 mmol) to $AlCl_3$ (0.4 mmol) to $Ti(Oi\text{-}Pr)_4$ (0.4 mmol) was 3:1:1 (Table 1, entries 1−4), and the 10 mmol % (*S*)-BINOL−$Ti(Oi\text{-}Pr)_2$ complex catalyst was formed from (*S*)-BINOL (0.025 mmol) and $Ti(Oi\text{-}Pr)_4$ (0.025 mmol) in a ratio of 1:1. The catalytic arylation was performed at room temperature. Under the initial conditions, 82% ee was achieved without BDMAEE (entry 1). Introducing 1 equiv of BDMAEE raised the enantioselectivity to 88% (PhLi:BDMAEE = 1:1) (entry 2), indicating that BDMAEE inhibited the racemic background reaction to some extent. Modification of the PhBr:*n*-BuLi ratio from 1:1 to 1:1.2 introduced a slight rise in the enantioselectivity to 89% (entries 2 and 3). A further change in the ratio to 1:1.4 led to a sharp decrease in the enantioselectivity to 73% (entries 2−4). With a concurrent increase in the amounts of PhLi and BDMAEE to 1.6 mmol with a PhLi:BDMAEE:$AlCl_3$ ratio of 4:4:1, the ee was slightly enhanced to 90% (entry 5). Further increasing the amounts of PhLi and BDMAEE decreased the enantioselectivity (entry 6). Replacement of the chiral ligand (*S*)-BINOL (**L1**) with (*S*)-H_8-BINOL (**L2**) raised the ee to 92% (entry 7). Screening of three other additives showed that the more easily available and cheap TMEDA achieved the highest enantioselectivity (93% ee) (entries 7−10). Thus, the expense of this protocol was further reduced. Experiments on the catalyst loading showed that 10 mmol % (*S*)-BINOL−$Ti(Oi\text{-}Pr)_2$ was optimal in this study

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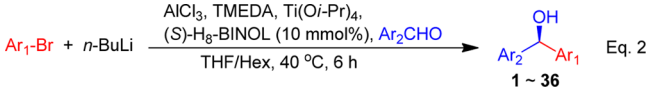
(entries 8, 11, and 12). Decreasing the amount of Ti(O*i*-Pr)$_4$ from 0.425 to 0.345 mmol induced a slight reduction in ee, while increasing the amount of the compound did not change the enantioselectivity (entries 8, 13, and 14). Taking consideration of the additive loading (entries 14−16), the slightly decreased amount of 1.2 mmol of TMEDA was ideal in view of the enantioselectivity (94% ee). This result indicated that the optimal proportion of PhLi to TMEDA was 4:3 (entry 16). The temperature markedly influenced the enantioselectivity (entries 16−20). At 0 °C, not only did the reaction become very sluggish so that the reaction time was greatly prolonged to 60 h, but also the enantioselectivity dropped to 90% ee (entries 16 and 17). Raising the temperature to 40 °C not only greatly shortened the reaction time from 24 to 6 h but also slightly raised the enantioselectivity to 96% ee (entry 19). Using a higher temperature depressed the enantioselectivity (entry 20). In the above investigations, a mixed solvent of THF and hexane was used. THF was used to dissolve PhBr and $AlCl_3$, while hexane was the solvent for *n*-BuLi. Therefore, the effect of using a single solvent on the enantioselectivity was investigated (entries 21−24). The THF/hexane mixed solvent was completely removed in vacuo and then another dried solvent was introduced into the reaction mixture in the experimental process. Both THF and the THF/hexane mixed solvent gave the same highest enantioselectivity (96% ee; entries 19 and 21). On the basis of operational convenience, procedure cost, and reduction of waste solvents, the THF/hexane mixture was selected as the preferred solvent. Finally, we investigated the PhLi loading in terms of the enantioselectivity and yield (entries 19, 25, and 26). The results clearly indicated that increasing the amount of PhLi to 2.0 mmol was ideal, as it gave a raised 96% yield (entry 25) while maintaining the high 96% ee.

With the finely optimized reaction conditions in hand, we explored the substrate scope of this protocol. We first examined the phenylation of aldehydes with PhBr as the starting material (Table 2, entries 1−15). Remarkable yields and enantioselectivities were obtained with these aldehydes. Electron-withdrawing and electron-donating groups in the benzene ring were both well-tolerated. The highest enantioselectivity was up to 96% ee (entries 1, 10, and 12). Heteroaryl aldehydes also afforded high yields and ee (entries 10 and 11). Aliphatic aldehydes gave lower yields because of their low reactivities. An α-branched aldehyde obtained high ee (92%) (entry 14). For the linear aldehyde, the enantioselectivity was depressed to 80% ee (entry 15). Next, we explored arylation of different aromatic aldehydes with various available aryl bromides as starting materials (entries 16−36). The results indicated that this process could be well-compatible with these aryl sources. Aryl aldehydes with either electron-withdrawing or electron-donating groups gave high enantioselectivities and yields. The highest enantioselectivity was up to 96% ee (entry 21). Heteroaryl aldehydes also resulted in ≥90% ee (entries 23, 27, and 31). Even aliphatic aldehydes achieved a high ee of 86% (entries 28 and 35).

We suppose that the LiCl side product generated in situ during the salt metathesis is chelated by TMEDA (Figure 1).[16] The chelation strongly suppresses the racemic background reaction catalyzed by LiCl, just as in Walsh's report with TEEDA[14] and our work with BDMAEE.[8c−e] The phenyl group is finally transferred to Ti by continuous transmetalation. The resulting PhTi(O*i*-Pr)$_3$ delivers the phenyl group to the aldehyde catalyzed by (*S*)-H$_8$-BINOL−Ti(O*i*-Pr)$_2$ in a highly enantioselective mode.

In summary, we have successfully developed a highly enantioselective catalytic arylation of aldehydes using cheap

Table 2. Catalytic Asymmetric Arylation of Aldehydes[a]



entry	Ar_1	Ar_2	yield (%)[b]	ee (%)[c]
1	Ph	3-MeOC$_6$H$_4$	92	96
2	Ph	4-MeOC$_6$H$_4$	94	92
3	Ph	3-MeC$_6$H$_4$	96	92
4	Ph	4-MeC$_6$H$_4$	95	94
5	Ph	2-ClC$_6$H$_4$	95	89
6	Ph	4-ClC$_6$H$_4$	95	92
7	Ph	4-BrC$_6$H$_4$	92	91
8	Ph	4-FC$_6$H$_4$	89	92
9	Ph	4-F$_3$CC$_6$H$_4$	94	90
10	Ph	2-thienyl	94	96
11	Ph	2-furyl	90	92
12	Ph	1-naphthyl	91	96
13	Ph	2-naphthyl	90	90
14	Ph	*c*-Hex	72	92
15	Ph	*n*-nonyl	71	80
16	4-FC$_6$H$_4$	Ph	98	93
17	4-FC$_6$H$_4$	2-naphthyl	85	91
18	4-FC$_6$H$_4$	1-naphthyl	92	94
19	4-ClC$_6$H$_4$	Ph	90	91
20	4-ClC$_6$H$_4$	4-MeOC$_6$H$_4$	83	88
21	4-ClC$_6$H$_4$	1-naphthyl	81	96
22	4-ClC$_6$H$_4$	4-FC$_6$H$_4$	87	90
23	4-ClC$_6$H$_4$	2-thienyl	87	90
24	3-MeOC$_6$H$_4$	Ph	94	86
25	3-MeOC$_6$H$_4$	4-ClC$_6$H$_4$	96	88
26	3-MeOC$_6$H$_4$	4-MeC$_6$H$_4$	93	87
27	3-MeOC$_6$H$_4$	2-thienyl	86	91
28	3-MeOC$_6$H$_4$	*c*-Hex	75	86
29	4-MeC$_6$H$_4$	Ph	95	92
30	4-MeC$_6$H$_4$	1-naphthyl	99	90
31	4-MeC$_6$H$_4$	2-thienyl	93	93
32	2-naphthyl	4-ClC$_6$H$_4$	84	86
33	2-naphthyl	4-MeOC$_6$H$_4$	98	86
34	2-naphthyl	1-naphthyl	89	93
35	2-naphthyl	*c*-Hex	79	86
36	2-naphthyl	2-thienyl	94	83

[a]2.0 mmol of Ar_1Li from Ar_1Br:*n*-BuLi = 1:1.2 at −78 °C, 0.25 mmol of Ar_2CHO, 0.5 mmol of $AlCl_3$, 0.525 mmol of Ti(O*i*-Pr)$_4$, and 1.5 mmol of TMEDA were used. [b]Isolated yields. [c]Determined with chiral HPLC. The configurations were determined by comparison of the retention times of major isomers in HPLC with the reported data.[8]

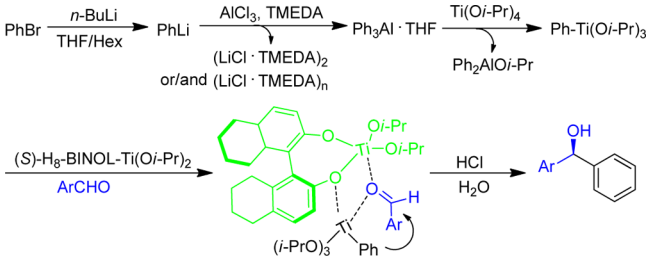


Figure 1. Proposed reaction mechanism.

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aryl bromides as starting aryl sources under the catalysis of the (*S*)-H_8-BINOL−Ti(O*i*-Pr)$_2$ complex under mild reaction conditions in one pot. Aryl bromides readily transfer aryls to aryllithiums following the conventional method. Addition of $AlCl_3$ allows aryl transfer to triarylaluminums and generates the achiral Lewis acid LiCl as well. Later introduction of Ti(O*i*-Pr)$_4$ produces aryltitaniums, which finally enantioselectively transfer aryls to aldehydes. LiCl promotes the racemic background reaction and reduces the enantioselectivity of the transformation. TMEDA strongly chelates LiCl and suppresses its catalytic activity, guaranteeing the excellent enantioselectivity in this study. This efficient protocol does not need salt-free aryltitanium intermediates, slow addition of reactive aryltitanium intermediates over a long period, or a change of one solvent to another during the reaction process. Therefore, this work demonstrates a cost-effective, operationally convenient, and thus a very practical method for the synthesis of enantiopure diarylmethanols.

EXPERIMENTAL SECTION

General. All of the reactions were performed under an argon atmosphere, and solvents were dried according to established procedures prior to use. All of the reagents were commercial. Reactions were monitored by thin-layer chromatography (TLC); column and preparative TLC purification were carried out using silica gel. Melting points were recorded on an X-4 melting point apparatus and are uncorrected. Optical rotations were recorded on a polarimeter. ^{1}H NMR and ^{13}C NMR spectra were measured on 400 and 100 MHz spectrometers, respectively, in $CDCl_3$ with TMS as an internal standard; chemical shifts are reported in parts per million. The determination of ee values was carried out using chiral HPLC with an OD-H, OB-H, AS-H, or AD-H column.

General Procedure for the Catalytic Asymmetric Arylation of Aldehydes. Freshly distilled bromobenzene (2.0 mmol, 0.21 mL) and 2.0 mL of dry THF were introduced into a dry 10 mL round-bottom flask equipped with a clean stir bar under an argon atmosphere. The flask was placed into a cold bath at −78 °C, and *n*-BuLi (1.8 M, 2.4 mmol, 1.33 mL) was added dropwise. After 1 h, the mixture was warmed to 0 °C, and a solution of $AlCl_3$ (67 mg, 0.5 mmol) in 1.0 mL of dry THF was added dropwise into the flask. After the flask was warmed to room temperature and kept stirring for about 12 h, TMEDA (1.5 mmol, 223.5 μL) was added. After 30 min of stirring, a mixture of (*S*)-H_8-BINOL (7.4 mg, 0.025 mmol) and Ti(O*i*-Pr)$_4$ (0.525 mmol, 155.4 μL), which had previously been stirred for about 15 min in 1.0 mL of dry THF, was introduced, and the resulting mixture was stirred for further 60 min. Then the aldehyde (0.25 mmol) was added to the flask at room temperature, and the flask was placed into an oil bath at 40 °C and kept stirring for about 6 h (checking with TLC until the reaction was complete). Two drops of icy water was added to the mixture to quench the reaction with a pipet, and then 3.0 mL of 5% HCl was further added into the mixture. The resulting mixture was extracted with ethyl acetate (8.0 mL × 3), and the organic layers were combined, washed with 2.0 mL of brine, dried with anhydrous Na_2SO_4, and condensed under reduced pressure to give an oily residue. The residue was then purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to furnish the pure diarylmethanol.

(S)-(3-Methoxyphenyl)(phenyl)methanol (**1**).[8c] Yield 49.3 mg, 92%; light-yellow oil; $[\alpha]_D^{25}$ = +7 (*c* 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 75:25, flow rate 1.0 mL/min, λ = 222.9 nm) t_r (major) = 7.8 min, t_r (minor) = 11.1 min, ee = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.64 (s, 1H), 3.73 (s, 3H), 5.71 (s, 1H), 6.75−6.76 (d, *J* = 4.0 Hz, 1H), 6.78−6.90 (d, 2H), 6.91−7.34 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 76.1, 112.0, 112.9, 118.8, 126.5, 127.6, 128.5, 129.5, 131.0, 143.6, 145.4, 159.7.

(S)-(4-Methoxyphenyl)(phenyl)methanol (**2**).[8c] Yield 50.4 mg, 94%; light-yellow oil; $[\alpha]_D^{25}$ = −19 (*c* 1.0, $CHCl_3$); HPLC (OJ-H, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 234.5 nm) t_r (major) = 40.6 min, t_r (minor) = 35.8 min, ee = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70 (s, 1H), 3.72 (s, 3H), 5.68 (s, 1H), 6.79−6.82 (d, *J* = 12 Hz, 2H), 7.20−7.32 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 75.7, 113.8, 126.3, 127.3, 127.8, 128.3, 130.9, 136.1, 143.9, 158.9.

(S)-Phenyl(m-tolyl)methanol (**3**).[8c] Yield 47.6 mg, 96%; light-yellow solid, mp 52−53 °C; $[\alpha]_D^{25}$ = −1 (*c* 1.0, $CHCl_3$); HPLC (OB-H, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 226.0 nm) t_r (major) = 15.0 min, t_r (minor) = 9.6 min, ee = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.34 (s, 1H), 5.75 (s, 1H), 7.05−7.07 (d, *J* = 8.0 Hz, 1H), 7.13−7.36 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 76.2, 123.5, 126.4, 127.1, 127.4, 128.3, 128.4, 138.1, 143.7.

(S)-Phenyl(p-tolyl)methanol (**4**).[8c] Yield 47.1 mg, 95%; white solid, mp 57−58 °C; $[\alpha]_D^{25}$ = −5 (*c* 1.0, $CHCl_3$); HPLC (OB-H, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 221.0 nm) t_r (major) = 12.9 min, t_r (minor) = 11.6 min, ee = 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 1H), 2.28 (s, 3H), 5.74 (s, 1H), 7.08−7.33 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 76.0, 126.4, 126.5, 127.4, 128.4, 129.1, 137.2, 140.9, 143.9.

(S)-(2-Chlorophenyl)(phenyl)methanol (**5**).[8c] Yield 51.9 mg, 95%; light-yellow oil; $[\alpha]_D^{25}$ = −16 (*c* 1.0, $CHCl_3$); HPLC (OJ-H, hexane/*i*-PrOH = 70:30, flow rate 1.0 mL/min, λ = 222.2 nm) t_r (major) = 12.9 min, t_r (minor) = 10.2 min, ee = 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.54 (s, 1H), 6.17 (s, 1H), 7.13−7.57 (m, 8H), 7.59−7.60 (d, *J* = 4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.6, 126.9, 127.0, 127.7, 127.9, 128.4, 128.7, 129.5, 132.4, 140.9, 142.1.

(S)-(4-Chlorophenyl)(phenyl)methanol (**6**).[8c] Yield 51.9 mg, 95%; light-yellow solid, mp 51−52 °C; $[\alpha]_D^{25}$ = +19 (*c* 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 85:15, flow rate 1.0 mL/min, λ = 225.0 nm) t_r (major) = 12.0 min, t_r (minor) = 9.0 min, ee = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (s, 1H), 5.70 (s, 1H), 7.21−7.40 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.5, 126.4, 127.8, 128.6, 133.2, 142.1, 143.3.

(S)-(4-Bromophenyl)(phenyl)methanol (**7**).[8c] Yield 60.5 mg, 92%; light-yellow solid, mp 73−75 °C; $[\alpha]_D^{25}$ = +19 (*c* 1.0, $CHCl_3$); HPLC (OB-H, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 230.0 nm) t_r (major) = 11.4 min, t_r (minor) = 9.1 min, ee = 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 1H), 5.77 (s, 1H), 7.23−7.32 (m, 2H), 7.33−7.40 (m, 4H), 7.42−7.45 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.5, 121.3, 126.4, 127.8, 128.1, 128.6, 131.4, 142.6, 143.3.

(S)-(4-Fluorophenyl)(phenyl)methanol (**8**).[8c] Yield 45.0 mg, 89%; light-yellow oil; $[\alpha]_D^{25}$ = +8 (*c* 1.0, $CHCl_3$); HPLC (OB-H, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 224.0 nm) t_r (major) = 18.4 min, t_r (minor) = 15.6 min, ee = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.77 (s, 1H), 5.68 (s, 1H), 6.93−6.99 (m, 2H), 7.22−7.53 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.5, 115.1, 115.3, 126.4, 127.7, 128.1, 128.2, 128.5, 139.5, 143.6, 160.9, 163.3.

(S)-Phenyl(4-(trifluoromethyl)phenyl)methanol (**9**).[8c] Yield 59.3 mg, 94%; light-yellow solid, mp 79−81 °C; $[\alpha]_D^{25}$ = +27 (*c* 1.0, $CHCl_3$); HPLC (OB-H, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 225.0 nm) t_r (major) = 10.2 min, t_r (minor) = 7.6 min, ee = 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (s, 1H), 5.80 (s, 1H), 7.27−7.35 (m, 5H), 7.45−7.47 (m, 2H), 7.55−7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.7, 125.3, 126.6, 128.0, 128.7, 143.1, 147.4.

(S)-Phenyl(thiophen-2-yl)methanol (**10**).[8c] Yield 44.7 mg, 94%; light-yellow solid, mp 49−52 °C; $[\alpha]_D^{25}$ = +27 (*c* 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 95:5, flow rate 1.0 mL/min, λ = 237.8 nm) t_r (major) = 16.9 min, t_r (minor) = 19.1 min, ee = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.72 (s, 1H), 5.96 (s, 1H), 6.83−6.91 (m, 2H), 7.21−7.41 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.3, 124.8, 125.4, 126.2, 126.6, 127.9, 128.5, 130.0, 130.9, 143.0, 148.1.

(S)-Furan-2-yl(phenyl)methanol (**11**).[8f] Yield 39.2 mg, 90%; light-yellow oil; $[\alpha]_D^{25}$ = −6 (*c* 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 95:5, flow rate 1.0 mL/min, λ = 218.9 nm) t_r (major) = 15.1 min, t_r (minor) = 20.9 min, ee = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (s, 1H), 5.74 (s, 1H), 6.06−6.07 (d, *J* = 4.0 Hz, 1H), 6.28 (s, 1H), 7.27−7.40 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 70.0, 107.4, 110.1, 126.5, 128.0, 128.4, 140.7, 142.5, 155.9.

(S)-Naphthalen-1-yl(phenyl)methanol (**12**).[8c] Yield 53.3 mg, 91%; colorless oil; $[\alpha]_D^{25}$ = −42 (*c* 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-

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PrOH = 75:25, flow rate 1.0 mL/min, λ = 225.8 nm) t_r (major) = 7.8 min, t_r (minor) = 17.1 min, ee = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.68 (s, 1H), 6.37 (s, 1H), 7.16−7.42 (m, 8H), 7.52−7.54 (d, J = 8.0 Hz, 1H), 7.74−7.82 (m, 2H), 7.92−7.94 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 73.5, 123.9, 124.5, 125.2, 125.5, 126.1, 127.0, 127.6, 128.4, 128.7, 130.6, 133.8, 138.7, 143.0.

*(S)-Naphthalen-2-yl(phenyl)methanol (**13**).*[7b] Yield 52.7 mg, 90%; white solid, mp 44−46 °C; $[\alpha]_D^{25}$ = +6 (c 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 92:8, flow rate 1.0 mL/min, λ = 235.7 nm) t_r (major) = 18.9 min, t_r (minor) = 22.9 min, ee = 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 (s, 1H), 5.77 (s, 1H), 7.19−7.10 (m, 6H), 7.39−7.42 (m, 2H), 7.66−7.73 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 76.3, 112.9, 124.7, 125.0, 125.9, 126.1, 126.6, 127.6, 128.0, 128.3, 128.5, 130.1, 131.0, 132.8, 133.2, 137.1, 141.0, 143.6, 151.4.

*(R)-Cyclohexyl(phenyl)methanol (**14**).*[8c] Yield 34.3 mg, 72%; white solid, mp 64−65 °C; $[\alpha]_D^{25}$ = +26 (c 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 98:2, flow rate 1.0 mL/min, λ = 213.8 nm) t_r (major) = 12.9 min, t_r (minor) = 11.6 min, ee = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86−1.59 (m, 12H), 4.33−4.34 (d, J = 4 Hz, 1H), 7.23−7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 26.0, 26.4, 28.7, 29.3, 44.8, 79.2, 126.8, 128.3, 129.1, 145.3.

*(R)-1-Phenyldecan-1-ol (**15**).*[8c] Yield 41.6 mg, 71%; colorless oil; $[\alpha]_D^{25}$ = +24 (c 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 98:2, flow rate 1.0 mL/min, λ = 209.7 nm) t_r (major) = 9.5 min, t_r (minor) = 10.3 min, ee = 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86−0.89 (m, 3H), 1.18−1.24 (m, 14H), 1.68−1.82 (m, 2H), 2.02 (s, 1H), 4.61−4.65 (t, J = 8.0 Hz, 1H), 7.25−7.33 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 25.7, 29.2, 29.5, 31.8, 39.0, 74.5, 125.8, 127.3, 128.2, 144.9.

*(R)-(4-Fluorophenyl)(phenyl)methanol (**16**).*[3d] Yield 49.5 mg, 98%; light-yellow oil; $[\alpha]_D^{25}$ = −11 (c 1.0, $CHCl_3$); HPLC (OB-H, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 210.0 nm) t_r (major) = 14.8 min, t_r (minor) = 20.0 min, ee = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 1H), 5.79 (s, 1H), 6.98−7.03 (m, 2H), 7.24−7.34 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.5, 121.3, 126.4, 127.8, 128.1, 128.6, 131.4, 142.6, 143.3.

*(S)-(4-Fluorophenyl)(naphthalen-2-yl)methanol (**17**).*[8c] Yield 53.6 mg, 85%; light-yellow oil; $[\alpha]_D^{25}$ = −43 (c 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 268.9 nm) t_r (major) = 9.1 min, t_r (minor) = 10.4 min, ee = 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 1H), 6.50 (s, 1H), 6.98−7.02 (m, 2H), 7.34−7.51 (m, 5H), 7.60−7.62 (d, J = 8.0 Hz, 1H), 7.81−7.88 (m, 2H), 7.97−7.98 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.6, 115.2, 115.4, 124.5, 125.0, 126.1, 126.3, 127.7, 128.0, 128.4, 132.9, 133.2, 139.3, 140.9.

*(S)-(4-Fluorophenyl)(naphthalen-1-yl)methanol (**18**).*[8c] Yield 58.0 mg, 92%; white solid, mp 54−56 °C; $[\alpha]_D^{25}$ = +4 (c 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 222.5 nm) t_r (major) = 8.6 min, t_r (minor) = 21.5 min, ee = 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 1H), 5.97 (s, 1H), 6.99−7.04 (t, J = 8.0 Hz, 2H), 7.36−7.51 (m, 5H), 7.78−7.86 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 73.0, 115.2, 115.4, 123.8, 124.5, 125.3, 125.6, 126.2, 128.6, 128.7, 130.5, 133.9, 138.5, 138.8, 160.9, 163.4.

*(R)-(4-Chlorophenyl)(phenyl)methanol (**19**).*[4c] Yield 49.2 mg, 90%; white solid, mp 52−53 °C; $[\alpha]_D^{25}$ = −16 (c 1.0, $CHCl_3$); HPLC (OB-H, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 223.2 nm) t_r (major) = 9.0 min, t_r (minor) = 12.9 min, ee = 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (s, 1H), 5.70 (s, 1H), 7.21−7.40 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.5, 126.4, 127.8, 128.6, 133.2, 142.1, 143.3.

*(R)-(4-Chlorophenyl)(4-methoxyphenyl)methanol (**20**).*[4c] Yield 51.6 mg, 83%; light-yellow oil; $[\alpha]_D^{25}$ = −21 (c 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 228.4 nm) t_r (major) = 15.1 min, t_r (minor) = 14.4 min, ee = 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 1H), 3.78 (s, 3H), 5.74 (s, 1H), 6.84−6.86 (d, J = 8.0 Hz, 2H), 7.22−7.29 (m, 6H); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 1H), 3.78 (s, 3H), 5.74 (s, 1H), 6.84−6.86 (d, J = 8.0 Hz, 2H), 7.22−7.29 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 74.9, 115.3, 115.5, 126.9, 127.7, 128.1, 128.2, 128.6, 133.4, 139.1, 142.0, 158.9.

*(S)-(4-Chlorophenyl)(naphthalen-1-yl)methanol (**21**).*[8c] Yield 54.1 mg, 81%; light-yellow oil; $[\alpha]_D^{25}$ = −64 (c 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 85:15, flow rate 1.0 mL/min, λ = 233.6 nm) t_r (major) = 10.8 min, t_r (minor) = 25.3 min, ee = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 1H), 6.45 (s, 1H), 7.24−7.32 (m, 4H), 7.41−7.48 (m, 3H), 7.55−7.57 (d, J = 8.0 Hz, 1H), 7.81−7.87 (m, 2H), 7.96−7.98 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 73.2, 123.8, 124.8, 125.3, 125.7, 126.3, 128.3, 128.6, 128.8, 130.5, 134.0, 138.4, 141.6.

*(R)-(4-Chlorophenyl)(4-fluorophenyl)methanol (**22**).*[4c] Yield 51.5 mg, 87%; light-yellow oil; $[\alpha]_D^{25}$ = −7 (c 1.0, $CHCl_3$); HPLC (OB-H, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 223.4 nm) t_r (major) = 13.1 min, t_r (minor) = 17.4 min, ee = 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 1H), 5.76 (s, 1H), 6.99−7.03 (t, J = 8.8 Hz, 2H), 7.25−7.31 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 74.9, 115.3, 115.5, 127.7, 128.1, 128.2, 128.6, 133.4, 139.1, 142.0, 161.0, 163.5.

*(S)-(4-Chlorophenyl)(thiophen-2-yl)methanol (**23**).*[8c] Yield 48.9 mg, 87%; light-yellow solid, mp 49−51 °C; $[\alpha]_D^{25}$ = +2 (c 1.0, $CHCl_3$); HPLC (AD-H, hexane/*i*-PrOH = 98:2, flow rate 1.0 mL/min, λ = 240.1 nm) t_r (major) = 23.4 min, t_r (minor) = 27.9 min, ee = 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.54 (s, 1H), 6.01 (s, 1H), 6.87−6.95 (m, 2H), 7.25−7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.7, 125.0, 125.7, 126.7, 127.6, 128.7, 133.7, 141.5, 147.6.

*(R)-(3-Methoxyphenyl)(phenyl)methanol (**24**).*[8c] Yield 50.4 mg, 94%; light-yellow oil; $[\alpha]_D^{25}$ = −10 (c 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 75:25, flow rate 1.0 mL/min, λ = 225.8 nm) t_r (major) = 10.4 min, t_r (minor) = 7.5 min, ee = 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 1H), 3.77 (s, 1H), 5.78 (s, 1H), 6.78−6.80 (m, 1H), 6.92−6.94 (m, 2H), 7.22−7.37 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 76.1, 112.0, 112.9, 118.8, 126.5, 127.6, 128.5, 129.5, 131.0, 143.6, 145.4, 151.3, 159.7.

*(R)-(4-Chlorophenyl)(3-methoxyphenyl)methanol (**25**).*[4c] Yield 59.7 mg, 96%; white solid, mp 66−67 °C; $[\alpha]_D^{25}$ = −2 (c 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 85:15, flow rate 1.0 mL/min, λ = 237.7 nm) t_r (major) = 16.8 min, t_r (minor) = 10.4 min, ee = 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 1H), 3.75−3.77 (m, 3H), 5.75 (s, 1H), 6.80−6.82 (d, J = 8.0 Hz, 1H), 6.90−6.91 (m, 2H), 7.22−7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 75.4, 112.0, 113.1, 118.8, 127.8, 128.6, 129.7, 130.1, 131.0, 133.3, 142.0, 145.0, 159.8.

*(R)-(3-Methoxyphenyl)(p-tolyl)methanol (**26**).*[3k] Yield 53.1 mg, 93%; light-yellow oil; $[\alpha]_D^{25}$ = −22 (c 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 224.8 nm) t_r (major) = 17.5 min, t_r (minor) = 12.6 min, ee = 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 4H), 3.77 (s, 3H), 5.75 (s, 1H), 6.77−7.26 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.1, 75.9, 111.9, 112.8, 118.7, 126.4, 129.1, 129.4, 137.2, 140.8, 145.6, 159.6.

*(S)-(3-Methoxyphenyl)(thiophen-2-yl)methanol (**27**).*[17] Yield 47.4 mg, 86%; light-yellow solid, mp 66−67 °C; $[\alpha]_D^{25}$ = −7 (c 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 226.8 nm) t_r (major) = 18.0 min, t_r (minor) = 15.3 min, ee = 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (s, 1H), 3.78 (s, 3H), 6.00 (s, 1H), 6.82−7.01 (m, 5H), 7.24−7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 72.2, 111.6, 113.5, 118.6, 124.9, 125.4, 126.6, 129.5, 144.7, 147.8, 159.7.

*(R)-Cyclohexyl(3-methoxyphenyl)methanol (**28**).*[17] Yield 41.3 mg, 75%; light-yellow oil; $[\alpha]_D^{25}$ = +16 (c 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 95:5, flow rate 1.0 mL/min, λ = 215.4 nm) t_r (major) = 19.7 min, t_r (minor) = 11.3 min, ee = 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92−1.25 (m, 5H), 1.37−1.40 (d, J = 12.0 Hz, 1H), 1.56−1.78 (m, 4H), 1.85 (s, 1H), 1.96−1.99 (d, J = 12.0 Hz, 1H), 3.81 (s, 3H), 4.33−4.34 (d, J = 4.0 Hz, 1H), 6.80−6.88 (m, 3H), 7.22−7.26 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 26.0, 26.4, 28.7, 29.3, 44.8, 55.1, 79.2, 112.1, 112.7, 119.0, 129.1, 145.3, 159.5.

*(R)-Phenyl(p-tolyl)methanol (**29**).*[8c] Yield 47.1 mg, 95%; white solid, mp 55−57 °C; $[\alpha]_D^{25}$ = +20 (c 1.0, $CHCl_3$); HPLC (OB-H, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 217.9 nm) t_r (major) = 7.3 min, t_r (minor) = 8.3 min, ee = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 1H), 2.28 (s, 3H), 5.74 (s, 1H), 7.08−7.33

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(m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 76.0, 126.4, 126.5, 127.4, 128.4, 129.1, 137.2, 140.9, 143.9.

*(S)-Naphthalen-1-yl(p-tolyl)methanol (**30**).*[8c] Yield 61.5 mg, 99%; light-yellow oil; $[\alpha]_D^{25}$ = −33 (*c* 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 281.6 nm) t_r (major) = 7.9 min, t_r (minor) = 16.6 min, ee = 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.37 (s, 1H), 6.47 (s, 1H), 7.10−7.12 (d, *J* = 8.0 Hz, 2H), 7.25−7.27 (d, *J* = 8.0 Hz, 2H), 7.38−7.49 (m, 3H), 7.63−7.65 (d, *J* = 8.0 Hz, 1H), 7.78−7.85 (m, 2H), 7.98−8.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 73.4, 123.9, 124.3, 125.3, 125.5, 125.5, 126.0, 127.0, 128.3, 128.7, 129.2, 130.6, 133.8, 137.3, 138.8, 140.2.

*(S)-Thiophen-2-yl(p-tolyl)methanol (**31**).*[17] Yield 47.5 mg, 93%; light-yellow solid, mp 64−65 °C; $[\alpha]_D^{25}$ = +12 (*c* 1.0, $CHCl_3$); HPLC (AD-H, hexane/*i*-PrOH = 95:5, flow rate 1.0 mL/min, λ = 232.2 nm) t_r (major) = 13.0 min, t_r (minor) = 15.1 min, ee = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.50 (s, 1H), 5.99 (s, 1H), 6.74−6.93 (m, 2H), 7.15−7.17 (d, *J* = 8.0 Hz, 2H), 7.23−7.24 (d, *J* = 4.0 Hz, 1H), 7.30−7.32 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 72.2, 124.7, 125.2, 126.2, 126.6, 129.1, 137.7, 140.2, 148.3.

*(R)-(4-Chlorophenyl)(naphthalen-2-yl)methanol (**32**).*[14b] Yield 56.4 mg, 84%; light-yellow solid, mp 85−86 °C; $[\alpha]_D^{25}$ = +11 (*c* 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 229.1 nm) t_r (major) = 16.8 min, t_r (minor) = 18.7 min, ee = 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 1H), 5.94 (s, 1H), 7.26−7.53 (m, 7H), 7.78−7.95 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.7, 124.5, 125.1, 126.1, 126.3, 127.7, 128.0, 128.6, 132.9, 133.2, 133.3, 140.6, 141.9.

*(R)-(4-Methoxyphenyl)(naphthalen-2-yl)methanol (**33**).*[14b] Yield 64.8 mg, 98%; light-yellow solid, mp 71−73 °C; $[\alpha]_D^{25}$ = −21 (*c* 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 226.1 nm) t_r (major) = 22.8 min, t_r (minor) = 19.0 min, ee = 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 1H), 3.78 (s, 3H), 5.95 (s, 1H), 6.85−6.87 (d, *J* = 8.0 Hz, 2H), 7.30−7.32 (d, *J* = 8.0 Hz, 2H), 7.39−7.41 (d, *J* = 8.0 Hz, 1H), 7.44−7.49 (m, 2H), 7.77−7.84 (m, 3H), 7.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 75.8, 113.8, 124.7, 125.8, 126.1, 127.6, 128.0, 128.2, 132.7, 133.2, 135.9, 141.3, 159.0.

*(S)-Naphthalen-1-yl(naphthalen-2-yl)methanol (**34**).*[8c] Yield 63.3 mg, 89%; light-yellow oil; $[\alpha]_D^{25}$ = −63 (*c* 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 70:30, flow rate 1.0 mL/min, λ = 222.5 nm) t_r (major) = 10.1 min, t_r (minor) = 17.0 min, ee = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (s, 1H), 6.66 (s, 1H), 7.23−7.91 (m, 13H), 8.08−8.10 (d, *J* = 8.0 Hz, 1H); 0.42 (s, 1H), 5.94 (s, 1H), 7.26−7.53 (m, 7H), 7.78−7.95 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.6, 117.2, 124.0, 124.7, 125.2, 125.7, 125.9, 126.2, 126.3, 126.6, 127.7, 127.9, 128.5, 132.8, 133.2, 133.3, 137.0.

*(R)-Cyclohexyl(naphthalen-2-yl)methanol (**35**).*[18] Yield 47.5 mg, 79%; light-yellow solid, mp 56−59 °C; $[\alpha]_D^{25}$ = +8 (*c* 1.0, $CHCl_3$); HPLC (OD-H, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 221.0 nm) t_r (major) = 11.1 min, t_r (minor) = 9.3 min, ee = 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11−1.79 (m, 11H), 2.01−2.04 (m, 1H), 4.54−4.55 (m, 1H), 7.45−7.96 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.0, 26.4, 28.8, 29.4, 44.9, 79.5, 124.7, 125.5, 125.7, 126.0, 127.6, 127.9, 132.9, 133.0, 141.0.

*(S)-Naphthalen-2-yl(thiophen-2-yl)methanol (**36**).*[17] Yield 56.5 mg, 94%; light-yellow oil; $[\alpha]_D^{25}$ = +4 (*c* 1.0, $CHCl_3$); HPLC (AS-H, hexane/*i*-PrOH = 98:2, flow rate 1.0 mL/min, λ = 241.7 nm); t_r (major) = 27.3 min, t_r (minor) = 35.3 min, ee = 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 1H), 5.82 (s, 1H), 6.90−6.95 (m, 2H), 7.24−7.44 (m, 1H), 7.47−7.51 (m, 3H), 7.81−7.95 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.3, 124.1, 125.2, 126.0, 126.3, 126.6, 127.8, 132.6, 132.9, 158.7.

Typical Procedure for the Synthesis of (*S*)-H$_8$-BINOL from (*S*)-BINOL.[19] (*S*)-BINOL (1.43 g, 5 mmol) and 5% Pd/C (1.5 g, 50% wet) were added to 50 mL of EtOH in a 100 mL high-pressure vessel. The reaction mixture was stirred under 10 MPa H_2 at 70 °C for about 7 h until no more H_2 consumption could be detected. The vessel was cooled to room temperature, after which Pd/C was filtered off and the vessel was washed with CH_2Cl_2 (3 × 50 mL). The organic layers were combined and condensed to dryness under reduced pressure to give a white solid. The solid was recrystallized with *n*-heptane to furnish (*S*)-H$_8$-BINOL as white crystals. Yield 1.40 g, 95%; mp 160−161 °C; $[\alpha]_D^{25}$ = −72 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65−1.77 (m, 10H), 2.12−2.33 (m, 5H), 2.73−2.76 (m, 5H), 4.57 (s, 2H), 6.82−6.84 (d, *J* = 8.0 Hz, 2H), 7.06−7.08 (d, *J* = 8.0 Hz, 2H).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra and HPLC chromatograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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