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Asymmetric synthesis of new chiral long chain alcohols

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ABSTRACT

Sixteen new chiral alcohols with alkyl (C_{11}–C_{19}) and aryl, substituted aryl, hetero aryl and biaryl groups **2a**–**2t** were synthesized by three different asymmetric reduction methods from their corresponding ketones **1a**–**1t**. Chiral $NaBH_4$ (method A), chiral BH_3 (method B) and chiral AIP (method C) were used as asymmetric reduction catalysts. Chiral $NaBH_4$ was modified by four different ligands **3a**–**3d**, chiral BH_3 and chiral AIP by four different ligands **4a**–**4d**. Ligand **4c** was synthesized for the first time in this work. Chiral $NaBH_4$ generated chiral alcohols of (*R*)-configuration and chiral BH_3 and chiral AIP of (*S*)-configuration with high enantiomeric excesses, were analysed by chiral HPLC. In order to determine the ee values by chiral HPLC, sixteen corresponding racemic alcohols, synthesized by reducing their corresponding ketones via $NaBH_4$, were used for chiral resolution on a Daicel OD HPLC column. The sixteen starting ketones were synthesized in this study by Friedel–Craft acylation. The new chiral alcohols were characterized by IR, NMR, (^1H and ^{13}C), MS, elemental analyses and specific rotation. The reduction methods A, B and C were applied to these ketones for the first time in this study and were compared with each other. The relationship between the structure of the ketone and the yield and the enantiomeric excess was discussed.

1. Introduction

Chiral alcohols are valuable substances for the food, drug, and cosmetic industries because of their biological activity which can depend on their enantiomeric purity. Enantiomerically pure chiral alcohols are important synthetic intermediates, therefore, a number of synthetic methods have been extensively investigated.[1,2] Chiral alcohols are well-known synthons and can be obtained from the corresponding prochiral ketones by asymmetric reduction.

Asymmetric reduction by means of chemical methods involves the use of expensive chiral reagents and environmentally hazardous heavy metals which are often employed.[3] The asymmetric reduction of ketones to enantiomerically enriched alcohols is an important synthetic operation. Chiral borones and borohydrides are useful reagents in asymmetric reductions.[4] The importance of designing new chiral reducing agents need not be restated. Although sodium borohydride ($NaBH_4$) is a very common reducing agent, sodium borohydride based chiral reducing agents are only a few in number.[5] The chiral modifications of borohydride have been by chiral auxiliaries containing hydroxy group (hydroxymonosaccharide derivatives[6]) or by hydroxy and carboxylic acid groups (amino acid,[7] tartaric acid,[8] mandelic acid[9] and amino alcohols[10] etc.). However, the asymmetric inductions are not good.

The catalytic enantioselective reduction of prochiral ketones stands as an alternative and complementary method for the synthesis of chiral secondary alcohols. In particular, the oxazaborolidine mediated enantioselective reduction of ketones with borane is a well-established methodology. Since the famous CBS (Corey–Bakshi–Shibata) oxazaborolidine catalyst was obtained by Corey et al.[11] from (*R*)- or (*S*)-proline, a number of new chiral oxazaborolidines have been synthesized and used widely in asymmetric reductions. Amongst the characteristics for the enantioselective reduction of prochiral ketones catalysed by the CBS catalyst are its high reaction rate and high enantioselectivity.

2. Results and discussion

Sixteen novel chiral alcohols with alkyl (C_{11}–C_{19}) and aryl, substituted aryl, hetero aryl and biaryl groups **2a**–**2t** were synthesized for the first time in this study by three different asymmetric reduction methods (A, B, C) of their corresponding ketones **1a**–**1t** (Scheme 1). Only **2a** has been synthesized as its (*R*)- and (*S*)-enantiomers[12] and **2t** as its (*S*)-enantiomer[13] by methods other than those used in this study.

In method A, $NaBH_4$ was chirally modified by pivalic acid and four different ligands **3a**–**3d** that are shown in Scheme 2.

The results of method A are summarized in Table 1. DIPGF[14] **3a**, BINAP[15] **3b**, L-menthol[16] **3c** and DIPM **3d** were used as asymmetric induction agents for chiral $NaBH_4$ reduction of the ketones **1a**–**1h**. Method A was applied to the ketones **1a**–**1h** for the first time in

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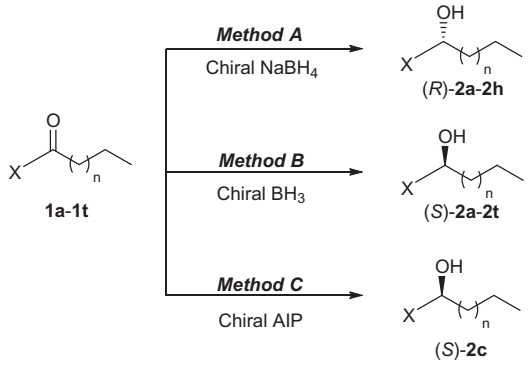
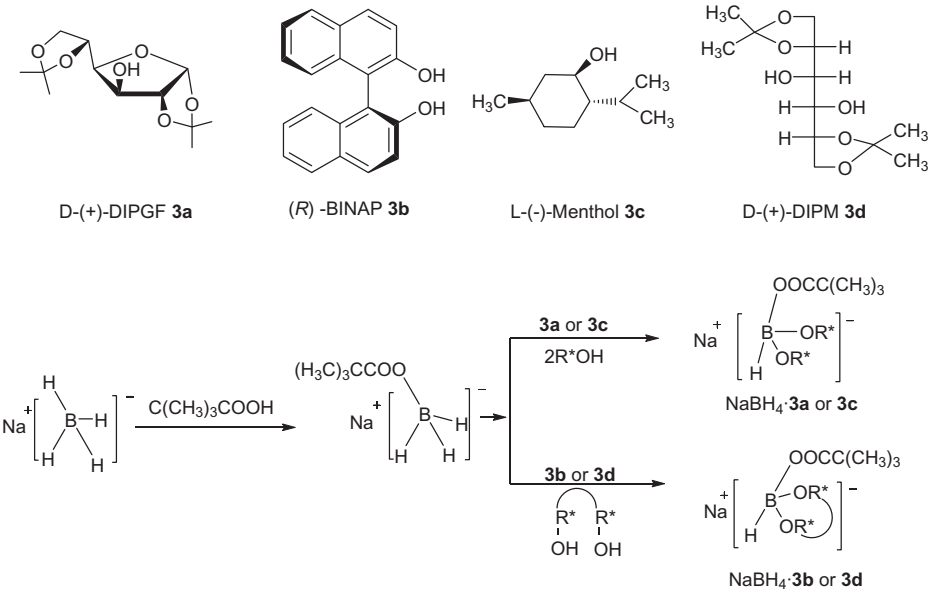
Ketone	Alcohol	X	n
1a	**2a**	Ph	9
1b	**2b**	Ph	10
1c	**2c**	Ph	11
1d	**2d**	Ph	12
1e	**2e**	Ph	13
1f	**2f**	Ph	16
1g	**2g**	Ph	17
1h	**2h**	*p*-Tolyl	10
1j	**2j**	*p*-$MeOC_6H_4$	11
1k	**2k**	*p*-BrC_6H_4	11
1m	**2m**	*p*-OHC_6H_4	11
1n	**2n**	2-Furyl	13
1p	**2p**	2-Thienyl	13
1r	**2r**	2-Piroyl	13
1s	**2s**	2-Naphthyl	10
1t	**2t**	Ph	*

* *p*-$C(CH_3)_3C_6H_4$



Scheme 1. Structures of the ketones and the three principal methods for asymmetric synthesis of new chiral alcohols.



Scheme 2. Chiral ligands and chiral modification of $NaBH_4$.

this work. DIPGF **3a** was chosen as the best chiral ligand for method A. Therefore, $NaBH_4$·**3a** was used in this study for the chiral reduction of the ketones **1a**–**1h** (Table 1) In method B, BH_3 was chirally modified by four different ligands **4a**–**4d**. Scheme 3; ligand **4c** was synthesized for the first time in this research.

For the selection of the best chiral ligand, ketone **1c** was reduced by the chiral catalysts BH_3·**4a**–**4d**, but the ee values obtained were low as can be seen from the Table 2. In the literature survey (*R*)-(+)-2-methyl-CBS-oxazaborolidine [(*R*)-Me-CBS] was the best catalyst[11b] giving very high ee values, therefore, ketone **1c** was reduced with (*R*)-Me-CBS, and also in this work a 92% ee value was obtained (Table 2, entry 5). All of the ketones **1a**–**1t** were enantioselectively reduced by (*R*)-Me-CBS with high ee values and the results are summarized in Table 3.

Boron is also contained in the catalyst (*R*)-Me-CBS, with a methyl substituent. This methyl substituent adds steric hindrance to the catalyst and so high ee values could be delivered. The other chiral BH_3 catalysts BH_3·**4a**–**4d** have no substituent on the boron atom and this might cause lower ee values.

In method C, chiral catalysts were prepared by the reaction of AIP (aluminium isopropoxide) with four different ligands **4a**–**4d** (Scheme 4), with the aim to examine the effect of a metal other than boron as the Lewis acid influencing enantioselectivity, coordination rate and the availability of the oxygen of the prochiral ketone. In addition, AIP is easily obtainable and inexpensive.

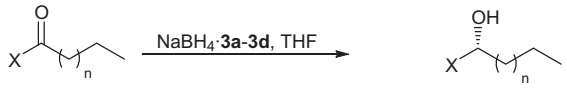
In method C, ketone **1c** was reduced by four chiral AIP catalysts AIP·**4a**–**4d**. Table 4. These catalysts were used for the asymmetric reduction of the ketone **1c** for the first time in this study. As a result, AIP·**4a** gave better ee values than the other chiral AIP catalysts, but was not as good as BH_3·**4a** and (*R*)-Me-CBS.

Amongst the ligands **4a**–**4d**, **4a** was the best and **4b** was the second best ligand (Tables 2 and 4). This may be due to the coordination ability of the nitrogen and oxygen of the chiral amino alcohols. Steric hindrance reduces the coordinating ability of the amino alcohols **4b**, **4c**, **4d** towards the metals boron and aluminium.

The low enantioselectivity of method A can be attributed to its salt structure. Coordination of boron (Fig. 1) with the oxygen of the ketone and the transfer of a hydride ion to the carbon atom of the ketone probably occurs at the same time but not via a stable cyclic complex as in B and C. This complex might be a four-membered cyclic system, which would not be easily formed because of the steric hindrance of the salt structure of chiral $NaBH_4$ and so it might not be stable. Therefore, low ee values were obtained.

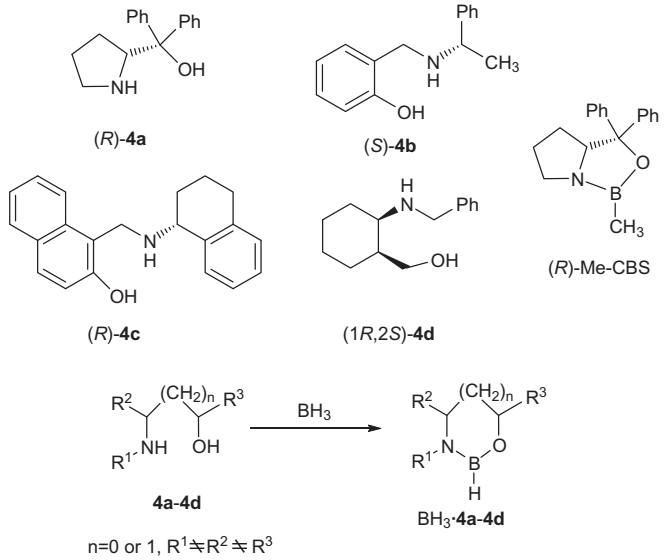
In method B according to the mechanistic model of Corey[17] (Fig. 2) boron is the Lewis acid portion of the chiral BH_3 catalyst and BH_3 was used in a greater amount. The free BH_3 coordinates

Table 1
Asymmetric reduction of prochiral ketones with method A



Entry	Ketone	Chiral ligand (equiv)	Alcohol	Yield (%)[a]	$[\alpha]_D^{25}$[b]	ee (%)[c]	Abs Conf.[d]
1	**1a**	**3a** (1 mmol)	**2a**	75	+8.3	26	(*R*)[e]
2	**1a**	**3c** (1 mmol)	**2a**	30	+6.7	21	(*R*)
3	**1a**	**3d** (0.5 mmol)	**2a**	61	+7.4	23	(*R*)
4	**1b**	**3a** (1 mmol)	**2b**	70	+9.8	26	(*R*)
5	**1b**	**3b** (0.5 mmol)	**2b**	70	+2.6	7	(*R*)
6	**1b**	**3c** (1 mmol)	**2b**	92	+5.6	15	(*R*)
7	**1b**	**3d** (0.5 mmol)	**2b**	76	+8.2	22	(*R*)
8	**1c**	**3a** (1 mmol)	**2c**	67	+14.2	33	(*R*)
9	**1c**	**3b** (0.5 mmol)	**2c**	65	+4.8	11	(*R*)
10	**1c**	**3c** (1 mmol)	**2c**	59	+8.2	22	(*R*)
11	**1c**	**3d** (0.5 mmol)	**2c**	50	+4.4	10	(*R*)
12	**1d**	**3a** (1 mmol)	**2d**	45	+11.2	31	(*R*)
13	**1d**	**3b** (0.5 mmol)	**2d**	60	+0.8	4	(*R*)
14	**1e**	**3a** (1 mmol)	**2e**	58	+6	39	(*R*)
15	**1e**	**3b** (0.5 mmol)	**2e**	60	0	0	(*RS*)
16	**1f**	**3a** (1 mmol)	**2f**	48	+16.4	64	(*R*)
17	**1g**	**3a** (1 mmol)	**2g**	40	+10	66	(*R*)
18	**1g**	**3d** (0.5 mmol)	**2g**	38	+2.6	14	(*R*)
19	**1h**	**3a** (1 mmol)	**2h**	95	+11.2	39	(*R*)

[a] Isolated yield of products.
[b] Specific rotations were measured in hexane **2a**–**2g** or chloroform **2h** (*c* 1.1).
[c] The ee values were determinated by HPLC analysis using a chiral column (Chiralcel OD).
[d] The absolute configuration of the products was assigned by comparing the sign of their specific rotation with the literature value of similar chiral alcohols **2a**–**2g**,[12] **2h**.[18]
[e] Based on $[\alpha]_D^{25} = -31$ (*c* 1, hexane), (*S*), 100% ee: Lit.[12].



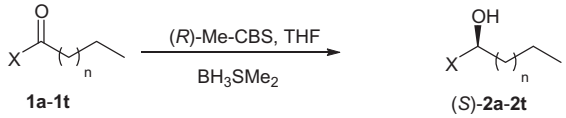
Scheme 3. Chiral ligands **4a**–**4d** and preparation of chiral catalysts BH_3·**4a**–**4d**.

Table 2
Asymmetric reduction of **1c** with chiral oxazaborolidine catalysts BH_3·**4a**–**4d**

Entry	Chiral catalyst	Yield[a] (%)	$[\alpha]_D^{25}$[b]	ee[c] (%)	Abs Conf.[d]
1	BH_3·**4a**	78	−30.6	71	(*S*)
2	BH_3·**4b**	65	+6.5	15	(*R*)
3	BH_3·**4c**	70	−2.2	5	(*S*)
4	BH_3·**4d**	60	+1.9	4	(*R*)
5	*R*-Me-CBS	80	−39.6	92	(*S*)

[a] Isolated yield of products.
[b] Specific rotations were measured in hexane (*c* 1.1).
[c] The ee values were determinated by HPLC analysis using a chiral column (Chiralcel OD).
[d] The absolute configuration of the products was assigned by comparing the sign of their specific rotation with the literature value of similar chiral alcohols (Lit.[12]).

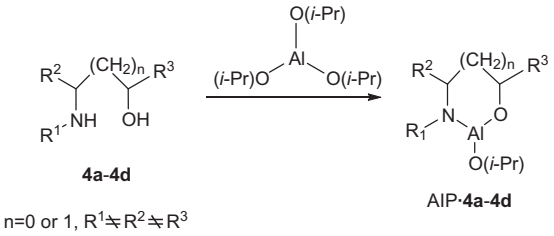
Table 3
Asymmetric reduction of prochiral ketones with method B [(*R*)-Me-CBS]



Entry	Ketone	Alcohol	Yield[a] (%)	$[\alpha]_D^{25}$[b]	ee[c] (%)	Abs Conf.[d]
1	**1a**	**2a**	95	−30.8	97	(*S*)
2	**1b**	**2b**	96	−35.2	95	(*S*)
3	**1c**	**2c**	80	−39.6	92	(*S*)
4	**1d**	**2d**	79	−17.6	86	(*S*)
5	**1e**	**2e**	73	−19.6	91	(*S*)
6	**1f**	**2f**	60	−18.4	72	(*S*)
7	**1g**	**2g**	70	−17	90	(*S*)
8	**1h**	**2h**	90	−28.6	100	(*S*)
9	**1j**	**2j**	60	−17.2	96	(*S*)
10	**1k**	**2k**	33	−15	99	(*S*)
11	**1m**	**2m**	20	−15.2	86	(*S*)
12	**1n**	**2n**	90	−11	95	(*S*)
13	**1p**	**2p**	22	−15.2	92	(*S*)
14	**1r**	**2r**	33	−10.5	88	(*S*)
15	**1s**	**2s**	30	−39.6	76	(*S*)
16	**1t**	**2t**	29	−10	17	(*S*)

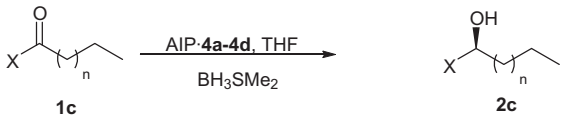
[a] Isolated yield of products.
[b] Specific rotations were measured in hexane (entry 1–7) or chloroform (entry 8–16) (*c* 1.1).
[c] The ee values were determinated by HPLC analysis using a chiral column (Chiralcel OD).
[d] The absolute configuration of the products was assigned by comparing the sign of their specific rotation with the literature value of similar chiral alcohols **2a**–**2g**,[12] **2h**–**2j**,[18] **2k**–**2m**,[19] **2n**–**2s**[20] and **2t**.[13]

to the Lewis basic nitrogen atoms of the chiral BH_3 catalyst and increases the Lewis acidity of the endocyclic boron atom to the ketone and also activates itself as a hydride donor to the carbon atom of the ketone. These conditions deliver a stable six-membered transition state, which is responsible for high ee values (Table 3, Fig. 2).



Scheme 4. Preparation of chiral catalysts AlP·**4a**–**4d**.

Table 4
Asymmetric reduction results of **1c** with chiral AlP catalysts **4a**–**4d**



Entry	Chiral catalyst	Yield[a] (%)	$[\alpha]_D^{25}$[b]	ee [c](%)	Abs Conf.[d]
1	**AlP·4a**	79	−25.4	59	(*S*)
2	**AlP·4b**	69	+6.9	16	(*R*)
3	**AlP·4c**	70	−2.4	7	(*S*)
4	**AlP·4d**	60	+4.5	11	(*R*)

[a] Isolated yield of products.
[b] Specific rotations were measured in hexane (*c* 1.1).
[c] The ee values were determinated by HPLC analysis using a chiral column (Chiralcel OD).
[d] The absolute configuration of the products was assigned by comparing the sign of their specific rotation with the literature value of similar chiral alcohols (Lit.[12]).

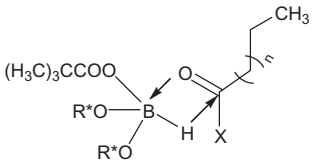


Figure 1. Possible transition state for method A.

In method C a six-membered coordination state was also formed but the Lewis acid ability of the aluminium of the chiral AlP catalyst is weaker than the boron in method B. This coordinated transition state may be formed with more difficulty than in method B because of the steric hindrance of the chiral aluminium catalyst. Furthermore, in method C the metals in the cyclic transition state are not the same; this may influence the balance and stability of the ring system, negatively. In method B the metals were the same and this configuration protects the stability and the balance of the six-membered ring system. Therefore, the ee values of method C were lower than in B but higher than for A. Note that both methods B and C take place under an inert N_2 atmosphere.

Method A was cheap and easy for work up, but the ee values were lower than B and C. Method B that needs an inert atmosphere is sensitive and the reagents are expensive, however, the best ee values were obtained with method B in this research. Method C was accomplished by inexpensive materials but the ee values were not better than B. (*R*)-Me-CBS is more expensive than AlP, but to achieve high ee values, method B might be the preferred (Table 5).

Table 5
The comparison of the results of asymmetric reduction of **1c** with the best chiral catalysts of the three methods

Method	Chiral catalyst	Yield (%)	$[\alpha]_D^{25}$	ee (%)	Abs Conf.
A	$NaBH_4$·**3a**	67	+14.2	33	(*R*)
B	(*R*)-Me-CBS	80	−39.6	92	(*S*)
C	AlP·**4a**	79	−25.4	59	(*S*)

3. Conclusion

Chiral $NaBH_4$ delivered chiral alcohols of an (*R*)-configuration and chiral BH_3 of an (*S*)-configuration with high enantiomeric excesses were analysed by chiral HPLC. The new chiral alcohols were characterized by IR, NMR, (^{1}H and ^{13}C), MS, elemental analyses and specific rotation. The sixteen starting ketones herein were synthesized by Friedel–Craft acylation.

Method A was performed only for **1a**–**1h** ketones because the ee values were low and method B was applied for all ketones **1a**–**1t**. Method A can be used for obtaining alcohols of an (*R*)-configuration and method B for an (*S*)-configuration. The absolute configuration of the novel chiral alcohols **2a**–**2t** was assigned by comparing the sign of their specific rotation with the literature value for similar chiral alcohols **2a**–**2g**,[12] **2h**–**2j**,[18] **2k**–**2m**,[19] **2n**–**2s**[20] and **2t.**[13]

The enantiomeric excesses of method B were better than method A and C. The reason may be related to the strength of the Lewis acid ability of boron. Boron in BH_3 is more reactive than the salt structure $NaBH_4$. The reaction time was the longest in method A and similar in B and C. With increasing alkyl chain lengths better steric hindrance and, therefore, better ee values were obtained. Substituted aryl and hetero aryl groups had positive inducing effects on ee values. Ketone **1t** having aryl groups on both sides could not show enough difference and as a result the lowest ee value was found.

The best asymmetric reduction method was B. The second was C and then A. The spectroscopic data of all alcohols from methods A, B, C were similar with each other. These new chiral alcohols **2a**–**2t** may have utility as chiral starting materials for the synthesis of several natural bioactive compounds and as chiral auxiliaries and chiral ligands in asymmetric syntheses.

4. Experimental

4.1. General

The majority of the chemicals used in this work were commercially available from Merck or Aldrich. Prochiral ketones as starting materials were synthesized by Friedel–Craft acylation.[21] The racemic alcohols were prepared by the reduction of the corresponding

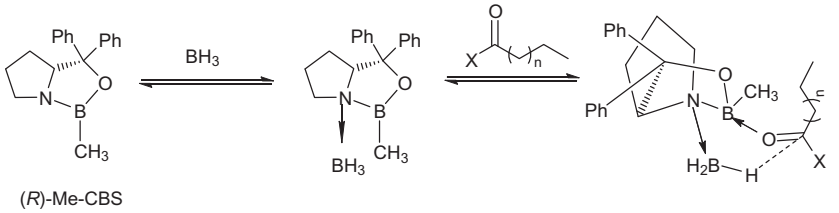


Figure 2. Coordination of the oxazaboralidine catalyst and the ketone.

ketones with $NaBH_4$ in methanol-THF. To prepare **4b** and **4c**, two amino alcohols were synthesized according to literature methods.[22] The reactions were monitored by TLC using silica gel plates and the products were purified by flash column chromatography on silica gel (Merck; 230–400 mesh) with hexane–ethyl acetate. NMR spectra were recorded at 500 MHz for ^1H and 125 MHz for ^{13}C using Me_4Si as the internal standard in $CDCl_3$. GC–MS were recorded on Agilent/QP2010 Plus. Specific rotations were measured with Optical Activity AA-55 digital polarimeter at room temperature. IR spectra were recorded on Mattson 1000. Melting points were determined with Bühi Melting Point B-540. Enantiomeric excesses (ee) of the product chiral alcohols were determined with Shimadzu/DGU-20A_5 HPLC apparatus fitted with a 25 cm Chiralcel OD (Daicel) chiral column.

4.2. General procedure for the reduction of prochiral ketones by method A

To a stirred suspension of $NaBH_4$ (0.5 mmol) in THF (4 ml) was added a solution of pivalic acid (0.5 mmol) in THF (4 ml). The solution was stirred 30 min and at the same time H_2 was formed. Then chiral ligand (**3a**–**3d**) (0.5 or 1 mmol) was added all at once, followed by another 4 ml of THF as a rinse. After stirring 3–4 h, the ketone (0.5 mmol) was added to the reaction solution all at once. The mixture was stirred at 25 °C for 3–4 days. Then work-up was carried out. The reaction mixture was hydrolysed by 1 M HCl with considerable gas evolution. The solution was extracted with ether (30 ml) and the aqueous layer was separated and was extracted once more with ether (80 ml). The ether layers were combined, washed once with water and dried over anhydrous Na_2SO_4. Evaporation was carried out under reduced pressure after filtration. The crude product containing alcohol and starting chiral ligand was separated by column chromatography (*n*-hexane/EtOAc 8:1).

4.3. General procedure for reduction of prochiral ketones by method B

4.3.1. General procedure for reduction of prochiral ketones by chiral oxazaborolidine catalysts BH_3·4a, 4b, 4c and 4d

To a solution of chiral amino alcohol **4a**–**4d** (0.1 mmol) in toluene (5 ml) was added BH_3·Me_2S (2 M in THF, 1.1 mmol, 0.55 ml) under nitrogen atmosphere at room temperature over a period of 30 min and stirred for another 30 min. The ketone (1 mmol) in toluene (5 ml) was added slowly over a period of 120 min then stirred at room temperature for another 30 min. The reaction mixture was quenched with 2 N NaOH and extracted twice with 10 ml of ether. The combined organic layers were washed with 2 N HCl and water, and dried over anhydrous Na_2SO_4, then concentrated under reduced pressure and passed through a silica column (*n*-hexane/EtOAc 8:1).

4.3.2. General procedure for the reduction of prochiral ketones by (*R*)-(+)-2-methyl-CBS-oxazaborolidine [(*R*)-Me-CBS]

In a typical procedure, to a solution (*R*)-Me-CBS (0.1 mmol, 0.1 ml of 1 M solution in toluene) was added, respectively BH_3·Me_2S (2 M in THF, 1.5 mmol, 0.75 ml) and the mixture was stirred under a nitrogen atmosphere, then cooled to 0 °C. After 10 min of stirring, the solution of ketone (1 mmol) in 5 ml of THF was simultaneously added within 40 min at 0 °C. The reaction mixture was maintained at rt for 1 h and then quenched with 2 M HCl. The solution was extracted with ether (30 ml). The aqueous layer was separated and was extracted once more with ether (80 ml). The ether layers were combined, washed once with water and dried over anhydrous Na_2SO_4. Evaporation was carried out under reduced pressure after filtration. The residue purified by column chromatography (*n*-hexane/EtOAc 8:1).

4.4. General procedure for the reduction of prochiral ketones by method C

At first, AIP (Aluminium isopropoxide) (0.6 mmol) was added to a solution of chiral amino alcohol **4a**–**4d** (0.5 mmol) in dry THF (5 ml), and the mixture was stirred at room temperature for 1 h under a nitrogen atmosphere. After a BH_3·Me_2S (2 M in THF, 5 mmol, 2.5 ml) was added, the ketone (5 mmol) in dry THF (10 ml) was added dropwise over a period of 1 h then stirred at room temperature for another 30 min. The reaction mixture was quenched with 2 M HCl and extracted twice with 30 ml of ether. The combined organic layers were washed with water, and dried over anhydrous Na_2SO_4, then concentrated on reduced pressure and passed through a silica column (*n*-hexane/EtOAc 8:1).

4.5. Spectroscopic data of chiral alcohols synthesized

4.5.1. (*S*)-1-Phenyl-1-dodecanol 2a

Mp 34.4–35.2 °C (lit.[12] mp 34.4–35.4 °C), $[\alpha]_D^{25} = -30.8$ (*c* 1.1, hexane) {lit.[12] $[\alpha]_D^{25} = -31$ (*c* 1, hexane)}, HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 2:98, flow rate: 1.0 ml/min, wavelength: 210 nm; R_t (retention time): 10.596 min for (*R*)-isomer, 12.338 min for (*S*)-isomer; purity: 1.7% for (*R*), 98.3% for (*S*). IR (neat, cm^{-1}): 3400, 3023, 2930, 2853, 1623, 1469, 1407, 1315, 769, 707 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.80 (t, 3H, J = 6.3 Hz), 1.12–1.39 (m, 18H), 1.58–1.74 (m, 2H), 1.80 (br s, 1H), 4.58 (t, 1H, J = 6.3 Hz), 7.18–7.22 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 14.07, 23, 26, 28.80–30.01, 32.20, 38.6, 75.01, 126.00, 126.85, 128.90, 145.2. MS *m*/*z*: 41, 79, 91, 104, 107, 120, 133, 244, 260, 262 (M^+). Anal. calcd for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C. 82.38; H, 11.19.

4.5.2. (*S*)-1-Phenyl-1-tridecanol 2b

Mp 28.2–29.3 °C, $[\alpha]_D^{25} = -35.2$ (*c* 1.1, hexane). HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 2:98, flow rate: 1.0 ml/min, wavelength: 210 nm; R_t (retention time): 10.203 min for (*R*)-isomer, 12.340 min for (*S*)-isomer; purity: 2.4% for (*R*), 97.6% for (*S*). IR (neat, cm^{-1}): 3400, 3023, 2930, 2853, 1623, 1469, 1407, 1315, 1050, 779, 725 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.82 (t, 3H, J = 6.3 Hz), 1.22–1.27 (m, 20H), 1.62–1.71 (m, 2H), 1.80 (br s, 1H), 4.58 (t, 1H, J = 7.3 Hz), 7.28–7.39 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 14.30, 22.89, 26.05, 28.80–30.01, 32.20, 38.6, 75.01, 126.00, 126.85, 128.90, 145.2. MS *m*/*z*: 43, 55, 79, 91, 107, 120, 133, 258, 274, 276 (M^+). Anal. calcd for $C_{19}H_{32}O$: C, 82.54; H, 11.66. Found: C. 82.54; H, 12.12.

4.5.3. (*S*)-1-Phenyl-1-tetradecanol 2c

Mp 52.8–53.2 °C, $[\alpha]_D^{25} = -39.6$ (*c* 1.1, hexane). HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 2:98, flow rate: 1.0 ml/min, wavelength: 210 nm; R_t (retention time): 9.120 min for (*R*)-isomer, 11.397 min for (*S*)-isomer; purity: 3.8% for (*R*), 96.2% for (*S*). IR (neat, cm^{-1}): 3369, 3023, 2923, 2853, 1691, 1469, 1384, 1269, 1123, 1038, 738, 707 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.82 (t, 3H, J = 6.3 Hz), 1.14–1.40 (m, 22H), 1.62–1.78 (m, 2H), 1.50 (br s, 1H), 4.58 (t, 1H, J = 7.3 Hz), 7.18–7.30 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 14.20, 23.89, 26.05, 29.50–30.01, 32.20, 38.6, 75.01, 126.00, 126.85, 128.90, 145.2. MS *m*/*z*: 43, 57, 79, 91, 107, 120, 133, 272, 274, 288, 290 (M^+). Anal. calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80. Found: C, 82.50; H, 11.47.

4.5.4. (*S*)-1-Phenyl-1-pentadecanol 2d

Mp 36.8–37.3 °C, $[\alpha]_D^{25} = -17.6$ (*c* 1.1, hexane). HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 2:98, flow rate: 1.0 ml/min, wavelength: 210 nm; R_t (retention time): 9.610 min for (*R*)-isomer, 11.451 min for (*S*)-isomer; purity: 6.7%

for (*R*), 93.3% for (*S*). IR (neat, cm^{-1}): 3372, 3030, 2946, 2865, 1675, 1483, 1402, 1316, 1050, 779, 698 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.82 (t, 3H, J = 6.8 Hz), 1.12–1.29 (m, 24H), 1.62–1.70 (m, 2H), 1.85 (br s, 1H), 4.56 (t, 1H, J = 7.8 Hz), 7.16–7.27 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 14.31, 22.90, 26.05, 29.56–29.90, 32.14, 39.35, 74.94, 126.11, 127.69, 128.64, 145.19. MS *m*/*z*: 43, 69, 79, 91, 107, 120, 133, 286, 304, 305 (M^+). Anal. calcd for $C_{21}H_{36}O$: C, 82.83; H, 11.92. Found: C, 82.99; H, 12.94.

4.5.5. (*S*)-1-Phenyl-1-hexadecanol 2e

Mp 60.5–61.2 °C, $[\alpha]_D^{25} = -19.6$ (*c* 1.1, hexane). HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 2:98, flow rate: 1.0 ml/min, wavelength: 210 nm; R_t (retention time): 9.204 min for (*R*)-isomer, 11.078 min for (*S*)-isomer; purity: 4.5% for (*R*), 95.5% for (*S*). IR (neat, cm^{-1}): 3372, 3043, 2946, 2854, 1669, 1483, 1402, 1316, 1023, 779, 698 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.85 (t, 3H, J = 6.8 Hz), 1.12–1.30 (m, 26H), 1.72–1.82 (m, 2H), 1.95 (br s, 1H), 4.68 (t, 1H, J = 7.3 Hz), 7.28–7.36 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 14.31, 22.90, 26.05, 29.56–29.90, 32.14, 39.35, 74.94, 126.11, 127.69, 128.64, 145.19. MS *m*/*z*: 43, 55, 69, 79, 107, 120, 133, 207, 316, 318 (M^+). Anal. calcd for $C_{22}H_{38}O$: C, 82.95; H, 12.03. Found: C, 82.84; H, 13.45.

4.5.6. (*S*)-1-Phenyl-1-nonadecanol 2f

Mp 50.5–51 °C, $[\alpha]_D^{25} = -18.4$ (*c* 1.1, hexane). HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 2:98, flow rate: 1.0 ml/min, wavelength: 210 nm; R_t (retention time): 9.555 min for (*R*)-isomer, 11.677 min for (*S*)-isomer; purity: 13.9% for (*R*), 86.1% for (*S*). IR (neat, cm^{-1}): 3407, 3025, 2947, 2861, 1686, 1483, 1409, 1325, 1077, 752, 698 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.80 (t, 3H, J = 6.8 Hz), 1.12–1.25 (m, 32H), 1.56–1.68 (m, 2H), 1.82 (br s, 1H), 4.60 (t, 1H, J = 7.3 Hz), 7.17–7.27 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 14.31, 22.90, 26.05, 29.57–30.01, 32.14, 39.35, 74.95, 126.11, 127.69, 128.64, 145.19. MS *m*/*z*: 43, 69, 79, 91, 107, 120, 147, 207, 342, 358 (M^+). Anal. calcd for $C_{25}H_{44}O$: C, 82.26; H, 12.30. Found: C, 81.39; H, 12.82.

4.5.7. (*S*)-1-Phenyl-1-Eicosanol 2g

Mp 70.2–71 °C, $[\alpha]_D^{25} = -17$ (*c* 1.1, hexane). HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 2:98, flow rate: 1.0 ml/min, wavelength: 210 nm; R_t (retention time): 8.254 min for (*R*)-isomer, 10.038 min for (*S*)-isomer; purity: 4.8% for (*R*), 95.2% for (*S*). IR (neat, cm^{-1}): 3407, 3040, 2946, 2871, 1685, 1483, 1409, 1325, 1050, 752, 698 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.85 (t, 3H, J = 6.8 Hz), 1.15–1.30 (m, 34H), 1.44 (br s, 1H), 1.61–1.72 (m, 2H), 4.70 (t, 1H, J = 7.3 Hz), 7.27–7.37 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 14.31, 22.90, 26.05, 29.57–30.01, 32.14, 39.35, 74.94, 126.11, 127.69, 128.64, 145.19. MS *m*/*z*: 43, 57, 79, 91, 107, 120, 147, 207, 356, 374 (M^+). Anal. calcd for $C_{26}H_{46}O$: C, 83.35; H, 12.66. Found: C, 83.19; H, 13.36.

4.5.8. (*S*)-1-(*p*-Methylphenyl)-1-tridecanol 2h

Mp 39.1–39.7 °C, $[\alpha]_D^{25} = -28.6$ (*c* 1.1, chloroform). HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 1:99, flow rate: 1.0 ml/min, wavelength: 210 nm; R_t (retention time): 16.679 min for (*R*)-isomer, 17.340 min for (*S*)-isomer; purity: 0% for (*R*), 100% for (*S*). IR (neat, cm^{-1}): 3392, 3038, 2923, 2853, 1646, 1469, 1269, 1261, 1107, 1046, 823, 738 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.80 (t, 3H, J = 6.8 Hz), 1.14–1.40 (m, 20H), 1.50 (br s, 1H), 1.58–1.80 (m, 2H), 2.28 (s, 3H), 4.68 (t, 1H, J = 7.3 Hz), 7.09 (d, 2H, J = 7.8 Hz), 7.16 (d, 2H, J = 7.8 Hz). ^{13}C NMR ($CDCl_3$): δ 14.20, 21.30, 23.01, 26.20, 29.00–30.01, 32.20, 39.35, 74.80, 126.01, 129.69, 136.54, 142.19. MS *m*/*z*: 41, 57, 77, 93, 121, 131, 145, 272, 288, 290 (M^+). Anal. calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80. Found: C, 82.41; H, 11.63.

4.5.9. (*S*)-1-(*p*-Methoxyphenyl)-1-tetradecanol 2j

Mp 44.9–45.4 °C, $[\alpha]_D^{25} = -17.2$ (*c* 1.1, chloroform). HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 2:98, flow rate: 1.0 ml/min, wavelength: 210 nm; R_t (retention time): 12.174 min for (*R*)-isomer, 12.926 min for (*S*)-isomer; purity: 1.8% for (*R*), 98.2% for (*S*). IR (neat, cm^{-1}): 3307, 3069, 2923, 2853, 1623, 1461, 1307, 1253, 1107, 1046, 807, 723 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.82 (t, 3H, J = 6.3 Hz), 1.12–1.35 (m, 22H), 1.50 (br s, 1H), 1.58–1.75 (m, 2H), 3.72 (s, 3H), 4.55 (t, 1H, J = 6.8 Hz), 6.80 (dd, 2H, J_1 = 1.9, J_2 = 6.8 Hz), 7.16 (dd, 2H, J_1 = 1.9, J_2 = 6.8 Hz). ^{13}C NMR ($CDCl_3$): δ 14.40, 23.01, 26.20, 29.40–30.01, 32.20, 39.05, 55.03, 75.00, 114.01, 115.09, 125.54, 139.19, 159.20. MS *m*/*z*: 43, 44, 69, 94, 121, 137, 147, 320 (M^+), 321. Anal. calcd for $C_{21}H_{36}O_2$: C, 78.70; H, 11.32. Found: C, 78.16; H, 10.97.

4.5.10. (*S*)-1-(*p*-Bromophenyl)-1-tetradecanol 2k

Mp 42.7–43.1 °C, $[\alpha]_D^{25} = -15$ (*c* 1.1, chloroform). HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 2:98, flow rate: 1.0 ml/min, wavelength: 210 nm; R_t (retention time): 10.249 min for (*S*)-isomer, 10.589 min for (*R*)-isomer; purity: 99.6% for (*S*), 0.4% for (*R*). IR (neat, cm^{-1}): 3353, 3069, 2923, 2846, 1600, 1476, 1353, 1223, 1130, 1076, 823, 723 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.80 (t, 3H, J = 6.8 Hz), 1.12–1.34 (m, 22H), 1.54–1.72 (m, 2H), 1.80 (br s, 1H), 4.53 (t, 1H, J = 7.3 Hz), 7.14 (dd, 2H, J_1 = 1.9, J_2 = 6.3 Hz), 7.39 (dd, 2H, J_1 = 1.9, J_2 = 6.3 Hz). ^{13}C NMR ($CDCl_3$): δ 14.50, 23.50, 26.20, 29.80–30.01, 32.20, 39.40, 74.00, 121.01, 127.90, 131.80, 144.19. MS *m*/*z*: 43, 55, 77, 106, 120, 157, 185, 368, 369 (M^+). Anal. calcd for $C_{20}H_{33}BrO$: C, 65.03; H, 9.00. Found: C, 65.41; H, 9.09.

4.5.11. (*S*)-1-(*p*-Hydroxyphenyl)-1-tetradecanol 2m

Mp 66.2–67.1 °C, $[\alpha]_D^{25} = -15.2$ (*c* 1.1, chloroform). HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 5:95, flow rate: 1.0 ml/min, wavelength: 210 nm; R_t (retention time): 20.772 min for (*R*)-isomer, 23.017 min for (*S*)-isomer; purity: 7% for (*R*), 93% for (*S*). IR (neat, cm^{-1}): 3407, 3030, 2923, 2853, 1630, 1469, 1307, 1284, 1123, 1053, 807, 723 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.82 (t, 3H, J = 6.8 Hz), 1.12–1.34 (m, 22H), 1.49 (br s, 1H), 1.56–1.76 (m, 2H), 4.45 (t, 1H, J = 6.8 Hz), 4.70 (br s, 1H), 6.74 (dd, 2H, J_1 = 1.9, J_2 = 6.3 Hz), 7.18 (dd, 2H, J_1 = 1.9, J_2 = 6.3 Hz). ^{13}C NMR ($CDCl_3$): δ 15.00, 23.10, 26.00, 29.40–30.01, 31.20, 38.30, 73.50, 114.20, 126.20, 136.10, 154.19. MS *m*/*z*: 41, 65, 77, 95, 107, 123, 133, 305, 306 (M^+). Anal. calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 78.22; H, 11.57.

4.5.12. (*S*)-1-(2-Furyl)-1-hexadecanol 2n

Mp 58.5–59.4 °C, $[\alpha]_D^{25} = -11$ (*c* 1.1, chloroform). HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 1.5:98.5, flow rate: 1.0 ml/min, wavelength: 210 nm; R_t (retention time): 10.221 min for (*R*)-isomer, 11.137 min for (*S*)-isomer; purity: 2.2% for (*R*), 97.8% for (*S*). IR (neat, cm^{-1}): 3346, 3023, 2923, 2853, 1607, 1476, 1276, 1153, 1107, 1046, 846, 753 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.82 (t, 3H, J = 6.8 Hz), 1.14–1.42 (m, 27H), 1.74–1.82 (m, 2H), 4.70 (t, 1H, J = 6.8 Hz), 6.15 (dd, 1H, J_1 = 1.0, J_2 = 3.4 Hz), 6.26 (dd, 1H, J_1 = 1.9, J_2 = 3.4 Hz), 7.30 (dd, 1H, J_1 = 1.0, J_2 = 1.9 Hz). ^{13}C NMR ($CDCl_3$): δ 14.25, 23.10, 25.90, 29.80–30.01, 32.10, 36.10, 68.00, 106.20, 111.01, 142.10, 157.20. MS *m*/*z*: 41, 69, 81, 97, 107, 121, 135, 290, 308 (M^+), 309. Anal. calcd for $C_{20}H_{36}O_2$: C, 77.86; H, 11.76. Found: C, 77.01; H, 11.86.

4.5.13. (*S*)-1-(2-Thenyl)-1-hexadecanol 2p

Mp 44.9–45.4 °C, $[\alpha]_D^{25} = -15.2$ (*c* 1.1, chloroform). HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 1.5:98.5, flow rate: 1.0 ml/min, wavelength: 210 nm; R_t (retention

time): 13.967 min for (*R*)-isomer, 14.697 min for (*S*)-isomer; purity: 4% for (*R*), 96% for (*S*). IR (neat, cm^{-1}): 3423, 3092, 2923, 2853, 1630, 1479, 1392, 1276, 1084, 1046, 800, 707 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.82 (t, 3H, J = 6.3 Hz), 1.12–1.42 (m, 26H), 1.48 (br s, 1H), 1.70–1.85 (m, 2H), 4.70 (t, 1H, J = 7.3 Hz), 6.88–6.92 (m, 2H), 7.16 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 14.20, 23.10, 25.90, 29.40–30.01, 32.20, 36.60, 74.20, 124.20, 125.50, 126.40, 147.20. MS *m*/*z*: 55, 79, 97, 113, 123, 139, 151, 281, 306, 324 (M^+). Anal. calcd for $C_{20}H_{36}OS$: C, 74.01; H, 11.18; S, 9.88. Found: C, 75.32; H, 10.82; S, 7.83.

4.5.14. (*S*)-1-(2-Pyrrolyl)-1-hexadecanol 2r

Mp 70.2–70.9 °C, $[\alpha]_D^{25} = -10.5$ (*c* 1.1, chloroform). HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 3:97, flow rate: 0.8 ml/min, wavelength: 210 nm; R_t (retention time): 14.465 min for (*R*)-isomer, 15.426 min for (*S*)-isomer; purity: 6.2% for (*R*), 93.8% for (*S*). IR (neat, cm^{-1}): 3392, 3107, 3023, 2923, 2853, 1730, 1584, 1461, 1384, 1290, 1138, 776, 730 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.82 (t, 3H, J = 7.3 Hz), 1.12–1.40 (m, 26H), 1.58 (br s, 1H), 1.60–1.85 (m, 2H), 3.70 (br s, 1H), 4.40 (td, 1H, J_1 = 1.4, J_2 = 7.3 Hz), 5.60–5.80 (m, 2H), 7.50 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 14.20, 23.10, 24.01, 29.10–30.01, 30.40, 32.20, 68.01, 126.02, 130.00, 131.04, 133.20. MS *m*/*z*: 43, 57, 71, 83, 113, 149, 167, 207, 253, 279. Anal. calcd for $C_{20}H_{37}NO$: C, 78.11; H, 12.13; N, 4.55. Found: C, 79.37; H, 12.16; N, 4.40.

4.5.15. (*S*)-1-(Naphthalen-2-yl)-1-tridecanol 2s

Mp 26–27 °C, $[\alpha]_D^{25} = -39.6$ (*c* 1.1, chloroform). HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 10:90, flow rate: 1.0 ml/min, wavelength: 210 nm; R_t (retention time): 7.850 min for (*S*)-isomer, 12.659 min for (*R*)-isomer; purity: 88.1% for (*S*), 11.9% for (*R*). IR (neat, cm^{-1}): 3346, 3023, 2923, 2853, 1607, 1476, 1276, 1153, 1107, 1046, 846, 753 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.80 (t, 3H, J = 6.3 Hz), 1.14–1.54 (m, 21H), 1.70–1.92 (m, 2H), 4.75 (t, 1H, J = 6.8 Hz), 7.40–8.20 (m, 7H). ^{13}C NMR ($CDCl_3$): δ 14.40, 23.10, 26.60, 29.80–30.01, 32.20, 38.80, 72.00, 123.00, 123.40, 125.10, 125.20, 126.20, 128.20, 129.20, 130.10, 134.10, 149.02. MS *m*/*z*: 43, 57, 77, 97, 115, 157, 181, 193, 221, 308, 326 (M^+). Anal. calcd for $C_{23}H_{34}O$: C, 84.60; H, 10.50. Found: C, 84.52; H, 10.23.

4.5.16. (*S*)-(4-*t*-Butylphenyl)(phenyl)methanol 2t

Mp 79.7–80.5 °C, $[\alpha]_D^{25} = -10$ (*c* 1.1, chloroform). HPLC analysis: Chiralcel OD chiral column, mobile phase *iso*-PrOH/hexane: 10:90, flow rate: 1.0 ml/min, wavelength: 210 nm; R_t (retention time): 8.803 min for (*S*)-isomer, 9.870 min for (*R*)-isomer; purity: 58.7% for (*S*), 41.3% for (*R*). IR (neat, cm^{-1}): 3229, 3030, 2959, 2855, 1599, 1449, 1339, 1270, 1110, 1011, 755, 630 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.12 (s, 9H), 2.20 (br s, 1H), 5.70 (s, 1H), 7.10–7.40 (m, 9H). ^{13}C NMR ($CDCl_3$): δ 32.14, 34.35, 76.04, 125.20, 126.50, 126.70, 127.50, 128.50, 141.00, 144.19, 150.80. MS *m*/*z*: 41, 51, 77, 91, 105, 119, 134, 183, 209, 225, 240 (M^+). Anal. calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 85.15; H, 8.12.

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