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Asymmetric organocatalytic oxy-Michael addition of alcohols to α,β-unsaturated aldehydes

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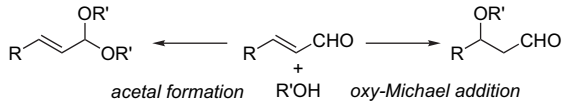
Abstract—A 1,4-addition of alcohols to α,β-unsaturated aldehydes was found to be efficiently promoted by biphenyldiamine-based catalyst **3** without formation of the acetals. An asymmetric variant of this reaction has also been performed by designing a novel axially chiral organocatalyst (*R*)-**10c**.

1. Introduction

β-Hydroxy carbonyl compounds and their alkoxy analogues serve as valuable building blocks and structural motifs in a variety of natural products,[1] and these compounds are usually prepared by the aldol reaction[2] and/or the subsequent alkylation of the resulting hydroxyl group. Alternatively, intermolecular 1,4-addition of alcohols to α,β-unsaturated carbonyl compounds also represents an attractive method for the direct synthesis of β-alkoxy carbonyl compounds. Such oxy-Michael additions of alcohols to α,β-unsaturated ketones or esters have recently been effected by several catalysts such as L-proline,[3] PMe_3,[4] DBU,[5] Tf_2NH,[6] and transition metal complexes;[7] however, the oxy-Michael addition of alcohols to α,β-unsaturated aldehydes remains a challenge, mainly because of the competitive acetal formation (Scheme 1).



Scheme 1.

In the field of organocatalysis, 1,4-addition reactions of heteroatom nucleophiles such as thiols,[8] amides,[9] carbamates,[10] and triazoles[11] to α,β-unsaturated aldehydes have been performed by iminium catalysis, and only a few reports have been made on organocatalytic conjugate addition of oxygen nucleophiles to α,β-unsaturated aldehydes.[12] Recently we also reported the organocatalytic oxy-Michael addition of simple alcohols to α,β-unsaturated aldehydes;[13] however, an asymmetric version of this process has remained elusive despite its potential application in organic synthesis. In this context, we are interested in the development of a novel secondary amine-type chiral catalyst for the 1,4-addition reaction of alcohols to α,β-unsaturated aldehydes. Herein we report that the biaryldiamine-based organocatalyst can be utilized to realize the first asymmetric oxy-Michael addition reaction of alcohols to α,β-unsaturated aldehydes.

2. Results and discussion

We first investigated the oxy-Michael addition reaction of methanol to 2-heptenal using *N*-methylaniline (**1**) as a catalyst since it has sufficient nucleophilicity to form the iminium salts of α,β-unsaturated aldehydes as a reactive intermediate, in addition to the ease of structural and electronical modifications. Thus, the oxy-Michael addition of methanol to 2-heptenal was carried out in $MeOH/H_2O$ (95:5) in the presence of 5 mol % of *N*-methylaniline (**1**) or its derivatives, and the results are summarized in Table 1. In the absence of the catalyst, small amounts of acetal **5** were obtained (entry 1), and the reaction with *N*-methylaniline (**1**) gave only trace amounts of the desired oxy-Michael adduct **4** (entry 2). We then surveyed acidic additives to improve the yield of the desired oxy-Michael adduct without loss of the favorable chemoselectivity. The addition of HCl cocatalyst accelerated both the oxy-Michael addition and the acetalization (entry 3). Use of a weaker acid such as TFA led to an increased ratio of oxy-Michael adduct **4** to acetal **5** (entry 4). Moreover, in the case of the weakly acidic additive **2**, the oxy-Michael addition occurred exclusively to give **4** in moderate yield (entry 5), while **2** itself was found not to catalyze the oxy-Michael addition (entry 6).

Keywords: Oxy-Michael addition; α,β-Unsaturated aldehyde; Organocatalyst; Iminium catalysis.
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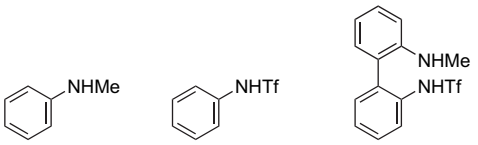
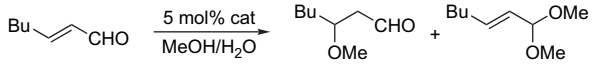


1 2 3

Based on these results, we then prepared the biphenyldiamine-based catalyst **3**, which has both secondary amine and acidic moieties in the molecule, and consequently, the reaction using **3** was found to proceed smoothly to give oxy-Michael adduct **4** in good yield (entry 7). It should be noted that the present reaction was significantly retarded without adding H_2O, probably due to deceleration of the iminium hydrolysis step in the catalytic cycle (entry 8).

Table 1. Oxy-Michael addition of methanol to 2-heptenal with aromatic amine-based catalysts[a]



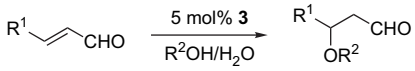
4 5

Entry	Catalyst	Time (h)	Yield[b] (%)	
			4	**5**
1	—	10	0	4
2	**1**	10	5	0
3	**1**+HCl[c]	4	23	29
4	**1**+TFA[d]	4	42	15
5	**1**+**2**[e]	10	51	0
6	**2**	10	0	10
7	**3**	10	87	0
8[f]	**3**	10	25	0

[a] Unless otherwise noted, the reaction of 2-heptenal (0.25 mmol) was carried out in the presence of 5 mol % of the catalyst in MeOH (950 μL) and H_2O (50 μL) at 0 °C.
[b] Isolated yield.
[c] HCl (5 mol %).
[d] TFA (5 mol %).
[e] **2** (5 mol %).
[f] Without H_2O.

Under optimized conditions, we then investigated the scope of the oxy-Michael addition between various α,β-unsaturated aldehydes and alcohols, and the representative results are summarized in Table 2. α,β-Unsaturated aldehydes, which have a primary alkyl or a secondary alkyl group at the β-position, were proved to be suitable substrates in the oxy-Michael addition of methanol (entries 1–4). The reaction of the sterically hindered *tert*-butyl-substituted analogue resulted in low yield of the product (entry 5). Cinnamaldehyde was unreactive (entry 6). In addition, catalyst **3** was also effective for the oxy-Michael addition of ethanol, propanol, allyl alcohol, and benzyl alcohol, giving the corresponding oxy-Michael adducts in moderate to good yields (entries 8, 10, 12, and 13). Unfortunately, however, this system was not suitable for secondary alcohol such as isopropanol (entry 11). Since benzyl and allyl groups can be easily removed from the products, both oxy-Michael adducts of benzyl and allyl alcohols serve as synthetic equivalents to aldol products. In each case, the addition of a proper amount of H_2O to the alcohol solvent is necessary to attain good chemical yields (entry 7 vs 8 and entry 9 vs 10). It should be noted that all the reactions proceeded without acetal formation.

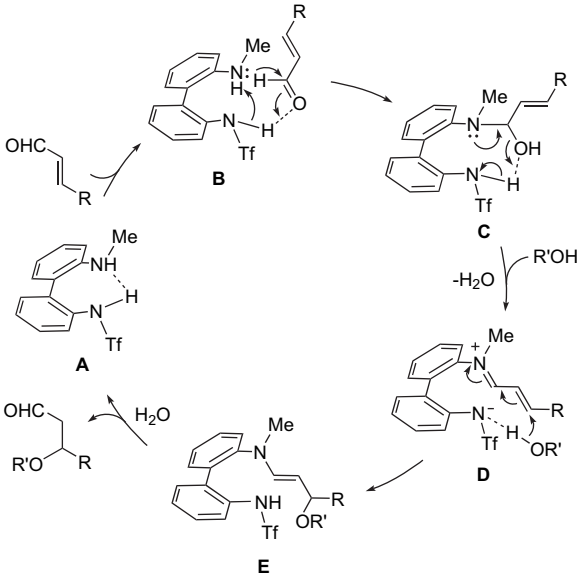
Table 2. Oxy-Michael addition of alcohols to α,β-unsaturated aldehydes catalyzed by biphenyldiamine-based catalyst **3**[a]



Entry	R^1	R^2	Time (h)	Yield[b,c] (%)
1	Bu	Me	10	87
2	Pr	Me	8	83
3	$BnCH_2$	Me	10	80
4	*i*-Pr	Me	10	72
5	*t*-Bu	Me	36	41
6	Ph	Me	24	<5
7	Bu	Et	23	63
8[d]	Bu	Et	22	81
9[d]	Bu	Pr	24	61
10[e]	Bu	Pr	24	72
11[e]	Bu	*i*-Pr	24	<5
12[e]	Bu	Allyl	40	72
13[e]	Bu	Bn	24	64

[a] Unless otherwise noted, the reaction of an α,β-unsaturated aldehyde (0.25 mmol) was carried out in the presence of 5 mol % of **3** in an alcohol (950 μL) and H_2O (50 μL) at 0 °C.
[b] Isolated yield.
[c] Acetal was not detected.
[d] Alcohol (970 μL) and H_2O (30 μL).
[e] Alcohol (990 μL) and H_2O (10 μL).

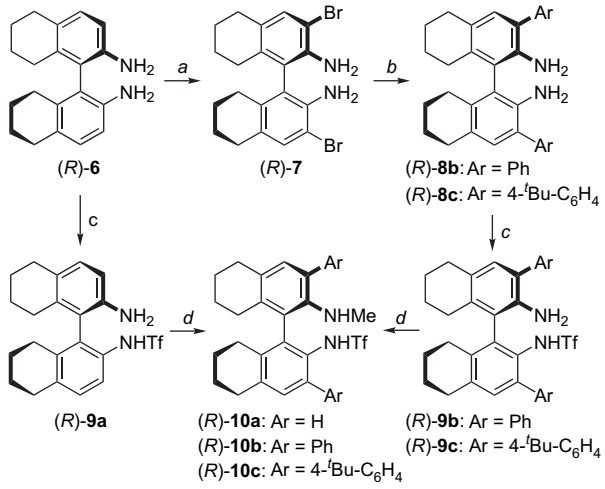
The proposed catalytic cycle is outlined in Scheme 2. This organocatalytic oxy-Michael addition reaction can be explained by iminium activation of α,β-unsaturated aldehydes by catalyst **A**. The first step is the formation of the iminium ion intermediate **D** with the assistance of acidic sulfonamide moiety via **B** and **C**. An alcohol then reacts as a nucleophile with this intermediate **D** to give the enamine intermediate **E**, which is followed by hydrolysis to yield the desired β-alkoxyaldehyde with regeneration of catalyst **A**. While we have not conducted a detailed study, the sulfonamide moiety might also activate the alcohol in the conjugate addition step (**D** to **E**).



Scheme 2. Proposed mechanism for the oxy-Michael addition of alcohols to α,β-unsaturated aldehydes.

We then turned our attention to the development of the asymmetric oxy-Michael addition reaction, and enantiopure

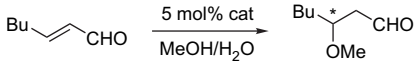
catalysts of type (*R*)-**10** were selected as axially chiral biphenyldiamine derivatives and prepared as follows (Scheme 3). Careful bromination of octahydrobinaphthyldiamine (*R*)-**6** with NBS yielded (*R*)-**7**, which was treated with arylboronic acids under standard Suzuki–Miyaura coupling conditions to give (*R*)-**8b** and (*R*)-**8c**. Trifluoromethanesulfonylation of diamines (*R*)-**6**, (*R*)-**8b**, and (*R*)-**8c** followed by methylation with MeOTf afforded (*R*)-**10a**–**c**, respectively.



Scheme 3. Reagents and conditions: (a) NBS, THF, 0 °C; (b) $ArB(OH)_2$, $Pd(OAc)_2$, PPh_3, $Ba(OH)_2 \cdot 8H_2O$, DME, H_2O, 80 °C; (c)Tf_2O, $^iPr_2NEt$, DMAP, CH_2Cl_2, 0 °C to rt; (d) MeOTf, CH_3CN, 80 °C.

With these new axially chiral organocatalysts, the oxy-Michael addition reaction of methanol to 2-heptenal was performed, and the results are summarized in Table 3. Attempted use of (*R*)-**10a** resulted in formation of the oxy-Michael adduct **4** with low enantioselectivity (entry 1); however, introduction of phenyl group at 3,3′-positions of octahydrobinaphthyl moiety enhanced the enantioselectivity (entry 2). Using the sterically more congested catalyst (*R*)-**10c**, the oxy-Michael adduct **4** was obtained with 68% ee albeit in low yield (entry 3). This low reactivity can be attributed to the low solubility of the catalyst (*R*)-**10c** in the MeOH/H_2O mixed-solvent system, and even 1 mol % of (*R*)-**10c** was not completely dissolved in it, giving a similar result (entry 4). Thus a minimum amount of toluene (100 μL) was added to dissolve the catalyst, and consequently, moderate yield was achieved at the expense of the reaction rate and enantioselectivity (entry 5).

Table 3. Asymmetric oxy-Michael addition of MeOH to 2-heptenal catalyzed by (*R*)-**10**[a]



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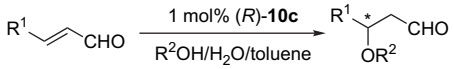
Entry	Catalyst	Time (h)	Yield[b] (%)	ee[c] (%)
1	(*R*)-**10a**	20	80	2
2	(*R*)-**10b**	14	46	37
3	(*R*)-**10c**	14	36	68
4[d]	(*R*)-**10c**	24	29	68
5[d,e]	(*R*)-**10c**	48	65	51

[a] The reaction of 2-heptenal (0.25 mmol) was carried out in the presence of 5 mol % of the catalyst in MeOH (950 μL) and H_2O (50 μL) at 0 °C.
[b] Isolated yield.
[c] Determined by GC analysis using chiral capillary column.
[d] Use of 1 mol % of the catalyst.
[e] Toluene (100 μL) was added.

Table 4. Asymmetric oxy-Michael addition of alcohol to α,β-unsaturated aldehydes catalyzed by (*R*)-**10c**[a]



Entry	R^1	R^2	Time (h)	Yield[b] (%)	ee[c] (%)
1	Bu	Me	48	65	51
2	Pr	Me	48	66	46
3	$BnCH_2$	Me	48	83	53
4[d,e]	Bu	Et	24	55	48
5[d,f]	Bu	Allyl	48	60	16

[a] The reaction of α,β-unsaturated aldehyde (0.25 mmol) was carried out in the presence of 1 mol % of (*R*)-**10c** in MeOH (950 μL), H_2O (50 μL), and toluene (100 μL) at 0 °C.
[b] Isolated yield.
[c] Determined by GC analysis using chiral capillary column.
[d] Use of 5 mol % of catalyst (*R*)-**10c**.
[e] EtOH (970 μL) and H_2O (30 μL).
[f] Allyl alcohol (990 μL) and H_2O (10 μL).

We then applied our system to several α,β-unsaturated aldehydes and alcohols and the results are shown in Table 4. Using 1 mol % of (*R*)-**10c**, the oxy-Michael addition of methanol to α,β-unsaturated aldehydes having a primary alkyl substituent at the β-position proceeded slowly to give the corresponding adducts with moderate enantioselectivity (entries 1–3). In the case of ethanol and allyl alcohol, catalyst (*R*)-**10c** was dissolved in the alcohol/H_2O mixed-solvent system without using toluene (entries 4 and 5). Unfortunately, however, the reaction with allyl alcohol resulted in low enantioselectivity (entry 5).

3. Conclusion

In summary, we have developed oxy-Michael addition of alcohols to α,β-unsaturated aldehydes catalyzed by biphenyldiamine-based catalyst **3**. Furthermore, using newly designed axially chiral organocatalyst (*R*)-**10c**, the asymmetric variant of this process has also been performed. Our efforts will be directed toward improving the efficiency of this and related catalyst systems. Further work aimed at the elucidation of the mechanism is also in progress.

4. Experimental

4.1. General information

Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. ^1H NMR spectra were measured on a JEOL JNM-FX400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million from tetramethylsilane as an internal standard. Data were reported as follows: chemical shift, integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad, and app=apparent), coupling constants (Hz), and assignment. ^{13}C NMR spectra were recorded on a JEOL JNM-FX400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in parts per million from the

residual solvent as an internal standard. Analytical gas–liquid phase chromatography (GLC) was performed on Shimadzu GC-14B instruments equipped with a flame ionization detector using an Astec Chiraldex B-DM (30 m×0.25 mm) column or a GL Science Chirasil-DEX CB (25 m×0.25 mm) column. The high-resolution mass spectra (HRMS) were performed on a Bruker microTOF. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by flash column chromatography on silica gel 60 (Merck 1.09386.9025, 230–400 mesh). In experiments requiring dry solvents, tetrahydrofuran (THF) was purchased from Kanto Chemical Co. Inc. as 'Dehydrated'. α,β-Unsaturated aldehydes were distilled and stored under an argon atmosphere at −17 °C. Other simple chemicals were purchased and used as such.

4.2. Synthesis and characterization of 3 and (*R*)-10a–c

4.2.1. 2′-Methylamino-2-trifluoromethanesulfonylamino-1,1′-biphenyl 3. To a stirred solution of 2-methylamino-2′-amino-1,1′-biphenyl[14] (198 mg, 1.0 mmol) and $^{i}Pr_2NEt$ (174 μL, 1.0 mmol) in CH_2Cl_2 (10 mL) was added Tf_2O (168 μL, 1.0 mmol) dropwise at −78 °C. After 3 h of stirring at −78 °C, the mixture was poured into water and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2=1:1 as an eluent) to afford **3** (182 mg, 0.55 mmol, 55% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (1H, d, J=7.6 Hz, Ar-H), 7.37–7.46 (4H, m, Ar-H), 7.17 (1H, dd, J=1.2, 7.6 Hz, Ar-H), 6.98 (1H, app t, Ar-H), 6.89 (1H, d, J=8.4 Hz, Ar-H), 2.83 (3H, s, NHC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 133.7, 132.5, 131.5, 131.4, 129.8, 129.0, 127.9, 125.9, 125.3, 120.1, 119.4 (q, J_{C-F}=324 Hz), 112.7, 31.3; IR (neat) 3340, 2360, 1364, 1271, 1225, 1196, 1140, 959, 822, 741, 597 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{14}F_3N_2O_2S$: 331.0723 ([M+H]$^+$); found: 331.0722 ([M+H]$^+$).

4.2.2. (*R*)-2,2′-Diamino-3,3′-dibromo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (*R*)-7. To a stirred solution of (*R*)-2,2′-diamino-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (292 mg, 1.00 mmol) in anhydrous THF (5 mL) was added NBS (356 mg, 2.00 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 1 min. The mixture was then quenched with saturated $NaHCO_3$ and saturated Na_2SO_3 at 0 °C, and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate=40:1 as an eluent) to afford (*R*)-**7** (446 mg, 0.99 mmol, 99% yield): $[\alpha]_D^{22}$ 30.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (2H, s, Ar-H), 3.72 (4H, br s, NH_2), 2.70 (4H, t, J=6.0 Hz, $ArCH_2$), 2.16–2.25 (2H, m, ArC*H*H), 2.03–2.13 (2H, m, ArCH*H*), 1.60–1.74 (8H, m, $CH_2CH_2CH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 135.6, 132.3, 129.0, 122.4, 107.0, 29.0, 26.7, 23.1, 22.9; IR (neat) 3472, 3375, 2930, 2855, 2359, 2332, 1601, 1456, 1013, 908, 733 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{23}Br_2N_2$: 449.0223 ([M+H]$^+$); found: 449.0211 ([M+H]$^+$).

4.2.3. (*R*)-2,2′-Diamino-3,3′-diphenyl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (*R*)-8b. A mixture of (*R*)-**7** (216 mg, 0.48 mmol), $Pd(OAc)_2$ (10.8 mg, 0.048 mmol), PPh_3 (50.3 mg, 0.192 mmol), $Ba(OH)_2\cdot 8H_2O$ (606 mg, 1.92 mmol), and phenylboronic acid (176 mg, 1.44 mmol) in degassed DME (5 mL) and H_2O (500 μL) was refluxed overnight. After cooling to room temperature, the resulting mixture was poured into water and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/diethyl ether=25:1 as an eluent) to afford (*R*)-**8b** (88 mg, 0.20 mmol, 41% yield): $[\alpha]_D^{24}$ −28.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (4H, d, J=7.6 Hz, Ar-H), 7.41 (4H, dd, J=7.6, 7.6 Hz, Ar-H), 7.30 (2H, t, J=7.6 Hz, Ar-H), 6.91 (2H, s, Ar-H), 3.53 (4H, br s, NH_2), 2.76 (4H, t, J=6.0 Hz, $ArCH_2$), 2.33–2.42 (2H, m, ArC*H*H), 2.22–2.31 (2H, m, ArCH*H*), 1.65–1.80 (8H, m, $CH_2CH_2CH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 138.8, 135.6, 130.3, 129.2, 128.6, 127.3, 126.8, 125.6, 122.3, 29.3, 27.0, 23.5, 23.3; IR (neat) 3468, 3374, 2926, 2855, 2342, 2237, 1605, 1589, 1458, 1435, 908, 775, 731, 702, 648 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{32}H_{33}N_2$: 445.2638 ([M+H]$^+$); found: 445.2640 ([M+H]$^+$).

4.2.4. (*R*)-2,2′-Diamino-3,3′-bis(4-*tert*-butylphenyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (*R*)-8c. Compound (*R*)-**8c** was prepared in a similar manner as described above using 4-*tert*-butylphenylboronic acid instead of phenylboronic acid (77% yield): $[\alpha]_D^{27}$ −64.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (8H, app s, Ar-H), 6.92 (2H, s, Ar-H), 3.54 (4H, br s, NH_2), 2.75 (4H, t, J=5.6 Hz, $ArCH_2$), 2.30–2.43 (2H, m, ArC*H*H), 2.17–2.30 (2H, m, ArCH*H*), 1.60–1.80 (8H, m, $CH_2CH_2CH_2CH_2$), 1.35 (18H, s, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 138.9, 137.1, 135.3, 130.3, 128.8, 127.2, 125.5, 122.3, 34.5, 31.4, 29.3, 27.0, 23.5, 23.3 (the signal for an aromatic carbon was not identified due to the overlap of peaks); IR (neat) 3451, 3348, 2959, 2936, 2914, 2833, 2363, 2330, 2236, 1605, 1589, 1458, 1393, 1362, 1263, 1244, 907, 837, 731 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{40}H_{49}N_2$: 557.3890 ([M+H]$^+$); found: 557.3892 ([M+H]$^+$).

4.2.5. (*R*)-2′-Amino-2-trifluoromethanesulfonylamino-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (*R*)-9a. To a stirred solution of (*R*)-**6** (146 mg, 0.50 mmol), $^{i}Pr_2NEt$ (87 μL, 0.50 mmol), and a catalytic amount of DMAP in CH_2Cl_2 (2 mL) was added Tf_2O (84 μL, 0.50 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was then quenched with saturated $NaHCO_3$ at 0 °C and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate=5:1 as an eluent) to afford (*R*)-**9a** (72 mg, 0.17 mmol, 34% yield): $[\alpha]_D^{22}$ −12.4 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (1H, d, J=8.4 Hz, Ar-H), 7.12 (1H, d, J=8.4 Hz, Ar-H), 6.97 (1H, d, J=8.0 Hz, Ar-H), 6.62 (1H, d, J=8.0 Hz, Ar-H), 4.41 (2H, br s, NH_2), 2.80 (2H, t, J=6.0 Hz, $ArCH_2$), 2.72 (2H, t, J=6.0 Hz, $ArCH_2$), 2.18–2.34 (2H, m, $ArCH_2$), 2.09 (2H, t, J=6.0 Hz, $ArCH_2$), 1.60–1.80 (8H, m, $CH_2CH_2CH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 137.4, 136.1, 135.8,

130.8, 130.4, 129.8, 128.5, 128.2, 119.5 (q, J_{C-F}=324 Hz), 118.7, 117.3, 113.6, 29.5, 29.1, 27.13, 27.08, 23.0, 22.94, 22.90, 22.6; IR (neat) 3304, 2932, 2859, 2359, 1614, 1476, 1412, 1356, 1217, 1194, 1142, 980, 735, 602 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{24}F_3N_2O_2S$: 425.1505 ($[M+H]^+$); found: 425.1503 ($[M+H]^+$).

4.2.6. (*R*)-2′-Amino-3,3′-diphenyl-2-trifluoromethanesulfonylamino-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (*R*)-9b. Compound (*R*)-**9b** was prepared in a similar manner as described above using (*R*)-**8b** instead of (*R*)-**6** (38% yield): $[\alpha]_D^{25}$ −152.1 (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.52 (10H, m, Ar-H), 7.17 (1H, s, Ar-H), 6.97 (1H, s, Ar-H), 3.53 (2H, br s, NH_2), 2.70–2.94 (4H, m, $ArCH_2$), 2.50–2.62 (1H, m, ArC*H*H), 2.26–2.44 (3H, m, $ArCH_2$), 1.60–1.86 (8H, m, $CH_2CH_2CH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 139.5, 139.4, 139.2, 137.4, 137.1, 137.0, 135.6, 132.1, 131.0, 129.4, 129.3, 129.1, 128.9, 128.2, 127.5, 127.3, 127.24, 127.19, 123.1, 118.6 (q, J_{C-F}=324 Hz), 29.7, 29.2, 27.8, 27.6, 23.1, 22.9, 22.7, 22.6; IR (neat) 3426, 3341, 2932, 2859, 2357, 2328, 1605, 1460, 1418, 1358, 1206, 1190, 1134, 910, 766, 735, 702 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{33}H_{32}F_3N_2O_2S$: 577.2131 ($[M+H]^+$); found: 577.2131 ($[M+H]^+$).

4.2.7. (*R*)-2′-Amino-3,3′-bis(4-*tert*-butylphenyl)-2-trifluoromethanesulfonylamino-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (*R*)-9c. Compound (*R*)-**9c** was prepared in a similar manner as described above using (*R*)-**8c** instead of (*R*)-**6** (38% yield): $[\alpha]_D^{22}$ −169.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (2H, d, *J*=8.0 Hz, Ar-H), 7.41 (2H, d, *J*=8.0 Hz, Ar-H), 7.39 (2H, d, *J*=8.0 Hz, Ar-H), 7.31 (2H, d, *J*=8.0 Hz, Ar-H), 7.17 (1H, s, Ar-H), 6.97 (1H, s, Ar-H), 3.55 (2H, br s, NH_2), 2.68–2.96 (4H, m, $ArCH_2$), 2.48–2.62 (1H, m, ArC*H*H), 2.22–2.44 (3H, m, $ArCH_2$), 1.57–1.85 (8H, m, $CH_2CH_2CH_2CH_2$), 1.36 (9H, s, *t*-Bu), 1.35 (9H, s, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 150.1, 139.6, 139.2, 137.5, 137.2, 136.8, 136.6, 136.1, 135.3, 132.0, 131.1, 129.0, 128.8, 127.6, 127.0, 125.7, 125.0, 123.0, 118.6 (q, J_{C-F}=324 Hz), 34.6, 34.5, 31.4, 31.3, 29.7, 29.2, 27.7, 27.6, 26.9, 23.1, 23.0, 22.6 (the signal for an aromatic carbon was not identified due to the overlap of peaks); IR (neat) 3428, 2959, 2936, 2864, 2839, 2322, 1607, 1460, 1408, 1362, 1269, 1206, 1188, 1136, 968, 910, 837, 775, 733, 631, 598, 577 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{41}H_{48}F_3N_2O_2S$: 689.3383 ($[M+H]^+$); found: 689.3381 ($[M+H]^+$).

4.2.8. (*R*)-2′-Methylamino-2-trifluoromethanesulfonylamino-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (*R*)-10a. To a stirred solution of (*R*)-**9a** (72 mg, 0.17 mmol) in CH_3CN (2 mL) was added MeOTf (19 μL, 0.17 mmol) at room temperature and the reaction mixture was stirred at 80 °C overnight. The reaction mixture was then quenched with saturated $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate=8:1 as an eluent) to afford (*R*)-**10a** (29 mg, 0.068 mmol, 40% yield): $[\alpha]_D^{26}$ −17.9 (*c* 0.8, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (1H, d, *J*=8.8 Hz, Ar-H), 7.12 (1H, d, *J*=8.8 Hz, Ar-H), 7.08 (1H, d, *J*=8.8 Hz, Ar-H), 6.56 (1H, d, *J*=8.8 Hz, Ar-H), 2.80 (2H, t, *J*=6.0 Hz, $ArCH_2$), 2.73 (2H, t, *J*=6.0 Hz, $ArCH_2$), 2.72 (3H, s, $NHCH_3$), 2.21 (2H, t, *J*=6.4 Hz, $ArCH_2$), 2.05 (2H, t, *J*=6.4 Hz, $ArCH_2$), 1.58–1.82 (8H, m, $CH_2CH_2CH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 137.7, 136.0, 135.5, 131.0, 130.6, 129.8, 127.7, 126.8, 119.5 (q, J_{C-F}=324 Hz), 117.7, 116.7, 108.4, 30.6, 29.5, 29.0, 27.2, 27.0, 23.13, 23.10, 22.9, 22.6; IR (neat) 3428, 3300, 2932, 2859, 2359, 2330, 1726, 1599, 1504, 1476, 1418, 1354, 1234, 1217, 1194, 1142, 806, 743, 602 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{26}F_3N_2O_2S$: 439.1662 ($[M+H]^+$); found: 439.1680 ($[M+H]^+$).

4.2.9. (*R*)-2′-Methylamino-3,3′-diphenyl-2-trifluoromethanesulfonylamino-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (*R*)-10b. Compound (*R*)-**10b** was prepared in a similar manner as described above using (*R*)-**9b** instead of (*R*)-**9a** (35% yield): $[\alpha]_D^{26}$ −95.3 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.28–7.49 (10H, m, Ar-H), 7.15 (1H, s, Ar-H), 7.01 (1H, s, Ar-H), 2.66–2.98 (4H, m, $ArCH_2$), 2.25–2.47 (4H, m, $ArCH_2$), 2.22 (3H, s, $NHCH_3$), 1.50–1.92 (8H, m, $CH_2CH_2CH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 139.6, 139.5, 138.8, 138.7, 137.7, 137.0, 132.3, 132.1, 131.8, 131.1, 129.4, 129.0, 128.9, 128.1, 127.5, 127.3, 127.1, 118.6 (q, J_{C-F}=323 Hz), 35.7, 29.71, 29.65, 29.4, 28.7, 27.4, 22.92, 22.89, 22.79 (the signals for two aromatic carbons were not identified due to the overlap of peaks); IR (neat) 3354, 2932, 2859, 2351, 1605, 1450, 1410, 1358, 1202, 1188, 1136, 974, 910, 770, 733, 702, 640, 602 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{34}H_{34}F_3N_2O_2S$: 591.2288 ($[M+H]^+$); found: 591.2297 ($[M+H]^+$).

4.2.10. (*R*)-3,3′-Bis(4-*tert*-butylphenyl)-2′-methylamino-2-trifluoromethanesulfonylamino-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (*R*)-10c. Compound (*R*)-**10c** was prepared in a similar manner as described above using (*R*)-**9c** instead of (*R*)-**9a** (53% yield): $[\alpha]_D^{24}$ −185.3 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (2H, d, *J*=8.4 Hz, Ar-H), 7.38 (2H, d, *J*=8.0 Hz, Ar-H), 7.31 (2H, d, *J*=8.0 Hz, Ar-H), 7.30 (2H, d, *J*=8.4 Hz, Ar-H), 7.15 (1H, s, Ar-H), 7.02 (1H, s, Ar-H), 2.65–2.97 (5H, m, $ArCH_2$), 2.30–2.50 (3H, m, $ArCH_2$), 2.23 (3H, s, $NHCH_3$), 1.54–1.92 (8H, m, $CH_2CH_2CH_2CH_2$), 1.37 (9H, s, *t*-Bu), 1.33 (9H, s, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 150.0, 141.7, 139.5, 139.0, 138.5, 137.5, 136.7, 136.5, 136.4, 132.2, 132.0, 131.7, 128.99, 128.96, 127.4, 125.8, 124.9, 118.6 (q, J_{C-F}=323 Hz), 35.7, 34.6, 34.5, 31.4, 31.3, 29.6, 29.4, 28.7, 27.4, 22.95, 22.90, 22.8 (the signals for two aromatic carbons and an aliphatic carbon were not identified due to the overlap of peaks); IR (neat) 3354, 2961, 2866, 2359, 2342, 1402, 1362, 1204, 1186, 1022, 912, 837, 783, 737 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{42}H_{50}F_3N_2O_2S$: 703.3539 ($[M+H]^+$); found: 703.3533 ($[M+H]^+$).

4.3. Representative procedure for the oxy-Michael addition of an alcohol to an α,β-unsaturated aldehyde and their characterization

To a solution of catalyst **3** (4.1 mg, 0.0125 mmol) in MeOH/H_2O (95:5 v/v, 0.25 M) was added (*E*)-2-heptenal (33 μL, 0.25 mmol) at 0 °C. Upon consumption of the starting material, the reaction mixture was directly purified by flash column chromatography on silica gel (pentane/diethyl ether=4:1 as an eluent) to afford 3-methoxyheptanal (31.4 mg, 0.218 mmol, 87% yield).

4.3.1. 3-Methoxyheptanal (entry 1 in Table 2 and entry 1 in Table 4). $[\alpha]_D^{24}$ 6.5 [*c* 2.2, $CHCl_3$ (51% ee)] in the case of entry 1 in Table 4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (1H, t, *J*=2.4 Hz, CHO), 3.71 (1H, m, C*H*OMe), 3.35 (3H, s, OMe), 2.60 (1H, ddd, *J*=2.4, 7.2, 16.4 Hz, C*H*HCHO), 2.52 (1H, ddd, *J*=2.0, 5.2, 16.4 Hz, CH*H*CHO), 1.25–1.65 (6H, m, $CH_2CH_2CH_2$), 0.91 (3H, t, *J*=7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 76.3, 56.8, 48.0, 33.6, 27.3, 22.8, 14.1; IR (neat) 2957, 2930, 2860, 2826, 2725, 2342, 1724, 1466, 1094, 1032, 748 cm^{-1}; HRMS (ESI-TOF) calcd for $C_8H_{16}O_2Na$: 167.1043 ([M+Na]$^+$); found: 167.1048 ([M+Na]$^+$); GLC analysis: Chiraldex B-DM (30 m×0.25 mm) column (carrier gas: N_2=74 kPa, He=98 kPa, 80 °C isotherm), retention time: 17.4 min and 18.5 min (major).

4.3.2. 3-Methoxyhexanal (entry 2 in Table 2 and entry 2 in Table 4). $[\alpha]_D^{28}$ 3.1 [*c* 2.14, $CHCl_3$ (46% ee)] in the case of entry 2 in Table 4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (1H, t, *J*=2.4 Hz, CHO), 3.72 (1H, m, C*H*OMe), 3.35 (3H, s, OMe), 2.62 (1H, ddd, *J*=2.4, 6.8, 16.0 Hz, C*H*HCHO), 2.53 (1H, ddd, *J*=2.4, 8.8, 16.0 Hz, CH*H*CHO), 1.33–1.65 (4H, m, CH_2CH_2), 0.94 (3H, t, *J*=7.6 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 76.1, 56.8, 48.0, 36.1, 18.4, 14.2; IR (neat) 2959, 2926, 2855, 2357, 1726, 1462, 1379, 1261, 1094, 1022, 768 cm^{-1}; HRMS (ESI-TOF) calcd for $C_7H_{14}O_2Na$: 153.0886 ([M+Na]$^+$); found: 153.0880 ([M+Na]$^+$); GLC analysis: Chiraldex B-DM (30 m×0.25 mm) column (carrier gas: N_2=74 kPa, He=98 kPa, 70 °C isotherm), retention time: 16.7 min and 17.9 min (major).

4.3.3. 3-Methoxy-5-phenylpentanal (entry 3 in Table 2 and entry 3 in Table 4). $[\alpha]_D^{26}$ 3.2 [*c* 1.47, $CHCl_3$ (53% ee)] in the case of entry 3 in Table 4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (1H, t, *J*=2.2 Hz, CHO), 7.21–7.30 (2H, m, Ar-H), 7.17–7.19 (3H, m, Ar-H), 3.74 (1H, m, C*H*OMe), 3.37 (3H, s, OMe), 2.62–2.76 (3H, m, PhCH_2 and C*H*HCHO), 2.56 (1H, ddd, *J*=2.0, 5.2, 16.4 Hz, CH*H*CHO), 1.78–1.98 (2H, m, BnCH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 141.5, 128.4, 128.3, 125.9, 75.4, 56.8, 47.8, 35.7, 31.2; IR (neat) 3026, 2926, 2849, 2826, 2725, 1722, 1603, 1454, 1364, 1186, 1115, 1080, 748, 700 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{16}O_2Na$: 215.1043 ([M+Na]$^+$); found: 215.1037 ([M+Na]$^+$). The enantiomeric excess was determined by reduction [2.0 equiv $NaBH_4$, MeOH (0.2 M)] to 3-methoxy-5-phenylpentanol: $[\alpha]_D^{27}$ 13.8 [*c* 0.6, $CHCl_3$ (53% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.35 (2H, m, Ar-H), 7.15–7.23 (3H, m, Ar-H), 3.71–3.85 (2H, m, CH_2OH), 3.45 (1H, m, C*H*OMe), 3.37 (3H, s, OMe), 2.66 (2H, t, *J*=8.0 Hz, PhCH_2), 2.60 (1H, br s, OH), 1.70–2.00 (4H, m, BnCH_2 and CH_2CH$_2$OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 128.4, 128.3, 125.8, 80.0, 60.7, 56.4, 35.4, 34.8, 31.2; IR (neat) 3389, 3026, 2938, 2880, 2824, 2359, 2340, 1495, 1454, 1364, 1184, 1080, 1053, 745, 698 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{18}O_2Na$: 217.1199 ([M+Na]$^+$); found: 217.1209 ([M+Na]$^+$); GLC analysis: Chirasil-DEX CB (25 m×0.25 mm) column (carrier gas: N_2=80 kPa, He=85 kPa, 130 °C isotherm), retention time: 60.8 min and 62.2 min (major).

4.3.4. 3-Methoxy-4-methylpentanal (entry 4 in Table 2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (1H, t, *J*=2.2 Hz, CHO), 3.53 (1H, m, C*H*OMe), 3.36 (3H, s, OMe), 2.55 (1H, ddd, *J*=2.4, 8.0, 16.0 Hz, C*H*HCHO), 2.46 (1H, ddd, *J*=1.8, 3.8, 16.0 Hz, CH*H*CHO), 1.96 (1H, m, C*H*Me$_2$), 0.92 (3H, d, *J*=8.0 Hz, CHCH_3), 0.90 (3H, d, *J*=8.0 Hz, CHCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 81.0, 57.5, 44.7, 30.5, 18.2, 17.1; IR (neat) 2957, 2924, 2855, 2363, 2336, 1730, 1516, 1456, 1377, 1314, 1098, 1024, 912, 743 cm^{-1}; HRMS (ESI-TOF) calcd for $C_7H_{14}O_2Na$: 153.0886 ([M+Na]$^+$); found: 153.0880 ([M+Na]$^+$).

4.3.5. 3-Methoxy-4,4-dimethylpentanal (entry 5 in Table 2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (1H, t, *J*=2.2 Hz, CHO), 3.40 (3H, s, OMe), 3.38 (1H, m, C*H*OMe), 2.59 (1H, app d, C*H*HCHO), 2.57 (1H, app dd, CH*H*CHO), 0.90 (9H, s, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 84.4, 60.0, 45.7, 35.7, 26.0; IR (neat) 2924, 2855, 2358, 2330, 1730, 1464, 1028, 912, 739 cm^{-1}; HRMS (ESI-TOF) calcd for $C_8H_{16}O_2Na$: 167.1043 ([M+Na]$^+$); found: 167.1050 ([M+Na]$^+$).

4.3.6. 3-Ethoxyheptanal (entry 8 in Table 2 and entry 4 in Table 4). $[\alpha]_D^{28}$ 6.9 [*c* 0.5, $CHCl_3$ (48% ee)] in the case of entry 4 in Table 4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (1H, t, *J*=2.4 Hz, CHO), 3.79 (1H, m, C*H*OEt), 3.52 (2H, m, OCH_2), 2.61 (1H, ddd, *J*=2.8, 7.2, 16.4 Hz, C*H*HCHO), 2.52 (1H, ddd, *J*=2.0, 4.8, 16.4 Hz, CH*H*CHO), 1.25–1.70 (6H, m, $CH_2CH_2CH_2$), 1.18 (3H, t, *J*=6.8 Hz, OCH$_2$CH_3), 0.91 (3H, t, *J*=7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 74.6, 64.5, 48.4, 34.1, 27.3, 22.7, 15.4, 14.0; IR (neat) 2959, 2932, 2862, 2723, 2363, 2338, 1724, 1456, 1371, 1346, 1099, 1076 cm^{-1}; HRMS (ESI-TOF) calcd for $C_9H_{18}O_2Na$: 181.1199 ([M+Na]$^+$); found: 181.1190 ([M+Na]$^+$); GLC analysis: Chiraldex B-DM (30 m×0.25 mm) column (carrier gas: N_2=74 kPa, He=98 kPa, 80 °C isotherm), retention time: 22.0 min and 23.1 min (major).

4.3.7. 3-Propoxyheptanal (entry 10 in Table 2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (1H, t, *J*=2.2 Hz, CHO), 3.78 (1H, m, C*H*OPr), 3.41 (2H, m, OCH_2), 2.61 (1H, ddd, *J*=2.4, 6.8, 16.0 Hz, C*H*HCHO), 2.51 (1H, ddd, *J*=2.0, 5.2, 16.0 Hz, CH*H*CHO), 1.20–1.67 (8H, m, CH_2CH_2CH_2 and OCH$_2$CH_2), 0.91 (6H, app t, CH_3 and OCH$_2$CH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 74.9, 71.0, 48.4, 34.1, 27.3, 23.2, 22.7, 14.0, 10.6; IR (neat) 2959, 2932, 2874, 2862, 2723, 2361, 2330, 1726, 1466, 1379, 1352, 1098, 1084, 1028 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{10}H_{20}O_2Na$: 195.1356 ([M+Na]$^+$); found: 195.1346 ([M+Na]$^+$); GLC analysis: Chiraldex B-DM (30 m×0.25 mm) column (carrier gas: N_2=74 kPa, He=98 kPa, 70 °C isotherm), retention time: 65.3 min and 68.2 min (major).

4.3.8. 3-Allyloxyheptanal (entry 12 in Table 2 and entry 5 in Table 4). $[\alpha]_D^{24}$ 2.2 [*c* 2.5, $CHCl_3$ (16% ee)] in the case of entry 5 in Table 4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (1H, t, *J*=2.2 Hz, CHO), 5.89 (1H, m, C*H*=CH$_2$), 5.26 (1H, dd, *J*=1.6, 17.6 Hz, CH=C*H*H), 5.16 (1H, dd, *J*=1.6, 10.4 Hz, CH=CH*H*), 4.01 (2H, m, CHOCH_2), 3.86 (1H, m, C*H*OCH$_2$), 2.63 (1H, ddd, *J*=2.4, 6.8, 16.4 Hz, C*H*HCHO), 2.53 (1H, ddd, *J*=2.0, 4.8, 16.4 Hz, CH*H*CHO), 1.25–1.70 (6H, m, $CH_2CH_2CH_2$), 0.91 (3H, t, *J*=6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 134.8, 117.0, 74.3, 70.2, 48.3, 34.0, 27.3, 22.7, 14.0; IR (neat) 2957, 2932, 2860, 2727, 2357, 1726, 1464, 1339, 1070, 1038, 924 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{10}H_{18}O_2Na$: 193.1199 ([M+Na]$^+$); found: 193.1197 ([M+Na]$^+$). The

enantiomeric excess was determined by conversion to 3-propoxyheptanal ($[\alpha]_D^{25}$ 2.3 [*c* 1.5, $CHCl_3$ (16% ee)]) by hydrogenation of an allyl group [H_2 (1 atm), 20 wt % Pd/C, THF (0.2 M)].

4.3.9. 3-Benzyloxyheptanal (entry 13 in Table 2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (1H, t, *J*=2.0 Hz, CHO), 7.22–7.40 (5H, m, Ar-H), 4.56 (1H, d, *J*=11.6 Hz, PhC*H*H), 4.51 (1H, d, *J*=11.6 Hz, PhCH*H*), 3.95 (1H, m, C*H*OBn), 2.67 (1H, ddd, *J*=2.4, 7.2, 16.4 Hz, C*H*HCHO), 2.56 (1H, ddd, *J*=2.0, 4.4, 16.4 Hz, CH*H*CHO), 1.27–1.75 (6H, m, $CH_2CH_2CH_2$), 0.91 (3H, t, *J*=6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 138.2, 128.4, 127.8, 127.7, 74.3, 71.2, 48.3, 33.9, 27.2, 22.7, 14.0; IR (neat) 2955, 2930, 2860, 1724, 1454, 1094, 1067, 1028, 735, 698 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{20}O_2Na$: 243.1356 ($[M+Na]^+$); found: 243.1362 ($[M+Na]^+$).

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