Supplementary Information

Bio-inspired asymmetric aldehyde arylations catalyzed by rhodium-cyclodextrin self-inclusion complexes

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1. General comments

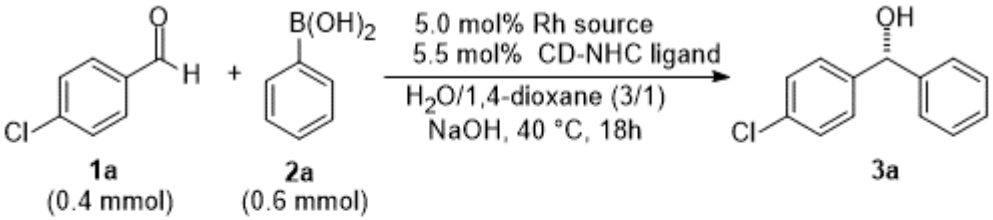
6-*O*-monotosyl cyclodextrins were prepared by the reported procedure.[s1] Other reagents were purchased from commercial sources and used without further purification.

Melting points were measured with a Stanford Research Systems MPA100 apparatus. Optical rotations were recorded by a Jasco P-2000 polarimeter. High performance liquid chromatography (HPLC) analyses were performed on Shimadzu LC-20AB coupled diode array-detector SPD-M20A with a ODS column (Kaseisorb LC ODS 2000-3 (4.6 mm I.D. × 150 mm)) or chiral columns (Daicel CHIRALCEL OB (4.6 mm I.D. × 250 mm), OD-3 (4.6 mm I.D. × 250 mm), AD-3 (4.6 mm I.D. × 250 mm)). ^{1}H NMR for 400 MHz and ^{13}C NMR for 100 MHz spectra were recorded by a JEOL JNM-Alice 400 spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra was obtained with a-cyano-4-hydroxycinnamic acid as a matrix on a BRUKER autoflex III. FAB mass spectroscopies (HRMS) were carried out by using a JEOL JMS-700 with polyethyleneglycol as a matrix. Elemental analyses were performed on Perkin Elmer 240C apparatus in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University.

2. Rh-catalyzed phenylation of *p*-chlorobenzaldehyde using CD–imidazolium salts.

Optimization of the reaction conditions was shown in Table S1.

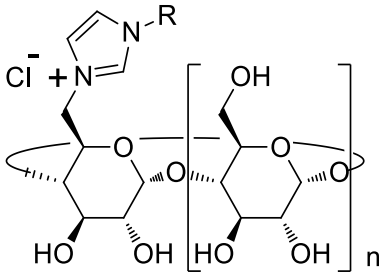
Table S1. Rh-catalyzed phenylation of *p*-chlorobenzaldehyde **1a**.



1a (0.4 mmol) **2a** (0.6 mmol) **3a**

entry	Rh source	CD-NHC ligand	Isolated yield (%)	ee (%)[a]
1	$[RhCl(cod)]_2$	---	76	----
2	$[RhCl(cod)]_2$	**L2**	68	0
3	$[RhCl(CH_2{=}CH_2)_2]_2$	**L2**	23	80
4[b]	$[RhCl(CH_2{=}CH_2)_2]_2$	**L2**	91	81
5	$[Rh(OAc)_2]_2$	---	n.d.	----
6	$[Rh(OAc)_2]_2$	**L2**	99	83
7[c]	$[Rh(OAc)_2]_2$	**L2**	88	70
8[d]	$[Rh(OAc)_2]_2$	**L2**	77	50
9	$RhCl_3{\cdot}H_2O$	**L2**	9	80
10	$[Rh(OAc)_2]_2$	**L1**	97	94
11	$[Rh(OAc)_2]_2$	**L4**	71	9
12	$[Rh(OAc)_2]_2$	**L3**	15	7
13[e]	$[Rh(OAc)_2]_2$	**L1**	99	95

[a]Determined by HPLC. [b]AgOAc (5.0 mol%) was added. [c]in H_2O/1,4-dioxane (1/3). [d]at 80 °C. [e]The reaction was performed with $[Rh(OAc)_2]_2$ (1.0 mol% of Rh) and CD-NHC ligand salt **L1** (1.1 mol%) for 6h.



L1: n = 7, R = Me **L3**: n = 5, R = Me
L2: n = 7, R = Mes **L4**: n = 5, R = Mes

3. Kinetic experiments

The kinetic experiments for the phenylation of aldehyde were performed by using TEG–benzaldehyde (**1y**) as a water-soluble substrate to ensure homogeneous reactions. Synthetic procedure of **1y** was described later. The concentration of product **3y** was measured quantitively by HPLC (ODS column/eluent: methanol–water) to calculate initial production rate of **3y**.

General procedure

Under N_2, $[Rh(OAc)_2]_2$ (4.4 mg, 0.010 mmol) and CD–imidazolium salt **L1** (γ-CD–$Im^+(Me)Cl^-$) (31 mg, 0.022 mmol) were added to the test tube. 0.40 mol/L NaOHaq (1.5 mL) and 1,4-Dioxane (0.20 mL) were added and stirred at 50 °C for 10 min. The complex mixture was added to the 1,4-dioxane (0.30 mL) solution of substrates (**1y**: 0.40 mmol, phenylboronic acid: 0.60 mmol) and stirred at 50 °C. The reaction solution samples (50 μL) were collected at fixed time intervals and quenched with NH_4Cl. The samples were diluted to 9 times with methanol. The diluted samples were analyzed with HPLC devices.

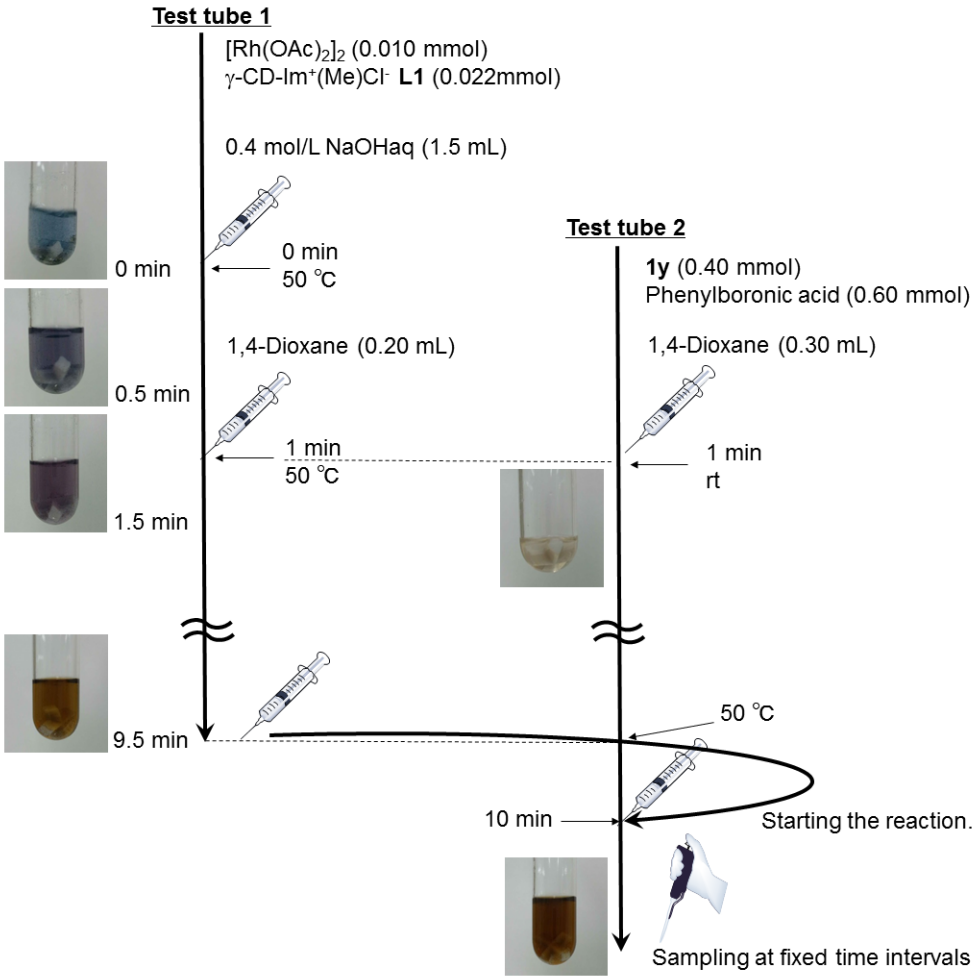


Figure S1. Schematic procedure of kinetic experiment.

Appendix

The reaction proceeded extremely slowly at lower concentrations of phenylboronic acid **2**, which is related to the pH of the reaction mixture. It is well known that boronic acids exist as anionic tetrahedral trihydroxyboronates in aqueous solutions of high pH.[s2] Therefore, the difference in the production rates can be attributed to the ionization equilibrium of the boronic acid.

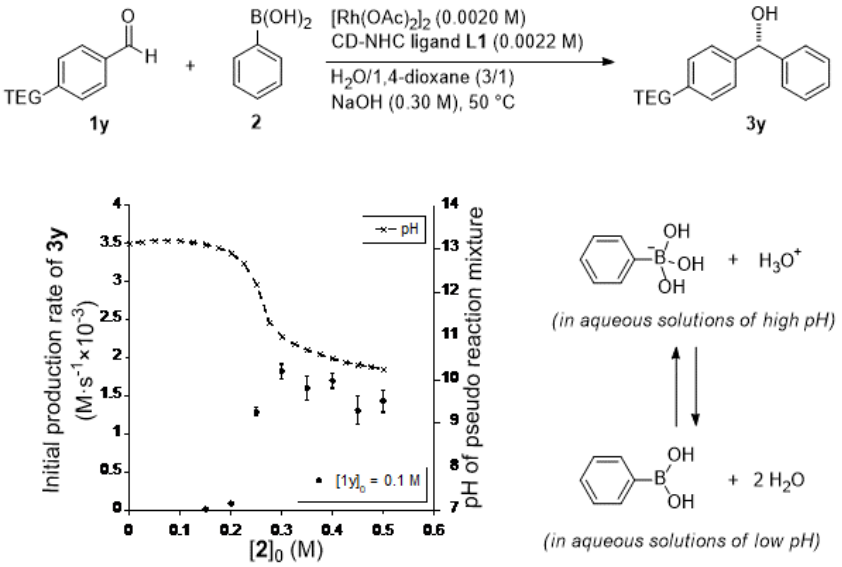
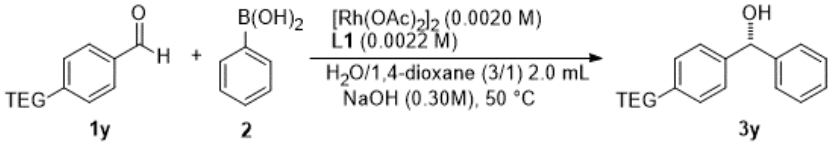


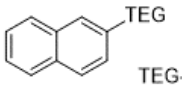
Figure S2. Kinetic experiments for the penylation of **1y** using CD–imidazolium salt **L1**. All data points are means ± 2SE, N = 4. The dashed curve is the pH of a pseudo-reaction mixture without a Rh source.

Table S2. Rh-catalyzed phenylation of TEG-benzaldehyde **1y**.



entry	$[\mathbf{1y}]_0$ (M)	$[\mathbf{2}]_0$ (M)	ee (%) of **3y**[a]
1	0.2	0.3	94%
2	0.5	0.3	94%
3	0.5	0.4	95%
4	0.5	0.5	95%
5[b]	0.1	0.3	95%
6[c]	0.1	0.3	95%
7[d]	0.1	0.3	95%

[a]Determined by HPLC. [b] [TEG-bearing naphthalene] = 0.1 M, [c] [TEG-bearing naphthalene] = 0.2 M, [d] [TEG-bearing naphthalene] = 0.3 M

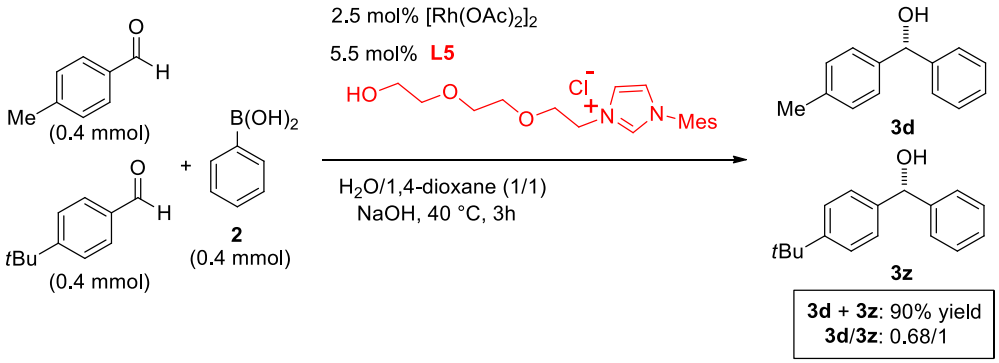


TEG-bearing naphthalene (as an inhibitor)

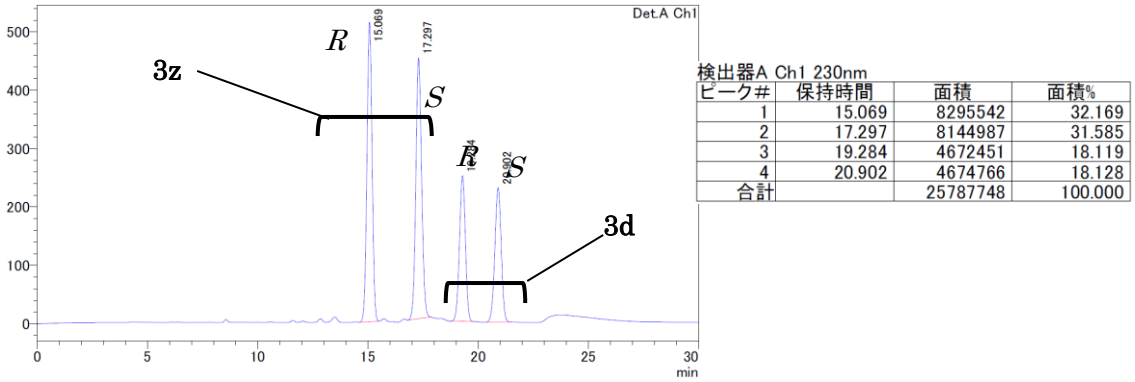
4. Competition experiments

The experiments were performed by similar procedure to general procedure of Rh-catalyzed phenylation in section 7.

Entry 1



HPLC condition: DAICEL CHIRALCEL OB, Hexane/IPA = 95/5, flow = 0.7 mL/min, wavelength = 230 nm, t_R = 15.1 min for (*R*)-**3z**, t_R = 17.3 min for (*S*)-**3z**, t_R = 19.3 min for (*R*)-**3d**, and t_R = 20.9 min for (*S*)-**3d**.



検出器A Ch1 230nm

ピーク#	保持時間	面積	面積%
1	15.069	8295542	32.169
2	17.297	8144987	31.585
3	19.284	4672451	18.119
4	20.902	4674766	18.128
合計		25787748	100.000

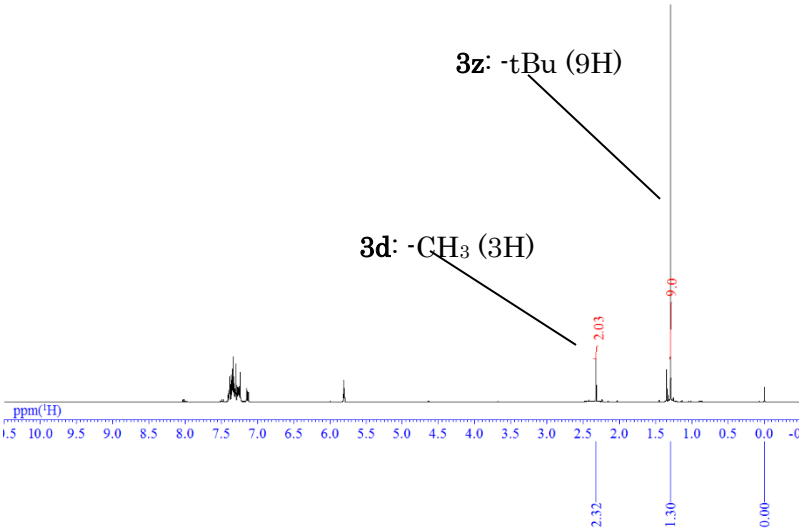
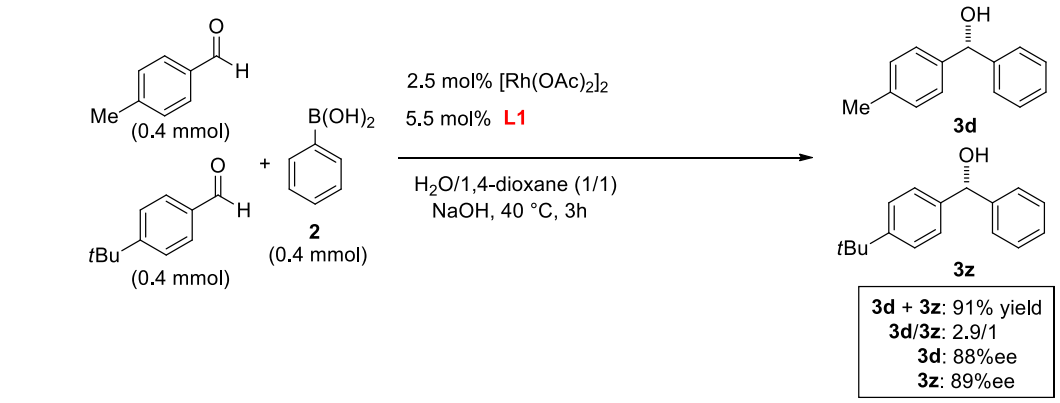
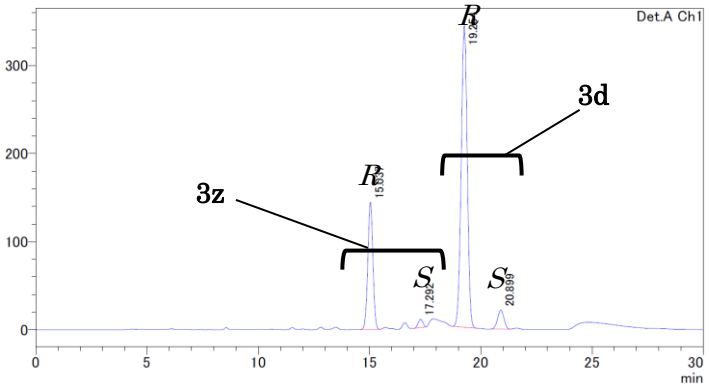


Figure S3. HPLC chat and ^{1}H NMR spectrum (in $CDCl_3$) of entry 1.

Entry 2





検出器A Ch1 230nm

ピーク#	保持時間	面積	面積%
1	15.037	2300834	24.569
2	17.292	137482	1.468
3	19.254	6501581	69.425
4	20.899	425036	4.539
合計		9364932	100.000

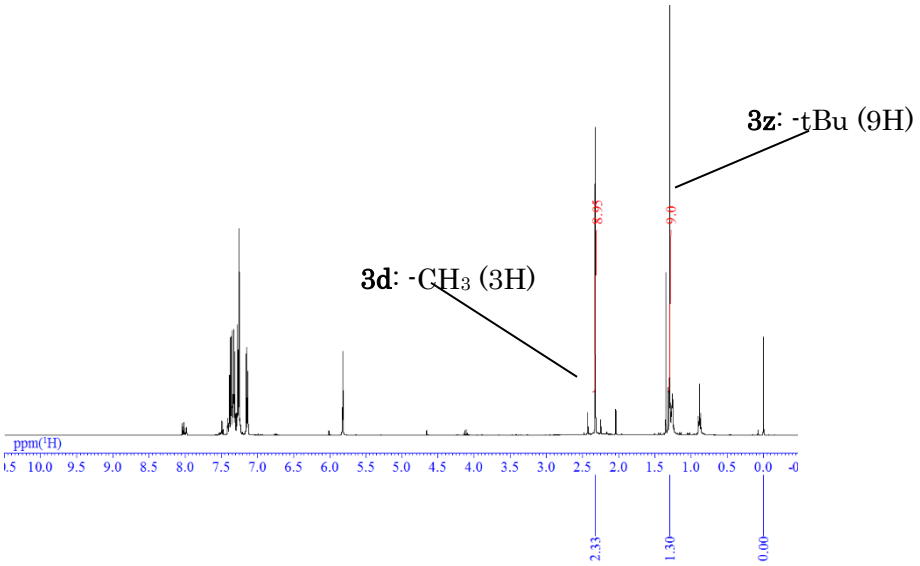


Figure S4. HPLC chat and ^{1}H NMR spectrum (in $CDCl_3$) of entry 2.

5. Synthetic procedures, and ^{1}H and ^{13}C NMR spectra of L1–L5

5-1. General synthetic procedure of CD–imidazolium salts (**L1**–**L4**)

These compounds were prepared under similar conditions with literature.[s3] 6-*O*-Monotosyl-γ-cyclodextrin (15.0 g, 10.3 mmol) and *N*-methylimidazole (2.54 g, 30.9 mmol) were dissolved in dry DMF (40 mL). The mixture was stirred under nitrogen at 90 °C for 4 day and cooled to room temperature. The reaction mixture was added to acetone (400mL) stirred vigorously. The white paste formed was filtered and dissolved in water. The solution was reprecipitated twice by pouring into acetone, and the resulting white paste was dried at 40 °C *in vacuo* to give γ-cyclodextrin–N-methylimidazolium tosylate as a white solid (12.3 g, 78%).

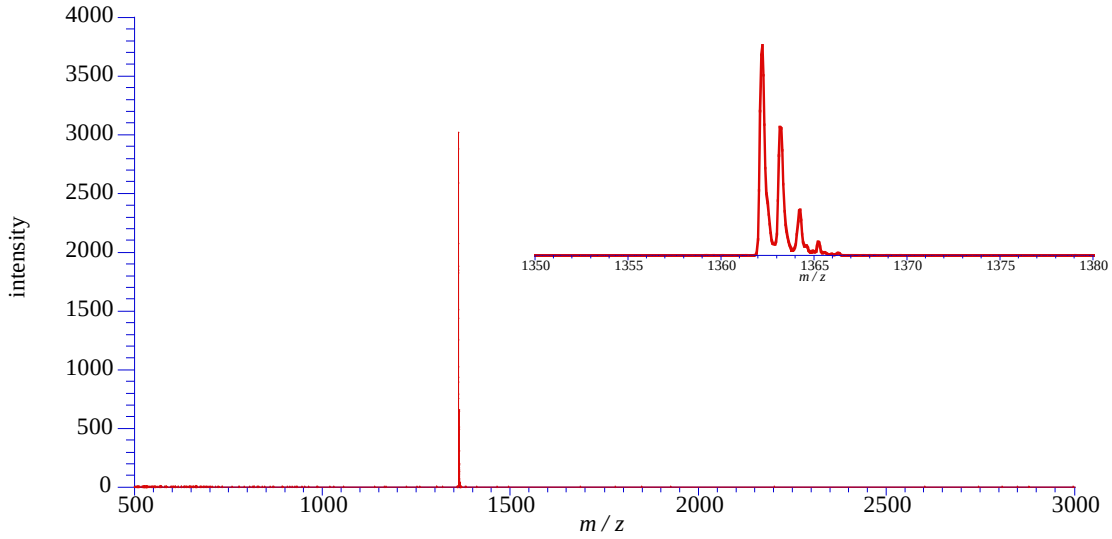
The tosylate (6.0 g, 3.9 mmol) was dissolved in deionized water (120 mL). The solution was contact with Amberlite IRA-900 resin (500 mL volumn) for 1 day and filtered, and the resin was washed with deionized water (240 mL). The whole filtrate was dried in vacuo to give CD–imidazolium salt **L1** (γ-CD–$Im^{+}(Me)Cl^{-}$) as a white solid (5.5 g, quantatively).

5-2. Synthetic procedure of TEG–imidazolium salt **L5**

2-[2-(2-chloroethoxy)ethoxy]ethanol (556 mg, 3.3 mmol) and *N*-mesitylimidazole (558 mg, 3.0 mmol) were dissolved in dry DMF (2.0 mL). The mixture was stirred under nitrogen at 90 °C for 2 day and cooled to room temperature. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel (9:1, CH_2Cl_2:MeOH and 7:3, CH_2Cl_2:MeOH) to give TEG–imidazolium salt **L5** (TEG–$Im^{+}(Mes)Cl^{-}$) as a pale yellow oil (195 mg, 18%).

5-3. CD–imidazolium salt **L1** (γ-CD–$Im^{+}(Me)Cl^{-}$)

78% yield (2steps); white solid; mp 241–246 °C, accompanied by decomposition; MALDI-TOF MS: (*m/z*) 1362 ([M-Cl^{-}]$^{+}$, $C_{52}H_{85}N_2O_{39}$, calcd. 1361); ^{1}H NMR (400MHz, D_2O, 25.0 °C) δ 7.59 (d, *J* = 2.0 Hz, 1H, Im-H), 7.52 (d, *J* = 2.0 Hz, 1H, Im-H), 5.16-5.09 (m, 8H, CD-H_1), 4.50-3.24 (m, 51H, CD-H, *N*-CH_3), The proton signals of N-CH=N(Im-H) and OH were dissapeared by deuterium exchange. These were observed as a singlet at 9.05 ppm and several peaks at 6.0–4.3 ppm in DMSO-d_6; ^{13}C NMR (100 MHz, D_2O, 25.0 °C) δ 124.25, 123.83, 102.61, 102.38–102.09 (overlapped), 82.95, 81.49, 81.22–81.05 (overlapped), 73.54–73.41 (overlapped), 73.08–72.22 (overlapped), 70.21, 61.20, 60.88-60.83 (overlapped), 60.30, 50.57, 36.45. Anal. Calcd for $C_{52}H_{85}ClN_2O_{39}\cdot H_2O$: C, 44.12; H, 6.19; N, 1.98%. Found: C, 44.18; H, 6.08; N, 1.89%.



Acquisition operation mode: Linear

Voltage polarity: Positive

Figure S5. MALDI-TOF mass spectrum of CD–imidazolium salt **L1** (γ-CD–$Im^{+}(Me)Cl^{-}$).

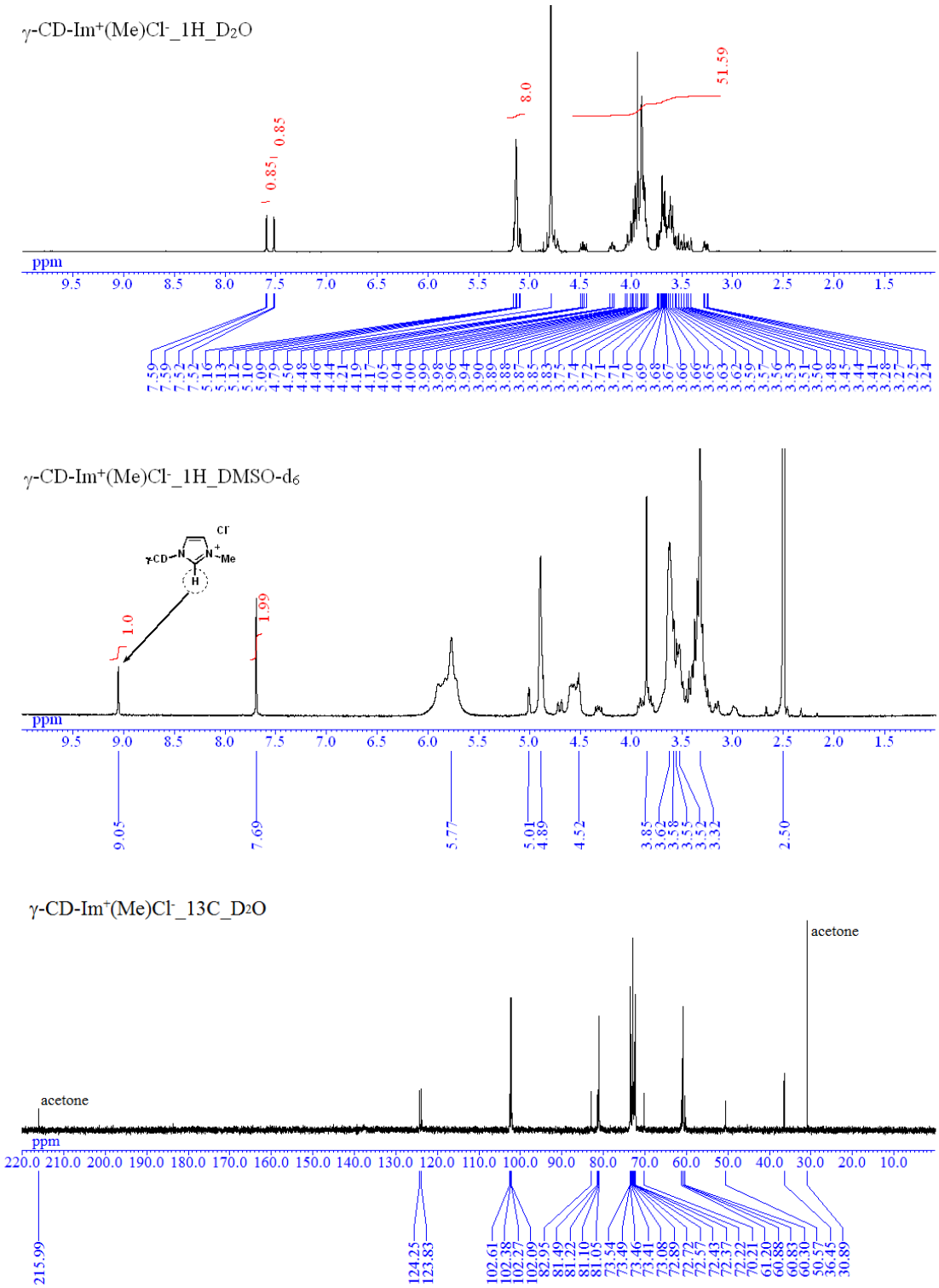
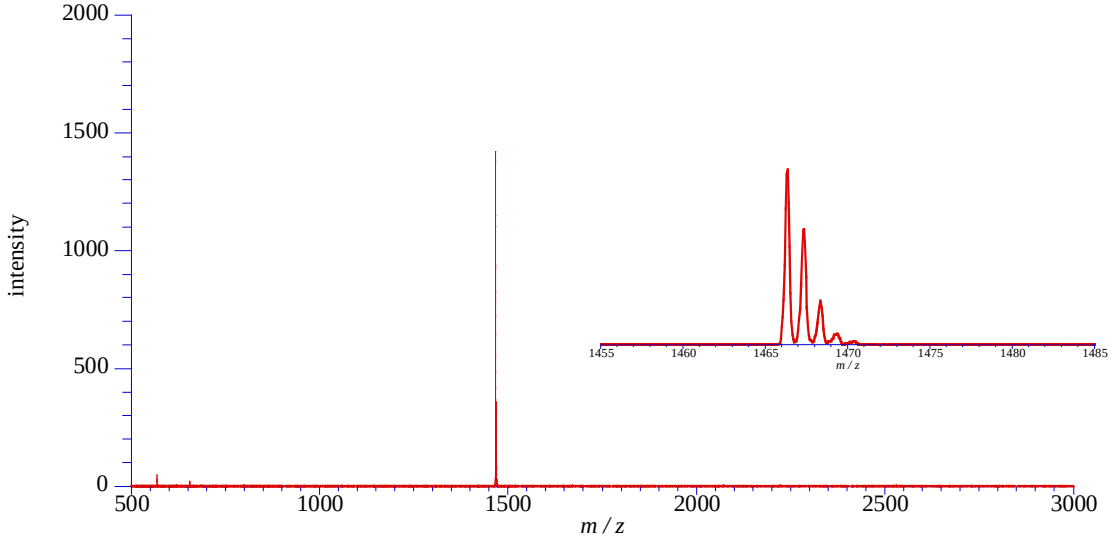


Figure S6. ^{1}H and ^{13}C NMR spectra of CD–imidazolium salt **L1** (γ-CD–$Im^{+}(Me)Cl^{-}$).

5-4. CD–imidazolium salt **L2** (γ-CD–$Im^{+}(Mes)Cl^{-}$)

59% yield (2 steps); white solid; mp 243–246 °C, accompanied by decomposition; MALDI-TOF MS: (*m/z*) 1466 ([M-Cl^{-}]$^{+}$, $C_{60}H_{93}N_2O_{39}$, calcd. 1466); ^{1}H NMR (400MHz, D_2O, 25.0 °C): δ 7.94 (d, *J* = 1.9 Hz, 1H, Im-H), 7.66 (d, *J* = 1.9 Hz, 1H, Im-H), 7.19(s, 2H, Ar-H(Mes)), 5.21–5.11 (m, 8H, CD-H_1), 4.68–3.39 (m, 48H, CD-H), 2.38 (s, 3H, *p*-Me(Mes)), 2.09–2.03 (m, 6H, *o*-Me(Mes)), The proton signals of N-CH=N(Im-H) and OH were dissapeared by deuterium exchange. These were observed as a singlet at 9.22 ppm and several peaks at 6.1–4.4 ppm in DMSO-d_6; ^{13}C NMR (100 MHz, D_2O, 25.0 °C) δ 142.14, 135.05, 131.33, 129.96, 124.85, 124.68, 102.72, 102.43–102.26 (overlapped), 101.66, 82.81, 81.55, 81.28–81.00 (overlapped), 80.29, 73.65–72.37 (overlapped), 70.10, 61.31, 60.94–60.68 (overlapped), 50.75, 20.95, 17.21–17.16 (overlapped). Anal. Calcd for $C_{60}H_{93}ClN_2O_{39}\cdot H_2O$: C, 47.42; H, 6.30; N, 1.84%. Found: C, 47.37; H, 6.20; N, 1.73%.



Acquisition operation mode: Linear

Voltage polarity: Positive

Figure S7. MALDI-TOF mass spectrum of CD–imidazolium salt **L2** (γ-CD–$Im^{+}(Mes)Cl^{-}$).

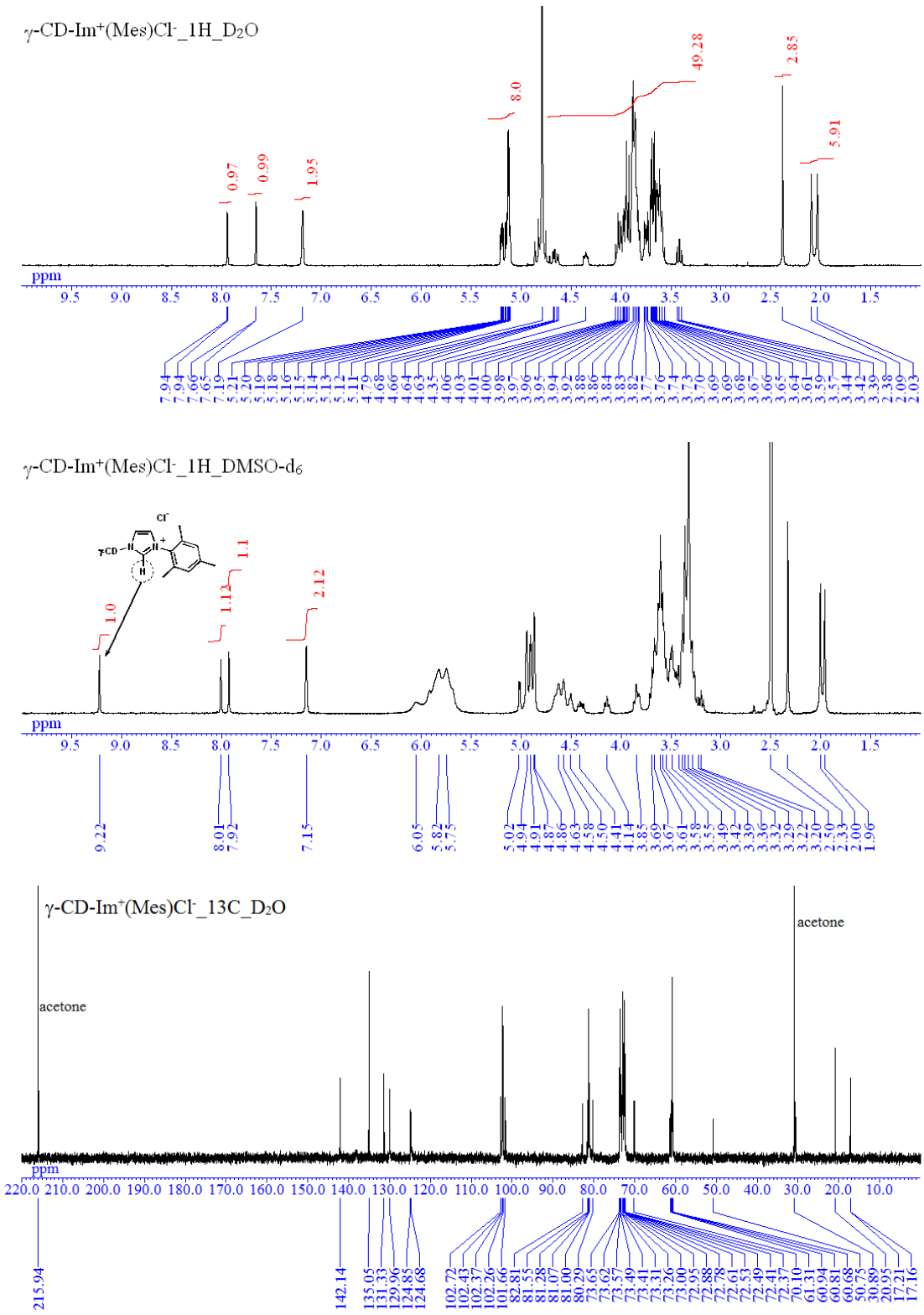
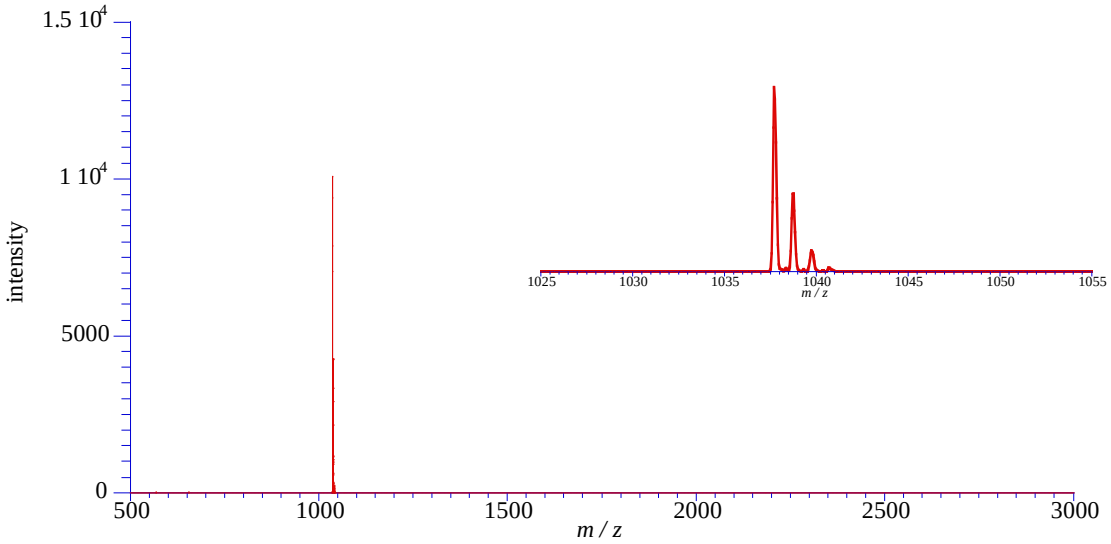


Figure S8. ^{1}H and ^{13}C NMR spectra of CD–imidazolium salt **L2** (γ-CD–Im^{+}(Mes)Cl^{-}).

5-5. CD–imidazolium salt **L3** (α-CD–$Im^{+}(Me)Cl^{-}$)

16% yield (2 steps); pale brown solid; mp 240–241 °C, accompanied by decomposition; MALDI-TOF MS: (*m/z*) 1038 ([M-Cl^{-}]$^{+}$, $C_{40}H_{65}N_2O_{29}$, calcd. 1037); ^{1}H NMR (400MHz, D_2O, 25.0 °C) δ 7.60 (d, *J* = 1.9 Hz, 1H, Im-H), 7.52 (d, *J* = 1.9 Hz, 1H, Im-H), 5.12–5.04 (m, 6H, CD-H_1), 4.52–3.22 (m, 39H, CD-H, *N*-CH_3), The proton signals of N-CH=N(Im-H) and OH were dissapeared by deuterium exchange. These were observed as a singlet at 9.16 ppm and several peaks at 5.6–4.4 ppm in DMSO-*d*$_6$; ^{13}C NMR (100 MHz, D_2O, 25.0 °C) δ 124.17, 123.87, 101.97–101.84 (overlapped), 83.07, 82.27, 81.88–81.78 (overlapped), 73.86–73.71 (overlapped), 73.23, 72.64–71.94 (overlapped), 70.39, 61.51, 61.07–60.92 (overlapped), 60.30, 50.57, 36.38. Anal. Calcd for $C_{40}H_{65}ClN_2O_{29}\cdot H_2O$: C, 44.02; H, 6.19; N, 2.57%. Found: C, 44.25; H, 6.01; N, 2.33%.



Acquisition operation mode: Linear

Voltage polarity: Positive

Figure S9. MALDI-TOF mass spectrum of CD–imidazolium salt **L3** (α-CD–$Im^{+}(Me)Cl^{-}$).

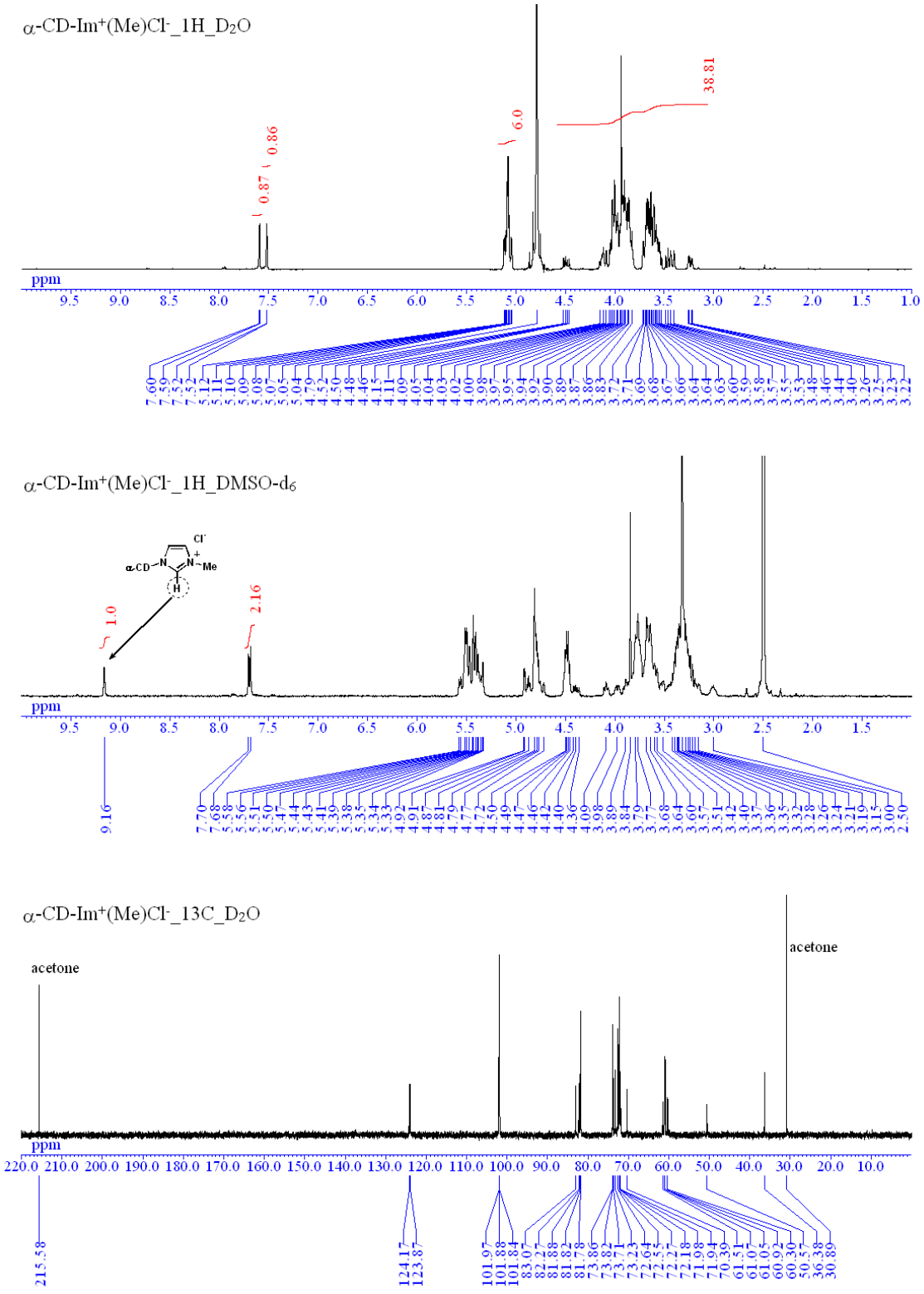
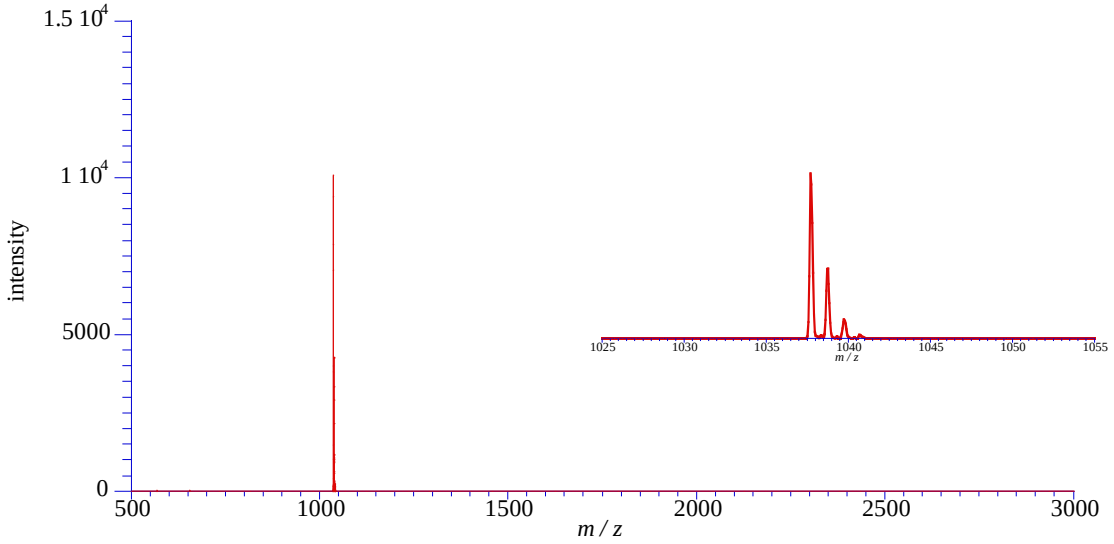


Figure S10. ^{1}H and ^{13}C NMR spectra of CD–imidazolium salt **L3** (α-CD–Im^{+}(Me)Cl^{-}).

5-6. CD–imidazolium salt **L4** (α-CD–$Im^+(Mes)Cl^-$)

32% yield (2 steps); pale brown solid; mp 246–252 °C, accompanied by decomposition; MALDI-TOF MS: (*m/z*) 1142 ([M-Cl^-]$^+$, $C_{48}H_{73}N_2O_{29}$, calcd. 1141); ^{1}H NMR (400MHz, D_2O, 25.0 °C) δ 7.91 (d, *J* = 1.9 Hz, 1H, Im-H), 7.70 (d, *J* = 1.9 Hz, 1H, Im-H), 7.22 (s, 2H, Ar-H(Mes)), 5.14–5.07 (m, 6H, CD-H_1), 4.33–3.32 (m, 36H, CD-H), 2.40 (s, 3H, *p*-CH_3(Mes)), 2.12–2.06 (m, 6H, *o*-CH_3(Mes)), The proton signals of N-CH=N(Im-H) and OH were dissapeared by deuterium exchange. These were observed as a singlet at 9.29 ppm and several peaks at 5.6–4.3 ppm in DMSO-d_6; ^{13}C NMR (100 MHz, D_2O, 25.0 °C) δ 141.51, 135.29, 131.54, 129.79–129.73 (overlapped), 124.96, 124.40, 102.32–101.94 (overlapped), 82.98, 82.23–81.90 (overlapped), 74.12–71.88 (overlapped), 69.78, 61.36–60.97 (overlapped), 50.69, 21.14, 17.17–17.08 (overlapped). HRMS (FAB): (*m/z*) 1141.4313 [M-Cl^-]$^+$, $C_{48}H_{73}N_2O_{29}$, calcd. 1141.4229.



Acquisition operation mode: Linear

Voltage polarity: Positive

Figure S11. MALDI-TOF mass spectrum of CD–imidazolium salt **L4** (α-CD–$Im^+(Mes)Cl^-$).

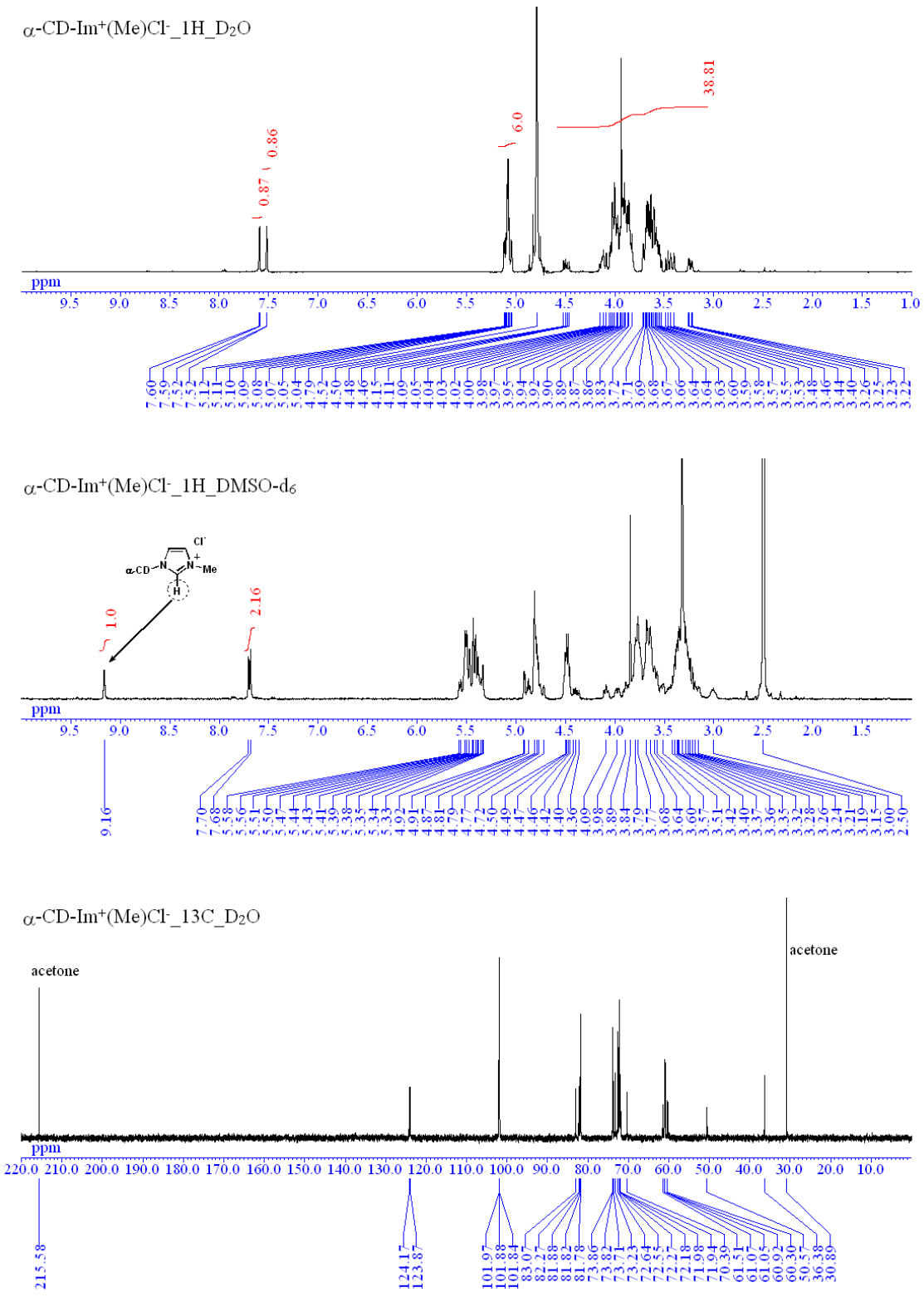


Figure S12. ^{1}H and ^{13}C NMR spectra of CD–imidazolium salt **L4** (α-CD–Im^{+}(Mes)Cl^{-}).

5-7. TEG–imidazolium salt **L5** (TEG–Im$^+$(Mes)Cl$^-$)

18% yield; pale yellow oil; ^{1}H NMR (400MHz, $CDCl_3$, 20.3 °C) δ 10.12 (s, 1H, Im-H), 8.10 (s, 1H, Im-H), 7.15 (s, 1H, Im-H), 7.01 (s, 2H, Ar-H(Mes)), 4.95 (t, *J* = 4.6 Hz, 2H, OCH_2CH_2O), 4.02 (t, *J* = 4.6 Hz, 2H, OCH_2CH_2O), 3.75–3.54 (m, 9H, OCH_2CH_2O, OH), 2.35 (s, 3H, *o*-CH_3(Mes)), 2.07 (s, 6H, *p*-CH_3(Mes)); ^{13}C NMR (100 MHz, $CDCl_3$, 25.0 °C) δ 140.89, 138.35, 134.24, 130.81, 129.57, 124.26, 122.69, 72.59, 70.08–70.05 (overlapped), 68.82, 60.92, 49.65, 20.96, 17.36. HRMS (FAB): (*m/z*) 319.2021 [M-Cl$^-$]$^+$, $C_{18}H_{27}N_2O_3$, calcd. 319.2016.

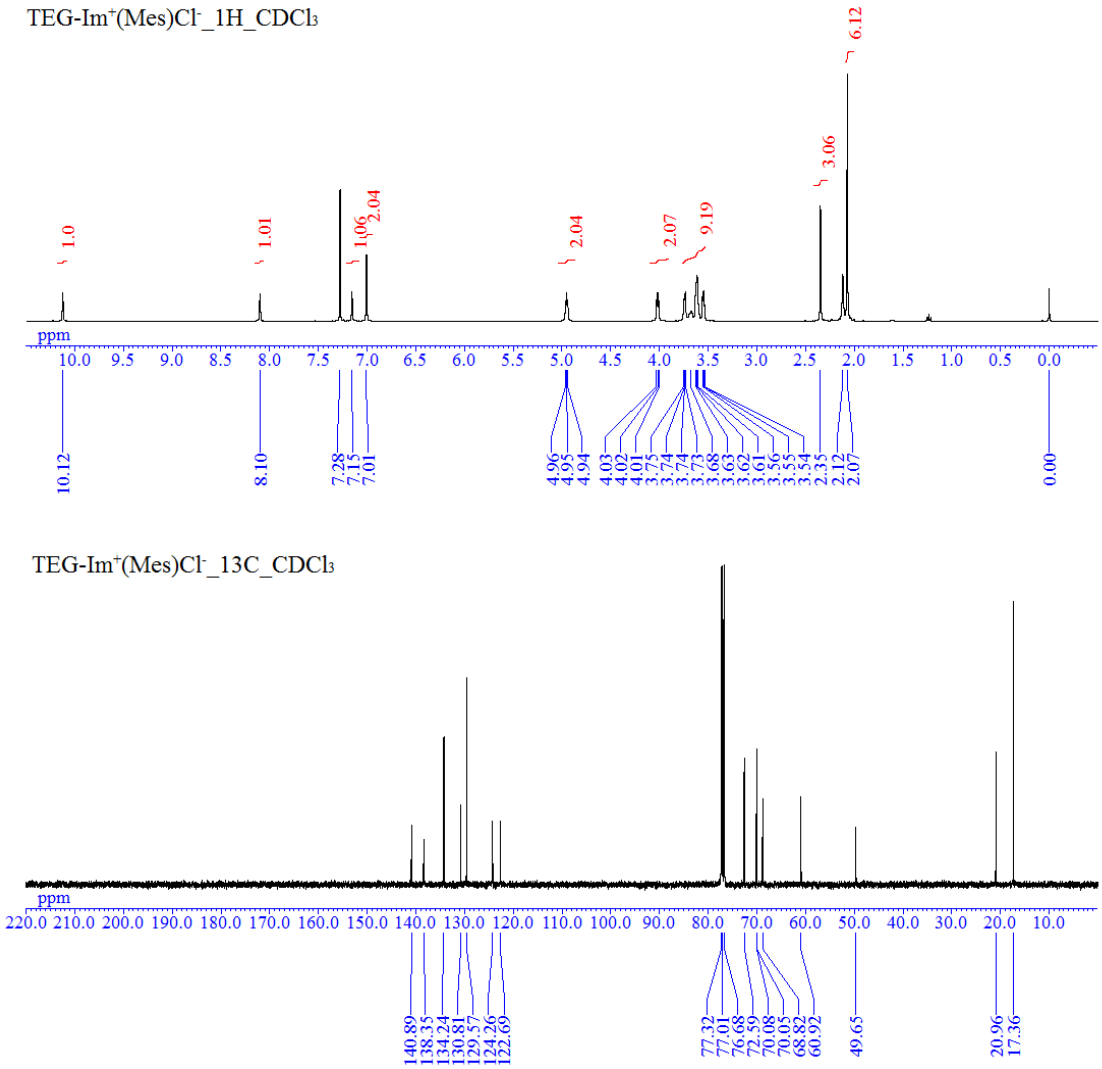


Figure S13. ^{1}H and ^{13}C NMR spectra of TEG–imidazolium salt **L5** (TEG–Im$^+$(Mes)Cl$^-$).

6. Synthetic procedure , and ^{1}H and ^{13}C NMR spectra of TEG–benzaldehyde (1y)

2-[2-(2-chloroethoxy)ethoxy]ethanol (9.6 g, 80 mmol) and 4-hydroxybenzaldehyde (13.6 g, 80 mmol) were dissolved in dry DMF (120 mL). And then, K_2CO_3 (22.0g, 160 mmol) was added to the mixture. The reaction mixture was stirred at 90 °C for 4 day and cooled to room temperature. The reaction mixture was neutralized with NH_4Cl, and extracted with CH_2Cl_2. The organic layer was dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (1:1, CH_2Cl_2:EtOAc) to give TEG–benzaldehyde (**1y**) as a pale yellow oil (16.6 g, 65.0 mmol).

1y: 81% yield; pale yellow oil; ^{1}H NMR (400MHz, $CDCl_3$, 19.3 °C) δ 9.87 (s, 1H, CHO), 7.83 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.03 (d, *J* = 9.0 Hz, 2H, Ar-H), 4.22 (t, *J* = 4.6 Hz, 2H, OCH_2CH_2O), 3.90 (t, *J* = 4.6 Hz, 2H, OCH_2CH_2O), 3.75–3.60 (m, 8H, OCH_2CH_2O), 2.96 (bs, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$, 19.1 °C) δ 190.56, 163.38, 131.56, 129.54, 114.46, 72.17, 70.37, 69.84, 68.94, 67.26, 61.12. HRMS (FAB): (*m/z*) 255.1232 $[M+H]^+$, $C_{13}H_{19}O_5$, calcd. 255.1227.

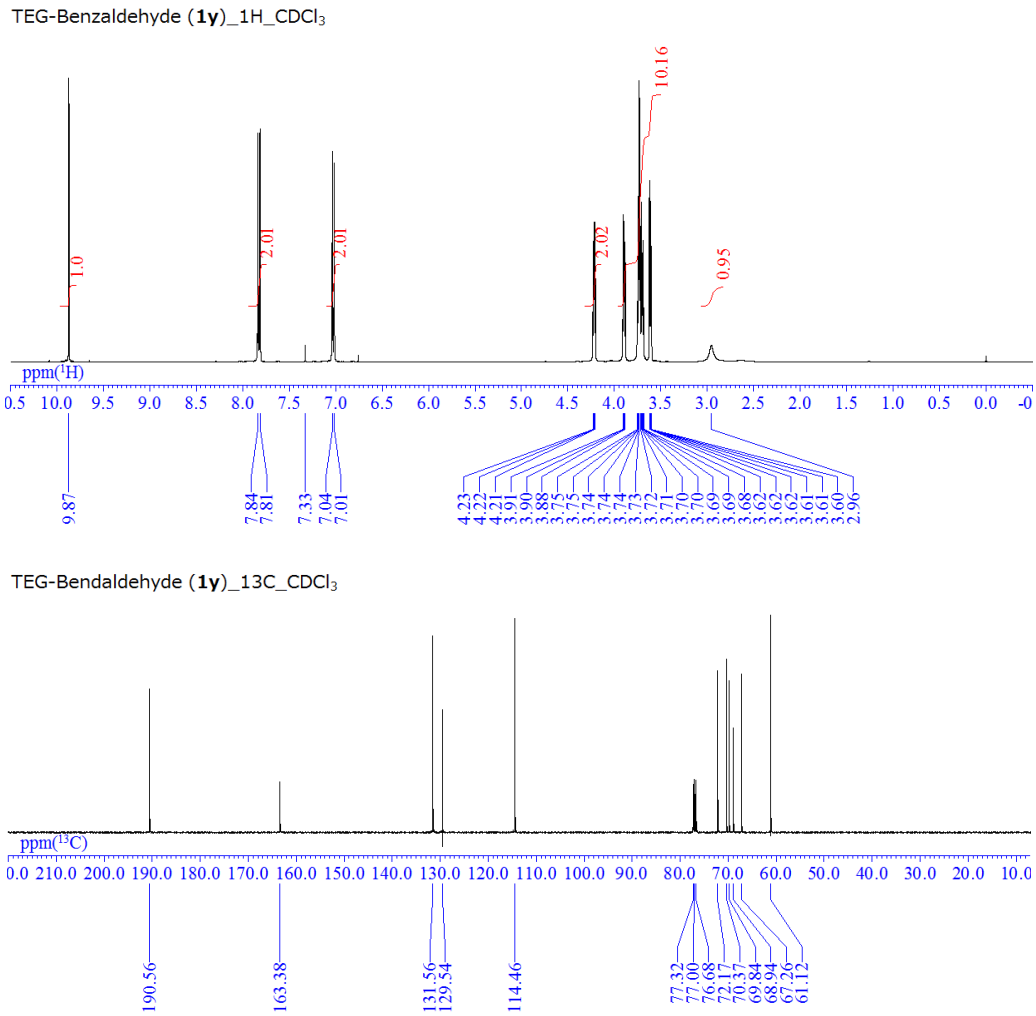


Figure S14. ^{1}H and ^{13}C NMR spectra of TEG–benzaldehyde (**1y**).

7. General procedure of Rh-catalyzed arylation

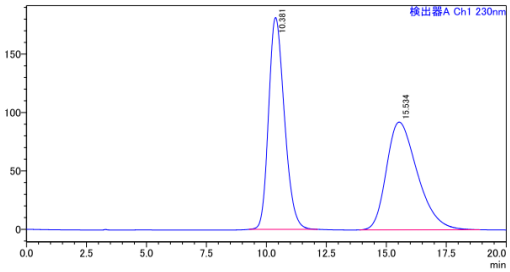
Under N_2, rhodium acetate dimer (1.8 mg, 0.0040 mmol), imidazolium salt (0.0088 mmol) were dissolved in degassed 1N NaOHaq (0.8 mL). To the solution, degassed water (2.2mL) and 1,4-dioxane (1.0 mL) were added and the mixed solution was stirred at 40 ℃ for 15 minutes. To the resulting Rh complex solution, boronic acid (1.2 mmol) and aldehyde (0.80 mmol) was added, and then the mixture was stirred at 40 ℃ for 6 hours. The reaction mixture was diluted with diethylether and filtered with short silica gel column, and then, the filtrate was concentrated. The desired arylcarbinol was isolated by a purification with the silica gel column (eluent: EtOAc/hexane mixture). The purity and optical purity of the product were analyzed by ^{1}H NMR analysis, optical rotation and HPLC analysis with chiral columns.

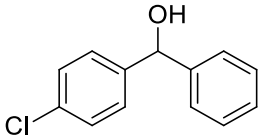
The standard racemic compounds were prepared by similar procedure using 1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride instead of CD–imidazolium salts.

8. HPLC charts and ^{1}H NMR spectra of arylcarbinols 3a–3y

8-1. (*R*)-*p*-Chlorophenyl(phenyl)carbinol (**3a**)

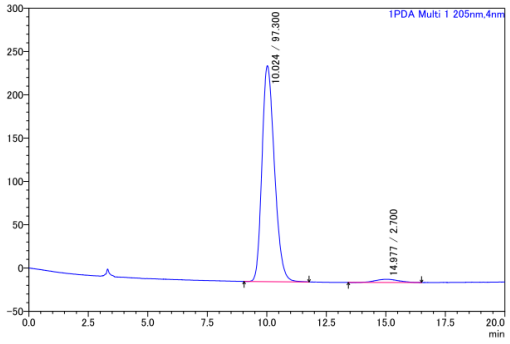
White solid; 99% yield, 95% ee; $[\alpha]_D^{23}$ = -20 (*c* = 0.40, $CHCl_3$), (lit.[s4] $[\alpha]_D^{30}$ = +18.6 (*c* = 0.40, $CHCl_3$) for 87% ee, (*S*)); HPLC condition: DAICEL CHIRALCEL OB, Hexane/IPA = 85/15, flow = 1.0 mL/min, wavelength = 205 nm, t_R = 10.0 min for (*R*) and t_R = 15.0 min for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.26 (m, 9H), 5.81 (d, J = 3.6 Hz, 1H), 2.21 (d, J = 3.6 Hz, 1H).

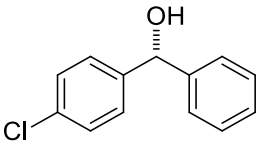




検出器A Ch1 230nm

ピーク#	保持時間	面積	面積%
1	10.381	8309195	50.079
2	15.534	8282965	49.921
合計		16592160	100.000





PDA Ch1 205nm

ピーク#	保持時間	面積%
1	10.024	97.300
2	14.977	2.700
合計		100.000

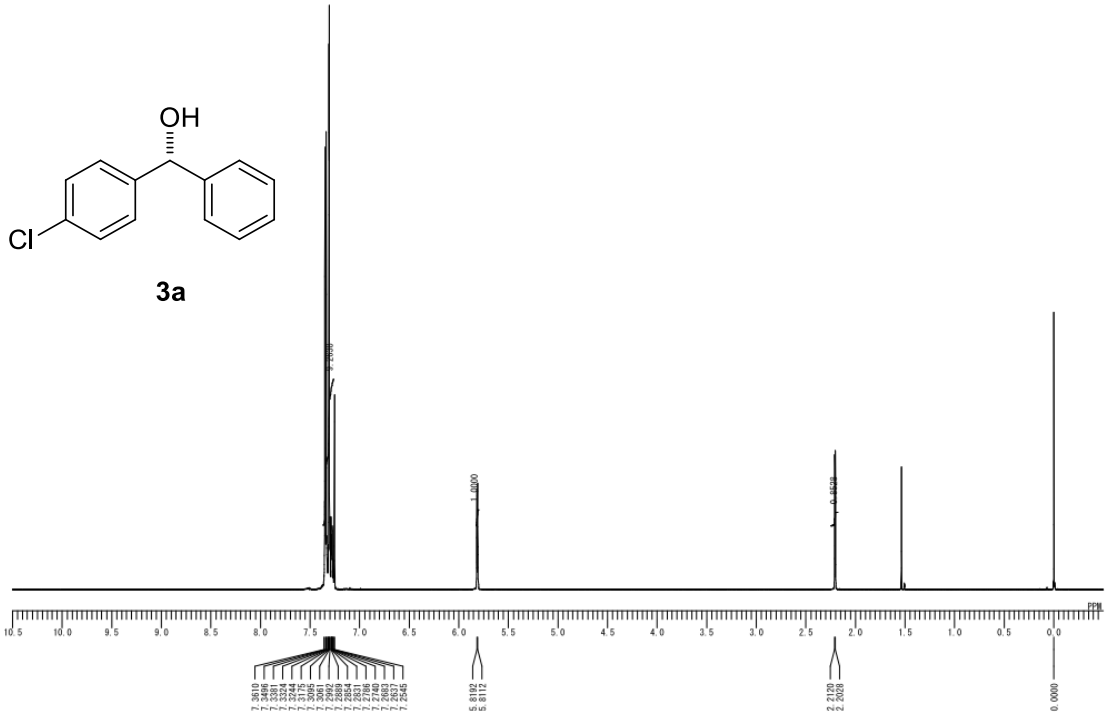
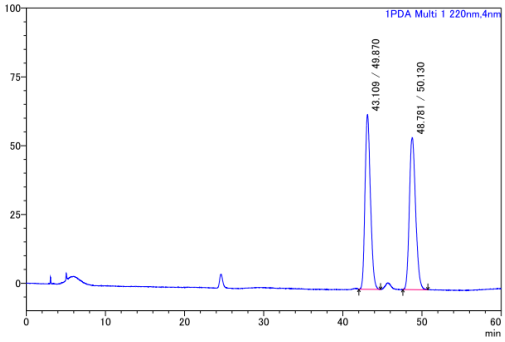
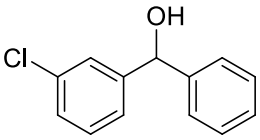


Figure S15. HPLC charts of **3a** and the racemic compound and ^{1}H NMR spectrum of **3a.**

8-2. (*R*)-*m*-Chlorophenyl(phenyl)carbinol (**3b**)

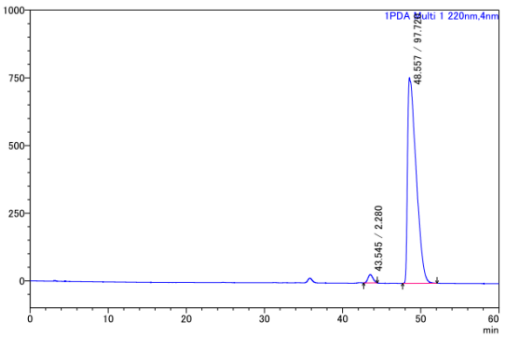
Colorless oil; 99% yield, 94% ee; $[\alpha]_D^{23}$ = -34 (*c* = 0.40, $CHCl_3$), (lit.[s5] $[\alpha]_D^{22}$ = +33.1 (*c* = 0.37, $CHCl_3$) for 96% ee, (*S*)); HPLC condition: DAICEL CHIRALCEL OD-3, Hexane/IPA = 98/2, flow = 1.0 mL/min, wavelength = 220 nm, t_R = 43.5 min for (*S*) and t_R = 48.6 min for (*R*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.17 (m, 9H), 5.68 (s, 1H), 2.70 (br, 1H).

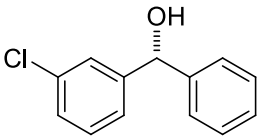




PDA Ch1 220nm

ピーク#	保持時間	面積	面積%
1	43.109	3028168	49.870
2	48.781	3043897	50.130
合計		6072065	100.000





PDA Ch1 220nm

ピーク#	保持時間	面積	面積%
1	43.545	1356645	2.280
2	48.557	58153761	97.720
合計		59510407	100.000

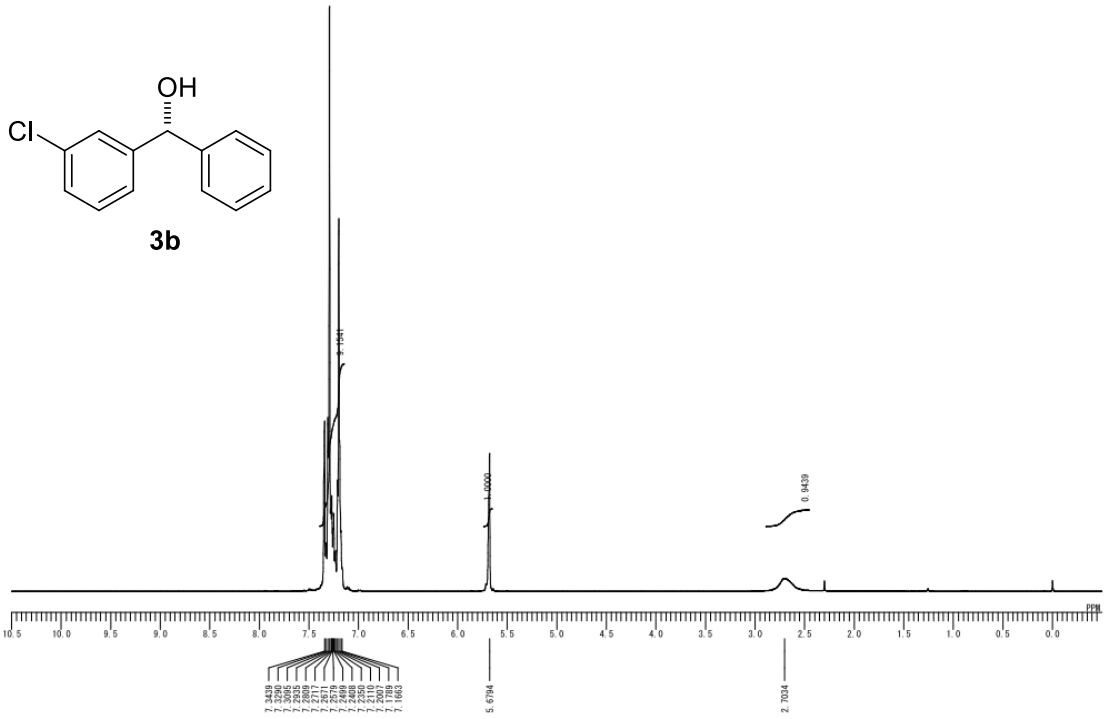
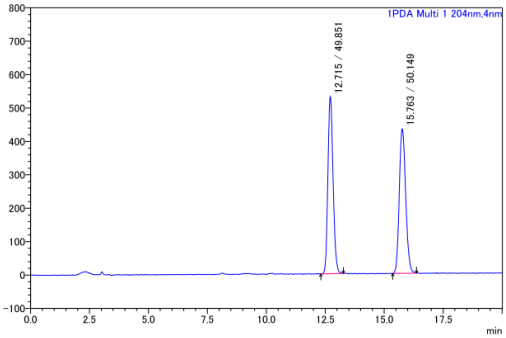
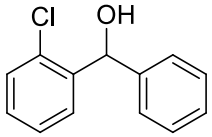


Figure S16. HPLC charts of **3b** and the racemic compound and ^{1}H NMR spectrum of **3b.**

8-3. (*R*)-*o*-Chlorophenyl(phenyl)carbinol (**3c**)

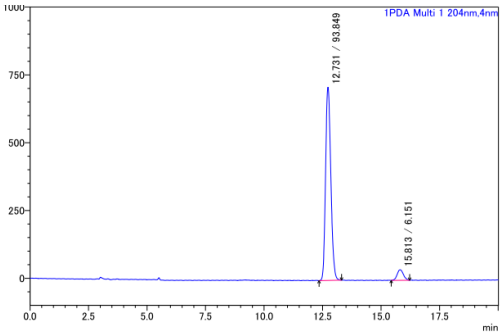
Colorless oil; 89% yield, 88% ee; $[\alpha]_D^{23}$ = +40 (*c* = 0.42, $CHCl_3$), (lit.[s5] $[\alpha]_D^{22}$ = -21.0 (*c* = 0.21, $CHCl_3$) for 93% ee, (*S*)); HPLC condition: DAICEL CHIRALCEL OD-3, Hexane/IPA = 95/5, flow = 1.0 mL/min, wavelength = 204 nm, t_R = 12.7 min for (*R*) and t_R = 15.8 min for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.7 Hz, 1.4 Hz, 1H), 7.41–7.20 (m, 8H), 6.23 (d, *J* = 4.1 Hz, 1H), 2.32 (d, *J* = 3.9 Hz, 1H).

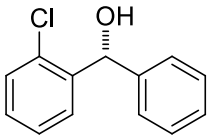




PDA Ch1 204nm

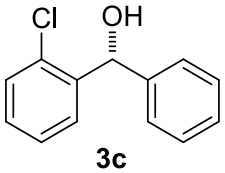
ピーク#	保持時間	面積	面積%
1	12.715	8113536	49.851
2	15.763	8162118	50.149
合計		16275654	100.000





PDA Ch1 204nm

ピーク#	保持時間	面積	面積%
1	12.731	11137372	93.849
2	15.813	729977	6.151
合計		11867349	100.000

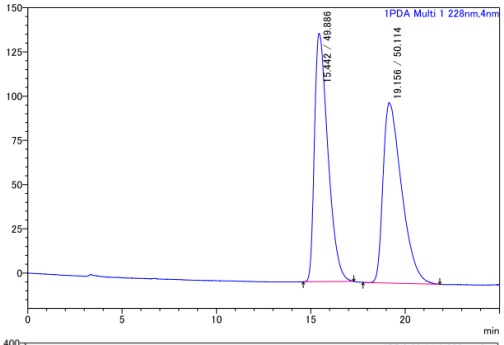


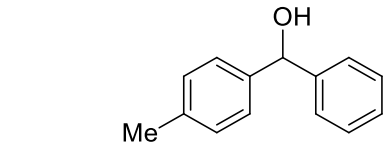
3c

Figure S17. HPLC charts of **3c** and the racemic compound and ^{1}H NMR spectrum of **3c.**

8-4. (*R*)-*p*-Methylphenyl(phenyl)carbinol (**3d**)

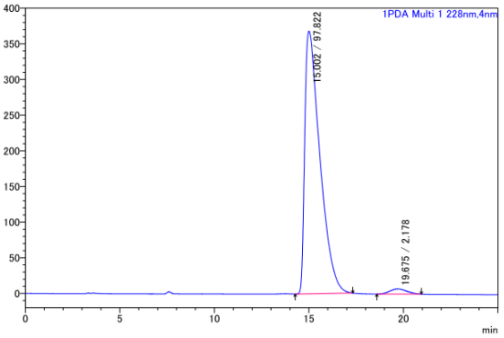
White solids; 90% yield, 96% ee; $[\alpha]_D^{23}$ = +10 (*c* = 0.40, $CHCl_3$), (lit.[s4] $[\alpha]_D^{21}$ = +19.6 (*c* = 0.80, $CHCl_3$) for 82% ee, (*R*)); HPLC condition: DAICEL CHIRALCEL OB, Hexane/IPA = 95/5, flow = 1.0 mL/min, wavelength = 228 nm, t_R = 15.0 min for (*R*) and t_R = 19.7 min for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.24 (m, 7H), 7.15–7.13 (m, 2H), 5.82 (d, *J* = 2.8 Hz, 1H), 2.33 (s, 3H), 2.15 (br, 1H).

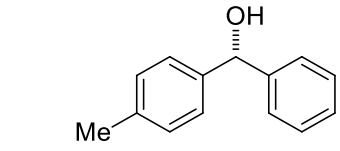




PDA Ch1 228nm

ピーク#	保持時間	面積	面積%
1	15.442	6951992	49.886
2	19.156	6983872	50.114
合計		13935864	100.000





PDA Ch1 228nm

ピーク#	保持時間	面積%	マーク
1	15.002	97.822	M
2	19.675	2.178	M
合計		100.000	

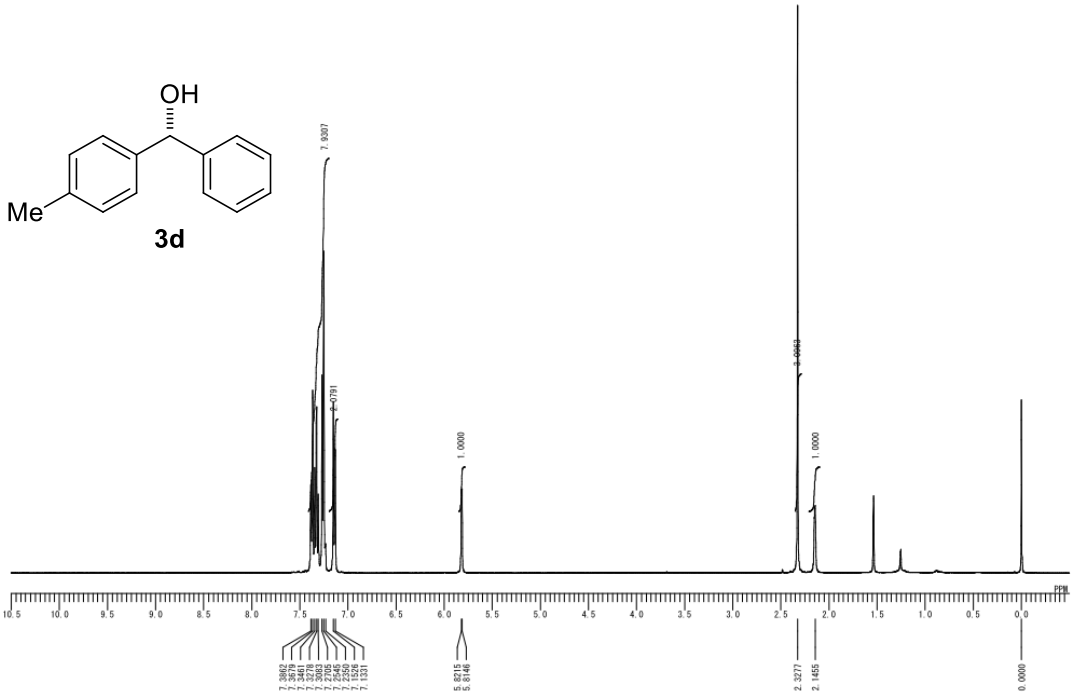
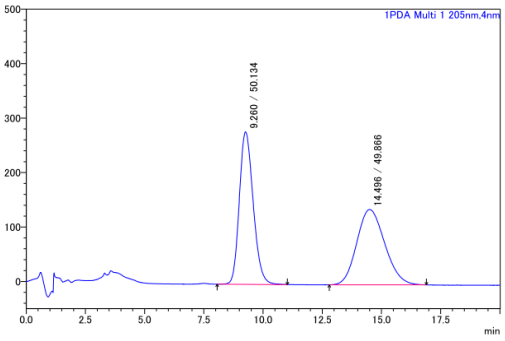
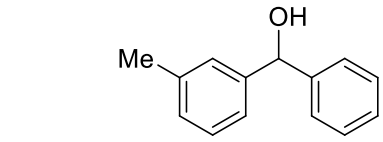


Figure S18. HPLC charts of **3d** and the racemic compound and ^{1}H NMR spectrum of **3d.**

8-5. (*R*)-*m*-Methylphenyl(phenyl)carbinol (**3e**)

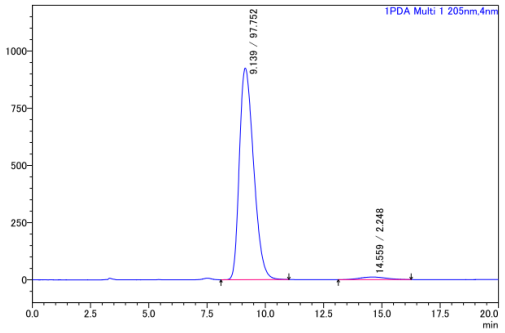
Colorless oil; 96% yield, 96% ee; $[\alpha]_D^{23}$ = +2 (*c* = 0.60, $CHCl_3$), (lit.[s6] $[\alpha]_D$ = -1.1 (*c* = 0.45, $CHCl_3$) for 91% ee, (*S*)); HPLC condition: DAICEL CHIRALCEL OB, Hexane/IPA = 85/15, flow = 1.0 mL/min, wavelength = 205 nm, t_R = 9.1 min for (*R*) and t_R = 14.6 min for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.06 (m, 9H), 5.80 (s, 1H), 2.33 (s, 3H), 2.20 (d, *J* = 2.8 Hz, 1H).

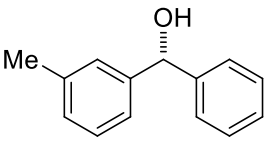




PDA Ch1 205nm

ピーク#	保持時間	面積	面積%
1	9.260	11420872	50.134
2	14.496	11359805	49.866
合計		22780678	100.000





PDA Ch1 205nm

ピーク#	保持時間	面積	面積%
1	9.139	39250902	97.752
2	14.559	902771	2.248
合計		40153673	100.000

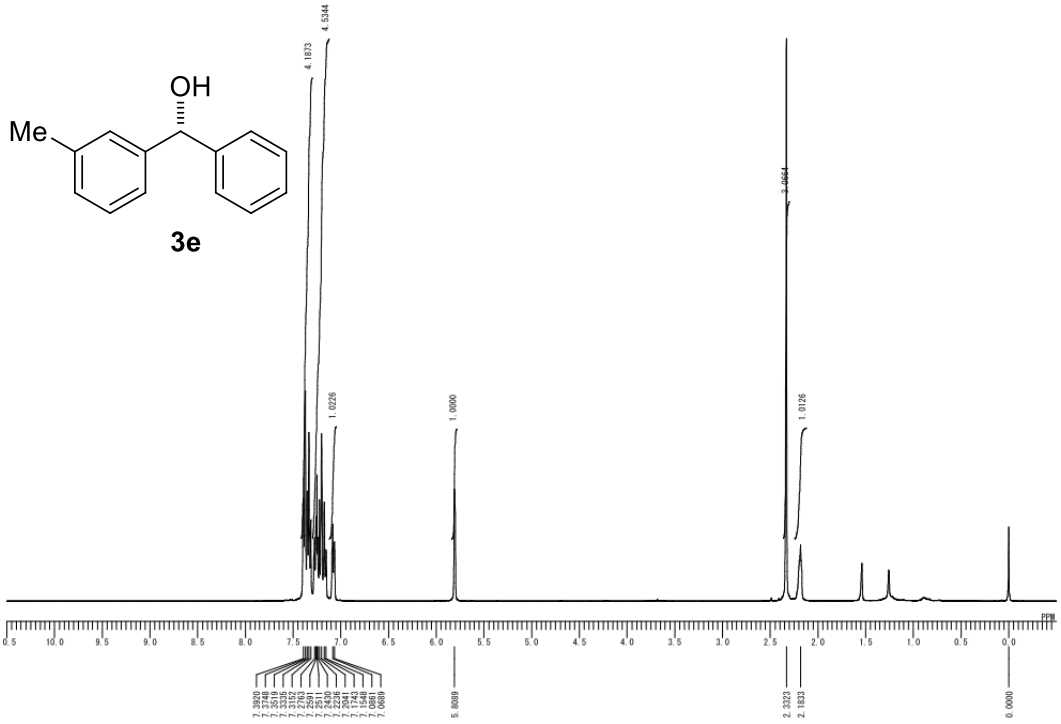
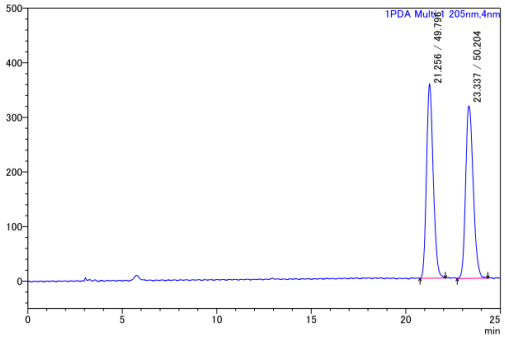
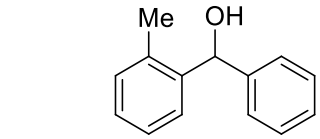


Figure S19. HPLC charts of **3e** and the racemic compound and ^{1}H NMR spectrum of **3e.**

8-6. (*R*)-*o*-Methylphenyl(phenyl)carbinol (**3f**)

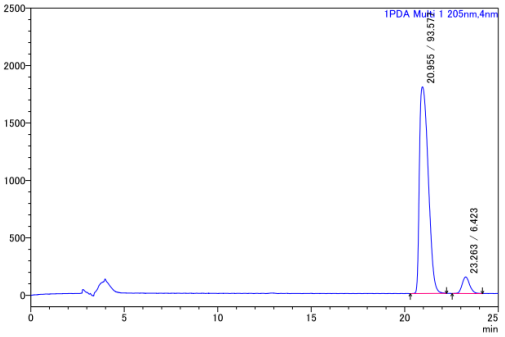
Colorless oil; 99% yield, 87% ee; $[\alpha]_D^{23}$ = -7 (*c* = 1.50, $CHCl_3$), (lit.[s7] $[\alpha]_D^{20}$ = -6.5 (*c* = 1.50, $CHCl_3$) for 80% ee, (*R*)); HPLC condition: DAICEL CHIRALCEL OD-3, Hexane/IPA = 97/3, flow = 1.0 mL/min, wavelength = 205 nm, t_R = 21.0 min for (*R*) and t_R = 23.3 min for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.51 (m, 1H), 7.33–7.13 (m, 8H), 6.01 (s, 1H), 2.25 (s, 3H), 2.10 (br, 1H).

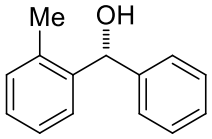




PDA Ch1 205nm

ピーク#	保持時間	面積	面積%
1	21.256	8748527	49.796
2	23.337	8820164	50.204
合計		17568691	100.000





PDA Ch1 205nm

ピーク#	保持時間	面積	面積%
1	20.955	59055013	93.577
2	23.263	4053270	6.423
合計		63108284	100.000

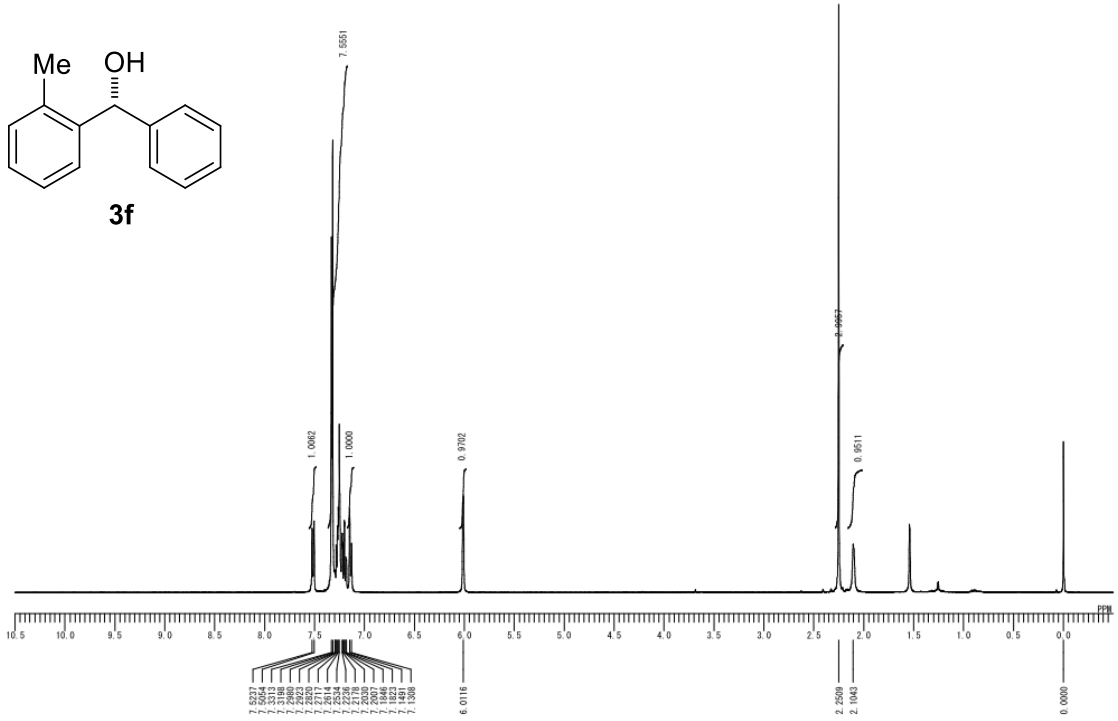
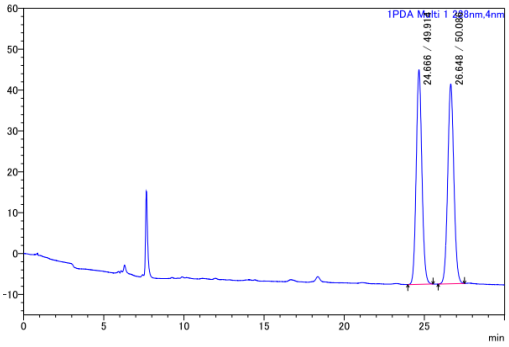
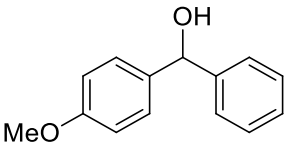


Figure S20. HPLC charts of **3f** and the racemic compound and ^{1}H NMR spectrum of **3f.**

8-7. (*R*)-*p*-Methoxyphenyl(phenyl)carbinol (**3g**)

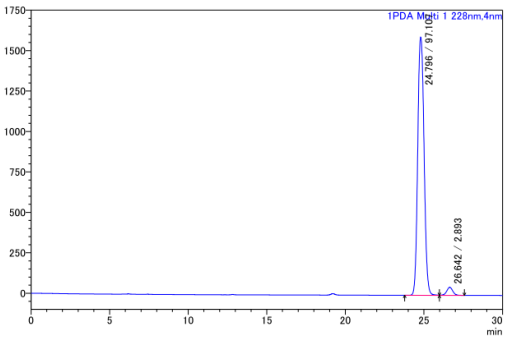
Colorless oil; 96% yield, 93% ee; $[\alpha]_D^{23}$ = +26 (*c* = 0.80, $CHCl_3$), (lit.[s4] $[\alpha]_D^{29}$ = +24.6 (*c* = 0.80, $CHCl_3$) for 90% ee, (*R*)); HPLC condition: DAICEL CHIRALCEL AD-3, Hexane/IPA = 90/10, flow = 0.5 mL/min, wavelength = 228 nm, t_R = 24.8 min for (*R*) and t_R = 26.6 min for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.24 (m, 7H), 6.87–6.85 (m, 2H), 5.80 (s, 1H), 3.78 (s, 3H), 2.17 (br, 1H).

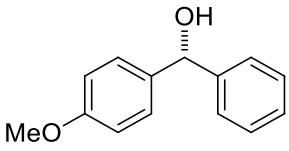




PDA Ch1 228nm

ピーク#	保持時間	面積	面積%
1	24.666	1298974	49.914
2	26.648	1303437	50.086
合計		2602411	100.000





PDA Ch1 228nm

ピーク#	保持時間	面積	面積%
1	24.796	44623271	97.107
2	26.642	1329191	2.893
合計		45952462	100.000

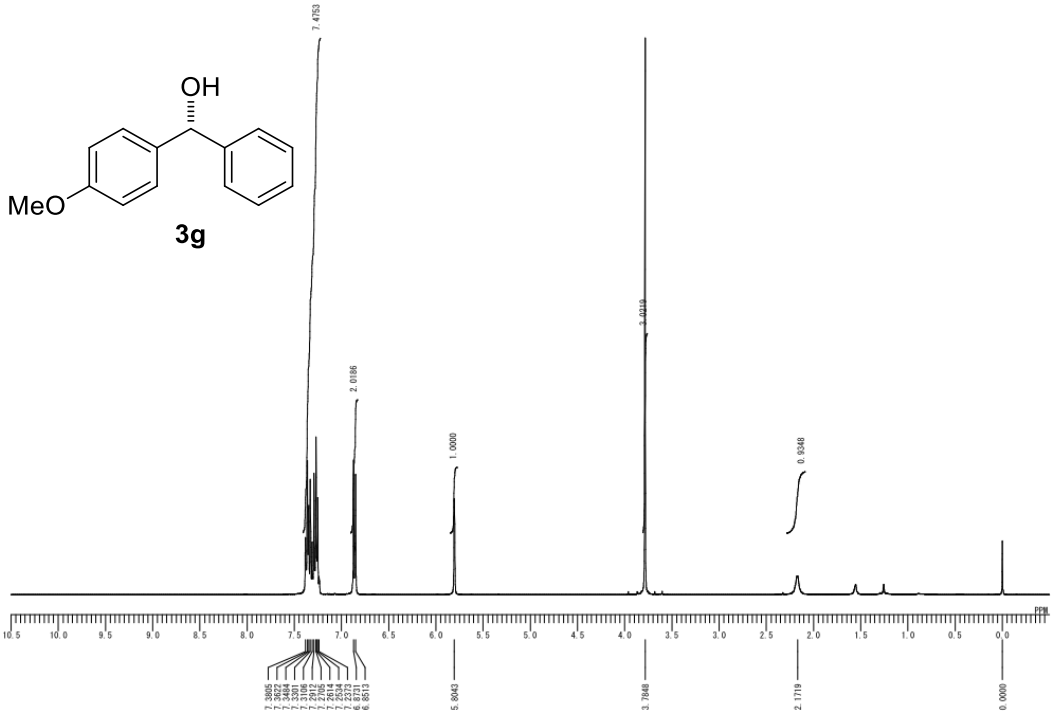
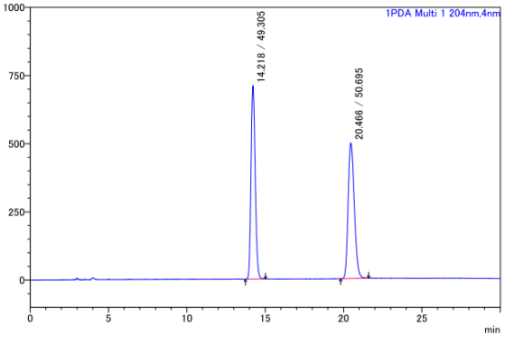
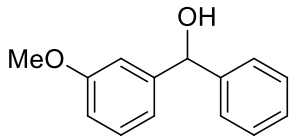


Figure S21. HPLC charts of **3g** and the racemic compound and ^{1}H NMR spectrum of **3g.**

8-8. (*R*)-*m*-Methoxyphenyl(phenyl)carbinol (**3h**)

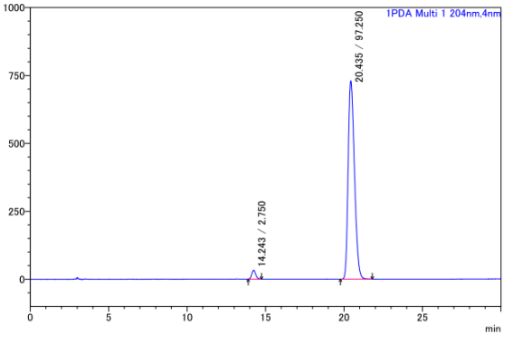
Colorless oil; 95% yield, 95% ee; $[\alpha]_D^{23}$ = -15 (*c* = 0.80, $CHCl_3$), (lit.[s5] $[\alpha]_D^{23}$ = +16.3 (*c* = 0.92, $CHCl_3$) for 94% ee, (*S*)); HPLC condition: DAICEL CHIRALCEL OD-3, Hexane/IPA = 90/10, flow = 1.0 mL/min, wavelength = 204 nm, t_R = 14.2 min for (*S*) and t_R = 20.4 min for (*R*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.24 (m, 6H), 6.96–6.95 (m, 2H), 6.83–6.81 (m, 1H), 5.77 (s, 1H), 3.78 (s, 3H), 2.71 (br, 1H).

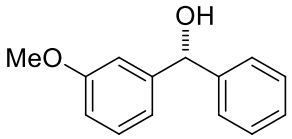




PDA Ch1 204nm

ピーク#	保持時間	面積	面積%
1	14.218	13143882	49.305
2	20.466	13514685	50.695
合計		26658567	100.000





PDA Ch1 204nm

ピーク#	保持時間	面積	面積%
1	14.243	576451	2.750
2	20.435	20386272	97.250
合計		20962723	100.000

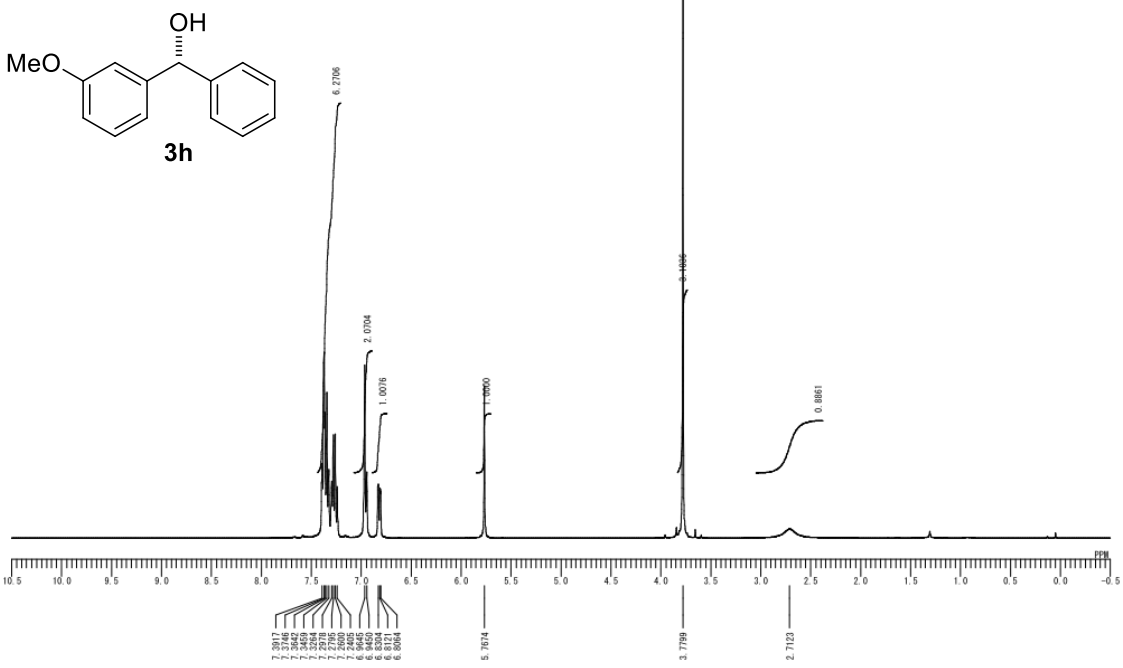
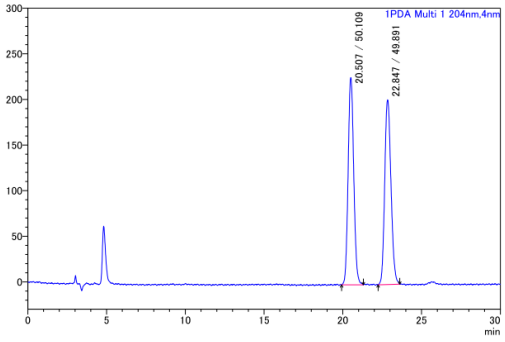
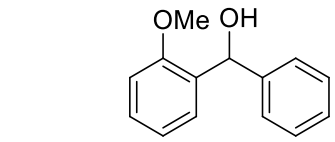


Figure S22. HPLC charts of **3h** and the racemic compound and ^{1}H NMR spectrum of **3h.**

8-9. (*R*)-*o*-Methoxyphenyl(phenyl)carbinol (**3i**)

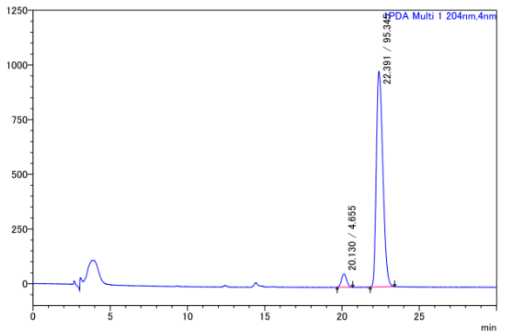
Colorless oil; 99% yield, 91% ee; $[\alpha]_D^{23}$ = +29 (*c* = 0.80, $CHCl_3$), (lit.[s5] $[\alpha]_D^{22}$ = -35.4 (*c* = 0.95, $CHCl_3$) for 95% ee, (*S*)); HPLC condition: DAICEL CHIRALCEL OD-3, Hexane/IPA = 95/5, flow = 1.0 mL/min, wavelength = 204 nm, t_R = 20.1 min for (*S*) and t_R = 22.4 min for (*R*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.22 (m, 7H), 6.96–6.88 (m, 2H), 6.06 (d, *J* = 5.6 Hz, 1H), 3.81 (s, 3H), 3.00 (d, *J* = 5.6 Hz, 1H).

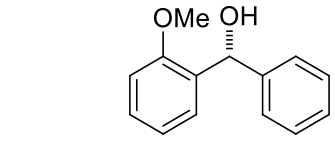




PDA Ch1 204nm

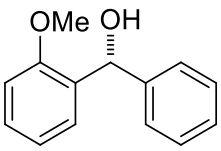
ピーク#	保持時間	面積	面積%
1	20.507	5623845	50.109
2	22.847	5599431	49.891
合計		11223276	100.000





PDA Ch1 204nm

ピーク#	保持時間	面積	面積%
1	20.130	1414655	4.655
2	22.391	28975996	95.345
合計		30390651	100.000

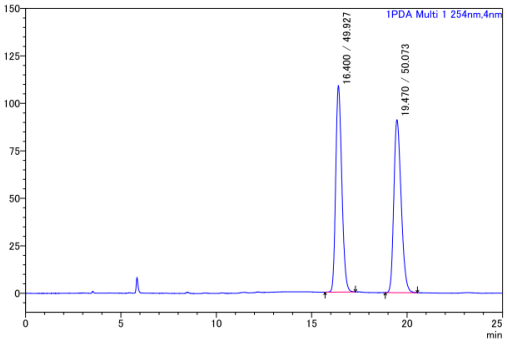


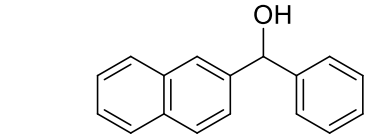
3i

Figure S23. HPLC charts of **3i** and the racemic compound and ^{1}H NMR spectrum of **3i.**

8-10. (*R*)-Naphthalen-2-yl(phenyl)carbinol (**3j**)

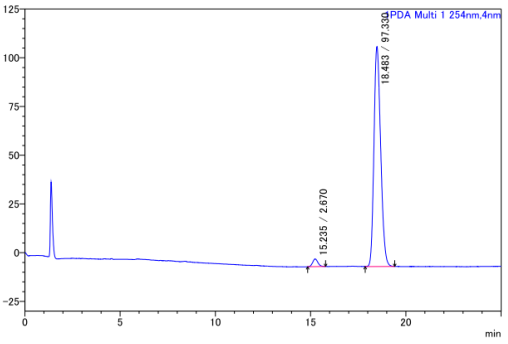
White solid; 88% yield, 94% ee; $[\alpha]_D^{23}$ = +10 (*c* = 0.40, benzene), (lit.[s5] $[\alpha]_D^{22}$ = -8.7 (*c* = 0.33, benzene) for 94% ee, (*S*)); HPLC condition: DAICEL CHIRALCEL OD-3, Hexane/IPA = 90/10, flow = 1.0 mL/min, wavelength = 254 nm, t_R = 15.2 min for (*S*) and t_R = 18.5 min for (*R*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.77 (m, 4H), 7.50–7.28 (m, 8H), 6.02 (s, 1H), 2.31 (s, 1H).

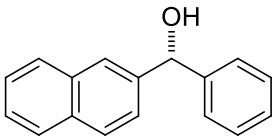




PDA Ch1 254nm

ピーク#	保持時間	面積	面積%
1	16.400	2424708	49.927
2	19.470	2431836	50.073
合計		4856544	100.000





PDA Ch1 254nm

ピーク#	保持時間	面積	面積%
1	15.235	75830	2.670
2	18.483	2764695	97.330
合計		2840524	100.000

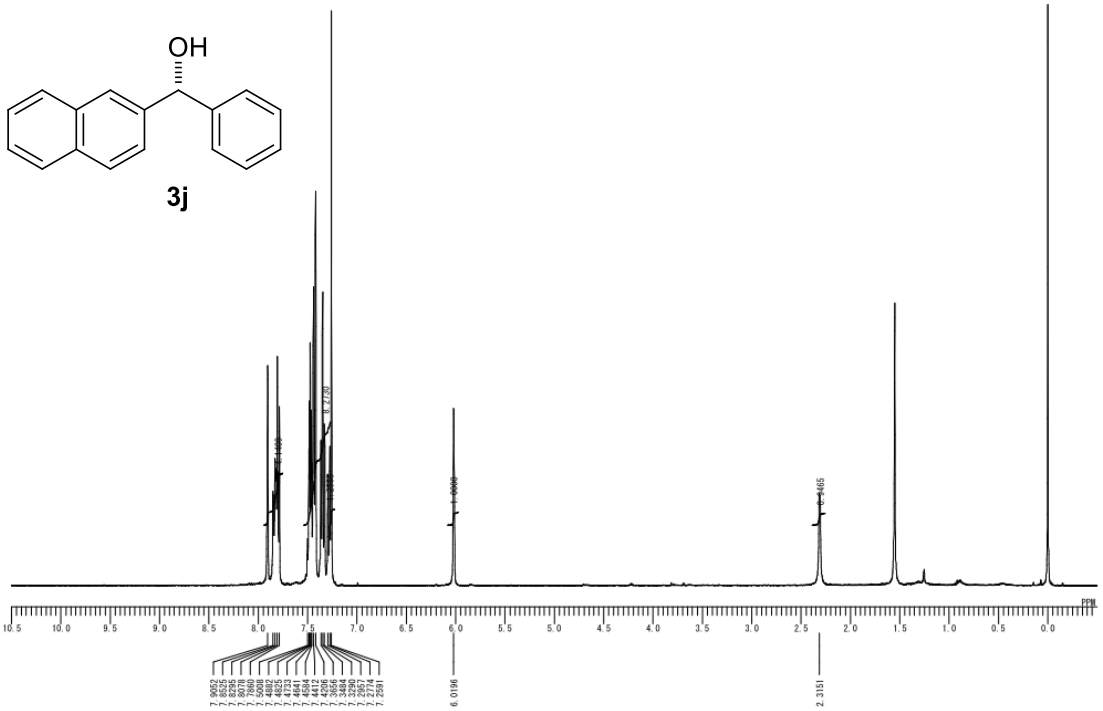
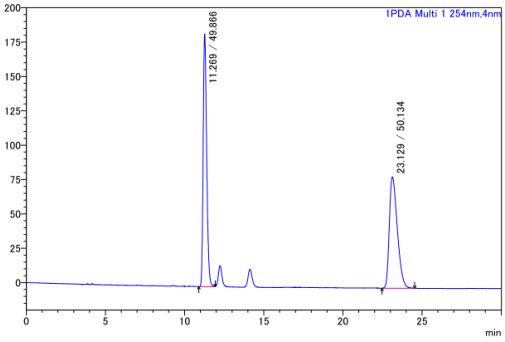
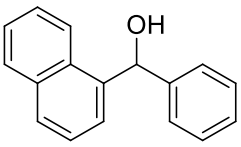


Figure S24. HPLC charts of **3j** and the racemic compound and ^{1}H NMR spectrum of **3j.**

8-11. (*R*)-Naphthalen-1-yl(phenyl)carbinol (**3k**)

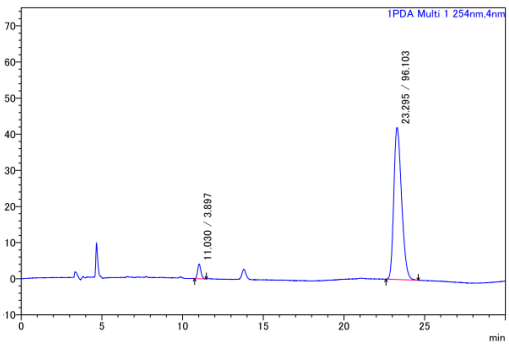
White solid; 75% yield, 92% ee; $[\alpha]_D^{23}$ = +60 (*c* = 0.40, $CHCl_3$), (lit.[s5] $[\alpha]_D^{22}$ = -46.3 (*c* = 0.30, $CHCl_3$) for 98% ee, (*S*)); HPLC condition: DAICEL CHIRALCEL OD-3, Hexane/IPA = 80/20, flow = 1.0 mL/min, wavelength = 254 nm, t_R = 11.0 min for (*S*) and t_R = 23.3 min for (*R*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–8.02 (m, 1H), 7.87–7.80 (m, 2H), 7.64–7.62 (m, 1H), 7.50–7.40 (m, 5H), 7.34–7.25 (m, 3H), 6.54 (s, 1H), 2.32 (br, 1H).

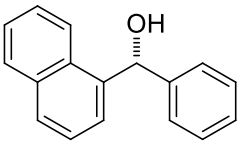




PDA Ch1 254nm

ピーク#	保持時間	面積	面積%
1	11.269	2821365	49.866
2	23.129	2836578	50.134
合計		5657943	100.000





PDA Ch1 254nm

ピーク#	保持時間	面積%	マーク
1	11.030	3.897	
2	23.295	96.103	
合計		100.000	

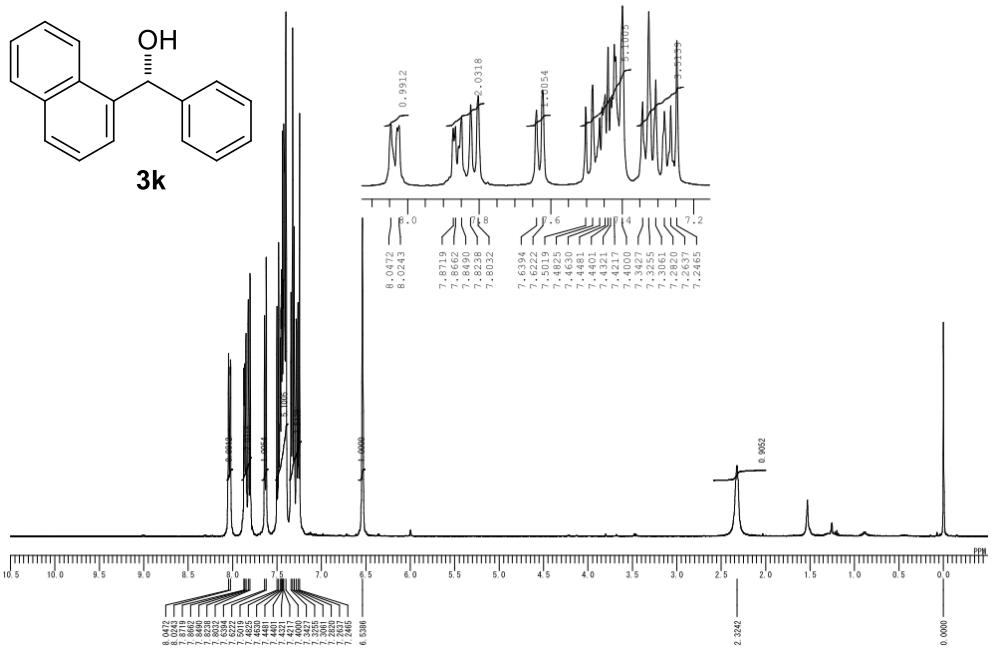
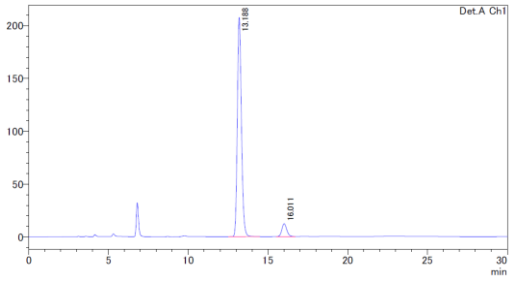
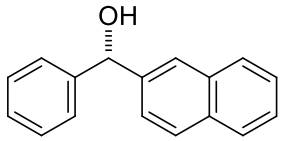


Figure S25. HPLC charts of **3k** and the racemic compound and ^{1}H NMR spectrum of **3k.**

8-12. (*S*)-Naphthalen-2-yl(phenyl)carbinol (**3l**)

White solid; 87% yield, 87% ee; HPLC condition: DAICEL CHIRALCEL OD-3, Hexane/IPA = 90/10, flow = 1.0 mL/min, wavelength = 254 nm, t_R = 13.2 min for (*S*) and t_R = 16.0 min for (*R*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.79 (m, 4H), 7.50–7.26 (m, 8H), 6.02 (s, 1H), 2.31 (s, 1H).





検出器A Ch1 254nm

ピーク#	保持時間	面積	面積%
1	13.188	3699502	93.493
2	16.011	257477	6.507
合計		3956979	100.000

The HPLC chart of Racemic compound (See. **3j**)

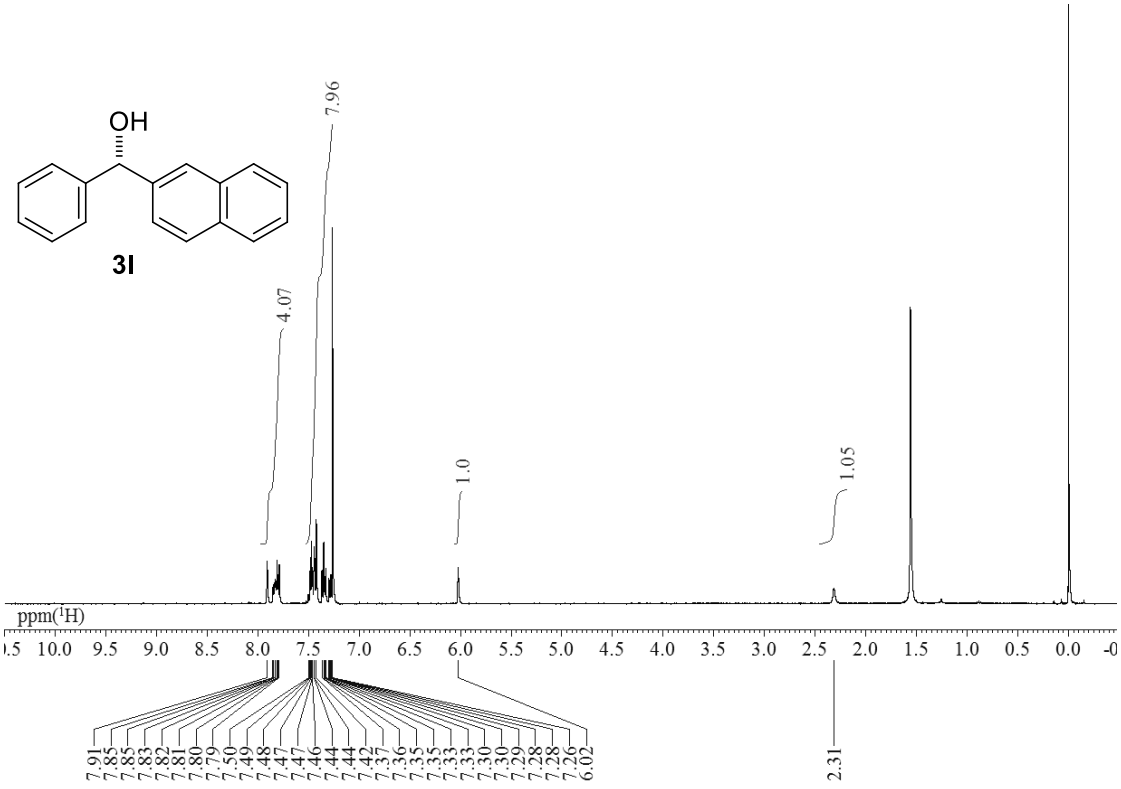
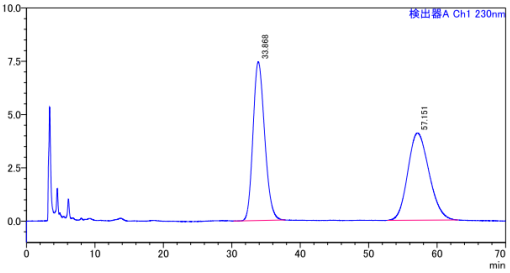
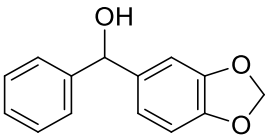


Figure S26. HPLC chart and ^{1}H NMR spectrum of **3l.**

8-13. (*S*)-1,3-Benzodioxol-5-yl(phenyl)carbinol (**3m**)

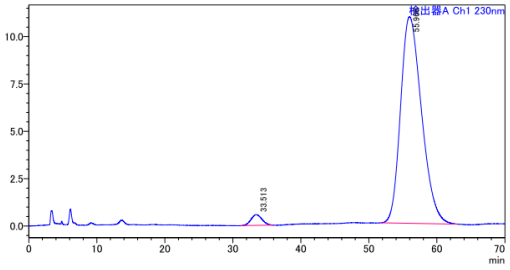
Pale yellow oil; 96% yield, 95% ee; $[\alpha]_D^{24}$ = -7 (*c* = 0.80, $CHCl_3$), (lit.[s4] $[\alpha]_D^{21}$ = +5.8 (*c* = 0.80, $CHCl_3$) for 81% ee, (*R*)); HPLC condition: DAICEL CHIRALCEL OB, Hexane/IPA = 90/10, flow = 1.0 mL/min, wavelength = 230 nm, t_R = 33.5 min for (*R*) and t_R = 56.0 min for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.31 (m, 4H), 7.28–7.24 (m, 1H), 6.85–6.83 (m, 2H), 6.76–6.74 (m, 1H), 5.92–5.91 (m, 2H), 5.74 (s, 1H), 2.43 (br, 1H).

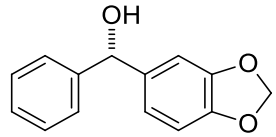




検出器A Ch1 230nm

ピーク#	保持時間	面積	面積%
1	33.868	880977	49.916
2	57.151	883925	50.084
合計		1764902	100.000





検出器A Ch1 230nm

ピーク#	保持時間	面積	面積%
1	33.513	64391	2.675
2	55.966	2342526	97.325
合計		2406917	100.000

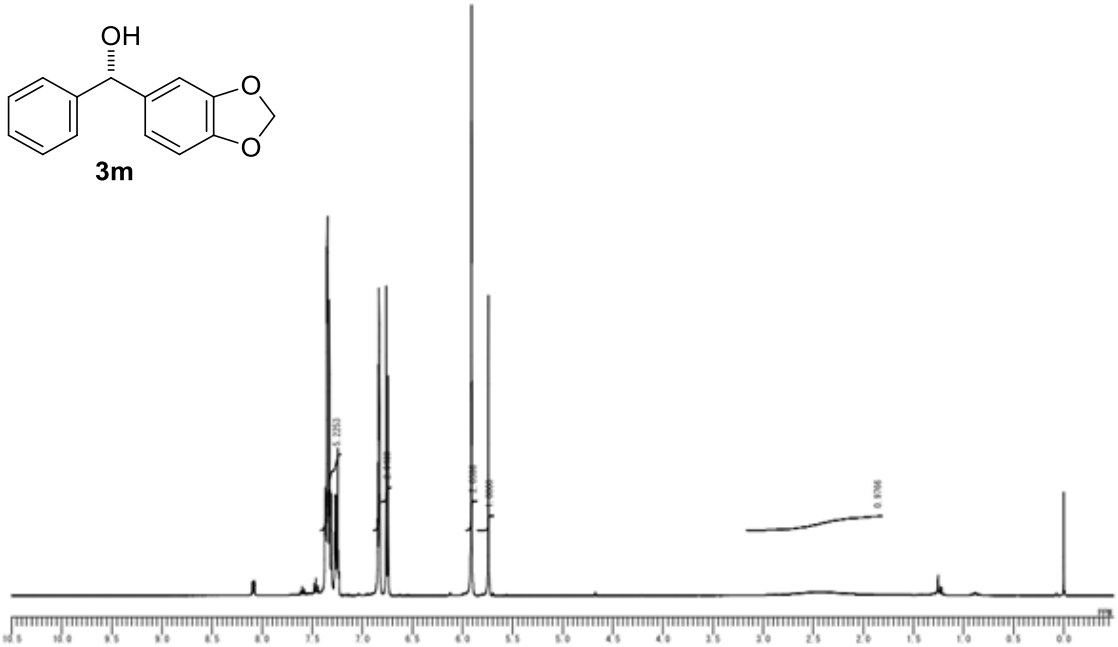
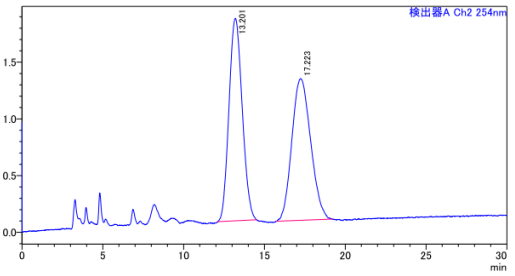
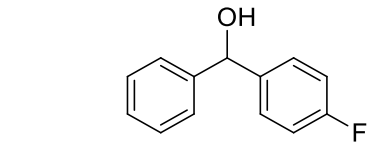


Figure S27. HPLC charts of **3m** and the racemic compound and ^{1}H NMR spectrum of **3m.**

8-14. (*S*)-*p*-Fluorophenyl(phenyl)carbinol (**3n**)

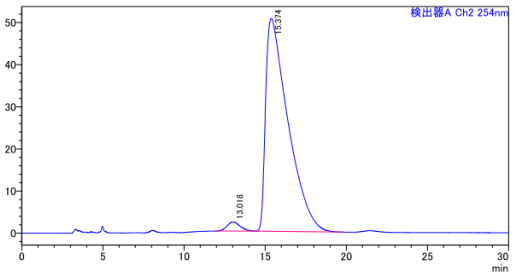
Colorless oil; 98% yield, 95% ee; $[\alpha]_D^{23}$ = +10 (*c* = 0.40, $CHCl_3$), (lit.[s8] $[\alpha]_D^{25}$ = -6.0 (*c* = 0.76, $CHCl_3$) for 94% ee, (*R*)); HPLC condition: DAICEL CHIRALCEL OB, Hexane/IPA = 80/20, flow = 1.0 mL/min, wavelength = 254 nm, t_R = 13.0 min for (*R*) and t_R = 15.4 min for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.24 (m, 7H), 7.03–6.98 (m, 2H), 5.80 (s, 1H), 2.34 (br, 1H).

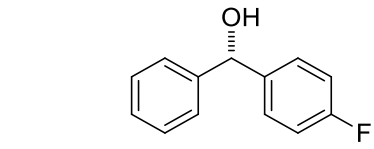




検出器A Ch2 254nm

ピーク#	保持時間	面積	面積%
1	13.201	101592	50.129
2	17.223	101071	49.871
合計		202663	100.000





検出器A Ch2 254nm

ピーク#	保持時間	面積	面積%
1	13.018	120666	2.431
2	15.374	4842177	97.569
合計		4962842	100.000

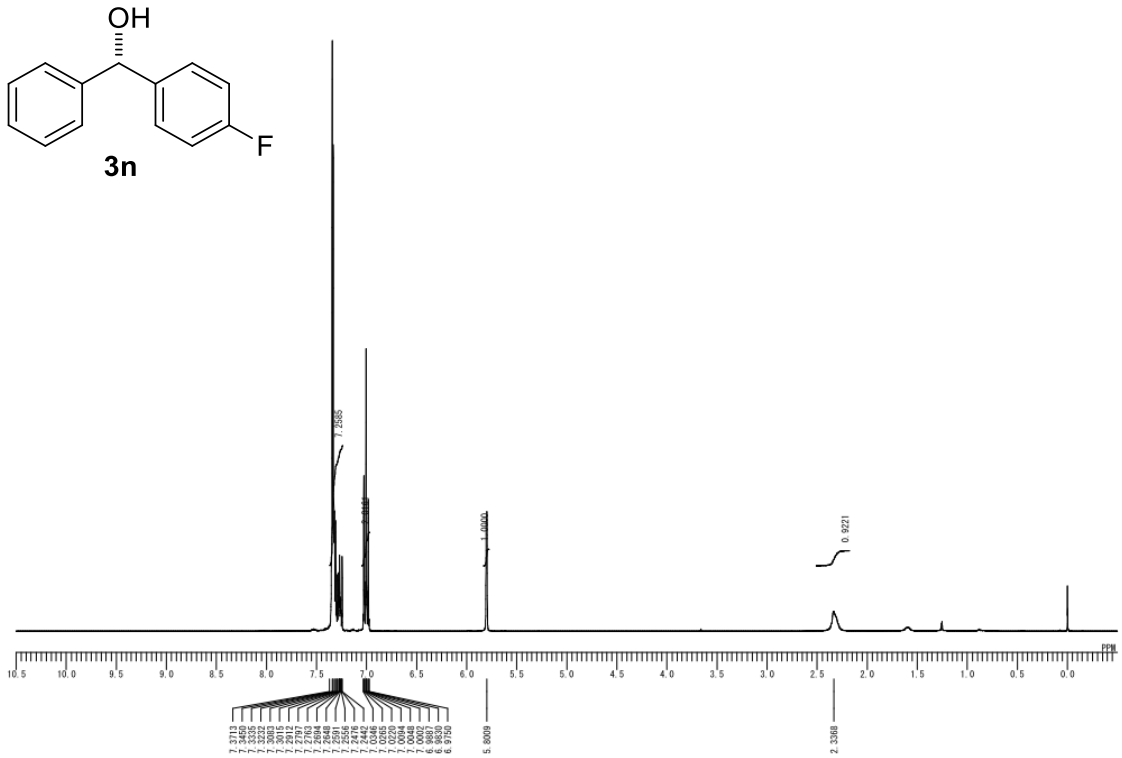
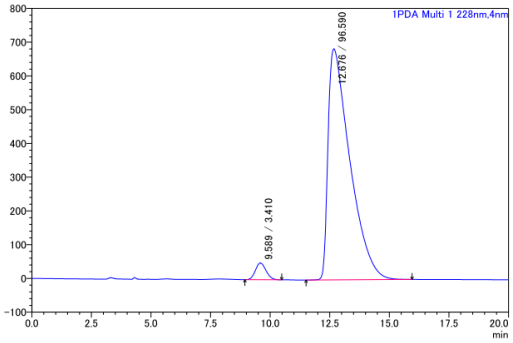
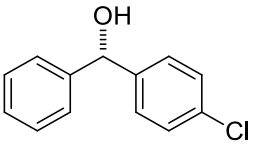


Figure S28. HPLC charts of **3n** and the racemic compound and ^{1}H NMR spectrum of **3n.**

8-15. (*S*)-*p*-Chlorophenyl(phenyl)carbinol (**3o**)

White solid; 91% yield, 93% ee; $[\alpha]_D^{23}$ = +19 (*c* = 0.40, $CHCl_3$), HPLC condition: DAICEL CHIRALCEL OB, Hexane/IPA = 85/15, flow = 1.0 mL/min, wavelength = 228 nm, t_R = 9.6 min for (*R*) and t_R = 12.7 min for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.26 (m, 9H), 5.81 (d, J = 3.6 Hz, 1H), 2.25 (d, J = 3.6 Hz, 1H).





PDA Ch1 228nm

ピーク#	保持時間	面積	面積%
1	9.589	1540235	3.410
2	12.676	43632985	96.590
合計		45173219	100.000

The HPLC chart of Racemic compound (See. **3a**)

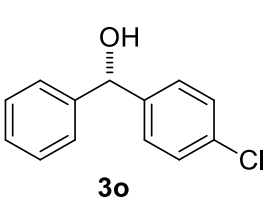
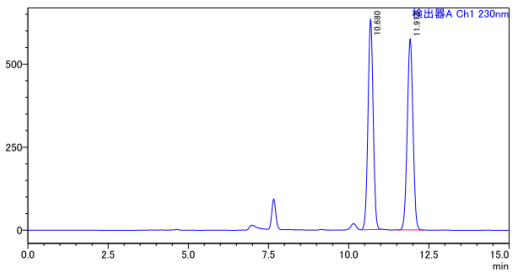
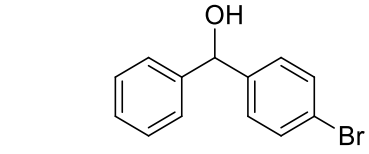


Figure S29. HPLC chart and ^{1}H NMR spectrum of **3o.**

8-16. (*S*)-*p*-Bromophenyl(phenyl)carbinol (**3p**)

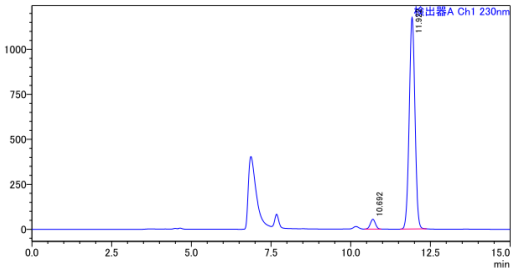
White solid; 81% yield, 92% ee; $[\alpha]_D^{24}$ = +16 (*c* = 0.30, $CHCl_3$), (lit.[s5] $[\alpha]_D^{22}$ = +18.2 (*c* = 0.30, $CHCl_3$) for 96% ee, (*S*)); HPLC condition: DAICEL CHIRALCEL AD-3, Hexane/IPA = 90/10, flow = 1.0 mL/min, wavelength = 230 nm, t_R = 10.7 min for (*R*) and t_R = 11.9 min for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.44 (m, 2H), 7.37–7.24 (m, 7H), 5.79 (s, 1H), 2.27 (s, 1H).

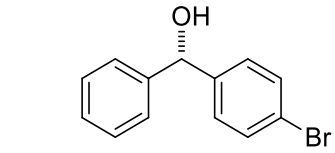




検出器A Ch1 230nm

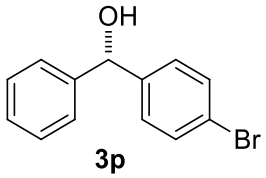
ピーク#	保持時間	面積	面積%
1	10.680	7069481	49.888
2	11.913	7101257	50.112
合計		14170738	100.000





検出器A Ch1 230nm

ピーク#	保持時間	面積	面積%
1	10.692	600793	3.928
2	11.922	14693676	96.072
合計		15294469	100.000

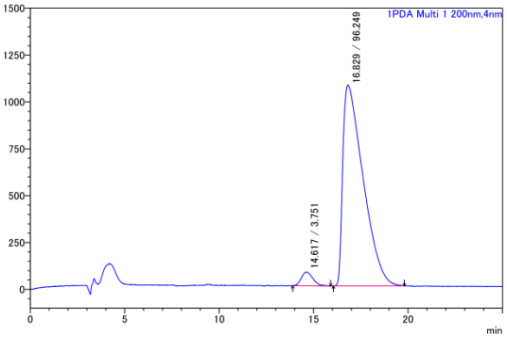


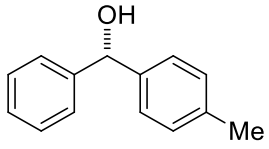
3p

Figure S30. HPLC charts of **3p** and the racemic compound and ^{1}H NMR spectrum of **3p.**

8-17. (*S*)-*p*-Methylphenyl(phenyl)carbinol (**3q**)

White solid; 87% yield, 92% ee; $[\alpha]_D^{23}$ = -22 (*c* = 0.80, $CHCl_3$), HPLC condition: DAICEL CHIRALCEL OB, Hexane/IPA = 95/5, flow = 1.0 mL/min, wavelength = 200 nm, t_R = 14.6 min for (*R*) and t_R = 16.8 min for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.24 (m, 7H), 7.15–7.13 (m, 2H), 5.82 (d, *J* = 2.8 Hz, 1H), 2.33 (s, 3H), 2.17 (br, 1H).





PDA Ch1 200nm

ピーク#	保持時間	面積	面積%
1	14.617	3117005	3.751
2	16.829	79989421	96.249
合計		83106426	100.000

The HPLC chart of Racemic compound (See. **3d**)

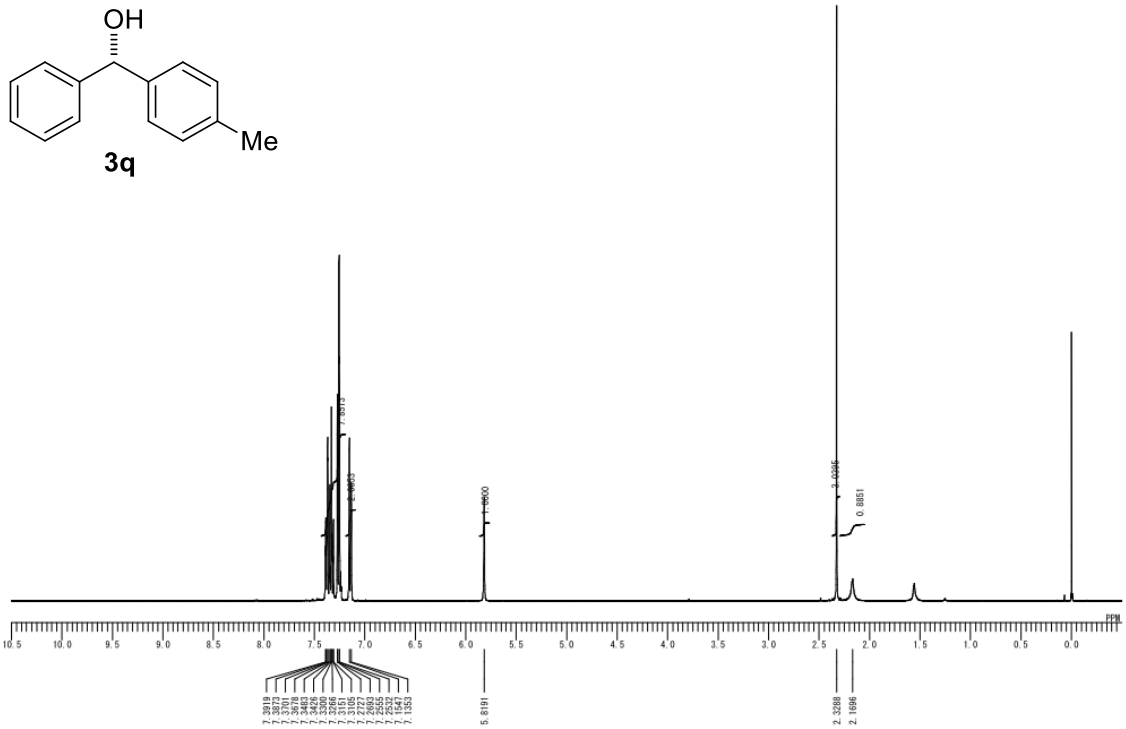
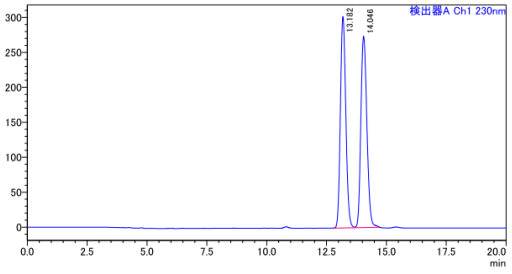
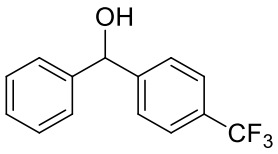


Figure S31. HPLC chart and ^{1}H NMR spectrum of **3q.**

8-18. (*S*)-*p*-Trifluorophenyl(phenyl)carbinol (**3r**)

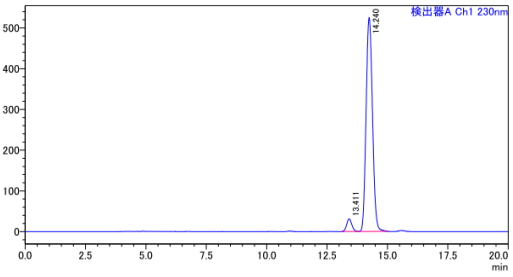
White solid; 93% yield, 90% ee; $[\alpha]_D^{23}$ = +32 (*c* = 0.25, $CHCl_3$), (lit.[s5] $[\alpha]_D^{22}$ = +34.3 (*c* = 0.25, $CHCl_3$) for 92% ee, (*S*)); HPLC condition: DAICEL CHIRALCEL OD-3, Hexane/IPA = 90/10, flow = 0.7 mL/min, wavelength = 230 nm, t_R = 13.4 min for (*R*) and t_R = 14.2 min for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.50 (m, 4H), 7.36–7.27 (m, 5H), 5.88 (s, 1H), 2.32 (s, 1H).

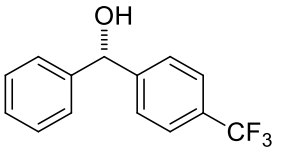




検出器A Ch1 230nm

ピーク#	保持時間	面積	面積%
1	13.182	4751270	49.821
2	14.046	4785360	50.179
合計		9536630	100.000





検出器A Ch1 230nm

ピーク#	保持時間	面積	面積%
1	13.411	460348	4.551
2	14.240	9655084	95.449
合計		10115432	100.000

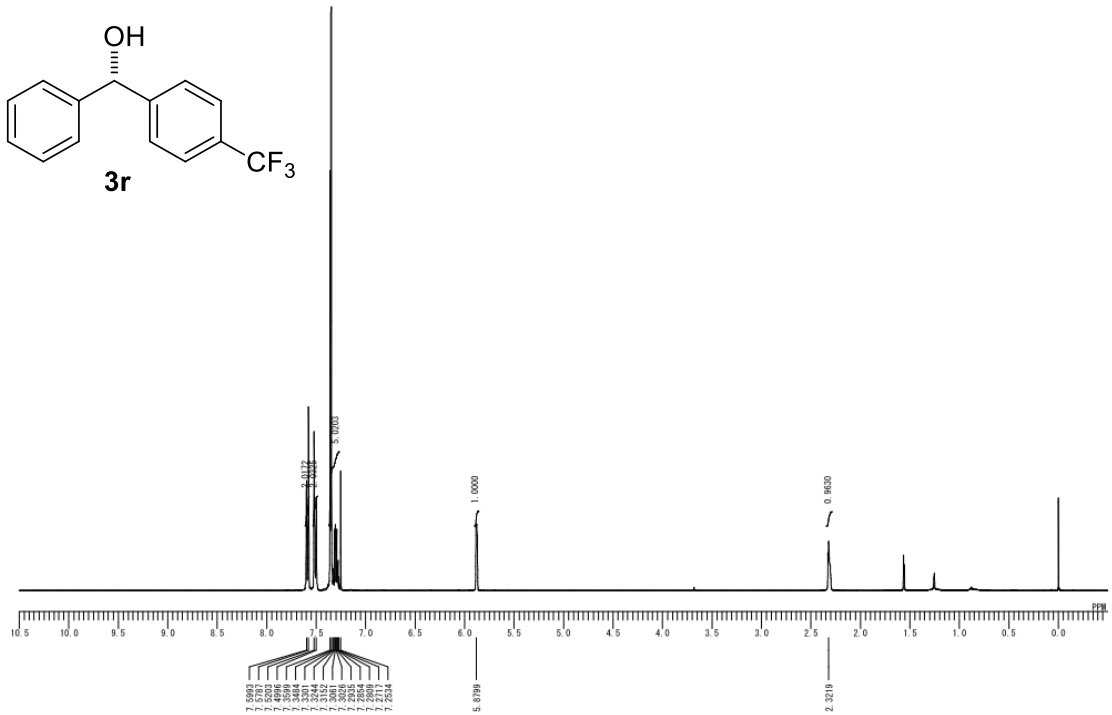
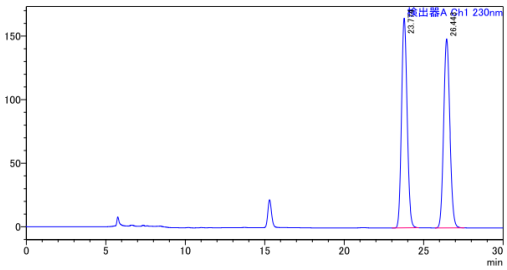
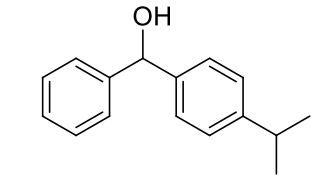


Figure S32. HPLC charts of **3r** and the racemic compound and ^{1}H NMR spectrum of **3r.**

8-19. (*S*)-*p*-Isopropylphenyl(phenyl)carbinol (**3s**)

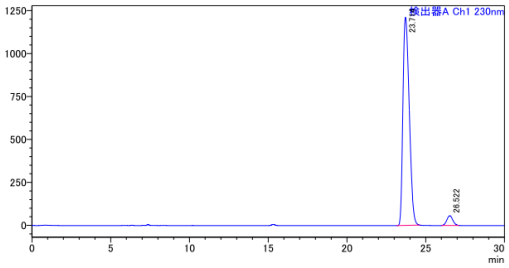
White solid; 99% yield, 92% ee; $[\alpha]_D^{23}$ = -13 (*c* = 0.80, $CHCl_3$), (lit.[s4] $[\alpha]_D^{24}$ = +11.2 (*c* = 0.80, $CHCl_3$) for 86% ee, (*R*)); HPLC condition: DAICEL CHIRALCEL OD-3, Hexane/IPA = 95/5, flow = 0.5 mL/min, wavelength = 230 nm, t_R = 23.7 min for (*S*) and t_R = 26.5 min for (*R*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.18 (m, 9H), 7.36–7.27 (m, 5H), 5.81 (d, *J* = 3.3 Hz, 1H), 2.88 (sept, *J* = 6.9 Hz, 1H), 2.22 (d, *J* = 3.6Hz, 1H), 1.22 (d, *J* = 6.8 Hz, 6H).

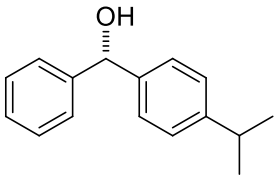




検出器A Ch1 230nm

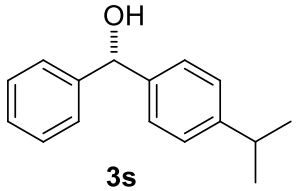
ピーク#	保持時間	面積	面積%
1	23.774	4034048	49.952
2	26.443	4041809	50.048
合計		8075857	100.000





検出器A Ch1 230nm

ピーク#	保持時間	面積	面積%
1	23.714	33583153	95.752
2	26.522	1490037	4.248
合計		35073190	100.000

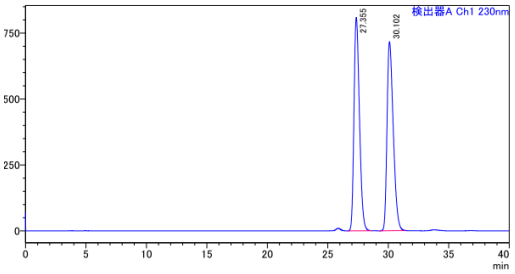


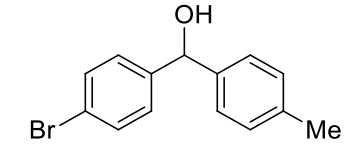
3s

Figure S33. HPLC charts of **3s** and the racemic compound and ^{1}H NMR spectrum of **3s.**

8-20. (*R*)-*p*-Bromophenyl(*p*-tolyl)carbinol (**3t**)

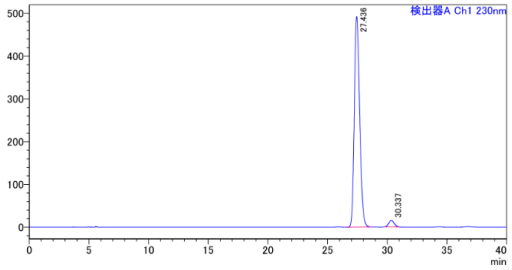
White solid; 86% yield, 94% ee; $[\alpha]_D^{23}$ = -9 (*c* = 0.40, $CHCl_3$), (lit.[s8] $[\alpha]_D^{28}$ = +25.0 (*c* = 1.00, $CHCl_3$) for 97% ee, (*S*)); HPLC condition: DAICEL CHIRALCEL OD-3, Hexane/IPA = 97/3, flow = 0.80 mL/min, wavelength = 230 nm, t_R = 27.4 min for (*R*) and t_R = 30.3 min for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.45 (m, 2H), 7.26–7.15 (m, 6H), 5.77 (s, 1H), 2.34 (s, 3H), 2.18 (br, 1H).

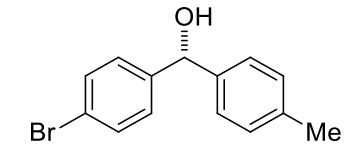




検出器A Ch1 230nm

ピーク#	保持時間	面積	面積%
1	27.355	25508644	49.813
2	30.102	25700420	50.187
合計		51209064	100.000





検出器A Ch1 230nm

ピーク#	保持時間	面積	面積%
1	27.436	15391971	96.853
2	30.337	500098	3.147
合計		15892069	100.000

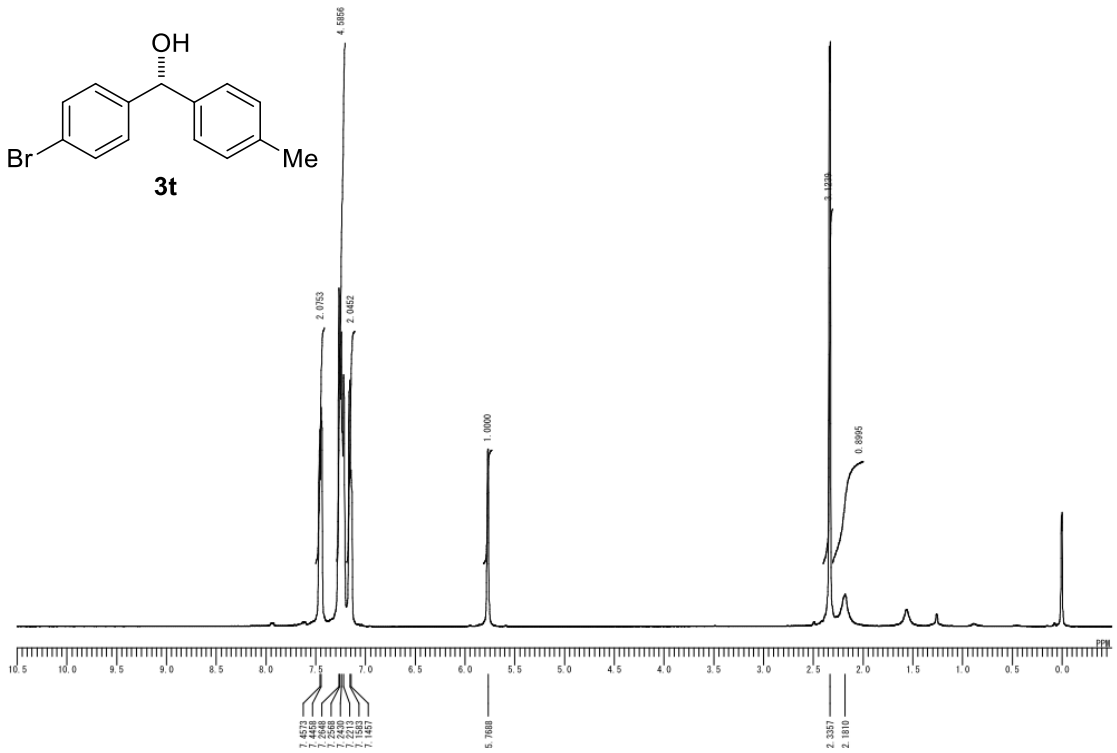
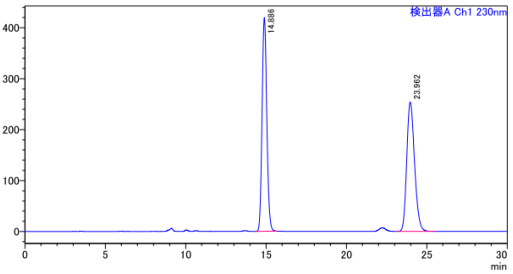
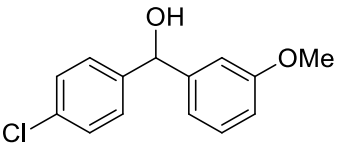


Figure S34. HPLC charts of **3t** and the racemic compound and ^{1}H NMR spectrum of **3t.**

8-21. (*S*)-*p*-Chlorophenyl(*m*-methoxyphenyl)carbinol (**3u**)

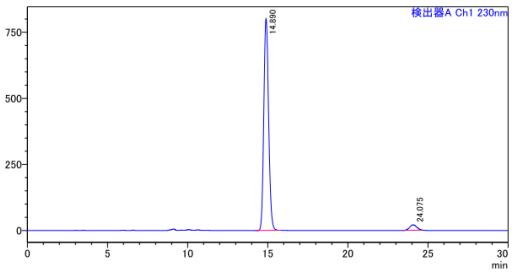
White solid; 96% yield, 93% ee; $[\alpha]_D^{23}$ = +2 (*c* = 0.40, $CHCl_3$), (lit.[s5] $[\alpha]_D^{22}$ = +1.3 (*c* = 0.41, $CHCl_3$) for 84% ee, (*S*)); HPLC condition: DAICEL CHIRALCEL OD-3, Hexane/IPA = 90/10, flow = 1.0 mL/min, wavelength = 230 nm, t_R = 14.9 min for (*S*) and t_R = 24.1 min for (*R*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.23 (m, 5H), 6.92–6.91 (m, 2H), 6.83–6.80 (m, 1H), 5.78 (s, 1H), 3.78 (s, 3H), 2.24 (br, 1H).

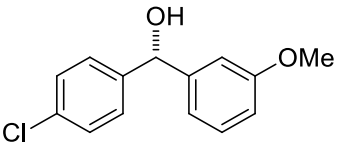




検出器A Ch1 230nm

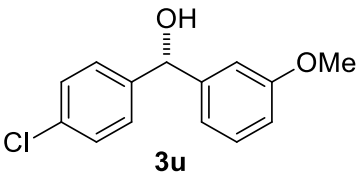
ピーク#	保持時間	面積	面積%
1	14.886	8630652	50.223
2	23.962	8554002	49.777
合計		17184654	100.000





検出器A Ch1 230nm

ピーク#	保持時間	面積	面積%
1	14.890	16839188	96.344
2	24.075	638947	3.656
合計		17478135	100.000

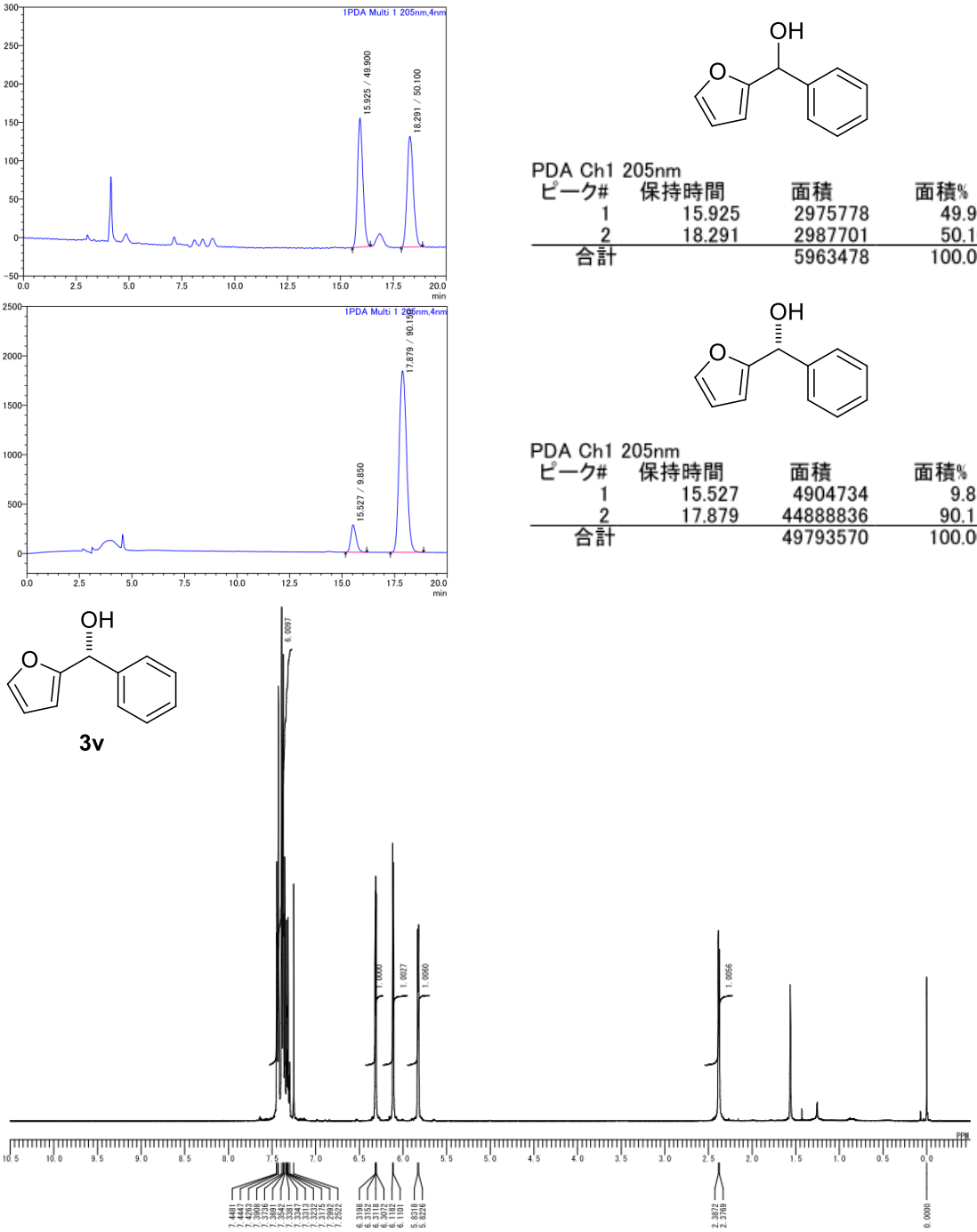


3u

Figure S35. HPLC charts of **3u** and the racemic compound and ^{1}H NMR spectrum of **3u.**

8-22. (*R*)-Furan-2-yl(phenyl)carbinol (**3v**)

Pale yellow oil; 96% yield, 80% ee; $[\alpha]_D^{23}$ = +6 (*c* = 0.80, $CHCl_3$), (lit.[s5] $[\alpha]_D^{22}$ = -4.71 (*c* = 0.64, $CHCl_3$) for 82% ee, (*S*)); HPLC condition: DAICEL CHIRALCEL OD-3, Hexane/IPA = 95/5, flow = 1.0 mL/min, wavelength = 205 nm, t_R = 15.5 min for (*S*) and t_R = 17.9 min for (*R*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.30 (m, 6H), 6.31 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.11 (d, *J* = 3.2 Hz, 1H), 5.83 (d, *J* = 3.7 Hz, 1H), 2.38 (d, *J* = 4.1 Hz, 1H).



PDA Ch1 205nm

ピーク#	保持時間	面積	面積%
1	15.925	2975778	49.900
2	18.291	2987701	50.100
合計		5963478	100.000

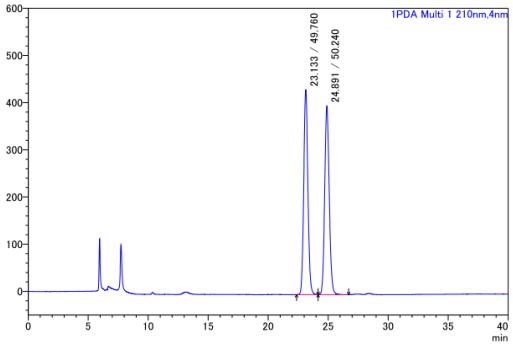
PDA Ch1 205nm

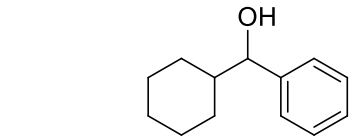
ピーク#	保持時間	面積	面積%
1	15.527	4904734	9.850
2	17.879	44888836	90.150
合計		49793570	100.000

Figure S36. HPLC charts of **3v** and the racemic compound and ^{1}H NMR spectrum of **3v.**

8-23. (*S*)-Cyclohexyl(phenyl)carbinol (**3w**)

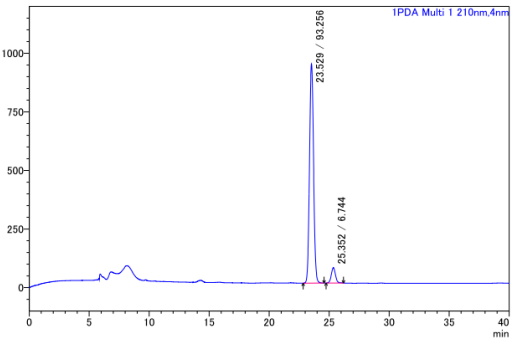
Colorless oil; 95% yield, 87% ee; $[\alpha]_D^{23}$ = -25 (*c* = 1.0, $CHCl_3$), (lit.[s6] $[\alpha]_D^{23}$ = +38.0 (*c* = 0.40, $CHCl_3$) for 96% ee, (*R*)); HPLC condition: DAICEL CHIRALCEL AD-3, Hexane/IPA = 97/3, flow = 0.5 mL/min, wavelength = 210 nm, t_R = 23.5 min for (*S*) and t_R = 25.4 min for (*R*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.22 (m, 5H), 4.36 (d, *J* = 6.9 Hz, 1H), 2.00–0.88 (m, 12H).

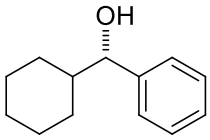




PDA Ch1 210nm

ピーク#	保持時間	面積	面積%
1	23.133	10426160	49.760
2	24.891	10526742	50.240
合計		20952902	100.000





PDA Ch1 210nm

ピーク#	保持時間	面積	面積%
1	23.529	21916838	93.256
2	25.352	1585063	6.744
合計		23501901	100.000

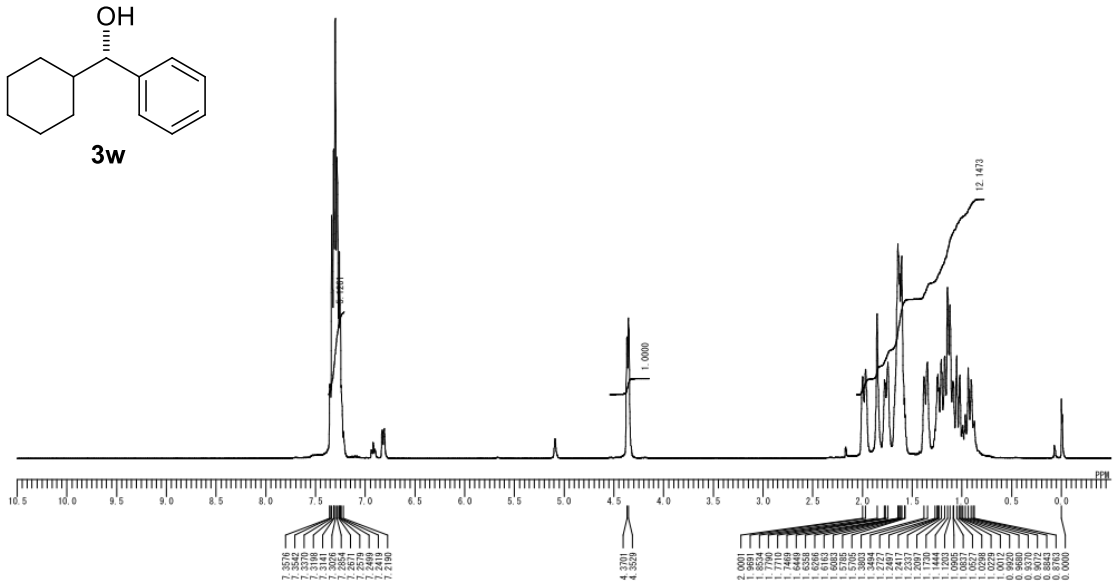
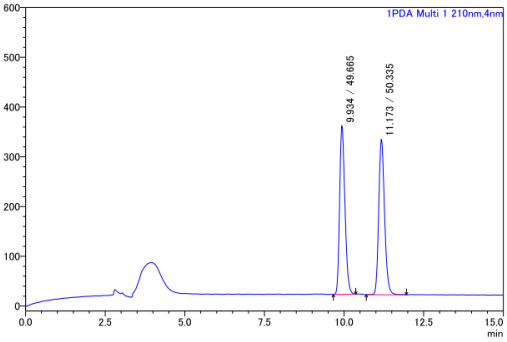
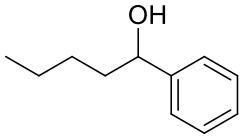


Figure S37. HPLC charts of **3w** and the racemic compound and ^{1}H NMR spectrum of **3w.**

8-24. (*S*)-1-Phenylpentan-1-ol (**3x**)

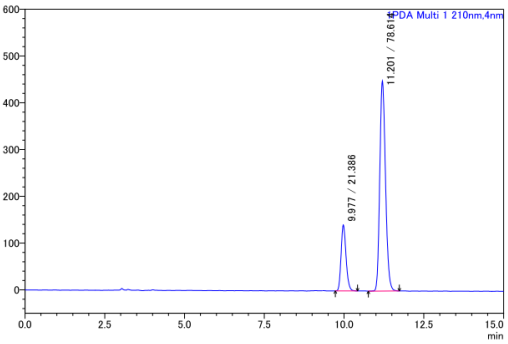
Colorless oil; 88% yield, 57% ee; $[\alpha]_D^{23}$ = -11 (*c* = 0.40, $CHCl_3$), (lit.[s6] $[\alpha]_D^{23}$ = -13.57 (*c* = 0.50, $CHCl_3$) for 80% ee, (*S*)); HPLC condition: DAICEL CHIRALCEL OD-3, Hexane/IPA = 97/3, flow = 1.0 mL/min, wavelength = 210 nm, t_R = 10.0 min for (*R*) and t_R = 11.2 min for (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.26 (m, 5H), 4.68–4.64 (m, 1H), 1.85–1.70 (m, 3H), 1.40–1.25 (m, 4H), 0.90–0.87 (m, 3H).

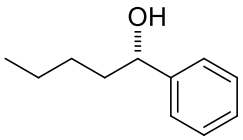




PDA Ch1 210nm

ピーク#	保持時間	面積	面積%
1	9.934	3933152	49.665
2	11.173	3986279	50.335
合計		7919431	100.000





PDA Ch1 210nm

ピーク#	保持時間	面積	面積%
1	9.977	1525119	21.386
2	11.201	5606340	78.614
合計		7131459	100.000

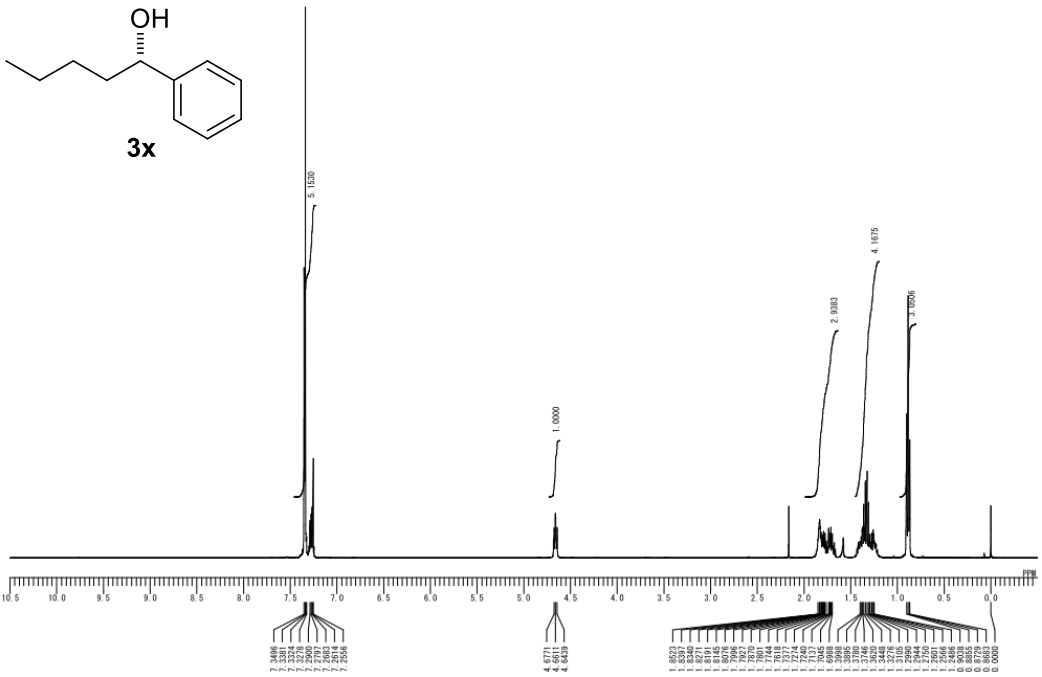
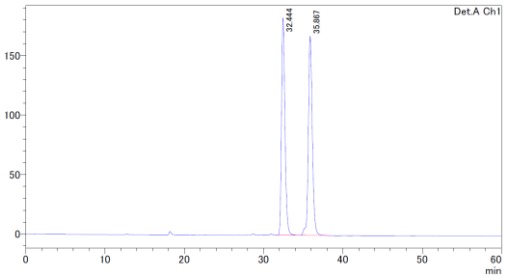
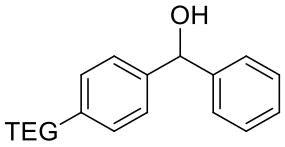


Figure S38. HPLC charts of **3x** and the racemic compound and ^{1}H NMR spectrum of **3x.**

8-25. (*R*)-*p*-TEGphenyl(phenyl)carbinol (**3y**)

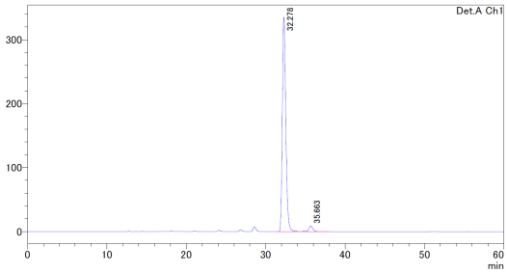
White solid; 60% yield, 94% ee; $[\alpha]_D^{20}$ = +9.5 (*c* = 1.0, CH_3OH),; HPLC condition: DAICEL CHIRALCEL AD-3 x 2, Hexane/IPA = 60/40, flow = 0.5 mL/min, wavelength = 230 nm, t_R = 32.3 min for (R) and t_R = 35.7 min for (S); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.23 (m, 7H), 6.86 (d, *J* = 9.0 Hz, 2H), 5.78 (d, *J* = 3.0 Hz, 1H), 4.10 (t, *J* = 4.8 Hz, 2H), 3.83 (t, *J* = 4.8 Hz, 2H), 3.72–3.57 (m, 8H), 2.63 (brs, 1H), 2.56 (d, *J* = 3.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.98, 144.00, 136.50, 128.33, 127.84, 127.29, 126.33, 114.45, 75.57, 72.44, 70.69, 70.20, 69.62, 67.23, 61.59. HRMS (FAB): (*m/z*) 355.1522 $[M+Na^+]^+$, $C_{19}H_{24}NaO_5$, calcd. 355.1516.

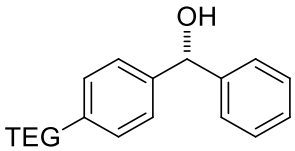




検出器A Ch1 230nm

ピーク#	保持時間	面積	面積%
1	32.444	5591513	49.121
2	35.867	5791730	50.879
合計		11383243	100.000





検出器A Ch1 230nm

ピーク#	保持時間	面積	面積%
1	32.278	10138328	97.060
2	35.663	307075	2.940
合計		10445403	100.000

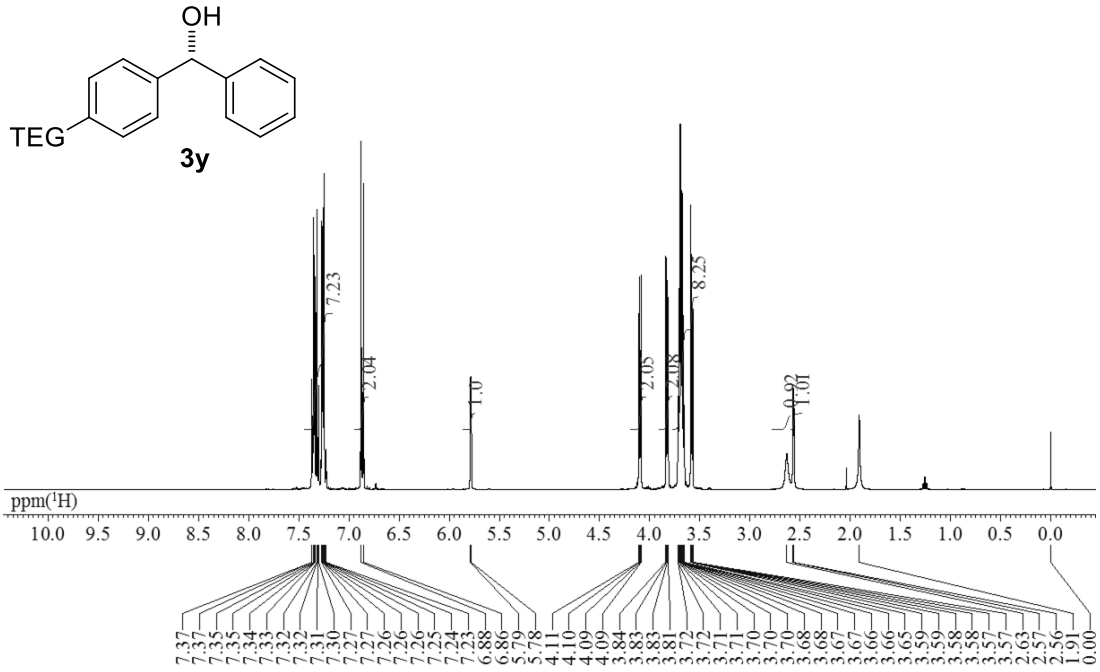


Figure S39. HPLC charts of **3y** and the racemic compound and ^{1}H NMR spectrum of **3y.**

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