

Supporting Information for

**Hetero-bifunctional catalyst manipulates carbonyl and alkynyl reductions of conjugated
alkynones in an aqueous medium**

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Experimental

1). General

All experiments, which are sensitive to moisture or air, were carried out under an Ar atmosphere using the standard Schlenk techniques. Tetraethoxysilane (TEOS), 1,4-bis(triethoxysilyl)ethane, cetyltrimethylammonium bromide (CTAB), fluorocarbon surfactant (FC-4: $[\text{C}_3\text{F}_7\text{O}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_2\text{CF}(\text{CF}_3)\text{CONH}(\text{CH}_2)_3\text{N}^+(\text{C}_2\text{H}_5)_2\text{CH}_3]\text{I}^-$), 4-(2-(trimethoxysilyl)ethyl)benzene-1-sulfonyl chloride, Triethylenediamine (DABCO), 4-(methylphenylsulfonyl)-1,2-diphenylethylenediamine [(S,S)-TsDPEN], (MesityleneRuCl₂)₂ were purchased from Sigma-Aldrich Company Ltd and used as received.

2). Characterization

Ru and Pd loading amounts in the catalysts were analyzed using an inductively coupled plasma optical emission spectrometer (ICP, Varian VISTA-MPX). Fourier transform infrared (FT-IR) spectra were collected on a Nicolet Magna 550 spectrometer using KBr method. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6380LV microscope operating at 20 kV. Transmission electron microscopy (TEM) images were performed on a JEOL JEM2010 electron microscope at an acceleration voltage of 220 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Perkin-Elmer PHI 5000C ESCA system. A 200 μm diameter spot size was scanned using a monochromatized Aluminum $K\alpha$ X-ray source (1486.6 eV) at 40 W and 15 kV with 58.7 eV pass energies. All the binding energies were calibrated by using the contaminant carbon ($\text{C}_{1s} = 284.6$ eV) as a reference. Nitrogen adsorption isotherms were measured at 77 K with a Quantachrome Nova 4000 analyzer. The samples were measured after being outgassed at 423 K overnight. Pore size distributions were calculated by using the BJH model. The specific surface areas (S_{BET}) of samples were determined from the linear parts of BET plots ($p/p_0 = 0.05$ -1.00). Solid state NMR experiments were explored on a Bruker AVANCE spectrometer at a magnetic field strength of 9.4 T with ^1H frequency of 400.1 MHz, ^{13}C frequency of 100.5 MHz, and ^{29}Si frequency of 79.4 MHz with 4 mm rotor at two spinning frequency of 5.5 kHz and 8.0 kHz, TPPM decoupling is applied in the during acquisition period. ^1H cross polarization in all solid state NMR experiments was employed using a contact time of 2 ms and the pulse lengths of 4 μs .

Figure S1. FT-IR spectra of **4** and catalyst **5**.

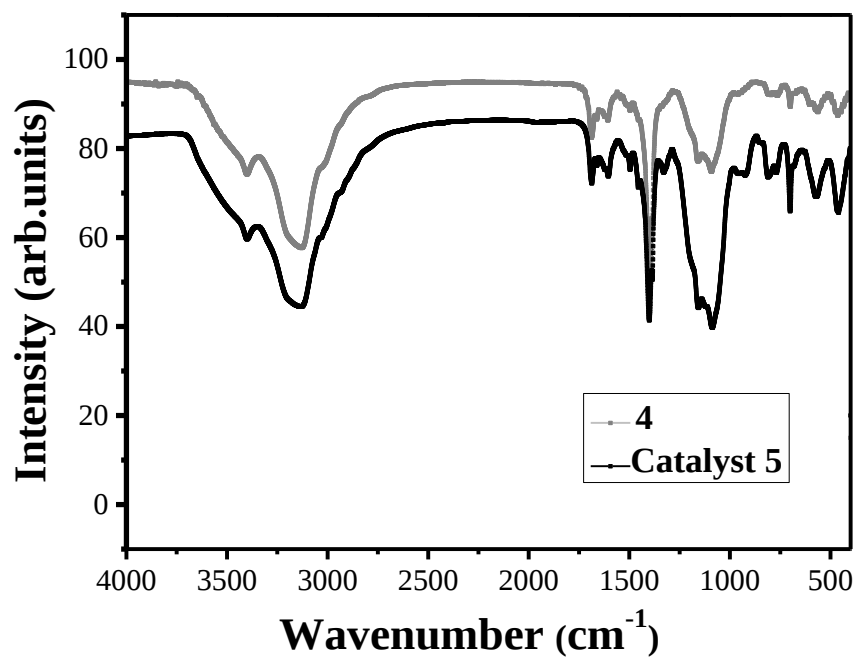


Figure S2. Small-angle powder XRD patterns of **4** and catalyst **5**.

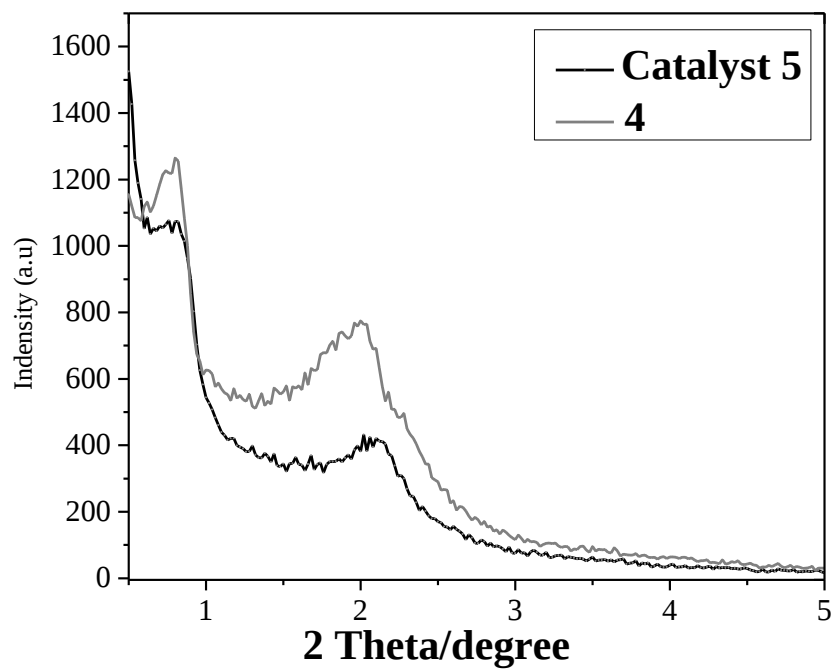
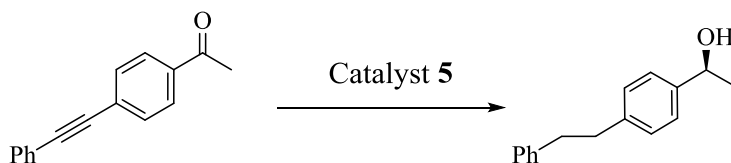


Table S1. Optimizing reaction conditions for the **5**-catalysed enantioselective cascade reactions of (4-(phenylethynyl)phenyl)ethanone.

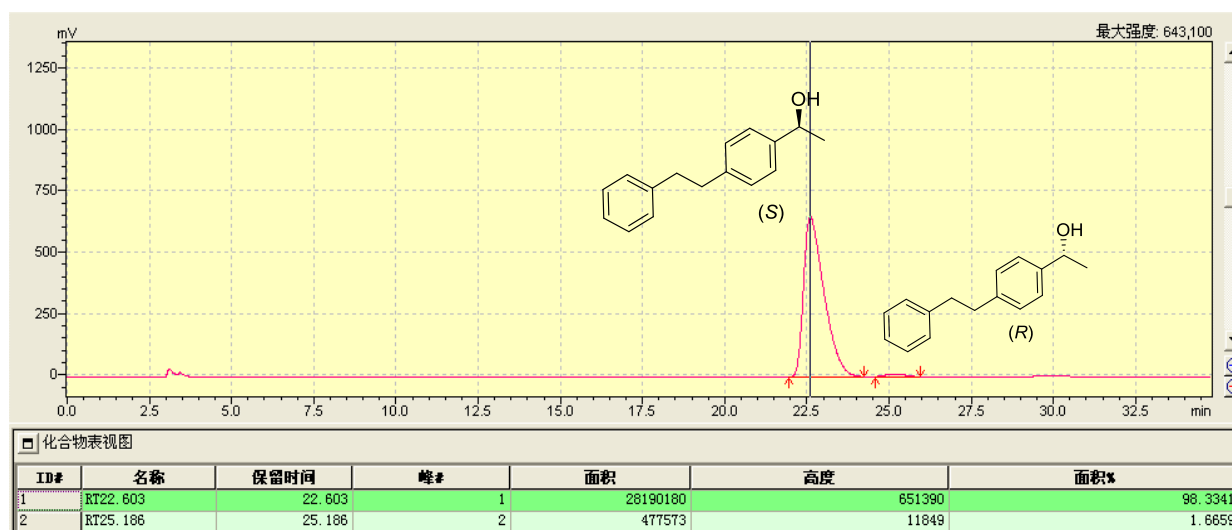
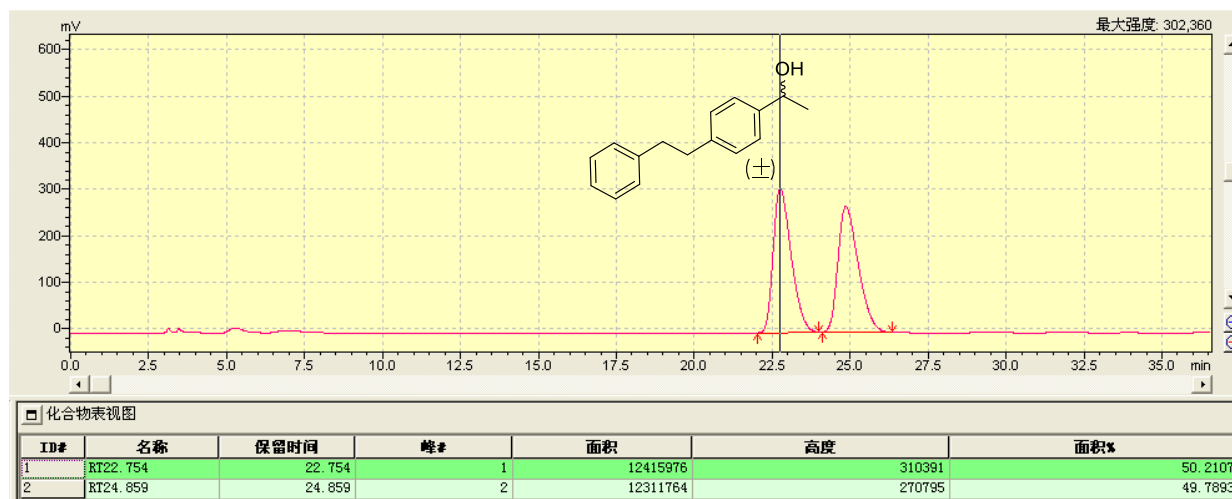


Entry	Ru-loading	H-resource	Solvent	℃	Time (h)	Yield (%)	ee (%)
1	2.0 mol%	HCOOH	/	60	8	/	/
2	2.0 mol%	<i>i</i> PrOH	/	60	8	/	/
3	2.0 mol%	HCOOH/NEt ₃	/	60	8	14	65
4	2.0 mol%	HCOONa	H ₂ O/ <i>i</i> PrOH (1:3)	50	6	34	94
5	2.0 mol%	HCOONa	H ₂ O/ <i>i</i> PrOH (1:3)	60	3	95	97
6	2.0 mol%	HCOONa	H ₂ O/ <i>i</i> PrOH (1:3)	70	1.5	97	92
7	2.0 mol%	HCOONa	H ₂ O/ <i>i</i> PrOH (1:2)	60	4	92	92
8	2.0 mol%	HCOONa	H ₂ O/ <i>i</i> PrOH (1:4)	60	2	98	93
9	2.0 mol%	HCOONa	H ₂ O/EtOH (1:3)	60	5	96	90
10	2.0 mol%	HCOONa	H ₂ O/MeOH (1:3)	60	5	97	89
11	1.75 mol%	HCOONa	H ₂ O/ <i>i</i> PrOH (1:3)	60	3	91	97
12	2.25 mol%	HCOONa	H ₂ O/ <i>i</i> PrOH (1:3)	60	3	96	96

Reaction conditions: Catalyst **5** (4.38 mol% of Pd based on ICP analysis), HCO₂Na (1.0 mmol), alkynone (0.10 mmol), and 2.0 mL of solvent were added sequentially to a 10.0 mL round-bottom flask. Yields were determined by ¹H-NMR analysis and *ee* values were determined by chiral HPLC analysis.

Figure 3. The HPLC analysis for chiral products. (Table 1 in manuscript: The selective ATH/reduction one-pot enantioselective cascade reductions of conjugated alkynones.)

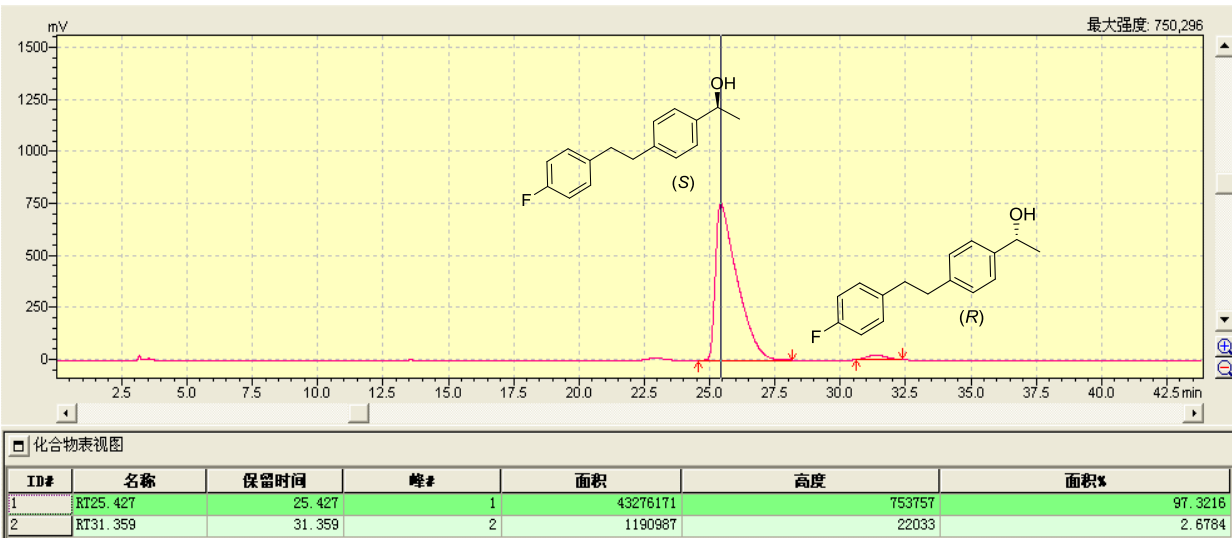
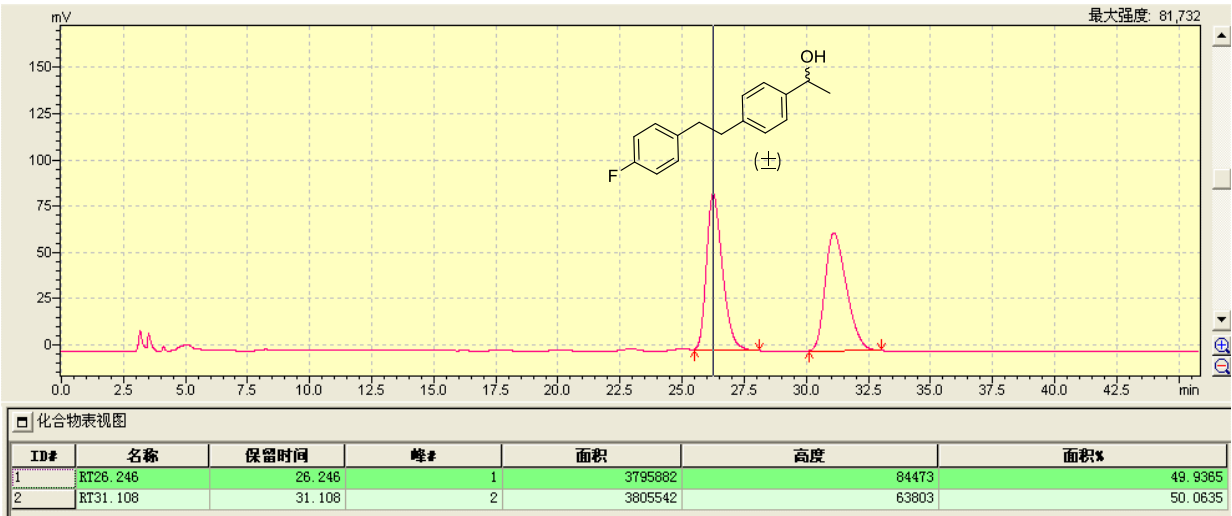
7a. (S)-1-(4-phenethylphenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C). [Literature (Chem. Eur. J. **2010**, 16, 6748): HPLC: Chiracel AD-H, eluent: n-hexane/2-propanol = 95/5, flow rate = 0.7 mL/min, detected at 254 nm, Retention time: 10.98 min (S), 12.16 min (R).]



Translation of Chinese to English is as follows:

	Name	ReTime [min]	Peak	Area	Heigh	Area%
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ID#	名称	保留时间	峰#	面积	高度	面积%
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2	RT25.186	25.186	2	477573	11849	1.6659

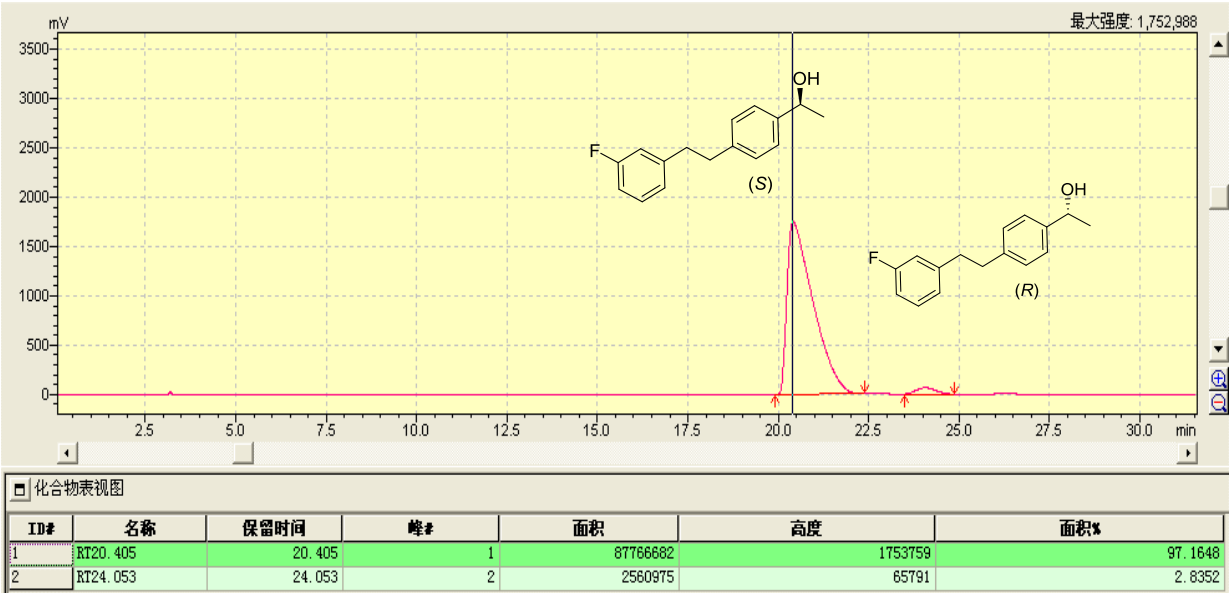
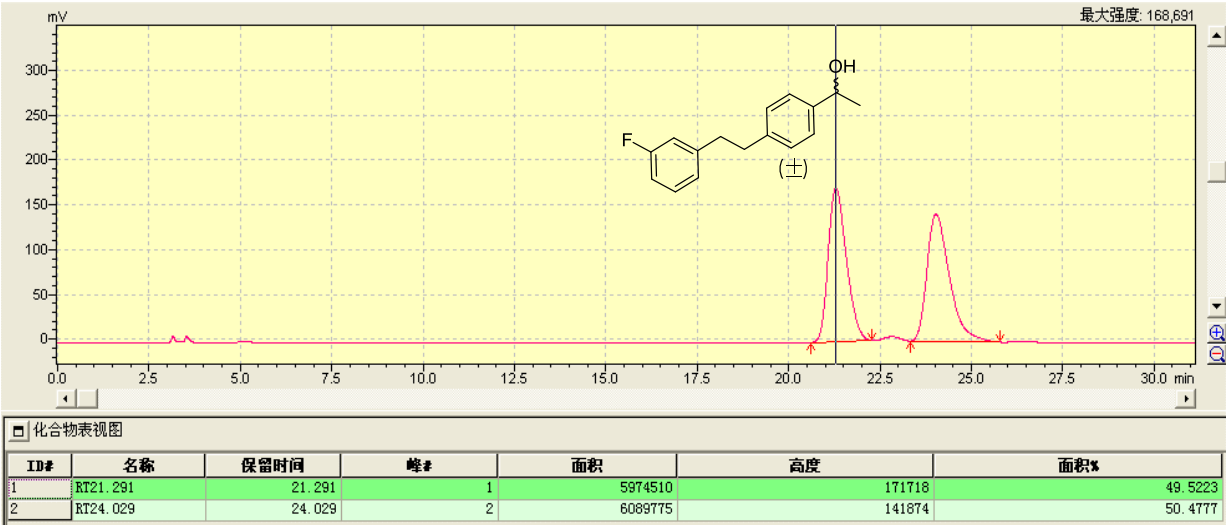
7b. (S)-1-(4-(4-fluorophenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).



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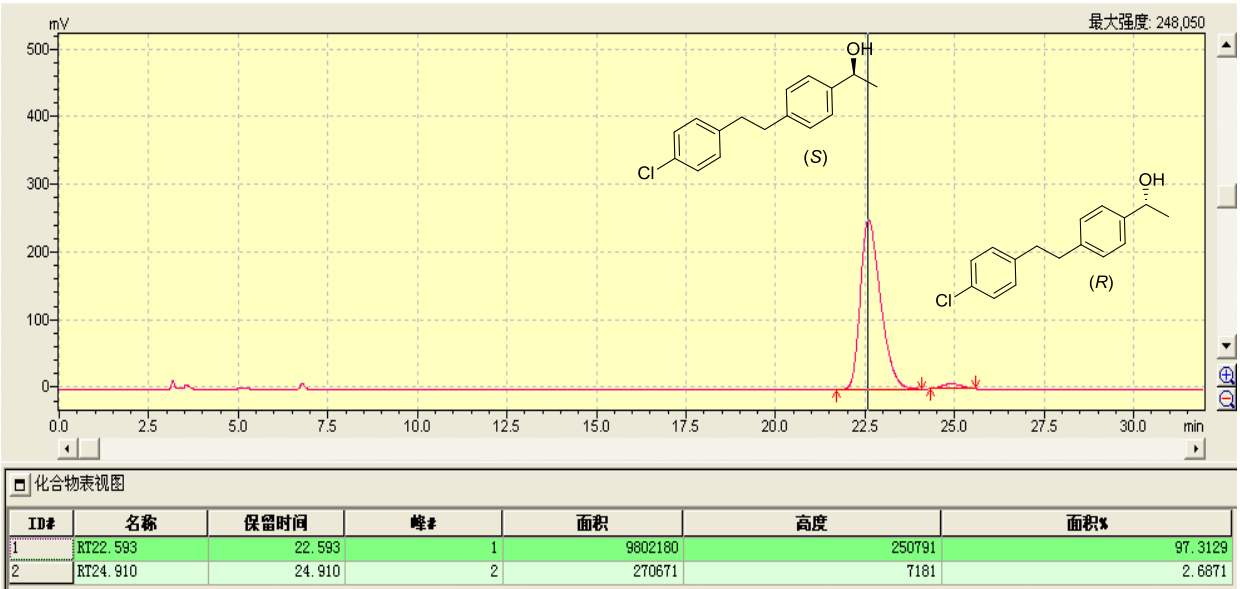
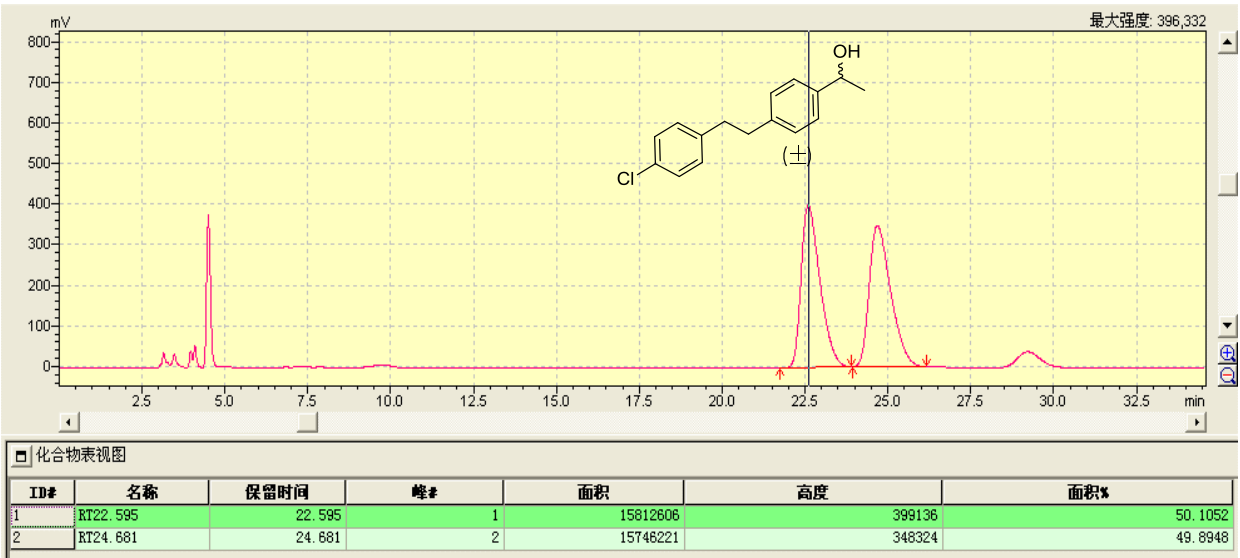
7c. (S)-1-(4-(3-fluorophenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).



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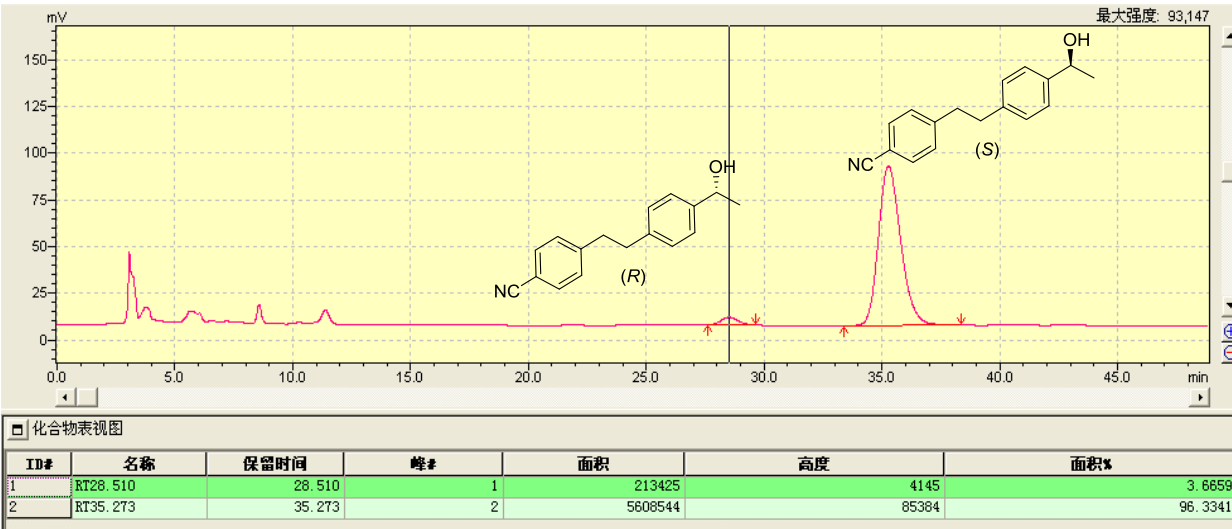
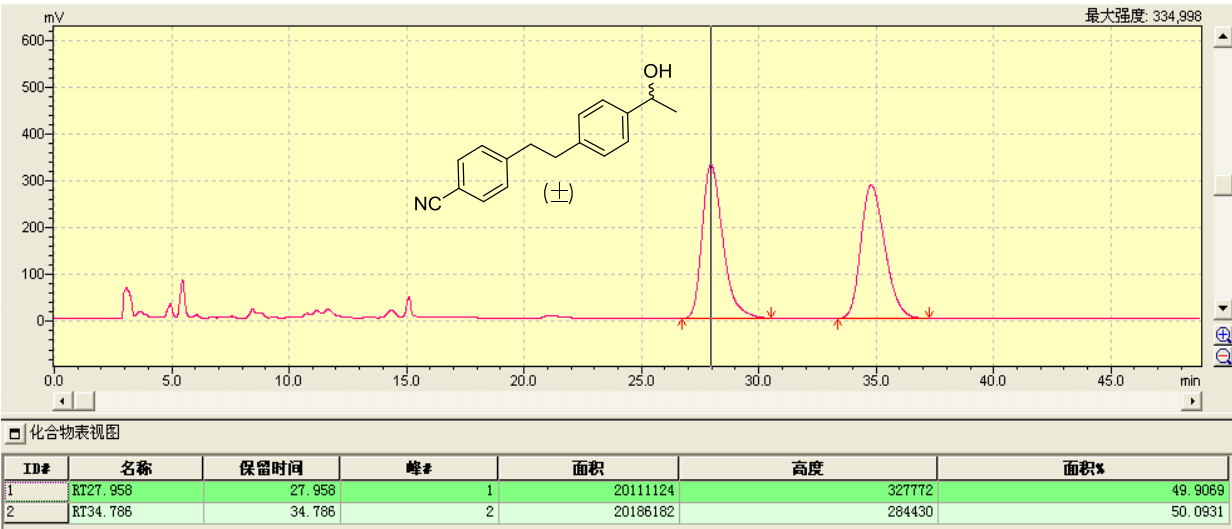
7d. (S)-1-(4-(4-chlorophenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).



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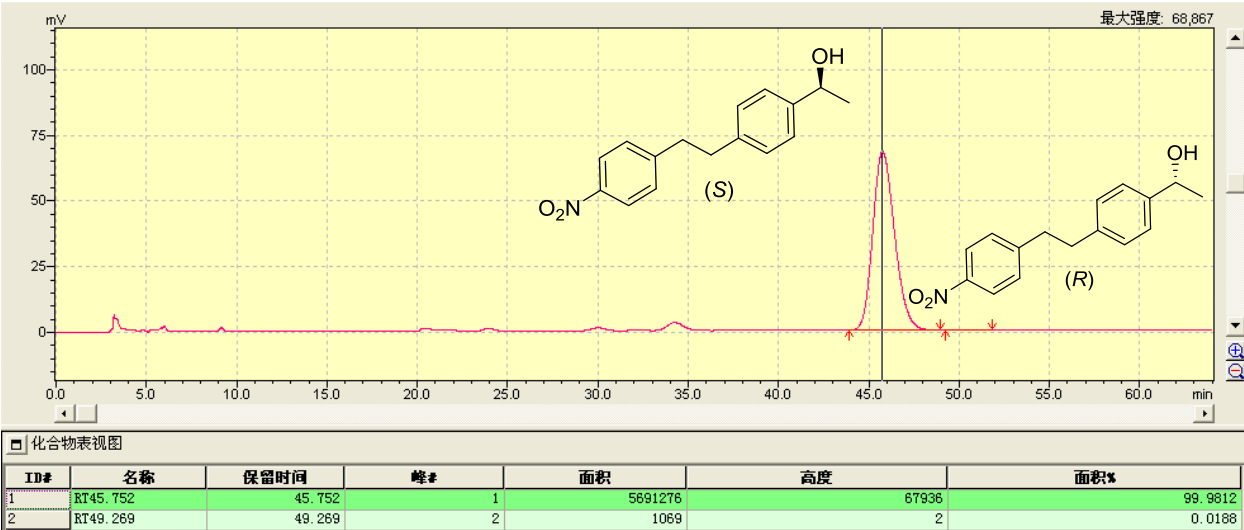
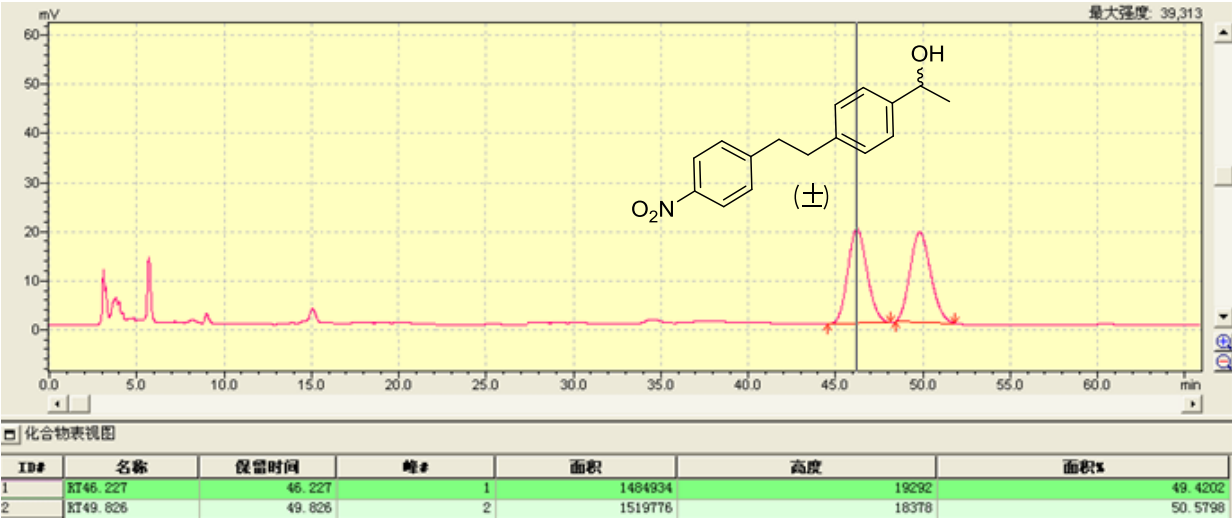
7e. (S)-4-(4-(1-hydroxyethyl)phenethyl)benzonitrile: (HPLC: Chiracel OD-H, detected at 215 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C).



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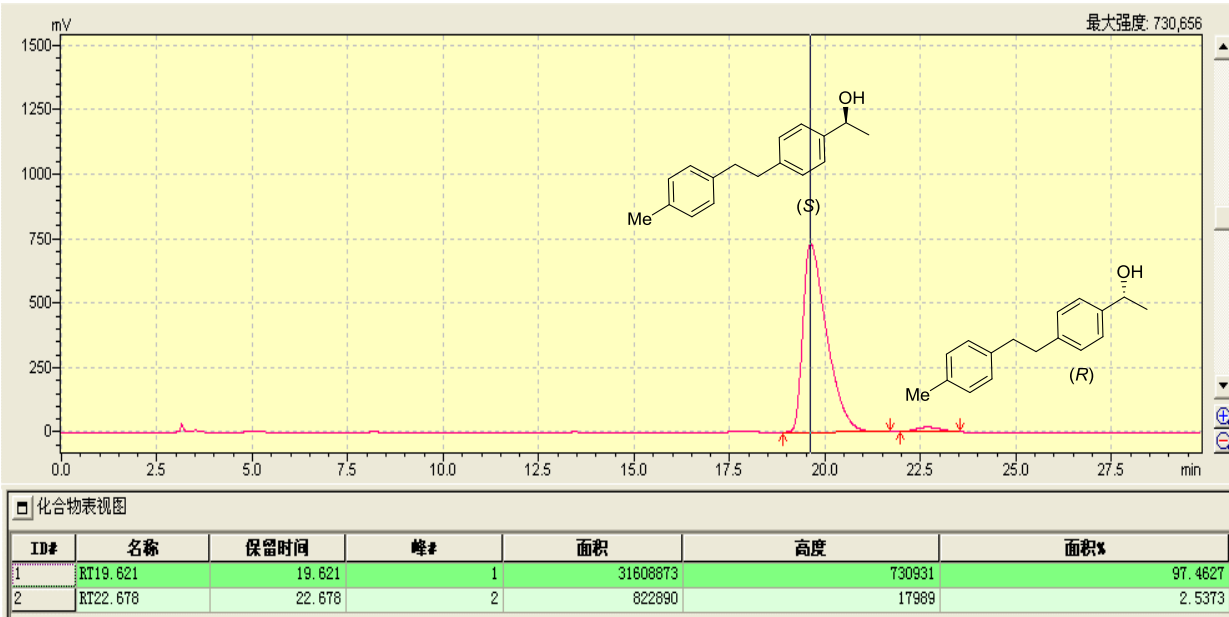
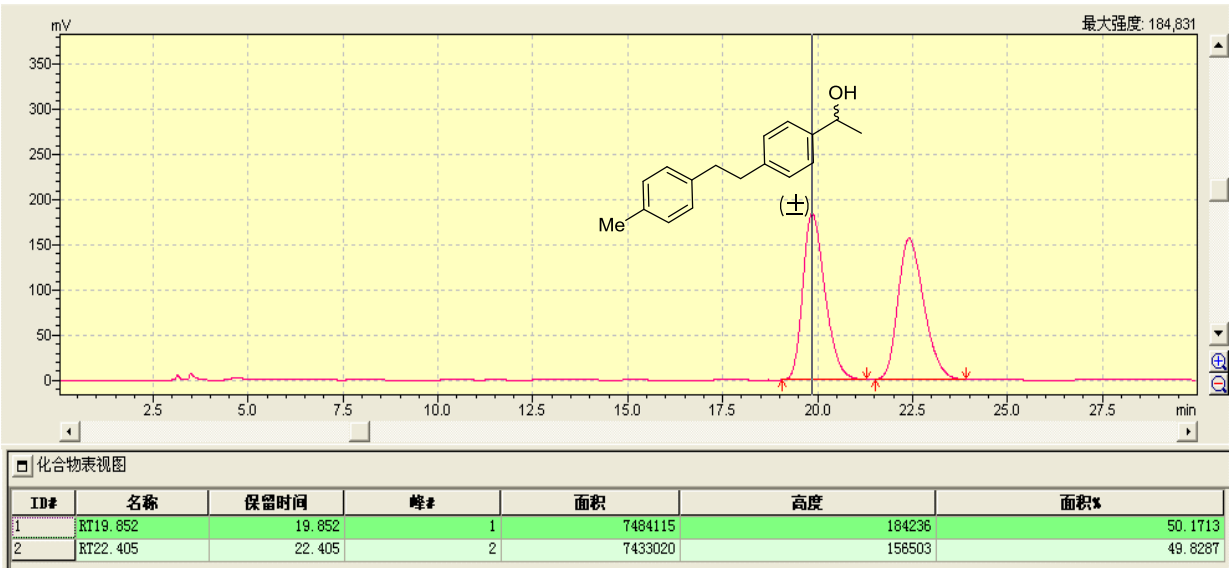
7f. (S)-1-(4-(4-nitrophenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 96/4, flow rate = 1.0 mL/min, 25 °C).



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	Name	ReTime [min]	Peak	Area	Heigh	Area%
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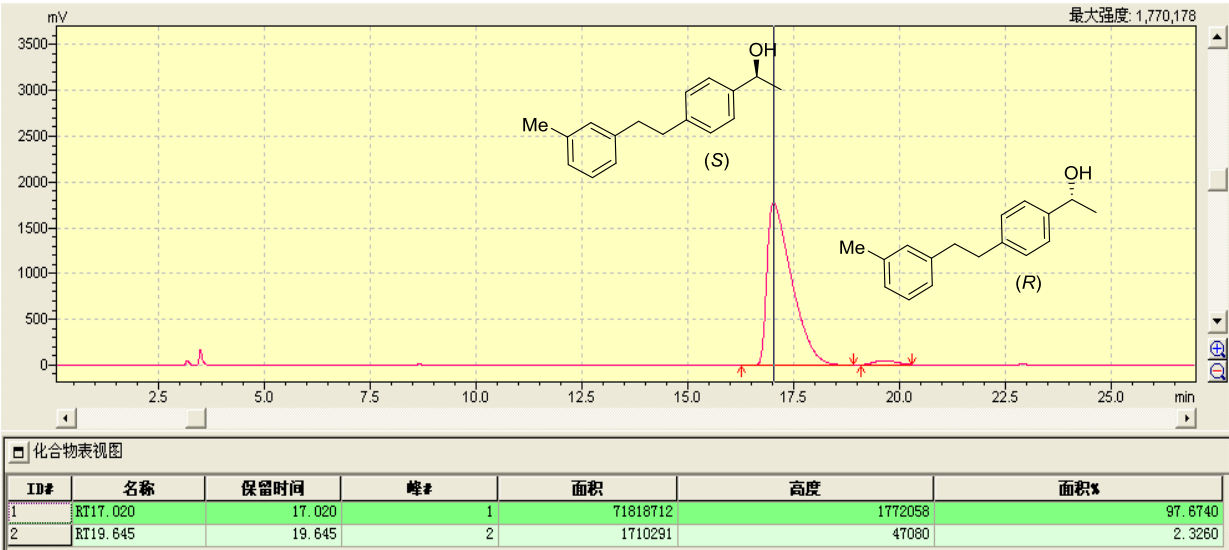
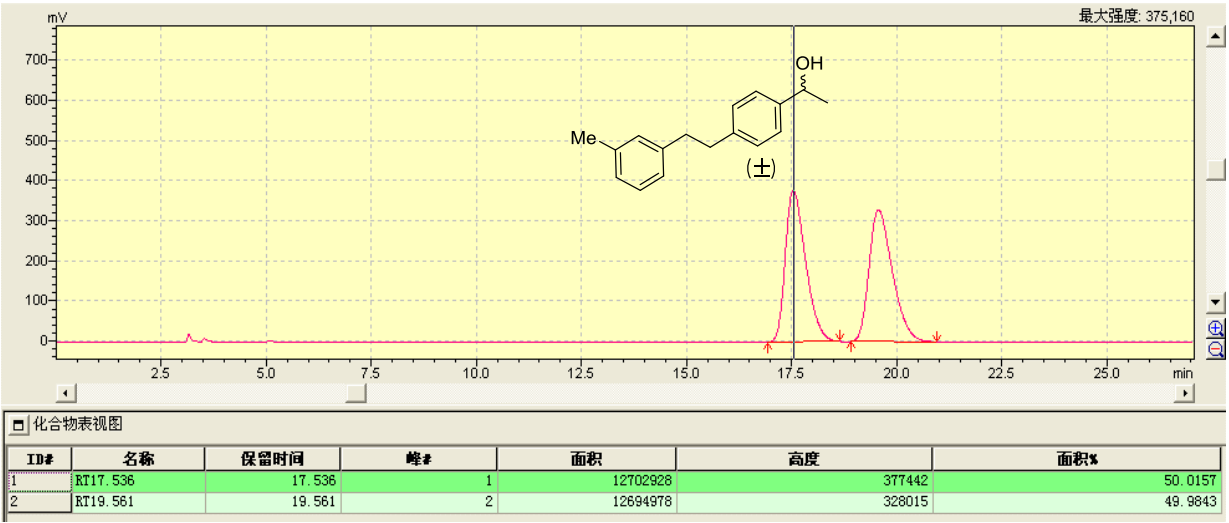
7g. (S)-1-(4-(4-methylphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).



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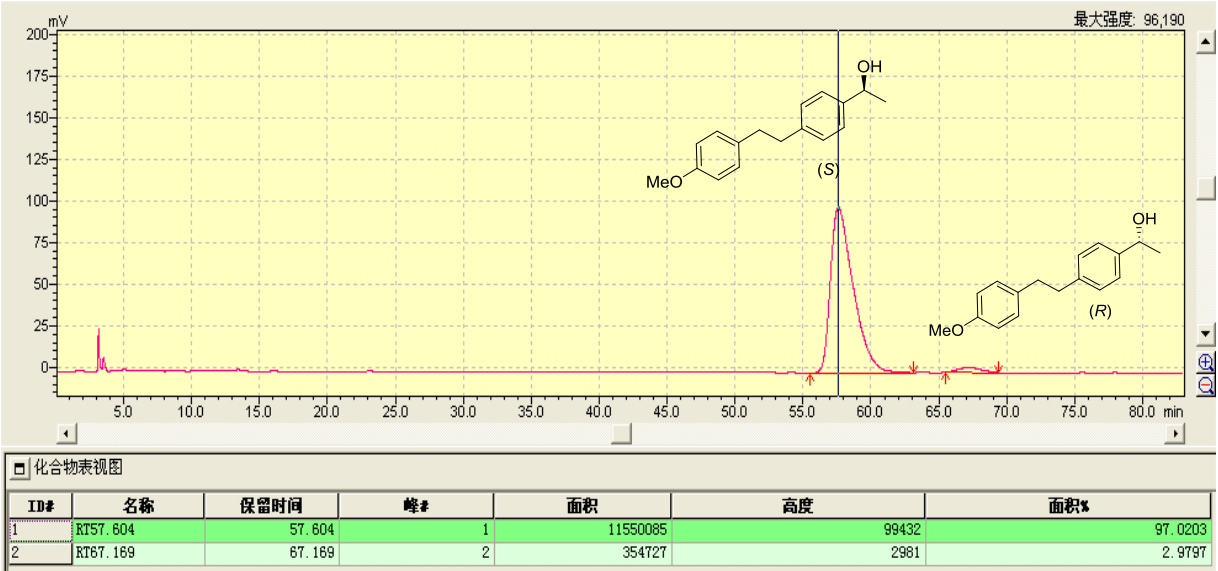
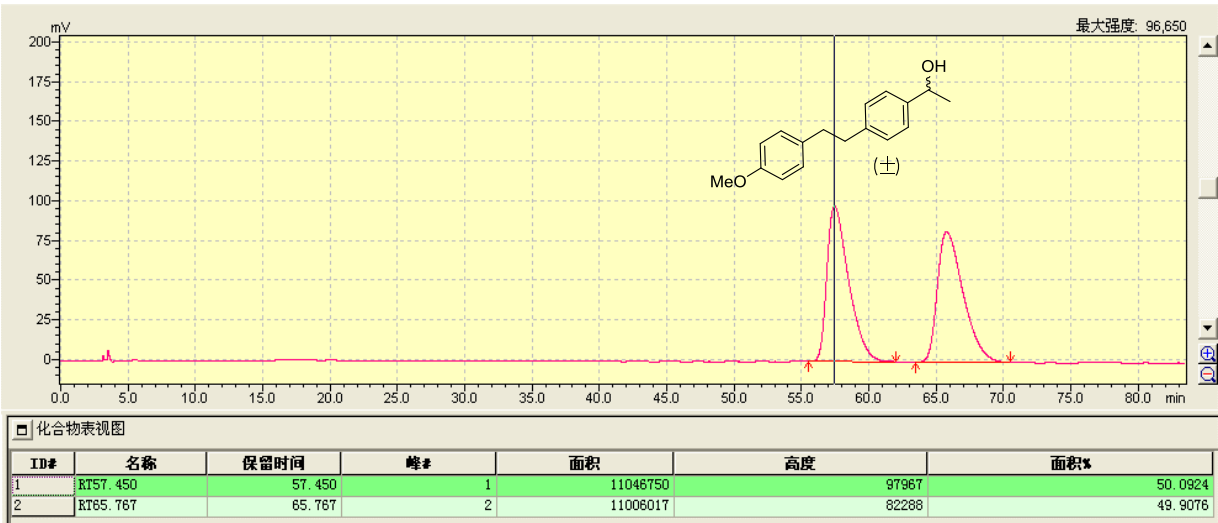
7h. (S)-1-(4-(3-methylphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).



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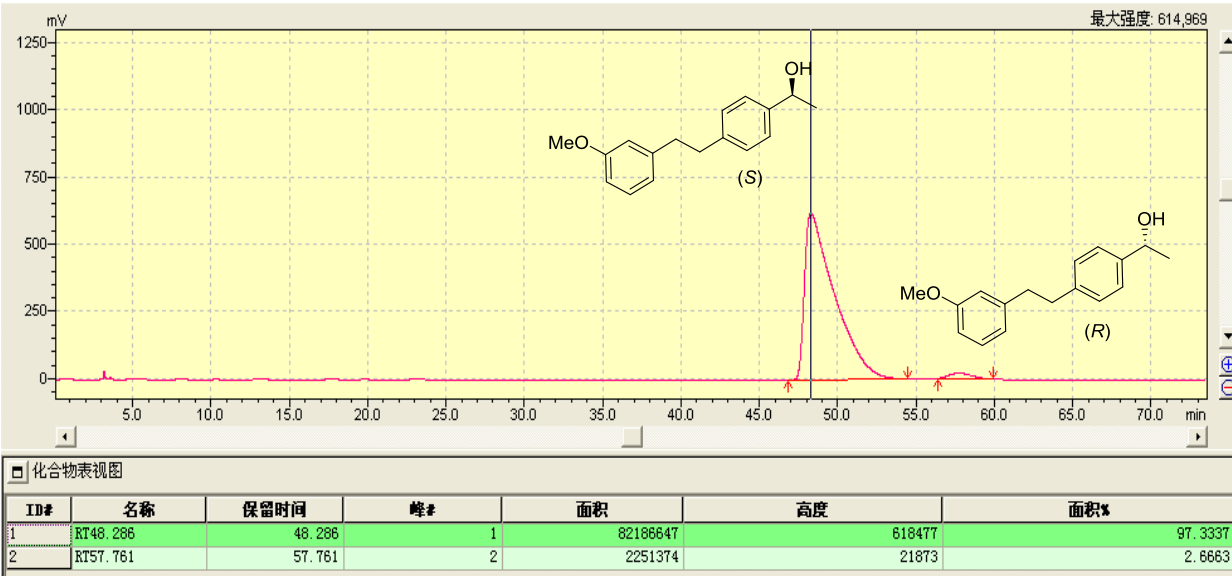
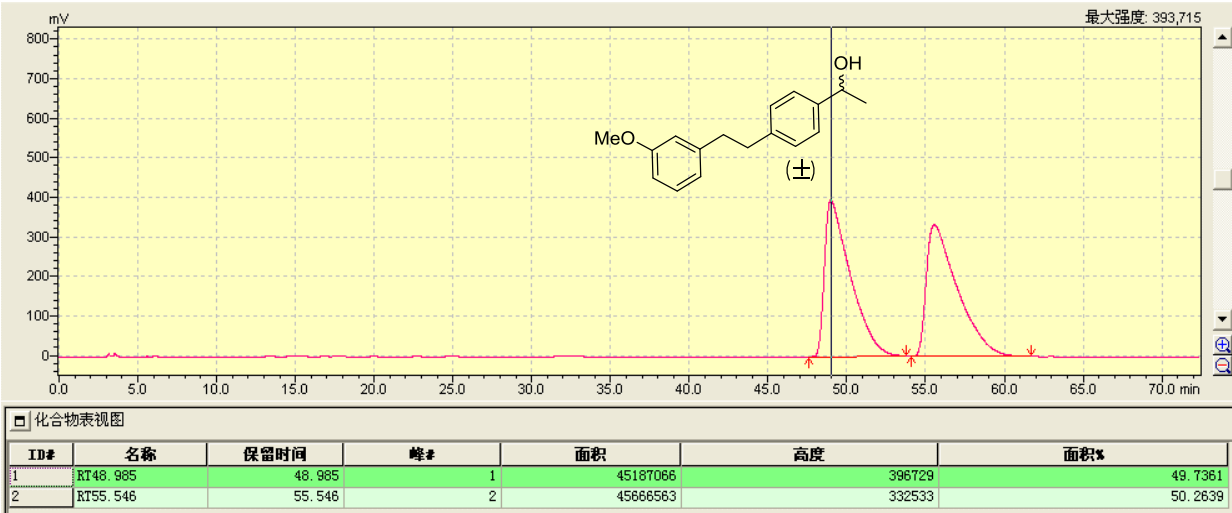
7i. (S)-1-(4-(4-methoxyphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).



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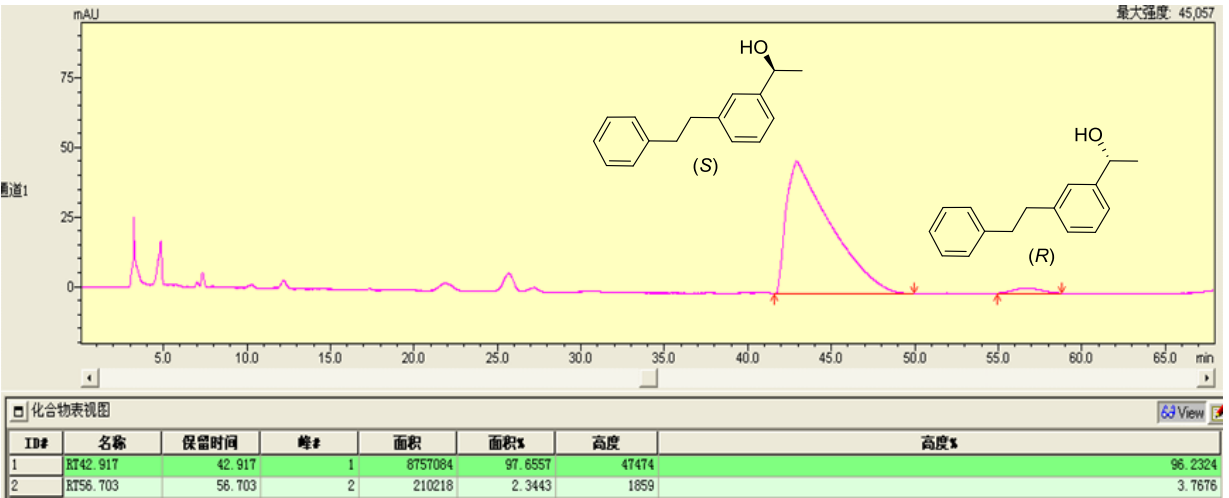
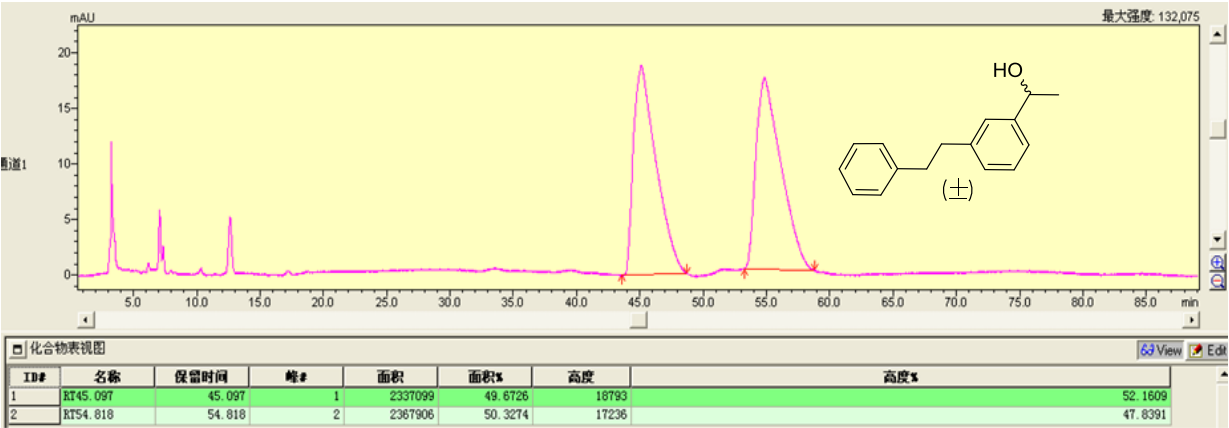
7j. (S)-1-(4-(3-methoxyphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).



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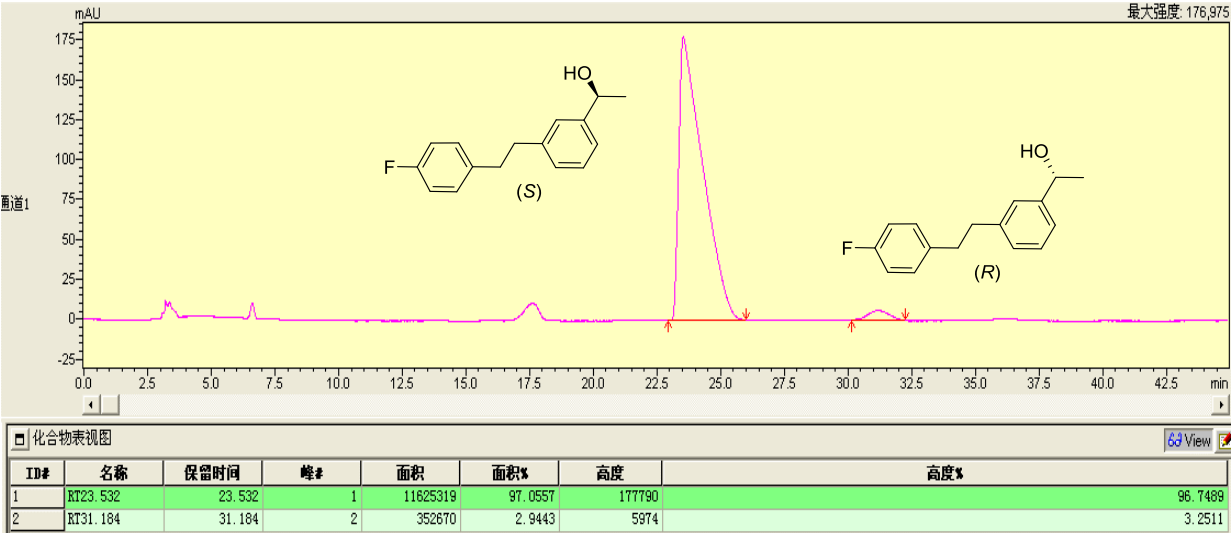
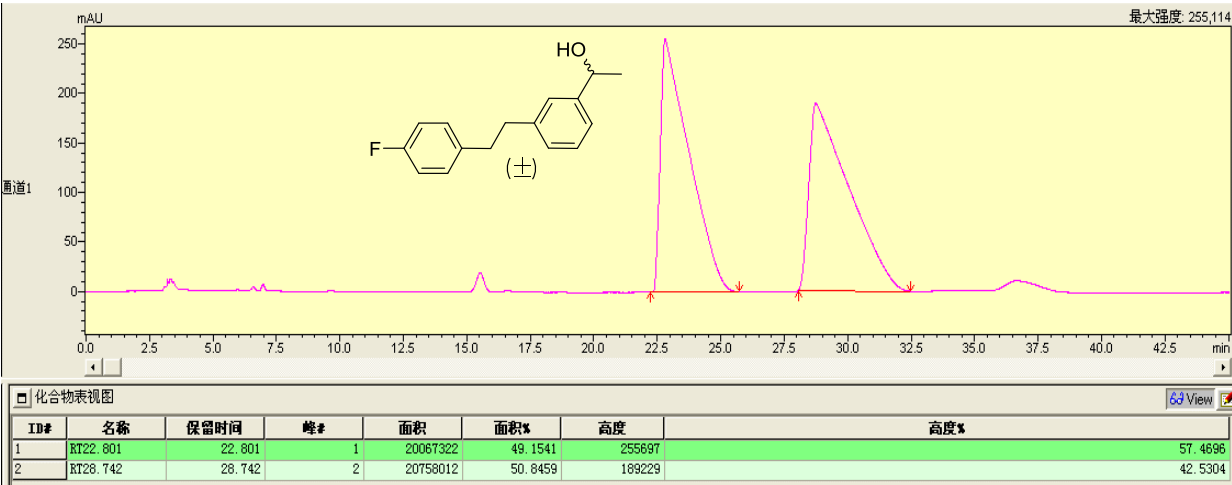
7k. (S)-1-(3-phenethylphenyl)ethan-1-ol: (HPLC: Chiracel OJ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).



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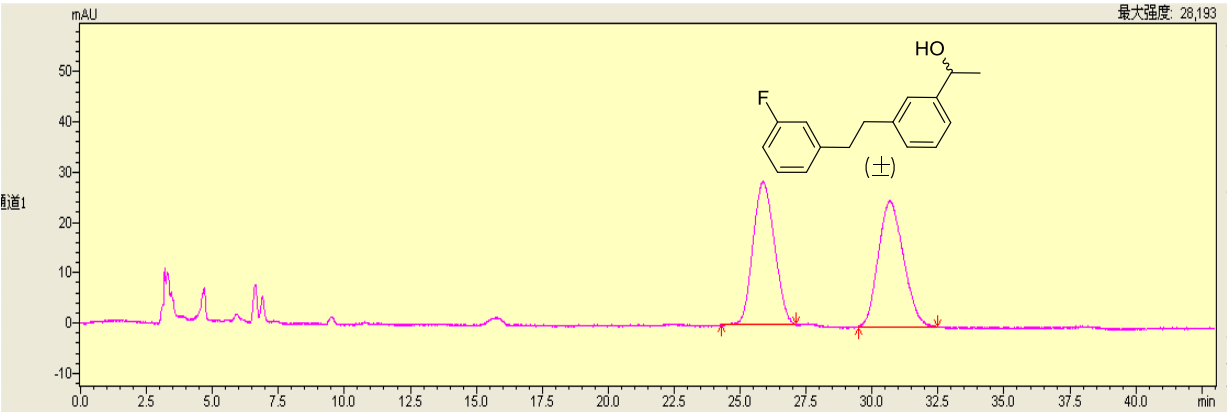
71. (S)-1-(3-(4-fluorophenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OJ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, 25 °C).



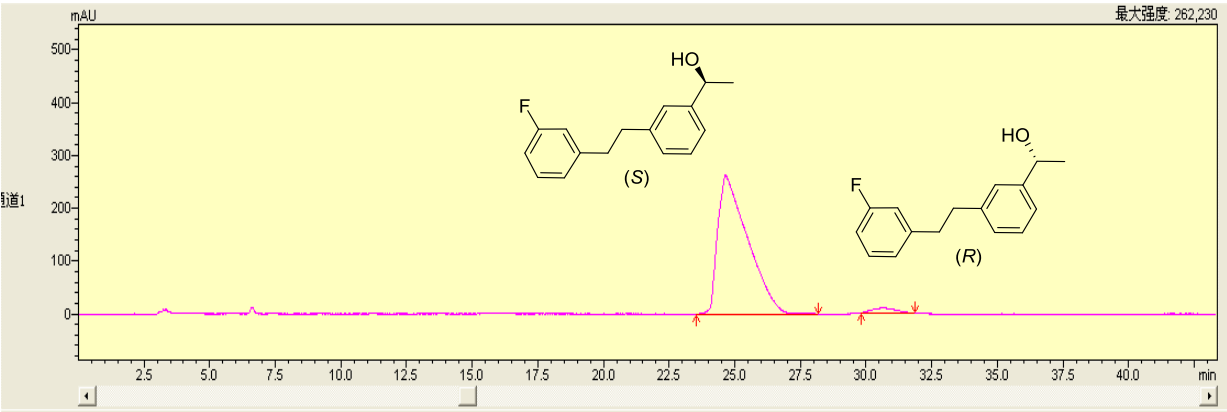
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7m. (S)-1-(3-(3-fluorophenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OJ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, 25 °C).



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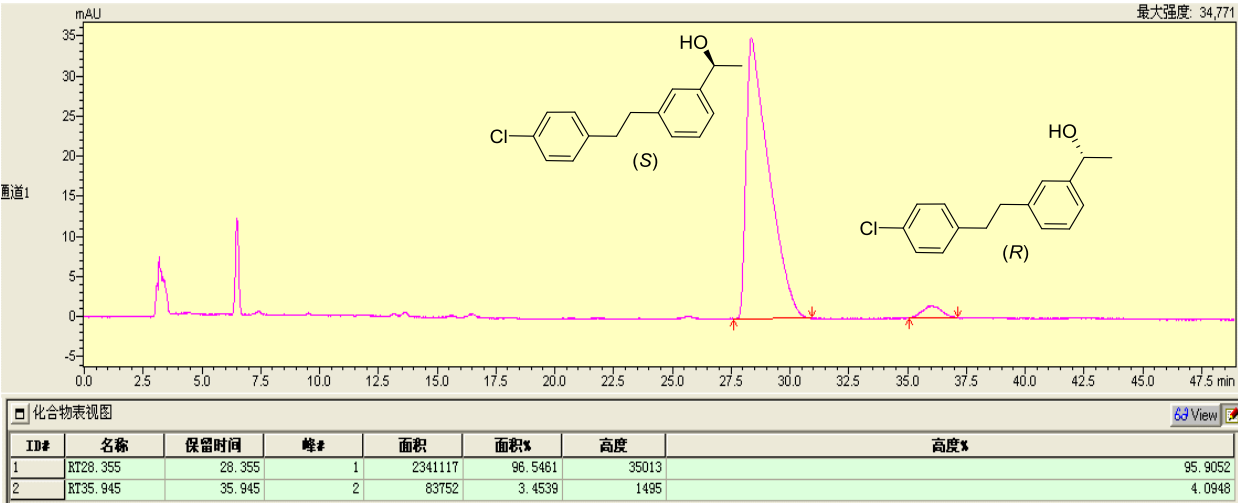
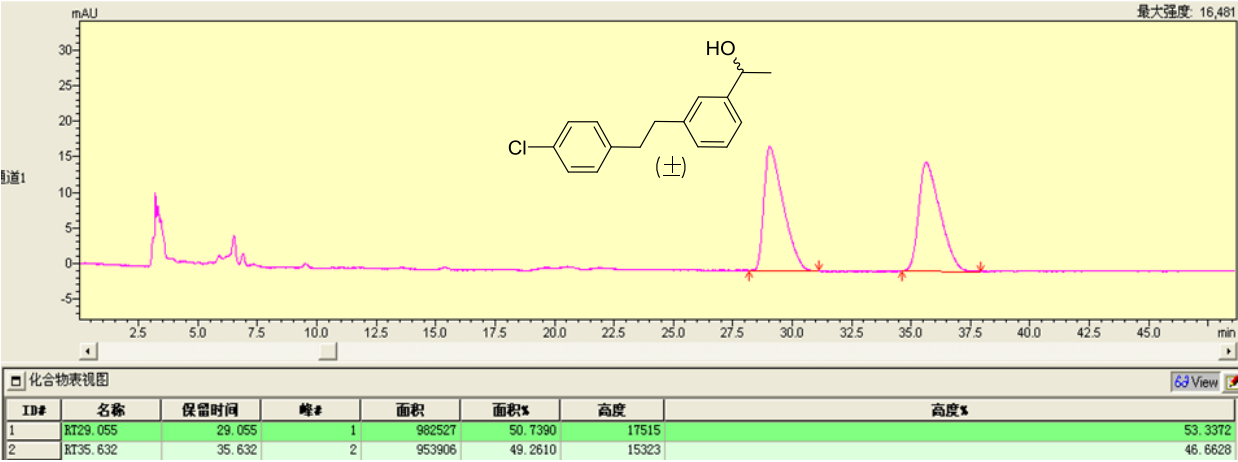


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Translation of Chinese to English is as follows:

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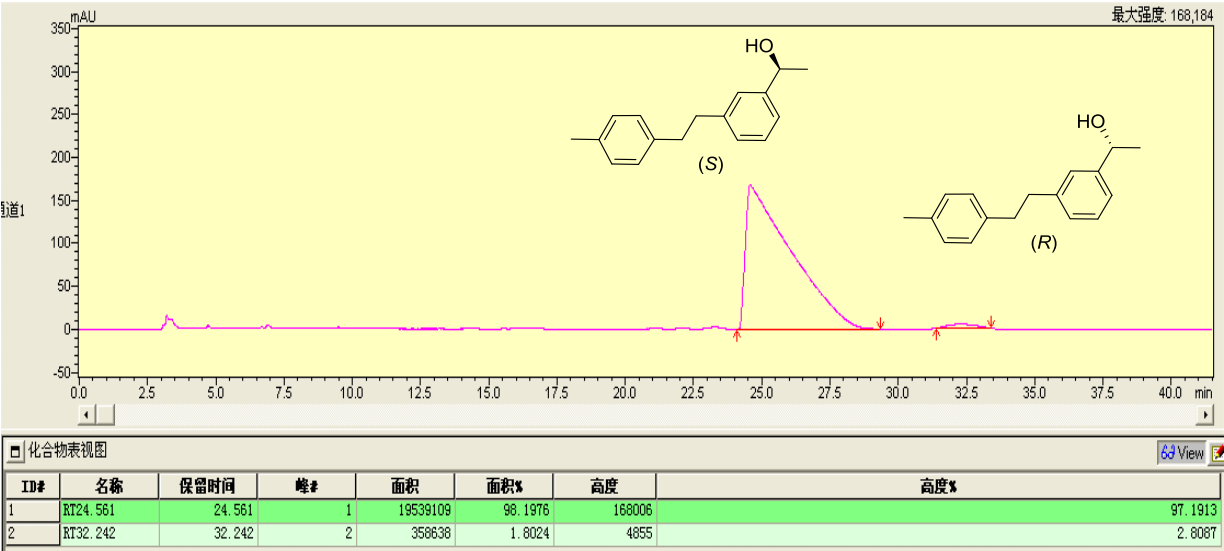
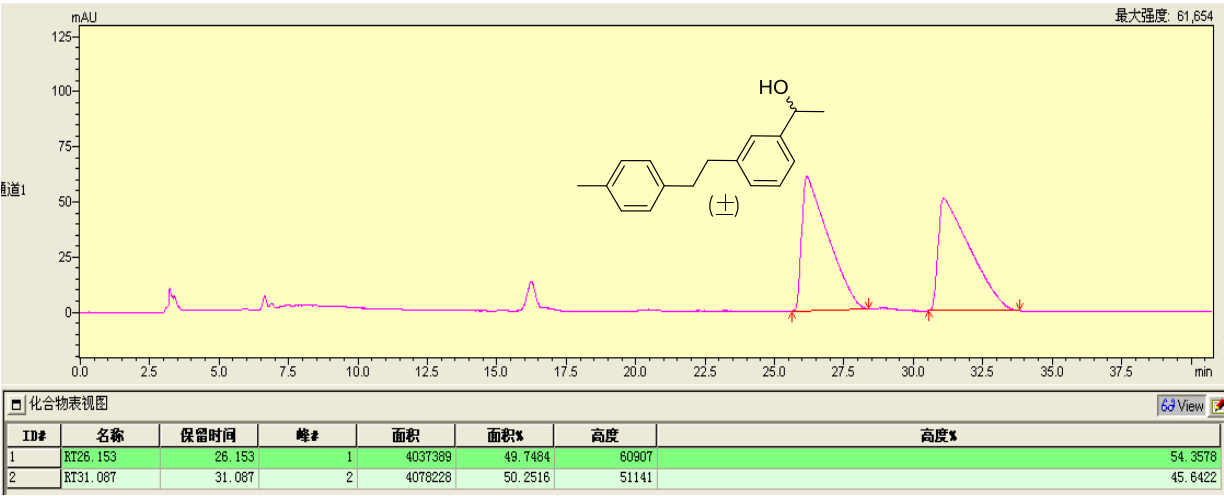
7n. (S)-1-(3-(4-chlorophenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OJ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, 25 °C).



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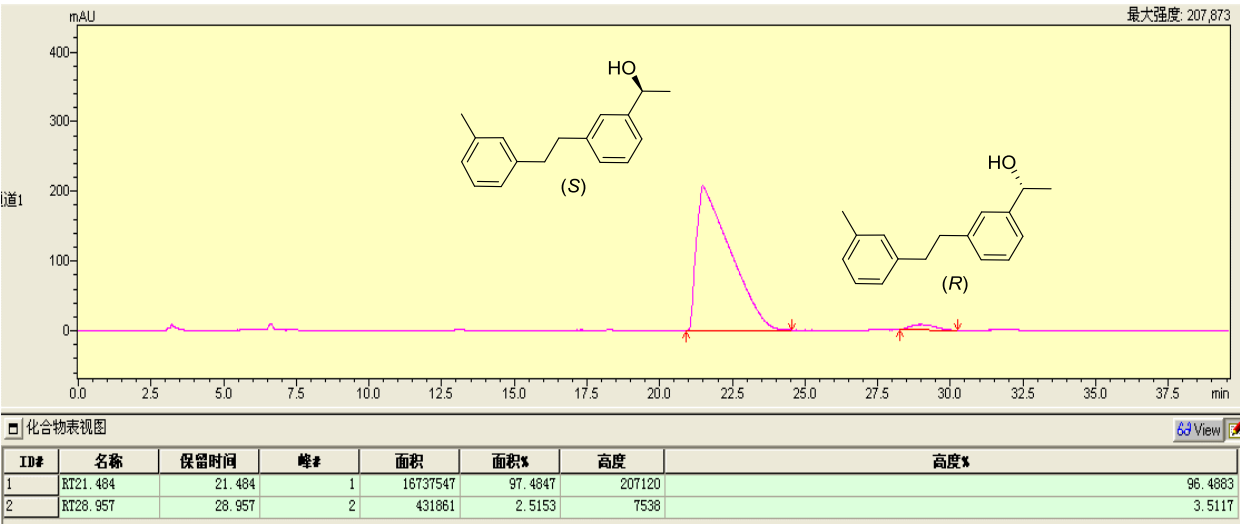
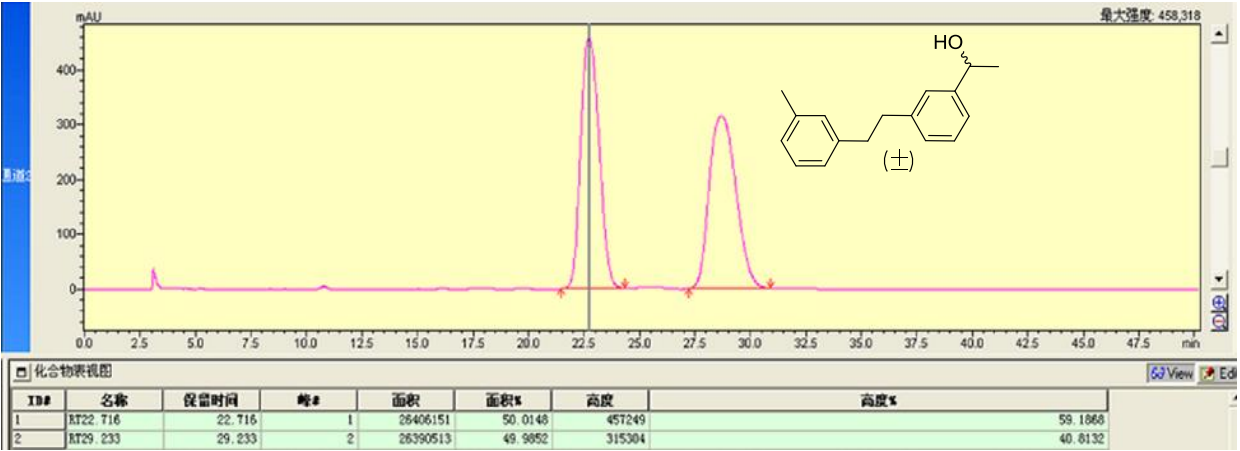
7o. (S)-1-(3-(4-methylphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OJ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, 25 °C).



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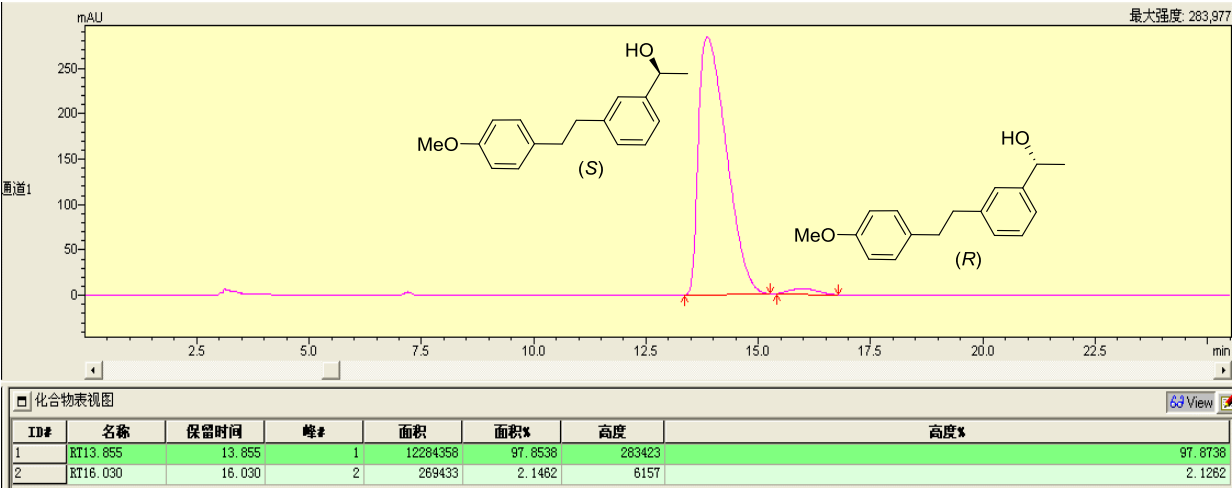
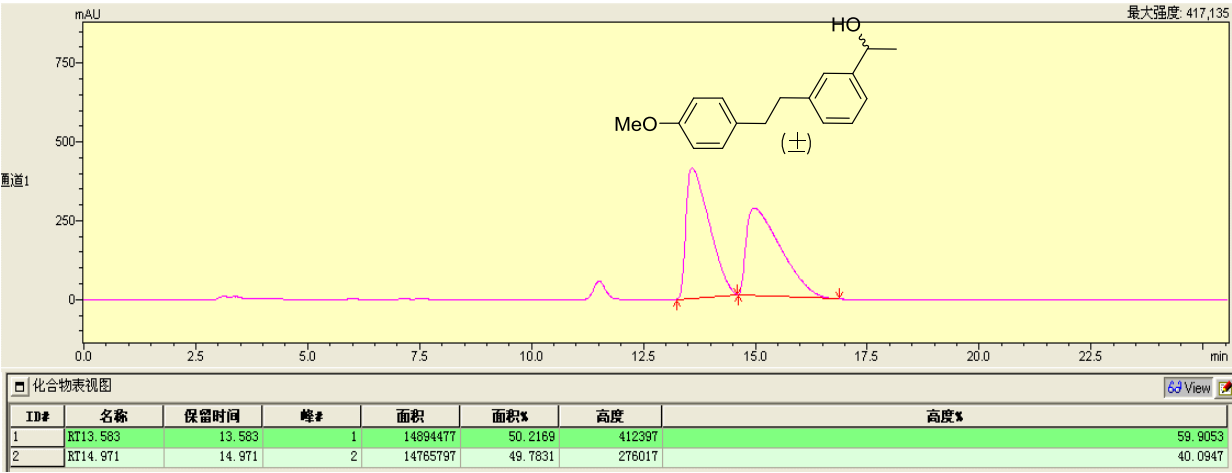
7p. (S)-1-(3-(3-methylphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OJ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, 25 °C).



Translation of Chinese to English is as follows:

	Name	ReTime [min]	Peak	Area	Area%	Heigh	Heigh%
	↑	↑	↑	↑	↑	↑	↑
ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT17.882	17.882	1	54328391	49.7262	1285639	50.7716

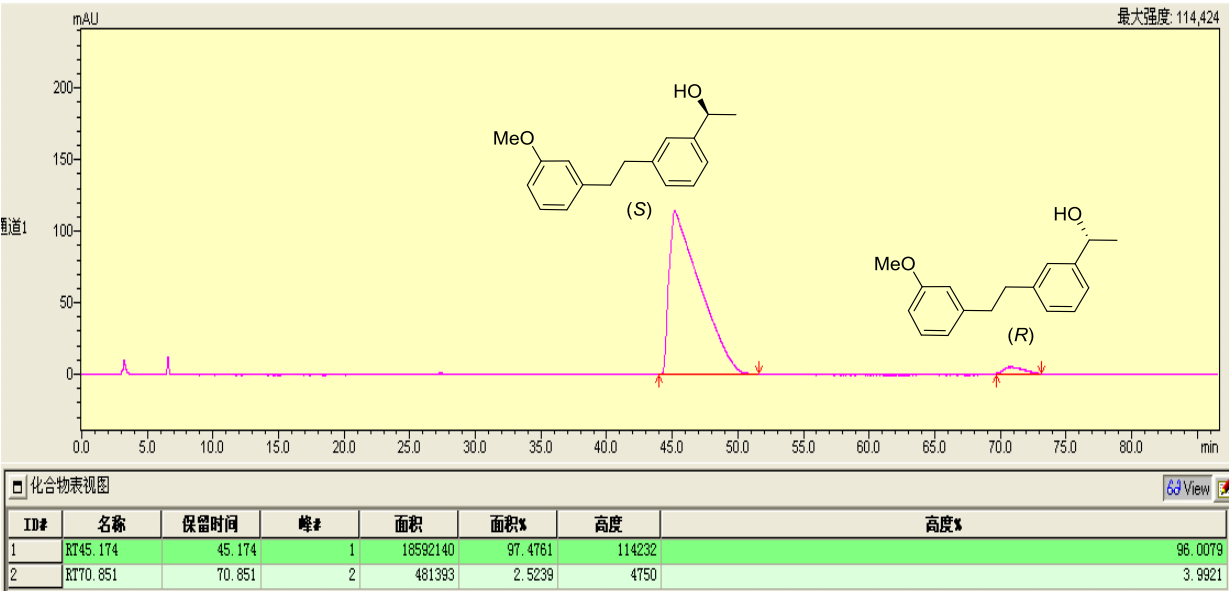
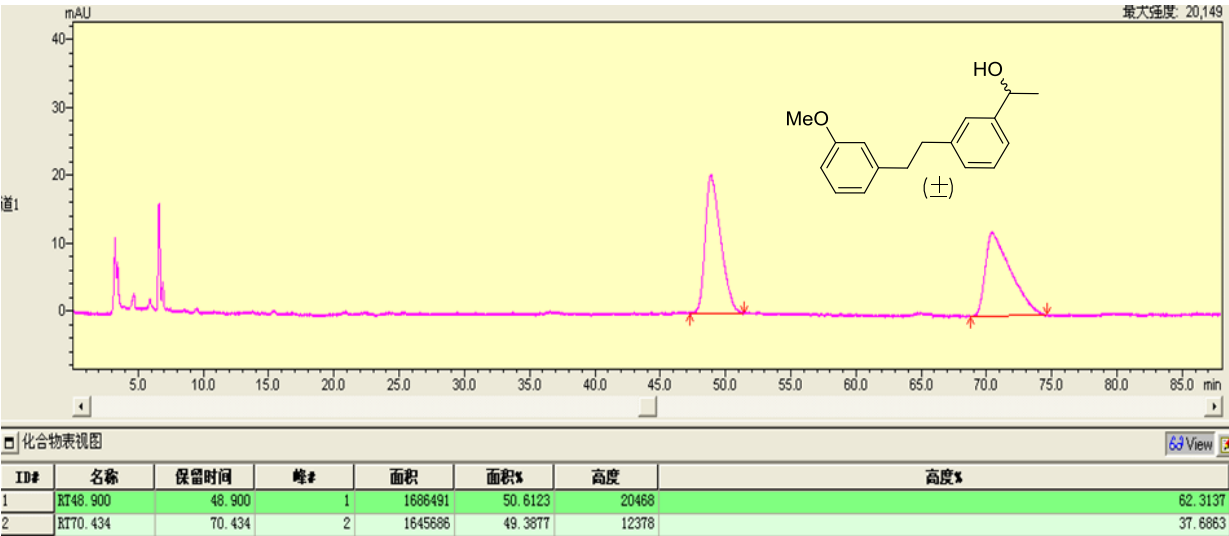
7q. (S)-1-(3-(4-methoxyphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel AS-H, detected at 254 nm, eluent: n-hexane/2-propanol = 96/4, flow rate = 1.0 mL/min, 25 °C).



Translation of Chinese to English is as follows:

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT22.603	22.603	1	28190180	651390	98.3341
2	RT25.186	25.186	2	477573	11849	1.6659

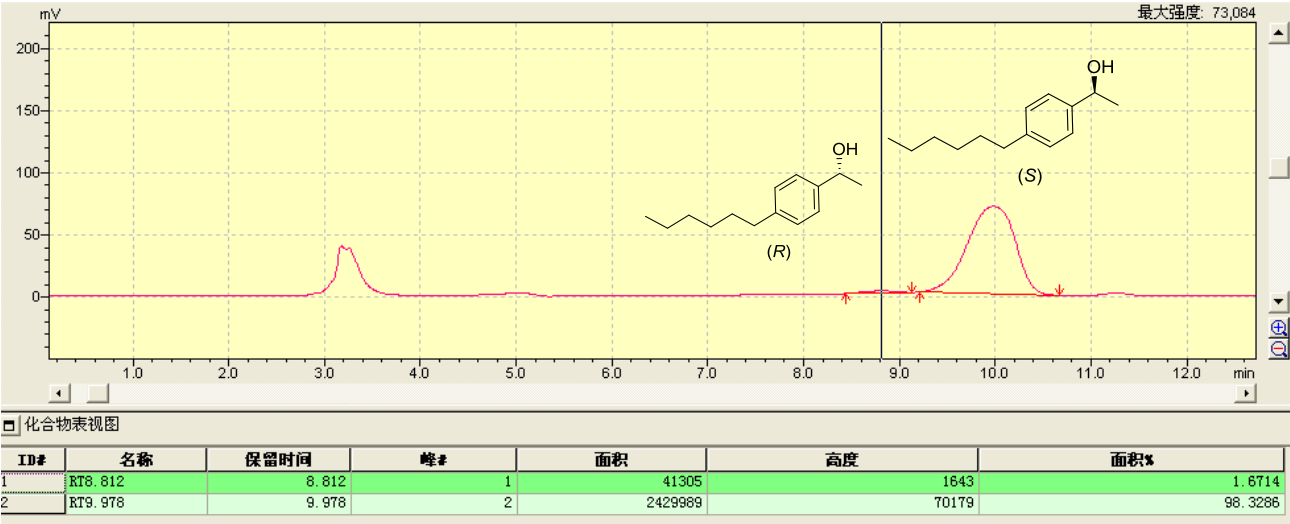
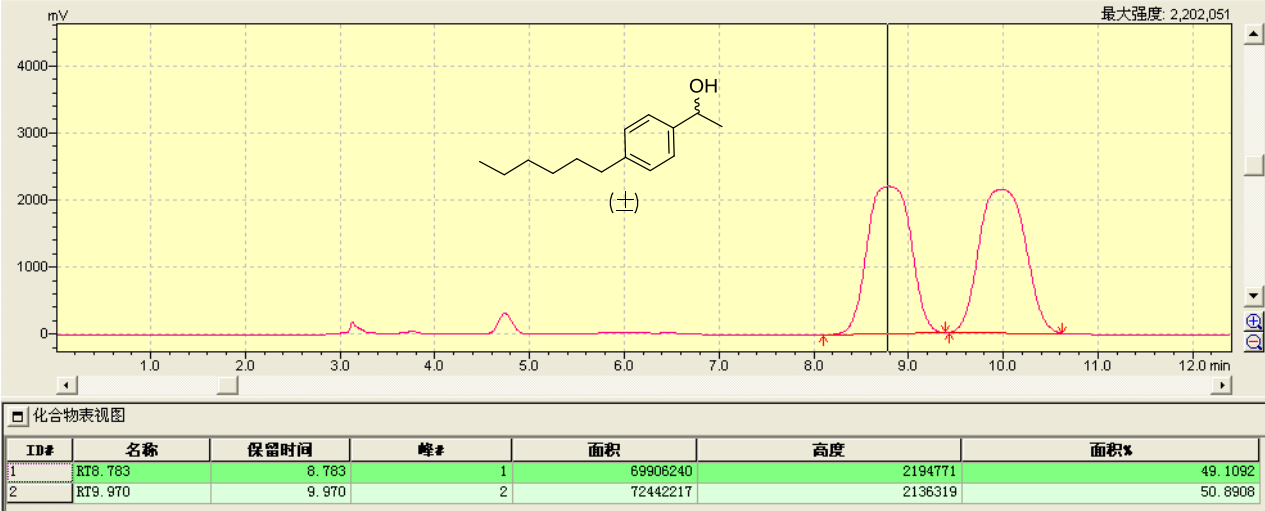
7r. (S)-1-(3-(3-methoxyphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OJ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, 25 °C).



Translation of Chinese to English is as follows:

	Name	ReTime [min]	Peak	Area	Heigh	Area%
	↑	↑	↑	↑	↑	↑
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT22.603	22.603	1	28190180	651390	98.3341
2	RT25.186	25.186	2	477573	11849	1.6659

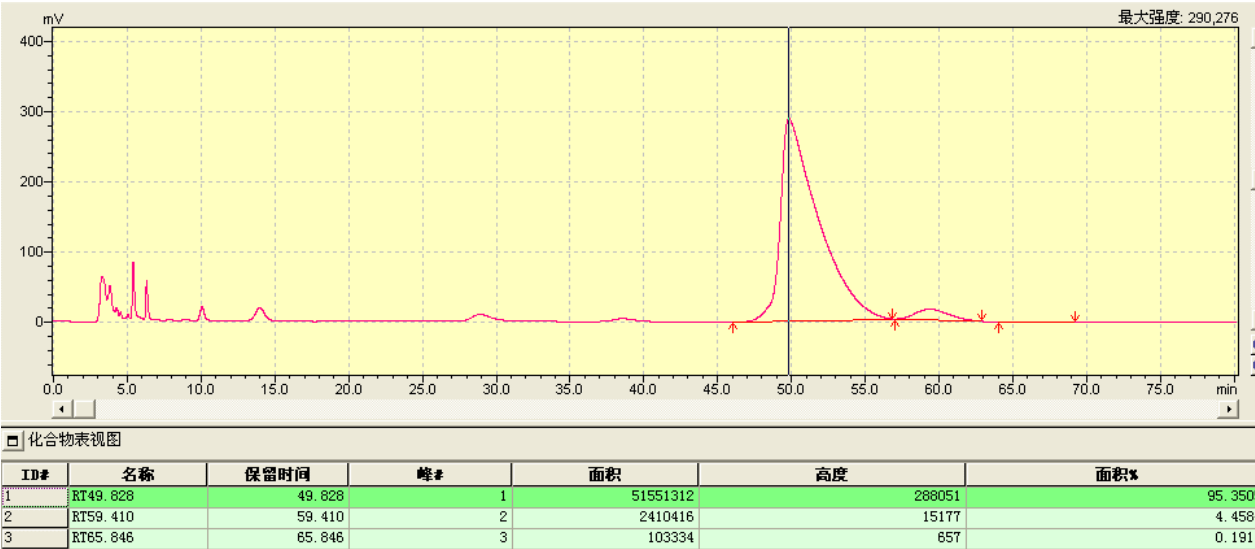
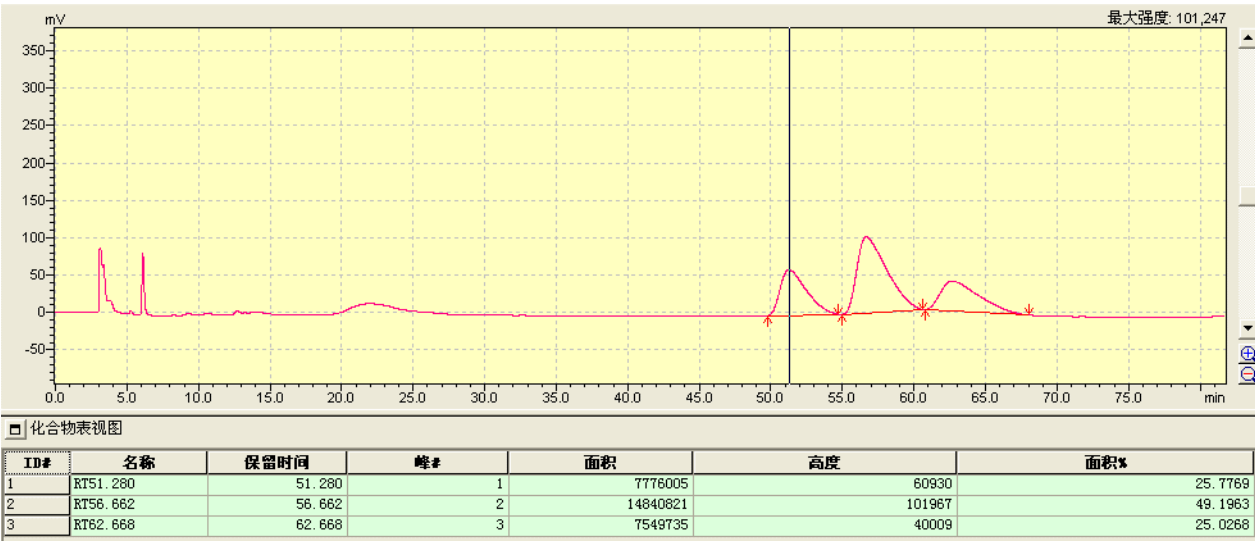
7s. (S)-1-(4-hexylphenyl)ethan-1-ol: (HPLC: Chiracel OD-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).



Translation of Chinese to English is as follows:

	Name	ReTime [min]	Peak	Area	Heigh	Area%
	↑	↑	↑	↑	↑	↑
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT22.603	22.603	1	28190180	651390	98.3341
2	RT25.186	25.186	2	477573	11849	1.6659

7t. (1S,1'S)-1,1'-(ethane-1,2-diylbis(4,1-phenylene))bis(ethan-1-ol): (HPLC: Chiracel OB-H, detected at 254 nm, eluent: n-hexane/2-propanol = 96/4, flow rate = 1.0 mL/min, 25 °C).

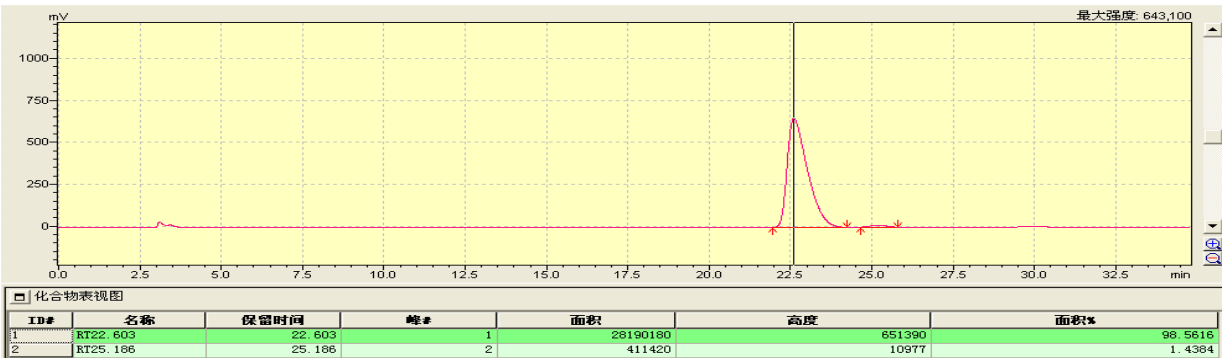


Translation of Chinese to English is as follows:

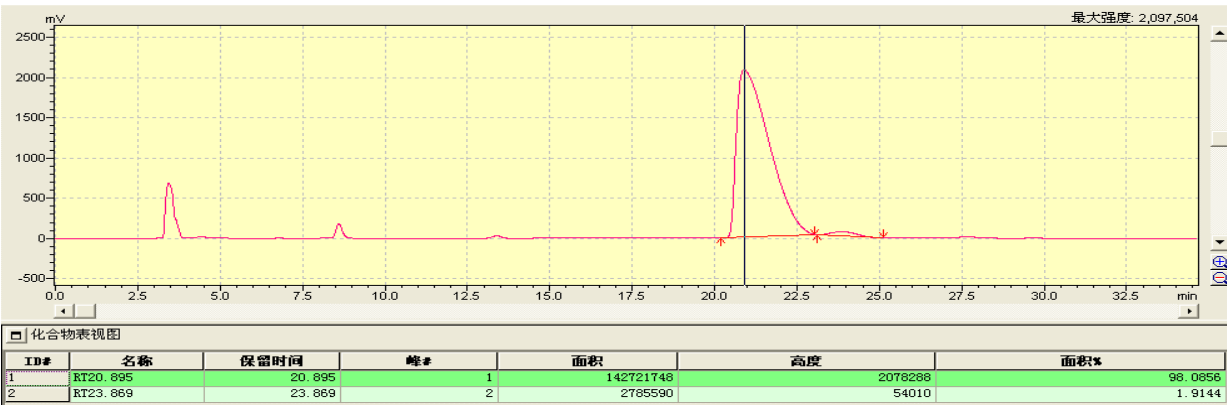
	Name	ReTime [min]	Peak	Area	Heigh	Area%
	↑	↑	↑	↑	↑	↑
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT22.603	22.603	1	28190180	651390	98.3341
2	RT25.186	25.186	2	477573	11849	1.6659

Figure 4. Reusability of catalyst 5 for the enantioselective cascade reductions of conjugated alkynones.

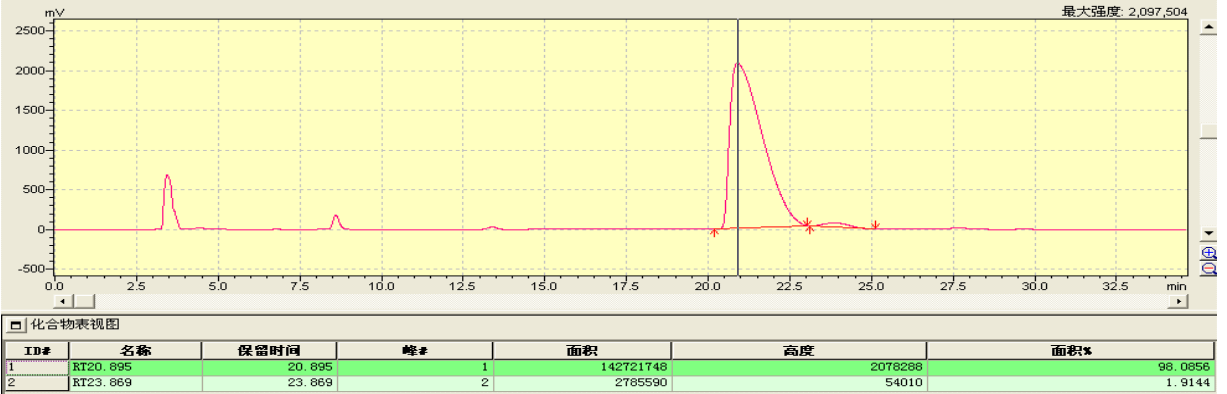
Recycle 1



Recycle 2



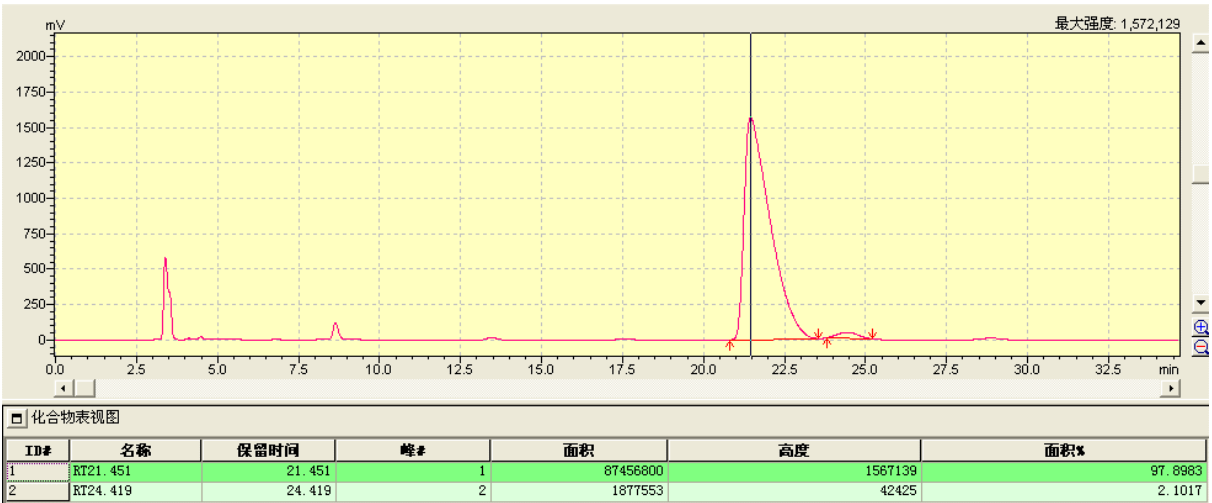
Recycle 3



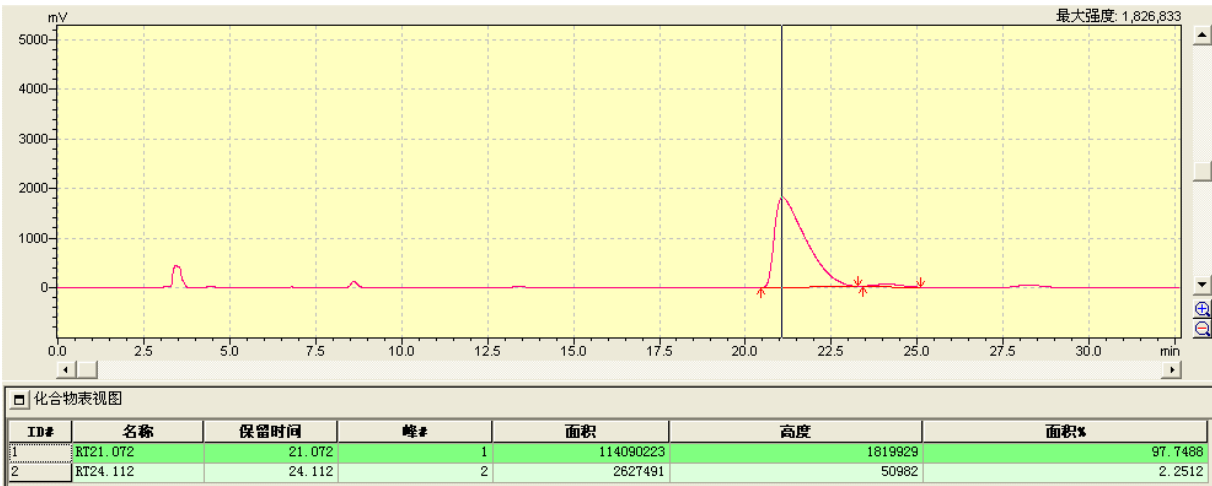
Translation of Chinese to English is as follows:

Name		ReTime [min]	Peak	Area	Heigh	Area%
		↑	↑	↑	↑	↑
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT22.603	22.603	1	28190180	651390	98.3341
2	RT25.186	25.186	2	477573	11849	1.6659

Recycle 4



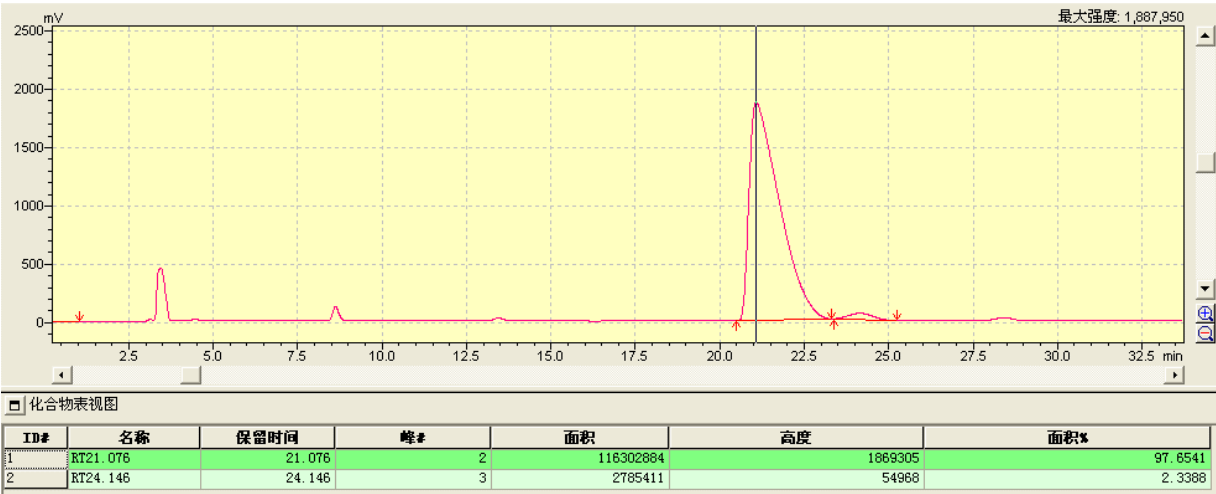
Recycle 5



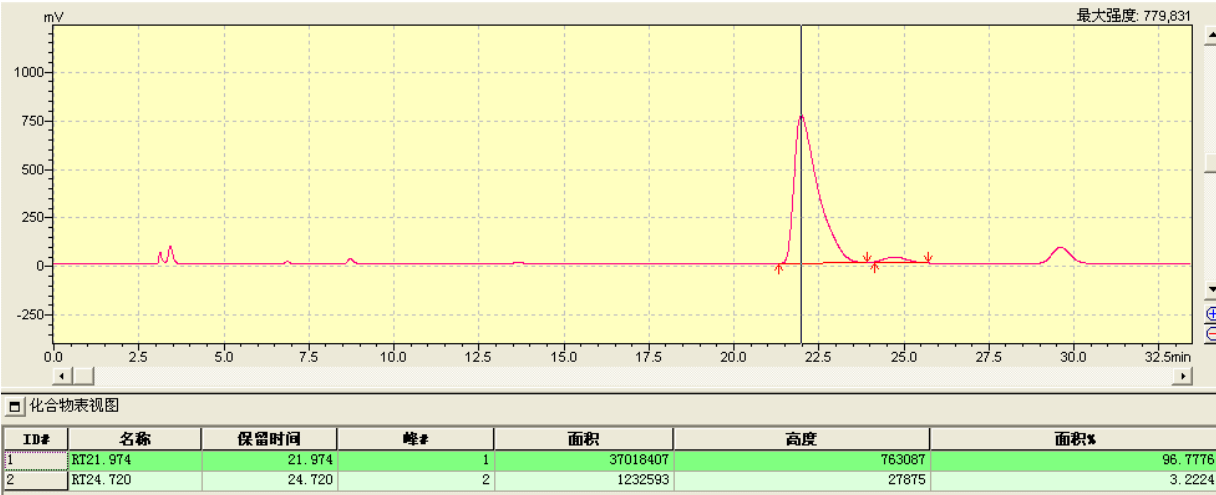
Translation of Chinese to English is as follows:

		ReTime				
		Name	[min]	Peak	Area	Heigh
				Area%		
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT22.603	22.603	1	28190180	651390	98.3341
2	RT25.186	25.186	2	477573	11849	1.6659

Recycle 6



Recycle 7



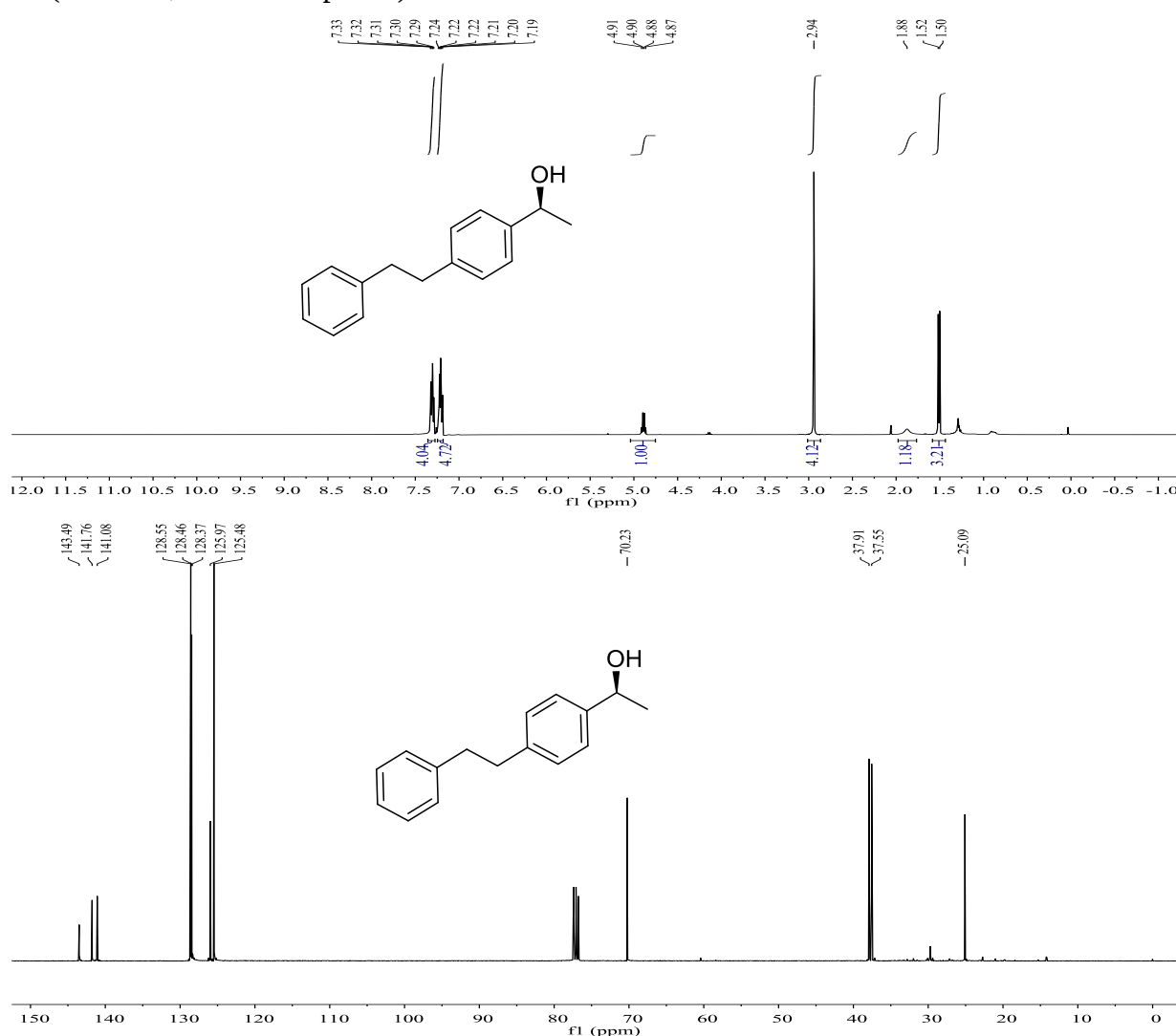
Translation of Chinese to English is as follows:

	Name	ReTime [min]	Peak	Area	Heigh	Area%
	↑	↑	↑	↑	↑	↑
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT22. 603	22. 603	1	28190180	651390	98. 3341
2	RT25. 186	25. 186	2	477573	11849	1. 6659

Figure 5. The characterizations of chiral products (**Table 1 in manuscript**).

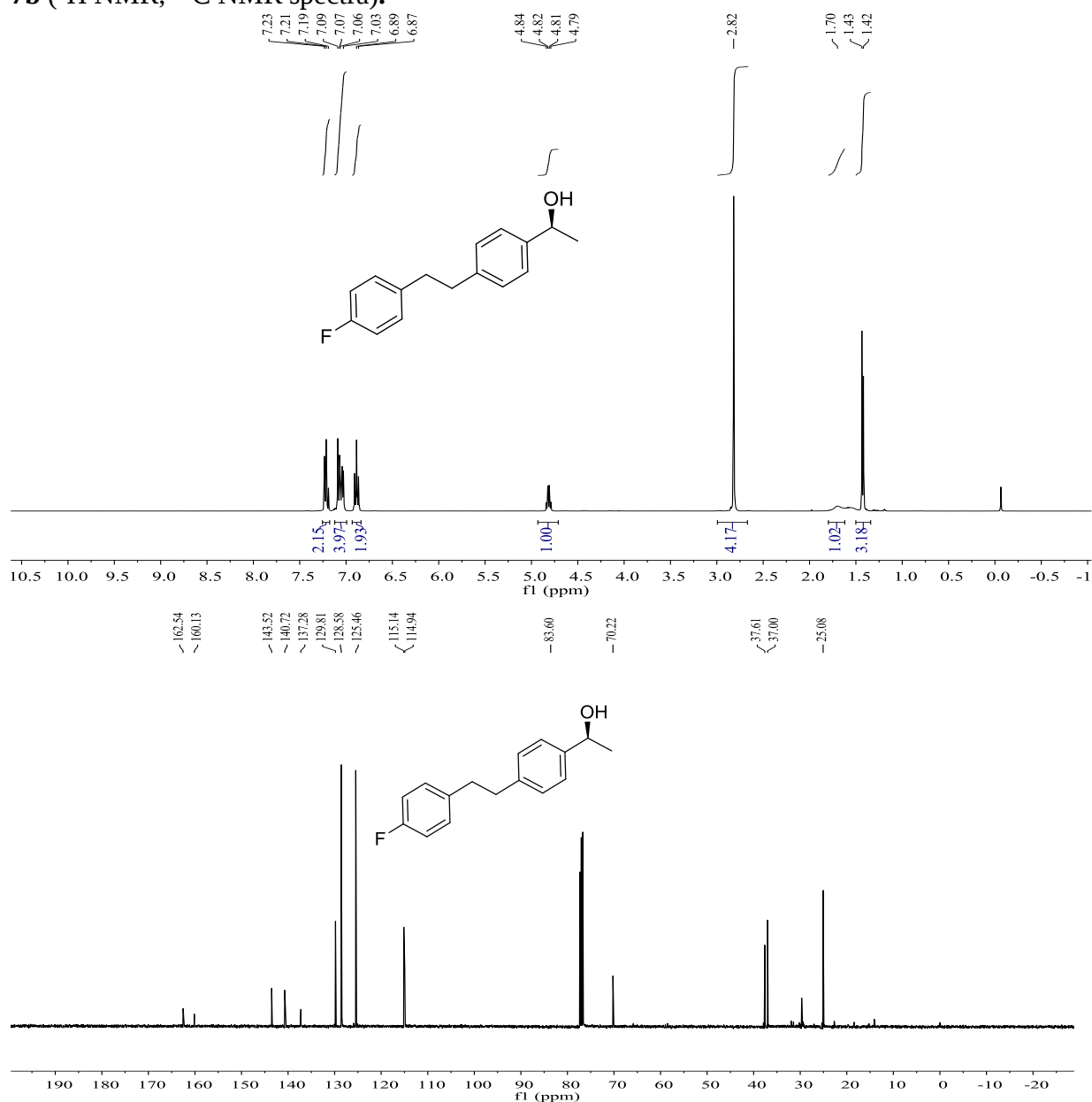
7a. (S)-1-(4-phenethylphenyl)ethan-1-ol. White solid, 99% yield, 97% *ee*. $[\alpha]_D^{25} = -25.891$ (c 0.216, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.31 (dd, *J* = 7.6, 5.7 Hz, 4H), 7.21 (dt, *J* = 8.2, 5.5 Hz, 5H), 4.89 (q, *J* = 6.4 Hz, 1H), 2.94 (s, 4H), 1.88 (brs, 1H), 1.51 (d, *J* = 6.6 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.5, 141.8, 141.0, 128.6, 128.5, 128.4, 126.0, 125.5, 70.2, 37.9, 37.6, 25.1. HRMS (ESI): *m/z* [M+Na]⁺ calculated for C₁₆H₁₈ONa⁺: 249.1250; found: 249.1251. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/*i*-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7a (¹H NMR, ¹³C NMR spectra).



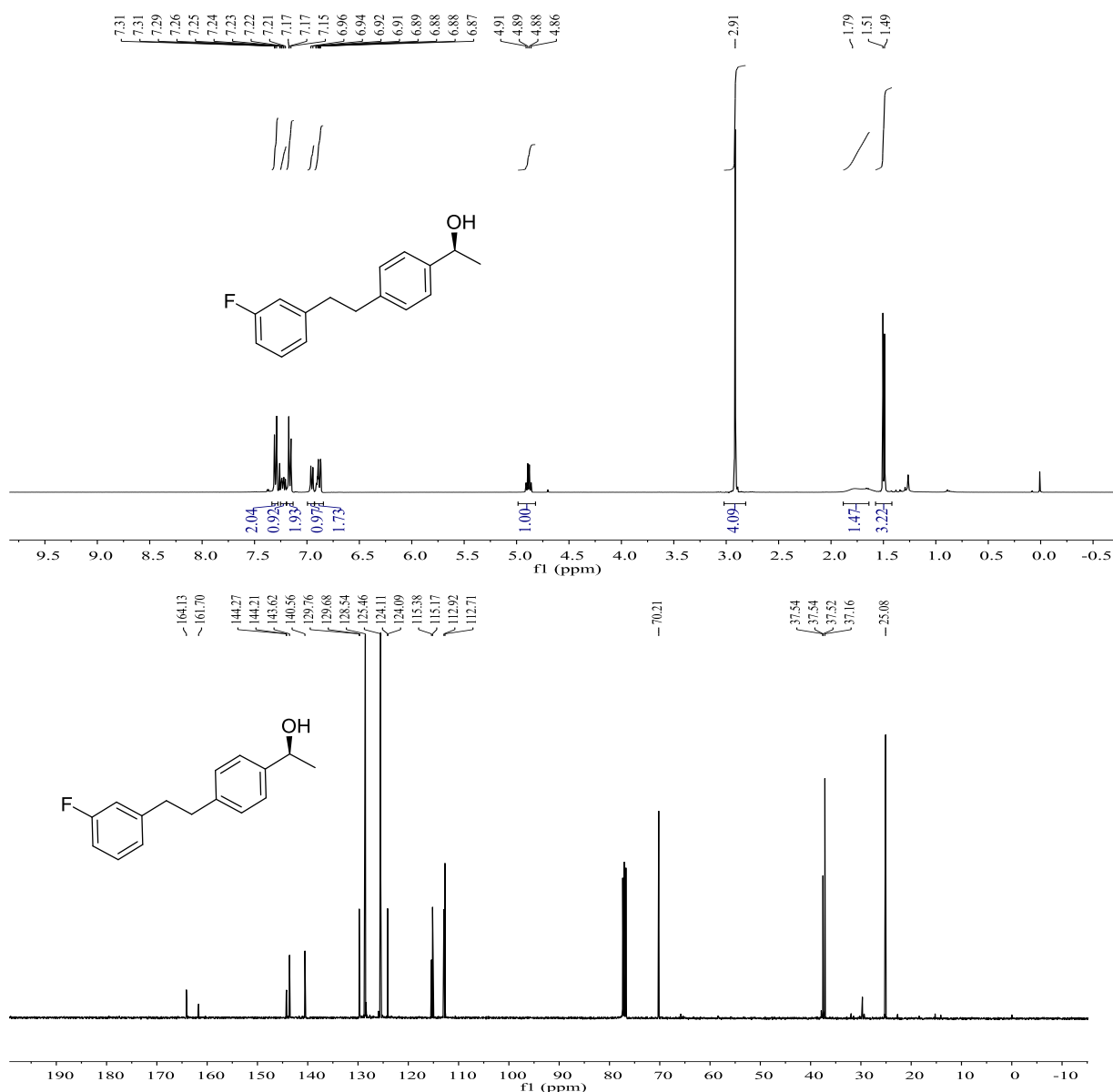
7b. (S)-1-(4-(4-fluorophenethyl)phenyl)ethan-1-ol. White solid, 93% yield, 95% *ee*. $[\alpha]_D^{25} = -29.648$ (c 0.256, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.21 (t, $J = 8.8$ Hz, 2H), 7.12 – 6.99 (m, 4H), 6.88 (d, $J = 8.6$ Hz, 2H), 4.82 (q, $J = 6.5$ Hz, 1H), 2.82 (s, 4H), 1.70 (brs, 1H), 1.43 (d, $J = 6.5$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 161.3 (d, $J = 243$ Hz), 143.5, 140.7, 137.3, 129.8, 128.6, 125.5, 114.9, 70.2, 37.6, 37.0, 25.1. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{17}\text{FONa}^+$: 267.1156; found: 267.1156. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/*i*-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7b (^1H NMR, ^{13}C NMR spectra).



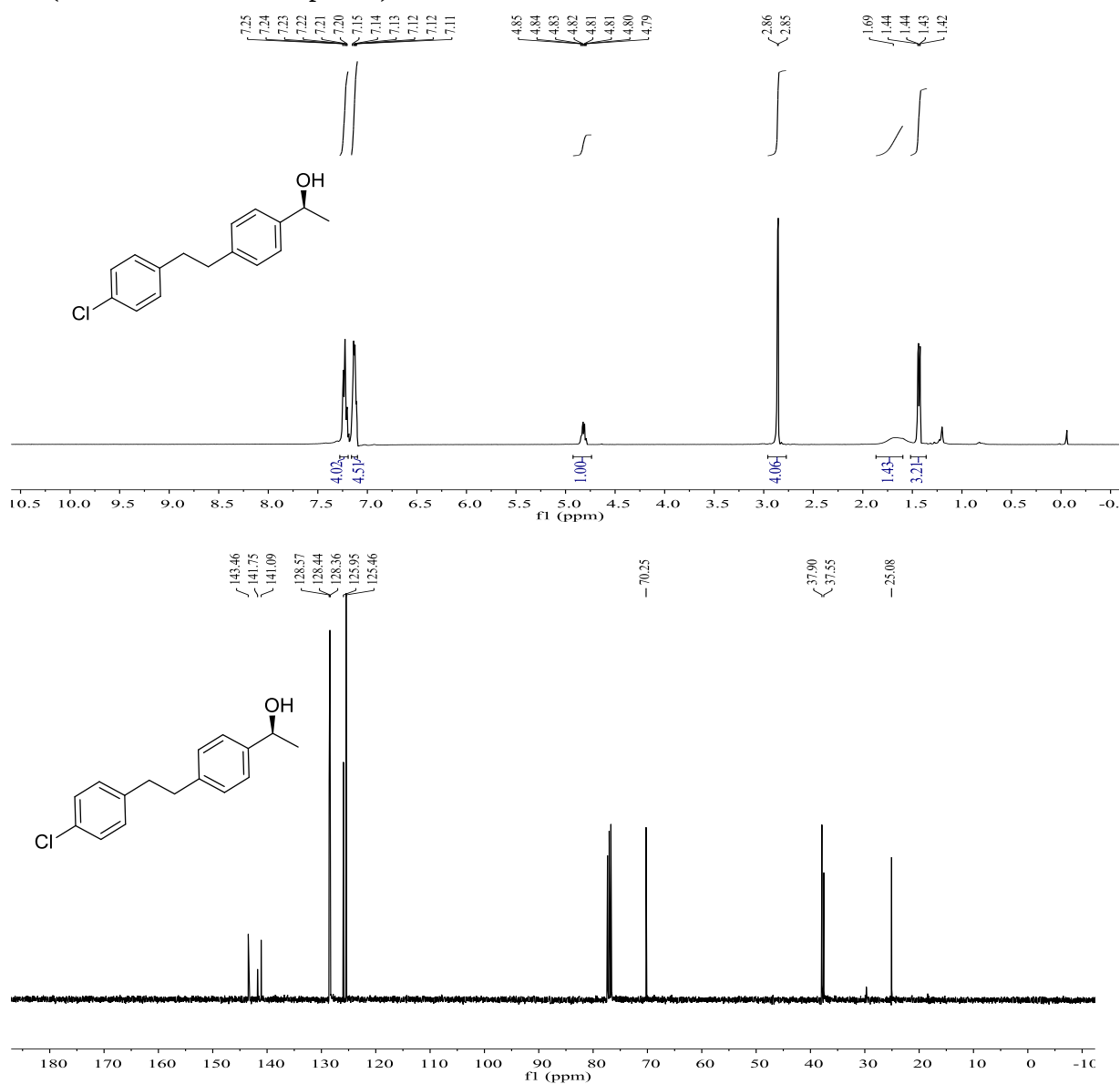
7c. (S)-1-(4-(3-fluorophenethyl)phenyl)ethan-1-ol. Yellow liquid, 92% yield, 94% ee. $[\alpha]_D^{25} = -28.785$ (c 0.378, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, $J = 8.2$ Hz, 2H), 7.25 – 7.20 (m, 1H), 7.16 (d, $J = 8.2$ Hz, 2H), 6.94 (d, $J = 7.7$ Hz, 1H), 6.93 – 6.87f (m, 2H), 4.89 (q, $J = 6.5$ Hz, 1H), 2.91 (s, 4H), 1.79 (brs, 1H), 1.50 (d, $J = 6.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 162.9 (d, $J = 245$ Hz), 144.2 (d, $J = 6.5$ Hz), 143.6, 140.6, 129.8 (d, $J = 8.7$ Hz), 128.5, 125.5, 124.1 (d, $J = 2.3$ Hz), 115.3 (d, $J = 20.9$ Hz), 112.8 (d, $J = 21.5$ Hz), 70.2, 37.6, 37.5, 37.2, 25.1. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{17}\text{FONa}^+$: 267.1156; found: 267.1158. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/*i*-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7c (^1H NMR, ^{13}C NMR spectra). (S)-1-(4-(3-fluorophenethyl)phenyl)ethan-1-ol.



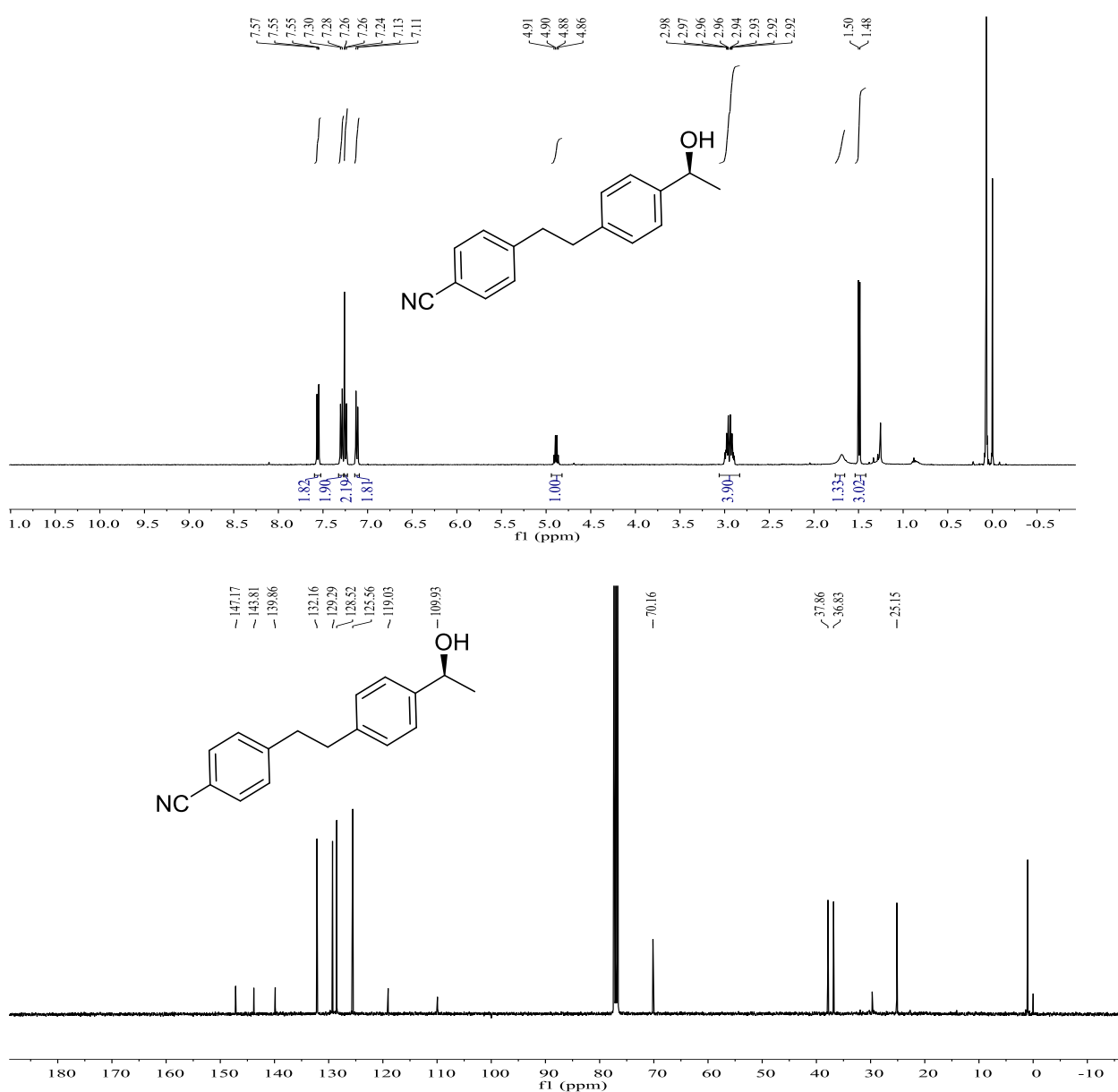
7d. (S)-1-(4-(4-chlorophenethyl)phenyl)ethan-1-ol. White solid, 94% yield, 95% ee. $[\alpha]_D^{25} = -33.289$ (c 0.216, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.20 (m, 4H), 7.16 – 7.10 (m, 4H), 4.82 (qd, $J = 6.4, 2.2$ Hz, 1H), 2.86– 2.85 (d, $J = 2.5$ Hz, 4H), 1.69 (brs, 1H), 1.43 (dd, $J = 6.7, 2.4$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 143.5, 141.8, 141.1, 128.6, 128.5, 128.4, 126.0, 125.5, 70.3, 37.9, 37.6, 25.1. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{17}\text{ClONa}^+$: 283.0860; found: 283.0861. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/*i*-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7d (^1H NMR, ^{13}C NMR spectra).



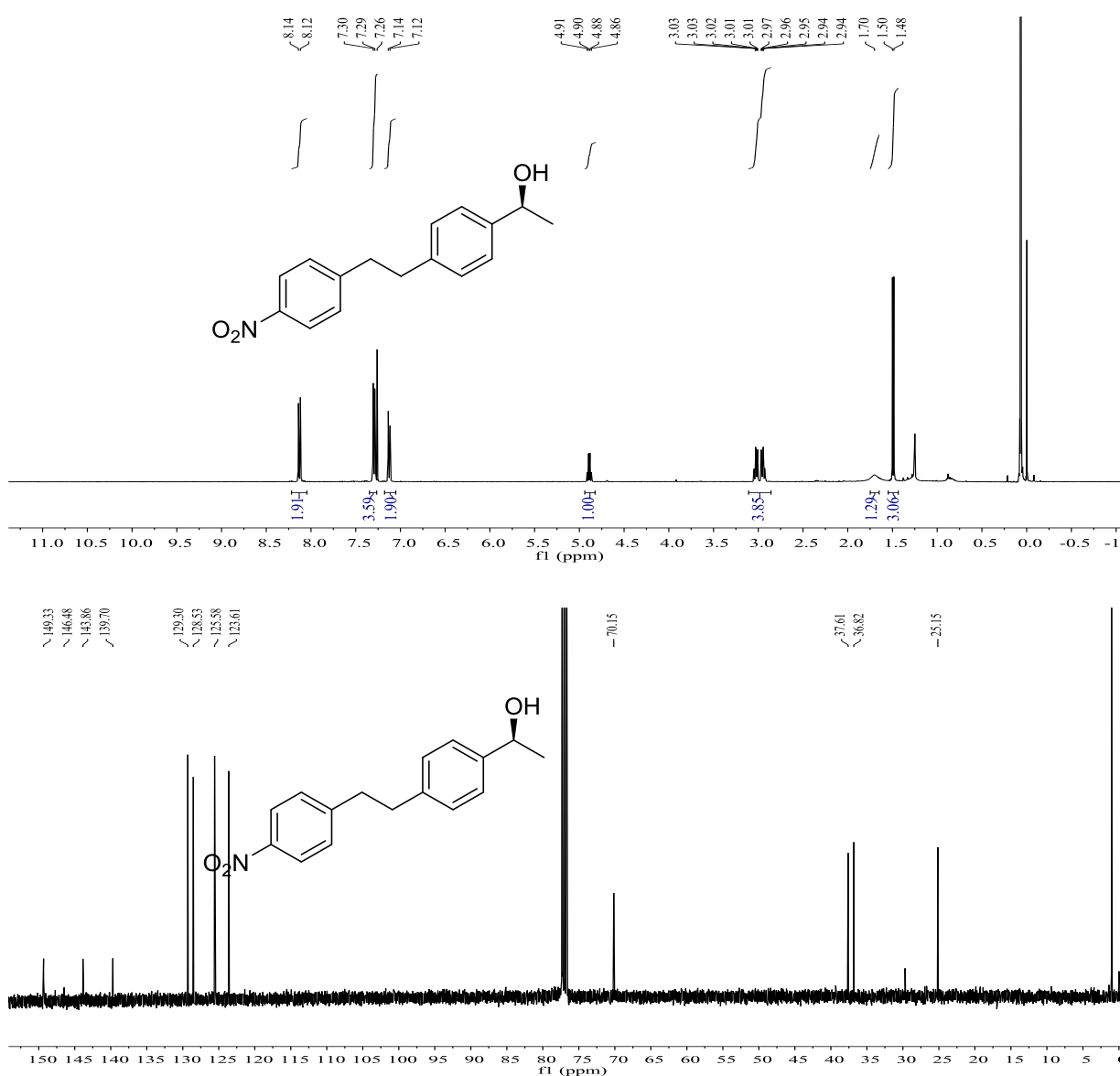
7e. (S)-4-(4-(1-hydroxyethyl)phenethyl)benzonitrile. White solid, 91% yield, 94% ee. $[\alpha]_D^{25} = -7.467$ (c 0.214, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, $J = 8.2$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.12 (d, $J = 8.1$ Hz, 2H), 4.89 (q, $J = 6.5$ Hz, 1H), 3.06 – 2.83 (m, 4H), 1.69 (brs, 1H), 1.49 (d, $J = 6.5$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 147.2, 143.8, 139.9, 132.2, 129.3, 128.5, 125.6, 119.0, 109.0, 70.2, 37.9, 36.8, 25.2. HRMS (ESI): m/z $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{17}\text{H}_{21}\text{N}_2\text{O}^+$: 269.1650; found: 269.1648. HPLC (Chiralpak OD-H, detector: 215 nm, elute: Hexane/*i*-PrOH = 95/5, flow rate: 1.0 mL/min, 25 °C).

7e (^1H NMR, ^{13}C NMR spectra).



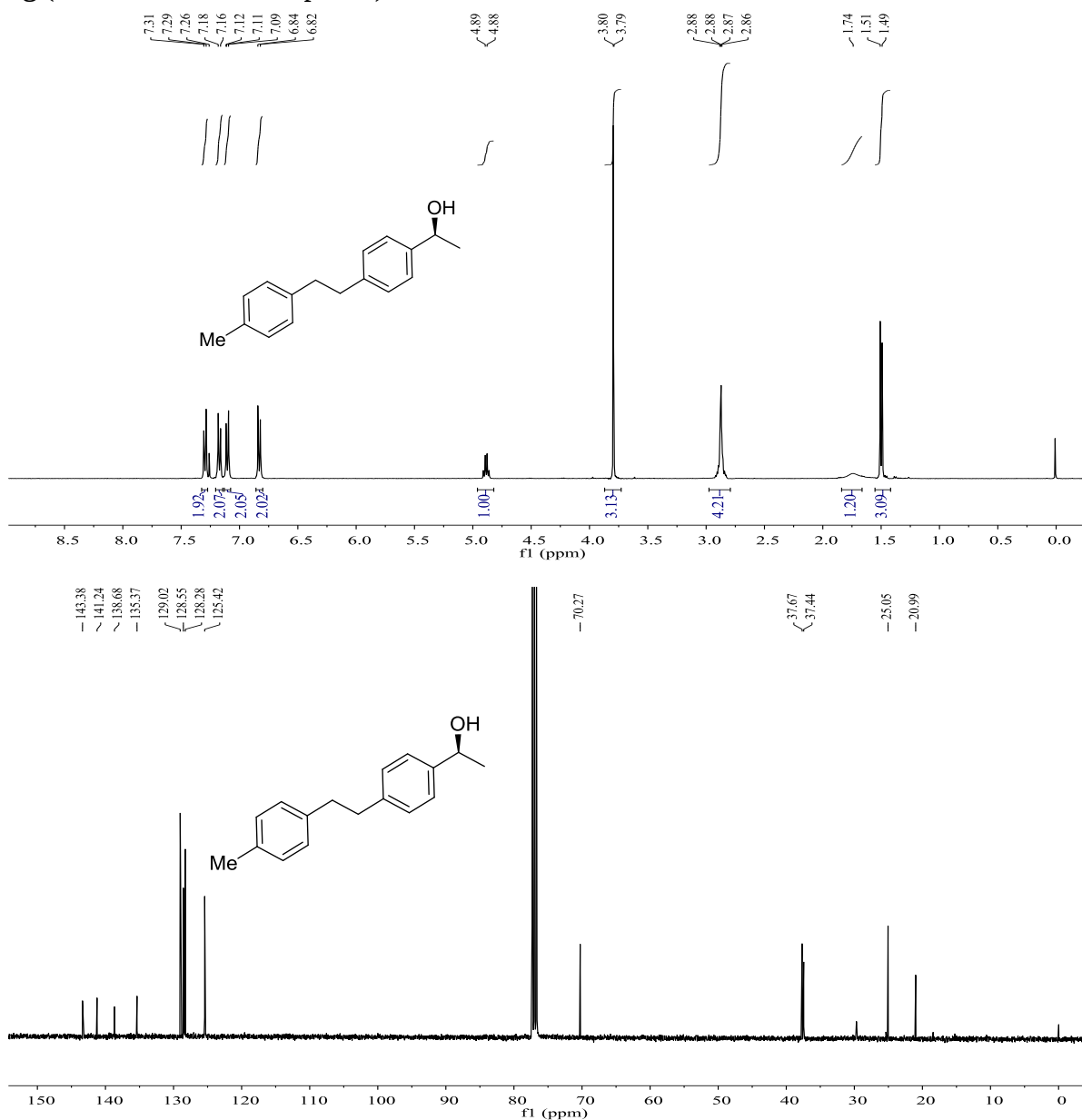
7f. (S)-1-(4-(4-nitrophenethyl)phenyl)ethan-1-ol. Brown solid, 83% yield, 99% ee. $[\alpha]_D^{25} = -4.781$ (c 0.376, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 4H), 7.13 (d, *J* = 8.1 Hz, 2H), 4.89 (q, *J* = 6.5 Hz, 1H), 3.03 – 2.94 (m, 4H), 1.70 (s, 1H), 1.49 (d, *J* = 6.5 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 149.3, 146.5, 143.9, 139.7, 129.3, 128.5, 125.6, 123.6, 70.2, 37.6, 36.8, 25.2. HRMS (ESI): *m/z* [M+NH₄]⁺ calculated for C₁₆H₂₁N₂O₃⁺: 289.1548; found: 289.1547. HPLC (Chiralpak OD-H, detector: 254 nm, elute: Hexane/*i*-PrOH = 96/4, flow rate: 1.0 mL/min, 25 °C).

7f (¹H NMR, ¹³C NMR spectra).



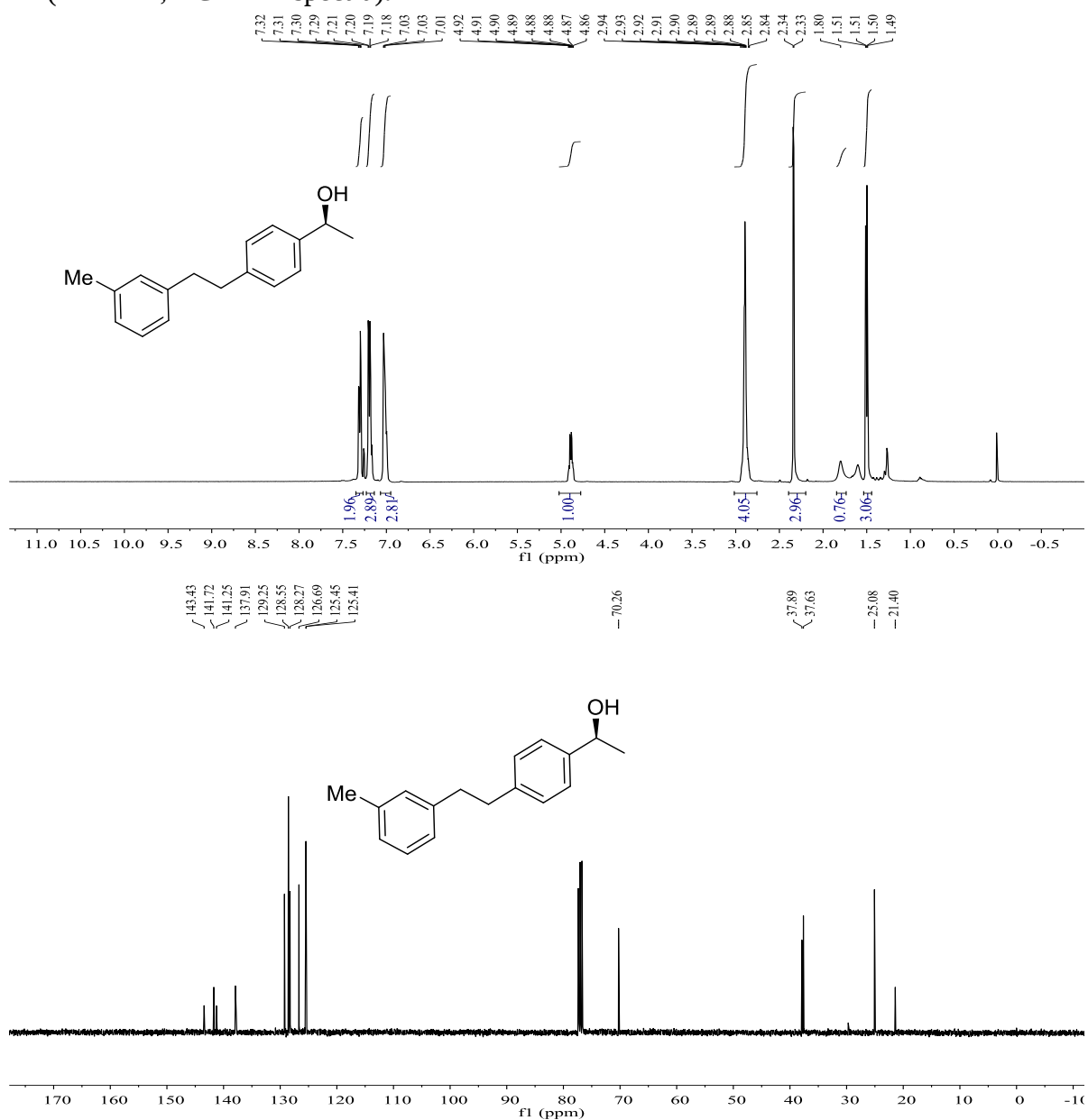
7g. (S)-1-(4-(4-methylphenethyl)phenyl)ethan-1-ol. White solid, 95% yield, 95% ee. $[\alpha]_D^{25} = -20.693$ (c 0.222, CHCl_3). ^1H NMR (400 MHz, CHCl_3) δ 7.30 (dc, $J = 7.9$ Hz, 2H), 7.17 (d, $J = 7.9$ Hz, 2H), 7.10 (d, $J = 8.5$ Hz, 2H), 6.83 (d, $J = 8.5$ Hz, 2H), 4.89 (d, $J = 6.3$ Hz, 1H), 3.80 (s, 3H), 2.87 (q, $J = 2.9$ Hz, 4H), 1.74 (brs, 1H), 1.50 (d, $J = 6.7$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 143.4, 141.2, 138.7, 135.4, 129.0, 128.6, 128.3, 125.4, 70.3, 37.6, 37.4, 25.1, 21.0. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{20}\text{ONa}^+$: 263.1406; found: 263.1409. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/*i*-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7g (^1H NMR, ^{13}C NMR spectra).



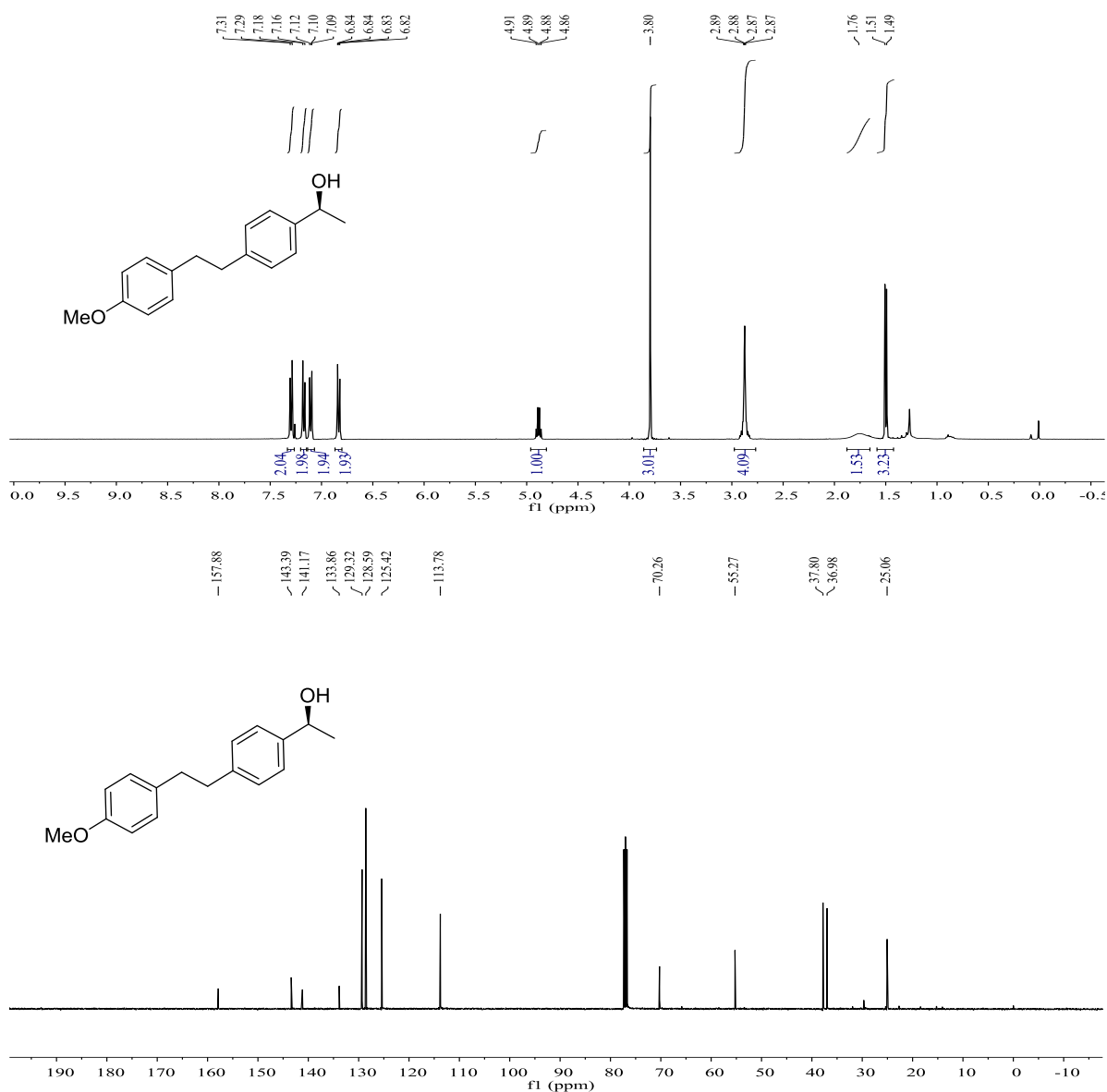
7h. (S)-1-(4-(3-methylphenethyl)phenyl)ethan-1-ol. White solid, 94% yield, 95% ee. $[\alpha]_D^{25} = -37.333$ (c 0.214, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.30 (dd, $J = 8.3, 2.9$ Hz, 2H), 7.20 (dd, $J = 8.1, 2.8$ Hz, 3H), 7.07 – 6.95 (m, 3H), 4.89 (qd, $J = 6.5, 2.8$ Hz, 1H), 2.90 (h, $J = 3.4, 2.5$ Hz, 4H), 2.34 (d, $J = 3.1$ Hz, 3H), 1.80 (brs, 1H), 1.53 – 1.44 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 143.4, 141.7, 141.3, 137.9, 129.3, 128.6, 128.3, 126.7, 125.5, 125.4, 70.3, 37.9, 37.6, 25.1, 21.4. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{20}\text{ONa}^+$: 263.1406; found: 263.1407. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/*i*-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7h (^1H NMR, ^{13}C NMR spectra).



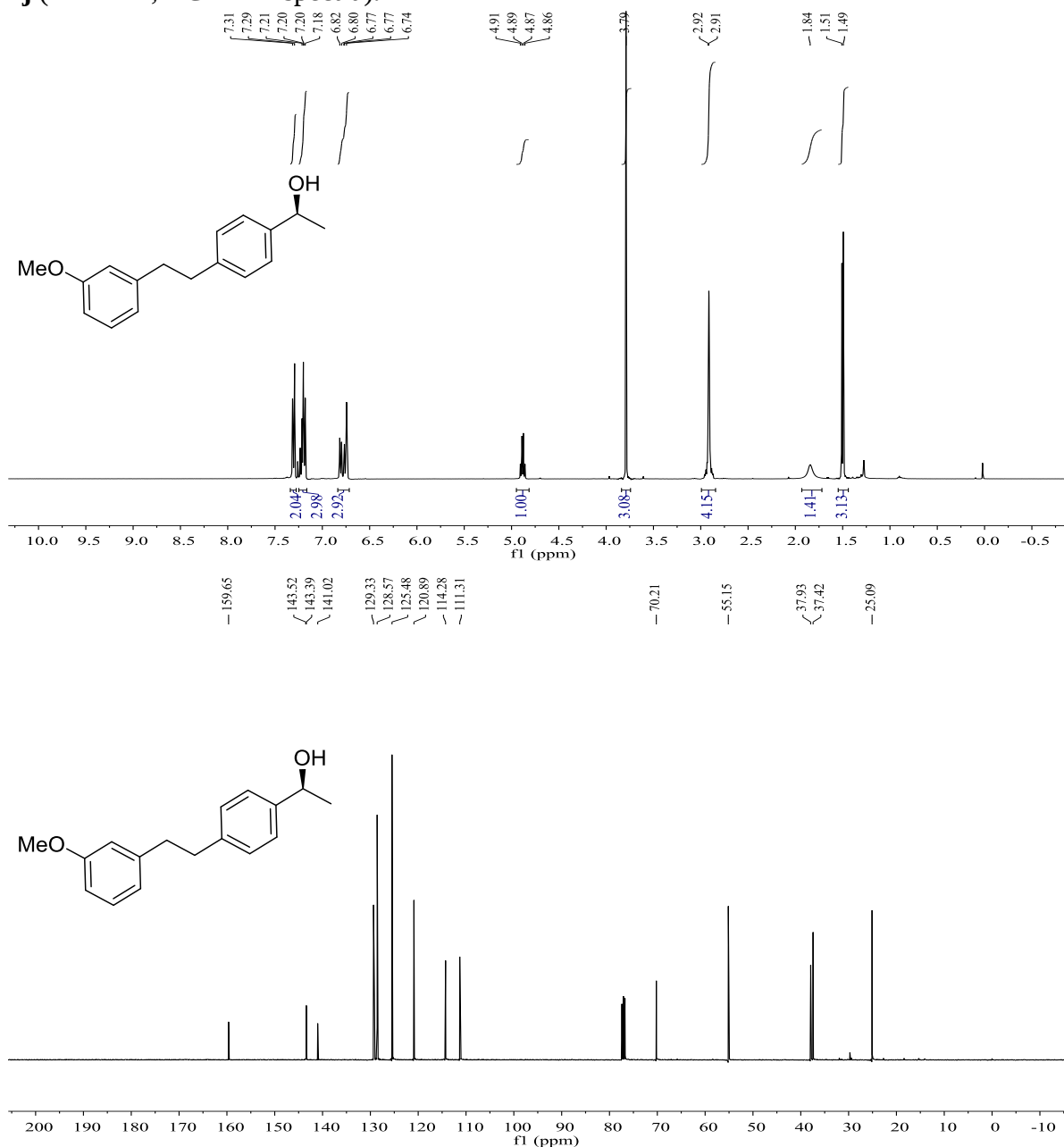
7i. (S)-1-(4-(4-methoxyphenethyl)phenyl)ethan-1-ol. White solid, 95% yield, 94% ee. $[\alpha]_D^{25} = -23.941$ (c 0.292, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, $J = 7.9$ Hz, 2H), 7.17 (d, $J = 7.9$ Hz, 2H), 7.11 (d, $J = 8.3$ Hz, 2H), 6.83 (d, $J = 8.4$ Hz, 2H), 4.88 (q, $J = 6.4$ Hz, 1H), 3.80 (s, 3H), 2.88 (q, $J = 3.0$ Hz, 4H), 1.76 (brs, 1H), 1.50 (d, $J = 6.6$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 157.9, 143.4, 141.2, 133.9, 129.3, 128.6, 125.4, 113.8, 70.3, 55.3, 37.8, 37.0, 25.1. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{Na}^+$: 279.1356; found: 279.1359. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/*i*-PrOH = 98/2, flow rate: 1.0 mL/min, 25 $^\circ\text{C}$).

7i (^1H NMR, ^{13}C NMR spectra).



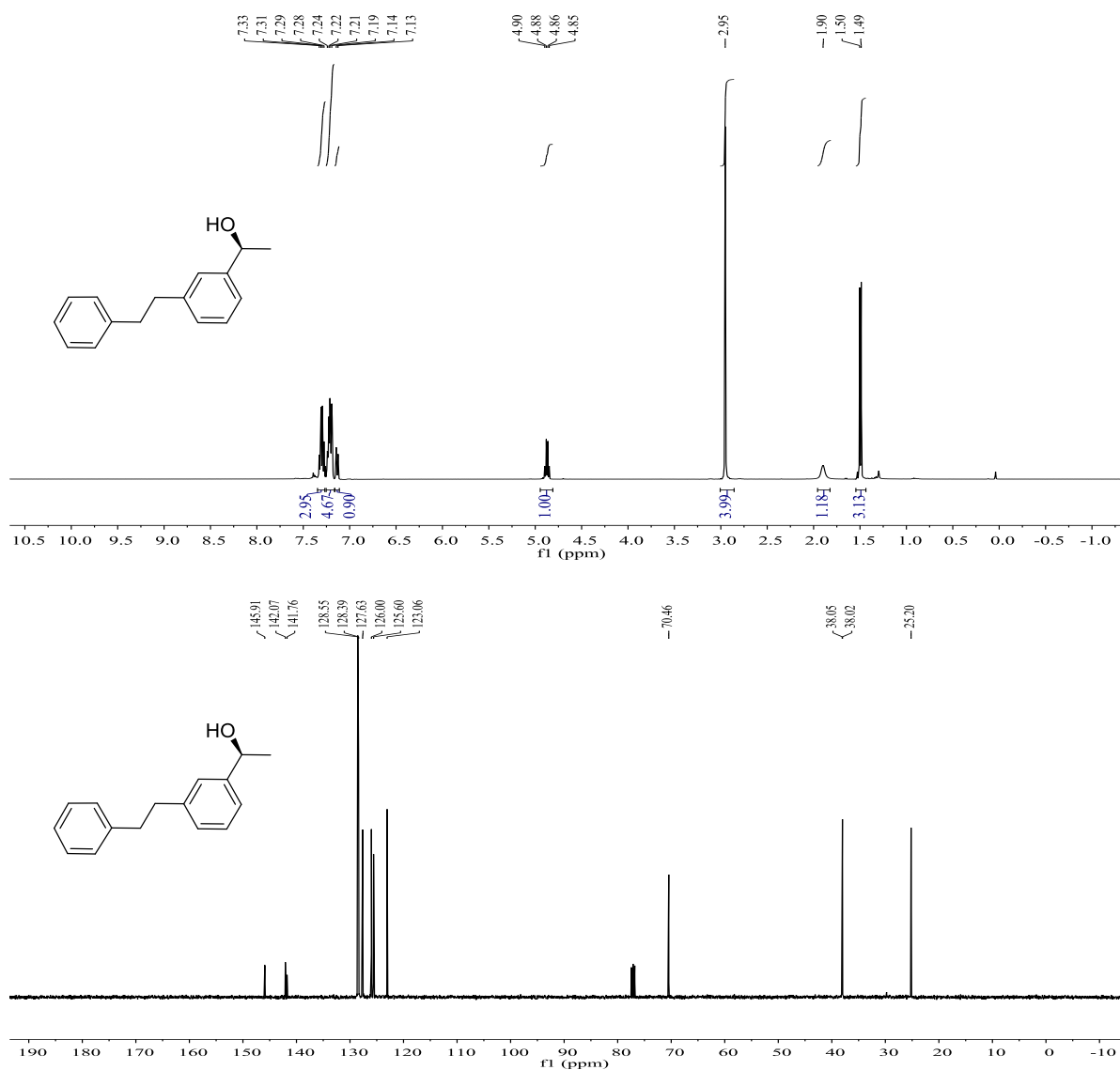
7j. (S)-1-(4-(3-methoxyphenethyl)phenyl)ethan-1-ol. White solid, 92% yield, 95% ee. $[\alpha]_D^{25} = -39.207$ (c 0.270, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, $J = 8.2$ Hz, 2H), 7.20 (dd, $J = 7.8, 5.8$ Hz, 3H), 6.84 – 6.72 (m, 3H), 4.88 (q, $J = 6.5$ Hz, 1H), 3.79 (s, 3H), 2.91 (s, 4H), 1.84 (brs, 1H), 1.50 (d, $J = 6.5$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 159.7, 143.5, 143.4, 141.0, 129.3, 128.6, 125.5, 120.9, 114.28, 111.3, 70.2, 55.2, 37.9, 37.4, 25.1. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{Na}^+$: 279.1356; found: 279.1361. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/*i*-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7j (^1H NMR, ^{13}C NMR spectra).



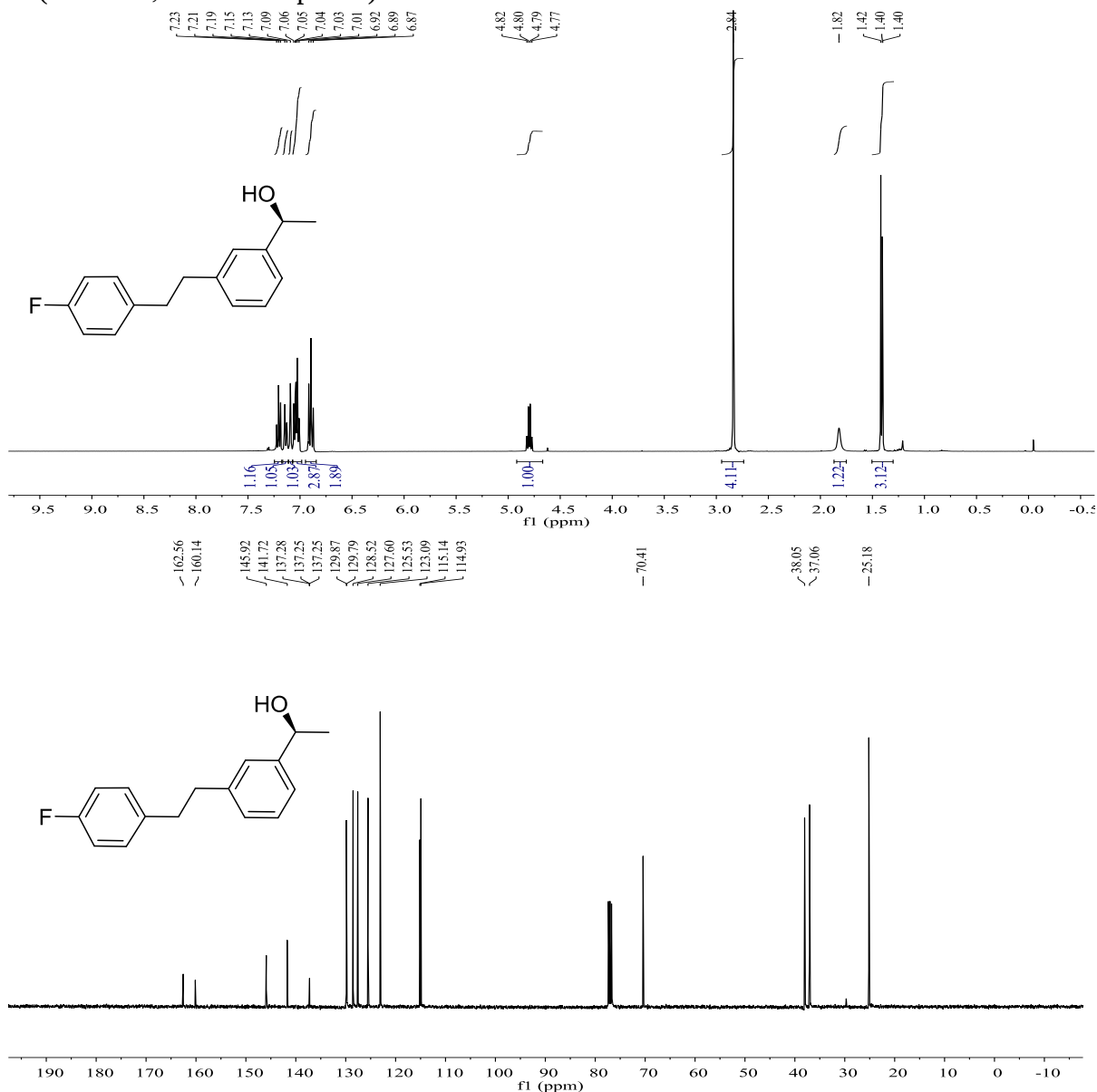
7k. (S)-1-(3-phenethylphenyl)ethan-1-ol. Yellow liquid, 93% yield, 95% ee. $[\alpha]_{\text{D}}^{25} = -21.766$ (c 0.468, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.30 (q, $J = 7.3$ Hz, 3H), 7.22 (dd, $J = 11.5, 7.5$ Hz, 5H), 7.13 (d, $J = 7.5$ Hz, 1H), 4.87 (q, $J = 6.5$ Hz, 1H), 2.95 (s, 4H), 1.90 (s, 1H), 1.50 (d, $J = 6.5$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.9, 142.1, 141.8, 128.6, 128.4, 127.6, 126.0, 125.6, 123.1, 70.5, 38.1, 38.0, 25.2. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{18}\text{ONa}^+$: 249.1250; found: 249.1252. HPLC (Chiralpak OJ-H, detector: 254 nm, elute: Hexane/*i*-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7k (^1H NMR, ^{13}C NMR spectra).



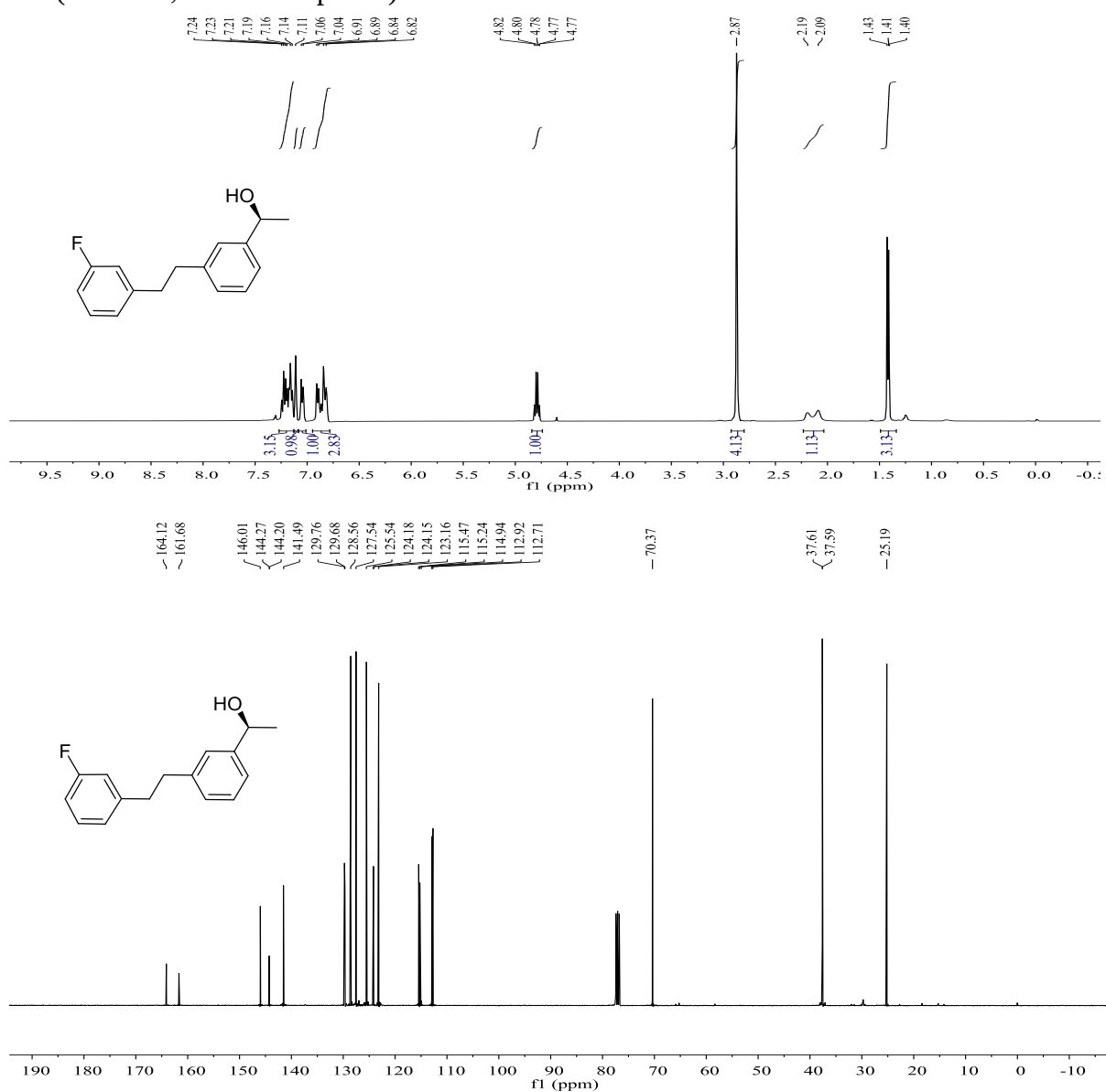
7l. (S)-1-(3-(4-fluorophenethyl)phenyl)ethan-1-ol. Yellow liquid, 91% yield, 94% ee. $[\alpha]_D^{25} = -33.116$ (c 0.386, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.21 (t, $J = 7.5$ Hz, 1H), 7.14 (d, $J = 7.6$ Hz, 1H), 7.09 (s, 1H), 7.07 – 6.99 (m, 3H), 6.89 (t, $J = 8.7$ Hz, 2H), 4.80 (q, $J = 6.4$ Hz, 1H), 2.84 (s, 4H), 1.82 (brs, 1H), 1.41 (d, $J = 6.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 161.4 (d, $J = 245$ Hz), 145.9, 141.7, 137.3 (d, $J = 3.2$ Hz), 129.8 (d, $J = 7.4$ Hz), 128.5, 127.6, 125.5, 123.1, 115.0 (d, $J = 21.5$ Hz), 70.4, 38.1, 37.1, 25.2. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{17}\text{FONa}^+$: 267.1156; found: 267.1158. HPLC (Chiralpak OJ-H, detector: 254 nm, elute: Hexane/*i*-PrOH = 97/3, flow rate: 1.0 mL/min, 25 °C).

7l (^1H NMR, ^{13}C NMR spectra).



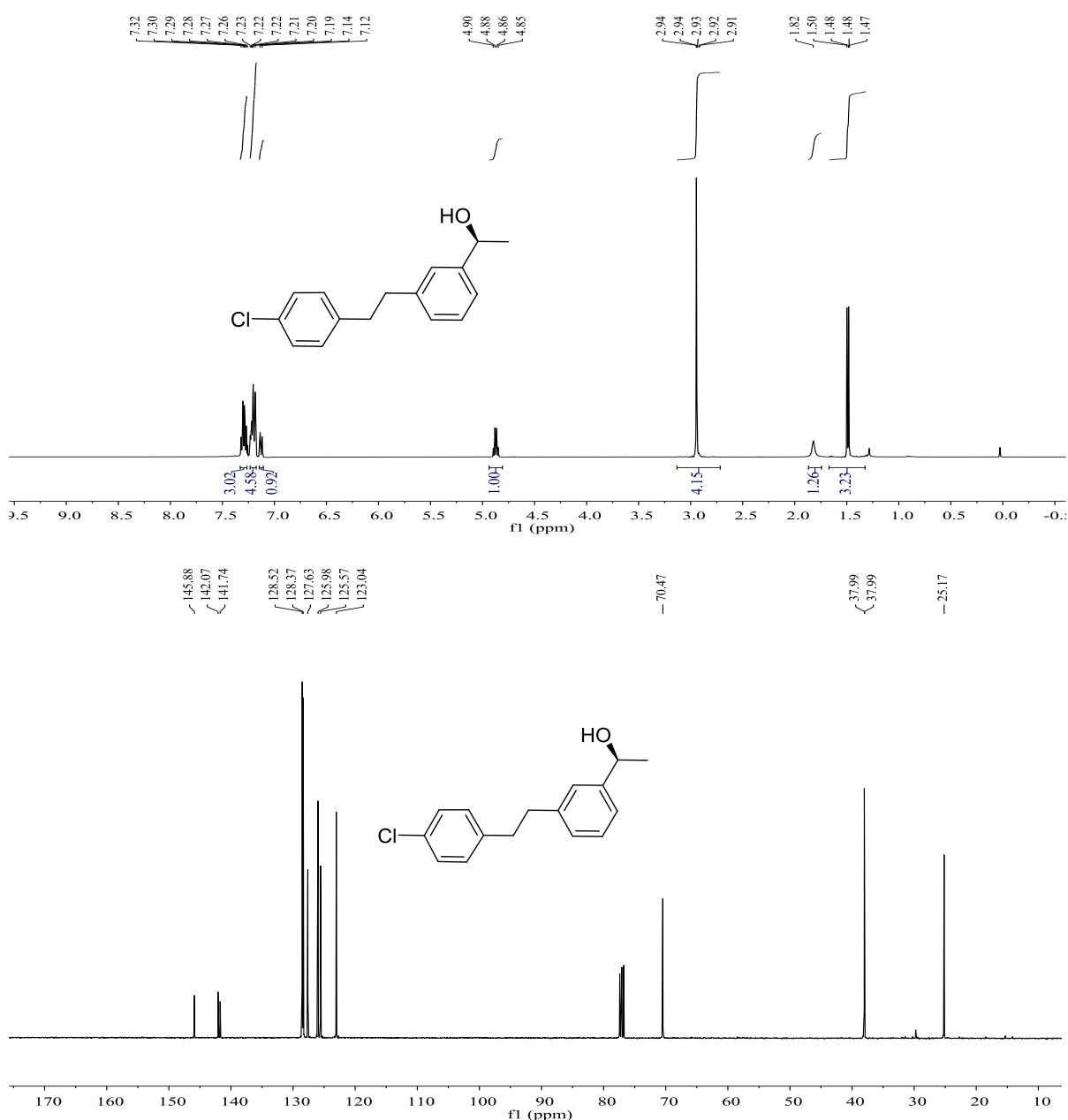
7m. (S)-1-(3-(3-fluorophenethyl)phenyl)ethan-1-ol. Yellow liquid, 90% yield, 94% ee. $[\alpha]_D^{25} = -22.323$ (c 0.340, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.27 – 7.13 (m, 3H), 7.11 (s, 1H), 7.05 (d, $J = 7.3$ Hz, 1H), 6.91 – 6.82 (m, 3H), 4.79 (q, $J = 6.4$ Hz, 1H), 2.87 (s, 4H), 2.19 – 2.09 (m, 1H), 1.42 (d, $J = 6.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.9 (d, $J = 245$ Hz), 146.1, 144.2 (d, $J = 7.2$ Hz), 141.5, 129.7 (d, $J = 8.4$ Hz), 128.6, 127.5, 125.4, 124.2 (d, $J = 2.7$ Hz), 123.2, 115.3 (d, $J = 21.1$ Hz), 112.8 (d, $J = 21.1$ Hz), 70.4, 37.6, 37.6, 25.2. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{17}\text{FONa}^+$: 267.1156; found: 267.1157. HPLC (Chiralpak OJ-H, detector: 254 nm, elute: Hexane/*i*-PrOH = 97/3, flow rate: 1.0 mL/min, 25 °C).

7m (^1H NMR, ^{13}C NMR spectra).



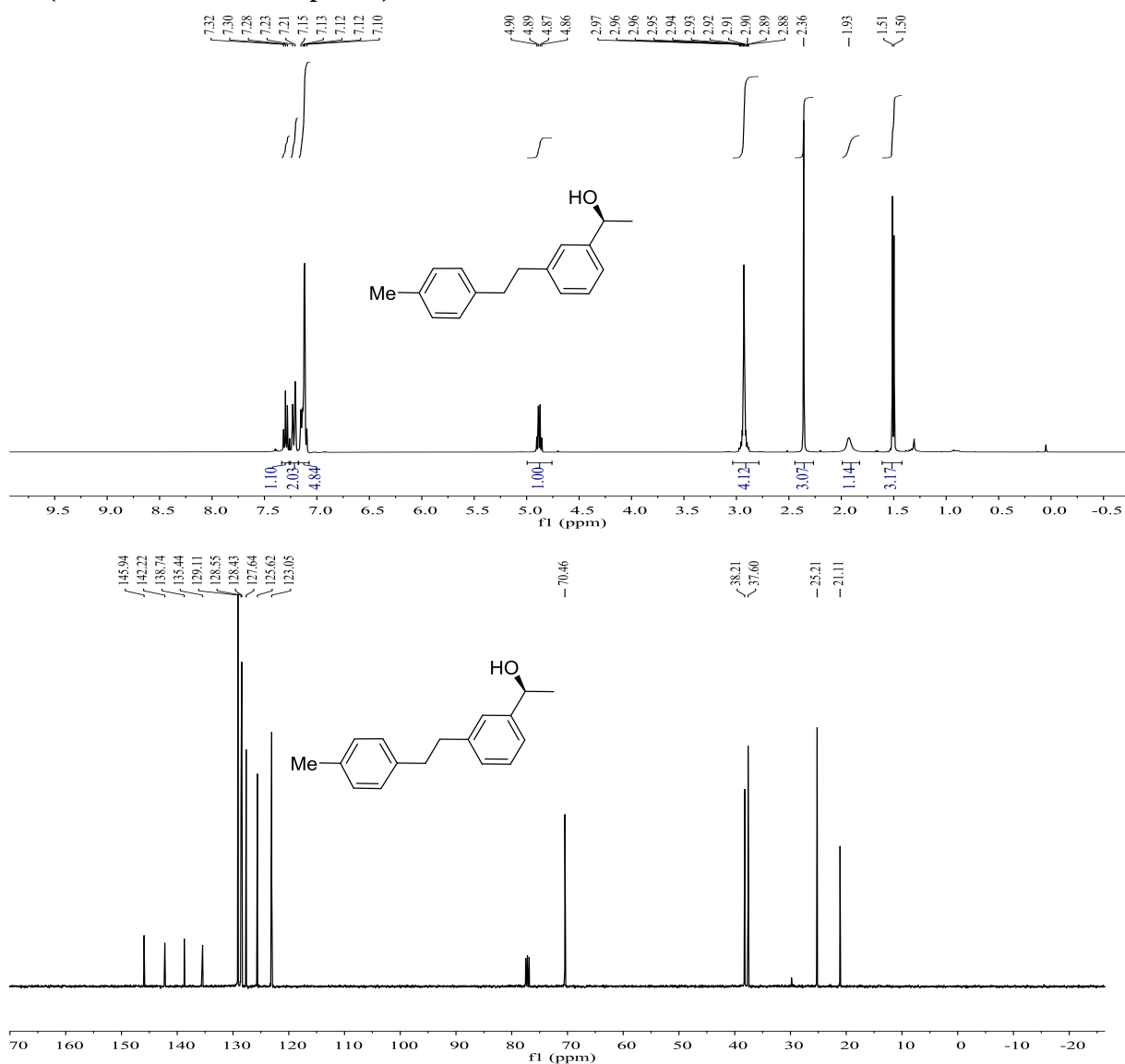
7n. (S)-1-(3-(4-chlorophenethyl)phenyl)ethan-1-ol. Yellow liquid, 91% yield, 93% ee. $[\alpha]_D^{25} = -23.839$ (c 0.310, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.26 (m, 3H), 7.21 (dt, $J = 8.3, 5.9$ Hz, 4H), 7.13 (d, $J = 7.4$ Hz, 1H), 4.87 (q, $J = 6.4$ Hz, 1H), 3.13 – 2.72 (m, 4H), 1.82 (brs, 1H), 1.49 (d, $J = 6.5$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.9, 142.1, 141.7, 128.5, 128.4, 127.6, 126.0, 125.6, 123.1, 70.5, 38.0, 37.9, 25.2. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{17}\text{ClONa}^+$: 283.0860; found: 283.0862. HPLC (Chiralpak OJ-H, detector: 254 nm, elute: Hexane/*i*-PrOH = 97/3, flow rate: 1.0 mL/min, 25 °C).

7n (^1H NMR, ^{13}C NMR spectra).



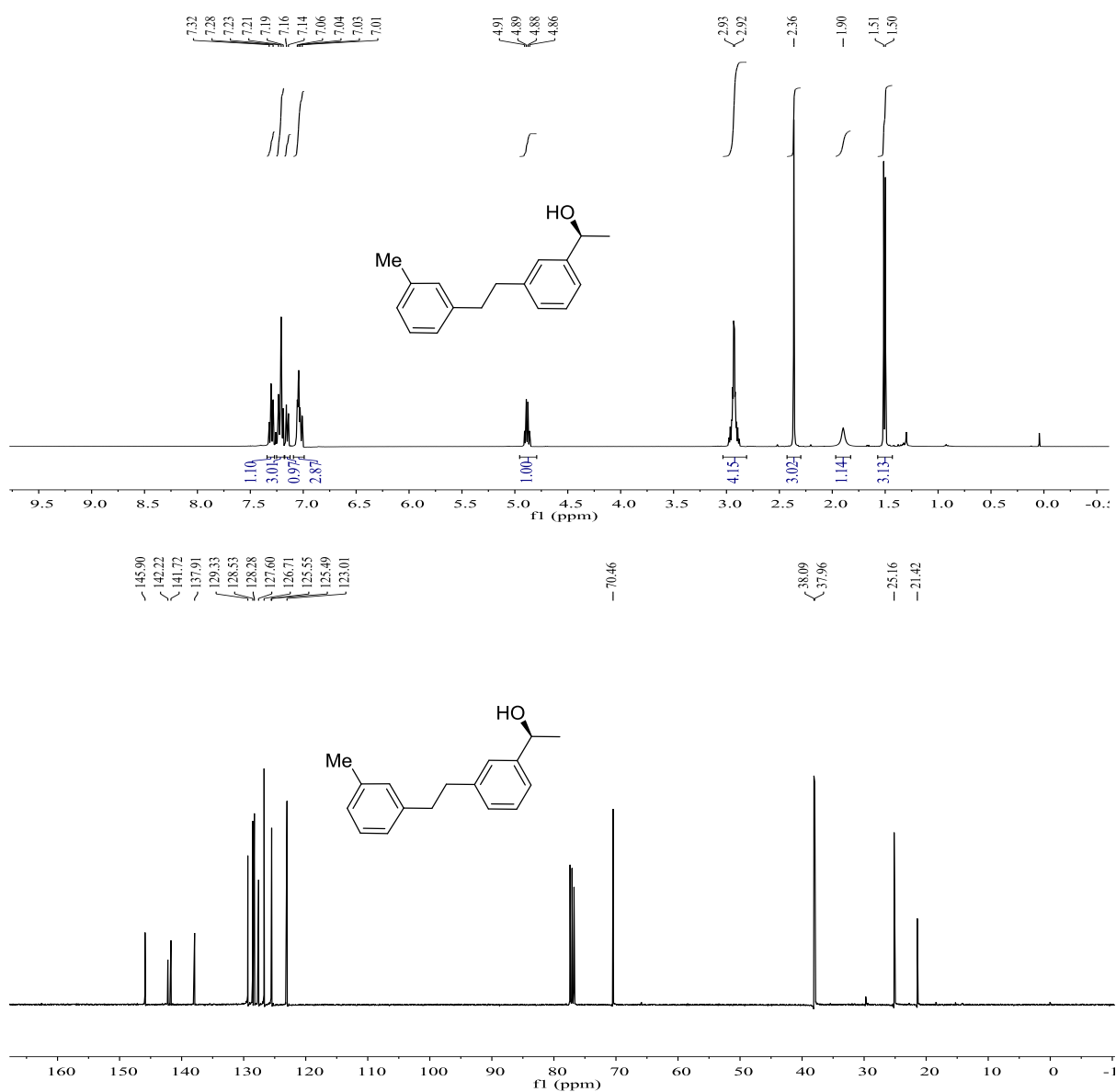
7o. (S)-1-(3-(4-methylphenethyl)phenyl)ethan-1-ol. Yellow liquid, 92% yield, 96% ee. $[\alpha]_D^{25} = -24.845$ (c 0.410, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.30 (t, $J = 7.5$ Hz, 1H), 7.22 (d, $J = 9.2$ Hz, 2H), 7.15 – 7.10 (m, 5H), 4.88 (q, $J = 6.4$ Hz, 1H), 2.97 – 2.88 (m, 4H), 2.36 (s, 3H), 1.93 (s, 1H), 1.50 (d, $J = 6.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.9, 142.2, 138.7, 135.4, 129.1, 128.6, 128.4, 127.6, 125.6, 123.1, 70.5, 38.2, 37.6, 25.2, 21.1. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{20}\text{ONa}^+$: 263.1406; found: 263.1414. HPLC (Chiralpak OJ-H, detector: 254 nm, elute: Hexane/*i*-PrOH = 97/3, flow rate: 1.0 mL/min, 25 °C).

7o (^1H NMR, ^{13}C NMR spectra).



7p. (S)-1-(3-(3-methylphenethyl)phenyl)ethan-1-ol. Yellow liquid, 92% yield, 95% ee. $[\alpha]_D^{25} = -22.688$ (c 0.493, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, $J = 14.9$ Hz, 1H), 7.25 – 7.18 (m, 3H), 7.15 (d, $J = 7.5$ Hz, 1H), 7.09 – 7.01 (m, 3H), 4.88 (q, $J = 6.6$ Hz, 1H), 2.93 (d, $J = 3.4$ Hz, 4H), 2.36 (s, 3H), 1.90 (brs, 1H), 1.51 (d, $J = 6.6$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.9, 142.2, 141.7, 137.9, 129.3, 128.5, 128.3, 127.6, 126.7, 125.6, 125.5, 123.0, 70.5, 38.1, 38.0, 25.2, 21.4. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{20}\text{ONa}^+$: 263.1406; found: 263.1409. HPLC (Chiralpak OJ-H, detector: 254 nm, elute: Hexane/*i*-PrOH = 97/3, flow rate: 1.0 mL/min, 25 °C).

7p (^1H NMR, ^{13}C NMR spectra).



7q. (S)-1-(3-(4-methoxyphenethyl)phenyl)ethan-1-ol. Yellow liquid, 92% yield, 96% ee.

$[\alpha]_D^{25} = -22.122$ (c 0.316, CHCl_3). ^1H NMR (400 MHz, CDCl_3)

δ 7.29 (t, $J = 7.5$ Hz, 1H), 7.25 – 7.16 (m, 2H), 7.11 (d, $J = 8.6$

Hz, 3H), 6.85 (d, $J = 8.5$ Hz, 2H), 4.87 (q, $J = 6.5$ Hz, 1H), 3.80

(s, 3H), 2.95 – 2.86 (m, 4H), 2.03 (brs, 1H), 1.49 (d, $J = 6.3$ Hz,

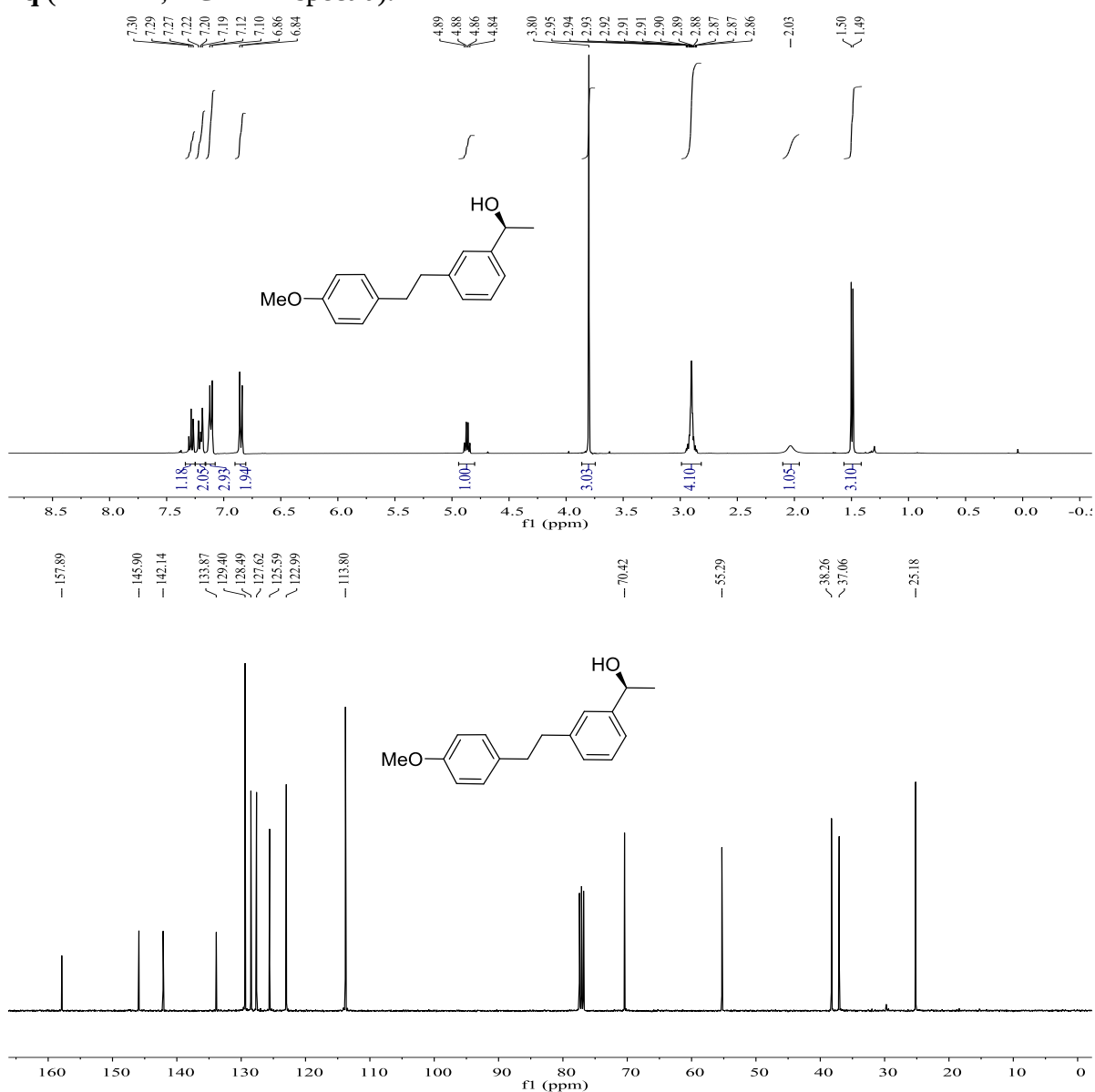
3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 157.9, 145.9, 142.1,

133.9, 129.4, 128.5, 127.6, 125.6, 123.0, 113.8, 70.4, 55.3, 38.3, 37.1, 25.2. HRMS (ESI): m/z

$[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{Na}^+$: 279.1356; found: 279.1364. HPLC (Chiralpak AS-H,

detector: 254 nm, elute: Hexane/*i*-PrOH = 96/4, flow rate: 1.0 mL/min, 25 °C).

7q (^1H NMR, ^{13}C NMR spectra).

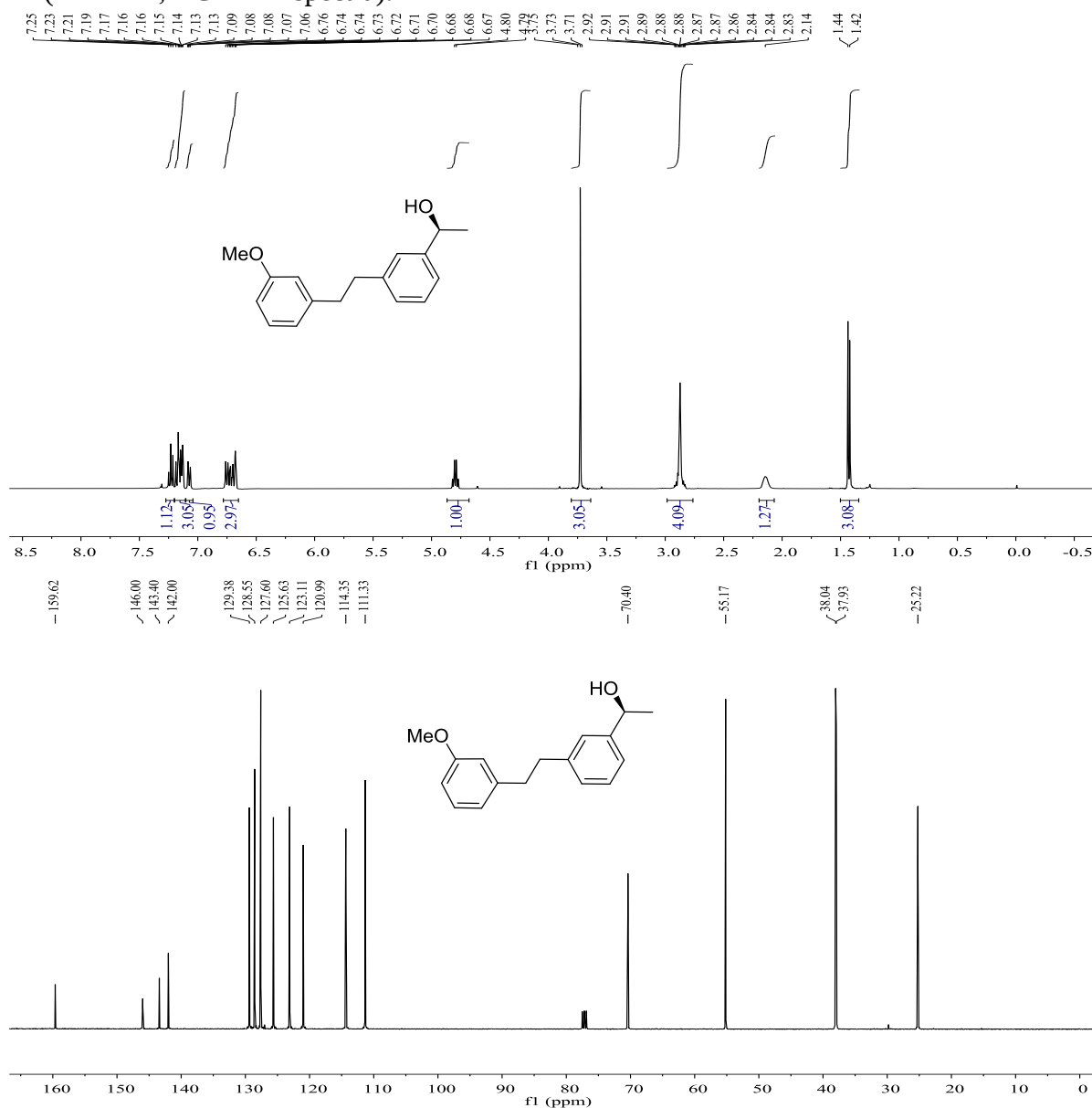


7r. (S)-1-(3-(3-methoxyphenethyl)phenyl)ethan-1-ol. Yellow liquid, 91% yield, 95% ee.

$[\alpha]_D^{25} = -24.247$ (c 0.486, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ

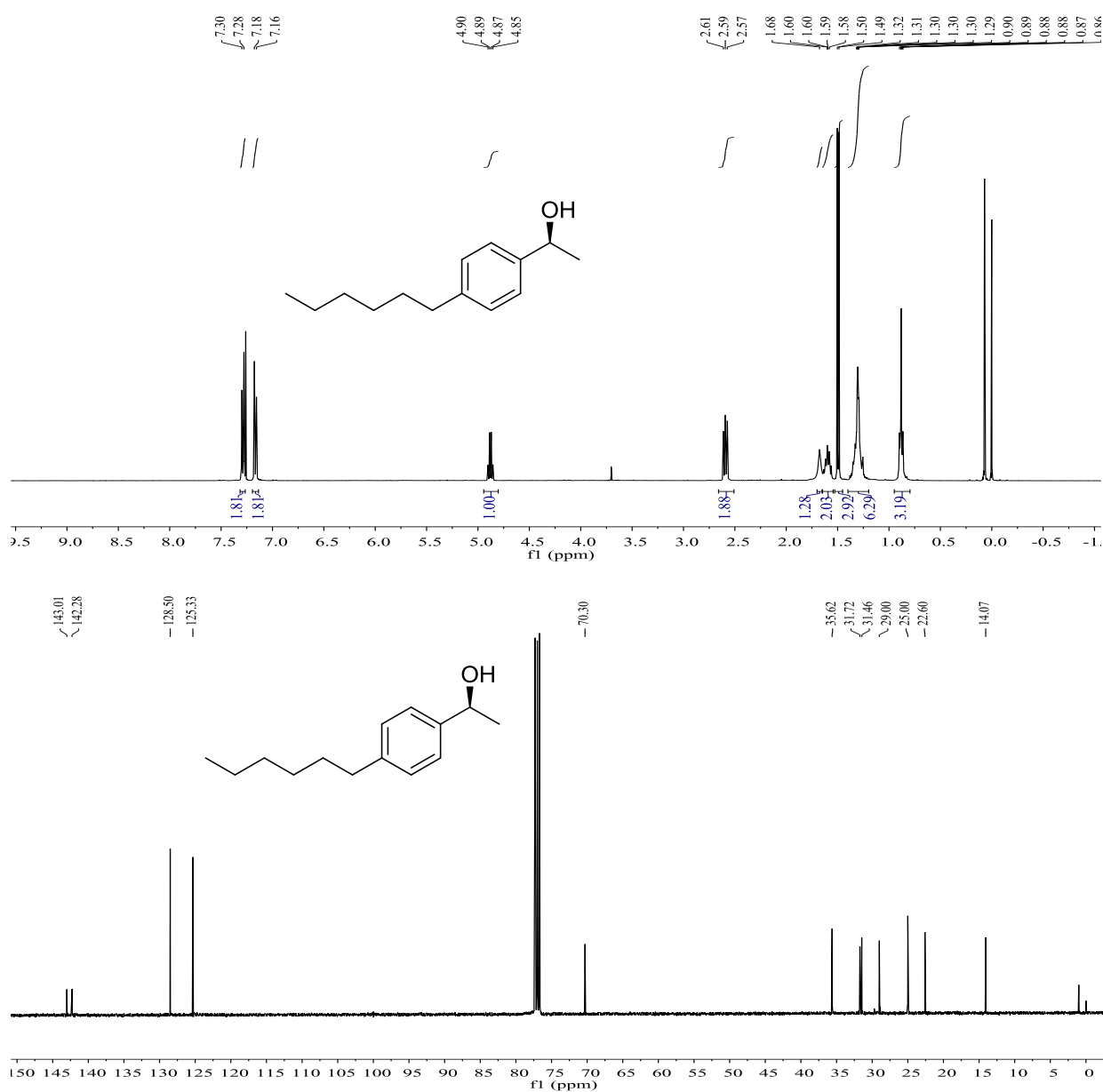
7.23 (t, $J = 7.4$ Hz, 1H), 7.20 – 7.11 (m, 3H), 7.10 – 7.04 (m, 1H), 6.78 – 6.65 (m, 3H), 4.80 (q, $J = 6.5$ Hz, 1H), 3.73 (s, 3H), 2.98 – 2.76 (m, 4H), 2.14 (brs, 1H), 1.43 (d, $J = 6.2$ Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 159.6, 146.0, 143.4, 142.0, 129.4, 128.6, 127.6, 125.6, 123.1, 121.1, 114.4, 111.3, 70.4, 55.2, 38.0, 37.9, 25.2. HRMS (ESI): m/z [M+Na]⁺ calculated for C₁₇H₂₀O₂Na⁺: 279.1356; found: 279.1364. HPLC (Chiralpak OJ-H, detector: 254 nm, elute: Hexane/*i*-PrOH = 97/3 flow rate: 1.0 mL/min, 25 °C).

7r (¹H NMR, ¹³C NMR spectra).



7s. (S)-1-(4-hexylphenyl)ethan-1-ol. Colorless liquid, 86% yield, 97% ee. $[\alpha]_D^{25} = -5.707$ (c 0.350, CHCl₃). ¹H NMR (400 MHz, CHCl₃) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 4.88 (q, *J* = 6.4 Hz, 1H), 2.66 – 2.57 (m, 2H), 1.68 (brs, 1H), 1.60 (ddd, *J* = 9.2, 4.6, 1.5 Hz, 2H), 1.49 (d, *J* = 6.4 Hz, 3H), 1.32 – 1.29 (m, 6H), 0.90 – 0.86 (m, 3H). ¹³C{¹H} NMR (100 MHz, CHCl₃) δ 143.0, 142.3, 128.5, 125.3, 70.3, 35.6, 31.7, 31.5, 29.0, 25.0, 22.6, 14.1. HRMS (ESI): *m/z* [M+NH₄]⁺ calculated for C₁₄H₂₆NO⁺: 224.2011; found: 224.2009. HPLC (Chiralpak OD-H, detector: 215 nm, elute: Hexane/*i*-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7s. (¹H NMR, ¹³C NMR spectra).



7t. (1S,1'S)-1,1'-(ethane-1,2-diylbis(4,1-phenylene))bis(ethan-1-ol). Colorless liquid, 86% yield, 99% ee, 21:1 dr. $[\alpha]_D^{25} = -9.939$ (c 0.422, CHCl₃). ¹H NMR (400 MHz, CHCl₃) δ 7.30 (d, *J* = 8.0 Hz, 4H), 7.18 (d, *J* = 8.0 Hz, 4H), 4.93 – 4.85 (m, 2H), 2.89 (s, 4H), 1.77 (brs, 2H), 1.49 (d, *J* = 9.3 Hz, 6H). ¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 143.4, 141.0, 128.5, 125.5, 70.3, 37.5, 25.1. HRMS (ESI): *m/z* [M+NH₄]⁺ calculated for C₁₈H₂₆NO⁺: 288.1960; found: 288.1958. (HPLC: Chiracel OB-H, detected at 254 nm, eluent: n-hexane/2-propanol = 96/4, flow rate = 1.0 mL/min, 25 °C).

7t. (¹H NMR, ¹³C NMR spectra).

