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Chiral Porous Organic Frameworks for Asymmetric Heterogeneous Catalysis and Gas Chromatographic Separation

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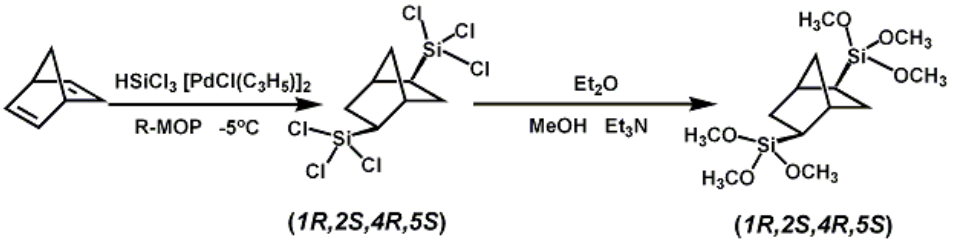
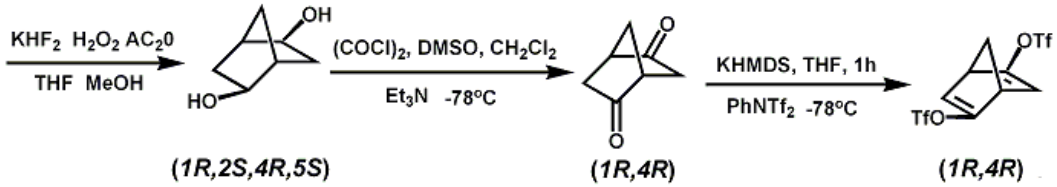
1. Materials and General Procedures.

All reagents and solvents used in these studies are commercially available and used without further purification. The IR (KBr pellet) spectra were recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a heating rate of 10 ^{o}C min^{-1} on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu Kα radiation. ^{1}H and ^{13}C NMR experiments were carried out on a MERCURYplus 400 spectrometer operating at resonance frequencies of 400 MHz. ICP-OES was performed on Optima 7300DV ICP-OES (Perkin Elmer Coporation, USA). Electrospray ionization mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane-methanol as mobile phase. Analytical high performance liquid chromatography (HPLC) was performed on YL-9100 HPLC with UV detection at 220 nm. Analytical CHIRALCEL AD-H and AS-H columns (4.6 mm × 25 cm) from Daicel were used. A SP-6890 system with a capillary control unit, a split injection port, and a flame ionization detector (FID) was used for all GC separations. Nitrogen (99.999%) was used as the carrier gas. The instrument control and data acquisition were carried out by the N-2000 software. SEM was conducted on a JEOL JSM-7401F electron microscope. A Shimadzu (Kyoto, Japan) TEM was conducted on a JEOL JEM-2100 electron microscope.

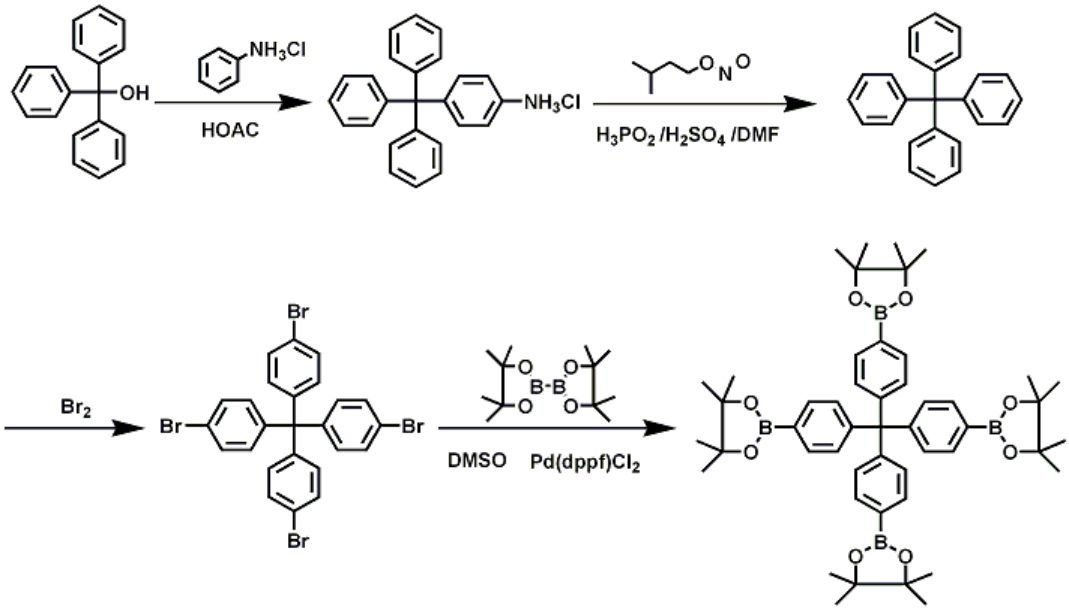
1. Synthesis of (1*R*,4*R*)-2,5-di(trifluoromethanesulfonyloxy)bicyclo-[2.2.1]hepta-2,5-diene and related precursors.





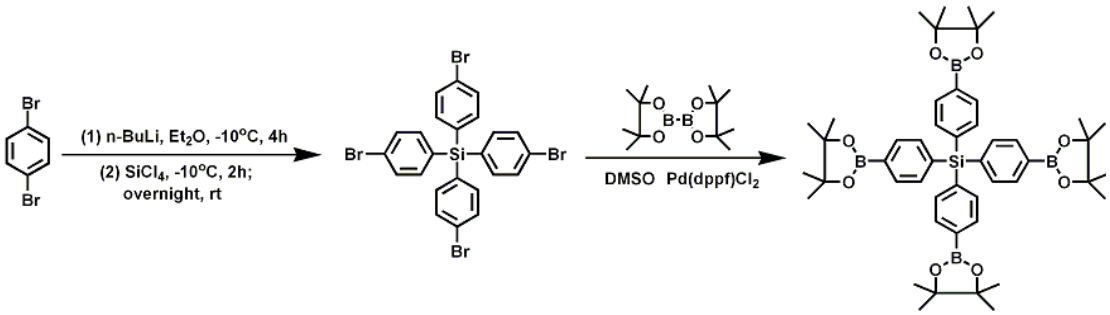
The (1*R*,4*R*)-2,5-di(trifluoromethanesulfonyloxy)bicyclo-[2.2.1]hepta-2,5-diene was synthesized according to the published procedures.[1-3] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.55 (t, 2H), 3.45 (m, 2H), 6.44 (dd, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 49.36, 72.10, 119.12, 122.75, 167.23 ppm.

Tetrakis[4-(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolanephenyl)]methane



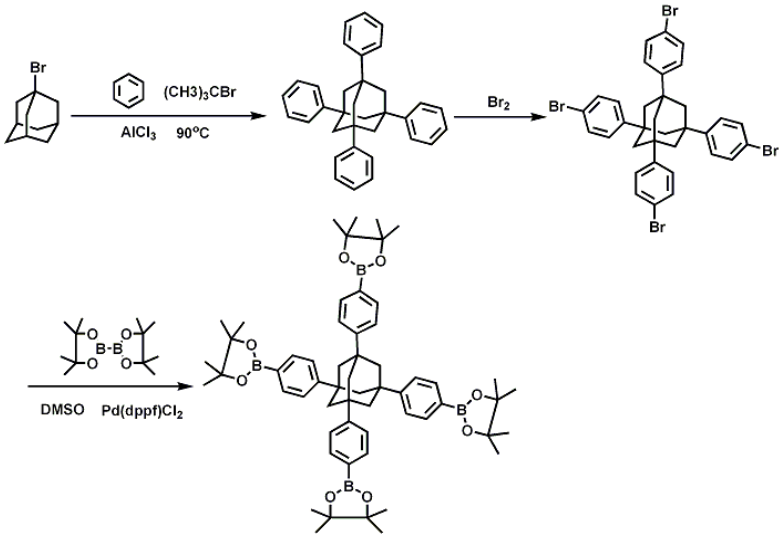
This compound was synthesized according to the published procedures.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67–7.65 (d, 8H), 7.29–7.26 (d, 8H), 1.31 (s, 48H). ^{13}C NMR(100 MHz, $CDCl_3$) δ: 149.7, 134.3, 130.5, 126.47, 83.9, 66.14, 25.1.

Tetrakis[4-(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolanephenyl)]silane



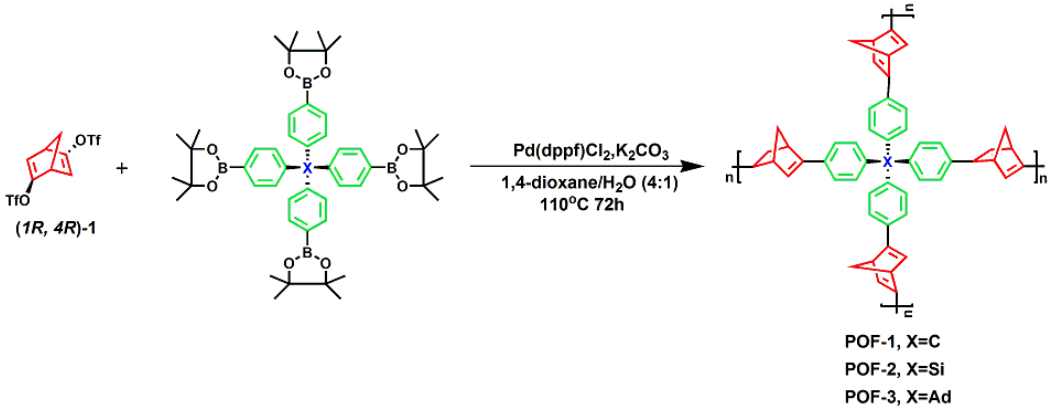
This compound was synthesized according to the published procedures.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80-7.78 (d, 8H), 7.56-7.54 (d, 8H), 1.34 (s, 48H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.48, 135.90, 134.14, 130.44, 84.09, 25.12.

1,3,5,7-tetrakis[4-(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolanephenyl)]adamantine



This compound was synthesized according to the published procedures. [6] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82-7.80 (d, 8H), 7.50-7.48 (d, 8H), 2.18 (s, 12H), 1.34 (s, 48H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.73, 135.24, 131.67, 124.70, 83.94, 47.17, 39.72, 25.09.

2. Synthesis of POFs and post-synthetic metalation



Synthesis of POF-1: A mixture of (1*R*, 4*R*)-bis-triflate (77.6 mg, 0.2 mmol), tetrakis[4-(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolanephenyl)]methane (82.4 mg, 0.10 mmol) and $PdCl_2$(dppf) (8.2 mg, 0.01 mmol) in 1, 4-dioxane (8 mL) was degassed by pump, purged with N_2. To the mixture was added an aqueous solution (2.0 mL) of K_2CO_3 (221.1 mg, 1.6 mmol) which bubbled by N_2. The mixture was stirred at 110 °C for 72 h, cooled at room temperature and poured into water. The precipitate was collected by filtration, thoroughly washed with water, THF, ethanol, dichloromethane and acetone, rigorously washed by Soxhlet extractions for 24 h with THF, ethanol, dichloromethane and acetone as solvent, respectively, and dried in vacuum to give **1** (48.2 mg, 91% yield) as off white solid. IR (KBr, cm^{-1}): 3425 (s), 3058 (w), 3028 (w), 2976 (w), 1604 (s), 1502 (s), 1361 (s), 1143 (s), 1089 (s), 1019 (s), 818 (m), 703 (w), 538 (w).

Synthesis of POF-2: A mixture of (1*R*, 4*R*)-bis-triflate (77.6 mg, 0.2 mmol), tetrakis[4-(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolanephenyl)]silane (84.0 mg, 0.10 mmol) and $PdCl_2$(dppf) (8.2 mg, 0.01 mmol) in 1, 4-dioxane (8 mL) was degassed by pump, purged with N_2. To the mixture was added an aqueous solution (2.0 mL) of K_2CO_3 (221.1 mg, 1.6 mmol) which bubbled by N_2. The mixture was stirred at 110 °C for 72 h, cooled at room temperature and poured into water. The precipitate was collected by filtration, thoroughly washed with water, THF, ethanol, dichloromethane and acetone, rigorously washed by Soxhlet extractions for 24 h with THF, ethanol, dichloromethane and acetone as solvent, respectively, and dried in vacuum to give POF-**2** (44.1 mg, 81% yield) as off white solid. IR (KBr, cm^{-1}): 3434 (s), 3063 (w), 3017 (w), 2968 (w), 1598 (s), 1429 (s), 1391 (s), 1108 (s), 1070 (s), 822 (m), 704 (m), 544 (m).

Synthesis of POF-3: A mixture of (1*R*, 4*R*)-bis-triflate (77.6 mg, 0.2 mmol), 1,3,5,7-tetrakis[4-(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolanephenyl)]adamantine (94.5 mg, 0.10 mmol) and $PdCl_2$(dppf) (8.2 mg, 0.01 mmol) in 1,4-dioxane (8 mL) was degassed by pump, purged with N_2. To the mixture was added an aqueous solution (2.0 mL) of K_2CO_3 (221.1 mg, 1.6 mmol) which bubbled by N_2. The mixture was stirred at 110 °C for 72 h, cooled at room temperature and poured into water. The precipitate was collected by filtration, thoroughly washed with water, THF, ethanol, dichloromethane and acetone, rigorously washed by Soxhlet extractions for 24 h with THF, ethanol, dichloromethane and acetone as solvent, respectively, and dried in vacuum to give POF-**3** (48.7 mg, 75% yield) as off white solid. IR (KBr, cm^{-1}): 3426 (s), 3086 (w), 3056 (w), 3028 (w), 2928 (m), 2897 (w), 2851 (m), 1607 (s), 1498 (m), 1445 (m), 1403 (m), 1335 (s), 1118 (w), 829 (m), 700 (m), 567 (w).

Post-synthetic metalation of POFs with $[Rh(C_2H_4)_2Cl]_2$.

Under an argon atmosphere, to a 10mL Schlenk tube with a Teflon cap was added POF **1** (5.3 mg, 0.01 mmol), $[Rh(C_2H_4)_2Cl]_2$ (1.95 mg, 0.005 mmol) and 0.5 mL 1,4-dioxane, the mixture was allowed to stir for overnight, and then the metalated **1** was centrifuged out of suspension and washed with THF. **2** and **3** were metalated in a similar procedure. ICP results: Rh, 24% for **1**-Rh (calc. 24.00% for $C_{45}H_{40}Cl_2Rh_2$); Rh, 24% for **2**-Rh (calc. 23.56.0% for $C_{44}H_{40}Cl_2Rh_2Si$); Rh, 24% for **3**-Rh (calc. 21.05% for $C_{54}H_{52}Cl_2Rh_2$),

3. A general procedure for the POF/Rh-catalyzed reaction

The in-situ generated **1**-Rh (0.004 mmol, 4 mol %), $ArB(OH)_2$ (0.4 mmol), enone/ester (0.2 mmol), degassed KOH aq. (1.0M in H_2O, 0.1 mL) was added sequentially. The mixture was stirred for 8 h at 50°C, quenched with saturated $NaHCO_3$ in water and extracted with Et_2O five times. The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The residue was flash chromatographed to afford the product. The reactions catalyzed by **2**-Rh and **3**-Rh were done in a similar way.

The viability of recycling POF-**1** was examined in the asymmetric 1,4-addition reaction of 3-methoxyphenylboronic acid with 2-cyclohexenone.

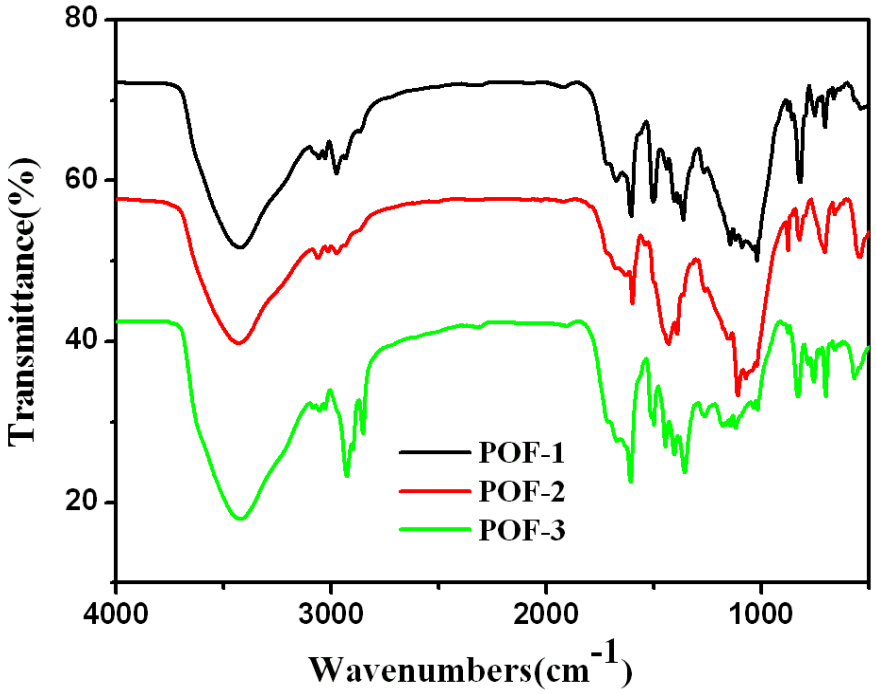
The catalysts can be easily recovered by simple filtration and washing with THF and Et_2O for several times, and then heating at 100 ºC for 4 hours under vacuum. The recycled POF-**1** was used for the next cycle with additional $[Rh(C_2H_4)_2Cl]_2$ (0.004 mmol, 4 mol % Rh, 1.55 mg) that is the same as described above.

4. Pretreatment and preparation of open tubular columns

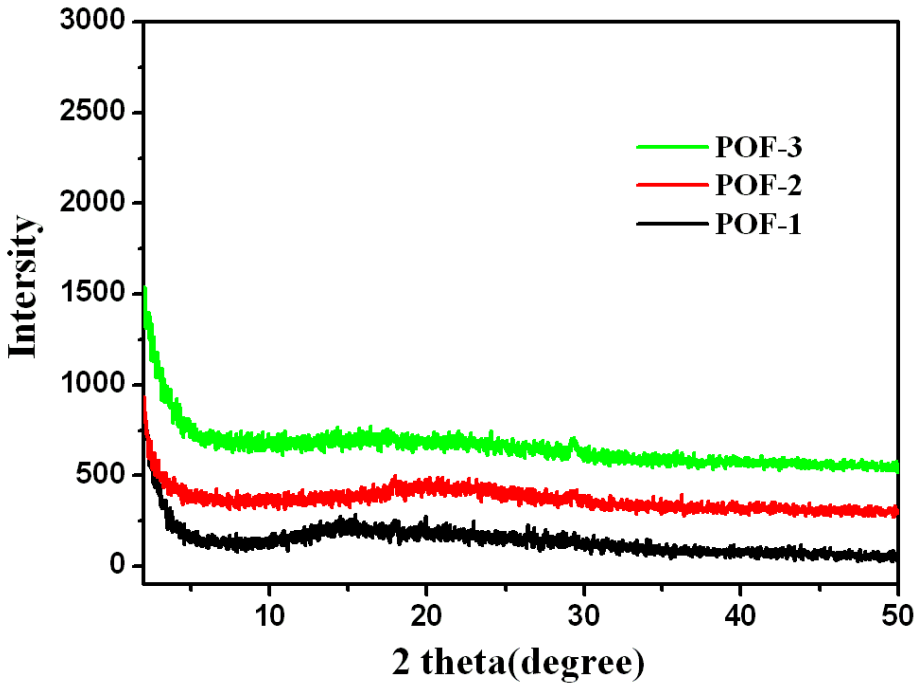
Untreated fused-silica open tubular column (Yongnian Optic Fiber Factory, Hebei, China) was filled with 1 M NaOH, sealed at both ends and maintained for 2h. The capillary was washed successively with ultrapure water for 1 h, 1M HCl for 2 h, ultrapure water until the outflow reached neutrality, and then purged wth nitrogen for 6 h at 120 ^oC.

The columns were prepared by a dynamic coating method. Briefly, 2 mL ethanol suspension of POF-**1** (5mg· mL^{-1}, grinded by ball mill pulverizer) was introduced into the open tubular column under gas pressure, and then pushed through the column at a rate of 50 $cm \cdot min^{-1}$ to leave a wet coating layer on the innerwall of the capillary column. A 15 m long buffer tube was attached to the end of the capillary column as a restrictor for avoiding acceleration of the solution plug near the end of the column. Finally, the coated open tubular column was flushed for 6h with nitrogen and then conditioned from 30 to 220 ^oC, increasing its temperature at a rate of 1 $^oC \cdot min^{-1}$, and finally at 220 ^oC for 3h.

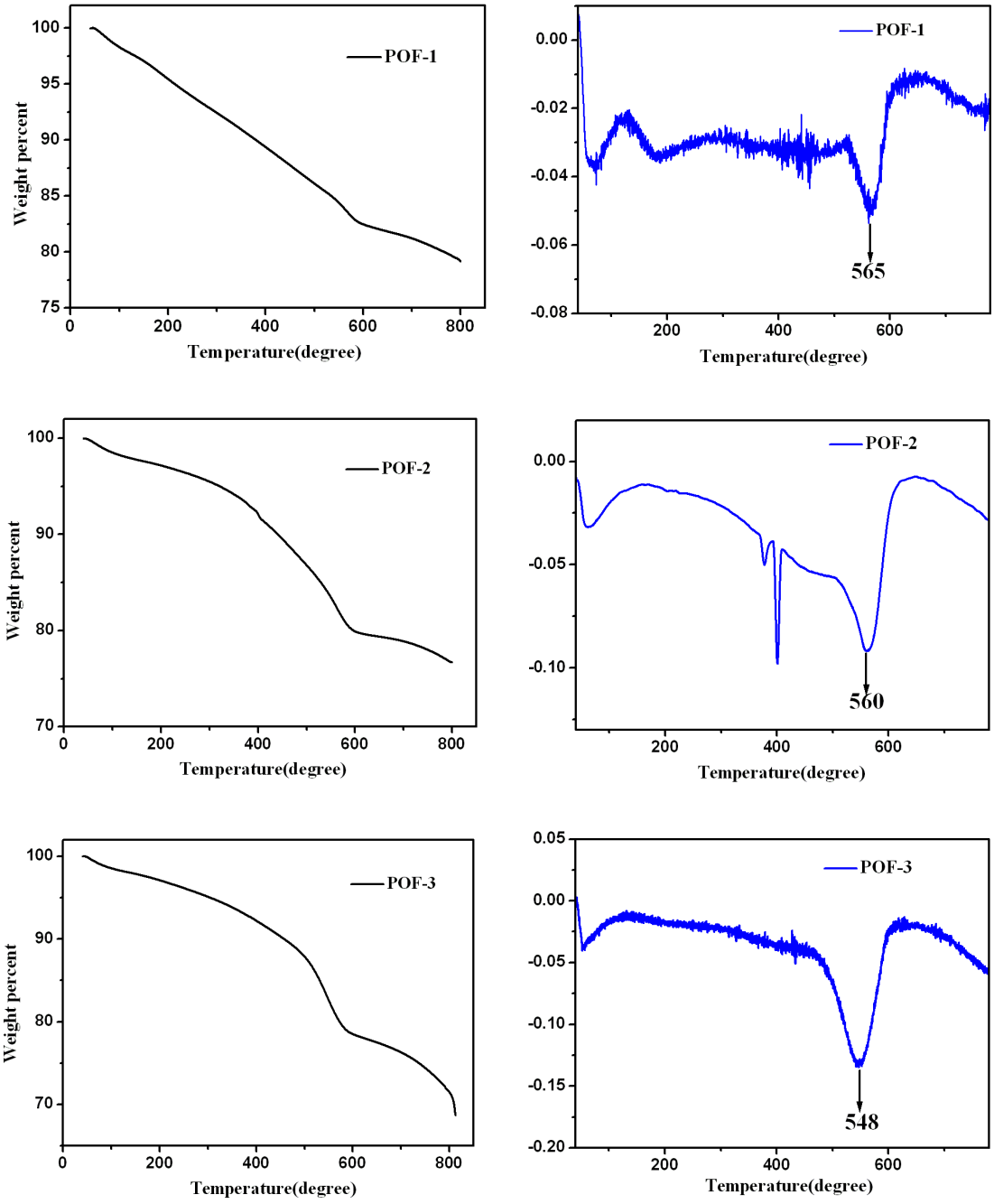
5. Figure S1. FT-IR spectra of the POFs



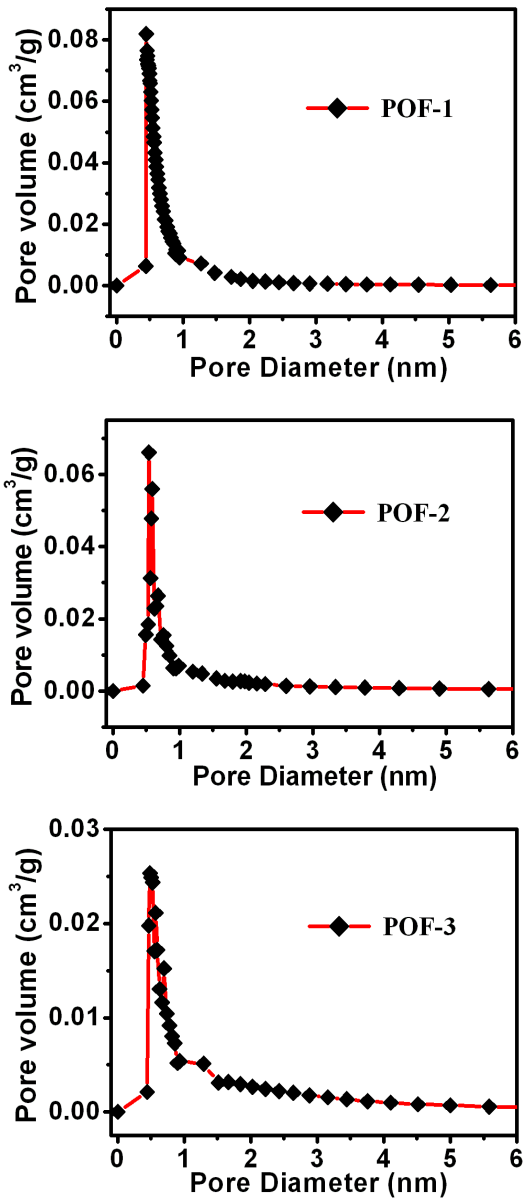
6. Figure S2. PXRD patterns of the POFs



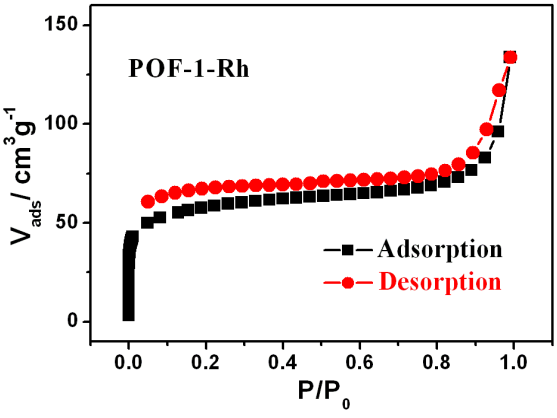
7. Figure S3. TGA and DSC curves of the POFs



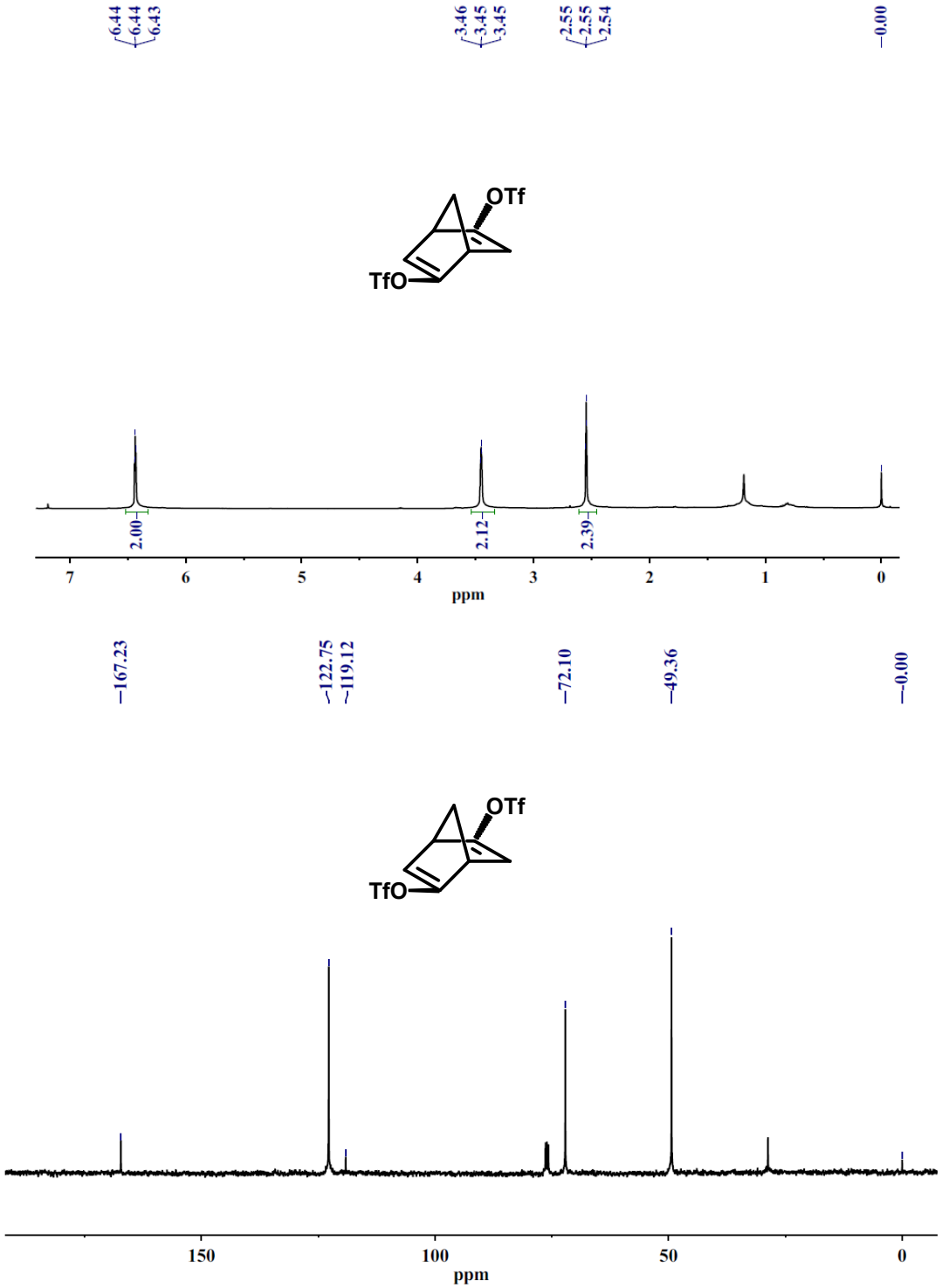
8. Figure S4. Pore size distributions of the POFs

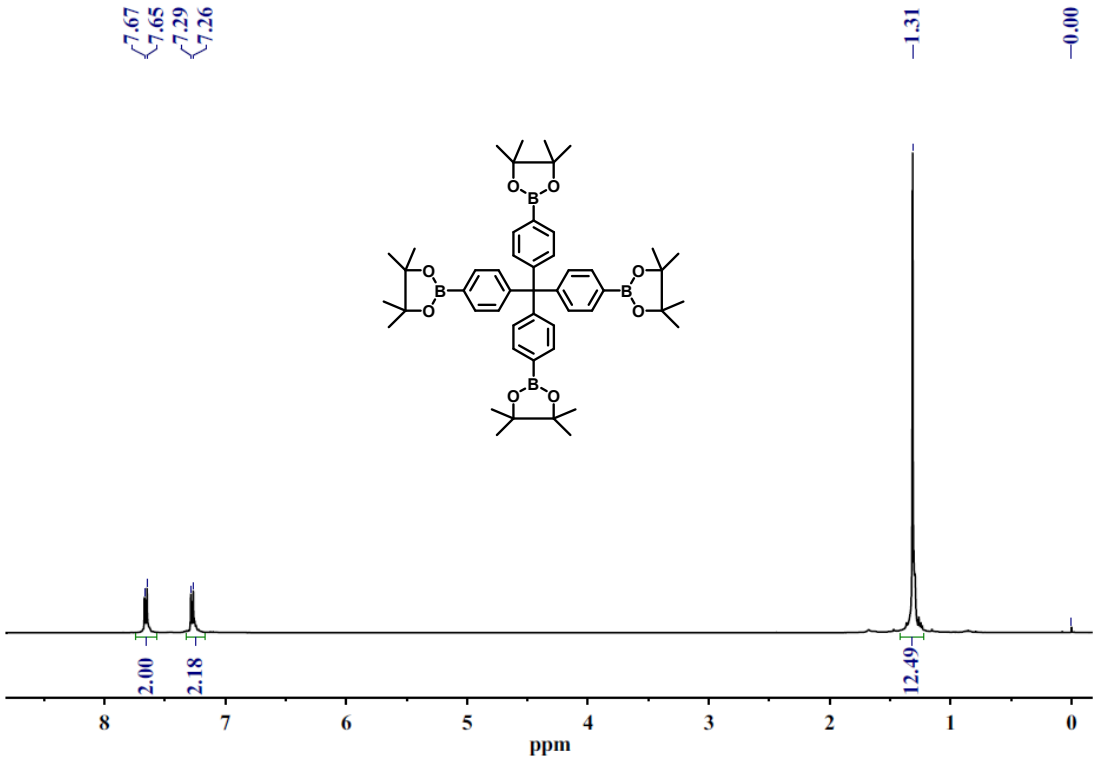


9. Figure S5. Nitrogen adsorption isotherm of POF-1-Rh



10. Figure S6. ^{1}H and ^{13}CNMR Spectra of the POFs and related precursors.

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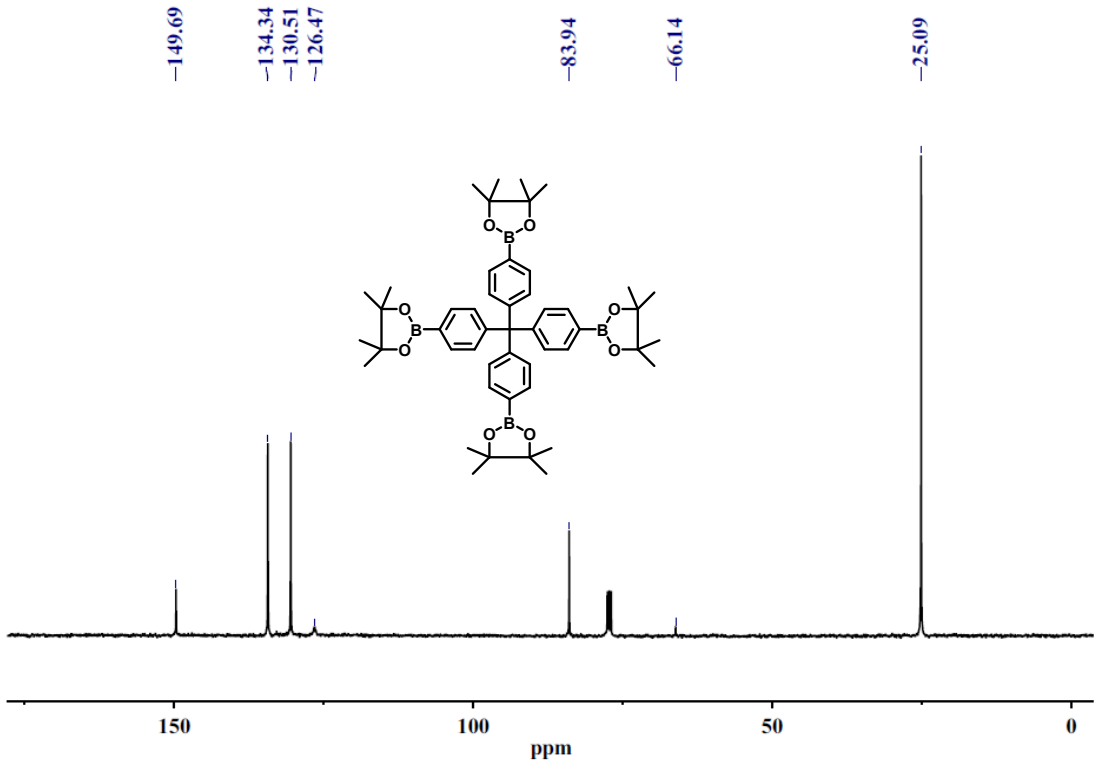
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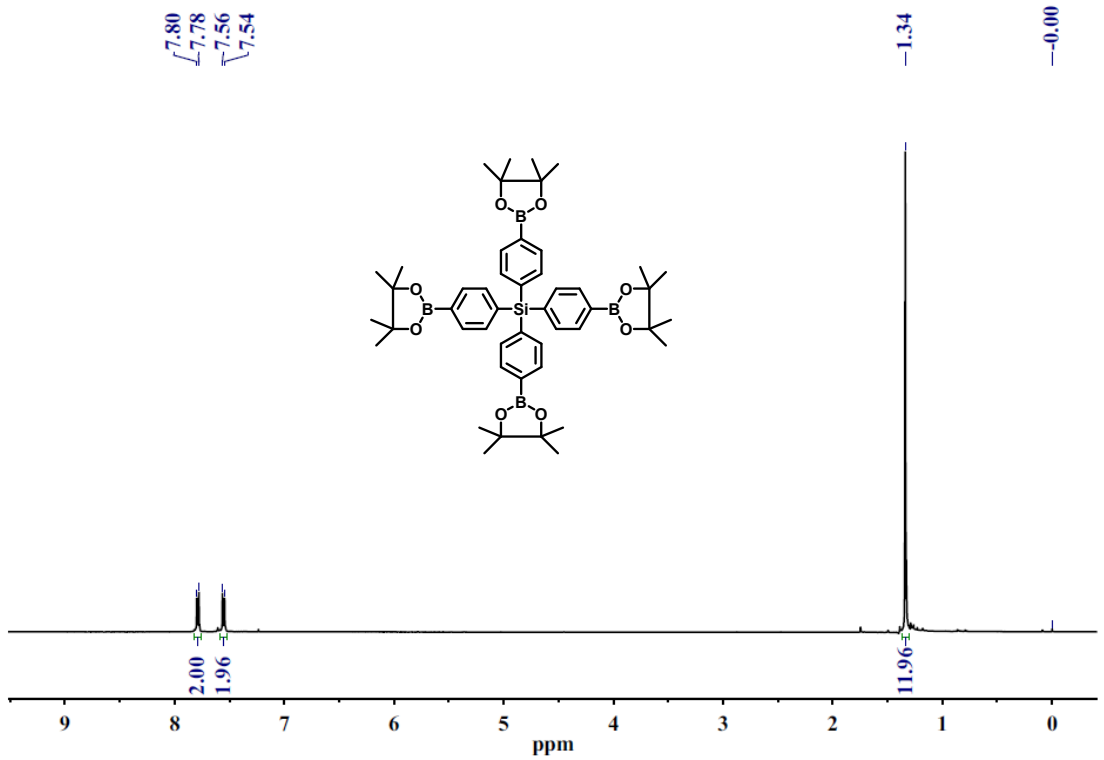
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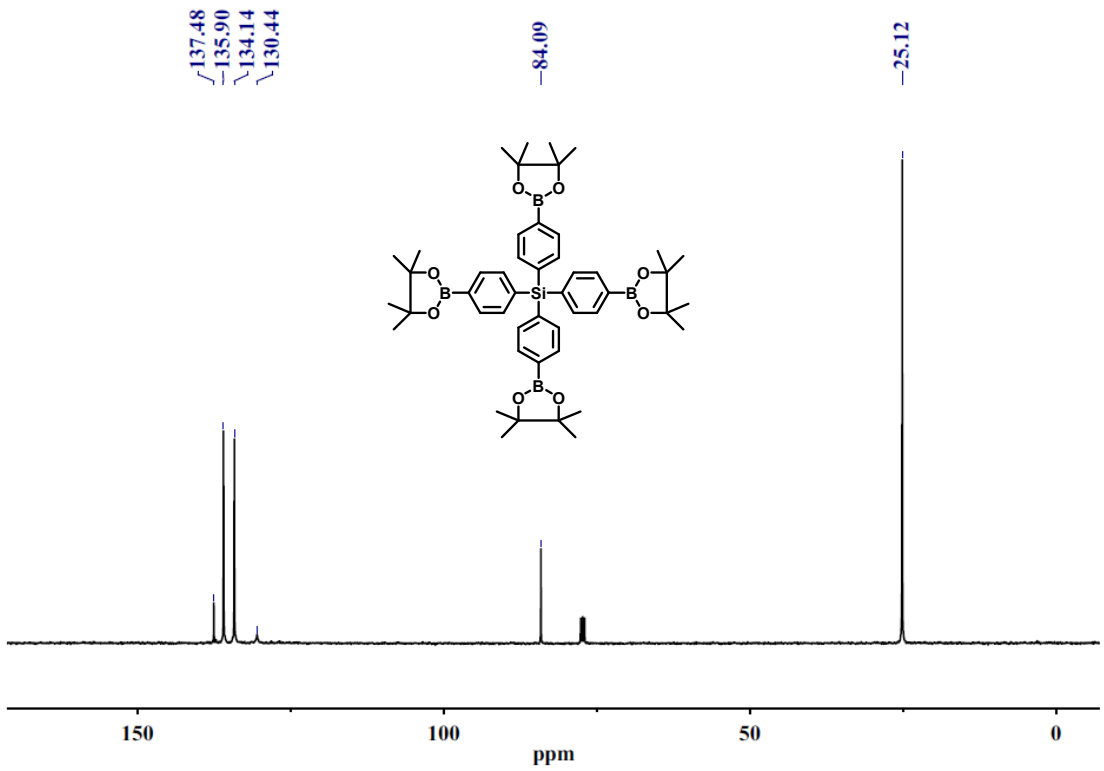
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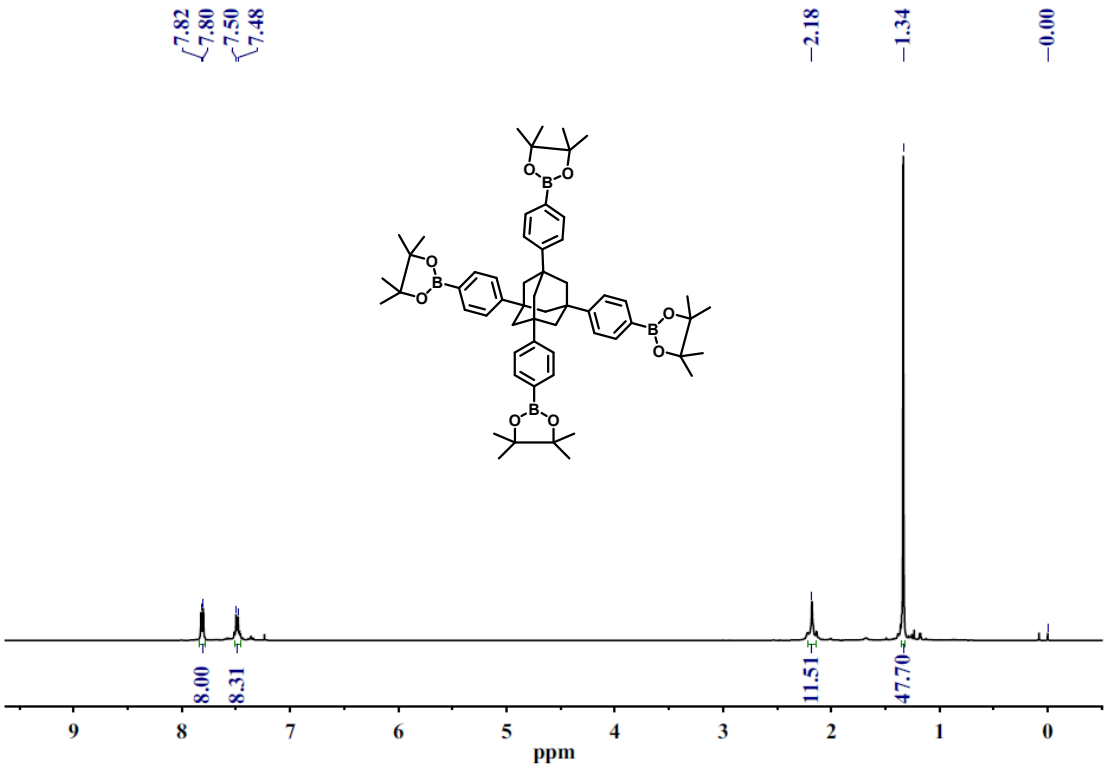
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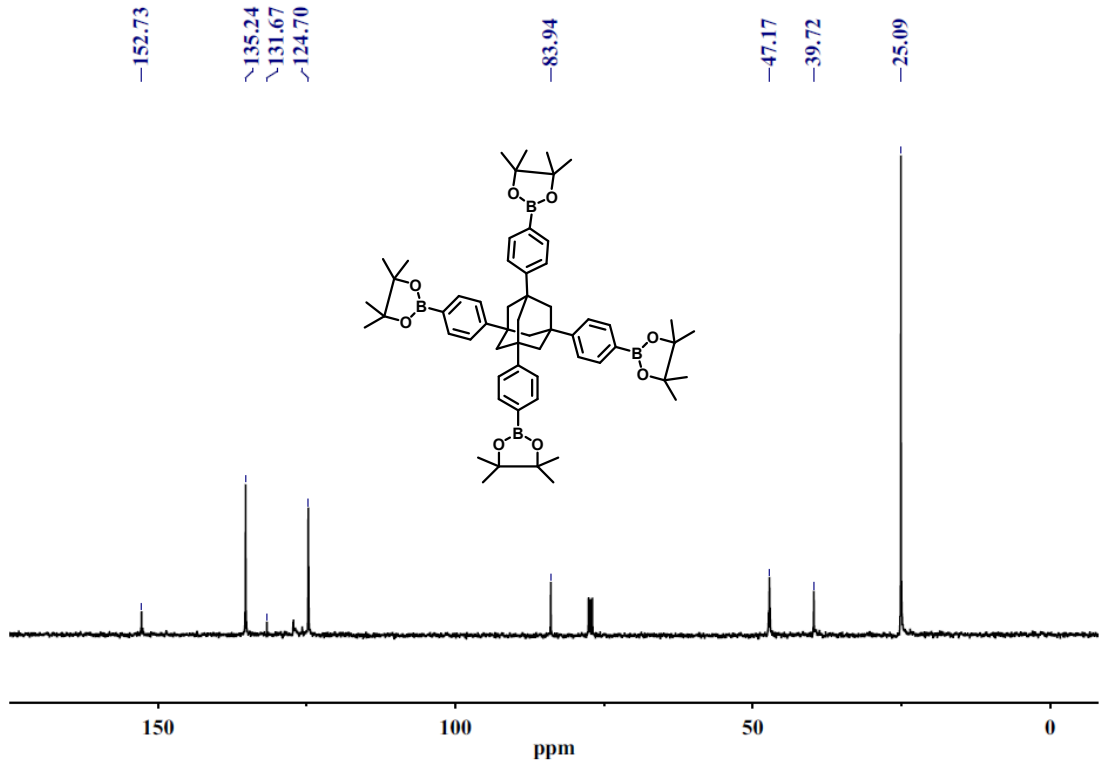
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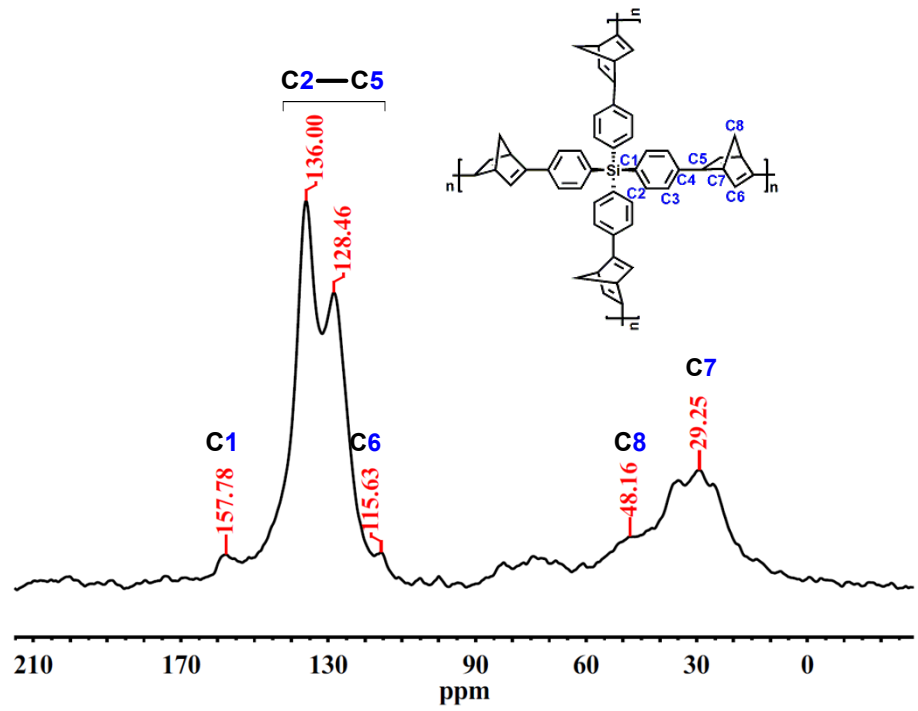
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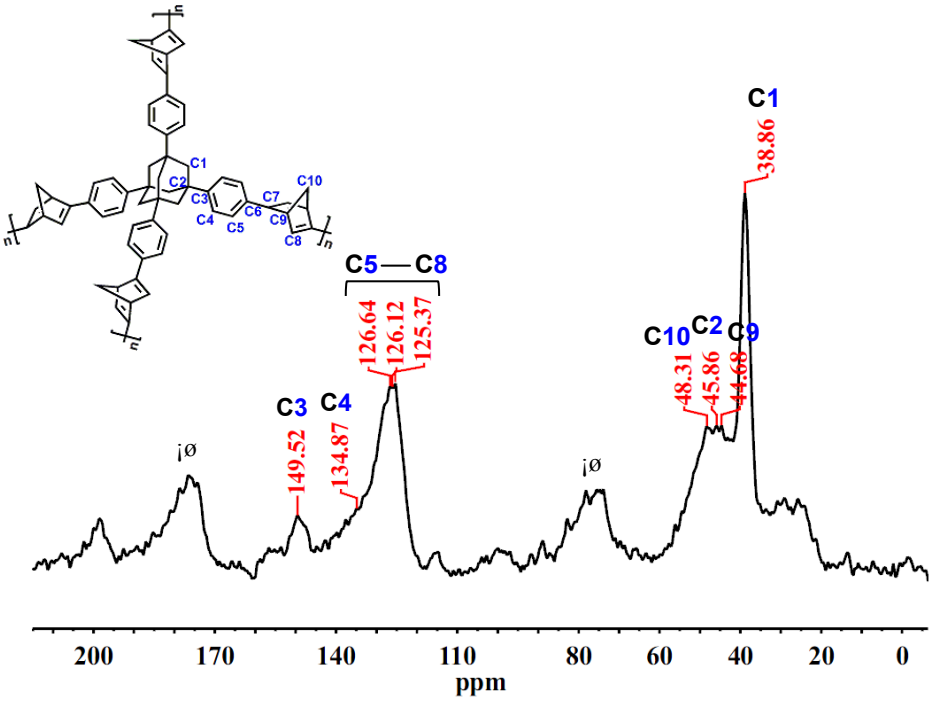
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C3
C4
C5
C6
C7
C8
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C10
C5—C8
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C10
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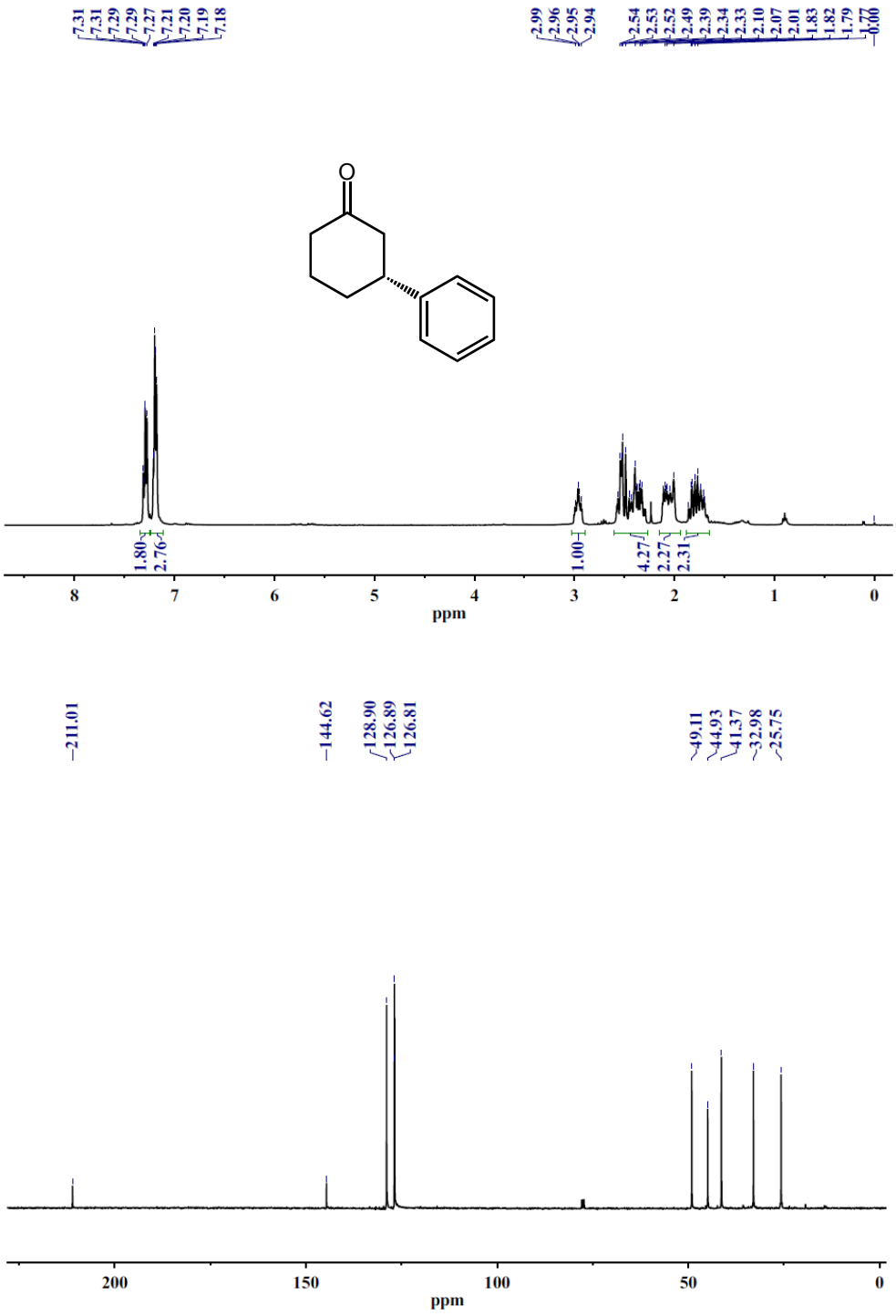
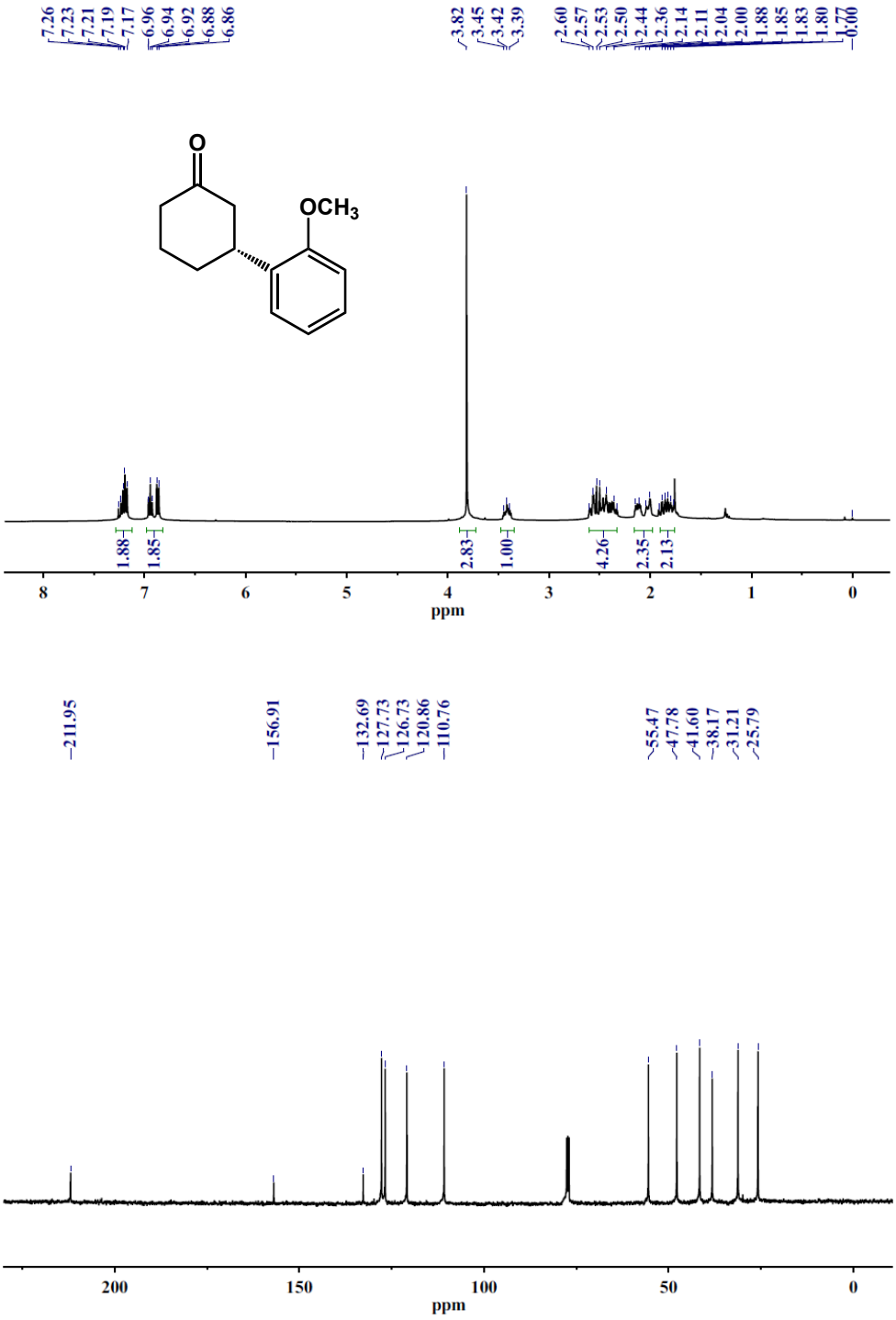
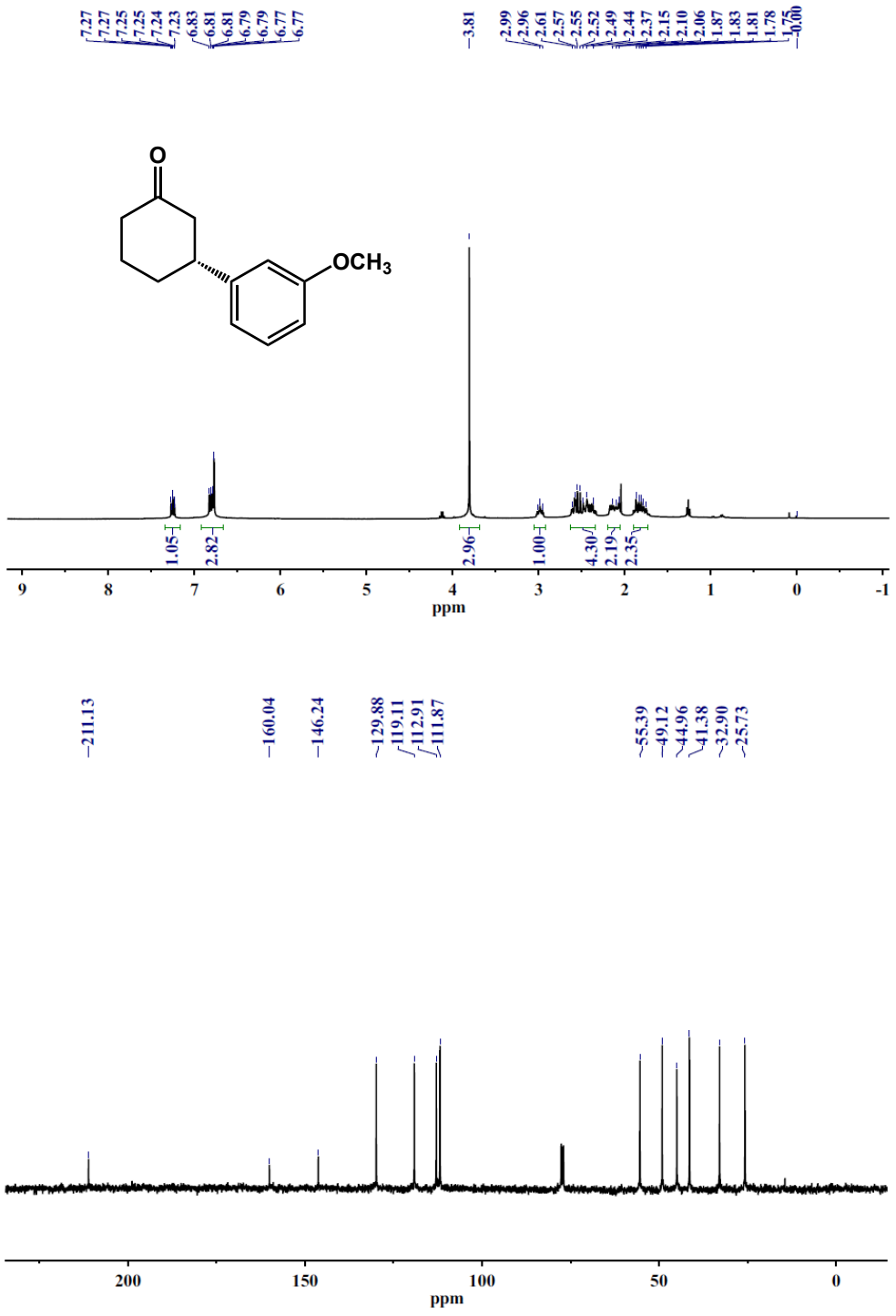


(*R*)-3-Phenyl-cyclohexanone: Purified by flash column chromatography (SiO_2, PE/EtOAc: 9:1), obtained as colorless oil (32.4mg, 93% yield). ^{1}HNMR (400MHz, $CDCl_3$): δ 7.31-7.27 (m, 2H), 7.21-7.18 (m, 3H), 2.99-2.94 (m, 1H), 2.57-2.33 (m, 4H), 2.11-2.01 (m, 2H), 1.86-1.70 (m, 2H). ^{13}CNMR (100MHz, $CDCl_3$): δ 211.01, 144.62, 128.90, 126.89, 126.81, 49.11, 44.93, 41.37, 32.98, 25.75.



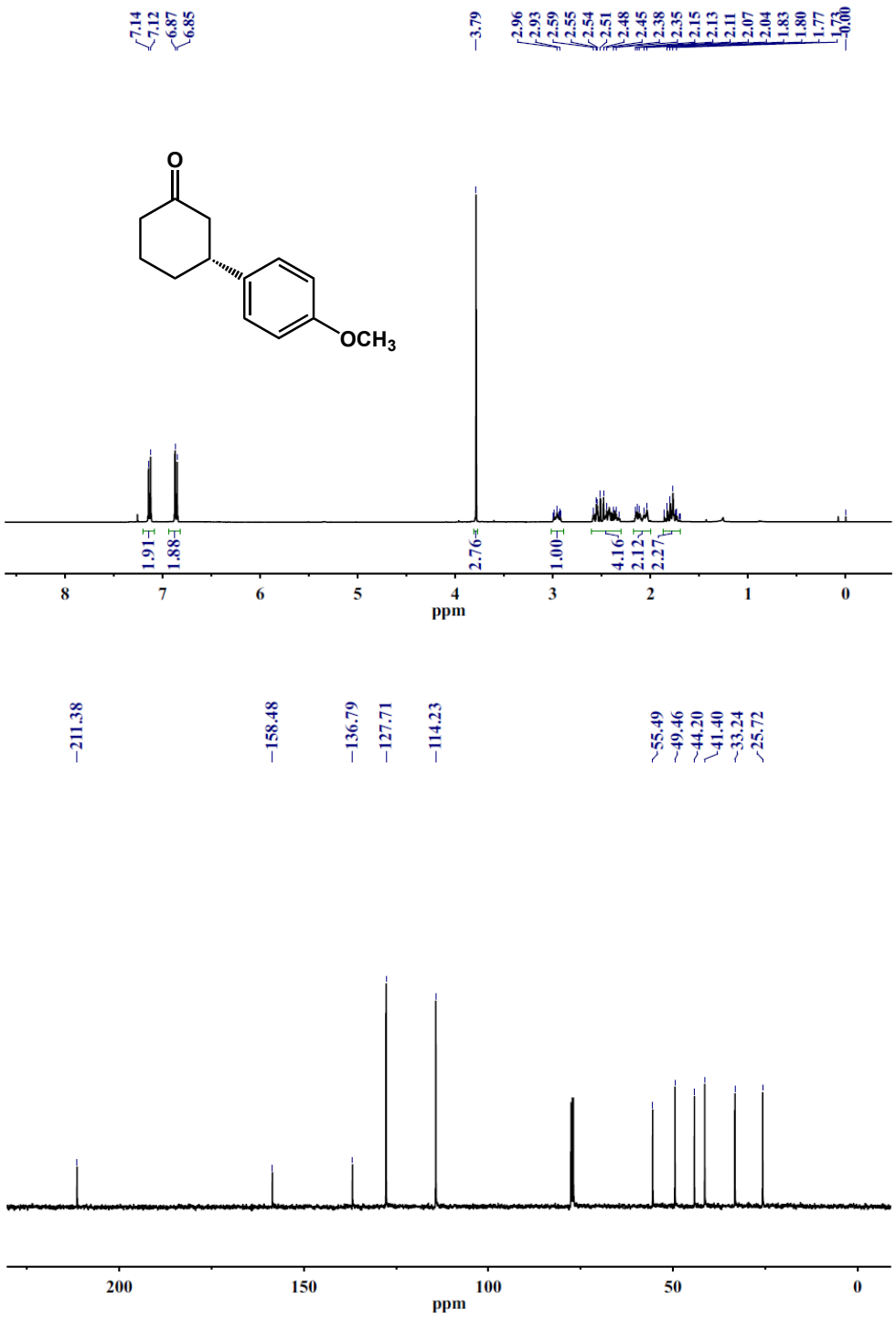
(*R*)-3-(2-methoxyphenyl)-cyclohexanone: Purified by flash column chromatography (SiO_2, PE/EtOAc: 15:1), obtained as colorless oil (36.8mg, 90% yield). ^{1}HNMR (400MHz, CDCl3): δ:7.26-7.17 (m, 2H), 6.96-6.86 (m, 2H), 3.82 (s,3H), 3.45-3.39 (m, 1H), 2.60-2.33 (m, 4H), 2.14-2.00 (m, 2H), 1.91-1.77 (m, 2H).

^{13}CNMR (100MHz, CDCl3): δ: 211.95, 156.91, 132.69, 127.73, 126.73, 120.86, 110.76, 55.47, 47.78, 41.60, 38.17, 31.21, 25.79.

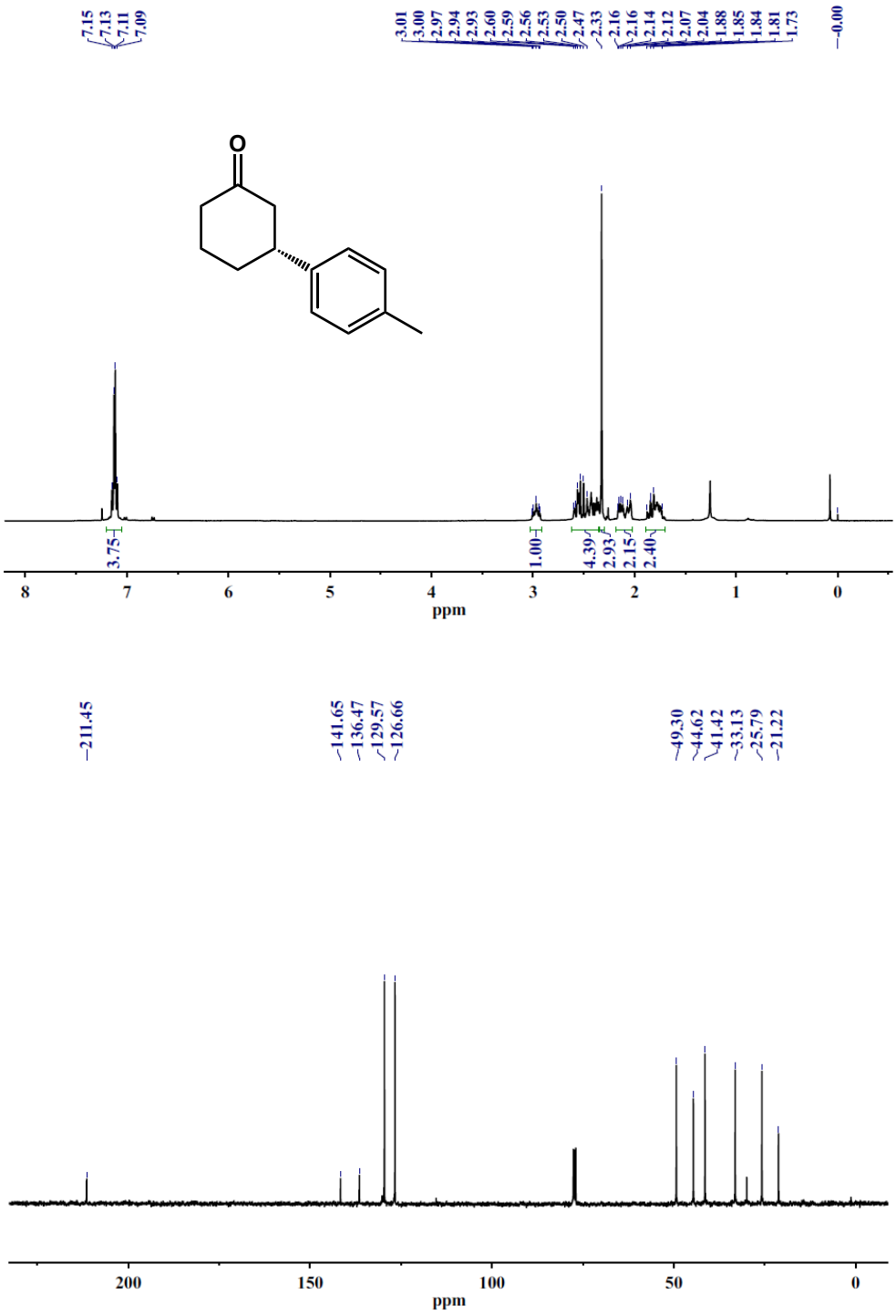


(*R*)-3-(3-methoxyphenyl)-cyclohexanone: Purified by flash column chromatography (SiO_2, PE/EtOAc: 9:1), obtained as colorless oil (37.6 mg, 92% yield). ^{1}HNMR (400MHz, $CDCl_3$): δ:7.27-7.23 (m, 1H), 6.83-6.77 (m, 3H), 3.81 (s,3H), 3.02-2.96 (m, 1H), 2.61-2.37 (m, 4H), 2.15-2.06 (m, 2H), 1.87-1.75 (m, 2H).

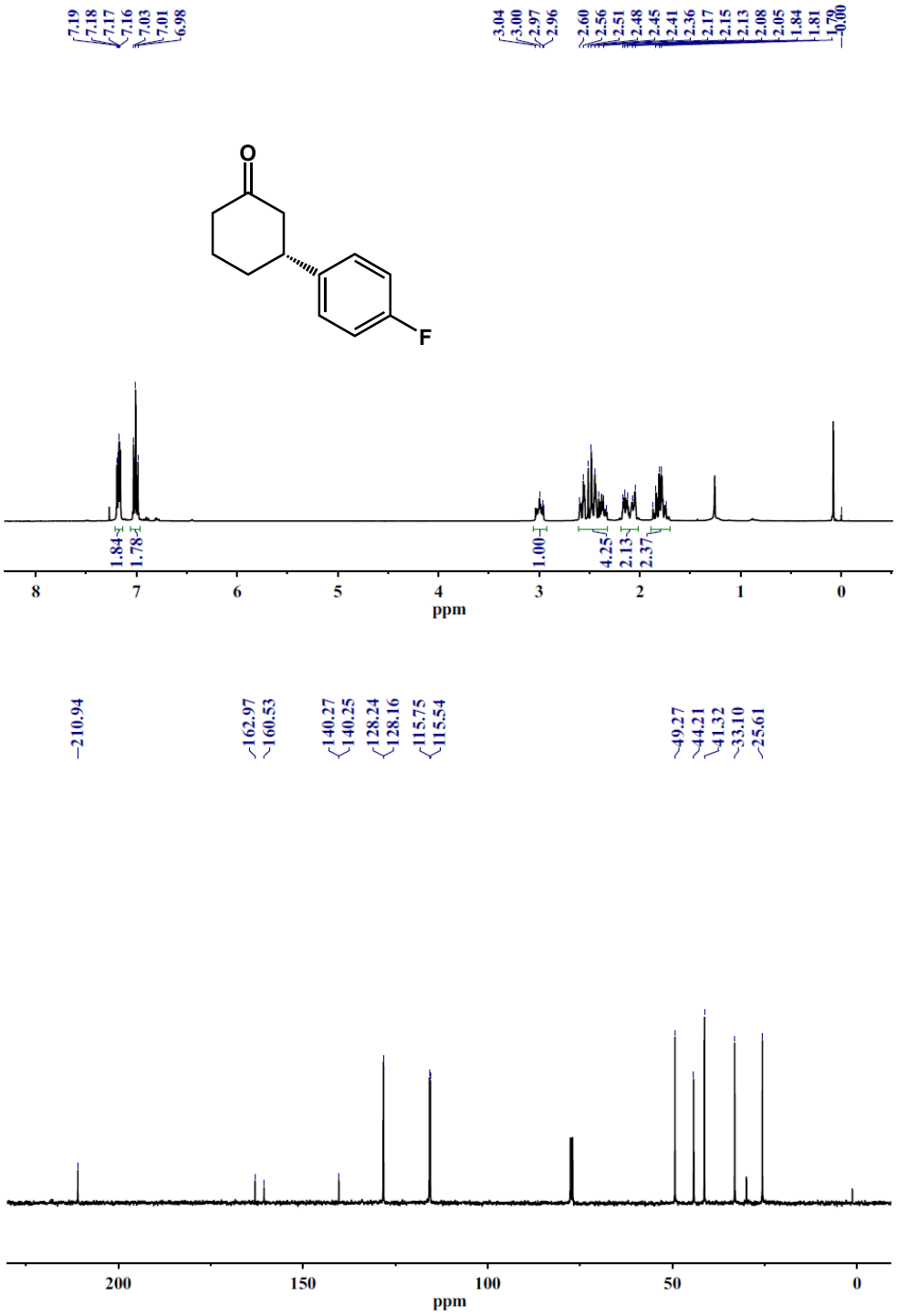
^{13}CNMR (100MHz, $CDCl_3$): δ: 211.13, 160.04, 146.24, 129.88, 119.11, 112.91, 111.87, 55.39, 49.12, 44.96, 41.38, 32.90, 25.73.



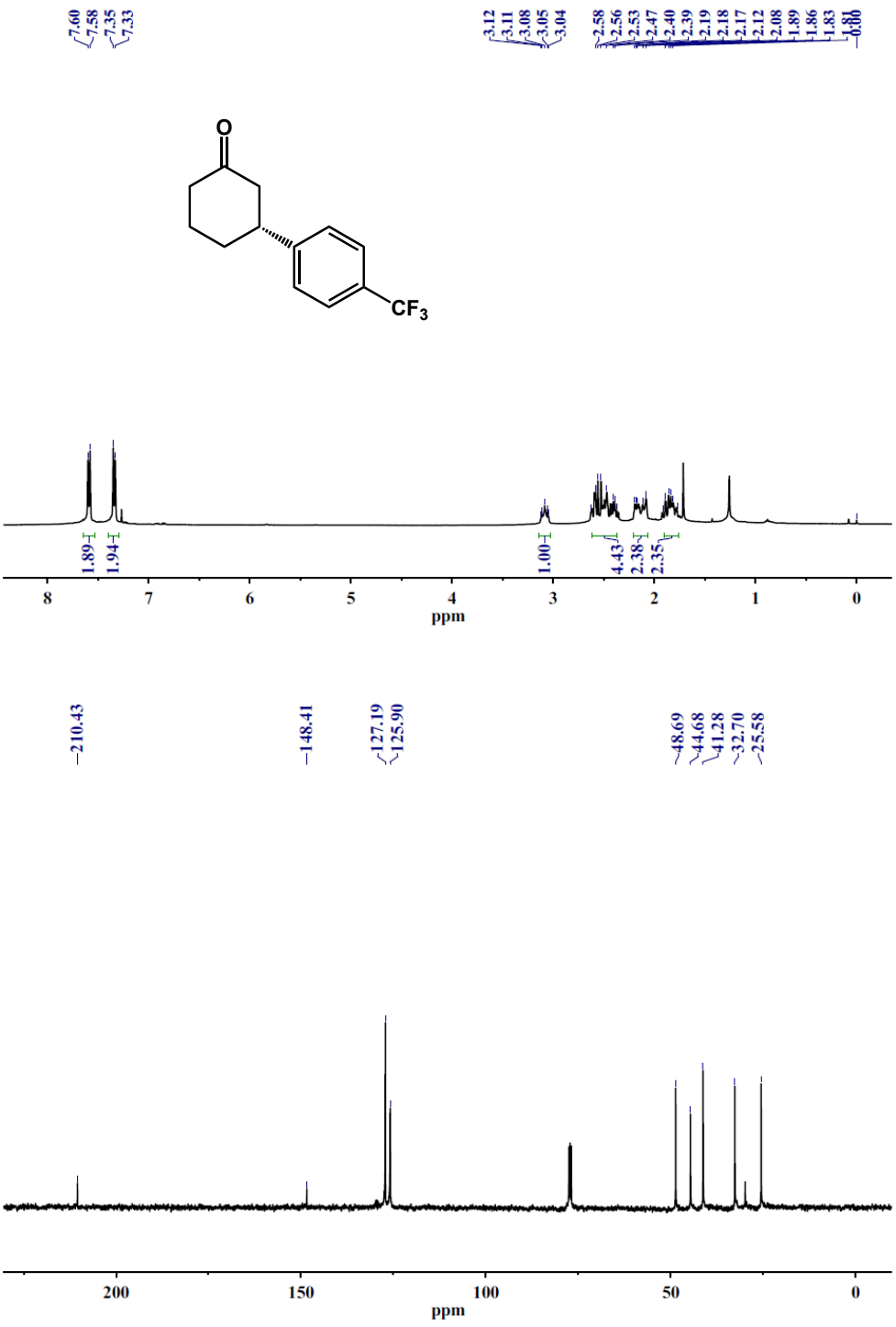
(*R*)-3-(4-methoxyphenyl)-cyclohexanone: Purified by flash column chromatography (SiO_2, PE/EtOAc: 15:1), obtained as colorless oil (37.5 mg, 92% yield). ^{1}HNMR (400 MHz, $CDCl_3$): δ:7.14-7.12 (d, 2H), 6.87-6.85 (d, 2H), 3.79 (s, 3H), 3.00-2.92 (m, 1H), 2.59-2.32 (m, 4H), 2.15-2.04 (m, 2H), 1.86-1.69 (m, 2H). ^{13}CNMR (100 MHz, $CDCl_3$): δ:211.38, 158.48, 136.79, 127.71, 114.23, 55.49, 49.46, 44.20, 41.40, 33.24, 25.72.



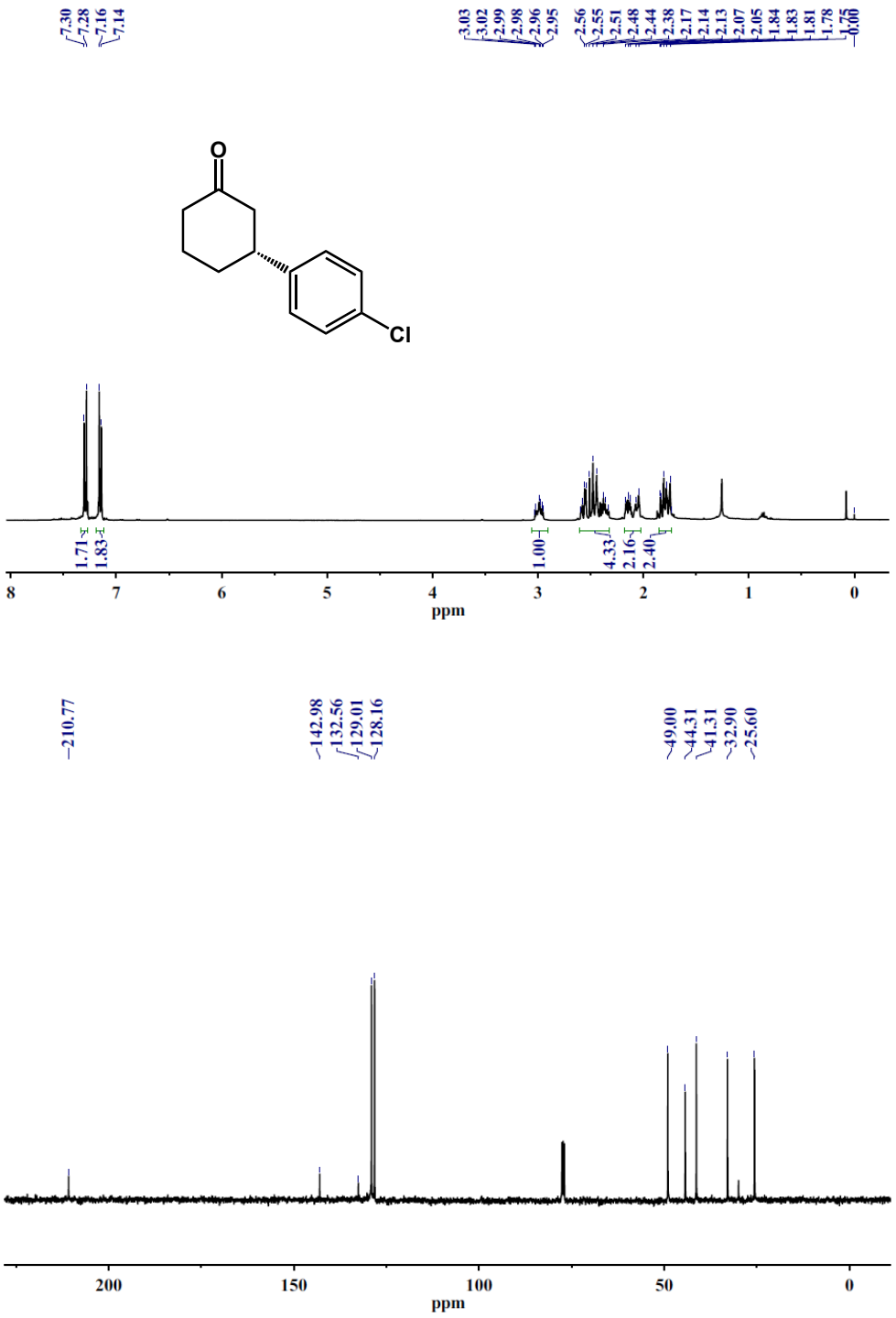
(*R*)-3-*p*-Tolyl-cyclohexanone: Purified by flash column chromatography (SiO_2, PE/EtOAc 9:1), obtained as colorless oil (33.5 mg, 89% yield). ^{1}HNMR (400MHz, CDCl3): δ:7.15-7.09 (m, 4H), 3.01-2.93 (m, 1H), 2.60-2.47 (m, 4H), 2.33 (s,3H), 2.16-2.04 (m, 2H), 1.88-1.73 (m, 2H). ^{13}CNMR (100MHz, $CDCl_3$): δ: 211.45, 141.65, 136.47, 129.57, 126.66, 49.30, 44.62, 41.42, 33.13, 25.79, 21.22.



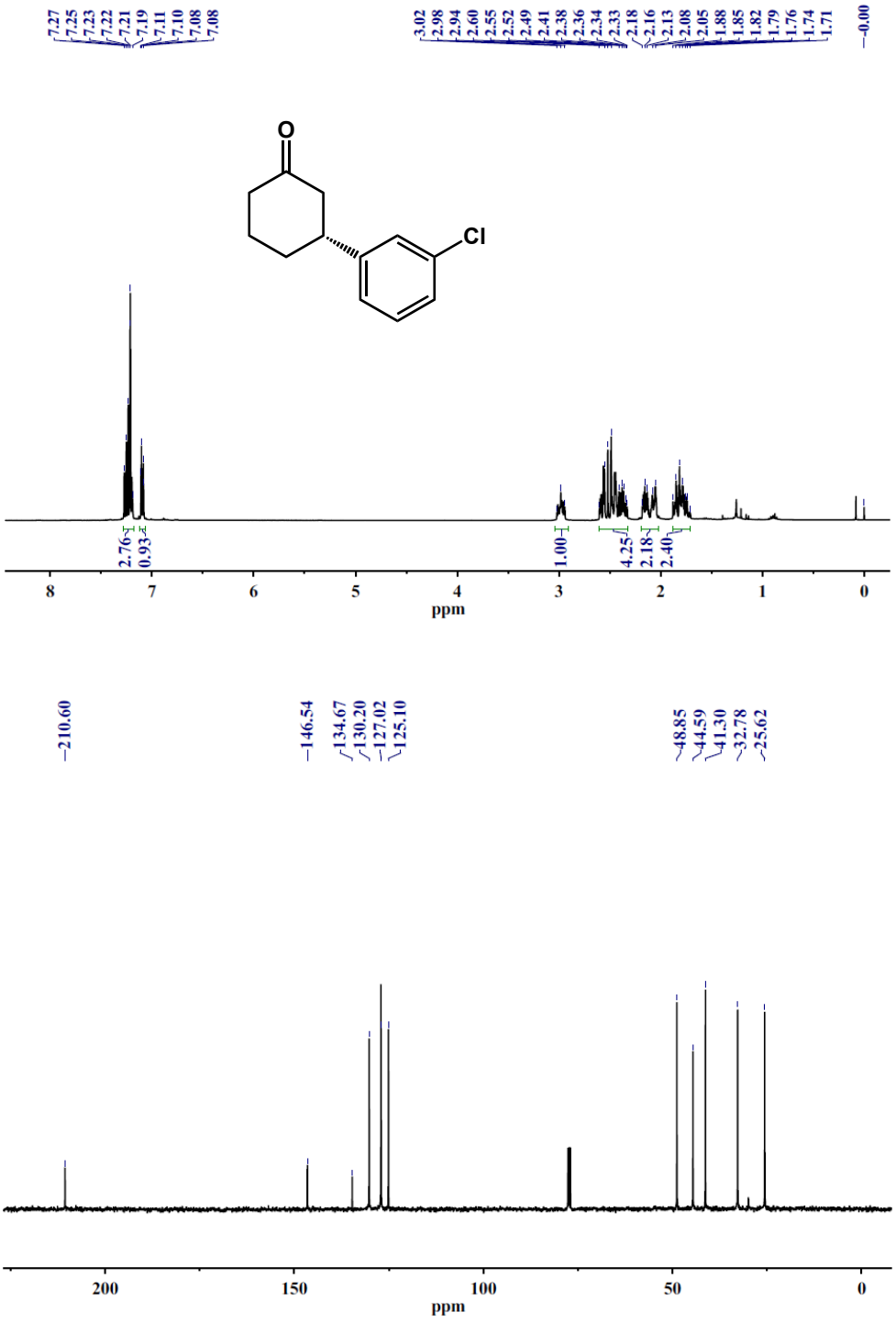
(*R*)-3-(4-Fluorophenyl)-cyclohexanone: Purified by flash column chromatography (SiO_2, PE/EtOAc 9:1), obtained as colorless oil (35.0 mg, 91% yield). ^{1}HNMR (400MHz, CDCl3): δ:7.19-7.16 (m, 2H), 7.03-6.98 (m, 2H) 3.04-2.96 (m, 1H), 2.60-2.33 (m, 4H), 2.17-2.05 (m, 2H), 1.87-1.74 (m, 2H). ^{13}CNMR (100MHz, $CDCl_3$): δ: 210.94, 162.97, 160.53, 140.27, 140.25, 128.24, 128.16, 115.75, 115.54, 49.27, 44.21, 41.32, 33.10, 25.61.



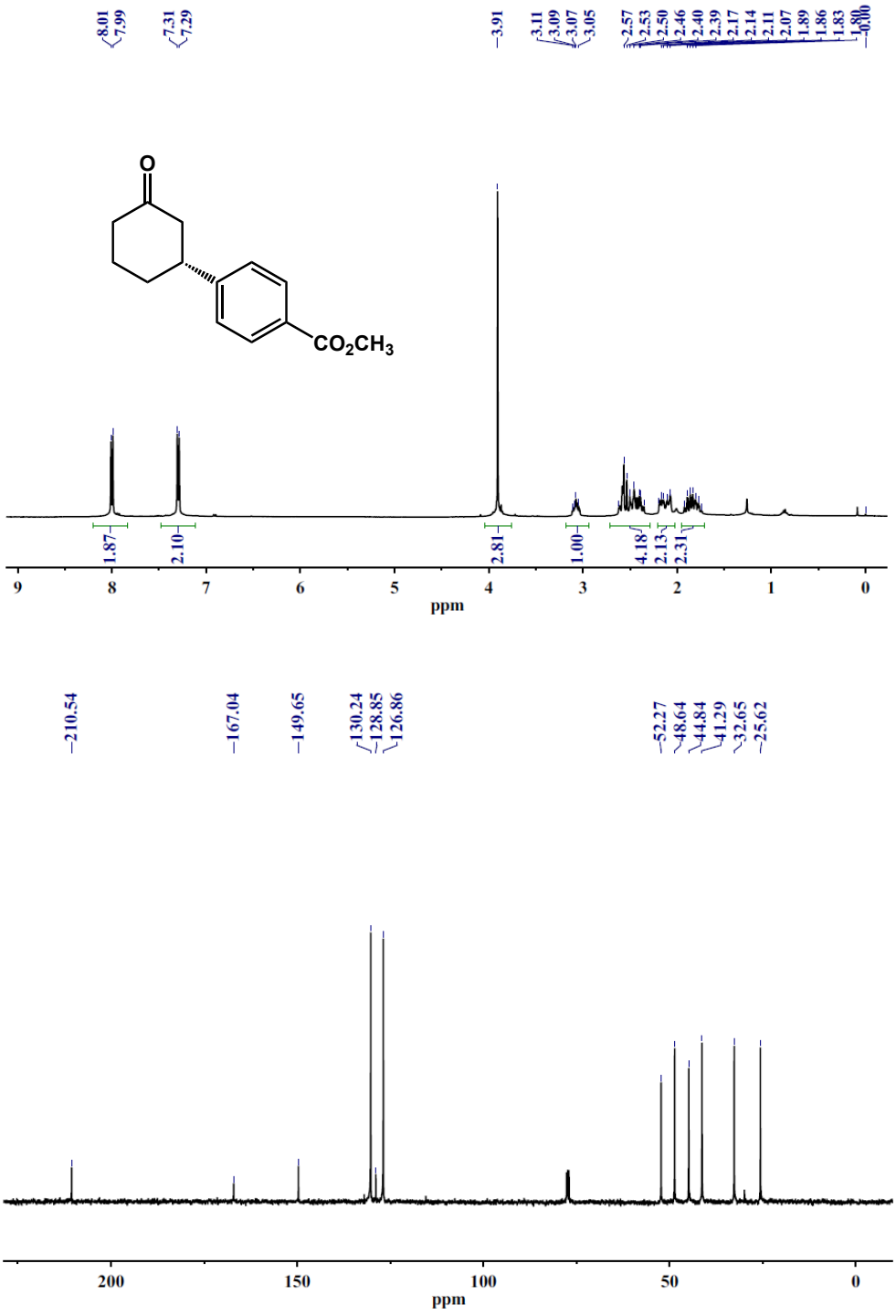
(*R*)-3-(4-(Trifluoromethyl)phenyl)-cyclohexanone: Purified by flash column chromatography (SiO_2, PE/EtOAc 15:1), obtained as colorless oil (44.6 mg, 92% yield). ^{1}HNMR (400MHz, CDCl3): δ:7.60-7.58 (d, 2H), 7.33-7.35 (d, 2H), 3.12-3.04 (m, 1H), 2.63-2.37 (m, 4H), 2.19-2.08 (m, 2H), 1.92-1.77 (m, 2H). ^{13}CNMR (100MHz, $CDCl_3$): δ: 210.43, 148.41, 127.19, 125.90, 48.69, 44.68, 41.28, 32.70, 25.58.



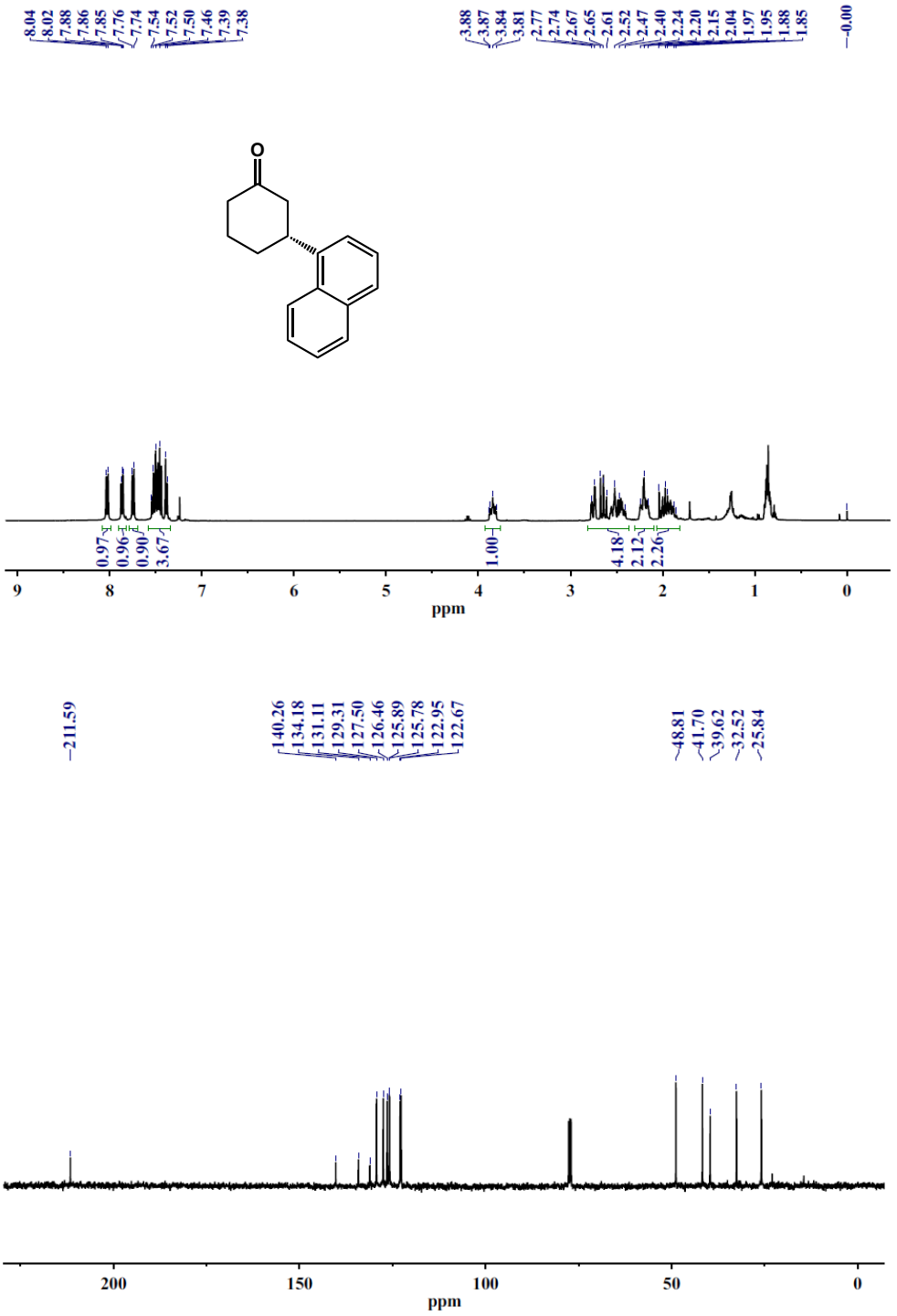
(*R*)-3-(4-Chlorophenyl)-cyclohexane: Purified by flash column chromatography (SiO_2, PE/EtOAc 9:1), obtained as colorless oil (37.6 mg, 90% yield). ^{1}HNMR (400MHz, CDCl3): δ:7.30-7.28 (d, 2H), 7.16-7.14 (d, 2H) 3.03-2.95 (m, 1H), 2.60-2.33 (m, 4H), 2.17-2.05 (m, 2H), 1.84-1.73 (m, 2H). ^{13}CNMR (100MHz, $CDCl_3$): δ: 210.77, 142.98, 132.56, 129.01, 128.16, 49.00, 44.31, 41.31, 32.90, 25.60.



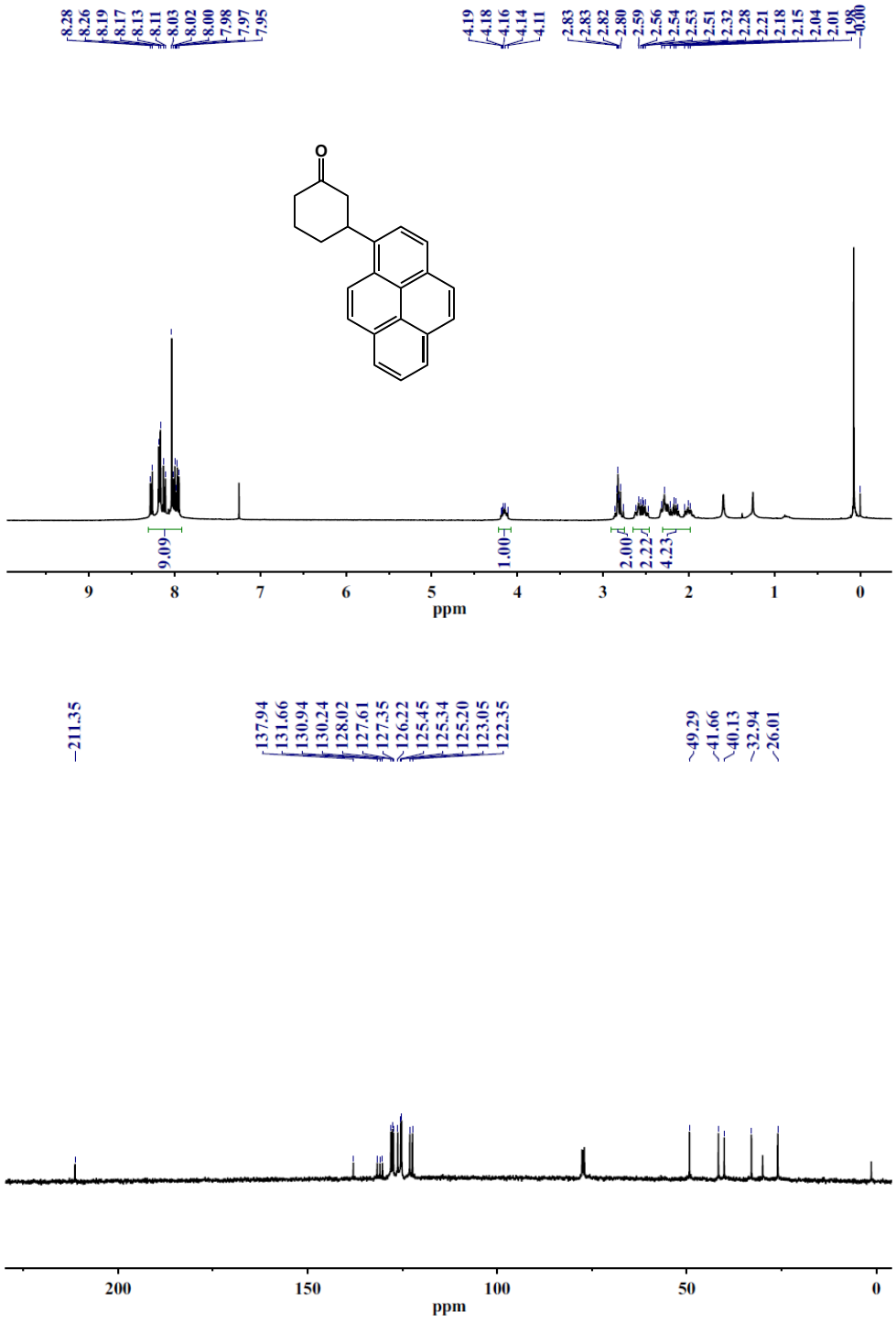
(*R*)-3-(3-Chlorophenyl)-cyclohexane: Purified by flash column chromatography (SiO_2, PE/EtOAc 9:1), obtained as colorless oil (38.0mg, 91% yield). ^{1}HNMR (400MHz, CDCl3): δ:7.27-7.19 (m, 3H), 7.11-7.08 (m, 1H), 3.02-2.94 (m, 1H), 2.60-2.33 (m, 4H), 2.18-2.05 (m, 2H), 1.88-1.71 (m, 2H). ^{13}CNMR (100MHz, $CDCl_3$): δ: 210.60, 146.54, 134.67, 130.20, 127.02, 125.10, 48.85, 44.59, 41.30, 32.78, 25.62.



(*R*)-3-(4-(Methoxycarbonyl)phenyl)-cyclohexanone: Purified by flash column chromatography (SiO_2, PE/EtOAc 5:1), obtained as colorless oil (40.9 mg, 88% yield). ^{1}HNMR (400MHz, CDCl3): δ:8.01-7.99 (d, 2H), 7.31-7.29 (d, 2H), 3.91(s, 1H), 3.11-3.05 (m, 1H), 2.62-2.35 (m, 4H), 2.19-2.07 (m, 2H), 1.92-1.74 (m, 2H). ^{13}CNMR (100MHz, $CDCl_3$): δ: 210.54, 167.04, 149.65, 130.24, 128.85, 126.86, 52.27, 48.64, 44.84, 41.29, 32.65, 25.62.

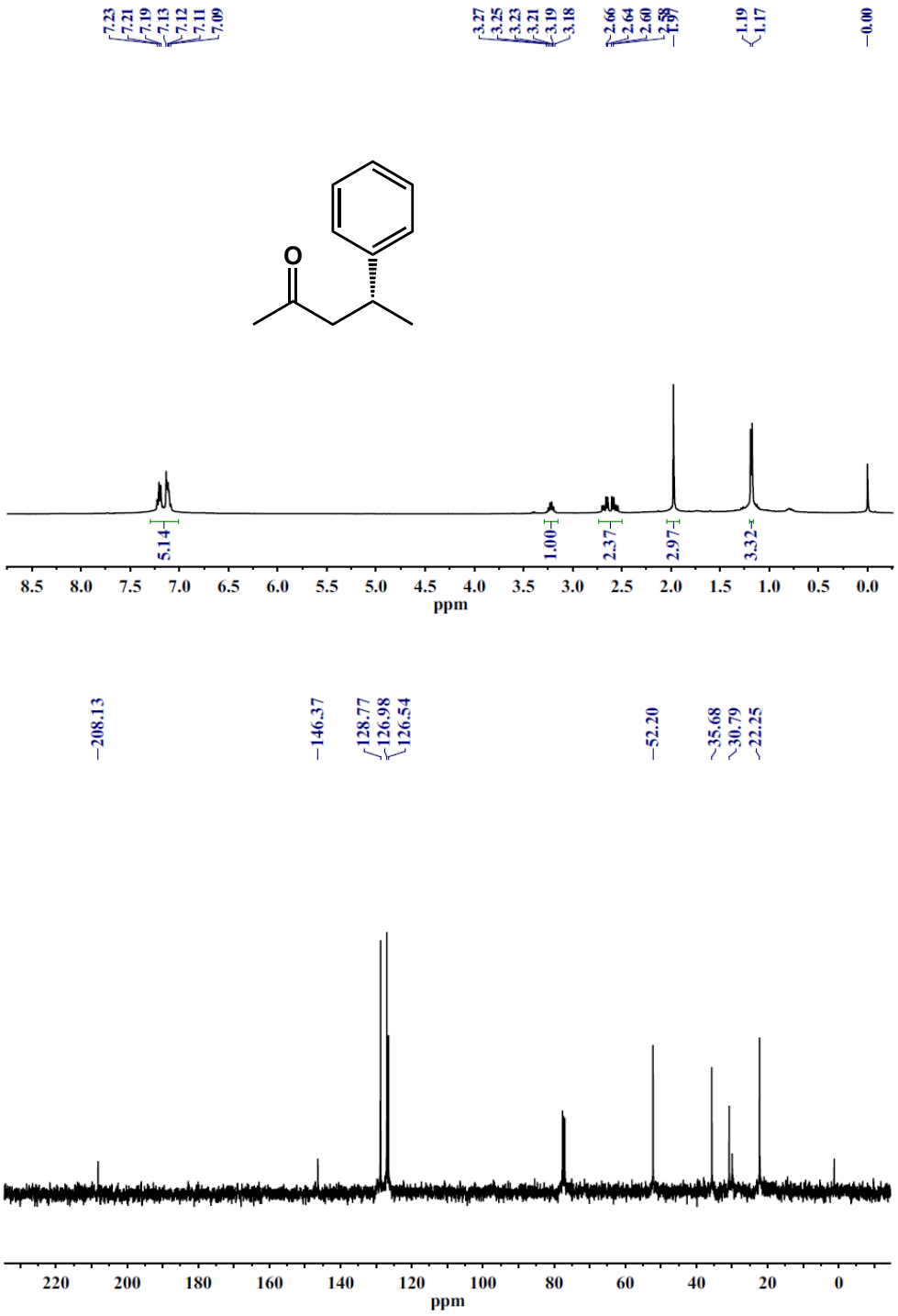


(*R*)-3-(Naphthalen-1-yl)cyclohexanone: Purified by flash column chromatography (SiO_2, PE/EtOAc 9:1), obtained as white solid (25.6 mg, 57% yield). ^{1}HNMR (400MHz, CDCl3): δ:8.04-8.02 (d, 1H), 7.88-7.85 (dd, 1H), 7.76-7.74 (d, 1H), 7.54-7.38 (m, 4H), 3.88-3.81 (m, 1H), 2.77-2.40 (m, 4H), 2.24-2.15 (m, 2H), 2.04-1.85 (m, 2H). ^{13}CNMR (100MHz, $CDCl_3$): δ: 211.59, 140.26, 134.18, 131.11, 129.31, 127.50, 126.46, 125.89, 125.78, 122.95, 122.67, 48.81, 41.70, 39.62, 32.52, 25.84.

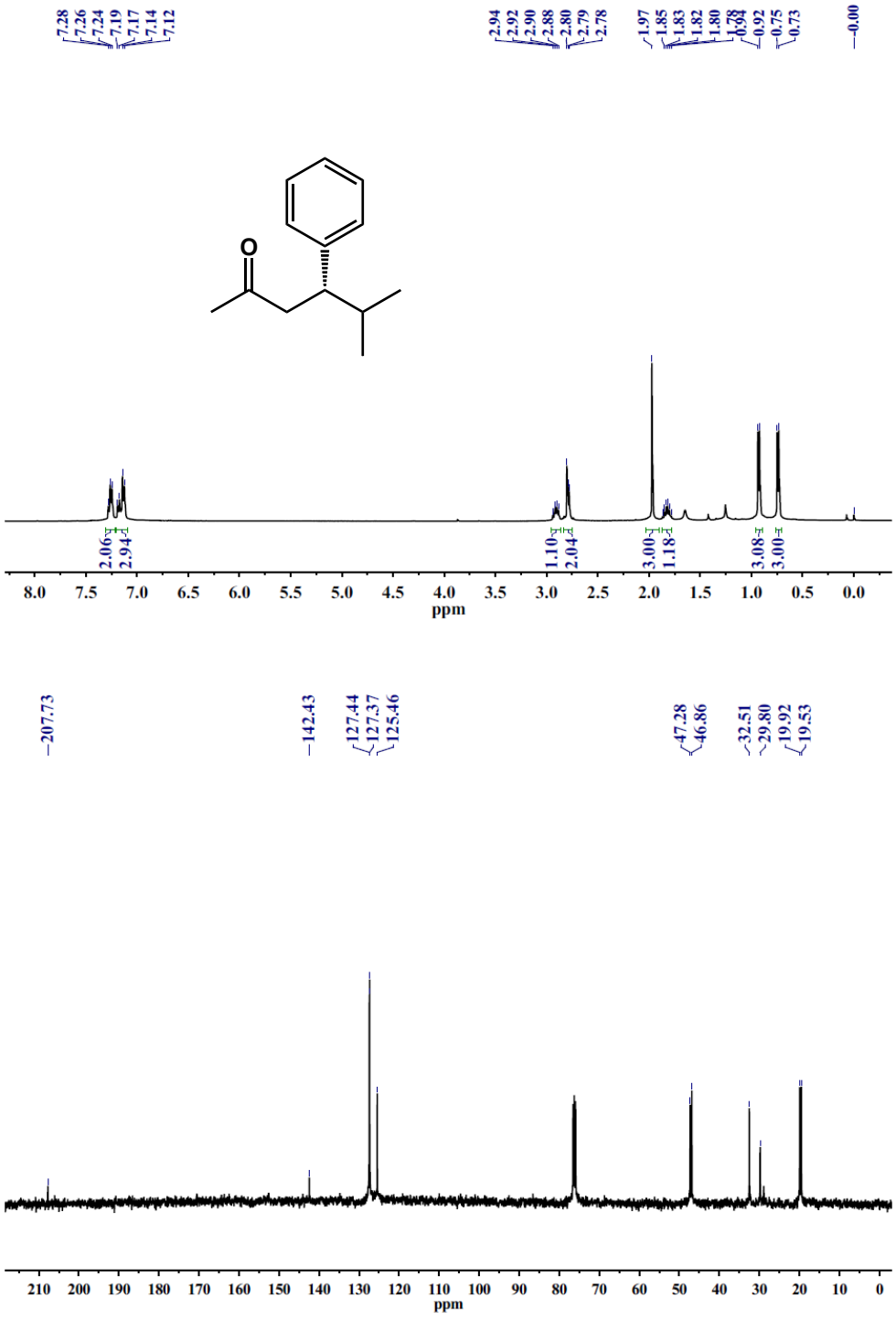


Homogeneous catalysis

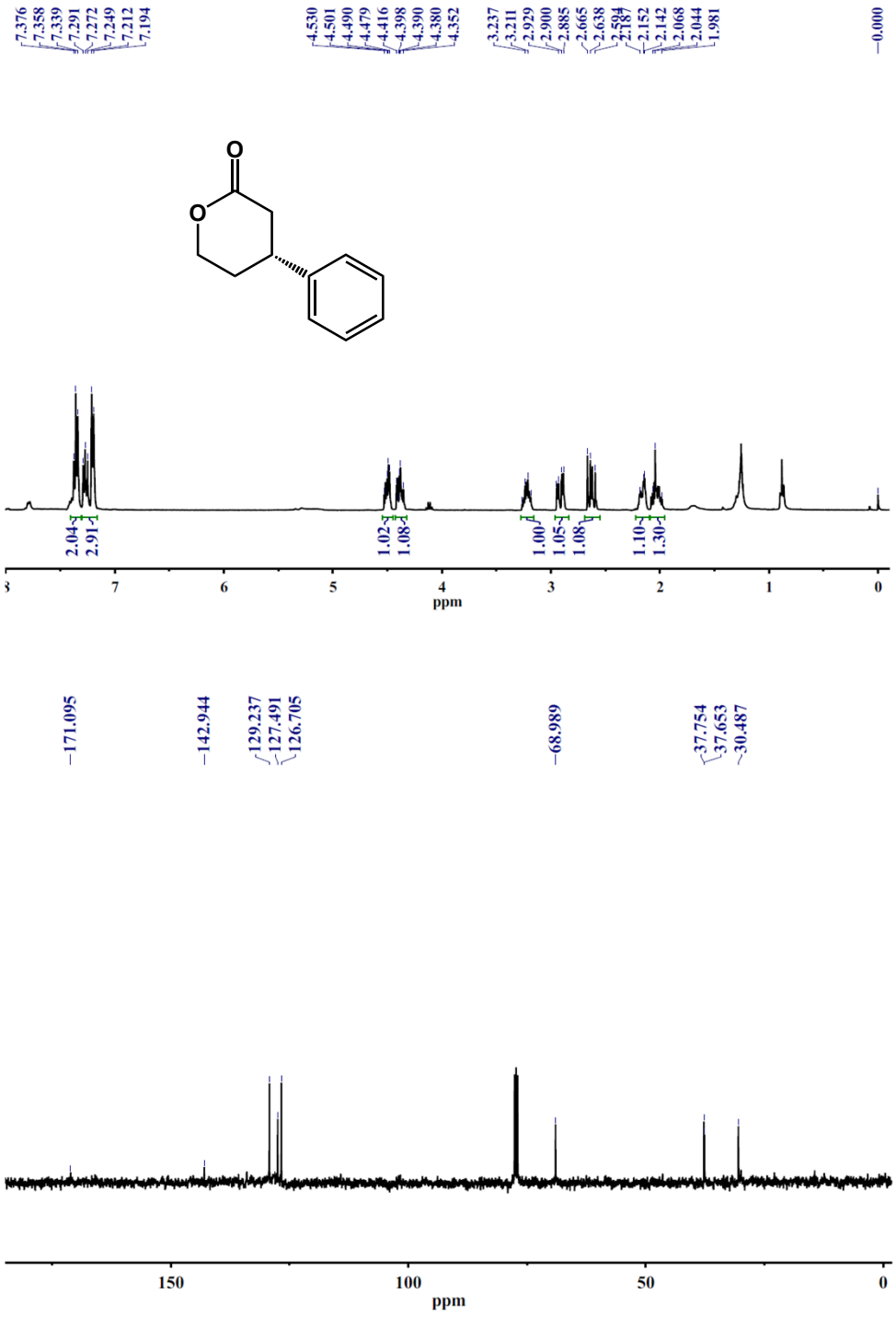
3-(1-Pyrenyl)cyclohexanone: ^{1}HNMR (400MHz, $CDCl_3$): δ: 8.28-7.95 (m, 9H), 4.19-4.11 (m, 1H), 2.86-2.76 (m, 2H), 2.62-2.47 (m, 2H), 2.32-1.98 (m, 4H), ^{13}CNMR (100MHz, $CDCl_3$): δ: 211.35, 137.94, 131.66, 130.94, 130.24, 128.02, 127.61, 127.35, 126.22, 125.45, 125.34, 125.20, 123.05, 122.35, 49.22, 41.66, 40.13, 32.94, 26.01.



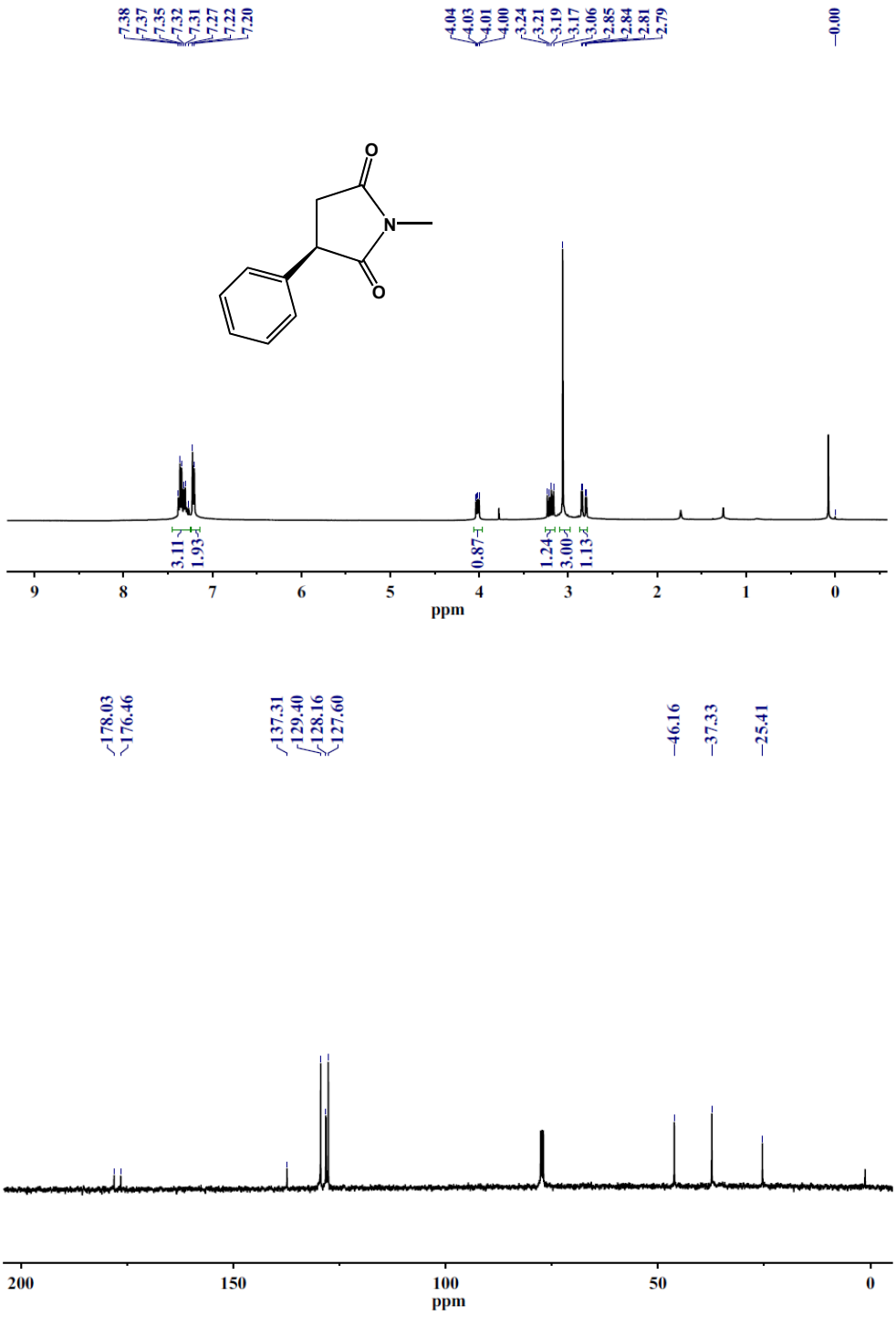
(*R*)-4-phenylpentan-2-one: Purified by flash column chromatography (SiO_2, PE/EtOAc 5:1), obtained as colorless oil (27.2 mg, 84% yield). ^{1}HNMR (400 MHz, $CDCl_3$): δ:7.23-7.09 (m, 5H), 3.27-3.18 (m, 1H), 2.70-2.54 (m, 2H), 1.97 (s, 3H), 1.19-1.17 (d, 3H). ^{13}CNMR (100 MHz, $CDCl_3$): δ: 208.13, 146.37, 128.77, 126.98, 126.54, 52.20, 35.68, 30.79, 22.25.



(*R*)-4-Phenyl-5-methyl-hexan-2-one: Purified by flash column chromatography (SiO_2, PE/EtOAc 5:1), obtained as colorless oil (20.9 mg, 55% yield). ^{1}HNMR (400 MHz, $CDCl_3$): δ:7.28-7.24 (m, 2H), 7.19-7.12 (m, 3H), 2.94-2.88 (m, 1H), 2.80-2.78 (m, 2H), 1.97(s, 3H), 1.87-1.78 (m, 1H), 0.94-0.92 (d, 3H), 0.75-0.73 (d, 3H). ^{13}CNMR (100 MHz, $CDCl_3$): δ: 207.73, 142.43, 127.44, 127.37, 125.46 47.28, 46.86, 32.51, 29.80, 19.92, 19.53.



(*R*)-4-phenyl-tetrahydro-2H-pyran-2-one: Purified by flash column chromatography (SiO_2, PE/EtOAc 5:1), obtained as colorless oil (25.7 mg, 73% yield).^{1}HNMR (400MHz, CDCl3): δ:7.38-7.34 (m, 2H), 7.29-7.19 (m, 3H), 4.53-4.48 (m, 1H), 4.42-4.35 (m, 1H), 3.26-3.18 (m, 1H), 2.95-2.88 (m, 1H), 2.67-2.59 (m, 1H), 2.19-2.14 (m, 1H), 2.07-1.98 (m, 1H). ^{13}CNMR (100MHz, $CDCl_3$): δ: 171.10, 142.94, 129.24, 127.49, 126.70, 68.99, 37.75, 37.65, 30.49.

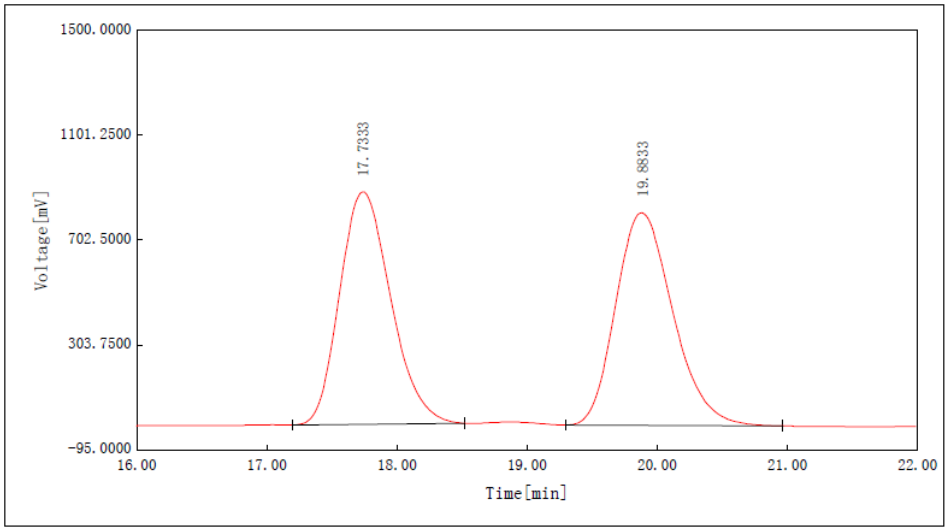


(*R*)-1-Methyl-3-phenyl-pyrrolidine-2,5-dione: Purified by flash column chromatography (SiO_2, PE/EtOAc 5:1), obtained as colorless oil (29.5 mg, 78% yield). ^{1}HNMR (400MHz, CDCl3): δ:7.38-7.27 (m, 3H), 7.22-7.20 (m, 2H), 4.53-4.48 (m, 1H), 4.04-4.00 (dd, 1H), 3.24-3.17 (dd, 1H), 3.06 (s, 3H), 2.85-2.79 (dd, 1H). ^{13}CNMR (100MHz, $CDCl_3$): δ: 178.03, 176.46, 137.31, 129.40, 128.16, 127.60, 46.16, 37.33, 25.41.

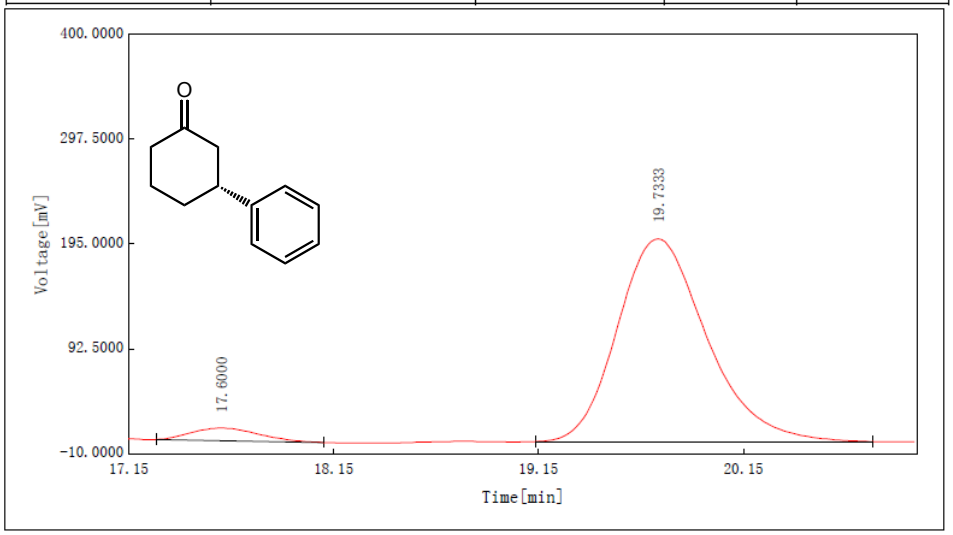
11. Figure S7. HPLC of the catalytic products

(*R*)-3-Phenyl-cyclohexanone

Column: CHIRALCEL AD-H column (4.6 mm × 25 cm) from Daicel. Column temperature: 25°C. hexane/iPrOH = 90/10; flow rate= 0.3 mL/min; t_{minor} = 17.600 min, t_{major} = 19.733 min; ee = 91%.



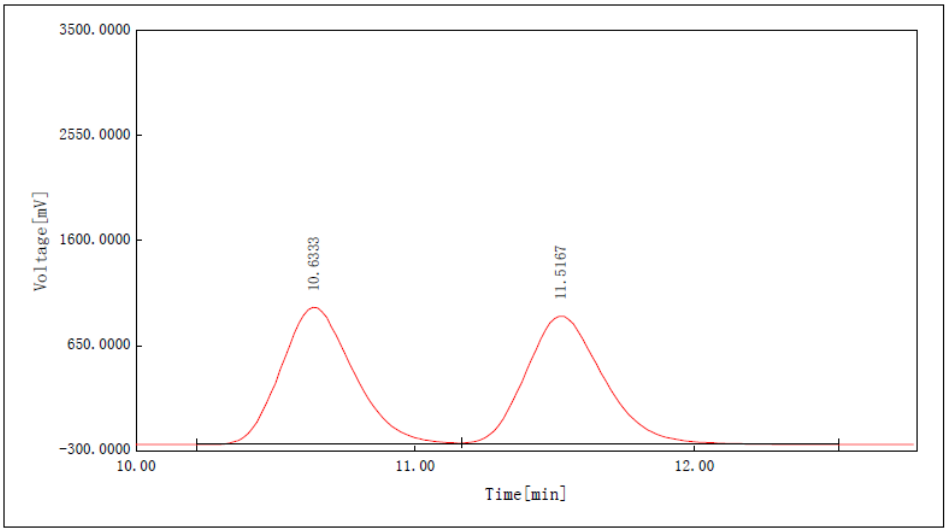
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	17.7333	24061.3323	FF	49.3516
2	19.8833	24693.5409	FF	50.6484
The Total		48754.8733		



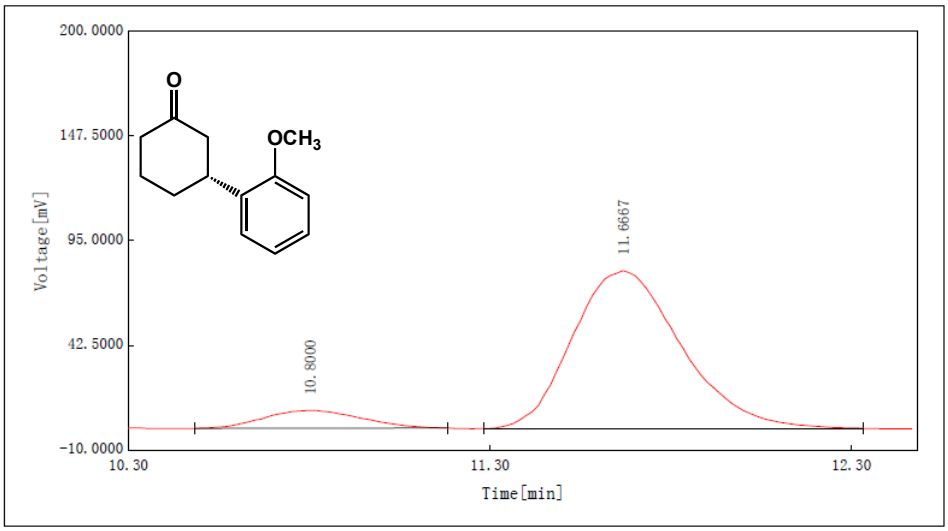
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	17.6000	278.9646	FF	4.4402
2	19.7333	6003.7155	BB	95.5598
The Total		6282.6801		

(*R*)-3-(2-methoxyphenyl)-cyclohexanone

Column: CHIRALCEL AD-H column (4.6 mm × 25 cm) from Daicel. Column temperature: 25°C. hexane/iPrOH = 95/5; flow rate= 0.7 mL/min; t_{minor} = 10.800 min, t_{major} = 11.667 min; ee = 82%.



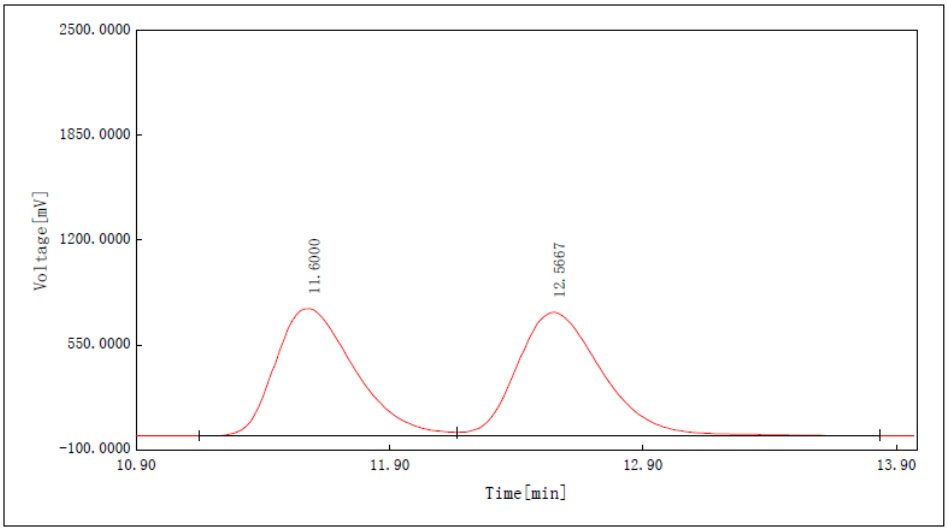
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	10.6333	22544.8633	BB	49.9572
2	11.5167	22583.4872	BB	50.0428
The Total		45128.3505		



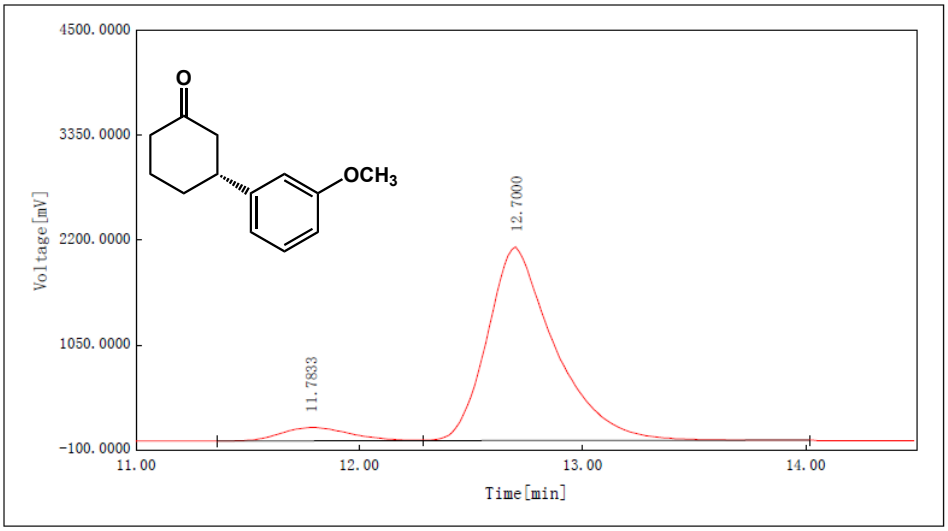
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	10.8000	166.9505	BB	9.1805
2	11.6667	1651.5906	BB	90.8195
The Total		1818.5412		

(*R*)-3-(3-methoxyphenyl)-cyclohexanone

Column: CHIRALCEL AD-H column (4.6 mm × 25 cm) from Daicel. Column temperature: 25°C. hexane/iPrOH = 97/3; flow rate= 1.0 mL/min; t_{minor} = 11.783 min, t_{major} = 12.700 min; ee = 87%.



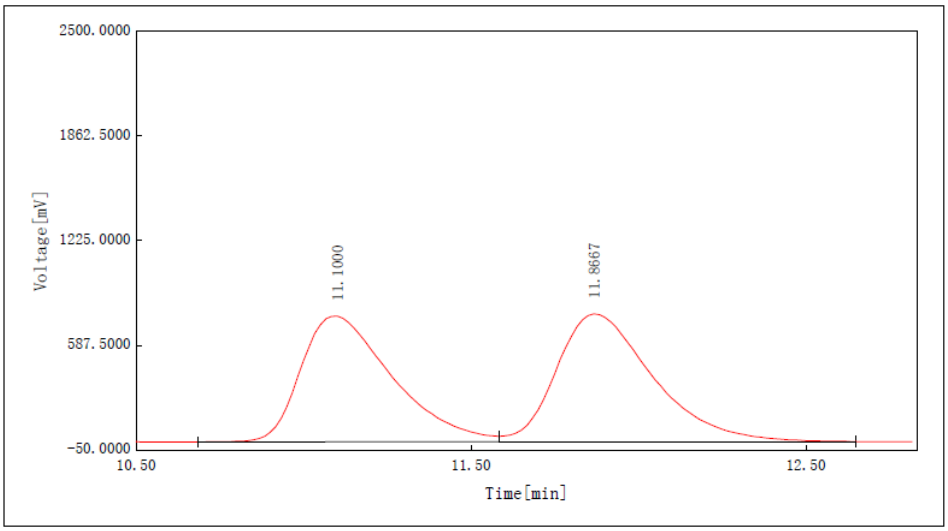
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	11.6000	17059.6424	BB	48.8909
2	12.5667	17833.6722	BB	51.1091
The Total		34893.3146		



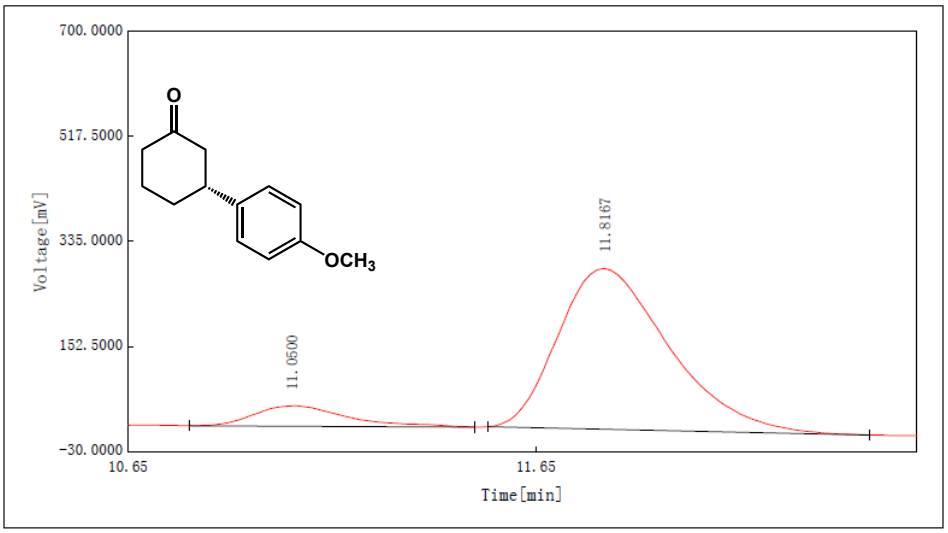
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	11.7833	3160.6973	BB	6.6066
2	12.7000	44680.9476	BB	93.3934
The Total		47841.6449		

(*R*)-3-(4-methoxyphenyl)-cyclohexanone

Column: CHIRALCEL AD-H column (4.6 mm × 25 cm) from Daicel. Column temperature: 25°C. hexane/iPrOH = 97/3; flow rate= 1.0 mL/min; t_{minor} = 11.050 min, t_{major} = 11.817 min; ee = 81%.



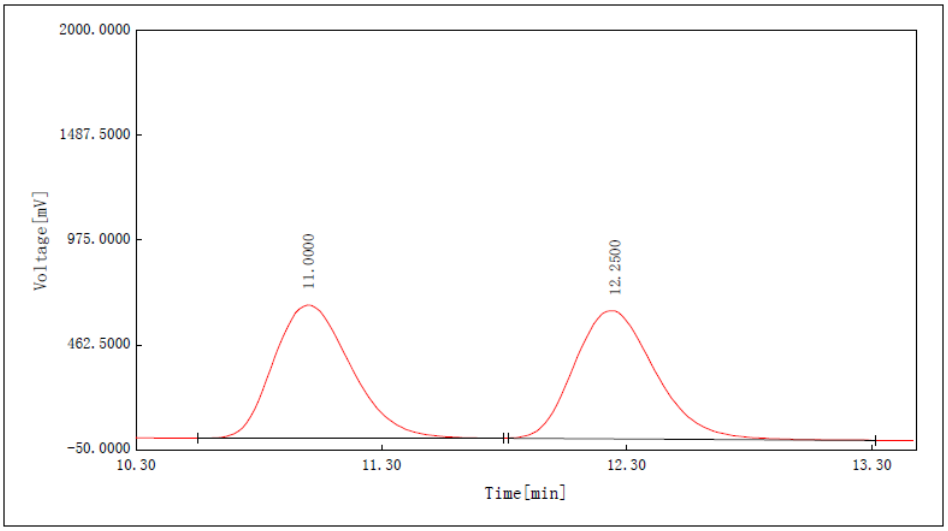
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	11.1000	14474.3075	BB	48.2587
2	11.8667	15518.8260	BB	51.7413
The Total		29993.1335		



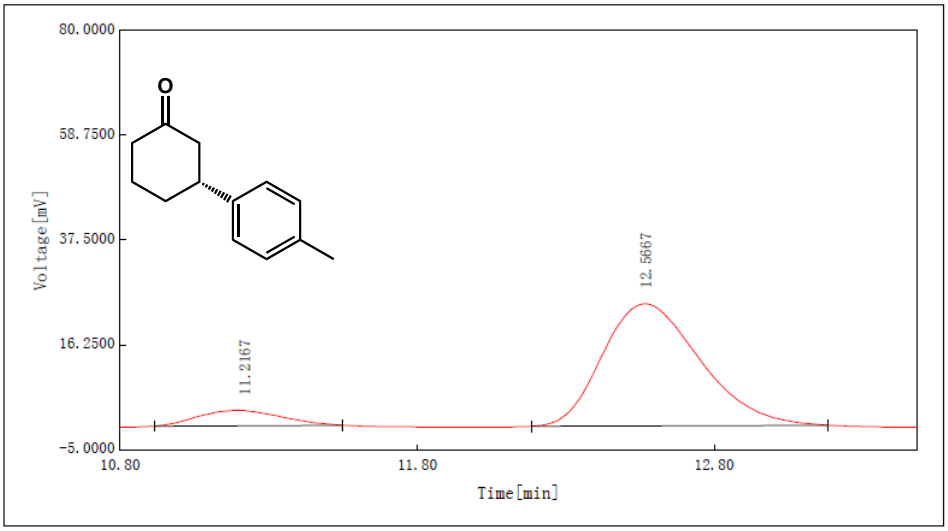
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	11.0500	555.3518	BB	9.5294
2	11.8167	5272.4128	BB	90.4706
The Total		5827.7647		

(*R*)-3-*p*-Tolyl-cyclohexanone

Column: CHIRALCEL AD-H column (4.6 mm × 25 cm) from Daicel. Column temperature: 25°C. hexane/iPrOH = 97/3; flow rate= 0.6 mL/min; t_{minor} = 11.217 min, t_{major} = 12.567 min; ee = 81%.



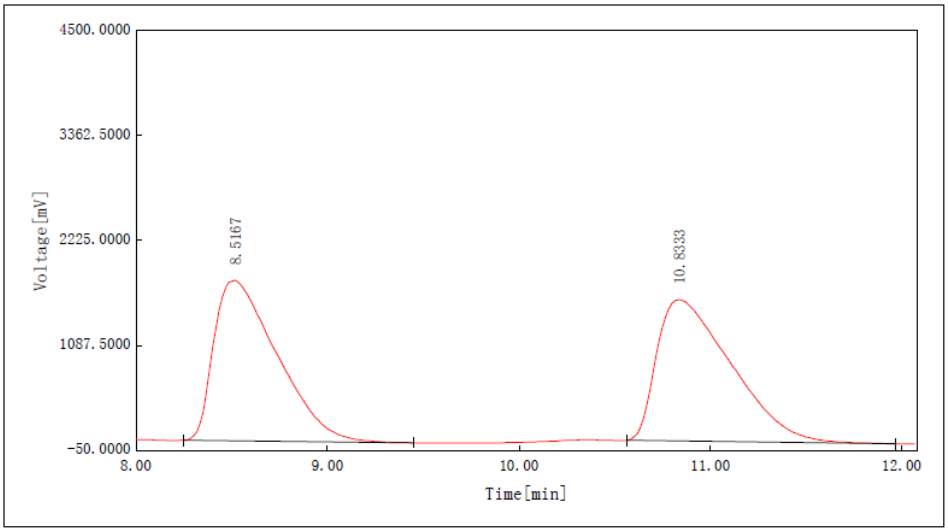
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	11.0000	14251.9198	BB	49.9154
2	12.2500	14300.2211	BB	50.0846
The Total		28552.1408		



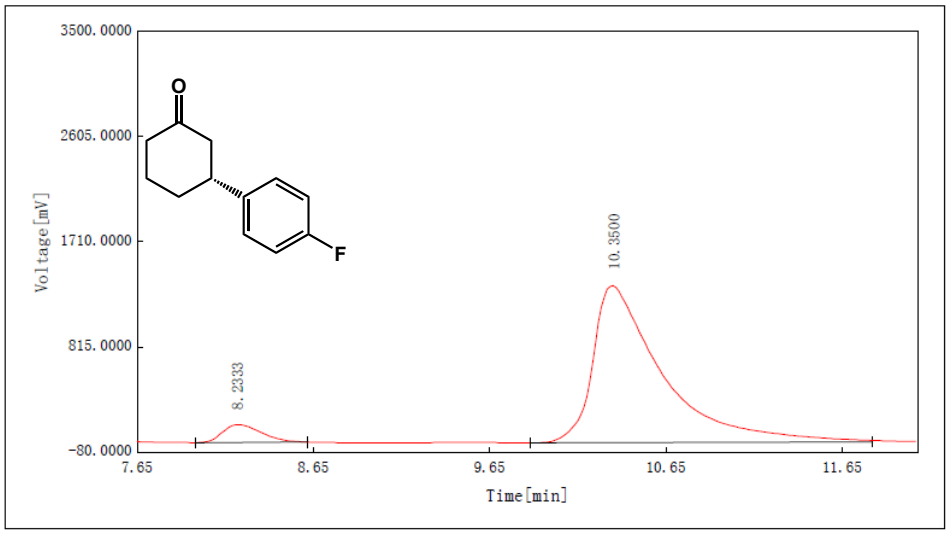
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	11.2167	60.0387	BB	9.5934
2	12.5667	565.7946	BB	90.4066
The Total		625.8333		

(*R*)-3-(4-Fluorophenyl)-cyclohexanone

Column: CHIRALCEL AD-H column (4.6 mm × 25 cm) from Daicel. Column temperature: 25°C. hexane/iPrOH = 97/3; flow rate= 1.0 mL/min; t_{minor} = 8.233 min, t_{major} = 10.350 min; ee = 88%.



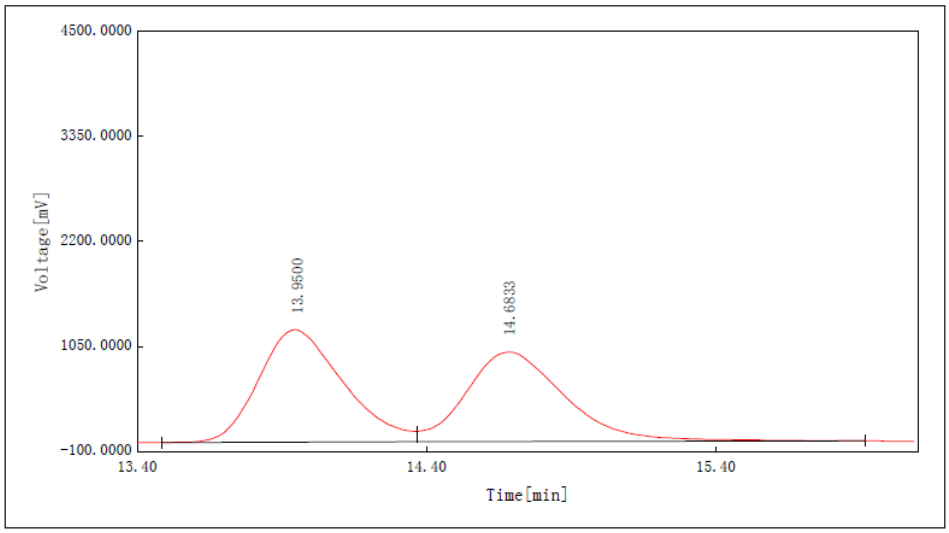
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	8.5167	39825.1101	BB	49.1697
2	10.8333	41170.1511	BB	50.8303
The Total		80995.2612		



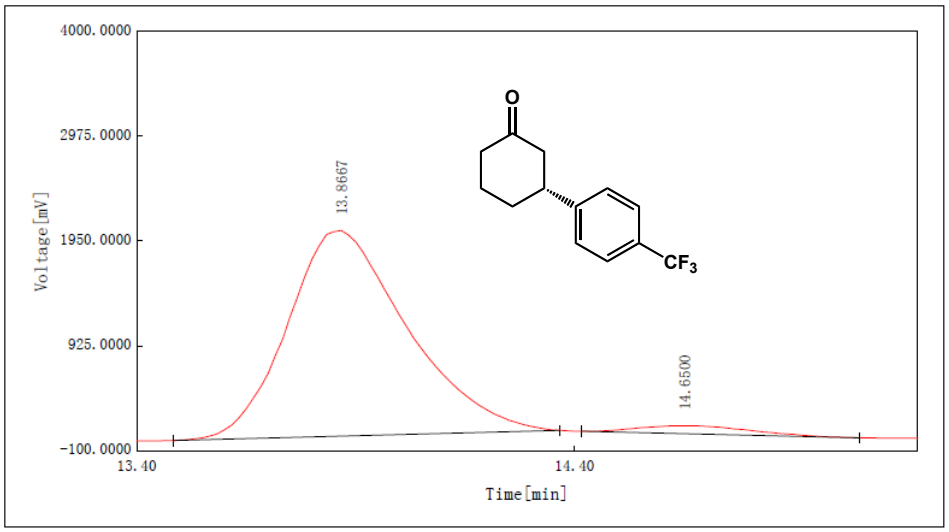
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	8.2333	2302.6773	BB	5.9191
2	10.3500	36599.9181	BB	94.0809
The Total		38902.5953		

(*R*)-3-(4-(Trifluoromethyl)phenyl)-cyclohexanone

Column: CHIRALCEL OD-H column (4.6 mm × 25 cm) from Daicel. Column temperature: 25°C. hexane/iPrOH = 90/10; flow rate= 0.5 mL/min; t_{major} = 13.867 min, t_{minor} = 14.650 min; ee = 93%.



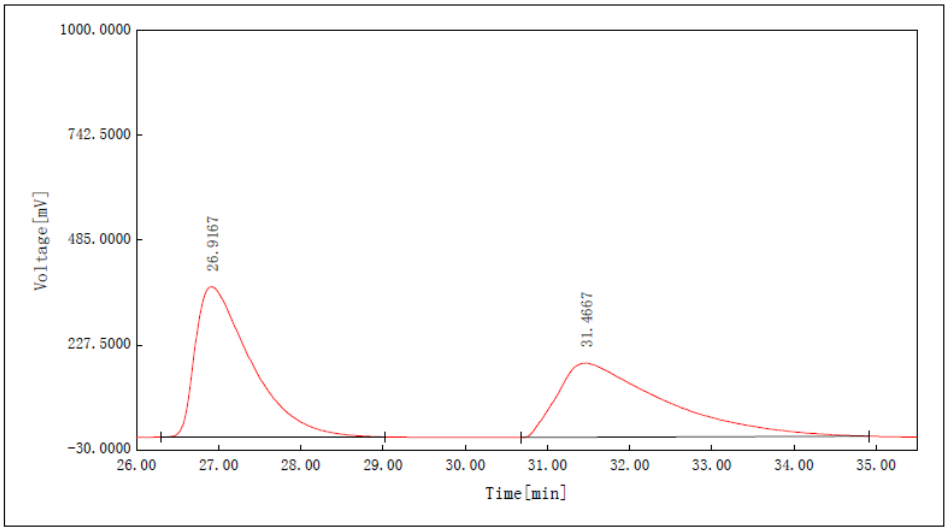
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	13.9500	24906.4181	BB	51.6249
2	14.6833	23338.5150	BB	48.3751
The Total		48244.9331		



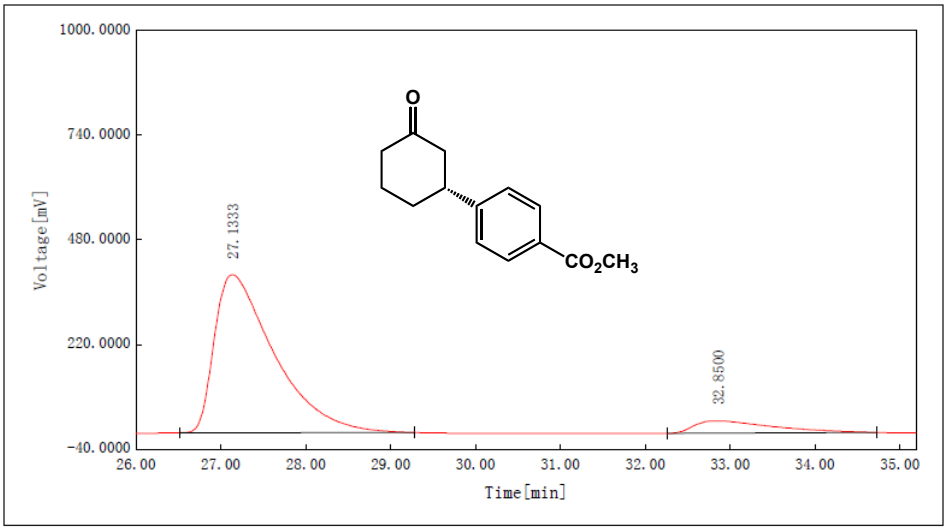
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	13.8667	38178.9101	BB	96.4463
2	14.6500	1406.7724	BB	3.5537
The Total		39585.6826		

(*R*)-3-(4-(Methoxycarbonyl)phenyl)-cyclohexanone

Column: CHIRALCEL AD-H column (4.6 mm × 25 cm) from Daicel. Column temperature: 25°C. hexane/iPrOH = 93/7; flow rate= 0.6 mL/min; t_{major} = 27.133 min, t_{minor} = 32.850 min; ee = 82%.



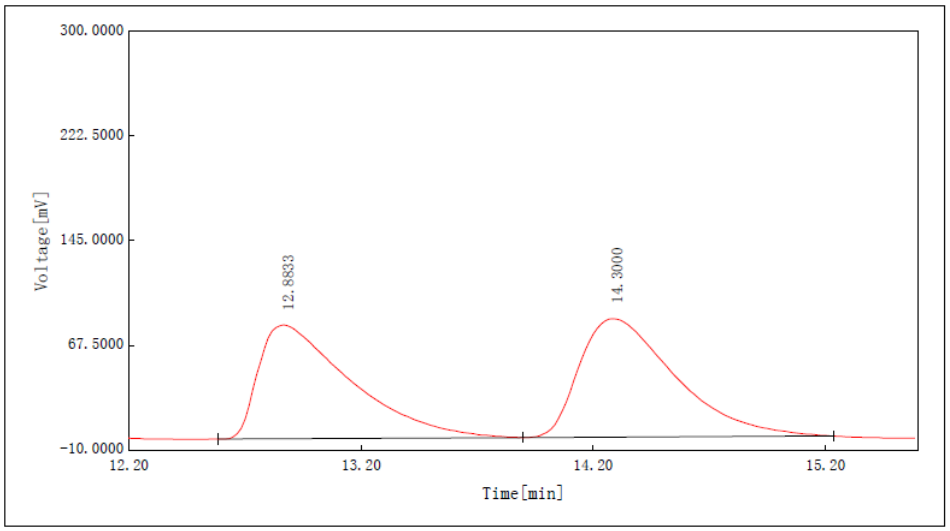
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	26.9167	17358.3386	BB	51.4688
2	31.4667	16367.5787	BB	48.5312
The Total		33725.9173		



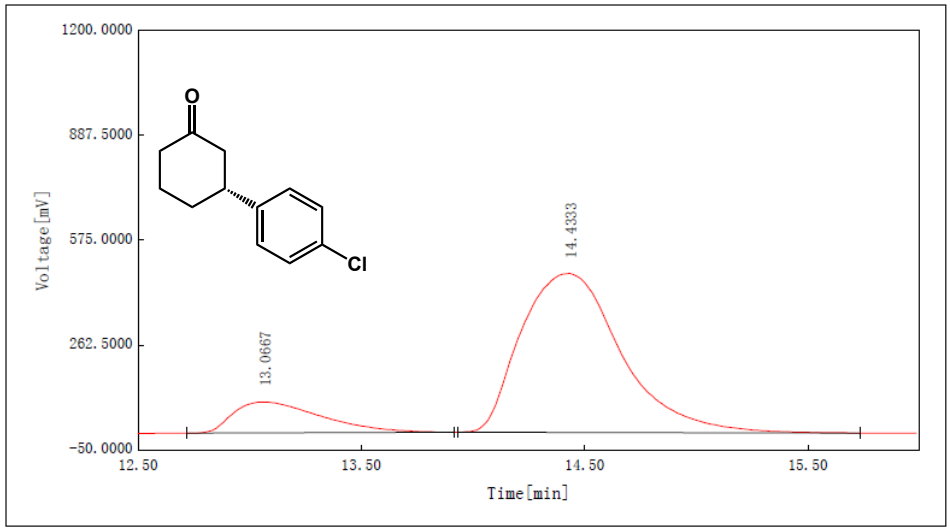
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	27.1333	19236.6204	BB	90.7485
2	32.8500	1961.1086	BB	9.2515
The Total		21197.7290		

(*R*)-3-(4-Chlorophenyl)-cyclohexane

Column: CHIRALCEL AD-H column (4.6 mm × 25 cm) from Daicel. Column temperature: 25°C. hexane/iPrOH = 98/2; flow rate= 0.8 mL/min; t_{minor} = 13.067 min, t_{major} = 14.433 min; ee = 71%.



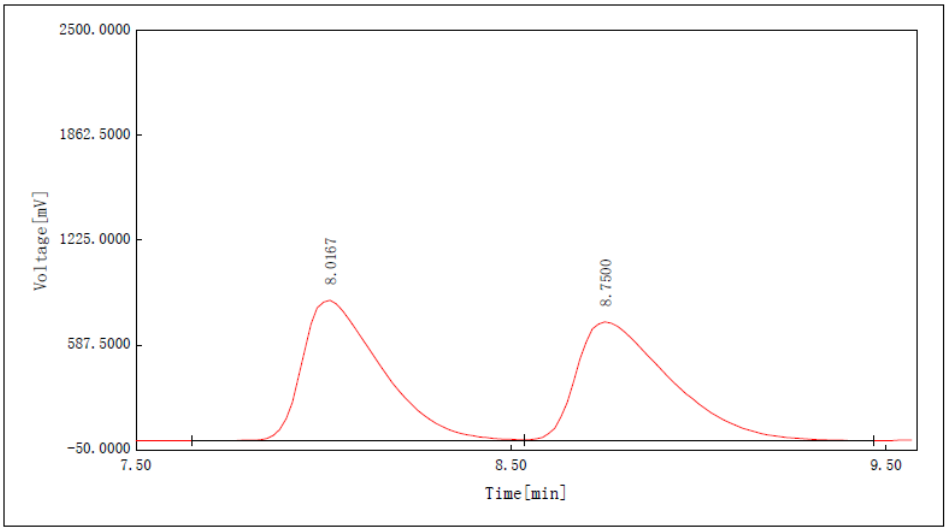
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	12.8833	2317.9003	BB	47.9825
2	14.3000	2512.8246	BB	52.0175
The Total		4830.7249		



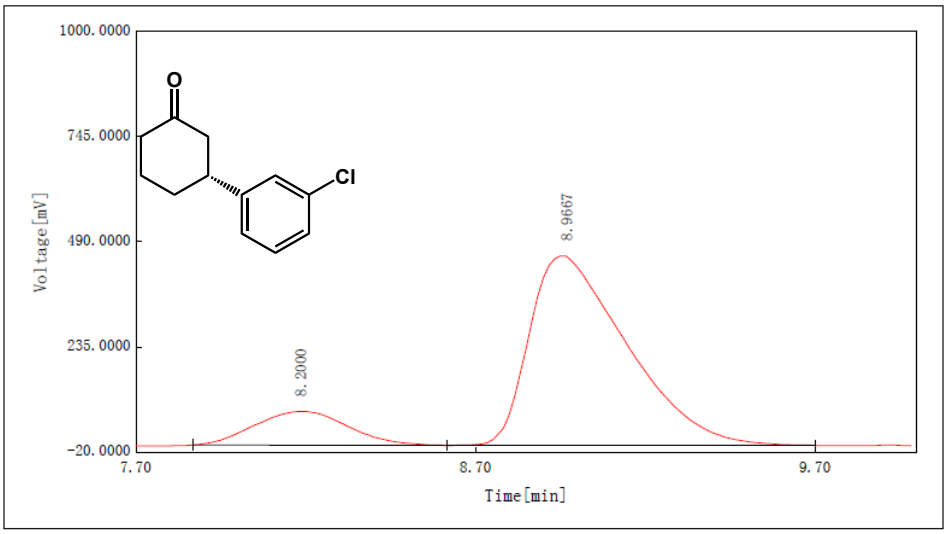
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	13.0667	2516.8729	BB	14.5534
2	14.4333	14777.2284	BB	85.4466
The Total		17294.1013		

(*R*)-3-(3-Chlorophenyl)-cyclohexane

Column: CHIRALCEL AD-H column (4.6 mm × 25 cm) from Daicel. Column temperature: 25°C. hexane/iPrOH = 90/10; flow rate= 0.7 mL/min; t_{minor} = 8.200 min, t_{major} = 8.967 min; ee = 71%.



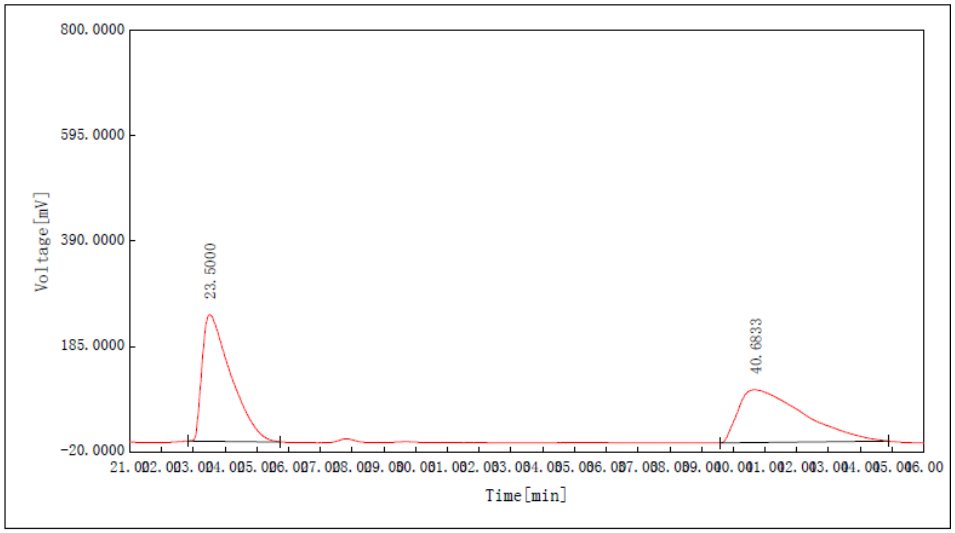
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	8.0167	12423.8823	BB	49.9793
2	8.7500	12434.1582	BB	50.0207
The Total		24858.0405		



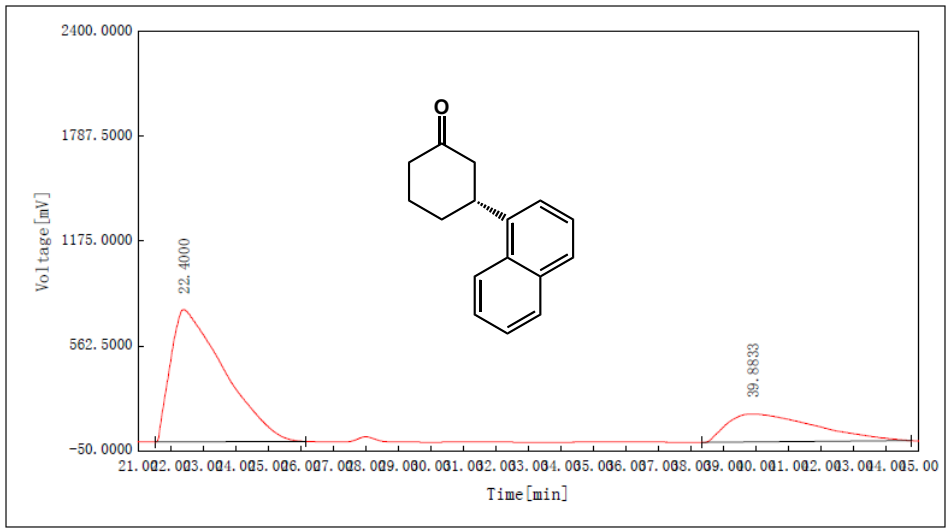
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	8.2000	1545.9400	FF	14.4716
2	8.9667	9136.6656	FF	85.5284
The Total		10682.6056		

(*R*)-3-(Naphthalen-1-yl)cyclohexanone

Column: CHIRALCEL AS-H column (4.6 mm × 25 cm) from Daicel. Column temperature: 25°C. hexane/iPrOH = 98/2; flow rate= 1.0 mL/min; t_{major} = 22.400 min, t_{minor} = 39.833 min; ee = 48%.



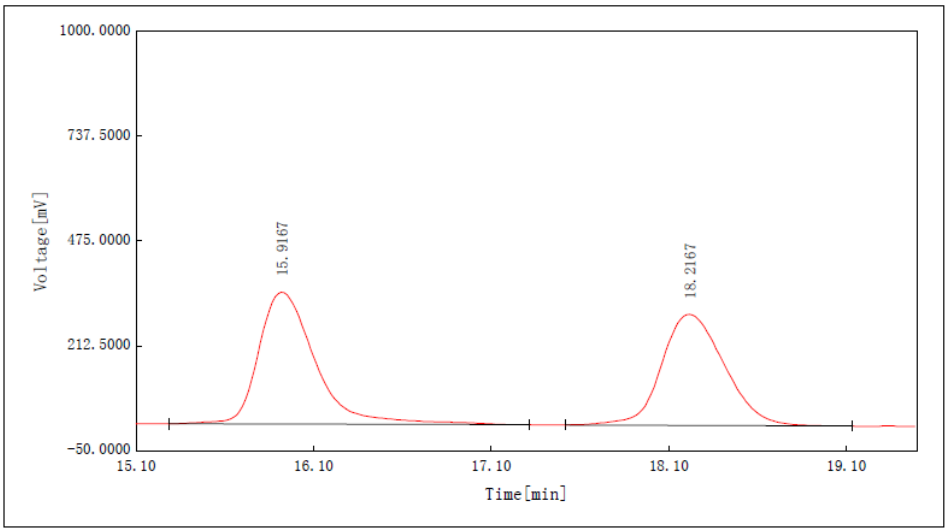
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	23.5000	15529.1114	BB	51.3022
2	40.6833	14740.7360	BB	48.6978
The Total		30269.8474		



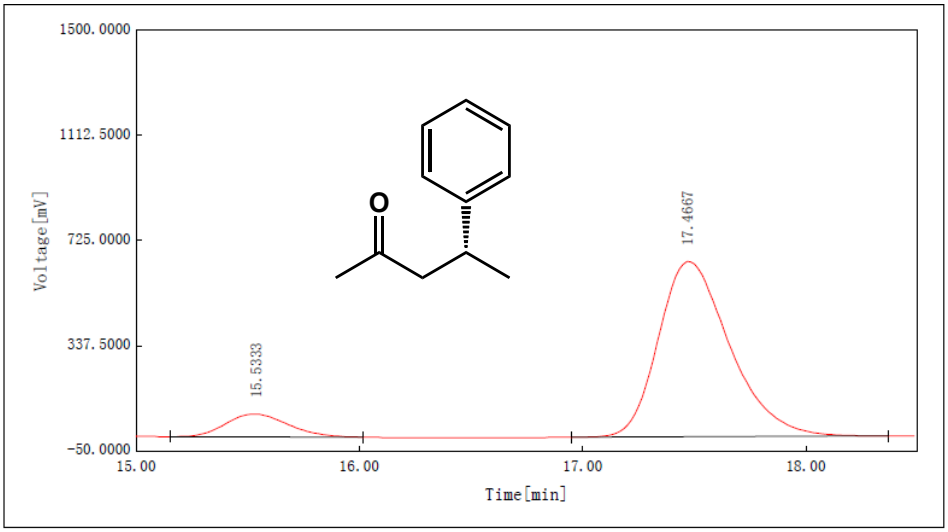
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	22.4000	88349.2605	BB	74.1919
2	39.8833	30732.8977	FF	25.8081
The Total		119082.1582		

(*R*)-4-phenylpentan-2-one

Column: CHIRALCEL AS-H column (4.6 mm × 25 cm) from Daicel. Column temperature: 25°C. hexane/iPrOH = 98/2; flow rate= 0.5 mL/min; t_{minor} = 15.533 min, t_{major} = 17.467 min; ee = 80%.



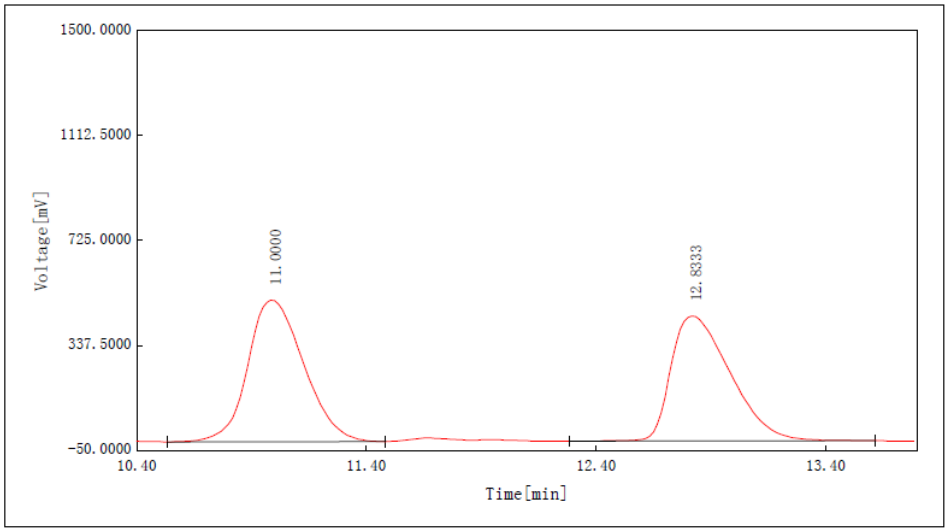
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	15.9167	7352.6642	BB	51.9024
2	18.2167	6813.6584	BB	48.0976
The Total		14166.3225		



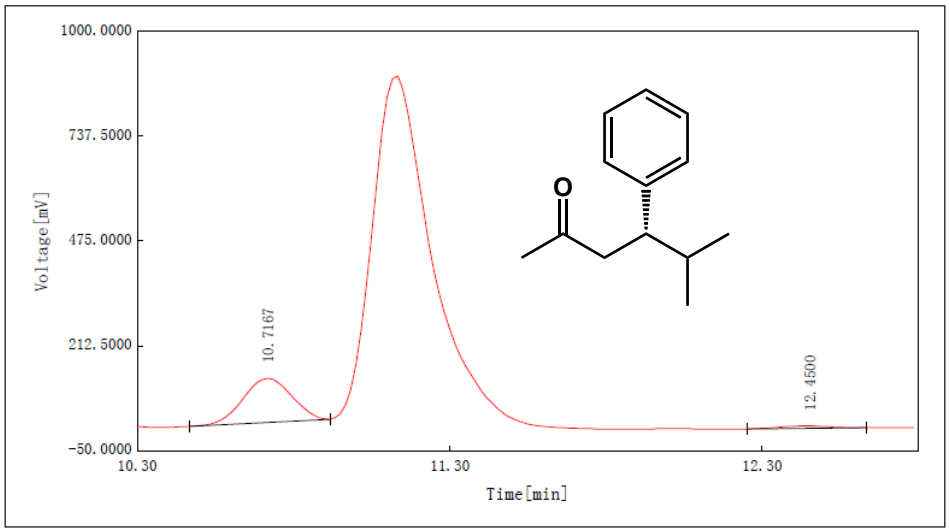
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	15.5333	1628.3591	BB	10.2069
2	17.4667	14325.0906	BB	89.7931
The Total		15953.4496		

(*R*)-4-Phenyl-5-methyl-hexan-2-one

Column: CHIRALCEL OD-H column (4.6 mm × 25 cm) from Daicel. Column temperature: 25°C. hexane/iPrOH = 99/1; flow rate= 0.7 mL/min; t_{major} = 10.717 min, t_{minor} = 12.450 min; ee = 90%.



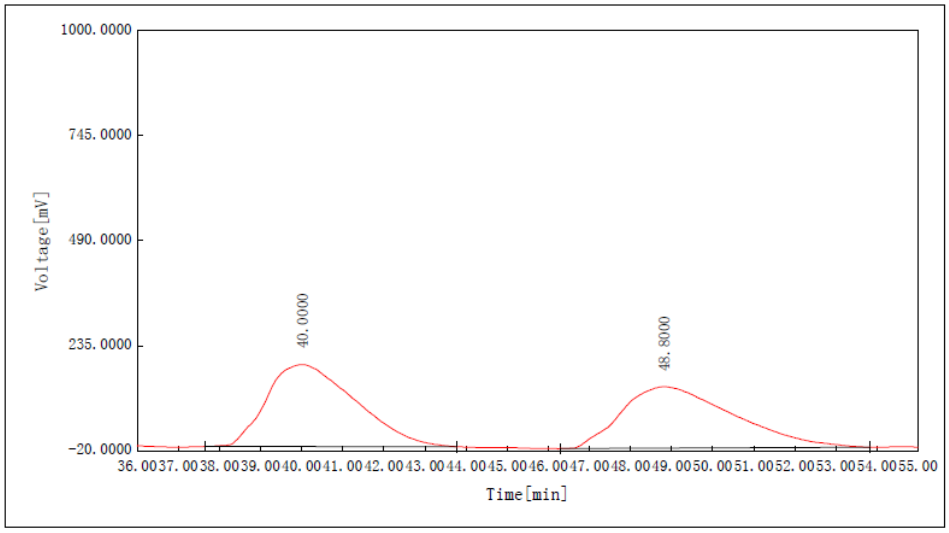
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	11.0000	8817.4654	BB	51.6785
2	12.8333	8244.6756	BB	48.3215
The Total		17062.1411		



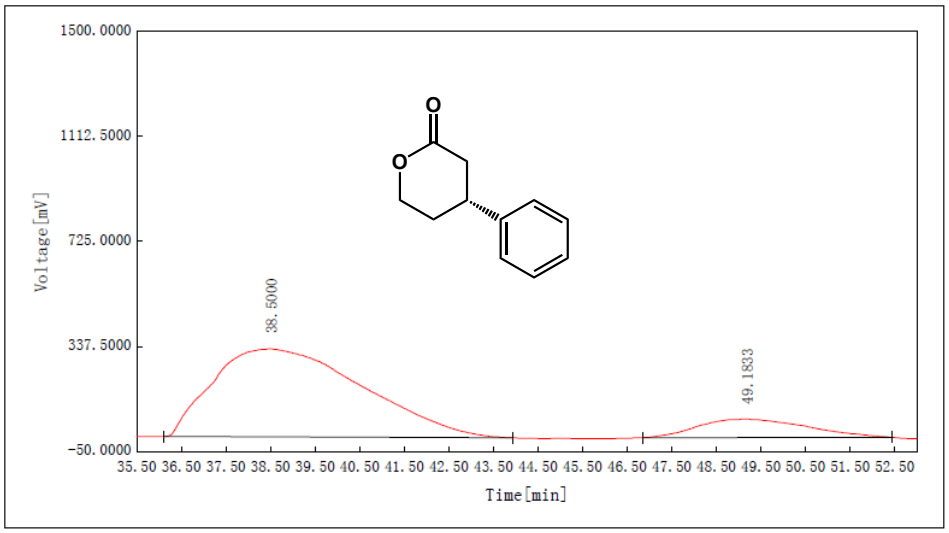
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	10.7167	1193.7641	BB	94.8111
2	12.4500	65.3340	BB	5.1889
The Total		1259.0981		

(*R*)-4-phenyl-tetrahydro-2H-pyran-2-one

Column: CHIRALCEL AS-H column (4.6 mm × 25 cm) from Daicel. Column temperature: 25°C. hexane/iPrOH = 80/20; flow rate= 1.0 mL/min; t_{major} = 38.500 min, t_{minor} = 49.183 min; ee = 74%.



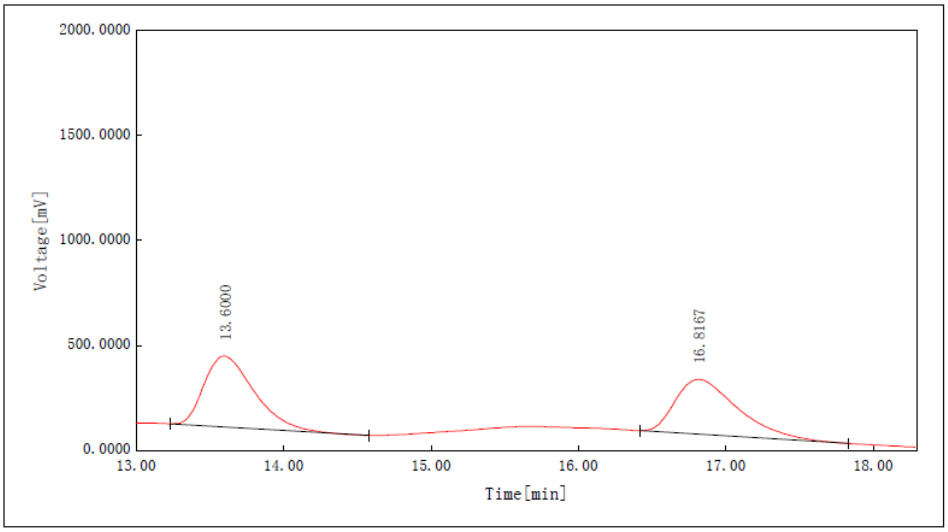
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	40.0000	29628.0592	BB	51.3403
2	48.8000	28081.1249	FF	48.6597
The Total		57709.1841		



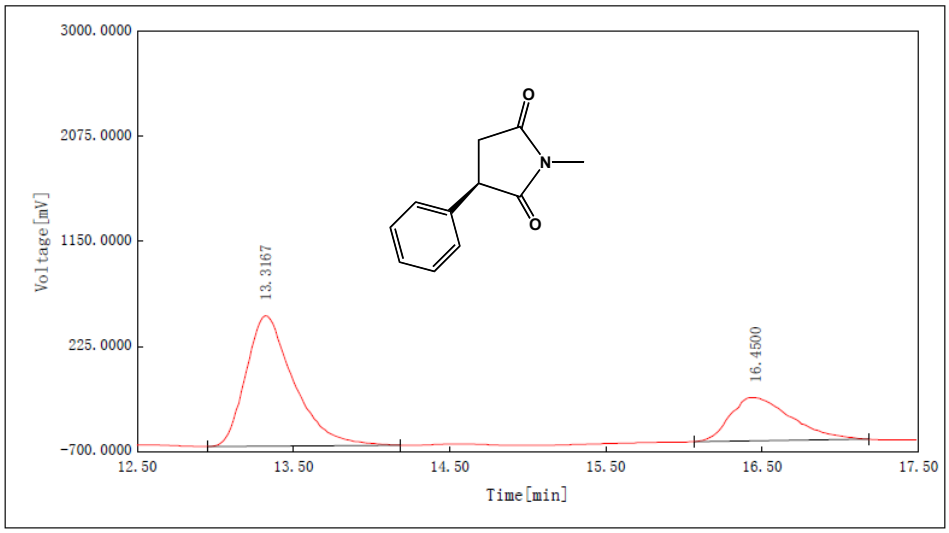
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	38.5000	75403.2310	BB	86.7358
2	49.1833	11531.1509	FF	13.2642
The Total		86934.3818		

(*R*)-1-Methyl-3-phenyl-pyrrolidine-2,5-dione

Column: CHIRALCEL AD-H column (4.6 mm × 25 cm) from Daicel. Column temperature: 25°C. hexane/iPrOH = 90/10; flow rate= 1.0 mL/min; t_{major} = 13.317 min, t_{minor} = 16.450 min; ee = 40 %.

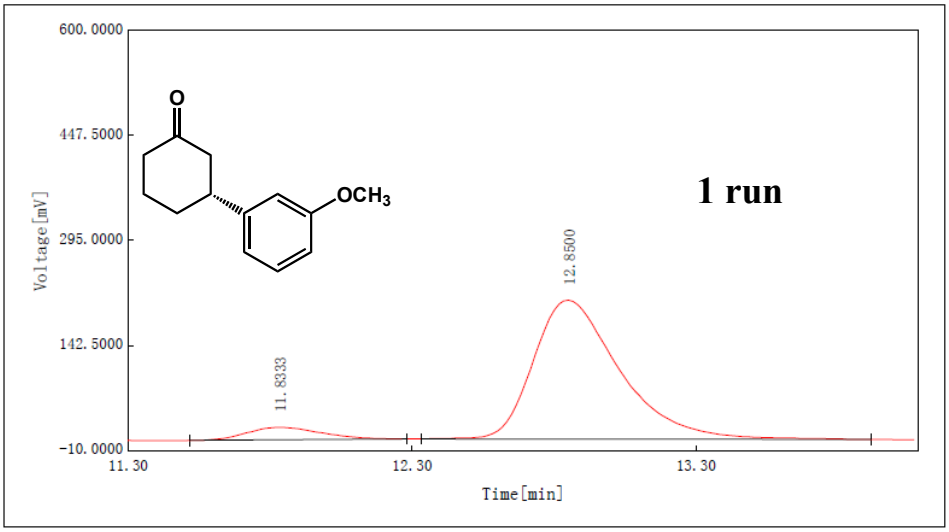


Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	13.6000	7894.9149	BB	50.6467
2	16.8167	7693.2982	BB	49.3533
The Total		15588.2131		

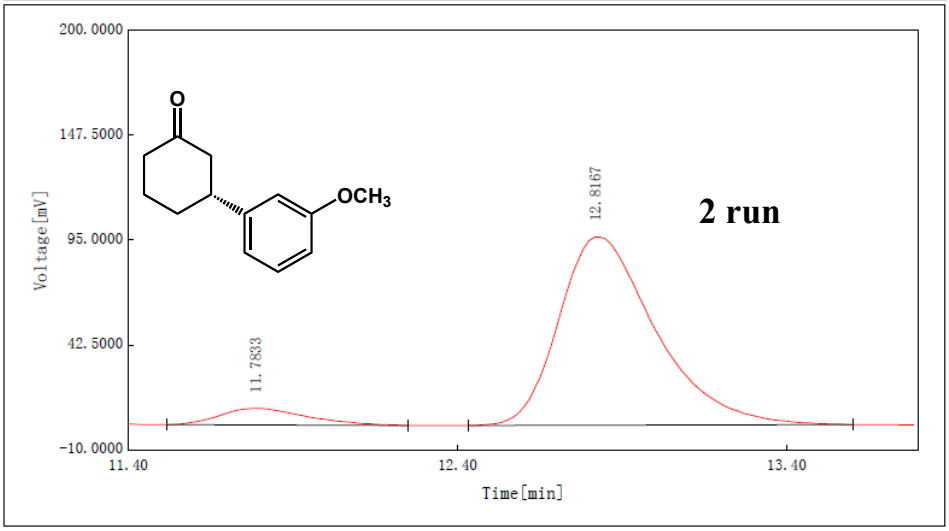


Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	13.3167	24341.3245	BB	70.1634
2	16.4500	10351.0029	BB	29.8366
The Total		34692.3274		

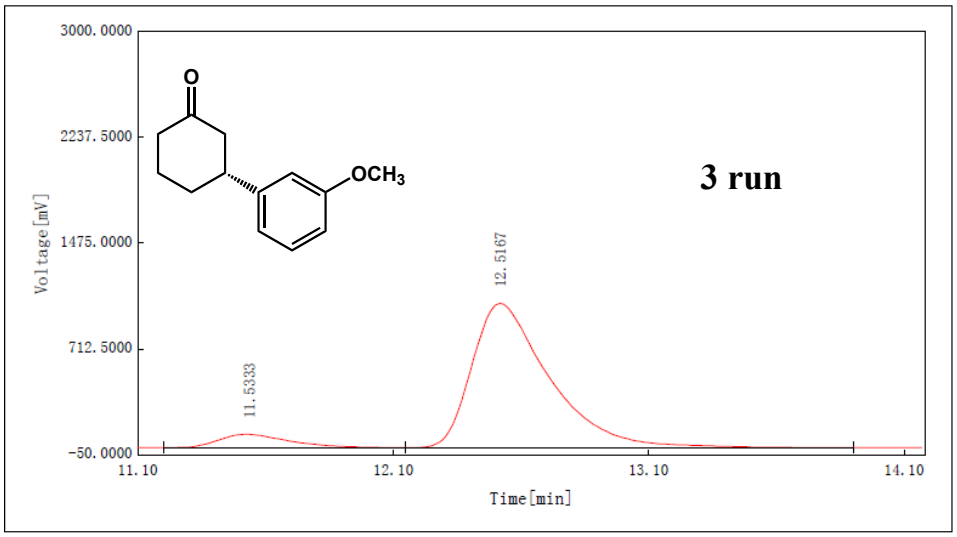
(*R*)-3-(3-methoxyphenyl)-cyclohexanone (6c) obtained with the recycled POF-1.



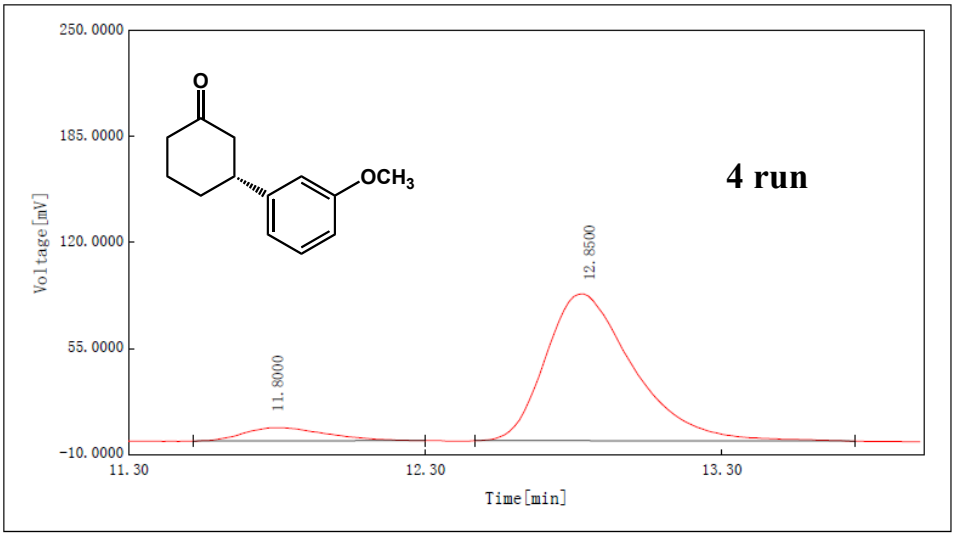
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	11.8333	328.5891	BB	7.1666
2	12.8500	4256.4211	BB	92.8334
The Total		4585.0102		



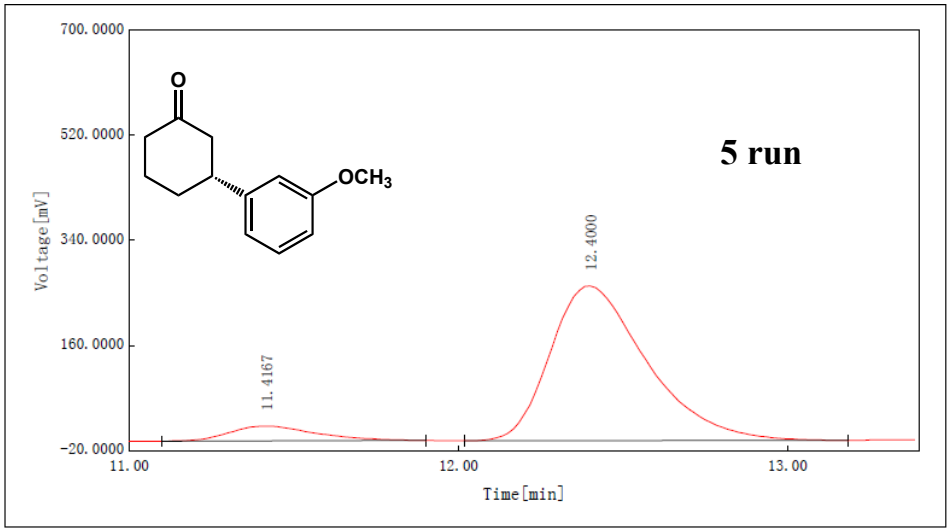
Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	11.7833	151.8992	BB	7.3193
2	12.8167	1923.4193	BB	92.6807
The Total		2075.3185		



Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	11.5333	1814.3140	BB	7.6532
2	12.5167	21892.3128	VB	92.3468
The Total		23706.6268		

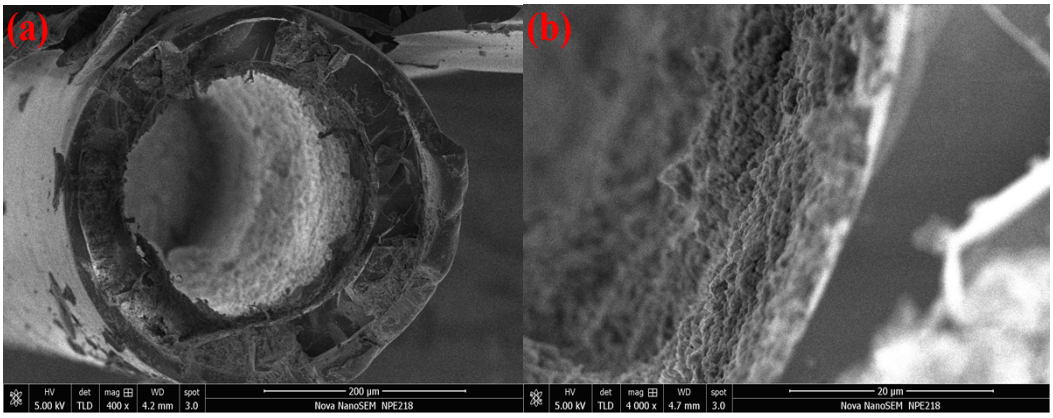


Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	11.8000	157.9788	BB	7.8587
2	12.8500	1852.2751	FF	92.1413
The Total		2010.2539		

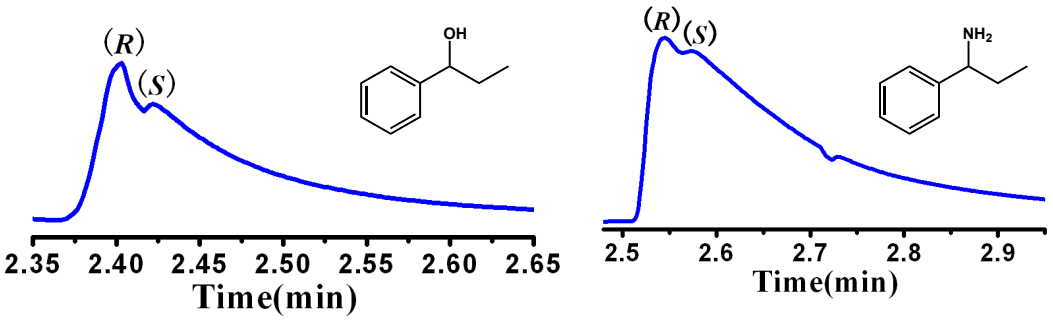


Serial Number	Retention Time[min]	Area[mAbs*s]	Type	Area%
1	11.4167	460.6256	BB	7.8702
2	12.4000	5392.1779	BB	92.1298
The Total		5852.8034		

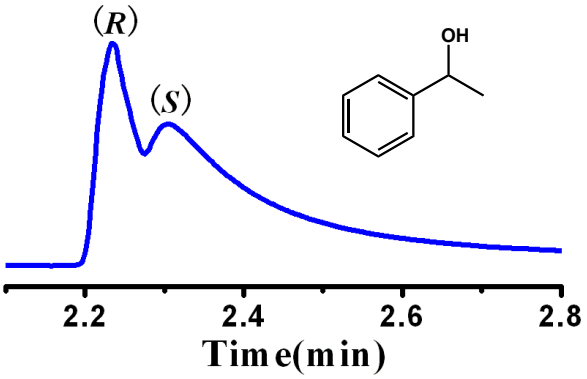
12. Figure S8. SEM images of the cross section of the **1**-coating GC column (a) and deposited on the inner wall of the GC column (b)



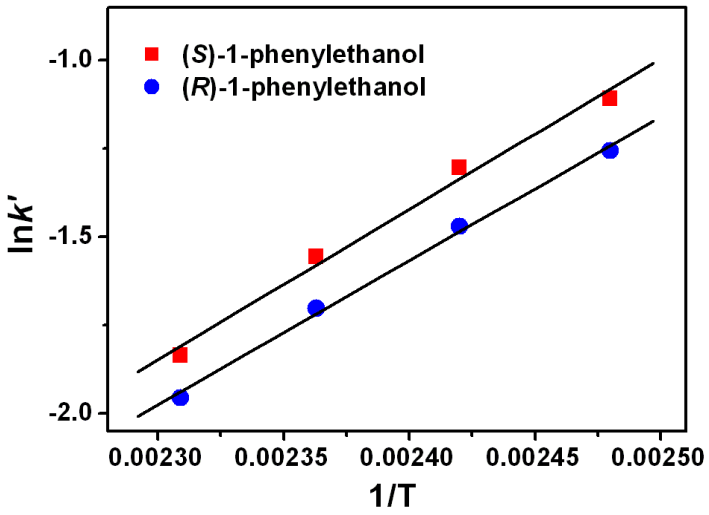
13. Figure S9 GC separation of racemic 1-phenylpropanol (left) and 1-phenylpropylamine (right) on the **1**-coating column.



14. Figure S10. GC separation of racemic 1-phenylethanol on the **1**-coating column after 30 h working time



15. Figure S11. Van't Hoff plots for enantiomers of 1-phenylethanol on the **1**-coating column



16. Table S1. McReynolds constants of the **1**-coating open tubular column.

benzene	1-butanol	2-pentanone	nitropropane	pyridine	av.
108	169	93	190	116	135

17. Table S2. Enantioseparation of racemates on the **1**-coating GC column

Racemates	Temp (^{o}C)	Retention factor (k_1)	Separation factor (α)
1-phenylethylamine	150	0.21	1.17
1-phenylpropylamine	140	0.42	1.04
1-phenylethanol	150	0.23	1.13
1-phenylpropanol	150	0.36	1.03

Separation factor (α) and retention factor (k_1) were obtained from the following equations:

$$\alpha = (t_2 - t_0)/(t_1 - t_0)$$

$$k_1 = (t_1 - t_0)/t_0$$

where t_0 is the column void time which was determined using n-pentane under the condition of the separation, where t_1 and t_2 represent the retention times of left- and right-handed enantiomers. Retention factor (k_1) is the first eluted enantiomer.

18. Table S3. Thermodynamic parameters for GC separation of 1-phenylethanol on the 1-coating column

	$\Delta_{ads}H_m$ (kJ/mol)	$\Delta(\Delta_{ads}H_m)$ (kJ/mol)	$\Delta_{ads}S_m + R\ln\Phi$ J/(K·mol)	$\Delta(\Delta_{ads}S_m)$ J/(K·mol)
(*R*)-1-phenylethanol	-34.0	-	-94.5	-
(*S*)-1-phenylethanol	-35.4	1.4	-96.8	2.3

The molar adsorption enthalpy change ($\Delta_{ads}H_m$) and molar adsorption entropy change ($\Delta_{ads}S_m$) of (*R*)- and (*S*)-1-phenylethanol were calculated from the following van't Hoff equation:

$$\ln k' = \frac{-\Delta_{ads}H_m}{RT} + \frac{\Delta_{ads}S_m}{R} + \ln\Phi$$

where k' is retention factor, R the gas constant, T the absolute temperature, and Φ the phase ratio.

$$T_{iso} = \frac{\Delta(\Delta_{ads}H_m)}{\Delta(\Delta_{ads}S_m)}$$

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