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Supporting Information

Ir-catalyzed asymmetric transfer hydrogenation of racemic quinolinyl-substituted tertiary alcohols

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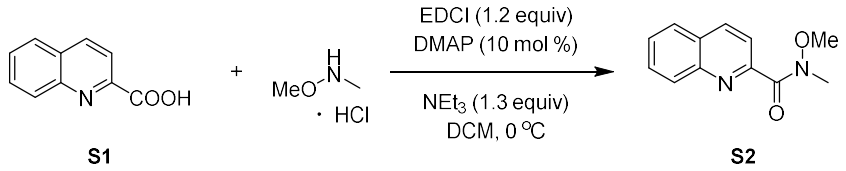
1.General Information

Unless otherwise noted, all the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under nitrogen atmosphere or in an argon-filled glove box. Purification of products was carried out by flash chromatography using silica gel (200-300 mesh). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Avance 400 MHz with tetramethylsilane as the internal standard. Chemical shifts are reported parts per million (ppm) referenced to $CDCl_3$ (δ 7.260 ppm) for ^{1}H NMR; $CDCl_3$ (δ 77.16 ppm) for ^{13}C NMR or C_6D_6 (δ 7.16 ppm) for ^{1}H NMR; $CDCl_3$ (δ 128.06 ppm) for ^{13}C NMR. Coupling constants (J) were expressed in Hz. The following abbreviations are used to describe peak patterns where appropriate: s (singlet), d (doublet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet), q (quartet), t (triplet) and td (triplet of doublets). Enantiomeric excess values were determined by high-performance liquid chromatography (HPLC) analysis using a chiral phase on Shimadzu LC-40A or Agilent Technologies 1260 Infinity II instrument in comparison with the authentic racemates. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Rudolph Autopol I polarimeter at 589 nm. The HR-ESI-MS spectra were measured using SCIEX X500R mass spectrometer (AB SCIEX, Framingham, MA, USA) or Waters Xevo G2-XS QTof. X-ray diffraction was measured on a Bruker APEX-II CCD diffractometer with Cu–Kα radiation. Hex refers to hexane, PE refers to petroleum ether, EA refers to ethyl acetate.

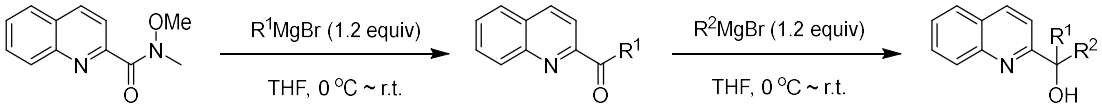
2. General Procedures for the Synthesis of Substrates

Procedure A



S1 **S2**

Step 1: NEt_3 (30.0 mmol, 1.3 equiv.) was added to a stirred solution of **S1** (50 mmol, 1.0 equiv.), EDCI (60 mmol, 1.2 equiv.), DMAP (5.0 mmol, 0.1 equiv.) and MeNH(OMe)•HCl (55 mmol, 1.1 equiv.) in DCM (100 mL) under N_2 atmosphere at 0 ℃ , then the reaction was stirred overnight. Subsequently, the reaction was quenched by saturated NH_4Cl solution (50 mL). The aqueous layer was extracted with EA (3 x 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation, which afforded the crude amide **S2** without further purification.



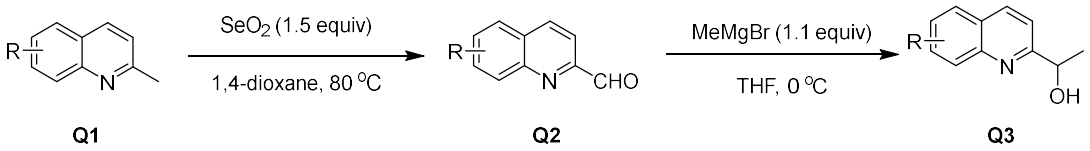
S2 **S3** **S4**

Step 2: Under N_2 atmosphere, to a stirred solution of **S2** (30 mmol, 1.0 equiv.) in THF (60 mL) was drop-wisely added R^1MgBr (36 mmol, 1.2 equiv.) at 0 ℃. Then the reaction mixture was stirred at RT for 24 h. The reaction was quenched by saturated NH_4Cl solution (40 mL). The aqueous layer was extracted with EA (3 x 30 mL). The combined organic layers were washed with brine (2 x 50 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using PE/EA=5/1 as eluent to give the corresponding product **Q3**.

Following a known literature method,[2] under N_2 atmosphere, to a stirred solution of **S3** (4 mmol, 1.0 equiv.) in THF (8 mL) was drop-wisely added R^2MgBr (4.8mmol, 1.2 equiv.) at 0 ℃. Then the reaction mixture was stirred at RT for 12 h. The reaction was quenched by saturated NH_4Cl solution (8 mL). The aqueous layer was extracted with EA (3 x 20 mL), and the combined organic layers were washed with brine (2 x 20 mL).

The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using PE/EA=10/1 as eluent to give the corresponding product **Q4**.

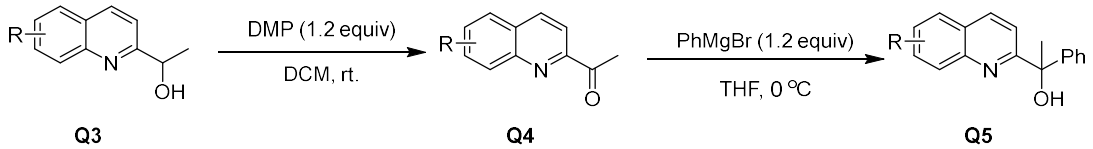
Procedure B



Q1 **Q2** **Q3**

Step 1: According to the reported literature[1]: To a two-necked round bottom flask was added quinaldine **Q1** (1.0 equiv.), SeO_2 (1.5 equiv.) and 1,4-dioxane. The reaction mixture was allowed to stir at 80 ℃ for 6 h. Then, the resulting mixture was quenched with saturated aqueous NaCl (20 mL). The mixture was extracted with EA (30 mL × 4) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated to afford the crude product **Q2**.

In an oven dried round-bottom flask, **Q2** (1.0 equiv.) was dissolved in anhydrous THF (30 mL), and then the Grignard reagent in THF (1.2 equiv.) was added at 0 ℃ under nitrogen atmosphere. The reaction mixture was warmed to room temperature and the progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EA (20 ml × 3). The combined organic layers were combined and dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using PE/EA=10/1 as eluent to give the corresponding product **Q3**.



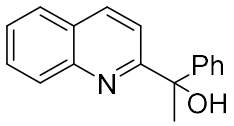
Q3 **Q4** **Q5**

Step 2: To a stirring solution of **Q3** (1.0 equiv.) in DCM (30 mL) was added Dess-Martin periodinane (DMP, 1.2 equiv.). The reaction mixture was allowed to proceed at room temperature and the progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was quenched with sat. $NaHCO_3$ aq. (30 mL) and extracted with DCM (20 mL×3). The combined organic layers were dried over

Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using PE/EA=20/1 as eluent to give the corresponding product **Q4**.

Following a known literature method,[2] under N_2 atmosphere, to a stirred solution of **Q4** (4 mmol, 1.0 equiv.) in THF (8 mL) was dropwisely added R_2MgBr (4.8 mmol, 1.2 equiv.) at 0 ℃. Then the reaction mixture was stirred at RT for 12 h. After the reaction was completed, the reaction mixture was quenched with saturated aqueous NH_4Cl (20 mL) and extracted with EA (20 ml × 3). The combined organic layers were combined and dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using PE/EA=10/1 as eluent to give the corresponding product **Q5.**

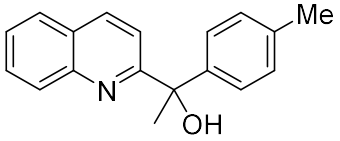
Compounds 1a,1b,1c,1d,1e,1g,1j have already been reported.[2]



1a
Chemical Formula: $C_{17}H_{15}NO$
Exact Mass: 249.1154

1-phenyl-1-(quinolin-2-yl)ethan-1-ol (1a)[2]

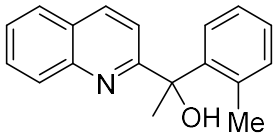
Following Procedure A, 20 mmol scale, white solid, 4.634 g, 93% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.46 – 7.44 (m, 3H), 7.25 – 7.20 (m, 3H), 7.16 – 7.13 (m, 1H), 6.63 (s, 1H), 1.93 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 164.3, 146.5, 145.5, 137.3, 130.0, 128.9, 128.3, 127.5, 127.2, 127.2, 126.7, 126.3, 118.5, 75.1, 28.6. **HRMS (ESI)**: calculated for $C_{17}H_{16}NO$ $[M+H]^+$ 250.1226, found 250.1234.



1b
Chemical Formula: $C_{18}H_{17}NO$
Exact Mass: 263.1310

1-(quinolin-2-yl)-1-(*p*-tolyl)ethan-1-ol (1b)

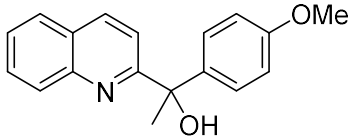
Following Procedure A, 4 mmol scale, white solid, 915.7 mg, 87% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.72 (m, 1H), 7.57 – 7.53 (m, 1H), 7.43 – 7.41 (m, 2H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.70 (s, 1H), 2.31 (s, 3H), 2.00 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 164.5, 145.5, 143.6, 137.3, 136.8, 129.9, 129.0, 128.9, 127.5, 127.1, 126.6, 126.2, 118.5, 74.9, 28.7, 21.0. **HRMS (ESI)**: calculated for $C_{18}H_{18}NO$ $[M+H]^+$ 264.1383, found 264.1387.



1c
Chemical Formula: $C_{18}H_{17}NO$
Exact Mass: 263.1310

1-(1,2-dihydroquinolin-2-yl)-1-(o-tolyl)ethan-1-ol (1c)

Following Procedure A, 2 mmol scale, colorless liquid, 387.1 mg, 73% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.84 – 7.76 (m, 3H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.34 (dt, *J* = 25.9, 7.6 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.52 (s, 1H), 2.06 (s, 3H), 2.04 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 165.4, 145.7, 142.3, 138.6, 137.5, 132.6, 130.1, 128.9, 128.2, 127.8, 127.2, 126.7, 125.7, 118.5, 76.5, 31.7, 21.3. **HRMS (ESI)**: calculated for $C_{18}H_{18}NO$ $[M+H]^+$ 264.1383, found 264.1391.

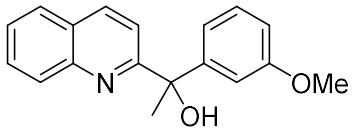


1d
Chemical Formula: $C_{18}H_{17}NO_2$
Exact Mass: 279.1259

1-(4-methoxyphenyl)-1-(quinolin-2-yl)ethan-1-ol (1d)

Following Procedure A, 2 mmol scale, white solid, 468.9 mg, 84% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.80 – 7.72 (m, 2H), 7.54 (t, *J* = 6.8 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 4.0 Hz, 1H), 3.78 (s, 3H), 2.00

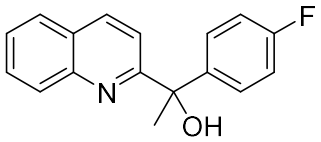
(s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 164.6, 158.7, 145.5, 138.7, 137.3, 130.0, 128.8, 127.6, 127.5, 127.1, 126.6, 118.5, 116.1, 114.7, 113.6, 74.8, 55.3, 28.8. **HRMS (ESI)**: calculated for $C_{18}H_{18}NO_2$ $[M+H]^+$ 280.1332, found 280.1333.



1e
Chemical Formula: $C_{18}H_{17}NO_2$
Exact Mass: 279.1259

1-(3-methoxyphenyl)-1-(quinolin-2-yl)ethan-1-ol (1e)

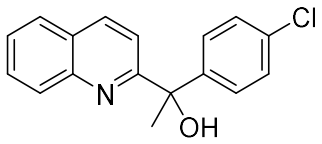
Following Procedure A, 4 mmol scale, white solid, 926.7 mg, 90% yield (for the last step); ^{1}H NMR (400 MHz,) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.13 (t, *J* = 8.8 Hz, 1H), 7.03 – 7.01 (m, 2H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.61 (s, 1H), 3.65 (s, 3H), 1.90 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 164.2, 159.7, 148.3, 145.6, 137.4, 130.0, 129.3, 128.9, 127.5, 127.2, 126.7, 118.8, 118.5, 112.5, 112.5, 75.1, 55.3, 28.8. **HRMS (ESI)**: calculated for $C_{18}H_{18}NO_2$ $[M+H]^+$ 280.1332, found 280.1341.



1f
Chemical Formula: $C_{17}H_{14}FNO$
Exact Mass: 267.1059

1-(4-fluorophenyl)-1-(quinolin-2-yl)ethan-1-ol (1f)

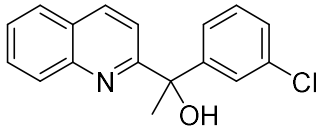
Following Procedure A, 4 mmol scale, white solid, 918.9 mg, 86% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.11 (dd, *J* = 15.6, 8,4 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.53 – 7.49 (m, 3H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.02 – 6.98 (m, 2H), 6.74 (s, 1H), 2.01 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 164.1, 162.0 (d, *J* = 245.8 Hz), 145.5, 142.4 (d, *J* = 3.2 Hz), 137.5, 130.1, 128.8, 128.1 (d, *J* = 8.2 Hz), 127.5, 127.2, 126.8, 118.3, 115.1 (d, *J* = 21.3 Hz), 74.7, 28.8. **^{19}F {^{1}H} NMR** (376 MHz, Chloroform-*d*) δ -115.80. **HRMS (ESI)**: calculated for $C_{17}H_{15}FNO$ $[M+H]^+$ 268.1132, found 268.1141.



1g
Chemical Formula: $C_{17}H_{14}ClNO$
Exact Mass: 283.0764

1-(4-chlorophenyl)-1-(quinolin-2-yl)ethan-1-ol (1g)

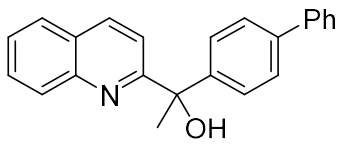
Following Procedure A, 4 mmol scale, white solid, 1.030 g, 91% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.69 (dd, *J* = 14.0, 7.2 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.49 – 7.46 (m, 1H), 7.30 (dd, *J* = 8.8, 4.6 Hz, 3H), 6.86 (s, 1H), 2.06 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 163.9, 145.7, 145.5, 137.7, 133.1, 130.2, 128.9, 128.5, 128.0, 127.7, 127.2, 126.9, 118.4, 75.1, 28.9. **HRMS (ESI)**: calculated for $C_{17}H_{15}ClNO$ $[M+H]^+$ 284.0837, found 284.0843.



1h
Chemical Formula: $C_{17}H_{14}ClNO$
Exact Mass: 283.0764

1-(3-chlorophenyl)-1-(quinolin-2-yl)ethan-1-ol (1h)

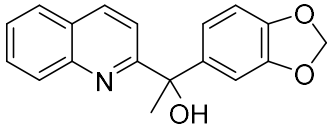
Following Procedure A, 4 mmol scale, white solid, 803.9 mg, 71% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 8.4, 4.4 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 6.8 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.31 – 7.21 (m, 2H), 6.73 (s, 1H), 1.99 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 163.5, 148.7, 145.5, 137.6, 134.3, 130.1, 129.6, 128.8, 127.5, 127.4, 127.2, 126.8, 126.7, 124.5, 118.2, 74.8, 28.6. **HRMS (ESI)**: calculated for $C_{17}H_{15}ClNO$ $[M+H]^+$ 284.0837, found 284.0843.



1i
Chemical Formula: $C_{23}H_{19}NO$
Exact Mass: 325.1467

1-([1,1'-biphenyl]-4-yl)-1-(quinolin-2-yl)ethan-1-ol (1i)

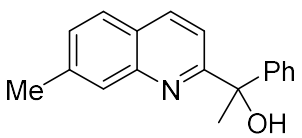
Following Procedure A, 2 mmol scale, white solid, 513.7 mg, 79% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.8 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.67 – 7.55 (m, 7H), 7.46 – 7.33 (m, 4H), 6.80 (s, 1H), 2.09 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 164.3, 145.6, 140.8, 140.1, 137.5, 130.0, 128.9, 128.8, 127.5, 127.3, 127.2, 127.1, 127.1, 126.8, 126.7, 118.5, 75.0, 28.7. **HRMS (ESI)**: calculated for $C_{23}H_{20}NO$ $[M+H]^+$ 326.1539, found 326.1545.



1j
Chemical Formula: $C_{18}H_{15}NO_3$
Exact Mass: 293.1052

1-(benzo[d][1,3]dioxol-5-yl)-1-(quinolin-2-yl)ethan-1-ol (1j)

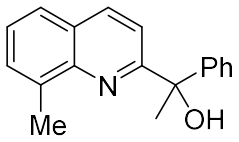
Following Procedure A, 4 mmol scale, white solid, 973.1 mg, 83% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 13.6, 8.4 Hz, 2H), 7.81 – 7.72 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.98 (s, 1H), 6.77 – 6.69 (m, 2H), 5.90 (d, *J* = 7.2 Hz, 2H), 1.97 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 164.3, 147.7, 146.7, 145.5, 140.7, 137.4, 130.0, 128.8, 127.5, 127.1, 126.7, 119.5, 118.4, 107.8, 107.4, 101.0, 74.9, 28.8. **HRMS (ESI)**: calculated for $C_{18}H_{16}NO_3$ $[M+H]^+$ 294.1125, found 294.1126.



1k
Chemical Formula: $C_{18}H_{17}NO$
Exact Mass: 263.1310

1-(7-methylquinolin-2-yl)-1-phenylethan-1-ol (1k)

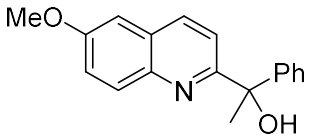
Following Procedure B, 2 mmol scale, white solid, 433.6 mg, 82% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.8 Hz, 1H), 7.91 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.18 (m, 2H), 6.76 (s, 1H), 2.59 (s, 3H), 2.01 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 164.2, 146.6, 145.74, 140.4, 137.0, 128.8, 128.3, 127.9, 127.1, 127.1, 126.3, 125.2, 117.6, 75.0, 28.6, 21.9. **HRMS (ESI)**: calculated for $C_{18}H_{18}NO$ $[M+H]^+$ 264.1383, found 264.1389.



1l
Chemical Formula: $C_{18}H_{17}NO$
Exact Mass: 263.1310

1-(8-methylquinolin-2-yl)-1-phenylethan-1-ol (1l)

Following Procedure B, 2 mmol scale, colorless liquid, 463.1 mg, 88% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 10.0 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 6.8 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.22 – 7.20 (m, 1H), 6.91 (s, 1H), 2.86 (s, 3H), 2.01 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 163.1, 146.6, 144.3, 137.7, 136.6, 130.3, 128.3, 127.2, 127.1, 126.4, 126.3, 125.5, 118.2, 75.1, 28.7, 17.9. **HRMS (ESI)**: calculated for $C_{18}H_{18}NO$ $[M+H]^+$ 264.1383, found 264.1390.

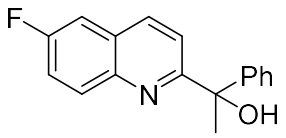


1m
Chemical Formula: $C_{18}H_{17}NO_2$
Exact Mass: 279.1259

1-(6-methoxyquinolin-2-yl)-1-phenylethan-1-ol (1m)

Following Procedure B, 2 mmol scale, white solid, 489.0 mg, 88% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (dd, *J* = 18.4, 8.8 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.42 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 9.2 Hz, 2H), 7.08 (d, *J* = 2.8 Hz, 1H), 6.67 (s, 1H), 3.94 (s, 3H), 2.04 (s, 3H). **^{13}C {^{1}H}**

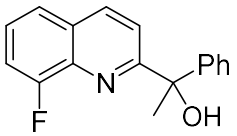
NMR (101 MHz, Chloroform-*d*) δ 161.9, 157.9, 146.8, 141.5, 136.1, 130.2, 128.3, 128.1, 127.1, 126.3, 122.4, 118.7, 105.2, 74.9, 55.6, 28.8. **HRMS (ESI)**: calculated for $C_{18}H_{18}NO_2$ $[M+H]^+$ 280.1332, found 280.1337.



1n
Chemical Formula: $C_{17}H_{14}FNO$
Exact Mass: 267.1059

1-(6-fluoroquinolin-2-yl)-1-phenylethan-1-ol (1n)

Following Procedure B, 4 mmol scale, white solid, 790.6 mg, 74% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.11 (dd, *J* =9.2, 5.2 Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.41 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.37 – 7.30 (m, 3H), 7.26 (d, *J* = 7.3 Hz, 1H), 6.54 (s, 1H), 2.02 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 163.8 (d, *J* = 2.8 Hz), 160.5 (d, *J* = 248.2 Hz), 146.3, 142.6, 136.7 (d, *J* = 5.2 Hz), 131.3 (d, *J* = 9.1 Hz), 128.4, 127.7 (d, *J* = 10.1 Hz), 127.3, 126.2, 120.0 (d, *J* = 25.7 Hz), 119.4, 110.7 (d, *J* = 21.7 Hz), 75.1, 28.7. **^{19}F {^{1}H} NMR** (376 MHz, Chloroform-*d*) δ -113.18. **HRMS (ESI)**: calculated for $C_{17}H_{15}FNO$ $[M+H]^+$ 268.1132, found 268.1131. **HRMS (ESI)**: calculated for $C_{17}H_{14}FNO$ $[M+H]^+$ 268.1132, found 268.1138.

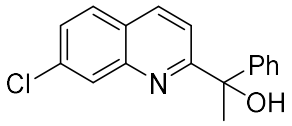


1o
Chemical Formula: $C_{17}H_{14}FNO$
Exact Mass: 267.1059

1-(8-fluoroquinolin-2-yl)-1-phenylethan-1-ol (1o)

Following Procedure B, 4 mmol scale, white solid, 871.9 mg, 77% yield (for the last step), **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.11 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.52 – 7.43 (m, 3H), 7.42 – 7.34 (m, 3H), 7.28 – 7.25 (m, 1H), 6.60 (s, 1H), 2.06 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 164.8, 158.2 (d, *J* = 258.6 Hz), 146.17, 137.1 (d, *J* = 3.1

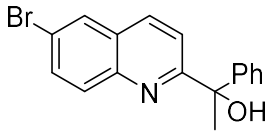
Hz), 128.37, 127.32, 126.5, 126.4, 126.30, 123.0 (d, J = 4.6 Hz), 119.54, 114.35, 114.16, 75.39, 28.65. **^{19}F {^{1}H} NMR** (376 MHz, Chloroform-*d*) δ -125.3. **HRMS (ESI)**: calculated for $C_{17}H_{14}FNO$ $[M+H]^+$ 268.1132, found 268.1141.



1p
Chemical Formula: $C_{17}H_{14}ClNO$
Exact Mass: 283.0764

1-(7-chloroquinolin-2-yl)-1-phenylethan-1-ol (1p)

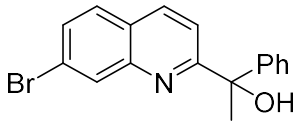
Following Procedure B, 4 mmol scale, white solid, 917.2 mg, 81% yield (for the last step), **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.53 – 7.48 (m, 3H), 7.34 – 7.29 (m, 3H), 7.25 (t, J = 7.2 Hz, 1H), 6.48 (s, 1H), 2.01 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 165.5, 146.1, 146.0, 137.1, 135.9, 128.7, 128.4, 127.9, 127.7, 127.3, 126.2, 125.5, 118.8, 75.2, 28.6. **HRMS (ESI)**: calculated for $C_{17}H_{15}ClNO$ $[M+H]^+$ 284.0837, found 284.0845.



1q
Chemical Formula: $C_{17}H_{14}BrNO$
Exact Mass: 327.0259

1-(6-bromoquinolin-2-yl)-1-phenylethan-1-ol (1q)

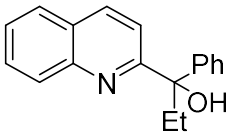
Following Procedure B, 4 mmol scale, white solid, 1.138 g, 87% yield (for the last step). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 – 7.94 (m, 3H), 7.80 (dd, J = 8.8, 2.0 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.34 – 7.31 (m, 3H), 7.26 – 7.23 (m, 1H), 6.47 (s, 1H), 2.01 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 164.9, 146.1, 144.2, 136.3, 133.4, 130.6, 129.5, 128.4, 128.2, 127.4, 126.2, 120.5, 119.5, 75.2, 28.6. **HRMS (ESI)**: calculated for $C_{17}H_{15}BrNO$ $[M+H]^+$ 328.0332, found 328.0338.



1r
Chemical Formula: $C_{17}H_{14}BrNO$
Exact Mass: 327.0259

1-(7-bromoquinolin-2-yl)-1-phenylethan-1-ol (1r)

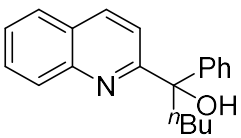
Following Procedure B, 4 mmol scale, white solid, 1.033 g, 79% yield (for the last step). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 – 7.94 (m, 3H), 7.80 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.30 (m, 3H), 7.25 (d, *J* = 7.6 Hz, 1H), 6.49 (s, 1H), 2.00 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 164.9, 146.1, 144.2, 136.3, 133.4, 130.6, 129.5, 128.4, 128.2, 127.4, 126.2, 120.5, 119.5, 75.2, 28.6. **HRMS (ESI)**: calculated for $C_{17}H_{15}BrNO$ $[M+H]^+$ 328.0332, found 328.0331.



1s
Chemical Formula: $C_{18}H_{17}NO$
Exact Mass: 263.1310

1-phenyl-1-(quinolin-2-yl)propan-1-ol (1s)

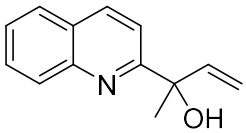
Following Procedure A, 4 mmol scale, white solid, 936.7 mg, 89% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (dd, *J* = 17.2, 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.64 (t, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.13 (q, *J* = 6.8 Hz, 1H), 6.61 (s, 1H), 2.41 – 2.26 (m, 2H), 0.80 (t, *J* = 7.2 Hz, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 163.1, 146.0, 145.5, 137.3, 129.9, 128.8, 128.3, 127.5 127.1, 127.0, 126.6, 126.4, 118.5, 77.5, 33.0, 8.0. **HRMS (ESI)**: calculated for $C_{18}H_{18}NO$ $[M+H]^+$ 264.1383, found 264.1387.



1t
Chemical Formula: $C_{20}H_{21}NO$
Exact Mass: 291.1623

1-phenyl-1-(quinolin-2-yl)pentan-1-ol (1t)

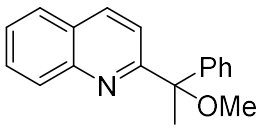
Following Procedure A, 4 mmol scale, white solid, 978.3 mg, 84% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 27.6, 8.4 Hz, 2H), 7.80 – 7.72 (m, 2H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.56 – 7.52 (m, 1H), 7.43 – 7.34 (m, 3H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.78 (s, 1H), 2.53 – 2.46 (m, 1H), 2.42 – 2.34 (m, 1H), 1.65 – 1.54 (m, 1H), 1.45 – 1.33(m, 2H), 1.18 – 1.07 (m, 1H), 0.91 (t, *J* = 7.2 Hz, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 163.3, 146.2, 145.5, 137.3, 129.9, 128.8, 128.3, 127.5, 127.1, 127.0, 126.6, 126.3, 118.5, 76.9, 40.2, 25.8, 23.1, 14.1. **HRMS (ESI)**: calculated for $C_{20}H_{22}NO$ $[M+H]^+$ 292.1696, found 292.1702.



1u
Chemical Formula: $C_{13}H_{13}NO$
Exact Mass: 199.0997

2-(quinolin-2-yl)but-3-en-2-ol (1u)

Following Procedure A, 4 mmol scale, white solid, 485.6 mg, 93% yield (for the last step); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.74 – 7.70 (m, 1H),7.74 – 7.70 (m, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 6.21 – 6.14 (m, 2H), 5.47 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.17 (dd, *J* = 10.8, 1.2 Hz, 1H), 1.70 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 163.2, 145.8, 143.6, 137.4, 129.9, 128.8, 127.5, 127.2, 126.6, 117.9, 113.6, 74.1, 27.9. **HRMS (ESI)**: calculated for $C_{13}H_{14}NO$ $[M+H]^+$ 200.1070, found 200.1071.



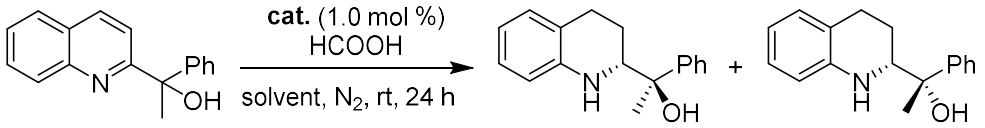
1v
Chemical Formula: $C_{18}H_{17}NO$
Exact Mass: 263.1310

2-(1-methoxy-1-phenylethyl)quinoline (1v)

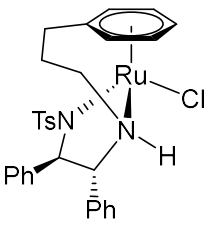
To a Schlenk tube containing **1a** (498.6 mg, 2 mmol, 1.0 equiv.) in DCM (8 mL) was added NaH (96 mg, 4 mmol, 2 equiv.) at 0 °C under nitrogen atmosphere. Then iodomethane (135.2 mg, 8 mmol, 4.0 equiv.) was added. The mixture was allowed to reflux at 40 °C in an oil bath for 72 h. After the stirring stopped, the reaction mixtures

were quenched with H_2O and extracted with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The crude residue was purified by column chromatography on silica gel (PE/EA = 20/1), affording the target compound as a white solid (194.7 mg with 37% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 18.0 Hz, 4H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 3.31 (s, 3H), 2.14 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 164.3, 147.1, 146.4, 136.2, 129.8, 129.1, 128.1, 127.4, 127.1, 126.8, 126.4, 126.0, 119.9, 82.9, 51.2, 23.5. **HRMS (ESI)**: calculated for $C_{18}H_{18}NO$ $[M+H]^+$ 264.1383, found 264.1391.

3. Reaction Conditions Optimization[a]



1a (*R*,*R*)-**2a** (*S*,*R*)-**2a**



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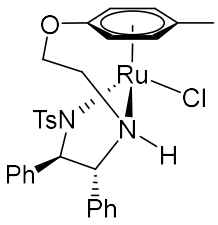

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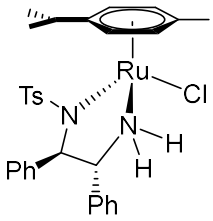

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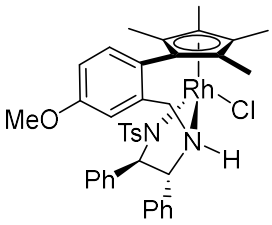

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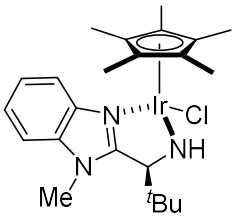

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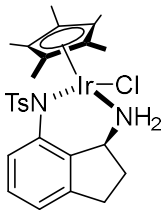


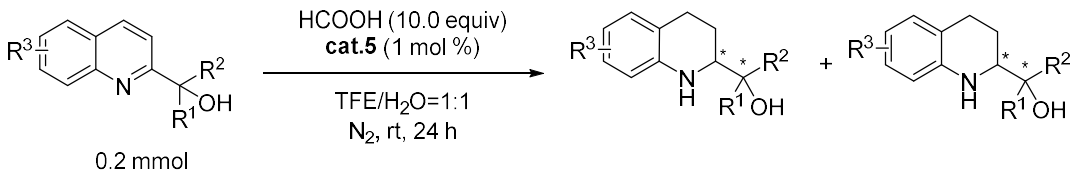
cat.6

			(*R*,*R*)-**2a**/(*S*,*R*)-**2a**	
entry	**cat.**	solvent (v/v)	yield (%)[b]	ee (%)[c]
1	**cat.1**	DCM	NR	-
2	**cat.2**	DCM	NR	-
3	**cat.3**	DCM	8/10	4/3
4	**cat.4**	DCM	8/8	8/7
5	**cat.5**	DCM	37/41	89/87
6	**cat.6**	DCM	trace	-
7	**cat.5**	TFE	36/35	95/90
8	**cat.5**	MeOH	30/33	90/92
9	**cat.5**	EtOH	34/33	89/88
10	**cat.5**	MeOH/H_2O = 1/1	38/40	93/94
11	**cat.5**	EtOH/H_2O = 1/1	42/41	96/95
12	**cat.5**	Toluene/H_2O = 1/1	40/39	95/97
13	**cat.5**	dioxane/H_2O = 1/1	39/40	94/90
14	**cat.5**	TFE/H_2O = 1/1	49/46	98/99
15	**cat.5**	toluene/H_2O = 1/1	39/36	96/98
16	**cat.5**	THF/H_2O = 1/1	43/44	98/97

17	**cat.5**	DCM/H_2O = 1/1	29/38	98/84
18	**cat.5**	TFE/H_2O = 3/1	48/46	92/96
18	**cat.5**	TFE/H_2O = 1/3	47/37	98/99
20[d]	**cat.5**	TFE/H_2O = 1/1	33/32	97/98
21[e]	**cat.1**	MeOH	6/10	33/63
22[e]	**cat.2**	MeOH	8/10	48/48
23[e]	**cat.3**	MeOH	1/5	-/-

[a]Reaction conditions: **1** (0.1 mmol), **cat.** (1 mol %), HCOOH (10.0 equiv.), 0.2 mL organic solvent and indicated amount of water, under an N_2 atmosphere at room temperature for 24 h; [b] Isolated yields; [c] The enantiomeric excess (ee) was determined by HPLC; [d] 5 equivalent of formic acid used; [e] HCOOH/NEt_3 = 5/2 (10.0 equiv.) as the hydrogen source.

3.General Procedure for Transfer Hydrogenation

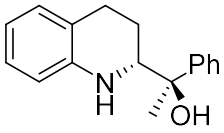


Under nitrogen atmosphere, substrate **1** (0.2 mmol, 1.0 equiv.) and catalyst (1 mol%) were added to a 10 mL sealed tube. 2,2,2-Trifluoroethanol (0.2 mL) and deionized water (0.2 mL) were sequentially introduced via syringe, followed by the dropwise addition of formic acid (2 mmol, 75 μL, 10.0 equiv.). The reaction was stirred at room temperature for 24 hours. Upon reaction completion, the mixture was diluted with ethyl acetate (10 mL) and water (10 mL), washed with saturated aqueous $NaHCO_3$ solution (5 mL). The aqueous layer was extracted with ethyl acetate (2 × 5 mL). The combined organic extracts were washed with saturated NaCl solution (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography (PE/EA = 10/1) to give the desired compound.

The racemic substrates of **2a**, **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2h**, **2i**, **2j**, **2k**, **2l**, **2m, 2n, 2o, 2s, 2t, 2v** were prepared according to the following procedure: under air atmosphere, substrate **1** (0.1 mmol), Pd/C (12.0 mg, 5.0 mol%), and anhydrous MeOH (1.0 mL) were added into an oven-dried 4 mL vial. The vial was then transferred to an autoclave and purged by three cycles of pressurization/venting with H_2 before pressurization with 20 bar of H_2 and stirred at 40 °C for 4 hours. Then the hydrogen was carefully released in the fume hood. After filtration through a layer of celite, the residue was purified by flash chromatography on silica gel to afford the corresponding product (eluent, Hex/EA = 10/1).

The racemic substrates of **2g**, **2h**, **2p**, **2q**, **2r**, **2u** were prepared according to the following procedure: in an argon-filled glove box, the substrate **1** (0.1 mmol, 1.0 equiv.), 1,1'-binaphthyl-2,2'-diyl hydrogen phosphate (0.01 mmol, 5 mol%), diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (HE, 0.5 mmol, 2.5 equiv.), and DCM (1.0 mL) were successively added into a 10 mL Schlenk tube. The reaction mixture was

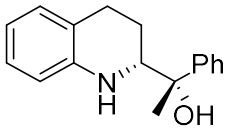
stirred at room temperature for 24 h. Then, the mixture was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to afford the corresponding product. (eluent: Hex/EA=10/1).



(*R,R*)-**2a**
Chemical Formula: $C_{17}H_{19}NO$
Exact Mass: 253.1467

(*R*)-1-phenyl-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*R,R*)-**2a**)

White solid, 0.2 mmol scale, 22.9 mg, 45% yield, 97% ee, $[\alpha]_{25}^{D}$ = -5.9 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.35; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.39 (m, 1H), 6.98 – 6.91 (m, 2H), 6.65 (t, *J* = 6.8 Hz, 1H), 6.39 (d, *J* = 8.4 Hz, 1H), 3.64 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.62 (s, 1H) 2.93 – 2.77 (m, 3H), 2.15 – 2.09 (m, 1H), 1.98 – 1.87 (m, 1H), 1.55 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 146.7, 144.5, 129.0, 128.6, 127.2, 126.7, 125.2, 122.0, 118.2, 115.3, 75.3, 59.6, 26.6, 25.0, 22.4. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H Column (hexane/isopropanol = 96/4, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 16.318 min (major), t_{R2} = 17.055 min (minor). **HRMS (ESI)**: calculated for $C_{17}H_{20}NO$ $[M+H]^+$ 254.1539, found 254.1537.

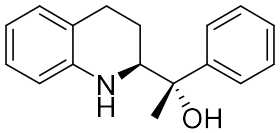


(*S,R*)-**2a**
Chemical Formula: $C_{17}H_{19}NO$
Exact Mass: 253.1467

(*S*)-1-phenyl-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*S,R*)-**2a**)

Colorless liquid, 0.2 mmol scale, 22.5 mg, 45% yield, 95% ee, $[\alpha]_{25}^{D}$ = +187.5 (*c* 0.3, CHCl3); TLC: PE/EA=10/1, R_f = 0.26; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 0.8 Hz, 2H), 7.01 – 6.92 (m, 2H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.56 (d, *J* = 7.9 Hz, 1H), 3.49 (dd, *J* = 10.4, 3.2 Hz, 1H), 2.78 – 2.63 (m, 2H), 2.51 (s, 1H), 1.75– 1.68 (m, 1H), 1.67 (s, 3H), 1.64 – 1.58 (m, 1H). **^{13}C**

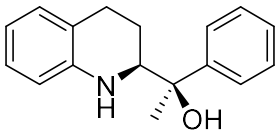
{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 144.9, 144.5, 129.1, 128.2, 127.1, 126.8, 125.5, 122.3, 118.0, 115.2, 75.3, 60.5, 26.6, 26.6, 22.9. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H Column (hexane/isopropanol = 96/4, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 19.308 min (minor), t_{R2} = 22.890 min (major). **HRMS (ESI)**: calculated for $C_{17}H_{20}NO$ $[M+H]^+$ 254.1539, found 254.1545.



(*S,S*)-**2a**
Chemical Formula: $C_{17}H_{19}NO$
Exact Mass: 253.1467

(*S*)-1-phenyl-1-((*S*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*S*,*S*)-2a)

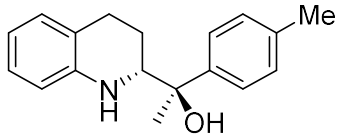
White solid, 4 mmol scale, 24.3 mg, 48% yield, 98% ee, $[\alpha]_{25}^{D}$= +2.6 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.35; **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H Column (hexane/isopropanol = 96/4, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 16.406 min (minor), t_{R2} = 17.152 min (major).



(*R,S*)-**2a**
Chemical Formula: $C_{17}H_{19}NO$
Exact Mass: 253.1467

(*R*)-1-phenyl-1-((*S*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*R*,*S*)-2a)

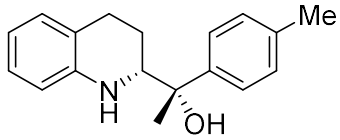
Colorless liquid, 0.2 mmol scale, 22.5 mg, 45% yield, 99% ee, $[\alpha]_{25}^{D}$ = -202.7 (*c* 0.3, $CHCl_3$); TLC: PE/ EA= 10/1, R_f= 0.26; **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H Column (hexane/isopropanol = 96/4, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 19.519 min (major), t_{R2} = 22.731 min (minor).



(*R,R*)-**2b**
Chemical Formula: $C_{18}H_{21}NO$
Exact Mass: 267.1623

(*R*)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)-1-(*p*-tolyl)ethan-1-ol ((*R,R*)-**2b**)

White solid, 0.2 mmol scale, 24.6 mg, 46% yield, 98% ee, $[\alpha]_{25}^{D}$ = -2.6 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.31; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.01 – 6.86 (m, 2H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 3.61 (dd, *J* = 10.8, 2.8, Hz, 2H), 2.86 (s, 1H), 2.85 – 2.76 (m, 2H), 2.38 (s, 3H), 2.10 (d, *J* = 15.8 Hz, 1H), 1.98 – 1.84 (m, 1H), 1.53 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 144.6, 143.6, 136.8, 129.3, 129.0, 126.7, 125.1, 122.0, 118.1, 115.2, 75.3, 59.6, 26.6, 25.1, 22.4, 21.0. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H Column (hexane/isopropanol = 96/4, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 15.899 min (major), t_{R2} = 20.229 min (major). **HRMS (ESI)**: calculated for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1695.

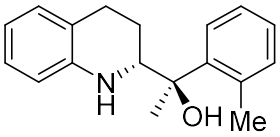


(*S,R*)-**2b**
Chemical Formula: $C_{18}H_{21}NO$
Exact Mass: 267.1623

(*S*)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)-1-(*p*-tolyl)ethan-1-ol ((*S,R*)-**2b**)

Colorless liquid, 0.2 mmol scale, 24.0 mg, 45% yield, 99% ee, $[\alpha]_{25}^{D}$ = +21.1 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.26; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.02 – 6.90 (m, 2H), 6.68 – 6.59 (m, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 4.01 (s, 1H), 3.52 – 3.42 (m, 1H), 2.80 – 2.62 (m, 2H), 2.46 (s, 1H), 2.36 (s, 3H), 1.78 – 1.71 (m, 1H), 1.64 (s, 3H), 1.60 (d, *J* = 17.8 Hz, 1H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 144.6, 141.9, 136.7, 129.1, 128.9, 126.7, 125.4, 122.3, 117.9, 115.2, 75.2, 60.5, 26.7, 26.5, 23.0, 21.0. **HPLC analysis**: The

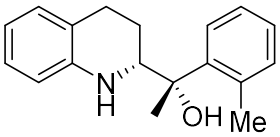
enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H Column (hexane/isopropanol = 96/4, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 17.295 min (minor), t_{R2} = 21.901 min (major). **HRMS (ESI)**: calculated for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1692.



(*R,R*)-**2c**
Chemical Formula: $C_{18}H_{21}NO$
Exact Mass: 267.1623

(*R*)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)-1-(o-tolyl)ethan-1-ol ((*R,R*)-**2c**)

Colorless liquid, 0.3 mmol scale, 37.0 mg, 46% yield, 98% ee, $[\alpha]_{25}^{D}$ = -17.0 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.39; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 5.6 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.50 (d, *J* = 7.6 Hz, 1H), 6.24 (s, 1H), 3.63 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.54 (s, 1H), 2.96 (s, 1H), 2.88 – 2.75 (m, 2H), 2.18 (s, 3H), 2.16 – 2.10 (m, 1H), 1.97 – 1.87 (m, 1H), 1.55 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 146.8, 144.3, 136.5, 128.9, 128.6, 127.2, 125.2, 119.2, 119.1, 115.9, 75.3, 59.6, 26.2, 25.1, 22.5, 21.0. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 18.028 min (major), t_{R2} = 34.489 min (minor). **HRMS (ESI)**: calculated for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1703.

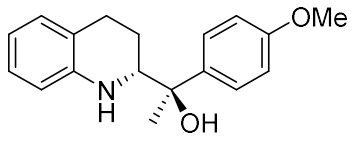


(*S,R*)-**2c**
Chemical Formula: $C_{18}H_{21}NO$
Exact Mass: 267.1623

(*S*)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)-1-(o-tolyl)ethan-1-ol ((*S,R*)-2c)

Colorless liquid, 0.3 mmol scale, 36.3 mg, 45% yield, 93% ee, $[\alpha]_{25}^{D}$ = +14.3 (*c* 0.1, $CHCl_3$); TLC: PE/EA= 10/1, R_f = 0.34; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 – 7.56 (m, 1H), 7.24 – 7.17 (m, 3H), 6.99 (q, *J* = 7.2 Hz, 2H), 6.69 (t, *J* = 7.2 Hz, 1H),

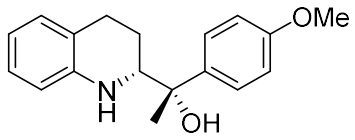
6.56 (d, *J* = 8.0 Hz, 1H), 3.83 (dd, *J* = 8.8, 4.8 Hz, 2H), 2.82 (s, 1H) 2.81 – 2.68 (m, 2H), 2.56 (s, 3H), 1.79 – 1.75 (m, 2H), 1.73 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 144.5, 142.7, 135.1, 132.7, 129.17, 127.2, 127.1, 126.8, 125.8, 122.7, 118.3, 115.5, 76.6, 57.9, 26.7, 26.5, 22.9, 22.8. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 16.106 min (minor), t_{R2} = 24.963 min (major). **HRMS (ESI)**: calculated for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1702.



(*R*,*R*)-**2d**
Chemical Formula: $C_{18}H_{21}NO_2$
Exact Mass: 283.1572

(*R*)-1-(4-methoxyphenyl)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*R*,*R*)-2d)

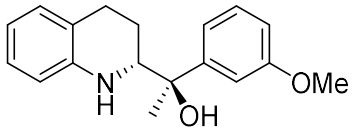
Colorless liquid, 0.3 mmol scale, 40.1 mg, 47% yield, 98% ee, $[\alpha]_{25}^{D}$ = -37.2 (*c* 0.1, $CHCl_3$); TLC: PE/EA= 10/1, R_f = 0.33; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.8 Hz, 2H), 7.06 – 6.85 (m, 4H), 6.64 (t, *J* = 6.8 Hz, 1H), 6.40 (d, *J* = 9.2 Hz, 1H), 3.84 (s, 3H), 3.67 (s, 1H), 3.59 (dd, *J* = 10.8, 2.8 Hz, 1H), 2.91 – 2.75 (m, 3H), 2.11 – 2.05 (m, 1H), 1.94 – 1.85 (m, 1H), 1.52 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 158.7, 144.6, 138.7, 129.0, 126.7, 126.4, 122.0, 118.0, 115.2, 113.9, 75.1, 59.7, 55.3, 26.7, 25.0, 22.4. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 15.206 min (major), t_{R2} = 22.093 min (minor). **HRMS (ESI)**: calculated for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645, found 284.1646.



(*S,R*)-**2d**
Chemical Formula: $C_{18}H_{21}NO_2$
Exact Mass: 283.1572

(*S*)-1-(4-methoxyphenyl)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*S,R*)-2d)

Colorless liquid, 0.3 mmol scale, 39.7 mg, 47% yield, 99% ee, $[\alpha]_{25}^{D}$ = +41.1 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.23; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.8 Hz, 2H), 7.00 – 6.90 (m, 4H), 6.63 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 4.11 (s, 1H), 3.82 (s, 3H), 3.45 (dd, *J* = 10.6, 2.8 Hz, 1H), 2.79 – 2.63 (m, 2H), 2.44 (s, 1H), 1.80 – 1.74 (m, 1H), 1.64 (s, 3H), 1.62 – 1.53 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.6, 144.6, 137.0, 129.0, 126.7, 122.2, 117.8, 115.1, 113.5, 75.1, 60.6, 55.3, 26.7, 26.3, 23.0. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 14.192 min (minor), t_{R2} = 18.489 min (major). **HRMS (ESI)**: calculated for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645, found 284.1649.

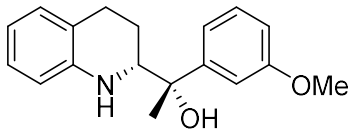


(*R,R*)-**2e**
Chemical Formula: $C_{18}H_{21}NO_2$
Exact Mass: 283.1572

(*R*)-1-(3-methoxyphenyl)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*R,R*)-**2e**)

Colorless liquid, 0.2 mmol scale, 26.8 mg, 47% yield, 98% ee, $[\alpha]_{25}^{D}$ = -6.9 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.17; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 (t, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 2.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.97 – 6.91 (m, 2H), 6.84 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 3.63 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.57 (s, 1H), 2.93 (s, 1H), 2.90 – 2.76 (m, 2H),

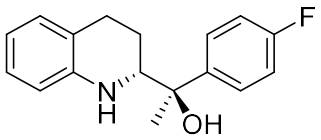
2.16– 2.11 (m, 1H), 1.98 – 1.89 (m, 1H), 1.52 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 159.9, 148.6, 144.5, 129.7, 129.0, 126.7, 122.1, 118.2, 117.4, 115.3, 112.3, 111.4, 75.2, 59.5, 55.3, 26.6, 25.1, 22.3. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t = 12.512min (minor), t_{R2} = 24.534 min (major). **(ESI)**: calculated for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645, found 284.1652.



(*S,R*)-**2e**
Chemical Formula: $C_{18}H_{21}NO_2$
Exact Mass: 283.1572

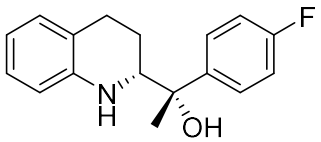
(*S*)-1-(3-methoxyphenyl)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*S,R*)-**2e**)

White solid, 0.2 mmol scale, 24.9 mg, 44% yield, 99% ee, $[\alpha]_{25}^{D}$ = +4.7 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f= 0.13; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 8.0 Hz, 1H), 7.09 (s, 1H), 7.04 – 6.92 (m, 3H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.56 (d, *J* = 7.6 Hz, 1H), 4.00 (s, 1H), 3.83 (s, 3H), 3.47 (dd, *J* = 10.0, 3.2 Hz, 1H), 2.77 – 2.64 (m, 2H), 2.54 (s, 1H), 1.73 – 1.57 (m, 1H), 1.64 (s, 3H), 1.21 (d, *J* = 6.0 Hz, 1H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 159.6, 146.7, 144.5, 129.2, 129.1, 126.8, 122.4, 118.0, 117.8, 115.2, 112.1, 111.6, 75.2, 60.4, 55.3, 26.6, 26.6, 22.9. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 13.523 min (major), t_{R2} = 18.711 min (minor). **HRMS (ESI)**: calculated for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645, found 284.1638.



(*R,R*)-**2f**
Chemical Formula: $C_{17}H_{18}FNO$
Exact Mass: 271.1372

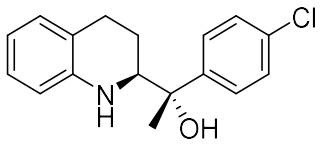
(*R*)-1-(4-fluorophenyl)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*R,R*)-**2f**) White solid, 0.2 mmol scale, 26.1 mg, 48% yield, 98% ee, $[\alpha]_{25}^{D}$ = -5.4 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.24; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (dd, *J* = 8.4, 5.2 Hz, 2H), 7.00 (t, *J* = 8.7 Hz, 2H), 6.87 (q, *J* = 7.2 Hz, 2H), 6.58 (t, *J* = 7.4 Hz, 1H), 6.32 (d, *J* = 8.0 Hz, 1H), 3.52 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.48 (s, 1H), 2.81 (s, 1H), 2.80 – 2.67 (m, 2H), 2.06 – 1.97 (m, 1H), 1.89 – 1.75 (m, 1H), 1.44 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 161.96 (d, *J* = 245.7 Hz), 144.3, 140.4 (d, *J* = 4.0Hz), 129.1, 127.0 (d, *J* = 8.0 Hz), 126.8, 122.0, 118.3, 115.5, 115.3 (d, *J* = 4.5 Hz), 75.1, 59.6, 26.5, 25.1, 22.4. **^{19}F {^{1}H} NMR** (376 MHz, Chloroform-*d*) δ -115.8. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H Column (hexane/isopropanol = 96/4, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 16.855 min (major), t_{R2} = 19.811 min (minor). **HRMS (ESI)**: calculated for $C_{17}H_{19}FNO$ $[M+H]^+$ 272.1445, found 272.1444.



(*S,R*)-**2f**
Chemical Formula: $C_{17}H_{18}FNO$
Exact Mass: 271.1372

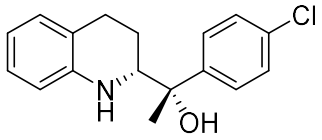
(*S*)-1-(4-fluorophenyl)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*S,R*)-**2f**) Colorless liquid, 0.2 mmol scale, 24.4 mg, 45% yield, 99% ee, $[\alpha]_{25}^{D}$ = +5.4 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.21; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.4 Hz, 1H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 6.8 Hz, 1H), 3.94 (s, 1H), 3.45 (dd, *J* = 10.4, 3.2 Hz, 1H), 2.78 – 2.61 (m, 2H), 2.54 (s, 1H), 1.64 (s, 3H), 1.69 – 1.42 (m, 2H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 161.9 (d, *J* = 245.3 Hz), 144.3, 140.5 (d, *J* = 3.2 Hz), 129.1, 127.2 (d, *J* = 8.0 Hz), 126.8, 122.3, 118.1, 115.3, 114.9 (d, *J* = 21.1 Hz), 75.0, 60.5, 26.9, 26.5, 22.9. **^{19}F {^{1}H} NMR** (376 MHz, Chloroform-*d*) δ -116.1. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H Column (hexane/isopropanol = 96/4, flow rate = 1.0 mL/min, T =

25 °C, UV detection at λ = 254 nm), t_{R1} = 20.122 min (major), t_{R2} = 22.526 min (minor). **HRMS (ESI)**: calculated for $C_{17}H_{19}FNO$ $[M+H]^+$ 272.1445, found 272.1444.



(*R,R*)-**2g**
Chemical Formula: $C_{17}H_{18}ClNO$
Exact Mass: 287.1077

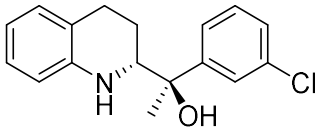
(*R*)-1-(4-chlorophenyl)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*R,R*)-**2g**) Colorless liquid, 0.2 mmol scale, 26.0 mg, 45% yield, 96% ee, $[\alpha]_{25}^{D}$ = -8.2 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.33; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 6.98– 6.92 (m, 2H), 6.66 (t, *J* = 8.0 Hz, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 3.60 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.54 (s, 1H), 2.92 (s, 1H), 2.88 – 2.77 (m, 2H), 2.13 – 2.07 (m, 1H), 1.95 – 1.85 (m, 1H), 1.52 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 145.3, 144.2, 133.1, 129.1, 128.7, 126.8, 126.8, 122.0, 118.4, 115.4, 75.1, 59.5, 26.5, 25.1, 22.3. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Phenomenex Chiralpak NQ-2 Column (hexane/isopropanol = 90/10, flow rate = 0.5 mL/min, T = 25 °C, UV detection at λ = 254 nm), t_{R1} = 8.893 min (minor), t_{R2} = 10.144 min (major). **HRMS (ESI)**: calculated for $C_{17}H_{19}ClNO$ $[M+H]^+$ 288.1150, found 288.1149.



(*S,R*)-**2g**
Chemical Formula: $C_{17}H_{18}ClNO$
Exact Mass: 287.1077

(*S*)-1-(4-chlorophenyl)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1ol ((*S,R*)-**2g**) Colorless liquid, 0.2 mmol scale, 25.6 mg, 45% yield, 99% ee, $[\alpha]_{25}^{D}$= +13.5 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.23; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.42 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 6.99 (t, J = 8.0 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 6.65 (t, J = 7.2 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 4.05 (s, 1H), 3.45 (dd, J = 10.0, 3.2 Hz, 1H), 2.76 – 2.58 (m, 3H), 1.63 (s, 3H), 1.59 – 1.51 (m, 2H). **^{13}C NMR** (101

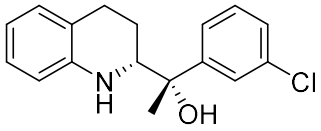
MHz, Chloroform-*d*) δ 144.3, 143.3, 132.9, 129.1, 128.3, 127.0, 126.8, 122.3, 118.2, 115.3, 75.0, 60.3, 27.0 26.5, 22.9. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Phenomenex Chiralpak NQ-2 Column (hexane/isopropanol = 90/10, flow rate = 0.5 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 9.058 min (minor), t_{R2} = 10.682 min (major). **HRMS (ESI)**: calculated for $C_{17}H_{19}ClNO$ $[M+H]^+$ 288.1150, found 288.1156.



(*R,R*)-**2h**
Chemical Formula: $C_{17}H_{18}ClNO$
Exact Mass: 287.1077

(*R*)-1-(3-chlorophenyl)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*R,R*)-**2h**)

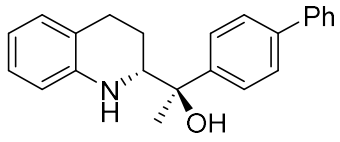
Colorless liquid, 0.2 mmol scale, 26.9 mg, 47% yield, 96% ee, $[\alpha]_{25}^{D}$ = -10.3 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.28; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (s, 1H), 7.41 – 7.24 (m, 3H), 6.95 (q, *J* = 7.4 Hz, 2H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H), 3.61 (dd, *J* = 11.0, 2.9 Hz, 1H), 3.52 (s, 1H), 2.96 (s, 1H), 2.91 – 2.73 (m, 2H), 2.17 – 2.07 (m, 1H), 1.99 – 1.83 (m, 1H), 1.52 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 149.1, 144.2, 134.8, 129.9, 129.1, 127.4, 126.8, 125.7, 123.4, 122.1, 118.5, 115.4, 75.1, 59.4, 26.5, 25.1, 22.3. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 90/10, flow rate = 0.8 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 11.962 min (major), t_{R2} = 12.952 min (minor). **HRMS (ESI)**: calculated for $C_{17}H_{19}ClNO$ $[M+H]^+$ 288.1150, found 288.1158.



(*S,R*)-**2h**
Chemical Formula: $C_{17}H_{18}ClNO$
Exact Mass: 287.1077

(*S*)-1-(3-chlorophenyl)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*S,R*)-**2h**)

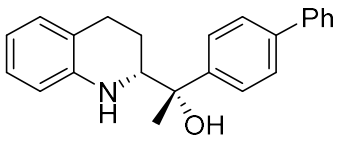
Colorless liquid, 0.2 mmol scale, 25.0 mg, 44% yield, 99% ee, $[\alpha]_{25}^{D}$ = +15.2 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.22; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (s, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 4.05 (s, 1H), 3.47 (dd, *J* = 9.6, 3.6 Hz, 1H), 2.79 – 2.65 (m, 2H), 2.60 (s, 1H), 1.63 (s, 3H), 1.61 – 1.57(m , 2H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 147.0, 144.2, 134.3, 129.4, 129.1, 127.2, 126.8, 125.8, 123.6, 122.4, 118.3, 115.4, 75.0, 60.3, 27.1, 26.4, 22.9. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 90/10, flow rate = 0.8 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 10.416 min (minor), t_{R2} = 13.161 min (major). **HRMS (ESI)**: calculated for $C_{17}H_{19}ClNO$ $[M+H]^+$ 288.1150, found 288.1147.



(*R,R*)-**2i**
Chemical Formula: $C_{23}H_{23}NO$
Exact Mass: 329.1780

(*R*)-1-([1,1'-biphenyl]-4-yl)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*R,R*)-**2i**)

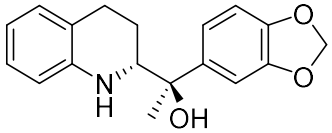
Colorless liquid, 0.3 mmol scale, 47.6 mg, 48% yield, 98% ee, $[\alpha]_{25}^{D}$ = -23.2 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.31; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 – 7.58 (m, 6H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.00 – 6.93 (m, 2H), 6.67 (t, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 1H), 3.69 (dd, *J* = 11.2, 2.8 Hz, 2H), 2.98 (s, 1H), 2.94 – 2.80 (m, 2H), 2.18 – 2.12 (m, 1H), 2.00 – 1.92 (m, 1H), 1.59 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 145.7, 144.5, 140.6, 140.1, 129.1, 128.9, 127.4, 127.3, 127.1, 126.8, 125.7, 122.1, 118.2, 115.3, 75.3, 59.6, 26.6, 25.1, 22.4. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 93/7, flow rate = 0.5 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 31.966 min (minor), t_{R2} = 34.792 min (major). **HRMS (ESI)**: calculated for $C_{23}H_{24}NO$ $[M+H]^+$ 330.1852, found 330.1858.



(*S,R*)-**2i**
Chemical Formula: $C_{23}H_{23}NO$
Exact Mass: 329.1780

(*S*)-1-([1,1'-biphenyl]-4-yl)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*S,R*)-**2i**)

Colorless liquid, 0.3 mmol scale, 47.0 mg, 48% yield, 98% ee, $[\alpha]_{25}^{D}$ = +49.6 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f= 0.31; $[\alpha]_{25}^{D}$ = +49.6 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.23; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.63 – 7.56 (m, 6H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.04 – 6.92 (m, 2H), 6.66 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 3.53 (dd, *J* = 10.4, 3.2 Hz, 1H), 2.81– 2.61 (m, 2H), 2.57 (s, 1H), 1.83–1.75 (m, 2H), 1.70 (s, 3H), 1.67 – 1.61 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 144.5, 143.9, 140.7, 139.9, 129.1, 128.8, 127.3, 127.1, 126.9, 126.8, 126.0, 122.3, 118.0, 115.2, 75.28, 60.5, 26.7, 26.7, 23.0. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 93/7, flow rate = 0.5 mL/min, T = 25 °C, UV detection at λ = 254 nm), t_{R1} = 32.997 min (minor), t_{R2} = 42.894 min (major). **HRMS (ESI)**: calculated for $C_{23}H_{24}NO$ $[M+H]^+$ 330.1852, found 330.1860.

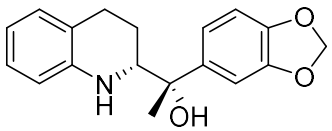


(*R,R*)-**2j**
Chemical Formula: $C_{18}H_{19}NO_3$
Exact Mass: 297.1365

(*R*)-1-(benzo[d][1,3]dioxol-5-yl)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*R,R*)-**2j**)

White solid, 0.2 mmol scale, 28.0 mg, 47% yield, 98% ee, $[\alpha]_{25}^{D}$ = -22.5 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.20; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.01 (d, *J* = 2.0 Hz, 1H), 6.98 – 6.92 (m, 3H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H), 5.98 (d, *J* = 2.0 Hz, 2H), 3.64 (s, 1H), 3.56 (dd, *J* = 11.2, 2.8 Hz,

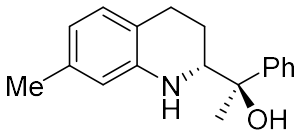
1H), 2.92 – 2.75 (m, 3H), 2.12 – 2.06 (m, 1H), 1.94 – 1.83 (m, 1H), 1.50 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 148.0, 146.6, 144.5, 140.9, 129.0, 126.8, 122.0, 118.3, 118.2, 115.3, 108.1, 106.1, 101.2, 75.2, 59.6, 26.6, 25.2, 22.4. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 17.858 min (minor), t_{R2} = 33.443 min (major). **HRMS (ESI)**: calculated for $C_{18}H_{20}NO_3$ $[M+H]^+$ 298.1438, found 298.1438.



(*S,R*)-**2j**
Chemical Formula: $C_{18}H_{19}NO_3$
Exact Mass: 297.1365

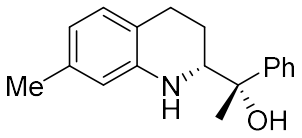
(*S*)-1-(benzo[d][1,3]dioxol-5-yl)-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)ethan-1-ol ((*S,R*)-**2j**)

White solid, 0.2 mmol scale, 28.2 mg, 47% yield, 99% ee, $[\alpha]_{25}^{D}$ = +18.6 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.13; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.02 (d, *J* = 1.6 Hz, 1H), 7.00 – 6.92 (m, 3H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.40 (t, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 5.96 (d, *J* = 2.0 Hz, 2H), 3.98 (s, 1H), 3.42 (dd, *J* = 10.4, 2.8 Hz, 1H), 2.78 – 2.65 (m, 2H), 2.45 (s, 1H), 1.79 – 1.73 (m, 1H), 1.62 (s, 3H), 1.62 – 1.55 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 147.6, 146.5, 144.5, 139.0, 129.1, 126.8, 122.3, 118.7, 118.0, 115.2, 107.8, 106.5, 101.0, 75.2, 60.6, 26.6, 26.6, 23.0. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 16.024 min (major), t_{R2} = 24.843 min (minor). **HRMS (ESI)**: calculated for $C_{18}H_{20}NO_3$ $[M+H]^+$ 298.1438, found 298.1443.



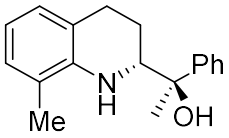
(*R,R*)-**2k**
Chemical Formula: $C_{18}H_{21}NO$
Exact Mass: 267.1623

(*R*)-1-((*R*)-7-methyl-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*R,R*)-**2k**) Colorless liquid, 0.3 mmol scale, 37.1 mg, 46% yield, 99% ee, $[\alpha]_{25}^{D}$ = -14.4 (*c* 0.1, $CHCl_3$); TLC: PE:EA=10/1, R_f = 0.36; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 – 7.55 (m, 1H), 7.25 – 7.18 (m, 3H)), 6.95 (q, *J* = 7.6 Hz, 2H), 6.65 (t, *J* = 8.0 Hz, 1H), 6.43 (d, *J* = 9.2 Hz, 1H), 3.90 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.70 (s, 1H), 2.95 (s, 1H), 2.93 – 2.77 (m, 2H), 2.57 (s, 3H), 2.08 – 2.03 (m, 1H), 1.98 – 1.87 (m, 1H), 1.64 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 144.6, 143.6, 135.7, 133.2, 129.1, 127.4, 126.8, 126.5, 126.0, 122.0, 118.1, 115.3, 76.6, 57.4, 26.7, 24.1, 22.7, 22.5. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 96/4, flow rate = 0.8 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 17.250 min (major), t_{R2} = 21.942 min (minor). **HRMS (ESI)**: calculated for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1695.



(*S,R*)-**2k**
Chemical Formula: $C_{18}H_{21}NO$
Exact Mass: 267.1623

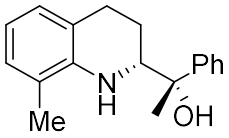
(*S*)-1-((*R*)-7-methyl-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*S,R*)-**2k**) Colorless liquid, 0.3 mmol scale, 37.7 mg, 47% yield, 99% ee, $[\alpha]_{25}^{D}$ = +53.8 (*c* 0.1, $CHCl_3$); TLC: PE:EA=10/1, R_f = 0.28; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 6.41 (s, 1H), 3.97 (s, 1H), 3.48 (dd, *J* = 10.4, 2.8 Hz, 1H), 2.75 – 2.60 (m, 3H), 2.24 (s, 3H), 1.76 – 1.69 (m, 3H), 1.66 (s, 3H),1.63 – 1.55 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 145.0, 144.3, 136.5, 129.0, 128.2, 127.1, 125.5, 119.4, 118.9, 115.8, 75.3, 60.5, 26.5, 26.3, 23.2, 21.1. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 96/4, flow rate = 0.8 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 23.111 min (minor), t_{R2} = 26.172 min (major). **HRMS (ESI)**: calculated for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1701.



(*R,R*)-**2l**
Chemical Formula: $C_{18}H_{21}NO$
Exact Mass: 267.1623

(*R*)-1-((*R*)-8-methyl-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*R,R*)-**2l**)

Colorless liquid, 0.3 mmol scale, 38.5 mg, 48% yield, 89% ee, $[\alpha]_{25}^{D}$ = -10.7 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.37; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.88 – 6.83 (m, 2H), 6.60 (t, *J* = 7.4 Hz, 1H), 3.61 (dd, *J* = 11.2, 2.9 Hz, 1H), 3.40 (s, 1H), 2.99 (s, 1H), 2.92 – 2.79 (m, 2H),, 2.14 – 2.11 (m, 1H), 1.97 – 1.89 (m, 1H), 1.82 (s, 3H), 1.60 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 146.7, 142.4, 128.6, 127.9, 127.2, 126.8, 125.1, 122.3, 121.5, 117.6, 75.3, 60.1, 26.8, 24.6, 22.2, 16.7. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 96/4, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 12.990 min (major), t_{R2} = 19.772 min (minor). **HRMS (ESI)**: calculated for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1705.

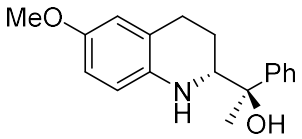


(*S,R*)-**2l**
Chemical Formula: $C_{18}H_{21}NO$
Exact Mass: 267.1623

(*S*)-1-((*R*)-8-methyl-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*S,R*)-**2h**)

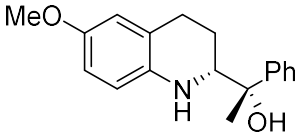
Colorless liquid, 0.3 mmol scale, 37.9 mg, 47% yield, 65% ee, $[\alpha]_{25}^{D}$ = +4.6 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.27; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.58 (t, *J* = 7.2 Hz, 1H), 3.79 (s, 1H), 3.50 (dd, *J* = 10.8, 3.2 Hz, 1H), 2.82 – 2.65 (m, 2H), 2.48 (s, 1H), 2.06 (s, 3H), 1.81 – 1.75 (m, 1H)), 1.69 (s, 3H), 1.61 – 1.57 (m, 1H)). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 144.9, 142.4,

128.2, 127.9, 127.1, 126.9, 125.5, 122.2, 121.6, 117.3, 75.5, 60.8, 27.0, 26.2, 22.8, 17.1. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 96/4, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 15.526 min (major), t_{R2} = 16.921 min (minor). **HRMS (ESI)**: calculated for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1701.



(*R,R*)-**2m**
Chemical Formula: $C_{18}H_{21}NO_2$
Exact Mass: 283.1572

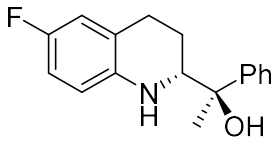
(*R*)-1-((*R*)-6-methoxy-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*R,R*)-**2m**) Colorless liquid, 0.3 mmol scale, 41.5 mg, 49% yield, >99% ee, $[\alpha]_{25}^{D}$ = -11.3 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.28; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 6.56 – 6.52 (m, 2H), 6.33 (d, *J* = 8.4 Hz, 1H), 3.71 (s, 3H), 3.58 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.31 (s, 1H), 3.09 (s, 1H), 2.93 – 2.75 (m, 2H), 2.17 – 2.11 (m, 1H), 1.97 – 1.87 (m, 1H)), 1.53 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 152.5, 146.9, 138.3, 128.6, 127.1, 125.1, 123.3, 116.4, 114.3, 112.9, 75.1, 59.8, 55.8, 26.9, 25.3, 22.4. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H Column (hexane/isopropanol = 96/4, flow rate = 0.8 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_R = 25.537 min. **HRMS (ESI)**: calculated for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645, found 286.1650.



(*S,R*)-**2m**
Chemical Formula: $C_{18}H_{21}NO_2$
Exact Mass: 283.1572

(*S*)-1-((*R*)-6-methoxy-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*S,R*)-**2m**) Colorless liquid, 0.3 mmol scale, 40.9 mg, 48% yield, 96% ee, $[\alpha]_{25}^{D}$ = +24.0 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.23; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.2 Hz,

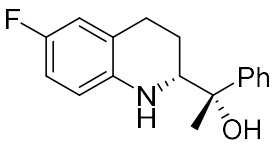
2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 6.61 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.55 – 6.53 (m, 2H), 3.71 (s, 3H), 3.42 (dd, *J* = 10.0, 34.0 Hz, 1H), 2.79 – 2.48 (m, 4H), 1.64 (s, 3H), 1.63 – 1.56 (m, 2H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 152.5, 145.0, 138.3, 128.2, 127.0, 125.3, 123.8, 116.5, 114.2, 112.9, 75.1, 60.7, 55.8, 27.0, 26.9, 22.9. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H Column (hexane/isopropanol = 96/4, flow rate = 0.8 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 28.991 min (minor), t_{R2} = 36.665 min (major). **HRMS (ESI)**: calculated for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645, found 286.1643.



(*R,R*)-**2n**
Chemical Formula: $C_{17}H_{18}FNO$
Exact Mass: 271.1372

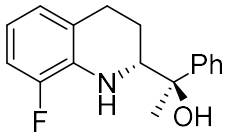
(*R*)-1-((*R*)-6-fluoro-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*R,R*)-**2n**)

Colorless liquid, 0.2 mmol scale, 25.6 mg, 47% yield, 91% ee, $[\alpha]_{25}^{D}$ = -11.9 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.29; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.70 – 6.62 (m, 2H), 6.31 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.59 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.48 (s, 1H), 2.95 (s, 1H), 2.90 – 2.86 (m, 1H), 2.78 – 2.74 (m, 1H), 2.13 – 2.10 (m, 1H), 1.96 – 1.82 (m, 1H), 1.54 (s, 3H). **^{13}C {^{1}H} NMR** ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.0 (d, *J* = 236.0 Hz), 146.6, 140.5 (d, *J* = 2.0 Hz), 128.6, 127.3, 125.2, 123.4 (d, *J* = 6.8 Hz), 116.0 (d, *J* = 7.6 Hz), 115.3, 115.0, 113.4, 113.2, 75.2, 59.7, 26.7, 25.0, 22.1. **^{19}F {^{1}H}NMR** (376 MHz, Chloroform-*d*) δ -126.9. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 90/10, flow rate = 0.8 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 9.306 min (minor), t_{R2} = 11.001 min (major). **HRMS (ESI)**: calculated for $C_{17}H_{19}FNO$ $[M+H]^+$ 272.1445, found 272.1443.



(*S,R*)-**2n**
Chemical Formula: $C_{17}H_{18}FNO$
Exact Mass: 271.1372

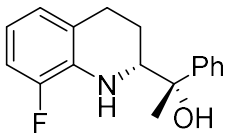
(*S*)-1-((*R*)-6-fluoro-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*S,R*)-**2n**) Colorless liquid, 0.2 mmol scale, 26.0 mg, 48% yield, 99% ee, $[\alpha]_{25}^{D}$ = +20.0 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.28; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 6.72 – 6.64 (m, 2H), 6.48 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.91 (s, 1H), 3.43 (dd, *J* = 10.4, 2.8 Hz, 1H), 2.77 – 2.59 (m, 2H), 2.57 (s, 1H), 1.72 – 1.68 (m, 1H), 1.65 (s, 3H), 1.61 – 1.52 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 155.9 (d, *J* = 235.9 Hz), 144.8, 140.6 (d, *J* = 2.0 Hz), 128.2, 127.1, 125.4, 123.7 (d, *J* = 6.8 Hz), 116.0 (d, *J* = 7.7 Hz), 115.3, 115.1, 113.4, 113.2, 75.2, 60.6, 26.8, 26.6, 22.7. **^{19}F {^{1}H} NMR** (376 MHz, Chloroform-*d*) δ -127.1. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 90/10, flow rate = 0.8 mL/min, T = 25 °C, UV detection at λ = 254 nm), t_{R1} = 12.163 min (major), t_{R2} = 14.230 min (minor). **HRMS (ESI)**: calculated for $C_{17}H_{19}FNO$ $[M+H]^+$ 272.1445, found 272.1449.



(*R,R*)-**2o**
Chemical Formula: $C_{17}H_{18}FNO$
Exact Mass: 271.1372

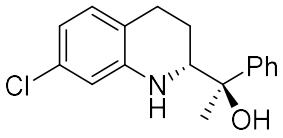
(*R*)-1-((*R*)-8-fluoro-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*R,R*)-**2o**) Colorless liquid, 0.3 mmol scale, 37.2 mg, 46% yield, 99% ee, $[\alpha]_{25}^{D}$ = -3.5 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.33; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 6.78 – 6.73 (m, 2H), 6.57 – 6.52 (m, 1H), 3.88 (s, 1H), 3.60 (dd, *J* = 11.2, 1.6 Hz, 1H), 2.91 – 2.79 (m, 3H), 2.11 – 2.05 (m, 1H), 1.95 – 1.85 (m, 1H), 1.59 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 151.3 (d, *J* = 239.8 Hz), 146.3, 133.0 (d, *J* = 11.9 Hz) 128.62, 127.36,

125.19, 124.2 (d, J = 3.3 Hz), 124.0 (d, J = 2.9 Hz)， 116.9 (d, J = 7.6 Hz), 112.3 (d, J = 18.3 Hz), 59.3, 26.4, 26.3, 24.6, 22.2. **^{19}F {^{1}H} NMR** (376 MHz, Chloroform-*d*) δ -137.4. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 95/5, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 9.563 min (major), t_{R2} = 15.354 min (minor). **HRMS (ESI)**: calculated for $C_{17}H_{19}FNO$ $[M+H]^+$ 272.1445, found 272.1449.



(*S,R*)-**2o**
Chemical Formula: $C_{17}H_{18}FNO$
Exact Mass: 271.1372

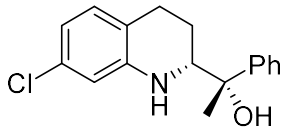
(*S*)-1-((*R*)-8-fluoro-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*S,R*)-**2o**) Colorless liquid, 0.3 mmol scale, 36.7 mg, 45% yield, 96% ee, $[\alpha]_{25}^{D}$ = +25.5 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.31; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 6.80 (dd, J = 11.8, 7.6 Hz, 1H), 6.72 (d, J = 7.6 Hz, 1H), 6.57 – 6.51 (m, 1H), 4.23 (s, 1H), 3.48 (dd, J = 10.4, 3.2 Hz, 1H), 2.75 –2.68 (m, 2H), 2.47 (s, 1H), 1.78 – 1.71 (m, 1H), 1.69 (s, 3H), 1.65 – 1.55 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 151.3 (d, J = 239.3 Hz), 144.6, 132.9 (d, J = 11.9 Hz), 128.2, 127.2, 125.5, 124.4 (d, J = 3.2 Hz), 124.0 (d, J = 2.9 Hz), 116.6 (d, J =7.6 239.3 Hz), 112.3 (d, J = 18.4 Hz), 59.8, 26.6, 26.3, 26.3, 22.7. **^{19}F {^{1}H} NMR** (376 MHz, Chloroform-*d*) δ -137.7. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 95/5, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 11.970 min (minor), t_{R2} = 13.408 min (major). **HRMS (ESI)**: calculated for $C_{17}H_{19}FNO$ $[M+H]^+$ 272.1445, found 272.1451.



(*R,R*)-**2p**
Chemical Formula: $C_{17}H_{18}ClNO$
Exact Mass: 287.1077

(*R*)-1-((*R*)-7-chloro-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*R,R*)-**2p**)

White solid, 0.2 mmol scale, 27.1 mg, 47% yield, 98% ee, $[\alpha]_{25}^{D}$ = -260.0 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.24; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.38 (s, 1H), 3.72 (s, 1H), 3.60 (dd, *J* = 10.8, 2.8 Hz, 1H), 2.78–2.74 (m, 2H), 2.71 (s, 1H), 2.08– 2.04 (m, 1H), 1.88 – 1.82 (m, 1H), 1.54 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 146.2, 145.6, 132.0, 129.9, 128.7, 127.4, 125.2, 120.3, 117.8, 114.6, 75.4, 59.5, 26.1, 24.7, 22.2. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 96/4, flow rate = 0.6 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 25.259 min (major), t_{R2} = 35.366 min (minor). **HRMS (ESI)**: calculated for $C_{17}H_{19}ClNO$ $[M+H]^+$ 288.1150, found 288.1147.

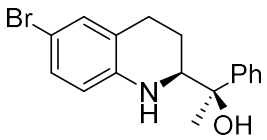


(*S,R*)-**2p**

Chemical Formula: $C_{17}H_{18}ClNO$

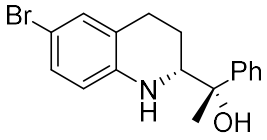
Exact Mass: 287.1077

(*S*)-1-((*R*)-7-chloro-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*S,R*)-**2p**) Colorless liquid, 0.2 mmol scale,27.7 mg, 48% yield, 89% ee, $[\alpha]_{25}^{D}$ = +257.2 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.23; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.51 (s, 1H), 4.11 (s, 1H) 3.46 (dd, *J* = 10.4, 3.2 Hz, 1H), 2.71 – 2.60 (m, 2H), 2.31 (s, 1H), 1.81 – 1.75 (m, 1H), 1.66 (s, 3H), 1.57 – 1.47 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 144.6, 144.5, 131.9, 129.9, 128.3, 127.3, 125.6, 120.4, 117.4, 114.4, 75.4, 60.2, 26.3, 26.2, 22.8. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 96/4, flow rate = 0.6 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 43.669 min (minor), t_{R2} = 54.625 min (major). **HRMS (ESI)**: calculated for $C_{17}H_{19}ClNO$ $[M+H]^+$ 288.1150, found 288.1149.



(*R,R*)-**2q**
Chemical Formula: $C_{17}H_{18}BrNO$
Exact Mass: 331.0572

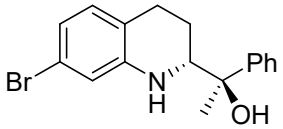
(*R*)-1-((*R*)-6-bromo-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*R,R*)-**2q**) Colorless liquid, 0.2 mmol scale, 31.8 mg, 48% yield, 98% ee, $[\alpha]_{25}^{D}$ = -23.1 (*c* 0.1, $CHCl_3$); TLC: PE:EA=10/1, R_f = 0.27; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.06 (s, 1H), 7.00 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.27 (d, *J* = 8.4 Hz, 1H), 3.66 (s, 1H), 3.59 (dd, *J* = 10.8, 2.8 Hz, 1H), 2.86 – 2.69 (m, 2H),2.74 (s, 1H), 2.09 – 2.03 (m, 1H), 1.90 – 1.79 (m, 1H), 1.54 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 146.3, 143.6, 131.4, 129.4, 128.7, 127.4, 125.2, 124.0, 116.6, 109.5, 75.4, 59.6, 26.4, 24.8, 22.0. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 19.705min (minor), t_{R2} = 25.981 min (minor). **HRMS (ESI)**: calculated for $C_{17}H_{19}BrNO$ $[M+H]^+$ 332.0645, found 332.0647.



(*S,R*)-**2q**
Chemical Formula: $C_{17}H_{18}BrNO$
Exact Mass: 331.0572

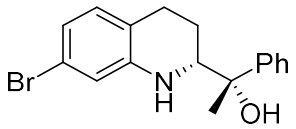
(*S*)-1-((*R*)-6-bromo-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*S,R*)-**2q**) White solid, 0.2 mmol scale, 30.4 mg, 46% yield, 98% ee, $[\alpha]_{25}^{D}$ = +7.6 (*c* 0.1, $CHCl_3$); TLC: PE:EA=10/1, R_f = 0.20; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 – 7.45 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 2H), 6.41 (d, *J* = 8.4 Hz, 1H), 4.06 (s, 1H), 3.45 (dd, *J* = 10.4, 2.8 Hz, 1H), 2.74 – 2.58 (m, 2H), 2.37 (s, 1H), 1.77 – 1.65 (m, 1H), 1.65 (s, 3H), 1.57 – 1.47 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 144.5, 143.6, 131.4, 129.4, 128.3, 127.2, 125.5, 124.2, 116.5, 109.3, 75.4, 60.4, 26.5, 26.4, 22.6. **HPLC analysis**: The enantiomeric excess was

determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 23.151 min (major), t_{R2} = 24.187 min (minor). **HRMS (ESI)**: calculated for $C_{17}H_{19}BrNO$ $[M+H]^+$ 332.0645, found 332.0637.



(*R,R*)-**2r**
Chemical Formula: $C_{17}H_{18}BrNO$
Exact Mass: 331.0572

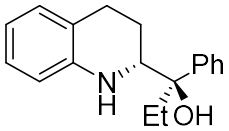
(*R*)-1-((*R*)-7-bromo-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*R,R*)-**2r**) Colorless liquid, 0.2 mmol scale, 29.8 mg, 45% yield, 98% ee, $[\alpha]_{25}^{D}$ = -0.8 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.29; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.06 (s, 1H), 7.00 (d, *J* = 10.6 Hz, 1H), 6.27 (d, *J* = 8.4 Hz, 1H), 3.66 (s, 1H), 3.59 (dd, *J* = 10.8, 2.8 Hz, 1H), 2.90 – 2.74 (m, 2H), 2.74 (s, 1H), 2.08 – 2.03 (m, 1H), 1.92 – 1.78 (m, 1H), 1.54 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 146.3, 143.6, 131.4, 129.4, 128.7, 127.4, 125.2, 124.0, 116.6, 109.5, 75.4, 59.6, 26.4, 24.8, 22.0. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 90/10, flow rate = 0.8 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 10.608 min (major), t_{R2} = 12.981 min (minor). **HRMS (ESI)**: calculated for $C_{17}H_{19}BrNO$ $[M+H]^+$ 332.0645, found 332.0639.



(*S,R*)-**2r**
Chemical Formula: $C_{17}H_{18}BrNO$
Exact Mass: 331.0572

(*S*)-1-((*R*)-7-bromo-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-ol ((*S,R*)-**2r**) Colorless liquid, 0.2 mmol scale, 31.2 mg, 47% yield, 93% ee, $[\alpha]_{25}^{D}$ = +10.4 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.24; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 2H), 6.41 (d, *J* = 8.4 Hz, 1H), 4.05 (s, 1H), 3.45 (dd, *J* = 10.4, 2.8 Hz, 1H), 2.70 – 2.59 (m, 2H), 2.36 (s, 1H), 1.77 – 1.71 (m, 1H), 1.65 (s, 3H), 1.56 – 1.48 (m, 1H). **^{13}C {^{1}H}**

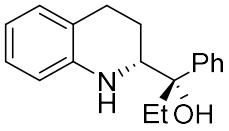
NMR (101 MHz, Chloroform-*d*) δ 144.5, 143.6, 131.4, 129.4, 128.3, 127.2, 125.5, 124.2, 116.5, 109.3, 75.3, 60.4, 26.5, 26.4, 22.6. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 90/10, flow rate = 0.8 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 13.309 min (minor), t_{R2} = 15.905 min (major). **HRMS (ESI)**: calculated for $C_{17}H_{19}BrNO$ $[M+H]^+$ 332.0645, found 332.0638.



(*R,R*)-**2s**
Chemical Formula: $C_{18}H_{21}NO$
Exact Mass: 267.1623

(*R*)-1-phenyl-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)propan-1-ol ((*R,R*)-**2s**)

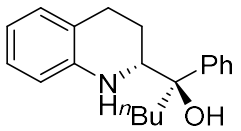
Colorless liquid, 0.2 mmol scale, 25.2 mg, 47% yield, 98% ee, $[\alpha]_{25}^{D}$ = -34.2 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.40; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.35 (d, *J* = 8.0 Hz, 1H), 3.68 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.40 (s, 1H), 2.98 (s, 1H), 2.96 – 2.77 (m, 2H), 2.24 – 2.18 (m, 1H), 2.05 – 1.94 (m, 2H), 1.83 – 1.76 (m, 1H), 0.69 (t, *J* = 7.2 Hz, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 144.5, 144.2, 129.1, 128.5, 127.1, 126.7, 126.0, 122.2, 118.3, 115.4, 77.9, 59.4, 30.1, 26.6, 22.1, 7.8. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 90/10, flow rate = 0.8 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 8.980 min (minor), t_{R2} = 9.556 min (major). **HRMS (ESI)**: calculated for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1700.



(*S,R*)-**2s**
Chemical Formula: $C_{18}H_{21}NO$
Exact Mass: 267.1623

(*S*)-1-phenyl-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)propan-1-ol ((*S,R*)-**2s**)

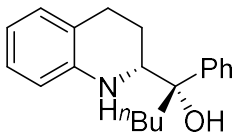
Colorless liquid, 0.2 mmol scale, 24.8 mg, 47% yield, 99% ee, $[\alpha]_{25}^{D}$ = +12.7 (*c* 0.1, $CHCl_3$); TLC: PE/EA=10/1, R_f = 0.33; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.70 – 6.58 (m, 2H), 4.15 (s, 1H), 3.53 (dd, *J* = 10.2, 3.2 Hz, 1H), 2.73 – 2.60 (m, 2H), 2.56 (s, 1H), 2.02 – 1.91 (m, 2H), 1.66 – 1.50 (m, 2H), 0.77 (t, *J* = 7.2 Hz, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 144.4, 142.3, 129.1, 128.1, 126.8, 126.7, 125.9, 122.7, 118.2, 115.5, 78.0, 60.1, 31.9, 26.5, 22.9, 7.8. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 90/10, flow rate = 0.8 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 13.477 min (minor), t_{R2} = 17.261 min (major). **HRMS (ESI)**: calculated for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1690.



(*R,R*)-**2t**
Chemical Formula: $C_{20}H_{25}NO$
Exact Mass: 295.1936

(*R*)-1-phenyl-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)pentan-1-ol ((*R,R*)-**2t**)

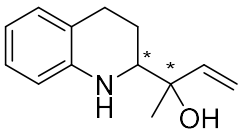
White solid, 0.2 mmol scale, 26.0 mg, 44% yield, 98% ee, $[\alpha]_{25}^{D}$ = -7.8 (*c* 0.1, $CHCl_3$); TLC: PE:EA=5/1, R_f = 0.17; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.34 (d, *J* = 8.0 Hz, 1H), 3.65 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.38 (s, 1H), 2.96 (s, 1H), 2.90 – 2.78 (m, 2H), 2.25 – 2.19 (m, 1H), 2.01 – 1.91 (m, 2H), 1.80 – 1.72 (m, 1H), 1.27 – 1.19 (m, 3H), 0.82 – 0.79 (m, 4H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 144.6, 144.5, 129.0, 128.5, 127.0, 126.7, 125.9, 122.2, 118.3, 115.4, 77.6, 59.6, 37.2, 26.6, 25.6, 23.2, 22.1, 14.0. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 90/10, flow rate = 0.8 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 6.638 min (minor), t_{R2} = 7.578 min (major). **HRMS (ESI)**: calculated for $C_{20}H_{26}NO$ $[M+H]^+$ 296.2009, found 296.2015.



(*S,R*)-**2t**
Chemical Formula: $C_{20}H_{25}NO$
Exact Mass: 295.1936

(*S*)-1-phenyl-1-((*R*)-1,2,3,4-tetrahydroquinolin-2-yl)pentan-1-ol ((*S,R*)-**2t**)

White solid, 0.2 mmol scale, 26.6 mg, 44% yield, 99% ee, $[\alpha]_{25}^{D}$ = +8.3 (*c* 0.1, $CHCl_3$); TLC: PE:EA= 5/1, R_f= 0.15; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.67 – 6.61 (m, 2H), 4.15 (s, 1H), 3.50 (dd, *J* = 10.0, 3.6 Hz, 1H), 2.72 – 2.60 (m, 2H), 2.56 (s, 1H), 2.03 – 1.93 (m, 1H), 1.89 – 1.82 (m, 1H), 1.64 – 1.47 (m, 3H), 1.38 – 1.29 (m, 3H), 1.00 – 0.92 (m, 1H), 0.84 (t, *J* = 7.2 Hz, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 144.4, 142.8, 129.0, 128.1, 126.8, 126.6, 125.7, 122.7, 118.2, 115.5, 77.7, 60.3, 39.2, 26.5, 25.6, 23.2, 22.8, 14.0. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 90/10, flow rate = 0.8 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 8.643 min (major), t_{R2} = 9.979 min (minor). **HRMS (ESI)**: calculated for $C_{20}H_{26}NO$ $[M+H]^+$ 296.2009, found 296.2008.

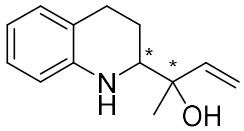


Chemical Formula: $C_{13}H_{17}NO$
Exact Mass: 203.1310

2-(1,2,3,4-tetrahydroquinolin-2-yl)but-3-en-2-ol (**2u-A**)

Colorless liquid, 0.2 mmol scale, 18.6 mg, 46% yield, 98% ee, $[\alpha]_{25}^{D}$ = -23.1 (*c* 0.1, $CHCl_3$); TLC: PE:EA=10/1, R_f= 0.29; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.97 (d, *J* = 7.6 Hz, 2H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 5.92 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.45 (d, *J* = 17.2 Hz, 1H), 5.25 (d, *J* = 10.8 Hz, 1H), 4.02 (s, 1H), 3.19 (dd, *J* = 11.2, 2.8 Hz, 1H), 2.89 – 2.74 (m, 2H), 2.34 (s, 1H), 2.06 (d, *J* = 12.8 Hz, 1H), 1.83 – 1.74 (m, 1H), 1.30 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 144.6, 143.8, 129.0, 126.8, 121.8, 117.8, 114.9, 114.2, 74.2, 58.0, 26.6, 22.6, 22.1. **HPLC**

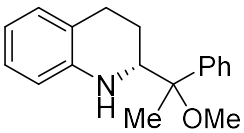
analysis: The enantiomeric excess was determined by HPLC on Phenomenex Chiralpak NQ-2 Column (hexane/isopropanol = 90/10, flow rate = 0.5 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 8.257 min (major), t_{R2} = 10.156 min (minor). **HRMS (ESI)**: calculated for $C_{13}H_{18}NO$ $[M+H]^+$ 204.1383, found 204.1383.



Chemical Formula: $C_{13}H_{17}NO$
Exact Mass: 203.1310

2-(1,2,3,4-tetrahydroquinolin-2-yl)but-3-en-2-ol (2u-B)

Colorless liquid, 0.2 mmol scale, 17.8 mg, 43% yield, 97% ee, $[\alpha]_{25}^{D}$ = +18.3 (*c* 0.1, $CHCl_3$); TLC: PE:EA=10/1, R_f = 0.21; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.96 (q, *J* = 7.2 Hz, 2H), 6.63 – 6.52 (m, 2H), 6.01 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.21 (d, *J* = 10.8 Hz, 1H), 4.27 (s, 1H), 3.28 (d, *J* = 13.6 Hz, 1H), 2.88 – 2.70 (m, 2H), 2.05 – 1.95 (m, 1H), 1.82 (s, 1H), 1.69 – 1.58 (m, 1H), 1.38 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 145.8, 141.0, 128.9, 126.8, 121.5, 117.3, 114.8, 114.5, 74.9, 59.7, 26.8, 24.7, 23.3. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Phenomenex Chiralpak NQ-2 Column (hexane/isopropanol = 90/10, flow rate = 0.5 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 9.123 min (major), t_{R2} = 9.977 min (minor). **HRMS (ESI)**: calculated for $C_{13}H_{18}NO$ $[M+H]^+$ 204.1383, found 204.1388.



Chemical Formula: $C_{18}H_{21}NO$
Exact Mass: 267.1623

2v

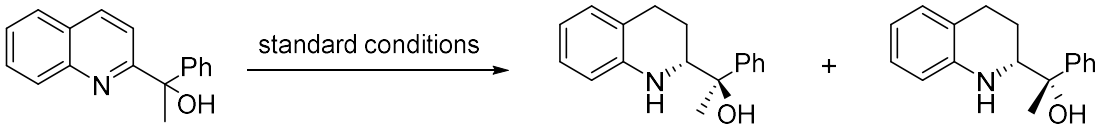
(2*R*)-2-(1-methoxy-1-phenylethyl)-1,2,3,4-tetrahydroquinoline (2v)

Colorless liquid, 0.2 mmol scale, 51.3 mg, 96% yield (mixture), dr: 1/1; 99% ee or 87% ee of each isomer, TLC: PE/EA= 40/1, R_f = 0.23; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.47 – 7.39 (m, 8H), 7.37 – 7.30 (m, 2H), 7.01 (t, *J* = 6.8 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 3H), 6.62– 6.56 (m, 3H), 6.36 (d, *J* = 7.2 Hz, 1H), 3.49 – 3.42 (m, 2H), 3.15 (s, 3H),

3.10 (s, 3H), 2.91 – 2.82 (m, 1H), 2.72 – 2.59 (m, 3H), 2.23 – 2.17(m, 1H), 1.65 (s, 3H), 1.61 (s, 3H), 1.59 –1.50 (m, 3H), 1.40 – 1.34 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 145.2, 144.9, 142.4, 141.7, 129.0, 128.9, 128.3, 128.3, 127.6, 127.6, 127.4, 127.2, 126.8, 126.62, 121.7, 121.3, 117.0, 116.6, 114.5, 114.1, 82.2, 80.9, 61.6, 61.0, 50.3, 50.3, 27.11, 27.1, 23.5, 23.3, 17.5, 14.5. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 96/4, flow rate = 0.5 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 8.763 min, t_{R2} = 10.387 min. **HRMS (ESI)**: calculated for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1696 or 268.1705.

4. Synthetic Applications

4.1 Gram-scale reaction of 1



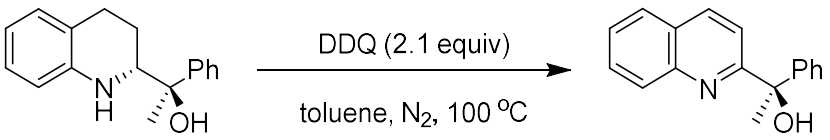
rac-**1**
1.00 g, 4 mmol

(*R,R*)-**2a**
46% yield, 97% ee

(*S,R*)-**2a**
43% yield, 95% ee

Under nitrogen atmosphere, substrate **1** (1.00 g, 4 mmol, 1.0 equiv.) and **cat.5** (23.1 mg, 0.04 mmol, 1 mol%) were added to a 100 mL round-bottom flask. TFE (8 mL) and H_2O (8 mL) were sequentially introduced via syringe, followed by the dropwise addition of HCOOH (1.5 mL, 40 mmol, 10.0 equiv.). The reaction was stirred at room temperature for 24 hours. Upon reaction completion, the mixture was diluted with ethyl acetate (40 mL) and water (40 mL). The organic phases were washed with saturated aqueous $NaHCO_3$ solution (30 mL) and then saturated NaCl solution (80 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography (PE/EA = 10/1) to give the desired compound (*R*,*R*)-**2a** as a white solid in 46% yield with 97% ee, and (*S*,*R*)-**2a** as a colorless liquid in 43% yield with 95% ee.

4.2 Synthesis of optically pure enantiomer of 1

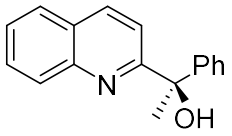


(*R,R*)-**2a**
0.5 mmol, 98% ee

(*R*)-**1a**
98% yield, 98% ee

Under nitrogen atmosphere, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 238.9 mg, 1.1 mmol, 2.1 equiv.) was added to a solution of (*R*,*R*)-**2a** (125.9, 0.5 mmol, 1.0 equiv.) in 4 mL toluene. And then the reaction mixture was stirred overnight at 100 °C. After the reaction was cooled to room temperature, the reaction was quenched by slow addition of water. The mixture was diluted and extracted with ethyl acetate (10 mL). Then the combined organic extracts were washed with saturated NaCl solution (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced

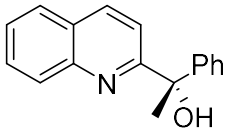
pressure. The crude mixture was purified by silica-gel column chromatography (PE/EA = 20/1) to give the desired compound (*R*)-**1a** as a white solid in 98% yield with 98% ee.



(*R*)-**1a**
Chemical Formula: $C_{17}H_{15}NO$
Exact Mass: 249.1154

(*R*)-1-phenyl-1-(quinolin-2-yl)ethan-1-ol (*R*)-**1a**

White solid, 0.5 mmol scale, 121.3 mg, 98% yield, 98% ee, $[\alpha]_{25}^{D}$ = -173.1 (*c* 0.5, $CHCl_3$). TLC: PE/EA=10/1, R_f = 0.2; **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H Column (hexane/isopropanol = 96/4, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 19.006 min (major), t_{R2} = 22.065 min (minor).

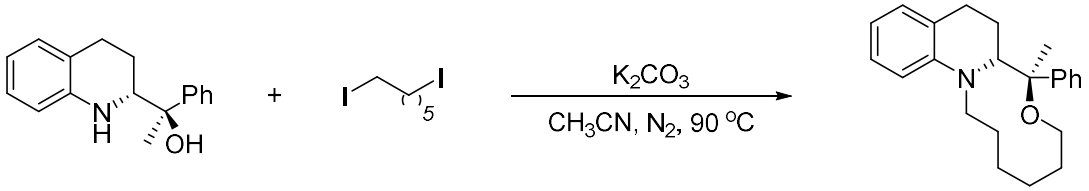


(*S*)-**1a**
Chemical Formula: $C_{17}H_{15}NO$
Exact Mass: 249.1154

(*S*)-1-phenyl-1-(quinolin-2-yl)ethan-1-ol (*S*)-**1a**

From (*S*,*R*)-**2a** (95% ee). White solid, 0.2 mmol scale, 48.3 mg, 97% yield, 95% ee, $[\alpha]_{25}^{D}$ = +286.2 (*c* 0.5, $CHCl_3$); **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H Column (hexane/isopropanol = 96/4, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 19.134 min (minor), t_{R2} = 22.153 min (major).

4.3 Synthesis of medium-sized ring compound 3

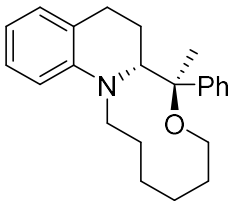


(*R*,*R*)-**2a**
97% ee

3
48% yield, 96% ee

According to the reported literature:[3] A Schlenk tube was charged with (*R*,*R*)-**2a**

(50.6 mg, 0.2 mmol, 1.0 equiv.), 1, 6-diiodihexane (135.2 mg, 0.4 mmol, 2.0 equiv.) and potassium carbonate (K_2CO_3, 30.4 mg, 0.22 mmol, 1.1 equiv.) and CH_3CN (4 mL). The mixture was allowed to reflux at 90 °C in an oil bath for 36 h. After the stirring stopped, the reaction mixtures were quenched with saturated ammonium chloride and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The crude residue was purified by column chromatography on silica gel (PE/EA = 10/1), affording the target compound **3** as yellow oil in 48% yield (321.8 mg) with 96% ee.

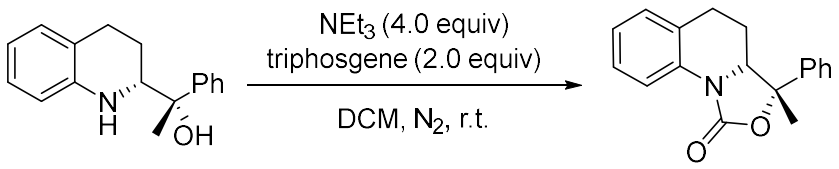


3
Chemical Formula: $C_{23}H_{29}NO$
Exact Mass: 335.2249

(*8R,8aR*)**-8-methyl-8-phenyl-1,2,3,4,5,6,8,8a,9,10-decahydro-[1,4]oxazecino[4,3-a] quinoline** (**3)**

Yellow oil, 0.2 mmol scale, 321.8 mg, 48% yield, 96% ee, $[\alpha]_{25}^{D}$ = -8.9 (*c* 0.1, $CHCl_3$); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 3.62 (dd, *J* = 5.6, 3.2 Hz, 1H), 3.23 – 3.15(m, 1H), 3.11 (t, *J* = 7.2 Hz, 2H), 3.06 – 3.01 (m, 1H), 2.65 – 2.60 (m, 2H), 2.32 – 2.20 (m, 2H), 1.74 – 1.67 (m, 2H), 1.51 (s, 3H), 1.32 – 1.30 (m, 2H), 1.22 – 1.19 (m, 2H), 1.07 – 1.00 (m, 2H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 149.0, 144.6, 129.4, 128.2, 126.89, 126.7, 125.0, 124.2, 116.6, 113.6, 77.8, 66.2, 52.6, 33.4, 30.1, 25.8, 25.4, 25.4, 24.8, 23.0, 7.0. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-3 Column (hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, T = 25 ℃, UV detection at λ = 254 nm), t_{R1} = 7.151 min (major), t_{R2} = 9.813 min (minor). **HRMS (ESI)**: calculated for $C_{17}H_{19}BrNO$ $[M+H]^+$ 336.2322, found 336.2321.

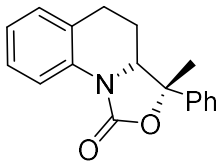
4.4 Synthesis of tricyclic compound 4



(*S,R*)-**2a**
95% ee

4
96% yield, 95% ee

Under nitrogen atmosphere (*S,R*)-**2a** (50.6 mg, 0.2 mmol, 1.0 equiv.) and triethylamine (67.5 μL, 0.8 mmol, 4 equiv.) were dissolved in 1 mL dry CH_2Cl_2. A solution of triphosgene (118.7 mg, 0.4 mmol, 2.0 equiv.) in 0.5 mL dry CH_2Cl_2 was added dropwise at 0 ℃ (ice bath) over a period of 15 min. Afterwards the ice bath was removed and the reaction mixture was allowed to warm up to room temperature and stirred for 3 h. The filtrate was washed with 10 mL H_2O and the aqueous layer was extracted with CH_2Cl_2 (3x5 mL). The combined organic layers were dried over Na_2SO_3, filtered and concentrated. The residue was purified by column chromatography (PE/EA= 5/1) to give the product **4** as a white solid with 96% yield (53.6 mg) and 95% ee.



4
Chemical Formula: $C_{18}H_{17}NO_2$
Exact Mass: 279.1259

(*3S,3aR*)-3-methyl-3-phenyl-3,3a,4,5-tetrahydro-1H-oxazolo[3,4-a]quinolin-1-one (4)

White solid, 0.2 mmol scale, 53.6 mg, 96% yield, 95% ee, $[\alpha]_{25}^{D}$ = +308.5 (*c* 0.5, $CHCl_3$); TLC: PE/EA=5/1, R_f = 0.21; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.4 Hz, 1H), 7.45 – 7.30 (m, 5H), 7.00 (t, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 4.01 (dd, *J* =12.4, 2.8 Hz, 1H), 2.90 – 2.72 (m, 2H), 1.94 (s, 3H), 1.72 – 1.66 (m, 1H), 1.07 – 0.97 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 154.2, 139.5, 135.3, 129.0, 128.5, 128.1, 127.1, 125.3, 124.7, 123.5, 118.8, 82.4, 65.0, 27.3, 27.1, 24.4. **HPLC analysis**: The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-3 Column (hexane/isopropanol = 90/10, flow rate = 1.0 mL/min,

T = 25 °C, UV detection at λ = 254 nm), t_{R1} = 13.011 min (major), t_{R2} = 16.972 min (minor). **HRMS (ESI)**: calculated for $C_{17}H_{18}NO$ $[M+H]^+$ 280.1332, found 280.1331.

5. References

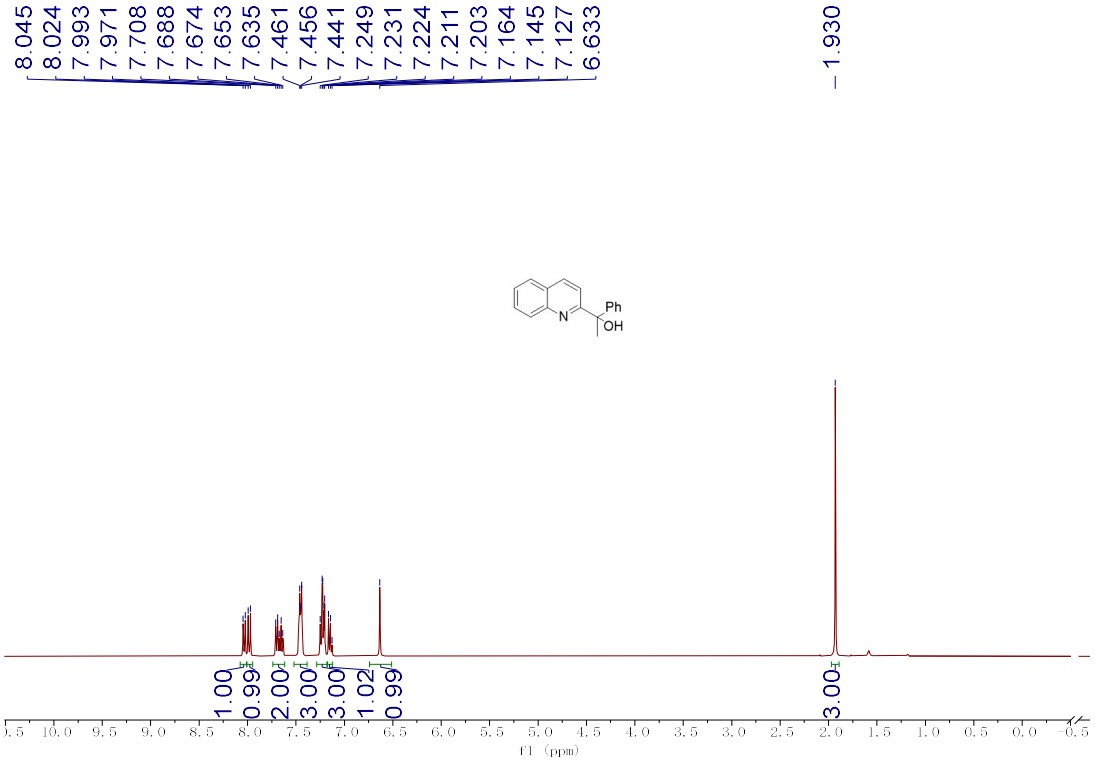
[1] Zhang, M.; Niu, T.; Liang, M.; Xu, F.; Du, Y.; Zhuang, H.; Song, R.-J.; Yang, H.; Yin, Q. Consecutive Asymmetric Transfer Hydrogenation of C2-Acylated Quinolines and Quinoxalines: A Diastereodivergent Synthesis of Enantioenriched Tetrahydroquinolines and Tetrahydroquinoxalines Bearing Endo- and Exocyclic Chirality. *J. Am. Chem. Soc.* **2025**, *147* (21), 18197-18207.

[2] Li, L.; Zhang, S. Q.; Cui, X.; Zhao, G.; Tang, Z.; Li, G. X. Catalytic Asymmetric Hydrogen Atom Transfer Based on a Chiral Hydrogen Atom Donor Generated from TBADT and Chiral BINOL. *Org. Lett.* **2024**, *26* (39), 8371-8376.

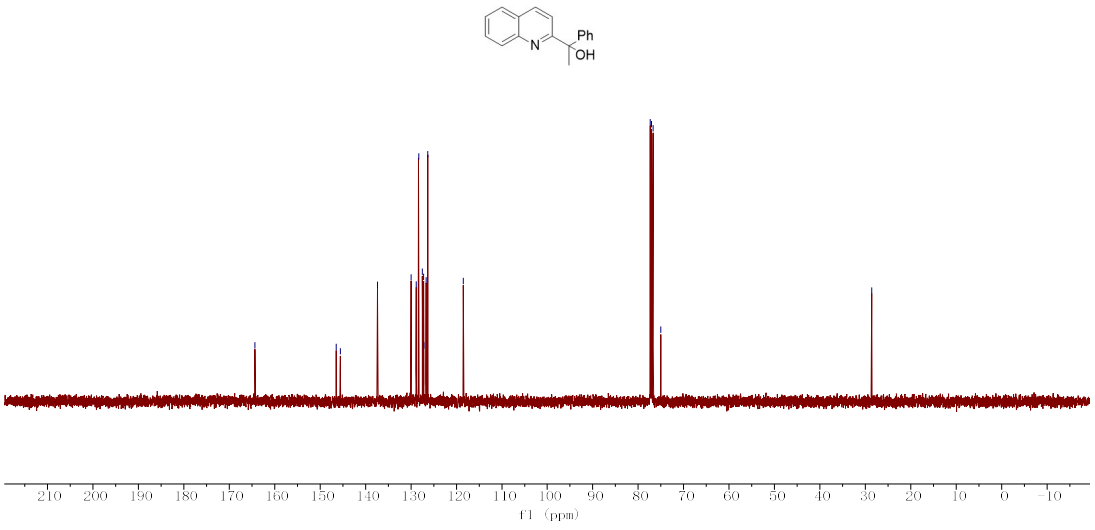
[3] Wang, M.; Zhang, C.; Ci, C.; Jiang, H.; Dixneuf, P. H.; Zhang, M. Room Temperature Construction of Vicinal Amino Alcohols via Electroreductive Cross-Coupling of N-Heteroarenes and Carbonyls. *J. Am. Chem. Soc.* **2023**, *145* (20), 10967-10973.

6. NMR Spectra

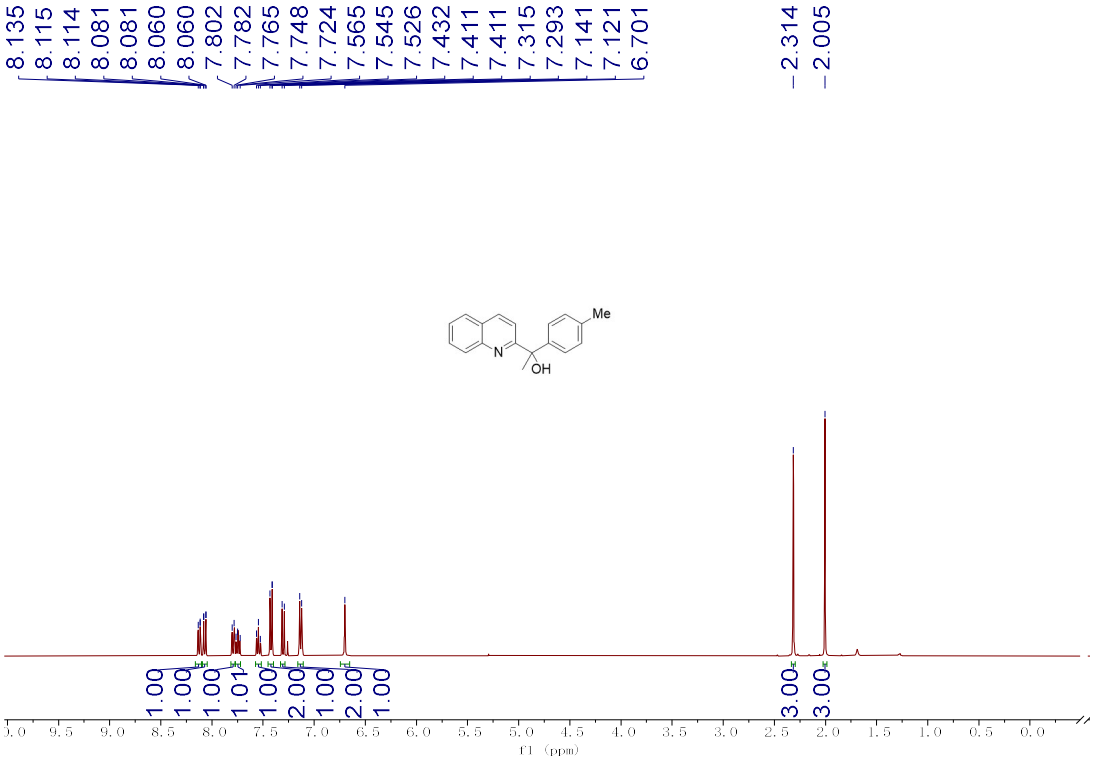
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1a**



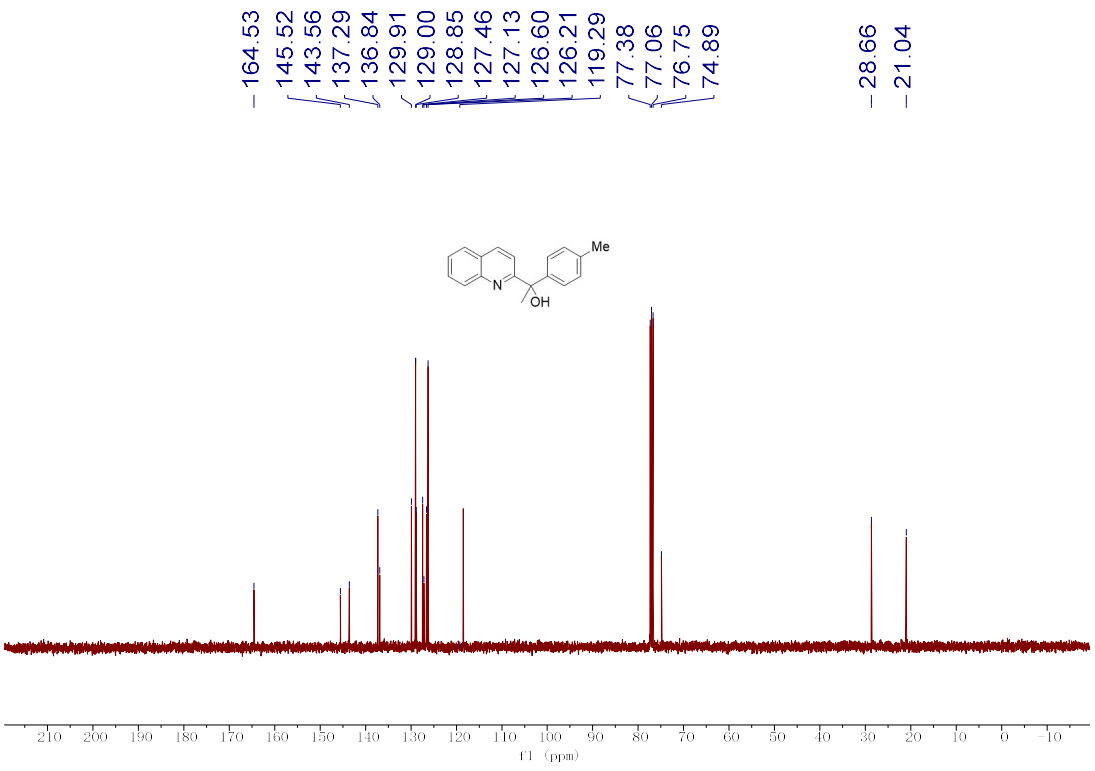
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1a**



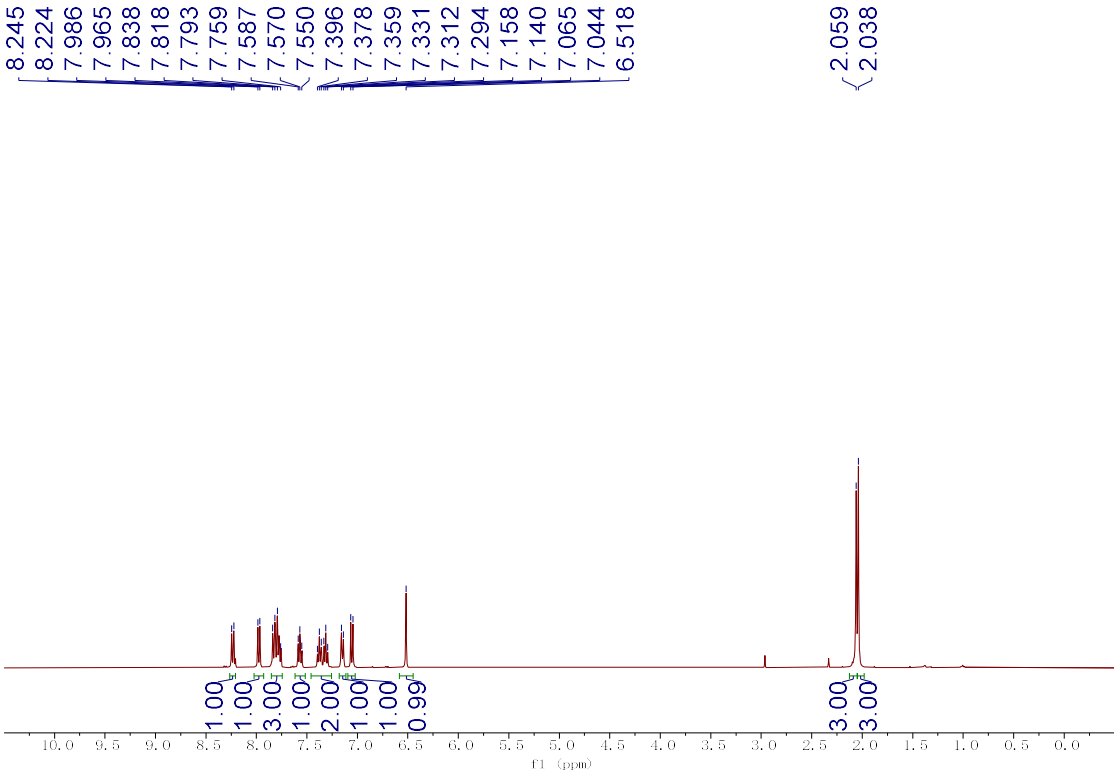
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1b**



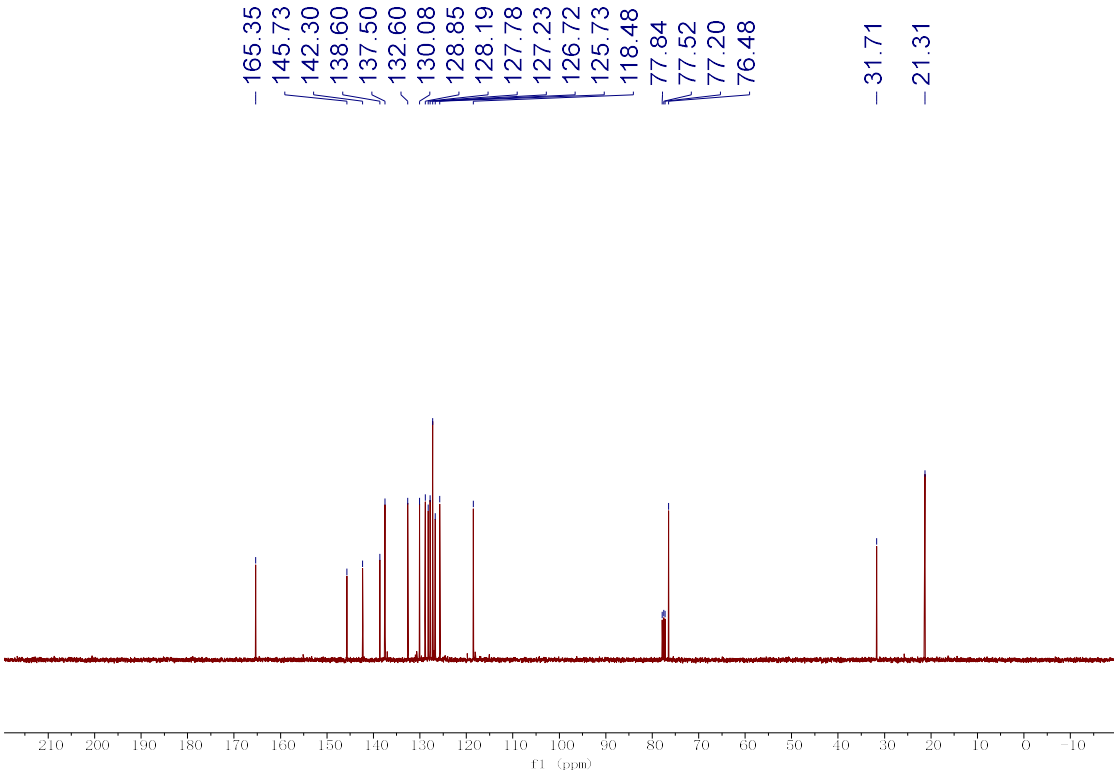
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1b**



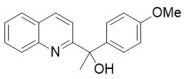
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1c**

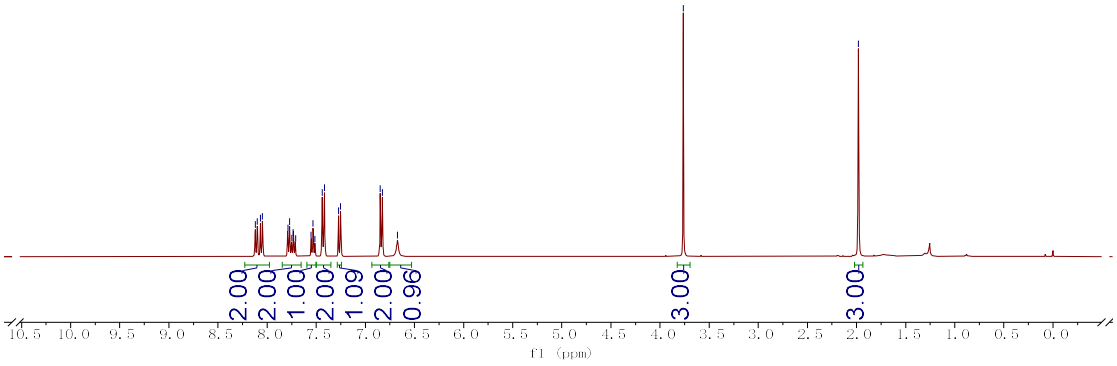


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1c**

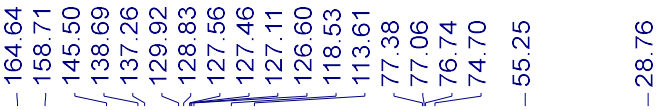


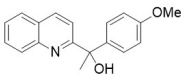
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1d**

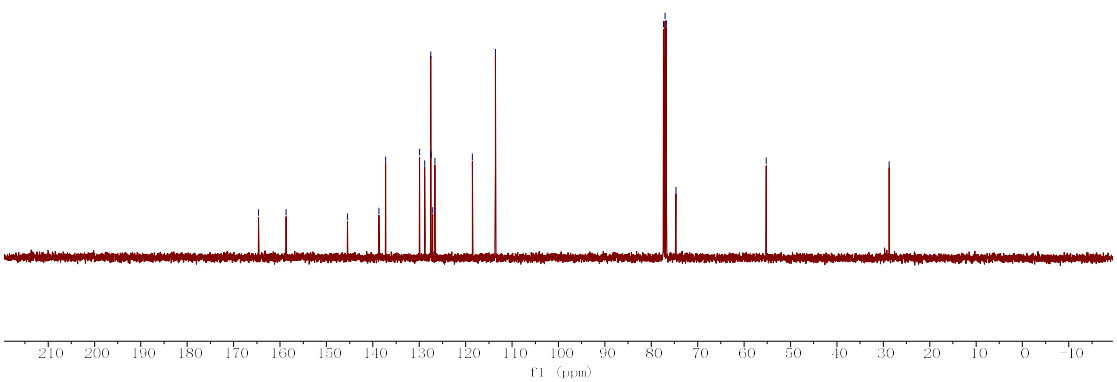




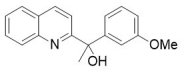
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1d**

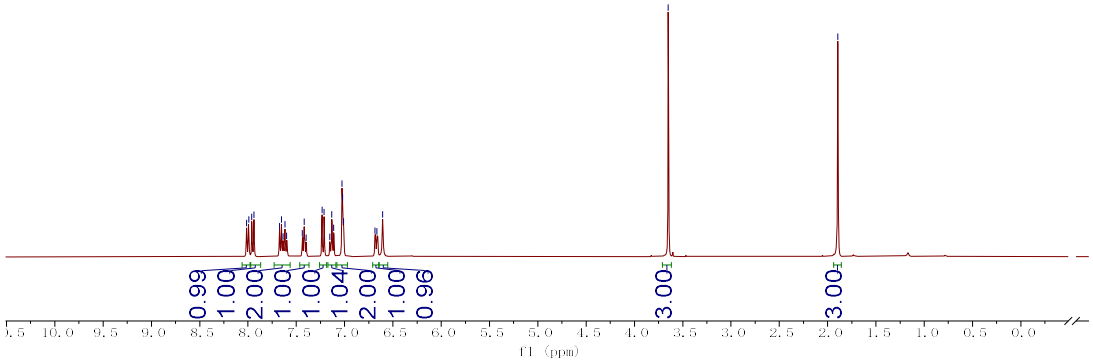




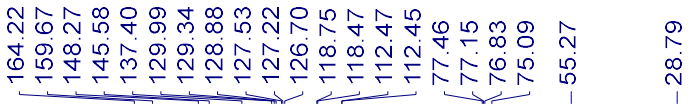


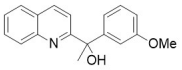
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1e**

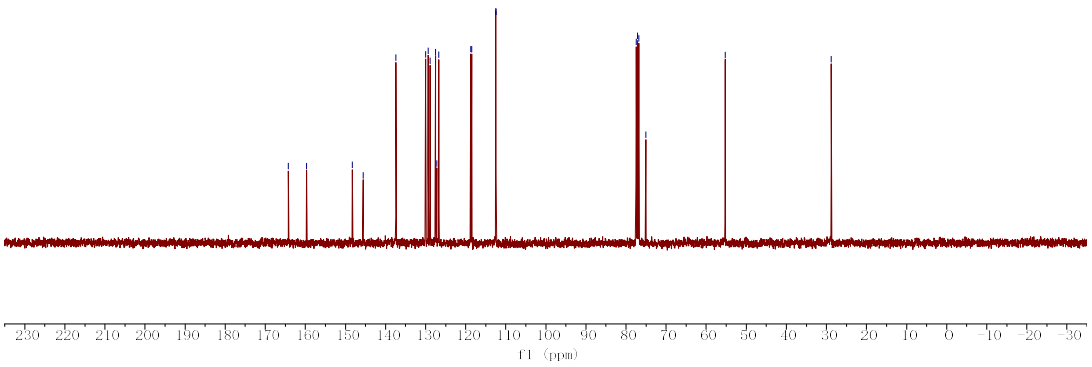




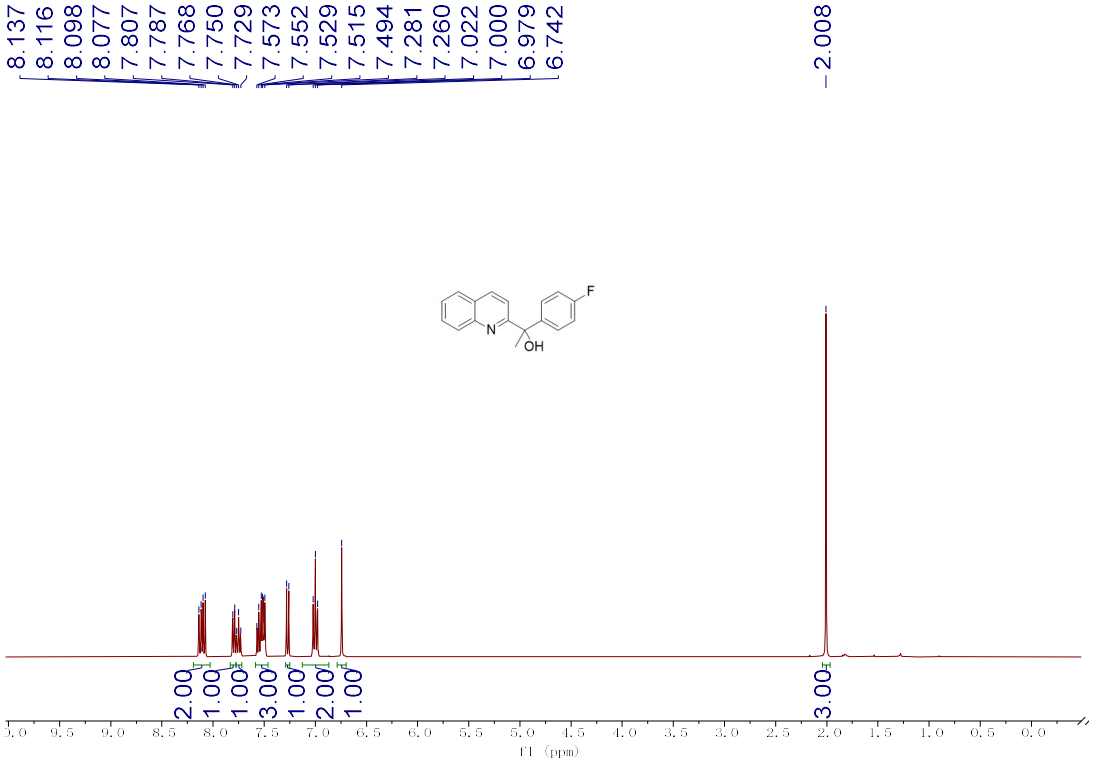
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1e**



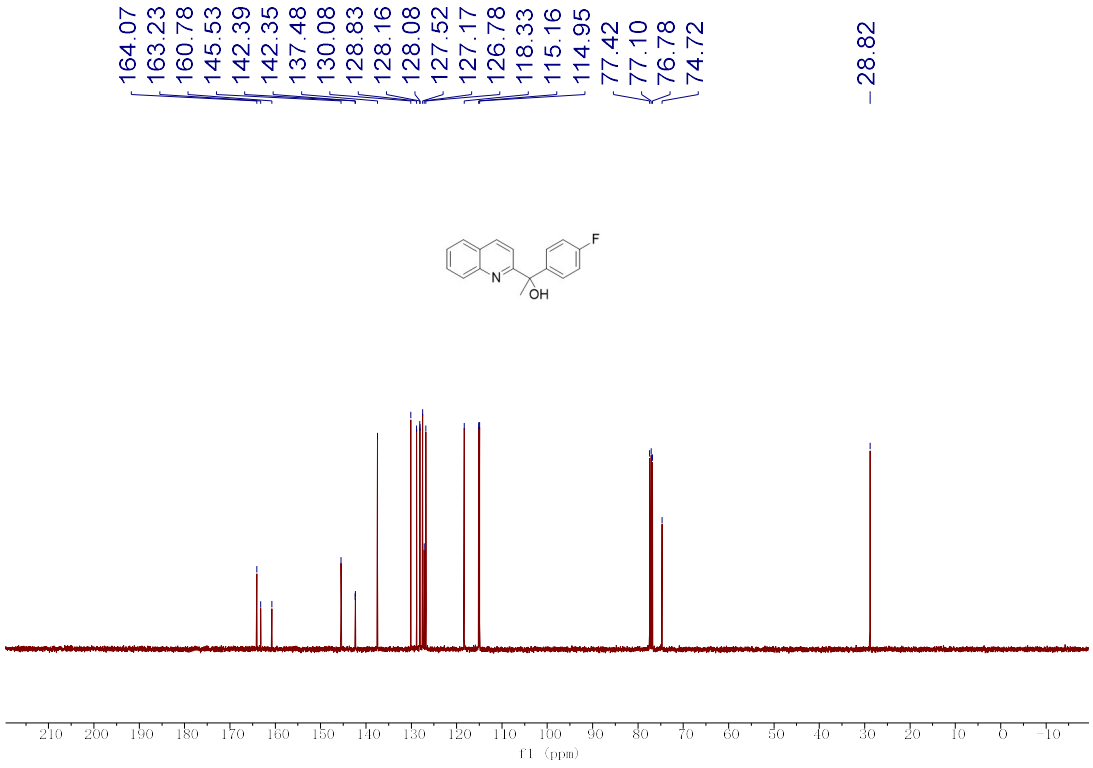




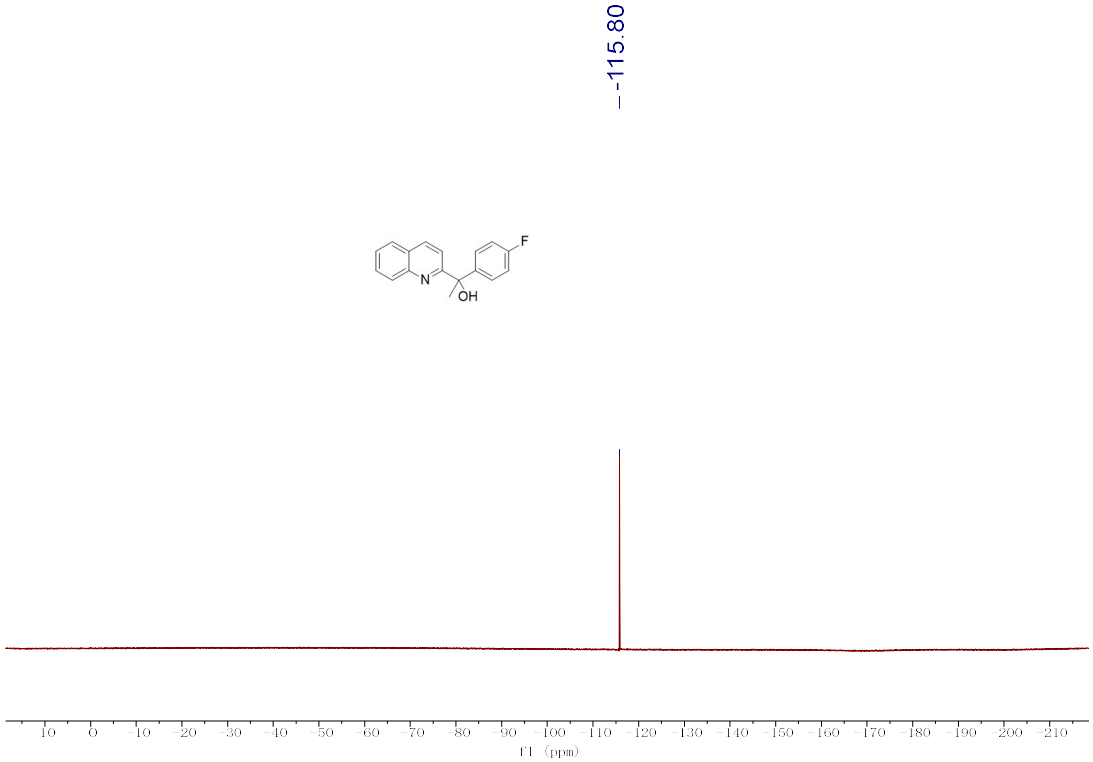
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1f**



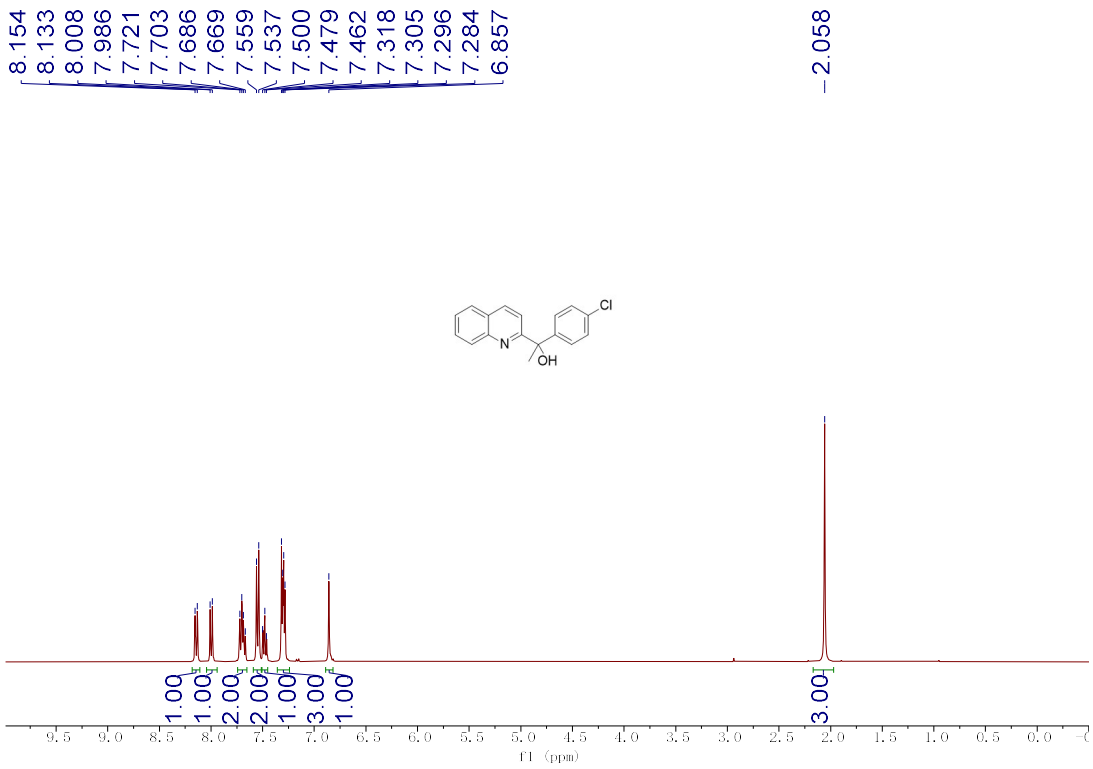
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1f**



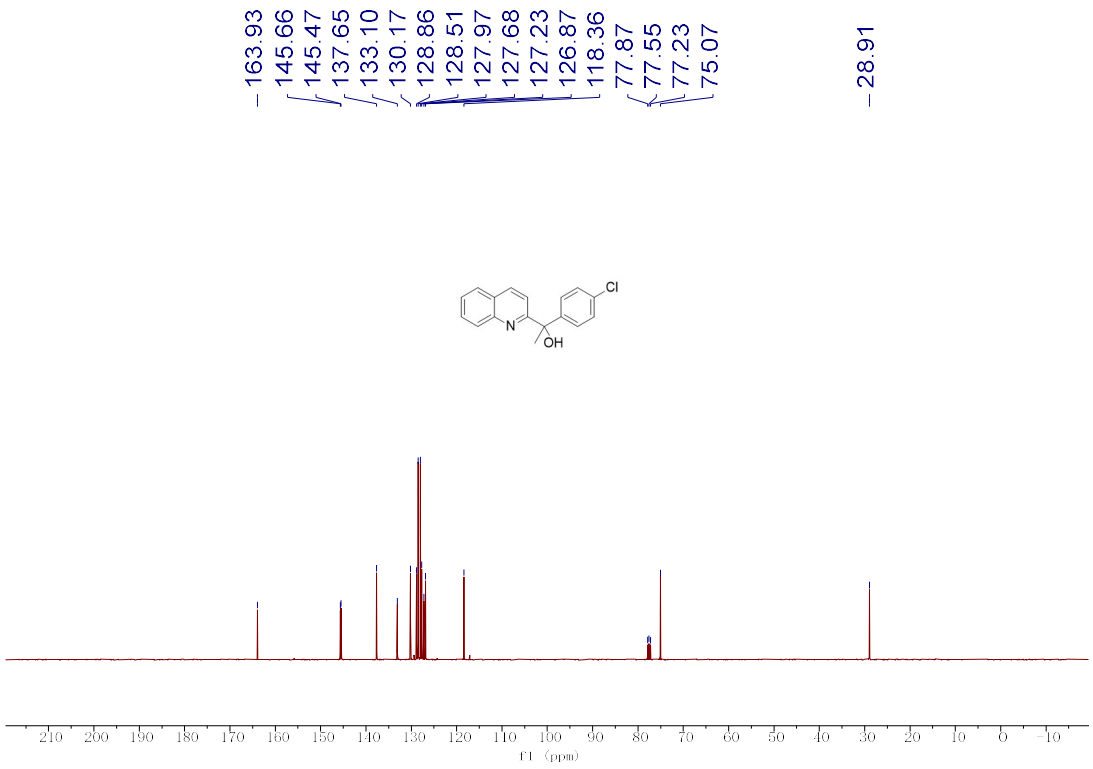
^{19}F {1H} NMR (376 MHz, $CDCl_3$) spectrum of **1f**



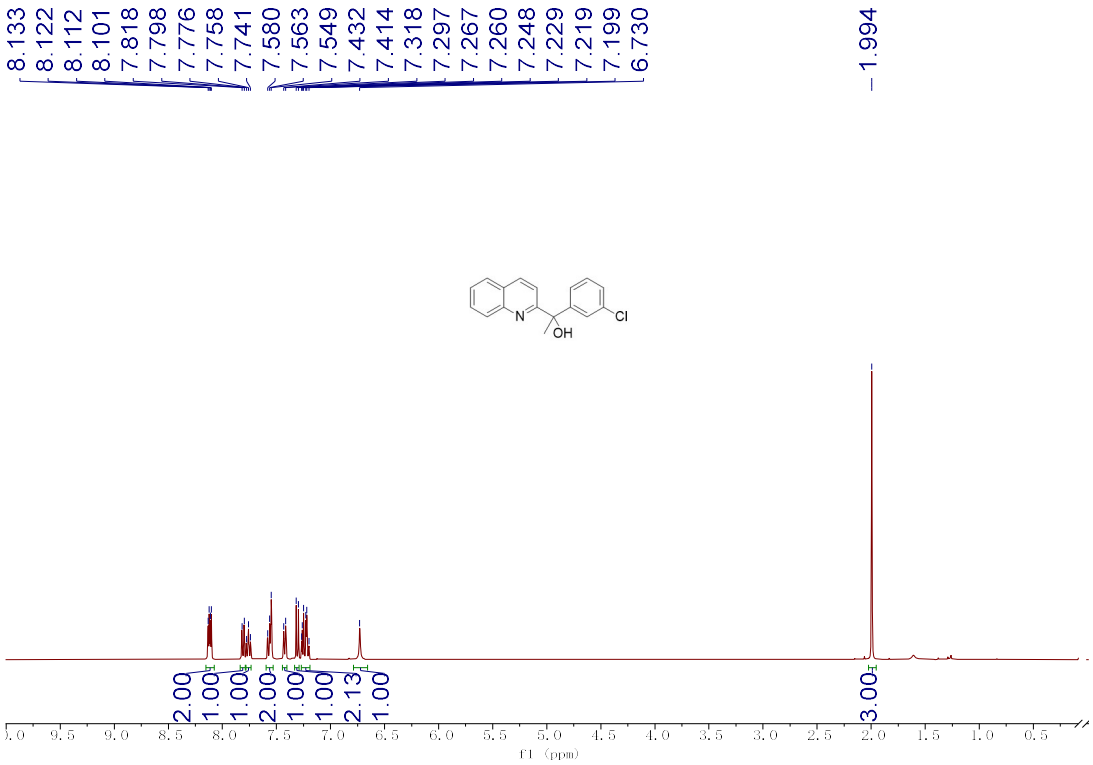
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1g**



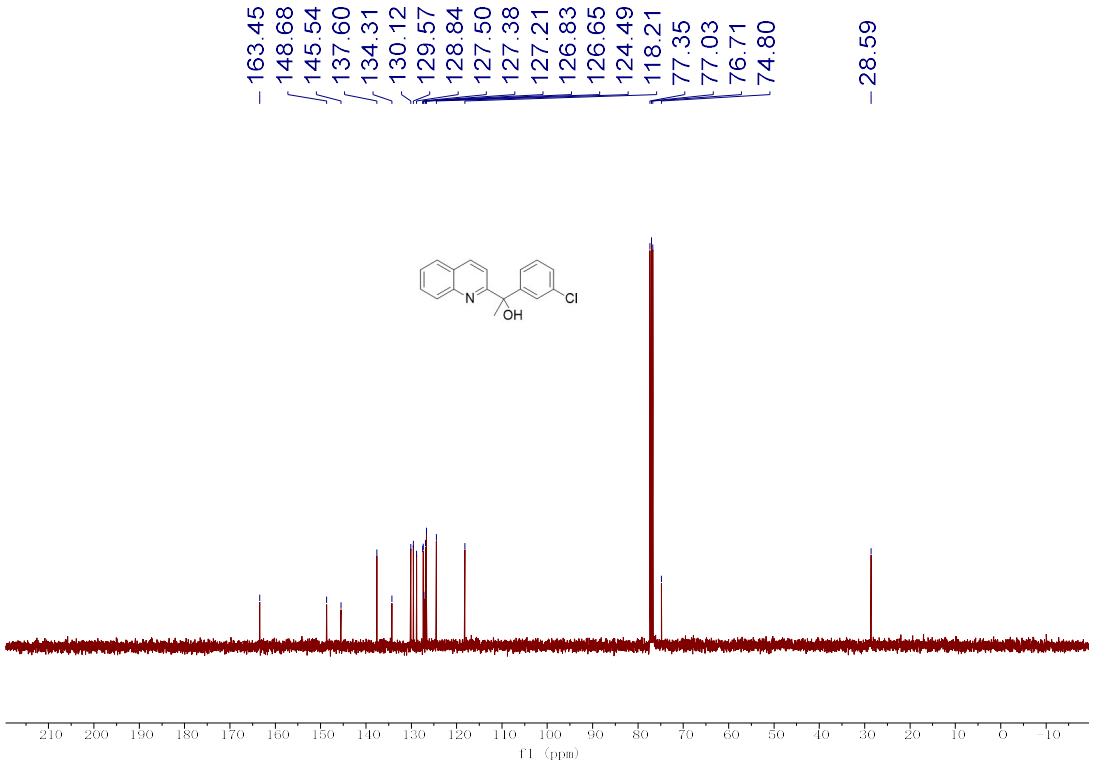
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1g**



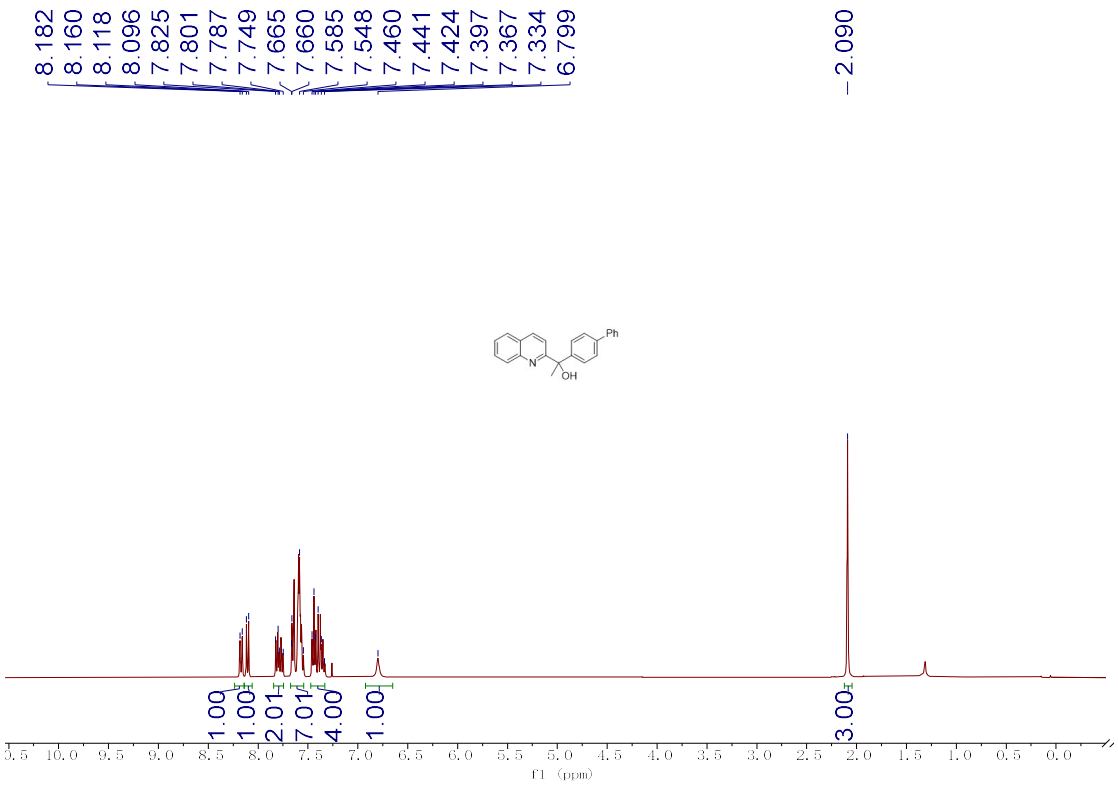
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1h**



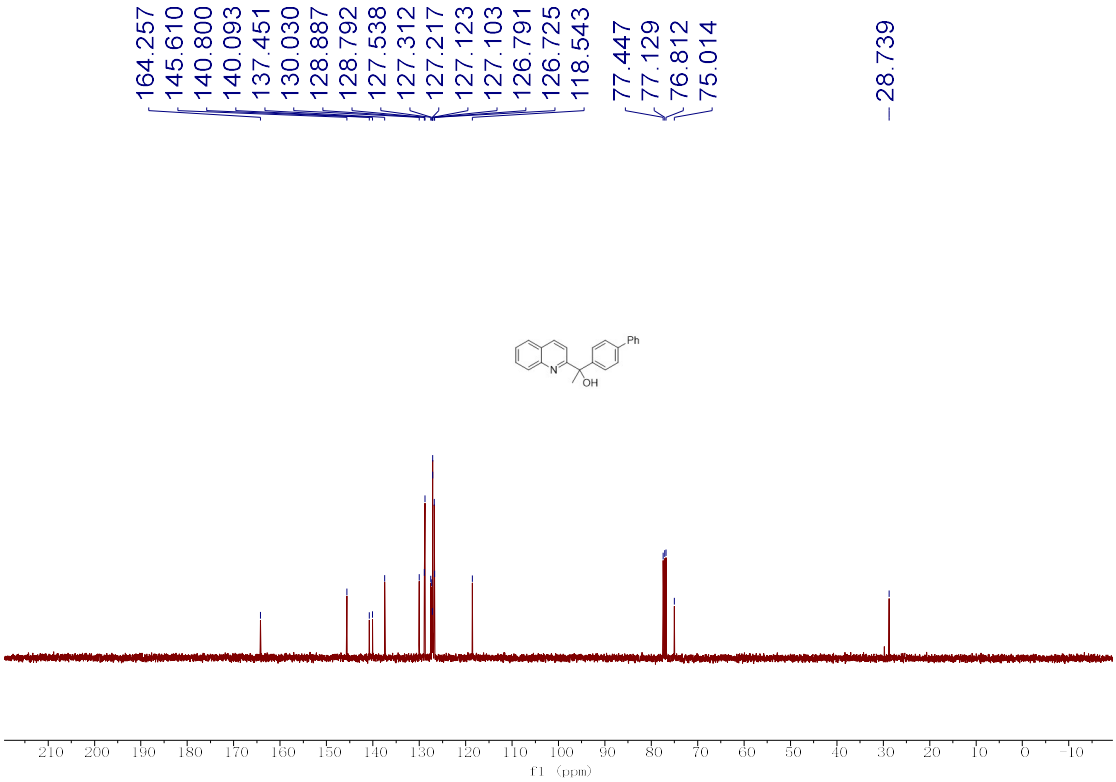
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1h**



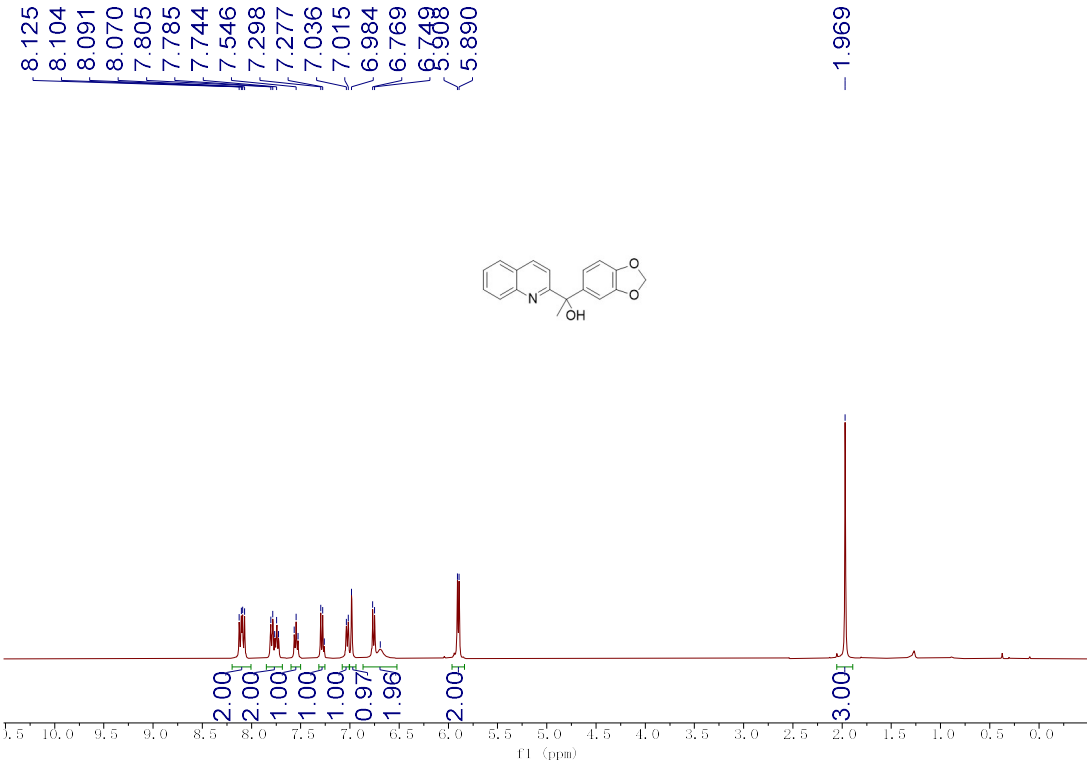
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1i**



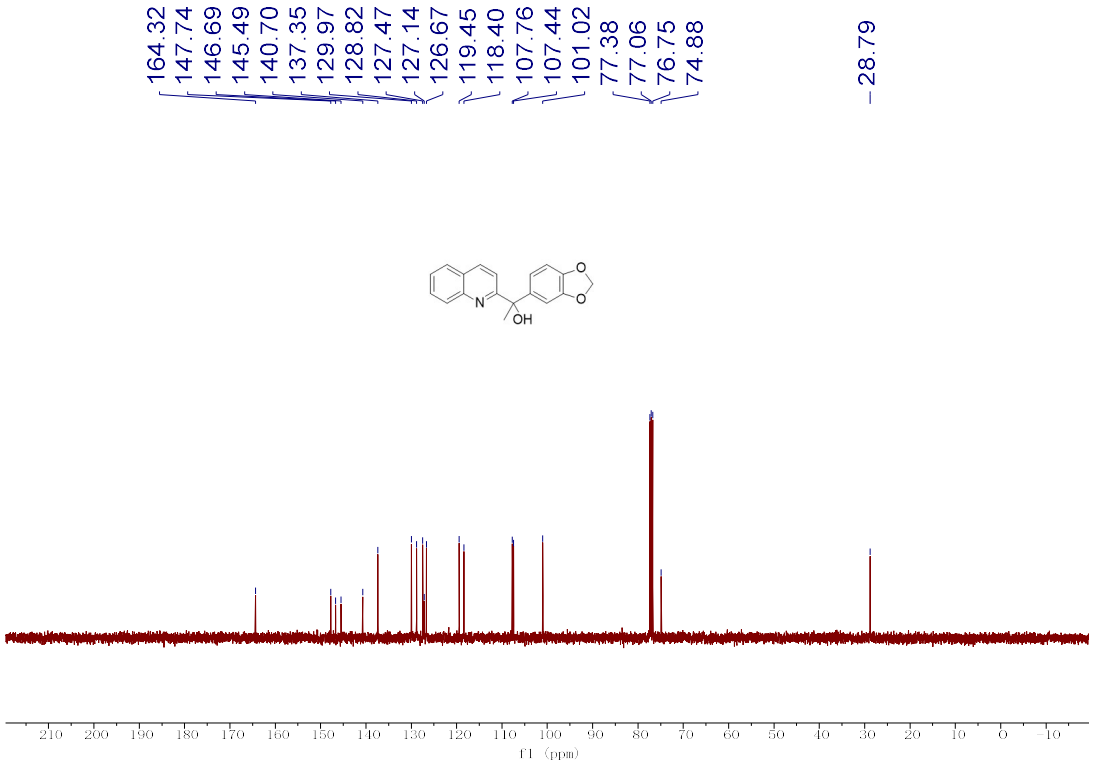
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1i**



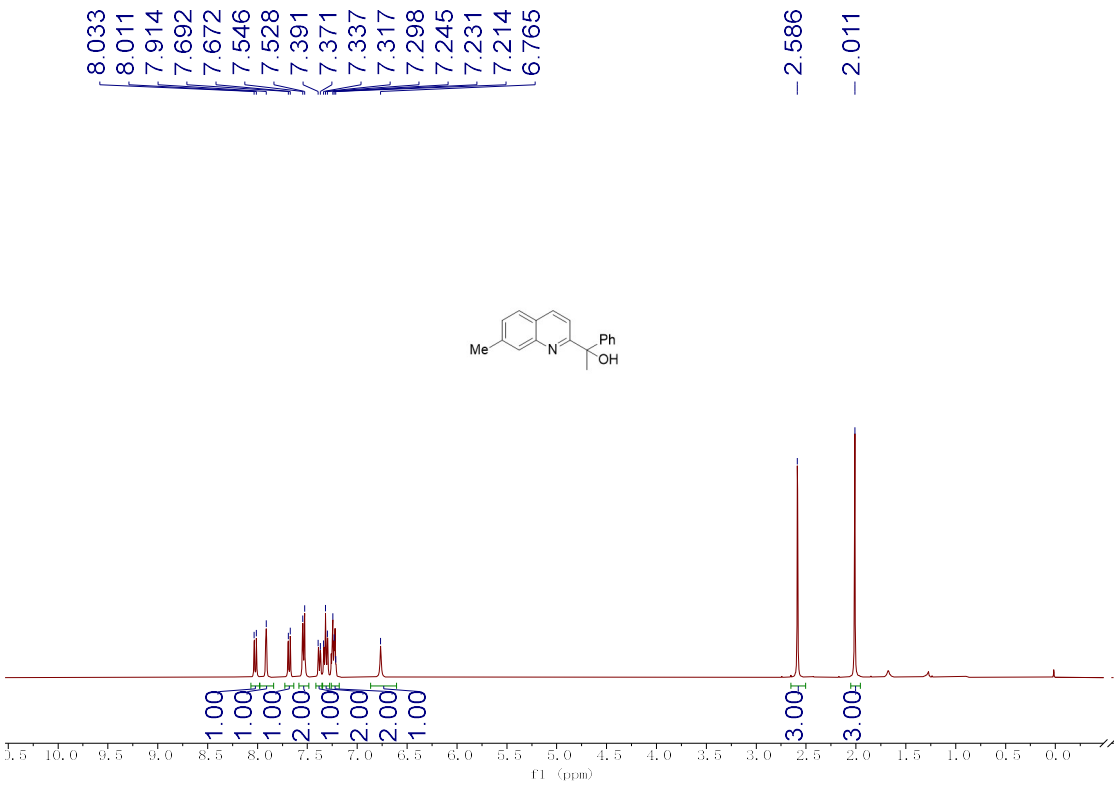
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1j**



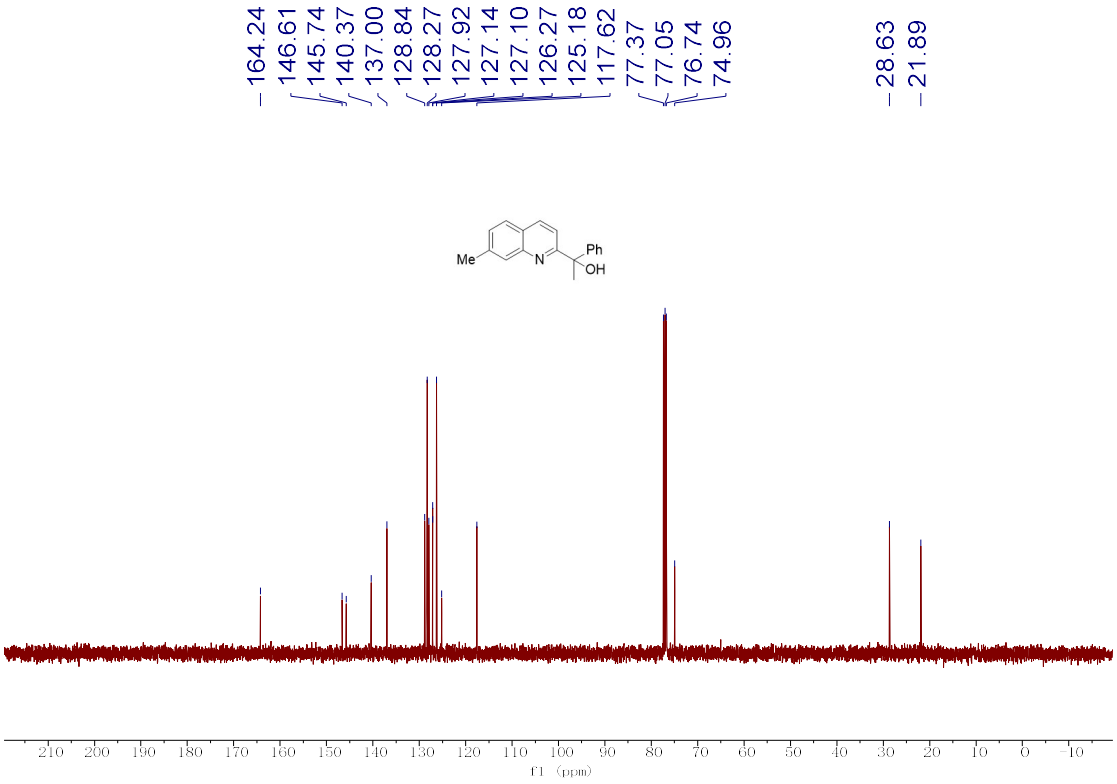
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1j**



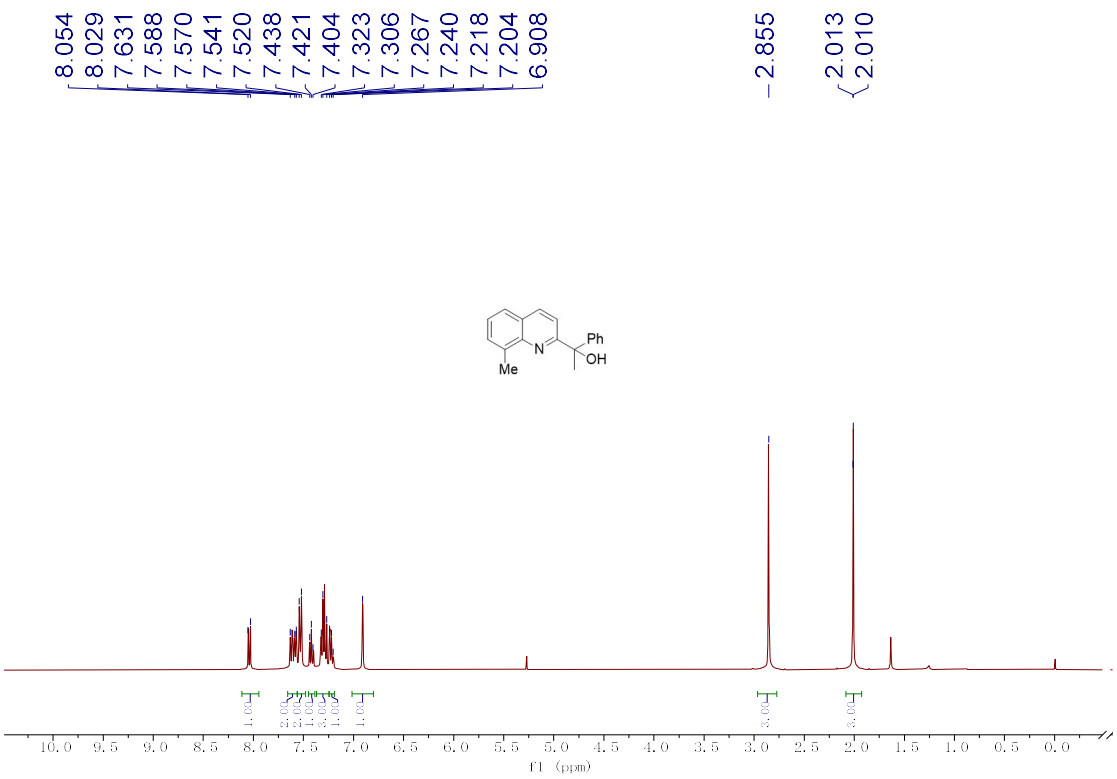
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1k**



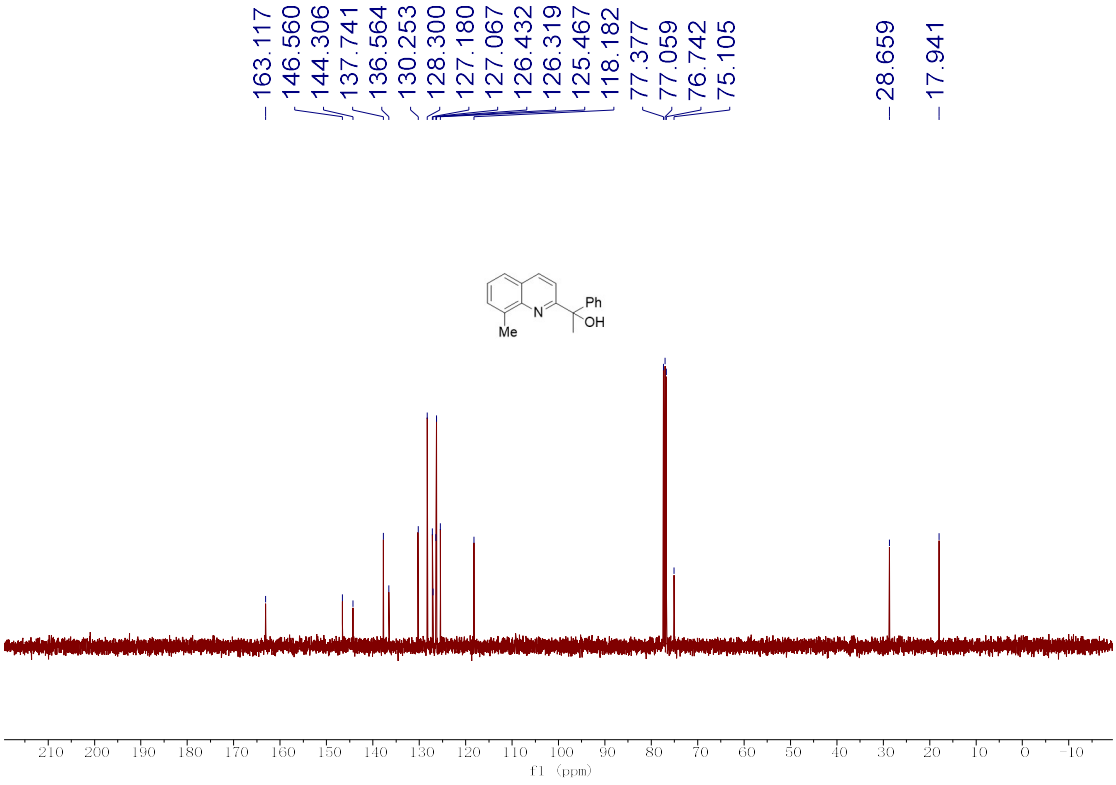
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1k**



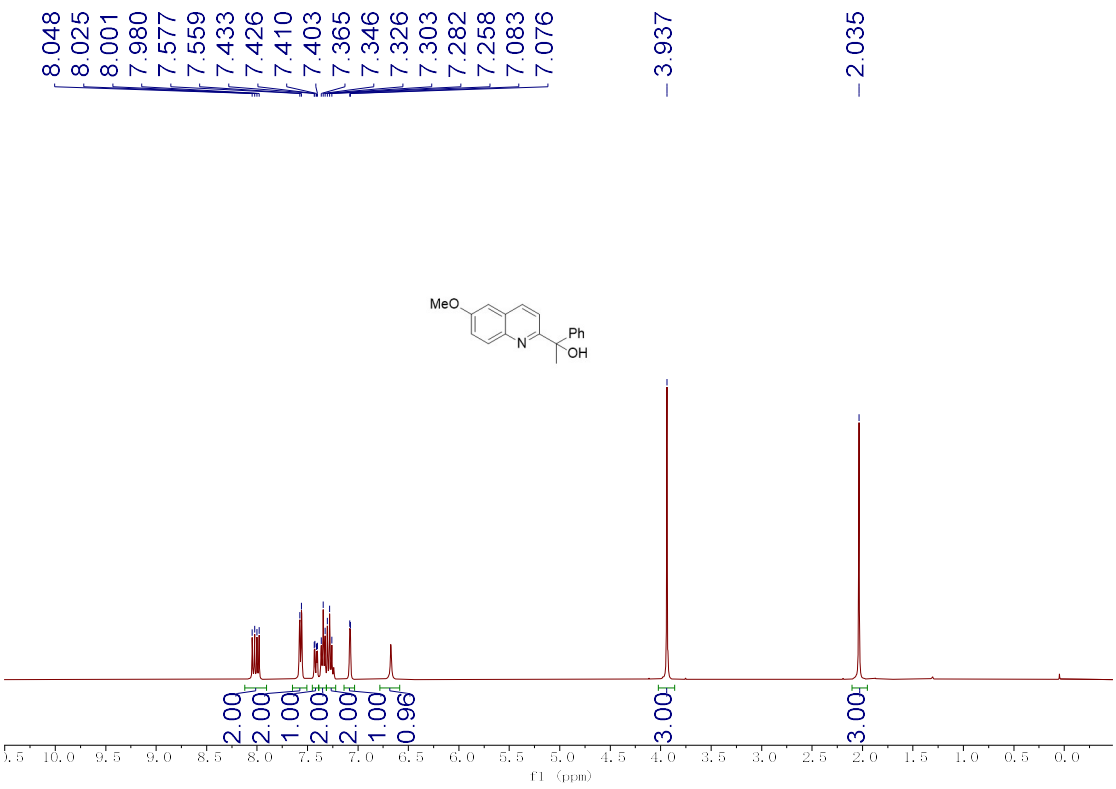
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1l**



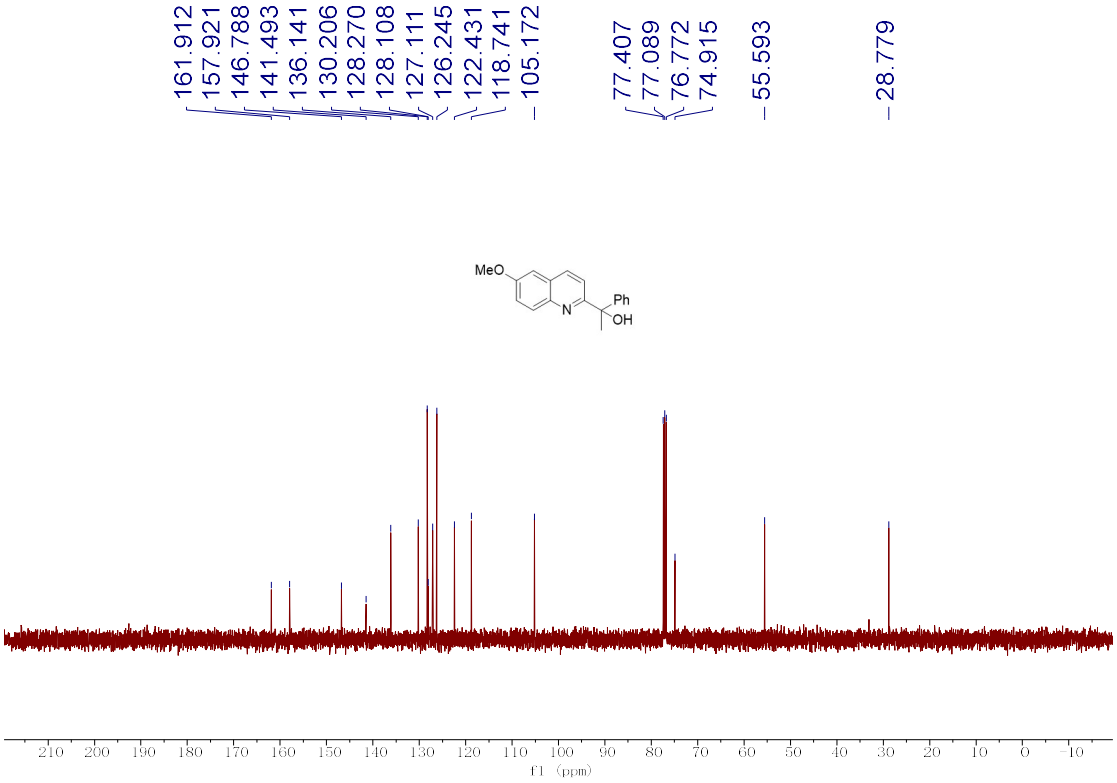
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1l**



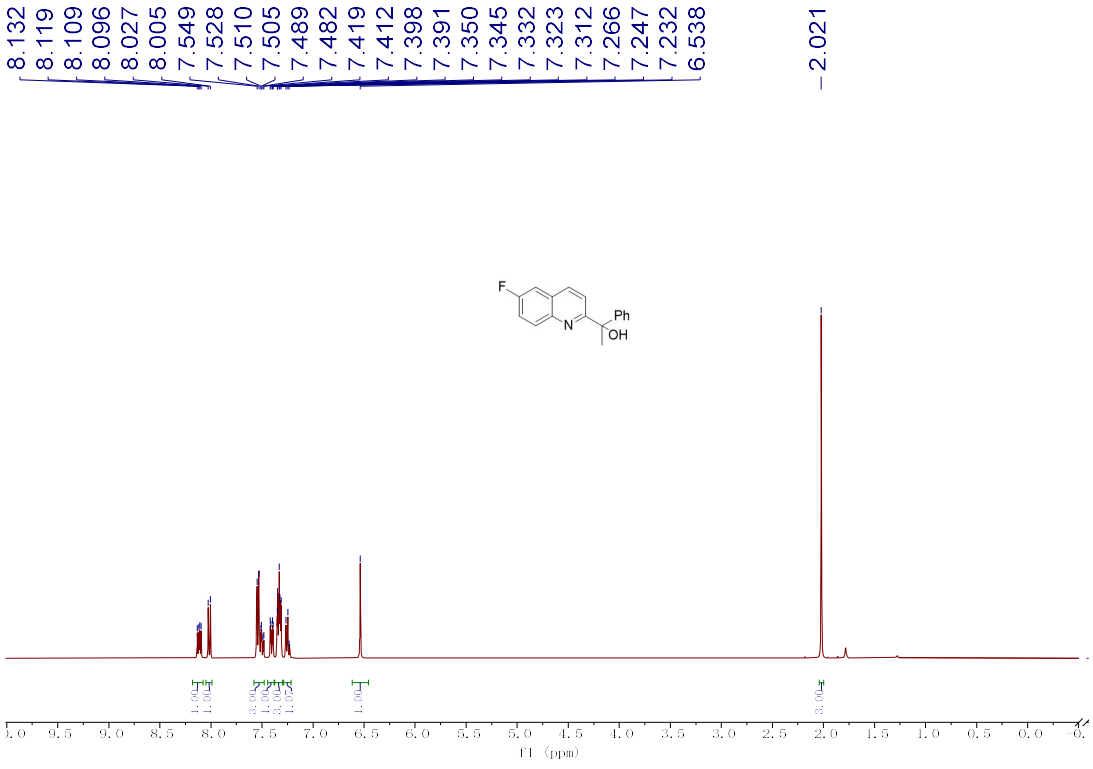
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1m**



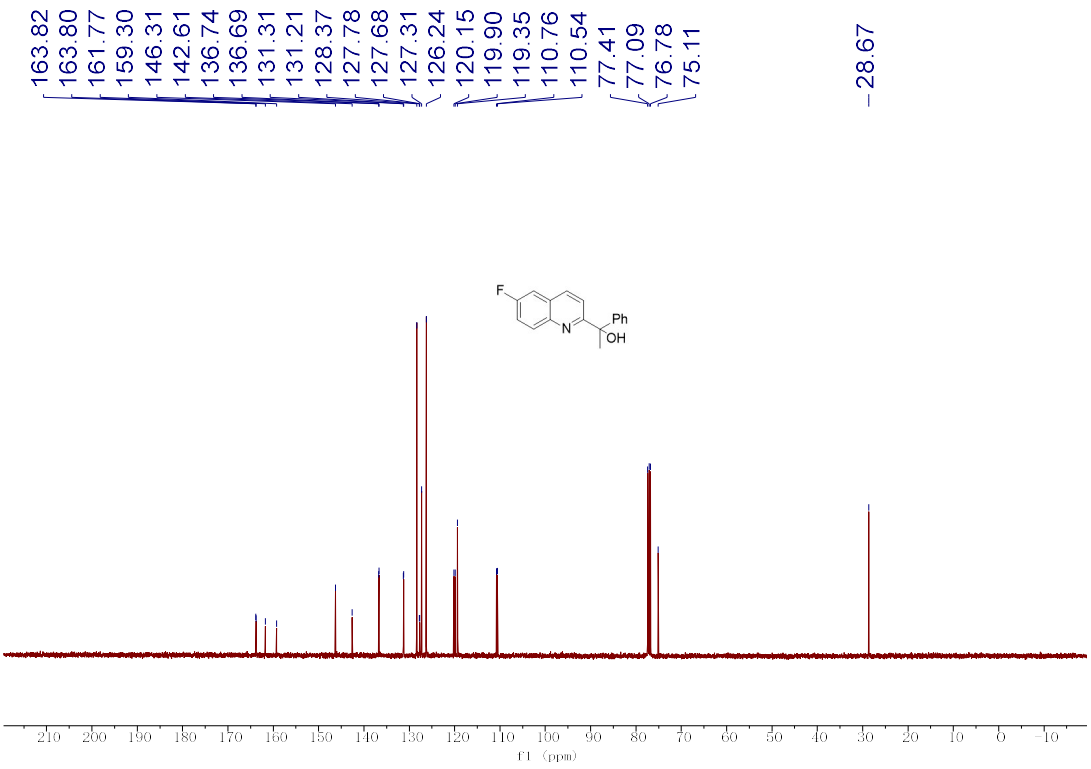
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1m**



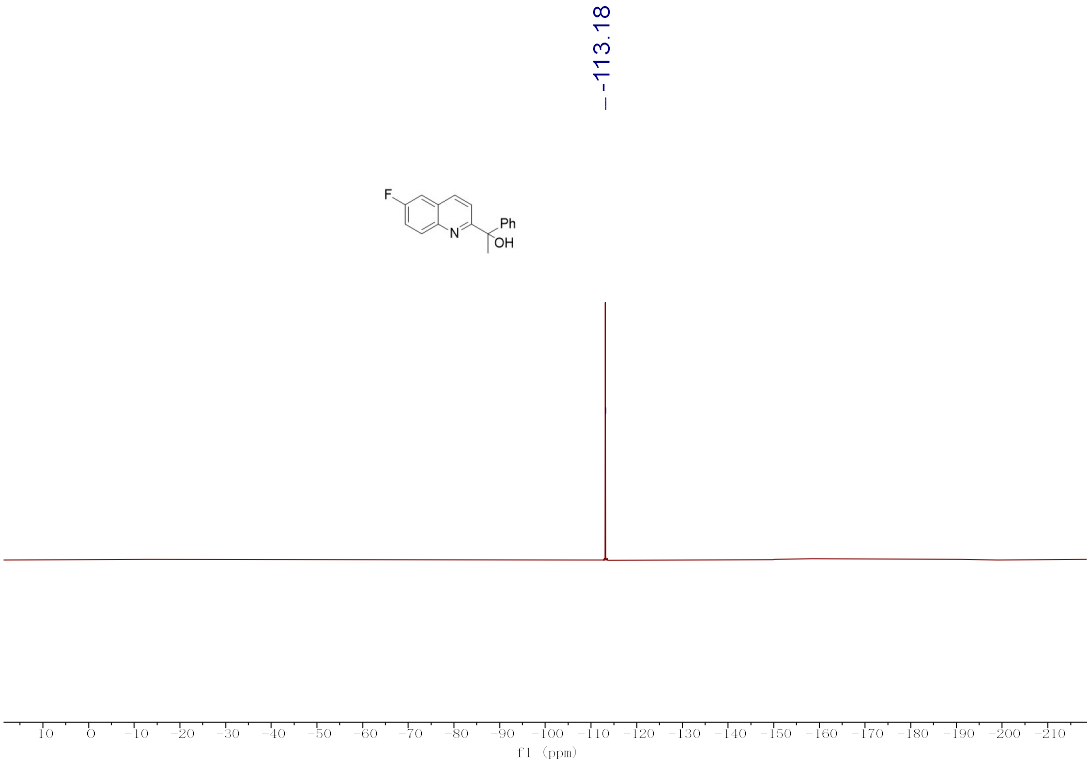
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1n**



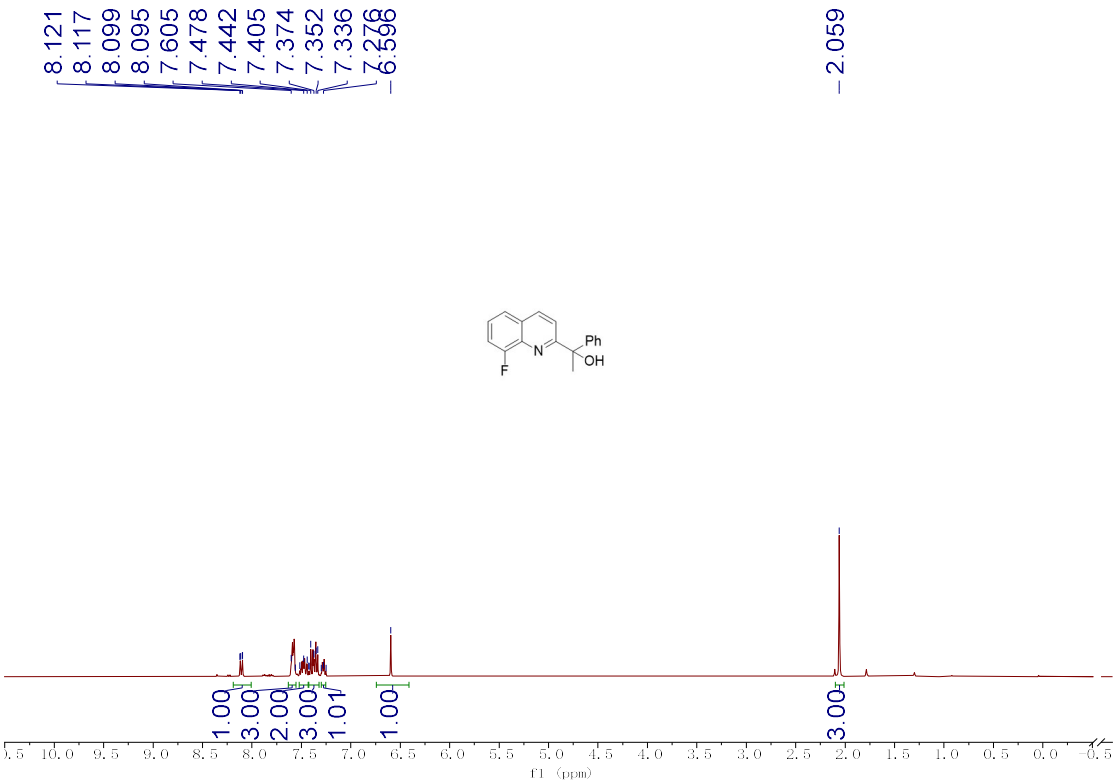
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1n**



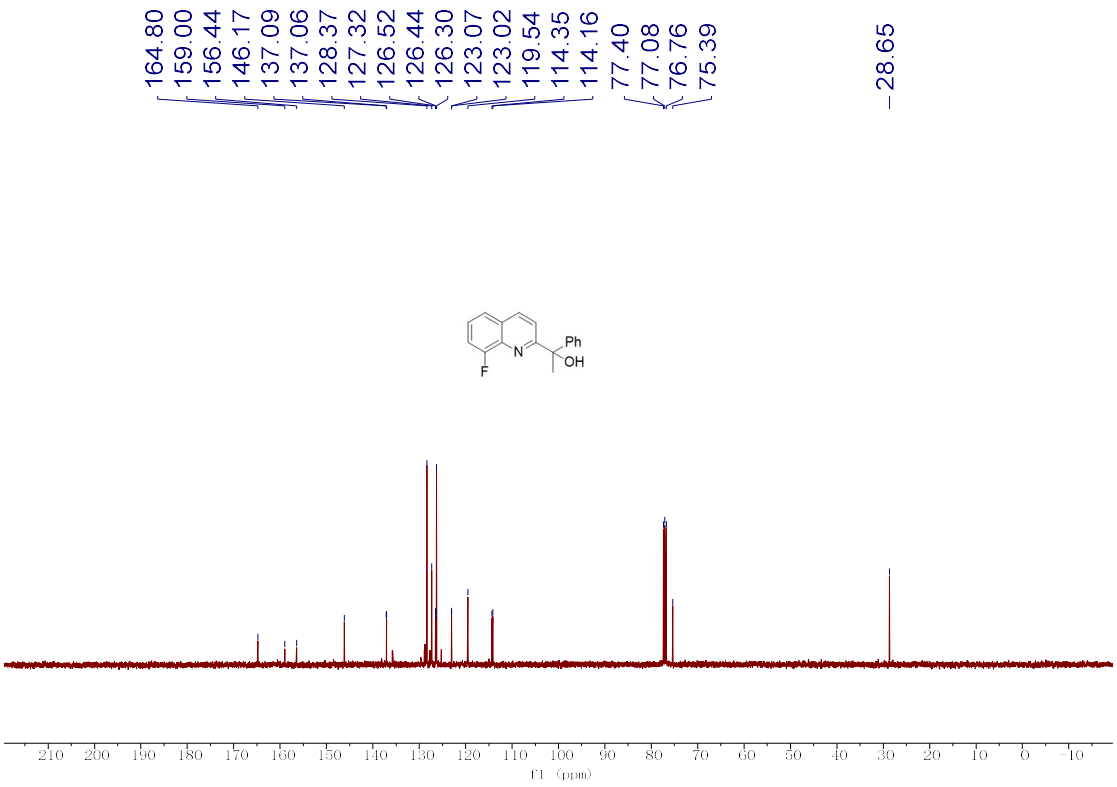
^{19}F {1H} NMR (376 MHz, $CDCl_3$) spectrum of **1n**



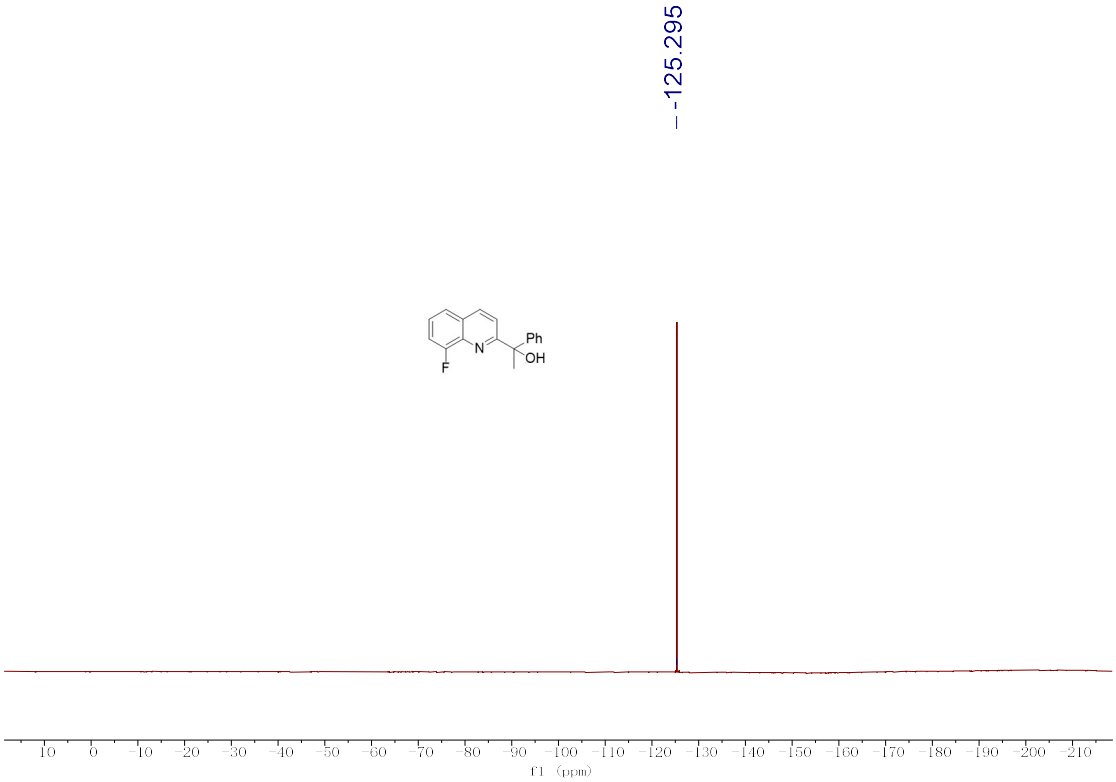
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1o**



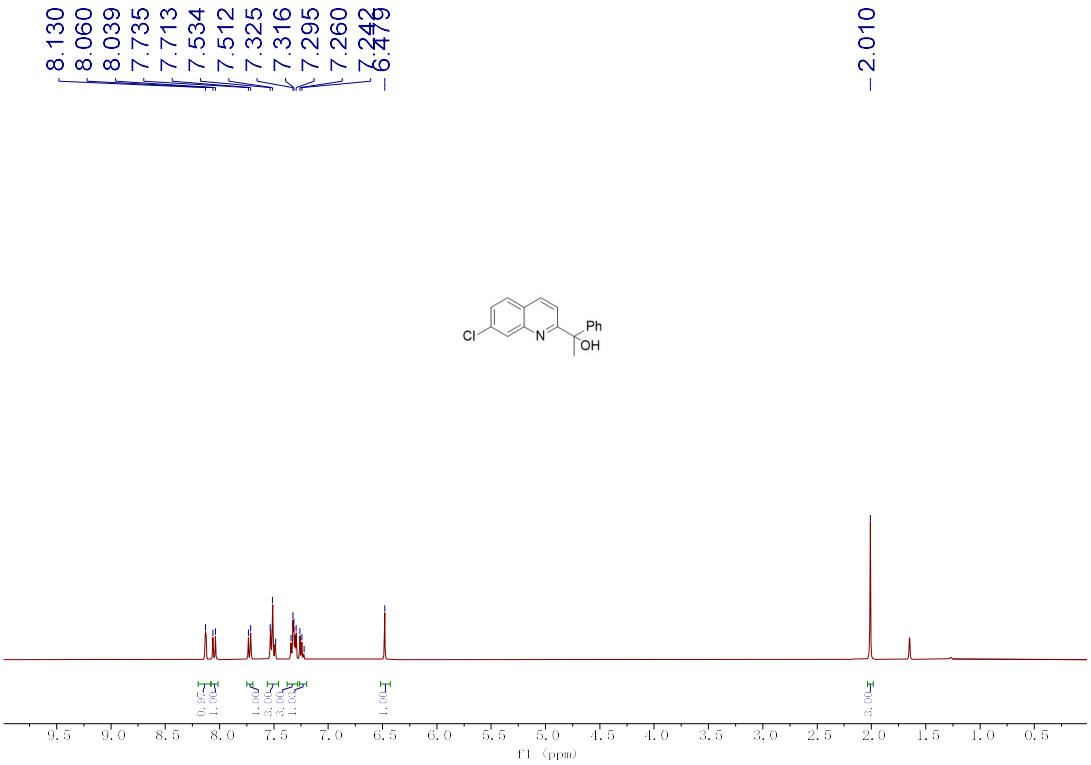
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1o**



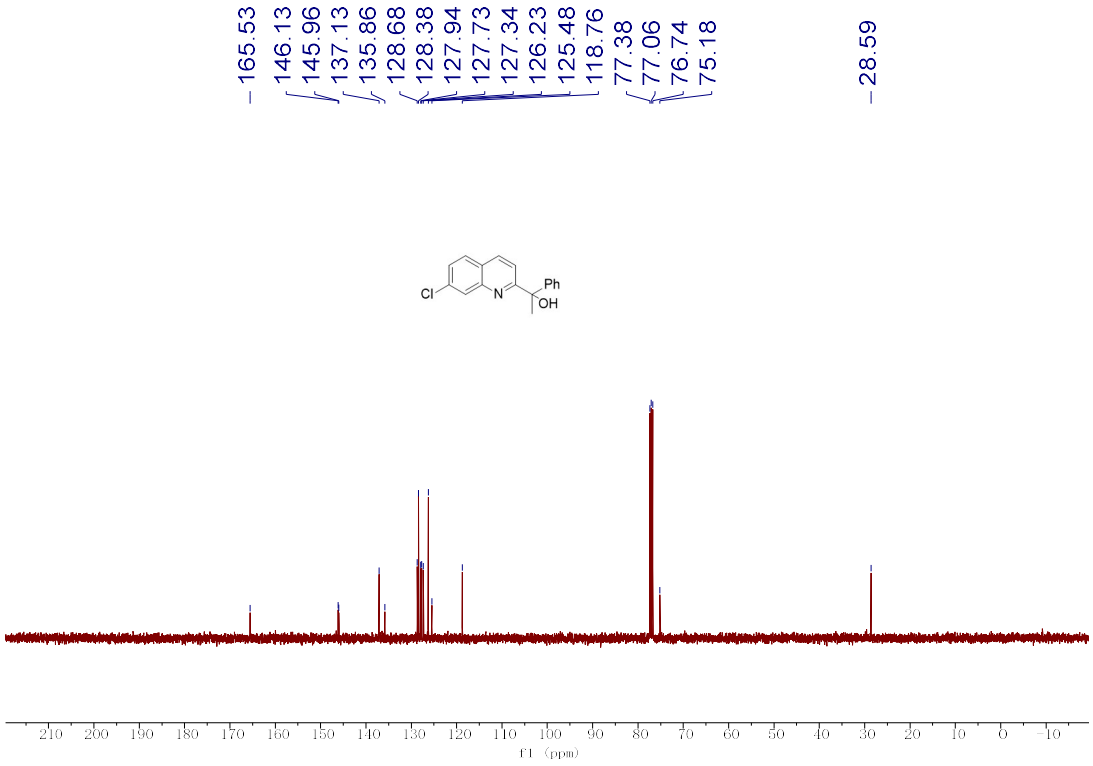
^{19}F {1H} NMR (376 MHz, $CDCl_3$) spectrum of **1o**



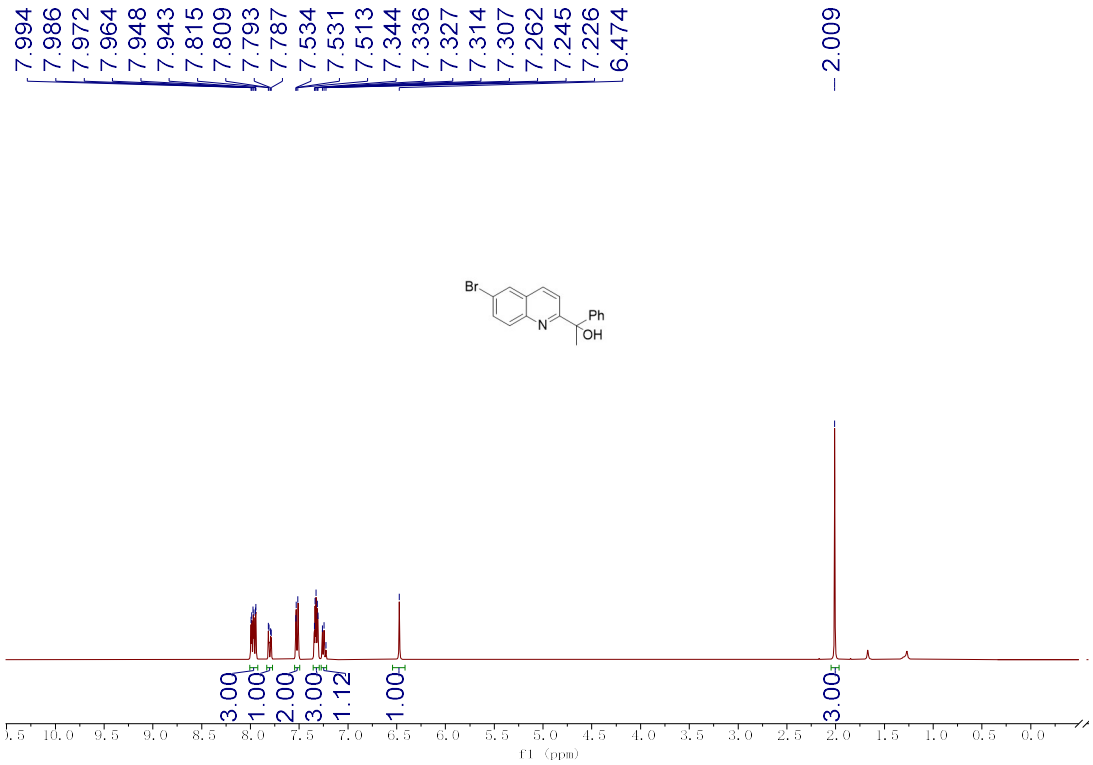
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1p**



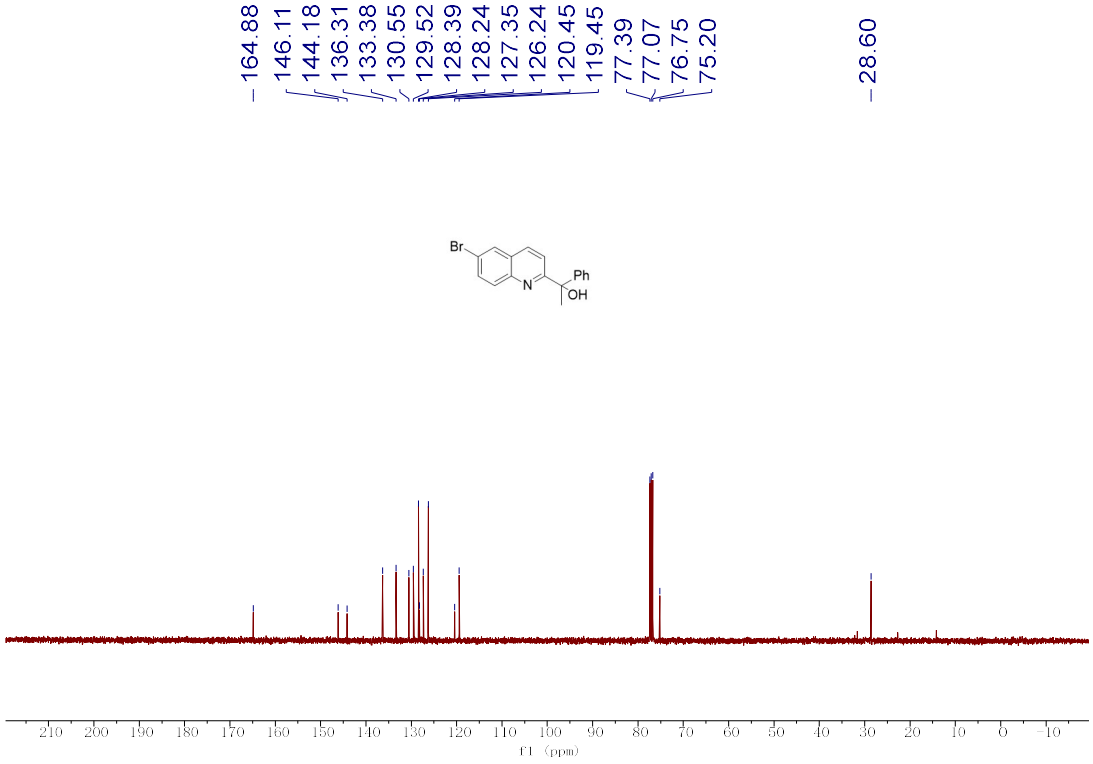
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1p**



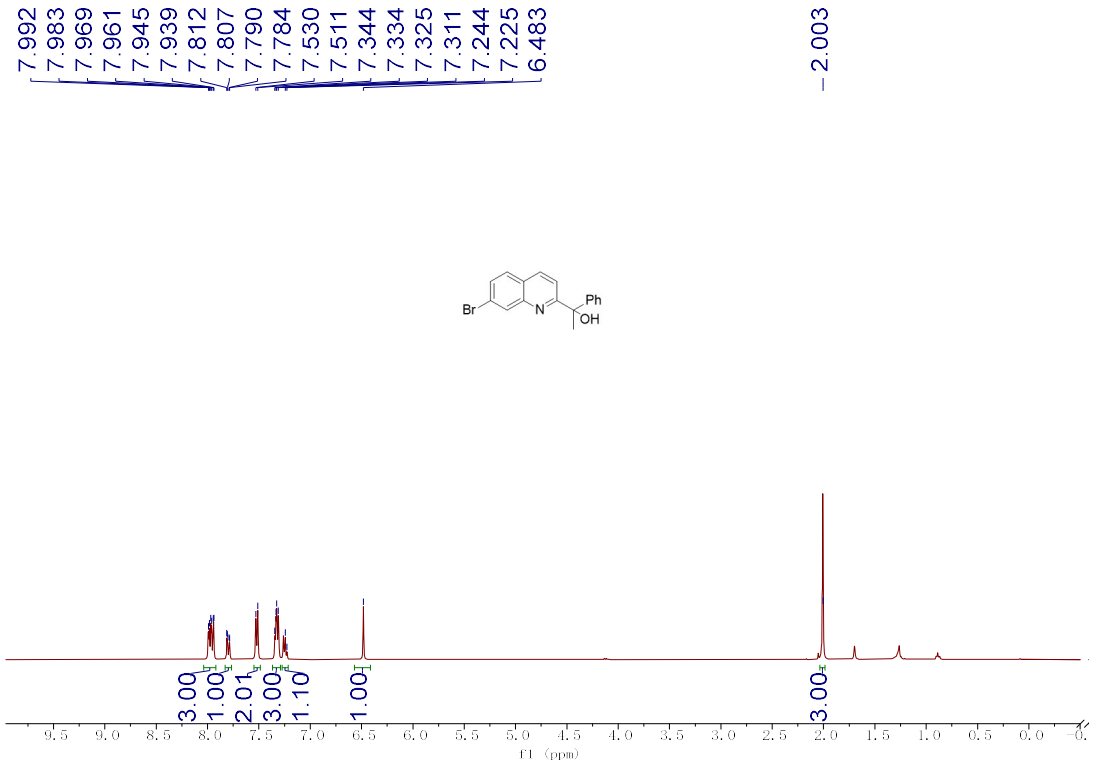
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1q**



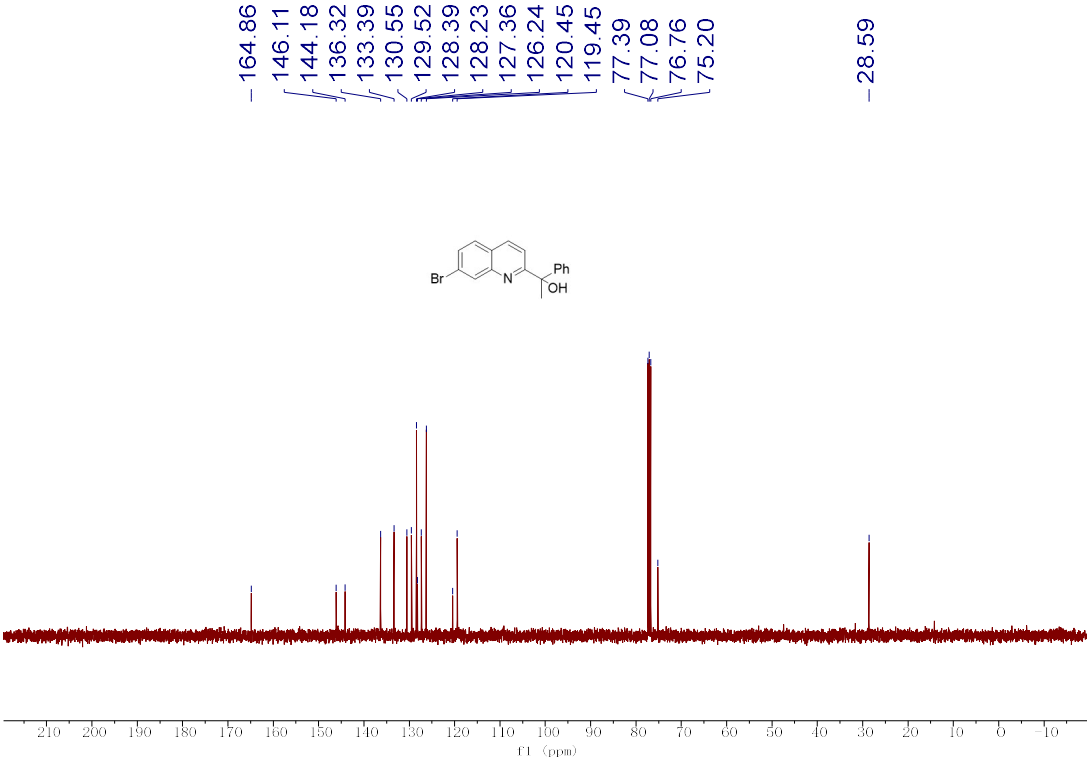
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1q**



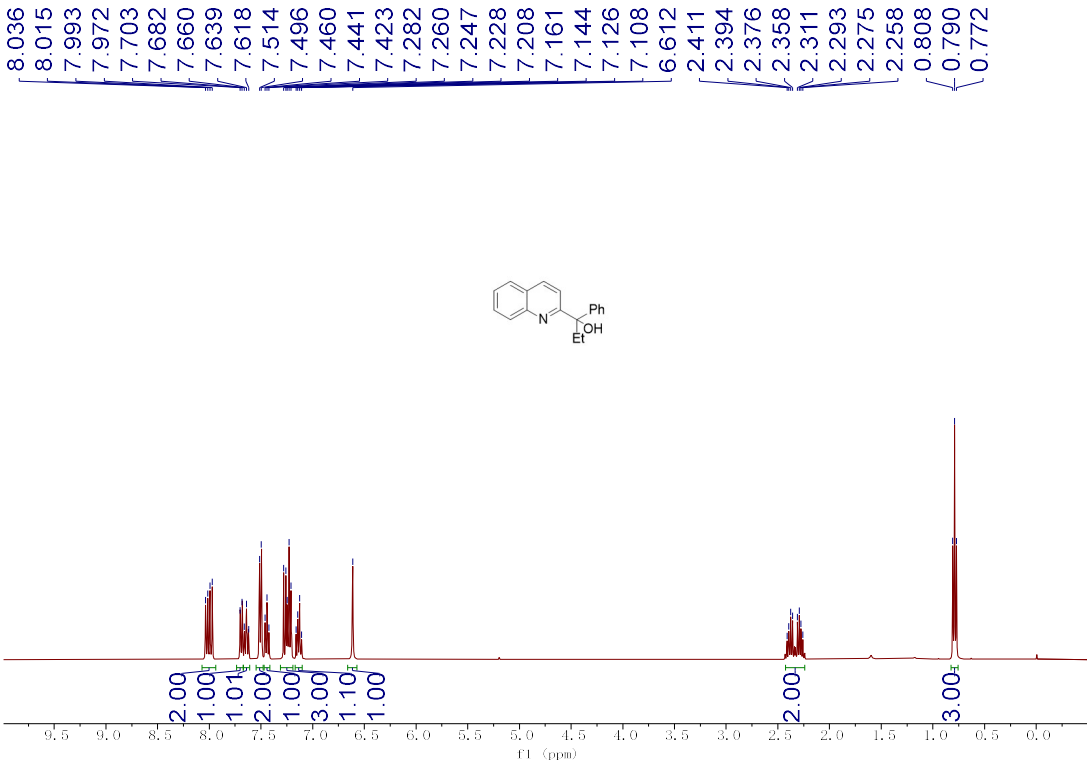
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1r**



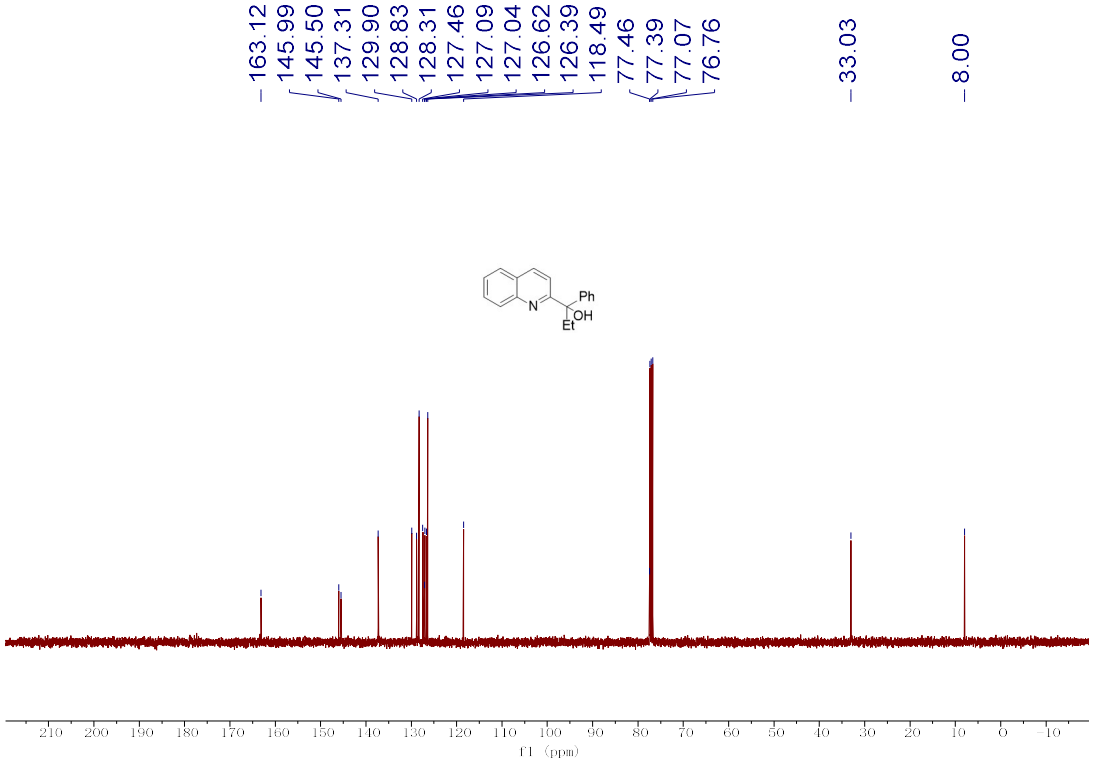
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1r**



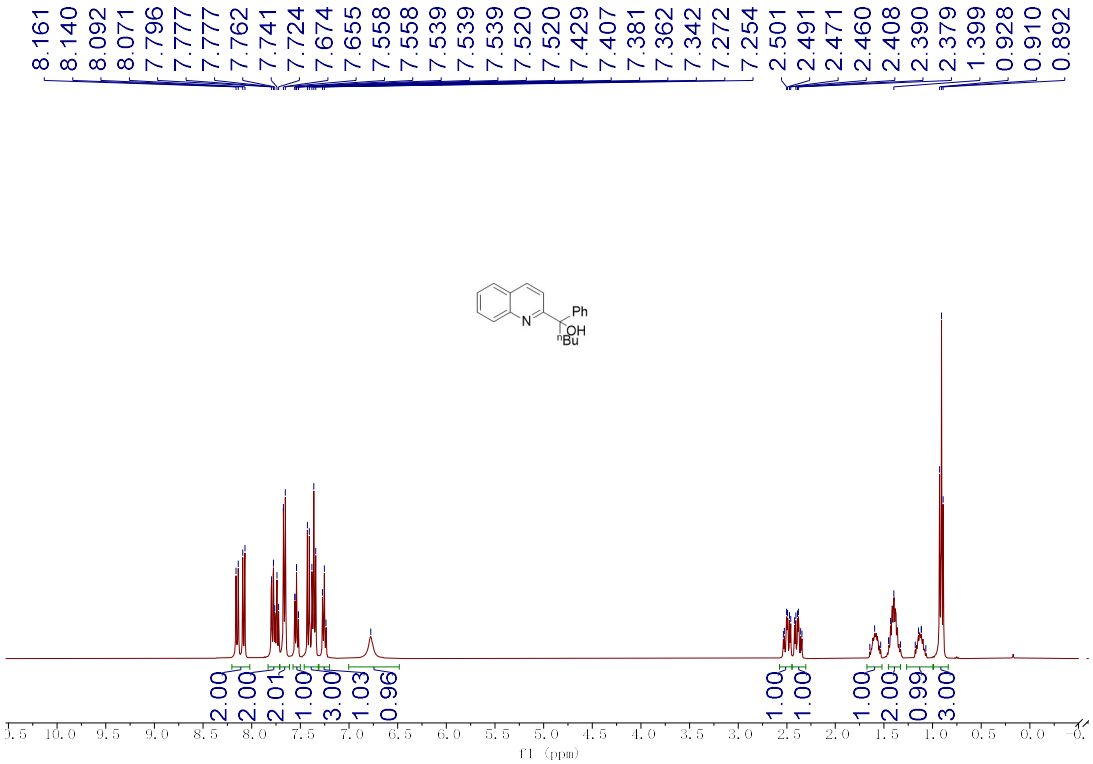
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1s**



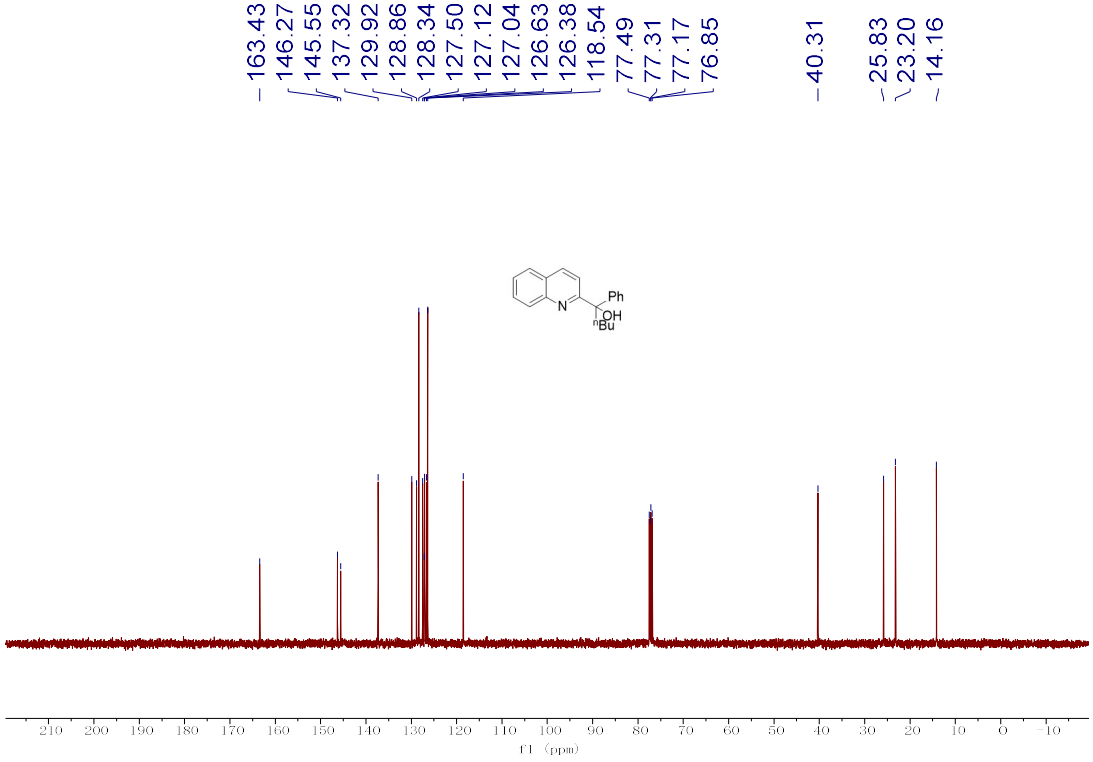
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1s**



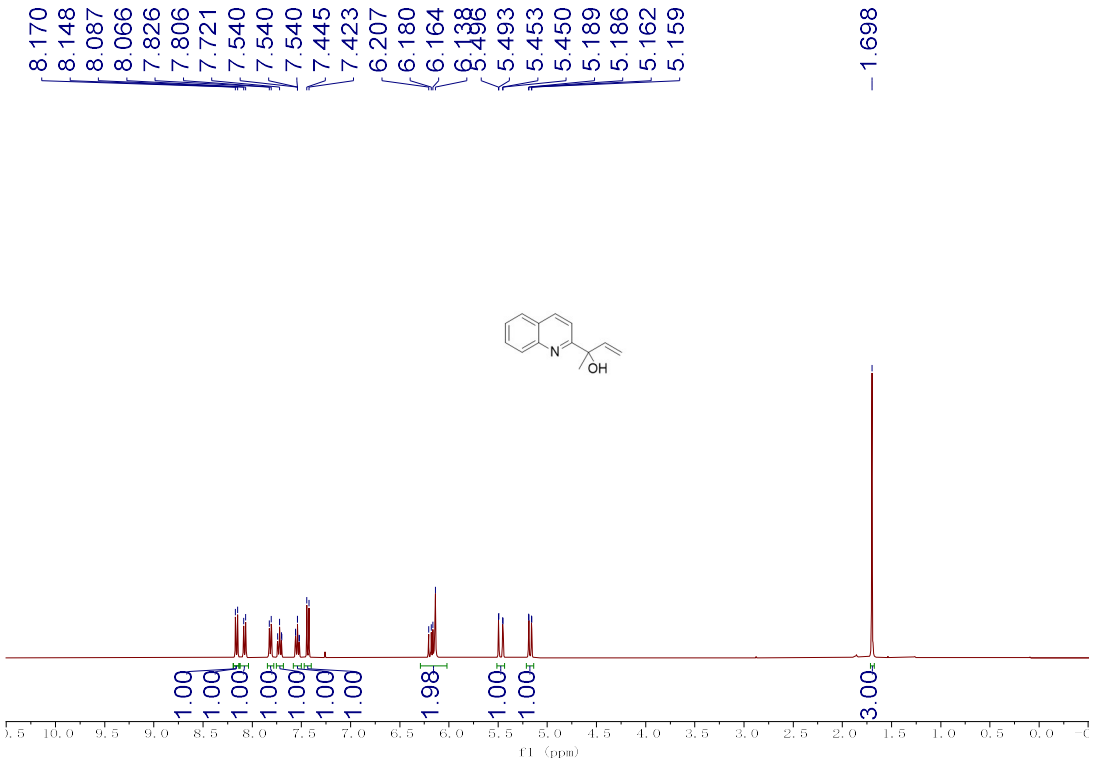
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1t**



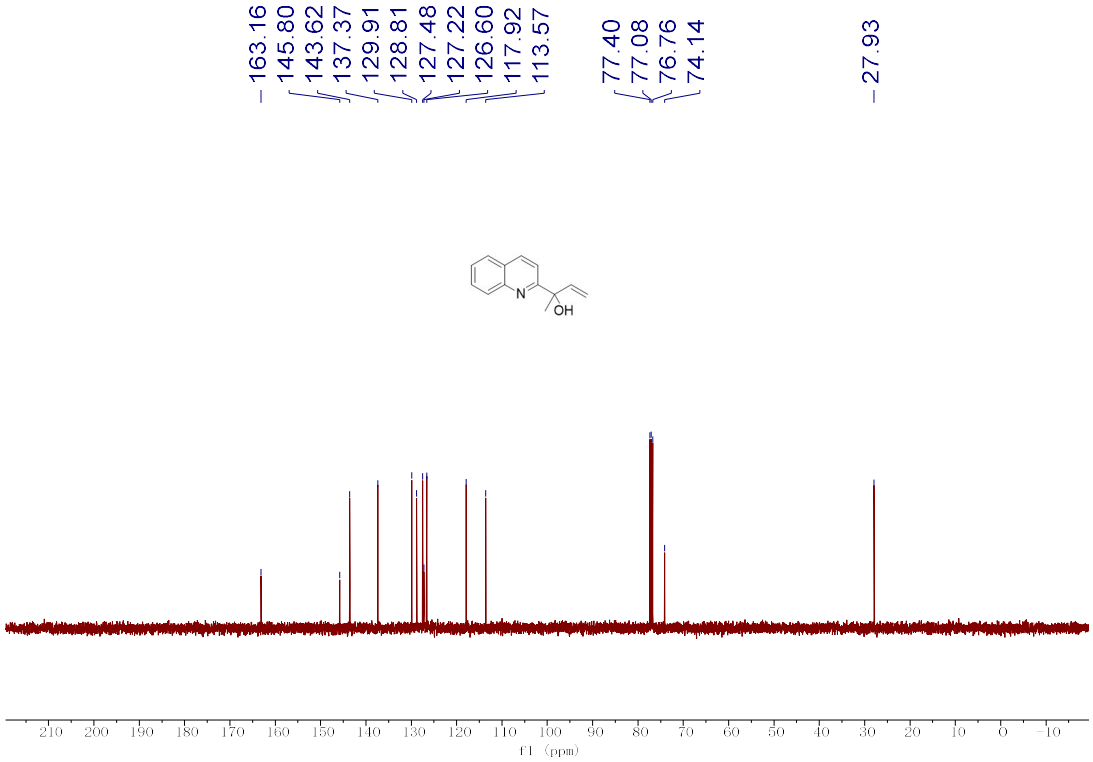
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1t**



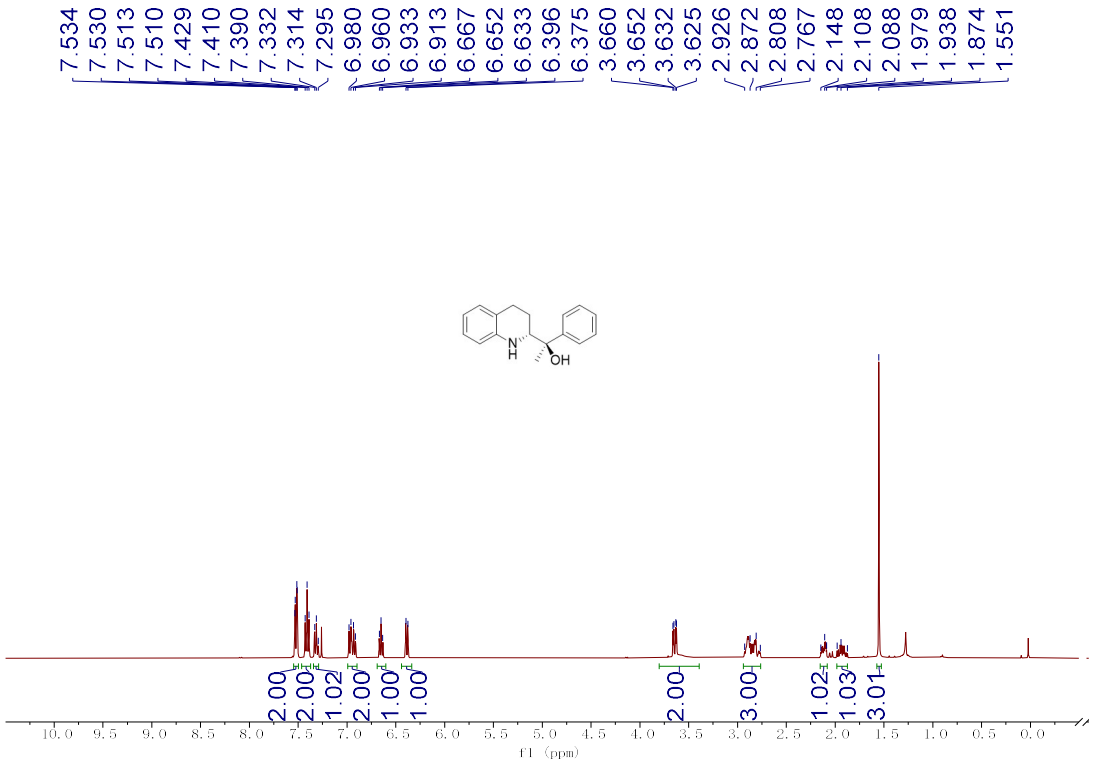
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1u**



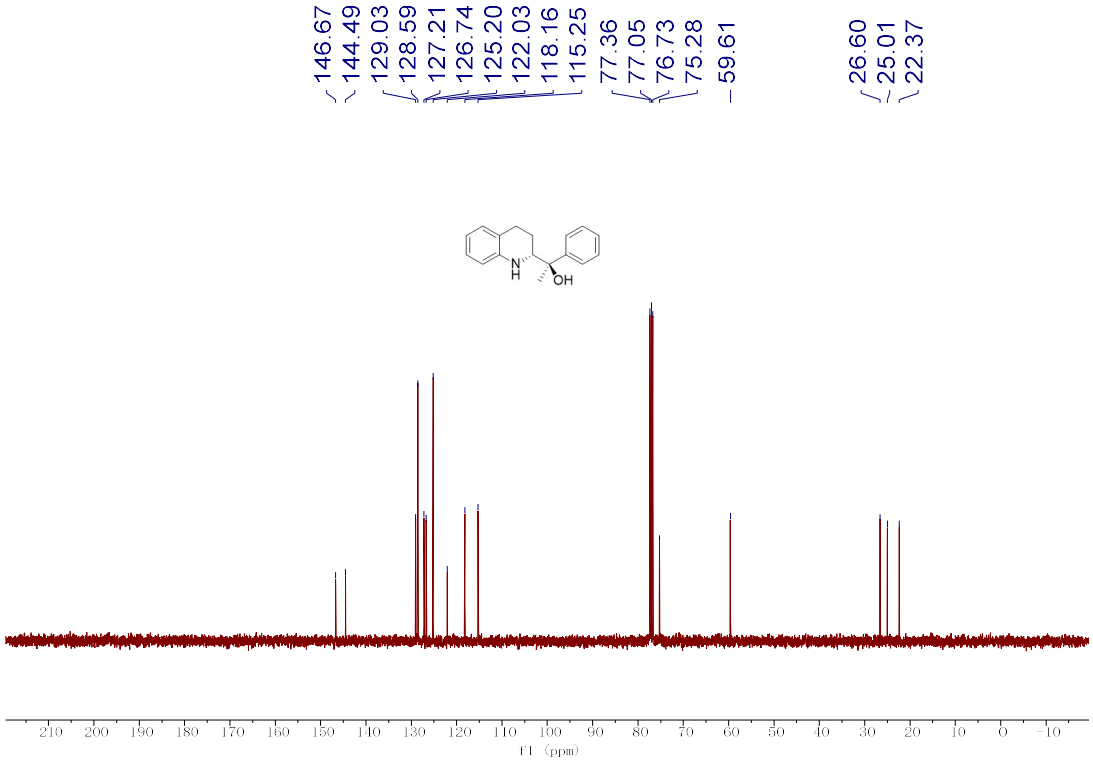
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **1u**



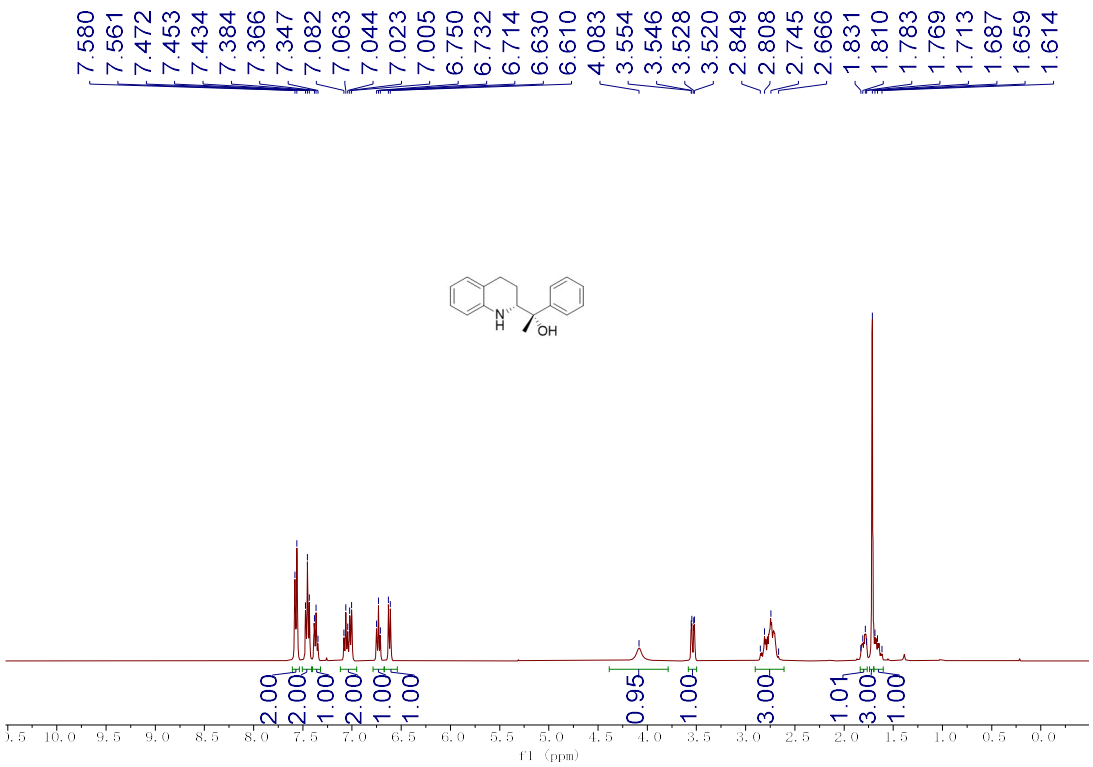
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2a**



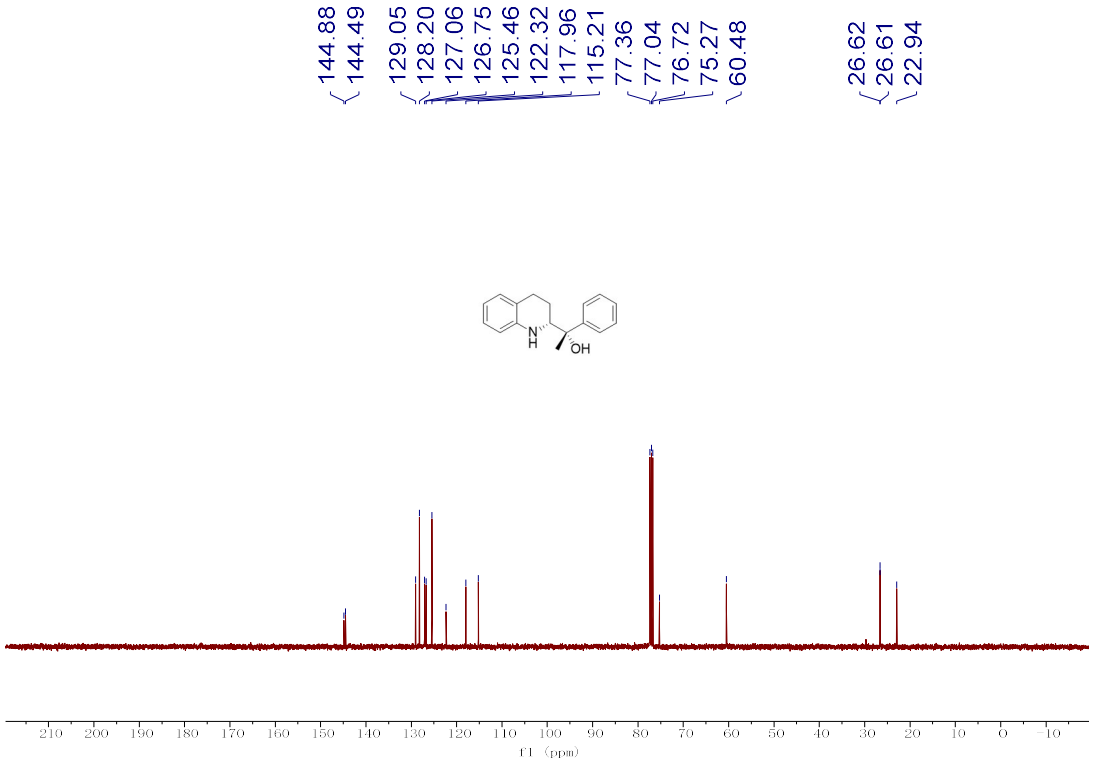
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2a**



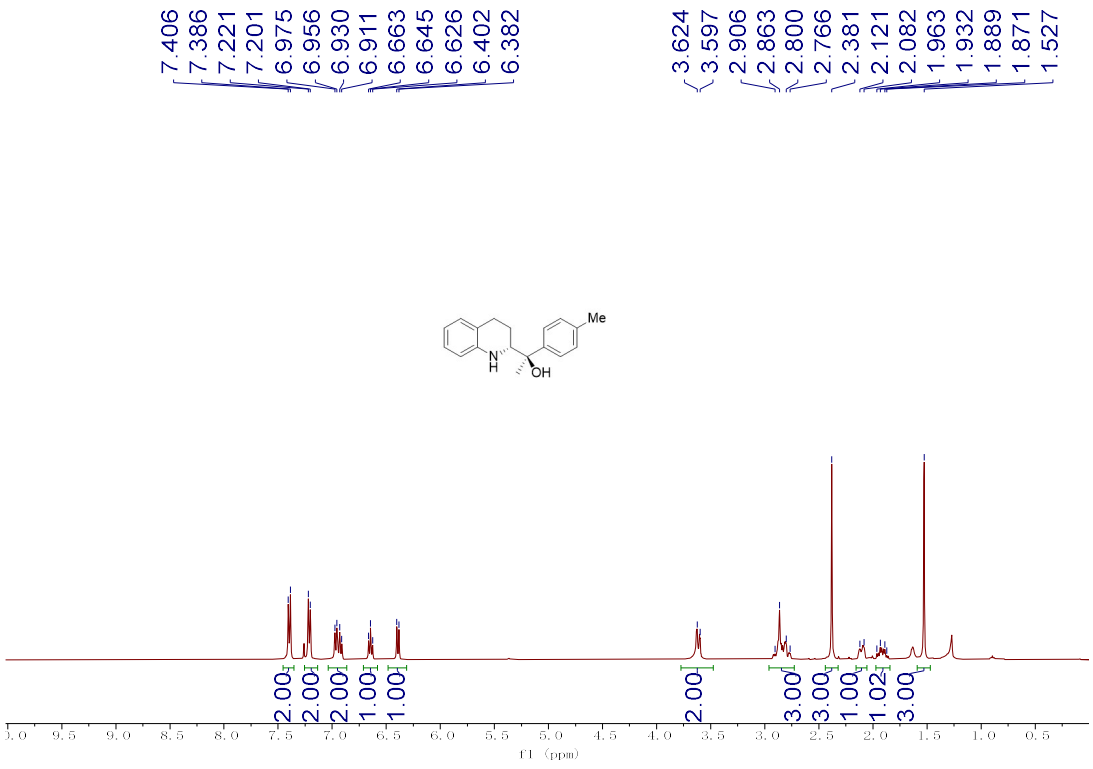
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2a**



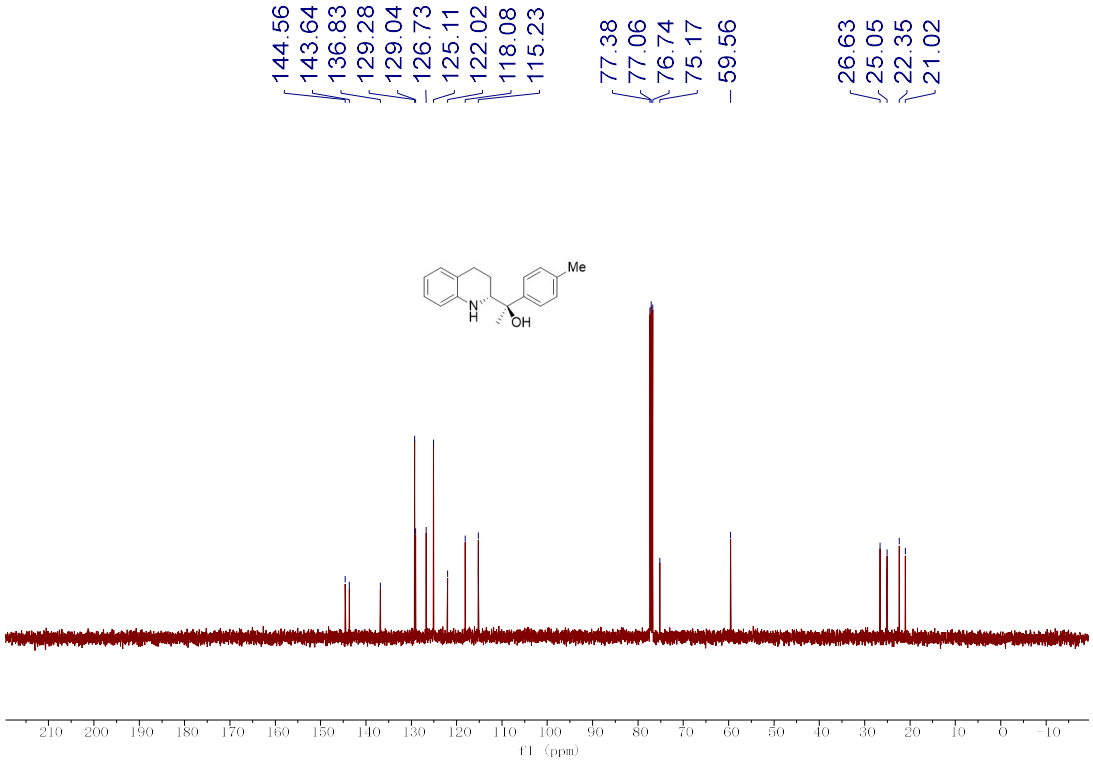
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2a**



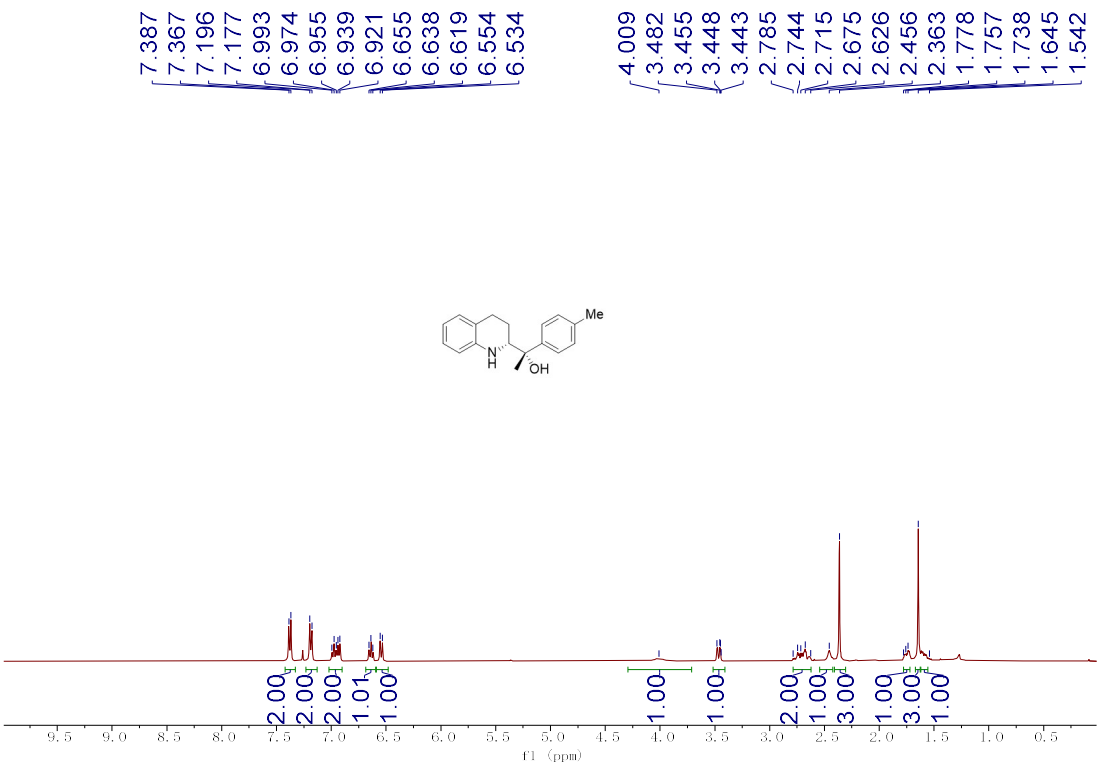
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2b**



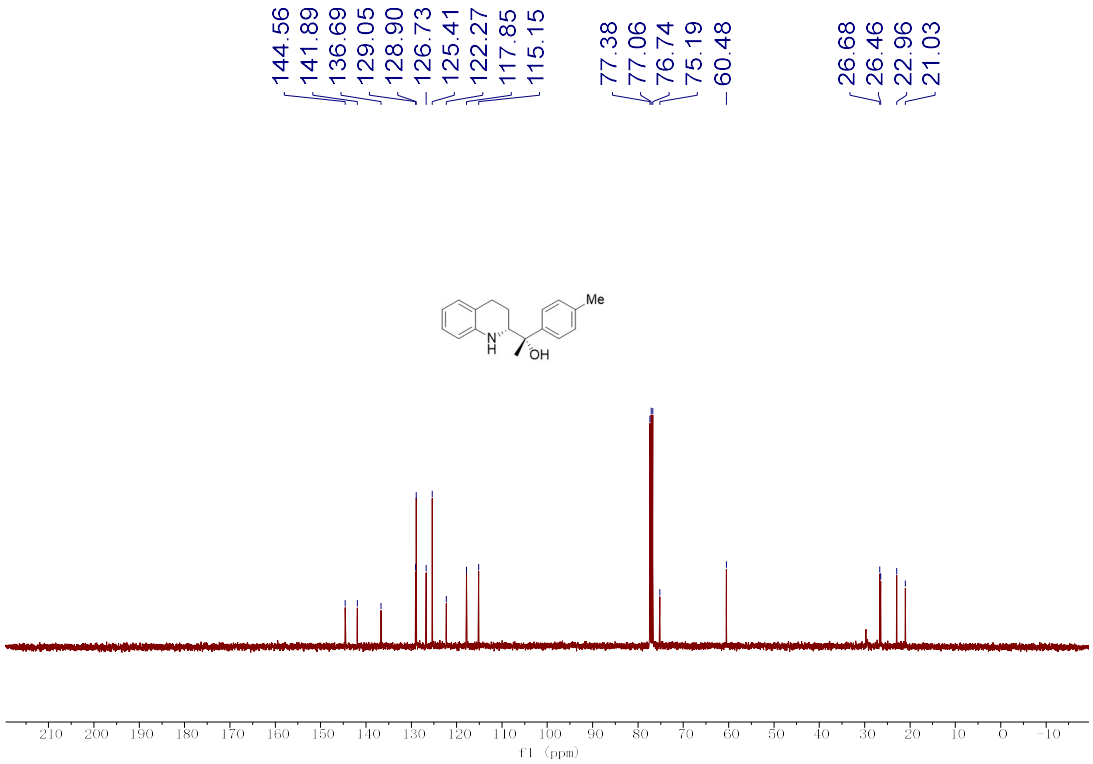
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2b**



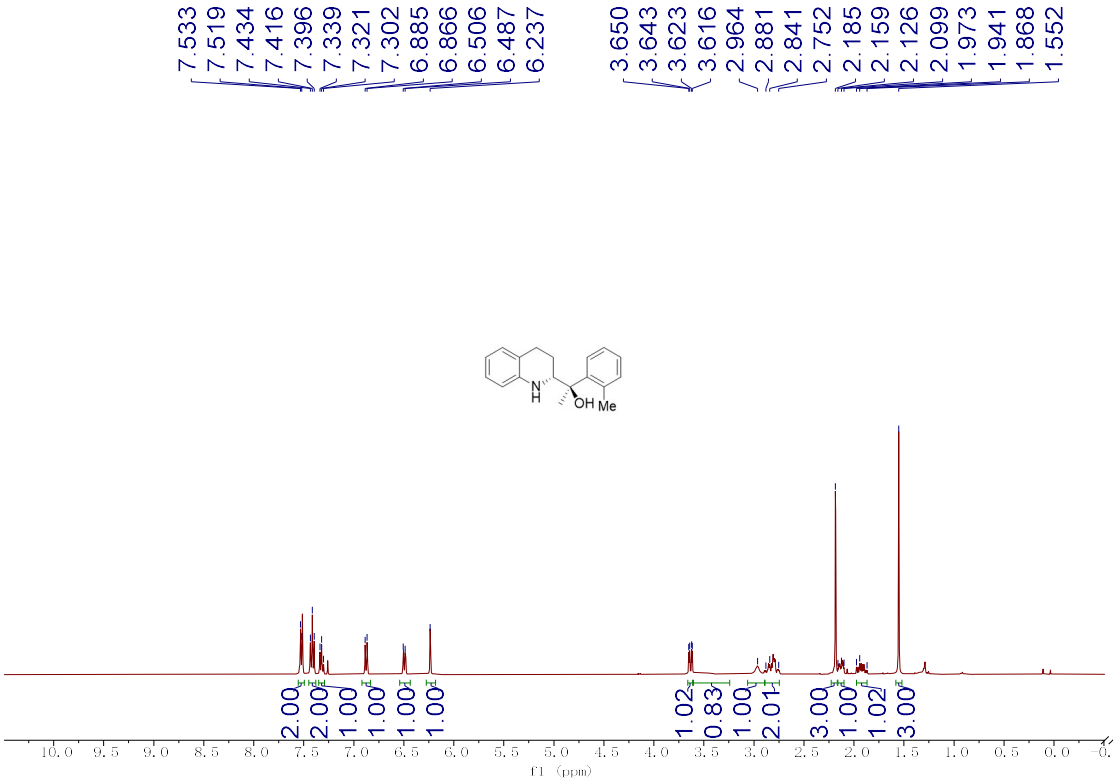
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2b**



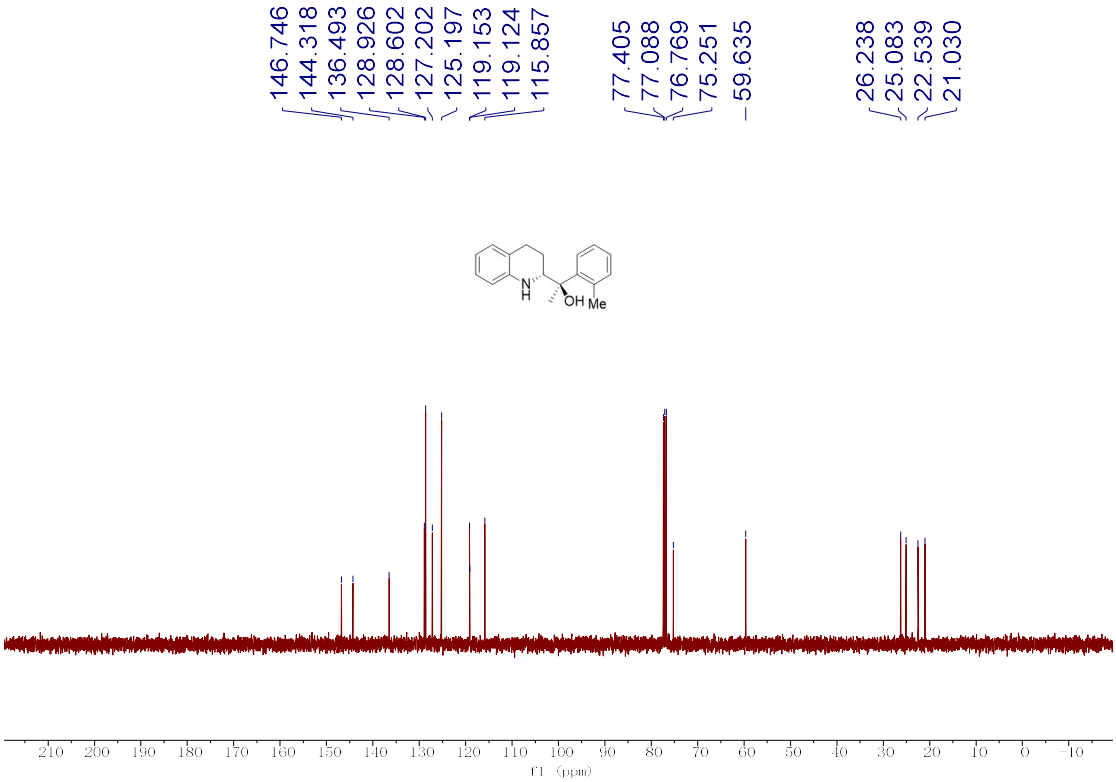
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2b**



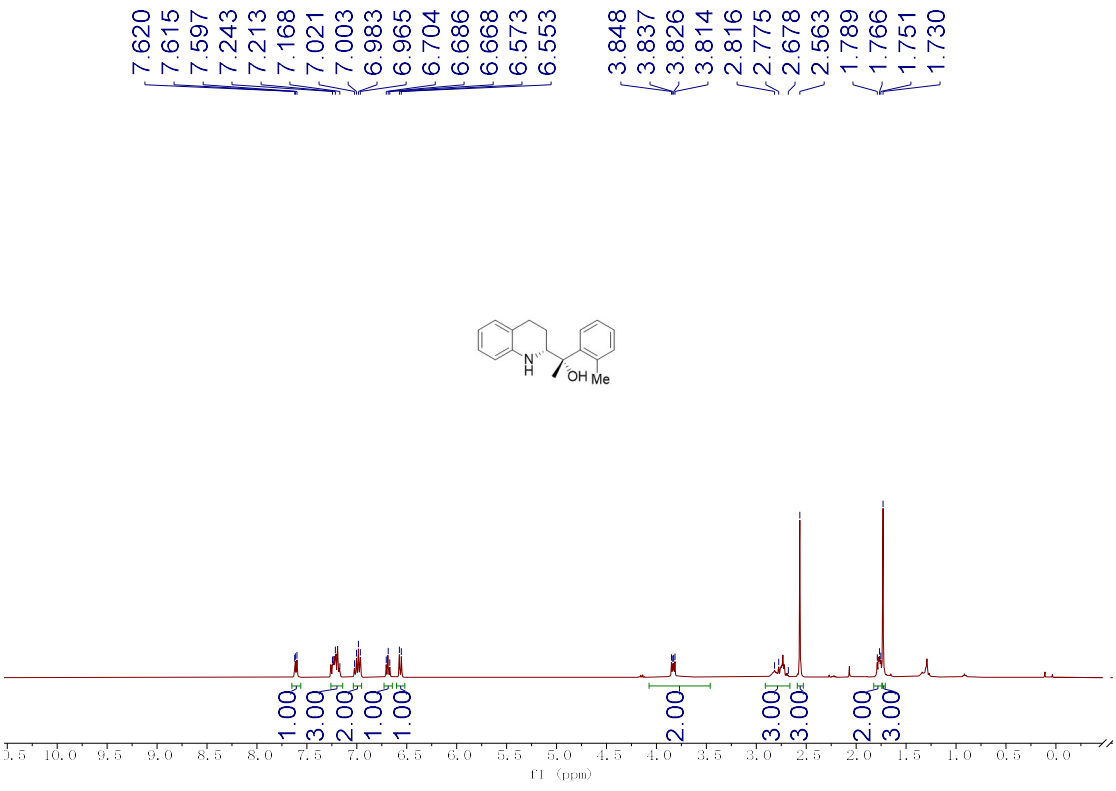
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2c**



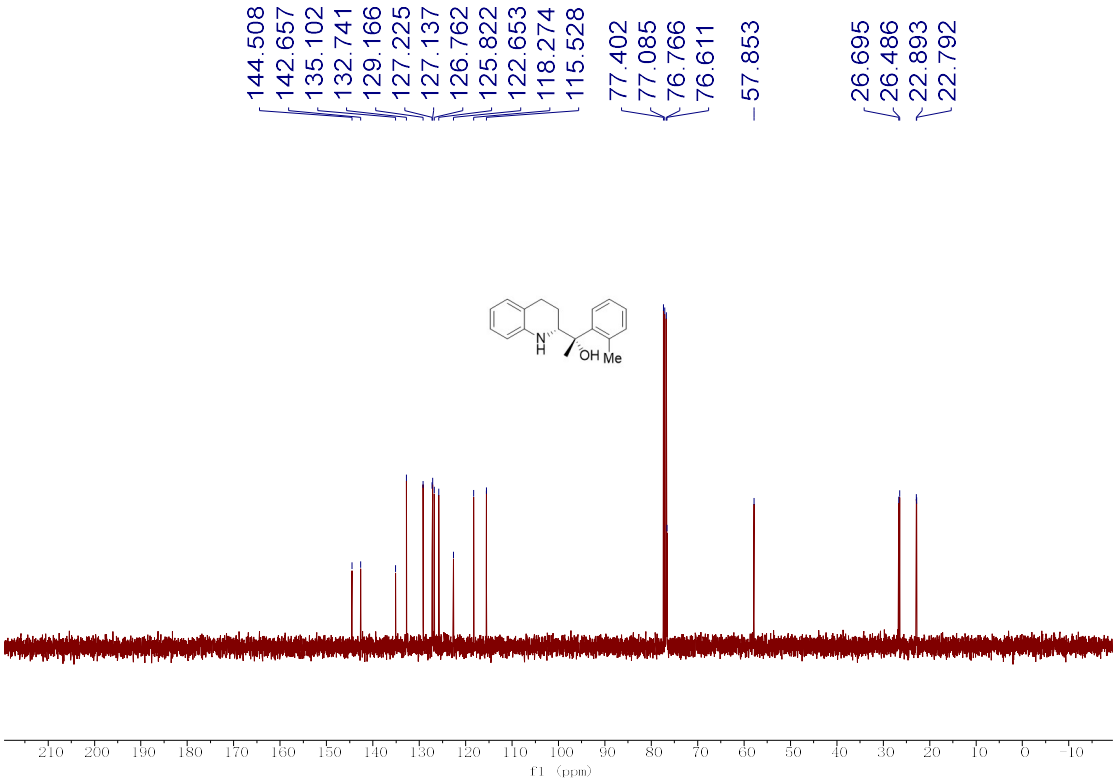
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2c**



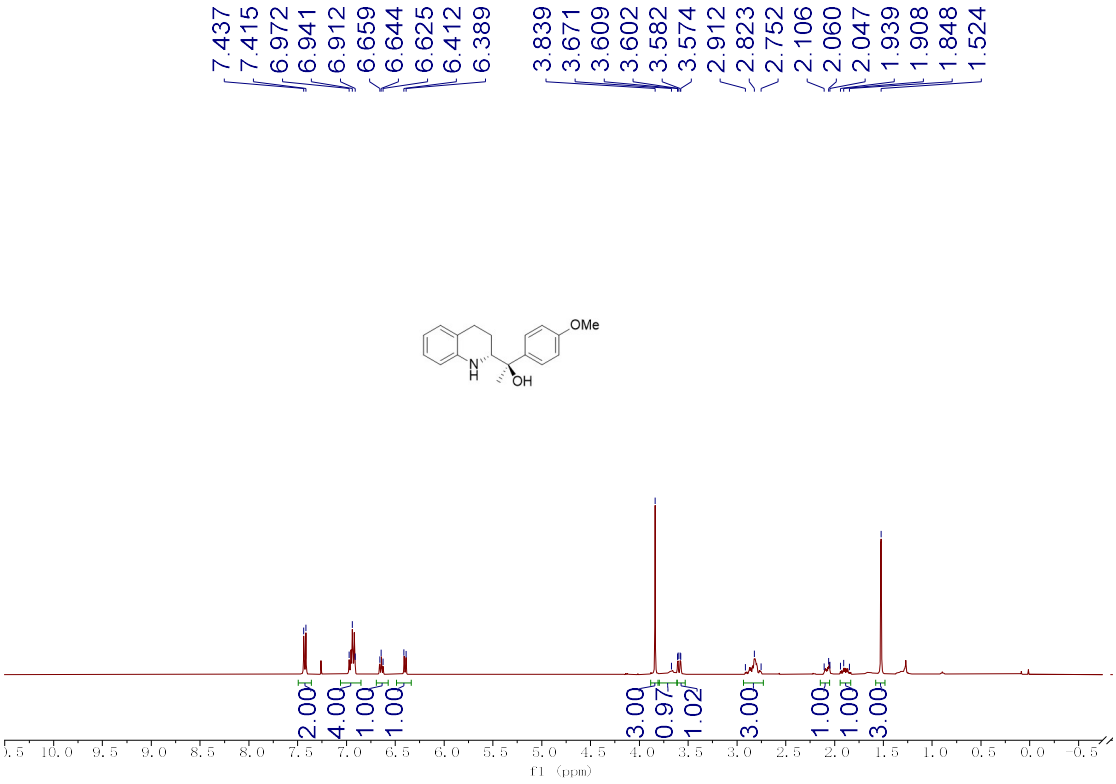
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2c**



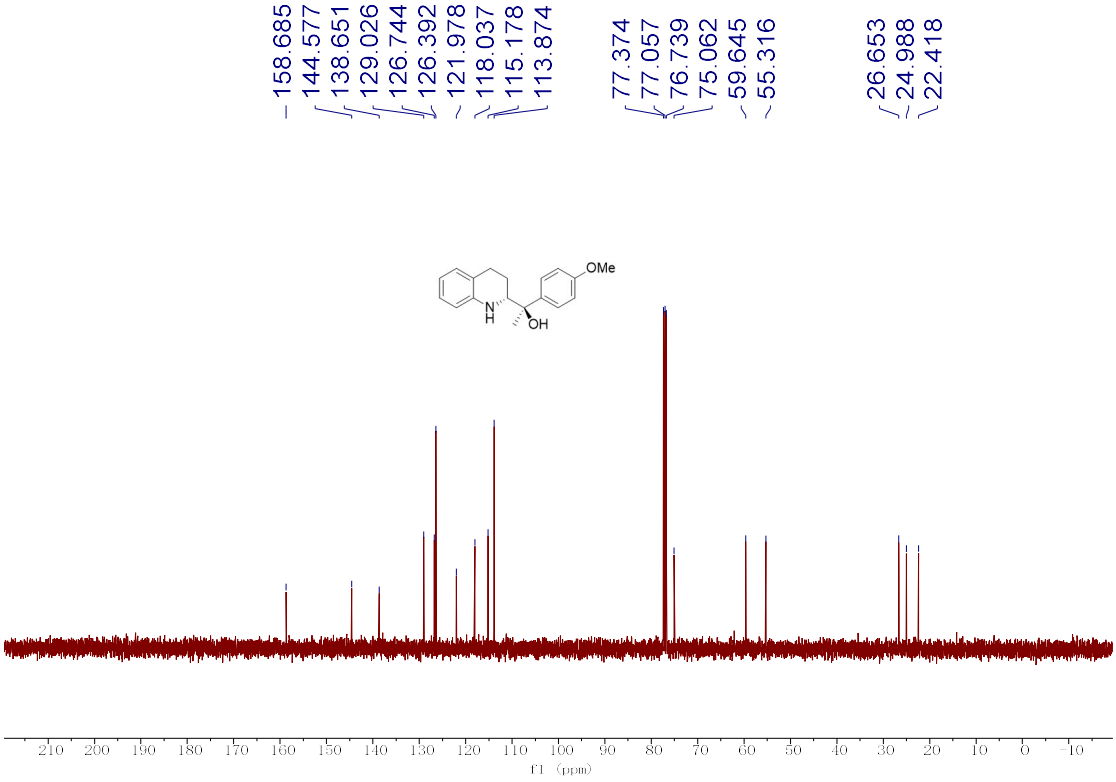
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2c**



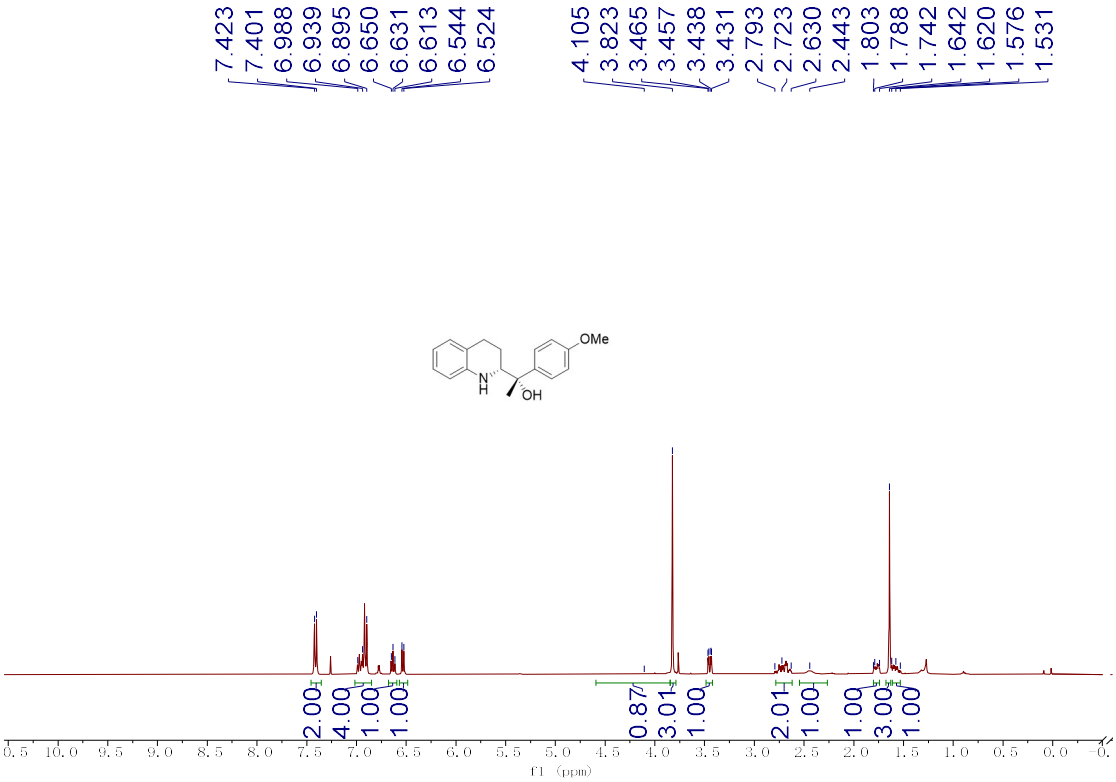
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2d**



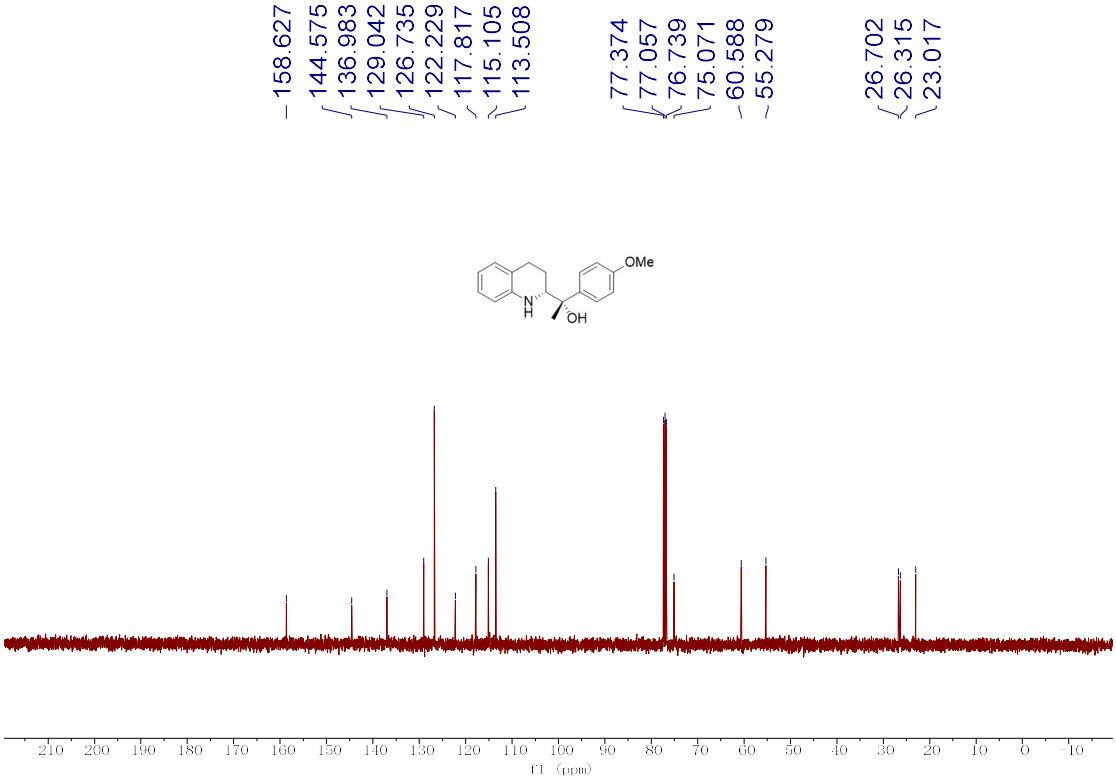
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2d**



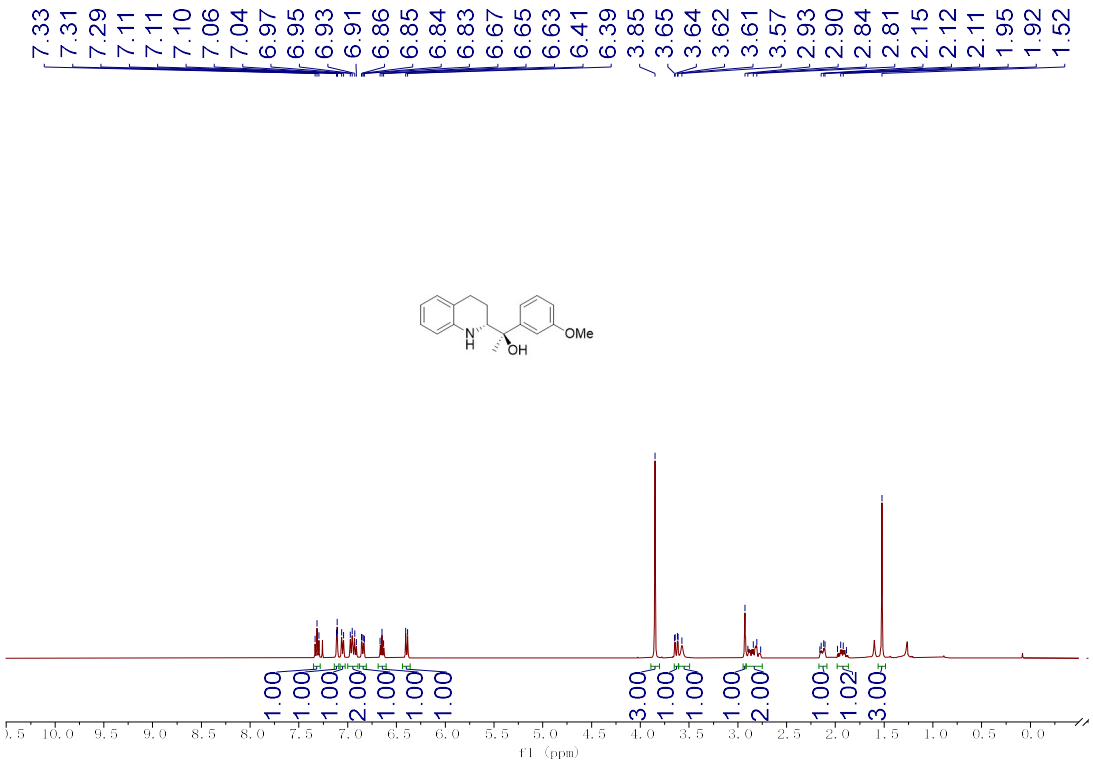
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2d**



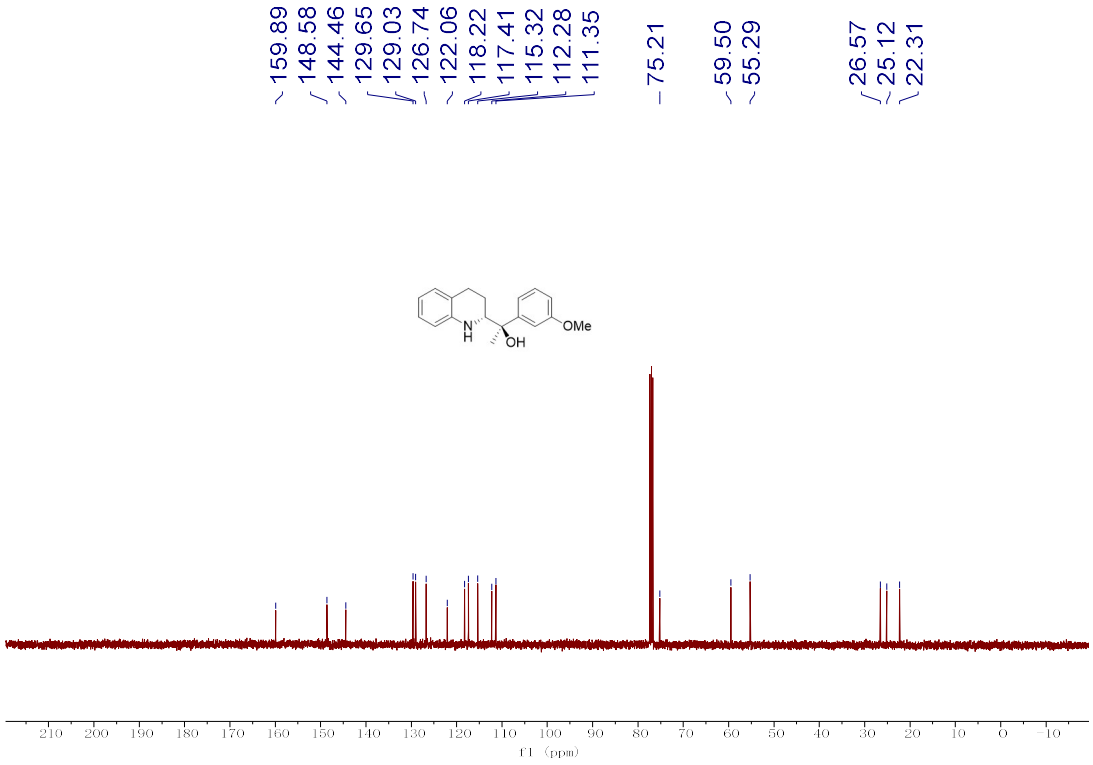
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2d**



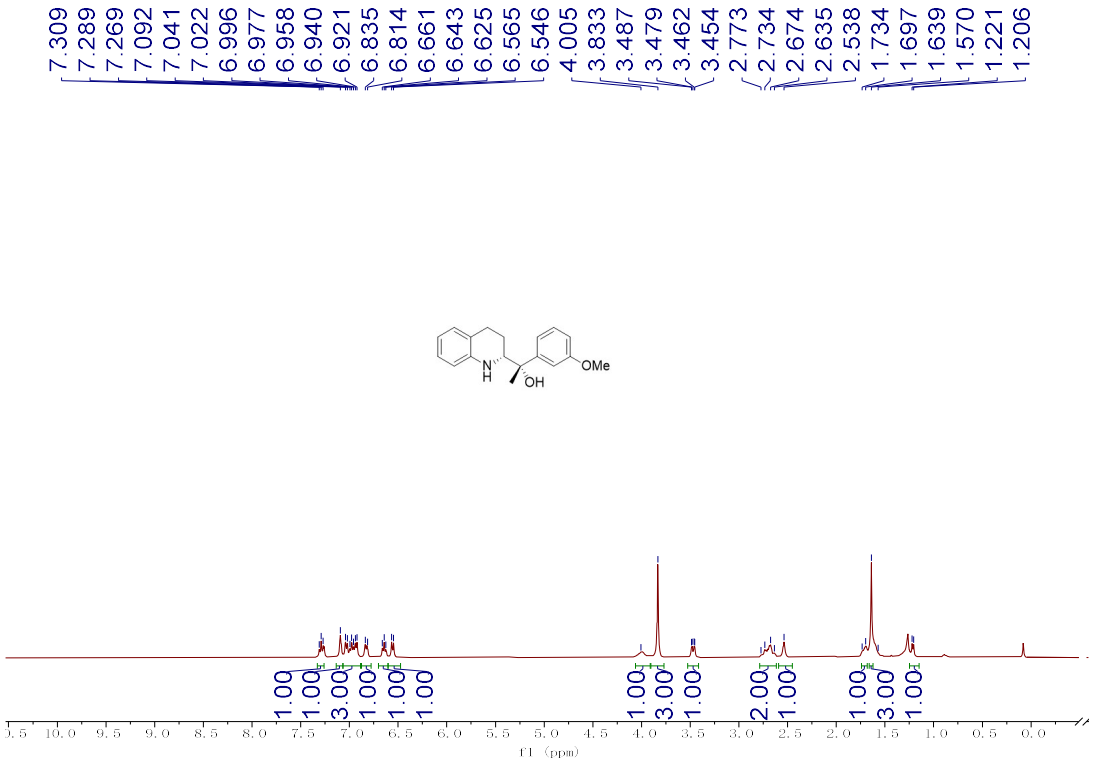
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2e**



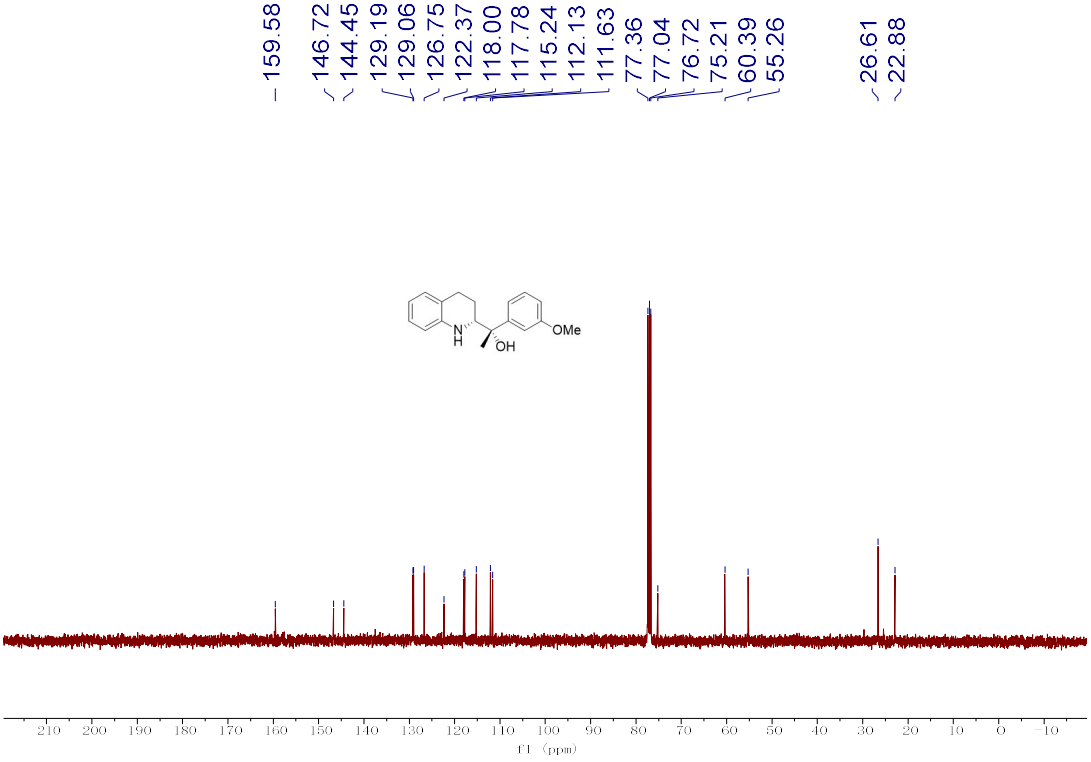
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2e**



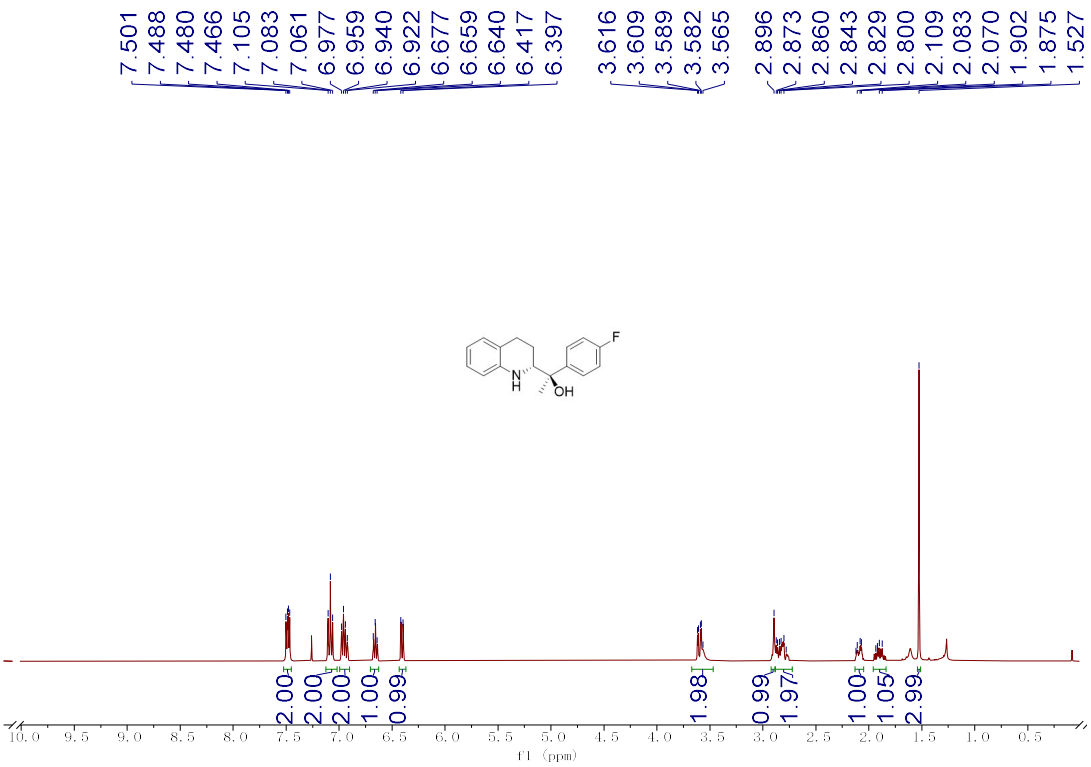
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2e**



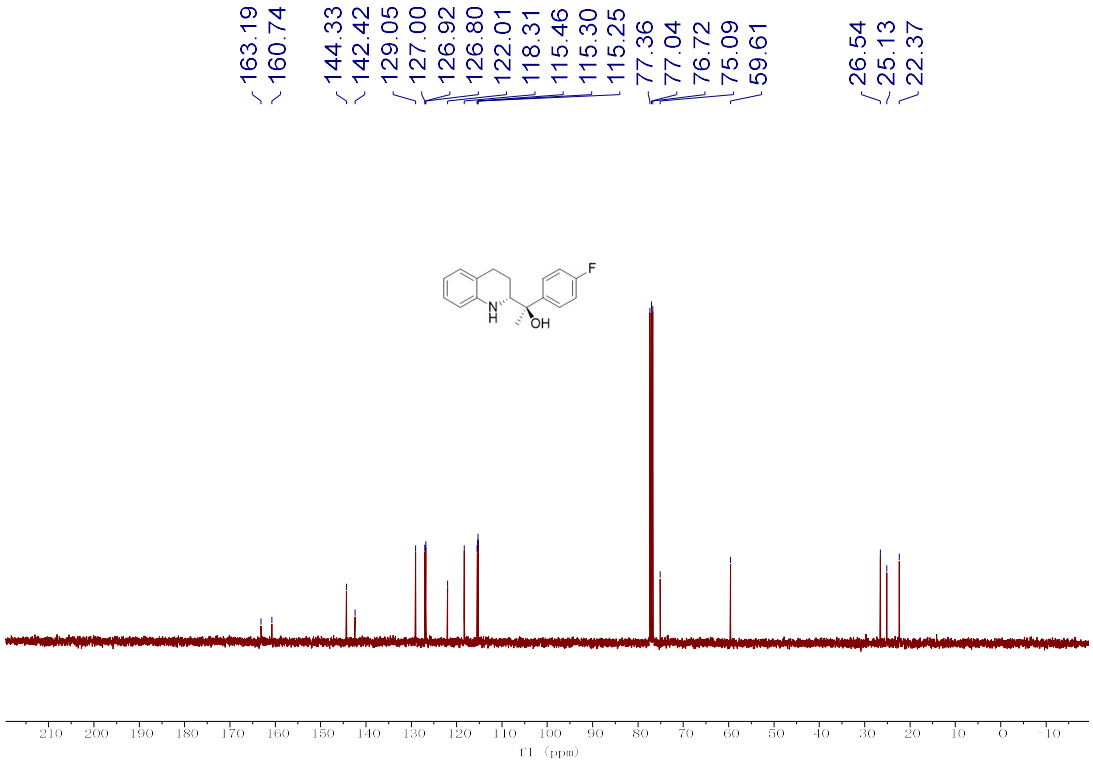
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2e**



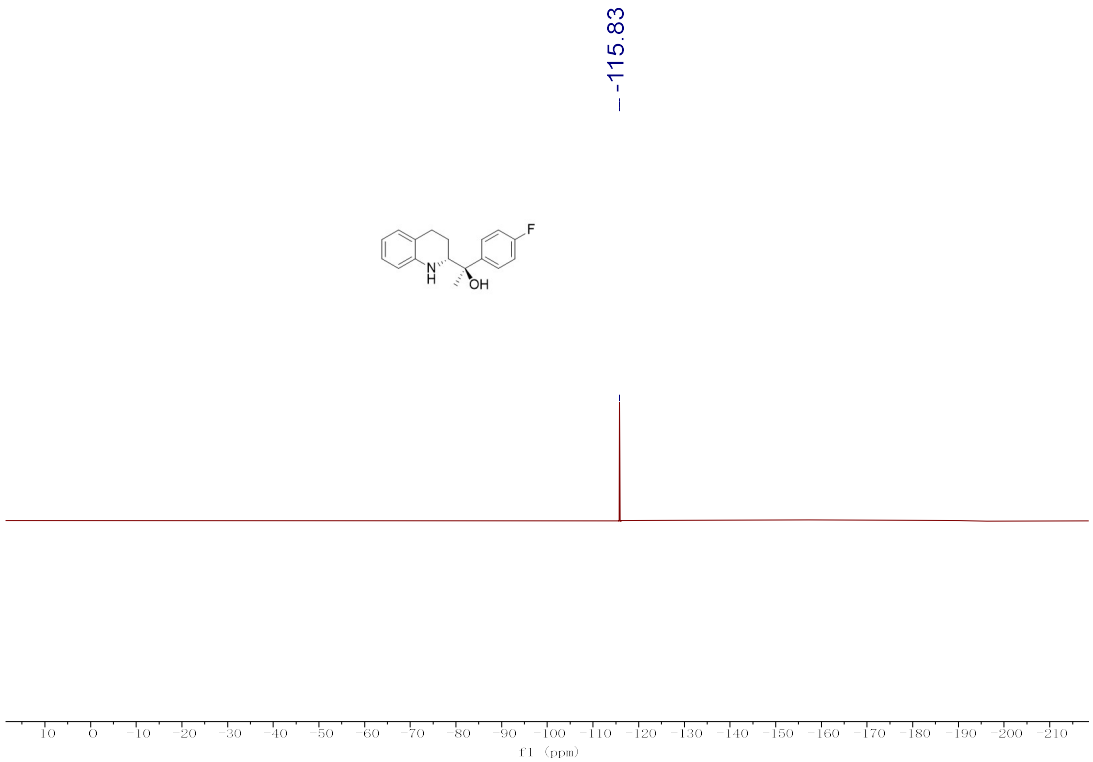
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2f**



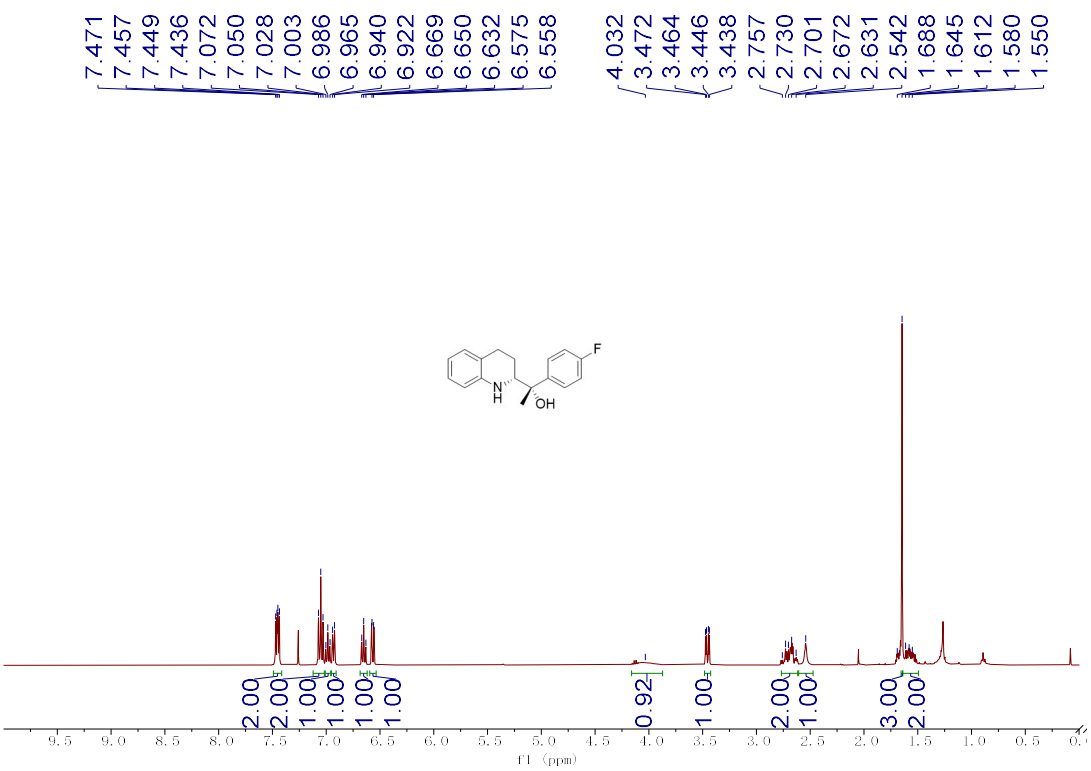
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2f**



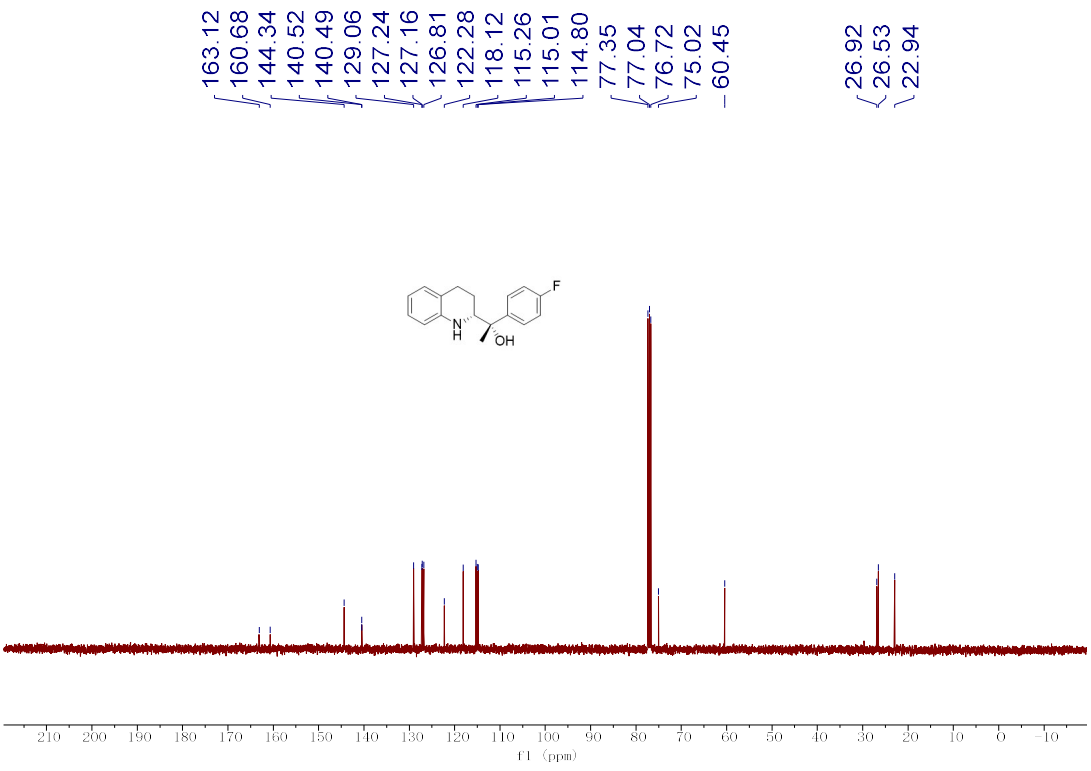
^{19}F {1H} NMR (376 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2f**



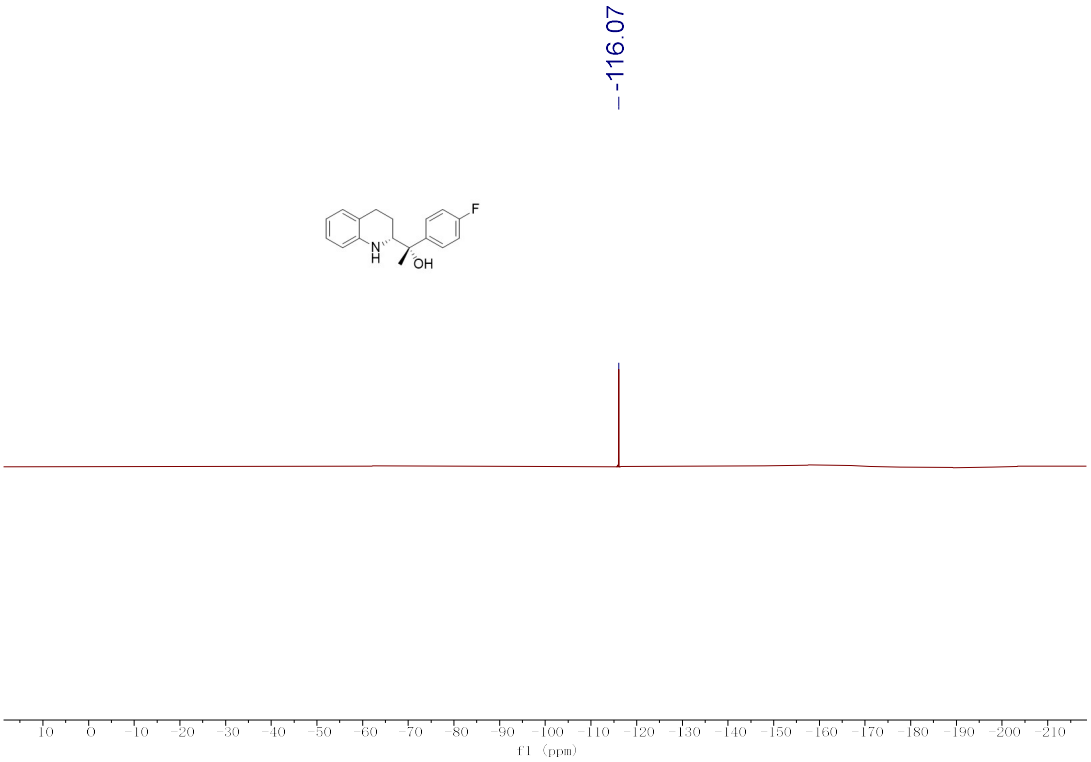
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2f**



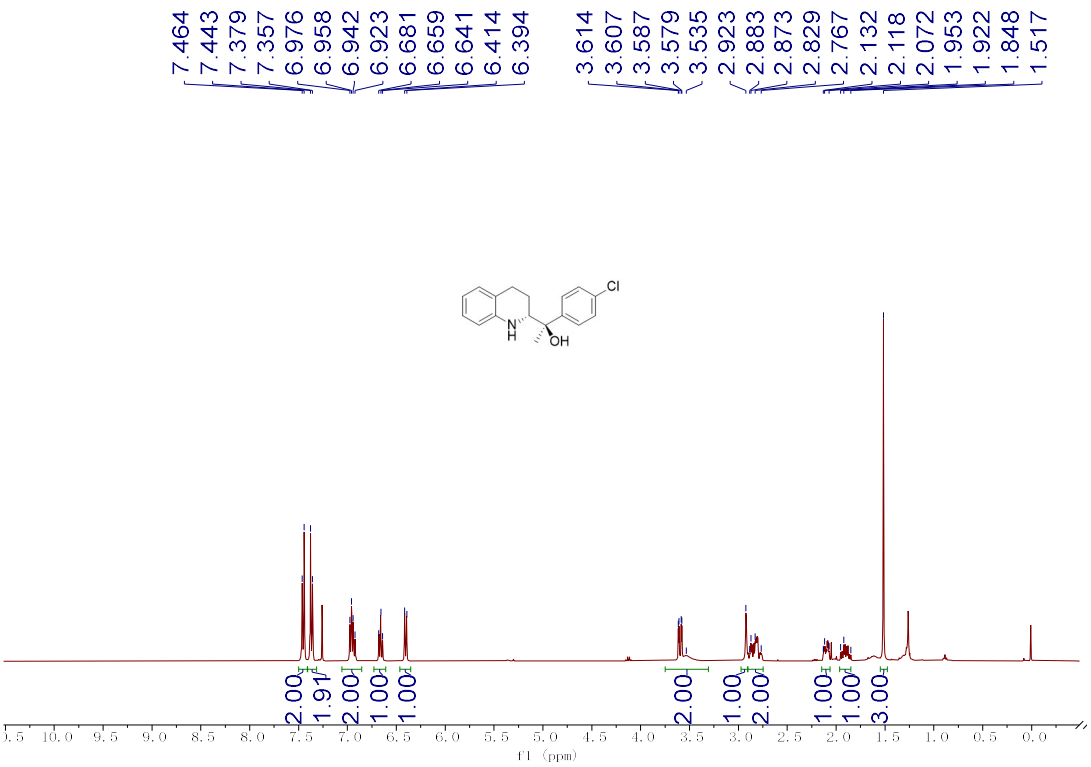
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2f**



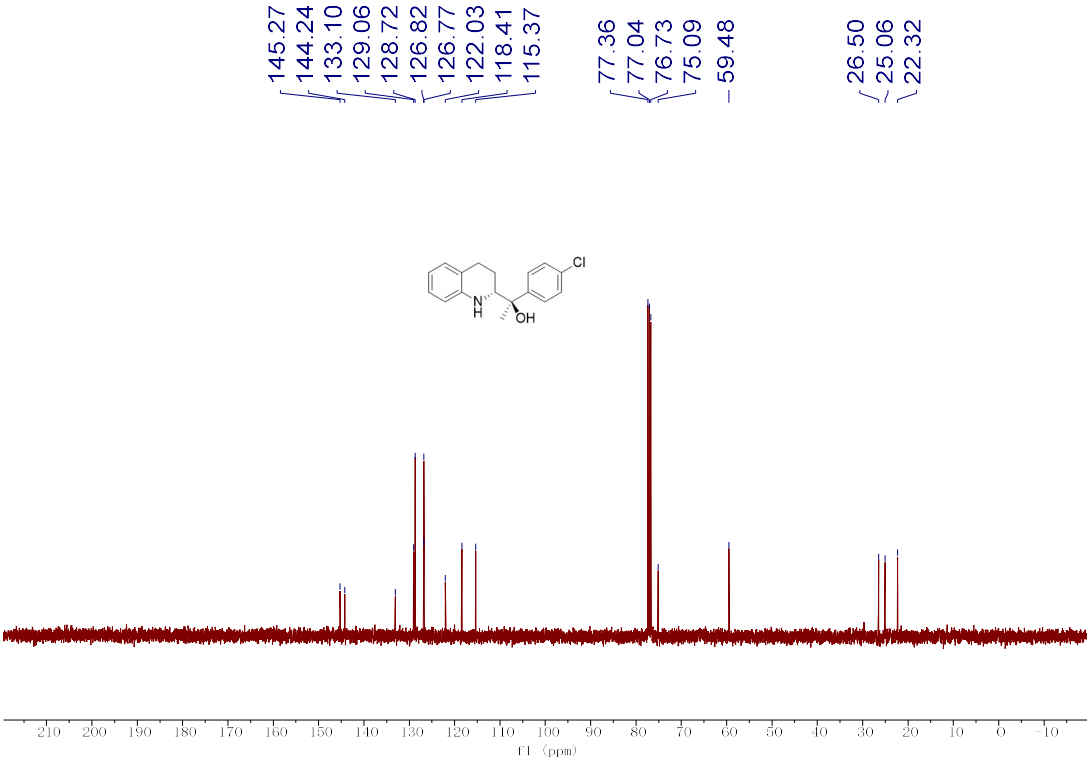
^{19}F {1H} NMR (376 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2f**



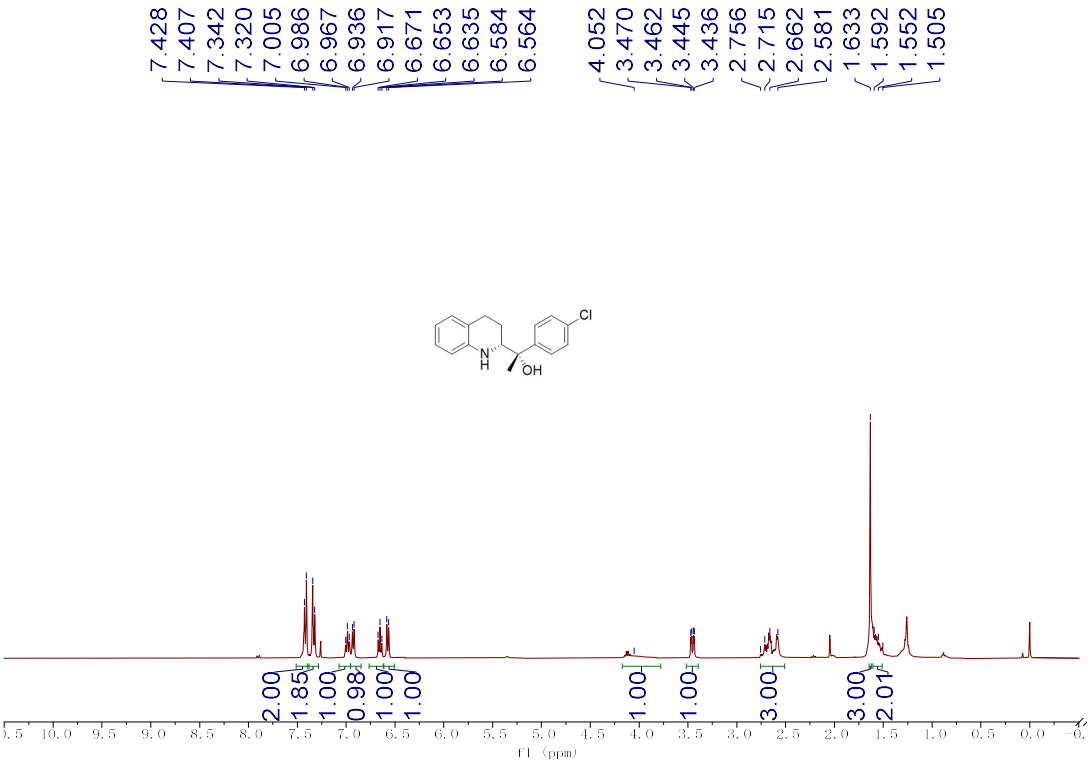
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2g**



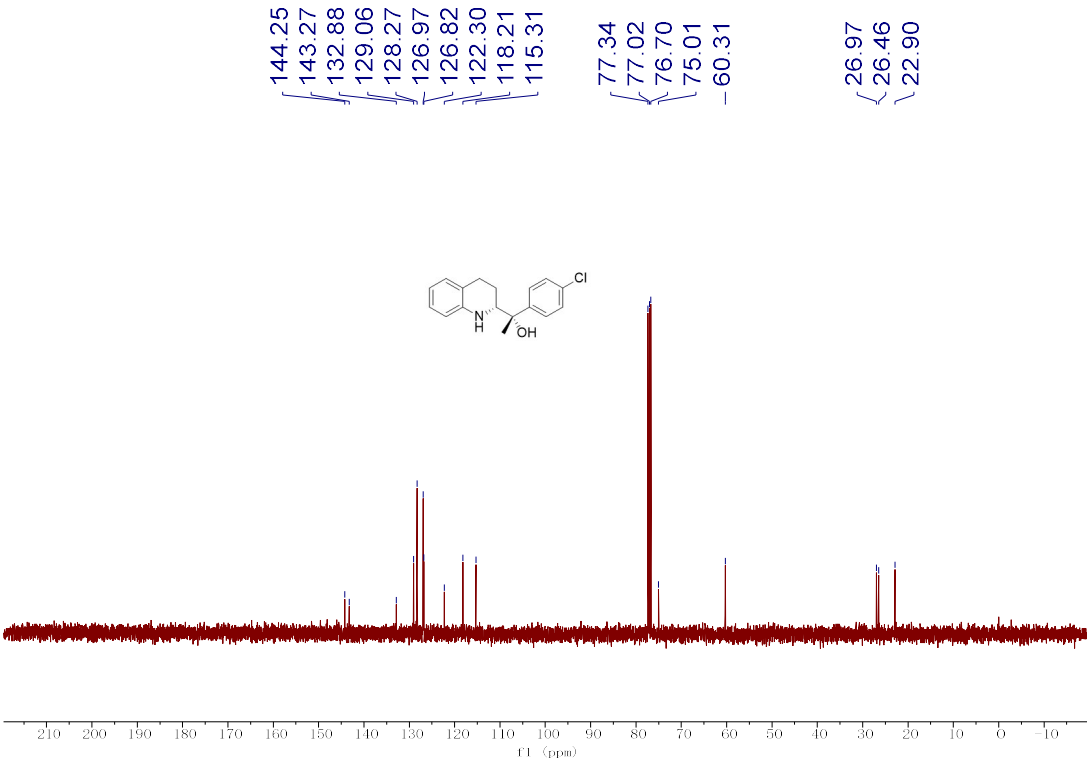
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2g**



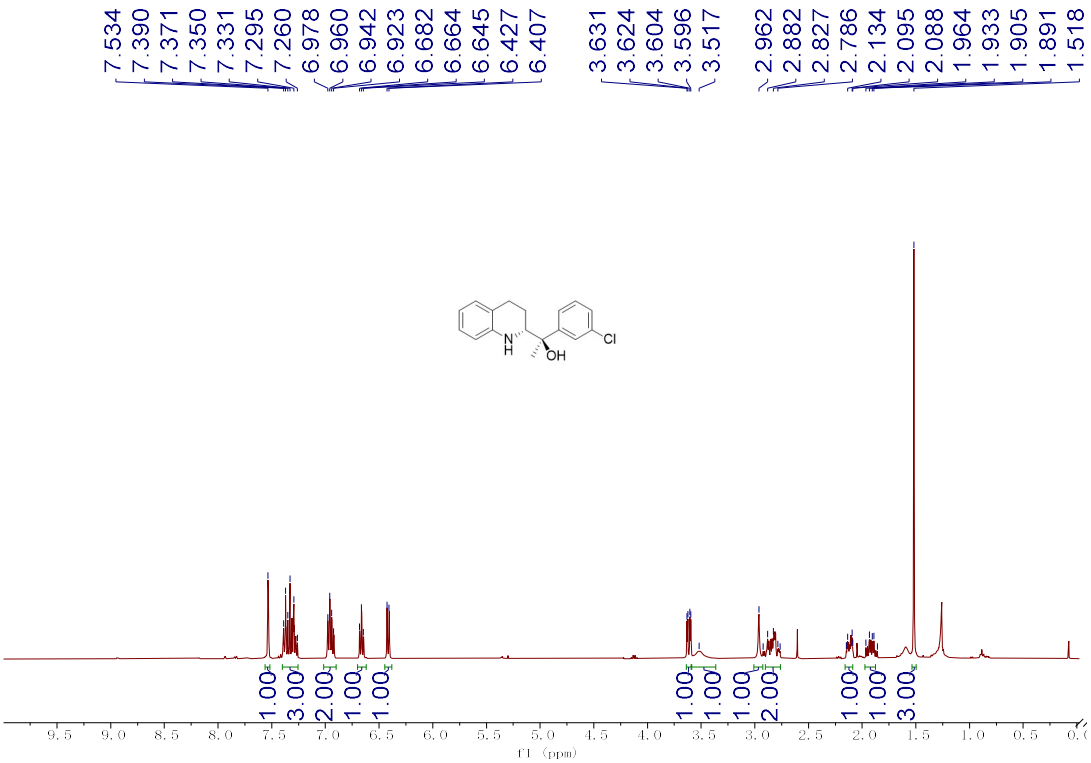
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2g**



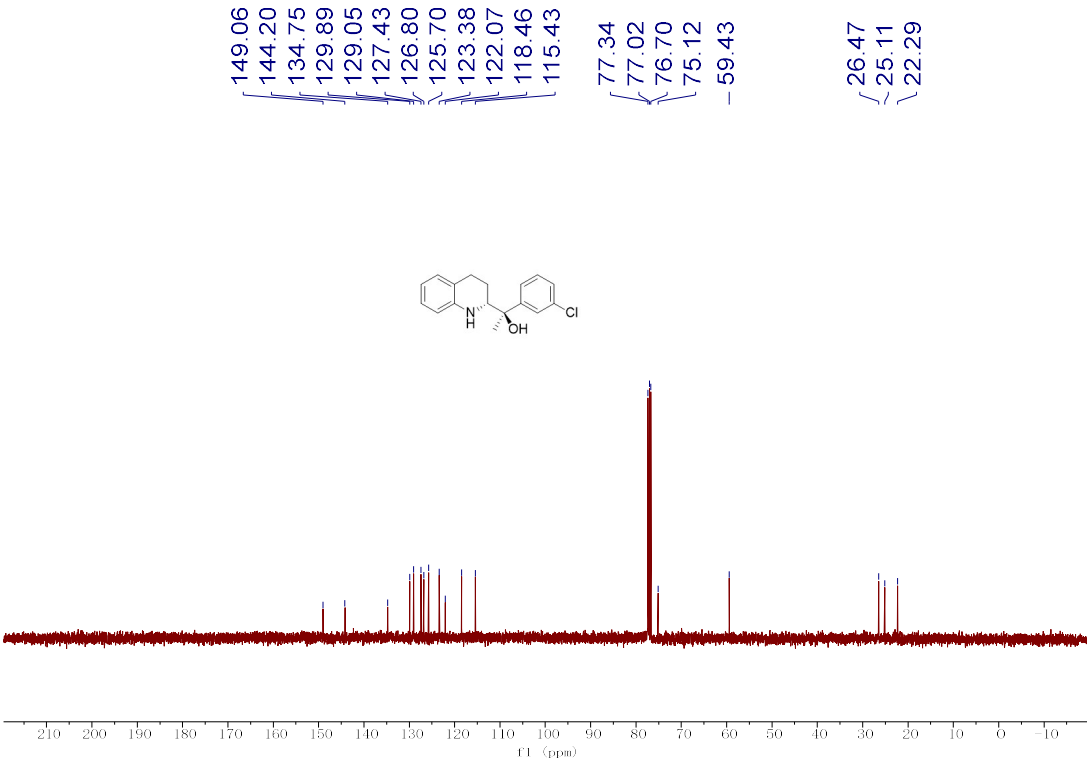
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2g**



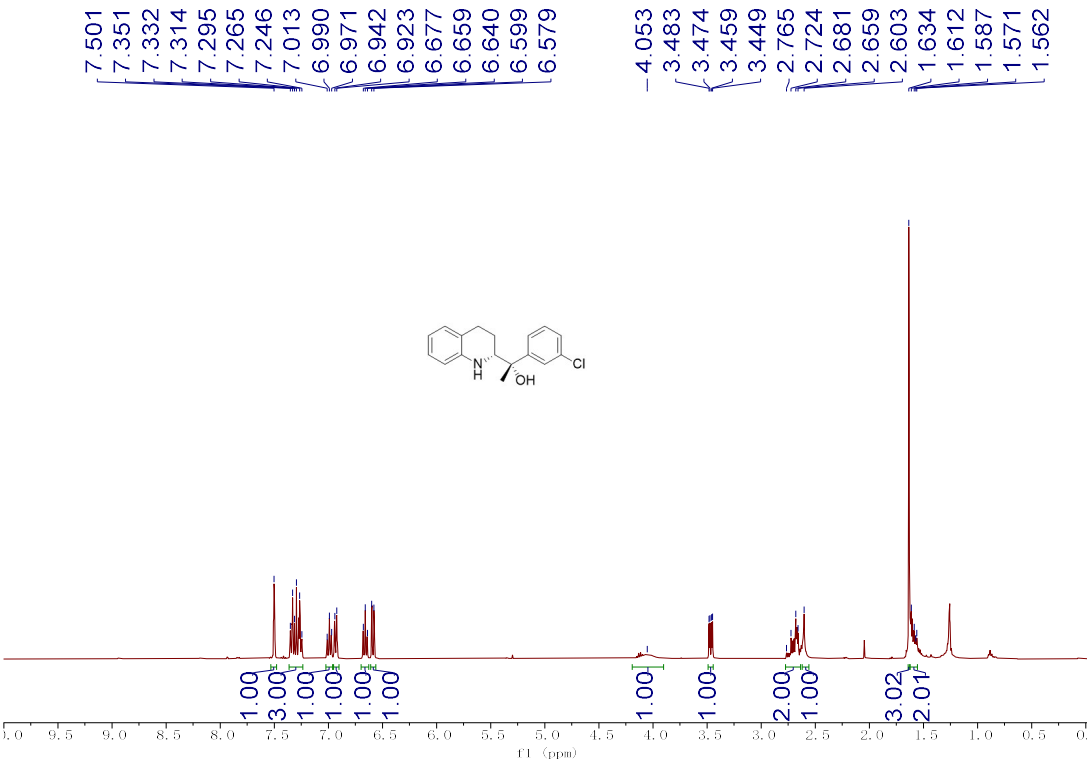
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2h**



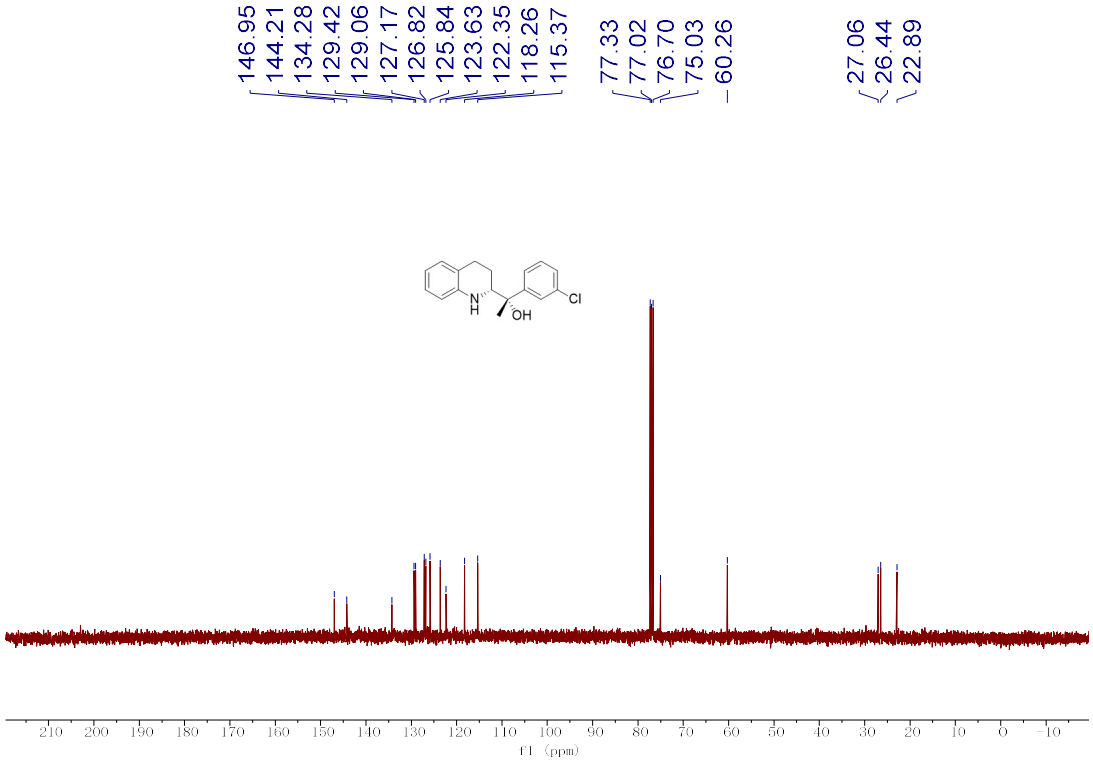
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2h**



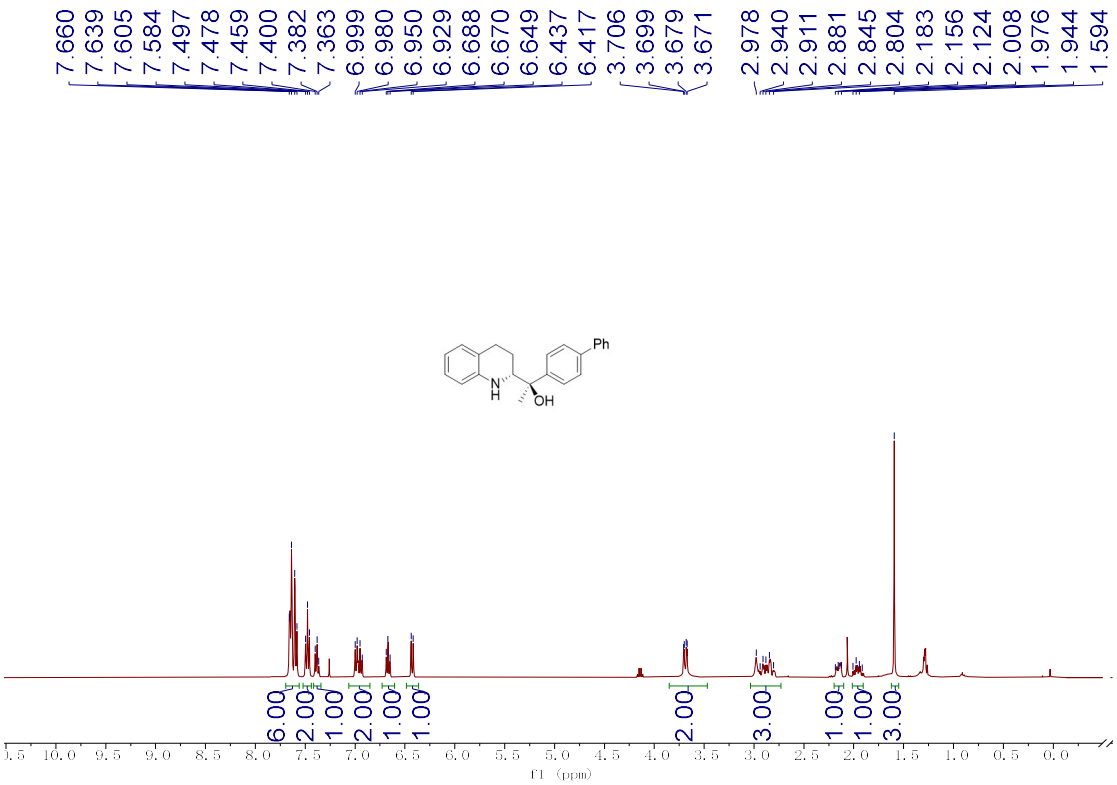
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2h**



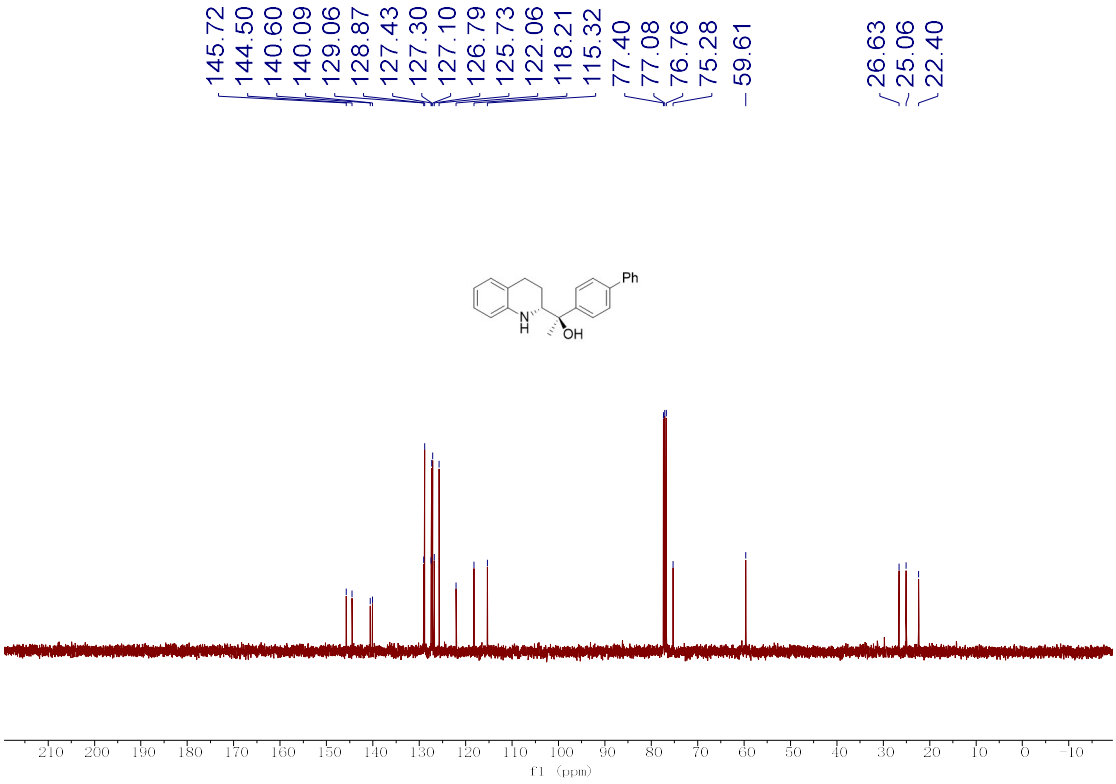
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2h**



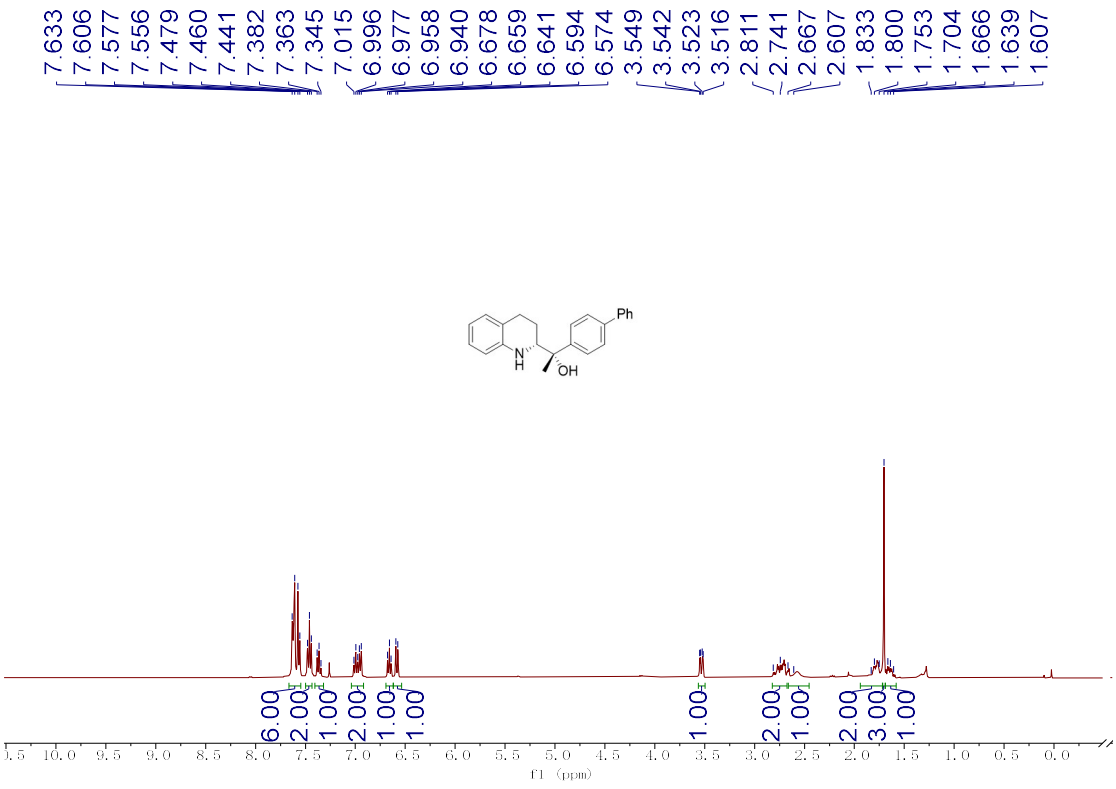
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2i**



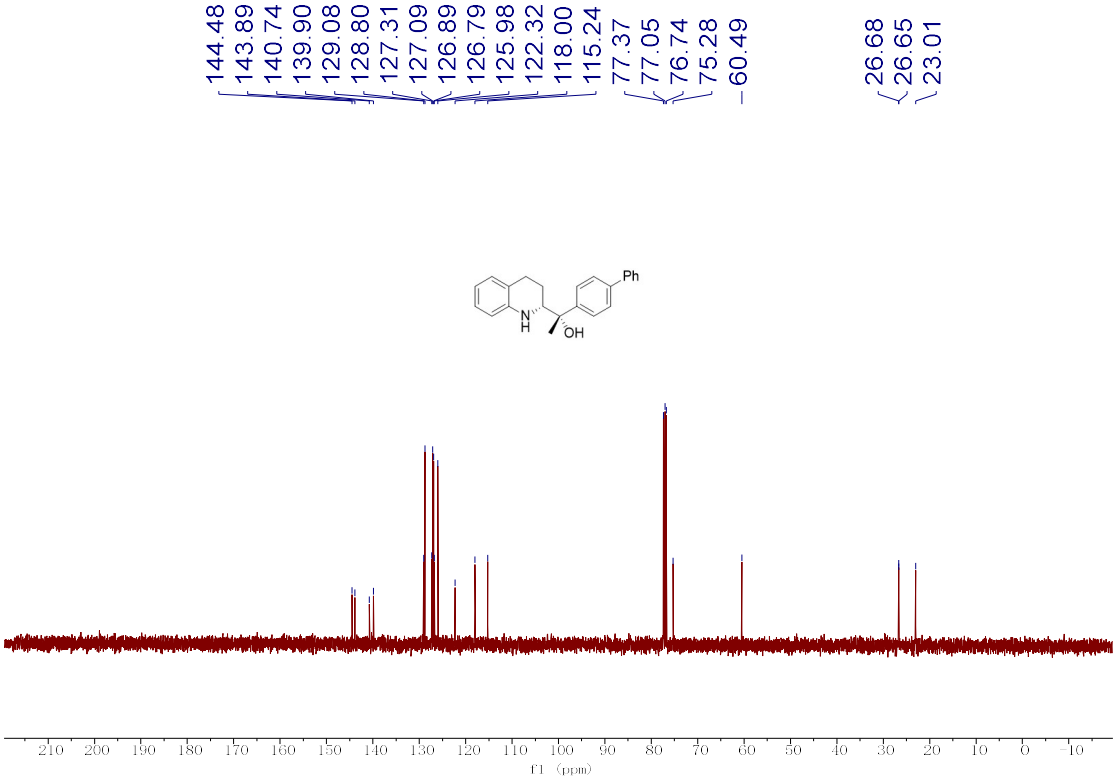
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2i**



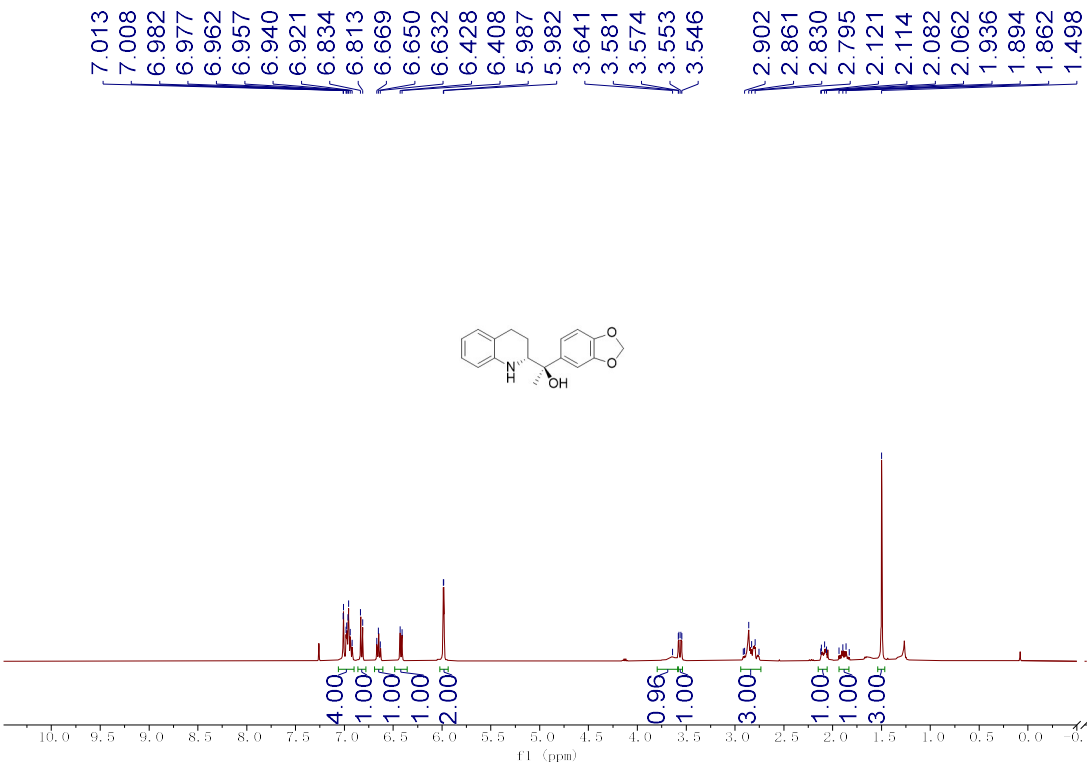
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2i**



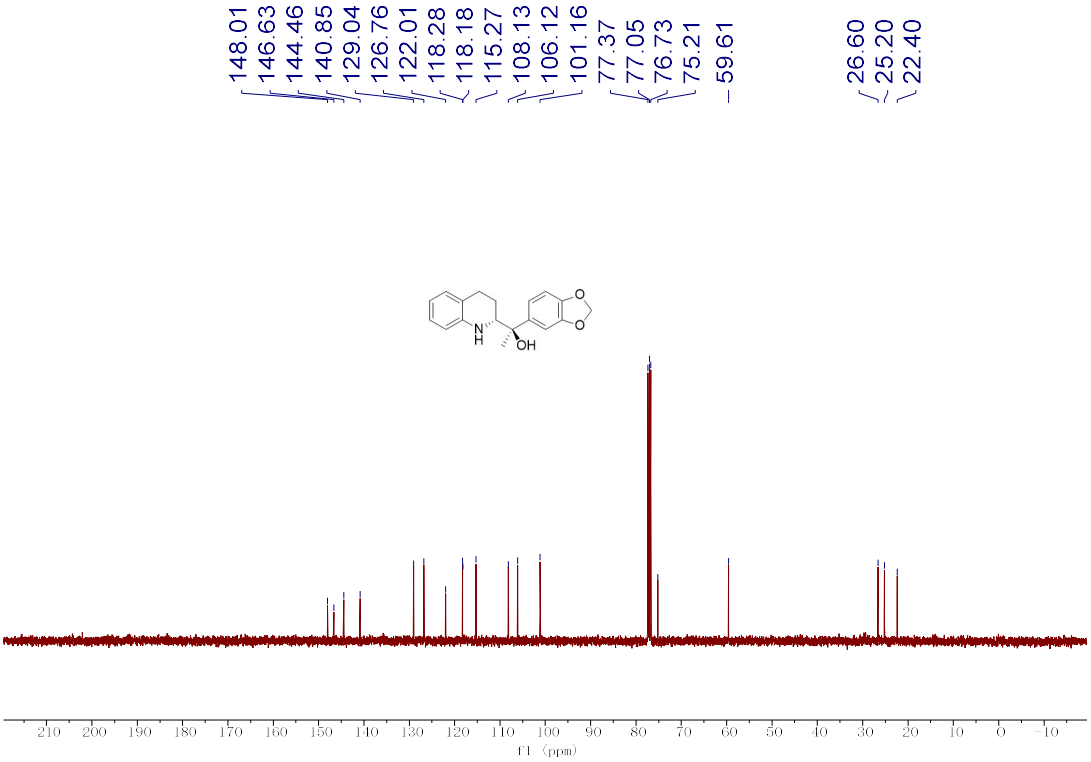
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2i**



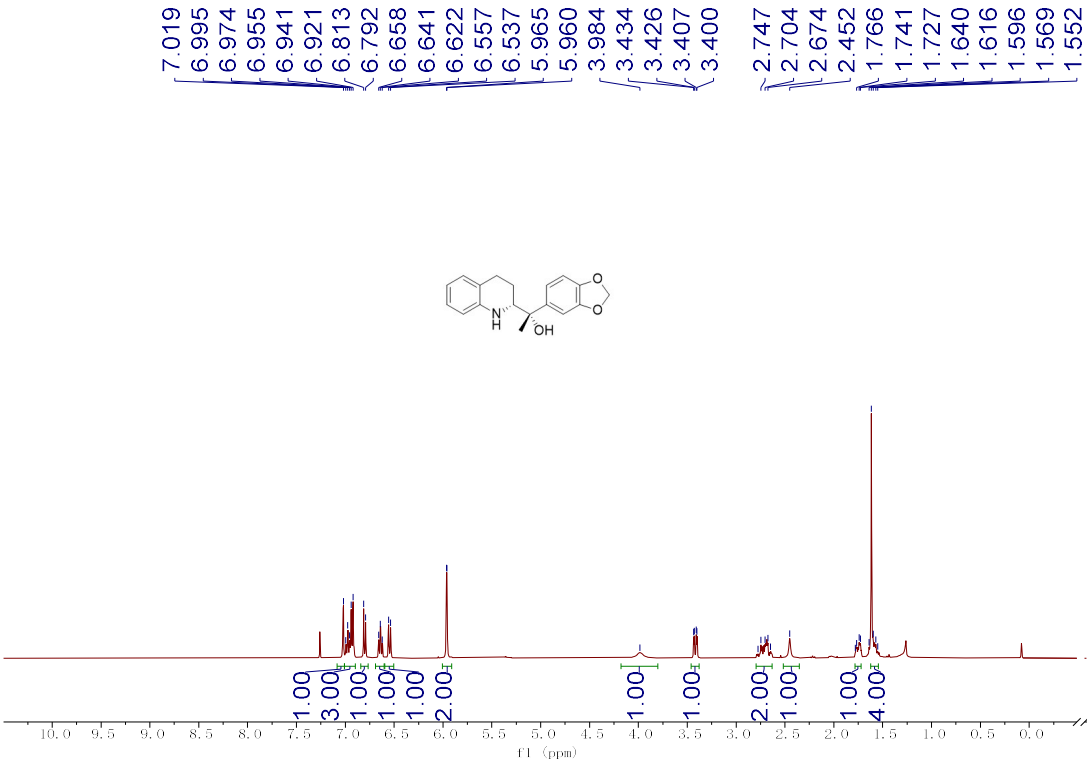
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2j**



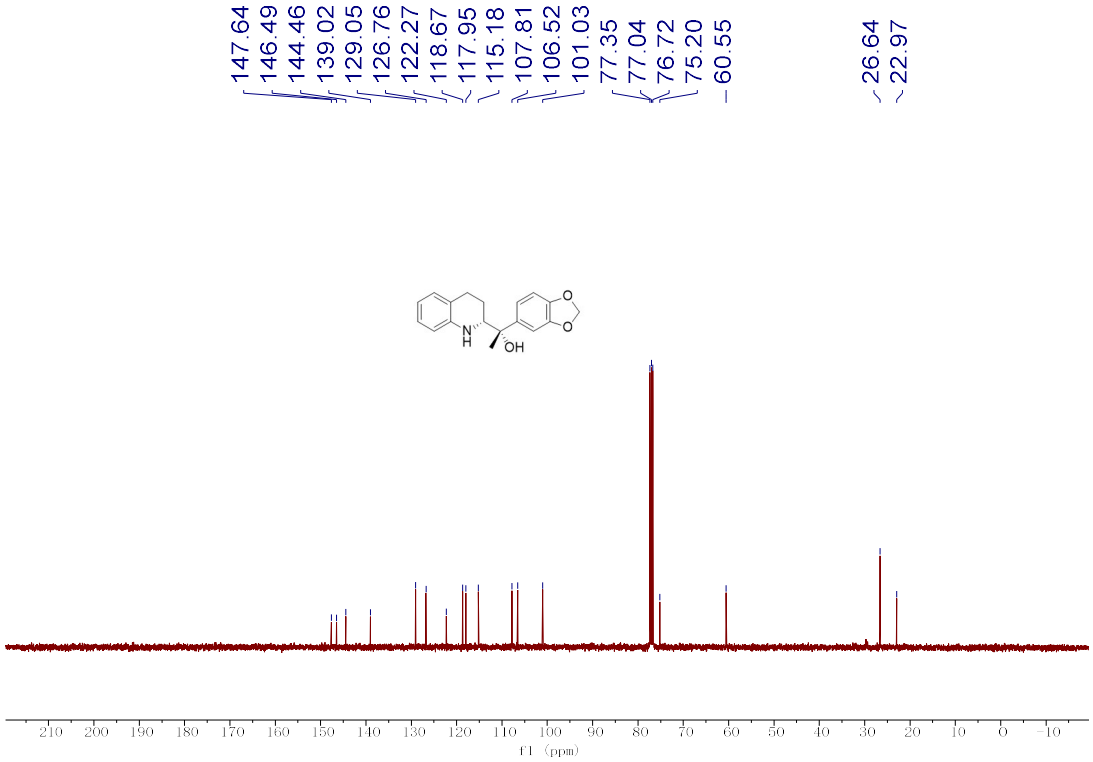
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2j**



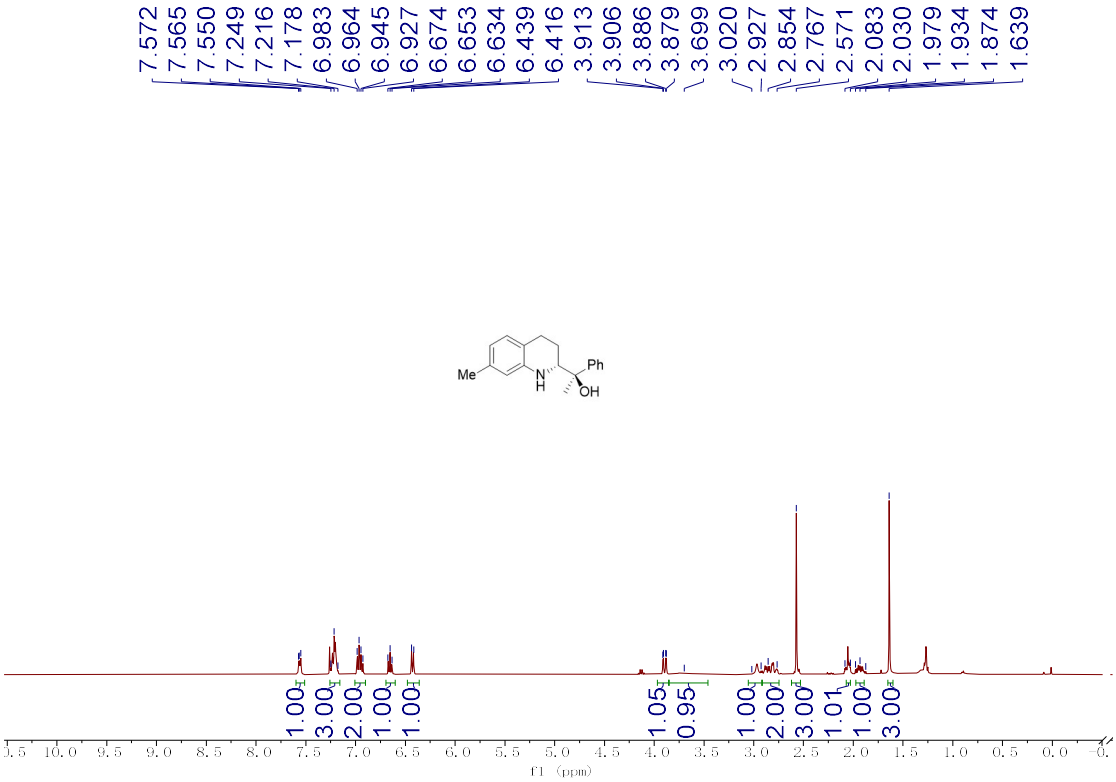
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2j**



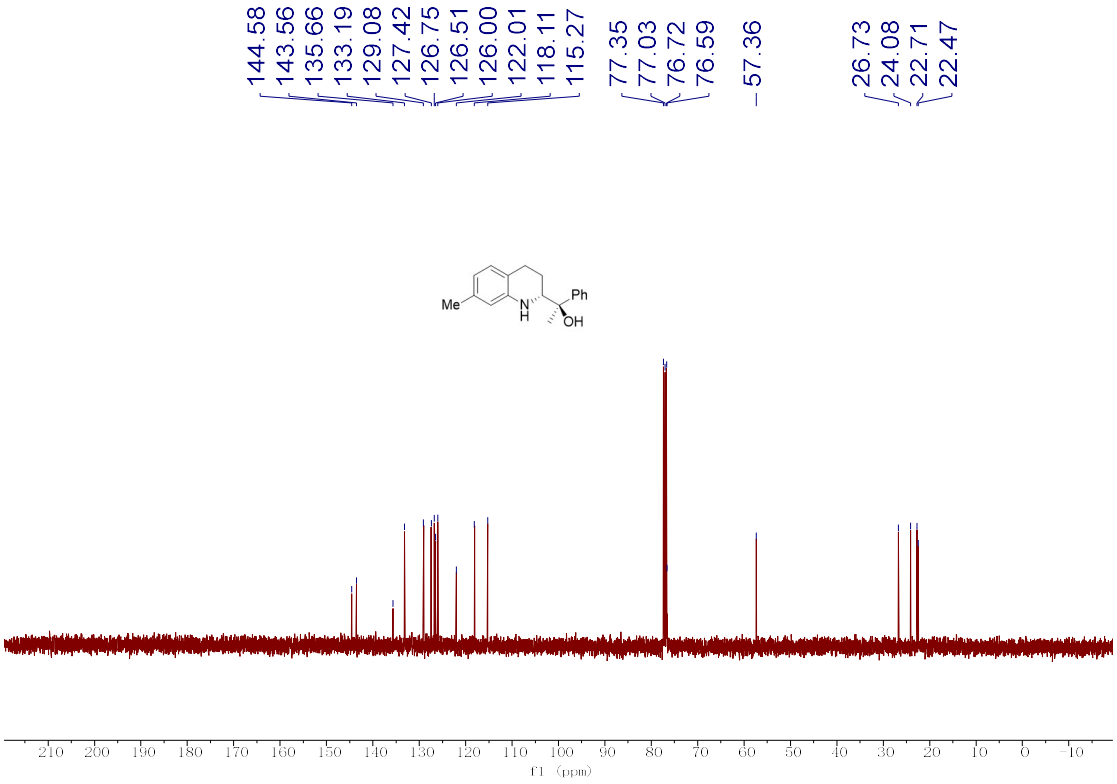
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2j**



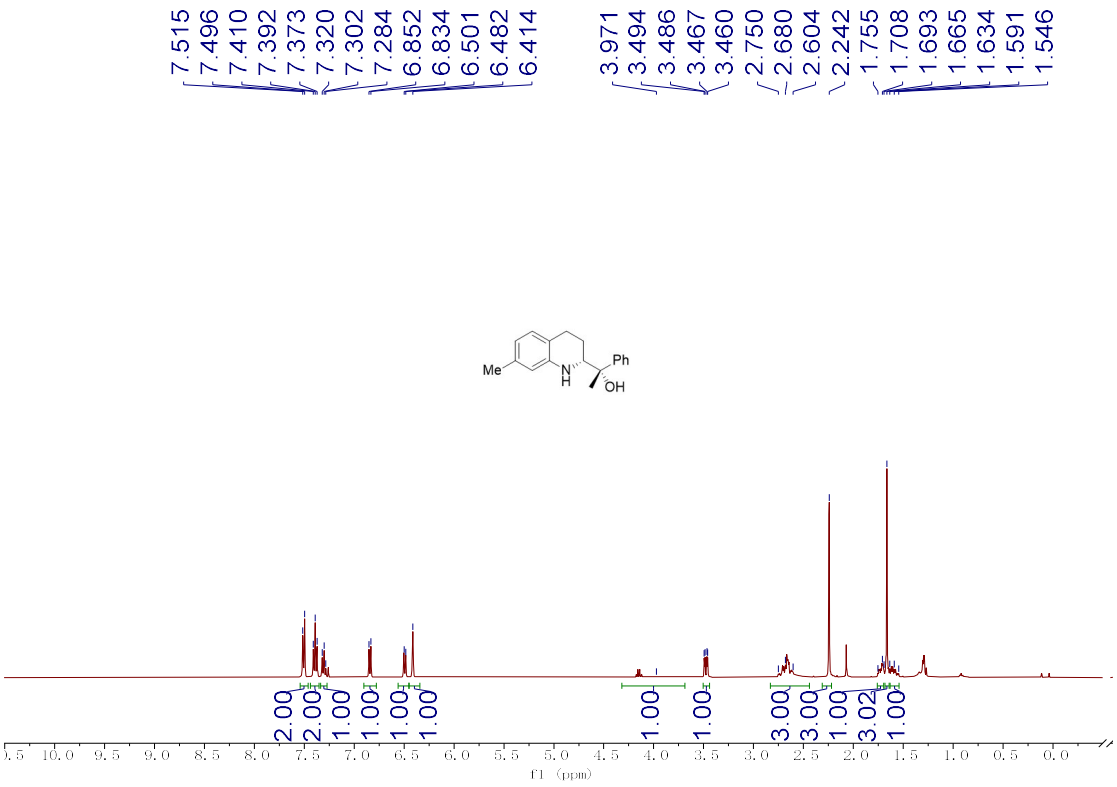
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2k**



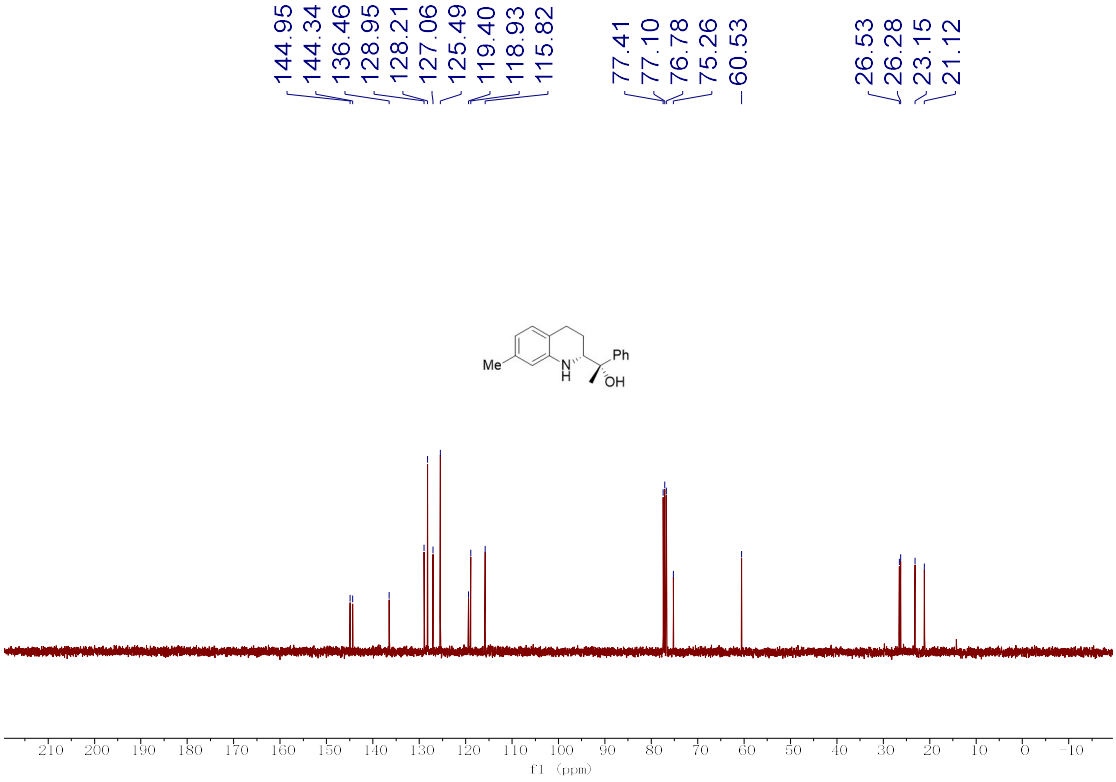
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2k**



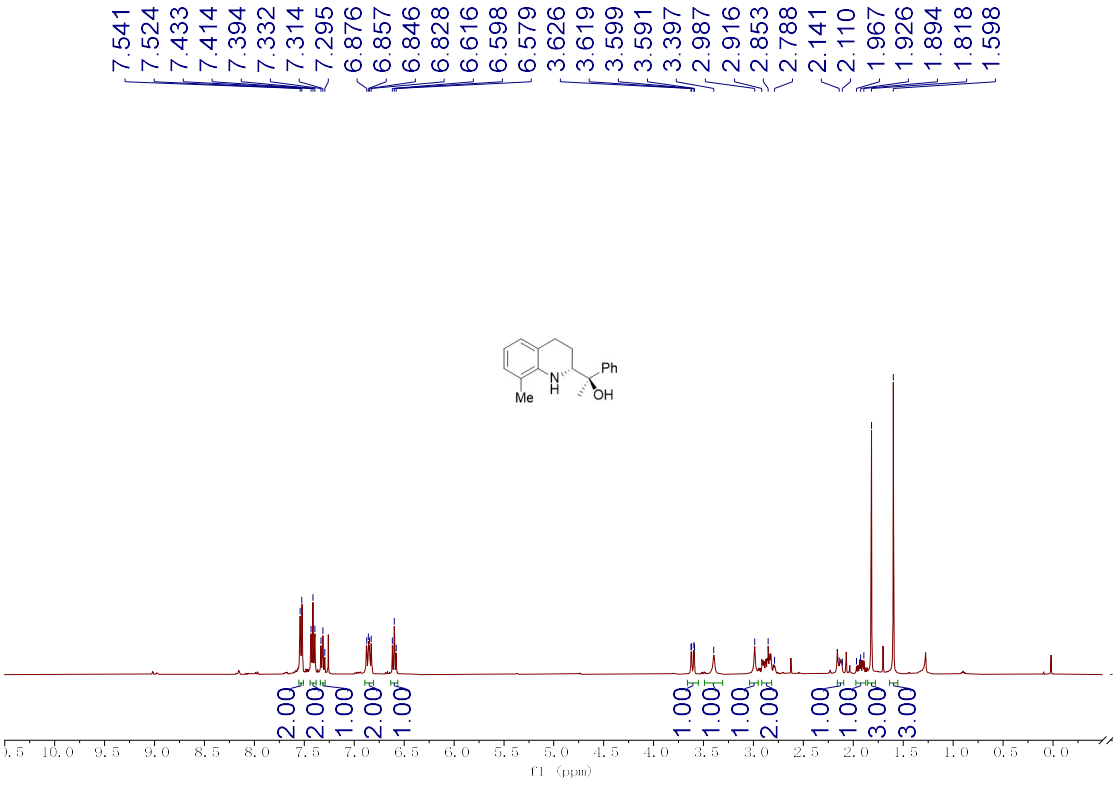
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2k**



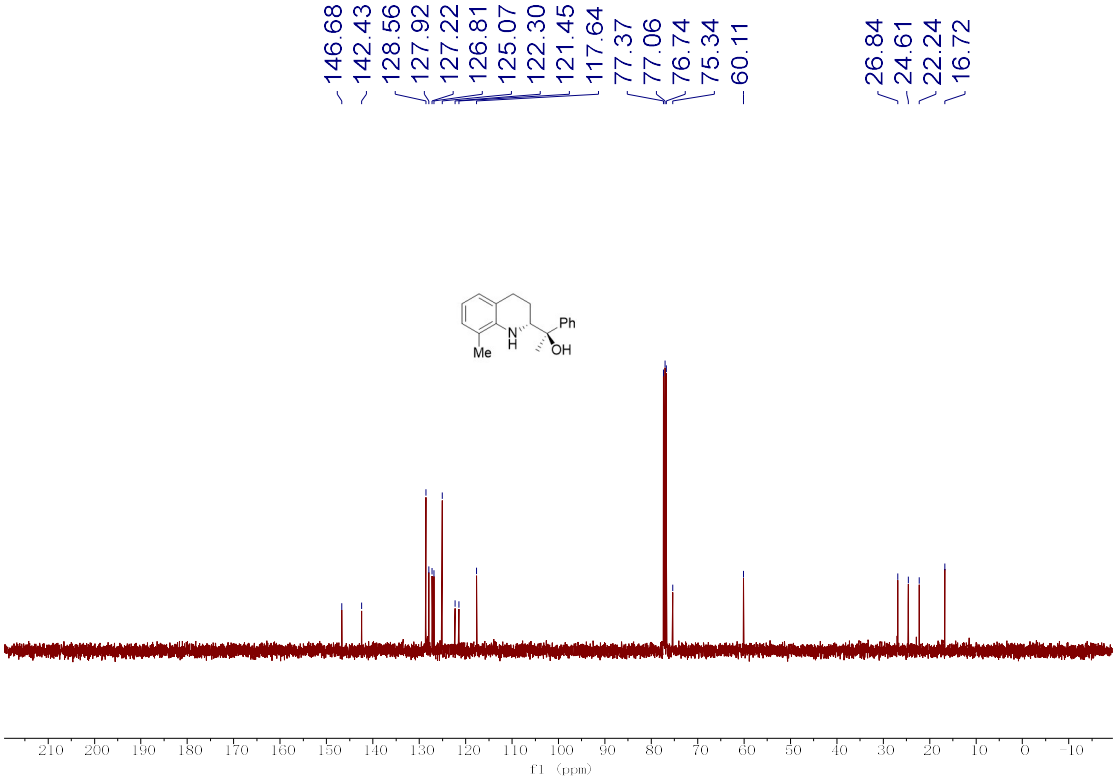
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2k**



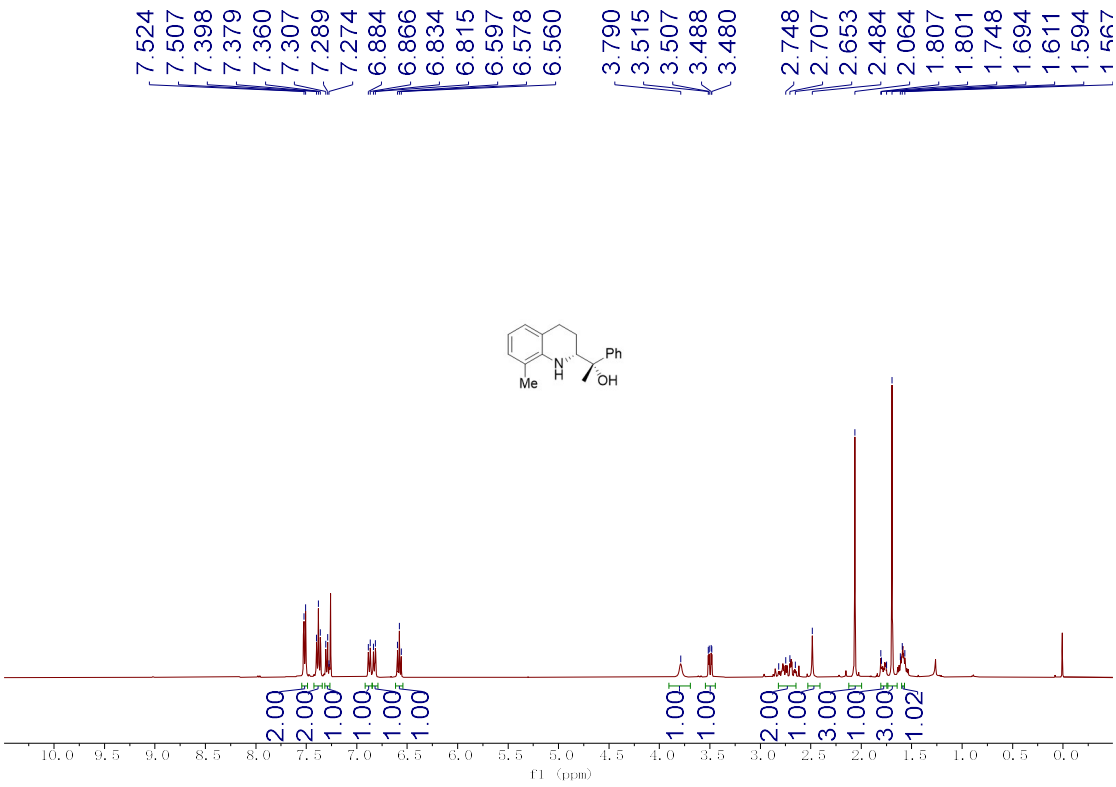
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2l**



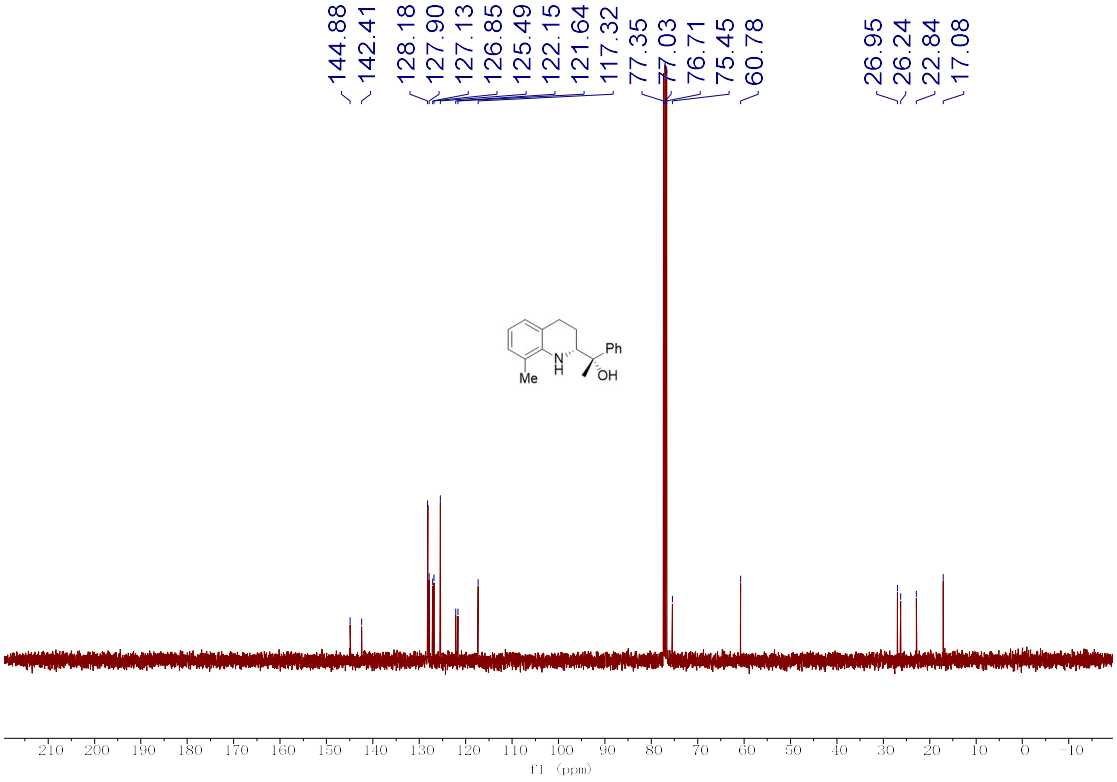
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2l**



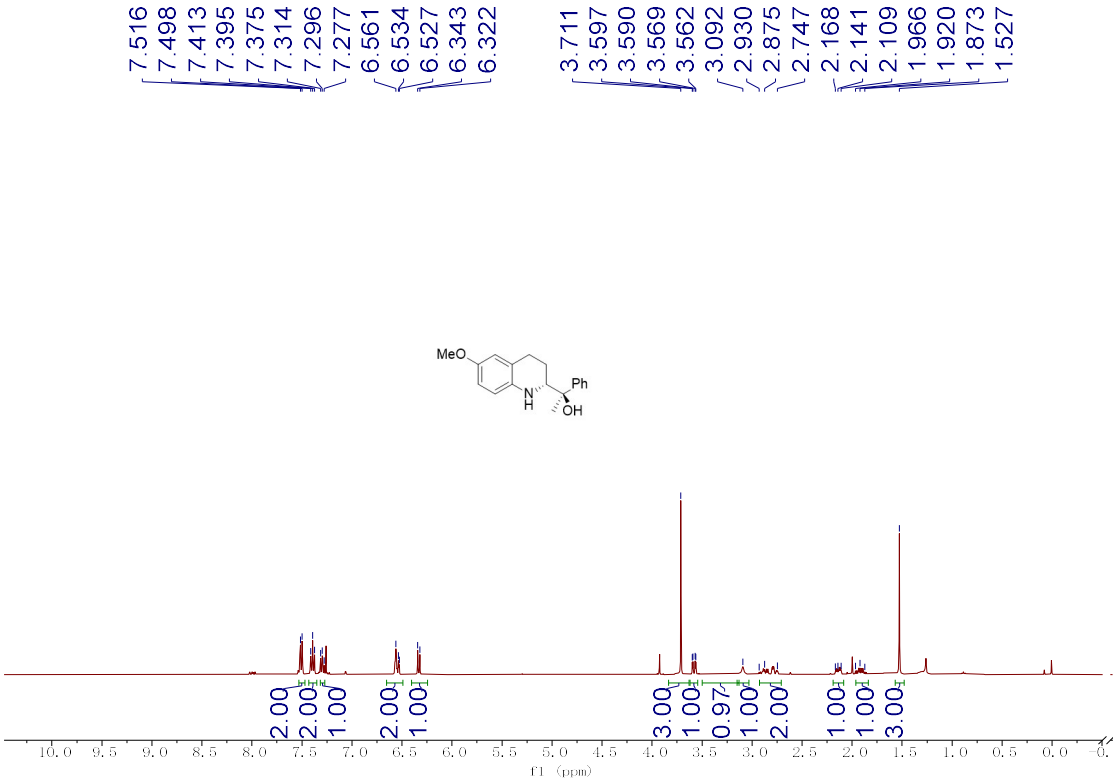
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2l**



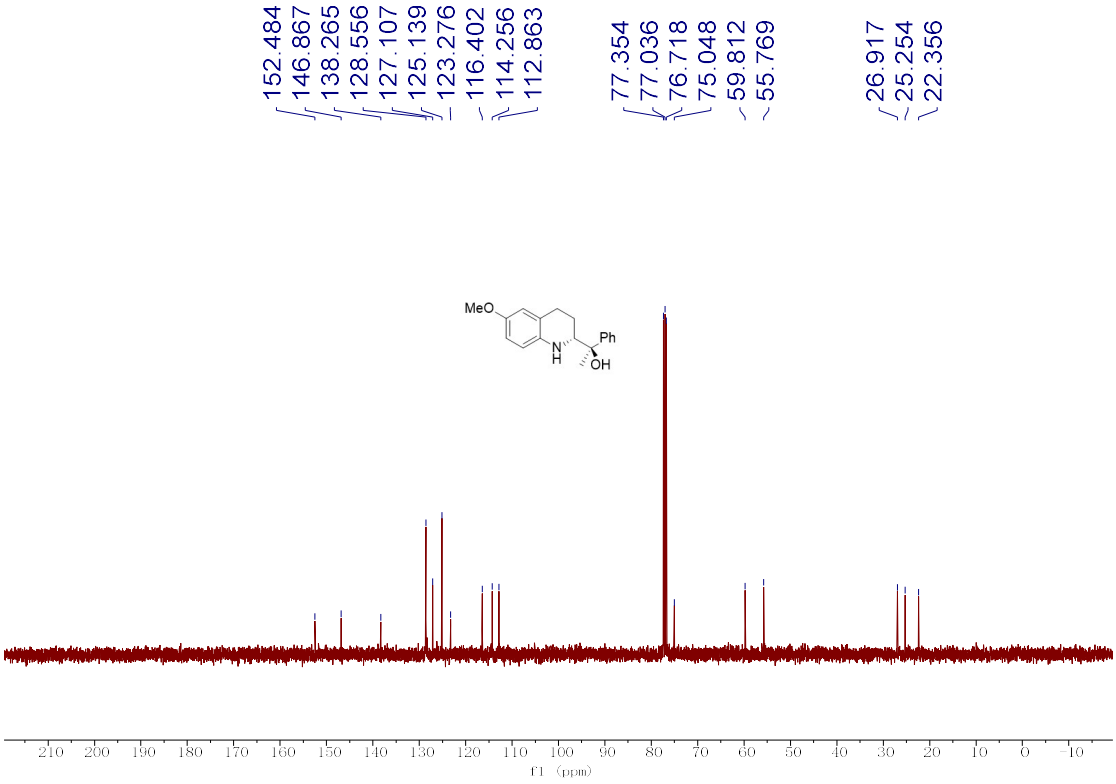
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2l**



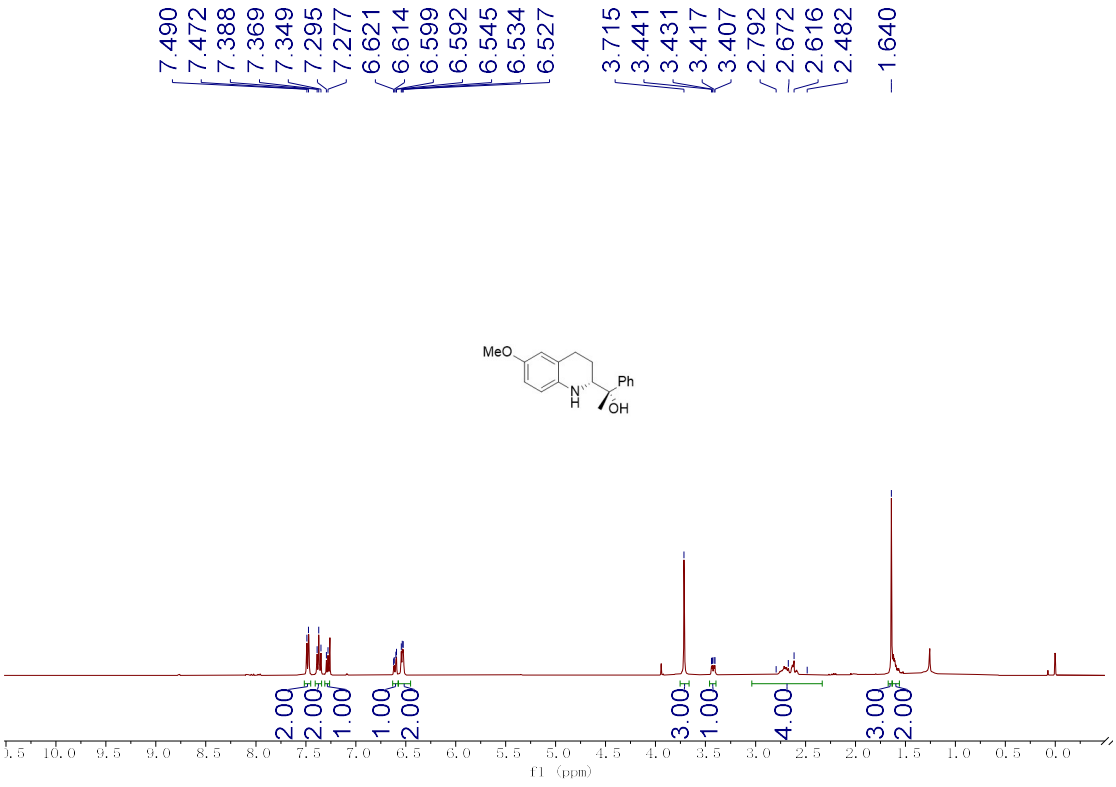
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2m**



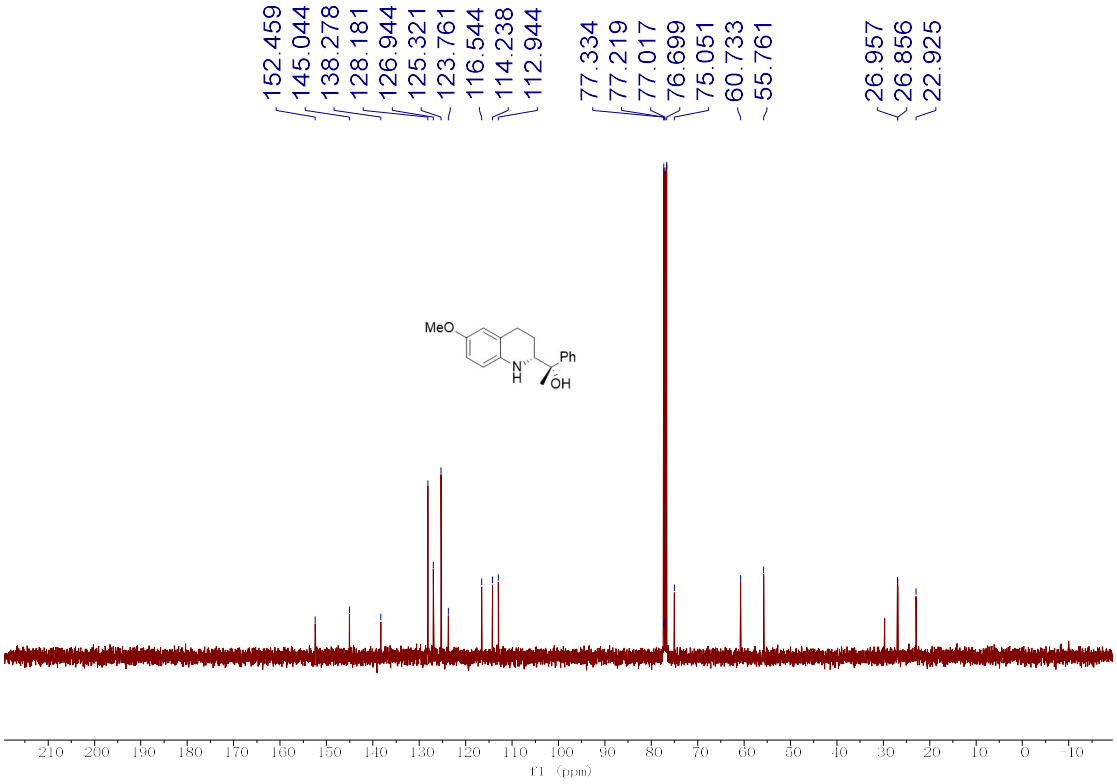
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2m**



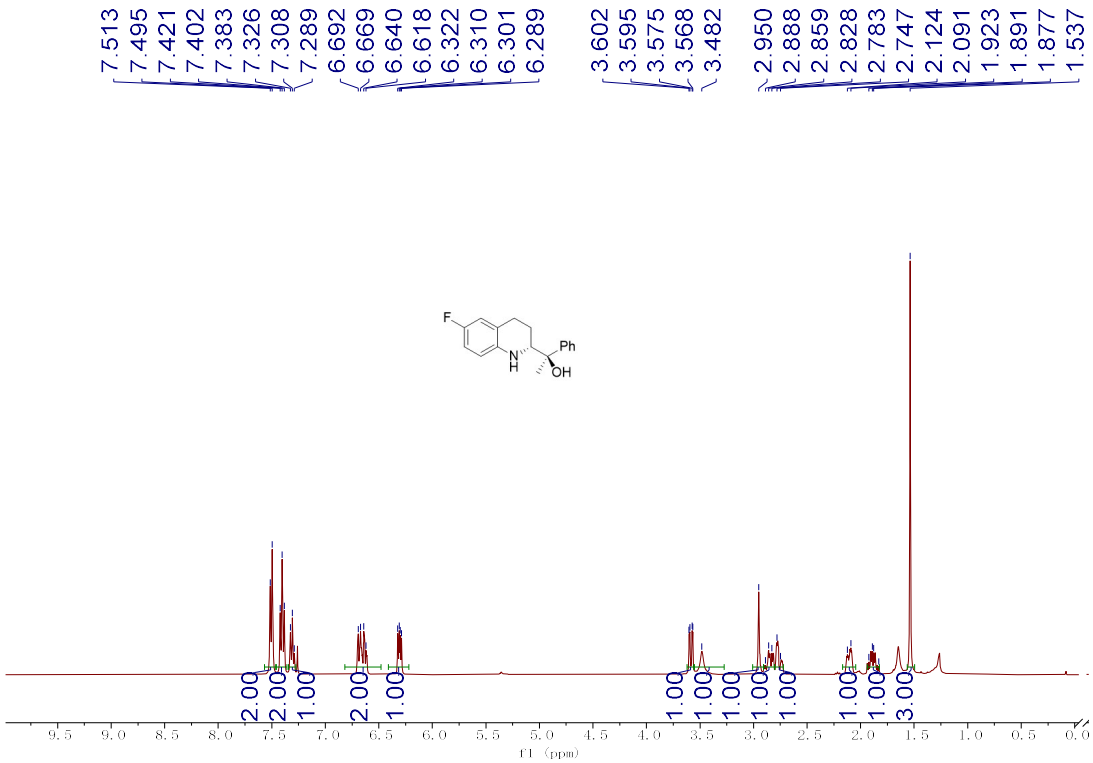
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2m**



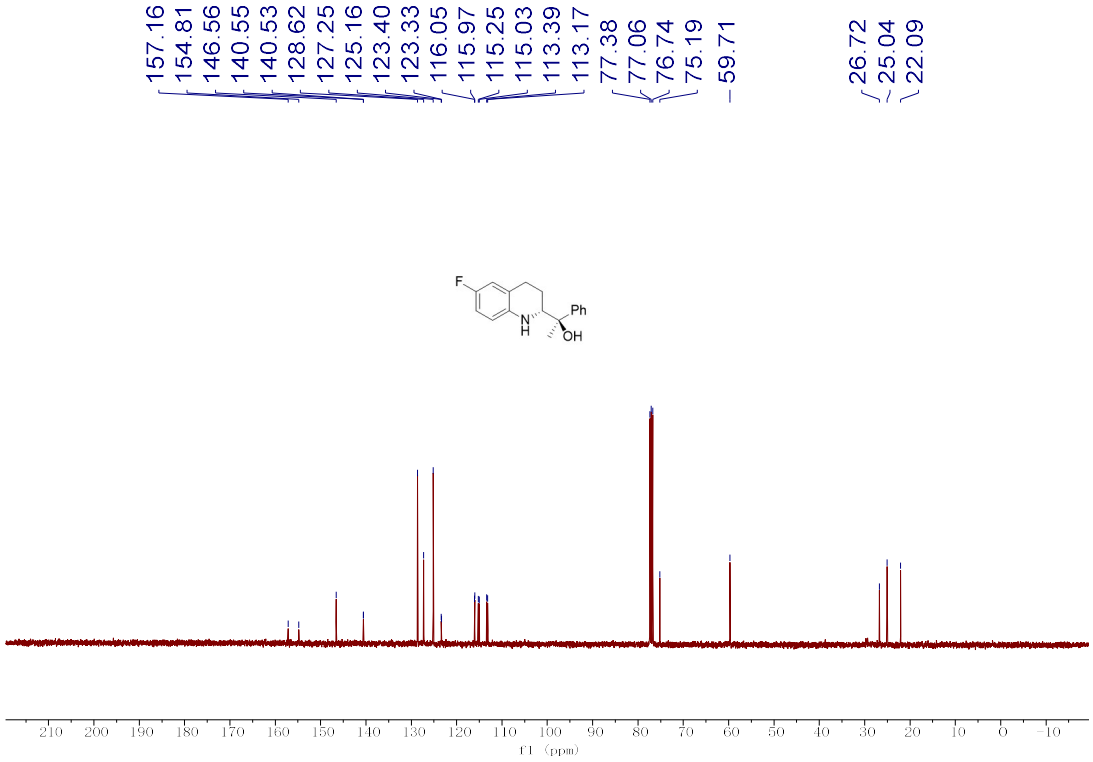
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2m**



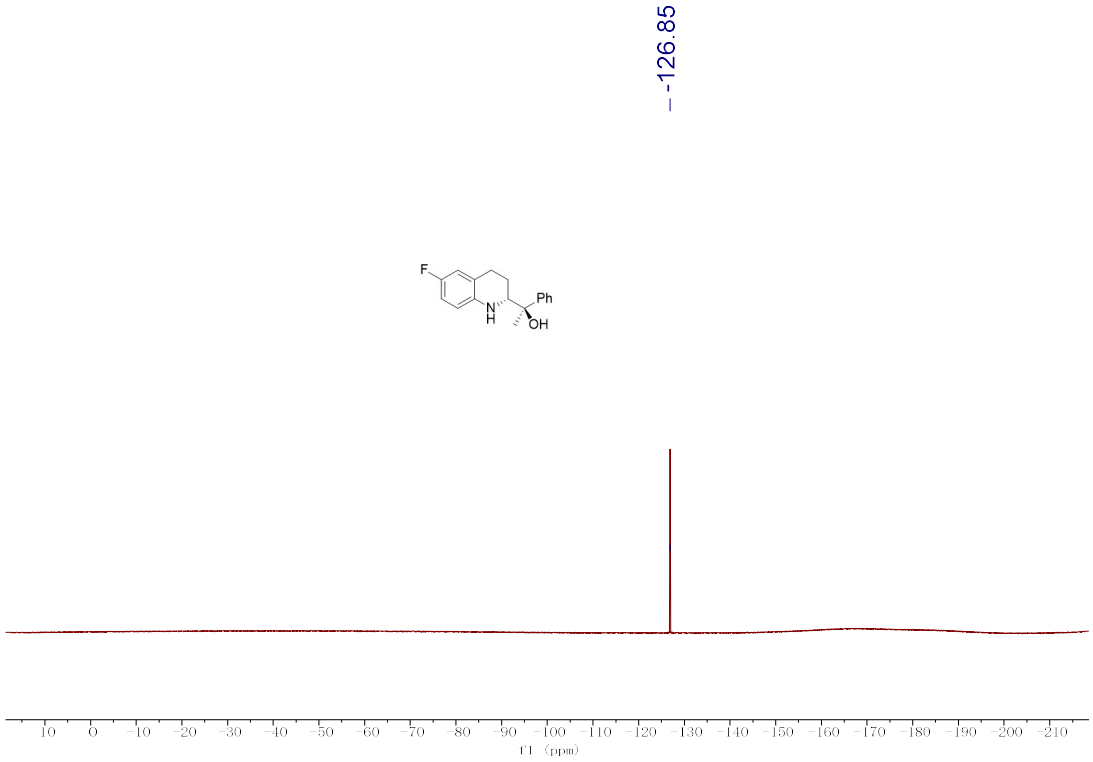
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2n**



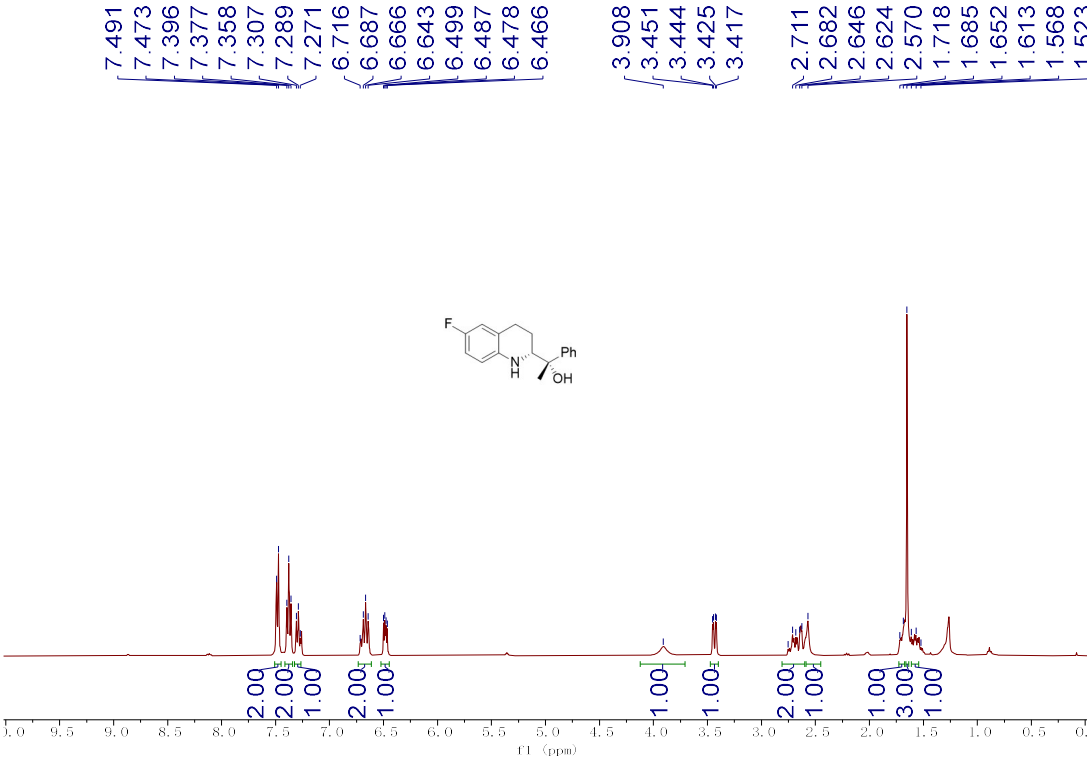
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2n**



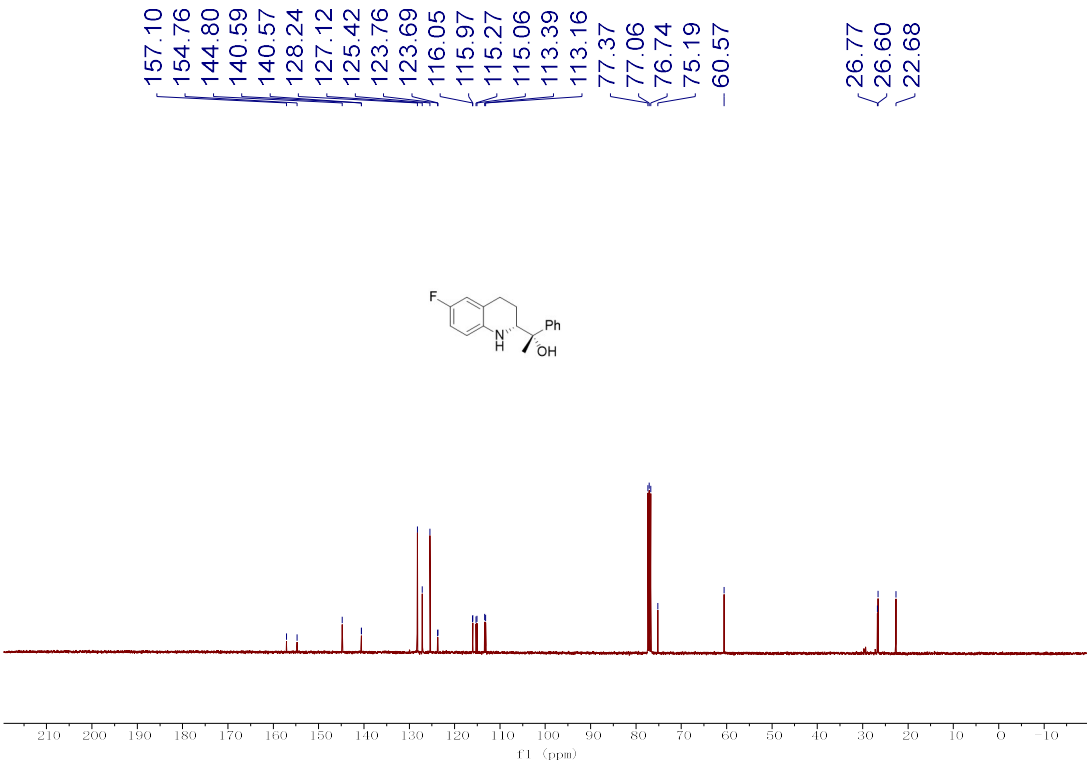
^{19}F {1H} NMR (376 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2n**



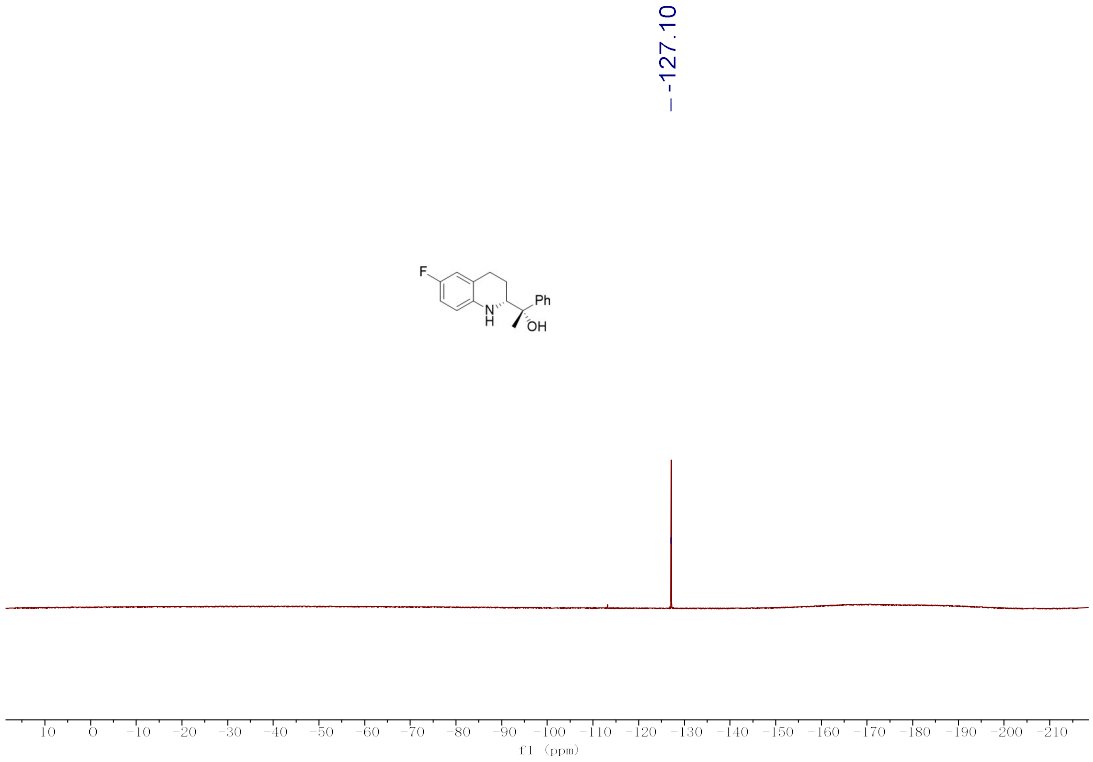
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2n**



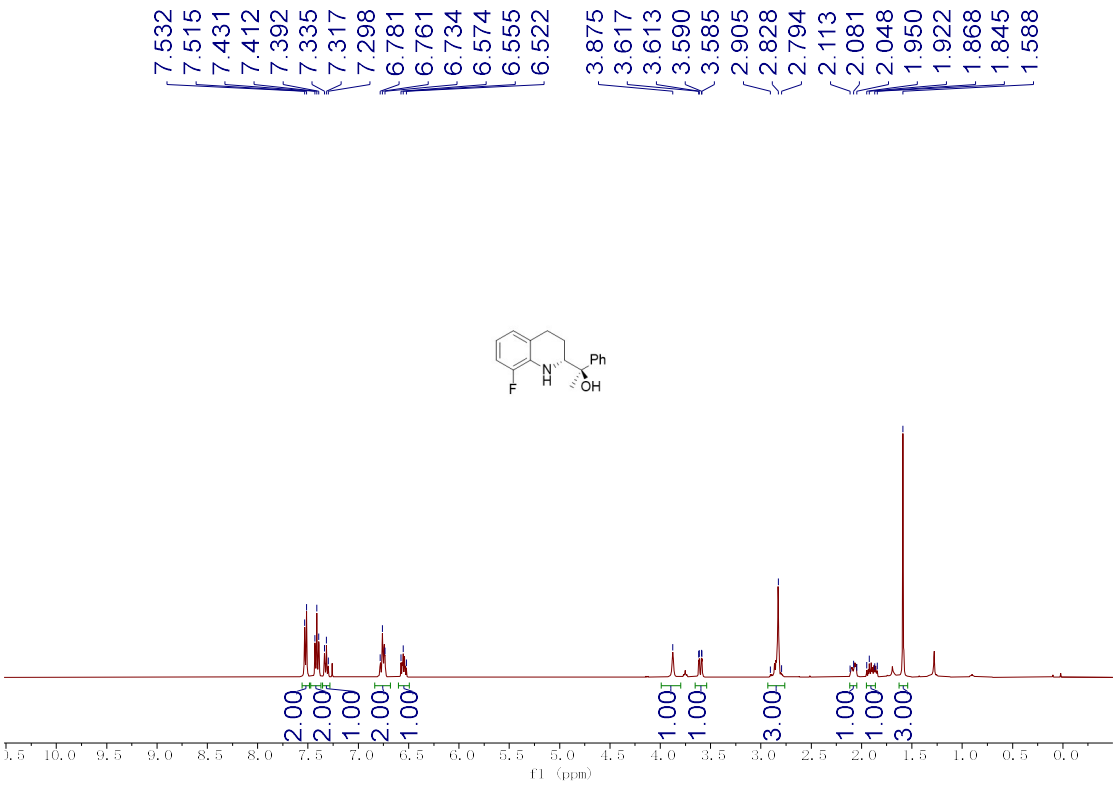
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2n**



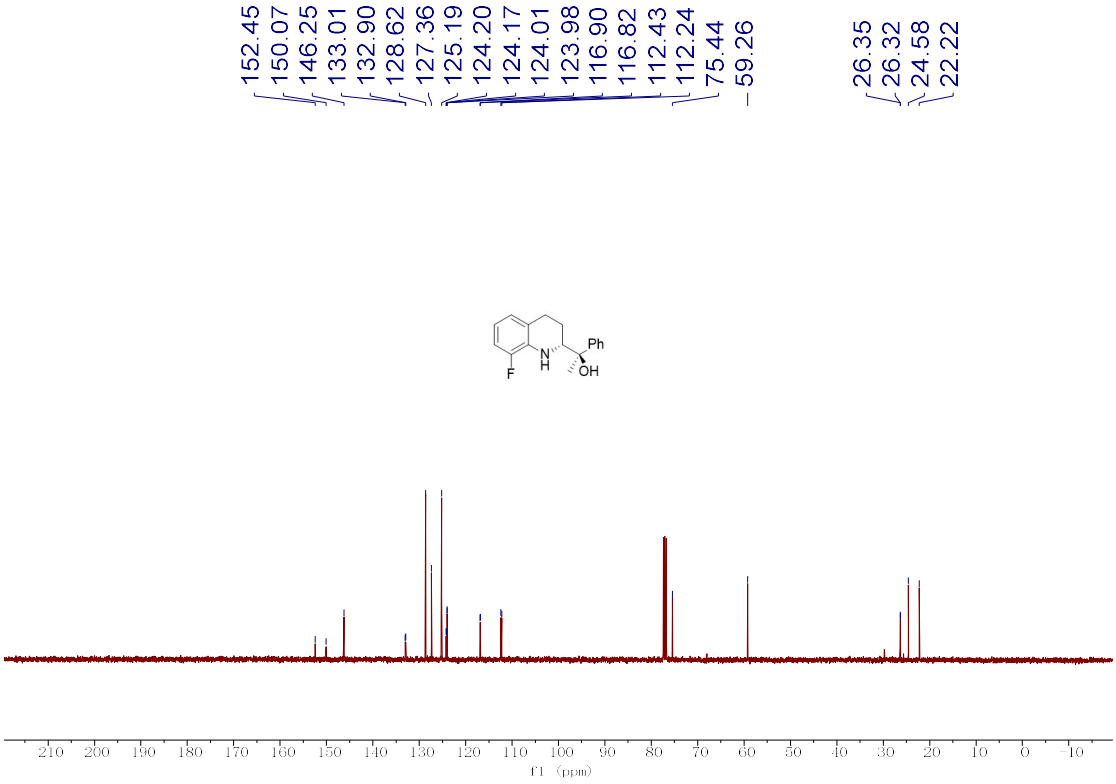
^{19}F {1H} NMR (376 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2n**



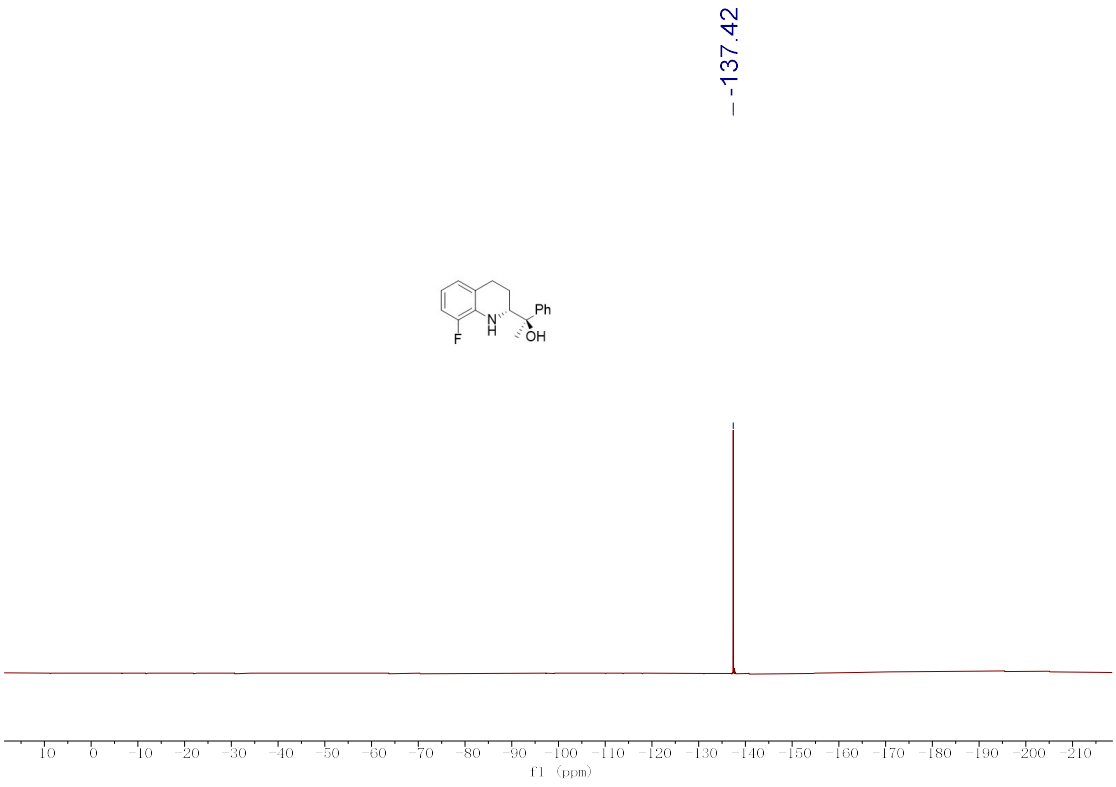
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2o**



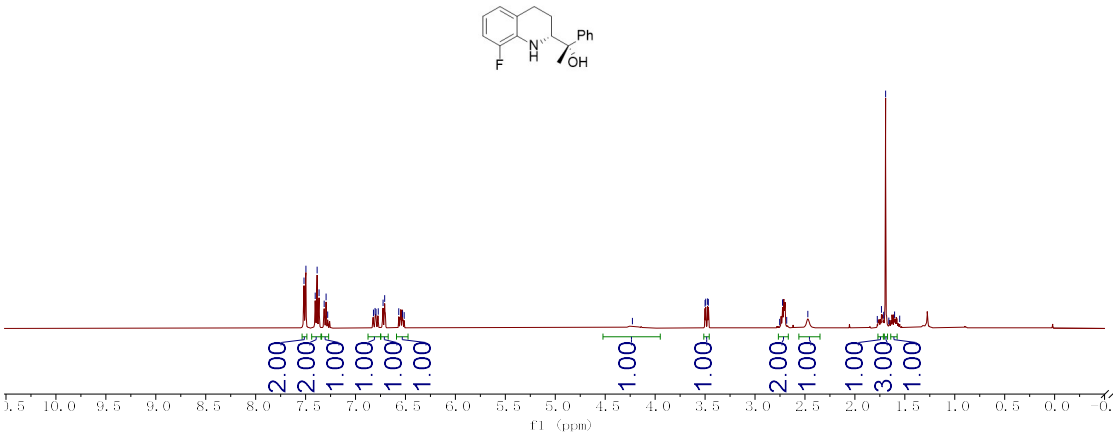
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2o**



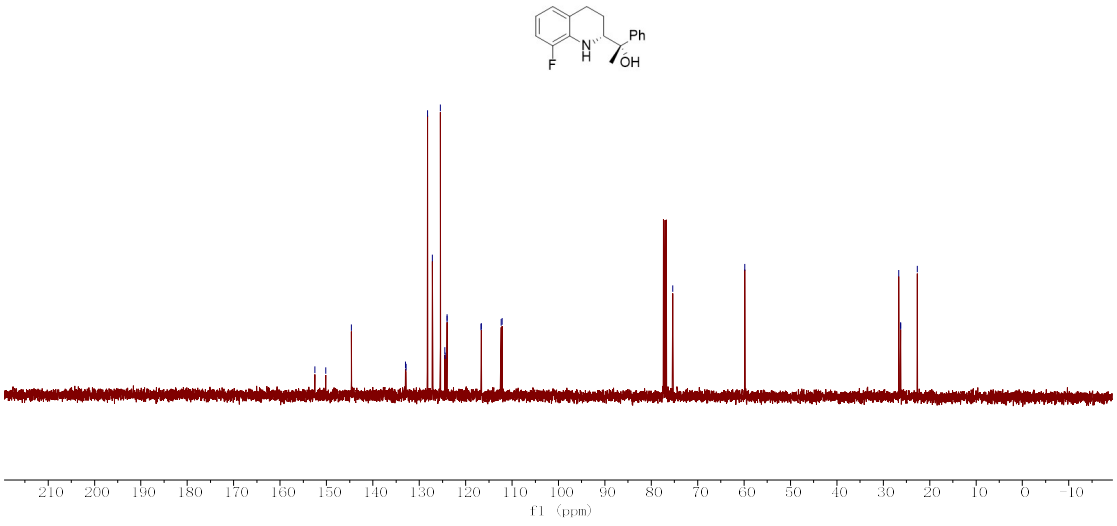
^{19}F {1H} NMR (376 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2o**



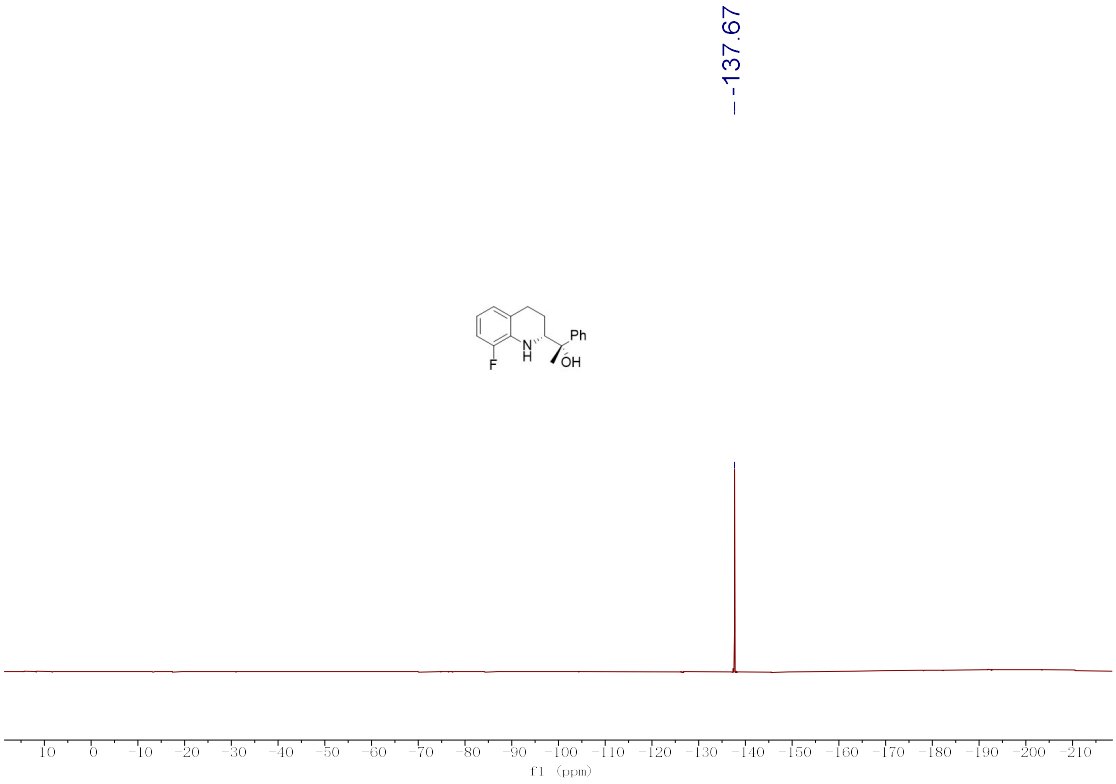
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2o**



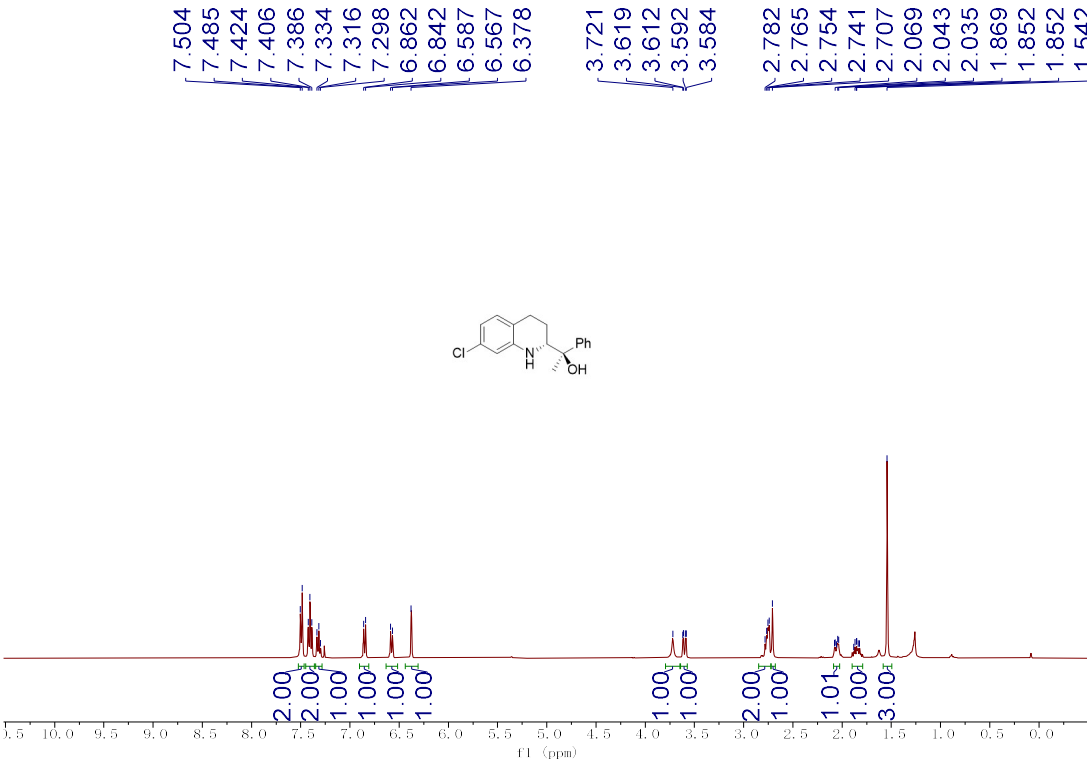
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2o**



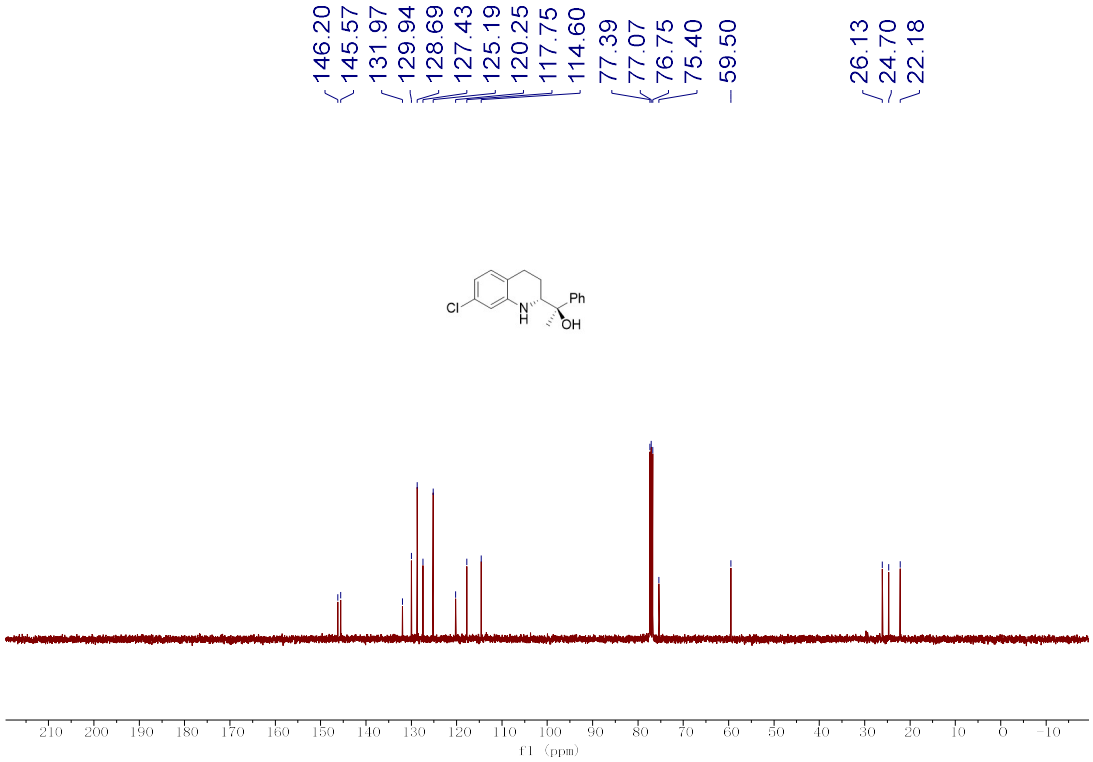
^{19}F {1H} NMR (376 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2o**



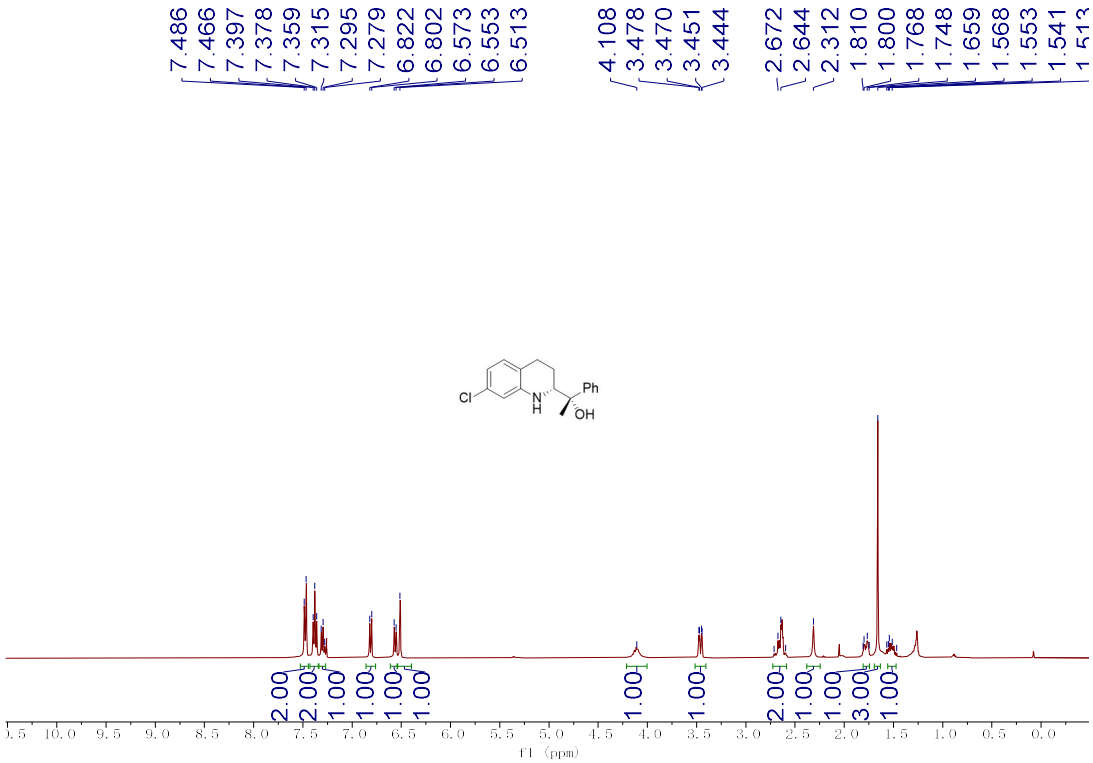
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2p**



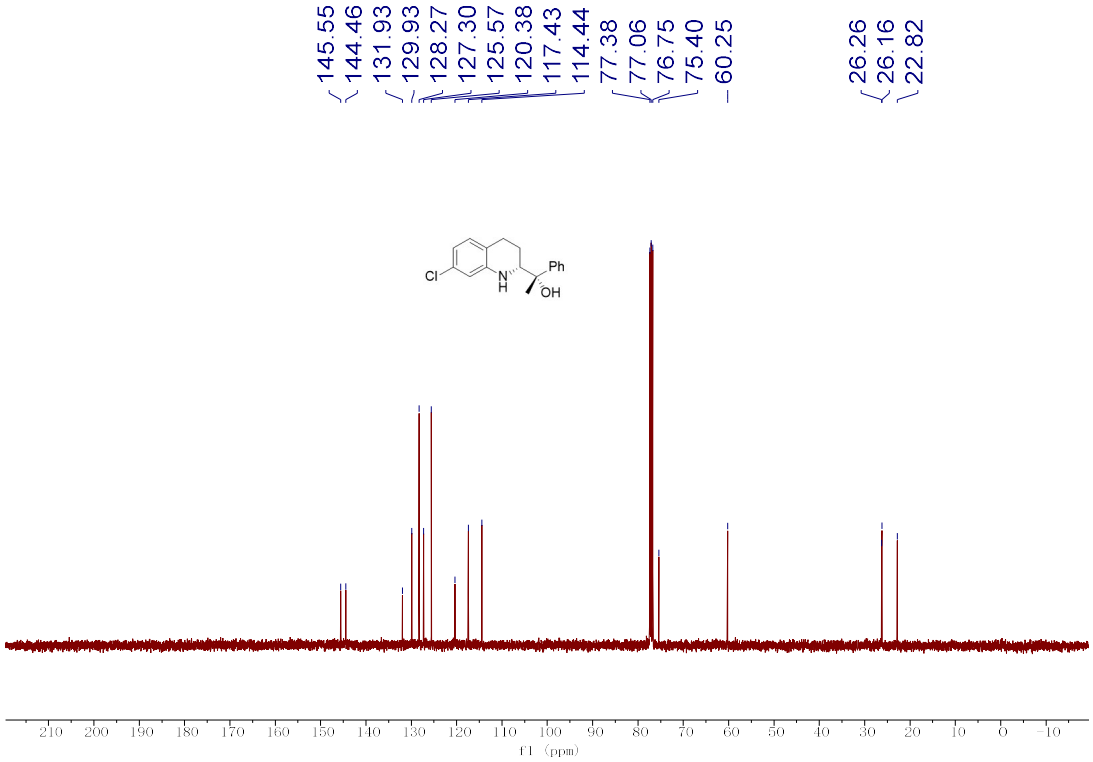
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2p**



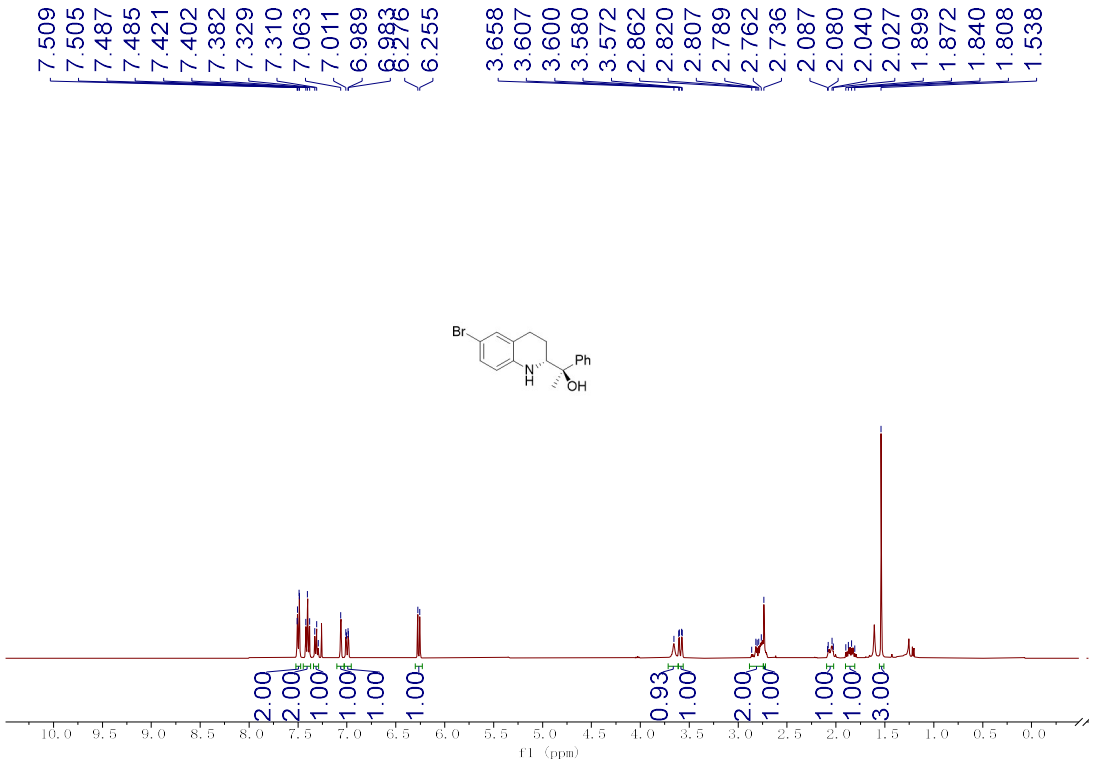
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2p**



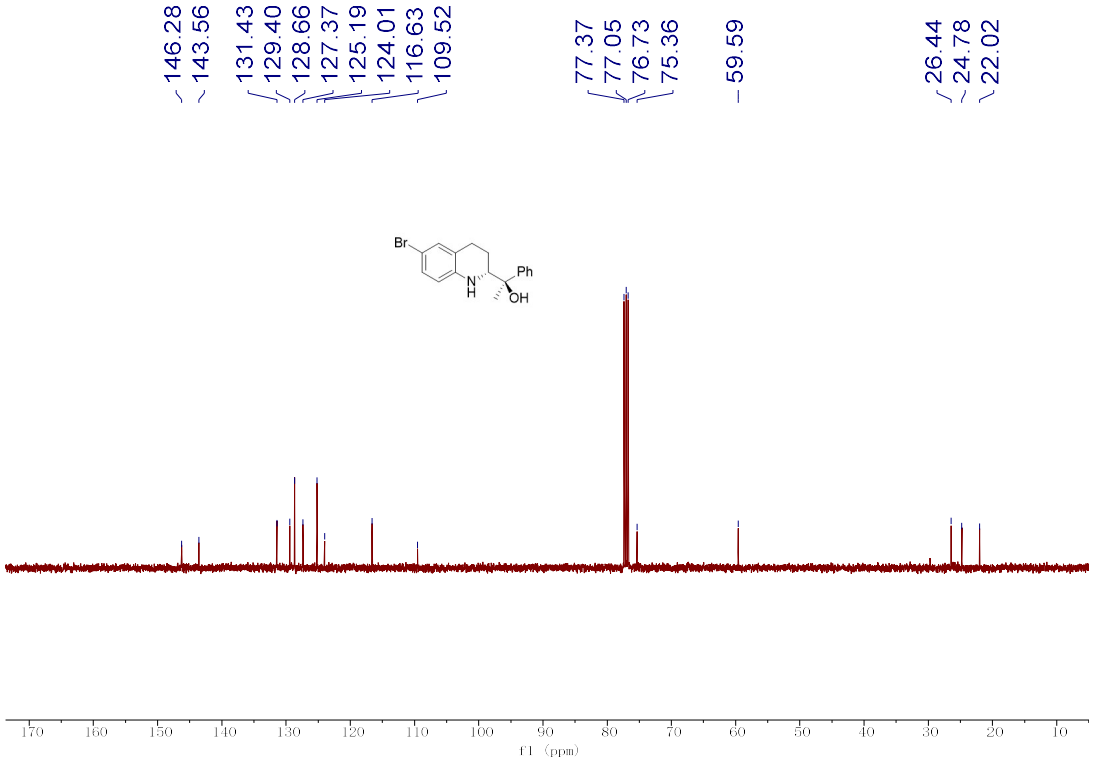
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2p**



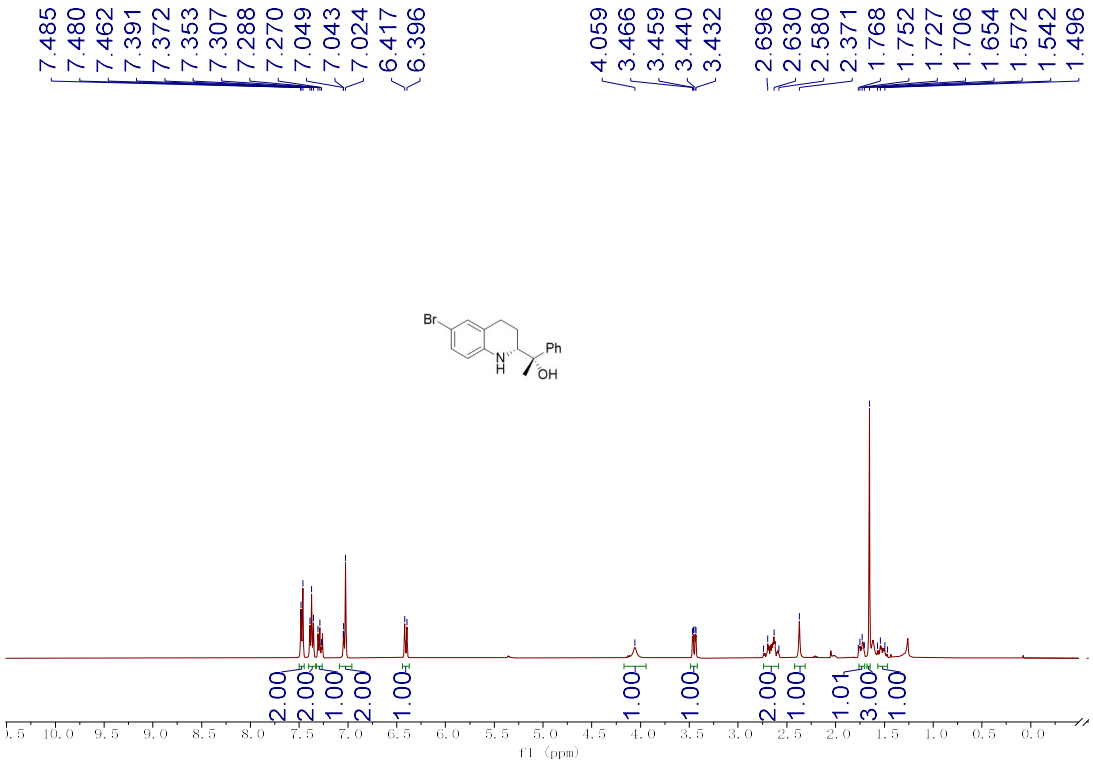
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2q**



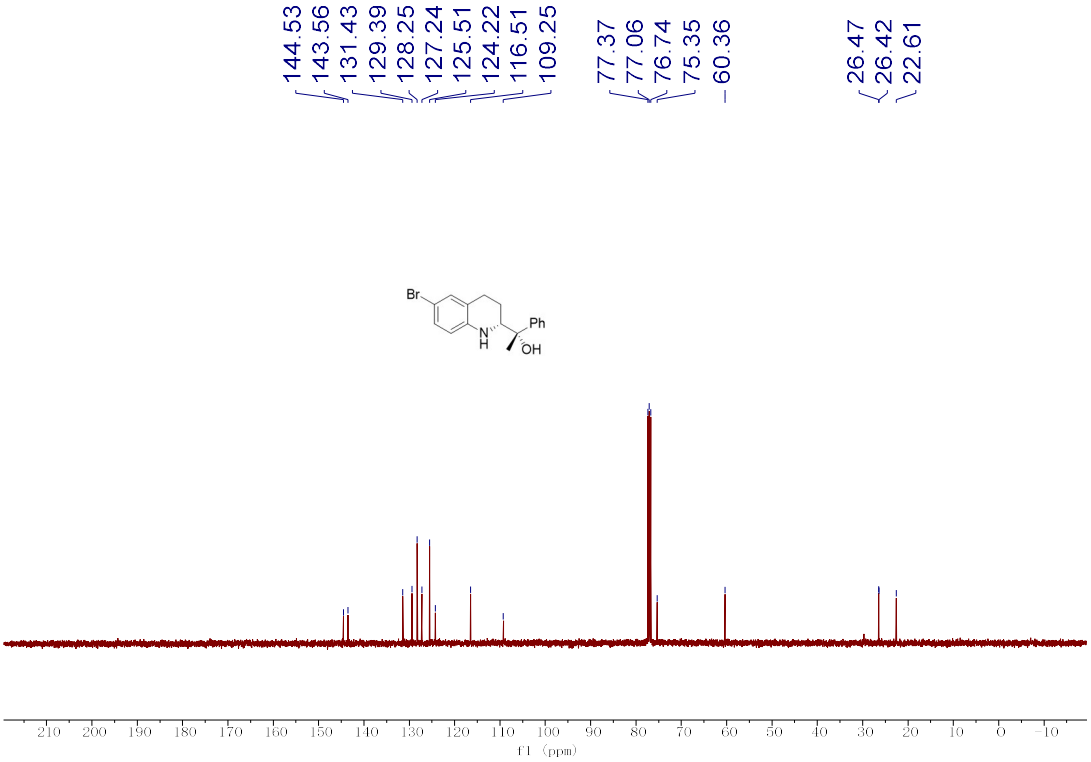
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R,R*)-**2q**



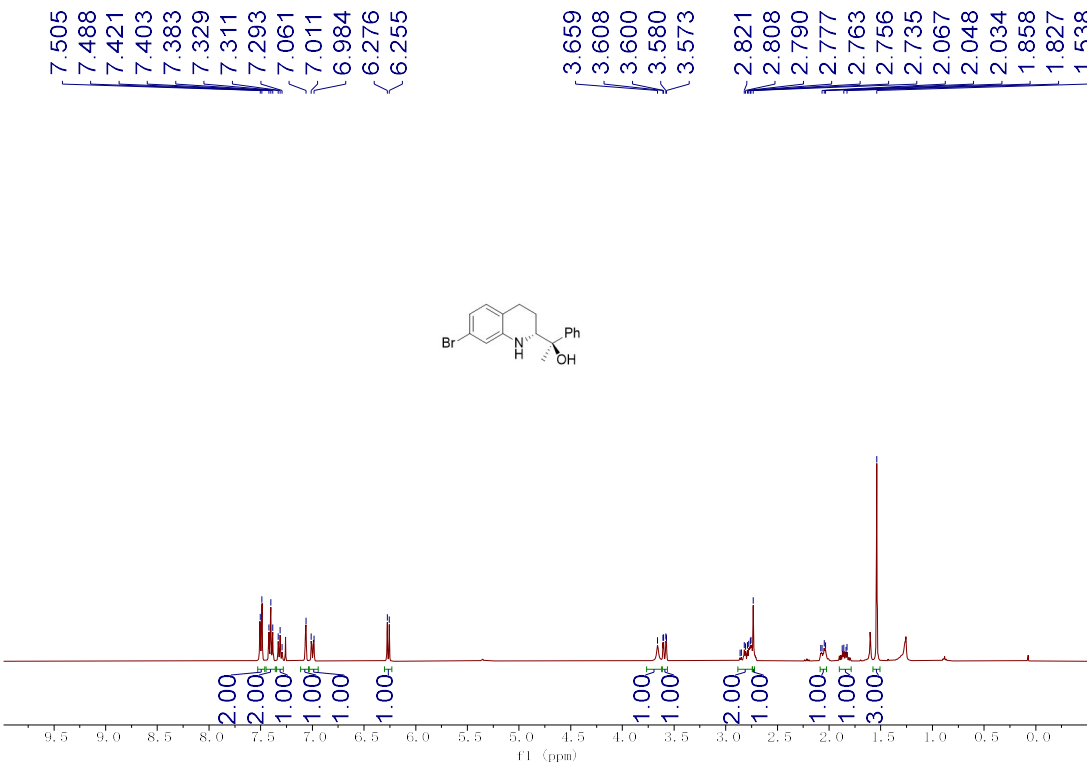
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S,R*)-**2q**



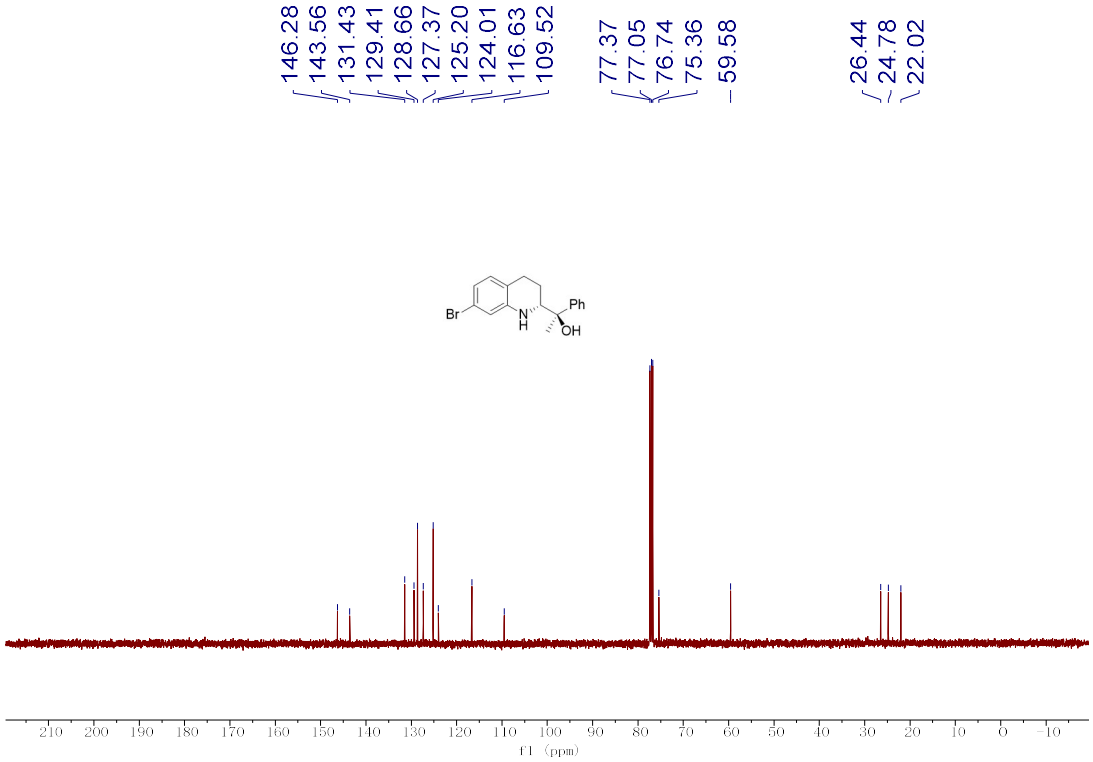
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2q**



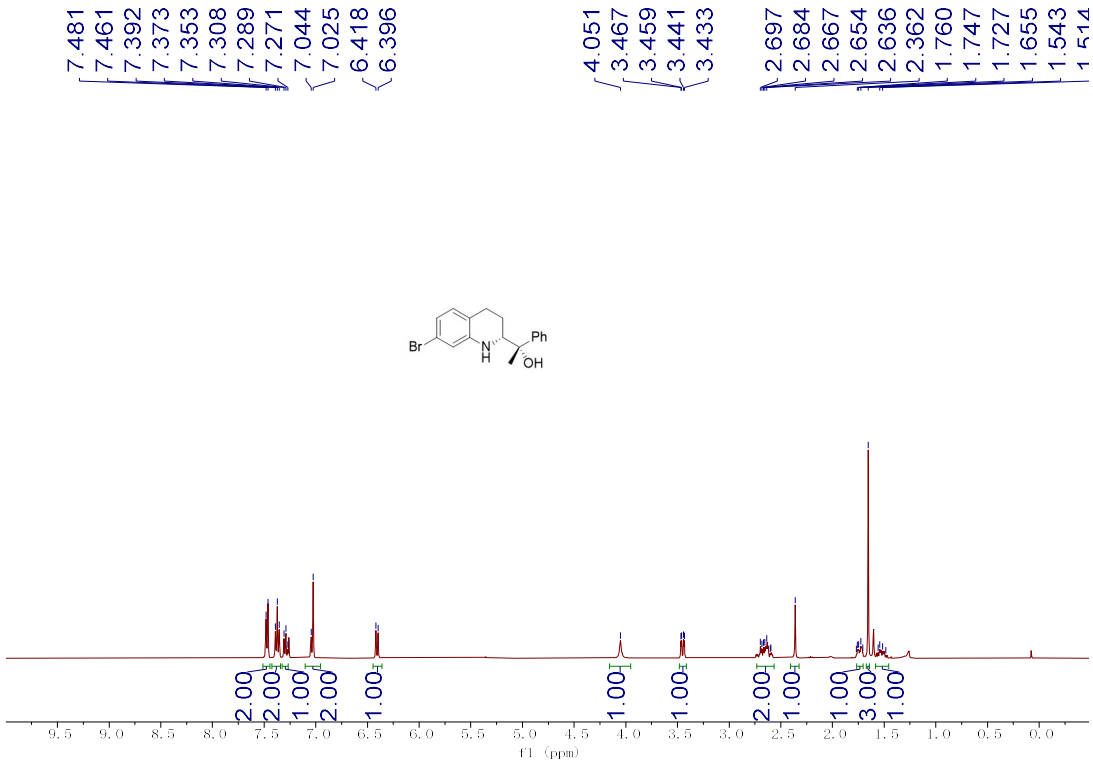
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2r**



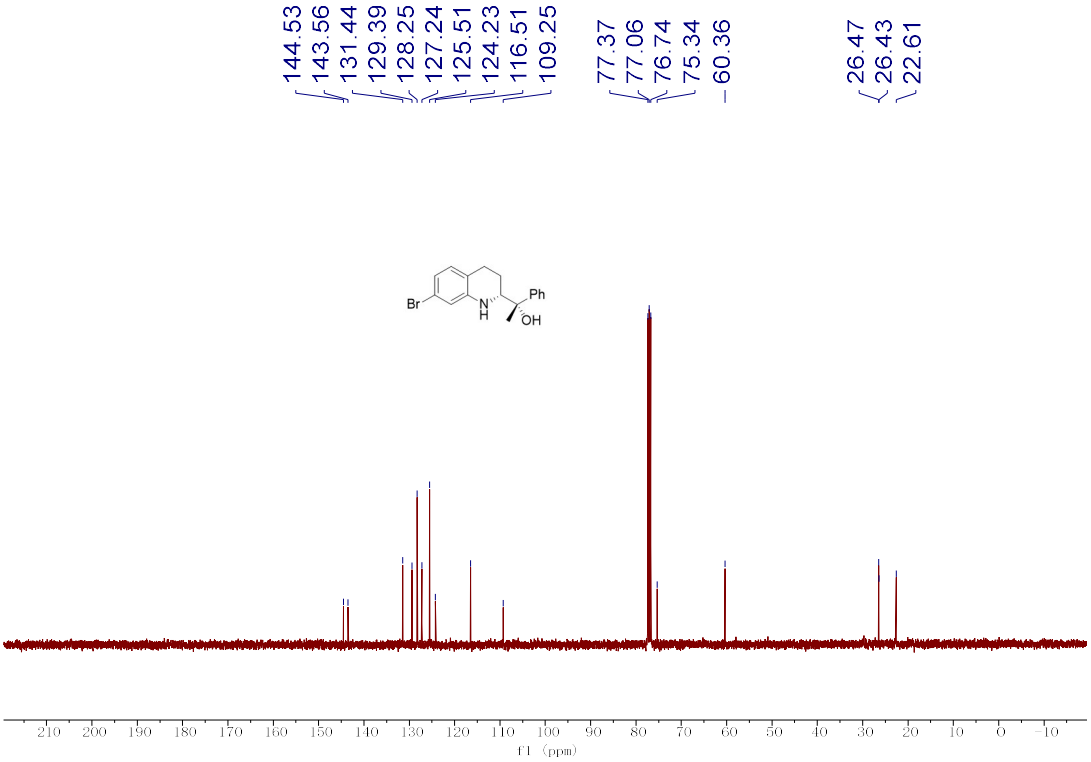
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2r**



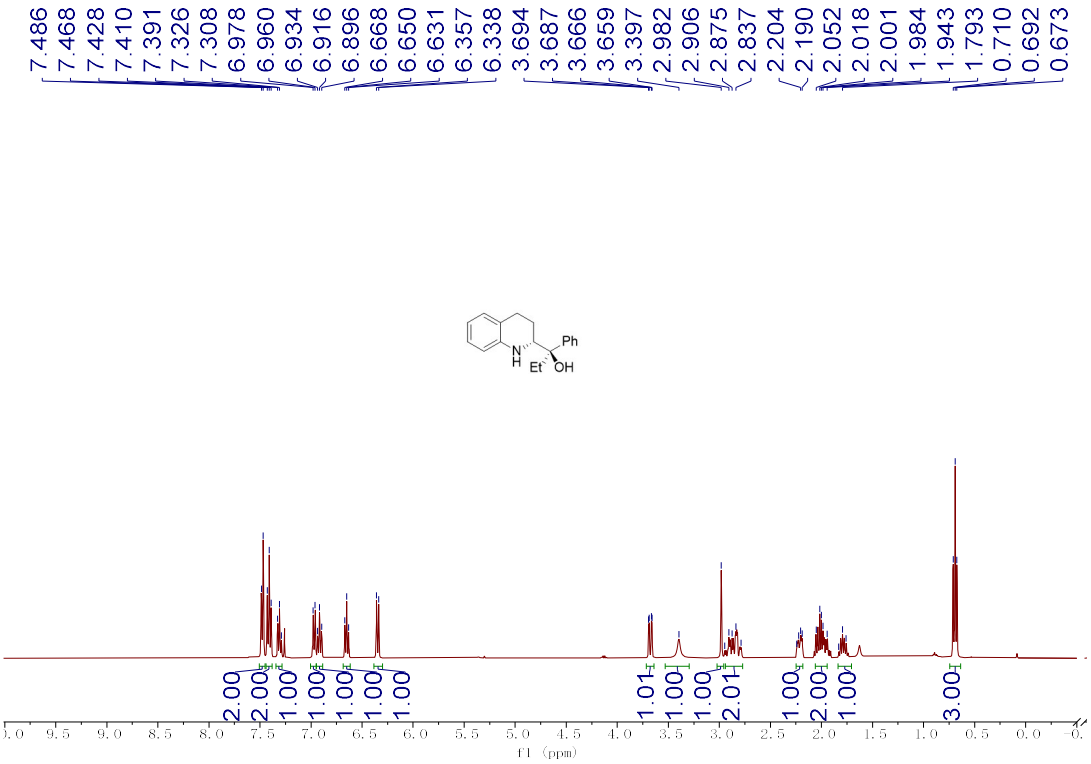
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2r**



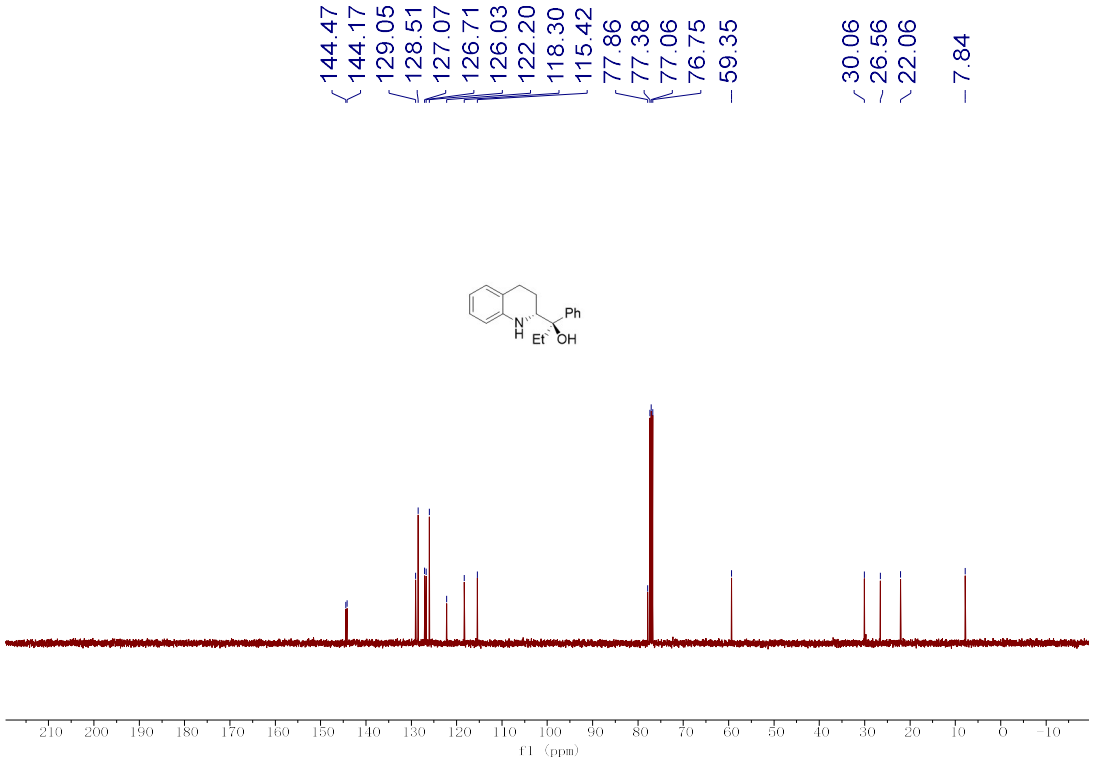
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2r**



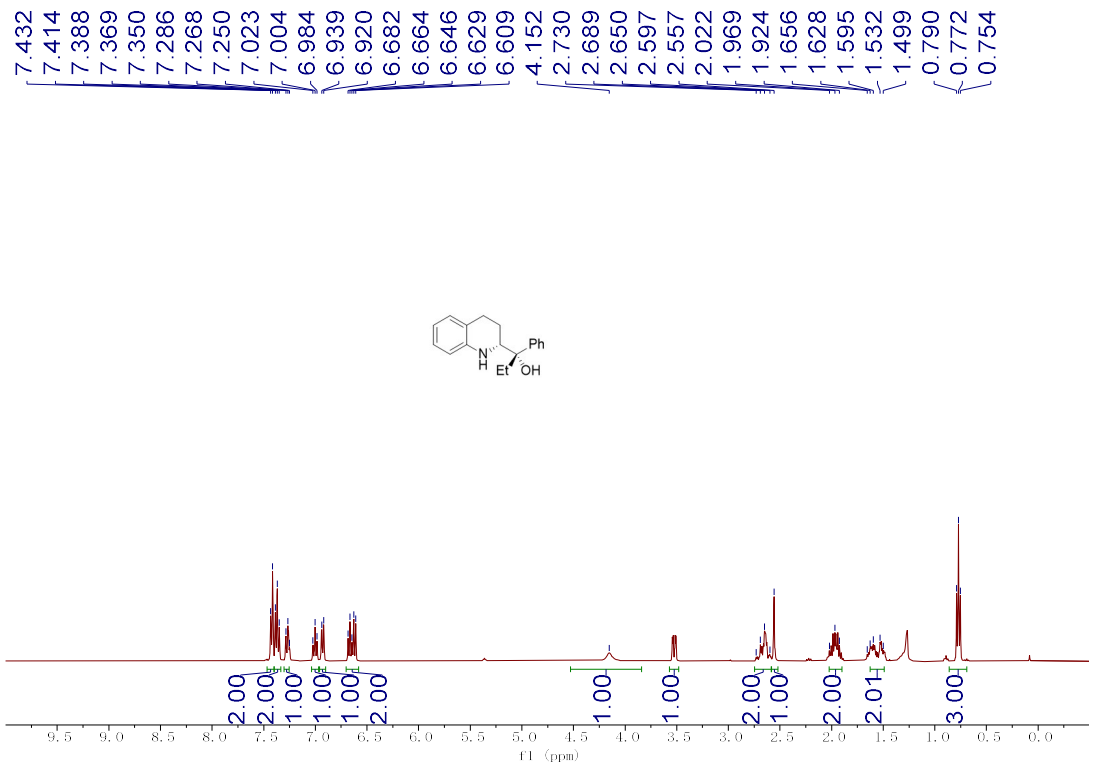
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2s**



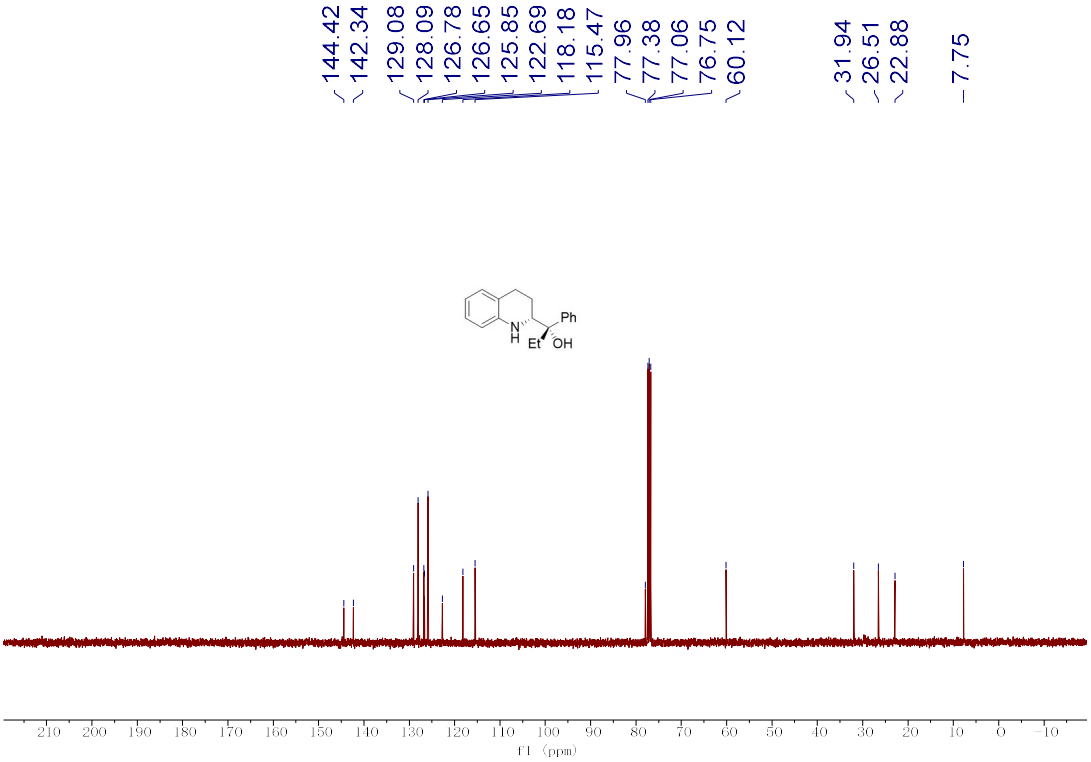
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2s**



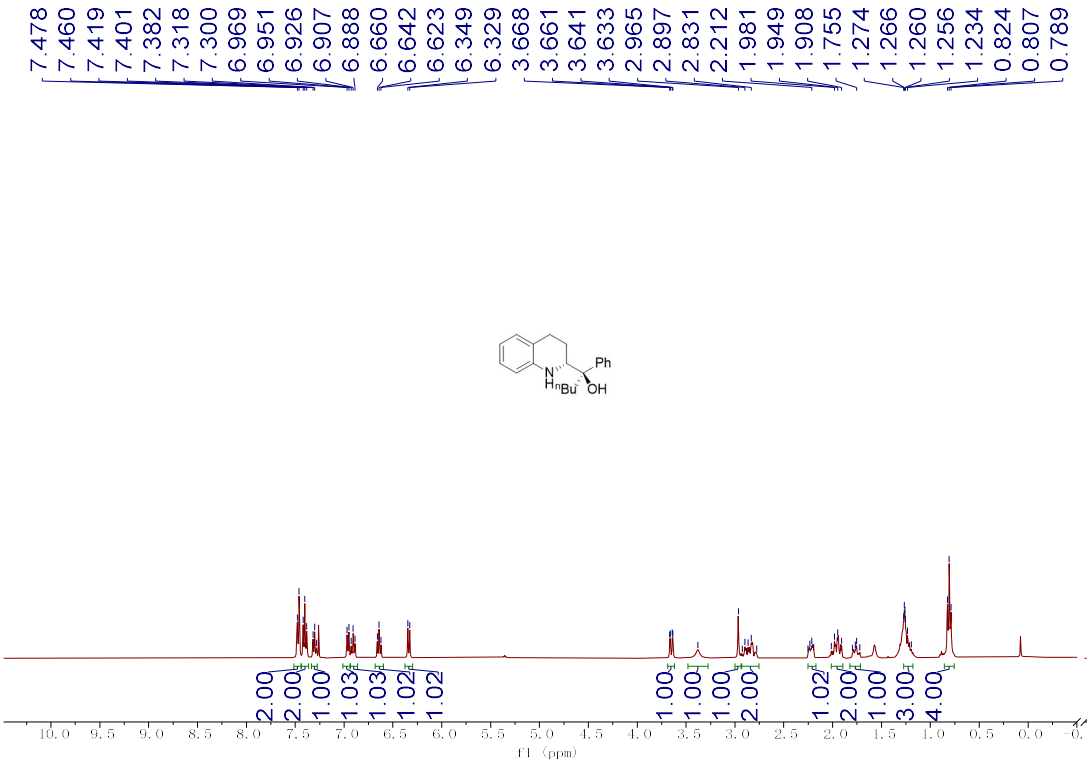
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2s**



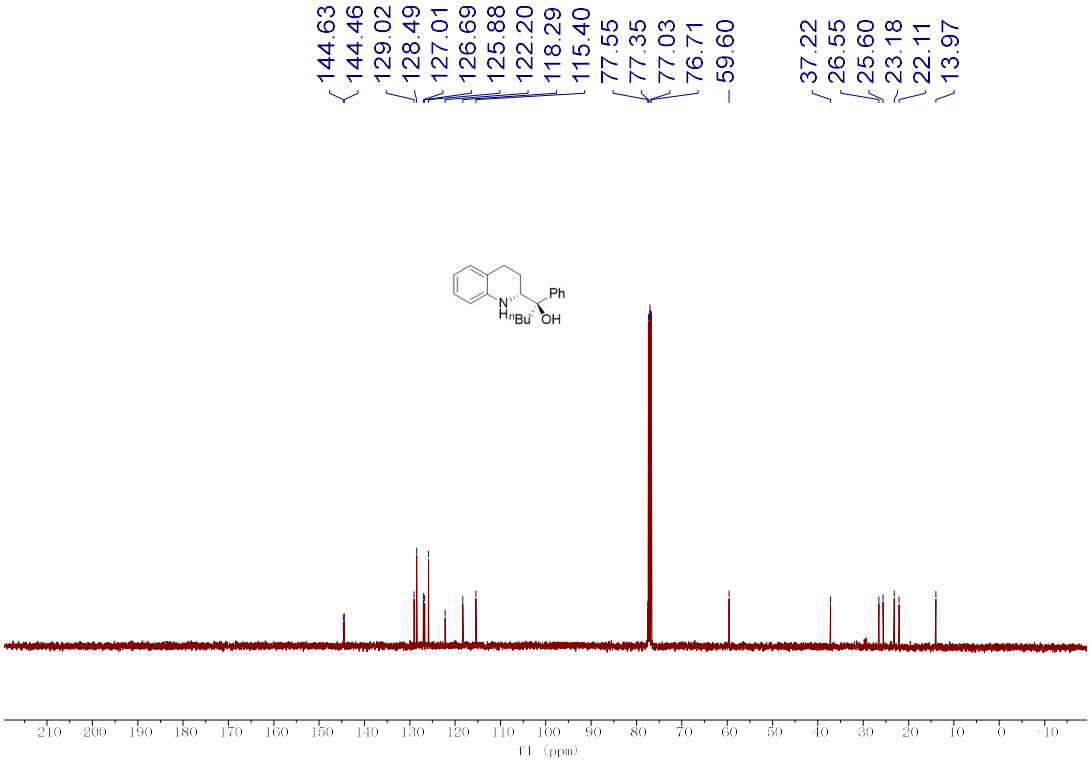
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2s**



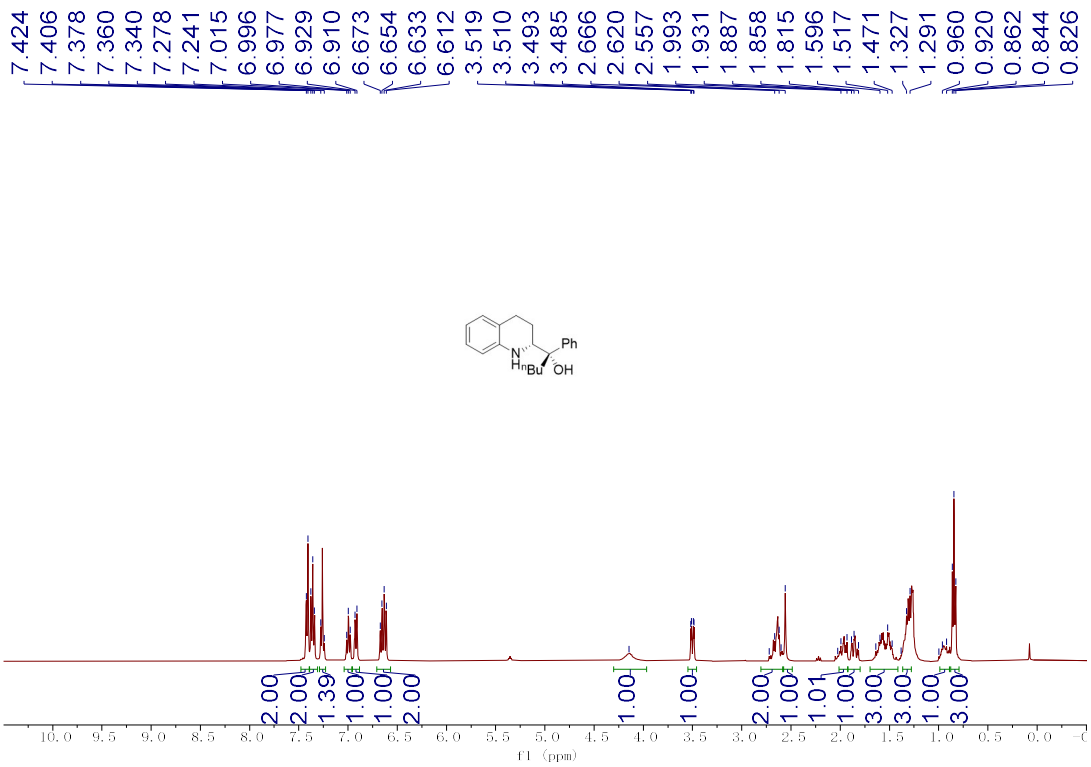
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2t**



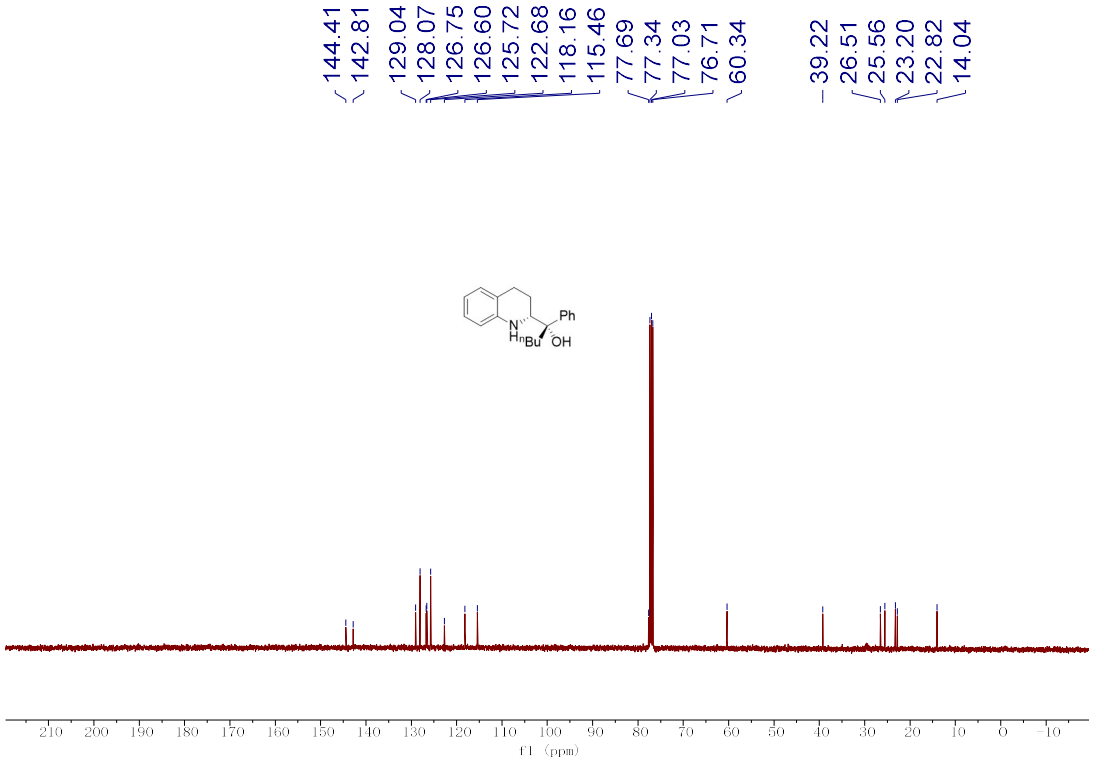
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*R*,*R*)-**2t**



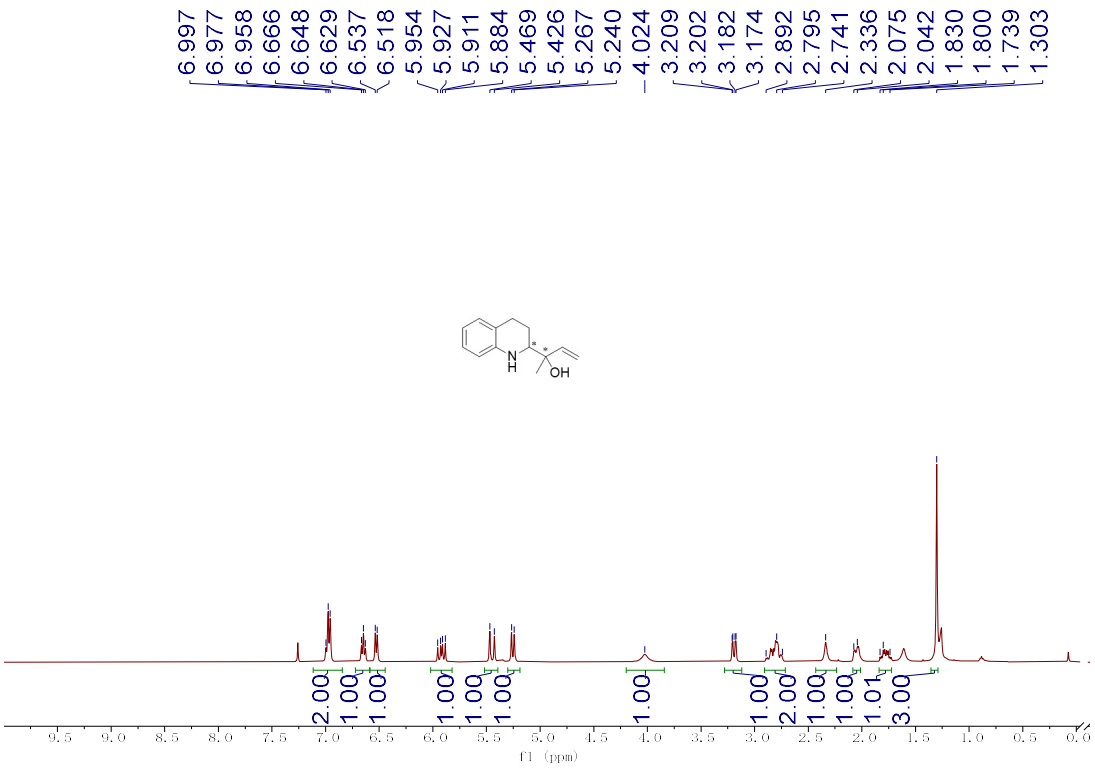
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2t**



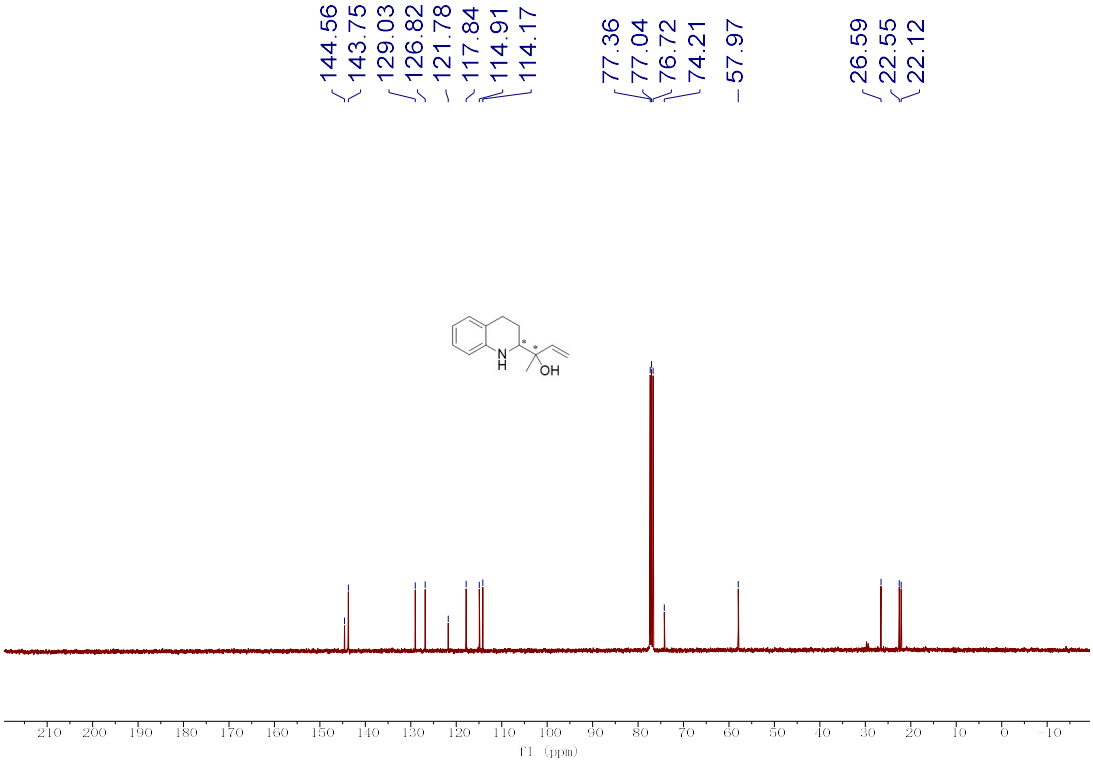
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (*S*,*R*)-**2t**



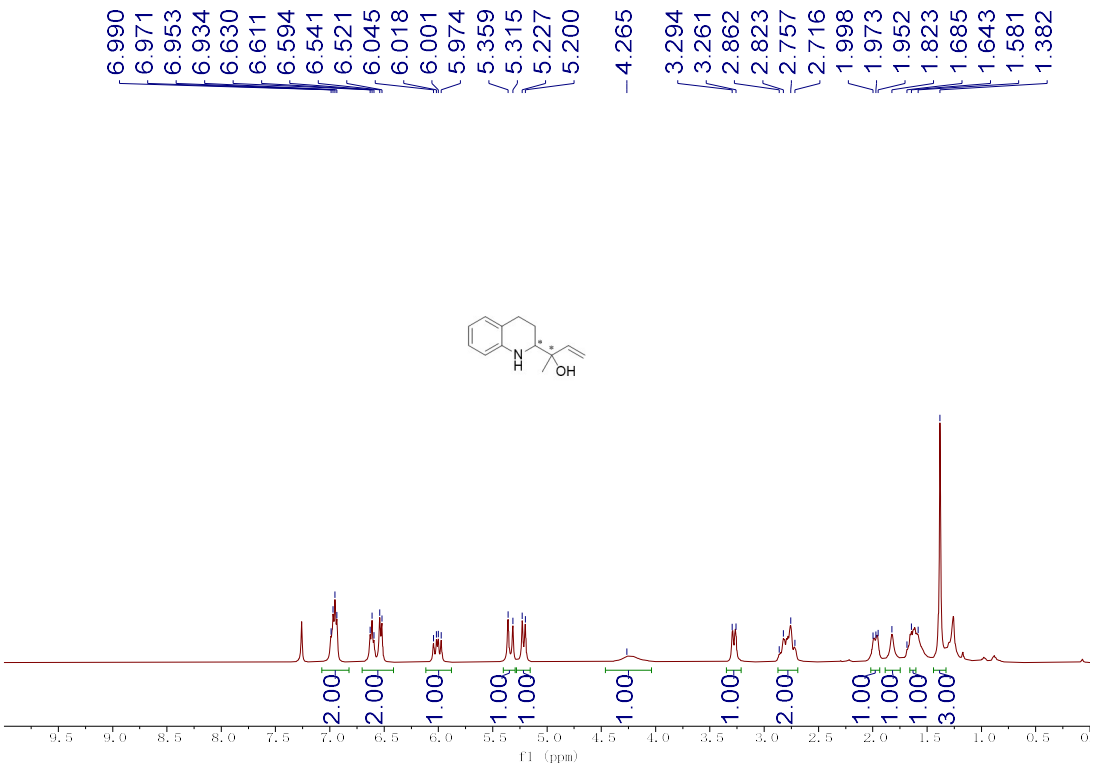
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2u-A**



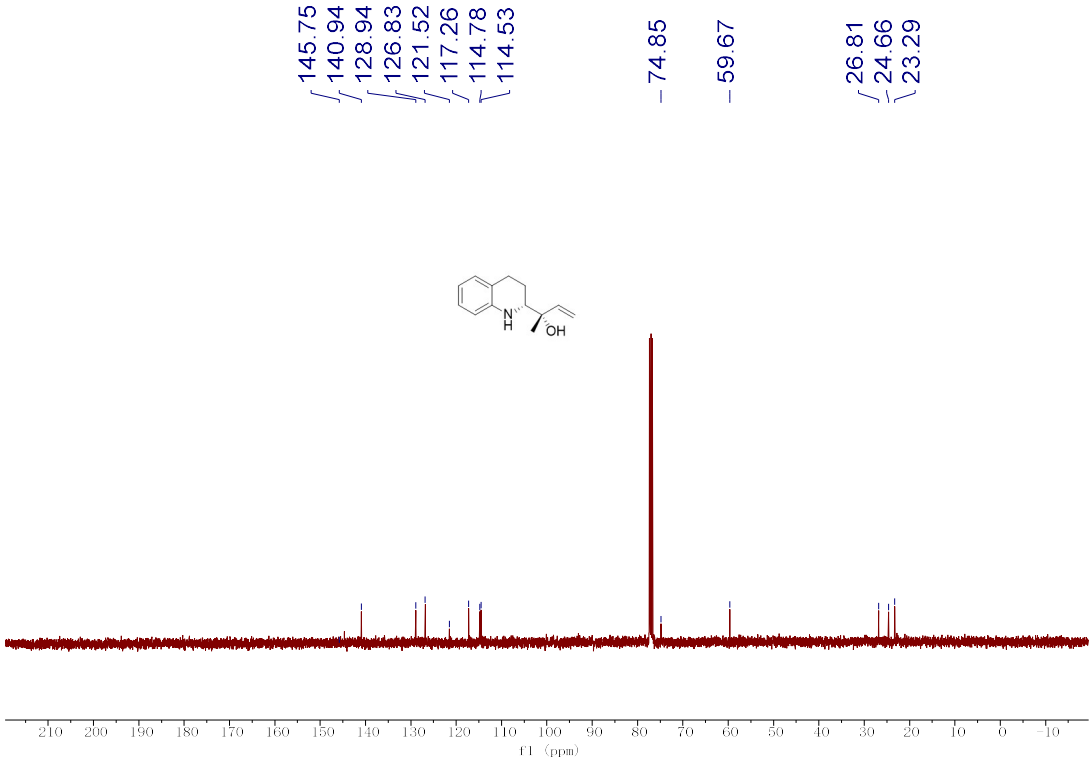
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **2u-A**



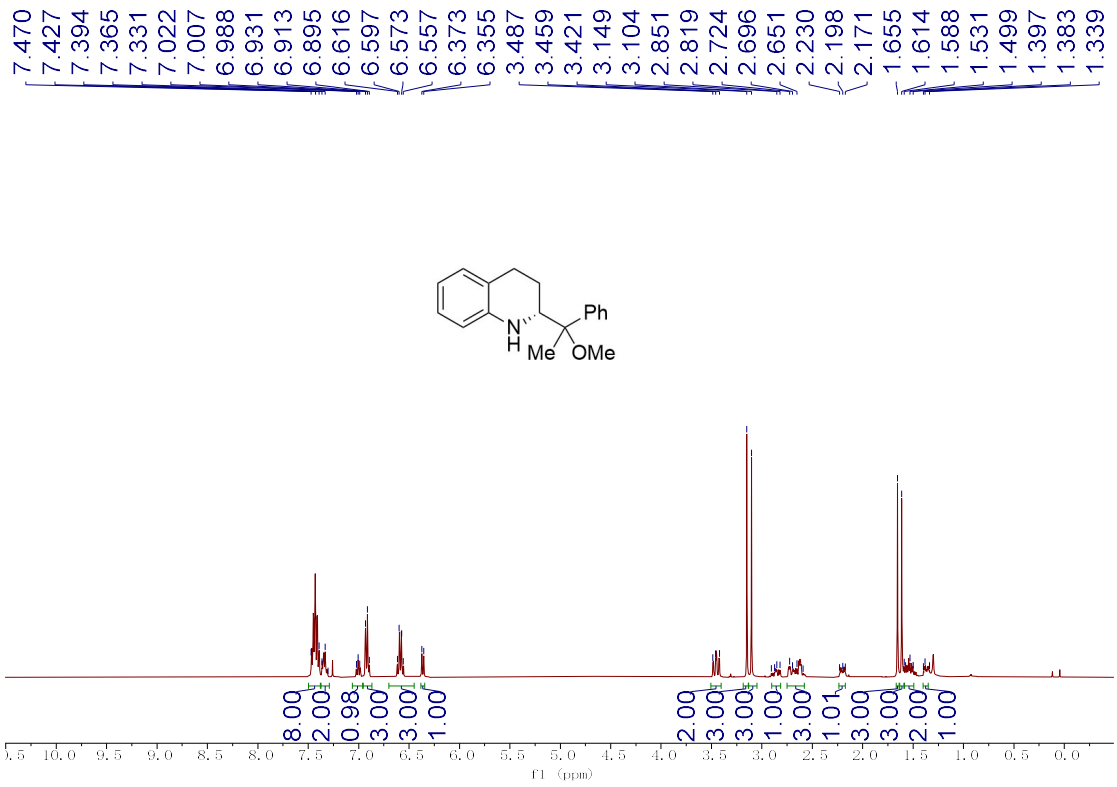
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2u-B**



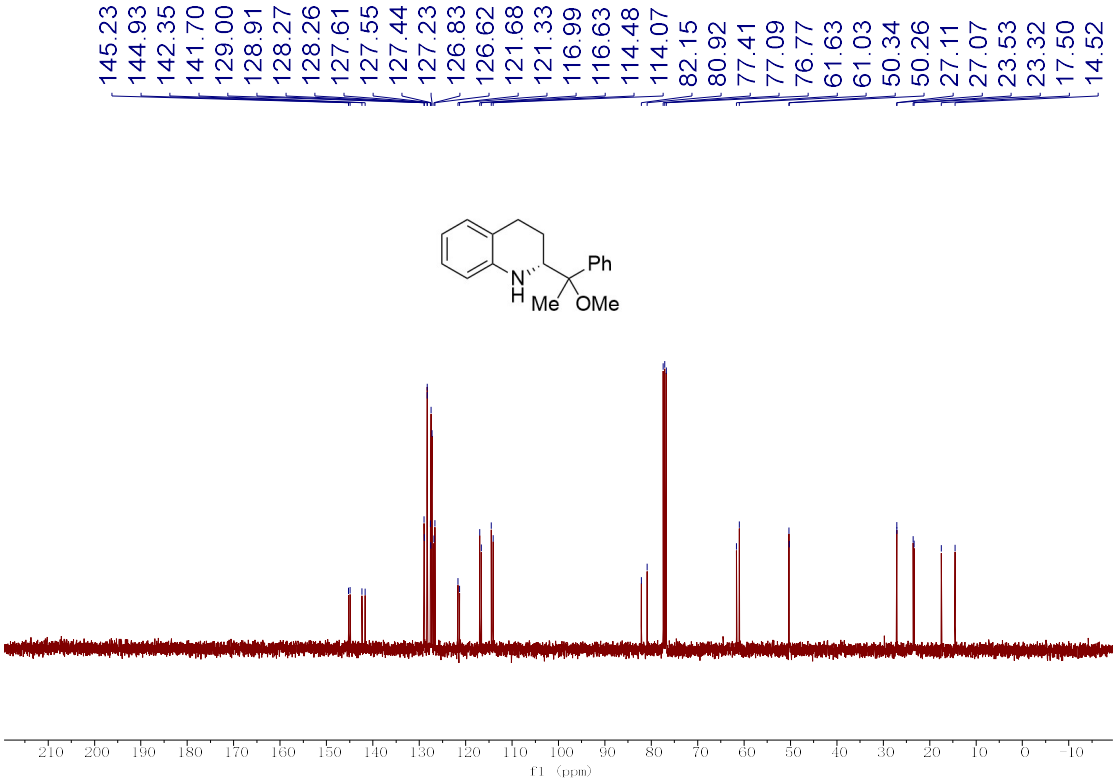
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **2u-B**



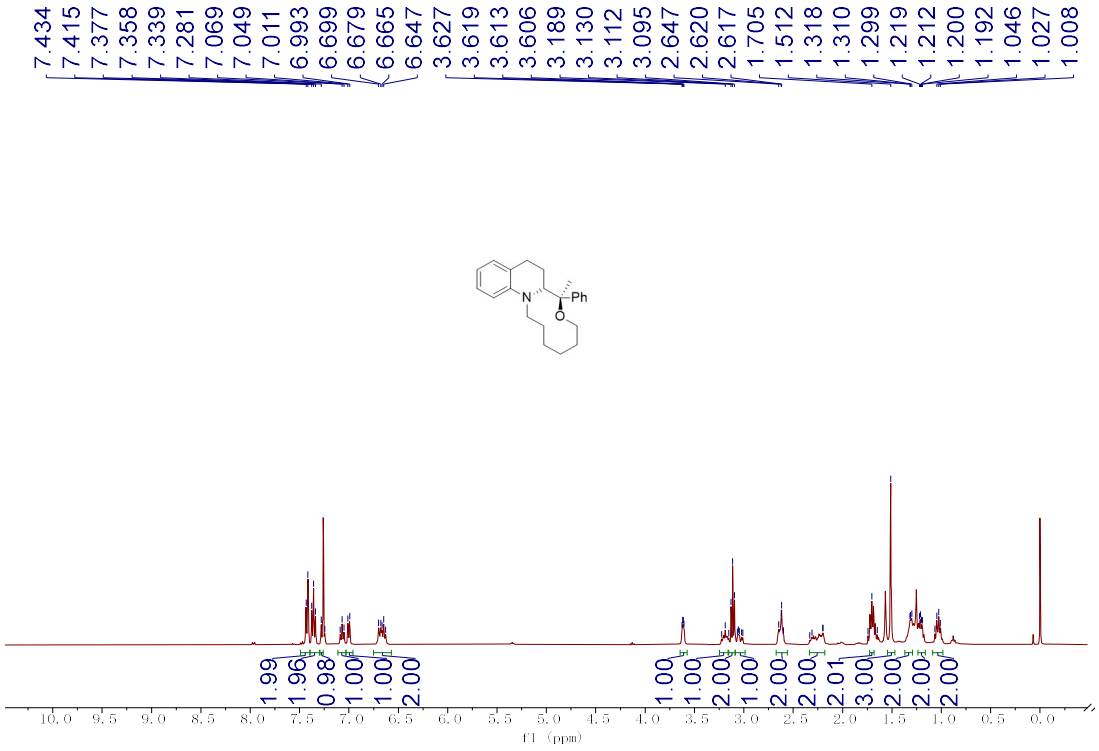
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2v**



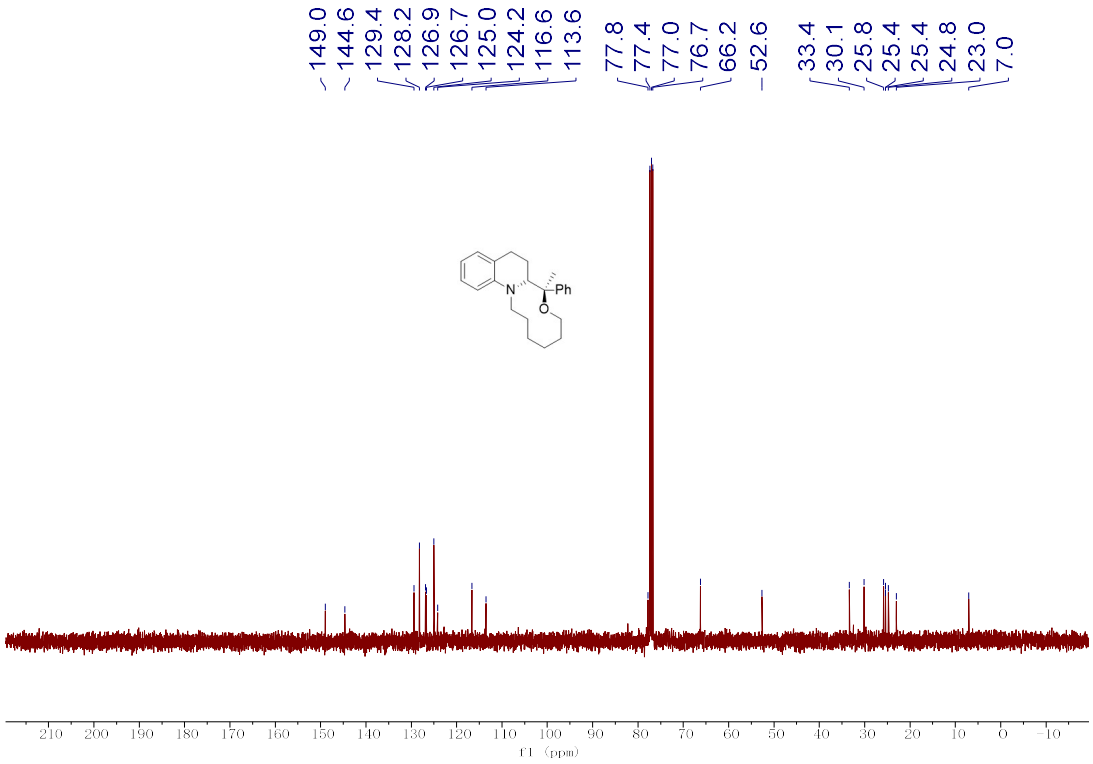
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **2v**



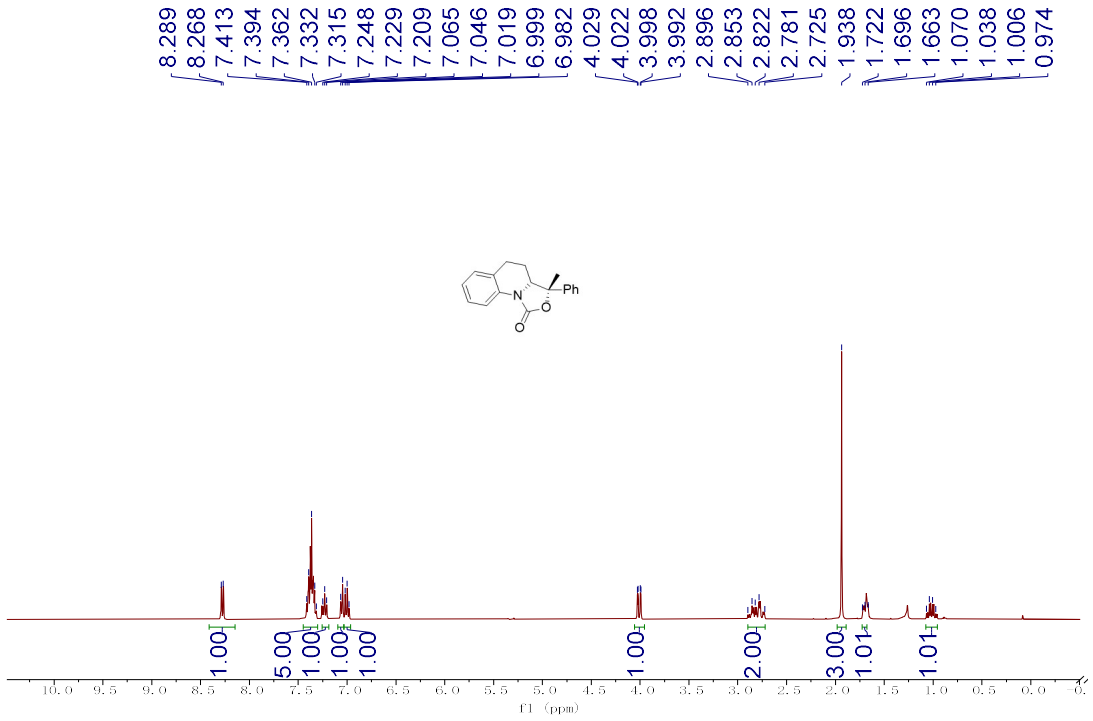
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3**



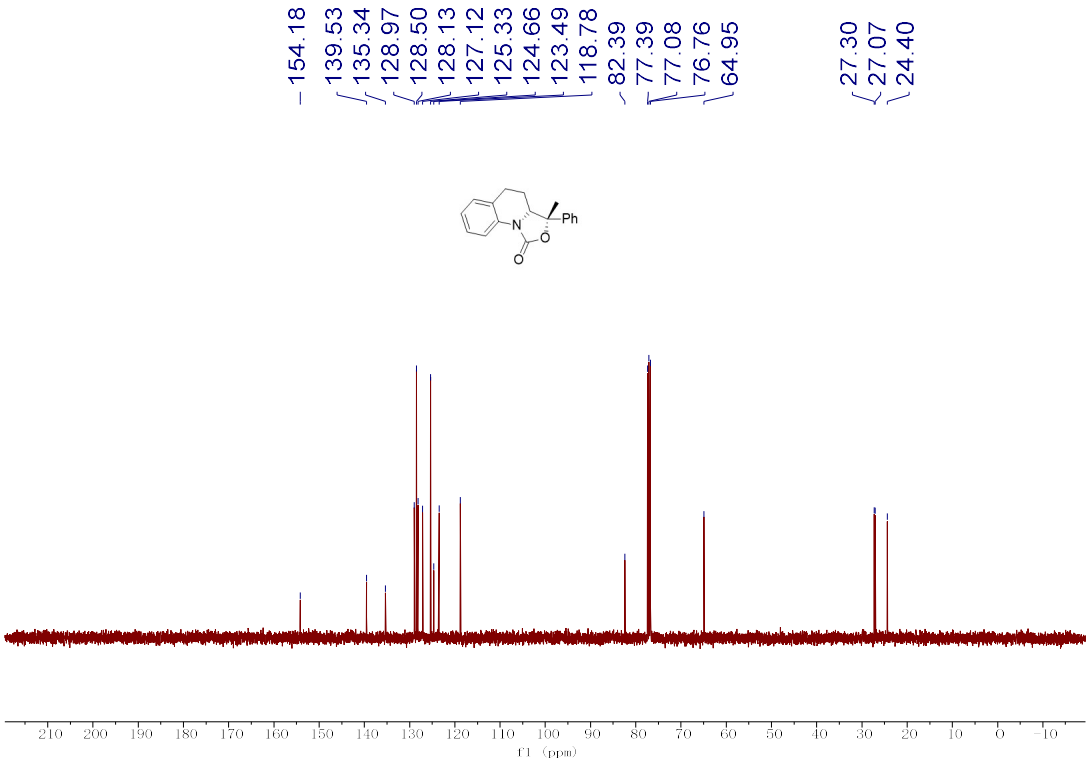
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3**



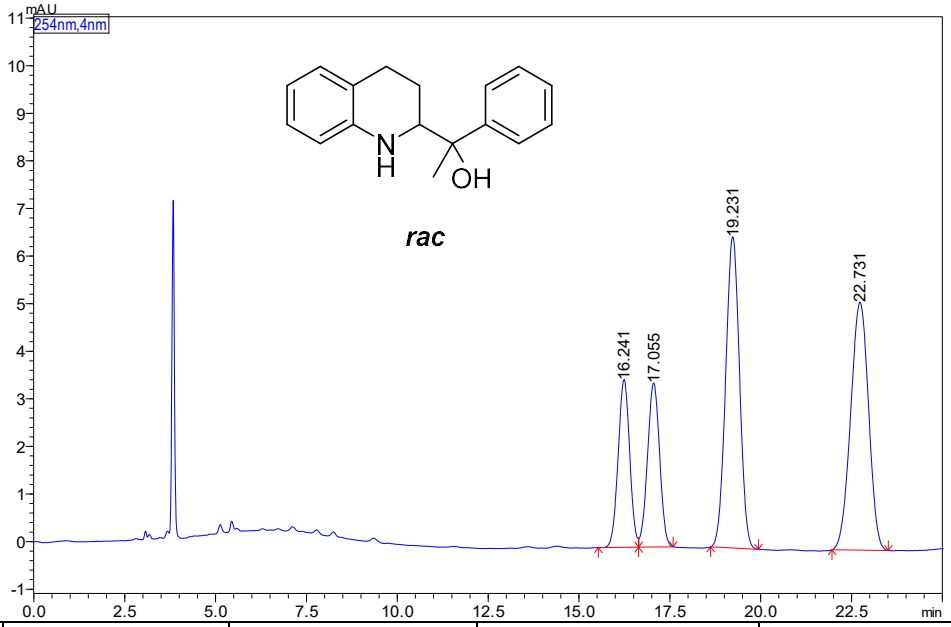
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4**



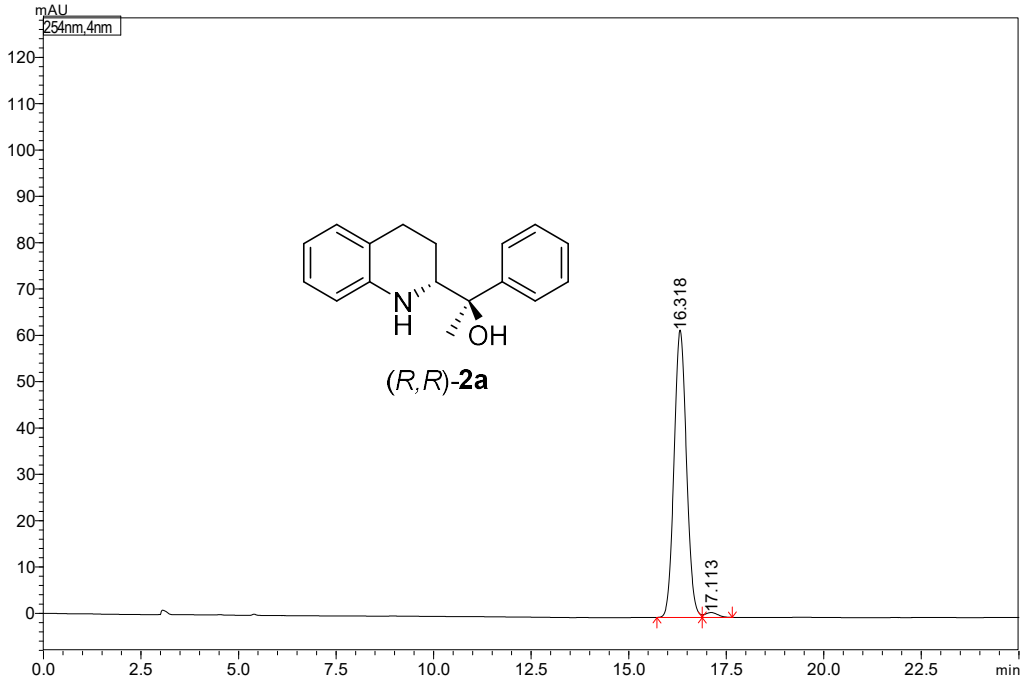
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of 4



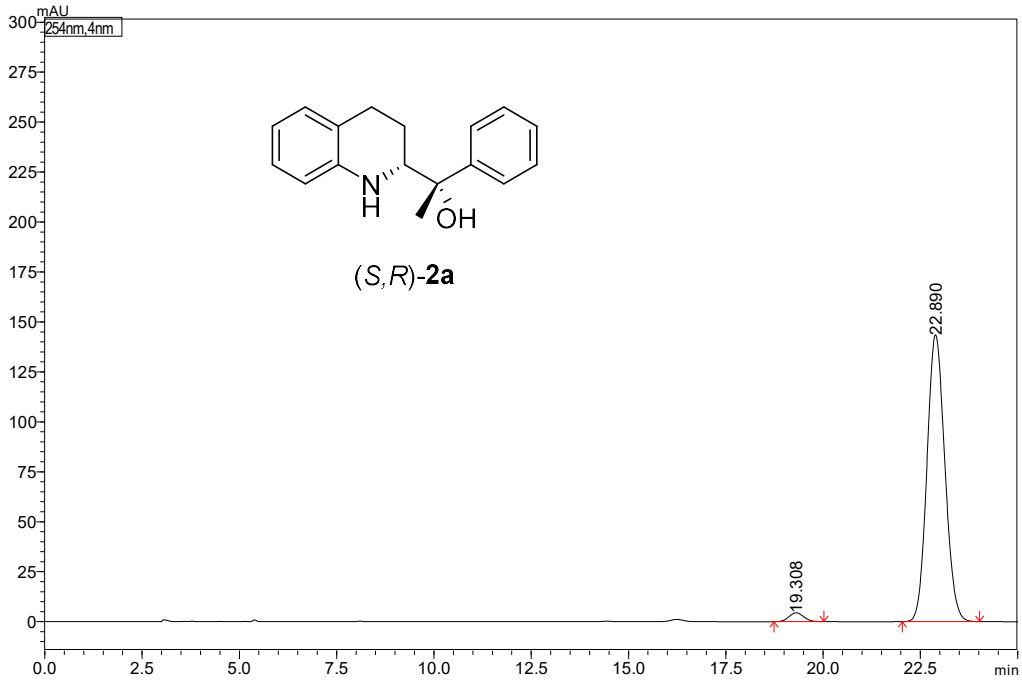
7. HPLC Spectra



Peak	Time (min)	Area (%)	Area	Height
峰号	保留时间	面积%	面积	高度
1	16.241	15.276	77842	3523
2	17.055	15.669	79848	3445
3	19.231	33.979	173150	6541
4	22.731	35.076	178744	5213
总计		100.000	509584	18723



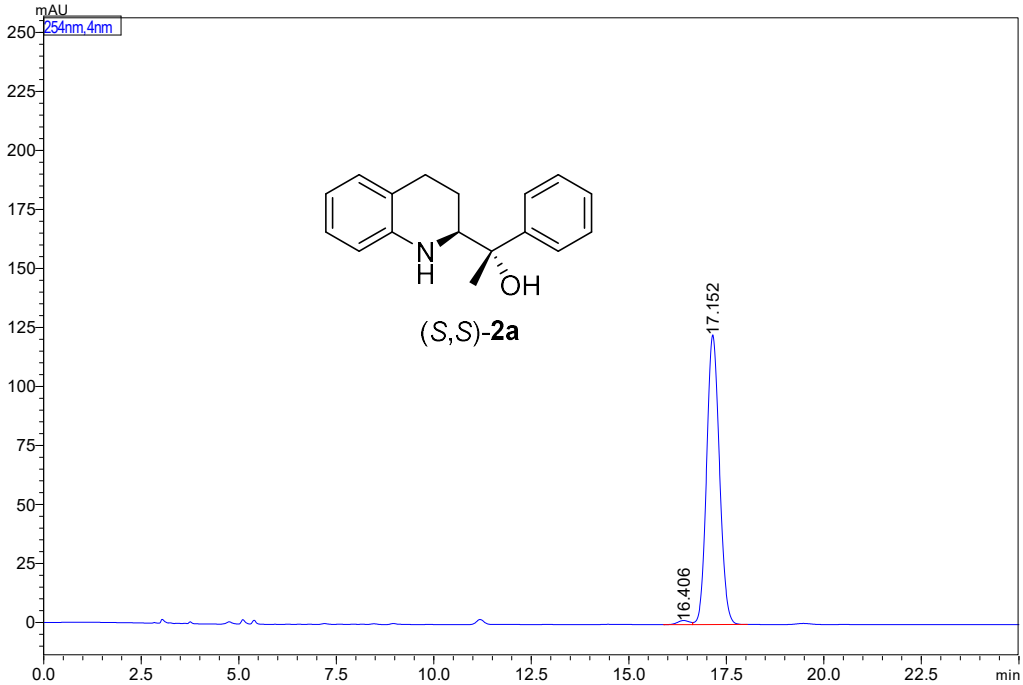
Peak	Time (min)	Area (%)	Area	Height
峰号	保留时间	面积%	面积	高度
1	16.318	98.306	1371002	62013
2	17.113	1.694	23626	1046
总计		100.000	1394628	63059



(*S*,*R*)-**2a**

Peak	Time (min)	Area (%)	Area	Height

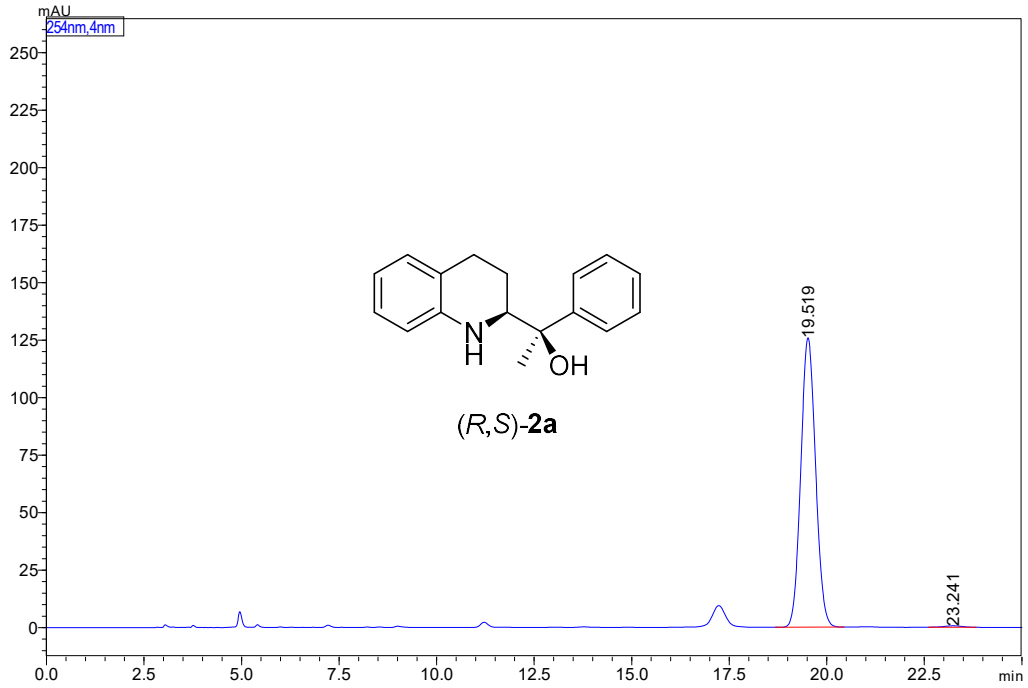
峰号	保留时间	面积%	面积	高度
1	19.308	2.517	118445	4445
2	22.890	97.483	4587390	143523
总计		100.000	4705836	147968



(*S*,*S*)-**2a**

Peak	Time (min)	Area (%)	Area	Height

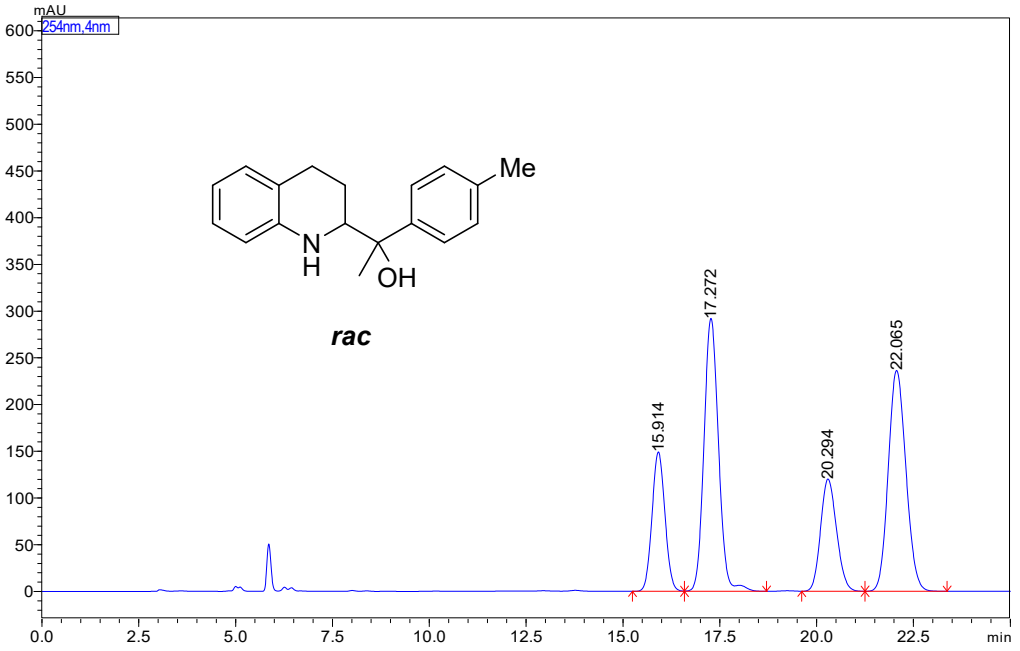
峰号	保留时间	面积%	面积	高度
1	16.406	1.275	36239	1716
2	17.152	98.725	2807139	122777
总计		100.000	2843378	124493



(*R*,*S*)-**2a**

Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	19.519	99.422	3320099	125829
2	23.241	0.578	19290	619
总计		100.000	3339389	126447



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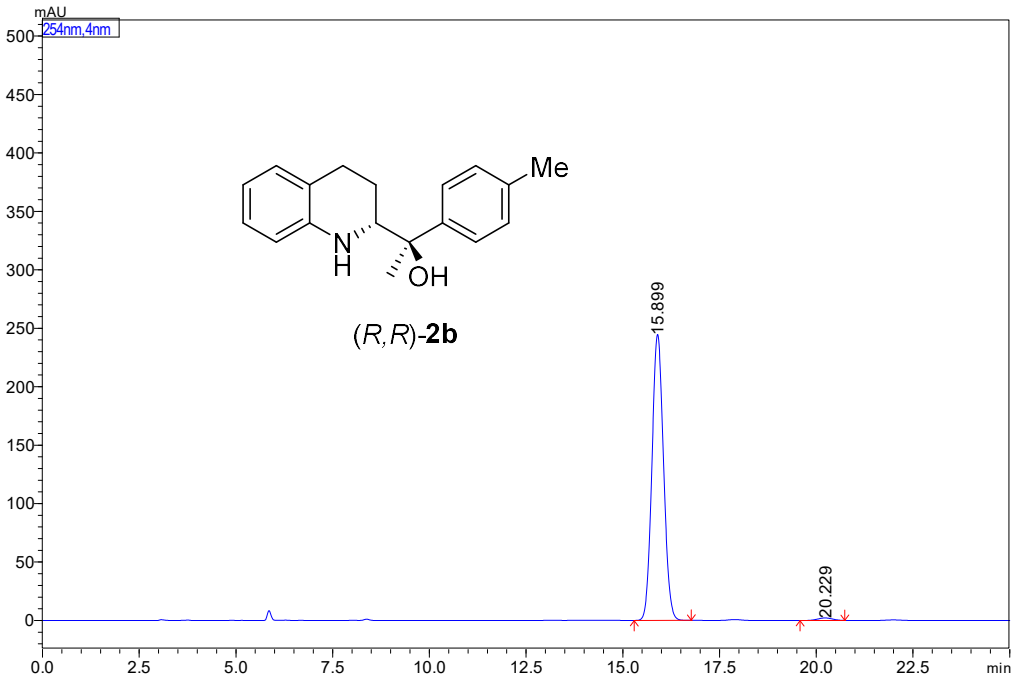
Peak	Time (min)	Area (%)	Area	Height

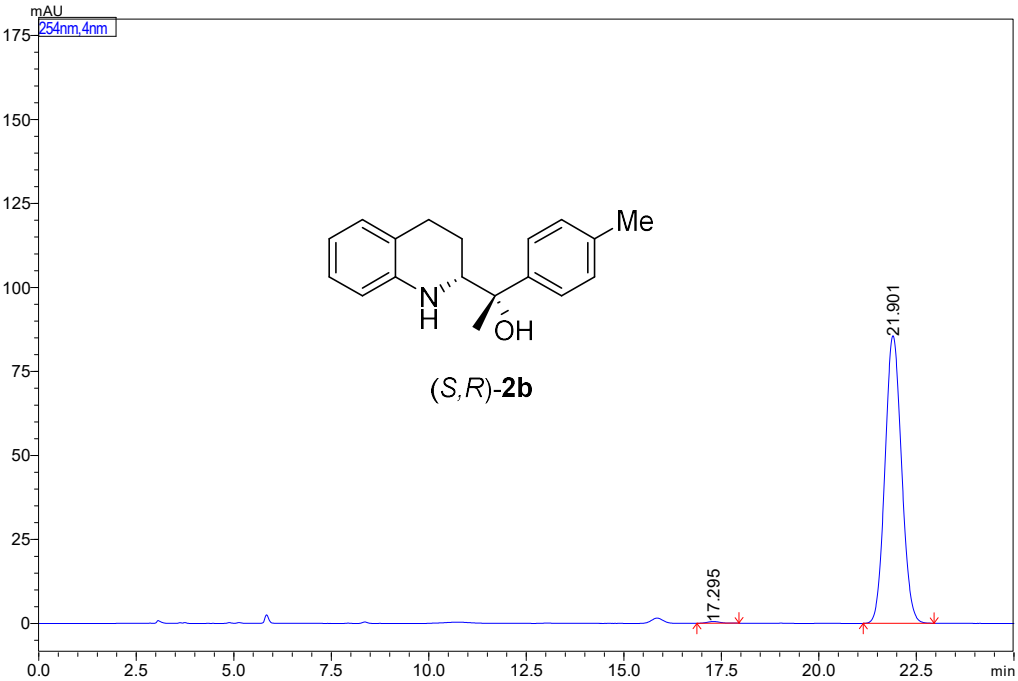
峰号	保留时间	面积%	面积	高度
1	15.914	15.681	3457745	149156
2	17.272	34.643	7638960	291987
3	20.294	15.664	3453902	120150
4	22.065	34.012	7499800	236259
总计		100.000	22050406	797553



(*R*,*R*)-**2b**

Peak	Time (min)	Area (%)	Area	Height

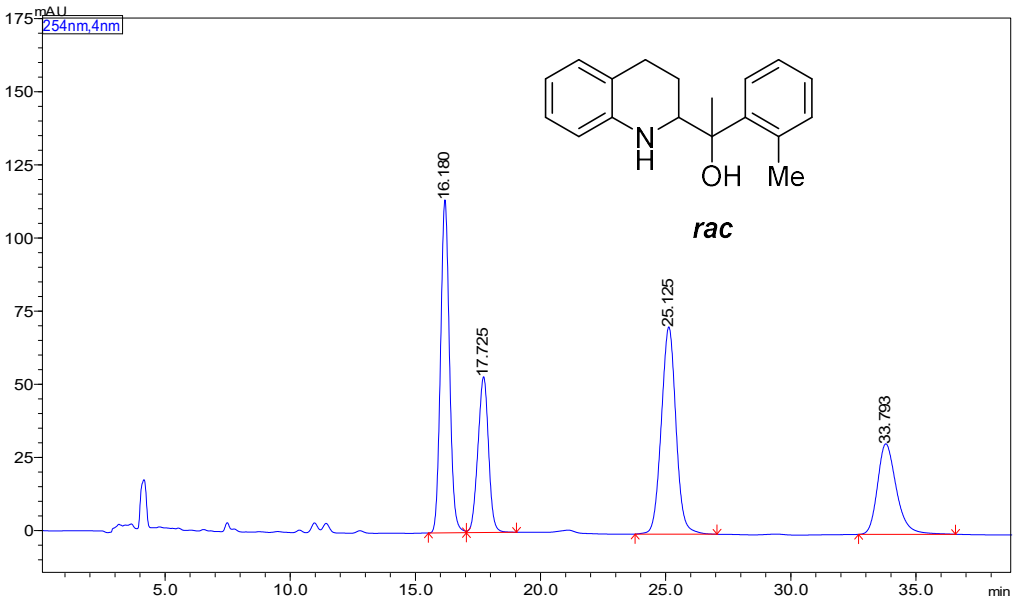
峰号	保留时间	面积%	面积	高度
1	15.899	98.896	5111600	244485
2	20.229	1.104	57062	2144
总计		100.000	5168663	246630



(*S*,*R*)-**2b**

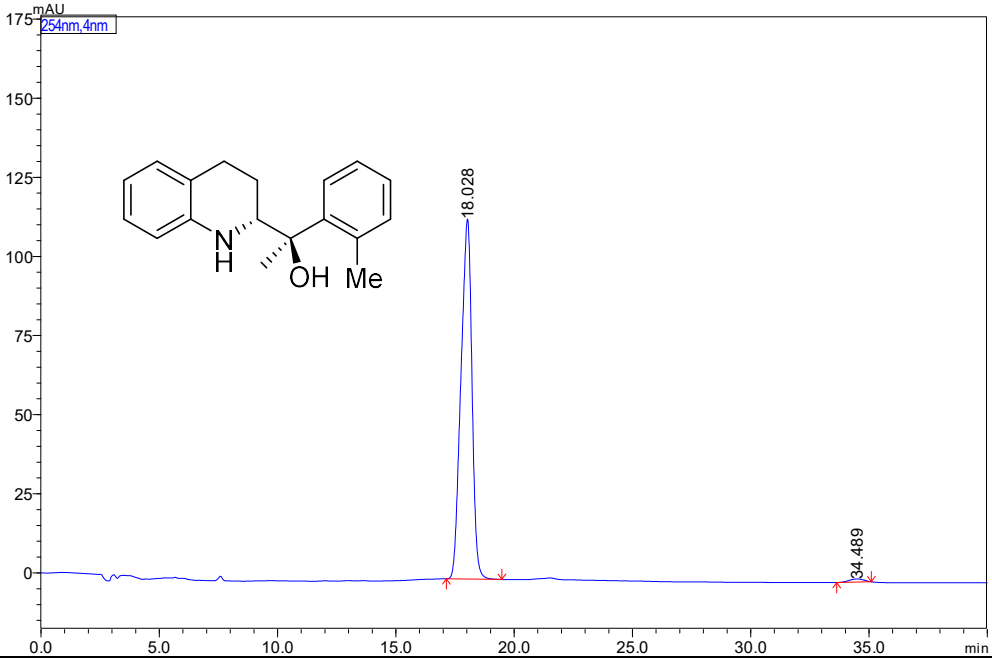
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	17.295	0.457	11594	511
2	21.901	99.543	2523999	85578
总计		100.000	2535593	86089



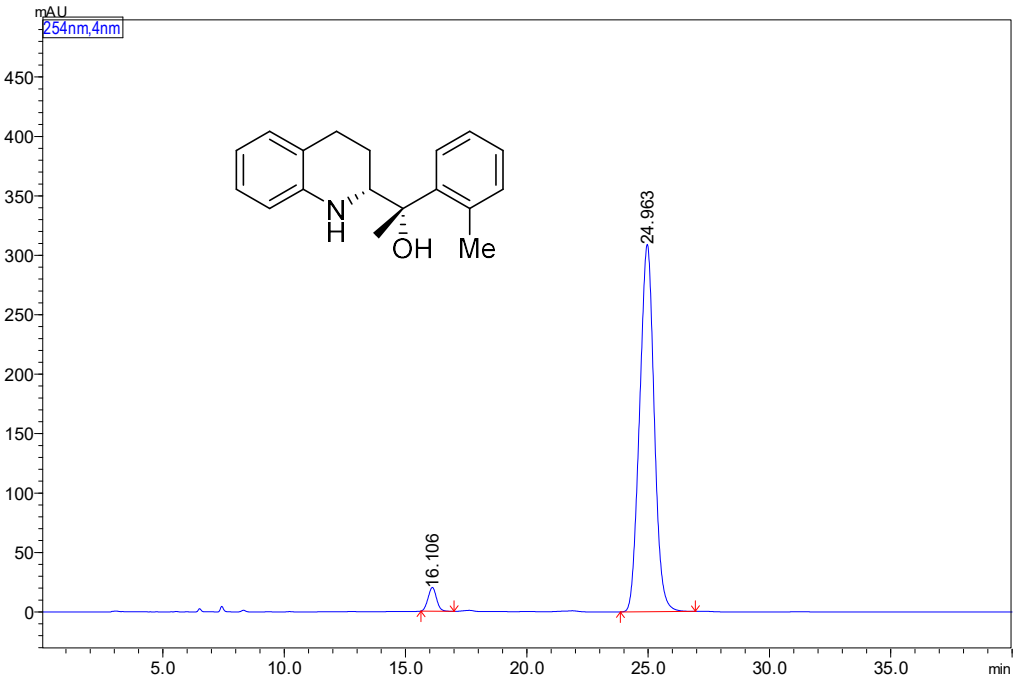
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	16.180	31.631	2814887	113857
2	17.725	17.664	1572004	53281
3	25.125	32.482	2890621	70821
4	33.793	18.223	1621730	30941
总计		100.000	8899242	268900



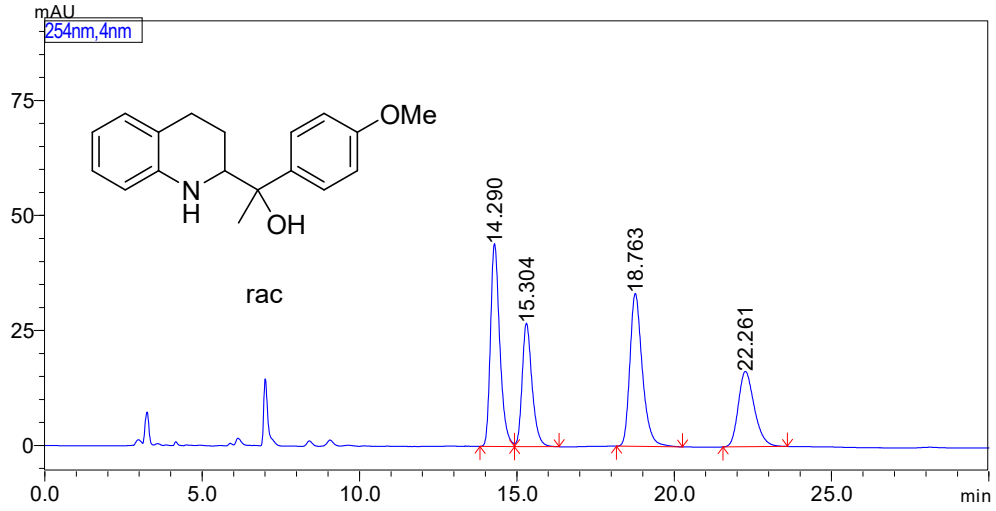
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	18.028	98.853	3677883	113745
2	34.489	1.147	42667	995
总计		100.000	3720550	114739



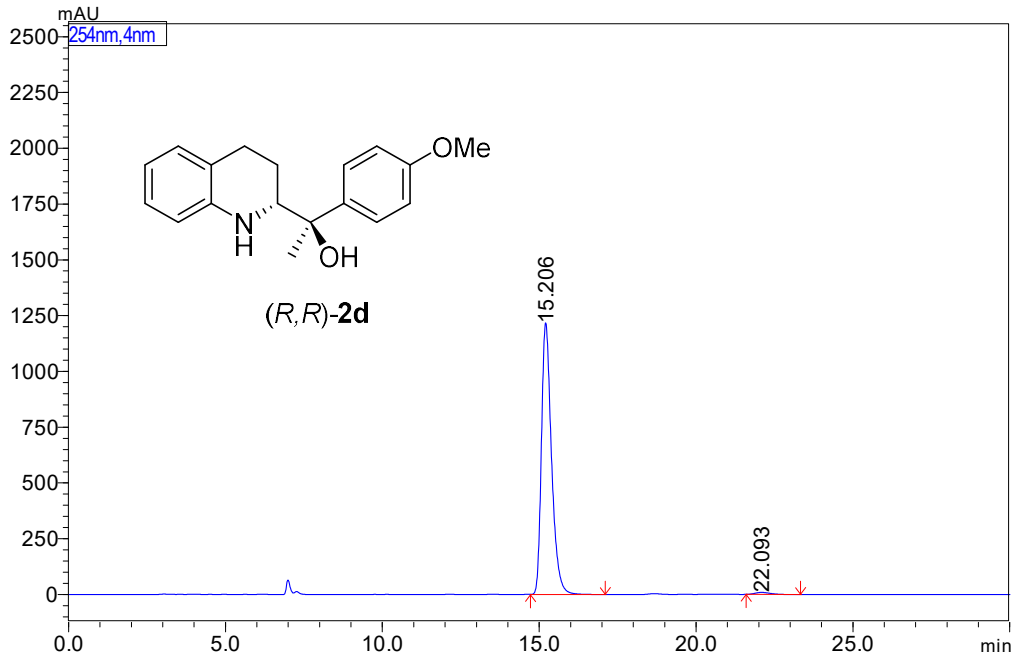
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	16.106	3.596	482262	19941
2	24.963	96.404	12928510	309061
总计		100.000	13410772	329002



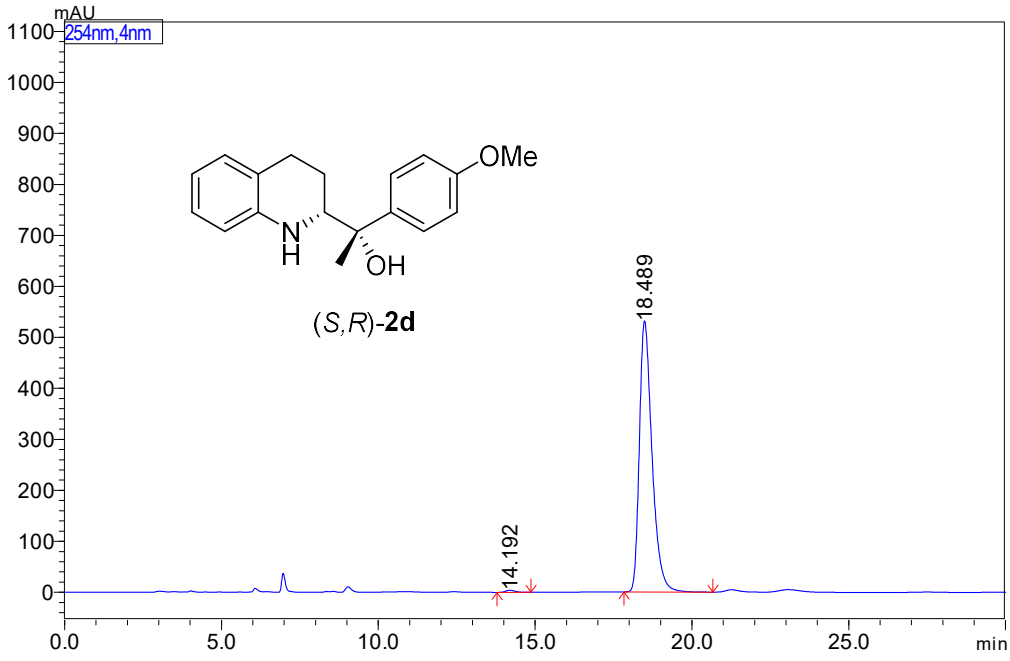
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	14.290	30.297	907172	44098
2	15.304	19.652	588430	26839
3	18.763	30.634	917261	33244
4	22.261	19.417	581385	16385
总计		100.000	2994247	120566



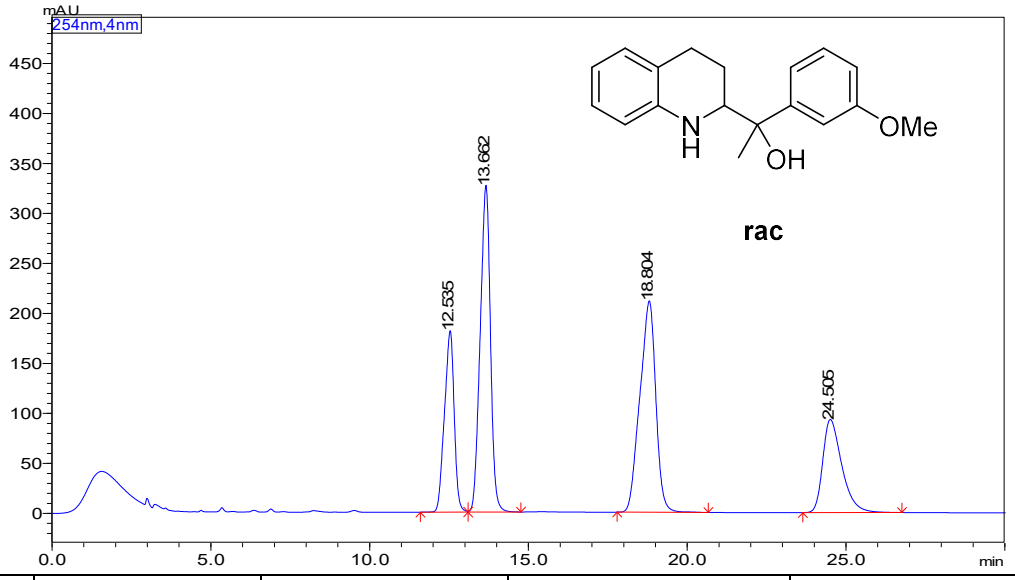
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	15.206	98.914	27176594	1217409
2	22.093	1.086	298481	8988
总计		100.000	27475075	1226398



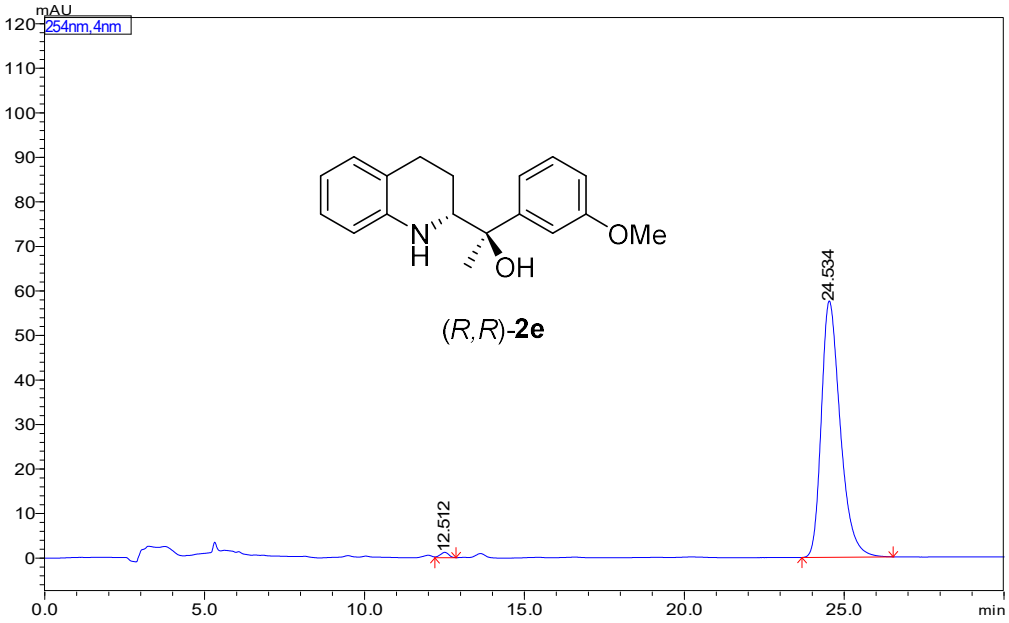
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	14.192	0.575	86091	4195
2	18.489	99.425	14899163	531634
总计		100.000	14985254	535829



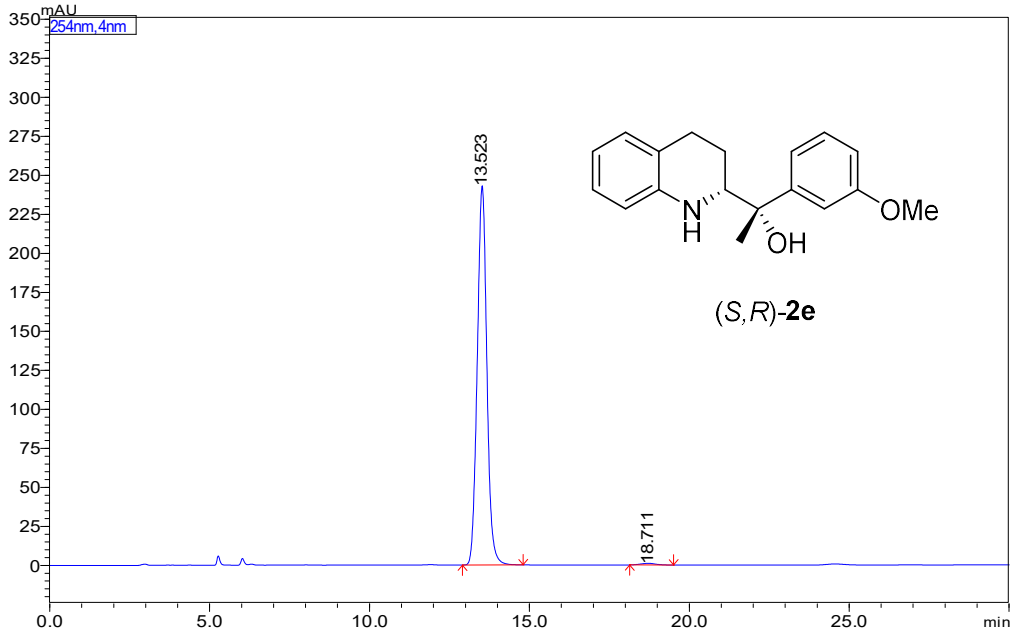
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	12.535	17.212	3864267	181526
2	13.662	32.665	7333592	326703
3	18.804	32.821	7368462	211359
4	24.505	17.301	3884288	93066
总计		100.000	22450609	812654



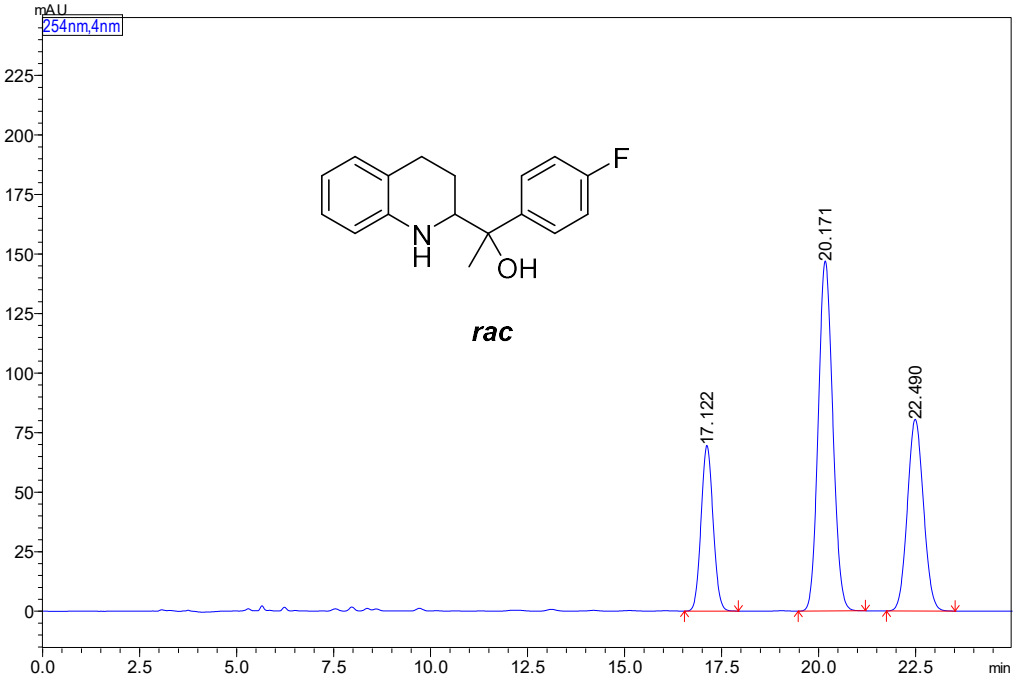
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	12.512	0.929	22206	1199
2	24.534	99.071	2367263	57564
总计		100.000	2389469	58763



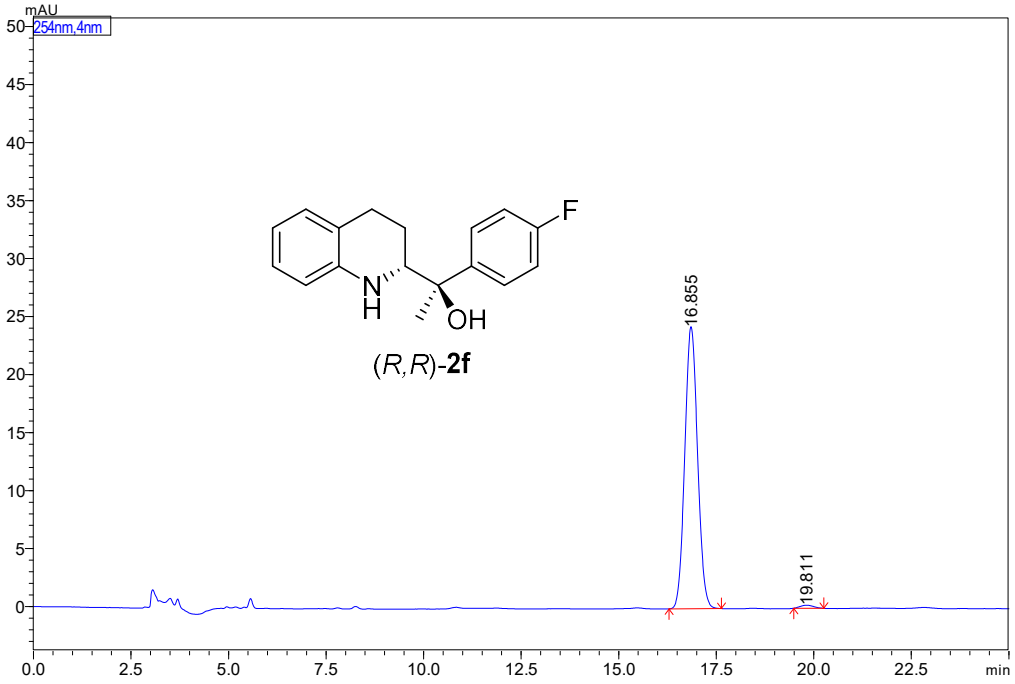
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	13.523	99.302	5064365	242959
2	18.711	0.698	35606	1070
总计		100.000	5099971	244030



Peak	Time (min)	Area (%)	Area	Height

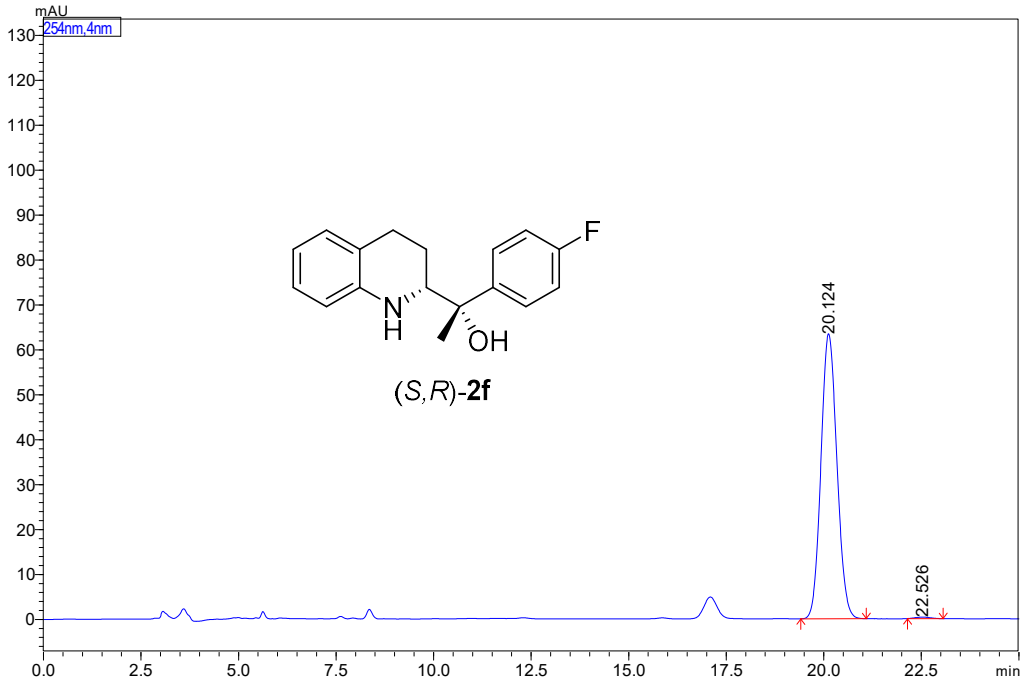
峰号	保留时间	面积%	面积	高度
1	17.122	19.619	1497891	69578
2	20.171	49.986	3816373	147021
3	22.490	30.395	2320606	80475
总计		100.000	7634870	297074



(*R*,*R*)-**2f**

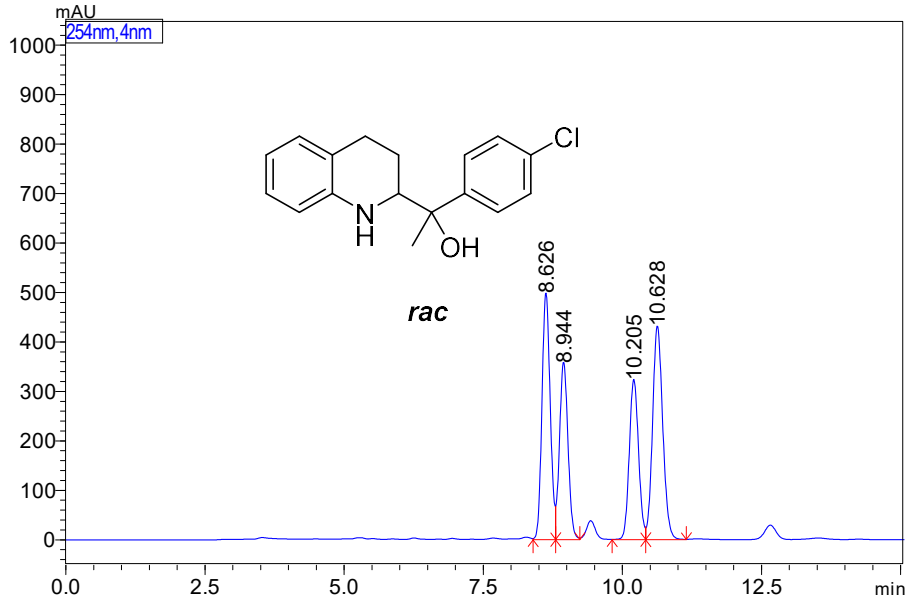
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	16.855	98.902	553277	24308
2	19.811	1.098	6143	264
总计		100.000	559420	24572

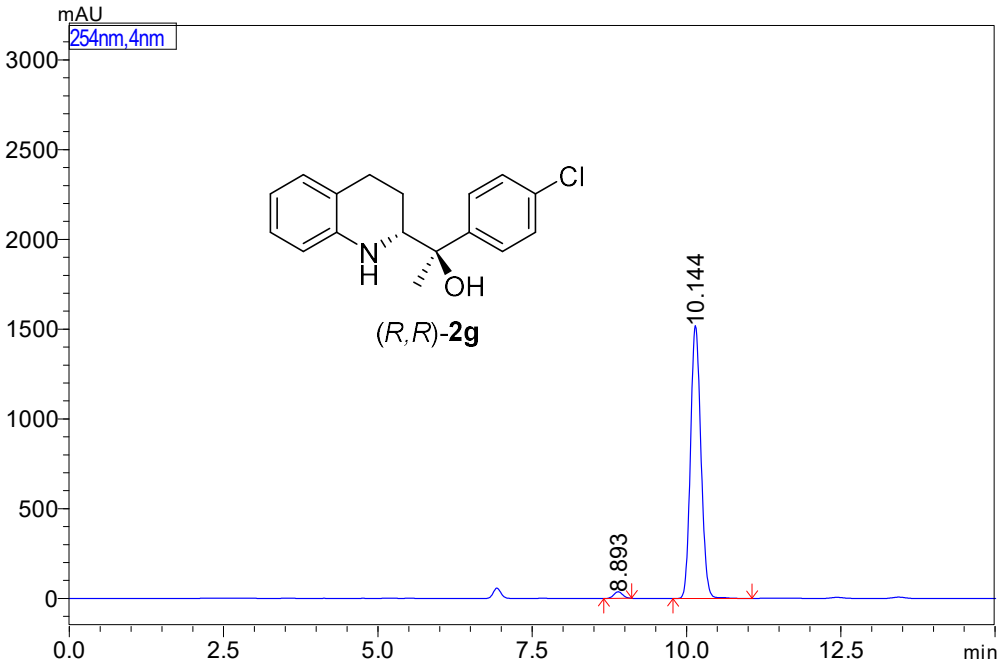


(*S*,*R*)-**2f**

Peak	Time (min)	Area (%)	Area	Height
峰号	保留时间	面积%	面积	高度
1	20.124	99.502	1804733	63445
2	22.526	0.498	9034	333
总计		100.000	1813767	63777

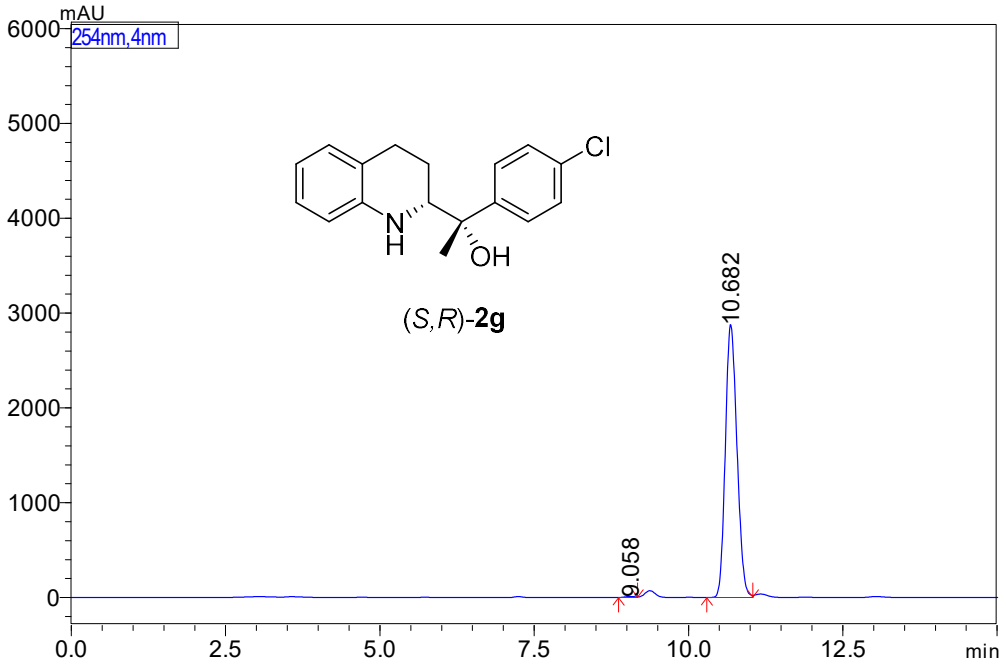


Peak	Time (min)	Area (%)	Area	Height
峰号	保留时间	面积%	面积	高度
1	8.626	28.327	5170859	498620
2	8.944	20.804	3797549	358262
3	10.205	20.672	3773614	323903
4	10.628	30.197	5512258	431597
总计		100.000	18254280	1612383



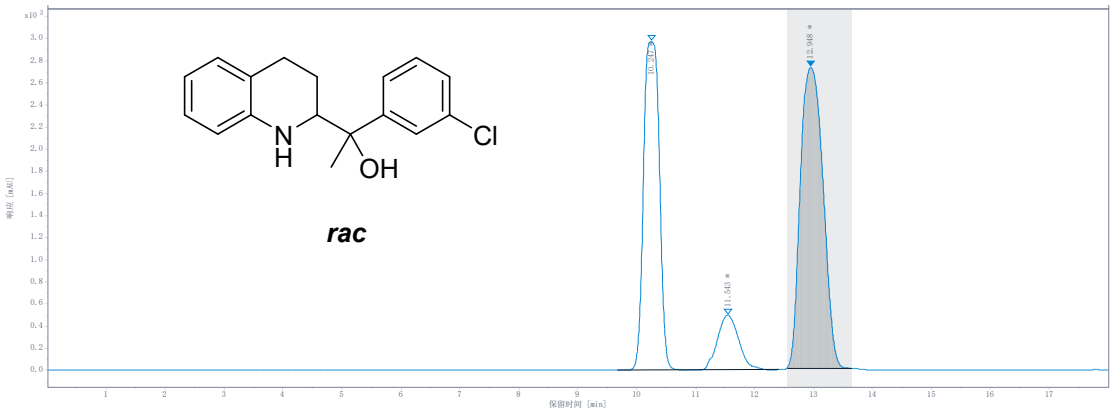
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	8.893	2.034	370370	36760
2	10.144	97.966	17838685	1519374
总计		100.000	18209055	1556134



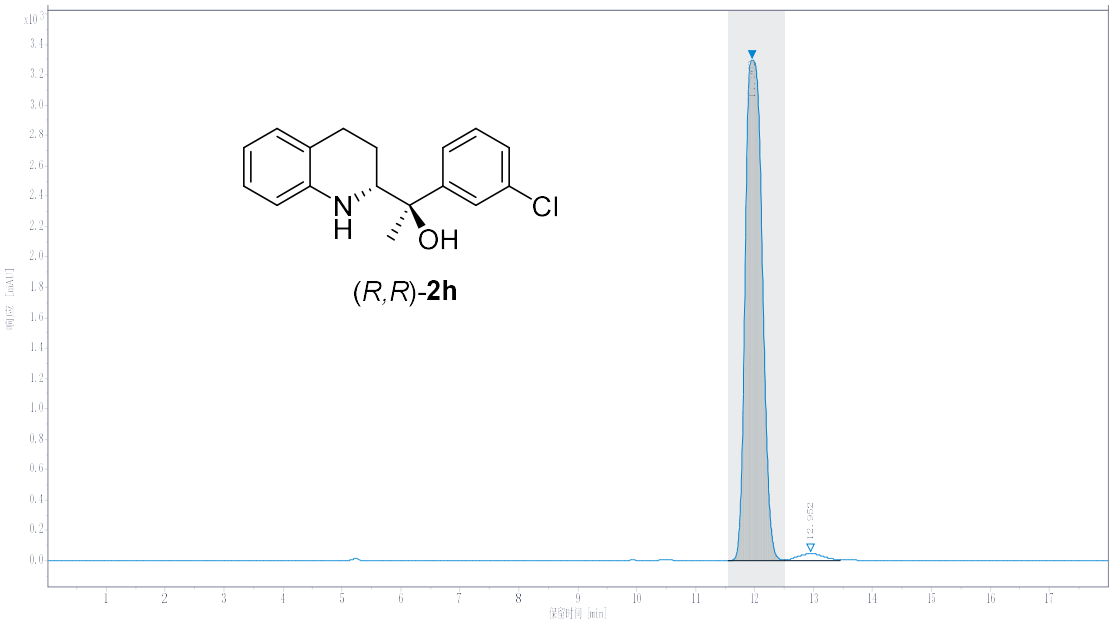
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	9.058	0.303	114458	10382
2	10.682	99.697	37709913	2876729
总计		100.000	37824371	2887111



Peak	Time (min)	Area	Area (%)	Height	Height (%)

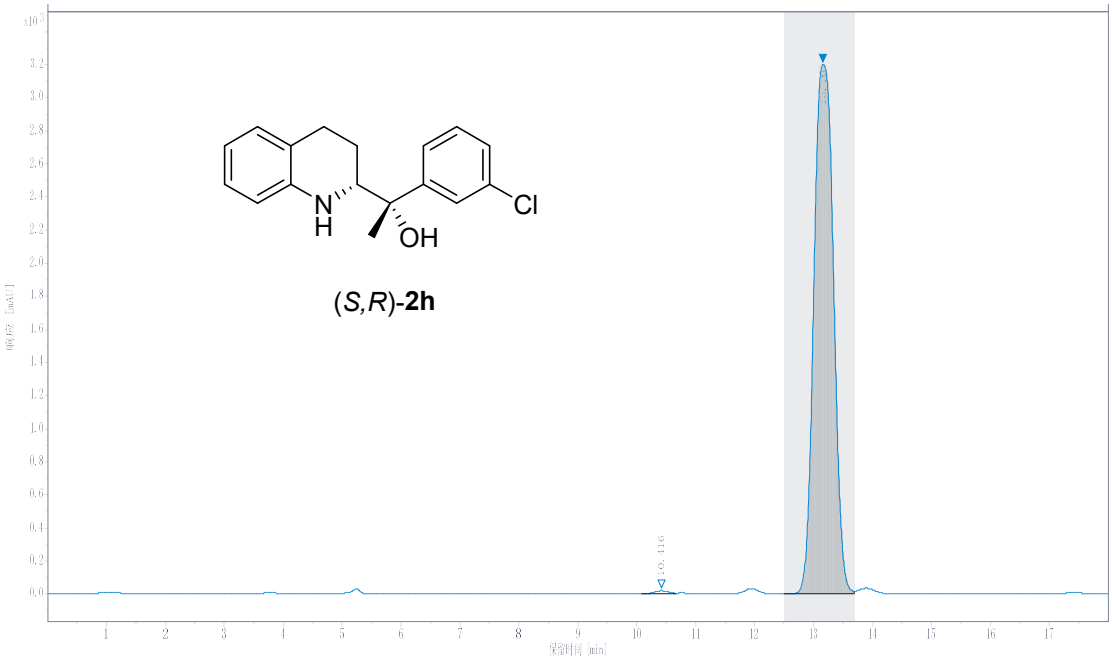
#	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%
1	10.247	54512.935	39.18	2972.572	48.06
2	11.543	12384.066	8.90	493.647	7.98
3	12.948	72244.836	51.92	2718.596	43.96



(*R*,*R*)-**2h**

Peak	Time (min)	Area	Area (%)	Height	Height (%)

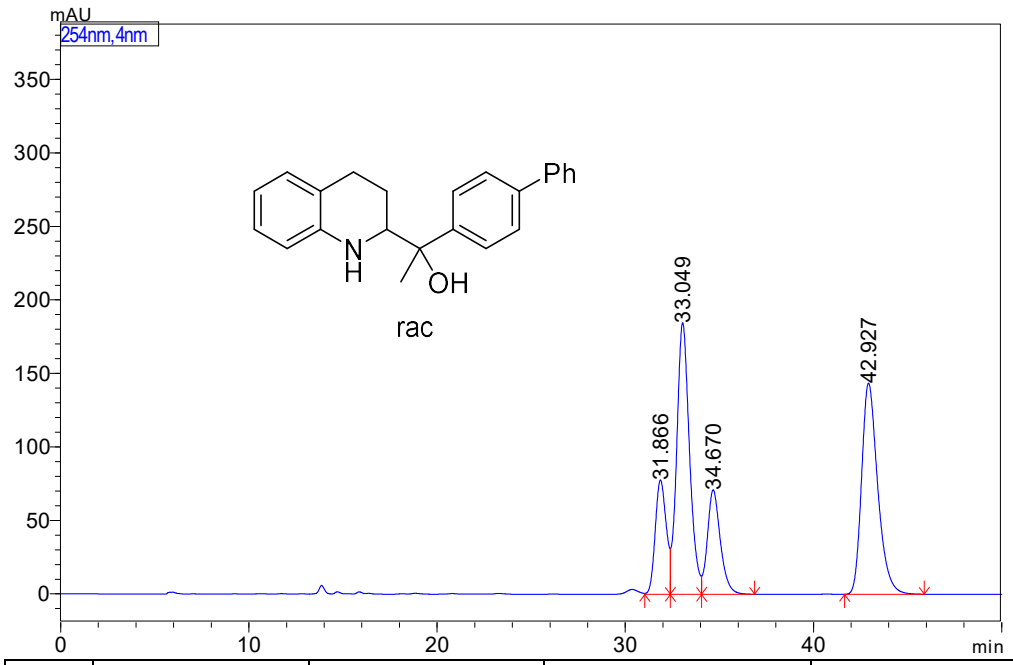
#	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%
1	11.962	65082.761	97.68	3297.418	98.54
2	12.952	1542.459	2.32	48.730	1.46



(*S*,*R*)-**2h**

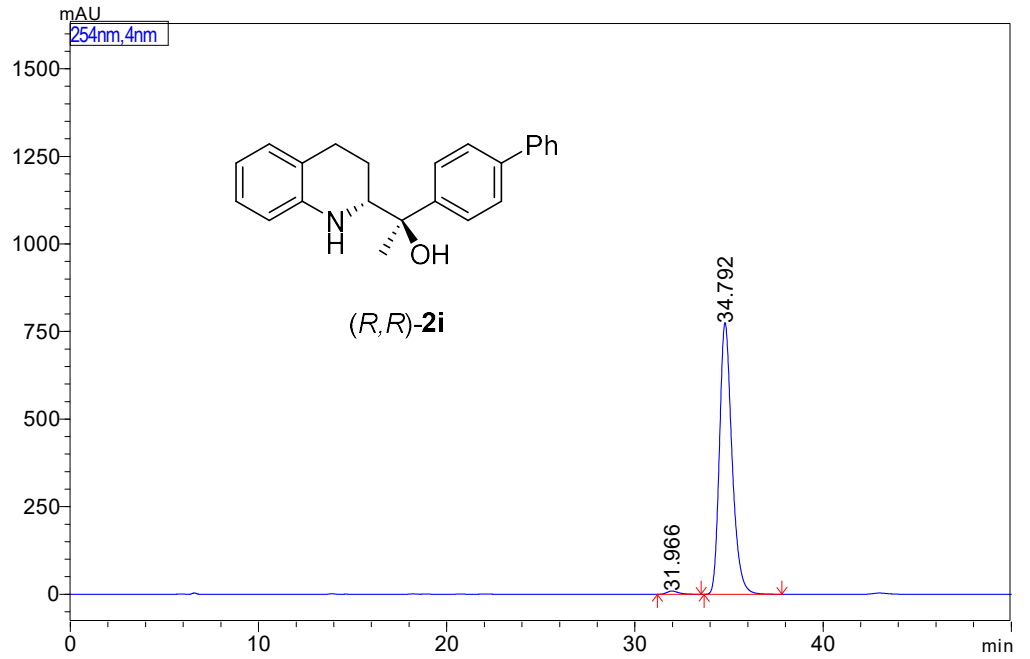
Peak	Time (min)	Area	Area (%)	Height	Height (%)

#	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%
1	10.416	379.965	0.51	21.438	0.66
2	13.161	74355.469	99.49	3202.520	99.34



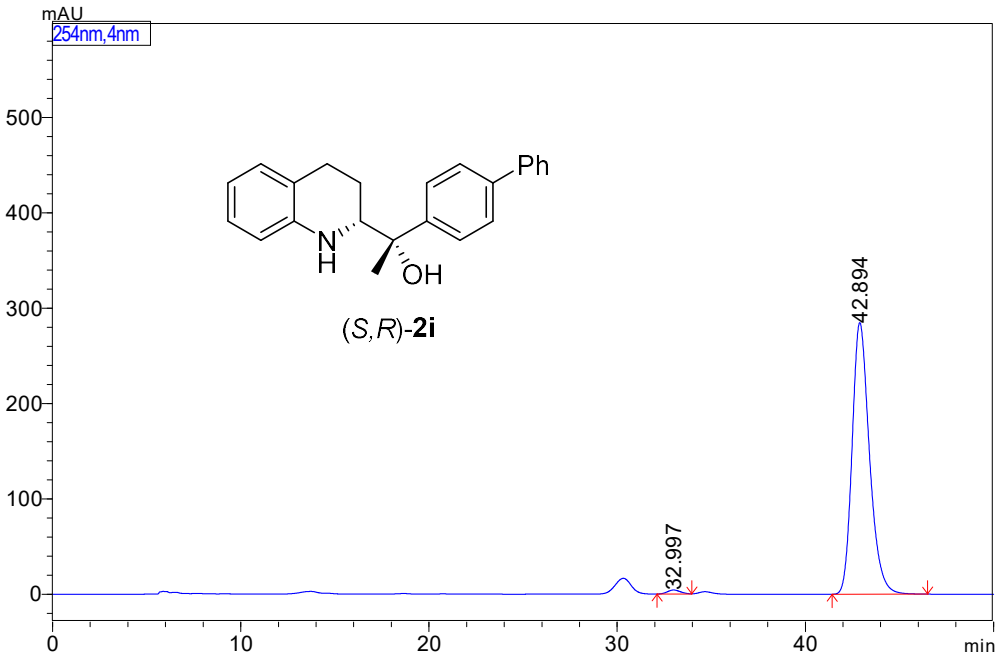
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	31.866	13.305	3180643	77787
2	33.049	36.577	8744192	184729
3	34.670	14.273	3412060	71051
4	42.927	35.845	8569185	143712
总计		100.000	23906080	477280



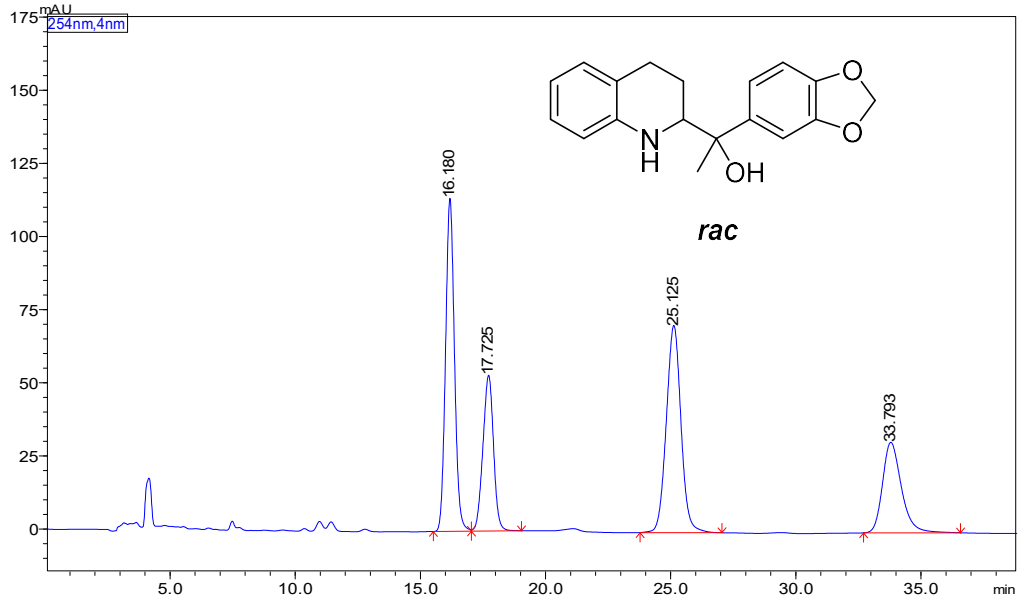
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	31.966	1.088	393726	9282
2	34.792	98.912	35803112	775442
总计		100.000	36196838	784723



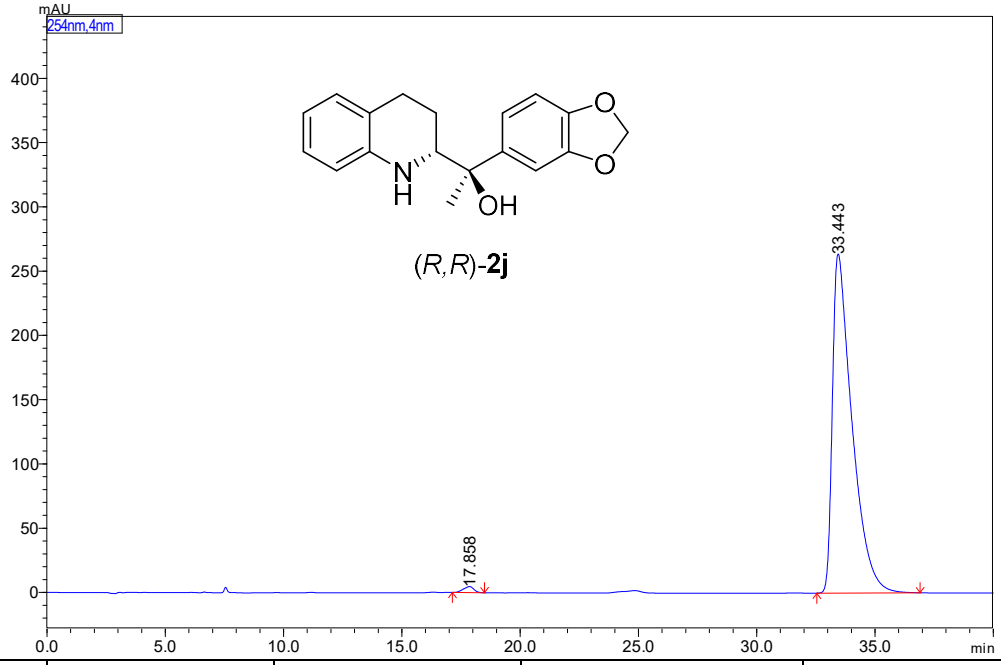
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	32.997	1.161	214513	4284
2	42.894	98.839	18258759	284879
总计		100.000	18473272	289163



Peak	Time (min)	Area (%)	Area	Height

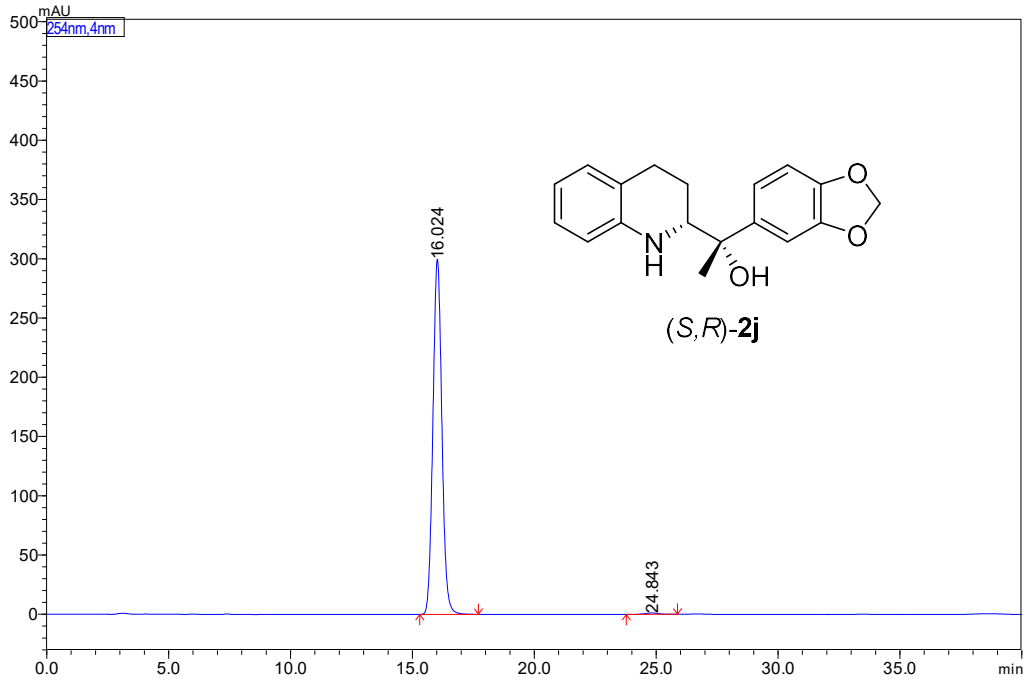
峰号	保留时间	面积%	面积	高度
1	16.180	31.631	2814887	113857
2	17.725	17.664	1572004	53281
3	25.125	32.482	2890621	70821
4	33.793	18.223	1621730	30941
总计		100.000	8899242	268900



(*R*,*R*)-**2j**

Peak	Time (min)	Area (%)	Area	Height

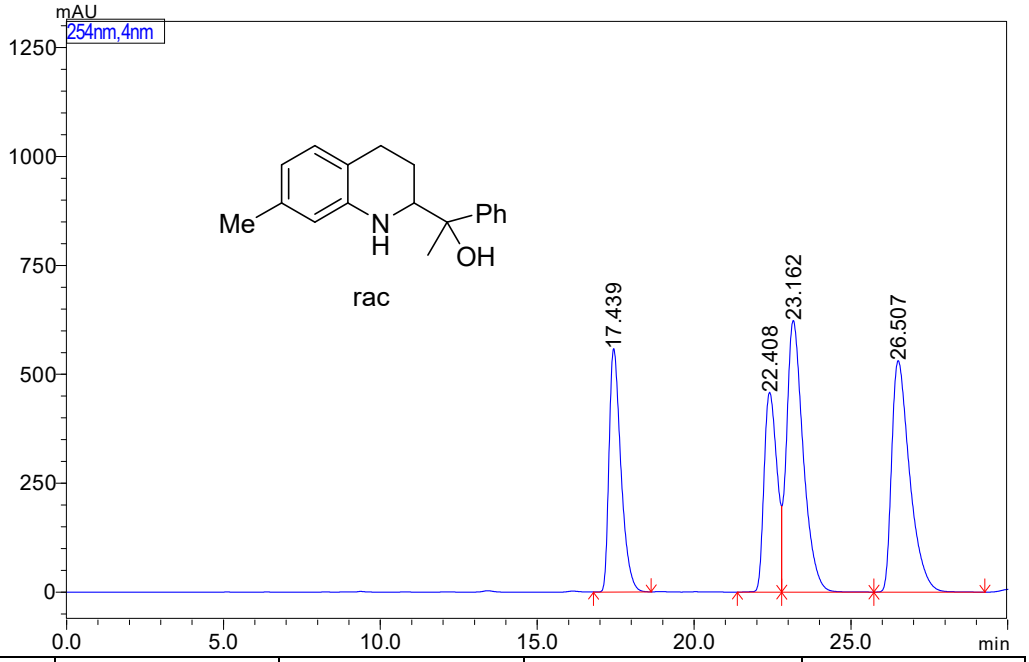
峰号	保留时间	面积%	面积	高度
1	17.858	0.924	141709	4669
2	33.443	99.076	15192984	263795
总计		100.000	15334694	268464



(*S*,*R*)-**2j**

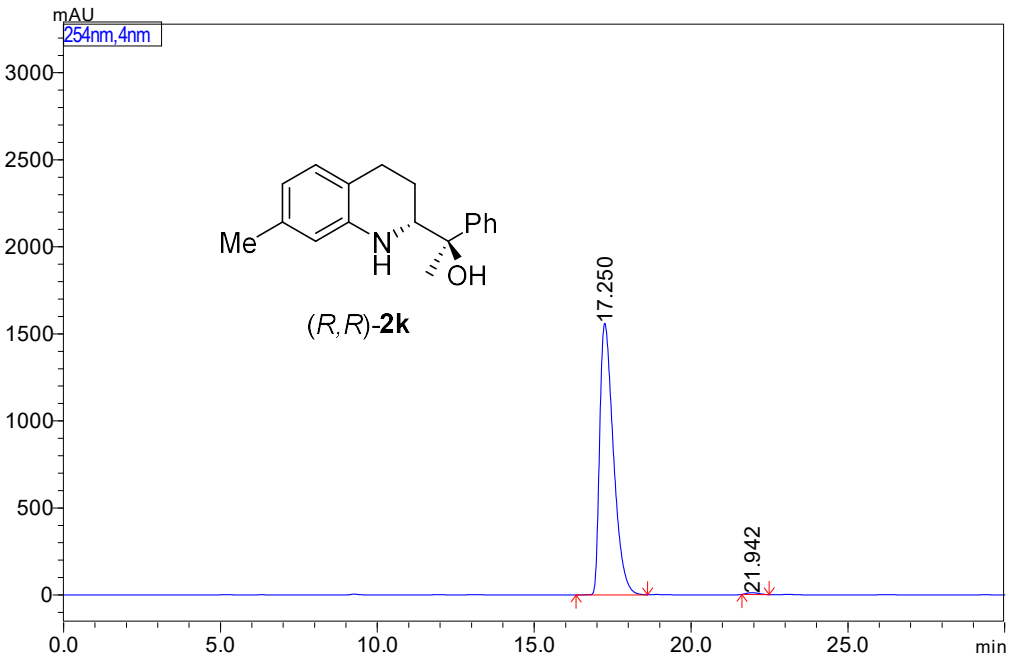
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	16.024	99.422	7679268	299831
2	24.843	0.578	44630	1180
总计		100.000	7723897	301011



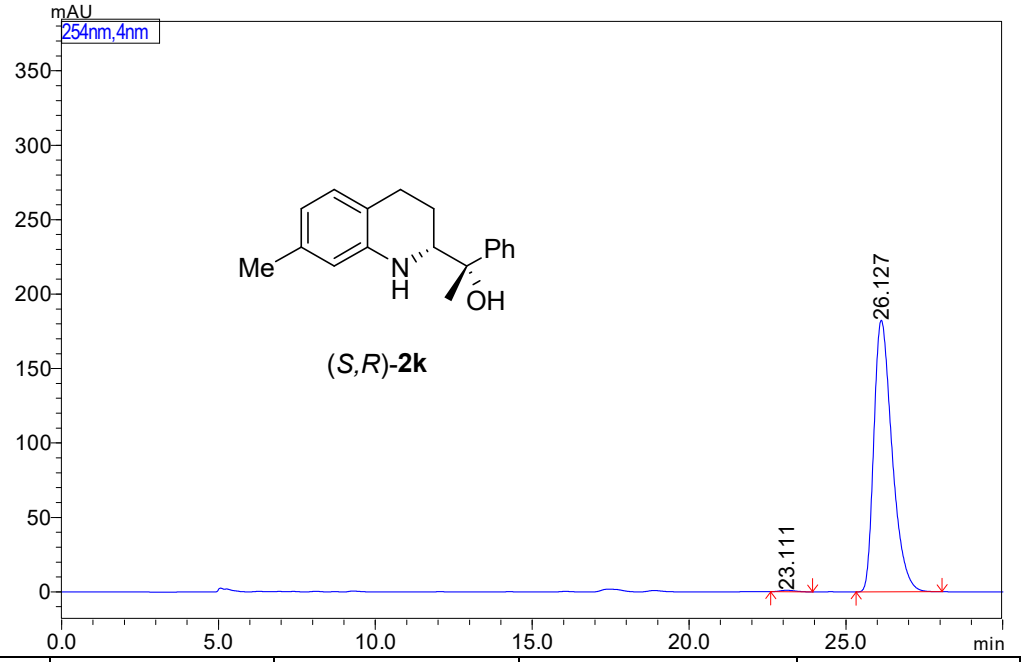
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	17.439	20.343	14697567	558521
2	22.408	18.297	13219508	458743
3	23.162	31.912	23055940	623363
4	26.507	29.448	21275363	531322
总计		100.000	72248378	2171950



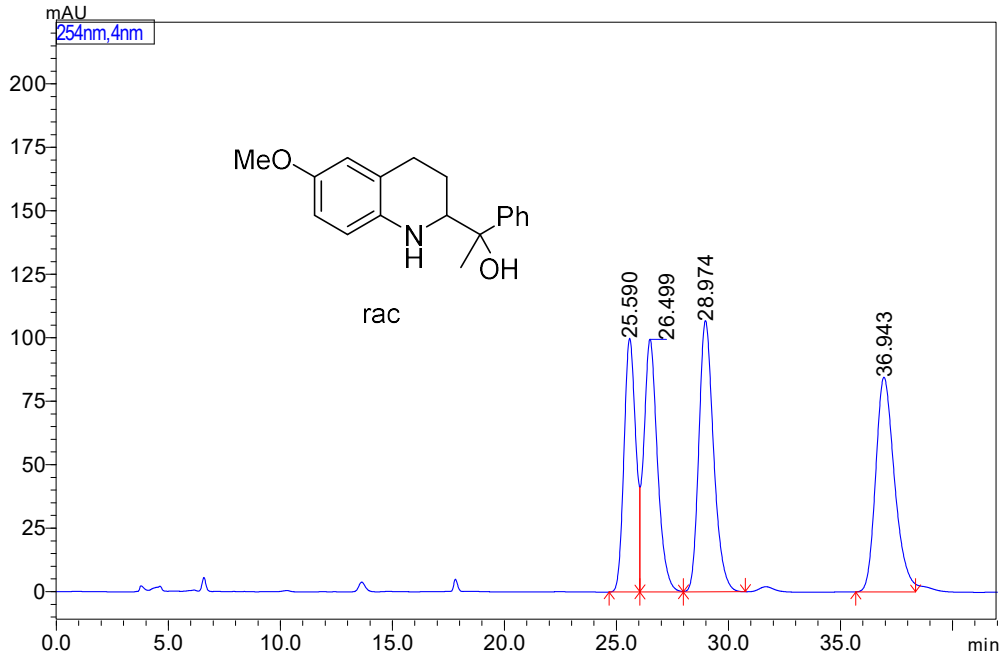
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	17.250	99.400	47467145	1560722
2	21.942	0.600	286574	10731
总计		100.000	47753719	1571452



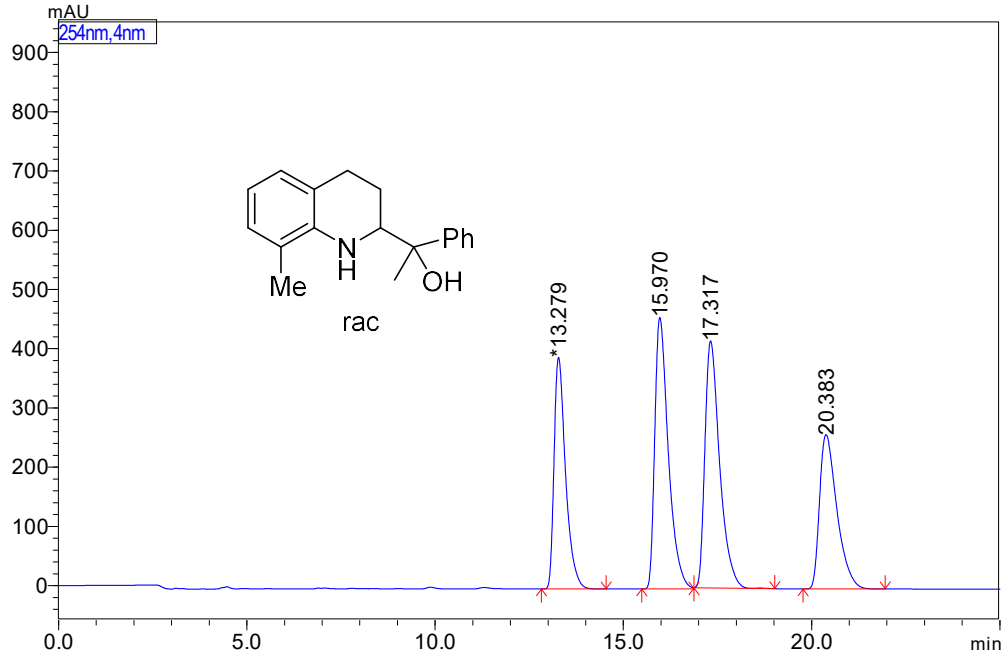
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	23.111	0.465	34453	1011
2	26.127	99.535	7371941	182401
总计		100.000	7406394	183412



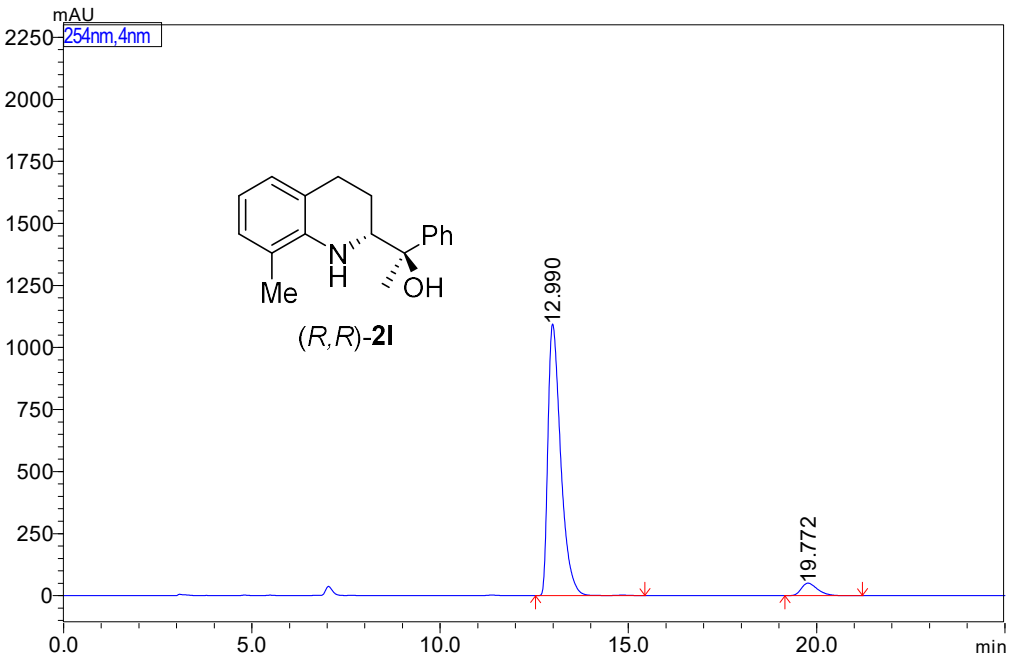
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	25.590	20.638	3656208	99962
2	26.499	23.854	4225785	99548
3	28.974	27.583	4886395	106828
4	36.943	27.925	4947151	84620
总计		100.000	17715540	390958



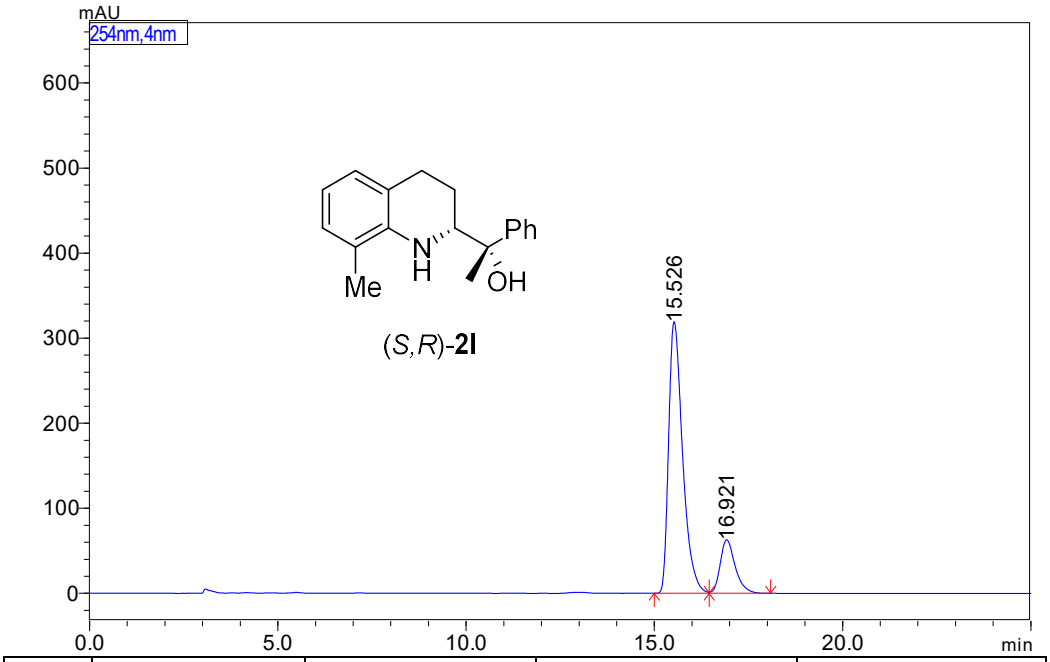
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	13.279	21.054	8316147	390940
2	15.970	29.017	11461279	458080
3	17.317	28.746	11354324	416849
4	20.383	21.182	8366495	260527
总计		100.000	39498245	1526396



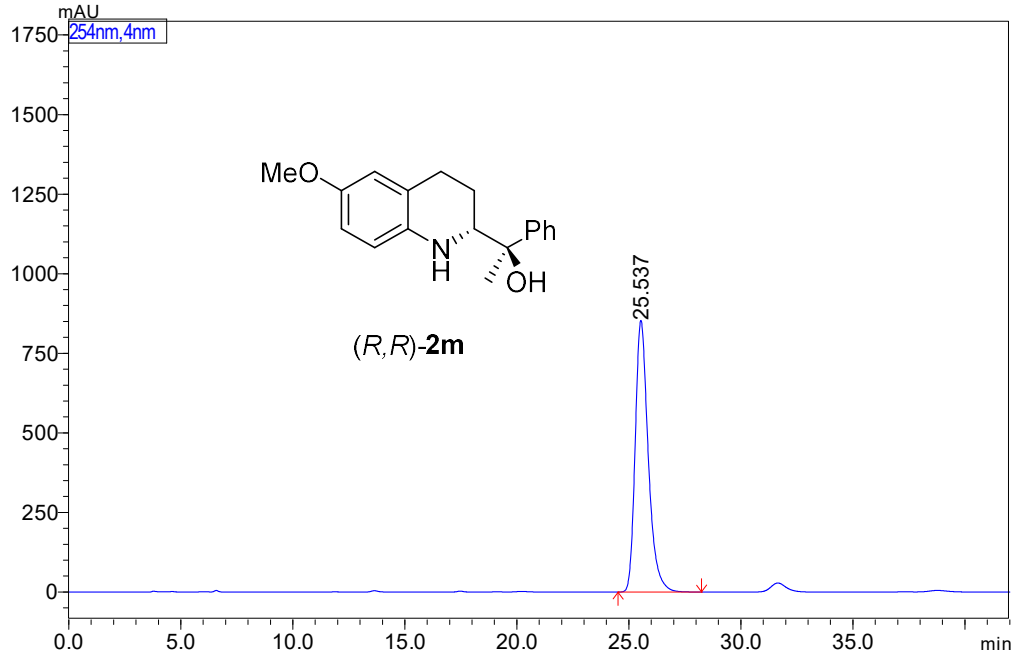
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	12.990	94.475	25809878	1094768
2	19.772	5.525	1509374	50487
总计		100.000	27319252	1145254



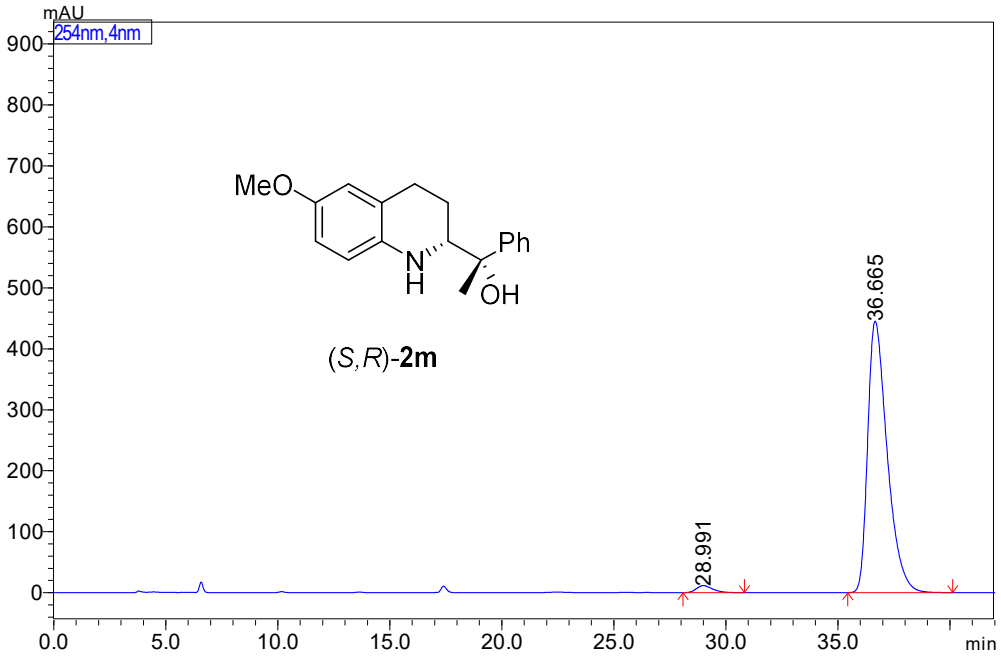
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	15.526	82.577	8246645	319344
2	16.921	17.423	1739963	62848
总计		100.000	9986608	382192



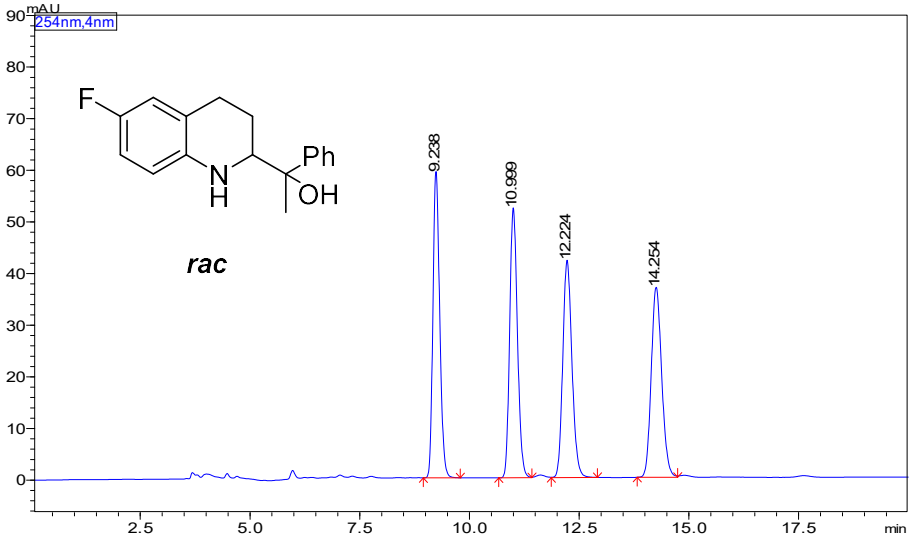
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	25.537	100.000	34582653	853486
总计		100.000	34582653	853486



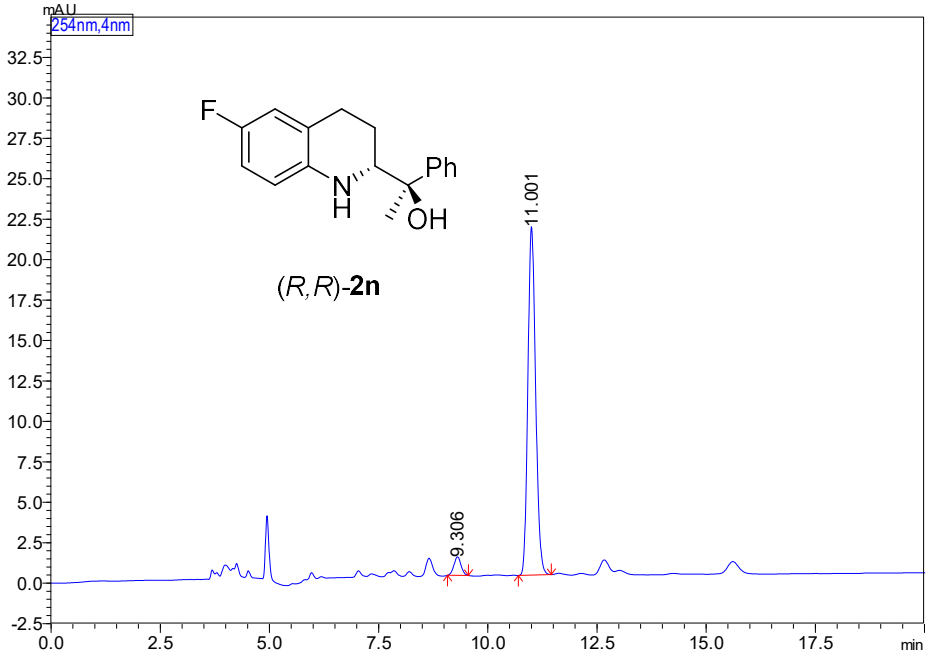
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	28.991	2.143	590679	11603
2	36.665	97.857	26973614	445272
总计		100.000	27564293	456875



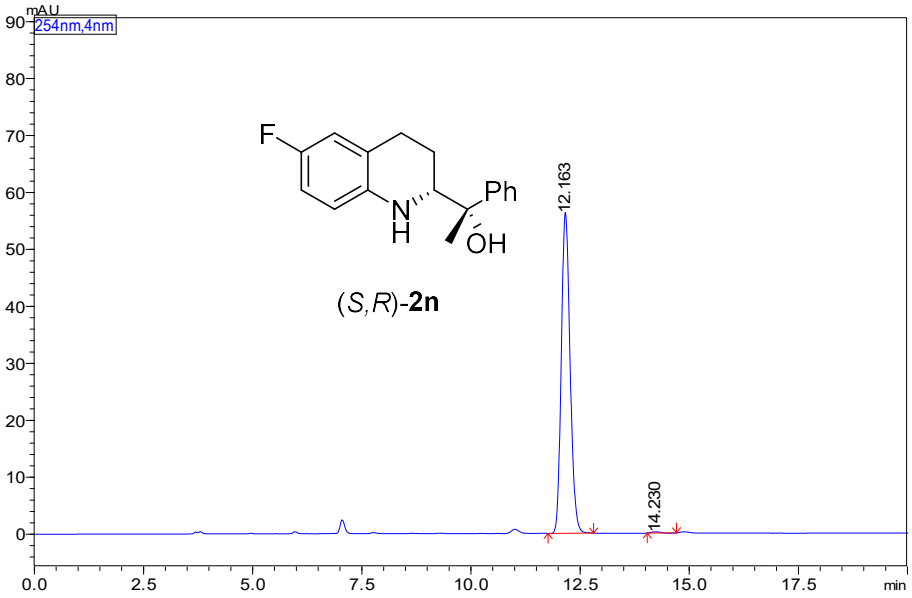
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	9.238	25.437	636735	59317
2	10.999	25.658	642260	52288
3	12.224	24.480	612768	42072
4	14.254	24.424	611373	36805
总计		100.000	2503136	190483



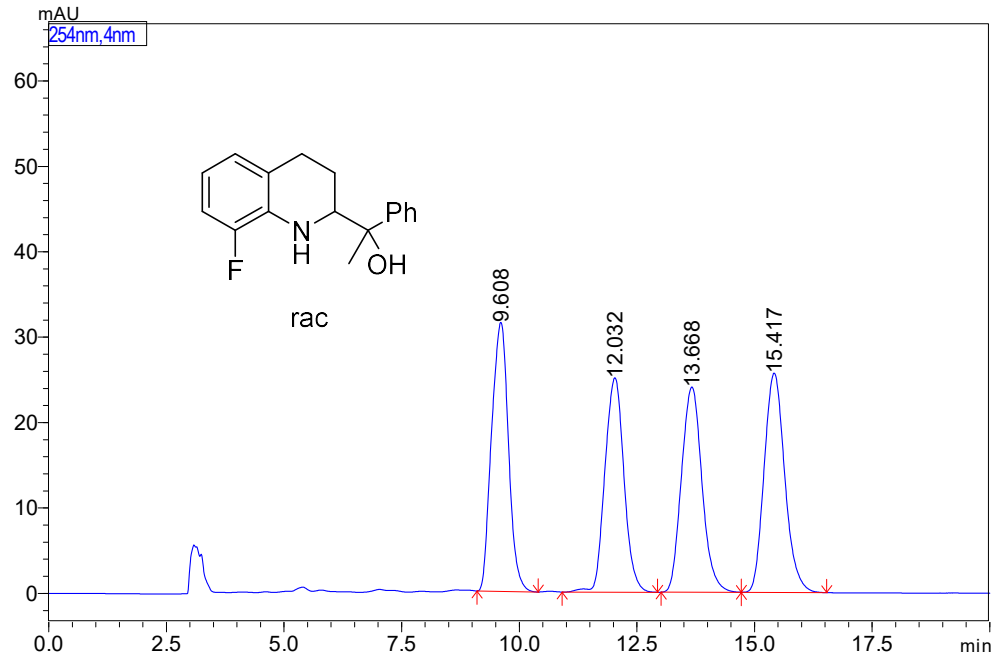
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	9.306	4.692	13095	1144
2	11.001	95.308	265977	21534
总计		100.000	279072	22679



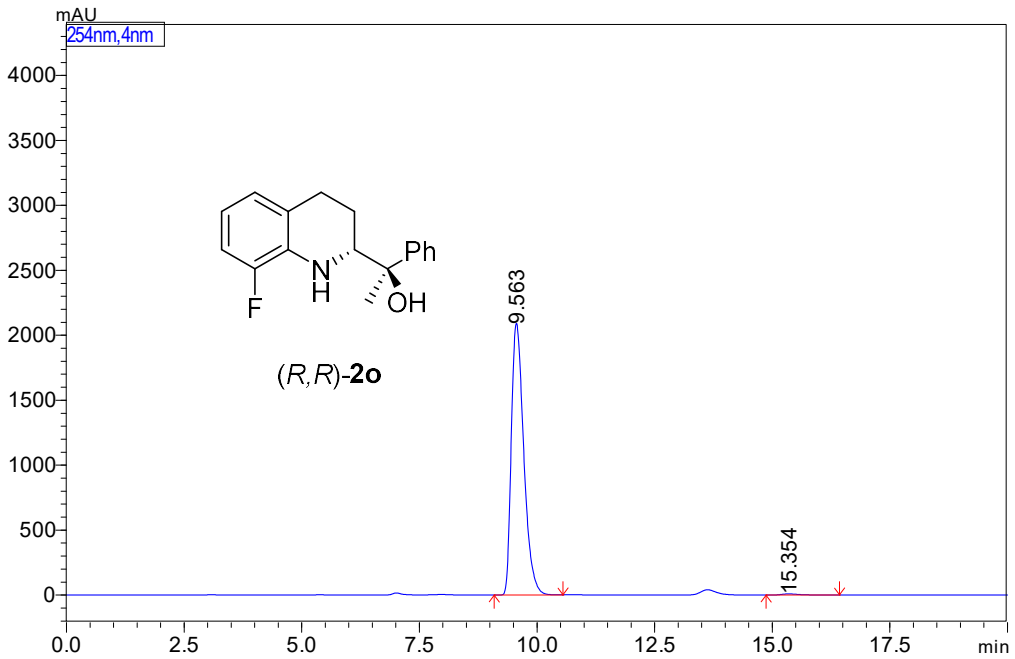
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	12.163	99.738	787883	56306
2	14.230	0.262	2072	207
总计		100.000	789955	56514



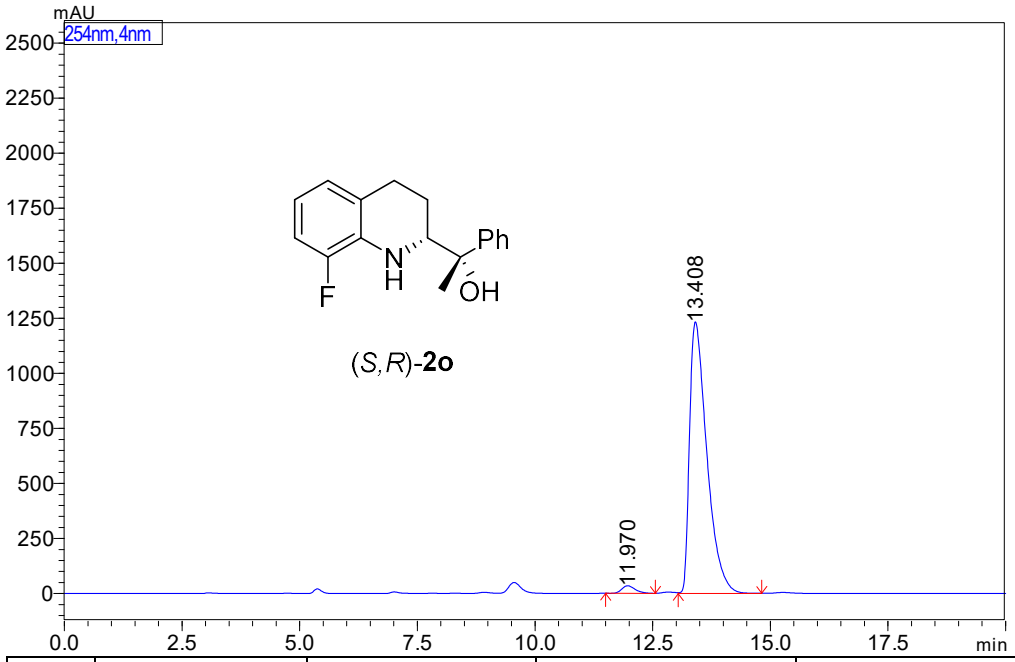
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	9.608	26.128	787610	31506
2	12.032	23.546	709783	25111
3	13.668	24.261	731347	24038
4	15.417	26.066	785741	25685
总计		100.000	3014482	106341



Peak	Time (min)	Area (%)	Area	Height

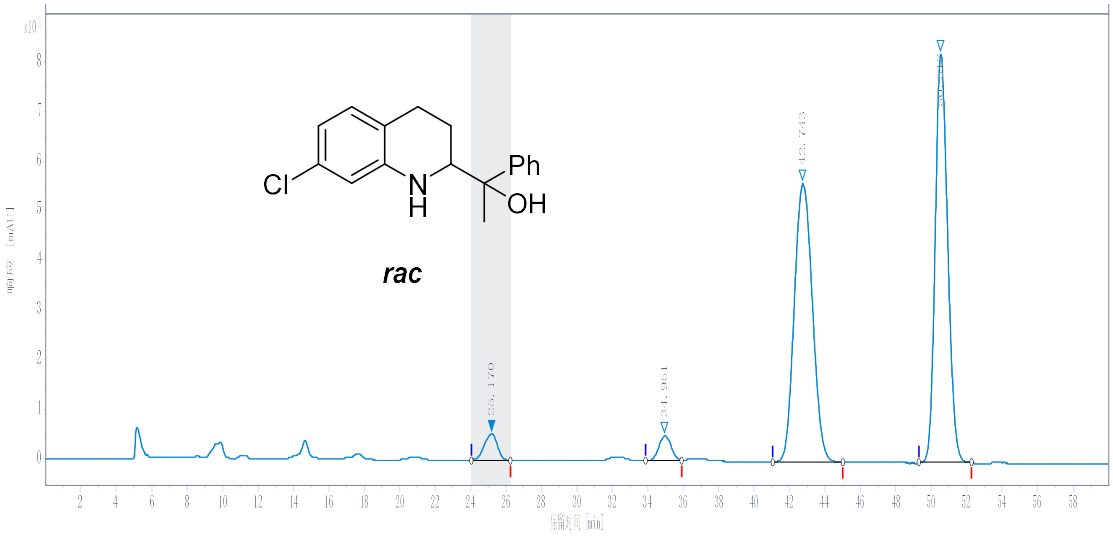
峰号	保留时间	面积%	面积	高度
1	9.563	99.415	38560913	2090206
2	15.354	0.585	227060	8657
总计		100.000	38787973	2098863



(*S*,*R*)-**2o**

Peak	Time (min)	Area (%)	Area	Height

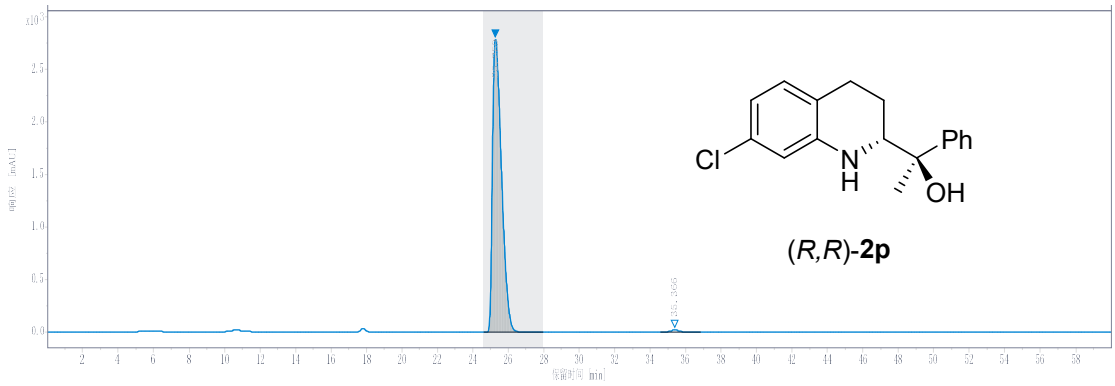
峰号	保留时间	面积%	面积	高度
1	11.970	2.103	678039	34376
2	13.408	97.897	31563338	1233822
总计		100.000	32241377	1268198



rac

Peak	Time (min)	Area	Area (%)	Height	Height (%)

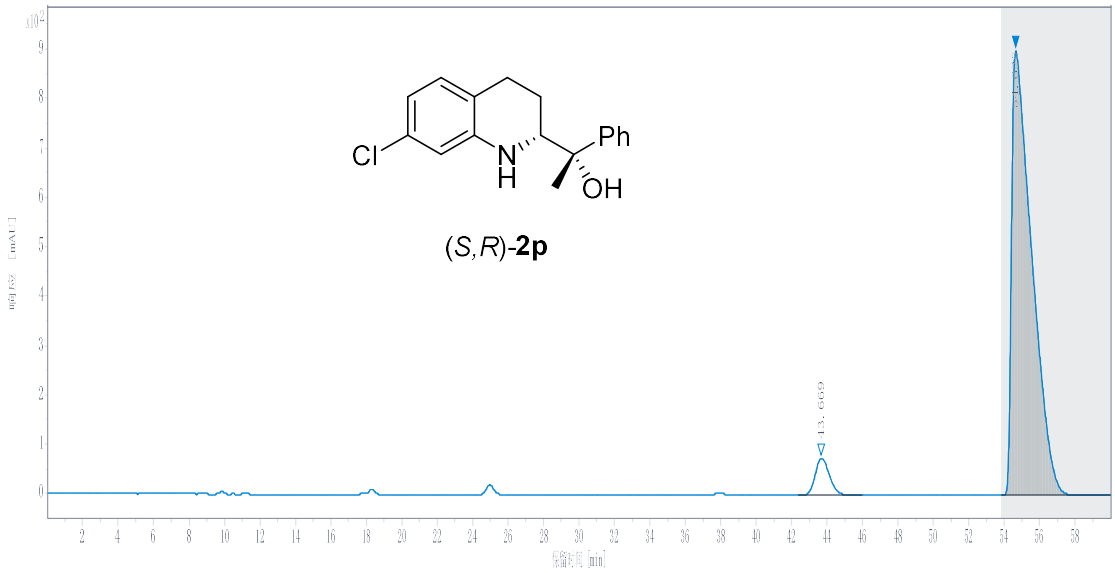
#	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%
1	25.170	265.846	3.11	5.255	3.53
2	34.951	243.026	2.84	4.985	3.34
3	42.743	3999.565	46.81	56.226	37.72
4	50.517	4036.282	47.24	82.577	55.41



(*R*,*R*)-**2p**

Peak	Time (min)	Area	Area (%)	Height	Height (%)

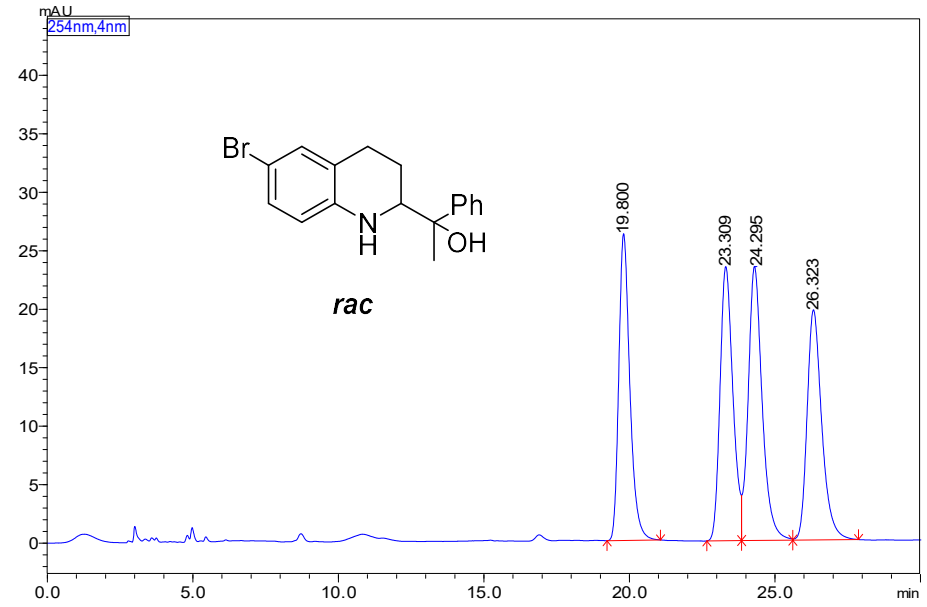
#	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%
1	25.259	98614.603	99.16	2781.161	99.23
2	35.366	837.179	0.84	21.686	0.77



(*S*,*R*)-**2p**

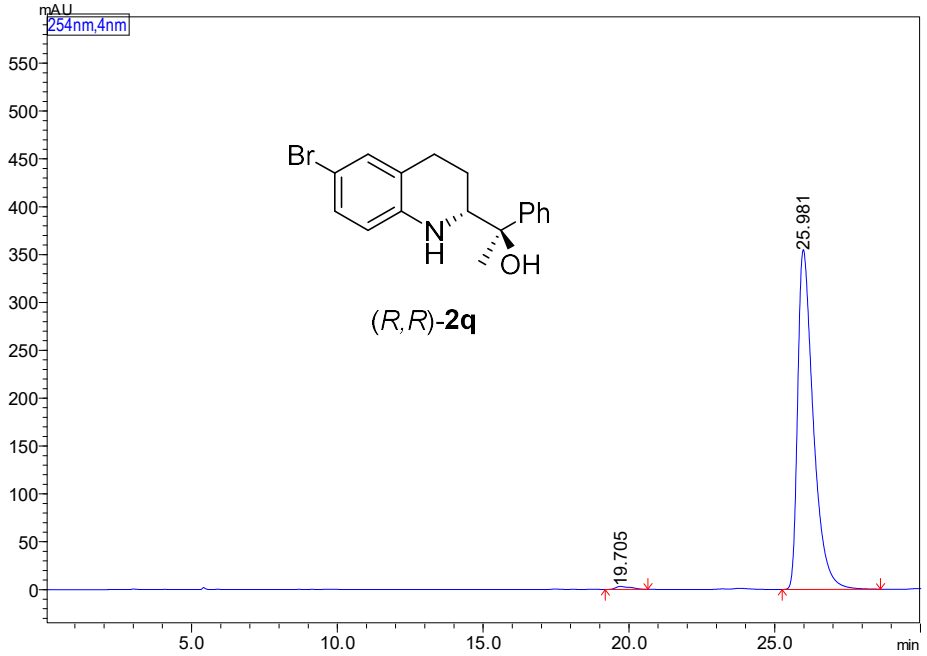
Peak	Time (min)	Area	Area (%)	Height	Height (%)

#	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%
1	43.669	4129.615	5.48	75.134	7.71
2	54.625	71204.602	94.52	899.952	92.29



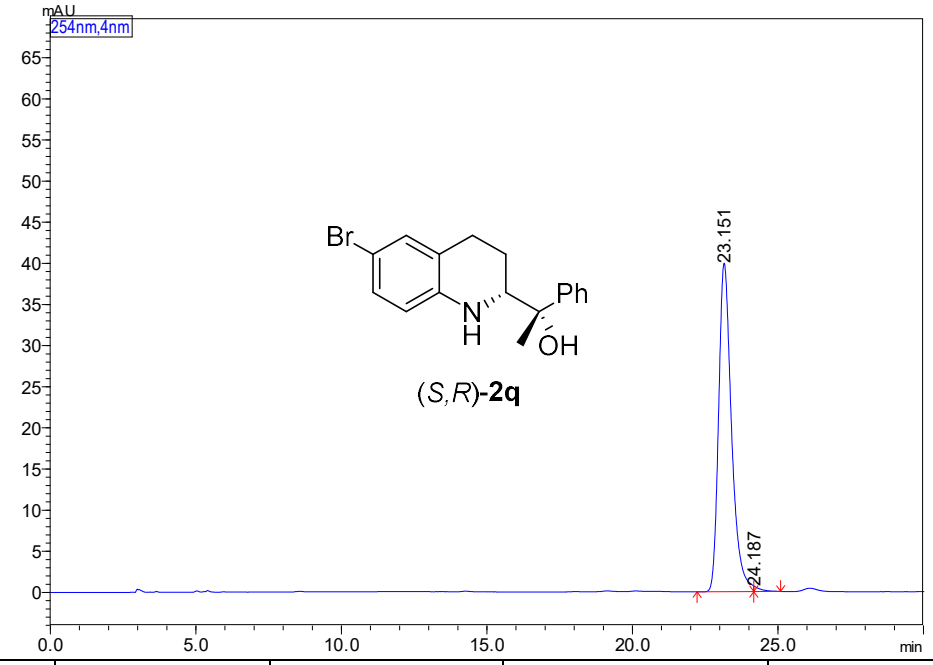
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	19.800	23.993	692956	26231
2	23.309	24.971	721200	23441
3	24.295	27.103	782774	23431
4	26.323	23.933	691213	19683
总计		100.000	2888143	92786



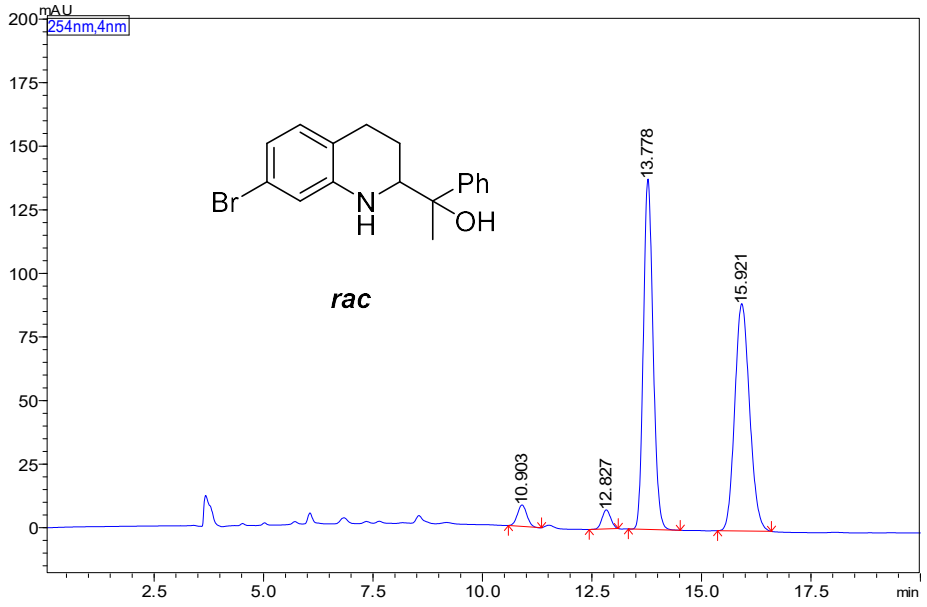
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	19.705	0.859	114329	3147
2	25.981	99.141	13187486	355077
总计		100.000	13301815	358225



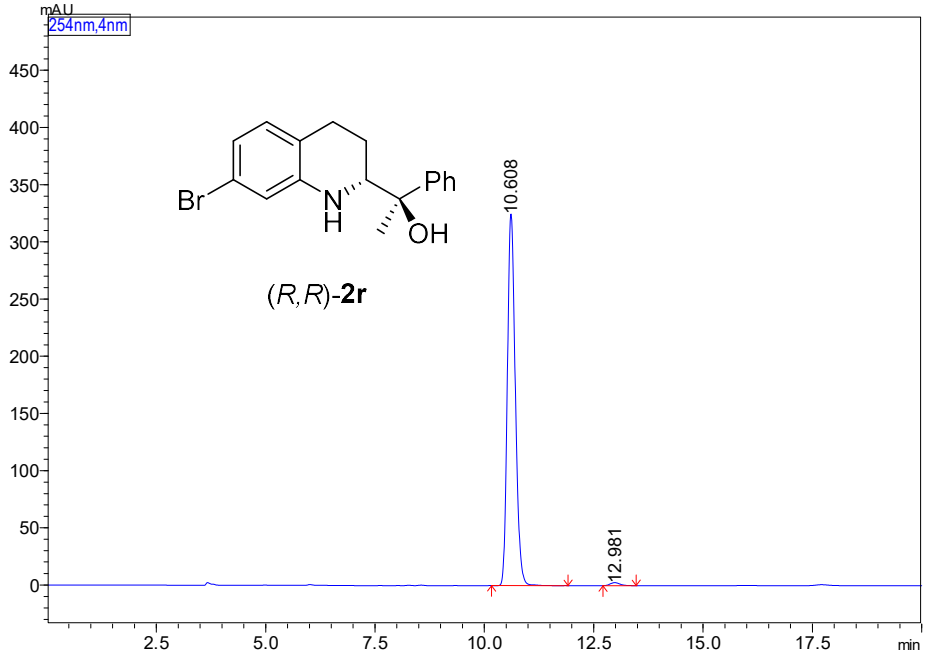
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	23.151	99.213	1227127	39921
2	24.187	0.787	9736	650
总计		100.000	1236864	40571



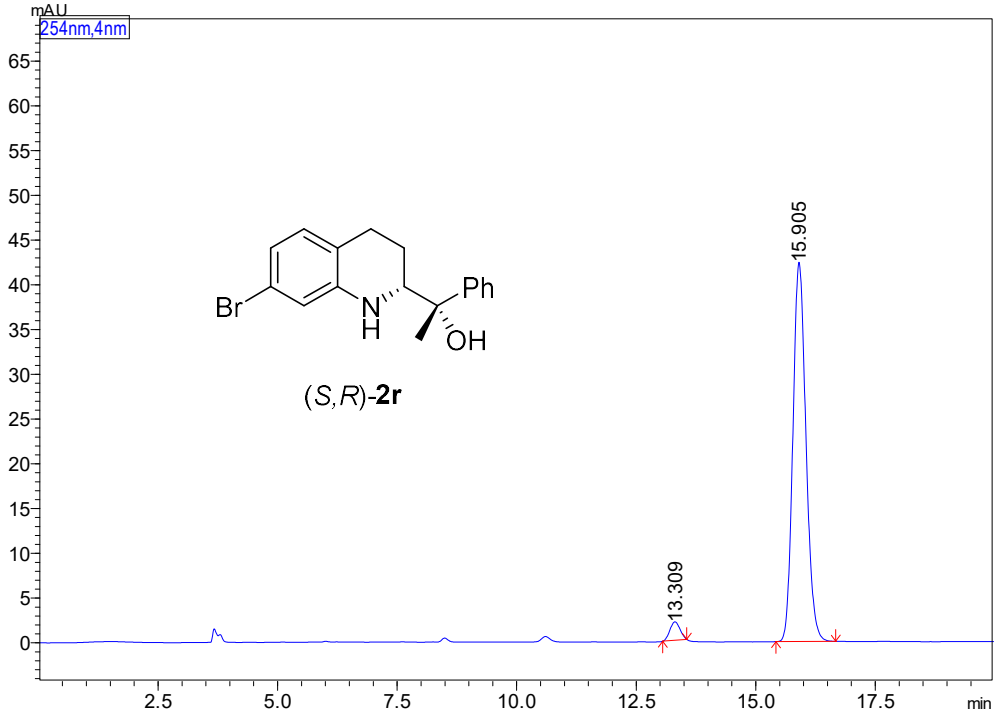
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	10.903	2.809	124991	8417
2	12.827	2.321	103268	7458
3	13.778	47.587	2117503	137810
4	15.921	47.283	2103973	89402
总计		100.000	4449735	243086



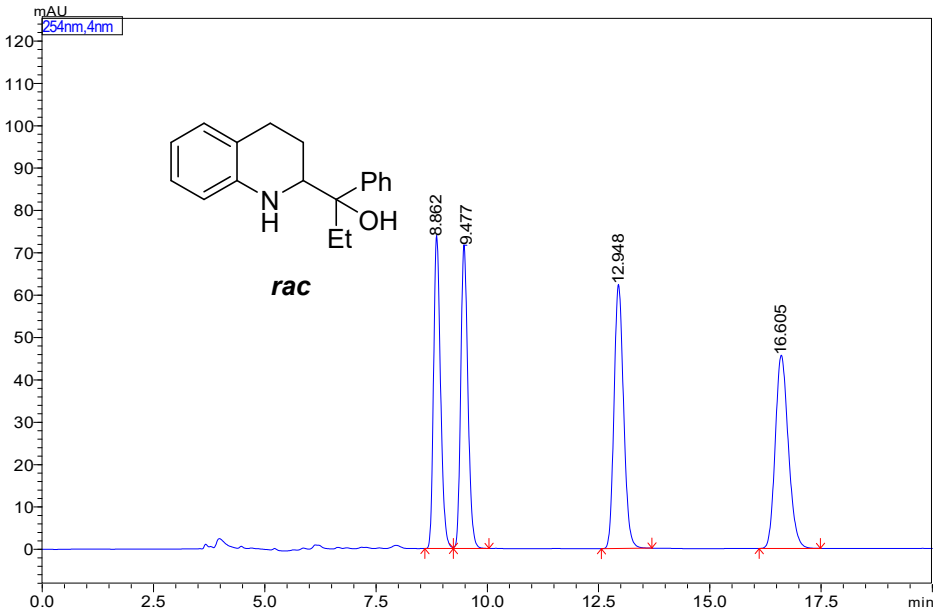
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	10.608	99.034	4110523	324706
2	12.981	0.966	40113	2655
总计		100.000	4150635	327361



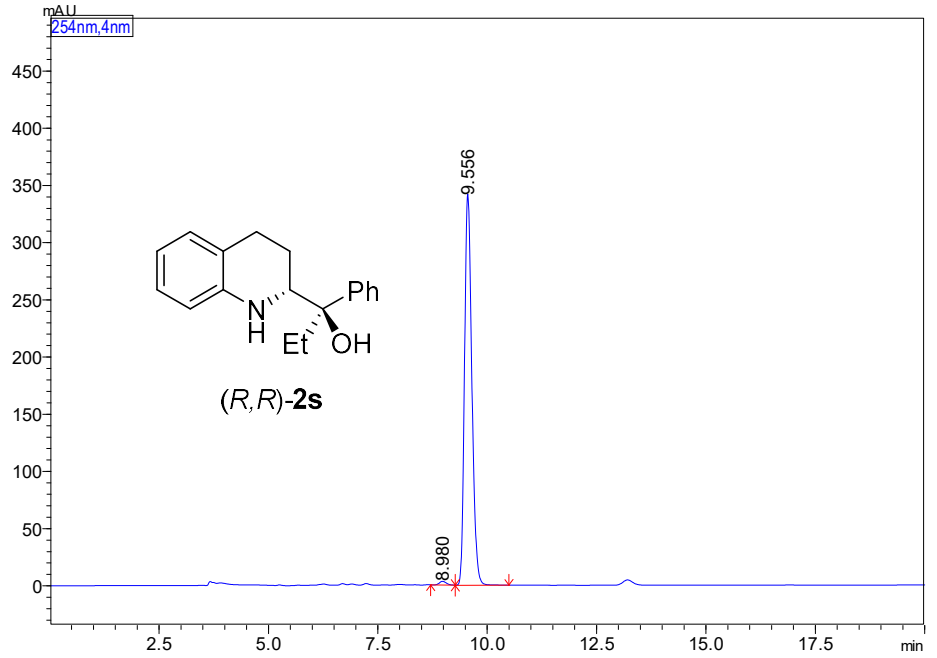
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	13.309	3.605	30128	2057
2	15.905	96.395	805585	42365
总计		100.000	835713	44421



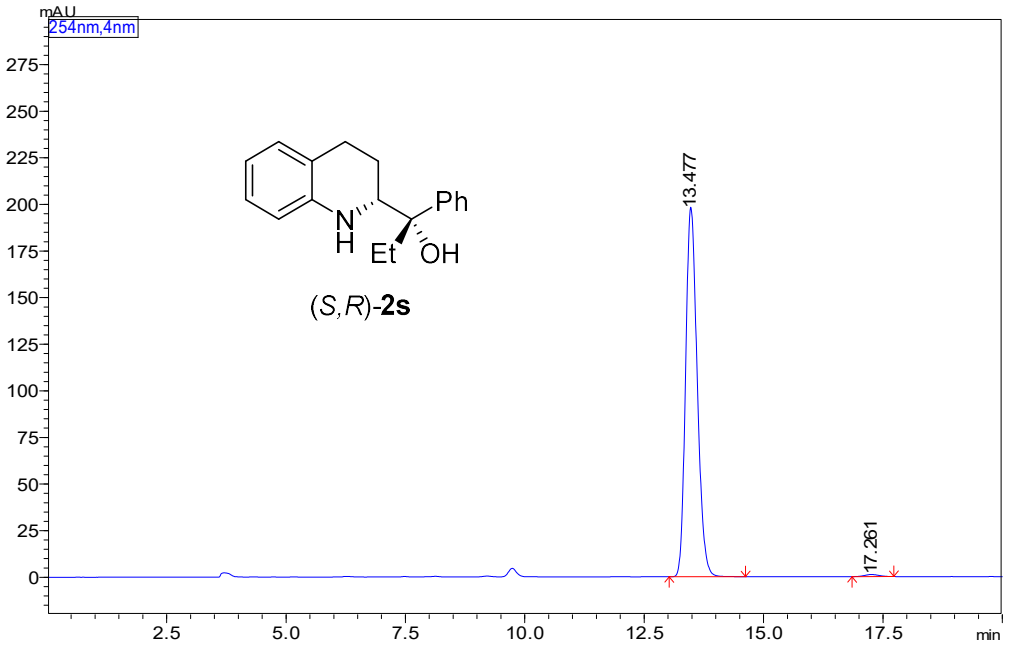
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	8.862	23.164	803373	73870
2	9.477	23.114	801608	71654
3	12.948	26.852	931246	62383
4	16.605	26.870	931897	45632
总计		100.000	3468124	253539

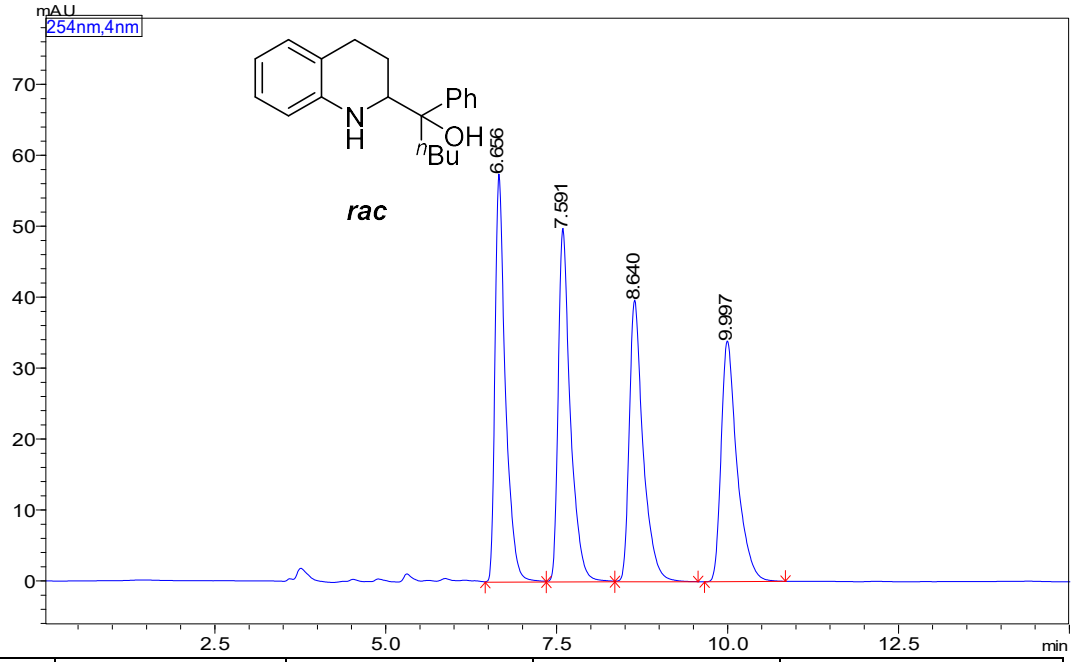


Peak	Time (min)	Area (%)	Area	Height

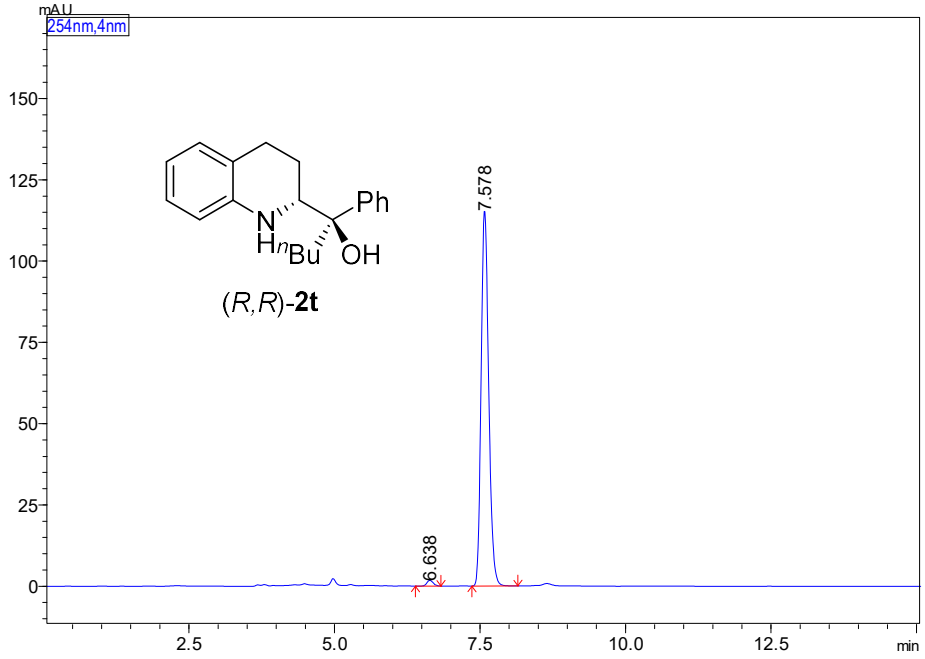
峰号	保留时间	面积%	面积	高度
1	8.980	0.860	34476	3180
2	9.556	99.140	3975261	341921
总计		100.000	4009737	345101



Peak	Time (min)	Area (%)	Area	Height
峰号	保留时间	面积%	面积	高度
1	13.477	99.302	3349416	198167
2	17.261	0.698	23537	1110
总计		100.000	3372953	199277

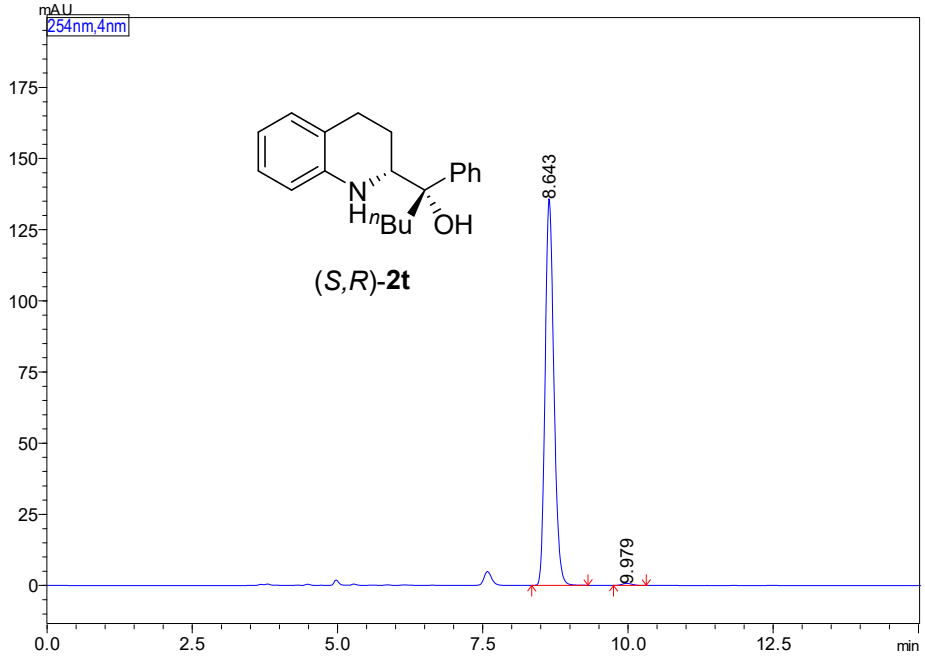


Peak	Time (min)	Area (%)	Area	Height
峰号	保留时间	面积%	面积	高度
1	6.656	26.175	611461	57525
2	7.591	26.338	615267	49839
3	8.640	23.935	559152	39725
4	9.997	23.552	550204	33934
总计		100.000	2336084	181023



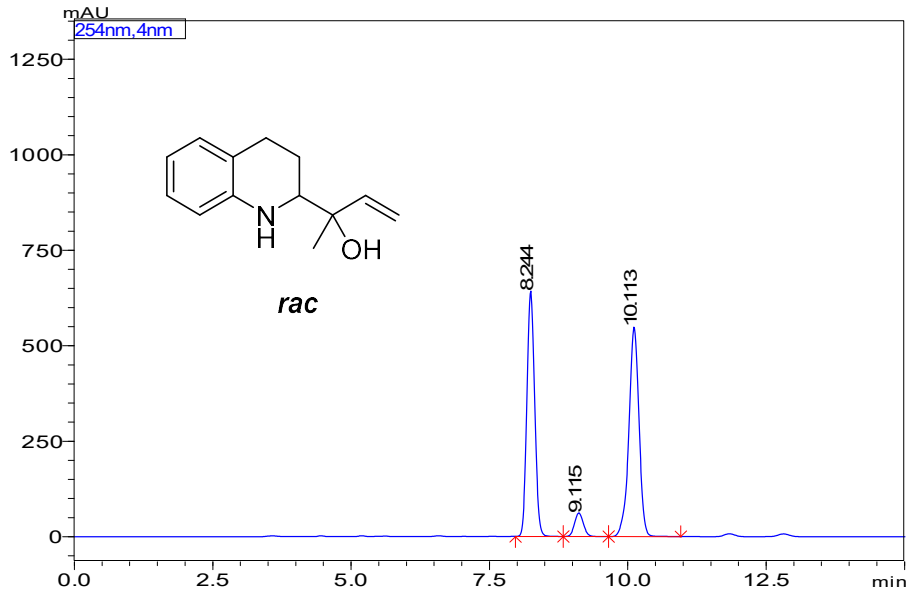
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	6.638	1.241	13154	1755
2	7.578	98.759	1046694	115245
总计		100.000	1059848	117000



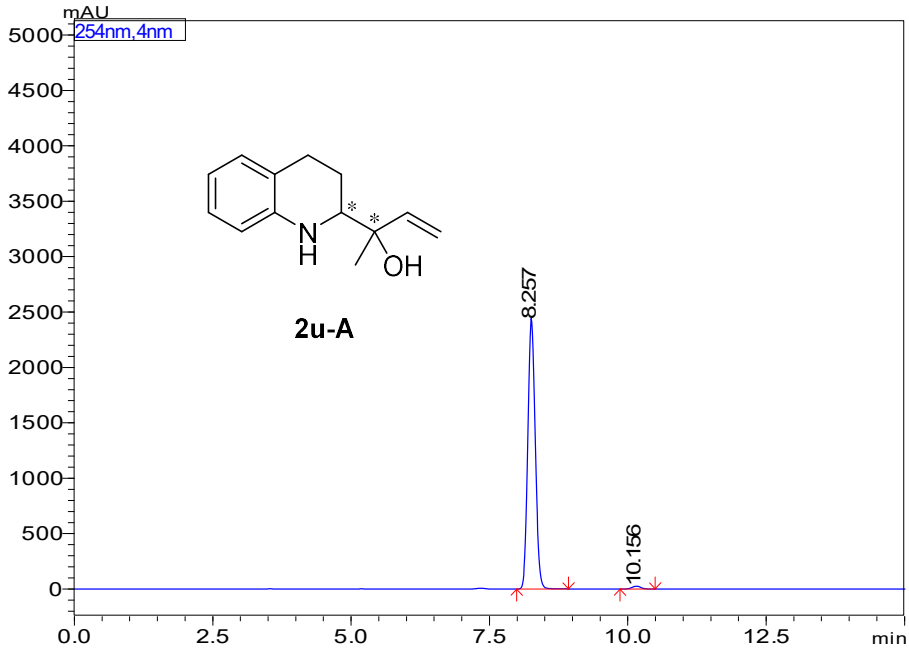
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	8.643	99.392	1423827	135833
2	9.979	0.608	8708	720
总计		100.000	1432535	136553



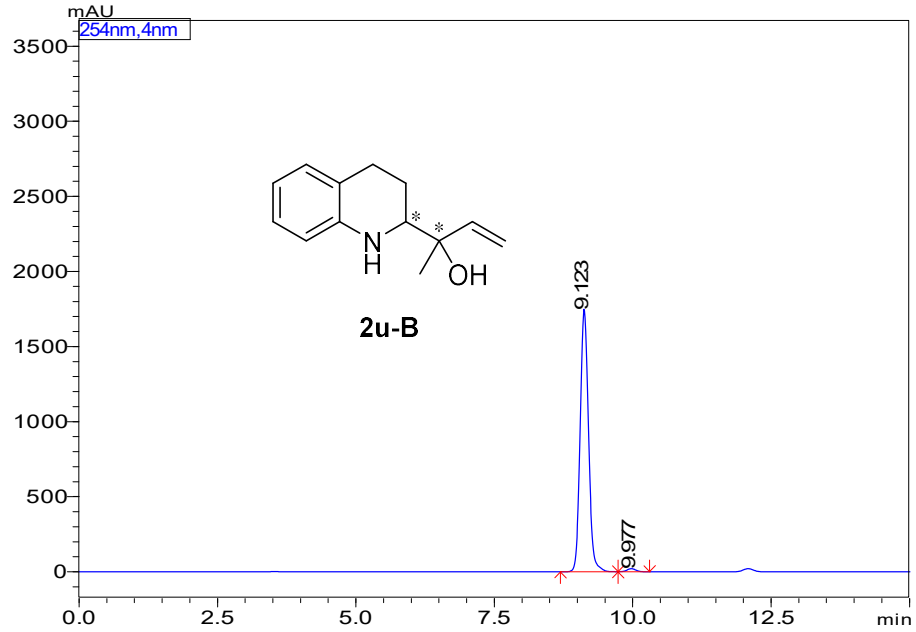
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	8.244	45.081	6325585	642924
2	9.115	4.997	701220	62141
3	10.113	49.922	7004915	548687
总计		100.000	14031720	1253752



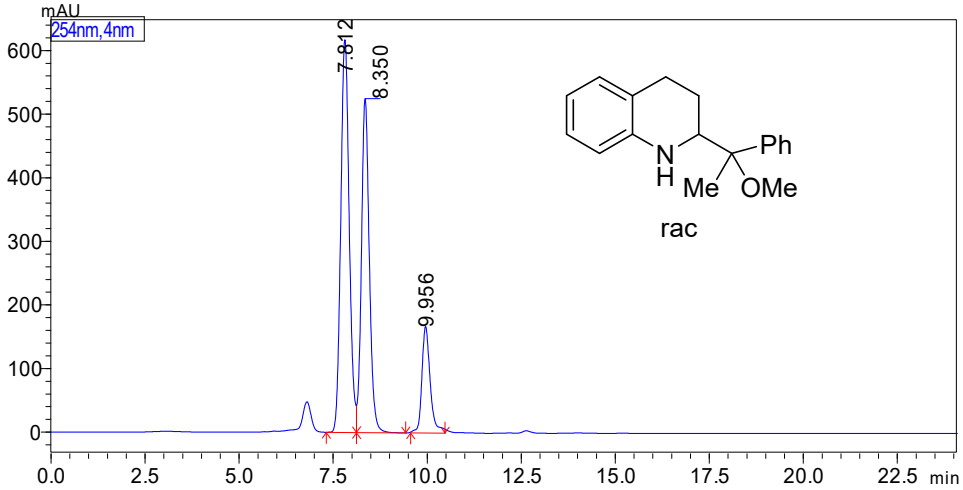
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	8.257	98.778	22932461	2441311
2	10.156	1.222	283677	25631
总计		100.000	23216138	2466942



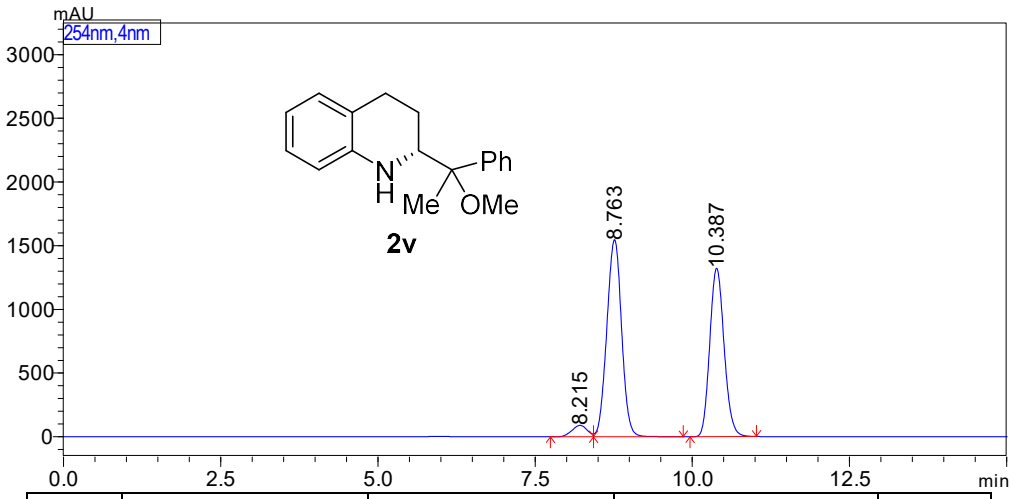
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	9.123	98.702	18398841	1747520
2	9.977	1.298	241981	21067
总计		100.000	18640821	1768587



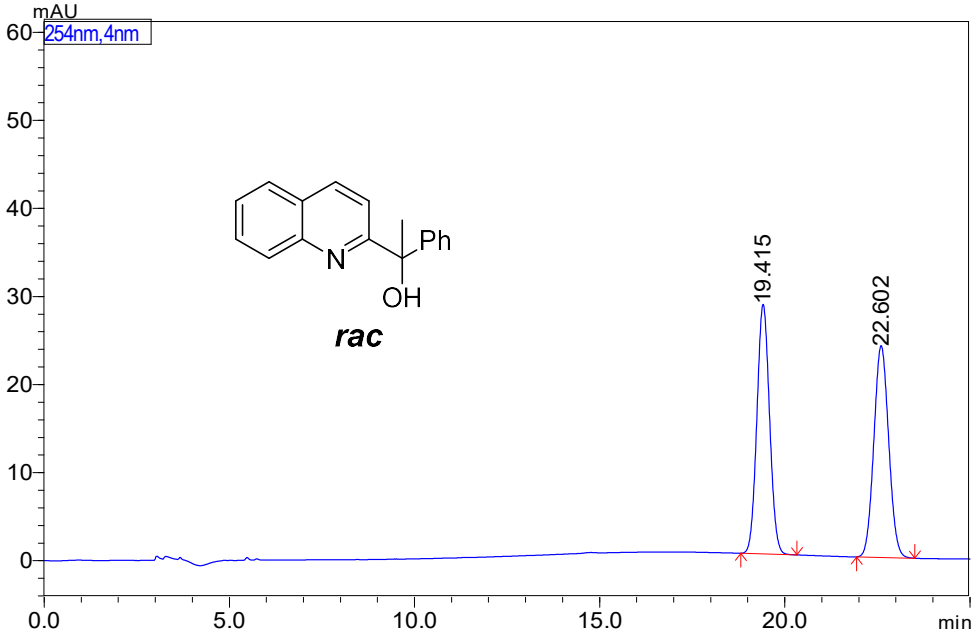
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	7.812	48.557	9659839	617605
2	8.350	38.448	7648845	525356
3	9.956	12.995	2585172	167680
总计		100.000	19893856	1310640



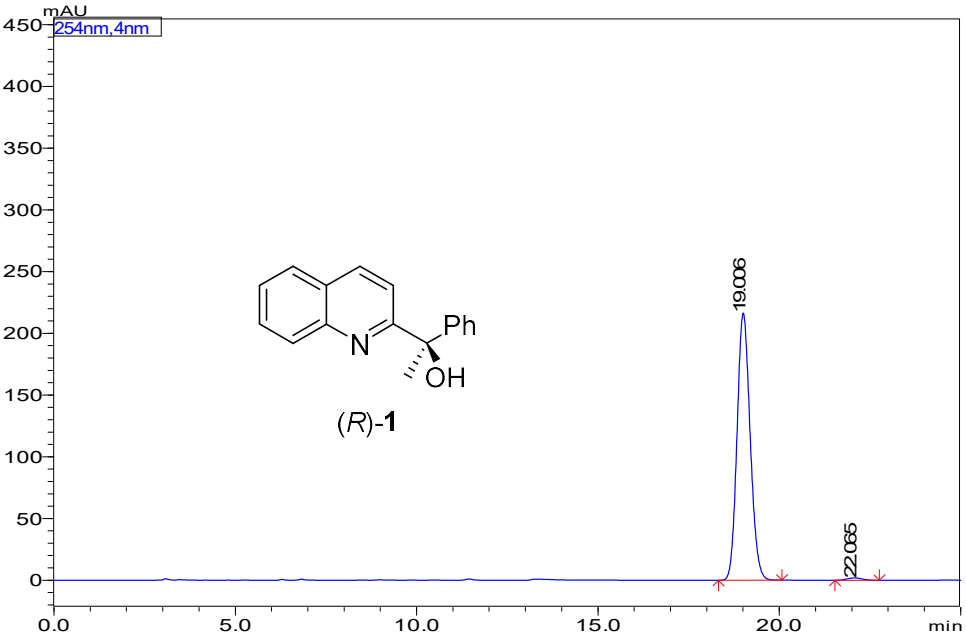
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	8.215	3.156	1508251	89768
2	8.763	52.894	25280516	1545574
3	10.387	43.950	21005759	1322502
总计		100.000	47794527	2957844



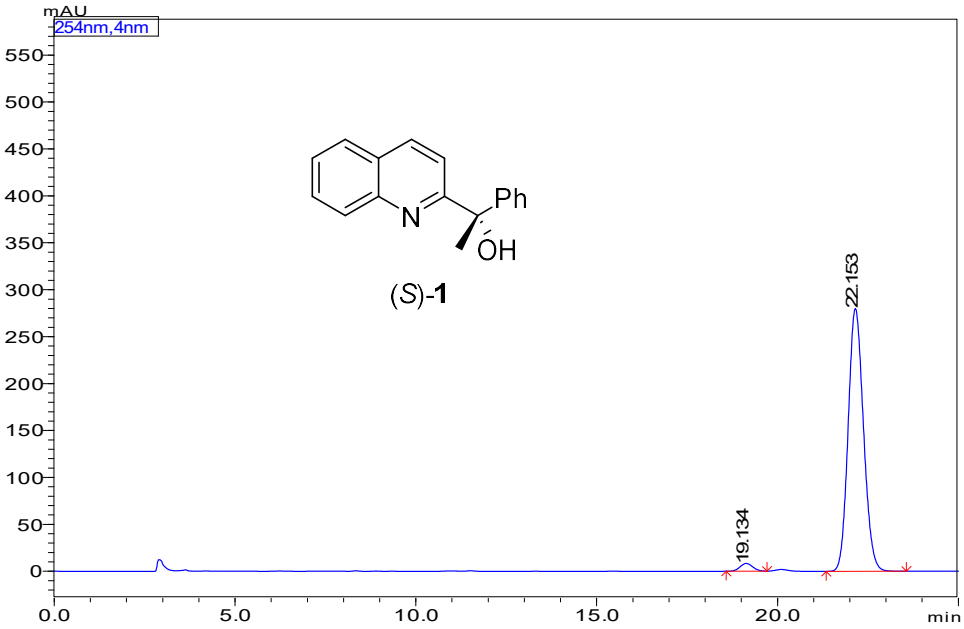
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	19.414	50.007	603125	25480
2	22.602	49.993	602957	21685
总计		100.000	1206081	47165



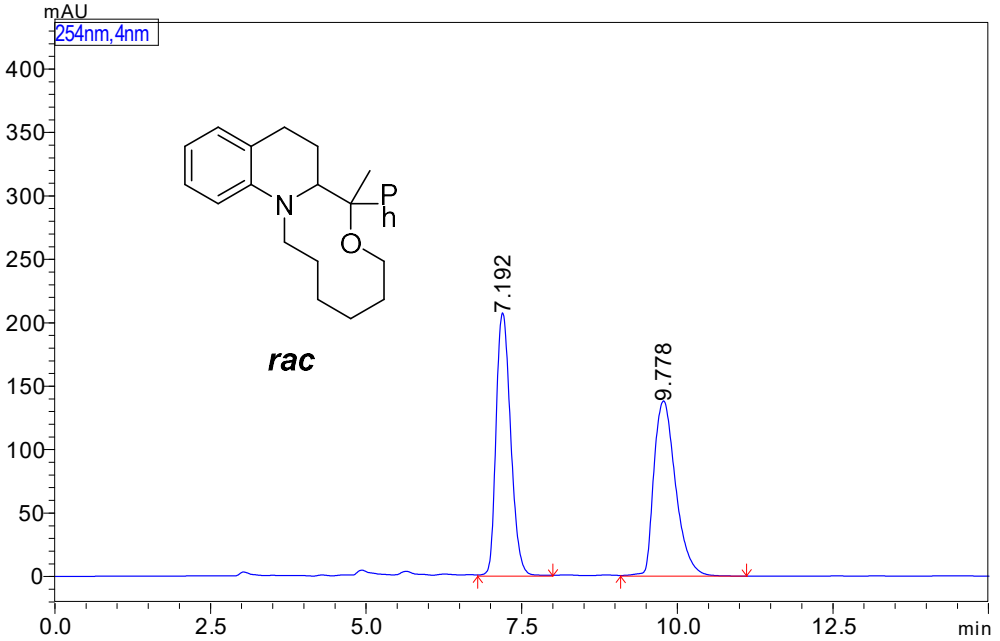
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	19.006	99.036	5439665	216444
2	22.065	0.964	52929	1870
总计		100.000	5492593	218313



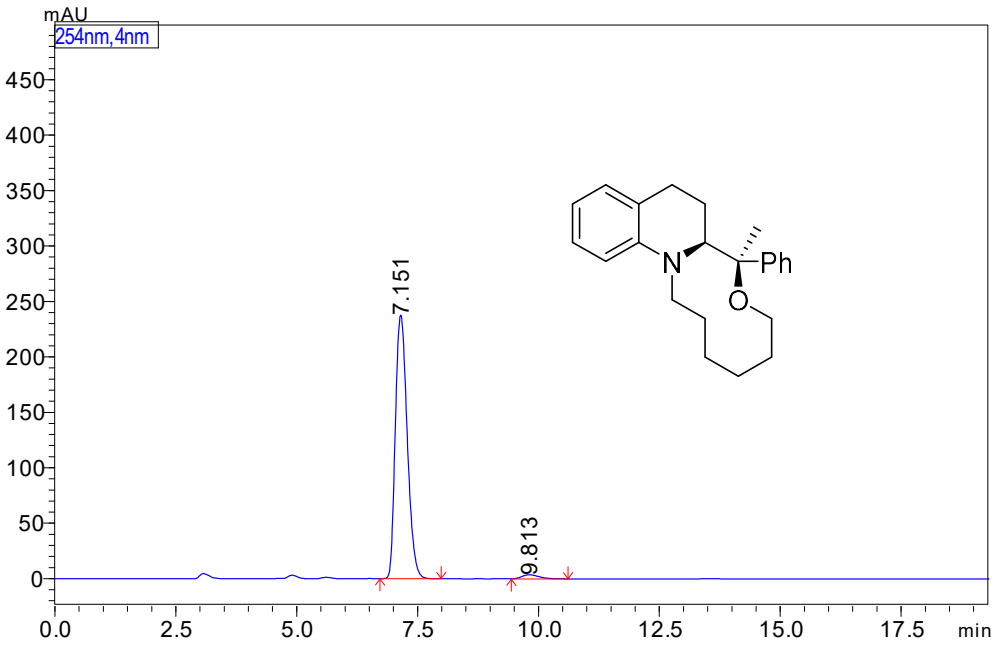
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	19.134	2.460	208292	8357
2	22.153	97.540	8257804	279998
总计		100.000	8466096	288355



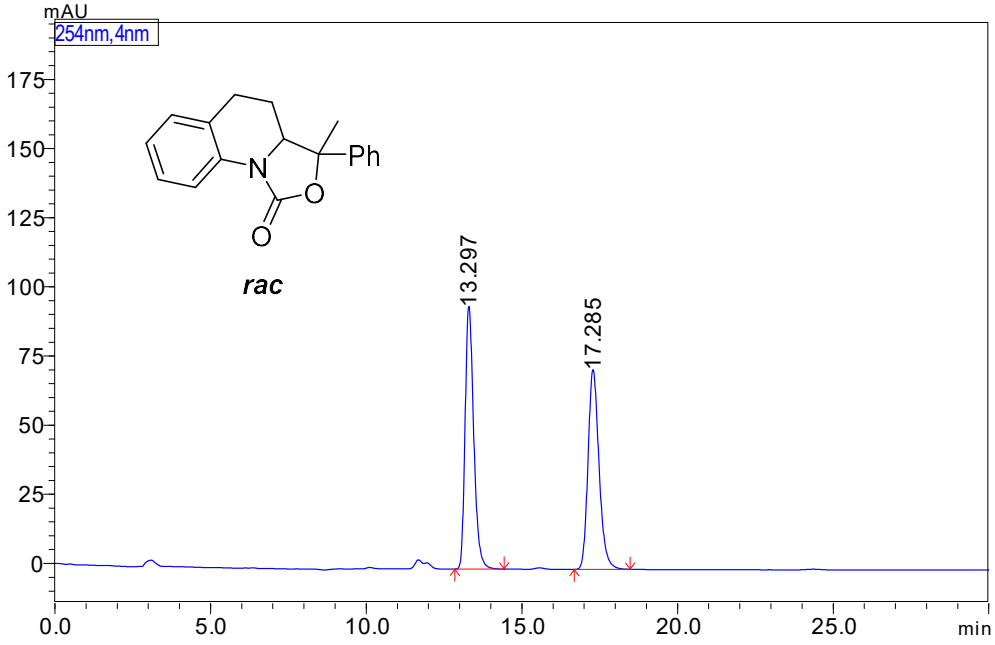
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	7.192	50.240	3396789	207533
2	9.778	49.760	3364271	138145
总计		100.000	6761060	345678



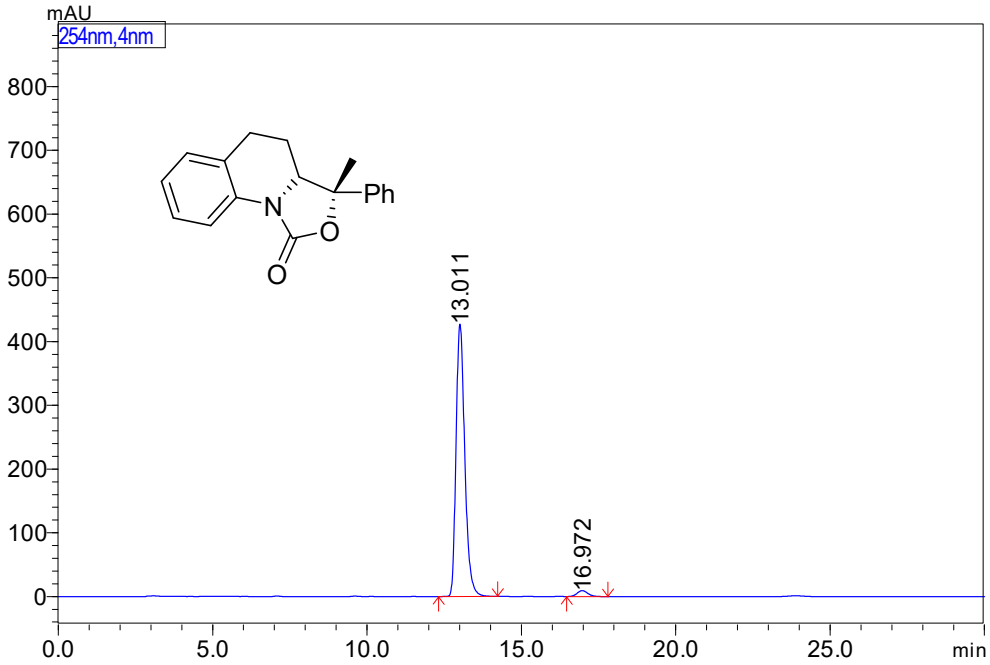
Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	7.151	97.802	4058814	237645
2	9.813	2.198	91233	3642
总计		100.000	4150047	241287



Peak	Time (min)	Area (%)	Area	Height

峰号	保留时间	面积%	面积	高度
1	13.297	50.699	1830284	94992
2	17.285	49.301	1779850	72260
总计		100.000	3610135	167251



Peak	Time (min)	Area (%)	Area	Height
峰号	保留时间	面积%	面积	高度
1	13.011	97.356	8431573	427528
2	16.972	2.644	229026	9438
总计		100.000	8660600	436967

8. Crystallographic Information

The crystal was obtained via slow evaporation of a solution of (*R*)-**1** (>99% ee) in DCM to hexane in a freezer.

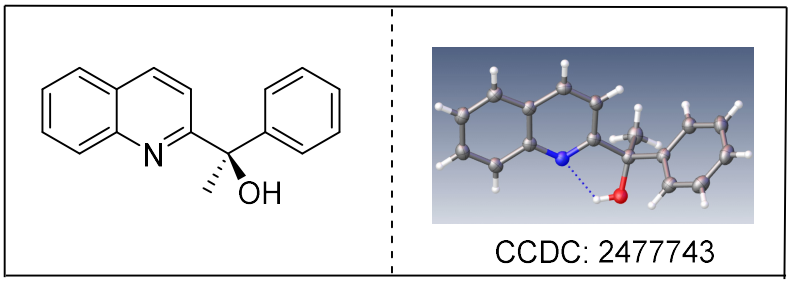


Figure 4. The X-ray structure of (*R*)-**1a**.

Table S1. Crystal data and structure refinement for (*R*)-**1a**

Bond precision: C-C = 0.0032 A Wavelength = 1.34138

Cell: a = 5.7891(7) b = 7.6847(9) c = 14.5137(18)

alpha = 90 beta = beta=93.419(6) gamma = 90

Temperature: 150 K

	Calculated	Reported
Volume	644.53(13)	644.53(13)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C17 H15 N O	C17 H15 N O
Sum formula	C17 H15 N O	C17 H15 N O
Mr	249.30	249.30
Dx,g cm-3	1.285	1.285
Z	2	2
Mu (mm-1)	0.398	0.414
F000	264.0	264.0
F000’	264.55	
h, k, lmax	7,9,18	7,9,18
Nref	2654[1431]	2630

Tmin, Tmax	0.917,0.940	0.619,0.751
Tmin'	0.917	
Correction method = # Reported T Limits:	T min=0.619	T max=0.751
AbsCorr = NONE		
Data completeness =1.84/0.99	Theta(max) = 57.101	
R(reflections) = 0.0358 (2506)	wR2(reflections) = 0.0908 (2630)	
S = 1.078	Npar = 17	

The crystal was obtained via slow evaporation of a solution of (*S*)-**1a** (>99% ee) in DCM to hexane in a freezer.

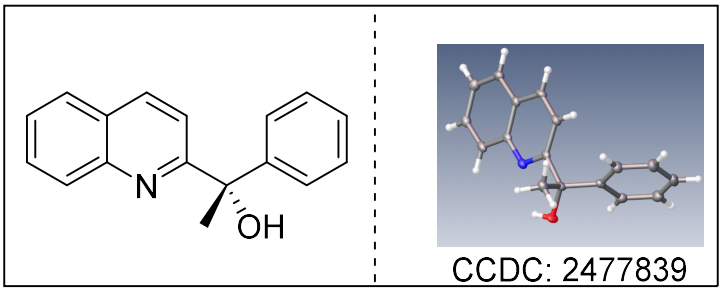


Figure 5. The X-ray structure of (*S*)-**1a**.

Table S2. Crystal data and structure refinement for (*S*)-**1a**

Bond precision: C-C = 0.0042 A	Wavelength = 1.54178	
Cell:	a = 5.7693(2)	b = 7.6573(2) c = 14.5001(5)
	alpha = 90	beta = 93.440(2) gamma = 90
Temperature: 100 K		
	Calculated	Reported
Volume	639.42(4)	639.42(4)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C17H15NO	2(C17H15NO)
Sum formula	C17H15NO	C34H30N2O2
Mr	249.30	498.60

Dx,g cm-3	1.295	1.295
Z	2	1
Mu (mm-1)	0.630	0.630
F000	264.0	264.0
F000’	264.74	
h, k, lmax	6,9,17	6,9,17
Nref	2349[1268]	2334
Tmin, Tmax	0.882,0.882	0.603,0.753
Tmin’	0.882	

Correction method = # Reported T Limits: T min=0.603 T max=0.753

AbsCorr = NONE

Data completeness =1.84/0.99	Theta(max) = 68.436
R(reflections) = 0.0454(2274)	wR2(reflections) = 0.1192(2334)
S = 1.045	Npar = 174

The crystal was obtained via slow evaporation of a solution of **4** (>99% ee) in DCM to hexane in a freezer.

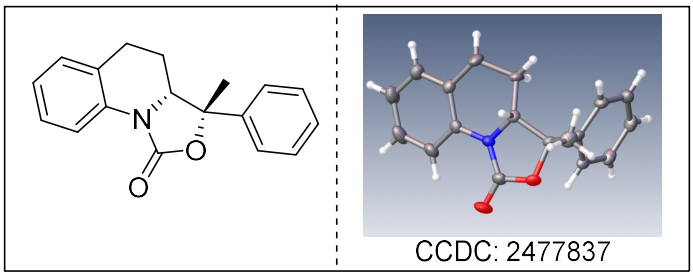


Figure 6. The X-ray structure of **4**.

Table S3. Crystal data and structure refinement for 4 .

Bond precision: C-C = 0.0026 A Wavelength = 1.54178

Cell: a = 6.1697(2) b = 12.7061(3) c = 18.3662(5)
alpha = 90 beta = 90 gamma = 90

Temperature: 179 K

	Calculated	Reported
Volume	1439.78(7)	1439.78(7)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab

Moiety formula	C18H17NO2	2(C18H17NO2)
Sum formula	C18H17NO2	C36H34N2O4
Mr	279.33	558.65
Dx,g cm-3	1.289	1.289
Z	4	2
Mu (mm-1)	0.670	0.670
F000	592.0	592.0
F000’	593.73	
h, k, lmax	7,15,22	7,15,22
Nref	2646[1555]	2639
Tmin, Tmax	0.935,0.935	0.691,0.753
Tmin’	0.935	

Correction method = # Reported T Limits: T min=0.691 T max=0.753

AbsCorr = NONE

Data completeness =1.70/1.00	Theta(max) = 68.412
R(reflections) = 0.0454(2274)	wR2(reflections) = 0.0835(2639)
S = 1.088	Npar = 191