Supporting Information

Kinetic Resolution of Azaflavanones via A RuPHOX-Ru Catalyzed Asymmetric Hydrogenation

Yue Zhu,[a] Jiayu Zhou,[a] Kai Xu,[b] Jing Li,[a] Jianxun Ye,[a] Yufei Lu,[a] Delong Liu,*,[a] and Wanbin Zhang[a,b]

[a] Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Pharmacy, 800 Dongchuan Road, Shanghai 200240, P. R. China

[b] Frontiers Science Center for Transformative Molecules, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China

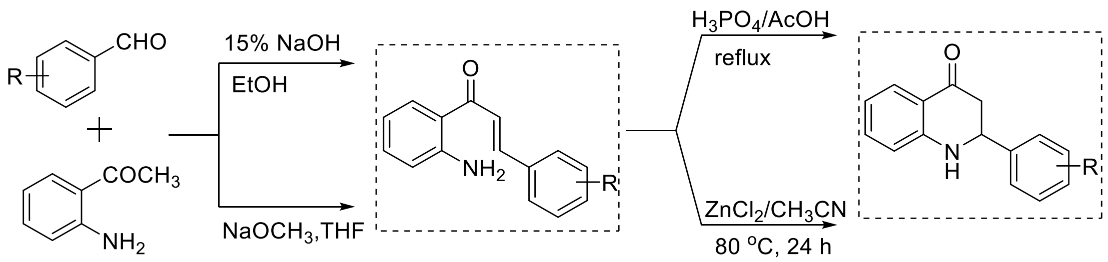
Fax: (+)-86-21-34207176; Phone: (+)-86-21-34207246; E-mail: dlliu@sjtu.edu.cn

Contents

1. General Information

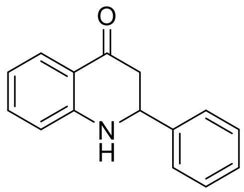
All the reactions were monitored by TLC using UV light to visualize the course of reaction. Anhydrous THF, DME, Et_2O, 1,4-dioxane and toluene were prepared by distillation over sodium-benzophenone prior to use. ^1H, ^{19}F and ^{13}C NMR spectra were obtained using a Varian MERCURY plus-400 or Bruker 500 spectrometer with TMS as an internal standard. HRMS was performed on a Bruck solariX FTICR Mass Spectrometer at the Instrumental Analysis Center of Shanghai Jiao Tong University. Melting points were measured with SGW X-4 micro melting point apparatus. Cinnamyl carbonates **1** were prepared according to literature procedures.[1] All commercially available reagents were used as received.

2. Preparation of Azaflavanones



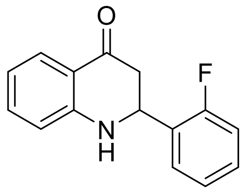
Preparation of 2-aryl-2,3-dihydroquinolin-4(1*H*)-one 1: To a solution of substituted benzaldhyde (20 mmol) and *o*-aminoacetophenone (20 mmol) in THF (80 mL) at 0 °C was added a solution of sodium ethoxide in MeOH (5 mL, 25 wt%). The solution was slowly warmed to room temperature and stirred for several hours. After the reaction was monitored by TLC to determine the consumption of starting materials, the solvent was removed by rotary evaporation under reduced pressure. The residue was diluted with saturated NH_4Cl solution (150 mL), extracted with DCM (125 mL × 3), and the organic phase was washed with saturated $NaHCO_3$ (150 mL), brine (150 ml) and dried over Na_2SO_4. After concentration in vacuo, the residue was purified by silica gel column chromatography (PE/EtOAc = 15/1) to obtain a yellow solid (3.22 g, 72%).

A solution of the above yellow solid in H_3PO_4:AcOH (1:1, 10 mL) was heated to 90 °C for several hours and the reaction was monitored by TLC. The reaction mixture was diluted with water (200 mL) and then extracted with DCM. The solution was washed with saturated $NaHCO_3$ and concentrated in vacuo. The residue was purified by silica gel column chromatography (PE/EtOAc = 30/1) to give the desired product. **1a-1p** were synthesized with this procedure. **1q-1w** were synthesized with the following procedures. The yellow solid (10 mmol) was dissolved in acetonitrile (40 mL), $ZnCl_2$ ether solution (11 mL, 1M) was added to it, and stirred at 80 °C for 24 h. After the reaction was monitored by TLC, the solvent was evaporated under reduced pressure, the oily substance obtained after spin-drying was diluted with saturated ammonium chloride solution, extracted with dichloromethane (125 mL × 3), and the organic phase was spin-dried to obtain a light-yellow solid. After recrystallization with 10% ethyl acetate and *n*-hexane, the target product (2.86 g, 89%) can be obtained.



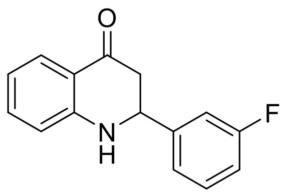
rac-**1a**

2,3-Dihydro-2-phenyl-4-quinolone (*rac*-1a):[1] Light yellow solid (2.86 g, 62%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 7.9, 1.6 Hz, 1H), 7.46 (d, J = 8.04, 2H), 7.42–7.30 (m, 4H), 6.79 (t, J = 7.48 Hz, 1H), 6.71 (d, J = 8.2 Hz, 1H), 4.74 (dd, J = 13.7, 3.9 Hz, 1H), 4.56 (s, 1H), 2.87 (dd, J = 16.3, 13.7 Hz, 1H), 2.78 (dd, J = 16.2, 3.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 151.5, 141.0, 135.4, 129.0, 128.4, 127.6, 126.6, 119.0, 118.4, 115.9, 58.5, 46.4.



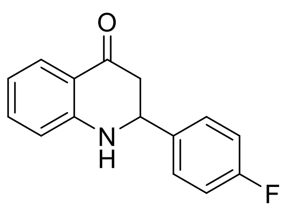
rac-**1b**

2-(2-Fluorophenyl)-2,3-dihydro-4(1*H*)-quinolinone (*rac*-1b):[2] Pale yellow solid (0.84 g, 35%). ^{1}H NMR (400MHz, $CDCl_3$) δ 7.88 (dd, J = 7.9, 1.6 Hz, 1H), 7.57 (td, J = 7.3, 1.7 Hz, 1H), 7.37–7.29 (m, 2H), 7.18 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 10.5 Hz, 1H), 6.81 (t, J = 7.4, 1H), 6.73 (d, J = 8.3 Hz, 1H), 5.14 (t, J = 7.9 Hz, 1H), 4.50 (s, 1H), 2.89 (d, J = 16.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 161.4, 159.0 (J = 248.1 Hz), 151.5, 135.5, 130.0, 129.8 (J = 8.4 Hz), 128.0, 127.9 (J = 12.8 Hz), 127.6, 127.5, 127.5, 124.7 (J = 3.6 Hz), 124.6, 119.1, 118.6, 116.0, 115.9, 115.7, 50.9 (J = 3.38 Hz), 44.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –118.8.



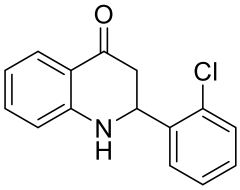
rac-**1c**

2-(3-Fluorophenyl)-2,3-dihydroquinolin-4(1*H*)-one (*rac*-1c):[3] Yellow solid (0.53 g, 22%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 7.9, 1.7 Hz, 1H), 7.39–7.33 (m, 2H), 7.26–7.18 (m, 2H), 7.04 (td, J = 8.4, 2.5 Hz, 1H), 6.81 (t, J = 7.5 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 4.76 (dd, J = 12.6, 4.7 Hz, 1H), 4.52 (s, 1H), 2.89–2.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9 (J = 2.1 Hz), 164.3, 161.8, 151.4 (J = 247.9 Hz), 135.3, 143.7, 143.6 (J = 6.8 Hz), 135.6, 130.6 (J = 8.2 Hz), 127.6, 122.3 (J = 2.9 Hz), 119.0, 118.7, 116.1 (J = 1.7 Hz), 115.5, 115.3 (J = 15.6 Hz), 113.7, 113.5 (J = 22.1 Hz), 58.0, 46.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –111.7.



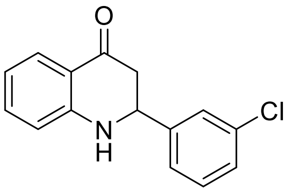
rac-**1d**

2-(4-Fluorophenyl)-2,3-dihydro-4(1*H*)-quinolinone (*rac*-1d):[4] Pale yellow solid (1.20 g, 50%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (dd, J = 7.9, 1.8 ,1H), 7.39–7.34 (m, 2H), 7.26–7.17 (m, 2H), 7.04 (td, J = 8.5, 2.6 Hz, 1H), 6.81 (t, J = 7.0 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 4.76 (dd, J = 12.7, 4.6 Hz, 1H), 4.53 (brs, 1H), 2.90–2.74 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 192.9, 164.3, 161.8 (J = 246.2 Hz), 151.5, 143.7, 135.6, 130.7, 130.6 (J = 8.4 Hz), 127.5, 122.3 (J = 3.3 Hz), 119.0, 118.6, 116.1, 115.4, 115.2 (J = 20.5 Hz), 113.7, 113.5 (J = 22.1 Hz), 57.9, 46.3; ^{19}F NMR (376 MHz, CDCl$_3$) δ –111.7.



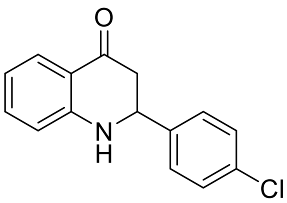
rac-**1e**

2-(2-Chlorophenyl)-2,3-dihydro-4(1*H*)-quinolinone (*rac*-1e):[5] A pale yellow solid (1.55 g, 60%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 (dd, J = 7.9, 1.7 Hz, 1H), 7.68 (dd, J = 7.5, 1.9 Hz, 1H), 7.41 (dd, J = 7.6, 1.8 Hz, 1H), 7.37–7.27 (m, 3H), 6.81 (t, J = 7.6 Hz, 1H), 6.74 (dd, J = 8.3 Hz, 1H) 5.25 (dd, J = 12.2, 3.7 Hz, 1H), 4.50 (s, 1H), 2.96 (dd, J = 16.4, 4.1 Hz, 1H), 2.83–2.76 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 192.8, 151.5, 138.3, 135.5, 132.7, 130.0, 129.3, 127.6, 127.5, 127.4, 119.1, 118.6, 116.1, 54.2, 44.0.



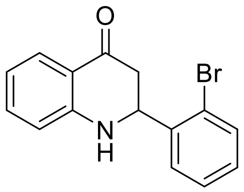
rac-**1f**

2-(3-Chlorophenyl)-2,3-dihydro-4(1H)-quinolinone (*rac*-1f):[5] Pale yellow solid (1.44 g, 56%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84 (dd, J = 7.96, 1.72 Hz, 1H), 7.40–7.32 (m, 5H), 6.79 (t, J = 7.36 Hz, 1H), 6.73 (d, J = 8.26 Hz, 1H), 4.74 (dd, J = 13.2, 4.2 Hz, 1H), 4.47 (s, 1H), 2.89–2.71 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 192.9, 151.4, 139.6, 135.5, 134.2, 129.2, 128.0, 127.6, 119.0, 118.7, 116.0, 57.9, 46.4.



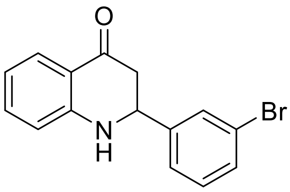
rac-**1g**

2-(4-Chlorophenyl)-2,3-dihydro-4(1*H*)-quinolinone (*rac*-1g):[4] Pale yellow solid (1.60 g, 62%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (dd, J = 7.96, 1.72 Hz, 1H), 7.40–7.32 (m, 5H), 6.79 (t, J = 7.4 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 4.74 (dd, J = 13.1, 4.3 Hz, 1H), 4.48 (s, 1H), 2.89–2.70 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 192.9, 151.3, 139.5, 135.5, 134.2, 129.2, 128.0, 127.6, 119.1, 118.7, 116.0, 57.9, 46.4.



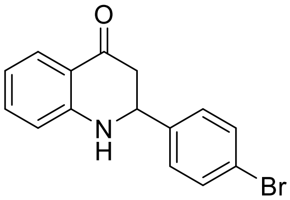
rac-**1h**

2-(2-Bromophenyl)-2,3-dihydro-4(1*H*)-quinolinone (*rac*-1h):[2] A pale yellow solid (1.45 g, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.69 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.48 (q, *J* = 7.4 Hz, 2H), 7.21 (td, *J* = 7.6, 1.92 Hz, 1H), 6.81 (t, *J* = 7.9 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 5.25 (dd, *J* = 12.2, 3.7 Hz, 1H), 4.50 (s, 1H), 2.97 (dd, *J* = 16.4, 4.2 Hz, 1H), 2.81–2.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 151.6, 139.9, 135.5, 133.3, 129.7, 128.2, 127.7, 127.7, 122.9, 119.1, 118.6, 116.1, 56.8, 44.2.



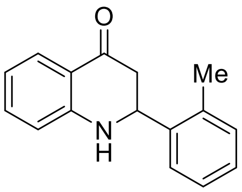
rac-**1i**

2-(3-Bromophenyl)-2,3-dihydro-4(1*H*)-quinolinone (*rac*-1i):[3] Pale yellow solid (1.81 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.9, 1.72 Hz, 1H), 7.65 (t, *J* = 1.9 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.39–7.34 (m, 2H), 7.29–7.27 (m, 1H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 4.74 (dd, *J* = 13.2, 4.3 Hz, 1H), 4.48 (s, 1H), 2.89–2.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 151.3, 143.4, 135.5, 131.6, 130.6, 129.8, 127.6, 125.3, 123.0, 119.1, 118.8, 116.0, 58.0, 46.4.



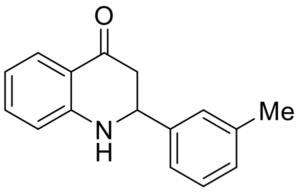
rac-**1j**

2-(4-Bromophenyl)-2,3-dihydro-4(1*H*)-quinolinone (*rac*-1j):[4] Pale yellow solid (1.87 g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.52 (dd, *J* = 6.4, 2.0 Hz, 2H), 7.37–7.31 (m, 3H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 4.73 (dd, *J* = 13.1, 4.3 Hz, 1H), 4.45 (brs, 1H), 2.85–2.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 151.4, 140.1, 135.5, 132.2, 128.3, 127.6, 122.3, 119.1, 118.7, 116.0, 58.0, 46.4.



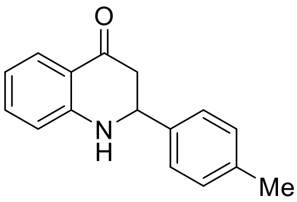
rac-**1k**

2,3-Dihydro-2-(2-methylphenyl)-4(1*H*)-quinolinone (*rac*-1k):[6] Pale yellow solid (1.18 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.67 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.37–7.28 (m, 2H), 7.25–7.19 (m, 2H), 6.80 (t, *J* = 7.9 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 5.03 (dd, *J* = 13.2, 4.4 Hz, 1H), 4.42 (brs, 1H), 2.85–2.72 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 132.8, 119.9, 116.2, 115.9, 111.8, 108.9, 108.5, 107.6, 106.7, 99.8, 99.2, 96.8, 35.4, 26.1.



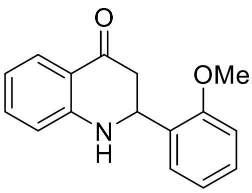
rac-**1l**

2,3-Dihydro-2-(3-methylphenyl)-4(1*H*)-quinolinone (*rac*-1l):[7] Pale yellow solid (1.30 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.37–7.22 (m, 4H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.79 (t, *J* = 6.9 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 4.72 (dd, *J* = 13.8, 3.8 Hz, 1H), 4.48 (brs, 1H), 2.92–2.85 (m, 1H), 2.76 (dd, *J* = 16.1, 3.8 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 151.7, 141.0, 138.8, 125.4, 129.2, 128.9, 127.6, 127.3, 123.7, 119.0, 118.4, 116.0, 58.5, 46.5, 21.5.



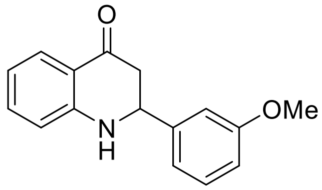
rac-**1m**

2,3-Dihydro-2-(4-methylphenyl)-4(1H)-quinolinone (*rac*-1m):[4] Pale yellow solid (1.42 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.36–7.27 (m, 3H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.70 (dd, *J* = 8.2, 1.0 Hz, 1H), 4.68 (dd, *J* = 13.8, 3.8 Hz, 1H), 4.53 (brs, 1H), 2.88–2.69 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 151.7, 138.3, 138.1, 135.4, 129.6, 127.6, 126.6, 119.0, 118.3, 116.0, 58.2, 46.5, 21.1.



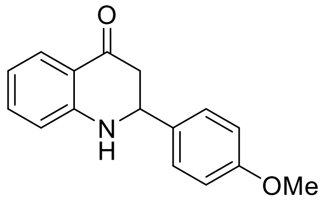
rac-**1n**

2-(2-Methoxyphenyl)-2,3-dihydroquinolin-4(1*H*)-one (*rac*-1n):[5,8] Yellow solid (0.87 g, 27%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.9, 4.0 Hz, 1H), 7.49 (dd, *J* = 9.2, 1.6 Hz, 1H), 7.34–7.28 (m, 2H), 6.99 (td, *J* = 7.5, 1.1 Hz, 1H), 6.91 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 5.18 (dd, *J* = 4.4 Hz, 1H), 4.63 (brs, 1H), 3.85 (s, 3H), 2.95–2.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 156.7, 152.0, 135.2, 129.1, 128.9, 127.6, 126.5, 120.9, 119.1, 118.1, 116.1, 110.6, 55.4, 51.3, 43.7.



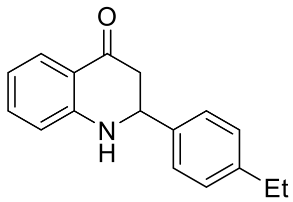
rac-**1o**

2-(3-Methoxyphenyl)-2,3-dihydroquinolin-4(1*H*)-one (*rac*-1o):[3] Yellow solid (0.98 g, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.36–7.29 (m, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.9–6.87 (m, 1H), 6.79 (td, *J* = 7.9, 1.0 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 4.72 (dd, *J* = 13.6, 4.0 Hz, 1H), 4.53 (brs, 1H), 3.83 (s, 3H), 2.91–2.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 160.0, 151.5, 142.7, 135.4, 130.1, 127.6, 119.0, 118.9, 118.5, 115.9, 113.7, 112.3, 58.5, 55.3, 46.5.



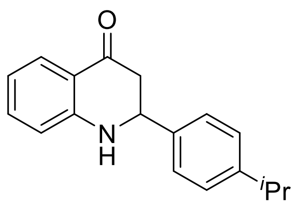
rac-**1p**

2-(4-Methoxyphenyl)-2,3-dihydroquinolin-4(1*H*)-one (*rac*-1p):[9] Yellow solid (1.12 g, 34%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.33 (td, *J* = 7.6, 1.6 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 4.70 (dd, *J* = 13.9, 3.4 Hz, 1H), 4.53 (brs, 1H), 3.82 (s, 3H), 2.91–2.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 159.7, 151.6, 135.4, 133.1, 127.9, 127.6, 119.0, 118.4, 115.9, 114.3, 57.9, 55.4, 46.6.



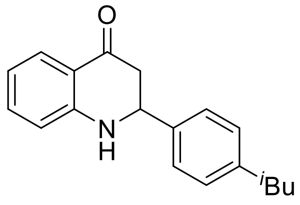
rac-**1q**

2,3-Dihydro-2-(4-ethylphenyl)-4(1*H*)-quinolinone (*rac*-1q):[10] Pale yellow solid (1.83 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.0, 1.76 Hz, 2H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 4.68 (dd, *J* = 13.8, 3.8 Hz, 1H), 4.53 (brs, 1H), 2.89–2.70 (m, 2H), 2.66 (q, *J* = 7.6 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 151.7, 138.3, 138.1, 135.4, 129.6, 127.6, 126.6, 119.0, 118.3, 116.0, 58.2, 46.5, 28.6, 15.6.



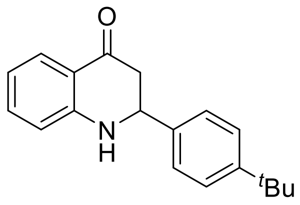
rac-**1r**

2,3-Dihydro-2-(4-isopropyl)-4(1H)-quinolinone (*rac*-1r):[11] Pale yellow solid (1.83 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 7.9, 1.6 Hz, 1H), 7.39–7.27 (m, 3H), 7.24 (d, J = 8.0 Hz, 2H), 6.75 (t, J = 7.4 Hz, 1H), 6.68 (d, J = 8.2 Hz, 1H), 4.68 (dd, J = 13.8, 3.8 Hz, 1H), 4.58 (brs, 1H), 2.95–2.81 (m, 2H), 2.72 (dd, J = 16.3, 3.9 Hz, 1H), 1.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 151.7, 149.3, 138.4, 135.4, 127.6, 127.0, 126.7, 119.0, 118.3, 116.0, 58.2, 46.4, 33.9, 24.0.



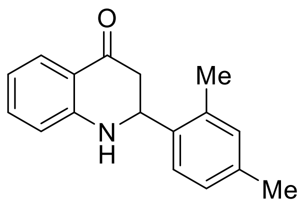
rac-**1s**

2,3-Dihydro-2-(4-isobutylphenyl)-4(1*H*)-quinolinone (*rac*-1s): Pale yellow solid (2.09 g, 75%). Mp 104–106 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 7.9, 1.6 Hz, 1H), 7.36–7.26 (m, 3H), 7.15 (d, J = 7.8 Hz, 2H), 6.74 (t, J = 7.4 Hz, 1H), 6.69 (d, J = 8.2 Hz, 1H), 4.66 (dd, J = 13.8, 3.8 Hz, 1H), 4.61 (brs, 1H), 2.86–2.68 (m, *2*H), 2.47 (d, J = 7.1 Hz, 2H), 1.91–1.79 (m, 1H), 0.91 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 151.8, 142.1, 138.3, 135.4, 129.7, 127.6, 126.4, 119.0, 118.3, 116.0, 58.2, 46.4, 45.1, 30.3, 22.4; IR (KBr): 3347, 2951, 2361, 1658, 1609, 1507, 1157, 758 cm^{-1}; HRMS (APCI) $C_{19}H_{21}NONa$ $[M+Na]^+$ calcd 302.1515, found 302.1516.



rac-**1t**

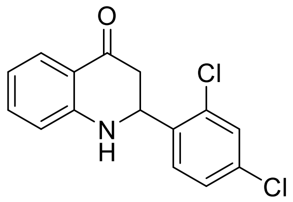
2,3-Dihydro-2-(4-tert-butylphenyl)-4(1*H*)-quinolinone (*rac*-1t):[3] Pale yellow solid (2.01 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 7.8, 1.4 Hz, 1H), 7.38 (q, J = 8.3 Hz, 4H), 7.30 (t, J = 7.6 Hz, 1H), 6.75 (t, J = 7.5 Hz, 1H), 6.68 (d, J = 8.2 Hz, 1H), 4.68 (dd, J = 13.6, 3.8 Hz, 1H), 4.59 (brs, 1H), 2.99–2.70 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 151.7, 151.5, 138.0, 135.4, 127.6, 126.4, 125.9, 119.0, 118.3, 116.0, 58.1, 46.4, 34.7, 31.4.



rac-**1u**

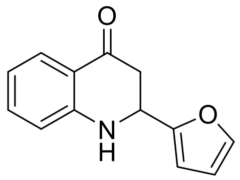
2-(2,4-Dimethylphenyl)-2,3-dihydroquinolin-4(1*H*)-one (*rac*-1u):[12] Yellow solid (1.38 g, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 7.9, 1.7 Hz, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 7.09 (d, J = 8.8 Hz, 1H), 7.02 (s, 1H), 6.79 (t, J = 7.9 Hz, 1H), 6.71 (d, J = 8.3 Hz, 1H), 4.98 (dd, J = 13.6, 4.0 Hz, 1H), 4.39 (brs, 1H), 2.84–2.69 (m, 2H), 2.33 (s, 6H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 193.6, 152.0, 137.8, 136.1, 135.3, 134.9, 131.7, 127.7, 127.4, 125.9, 119.0, 118.3, 116.0, 54.3, 45.4, 21.0, 19.0.



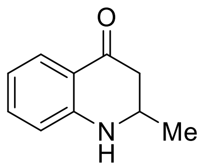
rac-**1v**

2-(2,4-Dichlorophenyl)-2,3-dihydroquinolin-4(1*H*)-one (*rac*-1v):[12] Yellow solid (0.88 g, 25%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.62 (d, *J* = 9.8 Hz, 1H), 7.43 (d, *J* = 2.2 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.30 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.82 (t, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 5.21 (dd, *J* = 12.9, 4.88 Hz, 1H), 4.50 (s, 1H), 2.93 (dd, *J* = 16.4, 4.1 Hz, 1H), 2.78–2.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 151.3, 137.1, 135.6, 134.5, 133.4, 129.8, 128.4, 127.9, 127.6, 118.9, 116.1, 53.9, 44.0.



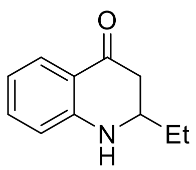
rac-**1w**

2-(Furan-2-yl)-2,3-dihydroquinolin-4(1*H*)-one (*rac*-1w):[4] Yellow solid (0.87 g, 34%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.39 (s, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 1H), 6.34 (s, 1H), 6.27 (d, *J* = 3.2 Hz, 1H), 4.84 (dd, *J* = 9.8, 4.2 Hz, 1H), 4.70 (s, 1H), 3.05–2.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 153.3, 150.5, 142.5, 135.5, 127.5, 119.3, 118.7, 116.0, 110.4, 106.9, 50.8, 42.0.



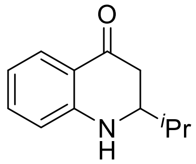
rac-**1x**

2-Methyl-2,3-dihydroquinolin-4(1*H*)-one (*rac*-1x):[13] Yellow solid (0.42 g, 26%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.00 Hz, 1H), 7.31–7.26 (m, 1H), 6.75–6.70 (m, 1H), 6.66 (dd, *J* = 8.20, 0.96 Hz, 1H), 4.35 (s, 1H), 3.81–3.74 (m, 1H), 2.66–2.42 (m, 2H), 1.33 (d, *J* = 6.32 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 151.6, 135.2, 127.5, 119.0, 118.0, 115.7, 49.1, 45.8, 21.3.



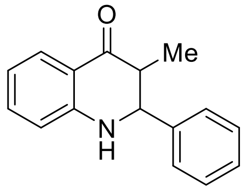
rac-**1y**

2-Ethyl-2,3-dihydroquinolin-4(1*H*)-one (*rac*-1y):[14] Yellow solid (0.81 g, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 7.92, 1.64 Hz, 1H), 7.29–7.24 (m, 1H), 6.72–6.68 (m, 1H), 6.65 (dd, J = 8.28, 1.04 Hz, 1H), 4.35 (s, 1H), 3.57–3.50 (m, 1H), 2.68–2.41 (m, 2H), 0.98 (t, J = 7.48 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 151.5, 135.1, 127.4, 119.0, 117.8, 115.7, 54.6, 43.4, 28.0, 9.63.



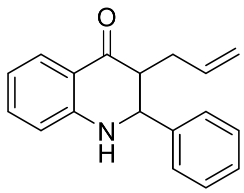
rac-**1z**

2-Isopropyl-2,3-dihydroquinolin-4(1*H*)-one (*rac*-1z):[15] Yellow solid (0.52 g, 27%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 7.92, 1.60 Hz, 1H), 7.31–7.27 (m, 1H), 6.73–6.67 (m, 2H), 4.31 (s, 1H), 3.45–3.39 (m, 1H), 2.64–2.49 (m, 2H), 1.91–1.83 (m,1H), 1.01 (d, J = 6.84 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 151.8, 135.2, 127.4, 119.0, 117.8, 115.8, 58.8, 40.7, 31.8, 18.3, 18.0.



rac-**1aa**

3-Methyl-2-phenyl-2,3-dihydroquinolin-4(1*H*)-one (*rac*-1aa): White solid (0.46 g, 19%). Mp 170–171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 9.56, 1.64 Hz, 1H), 7.46–7.30 (m, 6H), 6.77 (t, J = 7.60 Hz, 1H), 6.66 (dd, J = 8.20, 1.04 Hz, 1H), 4.53 (s, 1H), 4.31 (d, J = 12.84 Hz, 1H), 2.85–2.76 (m, 1H), 0.98 (d, J = 6.84 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 144.1, 142.3, 142.0, 129.0, 128.8, 128.7, 128.5, 128.0, 127.7, 127.2, 127.1, 124.9, 124.2, 117.8, 116.5, 113.6, 111.0, 73.3, 43.4, 42.6, 17.0, 15.3; IR (KBr): 3318, 2830, 1613, 1364, 752, 693 cm^{-1}; HRMS (APCI) $C_{16}H_{15}NONa$ $[M+H]^+$ calcd 238.1226, found 238.1322.



rac-**1ab**

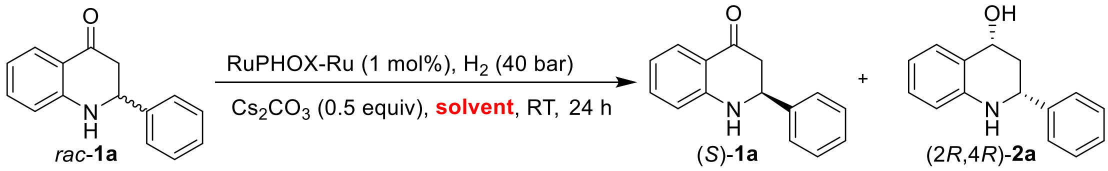
3-Allyl-2-phenyl-2,3-dihydroquinolin-4(1*H*)-one (*rac*-1ab): Yellow solid (0.52 g, 20%). Mp 100–101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 7.96, 1.64 Hz, 1H), 7.40–7.28 (m, 6H), 6.74 (t, J = 7.56 Hz, 1H), 6.64 (d, J = 8.20 Hz, 1H), 5.80–5.69 (m, 1H), 4.9 (dd, J = 17.12, 2.04 Hz, 1H), 4.57–4.52 (m, 2H), 2.90–2.84 (m, 1H), 2.61–2.54 (m, 1H), 2.18–2.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 150.6, 140.2, 135.3, 135.1, 128.8, 128.4, 127.8, 127.6, 118.8, 118.1, 117.3, 115.4, 61.0, 52.1, 31.0; IR (KBr): 3352, 2932, 1610, 1209, 920, 761 cm^{-1}; HRMS (APCI) $C_{18}H_{17}NONa$ $[M+H]^+$ calcd 264.1383, found 264.1385.

3. RuPHOX-Ru Catalyzed Asymmetric Hydrogenation of Azaflavanones

3.1 Optimization of the Reaction Conditions

The asymmetric hydrogenation of 2-phenyl-2,3-dihydroquinolin-4(1*H*)-one (*rac*-**1a**) using RuPHOX-Ru as a chiral catalyst was carried out in different solvents under 40 bar hydrogen pressure at room temperature over 24 h (Table S1). The reaction proceeded smoothly in protic solvents, such as MeOH, EtOH and *i*-PrOH, but with the desired product **2a** being obtained with unsatisfactory stereoselectivities (entries 1~3). When polar aprotic solvents (DCM, DCE, THF and 1,4-dioxane) were used, excellent drs and good ees of **2a** were obtained but with low reaction activity (entries 4~7). Only 50% conversion was afforded when toluene was used as a solvent. Considering the effect of the base on the reaction, we added H_2O with the aim to improve the solubility of the inorganic base Cs_2CO_3. To our delight, a mixed solvent system consisting of THF and H_2O gave the resolution product in excellent diastereoselectivities (entries 9~11).

Table S1. Screening of solvents[a]

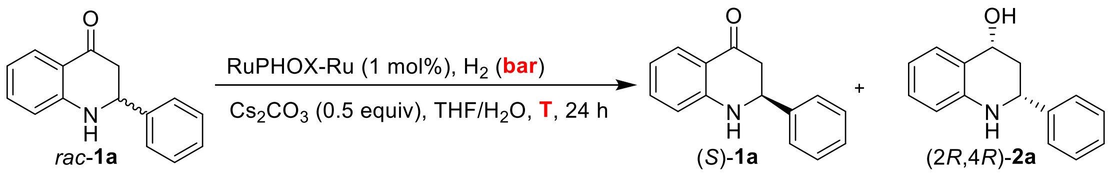


Entry	Solvent	Conv (%)[b]	See (%)[c]	Pee (%)[c]	dr[b]
1	MeOH	>99	-	0	>20:1
2	EtOH	58.8	90	58/84	5:1
3	*i*-PrOH	58.8	89	63/3	8:1
4	DCM	23	0	86	>20:1
5	DCE	10	0	86	>20:1
6	THF	25	45	87	>20:1
7	1,4-dioxane	11	8.6	58	>20:1
8	toluene	50	73	88	>20:1
9	toluene : H_2O	48	79	83	9:1
10	DCM : H_2O	NP	-	-	-
11	THF : H_2O	50	>99	98	>20:1

[a]Reaction conditions: **1a** (70.0 mg, 0.3 mmol), RuPHOX-Ru (1.0 mol%), in an indicated solvent in the presence of Cs_2CO_3 (0.5 equiv) under 40 bar H_2 pressure at 0 °C for 24 h; [b]Conversions and drs were determined by ^1H NMR; [c]The ee values were determined by HPLC using a chiral OD-H Daicel column.

The effect of the temperature and H_2 pressure on the asymmetric hydrogenation was also examined. As is shown in Table S2, only 15% conversion was observed when the reaction was carried out at 0 °C. Somewhat low enantioselectivity for (*S*)-**1a** was obtained with the reaction being conducted at a higher reaction temperature. Next, the asymmetric hydrogenation was carried out under different H_2 pressure (entries 4 and 5). Only 34% conversion was observed when the reaction was carried out under a hydrogen pressure of 30 bar. Excessive reduction and somewhat low enantioselectivity for **2a** were observed when 50 bar hydrogen pressure was used.

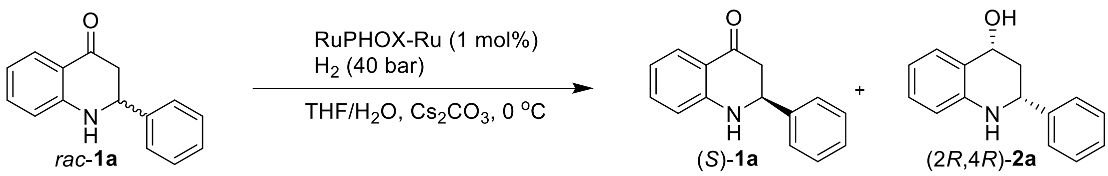
Table S2. Screening of reaction temperature[a]



Entry	Temp (°C)	H_2 (bar)	Conv (%)[b]	See (%)[c]	Pee (%)[c]	dr[b]
1	0	40	15	-	-	-
2	RT	40	50	>99	97	>20:1
3	40	40	50	95	97	>20:1
4	RT	30	34	76	95	>20:1
5	RT	50	53	>99	93	>20:1

[a]Reaction conditions: **1a** (70.0 mg, 0.3 mmol), RuPHOX-Ru (1.0 mol%), in THF/H_2O (1.5 + 0.5 mL) in the presence of Cs_2CO_3 (0.5 equiv) under certain H_2 pressure and temperature for 24 h; [b]Conversions and drs were determined by ^1H NMR; [c]The ee values were determined by HPLC using a chiral OD-H Daicel column.

3.2 General Procedure: RuPHOX-Ru Catalyzed Asymmetric Hydrogenation

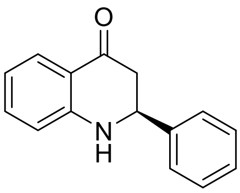


General Procedure: In a nitrogen-filled glovebox, a hydrogenation tube was charged with a stirring bar, substituted azaflavanones (0.30 mmol), (*S*,*S*)-RuPHOX-Ru (5.2 mg, 1 mol%) and Cs_2CO_3 (48.9 mg, 0.5 equiv, 0.15 mmol). THF (1.5 mL) and H_2O (0.5 mL) were then injected into the hydrogenation tube by a syringe. The hydrogenation tube was put into an autoclave. The system was evacuated and filled with hydrogen 3 times. The autoclave was charged with hydrogen to 40 bar hydrogen pressure, and the reaction mixture was stirred at room temperature for 24 h before releasing the hydrogen. H_2O was removed by anhydrous Na_2SO_4 and the solvent was evaporated to afford the crude product, which was purified by silica gel column chromatography to afford pure products (*S*)-**1a** and (*R*,*R*)-**2a**. The conversion of substrate was determined by ^1H NMR analysis of the crude product and the ee values were determined by HPLC with a chiral column using pure product.

Under the above reaction conditions, the asymmetric hydrogenation of substrates **1b-z** were carried out smoothly, affording the corresponding products (*S*)-**1b-z** and (*R*,*R*)-**2b-z**. However, the asymmetric hydrogenation could not occur when the 2,3-disubstituted substrates **1aa** and **1ab** were used.

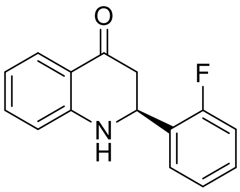
The product (*S*,*S*)-**2a** with opposite configuration was obtained in the above procedure by using (*R*,*R*)-RuPHOX-Ru as chiral catalyst instead of (*S*,*S*)-RuPHOX-Ru.

Gram scale synthesis: A 20 mL hydrogenation tube was charged with a stirrer bar, compound *rac*-**1a** (1.34 g, 6 mmol), RuPHOX-Ru (4.3 mg, 0.5 mol‰), and Cs_2CO_3 (1.95 g, 6 mmol) in an argon-filled glovebox. Then, THF (4.5 mL) and H_2O (1.5 ml) were injected into the tube by a syringe and the reaction tube was then put into an autoclave. The autoclave was evacuated and filled with hydrogen for 3 times, and then charged with hydrogen to 40 bar. After vigorous stirring at room temperature for 48 hours, the solvent was evaporated under reduced pressure to afford the crude product, which was determined by ^{1}HNMR analysis to determine the conversion of substrate. The crude product was passed through a short column of silicon (PE/EtOAc = 8/1) to afford (*S*)-**1a** (0.65 g, 49%, 99.6% ee) and (*R*,*R*)-**2a** (0.66 g, 49%, 98% ee, >20:1 dr).



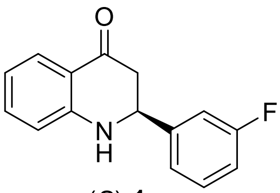
(*S*)-**1a**

(*S*)-2,3-Dihydro-2-phenyl-4-quinolone ((*S*)-1a): Light yellow solid (32.8 mg, 49%). $[\alpha]_D^{20}$ = +32.50 (*c* 0.560, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 29.381 min (major) and t_{R2} = 25.347 min (minor), ee = 99.6%.



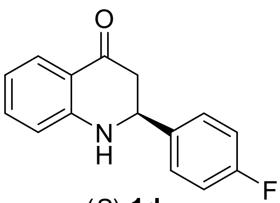
(*S*)-**1b**

(*S*)-2-(2-Fluorophenyl)-2,3-dihydro-4(1*H*)-quinolinone ((*S*)-1b):[5~6] Pale yellow solid (34.7 mg, 48%). $[\alpha]_D^{20}$ = +72.63 (*c* 0.690, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 29.608 min (major) and t_{R2} = 23.848 min (minor), ee = 97%.



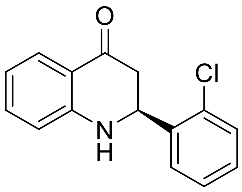
(*S*)-**1c**

(*S*)-2-(3-Fluorophenyl)-2,3-dihydroquinolin-4(1*H*)-one ((*S*)-1c): Yellow solid (35.5 mg, 49%). $[\alpha]_D^{20}$ = +15.86 (*c* 0.648, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 24.761 min (major) and t_{R2} = 23.005 min (minor), ee = 98%.



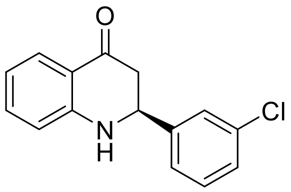
(*S*)-**1d**

(*S*)-2-(4-Fluorophenyl)-2,3-dihydro-4(1*H*)-quinolinone ((*S*)-1d): Pale yellow solid (35.5 mg, 49%). $[\alpha]_D^{20}$ = +17.88 (*c* 0.680, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 24.708 min (major) and t_{R2} = 22.968 min (minor), ee = 98%.



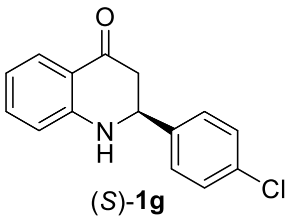
(*S*)-**1e**

(*S*)-2-(2-Chlorophenyl)-2,3-dihydro-4(1*H*)-quinolinone ((*S*)-1e):[4] Pale yellow solid (34 mg, 44%). $[\alpha]_D^{20}$ = –77.39 (*c* 0.690, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 29.117 min (major) and t_{R2} = 26.399 min (minor), ee = 96%.



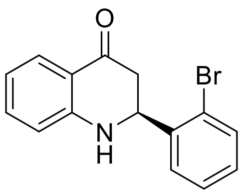
(*S*)-**1f**

(*S*)-2-(3-Chlorophenyl)-2,3-dihydro-4(1*H*)-quinolinone ((*S*)-1f): Pale yellow solid (35.6 mg, 46%). $[\alpha]_D^{20}$ = +19.00 (*c* 0.642, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 32.249 min (major) and t_{R2} = 27.441 min (minor), ee = 97%.



(*S*)-**1g**

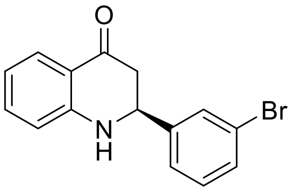
(*S*)-2-(4-Chlorophenyl)-2,3-dihydro-4(1*H*)-quinolinone ((*S*)-1g):[5] Pale yellow solid (37.8 mg, 49%). $[\alpha]_D^{20}$ = +17.33 (*c* 1.512, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 25.416 min (major) and t_{R2} = 23.524 min (minor), ee = 90%.



(*S*)-**1h**

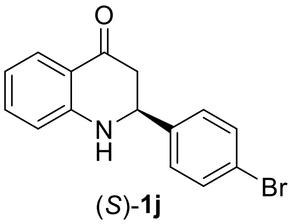
(*S*)-2-(2-Bromophenyl)-2,3-dihydro-4(1*H*)-quinolinone ((*S*)-1h): Pale yellow solid (39.0 mg, 43%). $[\alpha]_D^{20}$ = –102.95 (*c* 0.678, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 29.724 min (major) and t_{R2} = 27.760 min (minor), ee =

95%.



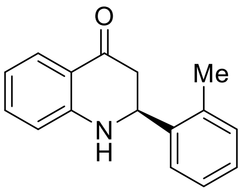
(*S*)-**1i**

(*S*)-2-(3-Bromophenyl)-2,3-dihydro-4(1*H*)-quinolinone ((*S*)-1i): Pale yellow solid (43.5 mg, 48%). $[\alpha]_D^{20}$ = +3.10 (*c* 0.826, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 25.792 min (major) and t_{R2} = 23.810 min (minor), ee = 98%.



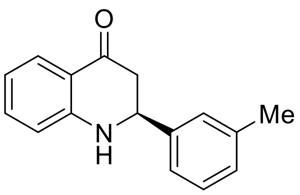
(*S*)-**1j**

(*S*)-2-(4-Bromophenyl)-2,3-dihydro-4(1*H*)-quinolinone ((*S*)-1j): Pale yellow solid (44.4 mg, 49%). $[\alpha]_D^{20}$ = +17.47 (*c* 0.916, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 34.082 min (major) and t_{R2} = 28.286 min (minor), ee = 98%.



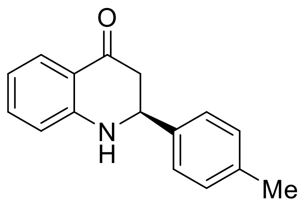
(*S*)-**1k**

(*S*)-2,3-Dihydro-2-(2-methylphenyl)-4(1*H*)-quinolinone ((*S*)-1k): Pale yellow solid (33.5 mg, 47%). $[\alpha]_D^{20}$ = –40.76 (*c* 0.628, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 43.920 min (major) and t_{R2} = 52.363 min (minor), ee = 96%.



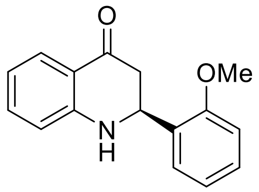
(*S*)-**1l**

(*S*)-2,3-Dihydro-2-(3-methylphenyl)-4(1*H*)-quinolinone ((*S*)-1l): Pale yellow solid (34.9 mg, 47%). $[\alpha]_D^{20}$ = +30.34 (*c* 0.646, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 27.227 min (major) and t_{R2} = 23.759 min (minor), ee = 99%.



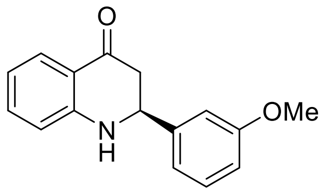
(*S*)-**1m**

(*S*)-2,3-Dihydro-2-(4-methylphenyl)-4(1*H*)-quinolinone ((*S*)-1m): Pale yellow solid (34.2 mg, 48%). $[\alpha]_D^{20}$ = +57.22 (*c* 0.488, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 32.132 min (major) and t_{R2} = 25.304 min (minor), ee = 99%.



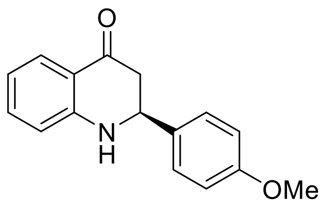
(*S*)-**1n**

(*S*)-2-(2-Methoxyphenyl)-2,3-dihydroquinolin-4(1*H*)-one ((*S*)-1n): Yellow solid (38.0 mg, 49%). $[\alpha]_D^{20}$ = +28.90 (*c* 0.706, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 37.831 min (major) and t_{R2} = 30.656 min (minor), ee = 99%.



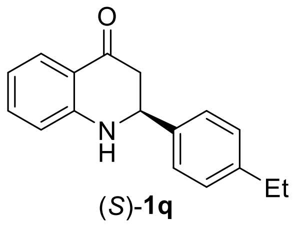
(*S*)-**1o**

(*S*)-2-(3-Methoxyphenyl)-2,3-dihydroquinolin-4(1*H*)-one ((*S*)-1o): Yellow solid (37.2 mg, 49%). $[\alpha]_D^{20}$ = +24.50 (*c* 0.702, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 35.171 min (major) and t_{R2} = 31.871 min (minor), ee = 98%.



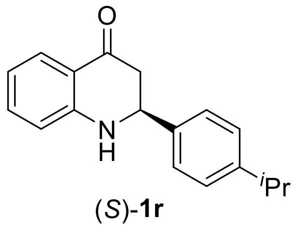
(*S*)-**1p**

(*S*)-2-(4-Methoxyphenyl)-2,3-dihydroquinolin-4(1*H*)-one ((*S*)-1p): Yellow solid (37.2 mg, 49%). $[\alpha]_D^{20}$ = +40.70 (*c* 0.690, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 46.970 min (major) and t_{R2} = 37.068 min (minor), ee = 96%.



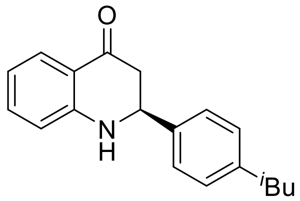
(*S*)-**1q**

(*S*)-2,3-Dihydro-2-(4-ethylphenyl)-4(1*H*)-quinolinone ((*S*)-**1q**): Pale yellow solid (37.7 mg, 49%). $[\alpha]_D^{20}$ = +47.91 (*c* 0.718, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 29.074 min (major) and t_{R2} = 23.415 min (minor), ee = 96%.



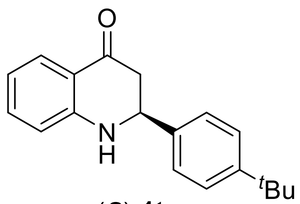
(*S*)-**1r**

(*S*)-2,3-Dihydro-2-(4-isopropyl)-4(1*H*)-quinolinone ((*S*)-**1r**): Pale yellow solid (39.8 mg, 49%). $[\alpha]_D^{20}$ = +52.86 (*c* 0.768, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 25.601 min (major) and t_{R2} = 20.951 min (minor), ee = 95%.



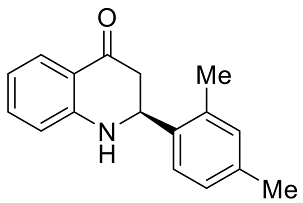
(*S*)-**1s**

(*S*)-2,3-Dihydro-2-(4-isobutylphenyl)-4(1*H*)-quinolinone ((*S*)-1s): Pale yellow solid (40.2 mg, 48%). $[\alpha]_D^{20}$ = +46.41 (*c* 0.780, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 22.933 min (major) and t_{R2} = 18.476 min (minor), ee = 95%.



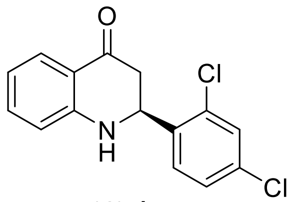
(*S*)-**1t**

(*S*)-2,3-Dihydro-2-(4-tert-butylphenyl)-4(1*H*)-quinolinone ((*S*)-1t): Pale yellow solid (40.2 g, 48%). $[\alpha]_D^{20}$ = +55.74 (*c* 0.770, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 23.073 min (major) and t_{R2} = 19.423 min (minor), ee = 93%.



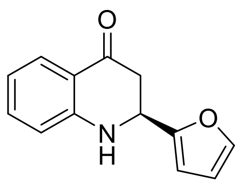
(*S*)-**1u**

(*S*)-2-(2,4-Dimethylphenyl)-2,3-dihydroquinolin-4(1*H*)-one ((*S*)-1u): Yellow solid (36.2 mg, 48%). $[\alpha]_D^{20}$ = –27.3 (*c* 0.674, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 24.943 min (major) and t_{R2} = 23.584 min (minor), ee = 99%.



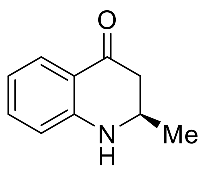
(*S*)-**1v**

(*S*)-2-(2,4-Dichlorophenyl)-2,3-dihydroquinolin-4(1*H*)-one ((*S*)-1v): Yellow solid (39.4 mg, 45%). $[\alpha]_D^{20}$ = –83.69 (*c* 0.726, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 29.334 min (major) and t_{R2} = 26.343 min (minor), ee = 99.7%.



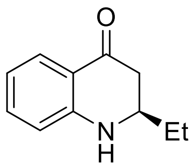
(*S*)-**1w**

(*S*)-2-(Furan-2-yl)-2,3-dihydroquinolin-4(1*H*)-one ((*S*)-1w): Yellow solid (32.2 mg, 48%). $[\alpha]_D^{20}$ = +339.86 (*c* 0.568, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 32.917 min (major) and t_{R2} = 23.795 min (minor), ee = 97%.



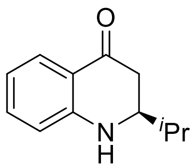
(*R*)-**1x**

(*R*)-2-Methyl-2,3-dihydroquinolin-4(1*H*)-one ((*R*)-1x): A light-yellow solid (22.52 mg, 46%). $[\alpha]_D^{20}$ = +114.63 (*c* 0.738, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 210 nm, flow rate = 0.8 mL/min) t_{R1} = 18.157 min (major) and t_{R2} = 19.374 min (minor), ee = 98%.



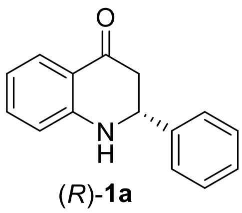
(*R*)-**1y**

(*R*)-2-Ethyl-2,3-dihydroquinolin-4(1*H*)-one (*R*-1y): A light-yellow solid (24.7 mg, 47%). $[\alpha]_D^{20}$ = +167.74 (*c* 0.402, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 210 nm, flow rate = 0.8 mL/min) t_{R1} = 15.602 min (major) and t_{R2} = 16.955 min (minor), ee = 98%.



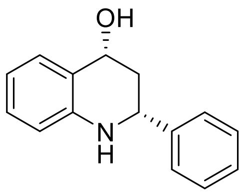
(*S*)-**1z**

(*S*)-2-Isopropyl-2,3-dihydroquinolin-4(1*H*)-one (*S*-1z): A light-yellow solid (26.7 mg, 47%) . $[\alpha]_D^{20}$ = +221.34 (*c* 0.510, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 210 nm, flow rate = 0.8 mL/min) t_{R1} = 12.993 min (major) and t_{R2} = 13.799 min (minor), ee = 98%.



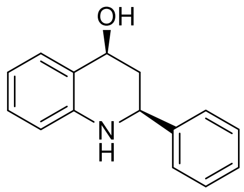
(*R*)-**1a**

(2*R*,4*R*)-2-phenyl-1,2,3,4-tetrahydroquinolin-4-ol ((*R*)-1a): Yellow solid (33.4 mg, 49%). $[\alpha]_D^{20}$ = –32.06 (*c* 0.660, acetone); HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 25.469 min (major) and t_{R2} = 29.569 min (minor), ee = 99.1% *ee*.



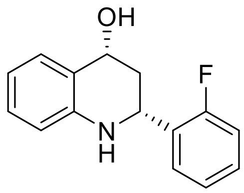
(2*R*,4*R*)-**2a**

(2*R*,4*R*)-1,2,3,4-Tetrahydro-2-phenyl-4-quinolinol ((2*R*,4*R*)-2a):[16] Light yellow solid (660 mg, 49%). $[\alpha]_D^{20}$ = +82.51 (*c* 1.084, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 6H), 6.99 (td, *J* = 7.6, 1.7 Hz, 1H), 6.67 (td, *J* = 7.4, 1.0 Hz, 1H), 6.41 (d, *J* = 7.9 Hz, 1H), 4.87 (dd, *J* = 10.4, 5.8 Hz, 1H), 4.39 (dd, *J* = 11.4, 2.7 Hz, 1H), 3.94 (brs, 1H), 2.48 (brs, 1H), 2.25–2.20 (m, 1H), 1.95–1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 143.3, 128.8, 128.6, 127.9, 127.0, 126.6, 124.5, 118.0, 114.1, 67.3, 55.7, 41.4; HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, UV = 210 nm, flow rate = 0.8 mL/min) t_{R1} = 47.755 min (major) and t_{R2} = 64.347 min (minor), ee = 98%.



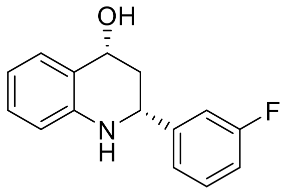
(2*S*,4*S*)-**2a**

(2*S*,4*S*)-1,2,3,4-Tetrahydro-2-phenyl-4-quinolinol ((2*S*,4*S*)-**2a):**[16] Light yellow solid (33.2 mg, 49%). $[\alpha]_D^{20}$ = –76.61 (*c* 0.684, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.43–7.26 (m, 6H), 7.06 (td, *J* = 7.6, 1.6 Hz, 1H), 6.74 (td, *J* = 7.2, 1.2 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 5.00 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.52 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.92 (brs, 1H), 2.40–2.32 (m, 1H), 2.08–1.98 (m, 1H) , 1.89 (brs, 1H); HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, UV = 210 nm, flow rate = 0.8 mL/min) t_{R1} = 47.815 min (major) and t_{R2} = 62.056 min (minor), ee = 94%.



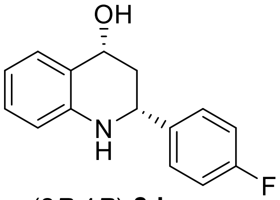
(2*R*,4*R*)-**2b**

(2*R*,4*R*)-2-(2-Fluorophenyl)-1,2,3,4-tetrahydro-4-quinolinol ((2*R*,4*R*)-**2b):** Pale yellow solid (35.8 mg, 49%). Mp 124-126 ºC; $[\alpha]_D^{20}$ = +56.29 (*c* 0.334, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.41 (td, *J* = 7.5, 1.9 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.28–7.24 (m, 1H), 7.13 (td, *J* = 7.4, 1.3 Hz, 1H), 7.09–7.02 (m, 2H), 6.75 (td, *J* = 7.4, 1.3 Hz, 1H), 6.53 (dd, *J* = 8.0, 1.3 Hz, 1H), 4.99 (dd, *J* = 9.7, 5.7 Hz, 1H), 4.91 (dd, *J* = 10.6, 3.0 Hz, 1H), 2.43–2.38 (m, 1H), 2.10–2.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 161.5, 159.1 (*J* = 246.4 Hz), 144.2, 130.3, 130.2 (*J* = 12.6 Hz), 129.1, 129.0 (*J* = 8.4 Hz), 128.7, 127.4, 124.5, 124.4 (*J* = 3.4 Hz), 118.2, 115.7, 115.5 (*J* = 21.8 Hz), 114.5, 67.0, 48.2 (*J* = 3.3 Hz), 39.2; ^{19}F NMR (376 MHz, $CDCl_3$) *δ* –119.7; IR (KBr): 2361, 2343, 1490, 1457, 1228, 751, 669, 418 cm^{-1}; HRMS (APCI) $C_{15}H_{14}FNONa$ $[M+Na]^+$ calcd 266.0952, found 266.0951; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 38.834 min (major) and t_{R2} = 31.842 min (minor), ee = 92%.



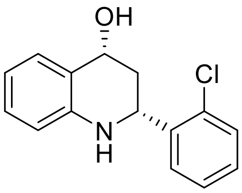
(2*R*,4*R*)-**2c**

(2*R*,4*R*)-2-(3-Fluorophenyl)-1,2,3,4-tetrahydroquinolin-4-ol ((2*R*,4*R*)-**2c):** Yellow solid (35.8 mg, 49%). Mp 95-97 ºC; $[\alpha]_D^{20}$ = +96.05 (*c* 0.314, acetone); ^{1}H NMR (400 MHz, $CDCl_3$, major rotamer): *δ* 7.39 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.33–7.28 (m, 1H), 7.16 (d, *J* = 7.7 Hz, 2H), 7.13 (dd, *J* = 9.8, 2.4 Hz, 1H), 7.06 (td, *J* = 7.6, 1.8 Hz, 1H), 6.98 (td, *J* = 7.3, 1.6 Hz, 1H), 6.75 (td, *J* = 7.4, 1.3 Hz, 1H), 6.52 (dd, *J* = 9.6, 1.2 Hz, 1H), 4.99 (dd, *J* = 10.2, 5.8 Hz, 1H), 4.52 (dd, *J* = 11.2, 2.9 Hz, 1H), 2.37–2.32 (m, 1H), 2.03–1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): *δ* 164.3, 161.9 (*J* = 247.3 Hz), 146.1, 146.0 (*J* = 6.8 Hz), 144.0, 130.4, 130.3 (*J* = 8.2 Hz), 128.7, 127.1, 124.4, 122.2 (*J* = 2.7 Hz), 118.2, 114.8, 114.6 (*J* = 21.2 Hz), 114.3, 113.6, 113.4 (*J* = 21.9 Hz), 67.1, 55.3 (*J* = 1.8 Hz), 41.3; ^{19}F NMR (376 MHz, $CDCl_3$) *δ* –112.3. IR (KBr): 3054, 2852, 2360, 1610, 1482, 1253, 750, 695 cm^{-1}; HRMS (APCI) $C_{15}H_{14}FNONa$ $[M+Na]^+$ calcd 266.0952, found 266.0952; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 37.032 min (major) and t_{R2} = 25.065 min (minor), ee = 95%.



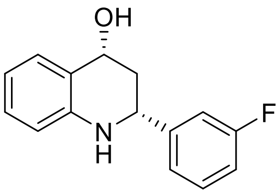
(2*R*,4*R*)-**2d**

(2*R*,4*R*)-2-(4-Fluorophenyl)-1,2,3,4-tetrahydro-4-quinolinol ((2*R*,4*R*)-**2d):**[17] A pale yellow solid (35.8 mg, 49%). $[\alpha]_D^{20}$ = +71.11 (*c* 0.522, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 1H), 7.34–7.29 (m, 1H), 7.19–7.13 (m, 2H), 7.13 (td, *J* = 7.4, 1.3 Hz, 1H), 7.08 (td, *J* = 7.8, 1.9 Hz, 1H), 6.98 (td, *J* = 8.4, 1.7 Hz, 1H), 6.76 (td, *J* = 7.4, 1.2 Hz, 1H), 6.54 (dd, *J* = 7.9, 1.2 Hz, 1H), 5.01 (dd, *J* = 10.1, 5.8 Hz, 1H), 4.00 (brs, 1H), 2.40–2.35 (m, 1H), 2.06–1.97 (m, 1H), 1.79 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 161.9 (*J* = 247.2 Hz), 146.1, 146.0 (*J* = 6.7 Hz), 144.0, 130.4, 130.3 (*J* = 8.3 Hz), 128.7, 127.1, 124.4, 122.2, 122.1 (*J* = 2.8 Hz), 118.2, 114.8, 114.6 (*J* = 21.2 Hz), 114.3, 113.6 (*J* = 21.9 Hz), 113.4, 67.1, 55.3 (*J* = 1.8 Hz), 41.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –112.4; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 37.062 min (major) and t_{R2} = 25.086 min (minor), ee = 94%.



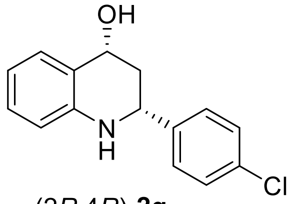
(2*R*,4*R*)-**2e**

(2*R*,4*R*)-2-(2-Chlorophenyl)-1,2,3,4-tetrahydro-4-quinolinol ((2*R*,4*R*)-**2e):** Pale yellow oil (38.2 mg, 49%). $[\alpha]_D^{20}$ = +176.67 (*c* 0.228, acetone); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.64 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.37 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.28 (td, *J* = 7.4, 1.7 Hz, 1H), 7.24–7.20 (m, 1H), 7.09 (td, *J* = 7.6, 1.6 Hz, 1H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 7.9 Hz, 1H), 5.08–5.02 (m, 2H), 3.96 (brs, 1H), 2.53–2.47 (m, 1H), 2.04–1.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 140.5, 132.7, 129.8, 128.7, 128.7, 127.4, 127.4, 127.3, 124.5, 118.3, 114.5, 67.1, 51.7, 38.9. IR (KBr): 2925, 2855, 2361, 2344, 1508, 1458, 1376, 752 cm^{-1}; HRMS (APCI) $C_{15}H_{14}ClNONa$ $[M+Na]^+$ calcd 266.0952, found 266.0952; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 43.752 min (major) and t_{R2} = 35.201 min (minor), ee = 95%.



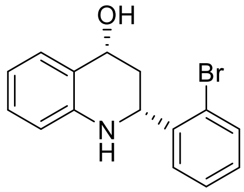
(2*R*,4*R*)-**2f**

(2*R*,4*R*)-2-(3-Chlorophenyl)-1,2,3,4-tetrahydro-4-quinolinol ((2*R*,4*R*)-**2f):** Pale yellow oil (38.2 mg, 49%). $[\alpha]_D^{20}$ = +88.80 (*c* 0.468, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 1.8 Hz, 4H), 7.07 (td, *J* = 7.8, 1.9 Hz, 1H), 6.75 (td, *J* = 7.4, 1.2 Hz, 1H), 6.52 (dd, J = 7.9, 1.2 Hz, 1H), 4.99 (dd, J = 10.2, 5.8 Hz, 1H), 4.55 (dd, J = 11.2, 2.8 Hz, 1H), 3.92 (brs, 1H), 2.35–2.29(m, 1H), 2.02–1.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 141.9, 133.5, 128.9, 128.7, 127.9, 127.0, 124.4, 118.2, 114.3, 67.2, 55.1, 41.4; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 54.847 min (major) and t_{R2} = 32.566 min (minor), ee = 92%.



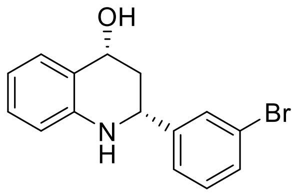
(2*R*,4*R*)-**2g**

(2*R*,4*R*)-2-(4-Chlorophenyl)-1,2,3,4-tetrahydro-4-quinolinol ((2*R*,4*R*)-2g):[18] Pale yellow solid (39.0 mg, 50%). $[\alpha]_D^{20}$ = +62.01 (*c* 103.4, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.5 Hz, 1H), 7.34–7.32 (m, 4H), 7.31–7.27 (m, 1H), 7.08 (td, J = 8.0 Hz, 1H), 6.77 (td, J = 7.4, 1.2 Hz, 1H), 6.55 (dd, J = 8.0, 1.2 Hz, 1H), 5.30 (dd, J = 10.2, 5.8 Hz, 1H), 4.55 (dd, J = 11.1, 2.8 Hz, 1H), 3.96 (brs, 1H), 2.40–2.34 (m, 1H), 2.10–1.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 141.8, 133.5, 128.9, 128.7, 127.9, 127.0, 124.4, 118.2, 67.2, 55.1, 41.4; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 37.127 min (major) and t_{R2} = 25.703 min (minor), ee = 92%.



(2*R*,4*R*)-**2h**

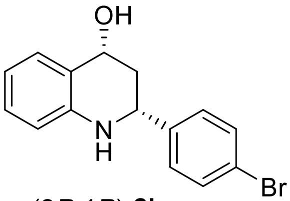
(2*R*,4*R*)-2-(2-Bromophenyl)-1,2,3,4-tetrahydro-4-quinolinol ((2*R*,4*R*)-2h): Pale yellow solid (39.2 mg, 43%). Mp 115-117 ºC; $[\alpha]_D^{20}$ = +85.38 (*c* 0.342, acetone); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.56 (dd, J = 7.8, 1.8 Hz, 1H), 7.53 (dd, J = 8.0, 1.3 Hz, 1H), 7.34 (d, J = 7.7 Hz, 1H), 7.25 (td, J = 7.4, 1.3 Hz, 1H), 7.07 (td, J = 7.5, 1.7 Hz, 1H), 7.01 (td, J = 7.6, 1.6 Hz, 1H), 6.70 (td, J = 7.4, 1.2 Hz, 1H), 6.50 (d, J = 8.0 Hz, 1H), 4.99 (dd, J = 10.0, 5.8 Hz, 1H), 4.90 (dd, J = 10.6, 2.8 Hz, 1H), 3.89 (brs, 1H), 2.45–2.40 (m, 1H), 1.96–1.83 (m, 1H), 1.69 (brs, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 144.9, 142.9, 132.7, 128.9, 128.0, 127.6, 126.7, 125.3, 122.3, 116.9, 114.2, 66.2, 54.4, 39.5; IR (KBr): 2925, 2855, 2361, 1458, 1376, 751, 669 cm^{-1}; HRMS (APCI) $C_{15}H_{14}BrNONa$ $[M+Na]^+$ calcd 266.0952, found 266.0952; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 46.849 min (major) and t_{R2} = 36.855 min (minor), ee = 96%.



(2*R*,4*R*)-**2i**

(2*R*,4*R*)-2-(3-Bromophenyl)-1,2,3,4-tetrahydro-4-quinolinol ((2*R*,4*R*)-2i): Pale yellow oil (42.9 mg, 47%). $[\alpha]_D^{20}$ = +105.77 (*c* 0.222, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, J = 1.8

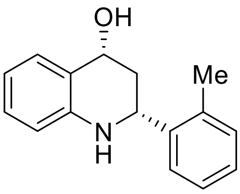
Hz, 1H), 7.42 (t, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.24–7.20 (m, 1H), 7.08 (td, *J* = 7.6, 1.8 Hz, 1H), 6.77 (dd, *J* = 7.4, 1.2 Hz, 1H), 6.54 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.02 (dd, *J* = 10.2, 5.8 Hz, 1H), 4.52 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.97 (brs, 1H), 2.40–2.34 (m, 1H), 2.05–1.97 (m, 1H); 1.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 145.7, 143.9, 131.0, 130.4, 129.7, 128.7, 127.0, 125.2, 124.4, 122.8, 118.3, 114.3, 67.1, 55.3, 41.4; IR (KBr): 2924, 2854, 2360, 2344, 1460, 750, 669 cm^{-1}; HRMS (APCI) $C_{15}H_{14}BrNONa$ $[M+Na]^+$ calcd 326.0151, found 326.0150; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 37.356 min (major) and t_{R2} = 26.892 min (minor), ee = 95%.



(2*R*,4*R*)-**2j**

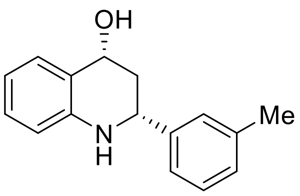
(2*R*,4*R*)-2-(4-Bromophenyl)-1,2,3,4-tetrahydro-4-quinolinol ((2*R*,4*R*)-**2j):**[18] Pale yellow solid (43.8 mg, 48%). $[\alpha]_D^{20}$ = +82.87 (*c* 0.376, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.47 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.76 (td, *J* = 7.4, 1.2 Hz, 1H), 6.52 (dd, *J* = 8.0, 1.1 Hz, 1H), 5.01 (dd, *J* = 10.2, 5.8 Hz, 1H), 4.53 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.95 (brs, 1H), 2.3–2.30 (m, 1H), 2.03–1.94 (m, 1H), 1.87 (brs, 1H); C NMR (100 MHz, $CDCl_3$) *δ* 144.0, 142.4, 131.9, 128.7, 128.3, 127.0, 124.4, 121.5, 118.2, 114.3, 67.1, 55.2, 41.4; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 54.498 min (major) and t_{R2} = 34.691 min (minor), ee = 98%.

Chemical Formula: $C_{16}H_{17}NO$



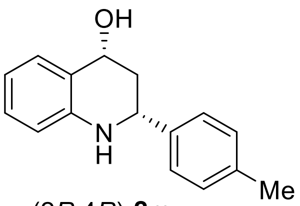
(2*R*,4*R*)-**2k**

(2*R*,4*R*)-2-(2-Methylphenyl)-1,2,3,4-Tetrahydro-4-quinolinol ((2*R*,4*R*)-**2k):** Pale yellow oil (35.2 mg, 49%). $[\alpha]_D^{20}$ = +84.44 (*c* 0.540, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.56 (d, *J* = 7.0 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.23–7.15 (m, 3H), 7.07 (td, *J* = 7.7, 1.8 Hz, 1H), 6.75 (td, *J* = 7.5, 1.2 Hz, 1H), 6.53 (dd, *J* = 7.9, 1.2 Hz, 1H), 5.04 (dd, *J* = 10.4, 5.9 Hz, 1H), 4.80 (dd, *J* = 11.1, 2.6 Hz, 1H), 4.88 (brs, 1H), 2.40–2.34 (m, 4H), 2.02–1.93 (m, 1H), 1.80 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 144.6, 141.1, 135.0, 130.8, 128.6, 127.5, 127.1, 126.7, 125.7, 124.5, 117.9, 114.2, 67.5, 51.6, 39.8, 19.1; IR (KBr): 3347, 2951, 2361, 1658, 1609, 1507, 758, 669 cm^{-1}; HRMS (APCI) $C_{16}H_{17}NONa$ $[M+Na]^+$ calcd 262.1202, found 262.1202 HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 40.851 min (major) and t_{R2} = 30.304 min (minor), ee = 98%.



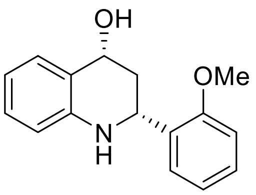
(2*R*,4*R*)-**2l**

(2*R*,4*R*)-2-(3-Methylphenyl)-1,2,3,4-Tetrahydro-4-quinolinol ((2*R*,4*R*)-**2l):** Pale yellow oil (35.2 mg, 49%). $[\alpha]_D^{20}$ = +89.24 (*c* 0.502, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 1H), 7.26–7.18 (m, 3H), 7.11 (d, *J* = 7.4 Hz, 1H), 7.06 (td, *J* = 9.8, 1.5 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 5.00 (dd, *J* = 10.3, 5.8 Hz, 1H), 4.49 (dd, *J* = 11.3, 2.7 Hz, 1H), 3.95 (brs, 1H), 2.38–2.33 (m, 4H), 2.07–1.99 (m, 1H), 1.85 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 143.3, 138.5, 128.7, 128.6, 128.6, 127.3, 127.0, 124.5, 123.6, 117.9, 114.1, 67.4, 55.7, 41.4, 21.5; IR (KBr): 2925, 2855, 2361, 1461, 1377, 747, 703, 669 cm^{-1}; HRMS (APCI) $C_{16}H_{17}NONa$ $[M+Na]^+$ calcd 262.1202, found 262.1202; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = min (major) and t_{R2} = min (minor), ee = 97%.



(2*R*,4*R*)-**2m**

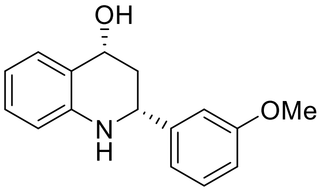
(2*R*,4*R*)-2-(4-Methylphenyl)-1,2,3,4-Tetrahydro-4-quinolinol ((2*R*,4*R*)-**2m):**[18] Pale yellow solid (33.7 mg, 47%). $[\alpha]_D^{20}$ = +100.21 (*c* 0.374, $CDCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.36–7.27 (m, 4H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 8.2 Hz 1H), 5.00 (dd, *J* = 10.3, 5.8 1H), 4.49 (dd, *J* = 11.3, 2.7 Hz, 1H), 2.38–2.33 (m, 4H), 2.07–1.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 141.1, 135.0, 130.7, 128.6, 127.0, 126.6, 125.7, 124.5,117.9, 114.2, 67.4, 51.6, 39.8, 19.1; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 44.048 min (major) and t_{R2} = 33.563 min (minor), ee = 98%.



(2*R*,4*R*)-**2n**

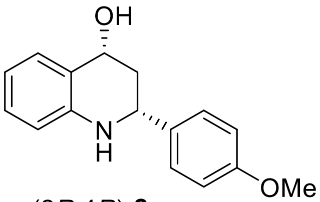
(2*R*,4*R*)-2-(2-Methoxyphenyl)-1,2,3,4-tetrahydroquinolin-4-ol ((2*R*,4*R*)-**2n):** White solid (37.5 mg, 49%). Mp 125-127 ºC; $[\alpha]_D^{20}$ = +196.6 (*c* 0.200, acetone); ^{1}H NMR (400 MHz, $CDCl_3$, major rotamer): δ 7.48 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.39 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.25 (d, *J* = 8.9 Hz, 1H), 7.06 (td, *J* = 7.6, 1.5 Hz, 1H), 6.96 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.73 (td, *J* = 8.5, 1.1 Hz, 1H), 6.54 (dd, *J* = 7.9, 1.0 Hz, 1H), 5.03–4.94 (m, 2H), 3.83 (s, 3H), 2.47–2.42 (m, 1H), 2.74 (q, *J* = 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): δ 156.7, 144.8, 137.1, 131.2, 128.5, 126.3, 124.6, 120.9, 117.8, 114.4, 110.5, 67.4, 55.4, 48.5, 38.5; IR (KBr): 2925, 2855, 2361, 2343, 1458, 1376, 1241, 751, 669 cm^{-1}; HRMS (APCI) $[M+Na]^+$ calcd

278.1151, found 278.1148; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 49.900 min (major) and t_{R2} = 43.384 min (minor), ee = 91%.



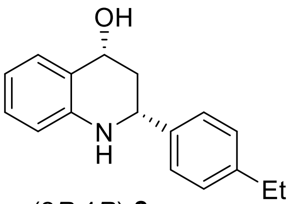
(2*R*,4*R*)-**2o**

(2*R*,4*R*)-2-(3-Methoxyphenyl)-1,2,3,4-tetrahydroquinolin-4-ol ((2*R*,4*R*)-**2o):** Yellow oil (37.5 mg, 49%). $[\alpha]_D^{20}$ = +37.93 (*c* 0.348, acetone); ^{1}H NMR (400 MHz, $CDCl_3$, major rotamer): δ 7.42 (d, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.25 (d, *J* = 8.9 Hz, 1H), 7.06 (td, *J* = 7.6, 1.5 Hz, 2H), 6.96 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.73 (td, *J* = 8.5, 1.1 Hz, 1H), 6.54 (dd, *J* = 7.9, 1.0 Hz, 1H), 5.03–4.94 (m, 2H), 3.81 (s, 3H), 2.47–2.42 (m, 1H), 2.78–2.70 (q, *J* = 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): δ 160.0, 145.0 144.2, 129.8, 128.6, 127.0, 124.4, 118.8, 117.9, 114.1, 113.2, 112.1, 67.3, 55.6, 55.3, 41.3; IR (KBr): 2923, 2836, 2361, 2344, 1608, 1485, 1312, 1258, 1039, 750, 669 cm^{-1}; HRMS (APCI) $C_{16}H_{17}NO_2Na$ $[M+Na]^+$ calcd 278.1151, found 278.1150; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 49.125 min (major) and t_{R2} = 35.430 min (minor), ee = 90%.



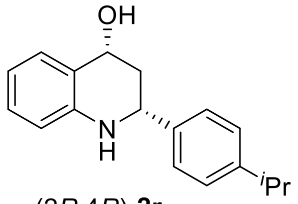
(2*R*,4*R*)-**2p**

(2*R*,4*R*)-2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroquinolin-4-ol ((2*R*,4*R*)-**2p):**[18] Yellow solid (37.5 mg, 48%). $[\alpha]_D^{20}$ = +57.07 (*c* 0.396, acetone); ^{1}H NMR (400 MHz, $CDCl_3$, major rotamer): δ 7.41 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.51 (d, *J* = 7.9 Hz, 1H), 5.02 (dd, *J* = 10.4, 5.8 Hz, 1H), 4.50 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.80 (s, 3H), 2.38–2.33 (m, 1H), 2.08–1.99 (m, 1H), 1.76 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): δ 159.2, 144.4, 135.3, 128.6, 127.7, 127.0, 124.5, 117.9, 114.1, 67.4, 55.4, 55.1, 41.5; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 74.571 min (major) and t_{R2} = 45.130 min (minor), ee = 93%.



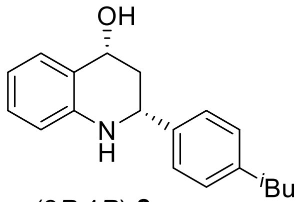
(2*R*,4*R*)-**2q**

(2*R*,4*R*)-2-(4-Ethylphenyl)-1,2,3,4-Tetrahydro-4-quinolinol ((2*R*,4*R*)-**2q):** Pale yellow oil (37.2 mg, 49%). $[\alpha]_D^{20}$ = +66.53 (*c* 0.478, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.05 (td, *J* = 7.8, 2.0 Hz, 1H), 6.73 (td, *J* = 7.4, 1.1 Hz, 1H), 6.49 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.00 (dd, *J* = 10.4, 6.0 Hz, 1H), 4.51 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.95 (brs, 1H), 2.65 (q, *J* = 7.5 Hz, 2H), 2.39–2.33 (m, 1H), 2.08–1.99 (m, 1H), 1.81 (brs, 1H), 1.24 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 144.0, 140.5, 128.6, 128.3, 127.0, 126.6, 124.5, 117.9, 114.1, 67.4, 55.4, 41.4, 28.6, 15.6; IR (KBr): 2924, 2854, 2362, 2345, 1608, 1459, 1037, 747, 669 cm^{-1}; HRMS (APCI) $C_{17}H_{19}NONa$ $[M+Na]^+$ calcd 276.1359, found 276.1359; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 34.862 min (major) and t_{R2} = 31.118 min (minor), ee = 93%.



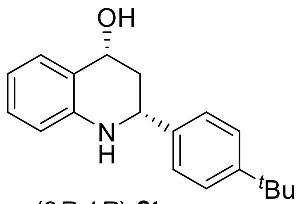
(2*R*,4*R*)-**2r**

(2*R*,4*R*)-2-(4-Isopropylphenyl)-1,2,3,4-Tetrahydro-4-quinolinol ((2*R*,4*R*)-**2r):** White oil (39.3 mg, 49%). $[\alpha]_D^{20}$ = +62.73 (*c* 0.440, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.39 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.3Hz, 2H), 7.21 (s, 1H), 7.06 (td, *J* = 7.9, 1.7 Hz, 1H), 6.74 (t, *J* = 7.3 Hz, 1H), 5.00 (dd, *J* = 10.3, 5.8 Hz, 1H), 4.55 (dd, *J* = 11.2, 2.7 Hz, 1H), 3.98 (brs, 1H), 2.99–2.87 (m, 1H), 2.46–2.37 (m, 1H), 2.15–2.02 (m, 1H), 1.70 (brs, 1H), 1.27 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 144.4, 140.6, 128.6, 127.0, 126.8, 126.6, 124.5, 117.8, 114.1, 67.4, 55.4, 41.3, 33.9, 24.0; IR (KBr): 2955, 2925, 2856, 2361, 2344, 1609, 1480, 1309, 748, 669 cm^{-1}; HRMS (APCI) $C_{18}H_{21}NONa$ $[M+Na]^+$ calcd 290.1515, found 290.1516; HPLC (Chiralcel IE-H, *n*-hexane/*i*-PrOH = 95/5, UV = 210 nm, flow rate = 0.7 mL/min) t_{R1} = 29.057 min (major) and t_{R2} = 23.128 min (minor), ee = 95%.



(2*R*,4*R*)-**2s**

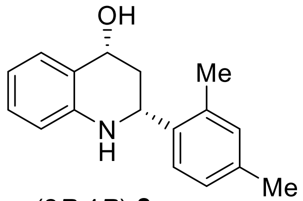
(2*R*,4*R*)-2-(4-Isobutylphenyl)-1,2,3,4-Tetrahydro-4-quinolinol ((2*R*,4*R*)-**2s):** Pale yellow solid (41.4 mg, 49%). Mp 105-107 ºC; $[\alpha]_D^{20}$ = +60.09 (*c* 0.446, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 5.00 (dd, *J* = 10.2, 5.8 Hz, 1H), 4.51 (d, *J* = 11.2, 3.0 Hz, 1H), 3.96 (brs, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 2.39–2.34 (m, 1H), 2.09–2.00 (m, 1H), 1.91–1.81 (m, 2H), 1.67 (brs, 1H), 0.91 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 141.4, 140.5, 129.5, 128.6, 127.0, 126.3, 124.5, 117.8, 114.1, 67.4, 55.4, 45.1, 41.4, 30.3, 22.4; IR (KBr): 2952, 2924, 2361, 2343, 1477, 1310, 1037, 747, 669 cm^{-1}; HRMS (APCI) $C_{19}H_{23}NONa$ $[M+Na]^+$ calcd 304.1672, found 304.1674; HPLC (Chiralcel IE-H, *n*-hexane/*i*-PrOH = 95/5, UV = 210 nm, flow rate = 0.7 mL/min) t_{R1} = 32.378 min (major) and t_{R2} = 27.039 min (minor), ee = 93%.



(2*R*,4*R*)-**2t**

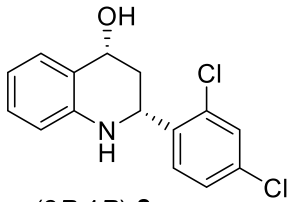
(2*R*,4*R*)-2-(4-*tert*-Butylphenyl)-1,2,3,4-Tetrahydro-4-quinolinol ((2*R*,4*R*)-**2t):** White solid

(41.4 mg, 49%). Mp 109-111 ºC; $[\alpha]_D^{20}$ = +63.08 (*c* 0.428, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.41–7.32 (m, 5H), 7.05 (td, *J* = 7.5, 1.6 Hz, 1H), 6.73 (td, *J* = 7.5, 1.3 Hz, 1H), 6.49 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.01 (dd, *J* = 10.3, 5.8 Hz, 1H), 3.96 (brs, 1H), 2.40–2.35 (m, 1H), 2.09–2.01 (m, 1H), 1.81 (brs, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 150.9, 144.4, 140.2, 128.6, 127.1, 126.3, 125.7, 124.5, 117.9, 114.1, 67.4, 55.4, 41.2, 34.6, 31.4; IR (KBr): 2954, 2924, 2361, 1609, 1480, 1310, 748, 577 cm^{-1}; HRMS (APCI) $[M+Na]^+$ calcd 304.1672, found 304.1672; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 21.702 min (major) and t_{R2} = 23.195 min (minor), ee = 93%.



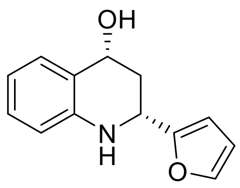
(2*R*,4*R*)-**2u**

(2*R*,4*R*)-2-(2,4-Dimethylphenyl)-1,2,3,4-tetrahydroquinolin-4-ol ((2*R*,4*R*)-2u): Colorless oil (37.2 mg, 49%). $[\alpha]_D^{20}$ = +80.13 (*c* 0.594, acetone); ^{1}H NMR (400 MHz, $CDCl_3$, major rotamer): *δ* 7.44 (t, *J* = 7.9 Hz, 2H), 7.10–7.00 (m, 3H), 6.75 (t, *J* = 6.9 Hz, 1H), 6.53 (d, *J* = 7.9 Hz, 1H), 5.05 (dd, *J* = 10.3, 5.8 Hz, 1H), 4.99 (dd, *J* = 10.6, 2.8 Hz, 1H), 3.86 (brs, 1H), 2.40–2.36 (m, 1H), 2.33 (d, *J* = 11.5 Hz, 1H), 1.66 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): *δ* 145.4, 139.0, 136.1, 134.7, 131.0, 127.5, 126.8, 126.6, 125.8, 125.4, 116.4, 113.8, 66.6, 51.4, 40.1, 20.1, 18.2; IR (KBr): 3527, 3373, 2921, 2864, 1610, 1481, 1311, 1038, 749, 573, 446 cm^{-1}; HRMS (APCI) $C_{17}H_{19}NONa$ $[M+Na]^+$ calcd 276.1359, found 276.1362; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 44.071 min (major) and t_{R2} = 30.267 min (minor), ee = 95%.



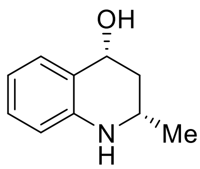
(2*R*,4*R*)-**2v**

(2*R*,4*R*)-2-(2,4-Dichlorophenyl)-1,2,3,4-tetrahydroquinolin-4-ol ((2*R*,4*R*)-2v): White solid (43.2 mg, 49%). Mp 166-168 ºC; $[\alpha]_D^{20}$ = +136.43 (*c* 0.560, acetone); ^{1}H NMR (400 MHz, $CDCl_3$, major rotamer): *δ* 7.58 (d, *J* = 7.6 Hz, 1H), 7.41–7.38 (m, 2H), 7.26–7.24 (m, 1H), 7.09 (td, *J* = 7.9, 2.2 Hz, 1H), 6.78 (td, *J* = 7.4, 2.2 Hz, 1H), 6.57 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.03 (dd, *J* = 9.7, 5.6 Hz, 1H), 4.97 (dd, *J* = 10.4, 3.0 Hz, 1H), 3.92 (brs, 1H), 2.47–2.42 (m, 1H), 1.97–1.89 (m, 1H), 1.80 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): *δ* 144.0, 139.3, 133.7, 133.2, 129.5, 128.8, 128.5, 127.7, 127.3, 124.4, 118.5, 114.6, 66.9, 51.3, 38.7; IR (KBr): 2925, 2855, 1746, 1467, 1378, 1253, 1099, 1039, 747, 572 cm^{-1}; HRMS (APCI) $C_{17}H_{19}NONa$ $[M+Na]^+$ calcd 316.0266, found 316.0263; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 60.496 min (major) and t_{R2} = 31.406 min (minor), ee = 92%.



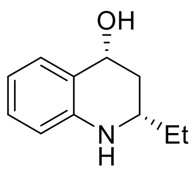
(2*R*,4*R*)-**2w**

(2*R*,4*R*)-2-(Furan-2-yl)-1,2,3,4-tetrahydroquinolin-4-ol ((2*R*,4*R*)-**2w):** Yellow solid (28.4 mg, 42%). Mp 109-111 ºC; $[\alpha]_D^{20}$ = –8.80 (*c* 0.190, acetone); ^{1}H NMR (400 MHz, $CDCl_3$, major rotamer): δ 7.38 (d, *J* = 6.6 Hz, 2H), 7.08 (td, *J* = 7.8, 1.8 Hz, 1H), 6.76 (td, *J* = 7.4, 1.2 Hz, 1H), 6.57 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.32 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 4.94 (dd, *J* = 8.5, 5.6 Hz, 1H), 4.66 (dd, *J* = 9.2, 3.4 Hz, 1H), 4.16 (brs, 1H), 2.51–2.46 (m, 1H), 2.30–2.23 (m, 1H), 1.70 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): δ 155.9, 143.3, 142.0, 128.8, 127.9, 127.0, 124.1, 118.3, 114.5, 110.3, 105.4, 66.3, 48.3, 36.7; IR (KBr): 2925, 2855, 2361, 1745, 1460, 1377, 1007, 746 cm^{-1}; HRMS (APCI) $[M+Na]^+$ calcd 238.0838, found 238.0838; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 36.105 min (major) and t_{R2} = 30.299 min (minor), ee = 90%.



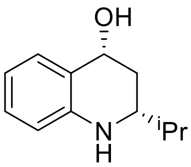
(2*S*,4*R*)-**2x**

(2*S*,4*R*)-2-Methyl-1,2,3,4-tetrahydroquinolin-4-ol ((2*S*,4*R*)-**2x):**[19] A white solid (36.2 mg, 49%). $[\alpha]_D^{20}$ = –37.72 (*c* 0.334, acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.72 Hz, 1H), 7.02 (t, *J* = 7.56 Hz, 1H), 6.70 (td, *J* = 7.44, 1.2 Hz, 1H), 6.46 (dd, *J* = 7.96, 1.20 Hz, 1H), 4.88 (dd, *J* = 10.56, 5.96 Hz, 1H), 3.56–3.48 (m, 1H), 2.23–2.18 (m,1H), 1.62–1.53 (m,1H), 1.21 (d, *J* = 6.28 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 128.4, 126.9, 124.7, 117.7, 114.0, 67.0, 46.4, 40.8, 22.4; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 210 nm, flow rate = 0.8 mL/min) t_{R1} = 20.648 min (major) and t_{R2} = 31.004 min (minor), ee = 98%.



(2*S*,4*R*)-**2y**

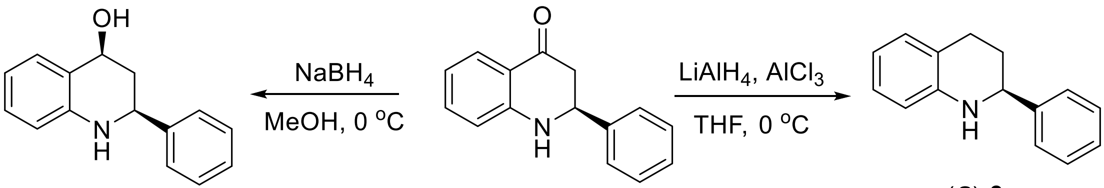
(2*S*,4*R*)-2-Ethyl-1,2,3,4-tetrahydroquinolin-4-ol ((2*S*,4*R*)-**2y):**[20] A white solid (25.52 mg, 48%). $[\alpha]_D^{20}$ = –32.84 (*c* 0.478, acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.68 Hz, 1H), 7.03 (t, *J* = 7.72 Hz, 1H), 6.70 (td, *J* = 7.36, 1.20 Hz, 1H), 6.48 (dd, *J* = 8.00, 1.20 Hz, 1H), 4.90 (dd, *J* = 10.48, 5.92 Hz, 1H), 3.36–3.29 (m, 1H), 2.29–2.24 (m, 1H), 1.59–1.54 (m, 2H), 0.99 (t, *J* = 7.48 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 128.4, 126.8, 124.9, 117.6, 114.0, 67.2, 52.2, 38.3, 29.2, 9.90; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 210 nm, flow rate = 0.8 mL/min) t_{R1} = 16.692 min (major) and t_{R2} = 23.687 min (minor), ee = 98%.



(2*R*,4*R*)-**2z**

(2*R*,4*R*)-2-Isopropyl-1,2,3,4-tetrahydroquinolin-4-ol ((2*R*,4*R*)**-2z)**:[21]A white solid (27.56 mg, 48%). $[\alpha]_D^{20}$ = –10.20 (*c* 0.510, acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.68 Hz, 1H), 7.03 (t, *J* = 7.68 Hz, 1H), 6.69 (td, *J* = 7.36, 1.16 Hz, 1H), 6.49 (dd, *J* = 7.96, 1.16 Hz, 1H), 4.90 (dd, *J* = 10.72, 5.88 Hz, 1H), 3.25–3.20 (m, 1H), 2.24–2.20 (m, 1H), 1.77–1.71 (m, 1H), 0.99 (dd, *J* = 6.84, 3.36 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 128.4, 126.6, 124.9, 117.4, 114.0, 67.5, 56.3, 35.3, 32.5, 18.3, 18.0; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 210 nm, flow rate = 0.8 mL/min) t_{R1} = 12.558 min (major) and t_{R2} = 14.799 min (minor), ee = 97%.

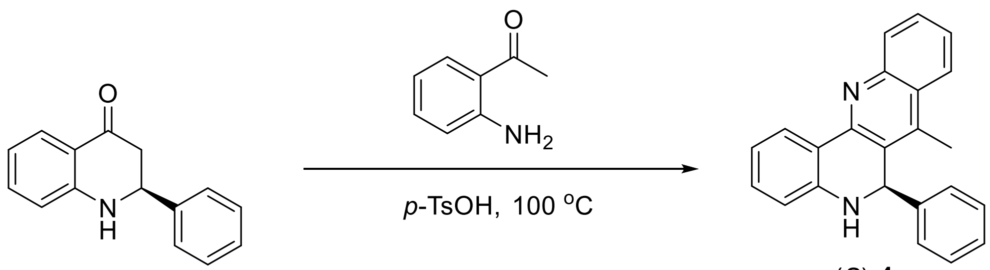
4. Transformation



(2*S*,4*S*)-**2a** (*S*)-**1a** (99% ee) (*S*)-**3**

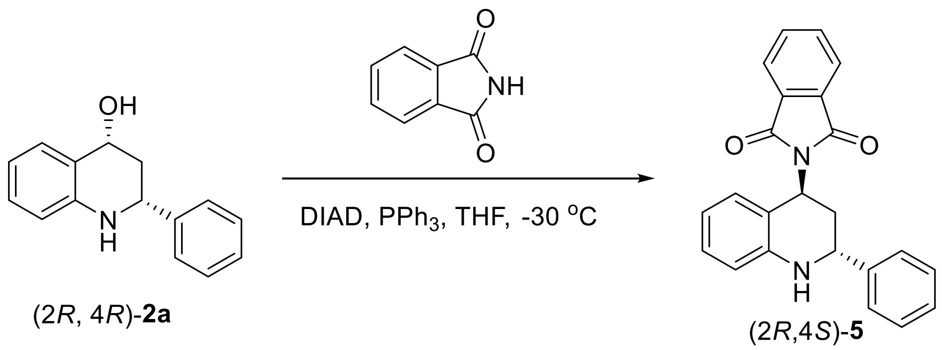
The synthesis of (2*S*,4*S*)**-2a:**[22] (*S*)**-1a** (44.6 mg, 0.2 mmol) was dissolved in MeOH (5 mL) and $NaBH_4$ (37.8 mg, 1.0 mmol) was added to the solution at 0 °C. After being stirred for 30 min, the reaction was quenched with H_2O (10 mL) and the resulting mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phase was dried over Na_2SO_4, concentrated under reduced pressure and the corresponding residue was purified by silica gel thin layer chromatography (EtOAc/*n*-hexane = 1/5) to give (2*S*,4*S*)**-2a** white solid (42.4 mg, 95%, 98% ee, >20:1). $[\alpha]_D^{20}$ = –135.39 (*c* 0.707, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 5H), 6.99 (td, *J* = 7.6, 1.7 Hz, 1H), 6.67 (td, *J* = 7.4, 1.0 Hz, 1H), 6.41 (d, *J* = 7.9 Hz, 1H), 4.87 (dd, *J* = 10.4, 5.8 Hz, 1H), 4.39 (dd, *J* = 11.4, 2.7 Hz, 1H), 3.94 (brs, 1H), 2.48 (brs, 1H), 2.25–2.20 (m, 1H), 1.95–1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 144.7, 129.3, 128.6, 127.4, 126.9, 126.5, 120.9, 117.2, 114.0, 55.3, 31.0, 26.4; HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, UV = 210 nm, flow rate = 0.8 mL/min) t_{R1} = 63.651 min (major) and t_{R2} = 48.190 min (minor), ee = 98%.

The synthesis of (*S*)**-3:**[22] (*S*)**-1a** (44.6 mg, 0.02 mmol) was dissolved in THF (2 mL) and $LiAlH_4$ (5.3 mg, 0.14 mmol) was added to the solution at 0 °C. The reaction mixture was warmed to room temperature and stirred for 30 min after being stirred for 1 h. Then, $AlCl_3$ (53.3 mg, 0.04 mmol) was added at room temperature under a N_2 atmosphere. After being stirred for 10 min, the reaction was quenched with H_2O. The mixture was extracted with CH_2Cl_2 (3 ×5 mL) and the combined organic phase was dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and purified by silica gel thin layer chromatography (EtOAc/*n*-hexanes = 1/10) to give (*S*)-**3** as a colorless oil (32.4 mg, 88%). $[\alpha]_D^{20}$ = –77.84 (*c* 0.388, acetone); ^{1}H NMR (400 MHz, $CDCl_3$, major rotamer): δ 7.39–7.27 (m, 5H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.64 (td, *J* = 7.3, 1.2 Hz, 1H), 6.52 (d, *J* = 7.3 Hz, 1H), 4.42 (dd, *J* = 9.2, 3.2 Hz, 1H), 4.02 (brs, 1H), 2.95–2.69 (m, 2H), 2.14–1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): δ 144.9, 144.8, 129.3, 128.6, 127.5, 126.9, 126.6, 120.9, 117.2, 114.0, 56.3, 31.0, 26.4; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 19.383 min (major) and t_{R2} = 17.183 min (minor), ee = 86%.



(*S*)-**4**

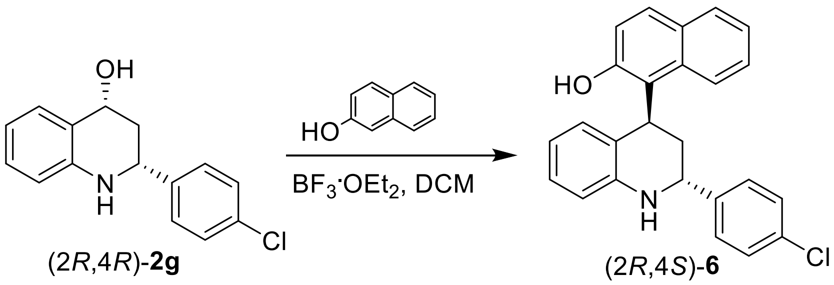
A mixture containing (*S*)-**1a** (111.6 mg, 0.5 mmol), 2-aminoacetophenone (120 μL, 0.10 mmol) and *p*-TsOH (83.6 mg, 0.5 mmol) was introduced into a Schlenk tube (10 mL) and stirred at 100 °C for 5 hours. After the reaction was completed, water (5 mL) and 10% NaOH was added to the mixture at room temperature. Then the mixture was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic phase was dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and purified by silica gel thin layer chromatography (EtOAc/*n*-hexanes = 1/10) to give (*S*)-**4**[23] (91.8 mg, 57%, 94% ee, >20:1). $[\alpha]_D^{20}$ = +4.00 (*c* 0.200, acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.13 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.68–7.63 (m, 1H), 7.47–7.43 (m, 1H), 6.20–7.12 (m, 1H), 6.93–6.87 (m, 1H), 6.52 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.90 (s, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6, major rotamer): δ 147.5, 146.1 143.9, 139.9, 131.2, 129.8, 128.9, 128.6, 128.5, 127.3, 126.8, 125.7, 125.5, 124.0, 121.0, 117.7, 115.0, 55.8, 13.0; HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80/20, UV = 210 nm, flow rate = 0.3 mL/min) t_{R1} = 32.525 min (major) and t_{R2} = 28.954 min (minor), ee = 94%.



(2*R*, 4*R*)-**2a**

(2*R*,4*S*)-**5**

Diisopropyl azodicarboxylate (DIAD) (0.16 mL, 0.81 mmol) was added dropwise to a stirred solution of (2*R*,4*R*)-**2a** (149 mg, 0.66 mmol), PPh_3 (204 mg, 0.0.78 mmol) and phthalimide (102 mg, 0.69 mmol) in dry THF (5 mL) at –30 °C before the mixture was warmed to room temperature and stirred for 1 h. Then the solvent was evaporated under reduced pressure to provide crude product which was purified by chromatography (PE/EtOAc = 10/1) to give (2*R*, 4*S*)-**5** as light-yellow solid (163 mg, 70%, 97% ee, >20:1). Mp 167–169 °C; $[\alpha]_D^{20}$ = –307.34 (*c* 0.856, acetone); ^{1}H NMR (400 MHz, $CDCl_3$, major rotamer): δ 7.82 (d, *J* = 3.0 Hz, 1H), 7.80 (d, *J* = 2.9 Hz, 1H), 7.70 (d, *J* = 3.2 Hz, 1H), 7.7.69 (d, *J* = 3.04 Hz, 1H), 7.40-7.27 (m, 5H), 7.11-7.02 (m, 1H), 6.94 (d, *J* = 7.24 Hz, 1H), 6.65 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.62 (td, *J* = 7.3, 1.1 Hz, 1H), 5.44 (t, *J* = 5.0 Hz, 1H), 4.77 (dd, *J* = 10.1, 3.5 Hz, 1H), 4.35 (brs, 1H), 2.44–2.39 (m, 1H), 2.33–2.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): δ 168.3, 145.8 143.7, 134.1, 132.0, 128.9, 128.7, 128.2, 127.7, 126.7, 123.3, 117.4, 117.0, 114.5, 53.0, 45.7, 37.3; IR (KBr): 3473, 2917, 2849, 1710, 1609, 1388, 1265, 1111, 746, 721, 530 cm^{-1}; HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, UV = 210 nm, flow rate = 0.7 mL/min) t_{R1} = 42.917 min (major) and t_{R2} = 63.785 min (minor), ee = 97%.



To a stirred solution of (2*R*,4*R*)-**2a** (130 mg, 0.5 mmol) and 2-naphthol (91 mg, 0.63 mmol) in CH_2Cl_2 (5 mL) was added $BF_3{\cdot}OEt_2$ (0.64 mL). The mixture was stirred at room temperature for 12 hours. Then the mixture was quenched by the addition of $NaHCO_3$ solution and was stirred for another 10 min. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4. Chromatography over silica gel using CH_2Cl_2/light petroleum (1:1) gave compound (2*R*,4*S*)-**6**[24] as light-yellow solid (110 mg, 63%, 95% ee, >20:1). ^{1}H NMR (400 MHz, $CDCl_3$, major rotamer): δ 7.80 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 11.3 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 3.0 Hz, 1H), 7.36–7.27 (m, 6H), 7.11–7.02 (m, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.07–7.02 (m, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.69 (t, *J* = 7.0 Hz, 1H), 5.86 (brs, 1H), 4.87 (t, *J* = 7.0 Hz, 1H), 4.59 (dd, *J* = 7.4, 3.6 Hz, 1H), 2.48–2.42 (m, 1H), 2.31–2.24 (m, 1H), 1.56 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): δ 152.8, 144.4 142.7, 133.1, 132.8, 129.7, 129.2, 129.0, 128.8, 127.8, 126.9, 123.3, 121.7, 120.9, 120.3, 118.9, 118.6, 115.1, 53.0, 36.1, 32.7; HPLC (Chiralcel IC-3, *n*-hexane/*i*-PrOH = 97/3, UV = 210 nm, flow rate = 0.7 mL/min) t_{R1} = 21.884 min (major) and t_{R2} = 12.148 min (minor), ee = 95%.

5. References

[1] K. J. Emery, T. Tuttle, A. R. Kennedy and J. A. Murphy, *Tetrahedron* 2016, **72**, 7875.

[2] M. Muthukrishnan, M. Mujahid, V. Punitharasu and D. A. Dnyaneshwar, *Synth. Commun.* 2010, **40**, 1391.

[3] J. Li, L. Jin, C. Yu and W. Su, *J. Chem. Res.* 2009, **3**, 170.

[4] R. P. Pandit, K. Sharma and Y. R. Lee, *Synthesis* 2015, 3881.

[5] K. H. Kumar, D. Muralidharan and P. T. Perumal, *Synthesis* 2004, 63.

[6] J. S. Mahanty, M. De, P. Das and N. G. Kundu, *Tetrahedron* 1997, **53**, 13397.

[7] R. Liu, Y. Zhang, K. Xu and G. Tan, *Synth. Commun.* 2017, **47**, 1.

[8] Y. Xia, Z.-Y. Yang, P. Xia, K. F. Bastow, Y. Tachibana, S.-C. Kuo, E. Hamel, T. Hackl and K.-H. Lee, *J. Med. Chem.* 1998, **41**, 1155.

[9] X. Zheng, H. Jiang, J. Xie, Z. Yin and H. Zhang, *Synth. Commun.* 2013, **43**, 1023.

[10] G.-F. Pan, L. Su, Y.-L. Zhang, S.-H. Guo and Y.-Q. Wang, *RSC Advances* 2016, **6**, 25375.

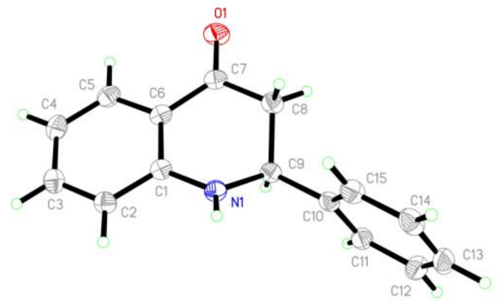
[11] K. Kanagaraj and K. Pitchumani, *J. Org. Chem.* 2013, **78**, 744.

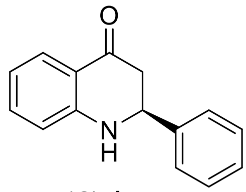
[12] C. Guo, X. Su, Z. Hou, S. Song, X. Yang, H. Xu, R. An, X. Liu and C. Han, CN108558756A, **2018**.

[13] R. Gosmini, V. L. Nguyen, J. Toum, C. Simon, J.-M. G. Brusq, G. Krysa, O. Mirguet, A. M. Riou-Eymard, E. V. Boursier, L. Trottet, P. Bamborough, H. Clark, C.-W. Chung, L. Cutler, E. H. Demont, R. Kaur, A. J. Lewis, M. B. Schilling, P. E. Soden, S. Taylor, A. L. Walker, M. D. Walker, R. K. Prinjha and E. Nicodème, *J. Med. Chem.* 2014, **57**, 8111.
[14] Y. Guo and S. R. Harutyunyan, *Angew. Chem. Int. Ed.* 2019, **58**,12950.
[15] J. P. Edwards, R. I. Higuchi, D. T. Winn, C. L. F. Pooley, T. R. Caferro, L. G. Hamann, L. Zhi, K. B. Marschke, M. E. Goldman and T. K. Jones, *Bioorg Med Chem Lett*. 1999, **9**, 1003.
[16] Y. Liu, J. Wei and C.-M. Che, *Chem. Commun.* 2010, **46**, 6926.
[17] P. M. Sabale, P. Walke and U. Solanki, *Indian J. Heterocyc. Chem.* 2015, 24, 265.
[18] A. R. Rao and J. N. Murthy, WO2009/087684A2, **2009**.
[19] B.-L. Lei, C.-H. Ding, X.-F. Yang, X.-L. Wan and X.-L. Hou, *J. Am. Chem. Soc.* 2009, **131**, 18250.
[20] J. Wang, K. Li, X. Zhou, W. Han, N. Wan, B. Cui, H. Wang, W. Yuan and Y. Chen *Tetrahedron Lett*. 2017, **58**, 2252.
[21] A. van Oeveren, B. A. Pio, C. M. Tegley, R. I. Higuchi, M. Wu, T. K. Jones, K. B. Marschke, A. Negro-Vilar and L. Zhi, *Bioorg Med Chem Lett*. 2007, **17**, 1523.
[22] K. Saito, Y. Moriya and T. Akiyama, *Org. Lett.* 2015, **17**, 3202.
[23] D. Mao, J. Tang, W. Wang, X. Liu, S. Wu, J. Yu and L. Wang, *Org. Biomol. Chem.* 2015, **13**, 2122.
[24] R. D. Devakaram, S. Black and N. Kumar, *Tetrahedron Lett.* 2012, **53**, 2269.

6. X-ray Crystal Structure Analysis

X-Ray Crystallography Data for (*S*)-**1a** (CCDC 2089632): A light yellow crystal suitable for X-ray crystallography was obtained from natural crystallization at room temperature under air.





(*S*)-**1a**

Figure The ORTEP drawing (50% probability for thermal ellipsoids) of (*S*)-**1a**

Bond precision: C-C = 0.0027 A Wavelength=1.54178

Cell:	a=5.4753(1)	b=13.6812(3)	c=15.3625(3)
	alpha=90	beta=90	gamma=90
Temperature:	173 K		

	Calculated	Reported
Volume	1150.79(4)	1150.78(4)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C15 H13 N O	C15 H13 N O
Sum formula	C15 H13 N O	C15 H13 N O
Mr	223.26	223.26
Dx,g cm-3	1.289	1.289
Z	4	4
Mu (mm-1)	0.637	0.637
F000	472.0	472.0
F000'	473.33	
h,k,lmax	6,16,18	6,16,18
Nref	2118[1259]	2109
Tmin,Tmax	0.892,0.909	0.673,0.753
Tmin'	0.892	

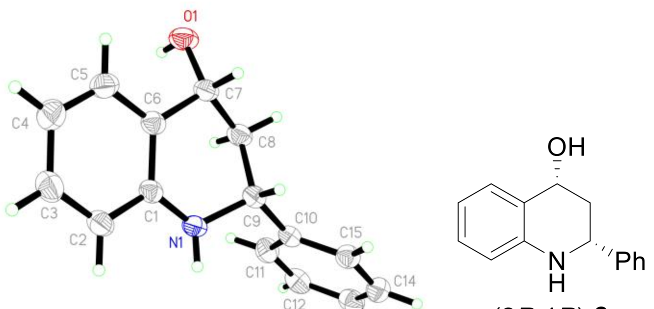
Correction method= # Reported T Limits: Tmin=0.673 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 1.68/1.00 Theta(max)= 68.254

R(reflections)= 0.0312(2052) wR2(reflections)= 0.0851(2109)

S = 1.058 Npar= 154

X-Ray Crystallography Data for (*R*,*R*)-**2a** (CCDC 2090799): A light yellow crystal suitable for X-ray crystallography was obtained from natural crystallization at room temperature under air.



(2*R*,4*R*)-**2a**

Figure The ORTEP drawing (50% probability for thermal ellipsoids) of (*R*,*R*)-2**a**

Bond precision:	C-C = 0.0024 A		Wavelength=1.54178
Cell:	a=5.4718(3)	b=13.1212(7)	c=16.6256(10)
	alpha=90	beta=90	gamma=90
Temperature:	298 K		

	Calculated	Reported
Volume	1193.66(12)	1193.66(12)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C15 H15 N O	C15 H15 N O
Sum formula	C15 H15 N O	C15 H15 N O
Mr	225.28	225.28
Dx,g cm-3	1.254	1.254
Z	4	4
Mu (mm-1)	0.615	0.615
F000	480.0	480.0
F000'	481.33	
h,k,lmax	6,15,20	6,15,20
Nref	2207[1311]	2196
Tmin,Tmax	0.906,0.918	0.672,0.753
Tmin'	0.906	

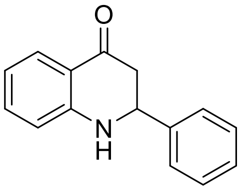
Correction method= # Reported T Limits: Tmin=0.672 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 1.68/1.00 Theta(max)= 68.413

R(reflections)= 0.0292(2093) wR2(reflections)= 0.0779(2196)

S = 1.026 Npar= 159

7. NMR Spectra



rac-**1a**

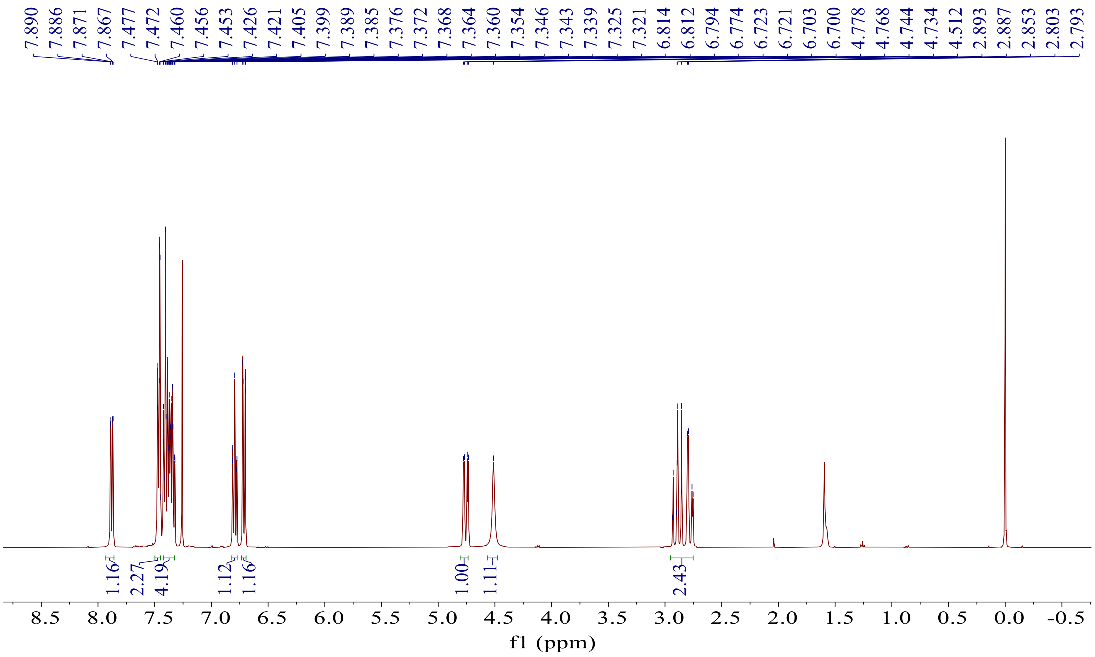


Figure S1 ^{1}H NMR Spectrum of *rac*-**1a** (400 MHz, $CDCl_3$)

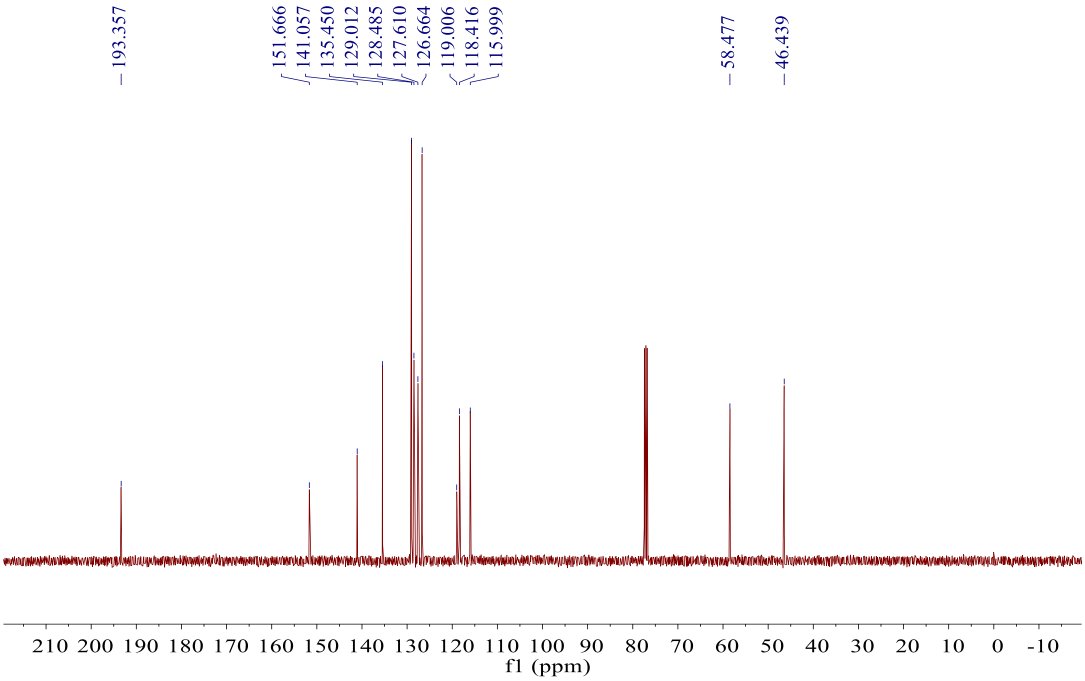
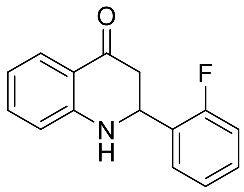


Figure S2 ^{13}C NMR Spectrum of *rac*-**1a** (100 MHz, $CDCl_3$)



rac-**1b**

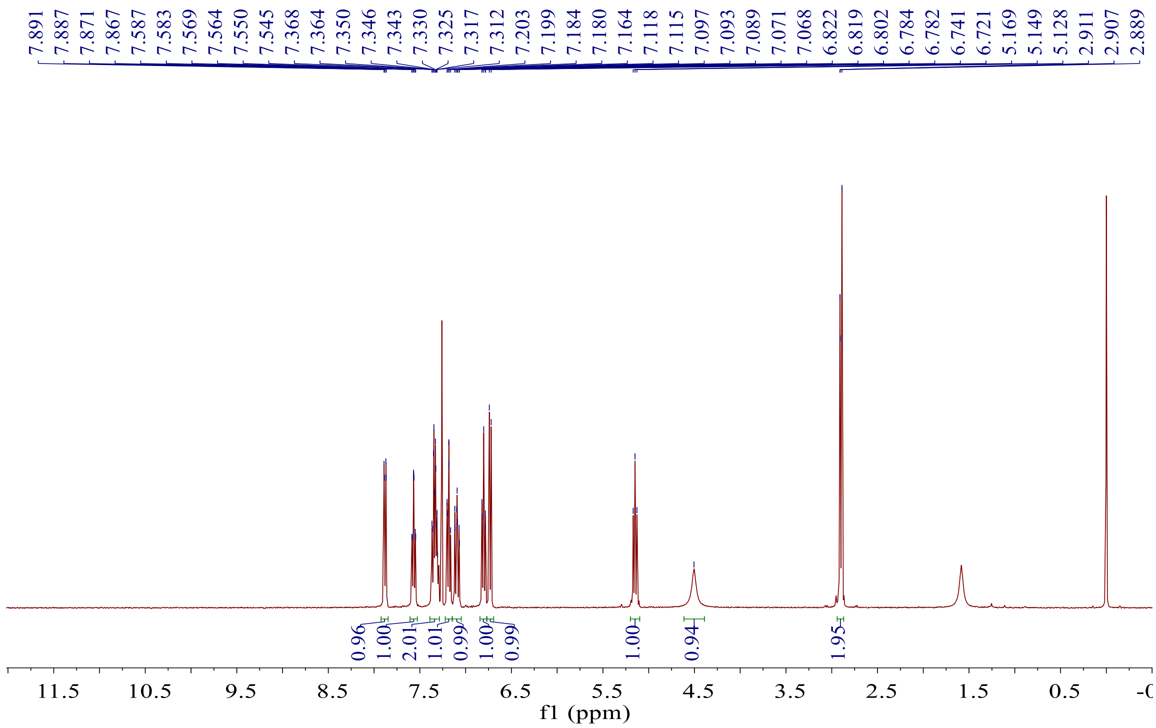


Figure S3 ^{1}H NMR Spectrum of *rac*-**1b** (400 MHz, $CDCl_3$)

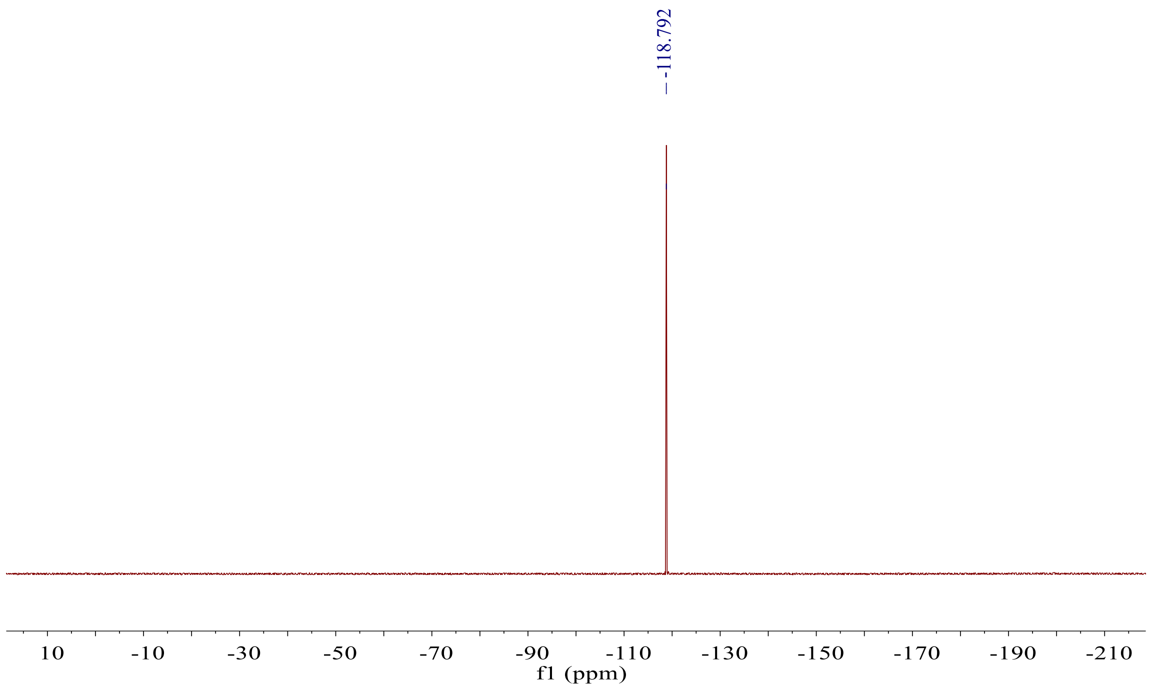


Figure S4 ^{19}F NMR Spectrum of *rac*-**1b** (376 MHz, $CDCl_3$)

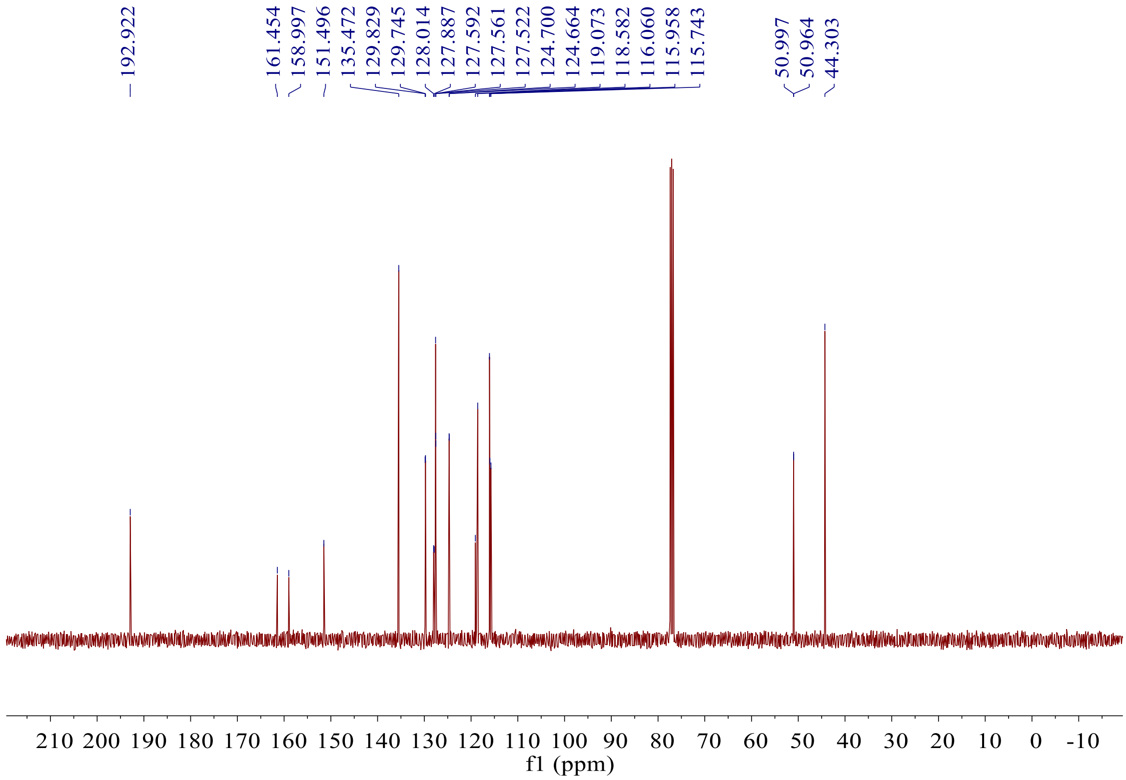
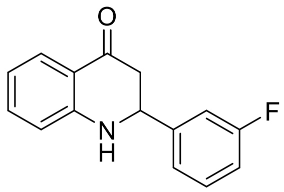


Figure S5 ^{13}C NMR Spectrum of *rac*-**1b** (100 MHz, $CDCl_3$)



rac-**1c**

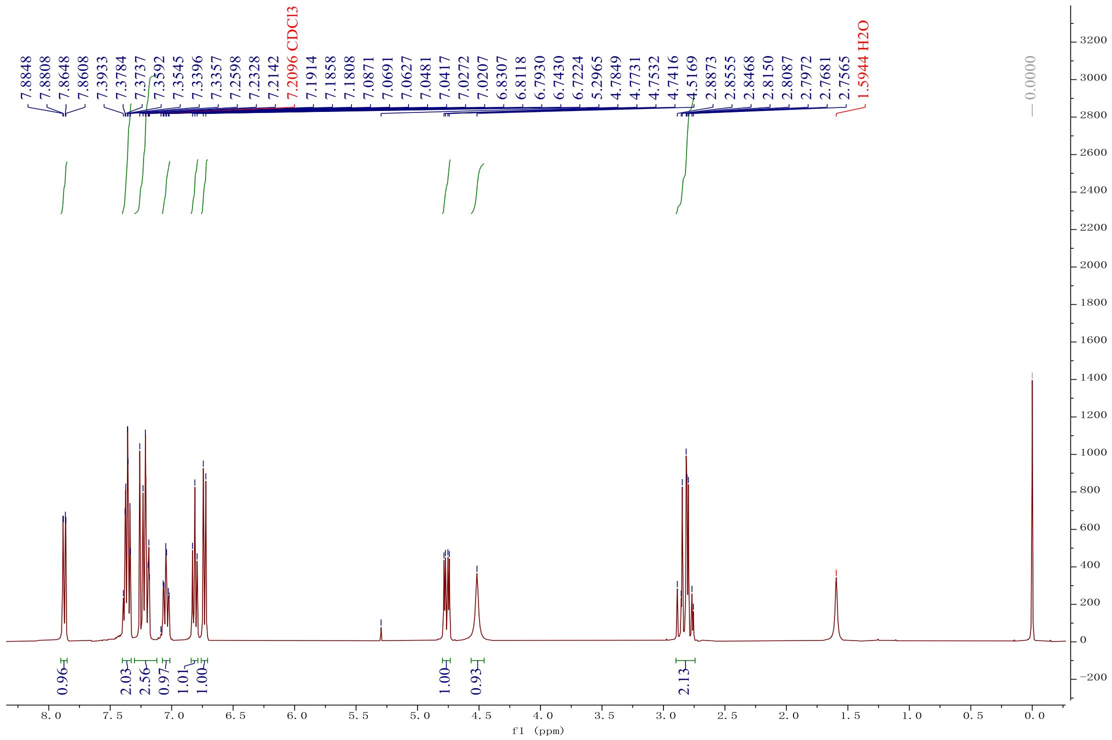


Figure S6 ^{1}H NMR Spectrum of *rac*-**1c** (400 MHz, $CDCl_3$)

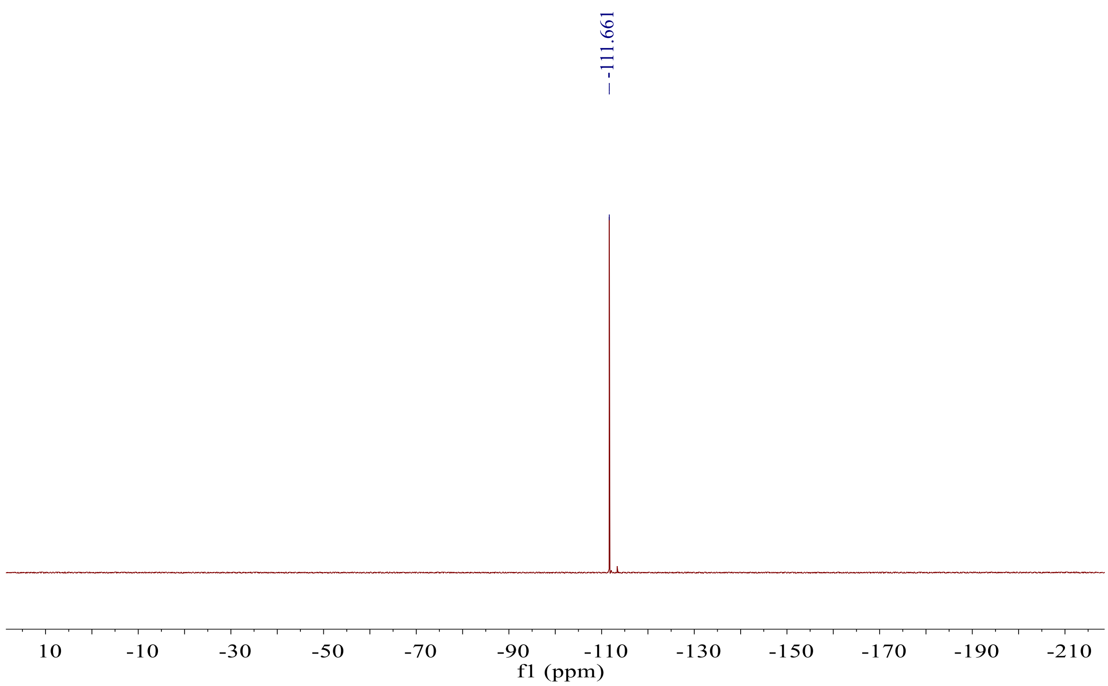


Figure S7 ^{19}F NMR Spectrum of *rac*-**1c** (376 MHz, $CDCl_3$)

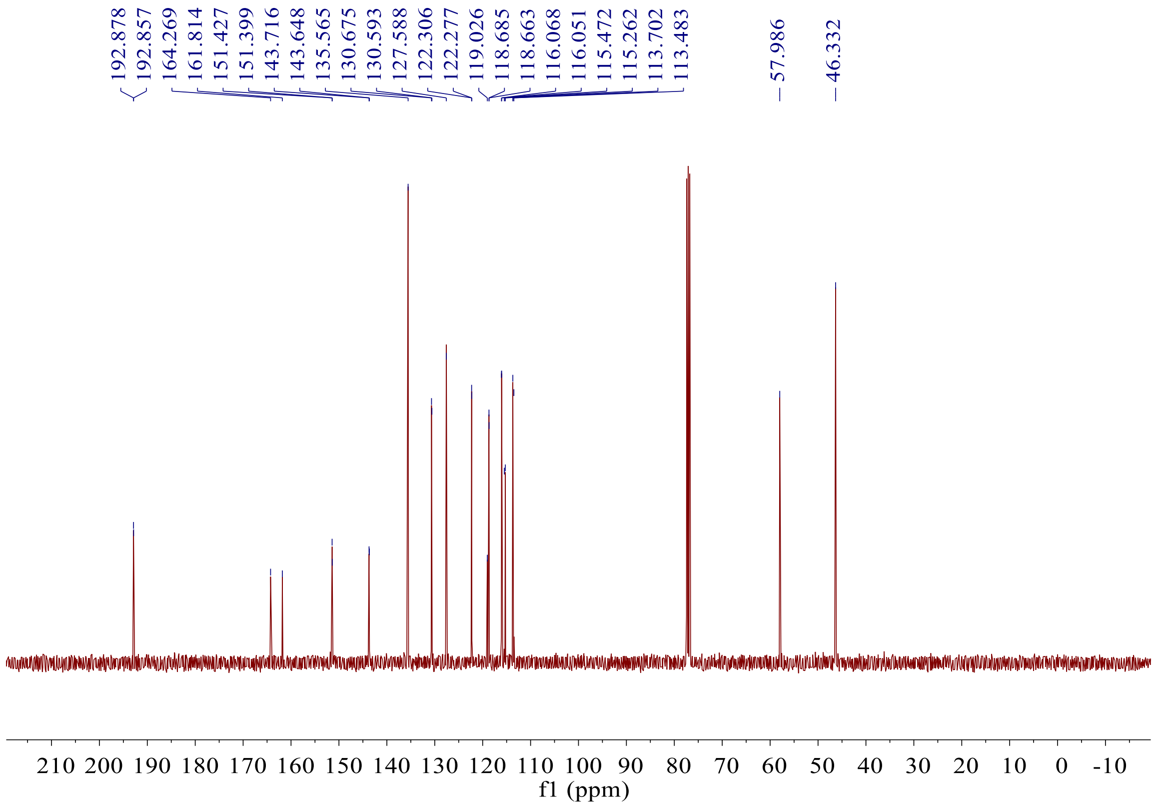
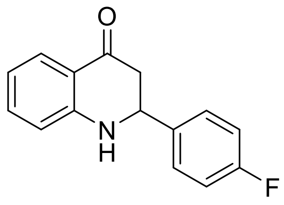


Figure S8 ^{13}C NMR Spectrum of *rac*-**1c** (100 MHz, $CDCl_3$)



rac-**1d**

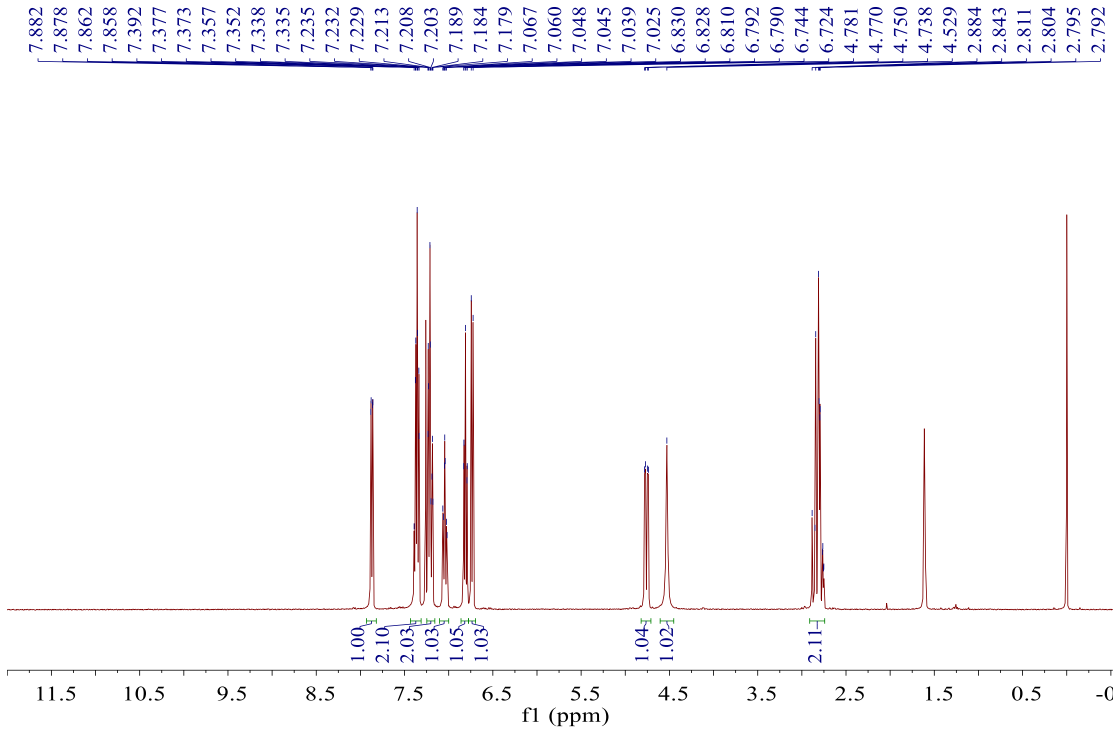


Figure S9 ^{1}H NMR Spectrum of *rac*-**1d** (400 MHz, $CDCl_3$)

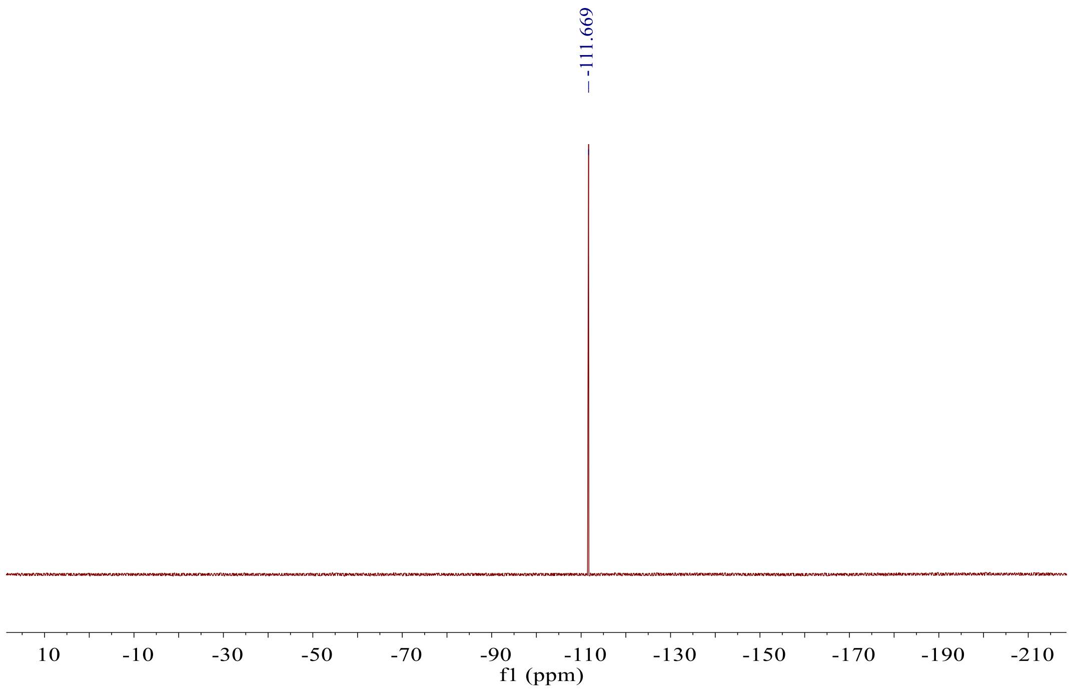


Figure S10 ^{1}H NMR Spectrum of *rac*-**1d** (376 MHz, $CDCl_3$)

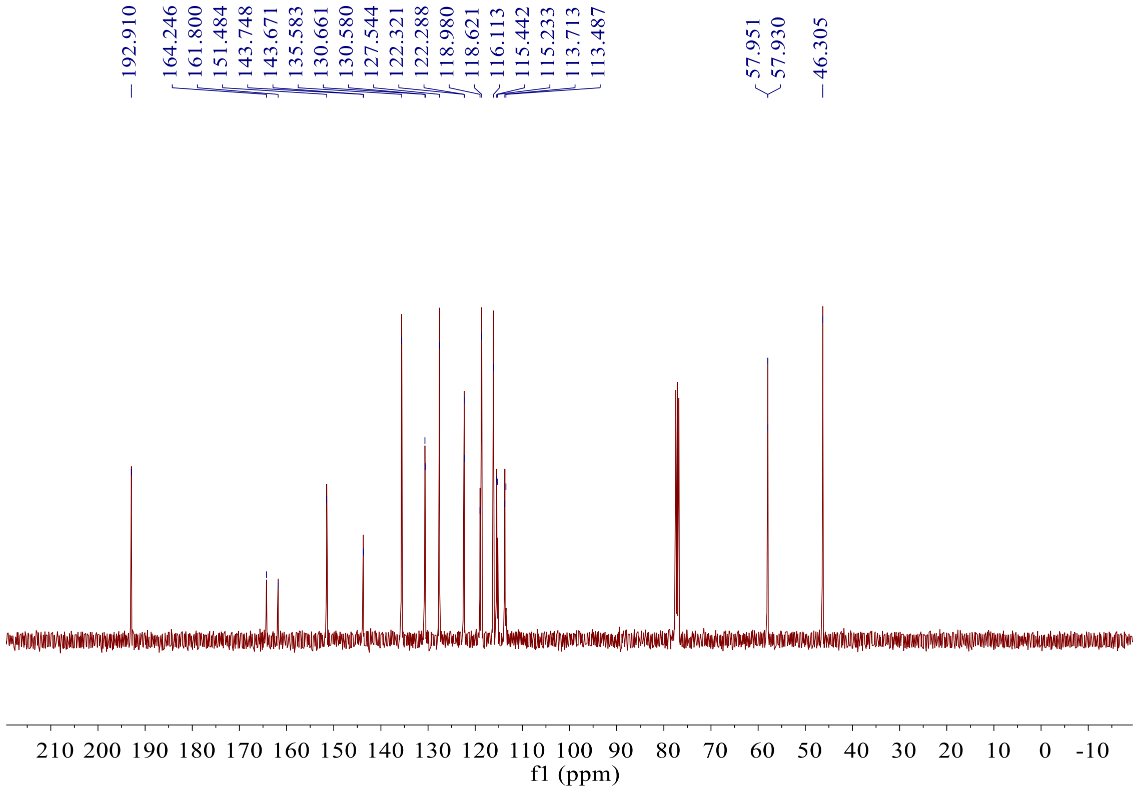
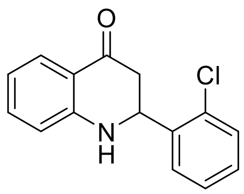


Figure S11 ^{13}C NMR Spectrum of *rac*-**1d** (100 MHz, $CDCl_3$)



rac-**1e**

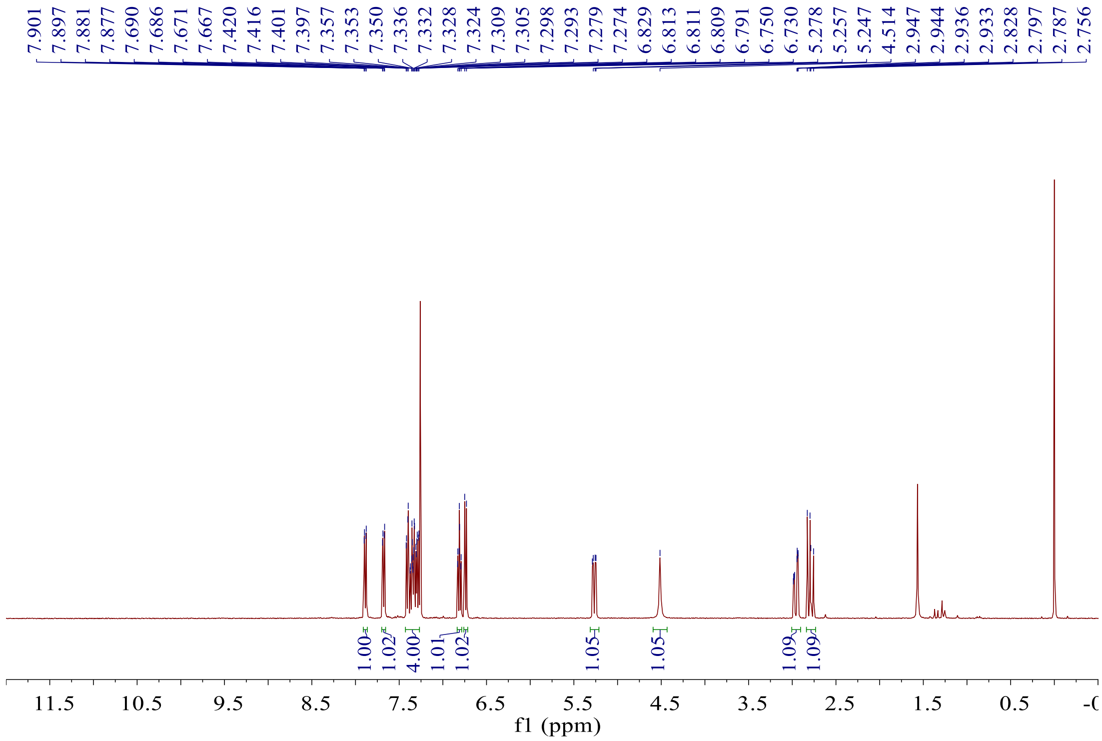


Figure S12 ^{1}H NMR Spectrum of *rac*-**1e** (400 MHz, $CDCl_3$)

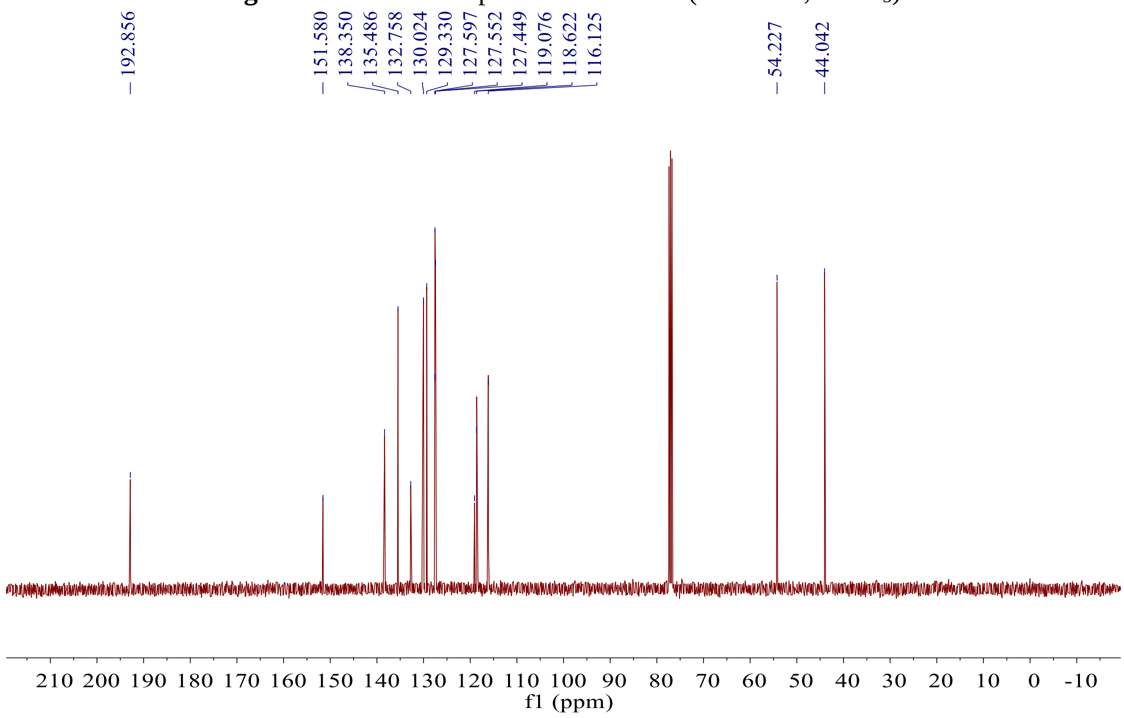
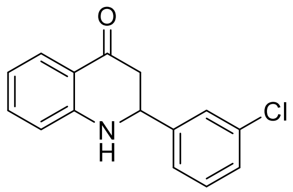


Figure S13 ^{13}C NMR Spectrum of *rac*-**1e** (100 MHz, $CDCl_3$)



rac-**1f**

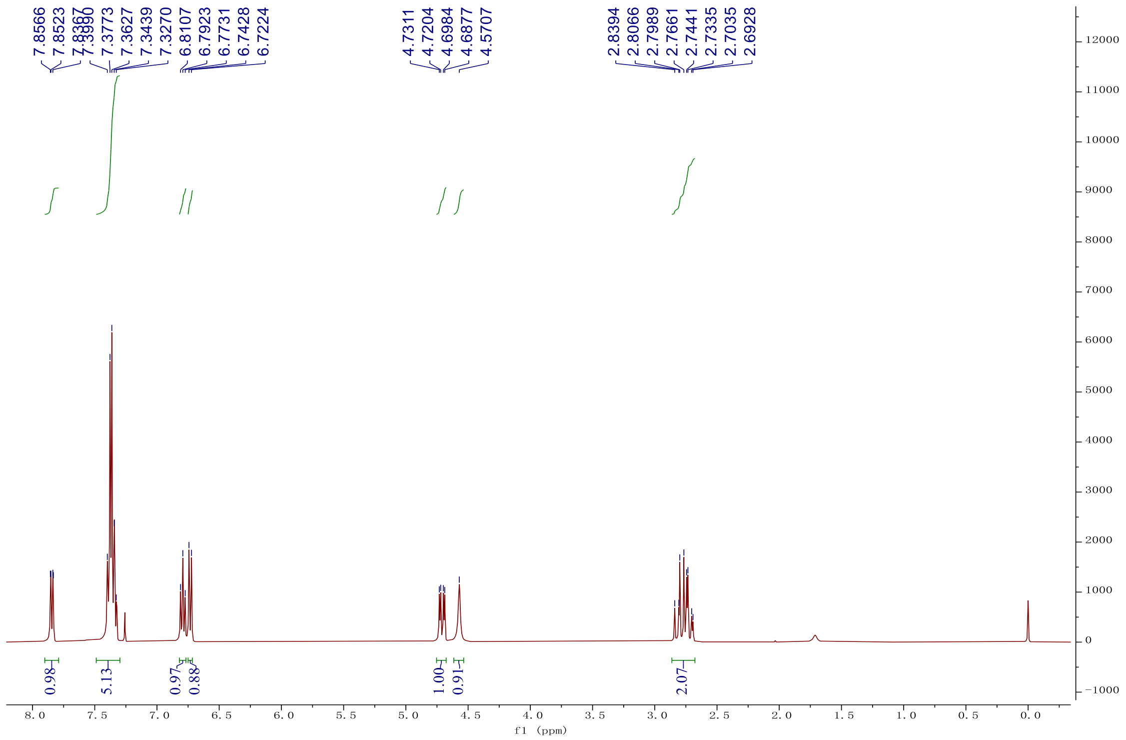


Figure S14 ^{1}H NMR Spectrum of *rac*-**1f** (400 MHz, $CDCl_3$)

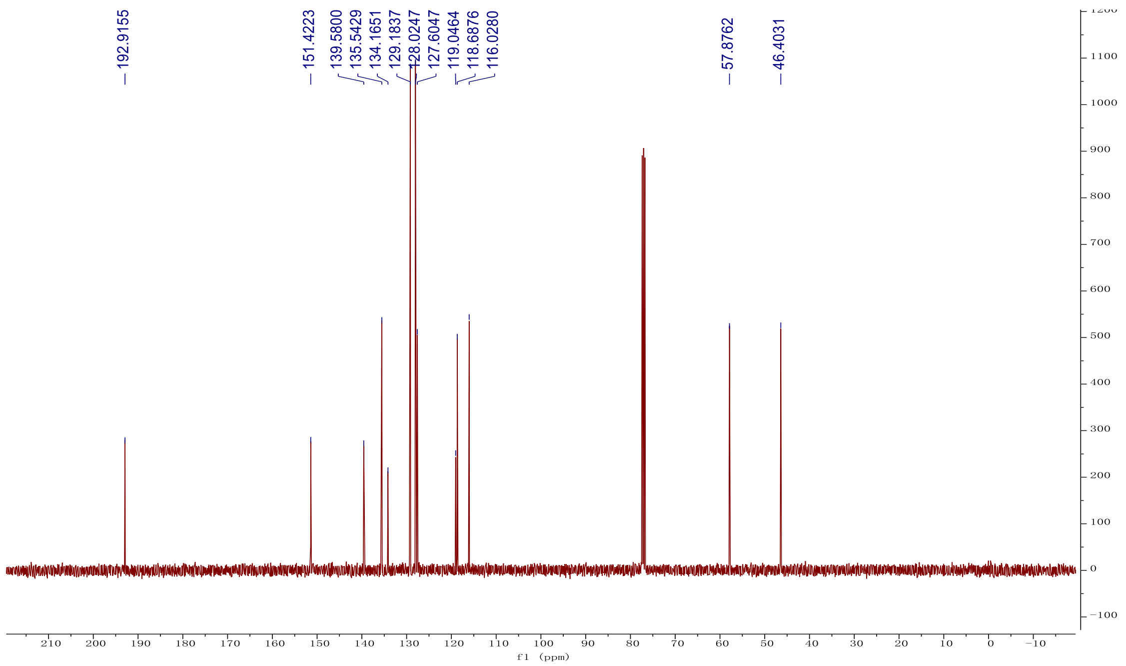
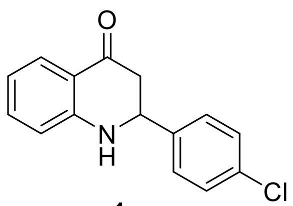


Figure S15 ^{13}C NMR Spectrum of *rac*-**1f** (100 MHz, $CDCl_3$)



rac-**1g**

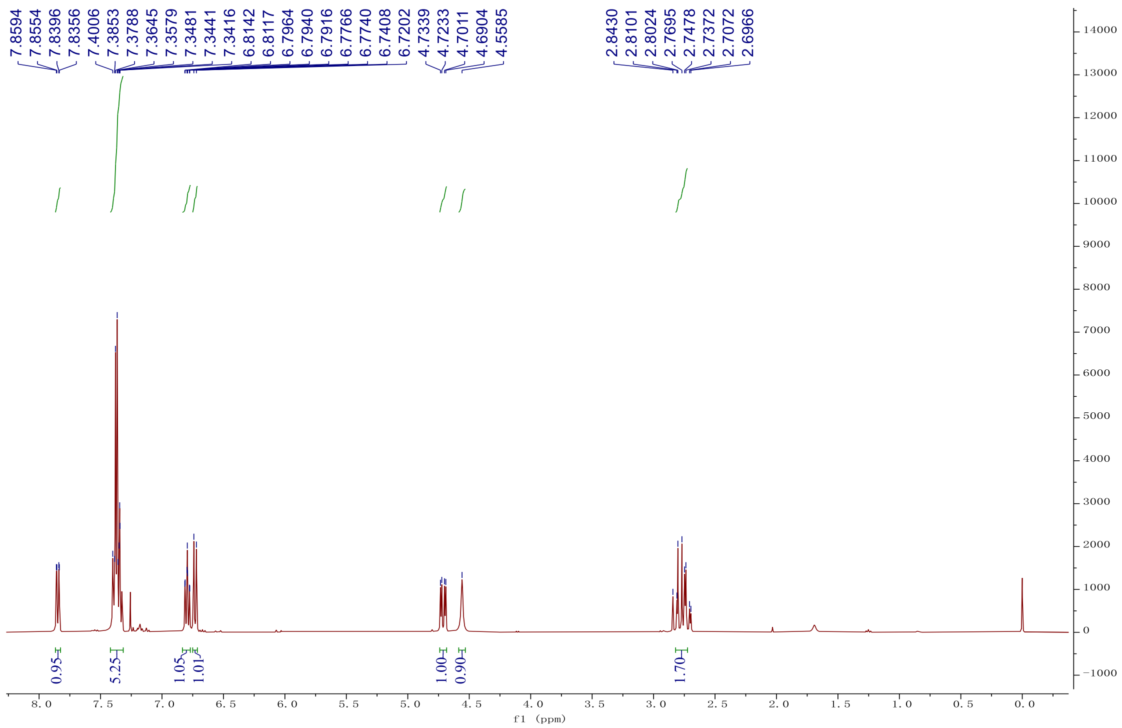


Figure S16 ^{1}H NMR Spectrum of *rac*-**1g** (400 MHz, $CDCl_3$)

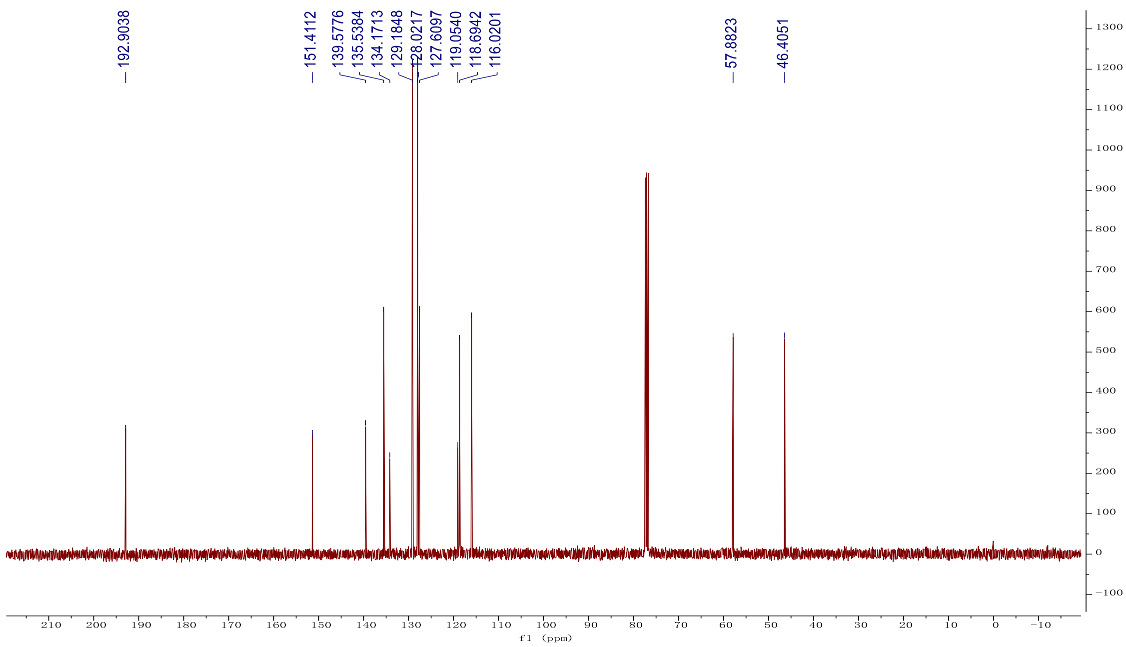
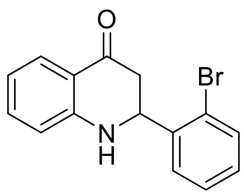


Figure S17 ^{13}C NMR Spectrum of *rac*-**1g** (100 MHz, $CDCl_3$)



rac-**1h**

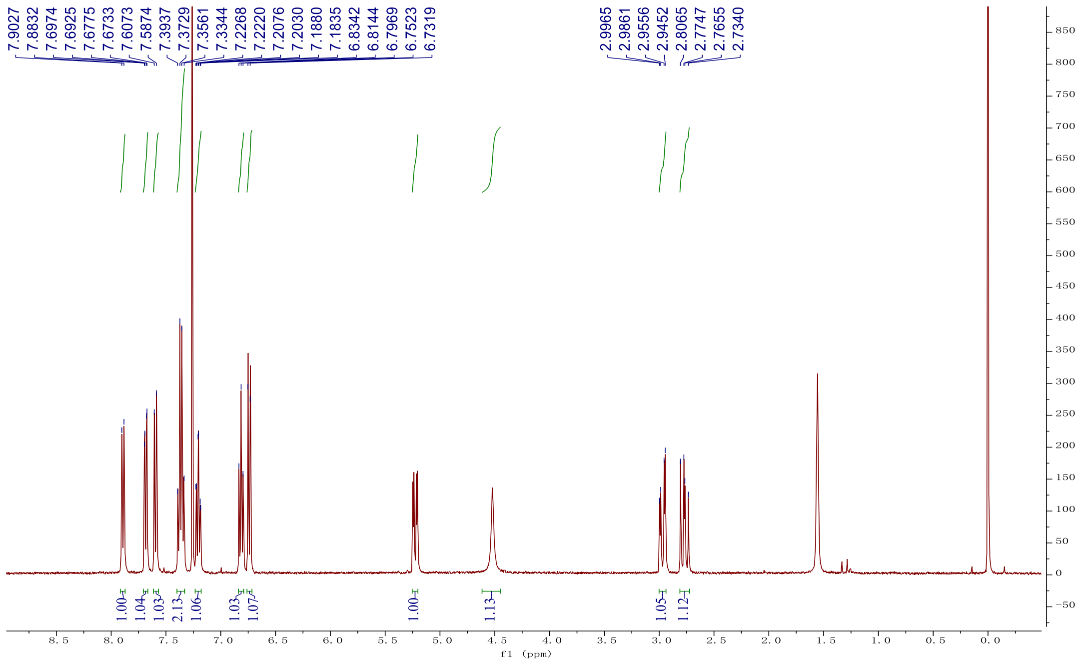


Figure S18 ^{1}H NMR Spectrum of *rac*-**1h** (400 MHz, $CDCl_3$)

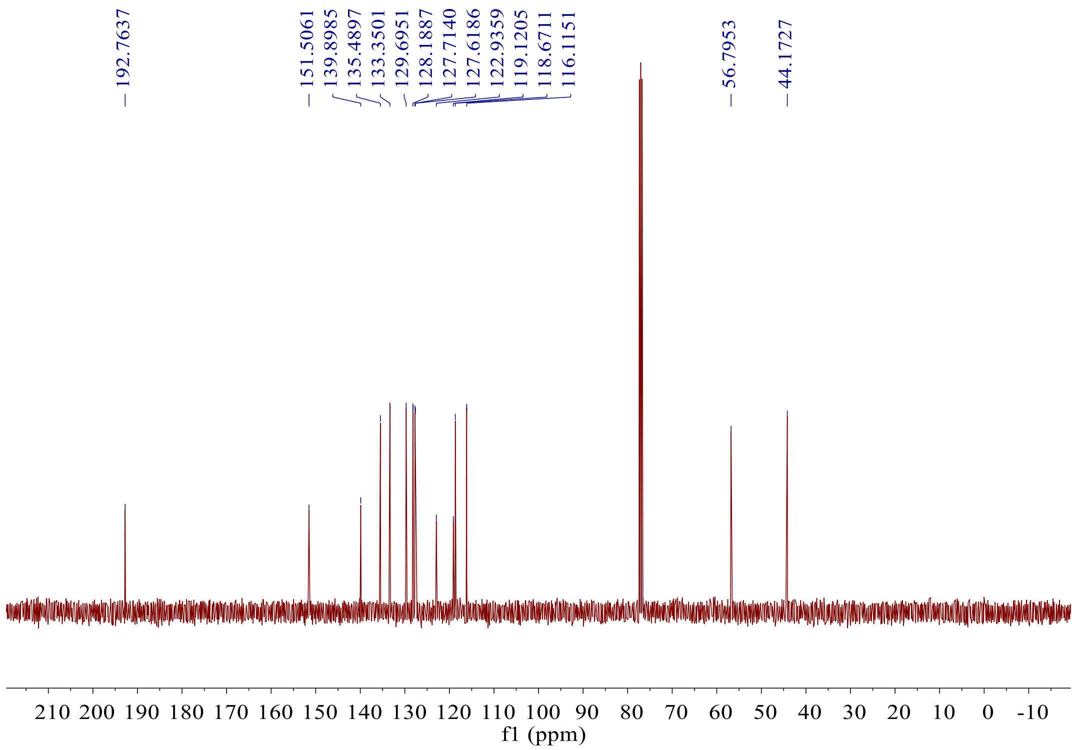
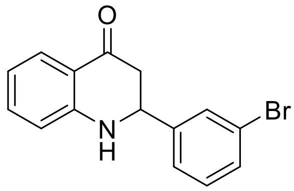


Figure S19 ^{13}C NMR Spectrum of *rac*-**1h** (100 MHz, $CDCl_3$)



rac-**1i**

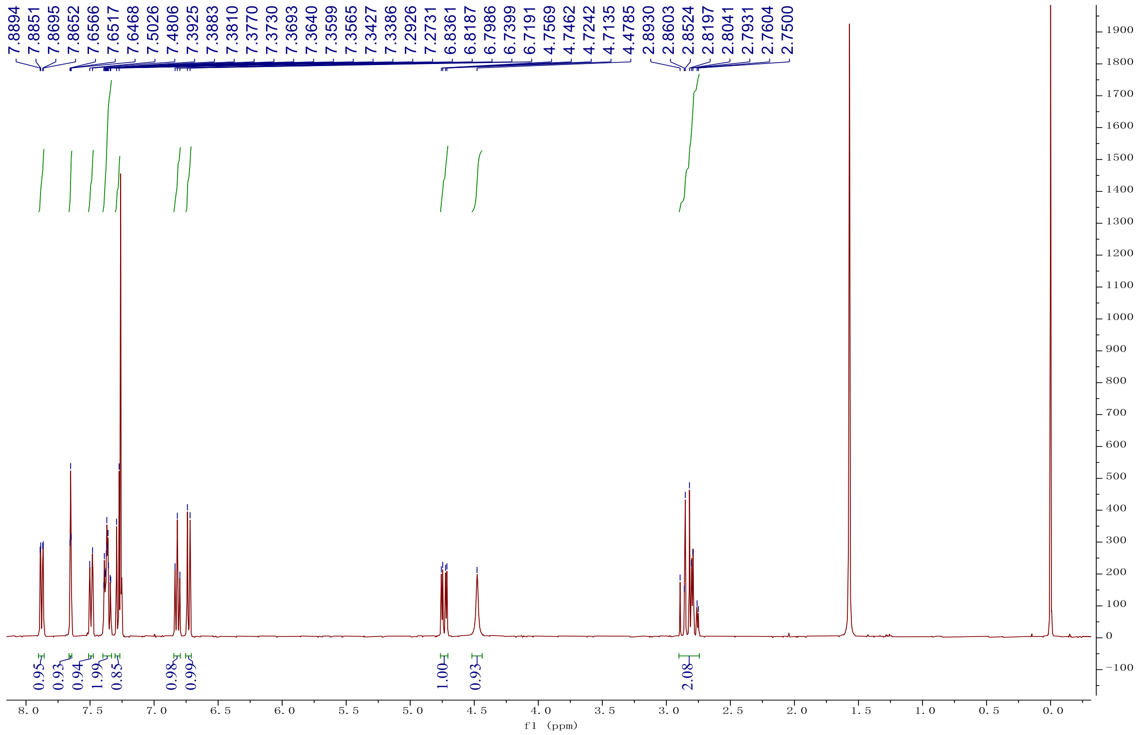


Figure S20 ^{1}H NMR Spectrum of *rac*-**1i** (400 MHz, $CDCl_3$)

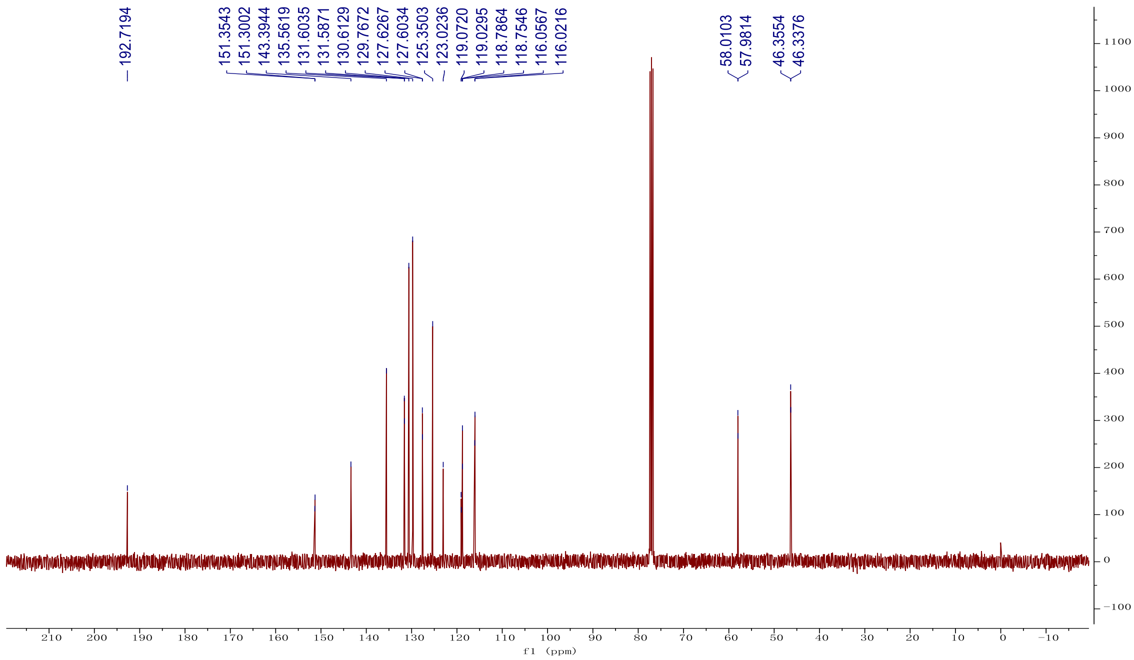
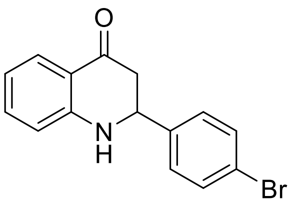


Figure S21 ^{13}C NMR Spectrum of *rac*-**1i** (100 MHz, $CDCl_3$)



rac-**1j**

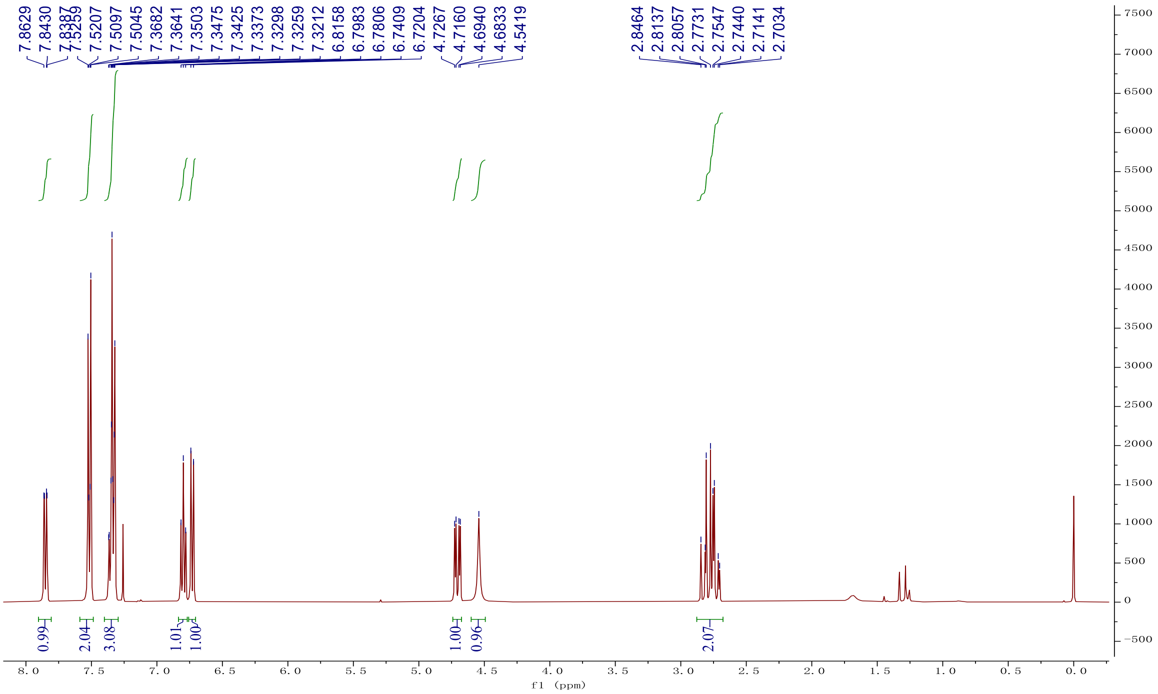


Figure S22 ^{1}H NMR Spectrum of *rac*-**1j** (400 MHz, $CDCl_3$)

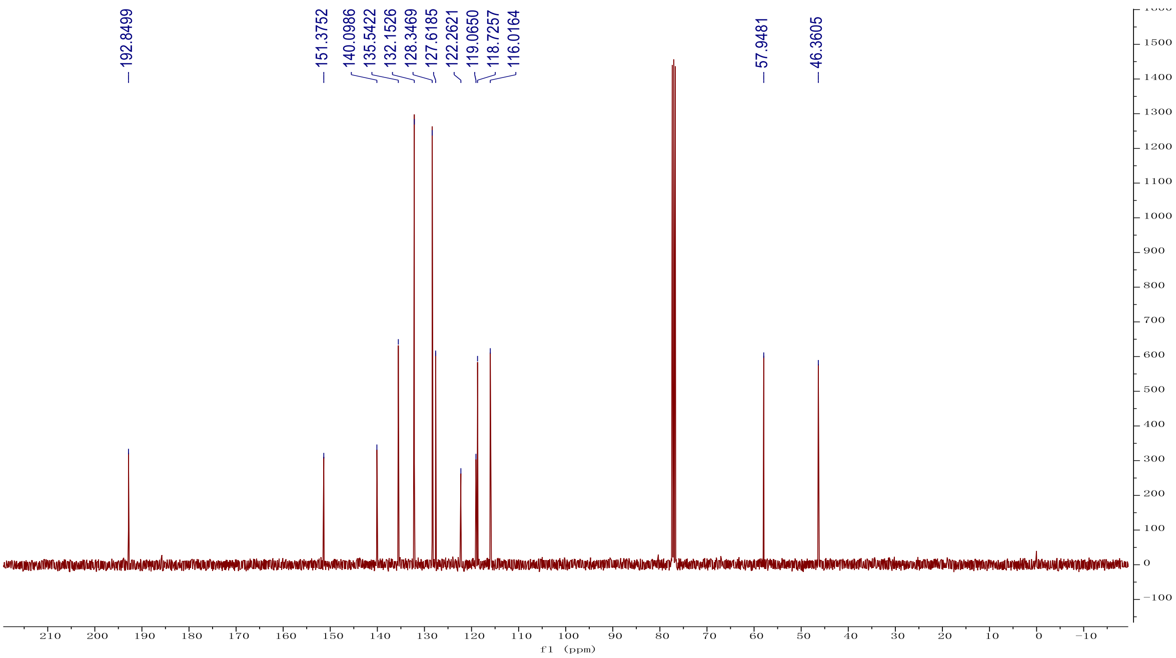
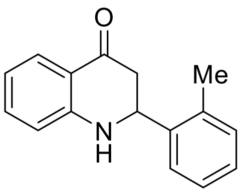


Figure S23 ^{13}C NMR Spectrum of *rac*-**1j** (100 MHz, $CDCl_3$)



rac-**1k**

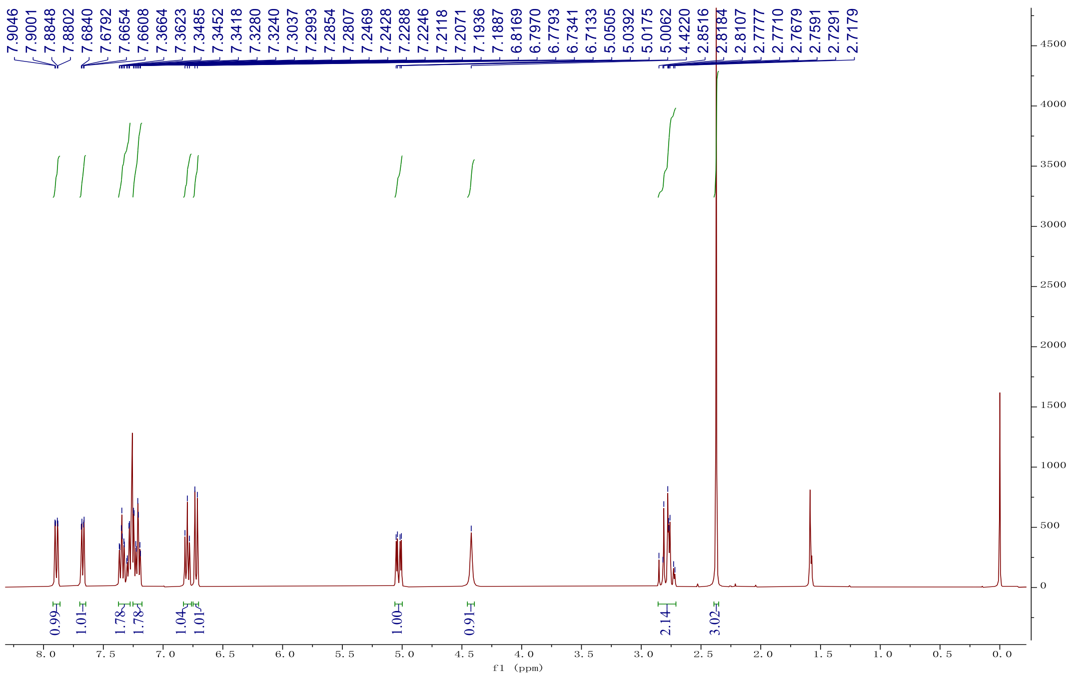


Figure S24 ^{1}H NMR Spectrum of *rac*-**1k** (400 MHz, $CDCl_3$)

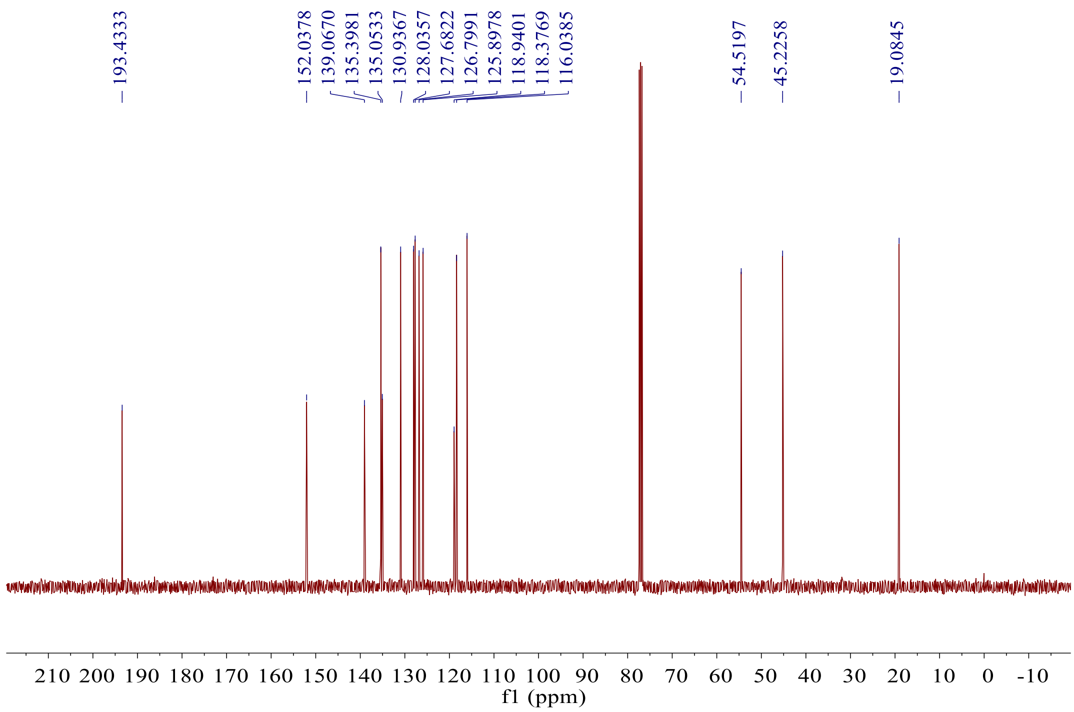
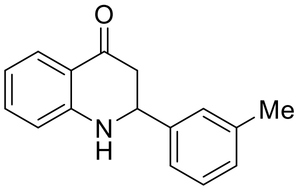


Figure S25 ^{13}C NMR Spectrum of *rac*-**1k** (100 MHz, $CDCl_3$)



rac-**1l**

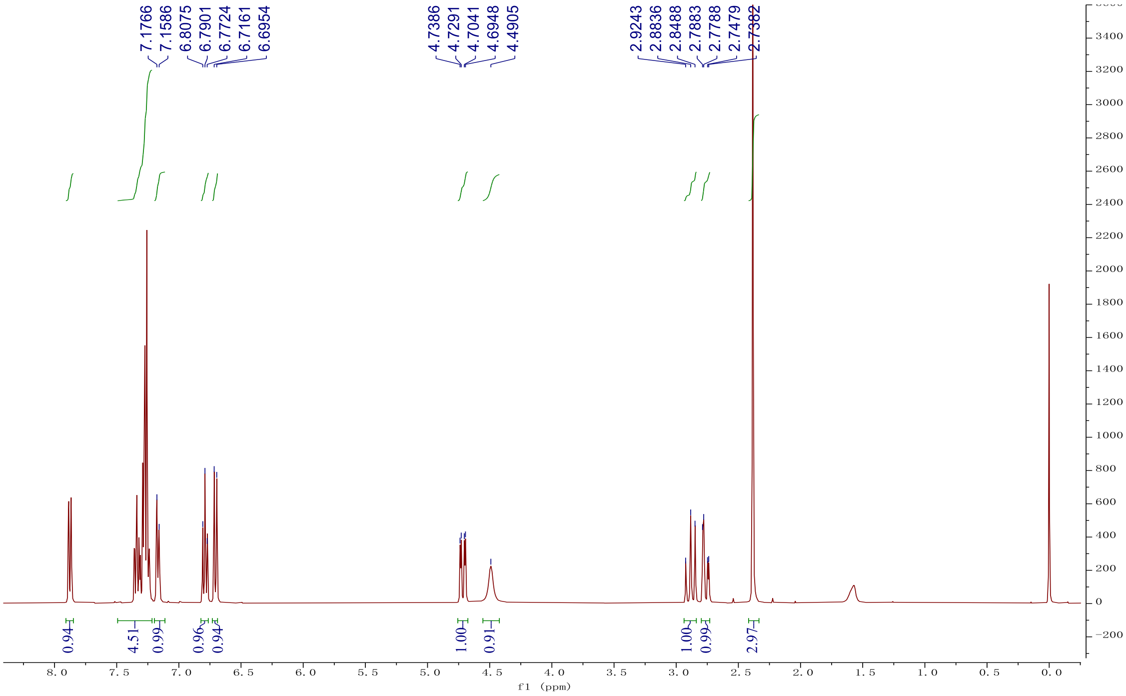


Figure S26 ^{1}H NMR Spectrum of *rac*-**1l** (400 MHz, $CDCl_3$)

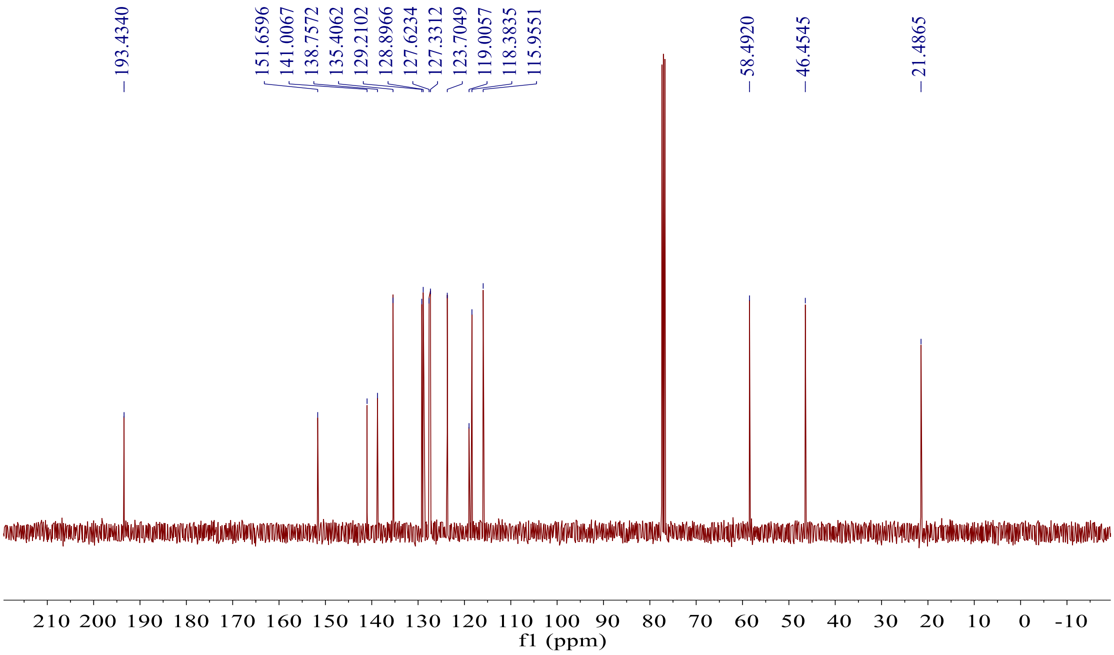
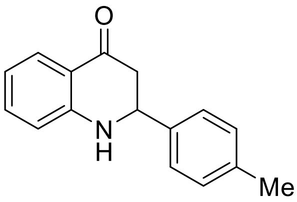


Figure S27 ^{13}C NMR Spectrum of *rac*-**1l** (100 MHz, $CDCl_3$)



rac-**1m**

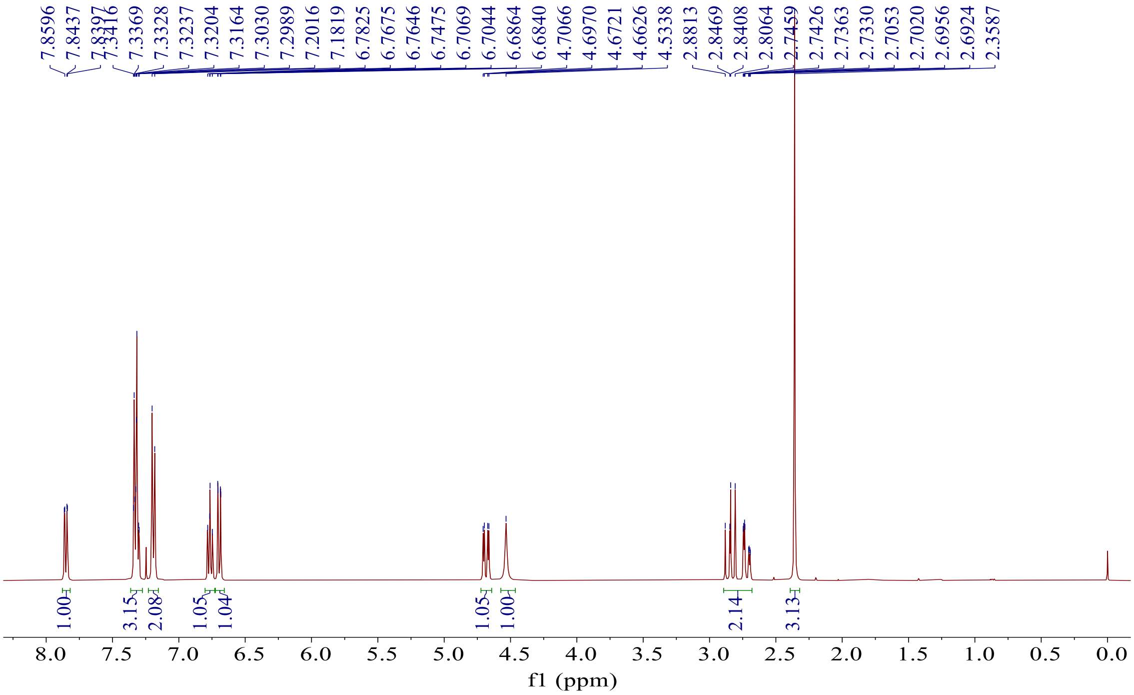


Figure S28 ^{1}H NMR Spectrum of *rac*-**1m** (400 MHz, $CDCl_3$)

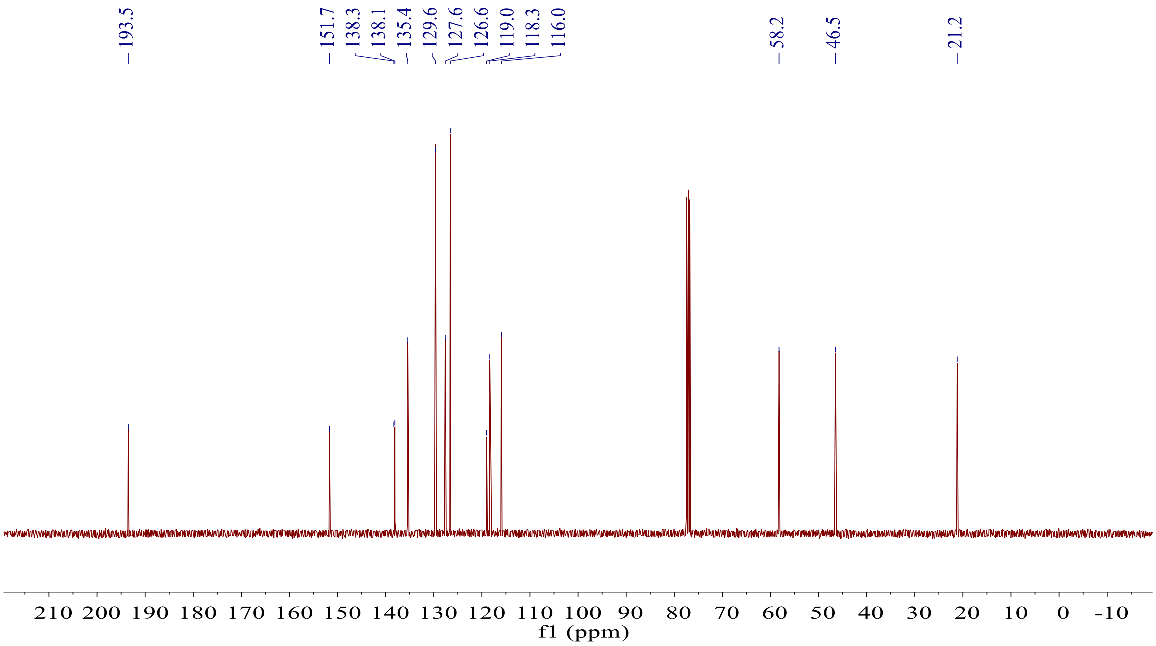
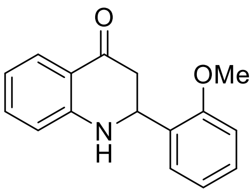


Figure S29 ^{13}C NMR Spectrum of *rac*-**1m** (100 MHz, $CDCl_3$)



rac-**1n**

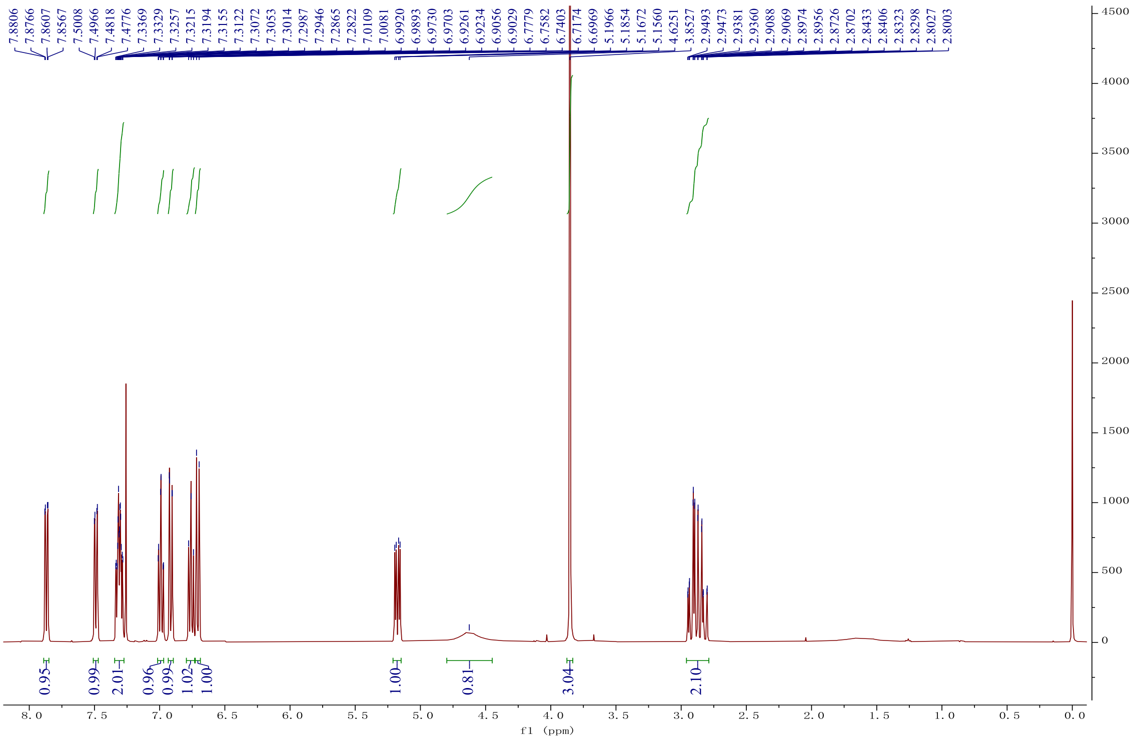


Figure S30 ^{1}H NMR Spectrum of *rac*-**1n** (400 MHz, $CDCl_3$)

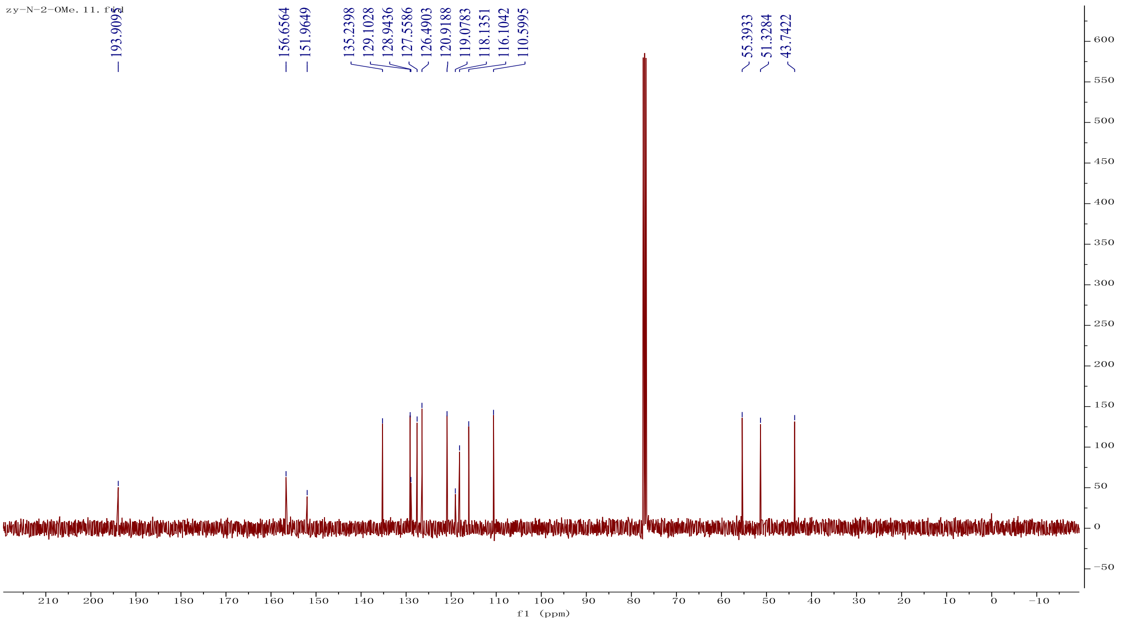
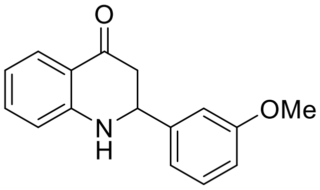


Figure S31 ^{13}C NMR Spectrum of *rac*-**1n** (100 MHz, $CDCl_3$)



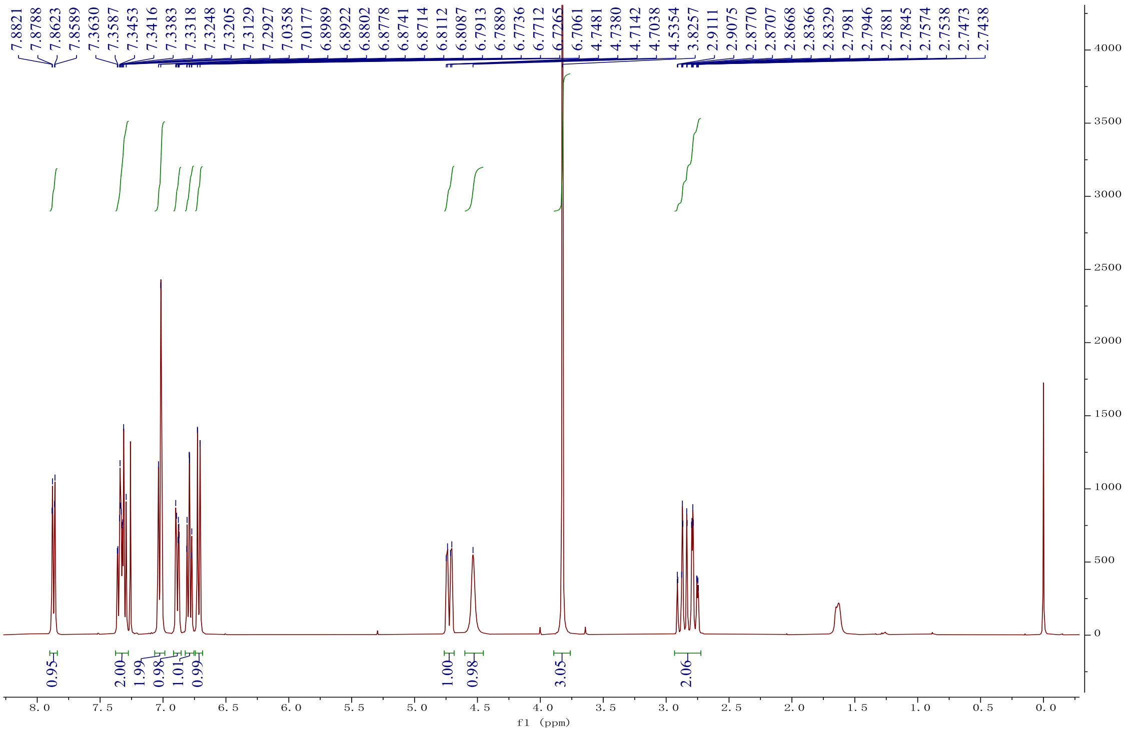


Figure S32 ^{1}H NMR Spectrum of *rac*-**1o** (400 MHz, $CDCl_3$)

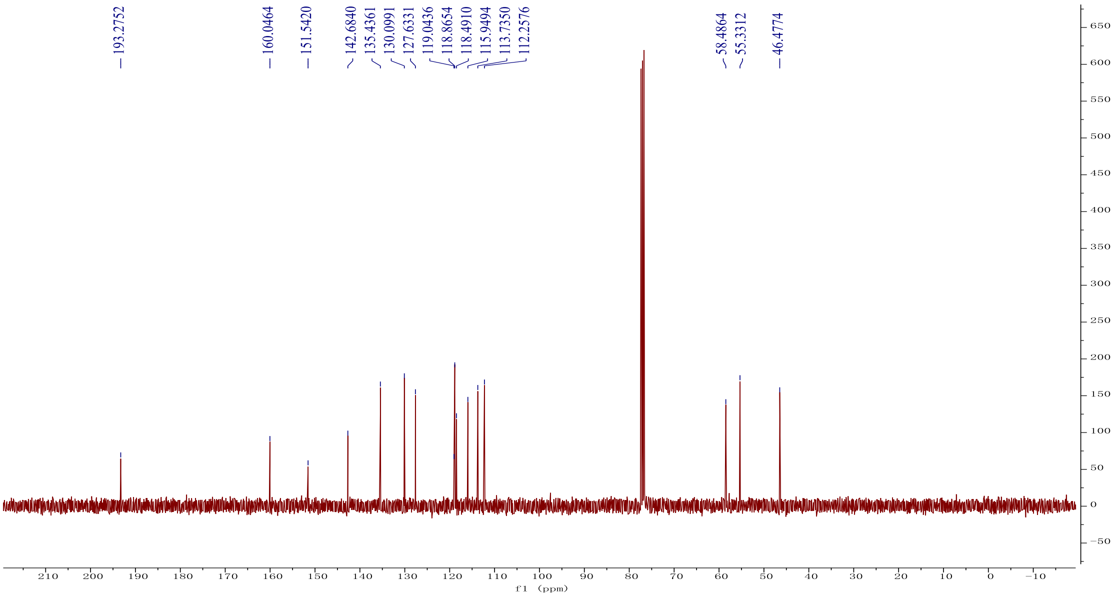
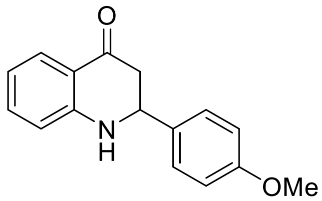


Figure S33 ^{13}C NMR Spectrum of *rac*-**1o** (100 MHz, $CDCl_3$)



rac-**1p**

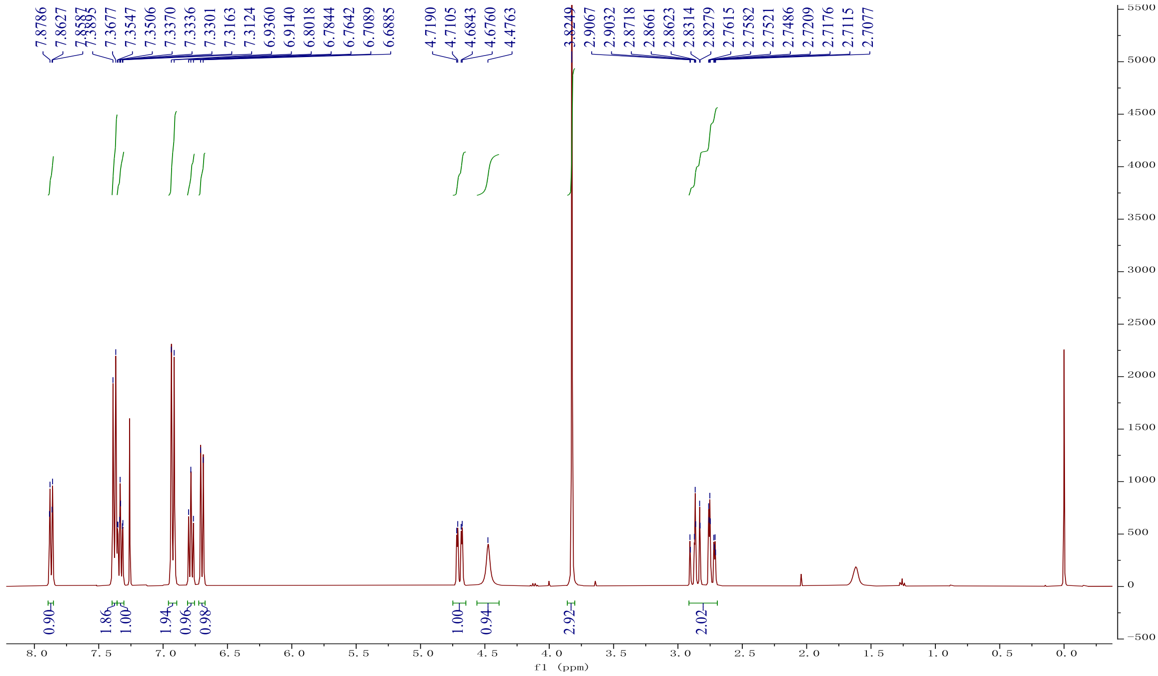


Figure S34 ^{1}H NMR Spectrum of *rac*-**1p** (400 MHz, $CDCl_3$)

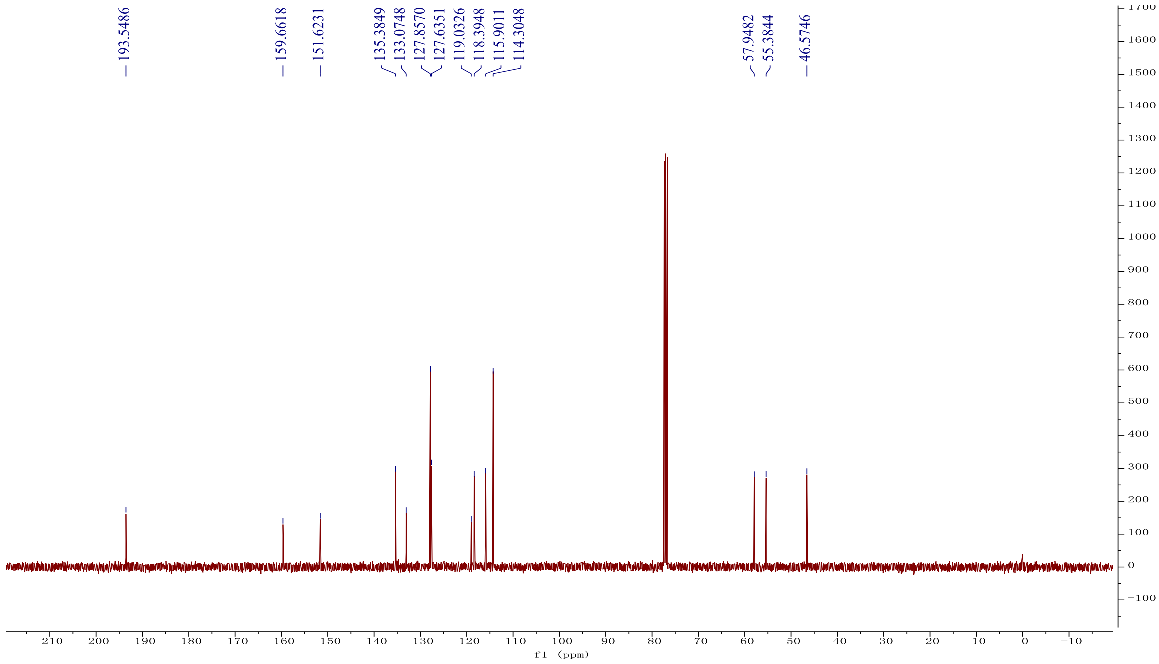
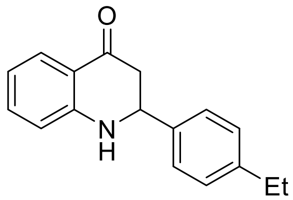


Figure S35 ^{13}C NMR Spectrum of *rac*-**1p** (100 MHz, $CDCl_3$)



rac-**1q**

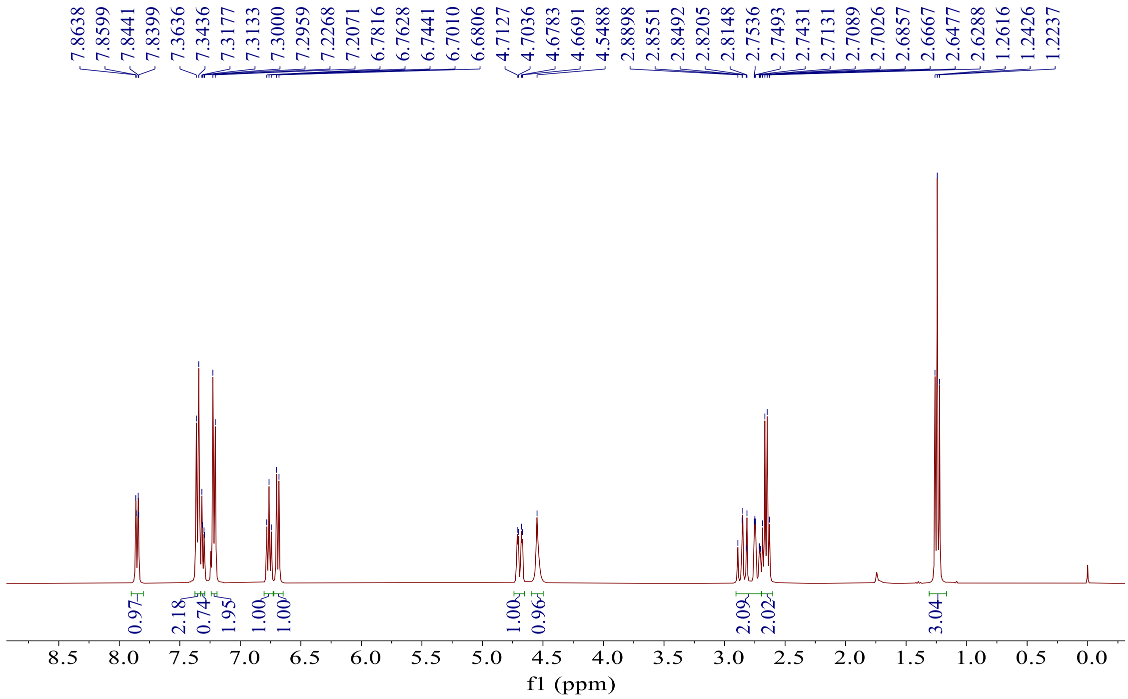


Figure S36 ^{1}H NMR Spectrum of *rac*-**1q** (400 MHz, $CDCl_3$)

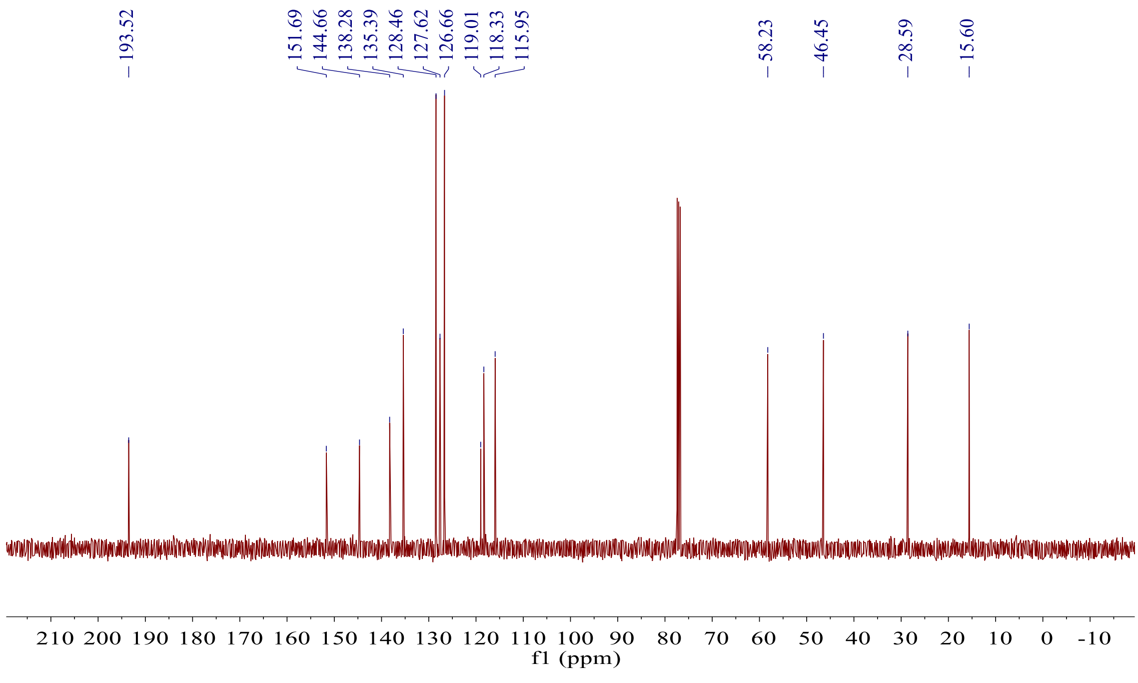
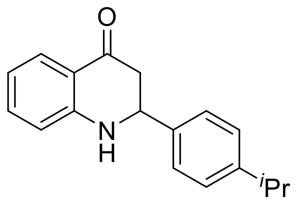


Figure S37 ^{13}C NMR Spectrum of *rac*-**1q** (100 MHz, $CDCl_3$)



rac-**1r**

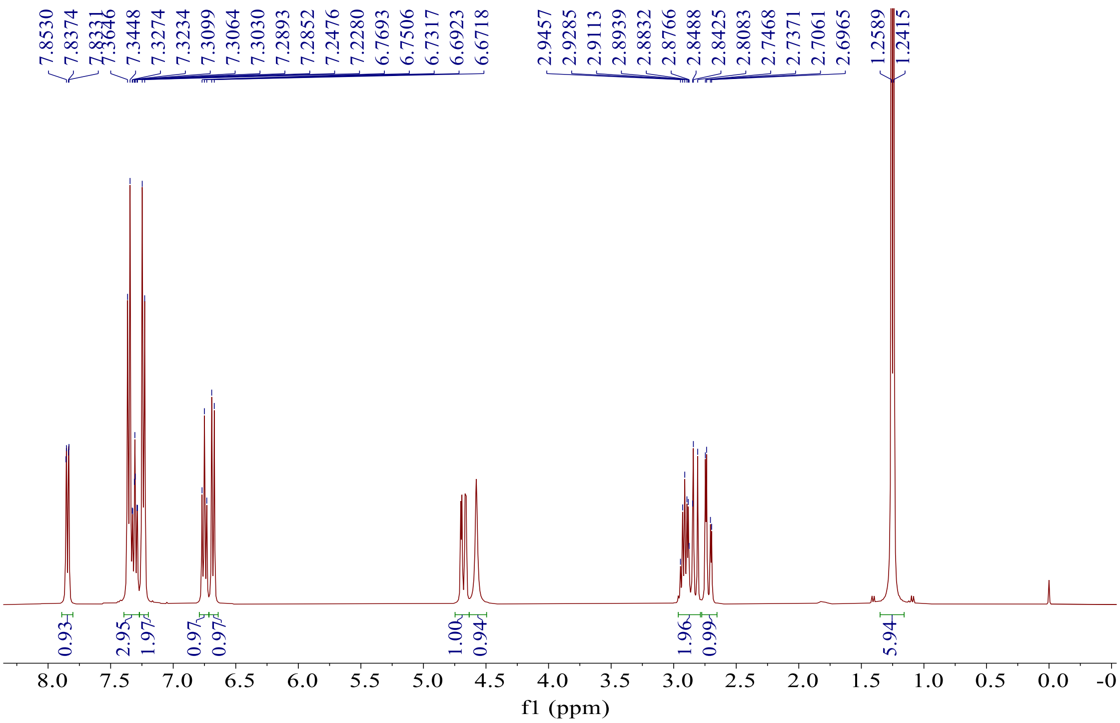


Figure S38 ^{1}H NMR Spectrum of *rac*-**1r** (400 MHz, $CDCl_3$)

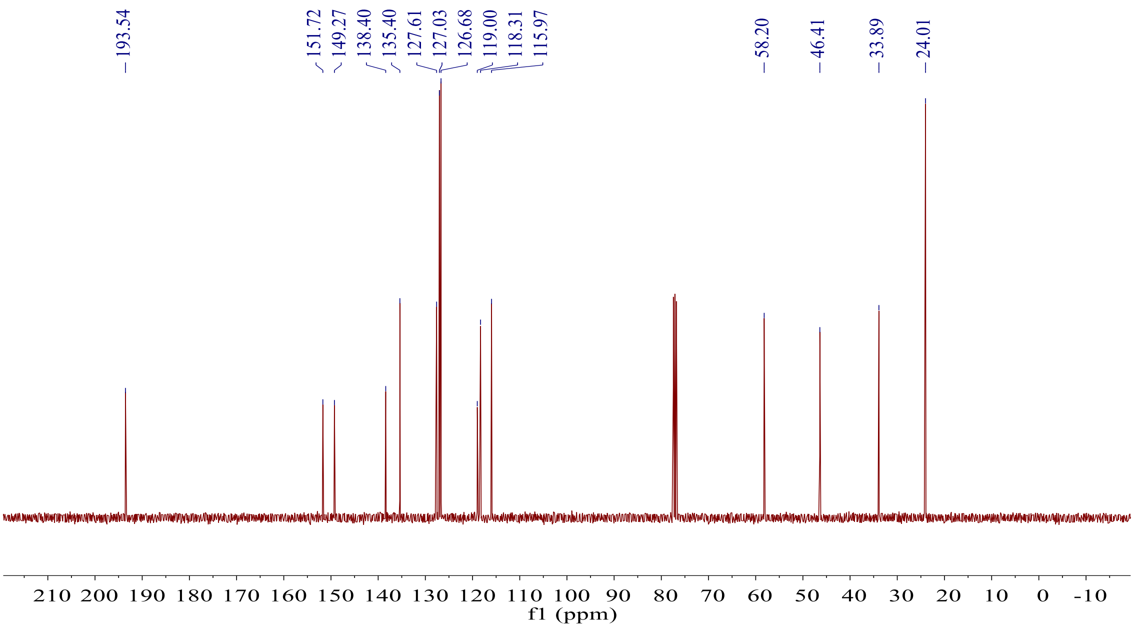
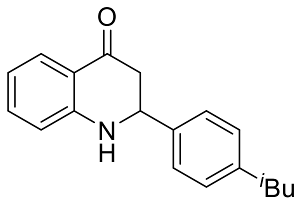


Figure S39 ^{13}C NMR Spectrum of *rac*-**1r** (100 MHz, $CDCl_3$)



rac-**1s**

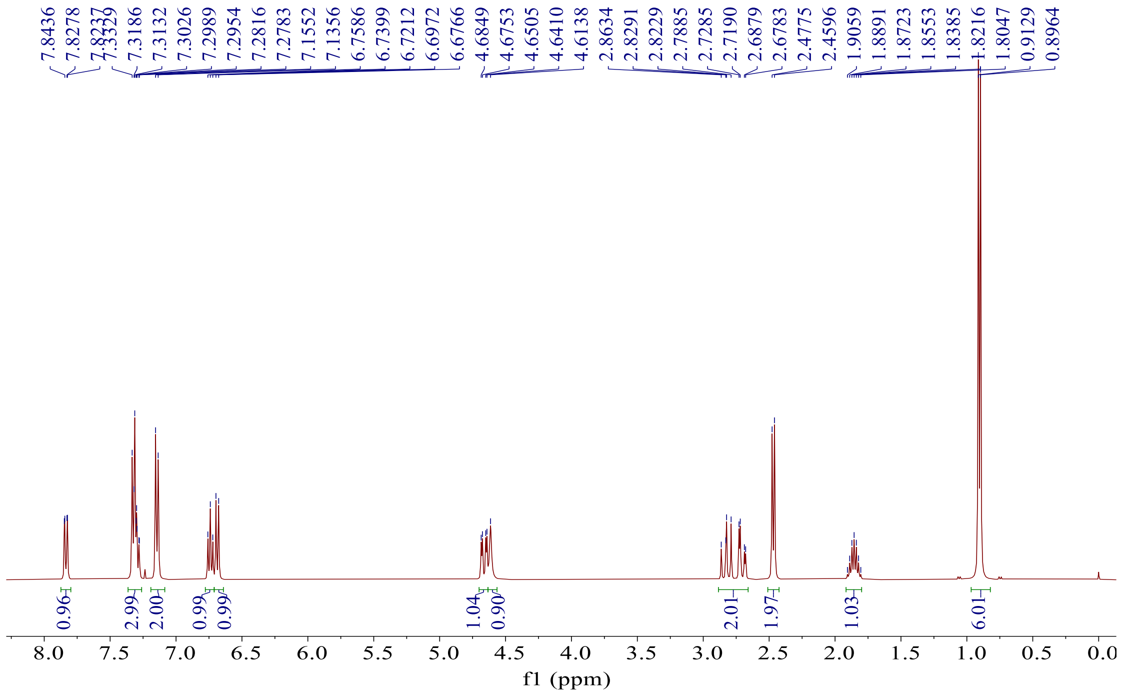


Figure S40 ^{1}H NMR Spectrum of *rac*-**1s** (400 MHz, $CDCl_3$)

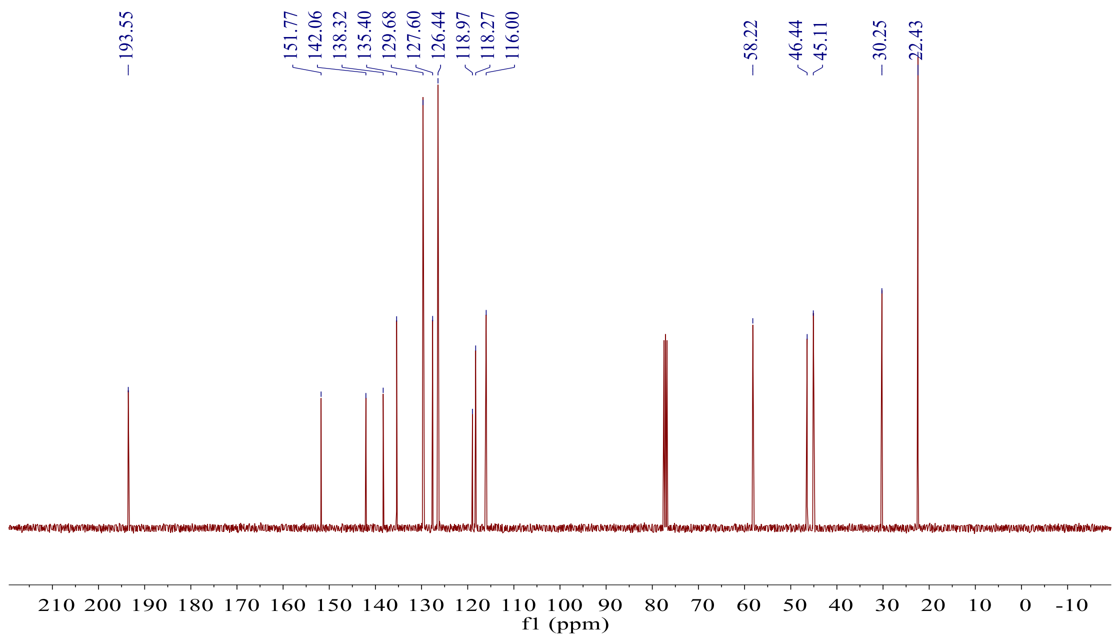
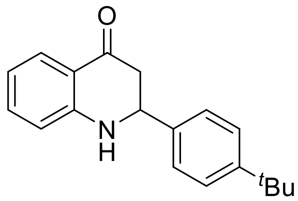


Figure S41 ^{13}C NMR Spectrum of *rac*-**1s** (100 MHz, $CDCl_3$)



rac-**1t**

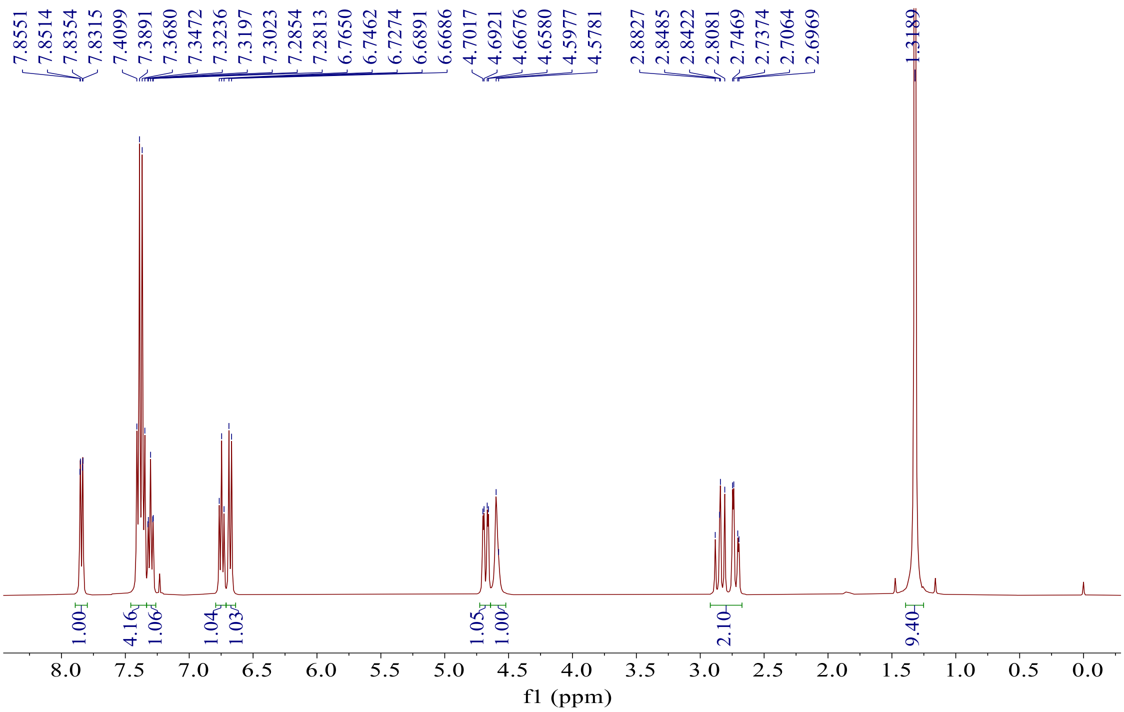


Figure S42 ^{1}H NMR Spectrum of *rac*-**1t** (400 MHz, $CDCl_3$)

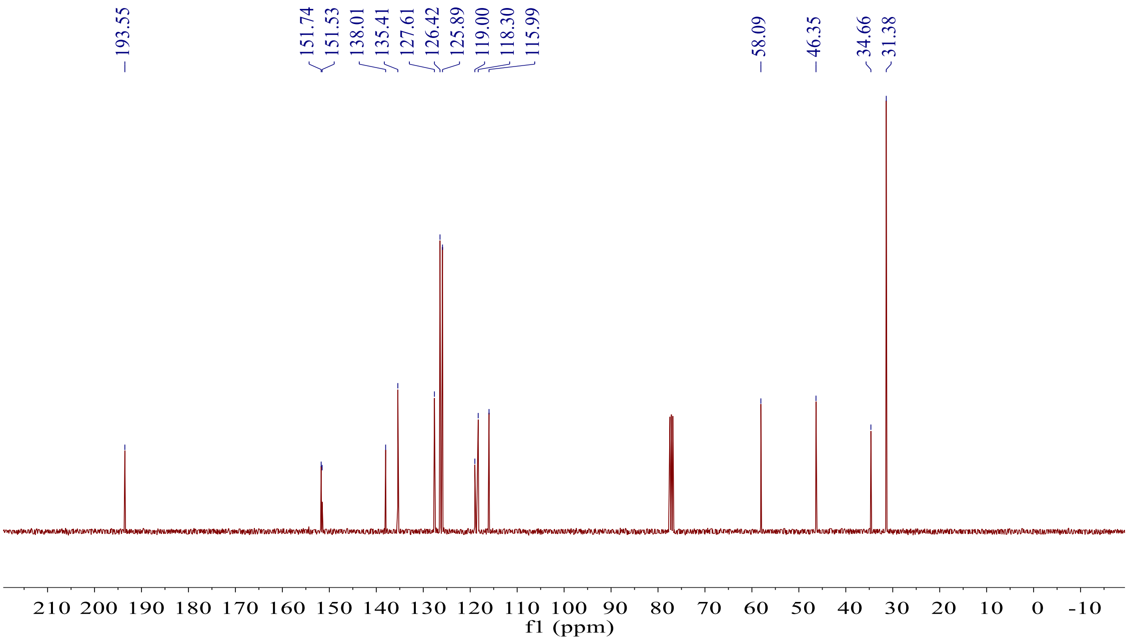
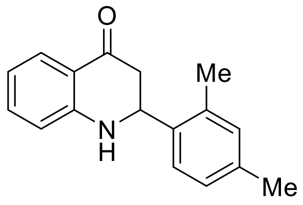


Figure S43 ^{13}C NMR Spectrum of *rac*-**1t** (100 MHz, $CDCl_3$)



rac-**1u**

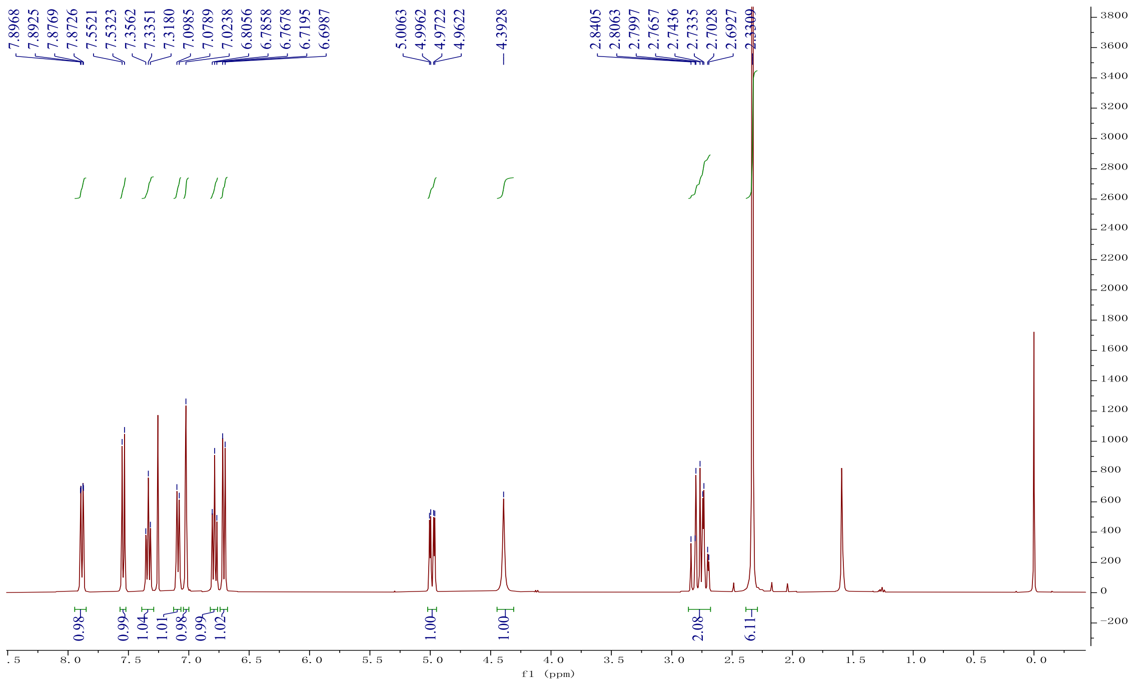


Figure S44 ^{1}H NMR Spectrum of *rac*-**1u** (400 MHz, $CDCl_3$)

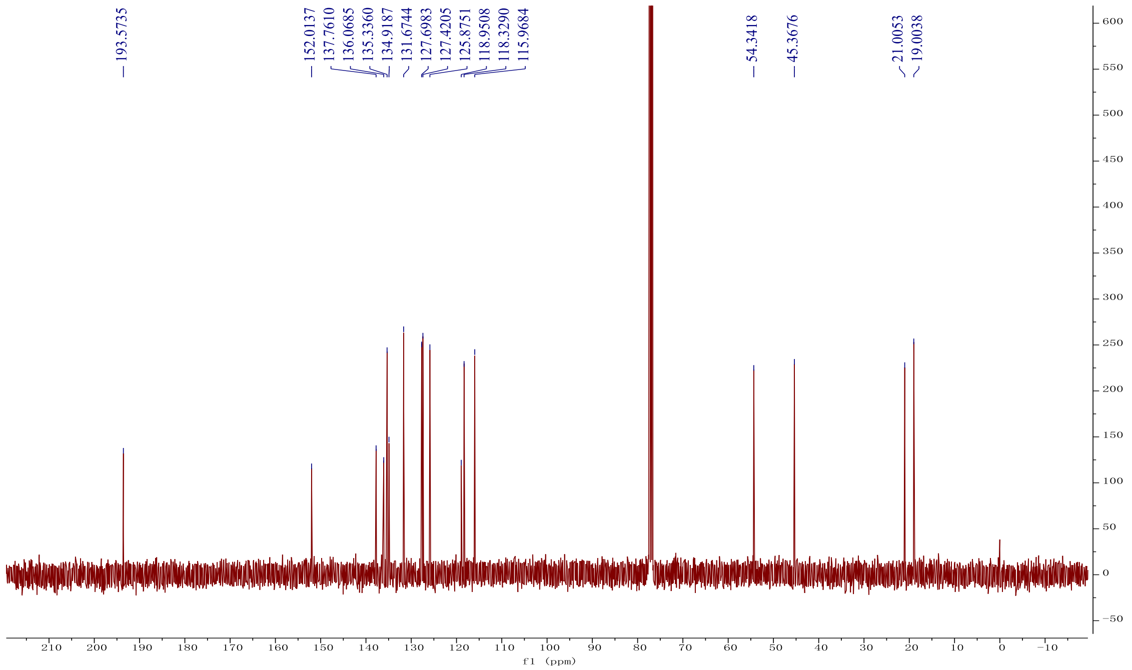
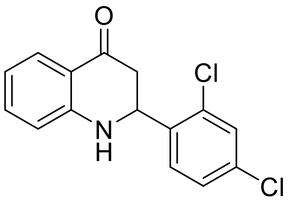


Figure S45 ^{13}C NMR Spectrum of *rac*-**1u** (100 MHz, $CDCl_3$)



rac-**1v**

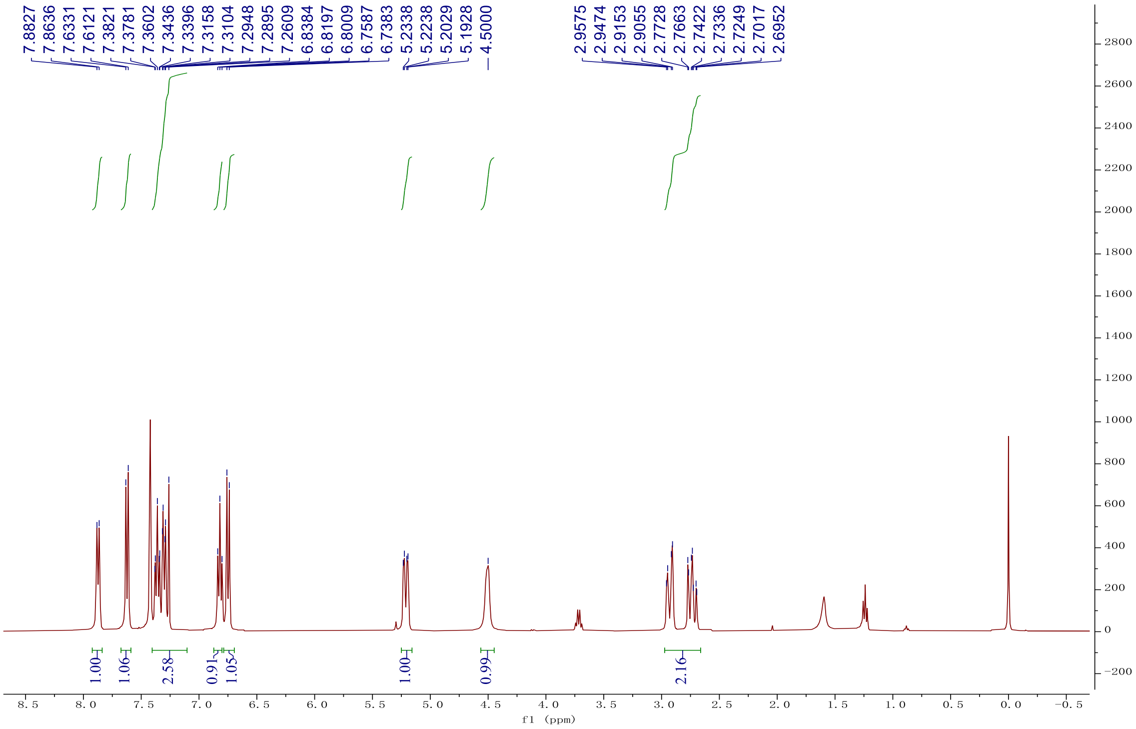


Figure S46 ^{1}H NMR Spectrum of *rac*-**1v** (400 MHz, $CDCl_3$)

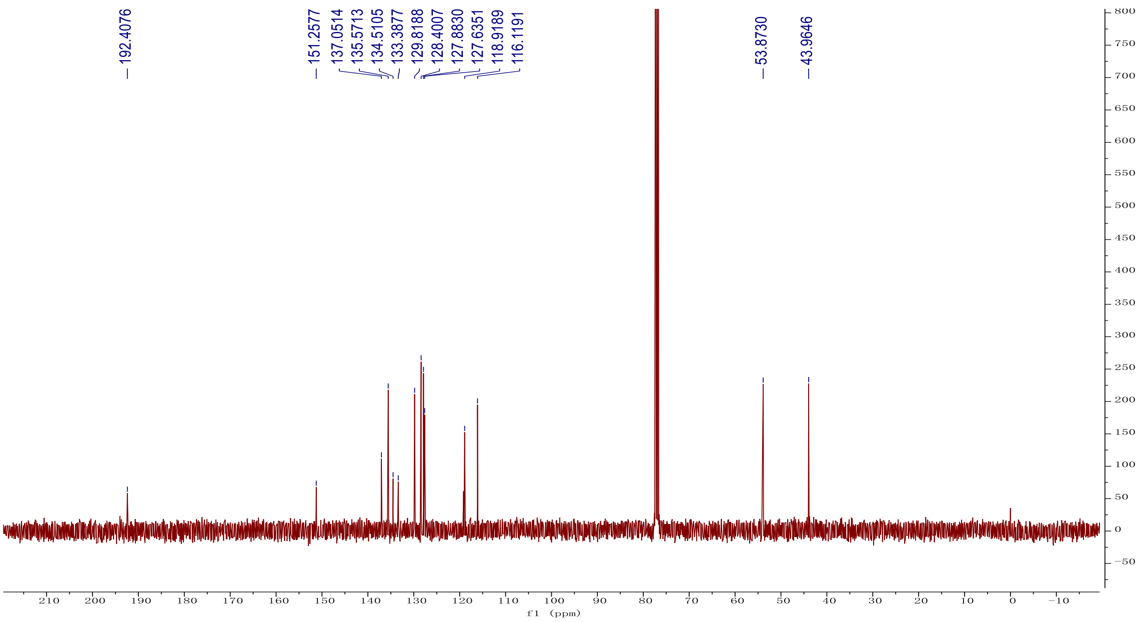
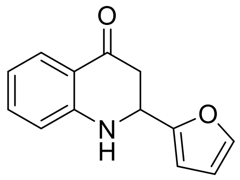


Figure S47 ^{13}C NMR Spectrum of *rac*-**1v** (100 MHz, $CDCl_3$)



rac-**1w**

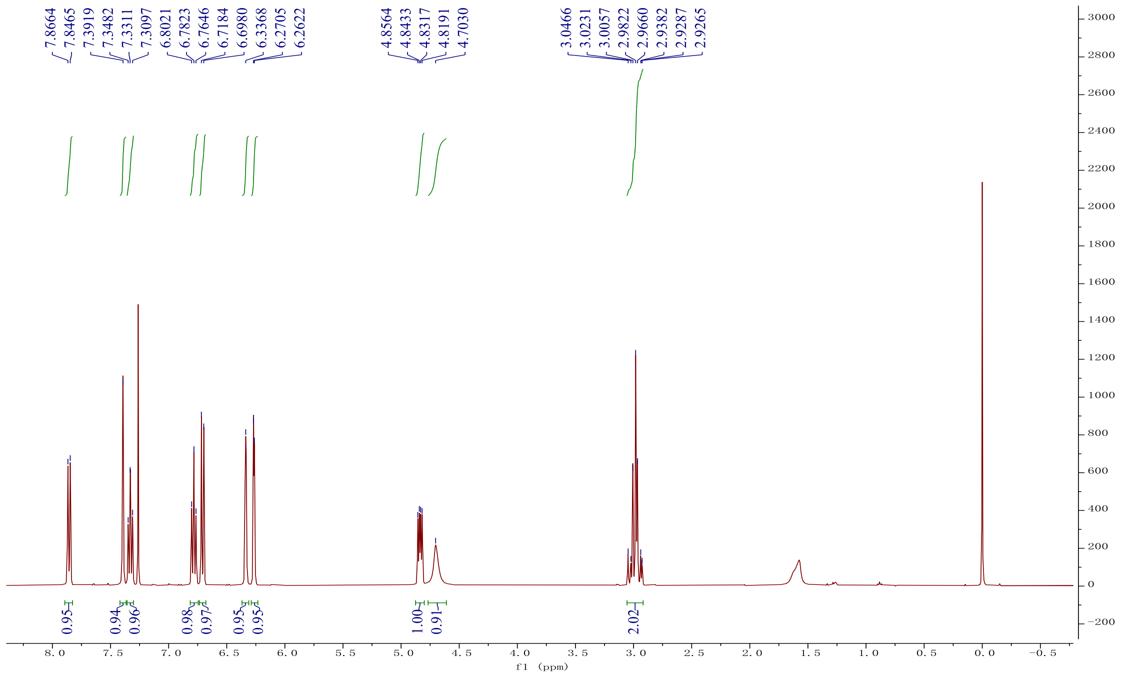


Figure S48 ^{1}H NMR Spectrum of *rac*-**1w** (400 MHz, $CDCl_3$)

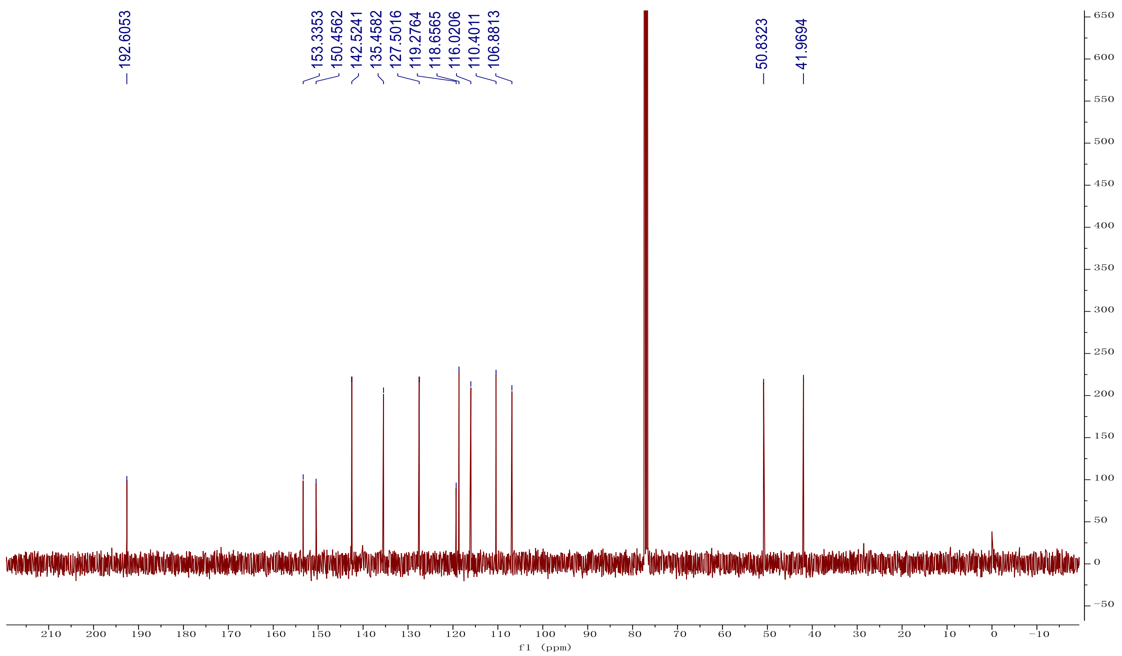
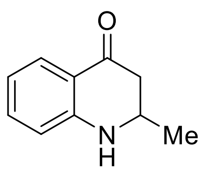


Figure S49 ^{13}C NMR Spectrum of *rac*-**1w** (100 MHz, $CDCl_3$)



rac-**1x**

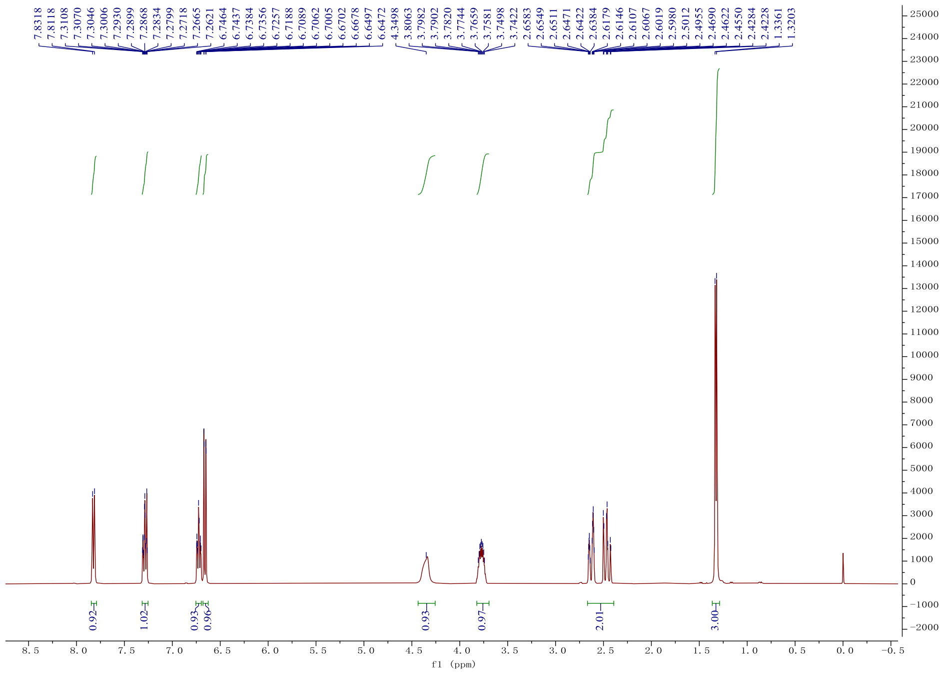


Figure S50 ^{1}H NMR Spectrum of *rac*-**1x** (400 MHz, $CDCl_3$)

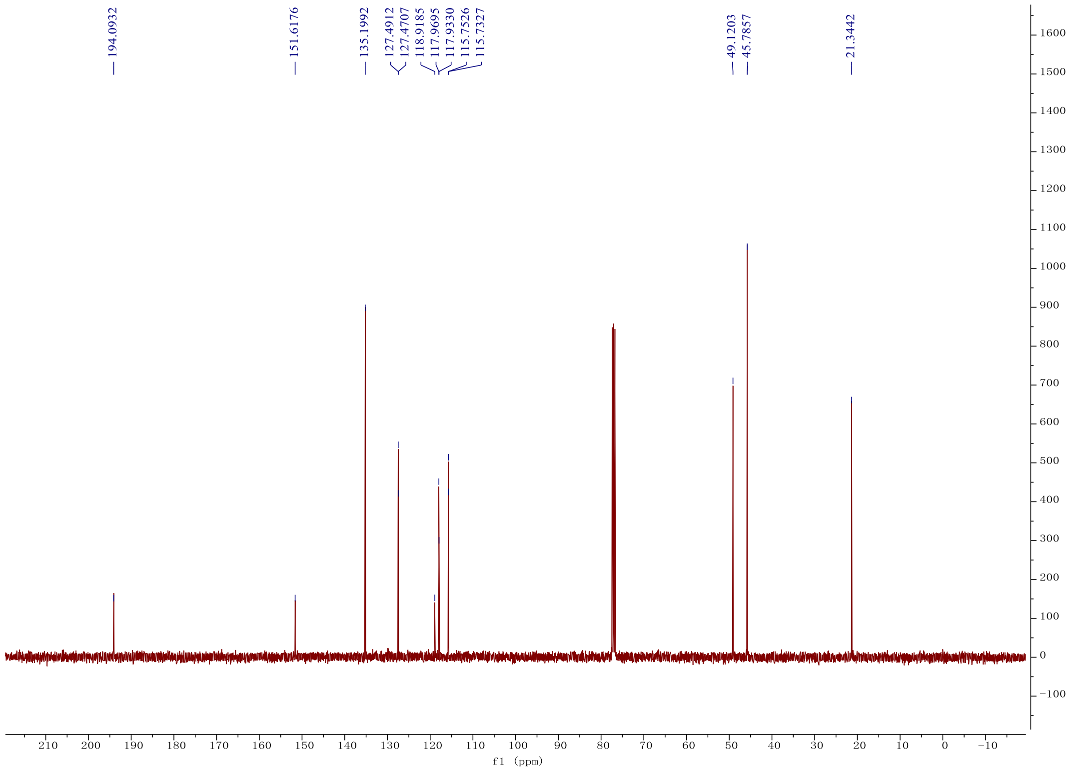
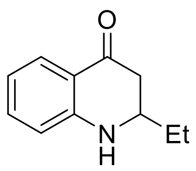


Figure S51 ^{13}C NMR Spectrum of *rac*-**1x** (100 MHz, $CDCl_3$)



rac-**1y**

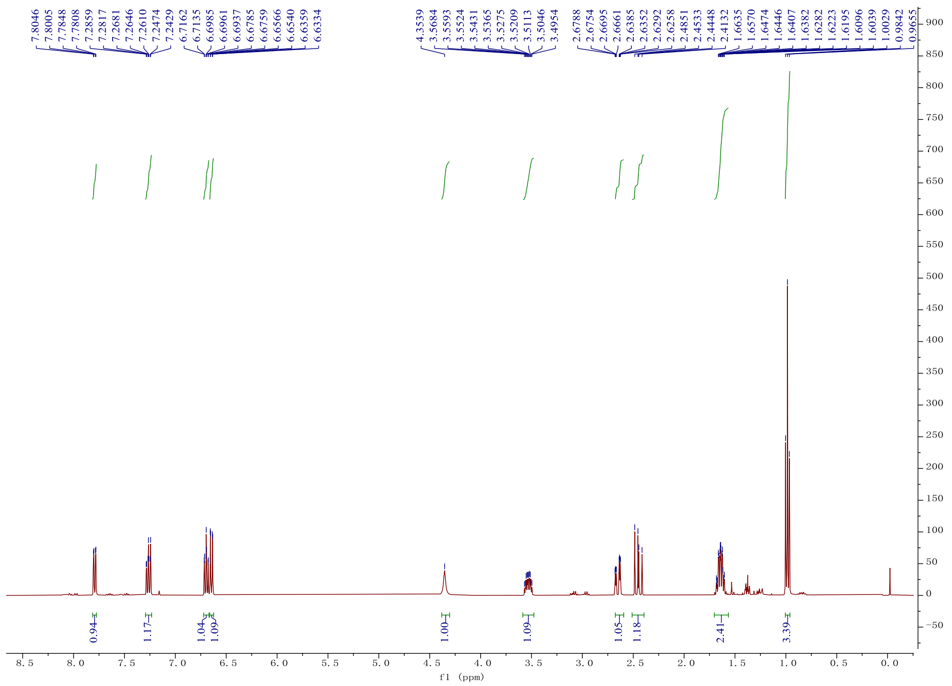


Figure S52 ^{1}H NMR Spectrum of *rac*-**1y** (400 MHz, $CDCl_3$)

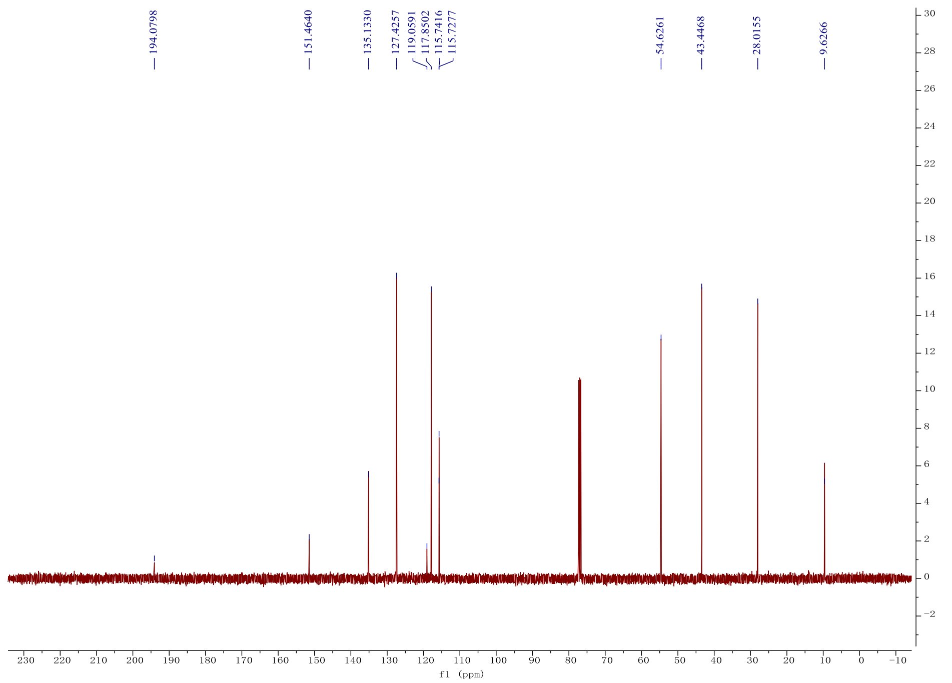
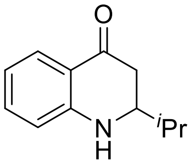


Figure S53 ^{13}C NMR Spectrum of *rac*-**1y** (100 MHz, $CDCl_3$)



rac-**1z**

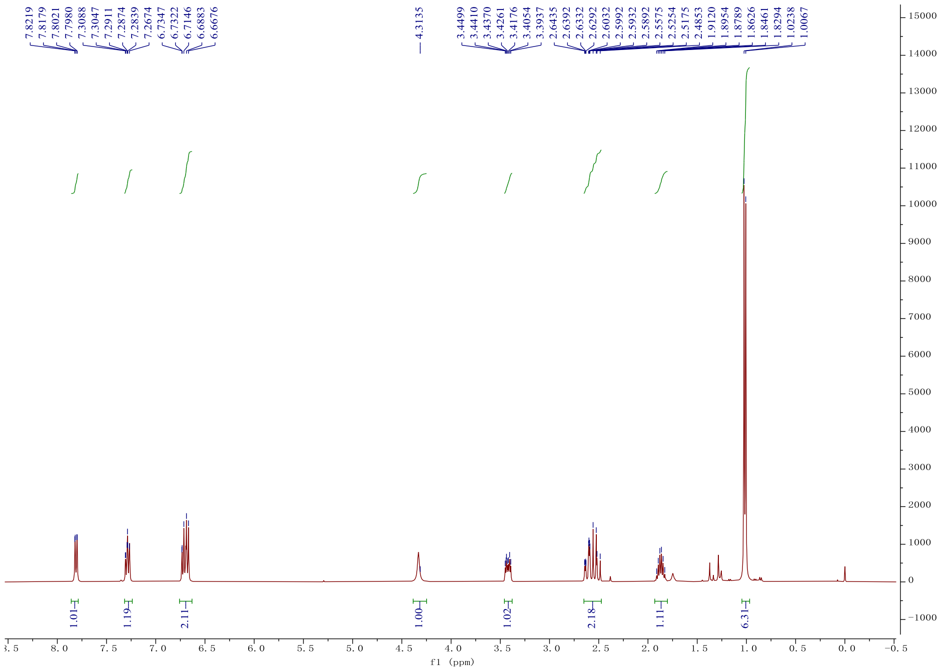


Figure S54 ^{1}H NMR Spectrum of *rac*-**1z** (400 MHz, $CDCl_3$)

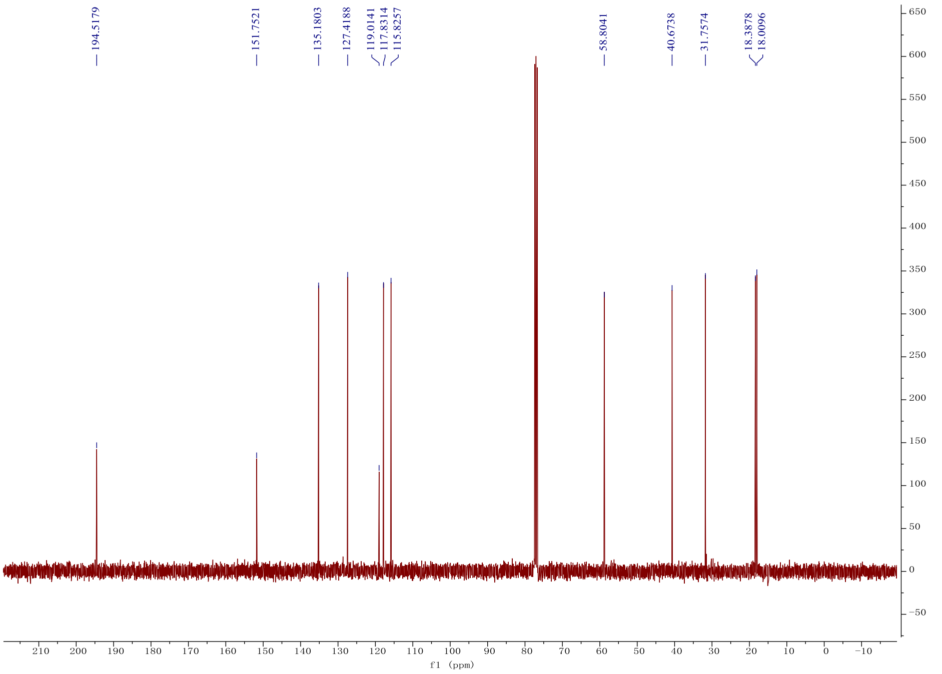
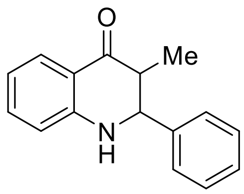


Figure S55 ^{13}C NMR Spectrum of *rac*-**1z** (100 MHz, $CDCl_3$)



rac-**1aa**

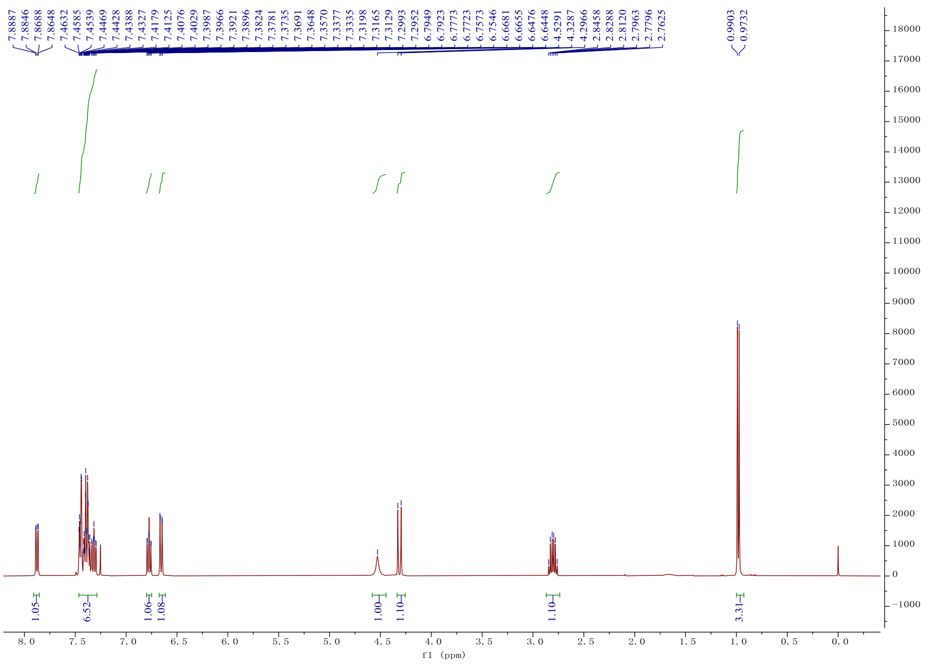


Figure S56 ^{1}H NMR Spectrum of *rac*-**1aa** (400 MHz, $CDCl_3$)

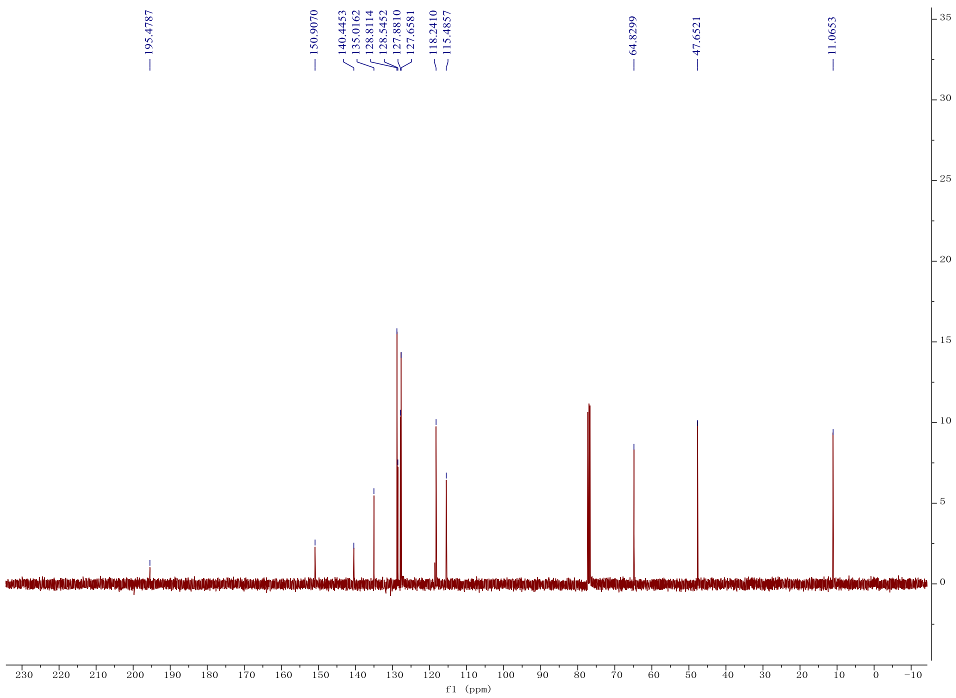
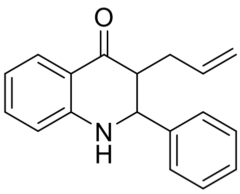


Figure S57 ^{13}C NMR Spectrum of *rac*-**1aa** (100 MHz, $CDCl_3$)



rac-**1ab**

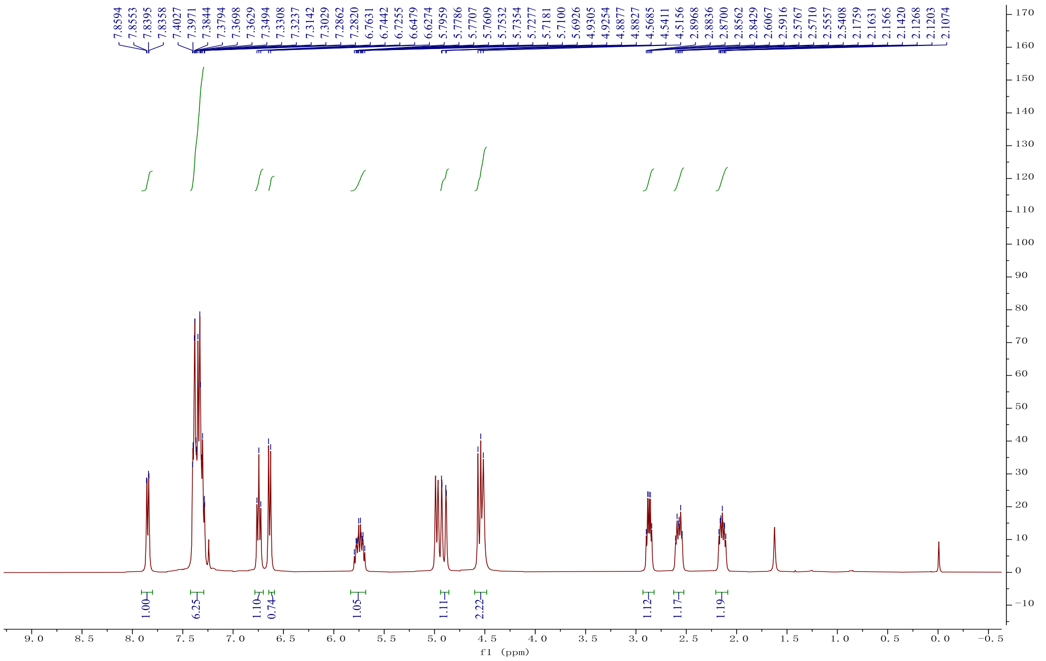


Figure S58 ^{1}H NMR Spectrum of *rac*-**1ab** (400 MHz, $CDCl_3$)

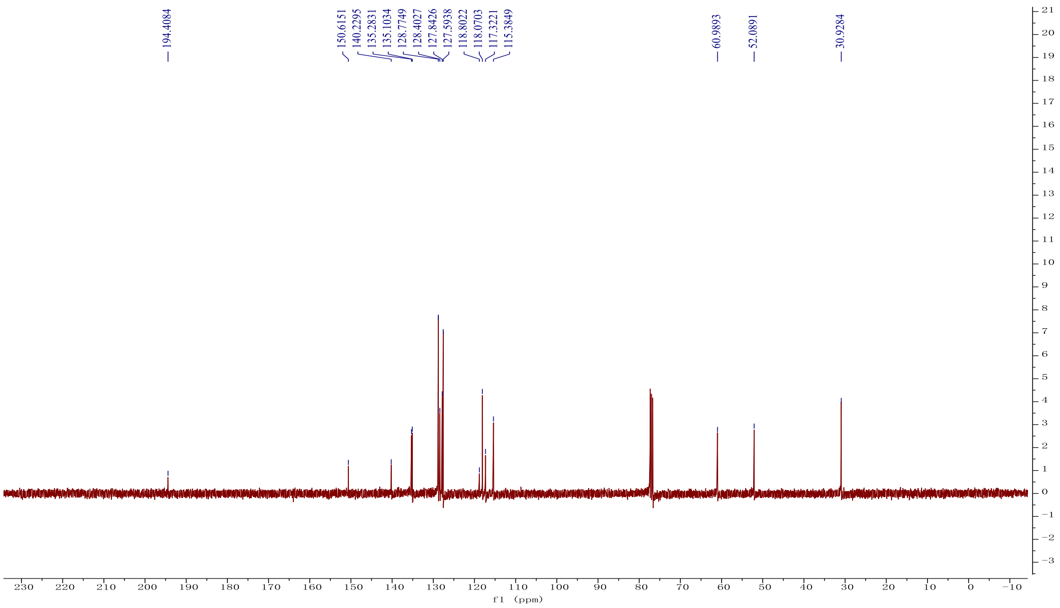
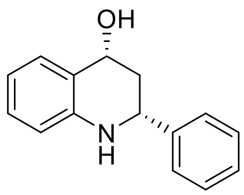


Figure S59 ^{13}C NMR Spectrum of *rac*-**1ab** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2a**

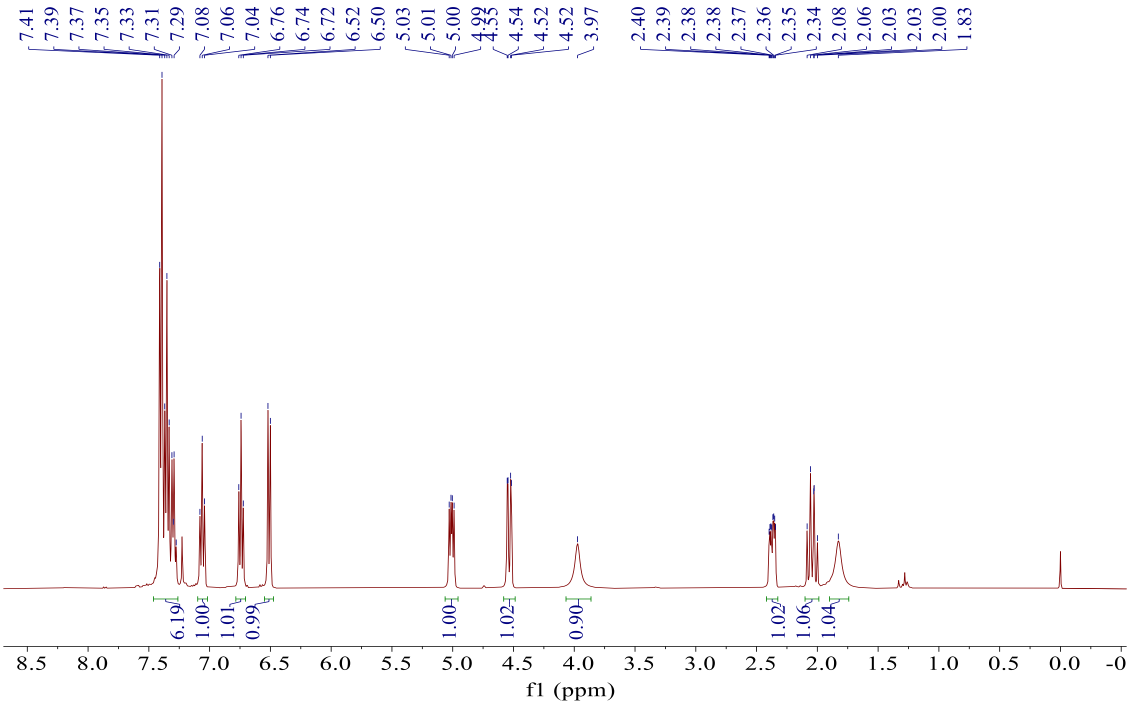


Figure S60 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2a** (400 MHz, $CDCl_3$)

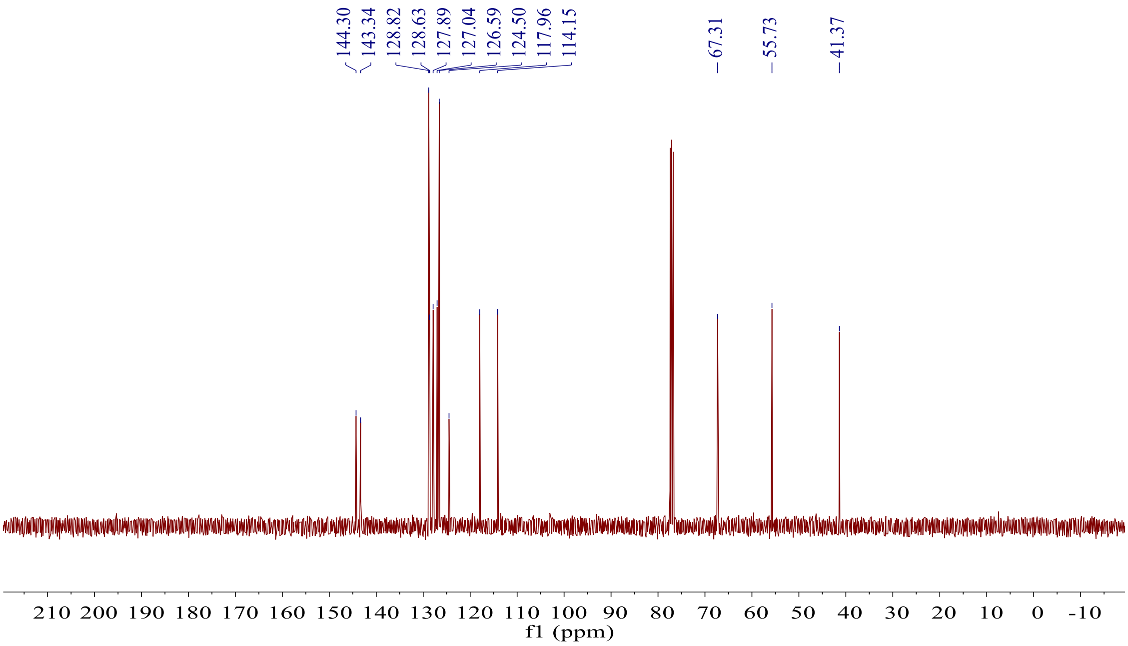
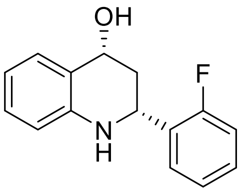


Figure S61 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2a** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2b**

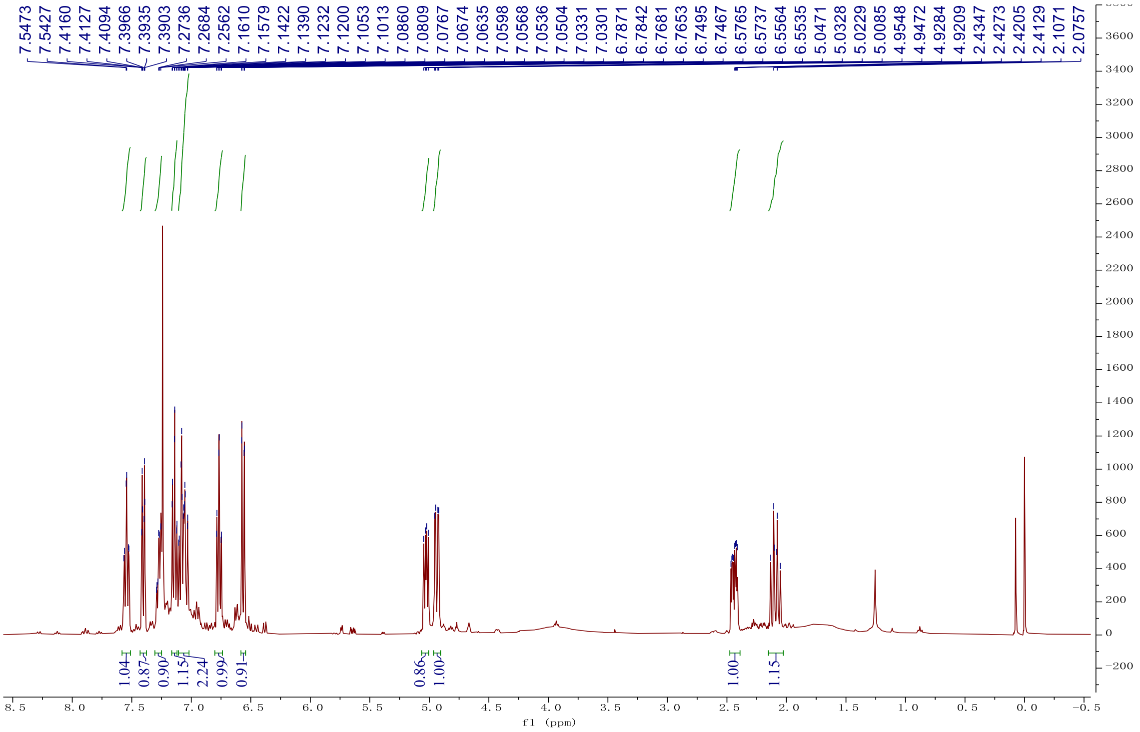


Figure S62 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2b** (400 MHz, $CDCl_3$)

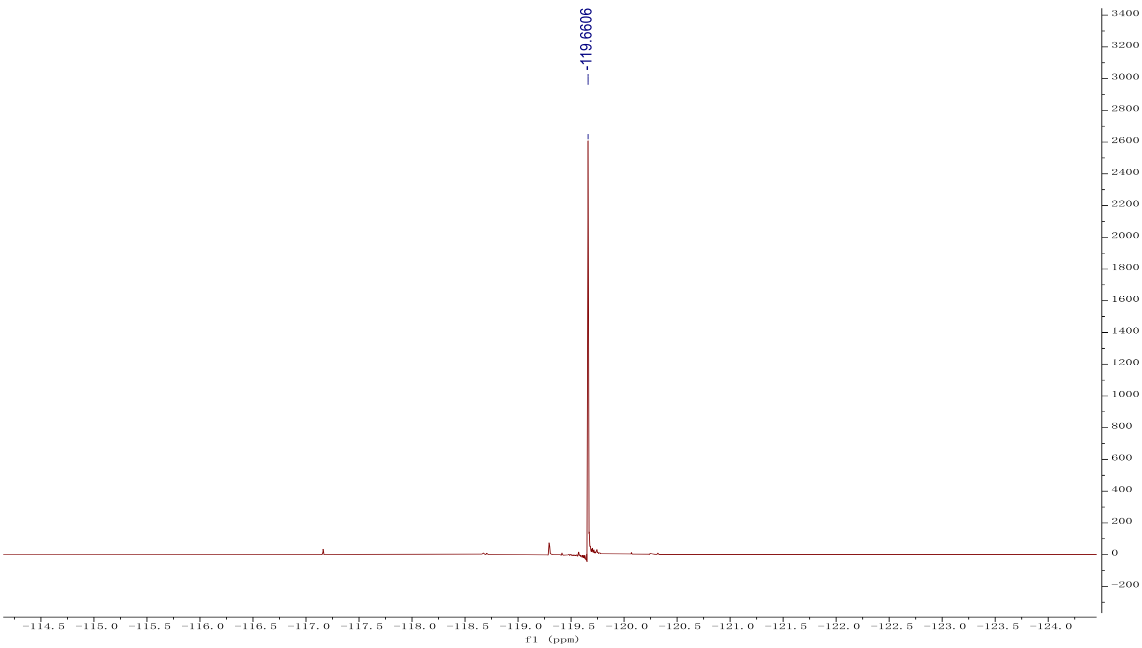


Figure S63 ^{19}F NMR Spectrum of (2*R*,4*R*)-**2b** (376 MHz, $CDCl_3$)

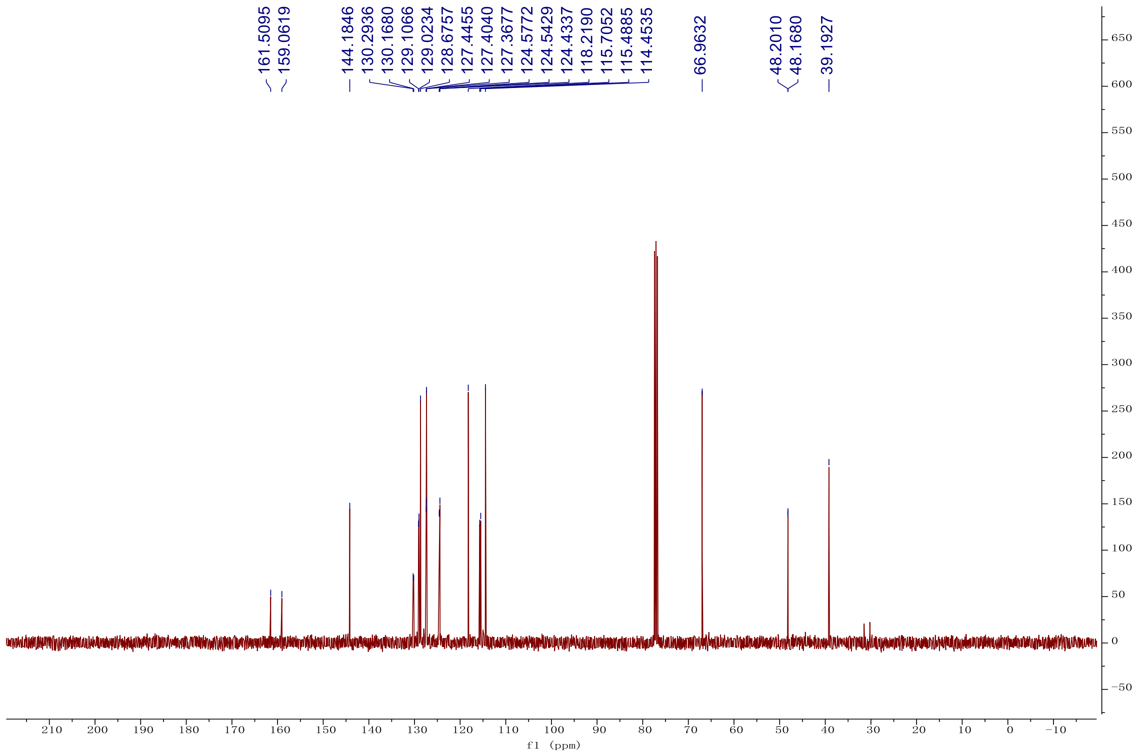
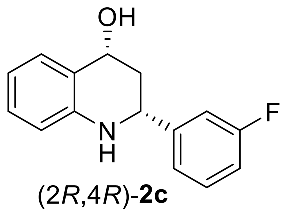


Figure S64 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2b** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2c**

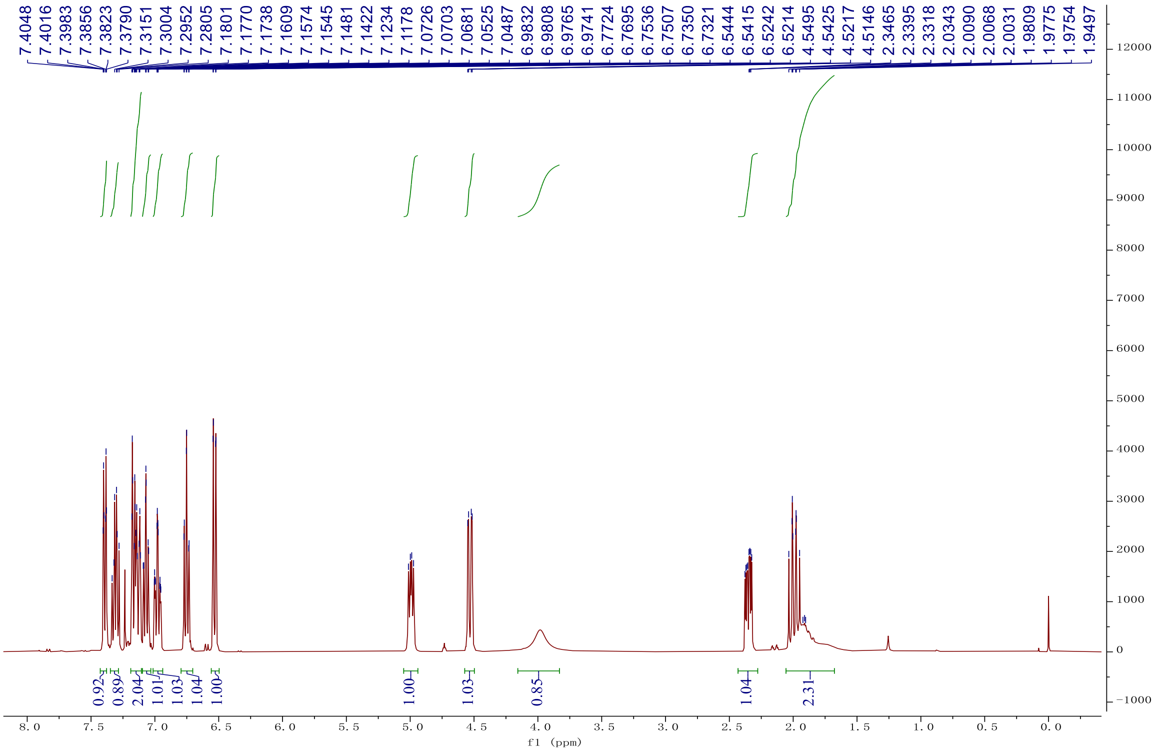


Figure S65 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2c** (400 MHz, $CDCl_3$)

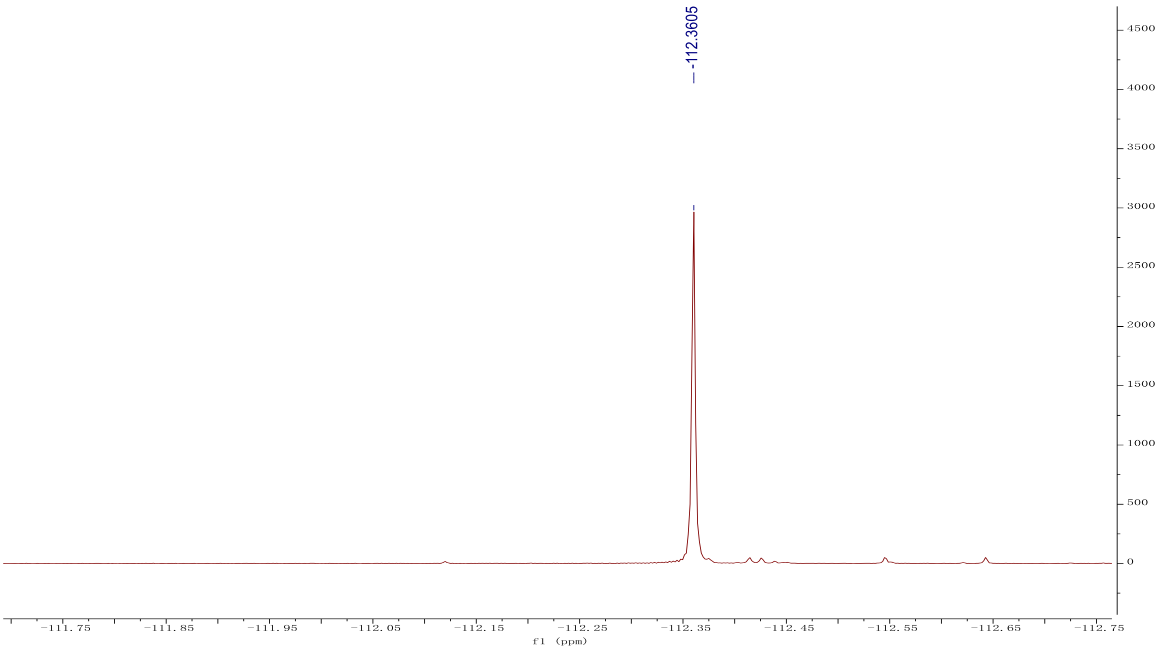


Figure S66 ^{19}F NMR Spectrum of (2*R*,4*R*)-**2c** (376 MHz, $CDCl_3$)

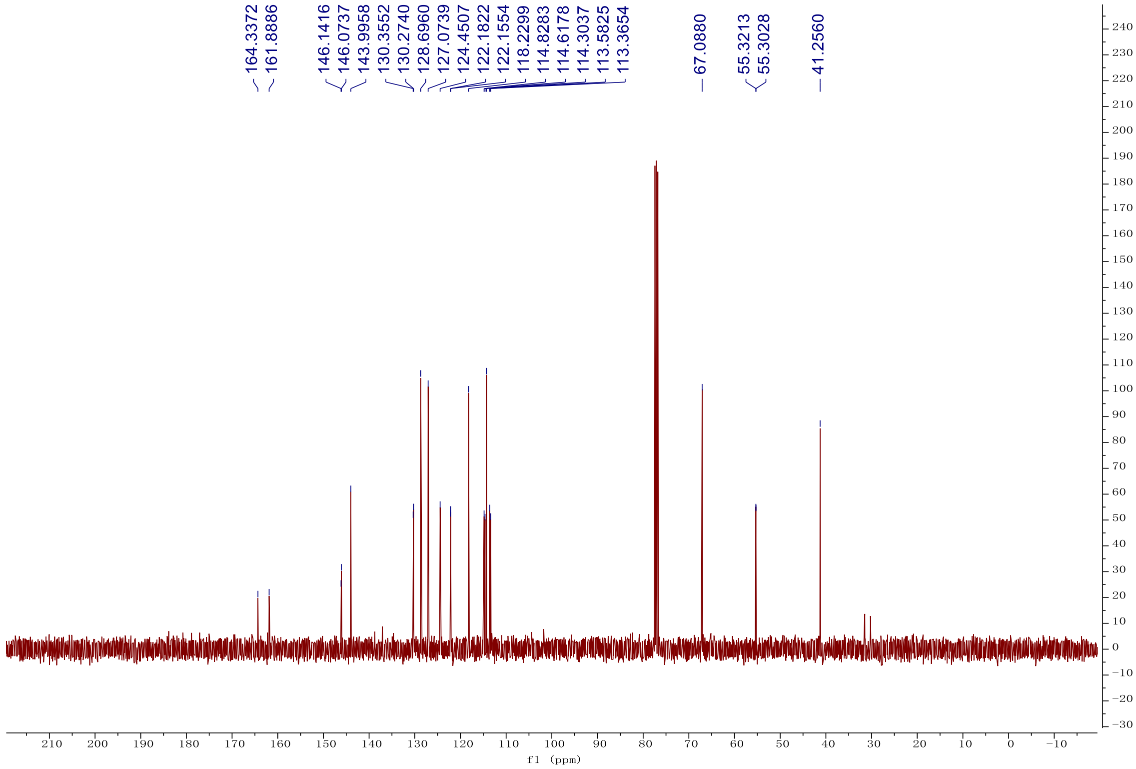
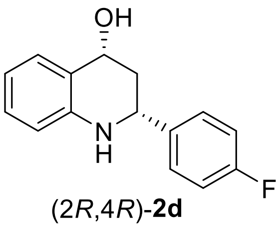


Figure S67 ^{13}C NMR Spectrum of (2*R*,4*R*)**-2c** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2d**

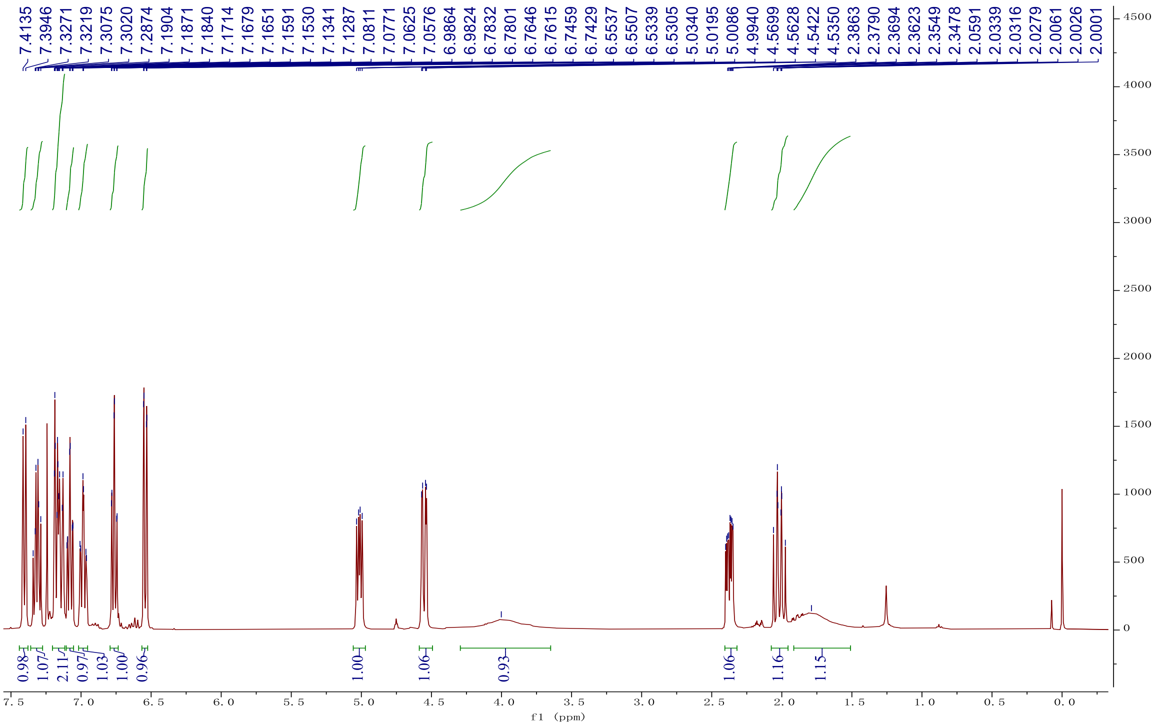


Figure S68 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2d** (400 MHz, $CDCl_3$)

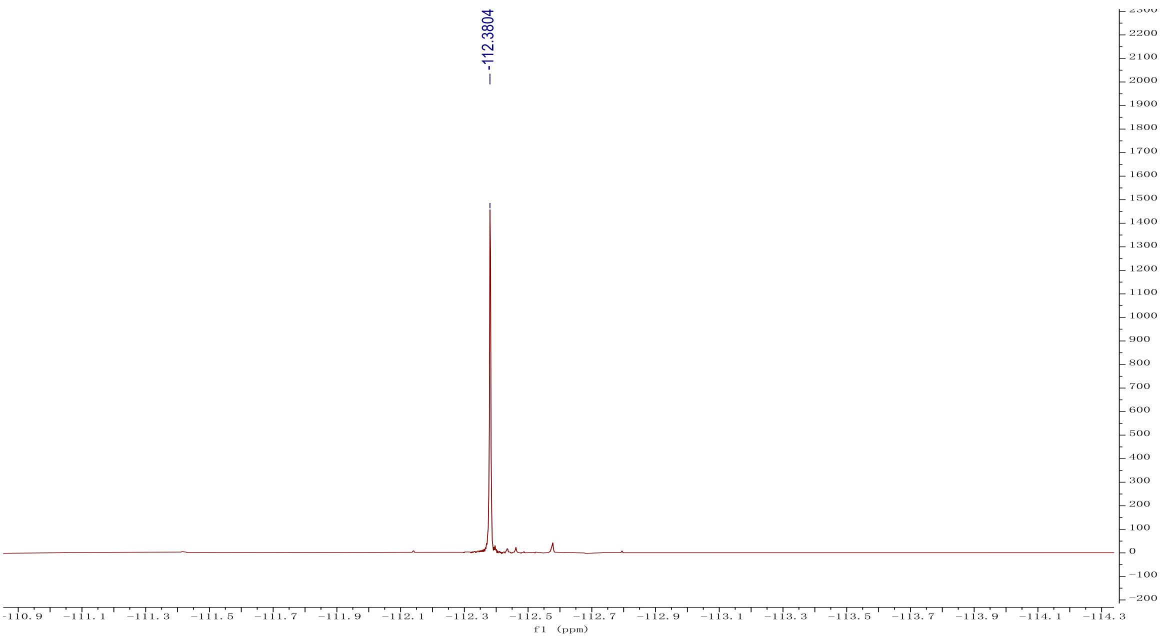


Figure S69 ^{19}F NMR Spectrum of (2*R*,4*R*)-**2d** (376 MHz, $CDCl_3$)

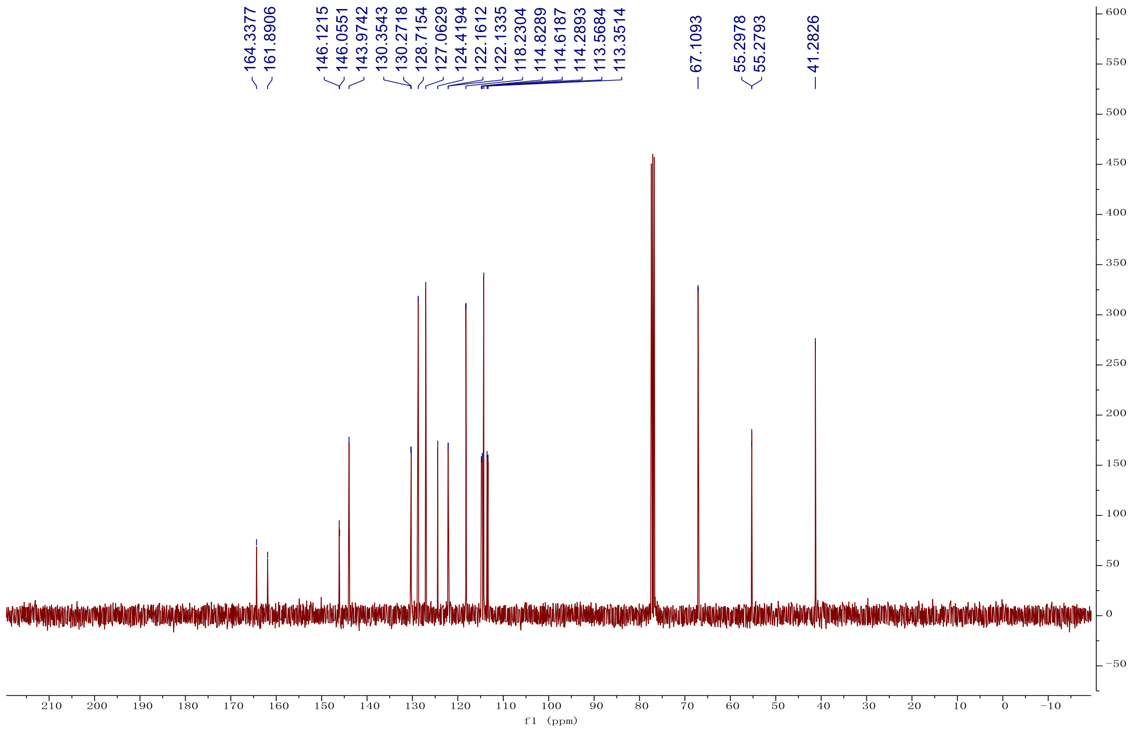
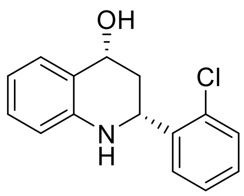


Figure S70 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2d** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2e**

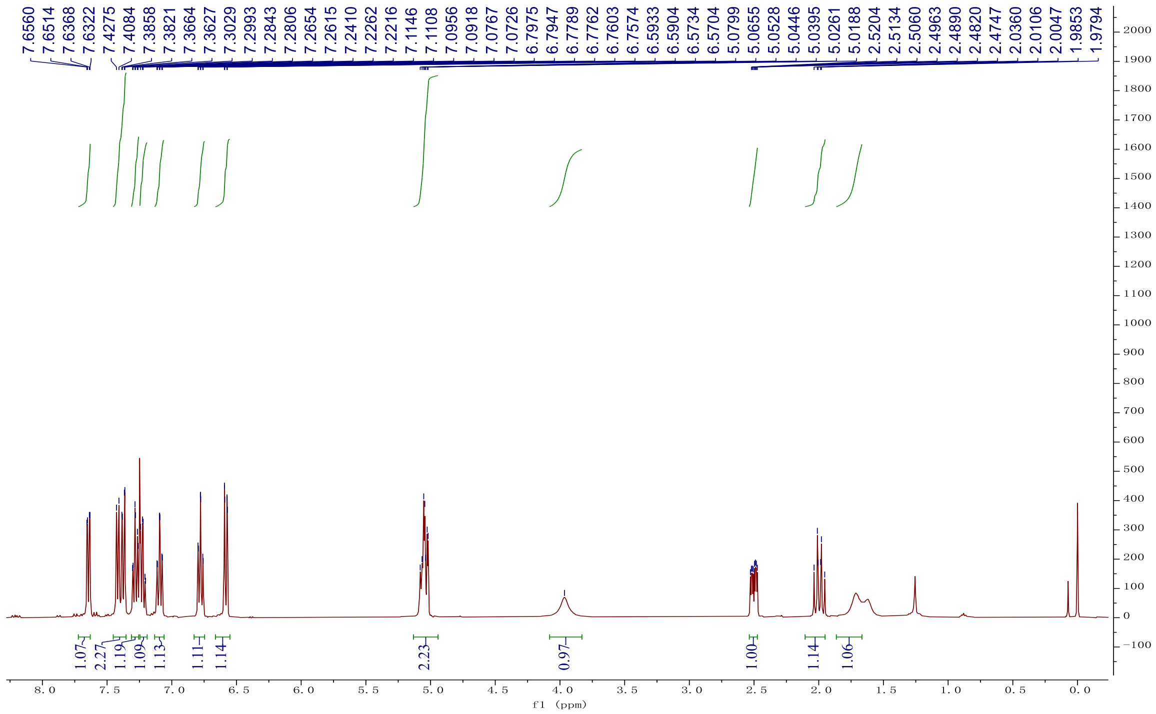


Figure S71 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2e** (400 MHz, $CDCl_3$)

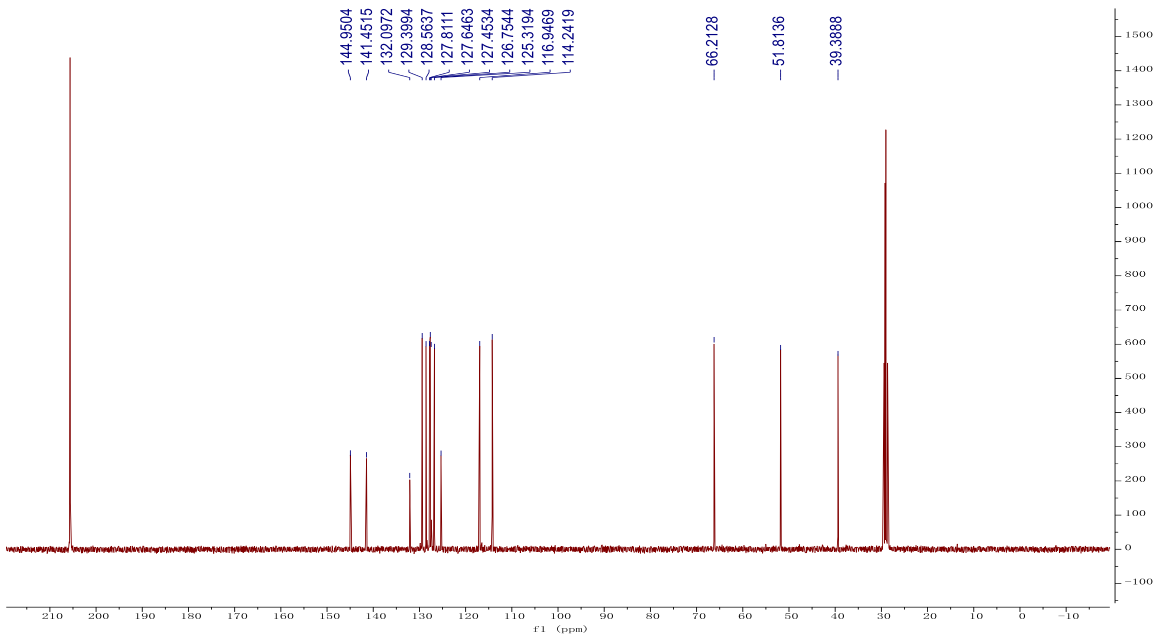
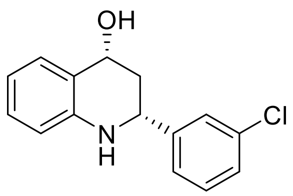


Figure S72 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2e** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2f**

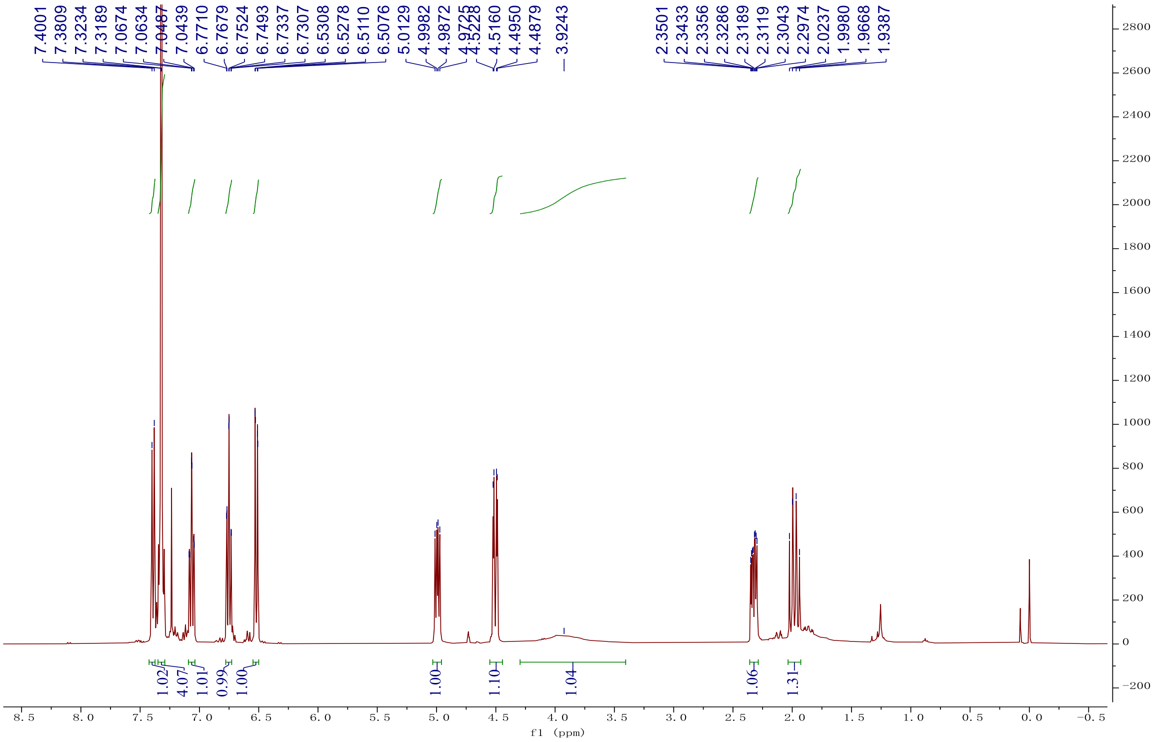


Figure S73 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2f** (400 MHz, $CDCl_3$)

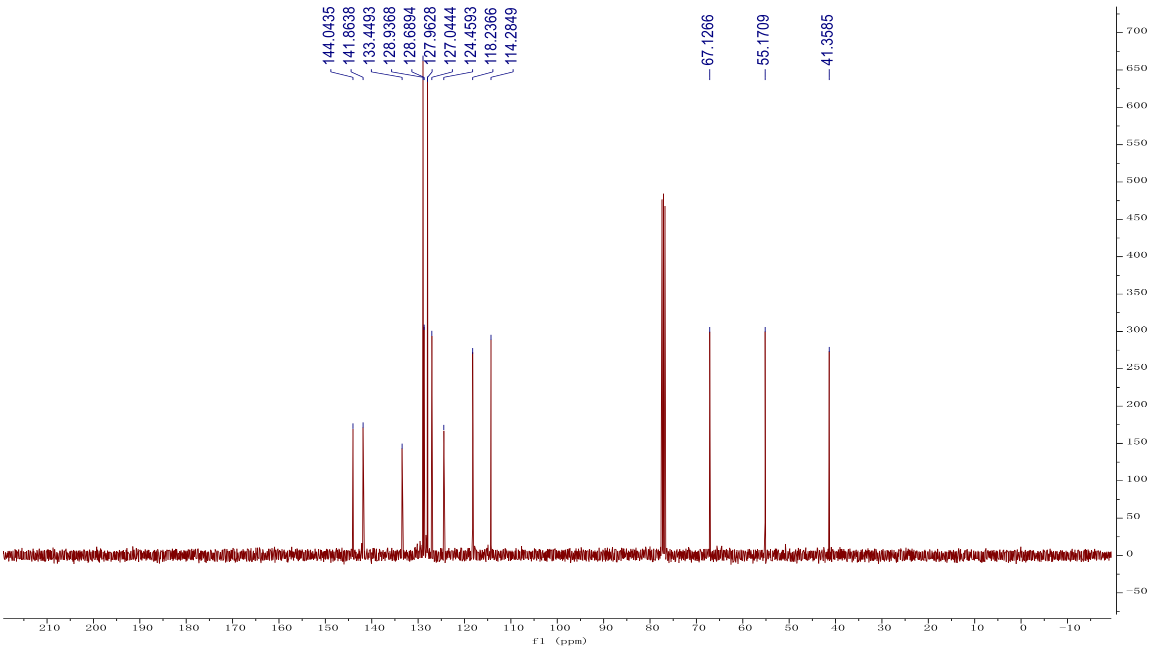
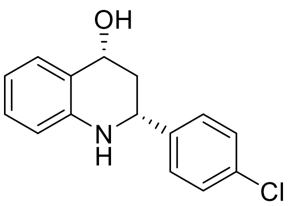


Figure S74 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2f** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2g**

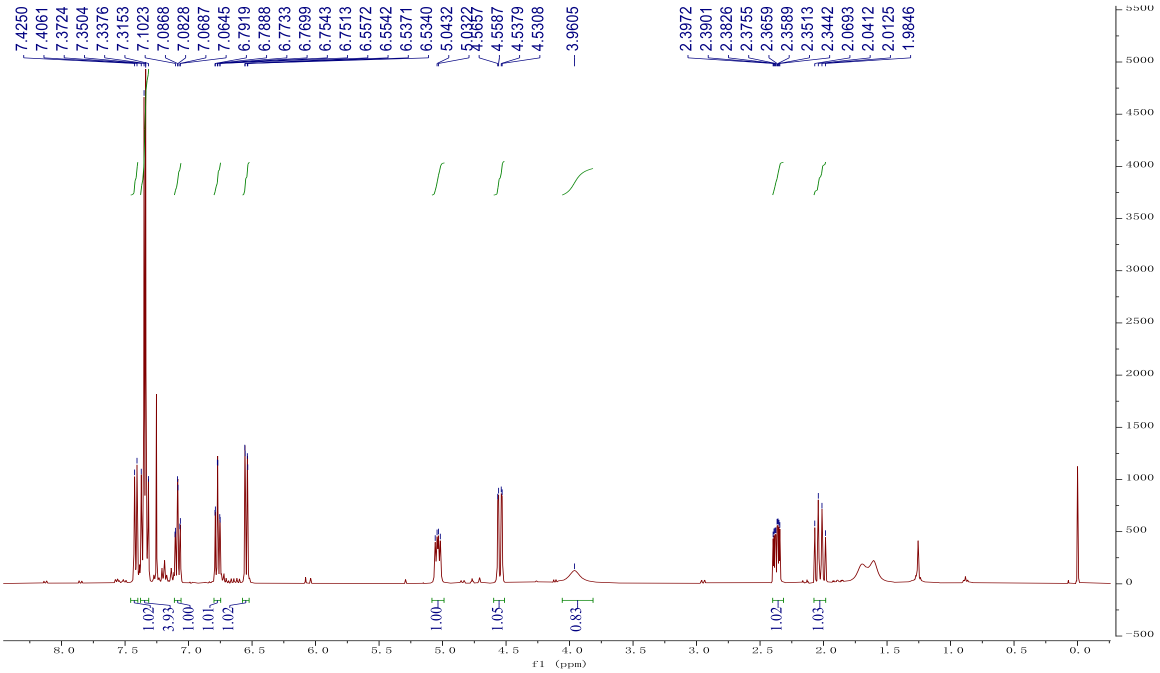


Figure S75 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2g** (400 MHz, $CDCl_3$)

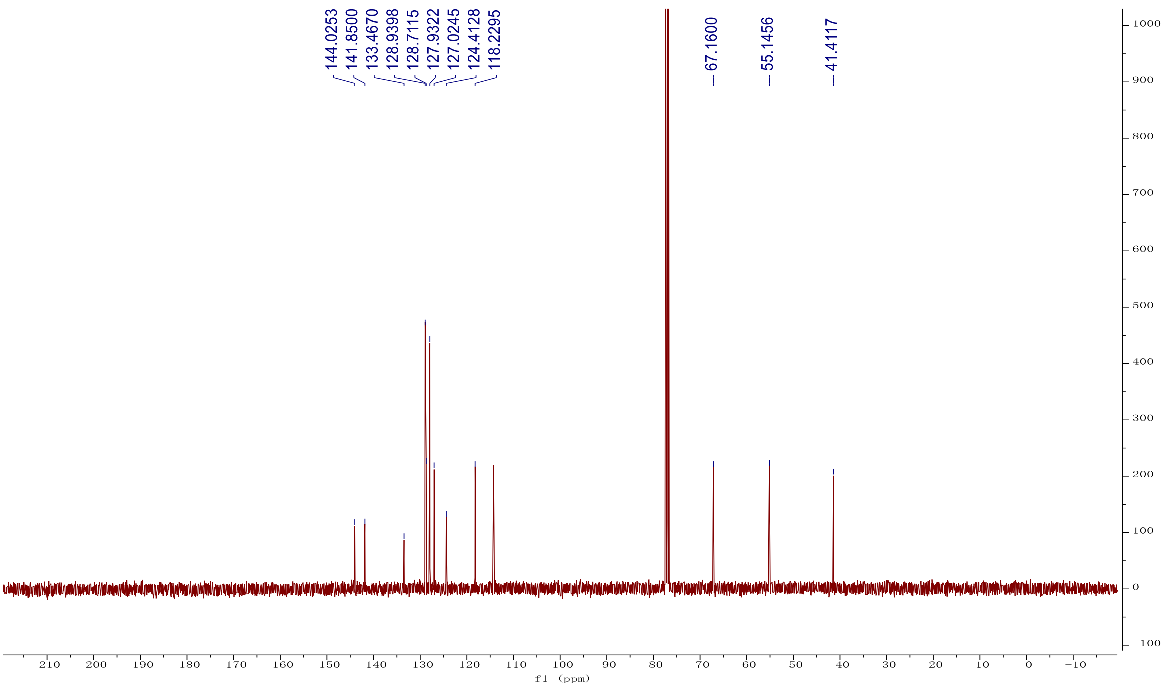
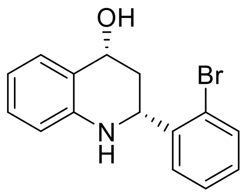


Figure S76 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2g** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2h**

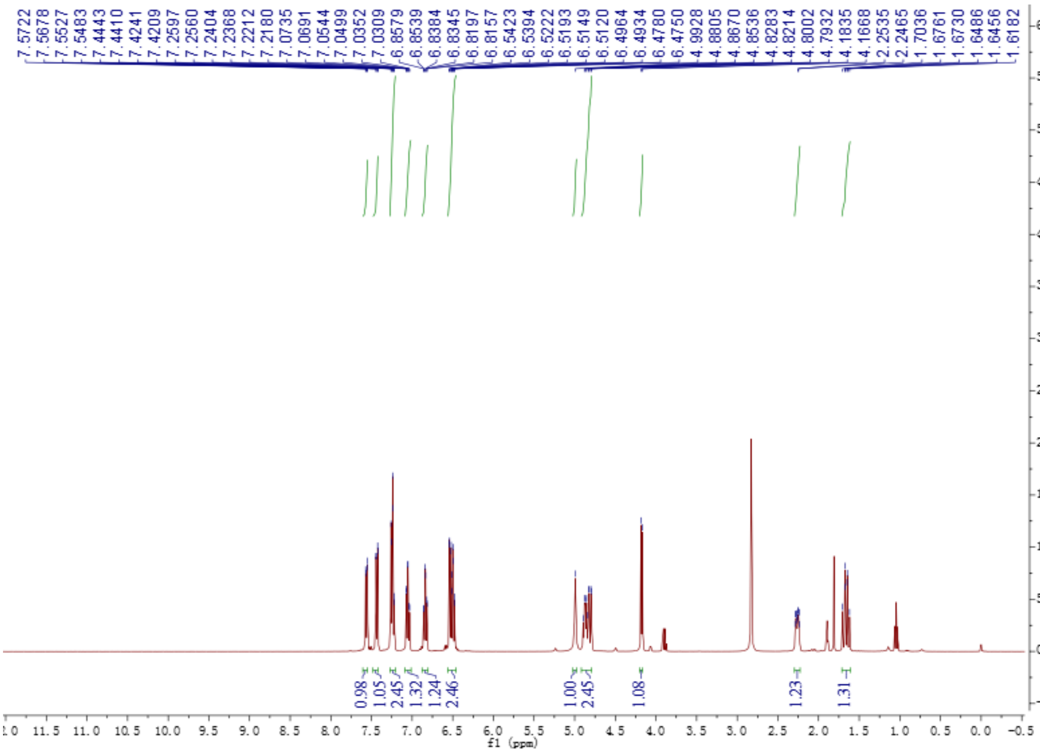


Figure S77 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2h** (400 MHz, $CDCl_3$)

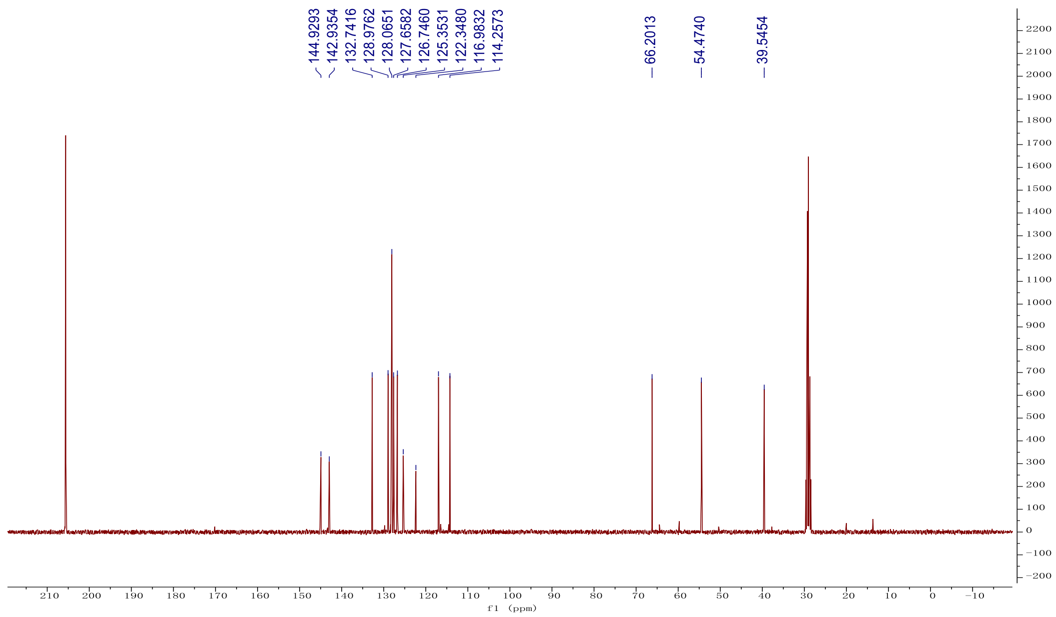
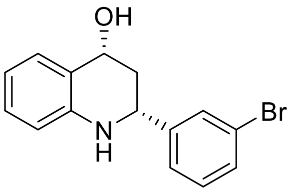


Figure S78 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2h** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2i**

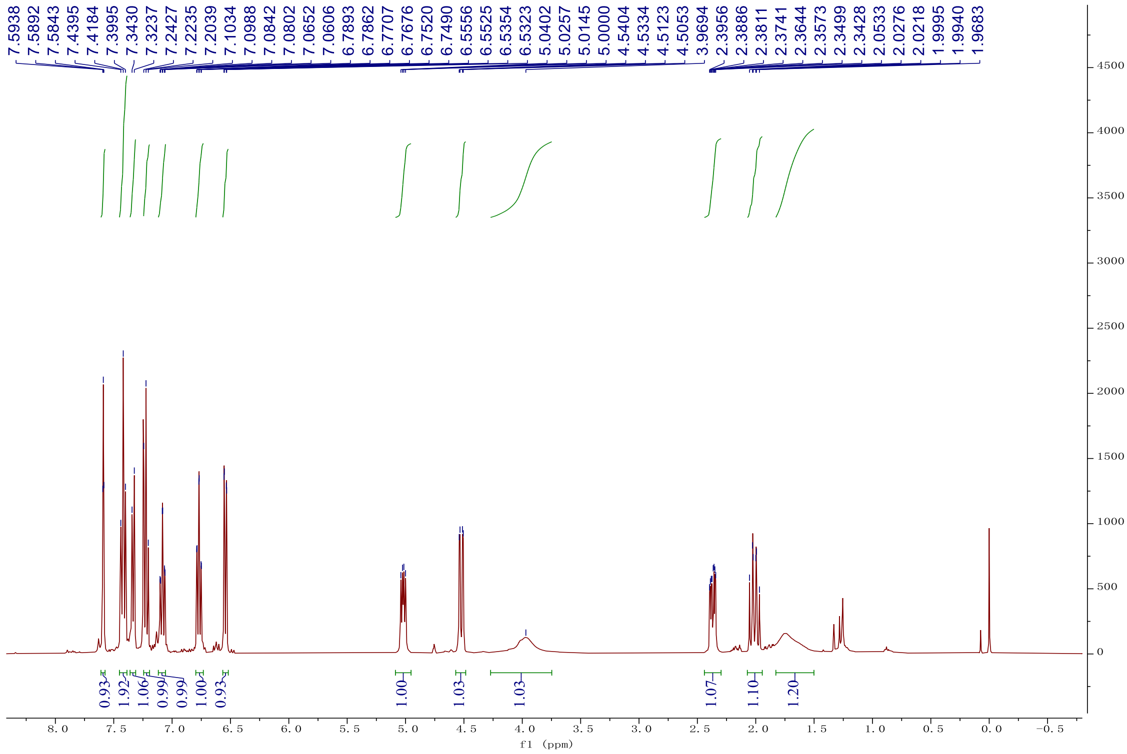


Figure S79 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2i** (400 MHz, $CDCl_3$)

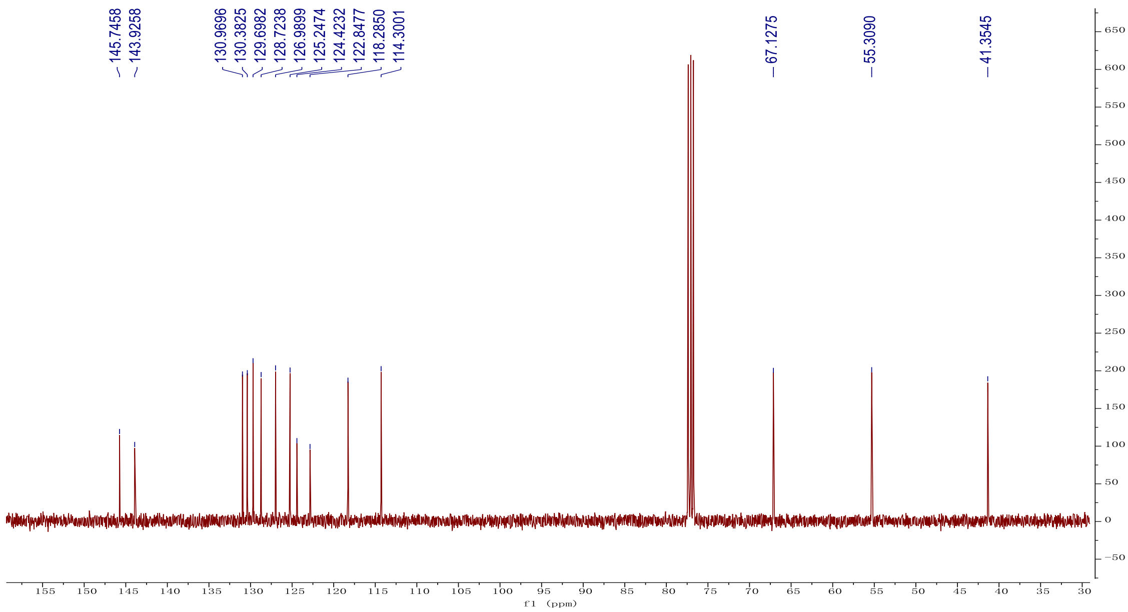
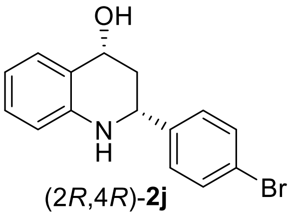


Figure S80 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2i** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2j**

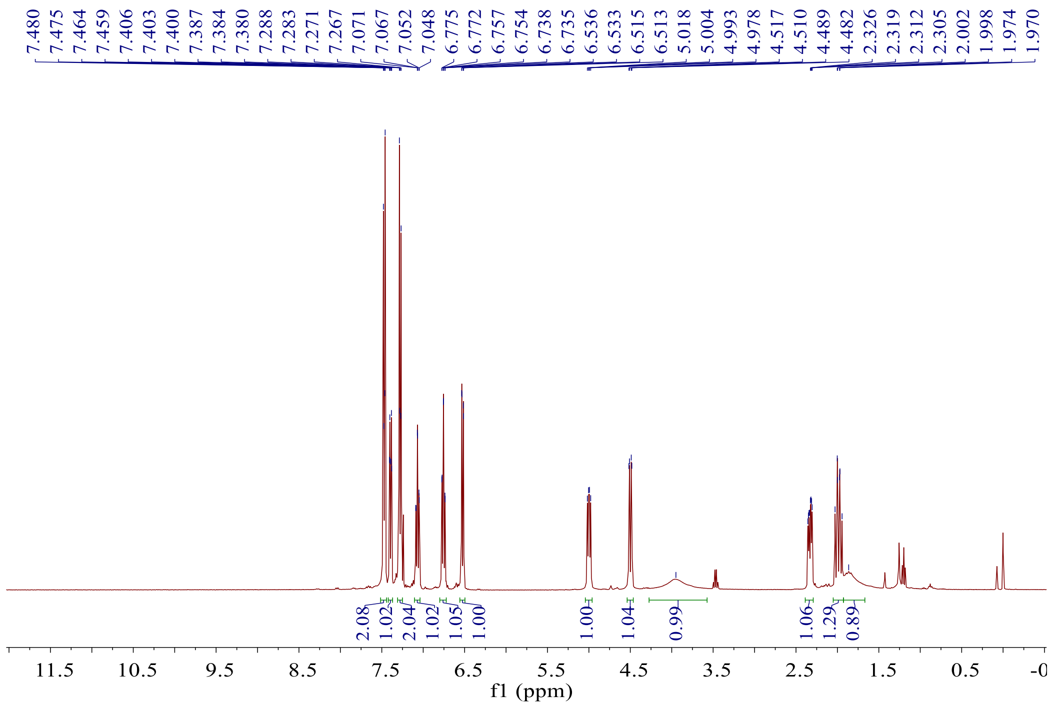


Figure S81 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2j** (100 MHz, $CDCl_3$)

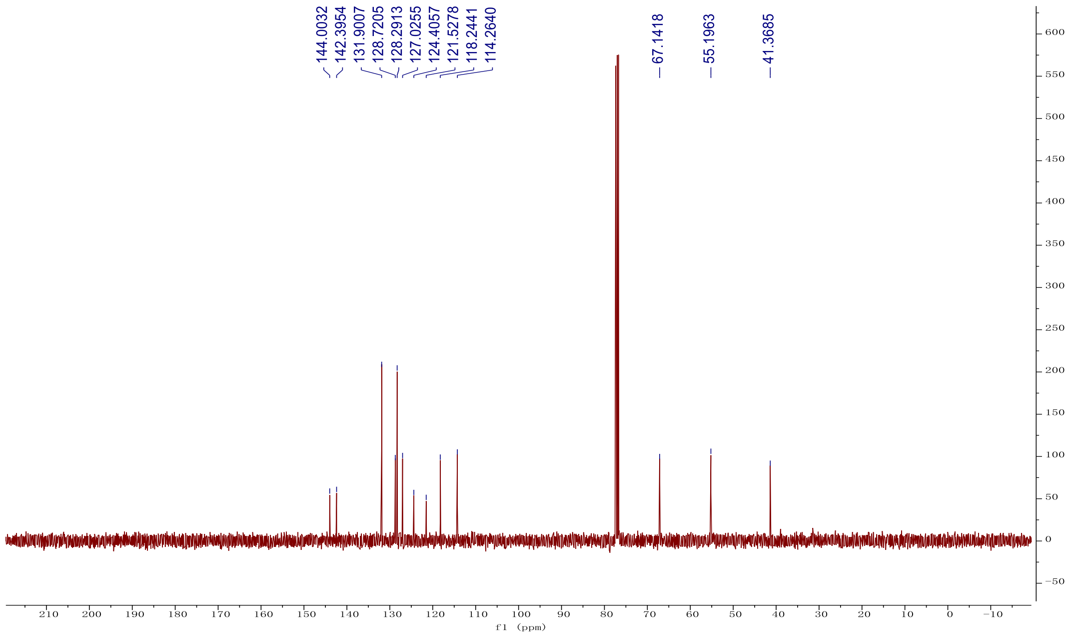
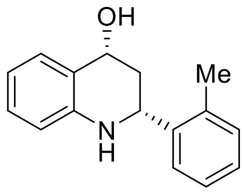


Figure S82 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2j** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2k**

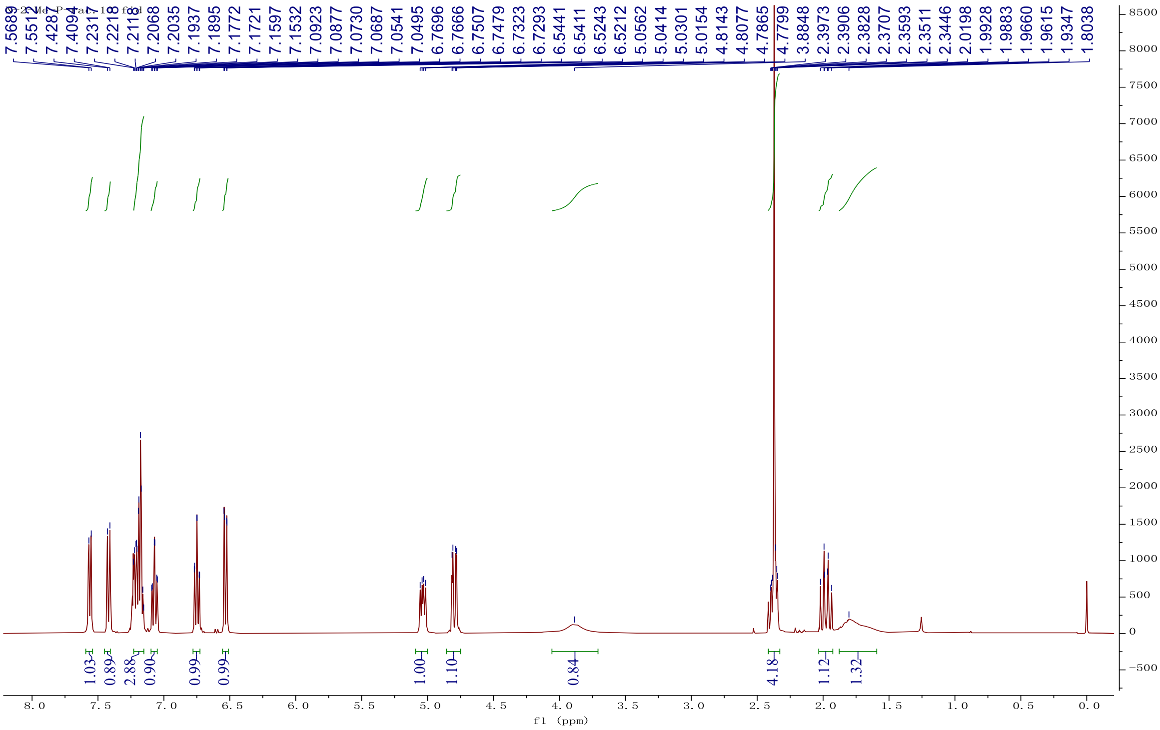


Figure S83 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2k** (100 MHz, $CDCl_3$)

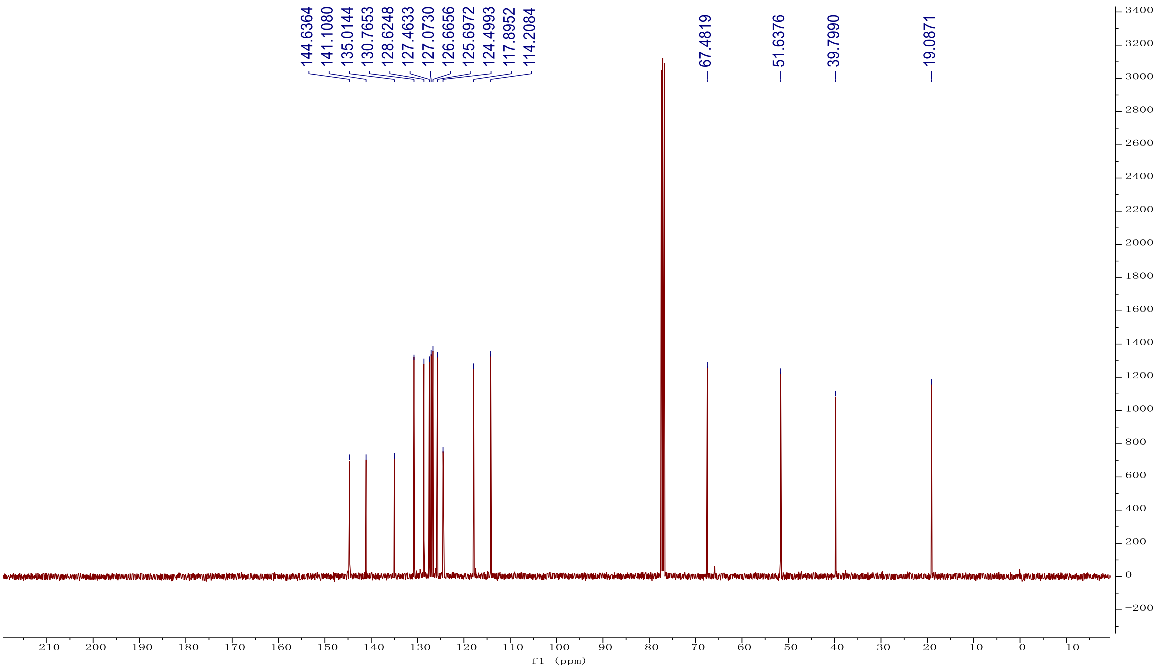
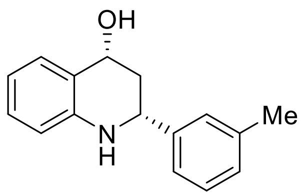


Figure S84 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2k** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2l**

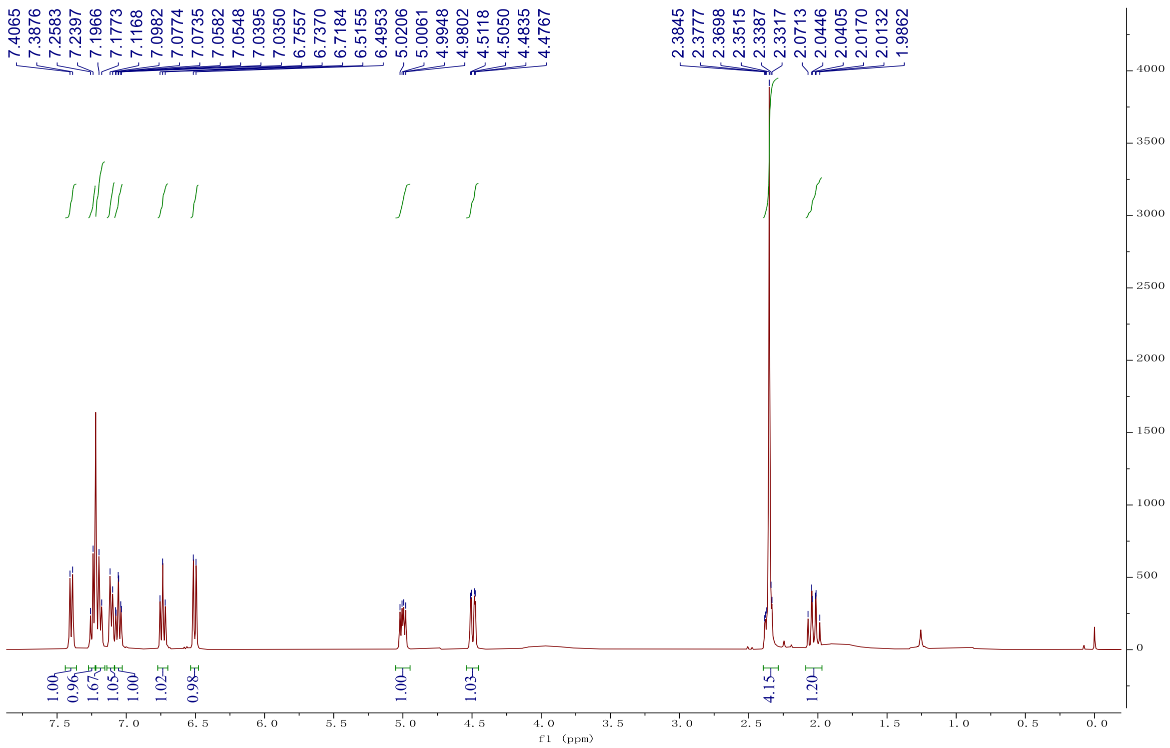


Figure S85 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2l** (400 MHz, $CDCl_3$)

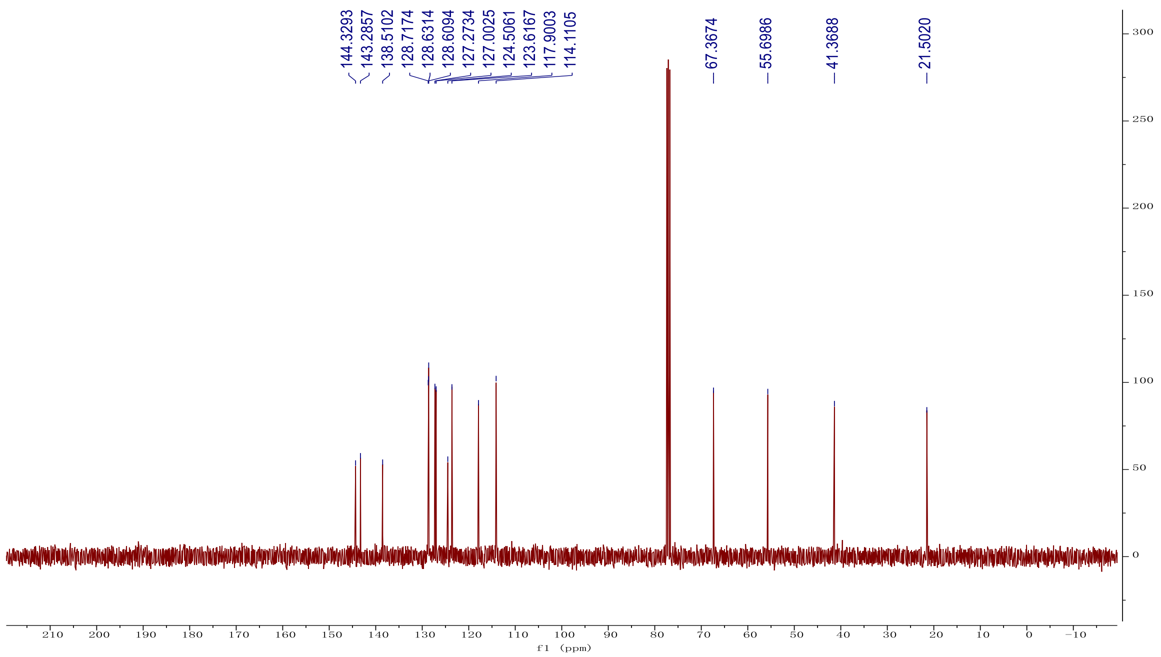
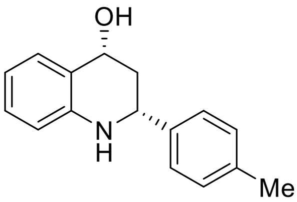


Figure S86 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2l** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2m**

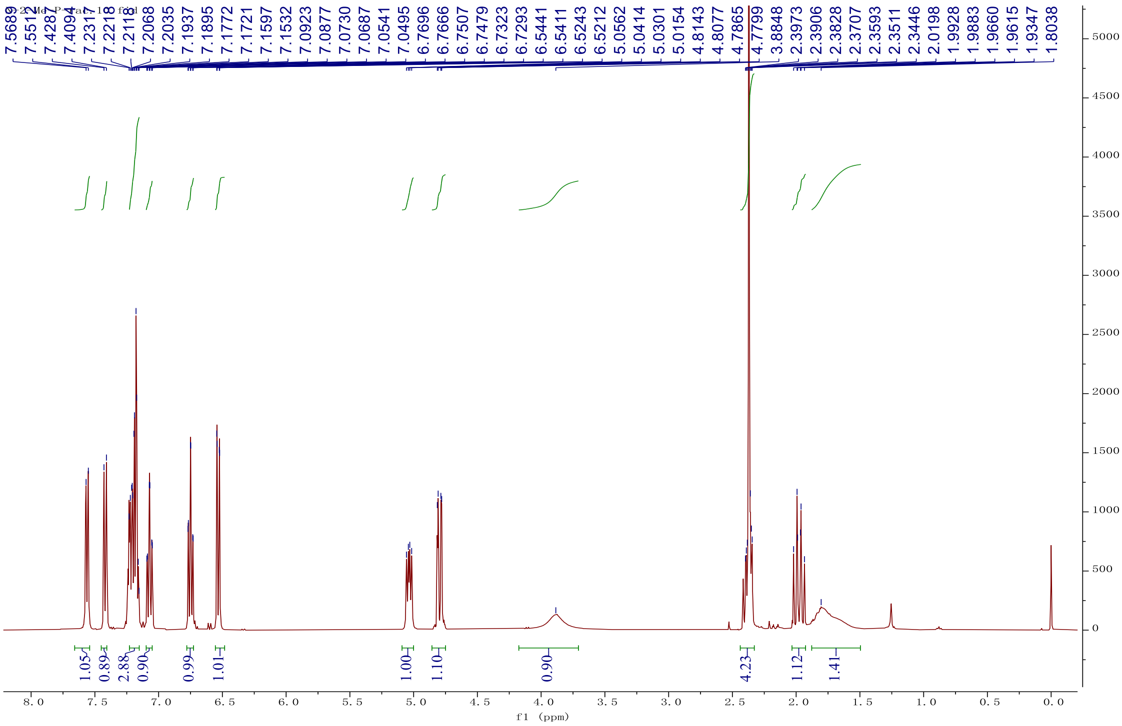


Figure S87 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2m** (400 MHz, $CDCl_3$)

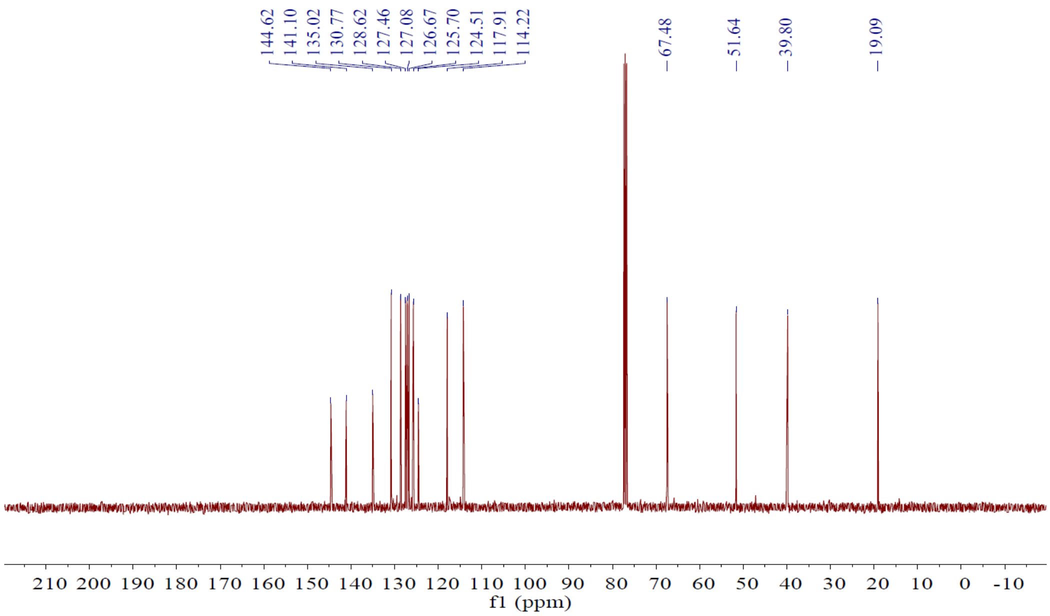
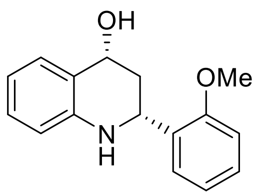


Figure S88 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2m** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2n**

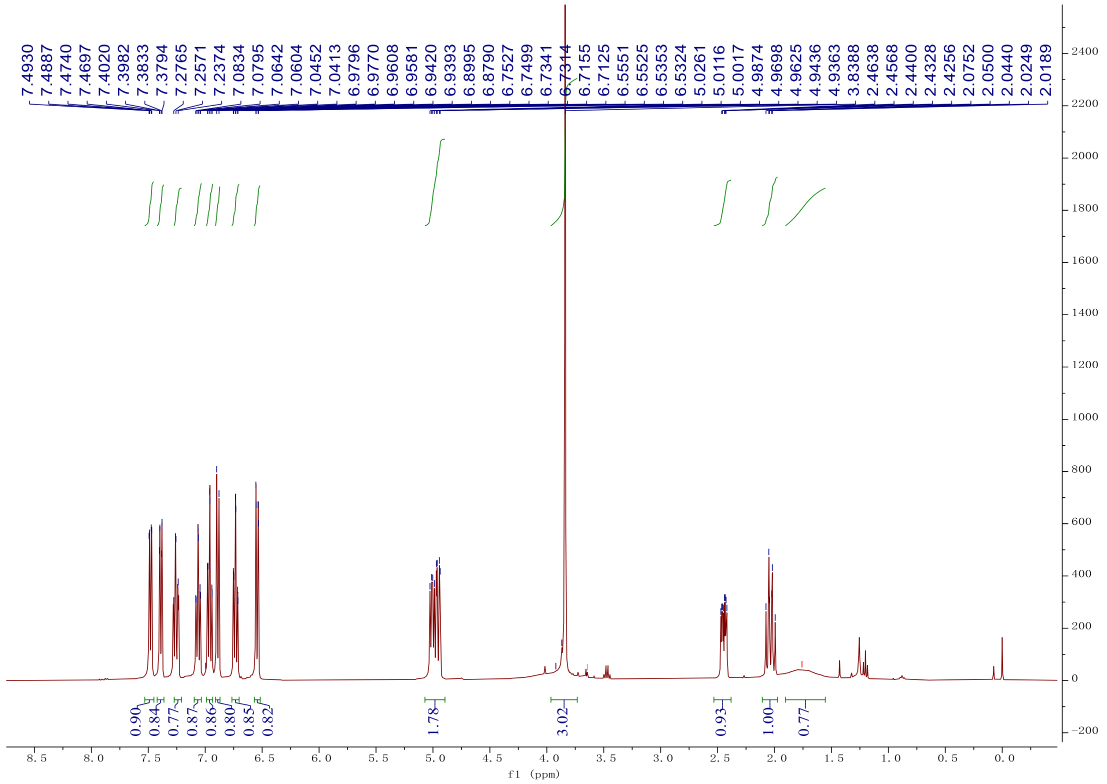


Figure S89 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2n** (400 MHz, $CDCl_3$)

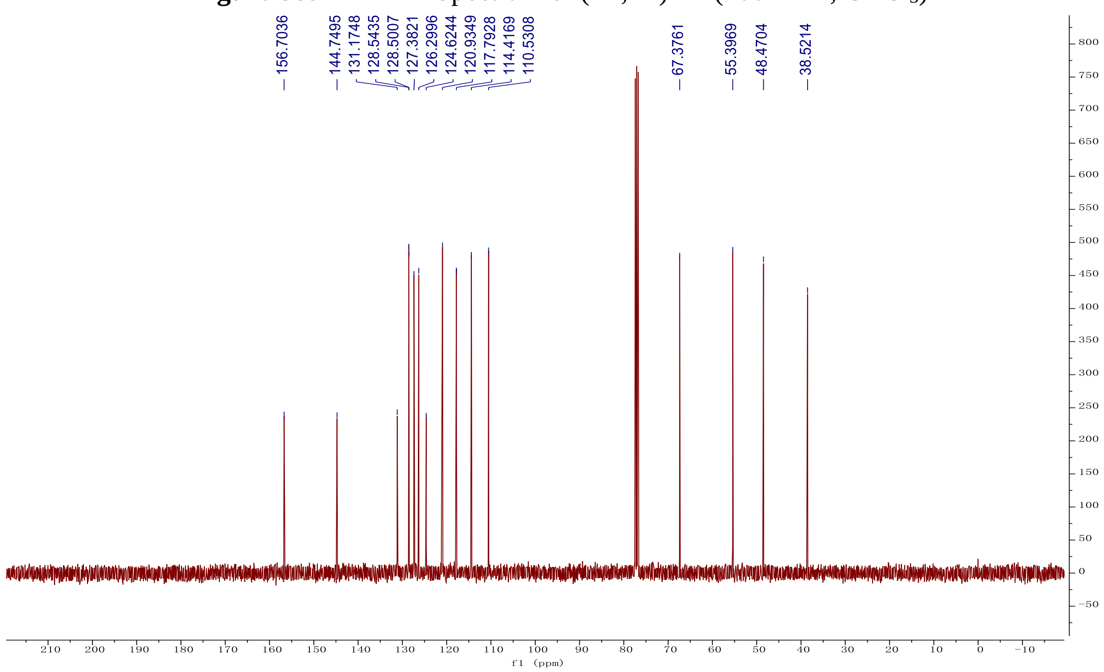
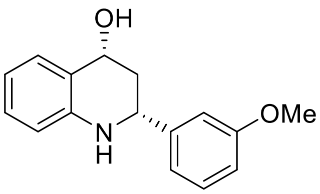


Figure S90 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2n** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2o**

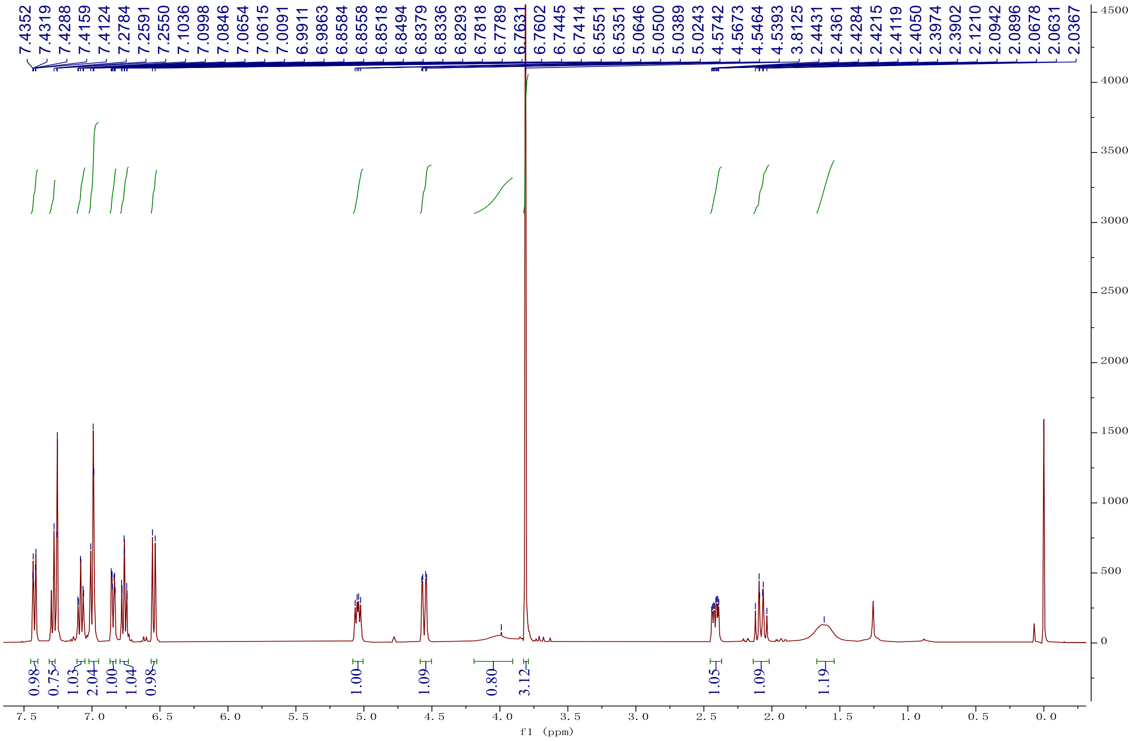


Figure S91 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2o** (400 MHz, $CDCl_3$)

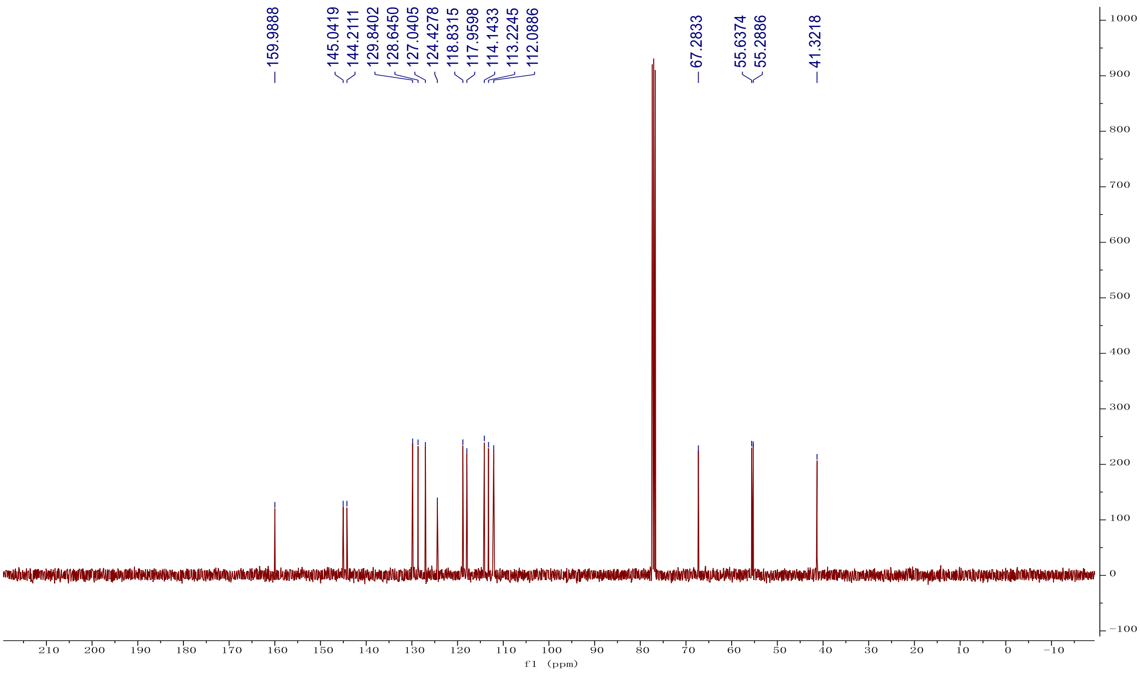
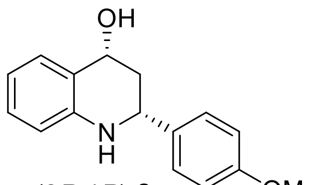


Figure S92 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2o** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2p**

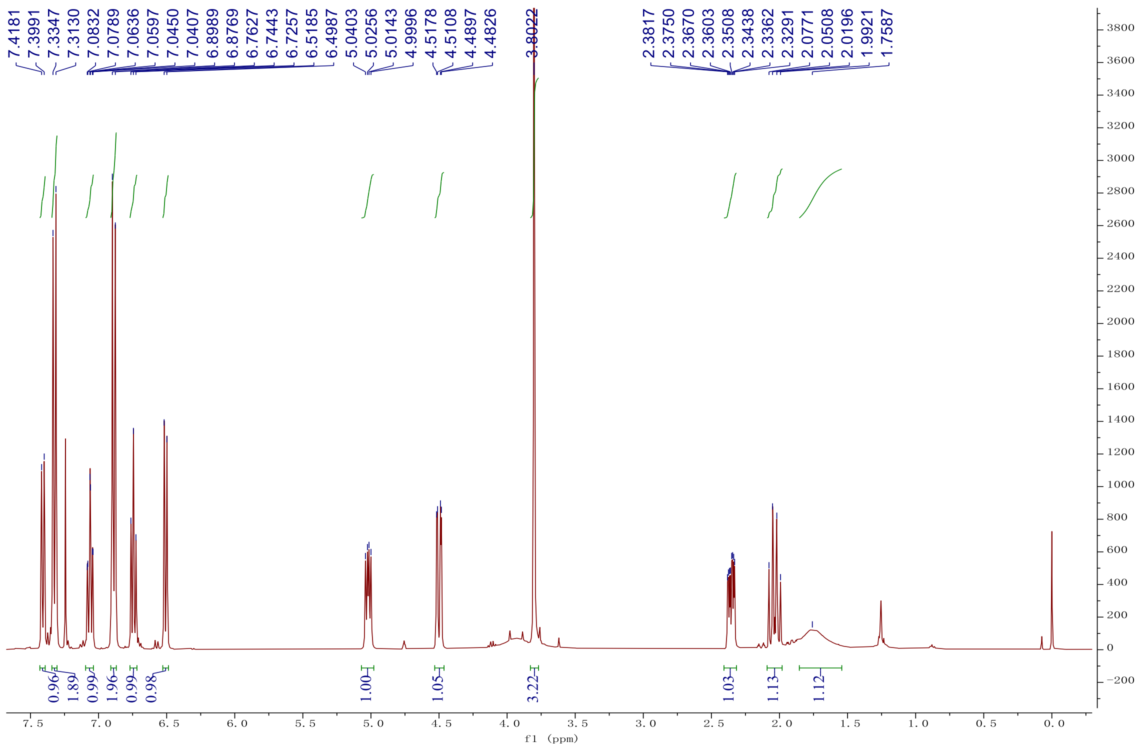


Figure S93 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2p** (400 MHz, $CDCl_3$)

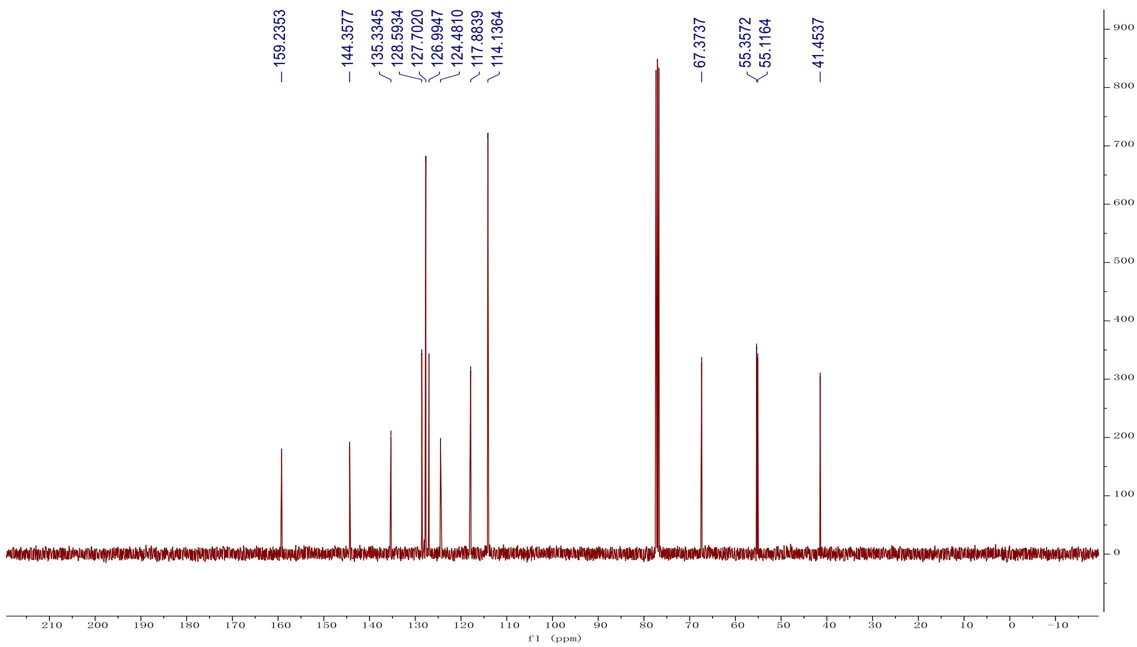
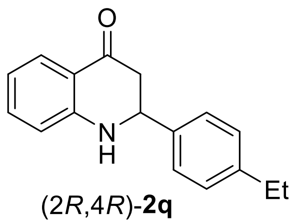


Figure S94 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2p** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2q**

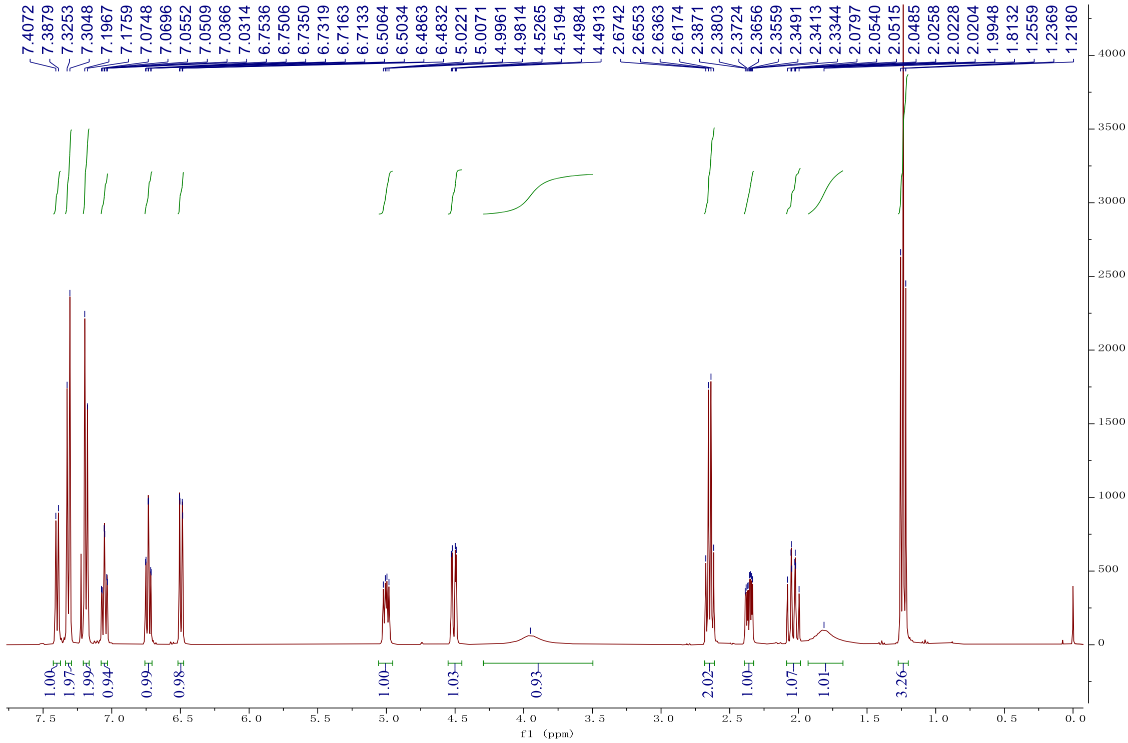


Figure S95 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2q** (400 MHz, $CDCl_3$)

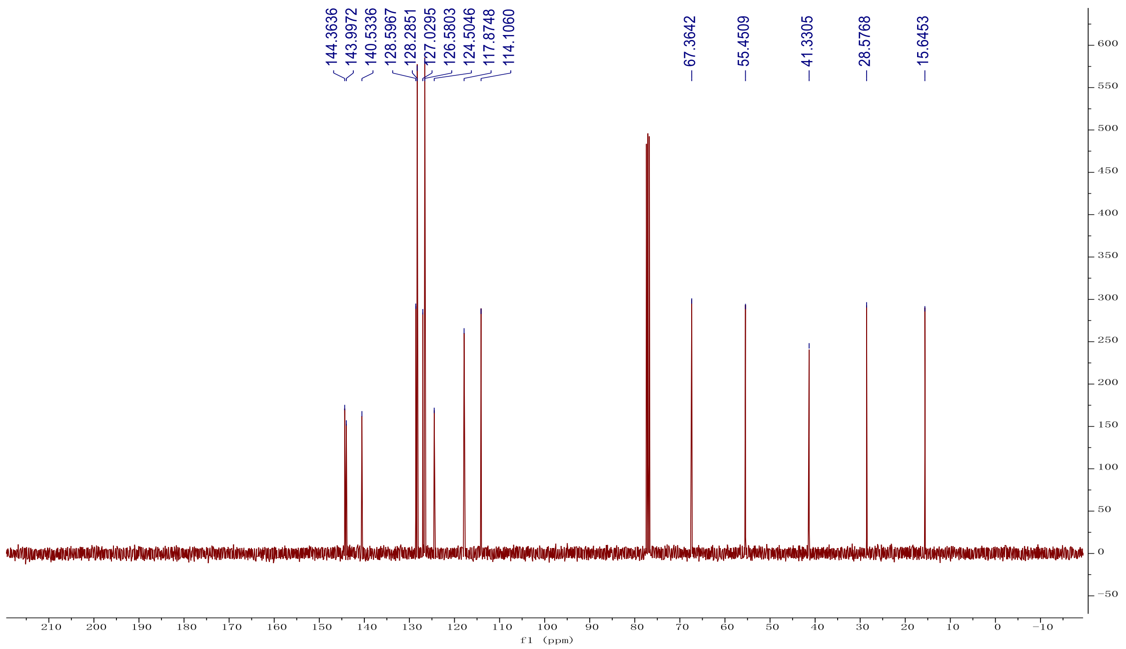
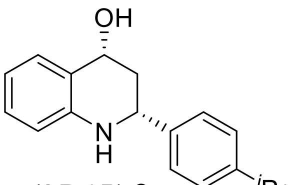


Figure S96 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2q** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2r**

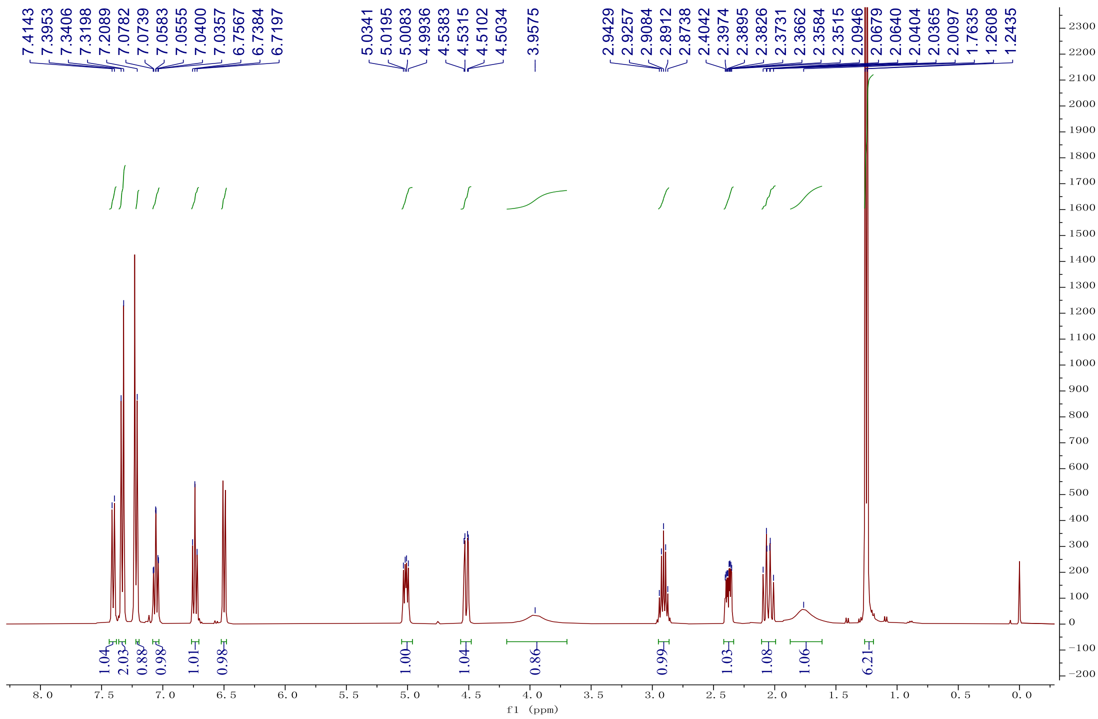


Figure S97 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2r** (400 MHz, $CDCl_3$)

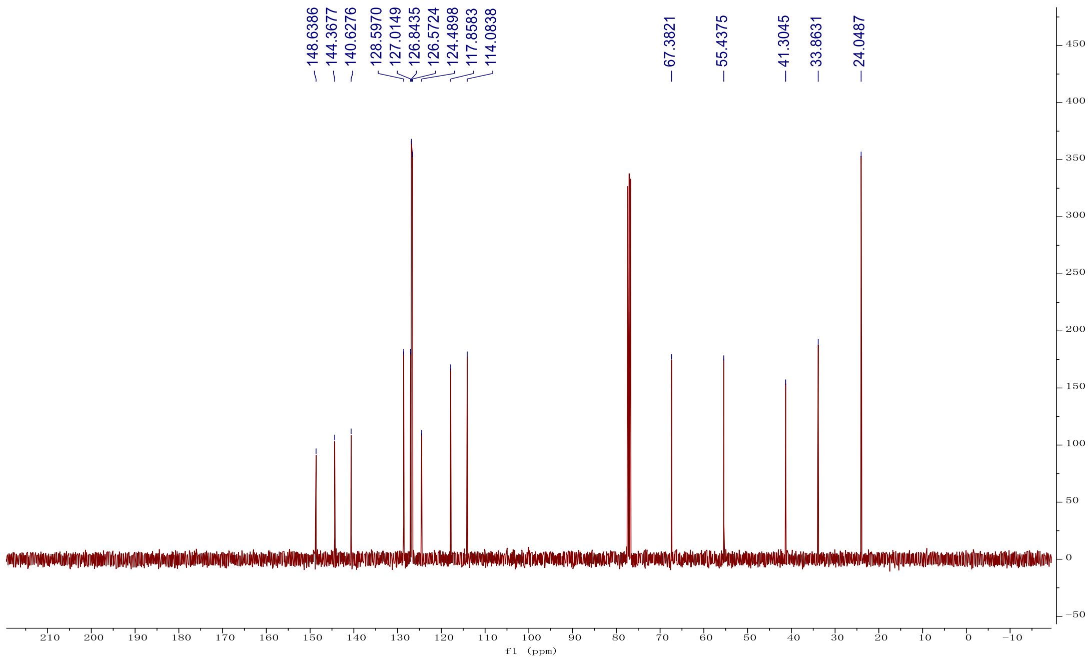


Figure S98 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2r** (100 MHz, $CDCl_3$)

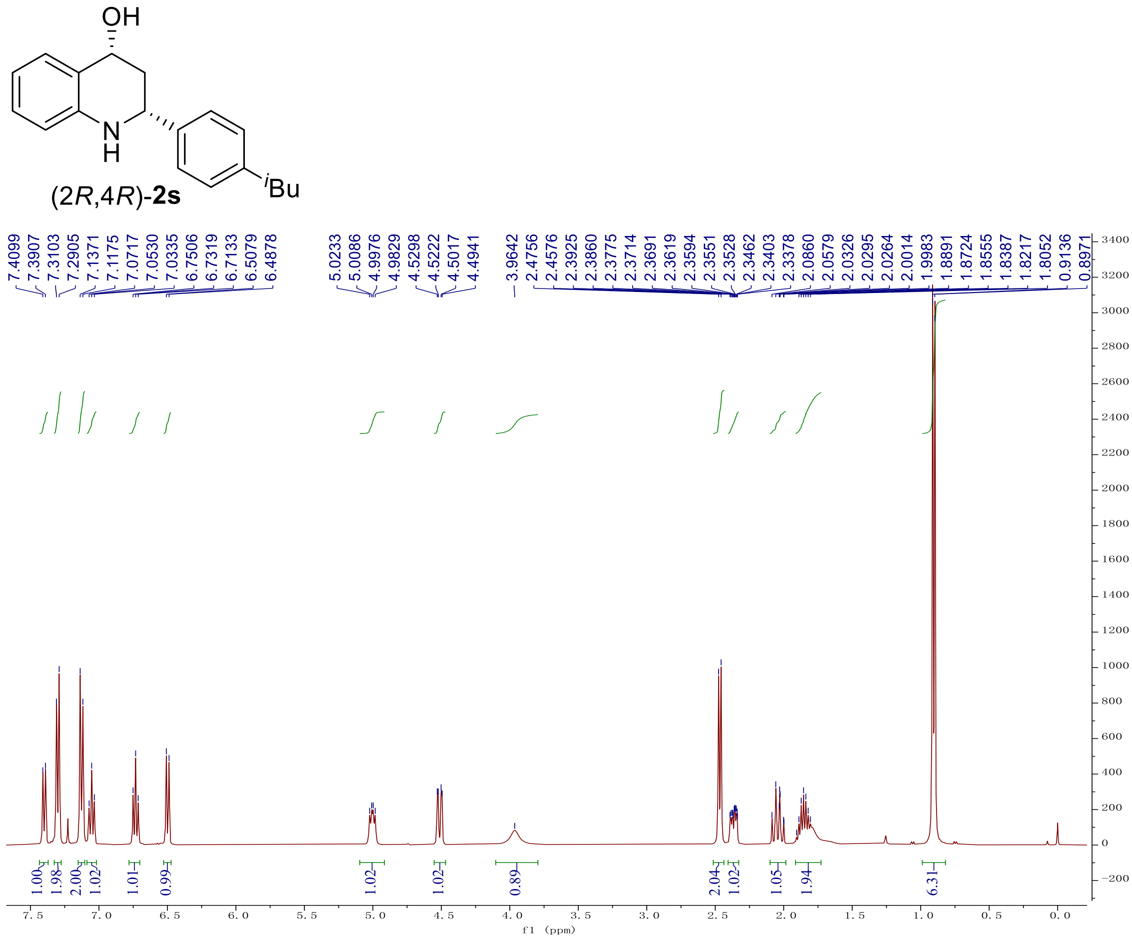


Figure S99 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2s** (400 MHz, $CDCl_3$)

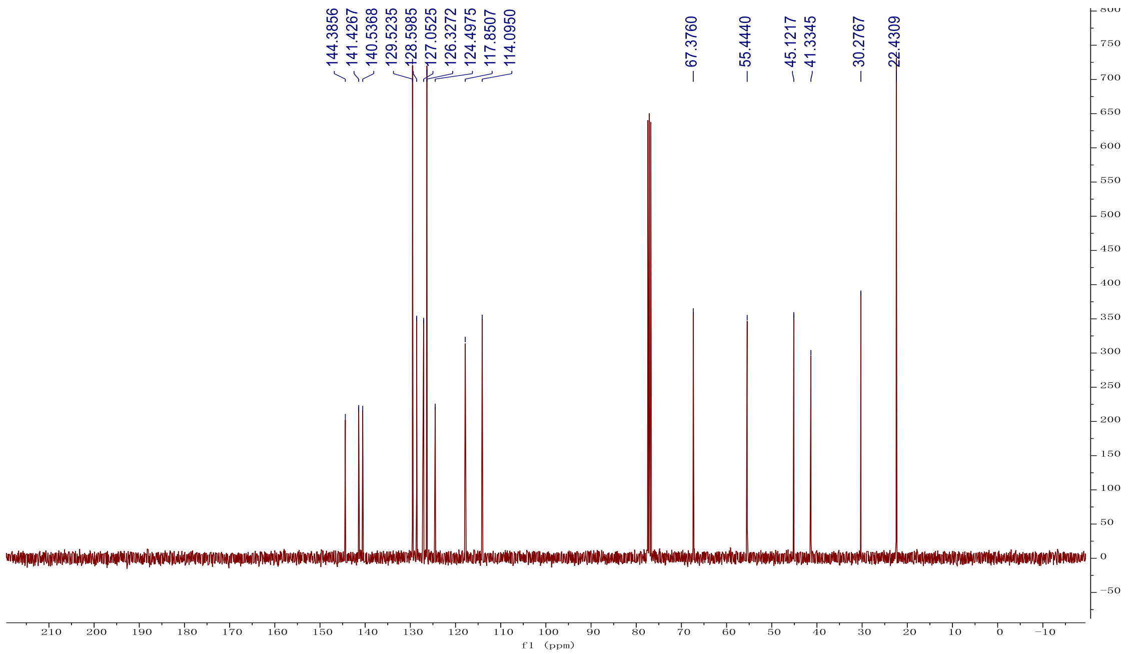
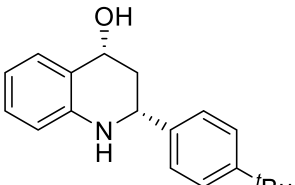


Figure S100 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2s** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2t**

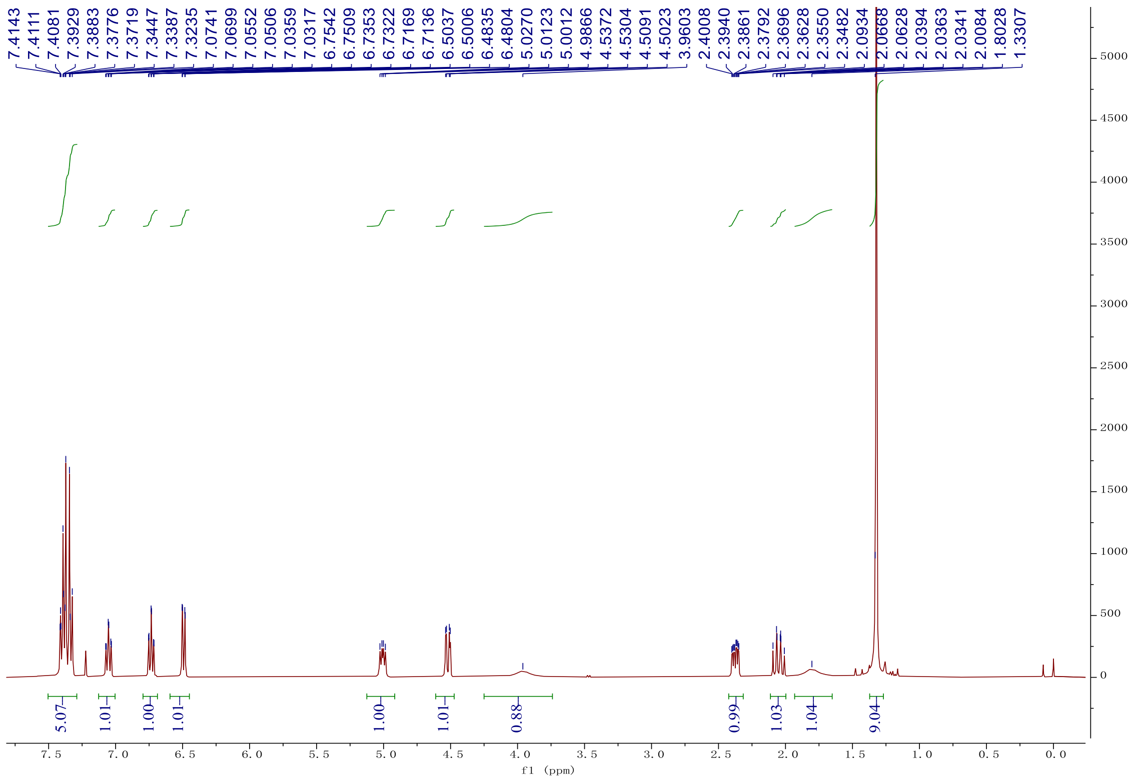


Figure S101 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2t** (400 MHz, $CDCl_3$)

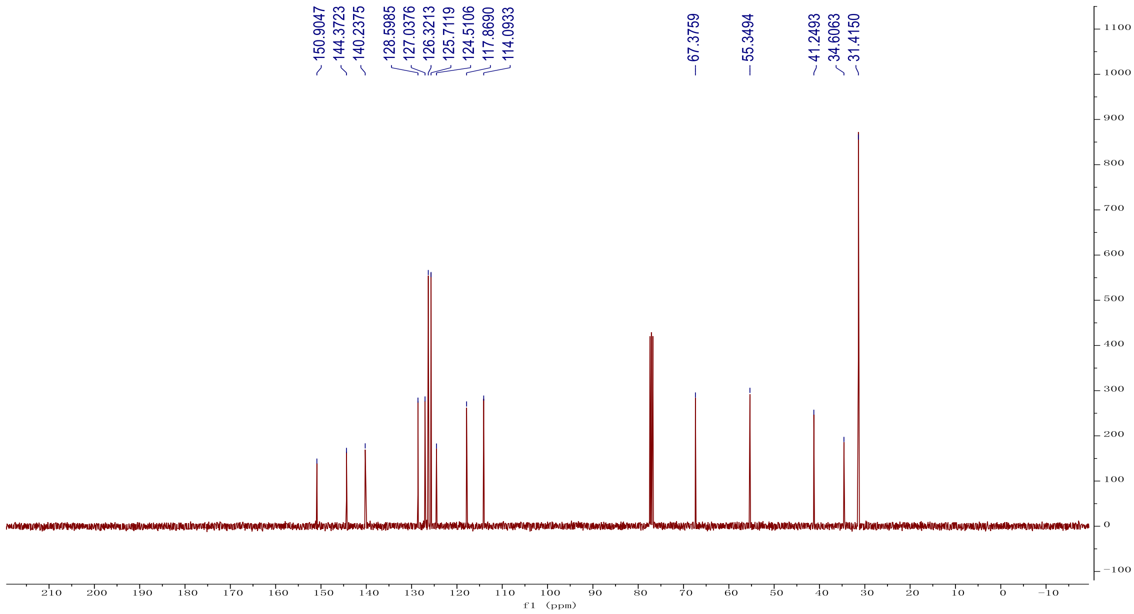
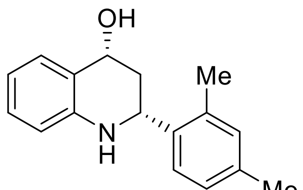


Figure S102 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2t** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2u**

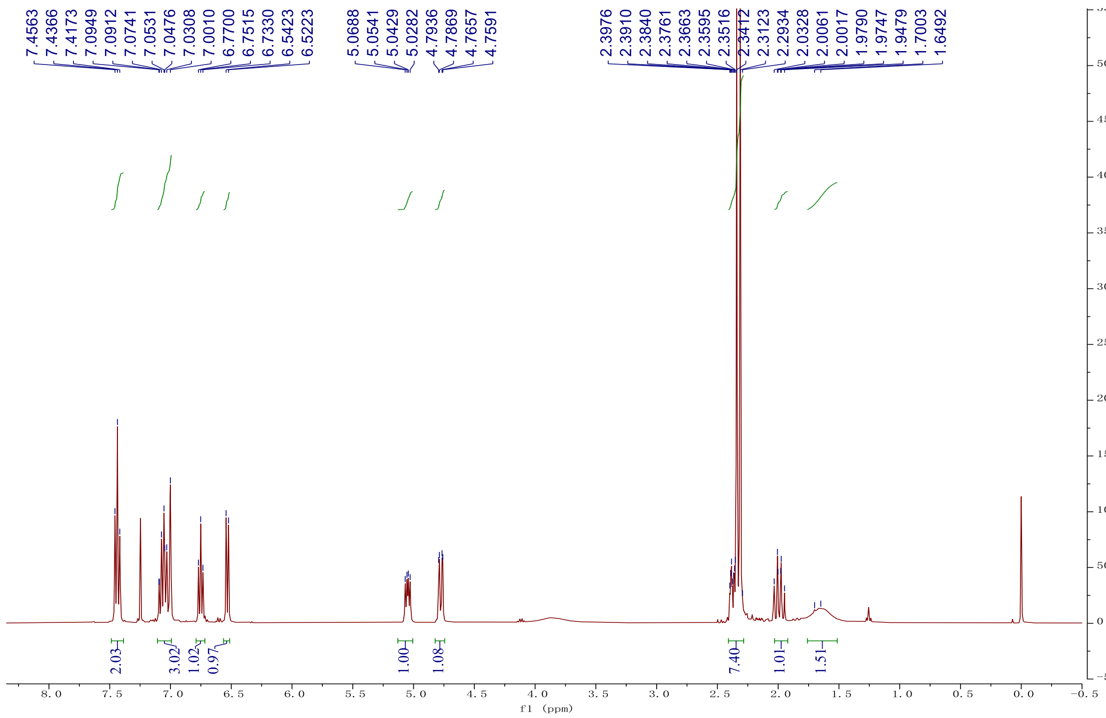


Figure S103 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2u** (400 MHz, $CDCl_3$)

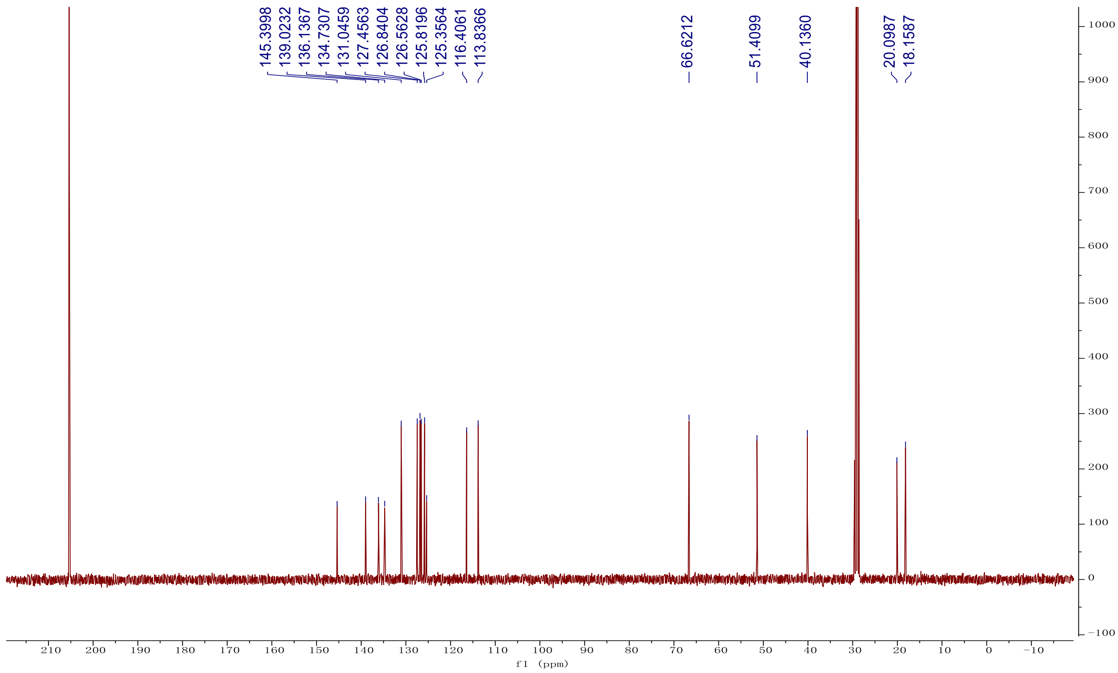
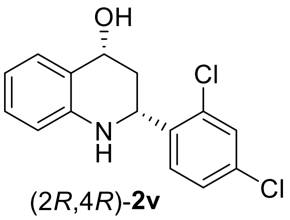


Figure S104 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2u** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2v**

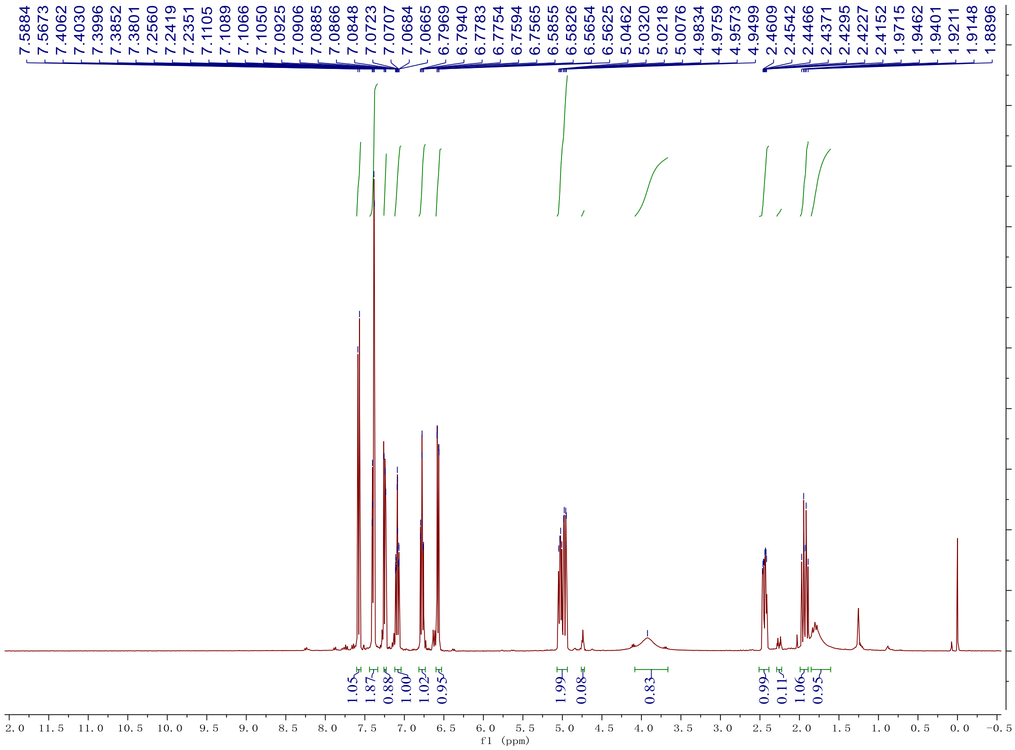


Figure S105 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2v** (400 MHz, $CDCl_3$)

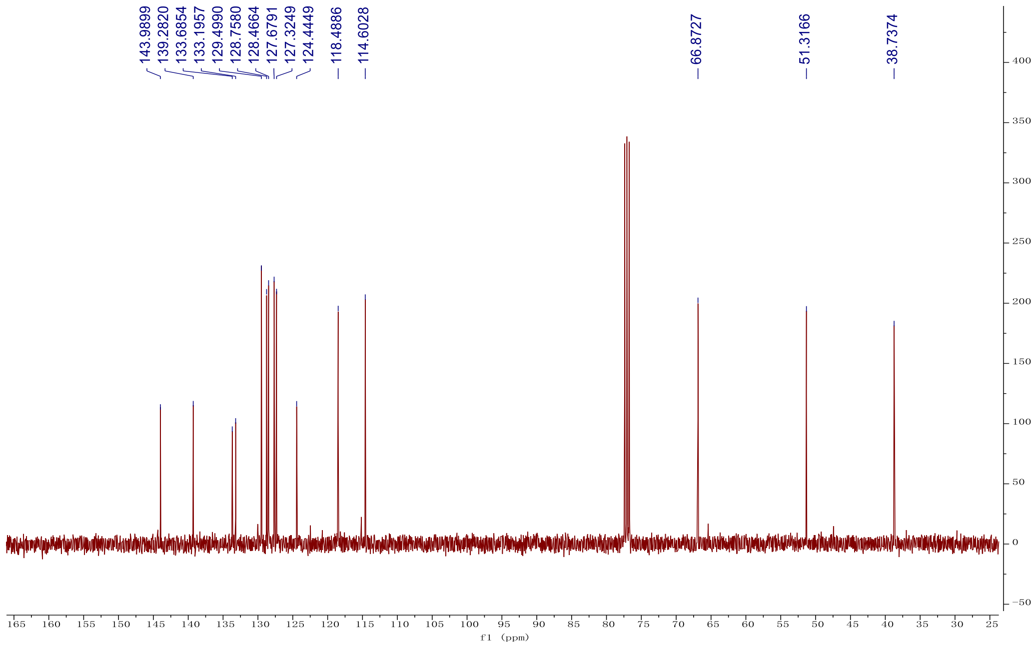
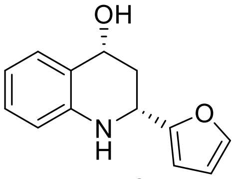


Figure S106 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2v** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2w**

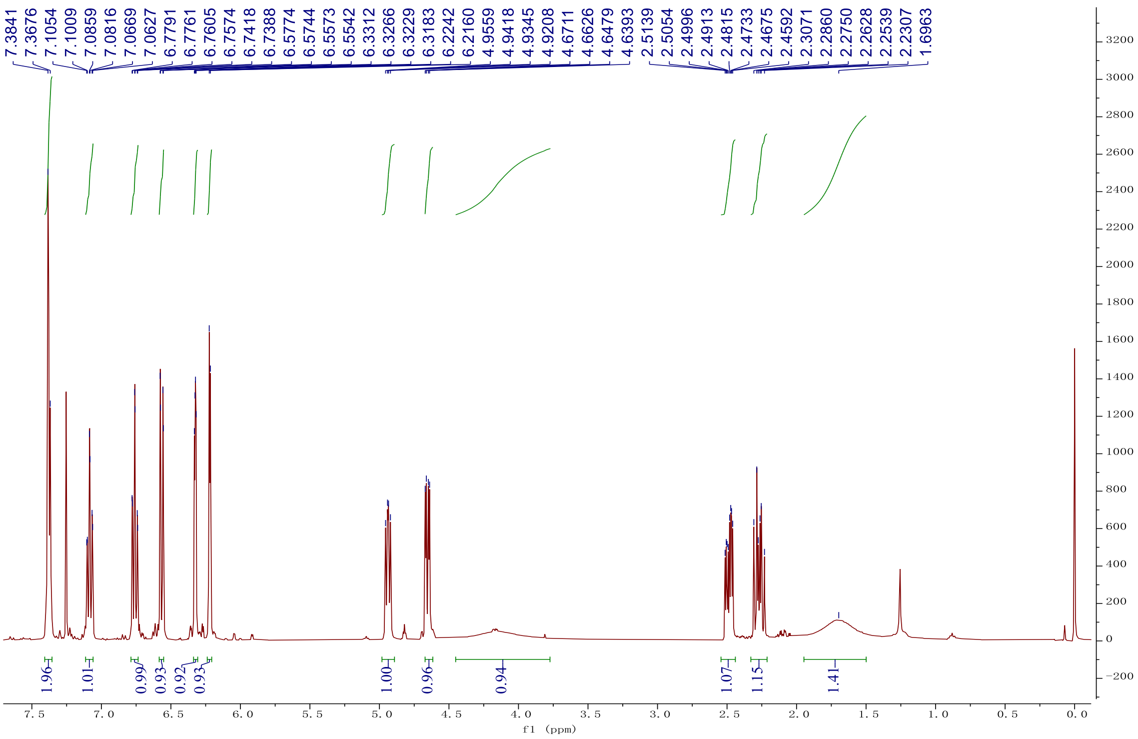


Figure S107 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2w** (400 MHz, $CDCl_3$)

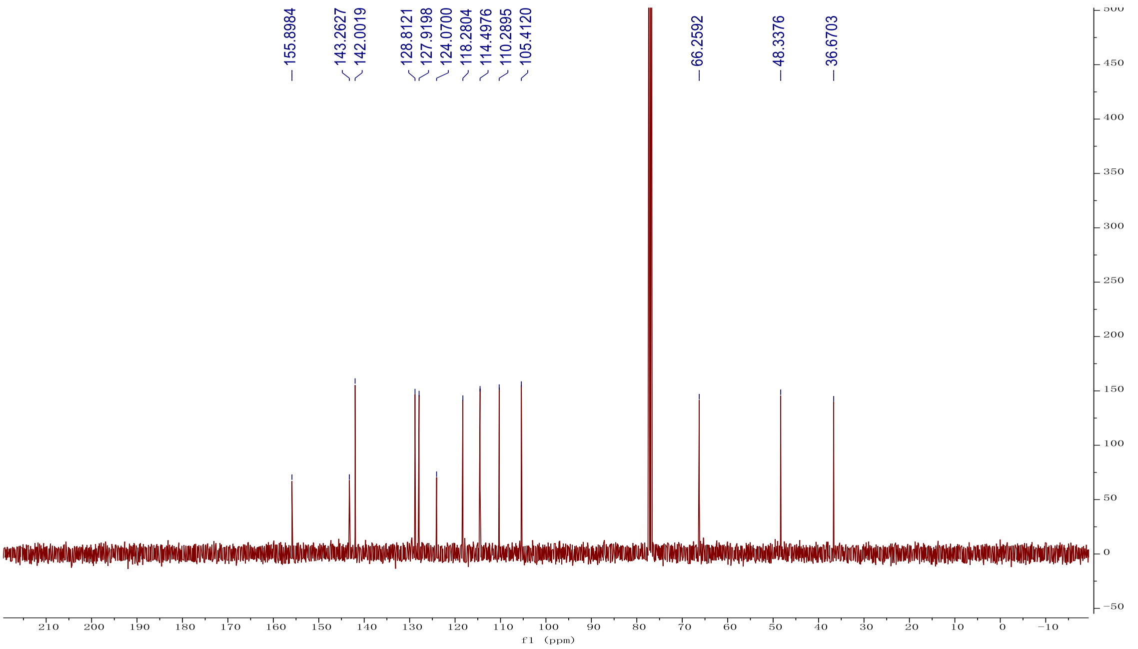
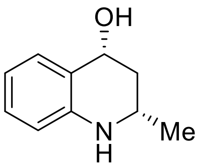


Figure S108 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2w** (100 MHz, $CDCl_3$)



(2*S*,4*R*)-**2x**

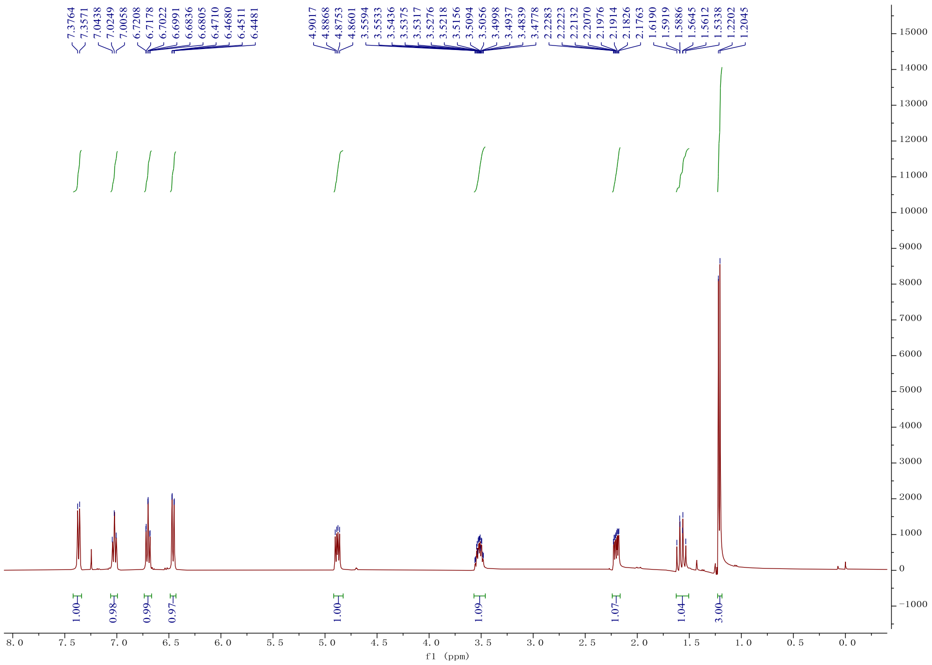


Figure S109 ^{1}H NMR Spectrum of (2*S*,4*R*)-**2x** (400 MHz, $CDCl_3$)

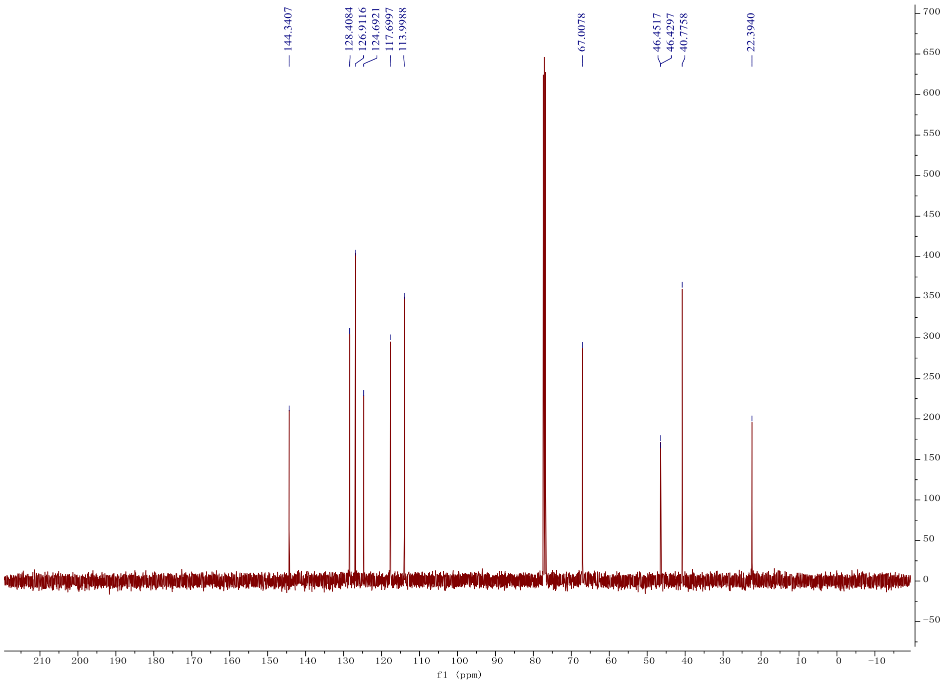
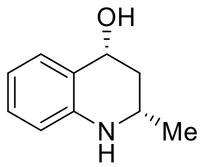


Figure S110 ^{13}C NMR Spectrum of (2*S*,4*R*)-**2x** (100 MHz, $CDCl_3$)



(2*S*,4*R*)-**2y**

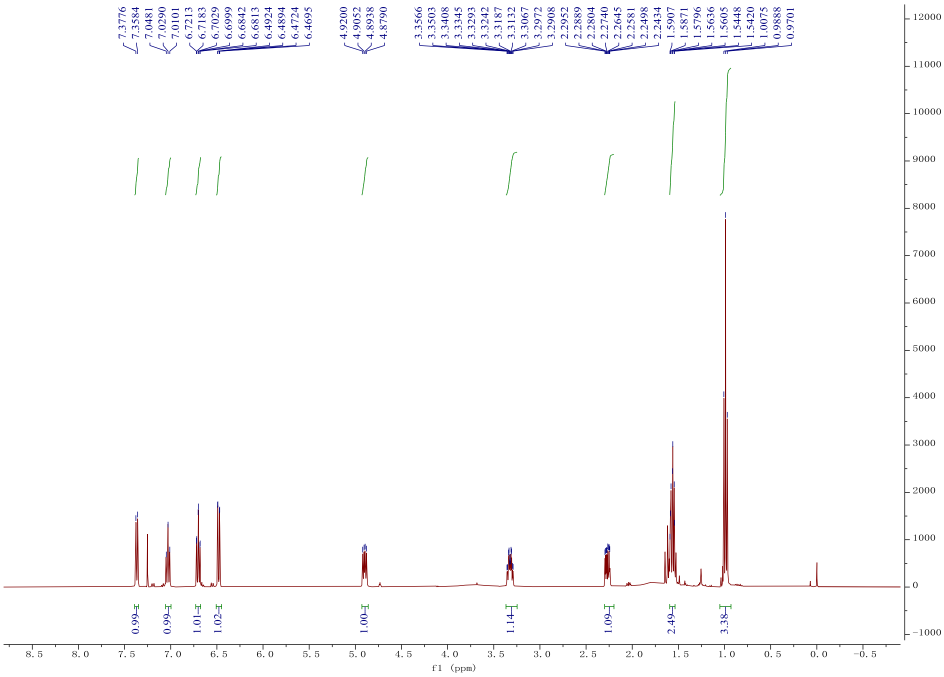


Figure S111 ^{1}H NMR Spectrum of (2*S*,4*R*)-**2y** (400 MHz, $CDCl_3$)

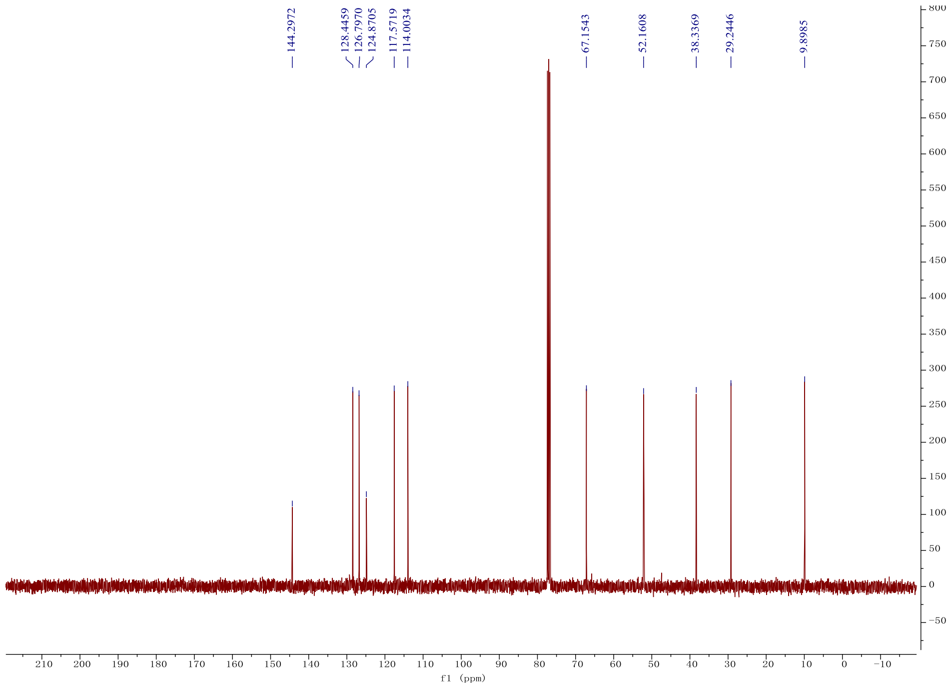
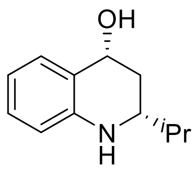


Figure S112 ^{13}C NMR Spectrum of (2*S*,4*R*)-**2y** (100 MHz, $CDCl_3$)



(2*R*,4*R*)-**2z**

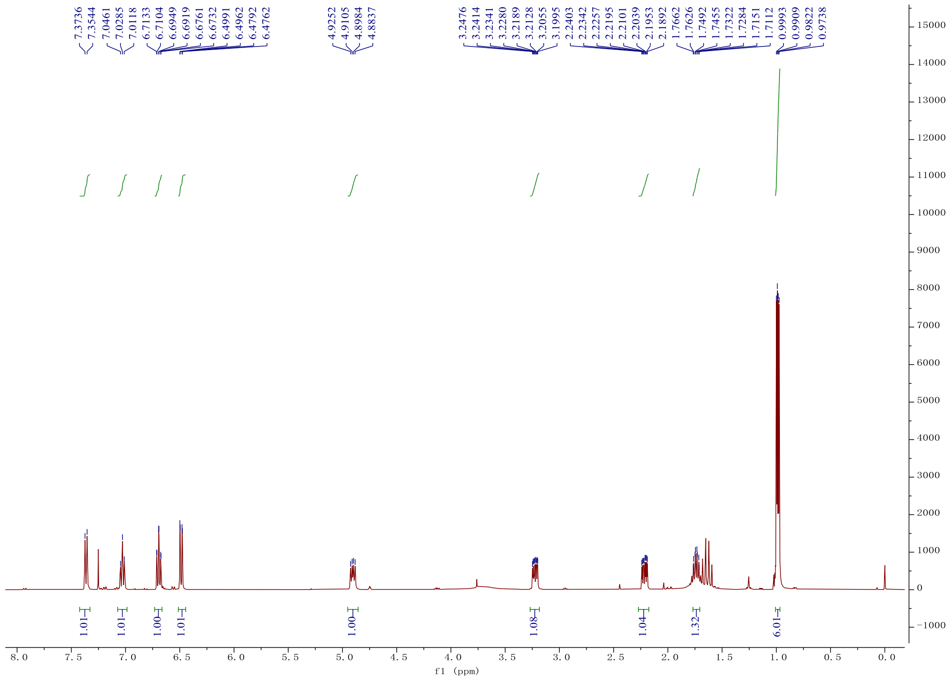


Figure S113 ^{1}H NMR Spectrum of (2*R*,4*R*)-**2z** (400 MHz, $CDCl_3$)

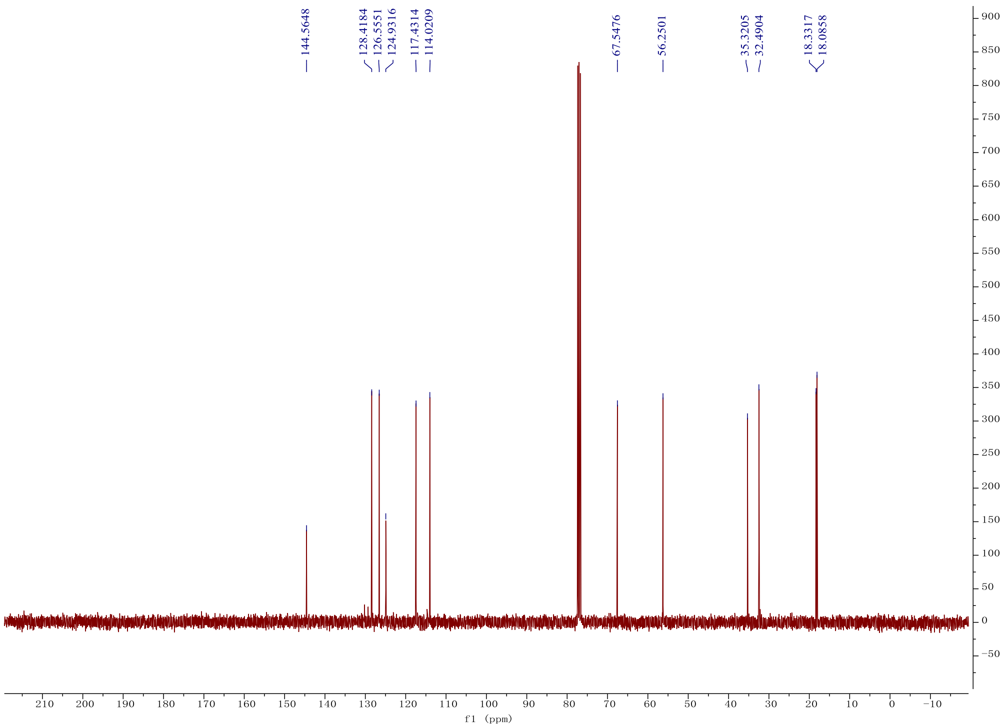
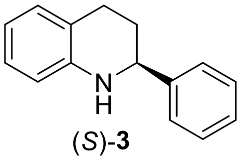


Figure S114 ^{13}C NMR Spectrum of (2*R*,4*R*)-**2z** (100 MHz, $CDCl_3$)



(*S*)-**3**

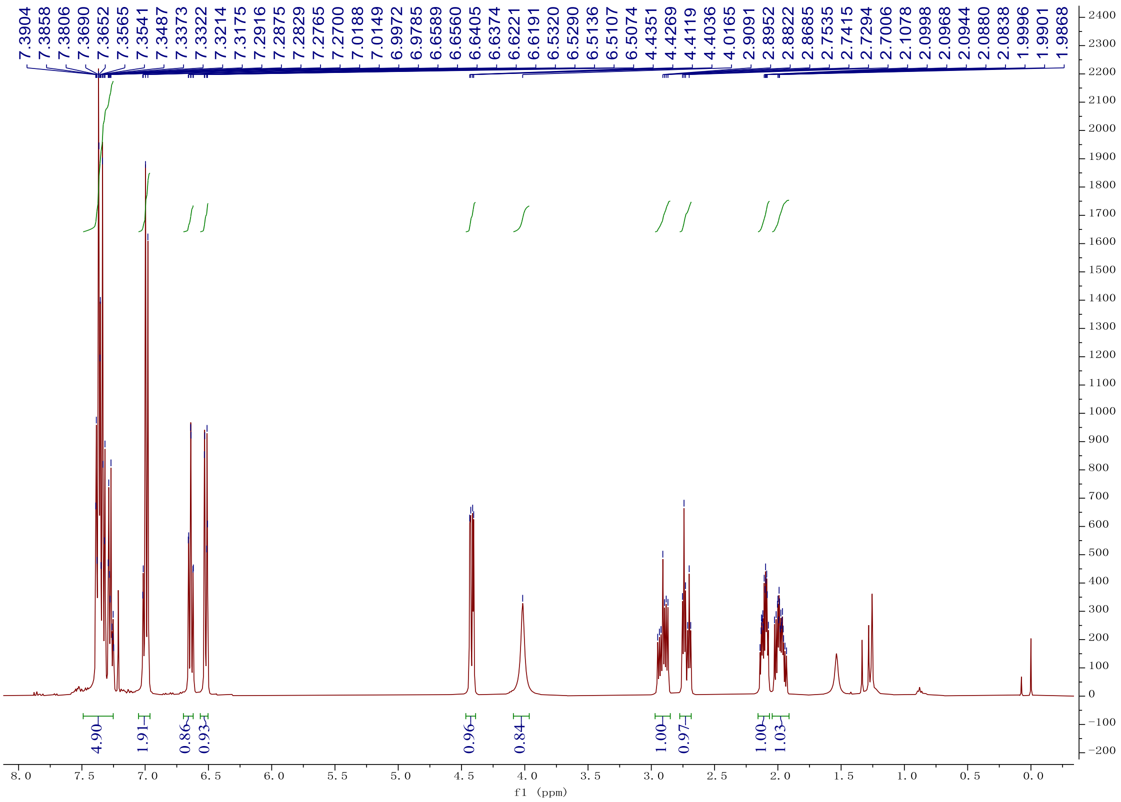


Figure S115 ^{1}H NMR Spectrum of (*S*)-**3** (400 MHz, $CDCl_3$)

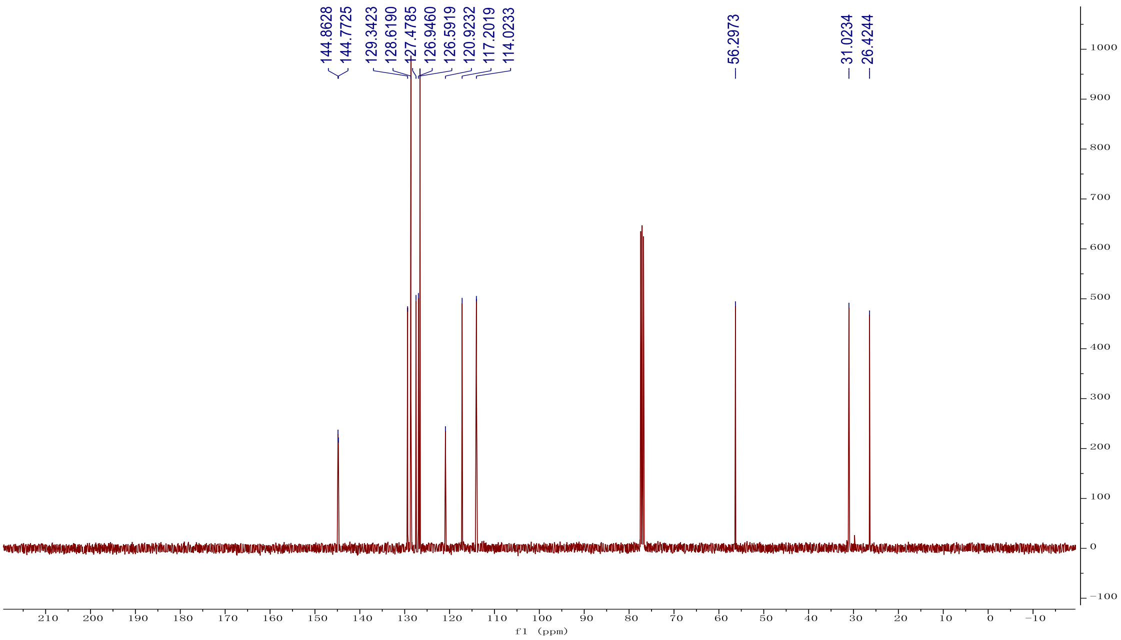
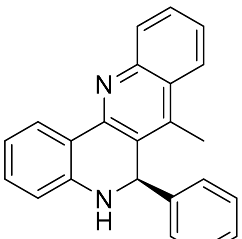


Figure S116 ^{13}C NMR Spectrum of (*S*)-**3** (100 MHz, $CDCl_3$)



(*S*)-**4**

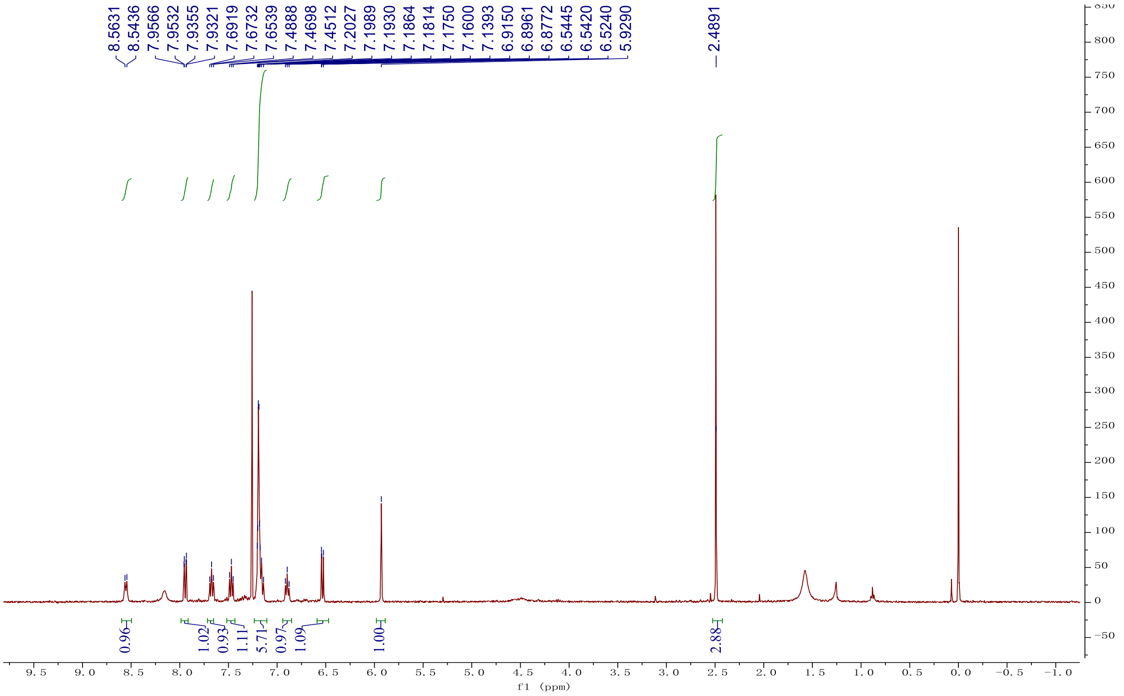


Figure S117 ^{1}H NMR Spectrum of (*S*)-**4** (400 MHz, $CDCl_3$)

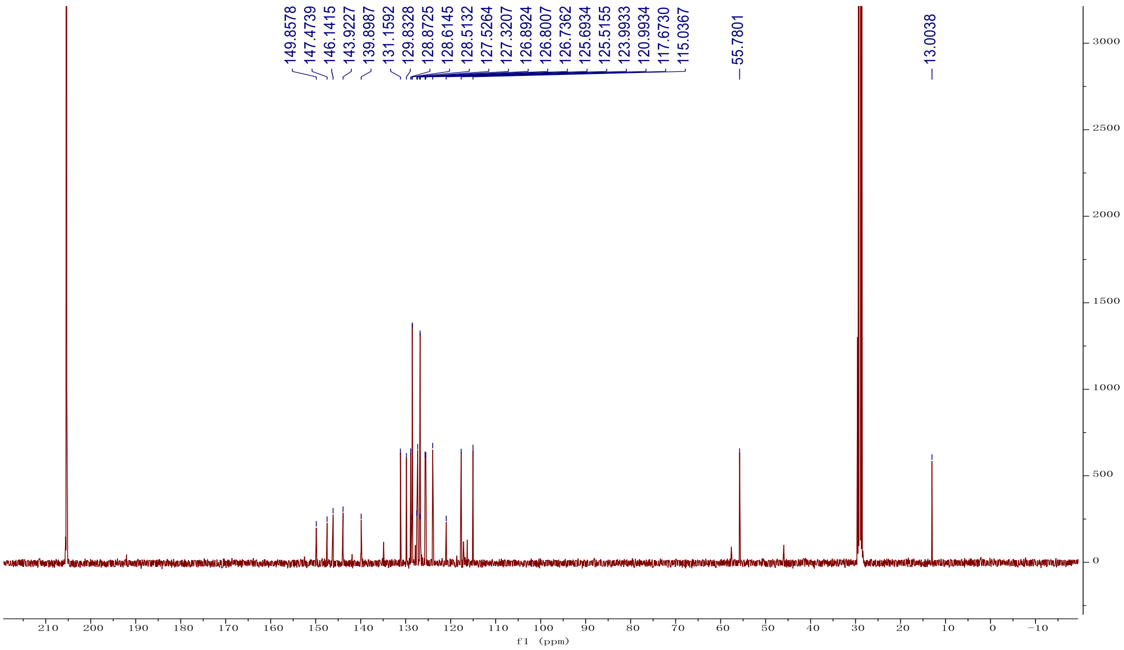
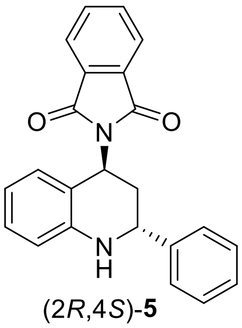


Figure S118 ^{13}C NMR Spectrum of (*S*)-**4** (100 MHz, $CDCl_3$)



(2*R*,4*S*)-**5**

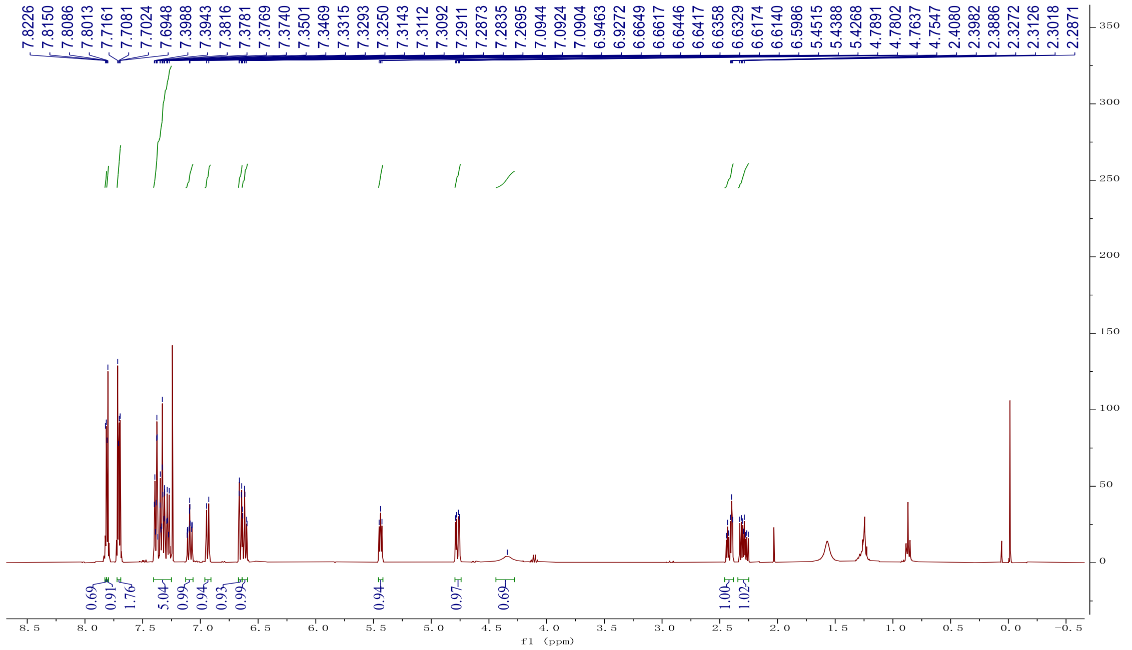


Figure S119 ^{1}H NMR Spectrum of (2*R*, 4*S*)-**5** (400 MHz, $CDCl_3$)

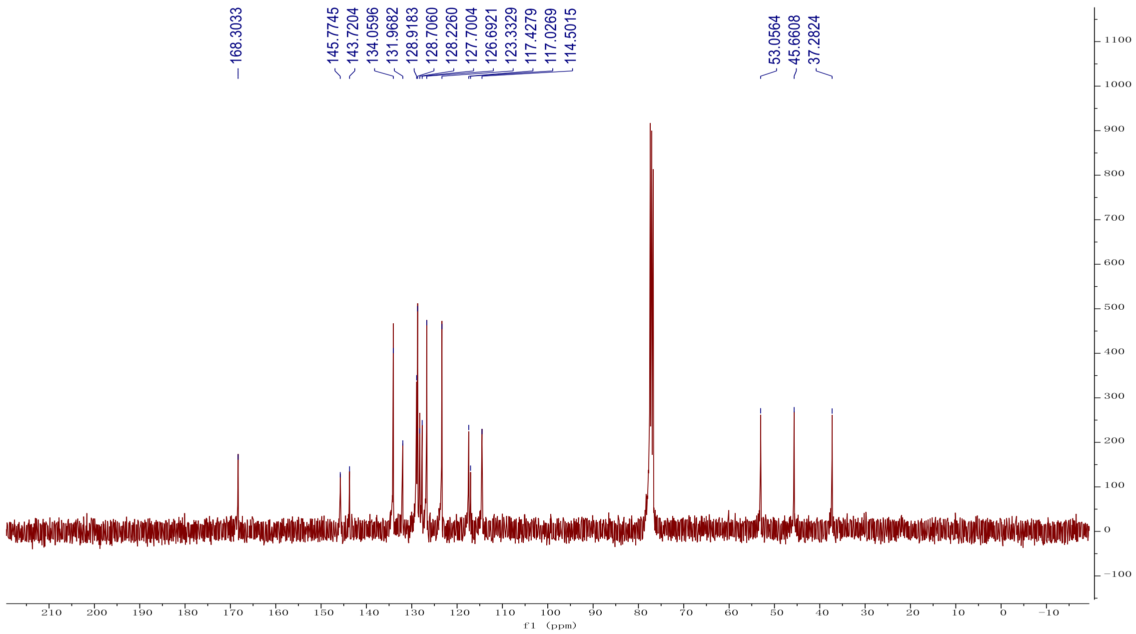
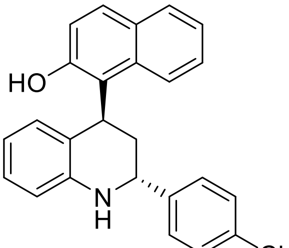


Figure S120 ^{13}C NMR Spectrum of (2*R*,4*S*)-**5** (100 MHz, $CDCl_3$)



(2*R*,4*S*)-**6**

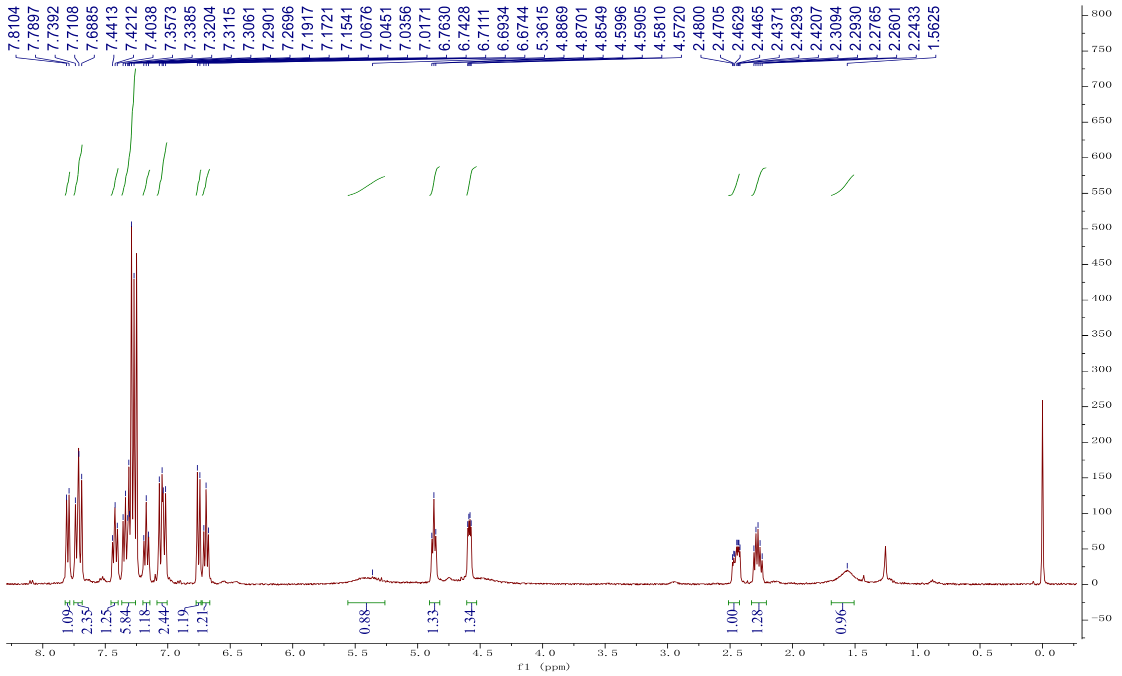


Figure S121 ^{1}H NMR Spectrum of (2*R*,4*S*)-**6** (400 MHz, $CDCl_3$)

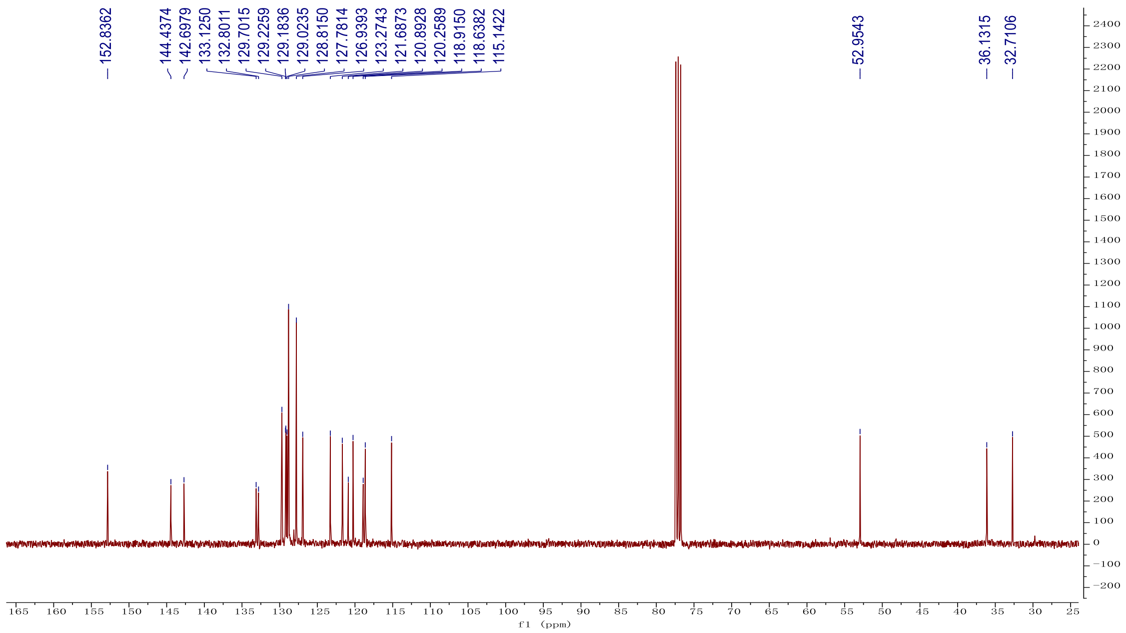
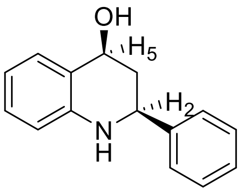
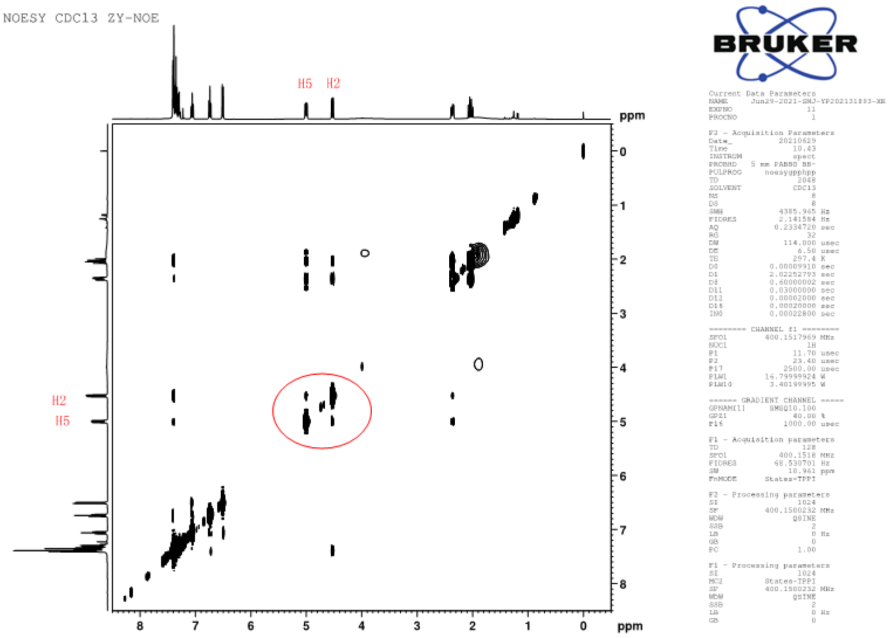


Figure S122 ^{13}C NMR Spectrum of (2*R*,4*S*)-**6** (100 MHz, $CDCl_3$)



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



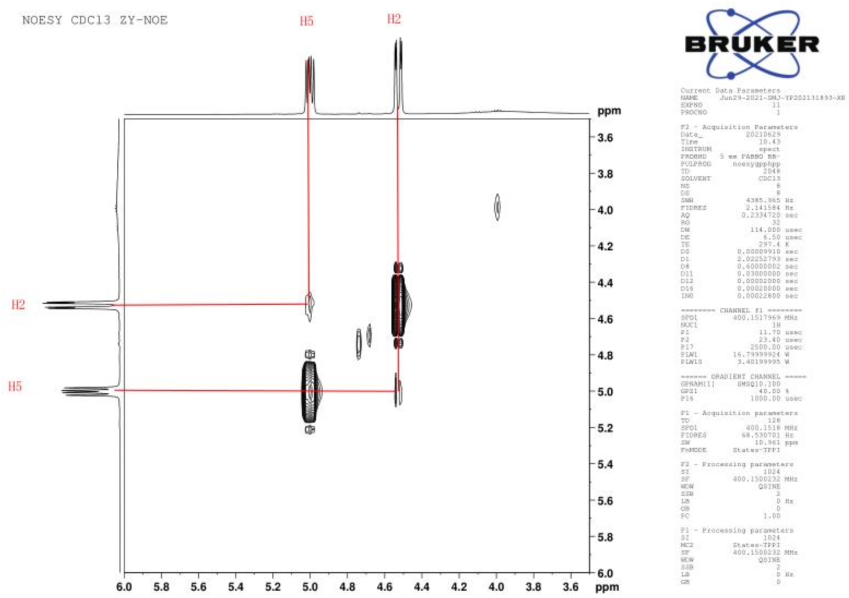
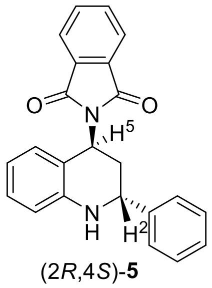
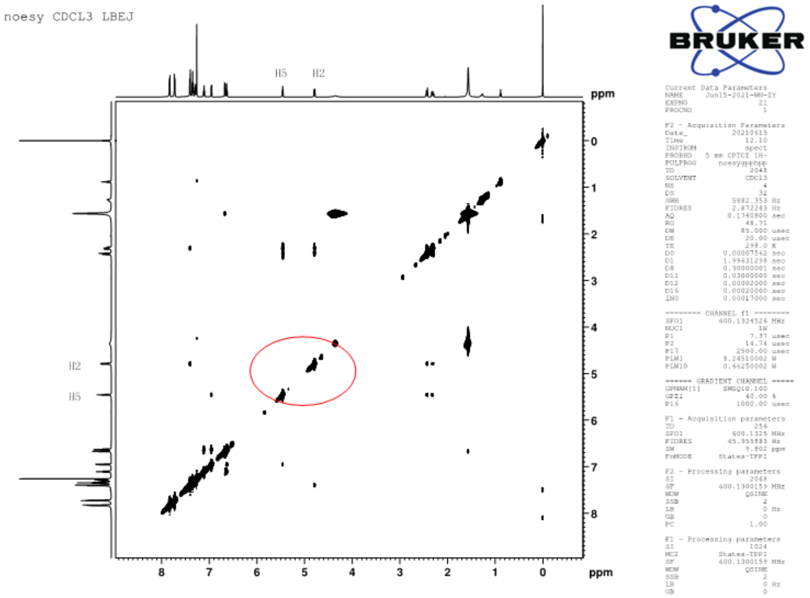


Figure S123 NOESY analysis of (*S*, *S*)-**2a**

From the NOESY spectrum of (*S*,*S*)-**2a**, it shows that H^2 has interactions to the H^5. We have confirmed the carbon connected with H^2 possess the *S*-configuration so that we can indicate the carbon links with H^5 possess the *S*-configuration.



(2*R*,4*S*)-**5**



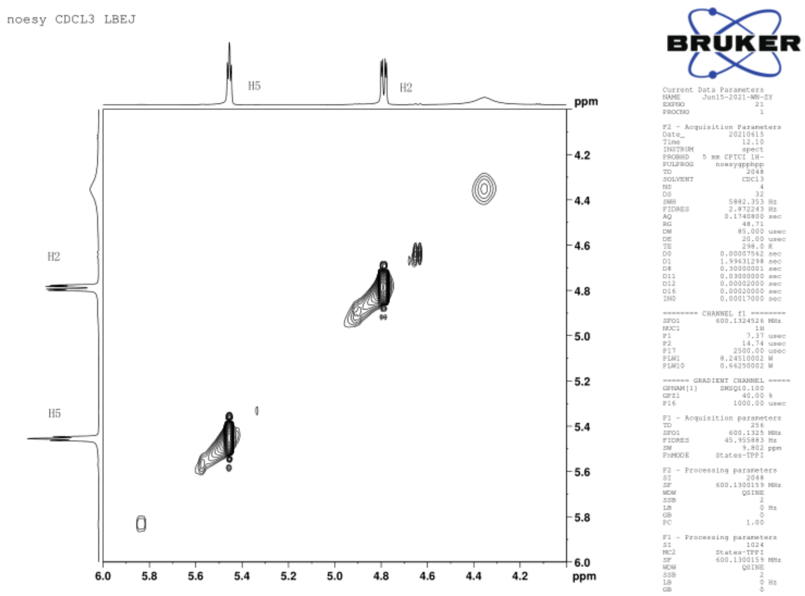
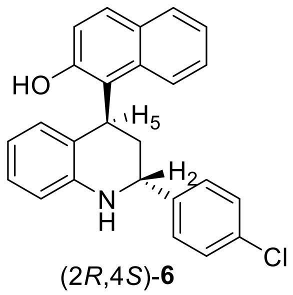
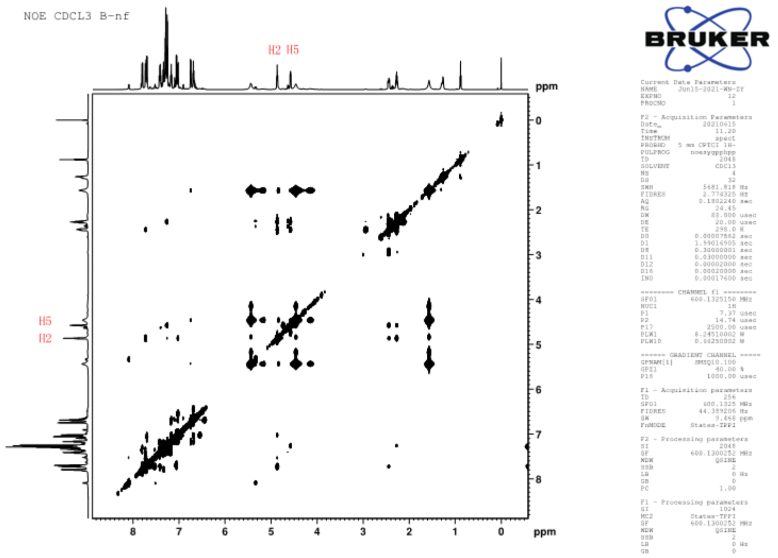


Figure S124 NOESY analysis of (2*R*, 4*S*)-**5**

From the NOESY spectrum of (2*R*,4*S*)-**5**, it shows that H^2 has no interactions to the H^5. We have confirmed the carbon connected with H^2 possess the *R*-configuration so that we can indicate the carbon links with H^5 possess the *S*-configuration.



(2*R*,4*S*)-**6**



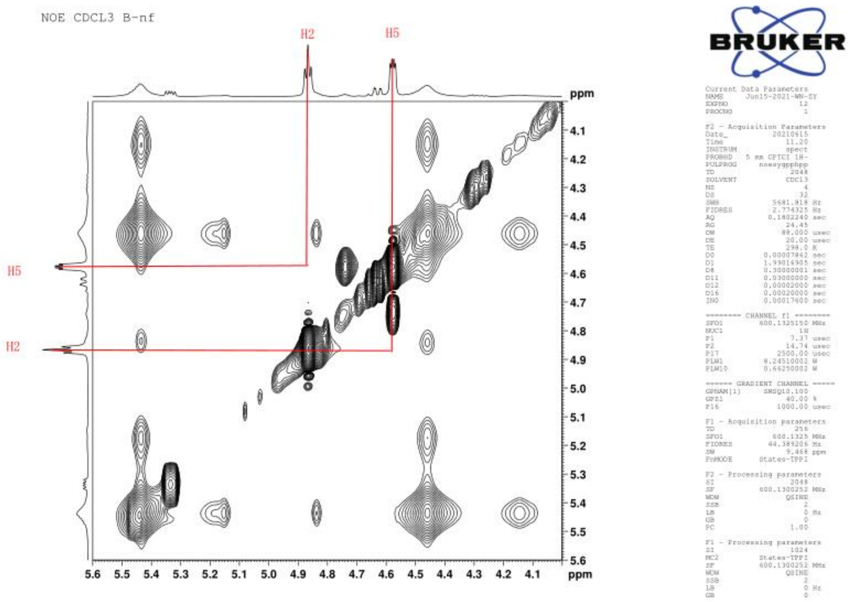
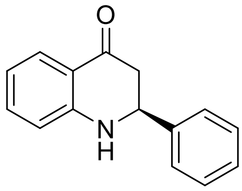


Figure S125 NOESY analysis of (2*R*, 4*S*)-**6**

From the NOESY spectrum of (2*R*,4*S*)-**6**, it shows that H^2 has no interactions to the H^5. We have confirmed the carbon connected with H^2 possess the *R*-configuration so that we can indicate the carbon links with H^5 possess the *S*-configuration.

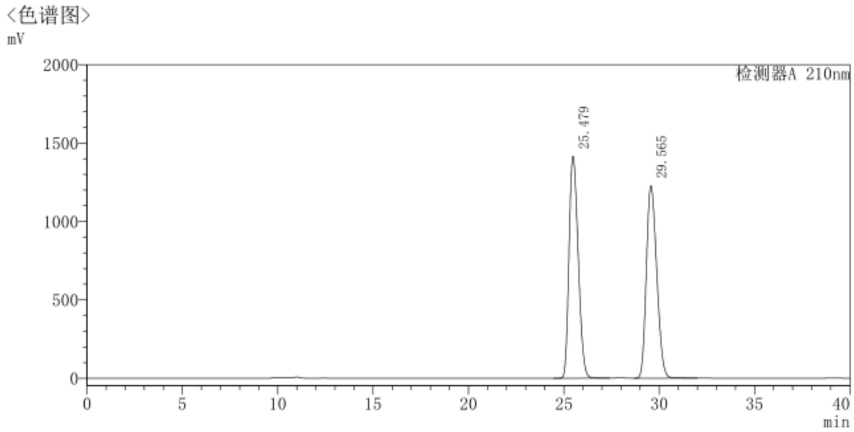
8. HPLC Data



(*S*)-**1a**

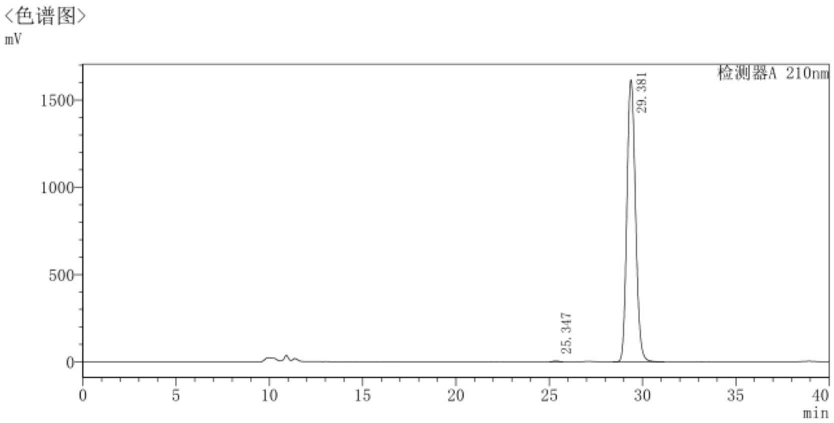
99.6% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



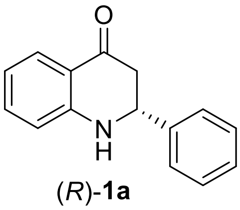
	Retention Time (min)	Area (%)
Peak 1	25.479	50.374
Peak 2	29.565	49.626

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	25.347	0.181	**99.6% ee**
Peak 2	29.381	99.819	

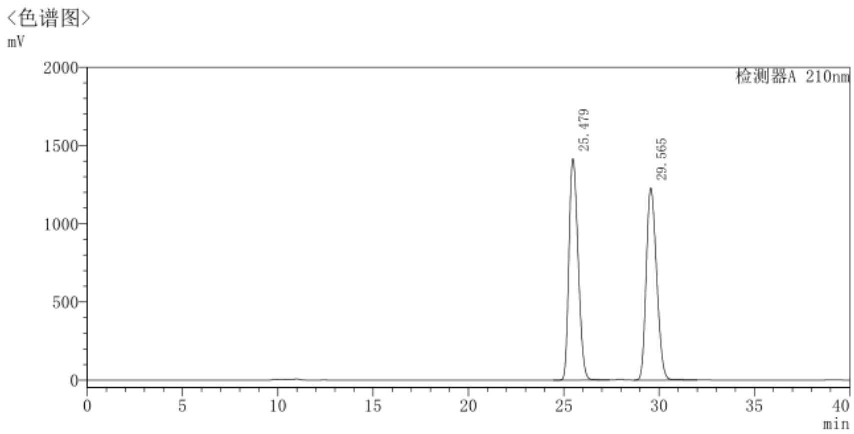
Figure S126 HPLC Data of (*S*)-**1a**



(*R*)-**1a**

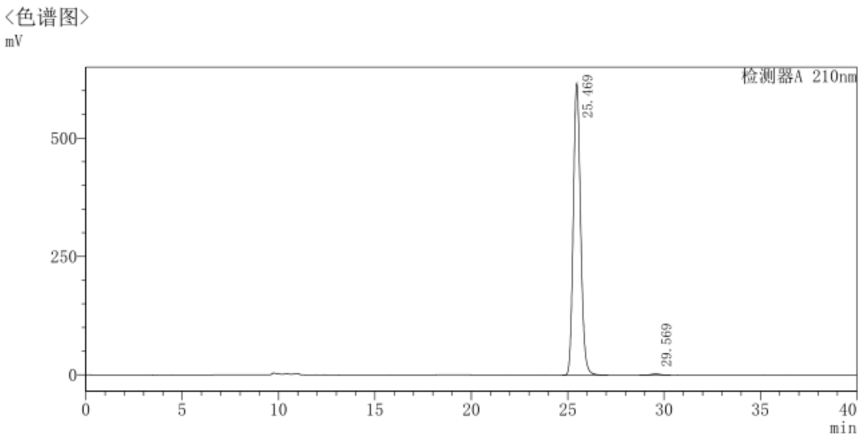
99.1% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-h column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



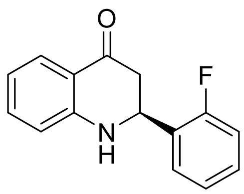
	Retention Time (min)	Area (%)
Peak 1	25.479	50.374
Peak 2	29.565	49.626

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	25.469	99.558	**99.1% ee**
Peak 2	29.569	0.442	

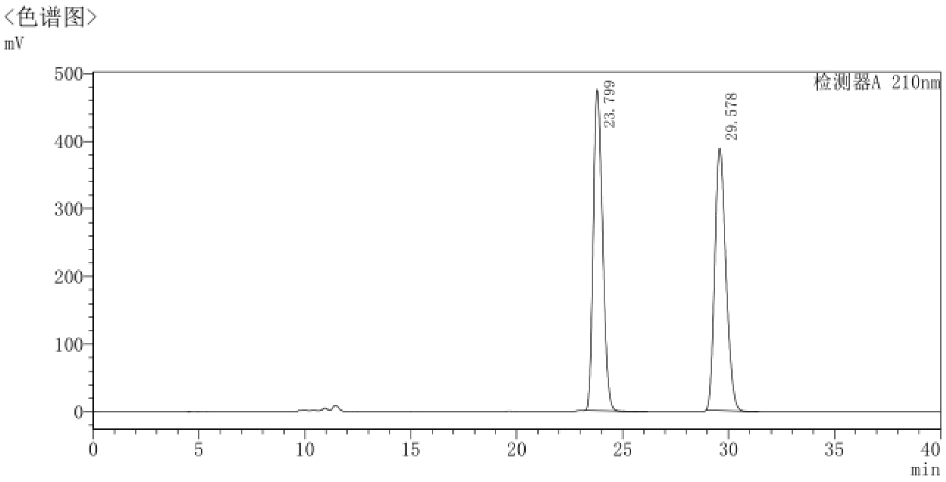
Figure S127 HPLC Data of (*R*)-**1a**



(*S*)-**1b**

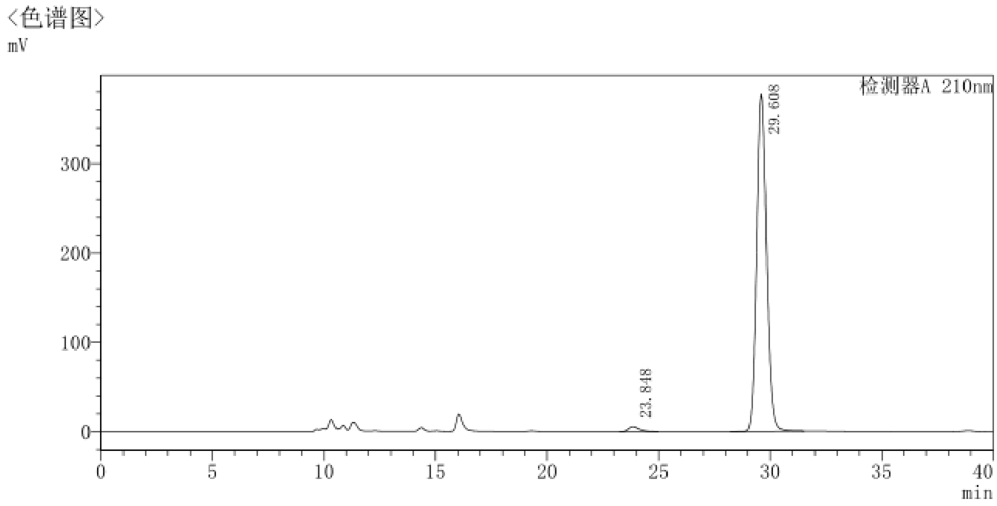
97% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



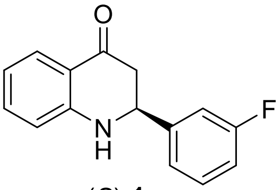
	Retention Time (min)	Area (%)
Peak 1	23.799	50.069
Peak 2	29.578	49.931

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	23.848	1.531	**97% ee**
Peak 2	29.608	98.469	

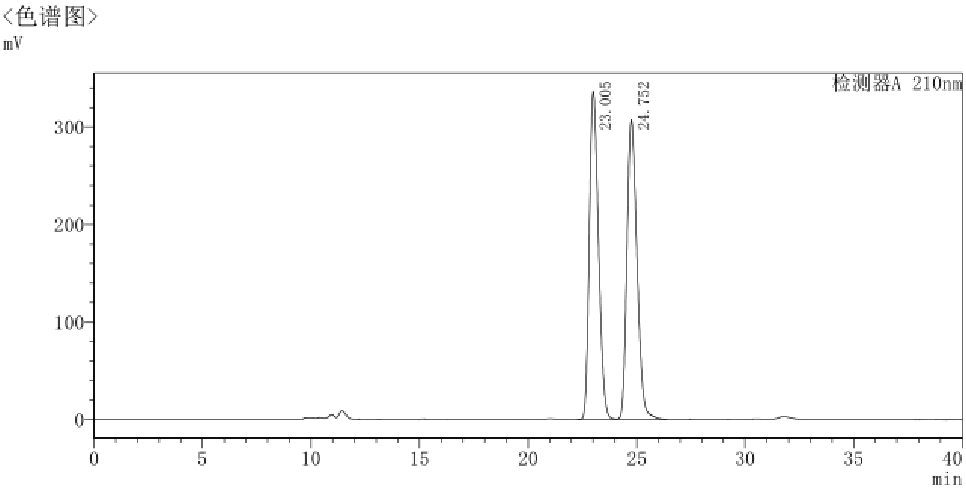
Figure S128 HPLC Data of (*S*)-**1b**



(*S*)-**1c**

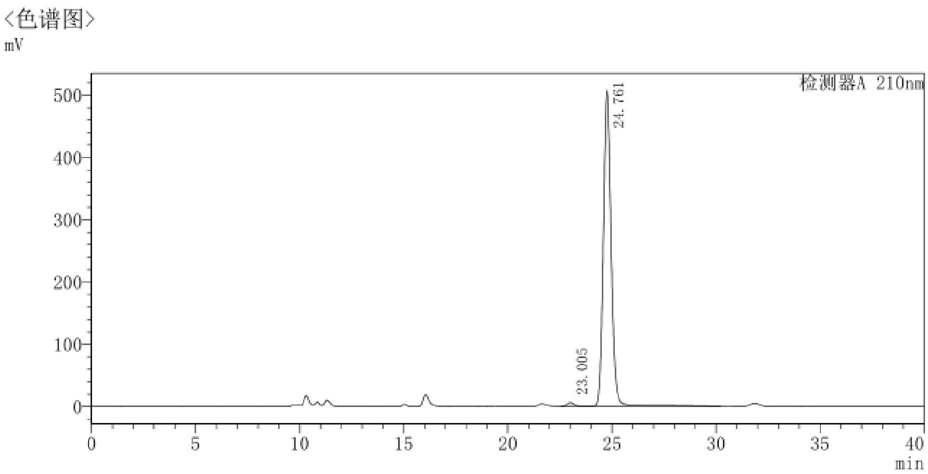
98% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



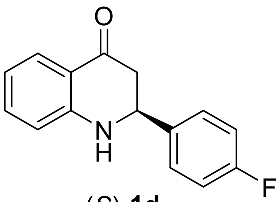
	Retention Time (min)	Area (%)
Peak 1	23.005	50.347
Peak 2	24.752	49.653

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	23.005	1.028	**98% ee**
Peak 2	24.761	98.972	

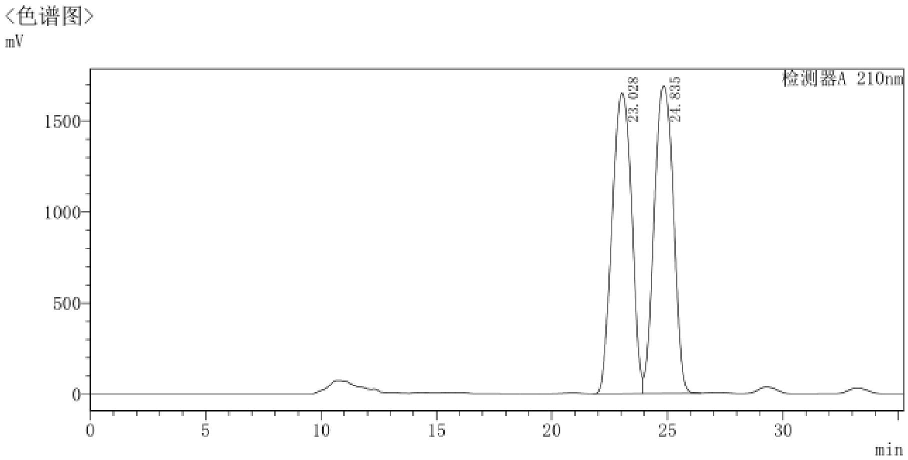
Figure S129 HPLC Data of (*S*)-**1c**



(*S*)-**1d**

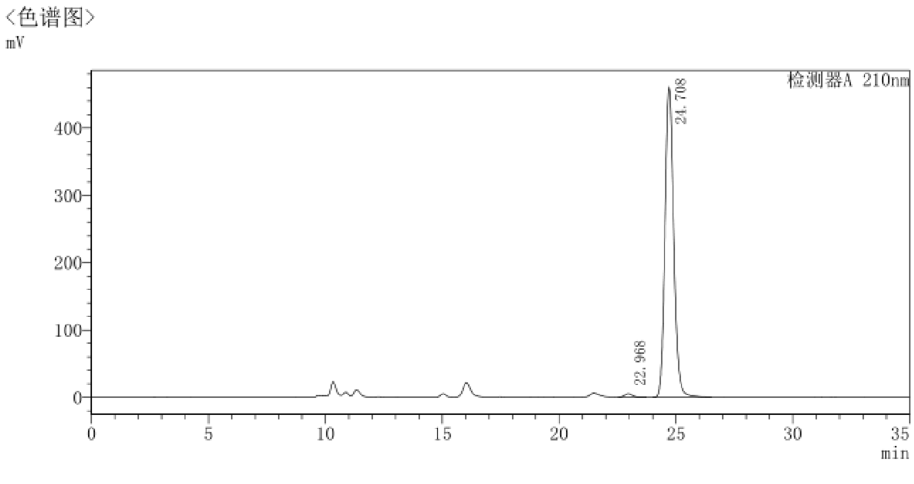
98% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



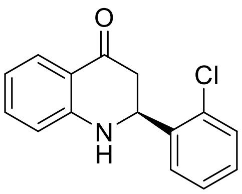
	Retention Time (min)	Area (%)
Peak 1	23.028	49.748
Peak 2	24.835	50.252

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	22.968	1.057	**98% ee**
Peak 2	24.708	98.943	

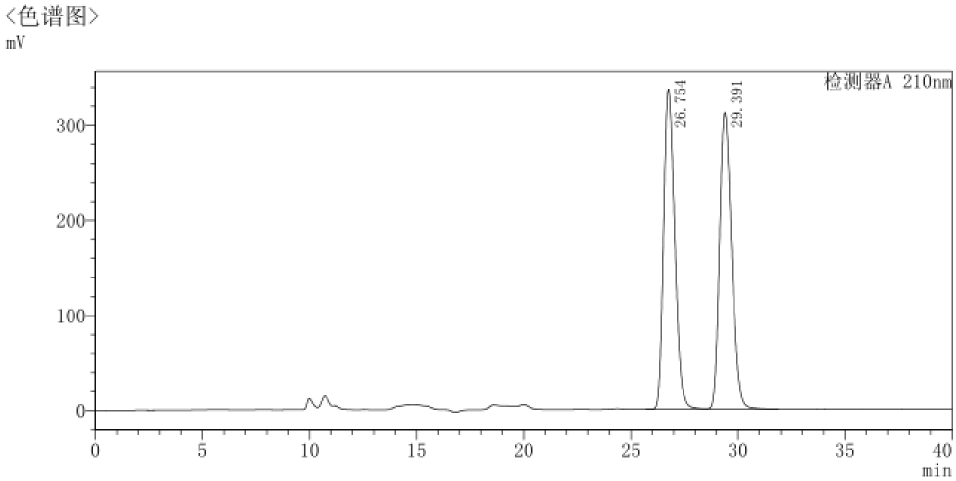
Figure S130 HPLC Data of (*S*)-**1d**



(*S*)-**1e**

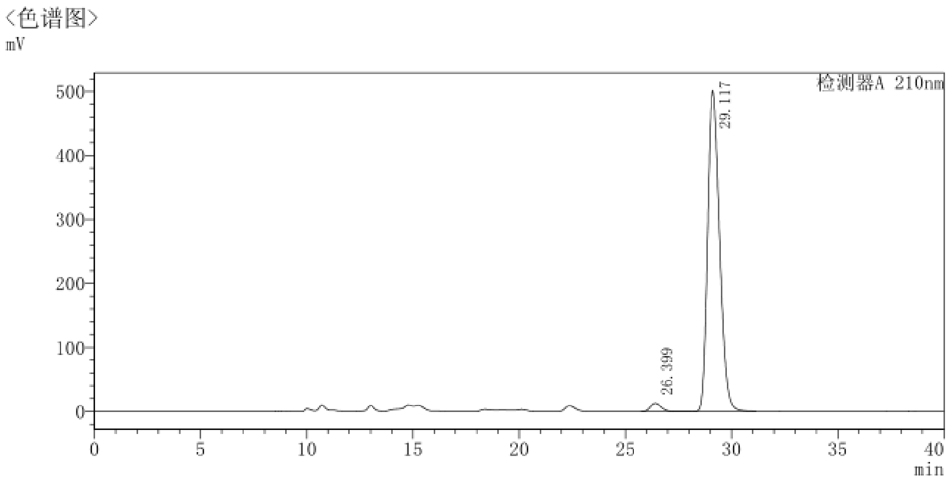
96% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



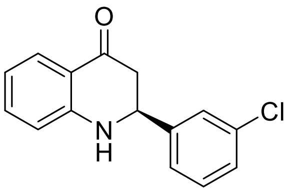
	Retention Time (min)	Area (%)
Peak 1	26.754	50.005
Peak 2	29.391	49.995

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	26.399	2.259	**96% ee**
Peak 2	29.117	97.741	

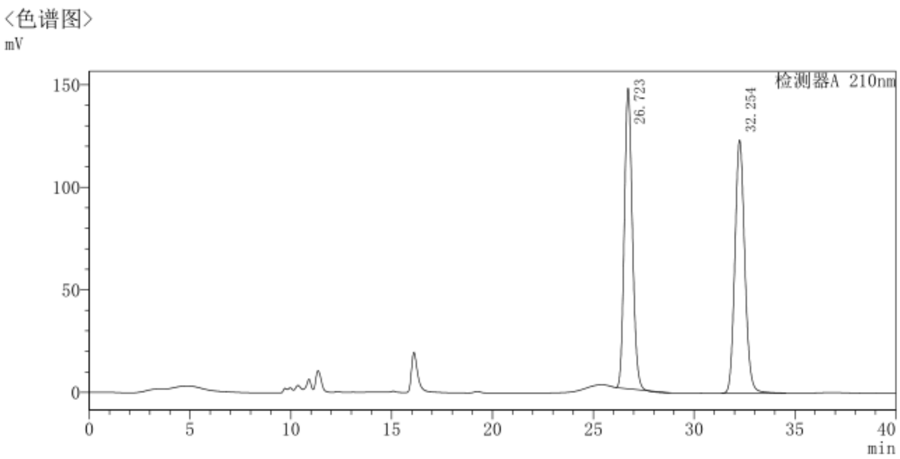
Figure S131 HPLC Data of (*S*)-**1e**



(S)-**1f**

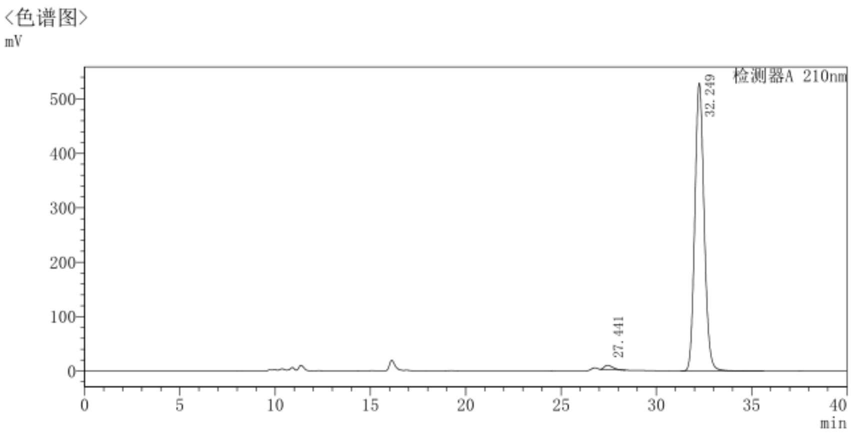
97% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



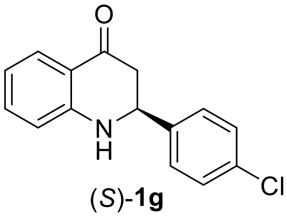
	Retention Time (min)	Area (%)
Peak 1	26.723	49.212
Peak 2	32.254	50.788

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	27.441	1.352	**97% ee**
Peak 2	32.249	98.648	

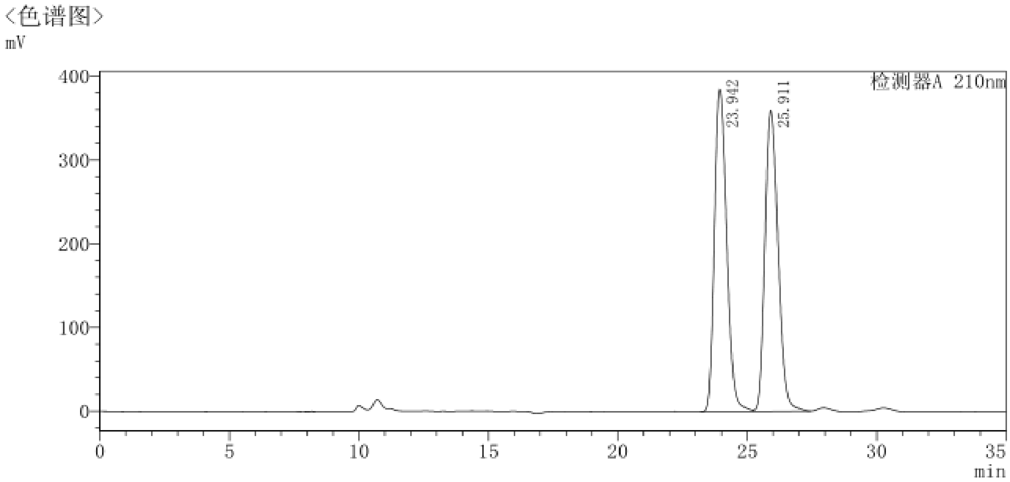
Figure S132 HPLC Data of (S)-**1f**



(*S*)-**1g**

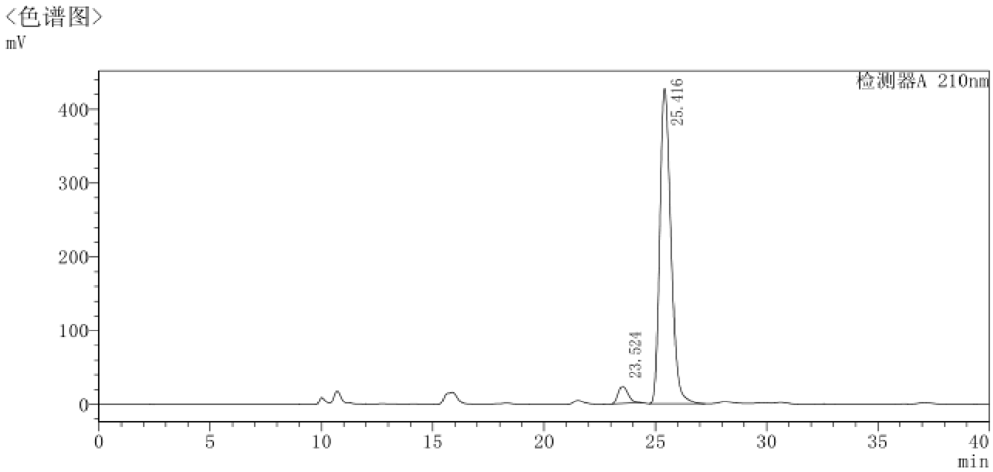
90% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



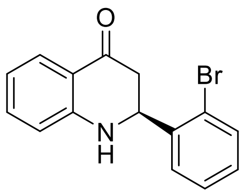
	Retention Time (min)	Area (%)
Peak 1	23.942	50.167
Peak 2	25.911	49.833

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	23.524	4.631	**90% ee**
Peak 2	25.416	95.369	

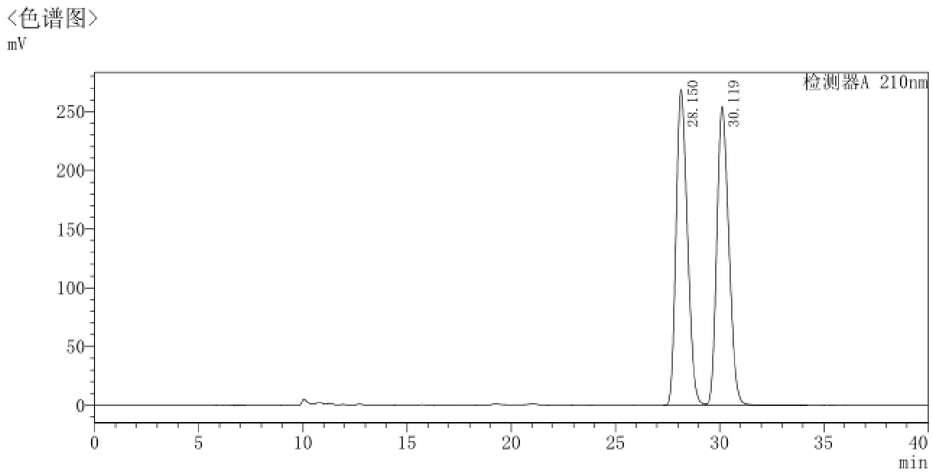
Figure S133 HPLC Data of (*S*)-**1g**



(S)-**1h**

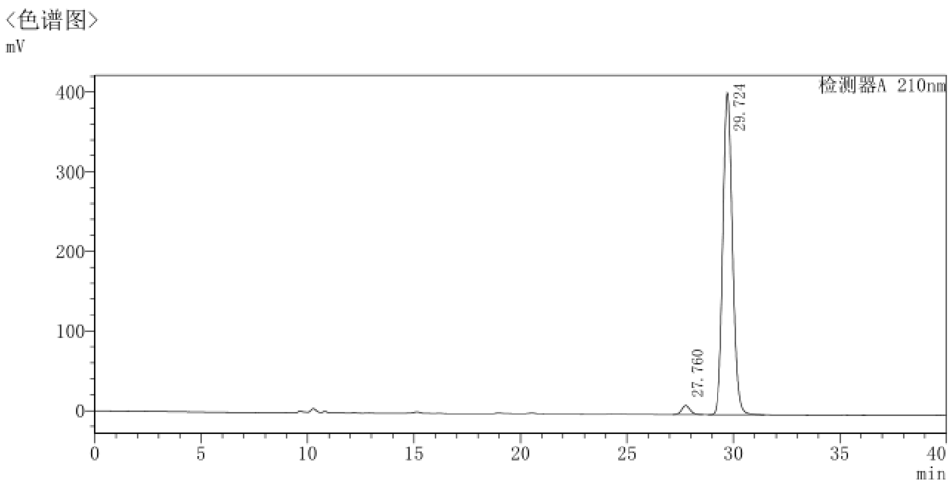
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



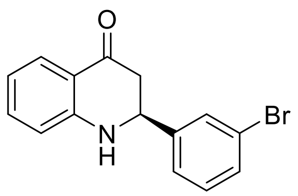
	Retention Time (min)	Area (%)
Peak 1	28.150	49.885
Peak 2	30.119	50.115

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	27.760	2.603	**95% ee**
Peak 2	29.724	97.397	

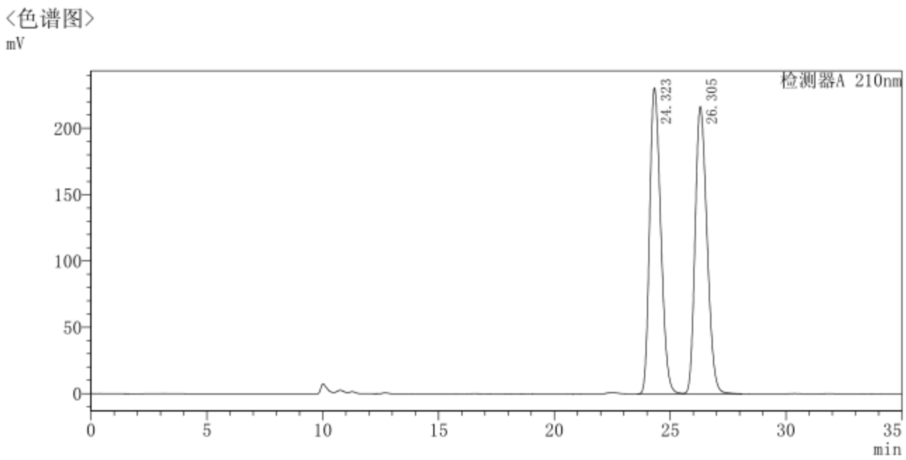
Figure S134 HPLC Data of (S)-**1h**



(*S*)-**1i**

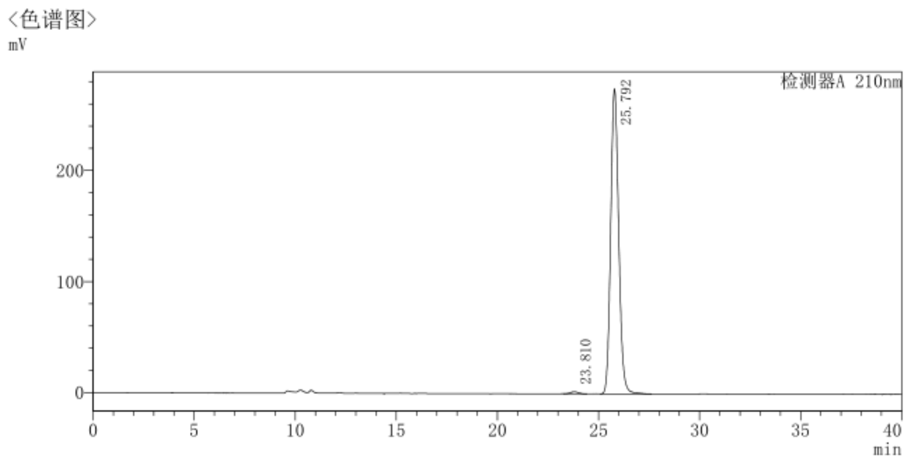
98% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



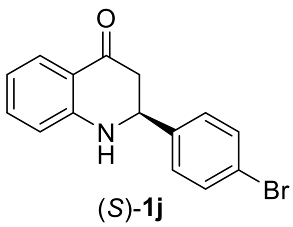
	Retention Time (min)	Area (%)
Peak 1	24.323	49.922
Peak 2	26.305	50.078

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	23.810	0.683	**98% ee**
Peak 2	25.792	99.317	

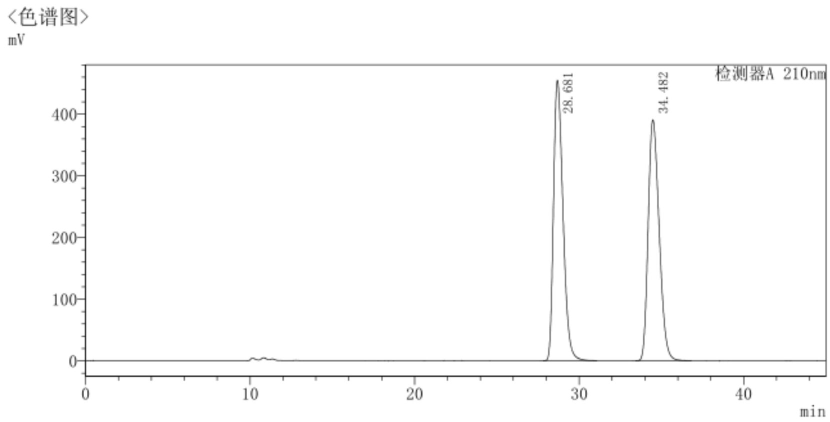
Figure S135 HPLC Data of (*S*)-**1i**



(*S*)-**1j**

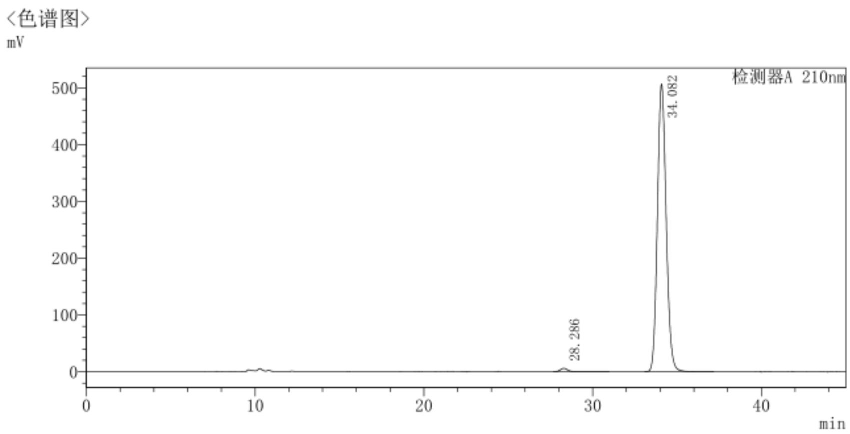
98% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



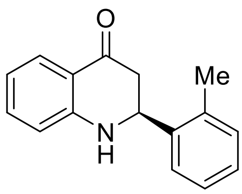
	Retention Time (min)	Area (%)
Peak 1	28.681	50.055
Peak 2	34.482	49.945

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	28.286	0.967	**98% ee**
Peak 2	34.082	99.033	

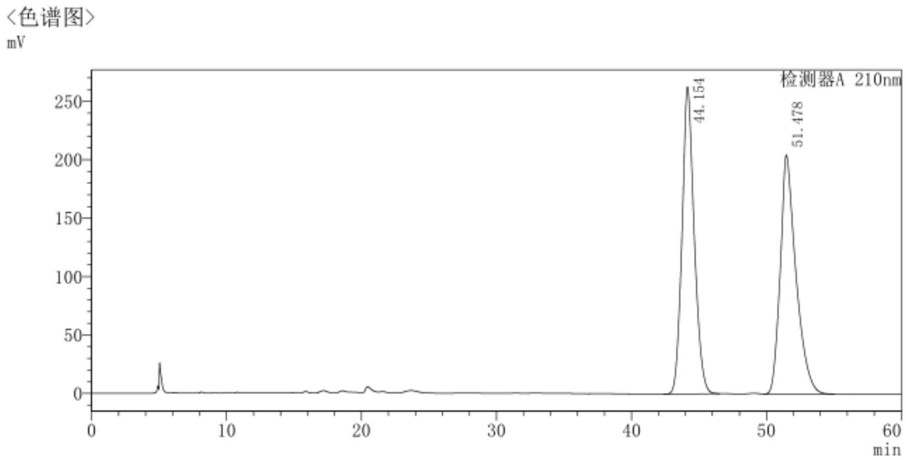
Figure S136 HPLC Data of (*S*)-**1j**



(*S*)-**1k**

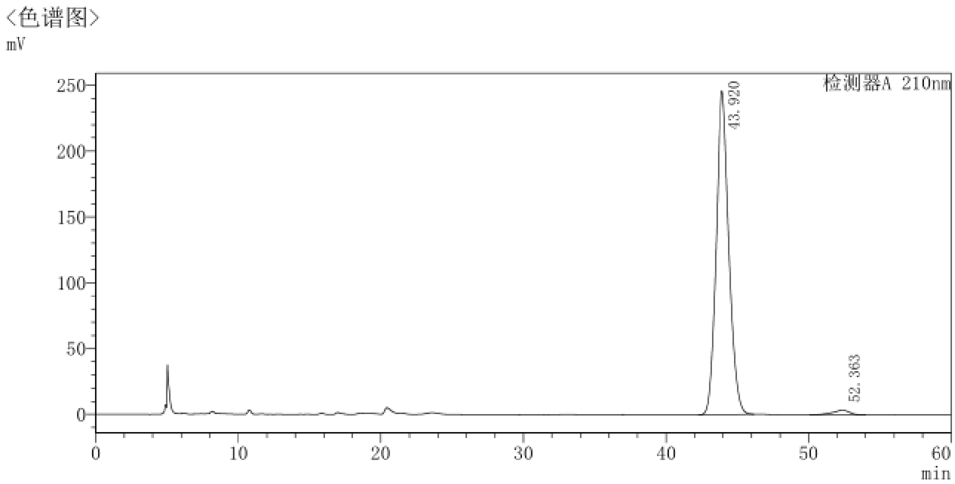
96% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



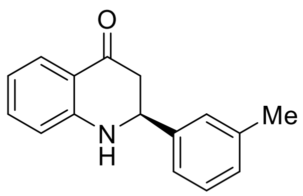
	Retention Time (min)	Area (%)
Peak 1	44.154	49.855
Peak 2	51.478	50.145

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	43.920	98.135	**96% ee**
Peak 2	52.363	1.865	

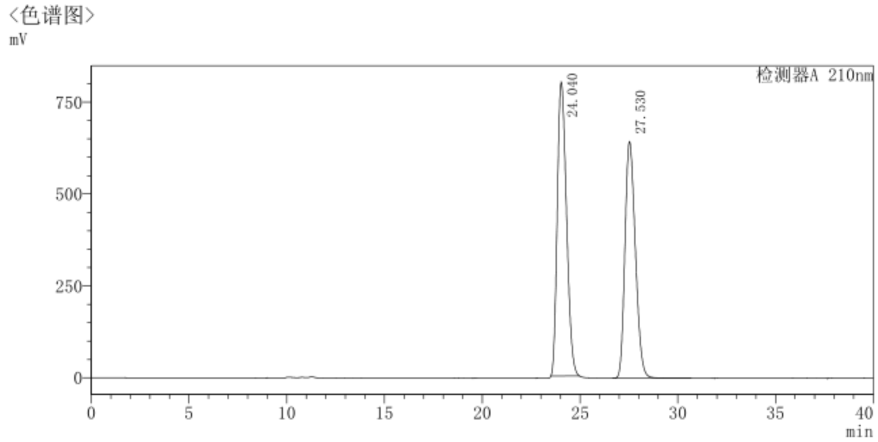
Figure S137 HPLC Data of (*S*)-**1k**



(*S*)-**1l**

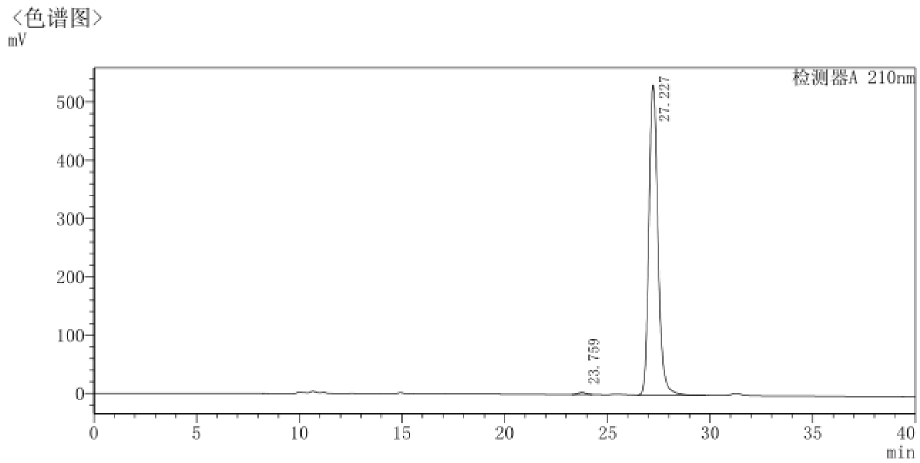
99% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



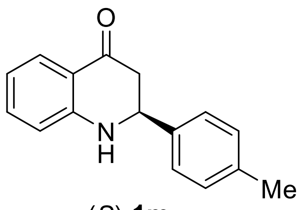
	Retention Time (min)	Area (%)
Peak 1	24.040	52.190
Peak 2	27.530	47.810

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	23.759	0.543	**99% ee**
Peak 2	27.227	99.457	

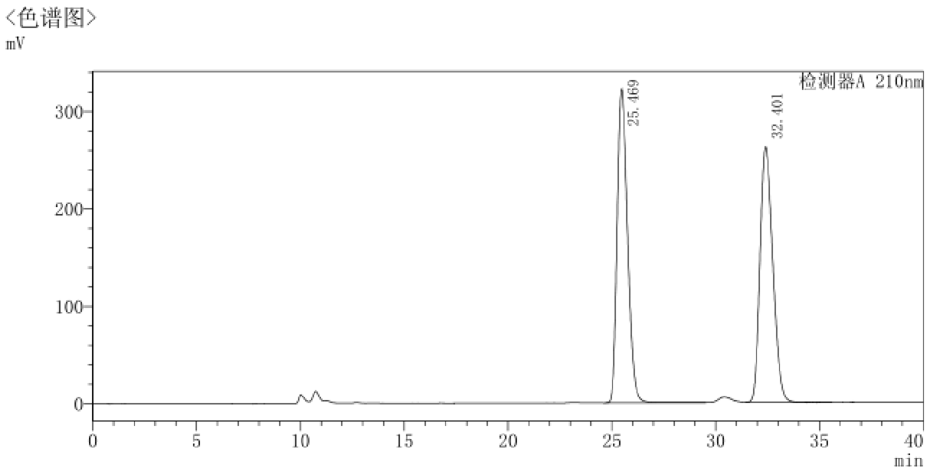
Figure S138 HPLC Data of (*S*)-**1l**



(*S*)-**1m**

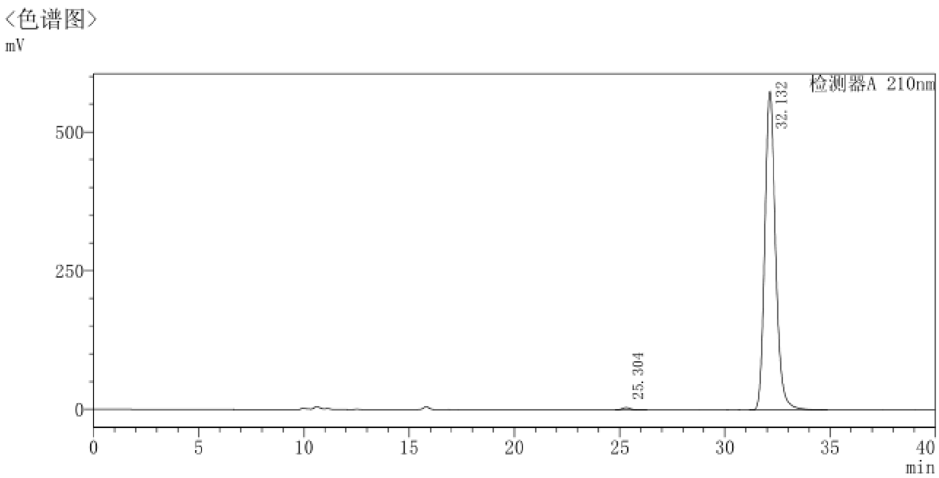
99% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



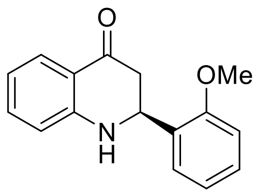
	Retention Time (min)	Area (%)
Peak 1	25.469	50.051
Peak 2	32.401	49.949

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	25.304	0.532	**99% ee**
Peak 2	32.132	99.468	

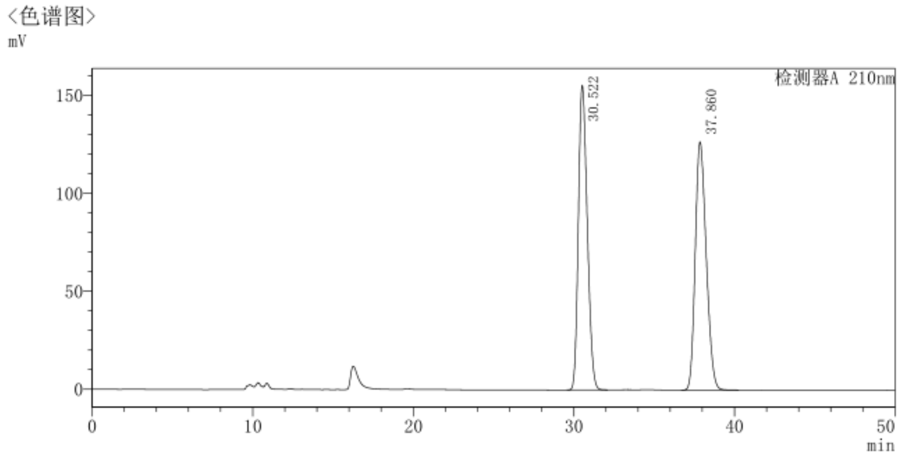
Figure S139 HPLC Data of (*S*)-**1m**



(*S*)-**1n**

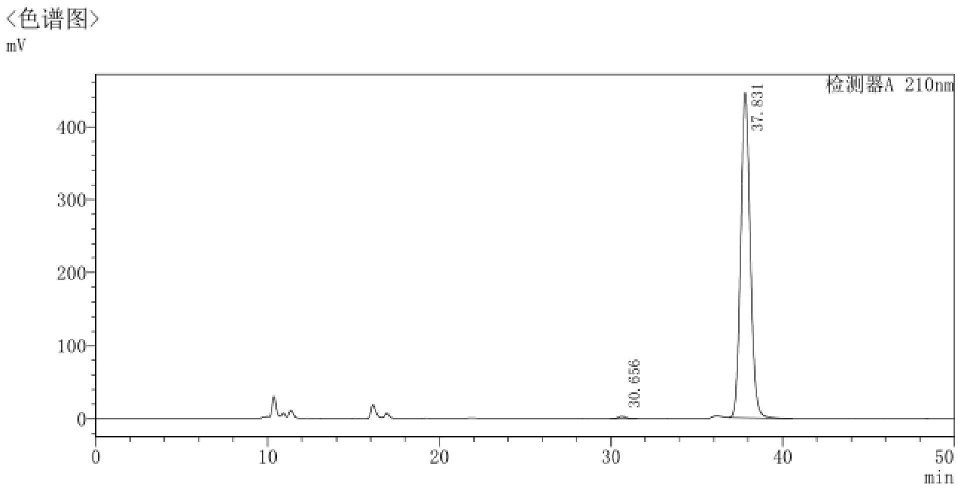
99% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



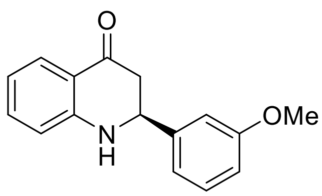
	Retention Time (min)	Area (%)
Peak 1	30.522	49.898
Peak 2	37.860	50.102

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	30.656	0.616	**99% ee**
Peak 2	37.831	99.384	

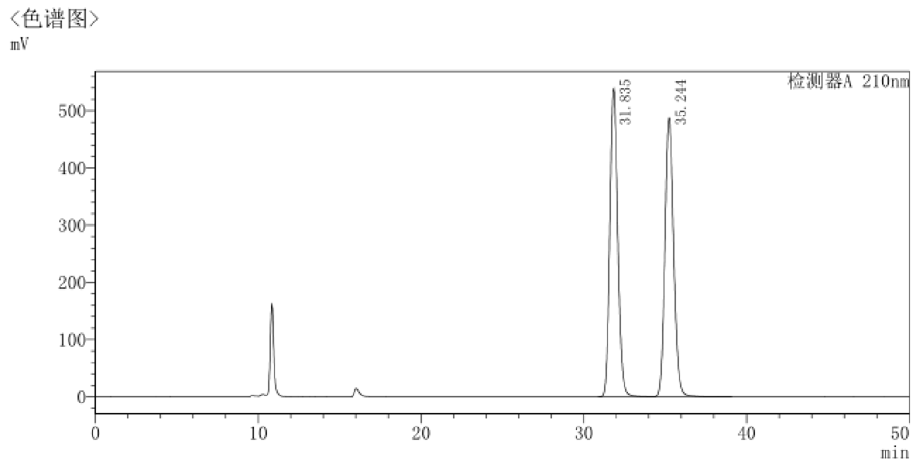
Figure S140 HPLC Data of (*S*)-**1n**



(*S*)-**1o**

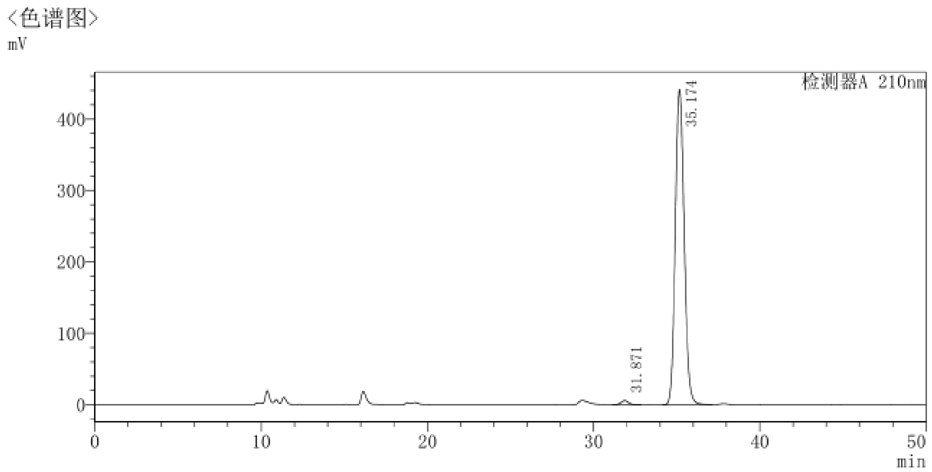
98% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



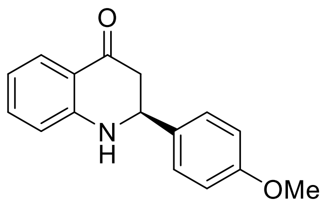
	Retention Time (min)	Area (%)
Peak 1	31.835	49.896
Peak 2	35.244	50.104

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	31.871	1.156	**98% ee**
Peak 2	35.174	98.844	

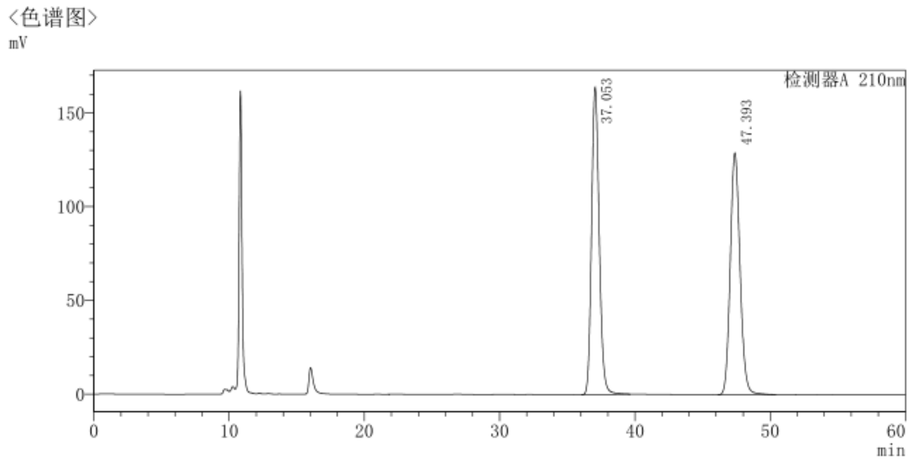
Figure S141 HPLC Data of (*S*)-**1o**



(S)-**1p**

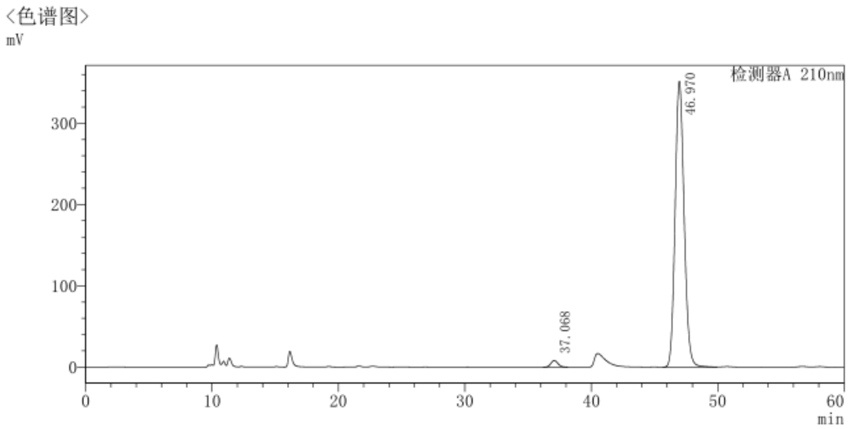
96% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



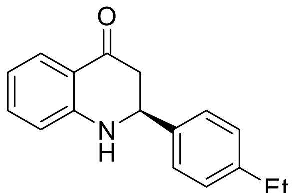
	Retention Time (min)	Area (%)
Peak 1	37.053	49.924
Peak 2	47.393	50.076

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	37.068	1.788	**96% ee**
Peak 2	46.970	98.212	

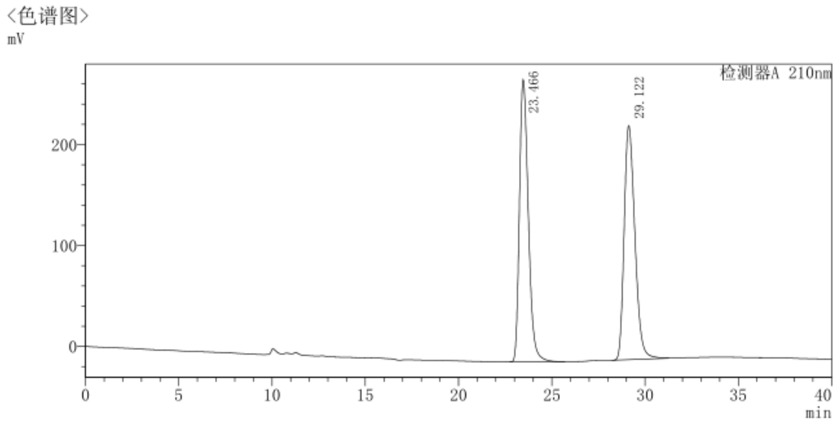
Figure S142 HPLC Data of (S)-**1p**



(*S*)-**1q**

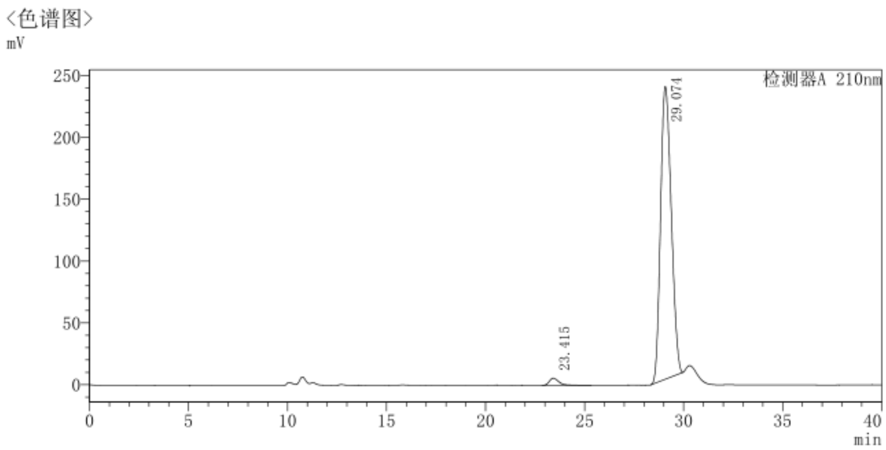
96% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



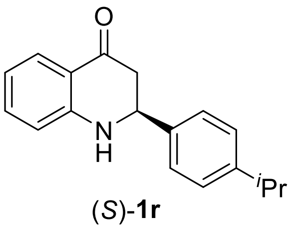
	Retention Time (min)	Area (%)
Peak 1	23.466	50.009
Peak 2	29.122	49.991

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	23.415	2.207	**96% ee**
Peak 2	29.074	97.793	

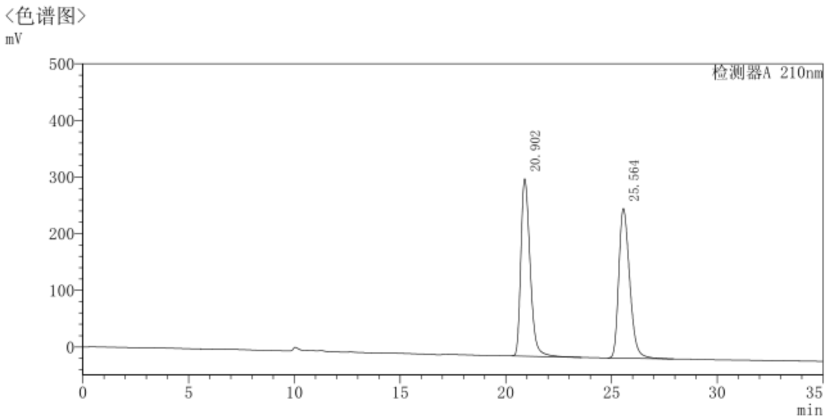
Figure S143 HPLC Data of (*S*)-**1q**



(*S*)-**1r**

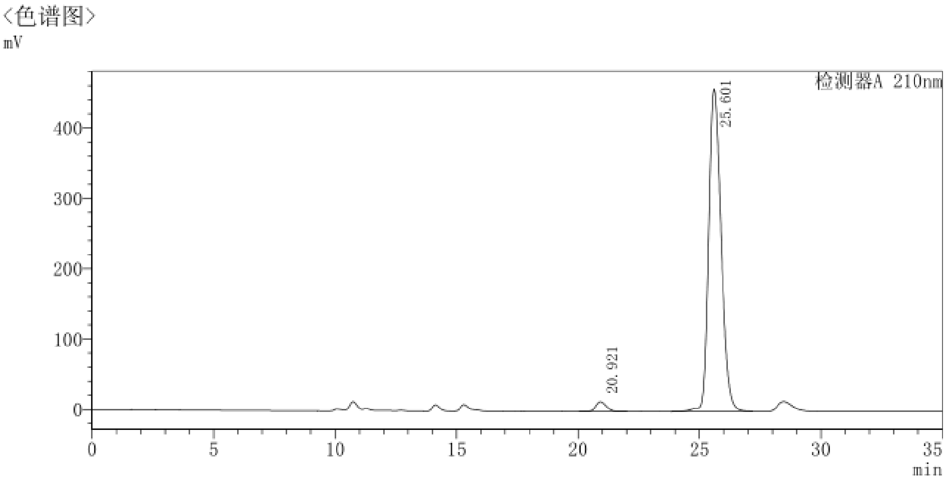
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



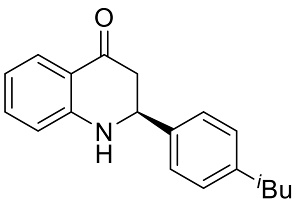
	Retention Time (min)	Area (%)
Peak 1	20.902	50.055
Peak 2	25.564	49.945

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	20.921	2.522	**95% ee**
Peak 2	25.601	97.478	

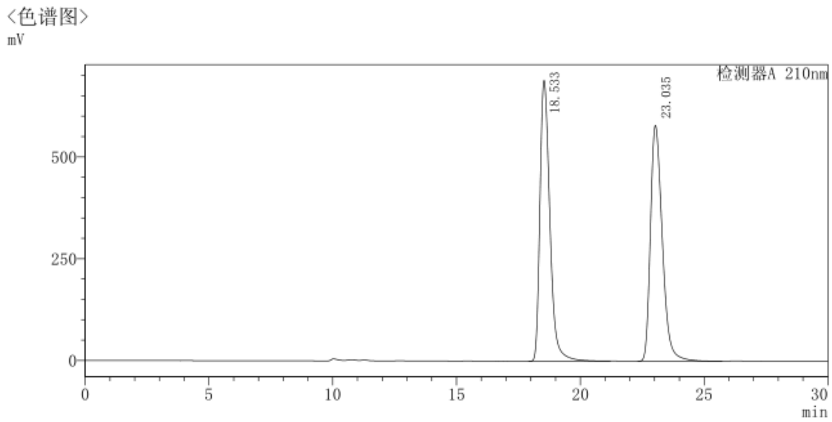
Figure S144 HPLC Data of (*S*)-**1r**



(*S*)-**1s**

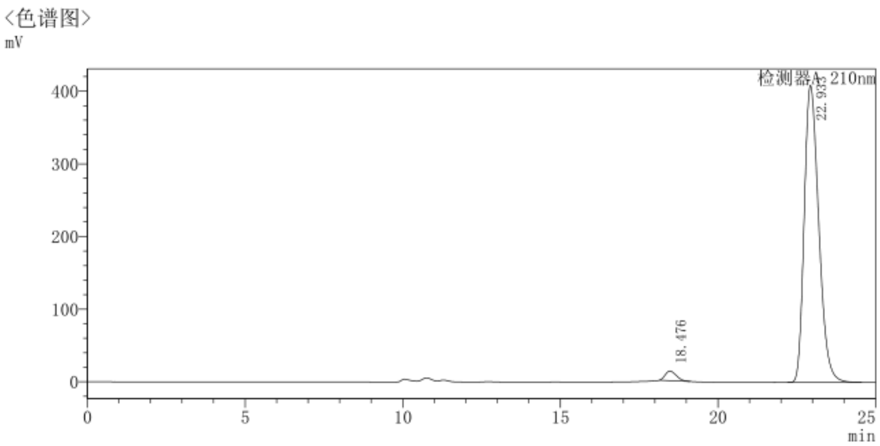
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



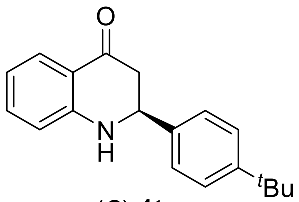
	Retention Time (min)	Area (%)
Peak 1	18.533	49.948
Peak 2	23.035	50.052

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	18.476	2.399	**95% ee**
Peak 2	22.933	97.601	

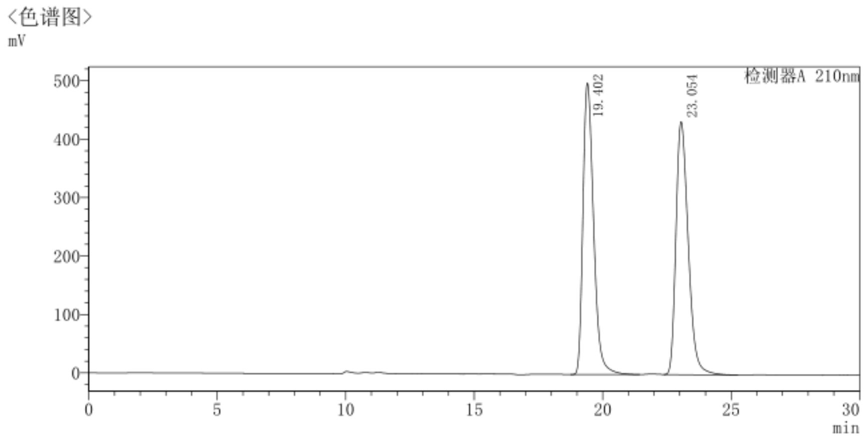
Figure S145 HPLC Data of (*S*)-**1s**



(*S*)-**1t**

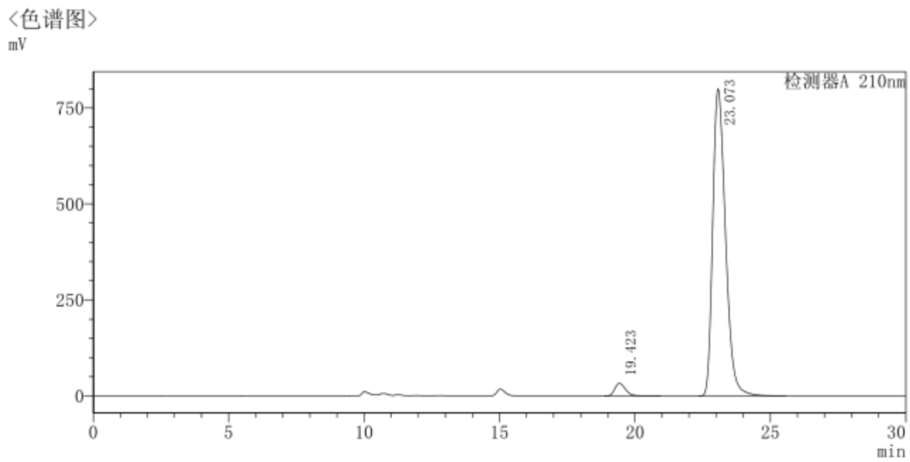
93% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



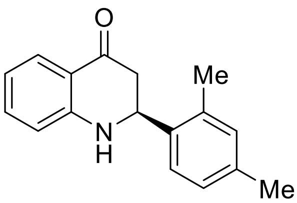
	Retention Time (min)	Area (%)
Peak 1	19.402	50.041
Peak 2	23.054	49.959

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	19.423	3.397	**93% ee**
Peak 2	23.073	96.603	

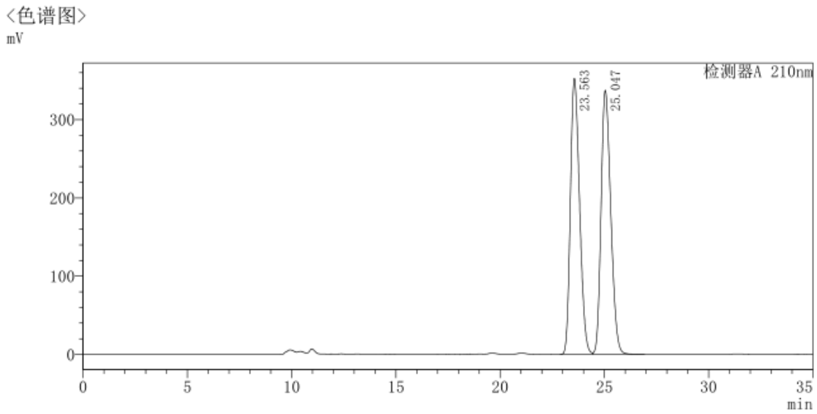
Figure S146 HPLC Data of (*S*)-**1t**



(*S*)-**1u**

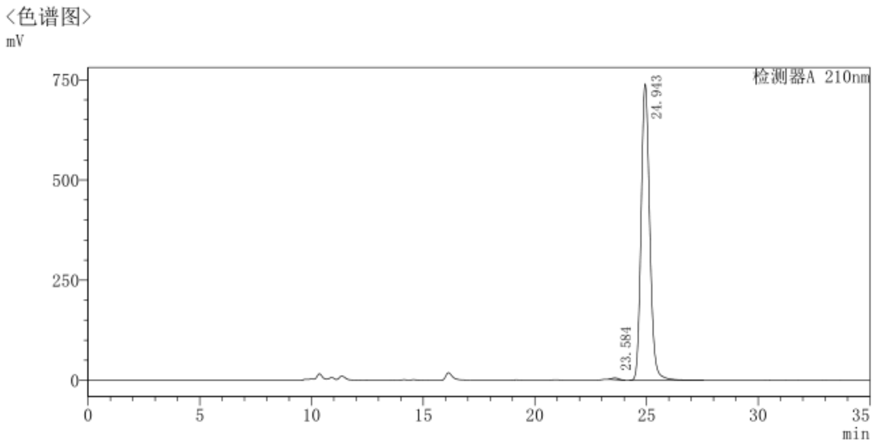
99% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



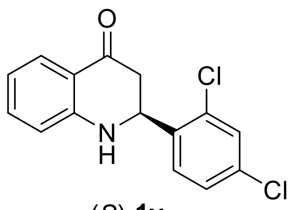
	Retention Time (min)	Area (%)
Peak 1	23.563	49.843
Peak 2	25.047	50.157

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	23.584	0.423	**99% ee**
Peak 2	24.943	99.577	

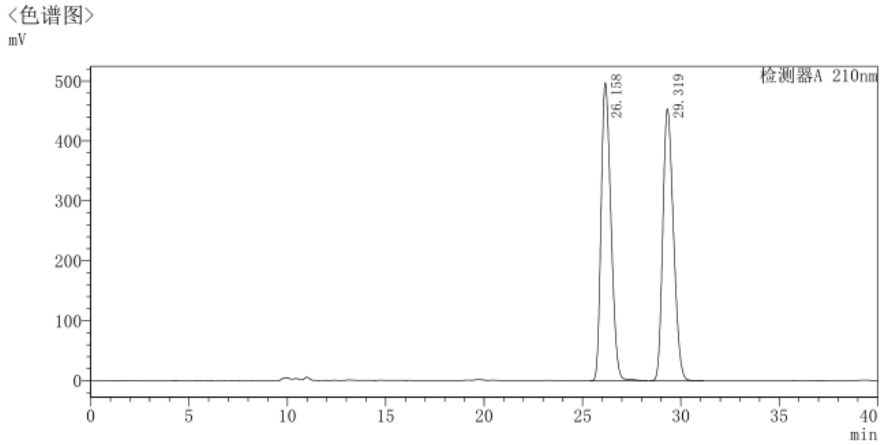
Figure S147 HPLC Data of (*S*)-**1u**



(*S*)-**1v**

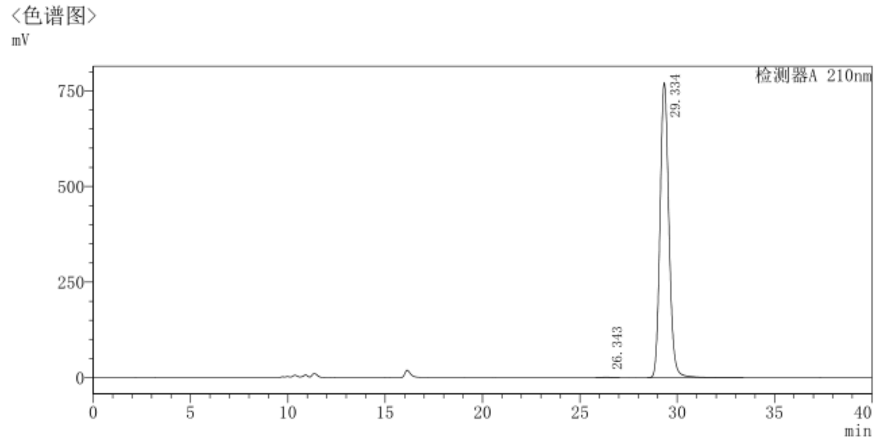
99.7% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



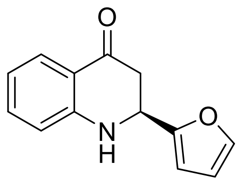
	Retention Time (min)	Area (%)
Peak 1	26.158	50.070
Peak 2	29.319	49.930

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	26.343	0.160	**99.7% ee**
Peak 2	29.334	99.840	

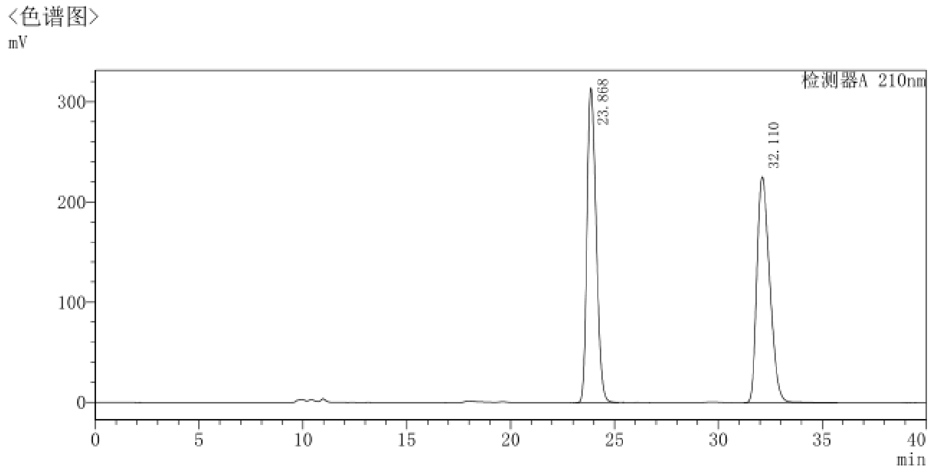
Figure S148 HPLC Data of (*S*)-**1v**



(*S*)-**1w**

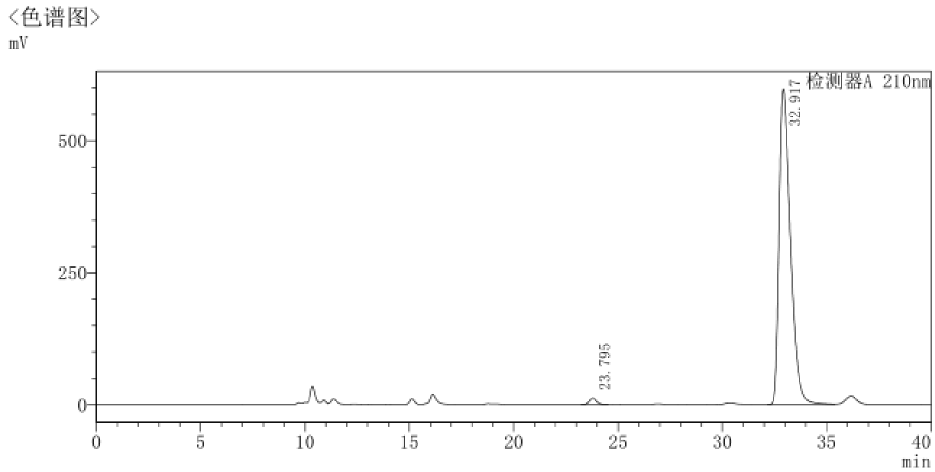
97% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



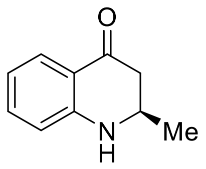
	Retention Time (min)	Area (%)
Peak 1	23.868	49.802
Peak 2	32.110	50.198

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	23.795	1.363	**97% ee**
Peak 2	32.917	98.637	

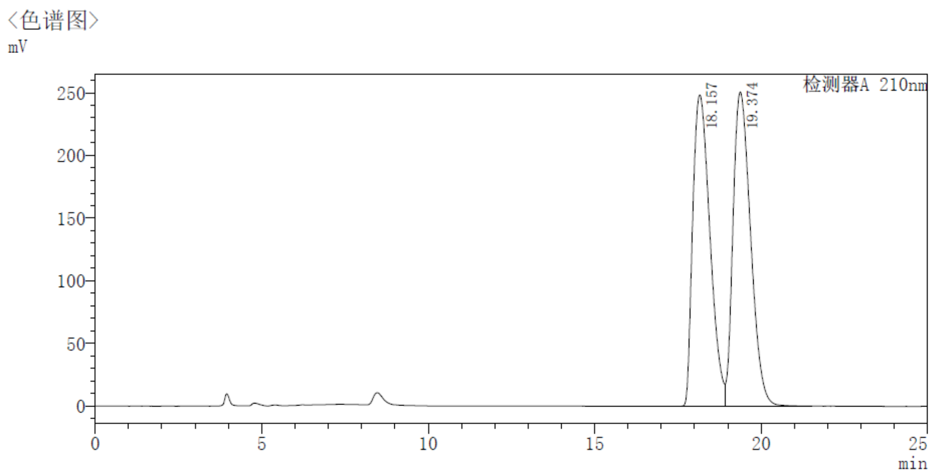
Figure S149 HPLC Data of (*S*)-**1w**



(*R*)-**1x**

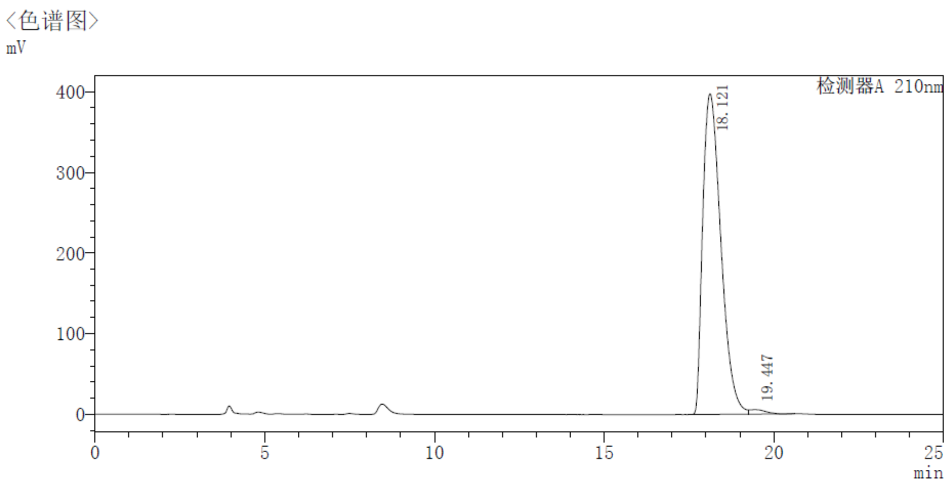
98% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OJ-H column, *n*-hexane/*i*-PrOH = 90/20, 0.8 mL/min, 210 nm.

Racemate:



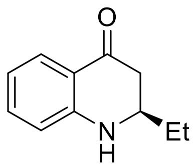
	Retention Time (min)	Area (%)
Peak 1	18.157	49.112
Peak 2	19.374	50.888

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	18.121	98.834	**98% ee**
Peak 2	19.447	1.166	

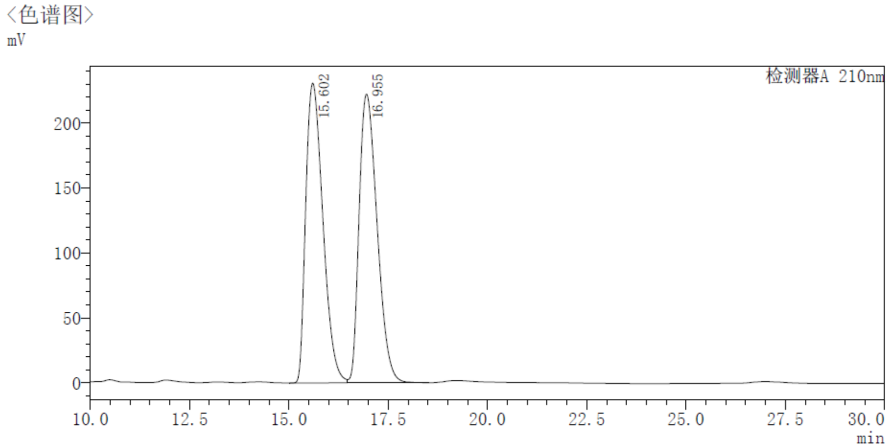
Figure S150 HPLC Data of (*R*)-**1x**



(*R*)-**1y**

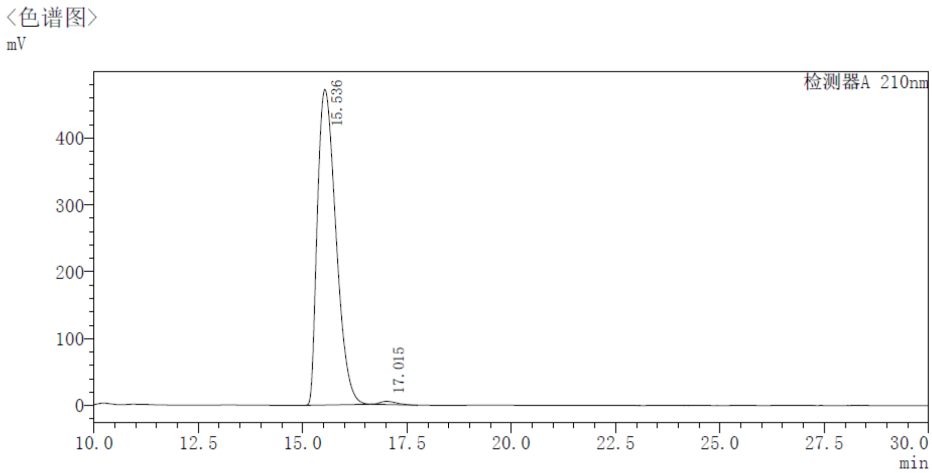
98% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OJ-H column, *n*-hexane/*i*-PrOH = 90/20, 0.8 mL/min, 210 nm.

Racemate:



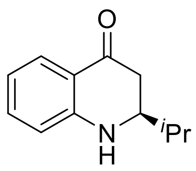
	Retention Time (min)	Area (%)
Peak 1	15.602	49.687
Peak 2	16.955	50.313

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	15.536	99.118	**98% ee**
Peak 2	17.015	0.882	

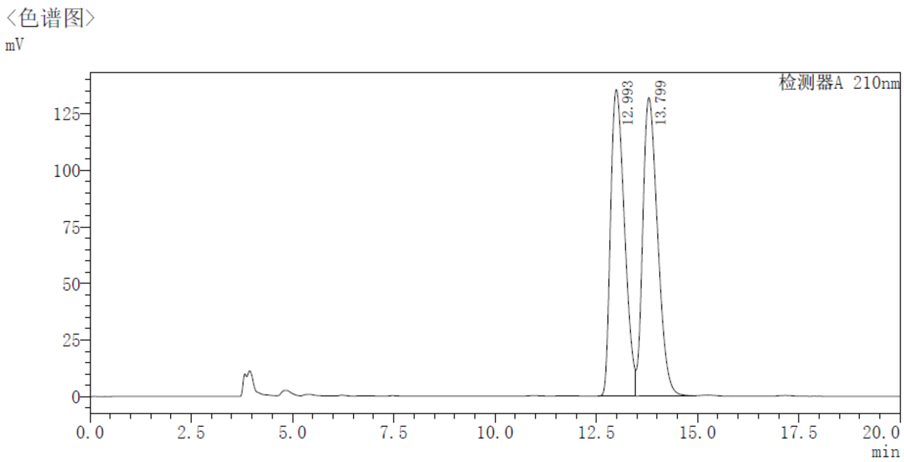
Figure S151 HPLC Data of (*R*)-**1y**



(*S*)-**1z**

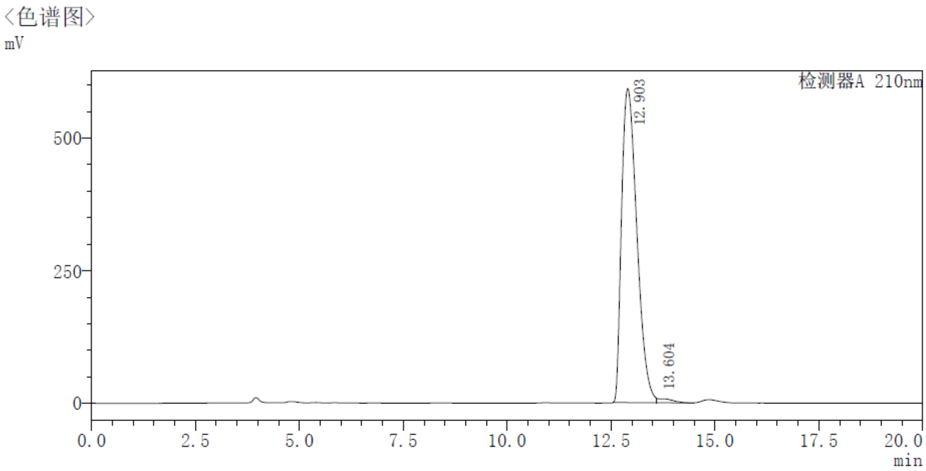
98% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OJ-H column, *n*-hexane/*i*-PrOH = 90/20, 0.8 mL/min, 210 nm.

Racemate:



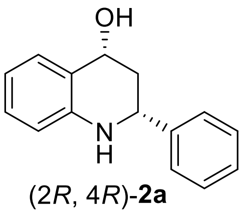
	Retention Time (min)	Area (%)
Peak 1	12.993	49.241
Peak 2	13.799	50.759

Chiral:



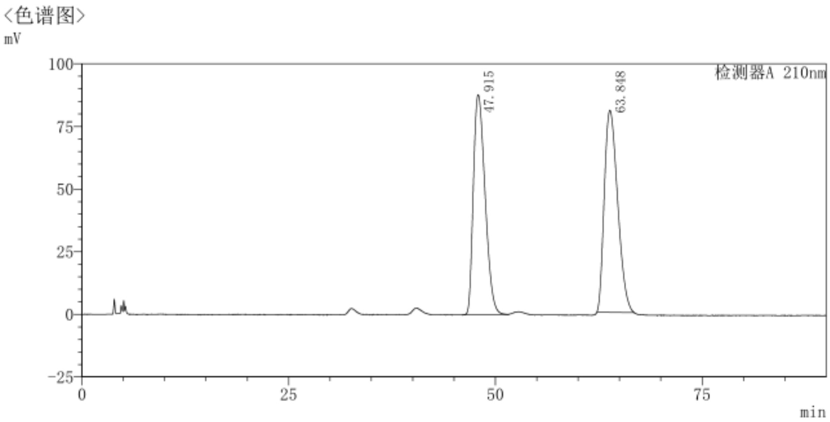
	Retention Time (min)	Area (%)	
Peak 1	12.903	98.767	**98% ee**
Peak 2	13.604	1.233	

Figure S152 HPLC Data of (*S*)-**1z**


(2*R*, 4*R*)-**2a**

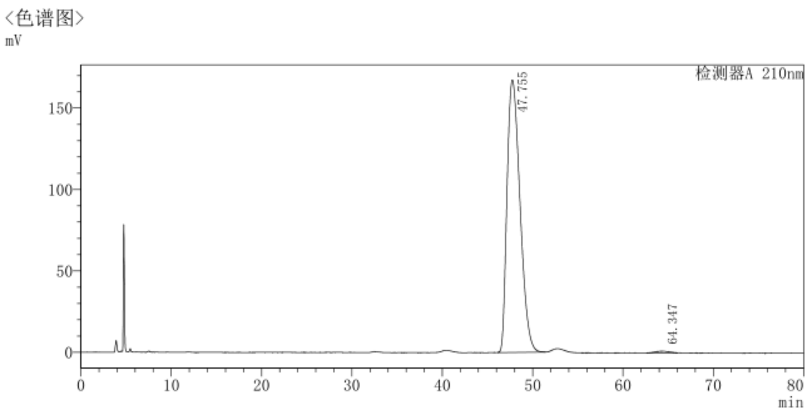
98% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OJ-H column, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 210 nm.

Racemate:



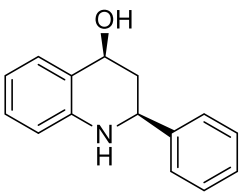
	Retention Time (min)	Area (%)
Peak 1	47.915	48.823
Peak 2	63.848	51.177

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	47.755	99.276	**98% ee**
Peak 2	64.347	0.724	

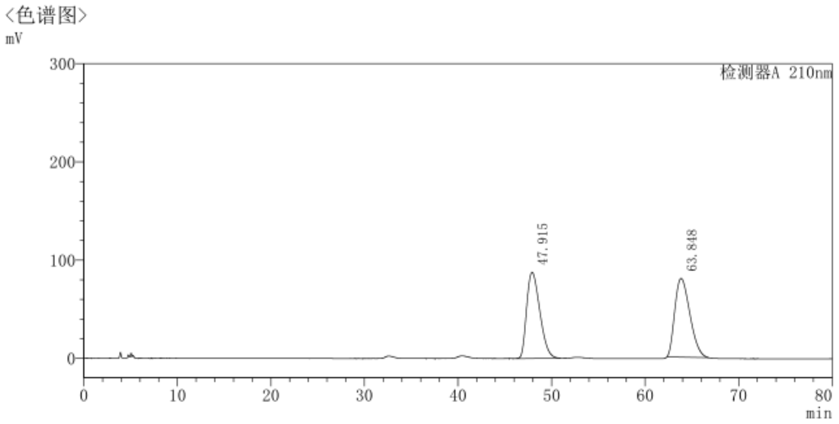
Figure S153 HPLC Data of (2*R*,4*R*)-**2a**



(2*S*,4*S*)-**2a**

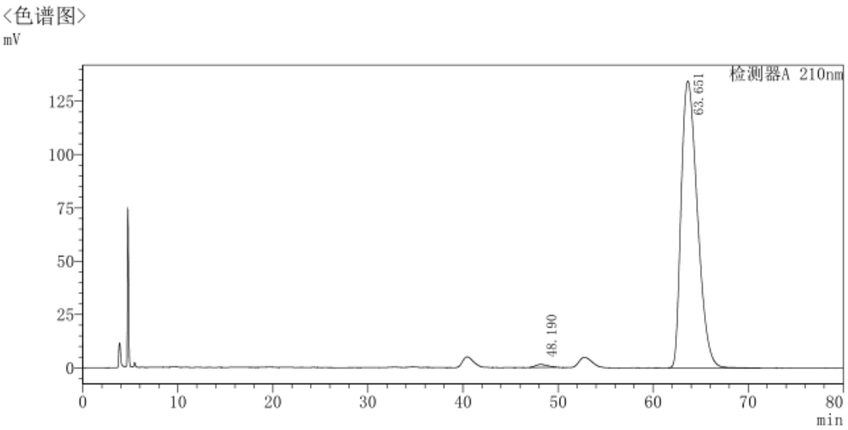
98% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OJ-H column, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 210 nm.

Racemate:



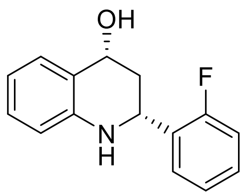
	Retention Time (min)	Area (%)
Peak 1	47.915	48.865
Peak 2	63.848	51.135

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	48.190	0.743	**98% ee**
Peak 2	63.651	99.257	

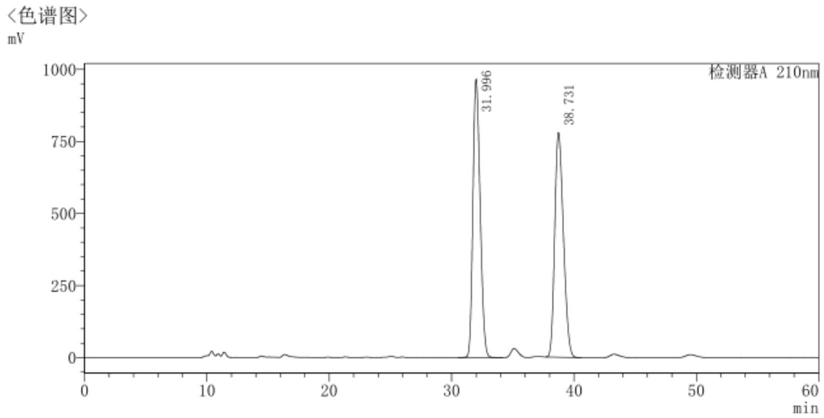
Figure S154 HPLC Data of (2*S*,4*S*)-**2a**



(2*R*,4*R*)-**2b**

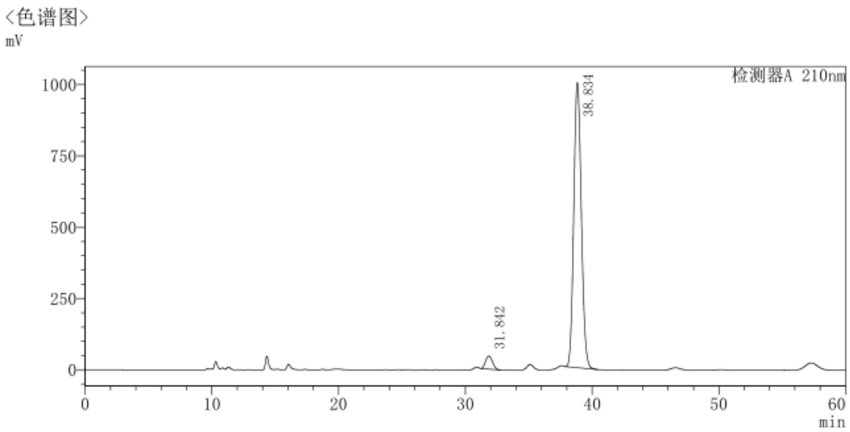
92% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



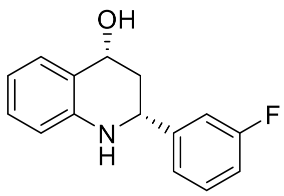
	Retention Time (min)	Area (%)
Peak 1	31.996	50.745
Peak 2	38.731	49.255

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	31.842	4.034	**92% ee**
Peak 2	38.834	95.966	

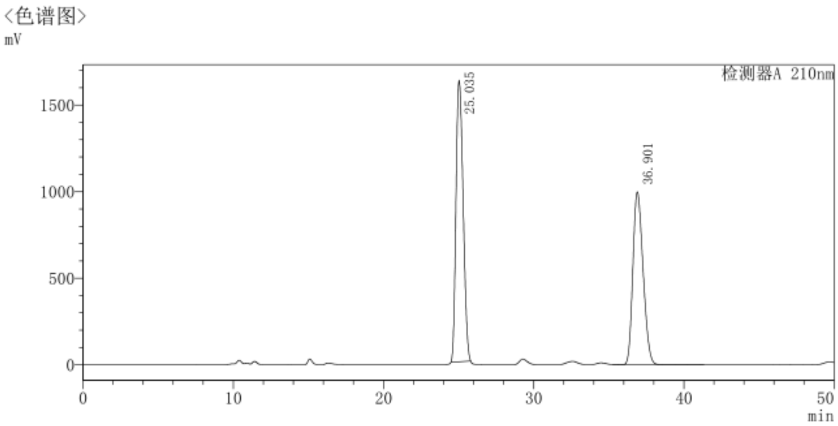
Figure S155 HPLC Data of (2*R*,4*R*)-**2b**



(2*R*,4*R*)-**2c**

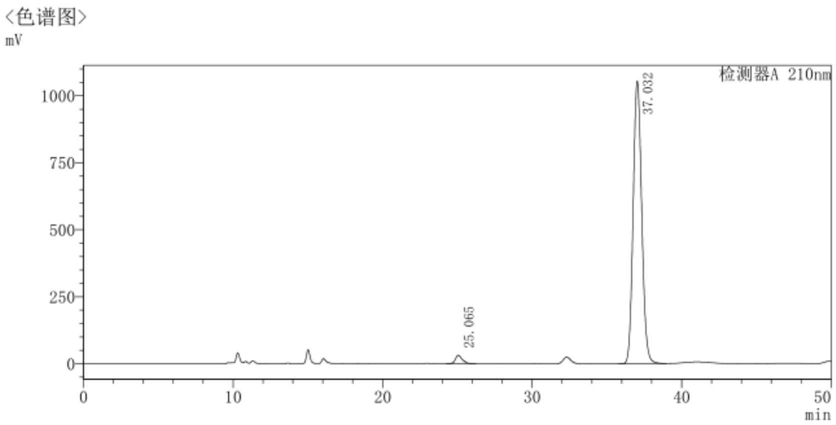
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



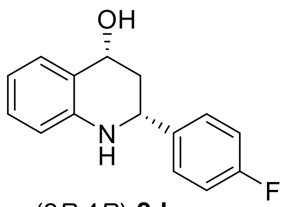
	Retention Time (min)	Area (%)
Peak 1	25.035	53.245
Peak 2	36.901	46.755

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	25.065	2.385	**95% ee**
Peak 2	37.032	97.615	

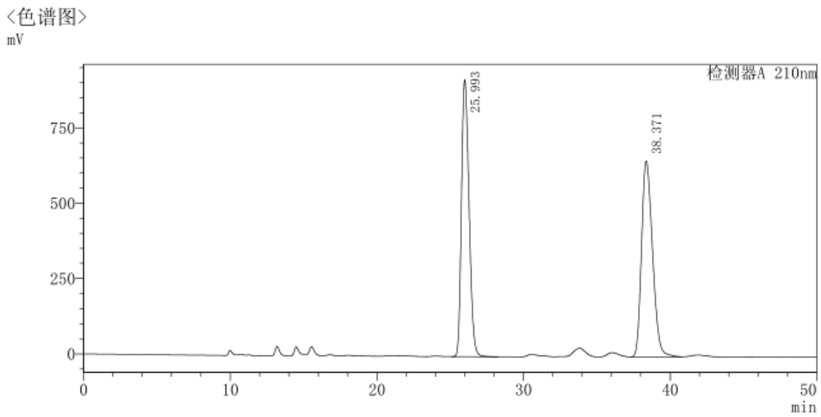
Figure S156 HPLC Data of (2*R*,4*R*)-**2c**



(2*R*,4*R*)-**2d**

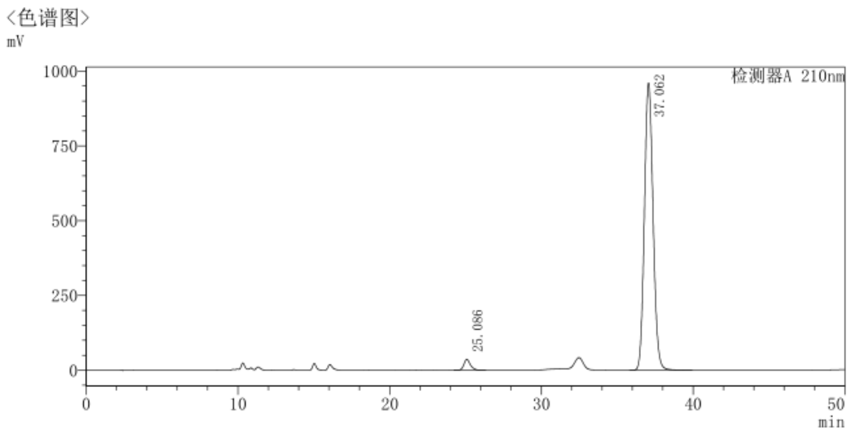
94% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



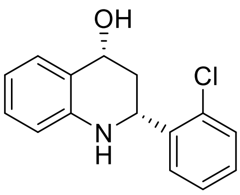
	Retention Time (min)	Area (%)
Peak 1	25.993	49.309
Peak 2	38.371	50.691

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	25.086	2.862	**94% ee**
Peak 2	37.062	97.138	

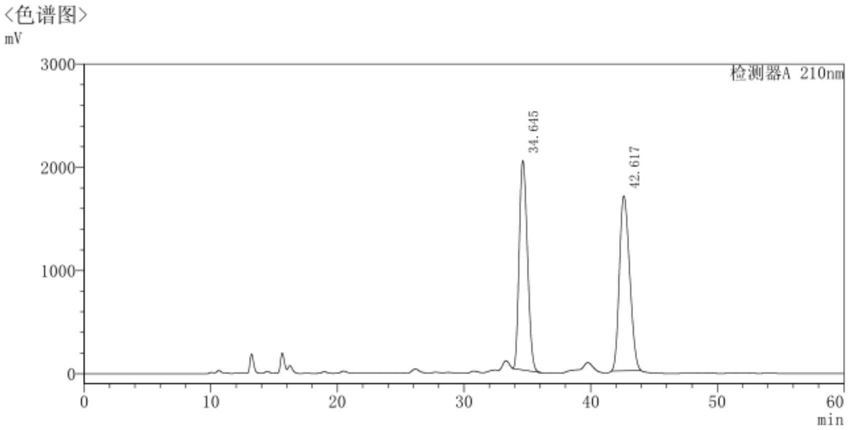
Figure S157 HPLC Data of (2*R*,4*R*)-**2d**



(2*R*,4*R*)-**2e**

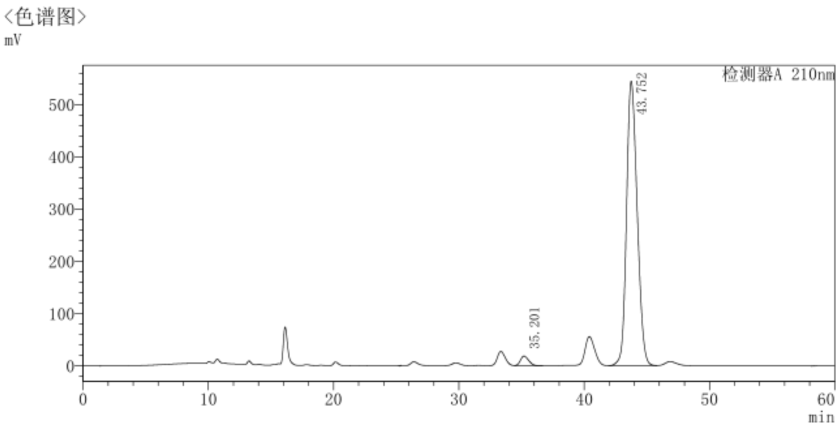
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



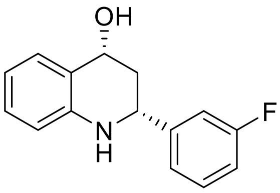
	Retention Time (min)	Area (%)
Peak 1	34.645	49.113
Peak 2	42.617	50.887

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	35.201	2.529	**95% ee**
Peak 2	43.752	97.471	

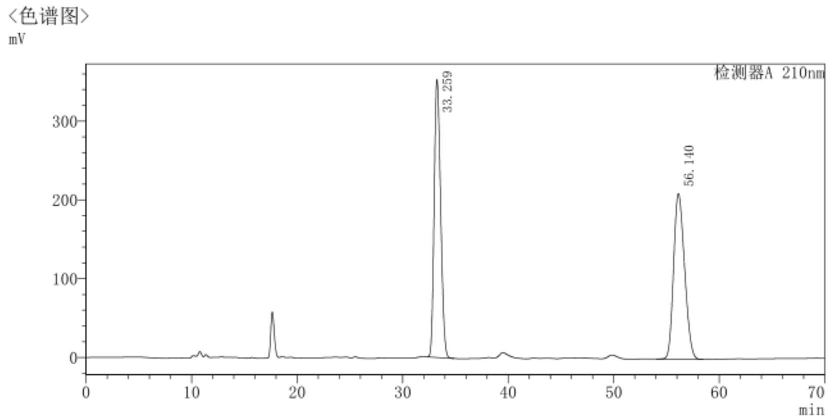
Figure S158 HPLC Data of (2*R*,4*R*)-**2e**



(2*R*,4*R*)-**2f**

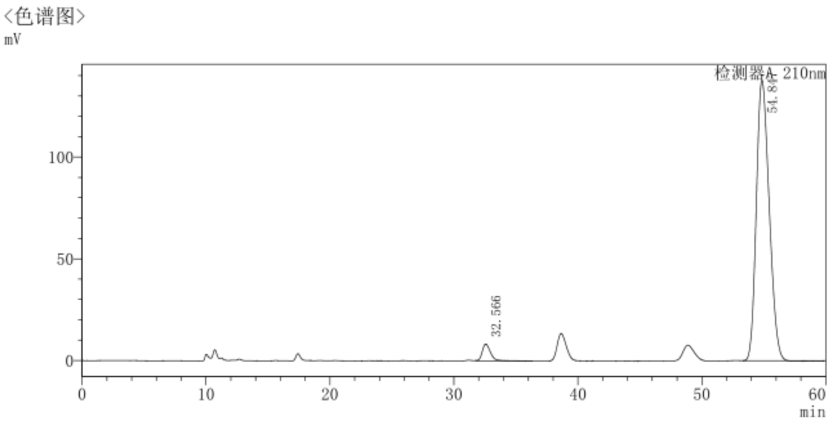
92% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



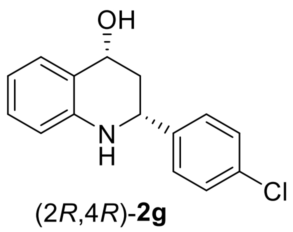
	Retention Time (min)	Area (%)
Peak 1	33.259	49.640
Peak 2	56.140	50.360

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	32.566	3.684	**92% ee**
Peak 2	54.847	96.316	

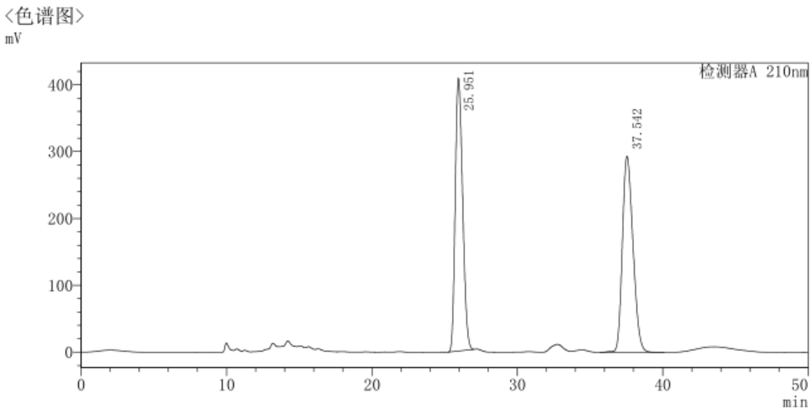
Figure S159 HPLC Data of (2*R*,4*R*)-**2f**



(2*R*,4*R*)-**2g**

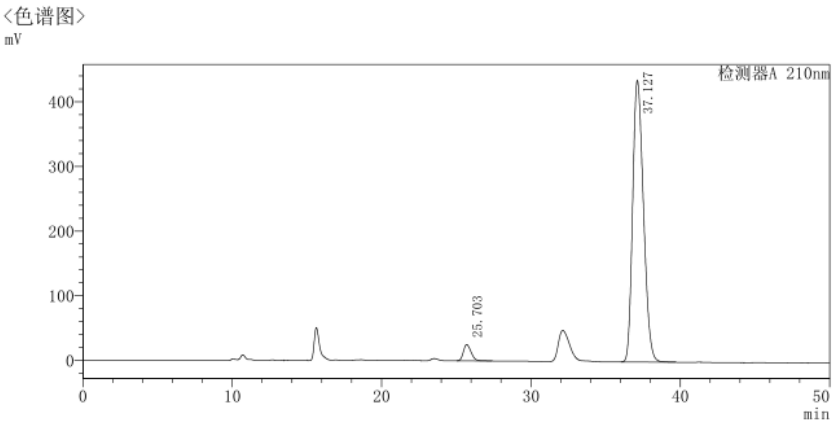
92% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



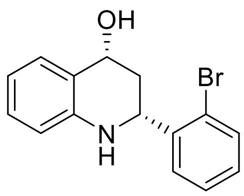
	Retention Time (min)	Area (%)
Peak 1	25.951	49.014
Peak 2	37.542	50.986

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	25.703	3.981	**92% ee**
Peak 2	37.127	96.019	

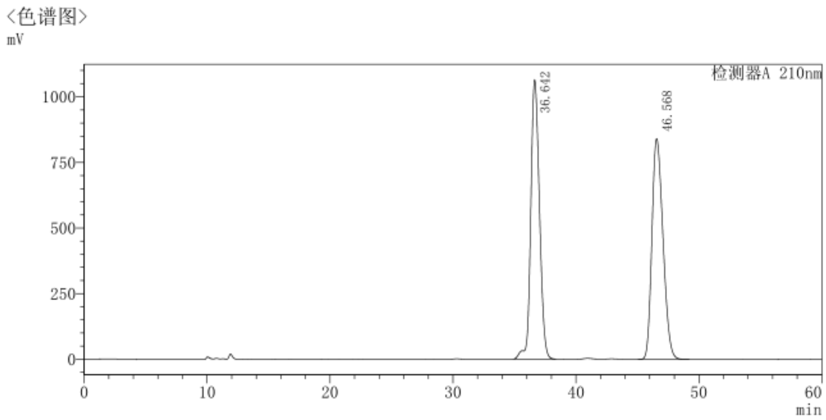
Figure S160 HPLC Data of (2*R*,4*R*)-**2g**



(2*R*,4*R*)-**2h**

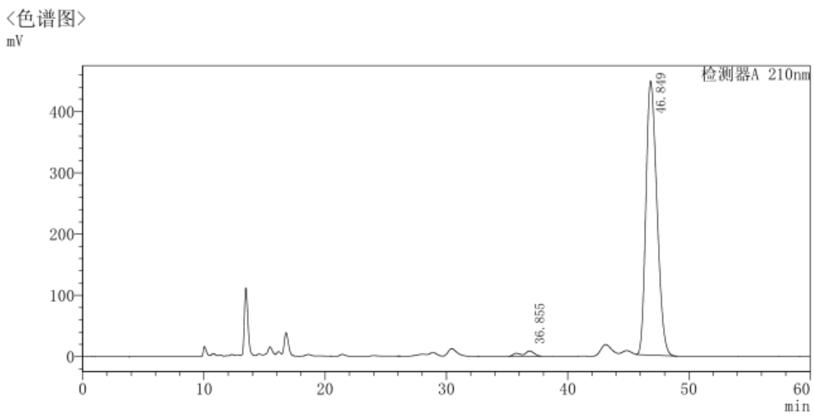
96% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



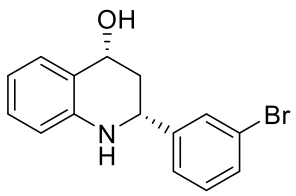
	Retention Time (min)	Area (%)
Peak 1	36.642	49.781
Peak 2	46.568	50.219

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	36.855	2.104	**96% ee**
Peak 2	46.849	97.896	

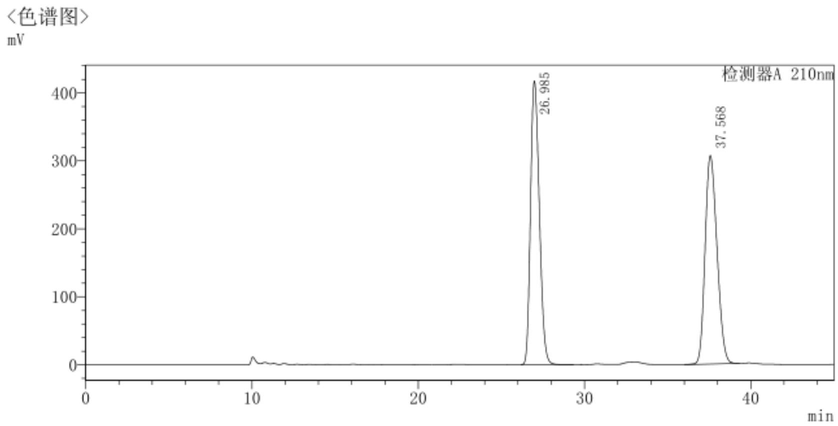
Figure S161 HPLC Data of (2*R*,4*R*)-**2h**



(2*R*,4*R*)-**2i**

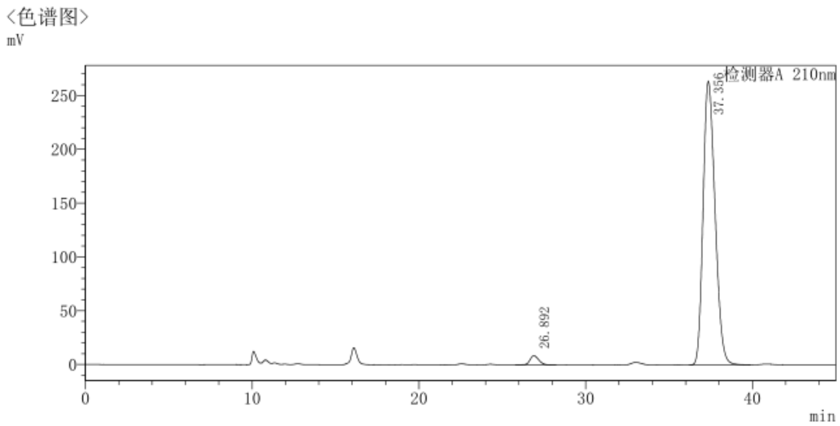
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



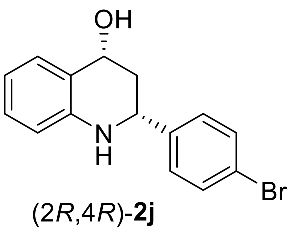
	Retention Time (min)	Area (%)
Peak 1	26.985	50.070
Peak 2	37.568	49.930

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	26.892	2.444	**95% ee**
Peak 2	37.356	97.556	

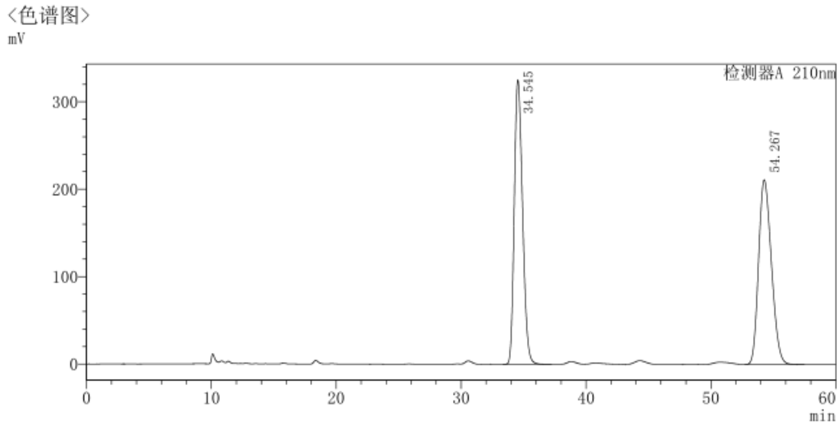
Figure S162 HPLC Data of (2*R*,4*R*)-**2i**



(2*R*,4*R*)-**2j**

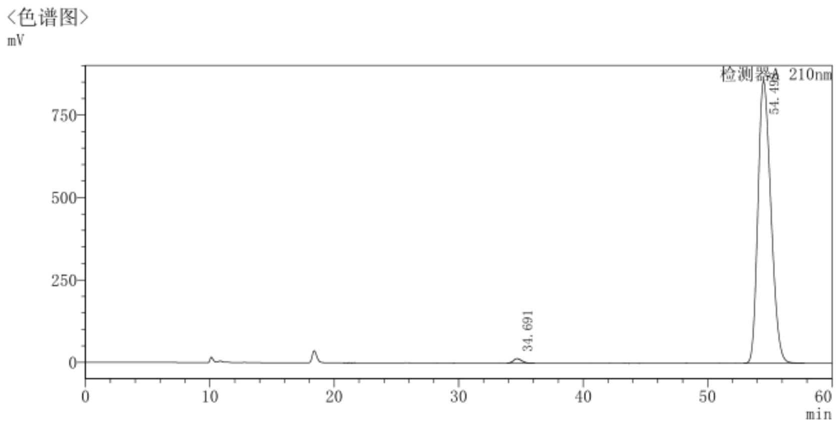
98% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



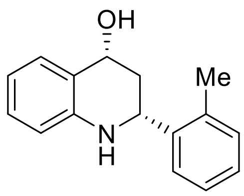
	Retention Time (min)	Area (%)
Peak 1	34.545	49.982
Peak 2	54.267	50.018

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	34.691	0.969	**98% ee**
Peak 2	54.498	99.031	

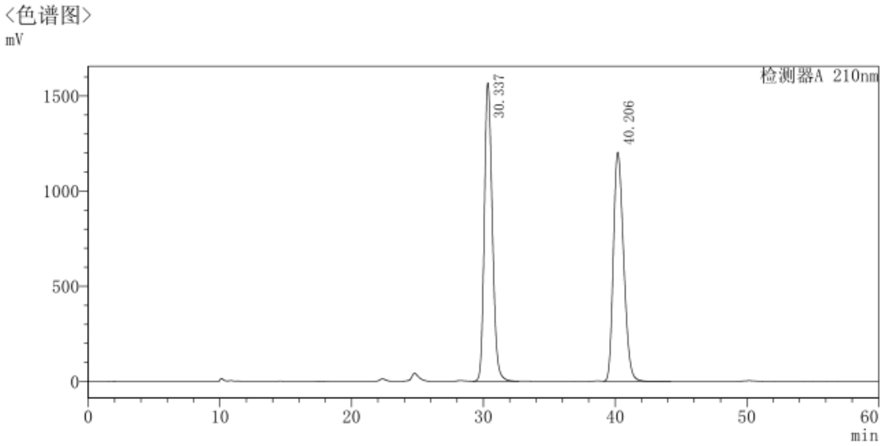
Figure S163 HPLC Data of (2*R*,4*R*)-**2j**



(2*R*,4*R*)-**2k**

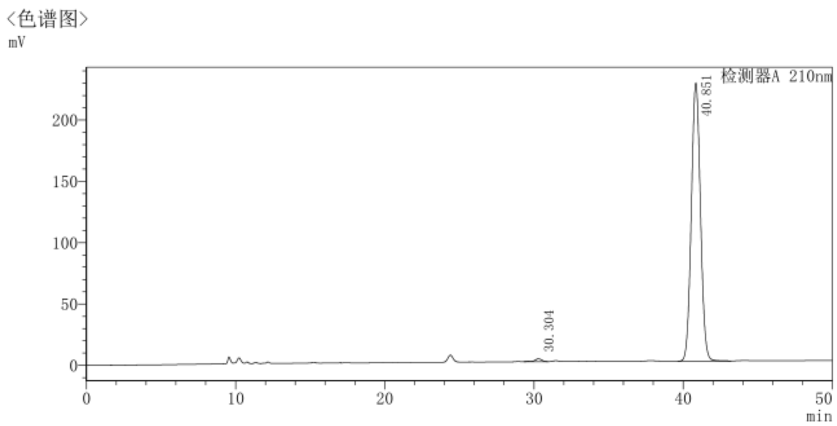
98% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



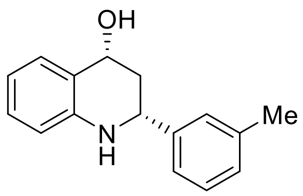
	Retention Time (min)	Area (%)
Peak 1	30.337	50.328
Peak 2	40.206	49.672

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	30.304	0.793	**98% ee**
Peak 2	40.851	99.207	

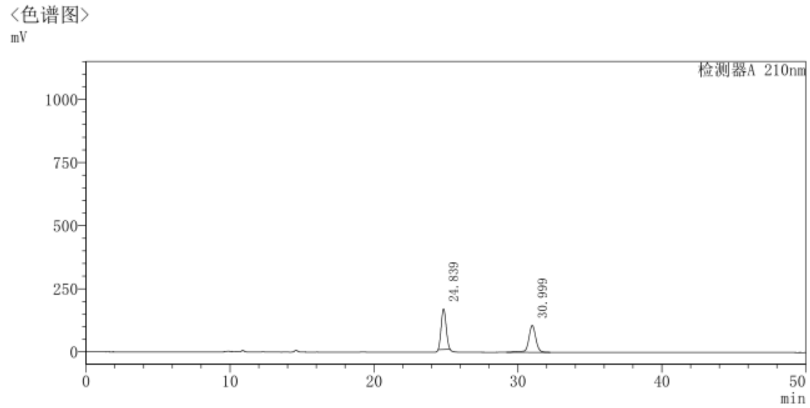
Figure S164 HPLC Data of (2*R*,4*R*)-**2k**



(2*R*,4*R*)-**2l**

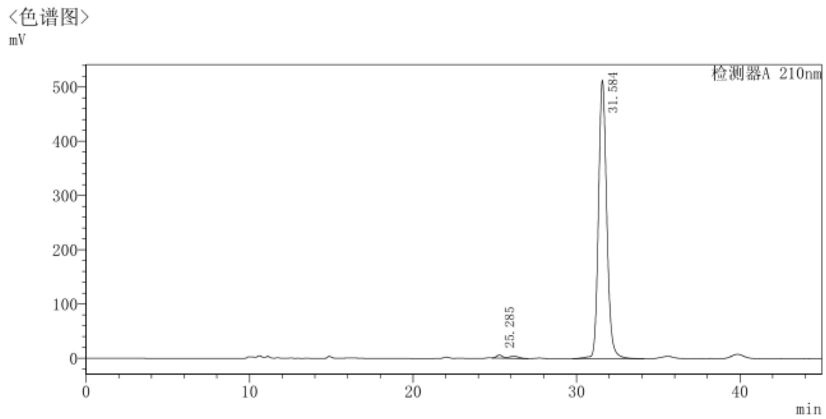
97% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



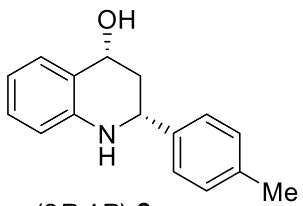
	Retention Time (min)	Area (%)
Peak 1	24.040	52.190
Peak 2	27.530	47.810

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	25.285	1.556	**97% ee**
Peak 2	31.584	98.444	

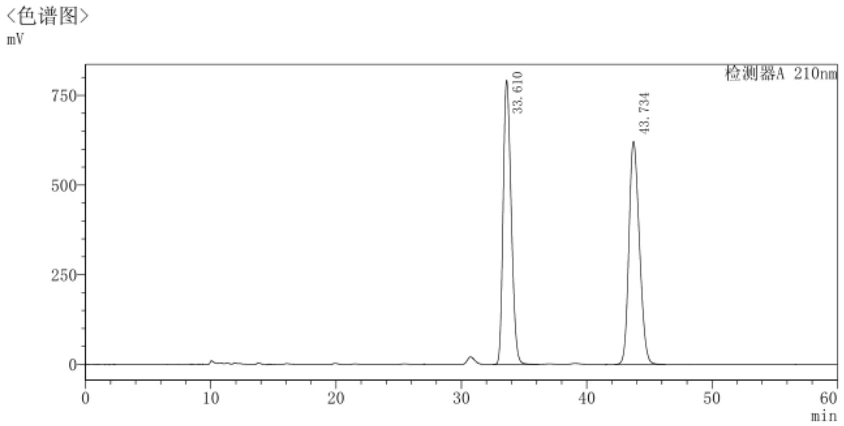
Figure S165 HPLC Data of (2*R*,4*R*)-**2l**



(2*R*,4*R*)-**2m**

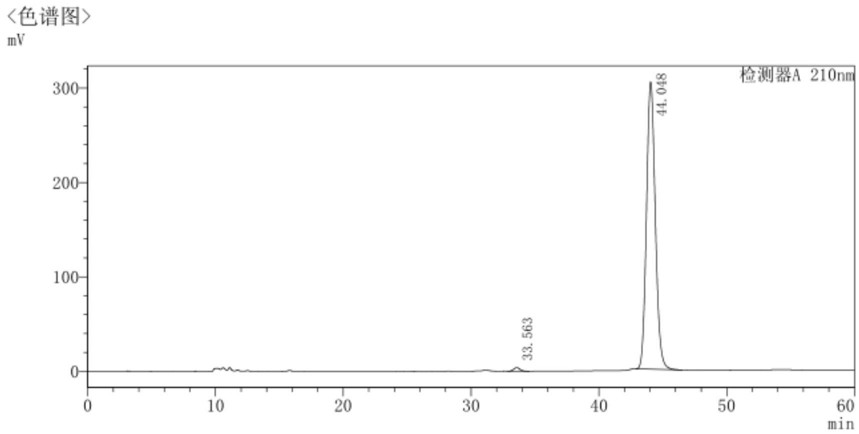
98% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



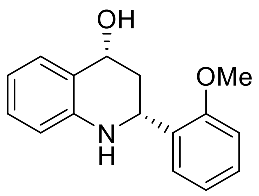
	Retention Time (min)	Area (%)
Peak 1	33.610	49.454
Peak 2	43.734	50.546

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	33.563	0.907	**98% ee**
Peak 2	44.048	99.093	

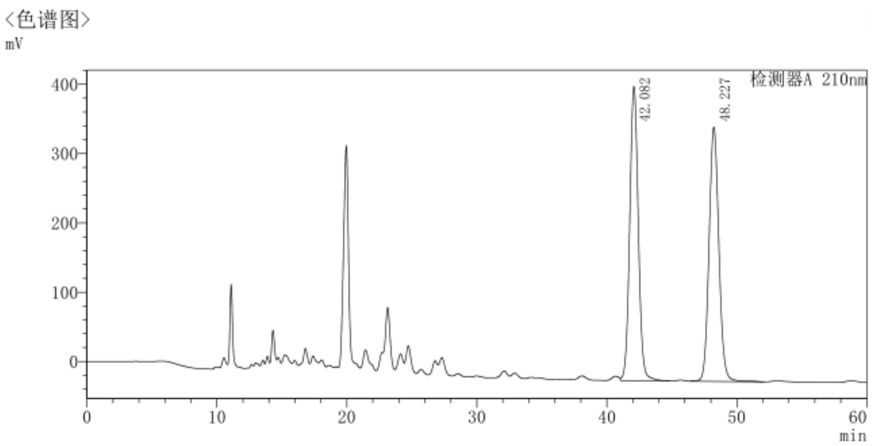
Figure S166 HPLC Data of (2*R*,4*R*)**-2m**



(2*R*,4*R*)-**2n**

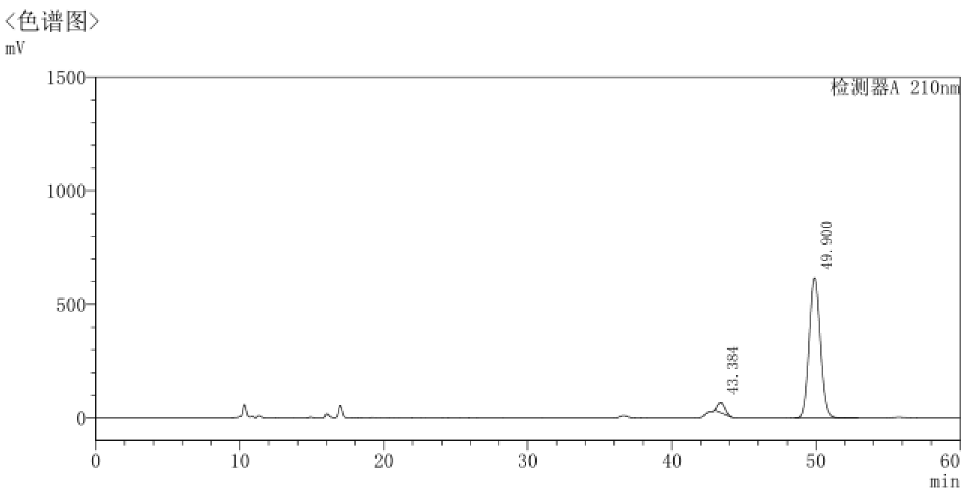
91% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



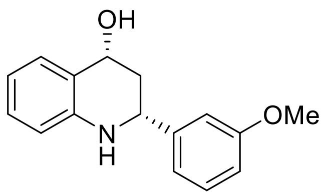
	Retention Time (min)	Area (%)
Peak 1	42.082	50.141
Peak 2	48.227	49.859

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	43.384	4.484	**91% ee**
Peak 2	49.900	95.516	

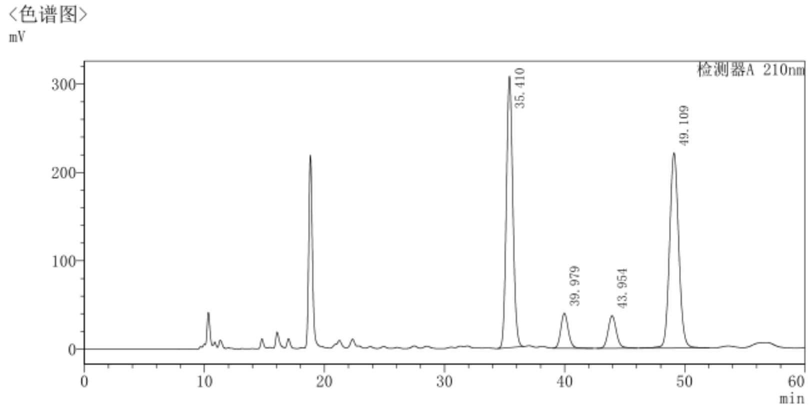
Figure S167 HPLC Data of (2*R*,4*R*)-**2n**



(2*R*,4*R*)-**2o**

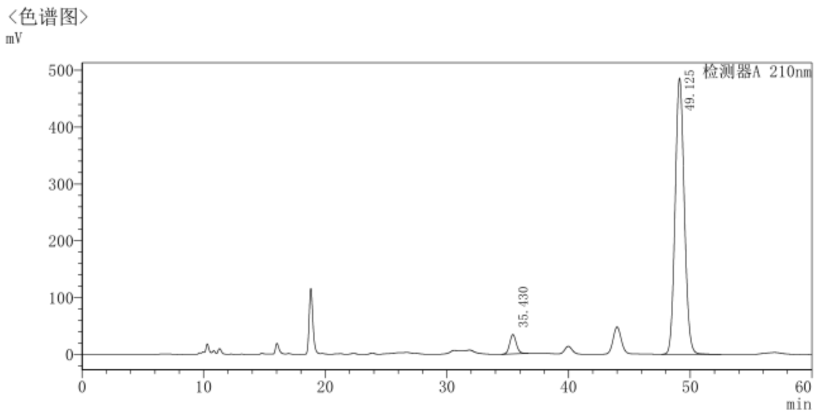
90% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



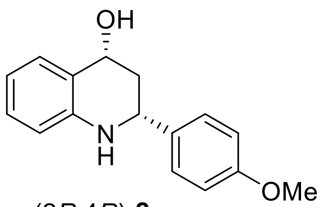
	Retention Time (min)	Area (%)
Peak 1	35.410	43.074
Peak 2	39.979	6.443
Peak 3	43.954	6.633
Peak 4	49.109	43.850

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	35.430	4.814	**90% ee**
Peak 2	49.125	95.186	

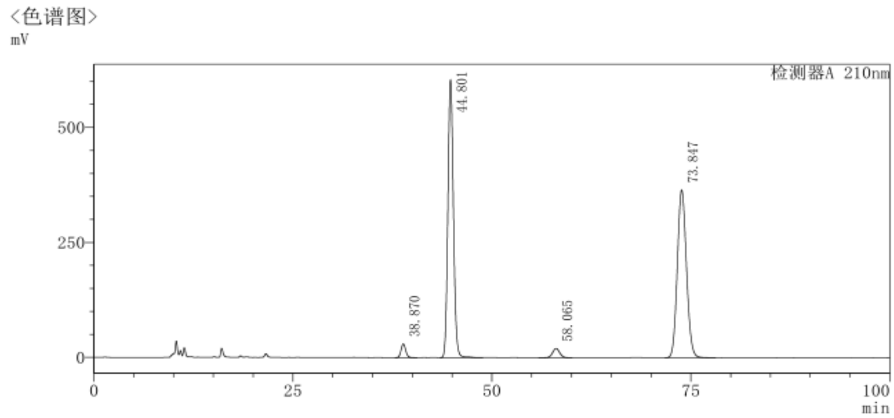
Figure S168 HPLC Data of (2*R*,4*R*)-**2o**



(2*R*,4*R*)-**2p**

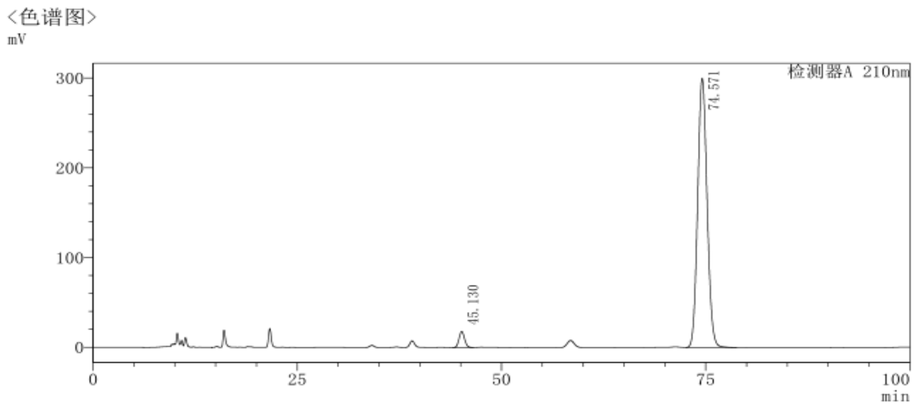
93% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



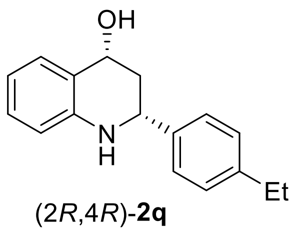
	Retention Time (min)	Area (%)
Peak 1	38.870	2.019
Peak 2	44.801	47.883
Peak 3	58.065	2.078
Peak 4	73.847	48.020

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	45.130	3.427	**93% ee**
Peak 2	74.571	96.573	

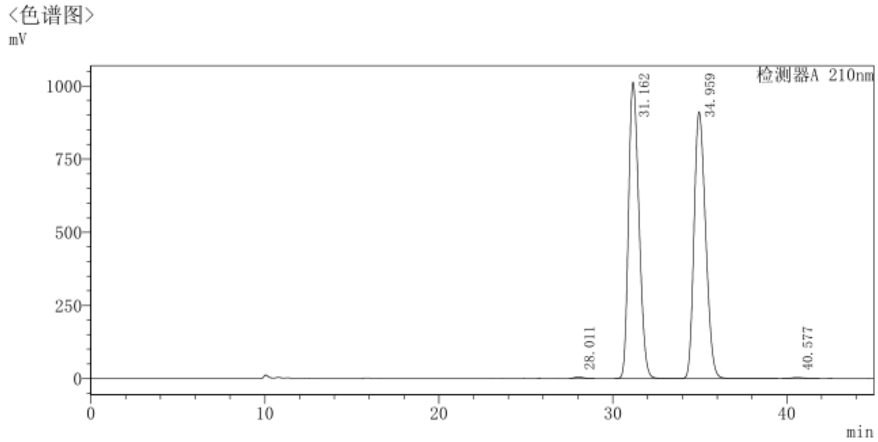
Figure S169 HPLC Data of (2*R*,4*R*)-**2p**



(2*R*,4*R*)-**2q**

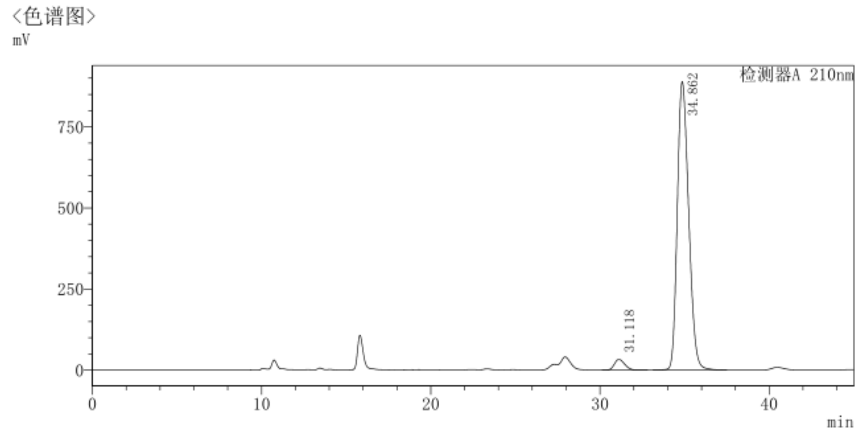
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



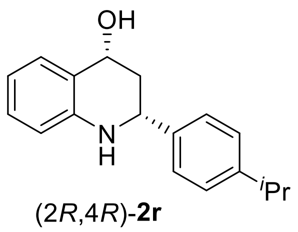
	Retention Time (min)	Area (%)
Peak 1	23.466	0.182
Peak 2	29.122	49.765
Peak 3	34.959	49.843
Peak 4	40.577	0.210

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	31.118	3.254	**93% ee**
Peak 2	34.862	96.746	

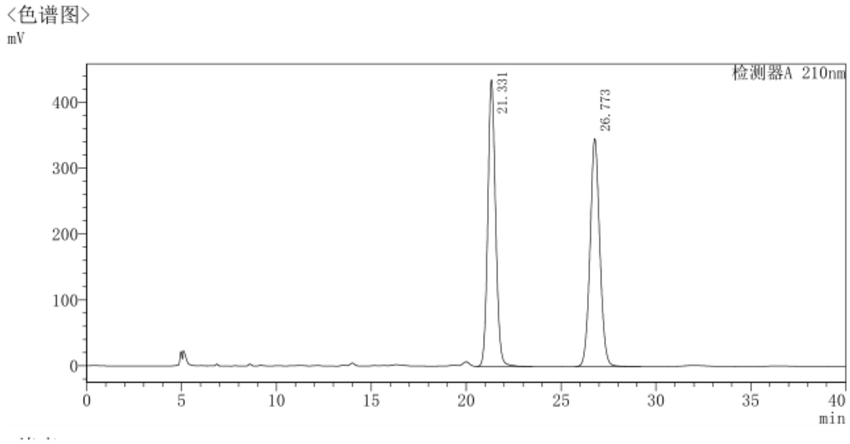
Figure S170 HPLC Data of (2*R*,4*R*)-**2q**



(2*R*,4*R*)-**2r**

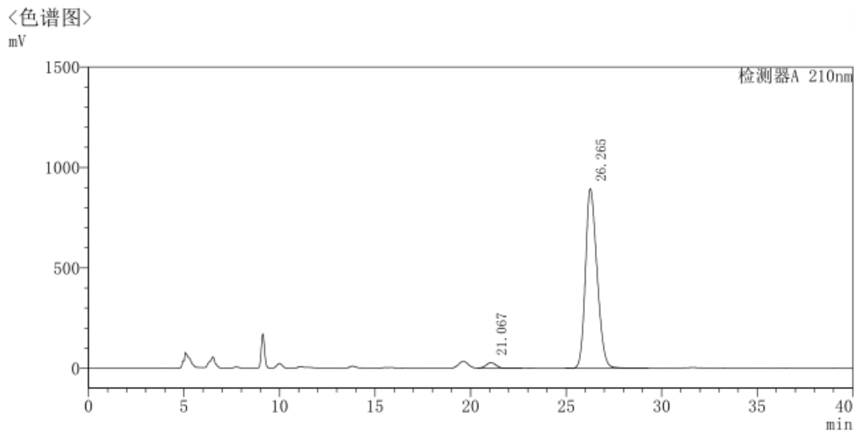
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IE-H column, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, 210 nm.

Racemate:



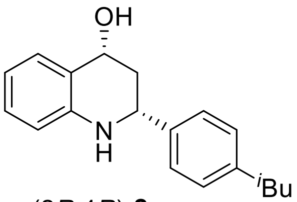
	Retention Time (min)	Area (%)
Peak 1	21.331	49.966
Peak 2	26.773	50.034

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	23.128	2.441	**95% ee**
Peak 2	29.057	97.559	

Figure S171 HPLC Data of (2*R*,4*R*)-**2r**

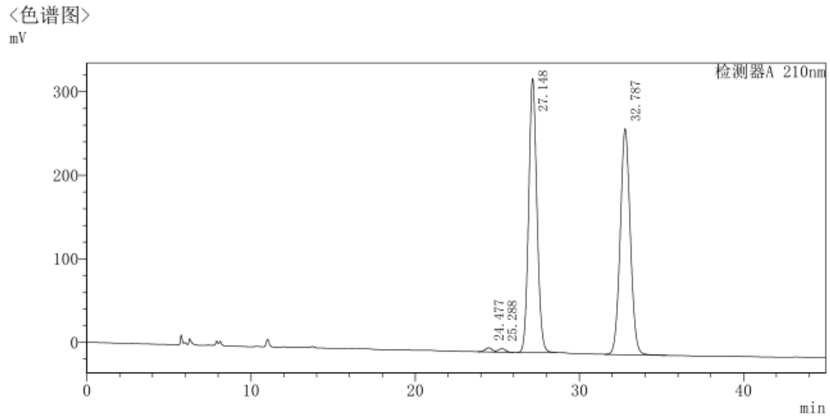


(2*R*,4*R*)-**2s**

v

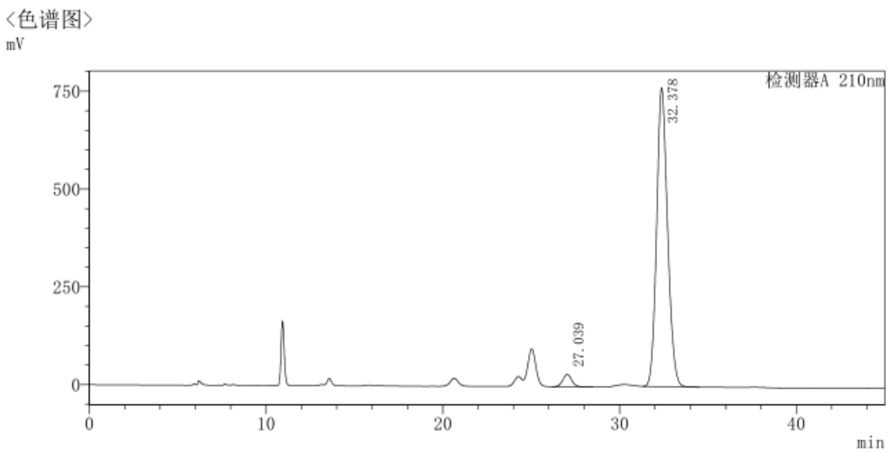
93% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IE-H column, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, 210 nm.

Racemate:



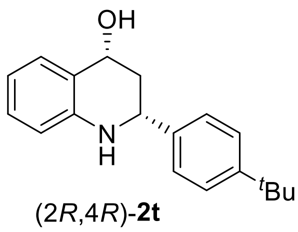
	Retention Time (min)	Area (%)
Peak 1	24.477	0.654
Peak 2	25.288	0.558
Peak 3	27.148	49.166
Peak 4	32.787	49.622

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	27.039	3.265	**93% ee**
Peak 2	32.378	96.735	

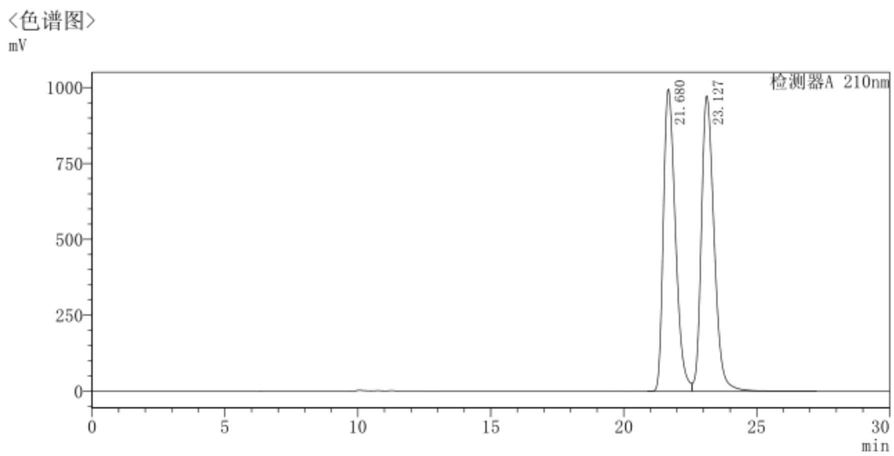
Figure S172 HPLC Data of (2*R*,4*R*)-**2s**



(2*R*,4*R*)-**2t**

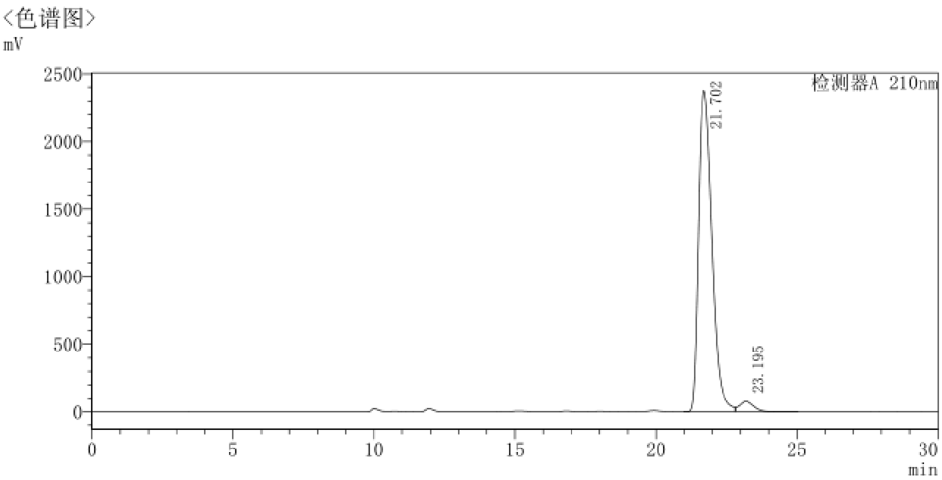
93% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



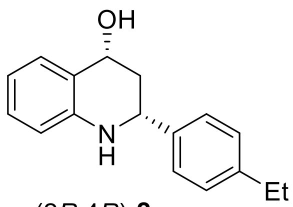
	Retention Time (min)	Area (%)
Peak 1	21.680	49.139
Peak 2	23.127	50.861

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	21.702	96.546	**93% ee**
Peak 2	23.195	3.454	

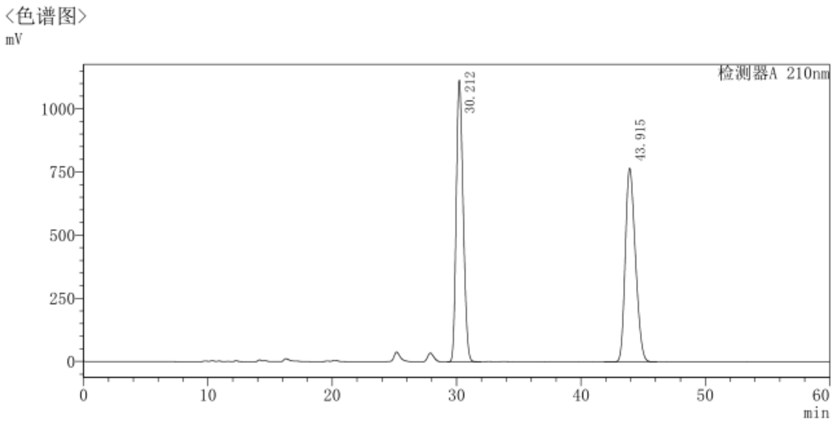
Figure S173 HPLC Data of (2*R*,4*R*)-**2t**



(2*R*,4*R*)-**2u**

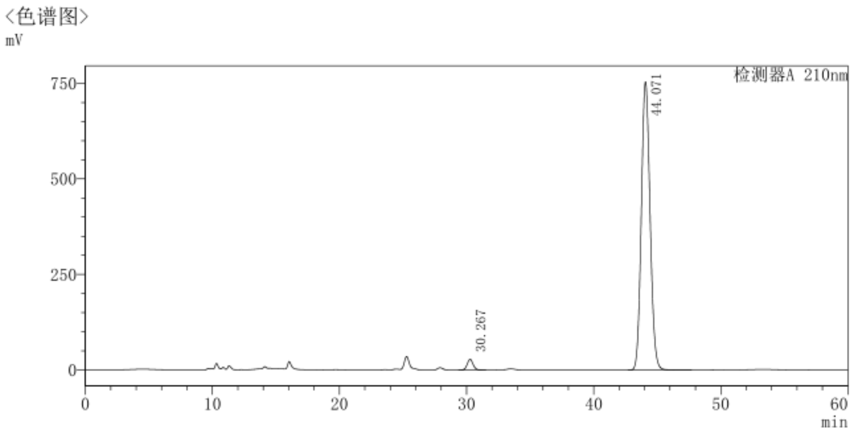
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



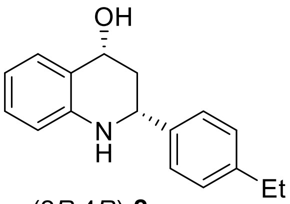
	Retention Time (min)	Area (%)
Peak 1	30.212	49.718
Peak 2	43.915	50.282

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	30.267	2.453	**95% ee**
Peak 2	44.071	97.547	

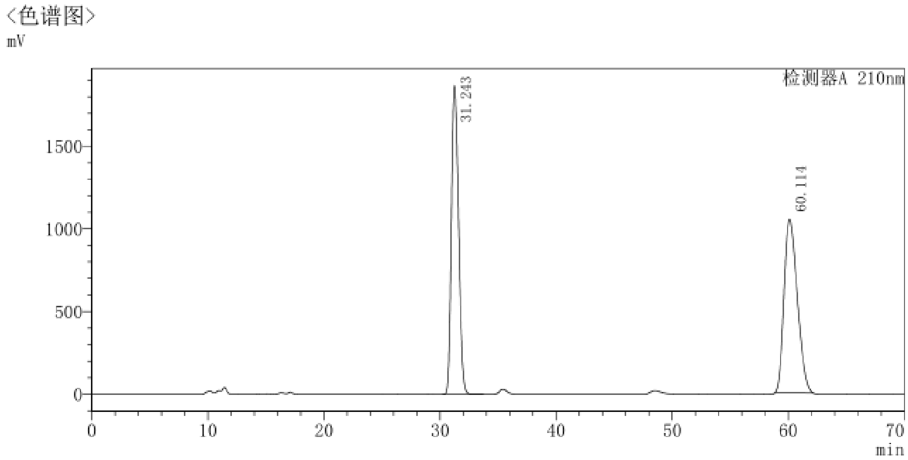
Figure S174 HPLC Data of (2*R*,4*R*)-**2u**



(2*R*,4*R*)-**2v**

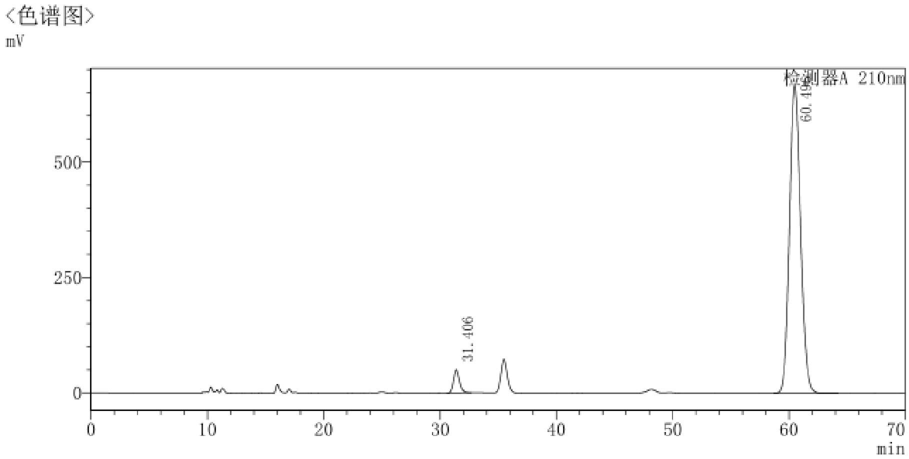
92% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



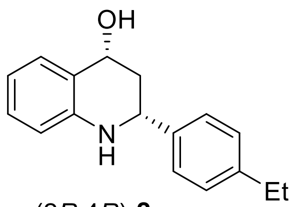
	Retention Time (min)	Area (%)
Peak 1	31.243	49.126
Peak 2	60.114	50.874

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	31.406	3.853	**92% ee**
Peak 2	60.496	96.147	

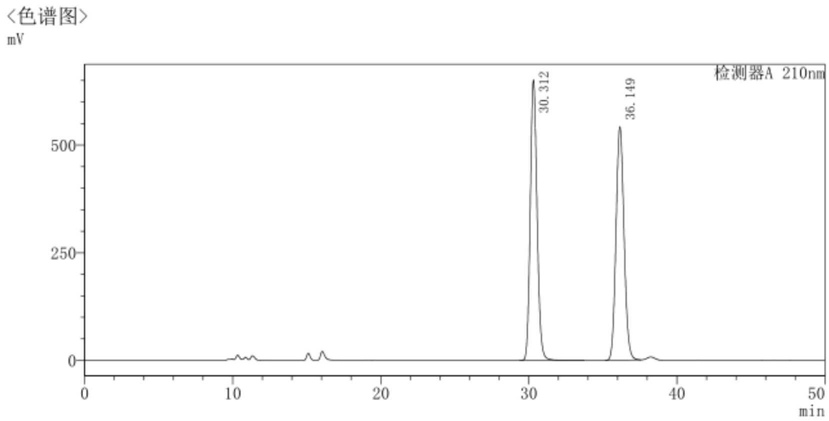
Figure S175 HPLC Data of (2*R*,4*R*)-**2v**



(2*R*,4*R*)-**2w**

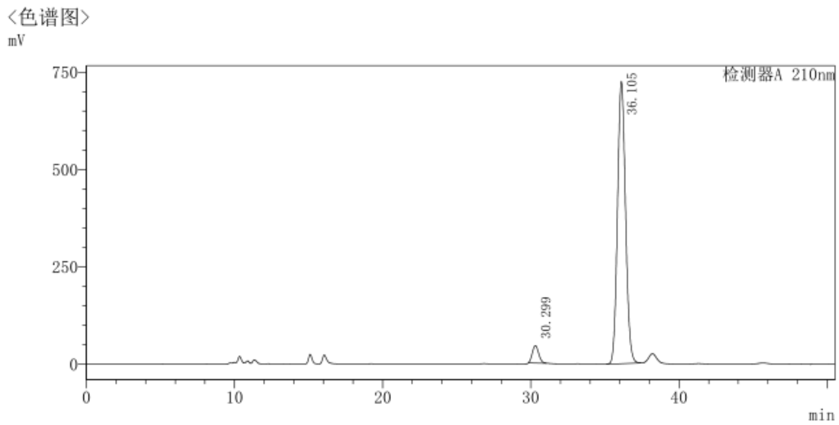
90% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



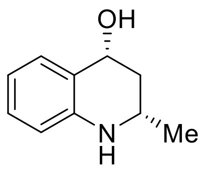
	Retention Time (min)	Area (%)
Peak 1	30.312	50.532
Peak 2	36.149	49.468

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	30.299	4.670	**90% ee**
Peak 2	36.105	95.330	

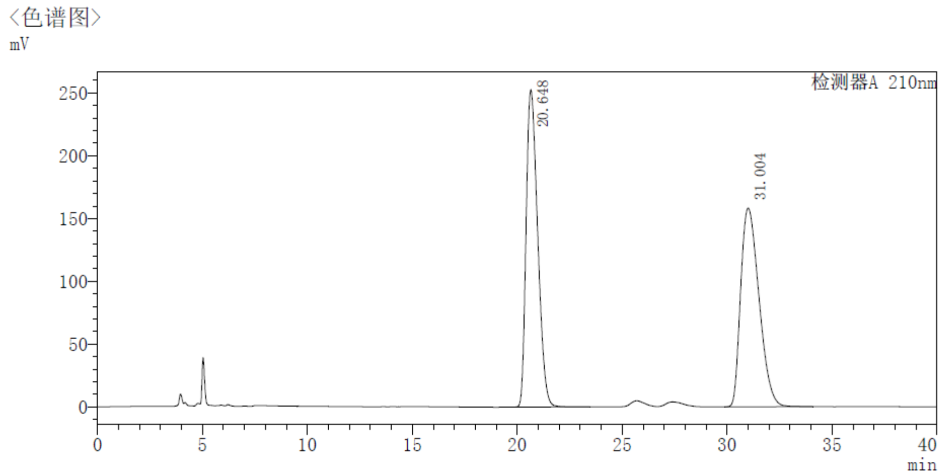
Figure S176 HPLC Data of (2*R*,4*R*)-**2w**



(2*S*,4*R*)-**2x**

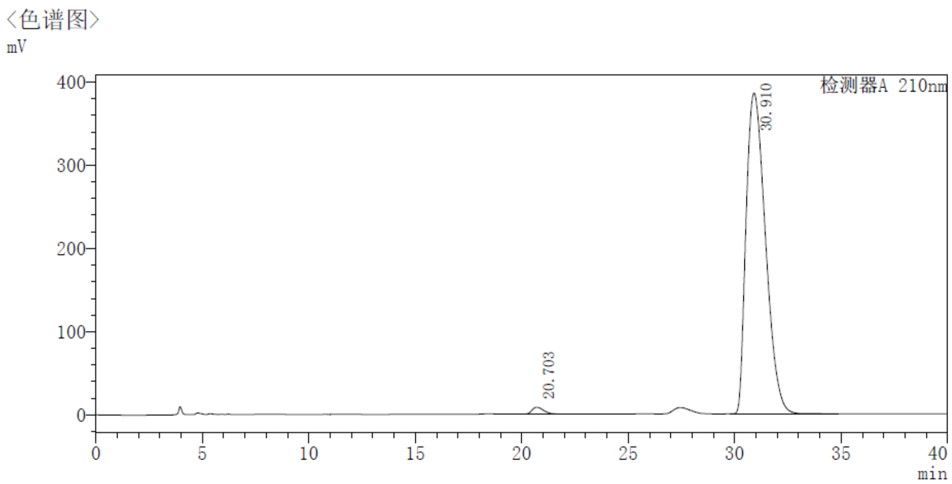
98% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OJ-H column, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 210 nm.

Racemate:



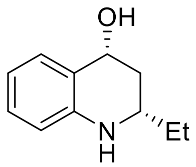
	Retention Time (min)	Area (%)
Peak 1	16.671	1.282
Peak 2	23.829	98.718

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	20.648	50.158	**98% ee**
Peak 2	31.004	49.842	

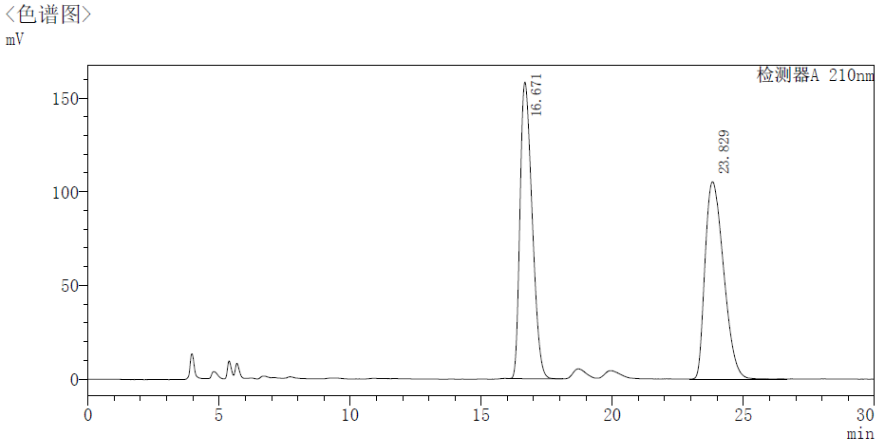
Figure S177 HPLC Data of (2*S*,4*R*)-**2x**



(2*S*,4*R*)-**2y**

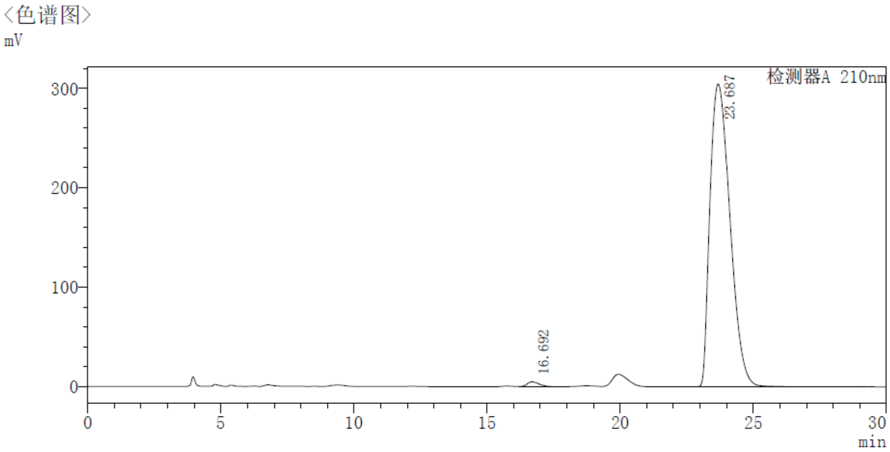
98% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OJ-H column, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 210 nm.

Racemate:



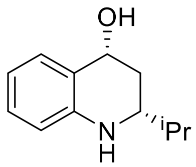
	Retention Time (min)	Area (%)
Peak 1	16.671	49.727
Peak 2	23.829	50.273

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	16.692	0.935	**98% ee**
Peak 2	23.687	99.065	

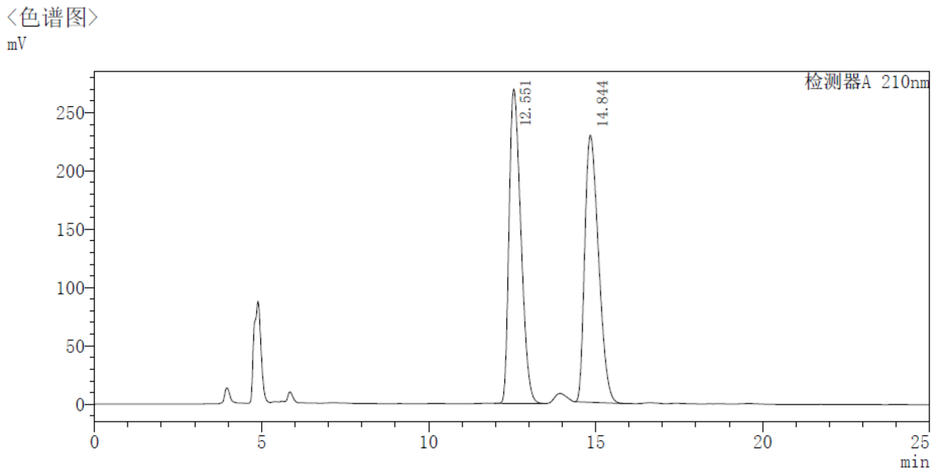
Figure S178 HPLC Data of (2*S*,4*R*)-**2y**



(2*R*,4*R*)-**2z**

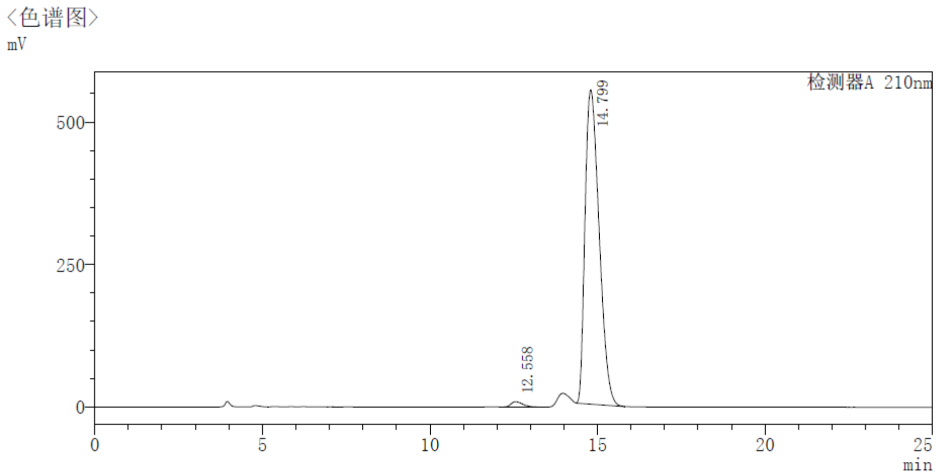
97% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OJ-H column, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 210 nm.

Racemate:



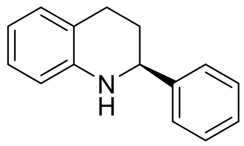
	Retention Time (min)	Area (%)
Peak 1	12.551	50.299
Peak 2	14.844	49.701

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	12.558	1.410	**97% ee**
Peak 2	14.799	98.590	

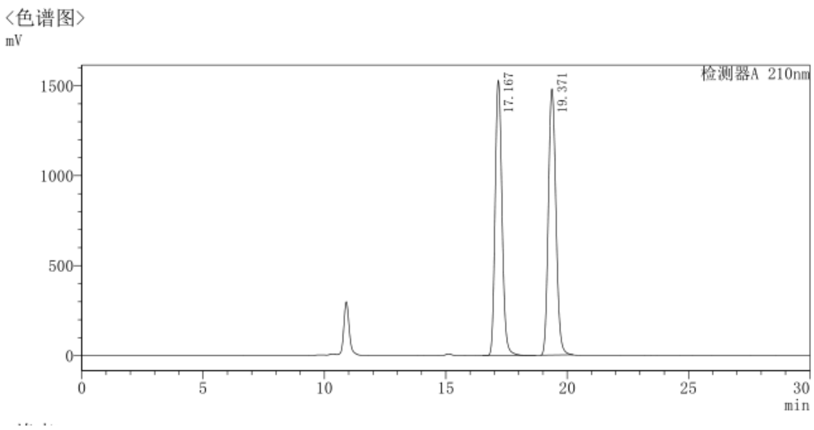
Figure S179 HPLC Data of (2*R*,4*R*)-**2z**



(*S*)-**3**

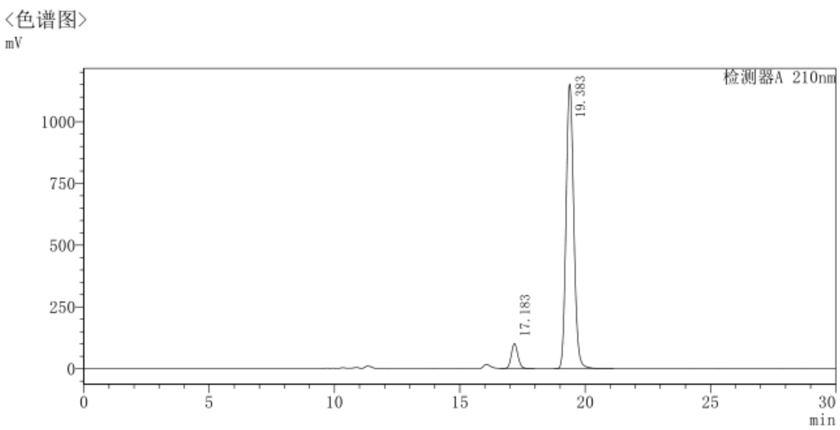
86% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



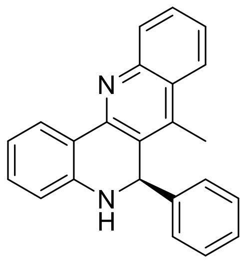
	Retention Time (min)	Area (%)
Peak 1	17.167	48.507
Peak 2	19.371	51.493

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	17.183	6.994	**86% ee**
Peak 2	19.383	93.006	

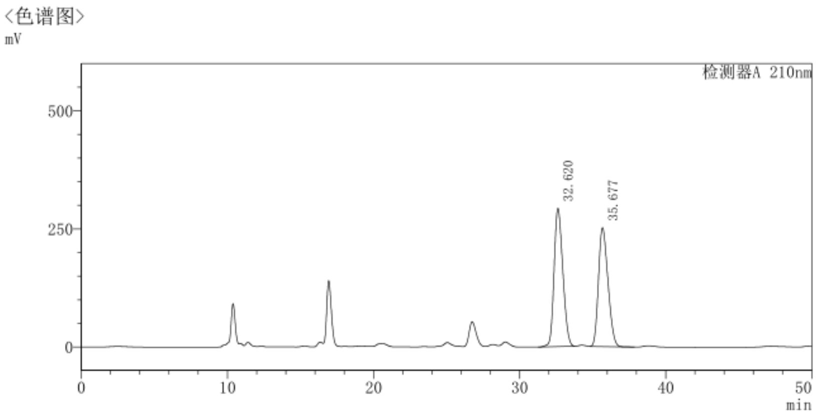
Figure S180 HPLC Data of (*S*)-**3**



(*S*)-**4**

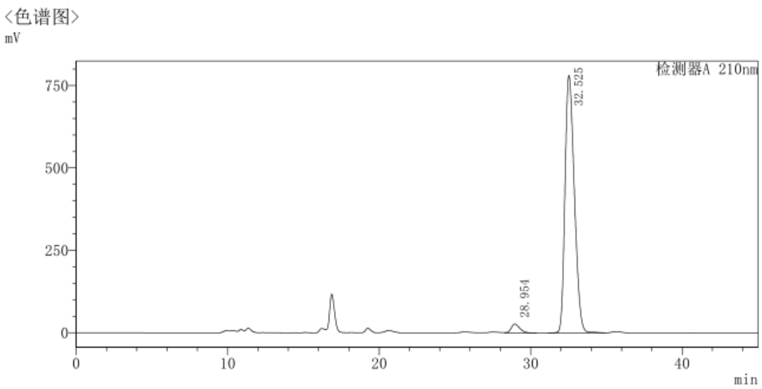
94% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80/20, 0.3 mL/min, 210 nm.

Racemate:



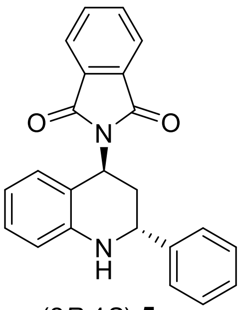
	Retention Time (min)	Area (%)
Peak 1	32.620	51.806
Peak 2	35.677	48.194

Chiral:



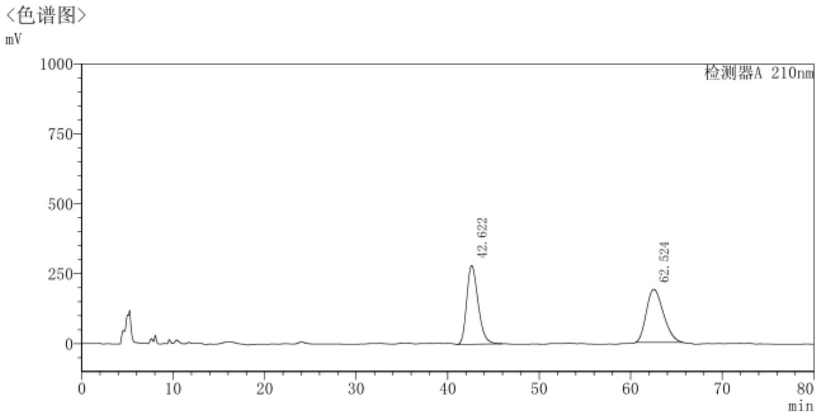
	Retention Time (min)	Area (%)	
Peak 1	28.954	2.923	**94% ee**
Peak 2	32.525	97.077	

Figure S181 HPLC Data of (*S*)-**4**



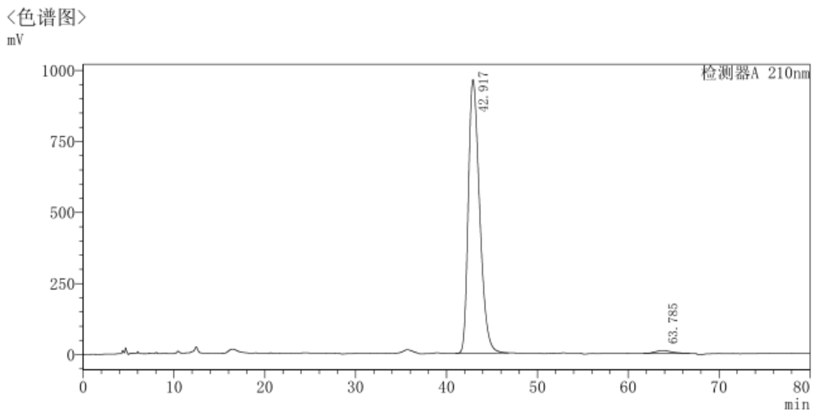
(2*R*,4*S*)-**5**

97% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, 210 nm.
Racemate:



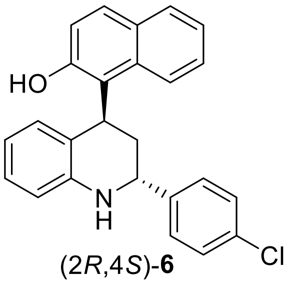
	Retention Time (min)	Area (%)
Peak 1	42.622	49.856
Peak 2	62.524	50.144

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	42.917	98.462	**97% ee**
Peak 2	63.785	1.538	

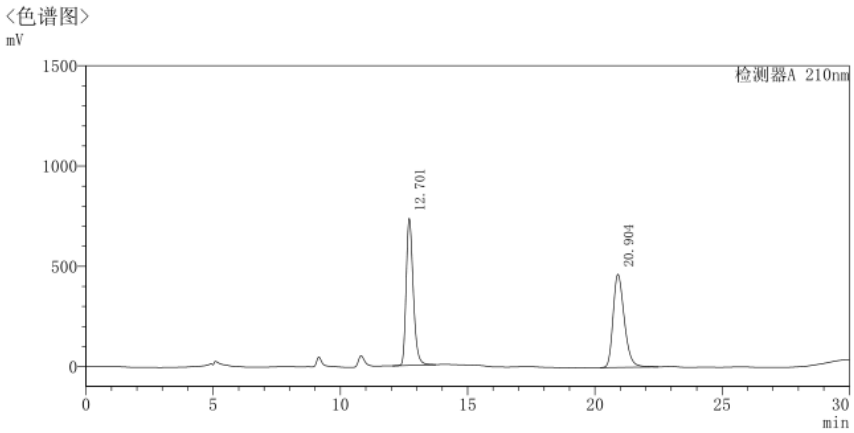
Figure S182 HPLC Data of (2*R*,4*S*)-**5**



(2*R*,4*S*)-**6**

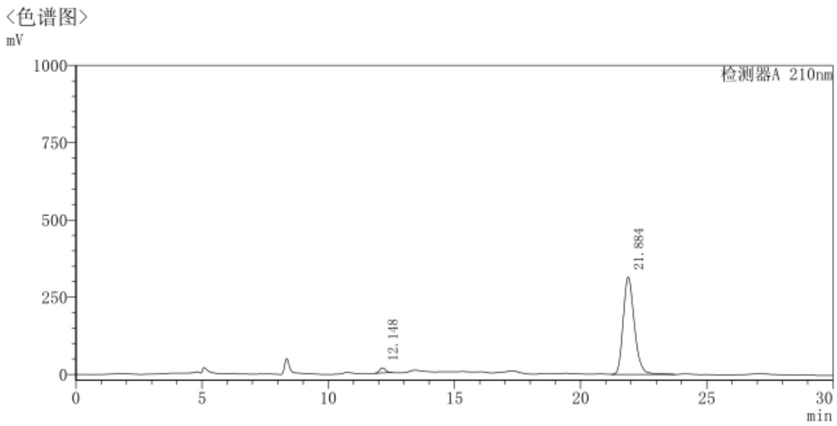
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 97/3, 0.7 mL/min, 210 nm.

Racemate:



	Retention Time (min)	Area (%)
Peak 1	12.701	49.991
Peak 2	20.904	50.009

Chiral:



	Retention Time (min)	Area (%)	
Peak 1	12.148	2.720	**95% ee**
Peak 2	21.884	97.280	

Figure S183 HPLC Data of (2*R*,4*S*)-**6**