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Supporting Information

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Supporting Information for

The Development of New Double Axially Chiral Phosphoric Acids and Their Catalytic Asymmetric Transfer Hydrogenation of Quinolines

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Contents of Supporting Information

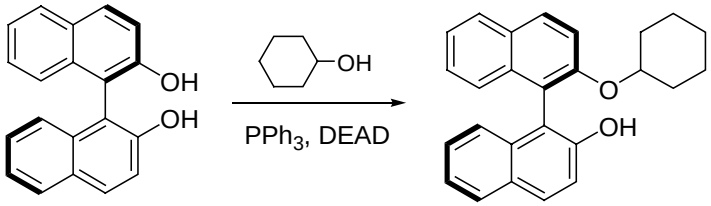
Experimental Details

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or under argon. Unless otherwise indicated, all commercially available compounds were used without further purification. THF was either distilled over benzophenone ketyl under nitrogen or purified by passing through a neutral alumina column under nitrogen. Et_2O was purified by passing through a neutral alumina column under nitrogen. CH_2Cl_2 was distilled over CaH_2 under nitrogen. DMF was distilled over CaH_2 under vacuum. DME was distilled over benzophenone ketyl under nitrogen. Column chromatography was carried out using silica gel (200-300 mesh). Melting points were measured on an XT-4 melting point apparatus and uncorrected. The ^1H NMR spectra were recorded on Varian Mercury Plus (300 MHz) or Bruker ARX-400 (400 MHz) spectrometer. ^{13}C NMR spectra and ^{31}P NMR spectra were recorded on Varian Mercury Plus spectrometer (75 MHz and 121 MHz, respectively). Infrared spectra were obtained on a Nicolet AVATAR 330 FT-IR spectrometer. Mass spectra were obtained on a VG ZAB-HS (EI) mass spectrometer or Thermo Finnigan LCQ Decaxp PLUS LC/MS spectrometer (ESI). Elemental analyses were carried out on an Elementar VARIO EL instrument. Optical rotations were measured on a Perkin-Elmer 341 LC spectrometer. The enantiomeric excesses of products were determined by analytical high performance liquid chromatography (HPLC) on Aglilent HP1100 liquid chromatograph equipped with a DVD detector using the Diacel Chiralcel OD-H or OJ columns. HPLC grade isopropyl alcohol and *n*-hexane were used as eluting solvents.

1. Synthesis of phosphoric acid catalysts

Compounds **2a**–**2c** were prepared in according to the literature procedures.[1]

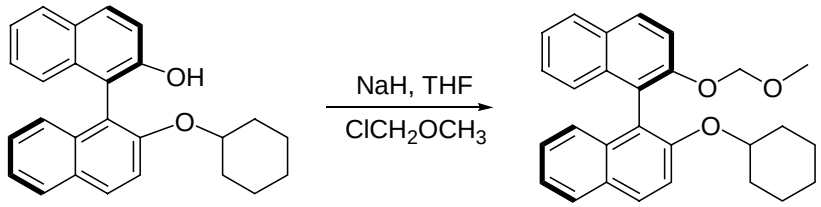
Synthesis of (R)-2'-Cyclohexyloxy-(1,1'-binaphthalen)-2-ol[2]



To a stirred solution of (*R*)-BINOL (8.58 g, 30 mmol), triphenylphosphine (7.86 g, 30 mmol) and cyclohexanol (9.0 g, 90 mmol) in THF (60 mL) was added DEAD (5.22 g, 30 mmol) in THF (40 mL) dropwise in 4 h at room temperature. After stirring for 20 h at the same temperature, the mixture was evaporated under reduced pressure and the residue was purified by

silica gel column chromatography to give (*R*)-BINOL monocyclohexanyl ether (4.3 g, 39% yield) from a petroleum ether (60–90 °C)–CH_2Cl_2–AcOEt (40:10: 1) eluent as a colorless oil and the unreacted (*R*)-BINOL (5.0 g, 58% yield) from a petroleum ether (60–90 °C)–CH_2Cl_2–AcOEt (10:10: 1) eluent. $[\alpha]_D^{20}$ = –55.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.93–1.64 (m, 10H), 4.06–4.15 (m, 1H), 5.14 (s, 1H), 7.05–7.34 (m, 8H), 7.74–7.81 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.9, 23.0, 25.2, 31.6, 76.9, 115.4, 117.2, 117.5, 117.6, 122.9, 124.0, 125.0, 125.1, 126.0, 126.8, 127.8, 127.9, 128.9, 129.3, 129.4, 130.3, 133.8, 134.2, 151.2, 154.3; IR (FT-IR, film): 2934, 2856, 1619, 1591, 1506, 1470, 1380, 1330, 1264, 1146, 814, 748 cm^{-1}; MS (70 ev EI): m/z (%) 412 (68), 330 (100), 298 (40), 285 (30), 270 (45), 239 (24). MS (70 ev EI): m/z (%) 368 (M^+, 20), 286 (100), 257 (8), 239 (10). HRMS (EI) calcd for $C_{26}H_{24}O_2$: 368.17763, found: 368.17844.

Synthesis of (R)-2-cyclohexyloxy-2'-(methoxymethoxy)-1,1'-binaphthalene ***2d***

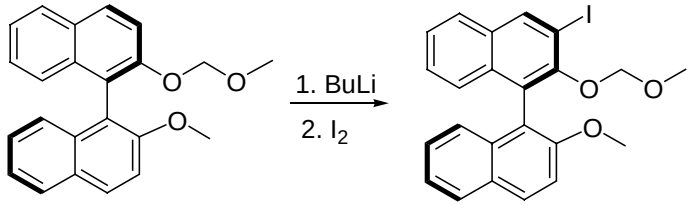


2d

To a stirred solution of (*R*)-BINOL monocyclohexyl ether (9.74 g, 26.47 mmol), in THF (60 mL) was added 1.81 g of NaH (53 mmol, 70% in mineral oil) at 0 °C. The reaction mixture was stirred for an additional 1 h at room temperature and then chloromethyl methyl ether (3.0 mL, 37 mmol) was added slowly at 0 °C. The reaction was followed with TLC and was complete within 6 h after the addition of chloromethyl methyl ether. The reaction mixture was added to 100 ml of water and the aqueous layer was separated and extracted three times with ethyl acetate. The organic layer was washed with water and brine. This was dried with Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography with petroleum ether (60–90 °C)-CH_2Cl_2-AcOEt (40:10: 1) as eluent to give **2d** (10.6 g, 97%) as a colorless oil. $[\alpha]_D^{20}$ = +64.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83–1.67 (m, 10H), 3.16 (s, 3H), 4.06–4.14 (m, 1H), 4.95 (d, *J* = 6.6 Hz, 1H), 5.04 (d, *J* = 6.9 Hz, 1H), 7.15–7.30 (m, 6H), 7.37 (d, *J* = 9.0 Hz, 1H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.79–7.89 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.2, 23.3, 25.3, 31.8, 32.1, 55.7, 77.1, 95.2, 117.1, 117.8, 121.6, 121.6, 123.5, 123.8, 125.4,

125.7, 125.9, 126.0, 127.7, 127.7, 128.9, 129.0, 129.2, 129.7, 134.0, 134.2, 152.8, 153.5; IR (FT-IR, film): 2933, 2854, 1621, 1592, 1260, 1237, 1147, 1035, 1015, 809, 749 cm^{-1}; MS (70 ev EI): m/z (%) 412 (M^+, 68), 330 (100), 298 (40), 285 (30), 270 (45), 239 (24). HRMS (EI) calcd for $C_{28}H_{28}O_3$: 412.20384, found: 412.20372.

*Synthesis of compounds **3a–3d.***[3]

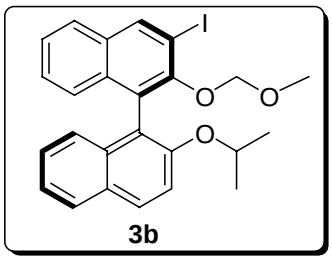


2a **3a**

General procedure: To a solution of **3a** (4.6 g, 13.4 mmol) in anhydrous THF (100 mL), *n*-BuLi (7.0 mL, 16 mmol, 2.3 M solution in hexane) was added dropwise at −78 °C, after warm to room temperature, the reaction mixture was stirred for 2 h. A solution of iodine (4.57 g, 36 mmol) in THF (20 mL) was added to the reaction mixture at −78°C, after stirring for an additional 1 h, saturated aqueous solution of $Na_2S_2O_3$ (30 ml) was added. After warm to room temperature, the mixture was stirred for 1 h at room temperature. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (3 × 40 mL). The combined organic layer was dried over anhydrous $NaSO_4$. After evaporation, the residue was purified by flash chromatography on silica gel column chromatography to give **3a** (4.7 g, 75% yield) from a petroleum ether(60–90 °C)–AcOEt (10: 1) eluent as a pale yellow oil.

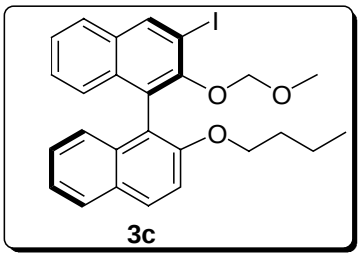
(*R*)-2-Methoxy-2'-(methoxymethoxy)-3'-iodo-1,1'-binaphthalene **3a**: $[\alpha]_D^{25}$ = +81.5 (*c* 0.8, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 2.65 (s, 3H), 3.71 (s, 3H), 4.57 (d, *J* = 5.4 Hz, 1H), 4.67 (d, *J* = 5.1 Hz, 1H), 7.02–7.36 (m, 7H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 8.43 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.5, 56.8, 92.9, 99.1, 113.2, 118.6, 123.7, 125.1, 125.5, 125.9, 126.3, 126.7, 126.8, 126.9, 127.8, 128.8, 130.1, 132.4, 133.7, 133.8, 139.3, 151.5, 155.0; IR (FT-IR, film): 2930, 1622, 1594, 1509, 1350, 1270, 1262, 1159, 1090, 986, 956, 813, 747 cm^{-1}; MS (70 ev EI): m/z (%) 470 (M^+, 100), 440 (42), 394 (55), 343 (20), 312 (25), 239 (55), 226 (35). HRMS (EI) calcd for $C_{23}H_{19}O_3I$: 470.03790, found: 470.03707.

(*R*)-2-Isopropoxy-2'-(methoxymethoxy)-3'-iodo-1,1'-binaphthalene **3b**: Reaction performed utilizing the same procedure for the preparation of **3a.** Yield 73%; a pale yellow oil; $[\alpha]_D^{20}$ = +93.8 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 0.95 (d, *J* = 6.0 Hz, 3H), 1.13 (d, *J* = 6.0 Hz, 3H), 2.77 (s, 3H), 4.43–4.54 (m, 1H), 4.62 (d, *J* = 5.1 Hz, 1H), 4.78 (d, *J* = 5.1 Hz, 1H), 7.12–7.38 (m, 7H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 8.48 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.2, 22.3, 56.8, 71.1, 92.8, 99.0, 115.7, 119.8, 123.6, 125.2, 125.3, 126.1, 126.3, 126.5, 126.6, 127.7, 128.7, 129.8, 132.3, 133.8, 134.0, 139.0, 151.5, 153.6; IR (FT-IR, film): 3060, 2974, 2932, 1621, 1592, 1507, 1466, 1439, 1385, 1260, 1243, 1112, 983, 953, 810, 749 cm^{-1}; MS (70 ev EI): m/z (%) 498 (M^+, 75), 456 (34), 424(30), 297 (75), 269 (40), 239 (45), 226 (48). HRMS (EI) calcd for $C_{25}H_{23}IO_3$: 498.06920, found: 498.06895.



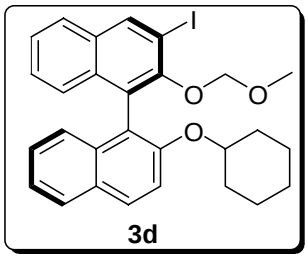
3b

(*R*)-2-Butoxy-2'-(methoxymethoxy)-3'-iodo-1,1'-binaphthalene **3c**: Reaction performed utilizing the same procedure for the preparation of **3a**. Yield 69%; a pale yellow oil; $[\alpha]_D^{20}$ = +54.1 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 0.66 (t, *J* = 7.5 Hz, 3H), 0.96–1.05 (m, 2H), 1.40–1.45 (m, 2H), 2.74 (s, 3H), 3.94–4.06 (m, 2H), 4.62 (d, *J* = 5.1 Hz, 1H), 4.73 (d, *J* = 5.4 Hz, 1H), 7.14–7.42 (m, 7H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 8.49 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 18.7, 31.3, 56.8, 69.0, 92.8, 99.1, 114.7, 119.2, 123.7, 125.2, 125.4, 126.1, 126.5, 126.7, 126.8, 126.9, 127.8, 128.9, 130.0, 132.4, 133.8, 133.9, 139.1, 151.5, 154.7; IR (FT-IR, film): 2928, 1593, 1508, 1463, 1350, 1271, 1159, 1085, 984, 956, 748 cm^{-1}; MS (70 ev EI): m/z (%) 512 (M^+, 100), 482 (10), 426(40), 297 (42), 269 (22), 239 (26), 226 (23). HRMS (EI) calcd for $C_{26}H_{25}O_3I$: 512.08485, found: 512.08375.



3c

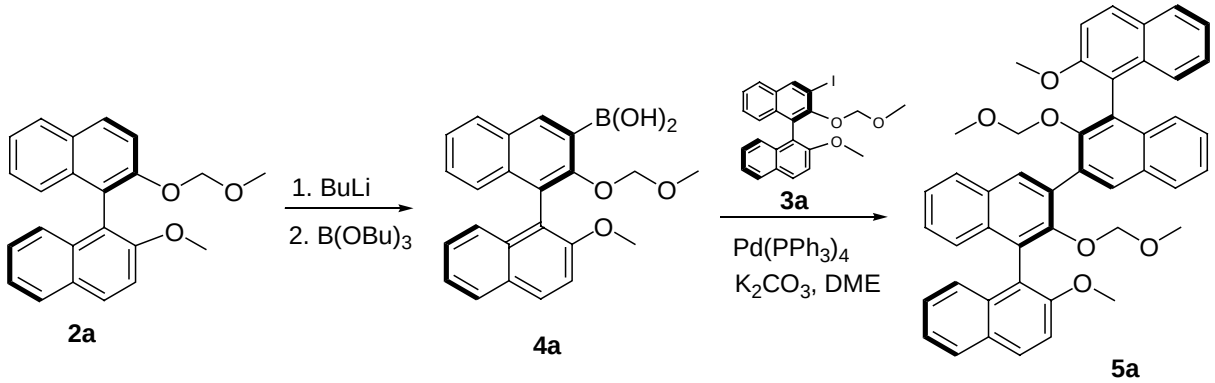
(*R*)-2-Cyclohexyloxy-2'-(methoxymethoxy)-3'-iodo-1,1'-binaphthalene **3d**: Reaction performed utilizing the same procedure for the preparation of 3a. Yield 76%; a pale yellow oil; $[\alpha]_D^{20}$ = +56.6 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 0.85–1.39 (m, 7H), 1.48–1.56 (m, 2H), 1.79–1.84 (m, 1H), 2.77 (s, 3H), 4.20–4.27 (m, 1H), 4.62 (d, *J* = 5.4 Hz, 1H), 4.78 (d, *J* = 5.1 Hz, 1H), 7.13–7.38 (m, 7H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 9.0 Hz,



3d

1H), 8.48 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.2, 23.4, 25.3, 31.8, 32.1, 56.9, 76.2, 92.8, 99.0, 115.6, 119.7, 123.5, 125.2, 125.3, 126.25, 126.34, 126.6, 126.7, 127.7, 128.7, 129.7, 132.3, 133.9, 134.0, 138.9, 151.5, 153.6; IR (FT-IR, film): 2932, 2855, 1621, 1592, 1508, 1466, 1349, 1270, 1236,1159, 983, 954, 747 cm^{-1}; MS (70 ev EI): m/z (%) 538 (M^+, 64), 456 (75), 426(30), 297 (54), 269 (22), 255 (30), 226 (24). HRMS (EI) calcd for $C_{28}H_{27}O_3I$: 538.10050, found: 538.10077.

*Synthesis of compounds **5a**–**5d**.*[3]



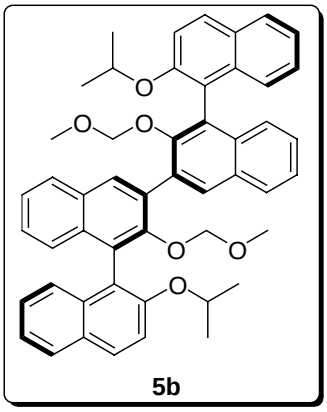
2a **4a** **5a**

Typical procedure: To a solution of **2a** (4.4 g, 12.8 mmol) in anhydrous THF (100 mL), *n*-BuLi 6.5 ml (15 mmol, 2.3 M solution in hexane) was added dropwise at −78 °C, followed by stirring at room temperature for 2 h. A solution of $B(OBu)_3$ (6.9 g, 30 mmol) in THF (10 mL) was added to the reaction mixture at -78°C. The mixture was then warmed to room temperature and stirred for another 9 h. A solution of 1N HCl (30 mL) was added and the organic layer was separated and the aqueous phase was extracted with AcOEt (3 × 40 mL). The combined organic layer was dried over anhydrous $NaSO_4$. After evaporation, the residue was combined with **3a** (4.7 g, 10 mmol), $Pd(PPh_3)_4$ (0.59 g, 0.51 mmol), DME (60 mL), H_2O (30 mL) and K_2CO_3 (5.56 g, 40 mmol). The resulting mixture was heated at reflux under argon for 48 h. Water (30 mL) was added and the organic layer was separated, the aqueous layer was extracted with AcOEt. The combined organic phases were dried over Na_2SO_4. After removal of the solvent, the residue was submitted to column chromatographic separation on silica gel with petroleum ether/ethyl acetate (5/1) as eluent to give **5a** (6.3 g, 92% yield) as a yellow foam.

(*R*,*R*)-2,2’’’-Dimethoxy-2’,2’’-di(methoxymethoxy)-1,1’:3’,3’’:1’’,1’’’-quaternaphthalene **5a**:

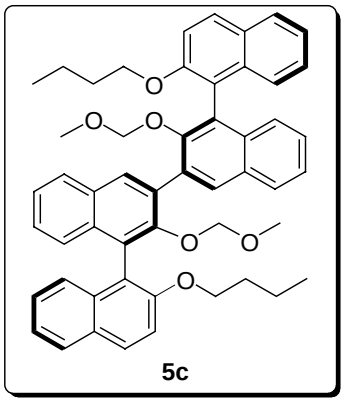
$[\alpha]_D^{25}$ = +171.9 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 6H), 3.74 (s, 6H), 4.50 (d, *J* = 5.7 Hz, 1H), 4.57 (d, *J* = 5.7 Hz, 1H), 7.19–7.41 (m, 14H), 7.80–7.95 (m, 6H), 8.18 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.7, 56.4, 98.6, 113.6, 119.6, 123.6, 124.9, 125.4, 125.6, 125.9, 126.1, 126.6, 127.7, 128.0, 128.9, 129.6, 130.6, 131.4, 133.1, 133.5, 134.1, 151.9, 155.1; IR (FT-IR, film): 3059, 2935, 2837, 1621, 1593, 1509, 1464, 1265, 1248, 1149, 1083, 985, 810, 749 cm^{-1}; MS (70 ev EI): m/z (%) 686 (M^+, 15), 610 (100), 582 (12), 452 (32). HRMS (EI) calcd for $C_{46}H_{38}O_6$: 686.26684, found: 686.26646.

(*R*,*R*)-2,2’’’-Diisopropoxy-2’,2’’-di(methoxymethoxy)-1,1’:3’,3’’:1’’,1’’’-quaternaphthalene **5b**:



Reaction performed utilizing the same procedure for the preparation of **5a**. Yield 86%; a yellow foam; $[\alpha]_D^{25}$ = +92.7 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 0.97 (d, *J* = 6.0 Hz, 6H), 1.21 (br s, 6H), 2.36 (s, 6H), 4.47–4.60 (m, 6H), 7.19–7.45 (m, 14H), 7.82–7.95 (m, 6H), 8.20 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.3, 22.5, 55.8, 55.9, 98.6, 123.6, 124.7, 125.7, 125.8, 125.9, 126.4, 127.7, 128.0, 129.1, 129.2, 129.33 130.5 131.8, 133.4 134.4, 151.8, 153.8; IR (FT-IR, film): 2975, 2928, 1621, 1592, 1507, 1467, 1387, 1264, 1242, 1157, 1112, 983, 807, 750 cm^{-1}; MS (70 ev EI): m/z (%) 742 (M^+, 28), 666 (35), 624 (33), 582 (75), 554 (16), 410 (14). HRMS (EI) calcd for $C_{50}H_{46}O_6$: 742.32944, found: 742.32896.

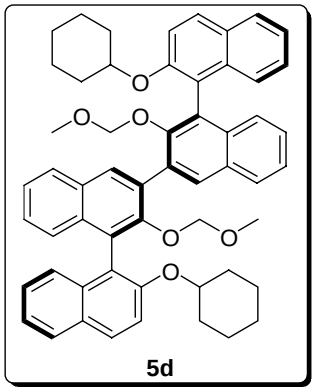
(*R*,*R*)-2,2’’’-Dibutoxy-2’,2’’-di(methoxymethoxy)-1,1’:3’,3’’:1’’,1’’’-quaternaphthalene **5c**:



Reaction performed utilizing the same procedure for the preparation of **5a**. Yield 85%; a yellow foam; $[\alpha]_D^{25}$ = +103.7 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 0.64–0.67 (m, 6H), 1.04 (br s, 4H), 1.45 (br s, 4H), 2.37 (s, 6H), 3.93–3.98 (m, 2H), 4.07–4.09 (m, 2H), 4.50 (d, *J* = 5.7 Hz, 2H), 4.58 (d, *J* = 5.7 Hz, 2H), 7.19–7.44 (m, 14H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.90–7.95 (m, 4H), 8.21 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 18.7, 31.4, 55.8, 98.6, 123.5, 124.8, 125.6, 125.8, 125.9, 126.2, 126.5, 127.7, 127.9, 129.0, 129.5, 130.5, 131.7, 132.6, 133.5, 134.2, 151.8, 154.7; IR (FT-IR, film): 3054, 2958, 2873, 1621, 1593, 1509, 1464, 1267, 1242, 1157, 1080, 983, 808, 749 cm^{-1}; MS (70 ev EI):

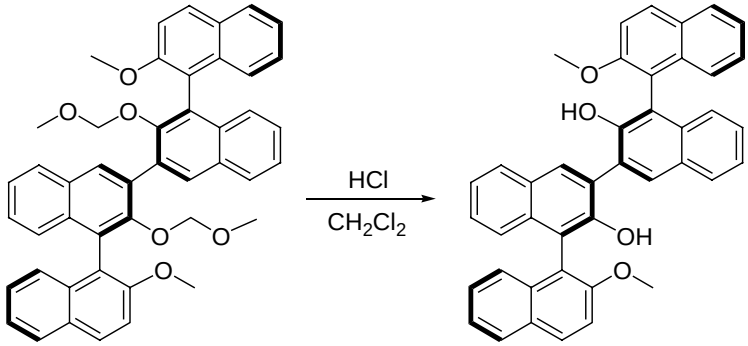
m/z (%) 770 (M^+, 20), 694 (100), 638 (28). HRMS (EI) calcd for $C_{52}H_{50}O_6$: 770.36074, found: 770.36030.

(*R*,*R*)-2,2’’’-Dicyclohexyloxy-2’,2’’-di(methoxymethoxy)-1,1’:3’,3’’:1’’,1’’’-quaternaphthalene



5d: Reaction performed utilizing the same procedure for the preparation of **5a**. Yield 85%; a yellow foam; $[\alpha]_D^{25}$ = +26.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84–1.92 (m, 20H), 2.36 (s, 6H), 4.24 (br s, 2H), 4.49 (d, *J* = 5.7 Hz, 2H), 4.58 (s, 2H), 7.20–7.45 (m, 14H), 7.82–7.94 (m, 6H), 8.20 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.4, 23.6, 25.4, 31.9, 32.3, 55.8, 98.6, 123.5, 124.7, 125.6, 125.8, 126.0, 126.3, 126.4, 127.6, 127.9, 129.0, 129.2, 130.4, 131.8, 132.4, 133.3, 134.4, 151.8, 153.6; IR (FT-IR, film): 3058, 2933, 2857, 1621, 1592, 1466, 1353, 1266, 1236, 1156, 1076, 982, 808, 749 cm^{-1}; MS (70 ev EI): m/z (%) 822 (M^+, 16), 746 (14), 664 (20), 582 (100), 554 (14), 410 (14). Anal. Calcd for $C_{56}H_{54}O_6$: C, 81.72; H, 6.61. Found: C, 81.52; H, 7.05.

*Synthesis of compounds **6a–6d.***

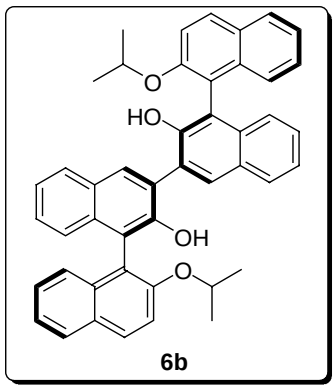


5a **6a**

Typical procedure: To a solution of **5a** (2.3 g, 3.35 mmol) in CH_2Cl_2 (60 mL) and MeOH (60 mL) was added 10 N HCl (20 mL) at 0 °C, the mixture was stirred at room temperature for 4 h. The reaction mixture was added to 40 mL of brine and the aqueous layer was separated and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layer was washed with water (40 mL), saturated $NaHCO_3$ (40 mL) and brine (40 mL). This was dried with Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography with petroleum ether (60–90 °C)–CH_2Cl_2–AcOEt (10:5:1) as eluent to give **6a** 1.84 g.

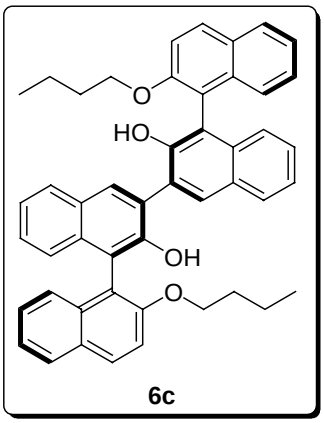
(*R*,*R*)-2,2’’’-Dimethoxy-1,1’:3’,3’’:1’’,1’’’-quaternaphthalene-2’,2’’-diol **6a**: A white powder, 92% yield.; m.p. 270 °C (dec.); $[\alpha]_D^{25}$ = +179.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (s, 6H), 5.72 (s, 2H), 7.09–7.44 (m, 14H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.92–7.99 (m, 4H), 8.17 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.7, 113.8, 116.6, 117.0, 123.8, 123.9, 124.8, 126.5, 127.1, 127.8, 128.1, 128.2, 129.3, 130.6, 131.4, 133.7, 133.9, 149.0, 155.7; IR (FT-IR, film): 3525, 3055, 2940, 2839, 1621, 1592, 1508, 1455, 1264, 1247, 1147, 1086, 810, 749 cm^{-1}; MS (70 ev EI): m/z (%) 598 (M^+, 100), 746 (14), 566 (8). HRMS (EI) calcd for $C_{42}H_{30}O_4$: 598.21441, found: 598.21317.

(*R*,*R*)-2,2’’’-Diisopropoxy-1,1’:3’,3’’:1’’,1’’’-quaternaphthalene-2’,2’’-diol **6b**: Reaction performed utilizing the same procedure for the preparation of **6a.** A white powder, 90% yield; m.p.242–244 °C; $[\alpha]_D^{25}$ = +78.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (d, *J* = 6.3 Hz, 6H), 1.05 (d, *J* = 6.3 Hz, 6H), 4.36–4.44 (m, 2H), 5.72 (s, 2H), 7.10–7.42 (m, 14H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.91–7.95 (m, 4H), 8.14 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.3, 72.7, 117.2, 118.2, 119.4, 123.6, 124.1, 125.1, 125.3, 126.3, 126.8, 128.0, 128.1, 129.1, 129.7, 130.2, 131.1, 133.7, 134.1, 149.2, 154.4; IR (FT-IR, film): 3522, 3056, 2974, 1621, 1591, 1504, 1465, 1263, 1240, 1110, 1002, 808, 749 cm^{-1}; MS (70 ev EI): m/z (%) 654 (M^+, 90), 612 (22), 570 (100), 552 (45), 426 (12), 255 (14). HRMS (EI) calcd for $C_{46}H_{38}O_4$: 654.27701, found: 654.27626.



6b

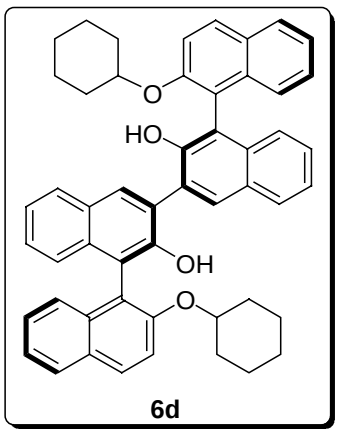
(*R*,*R*)-2,2’’’-Dibutoxy-1,1’:3’,3’’:1’’,1’’’-quaternaphthalene-2’,2’’-diol **6c**: Reaction performed utilizing the same procedure for the preparation of **6a.** A white powder, 94% yield; m.p.172–174 °C; $[\alpha]_D^{25}$ = +131.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.63 (t, *J* = 7.5 Hz, 6H), 0.99–1.09 (m, 4H), 1.37–1.47 (m, 4H), 3.94–4.00 (m, 4H), 5.66 (s, 2H), 7.11–7.36 (m, 12H), 7.42 (d, *J* = 9.0 Hz, 2H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.91–7.96 (m, 4H), 8.13 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 18.7, 31.2, 69.5, 115.7, 117.0, 117.5, 123.6, 123.9,



6c

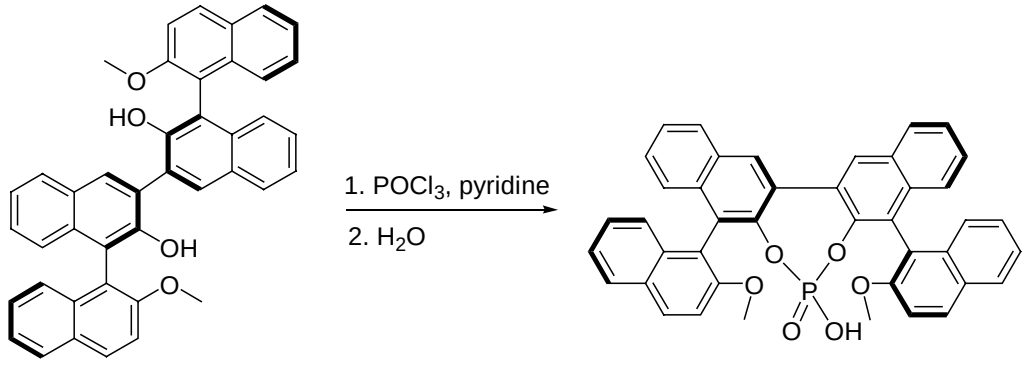
125.0, 126.3, 127.0, 127.7, 128.0, 128.1, 129.2, 129.4, 130.4, 131.1, 133.8, 134.0, 149.1, 155.2; IR (FT-IR, film): 3529, 3053, 2956, 2871, 1621, 1592, 1507, 1463, 1268, 1243, 1147, 1083, 808, 747 cm^{-1}; MS (70 ev EI): m/z (%) 682 (M^+, 100), 626 (12), 552 (10). HRMS (EI) calcd for $C_{48}H_{42}O_4$: 682.30831, found: 682.30918.

(*R*,*R*)-2,2'''-Dicyclohexyloxy-1,1':3',3'':1'',1'''-quaternaphthalene-2',2''-diol **6d**: Reaction performed utilizing the same procedure for the preparation of **6a.** A white powder, 88% yield; m.p.176–178 °C; $[\alpha]_D^{25}$ = +42.9 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 0.98–1.70 (m, 20H), 4.13–4.21 (m, 2H), 5.67 (s, 2H), 7.11–7.36 (m, 12H), 7.42 (d, *J* = 9.0 Hz, 2H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.90–7.95 (m, 4H), 8.11 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.27, 23.3, 25.3, 31.8, 31.9, 77.6, 117.2, 117.9, 119.1, 123.5, 124.0, 125.2, 125.3, 126.2, 126.8, 127.87, 127.95, 128.00, 129.1, 129.6, 130.1, 131.0, 133.8, 134.2, 149.3, 154.3; IR (FT-IR, film): 3524, 3058, 2934, 2855, 1620, 1591, 1505, 1451, 1358, 1265, 1235, 1146, 811, 748 cm^{-1}; MS (70 ev EI): m/z (%) 734 (M^+, 36), 652 (15), 570 (100), 426 (13), 255 (12). HRMS (EI) calcd for $C_{52}H_{46}O_4$: 734.33961, found: 734.33731.



6d

*Synthesis of chiral catalysts **1a–1d**.*[4]

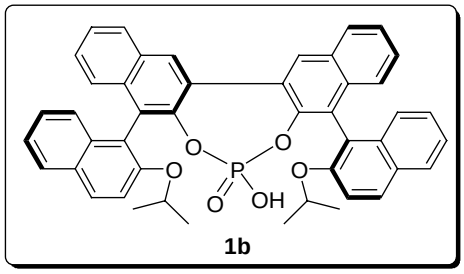


6a **1a**

Typical procedure: To a solution of **6a** (0.51 g, 0.85 mmol) in pyridine (4 mL) was added phosphorus oxychloride (200 μL, 2.1 mmol) at room temperature under N_2 and the reaction mixture was stirred at 70 °C for 3 h. Then water (3 mL) was added and the resulting suspension was stirred for the additional 3 h at 70 °C. After cooling, dichloromethane (50 mL) was added

and pyridine was removed by the reverse extraction with aqueous 6.0 N HCl (3 × 50 mL). The organic phase was dried over Na_2SO_4 and purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$ = 1/13) to yield (*R*,*R*)-4,4'-bis(2-methoxynaphthyl-1-yl)-2,2'-binaphthyl-3,3'-diyl hydrogen phsophate **1a** as a white solid (0.51 g, 91% yield). m.p.>300 °C; $[\alpha]_D^{25}$ = +189.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.13 (s, 6H), 6.77 (d, *J* = 8.7 Hz, 2H), 7.05–7.46 (m, 14H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 8.27 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.3, 114.2, 117.3, 123.3, 125.1, 125.6, 126.1, 126.3, 126.6, 127.7, 128.1, 128.5, 129.4, 129.9, 131.2, 133.5, 133.7, 144.8, 155.2; ^{31}P NMR (121 MHz, $CDCl_3$): δ –4.77; IR (FT-IR, film): 3059, 1622, 1593, 1509, 1272, 1264, 1249, 1090, 987, 866, 807, 747 cm^{-1}; MS (70 ev EI): m/z (%) 660 (26), 628 (32), 552 (58), 517 (30). HRMS (EI) calcd for $C_{42}H_{29}O_6P$: 660.17018, found: 660.17156.

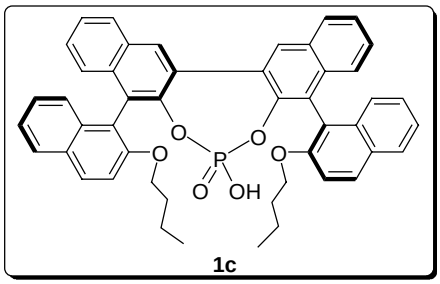
(*R*,*R*)-4,4'-Bis(2-isopropoxynaphthyl-1-yl)-2,2'-binaphthyl-3,3'-diyl hydrogen phsophate **1b**:



1b

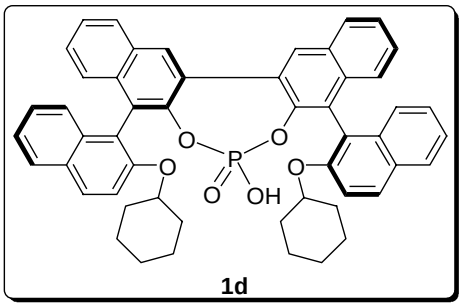
Reaction performed utilizing the same procedure for the preparation of **1a.** Yield 95%; a white powder; m.p. 260 °C (dec.); $[\alpha]_D^{25}$ = –8.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81 (d, *J* = 4.0 Hz, 6H), 0.98 (d, *J* = 5.6 Hz, 6H), 4.25 (br s, 2H), 6.93–7.25 (m, 12H), 7.41–7.56 (m, 6H), 8.01 (d, *J* = 8.1 Hz, 2H), 8.32 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.1, 22.3, 72.9, 117.6, 120.1, 123.7, 125.3, 125.4, 125.5, 125.9, 126.1, 126.4, 126.5, 127.3, 128.0, 129.4, 129.9, 131.2, 133.8, 144.9, 153.0; ^{31}P NMR (121 MHz, $CDCl_3$): δ –3.77; IR (FT-IR, film): 3056, 2974, 1622, 1592, 1508, 1468, 1244, 1111, 988, 746 cm^{-1}; MS (70 ev EI): m/z (%) 716(M^+, 2), 674 (2), 632 (4), 41 (100). HRMS (EI) calcd for $C_{46}H_{37}O_6P$: 716.23278, found: 716.23115.

(*R*,*R*)-4,4'-Bis(2-butoxynaphthyl-1-yl)-2,2'-binaphthyl-3,3'-diyl hydrogen phsophate **1c**: Reaction performed utilizing the same procedure for the preparation of **1a.** Yield 96%; a white powder; m.p.202–205°C; $[\alpha]_D^{25}$ = +80.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.45 (br s, 6H), 0.80 (br s, 4H), 1.21 (br s, 4H), 3.72 (br s, 4H), 5.35 (br s, 1H), 7.06–7.28 (m, 12H), 7.46 (t, *J* = 6.9 Hz, 2H), 7.69 (br s, 4H), 8.01 (d, *J* = 7.8 Hz, 2H), 8.29 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.4, 18.5, 30.9, 68.8, 115.0, 117.6, 123.3, 125.2, 125.6, 126.2, 126.4, 126.5, 127.7,



128.0, 128.8, 129.4, 129.9, 131.3, 133.6, 133.7, 144.4, 154.4; ^{31}P NMR (121 MHz, $CDCl_3$): δ –4.42; IR (FT-IR, film): 3060, 2956, 2871, 1622, 1593, 1510, 1466, 1273, 1245, 1019, 990, 888, 806, 744 cm^{-1}; MS (70 ev EI): m/z (%) 744 (M^+, 42), 688 (15), 670 (36), 632 (32), 614 (100), 316 (23), 267 (28). HRMS (EI) calcd for $C_{48}H_{41}O_6P$: 744.26408, found: 744.26462.

(*R*,*R*)-4,4'-Bis(2-cyclohexyloxynaphthyl-1-yl)-2,2'-binaphthyl-3,3'-diyl hydrogen phsophate **1d**:



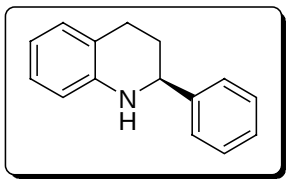
Reaction performed utilizing the same procedure for the preparation of **1a.** Yield 95%; A white powder; m.p. 217–220 °C; $[\alpha]_D^{25}$ = –100.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.78–1.46 (m, 18H), 1.72 (br s, 2H), 4.12 (br s, 2H), 4.38 (br s, 1H), 7.07–7.30 (m, 12H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.70 (br s, 4H), 8.04 (d, *J* = 8.1 Hz, 2H), 8.34 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.1, 23.3, 25.3, 31.6, 32.1, 77.9, 117.7, 120.7, 123.7, 125.3, 126.1, 126.3, 126.4, 127.1, 127.9, 129.4, 129.5, 129.6, 130.3, 131.1, 133.9, 145.3, 152.8; ^{31}P NMR (121 MHz, $CDCl_3$): δ –3.57; IR (FT-IR, film): 3061, 2933, 2855, 1622, 1592, 1508, 1449, 1329, 1248, 989, 868, 743 cm^{-1}; ESI-MS: m/z 795.6 (M–H), 796.5 (M^+). Anal. Calcd for $C_{52}H_{45}O_6P{\cdot}2H_2O$: C, 74.98; H, 5.93. Found: C, 75.08; H, 5.94.

2. Asymmetric Hydrogenation of quinolines.

Typical procedure: The quinoline **7** (0.1 mmol), catalyst **1** (0.2–1.0 mol%), Hantzsch dihydropyridine **9** (0.24 mmol) and Et_2O (3 mL) were added to a vial and the mixture was exposed to an argon atmosphere. The resulting yellow solution was allowed to stir at 35 °C for 12–20 h. The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel to afford the tetrahydroquinoline **8**. The yields and enantiomeric excesses are given in Table 3.

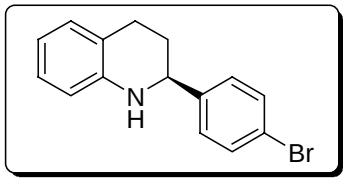
(*S*)-2-Phenyl-1,2,3,4-tetrahydroquinoline **8a**:

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.88–2.11 (m, 2H), 2.69 (dt, *J* = 16.2, 4.8 Hz, 1H), 2.82–2.91 (m,



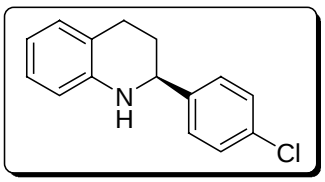
1H), 3.95 (s, 1H), 4.37 (dd, J = 9.3, 3.3 Hz, 1H), 6.48 (d, J = 7.5 Hz, 1H), 6.62 (td, J = 7.5, 0.9 Hz, 1H), 6.95–7.00 (m, 2H), 7.24–7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.3, 30.9, 56.1, 113.9, 117.0, 120.7, 126.4, 126.8, 127.3, 128.5, 129.2, 144.6, 144.7; $[\alpha]_D^{20}$ = –34.8 (*c* 1.1, $CHCl_3$, 96% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 95:5 at 0.6 mL/min), major isomer: t_R = 16.31 min, minor isomer: t_R = 21.04 min. lit.[5] $[\alpha]_D^{RT}$ = –37.7 (*c* 1.1, $CHCl_3$, 97% ee).

(*S*)-2-(4-Bromophenyl)-1,2,3,4-tetrahydroquinoline **8b**:



^{1}H NMR (300 MHz, $CDCl_3$): δ 1.87–2.00 (m, 1H), 2.04–2.13 (m, 1H), 2.70 (dt, J = 16.2, 4.8 Hz, 1H), 2.84–2.95 (m, 1H), 4.01 (br s, 1H), 4.40 (dd, J = 9.0, 3.0 Hz, 1H), 6.54 (d, J = 7.8 Hz, 1H), 6.66 (td, J = 7.5, 1.2 Hz, 1H), 6.98–7.04 (m, 2H), 7.23–7.28 (m, 2H), 7.44–7.48 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.1, 30.9, 55.6, 114.0, 117.4, 120.8, 121.0, 126.9, 128.2, 129.3, 131.6, 143.8, 144.3; IR (FT-IR, film): 3408, 2925, 1606, 1484, 1310, 1008, 824, 747 cm^{-1}; MS (70 ev EI): m/z (%) 287 (M^+, 70), 289 (68), 207 (22), 149 (25), 132 (100), 118 (35). HRMS (EI): calcd for $C_{15}H_{14}N^{79}Br$: 287.03096, found: 287.03110. $[\alpha]_D^{20}$ = –33.1 (*c* 1.1, $CHCl_3$, 97% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 90:10 at 0.6 mL/min), major isomer: t_R = 15.94 min, minor isomer: t_R = 28.56 min. The absolute configuration was tentatively assigned by analogy.

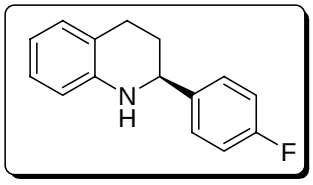
(*S*)-2-(4-Chlorophenyl)-1,2,3,4-tetrahydroquinoline **8c**:



^{1}H NMR (300 MHz, $CDCl_3$): δ 1.87–2.00 (m, 1H), 2.04–2.14 (m, 1H), 2.71 (dt, J = 16.2, 4.8 Hz, 1H), 2.84–2.96 (m, 1H), 4.02 (br s, 1H), 4.42 (dd, J = 9.0, 3.3 Hz, 1H), 6.54 (d, J = 7.8 Hz, 1H), 6.66 (td, J = 7.2, 1.2 Hz, 1H), 6.98–7.03 (m, 1H), 7.28–7.34 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.1, 30.9, 55.6, 114.0, 117.4, 120.8, 126.9, 127.9, 128.7, 129.3, 143.3, 144.4; IR (FT-IR, film): 3407, 2926, 2841, 1607, 1586, 1488, 1310, 1089, 1013, 828, 748 cm^{-1}; MS (70 ev EI): m/z (%) 243 (M^+, 100), 228 (13), 208 (8), 193 (10), 132 (100), 118 (33). HRMS (EI): calcd for $C_{15}H_{14}N^{35}Cl$: 243.08148, found: 243.08198. $[\alpha]_D^{20}$ = –40.4 (*c* 1.2, $CHCl_3$,

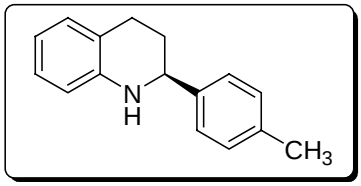
98% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 90:10 at 0.6 mL/in), major isomer: t_R = 15.26 min, minor isomer: t_R = 26.23 min. The absolute configuration was tentatively assigned by analogy.

(*S*)-2-(4-Fluorophenyl)-1,2,3,4-tetrahydroquinoline **8d**:



^{1}H NMR (300 MHz, $CDCl_3$): δ 1.88–2.00 (m, 1H), 2.03–2.12 (m, 1H), 2.71 (dt, *J* = 16.2, 4.8 Hz, 1H), 2.85–2.96 (m, 1H), 3.98 (br s , 1H), 4.40 (dd, *J* = 9.3, 3.3 Hz, 1H), 6.52 (dd, *J* = 8.4, 0.9 Hz, 1H), 6.65 (td, *J* = 7.5, 0.9 Hz, 1H), 6.97–7.05 (m, 4H), 7.30–7.37 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 31.1, 55.6, 114.0, 115.1, 115.4, 117.3, 120.8, 126.9, 128.0, 128.1, 129.3, 140.5, 144.5, 160.4, 163.7; IR (FT-IR, film): 3395, 2923, 1606, 1585, 1508, 1482, 1309, 1223, 1156, 833, 747 cm^{-1}; MS (70 ev EI): m/z (%) 227 (M^+, 100), 212 (20), 198 (5), 132 (40), 118 (18), 109 (15). HRMS (EI): calcd for $C_{15}H_{14}NF$: 227.11103, found: 227.11073. $[\alpha]_D^{20}$ = –41.3 (*c* 1.2, $CHCl_3$, 97% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 90:10 at 0.6 mL/min), major isomer: t_R = 13.42 min, minor isomer: t_R = 20.01 min. The absolute configuration was tentatively assigned by analogy.

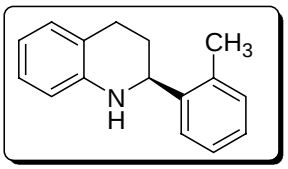
(*S*)-2-(4-Methylphenyl)-1,2,3,4-tetrahydroquinoline **8e**:



^{1}H NMR (300 MHz, $CDCl_3$): δ 1.87–2.12 (m, 2H), 2.34 (s, 3H), 2.71 (dt, *J* = 16.5, 4.8 Hz, 1H), 2.85–2.95 (m, 1H), 3.95 (br s, 1H), 4.37 (dd, *J* = 9.3, 3.3 Hz, 1H), 6.49 (d, *J* = 8.1 Hz, 1H), 6.62 (td, *J* = 7.5, 1.2 Hz, 1H), 6.96–7.01 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.0, 26.4, 31.0, 55.9, 113.9, 117.0, 120.8, 126.4, 126.8, 129.2, 129.2, 137.0, 141.8, 144.7; IR (FT-IR, film): 3408, 3015, 2922, 1607, 1585, 1481, 1310, 1273, 1105, 812, 746 cm^{-1}; MS (70 ev EI): m/z (%) 223 (M^+, 100), 208 (24), 193 (5), 132 (54), 118 (30), 105 (16). HRMS (EI): calcd for $C_{16}H_{17}N$: 223.13610, found: 223.13531. $[\alpha]_D^{20}$ = –22.8 (*c* 1.0, $CHCl_3$, 94% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 90:10 at 0.5 mL/min), major isomer: t_R = 13.17 min, minor isomer: t_R = 20.98 min. The absolute

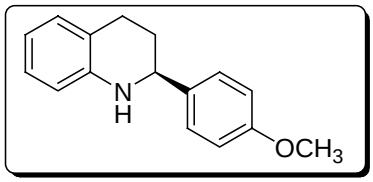
configuration was tentatively assigned by analogy.

(*S*)-2-(2-Methylphenyl)-1,2,3,4-tetrahydroquinoline **8f**:



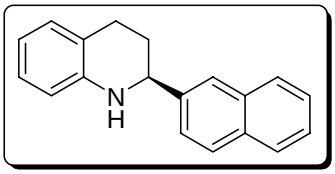
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.85–1.98 (m, 1H), 2.06–2.14 (m, 1H), 2.40 (s, 3H), 2.75 (dt, *J* = 16.5, 4.8 Hz, 1H), 2.88–2.98 (m, 1H), 3.93 (br s, 1H), 4.67 (dd, *J* = 9.3, 3.3 Hz, 1H), 6.54 (dd, *J* = 8.1, 0.9 Hz, 1H), 6.65 (td, *J* = 7.5, 1.2 Hz, 1H), 6.99–7.03 (m, 2H), 7.15–7.24 (m, 3H), 7.48–7.51 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.0, 26.5, 29.2, 51.1, 114.0, 117.0, 120.8, 126.0, 126.4, 126.9, 127.0, 129.3, 130.5, 134.7, 142.5, 145.0; $[\alpha]_D^{20}$ = –33.8 (*c* 1.0, $CHCl_3$, 86% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 90:10 at 0.6 mL/min), major isomer: t_R = 13.81 min, minor isomer: t_R = 15.83 min. lit.[5] $[\alpha]_D^{RT}$ = –31.0 (*c* 1.0, $CHCl_3$, 91% ee).

(*S*)-2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroquinoline **8g**:



^{1}H NMR (300 MHz, $CDCl_3$): δ 1.89–2.12 (m, 2H), 2.73 (dt, *J* = 16.5, 4.5 Hz, 1H), 2.86–2.97 (m, 1H), 3.80 (s, 3H), 3.99 (br s, 1H), 4.37 (dd, *J* = 9.3, 3.3 Hz, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 6.63 (t, *J* = 7.5 Hz, 1H), 6.86–7.02 (m, 4H), 7.28–7.32 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.5, 31.1, 55.3, 55.7, 113.90, 113.94, 117.1, 120.9, 126.8, 127.6, 129.2, 136.9, 144.8, 158.9; $[\alpha]_D^{20}$ = –24.3 (*c* 1.2, $CHCl_3$, 95% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 90:10 at 0.6 mL/min), major isomer: t_R = 13.87 min, minor isomer: t_R = 20.74 min. lit.[5] $[\alpha]_D^{RT}$ = –18.6 (*c* 1.0, $CHCl_3$, 98% ee).

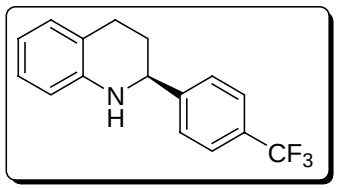
(*S*)-2-(Naphthyl-2-)-1,2,3,4-tetrahydroquinoline **8h**:



^{1}H NMR (300 MHz, $CDCl_3$): δ 2.04–2.22 (m, 2H), 2.75 (dt, *J* = 16.2, 4.5 Hz, 1H), 2.89–3.00 (m, 1H), 4.13 (br s, 1H), 4.58 (dd, *J* = 9.0, 3.5 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.64–6.69 (m, 1H), 7.00–7.09 (m, 2H), 7.44–7.51 (m, 3H), 7.59–7.84 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.4, 30.9, 56.3, 114.0, 117.2, 120.9, 124.8, 125.1, 125.7, 126.1, 126.9, 127.6, 127.8, 128.3, 129.3, 132.9, 133.4, 142.2, 144.6; $[\alpha]_D^{20}$ = –26.9 (*c* 1.0, $CHCl_3$, 97% ee).

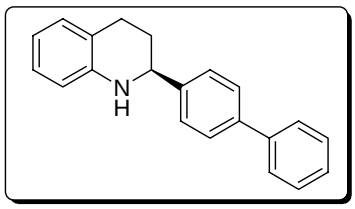
Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 90:10 at 0.6 mL/min), major isomer: t_R = 18.82 min, minor isomer: t_R = 32.83 min. lit.[5] $[\alpha]_D^{RT}$ = –26.1 (*c* 1.0, $CHCl_3$, >99% ee).

(*S*)-2-(4-Trifluoromethyl-phenyl)-1,2,3,4-tetrahydroquinoline **8i**:



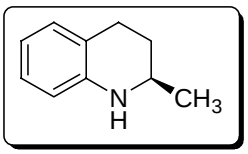
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.89–2.02 (m, 1H), 2.06–2.16 (m, 1H), 2.68 (dt, *J* = 16.5, 5.1 Hz, 1H), 2.84–2.94 (m, 1H), 4.01 (br s, 1H), 4.49 (dd, *J* = 8.7, 3.3 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 6.66 (td, *J* = 7.5, 0.9 Hz, 1H), 6.97–7.04 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.8, 30.8, 55.7, 114.1, 117.5, 120.7, 125.37, 125.42, 125.47, 126.8, 127.0, 129.3, 144.2, 148.9; $[\alpha]_D^{20}$ = –36.4 (*c* 1.4, $CHCl_3$, 98% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 90:10 at 0.6 mL/min), major isomer: t_R = 16.22 min, minor isomer: t_R = 24.46 min. lit.[5] $[\alpha]_D^{RT}$ = –31.8 (*c* 1.0, $CHCl_3$, >99% ee).

(*S*)-2-(1,1'-biphenyl-4-yl)-1,2,3,4-tetrahydroquinoline **8j**:



^{1}H NMR (300 MHz, $CDCl_3$): δ 1.96–2.19 (m, 2H), 2.75 (dt, *J* = 16.5, 4.5 Hz, 1H), 2.88–2.99 (m, 1H), 4.07 (br s, 1H), 4.47 (dd, *J* = 9.3, 3.3 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 1H), 6.67 (t, *J* = 7.2 Hz, 1H), 6.99–7.04 (m, 2H), 7.30–7.46 (m, 5H), 7.56–7.60 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.3, 30.9, 55.9, 114.0, 117.2, 120.9, 126.89, 126.96, 127.04, 127.2, 127.3, 128.7, 129.3, 140.4, 140.8, 143.8, 144.6; $[\alpha]_D^{20}$ = –12.4 (*c* 1.5, $CHCl_3$, 97% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 80:20 at 0.8 mL/min), major isomer: t_R = 12.22 min, minor isomer: t_R = 20.14 min. lit.[5] $[\alpha]_D^{RT}$ = –13.8 (*c* 1.0, $CHCl_3$, >99% ee).

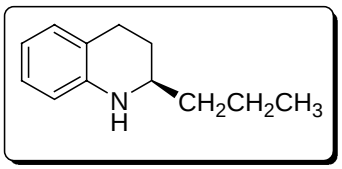
(*R*)-2-Methyl-1,2,3,4-tetrahydroquinoline **8k**:



^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (d, *J* = 6.3 Hz, 3H), 1.55–1.65 (m, 1H), 1.88–1.96 (m, 1H), 2.72–2.83 (m, 1H), 3.36–3.42 (m, 1H), 6.46 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.60 (td, *J* = 7.5, 1.2 Hz, 1H), 6.93–6.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.6, 26.6, 30.1, 47.1, 114.0, 117.0, 121.1, 126.7, 129.2, 144.7;

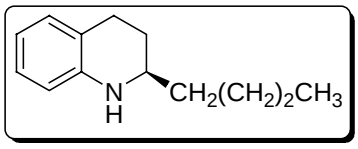
$[\alpha]_D^{20}$ = +72.4 (*c* 0.7, $CHCl_3$, 88% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OJ (hexanes: *i*-PrOH 99:1 at 0.7 mL/min), minor isomer: t_R = 26.64 min, major isomer: t_R = 31.62 min. lit.[6] $[\alpha]_D^{25}$ = +79.9 (*c* 1.01, $CHCl_3$, 94% ee).

(*R*)-2-Propyl-1,2,3,4-tetrahydroquinoline **8l**:



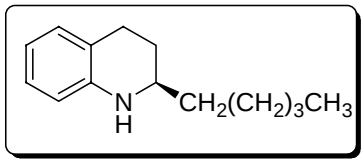
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.3 Hz, 3H), 1.32–1.58, 1.85–1.91 (m, 1H), 2.65–2.74 (m, 2H), 3.15–3.20 (m, 1H), 6.40 (d, *J* = 7.5 Hz, 1H), 6.52 (t, *J* = 7.5 Hz, 1H), 6.88 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 18.9, 26.4, 28.1, 38.9, 51.3, 114.0, 116.9, 121.4, 126.7, 129.2; $[\alpha]_D^{20}$ = +64.4 (*c* 1.2, $CHCl_3$, 94% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OJ (hexanes: *i*-PrOH 99:1 at 0.7 mL/min), minor isomer: t_R = 19.13 min, major isomer: t_R = 26.84 min. lit.[6] $[\alpha]_D^{25}$ = + 72.7 (*c* 1.58, $CHCl_3$, 93% ee).

(*R*)-2-Butyl-1,2,3,4-tetrahydroquinoline **8m**:



^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83 (t, *J* = 7.2 Hz, 3H), 1.22–1.56 (m, 7H), 1.81–1.90 (m, 1H), 2.58–2.77 (m, 2H), 3.09–3.17 (m, 1H), 3.65 (br s, 1H), 6.35–6.38 (m, 1H), 6.47–6.52 (m, 1H), 6.83–6.88 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 22.8, 26.4, 27.9, 28.1, 36.4, 51.5, 114.0, 116.8, 121.3, 126.7, 129.2, 144.7; $[\alpha]_D^{20}$ = +57.5 (*c* 0.8, $CHCl_3$, 94% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 99:1 at 0.6 mL / min), major isomer: t_R = 11.05 min, minor isomer: t_R = 12.29 min. lit.[5] $[\alpha]_D^{RT}$ = +71.1 (*c* 1.0, $CHCl_3$, 87% ee).

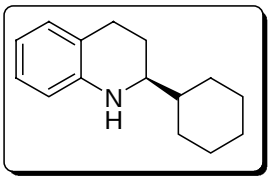
(*R*)-2-Pentyl-1,2,3,4-tetrahydroquinoline **8n**:



^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, *J* = 6.3 Hz, 3H), 1.26–1.65 (m, 9H), 1.90–1.99 (m, 1H), 2.67–2.82 (m, 2H), 3.18–3.28 (m, 1H), 3.63 (br s, 1H), 6.46 (d, *J* = 8.1 Hz, 1H), 6.59 (t, *J* = 7.5 Hz, 1H), 6.92–6.98 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.6, 25.3, 26.4, 28.1, 31.9, 36.6, 51.5, 114.0, 116.8, 121.3, 126.6, 129.2, 144.7; $[\alpha]_D^{20}$ = +60.7 (*c*

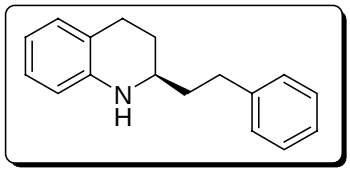
1.2, $CHCl_3$, 92% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 99:1 at 0.7 mL/min), major isomer: t_R = 9.13 min, minor isomer: t_R = 10.03 min. lit.[5] $[\alpha]_D^{RT}$ = +51.4 (*c* 1.0, $CHCl_3$, 90% ee).

(*R*)-2-Cyclohexyl-1,2,3,4-tetrahydroquinoline **8o**:



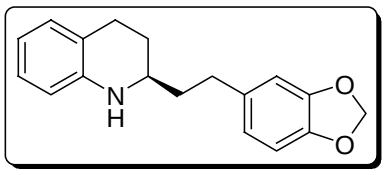
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00–1.43 (m, 7H), 1.65–1.95 (m, 6H), 2.71–2.80 (m, 2H), 3.00–3.07 (m, 1H), 3.79 (br s, 1H), 6.46 (d, *J* = 7.5 Hz, 1H), 6.57 (t, *J* = 7.2 Hz, 1H), 6.92–6.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.5, 26.2, 26.3, 26.4, 26.5, 28.6, 29.1, 42.4, 56.4, 113.9, 116.5, 121.3, 126.5, 129.0, 144.8; IR (FT-IR, film): 2923, 2851, 1607, 1585, 1483, 1448, 1310, 744 cm^{-1}; MS (70 eV EI): m/z (%) 215 (35), 132 (100), 117 (19). HRMS (EI) calcd for $C_{15}H_{21}N$: 215.16740, found: 215.16732. $[\alpha]_D^{20}$ = +47.7 (*c* 1.1, $CHCl_3$, 90% ee).Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 99:1 at 0.7 mL/min), major isomer: t_R = 9.87 min, minor isomer: t_R = 11.20 min. The absolute configuration was tentatively assigned by analogy.

(*R*)-2-(2-Phenethyl)-1,2,3,4-tetrahydroquinoline **8p**:



^{1}H NMR (300 MHz, $CDCl_3$): δ 1.59–1.71(m, 1H), 1.77–1.84 (m, 2H), 1.92–2.01 (m, 1H), 2.66–2.85 (m, 4H), 3.22–3.31 (m, 1H), 3.59 (br s, 1H), 6.42 (d, *J* = 8.1, Hz, 1H), 6.59 (td, *J* = 7.5, 1.2 Hz, 1H), 6.92–6.97 (m, 2H), 7.16–7.30 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.1, 27.9, 32.1, 38.1, 51.1, 114.1, 117.0, 121.2, 125.9, 126.7, 128.3, 128.4, 129.2, 141.8, 144.4; $[\alpha]_D^{20}$ = +64.9 (*c* 1.1, $CHCl_3$, 93% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OJ (hexanes: *i*-PrOH 95:5 at 0.8 mL / min), minor isomer: t_R = 39.80 min, major isomer: t_R = 44.15 min. lit.[5] $[\alpha]_D^{RT}$ = +63.9 (*c* 1.0, $CHCl_3$, 90% ee).

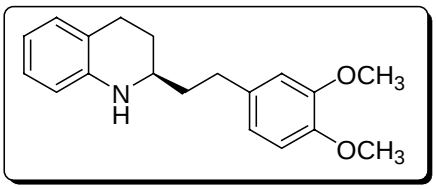
(*R*)-2-[2-(3,4-Methylenedioxyphenyl)ethyl]-1,2,3,4-tetrahydroquinoline **8q**:



^{1}H NMR (300 MHz, $CDCl_3$): δ 1.63–1.70(m, 1H), 1.74–1.81 (m, 2H), 1.95–2.00 (m, 1H), 2.62–2.81 (m, 4H), 3.25–3.29 (m, 1H), 3.65 (br s, 1H), 5.91 (s, 2H), 6.46 (d, *J* = 7.8 Hz,

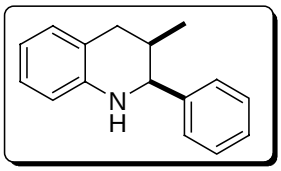
1H), 6.58–6.74 (m, 4H), 6.92–6.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 27.9, 31.8, 38.4, 51.0, 100.8, 108.2, 108.7, 114.1, 115.8, 117.1, 121.0, 121.3, 126.7, 129.2, 135.6, 144.4, 145.7, 147.6; $[\alpha]_D^{20}$ = +53.9 (*c* 1.4, $CHCl_3$, 90% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 80:20 at 0.8 mL / min), major isomer: t_R = 11.72 min, minor isomer: t_R = 14.25 min. lit.[5] $[\alpha]_D^{RT}$ = +50.7 (*c* 1.0, $CHCl_3$, 91% ee).

(*R*)-2-[2-(3,4-Dimethoxyphenyl)ethyl]-1,2,3,4-tetrahydroquinoline **8r**:



^{1}H NMR (300 MHz, $CDCl_3$): δ 1.66–1.69(m, 1H), 1.76–1.84 (m, 2H), 1.95–2.00 (m, 1H), 2.65–2.84 (m, 4H), 3.26–3.30 (m, 1H), 3.60 (br s, 1H), 3.84 (s, 3H), 3.85 (s, 3H), 6.43 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.59 (td, *J* = 7.5, 1.2 Hz, 1H), 6.72–6.80 (m, 3H), 6.92–6.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.1, 27.8, 31.7, 38.2, 51.1, 55.7, 55.8, 111.2, 111.5, 114.0, 116.9, 120.0, 121.1, 126.6, 129.1, 134.3, 144.3, 147.2, 148.8; $[\alpha]_D^{20}$ = +47.5 (*c* 1.5, $CHCl_3$, 95% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 80:20 at 0.8 mL / min), major isomer: t_R = 15.29 min, minor isomer: t_R = 16.98 min. lit.[5] $[\alpha]_D^{RT}$ = +40.0 (*c* 1.0, $CHCl_3$, 90% ee).

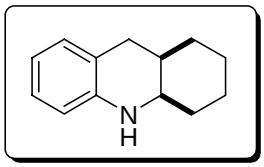
(*cis*)-3-Methyl-2-phenyl-1,2,3,4-tetrahydroquinoline **12a**:[7]



^{1}H NMR (300 MHz, $CDCl_3$): δ 0.742 (d, *J* = 6.9 Hz, 3H), 2.21–2.25 (m, 1H), 2.42 (dd, *J* = 16.1, 6.8 Hz, 1H), 2.90 (dd, *J* = 16.1, 5.0 Hz, 1H), 4.02 (br s, 1H), 4.44 (d, *J* = 3.3 Hz, 4H), 6.48 (d, *J* = 7.8 Hz, 1H), 6.58 (td, *J* = 8.4, 1.2 Hz, 1H), 6.91–6.98 (m, 2H), 7.16–7.27 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.1, 31.9, 33.3, 59.3, 113.7, 117.1, 120.0, 126.9, 127.1, 127.2, 128.1, 129.7, 142.9, 144.1; IR (FT-IR, film): 3400, 3024, 2961, 2909, 1608, 1586, 1489, 1452, 1270, 745, 702 cm^{-1}; MS (70 eV EI): m/z (%) 223 (100), 208 (10), 194 (33), 146 (65), 132 (15), 91 (20). HRMS (EI) calcd for $C_{16}H_{17}N$: 223.13610, found: 223.13693. $[\alpha]_D^{20}$ = +31.8 (*c* 1.1, $CHCl_3$, 82% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 90:10 at 0.6 mL/min), major isomer: t_R = 14.49 min, minor isomer: t_R = 17.33 min. The relative configuration was tentatively assigned by

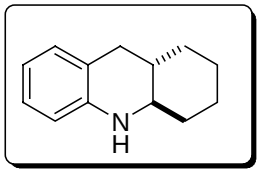
comparation with literature[7a] and NOE experiment.

(*rac*)-(*cis*)-1,2,3,4,4a,9a,10-Octahydroacridine:[8]



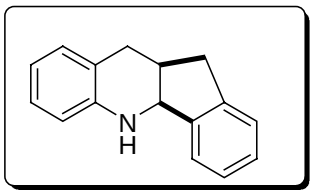
^{1}H NMR (300 MHz, $CDCl_3$): δ1.26–1.48 (m, 4H), 1.52–1.63 (m, 4H), 1.93–1.97 (m, 1H), 2.50 (dd, *J* = 16.2, 3.6 Hz, 1H), 2.89 (dd, *J* = 16.2, 5.1 Hz, 1H), 3.40 (br s, 1H), 3.49 (br s, 1H), 6.43 (d, *J* = 7.8 Hz, 1H), 6.56 (t, *J* = 7.1 Hz, 1H), 6.90–6.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7, 24.7, 27.2, 31.7, 32.5, 32.9, 50.0, 113.2, 116.3, 119.2, 126.5, 129.7, 143.9; IR (FT-IR, film): 3398, 2926, 2850, 1607, 1586, 1502, 1491, 1311, 1285, 744 cm^{-1}.

(*trans*)-1,2,3,4,4a,9a,10-Octahydroacridine **12b**:[8]



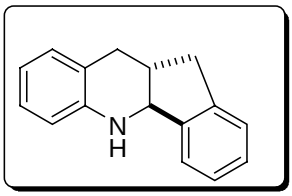
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94–1.08 (m, 1H), 1.22–1.37 (m, 3H), 1.41–1.56 (m, 1H), 1.73–1.87 (m, 4H), 2.47 (dd, *J* = 15.9, 11.7 Hz, 1H), 2.65 (dd, *J* = 16.2, 4.8 Hz, 1H), 2.83 (td, *J* = 10.2, 3.6 Hz, 1H), 3.49 (br s, 1H), 6.46 (d, *J* = 7.5 Hz, 1H), 6.59 (td, *J* = 7.5, 0.9 Hz, 1H), 6.92–6.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.6, 25.9, 31.9, 33.5, 34.5, 37.5, 56.0, 113.6, 116.9, 121.5, 126.6, 129.1, 144.5; IR (FT-IR, film): 2925, 2855, 1607, 1584, 1484, 1367, 1291, 909, 741 cm^{-1}; MS (70 eV EI): m/z (%) 187 (90), 186 (97), 156 (6), 144 (100), 130 (58), 118 (12). HRMS (EI) calcd for $C_{13}H_{17}N$: 187.13610, found: 187.13688. $[\alpha]_D^{20}$ = +108.8 (*c* 0.9, $CHCl_3$, 92% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 90:10 at 0.8 mL / min), major isomer: t_R = 6.44 min, minor isomer: t_R = 9.24 min. The relative *trans* configuration was assigned by comparation with literature.[8]

(*rac*)-(*cis*)-5,5a,10a,11-tetrahydro-10*H*-indeno[1,2-*b*]quinoline:[9]



^{1}H NMR (300 MHz, $CDCl_3$): δ 2.43 (dd, *J* = 16.5, 10.0 Hz, 1H), 2.71–2.81 (m, 3H), 3.12 (dd, *J* = 16.5, 7.5 Hz, 1H), 4.09 (br s, 1H), 4.79 (d, *J* = 6.3 Hz, 1H), 6.53–6.63 (m, 2H), 6.94–7.01 (m, 2H), 7.17–7.31 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.2, 36.7, 37.1, 59.0, 113.3, 117.0, 121.6, 123.8, 125.4, 126.6, 126.8, 127.5, 128.7, 141.5, 144.2, 146.1; IR (FT-IR, film): 3397, 3020, 2927, 1608, 1589, 1492, 1292, 1262, 739 cm^{-1}.

(*trans*)-5,5a,10a,11-tetrahydro-10*H*-indeno[1,2-*b*]quinoline **12c**:



^{1}H NMR (300 MHz, $CDCl_3$): δ 2.33–2.42 (m, 1H), 2.61 (dd, *J* = 14.6, 11.6 Hz, 1H), 2.95–3.13 (m, 3H), 4.21 (d, *J* = 10.5 Hz, 1H), 6.74–6.79 (m, 2H), 7.07 (dd, *J* = 8.1, 0.6 Hz, 2H), 7.20–7.31 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 33.2, 35.6, 45.5, 62.5, 117.0, 119.0, 121.2, 123.6, 124.9, 126.3, 126.9, 127.1, 130.5, 142.8, 143.3, 145.0; IR (FT-IR, film): 3046, 2925, 2846, 1606, 1578, 1494, 1468, 1350, 755, 747 cm^{-1}; MS (70eV EI): m/z (%) 221 (M^+, 98), 220 (100), 149 (25), 116 (18), 108 (28), 106 (55). HRMS (EI) calcd for $C_{16}H_{15}N$: 221.12045, found: 221.12084. $[\alpha]_D^{20}$ = +144.0 (*c* 0.9, $CHCl_3$, 91% ee). Enantiomeric excess of the product was measured by chiral stationary phase HPLC analysis using Chiracel-OD-H (hexanes: *i*-PrOH 92:8 at 0.8 mL / min): t_{major} = 13.21 min, t_{minor} = 16.54 min. The relative *trans* configuration was assigned by comparation with literature.[9]

References

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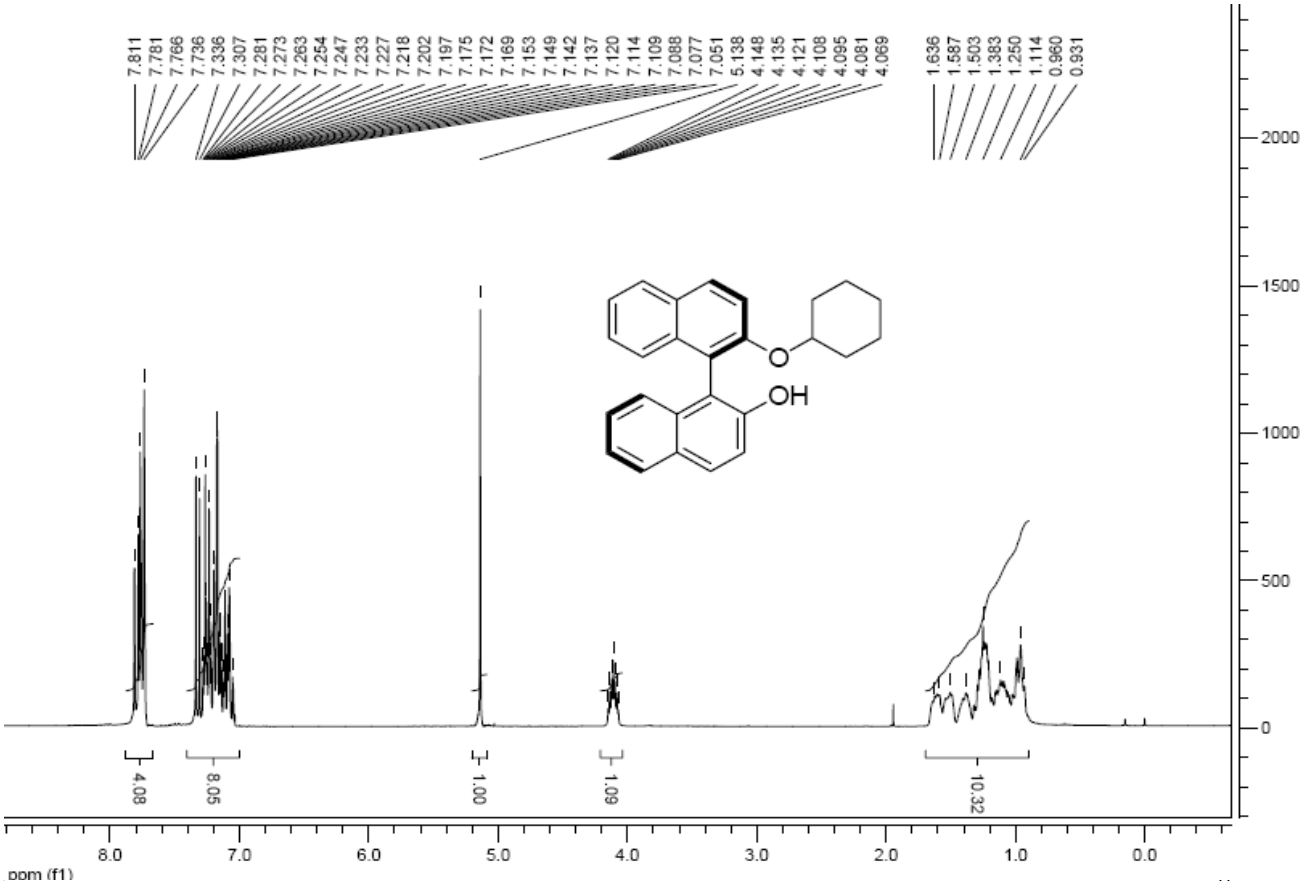
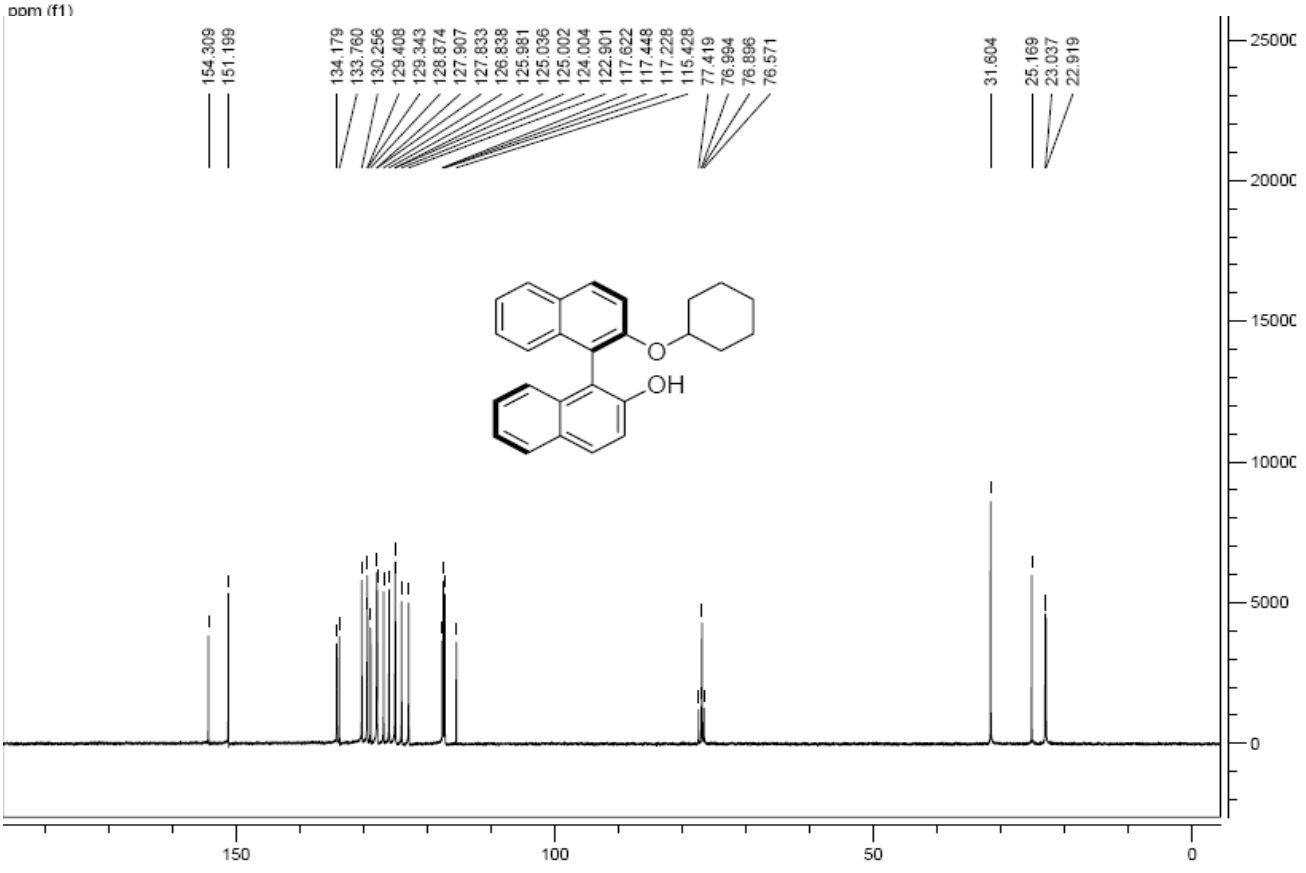
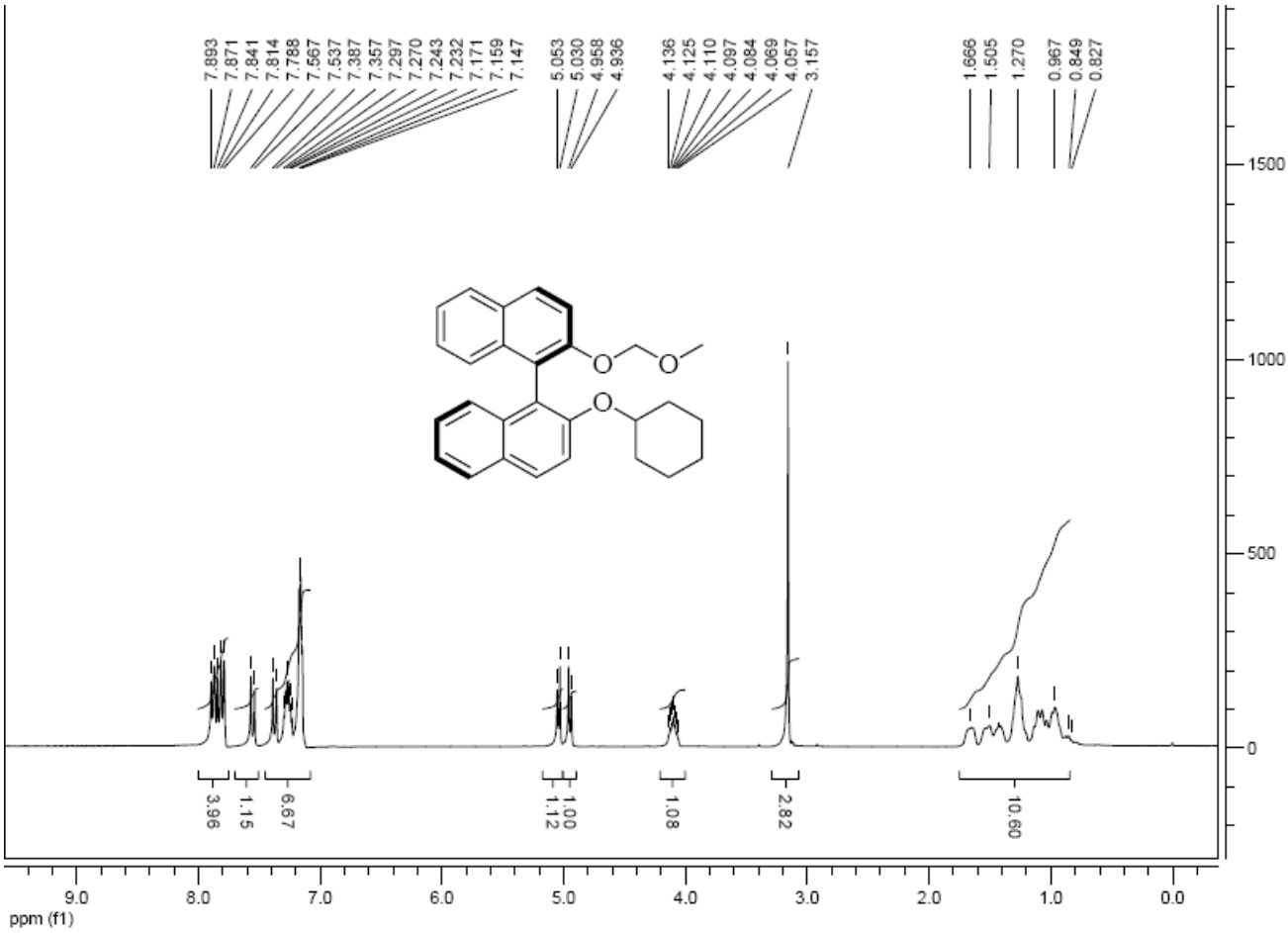
Copies of ^{1}H , ^{13}C NMR and ^{31}P NMR spectra of new BINOL derivatives



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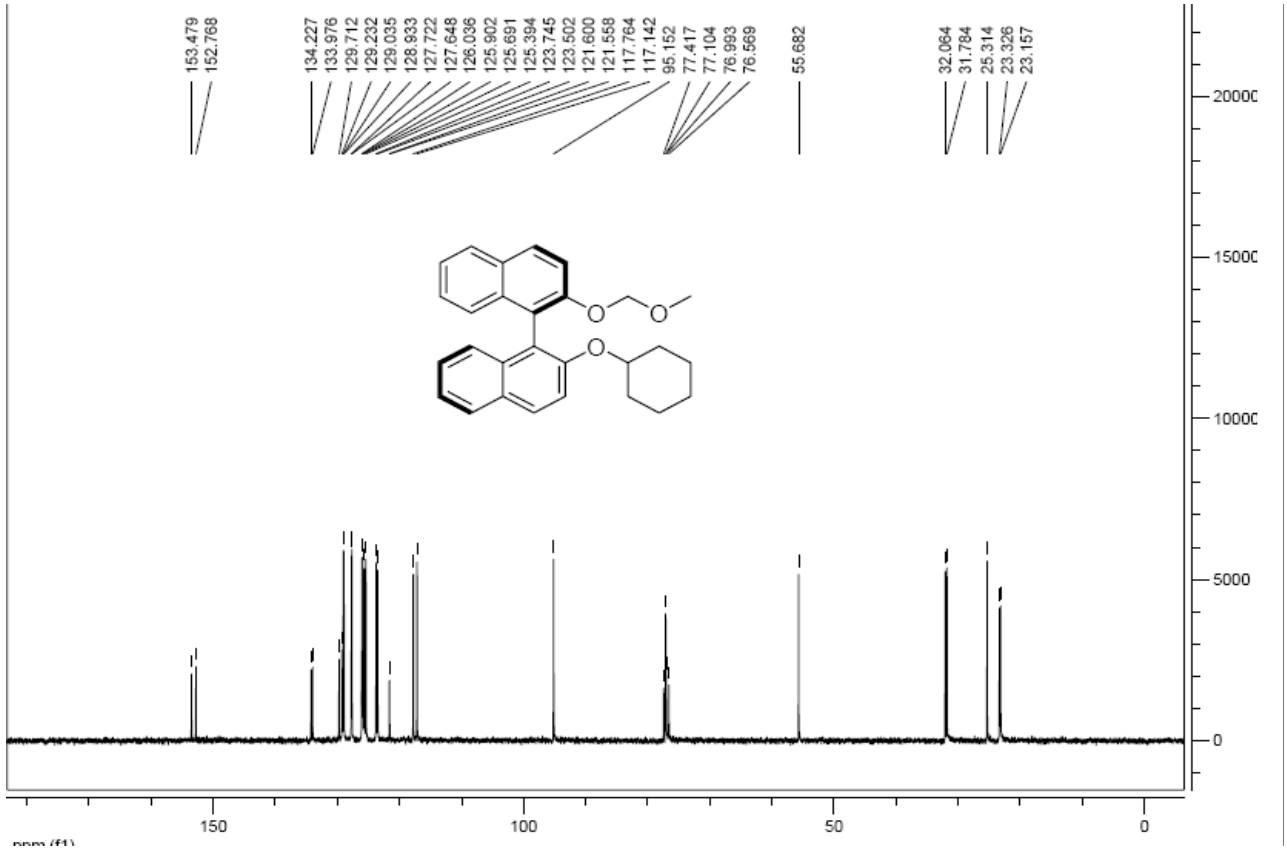
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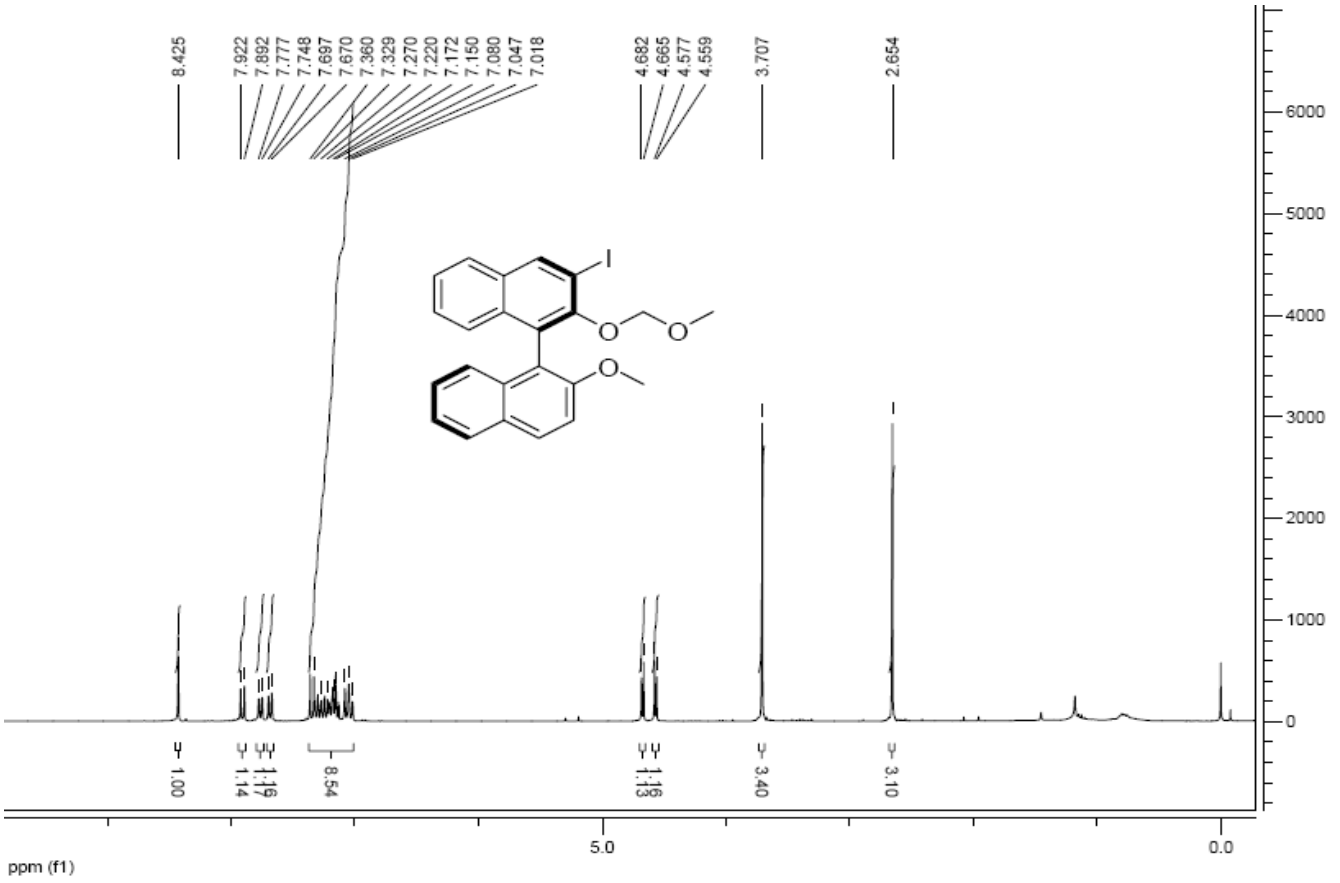
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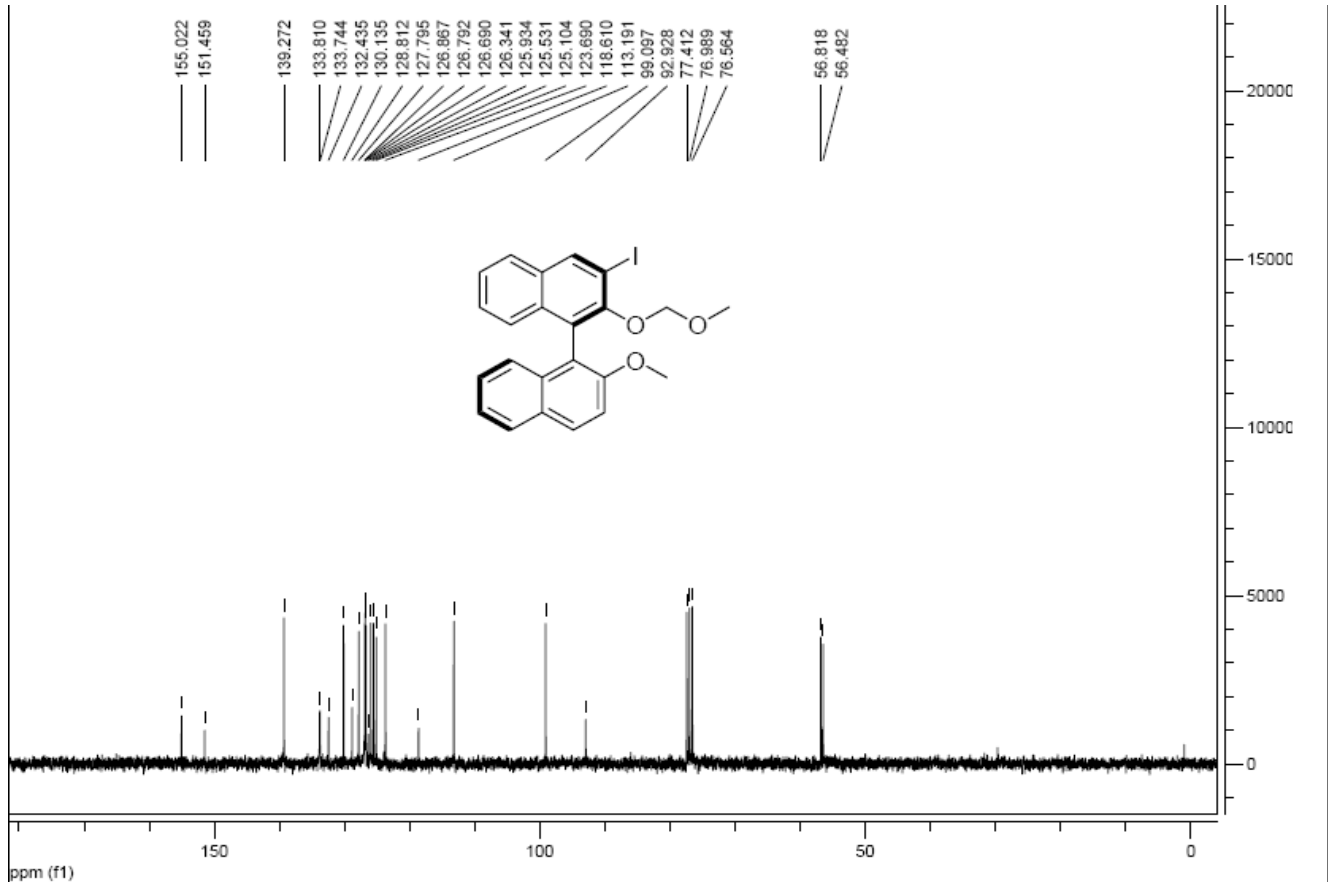
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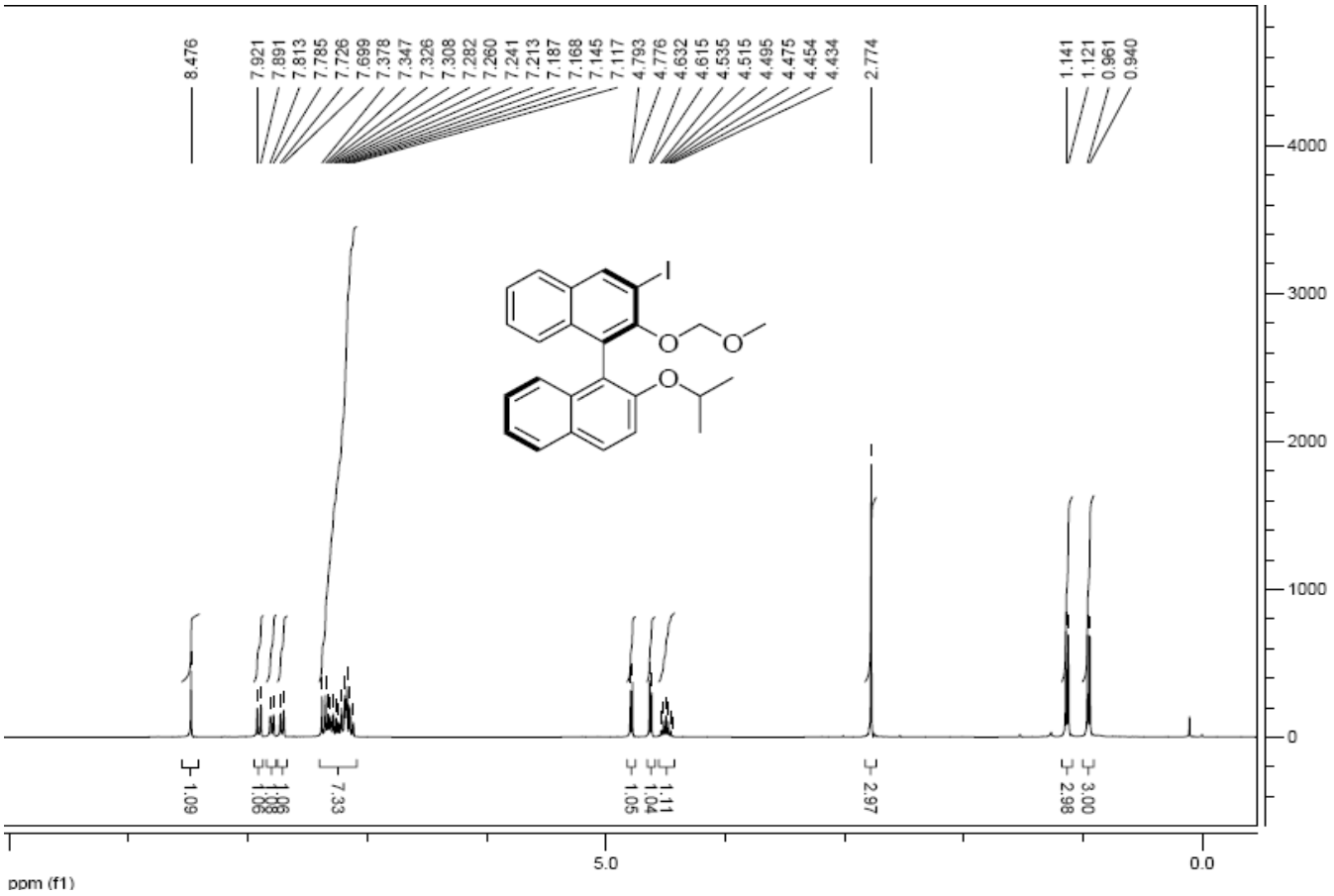
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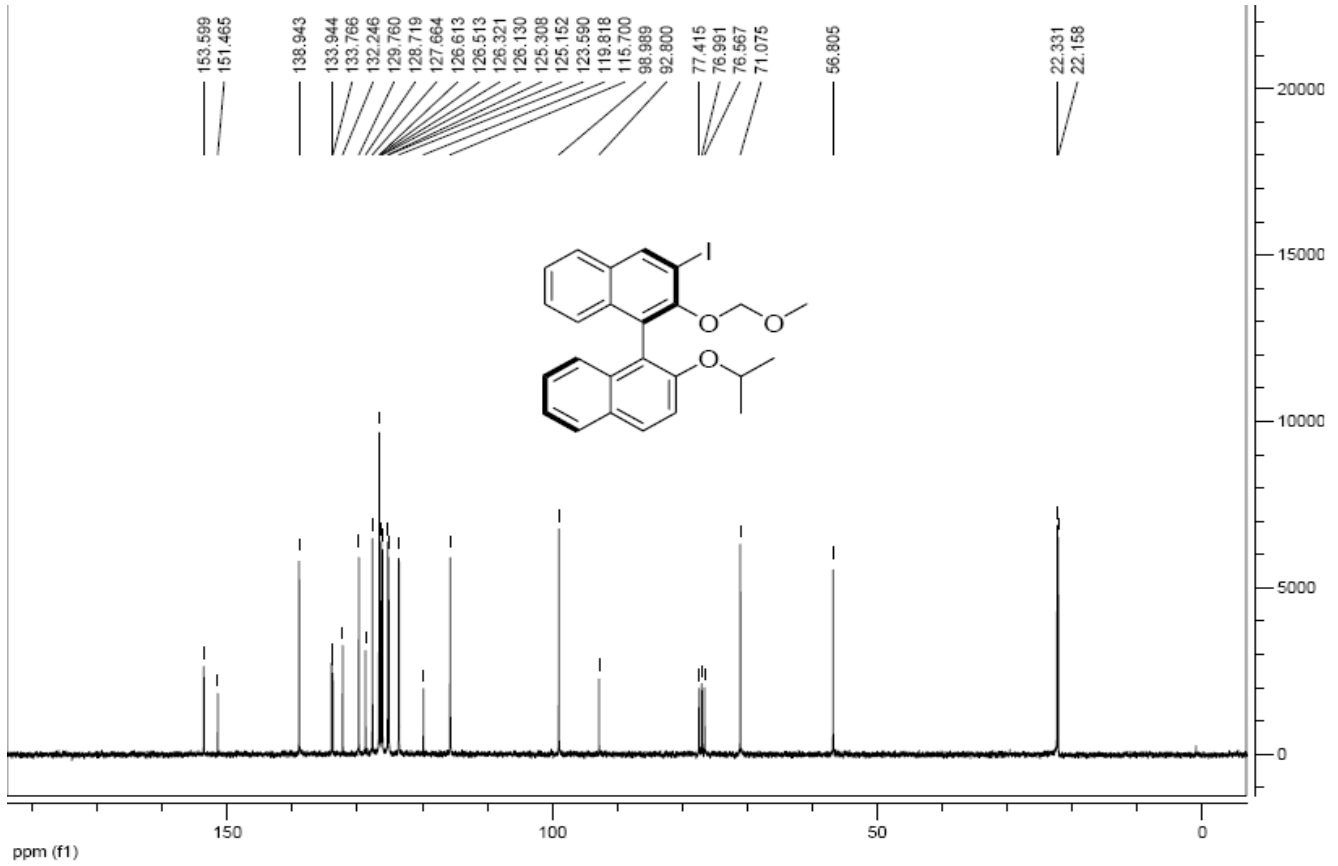
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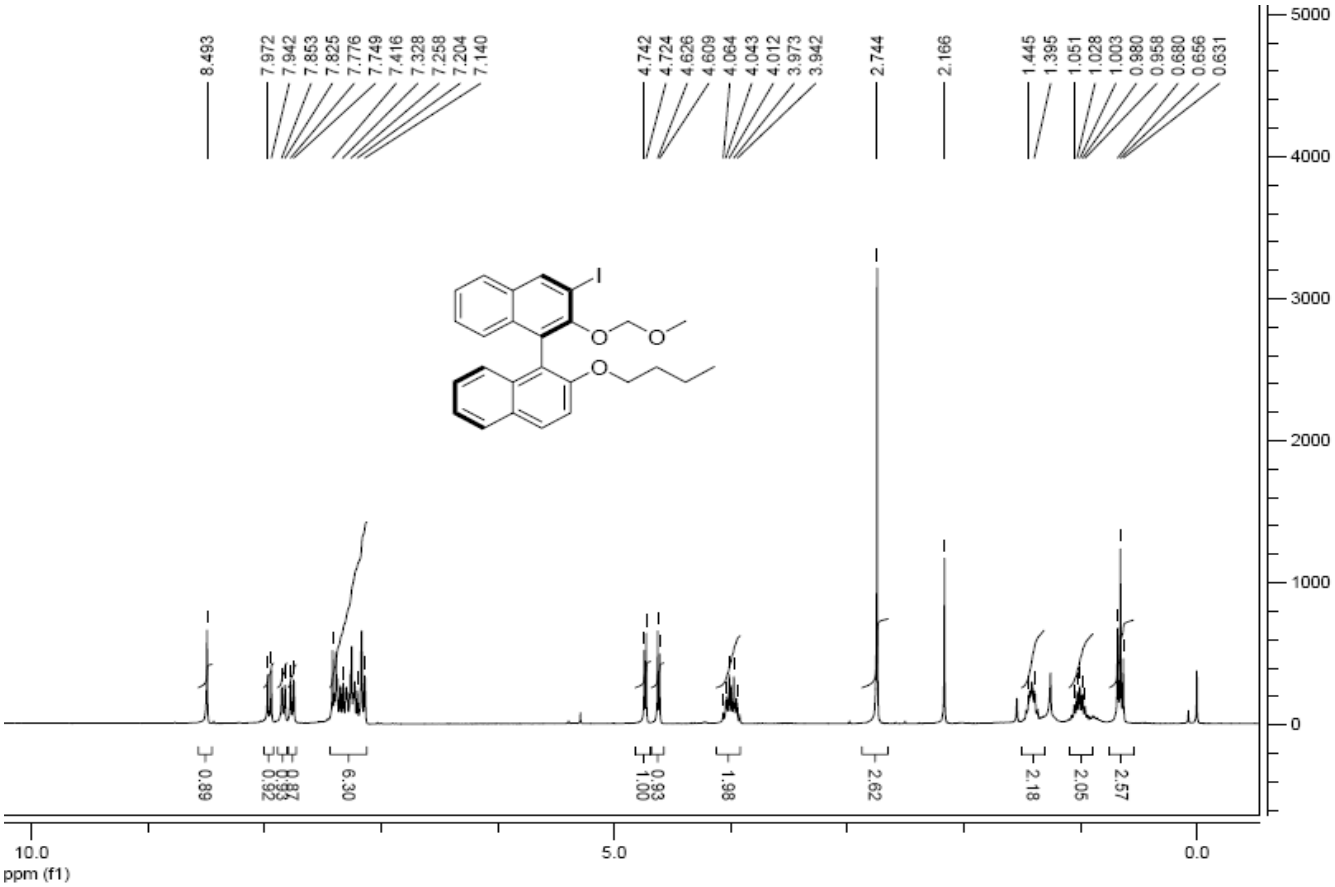
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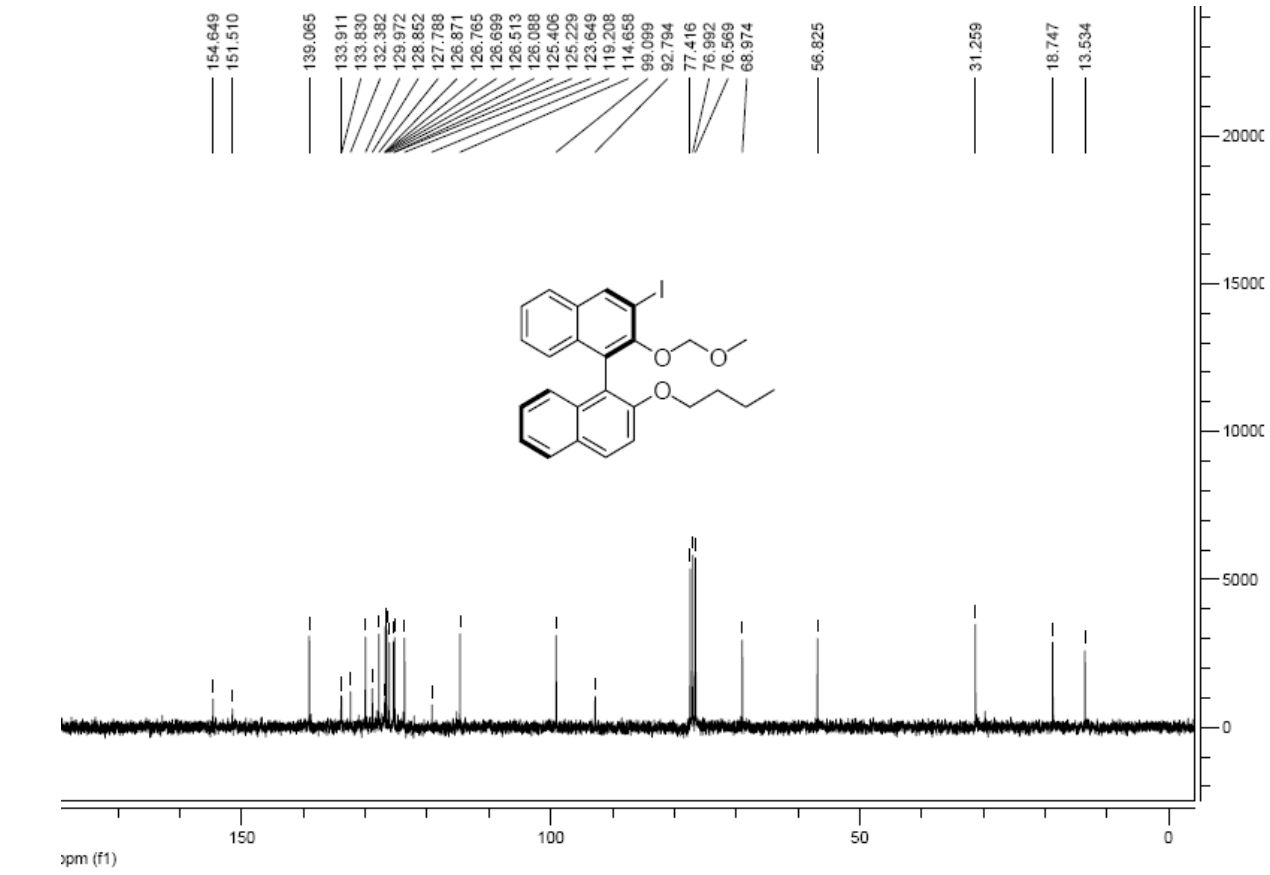
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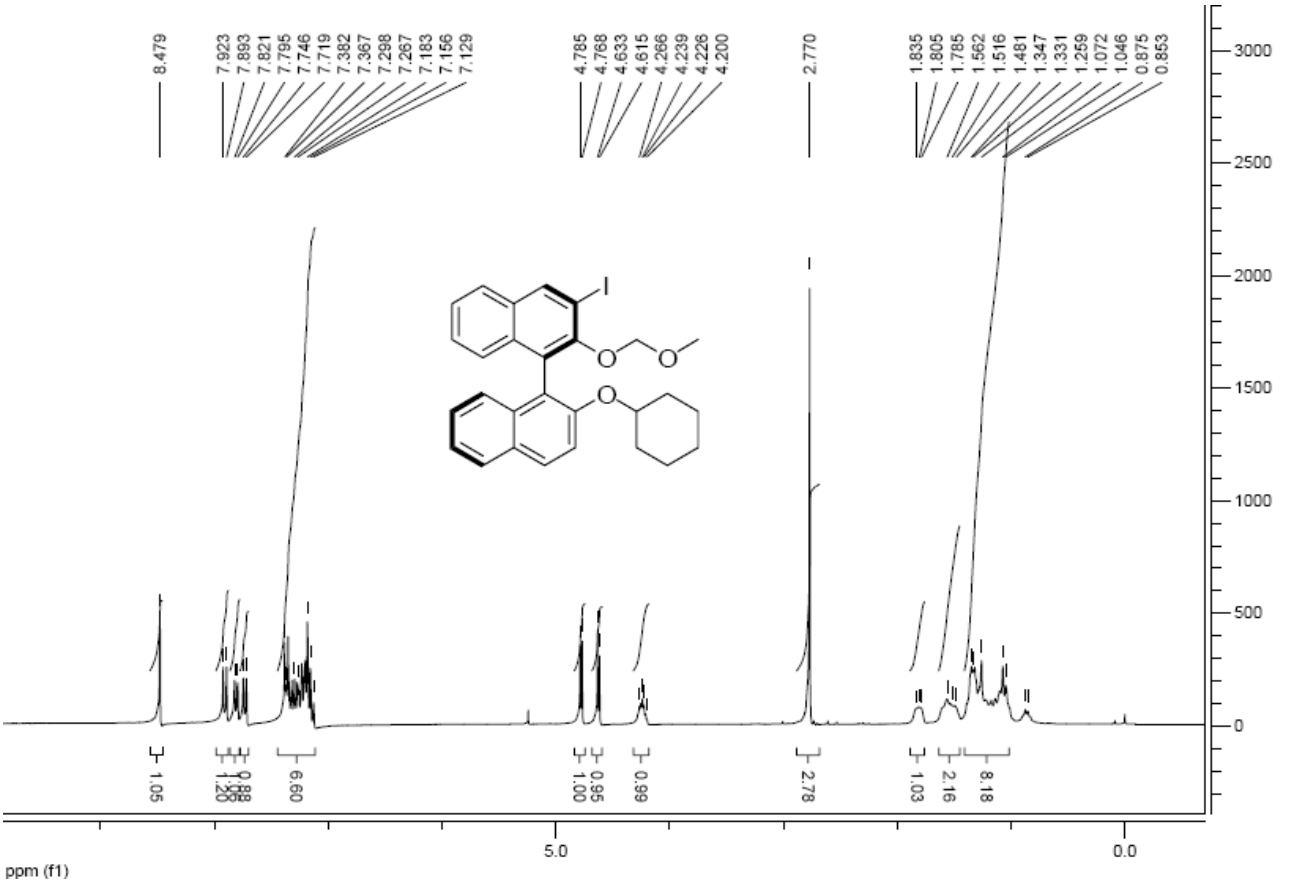
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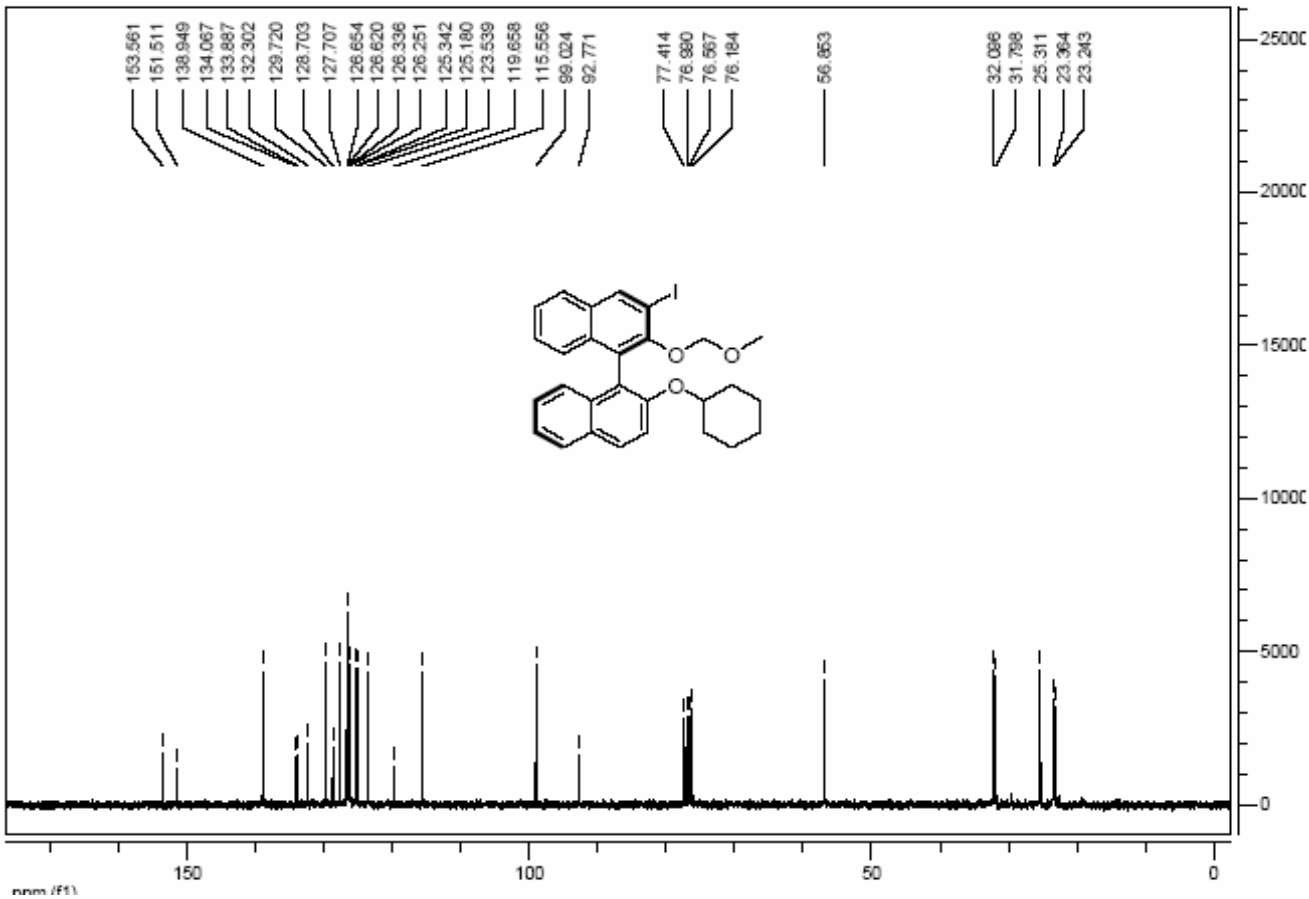
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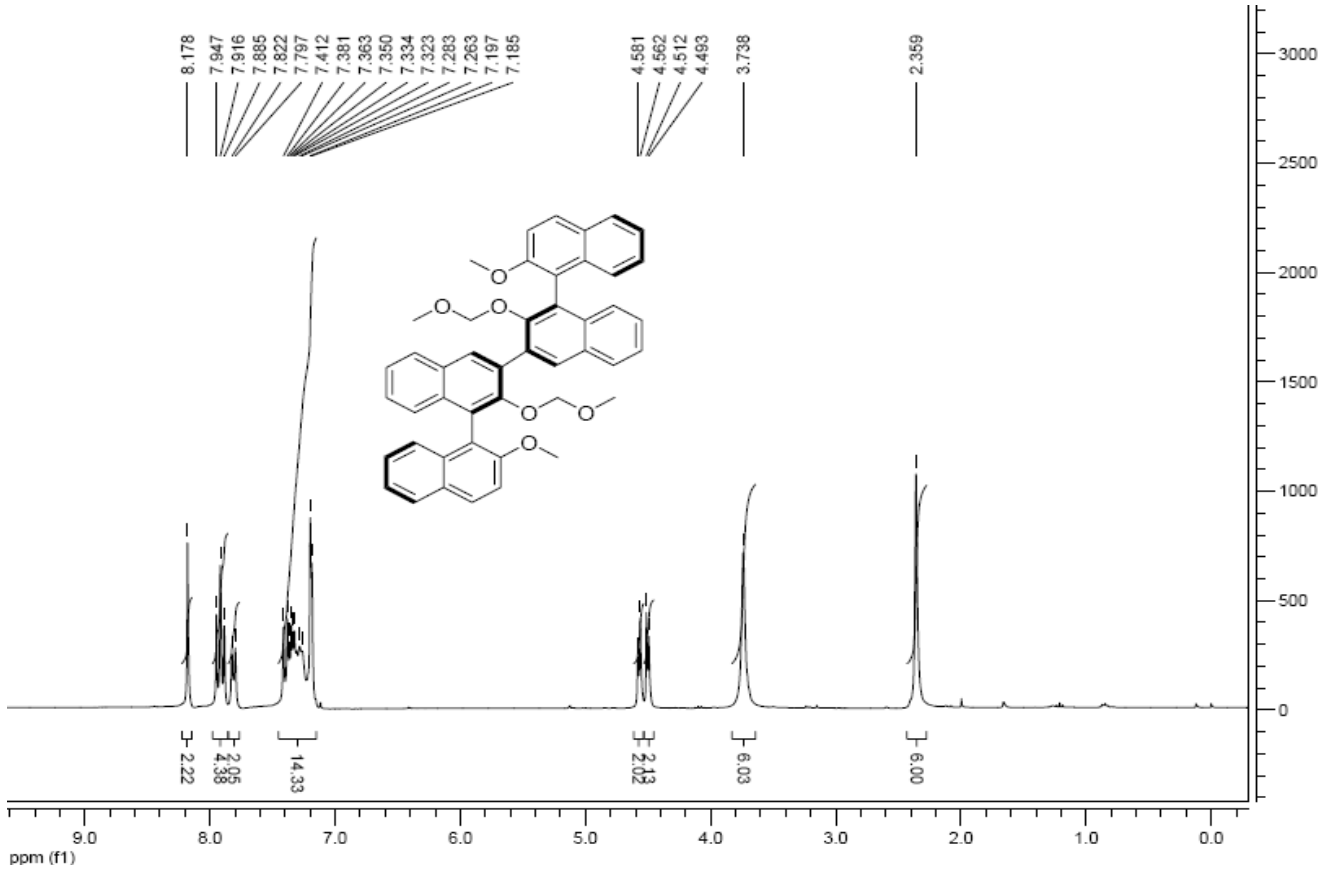
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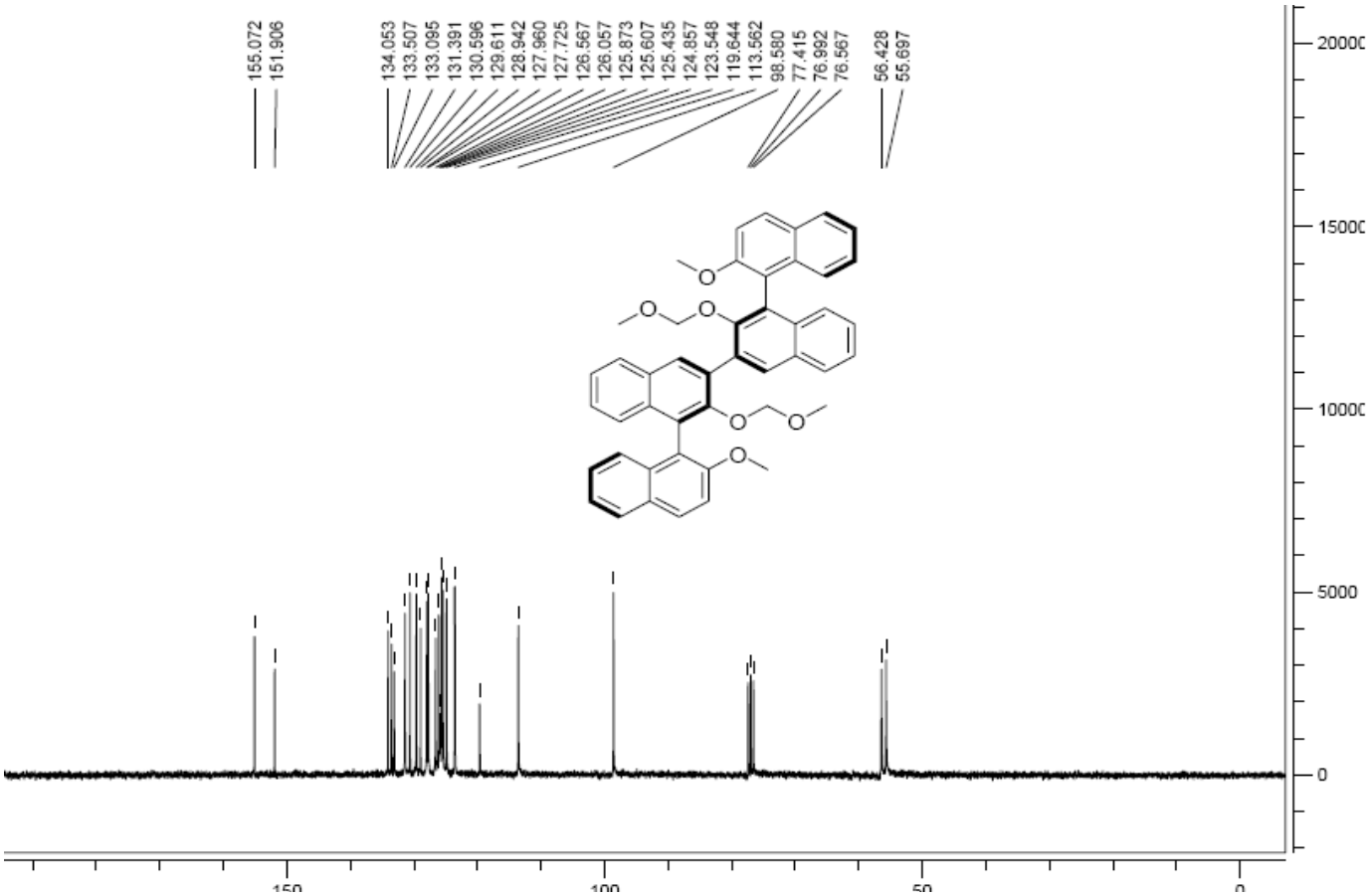
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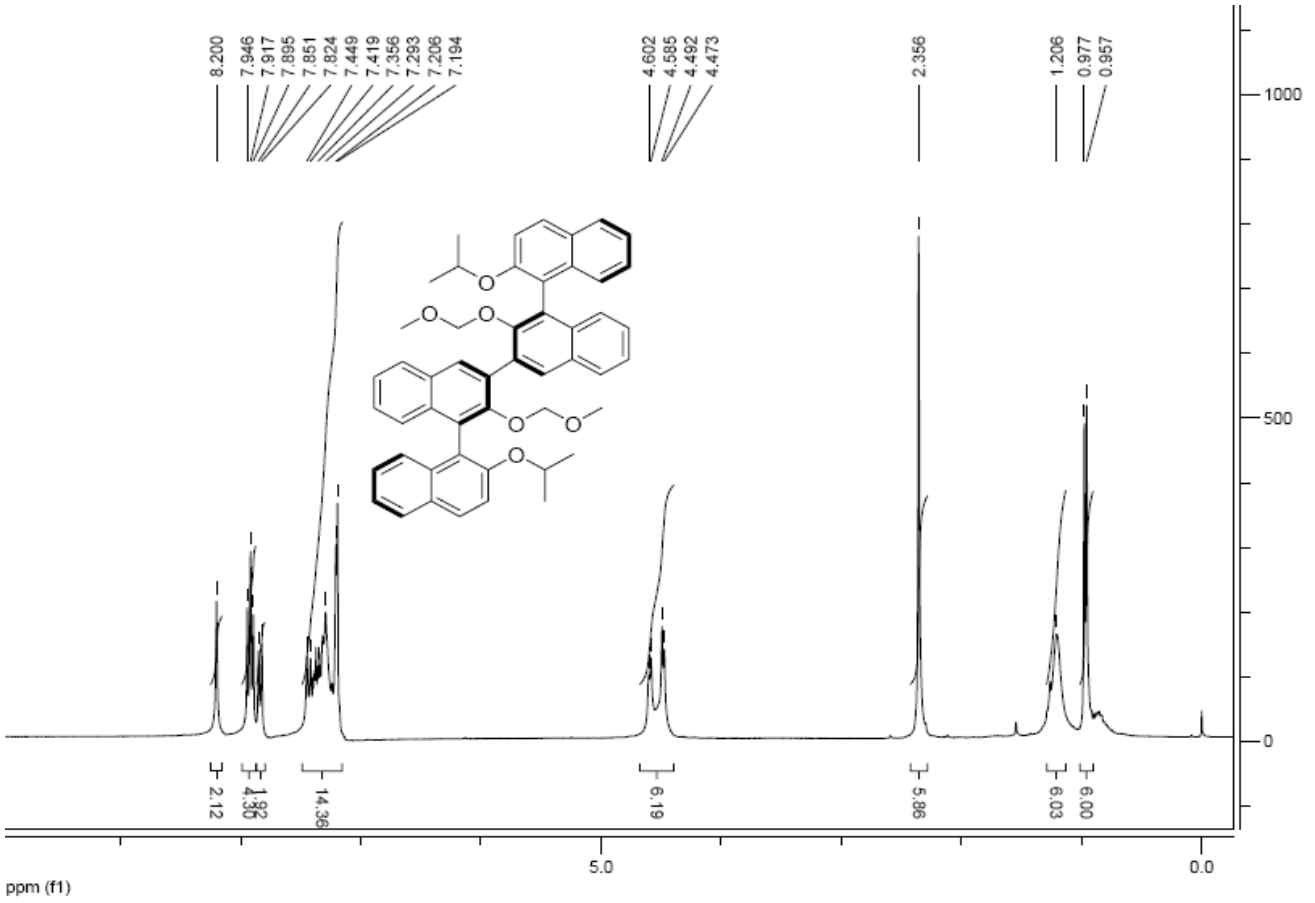
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6.19
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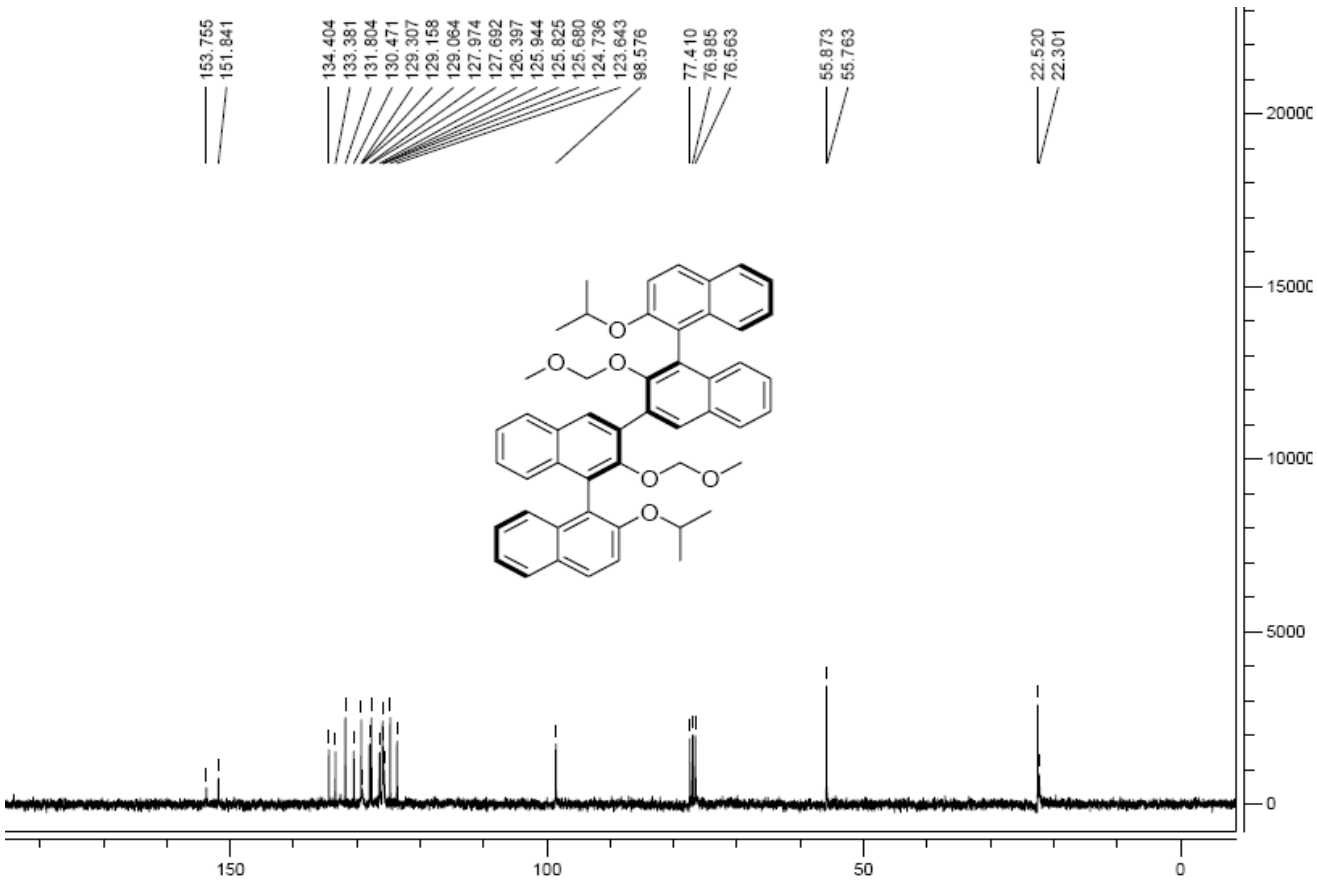
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125.825
125.680
124.736
123.643
98.576
77.410
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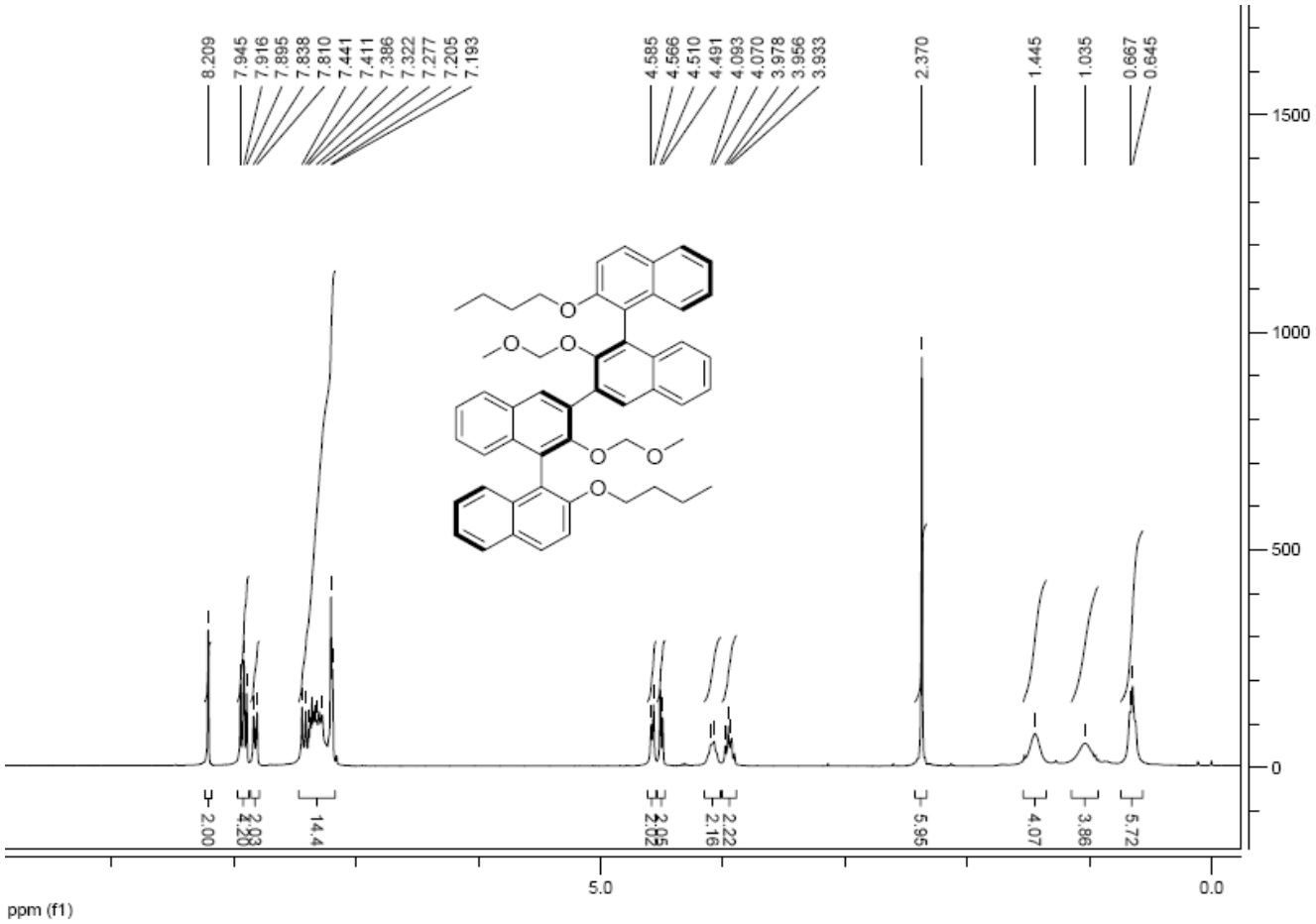
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7.322
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4.585
4.566
4.510
4.491
4.093
4.070
3.978
3.956
3.933
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1.445
1.035
0.667
0.645
2.00
2.03
14.4
2.05
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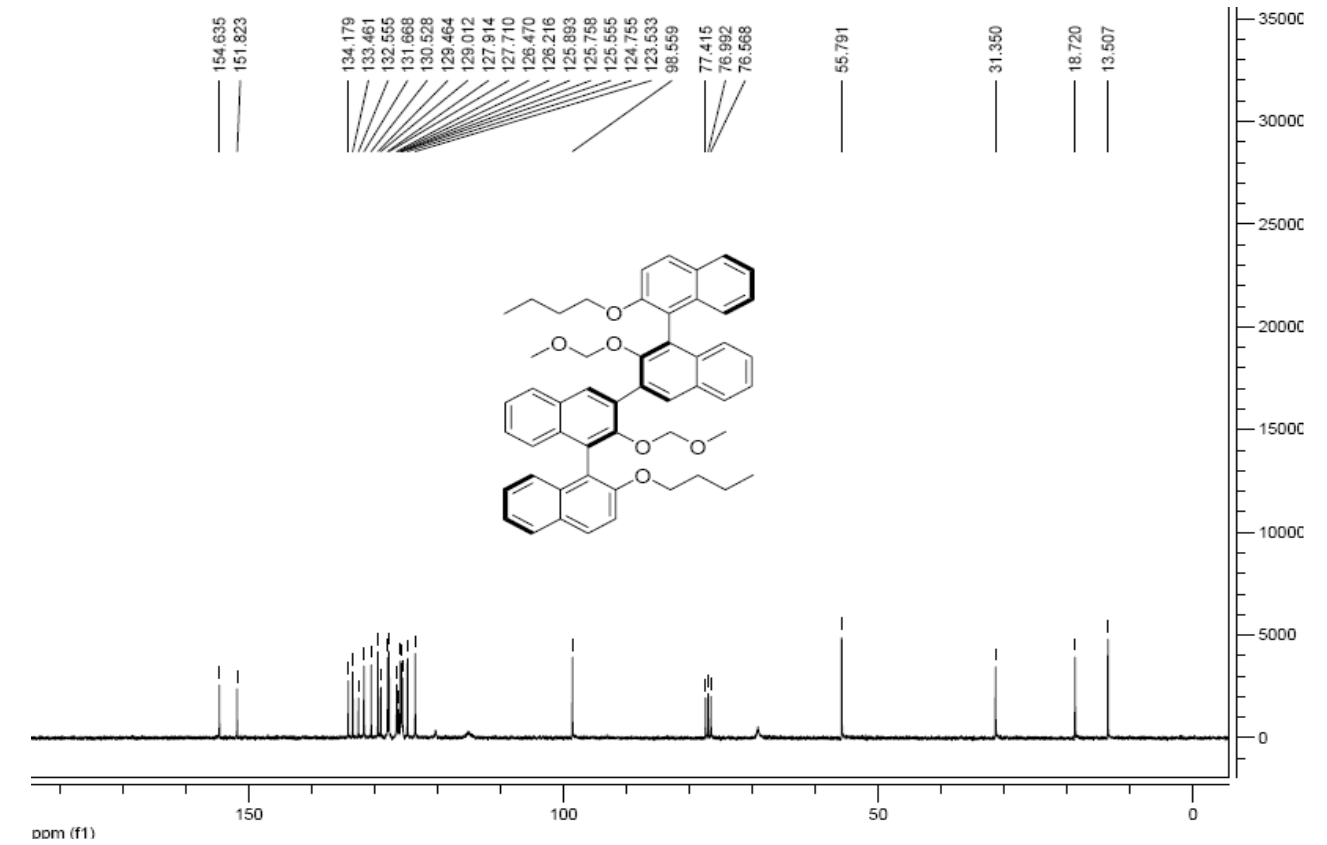
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126.216
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125.758
125.555
124.755
123.533
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76.992
76.568
55.791
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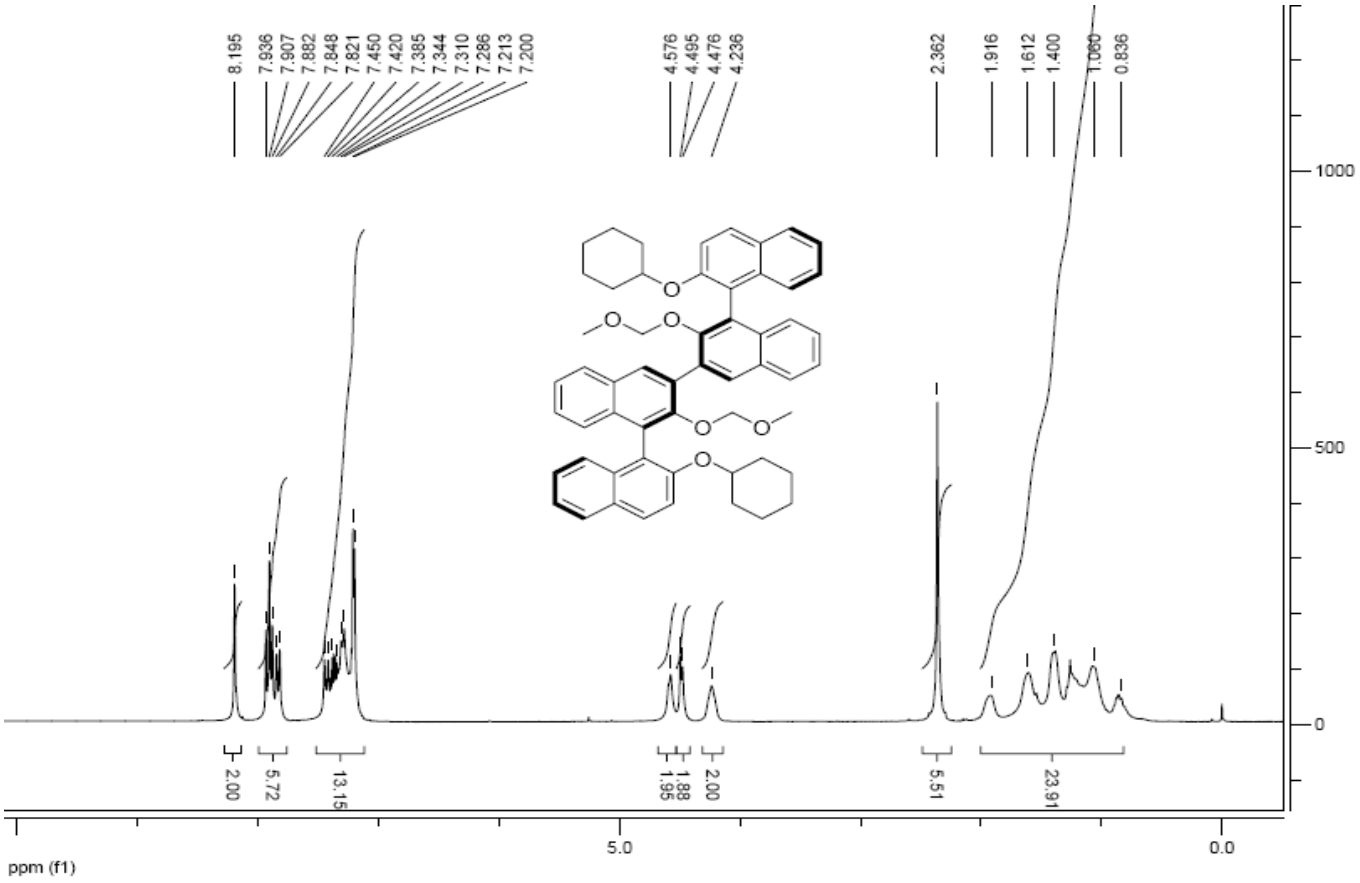
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7.420
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7.344
7.310
7.286
7.213
7.200
4.576
4.495
4.476
4.236
2.362
1.916
1.612
1.400
1.060
0.836
2.00
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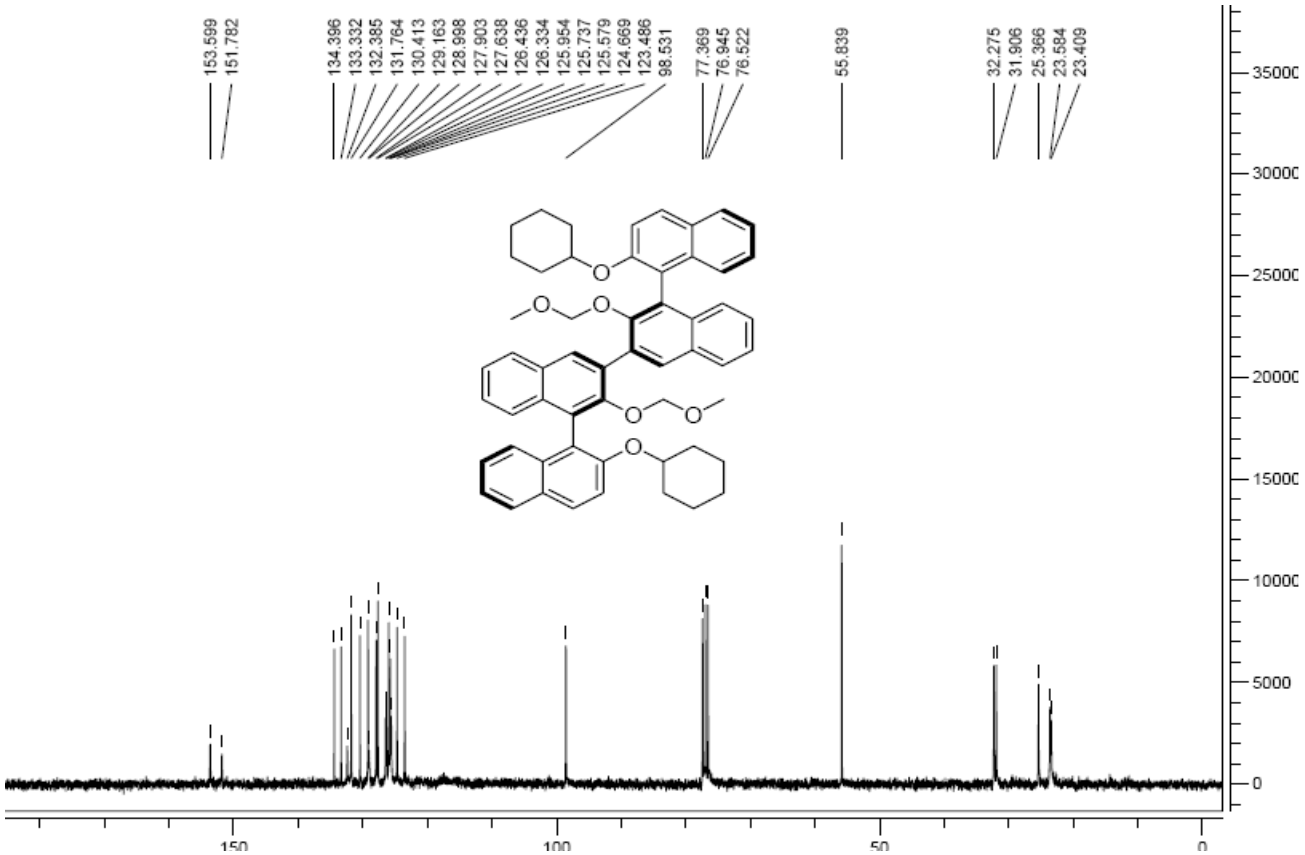
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76.945
76.522
55.839
32.275
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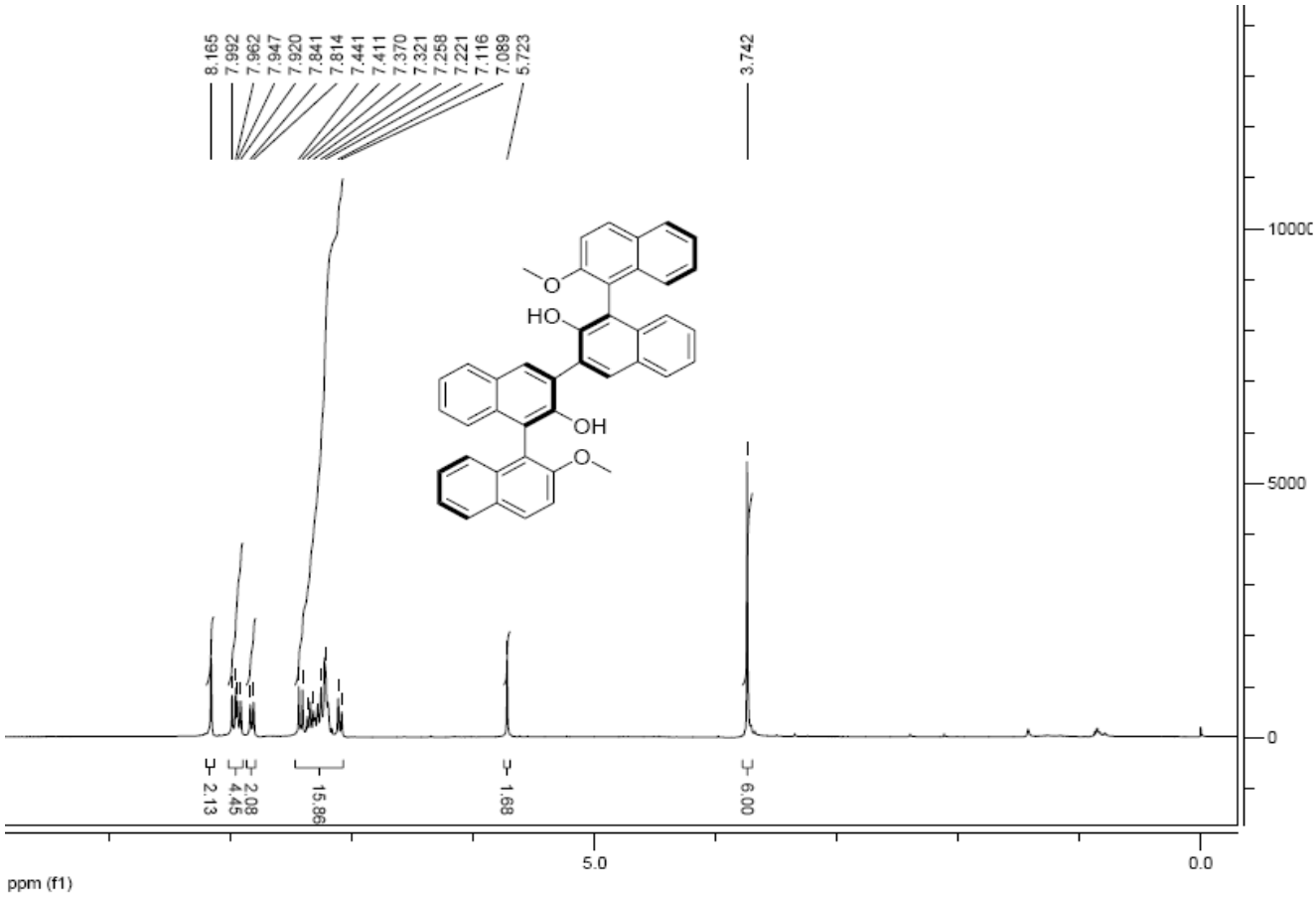
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7.221
7.116
7.089
5.723
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O
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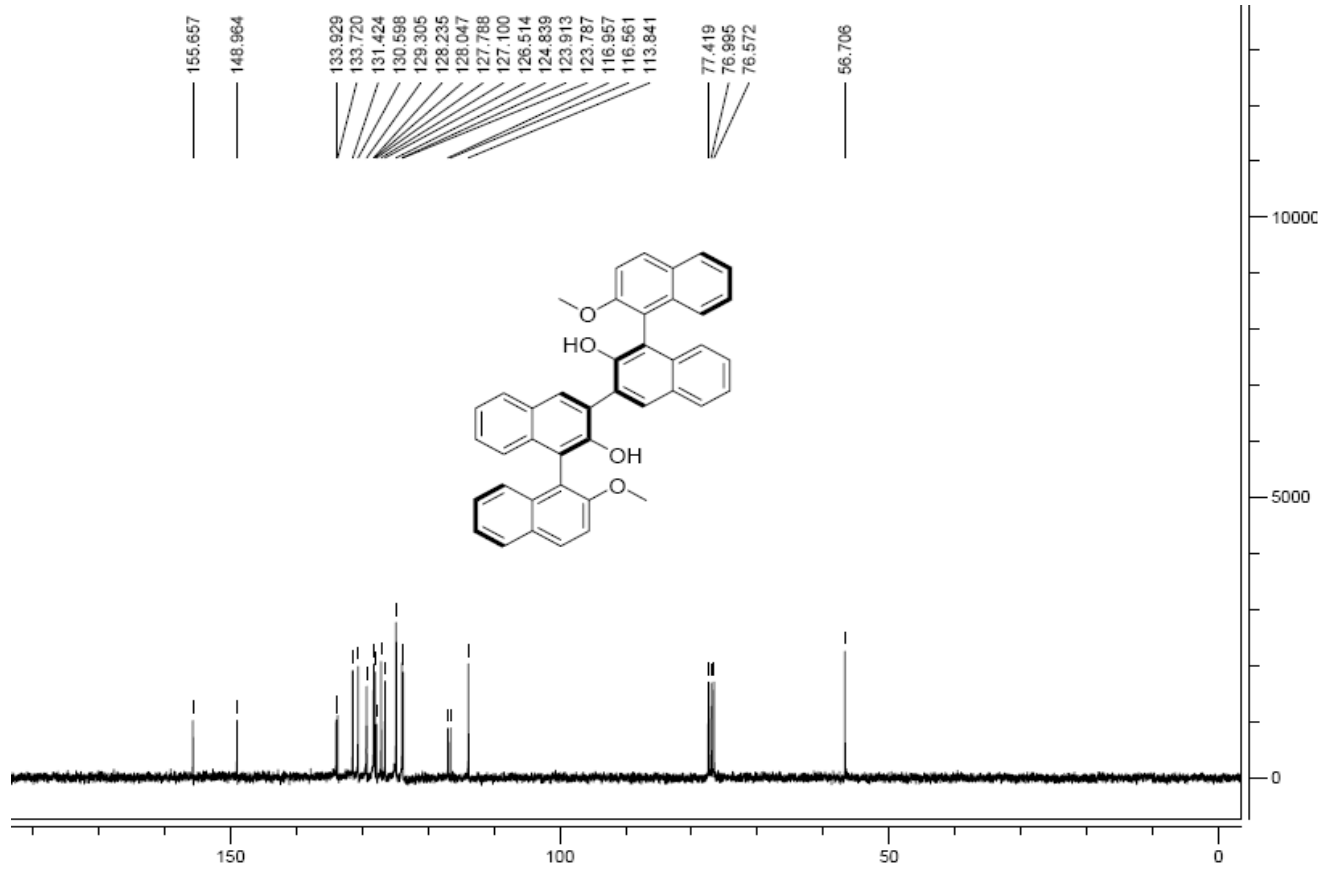
ppm (f1)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123.913
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76.995
76.572
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OH
O
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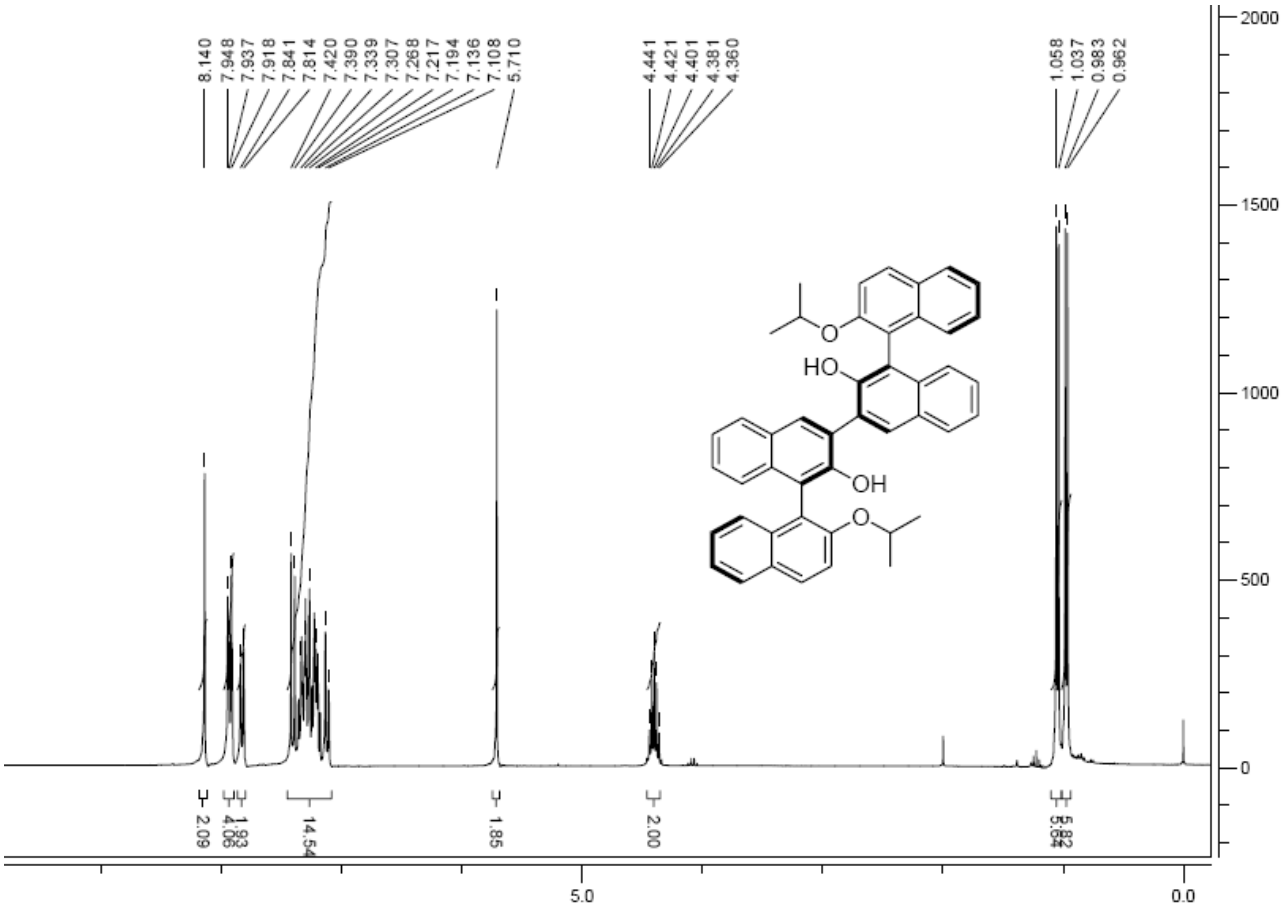
100
50
0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7.194
7.136
7.108
5.710
4.441
4.421
4.401
4.381
4.360
1.058
1.037
0.983
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14.54
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5.82
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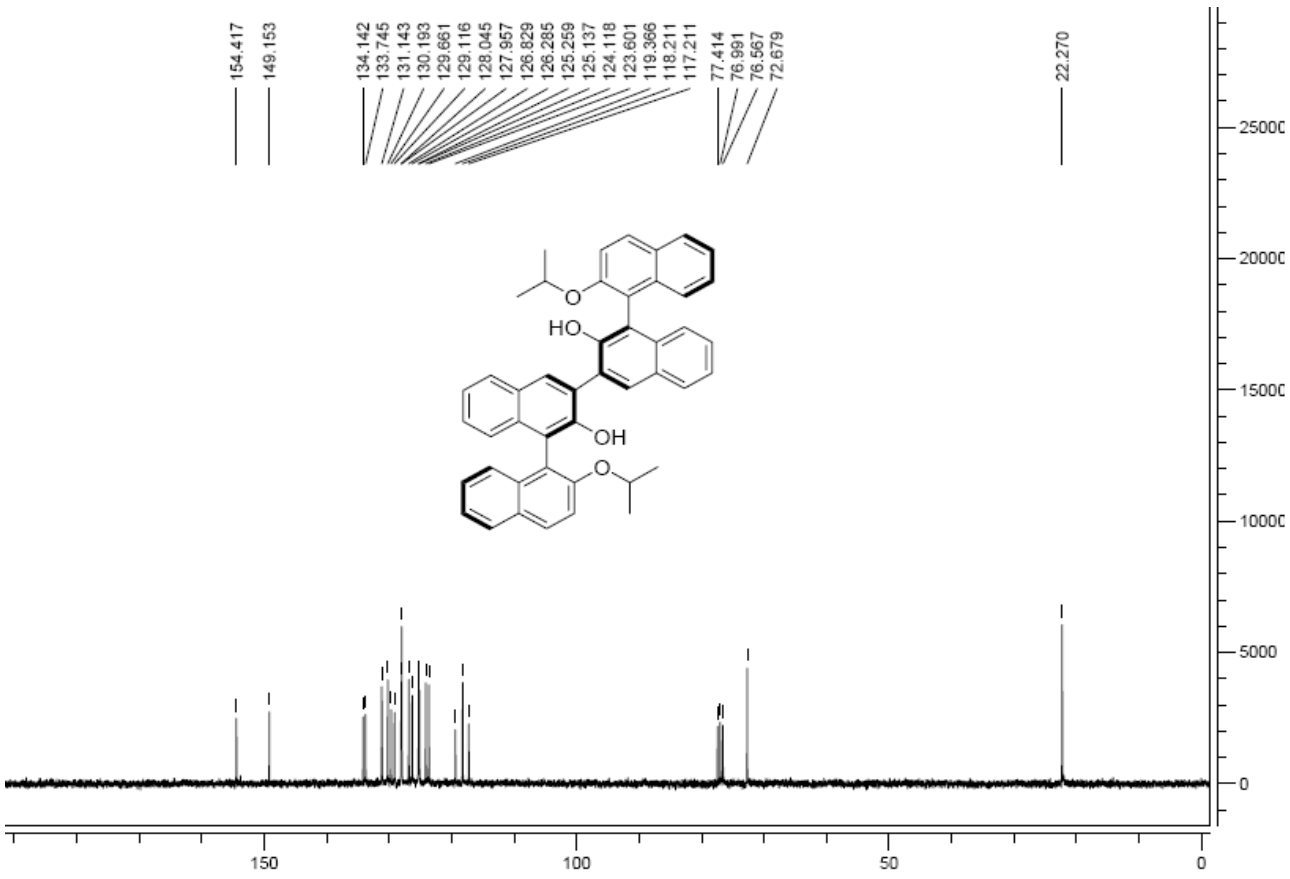
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126.829
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125.259
125.137
124.118
123.601
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117.211
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76.567
72.679
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OH
O
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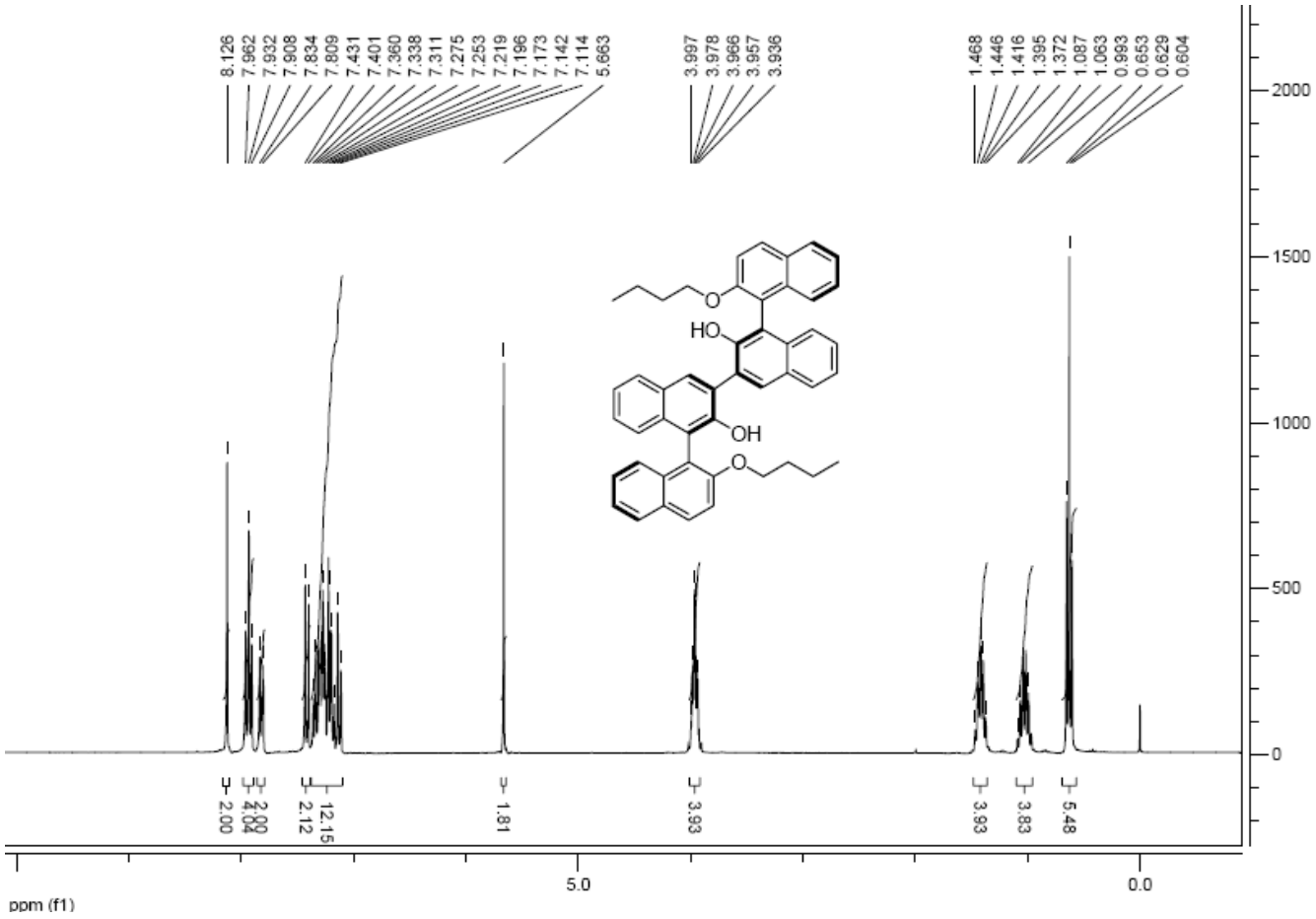
100
50
0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7.809
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7.275
7.253
7.219
7.196
7.173
7.142
7.114
5.663
3.997
3.978
3.966
3.957
3.936
1.468
1.446
1.416
1.395
1.372
1.087
1.063
0.993
0.653
0.629
0.604
HO
OH
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3.93
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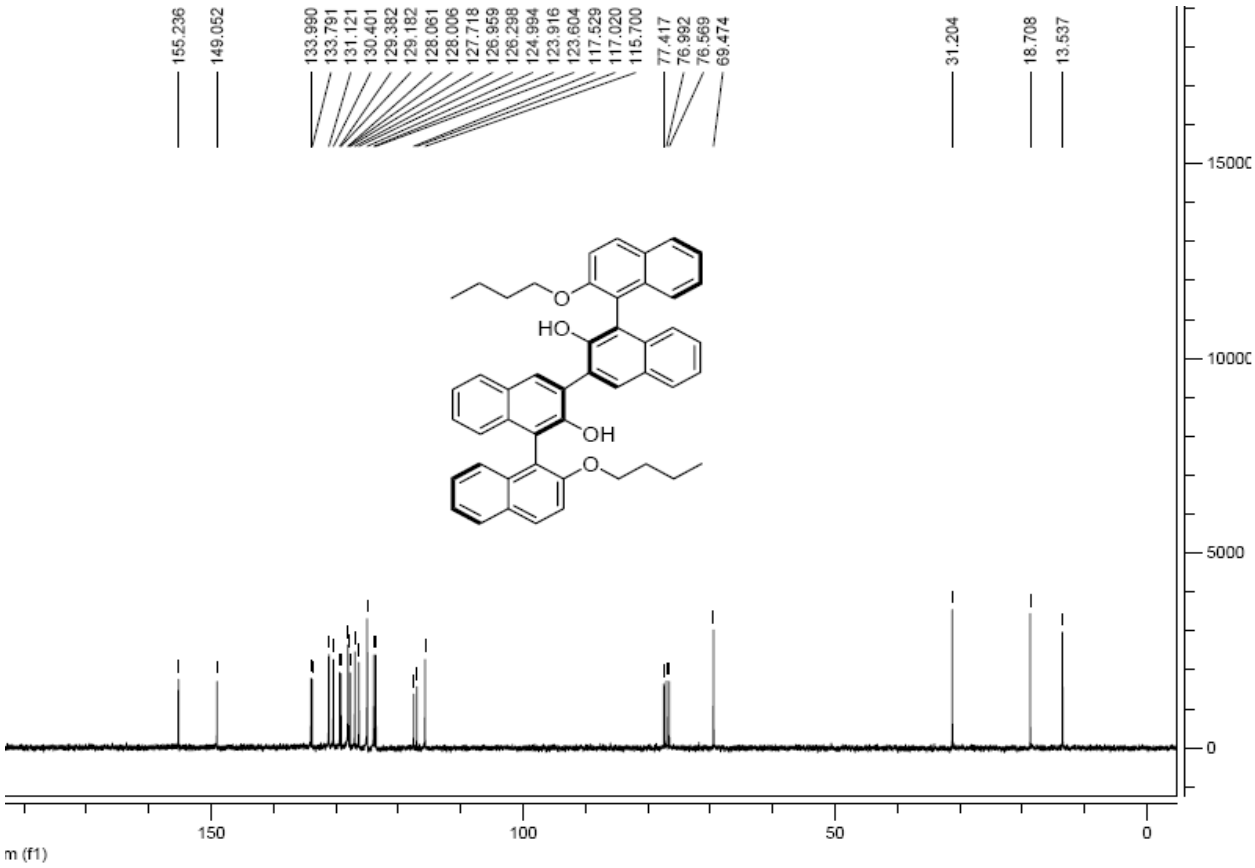
ppm (f1)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123.604
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117.020
115.700
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69.474
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OH
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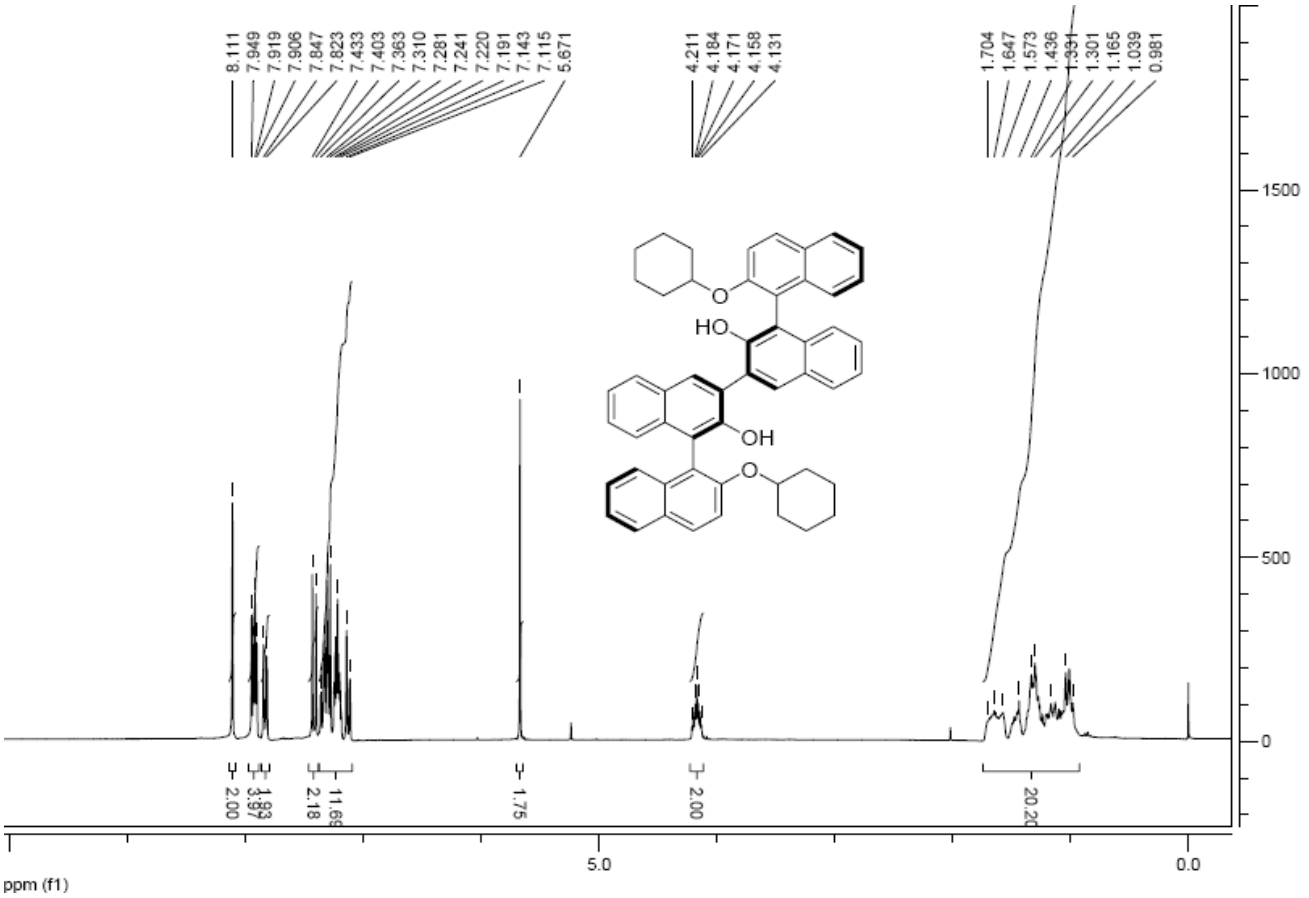
50
0
m (f1)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7.241
7.220
7.191
7.143
7.115
5.671
4.211
4.184
4.171
4.158
4.131
1.704
1.647
1.573
1.436
1.331
1.301
1.165
1.039
0.981
HO
OH
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1.93
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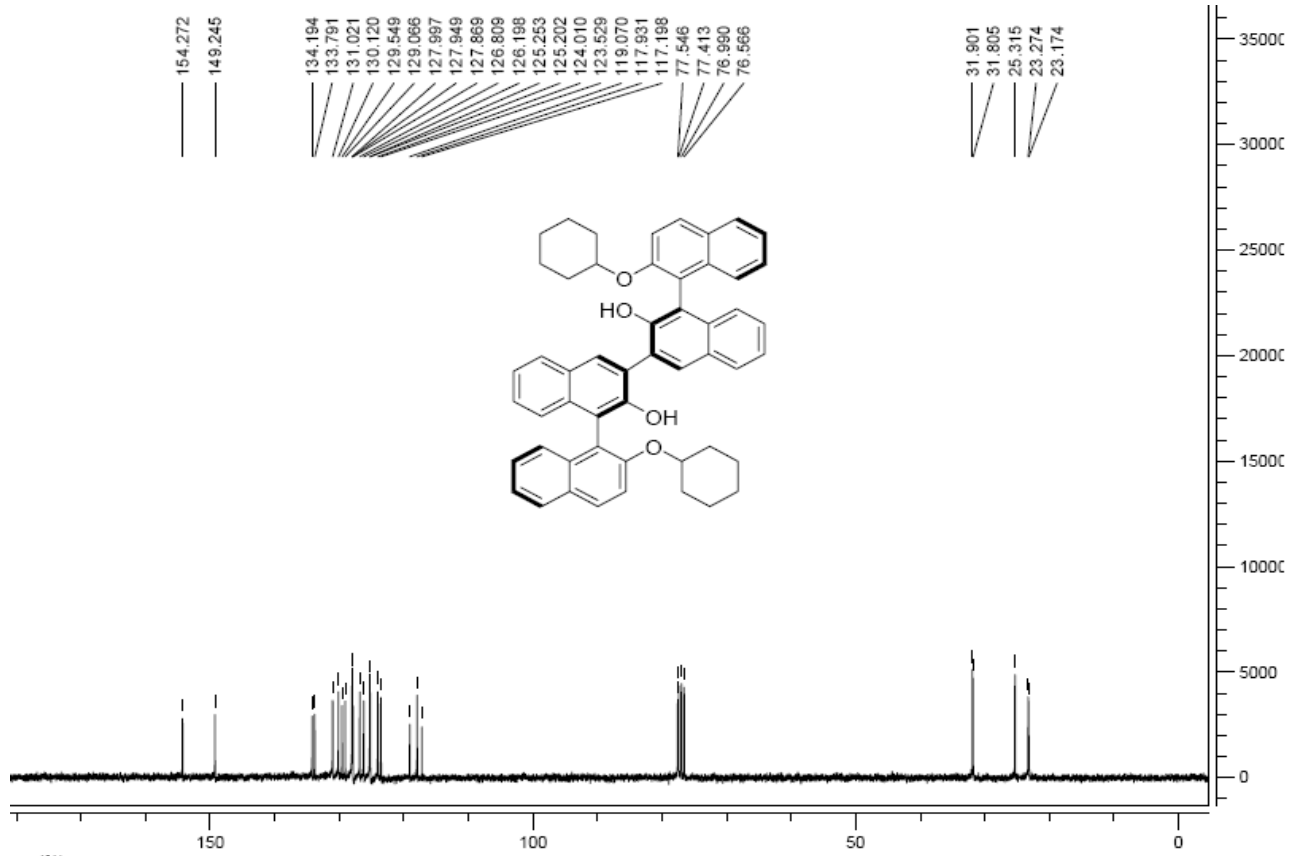
ppm (f1)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125.253
125.202
124.010
123.529
119.070
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117.198
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77.413
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HO
OH
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50
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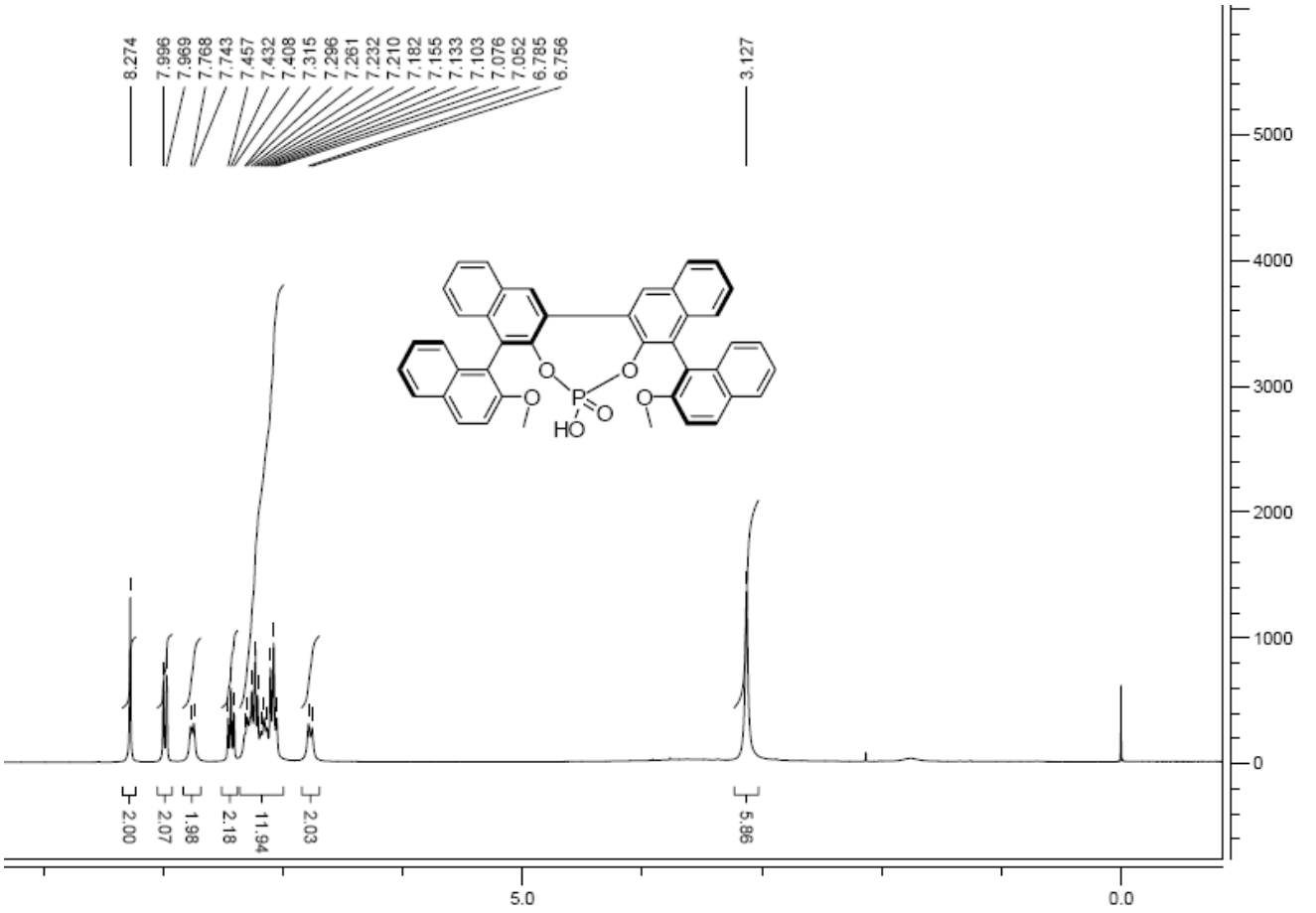
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7.232
7.210
7.182
7.155
7.133
7.103
7.076
7.052
6.785
6.756
3.127
HO
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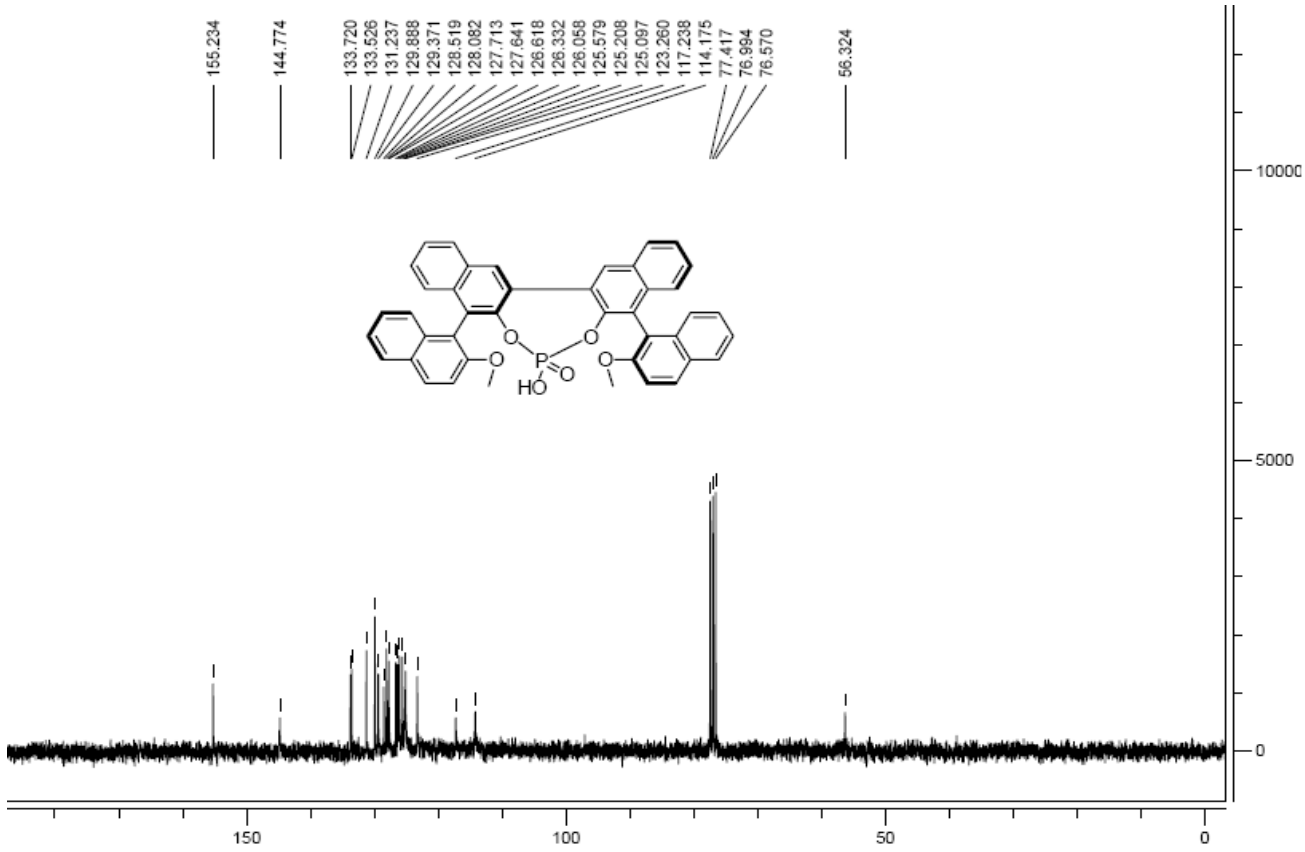
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128.519
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127.713
127.641
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126.332
126.058
125.579
125.208
125.097
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150
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50
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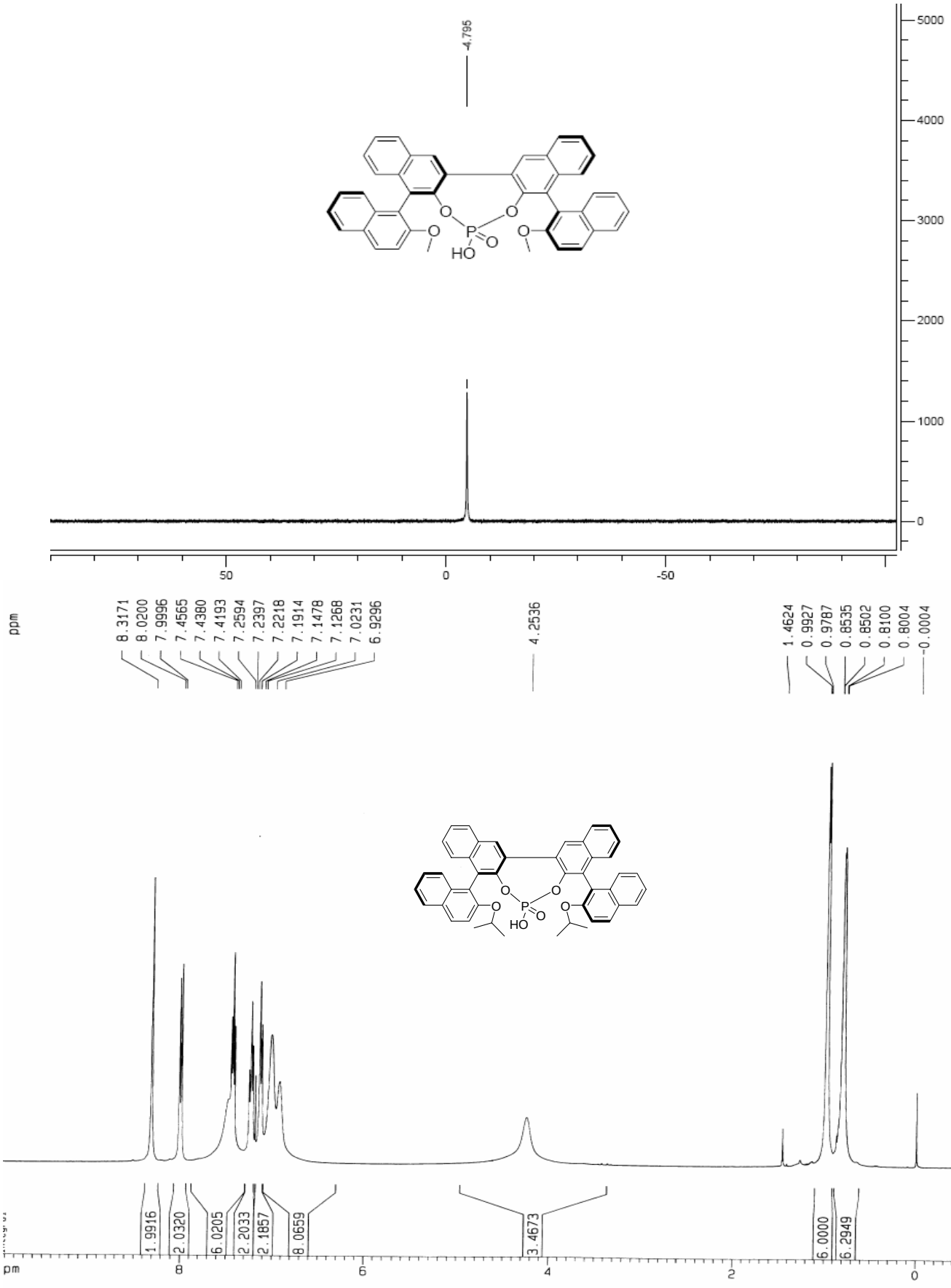
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-50
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7.2594
7.2397
7.2218
7.1914
7.1478
7.1268
7.0231
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1.4624
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0.9787
0.8535
0.8502
0.8100
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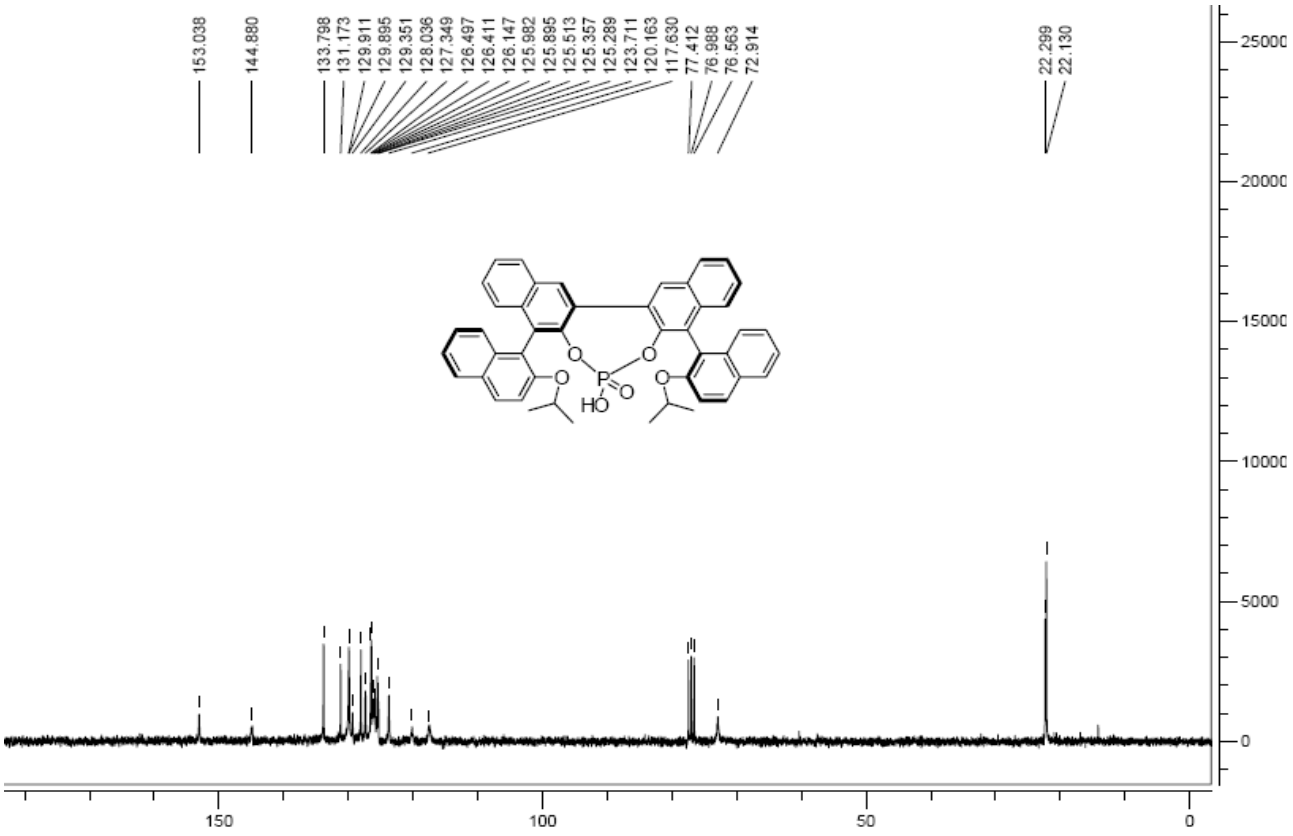
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120.163
117.630
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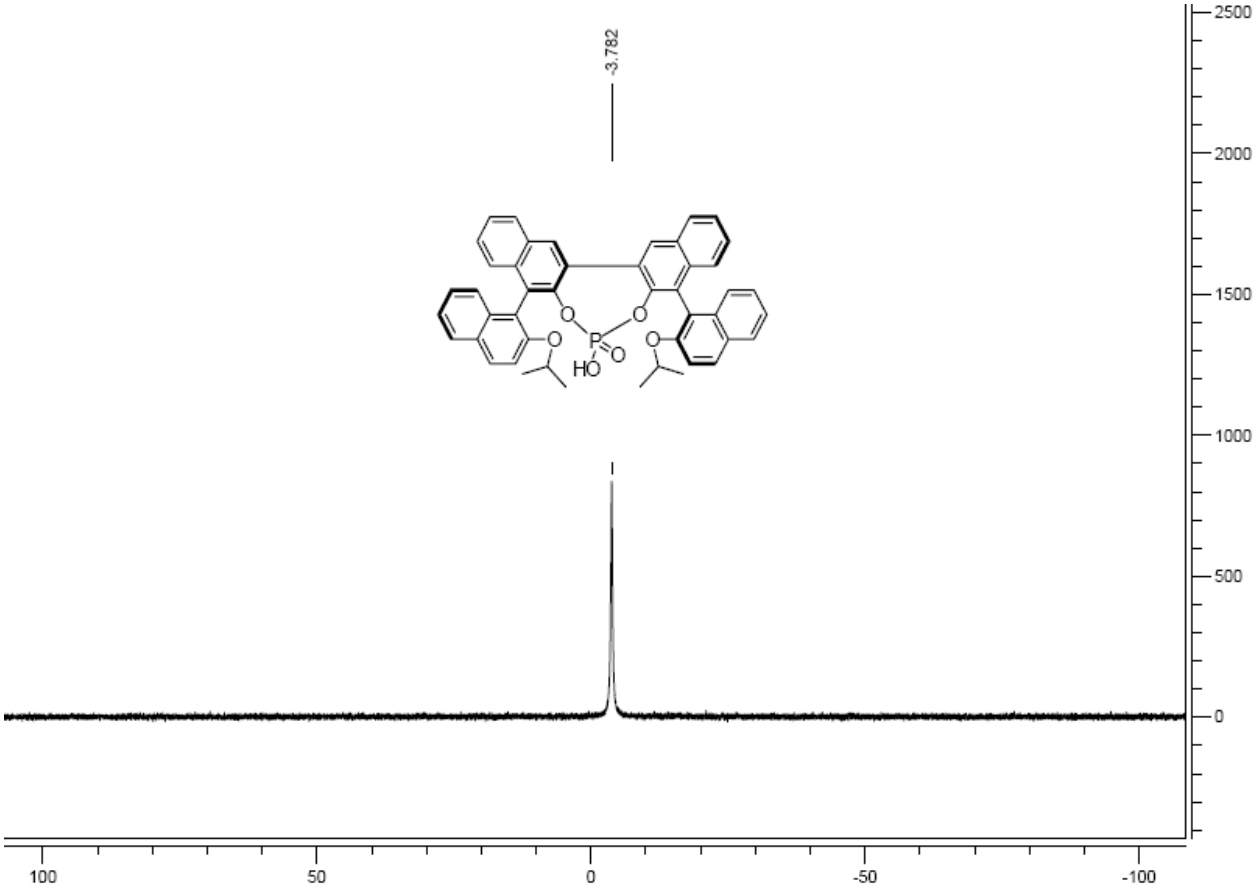
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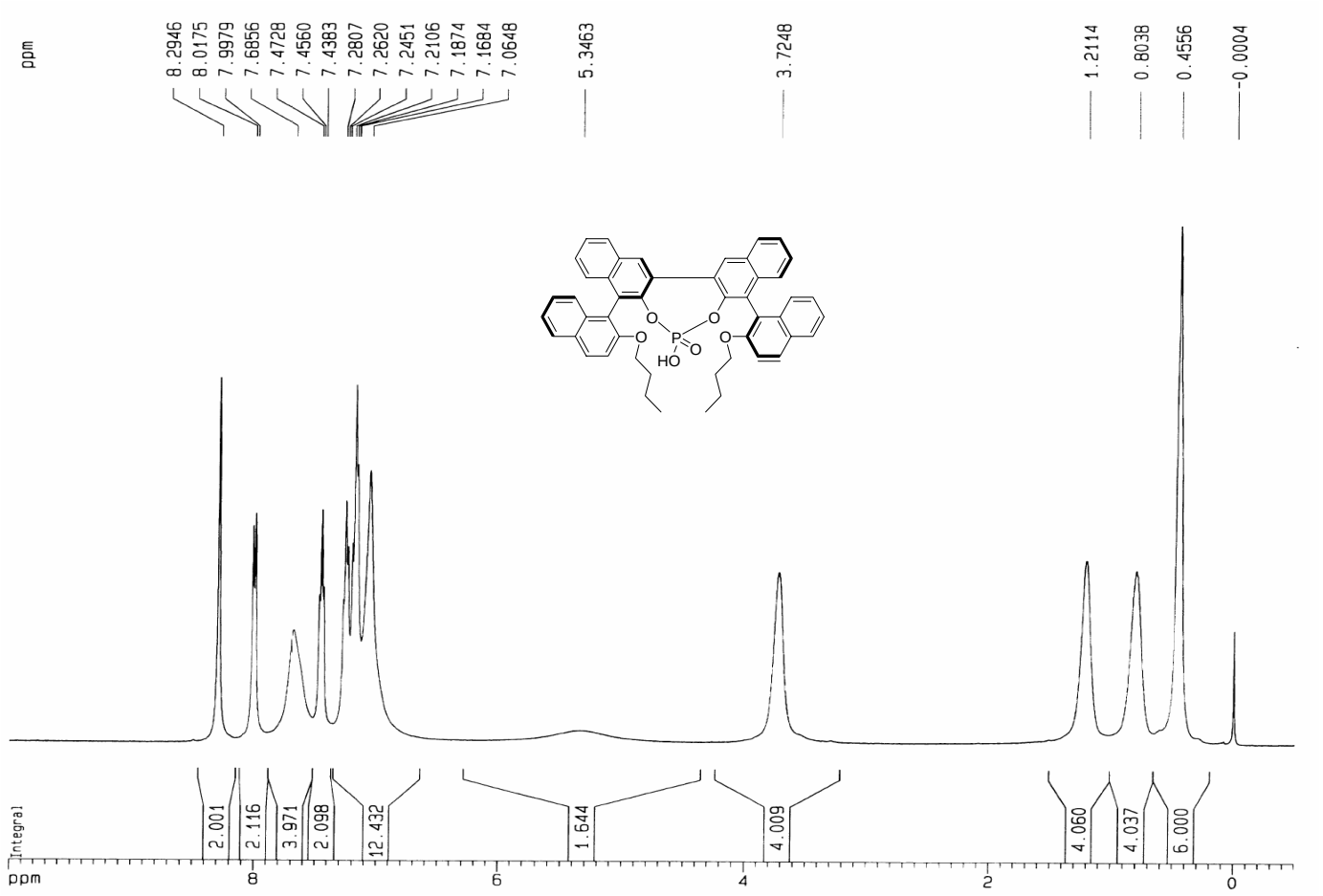
-100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7.2106
7.1874
7.1684
7.0648
5.3463
3.7248
1.2114
0.8038
0.4556
-0.0004
Integral
2.001
2.116
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12.432
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4.009
4.060
4.037
6.000
ppm
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6
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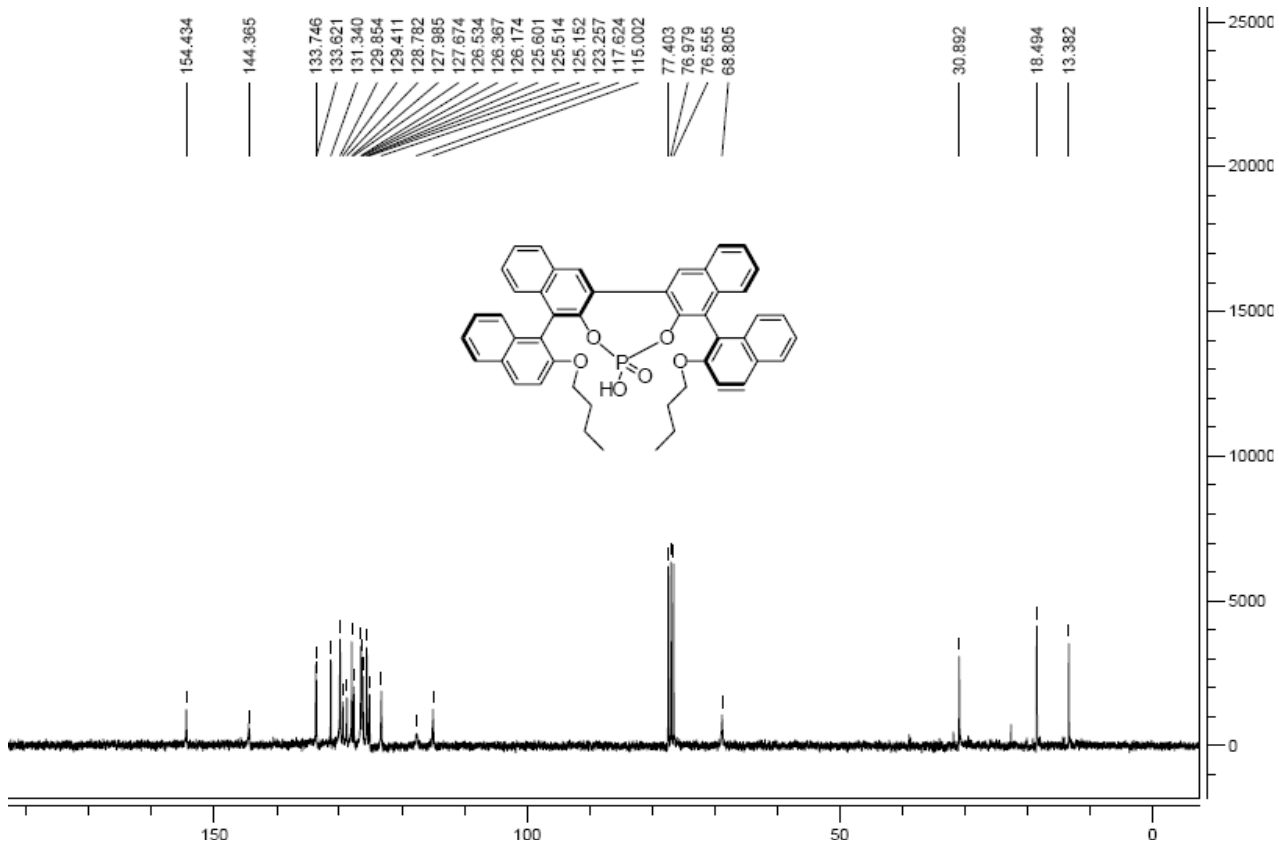
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126.174
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125.514
125.152
123.257
117.624
115.002
77.403
76.979
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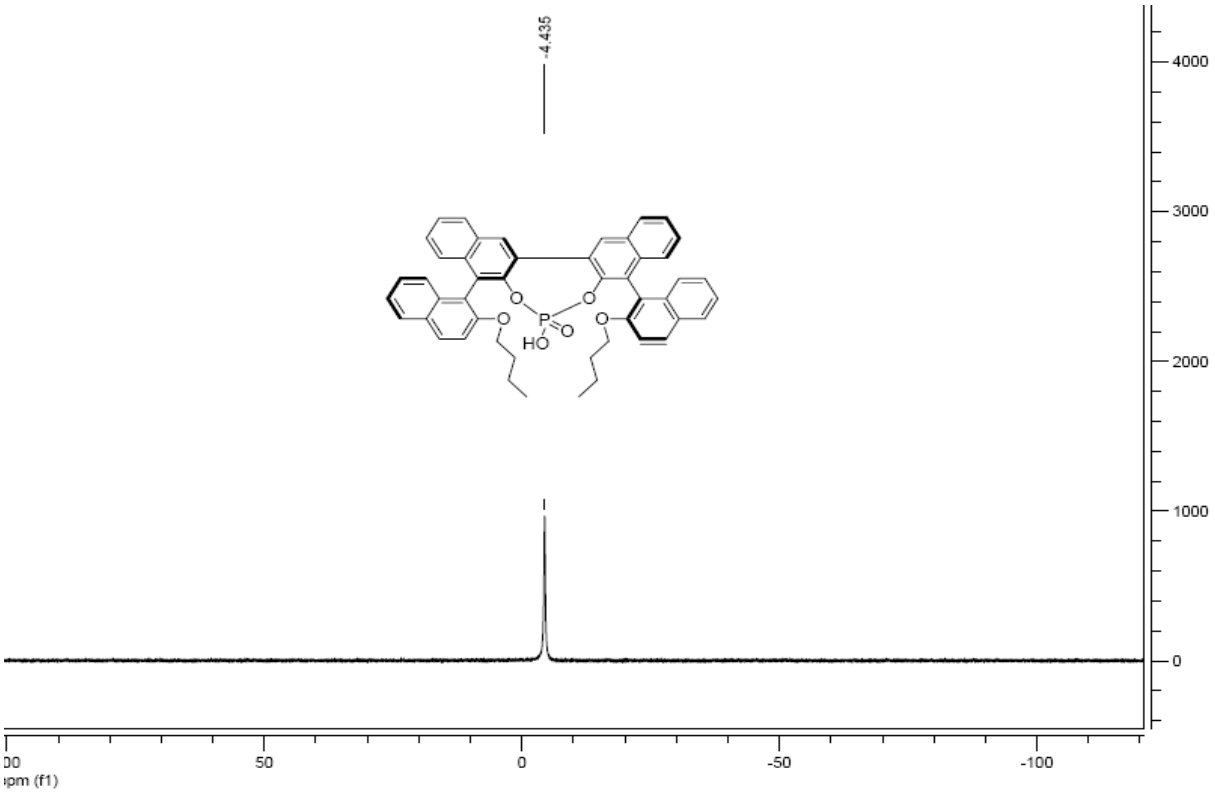
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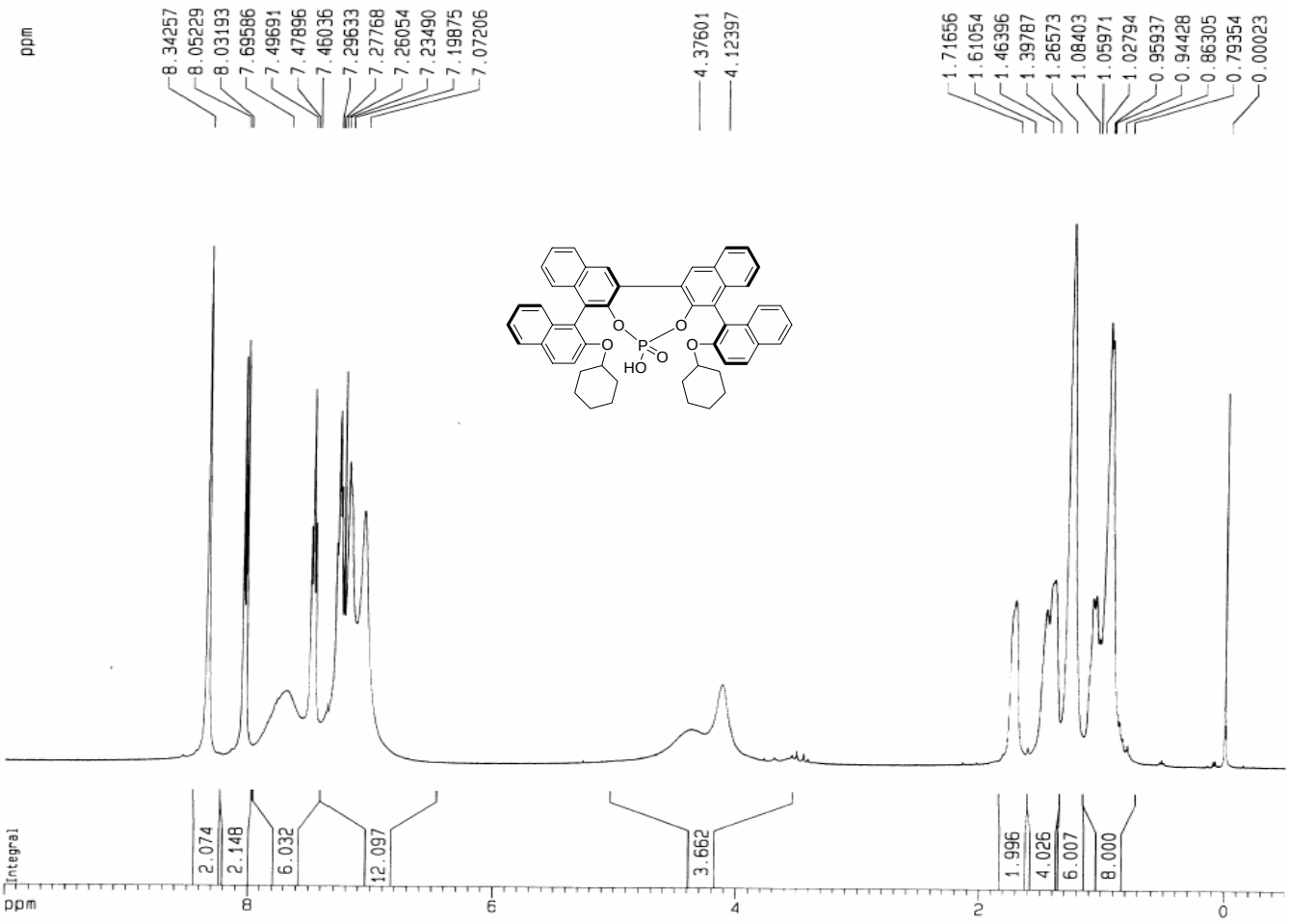
ppm (f1)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7.19875
7.07206
4.37601
4.12397
1.71656
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1.39787
1.26573
1.08403
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1.02794
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0.94428
0.86305
0.79354
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Integral
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1.996
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8.000
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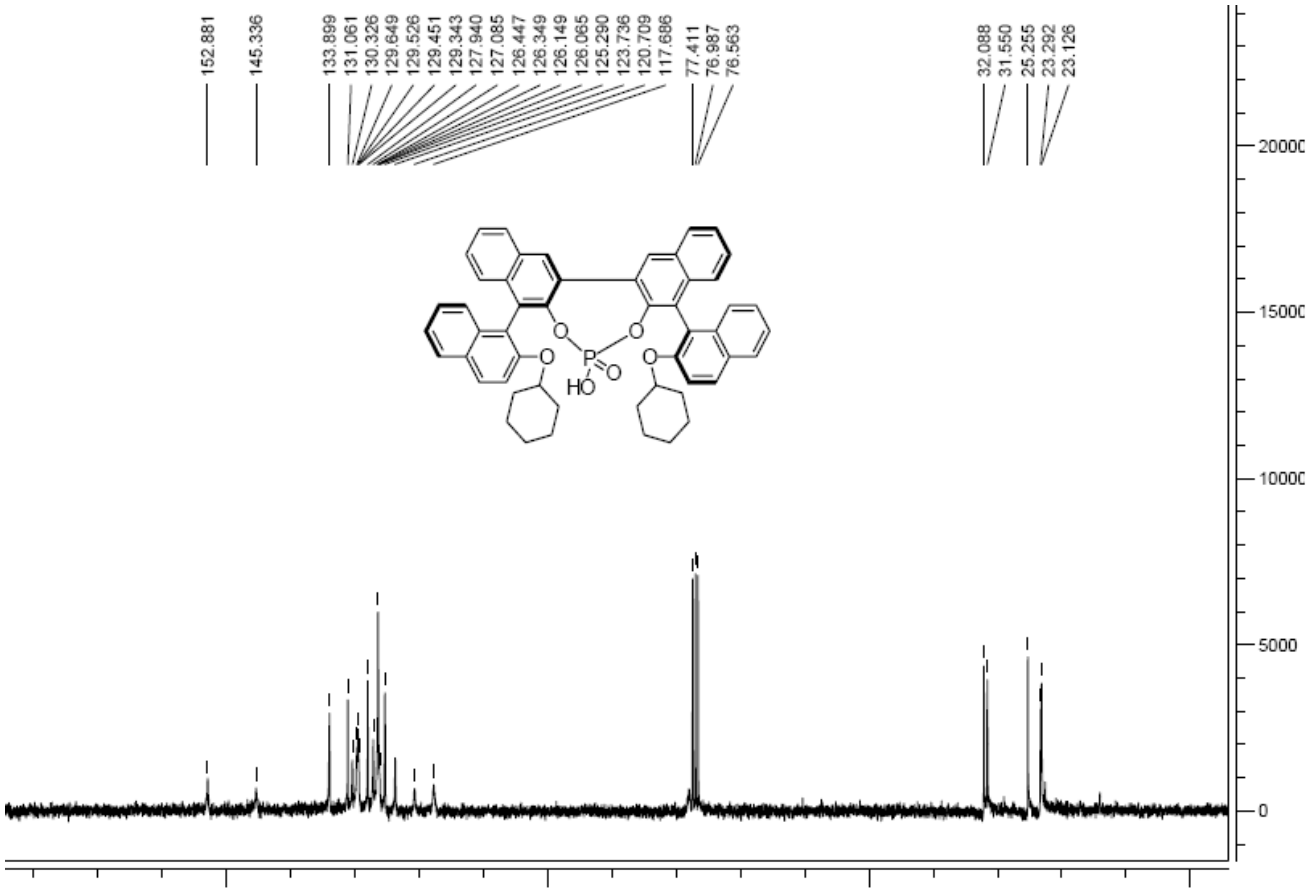
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126.349
126.149
126.065
125.290
123.736
120.709
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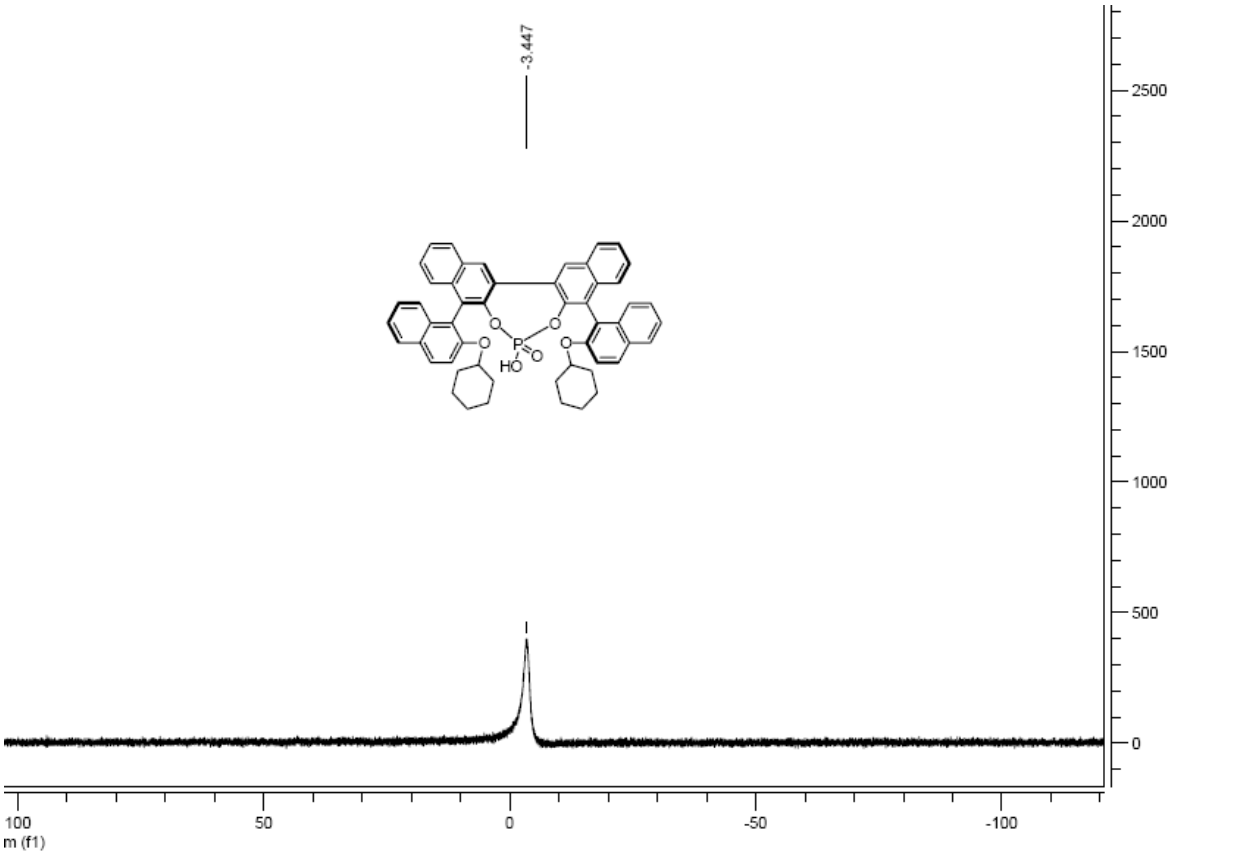
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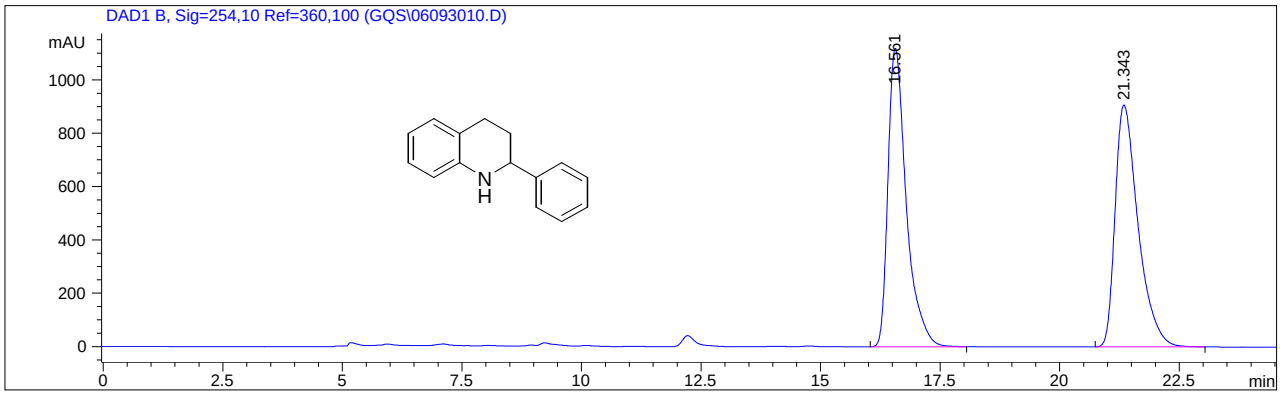
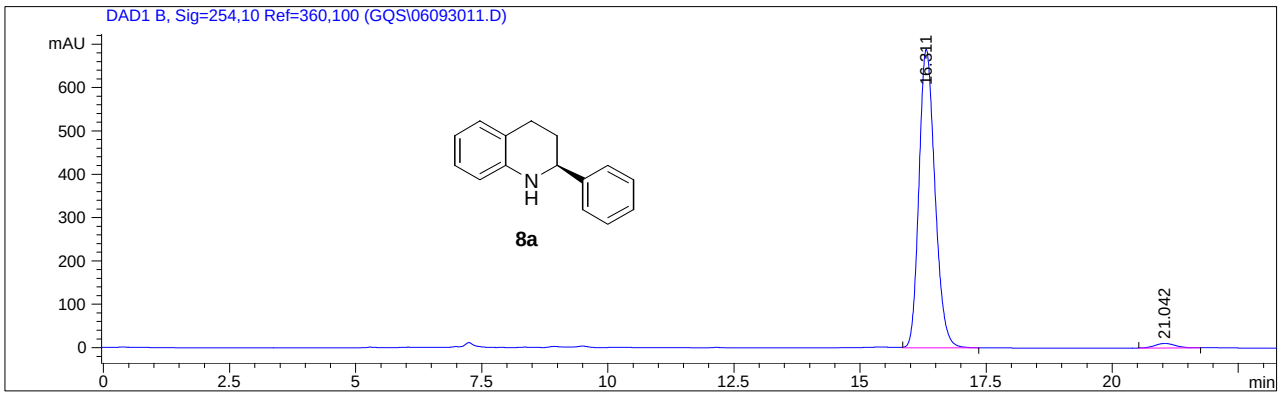
-100
m (f1)

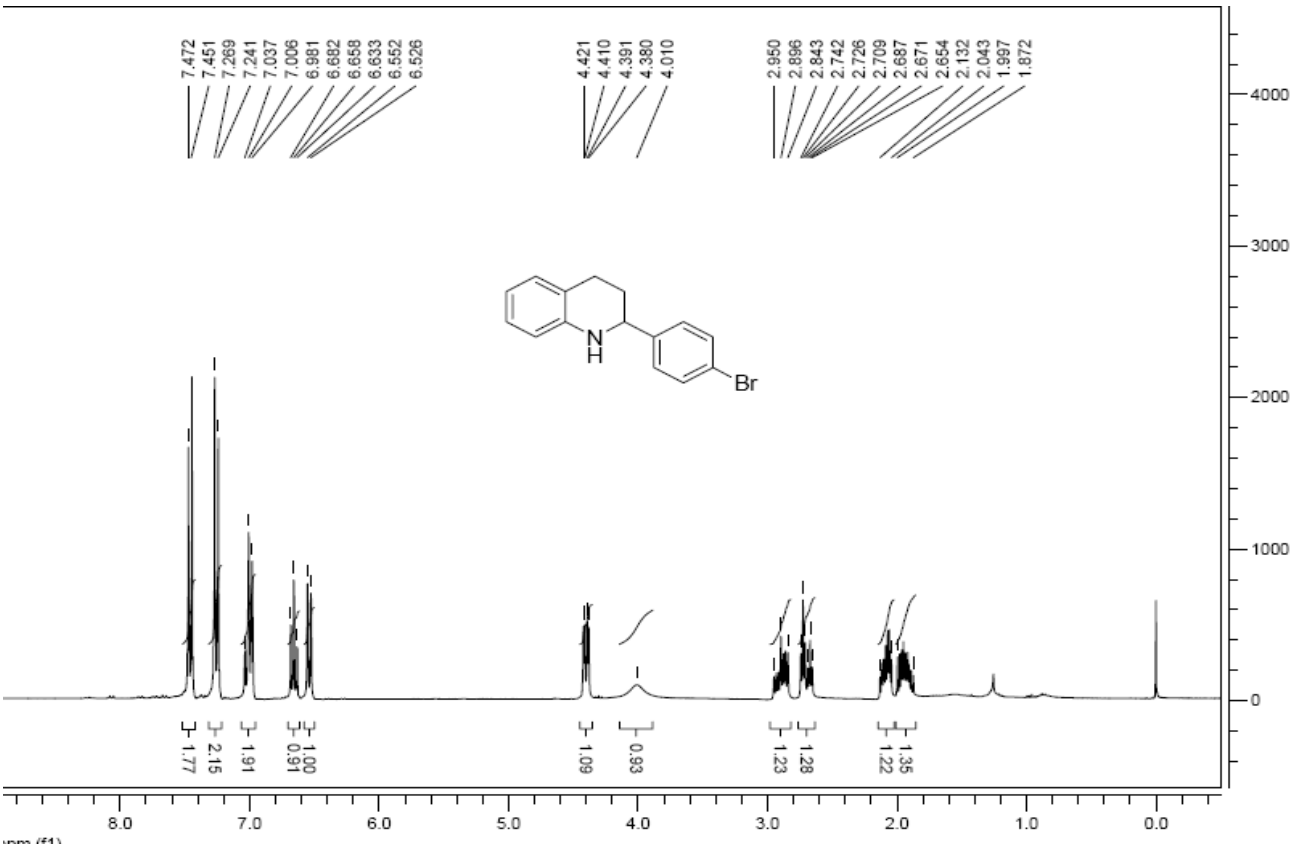
Copies of ^{1}H and ^{13}C NMR spectra, HPLC profiles of tetrahydroquinolines

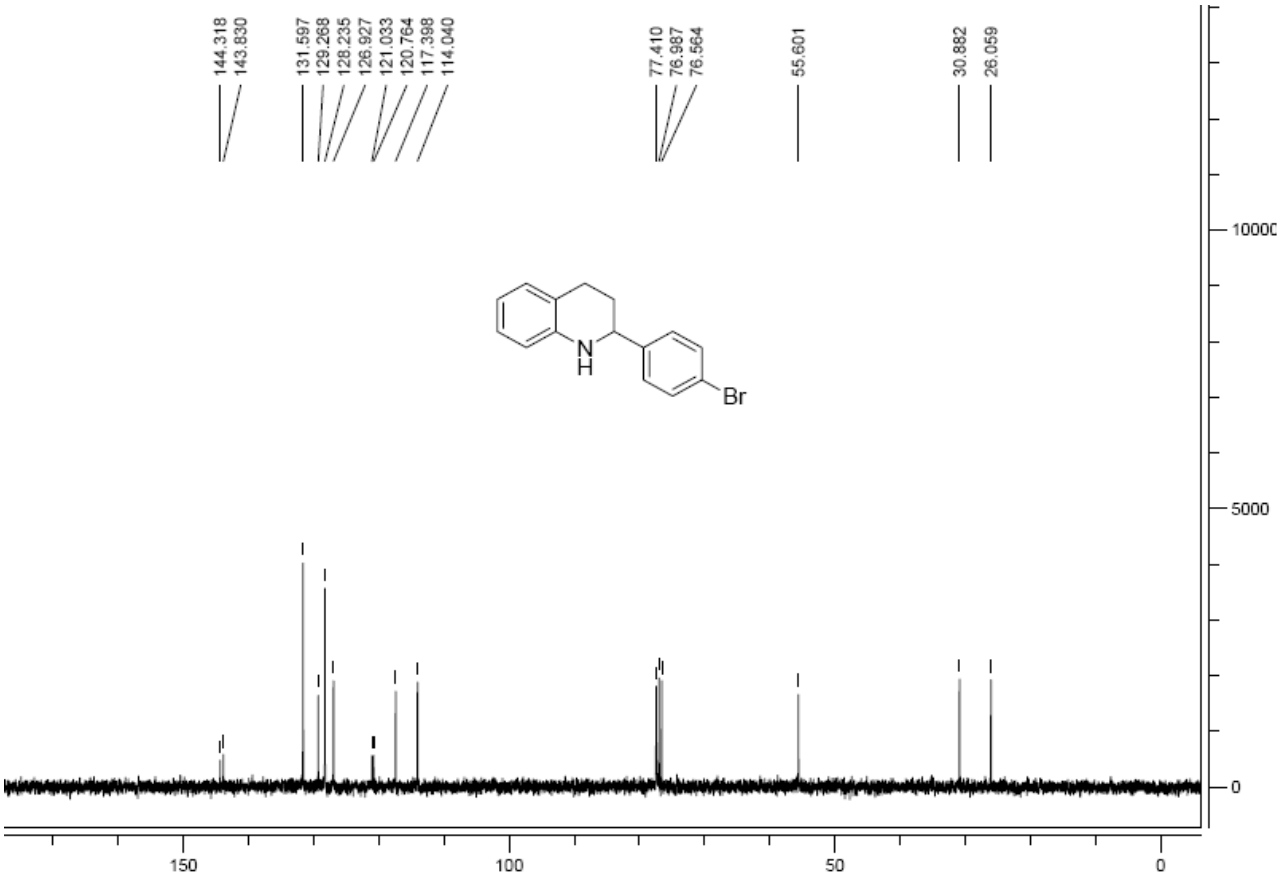


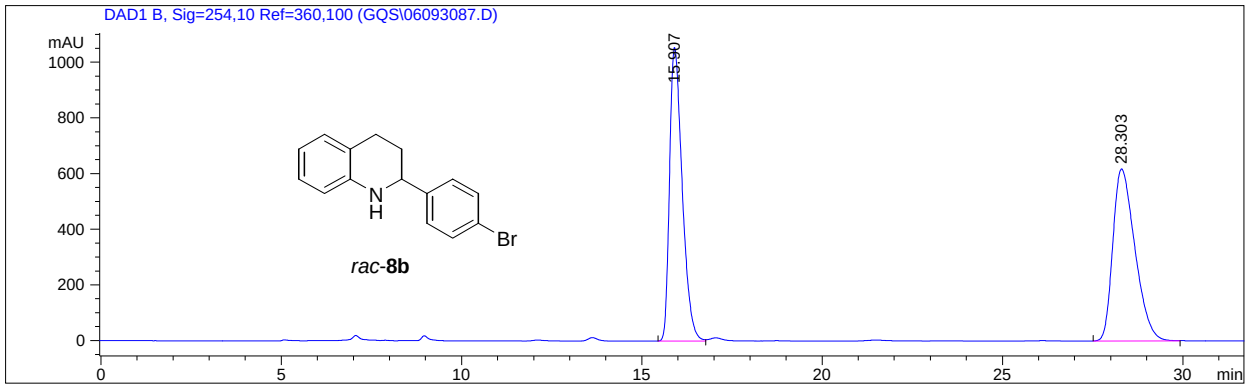
(*rac*)-2-phenyl-1,2,3,4-tetrahydroquinoline



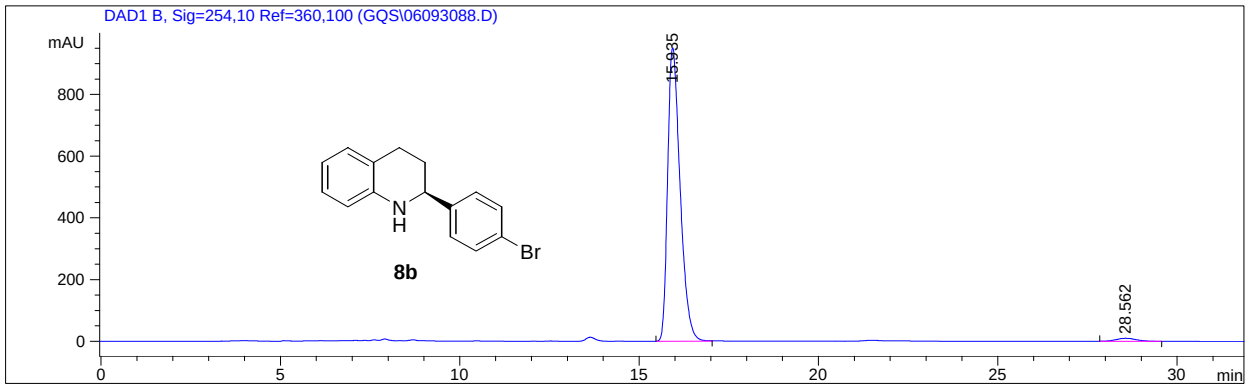
2-phenyl-1,2,3,4-tetrahydroquinoline



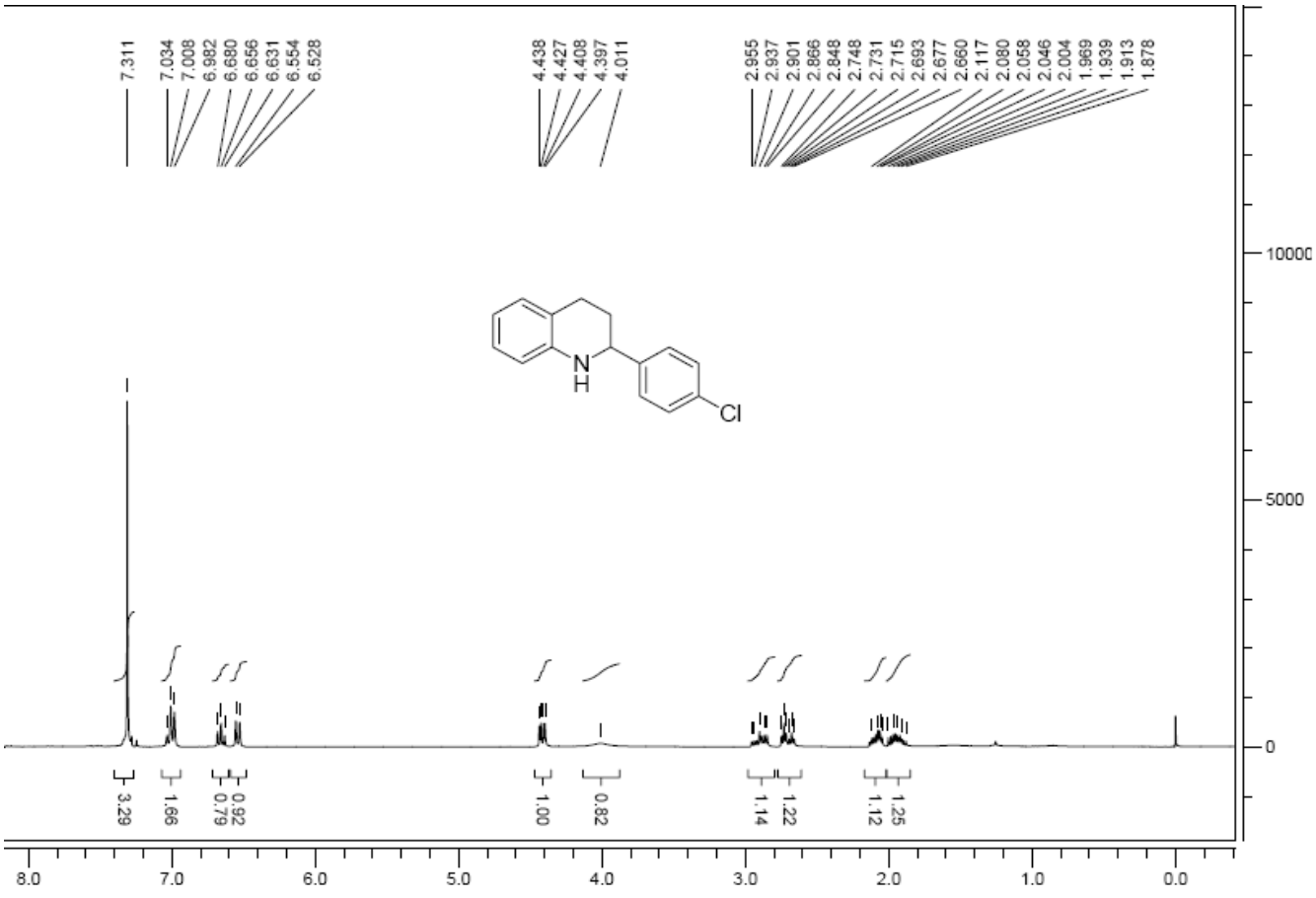




(*rac*)-2-(4-bromophenyl)-1,2,3,4-tetrahydroquinoline



(2-(4-bromophenyl)-1,2,3,4-tetrahydroquinoline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2.004
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1.939
1.913
1.878
N
H
Cl
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5000
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0.92
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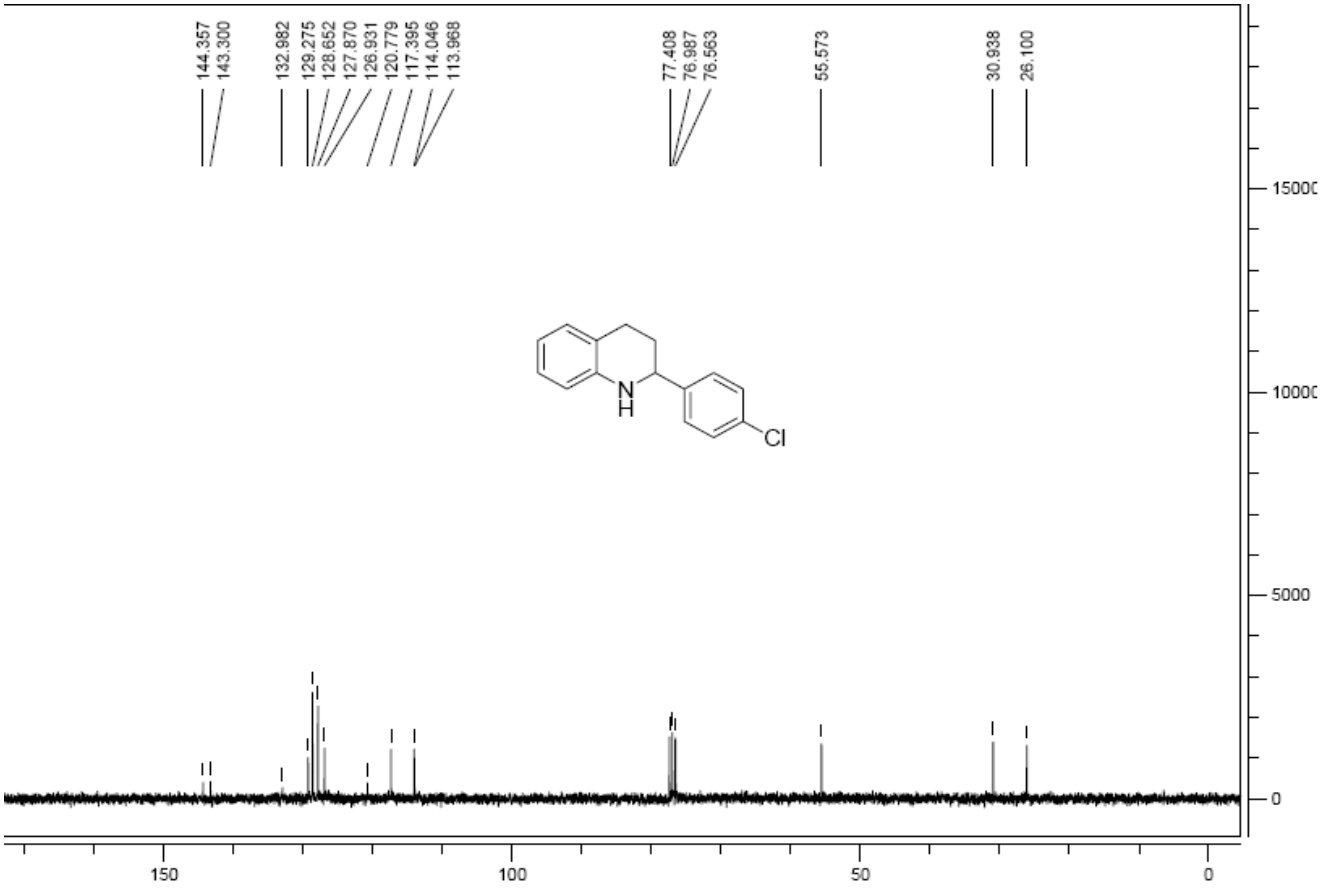
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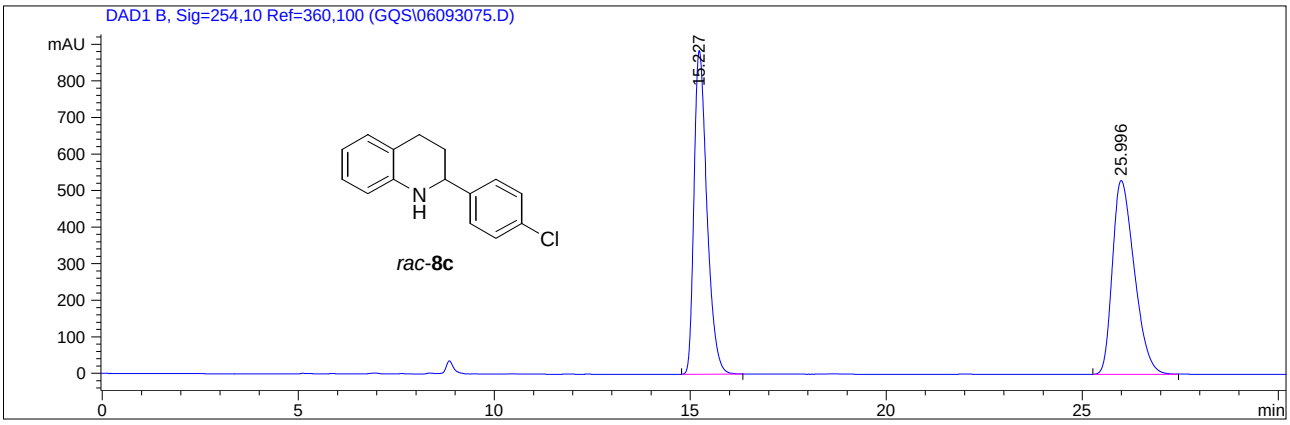
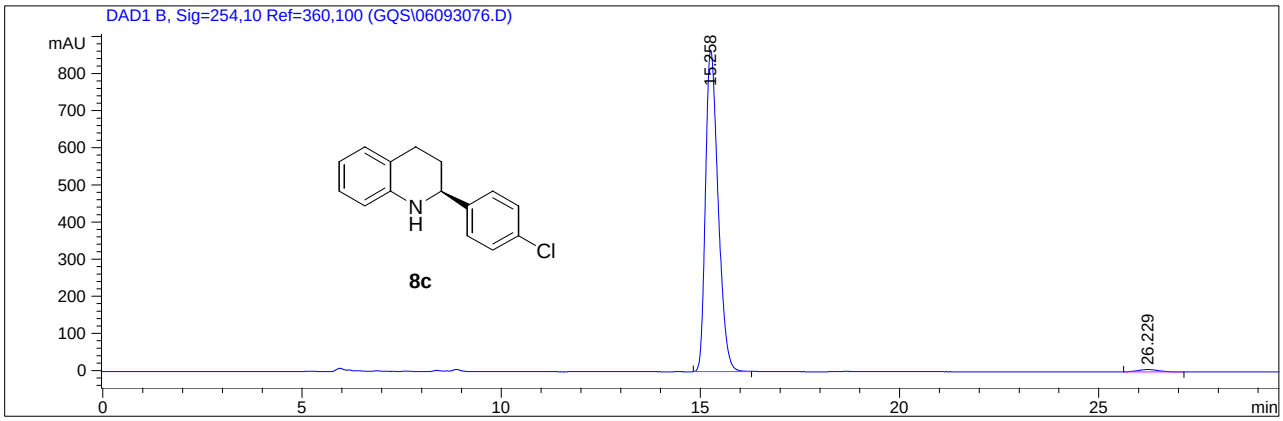
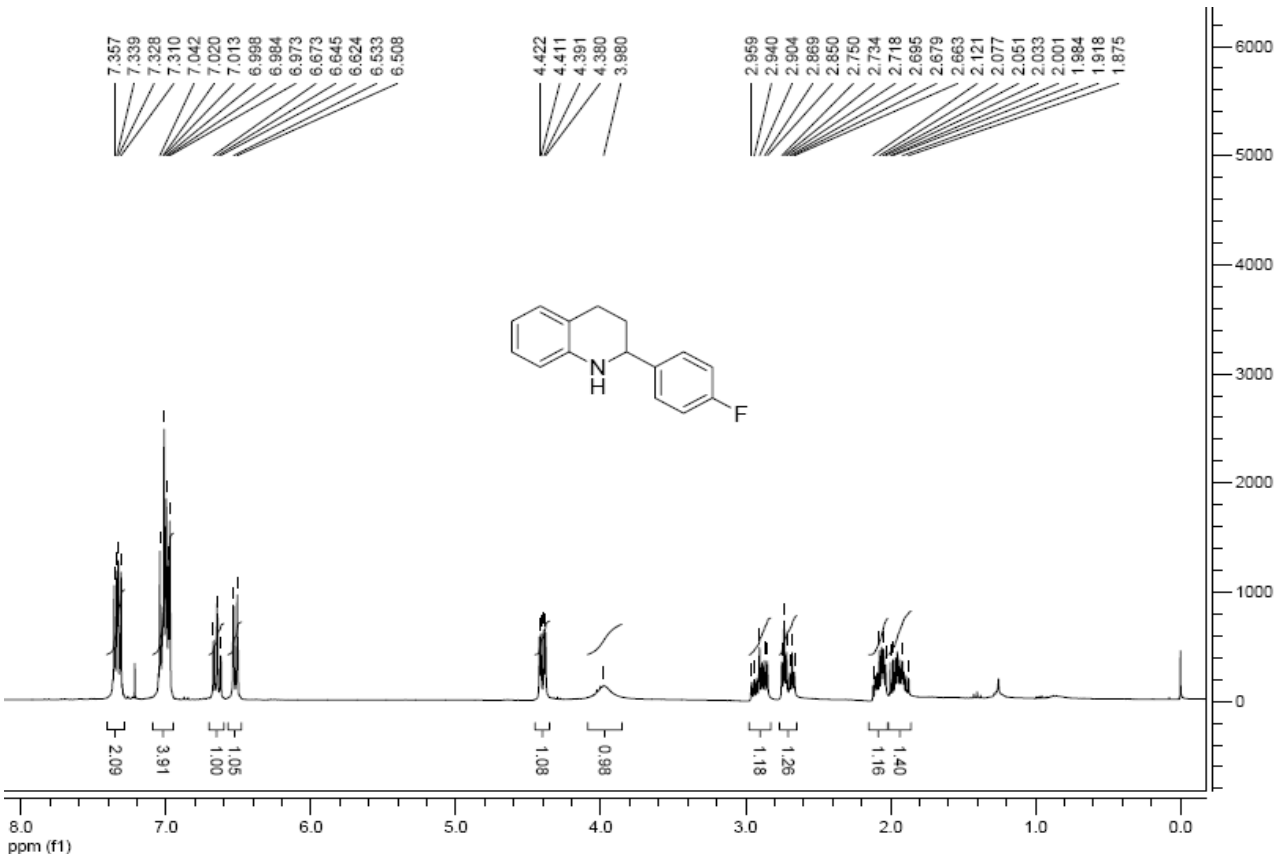
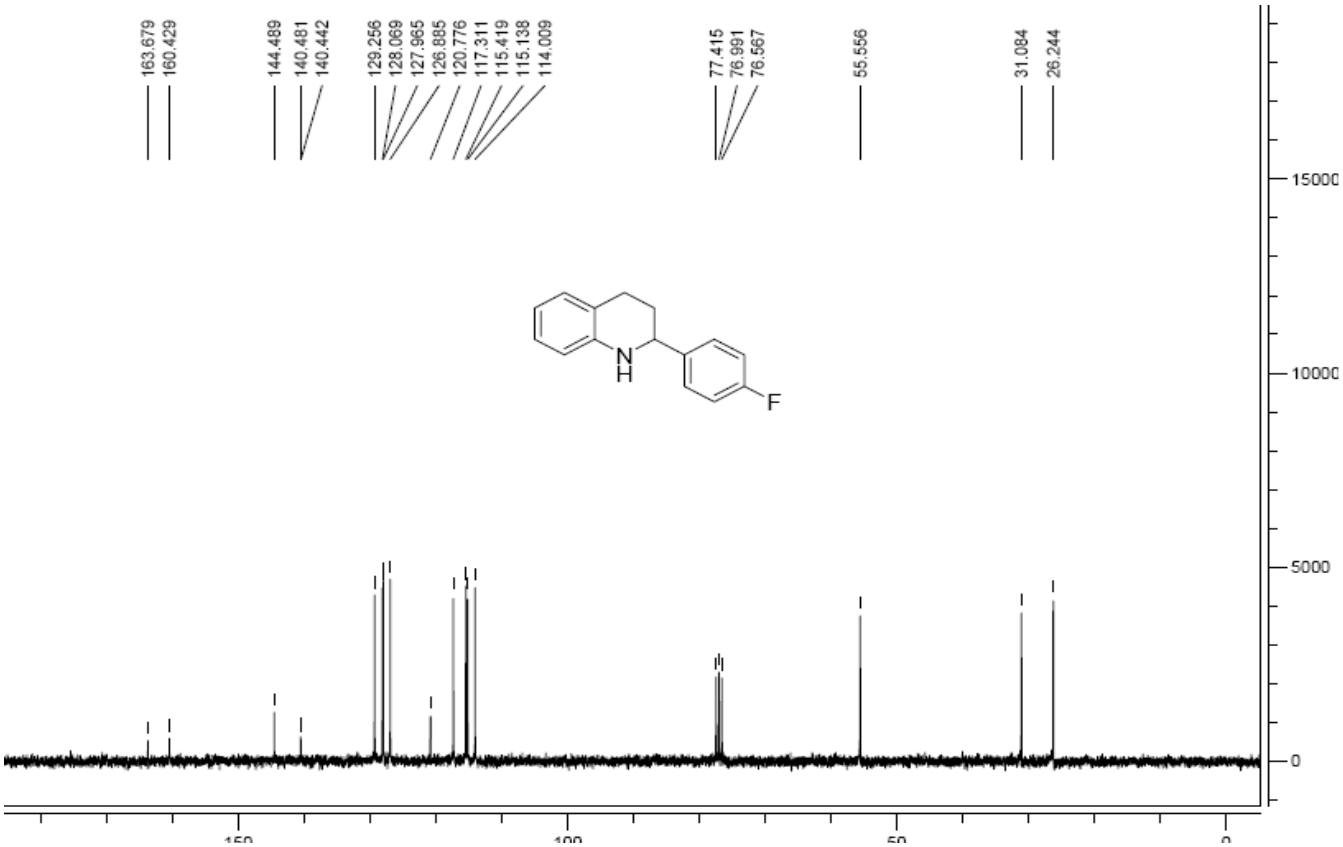


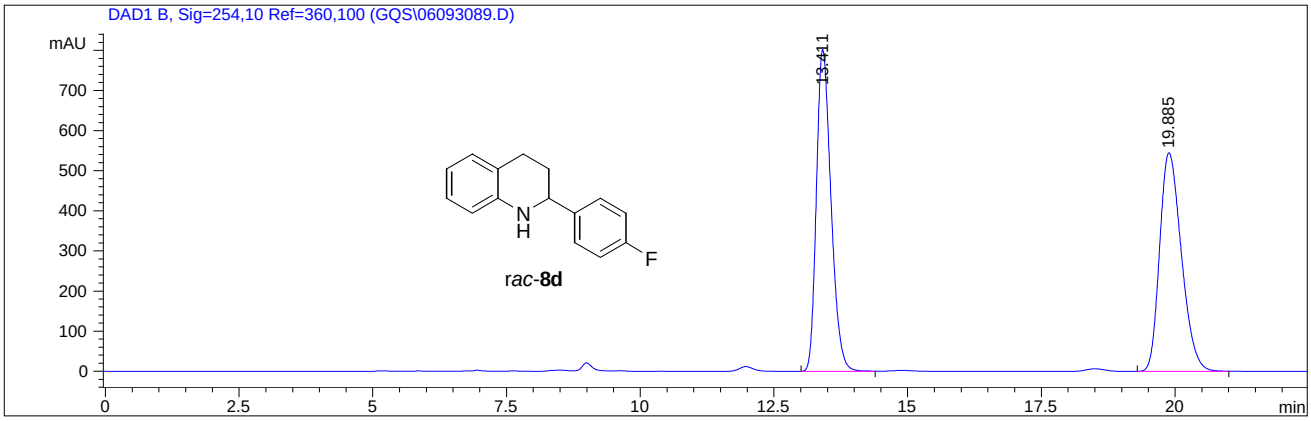
(*rac*)-2-(4-chlorophenyl)-1,2,3,4-tetrahydroquinoline



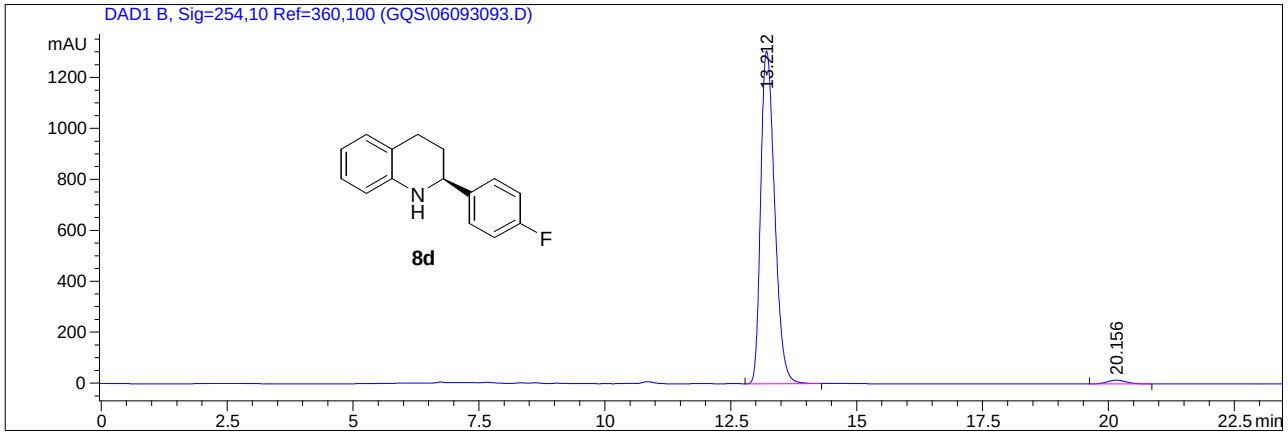
2-(4-chlorophenyl)-1,2,3,4-tetrahydroquinoline



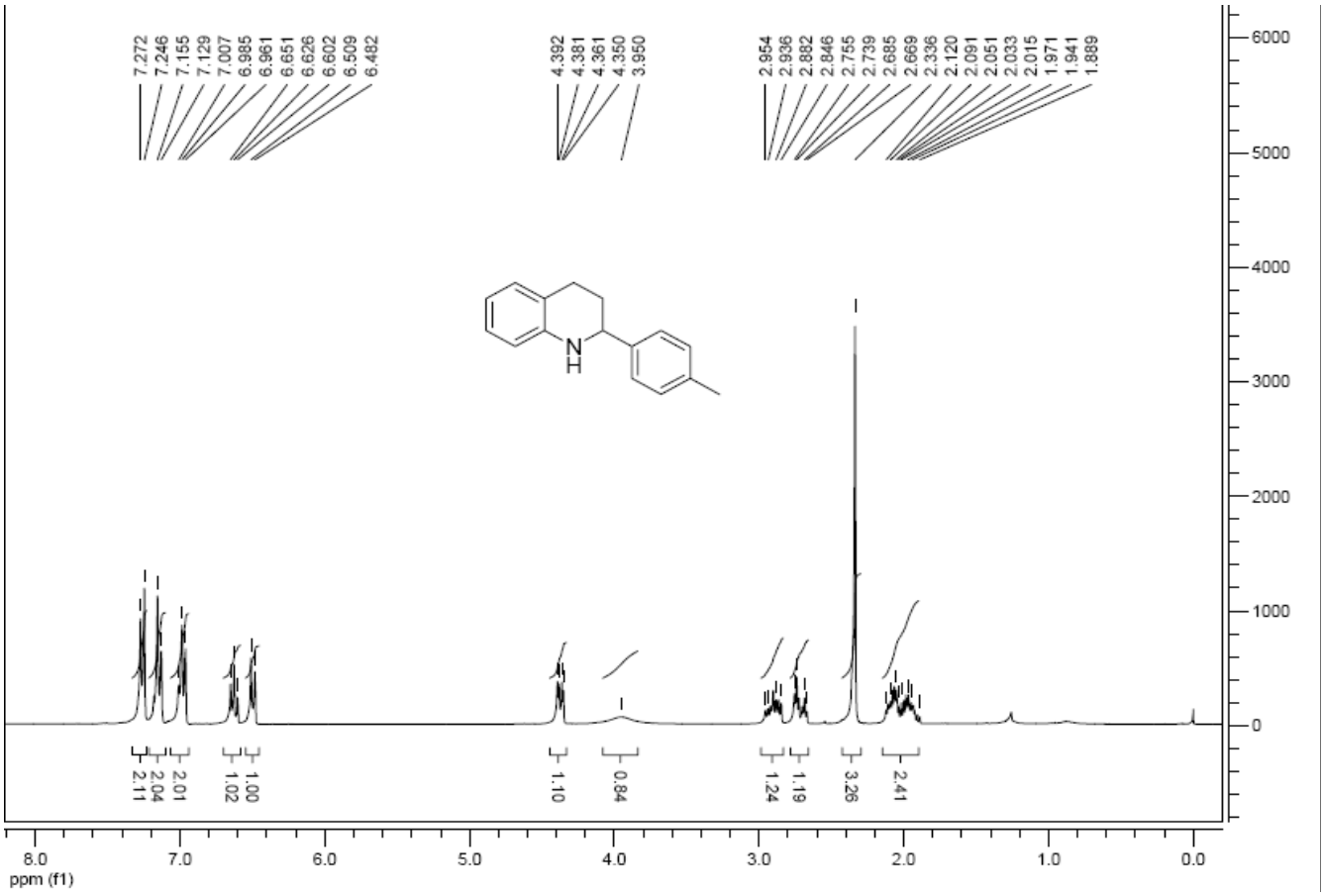




(*rac*)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline



2-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline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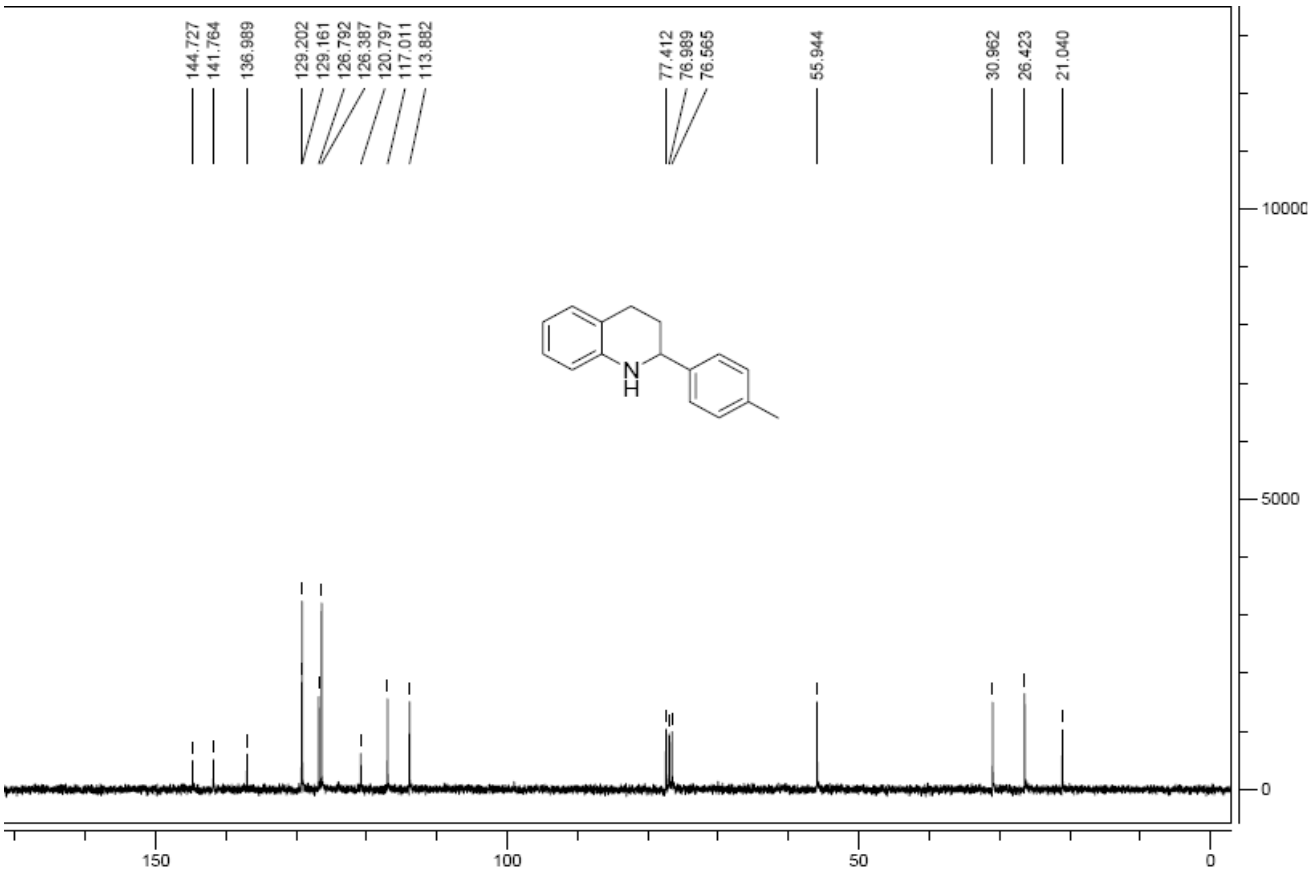
ppm (f1)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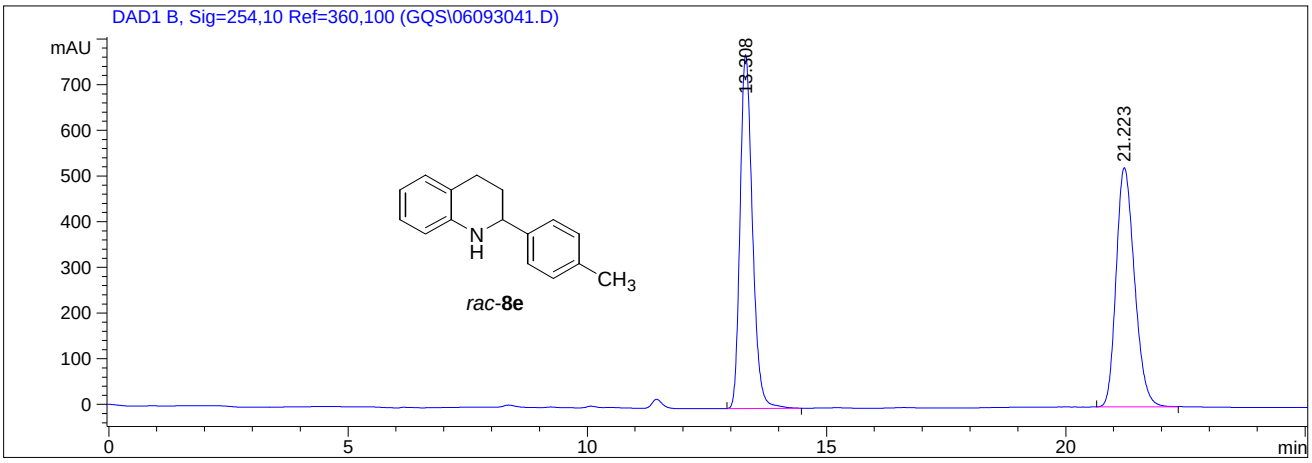
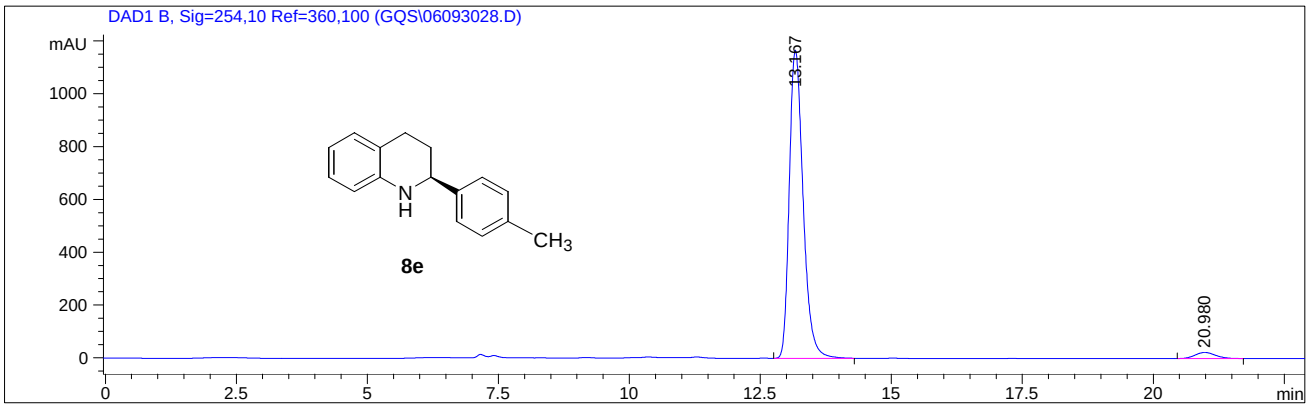
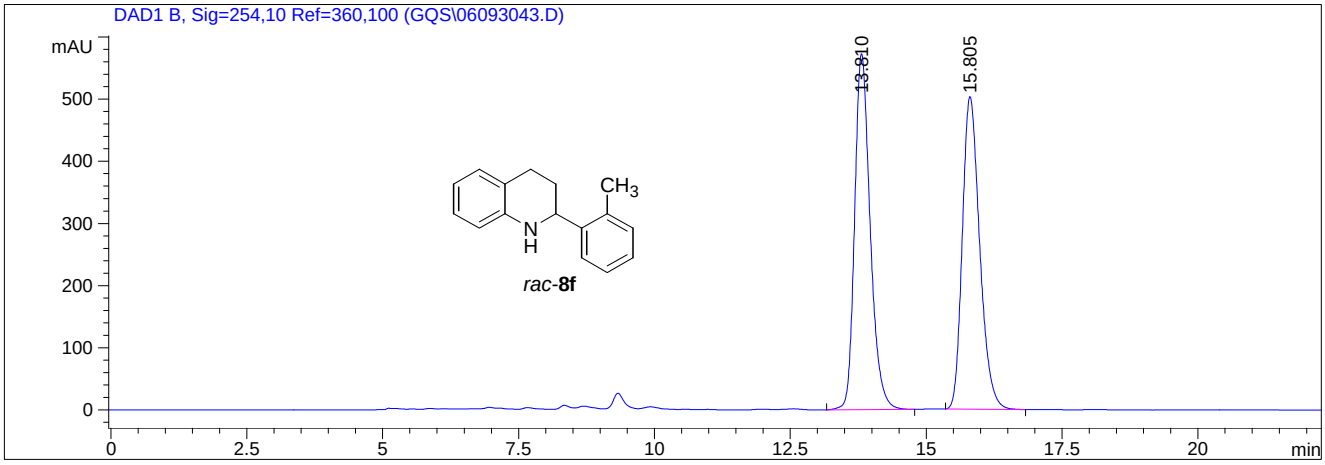


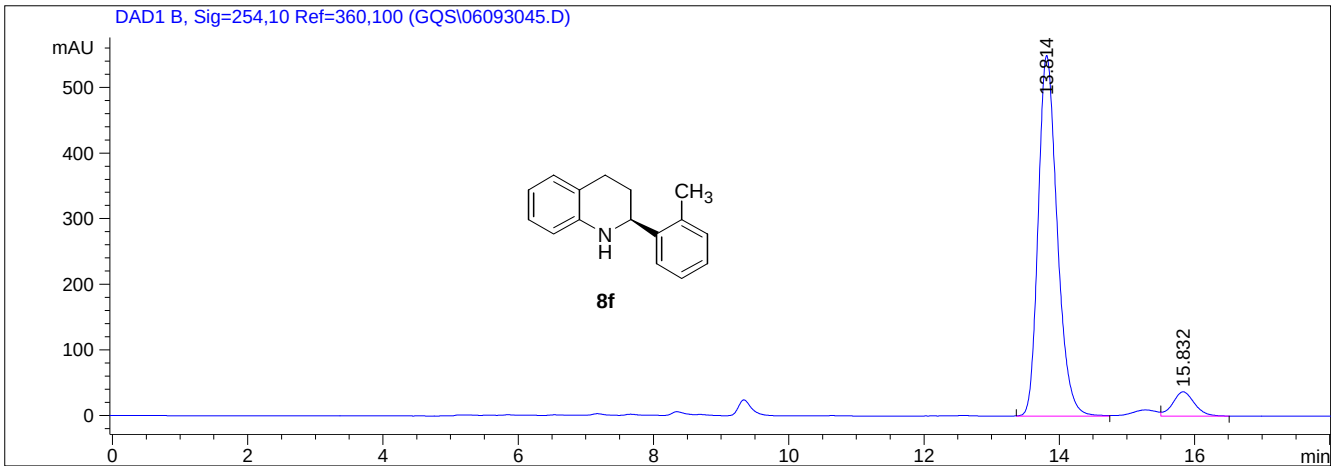
(*rac*)-2-(4-methylphenyl)-1,2,3,4-tetrahydroquinoline



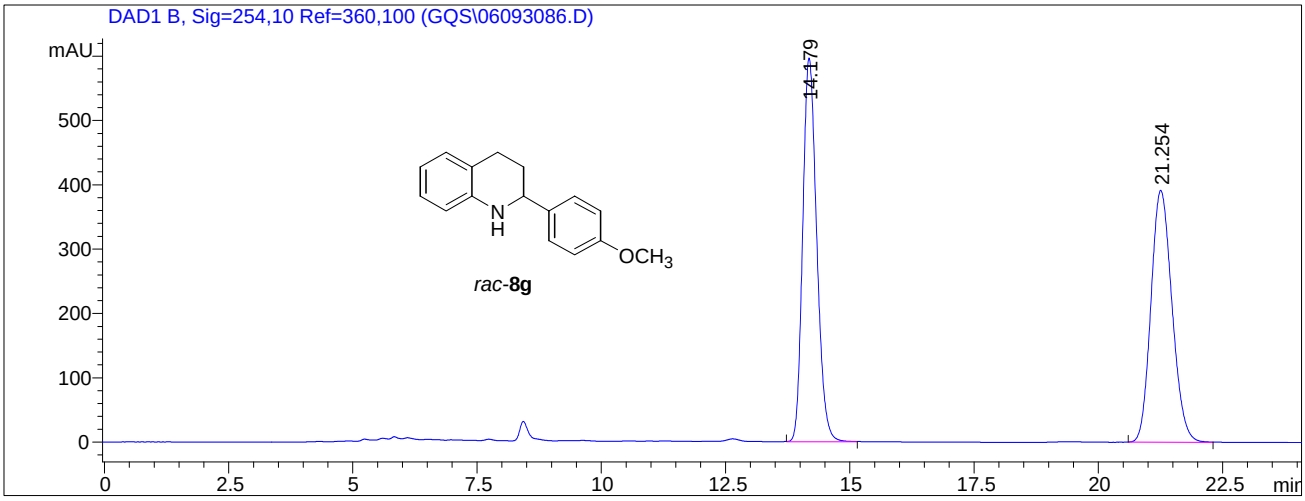
2-(4-methylphenyl)-1,2,3,4-tetrahydroquinoline



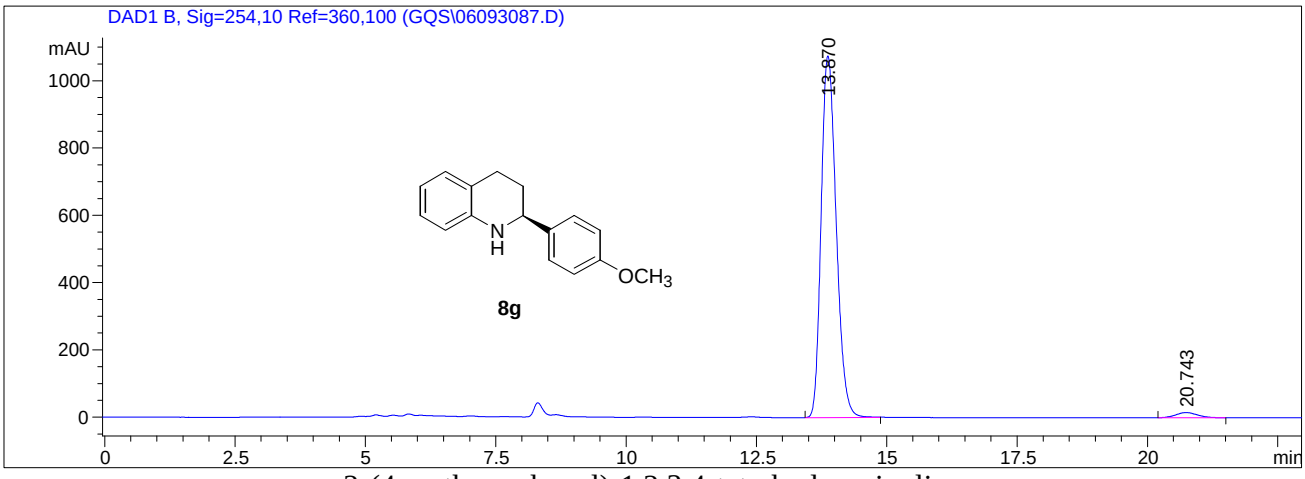
(*rac*)-2-(2-methylphenyl)-1,2,3,4-tetrahydroquinoline



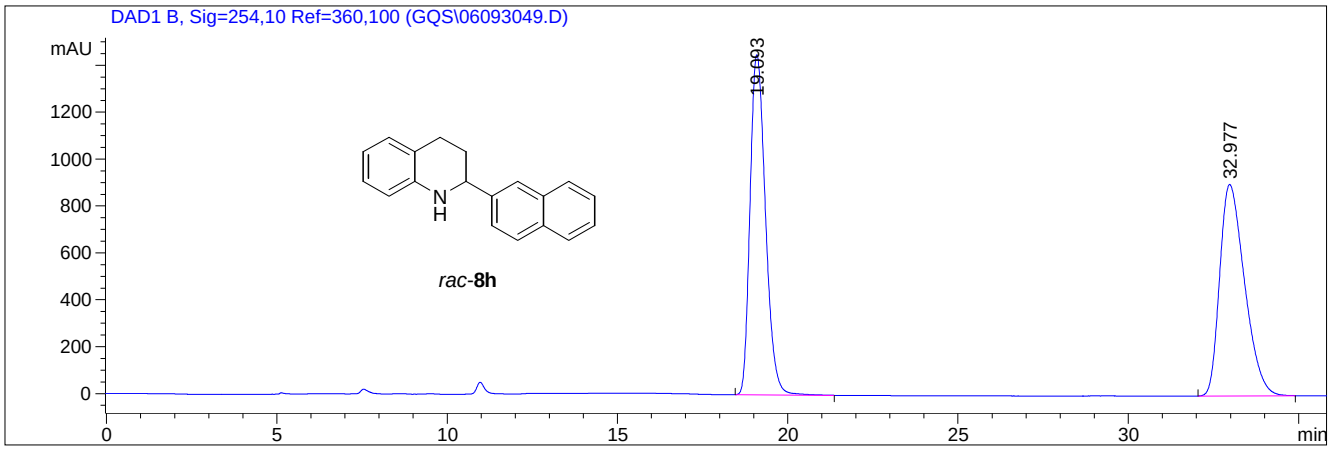
2-(2-methylphenyl)-1,2,3,4-tetrahydroquinoline



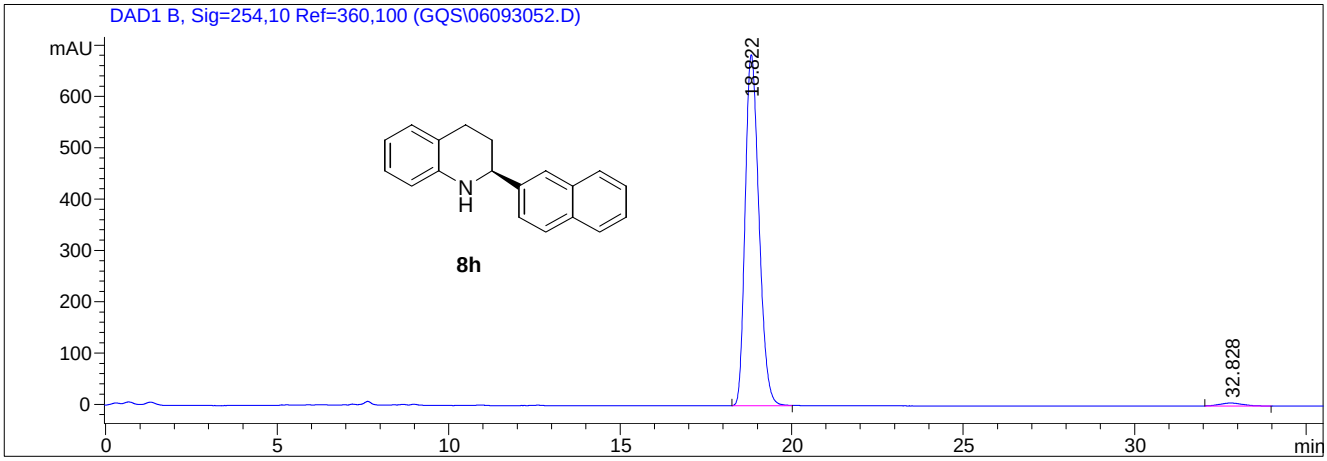
(*rac*)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline



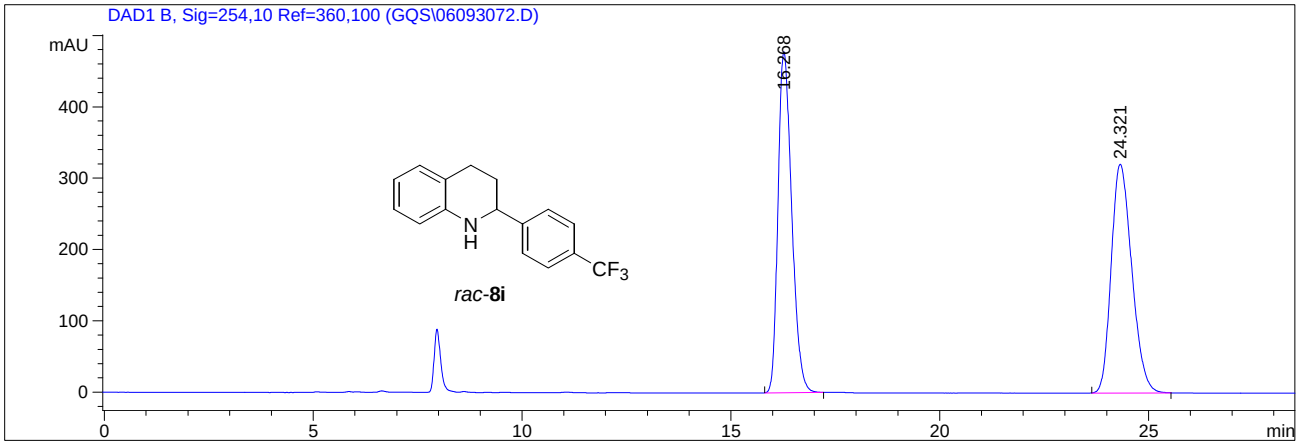
2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline



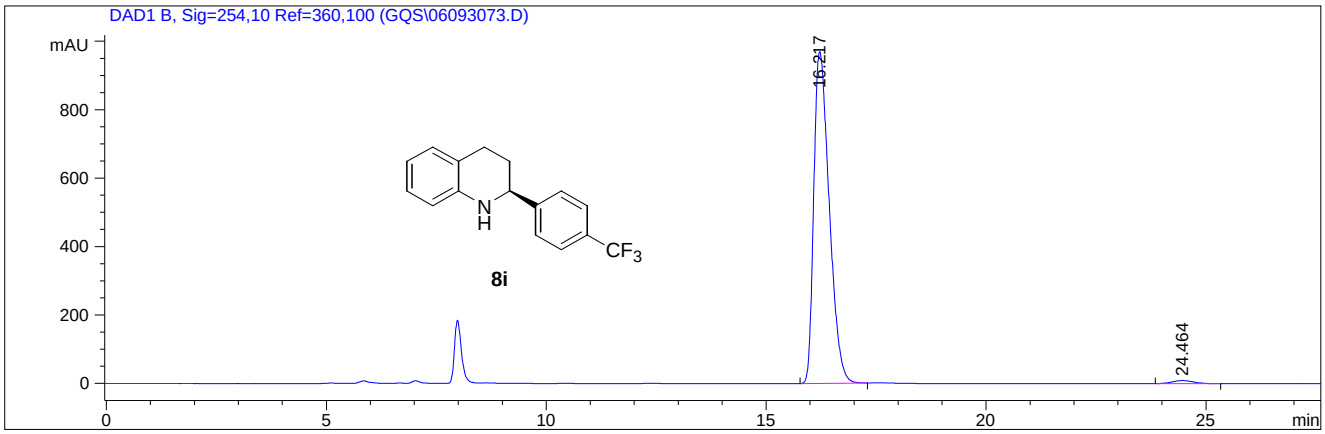
(rac)-2-(2-naphthyl)-1,2,3,4-tetrahydroquinoline



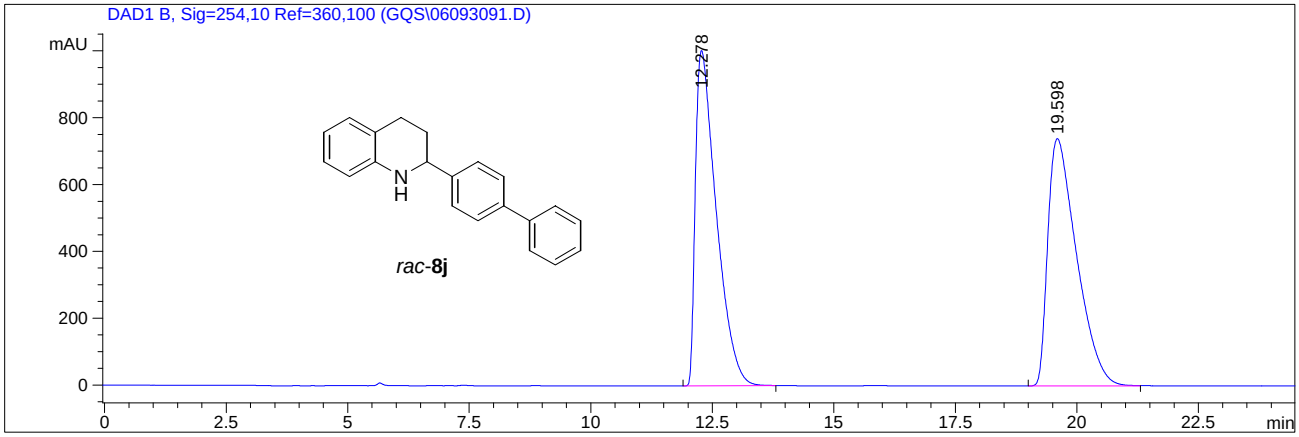
2-(2-naphthyl)-1,2,3,4-tetrahydroquinoline



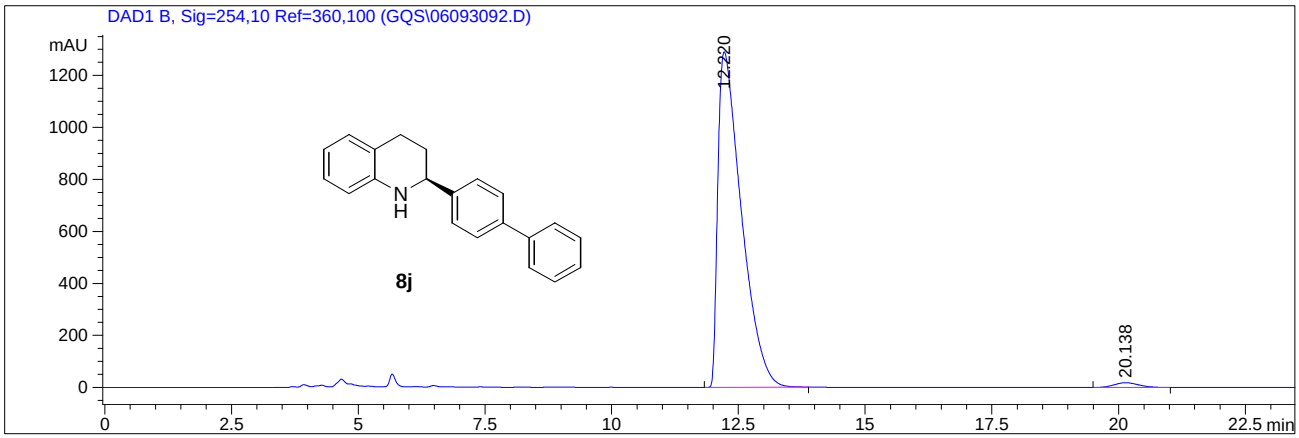
(*rac*)-2-(4-trifluoromethylphenyl)-1,2,3,4-tetrahydroquinoline



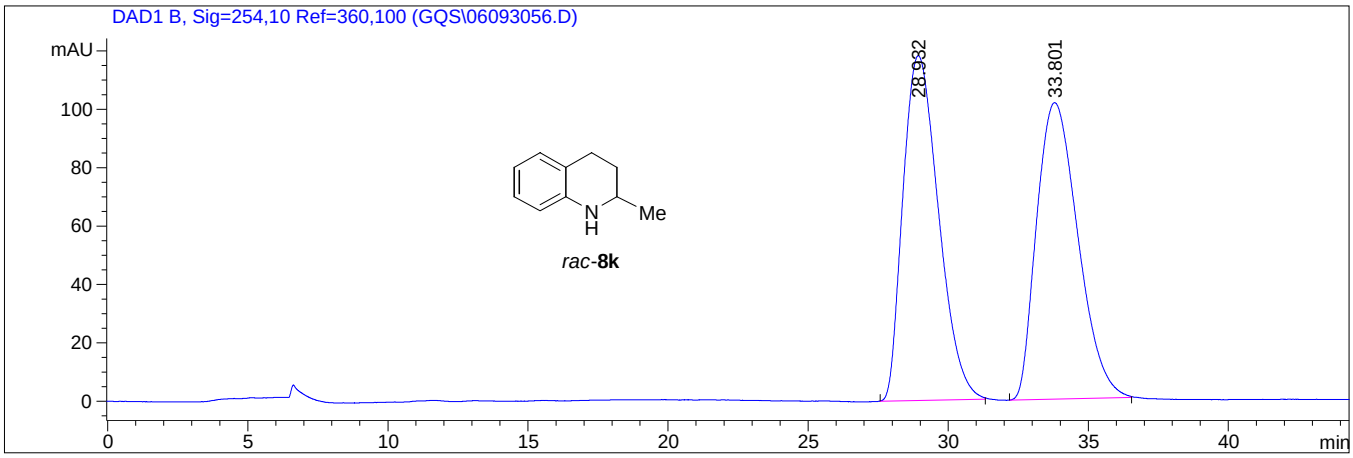
2-(4-trifluoromethylphenyl)-1,2,3,4-tetrahydroquinoline



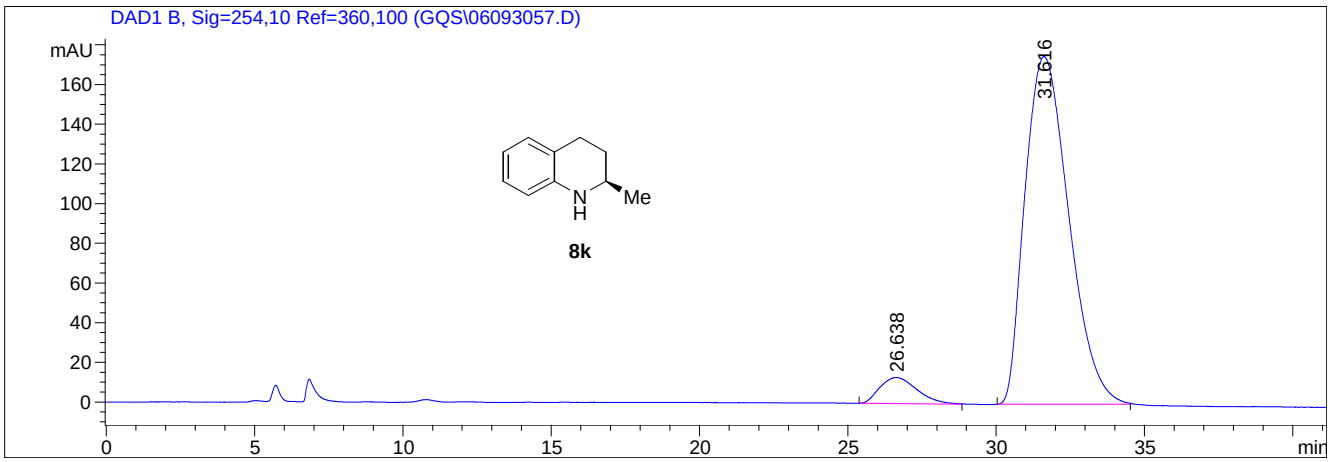
(*rac*)-2-(1,1’-biphenyl-4-yl)-1,2,3,4-tetrahydroquinoline



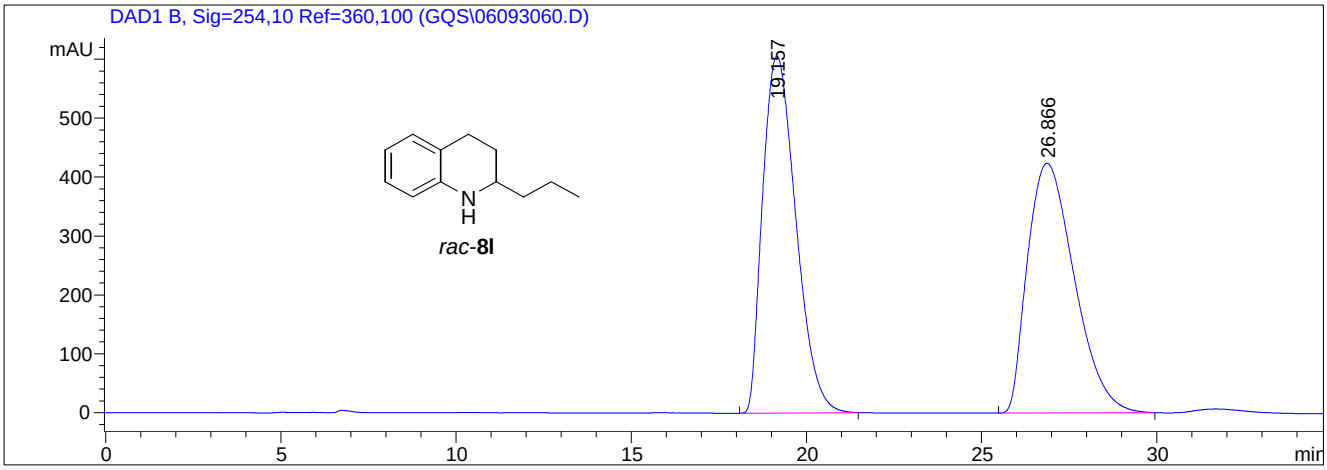
2-(1,1’-biphenyl-4-yl)-1,2,3,4-tetrahydroquinoline



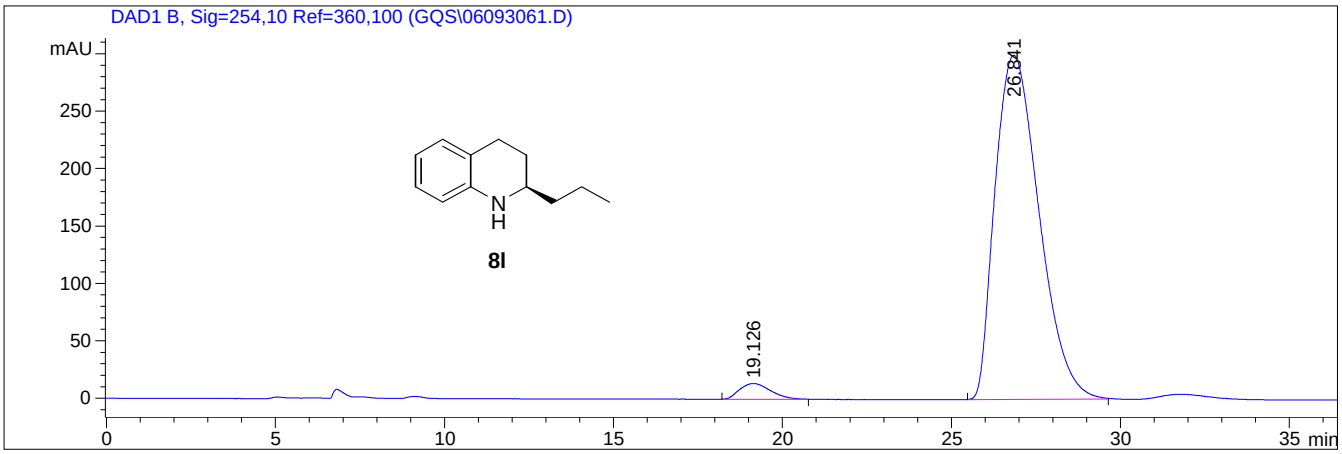
(*rac*)-2-methyl-1,2,3,4-tetrahydroquinoline



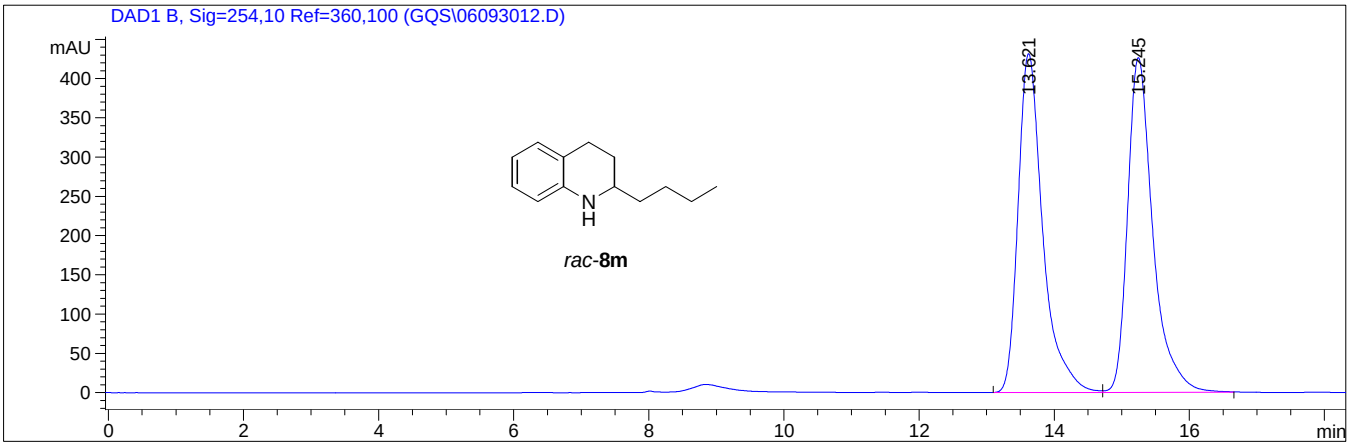
2-methyl-1,2,3,4-tetrahydroquinoline



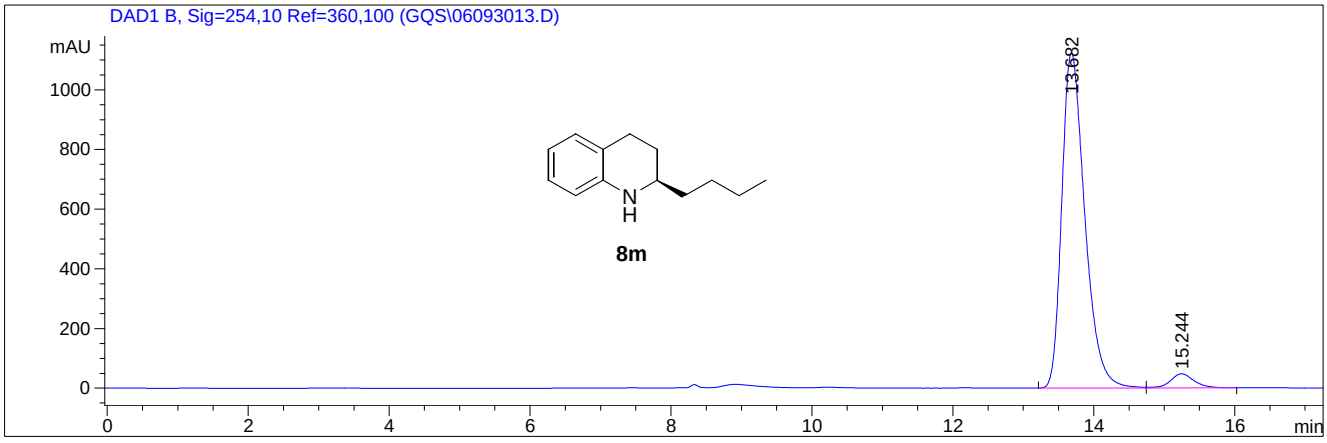
(*rac*)-2-propyl-1,2,3,4-tetrahydroquinoline



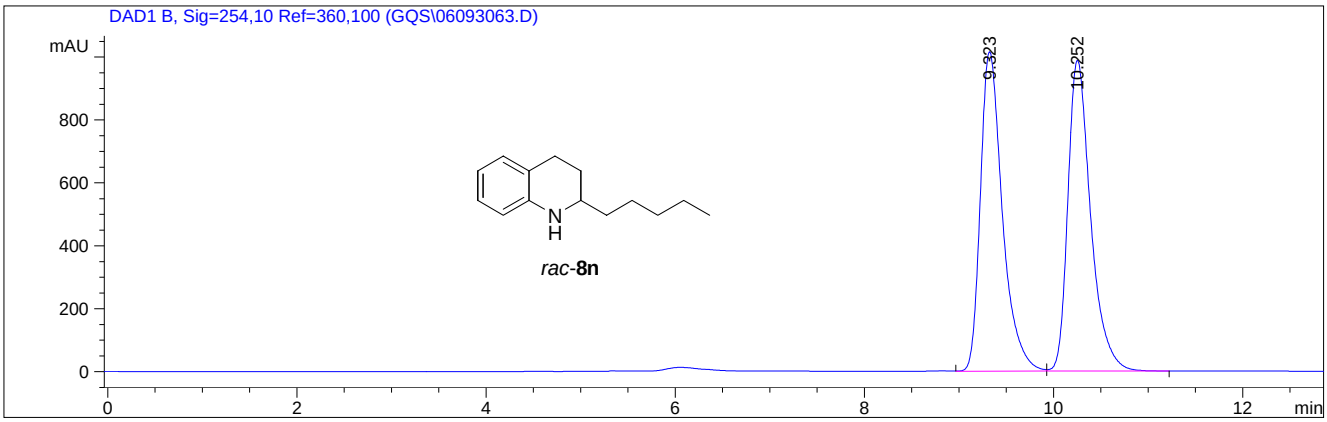
2-propyl-1,2,3,4-tetrahydroquinoline



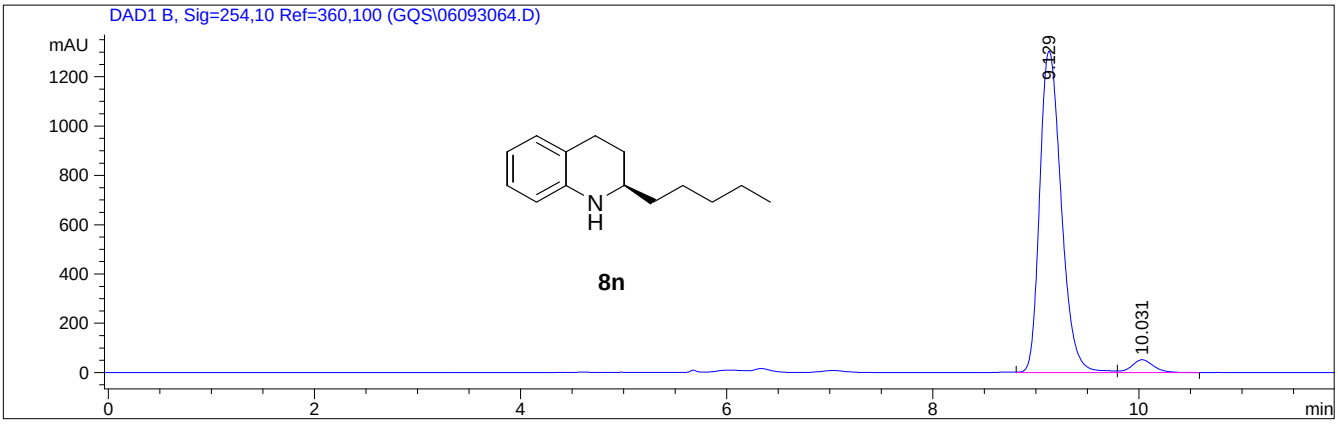
(*rac*)-2-butyl-1,2,3,4-tetrahydroquinoline



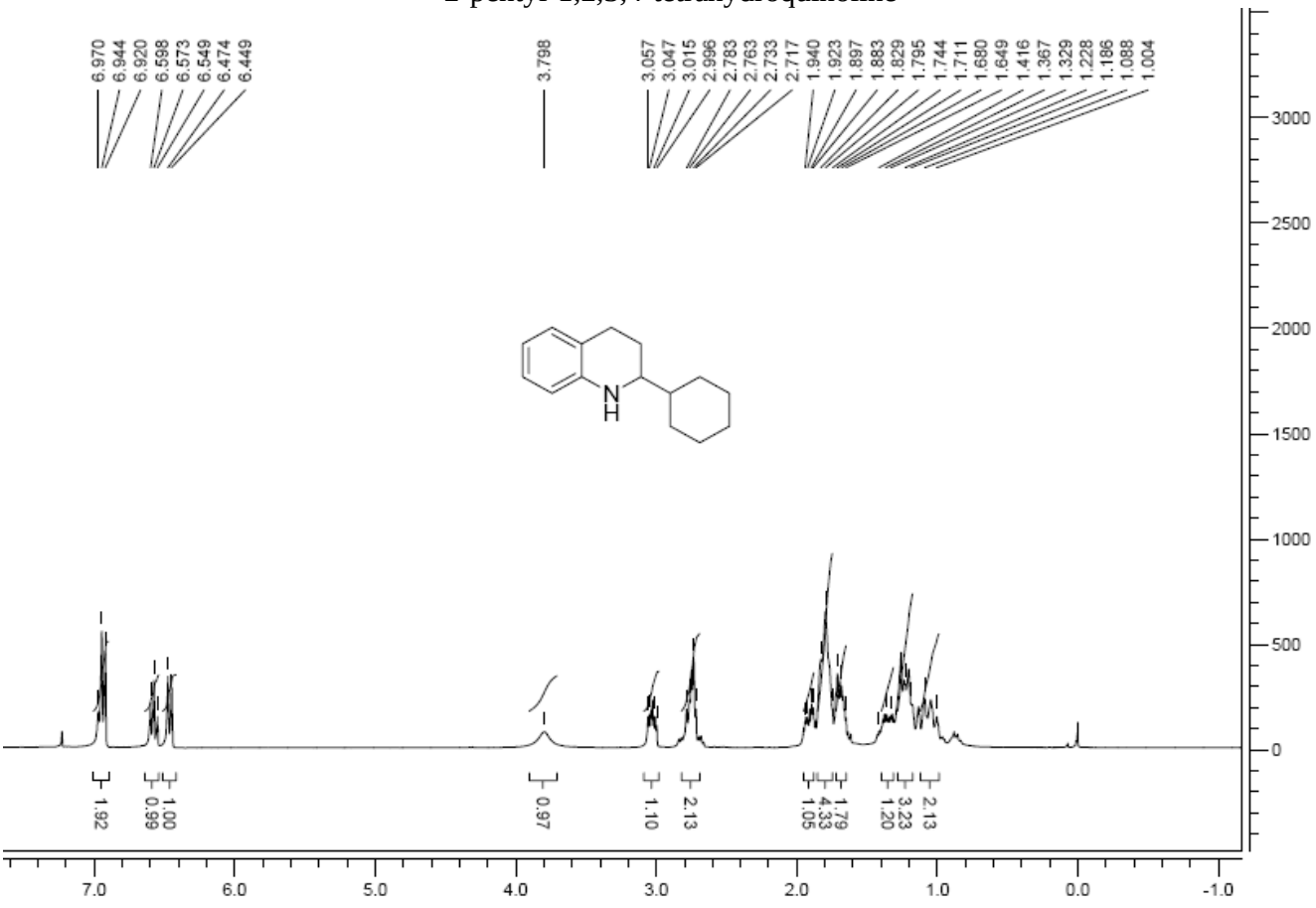
2-butyl-1,2,3,4-tetrahydroquinoline

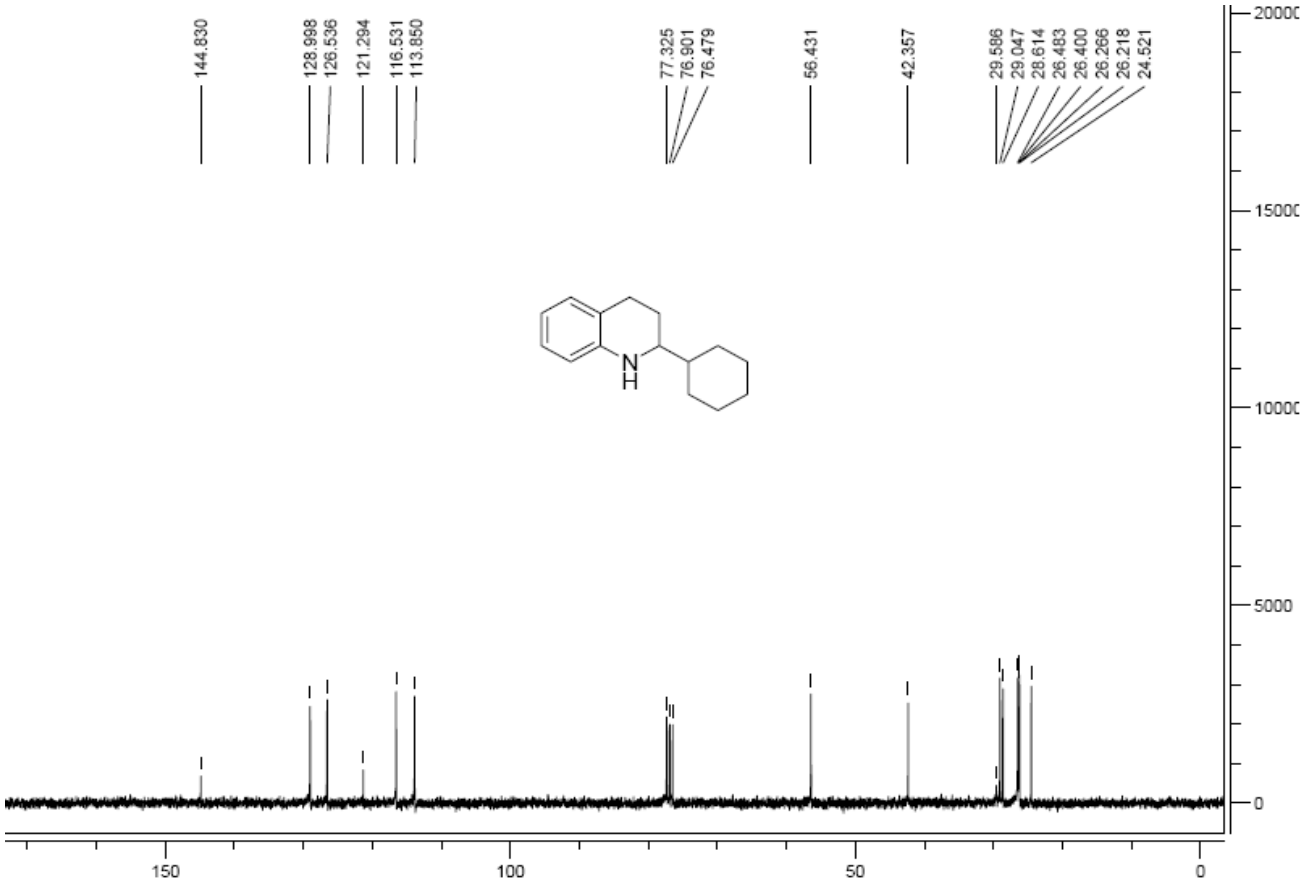


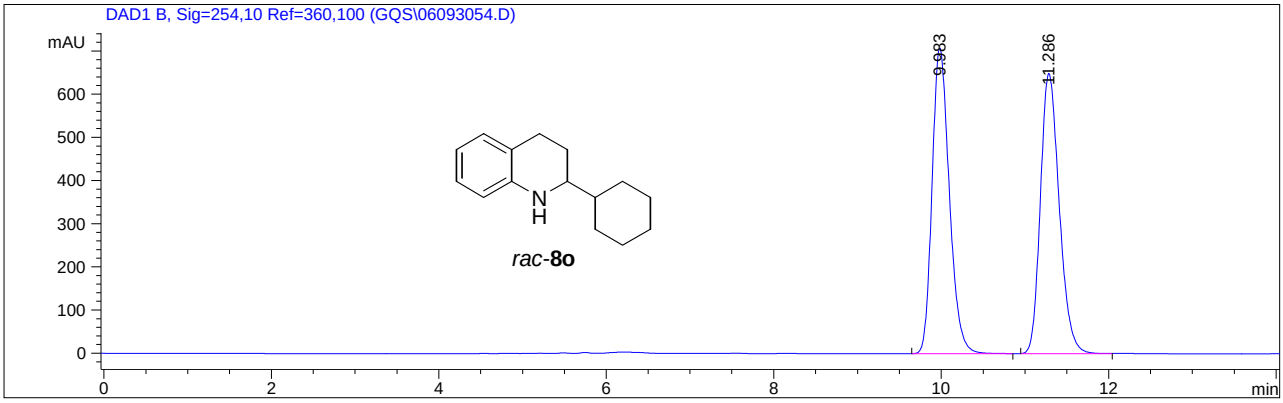
(*rac*)-2-pentyl-1,2,3,4-tetrahydroquinoline



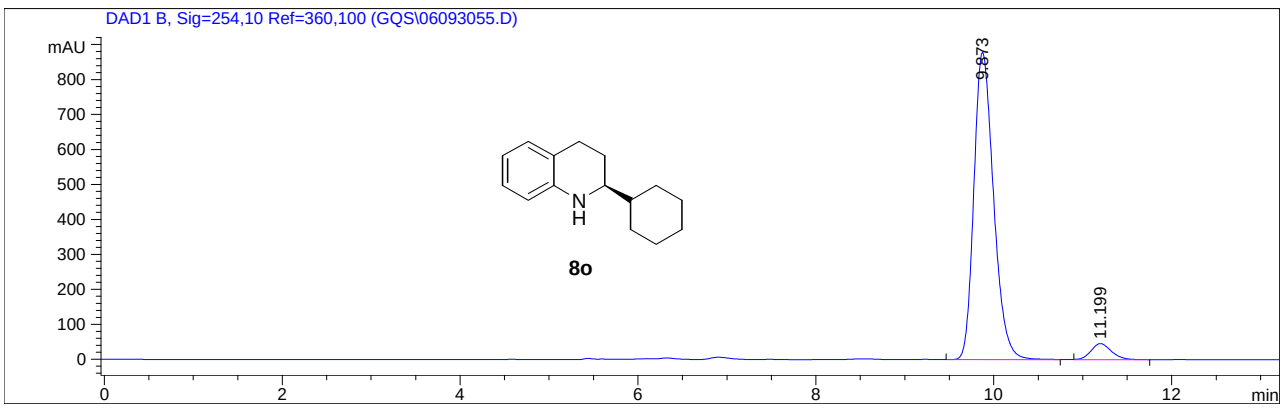
2-pentyl-1,2,3,4-tetrahydroquinoline



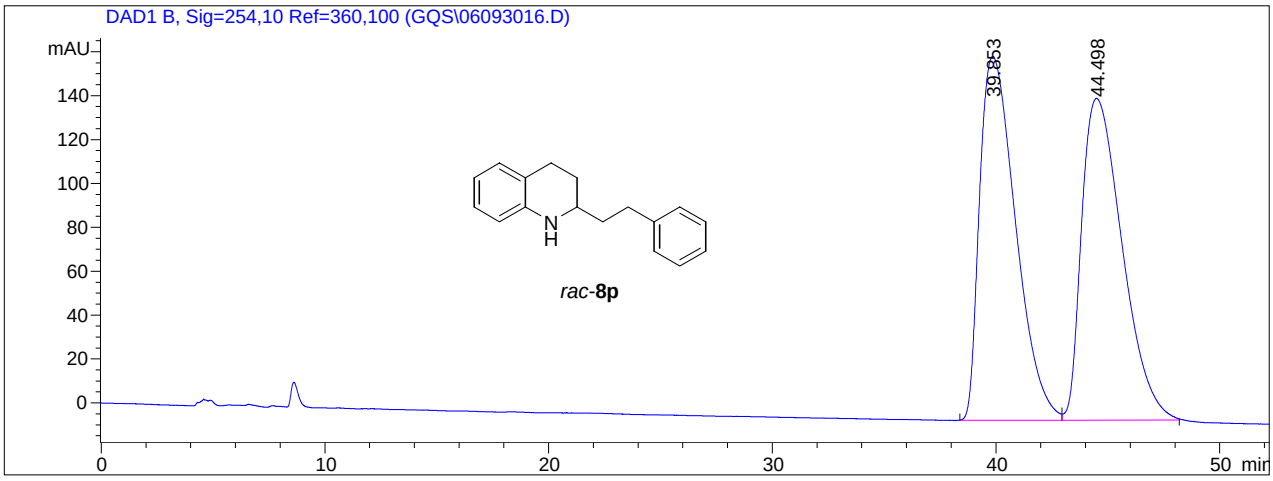




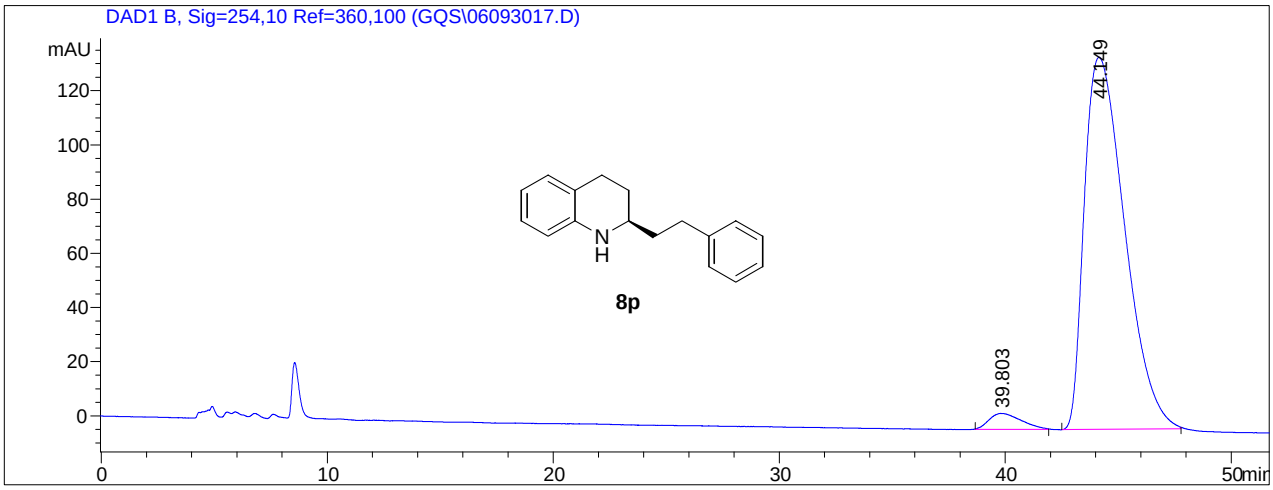
(*rac*)-2-cyclohexyl-1,2,3,4-tetrahydroquinoline



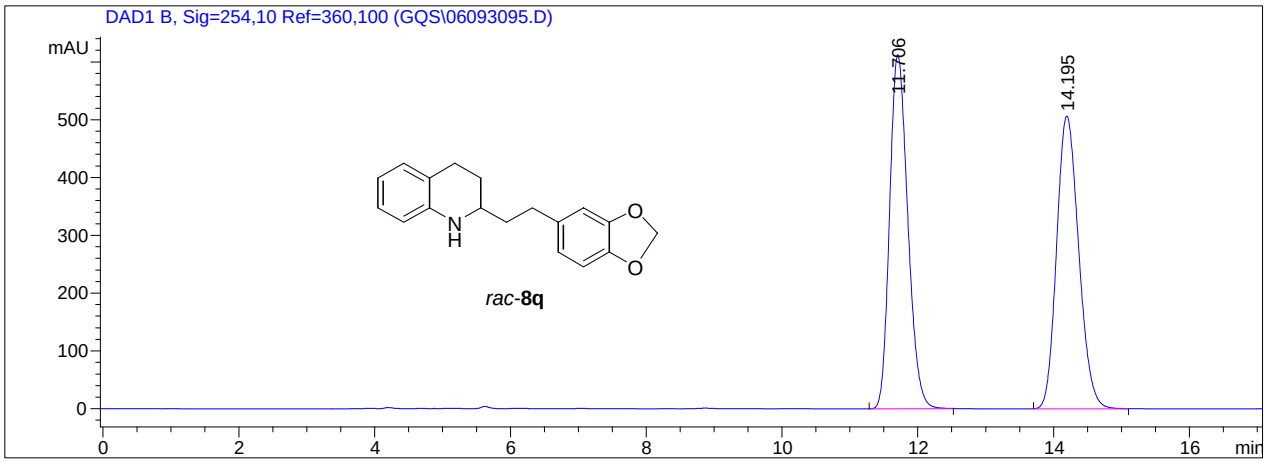
2-cyclohexyl-1,2,3,4-tetrahydroquinoline



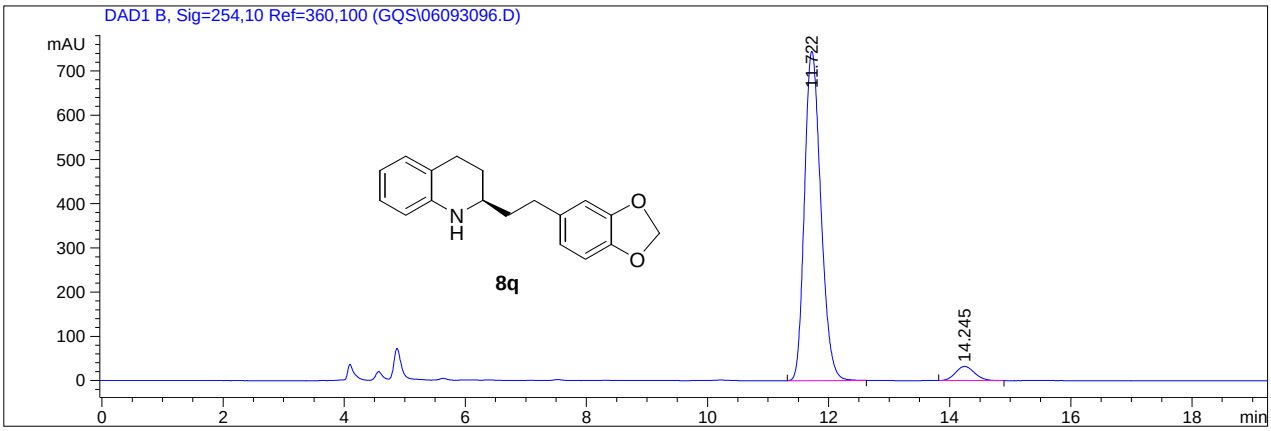
(*rac*)-2-(2-phenylethyl)-1,2,3,4-tetrahydroquinoline



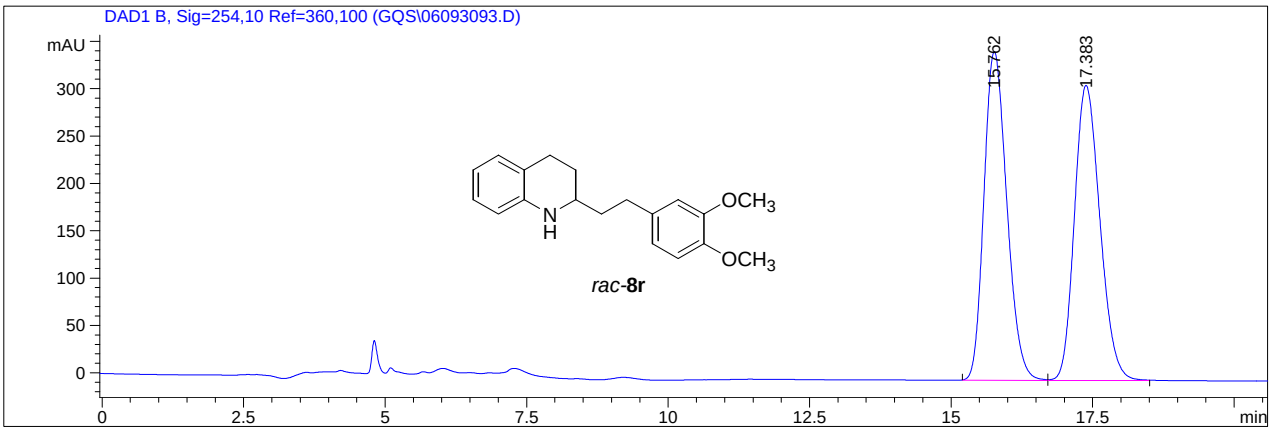
2-(2-phenylethyl)-1,2,3,4-tetrahydroquinoline



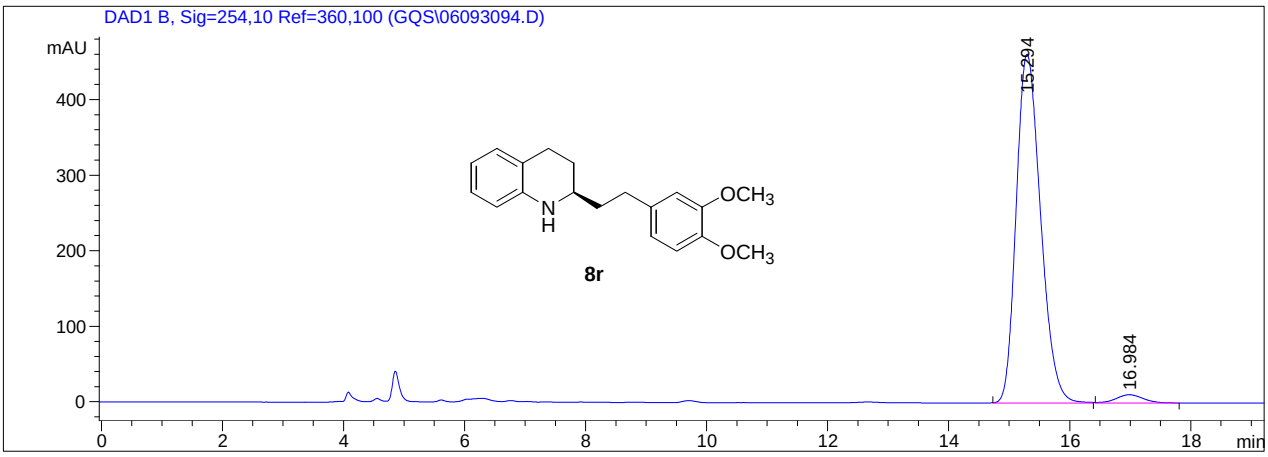
(*rac*)-2-[2-(3,4-methylenedioxyphenyl)ethyl]-1,2,3,4-tetrahydroquinoline



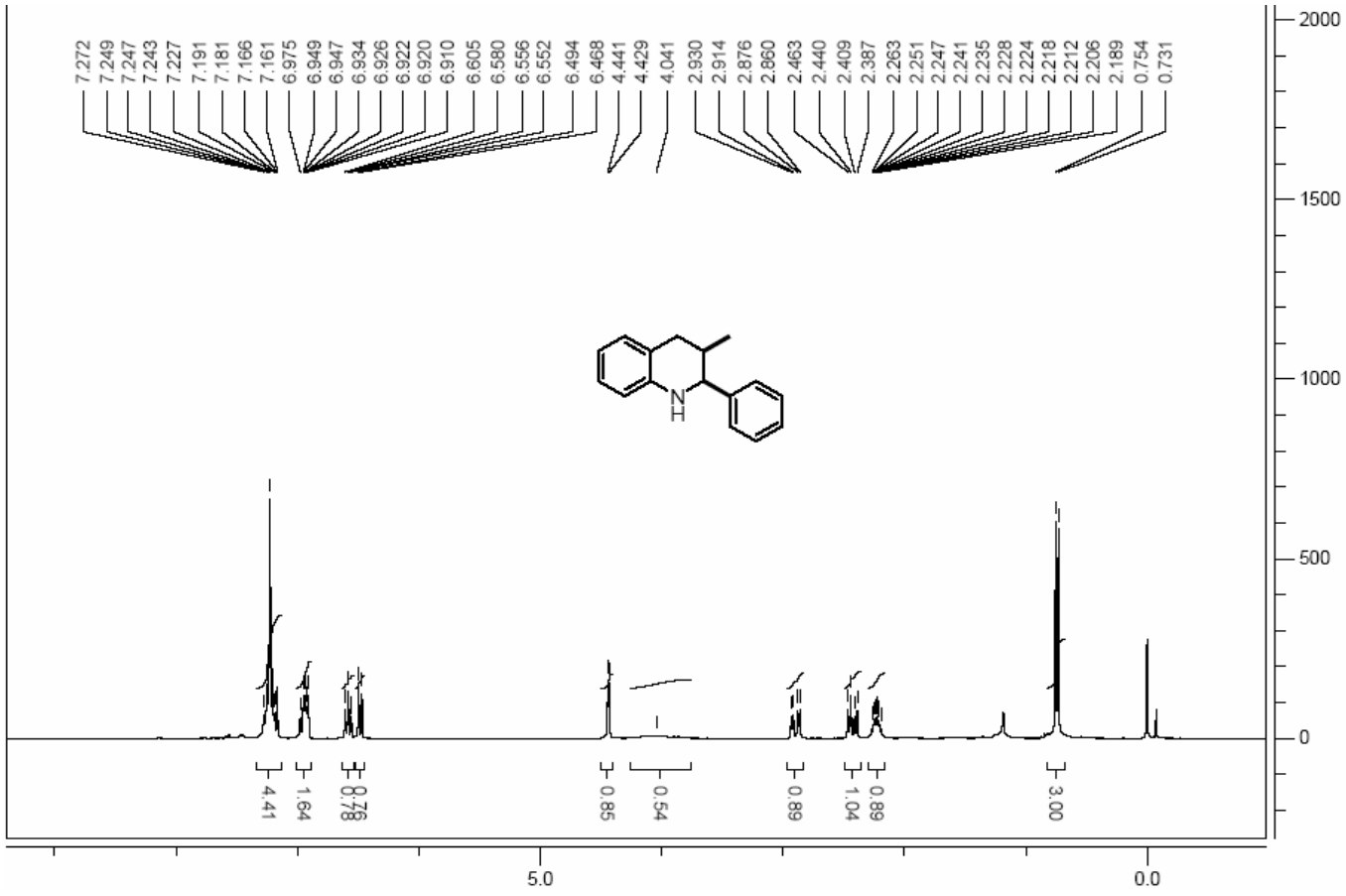
2-[2-(3,4-methylenedioxyphenyl)ethyl]-1,2,3,4-tetrahydroquinoline



(*rac*)-2-[2-(3,4-dimethoxyphenyl)ethyl]-1,2,3,4-tetrahydroquinoline



2-[2-(3,4-dimethoxyphenyl)ethyl]-1,2,3,4-tetrahydroquinoline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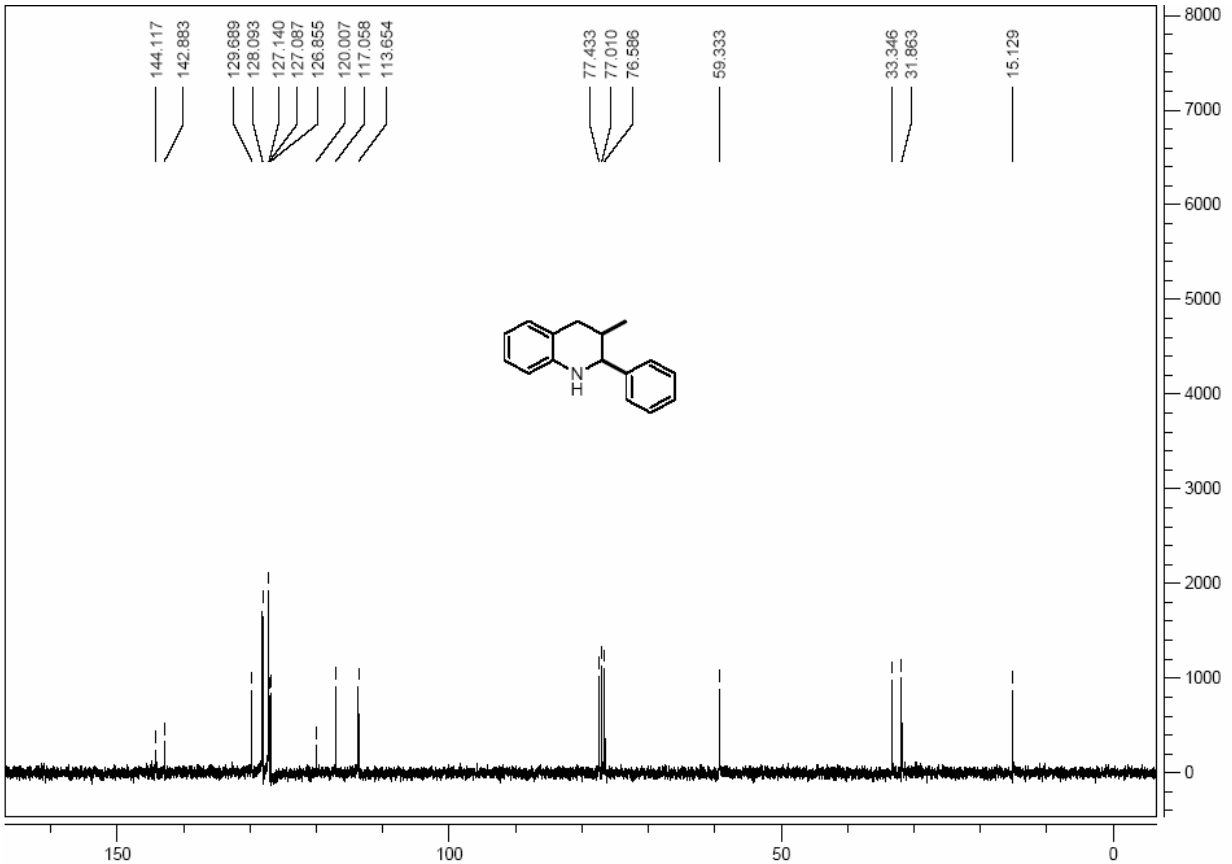
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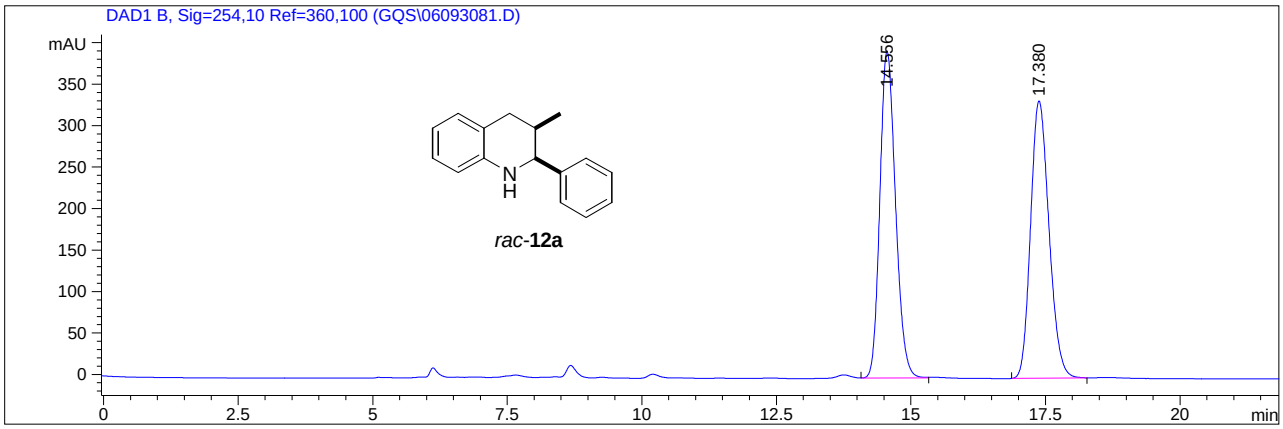
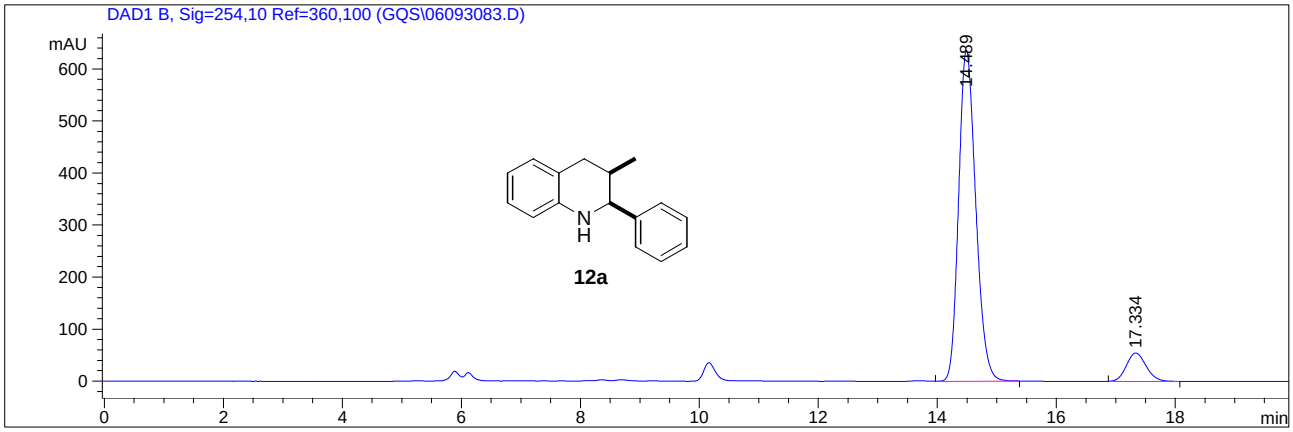
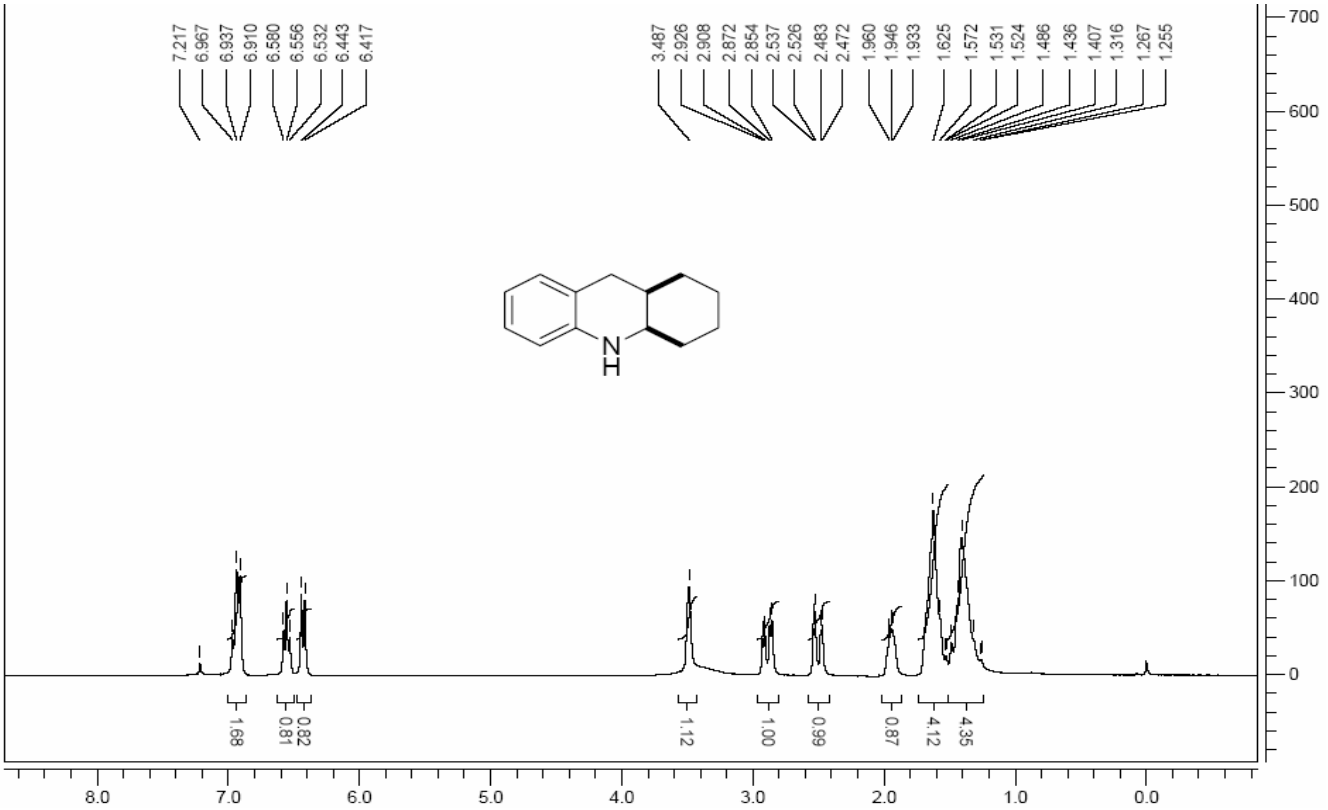
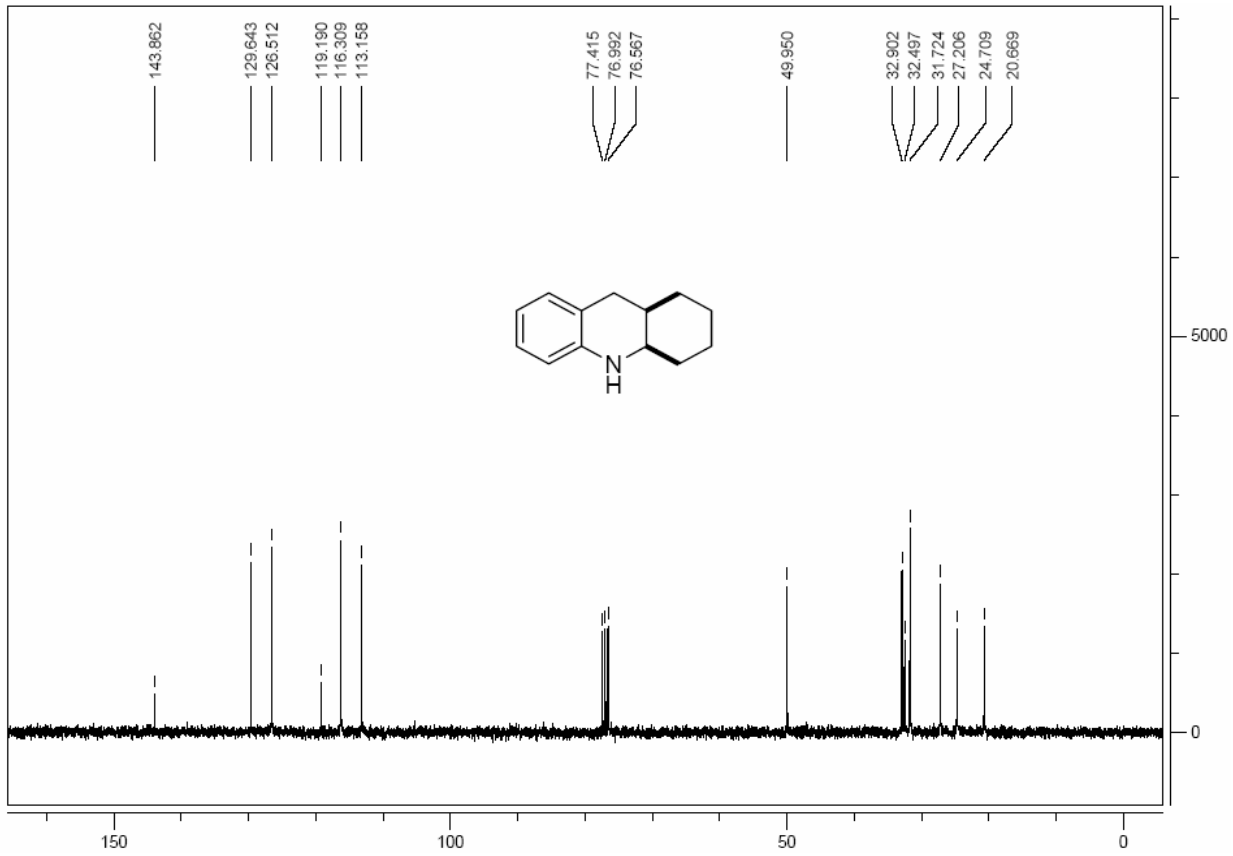


(*rac*)-(*cis*)-3-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline



(*cis*)-3-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline

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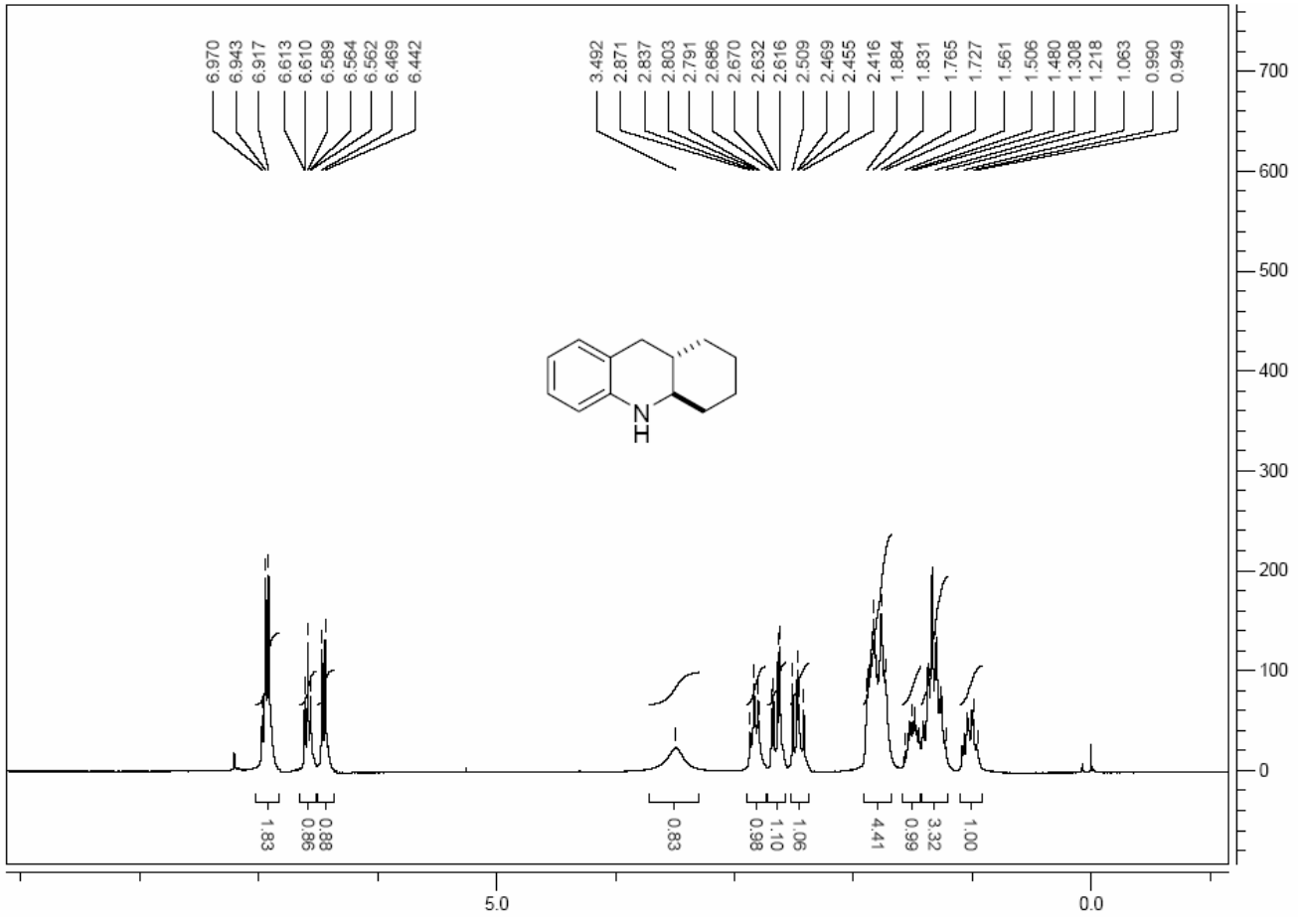
129.643
126.512
119.190
116.309
113.158
77.415
76.992
76.567
49.950
32.902
32.497
31.724
27.206
24.709
20.669
N
H
5000
0
150
100
50
0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6.943
6.917
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6.610
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6.562
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6.442
3.492
2.871
2.837
2.803
2.791
2.686
2.670
2.632
2.616
2.509
2.469
2.455
2.416
1.884
1.831
1.765
1.727
1.561
1.506
1.480
1.308
1.218
1.063
0.990
0.949
N
H
700
600
500
400
300
200
100
0
1.83
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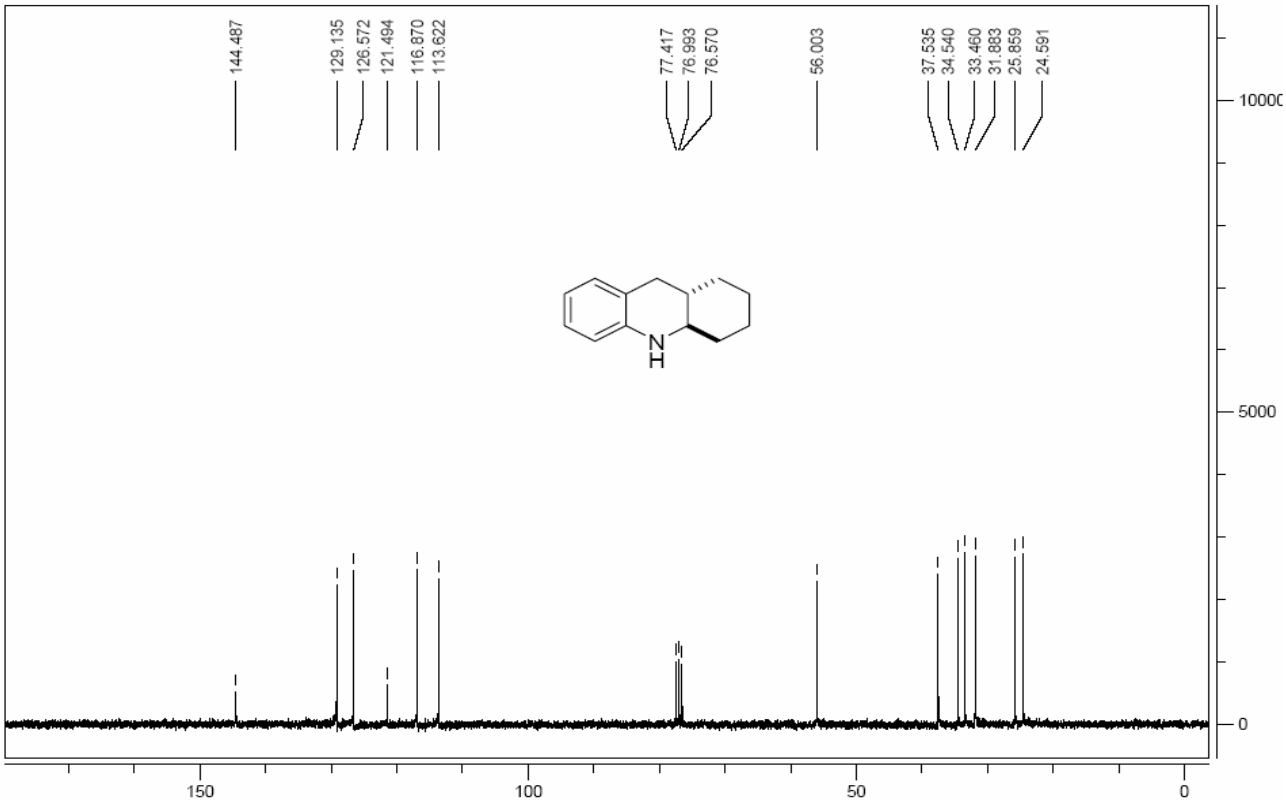
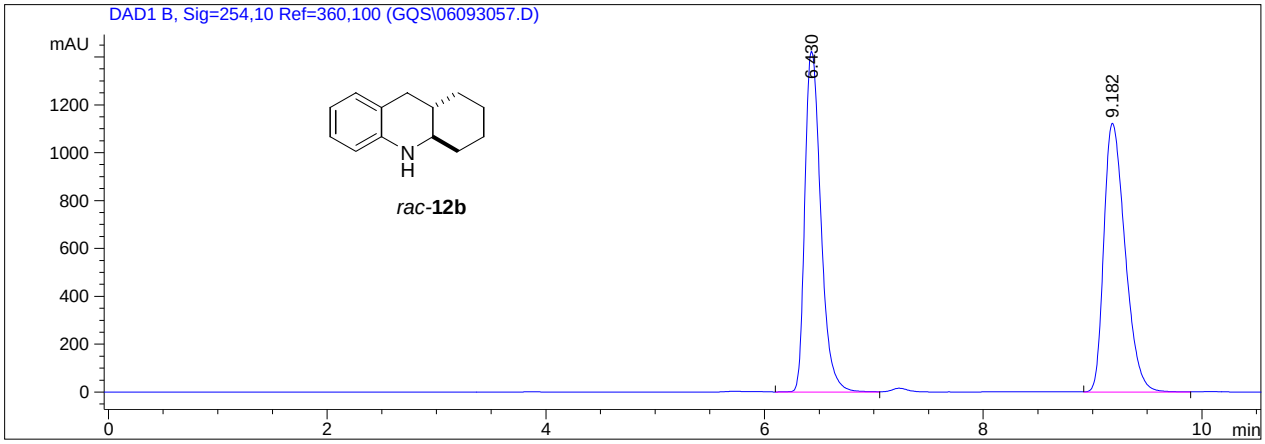
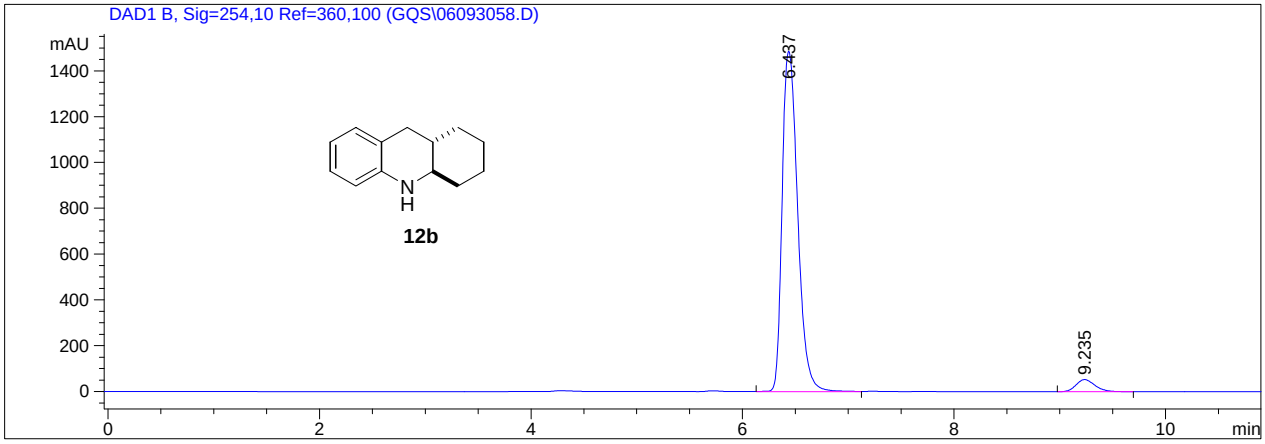
0.83
0.98
1.10
1.06
4.41
0.99
2.32
1.00
5.0
0.0

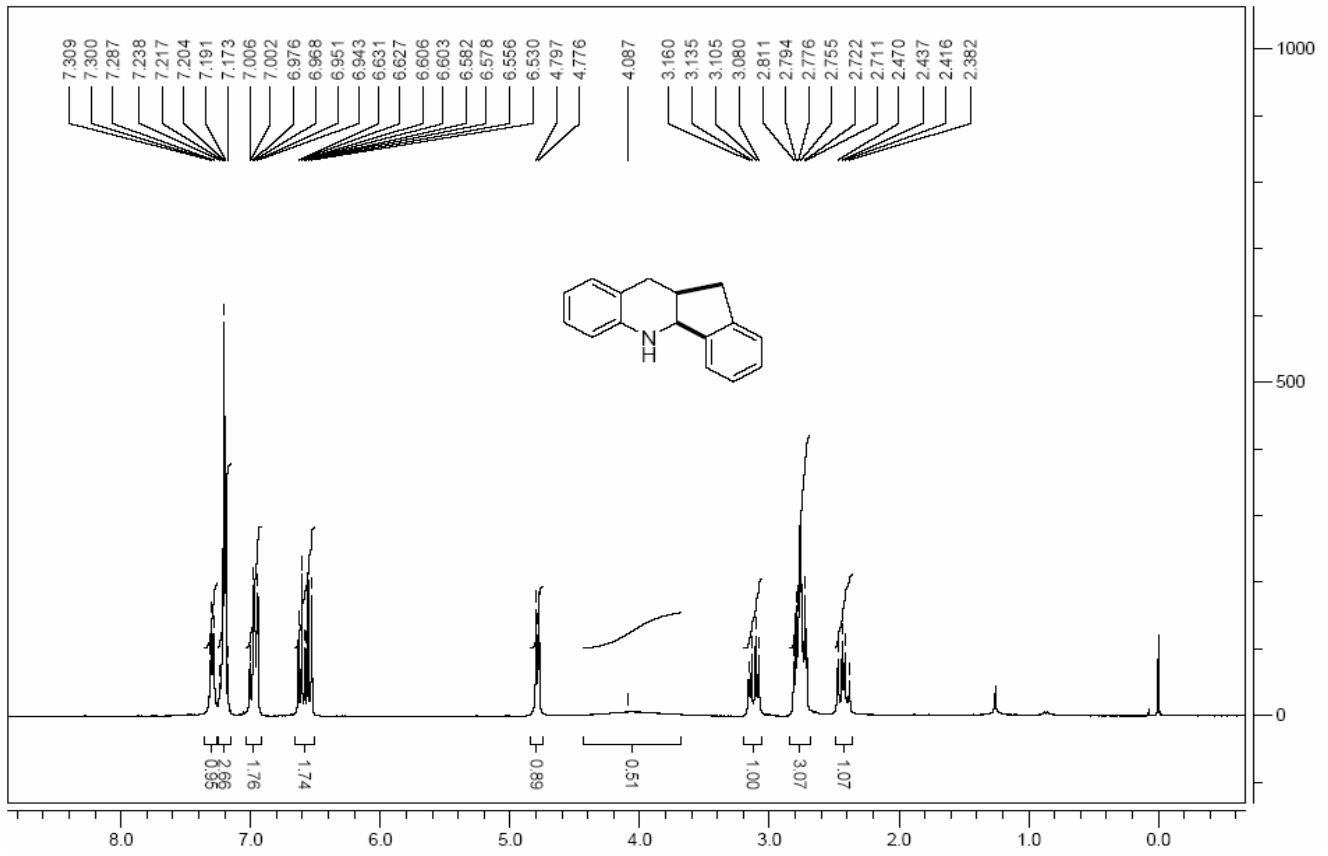




(*rac*)-(*trans*)-1,2,3,4,4a,9a,10-Octahydroacridine



(*trans*)-1,2,3,4,4a,9a,10-Octahydroacridine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7.204
7.191
7.173
7.006
7.002
6.976
6.968
6.951
6.943
6.631
6.627
6.606
6.603
6.582
6.578
6.556
6.530
4.797
4.776
4.087
3.160
3.135
3.105
3.080
2.811
2.794
2.776
2.755
2.722
2.711
2.470
2.437
2.416
2.382
N
H
0.89
1.76
1.74
0.89
0.51
1.00
3.07
1.07
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0
8.0
7.0
6.0
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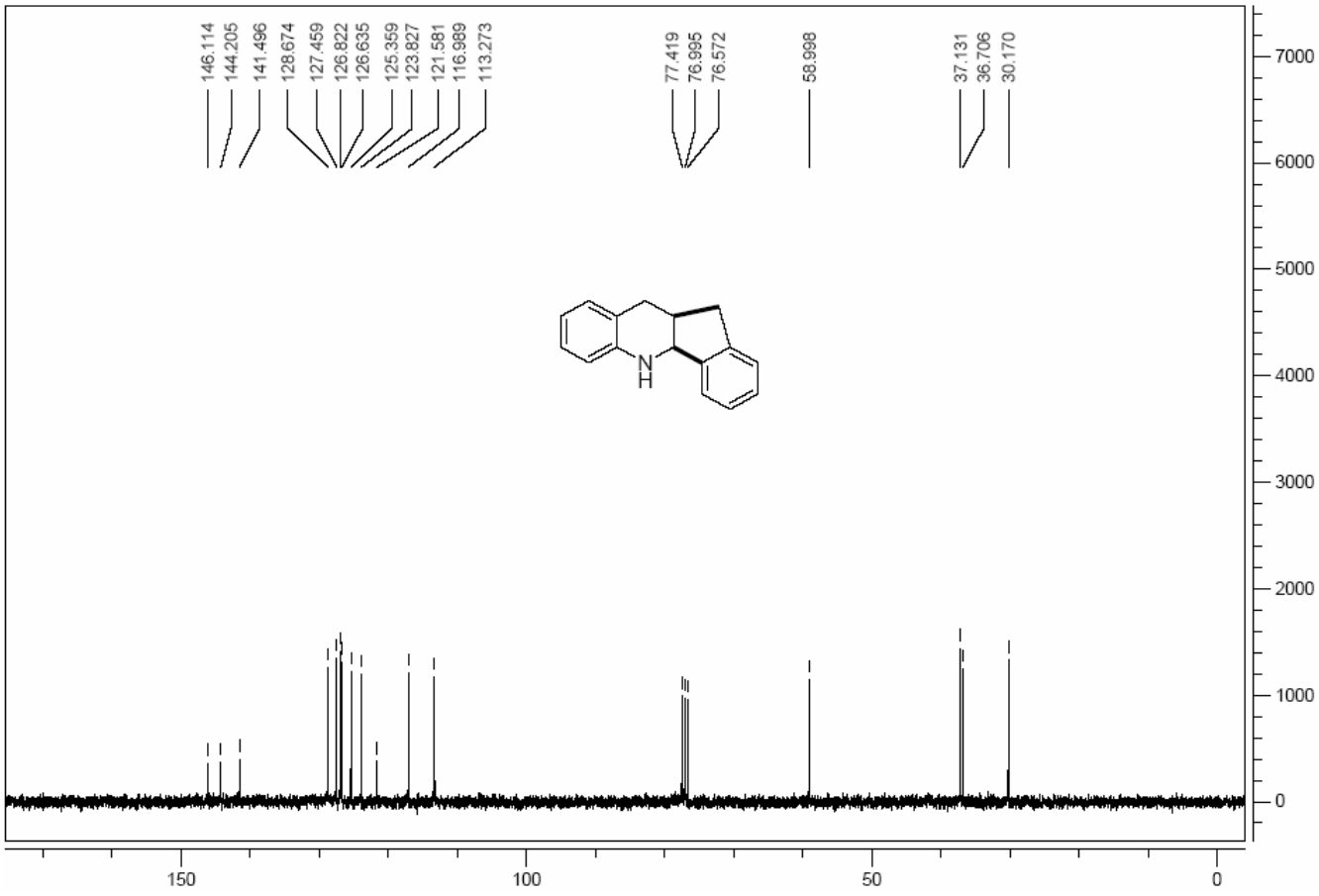
4.0
3.0
2.0
1.0
0.0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126.822
126.635
125.359
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121.581
116.989
113.273
77.419
76.995
76.572
58.998
37.131
36.706
30.170
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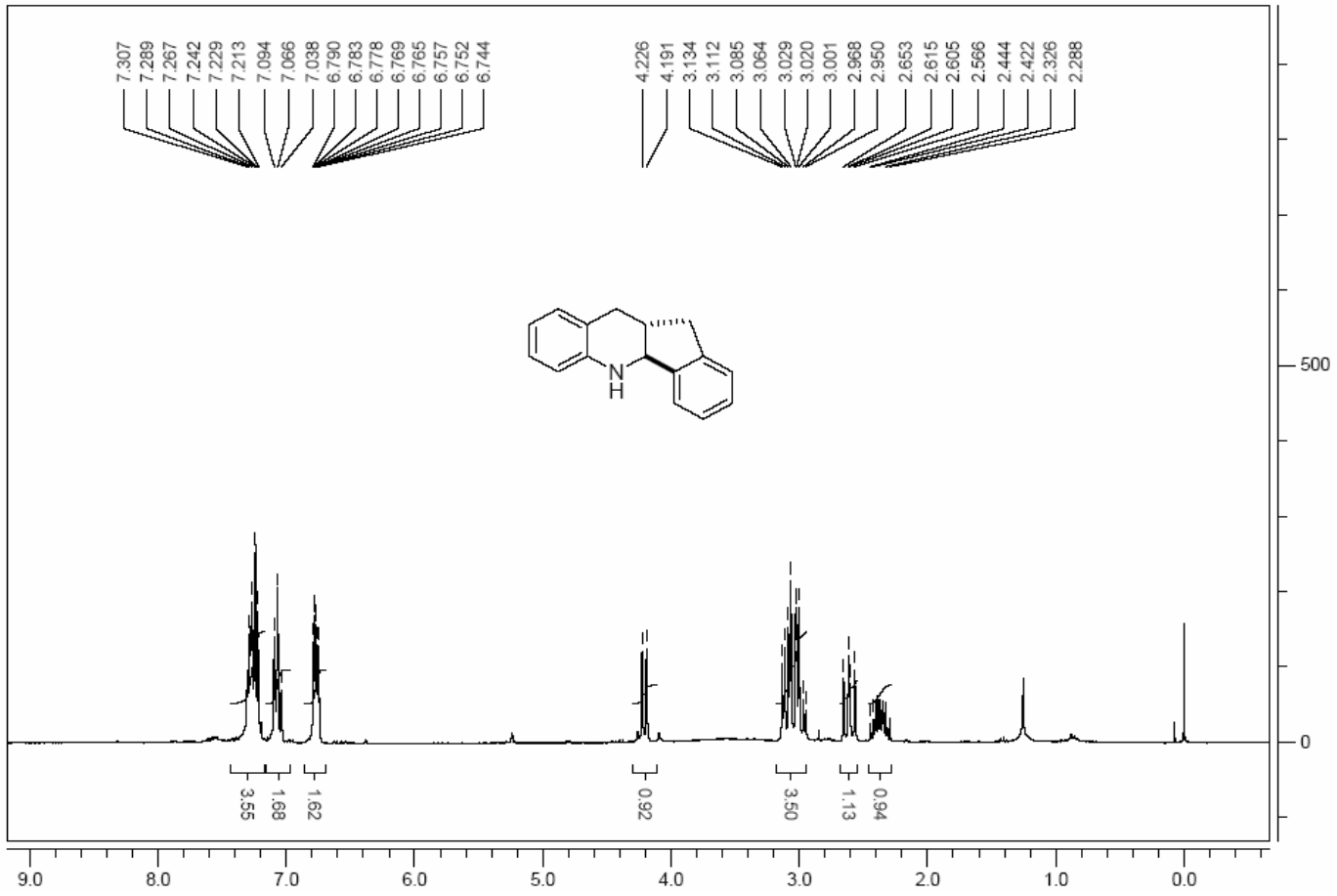
H
7000
6000
5000
4000
3000
2000
1000
0
150
100
50
0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7.267
7.242
7.229
7.213
7.094
7.066
7.038
6.790
6.783
6.778
6.769
6.765
6.757
6.752
6.744
4.226
4.191
3.134
3.112
3.085
3.064
3.029
3.020
3.001
2.968
2.950
2.653
2.615
2.605
2.566
2.444
2.422
2.326
2.288
N
H
500
0
3.55
1.68
1.62
0.92
3.50
1.13
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8.0
7.0
6.0
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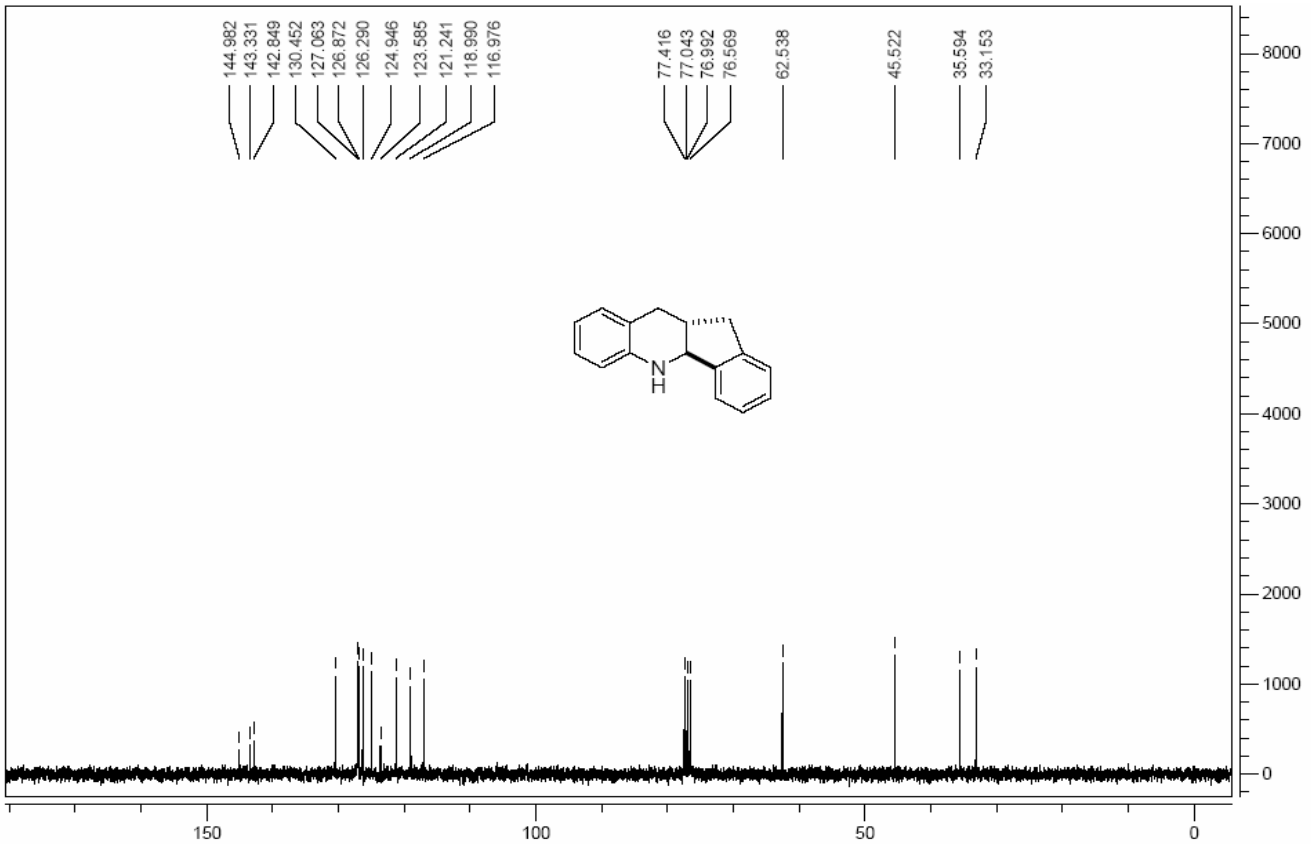
4.0
3.0
2.0
1.0
0.0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142.849
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126.872
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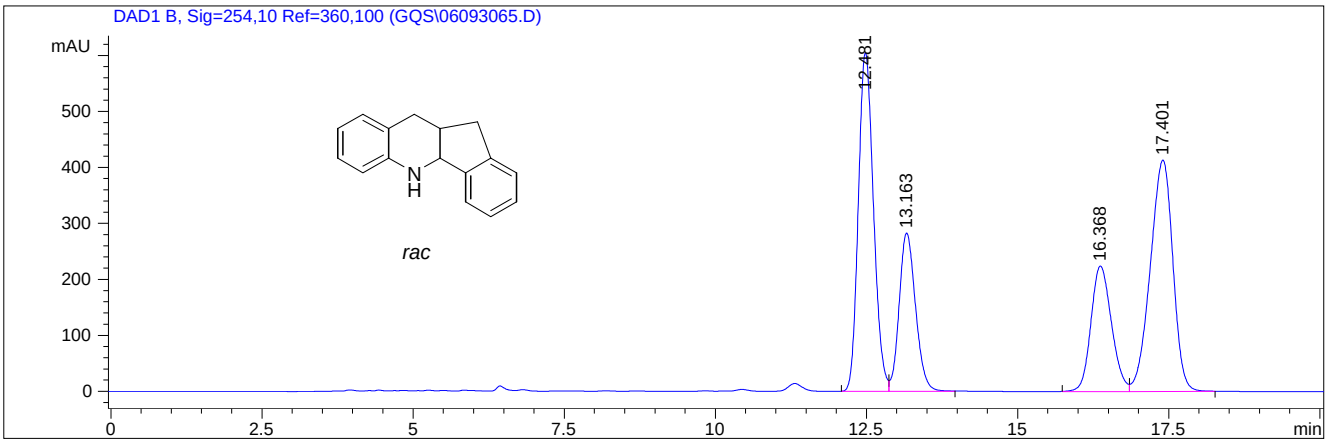
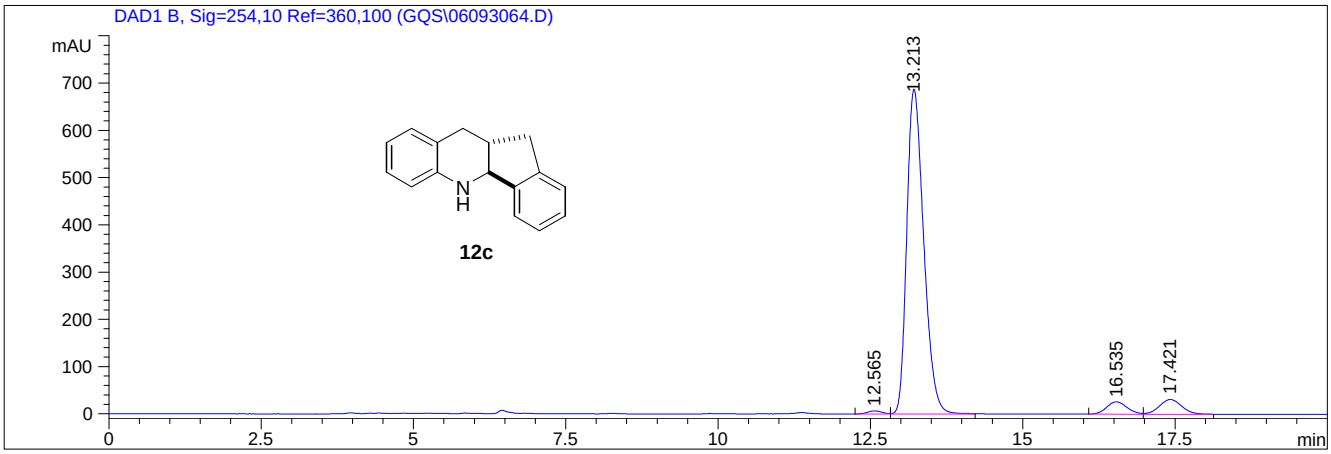
124.946
123.585
121.241
118.990
116.976
77.416
77.043
76.992
76.669
62.538
45.522
35.594
33.153
N
H
8000
7000
6000
5000
4000
3000
2000
1000
0
150
100
50
0



(*rac*)-5,5a,10a,11-tetrahydro-10*H*-indeno[1,2-*b*]quinoline



(*anti*)-5,5a,10a,11-tetrahydro-10*H*-indeno[1,2-*b*]quinoline