Supporting Information

Probing Evolution of Ar-BINMOL-derived Salen-Co(III) Complex for Asymmetric Henry Reactions of Aromatic Aldehydes: Salan-Cu(II) *versus* Salen-Co(III) Catalysis

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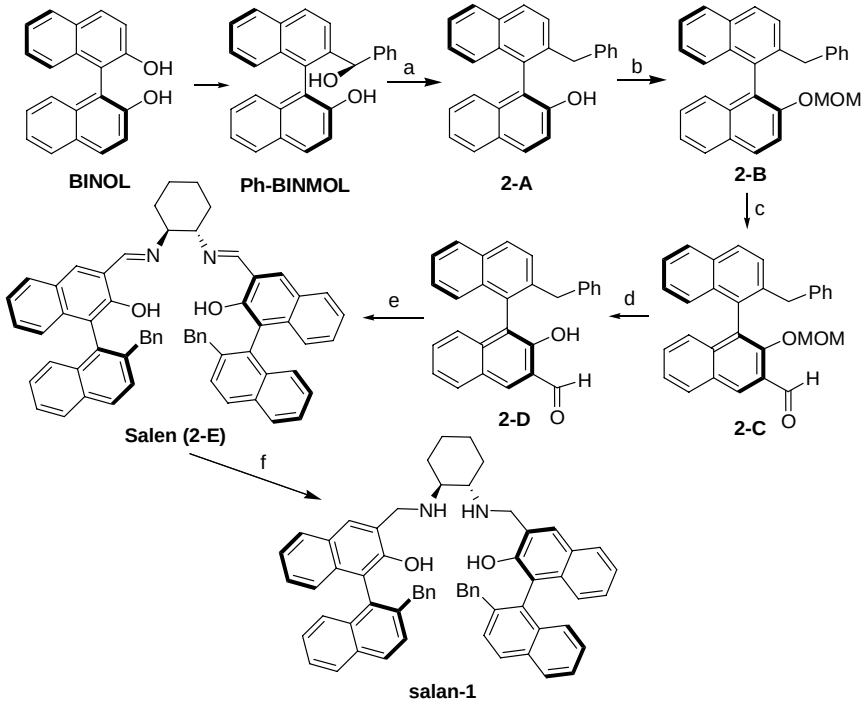
Contents

General information

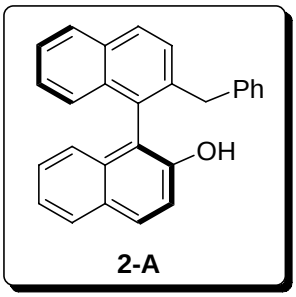
All reagents and solvents were used directly without purification. Flash column chromatography was performed over silica (200-300 mesh). Reactions were monitored by thin layer chromatography using silica gel. ^{1}H NMR and ^{13}C NMR (500 and 125MHz, respectively) spectra were recorded in $CDCl_3$, ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm, $(CD_3)_2CO$ at 2.05ppm). ^{13}C NMR chemical shifts are reported in ppm from tetramethyl silane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.20 ppm). Thin layer chromatography was performed using silica gel; F_{254} TLC plates and visualized with ultraviolet light. HPLC was carried out with a Waters 2695 Millennium system equipped with a photodiode array detector. The ESI-MS analysis of the samples was operated on an LCQ advantage mass spectrometer (ThermoFisher Company, USA), equipped with an ESI ion source in the positive ionization mode, with data acquisition using the Xcalibur software (Version 1.4).

2. The Synthesis of Salen and Salan Ligand

2.1. Schematic synthesis of salan 1-3



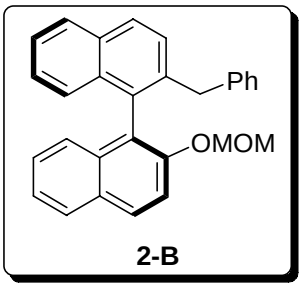
2.2 The synthesis of BINOL-derived product salan (1) from Ph-BINMOL:



2-A

Step a: To a solution of (*S, R*)-Ar-BINMOL (9.4g, >99%*ee*, 25 mmol) and NaI (22.5 g , 150 mmol) in dry acetonitrile (100 mL) were added TMSCl (13 mL , 150 mmol) at room temperature under Argon atmosphere. After the addition, the solution was allowed to stir at room temperature overnight. Then saturated sodium thiosulfate solution was added until the mixture turned colorless. The resultant mixture was extracted with DCM, and washed with water and saturated NaCl solution. The organic layer was dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography (hexanes/ethyl acetate = 5/1) to give the desired product **2-A** (9 g, 100% yield) as a white solid.^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (m, 3H), 7.52 (d, J = 8.4 Hz, 1H), 7.45 (t, J = 6.8 Hz, 1H) , 7.52-7.25 (m, 8H), 7.12 (d, J = 7.2 Hz, 2H), 6.99 (d, J = 8.0 Hz, 1H), 6.90 (d, J = 6.0 Hz, 1H), 4,62 (S, 1H) , 3.77 (S, 2H).^{13}C NMR ($CDCl_3$,100 MHz) δ 151.2, 140.5, 140.3, 133.7, 133.2, 132.8, 130.1, 129.3, 129.1, 129.1, 128.4, 128.3, 128.2, 127.0, 126.8, 126.1, 126.0, 125.8, 124.7, 124.7, 123.5, 117.5, 117.3, 77.4, 77.1, 76.8, 39.8 ppm. IR (neat, cm^{-1}): 3488, 3439, 3052, 3020, 2957, 2925, 1924, 1810, 1685, 1617, 1596, 1517, 1505, 1493, 1468, 1450, 1438, 1401, 1379, 1361, 1332, 1301, 1271, 1260, 1236, 1220, 1202, 1173, 1142, 1126, 1074, 1026, 975, 968, 948, 935, 910, 875, 868, 837, 816, 790, 769, 755, 717, 698, 684 cm^{-1}. Exact mass calcd for $C_{27}H_{20}O$ $[M+H]^+$, 361.15, Found 361.15.

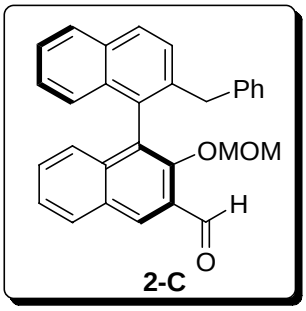
2.3 The synthesis of MOM-protected product (Step b):



2-B

To a solution of NaH (0.96 g, 40 mmol) in dry THF (150 mL) were added compound **2-A** (7.2 g, 20 mmol) which was dissolved in dry THF at 0 ^{o}C temperature under Argon atmosphere. The mixture was stirred for 1h, then MOMCl (3.06 mL, 40 mmol) was added at 0 ^{o}C. The mixture was allowed to stir at room temperature for 4h. After quenching with water, the resultant mixture was extracted with ethyl acetate, and washed with water and saturated NaCl solution. The organic layer was dried over $MgSO_4$, concentrated, and the residue was purified by column chromatography (hexanes/ethyl acetate = 10/1) to give the desired product **2-B** (7.28 g, 90% yield) as a pale yellow solid.^{1}HNMR($CDCl_3$,400 MHz) δ 7.93 (m, 4H), 7.59 (d, J = 9.2 Hz, H), 7.47-7.34 (m, 3H), 7.22 (s, 3H), 7.12-7.06 (m, 4H), 6.94 (s, 2H), 4.91 (m, 2H), 3.78 (s, 2H), 3.15 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.6, 141.1, 138.0, 134.0, 133.3, 132.7, 132.3, 129.7, 129.6, 129.2, 128.1, 128.0, 127.9, 127.9, 127.8, 126.5, 126.3, 126.0, 125.7, 125.4, 125.3, 124.1, 116.4, 94.6, 77.4, 77.1, 76.8, 55.8, 39.9 ppm. IR (neat, cm^{-1}): 3419, 3060, 3025, 2951, 2920, 2900, 2848, 2839, 1910, 1754, 1621, 1592, 1504, 1492, 1471, 1450, 1435, 1401, 1355, 1335, 1300, 1269, 1246, 1200, 1166, 1148, 1088, 1069, 1032, 1013, 946, 923, 897, 861, 843, 829, 812, 794, 784, 762, 747, 740, 718, 696, 683 cm^{-1}. Exact mass calcd for $C_{29}H_{24}O_2$ $[M+Na]^+$, 427.17, Found 427.17.

2.4 The synthesis of BINMOL-derived aldehyde (Step c):

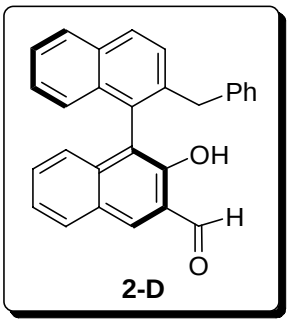


2-C

To a solution of compound **2-B** (4.04 g,10 mmol) in the dry THF (100 ml) were added TMEDA(1.8 ml, 12 mmol) in dry THF at -78 ^{o}C under Argon atmosphere. Then *n*-BuLi (9 ml, 14 mmol, 1.5 M in hexane) was added slowly in 1h. After the addition, the solution was allowed to stir at 0 ^{o}C for 30 min. The solution was then cooled to

-78 °C. A solution of dry DMF (10 mL, 13 mmol) in THF (10 mL) was added to the reaction and the solution was stirred for 30 min at -78 °C. The mixture was warmed to 0 °C and stirred for additional 1.5 h. After quenching with saturated NH_4Cl solution, 1 M HCl was added to the reaction mixture. The mixture was extracted with ethyl acetate, and washed with saturated $NaHCO_3$, water and saturated NaCl solution. The organic layer was dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography (hexanes/ethyl acetate = 20/1) to give the desired product **2-C** (3.24 g, 75% yield) as a pale yellow power. ^{1}H NMR (500 MHz, CDCl3) δ: 10.61 (s, 1H), 8.60 (s, 1H), 8.02-8.04 (d, J = 8 Hz, 1H), 7.90-7.93 (t, J = 9Hz, 2H) ,7.48-7.49 (d, J = 8.5, 1H), 7.43-7.4 (m, 2H), 7.25-7.30 (m, 2H), 7.19-7.20 (d, J = 8.5 Hz, 1H), 7.03-7.08 (m, 4H), 6.88-6.89 (d, J = 7.5Hz, 1H), 4.68-4.69 (m, 1H), 4.55-4.56 (m, 1H), 3.92-3.95 (d, J = 15.5 Hz, 1 H), 3.78-3.85 (d, J = 15.5 Hz, 1H), 2.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:153.2, 140.2, 138.9, 136.9, 133.3, 132.3, 131.8, 131.1, 130.1, 129.2 , 129.0, 128.6, 128.1, 128.0, 126.5, 126.2, 126.0, 125.9, 99.9, 57.0, 40.1 ppm. IR (neat, cm^{-1}): 3057, 2920, 1689, 1618, 1586, 1506, 1496, 1451, 1382, 1354, 1330, 1259, 1182, 1156, 1104, 1073, 1042, 963, 925, 879, 832, 807, 787, 754, 712, 698, 665 cm^{-1}. Exact mass calcd for $C_{30}H_{24}O_3$ $[M+Na]^+$, 455.16, Found 455.16.

2.5 The synthesis of deprotected BINMOL-derived aldehyde (Step d):

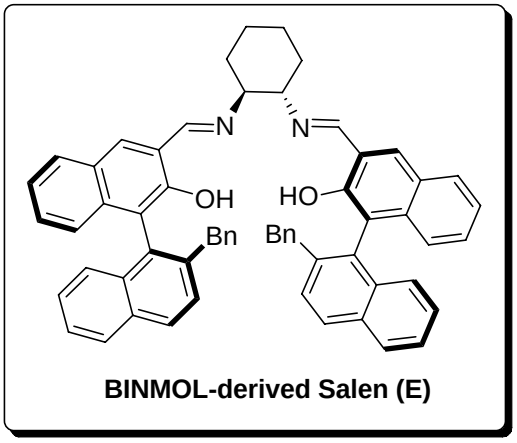


2-D

To a solution of compound **2-C** (3.03 g , 7 mmol) in THF (75 ml) were added slowly Conc. HCl (75 ml) at 0 °C. The mixture was stirred for 2 h at room temperature. Then water was added, The resultant mixture was extracted with ethyl acetate, and washed with saturated $NaHCO_3$, water and saturated NaCl solution. The organic layer was dried over Na_2SO_4, concentrated, and the residue was purified by column

chromatography (hexanes/ethyl acetate = 10/1) to give the desired product **2-D** (2.58 g , 95%yield) as a yellow power.^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.04 (s, H), 10.18 (s, H), 8.42 (s, H), 7.87 (d, J = 8.8 Hz, 3H), 7.70 (s, H), 7.46-7.43 (m, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.06 (s, 4H), 6.94 (d, J = 8.4 Hz, 3H), 3.78 (d, J = 5.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.8, 153.4, 140.7, 138.5, 138.0, 137.7, 132.9, 132.5, 130.6, 129.8, 129.2, 128.5, 128.2, 128.2, 128.1, 127.5, 126.4, 125.8, 125.7, 125.4, 125.2, 124.5, 122.1, 120.8, 39.9 ppm. IR (neat, cm^{-1}): 3428, 3150, 3059l, 2838, 1792, 1655, 1629, 1577, 1506, 1452, 1443, 1412, 1384, 1292, 1254, 1225, 1212, 1179, 1142, 1115, 1073, 1054, 1025, 952, 936, 923, 895, 879, 856, 809, 796, 778, 757, 711, 697, 681 cm^{-1}. Exact mass calcd for $C_{28}H_{20}O_2$ $[M]^+$, 388.15. Found 388.15;

2.6 The synthesis of BINMOL-derived salen (Step e):

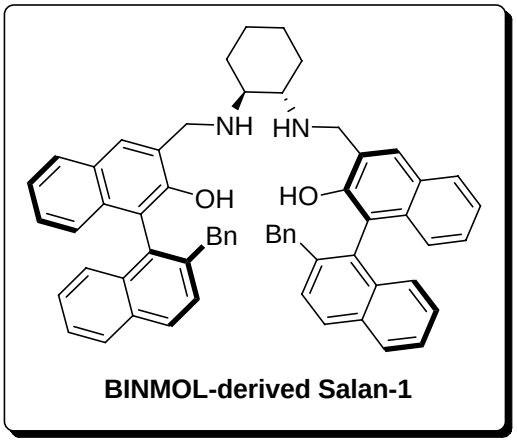


BINMOL-derived Salen (E)

To a solution of (1*S*,2*S*)- diaminocyclohexane tartrate (0.66 g , 2.5 mmol) and K_2CO_3 (0.7 g , 5 mmol) in 50% ethanol(12 ml) were added slowly compound **2-D** (1.94 g, 5 mmol) in ethanol(24ml) at room temperature. After the addition, the solution was allowed to stir at room temperature for 48h. The precipitate was collected by filtration, washed with ice ethanol, and dried in vacuum oven to obtain the product salen **2-E** (2.03 g , 95% yield) as a pale yellow power. ^{1}H NMR($CDCl_3$, 400 MHz) δ 8.45(s, H), 8.34 (s, H), 8.01 (t, J = 7.2 Hz, H), 7.90 (d, J = 8.8 Hz, 4H), 7.76 (t, J = 8.0 Hz, 4H), 7.49-7.46 (m, 3H), 7.40 (s, H), 7.38 (s, H), 7.30 (s, H), 7.22 (s, H), 7.11-7.08 (m, 7H), 7.00 (s, H), 6.97 (d, J = 8.0 Hz, 5H), 6.94 (s, H), 6.92 (s, H), 3.81 (d, J = 5.6 Hz, 4H), 3.32-3.30 (m, 2H), 1.99 (d, J = 13.6 Hz, 2H), 1.89 (d, J =8.8 Hz, 2H), 1.70 (d,

J =11.2 Hz, 2H), 1.46 (t, *J* = 10.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.8, 165.0, 154.4, 141.0, 138.4, 138.0, 133.3, 129.3, 129.2, 128.9, 128.3, 128.2, 128.2, 128.0, 126.4, 126.1, 125.8, 125.8, 125.7, 125.6, 125.5, 125.2, 125.2, 124.7, 124.5, 123.3, 120.4, 119.3, 39.9 ppm. IR(neat, cm^{-1}): 3403, 3055, 2929, 2856, 1629, 1597, 1506, 1494, 1443, 1380, 1348, 1294, 1258, 1180, 1143, 1115, 1062, 1024, 941, 915, 808, 746, 712, 697 cm^{-1}. Exact mass calcd for $C_{62}H_{50}N_2O_2$ $[M+H]^+$, 855.39, Found 855.39.

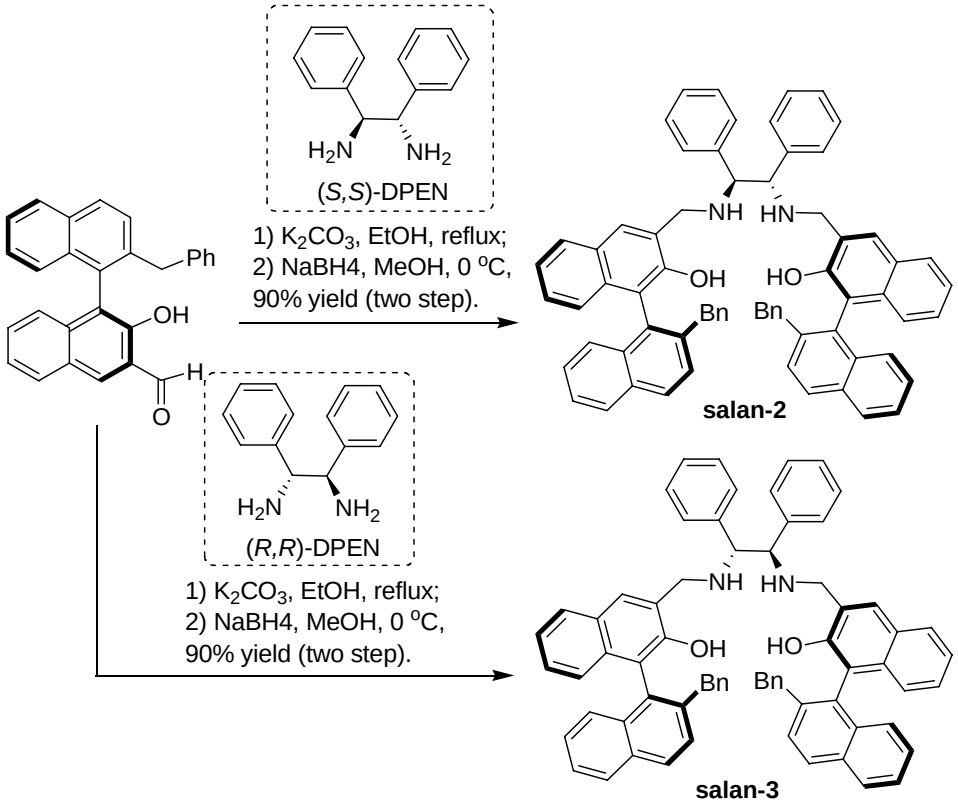
2.7 The synthesis of desired salan ligand (Step f):



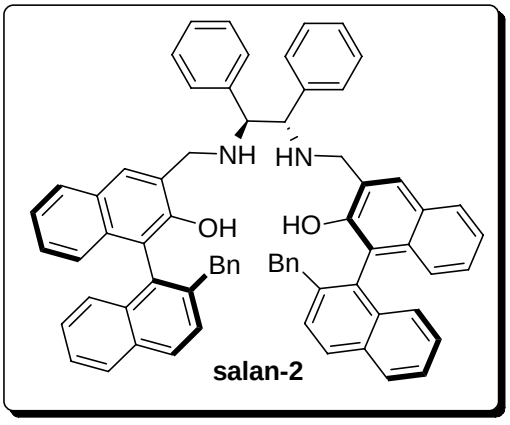
BINMOL-derived Salan-1

To a solution of compound **E** (1.71 g , 2 mmol) in MeOH (20 ml) were added $NaBH_4$ (0.08 g , 2.2 mmol) at 0 ^oC. After stirring for 2 h, water was added to quench the reaction. The solvent was removed under vacuum. The resultant mixture was extracted with DCM, and washed with water and saturated NaCl solution. The organic layer was dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography (hexanes/ethyl acetate = 10/1) to give the **BINMOL-derived Salan-1** (1.72 g, >99% yield) as a white solid.^{1}H NMR($CDCl_3$, 400 MHz) δ 7.87 (d, *J* = 8.4 Hz, 5H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.55 (s, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.35-7.29 (m, 6H), 7.21-7.16 (m, 4H), 7.13-7.08 (m, 5H), 7.03(d, *J* =8.4 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 4H), 4.13 (s, 4H), 3.77 (s, 4H), 2.43 (s, 2H), 2.08 (s, 2H), 1.52 (s, 2H), 1.09 (d, *J* = 4.4 Hz, 6H).$_{13}$C NMR ($CDCl_3$, 100 MHz) δ 153.3, 141.3, 138.1, 133.8, 133.2, 132.5, 129.3, 128.1, 128.1, 128.0, 128.0, 127.6, 127.4, 126.3, 126.2, 126.1, 125.6, 125.6, 125.3, 124.7, 123.2, 119.0, 60.2, 50.3, 50.2, 39.8, 30.5, 24.1 ppm. IR (neat, cm^{-1}): 3421, 3052, 3023, 2925, 2852, 1942, 1627, 1601, 1601, 1506, 1493,

1451, 1429, 1374, 1355, 1292, 1252, 1227, 1207, 1182, 1148, 1109, 1074, 1026, 939, 917, 885, 855, 829, 803, 783, 746, 717, 697 cm^{-1}. Exact mass calcd for $C_{62}H_{54}N_2O_2$ $[M+H]^+$, 859.42, Found 859.42.

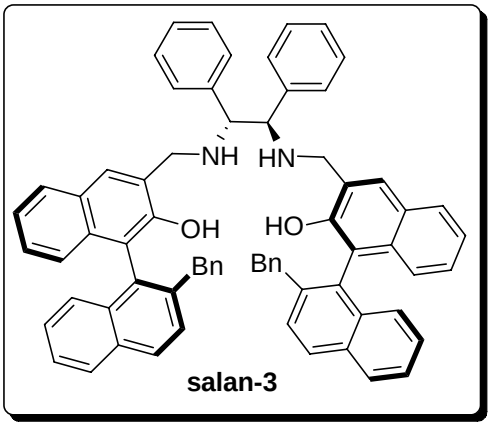


2.8 The synthesis of desired salan ligand 2 and 3.



To a solution of (1*S*,2*S*)-(-)-1,2-Diphenyl-1,2-ethanediamine (0.53 g , 2.5 mmol) and K_2CO_3 (0.7 g , 5 mmol) in 50% ethanol (12 mL) were added slowly **4** (1.94 g, 5 mmol) in ethanol(24ml) at room temperature. After the addition, the solution was allowed to stir at room temperature for 48h. The precipitate was collected by filtration, washed with ice ethanol, and dried in vacuum oven to obtain the product **salen-2** (2.24 g, 94%

yield) as a pale yellow power. To a solution of **salen-2** (1.90 g, 2 mmol) in MeOH (20 mL) were added $NaBH_4$ (0.08 g, 2.2 mmol) at 0 °C. After stirring for 2 h, water was added to quench the reaction. The solvent was removed under vacuum. The resultant mixture was extracted with DCM, and washed with water and saturated NaCl solution. The organic layer was dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography (hexanes/ethyl acetate = 10/1) to give **salan-2** (1.91 g, >99% yield) as a gray solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (d, J = 8.8 Hz, 6H), 7.18 (d, 11H), 7.10 (s, 7H), 7.04 (t, J = 8.4 Hz, 6H), 6.95 (t, J = 7.2 Hz, 8H), 6.83 (d, J = 8.0 Hz, 4H), 4.71 (s, 4H), 3.73 (d, J = 15.2 Hz, 4H), 3.55 (d, J = 15.2 Hz, 4H), 1.56 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.7, 138.7, 133.8, 133.2, 132.5, 130.0, 129.4, 128.1, 128.1, 128.0, 128.0, 127.7, 127.4, 126.3, 126.2, 126.1, 125.6, 125.6, 125.3, 124.7, 123.2, 119.0, 60.2, 50.3, 39.8. IR (neat, cm^{-1}): 3433, 3056, 3026, 2922, 2852, 1630, 1507, 1494, 1452, 1433, 1384, 1349, 1298, 1256, 1183, 1150, 1110, 1074, 1028, 888, 829, 783, 748, 716, 699 cm^{-1}. Exact mass calcd for $C_{70}H_{56}N_2O_2$ $[M+H]^+$, 957.4420. Found 957.4372.



salan-3

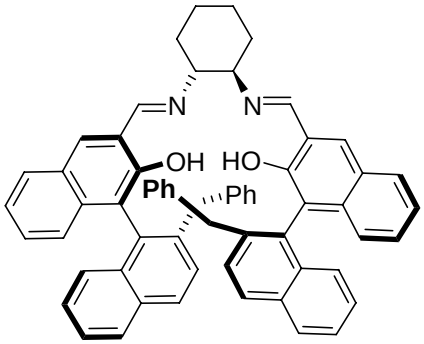
Using the same method, (1*R*,2*R*)-(-)-1,2-Diphenyl-1,2-ethanediamine can give **salan-3** (1.91 g, >99% yield) as a gray solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, J = 8.8 Hz, 6H), 7.15 (d, 11H), 7.07 (s, 7H), 7.01 (t, J = 8.4 Hz, 6H), 6.92 (t, J = 7.2 Hz, 8H), 6.80 (d, J = 8.0 Hz, 4H), 4.68 (s, 4H), 3.70 (d, J = 15.2 Hz, 4H), 3.52 (d, J = 15.2 Hz, 4H), 1.53 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.3, 139.3, 134.8, 134.2, 133.5, 131.0, 130.3, 129.1, 129.1, 129.0, 129.0, 128.7, 128.4,127.3, 127.2, 127.1, 126.6, 126.6, 126.3, 125.7, 124.2, 120.0, 61.2, 51.3, 40.8. IR (neat, cm^{-1}): 3435, 3056, 3026, 2922, 2852, 1629, 1506, 1494, 1452, 1433, 1384, 1349, 1255, 1183, 1149,

1110, 1027, 917, 889, 830, 804, 782, 748, 715, 699 cm^{-1}. Exact mass calcd for $C_{70}H_{56}N_2O_2$ $[M+H]^+$, 957.4420. Found 957.4363.

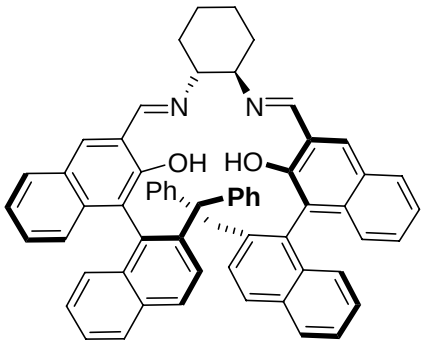
2.9 The Synthesis of Salen-5 Ligands

Similarly to the synthesis of salan ligand (1-3), the general procedure for the synthesis of salen liagnd 5 (5a-c):

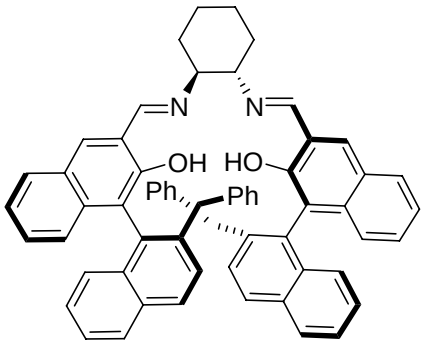
To a solution of (1*R*, 2*R*)-diaminocyclohexane tartrate (0.66 g, 2.5 mmol) and K_2CO_3(0.7 g, 5 mmol) in 50% ethanol (12 mL) were added slowly the Ar-BINMOL-derived aldehyde (1.94 g, 5 mmol) in ethanol (24 mL) at room temperature. After the addition, the solution was allowed to stir at room temperature for 48 hrs. The precipitate was collected by filtration, washed with ice ethanol, and dried in vacuum oven to obtain the product **5a** (2.03 g, 95% yield) as a pale yellow power.



(*R, R, S, S*)-5a: ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 12.99 (s, 2 H), 8.40 (s, 2 H), 7.85-7.87 (d, J = 11.5 Hz, 4 H), 7.69-7.73 (t, J = 10 Hz, 4 H), 7.42-7.44 (d, J = 11 Hz, 2 H), 7.31-7.35 (t, J = 10 Hz, 2 H), 7.15-7.26 (m, 4 H), 6.92-7.00 (m, 8 H), 6.84-6.97 (m, 8H), 3.73-3.83 (dd, J = 19, 27 Hz, 4 H), 3.26-3.28 (t, J = 4 Hz, 2H), 1.94-1.97 (d, J = 16.5Hz, 2H), 1.83-1.86 (d, J = 11Hz, 2 H), 1.66-1.68 (d, J = 12 Hz, 2H), 1.39-1.44 (t, J = 12.5Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.2, 154.5, 138.7, 136.1, 135.4, 135.0, 133.4, 133.2, 132.6, 132.0, 129.3, 129.0, 128.9, 128.4, 128.1, 127.5, 126.2, 126.0, 125.2, 124.9, 123.4, 120.6, 119.5, 73.2, 60.5, 39.5, 32.9, 24.2, 21.1, 14.3.

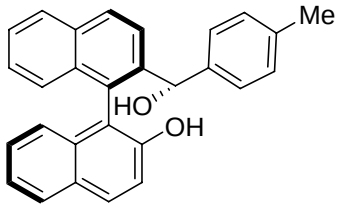


(*R, R, R, R*)- 5d: ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 13.29 (s, 2H), 8.39 (s, 2H), 7.89-7.90 (m, 4H), 7.38-7.42 (m, 6H), 7.32-7.34 (d, J = 8.0 Hz, 2H), 7.25-7.26 (m, 4H), 7.10-7.14 (m, 10H), 7.00-7.02 (d, J = 6.5, 4H), 6.91-6.92 (d, J = 8.0 Hz, 2H), 3.72-3.75 (d, J = 15.0 Hz, 2H), 3.58-3.61 (d, J = 15.0 Hz, 2H), 3.33-3.35 (t, J = 5.0 Hz, 2H), 2.04-2.07 (d, J = 13.5 Hz, 2H), 1.90-1.91 (d, J = 8.5 Hz, 2H), 1.76 -1.78 (d, J = 10.0 Hz, 2H), 1.47-1.50 (d, J = 10.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.1, 154.2, 141.3, 138.6, 135.3, 133.2, 133.0, 132.5, 131.9, 129.6, 128.8, 128.2, 128.17, 128.12, 128.06, 128.0, 126.2, 125.7, 124.6, 123.2, 120.3, 119.3, 73.2, 39.6, 32.5, 24.1.

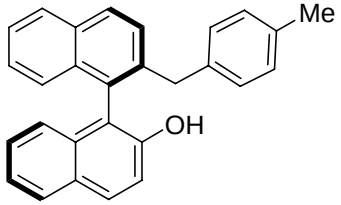


(*S, S, R, R*)-5e: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 13.09- 13.11 (m, 2H), 8.49 - 8.51 (m, 2H), 7.93-7.94 (m, 4H), 7.78 - 7.81 (m, 4H), 7.52 - 7.55 (m, 2H), 7.42-7.43 (m,2H), 7.33-7.34 (m, 2H), 7.26-7.27 (m, 2H), 6.94 -7.16 (m, 16H), 3.87-3.91 (m, 4H), 3.37 (s, 2H), 2.03-2.06 (d, J = 12.0 Hz, 2H), 1.93 (s, 2H), 1.77 (s, 2H), 1.51 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 165.1, 154.5, 141.1, 138.4, 135.3, 135.3, 135.3, 133.1, 132.1, 129.4, 128.9, 128.4, 128.1, 128.06, 127.4, 126.2, 125.9, 125.7, 125.3, 124.8, 123.3, 120.5, 119.4, 73.2, 40.0, 32.8, 24.2.

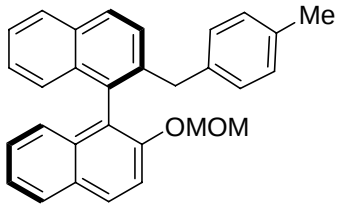
The synthesis of (*R,R,S,S*)-5b-c was similarly to that of 5a, and the characterization of product 5b-c was shown as following:



The characterization of product 5b-a (intermediate 1):^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.87-7.93 (m, 4H), 7.50-7.64 (m, 2H), 7.17-7.37 (m, 5H), 6.90-6.95 (m, 5H), 6.57 (s, 1H), 5.70 (s, 1H), 3.42 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 151.4, 141.5, 139.6, 136.6, 134.2, 133.1, 130.1, 129.4, 129.1, 128.7, 128.1, 128.09, 126.7, 126.6, 126.4, 126.1, 125.2, 123.5, 118.1, 117.4, 73.3, 21.0.

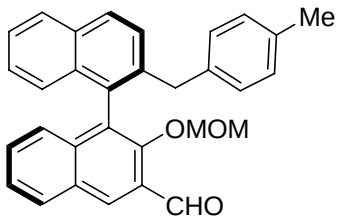


The characterization of product 5b-b (intermediate 2):^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.87-7.94 (m, 4 H), 7.44 - 7.53 (m, 2 H), 7.21-7.35 (m, 5H), 6.95-7.02 (m, 3 H), 6.81 - 6.8 (d, J = 7.6 Hz, 2H), 4.72 (s, 1H), 3.74 (s, 2H), 2.25 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.2, 140.7, 137.3, 135.5, 133.7, 133.3, 132.7, 130.0, 129.3, 129.2, 129.0 128.98, 128.8, 128.3, 128.2, 127.0, 126.7, 125.9, 124.7, 123.5, 117.5, 117.4, 39.3, 21.0.

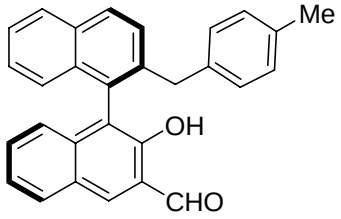


The characterization of product 5b-c (intermediate 3): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02-8.04 (d, J = 8.4 Hz, 1H), 7.93-7.95 (m, 3H), 7.65-7.68 (d, J = 8.8 Hz, 1H), 7.51 -7.53 (d, J = 8.8 Hz, 1H), 7.40 - 7.48 (m, 2H), 7.26-7.29 (m, 3H), 7.14-7.16 (d, J = 8.8 Hz, 1H), 7.00 - 7.02 (d, J = 8.0 Hz, 2H), 6.91-6.93 (d, J = 8.0 Hz, 2H), 5.04-5.06 (d, J = 7.2 Hz, 1H), 4.96 -4.97 (d, J = 7.2 Hz, 1H), 3.18 (s, 2H), 3.21 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 152.7, 138.4, 138.0, 135.1, 134.0, 133.4, 132.6, 132.4, 129.8 129.6, 129.2, 128.8, 127.9, 127.93, 127.8, 126.6, 126.3, 126.0, 125.2,

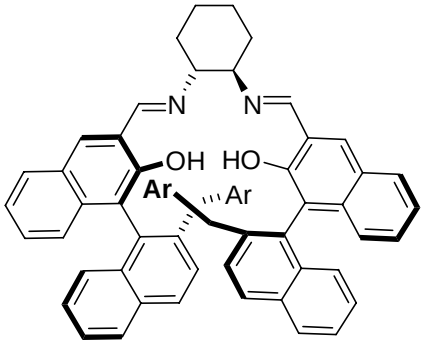
124.1, 122.9, 116.6, 94.8, 55.8, 39.4, 21.0.



The characterization of product 5b-d (intermediate 4): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 10.67 (s, 1H), 8.65(s, 1H), 8.06- 8.08 (d, J = 8.0 Hz, 1H), 7.93-7.97 (t, J = 8.0 Hz, 2H), 7.52-7.54 (d, J = 8.4 Hz, 1H), 7.45-7.49 (t, J = 7.2 Hz, 2H), 7.24-7.33 (m, 3H), 7.10-7.12 (d, J = 8.8 Hz, 1H), 6.92-6.94 (d, J = 8.0 Hz, 2H), 6.83 -6.85 (d, J = 7.8 Hz, 2H), 4.73-4.83 (d, J = 6.0 Hz, 1H), 4.61-4.62 (d, J = 6.0 Hz, 1H), 3.94 -3.97 (d, J = 11.2 Hz, 1H), 3.79-3.83 (d, J = 11.2 Hz, 1H), 3.07 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125MHz, $CDCl_3$) δ: 153.2, 139.3, 137.0 135.3, 133.4, 132.3, 132.3, 131.8, 131.0, 130.2, 129.2, 129.15, 129.0, 128.9, 128.6, 128.2, 128.09, 126.5, 126.3, 126.26, 126.0, 125.5, 99.9, 57.0, 39.6, 21.0.



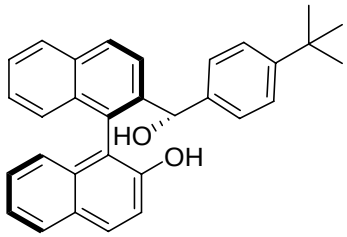
The characterization of product S5b-e (intermediate 5): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 10.45 (s 1H), 10.19 (s, 1H), 8.32 (s, 1H), 7.96-8.00 (d, J = 6.8, 1H), 7.92-7.94 (m, 2H), 7.23-7.51 (m, 6H), 7.10-7.12 (d, J = 8.0 Hz, 1H), 6.94-6.96 (d, J = 8.0 Hz, 2H), 6.87- 6.89 (d, J = 8.0 Hz, 2H), 3.75-3.85 (dd, J = 15.2, 21.2 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 196.8, 153.4, 138.0 137.9, 137.7, 135.3, 133.0, 132.6, 130.6, 130.5, 129.8, 129.2, 128.9, 128.5, 128.3, 128.2, 127.6, 126.4, 125.4, 124.4, 122.1, 120.9, 39.5, 21.0.



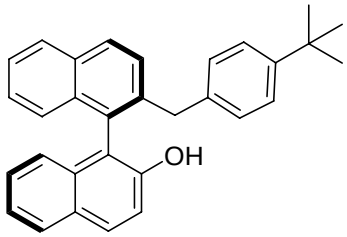
5b: Ar = *p*-MePh

The characterization of product (*R,R,S,S*)-5b: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.93-8.94 (d, J = 8.5 Hz, 2H), 7.9 (s, 4H), 7.81-7.84 (m, 4H), 7.55-7.58 (m, 2H), 7.44-7.46 (m, 2H), 7.34-7.37 (m, 2H), 7.29-7.32 (m, 2H), 7.17-7.20 (m, 2H), 7.09-7.12 (m, 2H), 6.95-7.02 (m, 10H), 4.22-4.25 (m, 2H), 3.85-3.92 (m, 2H), 3.41 (d, J = 1.0 Hz, 2H), 2.33-2.34 (d, J = 3.5 Hz, 6H), 1.95-1.96 (d, J = 4.5 Hz, 2H), 1.81 (s, 2H), 1.35-1.41 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ : 165.2, 154.5, 138.7, 135.4, 135.0, 133.4, 133.2, 132.6, 132.0, 129.3, 129.0, 128.9, 128.4, 128.1, 127.5, 126.2, 126.0, 125.2, 124.9, 123.4, 120.6, 119.5, 60.5, 39.5, 32.9, 24.2, 21.1, 14.3;

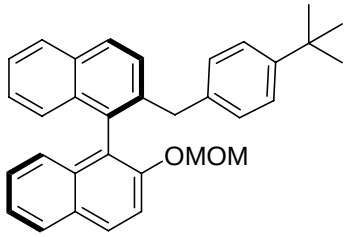
The synthesis and characterization of product (*R,R,S,S*)-5c:



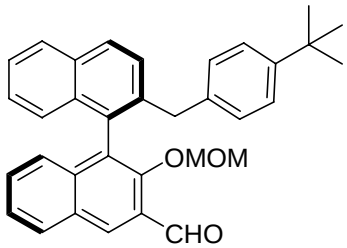
The characterization of product 5c-a(intermediate 1): ^{1}H NMR (400MHz,$CDCl_3$): 1.24 (s, 9 H), 2.91 (s, 1 H), 5.31 (s, CH_2Cl_2), 5.54 (s, 1 H), 5.76 (s, 1 H), 6.25 (d, J = 8.4 Hz, 1 H), 6.83 (d, J = 8.4 Hz, 2 H), 7.06 (t, J =8.0 Hz, 3 H), 7.19 (d, J = 8.4 Hz, 1 H), 7.26-7.31 (m, 3 H), 7.49 (t, J =8.0 Hz, 1 H), 7.70 (d, J = 8.4 Hz, 1 H), 7.88 (dd, J = 8.8, 16.0 Hz, 4 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): 31.3, 34.4, 53.5, 73.3, 117.1, 117.9, 123.5, 124.9, 124.97, 125.05, 125.9, 126.38, 126.44, 126.8, 127.9,128.1, 129.0, 129.5, 129.7, 130.1, 133.1, 133.4, 134.0, 139.4, 141.7, 149.99, 151.1.



The characterization of product 5c-b (intermediate-2): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.94-8.04 (m, 4H), 7.59-7.61 (dd, J_1 = 2.0 Hz, J_2 = 8.5 Hz, 1H), 7.53-7.55 (m, 1H), 7.45-7.47 (m, 1H), 7.36-7.42 (m, 3H), 7.23-7.29 (m, 3H), 7.08-7.10 (d, J = 8.5Hz, 1H), 6.94-6.96 (m, 2H), 5.00 (s, 1H), 3.86 (s, 2H), 1.37-1.38 (d, J = 4.0 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 151.3, 148.8, 140.7, 137.3, 133.9, 133.5, 132.8, 130.1, 129.3, 129.2, 128.9, 128.6, 128.2, 127.0, 126.04, 126.0, 125.3, 124.9, 123.5, 117.7, 117.5, 39.4, 34.4, 31.5;

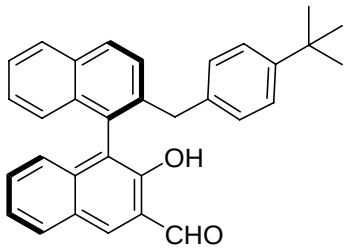


The characterization of product 5c-c (intermediate-3): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.95-8.06 (m, 4H), 7.60-7.70 (m, 2H), 7.40-7.49 (m, 2H), 7.21-7.32(m, 5H), 7.13-7.17 (m, 1H), 6.93-6.97 (m, 2H), 5.03-5.06 (m, 1H), 4.93-4.96 (m, 1H), 3.86-3.89 (m, 2H), 3.22-3.23 (m, 3H), 1.35-1.37 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 165.1, 154.2, 141.3, 138.6, 135.3, 133.2, 133.0, 132.5, 131.9, 129.6, 128.8, 128.2, 128.2, 128.1, 128.1, 128.0, 127.2, 126.2, 125.7, 125.2, 124.6, 123.2, 120.3, 119.3, 73.2, 39.6, 32.5, 24.1;

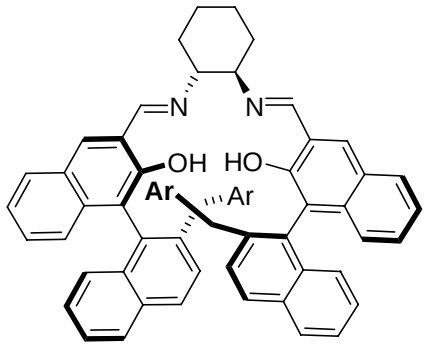


The characterization of product 5c-d (intermediate-4): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.64 (s, 1H), 8.62 (s, 1H), 8.04 (s, 1H), 7.92-8.02 (m, 2H), 6.98-7.31 (m, 9H), 6.77 (d, J = 8.4 Hz, 2H), 4.57-4.71 (m, 2H), 3.80-3.96 (m, 2H), 2.96 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 191.1, 153.1, 148.5, 139.2, 127.1, 137.0, 133.4,

132.3, 131.8, 131.1, 130.0, 129.1, 129.0, 128.7, 128.6, 128.4, 128.1, 126.3, 126.2, 126.0, 125.4, 124.9, 99.9, 39.7, 34.3, 31.4.



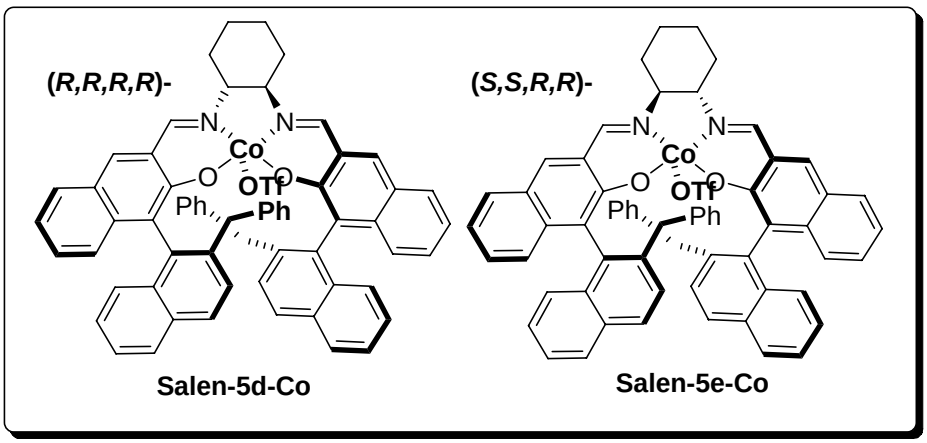
The characterization of product 5c-e (intermediate-5): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 10.43-10.45 (m, 1 H), 10.91 (s, 1 H), 8.31 (s, 1 H), 7.96-7.99 (s, 3 H), 6.87-7.60 (m, 11 H), 3.84-3.85 (m, 2 H), 1.29-1.31 (m, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 196.7, 153.4, 148.5, 138.8, 137.95, 137.88, 137.6, 133.0, 132.6, 130.7, 130.4, 129.8, 128.8, 128.5, 128.3, 127.5, 12.4, 125.8, 125.3, 125.0, 122.1, 120.9, 39.6, 34.3, 31.4.



5c: Ar = *p*-*t*-BuPh

The characterization of product (*R,R,S,S*)-5c/(Salen-5c): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 13.4 (s, 2H), 8.35 (s, 2H), 7.88-7.90 (dd, J = 3.0 Hz, 8.5 Hz, 4H), 7.47-7.49 (d, J = 8.5 Hz, 2H), 7.38- 7.42 (m, 2H), 7.29 (s, 2H), 7.22-7.23 (d, J = 3.5 Hz, 4H), 7.10-7.12 (dd, J = 2.0 Hz, 8.5Hz, 6H), 6.90-7.04 (m, 8H), 3.78-3.82 (d, J = 15.5 Hz, 2H), 3.64-3.67 (d, J = 15.5 Hz, 2H), 3.31-3.33 (dd, J = 4.0 Hz, 6.0 Hz, 2H), 2.07-2.10 (d, J = 13.5 Hz, 2H), 1.90-1.92 (d, J = 8.5 Hz, 2H), 1.77-1.79 (m, 2H), 1.47-1.51 (t, J = 5.0 Hz, 2H), 1.27 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ :165.2, 154.0, 148.4, 138.8, 138.0, 135.3, 133.2, 132.5, 131.9, 129.2, 128.7, 128.1, 127.2, 126.1, 126.09 ,125.1, 125.0,124.6,123.0, 120.2, 119.4, 39.4, 34.3, 32.3, 31.5, 21.1

3. The synthesis of (Salen)Co(III)-X catalysts[2]



Typical procedure of synthesis of (Salen)Co-OTf: deoxygenated toluene (ca. 11.6 mL) was added to salen (0.9405 g, 1.1 mmol) under N_2, and deoxygenated MeOH (ca. 11.6 mL) to $Co(OAc)_2 \cdot 4H_2O$ (545 mg, 2.2 mmol) under N_2. N_2 was bubbled through the resulting solutions for 20 min to ensure complete deoxygenation. The solution of $Co(OAc)_2 \cdot 4H_2O$ in MeOH (purple) was added via cannula under N_2 to the solution of 5 in toluene (yellow) to give a deep red solution. The resulting mixture was stirred for 30 min under an N_2 purge. Trifluoromethanesulfonic acid (97 μL, 1.1 mmol) and CH_2Cl_2 (16.6 mL) were added, and the resulting black solution stirred for an additional 2 h under an air atmosphere with vigorous stirring. Solvent was removed under reduced pressure, and the residue dissolved in minimal CH_2Cl_2. Excess insoluble $Co(OAc)_2 \cdot 4H_2O$ was removed via filtration through a Celite® pad, washing with CH_2Cl_2 (200 mL). Removal of solvent under reduced pressure provided complex 6 as a paramagnetic black solid (1.108g, >95%).

(*S,S,R,R*)-5e salen-Co-OTf: IR (KBr):3551, 3473, 3238, 3055, 2930, 2860, 2096, 1714, 1584, 1493, 1388, 1326, 1150, 1029, 957, 780, 638, 488, 408; ESI-MS (m/z): $[M]^+$calcd for $C_{62}H_{48}CoN_2O_2$ 911.30 found 911.80.

(*R,R,S,S*)-5a salen-Co-OTf: IR(KBr):3550, 3415, 3055, 2928, 1646, 1616, 1584, 1493, 1451, 1449, 1326, 1150, 1029, 757, 638, 510, 425; ESI-MS (m /z): $[M]^+$calcd for $C_{62}H_{48}CoN_2O_2$ 911.30 found 911.80.

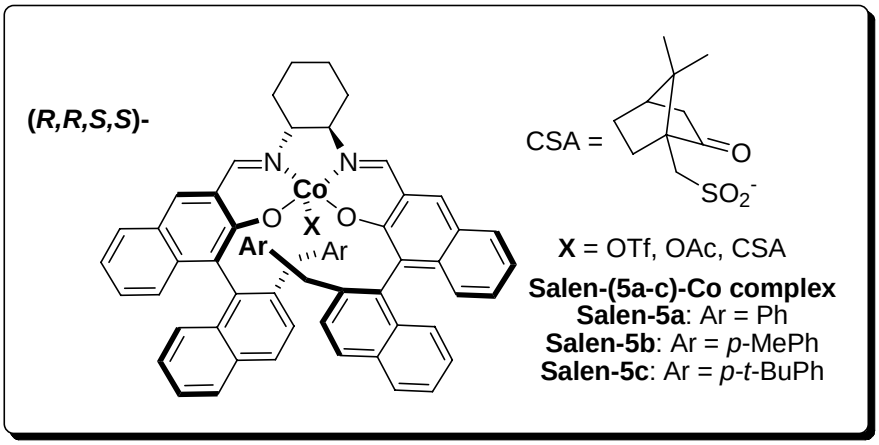
(***R,R,S,S***)**-5d salen-Co-OTf:** IR (KBr): 3473, 3414, 3055, 2929, 2859, 1616, 1584, 1492, 1450, 1327, 1029, 953, 783, 698, 511, 433. ESI-MS (m /z): $[M]^+$calcd for $C_{62}H_{48}CoN_2O_2$ 911.30 found 911.80.

(*R,R,R,R*)-5b Co-OTf: IR (KBr): 3551, 3473, 3415, 3237, 3051, 2926, 2858, 1616, 1584, 1507, 1445, 1347, 1150, 1028, 950, 861, 808, 755, 637, 498, 432; ESI-MS (m/z): $[M]^+$ calcd for $C_{64}H_{52}CoN_2O_2$ 939.33 found 939.35.

(*R,R,R,R*)-5c salen-Co-OTf: IR(KBr): 3550, 3473, 3415, 3235, 3053, 2958, 2865, 2067, 1910, 1616, 1507, 1387, 1295, 1150, 1115, 1028, 858, 813, 750, 637, 563, 507, 433. ESI-MS (m /z): $[M]^+$calcd for $C_{70}H_{66}CoN_2O_2$ 1023.43, found 1023.90.

Typical procedure of the synthesis of S5a-Co-OAc:

Typical procedure: deoxygenated toluene (ca. 11.6 mL) was added to salen ligand (881 mg, 1.03 mmol) under N_2, and deoxygenated MeOH (ca. 11.6 mL) to $Co(OAc)_2{\cdot}4H_2O$ (372 mg, 1.5mmol) under N_2. $N_2$was bubbled through the resulting solutions for 20 min to ensure complete deoxygenation. The solution of $Co(OAc)_2{\cdot}4H_2O$ in MeOH (purple) was added via cannula under N_2 to the solution of 5 in toluene (yellow) to give a deep red solution. With stirred, the resulting mixture was reflux for 2h under 80°C.Solvent was removed under reduced pressure, and the residue dissolved in minimal CH_2Cl_2. Excess insoluble $Co(OAc)_2{\cdot}4H_2O$ was removed via filtration through a Celite®pad, washing with CH_2Cl_2 (200 mL). Removal of solvent under reduced pressure provided (Salen) Co-OAc as a paramagnetic black solid (701mg, >70%). IR(KBr): 3551, 3474, 3414, 3237, 2925, 2854, 1616, 2361, 1584, 1587, 1551, 1507, 1348, 1148, 961, 802, 744, 716, 617, 503, 431. ESI-MS (m /z): $[M]^+$calcd for $C_{62}H_{48}CoN_2O_2$ 911.30, found 911.80.



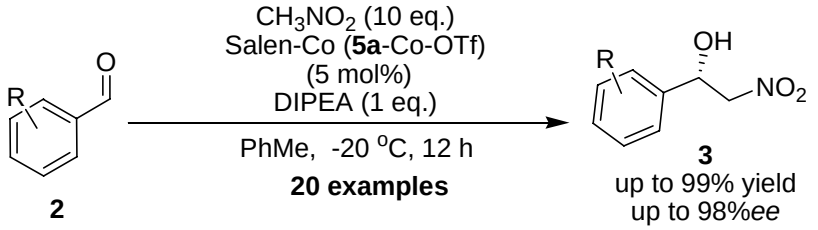
The synthesis of (*R,R,S,S*)-5a-Co-OTs:

A degassed solution of $Co(OAc)_2 \cdot 4\ H_2O$ (11.0 mg, 0.044 mmol) in 3 mL MeOH was added to a degassed solution of **5a** (37.7 mg, 0.040 mmol) in 3 mL toluene via a cannula under N_2. The combined red solution was purged with N_2 for 30 min and then LPTS (11.1 mg, 0.040 mmol) was added and followed by 5 mL of CH_2Cl_2. The mixture was stirred exposed to air for 1.5 h and concentrated, re-dissolved in CH_2Cl_2 and filtered over Celite®pad. The filtrate was concentrated and precipitated in pentane, to filter off a dark green crystalline solid that was air-dried; yield: 24 mg (70%). IR (KBr): 3550, 3472, 3413, 3238, 3054, 2929, 2859, 1714, 1616, 1584, 1492, 1425, 1349, 1123, 956,757, 622, 567, 488, 433. ESI-MS (m /z): $[M]^+$calcd for $C_{62}H_{48}CoN_2O_2$ 911.30, found 911.80.

The synthesis of (*R,R,S,S*)-5a-Co-OCSA:

Deoxygenated toluene (ca. 11.6 mL) was added to salen ligand (0.9405 mg, 1.1 mmol) under N_2, and deoxygenated MeOH (ca. 11.6 mL) to $Co(OAc)_2 \cdot 4H_2O$ (545 mg, 2.2 mmol) under N_2. N_2 was bubbled through the resulting solutions for 20 min to ensure complete deoxygenation. The solution of $Co(OAc)_2 \cdot 4H_2O$ in MeOH (purple) was added via cannula under N_2 to the solution in toluene (yellow) to give a deep red solution. The resulting mixture was stirred for 30 min under an N_2 purge. CSA acid (256 mg, 1.1 mmol) and CH_2Cl_2 (16.6 mL) were added, and the resulting black solution stirred for an additional 2 h under an air atmosphere with vigorous stirring. Solvent was removed under reduced pressure, and the residue dissolved in minimal CH_2Cl_2. Excess insoluble $Co(OAc)_2 \cdot 4H_2O$ was removed via filtration through a Celite®pad, washing with CH_2Cl_2 (200 mL). Removal of solvent under reduced pressure provided salen-**5a**-Co(III)-OCAS as a paramagnetic black solid (856 mg, 82% yield). IR (KBr): 3551, 3475, 3414, 3238, 3055, 2933, 2860, 1732, 1616, 1584, 1492, 1451, 1425, 1326, 1149, 1039, 780, 757, 717, 617, 488, 432. ESI-MS (m /z): $[M]^+$calcd for $C_{62}H_{48}CoN_2O_2$ 911.30, found 911.80.

4. General procedure for the asymmetric Henry reactions [3]



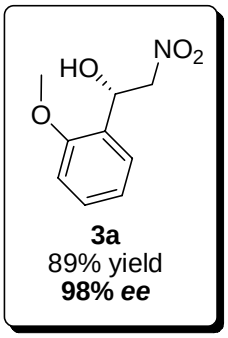
4.1 General procedure for the asymmetric salan-Cu(II)-catalyzed Henry reaction (Cu catalysis)

All reactions were performed on a 1 mmol scale with 10 mol% of Cu salt and 10 mol % of salan ligand (**1**) at a 0.5 M concentration using 10 equiv of nitromethane in EtOH. Reactions were run at 10 ^{o}C in a screw-capped vial for 48 h.

A representative procedure: salan ligand **1** (42.9 mg, 0.05 mmol) and and $Cu(OAc)_2 \cdot H_2O$ (10.0 mg, 0.05 mmol) were added to ethanol at ambient temperature. Stirring continued for ten minute and then nitromethane (0.27 mL, 10 mmol) and aromatic aldehyde (0.5 mmol) were added to the solution. After stirring for 48 hours, the mixture was then extracted with DCM and the organic extracts were combined, washed with brine, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was purified by column chromatography. All the products are known and confirmed by GC-MS, NMR, and HPLC.

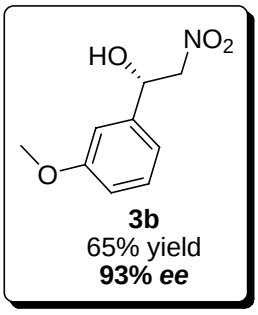
4.2 General procedure for the asymmetric salan-Co(III)-catalyzed Henry reaction (Co catalysis)

General procedure: To a screw cap vial containing a stir bar, cobalt complex (26.5 mg, 0.025 mmol, 5% mmol) was added. And then 2 mL toluene, 2-fluorobenzaldehyde (53 μL, 0.5 mmol), and DIPEA (83 μL, 0.5 mmol) was added to the vial. The reaction mixture was cooled down to -20 ºC, and then CH_3NO_2 (0.27 mL, 5 mmol) was added. The mixture was continued to stir at -20 ºC for 12 h. The reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 10/1) to give the nitroaldol adduct as a colorless oil.



3a
89% yield
98% *ee*

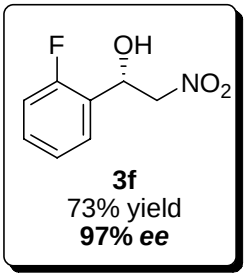
(*S*)-1-(2-Methoxyphenyl)-2-nitroethanol (**3a**) was obtained according to the general procedure (89% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 85:15 V/V, 0.8 mL/min, 215 nm); minor enantiomer t_r = 9.06min, major enantiomer t_r = 9.75 min; 98%*ee*. $[\alpha]^{14}_D$ = + 26.50^o (c 0.8, $CHCl_3$) ; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 (d, J = 7.0 Hz ,1 H), 7.32-7.35 (m, 1 H), 7.03 (t, J = 7.5 Hz, 1 H), 6.91 (d, J = 8.5 Hz, 1 H), 5.59-5.62 (m, 1 H), 4.61-4.64 (m, 1 H), 4.53-4.57 (m,1H), 3.87 (s, 3 H), 3.38 (d, J = 6.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 156.0, 129.8, 127.2, 126.0, 121.1, 110.5, 80.0, 67.9, 55.5; IR (KBr): 3549, 3414, 3239, 2940, 2068, 1618, 1553, 1491, 1382, 1287, 1243, 1121, 1075, 1025, 789, 758, 617, 487 cm^{-1};



3b
65% yield
93% *ee*

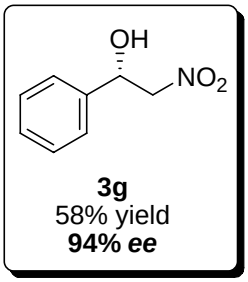
(*S*)-1-(3-Methoxyphenyl)-2-nitroethanol (**3b**) was obtained according to the general procedure (64% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 90:10 V/V, 0.8 mL/min, 215 nm); minor enantiomer t_r= 26.45 min, major enantiomer t_r = 35.29 min; 93% *ee*; $[\alpha]^{14}_D$ = + 9.82^o (c = 0. 47, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.30 (t, J = 8.0 Hz, 1 H), 6.94 (d, J = 6.5Hz, 2 H), 6.88 (dd, J = 2.5Hz, 8.5Hz, 1 H), 5.41 (dd, J = 2.5 Hz, 9.5 Hz, 1 H), 4.56-4.60 (m, 1 H), 4.49 (dd, J = 3.0 Hz, 13.0 Hz, 1 H), 3.81 (s, 3 H), 3.05 (s, 1H); ^{13}C NMR (125MHz, $CDCl_3$) δ: 160.1, 139.9, 130.1, 118.1, 114.4, 111.6, 81.3, 70.9,

55.3; IR (KBr): 3551, 2918, 2069,1617, 1552, 1488, 1382, 1324, 1125, 1075, 904, 844, 768, 730, 635, 493 cm^{-1};



3f
73% yield
97% *ee*

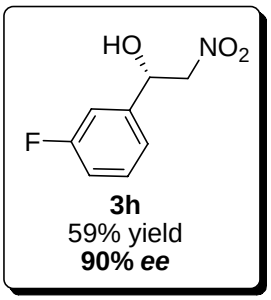
(*S*)-1-(2-Fluorophenyl)-2-nitroethanol (**3f**) was obtained according to the general procedure (92% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 95:5 V/V, 1mL/min, 215 nm); minor enantiomer t_r = 15.125 min, major enantiomer t_r = 15.711 min; 97% *ee*. $[\alpha]^{14}_D$ = +41.15^o (c = 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.55 (d, J = 7.5 Hz, 1 H), 7.39 (m, 1 H), 7.22 (d, J = 7.5 Hz, 1 H), 7.12 (m,1 H), 5.79 (dt, J = 8.5, 4.5 Hz, 1 H), 4.56-4.64 (m, 2 H), 3.39 (d, J = 1.1 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.33 (d, J_{CF} = 244.8 Hz), 130.50 (d, J_{CF} = 8.3 Hz), 127.62 (d, J_{CF} = 3.5Hz), 125.16 (d, J_{CF} =13.4 Hz), 124.89 (d, J_{CF} = 2.2 Hz), 115.62 (d, J_{CF} = 20.9 Hz), 79.70 (d, J_{CF} = 1.3 Hz), 65.44 (d, J_{CF} = 2.8 Hz); ^{19} F NMR (470 MHz, $CDCl_3$) δ: -118.352; IR(KBr): 3422, 2923, 1617, 1588, 1557, 1489, 1457, 1380, 1074, 1033, 897, 809, 762, 739,615 cm^{-1} ;



3g
58% yield
94% *ee*

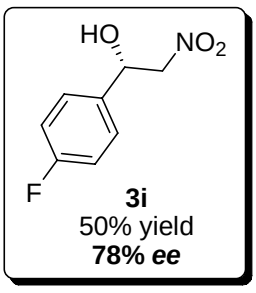
(*S*)-1-Phenyl-2-nitroethanol (**3g**) was obtained according to the general procedure as colorless oil (56% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 85:15 V/V, 0.8 mL/min, 215 nm); minor enantiomer t_r = 13.06 min, major enantiomer t_r = 15.85 min; 94% ee. $[\alpha]^{14}_D$ = +14.07 ^{o}(c = 0.8, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.43 - 7.35 (m, 5H), 5.45 (d, J = 10.0 Hz, 1 H), 4.62-4.57 (m, 1 H), 4.52-4.49 (m, 1 H) , 3.00 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.1, 129.1, 129.0, 126.0, 81.2, 71.0. IR (KBr): 3418, 3032,

2921, 1555, 1495, 1454, 1381, 1128, 1067, 897, 765, 700, 611, 524 cm^{-1};



3h
59% yield
90% *ee*

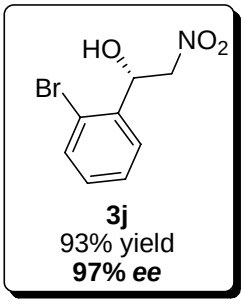
(*S*)-1-(3-Fluorophenyl)-2-nitroethanol (**3h**) was obtained according to the general procedure (59% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 85:15 V/V, 0.8 mL/min, 215 nm); minor enantiomer t_r = 11.19 min, major enantiomer t_r = 13.14 min; 90% *ee*. $[\alpha]^{14}_D$ = 17.1^o (c = 0.8, $CHCl_3$) ; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36-7.40 (m, 1H), 7.14-7.18 (m, 2H), 7.07 (td, J = 8.5 Hz, 1H), 5.46 (d, J = 9.5 Hz, 1H), 4.510- 4.60 (m, 2H), 3.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.02 (d, J_{CF} = 196.6 Hz), 140.63 (d, J_{CF} = 5.3 Hz), 130.73 (d, J_{CF} = 6.5 Hz), 121.57 (d, J_{CF} = 2.3 Hz), 115.90 (d, J_{CF}= 16.7 Hz), 113.12(d, J_{CF} = 18 Hz), 80.99, 70.31 (d, J_{CF} = 1Hz). ^{19}F-NMR (470 MHz, $CDCl_3$) δ: -111.440; IR (KBr): 3419, 2923, 1617, 1594, 1556, 1489, 1457, 1380, 1263, 1138, 1068, 893, 790, 710, 692 cm^{-1};



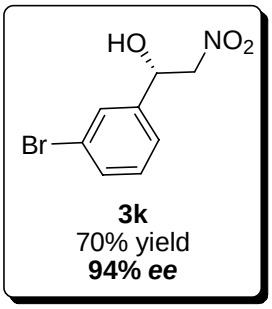
3i
50% yield
78% *ee*

(*S*)-1-(4-Fluorophenyl)-2-nitroethanol (**3i**) was obtained according to the general procedure (50% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 85:15 V/V, 0.8 mL/min, 215 nm); minor enantiomer t_r = 10.57 min, major enantiomer t_r = 12.40min; 78% *ee*. $[\alpha]^{17}_D$ = + 7.4^o (c 0.33, $CHCl_3$); ^{1}H NMR (500 MHz, CDCl3) δ: 7.37-7.39 (m, 2 H), 7.07-7.10 (m, 2 H), 5.44 (d, J = 8.5 Hz, 1 H), 4.55-4.60 (m, 2 H), 4.49 (dd, J = 3.0 Hz, 13.0 Hz, 1 H), 3.04 (s, 1 H) ;^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.9 (d, J_{CF} = 246.5 Hz), 134.0,

127.8 (d, J_{CF} = 8.1 Hz), 116.0 (d, J_{CF} = 21.6 Hz), 81.2, 70.3;[19] FNMR (470 MHz, $CDCl_3$): -112.5; IR (KBr): 3420, 2922, 1902,1688, 1606, 1555, 1511, 1419, 1379, 1225, 1160, 1078, 897, 839, 728, 565, 531 cm^{-1};

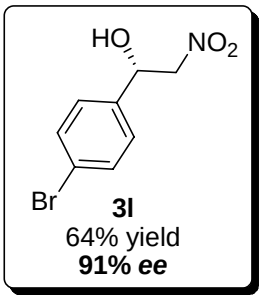


(*S*)-1-(2-Bromophenyl)-2-nitroethanol (**3j**) was obtained according to the general procedure (93% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 95:5 V/V, 1.0 mL/min, 215 nm); minor enantiomer t_r = 20.87 min, major enantiomer t_r = 22.49 min; 97% *ee*. $[\alpha]^{14}_D$ = +37.16° (c 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.63 (d, J = 7.5 Hz, 1 H), 7.54 (d, J = 8.0 Hz, 1 H), 7.38-7.23 (m, 1 H), 5.77 (d, J = 9.5 Hz, 1 H), 4.64-4.67 (dd, J = 2.0 Hz, 13.5 Hz ,1 H) , 4.38-4.43 (m, 1 H), 3.36 (s, 1 H); ^{13}C NMR (125MHz, $CDCl_3$) δ: 137.12, 133.0, 130.3, 128.3, 127.8, 121.5, 79.4, 70.1; IR (KBr): 3473, 2921, 1636, 1555, 1468, 1438, 1416, 1377, 1286, 1201, 1125, 1084, 1023, 899, 759, 732, 663, 610 ,445 cm^{-1};

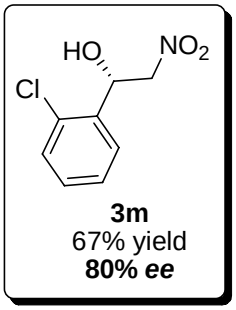


(*S*)-1-(3-Bromophenyl)-2-nitroethanol (**3k**) was obtained according to the general procedure (70% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 90:10 V/V, 0.8 mL/min, 215 nm); minor enantiomer t_r = 21.73 min, major enantiomer t_r = 28.05 min; 94% *ee* ; ^{1}H NMR (500 MHz, $CDCl_3$) 7.57 (s, 1 H), 7.49 (d, J = 7.5 Hz, 1H), 7.28-7.33 (m, 2H), 5.41 - 5.44 (m, 1H), 4.48-4.58 (m, 2H), 3.27 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 140.3,

132.1, 130.7, 129.1, 124.6, 123.1, 81.0, 70.2; IR (KBr): 3412, 2921, 1594, 1557, 1475, 1400, 1384, 1130, 1072, 898, 787, 694, 616 cm^{-1};

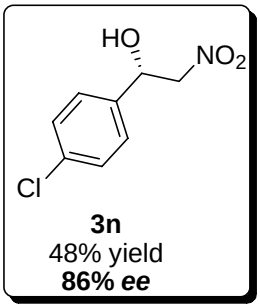


(*S*)--1-(4-Bromophenyl)-2-nitroethanol (**3l**) was obtained according to the general procedure (64% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 85:15 V/V, 0.8 mL/min, 215 nm); minor enantiomer t_r = 14.57 min, major enantiomer t_r = 19.00 min, 91% *ee*; $[\alpha]^{25}_D$ = + 19.80^o (c = 0.56, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.50 (d, J = 8.5 Hz, 2 H), 7.24 (d, J = 8.5 Hz, 2 H), 5.37 (dd, J = 3.0 Hz, 9.5 Hz, 1 H), 4.51-4.56 (m, 1H), 4.45 (dd, J = 3.5 Hz, 13.5 Hz, 1 H), 3.17 (s, 1 H); ^{13}C NMR (125 MHz,$CDCl_3$) δ: 137.3, 132.1, 127.7, 122.9, 81.0, 70.3; IR (KBr): 3414, 2068, 1638, 1618, 1558, 1489, 1385, 1129, 1073, 1011, 741, 618, 482 cm^{-1};



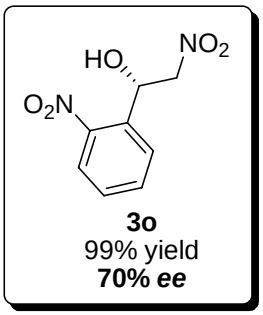
(*S*)-1-(2-Chlorophenyl)-2-nitroethanol (**3m**) was obtained according to the general procedure (67% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 85:15 V/V, 0.8 mL/min, 215 nm); minor enantiomer t_r = 11.98 min, major enantiomer t_r = 12.40min; 80%*ee*. $[\alpha]^{25}_D$ = +21.25^o (c 0.48, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.65 (dd, J = 1.0 Hz, 7.5 Hz, 1H), 7.28-7.38 (m, 3H) , 6.83 (d, J = 9.5 Hz, 1H), 4.66 (dd, J = 3.0 Hz, 13.5 Hz, 1 H), 4.45 (dd, J = 9.5 Hz, 13.5 Hz,1 H) , 4.49 (dd, J = 3.0 Hz, 13.5Hz, 1H), 3.25 (s, 1H) . ^{13}C NMR (125MHz, $CDCl_3$) δ: 136.7, 131.5, 129.9, 129.7, 127.6, 127.5, 79.4, 67.9;

IR (KBr): 3548, 3417, 2923, 1617, 1556, 1473, 1441, 1417, 1379, 1223, 1086, 1034, 898, 760, 739, 613, 467 cm^{-1};



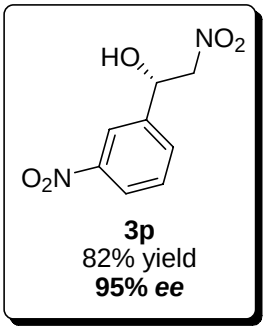
3n
48% yield
86% *ee*

(*S*)-1-(4-Chlorophenyl)-2-nitroethanol (**3n**) was obtained according to the general procedure (48% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 90:10 V/V, 0.8 mL/min, 215 nm); minor enantiomer t_r =18.17 min, major enantiomer t_r = 23.45 min; 86% *ee*.$[\alpha]^{14}_{D}$ = +18.48 °(c = 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.65 (dd, J = 1.0 Hz, 7.5 Hz, 1H), 7.28-7.38 (m, 3H) , 6.83 (d, J = 9.5 Hz, 1H) ,4.66 (dd, J = 3.0 Hz, 13.5 Hz, 1 H), 4.45 (dd, J = 9.5 Hz, 13.5 Hz, 1 H) , 4.49 (dd, J = 3.0 Hz, 13.5 Hz, 1 H), 3.25 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 136.7, 134.8, 129.2, 127.4, 81.0, 70.3.



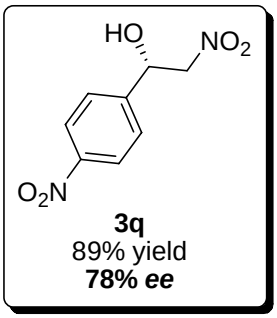
3o
99% yield
70% *ee*

(*S*)-(-)-2-Nitro-1-(2-nitrophenyl)ethanol (**3o**) was obtained according to the general procedure (99% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 90:10 V/V, 0.9 mL/min, 215 nm); minor enantiomer t_r = 16.95 min, major enantiomer t_r = 18.72 min, 70% *ee*. $[\alpha]^{25}_{D+}$ = 116.40° (c = 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.06 (dd, J = 1.0 Hz, 8.5 Hz, 1H), 7.73-7.76 (m, 1H), 7.53-7.56 (m, 1 H), 6.03 (d, J = 9.0 Hz), 4.85 (dd, J = 2.5 Hz, 14.0 Hz, 1H), 4.53-4.58 (m, 1H), 3.35 (d, J = 4.0 Hz); ^{13}C NMR (125 MHz, $(CD_3)_2CO$,δ): 147.2, 134.3, 134.1, 129.7, 128.7, 125.0, 80.1, 66.8; IR (KBr): 3550, 3415, 3238, 3081, 1639, 1557, 1518, 1382, 1348, 1082, 859, 838, 754, 618, 485 cm^{-1};



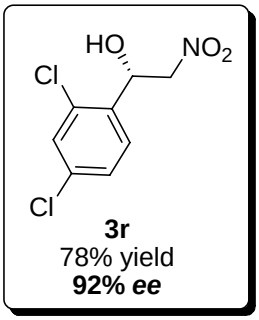
3p
82% yield
95% *ee*

(*S*)-(−)-2-Nitro-1-(3-nitrophenyl)ethanol (**3p**) was obtained according to the general procedure (82% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 85:15 V/V, 1mL/min, 215 nm); minor enantiomer t_r =16.07 min, major enantiomer t_r = 18.23 min; 95% *ee*; $[\alpha]^{17}_D$ = +53.2º (c = 0.6, $CHCl_3$), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 8.41 (s, 1 H), 8.19 (dd, J = 2.0 Hz, 8.5 Hz, 1 H), 7.97 (d, J = 7.5 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1 H), 5.68-5.71 (m, 1H), 5.57 (d, J = 4.5 Hz, 1 H), 4.92 (dd, J =3.5 Hz, 13 Hz, 1H), 4.72-4.76 (m, 1H); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ: 148.5, 142.7, 132.6, 129.9, 122.9, 121.1, 81.15, 69.6; IR (KBr): 3491, 3097, 2091, 1552, 1525, 1350, 1095, 1070, 919, 808, 735, 684 cm^{-1};



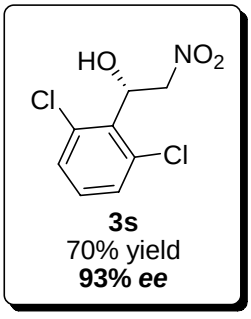
3q
89% yield
78% *ee*

(S)-2-Nitro-1-(4-nitrophenyl)ethanol (**3q**) was obtained according to the general procedure (89% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 90:10 V/V, 0.8 mL/min, 215 nm); minor enantiomer t_r = 21.4 min, major enantiomer t_r = 22.8 min, 78% *ee*; $[\alpha]^{14}_D$ = +21.28^o (c 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 8.22 (d, J = 9.0 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 5.62-5.65 (m, 1H), 4.53 (d, J = 4.0 Hz, 1H), 4.87 (dd, J = 3.5 Hz, 13.0 Hz, 1H), 4.65-4.69 (m, 1H); ^{13}C NMR (125MHz, $(CD_3)_2CO$) δ: 147.9, 147.6, 127.5, 123.5, 81.1, 69.8, 69.7.



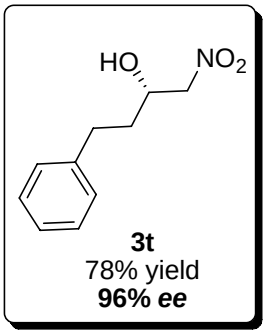
3r
78% yield
92% *ee*

(*S*)-1-(2,4-Dichlorophenyl)-2-nitroethanol (3r) was obtained according to the general procedure (89% yield). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane-isopropanol 90:10 V/V, 0.8 mL/min, 215 nm); minor enantiomer t_r = 16.57 min, major enantiomer t_r = 19.95 min; 92%*ee*. $[\alpha]^{17}_D$ = + 15.75^o (c = 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 7.71 (d, J = 8.5 Hz, 1H), 7.45 (d, J = 2.0 Hz, 1 H), 7.42 (dd, J = 2.0 Hz, 7.0 Hz, 1H), 5.77-5.80 (m, 1 H), 5.45-(d. J = 5.0 Hz, 1 H), 4.78 (dd, J = 3,0.0 Hz, 13.0 Hz, 1 H), 4.49-4.53 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 136.6, 134.2, 132.1, 129.5, 128.9, 127.8, 79.8, 67.3. IR (KBr): 3551, 3414, 2924, 1638, 1617, 1470, 1384, 1139, 1069, 858, 832 cm^{-1}.

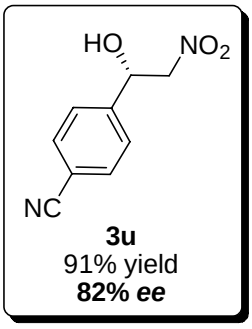


3s
70% yield
93% *ee*

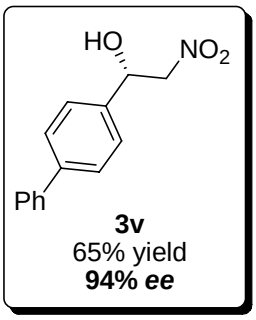
(*S*)-1-(2,6-Dichlorophenyl)-2-nitroethanol (**3s**) was obtained according to the general procedure (89% yield). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane-isopropanol 90:10 V/V, 0.8 mL/min, 215 nm); minor enantiomer t_r = 21.36 min, major enantiomer t_r = 22.59 min; 93%*ee*; $[\alpha]^{18}_D$ = -28.44^o (c = 0.8, $CHCl_3$) ; ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 7.47 (d, J = 7.0 Hz, 2H), 7.38 (dd, J = 7.5 Hz, 9.0 Hz, 1H), 6.37 (dd, J = 3.5 Hz, 10.0 Hz, 1H), 5.30 (dd, J = 10.0 Hz, 14.0 Hz, 1H), 4.78-4.81 (m, 1H), 2.14-2.19 (m, 1H); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ: 140.2, 135.65, 135.59, 135.53, 134.8, 82.9, 73.0; IR (KBr): 3538, 2920, 1617, 1550, 1437, 1380, 1098, 893, 772, 736, 634 cm^{-1};



(*S*)-1-Nitro-4-phenylbutan-2-ol (**3t**) was obtained according to the general procedure (78% yield). Enantiomeric excess was determined by HPLC with a Chiralcel IB column (*n*-hexane-isopropanol 92:8 V/V, 0.8 mL/min, 215 nm); minor enantiomer t_r =36.83 min, major enantiomer t_r = 34.8 min; 96% *ee*; $[\alpha]^{14}_D$ = -10.18 ^{o}(c = 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 7.24-7.31 (m, 4 H), 7.17-7.20 (m, 1 H), 4.63-4.65(d, J=6Hz, 1H), 4.57-4.60 (dd, J = 3.5 Hz, 12.5 Hz, 1 H), 4.31-4.47 (dd, J = 2.5,12.5Hz, 1 H), 4.25-4.28 (m, 1H), 2.83-2.89 (m, 1 H), 2.72-2.78 (m, 1 H), 1.80-1.91 (m, 2H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ: 141.7, 128.4, 128.3, 125.9, 81.3, 66.0, 35.9, 31.2. IR (KBr): 3551, 3473 , 2948, 2068, 1638, 1617, 1558, 1385, 1103, 881, 804 cm^{-1}.

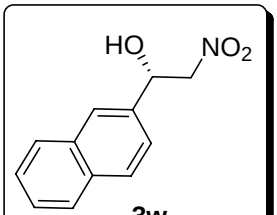


(S)-1-(4-Cyanophenyl)-2-nitroethanol (**3u**) was obtained according to the general procedure (82% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 90:10 V/V, 1mL/min, 215 nm); minor enantiomer t_r = 28.70 min, major enantiomer t_r = 33.73min, 83%*ee*. $[\alpha]^{20}_D$ = 23.7; ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 7.82-7.89 (m, 4H), 5.68-5.72 (m, 1H), 5.55 (d, J = 4.5 Hz, 1H), 4.93-4.96 (dd, J = 3.0 Hz, 13.0 Hz, 1 H), 4.75-4.79 (m, 1H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ: 145.6, 132.4, 127.2, 118.3, 111.8, 81.1, 70.0; IR (KBr): 3415, 2963, 2238, 1638, 1617, 1558, 1382, 1083, 904, 861 cm^{-1};



3v
65% yield
94% *ee*

(*S*)-1-(Biphenyl-4-yl)-2-nitroethanol (**3v**) was obtained according to the general procedure (50% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 90:10 V/V, 0.8 mL/min, 215 nm); minor enantiomer t_r = 30.94 min, major enantiomer t_r = 37.54 min; 94% *ee*. $[\alpha]^{25}_D$ = -13.48 (c = 0.56, $CHCl_3$). ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 7.67 (t, J = 8 Hz, 4 H), 7.560 (d, J = 8.0 Hz, 2 H), 7.47 (t, J = 7.5 Hz, 2 H), 7.38 (t, J = 7.5 Hz, 1H), 5.55-5.59 (m, 1H), 5.23 (d, J = 4.0 Hz, 1H), 4.81 (dd, J = 3.5 Hz, 12.5Hz, 1 H) , 4.67-4.72 (m, 1H); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ: 140.9, 140.5, 139.4 , 128.9 , 127.5 , 127.4, 127.0, 126.9 ,126.8, 81.7, 70.5; IR (KBr): 3550, 3475, 3238, 1637, 1617, 1546, 1384, 1123, 1075, 902, 841 $cm^{-1.}$



3w
65% yield
94% *ee*

(*S*)-1-(naphthalen-2-yl)-2-nitroethanol (**3w**) was obtained according to the general procedure (65% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane-isopropanol 50:50 V/V, 0.6 mL/min, 215 nm); minor enantiomer t_r = 16.13 min, major enantiomer t_r = 22.33 min; 94%*ee*. $[\alpha]^{20}_D$ = +55.19º (c = 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83-7.88 (m, 4 H), 7.53-7.54 (m, 2 H), 7.45 (d, J = 8.5 Hz, 1H), 5.59 (d, J = 10.0 Hz, 1H), 4.55-4.69 (m, 2 H), 2.81 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 135.6, 133.4, 133.2, 129.0, 128.1, 127.8, 126.7, 126.6, 125.3, 123.3, 81.2, 71.2; IR (KBr): 3478, 3415, 2938, 1618, 1551, 1412, 1165, 109, 903, 868, 829 cm^{-1}.

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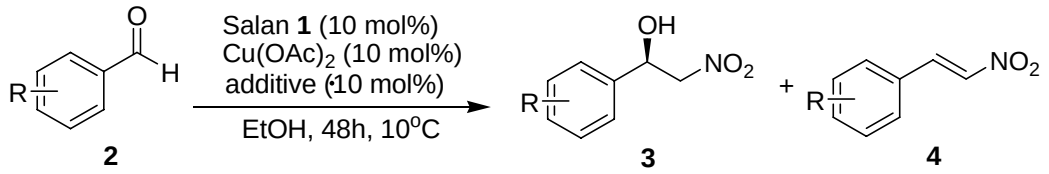
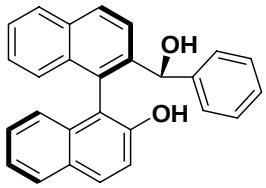
[2] a) X. Zheng, C. W. Jones, M. Weck, *Adv. Synth. Catal.* **2008**, *350*, 255-261; b) P. Yan, H. W. Jing, *Adv. Synth. Catal.* **2009**, *351*, 1325-1332; c) A. Sadhukhan, N. H. Khan, T. Roy, R. I. Kureshy, S. H. R. Abdi, H. C. Bajaj, *Chem. Eur. J.* **2012**, *18*, 5256-5260; d) J. M. Ready, E. N. Jacobsen, *J. Am. Chem. Soc.* **2001**, *123*, 2687-2688.

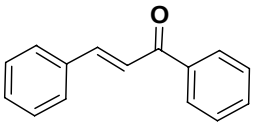
[3] For selected examples, see: a) T. Ooi, K. Doda, K. Maruoka, *J. Am. Chem. Soc.* **2003**, *125*, 2054-2055; b) B. M. Choudary, K. V. S. Ranganath, U. Pal, M. L. Kantam, B. Sreedhar, *J. Am. Chem. Soc.* **2005**, *127*, 13167-13171; c) T. Arai, M. Watanabe, A. Fujiwara, N. Yokoyama, A. Yanagisawa, *Angew. Chem. Int. Ed.* **2006**, *45*, 5978-5981; d) M. Bandini, F. Piccinelli, S. Tommasi, A. Umani-Ronchi, C. Ventrici, *Chem. Commun.* **2007**, 616-618; e) Y. Xiong, F. Wang, X. Huang, Y. Wen, X. Feng, *Chem. Eur. J.* **2007**, *13*, 829-833; f) N. Sanjeevakumar, M. Periasamy, *Tetrahedron: Asymmetry* **2009**, *20*, 1824-1847; g) W. Jin, X. Li, Y. Huang, F. Wu, B. Wan, *Chem. Eur. J.* **2010**, *16*, 8259-8261; h) K. Kodama, K. Sugawara, T. Hirose, *Chem. Eur. J.* **2011**, *17,* 13584-13592; i) B. V. S. Reddy, J. George, *Tetrahedron: Asymmetry* **2011**, *22*, 1169-1175; j) G. Lai, F. Guo, Y. Zheng, Y. Fang, H. Song, K. Xu, S. Wang, Z. Zha, Z. Wang, *Chem. Eur. J.* **2011**, *17*, 1114-1117; k) S. Milner, T. S. Thomas, A. R. Maguire, *Eur. J. Org. Chem.* **2012**, 3059-3067; l) K. Xu, G. Y. lai, Z. G. Zha, S. S. Pan, H. W. Chen, Z. Y. Wang, *Chem. Eur. J.* **2012**, *18*, 12357-12362; m) R. Boobalan, G. H. Lee, C. P. Chen, *Adv. Synth. Catal.* **2012**, *354*, 2511-2520; n) D. D. Qin, W. H. Lai, D. Hu, Z. Chen, A. A. Wu, Y. P. Ruan, Z. H. Zhou, H. B. Chen, *Chem. Eur. J.* **2012**, *18*, 10515-10518; o) T. Nitabaru, N. Kumagai, M. Shibasaki, *Angew. Chem. Int. Ed.* **2012**, *51*, 1644-1647; p) H. Li, X. Zhang, X. Shi, N. Ji, W. He, S. Y. Zhang, B. L. Zhang, *Adv. Synth. Catal.* **2012**, *354*, 2264-2274; q) D. D. Qin, W. Yu, J. D. Zhou, Y. C. Zhang, Y. P. Ruan, Z. H. Zhou, H. B. *Chem. Eur. J.* **2013**, *19*, 16541-116544; r) S. Kitagaki, T. Ueda, C. Mukai, *Chem. Commun.* **2013**, *49*, 4030-4032; s) H. X. He, W. Yang, D. M. Du, *Adv. Synth. Catal.* **2013**, *355*, 1137-1148.

Table S1. The effect of aromatic compound on the catalytic Henry reaction of substituted aromatic aldehydes

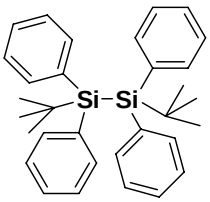




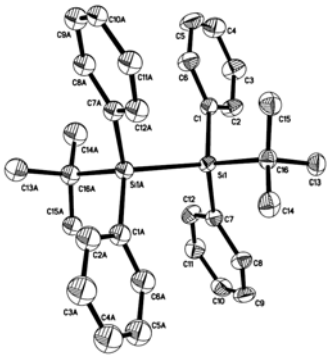
(*R, S*)-BINMOL

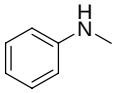
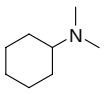
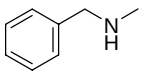


chalcone



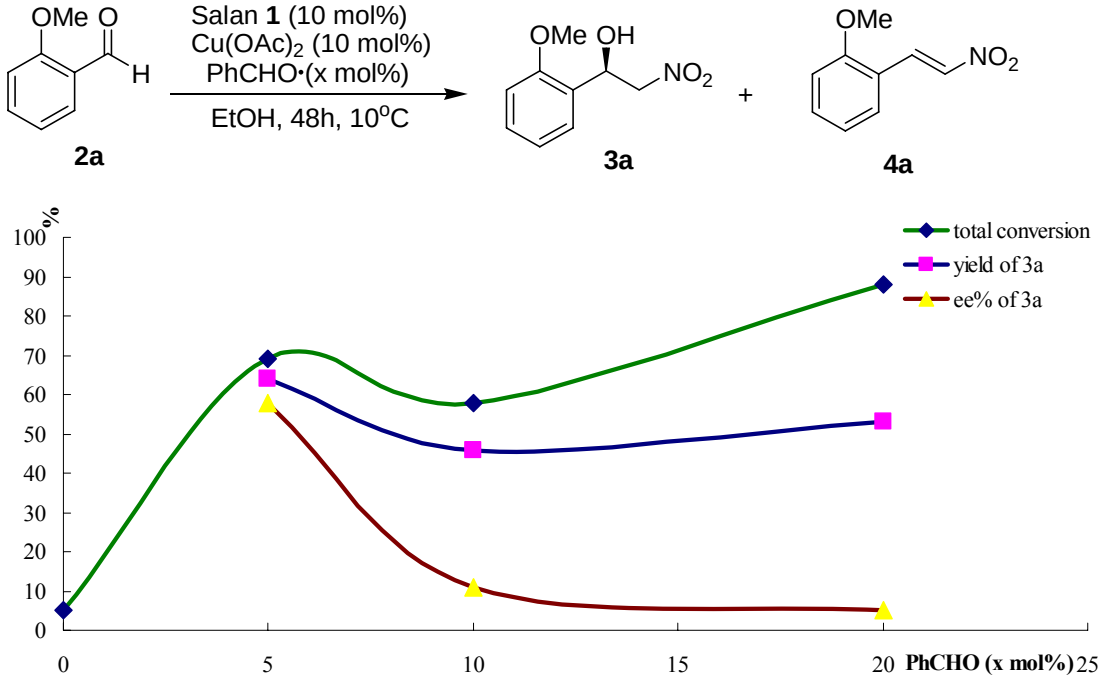
TBDPS-TBDPS



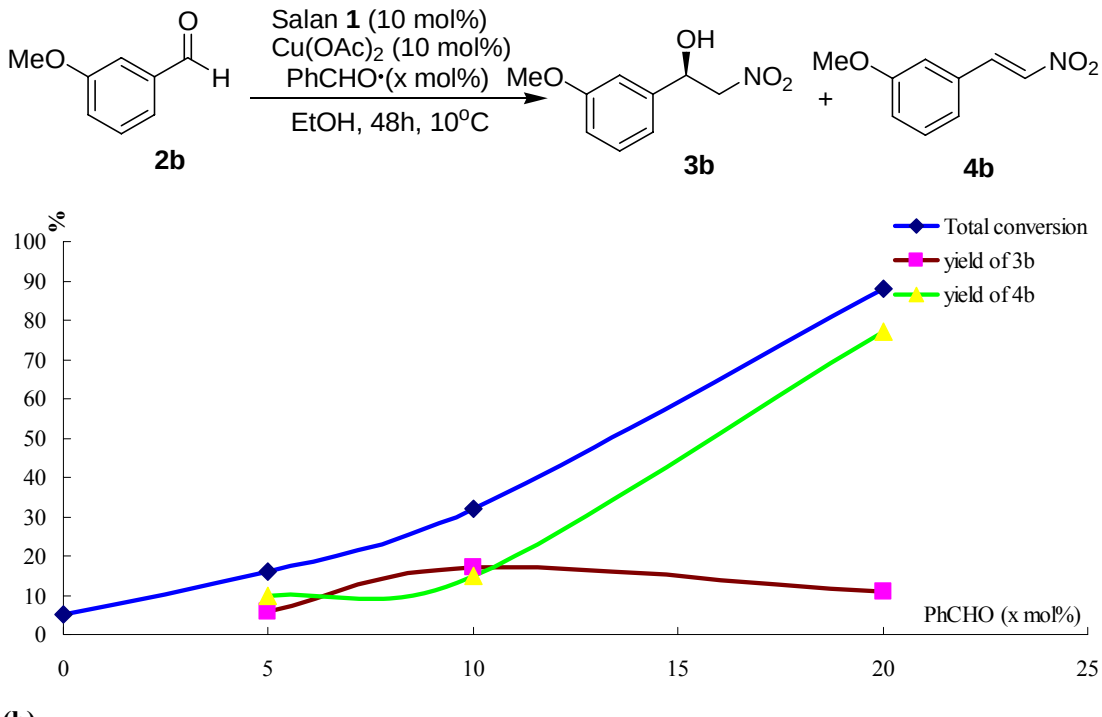
Entry	*Time (d)*	*Additive*	*Conversion (%)*	***3/4***	ee/%
1	2	PhCl	83 (√)	83:0	20
2	2	PhBr	48 (+)	0:48	---
3	2	PhI	53 (+)	28:25	0
4	2	chalcone	88 (√)	14:74	---
5	2	Ph-CH=CH-NO_2	75 (√)	19:56	---
6	5	TBDPS-TBDPS	75 (√)	75:0	30
7	2	TBDPS-TBDPS	25 (-)	25:0	40
8	5	$PhMeSiH_2$	73 (√)	73:0	40
9	5	1-ethynylbenzene	77 (√)	77:0	34
10	2	(*R*)-BINMOL	53 (+)	14:39	-
11	2	PhOH	70 (√)	22:48	5
12	2		46 (+)	46:0	16
13	2		20 (-)	20:0	44
14	2		46 (+)	46:0	32
15	2	PhCOOH	<10 (-)	5:0	---

[a]All reactions were carried out at -10 °C in a screw-capped vial for 48 h. [b] The conversion was determined by GC-MS, and the catalytic level was divied as Good (>70% yield, √), Moderate (40-70% yield, +), Poor (< 40% yield, -). [c] Enantiomeric excess was determined by HPLC using chiral columns.

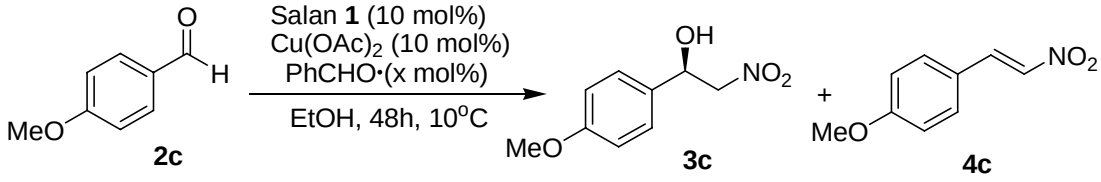
Figure S1. Benzaldehyde-assisted catalytic Henry reaction of substituted aromatic aldehydes **(a-e)** in accordance with Table 1 (Text)

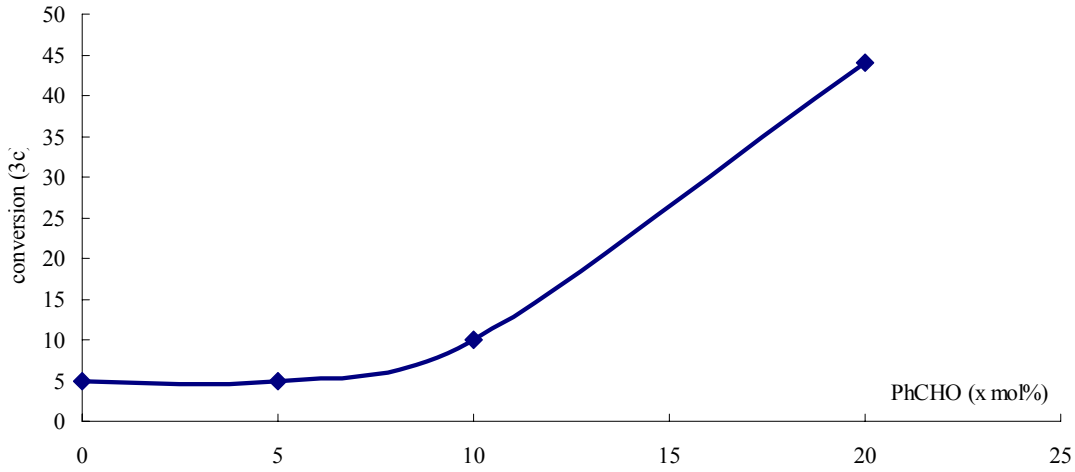


(a)

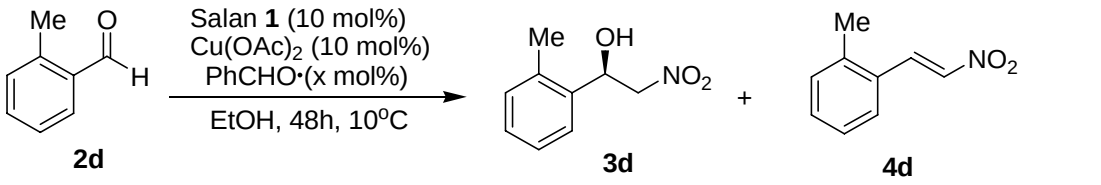


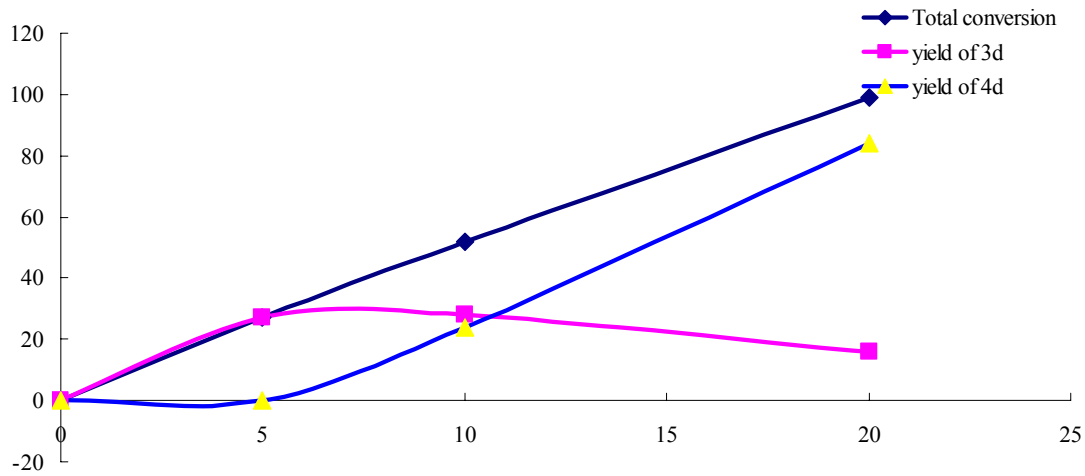
(b)


Salan 1 (10 mol%)
Cu(OAc)2 (10 mol%)
PhCHO·(x mol%)
EtOH, 48h, 10°C
MeO
O
H
OH
NO2
2c
3c
4c

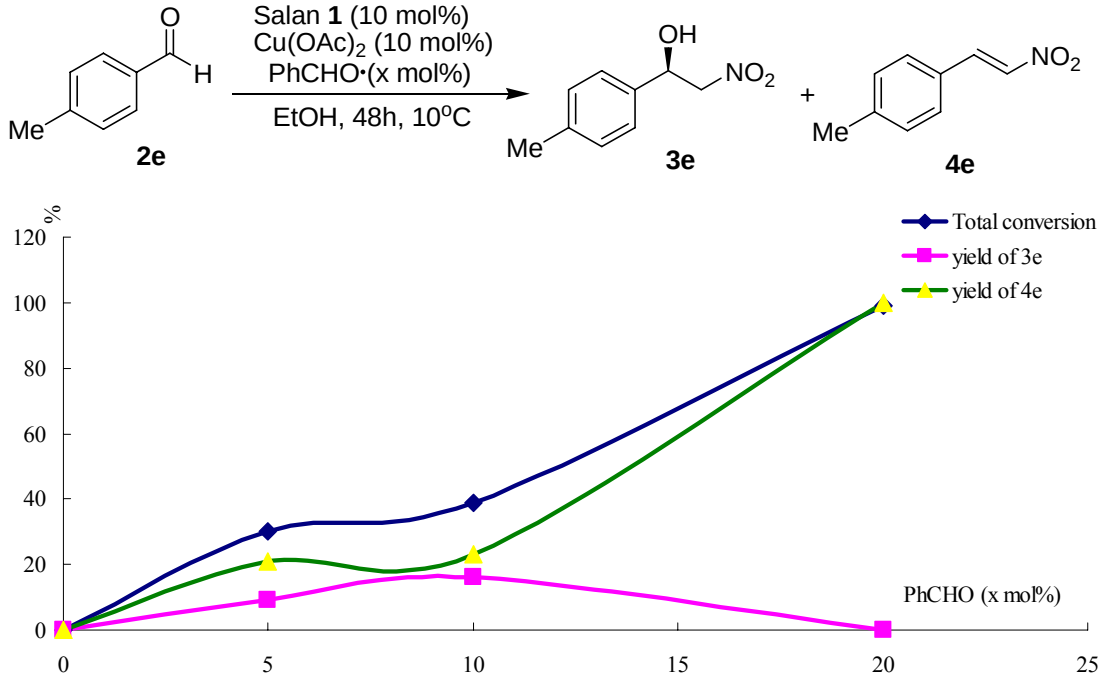

conversion (3c)
PhCHO (x mol%)
0
5
10
15
20
25
30
35
40
45
50

(c)


Salan 1 (10 mol%)
Cu(OAc)2 (10 mol%)
PhCHO·(x mol%)
EtOH, 48h, 10°C
Me
O
H
OH
NO2
2d
3d
4d


Total conversion
yield of 3d
yield of 4d
-20
0
20
40
60
80
100
120
0
5
10
15
20
25

(d)



(e)

Figure S2. The comparison of enantioselectivities and yields in the salen-Co (**1a**) catalyzed Henry reaction of F- or Br-substituted aromatic aldehydes.

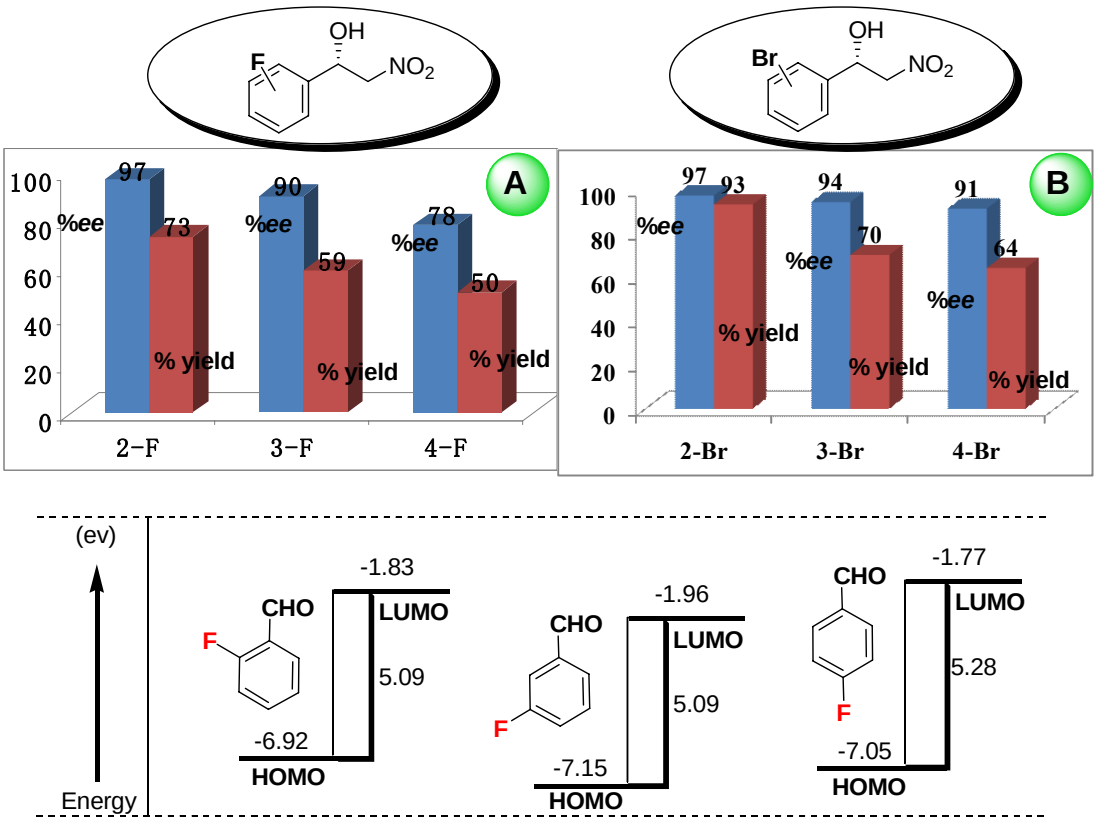
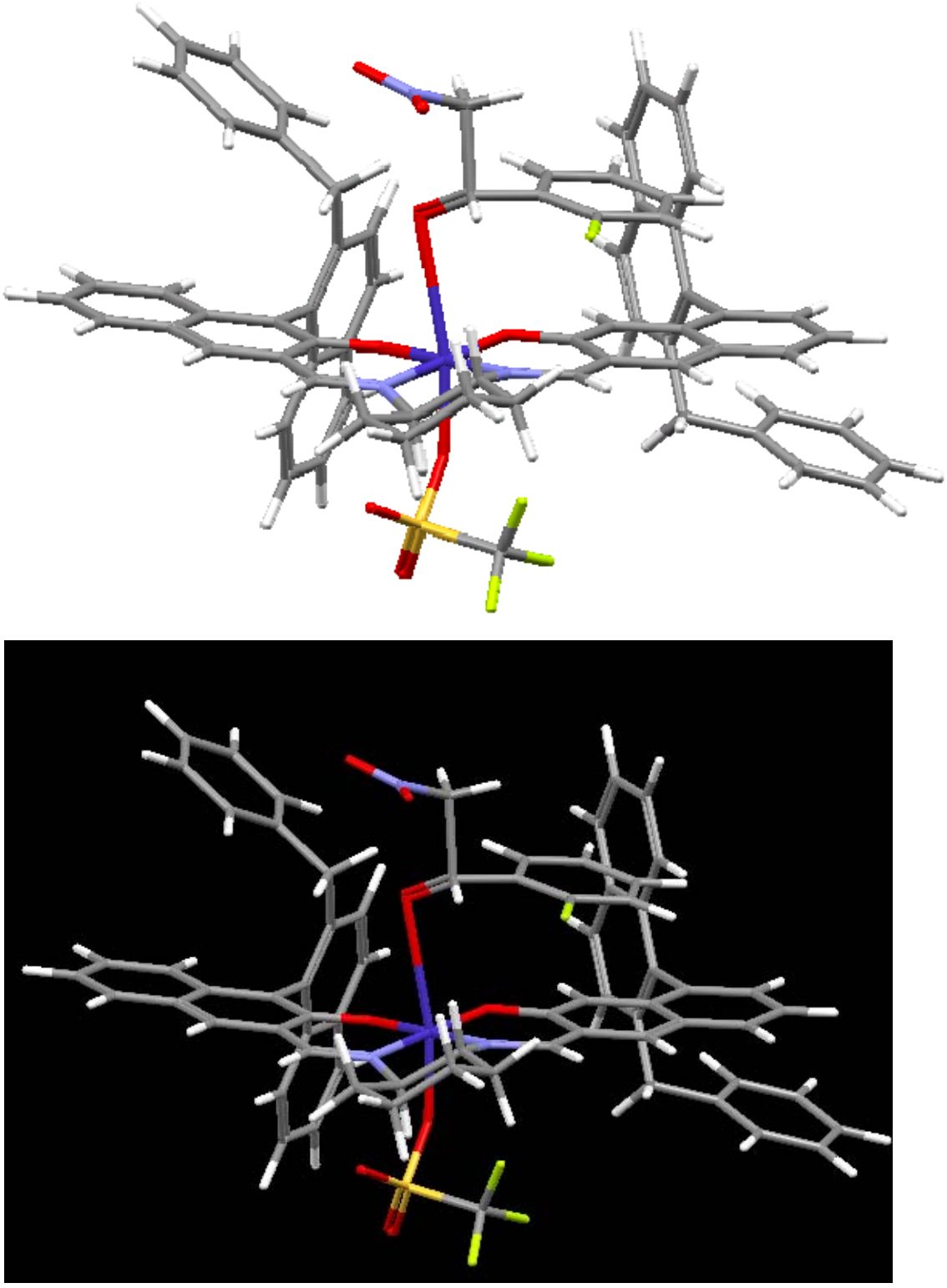
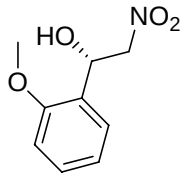
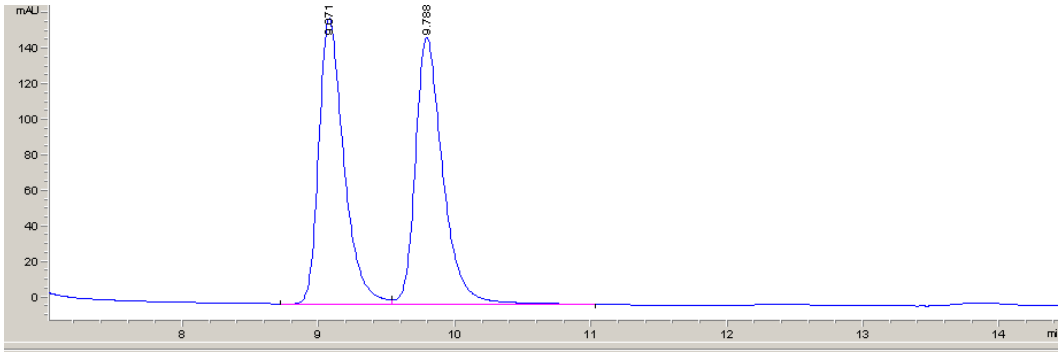


Figure S3. Optimized structures of the most reasonable catalyst-substructure complexes (*o*-fluorobenzaldehyde and (*R,R,S,S*)-salen (**5a**)-Co(III) catalyst) based on experimental results.

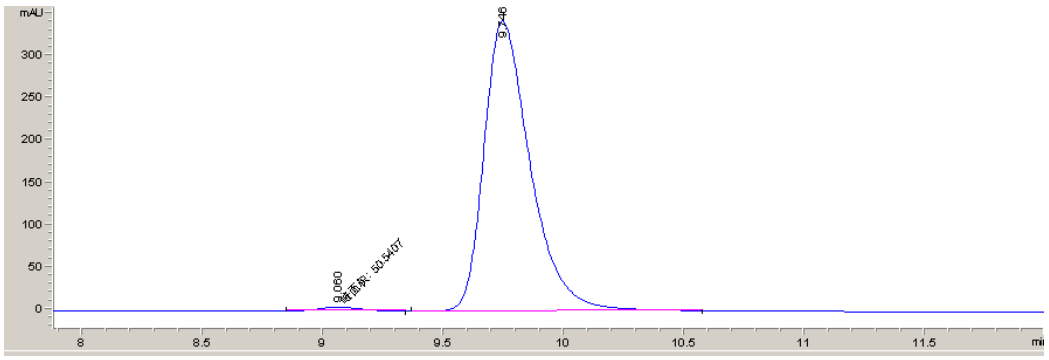


5. HPLC chromatograms of Henry products 3

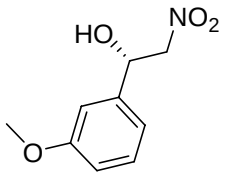


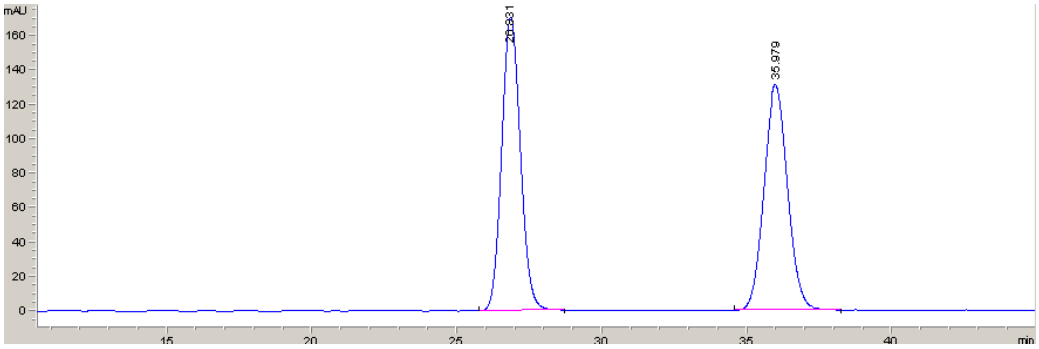


	Processed Chanel Descr	RT	Area	%Area	Height
1	215	9.071	2064.9	49.368	161
2	215	9.788	2117.8	50.632	151.6



	Processed Chanel Descr	RT	Area	%Area	Height
1	215	9.06	50.5	1.092	4.4
2	215	9.746	4576.1	98.908	342.6





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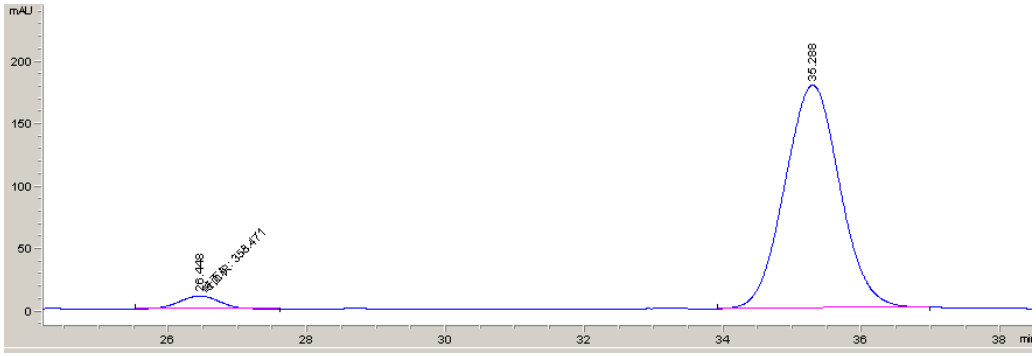
1	215	26.831	7569.8	49.943	170.6
2	215	35.979	7587	50.057	131.1



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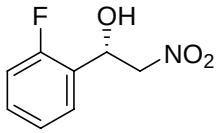
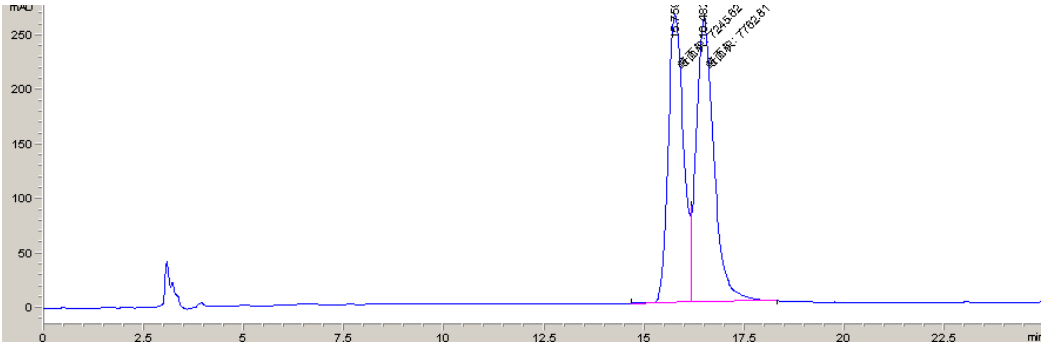
1	215	26.448	358.5	3.518	9.6
2	215	35.258	9846.8	96.487	178.5





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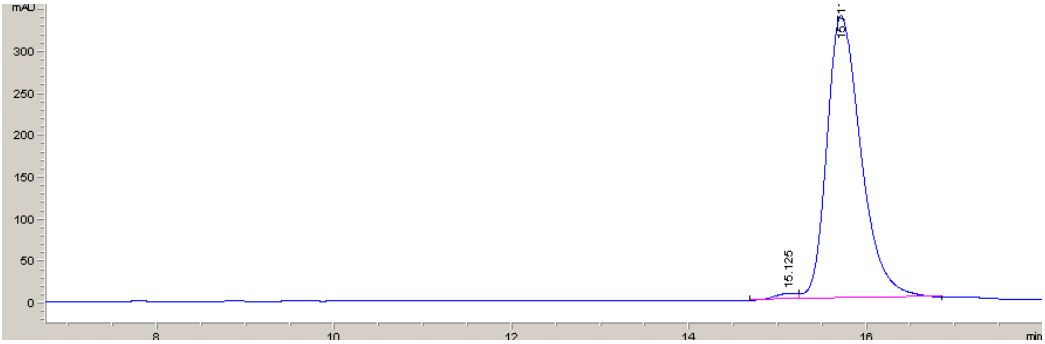
1	215	15.759	7245.6	48.313	263.5
2	215	16.482	7762.8	51.687	260.5



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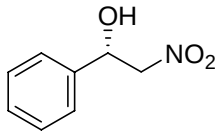
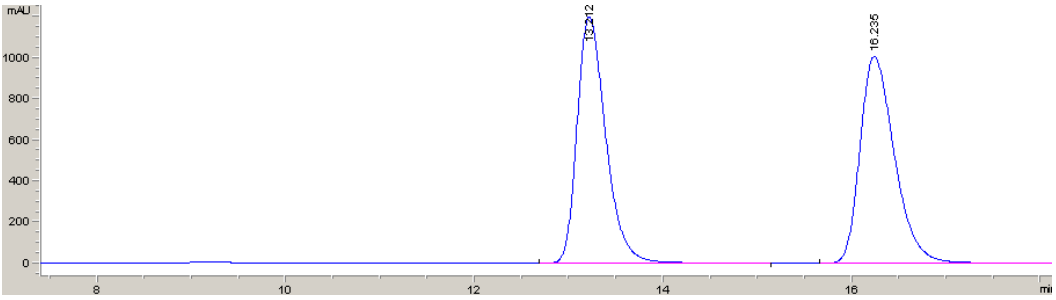
1	215	15.125	126.7	1.385	7.2
2	215	15.711	9024.3	98.615	337.4





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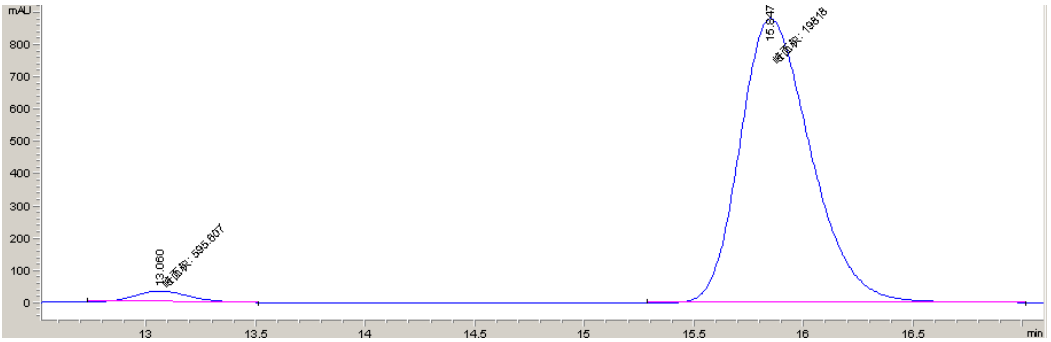
1	215	13.212	25355.5	49.783	1199.9
2	215	16.235	25576.5	50.217	1007.1



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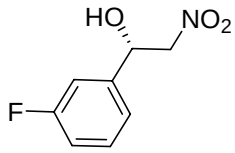
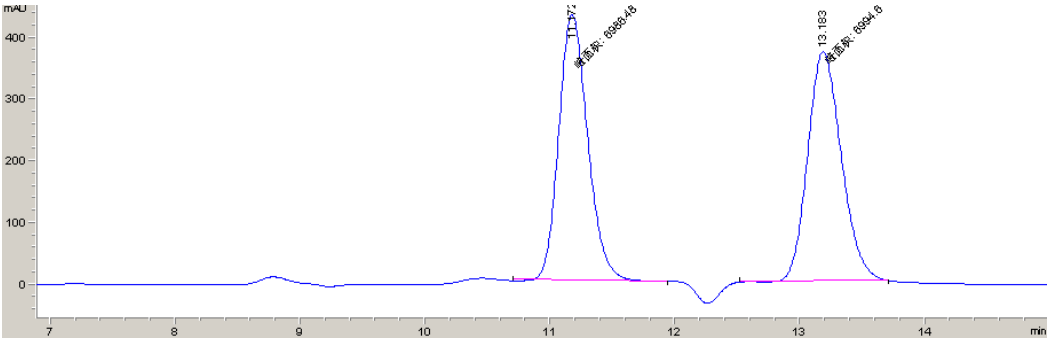
1	215	13.06	595.6	2.918	33.9
2	215	15.847	198.18	97.082	880.4





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1	215	11.172	6986.5	49.971	431.8
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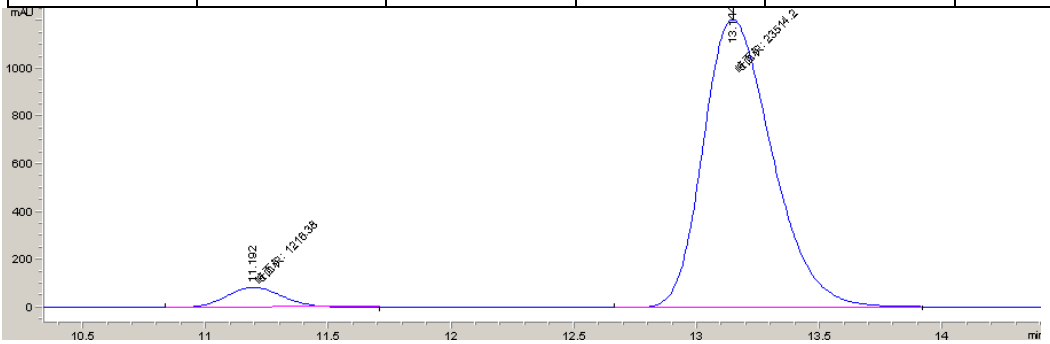

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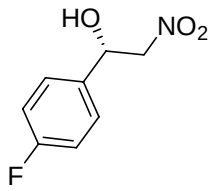
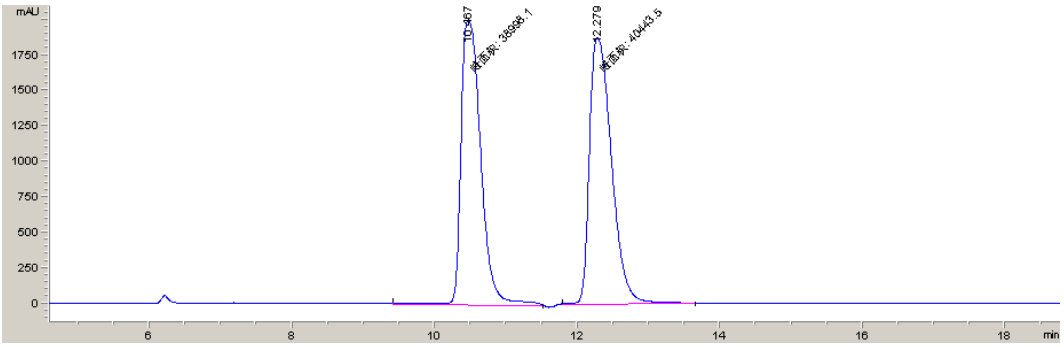
1	215	11.192	1216.4	4.919	81
2	215	13.144	23154.2	95.081	1205.1





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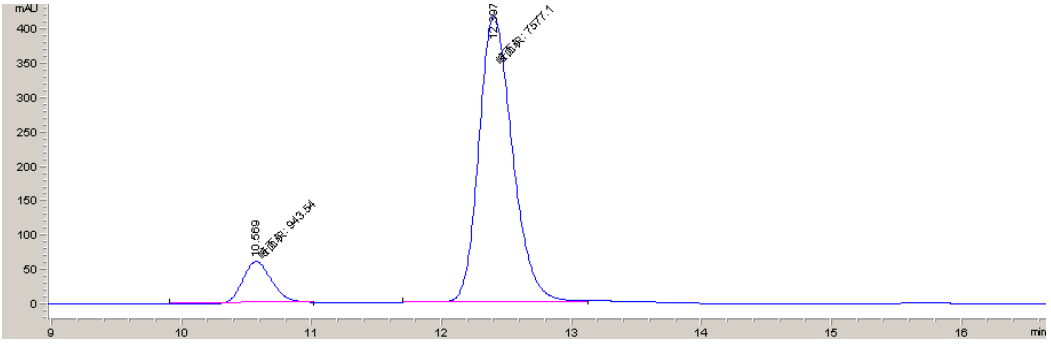
2	215	12.279	40443.5	50.910	1880.1



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1	215	10.569	943.5	11.074	60.8
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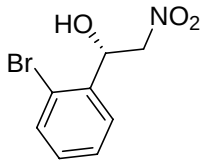

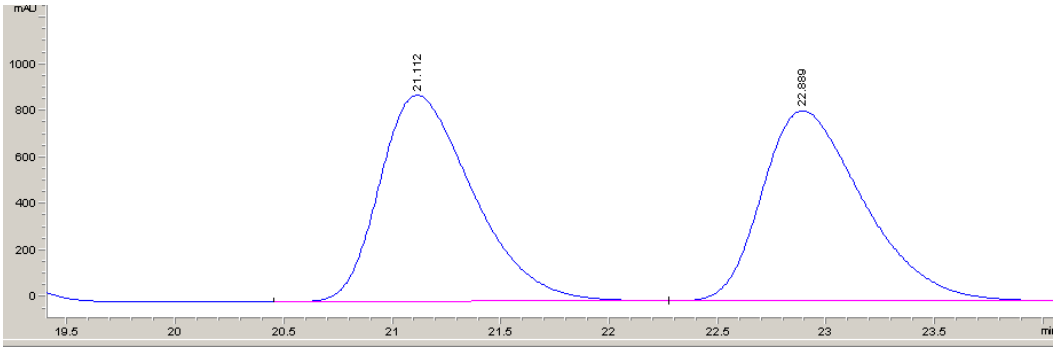

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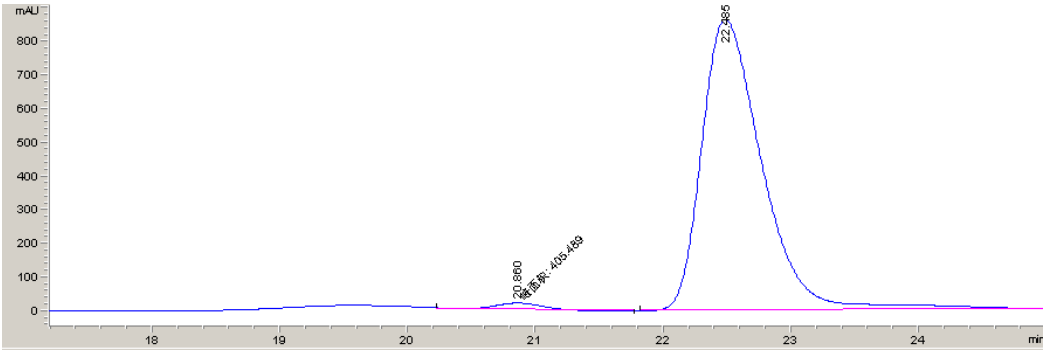
1	215	21.112	26655.5	50.075	887.6
2	215	22.889	26576.2	49.925	817.7



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1	215	20.86	405.5	1.401	17.5
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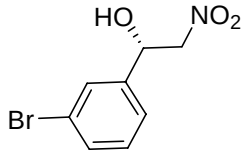

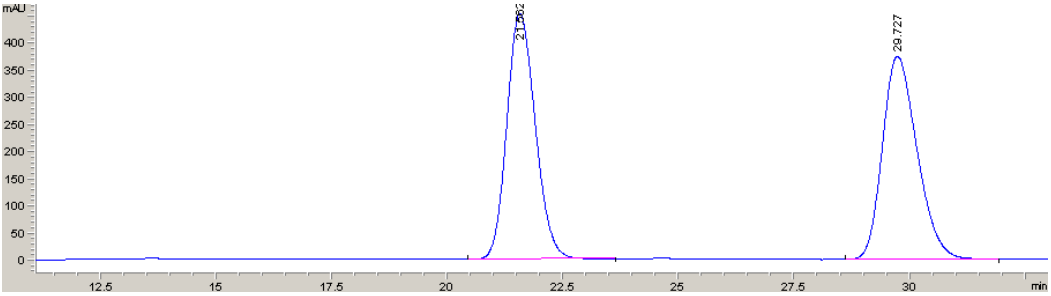

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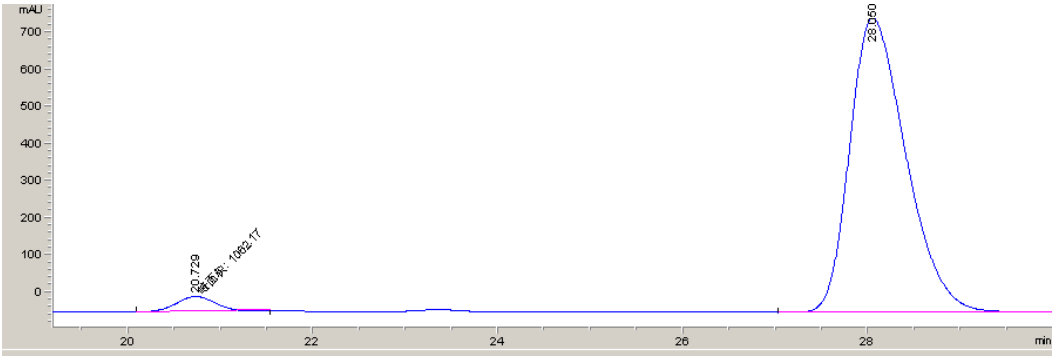
1	215	21.562	19435.9	49.923	453.4
2	215	29.727	19495.8	50.077	374.6



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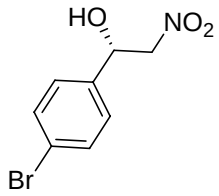
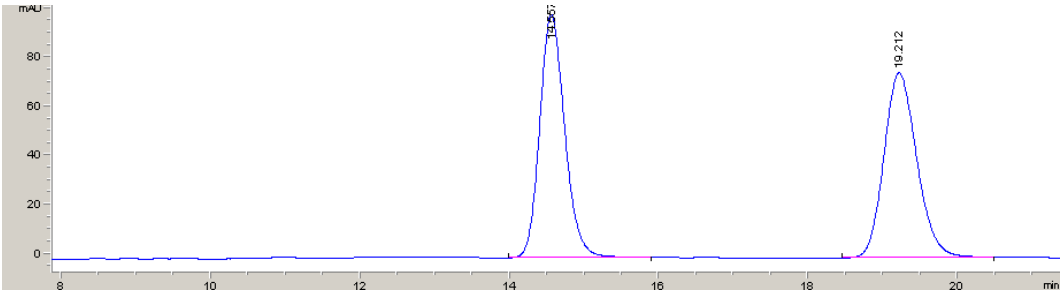
1	215	20.729	1062.2	3.076	38.4
2	215	28.05	33471.1	96.924	792.7





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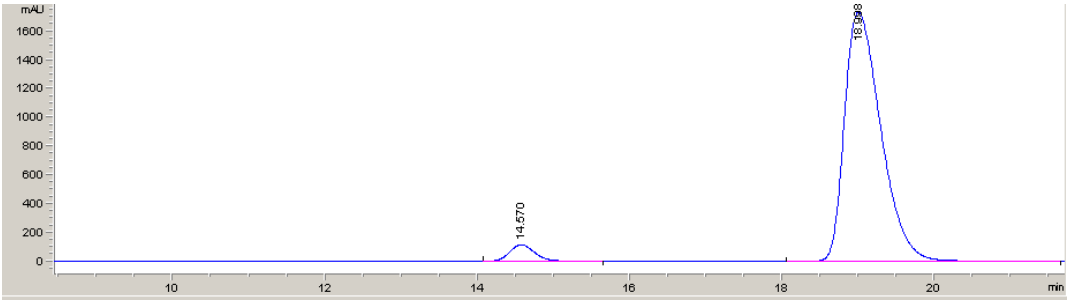
1	215	14.557	2306.7	50.054	99.2
2	215	19.212	2301.7	49.946	75.3



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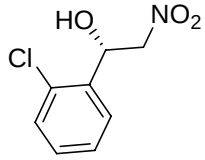
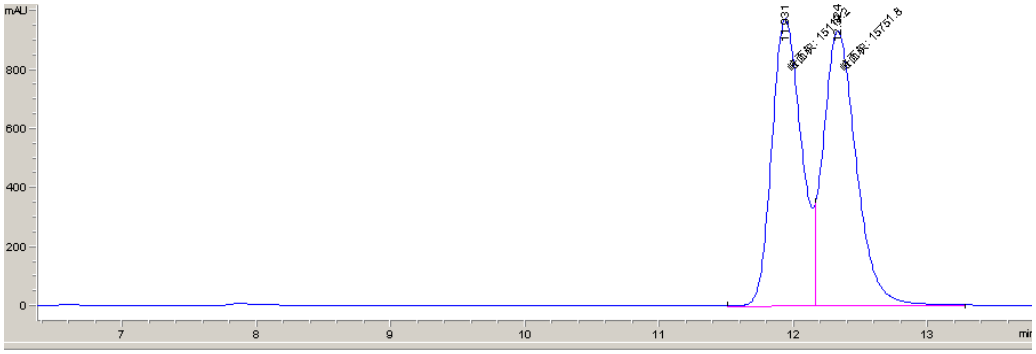
1	215	14.57	2652.9	4.423	115.9
2	215	18.998	57328.5	95.577	1732.3





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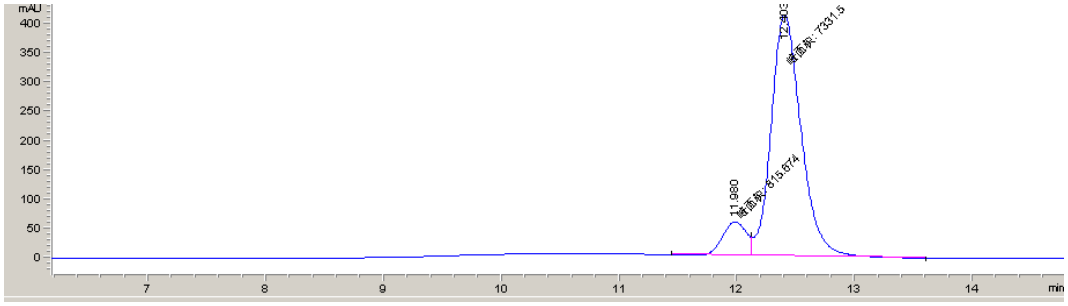
1	215	11.931	15119.2	48.975	974.8
2	215	12.424	15751.8	51.025	933.4



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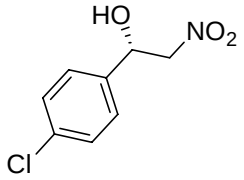
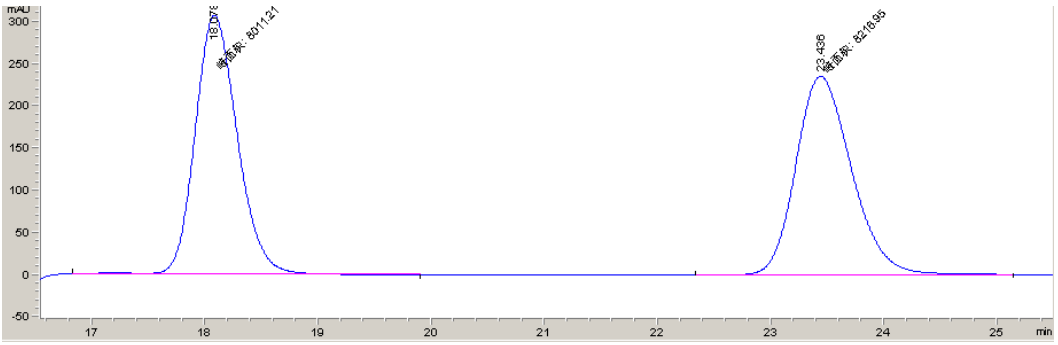
1	215	11.98	815.7	10.012	57.6
2	215	12.403	7331.5	89.988	412.6





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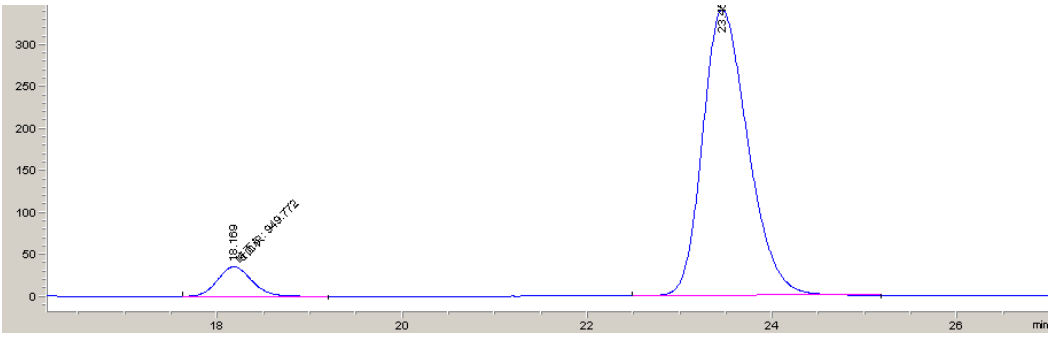
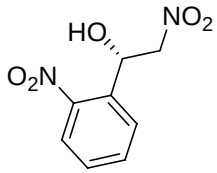
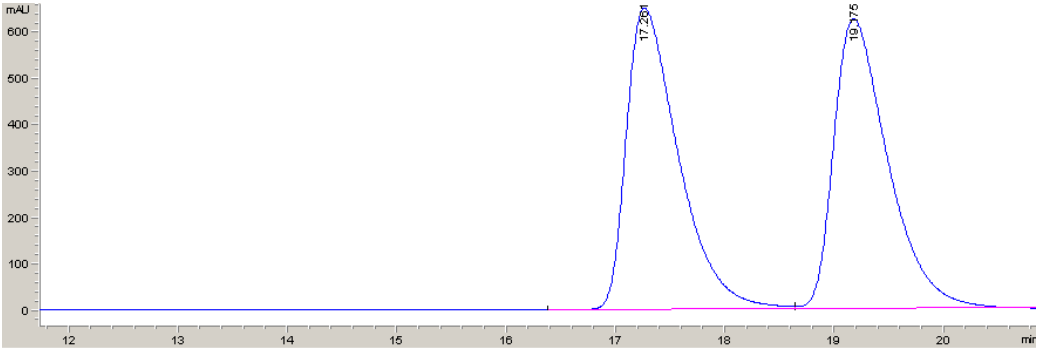
1	215	18.078	8011.2	49.366	307.4
2	215	23.466	8216.9	50.634	236.3

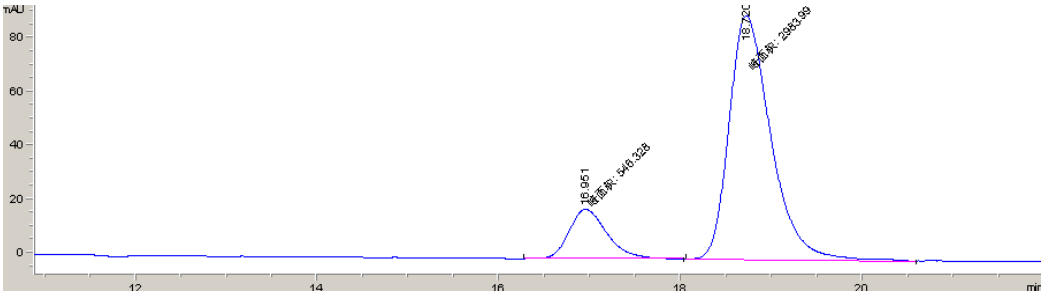


	Processed Chanel Descr	RT	Area	%Area	Height
1	215	18.169	949.8	7.524	35.7
2	215	23.453	11674	92.476	341.2





	Processed Chanel Descr	RT	Area	%Area	Height
1	215	17.261	21638.2	50.07	651.3
2	215	19.117	21577.7	49.97	625.6



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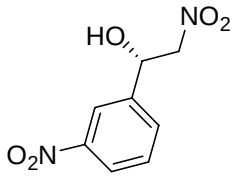
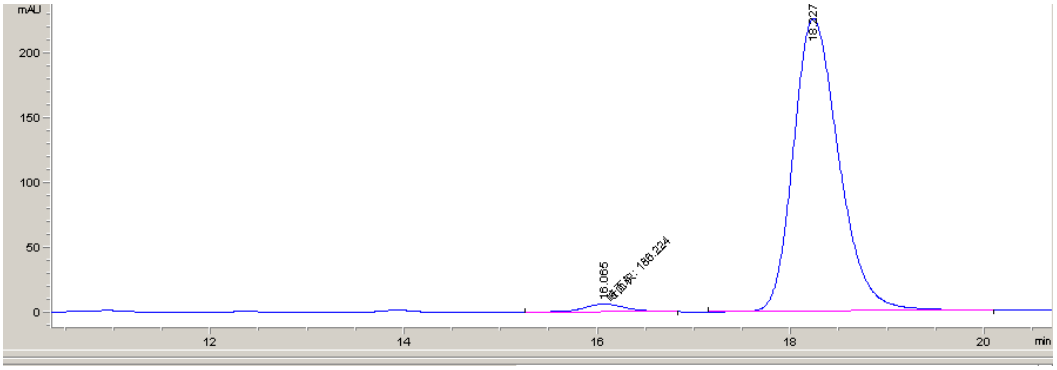
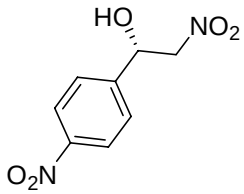
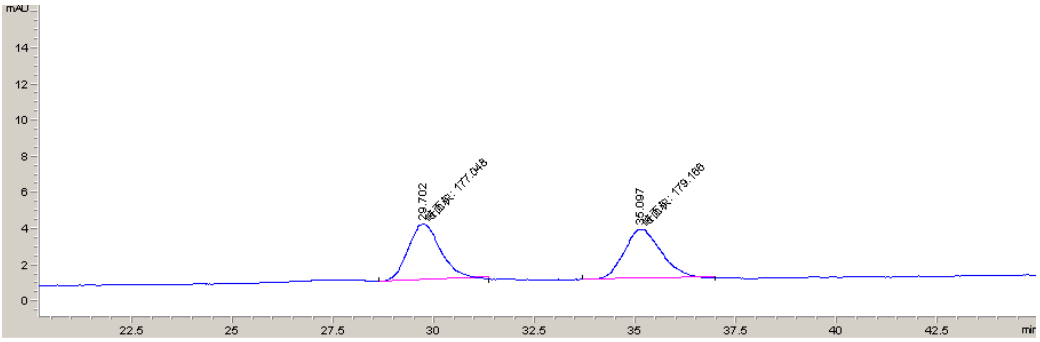
1	215	16.951	546.3	15.475	18.5
2	215	18.72	2984	84.525	91.7



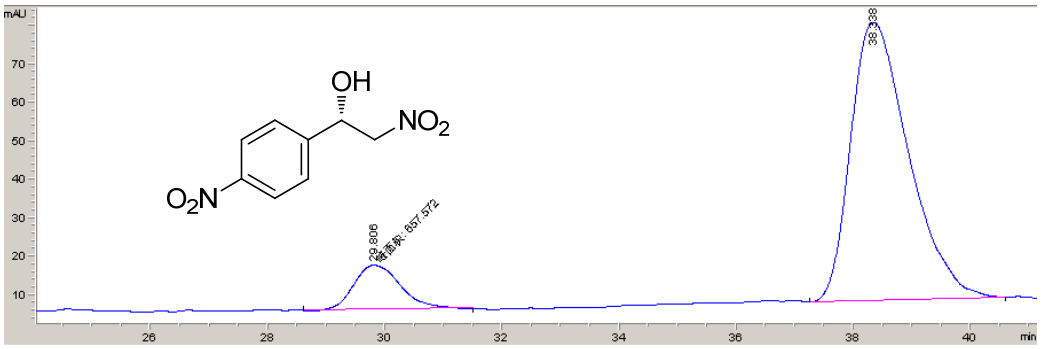


	Processed Chanel Descr	RT	Area	%Area	Height
1	215	16.065	186.2	2.453	6
2	215	18.227	7406.4	97.547	226.4

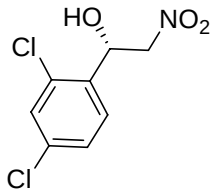


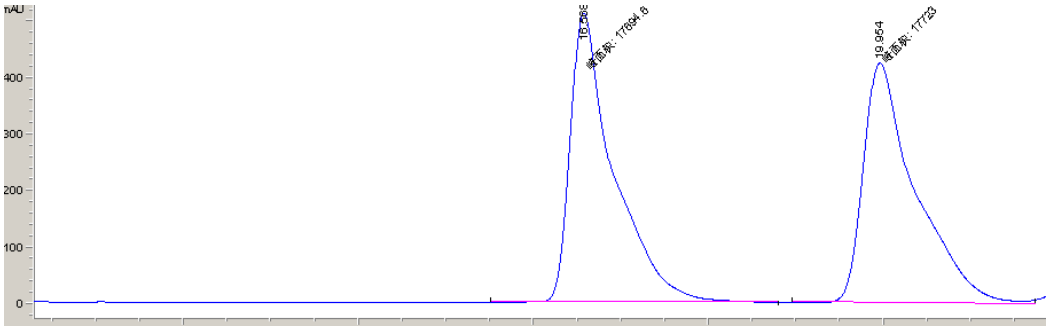


	Processed Chanel Descr	RT	Area	%Area	Height
1	215	29.702	177	49.703	3.1
2	215	35.097	179.2	50.297	2.8

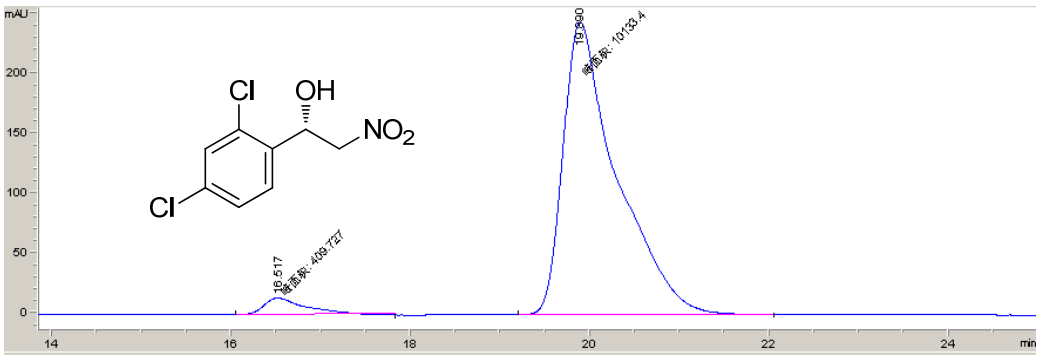


	Processed Chanel Descr	RT	Area	%Area	Height
1	215	29.806	657.6	11.644	11.7
2	215	38.338	4989.8	88.356	72.4

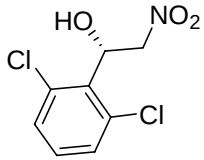


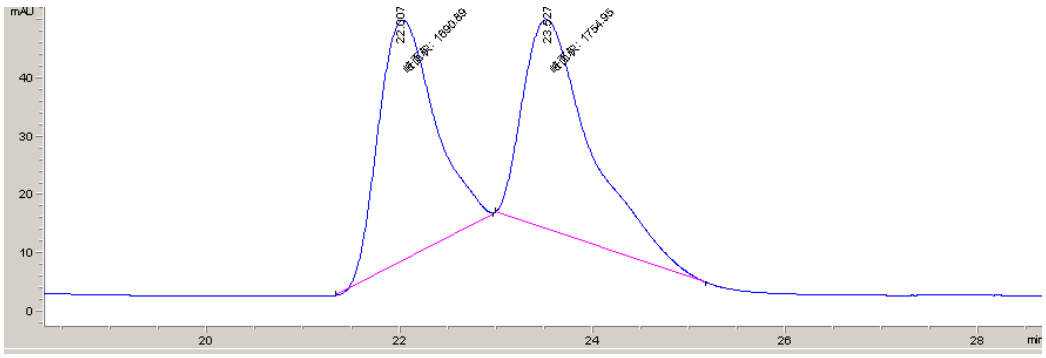


	Processed Chanel Descr	RT	Area	%Area	Height
1	215	16.568	17694.6	49.960	511.7
2	215	19.954	17723	50.040	424.7

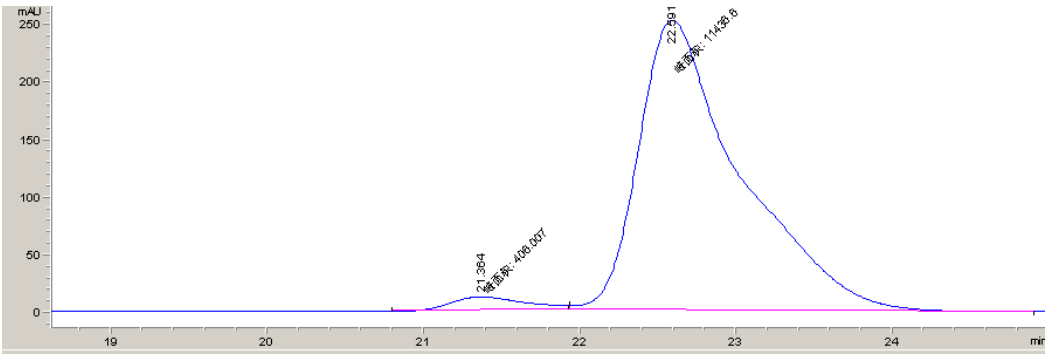


	Processed Chanel Descr	RT	Area	%Area	Height
1	215	16.517	409.7	3.886	13.4
2	215	19.89	10133.4	96.114	243.6

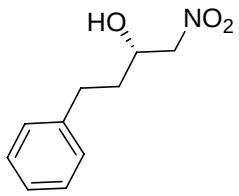


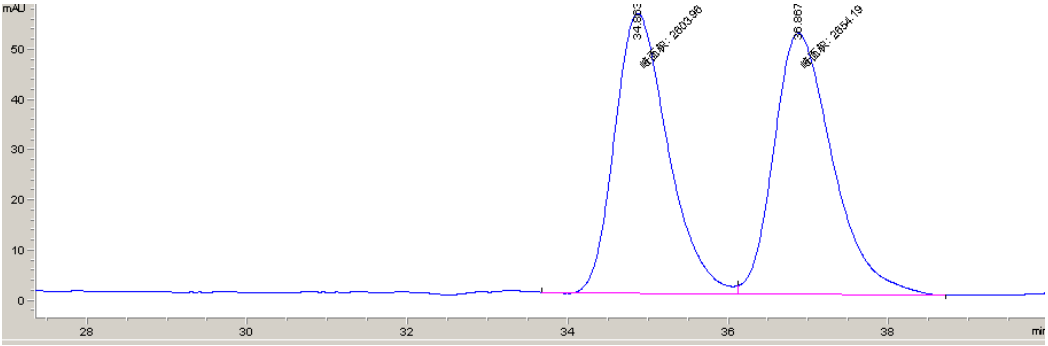


	Processed Chanel Descr	RT	Area	%Area	Height
1	215	22.007	1690.9	49.07	41.3
2	215	23.527	1754.9	50.93	35.8

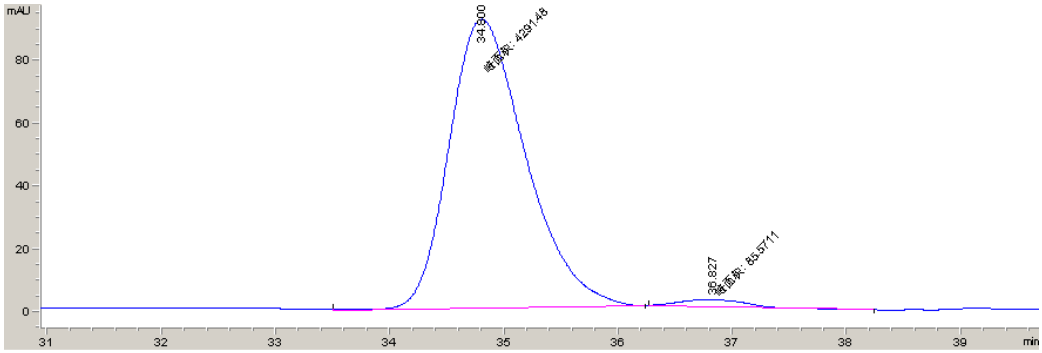


	Processed Chanel Descr	RT	Area	%Area	Height
1	215	21.364	406	3.428	12
2	215	22.591	11436.6	96.573	252.1

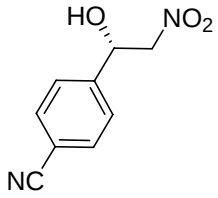


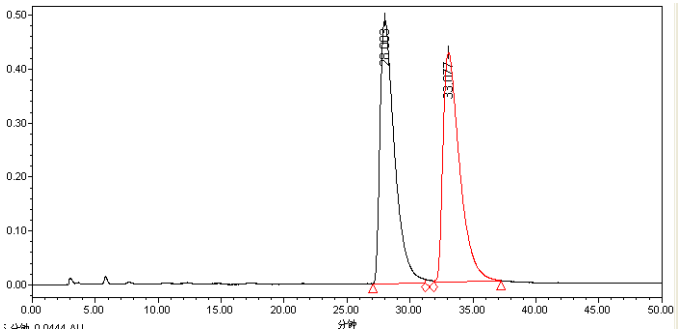


	Processed Chanel Descr	RT	Area	%Area	Height
1	215	34.863	2604	49.522	55.9
2	215	36.867	2654.2	50.478	52

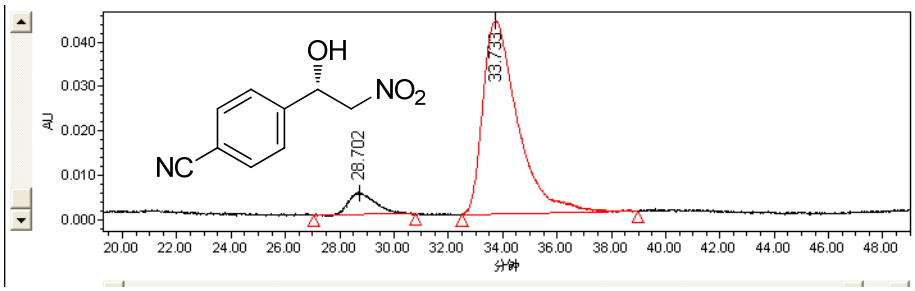


	Processed Chanel Descr	RT	Area	%Area	Height
1	215	34.8	4291.5	98.045	91.9
2	215	36.827	85.6	1.955	2.2

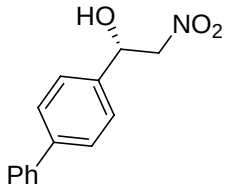


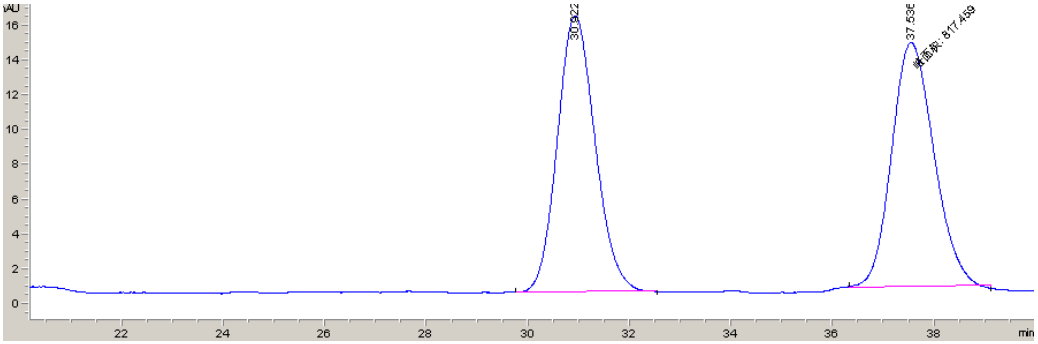


	Processed Chanel Descr	RT	Area	%Area	Height
1	215	28.003	39400329	50.12	489748
2	215	33.077	39204788	49.88	425163

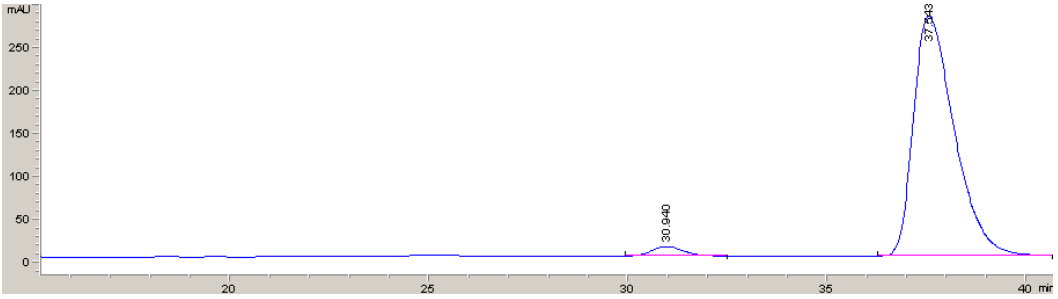


	Processed Chanel Descr	RT	Area	%Area	Height
1	215	28.702	345184	8.21	49.48
2	215	33.733	3860669	91.79	43435

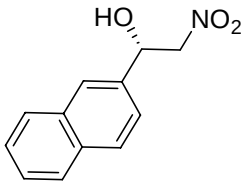


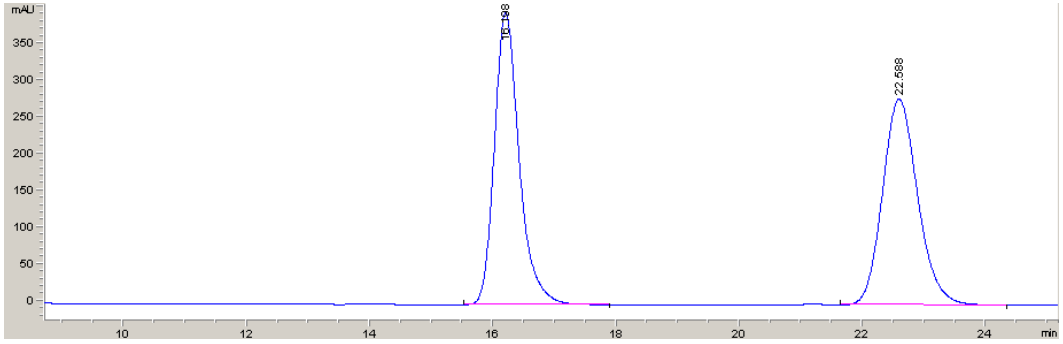


	Processed Chanel Descr	RT	Area	%Area	Height
1	215	30.922	822.4	50.151	15.9
2	215	37.536	87.5	49.849	14.1

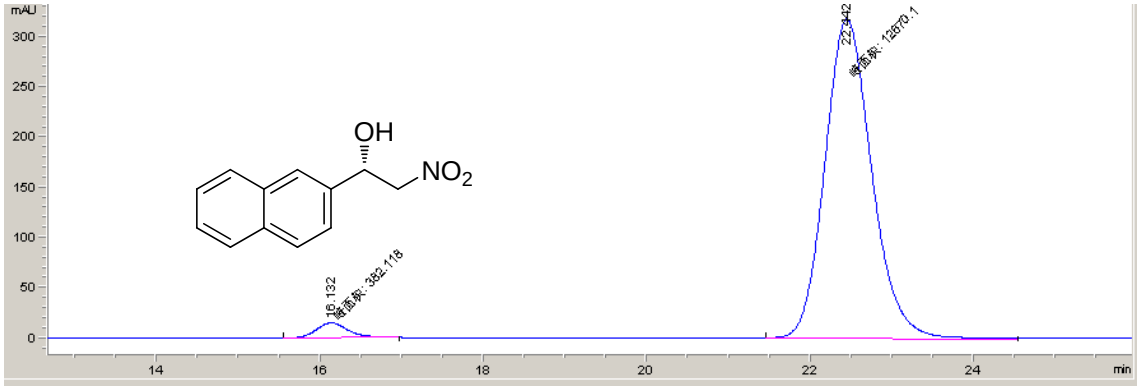


	Processed Chanel Descr	RT	Area	%Area	Height
1	215	30.94	600.8	2.938	11
2	215	37.543	19846.4	97.062	279



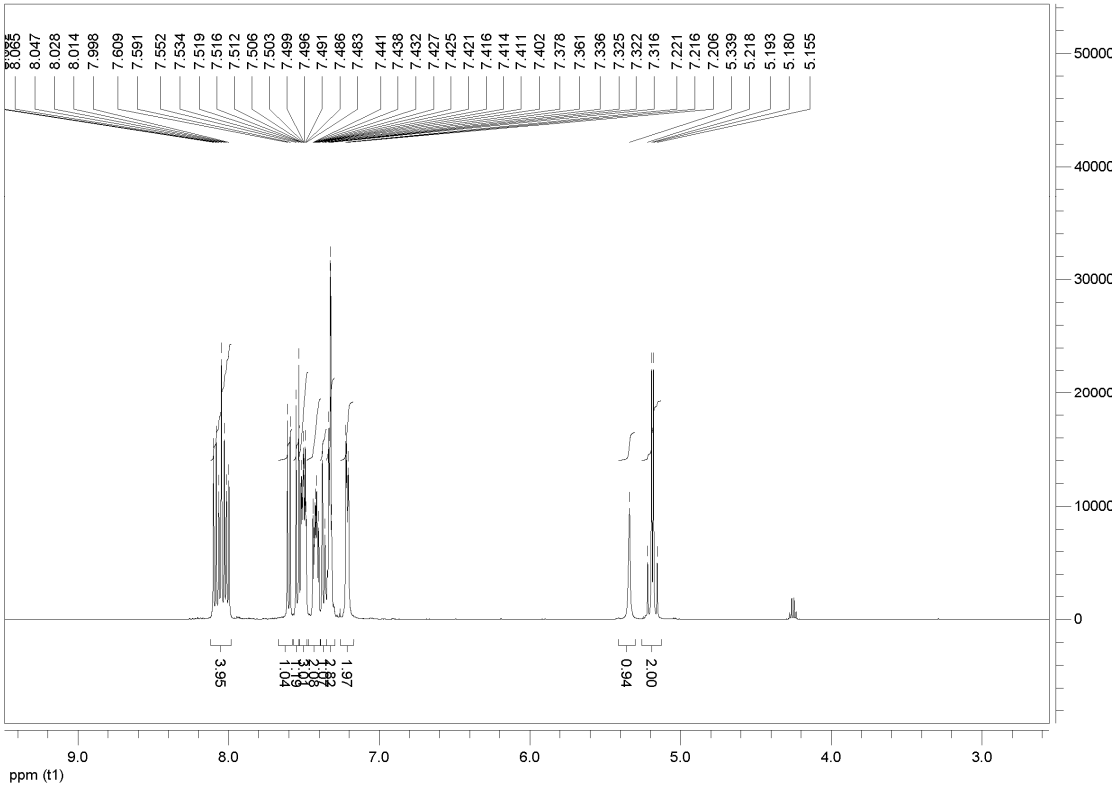


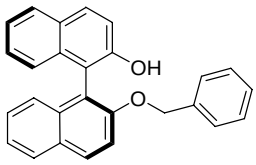
	Processed Chanel Descr	RT	Area	%Area	Height
1	215	16.198	11083.3	49.977	396.9
2	215	22.588	11093.7	50.023	279.6

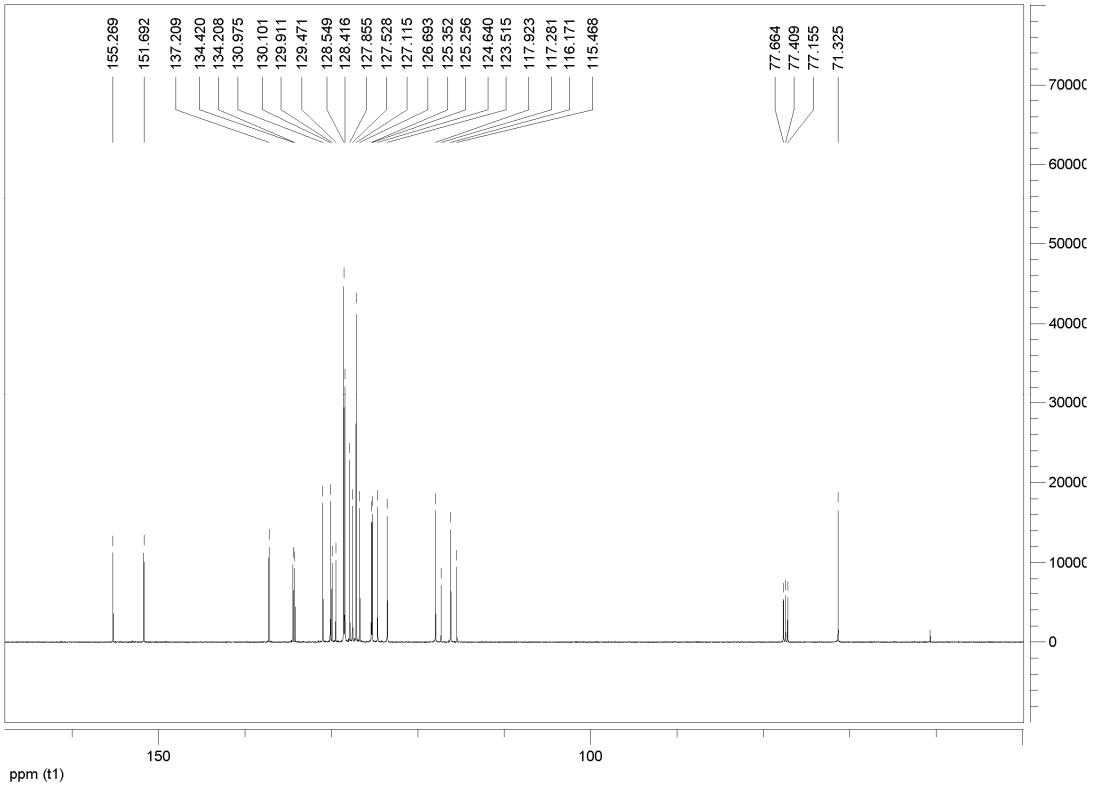


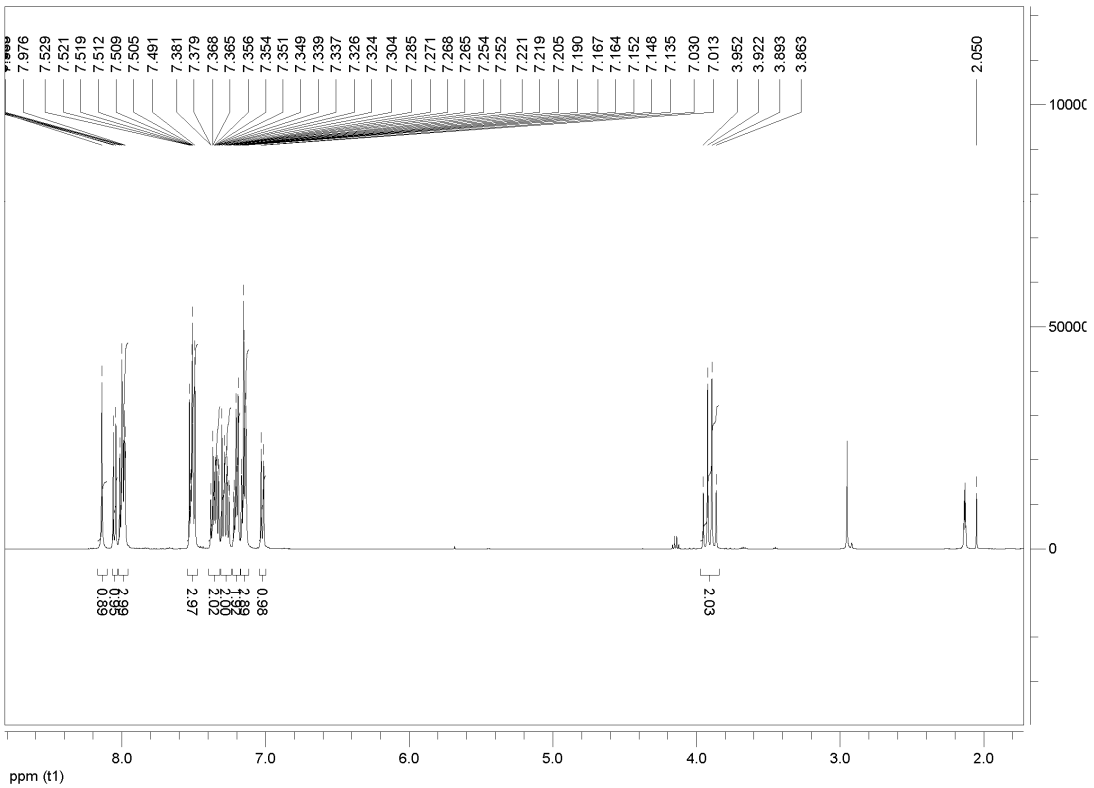
	Processed Chanel Descr	RT	Area	%Area	Height
1	215	16.132	382.1	2.938	14.5
2	215	22.332	12670.1	97.072	317.9

6. NMR Charts of salen and salan ligands and Compounds





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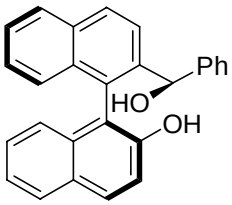
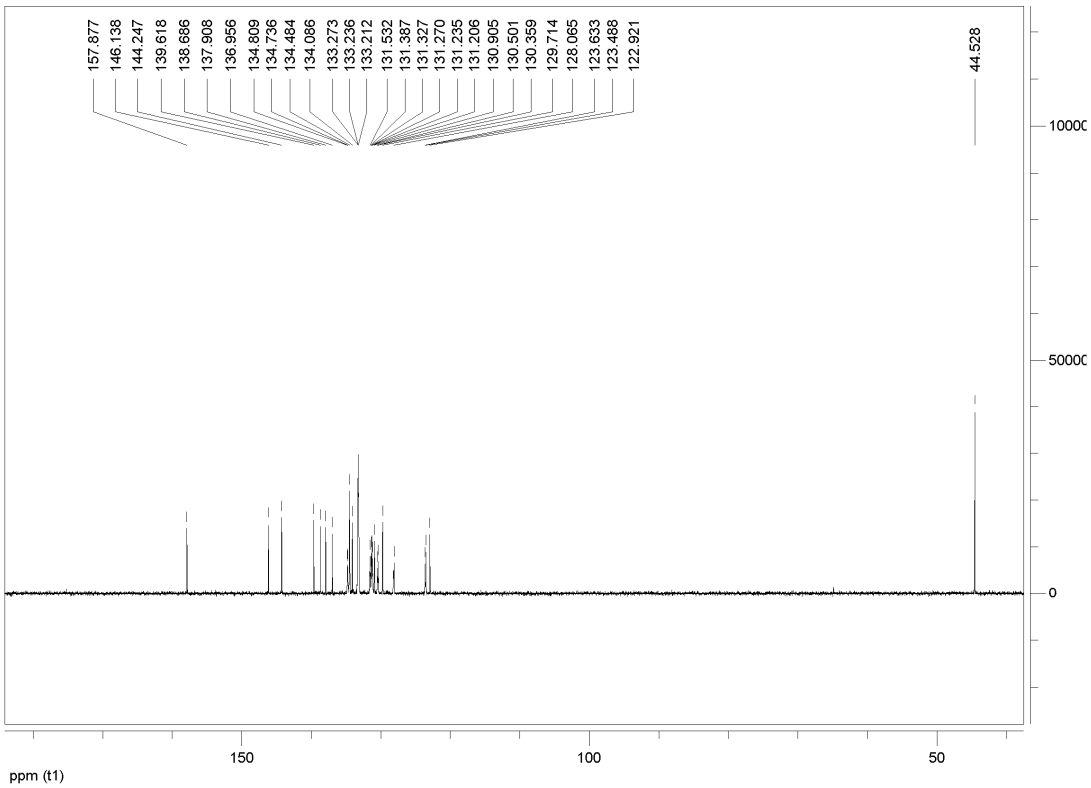
7.519
7.512
7.509
7.505
7.491
7.381
7.379
7.368
7.365
7.356
7.354
7.351
7.349
7.339
7.337
7.326
7.324
7.304
7.285
7.271
7.268
7.265
7.254
7.252
7.221
7.219
7.205
7.190
7.167
7.164
7.152
7.148
7.135
7.030
7.013
3.952
3.922
3.893
3.863
2.050
0.89
2.97
2.03
0.98
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


Ph
HO
OH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137.908
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134.809
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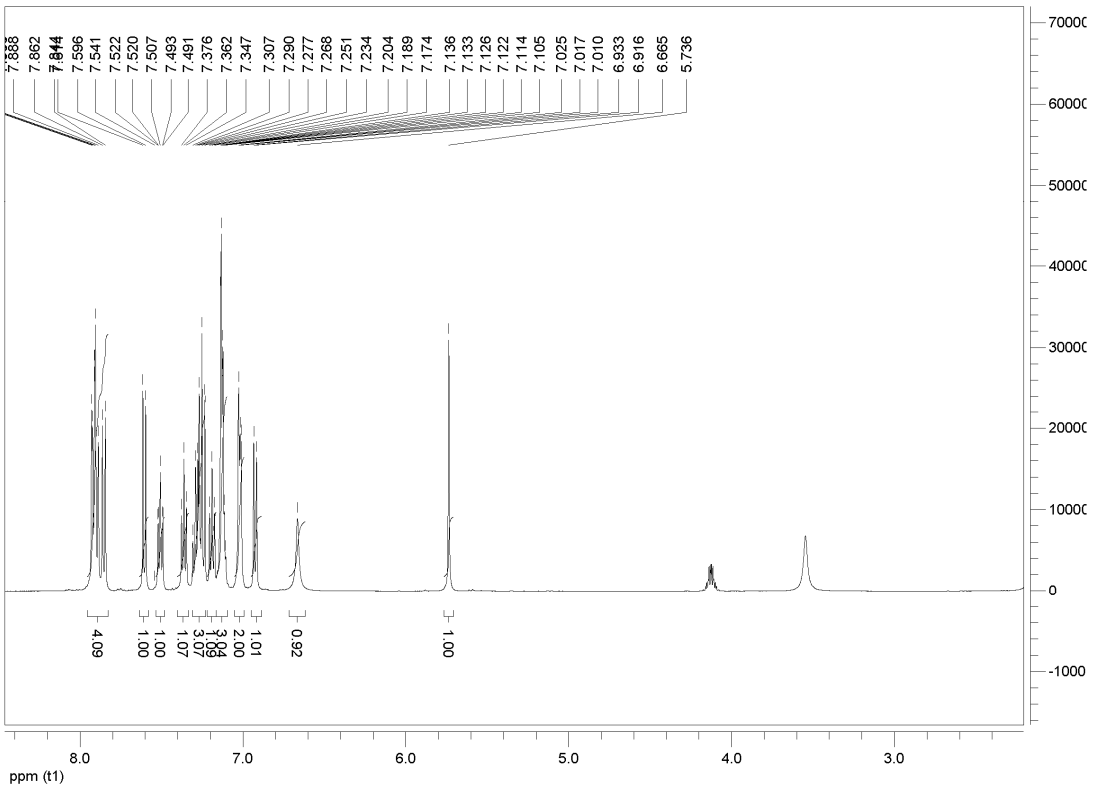
134.484
134.086
133.273
133.236
133.212
131.532
131.387
131.327
131.270
131.235
131.206
130.905
130.501
130.359
129.714
128.065
123.633
123.488
122.921
44.528
150
100
50
ppm (t1)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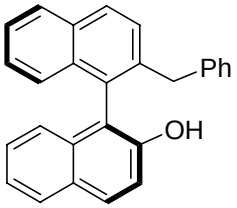
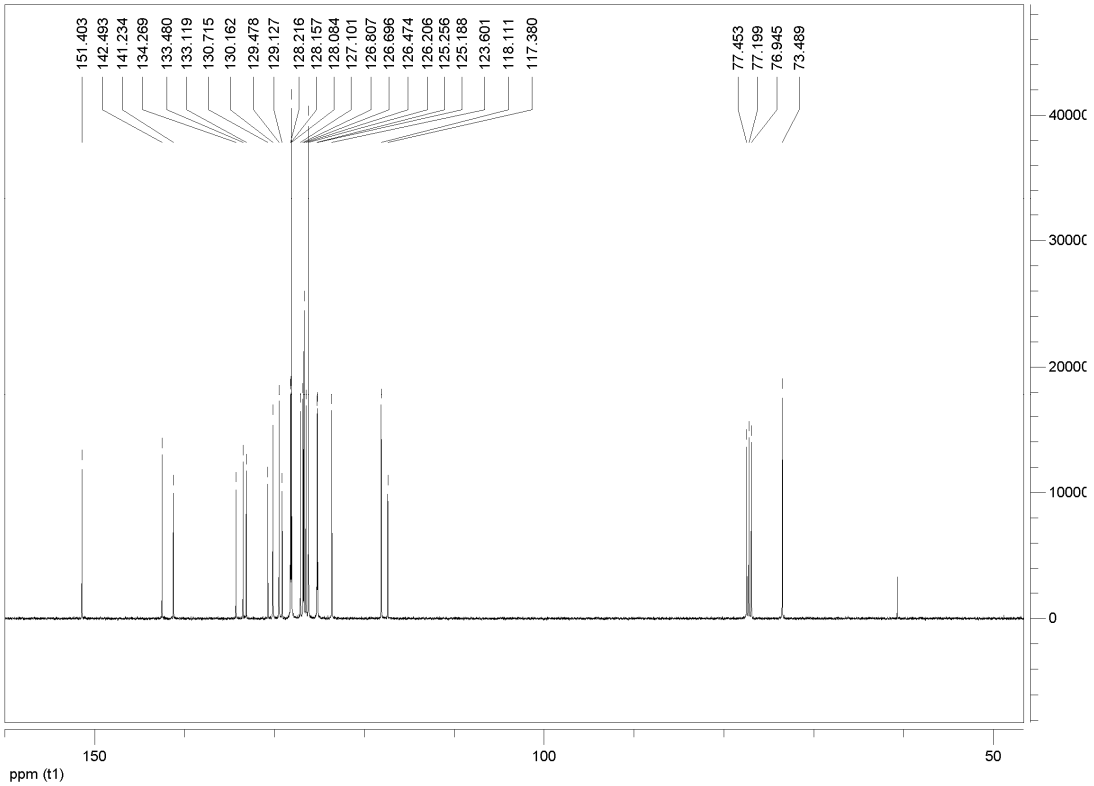
7.520
7.507
7.493
7.491
7.376
7.362
7.347
7.307
7.290
7.277
7.268
7.251
7.234
7.204
7.189
7.174
7.136
7.133
7.126
7.122
7.114
7.105
7.025
7.017
7.010
6.933
6.916
6.665
5.736
4.09
1.00
1.00
1.07
3.07
3.00
2.00
1.01
0.92
1.00
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)


Ph
OH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141.234
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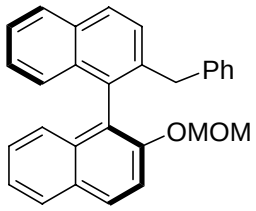
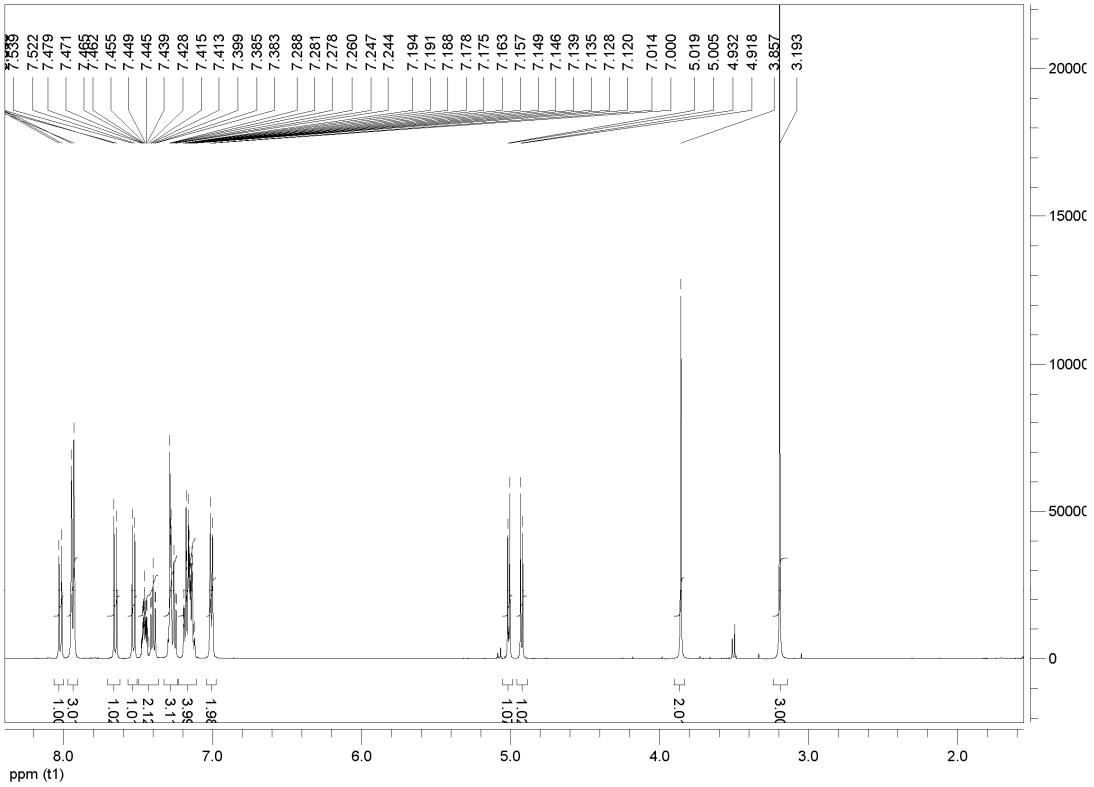
133.480
133.119
130.715
130.162
129.478
129.127
128.216
128.157
128.084
127.101
126.807
126.696
126.474
126.206
125.256
125.188
123.601
118.111
117.380
77.453
77.199
76.945
73.489
150
100
50
ppm (t1)


Ph
OMOM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7.445
7.439
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7.415
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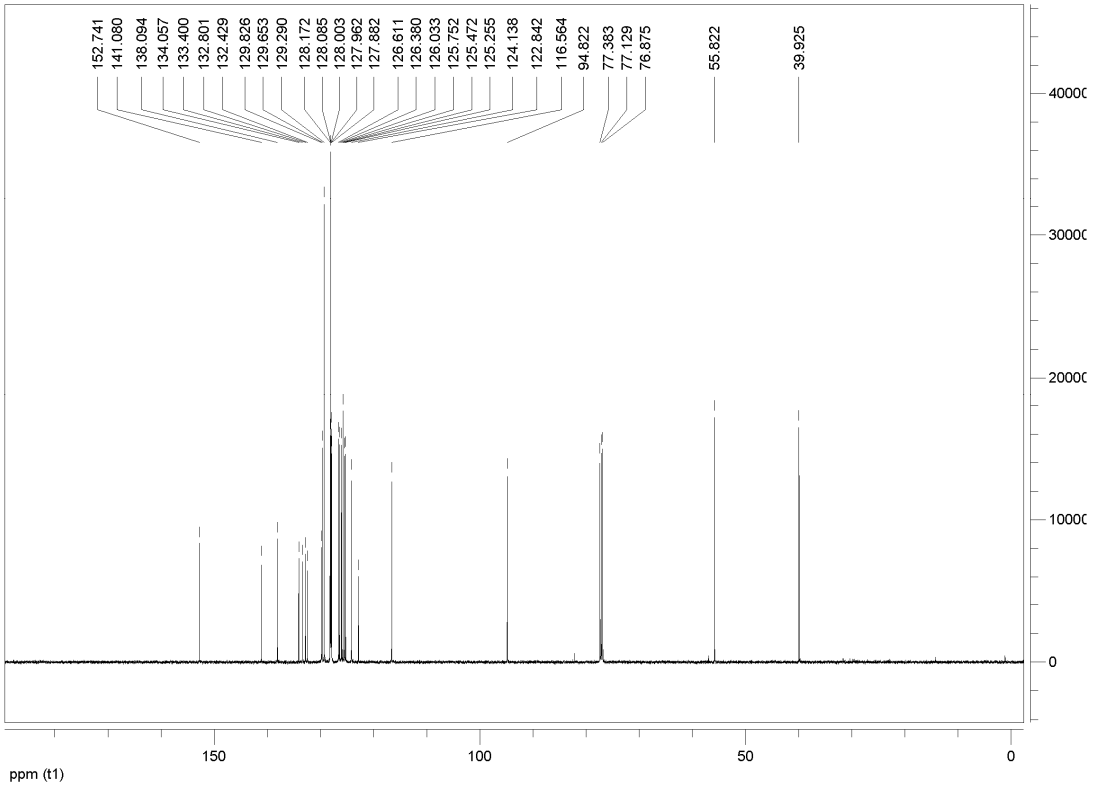
7.399
7.385
7.383
7.288
7.281
7.278
7.260
7.247
7.244
7.194
7.191
7.188
7.178
7.175
7.163
7.157
7.149
7.146
7.139
7.135
7.128
7.120
7.014
7.000
5.019
5.005
4.932
4.918
3.857
3.193
20000
15000
10000
50000
0
1.00
3.01
1.02
1.01
2.12
3.13
3.96
1.98
1.01
1.02
2.01
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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134.057
133.400
132.801
132.429
129.826
129.653
129.290
128.172
128.085
128.003
127.962
127.882
126.611
126.380
126.033
125.752
125.472
125.255
124.138
122.842
116.564
94.822
77.383
77.129
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55.822
39.925
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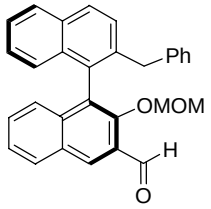
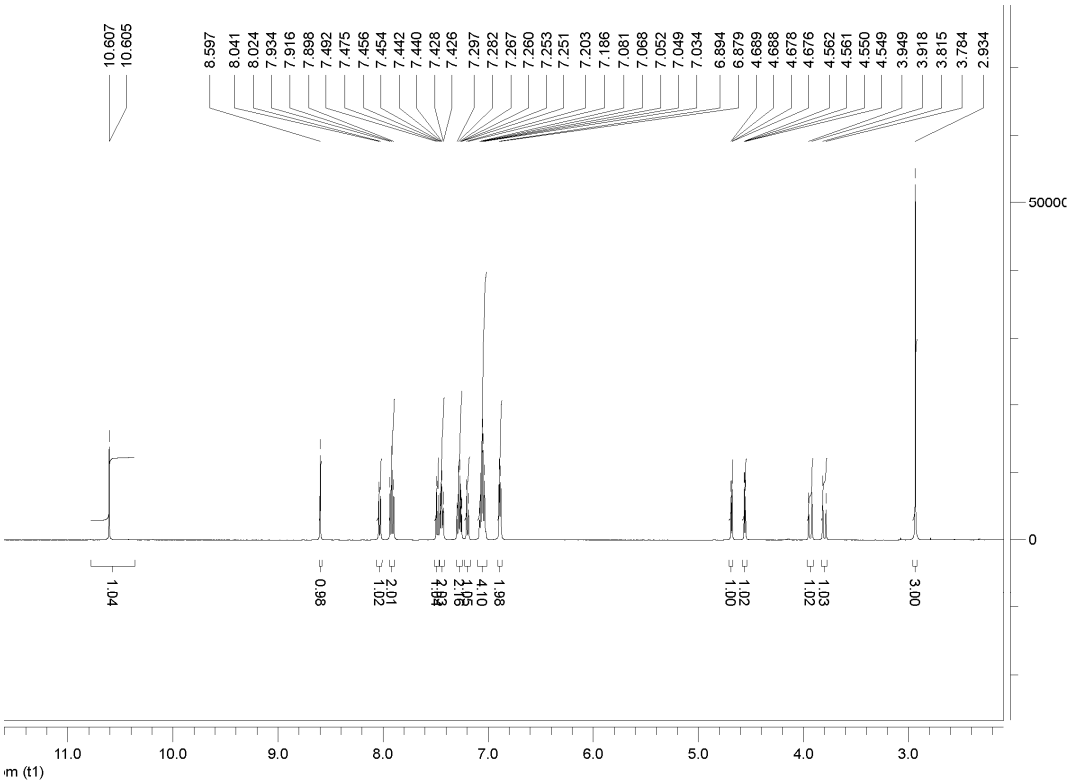
30000
20000
10000
0
150
100
50
0
ppm (t1)


Ph
OMOM
H
O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7.454
7.442
7.440
7.428
7.426
7.297
7.282
7.267
7.260
7.253
7.251
7.203
7.186
7.081
7.068
7.052
7.049
7.034
6.894
6.879
4.689
4.688
4.678
4.676
4.562
4.561
4.550
4.549
3.949
3.918
3.815
3.784
2.934
50000
0
1.04
0.98
2.01
1.02
2.16
4.10
1.98
1.02
1.00
1.03
1.02
3.00
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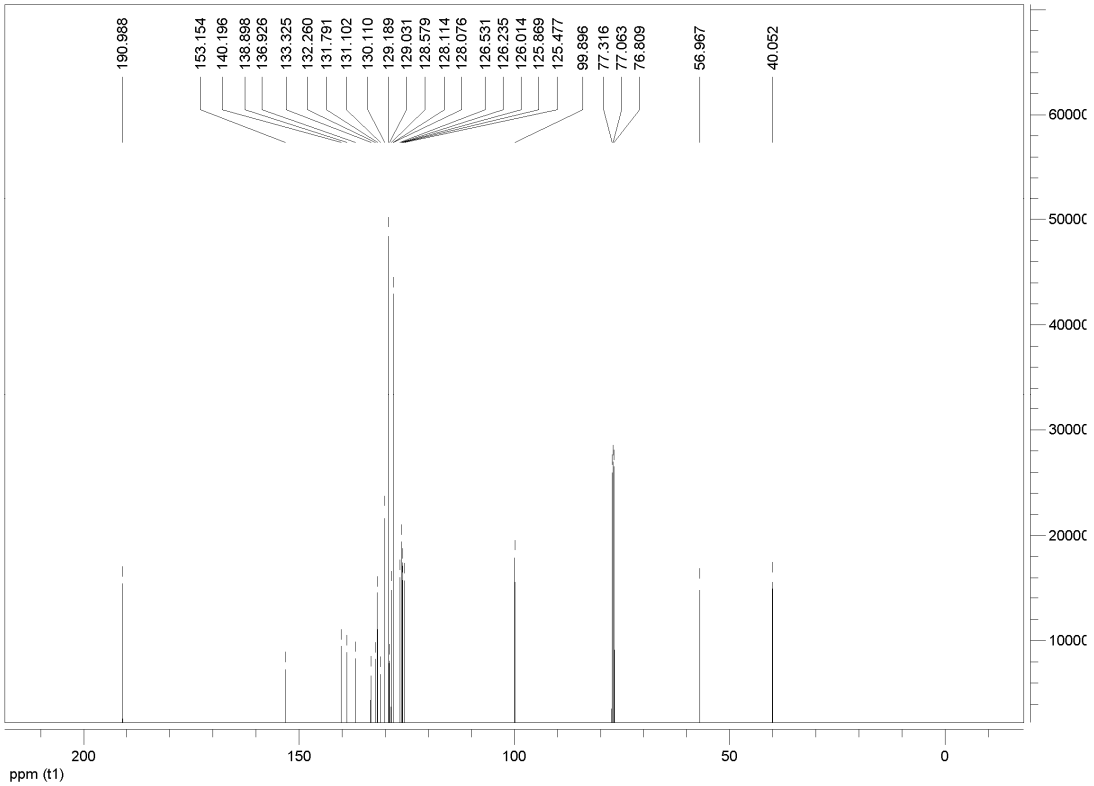
9.0
8.0
7.0
6.0
5.0
4.0
3.0
m (t1)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130.110
129.189
129.031
128.579
128.114
128.076
126.531
126.235
126.014
125.869
125.477
99.896
77.316
77.063
76.809
56.967
40.052
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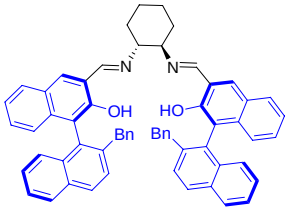
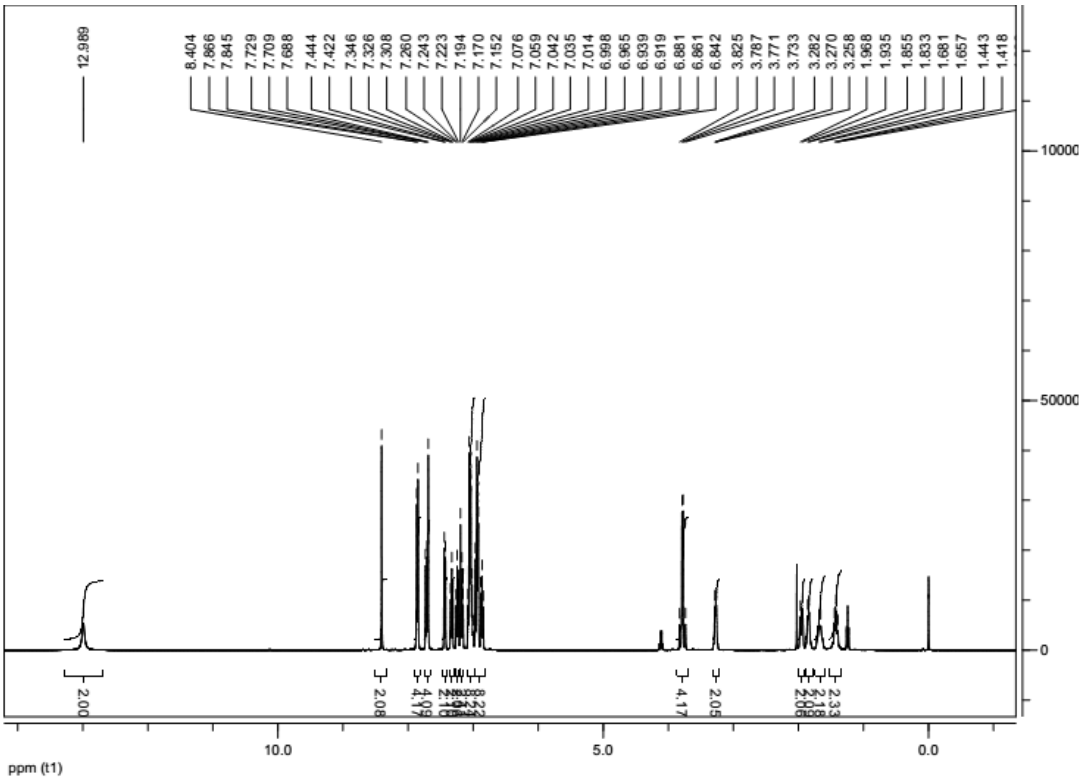
40000
30000
20000
10000
200
150
100
50
0
ppm (t1)


N
N
OH
HO
Bn
Bn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7.709
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7.444
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7.346
7.326
7.308
7.260
7.243
7.223
7.194
7.170
7.152
7.076
7.059
7.042
7.035
7.014
6.998
6.965
6.939
6.919
6.881
6.861
6.842
3.825
3.787
3.771
3.733
3.282
3.270
3.258
1.968
1.935
1.855
1.833
1.681
1.657
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1.418
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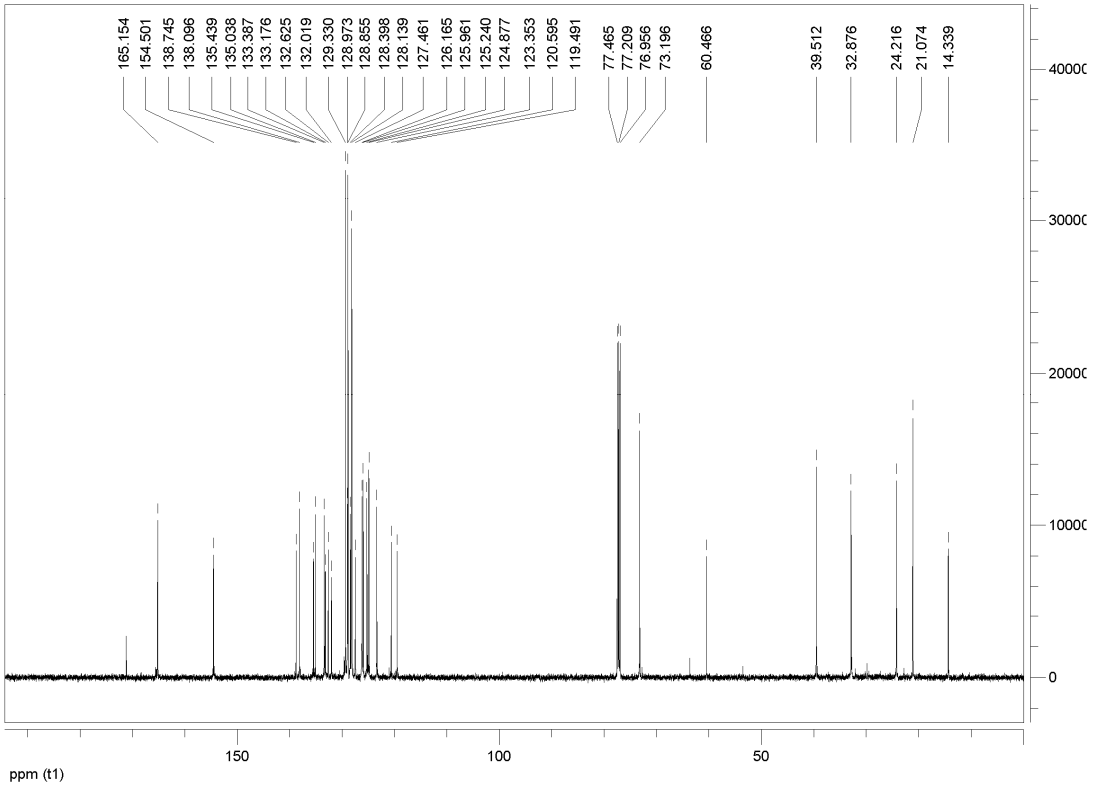
50000
0
2.00
2.08
4.17
2.05
10.0
5.0
0.0
ppm (t1)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135.038
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132.625
132.019
129.330
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128.855
128.398
128.139
127.461
126.165
125.961
125.240
124.877
123.353
120.595
119.491
77.465
77.209
76.956
73.196
60.466
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24.216
21.074
14.339
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30000
20000
10000
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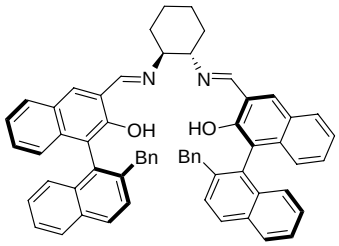
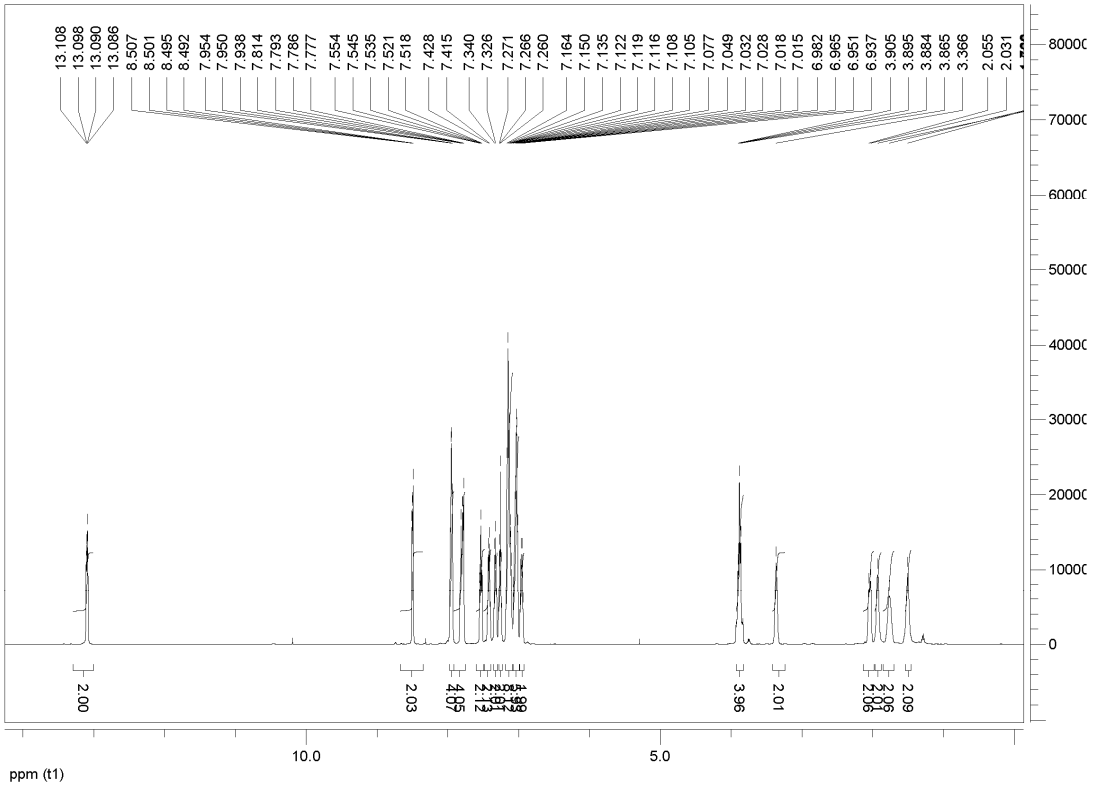
150
100
50
ppm (t1)


N
N
OH
HO
Bn
Bn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7.028
7.018
7.015
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6.965
6.951
6.937
3.905
3.895
3.884
3.865
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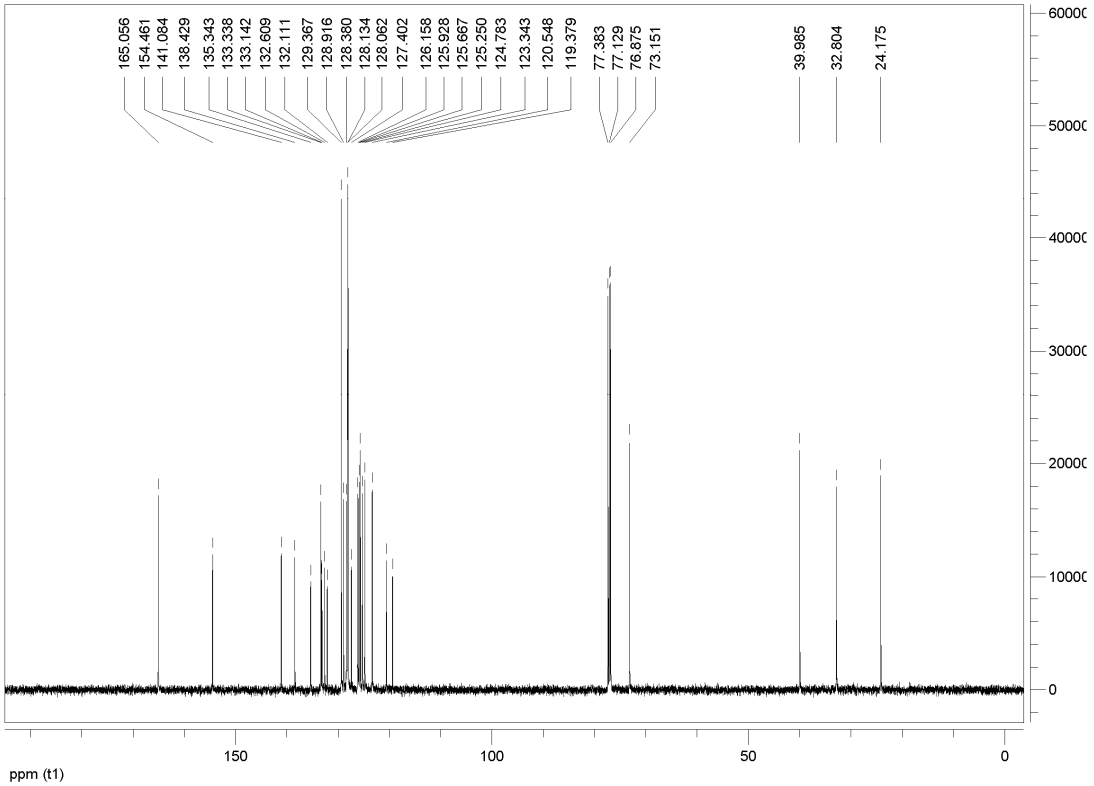
2.031
2.00
2.03
3.96
2.01
2.09
10.0
5.0
ppm (t1)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133.142
132.609
132.111
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128.380
128.134
128.062
127.402
126.158
125.928
125.667
125.250
124.783
123.343
120.548
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77.129
76.875
73.151
39.985
32.804
24.175
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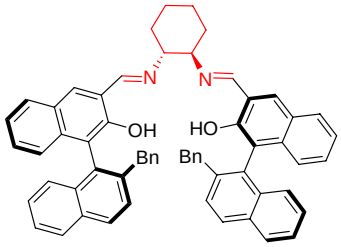
50
0
ppm (t1)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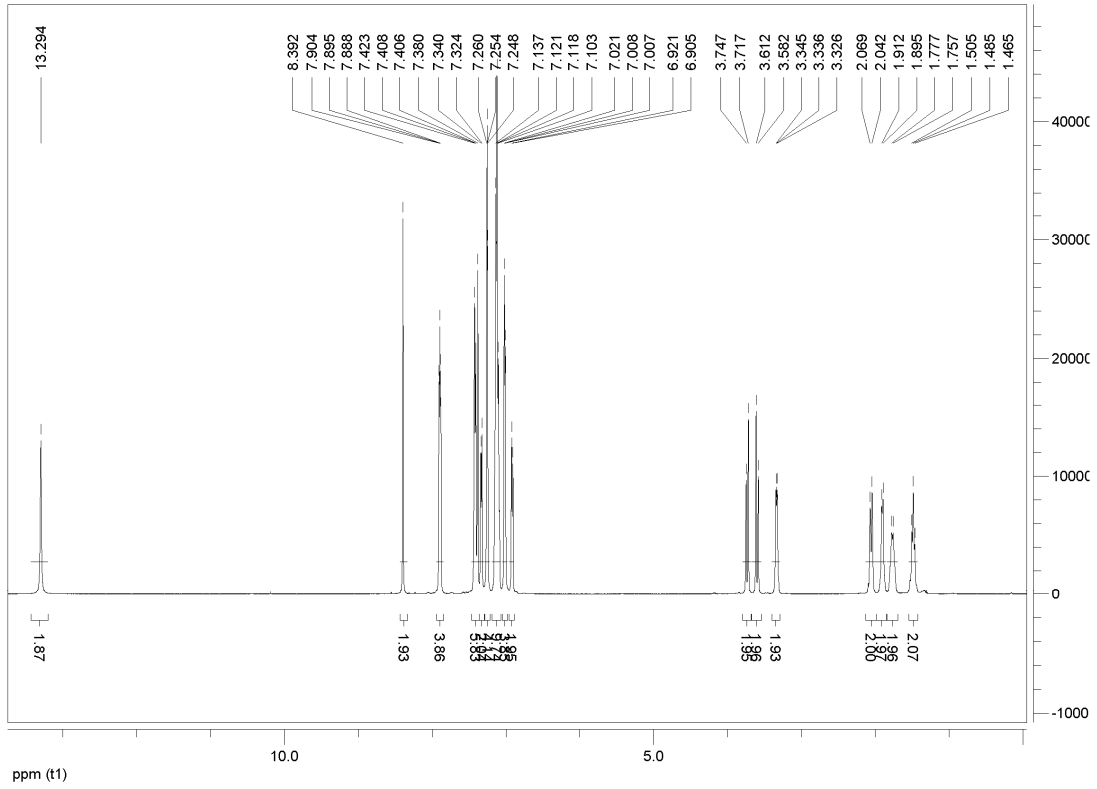
N
OH
HO
Bn
Bn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7.895
7.888
7.423
7.408
7.406
7.380
7.340
7.324
7.260
7.254
7.248
7.137
7.121
7.118
7.103
7.021
7.008
7.007
6.921
6.905
3.747
3.717
3.612
3.582
3.345
3.336
3.326
2.069
2.042
1.912
1.895
1.777
1.757
1.505
1.485
1.465
1.87
1.93
3.86
1.96
1.93
2.07
40000
30000
20000
10000
0
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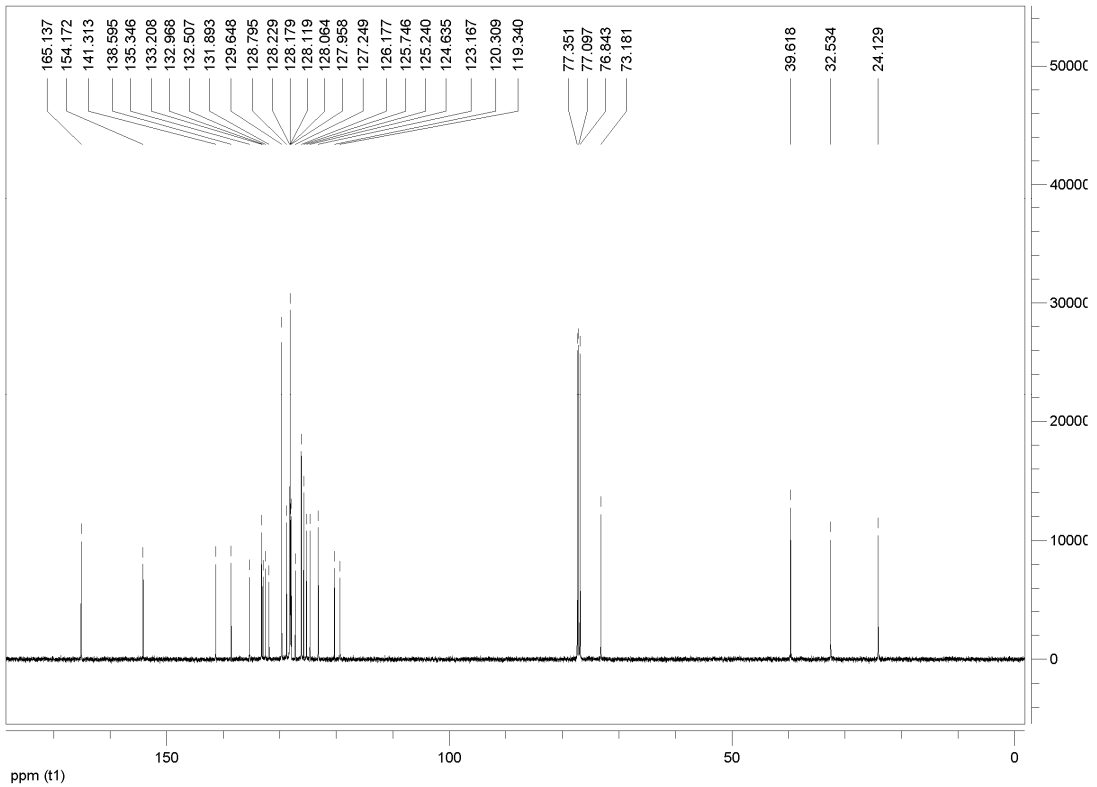
10.0
5.0
ppm (t1)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132.968
132.507
131.893
129.648
128.795
128.229
128.179
128.119
128.064
127.958
127.249
126.177
125.746
125.240
124.635
123.167
120.309
119.340
77.351
77.097
76.843
73.181
39.618
32.534
24.129
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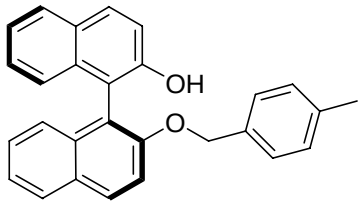
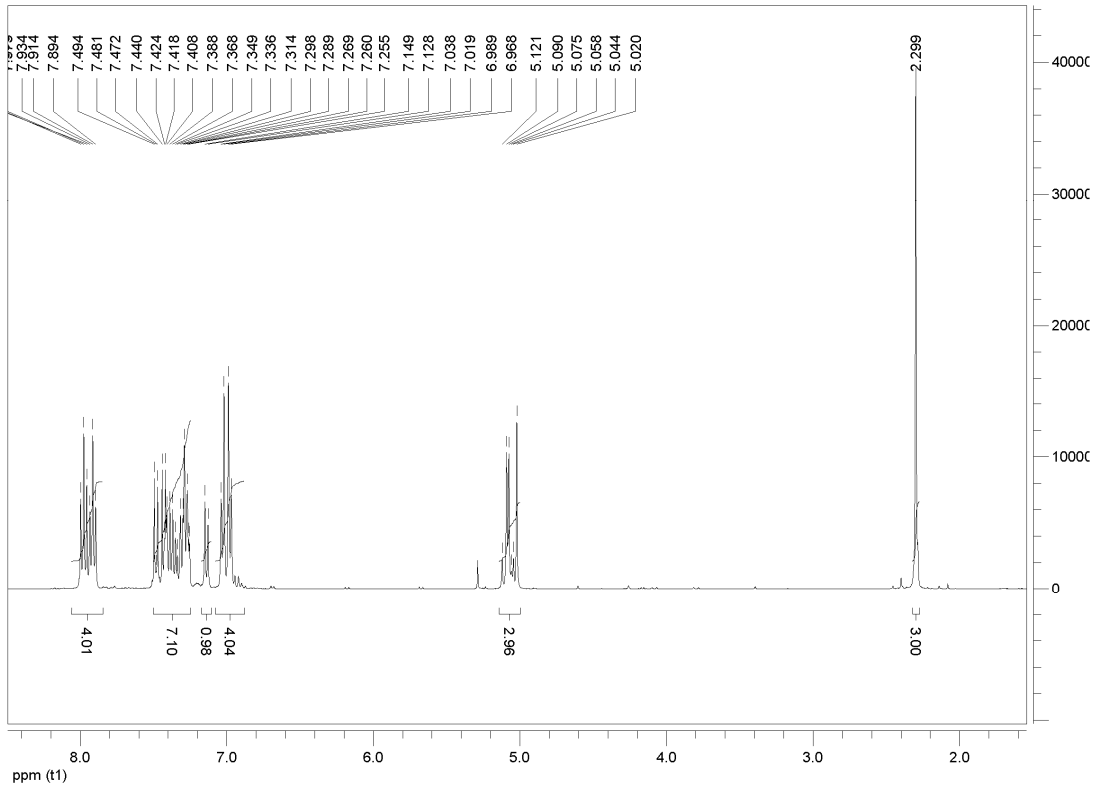
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)


OH
O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7.481
7.472
7.440
7.424
7.418
7.408
7.388
7.368
7.349
7.336
7.314
7.298
7.289
7.269
7.260
7.255
7.149
7.128
7.038
7.019
6.989
6.968
5.121
5.090
5.075
5.058
5.044
5.020
2.299
4.01
7.10
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4.04
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3.00
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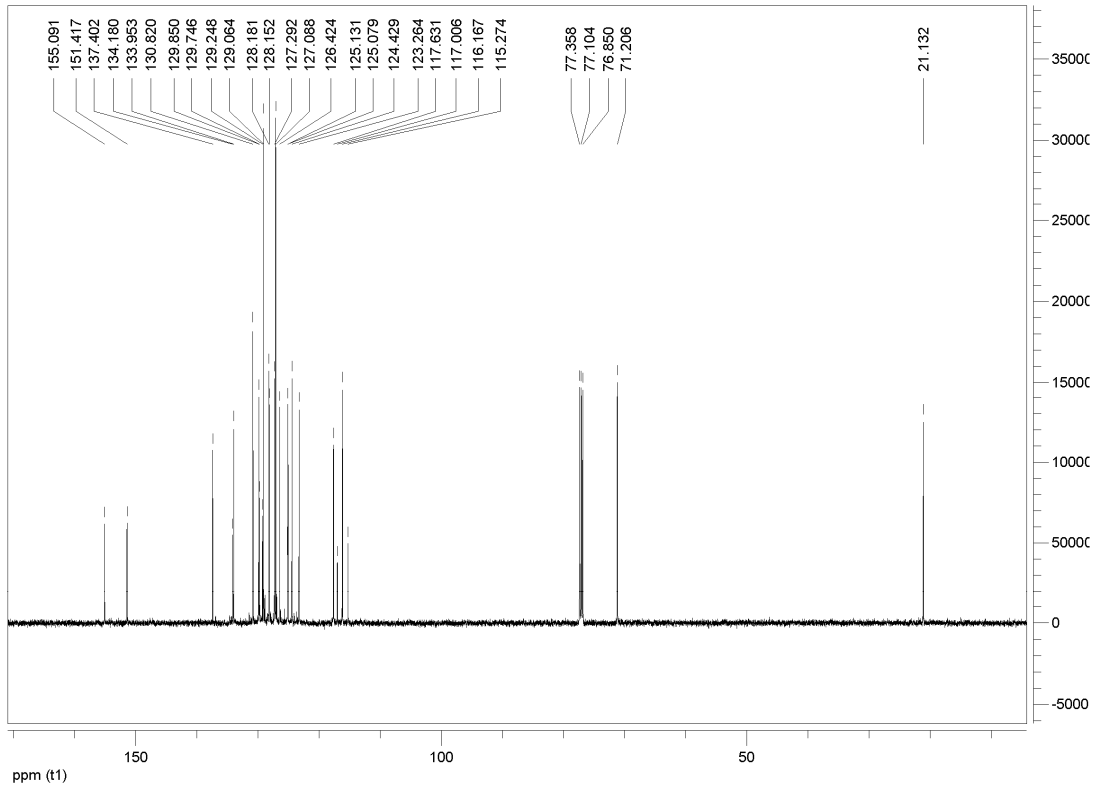
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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129.064
128.181
128.152
127.292
127.088
126.424
125.131
125.079
124.429
123.264
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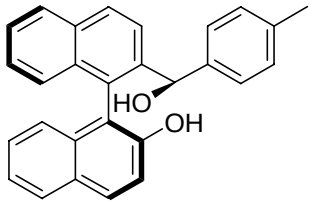
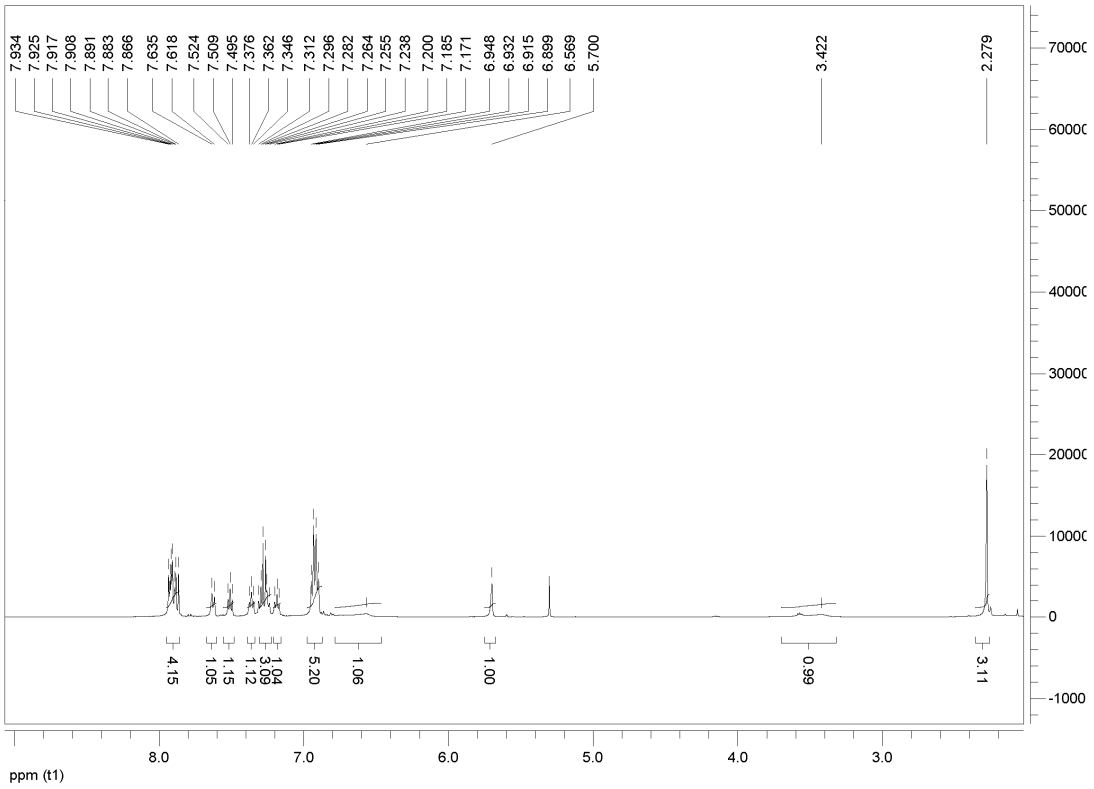
150
100
50
ppm (t1)


HO
OH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7.908
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7.883
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7.635
7.618
7.524
7.509
7.495
7.376
7.362
7.346
7.312
7.296
7.282
7.264
7.255
7.238
7.200
7.185
7.171
6.948
6.932
6.915
6.899
6.569
5.700
3.422
2.279
4.15
1.05
1.15
1.12
3.09
1.04
5.20
1.06
1.00
0.69
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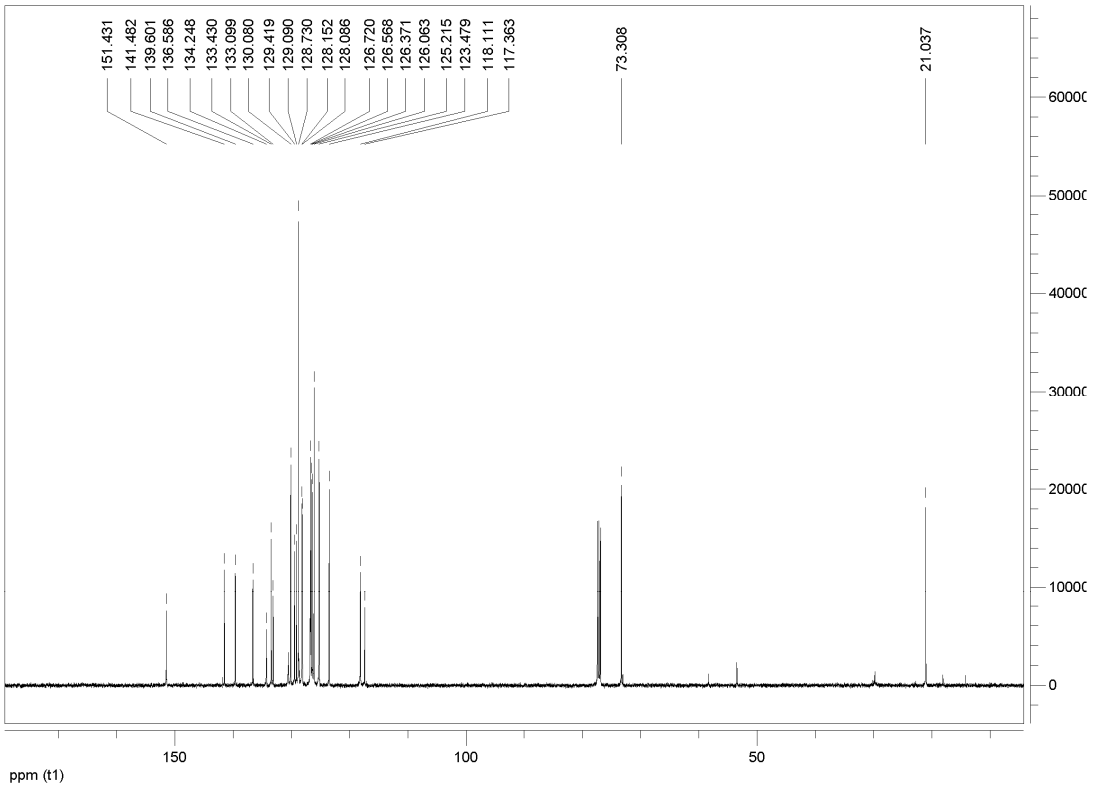
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)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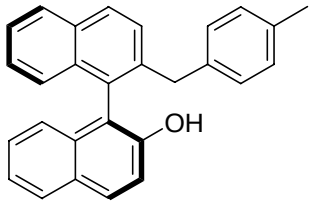
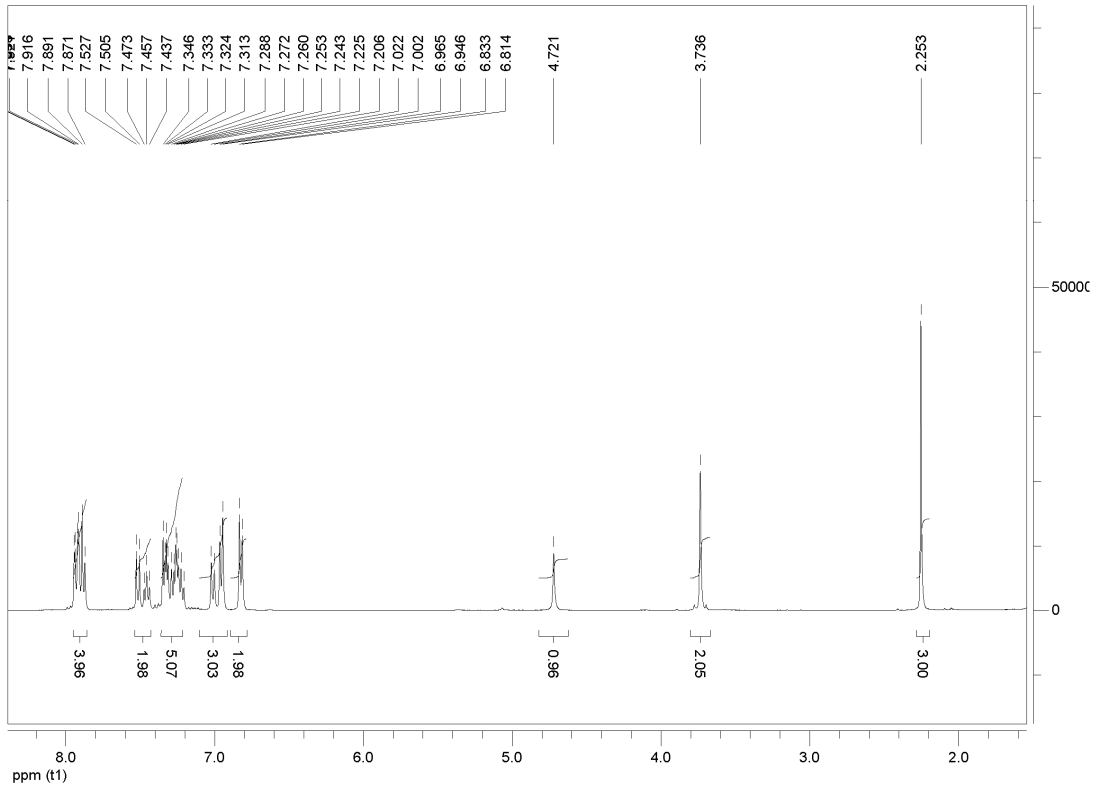
133.430
133.099
130.080
129.419
129.090
128.730
128.152
128.086
126.720
126.568
126.371
126.063
125.215
123.479
118.111
117.363
73.308
21.037
150
100
50
ppm (t1)


OH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7.473
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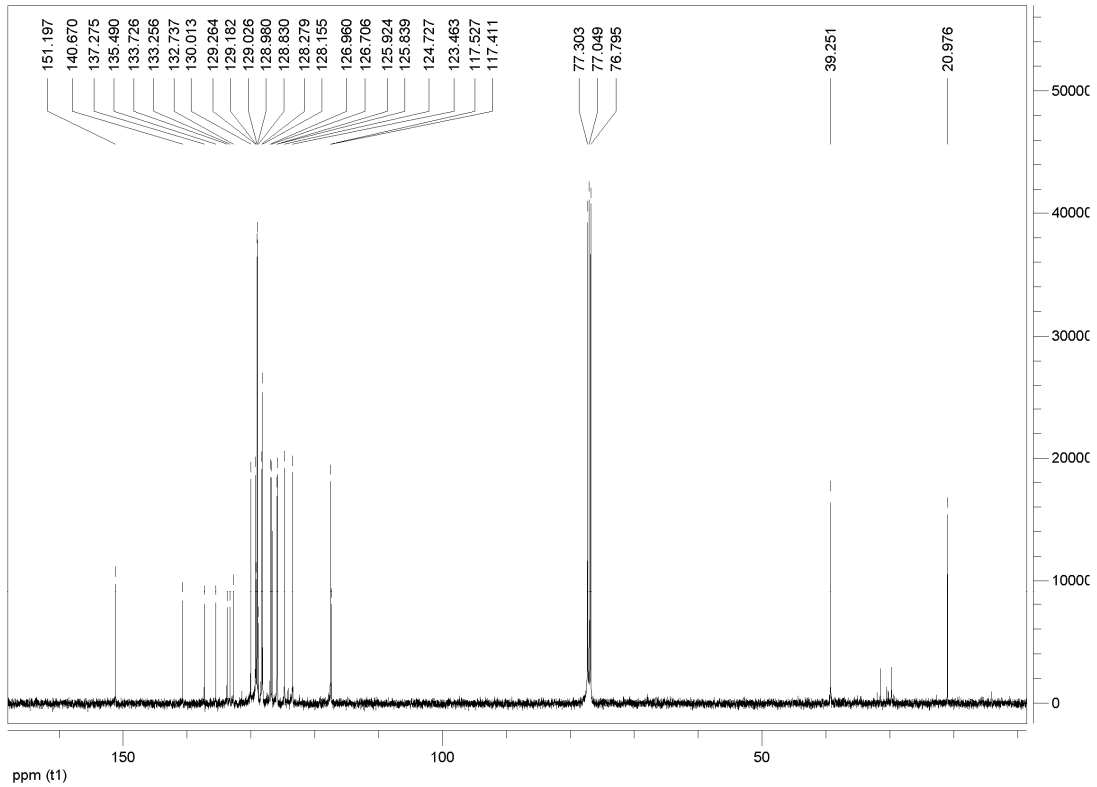
7.437
7.346
7.333
7.324
7.313
7.288
7.272
7.260
7.253
7.243
7.225
7.206
7.022
7.002
6.965
6.946
6.833
6.814
4.721
3.736
2.253
3.96
1.98
5.07
3.03
1.98
0.96
2.05
3.00
50000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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133.256
132.737
130.013
129.264
129.182
129.026
128.980
128.830
128.279
128.155
126.960
126.706
125.924
125.839
124.727
123.463
117.527
117.411
77.303
77.049
76.795
39.251
20.976
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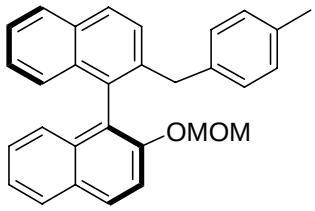
30000
20000
10000
0
150
100
50
ppm (t1)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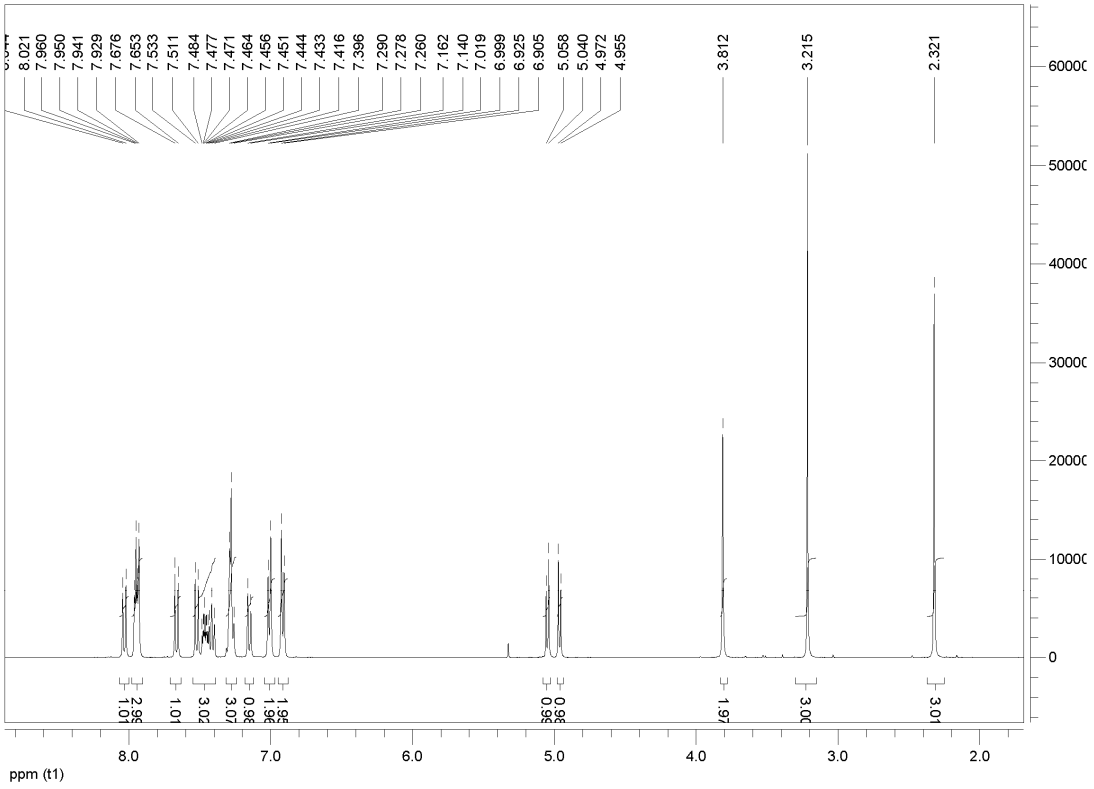
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7.676
7.653
7.533
7.511
7.484
7.477
7.471
7.464
7.456
7.451
7.444
7.433
7.416
7.396
7.290
7.278
7.260
7.162
7.140
7.019
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5.040
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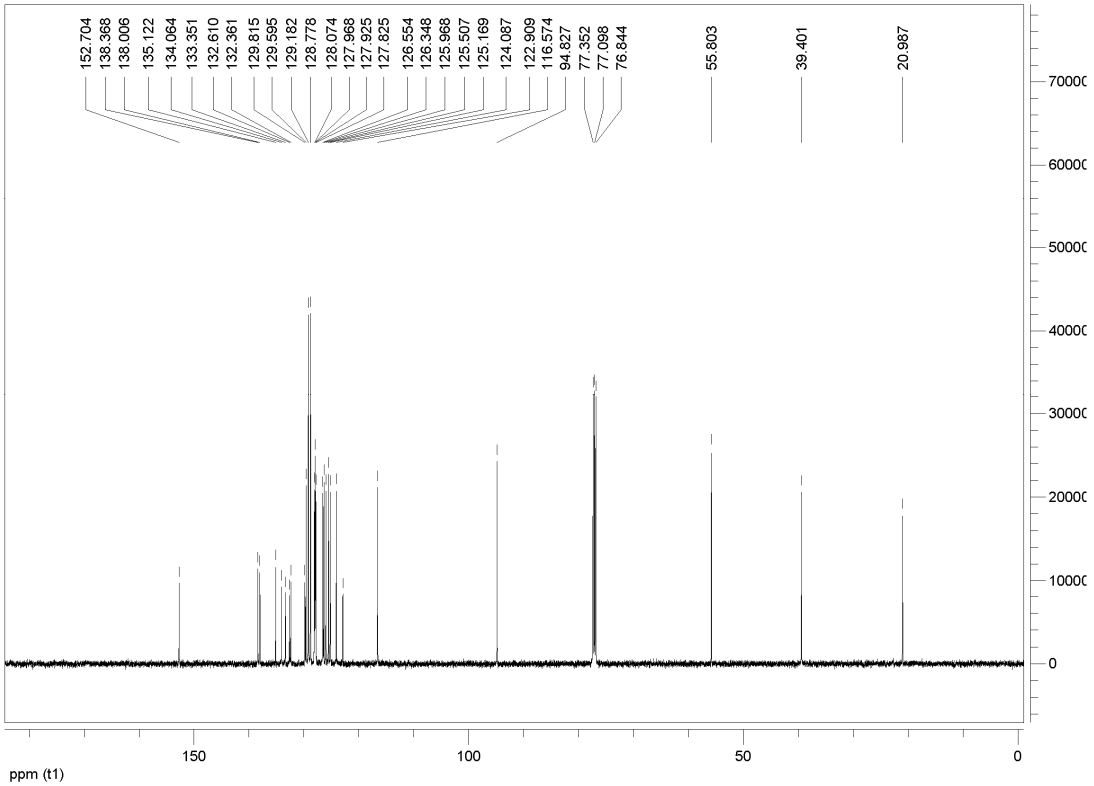
ppm (t1)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133.351
132.610
132.361
129.815
129.595
129.182
128.778
128.074
127.968
127.925
127.825
126.554
126.348
125.968
125.507
125.169
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116.574
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77.352
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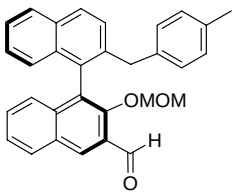
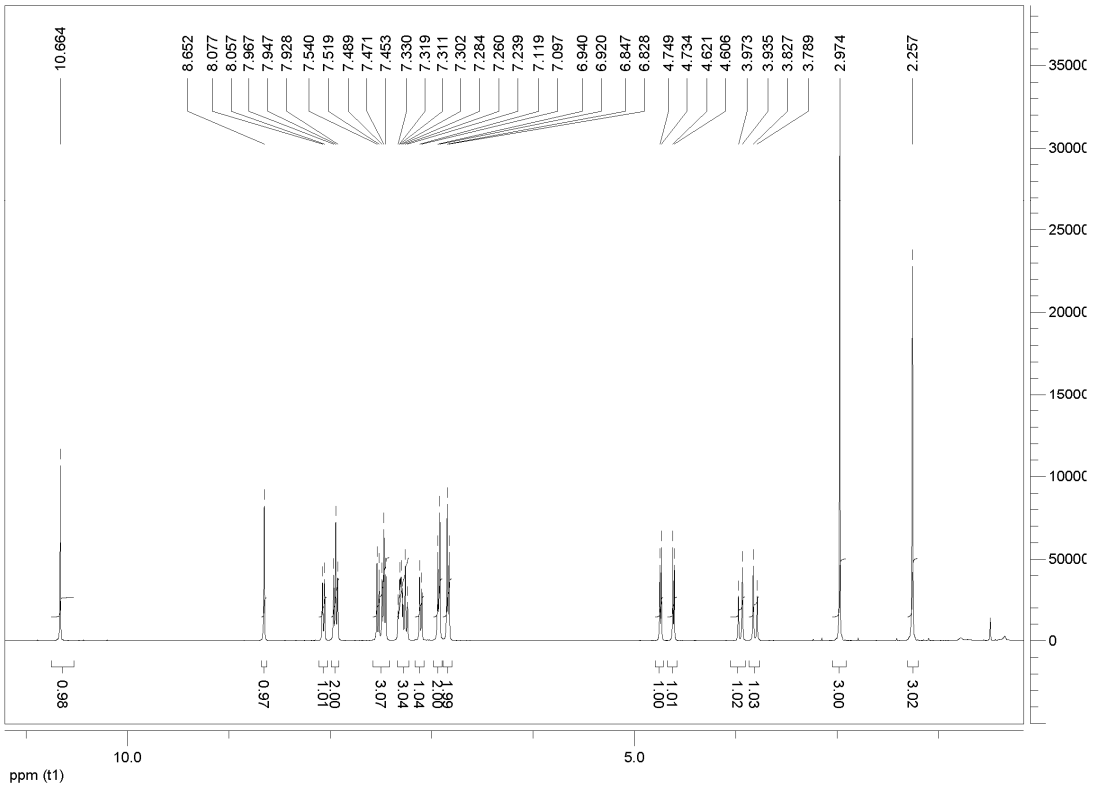
55.803
39.401
20.987
ppm (t1)


OMOM
H
O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7.928
7.540
7.519
7.489
7.471
7.453
7.330
7.319
7.311
7.302
7.284
7.260
7.239
7.119
7.097
6.940
6.920
6.847
6.828
4.749
4.734
4.621
4.606
3.973
3.935
3.827
3.789
2.974
2.257
0.98
0.97
2.00
1.01
3.07
3.04
1.04
1.99
2.00
1.01
1.00
1.02
1.03
3.00
3.02
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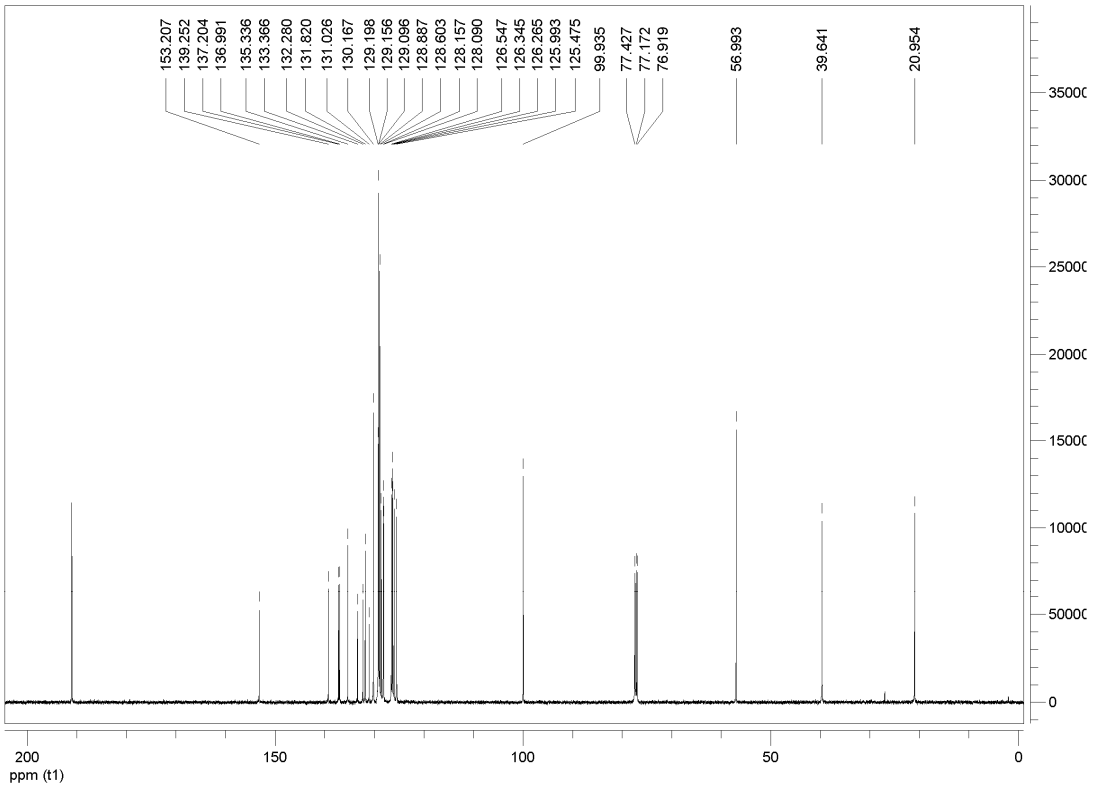
5.0
ppm (t1)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131.820
131.026
130.167
129.198
129.156
129.096
128.887
128.603
128.157
128.090
126.547
126.345
126.265
125.993
125.475
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77.172
76.919
56.993
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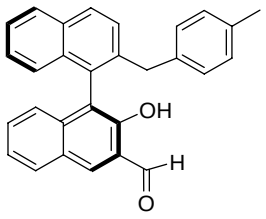
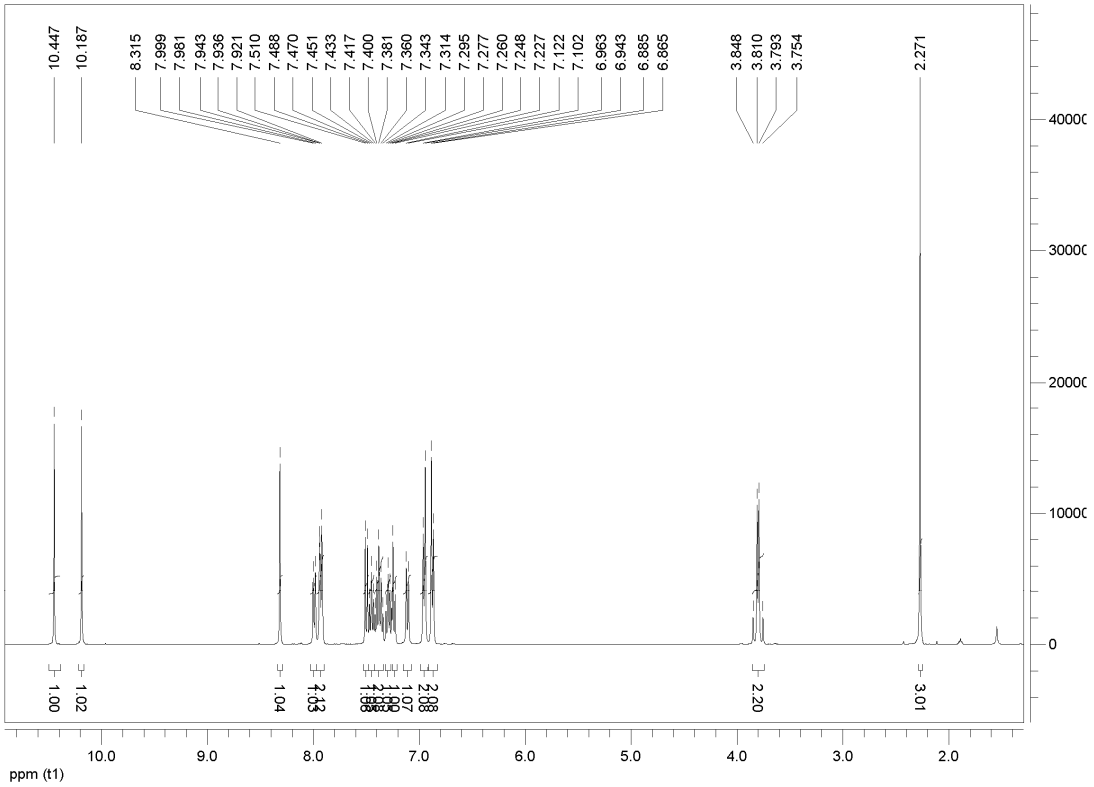
200
150
100
50
0
ppm (t1)


OH
H
O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7.921
7.510
7.488
7.470
7.451
7.433
7.417
7.400
7.381
7.360
7.343
7.314
7.295
7.277
7.260
7.248
7.227
7.122
7.102
6.963
6.943
6.885
6.865
3.848
3.810
3.793
3.754
2.271
1.00
1.02
1.04
2.13
2.08
1.07
2.08
2.20
3.01
40000
30000
20000
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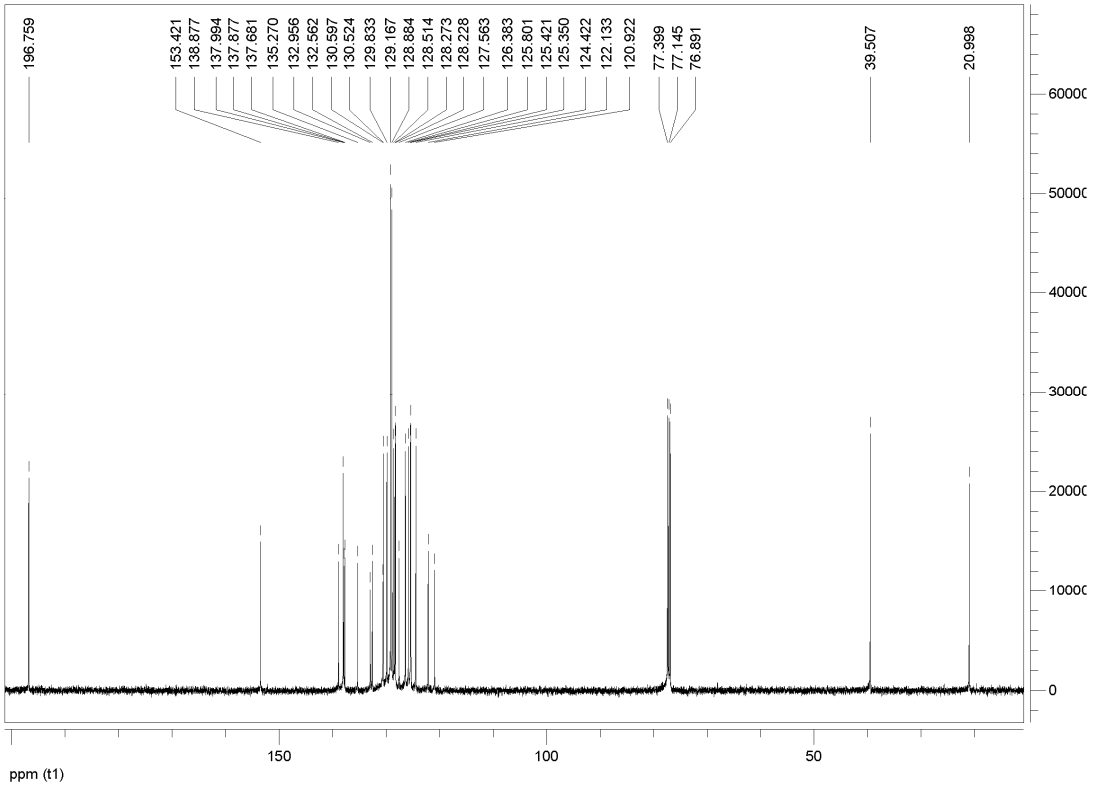
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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137.681
135.270
132.956
132.562
130.597
130.524
129.833
129.167
128.884
128.514
128.273
128.228
127.563
126.383
125.801
125.421
125.350
124.422
122.133
120.922
77.399
77.145
76.891
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20.998
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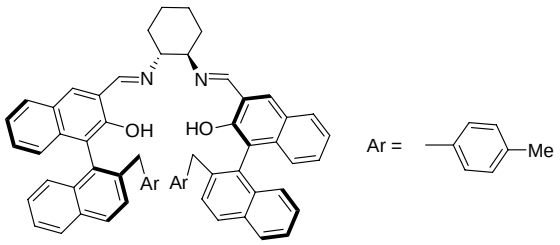
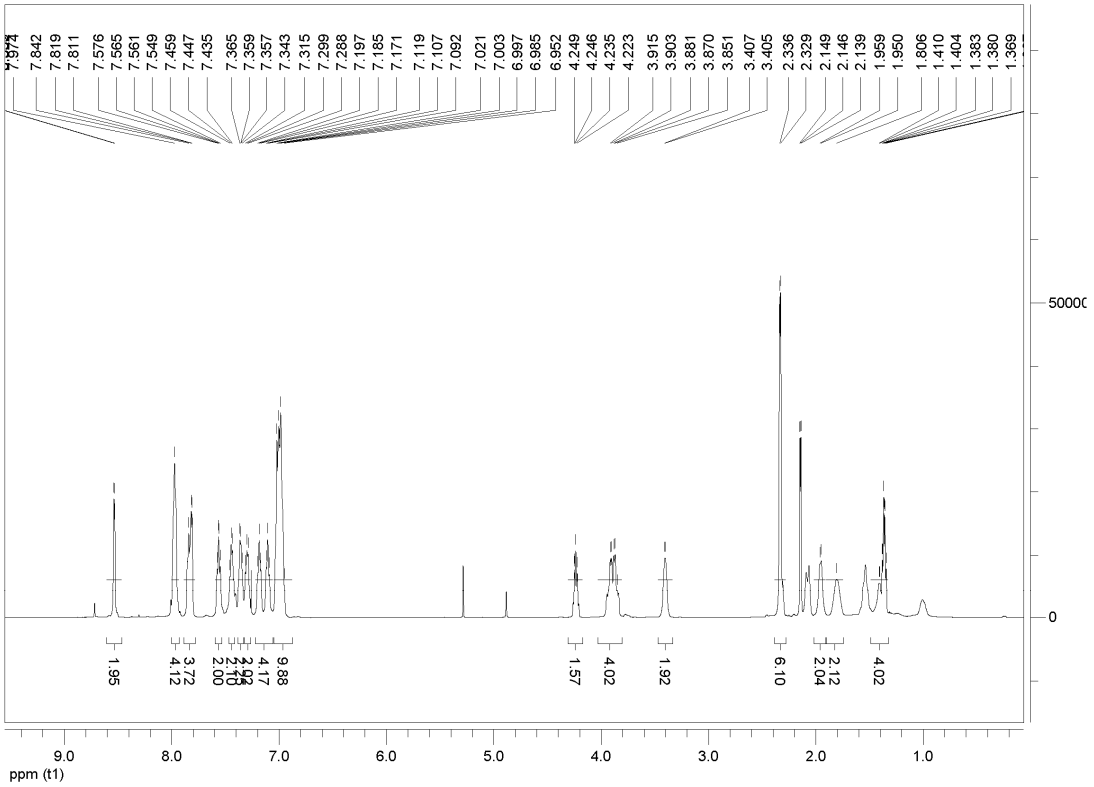
50000
40000
30000
20000
10000
0
150
100
50
ppm (t1)


N
N
OH
HO
Ar
Ar
Ar =
Me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7.549
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7.447
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7.365
7.359
7.357
7.343
7.315
7.299
7.288
7.197
7.185
7.171
7.119
7.107
7.092
7.021
7.003
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6.985
6.952
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4.246
4.235
4.223
3.915
3.903
3.881
3.870
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3.407
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2.336
2.329
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2.146
2.139
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1.950
1.806
1.410
1.404
1.383
1.380
1.369
1.95
4.12
3.72
2.00
2.10
2.25
2.22
4.17
9.88
1.57
4.02
1.92
6.10
2.04
2.12
4.02
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7.0
6.0
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3.0
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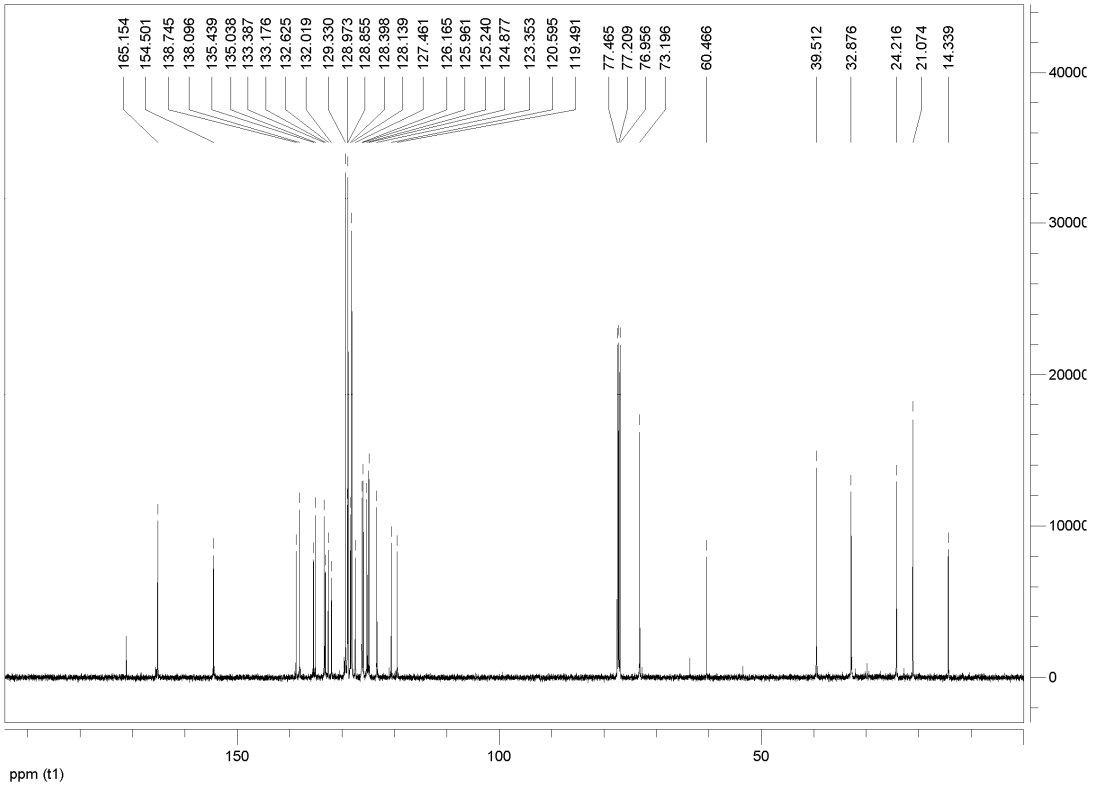
1.0
ppm (t1)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132.019
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128.139
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126.165
125.961
125.240
124.877
123.353
120.595
119.491
77.465
77.209
76.956
73.196
60.466
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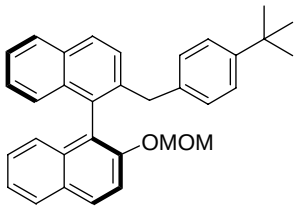
100
50
ppm (t1)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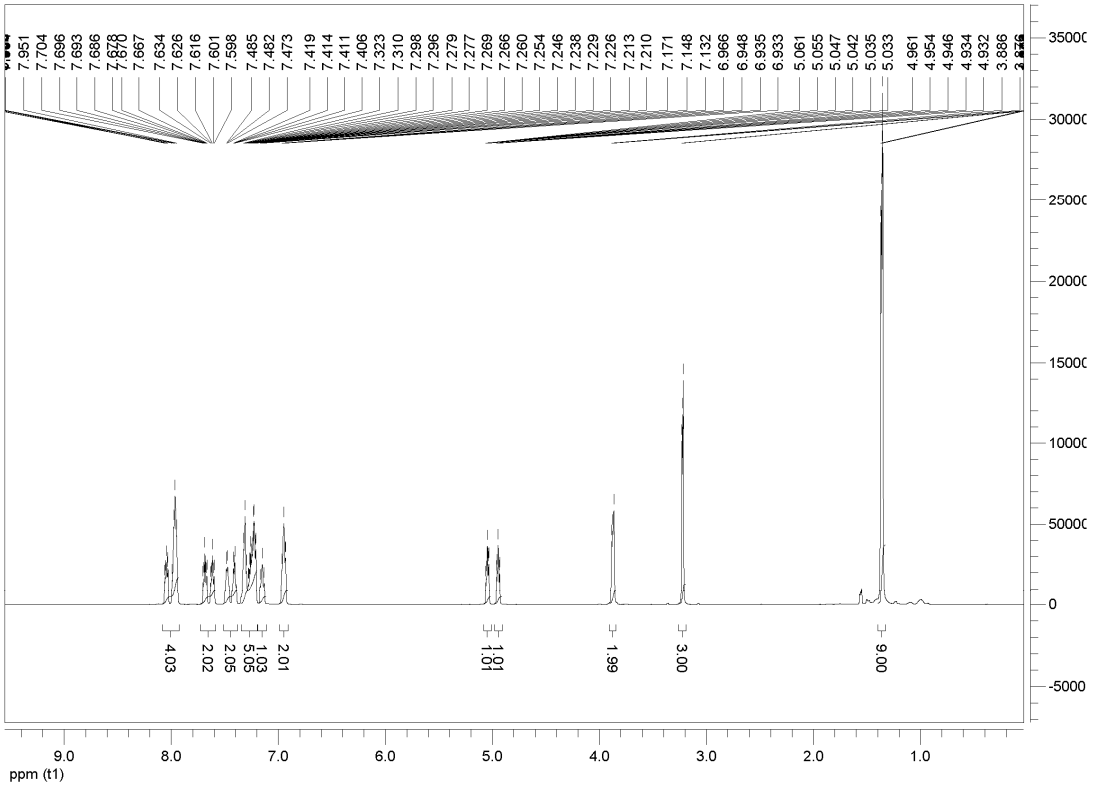
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7.473
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7.411
7.406
7.323
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7.254
7.246
7.238
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7.213
7.210
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7.148
7.132
6.966
6.948
6.935
6.933
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5.055
5.047
5.042
5.035
5.033
4.961
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4.946
4.934
4.932
3.886
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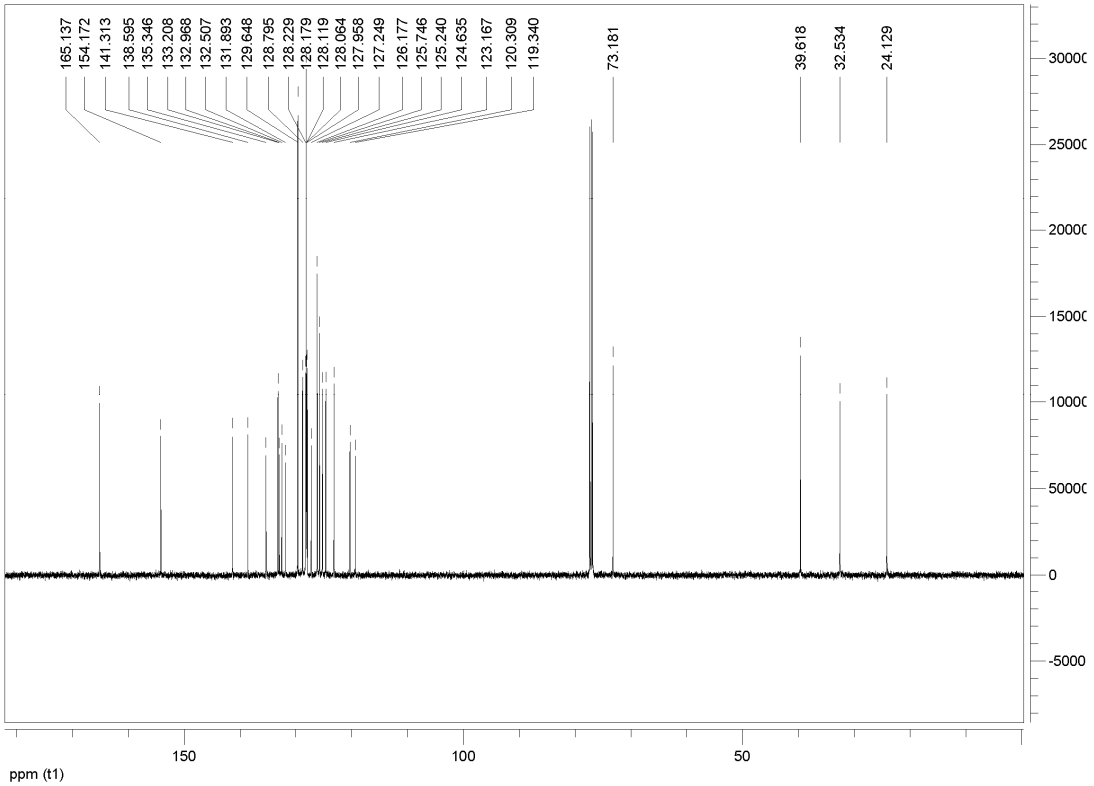
5.05
1.03
2.01
1.01
1.01
1.99
3.00
9.00
ppm (t1)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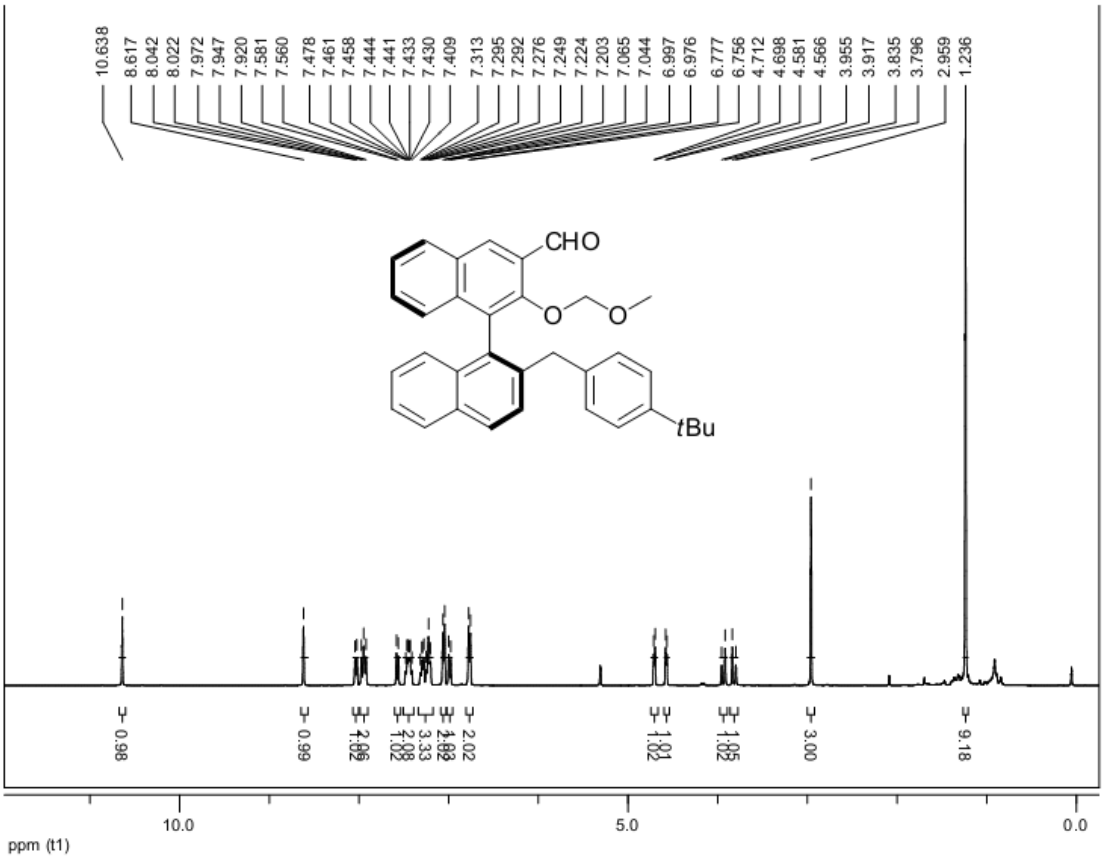
129.648
128.795
128.229
128.179
128.119
128.064
127.958
127.249
126.177
125.746
125.240
124.635
123.167
120.309
119.340
73.181
39.618
32.534
24.129
ppm (t1)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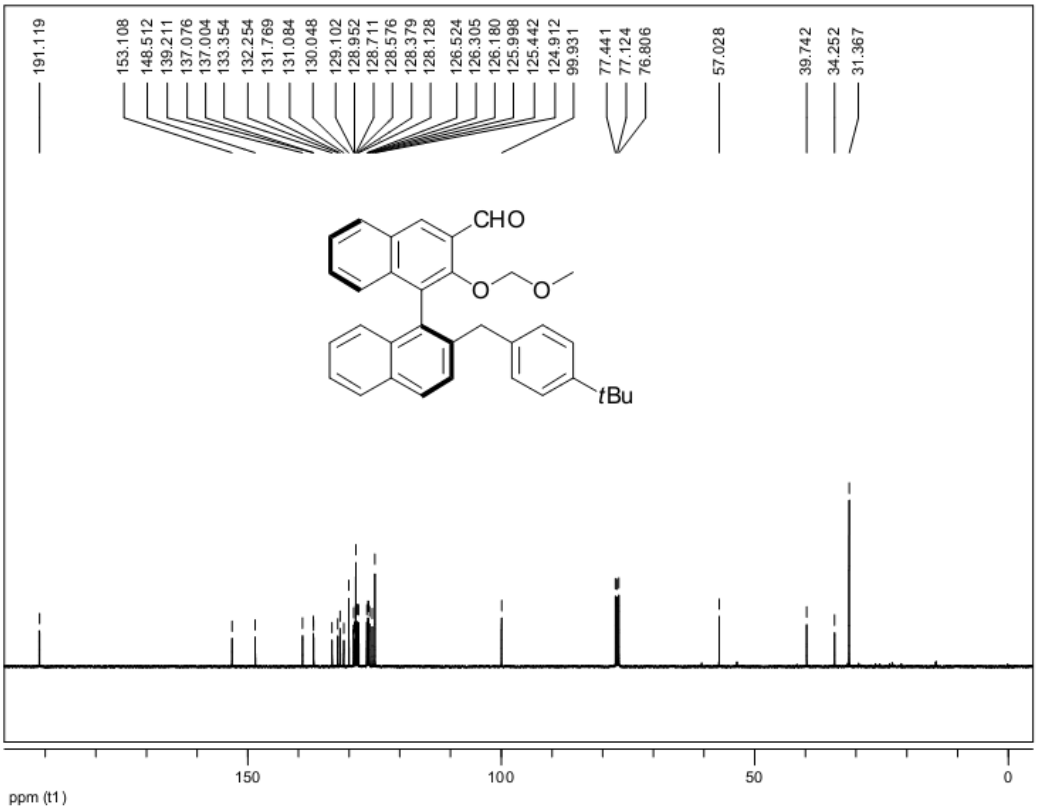
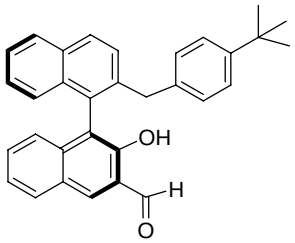
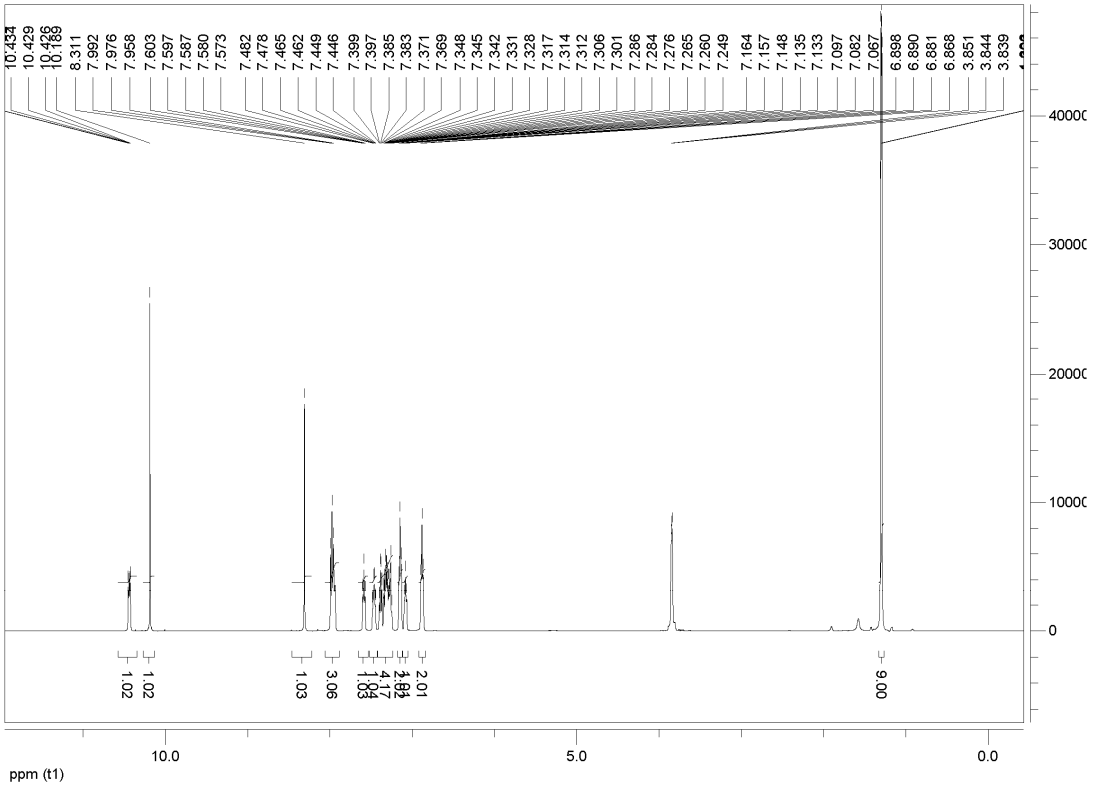
8.617
8.042
8.022
7.972
7.947
7.920
7.581
7.560
7.478
7.461
7.458
7.444
7.441
7.433
7.430
7.409
7.313
7.295
7.292
7.276
7.249
7.224
7.203
7.065
7.044
6.997
6.976
6.777
6.756
4.712
4.698
4.581
4.566
3.955
3.917
3.835
3.796
2.959
1.236
CHO
O
O
tBu
0.98
0.99
2.02
1.01
1.05
3.00
9.18
10.0
5.0
0.0
ppm (t1)


191.119
153.108
148.512
139.211
137.076
137.004
133.354
132.254
131.769
131.084
130.048
129.102
128.952
128.711
128.576
128.379
128.128
126.524
126.305
126.180
125.998
125.442
124.912
99.931
77.441
77.124
76.806
57.028
39.742
34.252
31.367
CHO
O
O
tBu
150
100
50
0
ppm (t1)


OH
H
O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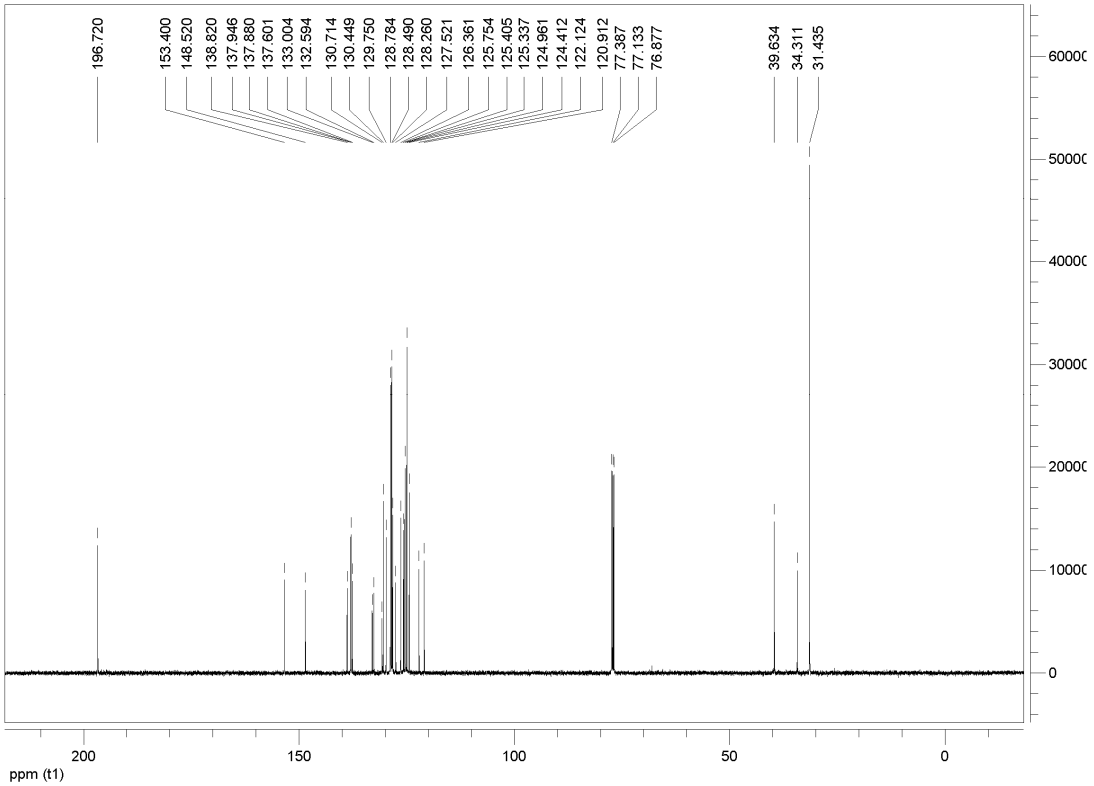
10.429
10.426
10.189
8.311
7.992
7.976
7.958
7.603
7.597
7.587
7.580
7.573
7.482
7.478
7.465
7.462
7.449
7.446
7.399
7.397
7.385
7.383
7.371
7.369
7.348
7.345
7.342
7.331
7.328
7.317
7.314
7.312
7.306
7.301
7.286
7.284
7.276
7.265
7.260
7.249
7.164
7.157
7.148
7.135
7.133
7.097
7.082
7.067
6.898
6.890
6.881
6.868
3.851
3.844
3.839
1.02
1.02
1.03
3.06
6.00
2.01
40000
30000
20000
10000
0
10.0
5.0
0.0
ppm (t1)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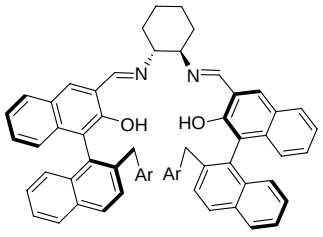
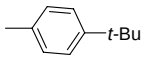
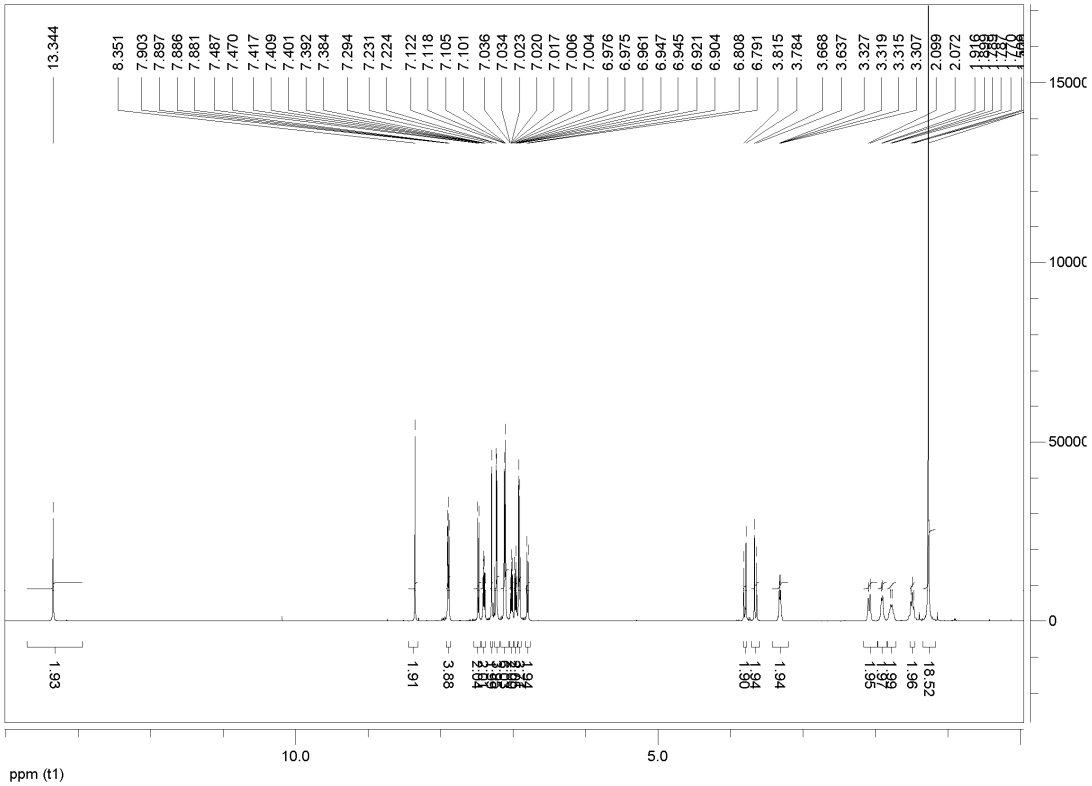
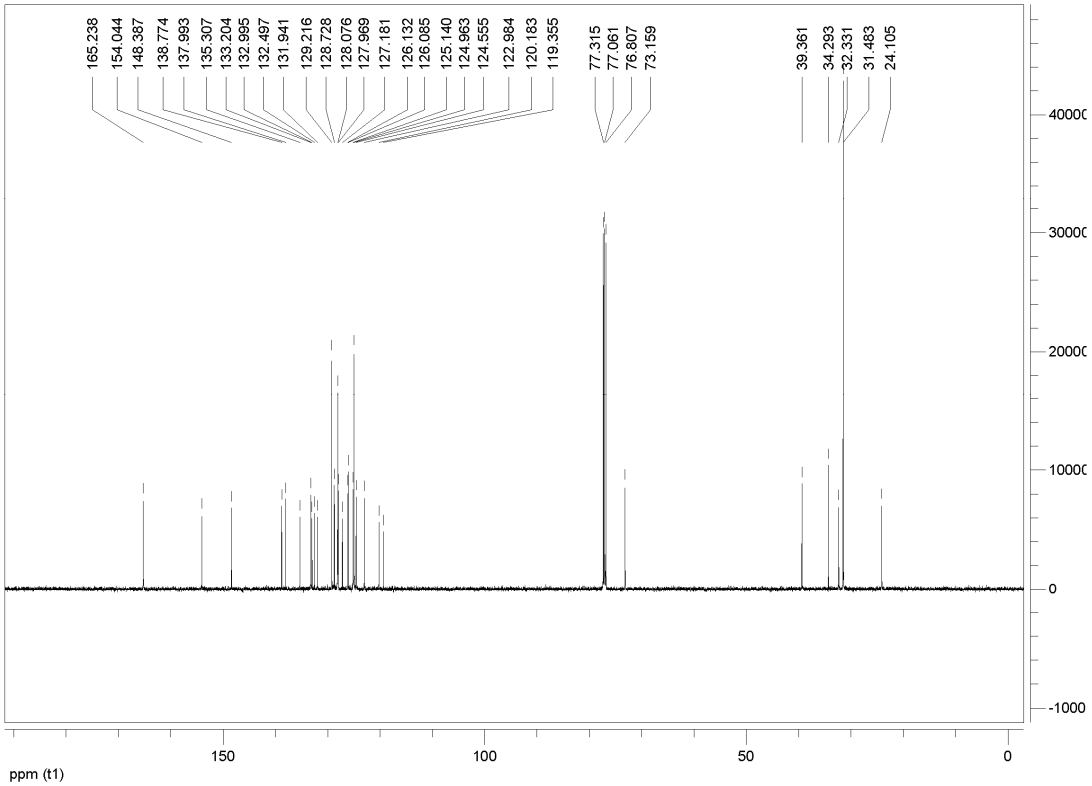
153.400
148.520
138.820
137.946
137.880
137.601
133.004
132.594
130.714
130.449
129.750
128.784
128.490
128.260
127.521
126.361
125.754
125.405
125.337
124.961
124.412
122.124
120.912
77.387
77.133
76.877
39.634
34.311
31.435
60000
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)


N
N
OH
HO
Ar
Ar

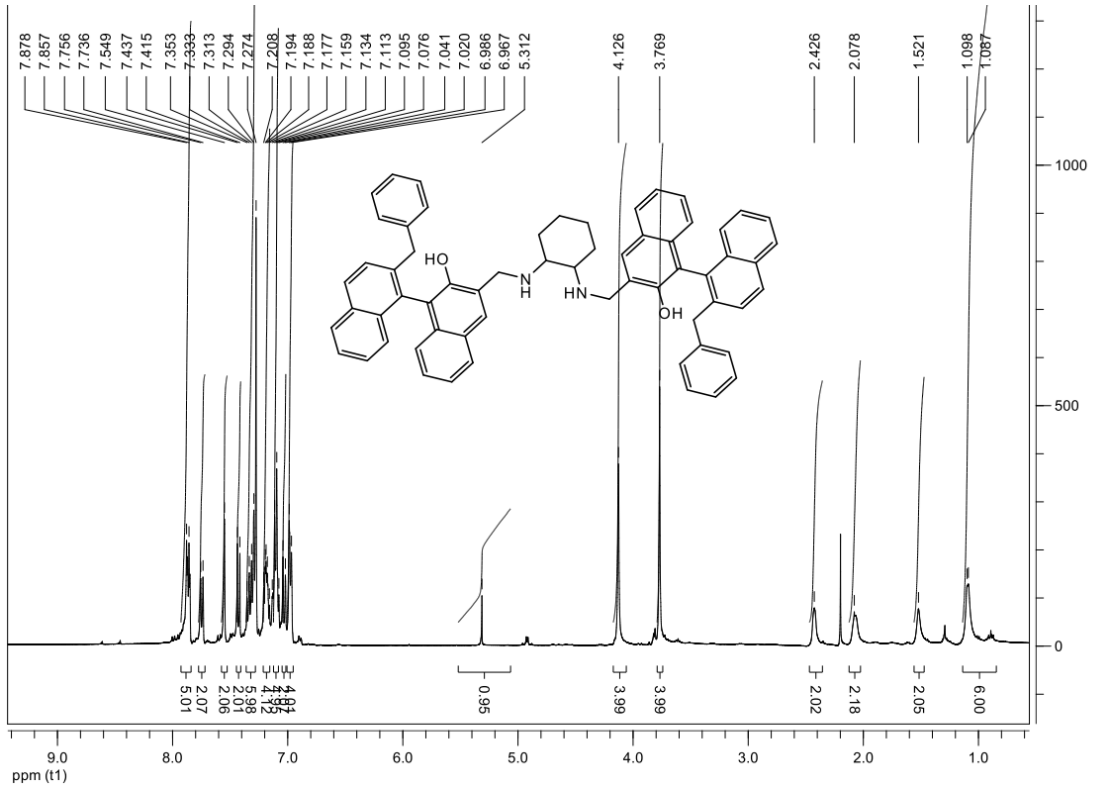
Ar = 
t-Bu


13.344
8.351
7.903
7.897
7.886
7.881
7.487
7.470
7.417
7.409
7.401
7.392
7.384
7.294
7.231
7.224
7.122
7.118
7.105
7.101
7.036
7.034
7.023
7.020
7.017
7.006
7.004
6.976
6.975
6.961
6.947
6.945
6.921
6.904
6.808
6.791
3.815
3.784
3.668
3.637
3.327
3.319
3.315
3.307
2.099
2.072
1.93
1.91
3.88
1.94
1.90
1.94
1.96
1.97
1.96
18.52
15000
10000
5000
0
10.0
5.0
ppm (t1)

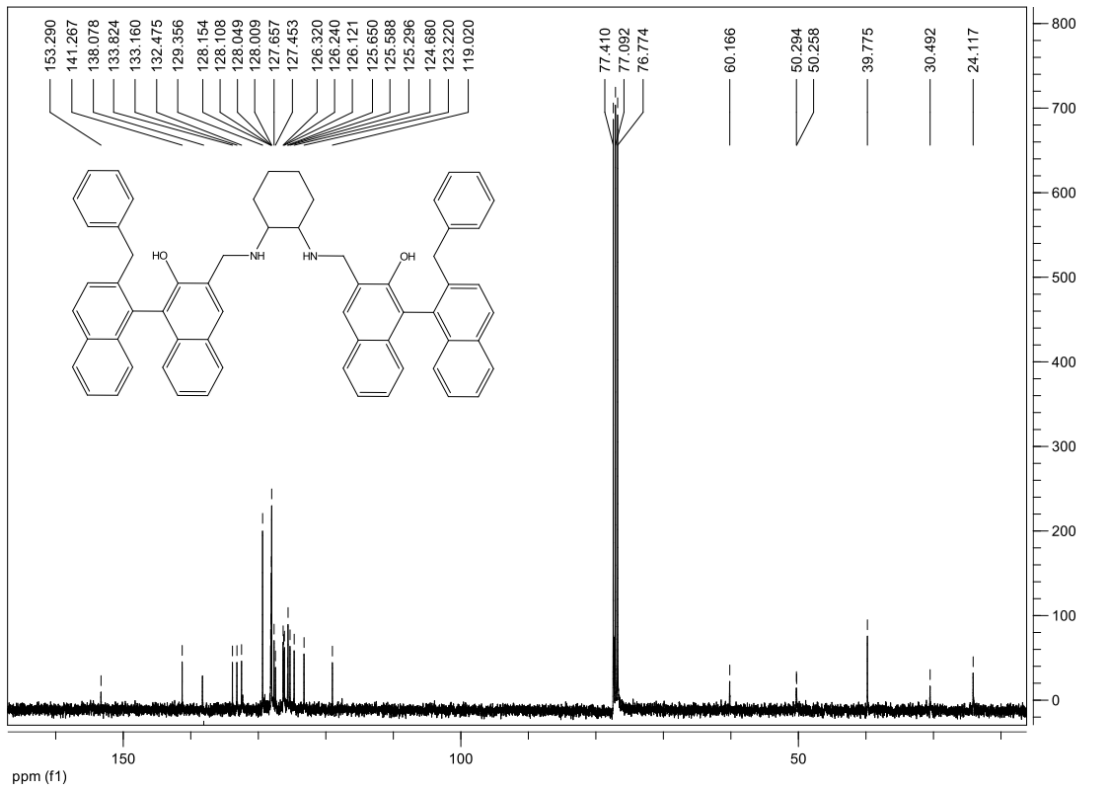

165.238
154.044
148.387
138.774
137.993
135.307
133.204
132.995
132.497
131.941
129.216
128.728
128.076
127.969
127.181
126.132
126.085
125.140
124.963
124.555
122.984
120.183
119.355
77.315
77.061
76.807
73.159
39.361
34.293
32.331
31.483
24.105
40000
30000
20000
10000
0
-1000
150
100
50
0
ppm (t1)

Salan ligand 1:

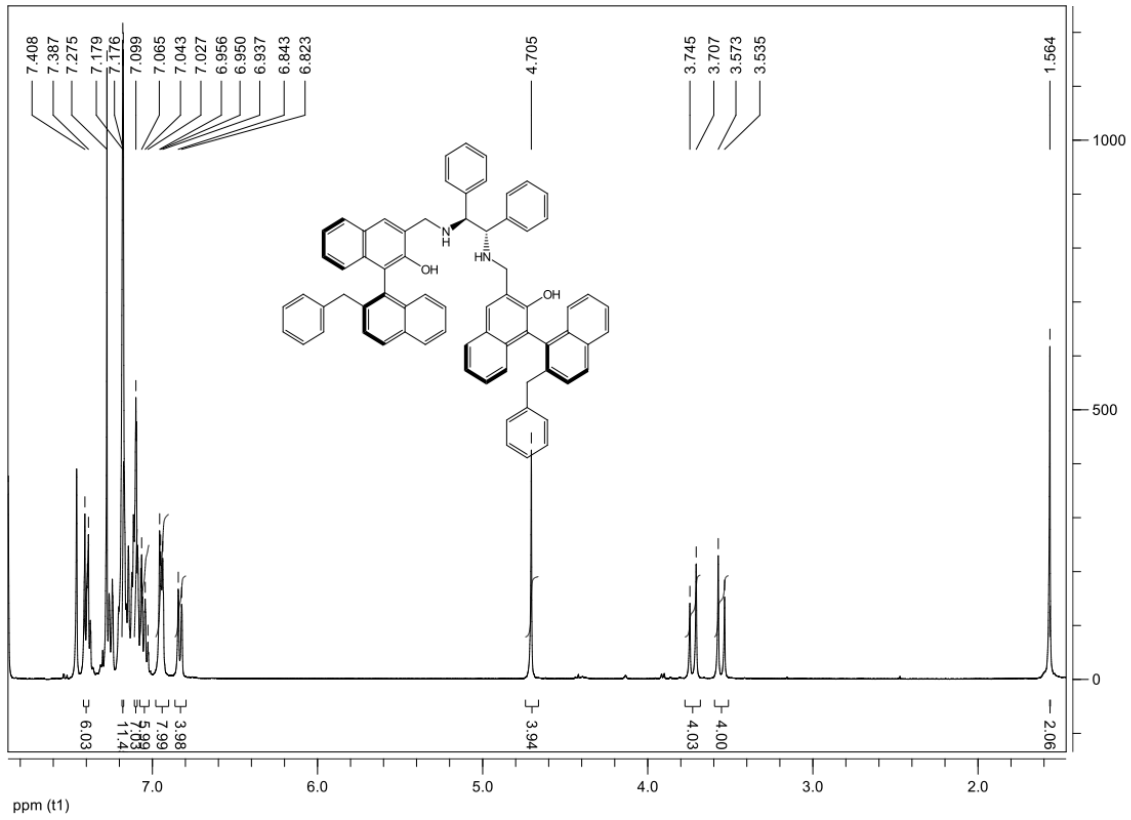
^{1}H NMR



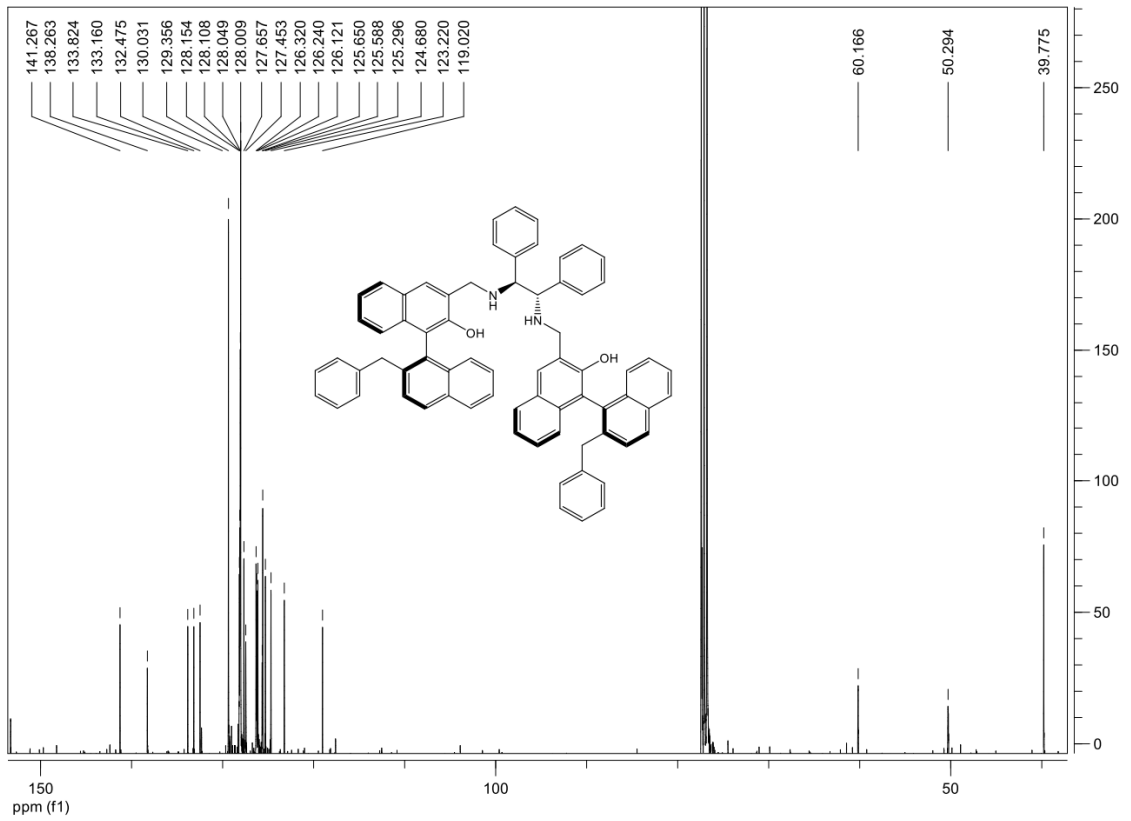
^{13}C NMR



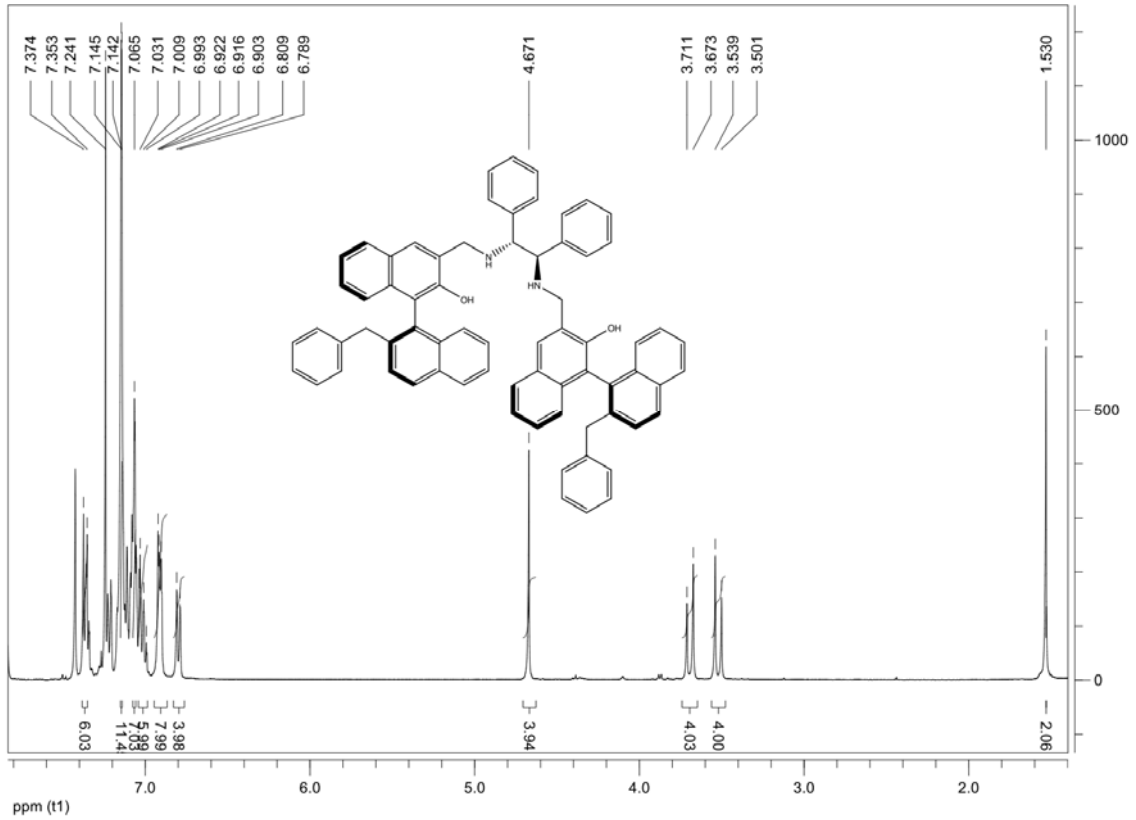
^{1}H NMR



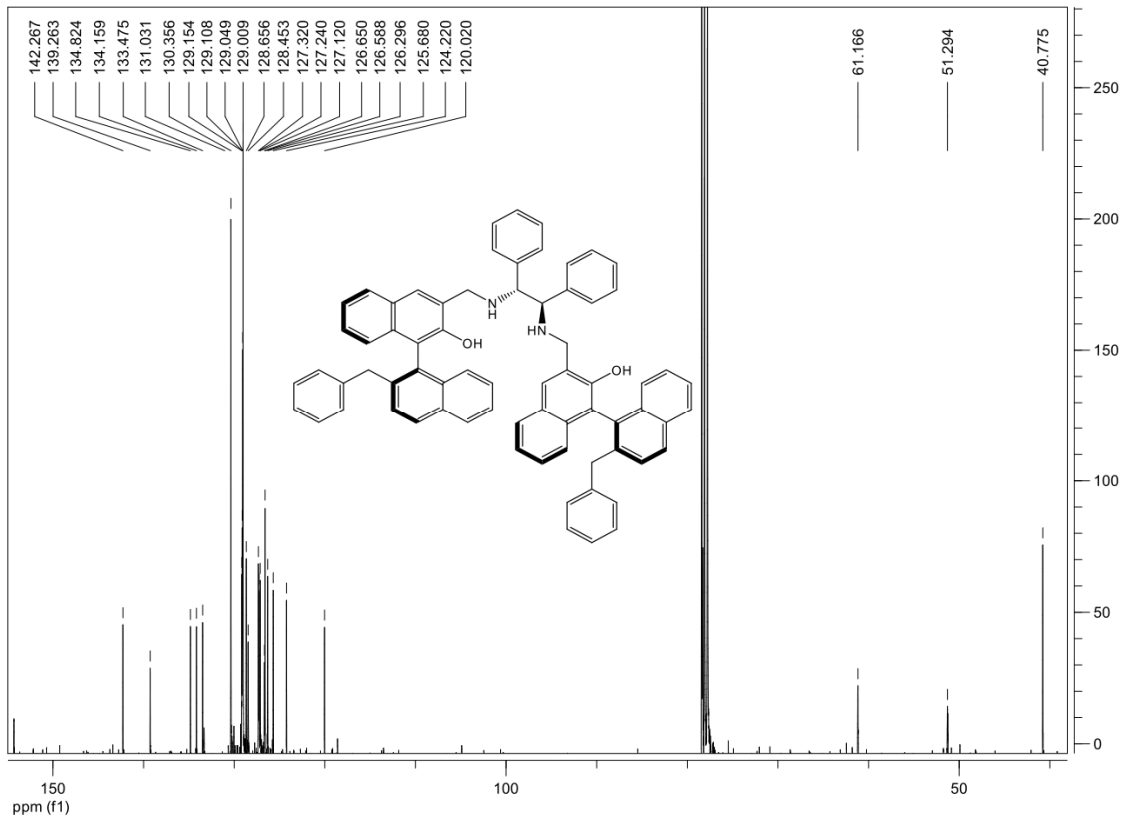
^{13}C NMR

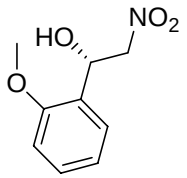


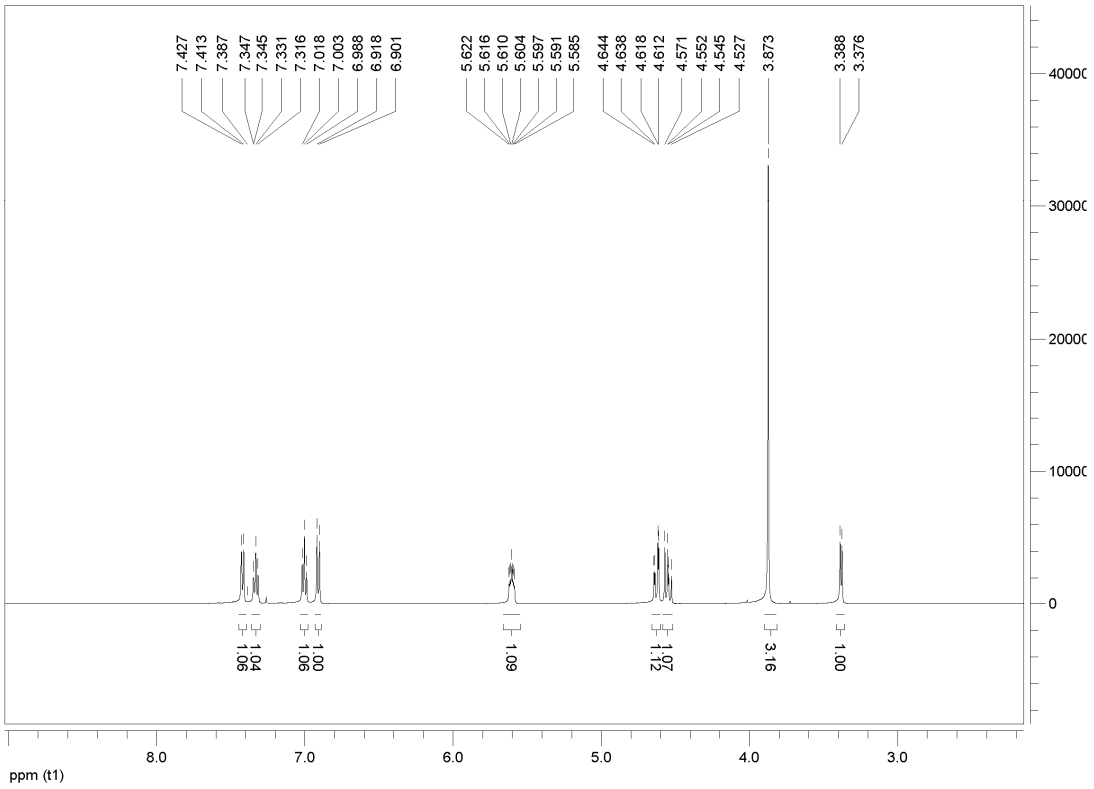
TM salan-3:[1]HNMR



[13]C NMR




HO
NO2
O


7.427
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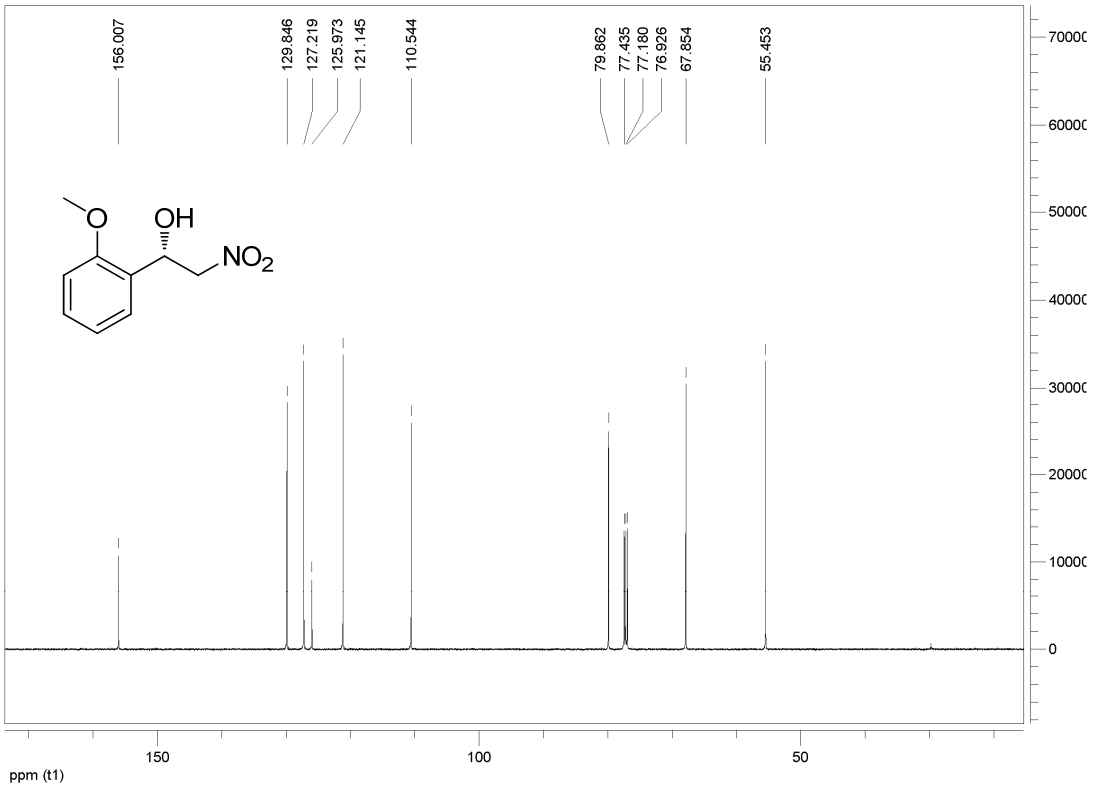
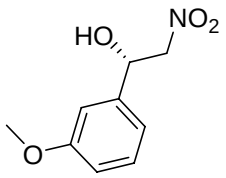
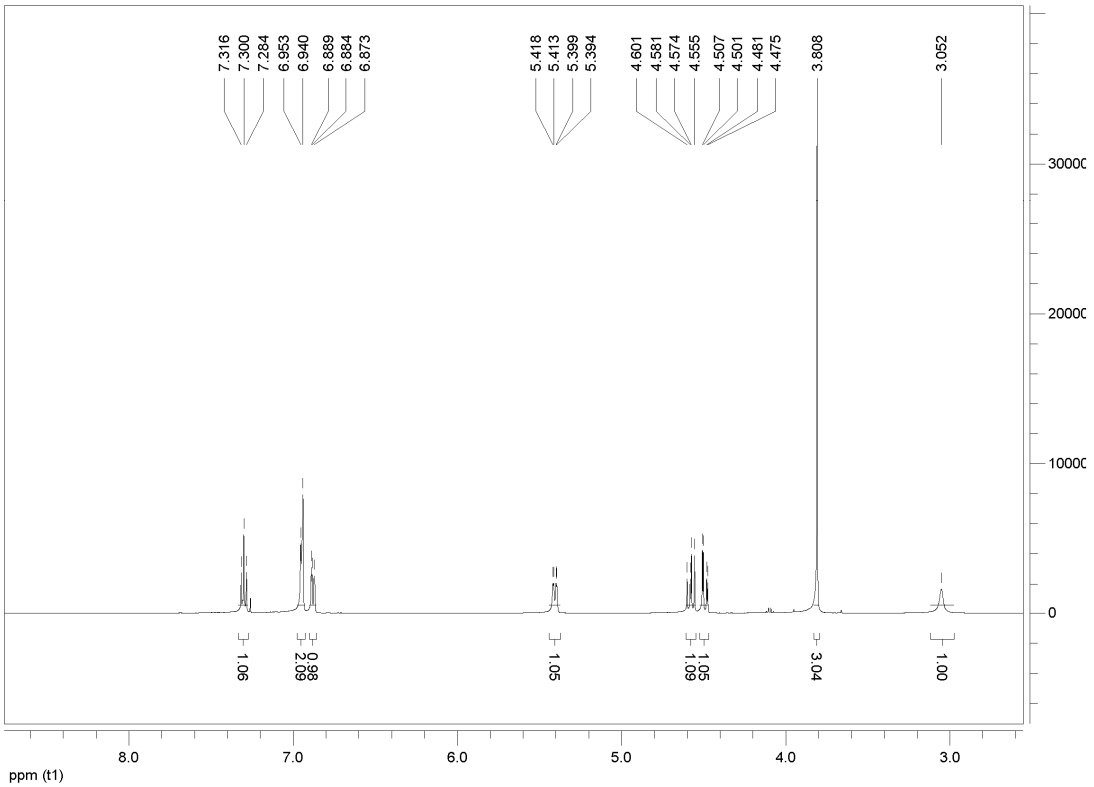
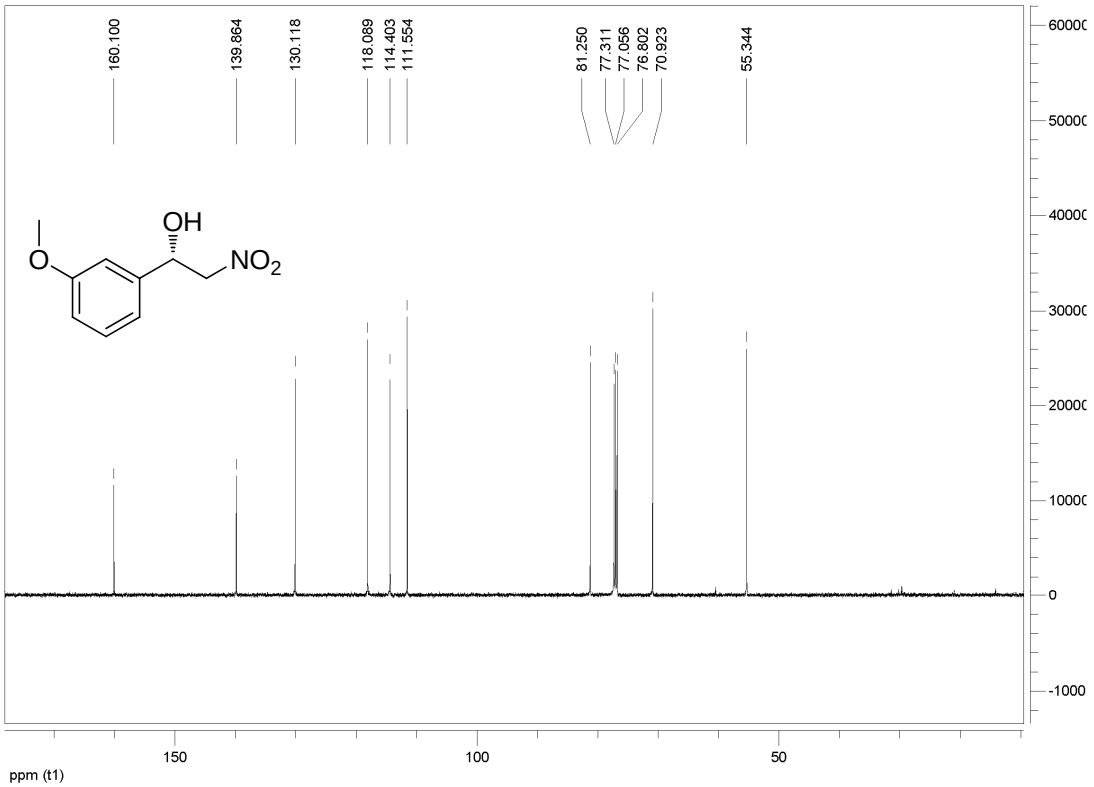
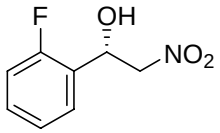
7.387
7.347
7.345
7.331
7.316
7.018
7.003
6.988
6.918
6.901
5.622
5.616
5.610
5.604
5.597
5.591
5.585
4.644
4.638
4.618
4.612
4.571
4.552
4.545
4.527
3.873
3.388
3.376
1.06
1.04
1.08
1.00
1.09
1.12
1.07
3.16
1.00
40000
30000
20000
10000
0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

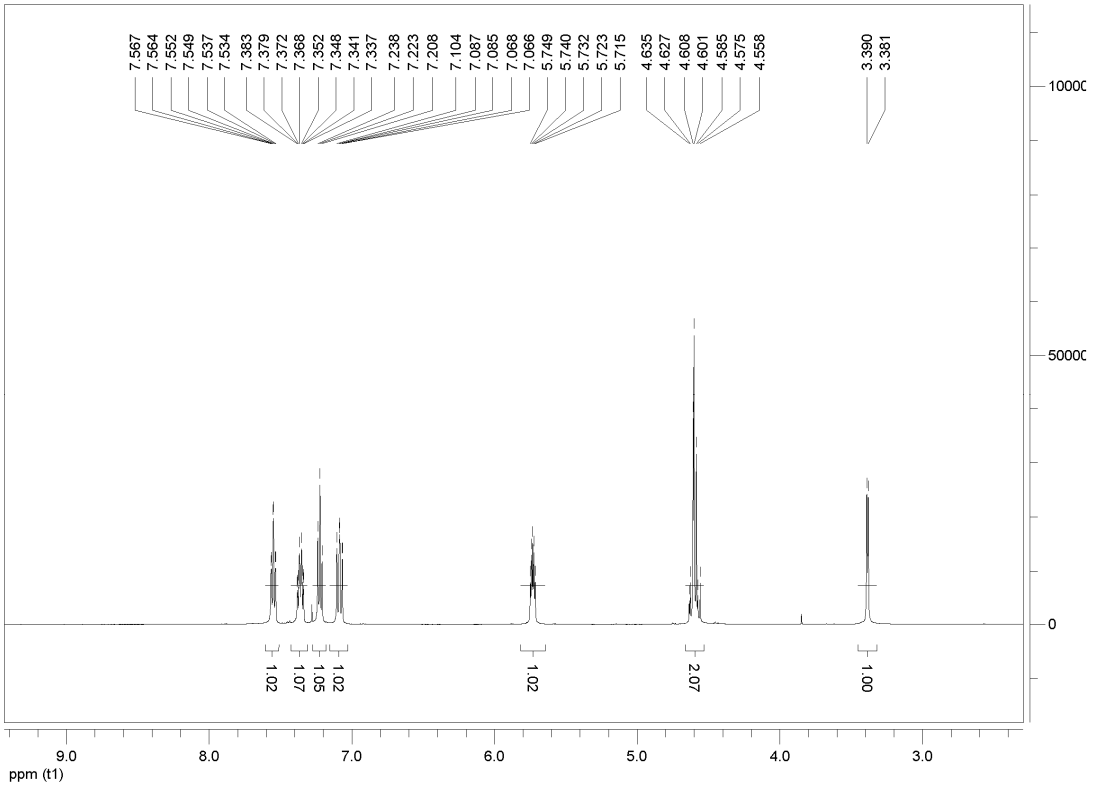

156.007
129.846
127.219
125.973
121.145
110.544
79.862
77.435
77.180
76.926
67.854
55.453
O
OH
NO2
70000
60000
50000
40000
30000
20000
10000
0
150
100
50
ppm (t1)

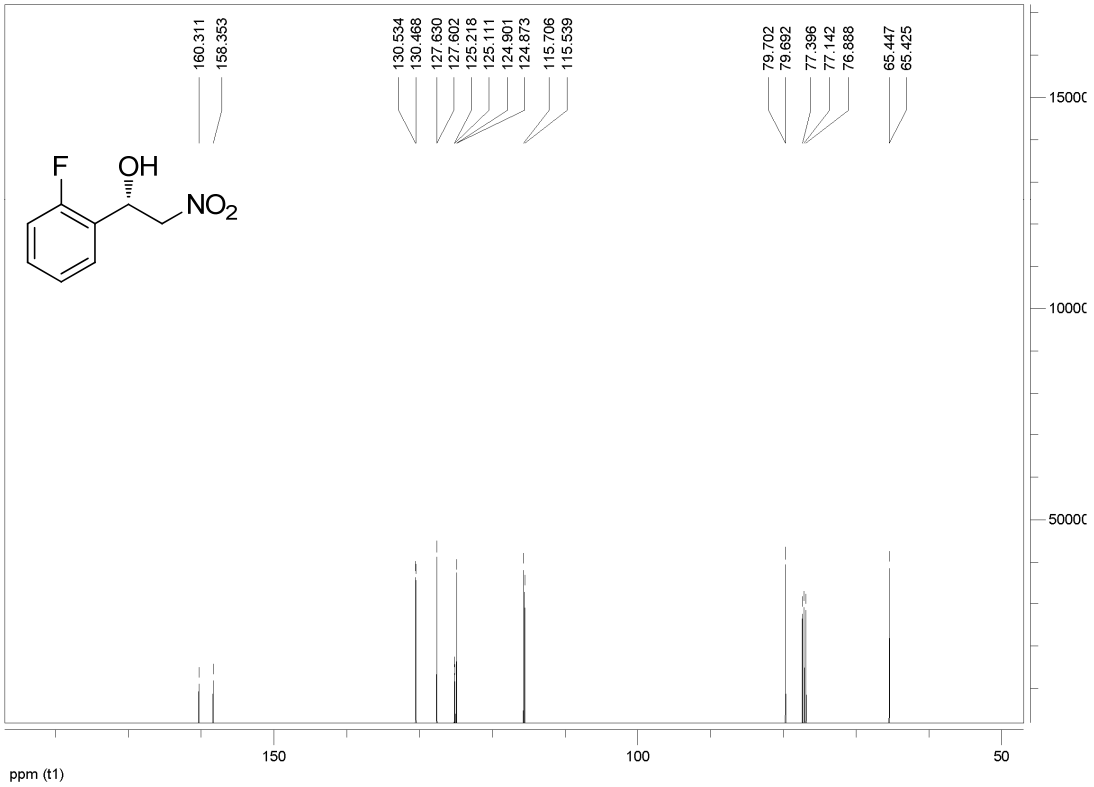

HO
NO2
O

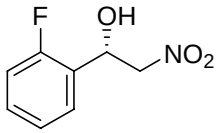

7.316
7.300
7.284
6.953
6.940
6.889
6.884
6.873
5.418
5.413
5.399
5.394
4.601
4.581
4.574
4.555
4.507
4.501
4.481
4.475
3.808
3.052
1.90
2.09
0.98
1.05
1.60
1.50
3.04
1.00
30000
20000
10000
0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

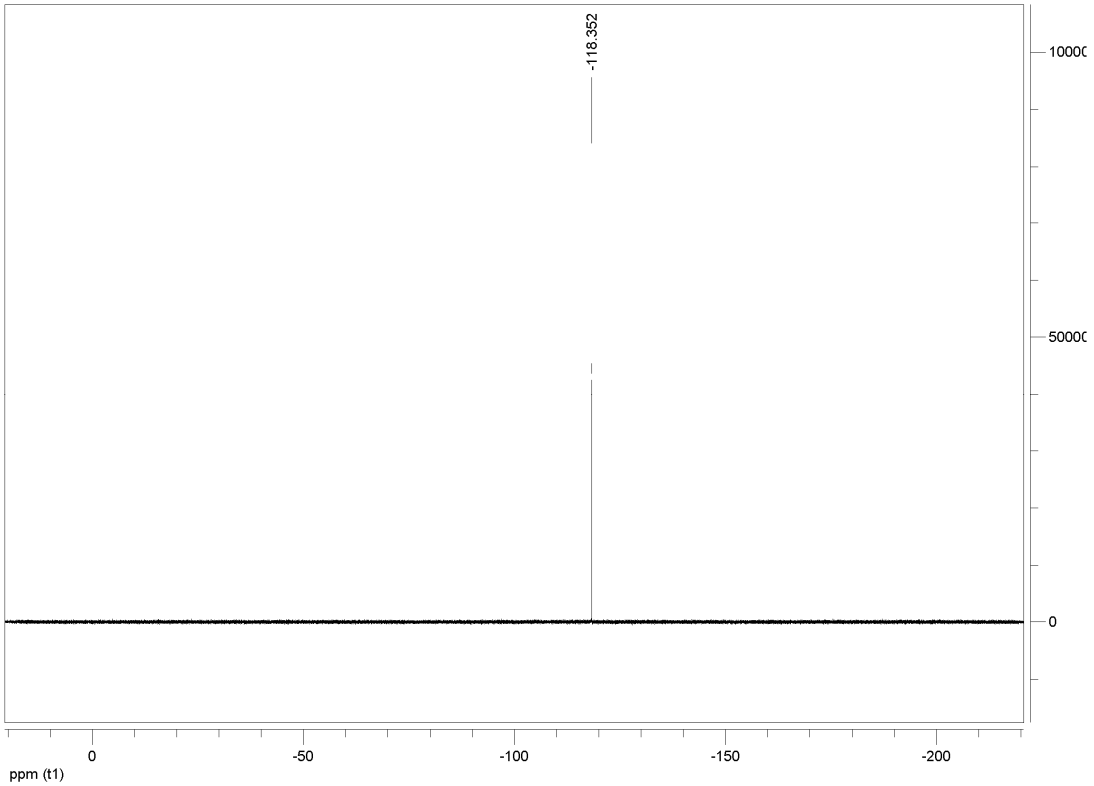

160.100
139.864
130.118
118.089
114.403
111.554
81.250
77.311
77.056
76.802
70.923
55.344
OH
O
NO2
60000
50000
40000
30000
20000
10000
0
-1000
150
100
50
ppm (t1)

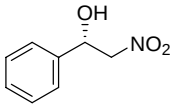

F
OH
NO2

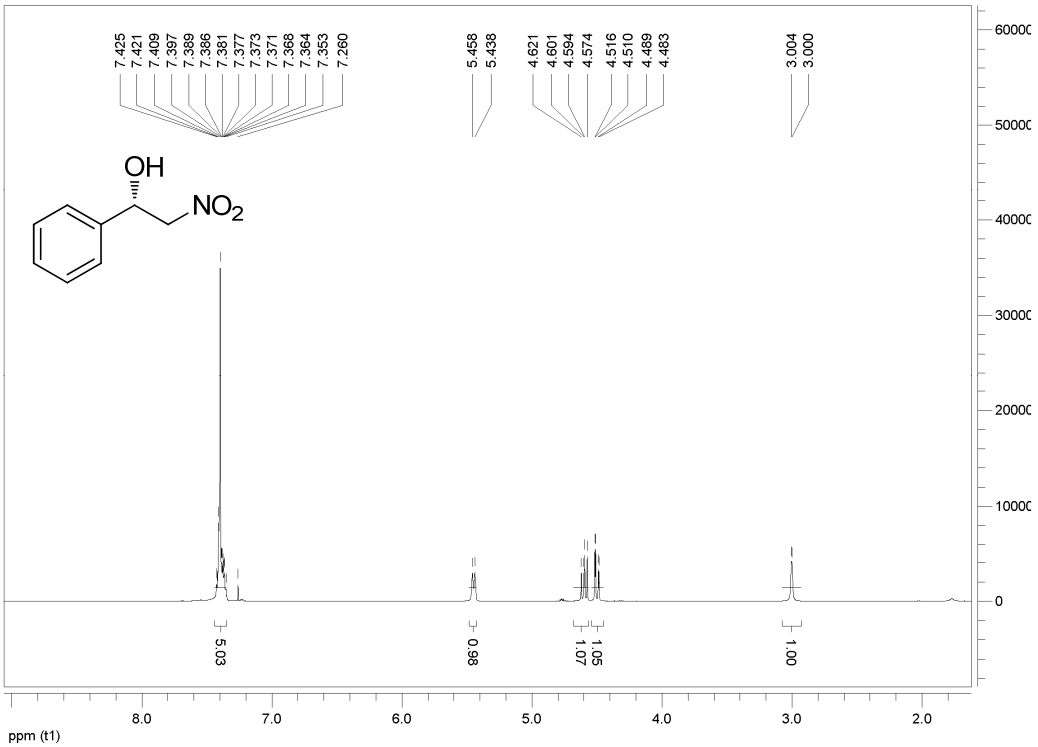

7.567
7.564
7.552
7.549
7.537
7.534
7.383
7.379
7.372
7.368
7.352
7.348
7.341
7.337
7.238
7.223
7.208
7.104
7.087
7.085
7.068
7.066
5.749
5.740
5.732
5.723
5.715
4.635
4.627
4.608
4.601
4.585
4.575
4.558
3.390
3.381
10000
50000
0
1.02
1.07
1.05
1.02
1.02
2.07
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)


160.311
158.353
130.534
130.468
127.630
127.602
125.218
125.111
124.901
124.873
115.706
115.539
79.702
79.692
77.396
77.142
76.888
65.447
65.425
15000
10000
50000
F
OH
NO2
150
100
50
ppm (t1)


F
OH
NO2


-118.352
10000
50000
0
0
-50
-100
-150
-200
ppm (t1)


OH
NO2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7.389
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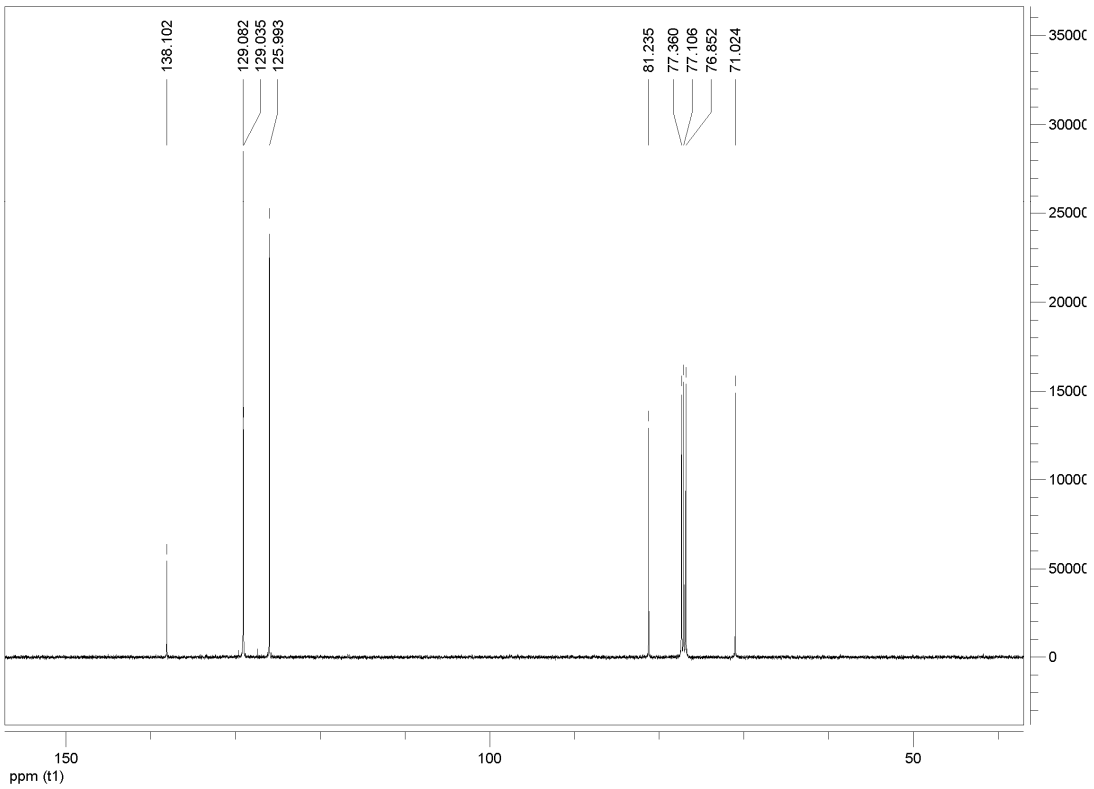
7.381
7.377
7.373
7.371
7.368
7.364
7.353
7.260
5.458
5.438
4.621
4.601
4.594
4.574
4.516
4.510
4.489
4.483
3.004
3.000
OH
NO2
60000
50000
40000
30000
20000
10000
0
5.03
0.98
1.07
1.06
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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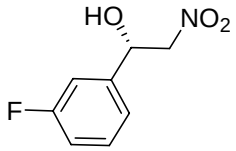
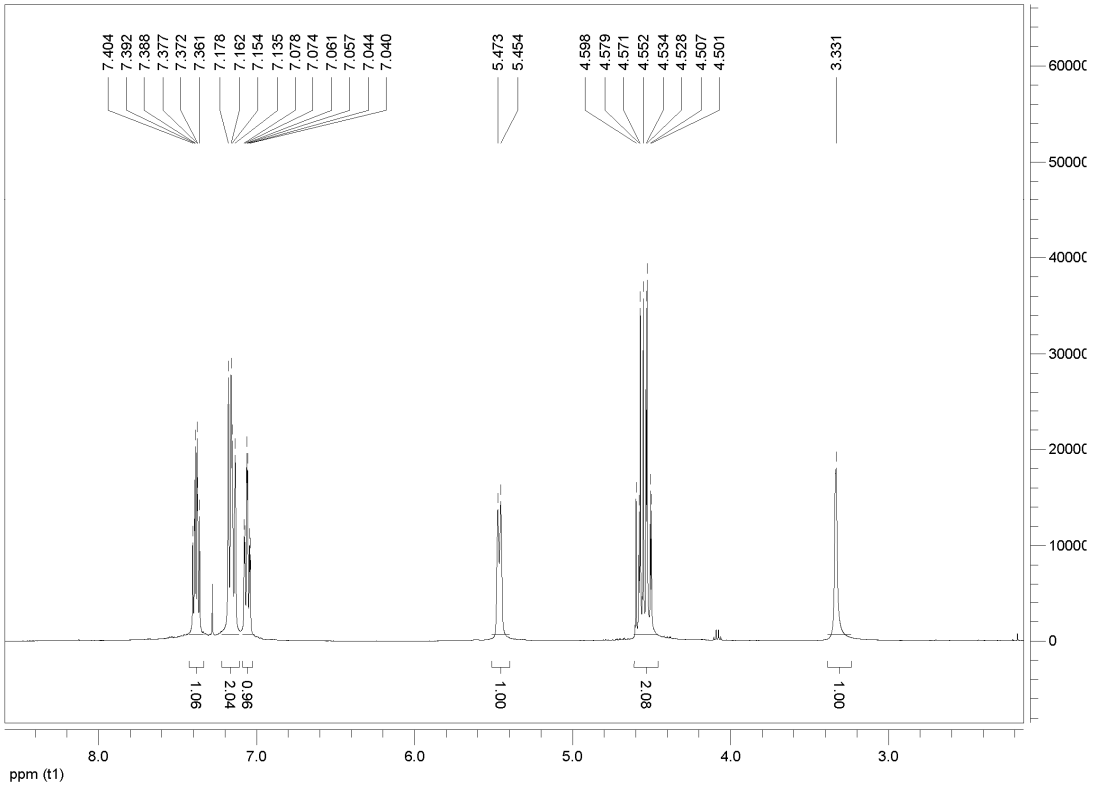
129.035
125.993
81.235
77.360
77.106
76.852
71.024
ppm (t1)


HO
NO2
F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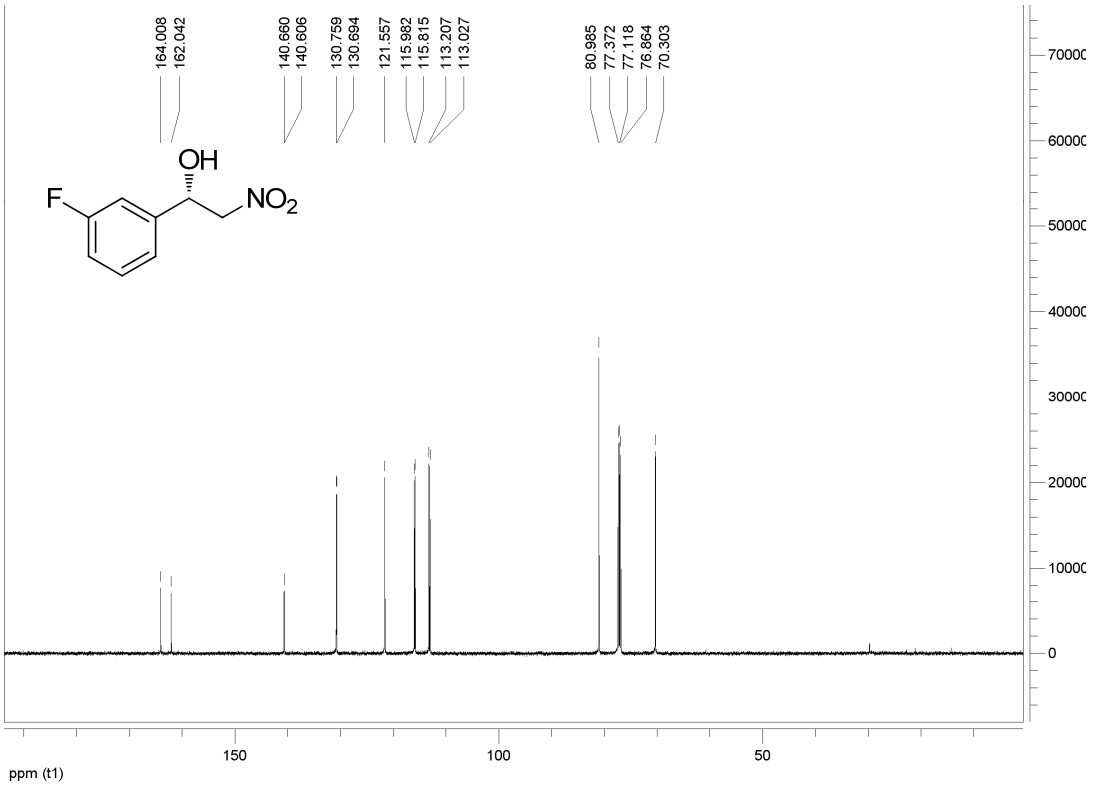
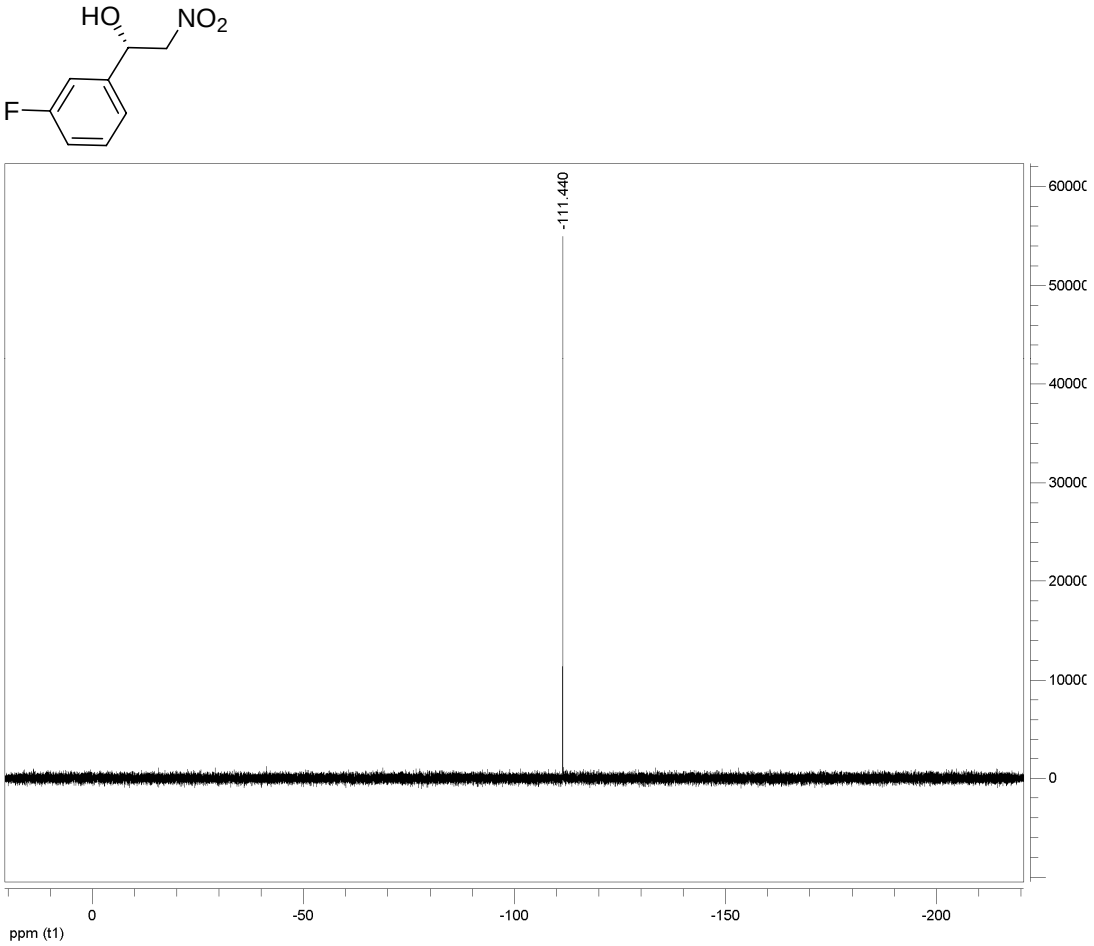
7.392
7.388
7.377
7.372
7.361
7.178
7.162
7.154
7.135
7.078
7.074
7.061
7.057
7.044
7.040
5.473
5.454
4.598
4.579
4.571
4.552
4.534
4.528
4.507
4.501
3.331
1.06
2.04
0.96
1.00
2.08
1.00
ppm (t1)


164.008
162.042
140.660
140.606
130.759
130.694
121.557
115.982
115.815
113.207
113.027
80.985
77.372
77.118
76.864
70.303
OH
F
NO2
70000
60000
50000
40000
30000
20000
10000
0
150
100
50
ppm (t1)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NO2
F
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40000
30000
20000
10000
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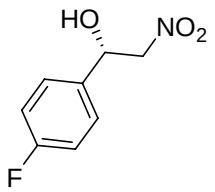
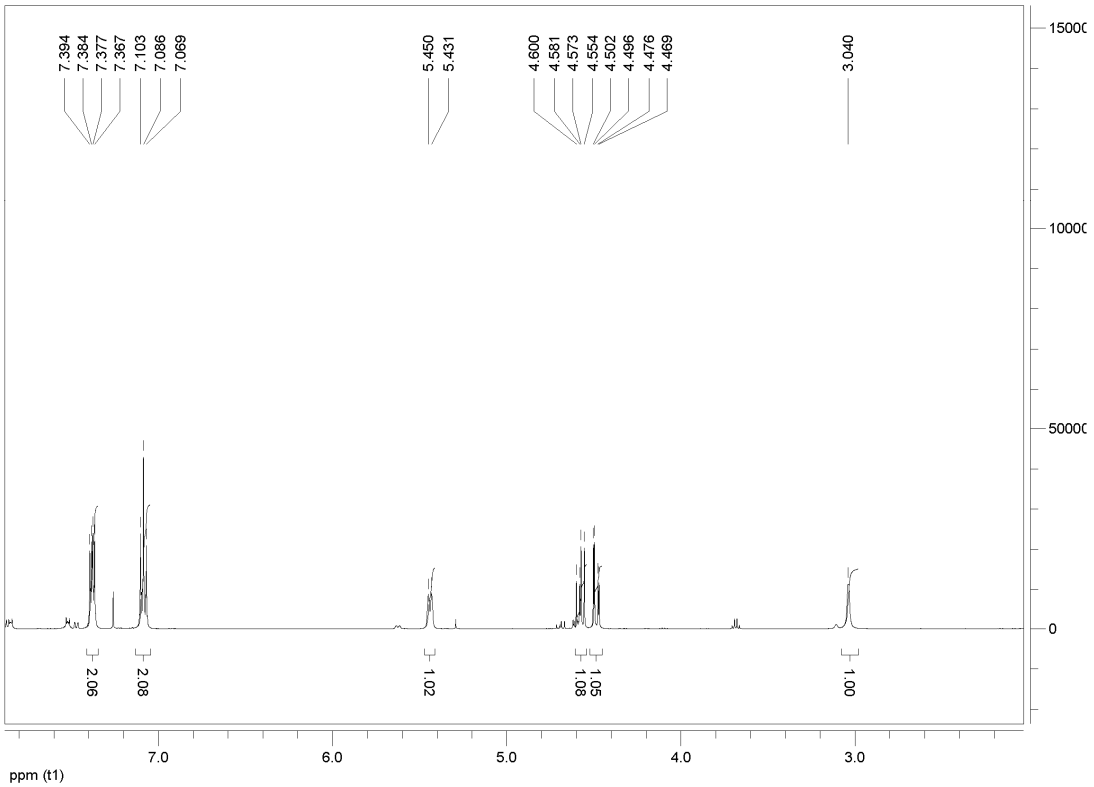
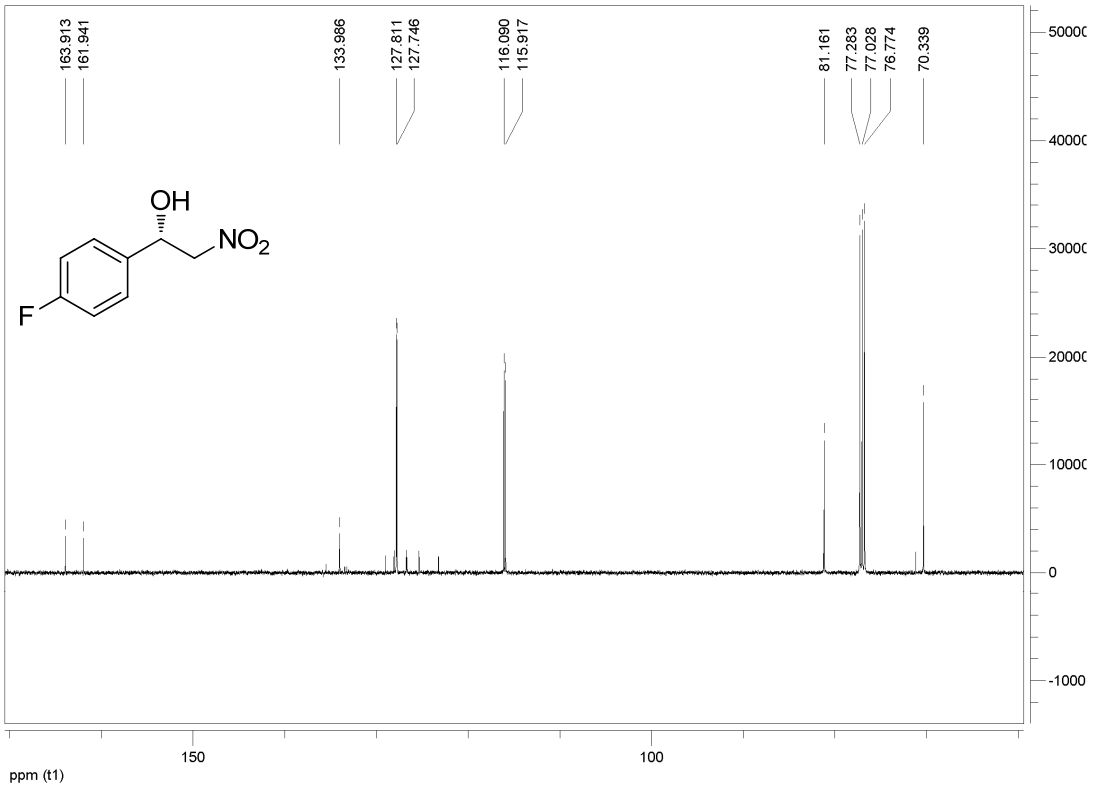
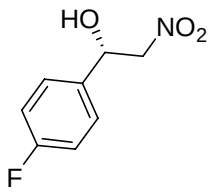
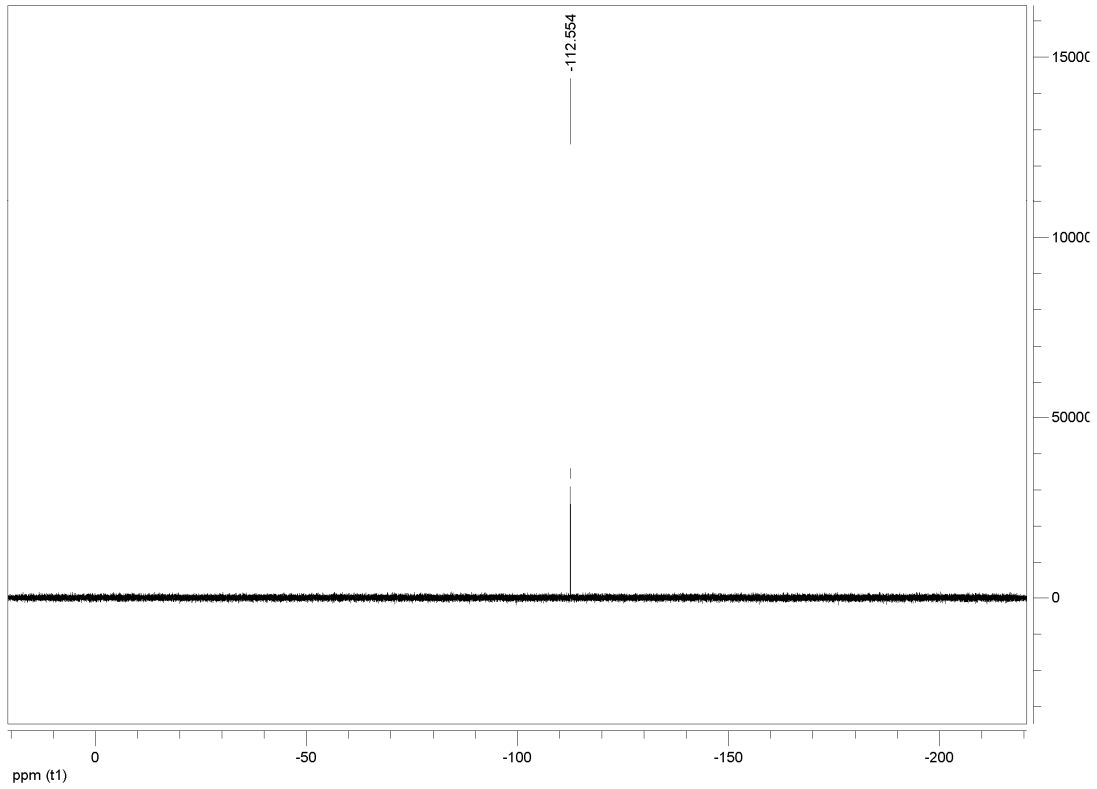
0
-50
-100
-150
-200
ppm (t1)

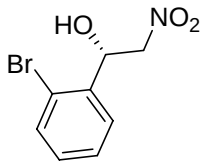

HO
NO2
F

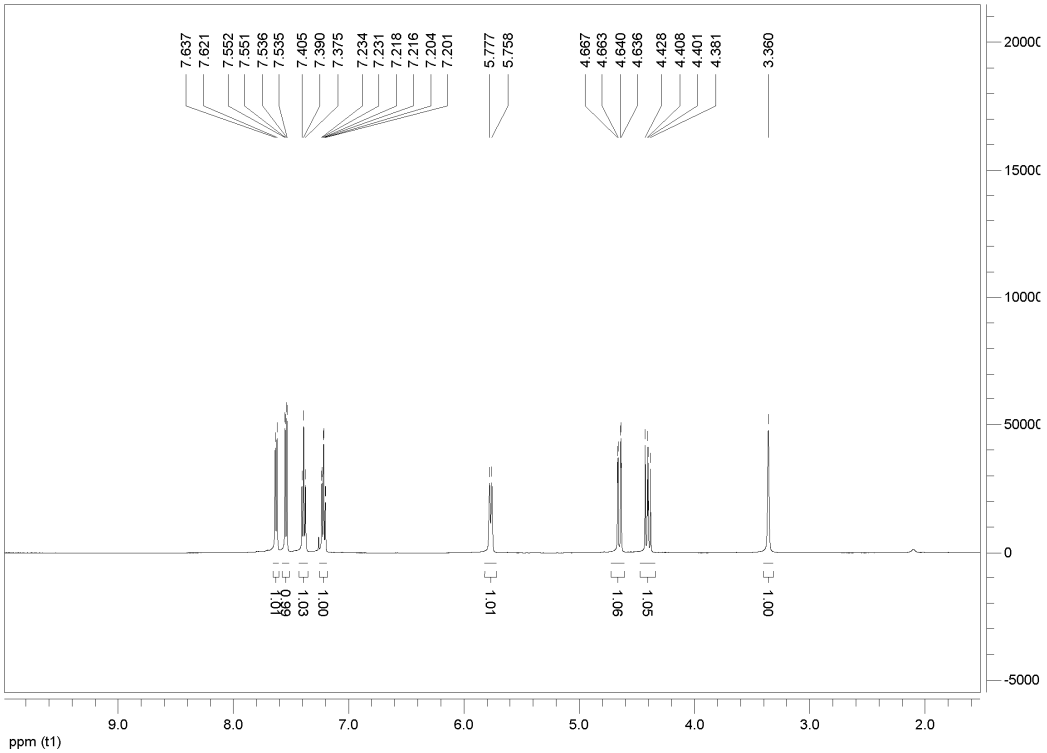

7.394
7.384
7.377
7.367
7.103
7.086
7.069
5.450
5.431
4.600
4.581
4.573
4.554
4.502
4.496
4.476
4.469
3.040
2.06
2.08
1.02
1.08
1.05
1.00
7.0
6.0
5.0
4.0
3.0
ppm (t1)

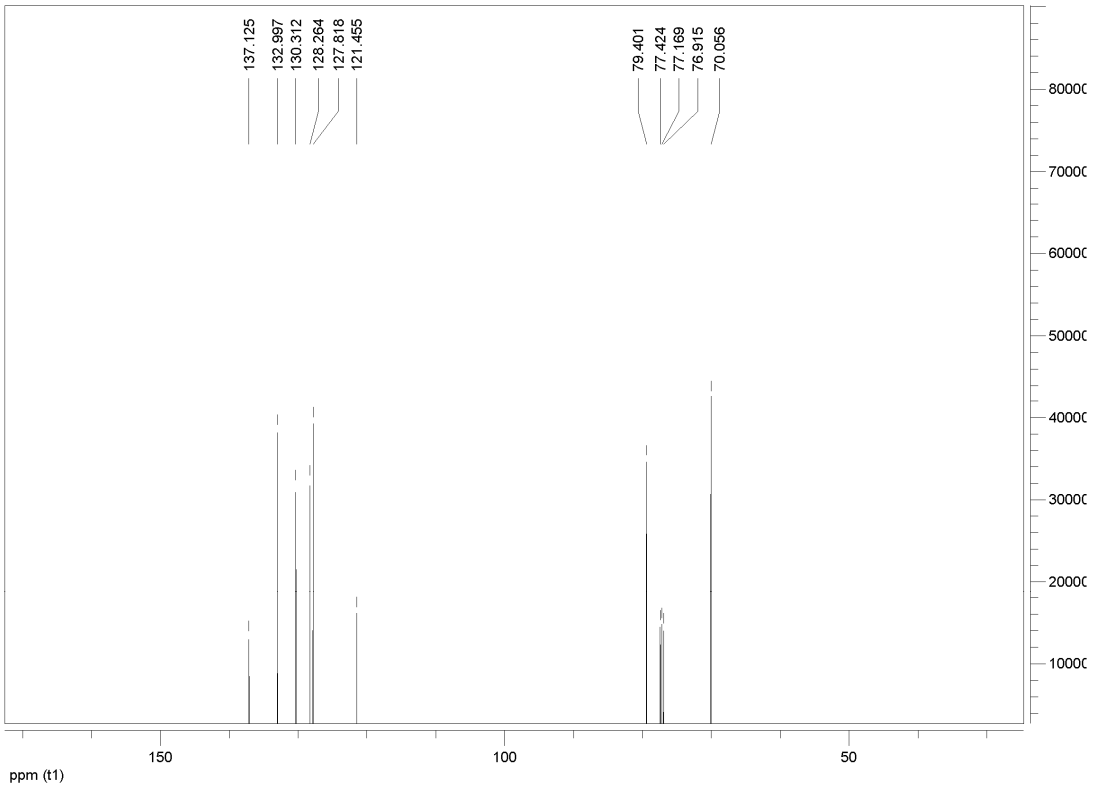

163.913
161.941
133.986
127.811
127.746
116.090
115.917
81.161
77.283
77.028
76.774
70.339
OH
NO2
F
150
100
ppm (t1)

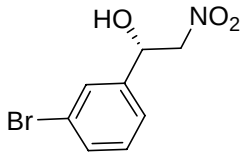

HO
NO2
F

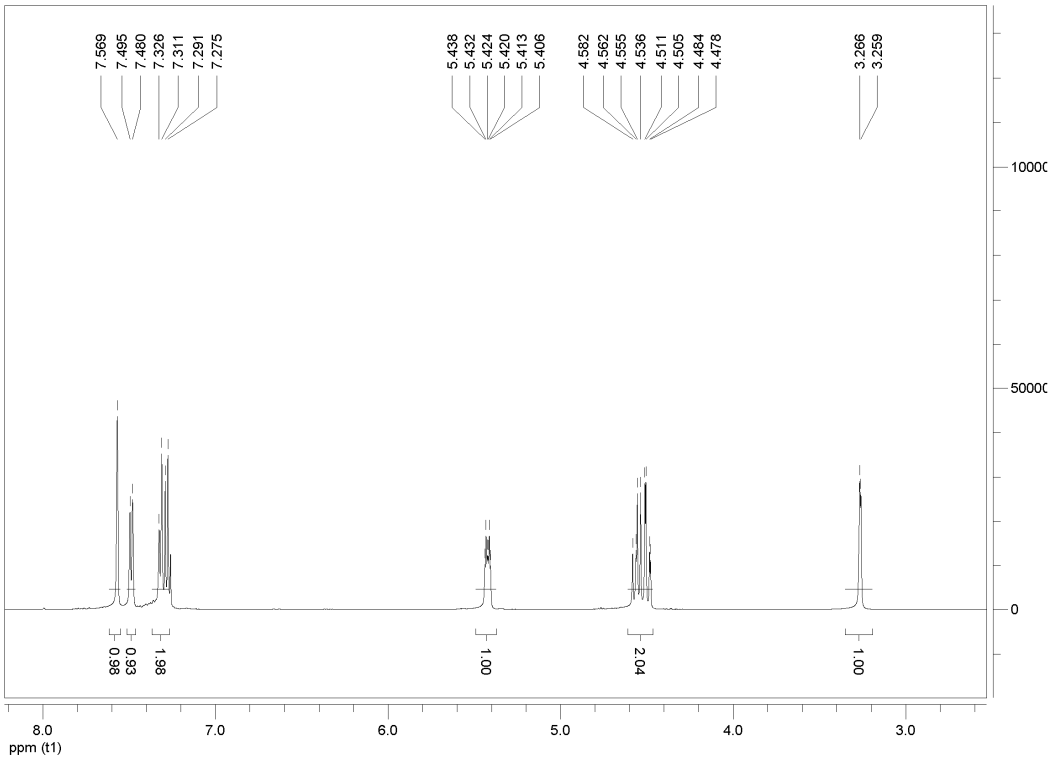

-112.554
15000
10000
50000
0
0
-50
-100
-150
-200
ppm (t1)

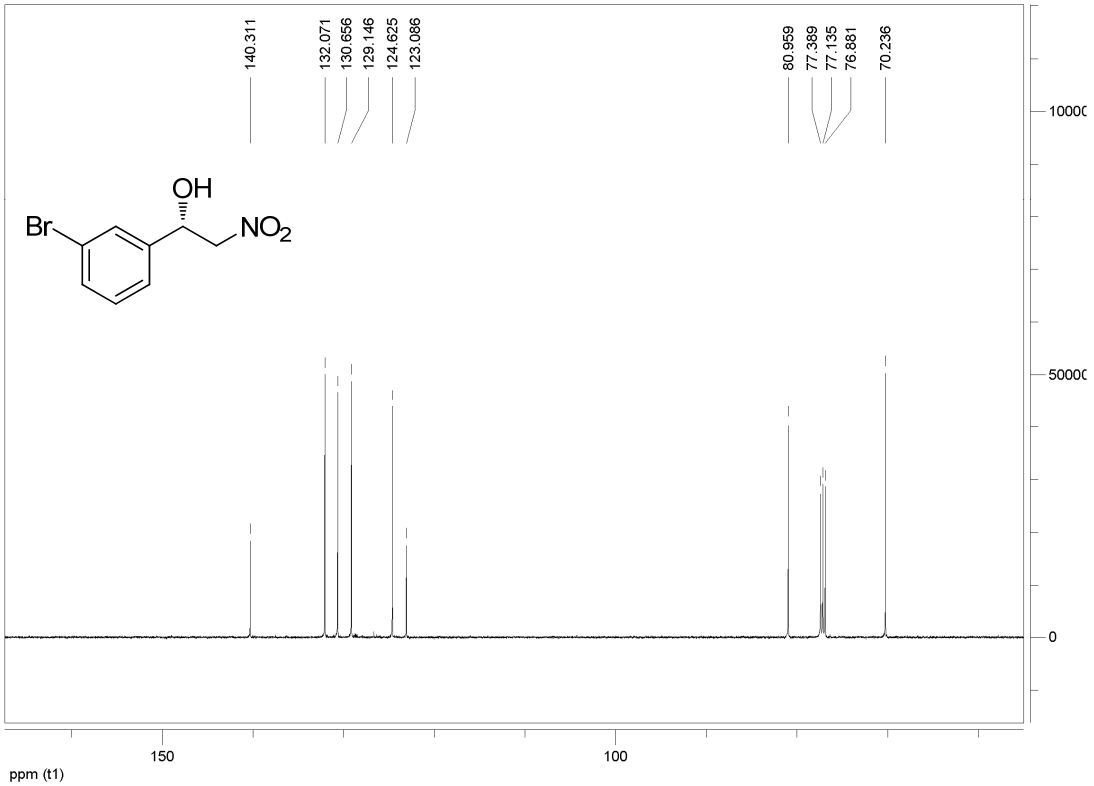

HO
NO2
Br

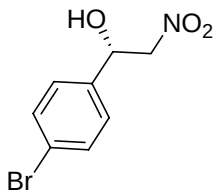

7.637
7.621
7.552
7.551
7.536
7.535
7.405
7.390
7.375
7.234
7.231
7.218
7.216
7.204
7.201
5.777
5.758
4.667
4.663
4.640
4.636
4.428
4.408
4.401
4.381
3.360
1.01
0.89
0.88
1.03
1.00
1.01
0.96
1.06
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

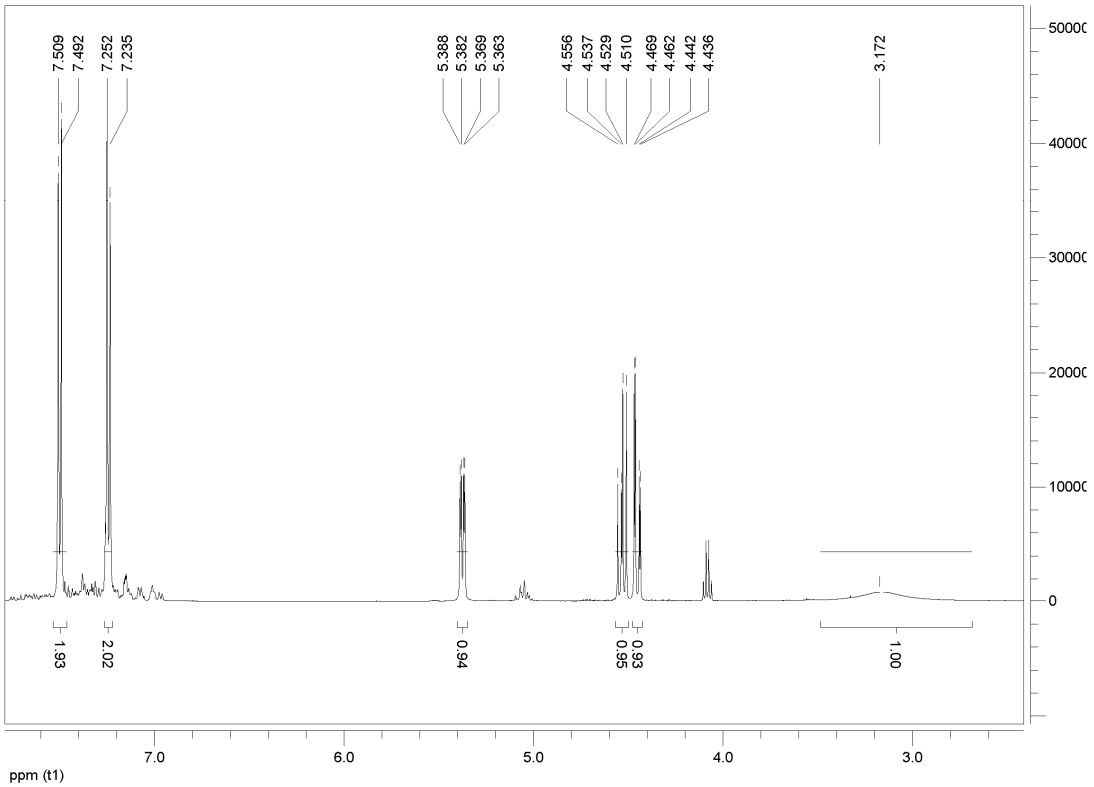

137.125
132.997
130.312
128.264
127.818
121.455
79.401
77.424
77.169
76.915
70.056
150
100
50
ppm (t1)

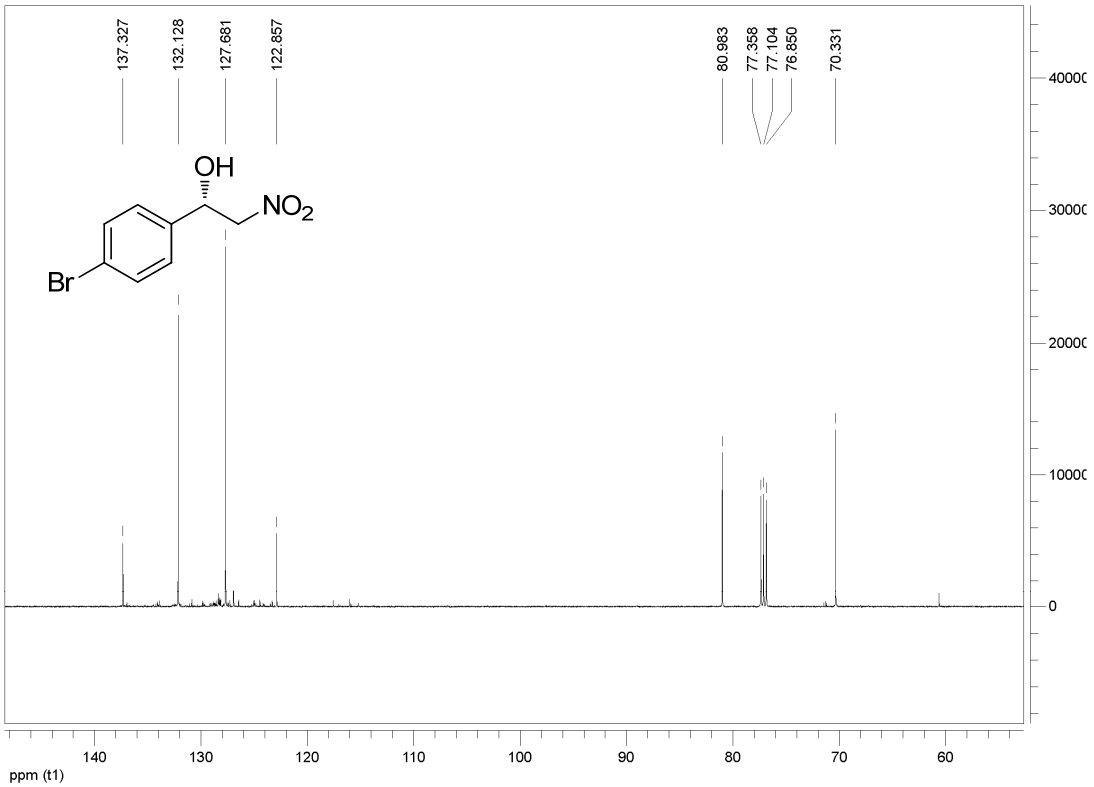

HO
NO2
Br

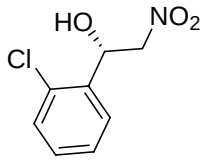

7.569
7.495
7.480
7.326
7.311
7.291
7.275
5.438
5.432
5.424
5.420
5.413
5.406
4.582
4.562
4.555
4.536
4.511
4.505
4.484
4.478
3.266
3.259
10000
50000
0
0.98
0.93
1.98
1.00
2.04
1.00
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

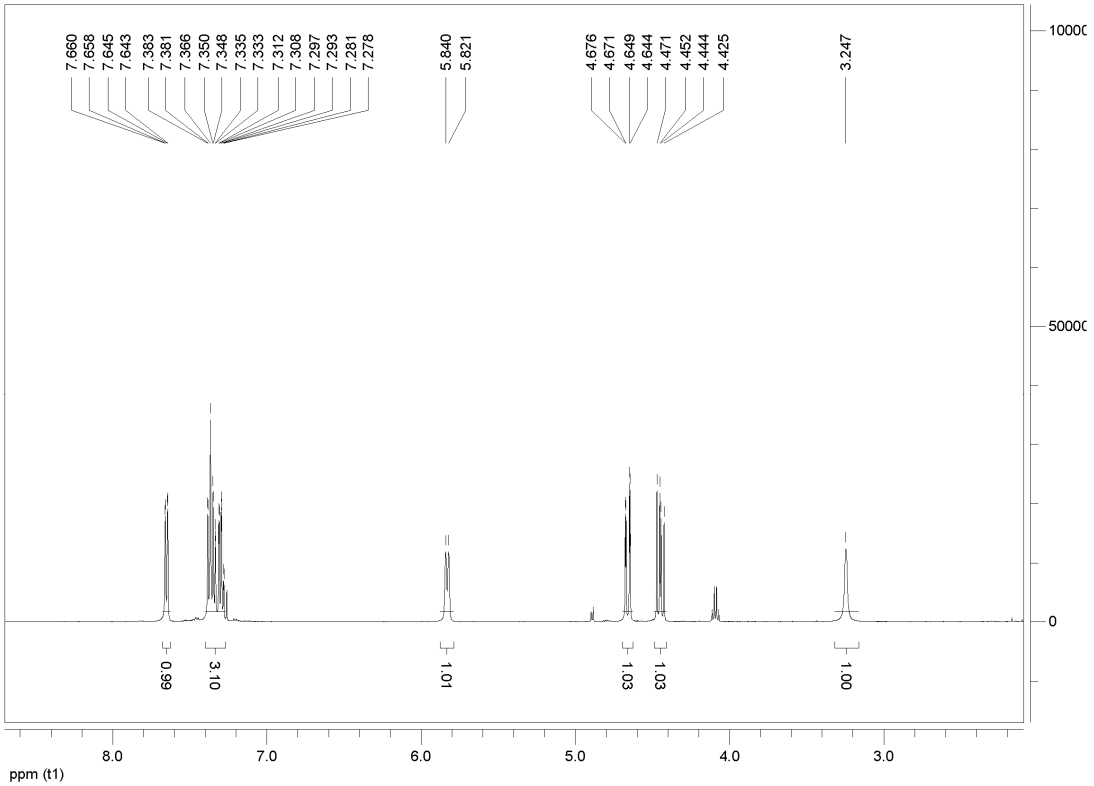

140.311
132.071
130.656
129.146
124.625
123.086
80.959
77.389
77.135
76.881
70.236
OH
Br
NO2
10000
50000
0
150
100
ppm (t1)

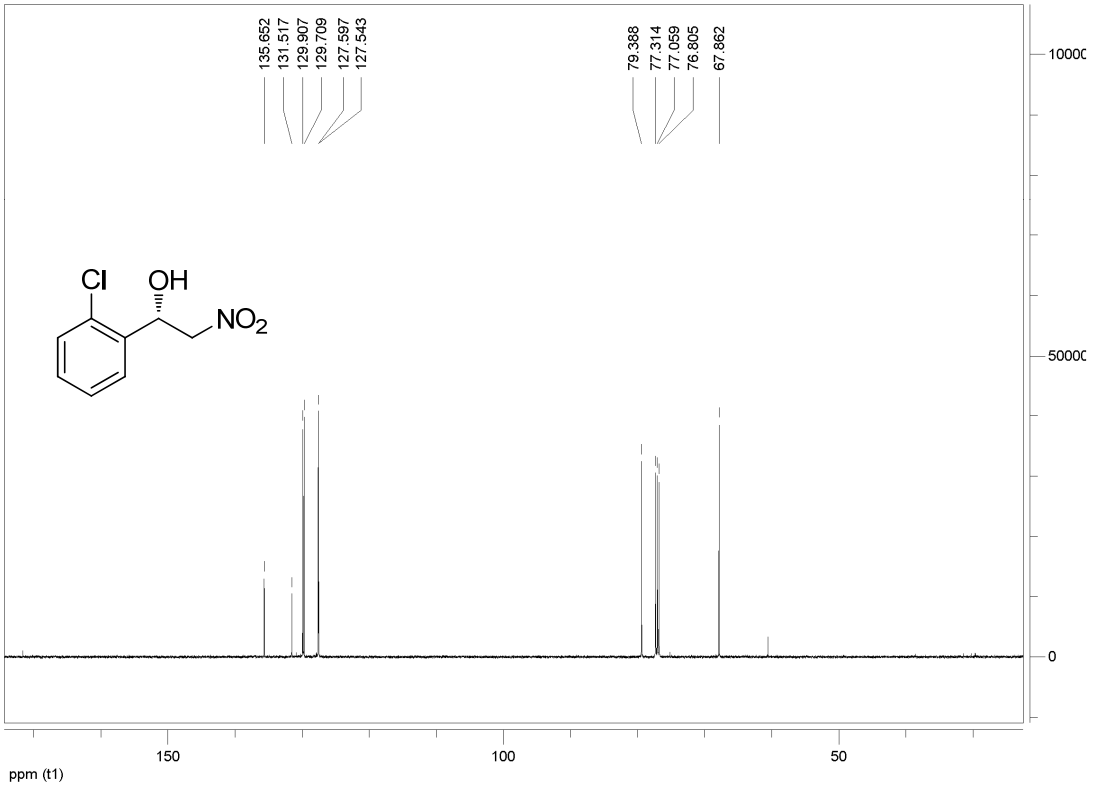

HO
NO2
Br

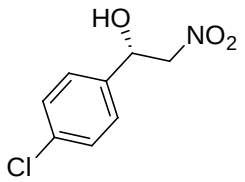

7.509
7.492
7.252
7.235
5.388
5.382
5.369
5.363
4.556
4.537
4.529
4.510
4.469
4.462
4.442
4.436
3.172
1.63
2.02
0.94
0.95
0.93
1.00
7.0
6.0
5.0
4.0
3.0
ppm (t1)

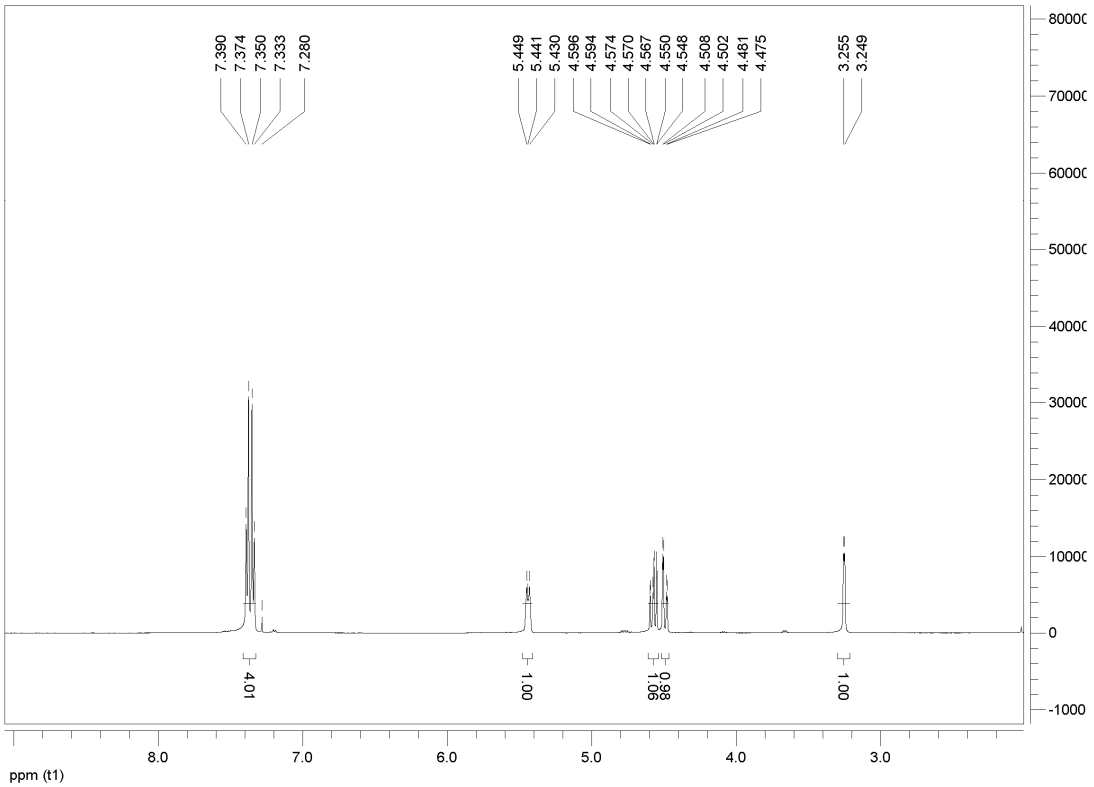

137.327
132.128
127.681
122.857
80.983
77.358
77.104
76.850
70.331
OH
NO2
Br
140
130
120
110
100
90
80
70
60
ppm (t1)

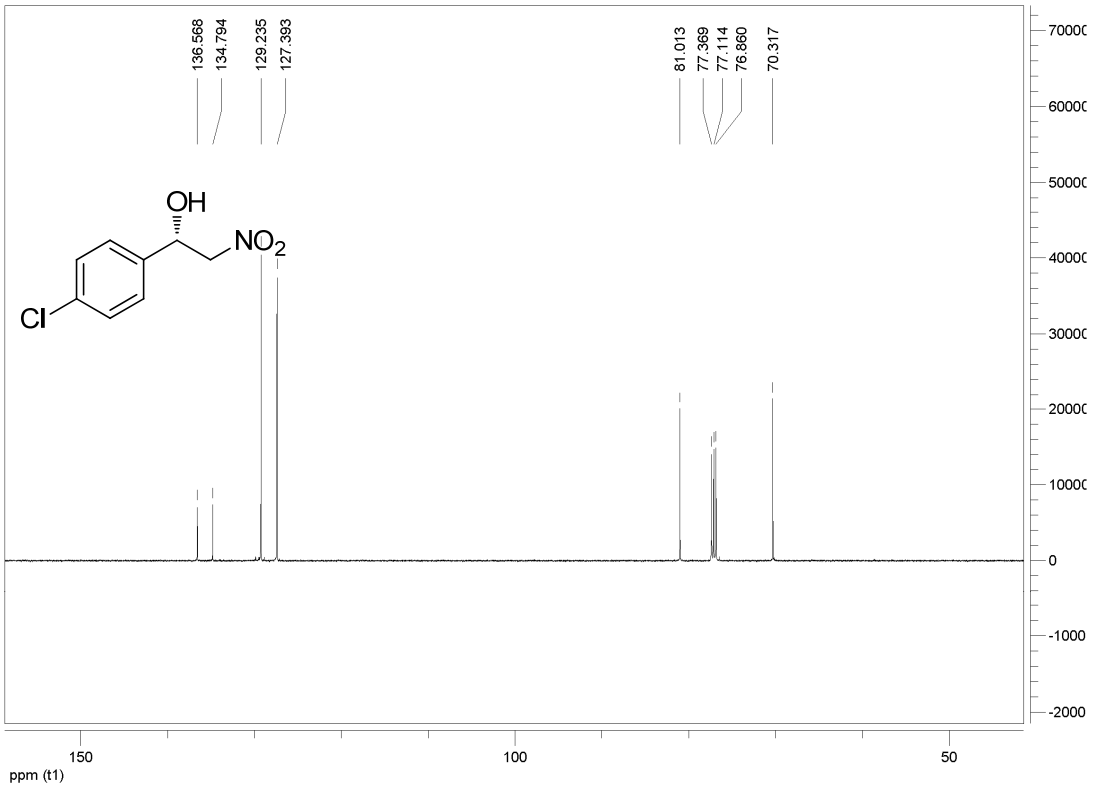

HO
NO2
Cl

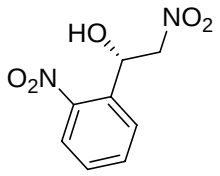

7.660
7.658
7.645
7.643
7.383
7.381
7.366
7.350
7.348
7.335
7.333
7.312
7.308
7.297
7.293
7.281
7.278
5.840
5.821
4.676
4.671
4.649
4.644
4.471
4.452
4.444
4.425
3.247
0.99
3.10
1.01
1.03
1.03
1.00
10000
50000
0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

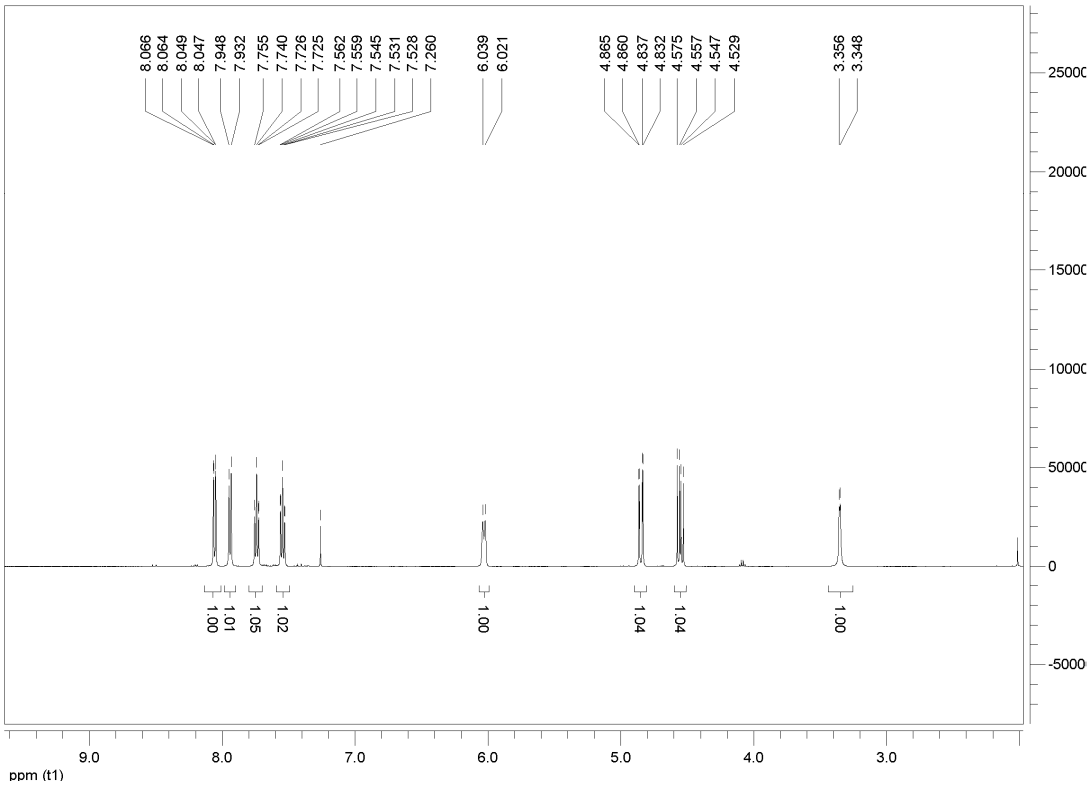

135.652
131.517
129.907
129.709
127.597
127.543
79.388
77.314
77.059
76.805
67.862
Cl
OH
NO2
10000
50000
0
150
100
50
ppm (t1)

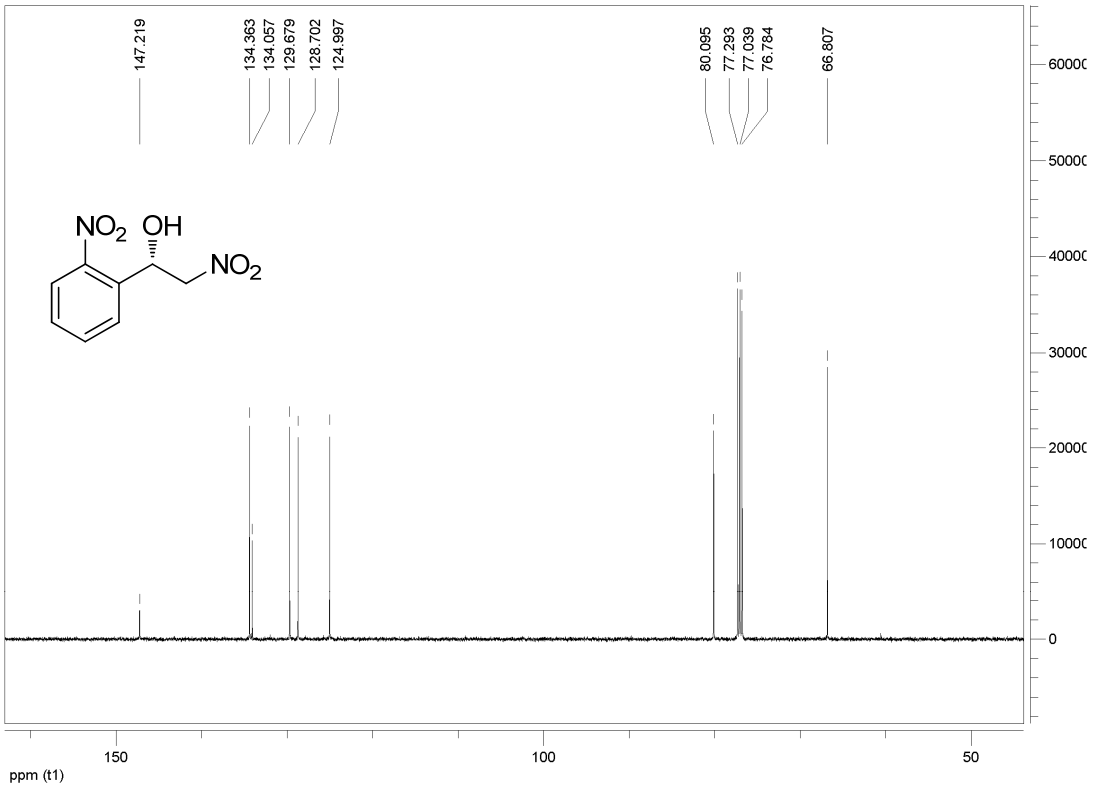

HO
NO2
Cl

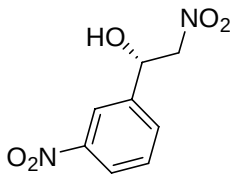

7.390
7.374
7.350
7.333
7.280
5.449
5.441
5.430
4.596
4.594
4.574
4.570
4.567
4.550
4.548
4.508
4.502
4.481
4.475
3.255
3.249
4.01
1.00
0.98
1.06
1.00
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

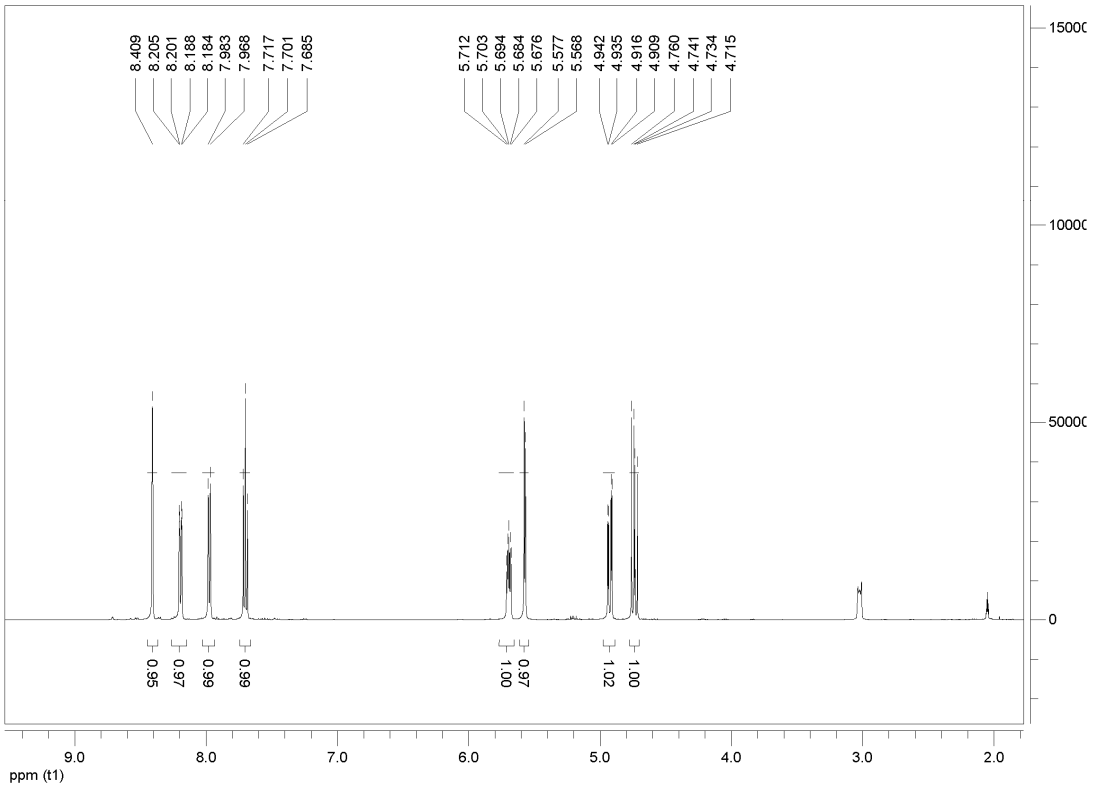

136.568
134.794
129.235
127.393
81.013
77.369
77.114
76.860
70.317
OH
NO2
Cl
150
100
50
ppm (t1)

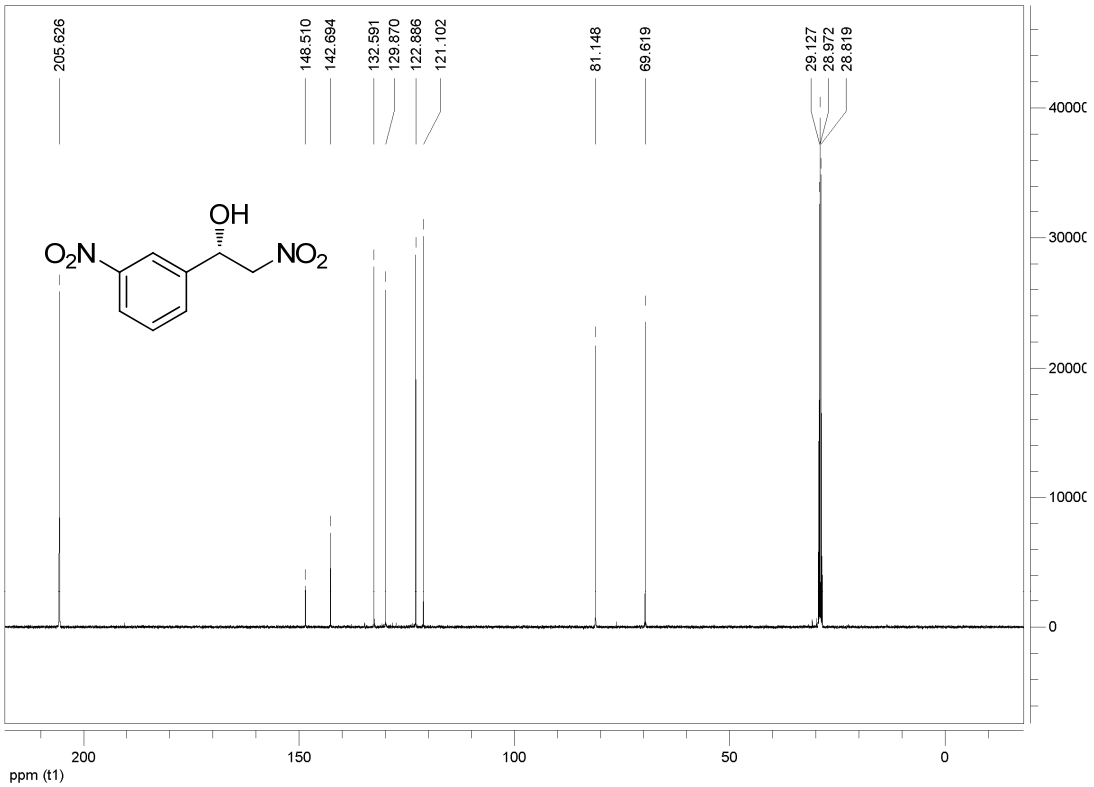

HO
NO2
O2N

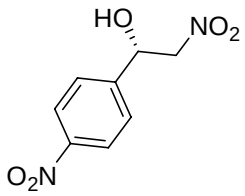

8.066
8.064
8.049
8.047
7.948
7.932
7.755
7.740
7.726
7.725
7.562
7.559
7.545
7.531
7.528
7.260
6.039
6.021
4.865
4.860
4.837
4.832
4.575
4.557
4.547
4.529
3.356
3.348
1.00
1.01
1.05
1.02
1.00
1.04
1.04
1.00
25000
20000
15000
10000
5000
0
-5000
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

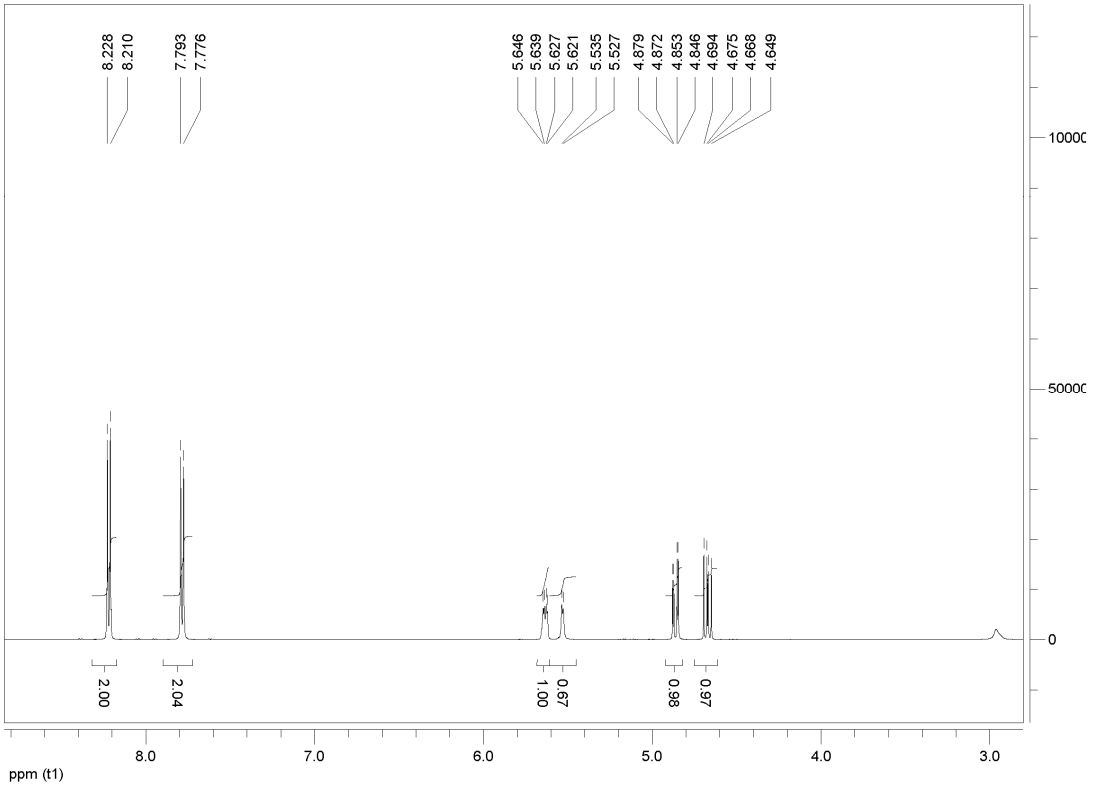

147.219
134.363
134.057
129.679
128.702
124.997
80.095
77.293
77.039
76.784
66.807
NO2
OH
NO2
60000
50000
40000
30000
20000
10000
0
150
100
50
ppm (t1)

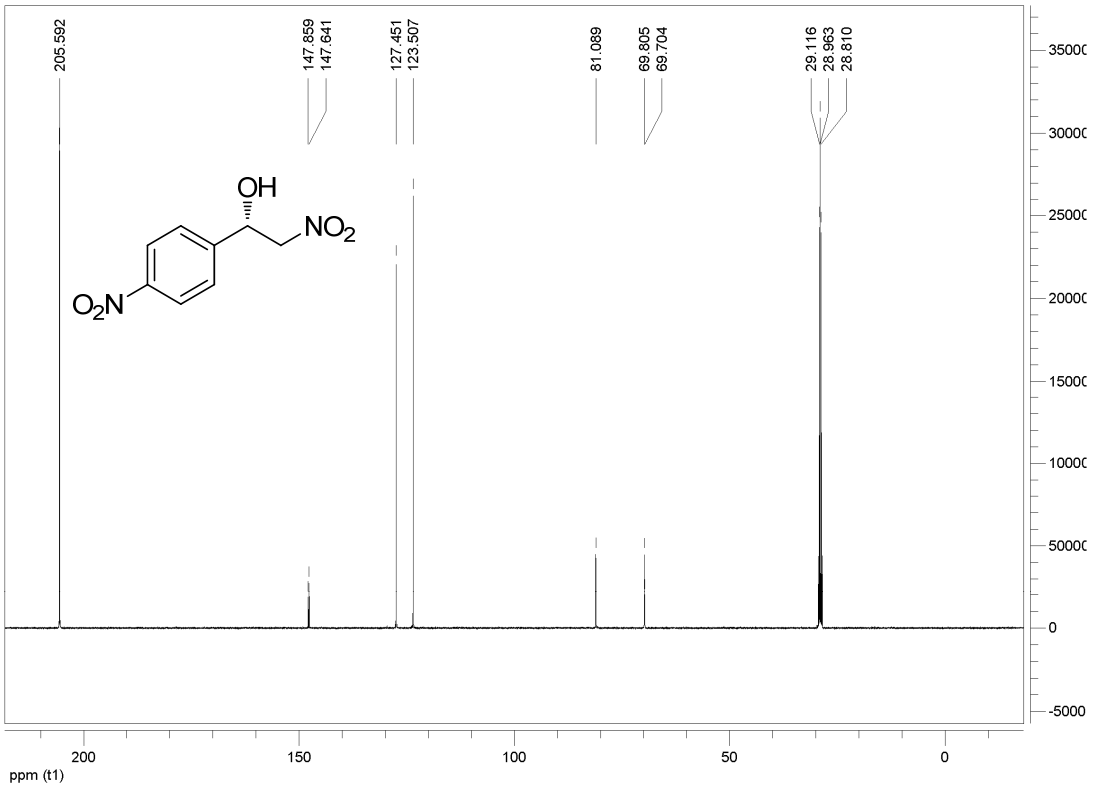

HO
NO2
O2N

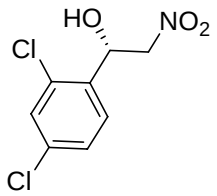

8.409
8.205
8.201
8.188
8.184
7.983
7.968
7.717
7.701
7.685
5.712
5.703
5.694
5.684
5.676
5.577
5.568
4.942
4.935
4.916
4.909
4.760
4.741
4.734
4.715
0.95
0.97
0.99
0.99
1.00
0.97
1.02
1.00
15000
10000
50000
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

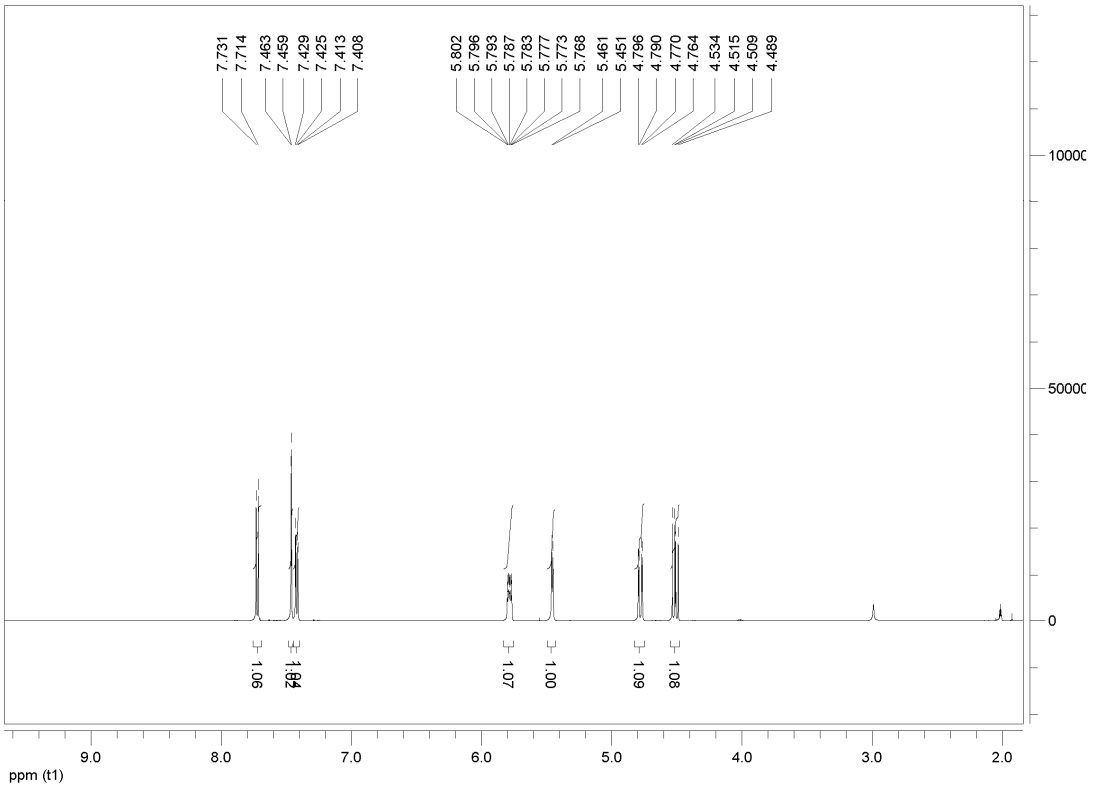

205.626
148.510
142.694
132.591
129.870
122.886
121.102
81.148
69.619
29.127
28.972
28.819
OH
O2N
NO2
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)

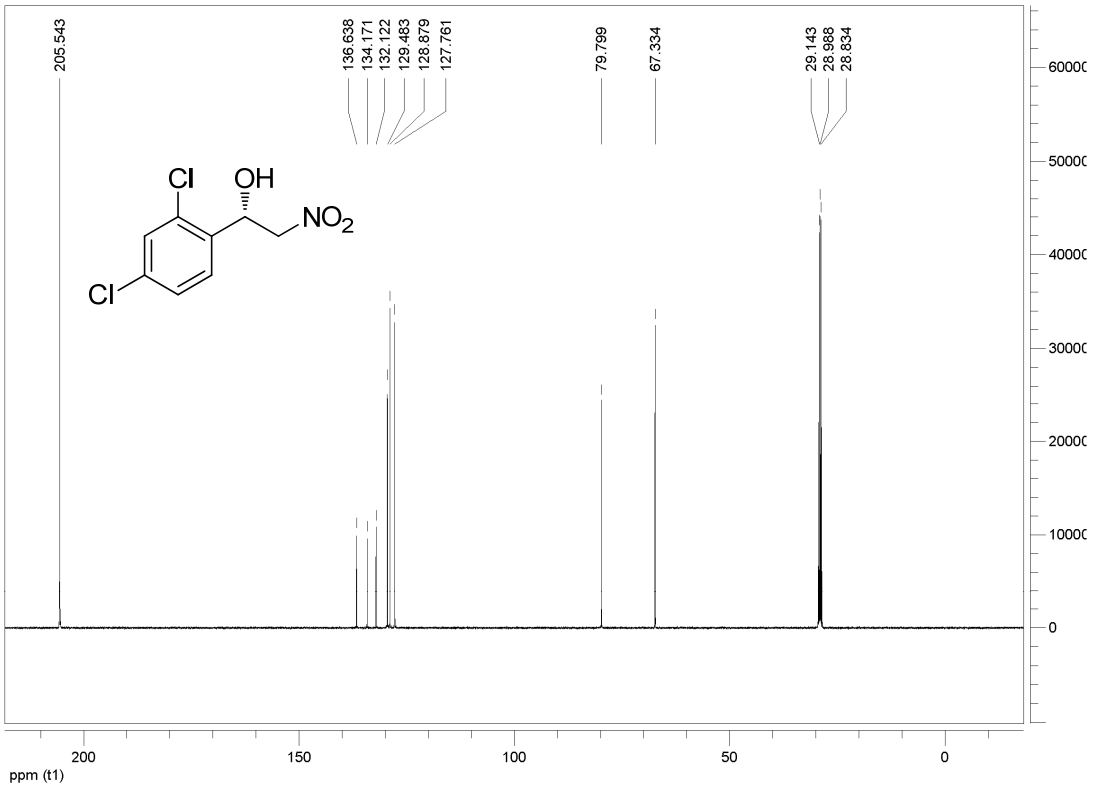

HO
NO2
O2N

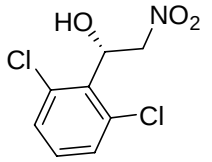

8.228
8.210
7.793
7.776
5.646
5.639
5.627
5.621
5.535
5.527
4.879
4.872
4.853
4.846
4.694
4.675
4.668
4.649
2.00
2.04
1.00
0.67
0.98
0.97
10000
50000
0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

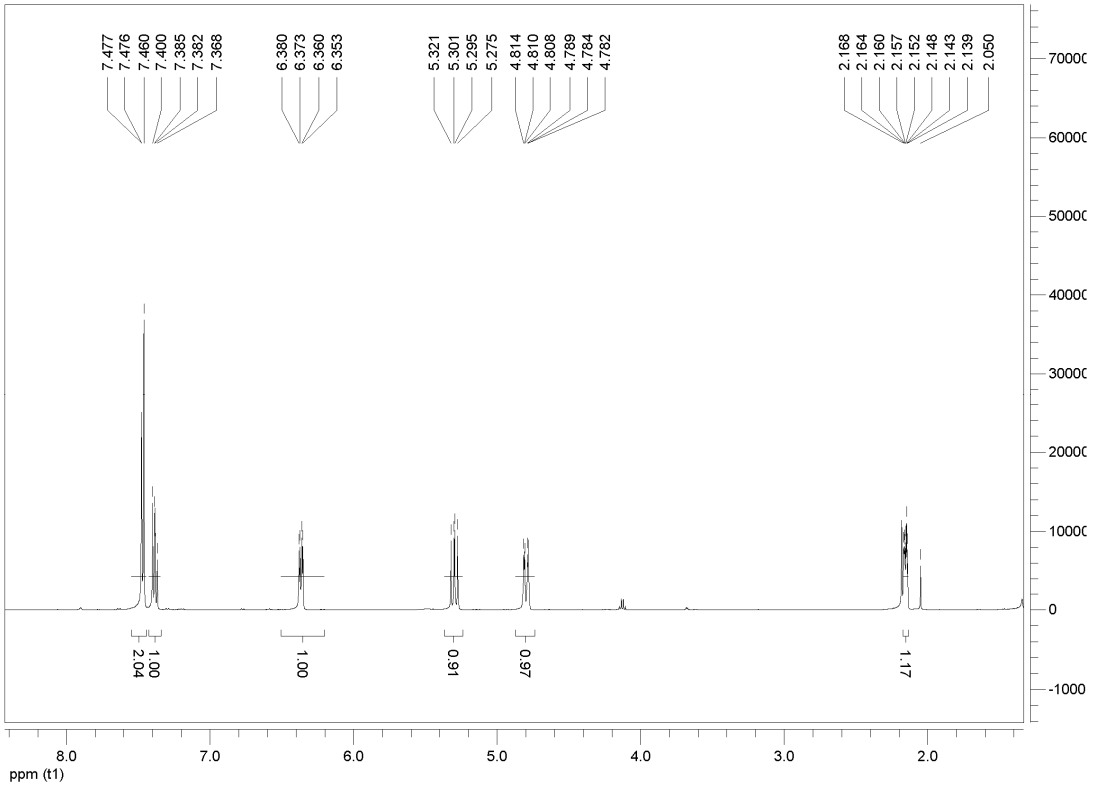

205.592
147.859
147.641
127.451
123.507
81.089
69.805
69.704
29.116
28.963
28.810
OH
NO2
O2N
35000
30000
25000
20000
15000
10000
50000
0
-5000
200
150
100
50
0
ppm (t1)

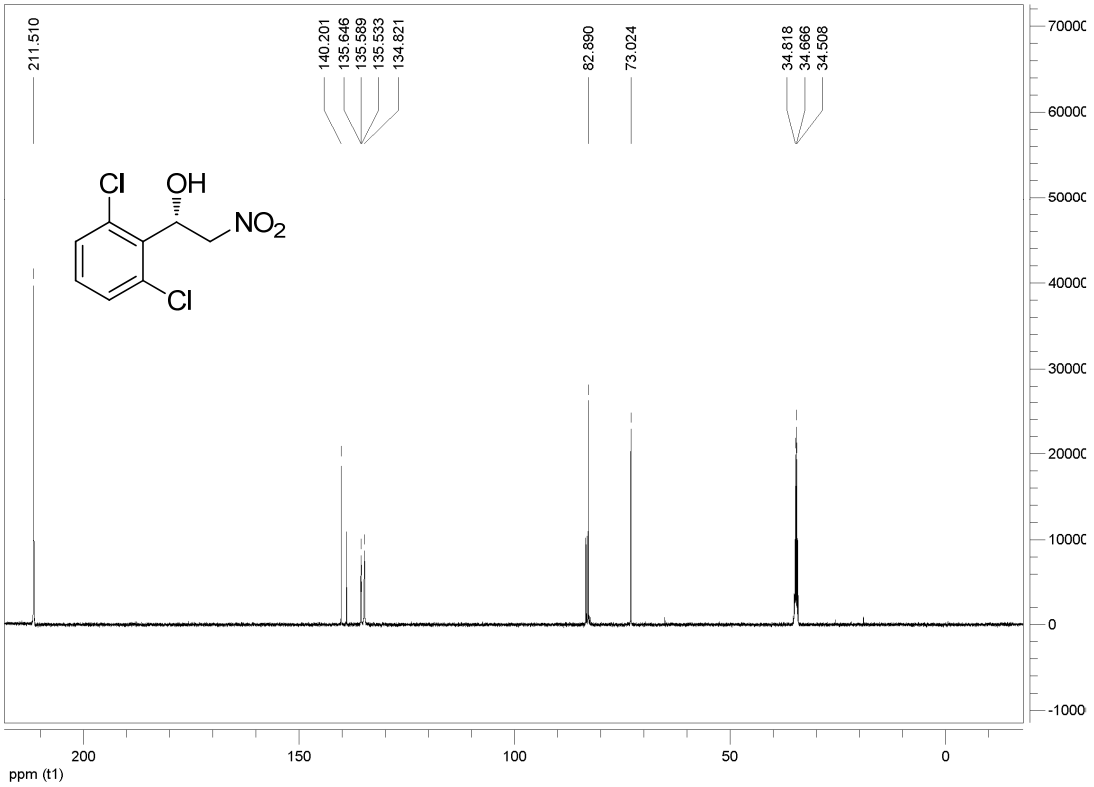

HO
NO2
Cl
Cl

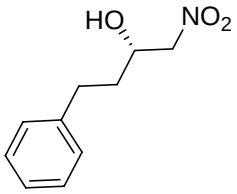

7.731
7.714
7.463
7.459
7.429
7.425
7.413
7.408
5.802
5.796
5.793
5.787
5.783
5.777
5.773
5.768
5.461
5.451
4.796
4.790
4.770
4.764
4.534
4.515
4.509
4.489
1.06
1.07
1.00
1.09
1.08
10000
50000
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

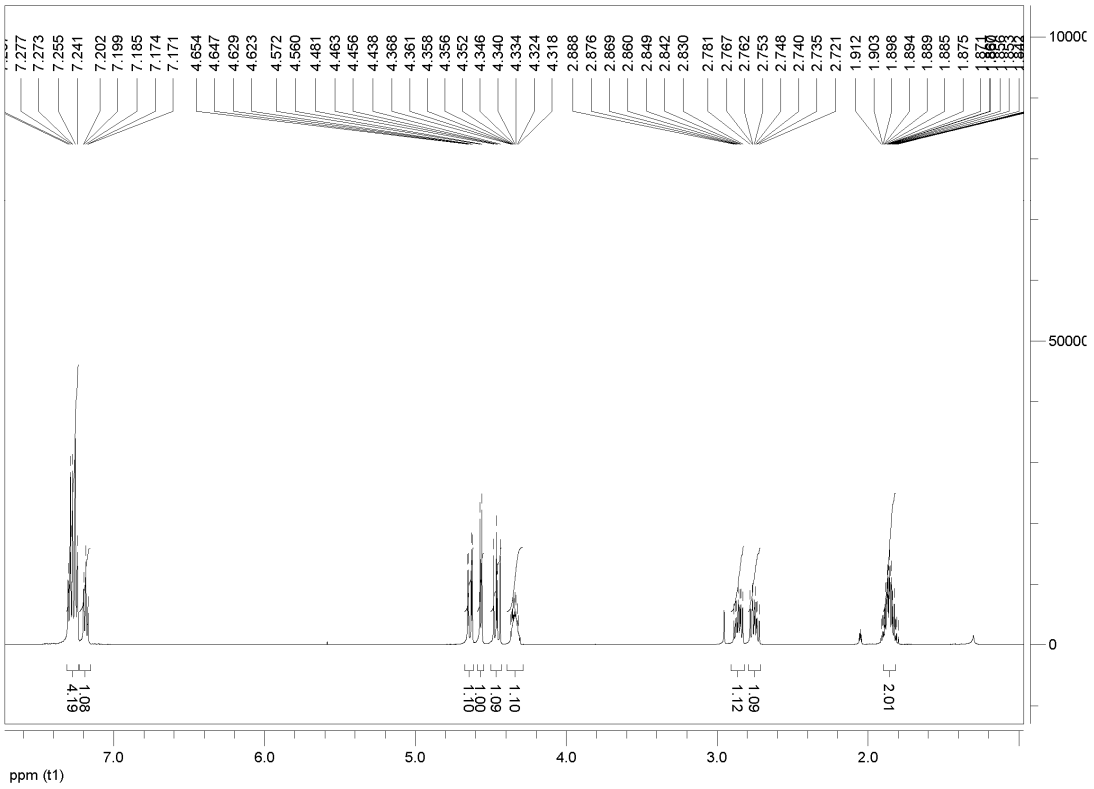

205.543
136.638
134.171
132.122
129.483
128.879
127.761
79.799
67.334
29.143
28.988
28.834
Cl
OH
NO2
Cl
60000
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)

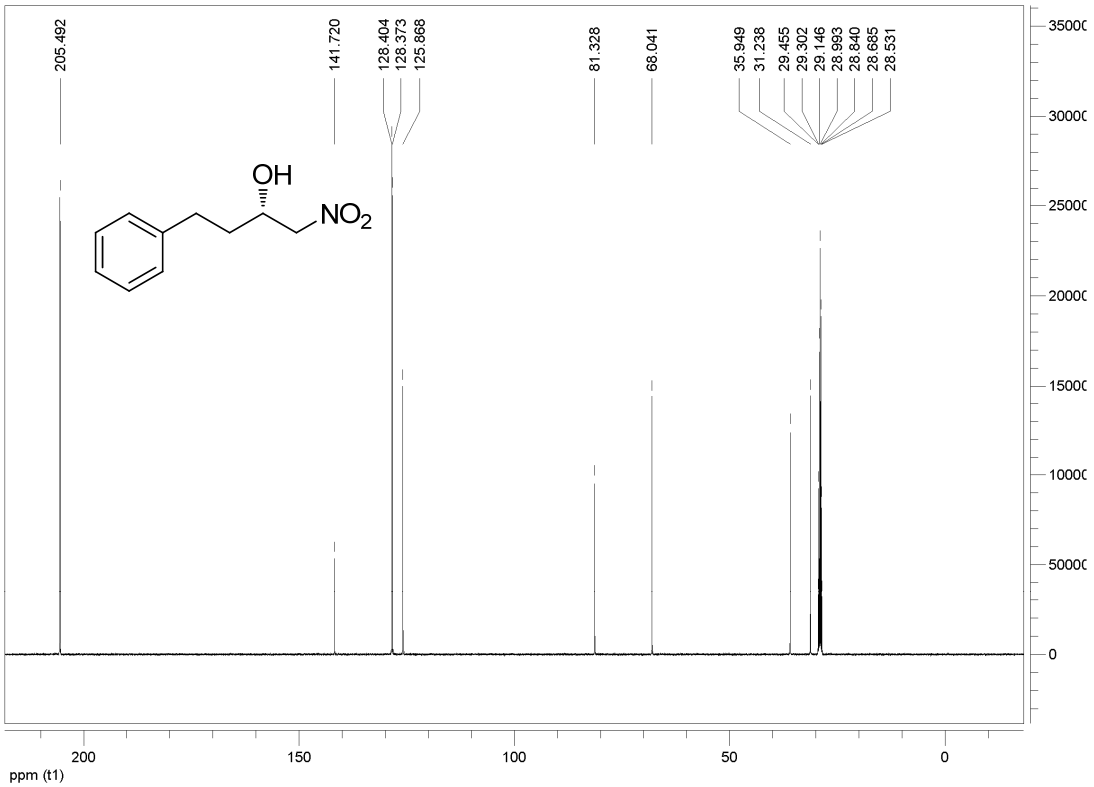

HO
NO2
Cl
Cl

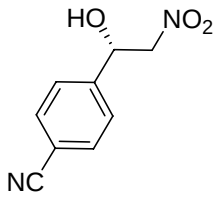

7.477
7.476
7.460
7.400
7.385
7.382
7.368
6.380
6.373
6.360
6.353
5.321
5.301
5.295
5.275
4.814
4.810
4.808
4.789
4.784
4.782
2.168
2.164
2.160
2.157
2.152
2.148
2.143
2.139
2.050
2.04
1.00
1.00
0.91
0.97
1.17
ppm (t1)

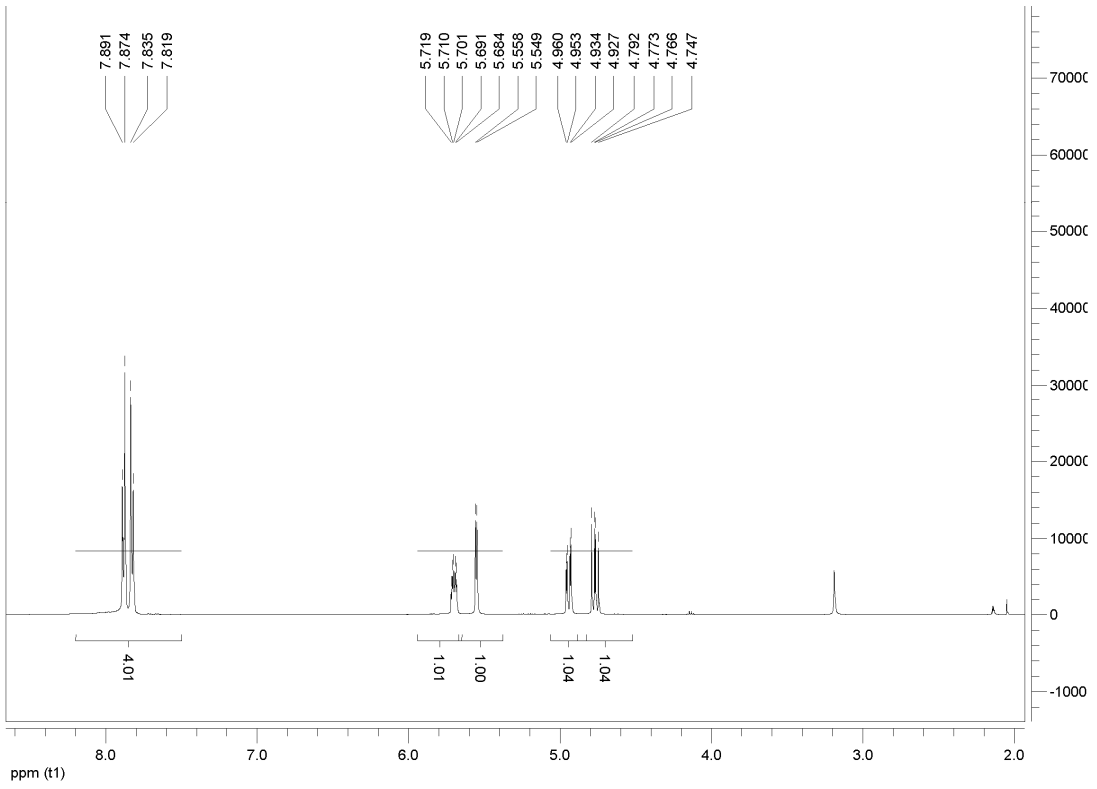

211.510
140.201
135.646
135.589
135.533
134.821
82.890
73.024
34.818
34.666
34.508
Cl
OH
NO2
Cl
ppm (t1)

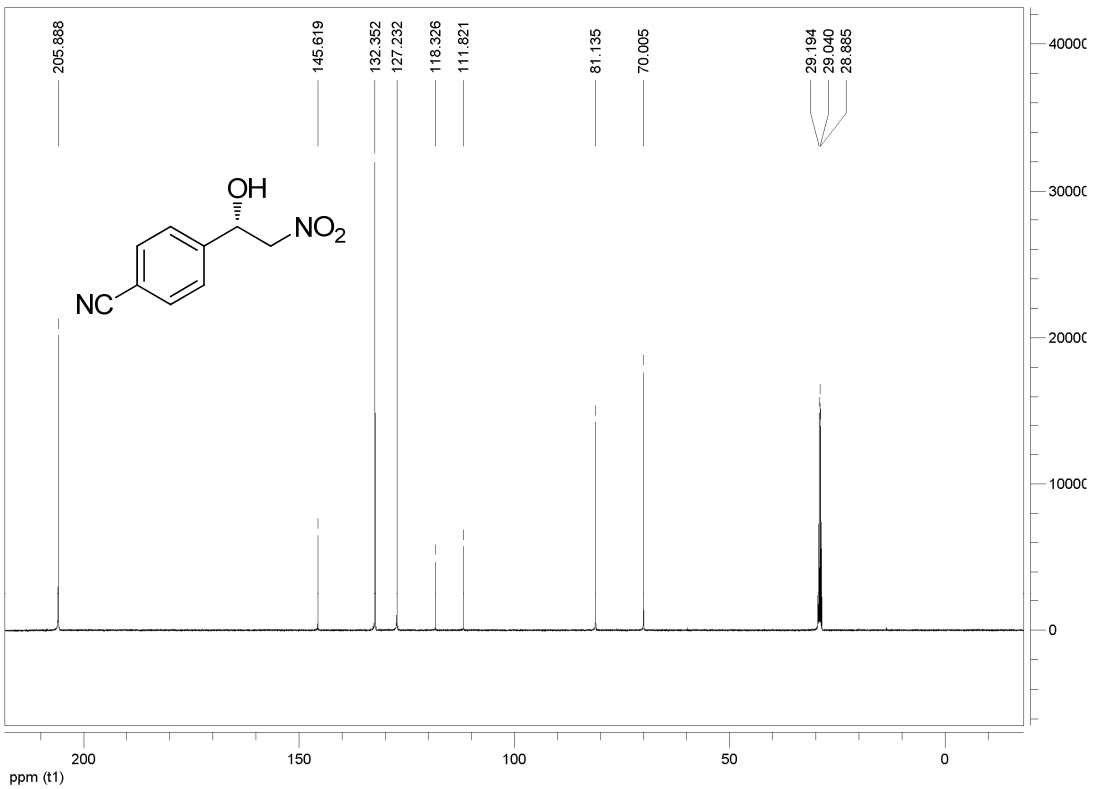

HO
NO2

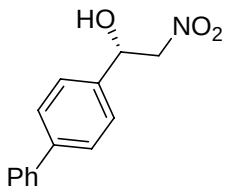

7.277
7.273
7.255
7.241
7.202
7.199
7.185
7.174
7.171
4.654
4.647
4.629
4.623
4.572
4.560
4.481
4.463
4.456
4.438
4.368
4.361
4.358
4.356
4.352
4.346
4.340
4.334
4.324
4.318
2.888
2.876
2.869
2.860
2.849
2.842
2.830
2.781
2.767
2.762
2.753
2.748
2.740
2.735
2.721
1.912
1.903
1.898
1.894
1.889
1.885
1.875
1.08
4.19
1.00
1.10
1.09
1.10
1.09
1.12
2.01
10000
50000
0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

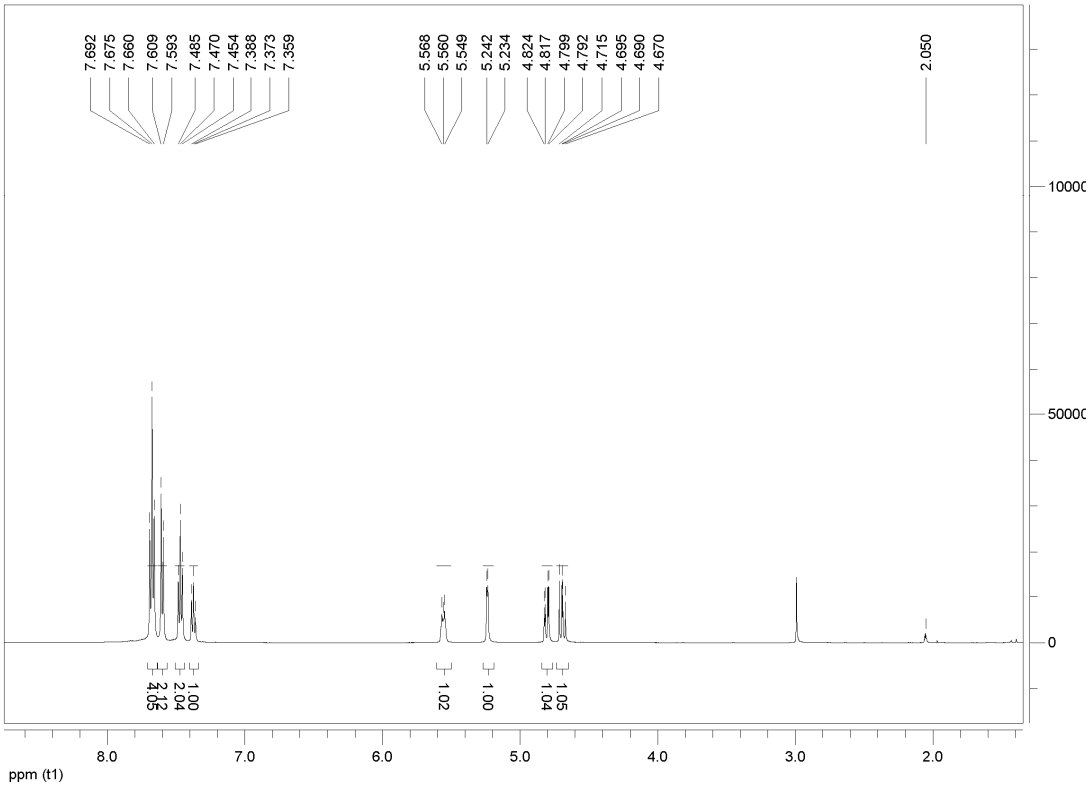

205.492
141.720
128.404
128.373
125.868
81.328
68.041
35.949
31.238
29.455
29.302
29.146
28.993
28.840
28.685
28.531
OH
NO2
35000
30000
25000
20000
15000
10000
50000
0
200
150
100
50
0
ppm (t1)

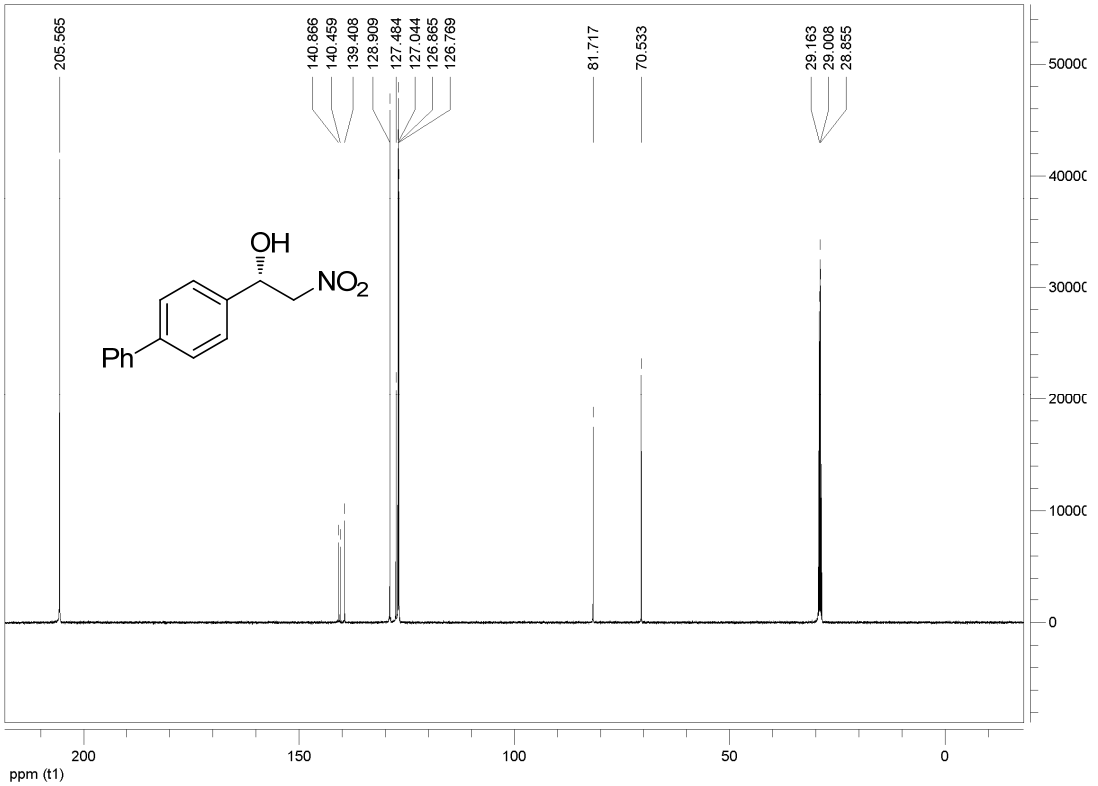

HO
NO2
NC

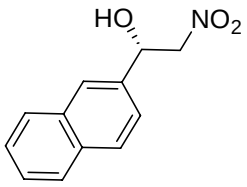

7.891
7.874
7.835
7.819
5.719
5.710
5.701
5.691
5.684
5.558
5.549
4.960
4.953
4.934
4.927
4.792
4.773
4.766
4.747
4.01
1.01
1.00
1.04
1.04
ppm (t1)

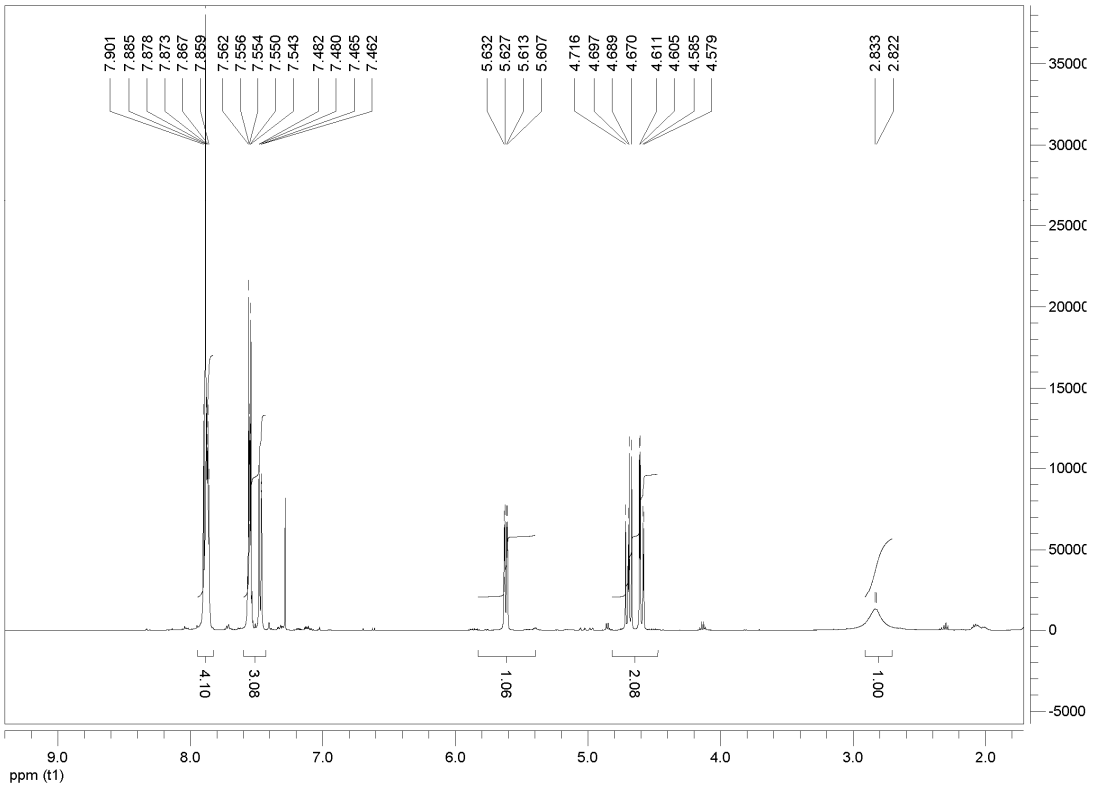

205.888
145.619
132.352
127.232
118.326
111.821
81.135
70.005
29.194
29.040
28.885
OH
NO2
NC
ppm (t1)

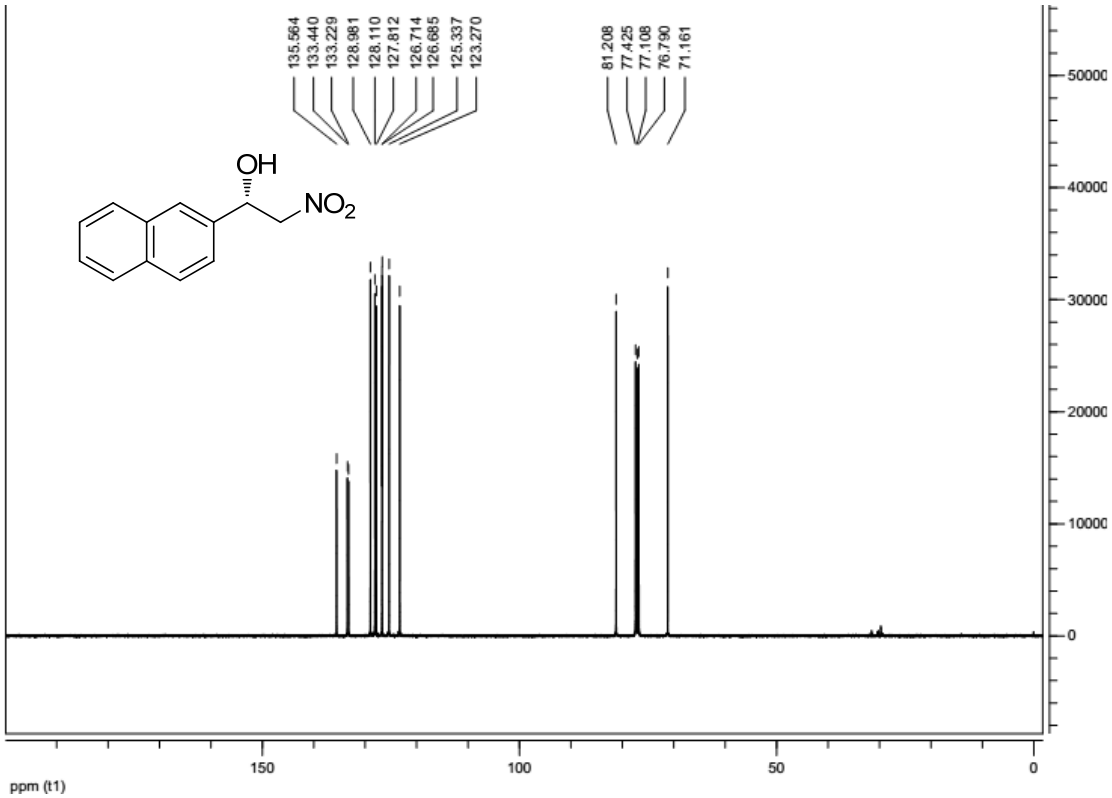

HO
NO2
Ph


7.692
7.675
7.660
7.609
7.593
7.485
7.470
7.454
7.388
7.373
7.359
5.568
5.560
5.549
5.242
5.234
4.824
4.817
4.799
4.792
4.715
4.695
4.690
4.670
2.050
2.05
2.04
1.00
1.02
1.00
1.04
1.05
10000
50000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


205.565
140.866
140.459
139.408
128.909
127.484
127.044
126.865
126.769
81.717
70.533
29.163
29.008
28.855
OH
NO2
Ph
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)


HO
NO2


7.901
7.885
7.878
7.873
7.867
7.859
7.562
7.556
7.554
7.550
7.543
7.482
7.480
7.465
7.462
5.632
5.627
5.613
5.607
4.716
4.697
4.689
4.670
4.611
4.605
4.585
4.579
2.833
2.822
4.10
3.08
1.06
2.08
1.00
ppm (t1)


135.564
133.440
133.229
128.981
128.110
127.812
126.714
126.685
125.337
123.270
81.208
77.425
77.108
76.790
71.161
OH
NO2
ppm (t1)