Supporting Information

Enantioselective Cyanosilylation of Aldehydes Catalyzed by Multistereogenic Salen-Mn(III) Complex With Rotatable Benzylic Group As a Helping Hand

Yun-Long Wei[a], Wei-Sheng Huang[a], Yu-Ming Cui[a], Ke-Fang Yang*[a], Zheng Xu[a], Li-Wen Xu*[a,b]

[a] Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education (MOE), Hangzhou Normal University, Hangzhou 311121; Tel: +86-571-28867756; E-mail: liwenxu@hznu.edu.cn

[b] State Key Laboratory for Oxo Synthesis and Selective Oxidation,
Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, P. R. China; E-mail: licpxulw@yahoo.com

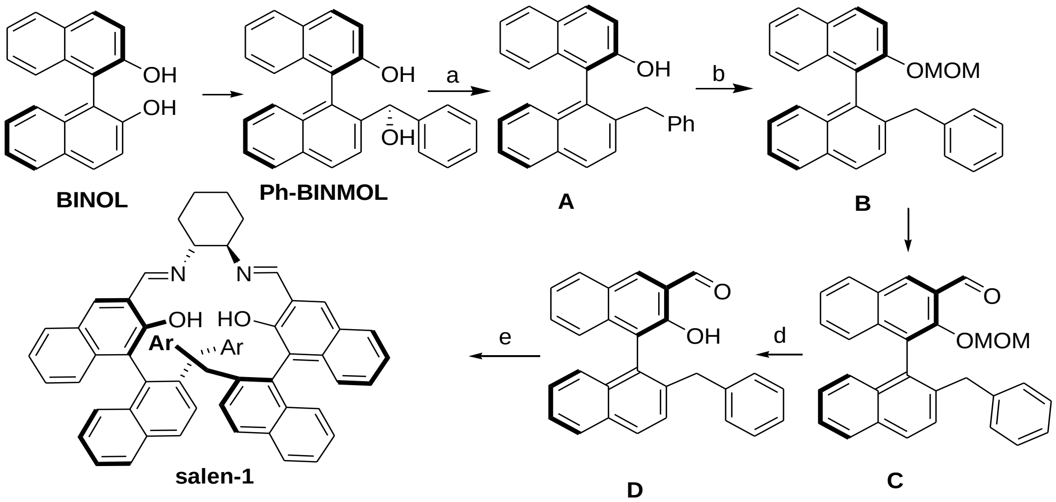
Table of Contents

S-1. 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, ^{13}C-NMR, ^{19}F-NMR were respectively recorded at 400 or 500 MHz, 101 or 126 MHz and 376 or 471 MHz respectively, ^{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.

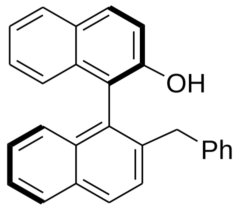
S-2. The Synthesis of Salen Ligands

2.1. Schematic synthesis of Salen 1-3



salen-**1a**: Ar = Ph
salen-**1b**: Ar = *p*(*t*-Bu)Ph
salen-**1c**: Ar = o-MePh
salen-**1d**: Ar = 1-napthyl

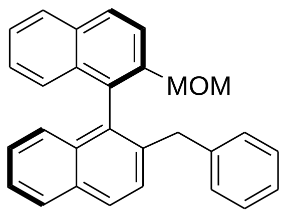
1.2 The synthesis of BINOL-derived product salen-1a from Ph-BINMOL:



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 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.

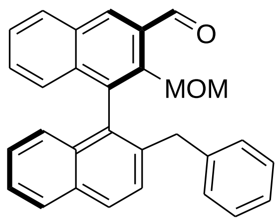
1.3 The synthesis of MOM-protected product (Step b):



B

To a solution of NaH (0.96 g, 40 mmol) in dry THF (150 mL) were added compound **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 **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.

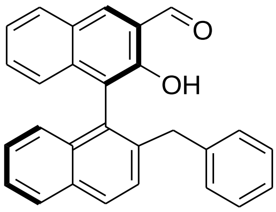
1.4 The synthesis of BINMOL-derived aldehyde (Step c):



C

To a solution of compound **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 cooled to -78 ^{o}C. A solution of dry DMF (10 ml, 13 mmol) in dry THF(10 ml) were added. The solution was stirred for 30 min at -78 ^{o}C, then warmed to 0℃. At 0 ^{o}C, it was stirred for 1.5 h. After quenching with saturated NH_4Cl solution, 1 M HCl aqueous solution 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 = 20/1) to give the desired product **C** (3.24 g, 75% yield) as a pale yellow power. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 10.60 (s, H), 8.60 (s, H), 8.04 (d, *J*=8.0 Hz, H), 7.92 (t, *J*=8.0 Hz, 3H), 7.49-7.43 (m, 3H), 7.27 (s, 3H), 7.19 (d, *J*=8.4 , H), 7.08-7.03 (m, 4H), 6.89 (d, *J*=7.6 Hz , 2H), 4.62 (m, 2H), 3.86 (m, 2H), 2.93 (s, 3H).**^{13}C NMR** ($CDCl_3$, 100 MHz) δ 191.1, 153.1, 140.2, 138.9, 136.9, 133.3, 132.2, 131.9, 131.0, 130.1, 130.1, 129.2, 129.2, 129.1, 128.9, 128.6, 128.1, 128.1, 126.6, 126.2, 126.2, 126.1, 125.9, 125.5, 99.9, 77.4, 77.1, 76.8, 57.0, 40.0 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.

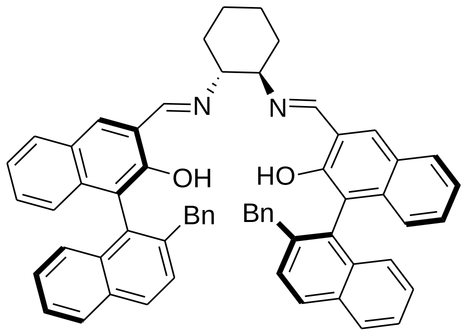
1.5 The synthesis of deprotected BINMOL-derived aldehyde (Step d):



D

To a solution of compound **C** (3.03 g , 7 mmol) in THF (75 ml) were added slowly Conc. HCl (75 ml) at 0 ^{o}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 **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, 77.4, 77.1, 76.8, 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;

1.6 The synthesis of BINMOL-derived salen:

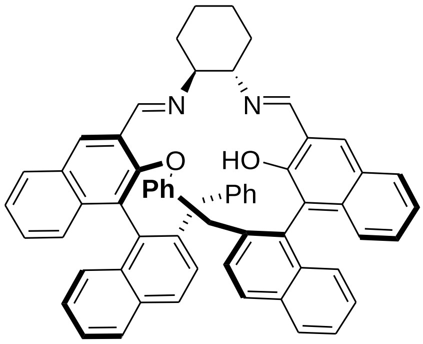


BINMOL-derived Salen

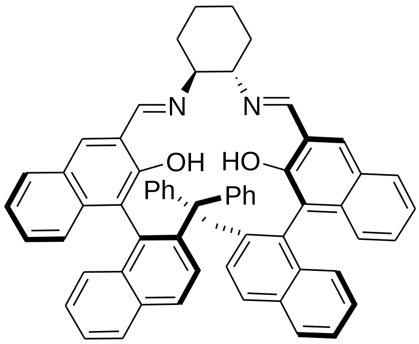
To a solution of (1R,2R)- diaminocyclohexane tartrate (0.66 g , 2.5 mmol) and K_2CO_3 (0.7 g , 5 mmol) in 50% ethanol(12 ml) were added slowly compound **D** (1.94 g, 5 mmol) in ethanol(24ml) at room temperature. After the addition, the solution was allowed to stir at room temperature for 48h. The precipitate was collected by filtration, washed with ice ethanol, and dried in vacuum oven to obtain the product **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, 77.4, 77.1 , 76.8, 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.

1.7 The Synthesis of Salen Ligands:

Similarly to the synthesis of salen ligands (2-3):

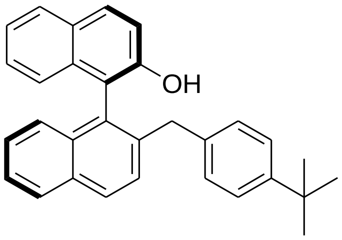


Salen-2: **^{1}H-NMR** (500 MHz, $CDCl_3$) δppm: 7.53-7.54 (m, 2H), 7.97 (s, 4H), 7.81-7.84 (m, 4H), 7.55-7.58 (m, 2H), 7.43-7.45 (m, 2H), 7.34-7.37 (m, 2H), 7.29-7.31 (m, 2H), 7.09-7.20 (m, 4H), 6.99-7.02 (m, 10H), 4.22-4.25 (m, 2H), 3.85-3.92 (m, 4H), 3.40-3.41 (d, 2H), 2.33-2.34 (d, 6H), 1.95-1.96 (d, 2H), 1.81 (s, 2H), 1.35-1.41 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δppm: 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. **FTIR ν_{max} (KBr)/cm^{-1}:** 3053, 2930, 2854, 2659, 1946, 1628, 1507, 1445, 1347, 1257, 1147, 1099, 943, 890, 804, 745, 713, 698, 496, 434.

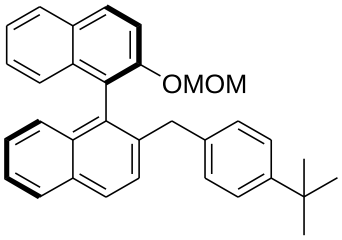


Salen-3: **^{1}H NMR** (500 MHz, $CDCl_3$) δppm: 13.09- 13.11 (m, 2H), 8.49 - 8.51 (m, 2H), 7.93-7.94 (m, 4H), 7.78 - 7.81 (m, 4H), 7.52 - 7.55 (m, 2H), 7.42-7.43 (m,2H), 7.33-7.34 (m, 2H), 7.26-7.27 (m, 2H), 6.94 -7.16 (m, 16H), 3.87-3.91 (m, 4H), 3.37 (s, 2H), 2.03-2.06 (d, J = 12.0 Hz, 2H), 1.93 (s, 2H), 1.77 (s, 2H), 1.51 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δppm : 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.

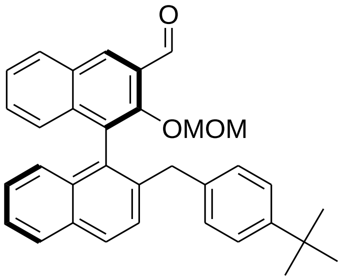
1.8 The synthesis and characterization of product Salen-1b:



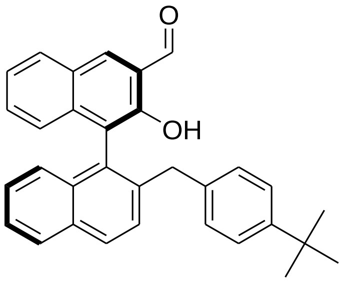
The characterization of product Salen1b-A: ^{1}H NMR (500 MHz, $CDCl_3$) δppm: 7.94-8.04 (m, 4H), 7.59-7.61 (dd, J = 2.0, 8.5 Hz, 1H), 7.53-7.55 (m, 1H), 7.45-7.47 (m, 1H), 7.36-7.42 (m, 3H), 7.23-7.29 (m, 3H), 7.08-7.10 (d, J = 8.5Hz, 1H), 6.94-6.96 (m, 2H), 5.00 (s, 1H), 3.86 (s, 2H), 1.37-1.38 (d, J = 4.0 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δppm : 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; FTIR ν_{max} (KBr)/cm^{-1}: 3508, 3055, 2961, 2867, 2355, 1907, 1619, 1595, 1515, 1468, 1266, 1201, 1175, 1143, 1022, 816, 746, 561, 432.



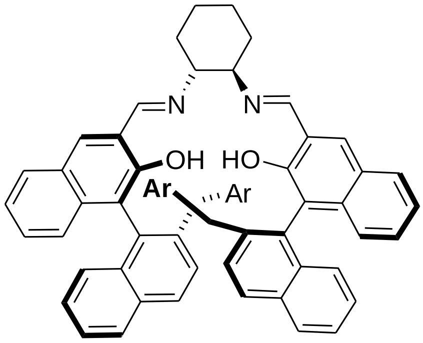
The characterization of product Salen1b-B: ^{1}H NMR (500 MHz, $CDCl_3$) δpm: 13.3 (s, 2H), 8.39 (s, 2H), 7.89-7.90 (m, 4H), 7.38-7.42 (m, 6H), 7.32-7.34 (d, J = 8.0 Hz, 2H), 7.25- 7.26 (t, J = 3.0 Hz, 4H), 7.10-7.14 (m, 10H), 7.01-7.02 (d, J = 7.0 Hz, 4H), 6.91-6.92 (d, J = 8.0 Hz, 2H), 3.72-3.75 (d, J = 15.0 Hz, 2H), 3.58-3.61 (d, J = 15.0 Hz, 2H), 3.32-3.35 (d, J = 13.5 Hz, 2H), 2.04-2.07 (d, J = 13.5 Hz, 2H), 1.47-1.51 (t, J = 10.0 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δppm : 165.1, 154.2, 141.3, 138.6, 135.3, 133.2, 133.0, 132.5, 131.9, 129.6, 128.8, 128.1, 128.06, 128.0, 127.2, 126.2, 125.2, 124.6, 123.2, 120.3, 119.3, 73.2, 39.6, 32.5, 24.1; **FTIR ν_{max} (KBr)/cm^{-1}**: 3458, 3054, 2960, 2902, 2358, 1914, 1622, 1593, 1507, 1362, 1244, 1197, 1067, 1034, 1015, 922, 812, 749, 561.



The characterization of product Salen1b-C: **^{1}H NMR** (400 MHz, $CDCl_3$) δppm: 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, $CDCl_3$) δppm: 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. **FTIR ν_{max} (KBr)/cm^{-1}**: 3456, 3054, 2960, 2903, 2868, 2359, 1911, 1690, 1619, 1587, 1508, 1450, 1268, 1157, 1075, 966, 925, 815, 756, 563.



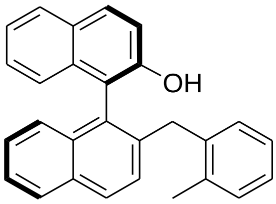
The characterization of product Salen1b-D: **^{1}H NMR** (500 MHz, $CDCl_3$) δppm: 10.43-10.45 (m, 1 H), 10.91 (s, 1 H), 8.31 (s, 1 H), 7.96-7.99 (s, 3 H), 6.87-7.60 (m, 11 H), 3.84-3.85 (m, 2 H), 1.29-1.31 (m, 9 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δppm : 196.7, 153.4, 148.5, 138.8, 137.95, 137.88, 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. **FTIR ν_{max} (KBr)/cm^{-1}:** 3202, 3054, 2960, 2859, 1918, 1653, 1629, 1504, 1411, 1386, 1339, 1295, 1116, 1055, 936, 838, 815, 777, 754, 604, 434.



1b: Ar = *p*-*t*-BuPh

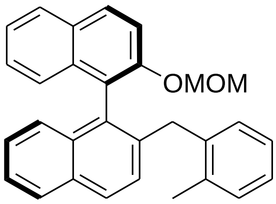
The characterization of product Salen-1b: [1]H NMR (500 MHz, $CDCl_3$) δppm: 13.4 (s, 2H), 8.35 (s, 2H), 7.88-7.90 (dd, J = 3.0 Hz, 8.5 Hz, 4H), 7.47-7.49 (d, J = 8.5 Hz, 2H), 7.38- 7.42 (m, 2H), 7.29 (s, 2H), 7.22-7.23 (d, J = 3.5 Hz, 4H), 7.10-7.12 (dd, J = 2.0 Hz, 8.5Hz, 6H), 6.90-7.04 (m, 8H), 3.78-3.82 (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, $CDCl_3$) δppm :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. **FTIR ν_{max} (KBr)/cm^{-1}**: 3053, 2959, 2861, 2361, 1910, 1630, 1507, 1442, 1344, 1258, 1145, 1117, 1022, 943, 812, 747, 566, 433.

1.9 The synthesis and characterization of product Salen 1c:



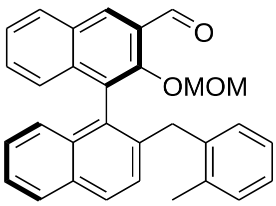
The characterization of product Salen1c-A:

[1]H NMR (500 MHz, CDCl3) δppm:7.9-8.03(m, 4 H), 7.54-7.57(td, J=1, 6.5 Hz, 1 H), 7.33-7.48(m, 6 H), 7.16-7.21(m, 4 H), 7.08-7.09(d, J=7Hz, 1 H), 4.96(s, 1 H), 3.86-3.96(q, J=16.5Hz, 2 H), 2.09(s, 3H); **13C NMR** (125 MHz, CDCl3) δppm: 151.2, 139.9, 138.3, 136.7, 13.6, 133.4, 132.7, 130.3, 130.3, 130.1, 129.5, 129.4, 129.2, 128.3, 128.2, 127.6, 127.1, 126.8, 126.3, 126.1, 126.0, 125.8, 124.4, 123.6, 117.8, 117.5, 37.1, 19.7; **FTIR ν_{max} (KBr)/cm^{-1}**: 3454, 2084, 1632, 1508, 1457, 1340, 1178, 1143, 494.



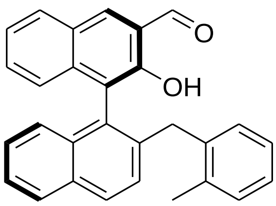
The characterization of product Salen1c-B:

^{1}H NMR (500 MHz, $CDCl_3$) δppm: 8.05-8.16(m, 4 H), 7.80-7.83(m, 1 H), 7.70-7.74(m, 1 H), 7.20-7.59(m, 7 H), 7.01-7.10(dd, J=7 Hz, 2 H), 6.91(s, 1H), 5.16-5.18(m, 1H), 5.06-5.08(m, 1H), 4.01(s, 2H), 3.33-3.45(m, 3H), 2.37(s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δppm:152.8, 141.1, 138.4, 137.6, 134.2, 133.6, 132.9, 132.6, 130.3, 130.0, 129.8, 128.4, 128.0, 126.7, 126.6, 126.5, 126.4, 125.7, 125.4, 124.3, 123.7, 116.7, 94.9, 55.9, 40.1,21.5; **FTIR ν_{max} (KBr)/cm^{-1}**: 3529, 3485, 3044, 2958, 2924, 1905, 1594, 1507, 1304, 1196, 1147, 1067, 1034, 924, 808, 745, 440.



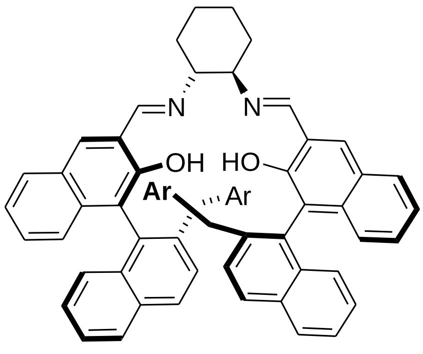
The characterization of product Salen1c-C:

^{1}H NMR (500 MHz, $CDCl_3$) δppm: 10.65 (s, 1H), 8.4(s, 1H), 8.07-8.09(d, J =8 Hz, 1H), 7.91-7.95 (t, J= 9Hz, 2H), 7.46-7.51(dd, J=7.5, 14.5Hz, 2 H), 7.24-7.37(m, 4H), 7.18-7.19(d, J=8.5Hz, 1H), 7.00-7.08(m, 4H), 4.76-4.77(d, J=6Hz, 1H), 4.61-4.63(d, J=Hz, 1H), 4.02-4.06(d, J=16.5Hz, 1H), 3.76-3.79(d, J=17Hz, 1H), 2.97(s, 3H), 2.04(s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δppm: 190.1, 152.3, 138.1, 136.7 , 136.7, 133.4, 133.2, 131.9, 131.2, 130.4, 130.3, 130.1,129.3, 129.2, 129.1 128.6, 128.1, 127.2, 126.5, 126.4, 126.2, 126.1, 125.9, 125.4, 100.0, 57.0, 37.4, 19.7; **FTIR ν_{max} (KBr)/cm^{-1}**: 3458, 2359, 1687, 1654, 1581, 1508, 1355, 1260, 1180, 1155, 1104, 964, 810, 755, 554, 500.



The characterization of product Salen1c-D:

^{1}H NMR (500 MHz, $CDCl_3$) δppm: 10.66(s ,1H), 8.66(s, 1H), 8.0-8.08(d, J=8Hz, 1H), 7.94-7.98(dd, J=9,11.5Hz, 2H), 7.45-7.55(m, 3H), 7.25-7.33(m, 3H), 7.08-7.12(m, 4H), 6.93-6.95(d, J=8Hz, 2H), 4.74-4.75(d, J=5.5Hz, 1H), 4.61-4.62(d, J=5.5Hz, 1H), 3.98-4.00(d, J=15.5Hz, 1H), 3.84-3.88(d, J=5.5Hz, 1H), 2.98(s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δppm:191.0, 153.2, 138.9, 136.9, 133.4, 132.3, 132.2, 131.1, 130.2, 129.2, 129.1, 129.0, 128.6, 128.2, 126.6, 126.3, 126.0, 125.9, 125.5, 99.9, 57.0, 40.1; **FTIR ν_{max} (KBr)/cm^{-1}**: 3478, 3054, 2855, 2354, 1658, 1631, 1504, 1338, 1296, 1118, 933, 895, 815, 749, 507, 434.

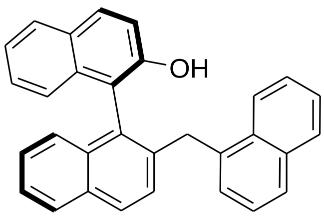


salen1c: Ar = *o*-MePh

The characterization of product Salen1c:

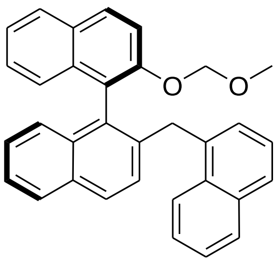
^{1}H NMR (400 MHz, $CDCl_3$) δppm: 13.03(s, 2H), 8.40(s, 2H), 7.80-7.86(m, 4H), 7.68-7.72(t, J=8.8Hz, 4H), 7.31-7.35(t, J=8.8Hz, 2H), 7.17-7.26(m, 8H), 6.98-7.05(m, 12H), 6.87-6.91(t, J=8Hz, 2H), 3.81-3.84(d, J=16Hz, 2H), 3.68-3.72(d, J=16Hz, 2H), 3.26-3.28(m, 2H), 1.95(s, 6H), 1.83-1.85(d, J=8.8Hz, 2H), 1.66-1.68(d, J=6Hz, 2H), 1.36-1.48(m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δppm:165.0, 154.3, 138.7, 137.8, 136.7, 135.0, 133.2, 133.0, 132.4, 132.0, 130.5, 129.8, 128.8, 128.2, 128.0, 127.9, 127.4, 127.1, 126.1, 126.0, 125.7, 125.6, 125.0, 124.7, 123.2, 120.5, 119.3, 73.0, 37.1, 32.7, 24.1, 19.6; **FTIR ν_{max} (KBr)/cm^{-1}**: 3054, 2934, 2858, 2836, 1633, 1508, 1462, 1301, 1259, 1215, 1143, 947, 882, 859, 769, 747, 619, 434.

The synthesis and characterization of product Salen-1d:



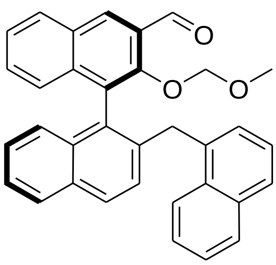
The characterization of product Salen1d-A:

^{1}H NMR (400 MHz, $CDCl_3$) δppm:7.81-7.86(dd, J=8Hz, 2H), 7.76-7.78(d, J=8.4Hz, 1H), 7.71-7.73(d, J=8Hz, 1H), 7.72-7.9(m, 3H), 7.34-7.38(t, J=7.2Hz, 1H), 7.12-7.32(m,11H), 5.19(s, 1H), 3.61-3.64(t, J=6.4Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δppm:151.4, 139.9, 136.1, 133.9, 133.8, 133.3, 132.7, 132.2, 130.1, 129.4, 129.2, 129.1, 128.6, 128.4, 128.2, 128.0, 127.5, 127.2, 127.0, 126.8, 125.9, 125.8, 125.5, 125.5, 124.8, 124.4, 123.6, 117.8, 117.4, 68.0, 36.7, 25.6; **FTIR ν_{max} (KBr)/cm^{-1}:** 3486, 3055, 2359, 1620, 1595, 1507, 1379, 1262, 1201, 1174, 1143, 817, 749, 419.



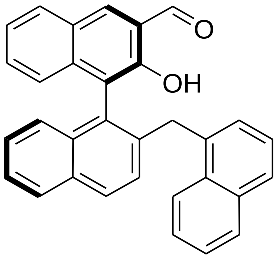
The characterization of product Salen1d-B:

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm:7.82-7.84(d, J=9.2Hz, 1H), 7.76-7.78(d, J=8Hz, 1H), 7.62-7.73 (m, 4H), 7.55-7.57 (d, J=8.4Hz, 1H), 7.48-7.50(d, J=9.2Hz, 1H), 7.08-7.26(m, 11H), 4.94-4.96(d, J=6.8Hz, 1H), 4.86-4.87(d, J=6.8Hz, 1H), 4.16-4.20(d, J=16.4, 1H), 4.03-4.07(d, J=16.8Hz, 1H), 3.04(s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm: 152.7, 137.9, 136.6, 133.9, 133.4, 132.6, 132.4, 132.0, 129.8, 128.5, 128.2, 128.0, 127.9, 127.8, 127.3, 127.0, 126.7, 126.3, 126.0, 125.6, 125.5, 125.4, 125.2, 124.8, 124.3, 122.9, 116.7, 95.2, 55.9, 37.2; **FTIR ν_{max} (KBr)/cm^{-1}:** 3462, 1636, 1507, 1472, 1397, 1259, 1240, 1196, 1066, 1032, 749.



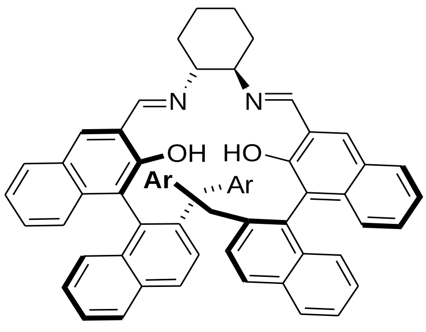
The characterization of product Salen1d-C:

[1]**H NMR** (400 MHz, $CDCl_3$) δppm: 10.56(s,1H), 8.52(s, 1H), 7.97-7.99(d, J=8Hz, 1H), 7.82-7.84(d, J=8Hz, 1H), 7.68-7.77(m,3H), 7.59-7.61(d, J=8Hz, 1H), 7.37-7.44(m, 2H), 7.28-7.34(dd, J=6.8, 15.2Hz, 2H), 7.13-7.28(m, 7H), 4.73-4.74(d, J=6Hz, 1H), 4.58-4.59(d, J=6Hz, 1H), 4.37-4.42(d, J=16.8Hz, 1H), 4.14-4.18(d, J=16.4Hz, 1H), 2.9(s, 3H); [13]**C NMR** (100 MHz, $CDCl_3$) δ ppm: 190.9, 153.2, 138.7, 136.6, 135.9, 133.8, 133.3, 133.2, 133.0, 132.2, 132.0, 130.8, 129.2, 129.0, 128.5, 128.5, 128.1, 128.0, 127.3, 127.0, 126.5, 126.1, 125.5, 125.3, 124.4, 100.1, 57.0, 37.1; **FTIR ν_{max} (KBr)/cm^{-1}**: 3453, 2280, 1685, 1636, 1356, 1157, 1074, 962, 749.



The characterization of product Salen1d-D:

[1]H NMR (400 MHz, $CDCl_3$) δppm: 10.50(s, 1H), 10.04(s, 1H), 8.14(s, 1H), 7.85-7.88(dd, J=3.6, 6.8Hz, 1H ,) 7.79-7.81(d, J=8Hz, 1H), 7.69-7.74(m, 2H), 7.58-7.60(d, J=8Hz, 1H), 7.28-7.37(m, 4H), 7.12-7.24(m, 7H), 4.26-4.30(d, J=16.4Hz, 1H), 4.11-4.15(d, J=16.4Hz, 1H); [13]**C NMR** (101 MHz, $CDCl_3$) δppm: 196.8, 153.3, 138.3, 138.0, 137.6, 136.2, 133.6, 132.9, 132.5, 132.2, 130.5, 130.4, 129.9, 128.4, 128.2, 128.0, 127.6, 126.9, 126.3, 125.7, 125.4, 125.2, 124.6, 124.5, 122.1, 37.0. **FTIR ν_{max} (KBr)/cm^{-1}**: 3184, 3049, 2913, 2842, 1943, 1653, 1626, 1504, 1384, 1292, 1177, 895, 827, 793, 774, 752, 507, 431.



Ar=1-napthyl

The characterization of product Salen 1d:

^{1}H NMR (400 MHz, $CDCl_3$) δppm: 13.19(s, 2H), 8.42(s, 2H), 7.79-7.87(m, 4H), 7.62-7.74(m, 10H), 7.47-7.55(m, 2H), 7.18-7.36 (m, 16H), 7.09-7.11 (m, 4H), 6.88-6.94(m, 2 H), 4.28-4.35(m, 2 H), 4.12-4.17(m, 2 H), 3.12-3.32(m, 2 H), 1.40-2.00(m, 8H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm: 162.6, 151.9, 135.7, 134.1, 132.6, 131.3, 130.9, 130.6, 129.9, 129.3, 128.1, 127.4, 126.5, 126.4, 126.0, 125.9, 125.8, 125.7, 125.6, 125.1, 125.0, 124.9, 124.7, 124.3, 123.7, 123.4, 123.2, 123.1, 123.0, 122.9, 122.8, 122.7, 122.5, 122.4, 122.3, 120.9, 118.1, 116.9, 70.7, 34.5, 30.3, 21.7; **FTIR ν_{max} (KBr)/cm^{-1}:** 3179, 3050, 3008, 2929, 2857, 2302, 1919, 1629, 1507, 1442, 1383, 1342, 1295, 1115, 944, 858, 776, 749, 432.

S-3. The synthesis of (Salen)Mn(III)-X catalysts

3.1 Typical procedure of synthesis of (Salen)Mn(III)-Cl:

Salen(1.57g，1.83 mmol，1eq) and manganese(II) acetate tetrahydrate (1.34, 5.47mmol, 3eq) were added to 20 mL of ethanol, and the mixture was refluxed for 3 h in air. Upon cooling, 20 mL of an aqueous saturated sodium chloride solution was added, and after stirring for 2h, anadditional 10 mL of water was added. The mixture was then extracted with 20 mL of dichloromethane. The combined organic portions were then washed with 5 mL of water and dried over MgSO4. The solvent was removed by rotary evaporation,the dark brown solid is dissolved in 20 mL of methylene chloridein a1-L, round-bottomed flask.Heptane (100 mL) is added, and the methylene chloride is removed by reduced pressure rotary evaporation. After complete removal of the methylene chloride, the brown slurry is stirred for 1 hr at ≤5°C in an ice bath. The brown solid is collected by vacuum filtration and allowed to air dry. Heating of the solid at 50-60 ℃ under high vacuum removes any residual solvent to yield the brown product (1.60 g, 93% yield). Element Analysis: Calcd for $C_{62}H_{48}MnN_2O_2$: C 78.88, H：5.13, N: 2.99 Found:C 78.29, H:4.63, N: 2.80

C1a: **FTIR ν_{max} (KBr)/cm^{-1}**: 3644，3054，2925，2857，1948，1610，1492，1309，1189，952，800，758， 689,537**. ESI-MS (m /z)**: $[M]^+$calcd for $C_{62}H_{48}MnN_2O_2$ 907.3, found 907.3.

C1b: **FTIR ν$_{max}$ (KBr)/cm^{-1}**: 3645, 3052, 2955, 2902, 2862, 1909, 1609, 1508, 1310, 952, 860, 757, 689, 567; **ESI-MS (m /z)**: $[M]^+$calcd for $C_{70}H_{64}MnN_2O_2$ 1019.4, found 1019.4.

C1c: **FTIR ν$_{max}$ (KBr)/cm^{-1}**: 3645, 3051, 2931, 2858, 1914, 1609, 1449, 1320, 1222, 1189, 952, 760, 688, 569; **ESI-MS (m /z):** $[M]^+$calcd for $C_{64}H_{52}MnN_2O_2$ 935.3, found 935.3.

C1d: **FTIR ν$_{max}$ (KBr)/cm^{-1}:** 3436, 3048, 2934, 2858, 1940, 1609, 1555, 1507, 1447, 1347, 1371, 1026, 951, 758, 689, 570; **ESI-MS (m /z):** $[M]^+$calcd for $C_{70}H_{52}MnN_2O_2$ 1007.3, found1007.3.

C2: **FTIR ν$_{max}$ (KBr)/cm^{-1}:** 3645，3045，3025，2930，2857，1947，1609，1493，1449, 1347， 951，802，745，715，568. **ESI-MS (m /z):** $[M]^+$calcd for $C_{62}H_{48}MnN_2O_2$ 907.3, found 907.3.

C3: **FTIR ν$_{max}$ (KBr)/cm^{-1}: 3**645，3053，2931，2858，1609，1449，1309，1221，1189，951，759，690，658，537. **ESI-MS (m /z):** $[M]^+$calcd for $C_{62}H_{48}MnN_2O_2$ 907.3, found 907.3.

3.2 Typical procedure of synthesis of (Salen)Mn-OAc:

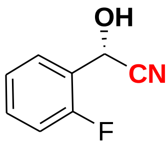
An appropriate amount of salen ligands (**Salen-1a**, 0.253 mmol, 0.216 g) was separately dissolved in absolute ethanol in nitrogen atmosphere under vigorous stirring. Then was added $Mn(OAc)_2$ $4H_2O$ (0.253 mmol, 0.062 g), and the resulting mixture was refluxed for 7 h in nitrogen atmosphere until the complete reaction of ligand compound (checked by TLC). Finally, the precipitate complexes were recovered by filtration, and washed several times with absolute ethanol and dichloromethane, dried in vacuum at 65 ℃ for 5 h, and again purified by re-crystallization in acetone to get the brown product in a 88% yield. **FTIR ν$_{max}$ (KBr)/cm^{-1}:** 3643，3203，3054，2933，2859，1946，1819，1610， 1554，1422，1323，1027，952，801，757，689，567，535. **ESI-MS (m /z):** $[M]^+$calcd for $C_{62}H_{48}MnN_2O_2$ 907.3, found 907.3.

3.3 Typical procedure of synthesis of (Salen)Mn-OTf:

Manganese(II) acetate tetrahydrate (1.55 g, 6.32 mmol) was added to the solution of Salen 1a (2.7g, 3.16 mmol) in N,N-dimethylformamide (20 mL). The resulting solution was heated at 100 ℃ for 3 h. After cooling, the solvent was removed by evaporation under reduced pressure, and then dried in vacuo at 80 ℃ for 12 h. The residue dissolved in CH_2Cl_2 (200 mL) was washed with aqueous trifluoromethanesulfonic acid solution (0.5 M, 100 mL × 3). The organic layer was dried over $MgSO_4$, and the solvent was removed by evaporation under reduced pressure. The residue was then dissolved in CH_2Cl_2 (~10 mL), and the resulting solution was passed through a membrane filter (Millex®-FG, pore size 0.20 μm, diameter 25 mm, S22 Millipore). The addition of pentane (~50 mL) afforded Mn (III) (2.77, 2.62 mmol) as a brown solid in a 83% yield. **FTIR ν_{max} (KBr)/cm^{-1}:** 3183，3055，2933，2858，1651，1610，1505，1451，1347，1245，1152，1029，804，747，638，571，510. **ESI-MS (m /z):** $[M]^+$calcd for $C_{62}H_{48}MnN_2O_2$ 907.3, found 907.3.

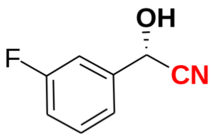
S-4. General procedure for the asymmetric cyanosilylation

General procedure of silylcyanation of the aldehydes catalyzed by Mn(salen) and POPh3: The aldehyde (0.5 mmol) was added to a stirred DCE solution of the catalyst [3 mol% Mn(salen), 20 mol% Ph_3PO] and the mixture stirred for 30 min at –10 ℃. TMSCN (0.75 mmol) was then added with a syringe and the mixture was stirred at the same temperature for 24 h. The solvent was then evaporated, 2N HCl (10 mL) was added, and the mixture was stirred vigorously at room temp. for 2 h to hydrolyze the trimethylsilyl ether. After addition of ethylacetate (10 ml), the mixture was stirred for 30 min. The organic layer was separated and washed with H_2O. The aqueous layer was extracted with ethyl acetate (2 ×20 mL), and the combined organiclayers were washed with brine and dried with Na_2SO_4.The crude product was further purified by flash chromatography and ee % was determined by chiral high pressureliquid chromatography (HPLC) column .



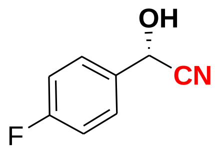
3a
94%yield
88%ee

2-Hydroxy-2-(2- Fluorophenyl) acetonitrile (**3a**) (yellow oil) was obtained according to the general procedure (94% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column(n-hexane-isopropanol 95:5 V/V, 0.8 mL/min, 210 nm); minor enantiomer tr =18.693 min, major enantiomer tr = 17.504 min; 88% *ee*; $[\alpha]^{18}_{D}$ -28.44^{o} (c 1.0, $CHCl_3$) ; [lit.[4] $[\alpha]^{D}_{20}$+21.9 (c3.60 , $CHCl_3$), 84% ee (R)]. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ ppm: 7.60-7.4（td，J=1.2, 6.4Hz, 1H）, 7.41-7.46 (m, 1H), 7.22-7.26 (t, J= 7.8Hz, 1H), 7.11-7.16(t, 9.2Hz, 1H), 5.77(s, 1H), 3.48(s, 1H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ ppm: 161.2, 158.7, 131.8-131.9 (s, J_{CF}=8.2Hz, 1C), 128.4, 124.9-125.0 (s, J_{CF}=3.7Hz, 1C), 122.8-122. 9 (s, J_{CF}=4.2Hz, 1C), 118, 115.9-116.1 (s, J_{CF}=20.4Hz, 1C), 57.9-58.0 (s, J_{CF}=4.9Hz, 1C); ^{19} **FNMR** (470 MHz, $CDCl_3$): -118.2; **IR(KBr)**: 3405, 2959, 2852, 2362, 1617, 1492, 1459, 1231, 1030, 759.



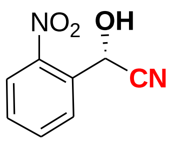
3b
81% yield
75% *ee*

2-Hydroxy-2-(3- Fluorophenyl) acetonitrile (**3b**) (yellow oil) was obtained according to the general procedure (81% yield). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column(n-hexane-isopropanol 95:5 V/V, 0.8 mL/min, 210 nm); minor enantiomer tr = 21.36 min, major enantiomer tr = 22.59 min; 75% *ee* ; $[\alpha]^{18}_{D}$ -20.05^{o} (c 1.0, $CHCl_3$) ; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ ppm: 7.11 (dt, *J* = 8.4, 8. 3, 2.2 Hz, 1H), 7.33-7.18 (m, 1H), 7.40 (dd, *J* = 13.8, 7.9 Hz, 1H), 5.53 (s, 1H), 3.93 (d, J = 2.8 Hz, 1H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ ppm：164.21 (s, 1C), 161.74 (s, 1C), 137.46 (d, J_{CF} = 7.31 Hz, 1C), 130.87 (d, J_{CF} = 8.30 Hz, 1C), 122.14 (d, J_{CF} = 3.03 Hz,1C), 118.55 (s, 1C), 116.91 (s, 1C), 116.70 (s, 1C), 113.89 (s, 1C), 113.65 (s, 1C), 62.77 (s, 1C); ^{19}**F-NMR** (470 MHz, $CDCl_3$) δppm: -110.9; **IR(KBr)**: 3445, 2968, 2923, 2851, 2061, 1619, 1453, 1265, 1137, 1051, 868, 757



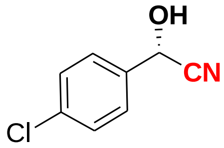
3c
98% yield
74% *ee*

2-Hydroxy-2-(3- Fluorophenyl) acetonitrile (**3c**) (yellow oil) was obtained according to the general procedure (98% yield). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column(n-hexane-isopropanol 95:5 V/V, 0.8 mL/min, 210 nm); minor enantiomer tr = 20.464 min, major enantiomer tr = 18.488 min; 74% *ee*;$[\alpha]^{18}_{D}$ -26.4^{o} (c 1.0, $CHCl_3$) ;[lit.[4]$[\alpha]_{20}^{D}$+36.4 (c 6.4, $CHCl_3$) for R-enantiomer in 94%ee]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm: 7.50 (dd, J = 8.4, 5.2 Hz, 1H), 7.16-7.06 (m, 1H), 5.51 (s, 1H), 3.68 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm: 164.7-164.2(d, J_{CF}=48.1Hz,1C), 131.2-131.1(d, J_{CF}=3.2Hz, 1C), 128.7-128.6 (d, J_{CF}=8.4Hz, 1C), 118.8, 116.3-116.1(d, J_{CF}=21.0Hz, 1C), 62.9; **^{19}F-NMR** (470 MHz, $CDCl_3$) δppm: -110.9; **IR (KBr):** 3430, 2959, 2924, 2853, 2361, 1605, 1510, 1234, 1039, 836, 749.



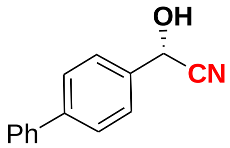
3d
96% yield
80% *ee*

2-Hydroxy-2-(4-Nitrophenyl)acetonitrile (**3d**) was obtained according to the general procedure (96% yield). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column(n-hexane-isopropanol 95:5 V/V, 0.8 mL/min, 210 nm); minor enantiomer tr = 19.831 min, major enantiomer tr = 18.258 min; 80% *ee*;$[\alpha]^{18}_{D}$ -70.4^{o} (c 1.0, $CHCl_3$) ; **^{1}H NMR** (400 MHz,$CDCl_3$) δppm: 8.16-8.18(dd, J=1, 8Hz, 1H)，7.97-7.99(d, J=7.5Hz, 1H), 7.77-7.80(t, J=8Hz, 1H), 7.61-7.65(t, J=8Hz，1H), 6.20(s, 1H), 4.15(s, 1H); **^{13}C NMR** (100 MHz,$CDCl_3$) δppm: 146.9, 134.8, 130.9, 130.8, 129.3, 125.8, 117.6, 60.4; **IR (KBr):**3492, 3399, 3111, 2966, 2934, 2854, 2249, 1524, 1346, 1186, 1040, 786, 741, 704.



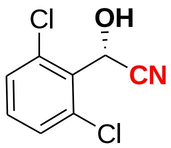
3e
72% yield
78% *ee*

2-Hydroxy-2-(4-Chlorophenyl)acetonitrile (**3e**) (yellow oil) was obtained according to the general procedure (72% yield). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column(n-hexane-isopropanol 95:5 V/V, 0.8 mL/min, 210 nm); minor enantiomer tr = 13.941 min, major enantiomer tr = 12.299 min; 78% *ee* ;$[\alpha]^{18}_{D}$ -31.9^{o} (c 1.0, $CHCl_3$) ; [lit.[1] $[\alpha\ \ ]_D$ +27.2 (c 1.50, $CHCl_3$) for R enantiomer in 66% ee]; **^{1}H NMR** (500 MHz, $CDCl_3$) δppm: 7.39-7.46 (m , 4 H), 5.29 (s, 1 H), 3.65 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δppm: 133.8 , 131.0 , 129.5, 129.4 , 128.0 , 118.7, 62.8; **IR(KBr):** 3418, 2957, 2922, 2852, 2361, 2341, 1598, 1409, 1193, 1015, 837..



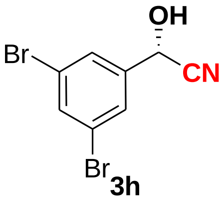
3f
71% yield
71% *ee*

2-Hydroxy-2-(4-phenylphenyl) acetonitrile (**3f**) was obtained according to the general procedure (71% yield). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column(n-hexane-isopropanol 95:5 V/V, 0.8 mL/min, 210 nm); minor enantiomer tr = 21.36 min, major enantiomer tr = 22.59 min; 71% *ee*;$[\alpha]^{18}_{D}$ -25.3^{o} (c 1.0, $CHCl_3$) ; **^{1}H NMR** (400 MHz ,$CDCl_3$) δppm: 7.74-7.76(d, J =8Hz, 2H), 7.67-7.70(m,4H),7.47-7.50(t, J=8 Hz, 2H), 7.38-7.41(t, J=7.5Hz, 1Hz), 6.04-6.05(d, J=6.4Hz, 1H), 5.84-5.86(d, J=6Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δppm: 147.6, 145.4, 141.5, 134.1, 132.7, 132.5, 132.3, 132.2, 125.0, 67.6; **IR(KBr):** 3413, 2963, 2922, 2852, 2239, 1487, 1409, 1273, 1193, 1027, 762.



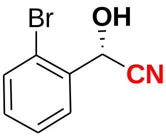
3g
94% yield
66% *ee*

2-Hydroxy-2-(2,6-diChlorophenyl) acetonitrile (**3g**) (yellow solid) was obtained according to the general procedure (94% yield). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column(n-hexane-isopropanol 95:5 V/V, 0.8 mL/min, 210 nm); minor enantiomer tr = 13.97 min, major enantiomer tr = 16.577 min; 66% *ee*; **$[\alpha]^{18}_{D}$** –53.4^{o} (c 0.8, $CHCl_3$) ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm: 7.27-7.39 (m, 3 H), 6.29 (s, 1 H), 3.64 (s, 1 H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ ppm :135.1 , 131.6 , 129.4, 117.1, 59.1 ; **IR (KBr)**: 3374, 3078, 2934, 2252, 1738, 1560, 1426, 1189, 1035, 861, 744, 664.



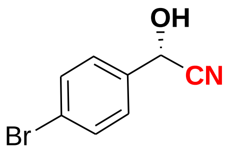
3h
81% yield
82% *ee*

2-Hydroxy-2-(3,5-diBromophenyl)acetonitrile (**3h**) (yellow solid) was obtained according to the general procedure (81% yield). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column(n-hexane-isopropanol 95:5 V/V, 0.8 mL/min, 210 nm); minor enantiomer tr = 21.36 min, major enantiomer tr = 22.59 min; 82% *ee*. **$[\alpha]^{18}_{D}$** –15.3^{o} (c 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δppm:7.71 (s, 1 H), 7.60 (s, 2 H), 5.50 (s, 1 H), 4.10 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 138.7 , 135.4 , 128.3, 123.6 , 118.1 , 61.9. **IR (KBr):** 3388, 3085, 2928, 2852, 2685, 2255, 1564, 1438, 1045, 936, 784, 732, 603.



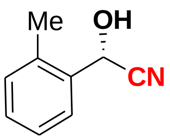
3i
81% yield
67% *ee*

2-Hydroxy-2-(2-Bromophenyl) acetonitrile (**3i**) (yellow oil) was obtained according to the general procedure (81% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column(n-hexane-isopropanol 95:5 V/V, 1 mL/min, 210 nm); minor enantiomer tr = 13.654 min, major enantiomer tr = 12.608 min; 67% *ee*; **$[\alpha]^{18}_{D}$** 8.4^{o} (c 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.72 (d, J = 7.74 Hz, 1H), 7.61 (d, J = 7.99 Hz, 1H), 7.42 (t, J = 7.58 Hz, 1H), 7.29 (t, J = 7.70 Hz, 1H), 5.83 (s, 1H), 3.76 (s, 1H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ ppm: 134.45, 133.37, 131.31, 128.60, 128.33, 122.35, 118.05, 63.12; **IR (KBr)**: 3389, 3058, 2913, 2805, 2249, 1591, 1571, 1243, 1031, 750, 637, 608.



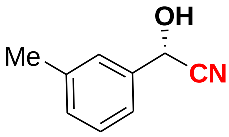
3j
72% yield
78% *ee*

2-Hydroxy-2-(2-diBromophenyl) acetonitrile (**3j**) was obtained according to the general procedure (72% yield). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column(n-hexane-isopropanol 95:5 V/V, 0.8 mL/min, 210 nm); minor enantiomer tr = 15.197 min, major enantiomer tr = 12.888 min; 78% *ee*. $[\alpha]^{18}_{D}$ –21,2^{o} (c 1.0, $CHCl_3$); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ ppm: 7.56 (d, J = 8.35 Hz, 1H), 7.37 (d, J = 8.32 Hz, 1H), 5.49 (s, 1H), 4.42-3.14 (m, 1H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ ppm: 134.2, 132.4, 128.2, 124.1, 118.6, 62.9; **IR (KBr):**3391, 1958, 2923, 2852, 2254, 1697, 1592, 1491, 1404, 1038, 841, 797, 615.



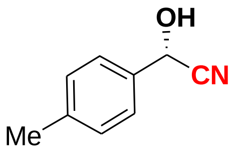
3k
71% yield
71% *ee*

2-Hydroxy-2-(2-Methylphenyl)acetonitrile (**3k**) (yellow oil) was obtained according to the general procedure (71% yield). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column(n-hexane-isopropanol 95:5 V/V, 0.8 mL/min, 210 nm); minor enantiomer tr = 12.868 min, major enantiomer tr = 11.066 min; 71% *ee*. $[\alpha]^{18}_{D}$ –11.8^{o} (c1.0, $CHCl_3$); lit.[1] $[\alpha]_D$+21.3 (c1.03, $CHCl_3$), 51% ee (R). ^{1}**H NMR** (400 MHz, $CDCl_3$) δ ppm: 7.22-7.32 (m, 4 H), 5.46 (s, 1 H), 3.60 (s, 1 H), 2.39 (s, 3 H); ^{13}**C NMR** (100 MHz,$CDCl_3$) δ ppm :139.2，135.2, 130.6, 129.0, 127.4 , 123.7, 119.1, 63.5 , 21.3; **IR (KBr):** 3412, 2957, 2924, 2853, 2247, 1692, 1600, 1491, 1462, 1038, 753.



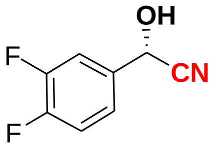
3l
71% yield
78% *ee*

2-Hydroxy-2-(3-Methylphenyl) acetonitrile (**3l**) (yellow oil) was obtained according to the general procedure (71% yield). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column(n-hexane-isopropanol 95:5 V/V, 0.8 mL/min, 210 nm); minor enantiomer tr = 13.093 min, major enantiomer tr = 11.292 min; 78% *ee*. $[\alpha]^{18}_{D}$ –14.1° (c 1.0, $CHCl_3$); lit.[1]$[\alpha]_D$+41.2(c 2.29 , $CHCl_3$), 91% ee (R). **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm: 7.22-7.33 (m, 4 H), 5.47 (s, 1 H), 3.49 (s, 1 H), 2.39 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm: 139.2, 135.3, 130.6 , 129.1, 127.3,123.7, 119.0, 63.58, 21.32; **IR (KBr)**: 3325, 2957, 2923, 2853, 2249, 1694, 1609, 1461, 1156, 1038, 793, 747, 700.



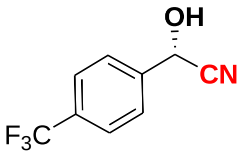
3m
72% yield
75% *ee*

2-Hydroxy-2-(4-Methylphenyl) acetonitrile (**3m**) (yellow oil) was obtained according to the general procedure (72% yield). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column(n-hexane-isopropanol 95:5 V/V, 0.8 mL/min, 210 nm); minor enantiomer tr = 14.196 min, major enantiomer tr = 12.746 min; 75% *ee*. $[\alpha]^{18}_{D}$ –12.3° (c 1.0, $CHCl_3$); lit.[1]$[\alpha]_D$+47.4 (c1.61 , $CHCl_3$), 92% ee (R). **^{1}H NMR** (400 MHz, $CDCl_3$)δ ppm: 7.40 (d, J = 7.9Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 5.47 (s, 1H), 3.42 (s, 1H), 2.38 (s, 3 H); **^{13}C NMR** (100 MHz,$CDCl_3$) δ ppm: 139.9 , 132.6, 129.8, 126.7, 119.1, 63.4, 21.2; **IR(KBr) :** 3419, 2956, 2923, 2854, 2248, 1681, 1514,1260, 1037, 929, 814, 762, 606, 528.



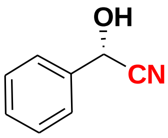
3n
84% yield
90% *ee*

2-Hydroxy-2-(3,4-difluorophenyl)acetonitrile (**3n**) (yellow oil) was obtained according to the general procedure (84% yield). Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column(n-hexane-isopropanol (97:3V/V, 0.8 mL/min, 210 nm); minor enantiomer tr = 21.36 min, major enantiomer tr = 33.22 min; 90% *ee*. **$[\alpha]^{18}_D$** -25.6^o (c 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz,$CDCl_3$) δ ppm: 7.34 (dd, *J* = 13.47, 5.31 Hz, 1H), 7.23 (m, 2H), 5.51 (s, 1H), 4.04 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm: 151.7-152.4(d, J_{CF}=14.8, 55Hz, 1C)，149.2 -149.9（d，J_{CF}=14.8, 55Hz, 1C），132-132.1（t，J_{CF}=4.9Hz, 1C），122.8-122.9（t，J_{CF}= 8.4Hz, 1C）118.0-118.4（d，J_{CF}=16.6，23.2Hz, 1C）, 155.9-116.1（d，J_{CF}=2, 17.6Hz, 1C），62.3（s，1C）; **^{19}F NMR** (470 MHz, $CDCl_3$) δ ppm: -135.18, -135.22, -135.32, -135.37; **IR(KBr):** 3417, 2957, 2924, 2854, 2253, 1707, 1616, 1521, 1437, 1289, 1119, 875, 825, 772.



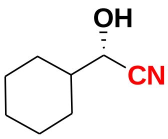
3o
83% yield
83% *ee*

2-hydroxy-2-(4-(trifluoromethyl)phenyl)acetonitrile (**3o**) (yellow oil) was obtained according to the general procedure (83% yield). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column(n-hexane-isopropanol 95:5 V/V, 0.8 mL/min, 210 nm); minor enantiomer tr = 21.36 min, major enantiomer tr = 22.59 min; 83% *ee*. **$[\alpha]^{18}_D$** -23.9^o (c 1.0, $CHCl_3$);lit.[1]$[\alpha]_D$+19.0 (c1.76 , $CHCl_3$), 80% ee (R). **^{1}H NMR** (400 MHz,$CDCl_3$) δ ppm: 7.68-7.70 (d, J=8.4Hz, 2 H), 7.61-7.63 (d, J=8.4Hz, 2H), 5.61 (s, 1 H), 4.02 (s, 1H); **^{13}C NMR** (100 MHz,$CDCl_3$) δ ppm: 138.7, 126.9, 126.2, 126.1, 118.5, 62.8; **^{19}F NMR** (470 MHz,$CDCl_3$) δ ppm: -62.90; **IR(KBr):** 3407, 2926, 2854, 2644, 2254, 1928, 1703, 1422, 1327, 1113, 850, 606.



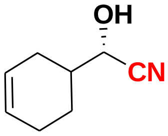
3p
65% yield
71% *ee*

2-Hydroxy-phenylacetonitrile (**3p**) was obtained according to the general procedure (65% yield). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column(n-hexane-isopropanol 95:5 V/V, 0.8 mL/min, 210 nm); minor enantiomer tr = 23.449 min, major enantiomer tr = 21.826 min; 71% *ee*. $[\alpha]^{18}_{D}$ –27.3^{o} (c 1.0, $CHCl_3$);lit.[3]$[\alpha]^{D}_{24}$ +36.8 (c 2.0, CHCl3), 85% ee (R). **^{1}H NMR** (400 MHz,$CDCl_3$) δppm: 7.42-7.52(m, 5H), 5.51(s, 1H), 3.59 (s, 1H); **^{13}C NMR** (100 MHz,$CDCl_3$) δ ppm: 135.2, 129.8, 129.2, 126.7, 118.9, 63.6; **IR(KBr):** 3425, 3064, 2928, 2852, 1485, 1275, 1260, 1192, 1040, 932, 749, 697.



3q
83% yield

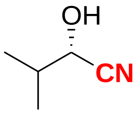
2-cyclohexyl-2-hydroxyacetonitrile (3q) was obtained according to the general procedure (83% yield).[α]21D –7.3o (c 1.0, CHCl3); lit.[3] $[\alpha□]^{D}_{24}$ +6.1 (c = 3.80, $CHCl_3$) for R enantiomer in 65% ee; 1H NMR (400 MHz,CDCl3) δ ppm: 4.24-4.25(d, J=6Hz, 1H), 3.59(s, 1H), 1.68-1.89(m, 6H), 1.10-1.28(m, 5H); 13C NMR (100 MHz, CDCl3) δ ppm:119.5, 42.2, 28.2, 27.9, 25.9, 25.5, 25.4.IR(KBr): 3448, 2931, 2856, 1636, 1451, 1265, 1043, 747, 704.



3r
92% yield

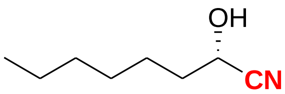
2-(cyclohex-3-enyl)-2-hydroxyacetonitrile(**3r**)was obtained according to the general procedure (92% yield). $[\alpha]^{21}_{D}$ –4.7^{o} (c 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$)
δ ppm:5.64-5.72(dd, J=20.4, 11.6Hz, 2H), 4.34-4.36(dd, J=2.8, 6.8Hz, 1H), 3.41(s, 1H), 1.93-2.26(m, 6H), 1.24(s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm: 127.1,

124.7, 119.4, 38.4, 38.3, 26.7, 26.7, 24.3, 23.9, 23.8. **IR(KBr):** 3446, 3029, 2920, 2847, 2245, 2092, 1652, 1438, 1266, 1084, 1054, 741, 657.



3s
83% yield

2-hydroxy-3-methylbutanenitrile(**3s**)was obtained according to the general procedure (83%yield).**[α]^{21}$_{D}$**–5.3^{o}(c1.0,$CHCl_3$);lit.[5][α]^{D}$_{19}$-15.4(c=2.1,$CHCl_3$) ,90%ee,(S)-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 4.26-4.28(d, J=6Hz, 1H), 3.02(s, 1H), 1.24(s, 1H), 1.05-1.10(m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm:119.2, 67.0, 33.1, 17.7, 17.2.**IR(KBr):** 3432, 2964, 2917, 2849, 2248, 1651, 1470, 1275, 1260, 1064, 971, 763, 749.



3t
81% yield

2-hydroxyoctanenitrile(**3t**)was obtained according to the general procedure (81% yield). **[α]^{21}$_{D}$** –6.1^{o} (c 1.0, $CHCl_3$);lit.[2][α]^{D}$_{26}$+9.1 (c 2.82 , CHCl3), 66% ee (R). **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm: 4.43-4.47(t, J=6.8Hz, 1H), 3.42(s, 1H), 1.80-1.85(dd, J=6.8Hz, 15.2Hz, 2H), 1.44-1.51(td, J=6.8, 11Hz, 2H), 1.24-1.37(m, 6H), 0.86-0.90(t, J=6.4Hz, 3H);**^{13}C NMR** (300 MHz,$CDCl_3$) δ ppm:120.2, 61.3, 35.1, 31.5, 26.6, 24.5, 22.5, 14.0; **IR(KBr):** 3448, 2956, 2928, 2829, 2359, 1635, 1457, 1275, 1261, 1070, 748.

Refereces:

[1] B. R. Matthews, W. R. Jackson, G. S. Jayatilake, C. Wilshire, H. A. Jacobs, Aust. J. Chem. 1988, 41, 1697−1709.

[2] H. Nitta, D. Yu, M. Kudo, A. Mori, S. Inoue, J. Am. Chem. Soc. 1992, 114, 7969−7975.

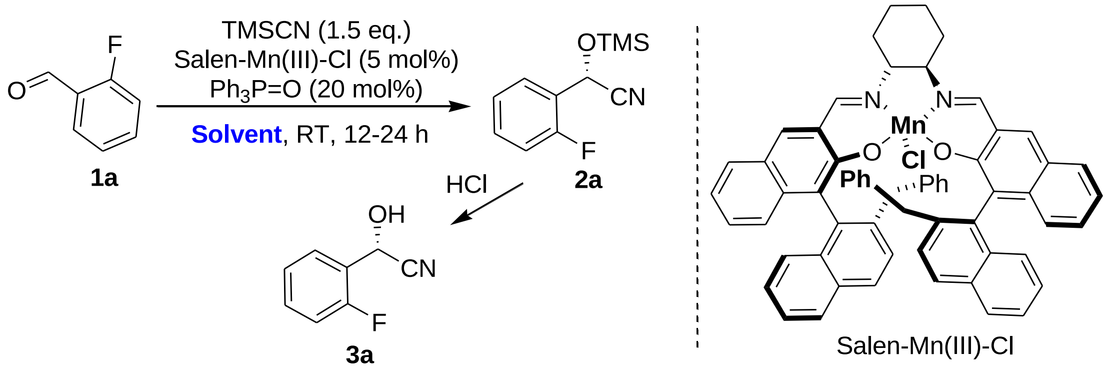
[3] M. Hayashi, Y. Miyamoto, T. Inoue, M. Oguni, J. Org. Chem. 1993,

58, 1515−1522.

[4] S. Han, P. Chen, G. Lin, H. Huang, Z. Li, Tetrahedron: Asymmetry 2001, 12, 843−846.

[5]Y.Hamashima,D.Sawada,M.Kanai,M.Shibasaki,J.Am.Chem.Soc.1999, 121,2641‐2642.

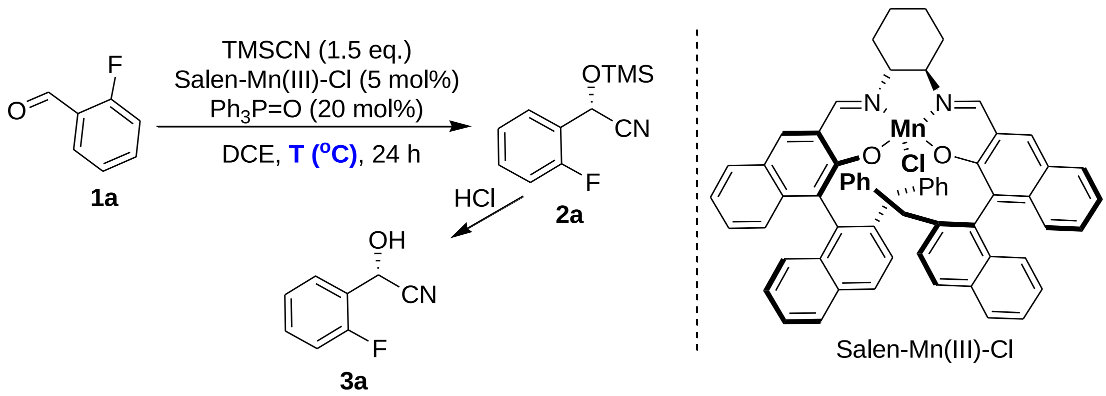
Table S1. Screening of solvents in the Salen-Mn catalyzed cyanosilylation reaction of aldehyde **1a**



Entry	Solvent	Time (h)	Yield (%)	*Ee* (%)
1	DCM	12	90	64
2	Toluene	12	54	30
3	THF	12	69	44
4	Et_2O	12	49	23
5	CH_3CN	12	56	11
6	EtOH	12	54	6
7	1,4-dioxane	12	56	6
8	$PhCF_3$	12	82	45
9	$CHCl_3$	12	41	38
10	Xylene	12	81	36
11	DCE	24	91	79
12	PhCl	24	89	60

13	PhBr	24	86	59
14	CH_2Br_2	24	71	52
15	*i*-PrOH	24	51	-7

Table S2. The effect of temperature on the Salen-Mn catalyzed cyanosilylation reaction of aldehyde **1a**



Entry	Temperature (°C)	Yield (%)	*Ee* (%)
1	20	91	79
2	0	92	83
3	-5	90	82
4	-10	94	88
5	-20	82	67
6	-30	33	56

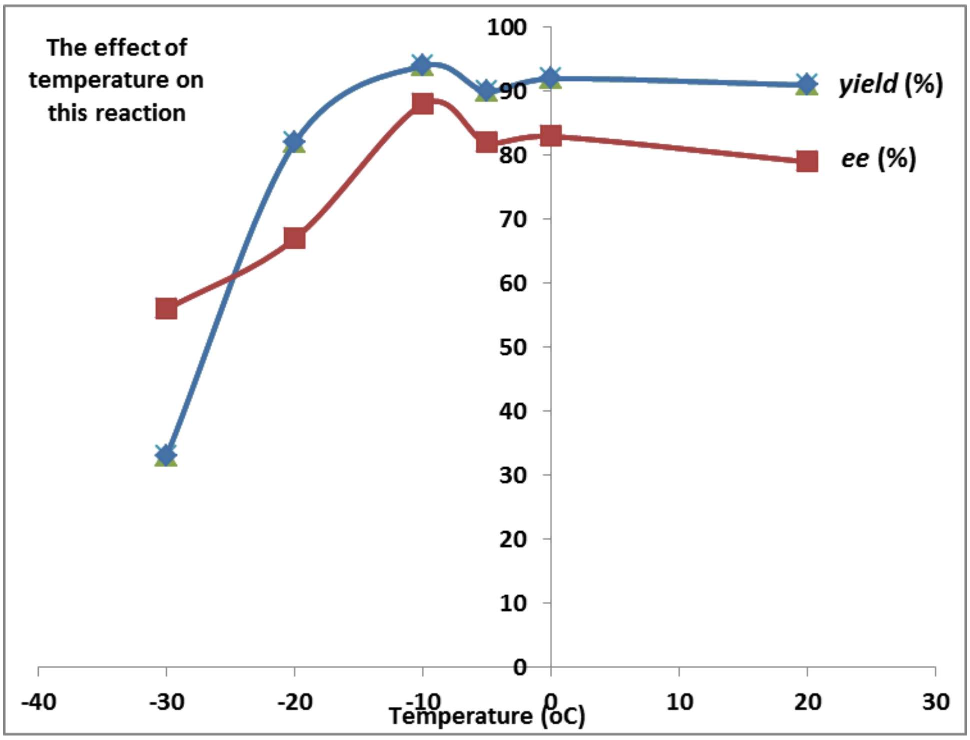
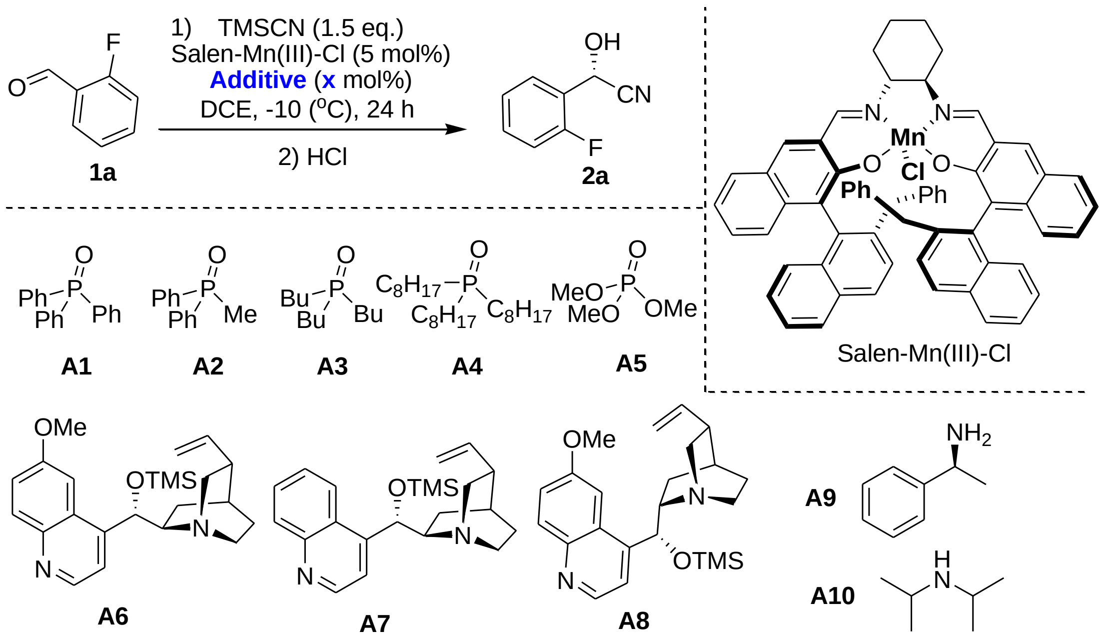


Table S3. The effect of phosphine oxide on the Salen-Mn catalyzed cyanosilylation reaction of aldehyde **1a**[a]



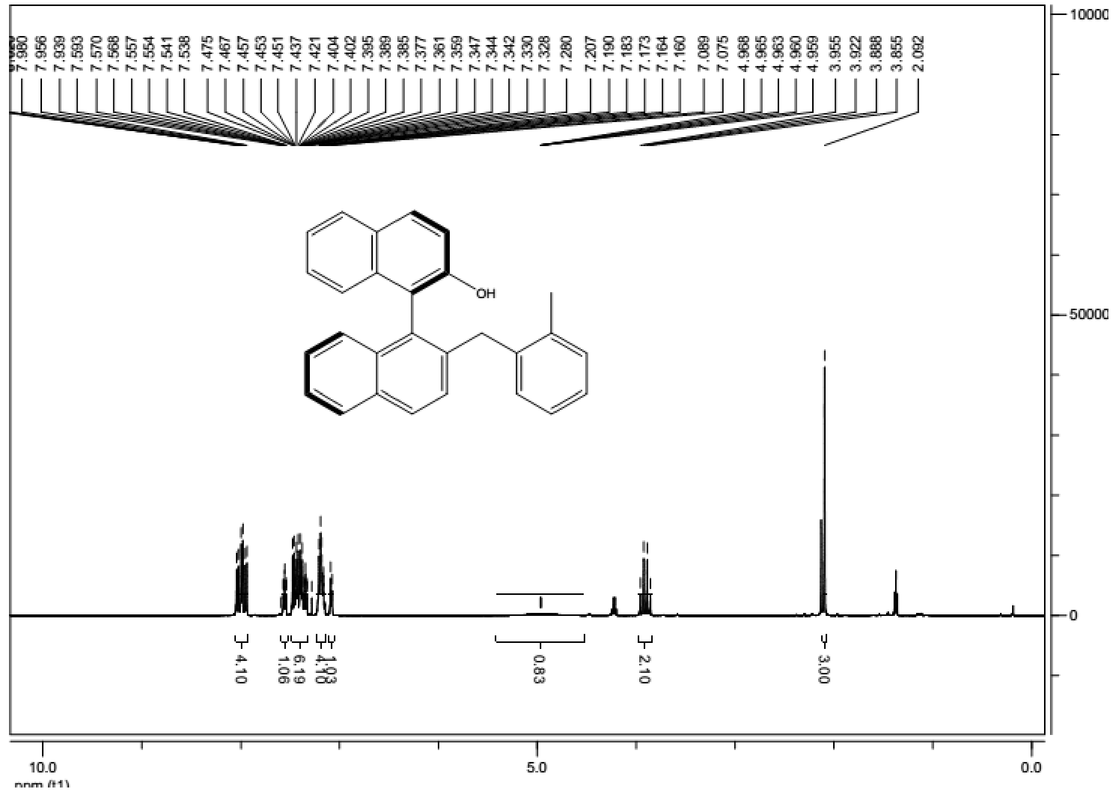
Entry	Additive (x mol%)	Yield (%)[b]	*Ee* (%)[c]
1	**A1** (10)	90	85
2	**A1** (20)	94	88
3	**A1** (30)	95	86
4	**A1** (40)	61	68
5	**A1** (50)	95	85
6	**A1** (75)	90	84
7	**A1** (100)	78	80
8	**A2** (20)	61	72
9	**A3** (20)	71	71
10	**A4** (20)	73	74
11	**A5** (20)	79	73
12	AgF (10)[c]	<5	-
13	$AgSbF_6$ (10)[c]	<5	-
14	$AgClO_4$ (10)[c]	<5	-
15	AgOTf (10)[c]	<5	-

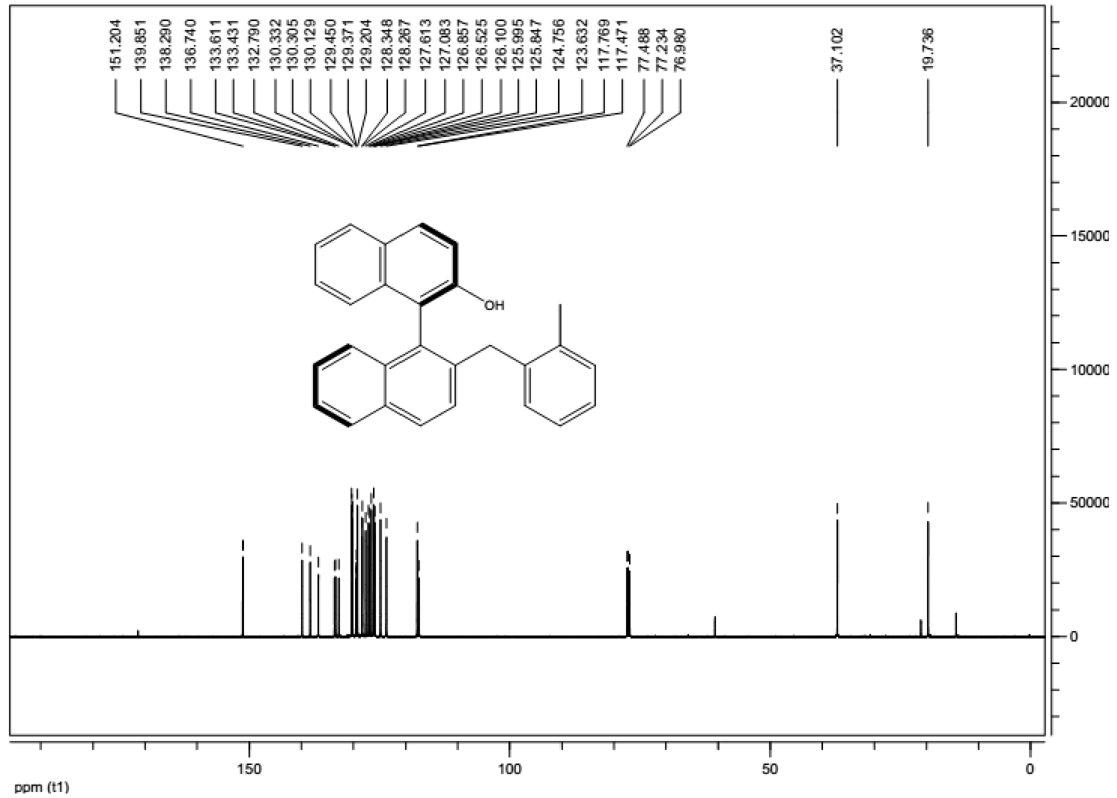
16	**A6** (10)[c]	73	67
17	**A7** (10)[c]	71	67
18	**A8** (10)[c]	70	64
19	**A9** (10)[c]	<20	50
20	**A10** (10)[c]	<20	65
21	DMAP (10)[c]	<20	32
22	DIPEA (10)[c]	<20	51
23	H_2O_2 (10)[c]	<20	36
24	PhIO (5)[c]	40	32
25	NFSI (10)[c]	<10	72
26	Selectfluor (10)[c]	<10	76

[c] Entries 12-26, except the second additive, the use of 20 mol% of triphenylphosphine oxide was also necessary.

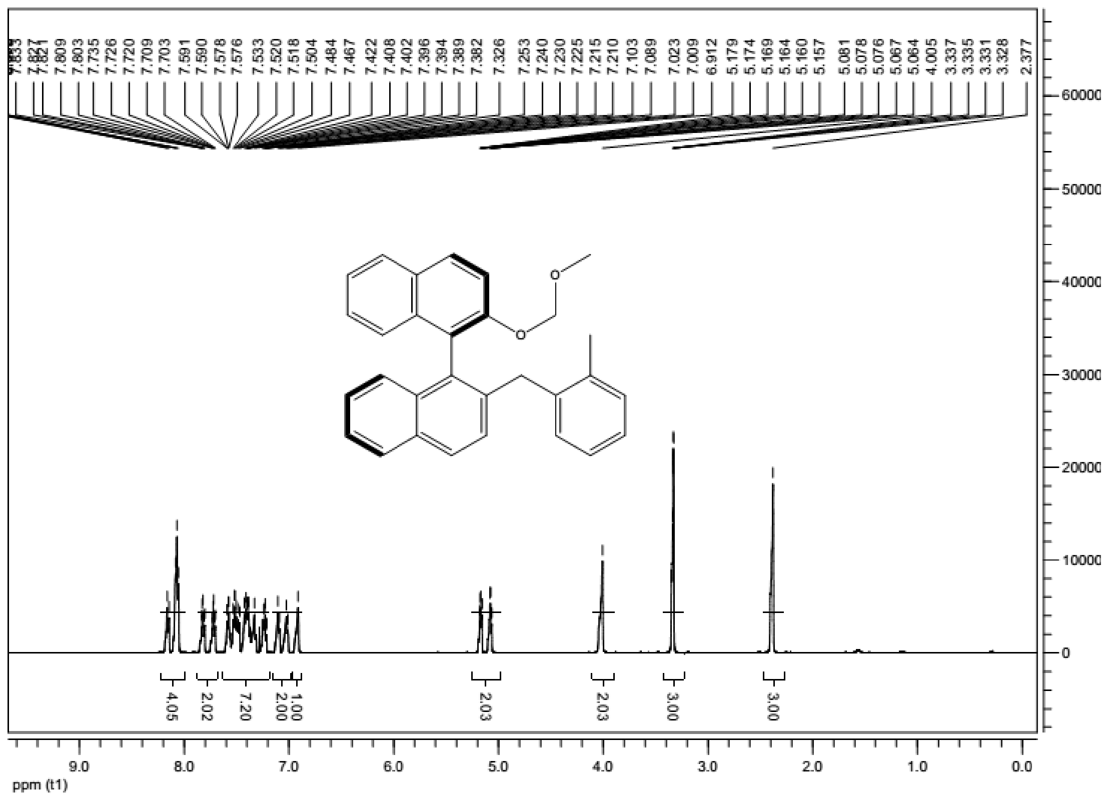
S-5. NMR Charts of Salen ligands and products

Salen 1c-A





Salen 1c-B


7.833 7.827 7.821 7.809 7.803 7.735 7.726 7.720 7.709 7.703 7.591 7.590 7.578 7.576 7.533 7.520 7.518 7.504 7.484 7.467 7.422 7.408 7.402 7.396 7.394 7.389 7.382 7.326 7.253 7.240 7.230 7.225 7.215 7.210 7.103 7.089 7.023 7.009 6.912 5.179 5.174 5.169 5.164 5.160 5.157 5.081 5.078 5.076 5.067 5.064 4.005 3.337 3.335 3.331 3.328 2.377
O
O
4.05
2.02
7.20
2.00
1.00
2.03
2.03
3.00
3.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)
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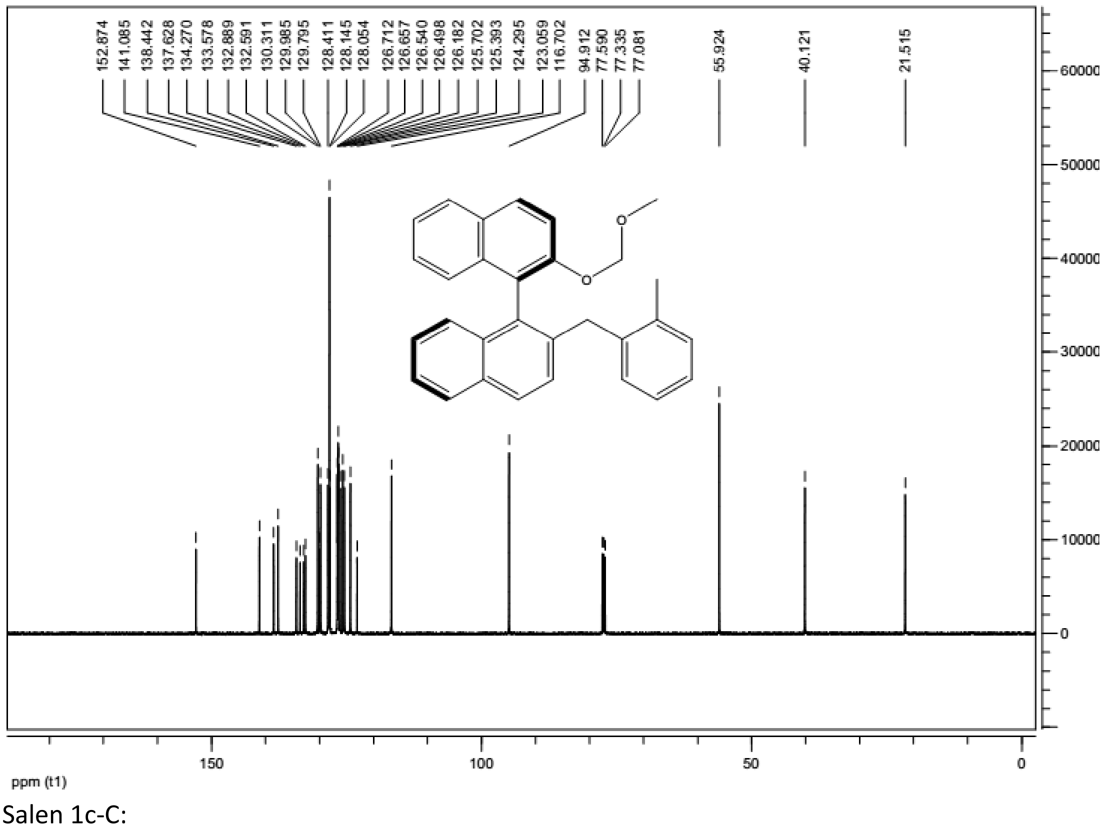
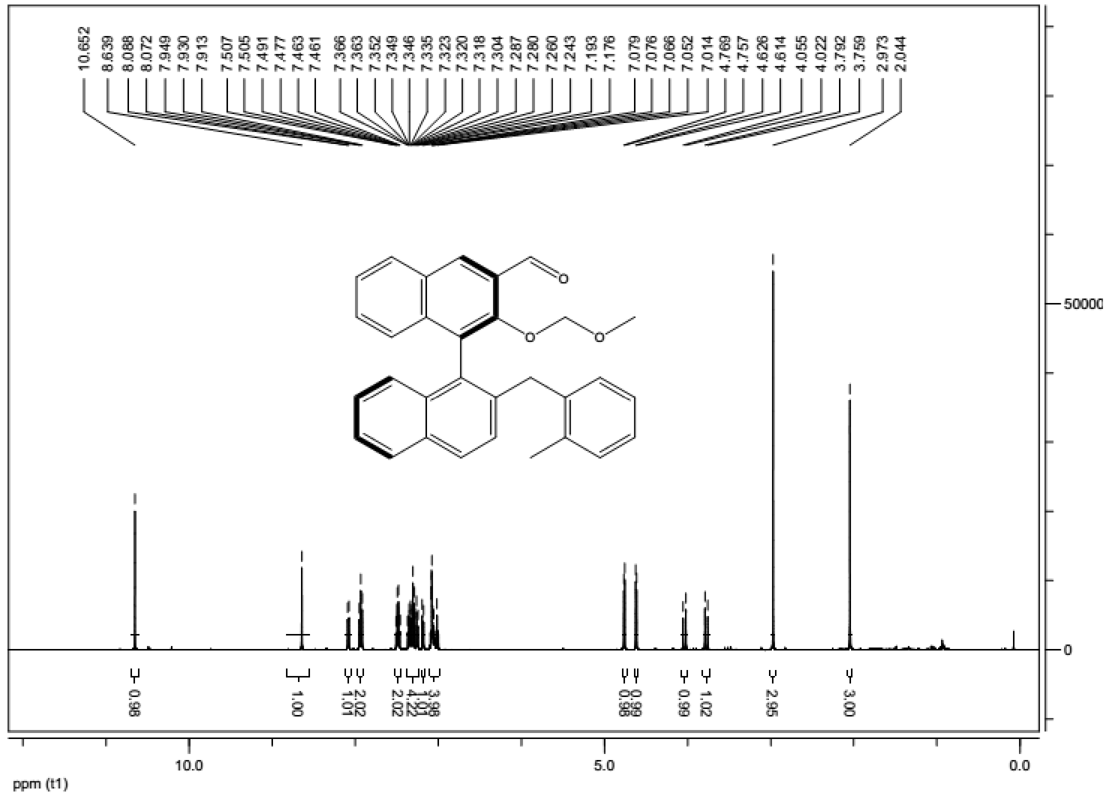

152.874 141.085 138.442 137.628 134.270 133.578 132.889 132.591 130.311 129.985 129.795 128.411 128.145 128.054 126.712 126.657 126.540 126.498 126.182 125.702 125.393 124.295 123.059 116.702 94.912 77.590 77.335 77.081 55.924 40.121 21.515
O
O
150 100 50 0
ppm (t1)
60000 50000 40000 30000 20000 10000 0

Salen 1c-C: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7.505
7.491
7.477
7.463
7.461
7.366
7.363
7.352
7.349
7.346
7.335
7.323
7.320
7.318
7.304
7.287
7.280
7.260
7.243
7.193
7.176
7.079
7.076
7.066
7.052
7.014
4.769
4.757
4.626
4.614
4.055
4.022
3.792
3.759
2.973
2.044
50000
0
0.98
1.00
1.01
2.02
2.02
4.22
3.98
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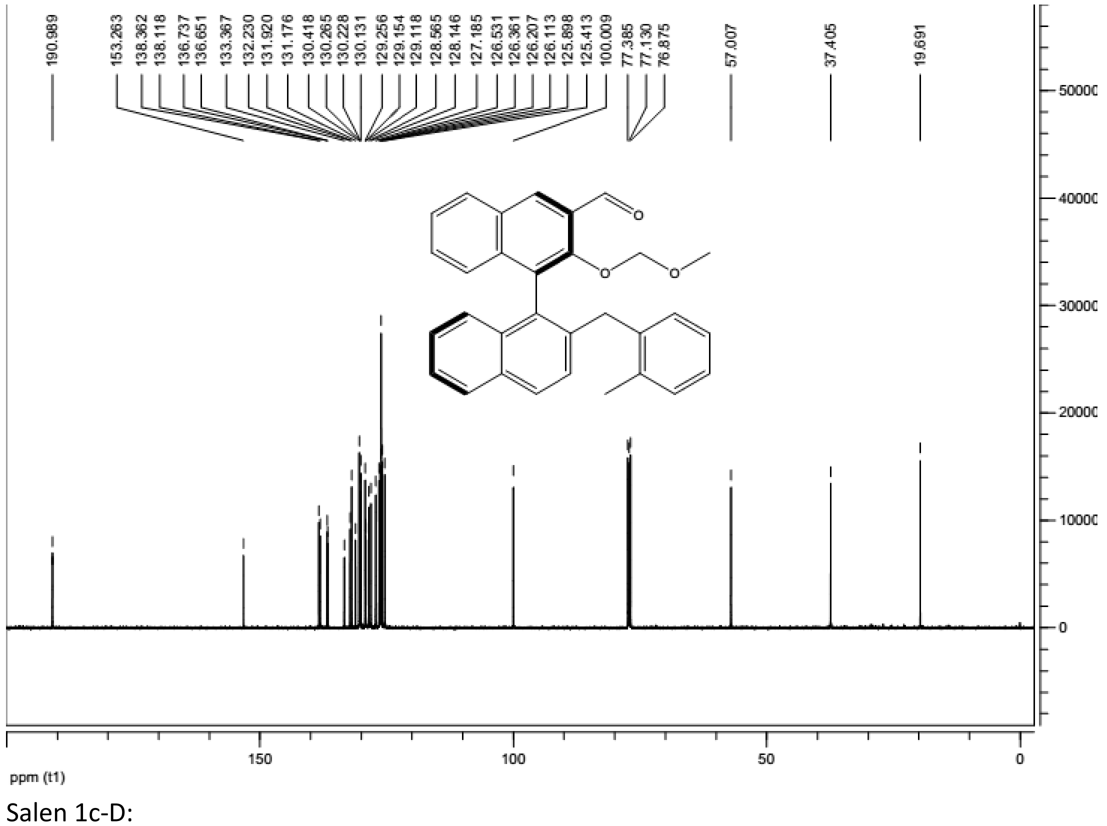
0.99
0.99
1.02
2.95
3.00
10.0
5.0
0.0
ppm (t1)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132.230
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131.176
130.418
130.265
130.228
130.131
129.256
129.154
129.118
128.565
128.146
127.185
126.531
126.361
126.207
126.113
125.898
125.413
100.009
77.385
77.130
76.875
57.007
37.405
19.691
50000
40000
30000
20000
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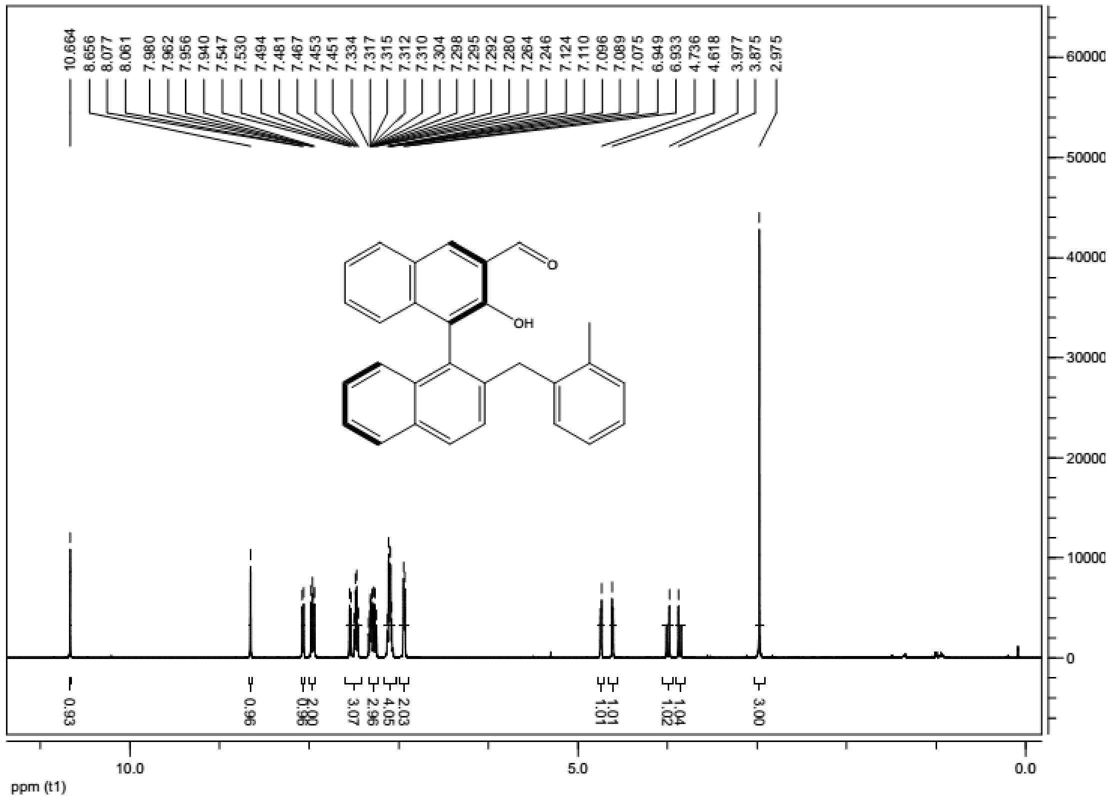
0
150
100
50
0
ppm (t1)

Salen 1c-D: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7.980
7.962
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7.940
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7.530
7.494
7.481
7.467
7.453
7.451
7.334
7.317
7.315
7.312
7.310
7.304
7.298
7.295
7.292
7.280
7.264
7.246
7.124
7.110
7.096
7.089
7.075
6.949
6.933
4.736
4.618
3.977
3.875
2.975
OH
O
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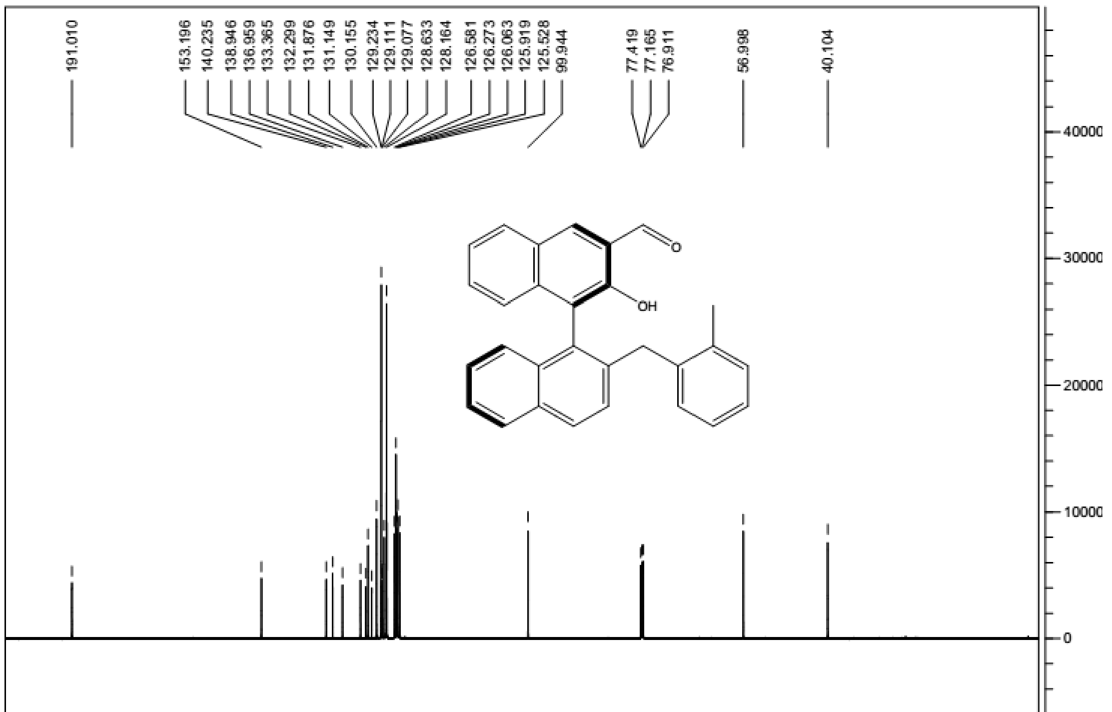
0.96
0.96
2.00
3.07
2.96
4.05
2.03
1.01
1.01
1.02
1.04
3.00
10.0
5.0
0.0
ppm (t1)
60000
50000
40000
30000
20000
10000
0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133.365
132.299
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129.234
129.111
129.077
128.633
128.164
126.581
126.273
126.063
125.919
125.528
99.944
77.419
77.165
76.911
56.998
40.104
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O
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150
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50
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ppm (t1)
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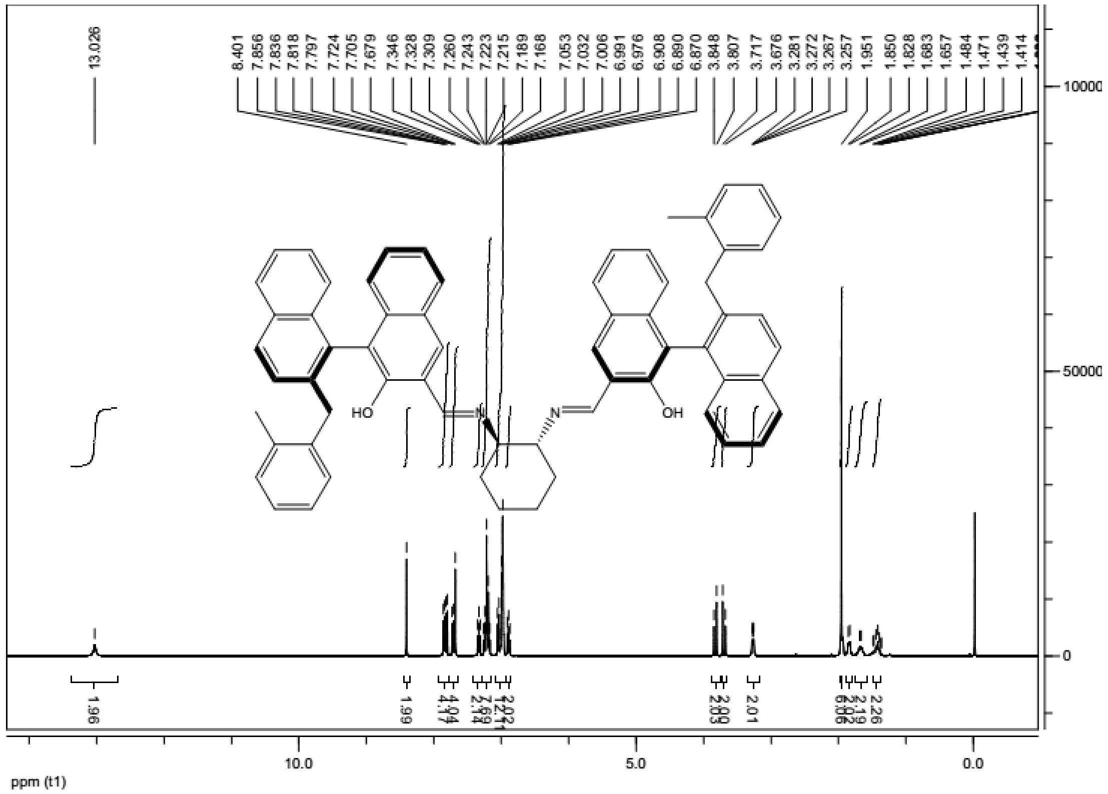
30000
20000
10000
0

Salen 1c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7.260
7.243
7.223
7.215
7.189
7.168
7.053
7.032
7.006
6.991
6.976
6.908
6.890
6.870
3.848
3.807
3.717
3.676
3.281
3.272
3.267
3.257
1.951
1.850
1.828
1.683
1.657
1.484
1.471
1.439
1.414
HO
OH
N
N
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1.99
4.04
4.17
2.44
2.69
2.11
4.02
2.00
2.03
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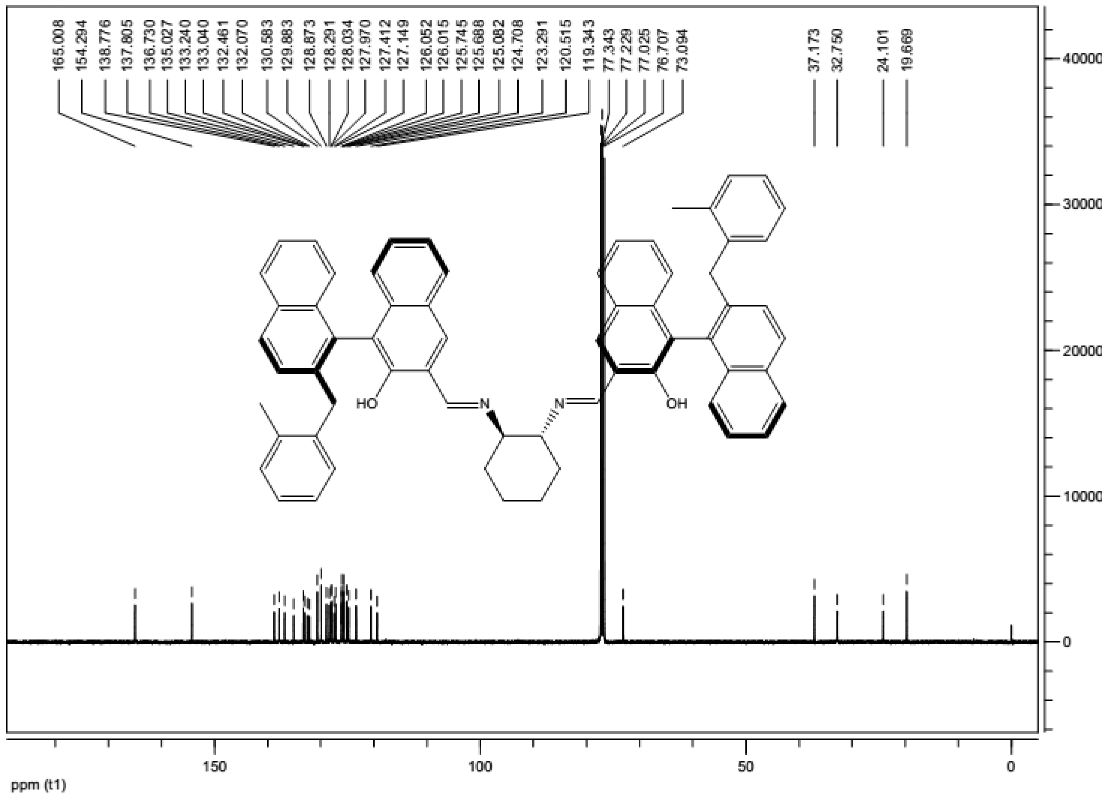
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128.291
128.034
127.970
127.412
127.149
126.052
126.015
125.745
125.688
125.082
124.708
123.291
120.515
119.343
77.343
77.229
77.025
76.707
73.094
37.173
32.750
24.101
19.669
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N
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ppm (t1)
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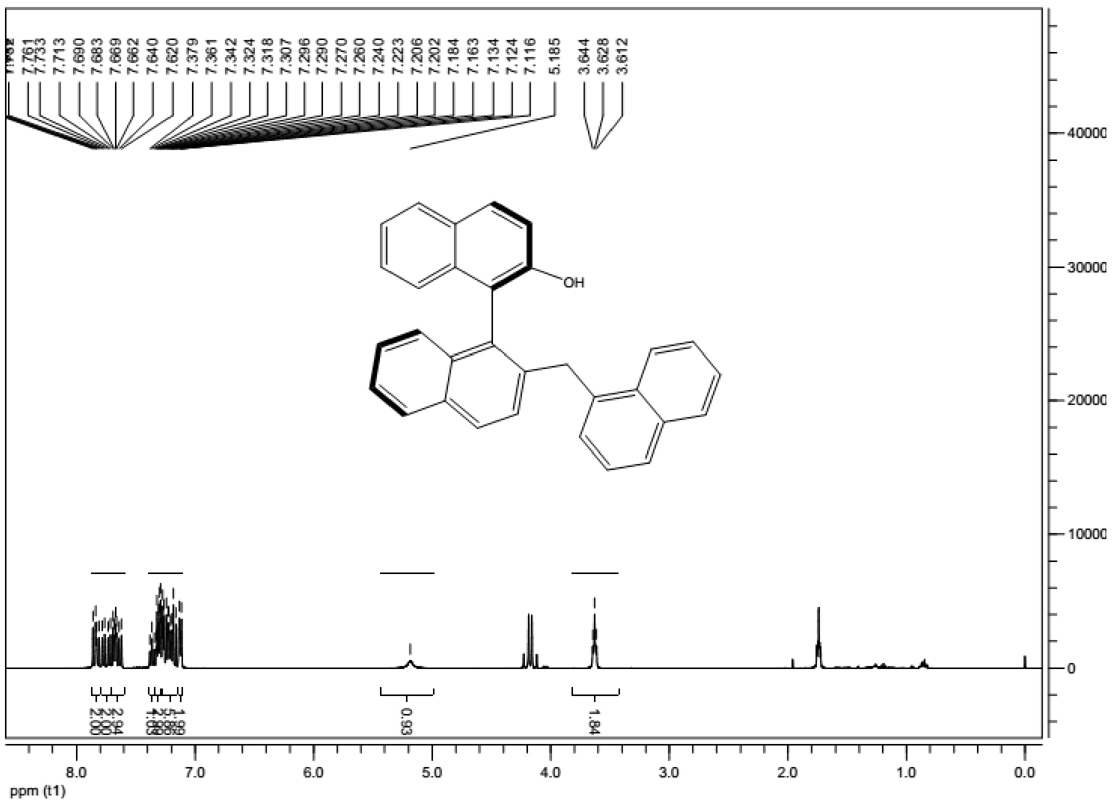
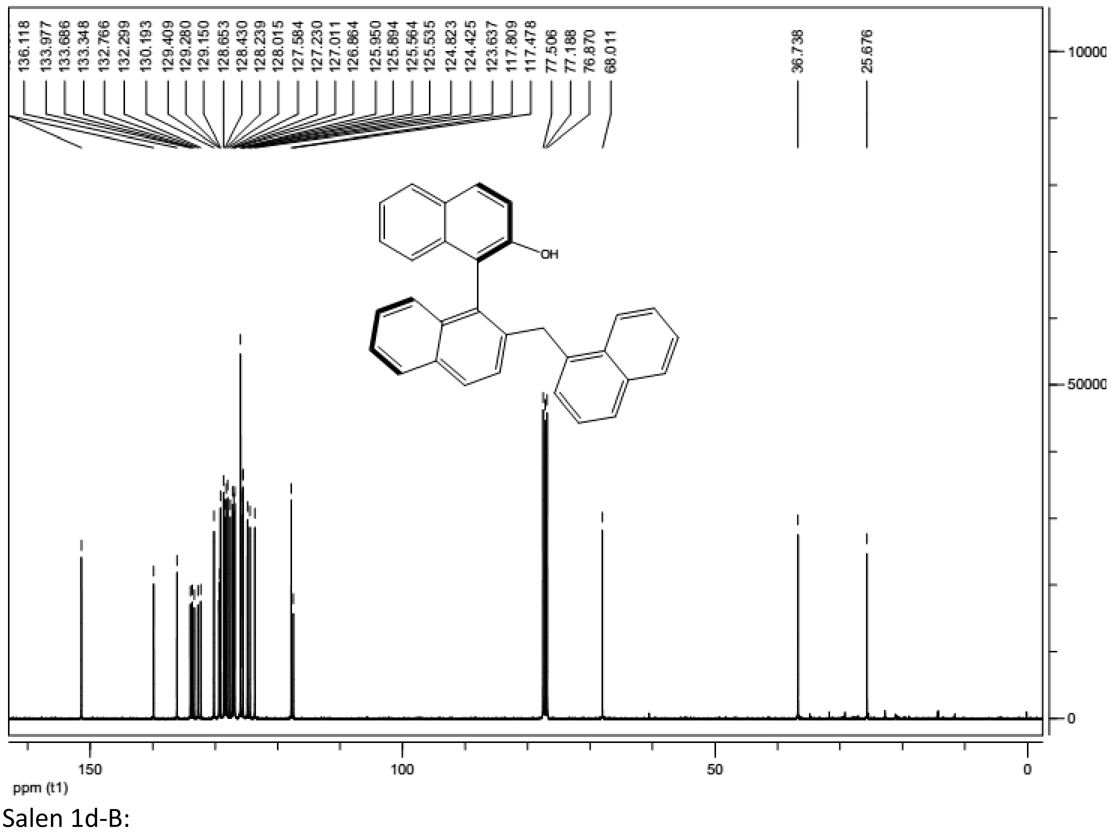
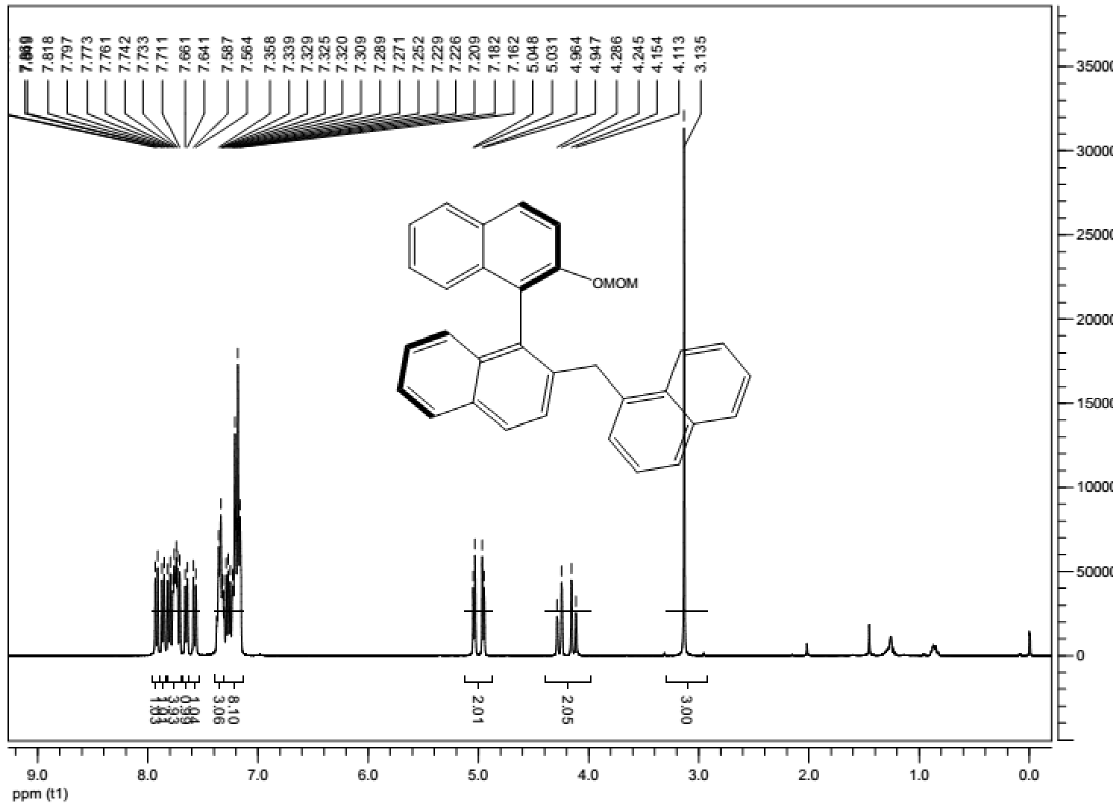
0

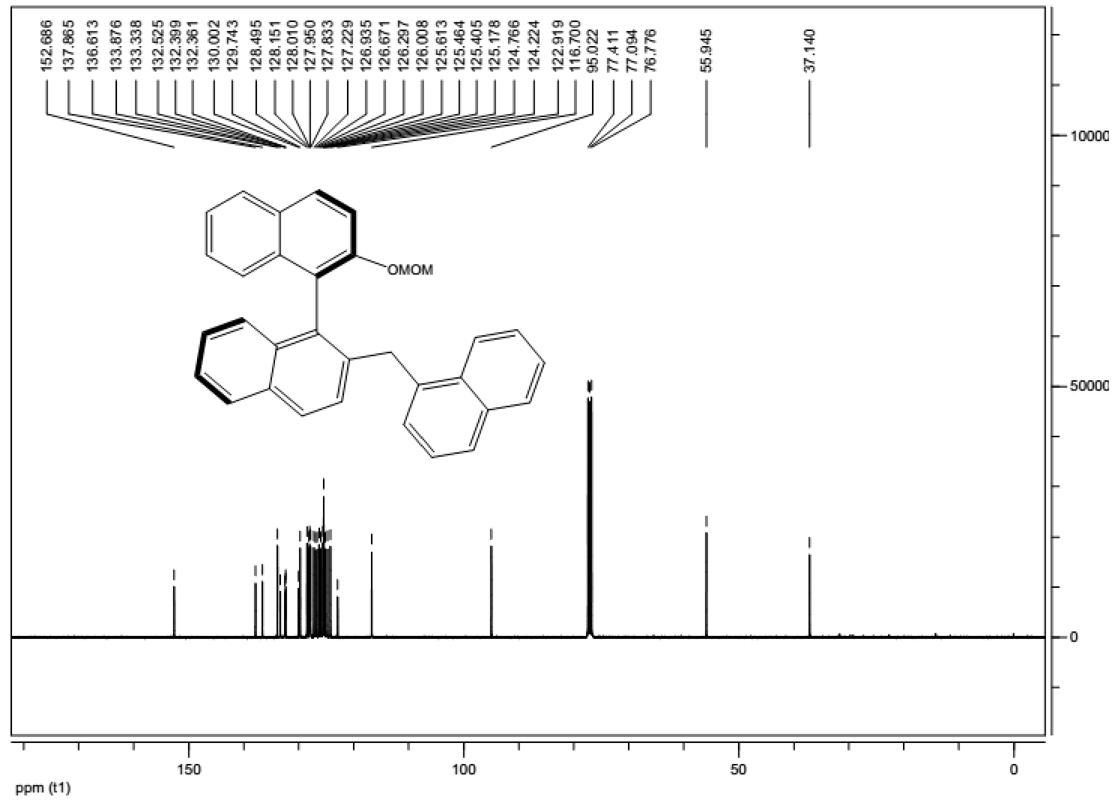
Salen 1d-A:



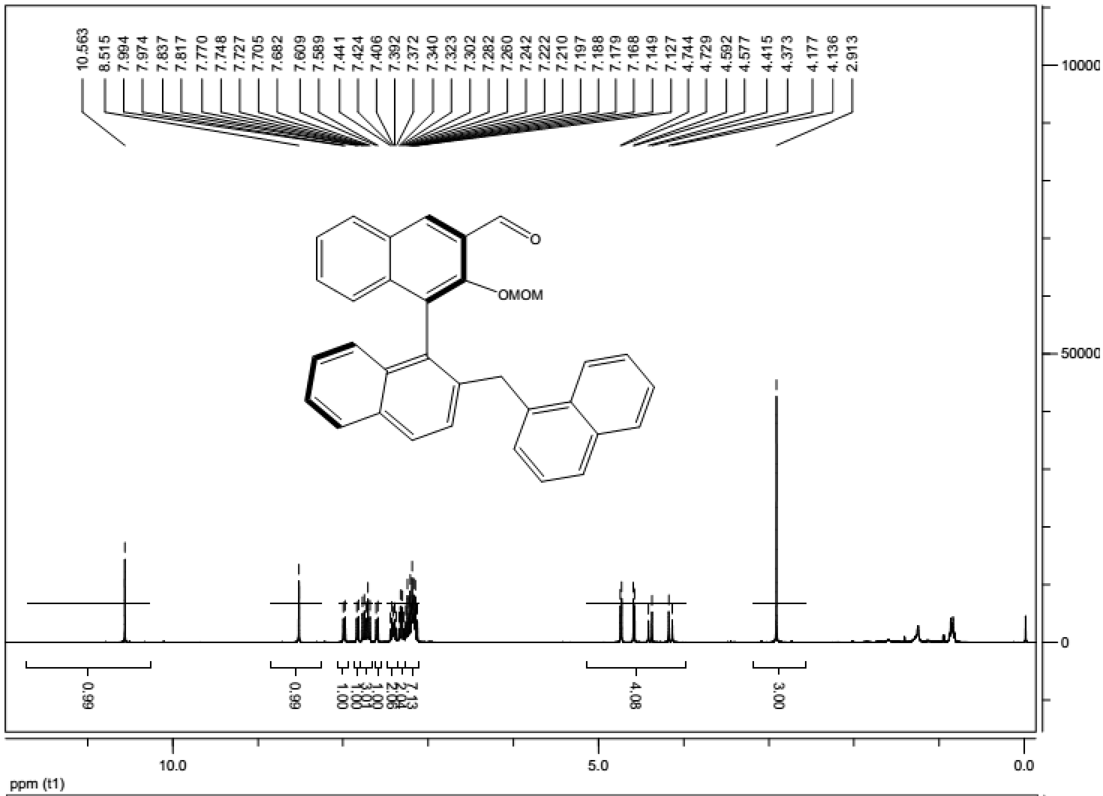


Salen 1d-B:





Salen 1d-C:



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7.589
7.441
7.424
7.406
7.392
7.372
7.340
7.323
7.302
7.282
7.260
7.242
7.222
7.210
7.197
7.188
7.179
7.168
7.149
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4.744
4.729
4.592
4.577
4.415
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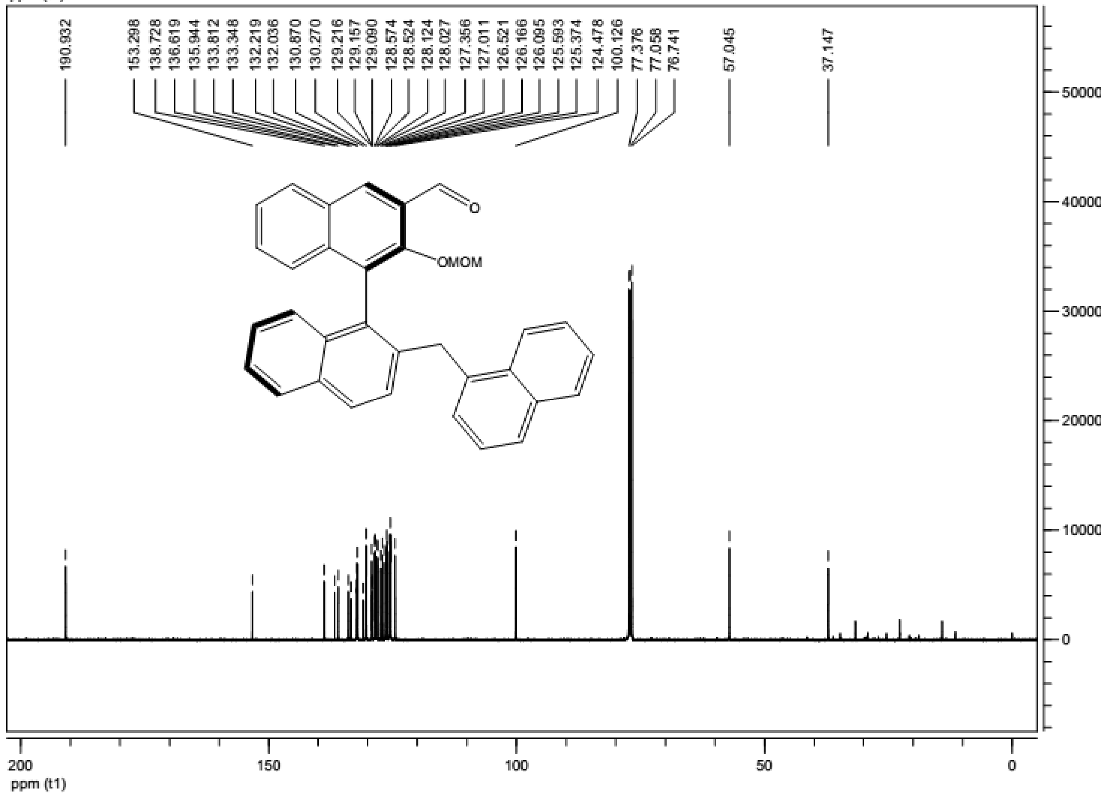
3.00
ppm (t1)



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127.356
127.011
126.521
126.166
126.095
125.593
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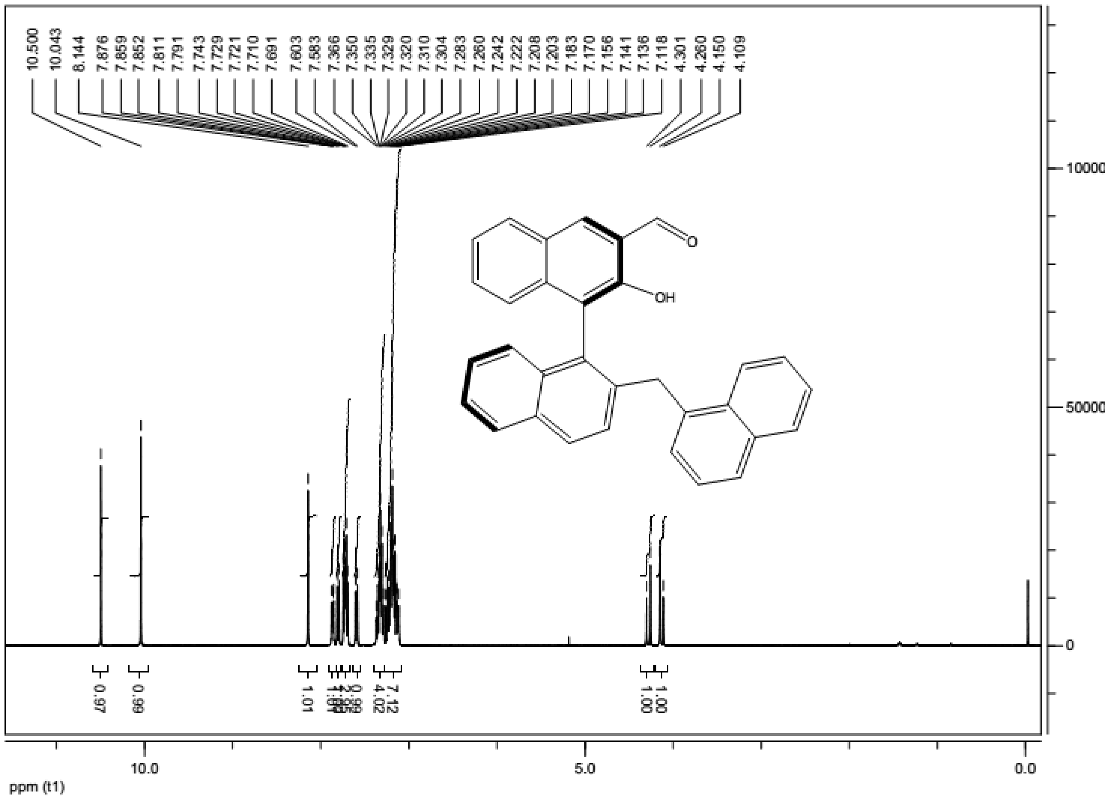
ppm (t1)

Salen 1d-D: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7.691
7.603
7.583
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7.335
7.329
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7.310
7.304
7.283
7.260
7.242
7.222
7.208
7.203
7.183
7.170
7.156
7.141
7.136
7.118
4.301
4.260
4.150
4.109
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O
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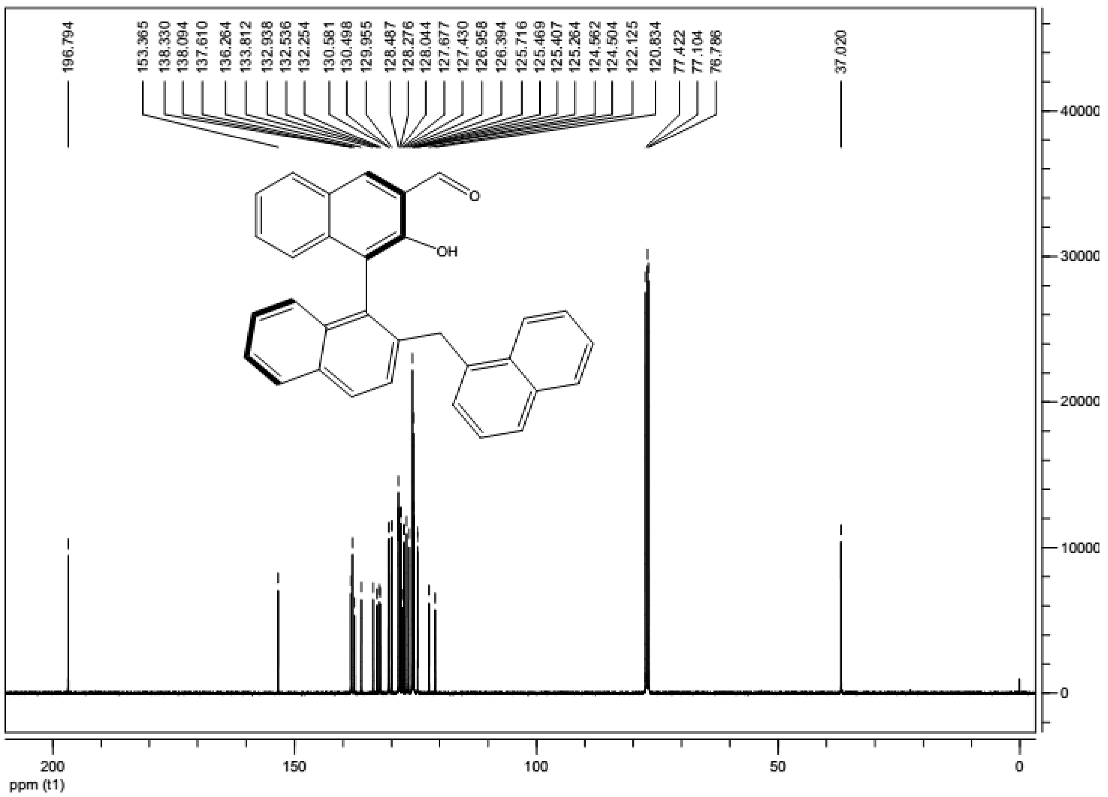
5.0
0.0
ppm (t1)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128.276
128.044
127.677
127.430
126.958
126.394
125.716
125.469
125.407
125.264
124.562
124.504
122.125
120.834
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77.104
76.786
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O
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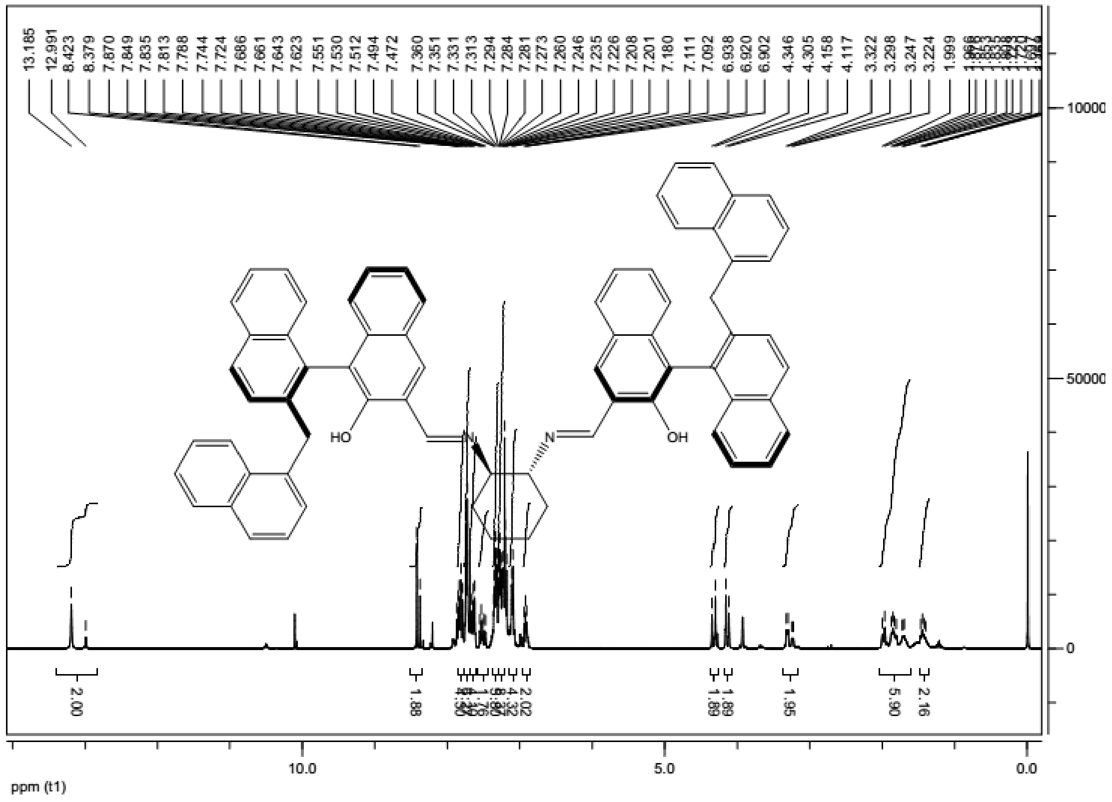
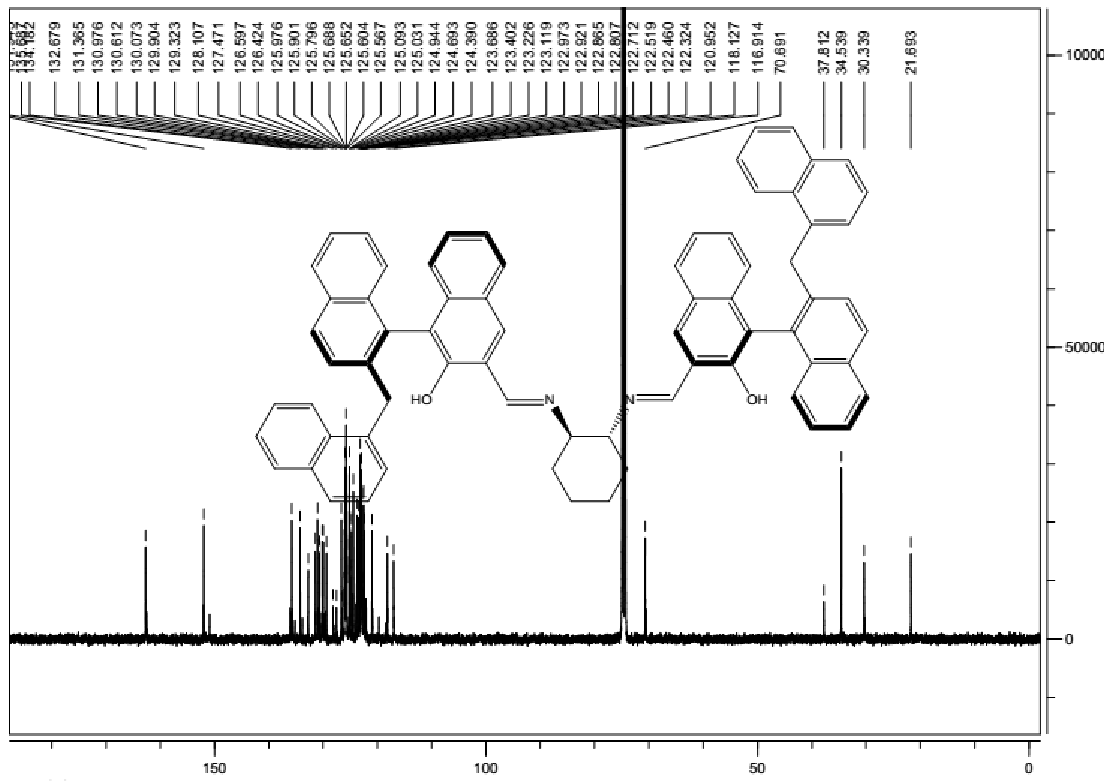
0
ppm (t1)

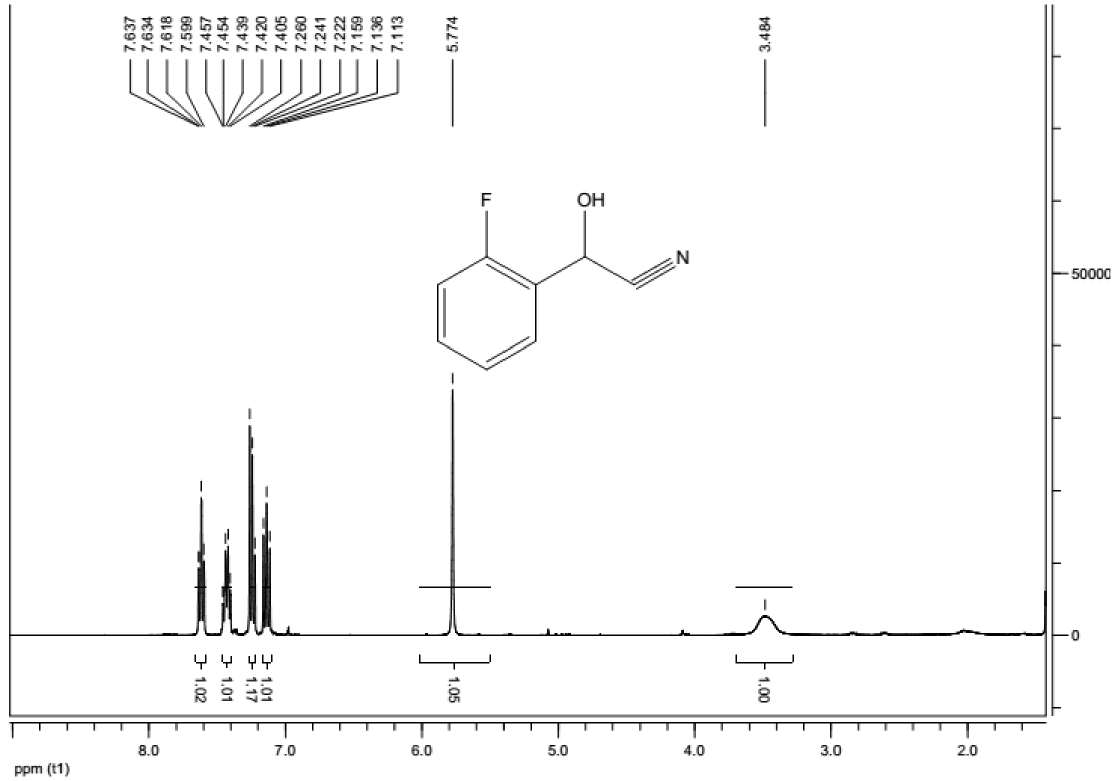
Salen 1d





NMR Charts of Compounds:

3a: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7.159
7.136
7.113
5.774
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F
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1.01
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1.00
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7.0
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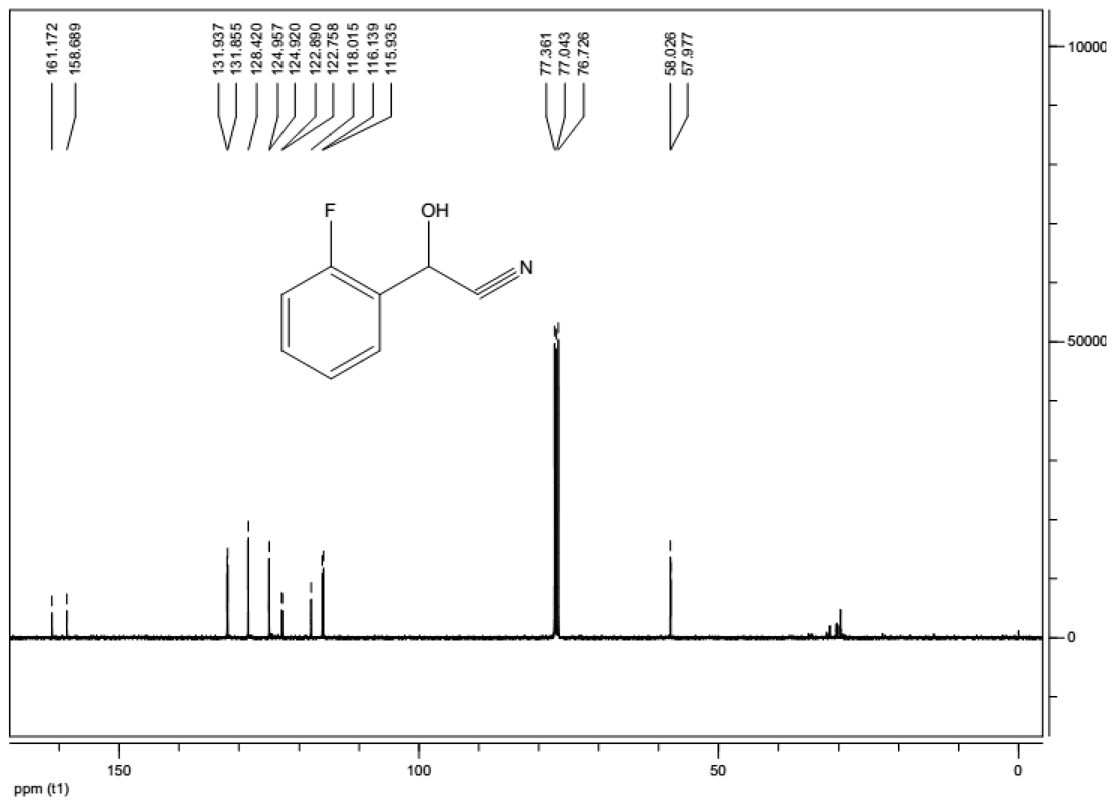
4.0
3.0
2.0
ppm (t1)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118.015
116.139
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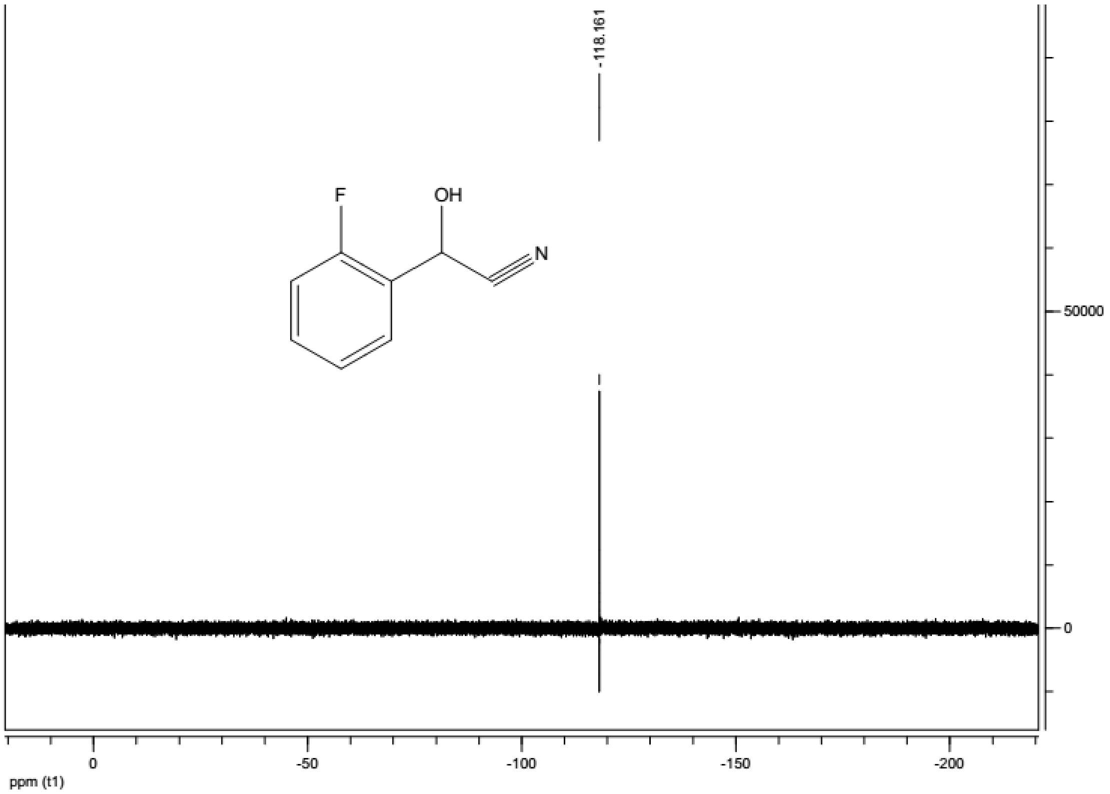
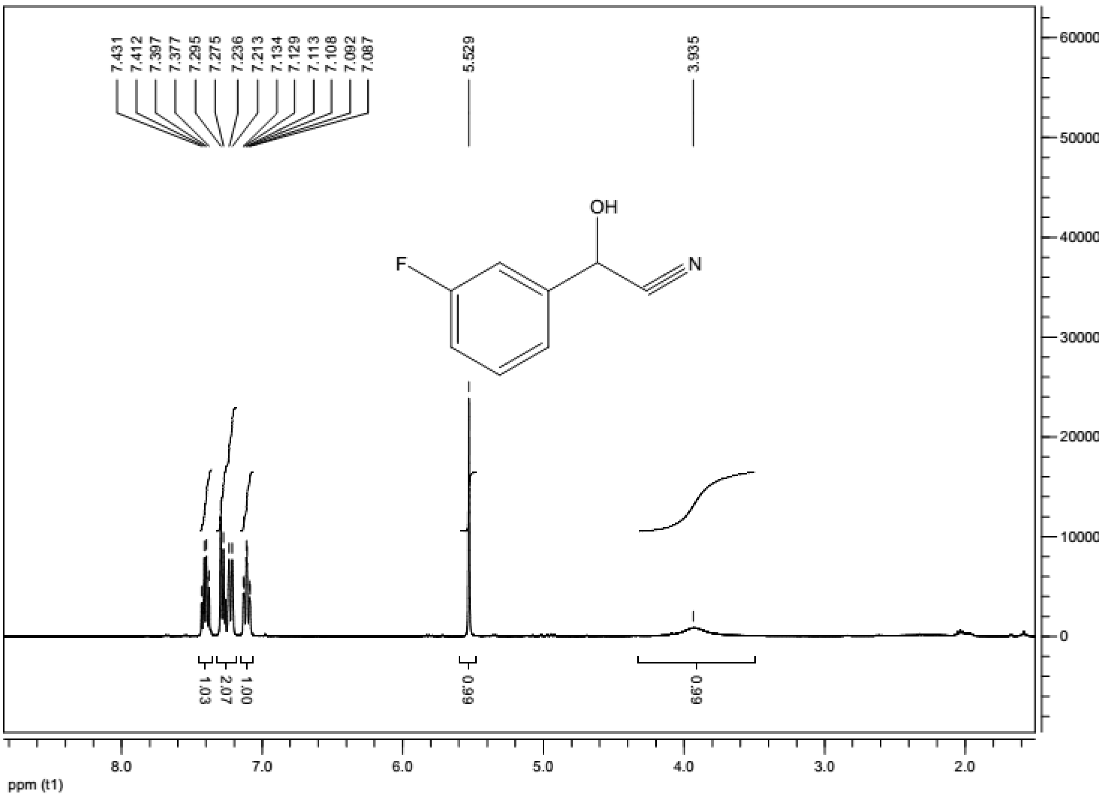
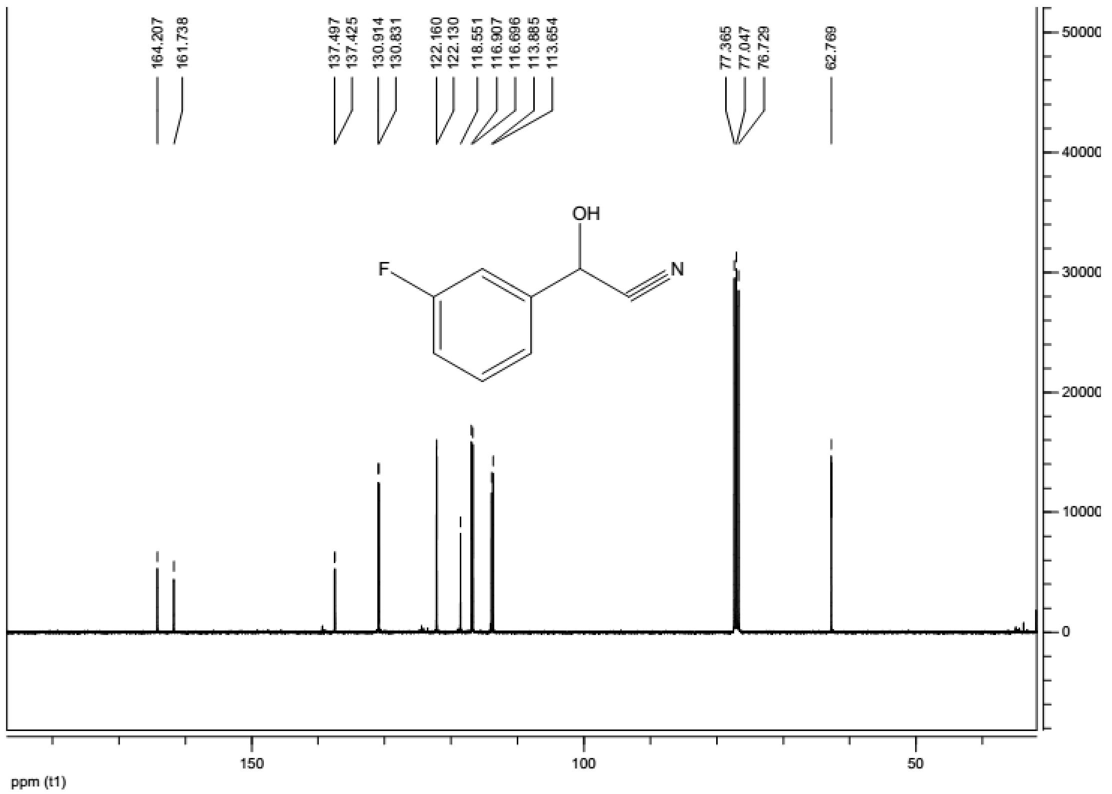
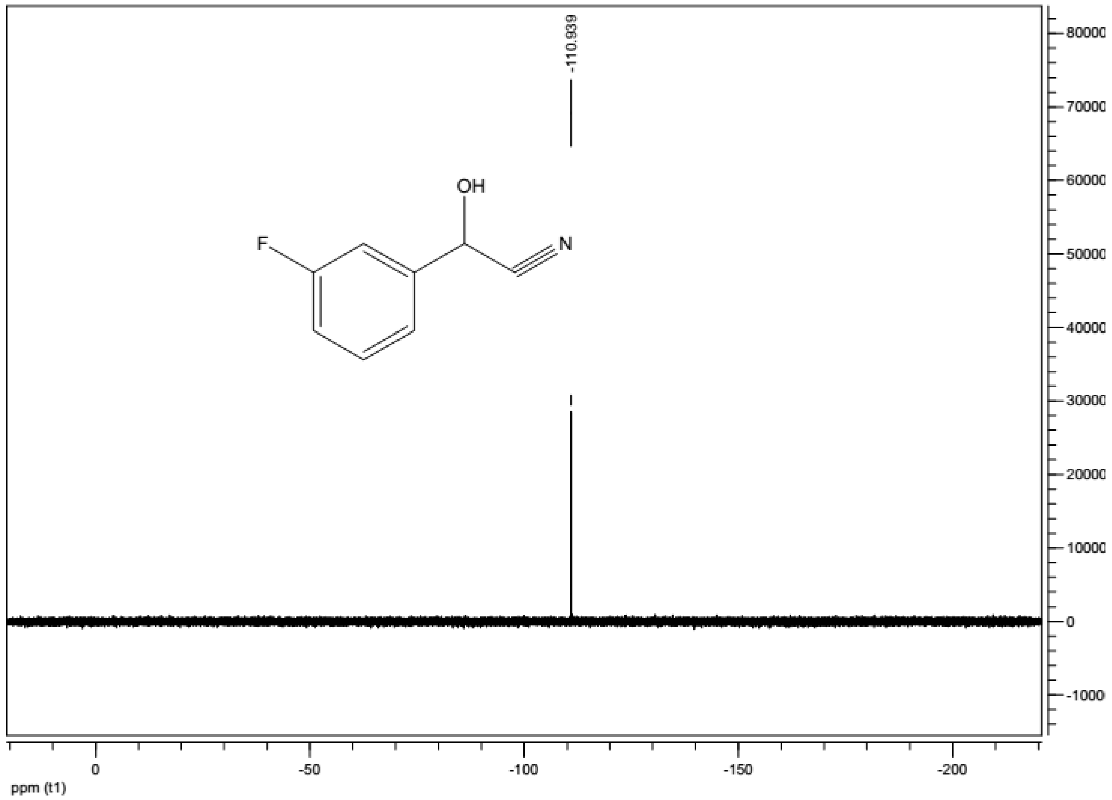
77.361
77.043
76.726
58.026
57.977
F
OH
N
10000
50000
0
150
100
50
0
ppm (t1)


-118.161
F
OH
N
50000
0
0
-50
-100
-150
-200
ppm (t1)

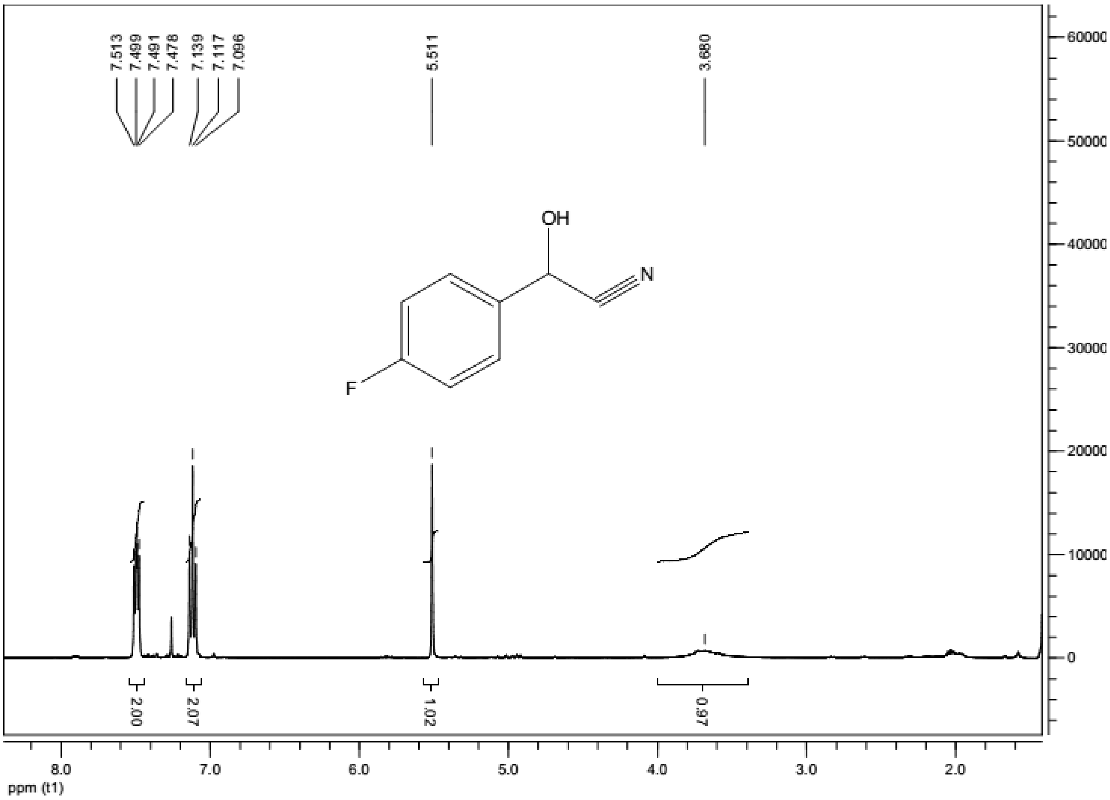
3b:

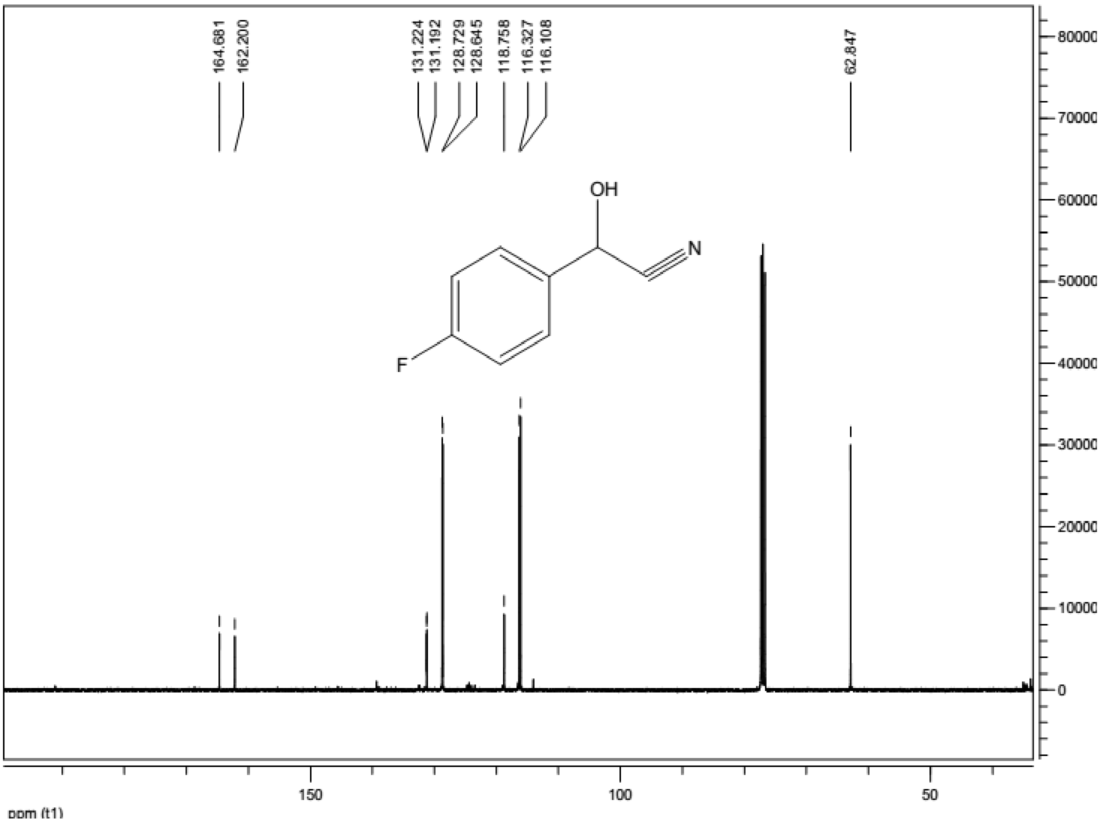

7.431
7.412
7.397
7.377
7.295
7.275
7.236
7.213
7.134
7.129
7.113
7.108
7.092
7.087
5.529
3.935
OH
F
N
1.03
2.07
1.00
0.99
0.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)
60000
50000
40000
30000
20000
10000
0

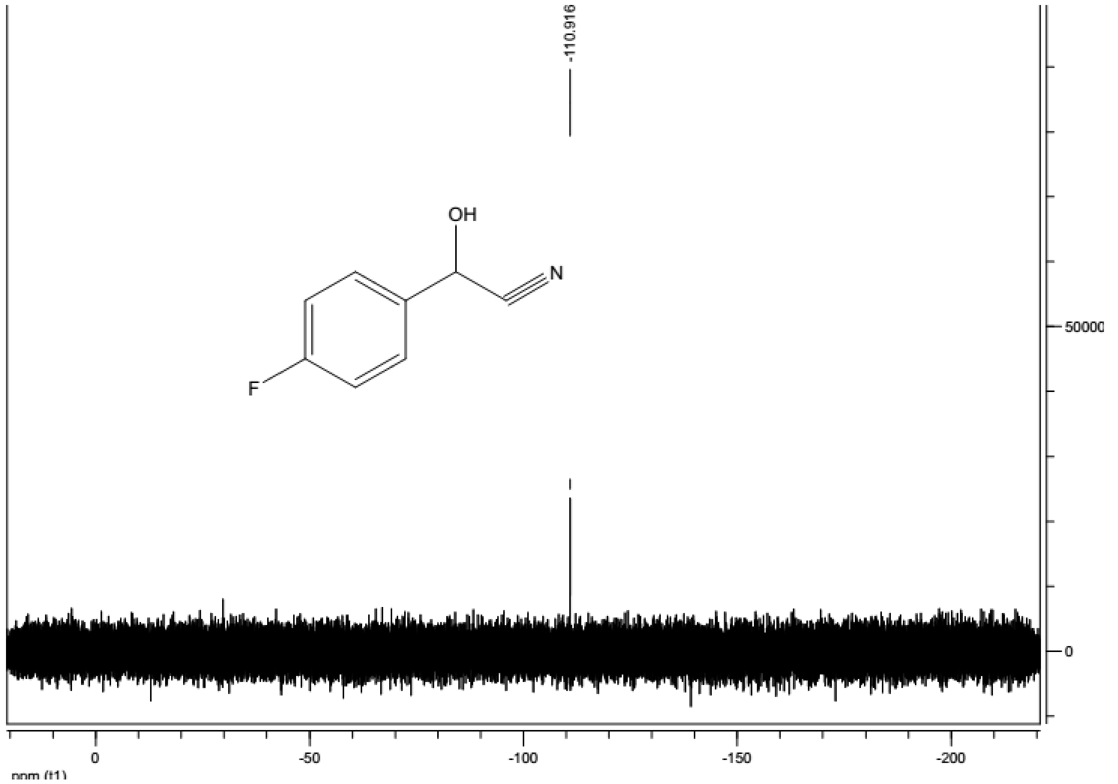

164.207
161.738
137.497
137.425
130.914
130.831
122.160
122.130
118.551
116.907
116.696
113.885
113.654
77.365
77.047
76.729
62.769
OH
F
N
50000
40000
30000
20000
10000
0
150
100
50
ppm (t1)


-110.939
OH
F
N
80000
70000
60000
50000
40000
30000
20000
10000
0
-1000
0
-50
-100
-150
-200
ppm (t1)

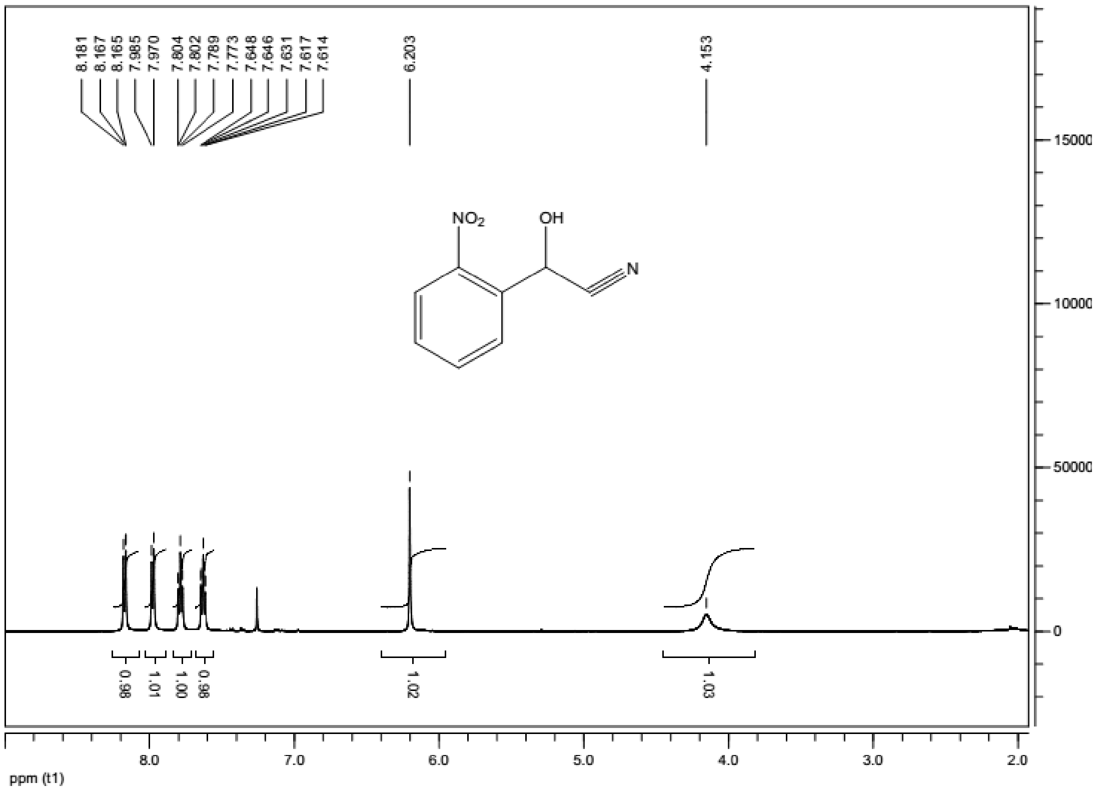
3c:

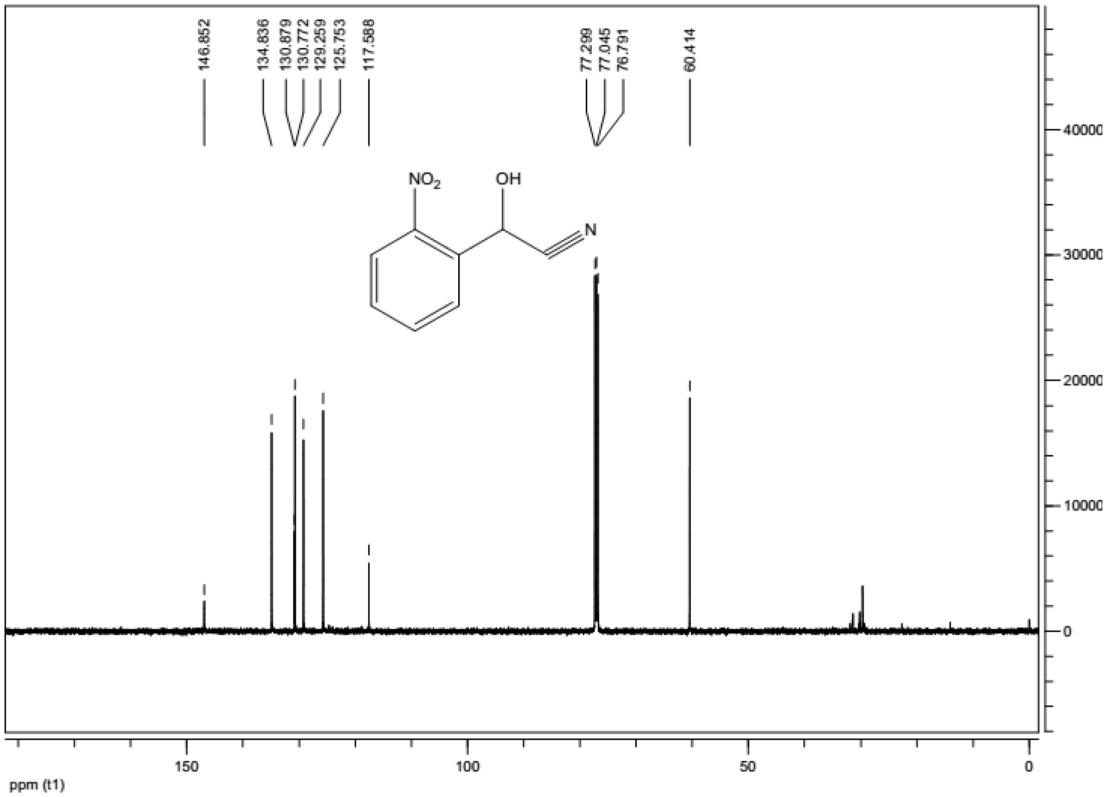

7.513
7.499
7.491
7.478
7.139
7.117
7.096
5.511
3.680
OH
N
F
2.00
2.07
1.02
0.97
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


164.681
162.200
131.224
131.192
128.729
128.645
118.758
116.327
116.108
62.847
OH
N
F
150
100
50
ppm (t1)

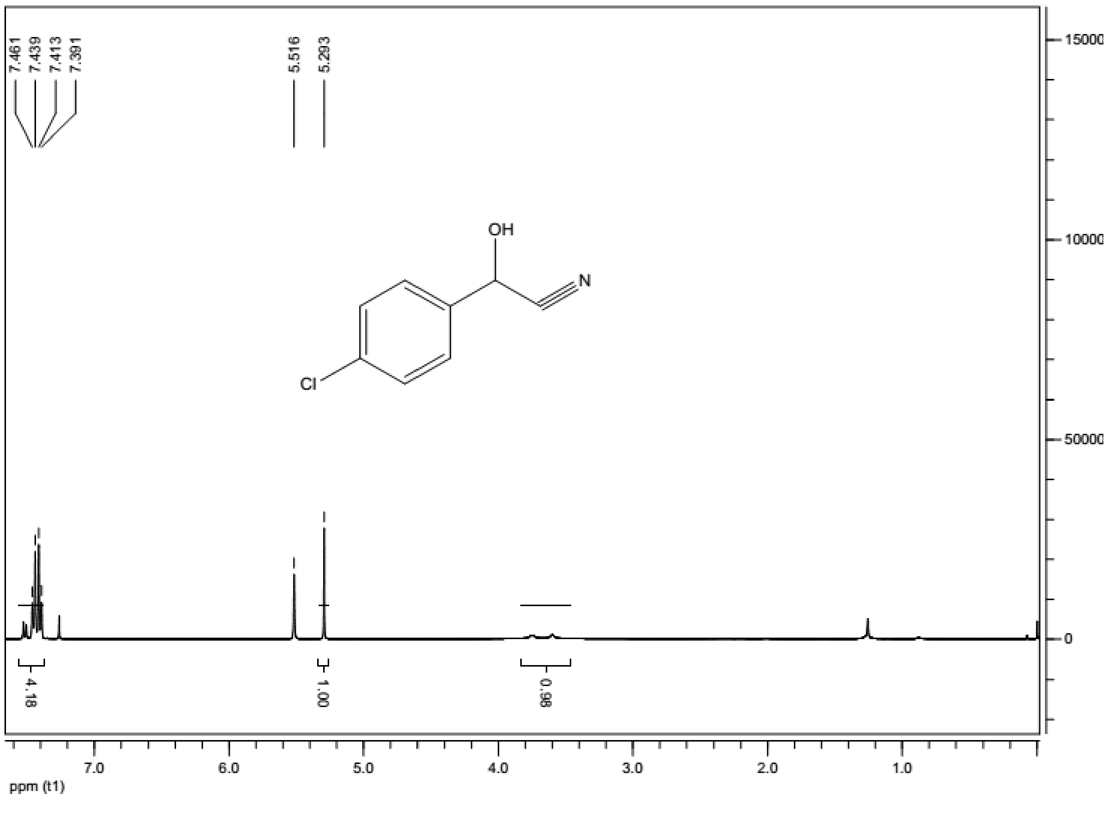

-110.916
OH
N
F
50000
0
0
-50
-100
-150
-200
ppm (t1)

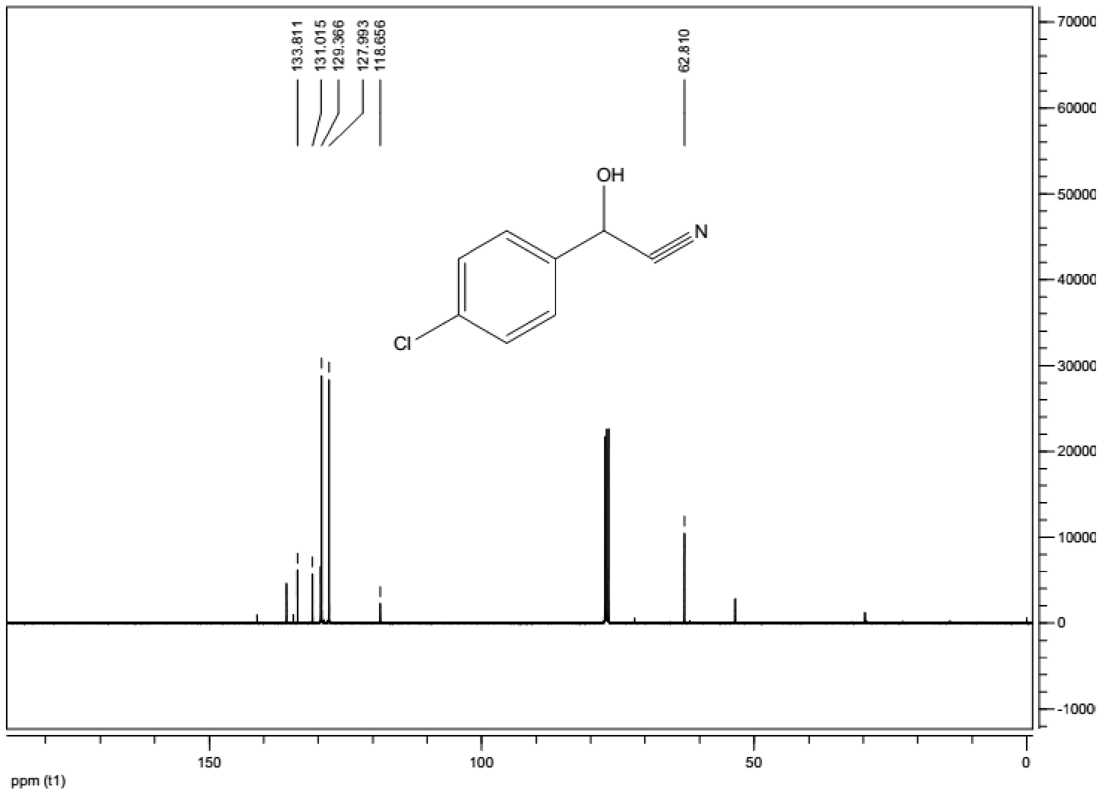
3d:


8.181
8.167
8.165
7.985
7.970
7.804
7.802
7.789
7.773
7.648
7.646
7.631
7.617
7.614
6.203
4.153
NO_2
OH
N
15000
10000
50000
0
0.98
1.01
1.00
0.98
1.02
1.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

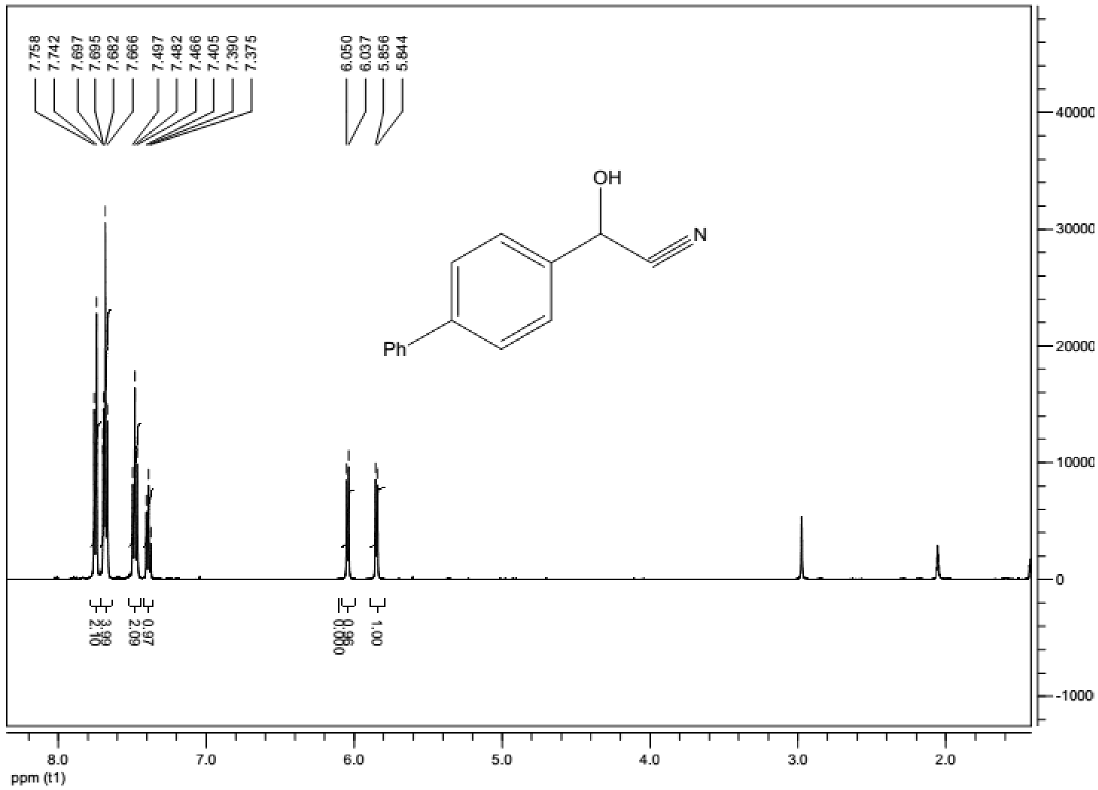

146.852
134.836
130.879
130.772
129.259
125.753
117.588
77.299
77.045
76.791
60.414
NO2
OH
N
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)

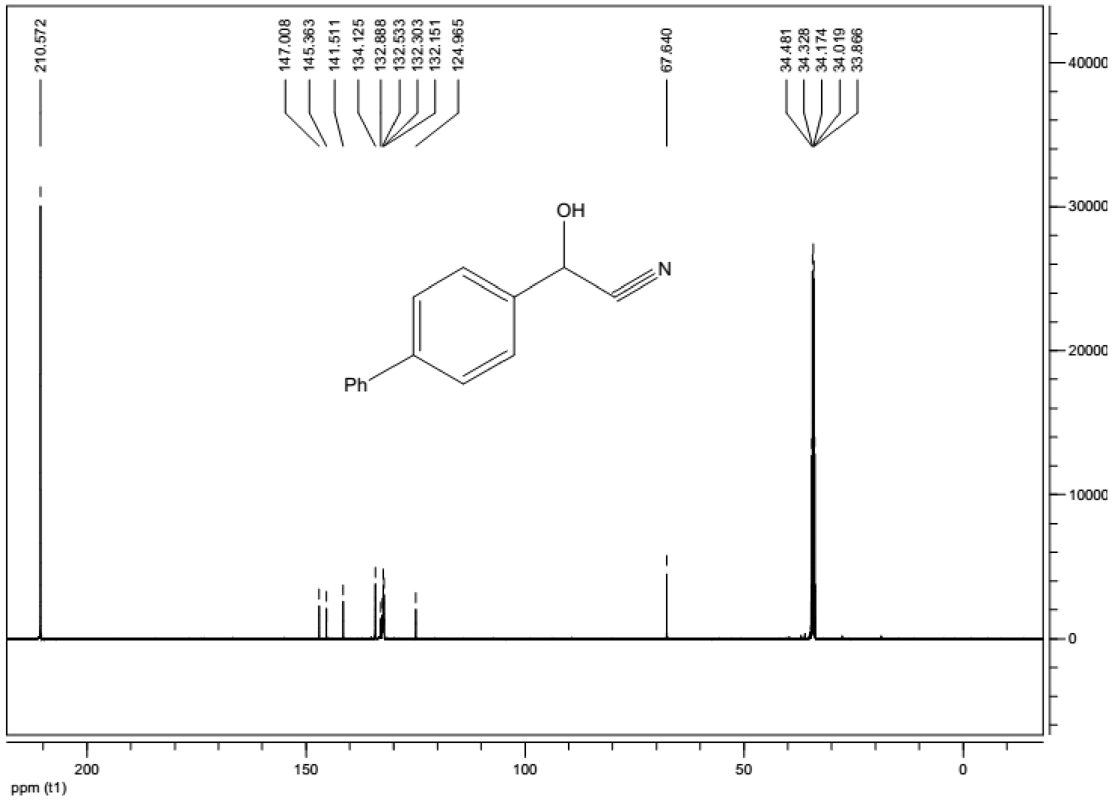
3e:


7.461
7.439
7.413
7.391
5.516
5.293
OH
N
Cl
15000
10000
50000
0
4.18
1.00
0.98
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

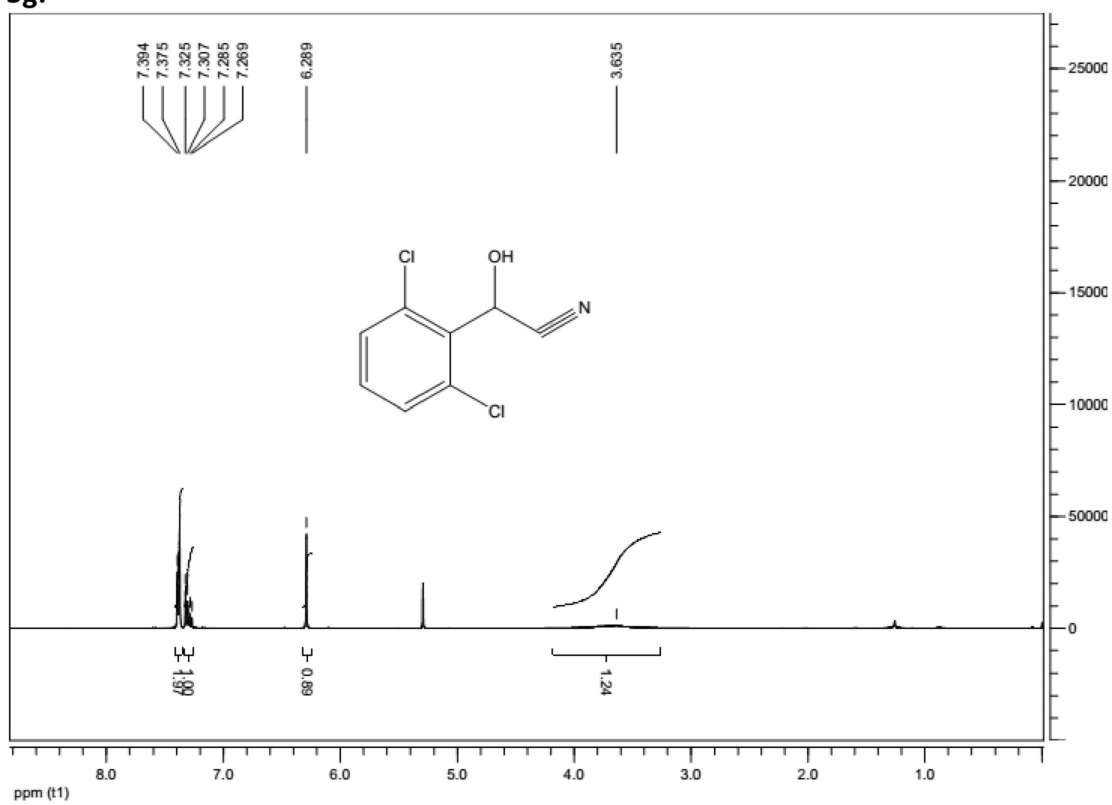

133.811
131.015
129.366
127.993
118.656
62.810
OH
N
Cl
150
100
50
0
ppm (t1)
70000
60000
50000
40000
30000
20000
10000
0
-1000

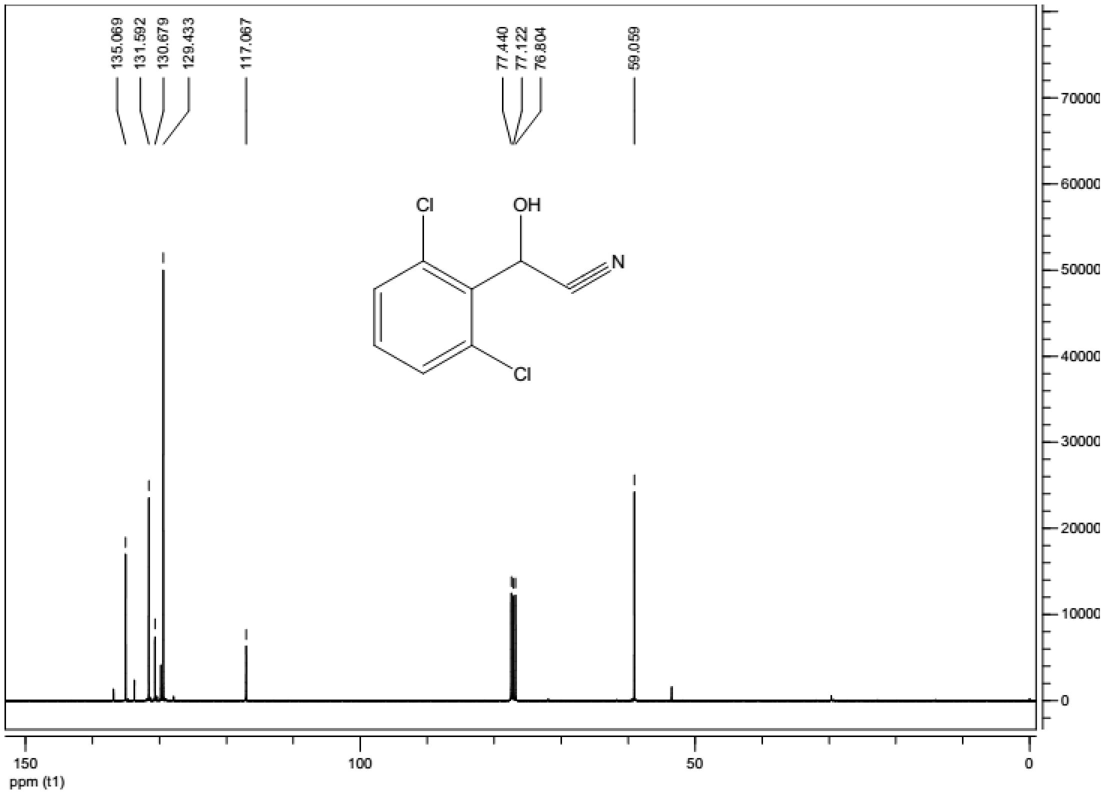
3f:


7.758
7.742
7.697
7.695
7.682
7.666
7.497
7.482
7.466
7.405
7.390
7.375
6.050
6.037
5.856
5.844
OH
N
Ph
3.99
2.10
2.09
0.97
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)
40000
30000
20000
10000
0
-1000

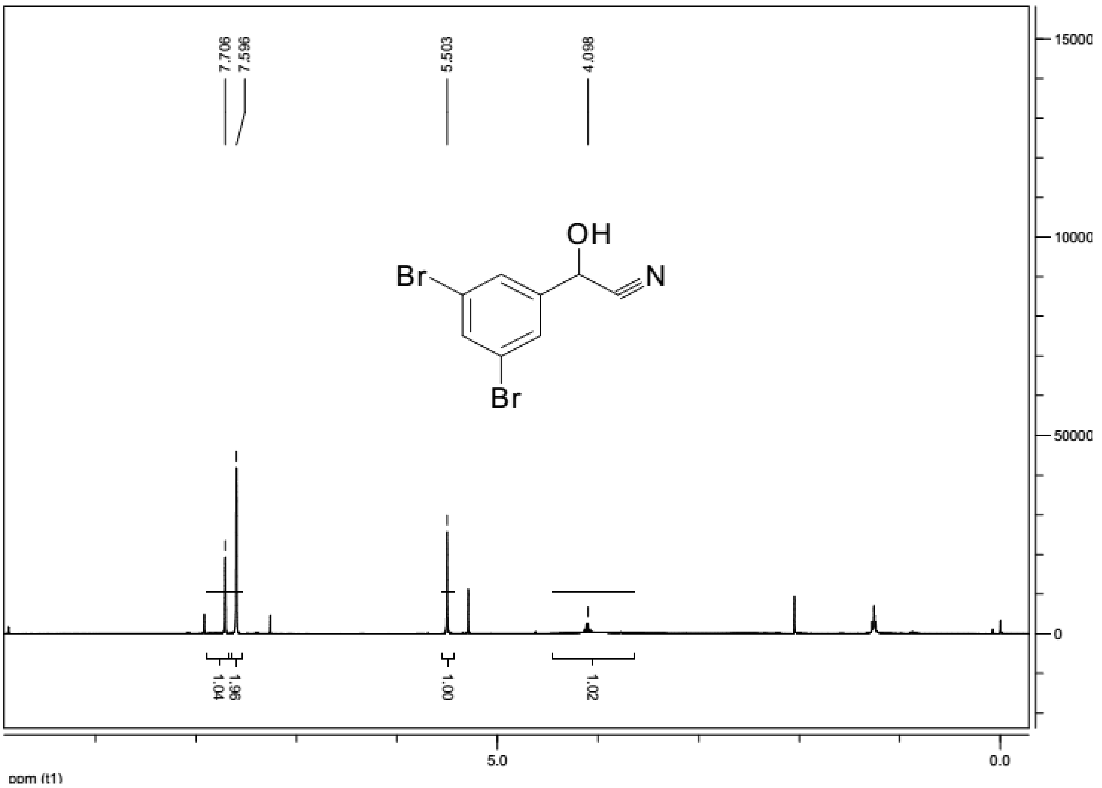

210.572
147.008
145.363
141.511
134.125
132.888
132.533
132.303
132.151
124.965
67.640
34.481
34.328
34.174
34.019
33.866
OH
N
Ph
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)

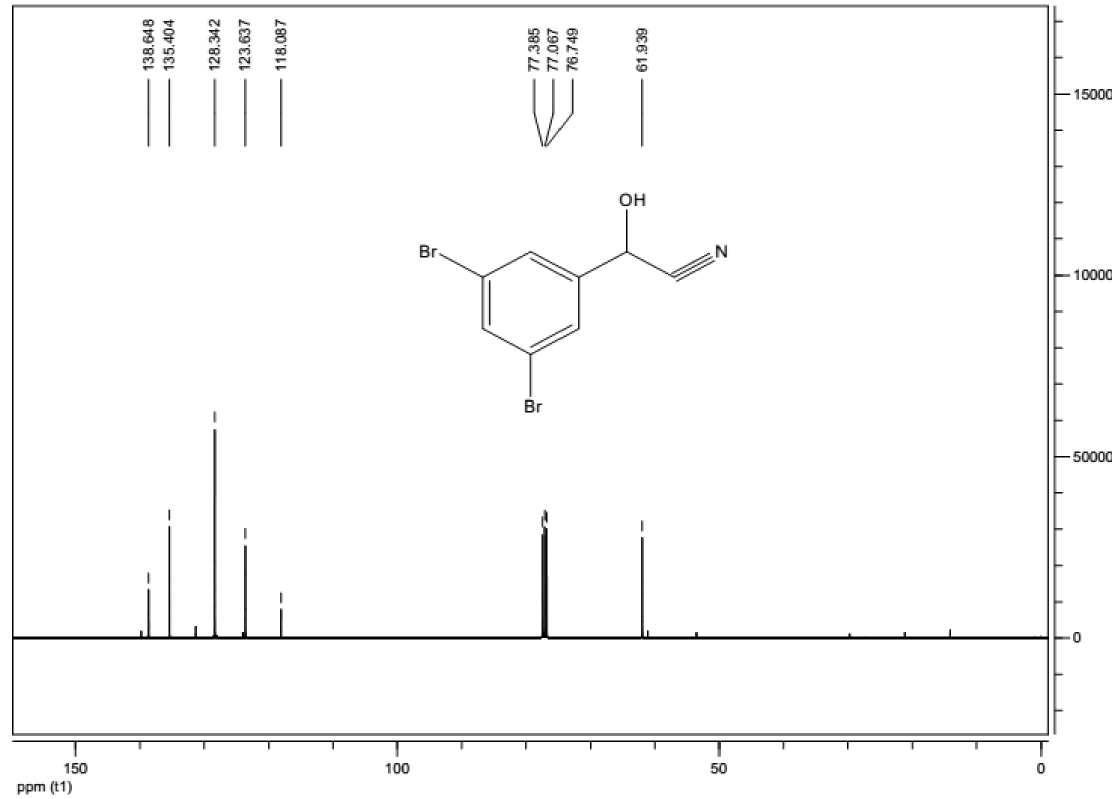
3g:


7.394
7.375
7.325
7.307
7.285
7.269
6.289
3.635
Cl
OH
N
Cl
25000
20000
15000
10000
50000
0
1.97
1.00
0.89
1.24
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

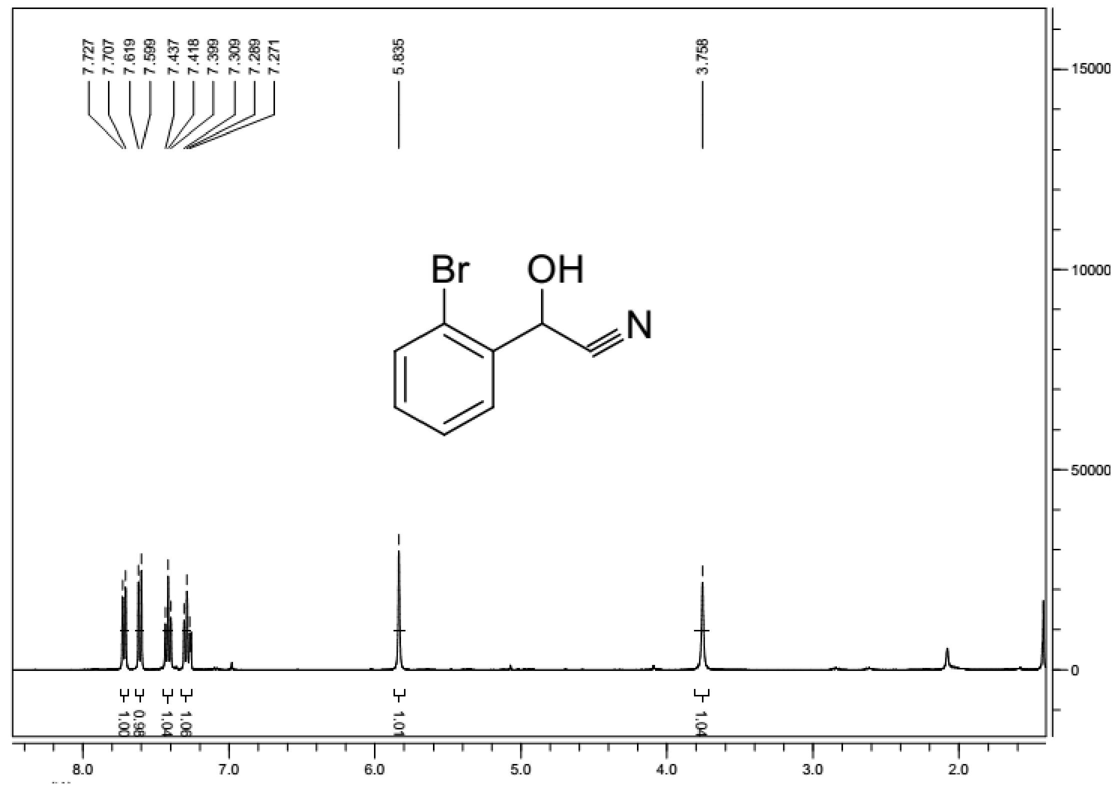

135.069
131.592
130.679
129.433
117.067
77.440
77.122
76.804
59.059
Cl
OH
N
Cl
70000
60000
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)

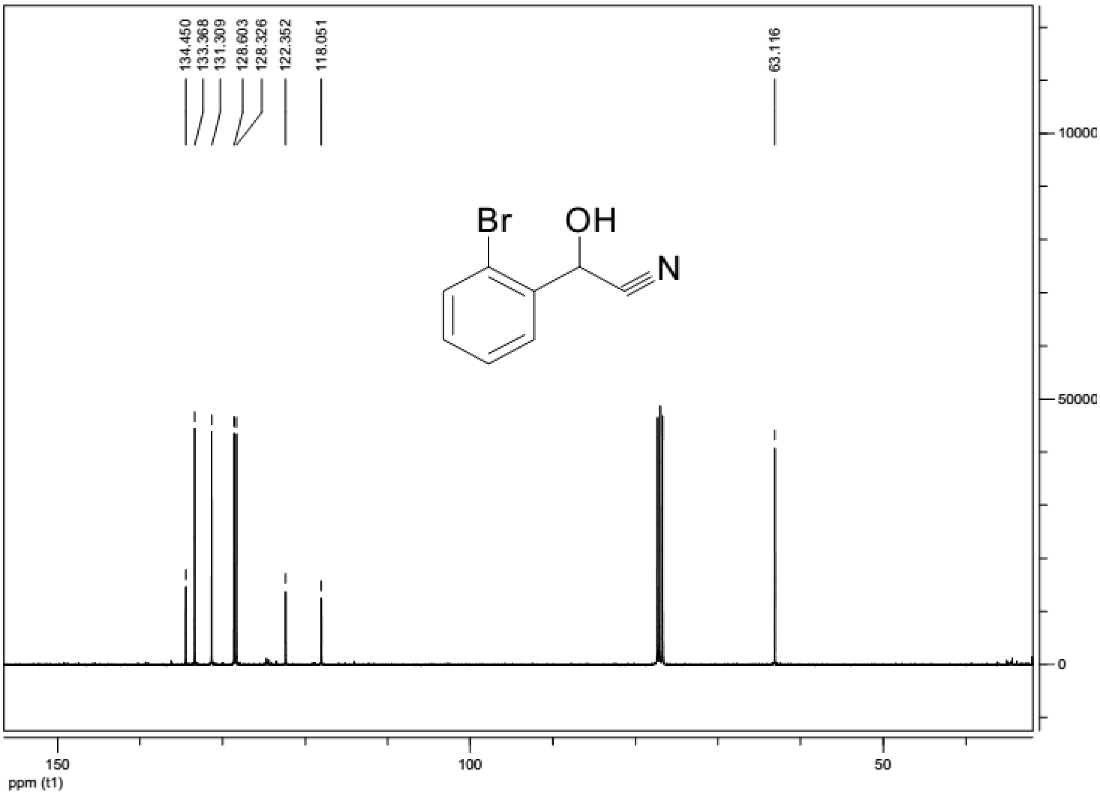
3h:


7.706
7.596
5.503
4.098
OH
Br
N
Br
15000
10000
50000
0
1.04
1.96
1.00
1.02
5.0
0.0
ppm (t1)

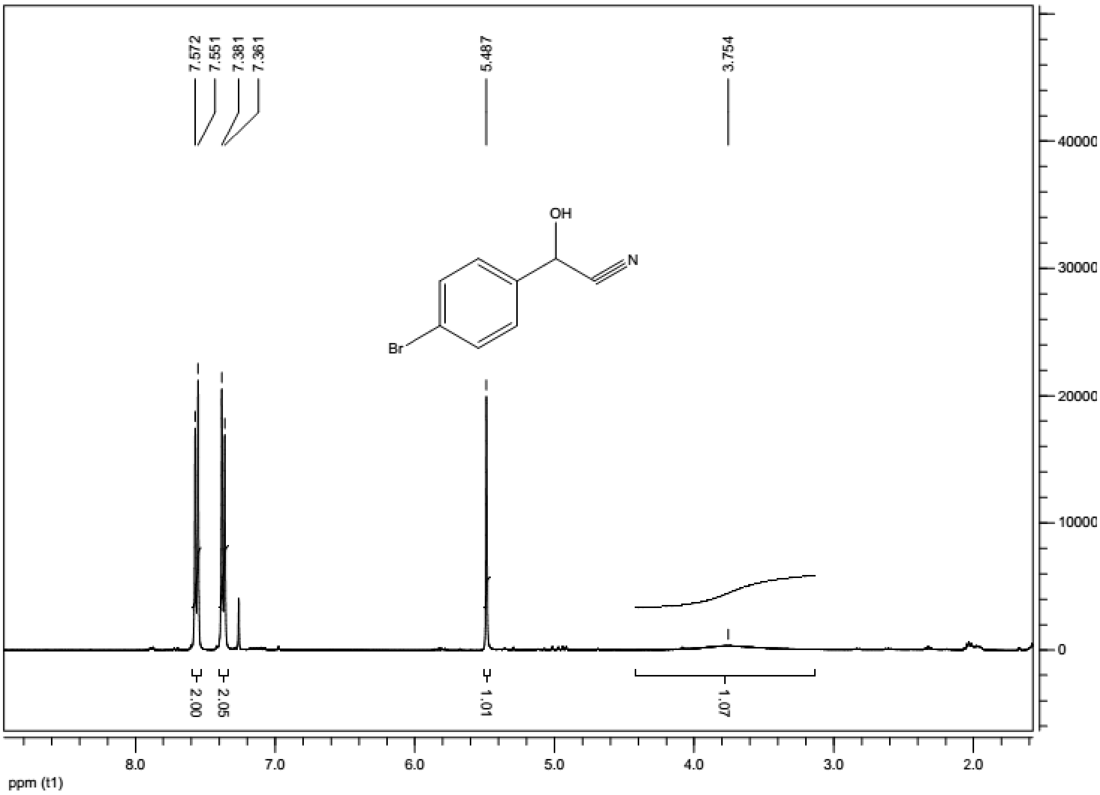

138.648
135.404
128.342
123.637
118.087
77.385
77.067
76.749
61.939
OH
Br
N
Br
15000
10000
50000
0
150
100
50
0
ppm (t1)

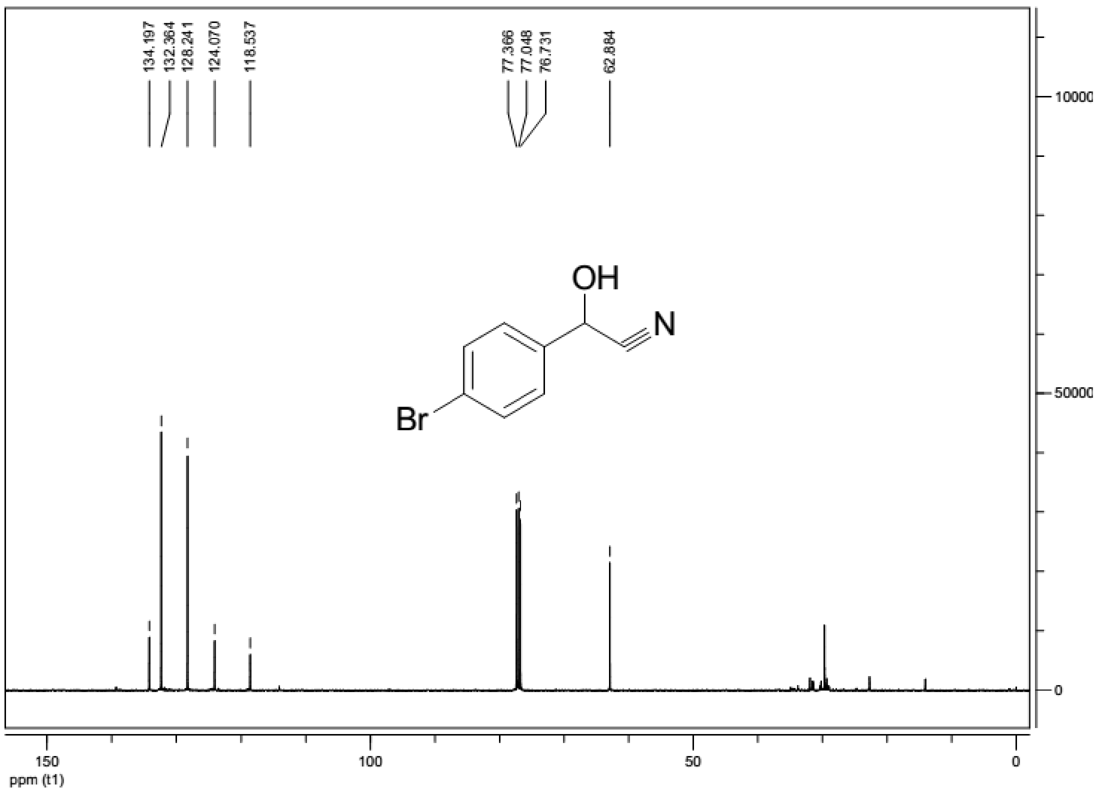
3i:


7.727
7.707
7.619
7.599
7.437
7.418
7.399
7.309
7.289
7.271
5.835
3.758
Br
OH
N
15000
10000
50000
0
1.00
0.96
1.04
1.06
1.01
1.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0

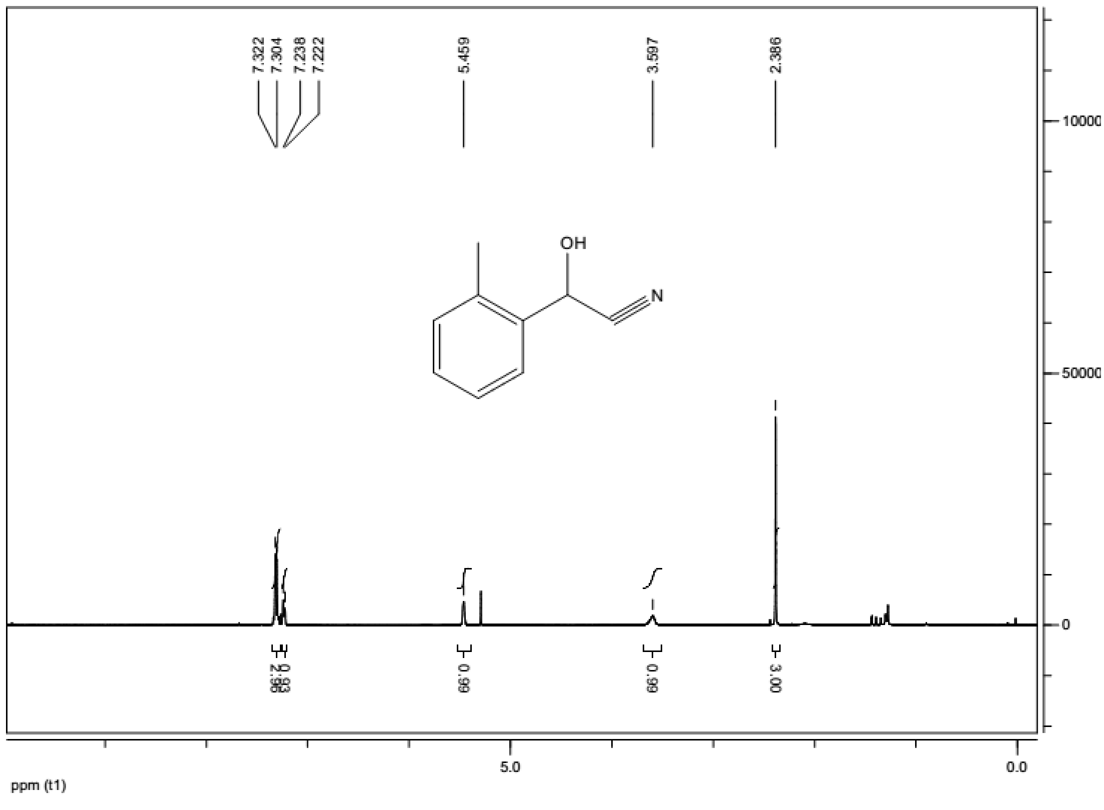

134.450
133.368
131.309
128.603
128.326
122.352
118.051
63.116
Br
OH
N
10000
50000
0
150
100
50
ppm (t1)

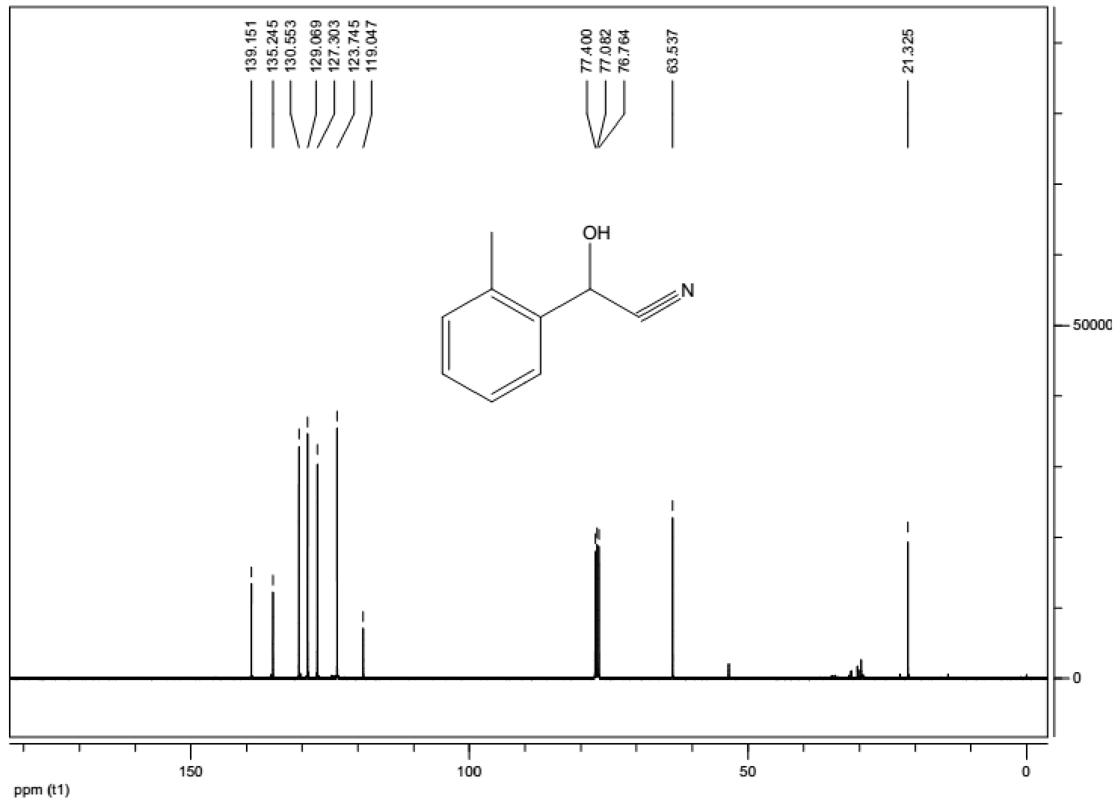
3j:


7.572
7.551
7.381
7.361
5.487
3.754
OH
N
Br
40000
30000
20000
10000
0
2.00
2.05
1.01
1.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

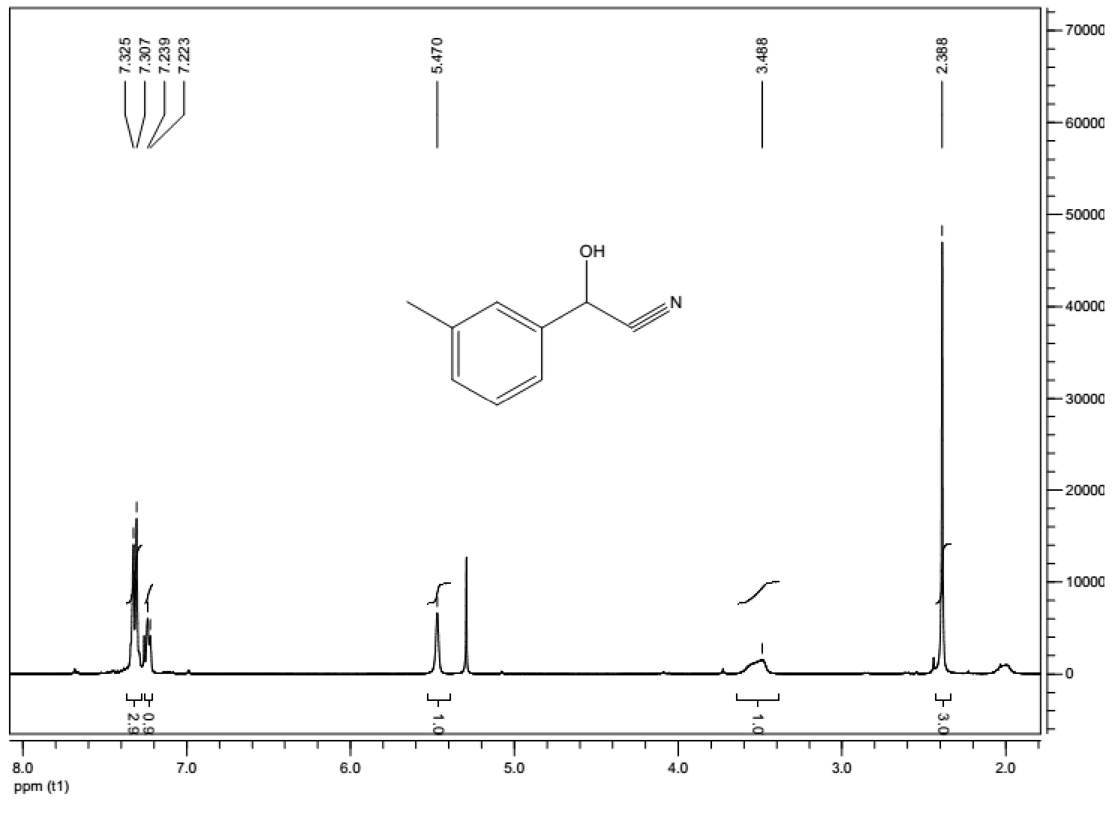

134.197
132.364
128.241
124.070
118.537
77.366
77.048
76.731
62.884
OH
N
Br
10000
50000
0
150
100
50
0
ppm (t1)

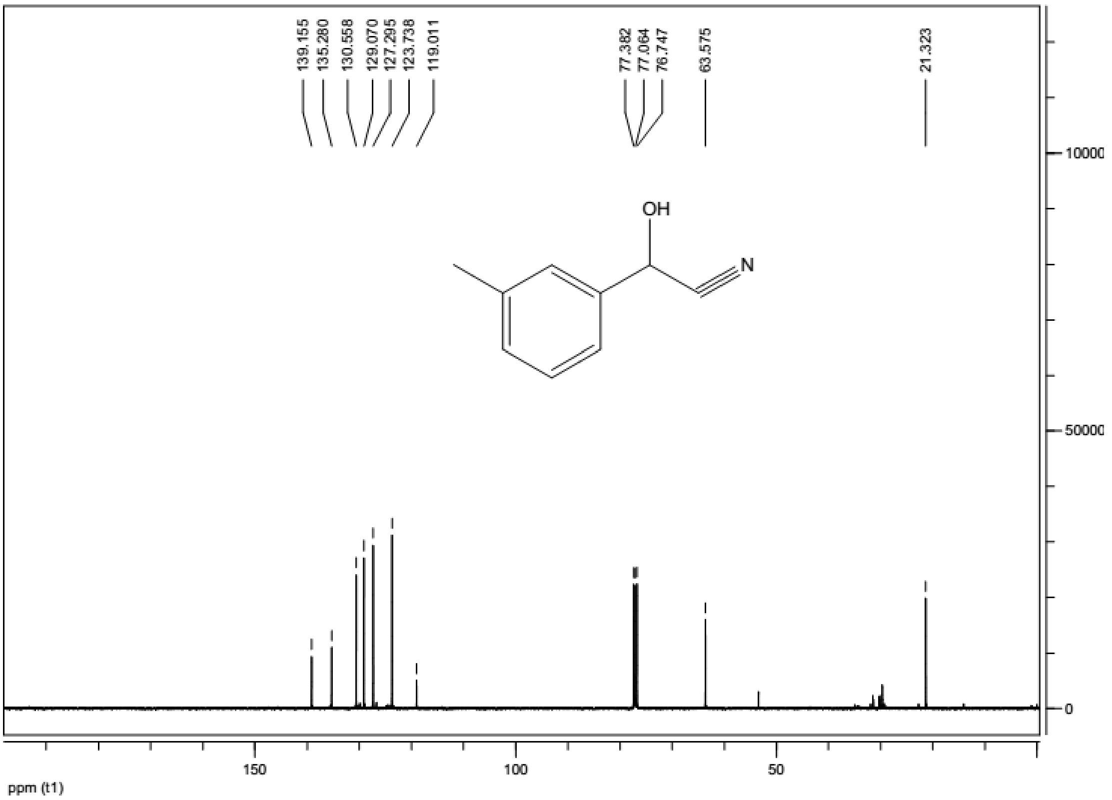
3k:


7.322
7.304
7.238
7.222
5.459
3.597
2.386
OH
N
10000
50000
0
2.96
0.93
0.99
0.99
3.00
5.0
0.0
ppm (t1)

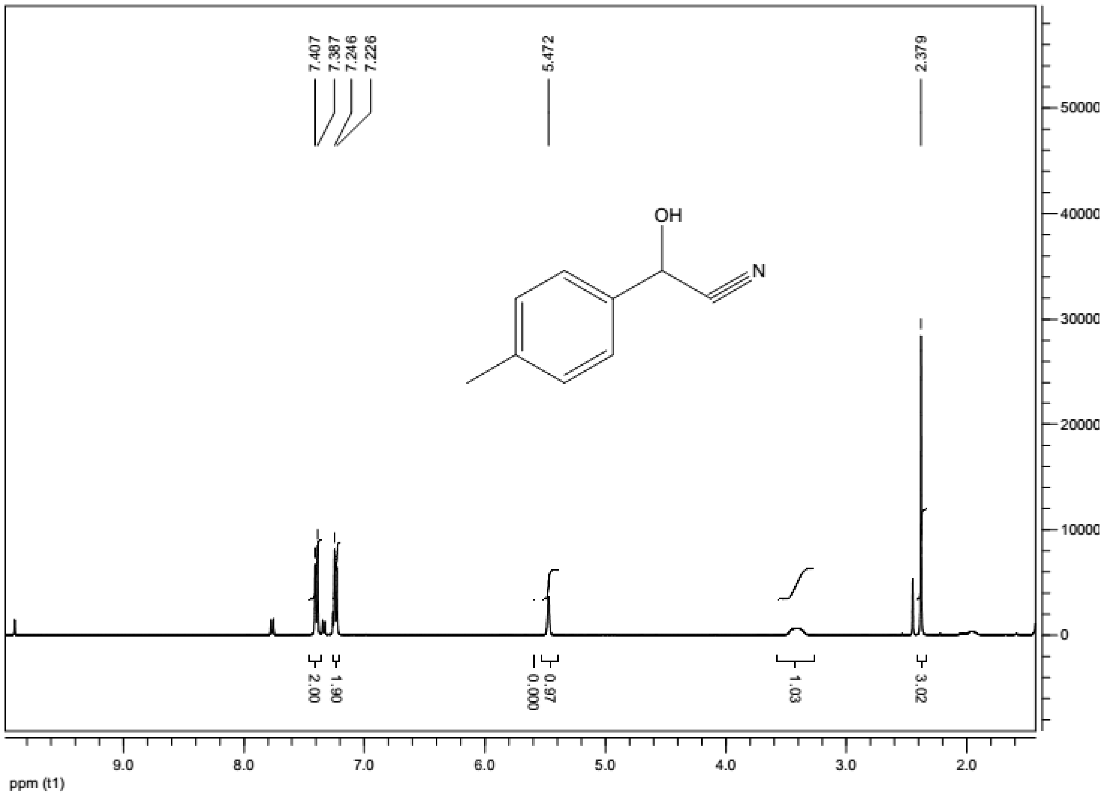

139.151
135.245
130.553
129.069
127.303
123.745
119.047
77.400
77.082
76.764
63.537
21.325
OH
N
50000
0
150
100
50
0
ppm (t1)

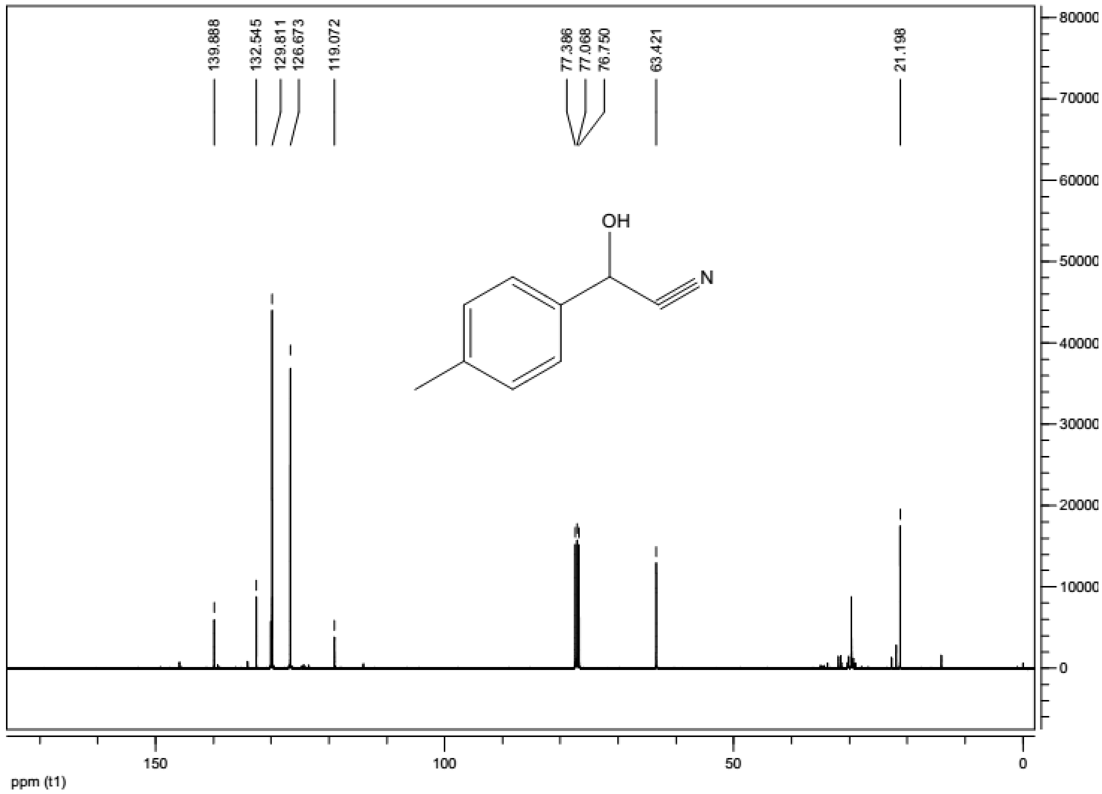
3l:


7.325
7.307
7.239
7.223
5.470
3.488
2.388
OH
N
70000
60000
50000
40000
30000
20000
10000
0
2.9
0.9
1.0
1.0
3.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


139.155
135.280
130.558
129.070
127.295
123.738
119.011
77.382
77.064
76.747
63.575
21.323
OH
N
10000
50000
0
150
100
50
ppm (t1)

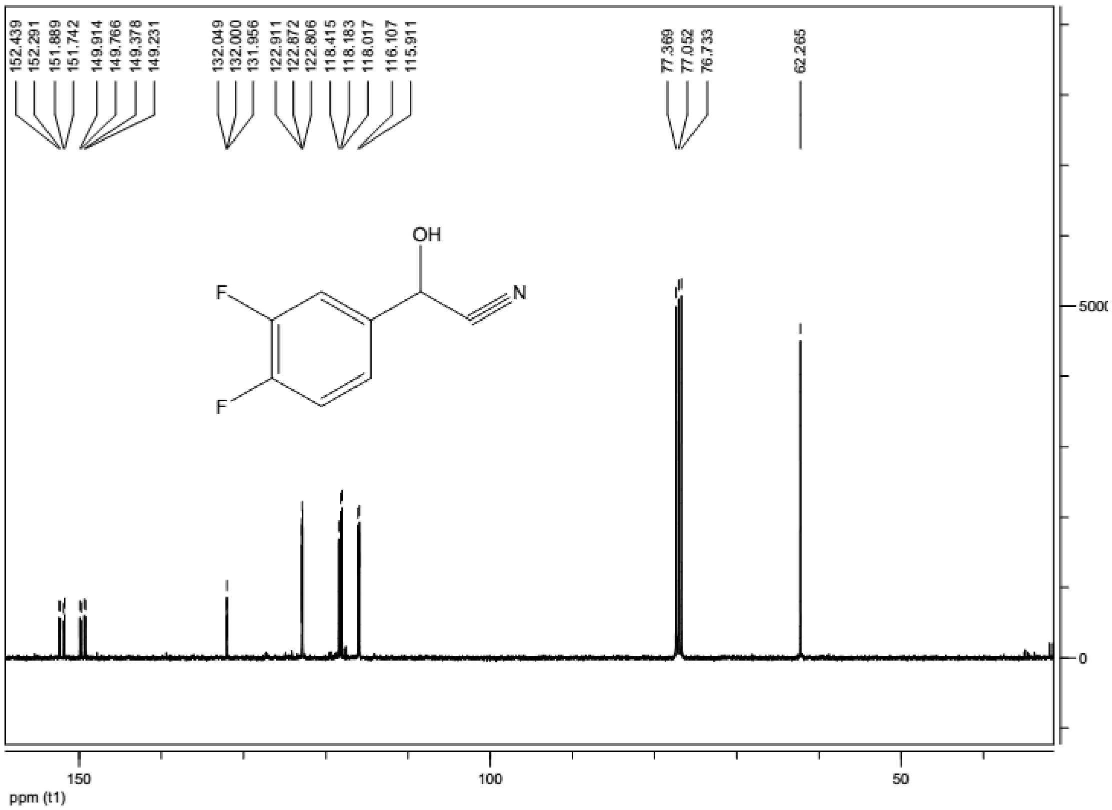
3m:

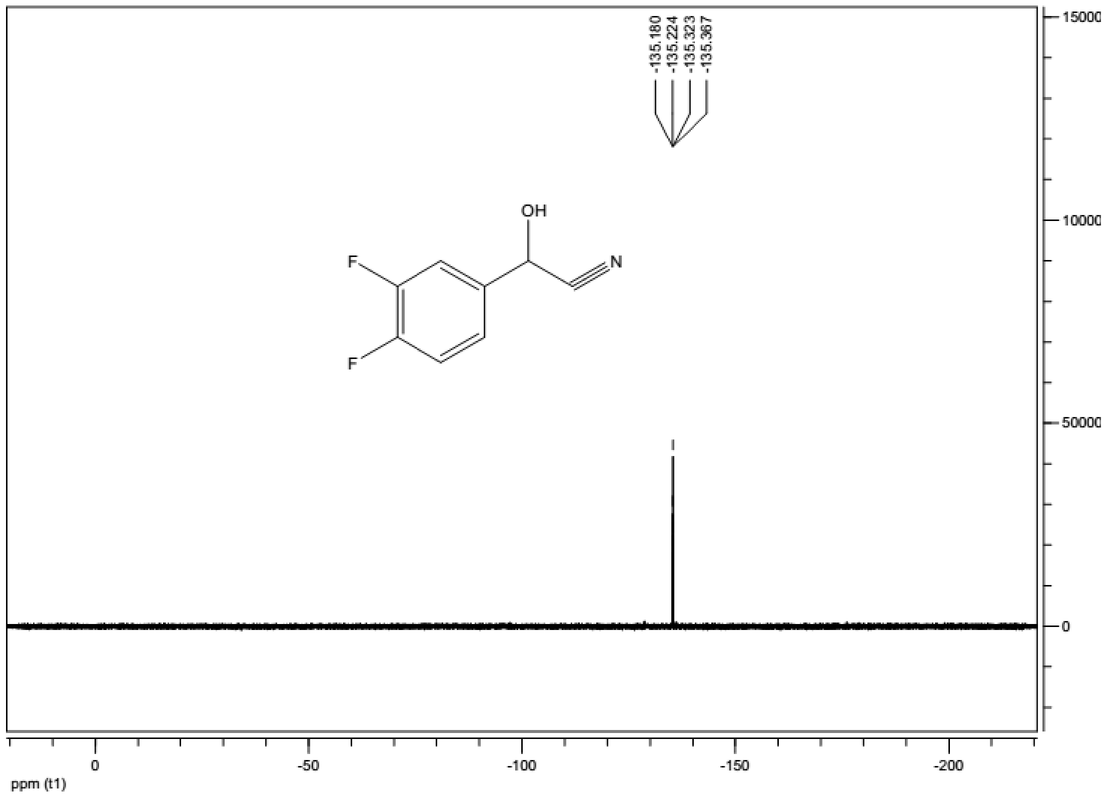

7.407
7.387
7.246
7.226
5.472
2.379
OH
N
50000
40000
30000
20000
10000
0
2.00
1.90
0.000
0.97
1.03
3.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


139.888
132.545
129.811
126.673
119.072
77.386
77.068
76.750
63.421
21.198
OH
N
150
100
50
0
ppm (t1)

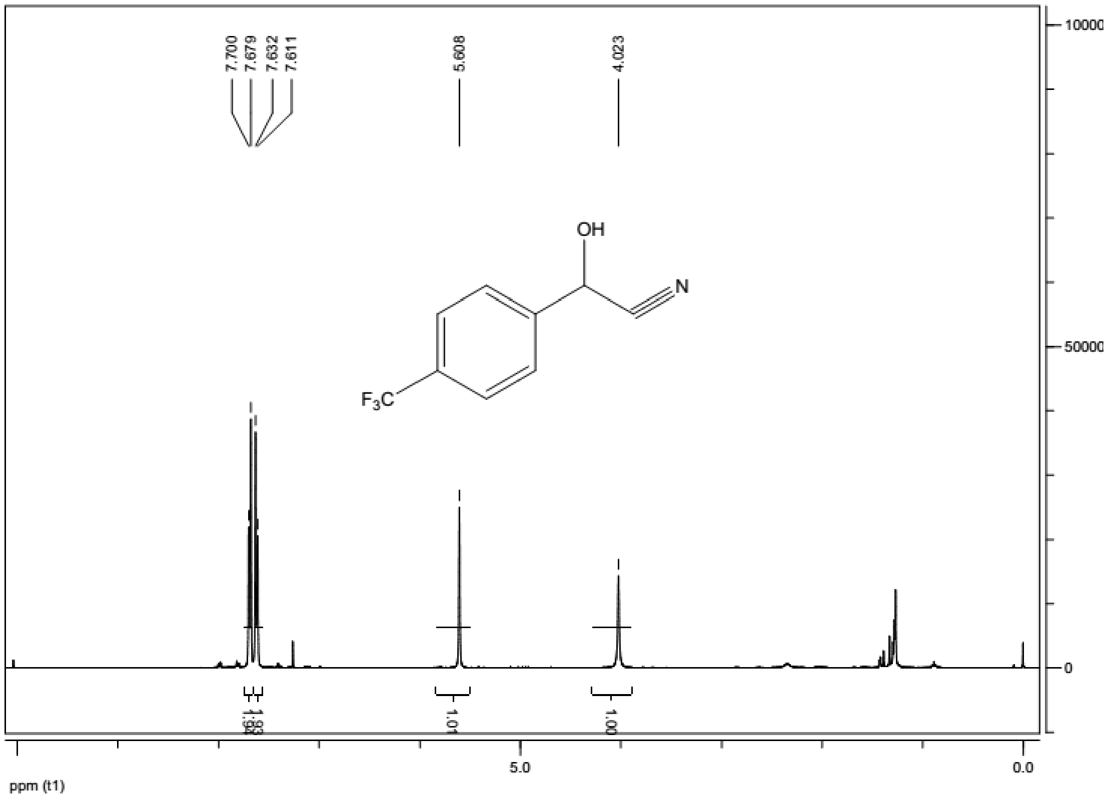
3n:


7.365
7.343
7.323
7.319
7.246
7.231
7.209
7.187
5.511
3.983
OH
F
F
N
3.10
0.98
1.00
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

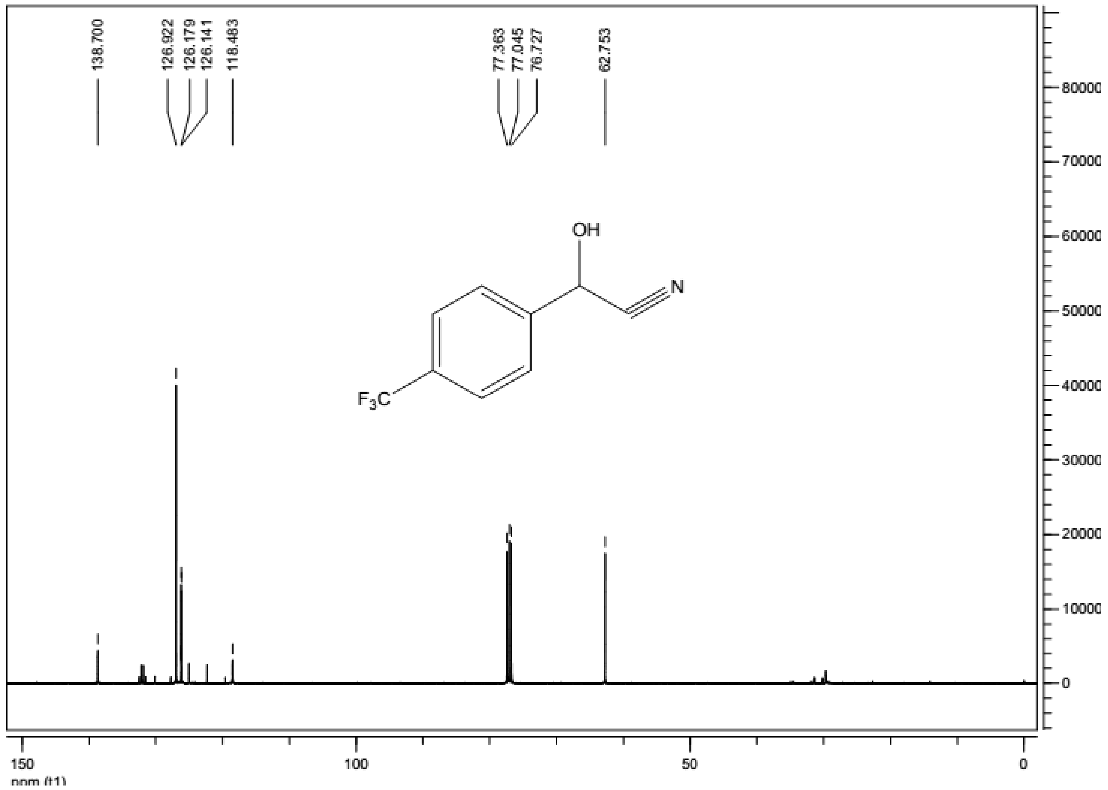

152.439
152.291
151.889
151.742
149.914
149.766
149.378
149.231
132.049
132.000
131.956
122.911
122.872
122.806
118.415
118.183
118.017
116.107
115.911
77.369
77.052
76.733
62.265
OH
F
N
F
5000
0
150
100
50
ppm (t1)


-135.180
-135.224
-135.323
-135.367
OH
F
N
F
15000
10000
50000
0
0
-50
-100
-150
-200
ppm (t1)

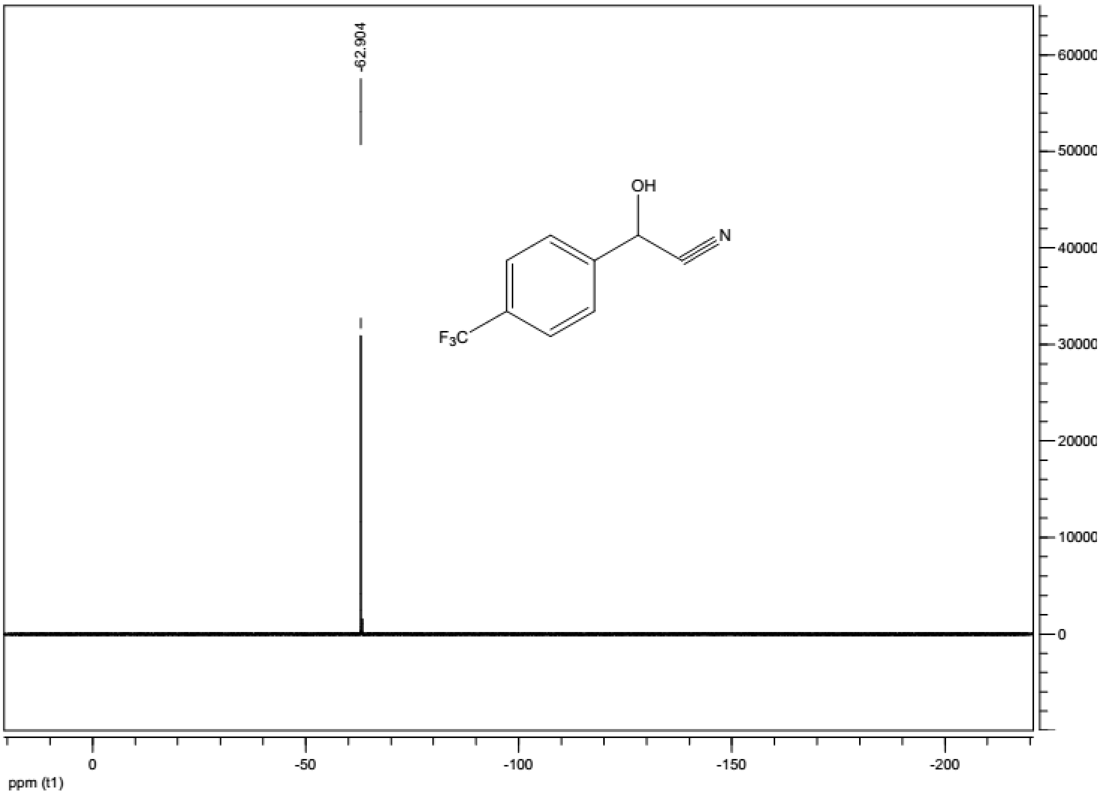
3o:



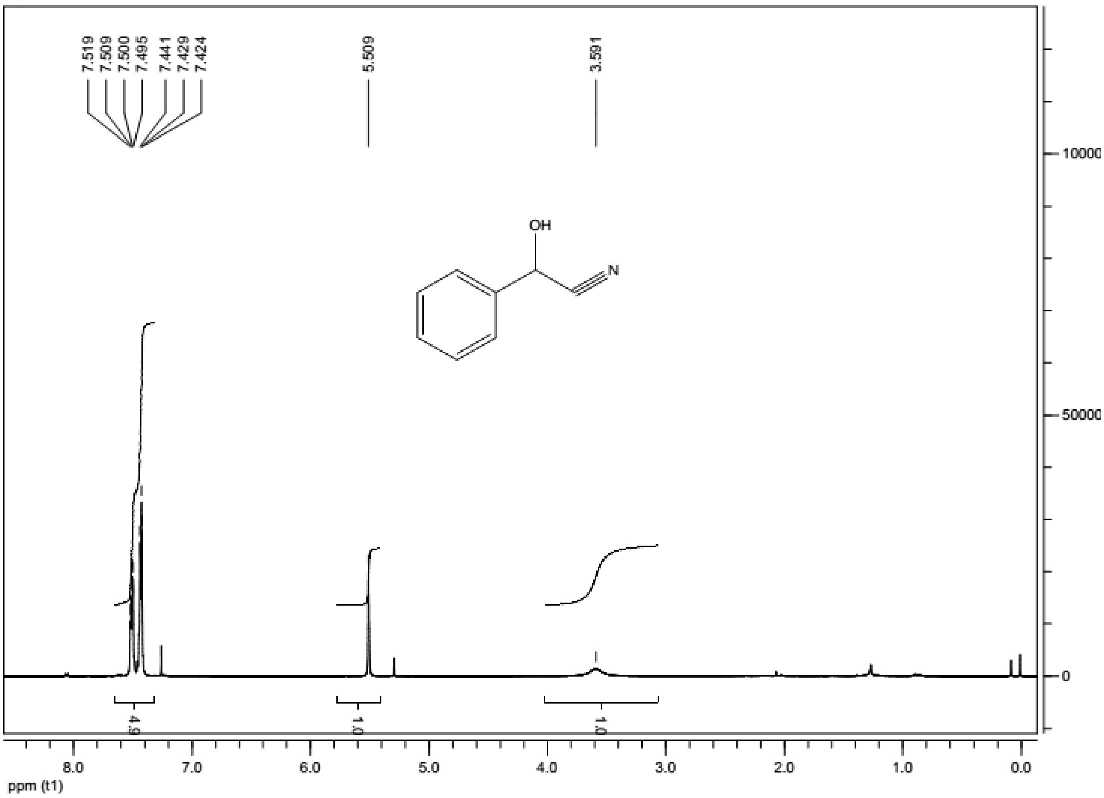
7.700
7.679
7.632
7.611
5.608
4.023
OH
N
F3C
1.93
1.01
1.00
5.0
0.0
ppm (t1)

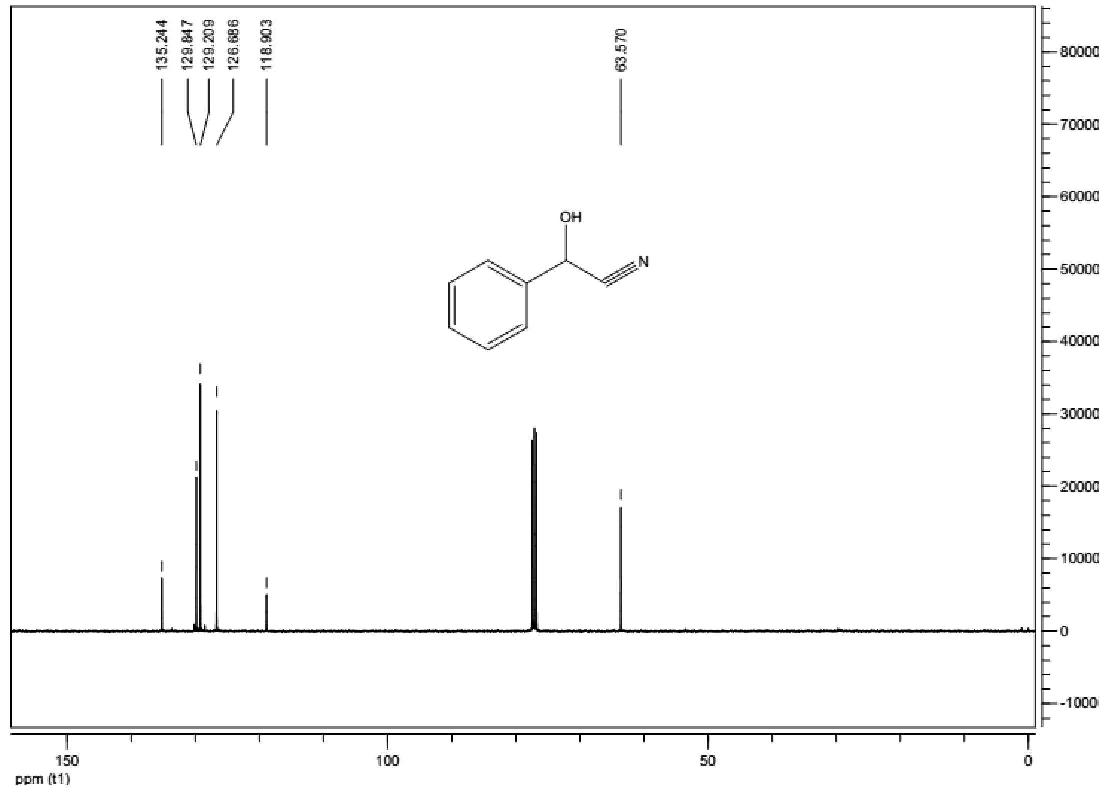


138.700
126.922
126.179
126.141
118.483
77.363
77.045
76.727
62.753
OH
N
F3C
150
100
50
0
ppm (t1)

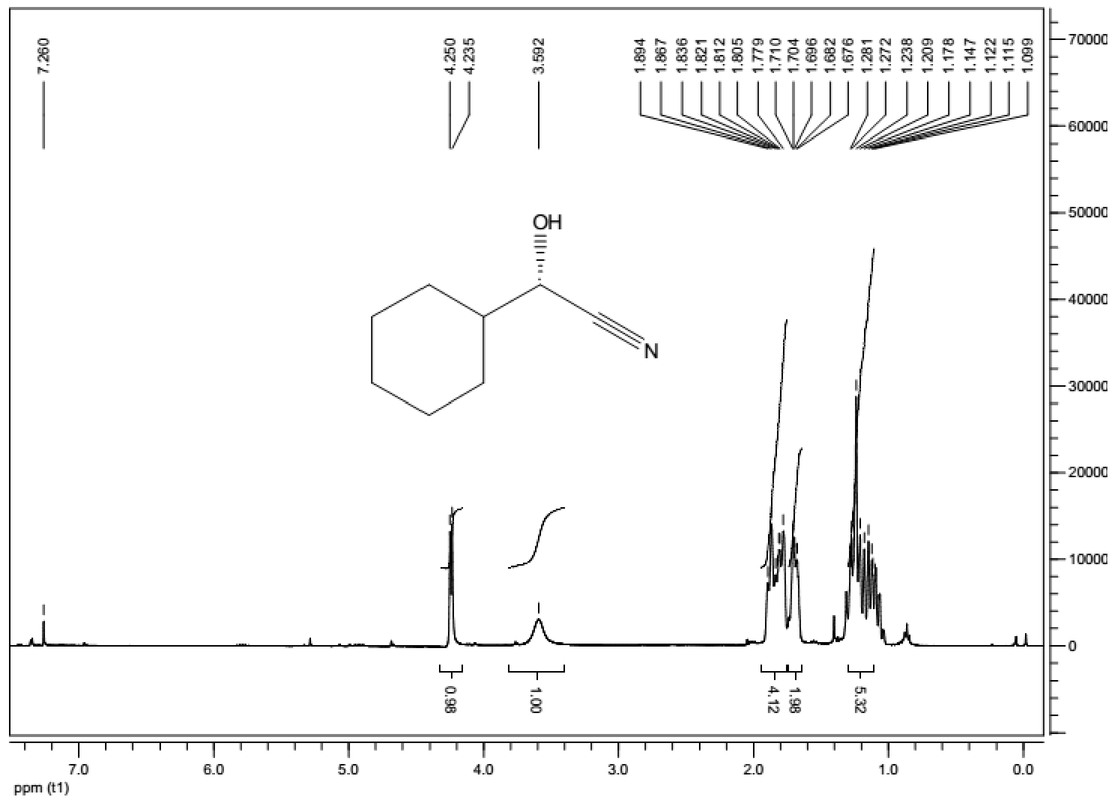

-62.904
OH
N
F3C
60000
50000
40000
30000
20000
10000
0
0
-50
-100
-150
-200
ppm (t1)

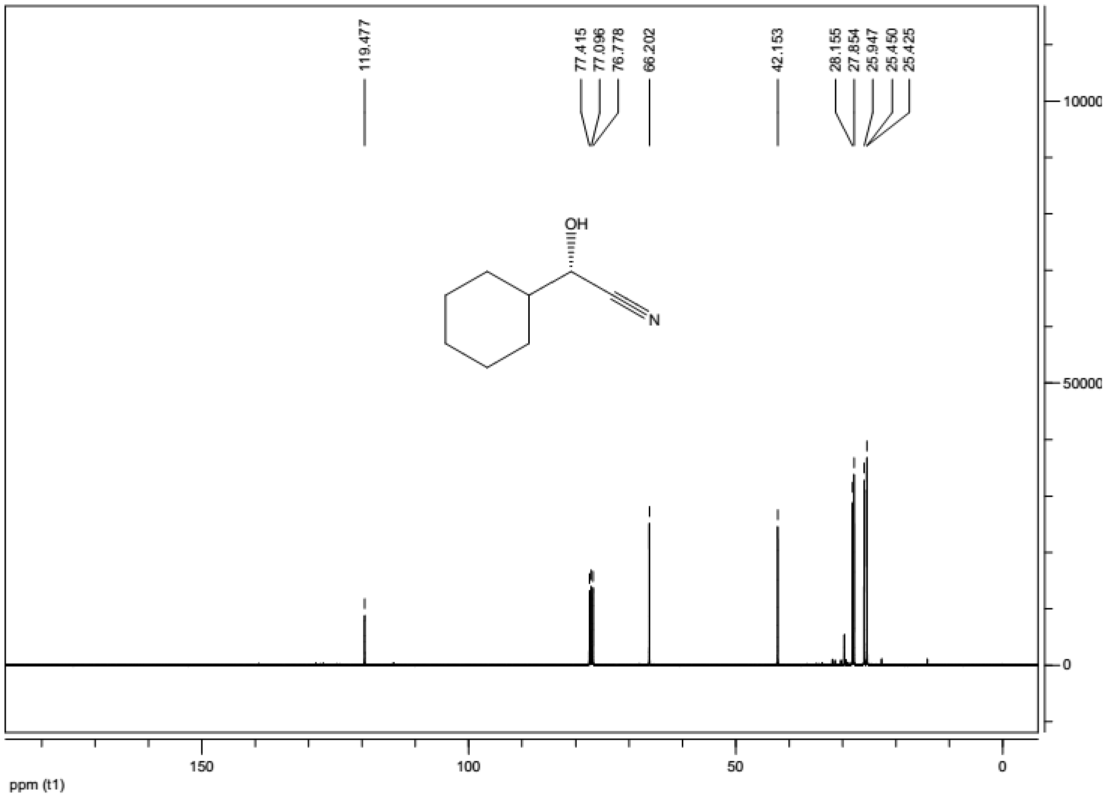
3p:


7.519
7.509
7.500
7.495
7.441
7.429
7.424
5.509
3.591
OH
N
10000
50000
0
4.9
1.0
1.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

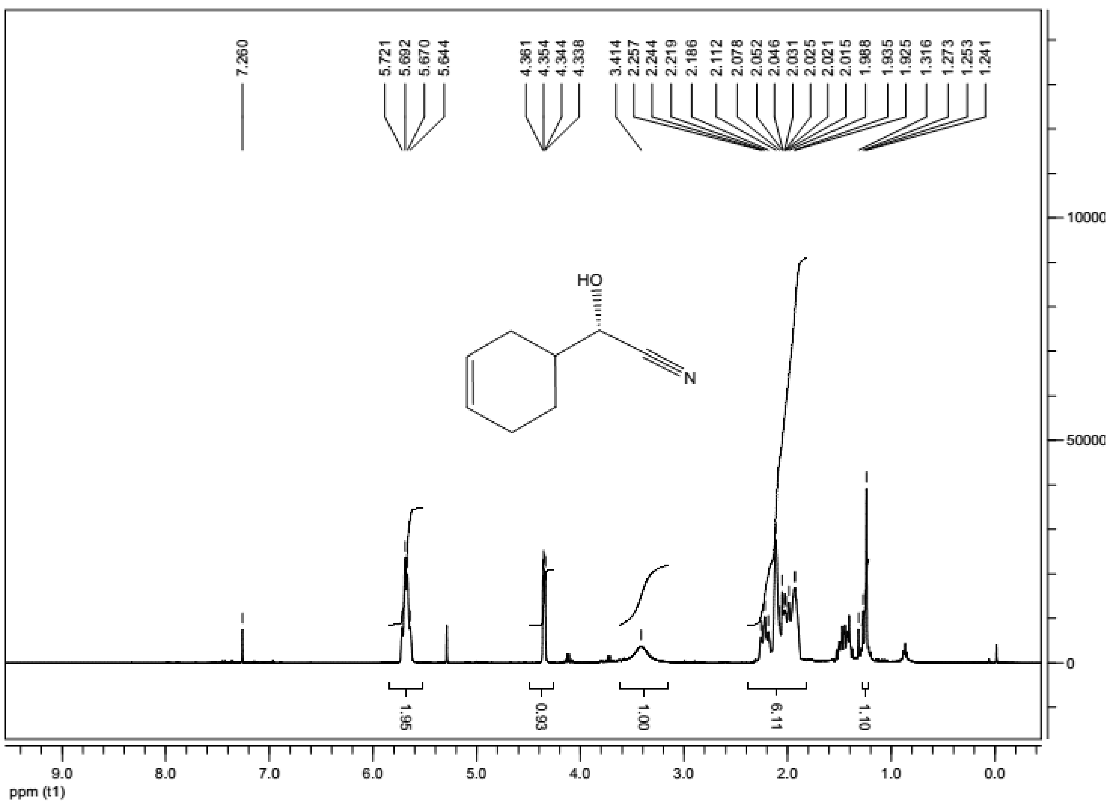

135.244
129.847
129.209
126.686
118.903
63.570
OH
N
ppm (t1)

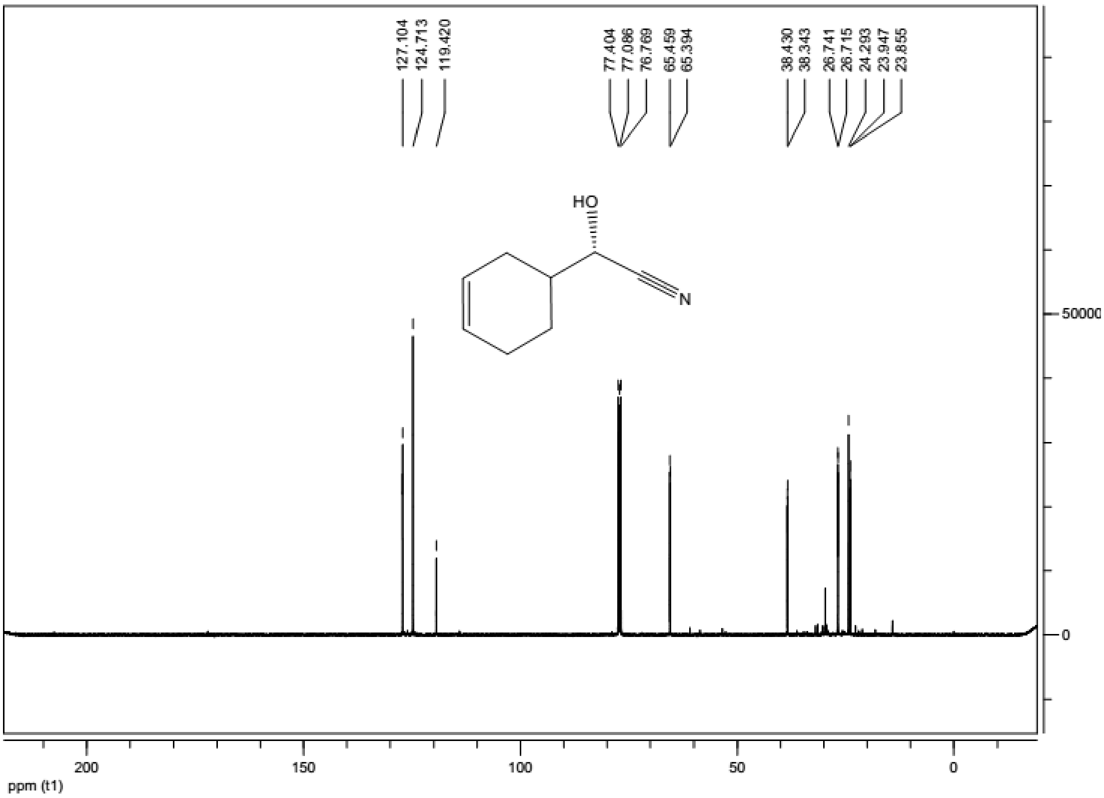
3q:


7.260
4.250
4.235
3.592
1.894
1.867
1.836
1.821
1.812
1.805
1.779
1.710
1.704
1.696
1.682
1.676
1.281
1.272
1.238
1.209
1.178
1.147
1.122
1.115
1.099
OH
N
0.98
1.00
4.12
1.98
5.32
ppm (t1)

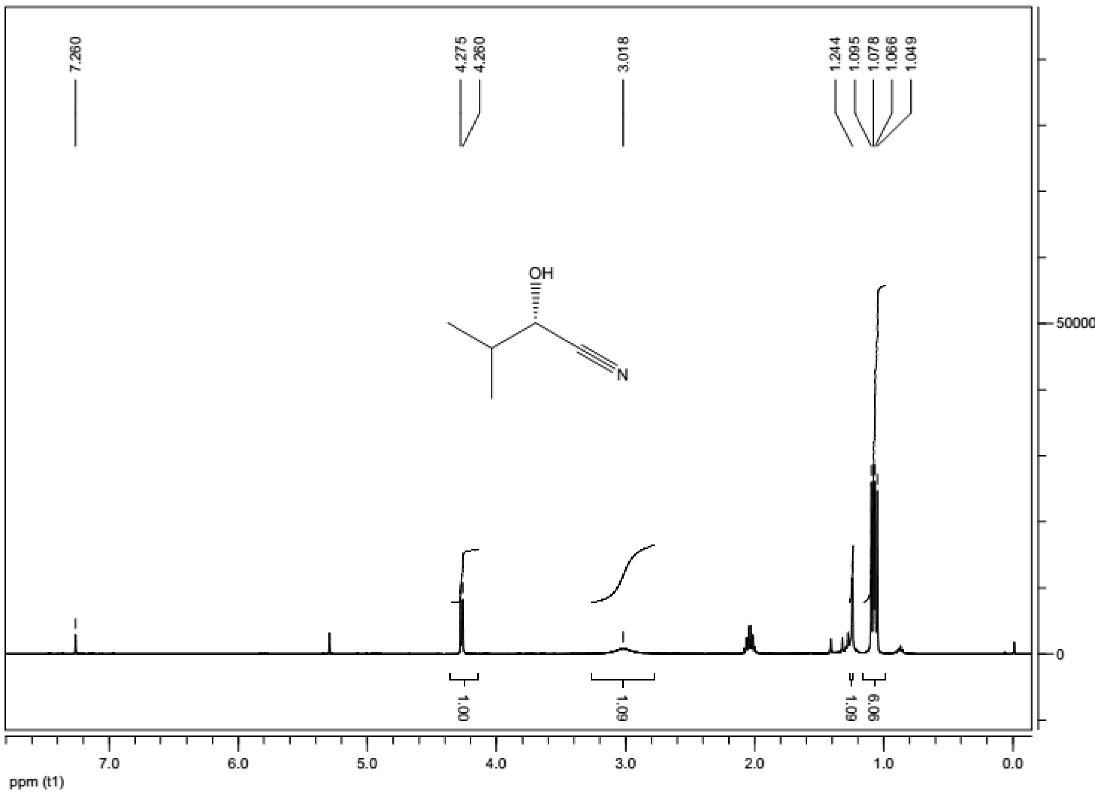

119.477
77.415
77.096
76.778
66.202
42.153
28.155
27.854
25.947
25.450
25.425
OH
N
10000
50000
0
150
100
50
0
ppm (t1)

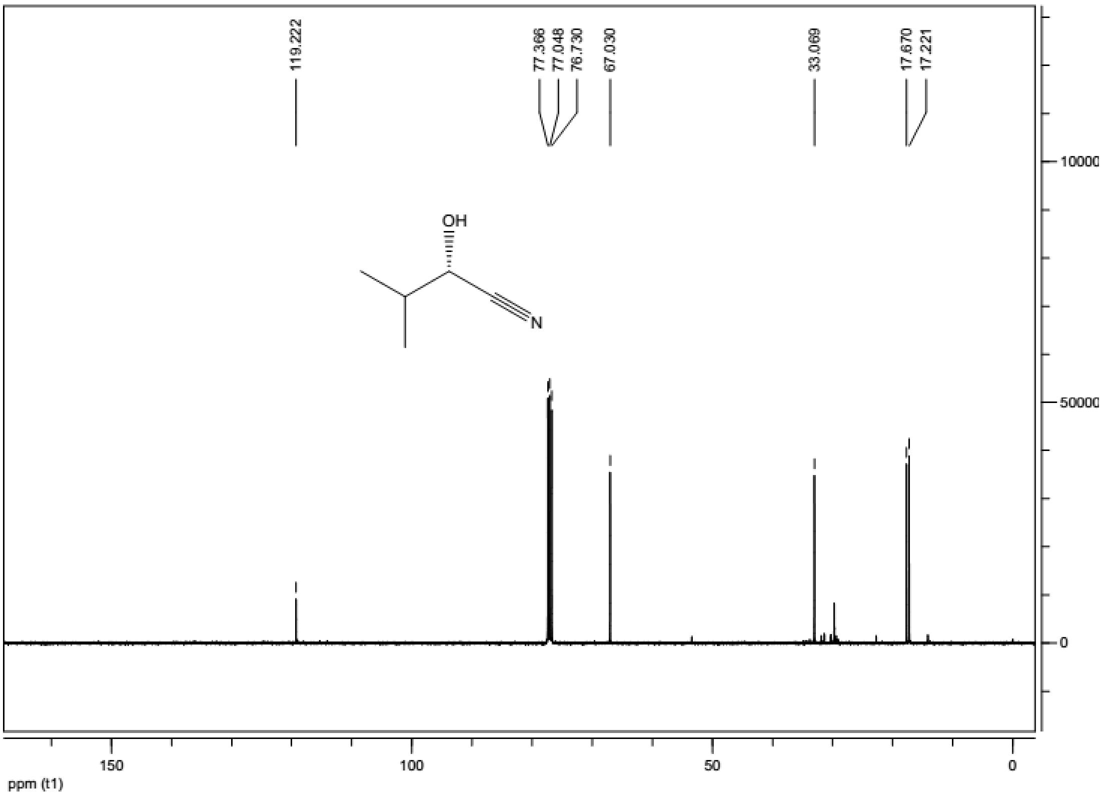
3r:


7.260
5.721
5.692
5.670
5.644
4.361
4.354
4.344
4.338
3.414
2.257
2.244
2.219
2.186
2.112
2.078
2.052
2.046
2.031
2.025
2.021
2.015
1.988
1.935
1.925
1.316
1.273
1.253
1.241
HO
N
10000
50000
0
1.95
0.93
1.00
6.11
1.10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

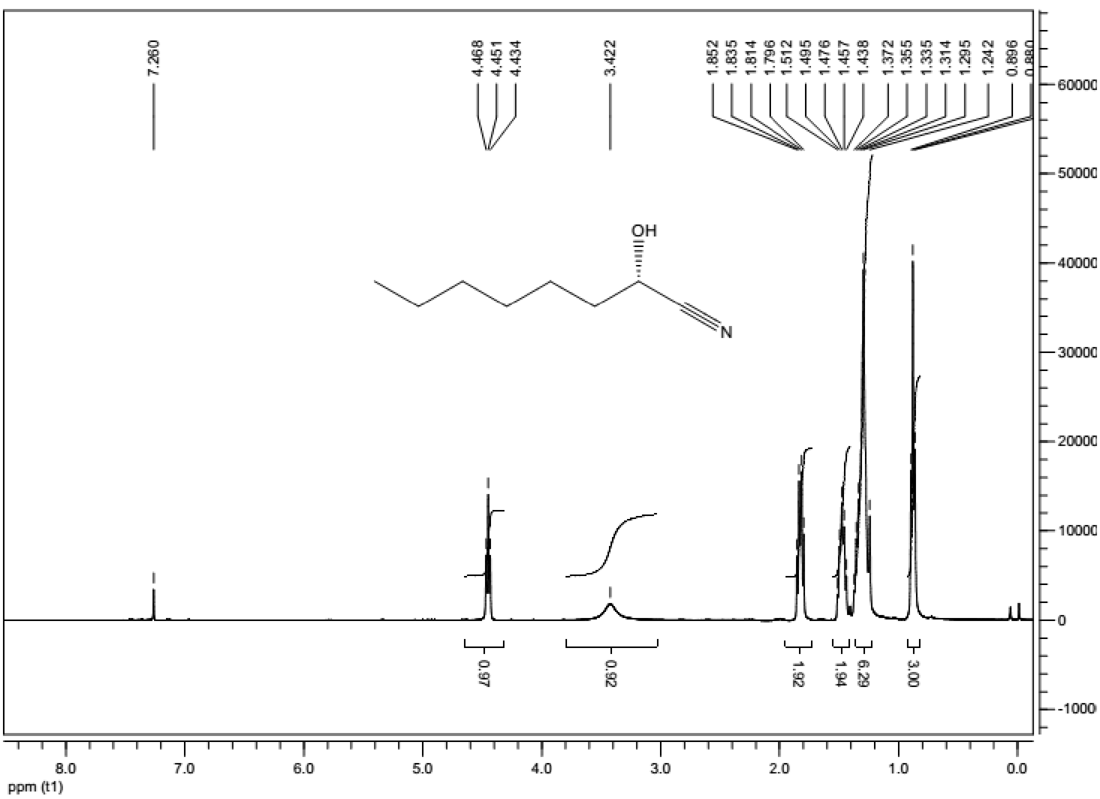

127.104
124.713
119.420
77.404
77.086
76.769
65.459
65.394
38.430
38.343
26.741
26.715
24.293
23.947
23.855
HO
N
50000
0
200
150
100
50
0
ppm (t1)

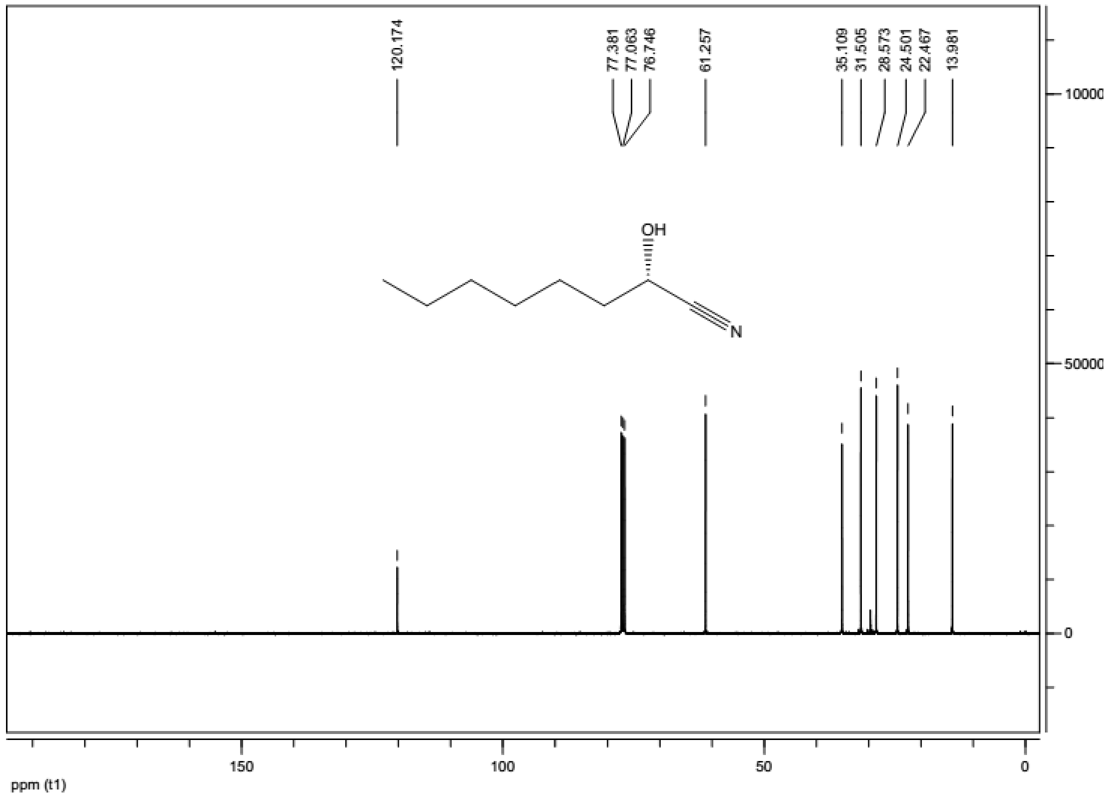
3s:


7.260
4.275
4.260
3.018
1.244
1.095
1.078
1.066
1.049
OH
N
50000
0
1.00
1.09
1.09
6.06
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

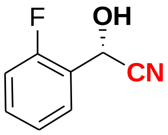

119.222
77.366
77.048
76.730
67.030
33.069
17.670
17.221
OH
N
ppm (t1)

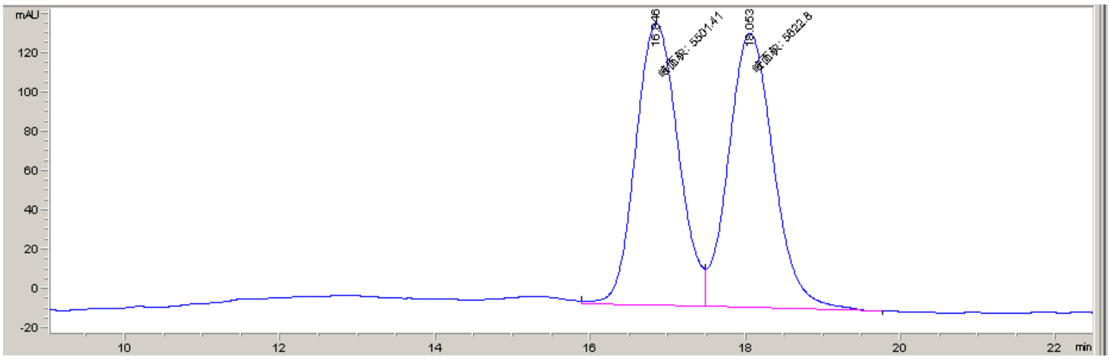
3t:


7.260
4.468
4.451
4.434
3.422
1.852
1.835
1.814
1.796
1.512
1.495
1.476
1.457
1.438
1.372
1.355
1.335
1.314
1.295
1.242
0.896
0.880
OH
N
0.97
0.92
1.92
1.94
6.29
3.00
ppm (t1)

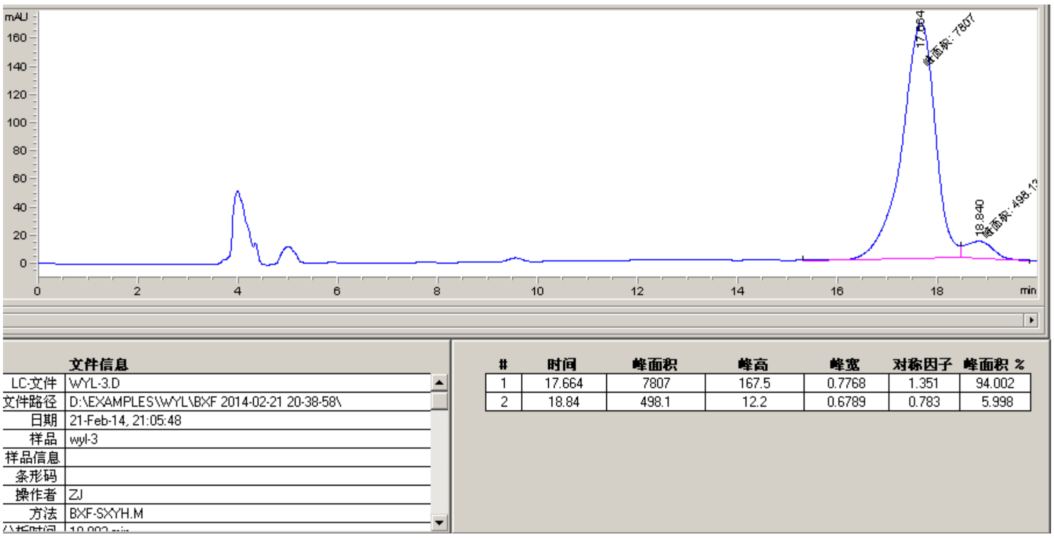

120.174
77.381
77.063
76.746
61.257
35.109
31.505
28.573
24.501
22.467
13.981
OH
N
10000
50000
0
150
100
50
0
ppm (t1)

S-6. HPLC chromatograms of Compounds 3

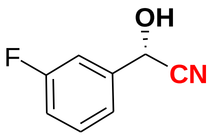




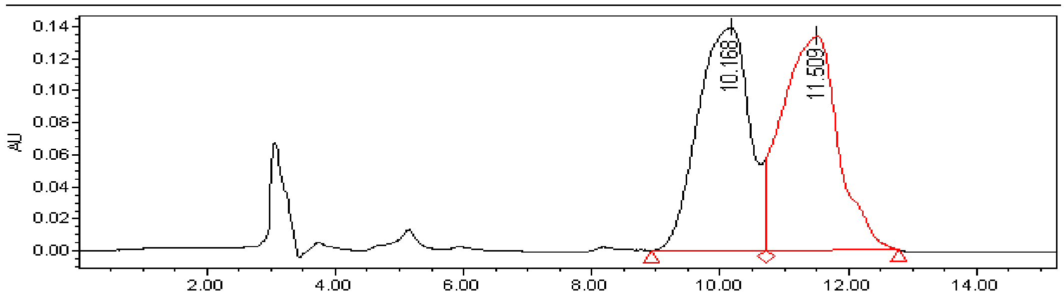
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	16.846	5501.4	49.454	143.5
2	210	18.053	5622.8	50.546	139.5



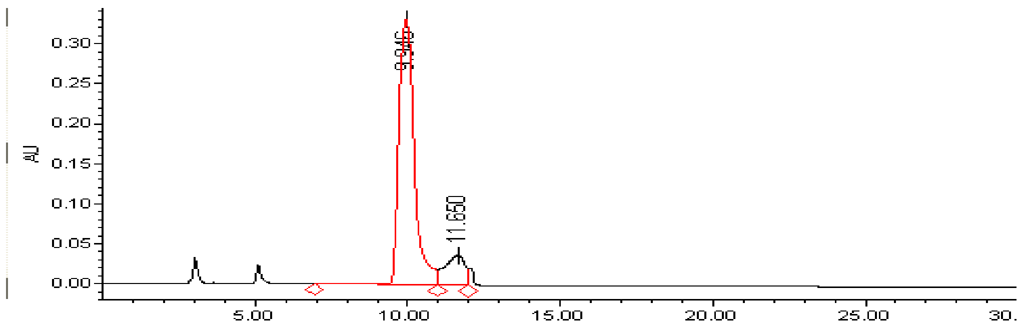
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	17.664	7807	94.002	167.5
2	210	18.84	498.1	5.998	12.2



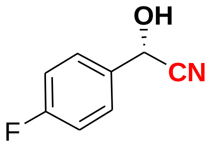
3b
81% yield
75% *ee*



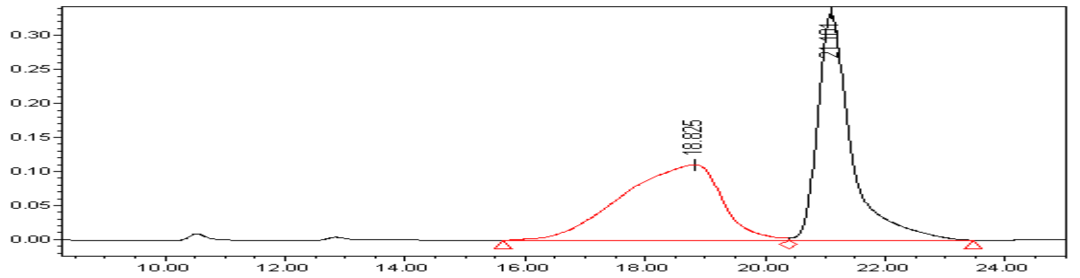
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	10.169	7817667	49.07	138869
2	210	11.509	8115473	50.93	133215



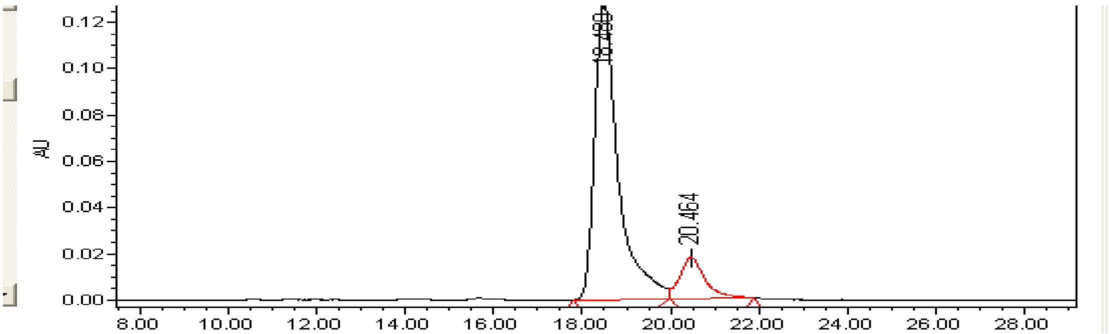
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	9.946	11692001	86.32	138869
2	210	11.650	1698456	12.68	133215



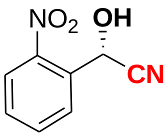
3c
98% yield
74% *ee*



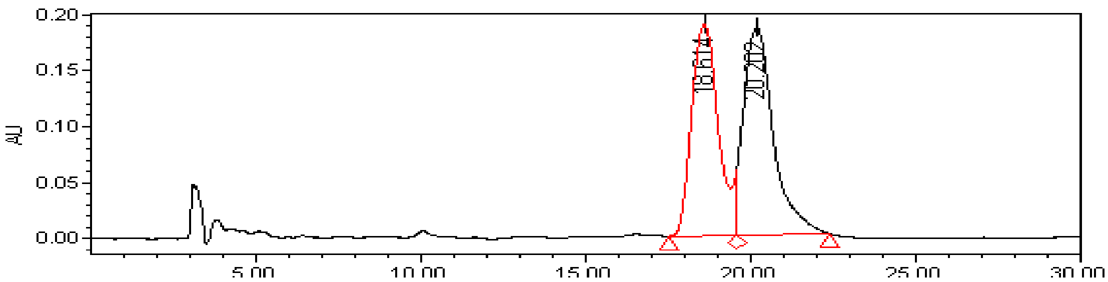
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	18.825	12817440	49.66	111092
2	210	21.101	12994209	50.34	333222



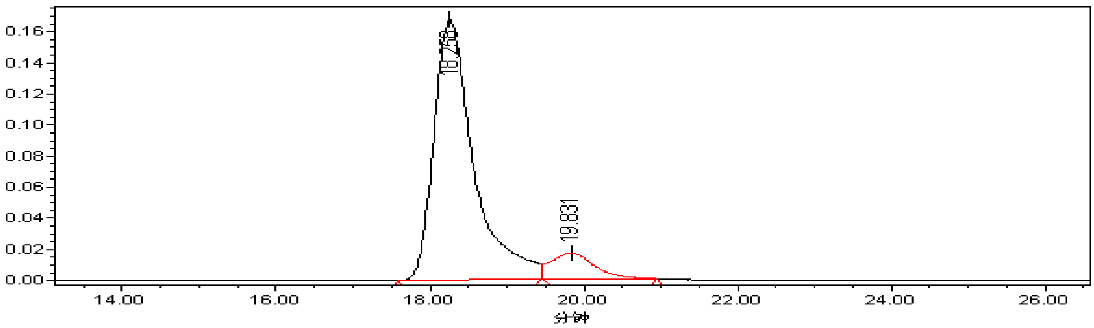
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	18.488	4801350	87.05	183618
2	210	20.464	714078	12.95	25252



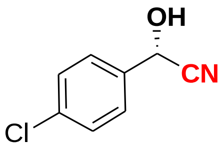
3d
96% yield
80% *ee*



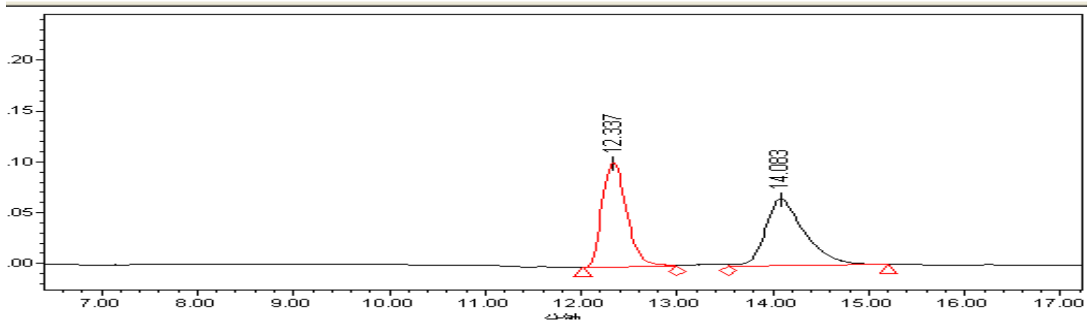
	Processed Chanel Descr	RT	Area	%Area	Height
1	210	18.614	10711425	48.10	188181
2	210	20.202	11559311	51.90	184655



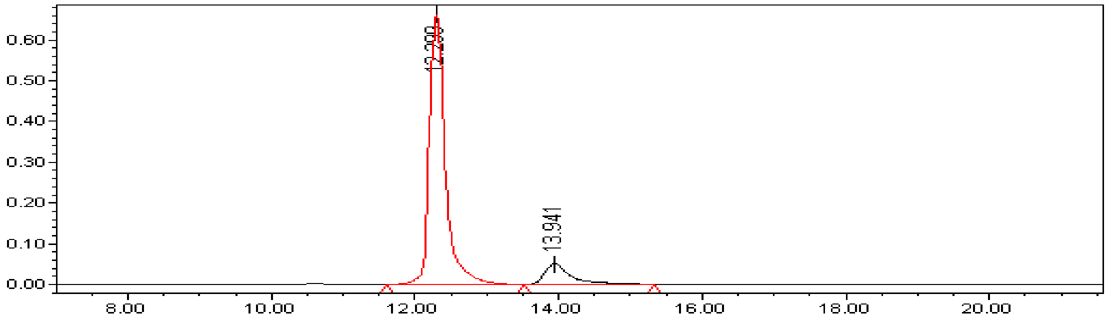
	Processed Chanel Descr	RT	Area	%Area	Height
1	210	18.258	6040570	90.04	167714
2	210	19.831	668192	9.96	17051



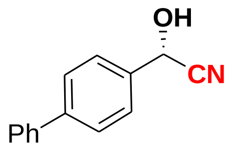
3e
72% yield
78% *ee*



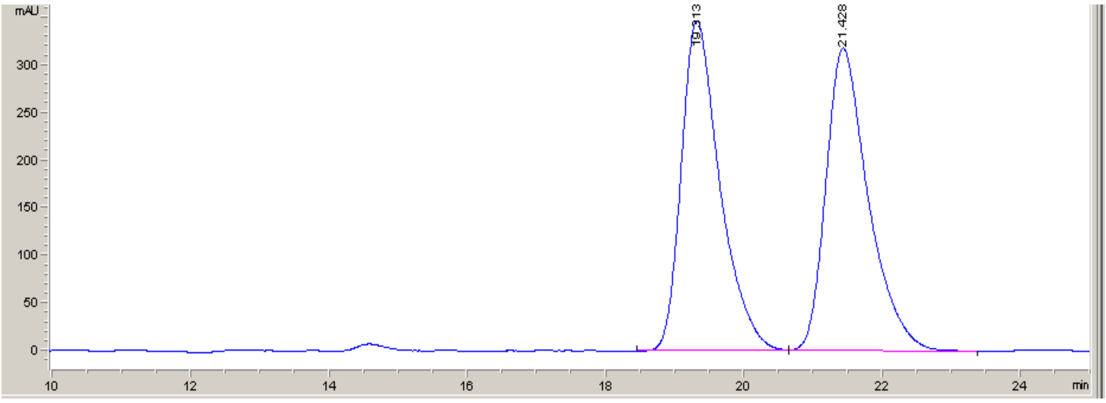
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	12.337	1848249	49.94	102496
2	210	14.083	1852516	50.06	65181



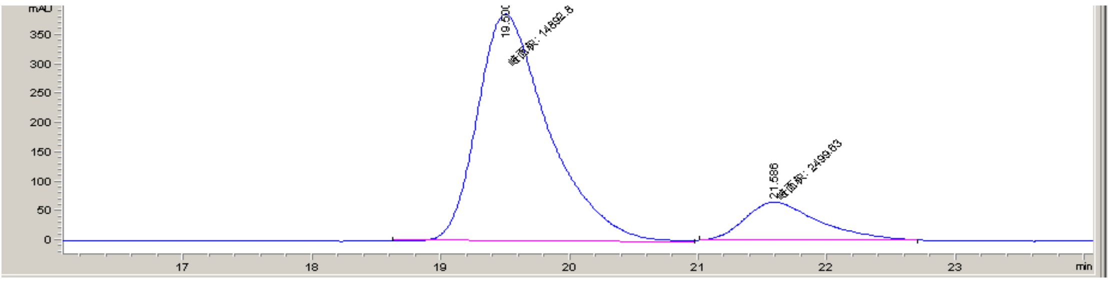
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	12.299	10240711	88.93	661342
2	210	13.941	1288333	11.07	49857



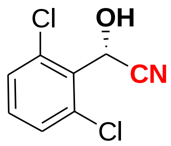
3f
71% yield
71% *ee*



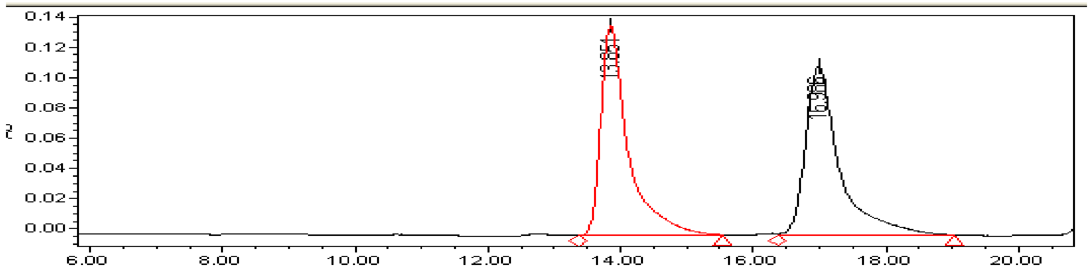
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	19.313	135101	49.782	347
2	210	21428	136285	50.218	318.3



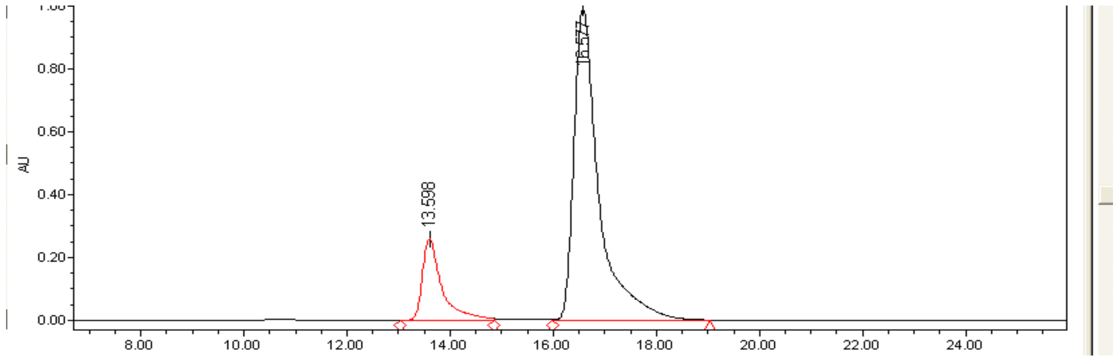
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	19.5	14892.8	85.6283	386.9
2	210	21.586	2499.6	14.377	63.5



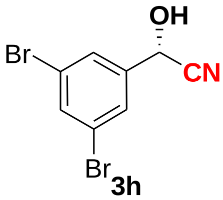
3g
94% yield
66% *ee*



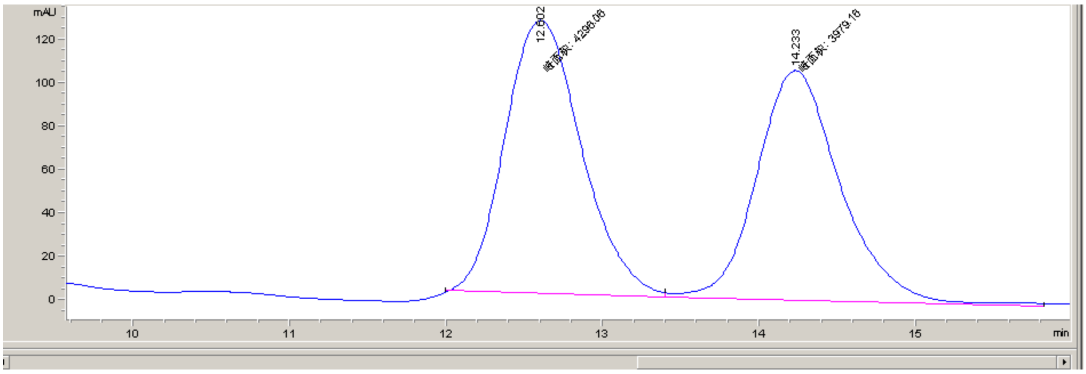
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	13.851	14892.8	85.6283	386.9
2	210	16.986	2499.6	14.377	63.5



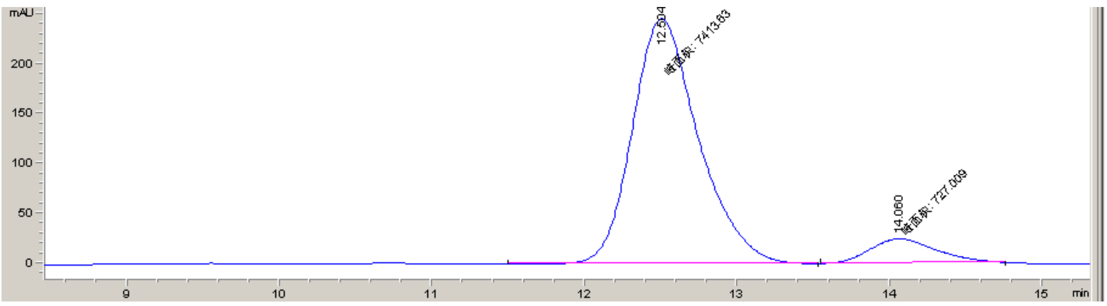
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	13.598	6782412	16..97	258624
2	210	16.577	33181786	83.03	990106



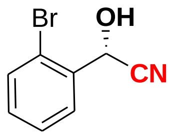
3h
81% yield
82% *ee*



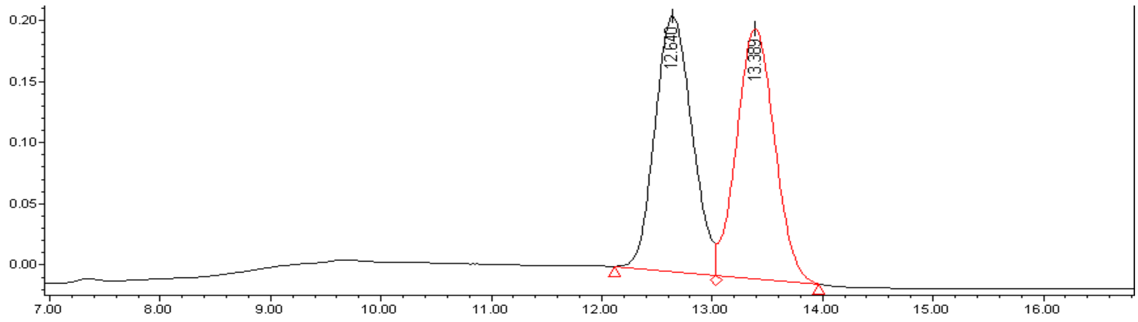
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	12.602	4296.1	51.915	125.9
2	210	14.233	3979.2	48.085	105.9



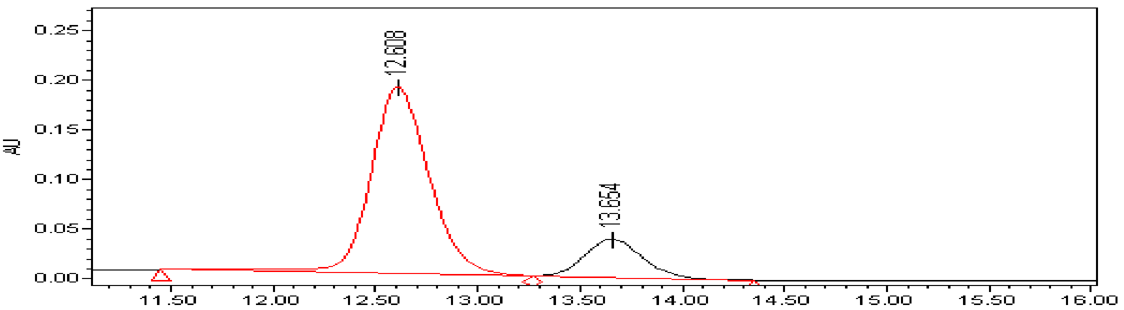
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	12.504	7413.6	91.069	145.8
2	210	14.06	2499.6727	8.931	24.2



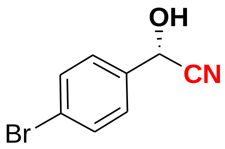
3i
81% yield
67% *ee*



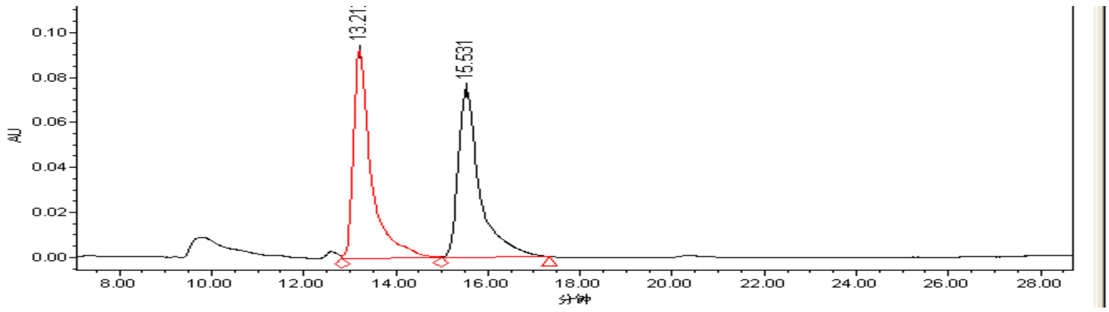
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	12.640	4860600	50.06	208562
2	210	13.389	4849388	49.94	204079



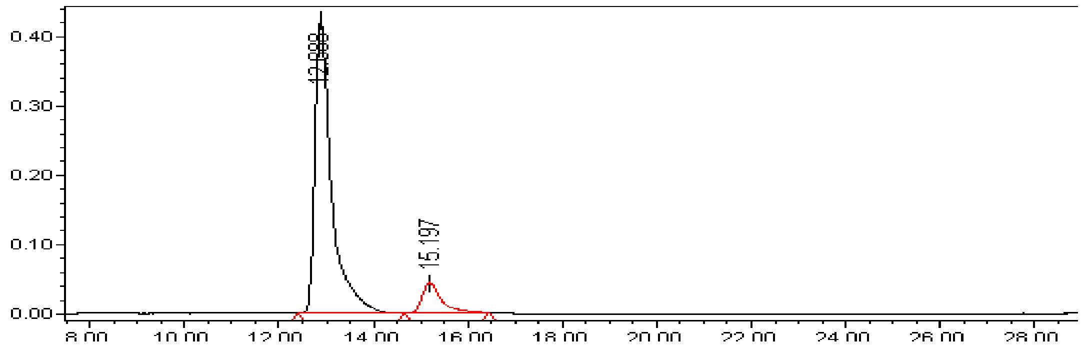
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	12.608	3756088	83.46	188310
2	210	13.664	759342	16.54	18697



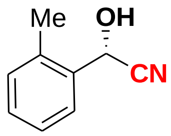
3j
72% yield
78% *ee*



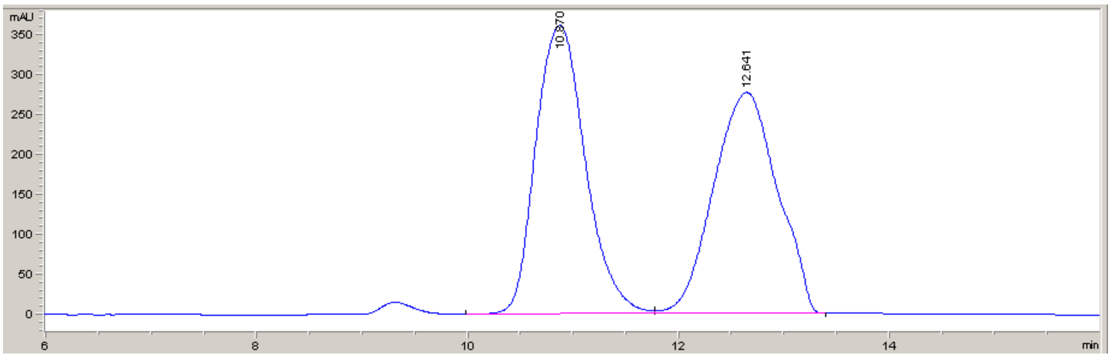
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	13.212	2496844	50.73	92279
2	210	15.531	2424717	49.27	74772



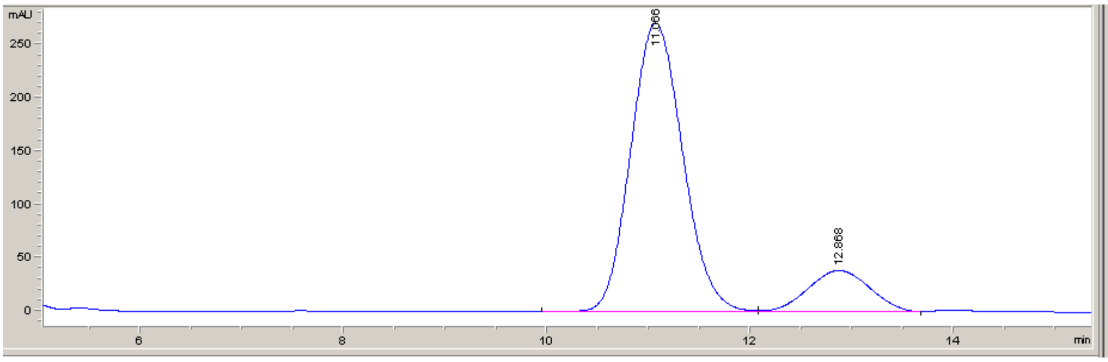
	Processed Chanel Descr	RT	Area	%Area	Height
1	210	12.888	10287943	89.11	188310
2	210	15.197	1257478	10.89	18697



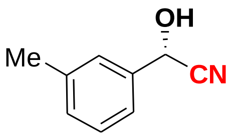
3k
71% yield
71% *ee*



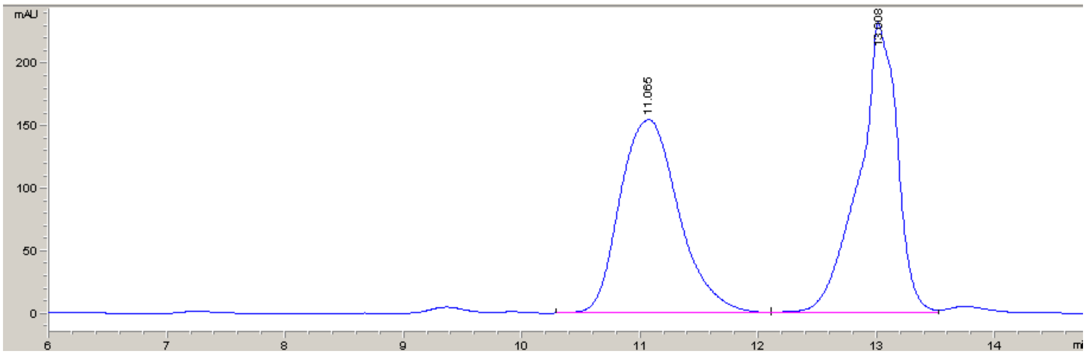
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	10.87	11849.3	50.352	361.3
2	210	12.641	11683.4	49.648	276.8



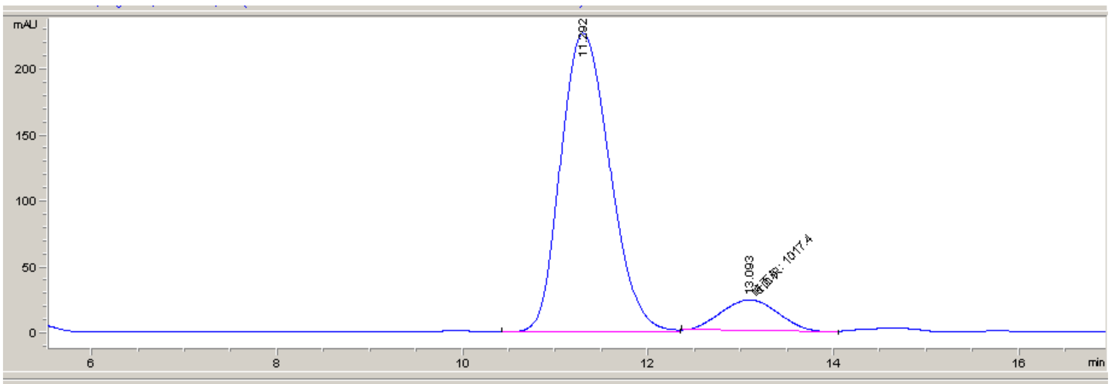
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	11.066	9639.2	85.536	271.2
2	210	12.868	1629.9	14.464	38.7



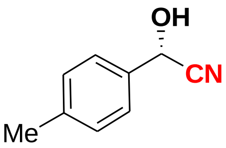
3l
71% yield
78% *ee*



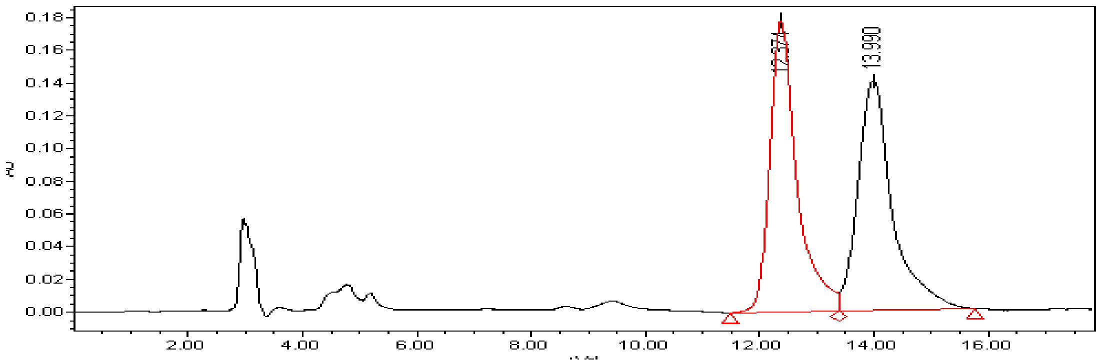
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	11.065	5347.3	50.431	154.5
2	210	13.008	5255.9	49.569	231.9



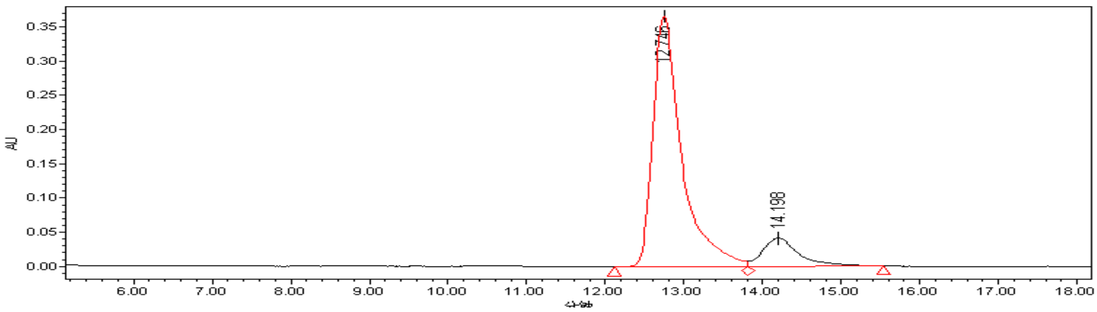
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	11.292	8357.2	89.147	22.5
2	210	13.093	1017.4	10.853	23.7



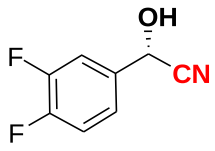
3m
72% yield
75% *ee*



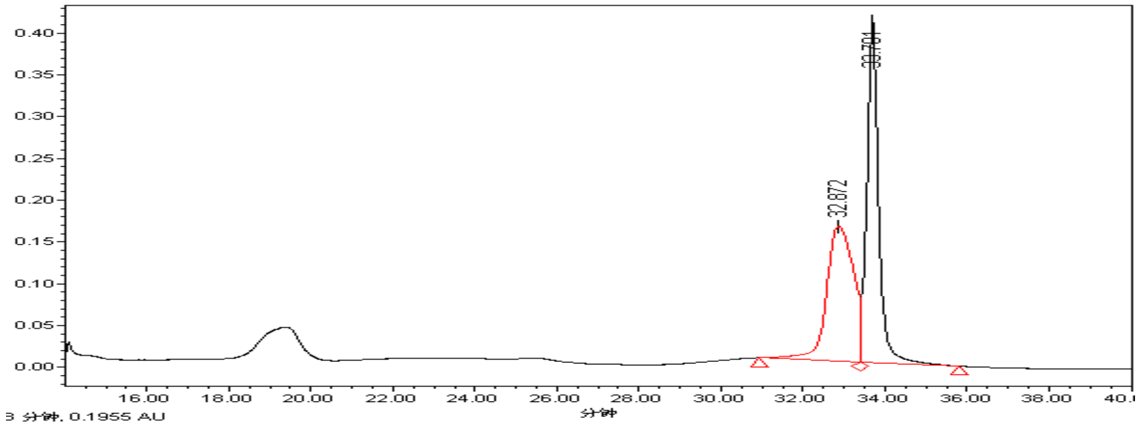
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	12.374	5891259	49.89	177881
2	210	13.990	59.16406	50.11	140500



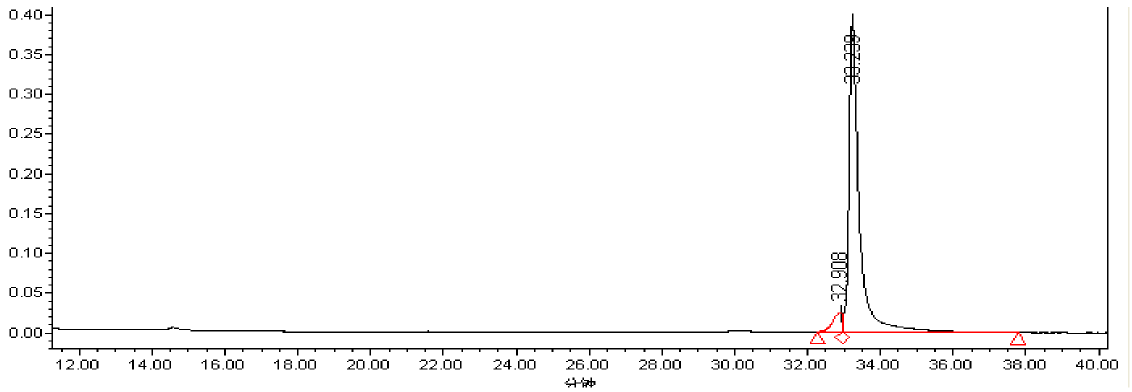
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	12. 746	9333394	87.56	365714
2	210	14.196	1326161	12.44	41386



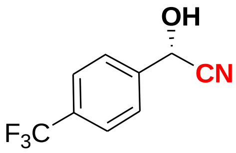
3n
84% yield
90% *ee*



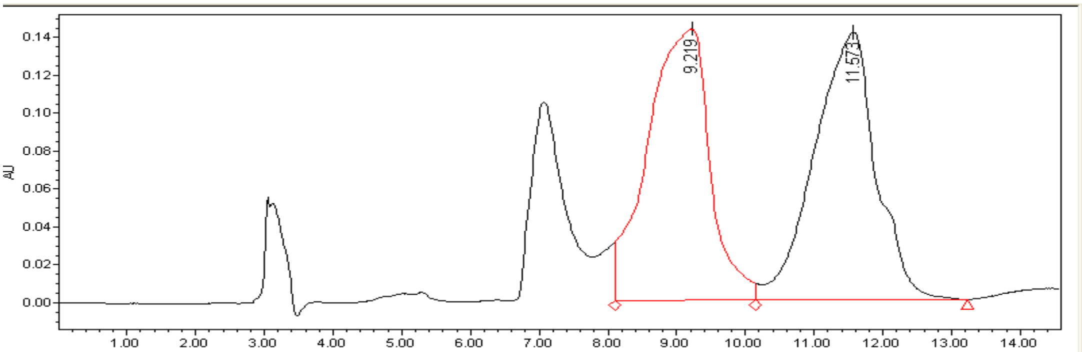
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	32.872	7338301	47.19	161882
2	210	33.701	8212877	52.81	400403



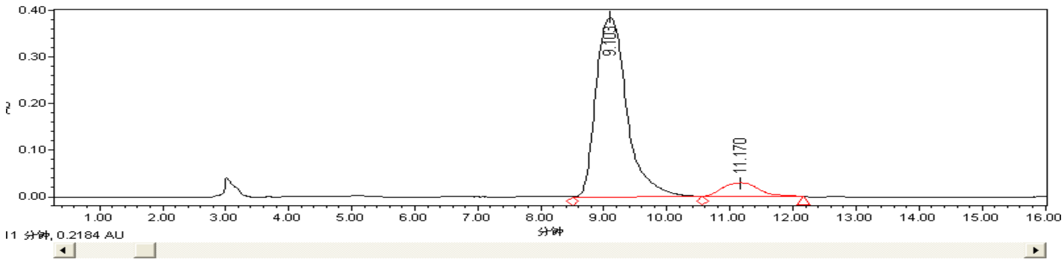
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	32.908	410138	5.10	23967
2	210	33.239	7627099	94.90	390290



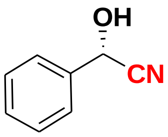
3o
83% yield
83% *ee*



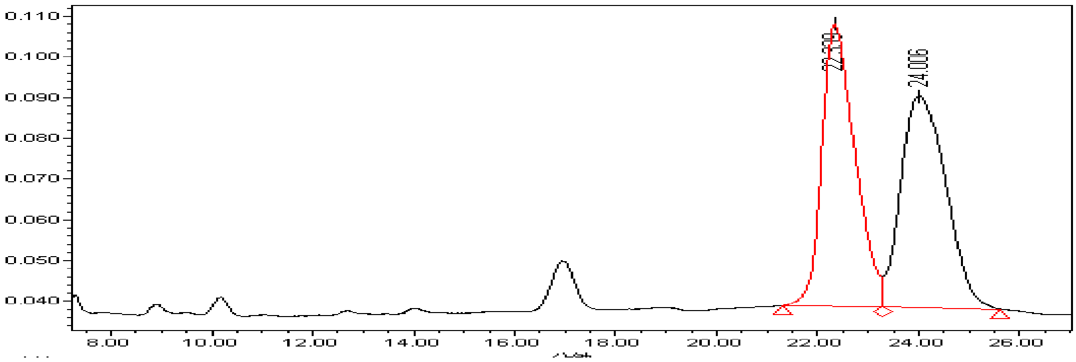
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	9.219	9025977	50.65	143163
2	210	11.573	8792871	49.35	141162



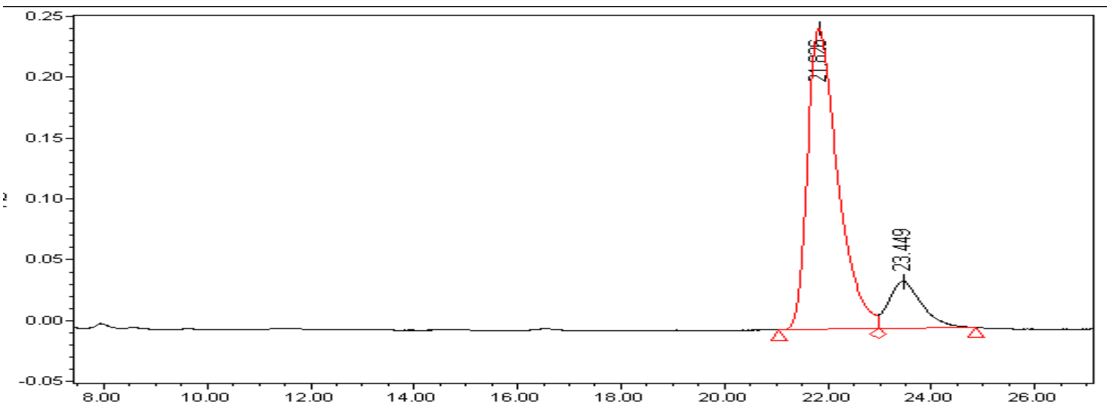
	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	9.103	12501667	91.44	384811
2	210	11.170	1226349	8.56	29639



3p
65% yield
71% *ee*



	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	22.339	3160665	49.3	59240
2	210	24.006	3250749	50.70	52047



	Processed Chanel Descr	Time/min	Area	%Area	Height
1	210	21.826	10000777	85.41	247014
2	210	23.449	1721857	14.59	38682