Betti's base for crystallization-induced diastereoisomer transformations: deracemization of α-substituted 4-*p*-methoxybenzyl-butyrraldehydes and synthesis of enantiopure primary amines. Synthesis of enantiopure Amorolfine and Fenpropimorph.

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Electronic Supporting Information

Content

Ethyl 4-((4-metoxybenzyl)oxy)butanoate, 2. The ethyl 4-hydroxybutanoate[1] was protected using 4-methoxybenzyl trichloroacetimidate[2] as described by Jacobsen[3] to give, after distillation at 121-123 °C /0.2 mm, 17.4 g (86 %) of protected ester **2**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (m, 2H), 6.87 (m, 2H), 4.42 (s, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.47 (t, *J* = 6.2 Hz, 2H), 2.40 (t, *J* = 7.4 Hz, 2H), 1.92 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 159.1, 130.4, 129.2, 113.7, 72.5, 68.9, 60.2, 55.2, 31.1, 25.1, 14.2; IR (film) cm^{-1}: 2936.2, 2859.3, 1733.4, 1614.33, 1514.3, 1248.4, 1175.1, 1100.9, 1034.9, 820.7.

Alkylation of Ethyl 4-((4-metoxybenzyl)oxy)butanoate: preparation of 3a-f. The reactions were conducted in oven-dried glassware and under nitrogen. To a cooled 1M LDA at -75 °C (1.1 eq, freshly prepared from diisopropylamine dissolved in dry THF and *n*-BuLi 2.5 M in hexane) the ester (1 eq) in dry THF (0.25 mL/mmol) was added in 20 min. The reaction was stirred at -75 °C for 40 min then alkylbromide[4] (1,5 eq) in dry HMPA (80 µL/mmol) was added. The reaction was stirred at -75 °C for 40 min then at -40 °C for two hours (the reaction was monitored by TLC), and quenched with saturated aqueous ammonium chloride solution. The reaction was left to warm at room temperature and the organic solvent evaporated under vacuum. The residue was partitioned between Et_2O and water. The organic layer was separated, washed with water, 1N HCl, water, brine, dried on $MgSO_4$ and the solvent distilled under reduced pressure.

Ethyl 2-benzyl-4-((4-methoxybenzyl)oxy)butanoate, 3a. From the crude **3a** was isolated by bulb to bulb distillation, as a colorless oil, with 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.13 (m, 7H), 6.86 (m, 2H), 4.37 (s, 2H), 4.00 (m, 2H), 3.78 (s, 3H), 3.50-3.39 (m, 2H), 2.39 (dd, *J* = 12.4 and 7.6 Hz, 1H), 2.87-2.73 (m, 2H), 1.97 (m, 1H), 1.78 (m, 1H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.3, 159.1, 139.1, 130.4, 129.2, 128.9, 128.2, 126.3, 113.6, 72.5, 67.7, 60.1, 55.2, 44.5, 38.5, 31.8, 14.0; IR (film) cm^{-1}: 2935.6, 2660.2, 1730.8, 1613.7, 1514.3, 1248.7, 1174.0, 1098.5, 1034.1, 820.3, 745.33, 700.95.

Ethyl 2-(4-fluorobenzyl)-4-((4-methoxybenzyl)oxy)butanoate, 3b. From the crude **3b** was purified by flash chromatography on silica, as a colorless oil, with 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (m, 2H), 7.10 (m, 2H), 6.94 (m, 2H), 6.86 (m, 2H), 4.38 (s, 2H), 4.00 (dq, *J* = 7.1 and 1.6 Hz, 2H), 3.79 (s, 3H), 3.50-3.39 (m, 2H), 2.91-2.71 (m, 3H), 1.96 (m, 1H), 1.77 (m, 1H), 1.10 (t, *J* = 7.1, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.1, 161.5 (d, *J* = 244.3Hz), 159.1, 134.76 (d, *J* = 3.2Hz), 130.33 (d, *J* = 7.3 Hz), 129.2, 115.0 (d, *J* = 21 Hz), 113.7, 72.6, 67.6, 60.2, 55.2, 44.7, 37.7, 31.9, 14.2; IR (film) cm^{-1}: 2954.2, 2936.4, 2861.0, 1730.6, 1612.9, 1511.7, 1248.8, 1222.3, 1175.0, 1159.4, 1098.4, 1035.1, 823.1.

Ethyl 2-(2-((4-methoxybenzyl)oxy)ethyl)pent-4-enoate, 3c. From the crude **3c** was purified by flash chromatography on silica, as a colorless oil, with 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (m, 2H), 6.87 (m, 2H), 5.73 (m, 1H), 5.08-4.99 (m, 2H), 4.40 (m, 2H), 4.10 (m, 2H), 3.80 (s, 3H), 3.50-3.40 (m, 2H), 2.62 (m, 1H), 2.41-2.31 (m, 1H), 2.29-2.22 (m, 1H), 1.99-1.90 (m, 1H), 1.81-1.72 (m, 1H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.1, 159.0, 135.1, 130.4, 129.1, 116.7, 113.6, 72.4, 67.5, 60.0, 55.1, 42.1, 36.4, 31.5, 14.1. IR (film) cm^{-1}: 2954.2, 2934.5, 2859.3, 1730.8, 1613.3, 1518.9, 1249.1, 1178.0, 1096.7, 1035.9, 819.6.

Ethyl (*E*)-2-(2-((4-methoxybenzyl)oxy)ethyl)-5-phenylpent-4-enoate, 3d. From the crude **3d** was purified by flash chromatography on silica, as a light yellow oil, with 76% of yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.22 (m, 6H), 7.22-7.16 (m, 1H), 6.86 (m, 2H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.13 (dt, *J* = 15.8 and 7.2 Hz, 1H), 4.41 (s, 2H), 4.09 (m, 2H), 3,79 (s, 3H), 3.53-3.42 (m, 2H), 2.70 (m, 1H), 2.55-2.47 (m, 1H), 2.44-2.36 (m, 1H), 2.05-1.94 (m, 1H), 1.86-1.77 (m, 1H), 1.20 (t, *J* = 7.2 Hz 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.3, 159.1, 137.3, 132.1, 130.5, 129.2, 128.5, 127.1, 127.0, 126.1, 113.7, 72.6, 67.7, 60.3, 55.3, 42.6, 35.8, 31.7, 14.3; IR (film) cm^{-1}: 2935.5, 2858.7, 1730.3, 1613.2, 1513.7, 1248.4, 1174.3, 1098.4, 1035.0, 967.7, 820.9, 744.1, 694.3.

Ethyl 4-((4-methoxybenzyl)oxy)-2-(pyridin-3-ylmethyl)butanoate, 3e. From the crude **3e** was purified by flash chromatography on silica, as a light yellow oil, with 37% yield. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.45 (dd, *J* = 4.7 and 1.6 Hz, 1H), 8.43 (d, *J* = 2 Hz, 1H), 7.48 (m, 1H), 7.27-7.17 (m, 3H), 6.87 (m, 2H), 4.40 (s, 2H), 4.01 (m, 2H), 3.79 (m, 3H), 3.52-3.41 (m, 2H), 2.94-2.76 (m, 3H), 2.00 (m, 1H), 1.80 (m, 1H), 1.10 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 174.7, 159.1, 150.2, 147.8, 136.4, 134.5, 130.3, 129.2, 123.2, 113.7, 72.6, 67.4, 60.3, 55.2, 44.2, 35.5, 32.0, 14.0; IR (film) cm^{-1}: 2936.2, 2862.0, 1729.1, 1613.4, 1514.2, 1248.6, 1181.3, 1100.9, 1032.3, 821.9, 715.8.

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4 Thiophene **3f** was obtained from 2-(chloromethyl)thiophene prepared as described by T.-H. Fu, W. T. McElroy, M. Shamszad, R. W. Heidebrecht, Jr., B. Gulledge, S. F. Martin *Tetrahedron*, 2013, **69**, 5588-5603

Ethyl 4-((4-methoxybenzyl)oxy)-2-(thiophen-2-ylmethyl) butanoate, 3f. From the crude **3f** was purified by flash chromatography on silica, as a light yellow oil, with 38% yield. ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.24 (m,2H), 7.11 (dd, *J* = 5.3 and 1.2 Hz, 1H), 6.89 (dd, *J* = 5.0 and 3.4 Hz, 1H), 6.87 (m, 2H), 6.78 (m, 1H), 4.39 (s, 2H), 4.06 (m, 2H),3.79 (s, 3H), 3.51-3.43 (m, 2H), 3.16 (dd, *J* = 14.8 and 8.4Hz, 1H), 3.00 (dd, *J* = 14.8 and 6.3 Hz, 1H), 2.85 (m, 1H), 1.98 (m, 1H), 1.83 (m,1H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 174.9, 159.1, 141.4, 130.4, 129.2, 126.7, 125.63, 123.7, 113.7, 72.6, 67.6, 60.4, 55.2, 44.9, 32.3, 31.7, 14.1.

Reduction of esters 3a-c,e,f to aldehydes 4a-c,e,f with DIBAL: general procedure. The reactions were conducted in oven-dried glassware and under nitrogen. Ester (1 eq) was dissolved in CH_2Cl_2 (3 mL, mmol^{-1}) and cooled at -70 °C. DIBAL-H (1M in CH_2Cl_2, 1.1 eq) was added in 60-80 min. The reaction was stirred at -70 °C until complete ester consumption, monitored by TLC. The reaction was quenched by MeOH (0.4 mL/mmol of hydride) addition at -70 °C and left to warm at room temperature. The reaction mixture was poured over an ice cooled 1N water solution of HCl (6.7 mL mmol^{-1} of hydride), and stirred for 60 min. The aqueous phase was separated and extracted with Et_2O, the combined organic phases were washed with water, brine and dried on Na_2SO_4. After solvent evaporation, the crude was flash chromatographed on a column of silica gel.

2-Benzyl-4-((4-methoxybenzyl)oxy)butanal, 4a. It was isolated with 58% yield, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.68 (d, *J* = 2.2 Hz, 1H), 7.30-7.12 (m, 7H), 6.87 (m, 2H), 4.36 (s, 2H), 3.79 (s, 3H), 3.45 (m, 2H), 3.00 (dd, *J* = 13.4 and 6.5 Hz, 1H), 2.77 (m, 1H), 2.70 (dd, *J* = 13.4 and 7.5 Hz, 1H), 1.95 (m, 1H), 1.82-1.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.1, 159.2, 138.6, 130.2, 129.3, 129.0, 128.5, 126.4, 113.8, 72.3, 67.2, 55.2, 50.8, 34.9, 29.0; IR (film) cm^{-1}: 2934.3, 2858.8, 2710.1, 1722.9, 1613.6, 1514.4, 1248.2, 1174.3, 1099.1, 1033.8, 820.3, 745.5, 701.0.

2-(4-Fluorobenzyl)-4-((4-methoxybenzyl)oxy)butanal, 4b. It was isolated with 82% yield, as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.67(d, *J* = 2.0 Hz, 1H), 7.21 (m, 2H), 7.09 (m, 2H), 6.95 (m, 2H), 6.87 (m, 2H), 4.37 (s, 2H), 3.80 (s, 3H), 3.46 (m, 2H), 2.97 (dd, *J* = 13.8 and 7.1 Hz, 1H), 2.74 (m, 1H), 2.67 (dd, J = 13.8 and 7.3 Hz, 1H), 1.94 (m, 1H), 1.76 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 203.8, 162.3, 160.7, 159.2, 134.34, 134.32, 130.40, 130.37, 130.1, 129.3, 115.4, 115.2, 113.8, 72.7, 67.1, 55.2, 50.9, 34.0, 29.0; IR (film) cm^{-1}: 2935.4, 2860.4, 2723.9, 1723.6, 1612.3, 1511.8, 1248.6, 1221.9, 1099.8, 1034.9, 822.5, 758.2.

2-(2-((4-Methoxybenzyl)oxy)ethyl)pent-4-enal, 4c. It was isolated with 83% yield, as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.64 (d, *J* = 2.2 Hz, 1H), 7.22 (m, 2H), 6.87 (m, 2H), 5.73 (m, 1H), 5.09-5.03 (m, 2H), 4.39 (s, 2H), 3.80 (s, 3H), 3.48 (m, 2H), 2.53 (m, 1H), 2.41 (m, 1H), 2.22 (m, 1H), 1.97 (m, 1H), 1.78 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.1, 159.2, 134.8, 130.2, 129.2, 117.3, 113.7, 72.6, 67.1, 55.2, 48.6, 34.9, 28.7; IR (film) cm^{-1}: 2963.0, 2913.6, 2850.6, 1723.1, 1612.9, 1513.4, 1259.6, 1094.0 1033.1, 800.1.

4-((4-Methoxybenzyl)oxy)-2-(pyridin-3-ylmethyl)butanal, 4e. It was isolated with 77% yield, as a light yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.69 (d, *J* = 2.0 Hz, 1H), 8.45 (dd, *J* = 7.4 and 1.4 Hz, 1H), 8.42 (d, *J* = 2 Hz, 1H), 7.47 (m, 1H), 7.23-7.18 (m, 3H), 6.88 (m, 2H), 4.38 (s, 2H), 3.79 (s, 3H), 3.52-3.43 (m, 2H), 3.01 (dd, *J* = 14.3 and 7.2 Hz, 1H), 2.78 (m, 1H), 2.68 (dd, *J* = 14.3 and 7.1 Hz, 1H), 1.95 (m, 1H), 1.80 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 203.1, 159.2, 150.2, 147.8, 136.4, 134.3, 129.9, 129.2, 123.3, 113.7, 72.6, 66.7, 55.2, 50.4, 31.5, 28.9. IR (film) cm^{-1}: 2922.5, 2859.5, 1722.4, 1612.7, 1513.7, 1247.9, 1098.2, 1030.6, 820.2, 715.1.

4-((4-Methoxybenzyl)oxy)-2-(thiophen-2-ylmethyl)butanal, 4f. The crude was flash chromatographed to give **4f** with 65% yield, as a light yellow oil and the corresponding alcohol **6f** with 27% yield; ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 9.70 (d, *J* = 1.9 Hz, 1H), 7.13 (dd, *J* = 5.3 and 1.2 Hz, 1H), 7.22 (m, 2H), 6.9 (dd, *J* = 5.3 and 3.5 Hz, 1H), 6.87 (m, 2H), 6.67 (m, 1H), 4.39 (s, 2H), 3.80 (s, 3H), 3.49 (m, 2H), 3.31 (dd, *J* = 15.2 and 7.0 Hz, 1H), 2.97 (dd, *J* = 15.2 and 7.0 Hz, 1H), 2.79 (m, 1H), 1.99 (m, 1H), 1.85 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 203.5, 159.2, 141.0, 130.1, 129.2, 126.8, 125.7, 123.9, 113.7, 72.6, 66.9, 55.2, 50.9, 28.8, 28.6.

(*E*)-2-(2-((4-Methoxybenzyl)oxy)ethyl)-5-phenylpent-4-enal, 4d. To a $LiAlH_4$ suspension (0.270 g, 7.0 mmol) in dry THF (40 mL), a solution of **3d** (2.35 g, 7.0 mmol) in dry THF (70 mL) was added dropwise and under N_2. The reaction mixture was first stirred at room temperature for 0.5 hour, then at 70 °C. After 2 h the reaction was cooled at –10 °C and the hydride excess quenched with saturated aqueous solution of NH_4Cl (1.5 mL). Warmed to room temperature, the reaction mixture was stirred until a gray solid material was separated from the organic phase. After filtration on büchner, the solid material was washed three times with CH_2Cl_2. The organic phase was dried on $MgSO_4$, and after solvent evaporation the residue was bulb to bulb distilled to give **6d** (2.05 g, 90%) as a colorless oil. A round bottomed flask was charged with CH_2Cl_2 (2,8 mL), PIPO (0.059 g, 1.5 mol%), alcohol **6d** (2.046 g, 6.2 mmol) and KBr (0.074 g, 0.62 mmol) dissolved in water (1.5 mL). The resulting suspension was stirred vigorously and cooled to 0 °C. A 10.5% solution of NaClO (5.18 mL, 7.26 mmol, at pH=9.5 obtained by addition of saturated aqueous solution of $NaHCO_3$ to commercial available bleach) was added dropwise in about 60 min, keeping the temperature below 5 °C. The reaction was followed

by TLC and after one hour, the reaction was quenched with 10% ascorbic acid (5 mL) and filtered to remove the solid material. Filtrate was extracted with Et_2O (3 x 15 mL) and the combined organic phases were dried on Na_2SO_4. After solvent evaporation the crude was flash chromatographed, and bulb to bulb distilled to give 1.61 g (80%) of aldehyde **4d**, as light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.69 (d, *J* = 1.8 Hz, 1H), 7.33- 7.18 (m, 7H), 6.89- 6.85 (m, 2H), 6.41 (d, *J* = 15.9 Hz, 1H), 6.12 (m, 1H), 4.40 (s, 2H), 3.80 (s, 3H), 3.54-3.47 (m, 2H), 2.66-2.53 (m, 2H), 2.43-2.34 (m, 1H), 2.07-1.97 (m, 1H), 1.88-1.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.1, 159.2, 137.1, 132.5, 130.2, 129.3, 128.5, 127.3, 126.5, 126.1, 113.8, 72.7, 67.1, 55.2, 49.1, 32.2, 28.8; IR (film) cm^{-1}: 3025.8, 2929.9, 2858.6, 1721.9, 1612.2, 1512.6, 1248.3, 1094.3, 1034.5, 968.4, 819.8, 744.0, 694.0.

(*R*)-2-Benzylbutan-1,4-diol, (*R*)-7a. To a well stirred solution of monoprotected diol (*R*)-**6a** (588 mg, 1.95mmol) in CH_2Cl_2-H_2O 20:1 (4.0 mL), cooled at -5 °C, DDQ (421 mg, 1.95 mmol) was added in 8 portions (15 min). The reaction was left to warm at rt and after 1 hour filtered on celite and washed with CH_2Cl_2 (3 x 5 mL). The combined organic solutions were washed with saturated aqueous solution of $NaHCO_3$ then dried on Na_2SO_4. After solvent evaporation and flash-chromatography, diol (*R*)-**7a**, 0.425 mg (73%) was obtained as a colorless oil; $[\alpha]_D^{24}$ +2.7 (c 1.8, EtOAc), [Lit.[5] $[\alpha]_D^{24}$ +6.6 (c 1.5, EtOAc)]; ^{1}H and ^{13}C NMR were identical to those previously reported.5

(*R*)-2-Allylbutane-1,4-diol, (*R*)-7c. The *O*-deprotection of the diol **(*R*)-6c** (380 mg, 1.52 mmol) was carried out as before on (*R*)-**6a**. After solvent evaporation and flash-chromatography, (*R*)-**7c**, 142 mg (72%), was obtained as a colorless oil; $[\alpha]_D^{26}$ –4.1 (c 1.46, MeOH); ^{1}H NMR (400 MHz): δ 5.77 (m, 1H); 5.07-5.01 (m, 2H), 3.80 (bs, 2H); 3.75 (m, 1H); 3.66-3.59 (m, 2H); 3.45 (dd, *J*=10.8 e 7.1 Hz, 1H); 2.07 (m, 2H); 1.79-1.65 (m, 2H); 1.62-1.52 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 136.5; 116.4; 65.7; 60.8; 39.9; 36.3; 35.2; IR (film) cm^{-1}: 3386.8; 2923.5; 1639.2; 1441.1; 1034.9; 912.5; 799.0.

(*R*)-2-Propylbutane-1,4-diol, (*R*)-8c. A suspension of PtO_2[6] (3 mg) in MeOH (5 mL) was prehydrogenated in a Parr hydrogenator under 15 psi of H_2 for 30 min before the addition of unsaturated diol **(*R*)-7c** (65 mg, 0.499 mmol). The suspension was shaken under 7 psi of H_2 for 1 hour. After filtration through Celite and solvent evaporation 65 mg (98%) of saturated diol **(*R*)-8c** were obtained; $[\alpha]_D^{26}$ - 3.3 (c 1.25, MeOH) [lit.[7] $[\alpha]_D^{20}$ –10.2 (c 1.0, MeOH)]; ^{1}H and ^{13}C NMR were identical to those previously reported.7

***tert*-Butyl (*R*)-(3-(benzo[*d*][1,3]dioxol-5-yl)-2-methylpropyl) carbamate, (–)-14a**. NaOH 2M aq. (3.3 mL, 6.6 mmol) was added dropwise to a suspension of (*R*)-[**12a**·HCl] (344 mg, 1.5 mmol) in *t*-BuOH (2.0 mL). The reaction was stirred at rt and followed by TLC. After 1 hour, a small amount (0.5 mL) of reaction mixture was taken to isolate and characterize the amine (*R*)-**12a**,[8] then dissolved in *t*-BuOH (0.5 mL) and added to the reaction mixture. A di-*tert*-butyl dicarbonate (445 mg, 2.0 mmol) solution in *t*-BuOH (0.7 mL) was then added in 45 min. The reaction was monitored by TLC and after 6 hours, the aqueous phase was separated with 20 mL of Et_2O in a separating funnel. The organic phase was dried on Na_2SO_4 and the crude product purified by flash chromatography to give 396 mg (90%) of (–)-**14a** with dr = 97.4:2.6, determinate by HPLC analysis using a Phenomenex® Lux Amylose-2, *n*-hexane/*i*-PrOH = 90:10, 1 mL min^{-1}, λ = 230 nm, 25 °C, minor isomer tr = 9.2 min and major isomer tr = 10.9 min; $[\alpha]_D^{20}$ –9.4 (c 0.84, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 6.72(d, *J* = 7.7 Hz, 1H), 6.64 (d, *J* = 1.0 Hz, 1H), 6.59 (d, *J* = 7.7 and 1.0 Hz, 1H), 5.92 (s, 2H), 4.55 (bs, 1H), 3.08 (m,1H), 2.97 (m, 1H), 2.60 (d, *J* = 13.5 and 5.8 Hz, 1H), 2.30 (d, *J* = 13.5 and 8.5 Hz, 1H), 1.85 (m, 1H), 1.44 (s, 9H), 0.86 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 156.0, 147.5, 145.7, 134.2, 121.8, 109.3, 108.0, 100.7, 79.0, 46.2, 40.6, 35.9, 28.4, 17.3.

(*R*)-3-(Benzo[d][1,3]dioxol-5-yl)-*N*,2-dimethylpropane-1-amine hydrochloride, (–)-15a. To a solution of (–)-**14a** (433 mg, 1.48 mmol) in THF (2 mL), cooled with an ice bath, 60% NaH in mineral oil (71 mg, 1.78 mmol) was added. After 30 min to the cooled reaction methyl iodide was added (0.14 mL, 2.29 mmol), and stirred at rt for 3 hrs. The reaction was quenched, at 0 °C, with saturated aqueous NH_4Cl. The organic solvent was removed and the crude extracted with Et_2O. The ethereal solution was washed with water, brine and dried on Na_2SO_4. After solvent evaporation, the crude was dissolved in CH_2Cl_2, cooled at 0 °C and CF_3COOH (1 mL) was added. The reaction mixture was stirred at rt for one hour

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6 With Pd(0) on carbon also (*Z*,*E*)-2-(prop-1-en-1-yl)butane-1,4-diol, along with **8c**, was isolated

7 N. Lee, Y.-W. Kim, Y. Chang, H. K. Kim, S. S. Jew, D.-K. Kim, *Tetrahedron Lett.*, 1996, **37**, 2429-2432

8 The amine (*R*)-(–)-**12a** was extracted with Et_2O, and after solvent evaporation the crude was filtered through plug of silica gel, washing with 10% Et_2O in hexanes then the amine recovered with 3% of NH_4OH_{con} in CH_2Cl_2-MeOH=4:1; (*R*)-(–)-**12a** was isolated as light yellow liquid material; $[\alpha]_D^{22}$-5.0 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 6.72 (d, *J* = 7.8 Hz, 1H), 6.65 (s, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 5.91 (s, 2H), 2.94 (bs, 2H), 2.68 (dd, *J* = 12.7 and 5.6 Hz, 1H), 2.60 (dd, *J* = 13.6 and 6.2 Hz, 1H), 2.52 (dd, *J* = 12.7 and 7.1 Hz, 1H), 2.31 (dd, *J* = 13.6 and 8.2 Hz, 1H), 1.78 (m, 1H), 0.89 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 147.4, 145.6, 134.2, 121.7, 109.2, 107.9, 100.6, 47.1, 40.5, 37.6, 17.1.

and then concentrated. Saturated aqueous $NaHCO_3$ (3 mL) was added to the residue under stirring. A progressive color change was observed, which ceased after two hours. The product was extracted with $CHCl_3$ (3 x 2 mL) and the organic phase washed with brine-H_2O 1:1 (2 mL), brine (1 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the residue dissolved in anhydrous Et_2O (3 mL) and HCl 2M in Et_2O (1.5 mL) added. The resulting suspension was stirred for 45 min, then it was filtrated. The solid was washed with anhydrous Et_2O and dried under reduced pressure to give 285 mg (79%) of (*R*)-**15a**. Crystallized from CH_3CN, mp = 145-148 °C; $[\alpha]_D^{22}$ –1.8 (c 1.4, MeOH); ^{1}H NMR (600 MHz, CD_3OD): *δ* 6.74 (d, *J* = 7.8 Hz, 1H), 6.73 (bs, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 5.90 (s, 2H), 2.95 (m,1H), 2.86 (m, 1H), 2.70 (s, 3H), 2.68 (m, 1H), 2.42 (dd, *J* = 13.4 and 8.4 Hz, 1H), 2.13 (m, 1H), 0.99 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD): *δ* 150.1, 148.5, 134.9, 124.1, 111.1, 110.0, 103.1, 56.9, 42.0, 35.2 (broad), 35.1, 18.1.

***tert*-Butyl (*S*)-(3-(4-(tert-butyl)phenyl)-2-methylpropyl)carbamate, (+)-14c**. (*S*)-**12c**·HCl (482 mg, 2.0 mmol) was subjected to react with NaOH 2M aq. in *t*-BuOH as previously described for (*R*)-**12a**. After 1 hour, a small amount (0.5 mL) of reaction mixture was taken to isolate and characterize the amine (*S*)-**12c**.[9] The reaction was continued as before for (*R*)-**14a** to give to 520 mg (85%) of (*S*)-**14c**; $[\alpha]_D^{26}$ +10.1 (c 1.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.29 (m, 2H), 7.07 (m, 2H), 4.54 (bs, 1H), 3.10 (m,1H), 2.99 (m, 1H), 2.64 (m, 1H), 2.36 (dd, *J* = 13.7 and 8.2 Hz, 1H), 1.91 (m, 1H), 1.44 (s, 9H), 1.30 (s, 9H), 0.88 (d, (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 156.0, 148.6, 137.2, 128.7, 125.1, 79.0, 46.3, 40.4, 35.7, 34.3, 31.4, 28.4, 17.5.

(*S*)-3-(4-(*tert*-Butyl)phenyl)-*N*,2-dimethylpropane-1-amine hydrochloride, (+)-15c. The carbamate (*S*)-**14c** (510 mg, 1.7 mmol) was subjected to methylation and *N*-Boc deprotection as described before for (*R*)-**14a**. 348 mg (80%) of hydrochloride (*S*)-**15c** was obtained, which was crystallized from *i*-PrOH to give a white solid; mp = 219-220 °C; $[\alpha]_D^{25}$ +8.1 (c 1.2, MeOH); ^{1}H NMR (600 MHz, CD_3OD): *δ* 7.34 (m, 2H), 7.12 (m, 2H), 2.95 (dd, *J* = 12.5 and 5.3 Hz, 1H), 2.84 (dd, *J* = 12.5 and 8.7 Hz, 1H), 2.68 (s, 3H), 2.68 (dd, *J* = 13.7 and 6.5 Hz, 1H), 2.48 (dd, *J* = 13.7 and 8.2 Hz, 1H), 2.13 (m,1H), 1.29 (s, 9H), 0.99 (d, (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD): *δ* 151.3, 138.0, 130.7, 127.3, 57.0, 41.8, 36.1, 35.2, 35.0, 32.6, 18.2.

(*S*)-*N*-(3-(4-(*tert*-Butyl)phenyl)-2-methylpropyl)-N,4-dimethyl benzenesulfonamide, (+)-16c. Pyridine (0.240 mL, 3 mmol) and TsCl (378 mg, 2 mmol) were consecutively added to a cooled solution of (*S*)-**15c** (340 mg, 1.3 mmol) in CH_2Cl_2 (2 mL). After 4 h at 0 °C, the reaction was left at room temperature for 20 hours. Et_2O (10 mL) was added and the solution was washed with water (3 x 1 mL) and brine (1 mL) and dried with Na_2SO_4. The residue was purified by flash chromatography to give 349 mg (72%) of (+)-**16c** with dr = 95.8:4.2, determined by HPLC analysis using a CHIRALCEL® OJ-H, *n*-hexane/*i*-PrOH = 85:15, 1 mL, min^{-1}, λ = 220 nm, 25 °C, minor isomer tr = 38.6 min and major isomer tr = 45.4 min; $[\alpha]_D^{26}$ +20.4 (c 1.67, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.65 (m, 2H), 7.30 (m, 2H), 7.29 (m, 2H), 7.07 (m, 2H), 2.86 (dd, *J* = 13.0 and 6.9 Hz, 1H), 2.81 (dd, *J* = 13.0 and 7.9 Hz, 1H), 2.75 (dd, *J* = 13.7 and 5.3 Hz, 1H), 2.70 (s, 3H), 2.42 (s, 3H), 2.33 (dd, *J* = 13.7 and 8.9 Hz, 1H), 2.01 (m, 1H), 1.31 (s, 9H), 0.92 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 148.7, 143.1, 137.1, 134.4, 129.6, 128.7, 127.4, 125.1, 56.3, 40.1, 35.3, 34.3, 33.5, 31.4, 21.4, 17.3.

(*R*)-*N*-(2-(4-Methoxy-3-(3-methoxypropoxy)benzyl)-3-methylbutyl)-4-methylbenzenesulfonamide, (+)-14b. To a cooled solution of hydrochloride (*R*)-**12b**·HCl (165 mg, 0.5 mmol) in CH_2Cl_2 (3 mL), 10% water solution of Na_2CO_3 (0.5 mL) was added. The mixture was stirred at rt for 60 min then the aqueous solution was separated and extracted with CH_2Cl_2 (2 mL). The combined organic phases were washed with water, brine and dried on Na_2SO_4. A small amount of amine (*R*)-**12b** was isolated for the characterization.[10] To the crude dissolved in CH_2Cl_2 (2 mL) the *i*-$PrNEt_2$ (0.267 mL, 1.5 mmol) and TsCl (110 mg, 0.575 mmol) were added in succession at 0 °C. The reaction was left at rt for 20 h, then quenched with Et_2O (10 mL) addition, washed with water (1 mL), brine (1 mL) and dried on Na_2SO_4. After solvent evaporation the crude was flash chromatographed to give 191 mg (85%) of (*R*)-**14b**, with dr = 99.8:0.2 determined by HPLC analysis using a CHIRALCEL® AD-H, *n*-hexane/*i*-PrOH = 85:15, 1 mL, min^{-1}, λ = 230 nm, 25 °C, minor isomer t_r = 14.3 min, major isomer t_r = 15.3 min; crystallized from *i*-Pr_2O, mp = 65-67 °C; $[\alpha]_D^{24}$ +21.1 (c 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.63 (m, 2H), 7.26 (m, 2H), 6.74 (d, *J* = 8.1 Hz, 1H), 6.64 (d, *J* = 1.8 Hz, 1H), 6.59 (dd, *J* = 8.1 and 1.8 Hz, 1H), 4.30 (m, 1H), 4.07 (t, *J* = 6.5 Hz, 2H), 3.84 (s, 3H), 3.57 (t, *J* = 6.3 Hz, 2H), 3.36 (s, 3H), 2.89 (m, 1H), 2.78 (m, 1H), 2.60 (dd, *J* =

9 The amine (*S*)-**12c** was isolated as described before for (*R*)-**12a**, ref 40, and characterized; $[\alpha]_D^{24}$ –4.3 (c 1.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.29 (m, 2H), 7.08 (m, 2H), 2.66 (m,2H), 2.51 (dd, *J* = 12.7 and 6.8 Hz, 1H), (dd, *J* = 13.5 and 8.1 Hz, 1H), 1.75 (m, 1H) 1.31 (s, 9H), 1.20 (bs, 2H), 0.89 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 148.4, 137.8, 128.7, 125.0, 48.0, 40.4, 38.4, 34.3, 31.3, 17.4

10 (+)-(*R*)-**12b**, light yellow oil; $[\alpha]_D^{24}$ +10.6 (c 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 6.78 (d, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 2.0 Hz, 1H), 6.70 (dd, *J* = 8.2 and 2.0 Hz, 1H), 4.10 (t, *J* = 6.5 Hz, 2H), 3.83 (s, 3H), 3.57 (t, *J* = 6.1 Hz, 2H), 3.35 (s, 3H), 2.60 (m, 3H), 2.38 (dd, *J* = 13.9 and 9.1 Hz, 1H), 2.10 (m, 2H), 1.83 (m, 1H) 1.49 (m, 1H), 1.04 (bs, 2H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 148.1, 147.3, 134.2, 121.0, 114.0, 111.5, 69.2, 65.9, 58.5, 55.9, 49.4, 42.2, 34.6, 29.5, 27.5, 19.4, 18.7

14.0 and 5.5 Hz, 1H), 2.42 (s, 3H), 2.31 (dd, *J* = 14.0 and 9.2 Hz, 1H), 2.09 (m, 2H), 1.75 (m, 1H), 1.56 (m, 1H), 0.88 (d, *J* = 6.9 Hz, 3H), 0.86 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 148.4, 147.7, 143.1, 136.7, 133.0, 129.5, 127.0, 121.0, 114.0, 111.8, 69.3, 66.0, 58.6, 56.0, 46.0, 43.7, 34.6, 29.5, 28.0, 21.4, 19.1, 19.0.

(*R*)-4-Methyl-*N*-(2-methyl-3-(4-(*tert*-pentyl)phenyl)propyl) benzenesulfonammide, (–)-14d. To a cooled solution of amine hydrochloride (*R*)-**12d**·HCl (64 mg, 0.25 mmol) in CH_2Cl_2 (3 mL), 10% water solution of Na_2CO_3 (0.25 mL) was added. A small amount of amine (*R*)-**12d** was isolated for the characterization.[11] (*R*)-**12d** was left to react with TsCl under the same conditions above described for (*R*)-**12b**. Isolated 91 mg (97%) of (*R*)-**14d** as a waxy material, with dr = 99.4:0.6, determinate by HPLC CHIRALPAK® AD-H, *n*-hexane/*i*-PrOH = 95:5, 0.75 mL min^{-1}, λ = 230 nm, 25 °C, minor isomer t_r = 21.4, major isomer t_r = 23,2; crystallized from *n*-hexane as a colorless solid; mp = 63-65 °C; $[\alpha]_D^{24}$ –18.5 (c 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.70 (m, 2H), 7.29 (m, 2H), 7.19 (m, 2H), 6.97 (m, 2H), 4.43 (m, 1H),2.86 (m, 1H), 2.77 (m, 1H), 2.57 (dd, *J* = 13.6 and 6.5 Hz, 1H), 2.42 (s, 3H), 2.34 (dd, *J* = 13.6 and 7.8 Hz, 1H), 1.87 (m, 1H), 1.61 (q, *J* = 7.5 Hz, 2H), 1.25 (s, 6H), 0.86 (d, *J* = 6.7 Hz, 3H), 0.67 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 147.3, 143.3, 137.0, 136.4, 129.6, 128.6, 127.1, 125.9, 48.7, 40.1, 37.6, 36.8, 35.1, 20.4, 21.5, 17.6, 9.1.

(*S*)-4-Methyl-*N*-(2-methyl-3-(4-(*tert*-pentyl)phenyl)propyl) benzenesulfonammide, (+)-14d. 0.70 mg (0.27 mmol) of amine hydrochloride (*S*)-**12d**·HCl were treated as described above for the enantiomer (*R*)-**12d**·HCl. A small amount of amine (*S*)-**12d** was isolated for the characterization.[12] 92 mg (91%) of amide (*S*)-**14d** was obtained, as a semisolid material, with dr = 99.7:0.3, determined by HPLC CHIRALPAK® AD-H, as for its enantiomer (*R*)-**14d**; crystallized from *n*-hexane as a colorless solid; $[\alpha]_D^{24}$ +16.4 (c 1.1, $CHCl_3$). ^{1}H and ^{13}C NMR are in agreement with its enantiomer previously reported.

Preparation of diols *meso* and (*S*,*S*)-18 from mono-protected diols (*R*,S)- and (*S*,S)-17: general procedure. An 1:1 mixture of (*R*,*S*)- and (*S*,*S*)-1-(benzyloxy)propan-2-yl)oxy)propan-1-ol [(*R*,*S*)- and (*S*,*S*)-**17**] was prepared as described in the literature,[13] and the isomers were separated by flash chromatography on silica gel. Each isomer was separately subjected to hydrogenolysis under the following conditions: 5% Pd/C (10% w/w) was added to a solution of the substrate in MeOH (7 mL mmol^{-1}). The reaction was conducted in a Parr hydrogenator with 2 bar of H_2 for 16-18 hours.

***meso*-((1-Hydroxypropan-2-yl)oxy)propan-1-ol, *meso*-18**. *Meso*-**18** (92%) was obtained as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 4.00 (bs, 2H), 3.66 (m, 2H), 3.60 (dd, *J* = 11.5 and 2.9 Hz, 2H), 3.48 (dd, J = 11.5 and 8.1 Hz, 2H), 1.11 (d, J = 6.4 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ ppm 76.3, 66.7, 17.8.

(*S*)-2-(((*S*)-1-Hydroxypropan-2-yl)oxy)propan-1-ol, (+)-18. (*S*,*S*)-**18** (86%) was obtained as a colorless oil; $[\alpha]_D^{25}$ +86.8 (c 1.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 4.00 (bs, 2H), 3.66 (m, 2H), 3.60 (dd, *J* = 11.5 and 2.9 Hz, 2H), 3.48 (dd, J = 11.5 and 8.1 Hz, 2H), 1.11 (d, J = 6.4 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ ppm 73.0, 66.4, 16.1.

Preparation of tosyl derivatives *meso*- and (*S*,*S*)-19 from diols *meso*- and (*S*,*S*)-18: general procedure. TsCl (2 eq) was added to an ice-water cooled solution of diol in anhydrous pyridine (1.5 mL mmol^{-1}), and stirred at the same temperature for 10 h, then left in the refrigerator at 4 °C for 30 h. Water-ice (15 mL mmol^{-1}) was added and the heterogeneous mixture stirred for one hour.

***meso*-Oxybis(propane-2,1-diyl) bis(4-methylbenzenesulfonate), *meso*-19**. The above reaction mixture was extracted with CH_2Cl_2 (4 x 5 mL). 3N HCl aq. (8 mL) was added to the organic solution under vigorous agitation for 45 min. The organic phase was separated, washed with water (3 x 5 mL), brine (3 mL) and dried on Na_2SO_4. After solvent distillation, the crude was flash chromatographed, on silica gel, to give the target *meso*-**19** (88%) product as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* ppm 7.78 (m, 4H), 7.35 (m, 4H), 3.81 (dd, J = 10.2 and 4.5 Hz, 2H), 3.87 (dd, J = 10.2 and 6.2 Hz, 2H), 2.71 (m, 2H), 2.45 (s, 6H), 1.06 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 144.8, 132.7, 129.8, 127.9, 72.5, 71.9, 21.6, 17.5.

(2*S*,2'*S*)-Oxybis(propane-2,1-diyl) bis(4-methylbenzenesulfonate), (*S*,*S*)-19. A solid product was recovered by filtration from the above reaction mixture, then dissolved in CH_2Cl_2 (10 mL). The organic solution was washed with 2N HCl aq. (2 mL), water (2 x 2 mL) and brine (2 mL). The organic solution was dried on Na_2SO_4 and the solvent distilled. The crude was crystallized from MeOH (4 mL g^{-1}) to give (*S*,*S*)-**19** (86%), as white solid material; $[\alpha]_D^{23}$ +3.8 (c 1.3, $CHCl_3$), [lit.[13] $[\alpha]_D^{29}$

11 (+)-(*R*)-**12d**, light yellow oil; $[\alpha]_D^{22}$ +1.1 (c 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.22 (m, 2H), 7.08(m, 2H), 2.69 (dd, *J* = 12.6 and 5.6 Hz, 1H), 2.65 (dd, *J* = 13.5 and 6.3 Hz, 1H), 2.53 (dd, *J* = 12.6 and 7.1 Hz, 1H), 2.37 (dd, *J* = 13.5 and 8.0 Hz, 1H), 2.27 (bs, 2H), 1.81 (m, 1H), 1.62 (q, *J* = 7.5 Hz, 2H), 1.26 (s, 6H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.67 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 146.8, 137.5, 128.6, 125.7, 47.9, 40.4, 38.2, 37.5, 36.8, 28.4 (2 C's),17.4, 9.1.

12 (–)-(*S*)-**12d**, light orange oil; $[\alpha]_D^{22}$ –1.2 (c 0.9, $CHCl_3$); ^{1}H and ^{13}C NMR were identical to those of its enantiomer

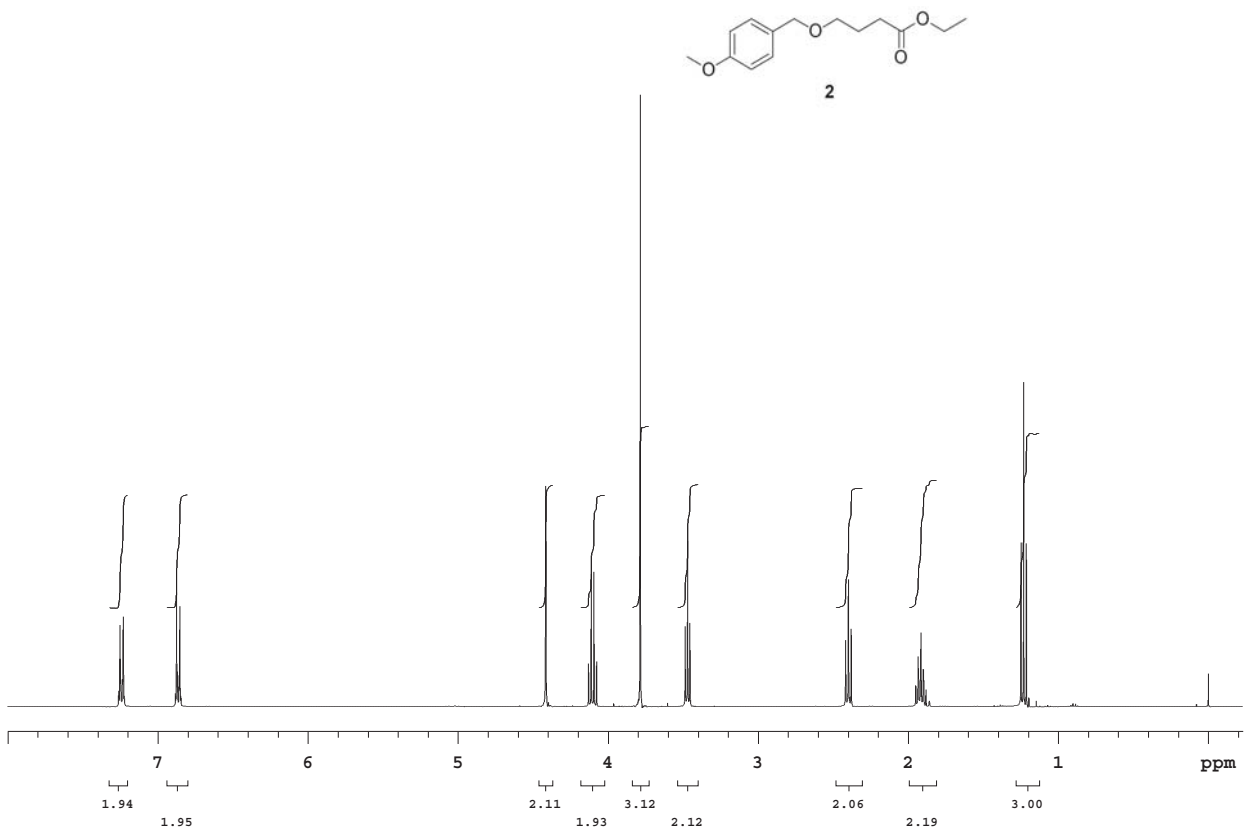
13 K. Ogasahara, K. Hirose, Y. Tobe and K. Naemura, *J. Chem. Soc., Perkin Trans. 1*, 1997, 3227-3236

+3.4 (c 0.99, $CHCl_3$)]; ^1H NMR spectra coincided with those previously reported;[13] ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 144.9, 132.9, 129.8, 127.9, 73.0, 72.5, 21.6, 17.1.

Preparation of diiodo derivatives *meso*- and (*S*,*S*)-20 from the corresponding tosyl derivatives 19: general procedure. To a saturated solution of NaI (4 eq) in dry acetone (0.5 mL $mmol^{-1}$), under stirring and nitrogen, ditosyl derivative was added. The reaction was heated to 60 °C for 18 hours. The suspension was diluted with Et_2O and washed with and brine and dried with $MgSO_4$.

***meso*-1-Iodo-2-((1-iodopropan-2-yl)oxy)propane, *meso*-20**. *Meso*-**20** (85% yield) was purified by flash chromatography on silica gel to give a light red oil; ^1H NMR (400 MHz, $CDCl_3$): δ 3.58 (m, 2H), 3.28 (dd, *J* = 10.1 and 5.2 Hz, 2H), 3.16 (dd, *J* = 10.1 and 6.2 Hz, 2H), 1.29 (d, J = 6.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 73.8, 20.8, 11.2.

(*S*)-1-Iodo-2-(((S)-1-iodopropan-2-yl)oxy)propane, (*S*,*S*)-20. (*S*,*S*)-**20** (85%) was purified as its *meso*-isomer; $[\alpha]_D^{23}$ +11.0 (c 2.0 , $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 3.57 (m, 2H), 3.18 (m, 4H), 1.29 (d, *J* = 6.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 73.8, 21.1, 11.3.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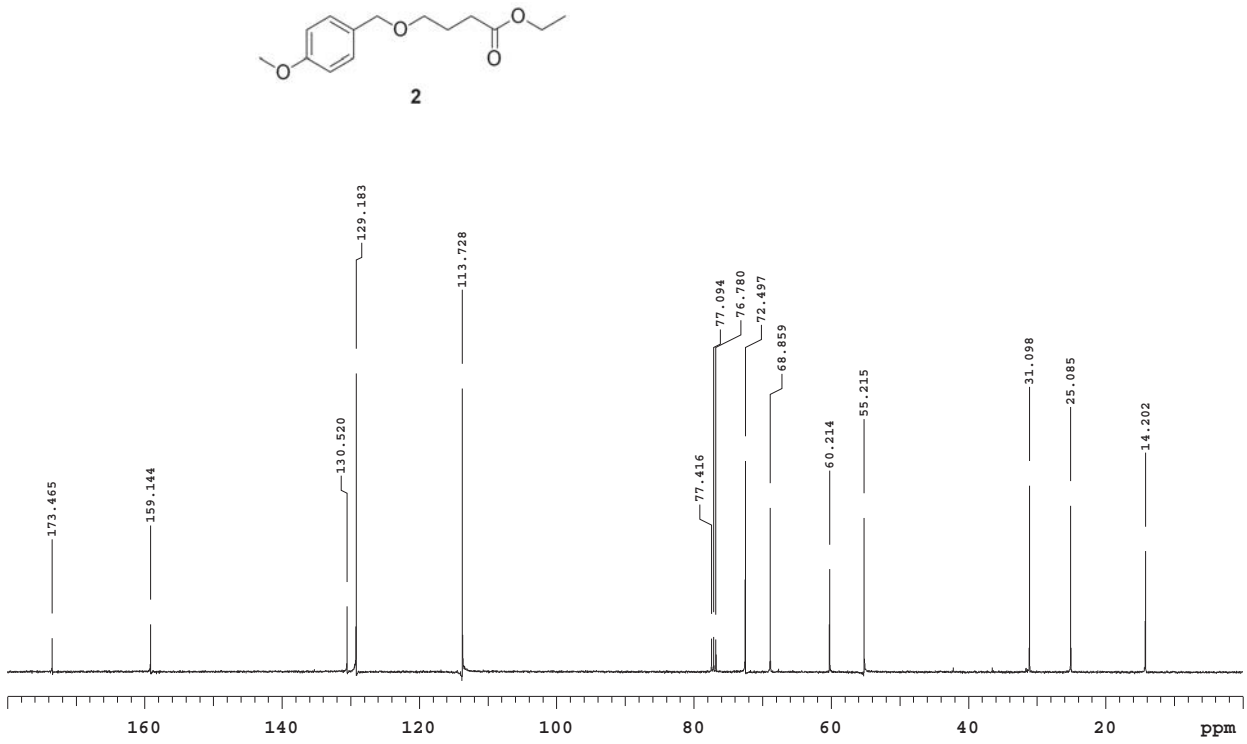
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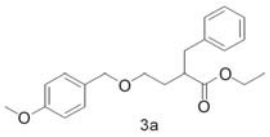
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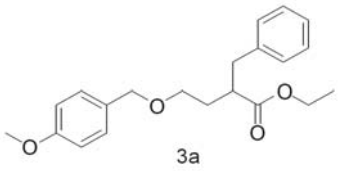
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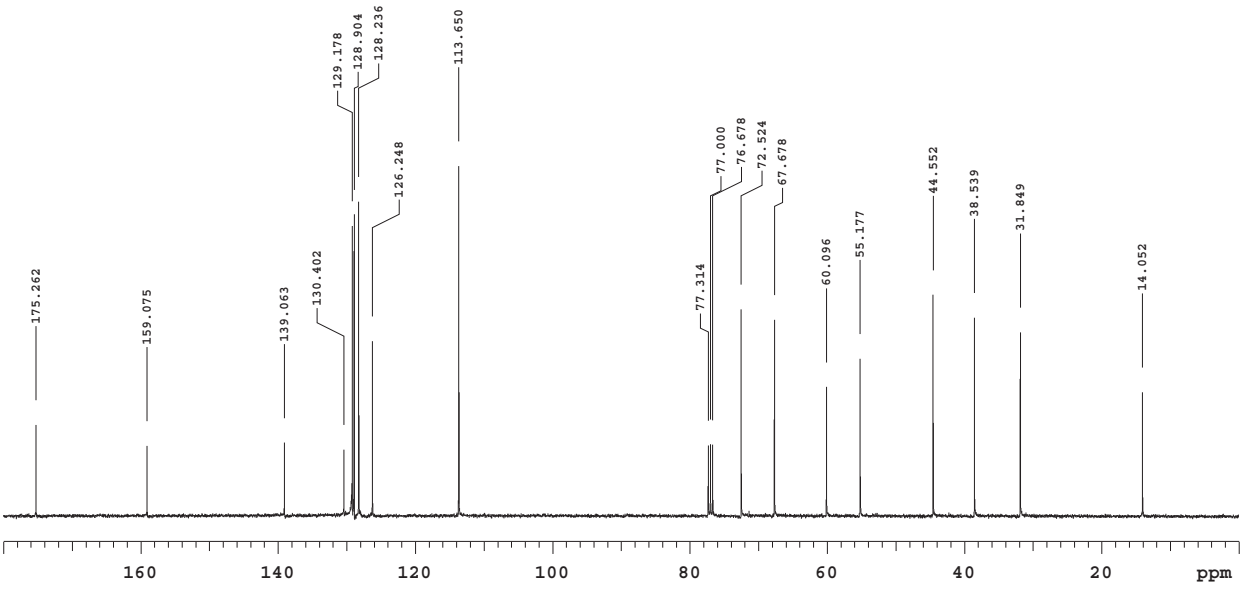
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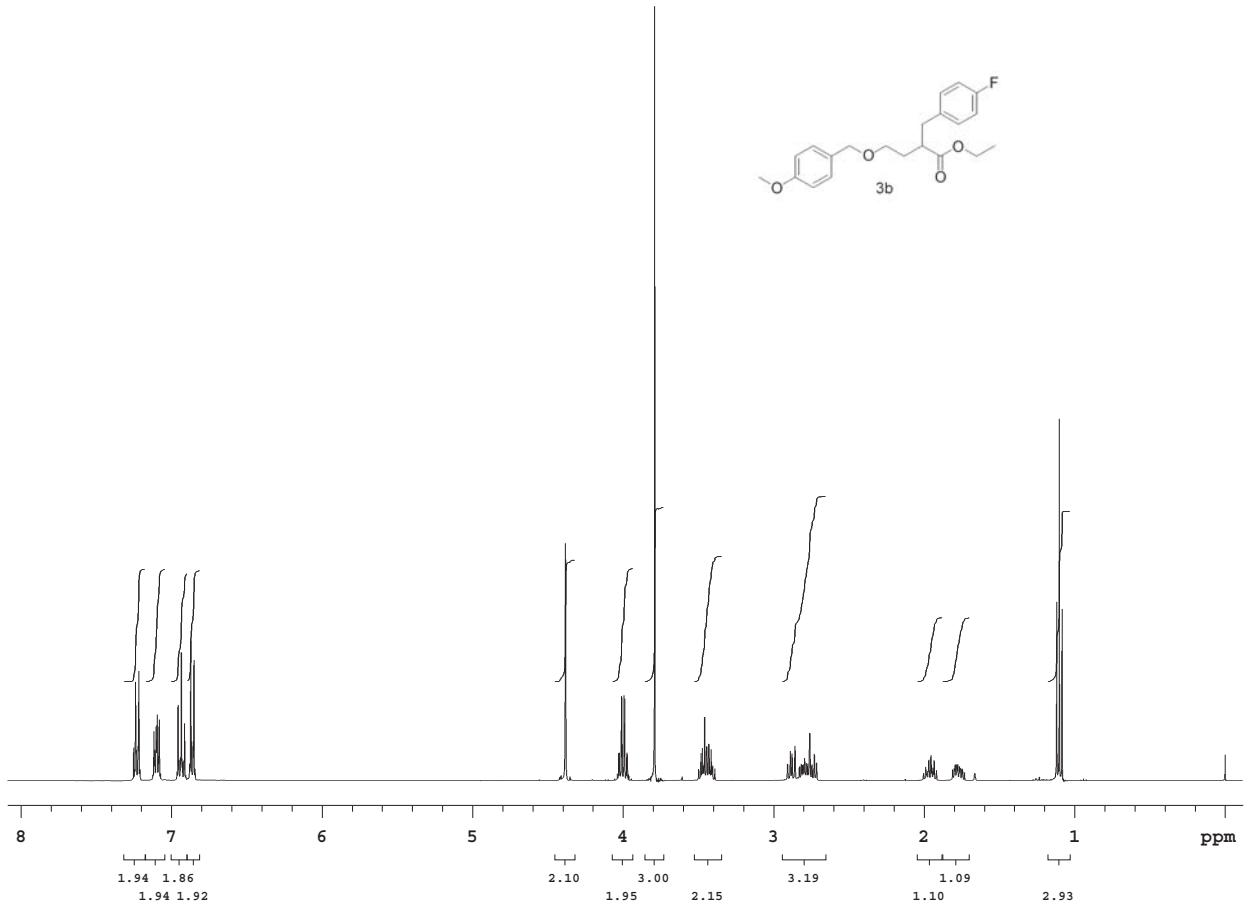
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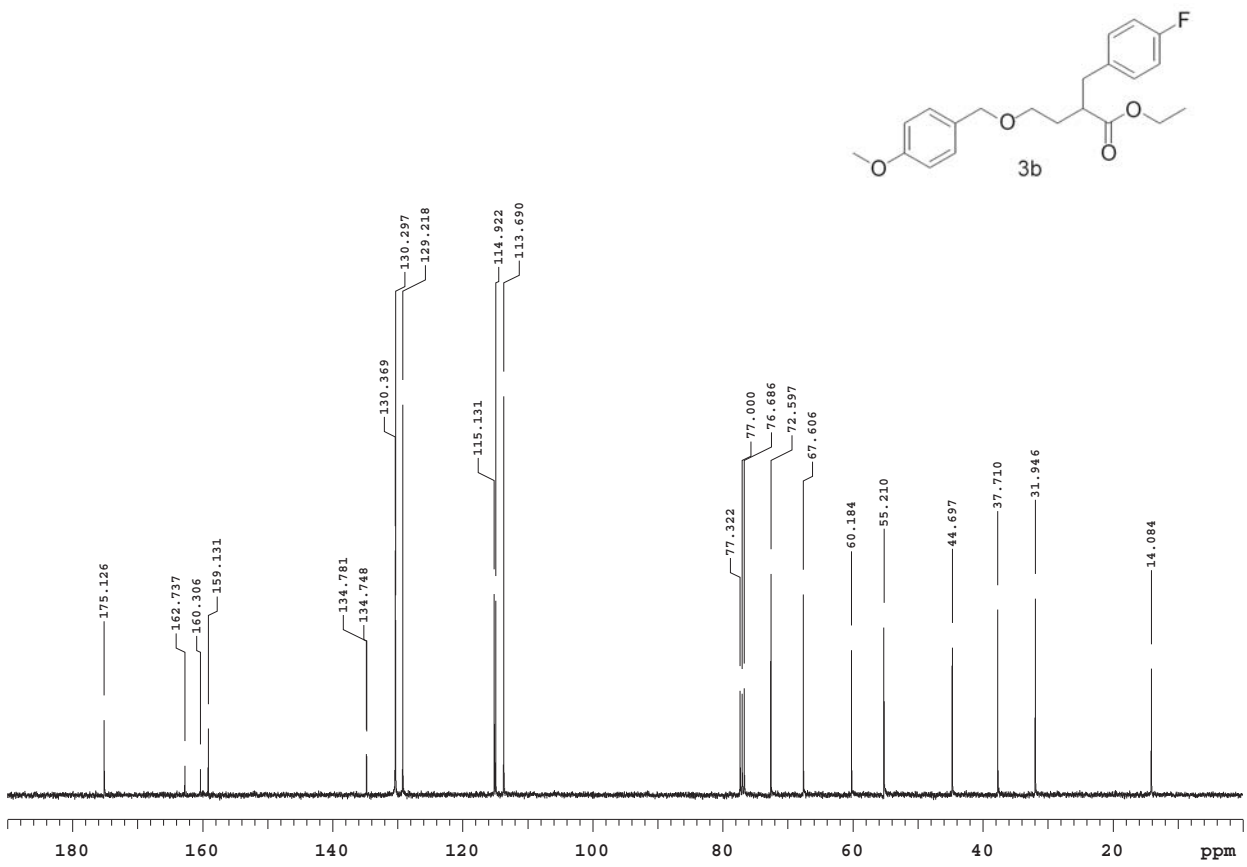
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72.597
67.606
60.184
55.210
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37.710
31.946
14.084
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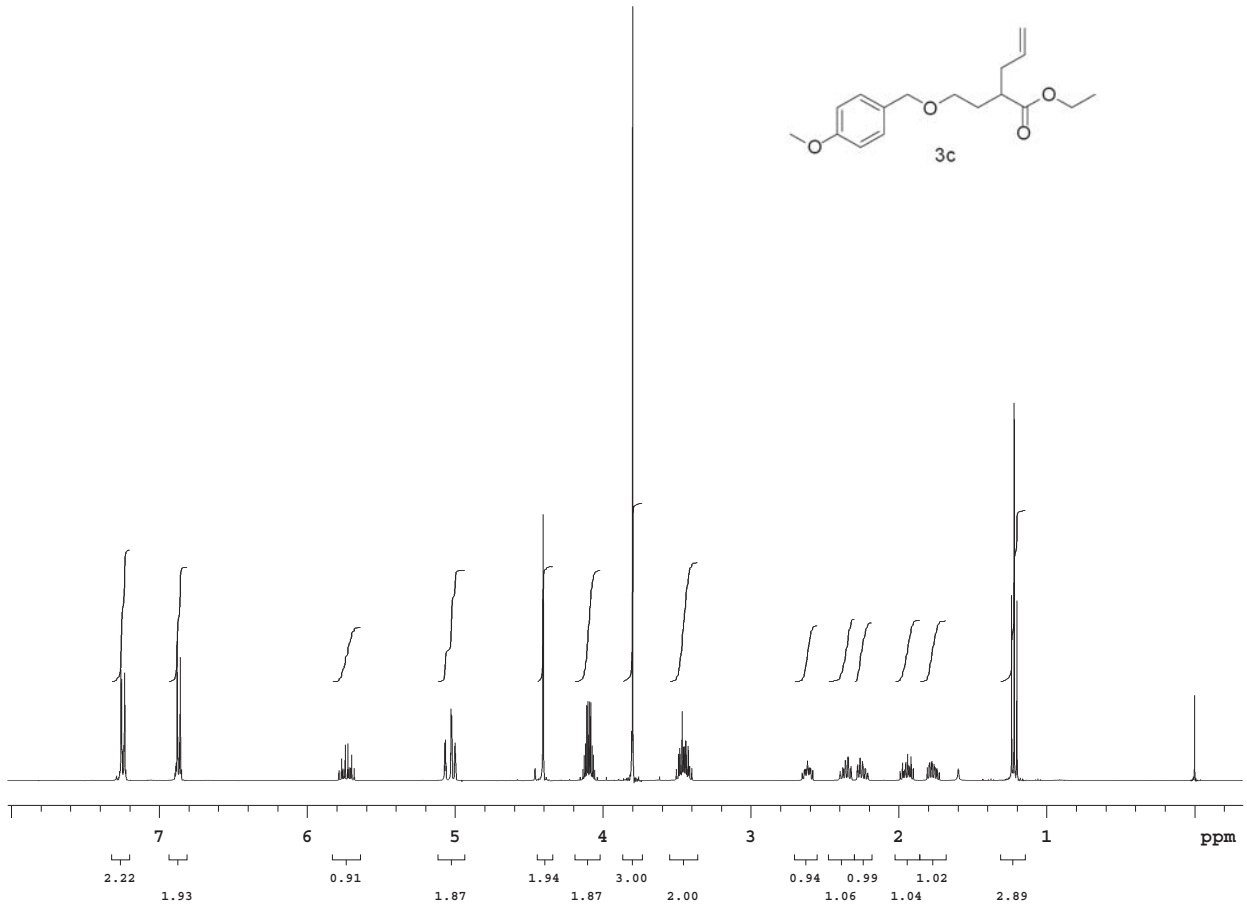
140
120
100
80
60
40
20
ppm


3c
7
6
5
4
3
2
1
ppm
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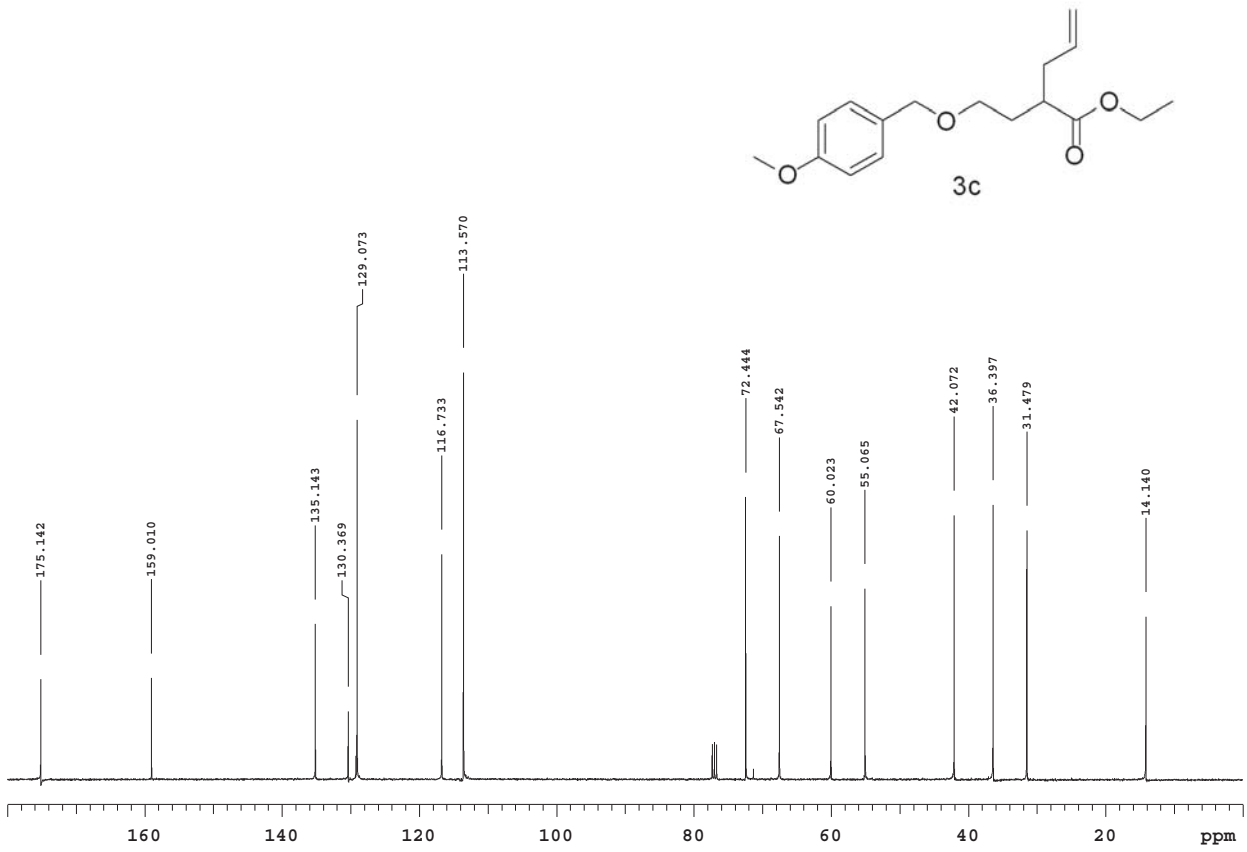
0.91
1.87
1.94
1.87
3.00
2.00
0.94
1.06
0.99
1.04
1.02
2.89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42.072
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31.479
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140
120
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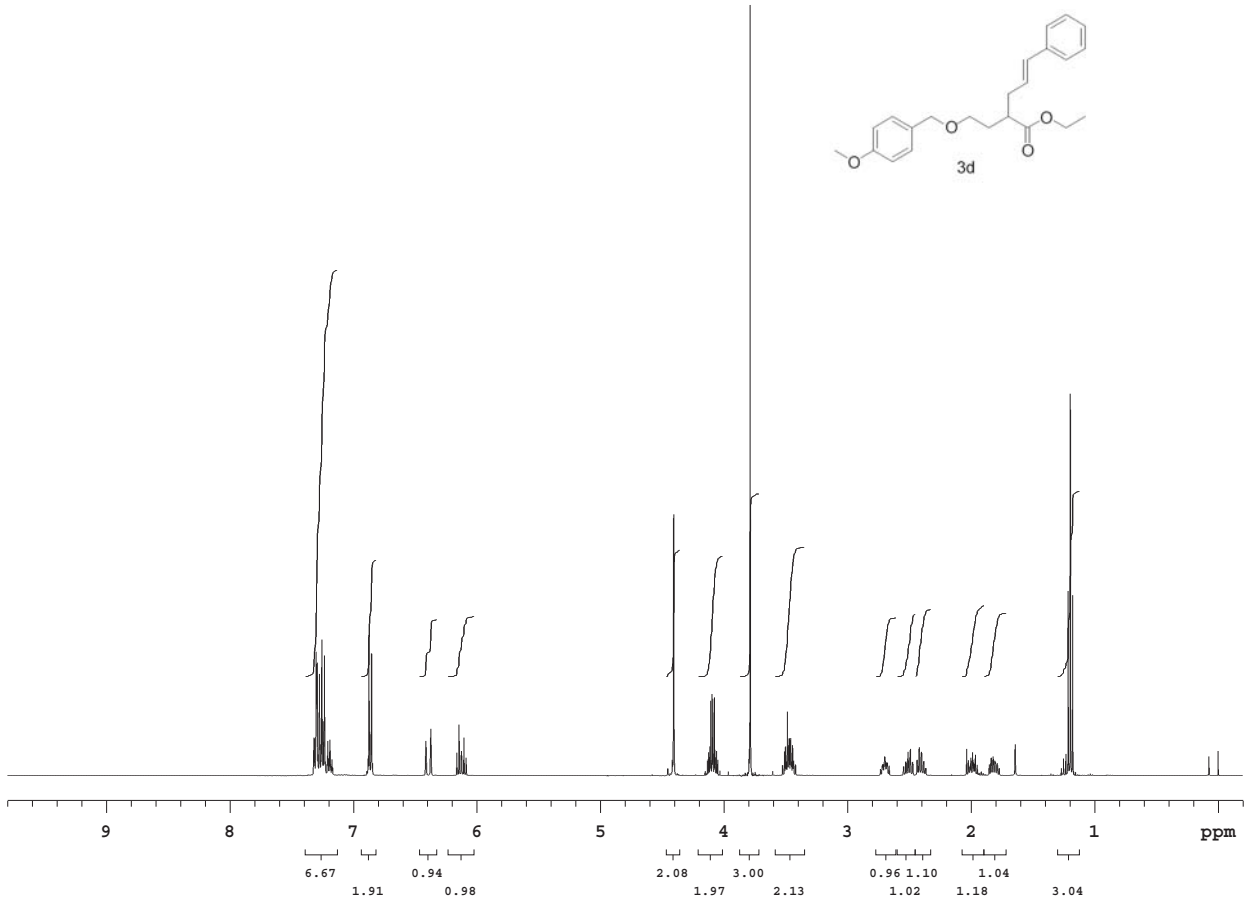
60
40
20
ppm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8
7
6
5
4
3
2
1
ppm
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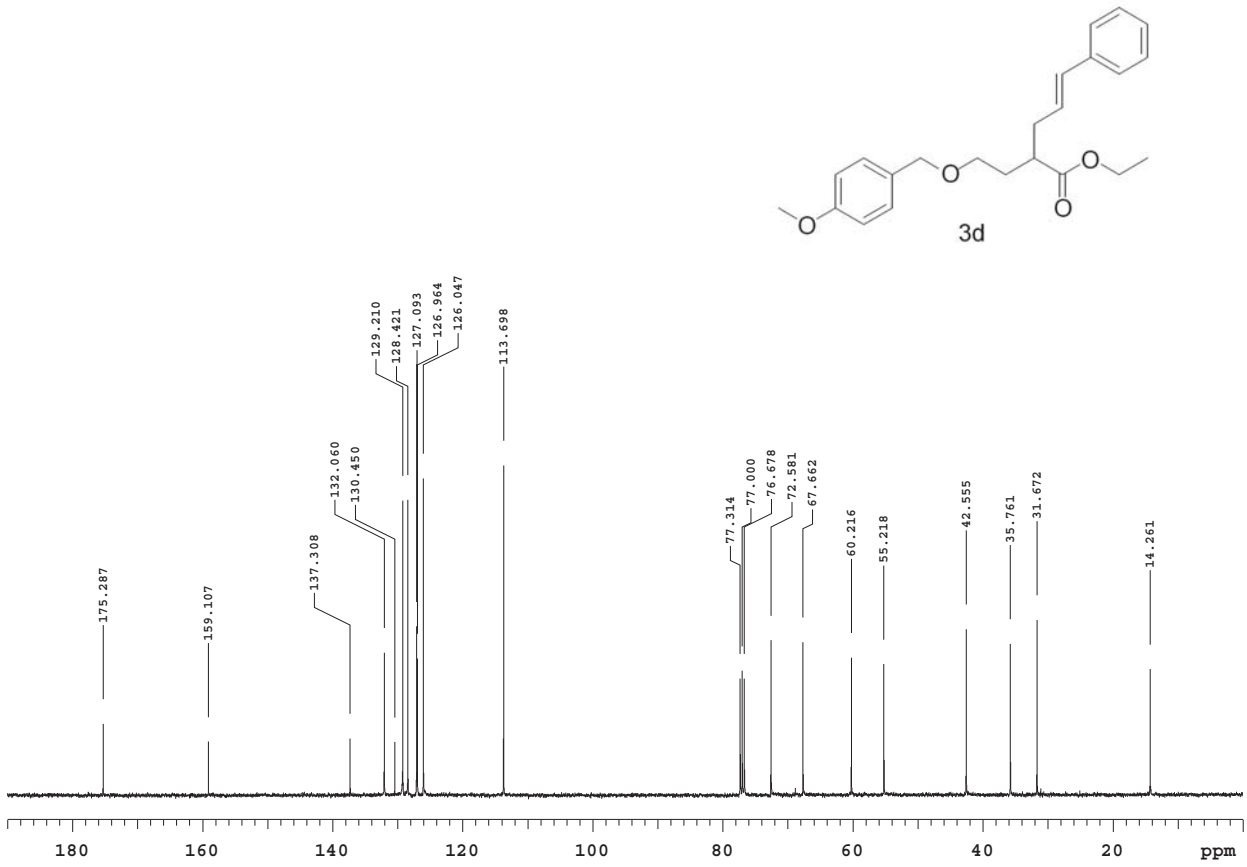
1.97
3.00
2.13
0.96
1.02
1.10
1.04
1.18
3.04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126.047
113.698
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77.000
76.678
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67.662
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60
40
20
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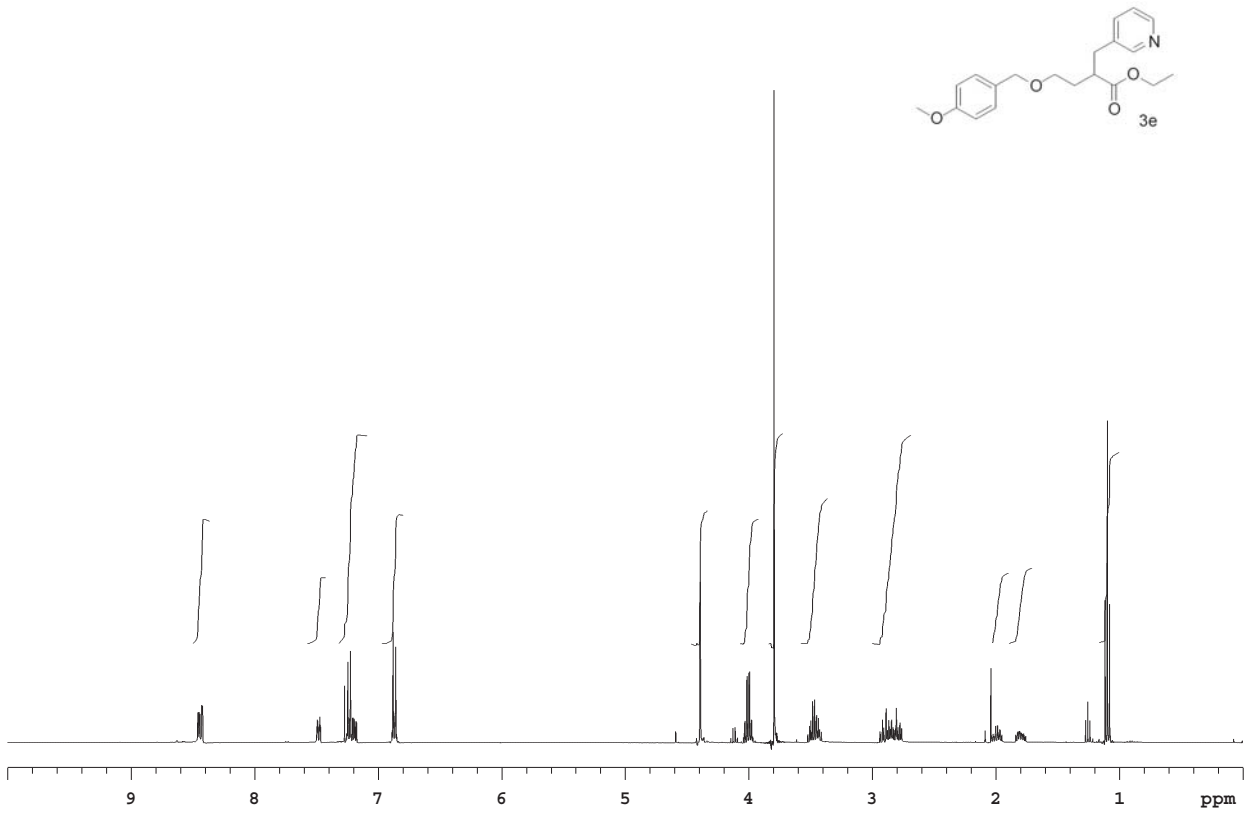
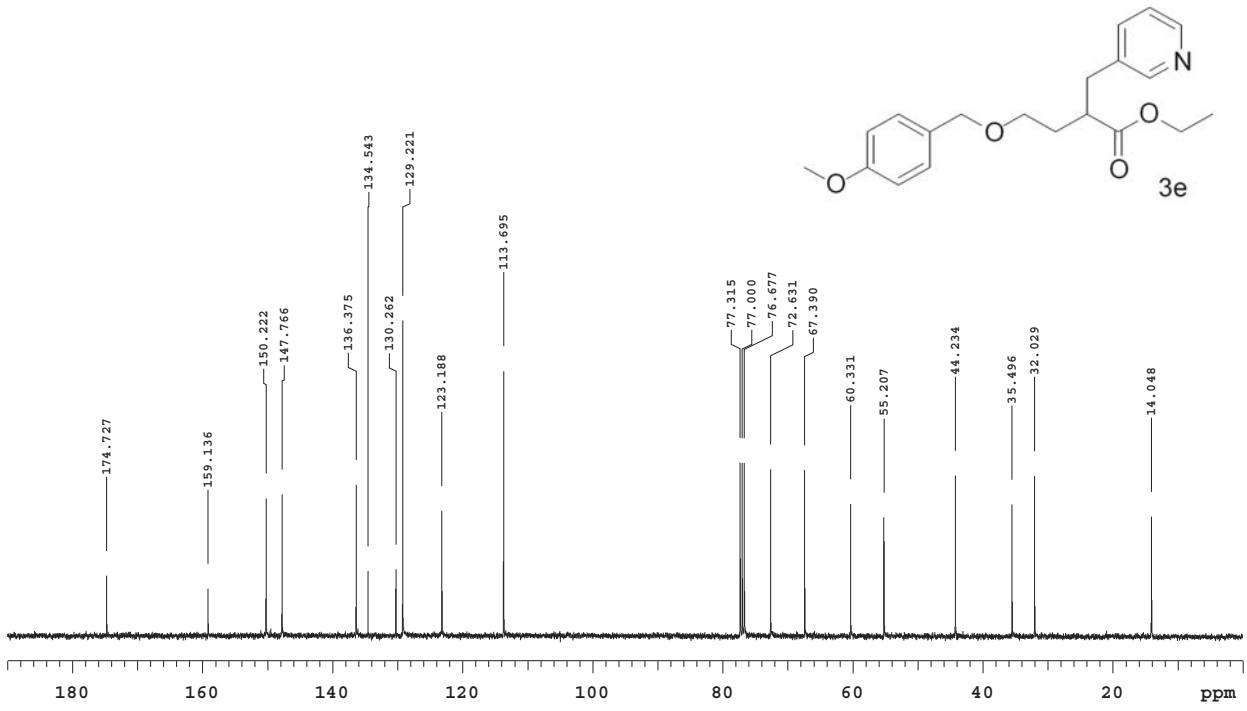

N
O
O
O
O
3e
9
8
7
6
5
4
3
2
1
ppm


N
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O
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O
3e
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150.222
147.766
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134.543
130.262
129.221
123.188
113.695
77.315
77.000
76.677
72.631
67.390
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35.496
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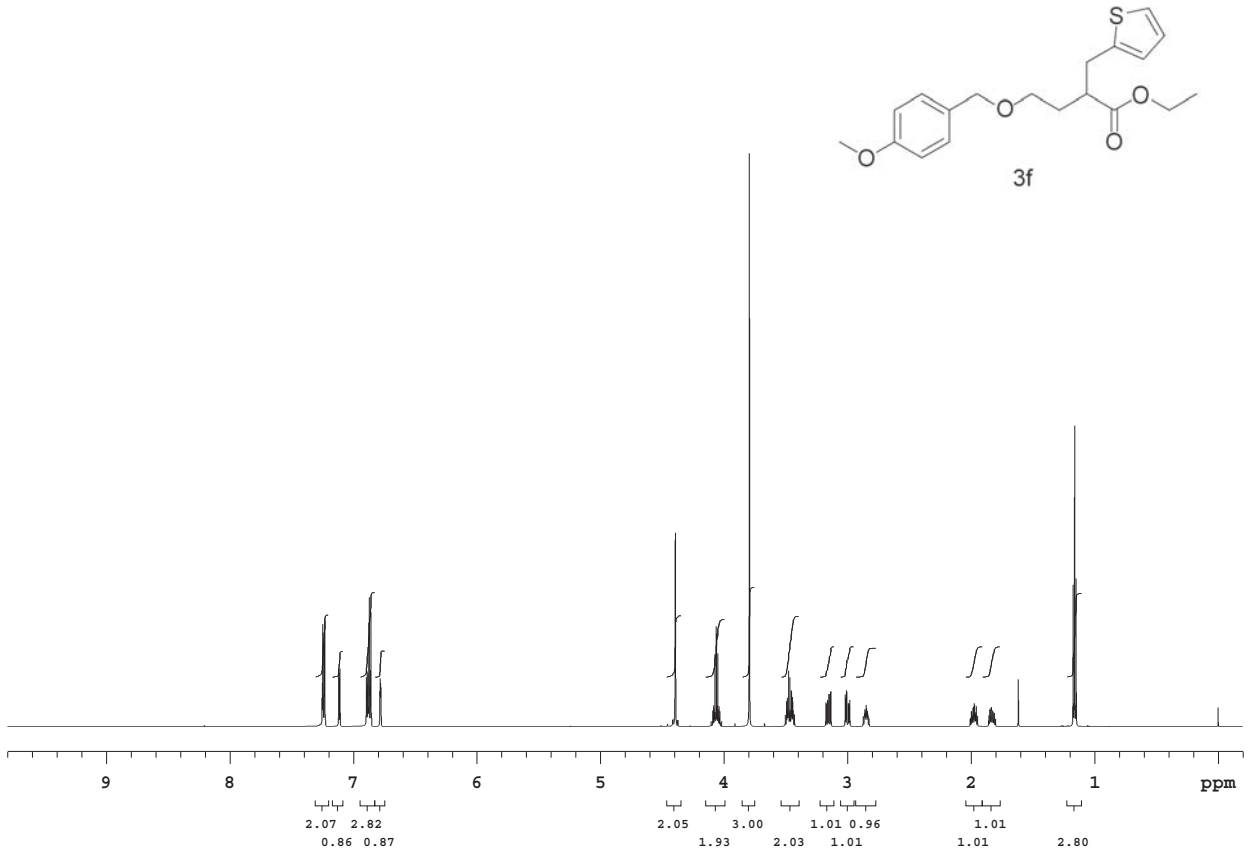
160
140
120
100
80
60
40
20
ppm


S
O
O
O
O
3f
9
8
7
6
5
4
3
2
1
ppm
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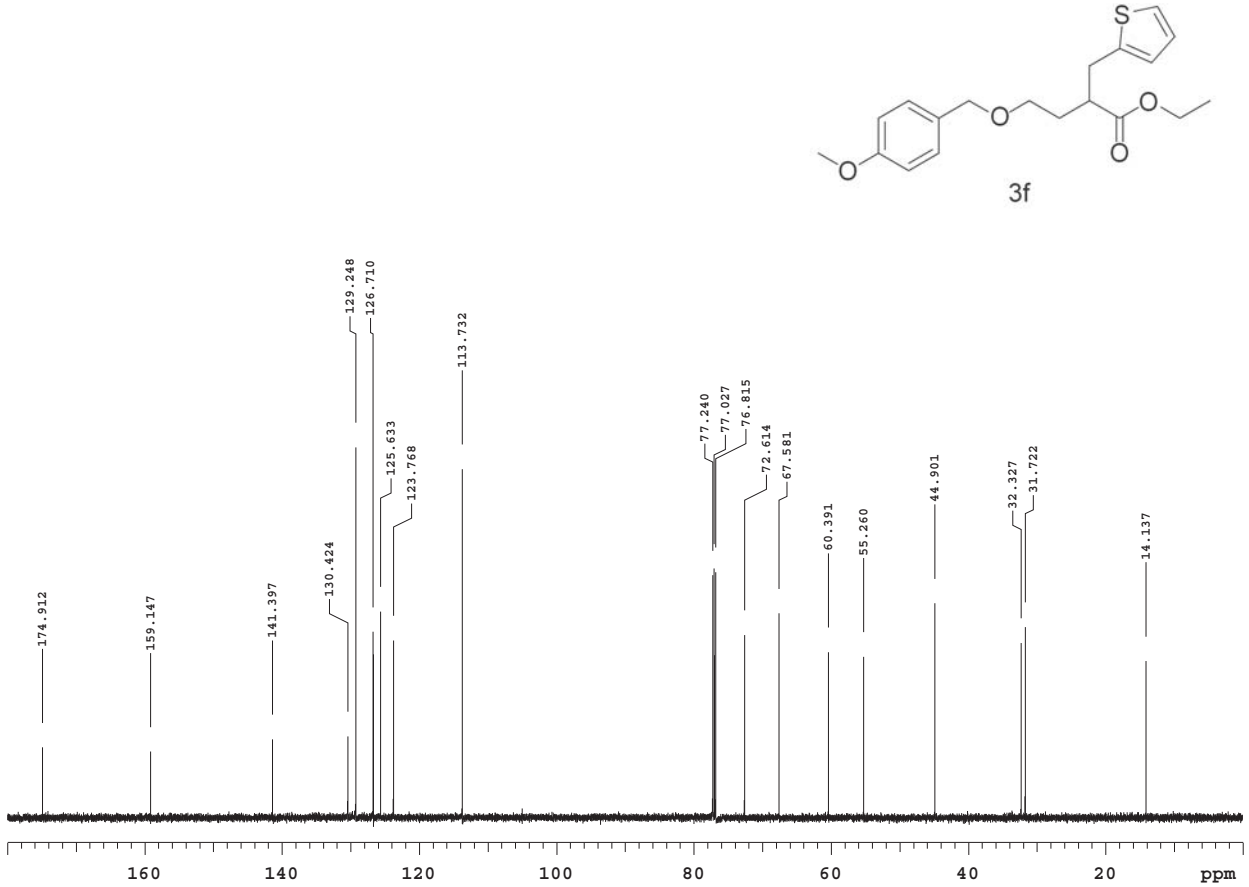
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O
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72.614
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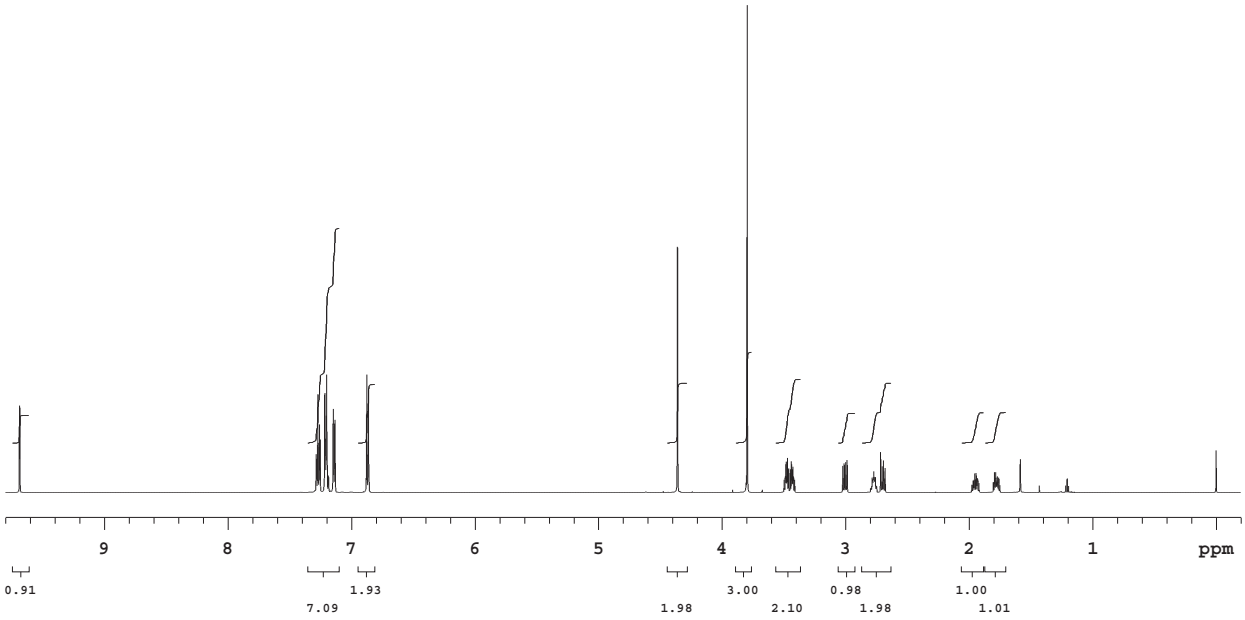
80
60
40
20
ppm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8
7
6
5
4
3
2
1
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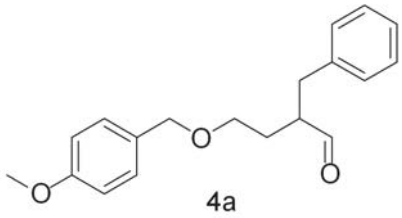
1.00
1.01


O
O
O

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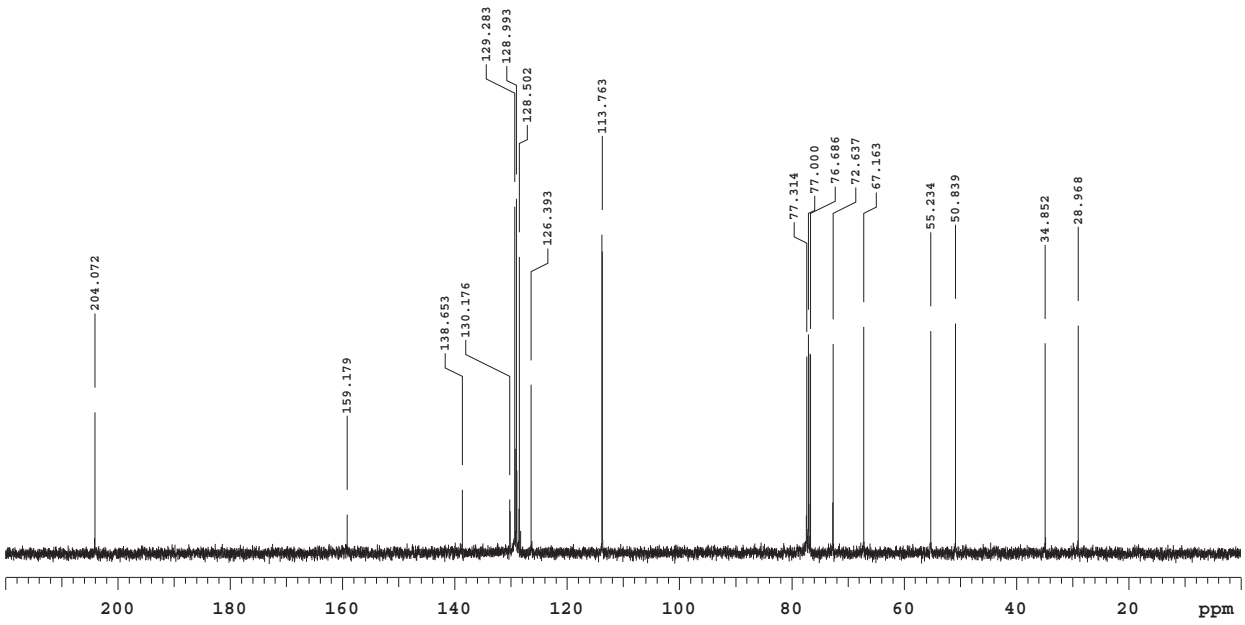
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77.314
77.000
76.686
72.637
67.163
55.234
50.839
34.852
28.968
200
180
160
140
120
100
80
60
40
20
ppm

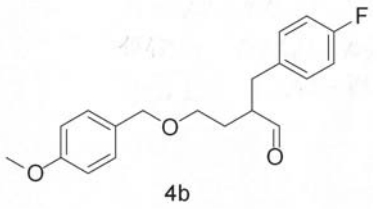
2.F.Benzil.4.PMB.O.Butirraldeide

Archive directory:
Sample directory:
File: PROTON

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: rosini
INOVA-600 "i600"

Pulse 45.0 degrees
Acq. time 3.000 sec
Width 9611.9 Hz
4 repetitions
OBSERVE H1, 599.7275851 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 18 sec



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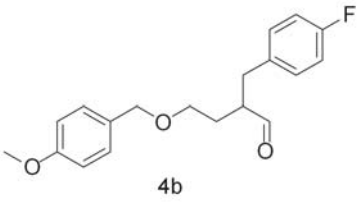

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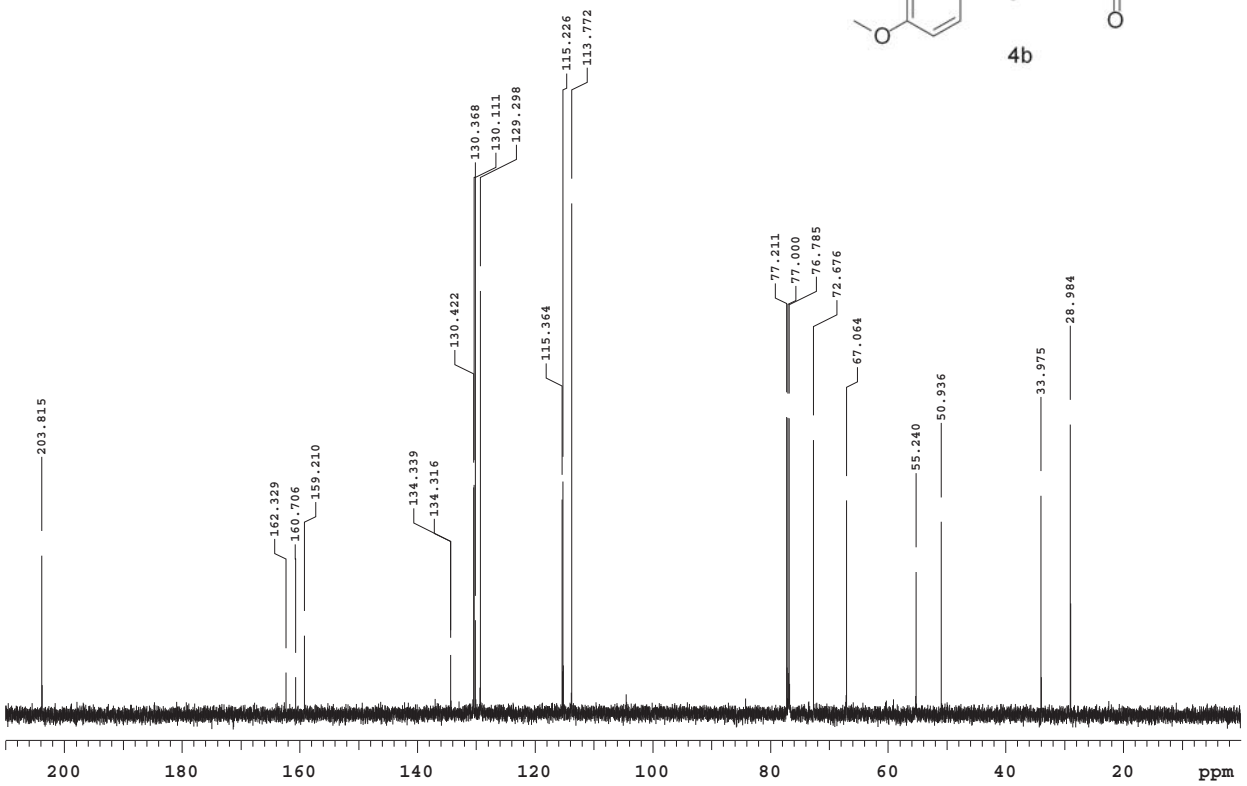

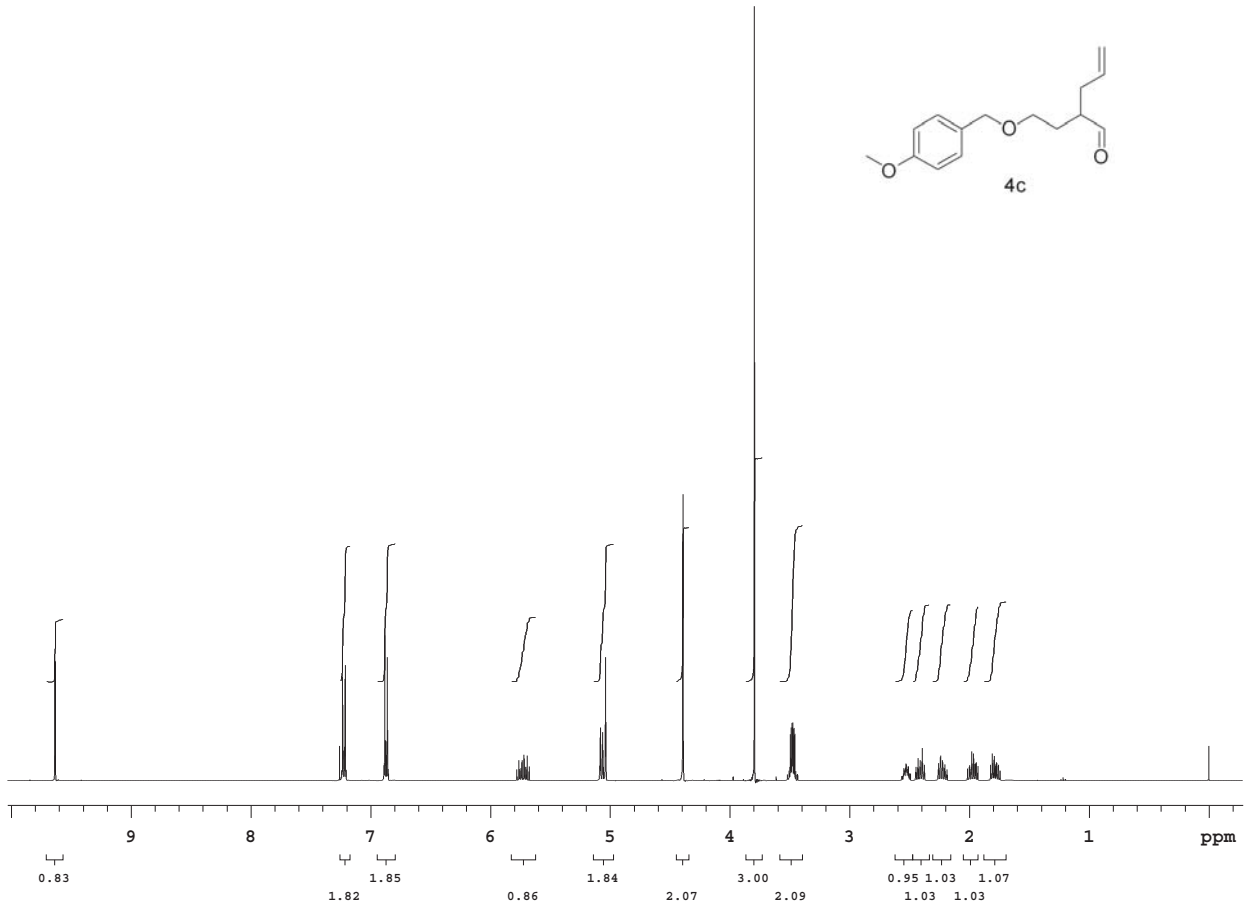
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6
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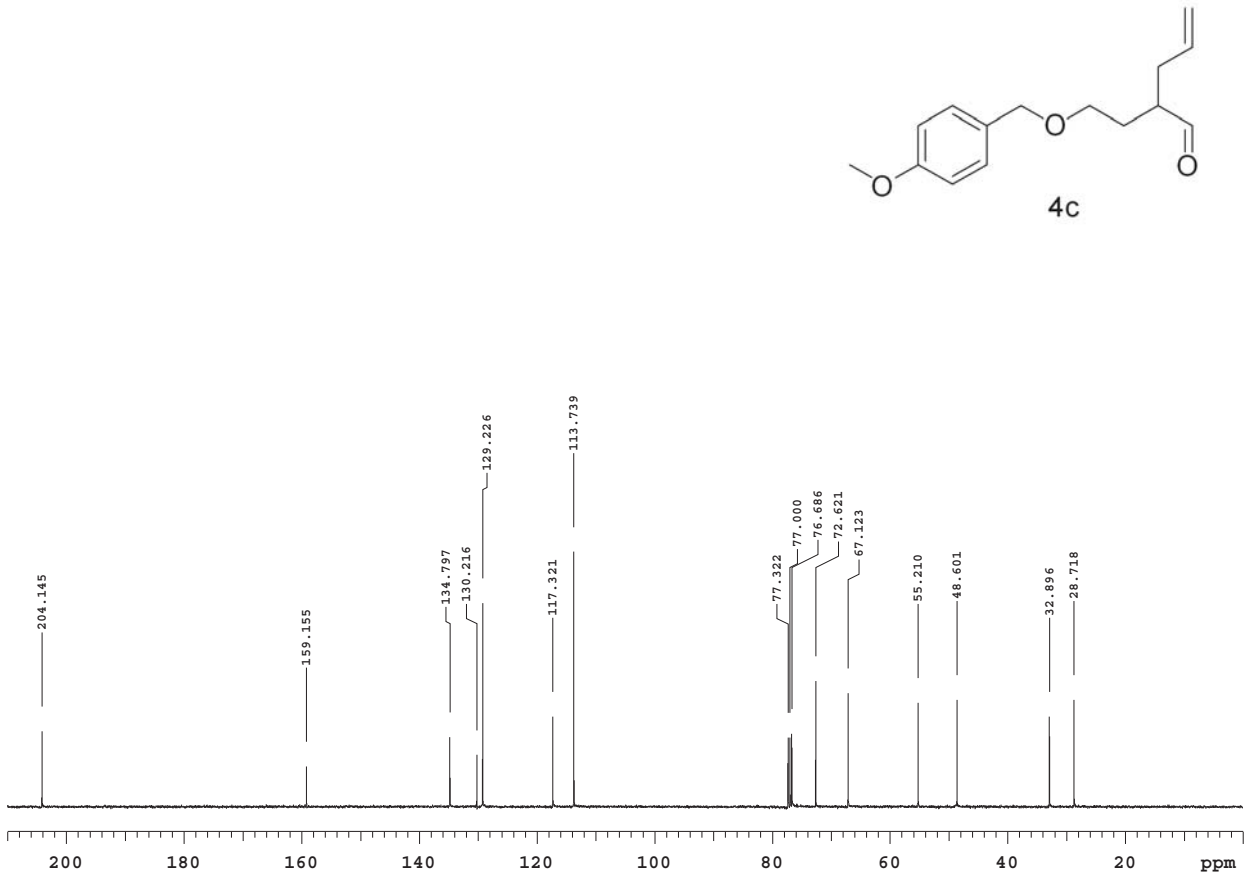
1.03
1.07
1.03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140
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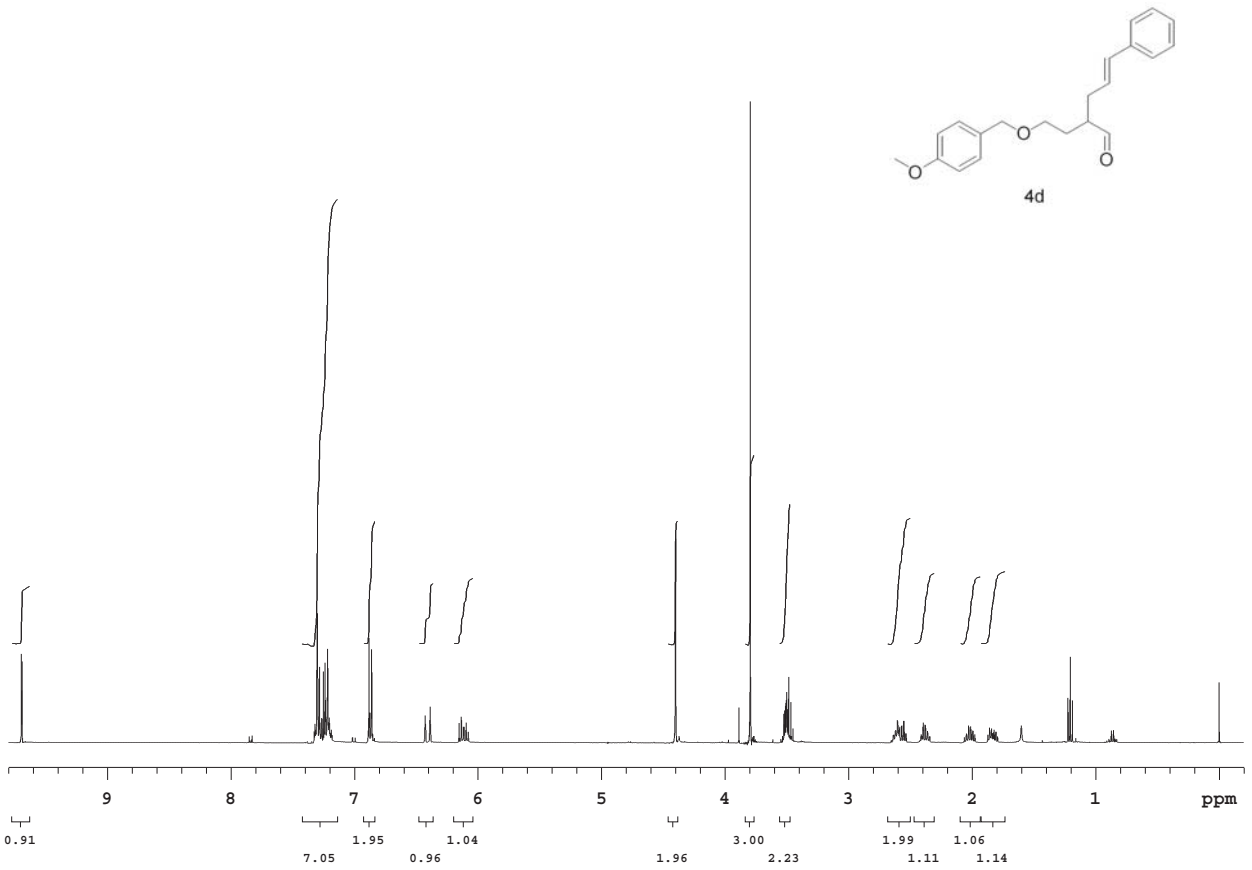
100
80
60
40
20
ppm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8
7
6
5
4
3
2
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0.96
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1.96
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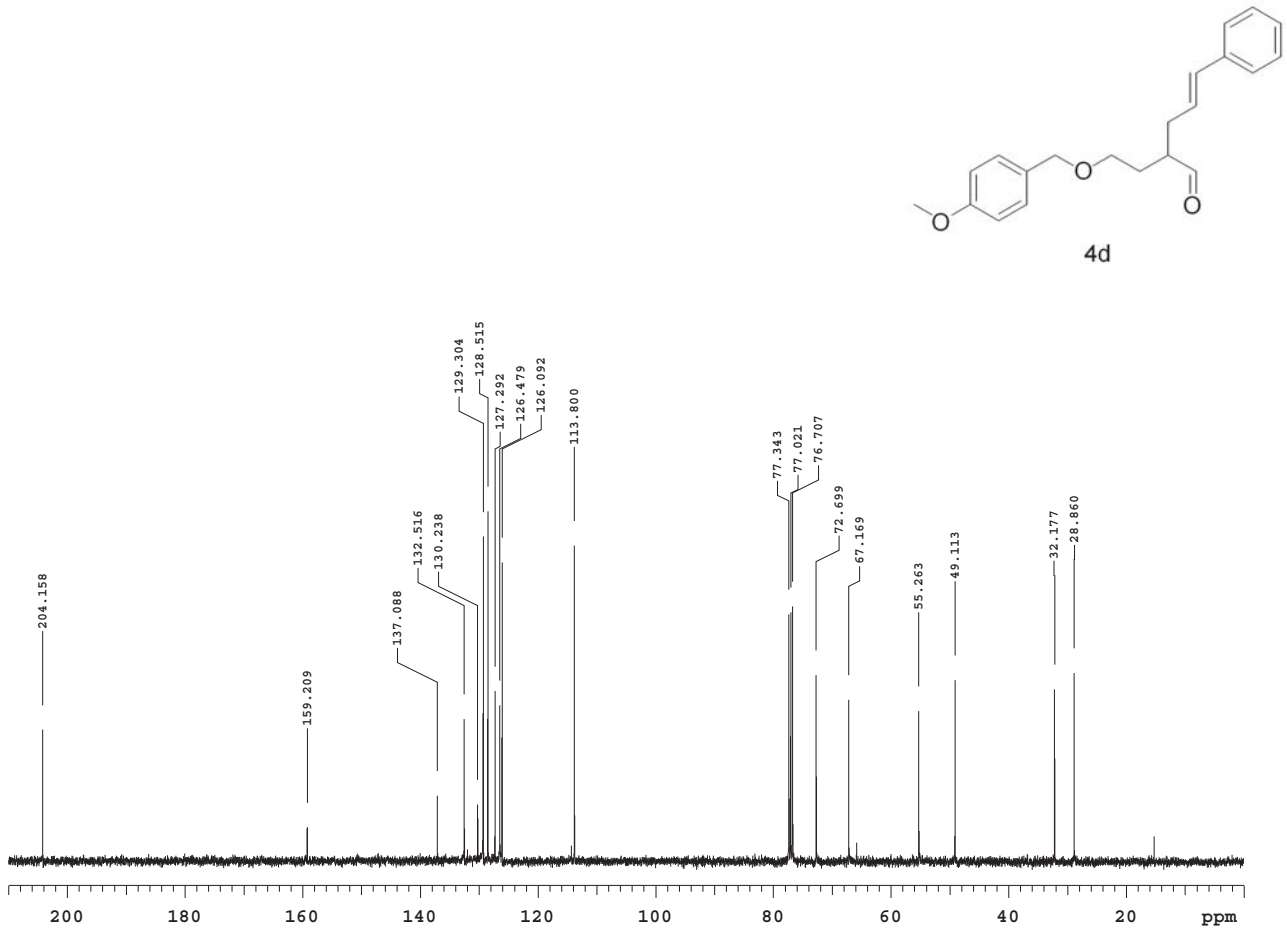
1.06
1.14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76.707
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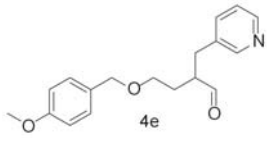
200
180
160
140
120
100
80
60
40
20
ppm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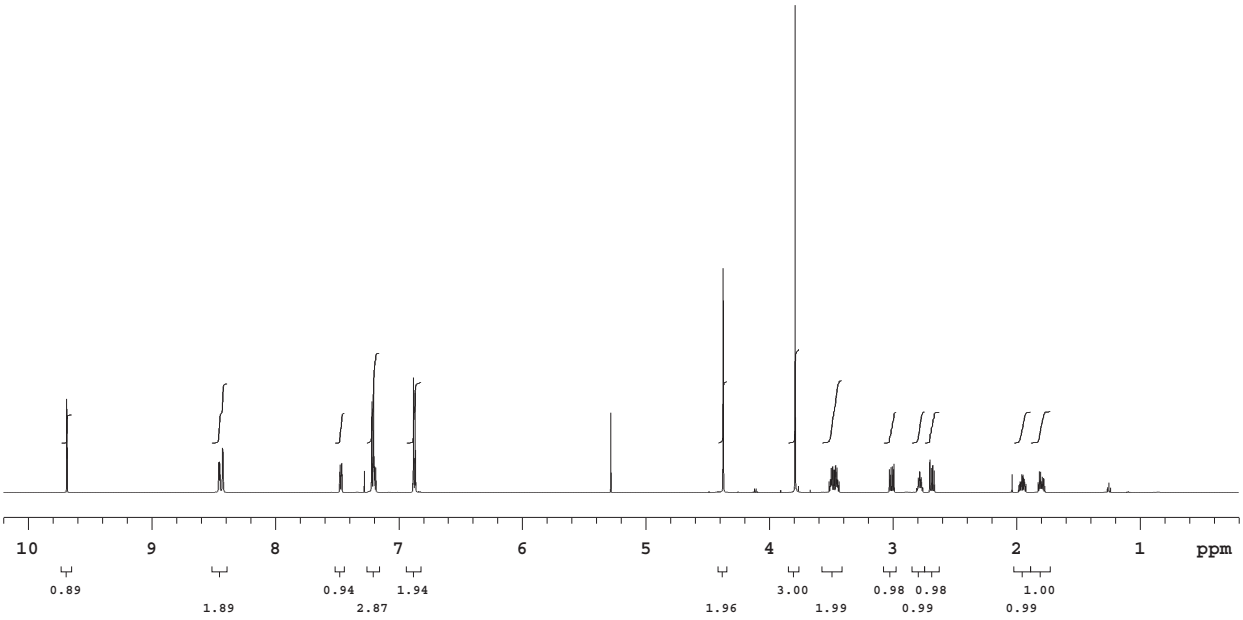
O
O
4e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8
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6
5
4
3
2
1
ppm
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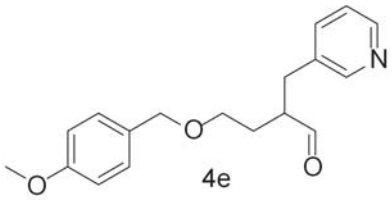
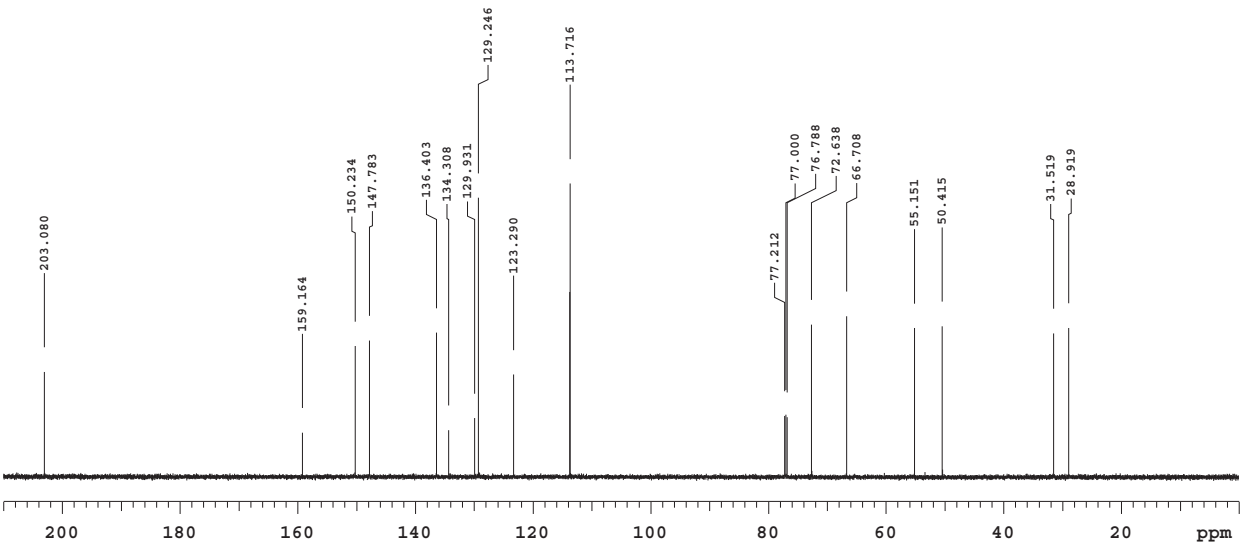
2.87
1.94
1.96
3.00
1.99
0.98
0.99
0.98
0.99
1.00
0.99


N
O
O
O
4e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76.788
72.638
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50.415
31.519
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140
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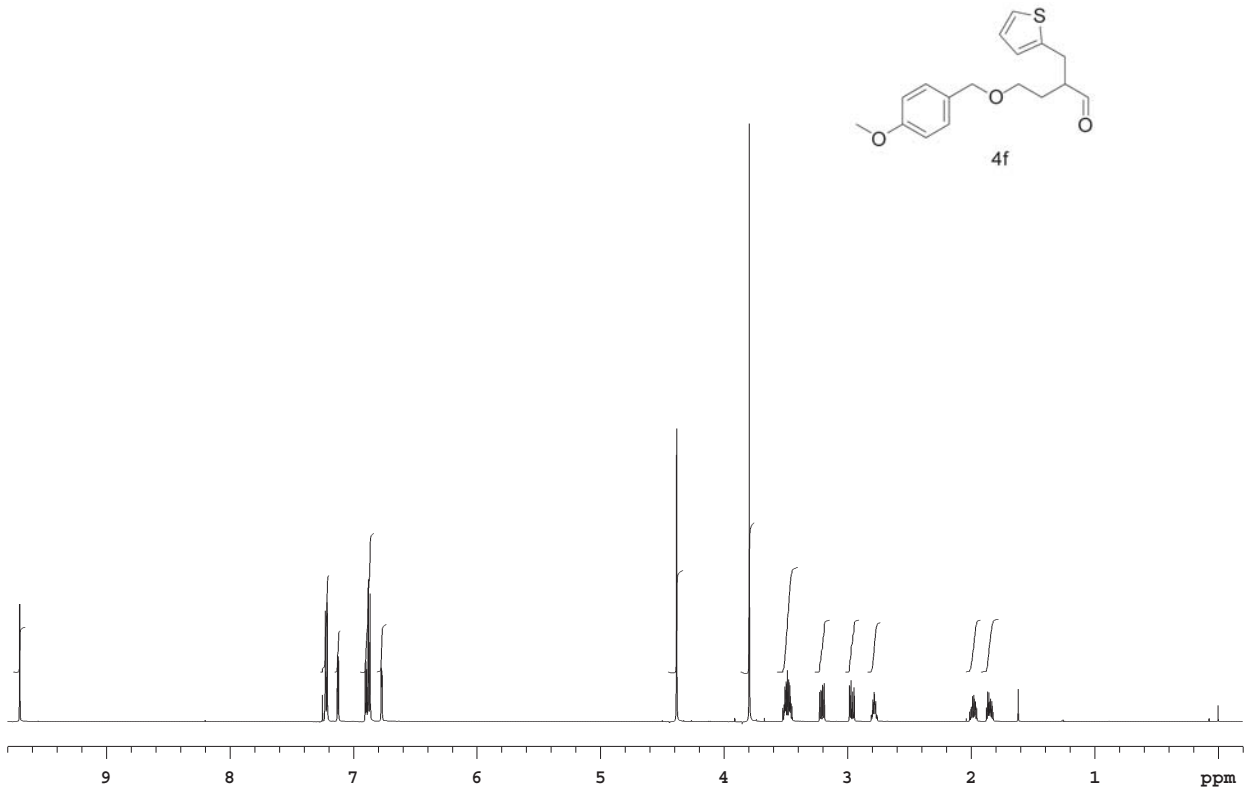
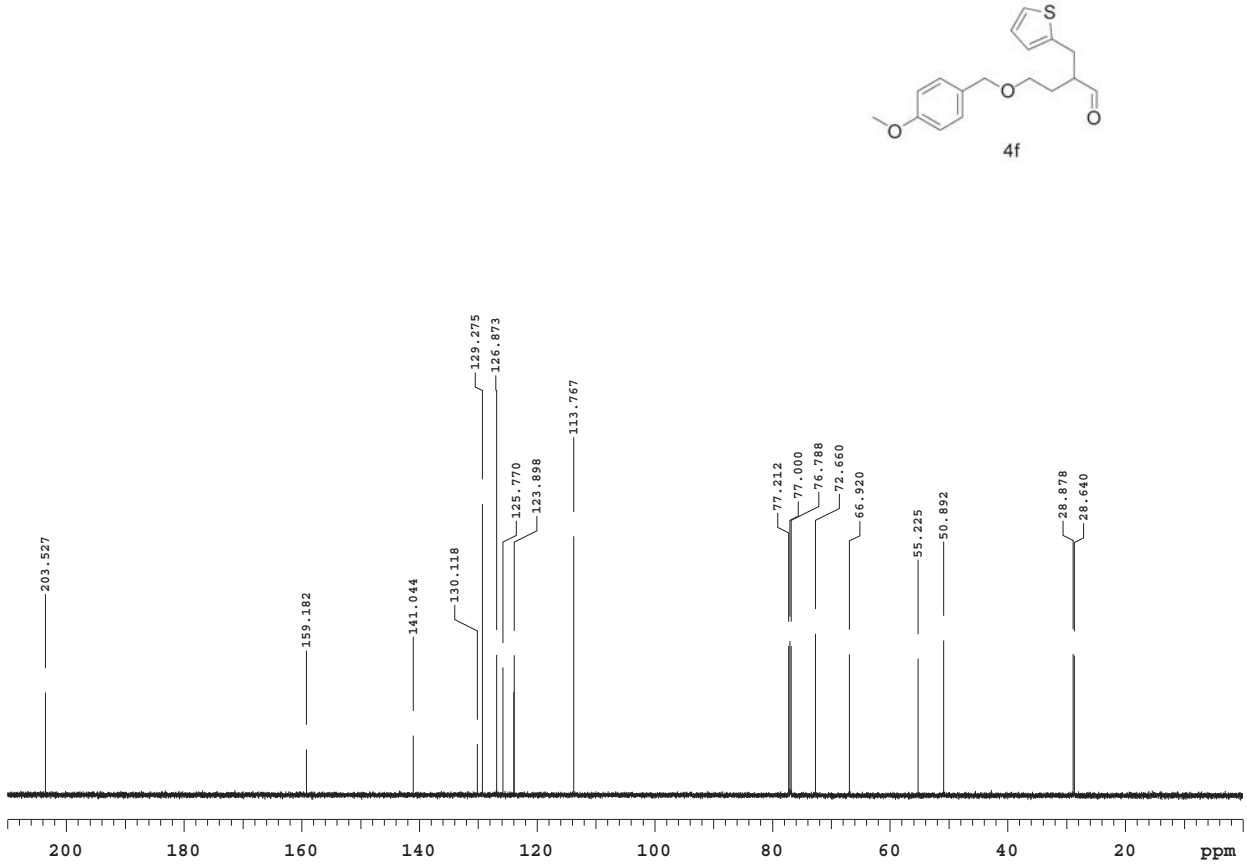
80
60
40
20
ppm


S
O
O
4f
9
8
7
6
5
4
3
2
1
ppm


S
O
O
4f
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123.898
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77.000
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72.660
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200
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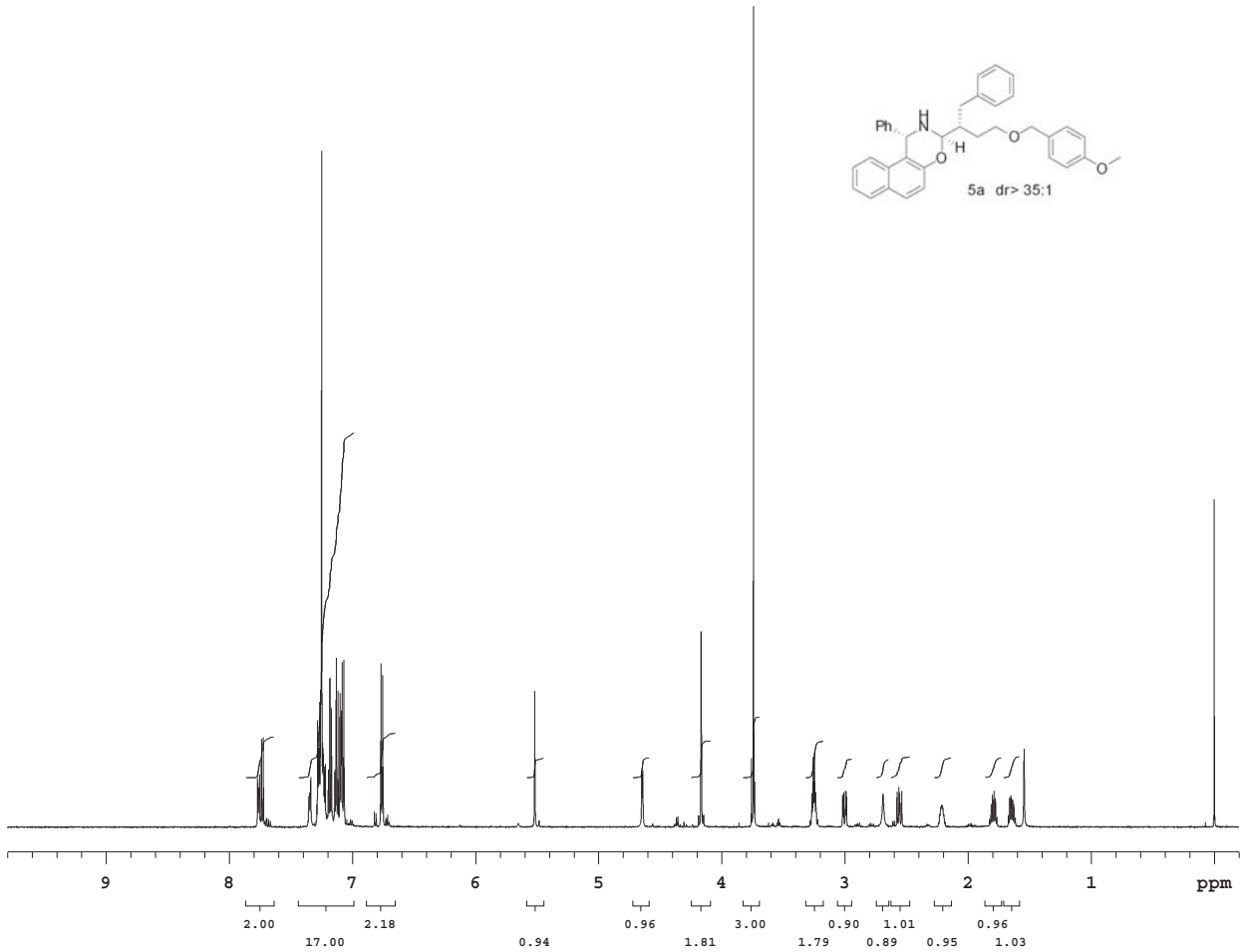
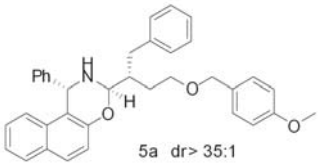
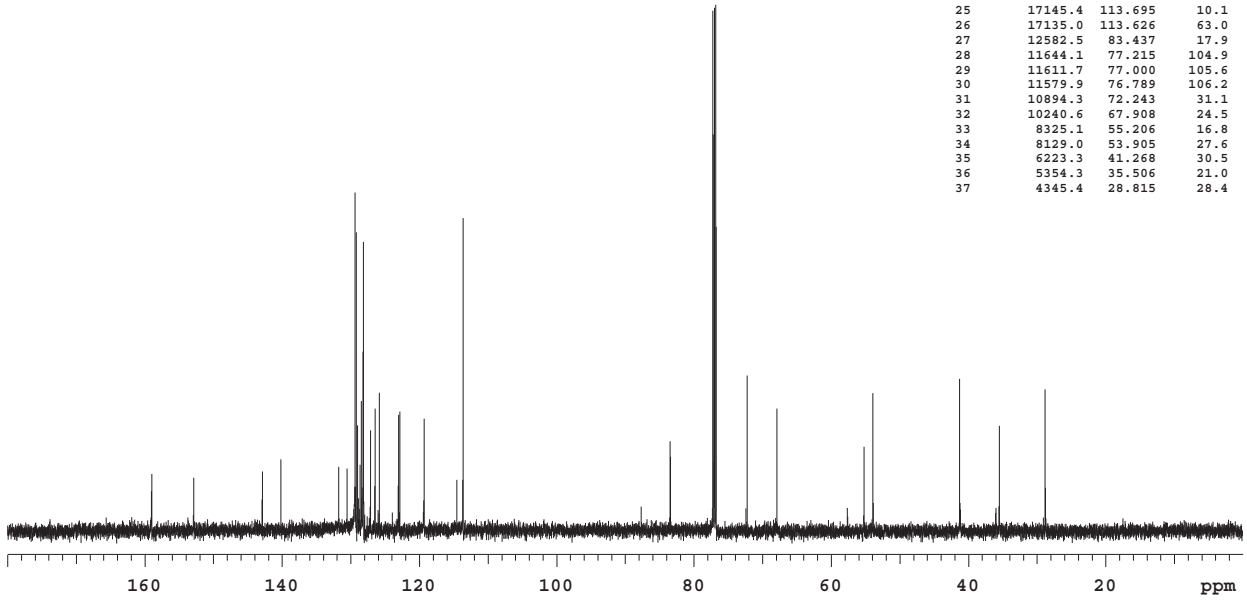
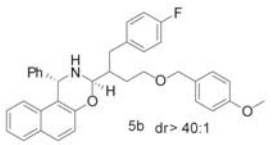
140
120
100
80
60
40
20
ppm

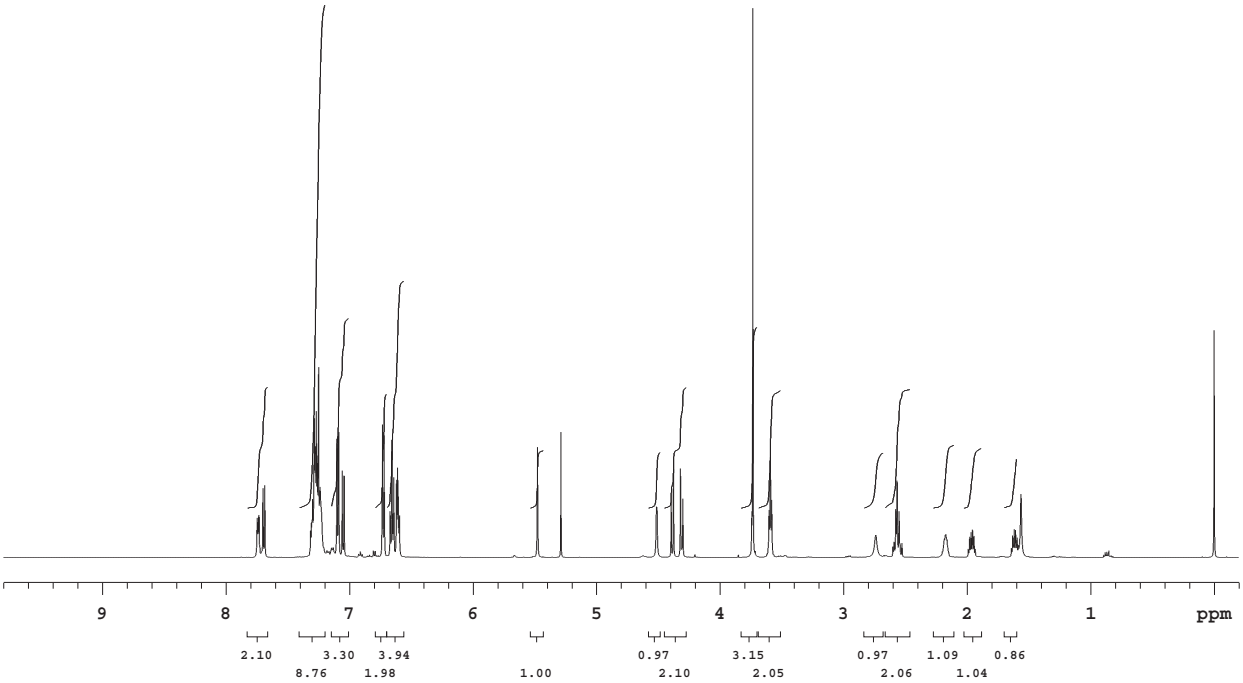


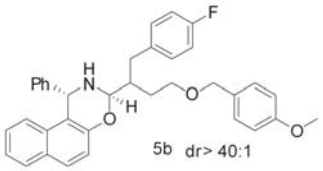


INDEX	FREQUENCY	PPM	HEIGHT
1	23977.3	158.999	11.3
2	23055.1	152.884	10.5
3	21546.3	142.878	11.8
4	21137.8	140.170	14.3
5	19866.8	131.741	12.7
6	19681.1	130.510	12.4
7	19508.7	129.367	64.4
8	19506.4	129.351	68.2
9	19498.3	129.298	8.6
10	19479.8	129.175	60.1
11	19451.4	128.987	21.1
12	19434.1	128.872	6.3
13	19398.2	128.634	13.2
14	19367.0	128.427	26.0
15	19349.6	128.312	8.5
16	19329.3	128.177	58.2
17	19321.8	128.127	47.6
18	19170.2	127.122	20.1
19	19070.2	126.459	24.5
20	18976.4	125.837	27.7
21	18554.7	123.040	23.2
22	18525.8	122.849	23.9
23	17992.4	119.311	22.4
24	17269.8	114.520	10.1
25	17145.4	113.695	10.1
26	17135.0	113.626	63.0
27	12582.5	83.437	17.9
28	11644.1	77.215	104.9
29	11611.7	77.000	105.6
30	11579.9	76.789	106.2
31	10894.3	72.243	31.1
32	10240.6	67.908	24.5
33	8325.1	55.206	16.8
34	8129.0	53.905	27.6
35	6223.3	41.268	30.5
36	5354.3	35.506	21.0
37	4345.4	28.815	28.4









INDEX	FREQUENCY	PPM	HEIGHT
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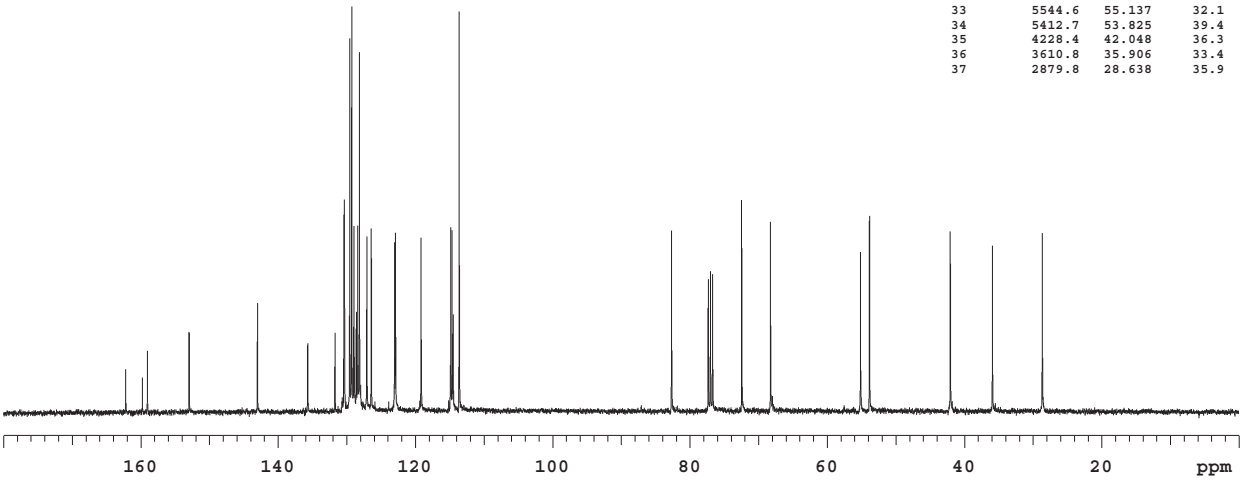
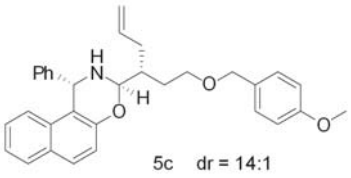
2	16066.3	159.767	6.7
3	15992.7	159.034	12.1
4	15381.5	152.957	15.9
5	14380.2	142.999	21.7
6	13646.0	135.698	13.2
7	13643.5	135.674	13.6
8	13243.7	131.698	15.7
9	13114.1	130.410	39.7
10	13109.3	130.361	30.7
11	13106.0	130.329	42.7
12	13028.3	129.556	75.3
13	12999.2	129.267	81.7
14	12967.6	128.953	37.4
15	12932.0	128.598	20.0
16	12911.0	128.389	37.4
17	12886.7	128.148	72.5
18	12777.4	127.061	35.3
19	12711.8	126.409	36.8
20	12369.4	123.004	34.0
21	12357.3	122.883	36.0
22	11981.7	119.148	35.0
23	11548.6	114.842	37.1
24	11527.5	114.632	36.5
25	11510.5	114.463	19.5
26	11423.1	113.594	80.7
27	8312.3	82.659	36.4
28	7775.6	77.322	26.6
29	7743.2	77.000	28.2
30	7711.6	76.686	27.6
31	7285.0	72.444	42.6
32	6862.5	68.242	38.2
33	5544.6	55.137	32.1
34	5412.7	53.825	39.4
35	4228.4	42.048	36.3
36	3610.8	35.906	33.4
37	2879.8	28.638	35.9





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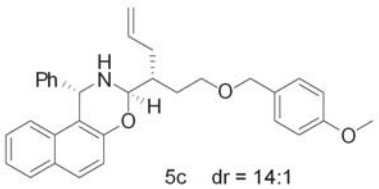

5c dr = 14:1

INDEX	FREQUENCY	PPM	HEIGHT
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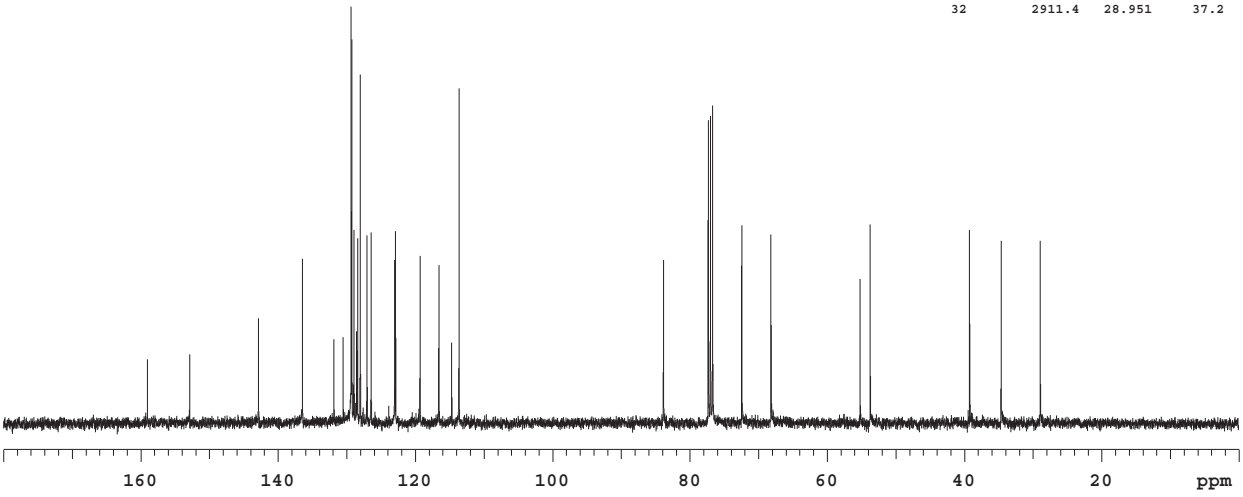
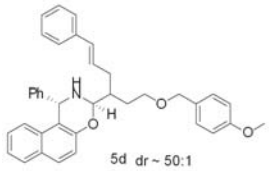
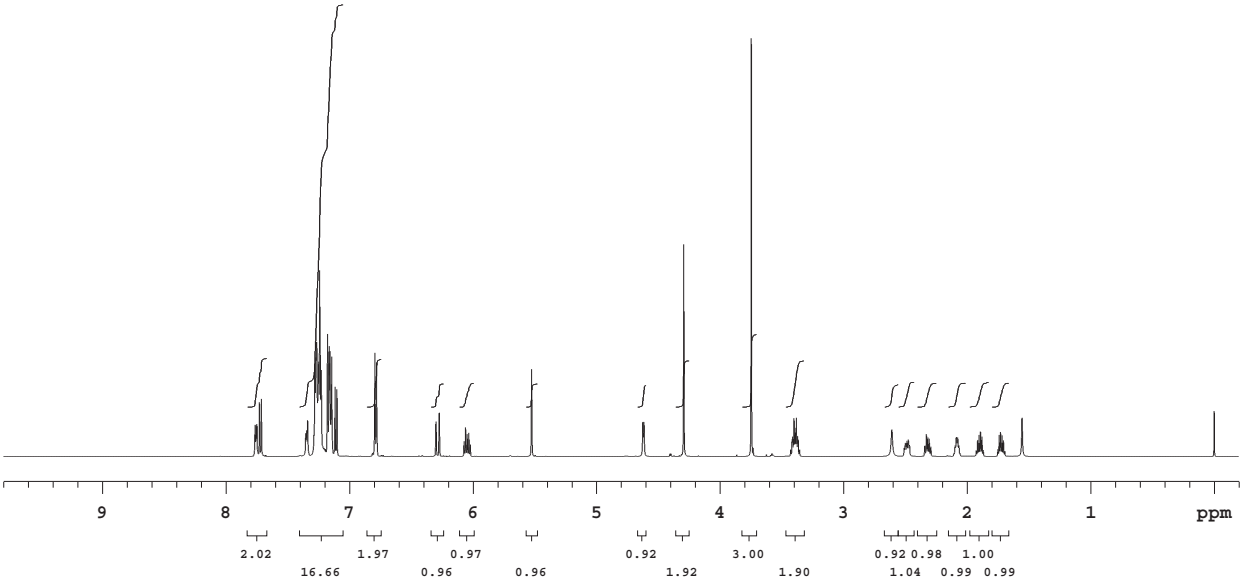
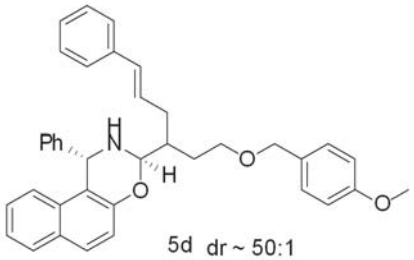
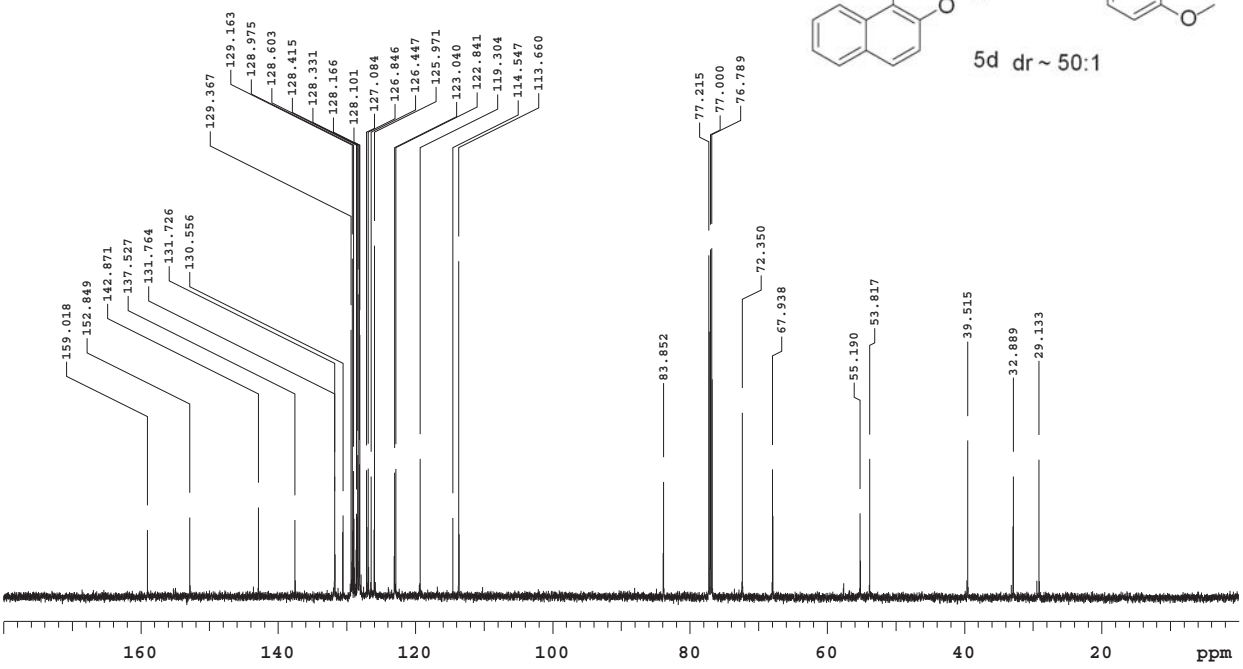
4	13720.4	136.439	33.6
5	13259.0	131.851	17.3
6	13123.9	130.506	17.7
7	13006.5	129.339	84.5
8	12995.1	129.226	77.9
9	12966.8	128.945	39.4
10	12929.6	128.574	18.9
11	12912.6	128.405	37.7
12	12872.9	128.011	70.8
13	12774.2	127.029	38.3
14	12714.3	126.433	38.9
15	12368.6	122.996	33.2
16	12355.7	122.867	39.1
17	11997.0	119.301	34.1
18	11722.6	116.572	32.2
19	11533.2	114.689	16.6
20	11432.0	113.682	10.0
21	11426.4	113.626	68.1
22	8431.3	83.842	33.3
23	7775.6	77.322	61.6
24	7743.2	77.000	62.4
25	7711.6	76.686	64.5
26	7284.2	72.436	40.3
27	6856.0	68.178	38.4
28	5549.5	55.185	29.5
29	5402.2	53.720	40.4
30	3945.9	39.239	39.3
31	3484.5	34.651	37.2
32	2911.4	28.951	37.2

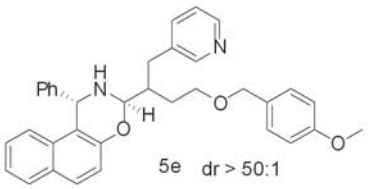


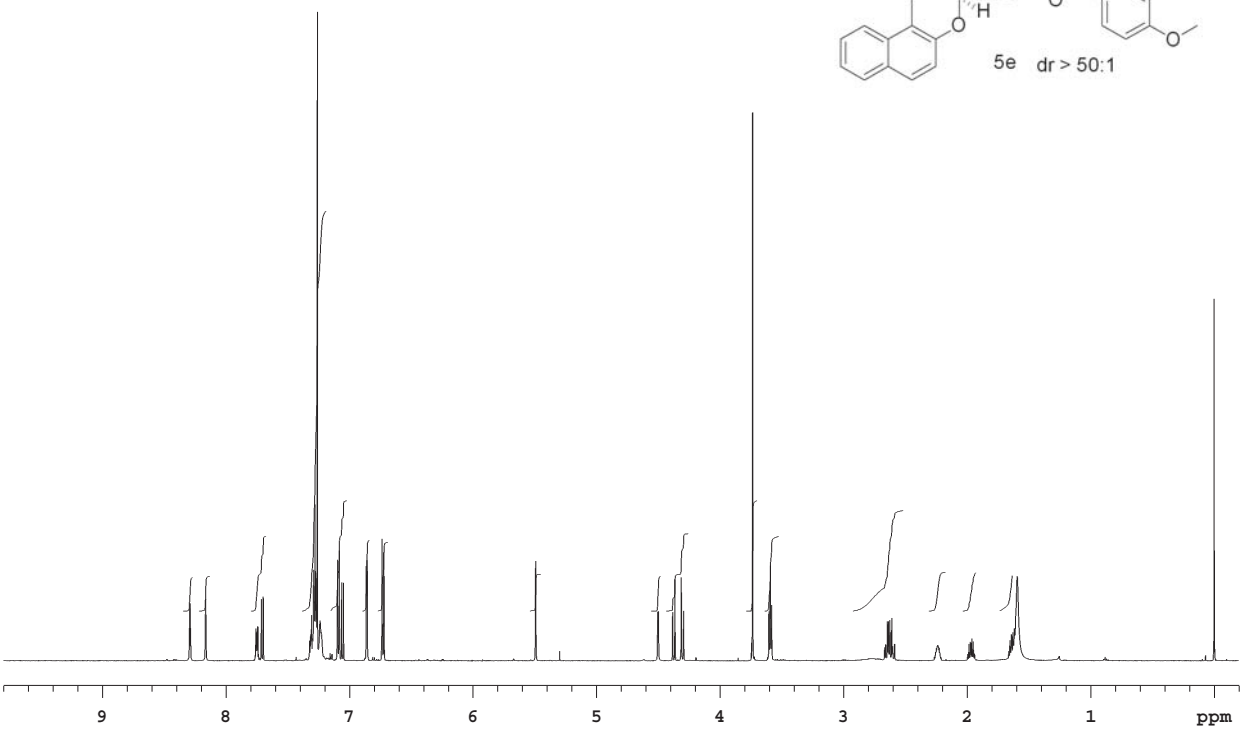

Ph
N
H
O
O
O
5d dr ~ 50:1

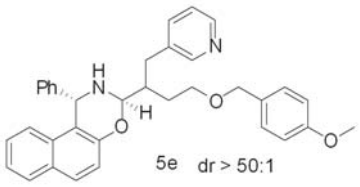

9
8
7
6
5
4
3
2
1
ppm
2.02
16.66
1.97
0.96
0.97
0.96
0.92
1.92
3.00
1.90
0.92
1.04
0.98
0.99
1.00
0.99


Ph
N
H
O
O
O
5d dr ~ 50:1

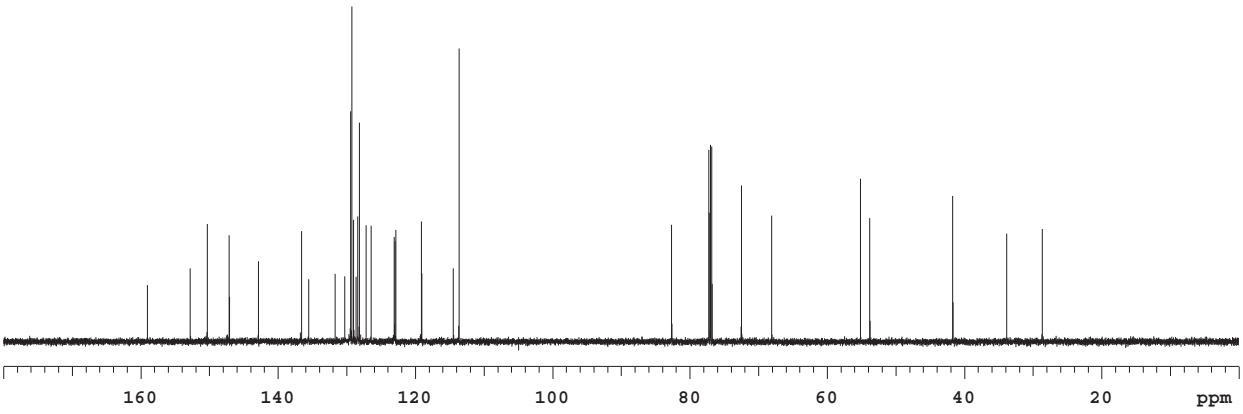

159.018
152.849
142.871
137.527
131.764
131.726
130.556
129.367
129.163
128.975
128.603
128.415
128.331
128.166
128.101
127.084
126.846
126.447
125.971
123.040
122.841
119.304
114.547
113.660
83.852
77.215
77.000
76.789
72.350
67.938
55.190
53.817
39.515
32.889
29.133
160
140
120
100
80
60
40
20
ppm

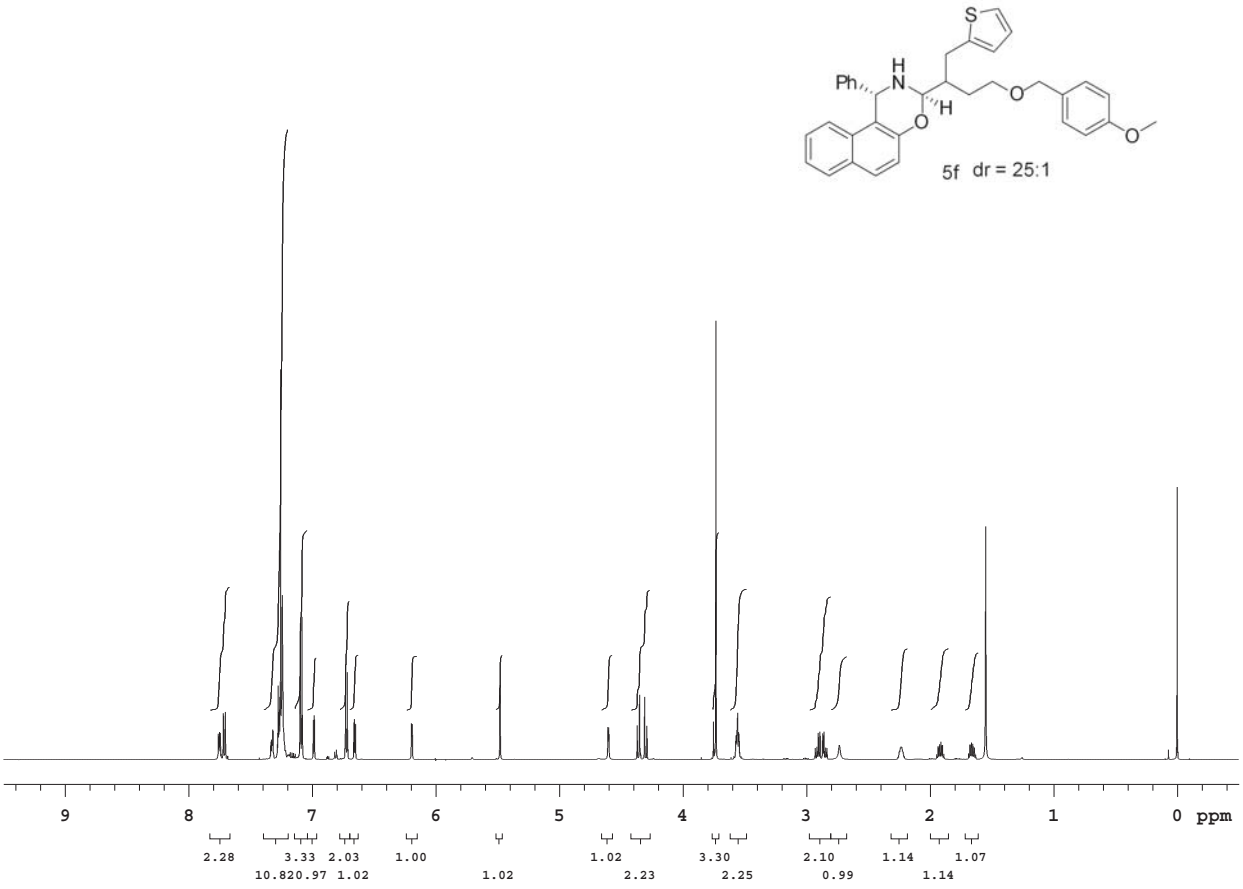


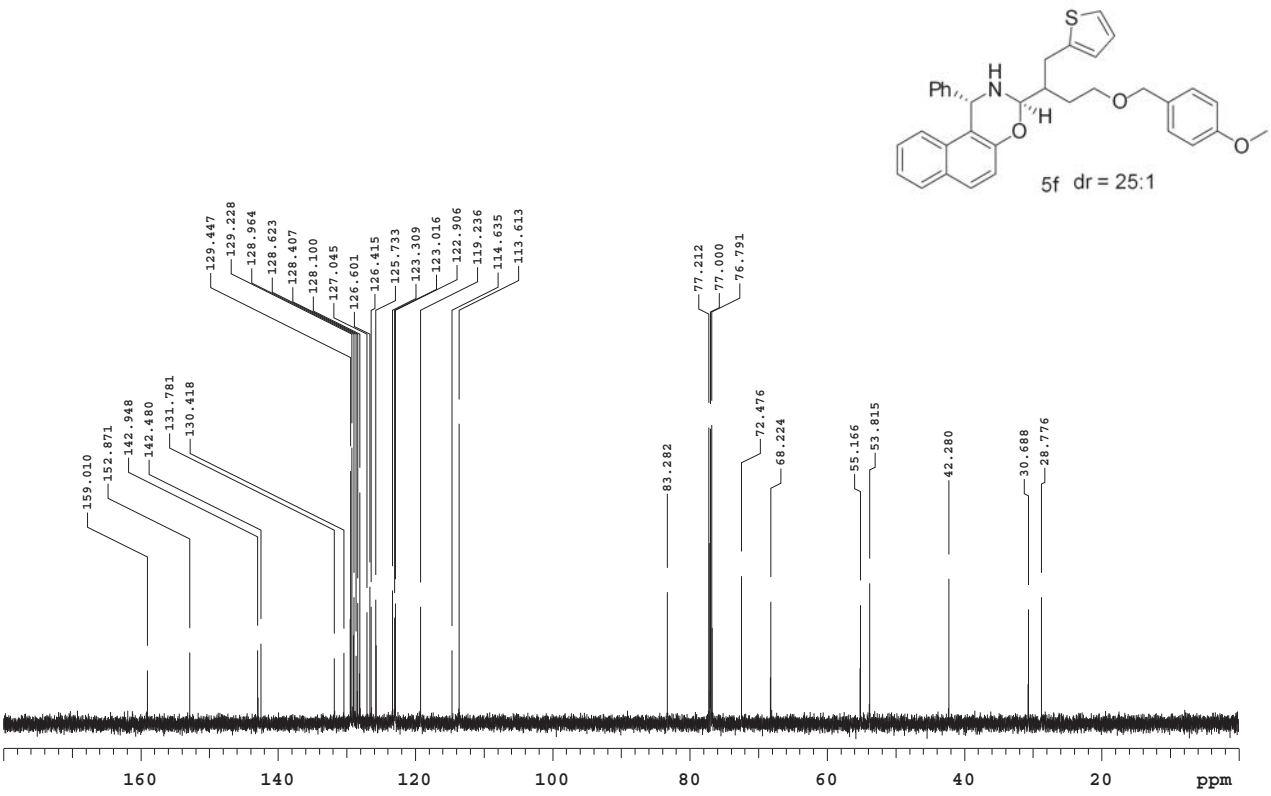


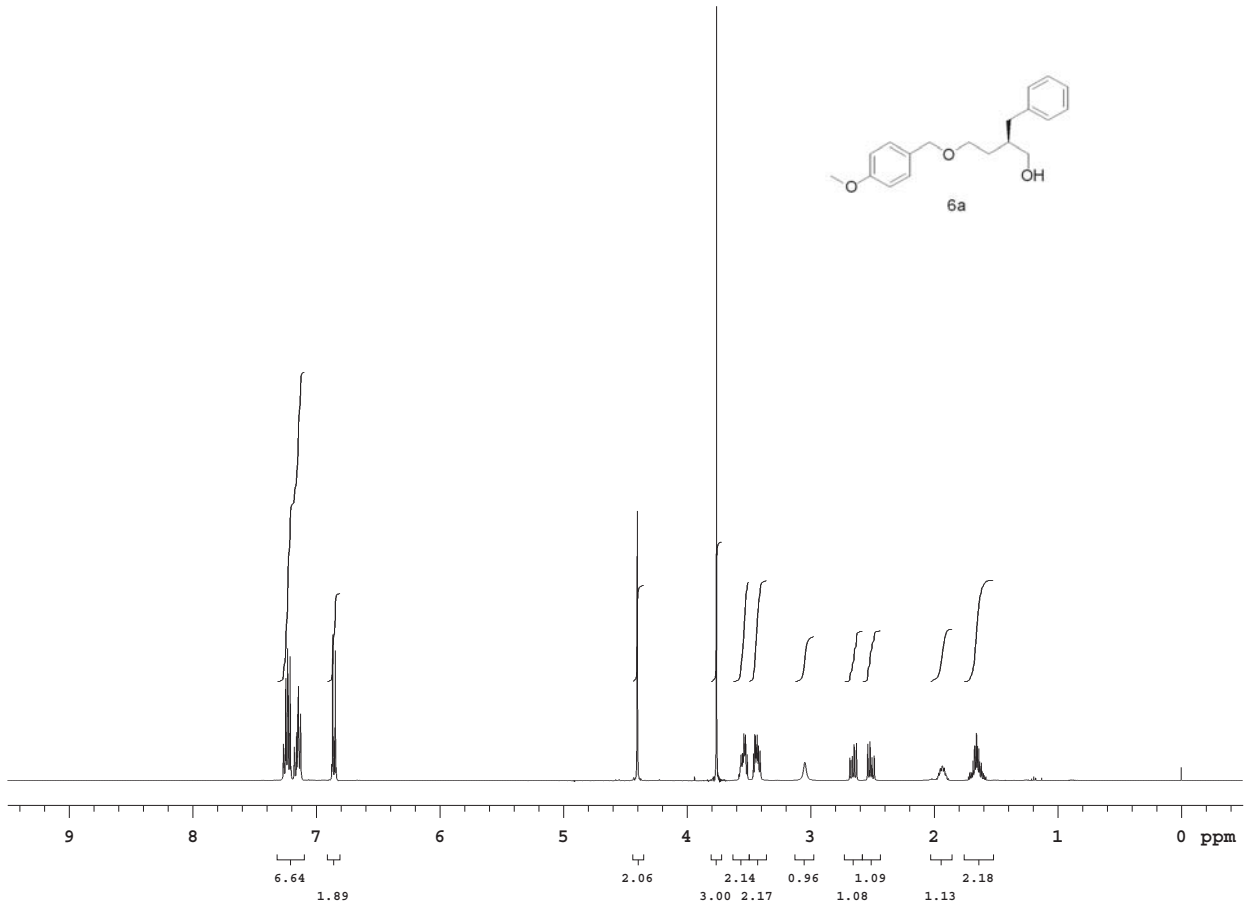


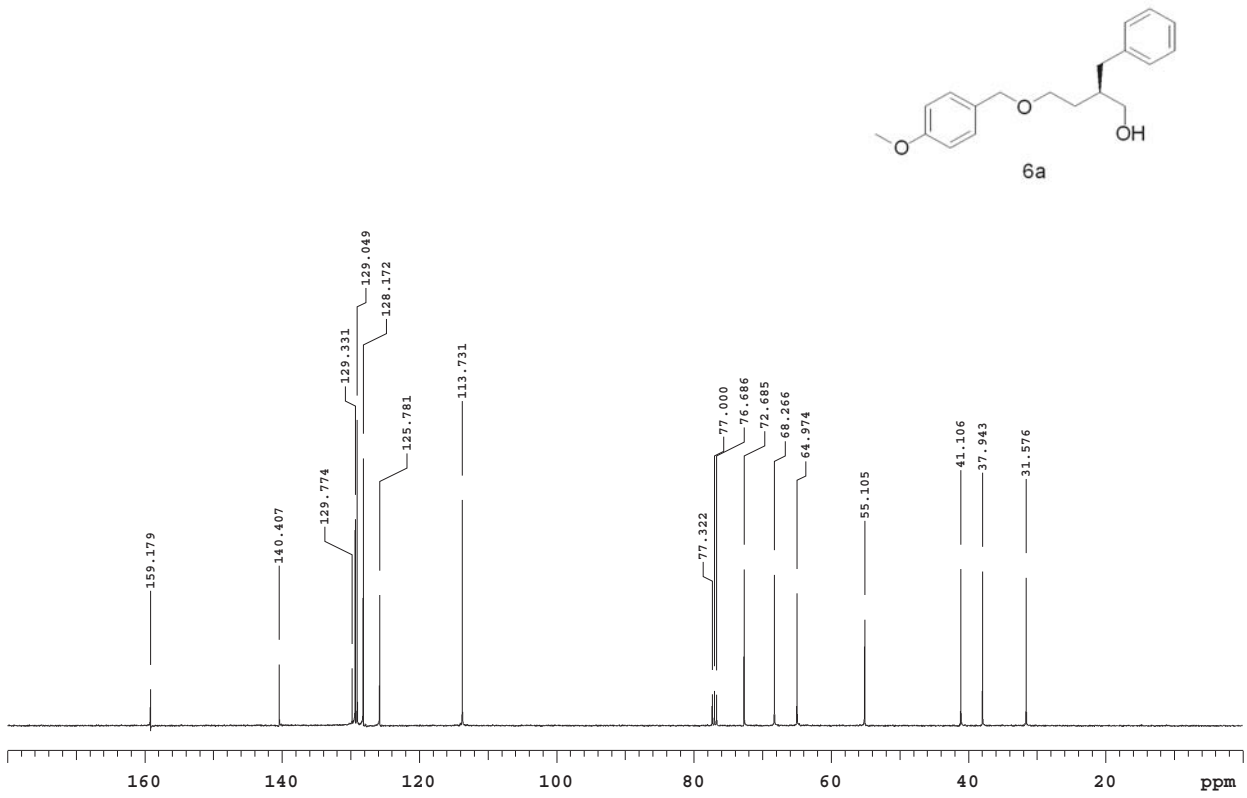
INDEX	FREQUENCY	PPM	HEIGHT
1	23982.3	159.032	11.5
2	23038.8	152.776	14.9
3	22667.7	150.314	23.8
4	22182.7	147.098	21.5
5	21545.3	142.872	16.2
6	20594.1	136.564	22.4
7	20436.7	135.520	12.7
8	19856.2	131.671	13.7
9	19642.4	130.253	13.2
10	19518.7	129.433	46.6
11	19491.6	129.253	67.8
12	19454.1	129.004	24.7
13	19396.6	128.623	13.1
14	19361.3	128.389	25.4
15	19325.9	128.154	44.3
16	19176.2	127.162	23.6
17	19065.2	126.426	23.5
18	18556.5	123.052	21.2
19	18543.8	122.968	20.3
20	18525.0	122.843	22.6
21	17957.7	119.082	24.3
22	17258.4	114.445	14.9
23	17132.0	113.606	59.3
24	12463.5	82.648	23.6
25	11643.8	77.212	38.8
26	11611.7	77.000	39.8
27	11579.7	76.788	39.5
28	10932.9	72.498	31.6
29	10264.0	68.063	25.5
30	8314.2	55.133	32.9
31	8109.8	53.778	25.0
32	6286.5	41.687	29.5
33	5103.9	33.845	21.9
34	4322.9	28.666	22.8

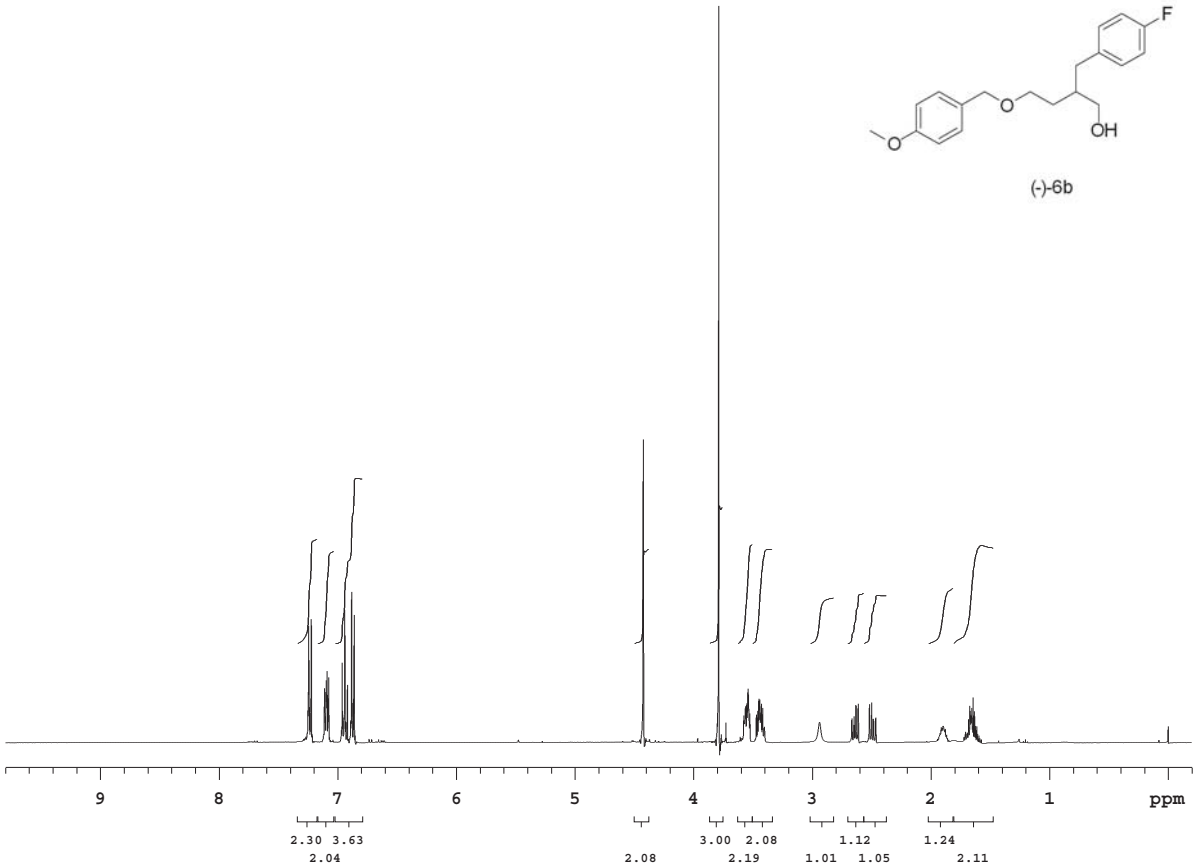


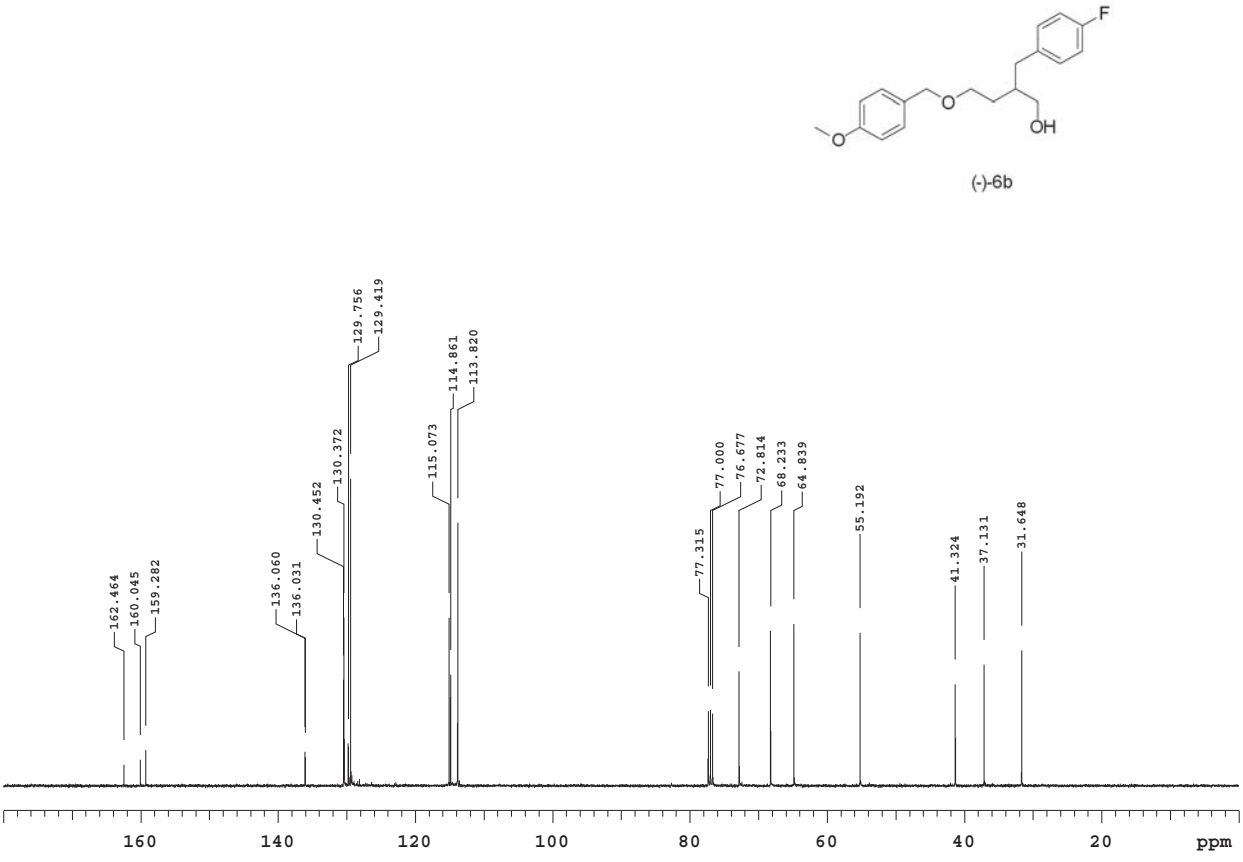

S
H
N
Ph
O
H
O
O
5f dr = 25:1
9
8
7
6
5
4
3
2
1
0 ppm
2.28
3.33
2.03
1.00
1.02
1.02
2.23
3.30
2.25
2.10
0.99
1.14
1.14
1.07
10.82
0.97
1.02

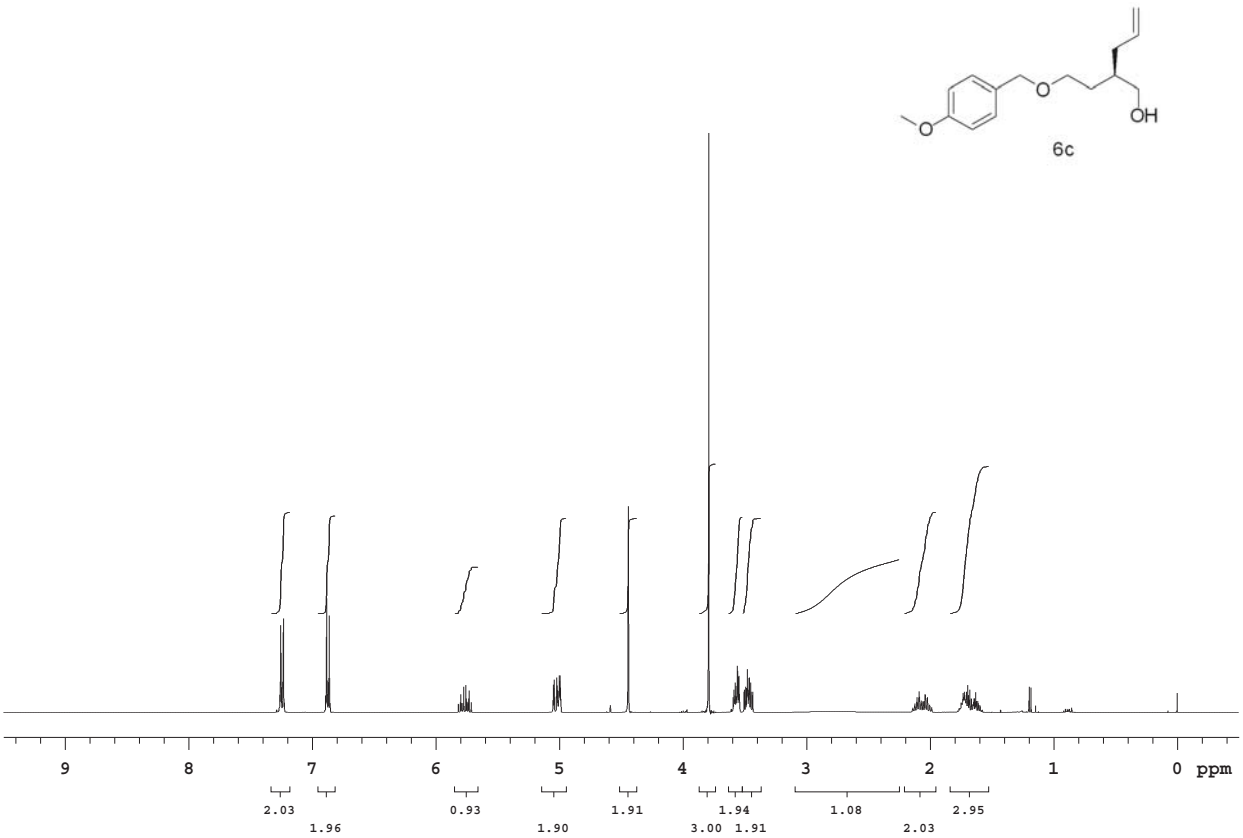

S
H
N
Ph
O
H
O
O
5f dr = 25:1
129.447
129.228
128.964
128.623
128.407
128.100
127.045
126.601
126.415
125.733
123.309
123.016
122.906
119.236
114.635
113.613
77.212
77.000
76.791
159.010
152.871
142.948
142.480
131.781
130.418
83.282
72.476
68.224
55.166
53.815
42.280
30.688
28.776
160
140
120
100
80
60
40
20
ppm

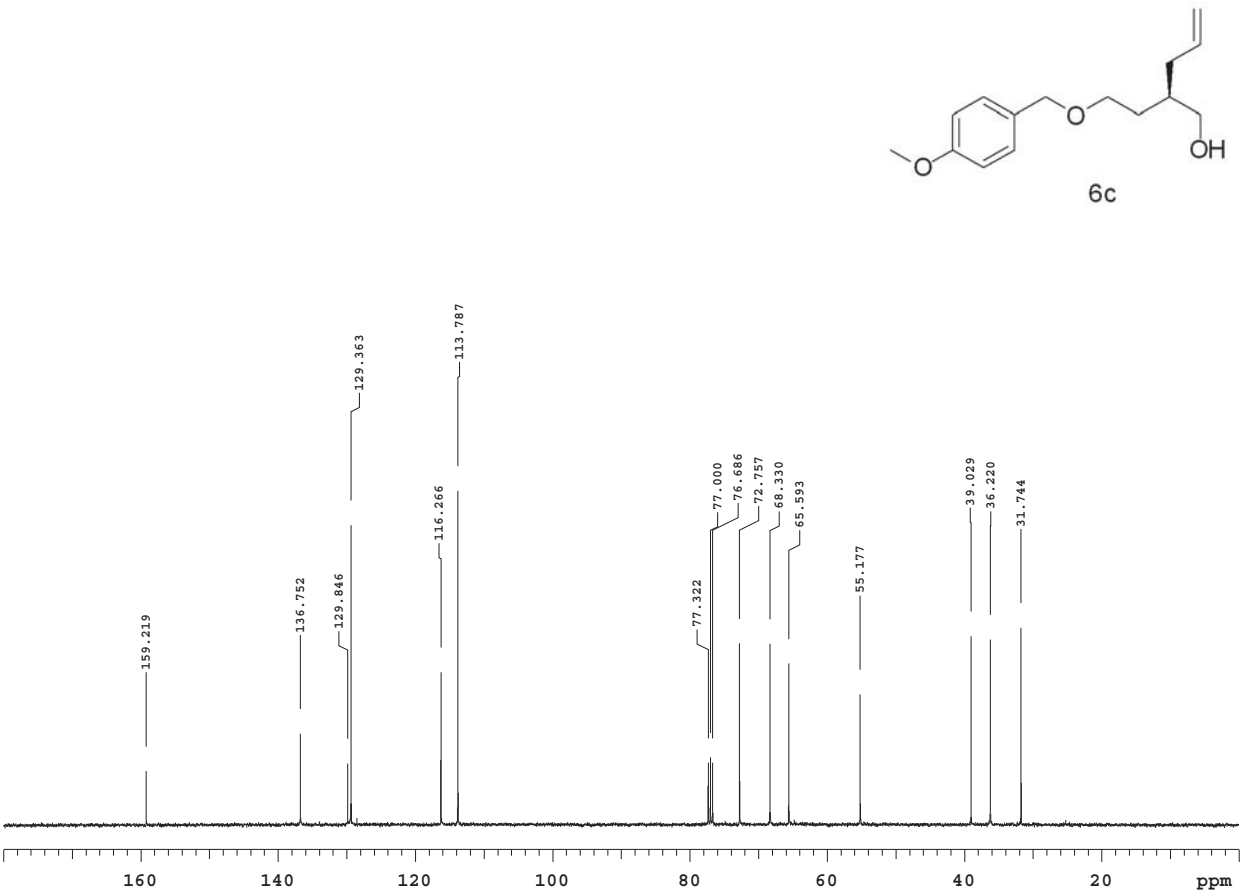

OH
6a
9
8
7
6
5
4
3
2
1
0 ppm
6.64
1.89
2.06
3.00
2.14
2.17
0.96
1.09
1.08
2.18
1.13

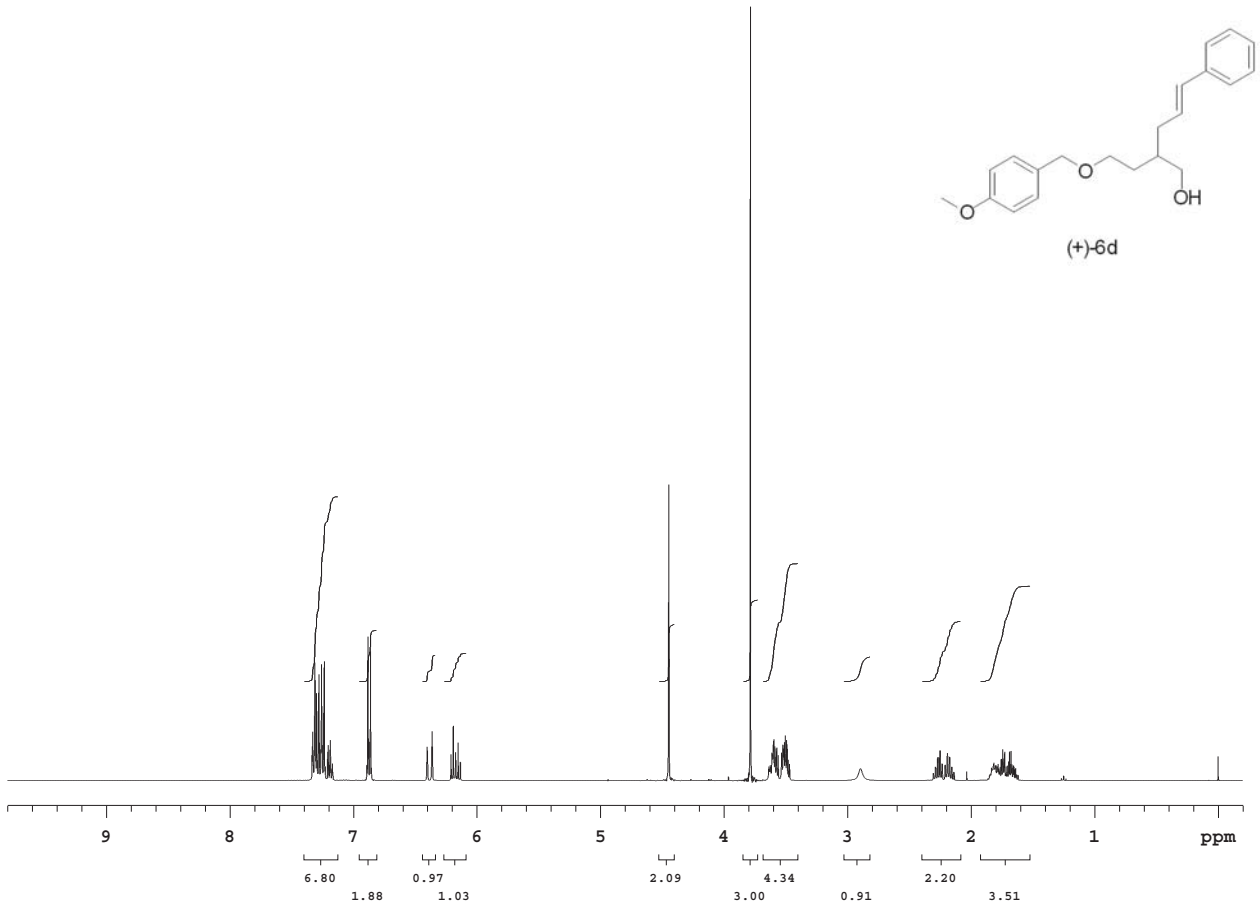

OH
6a
159.179
140.407
129.774
129.331
129.049
128.172
125.781
113.731
77.322
77.000
76.686
72.685
68.266
64.974
55.105
41.106
37.943
31.576
160
140
120
100
80
60
40
20
ppm

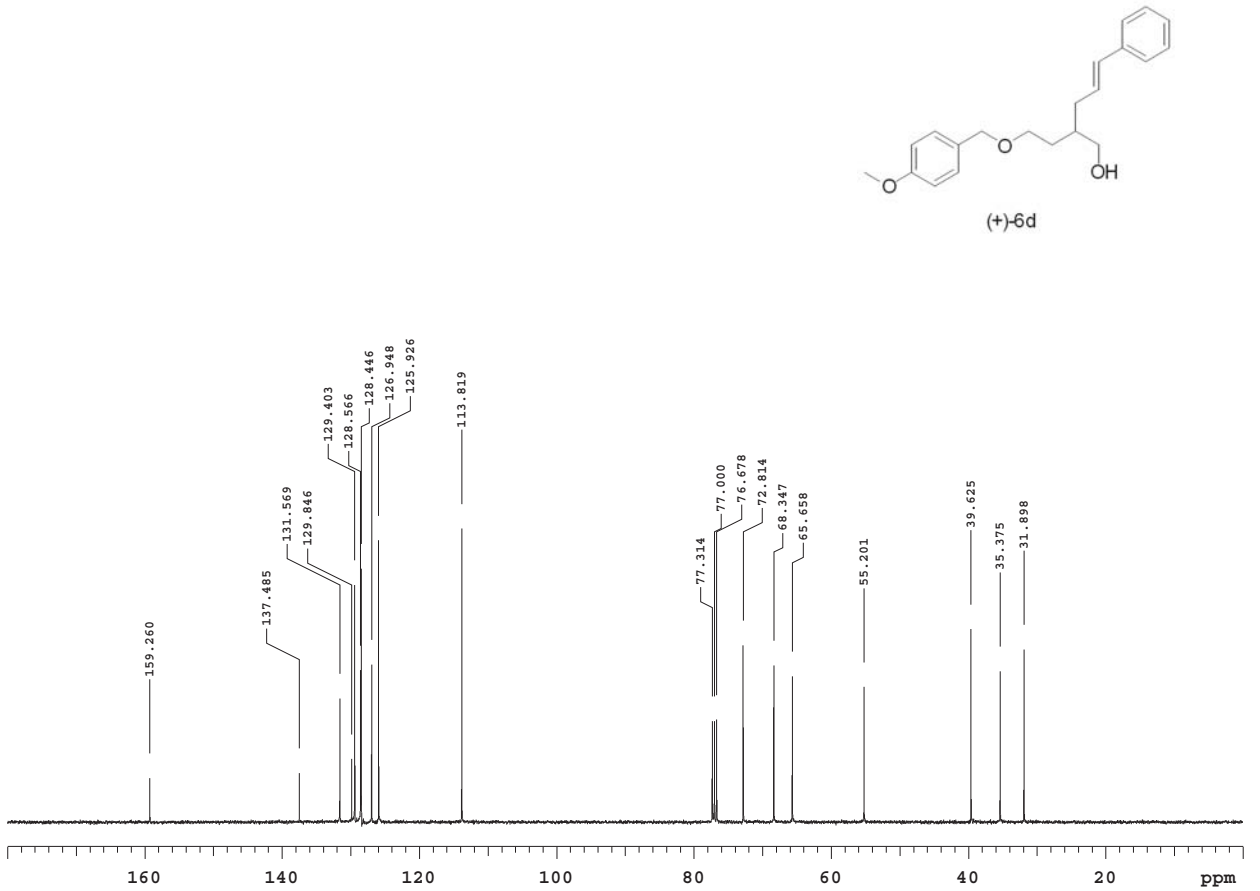

F
O
O
OH
(-)-6b
9
8
7
6
5
4
3
2
1
ppm
2.30 3.63
2.04
2.08
3.00 2.08
2.19
1.12
1.01 1.05
1.24
2.11

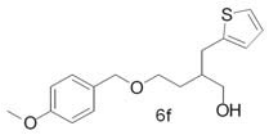

F
O
O
OH
(-)-6b
162.464
160.045
159.282
136.060
136.031
130.452
130.372
129.756
129.419
115.073
114.861
113.820
77.315
77.000
76.677
72.814
68.233
64.839
55.192
41.324
37.131
31.648
160
140
120
100
80
60
40
20
ppm

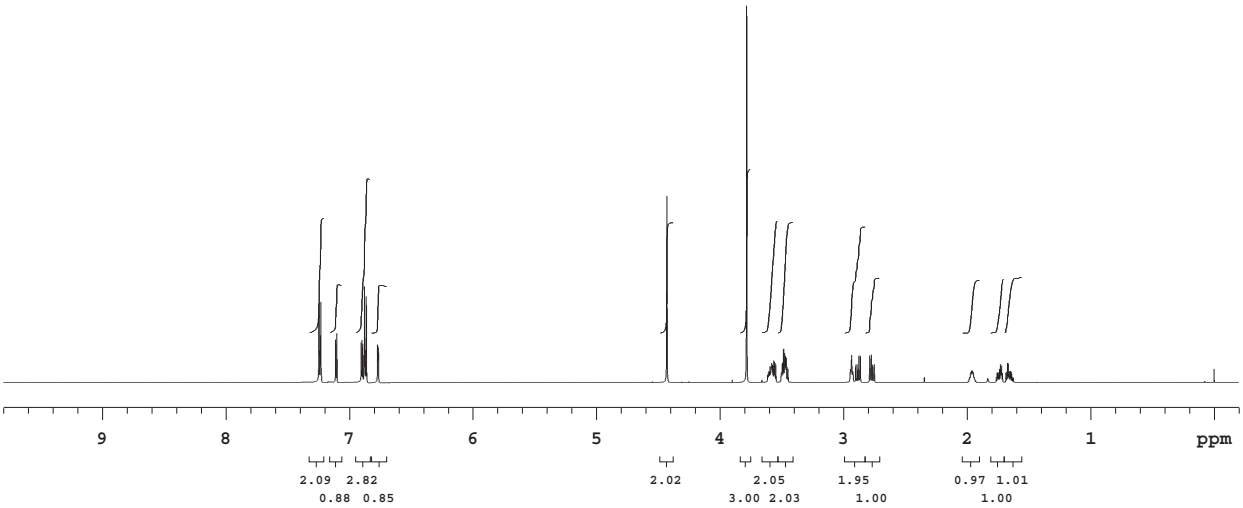

O
OH
O
6c
9
8
7
6
5
4
3
2
1
0 ppm
2.03
1.96
0.93
1.90
1.91
3.00
1.94
1.91
1.08
2.03
2.95

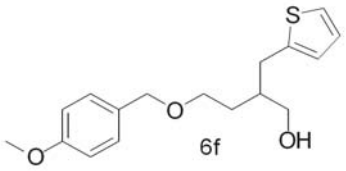

O
OH
O
6c
159.219
136.752
129.846
129.363
116.266
113.787
77.322
77.000
76.686
72.757
68.330
65.593
55.177
39.029
36.220
31.744
160
140
120
100
80
60
40
20
ppm

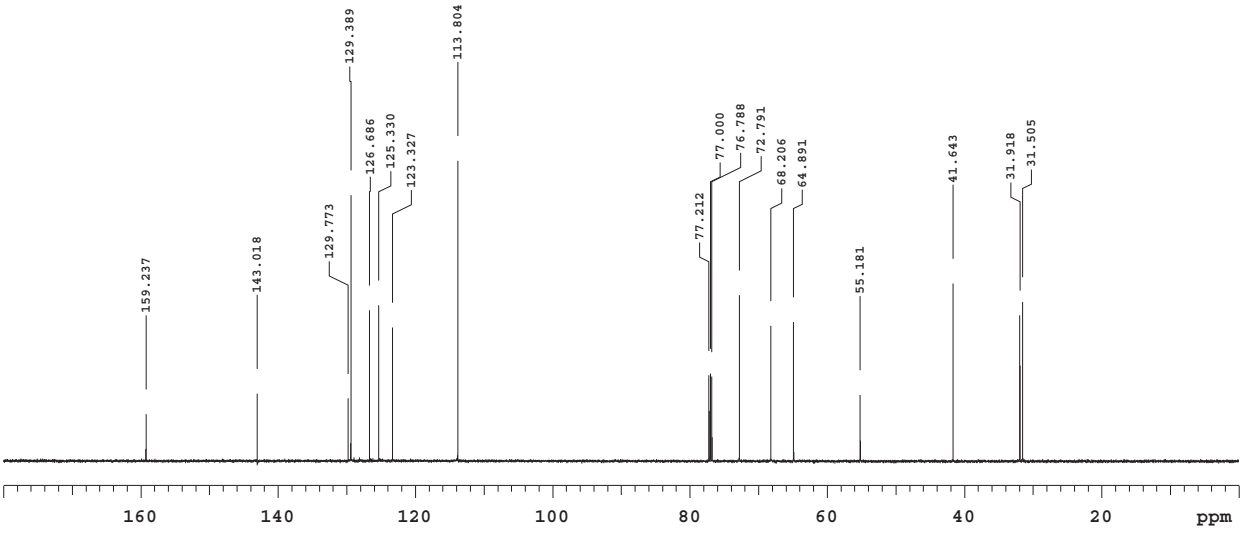

O
OH
O
(+)-6d
9
8
7
6
5
4
3
2
1
ppm
6.80
1.88
0.97
1.03
2.09
4.34
3.00
0.91
2.20
3.51

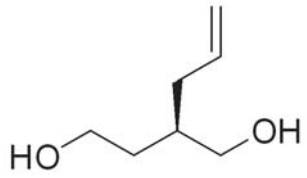

O
OH
O
(+)-6d
159.260
137.485
131.569
129.846
129.403
128.566
128.446
126.948
125.926
113.819
77.314
77.000
76.678
72.814
68.347
65.658
55.201
39.625
35.375
31.898
160
140
120
100
80
60
40
20
ppm


S
O
6f
OH
O

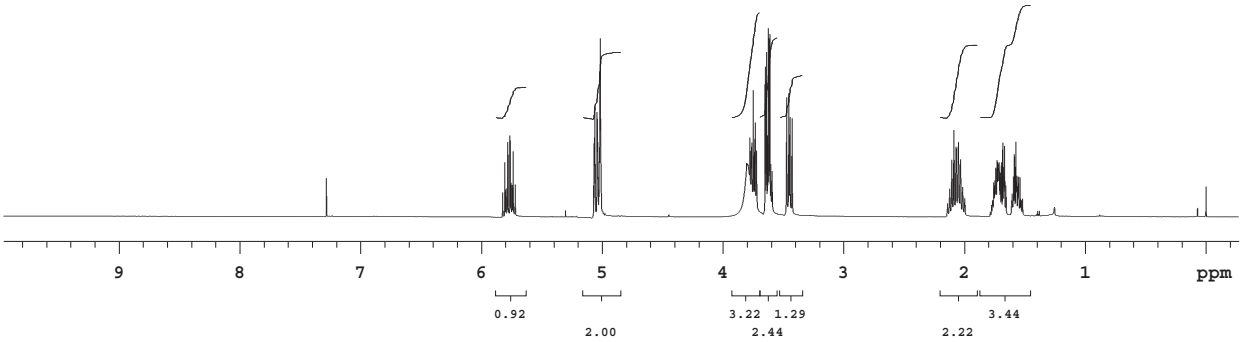

9
8
7
6
5
4
3
2
1
ppm
2.09
2.82
0.88
0.85
2.02
2.05
3.00
2.03
1.95
1.00
0.97
1.01
1.00

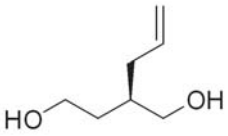

S
O
6f
OH
O


159.237
143.018
129.773
129.389
126.686
125.330
123.327
113.804
77.212
77.000
76.788
72.791
68.206
64.891
55.181
41.643
31.918
31.505
160
140
120
100
80
60
40
20
ppm

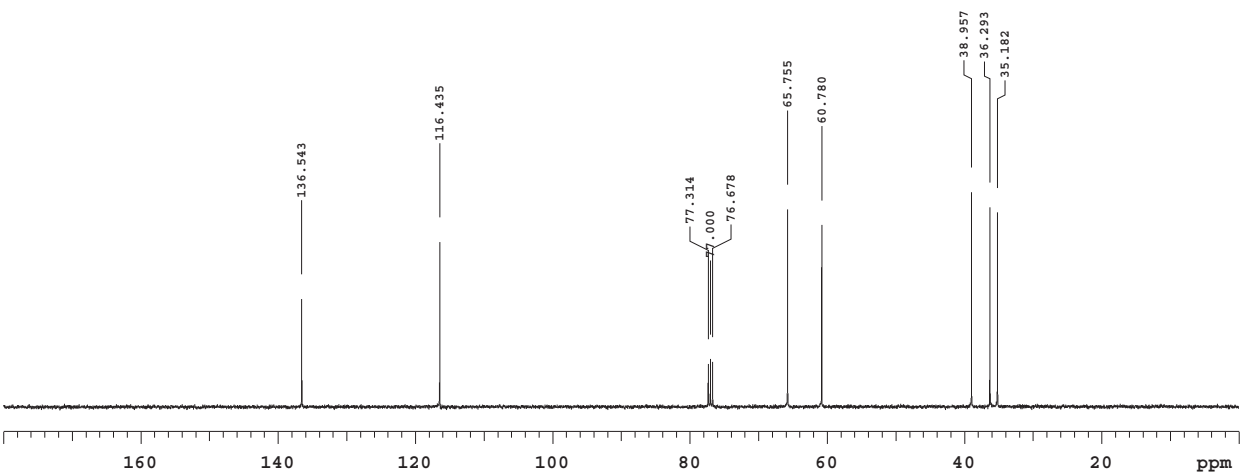

HO
OH

7c


9
8
7
6
5
4
3
2
1
ppm
0.92
2.00
3.22
1.29
2.44
2.22
3.44


HO
OH

7c


136.543
116.435
77.314
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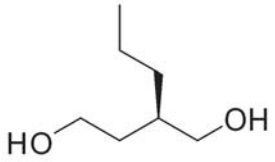
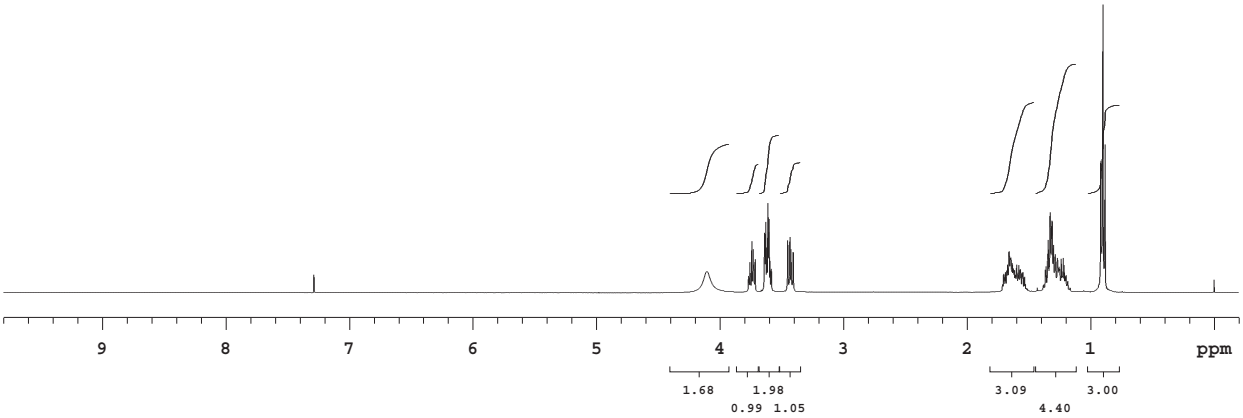
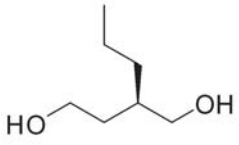
76.678
65.755
60.780
38.957
36.293
35.182
160
140
120
100
80
60
40
20
ppm

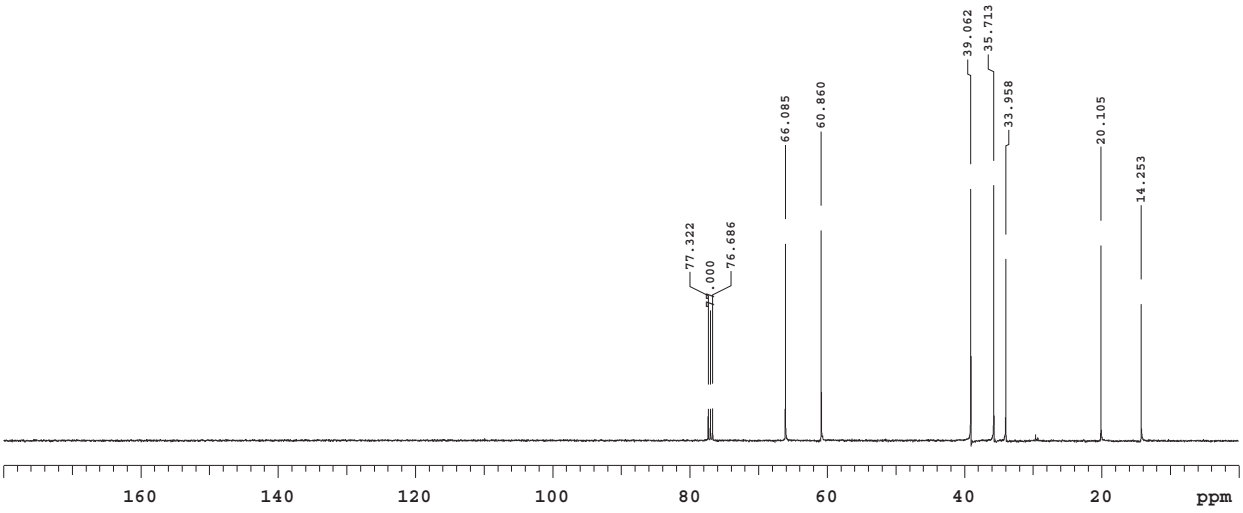

HO
OH

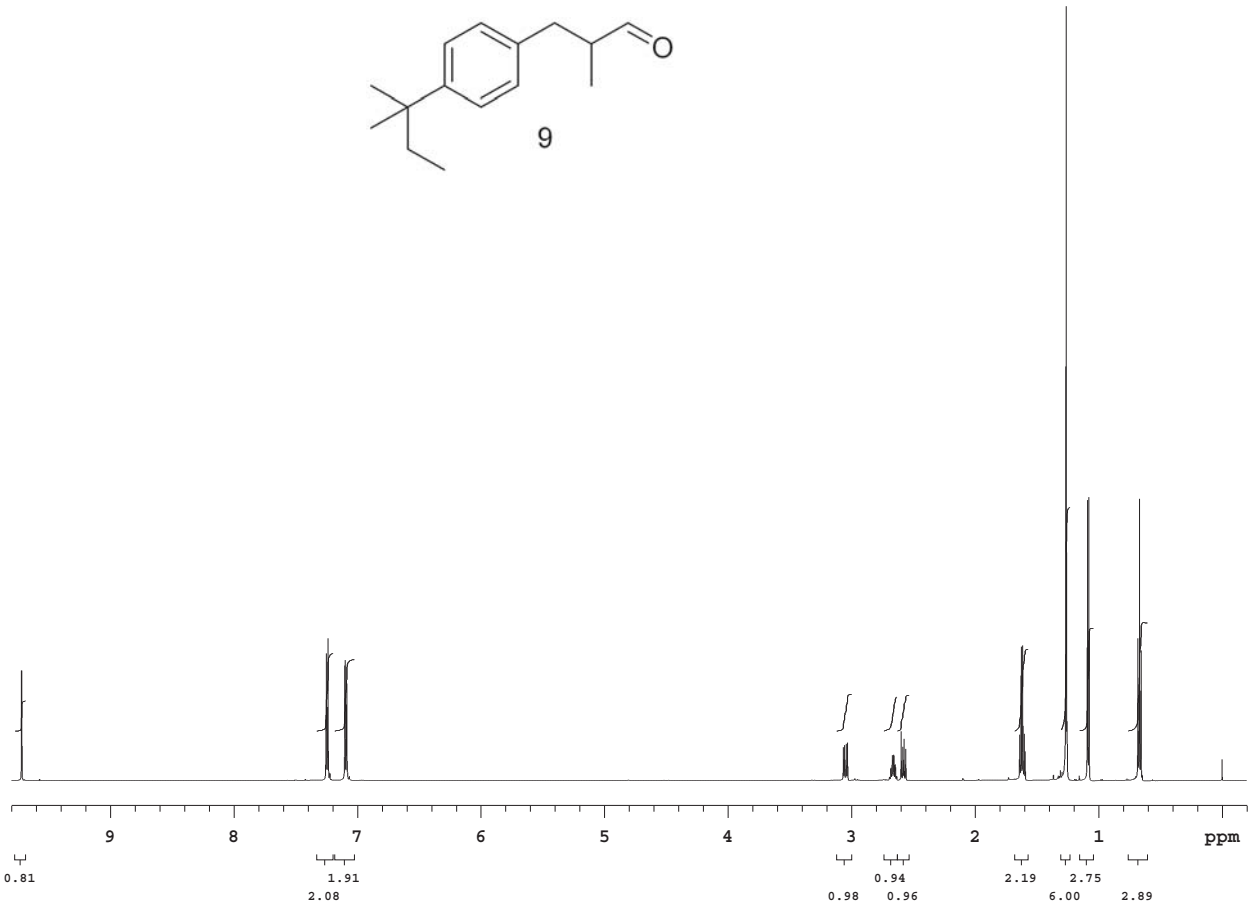
8c

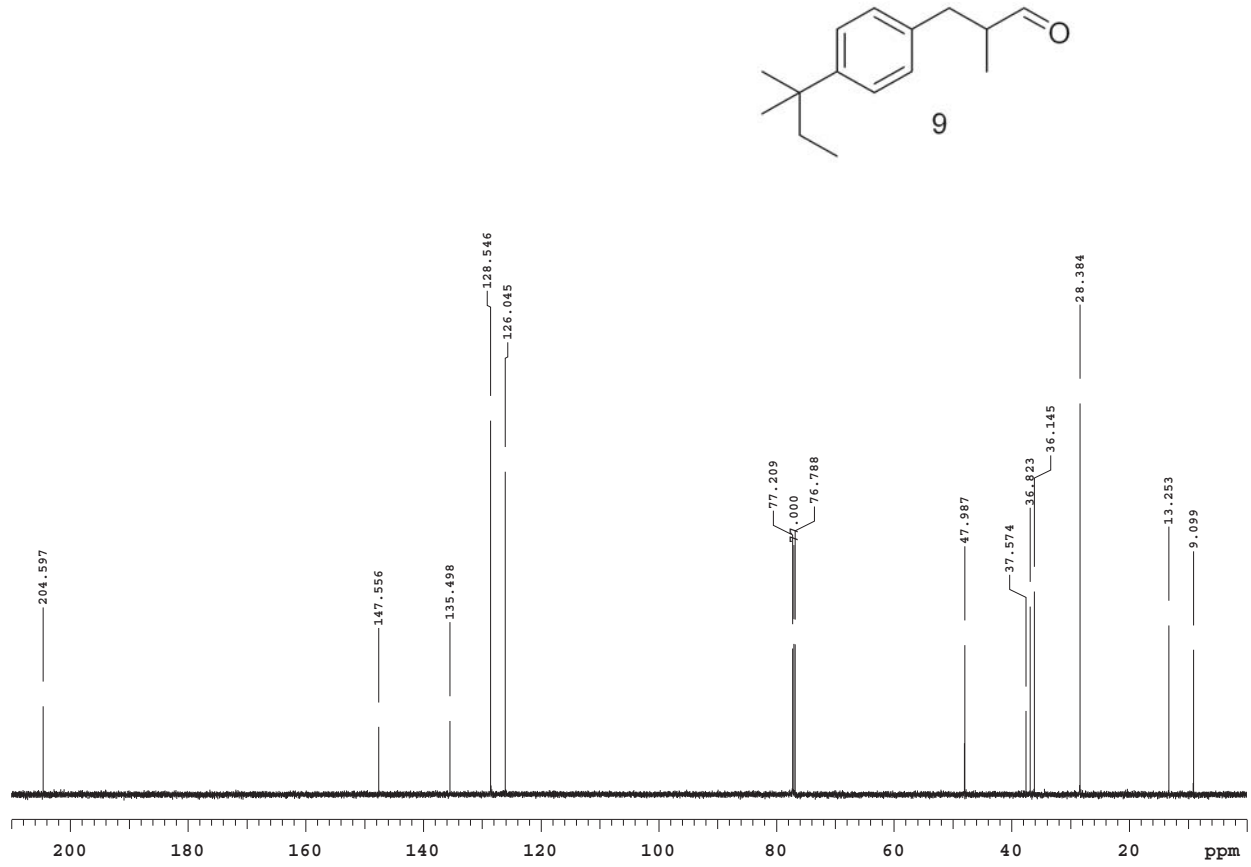

9
8
7
6
5
4
3
2
1
ppm
1.68
1.98
0.99 1.05
3.09
3.00
4.40

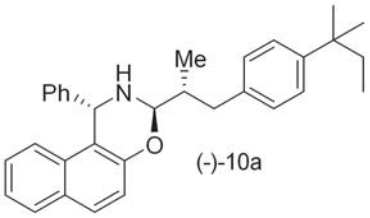

HO
OH

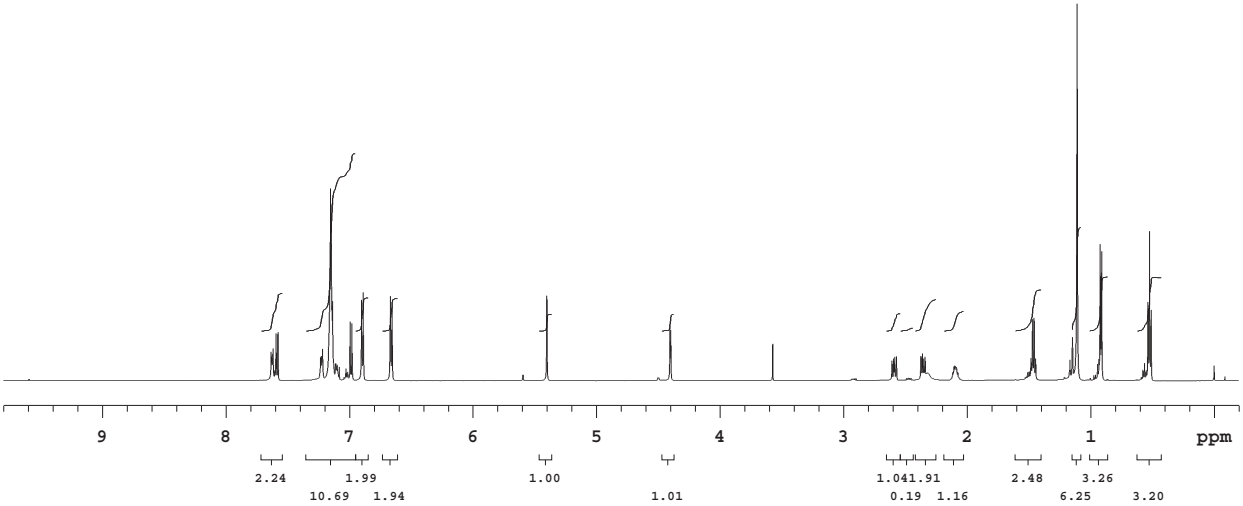
8c

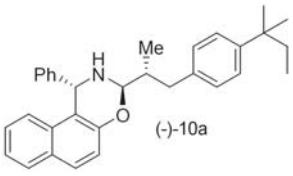

77.322
77.000
76.686
66.085
60.860
39.062
35.713
33.958
20.105
14.253
160
140
120
100
80
60
40
20
ppm


O
9
9
8
7
6
5
4
3
2
1
ppm
0.81
1.91
2.08
0.98
0.94
0.96
2.19
2.75
6.00
2.89


O
9
204.597
147.556
135.498
128.546
126.045
77.209
77.000
76.788
47.987
37.574
36.823
36.145
28.384
13.253
9.099
200
180
160
140
120
100
80
60
40
20
ppm







INDEX	FREQUENCY	PPM	HEIGHT
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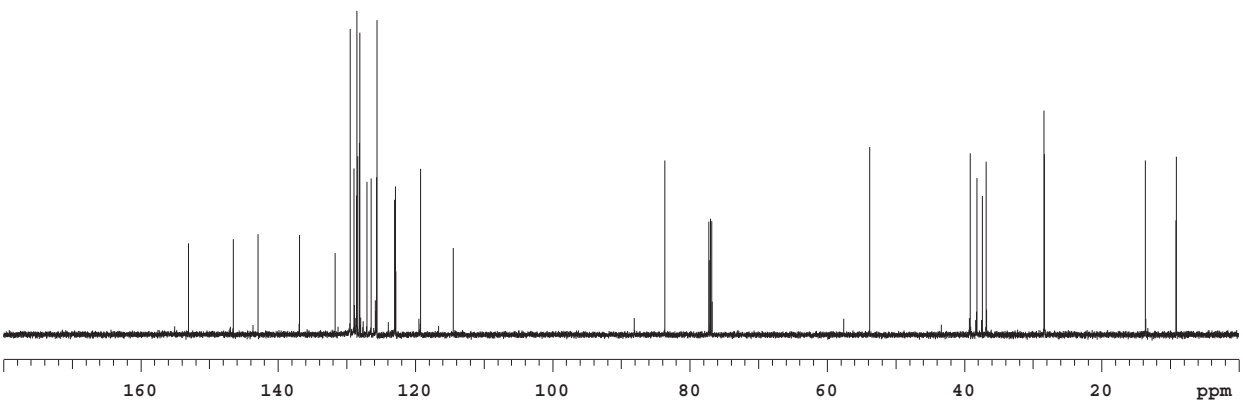
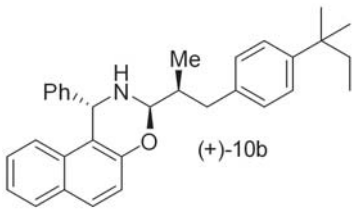
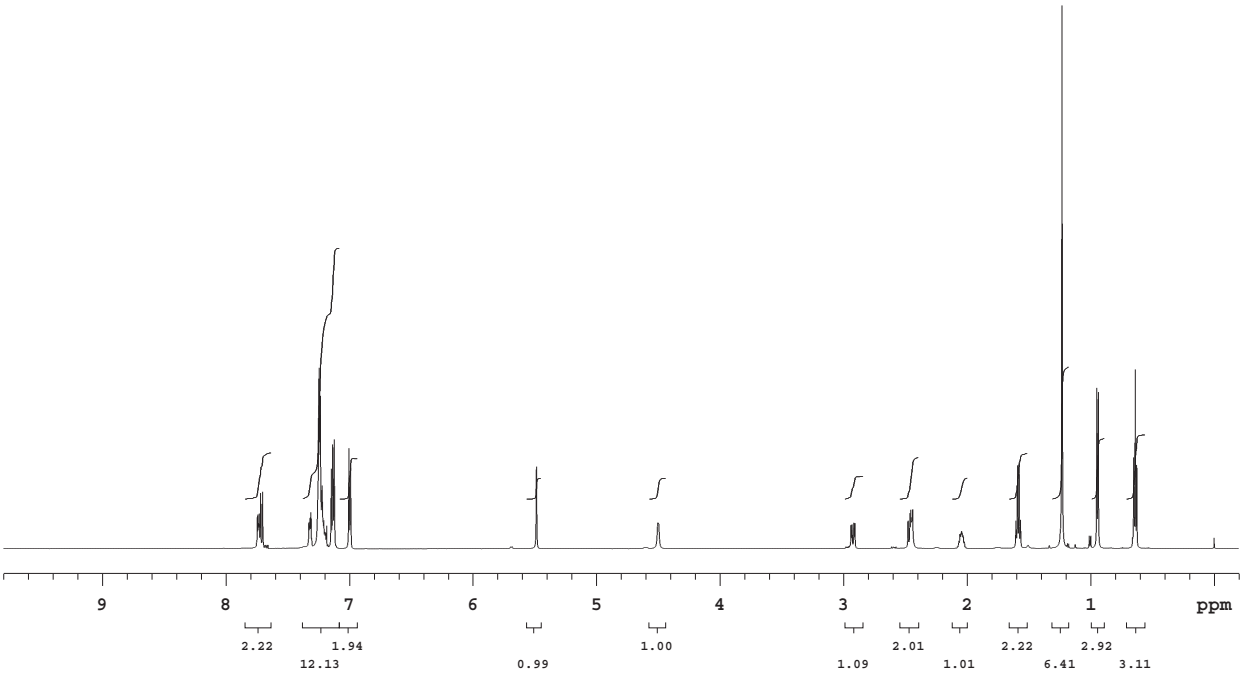
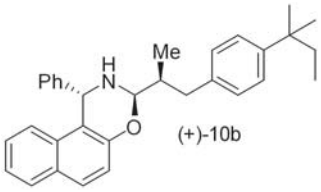
3	21548.0	142.890	20.3
4	20640.0	136.868	20.2
5	19857.3	131.678	16.5
6	19525.3	129.477	61.8
7	19441.9	128.924	33.7
8	19385.0	128.546	28.1
9	19382.8	128.532	65.5
10	19361.3	128.389	36.1
11	19319.3	128.111	61.1
12	19158.5	127.045	30.9
13	19065.2	126.426	31.6
14	18942.0	125.609	63.6
15	18546.5	122.986	27.3
16	18528.9	122.869	30.0
17	17981.5	119.239	33.5
18	17259.5	114.452	17.6
19	12613.7	83.644	35.2
20	11643.8	77.212	22.9
21	11611.7	77.000	23.4
22	11579.7	76.788	22.9
23	8112.6	53.796	37.9
24	5902.0	39.138	36.7
25	5759.5	38.193	31.6
26	5639.1	37.394	28.0
27	5550.7	36.808	35.0
28	4282.5	28.398	45.3
29	4276.5	28.358	36.5
30	2056.0	13.634	35.3
31	1379.4	9.147	36.0

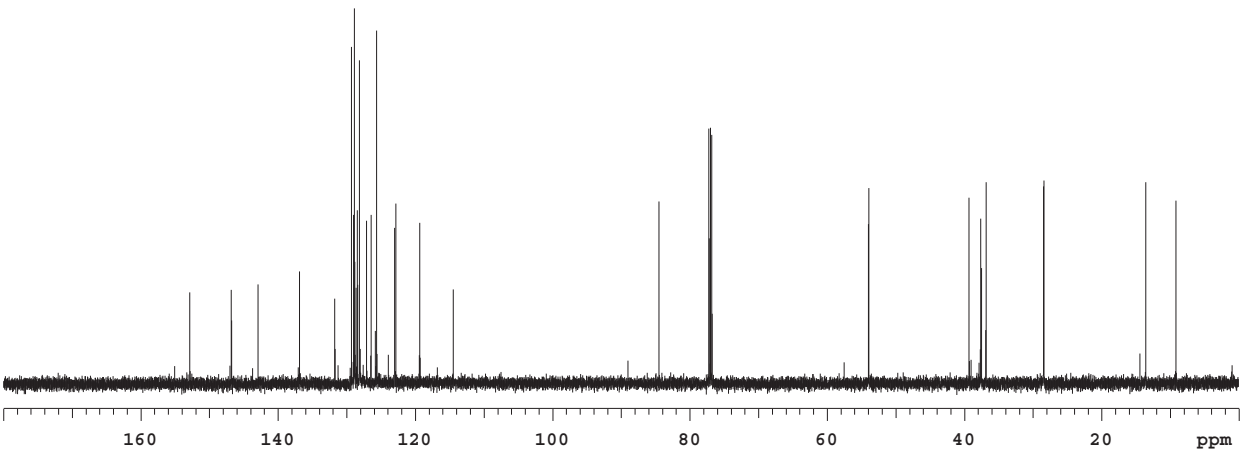


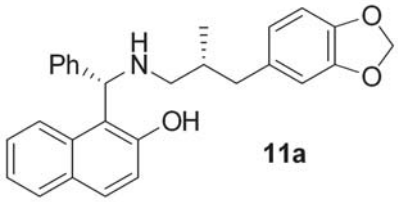




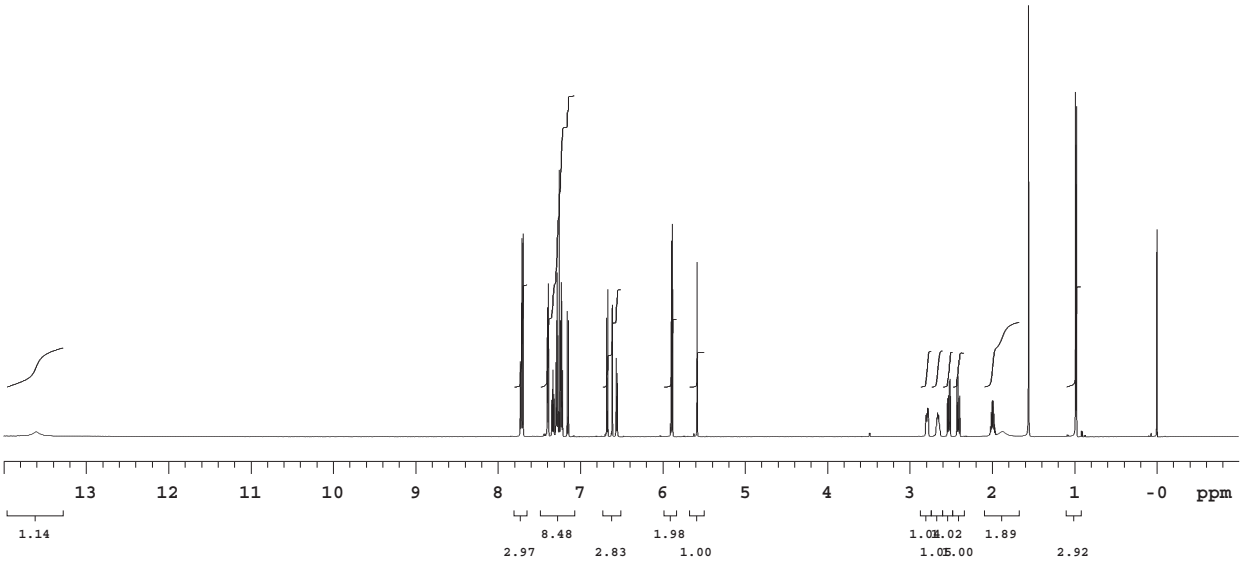


INDEX	FREQUENCY	PPM	HEIGHT
1	23053.7	152.875	18.5
2	22136.3	146.791	19.0
3	21552.4	142.919	20.1
4	20642.2	136.883	22.7
5	19862.8	131.715	17.2
6	19497.7	129.294	68.1
7	19450.2	128.979	34.1
8	19431.4	128.854	75.9
9	19394.4	128.609	19.4
10	19365.7	128.418	35.0
11	19325.9	128.154	65.4
12	19166.3	127.096	32.9
13	19069.6	126.455	34.1
14	18945.3	125.631	71.4
15	18552.1	123.023	31.5
16	18524.4	122.840	36.4
17	17995.3	119.331	32.5
18	17265.1	114.489	19.1
19	12741.8	84.494	36.9
20	11643.8	77.212	51.6
21	11611.7	77.000	51.8
22	11579.7	76.788	50.3
23	8135.8	53.950	39.5
24	5928.0	39.310	37.6
25	5676.7	37.643	33.4
26	5652.4	37.482	23.4
27	5557.4	36.852	40.7
28	4289.7	28.446	39.9
29	4284.7	28.413	41.1
30	2047.2	13.575	40.8
31	1381.0	9.158	37.0




Ph
H
N
OH
O
O

11a


13
12
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
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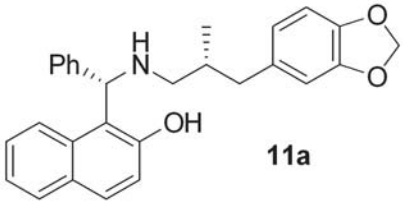
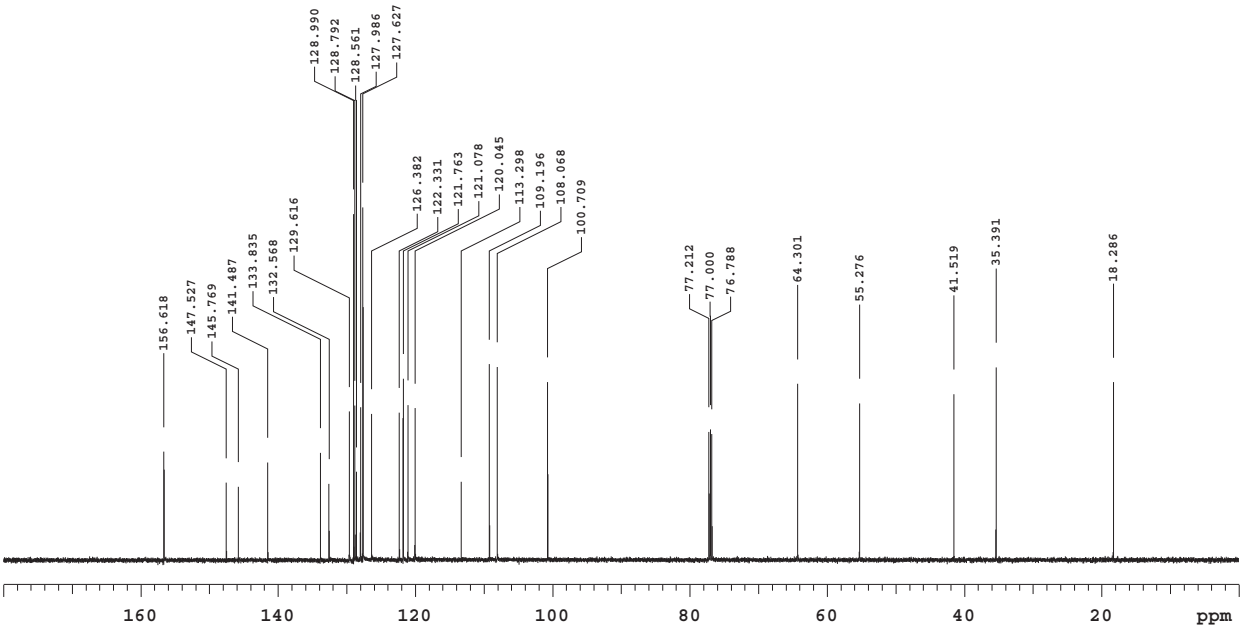
2.97
8.48
2.83
1.98
1.00
1.02
1.89
5.00
2.92


Ph
H
N
OH
O
O

11a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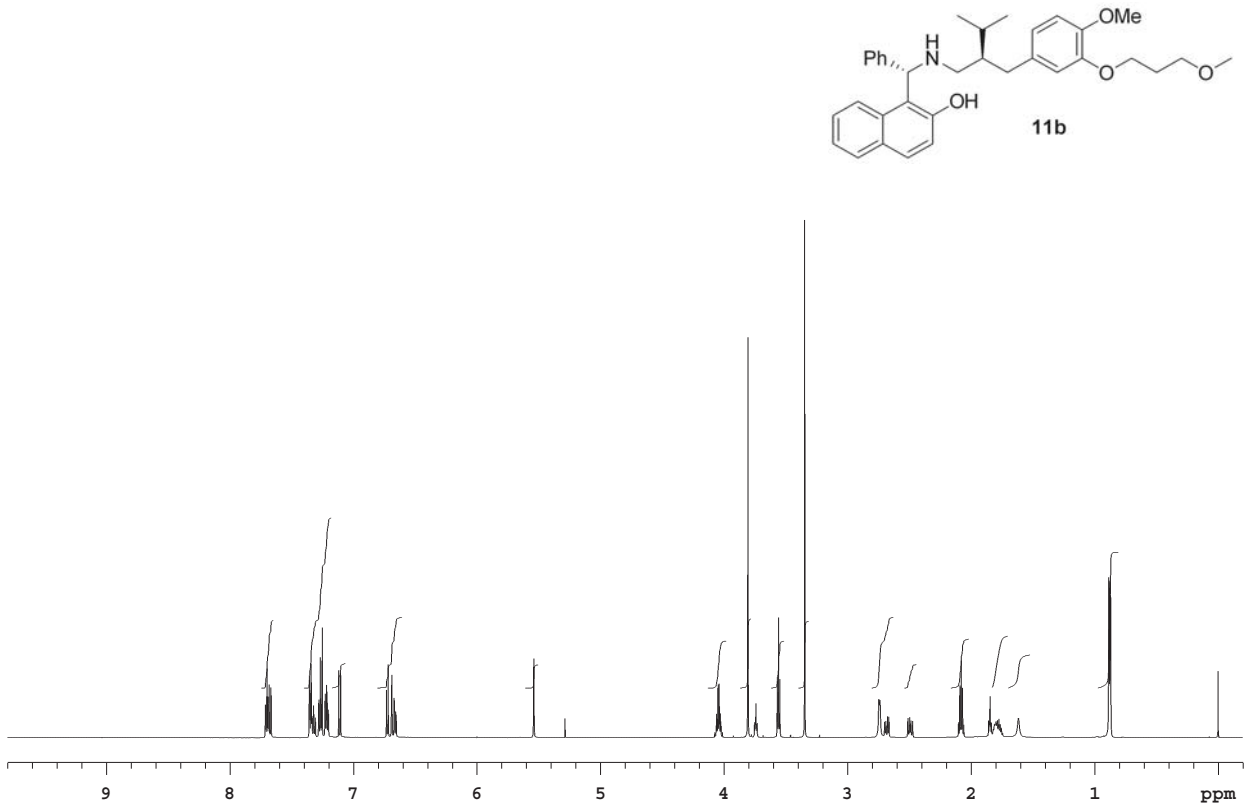
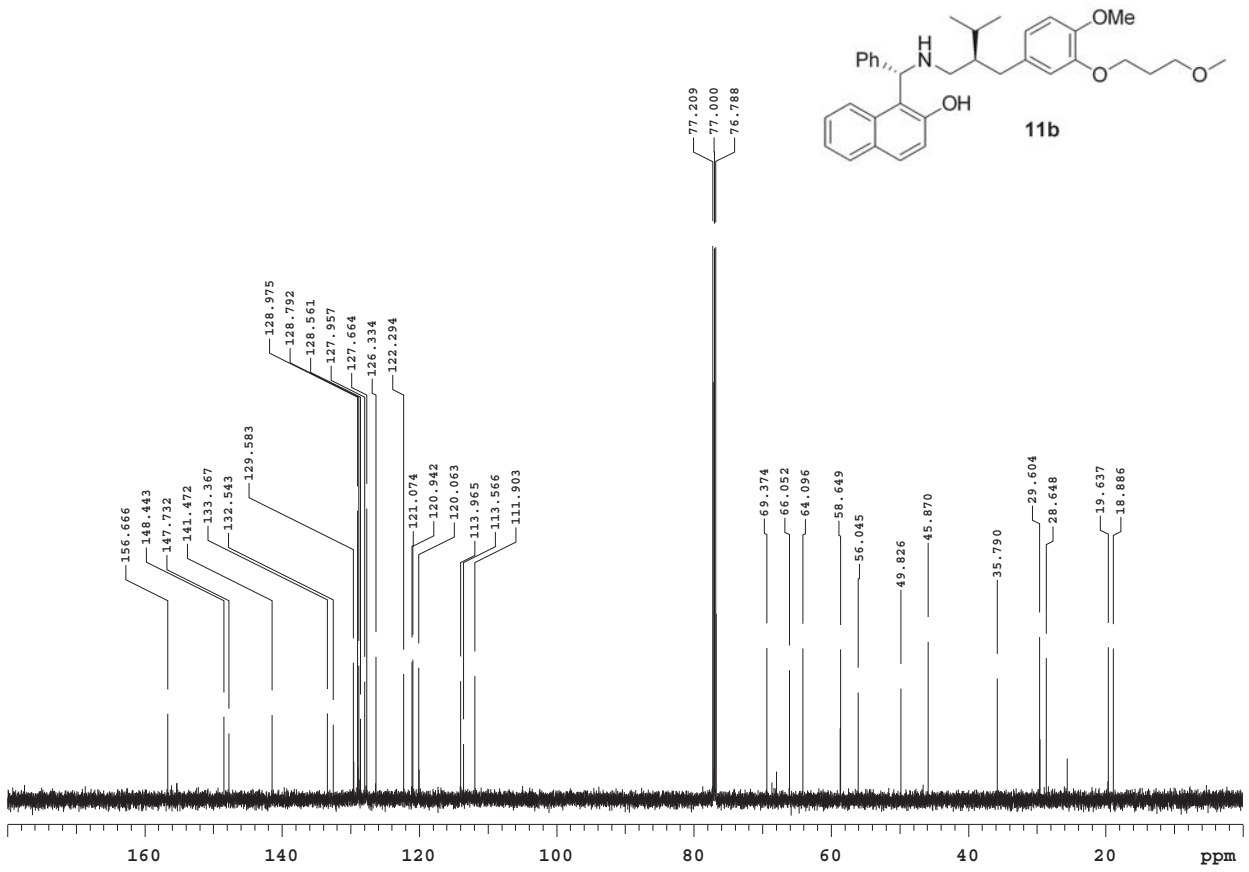
147.527
145.769
141.487
133.835
132.568
129.616
128.990
128.792
128.561
127.986
127.627
126.382
122.331
121.763
121.078
120.045
113.298
109.196
108.068
100.709
77.212
77.000
76.788
64.301
55.276
41.519
35.391
18.286
160
140
120
100
80
60
40
20
ppm


OMe
Ph
H
N
OH
O
O
11b
9
8
7
6
5
4
3
2
1
ppm


OMe
Ph
H
N
OH
O
O
11b
77.209
77.000
76.788
128.975
128.792
128.561
127.957
127.664
126.334
122.294
121.074
120.942
120.063
113.965
113.566
111.903
156.666
148.443
147.732
141.472
133.367
132.543
129.583
69.374
66.052
64.096
58.649
56.045
49.826
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35.790
29.604
28.648
19.637
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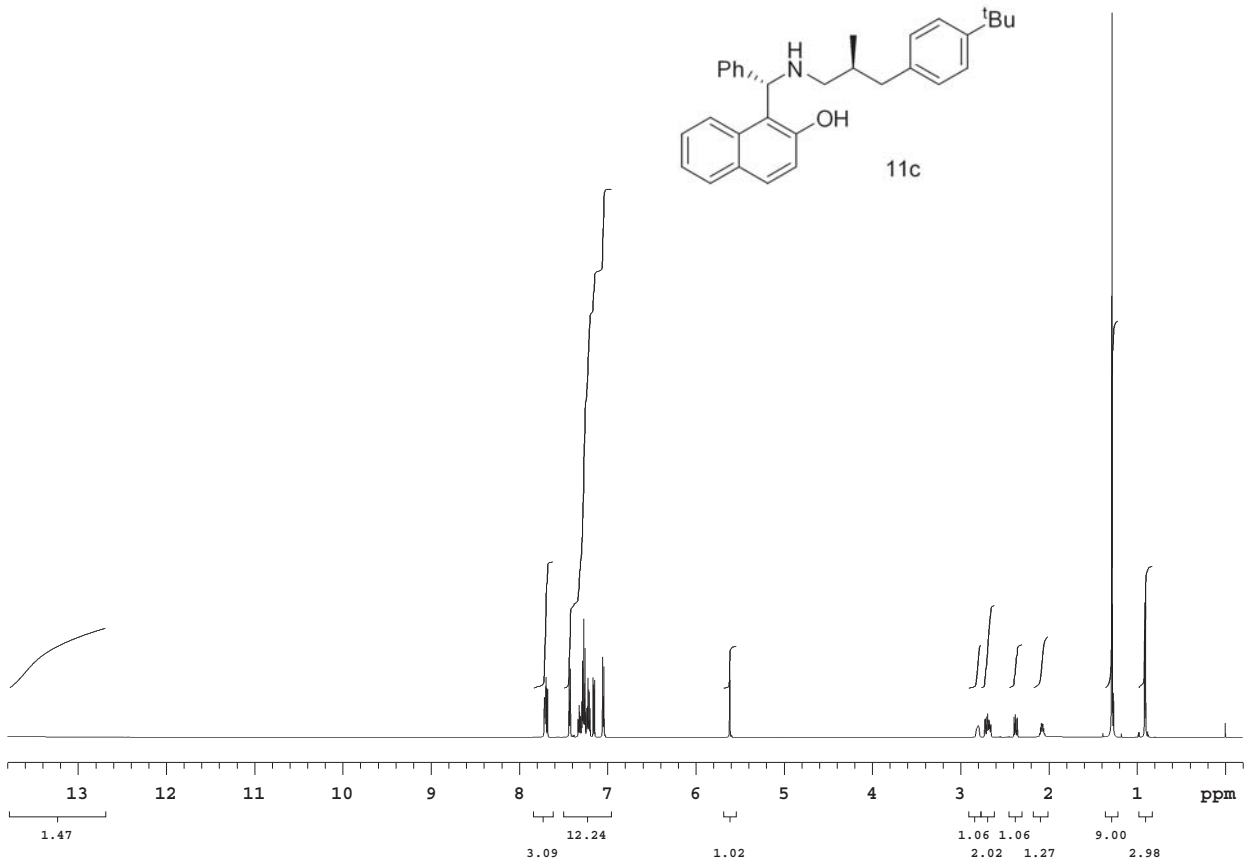
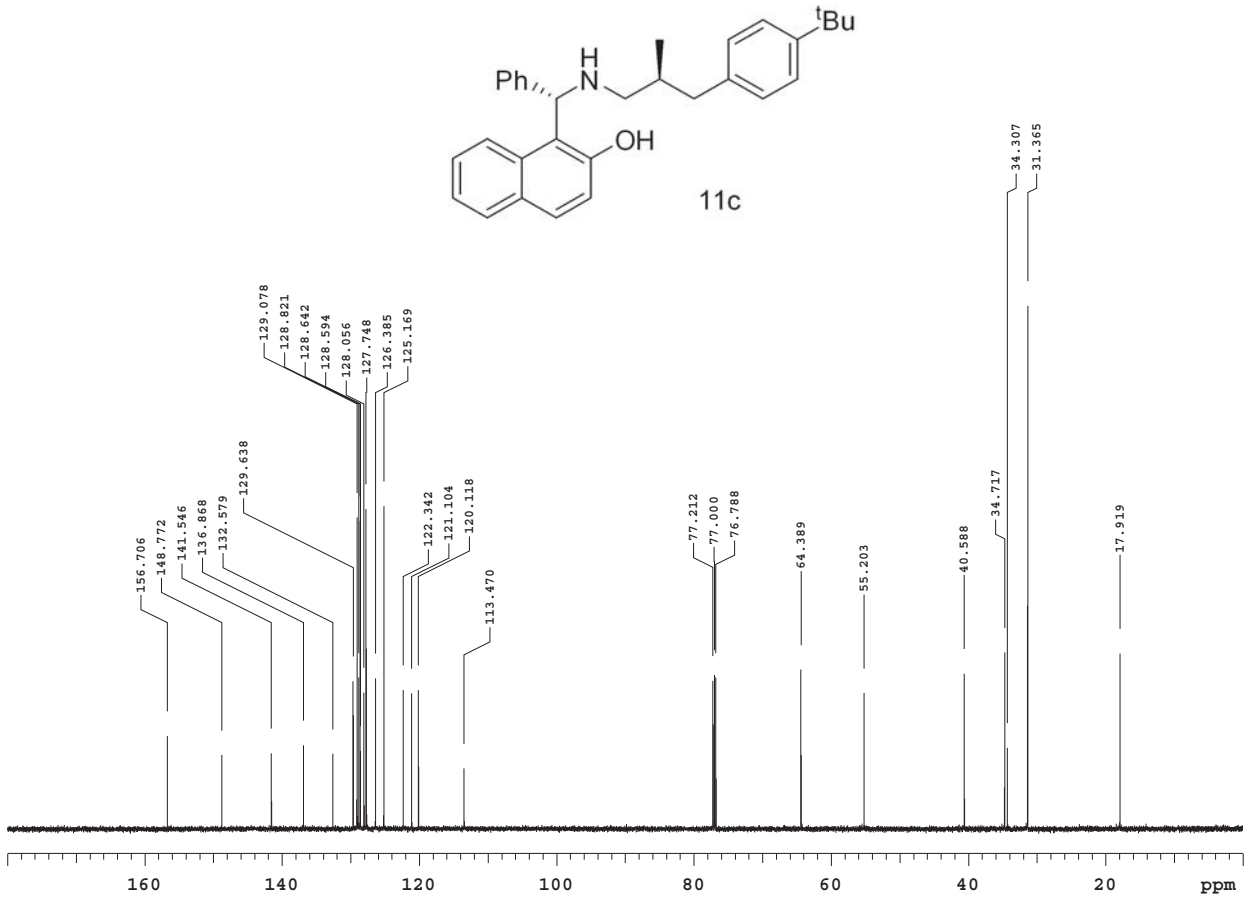
140
120
100
80
60
40
20
ppm


tBu
Ph
H
N
OH
11c
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.47
3.09
12.24
1.02
1.06
2.02
1.06
1.27
9.00
2.98


tBu
Ph
H
N
OH
11c
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128.821
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128.594
128.056
127.748
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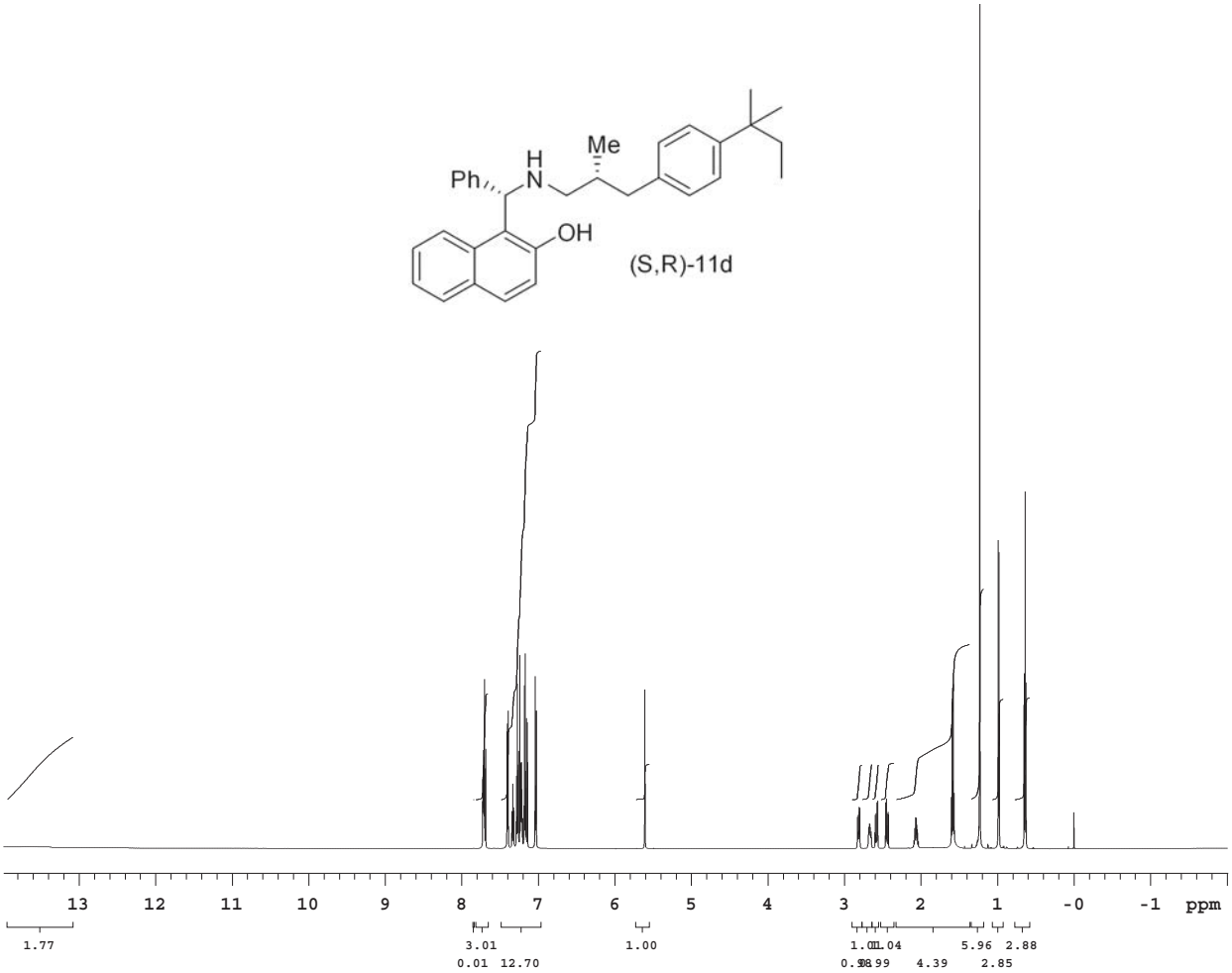
125.169
129.638
122.342
121.104
120.118
113.470
156.706
148.772
141.546
136.868
132.579
77.212
77.000
76.788
64.389
55.203
40.588
34.717
34.307
31.365
17.919
160
140
120
100
80
60
40
20
ppm


Ph
H
N
Me
OH
(S,R)-11d
13
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
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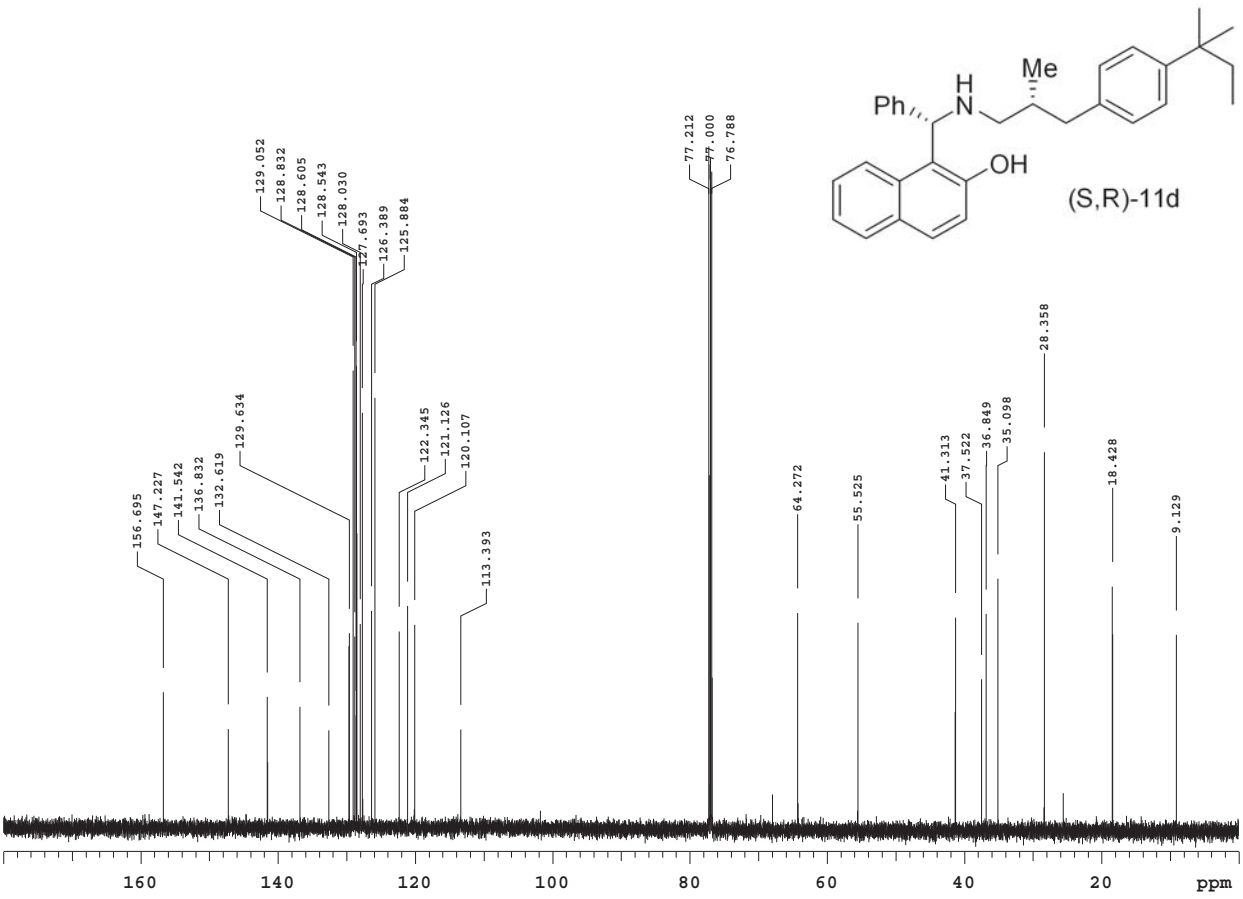
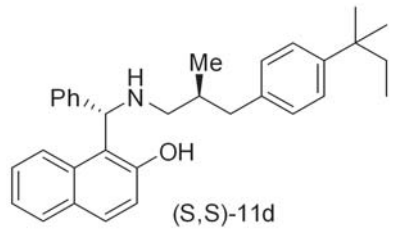
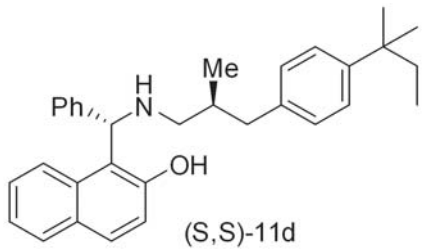
3.01
0.01
12.70
1.00
1.04
4.39
5.96
2.88
2.85


Ph
H
N
Me
OH
(S,R)-11d
129.052
128.832
128.605
128.543
128.030
127.693
126.389
125.884
77.212
77.000
76.788
156.695
147.227
141.542
136.832
132.619
129.634
122.345
121.126
120.107
113.393
64.272
55.525
41.313
37.522
36.849
35.098
28.358
18.428
9.129
160
140
120
100
80
60
40
20
ppm

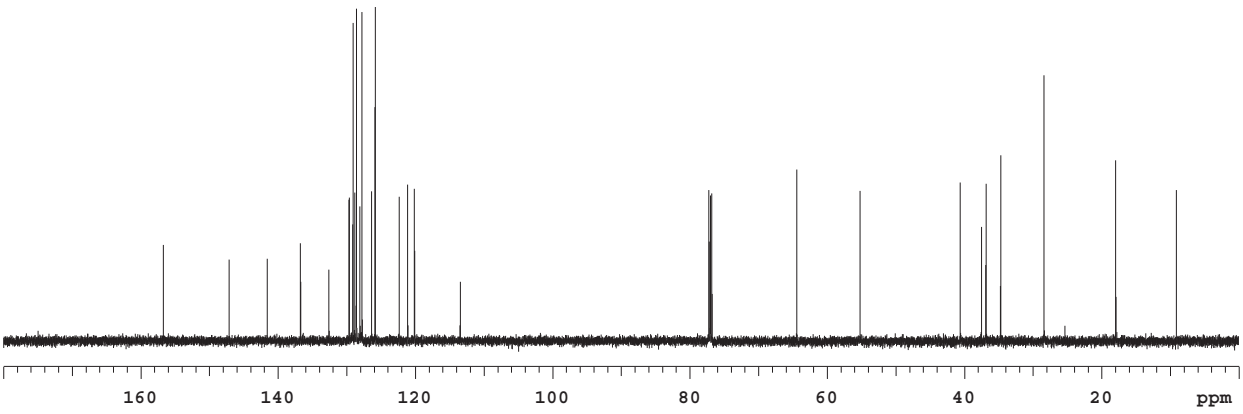


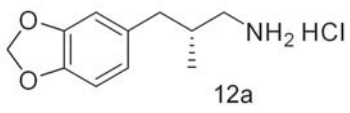
(S,S)-11d



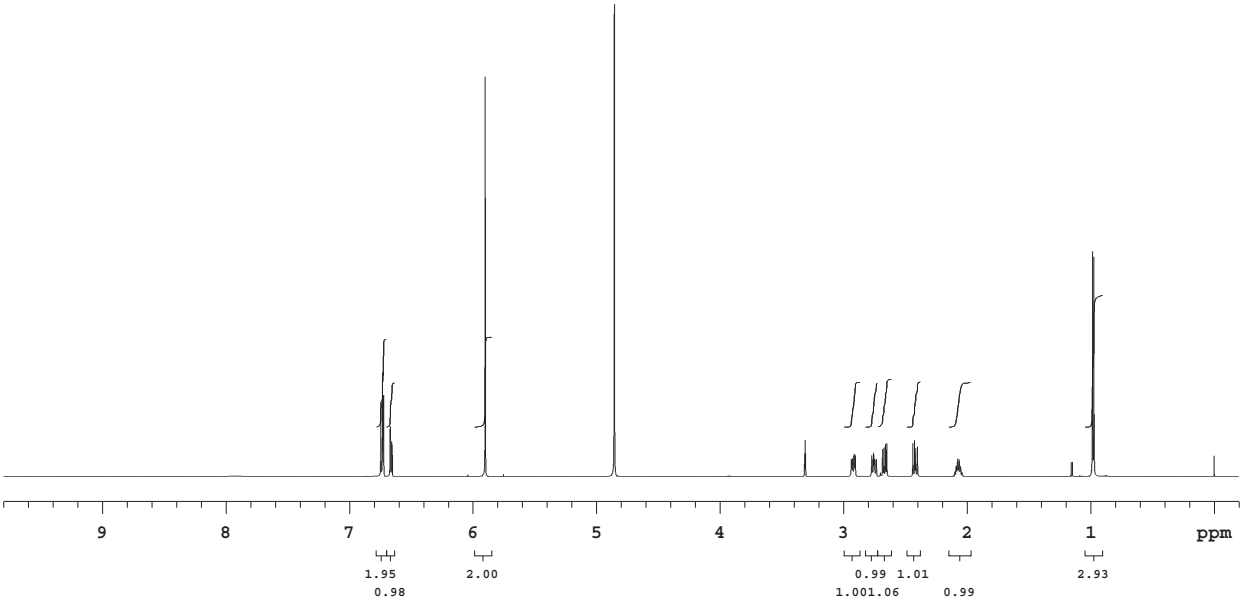
(S,S)-11d

INDEX	FREQUENCY	PPM	HEIGHT
1	23632.1	156.710	19.6
2	22183.2	147.102	16.6
3	21346.4	141.553	16.8
4	20617.9	136.722	19.9
5	19993.2	132.579	14.5
6	19549.1	129.634	29.1
7	19465.7	129.081	64.4
8	19425.9	128.817	30.1
9	19392.2	128.594	17.5
10	19386.7	128.557	67.4
11	19312.1	128.063	27.4
12	19266.3	127.759	66.7
13	19058.0	126.378	30.4
14	18978.5	125.851	67.7
15	18448.2	122.334	29.3
16	18262.6	121.104	31.8
17	18114.0	120.118	30.9
18	17108.8	113.452	12.1
19	11643.8	77.212	30.6
20	11611.7	77.000	29.5
21	11579.7	76.788	30.0
22	9714.9	64.422	34.8
23	8323.6	55.195	30.5
24	6122.4	40.599	32.2
25	5658.5	37.522	23.2
26	5557.9	36.856	31.9
27	5235.3	34.717	37.7
28	4282.5	28.398	53.9
29	2706.1	17.945	36.6
30	1376.6	9.129	30.7




O
O
NH2 HCl

12a


9
8
7
6
5
4
3
2
1
ppm
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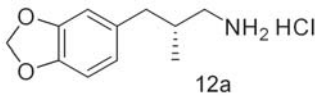
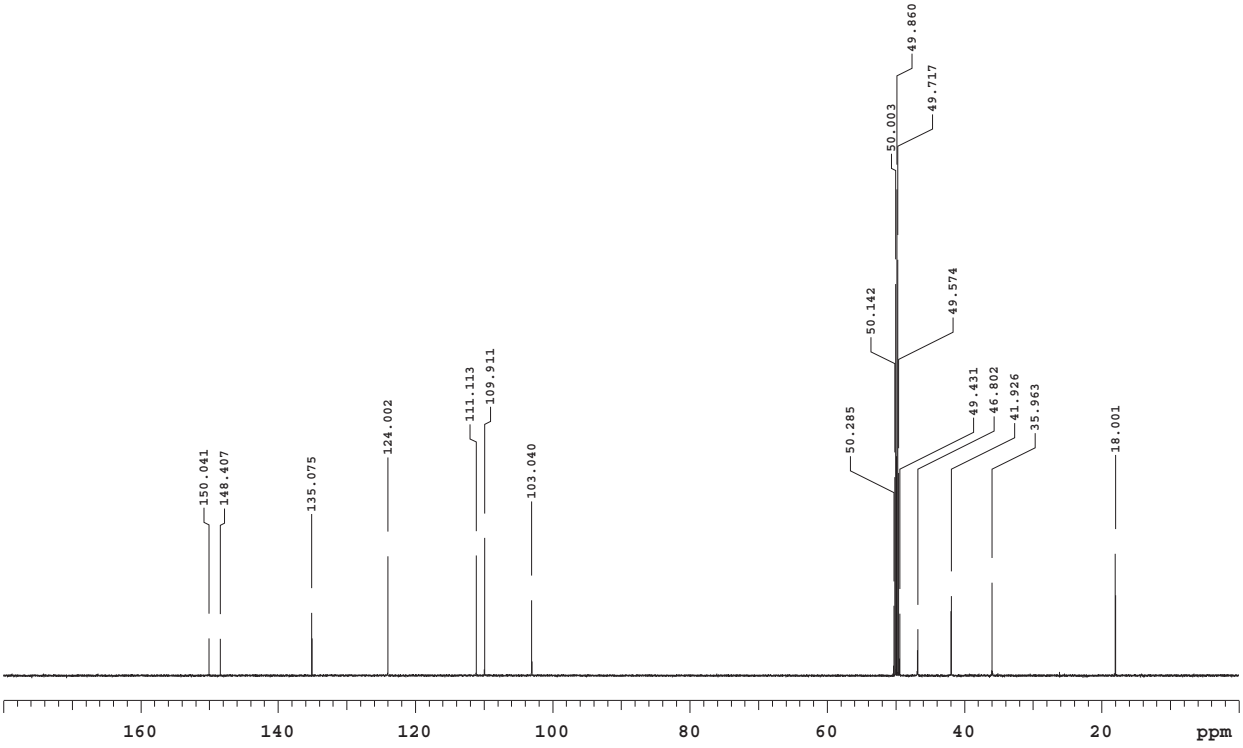
2.00
0.99
1.00
1.06
1.01
0.99
2.93


O
O
NH2 HCl

12a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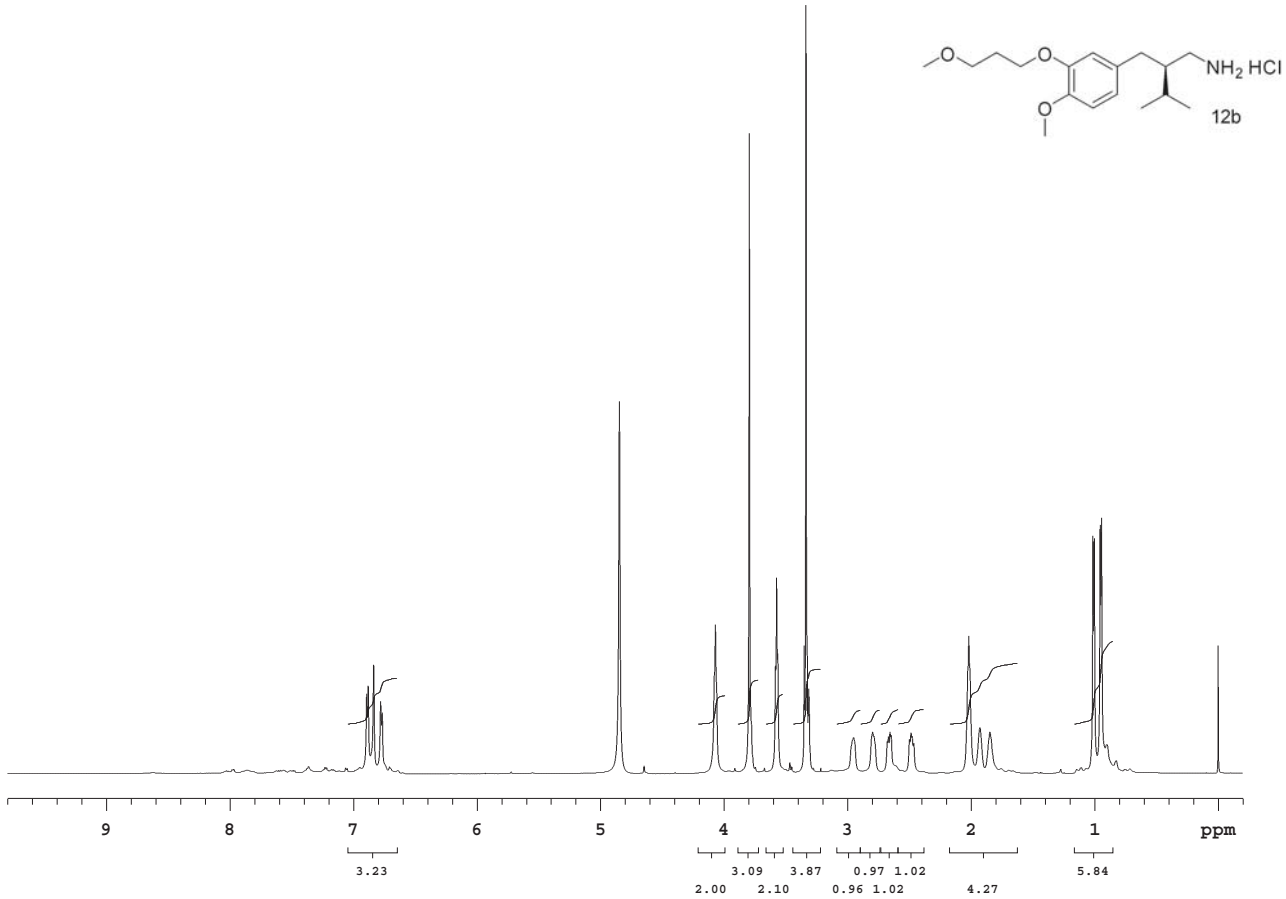
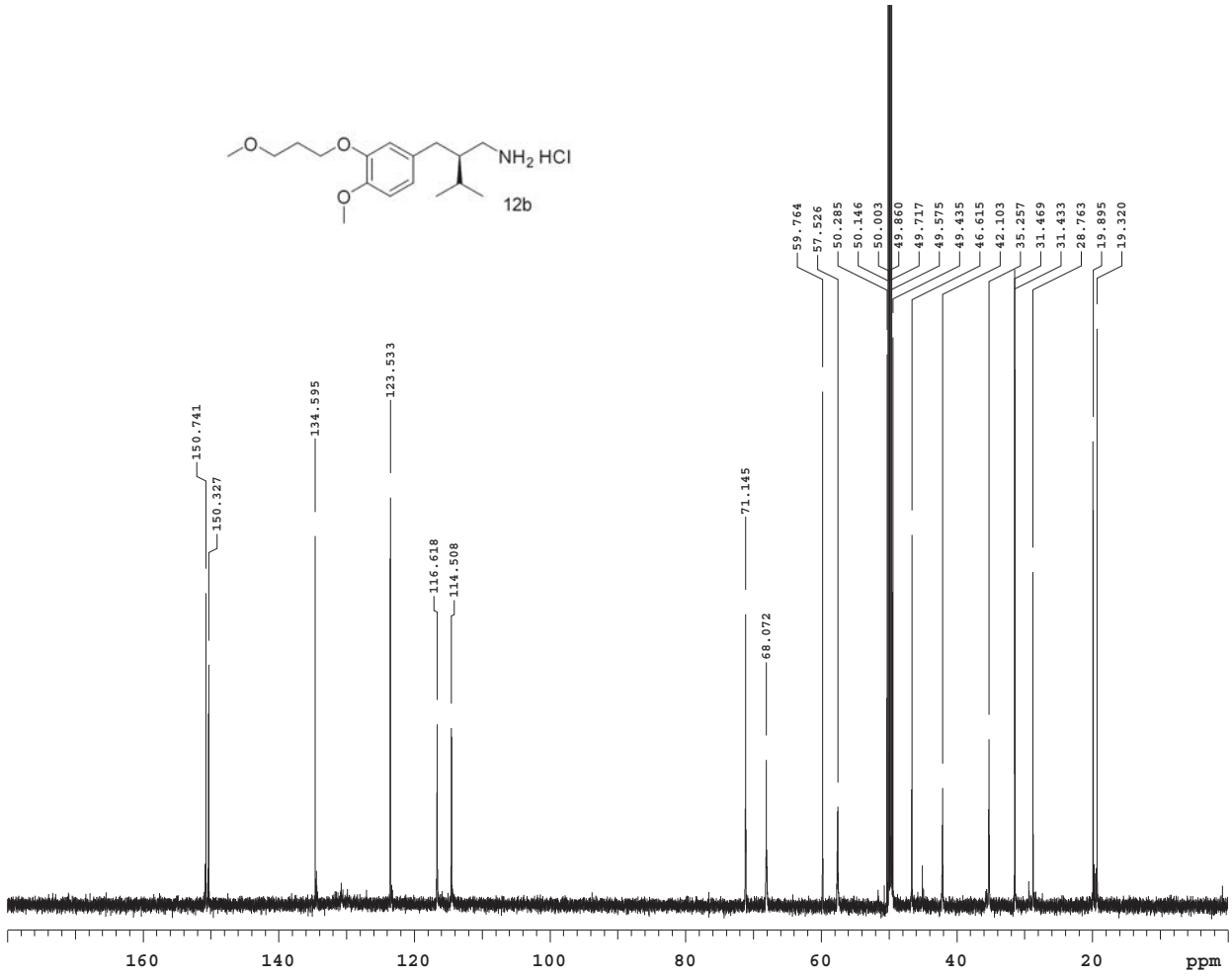
124.002
111.113
109.911
103.040
50.285
50.142
50.003
49.860
49.717
49.574
49.431
46.802
41.926
35.963
18.001
160
140
120
100
80
60
40
20
ppm


NH2 HCl
12b
9
8
7
6
5
4
3
2
1
ppm
3.23
2.00
3.09
2.10
3.87
0.96
0.97
1.02
1.02
4.27
5.84


NH2 HCl
12b
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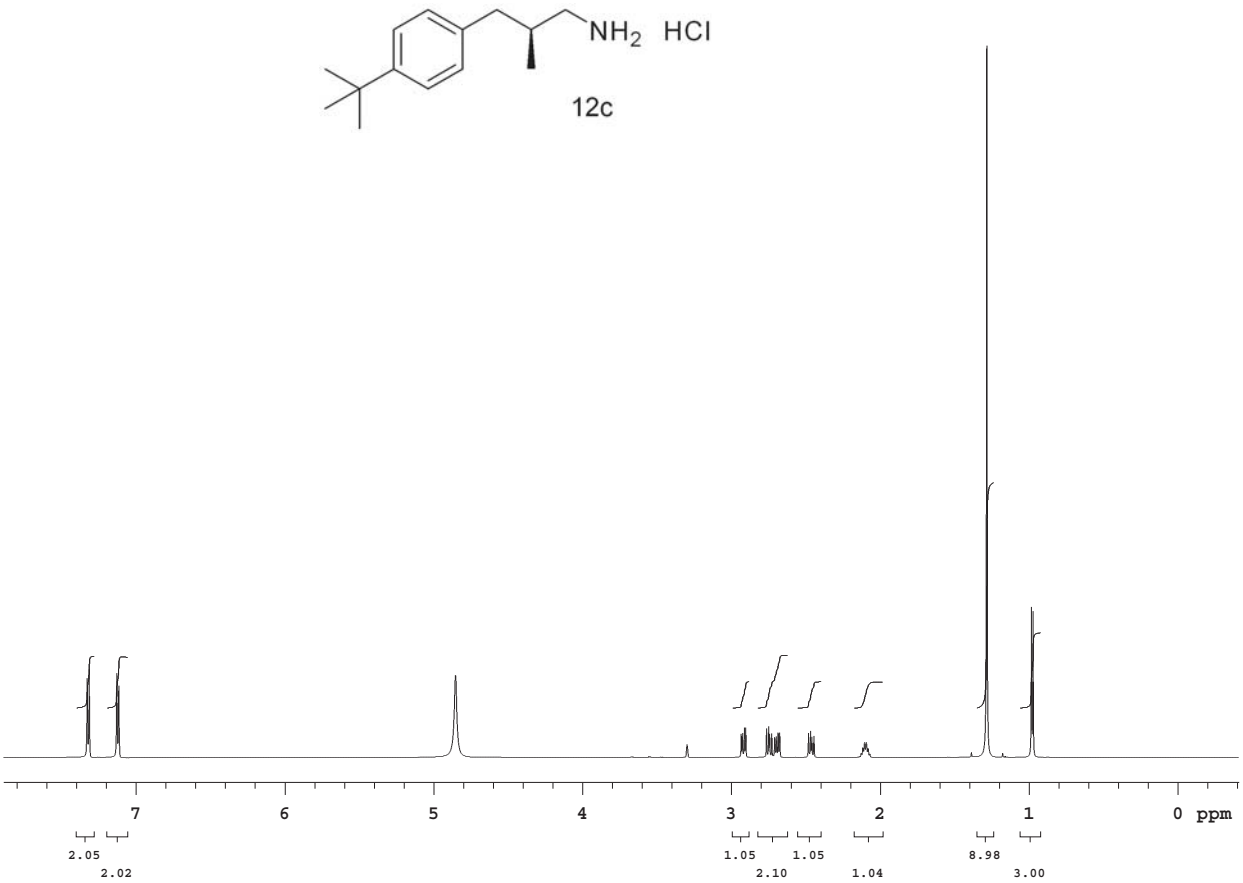
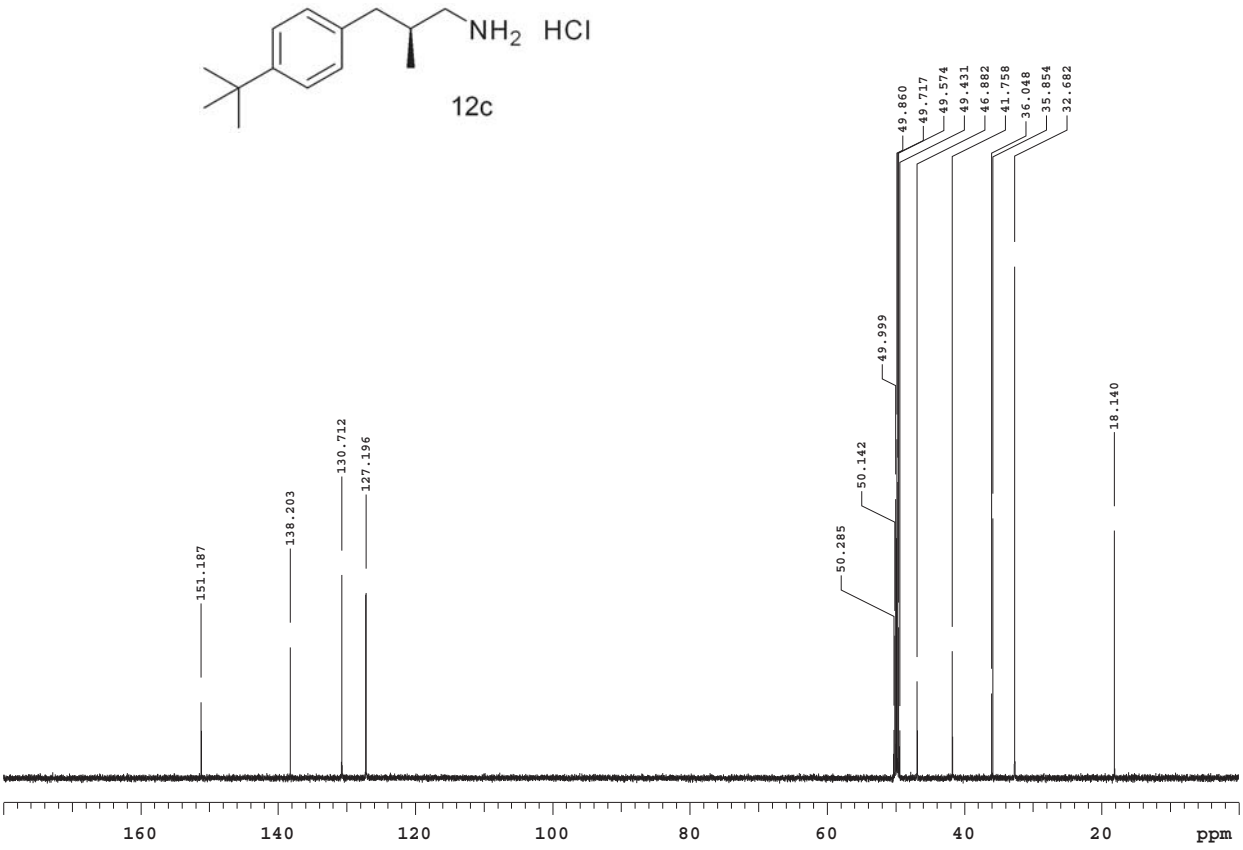
57.526
50.285
50.146
50.003
49.860
49.717
49.575
49.435
46.615
42.103
35.257
31.469
31.433
28.763
19.895
19.320
150.741
150.327
134.595
123.533
116.618
114.508
71.145
68.072
160
140
120
100
80
60
40
20
ppm


NH2 HCl
12c
7
6
5
4
3
2
1
0 ppm
2.05
2.02
1.05
2.10
1.05
1.04
8.98
3.00


NH2 HCl
12c
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138.203
130.712
127.196
50.285
50.142
49.999
49.860
49.717
49.574
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41.758
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32.682
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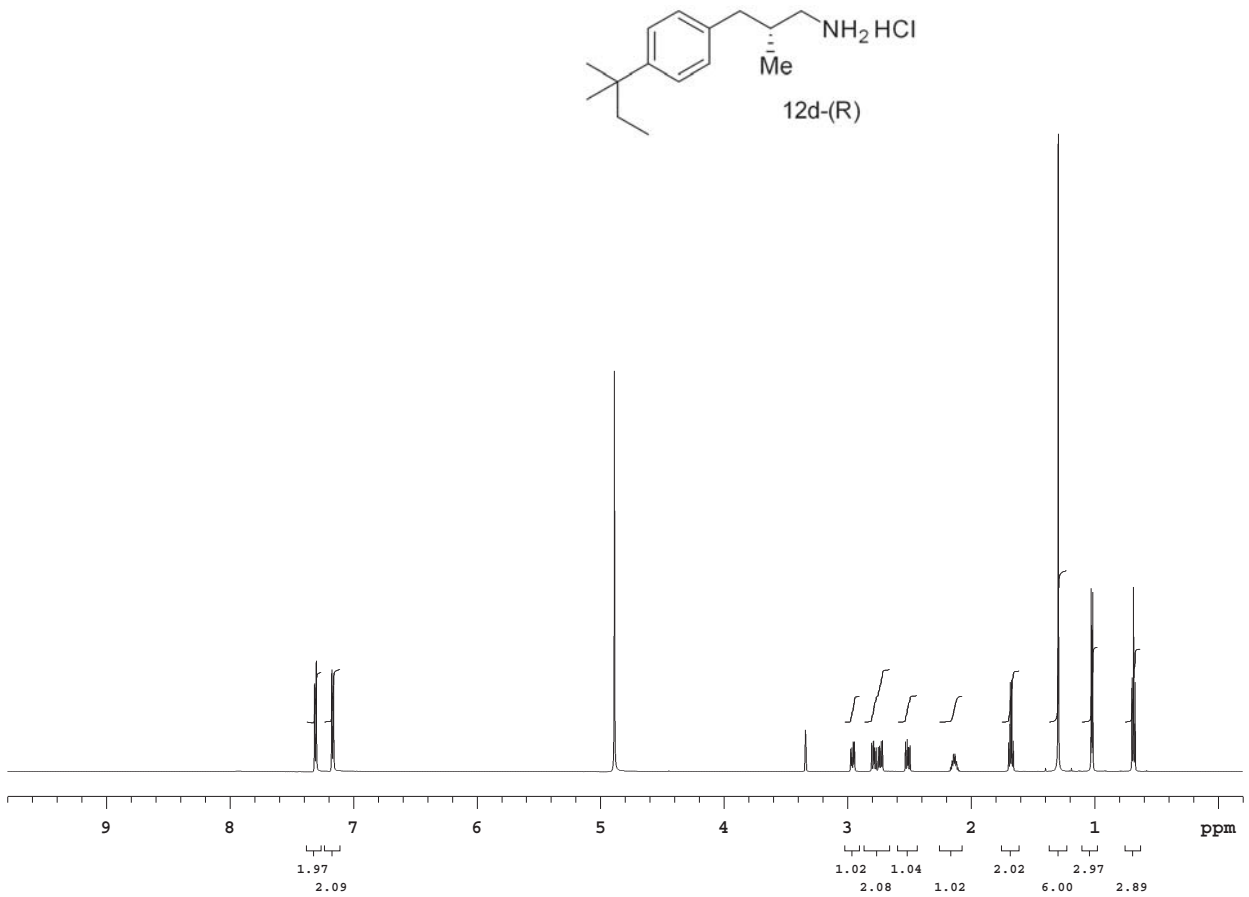
140
120
100
80
60
40
20
ppm


NH2 HCl
Me
12d-(R)
9
8
7
6
5
4
3
2
1
ppm
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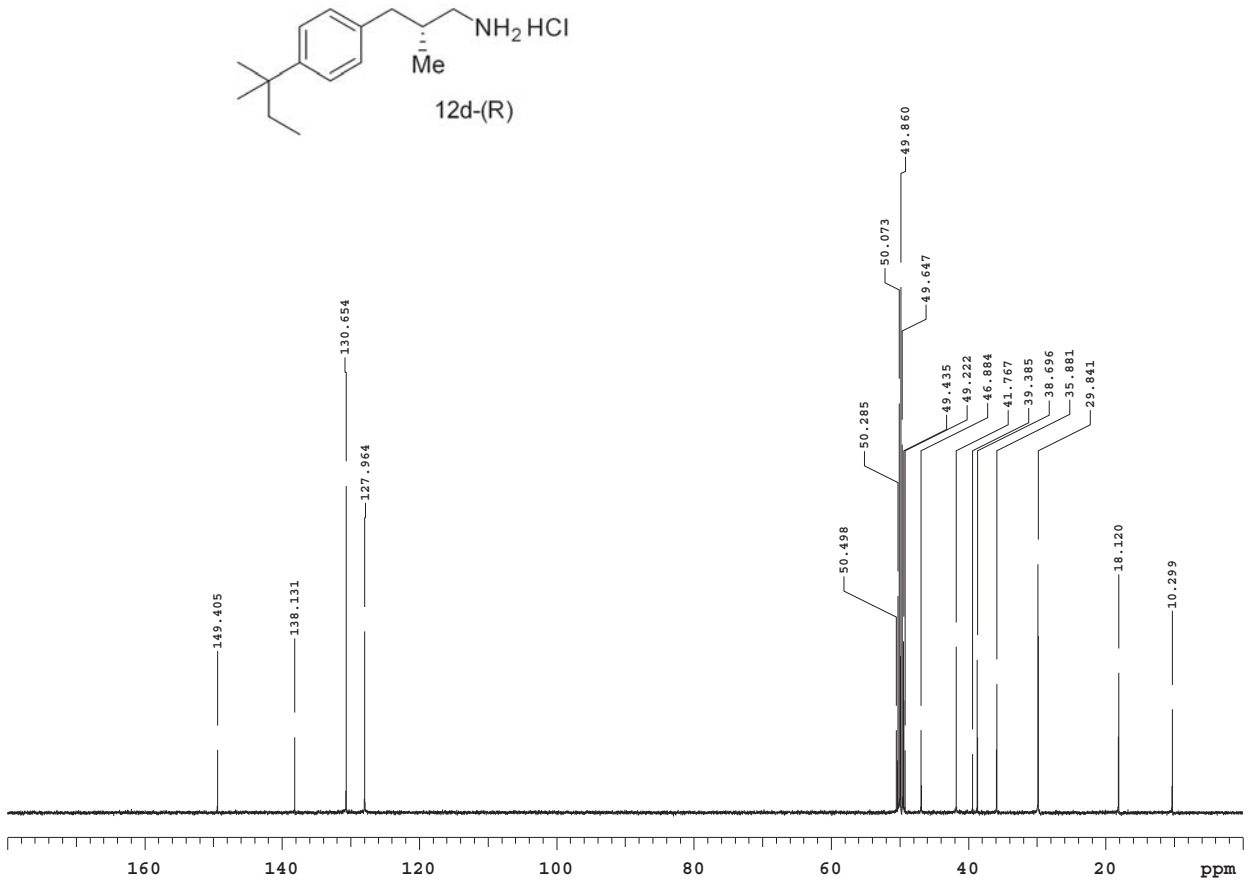
2.09
1.02
1.04
2.08
1.02
2.02
2.97
6.00
2.89


NH2 HCl
Me
12d-(R)
149.405
138.131
130.654
127.964
50.498
50.285
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49.435
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46.884
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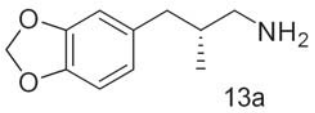
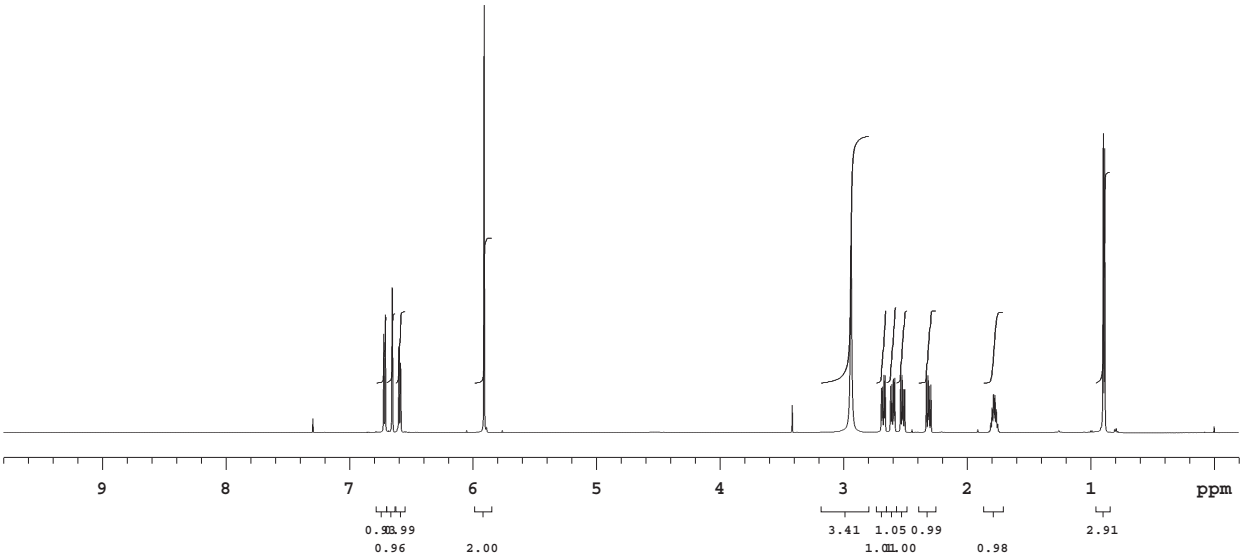
120
100
80
60
40
20
ppm


O
O
NH2

13a


9
8
7
6
5
4
3
2
1
ppm
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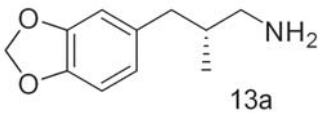
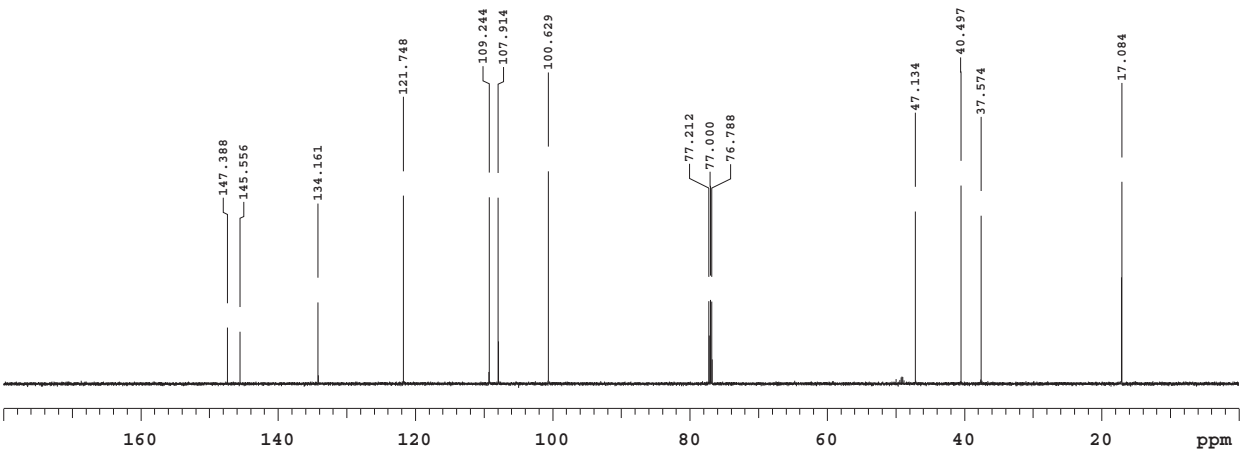
2.00
3.41
1.05
0.99
2.91
0.98


O
O
NH2

13a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145.556
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109.244
107.914
100.629
77.212
77.000
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37.574
17.084
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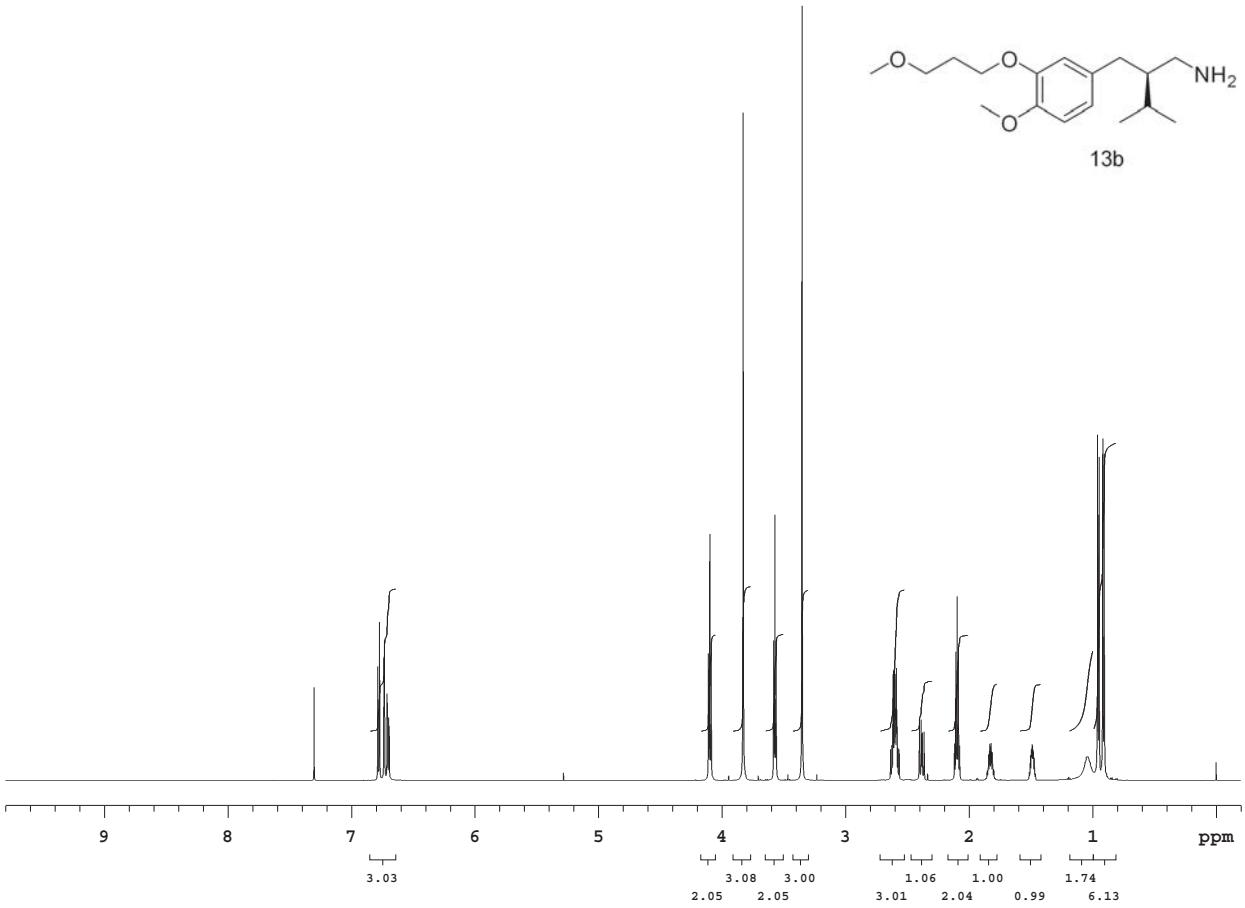
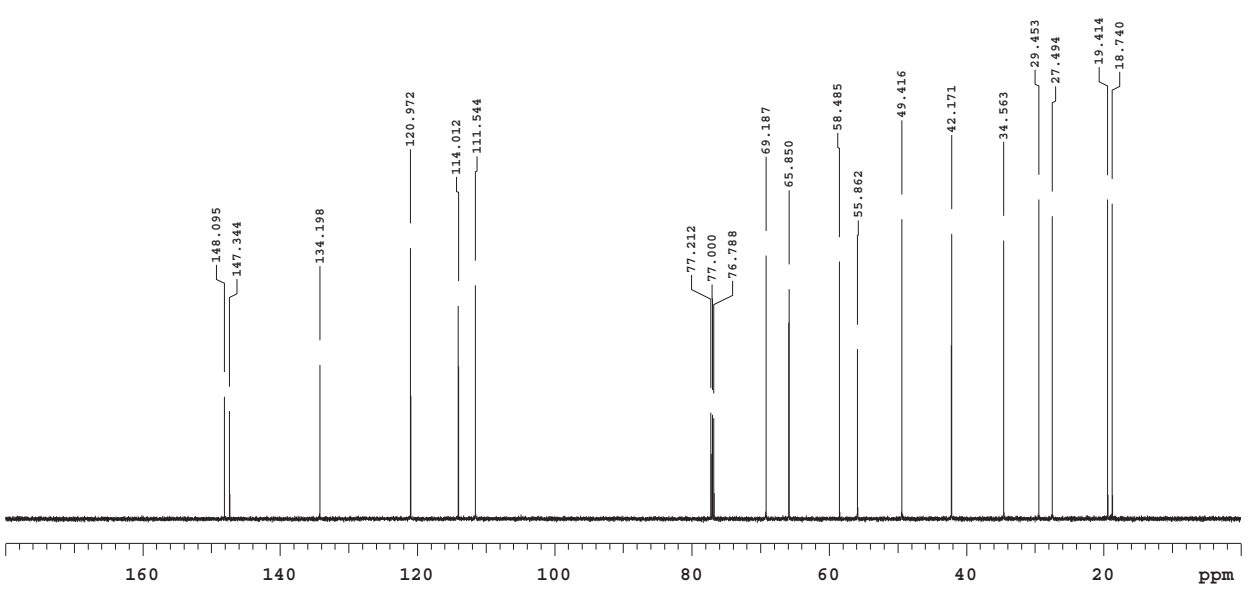
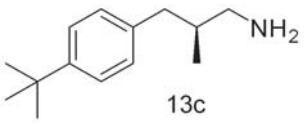
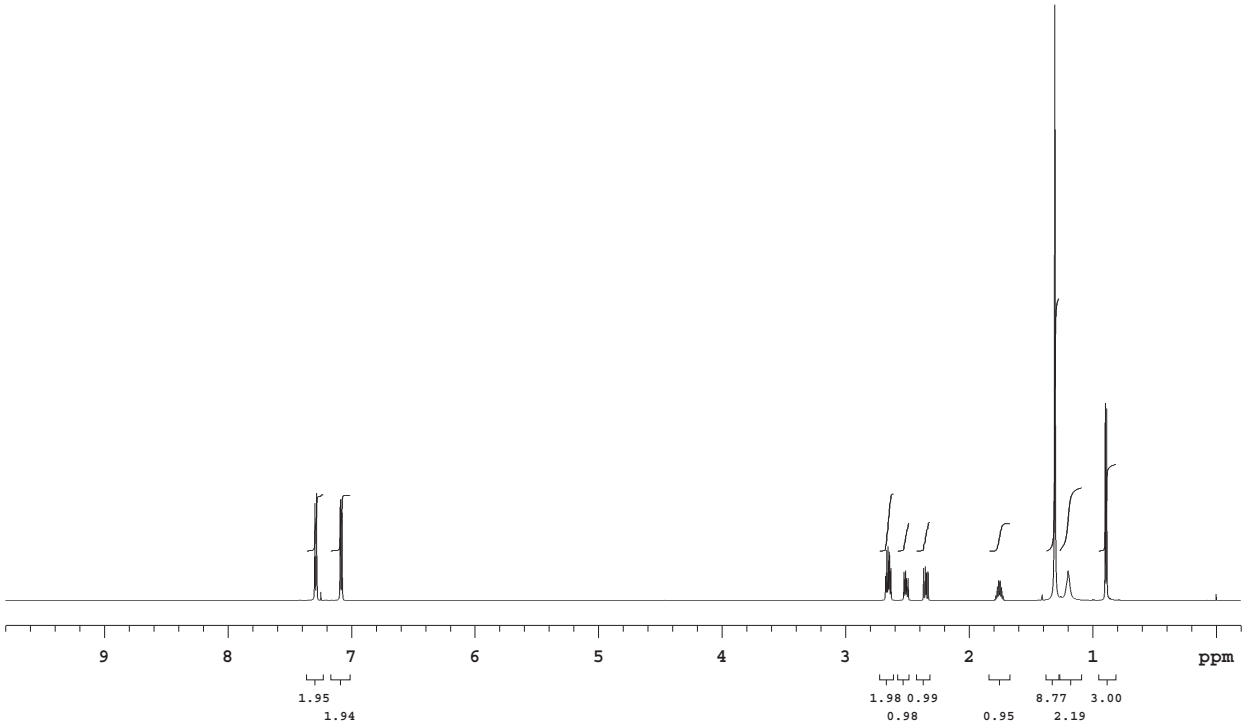
140
120
100
80
60
40
20
ppm

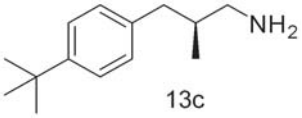

13b
9
8
7
6
5
4
3
2
1
ppm
3.03
2.05
3.08
2.05
3.00
3.01
1.06
2.04
1.00
0.99
1.74
6.13


13b
148.095
147.344
134.198
120.972
114.012
111.544
77.212
77.000
76.788
69.187
65.850
58.485
55.862
49.416
42.171
34.563
29.453
27.494
19.414
18.740
160
140
120
100
80
60
40
20
ppm

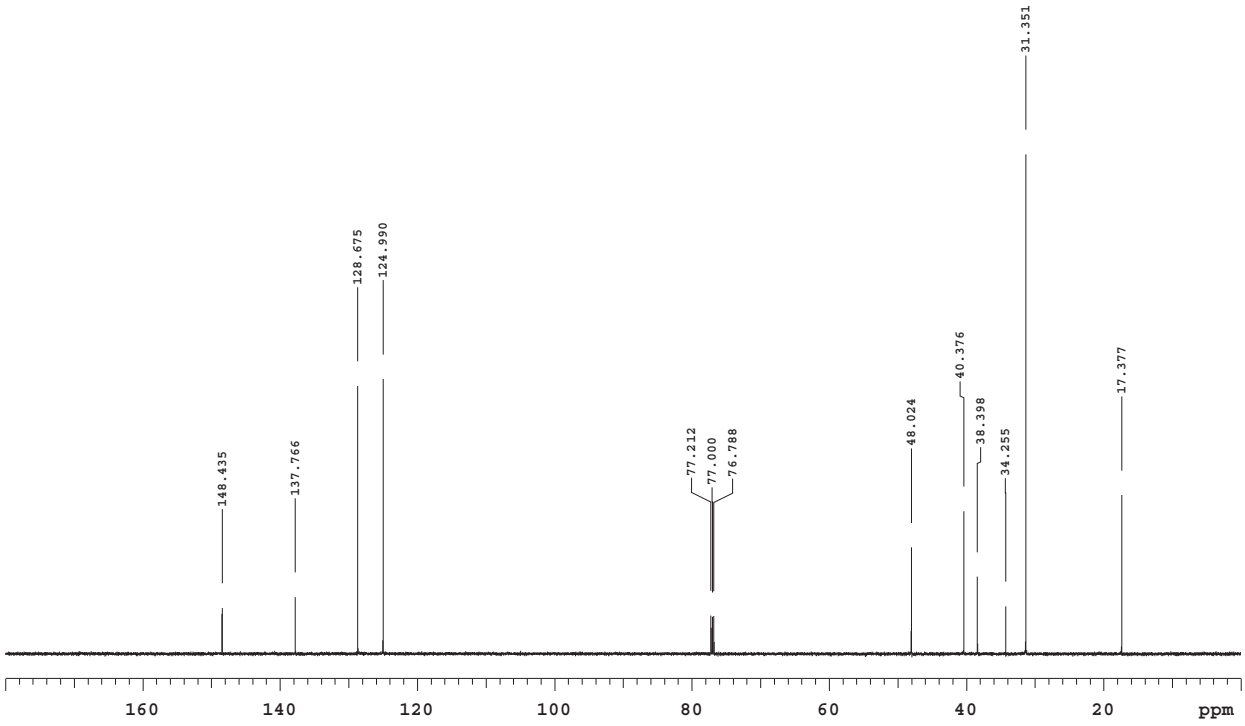

NH2

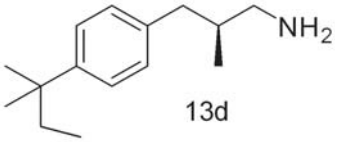
13c


9
8
7
6
5
4
3
2
1
ppm
1.95
1.94
1.98
0.98
0.99
0.95
8.77
2.19
3.00

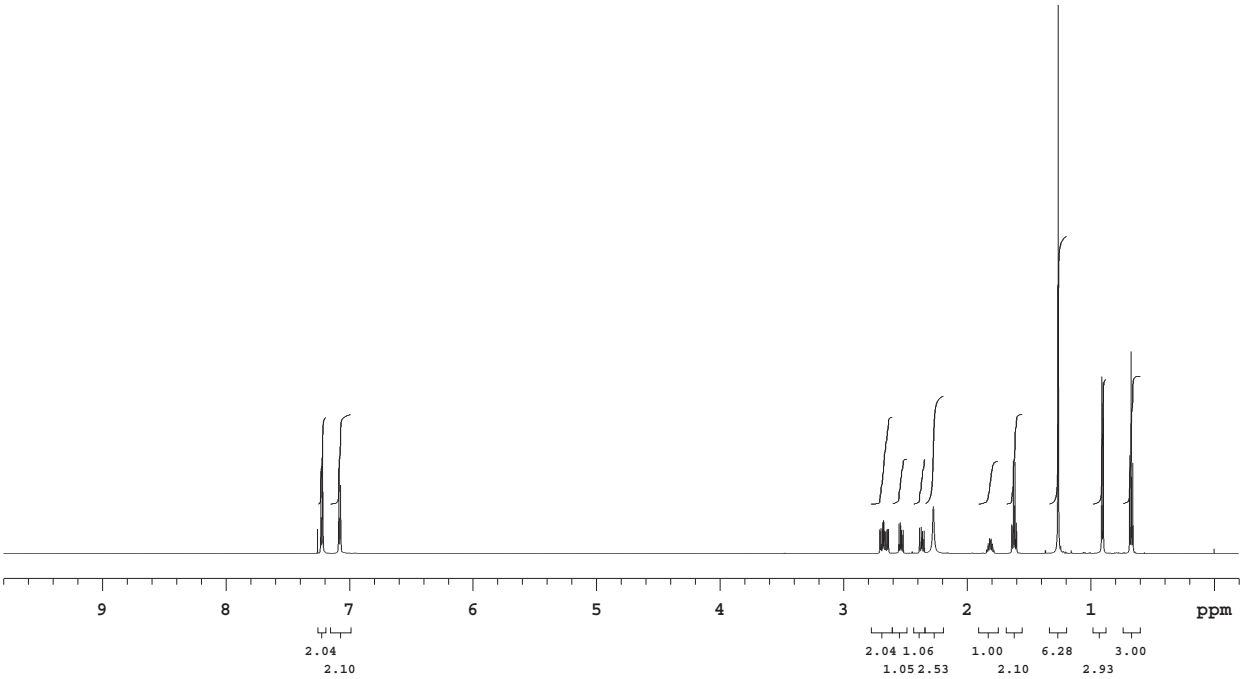

NH2

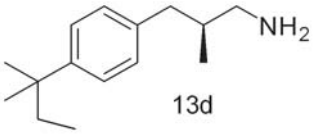
13c


148.435
137.766
128.675
124.990
77.212
77.000
76.788
48.024
40.376
38.398
34.255
31.351
17.377
160
140
120
100
80
60
40
20
ppm

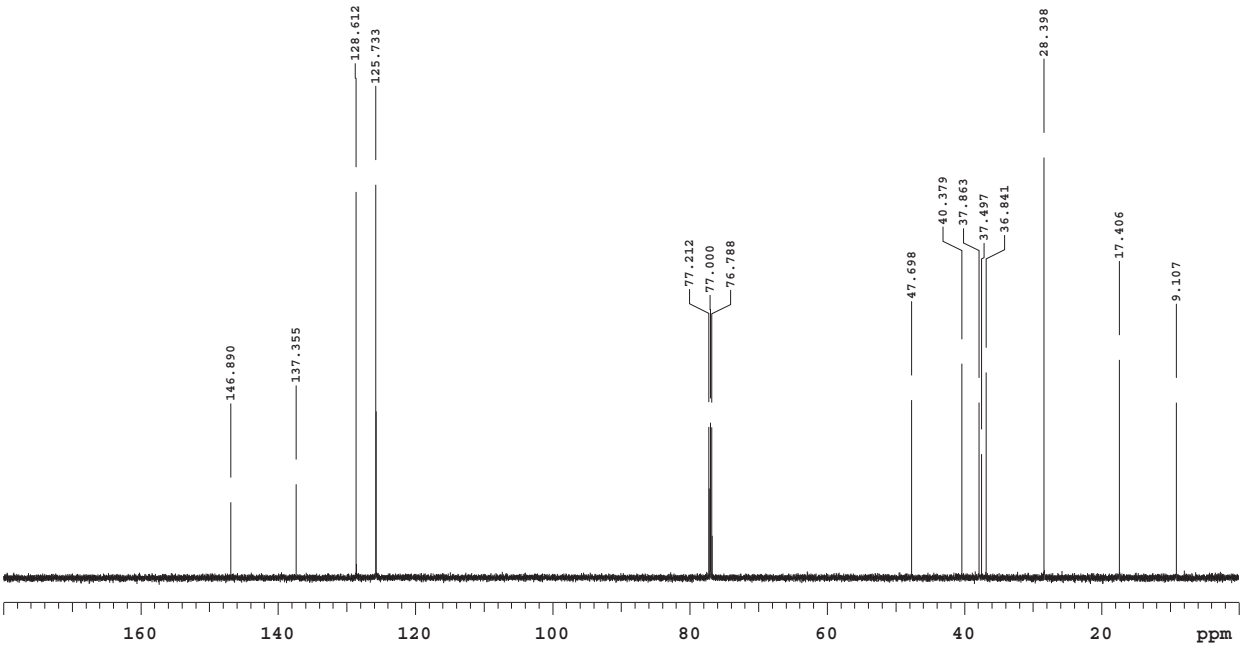

NH2

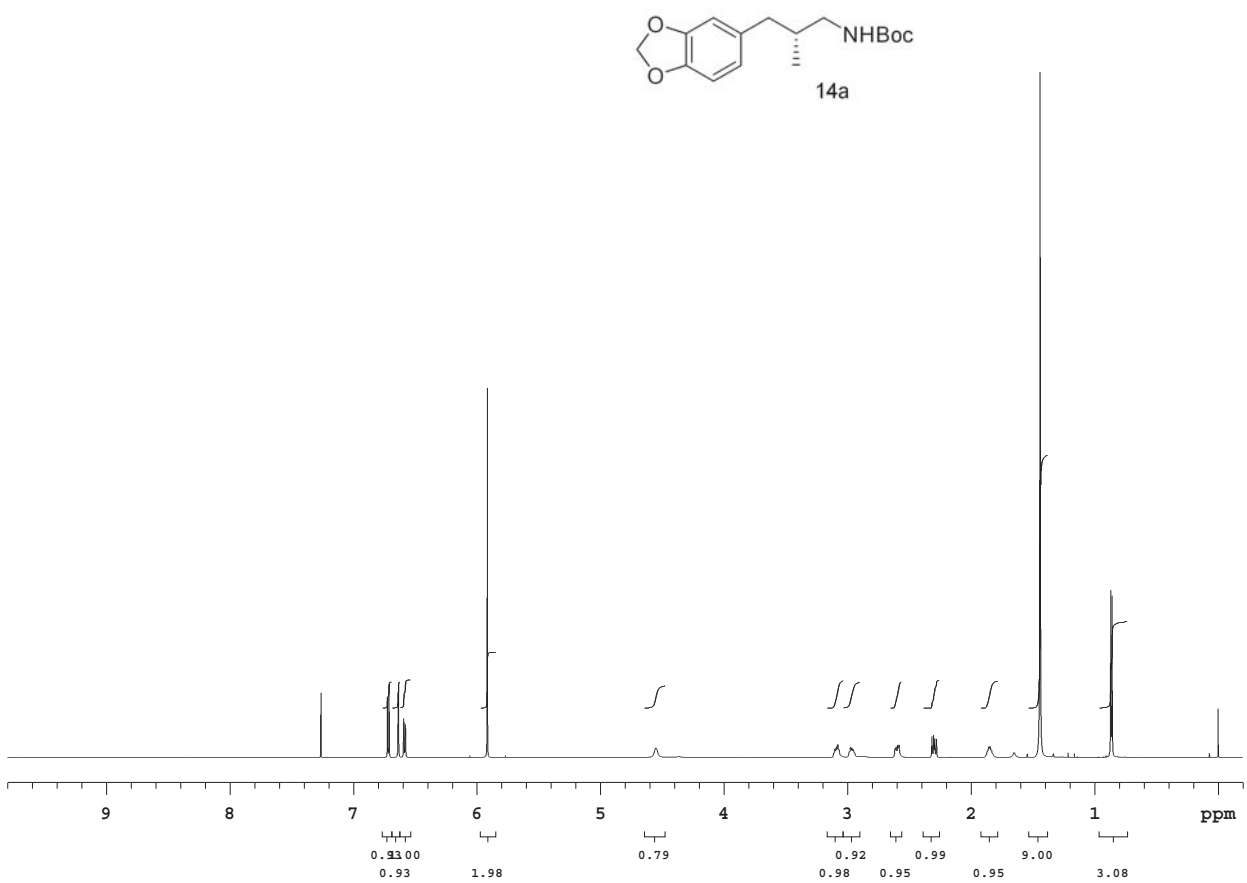
13d

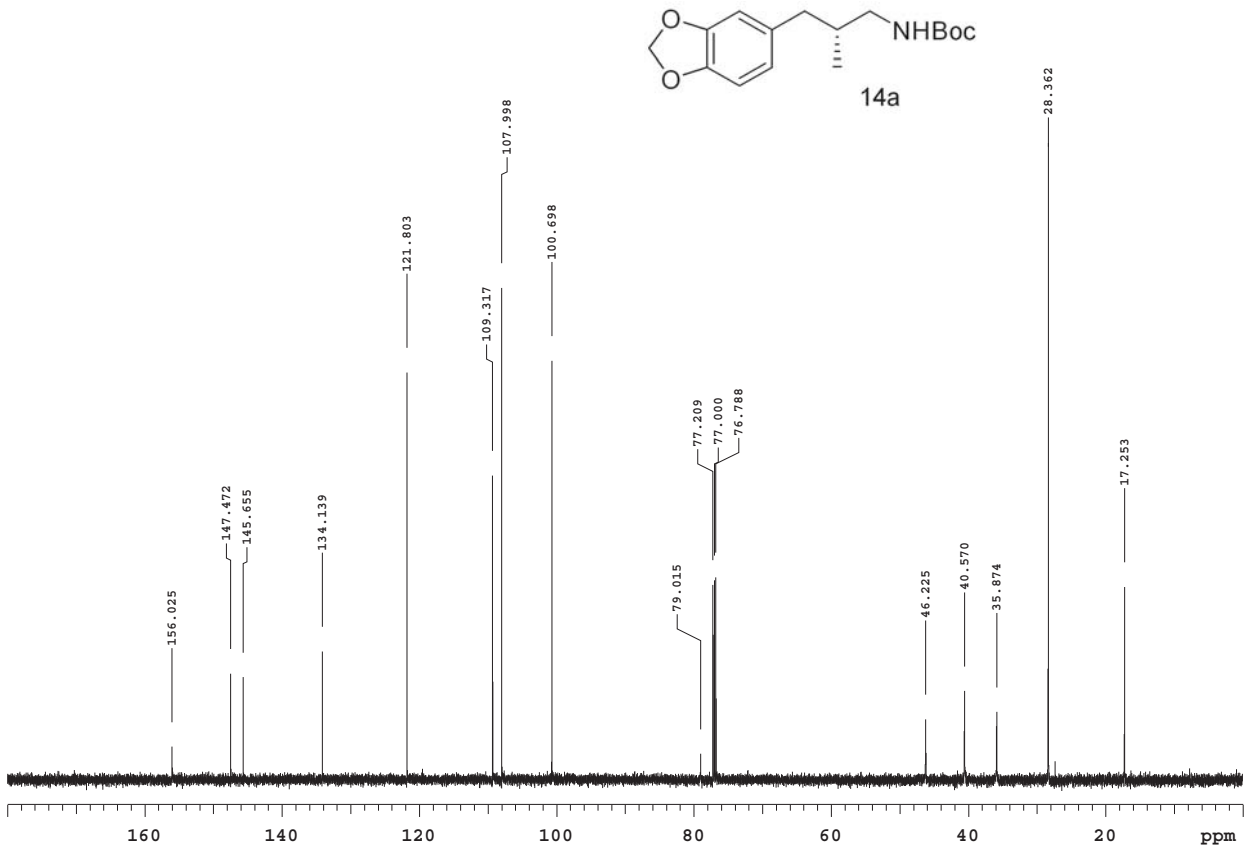

9
8
7
6
5
4
3
2
1
ppm
2.04
2.10
2.04
1.05
1.06
2.53
1.00
2.10
6.28
2.93
3.00

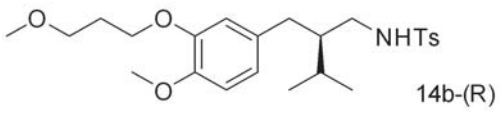

NH2

13d

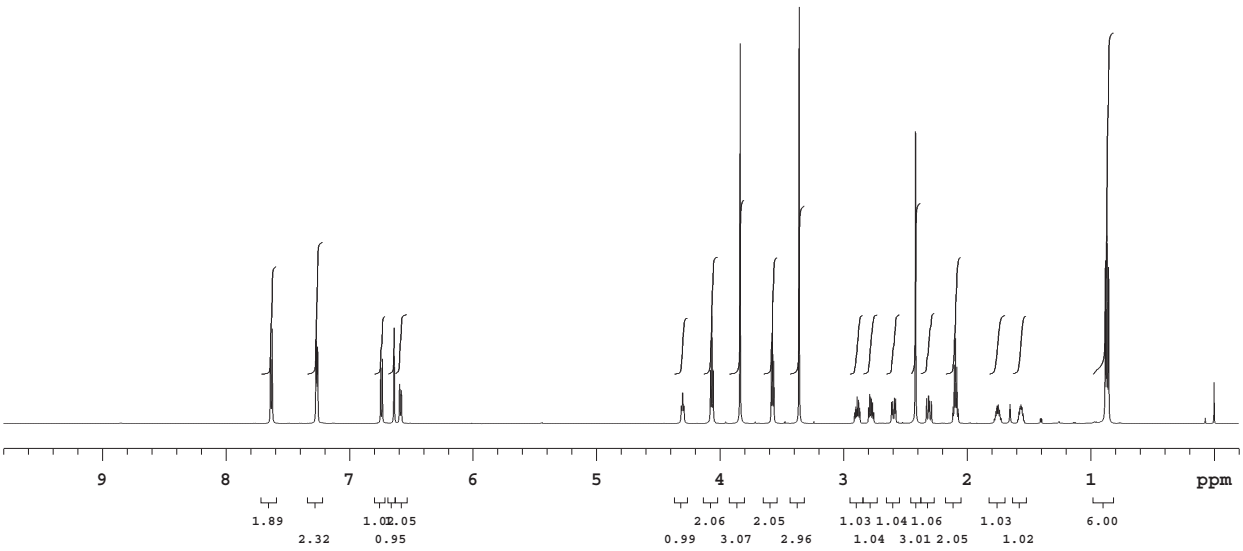

146.890
137.355
128.612
125.733
77.212
77.000
76.788
47.698
40.379
37.863
37.497
36.841
28.398
17.406
9.107
160
140
120
100
80
60
40
20
ppm

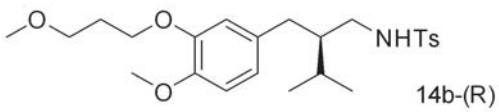

NHBoc
14a
9
8
7
6
5
4
3
2
1
ppm
0.93
1.98
0.79
0.98
0.95
0.99
0.95
9.00
3.08


NHBoc
14a
156.025
147.472
145.655
134.139
121.803
109.317
107.998
100.698
79.015
77.209
77.000
76.788
46.225
40.570
35.874
28.362
17.253
160
140
120
100
80
60
40
20
ppm

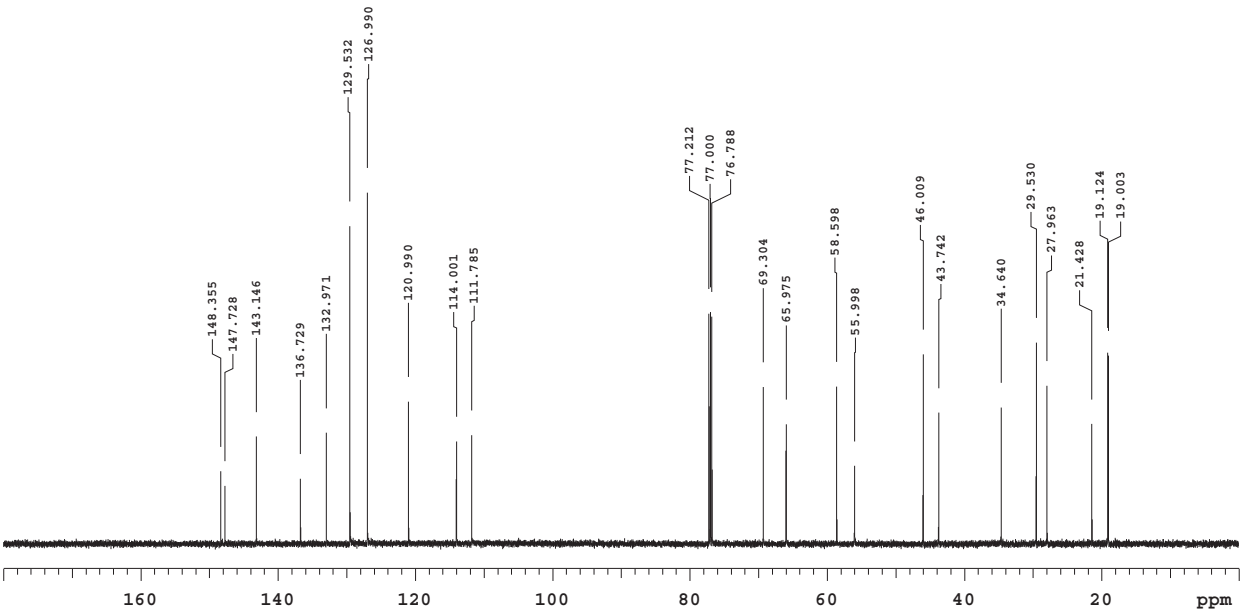

O
O
NHTs
O

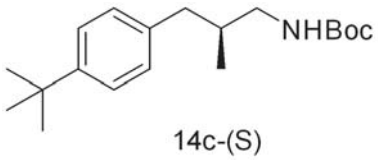
14b-(R)


9
8
7
6
5
4
3
2
1
ppm
1.89
2.32
1.01
1.05
0.95
0.99
2.06
3.07
2.05
2.96
1.03
1.04
1.04
3.01
1.06
2.05
1.03
1.02
6.00

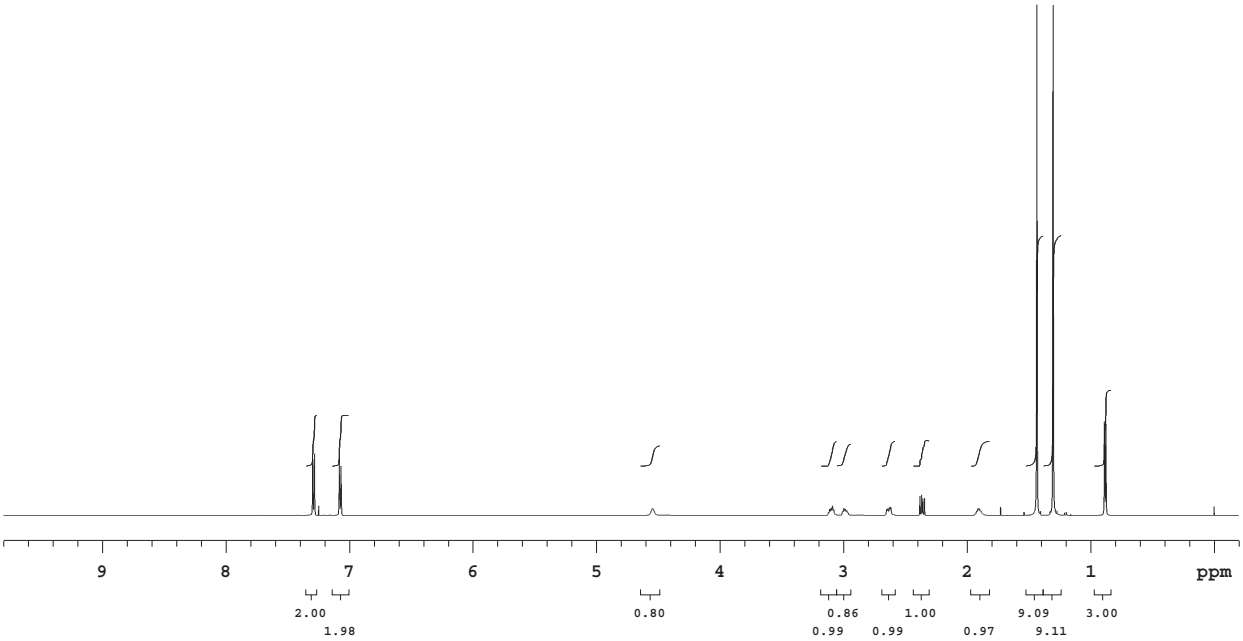

O
O
NHTs
O

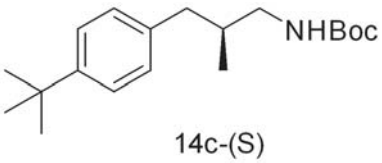
14b-(R)


148.355
147.728
143.146
136.729
132.971
129.532
126.990
120.990
114.001
111.785
77.212
77.000
76.788
69.304
65.975
58.598
55.998
46.009
43.742
34.640
29.530
27.963
21.428
19.124
19.003
160
140
120
100
80
60
40
20
ppm


NHBoc

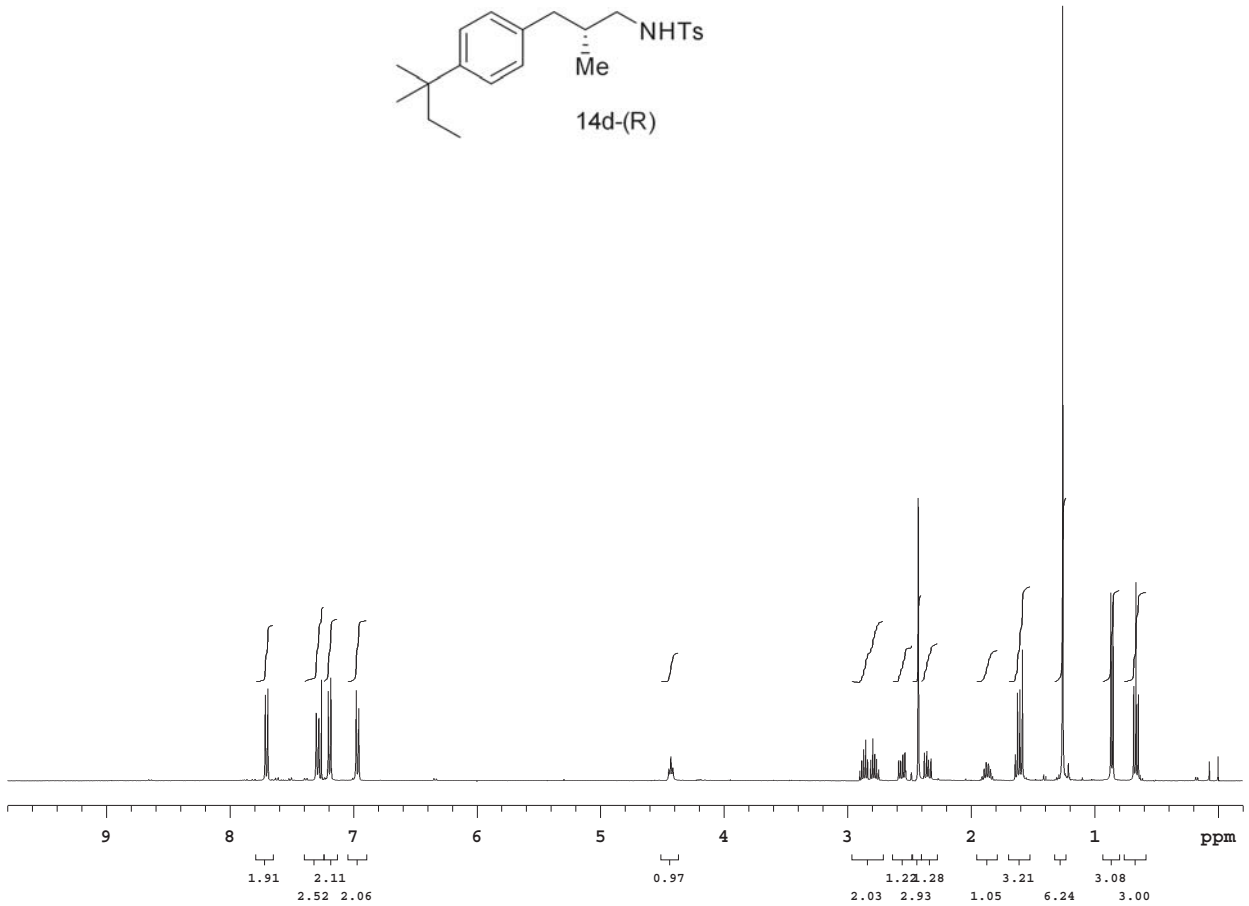
14c-(S)

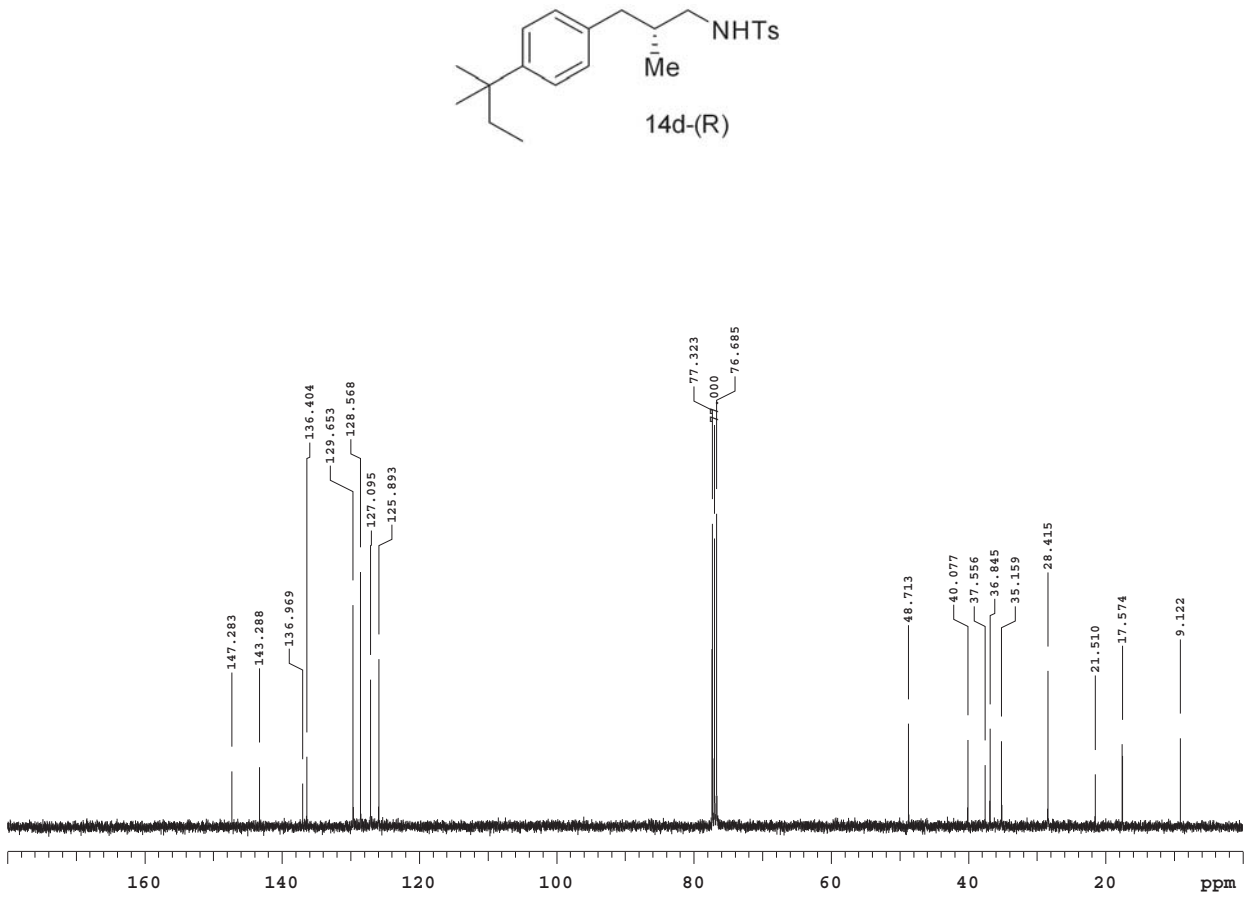

9
8
7
6
5
4
3
2
1
ppm
2.00
1.98
0.80
0.86
0.99
1.00
0.99
0.97
9.09
9.11
3.00

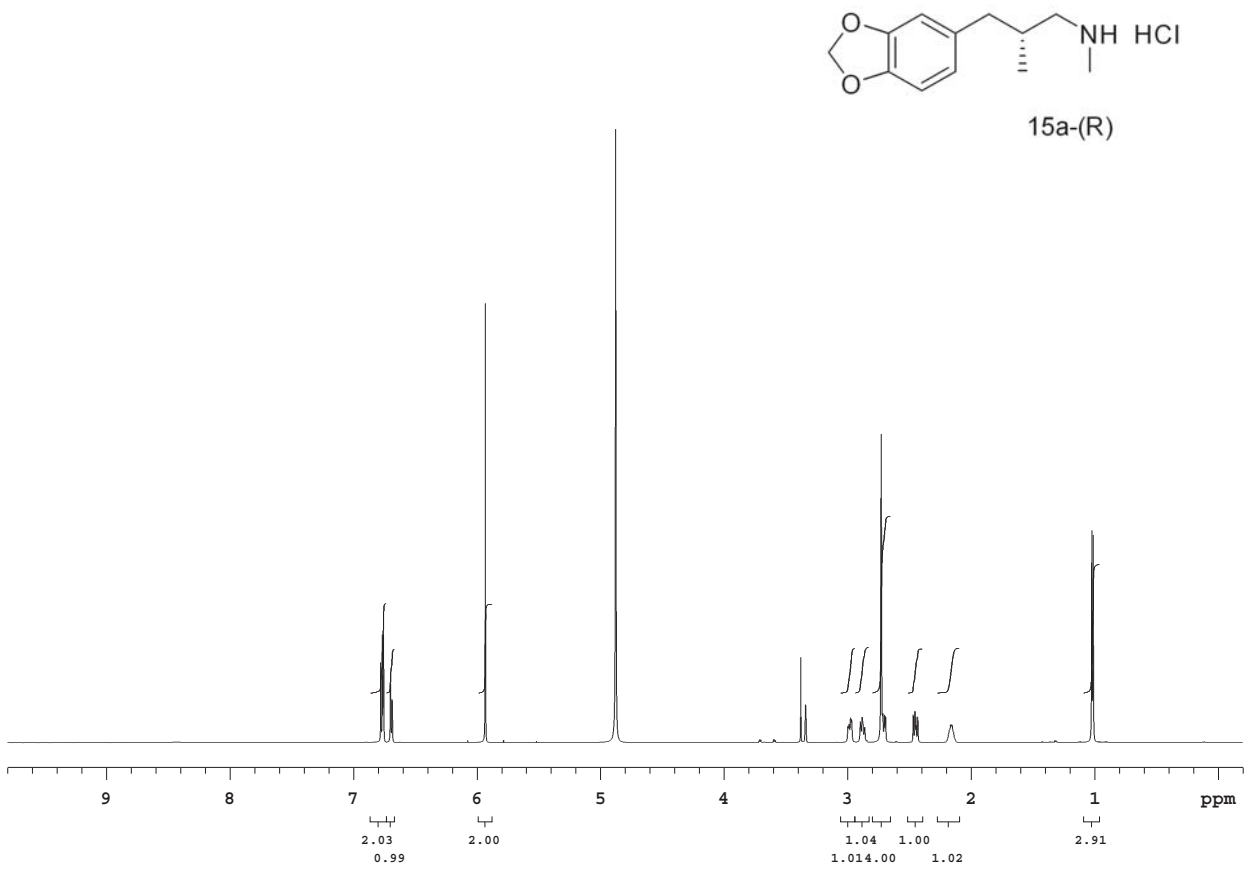

NHBoc

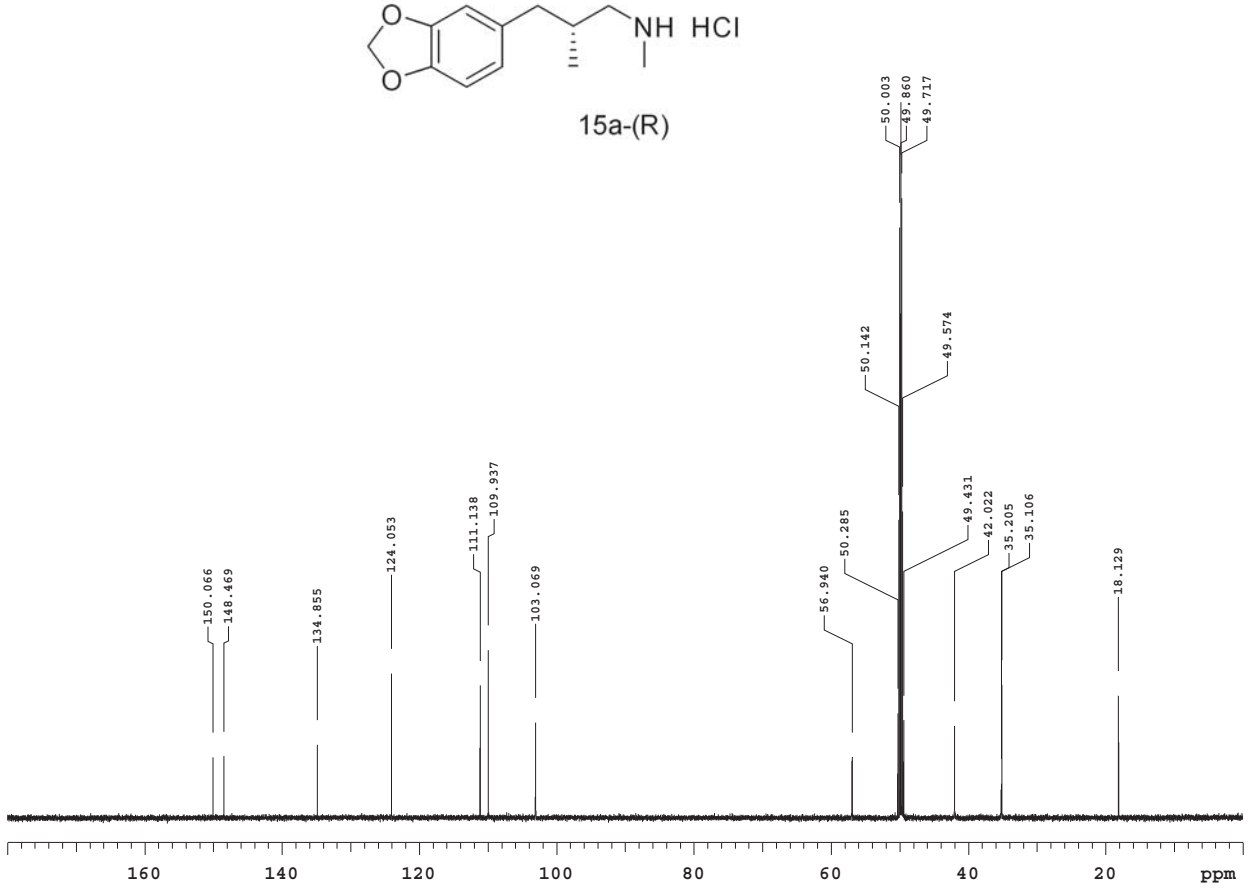
14c-(S)

156.050
148.655
137.227
128.689
125.118
78.963
77.212
77.000
76.788
46.350
40.394
35.669
34.303
31.373
28.391
17.480
160
140
120
100
80
60
40
20
ppm


NHTs
Me
14d-(R)
9
8
7
6
5
4
3
2
1
ppm
1.91
2.11
2.52
2.06
0.97
2.03
1.22
1.28
2.93
1.05
3.21
6.24
3.08
3.00


NHTs
Me
14d-(R)
147.283
143.288
136.969
136.404
129.653
128.568
127.095
125.893
77.323
77.000
76.685
48.713
40.077
37.556
36.845
35.159
28.415
21.510
17.574
9.122
160
140
120
100
80
60
40
20
ppm


NH HCl
15a-(R)
9
8
7
6
5
4
3
2
1
ppm
2.03
0.99
2.00
1.04
1.00
1.01
4.00
1.02
2.91

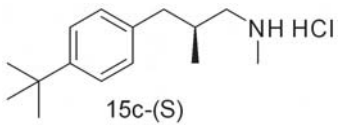

NH HCl
15a-(R)
50.003
49.860
49.717
50.142
49.574
150.066
148.469
134.855
124.053
111.138
109.937
103.069
56.940
50.285
49.431
42.022
35.205
35.106
18.129
160
140
120
100
80
60
40
20
ppm

GF-28B-NMeHCl

File: xp

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: rosini
INOVA-600 "i600"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.995 sec
Width 9595.8 Hz
Single scan
OBSERVE H1, 599.7299254 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 12 sec



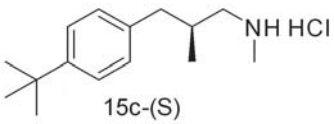
15c-(S)

GF-28B-NMeHCl

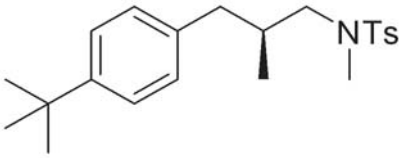
Sample: GF-28B-NMeHCl
File: xp

Pulse Sequence: s2pul
Solvent: cd3od
Temp. 25.0 C / 298.1 K
Operator: rosini
INOVA-600 "i600"

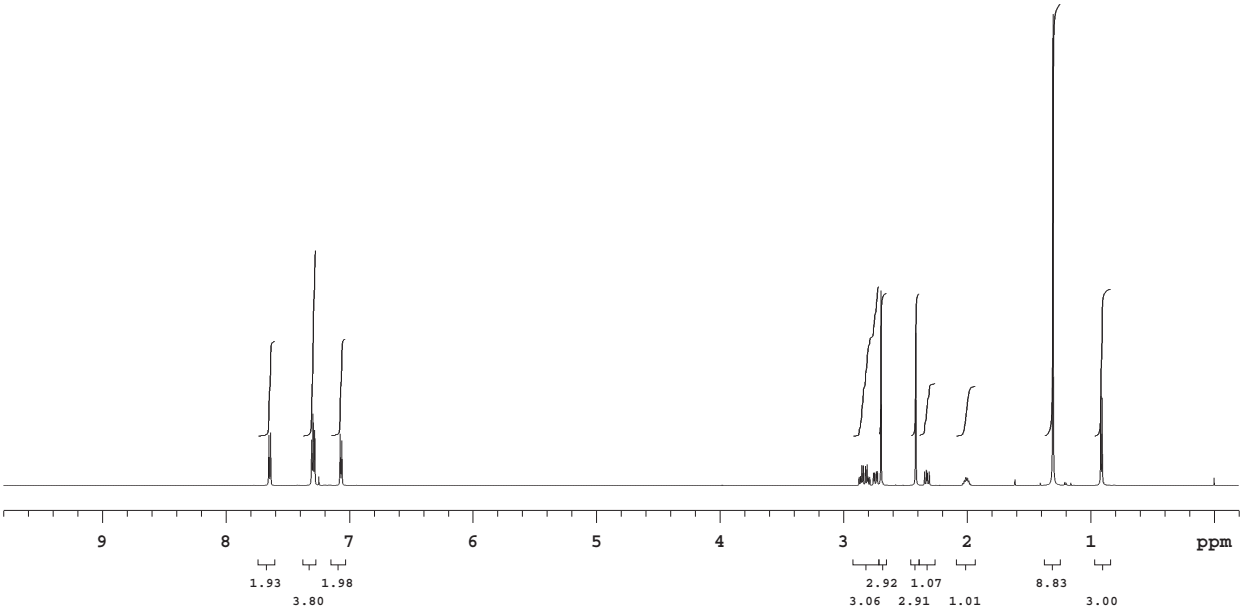
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 36199.1 Hz
528 repetitions
OBSERVE C13, 150.8018786 MHz
DECOUPLE H1, 599.7329490 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Sq. sine bell 1.000 sec
Shifted by -1.000 sec
FT size 131072
Total time 33 min, 29 sec

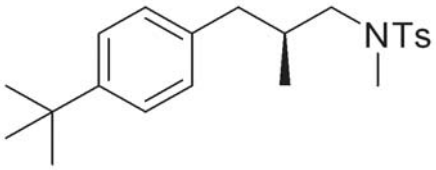


15c-(S)

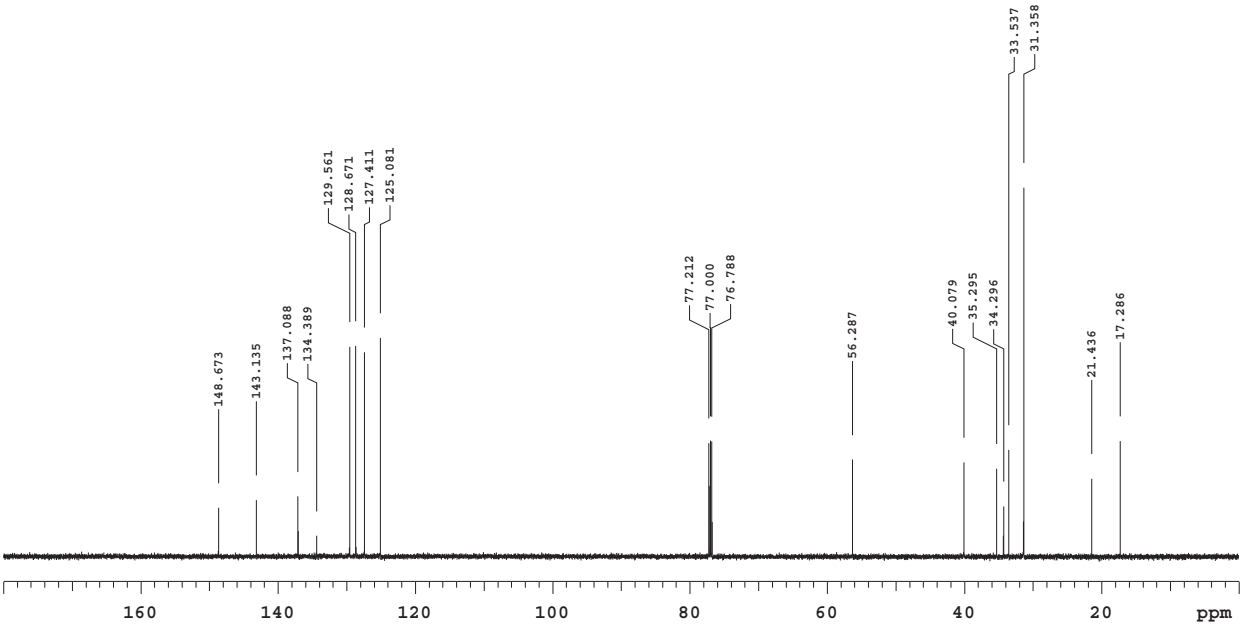

NTs

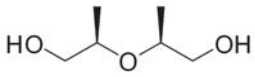
16c-(S)


9
8
7
6
5
4
3
2
1
ppm
1.93
1.98
3.80
2.92
1.07
3.06
2.91
1.01
8.83
3.00

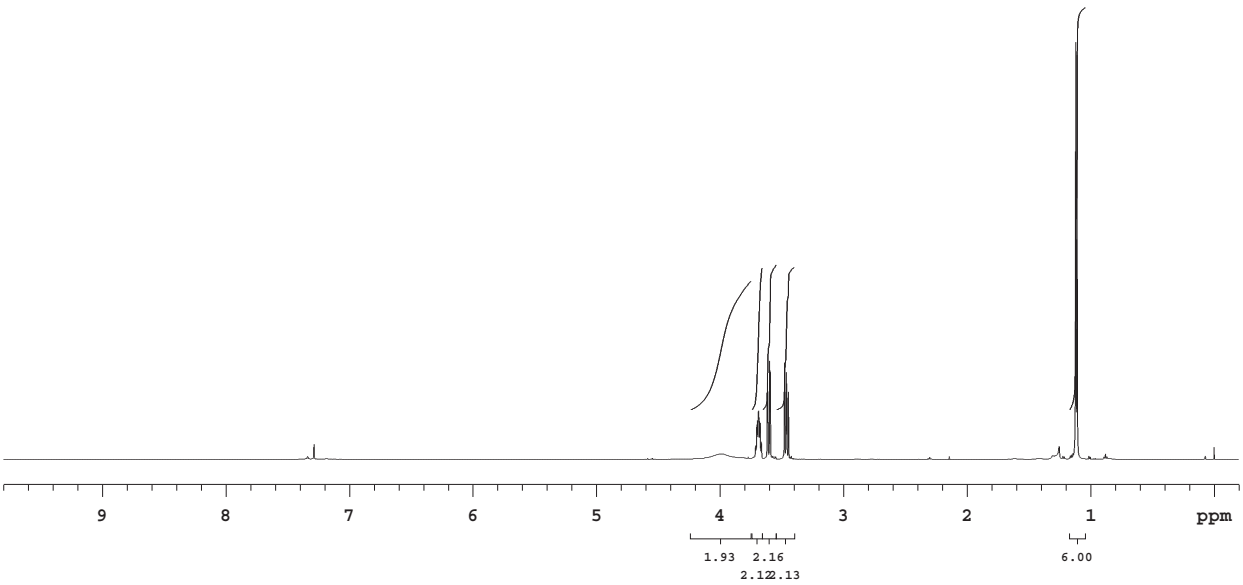

NTs

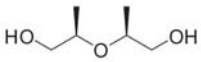
16c-(S)


148.673
143.135
137.088
134.389
129.561
128.671
127.411
125.081
77.212
77.000
76.788
56.287
40.079
35.295
34.296
33.537
31.358
21.436
17.286
160
140
120
100
80
60
40
20
ppm

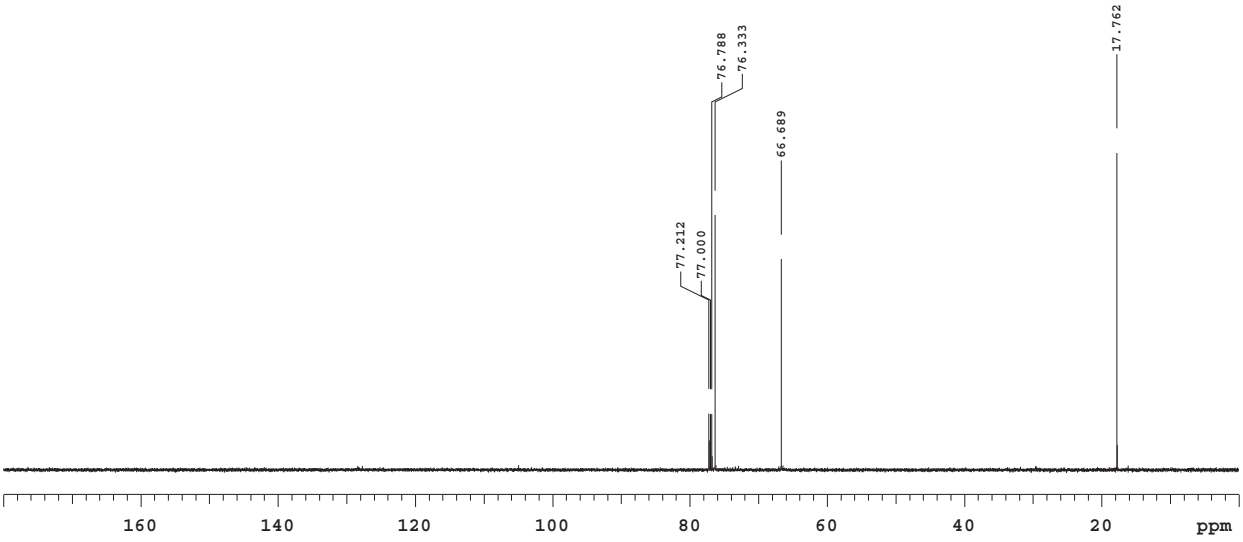


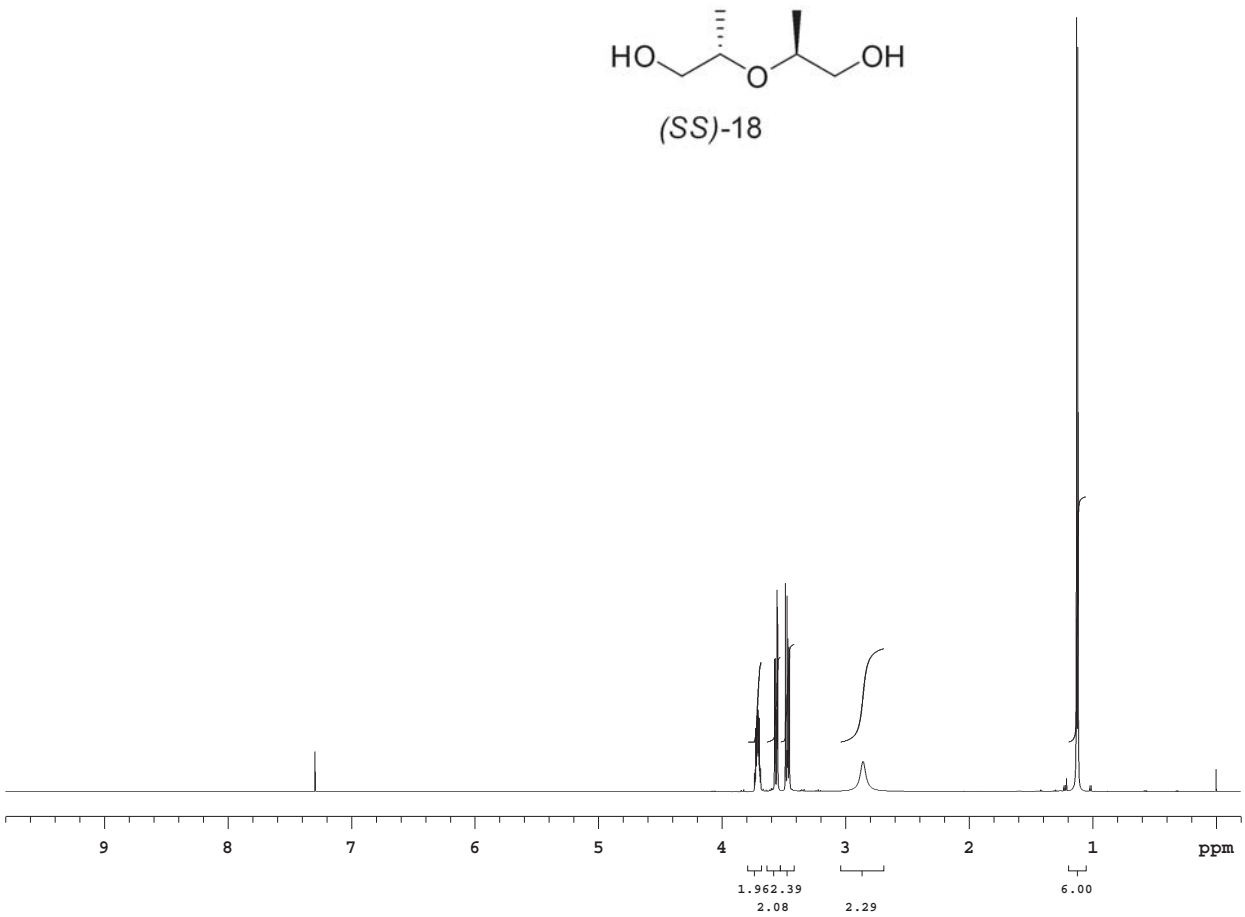
meso-18

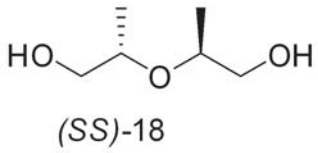


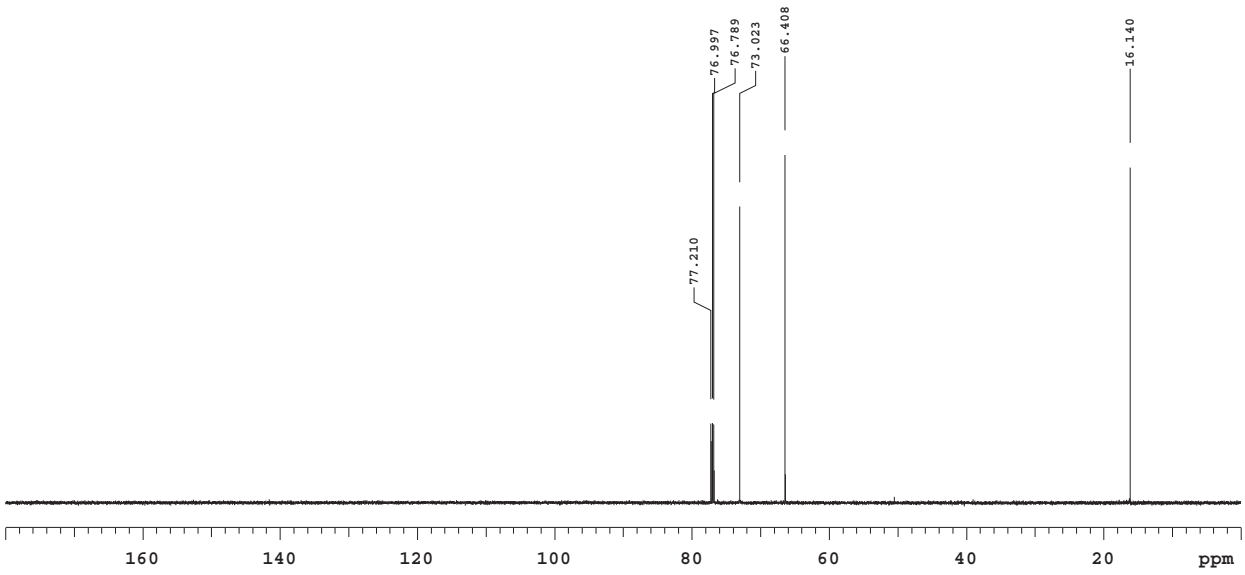


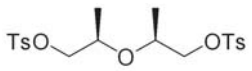
meso-18



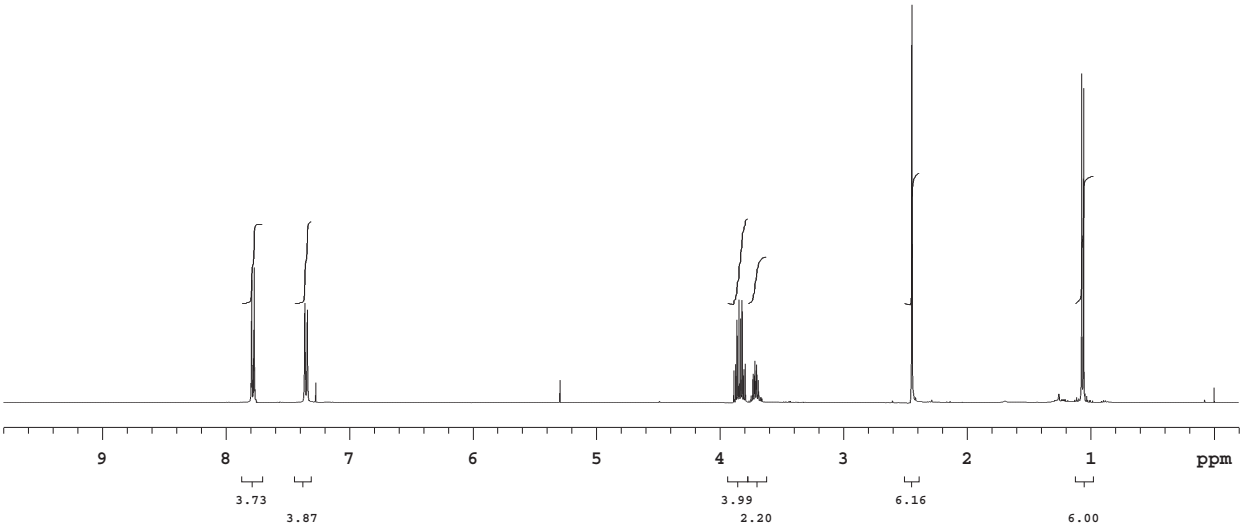

HO
O
OH
(SS)-18
9
8
7
6
5
4
3
2
1
ppm
1.96
2.39
2.08
2.29
6.00

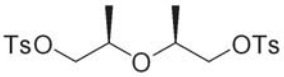

HO
O
OH
(SS)-18


76.997
76.789
73.023
66.408
16.140
77.210
160
140
120
100
80
60
40
20
ppm

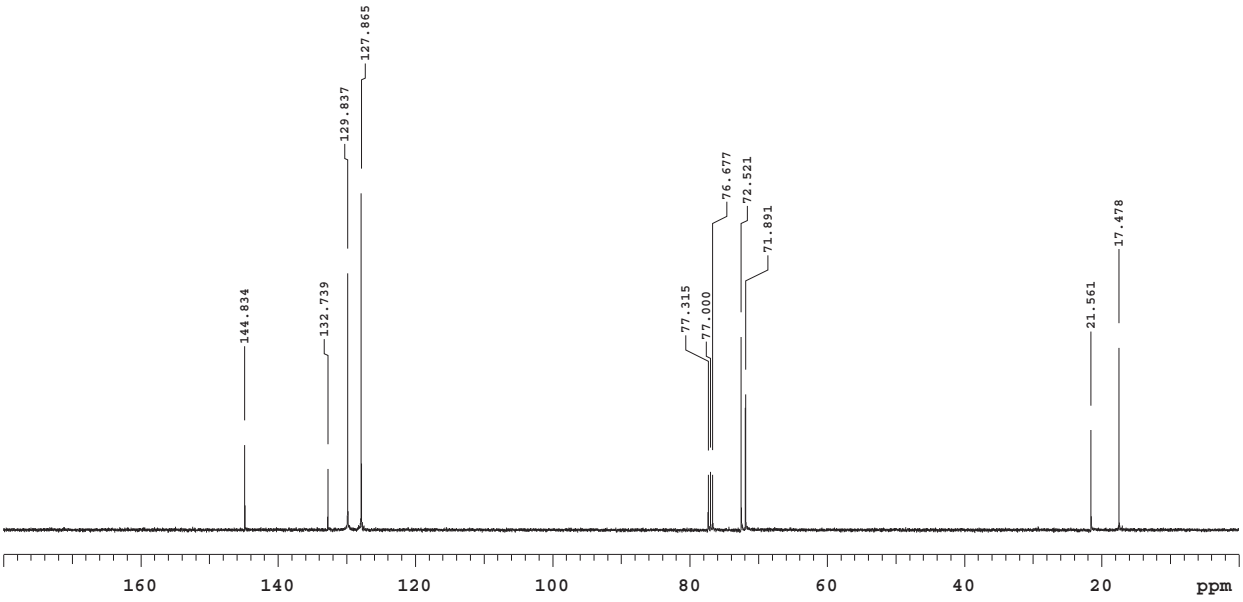


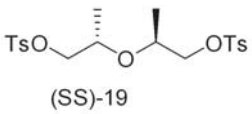
19-meso



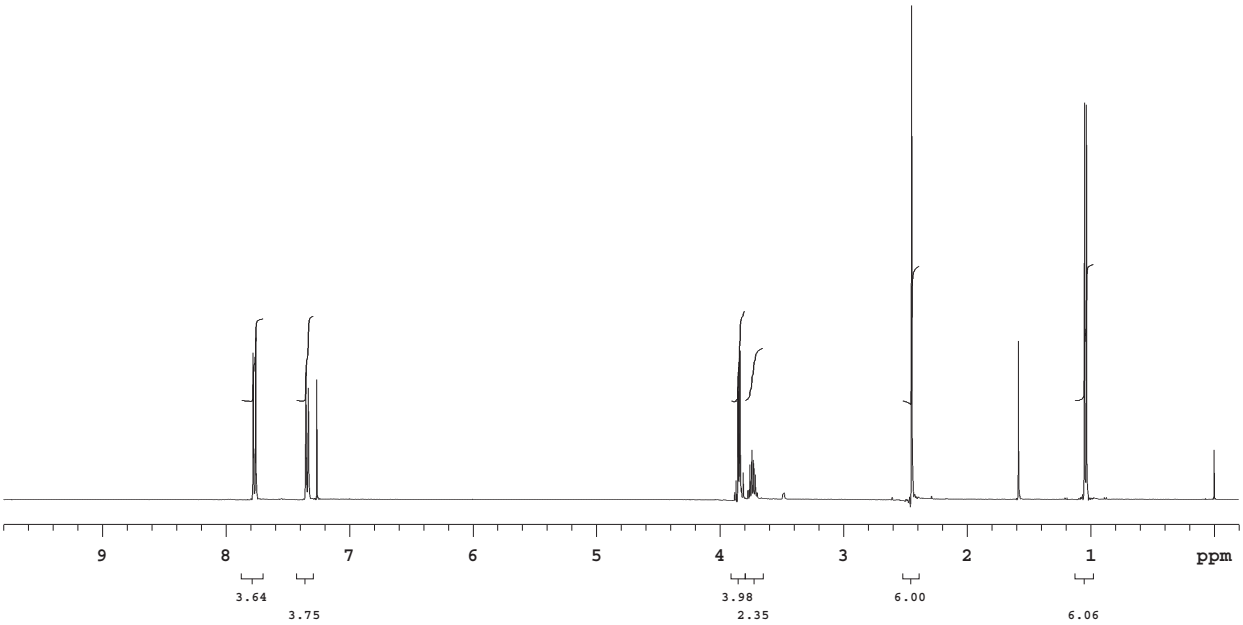


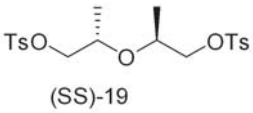
19-meso



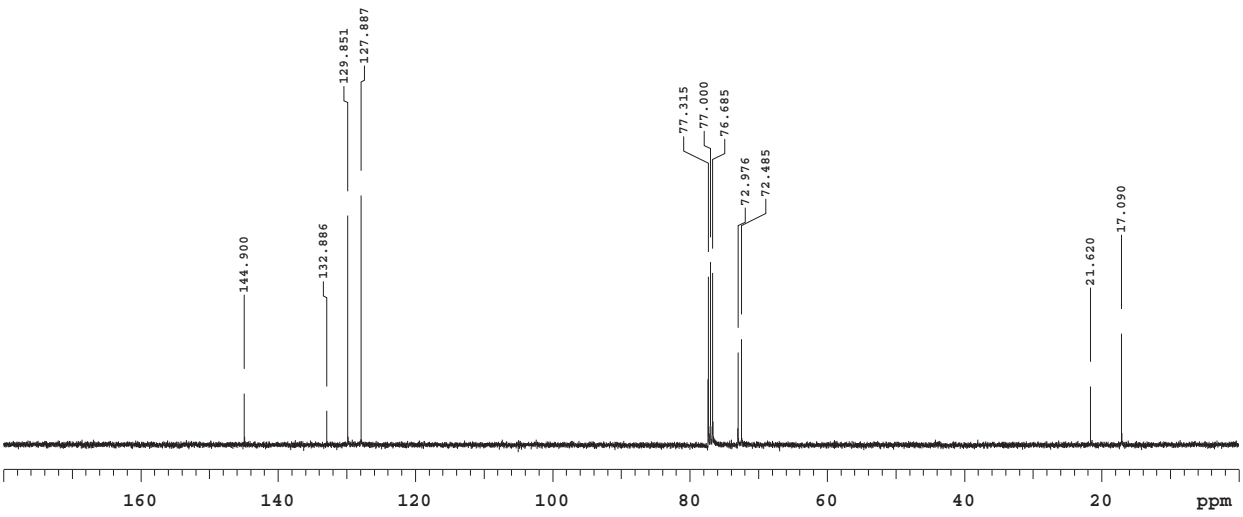

TsO
O
OTs

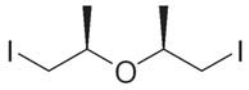
(SS)-19


9
8
7
6
5
4
3
2
1
ppm
3.64
3.75
3.98
2.35
6.00
6.06

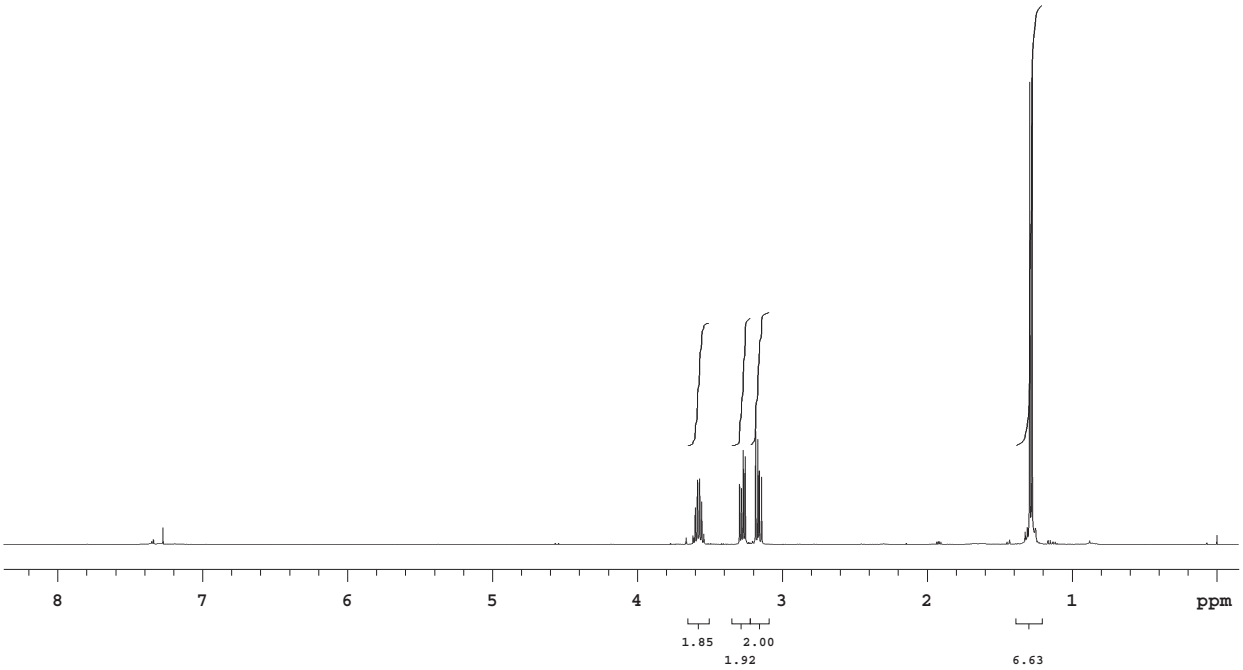

TsO
O
OTs

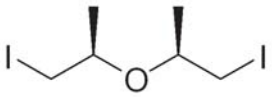
(SS)-19


144.900
132.886
129.851
127.887
77.315
77.000
76.685
72.976
72.485
21.620
17.090
160
140
120
100
80
60
40
20
ppm

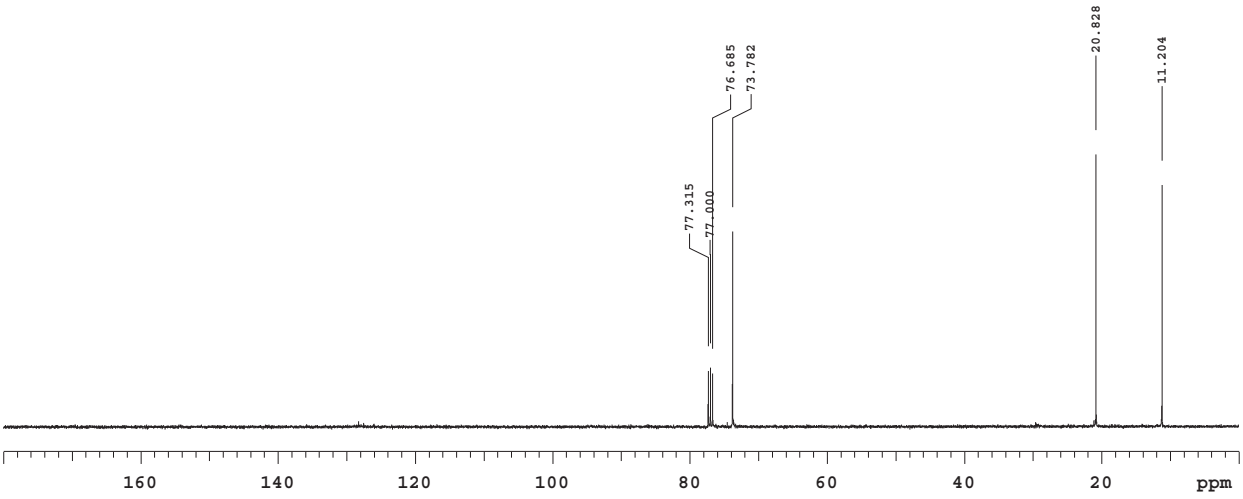


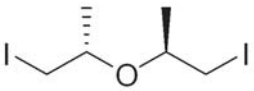
meso-20



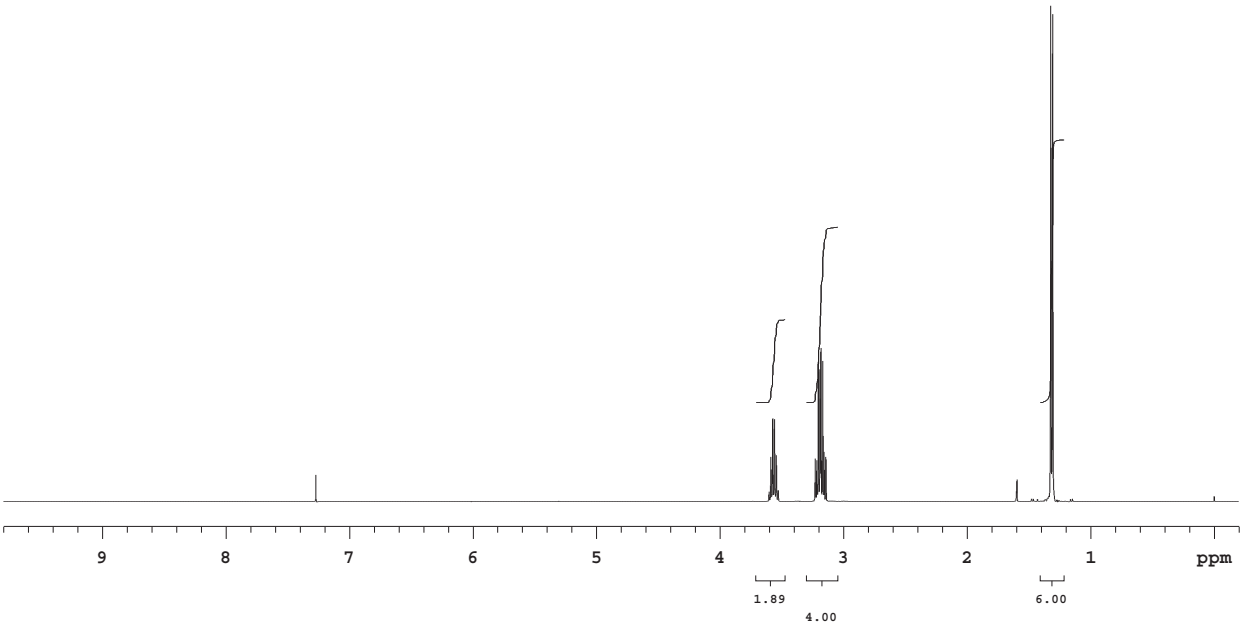


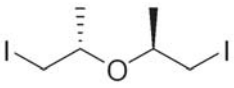
meso-20



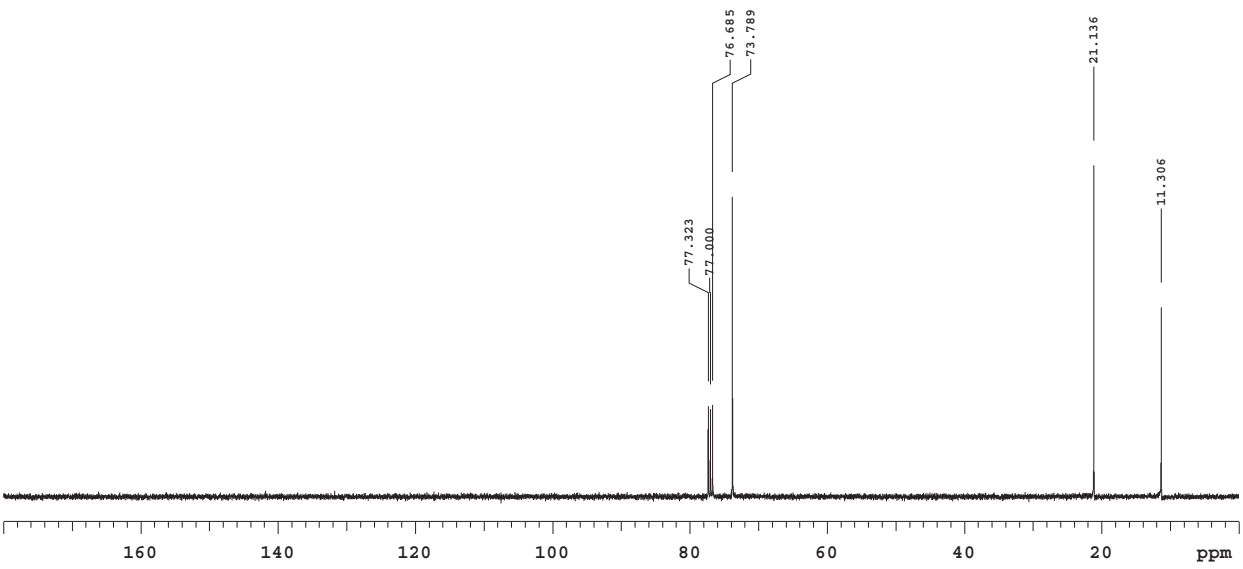


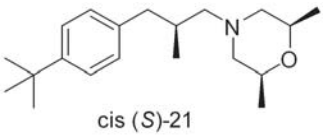
(SS)-20


9
8
7
6
5
4
3
2
1
ppm
1.89
4.00
6.00

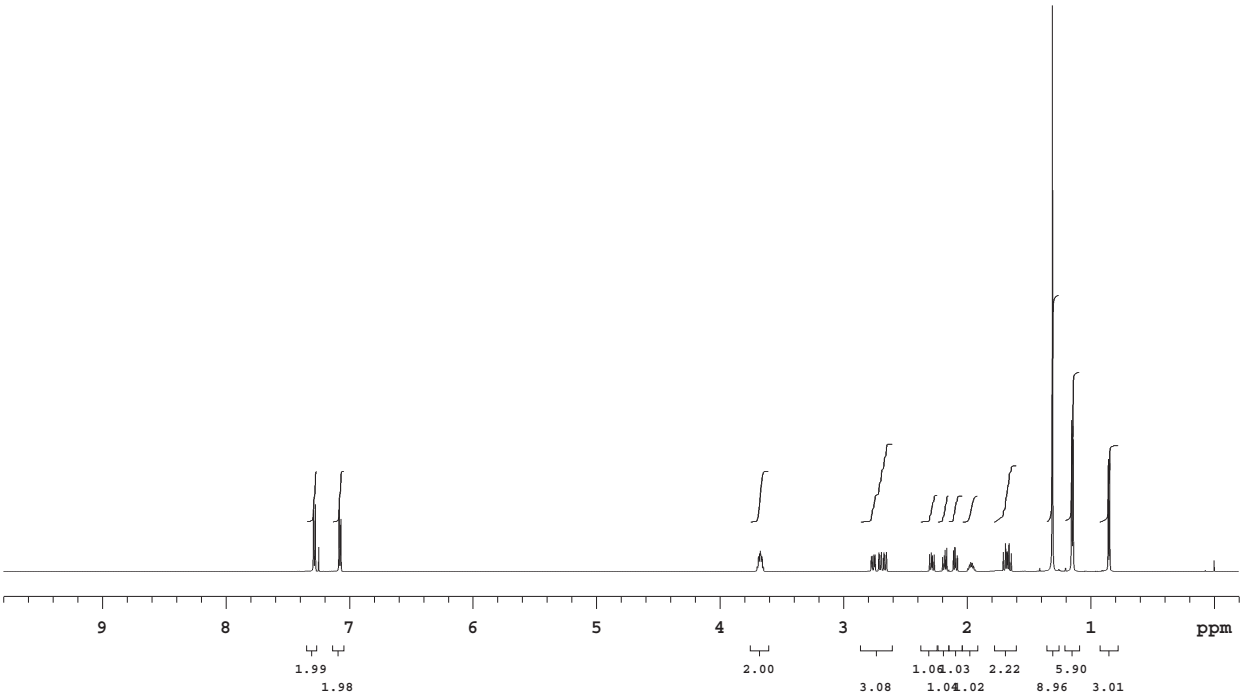


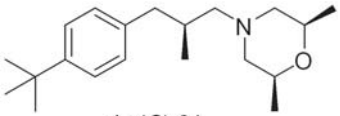
(SS)-20


76.685
73.789
77.323
77.000
21.136
11.306
160
140
120
100
80
60
40
20
ppm

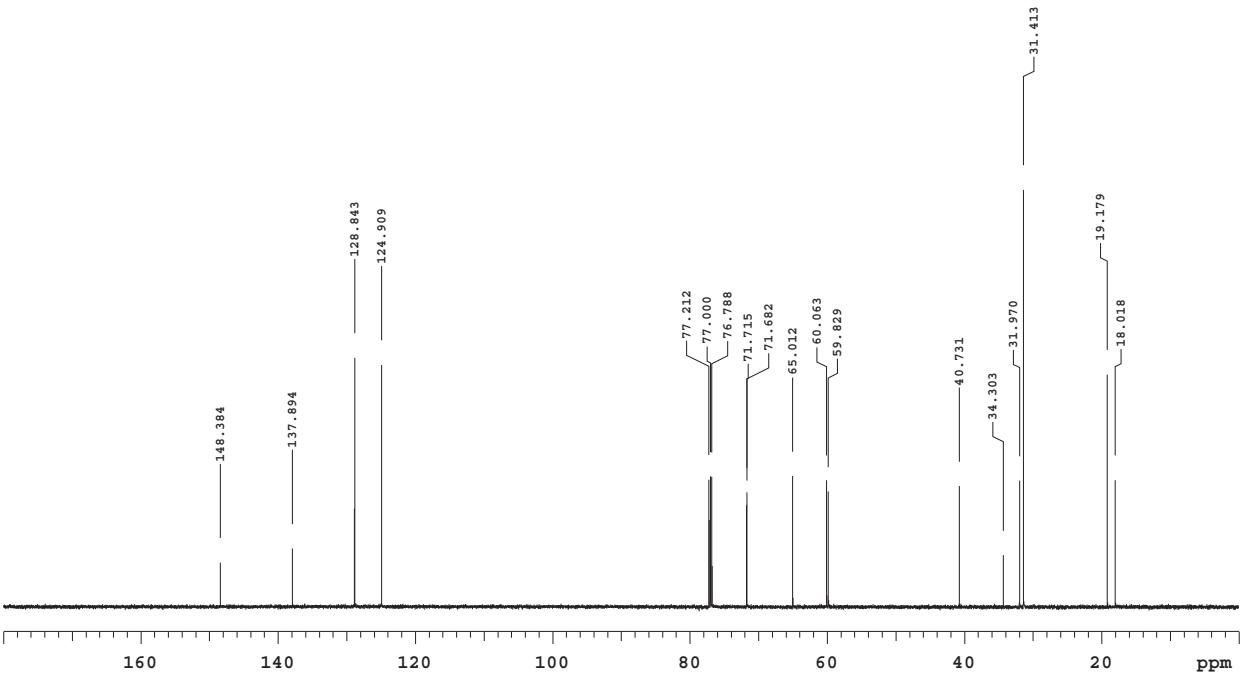


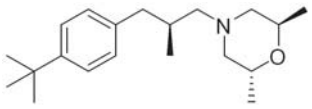
cis (*S*)-21



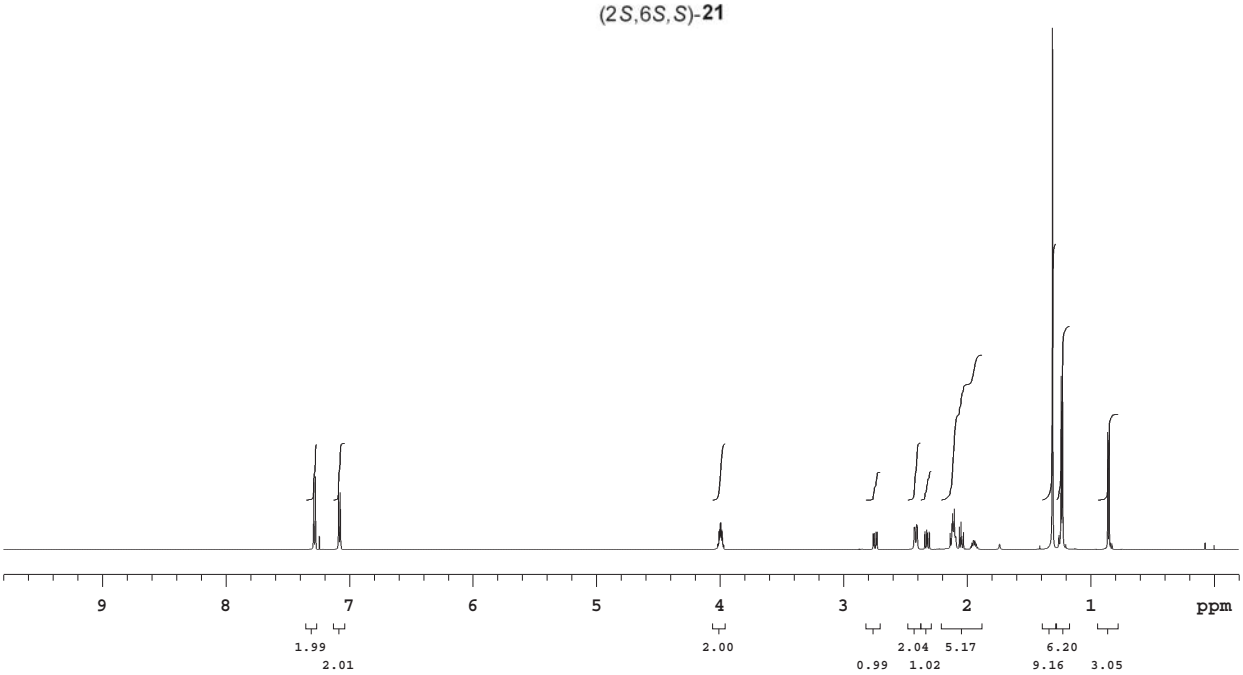


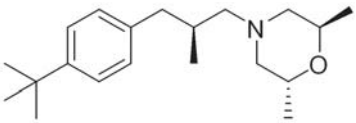
cis (*S*)-21



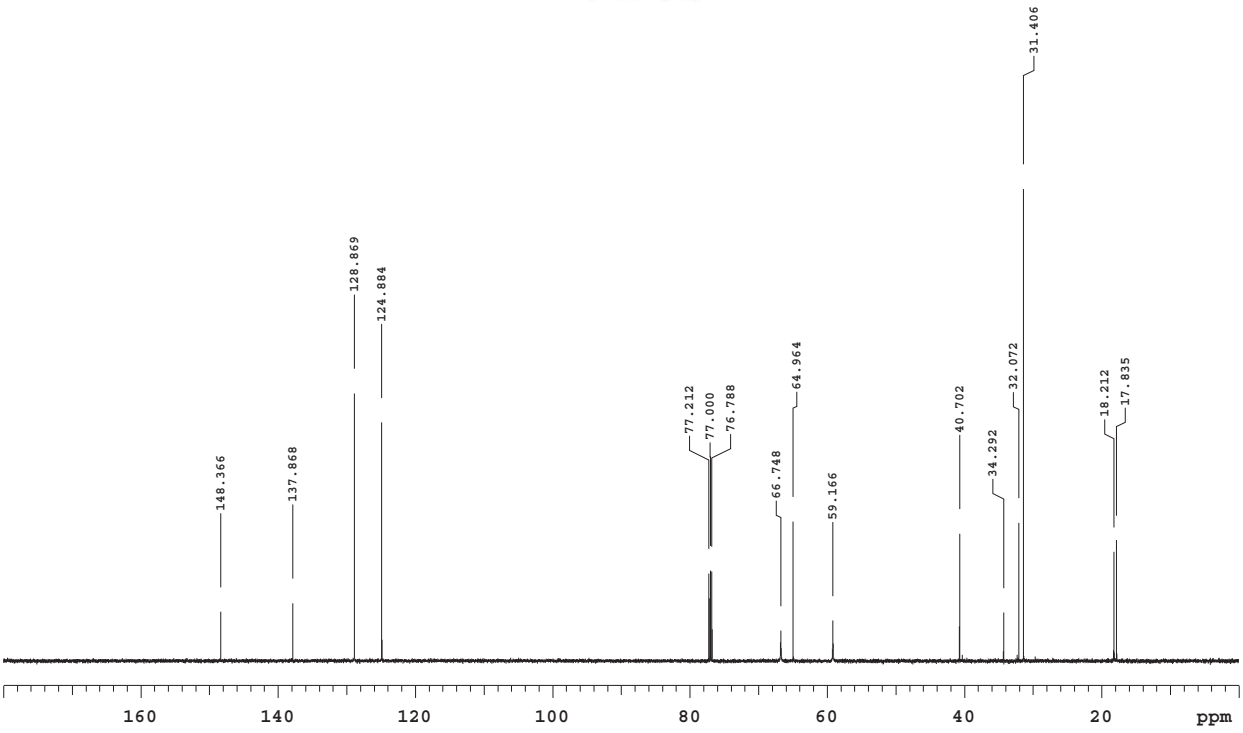


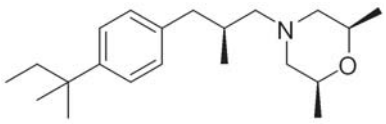
(2*S*,6*S*,*S*)-**21**



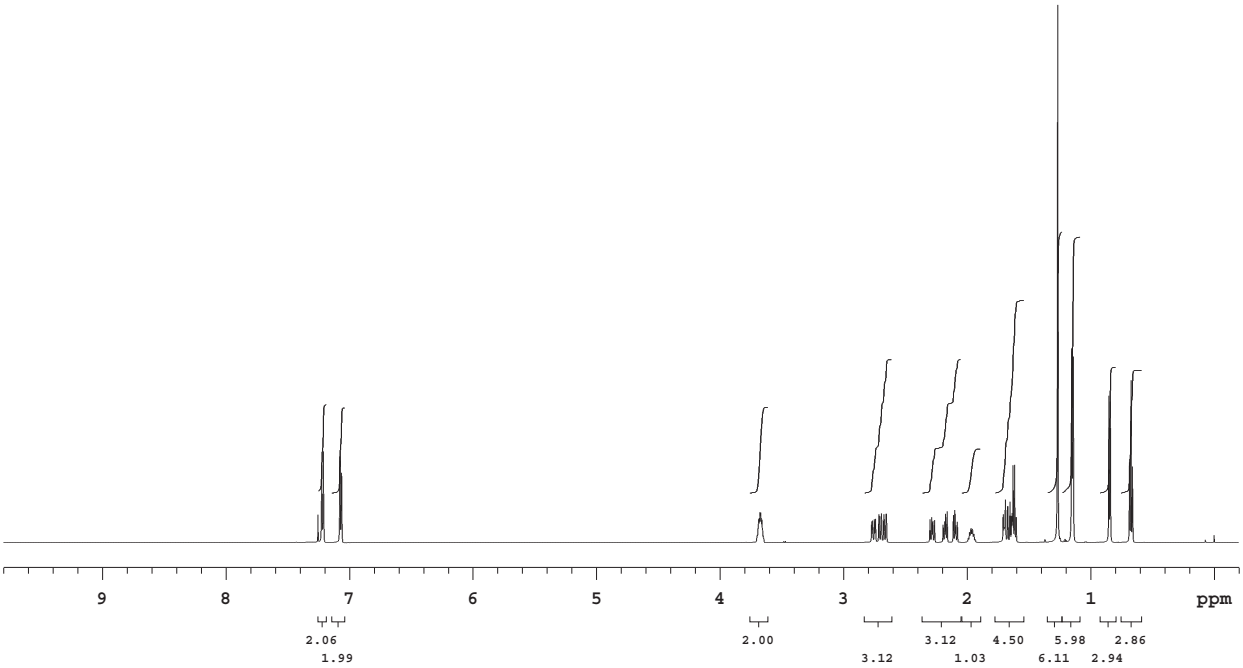


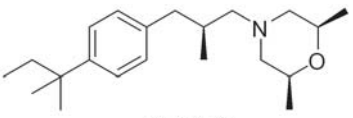
(2*S*,6*S*,*S*)-**21**



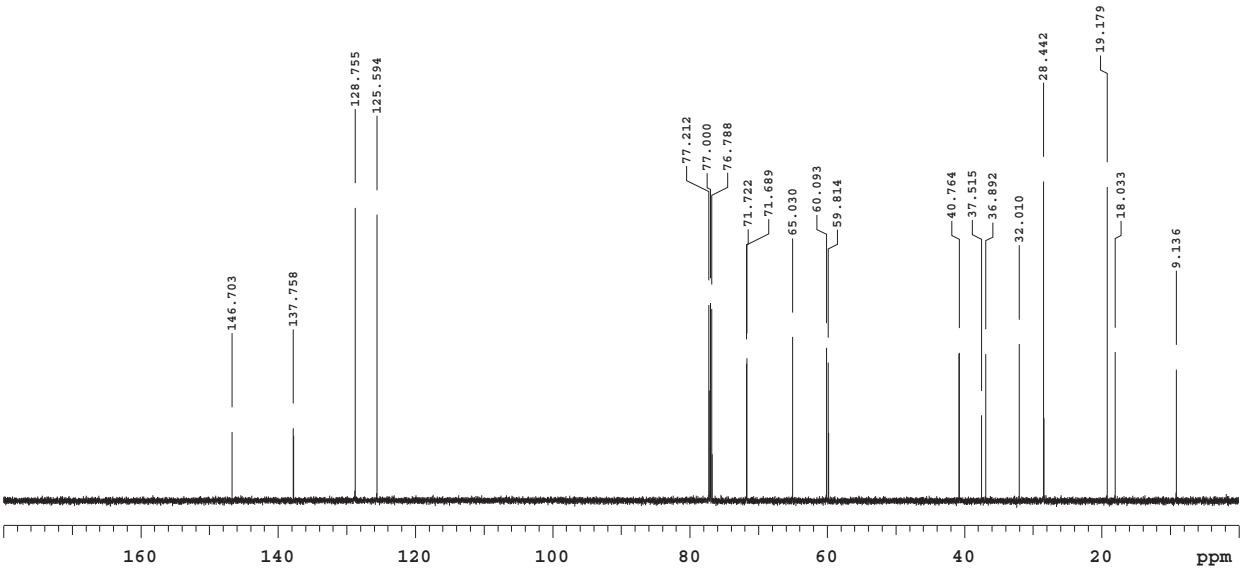


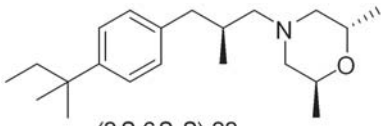
cis (*S*)-22



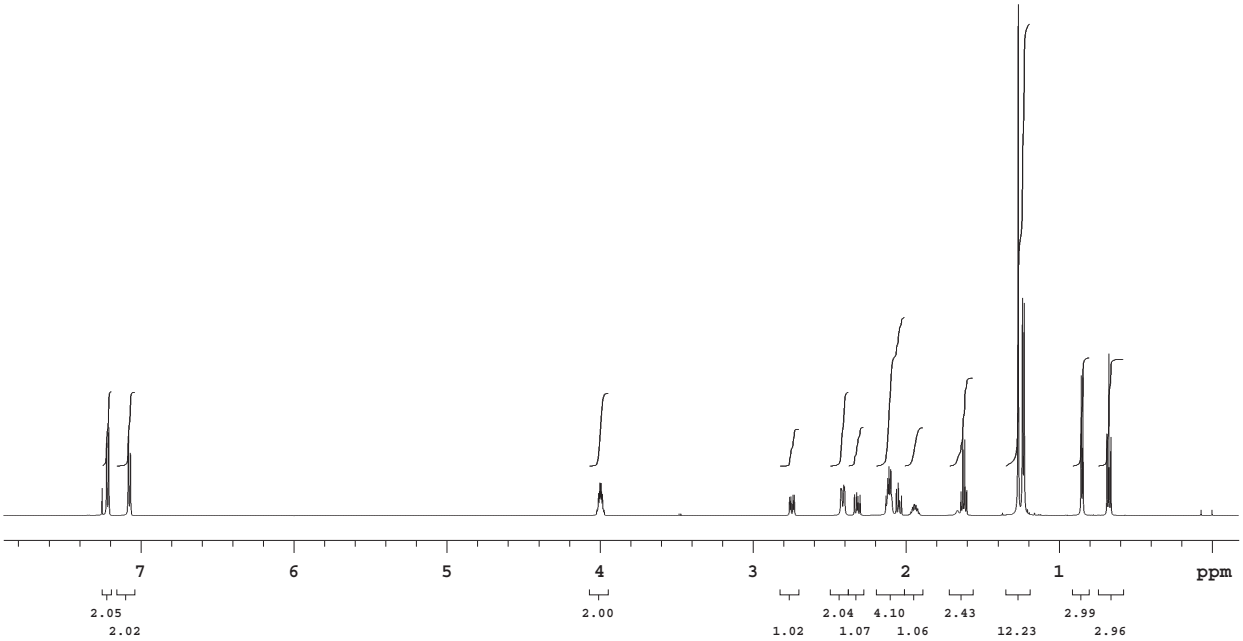


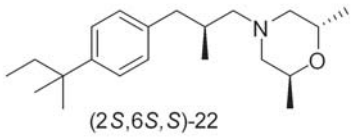
cis (*S*)-22



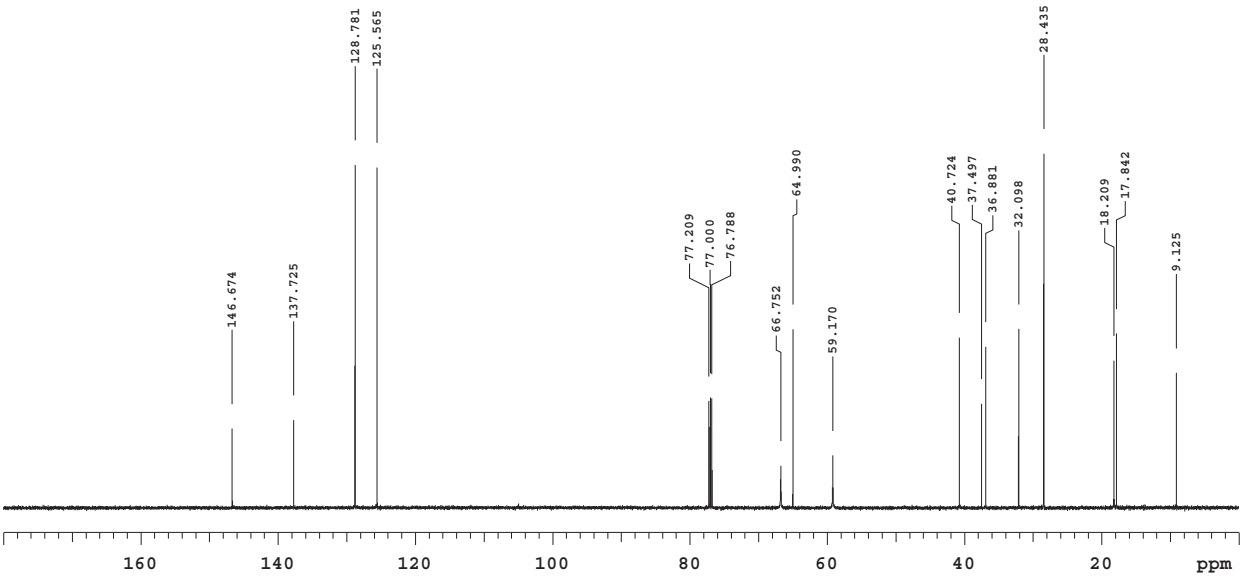


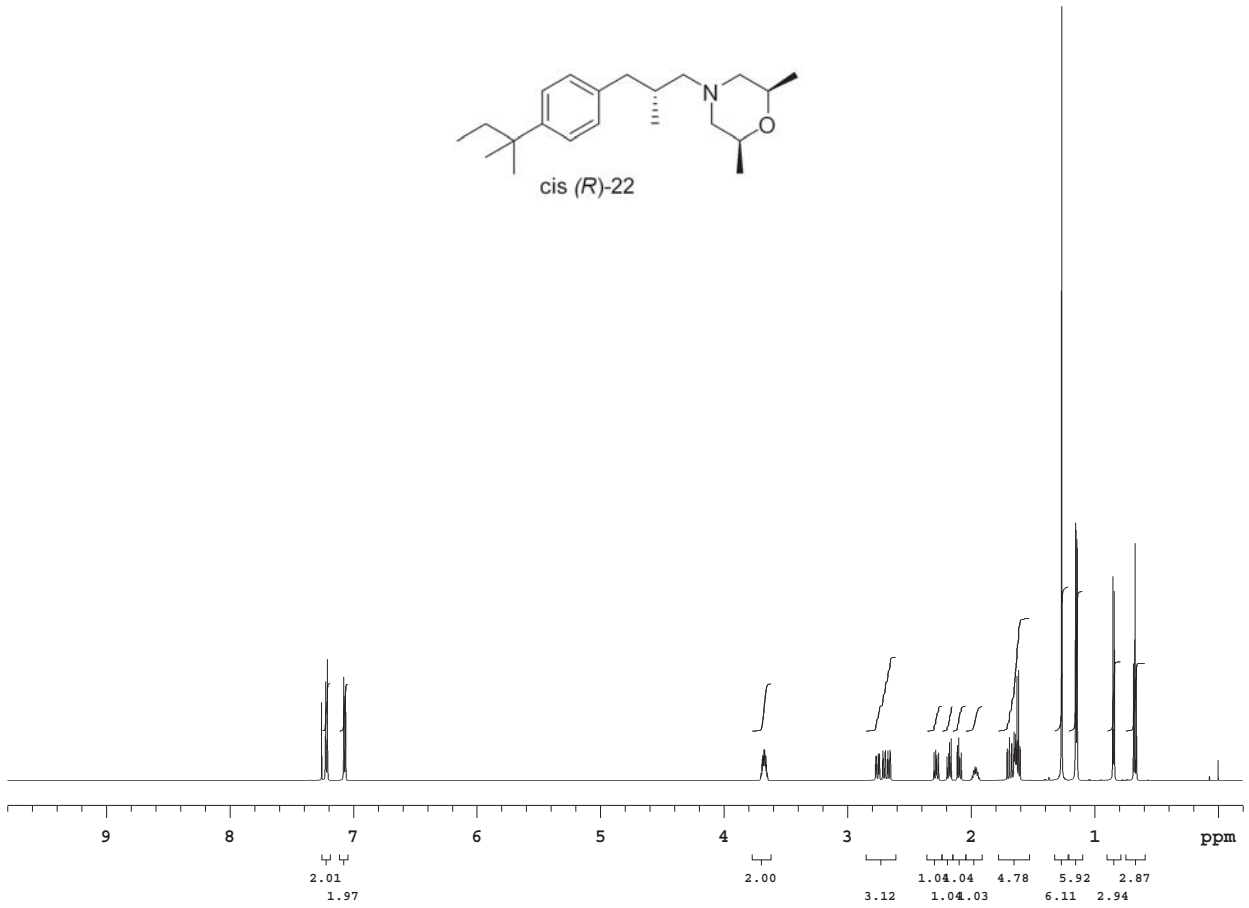
(2*S*,6*S*,*S*)-22

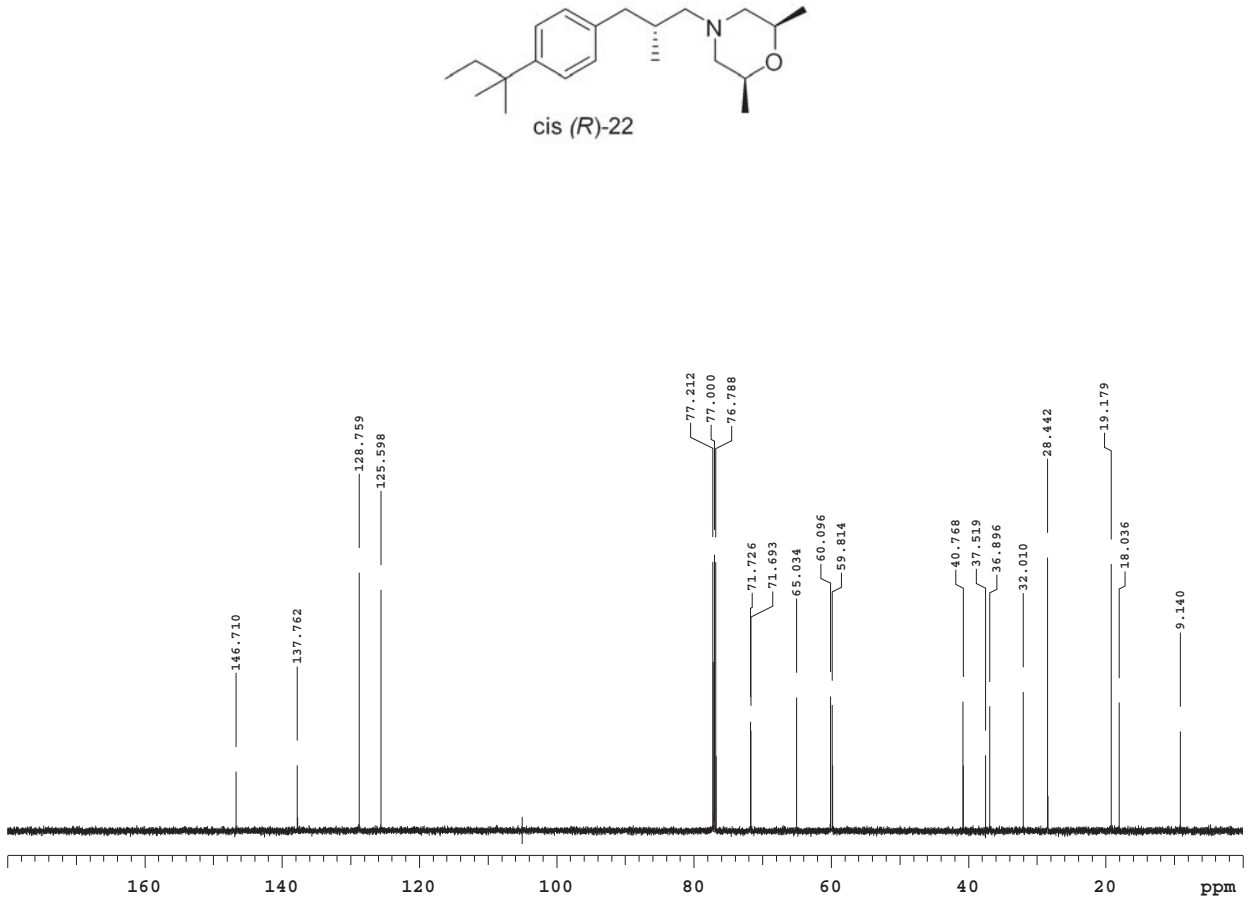


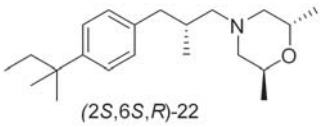


(2*S*,6*S*,*S*)-22

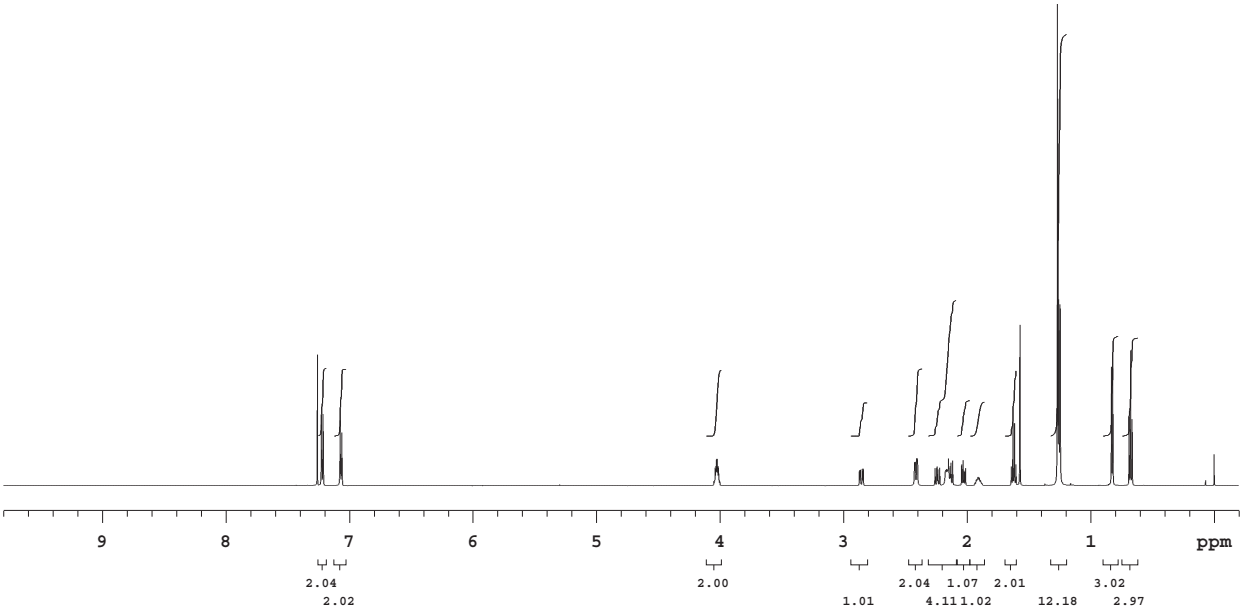


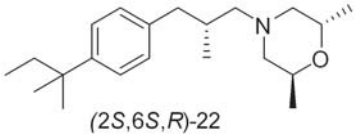

cis (R)-22
9
8
7
6
5
4
3
2
1
ppm
2.01
1.97
2.00
3.12
1.04
1.04
1.04
1.03
4.78
5.92
6.11
2.87
2.94


cis (R)-22
146.710
137.762
128.759
125.598
77.212
77.000
76.788
71.726
71.693
65.034
60.096
59.814
40.768
37.519
36.896
32.010
28.442
19.179
18.036
9.140
160
140
120
100
80
60
40
20
ppm



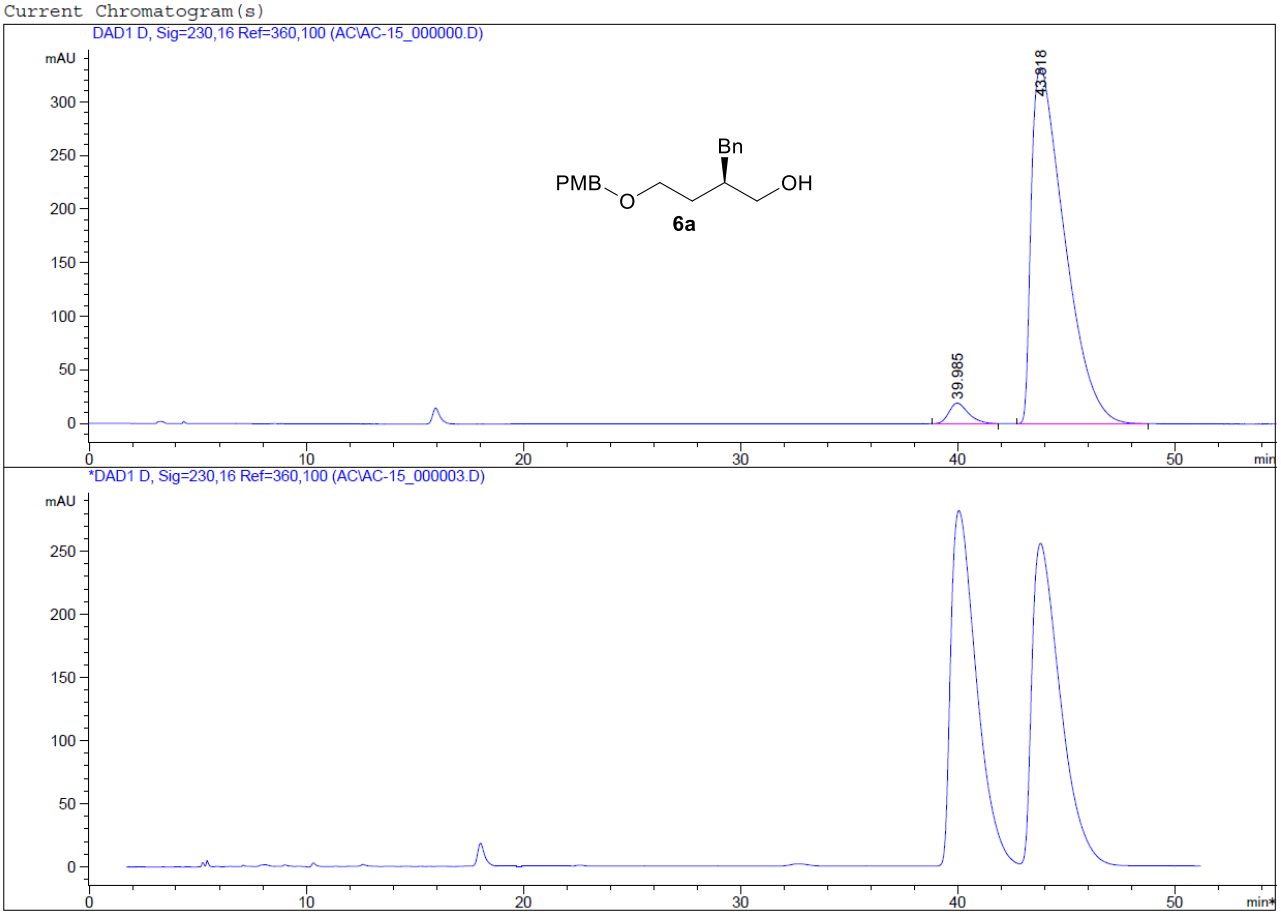
(2*S*,6*S*,*R*)-22





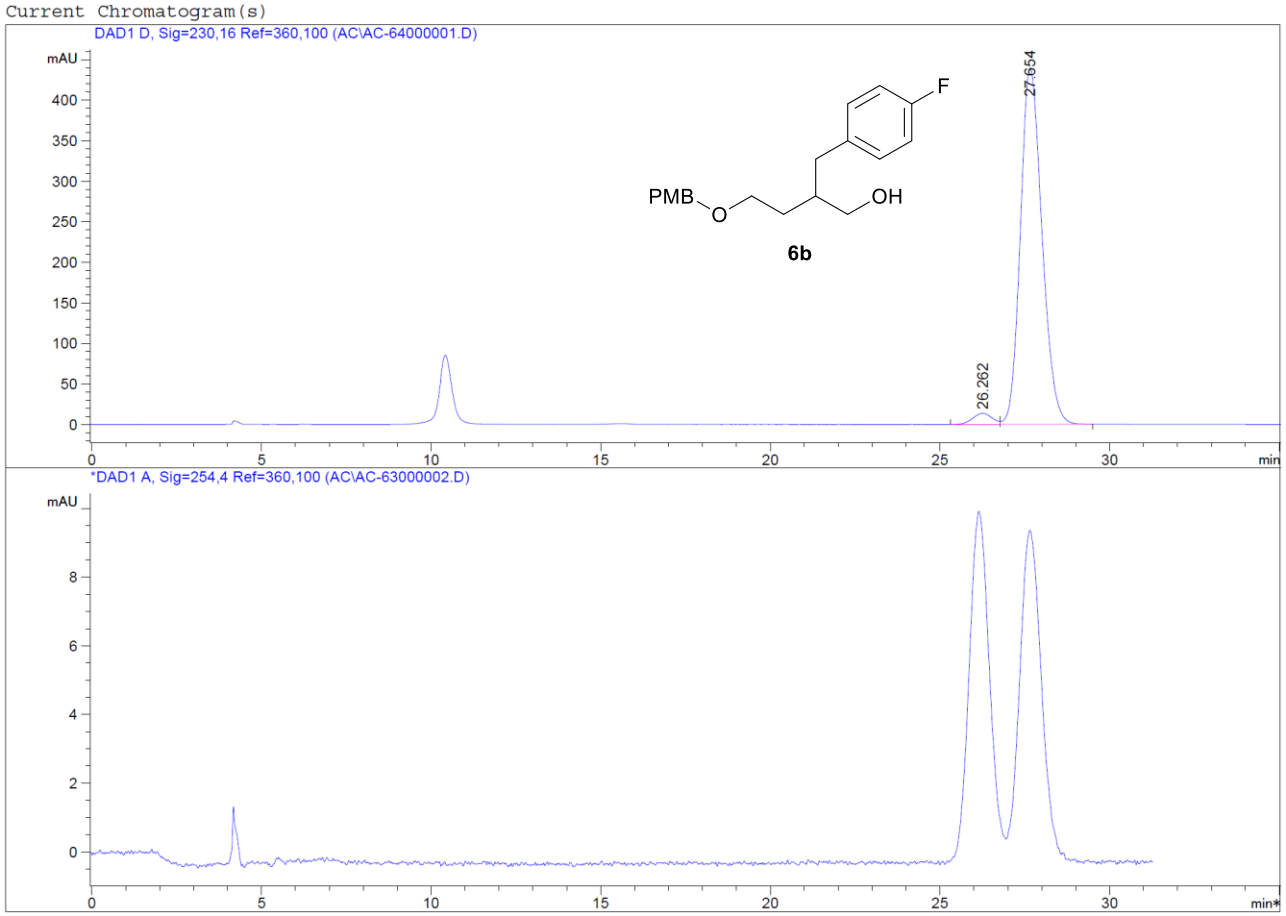
(2*S*,6*S*,*R*)-22

Current Chromatogram(s)



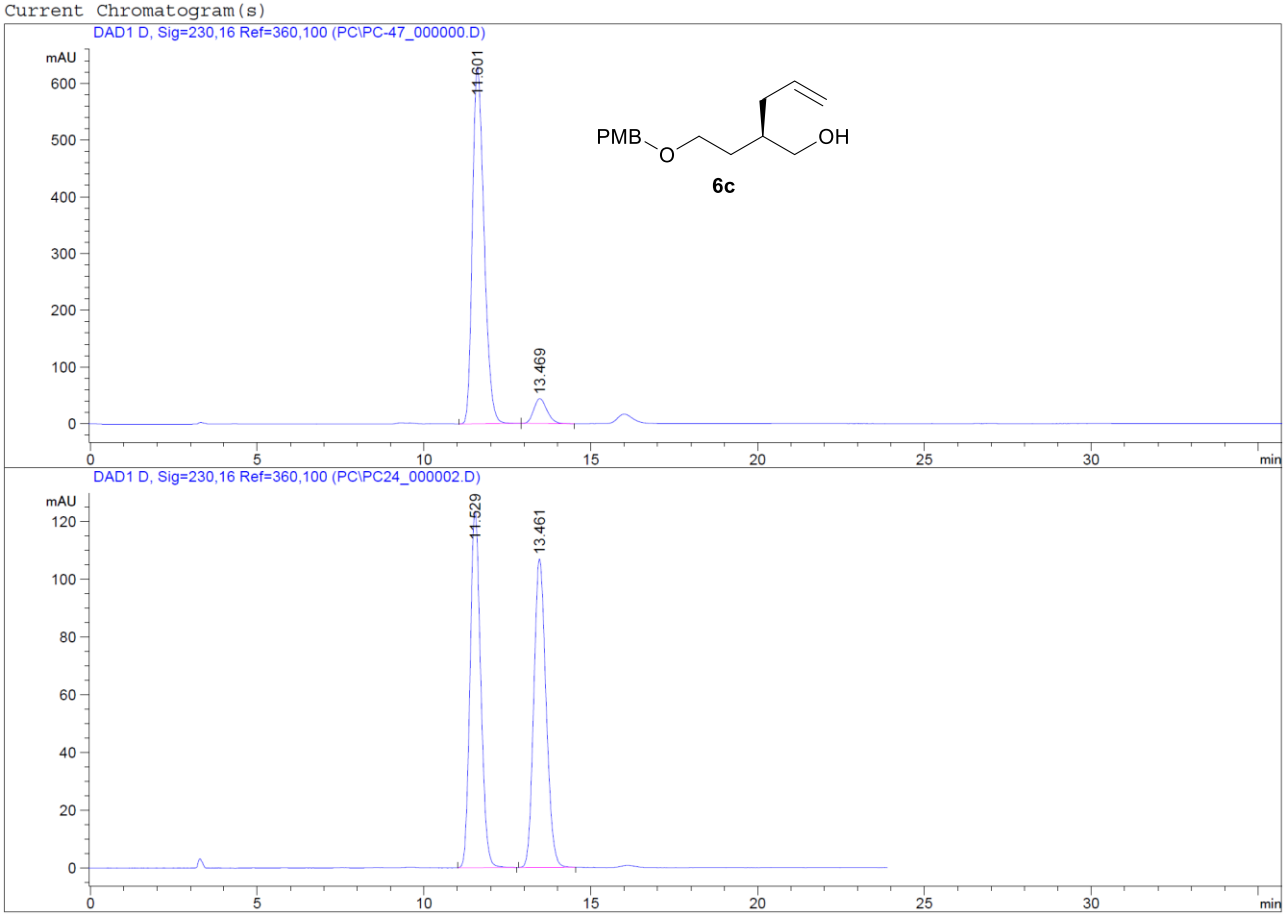

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  39.985 BB    0.8103 1196.62036   19.11609   3.2919
   2  43.818 BB    1.4972 3.51538e4   332.03162  96.7081

Totals :                  3.63505e4   351.14770
```

Current Chromatogram(s)



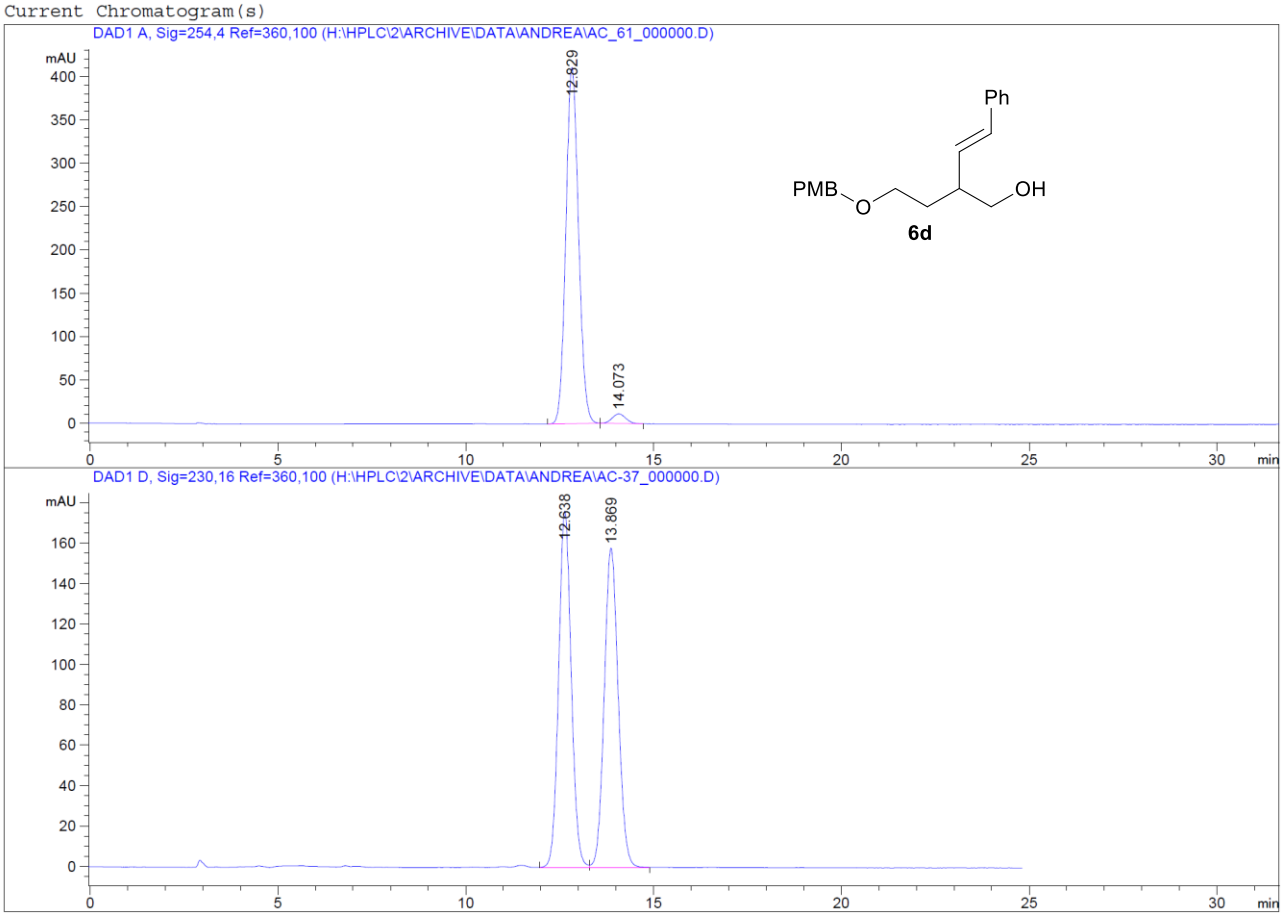

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  26.262 BV    0.5849  545.34912   13.68555   2.7346
   2  27.654 VB    0.6806 1.93973e4   439.73160  97.2654

Totals :                  1.99426e4   453.41715
```

Current Chromatogram(s)



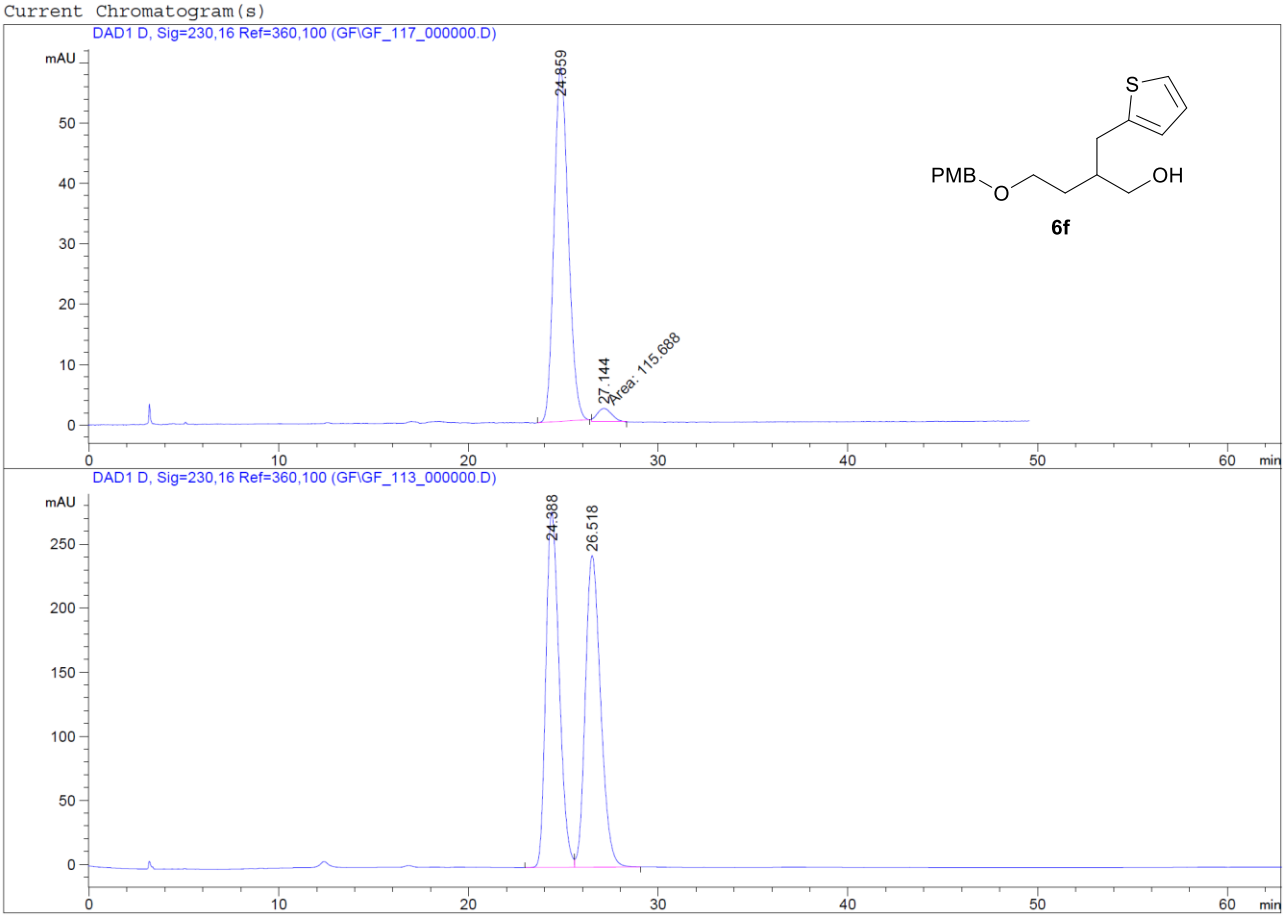

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.601 BB    0.3761 1.52027e4   628.81476  92.6356
   2  13.469 BB    0.4251 1208.59167   43.91069   7.3644

Totals :                  1.64113e4   672.72544
```

Current Chromatogram(s)



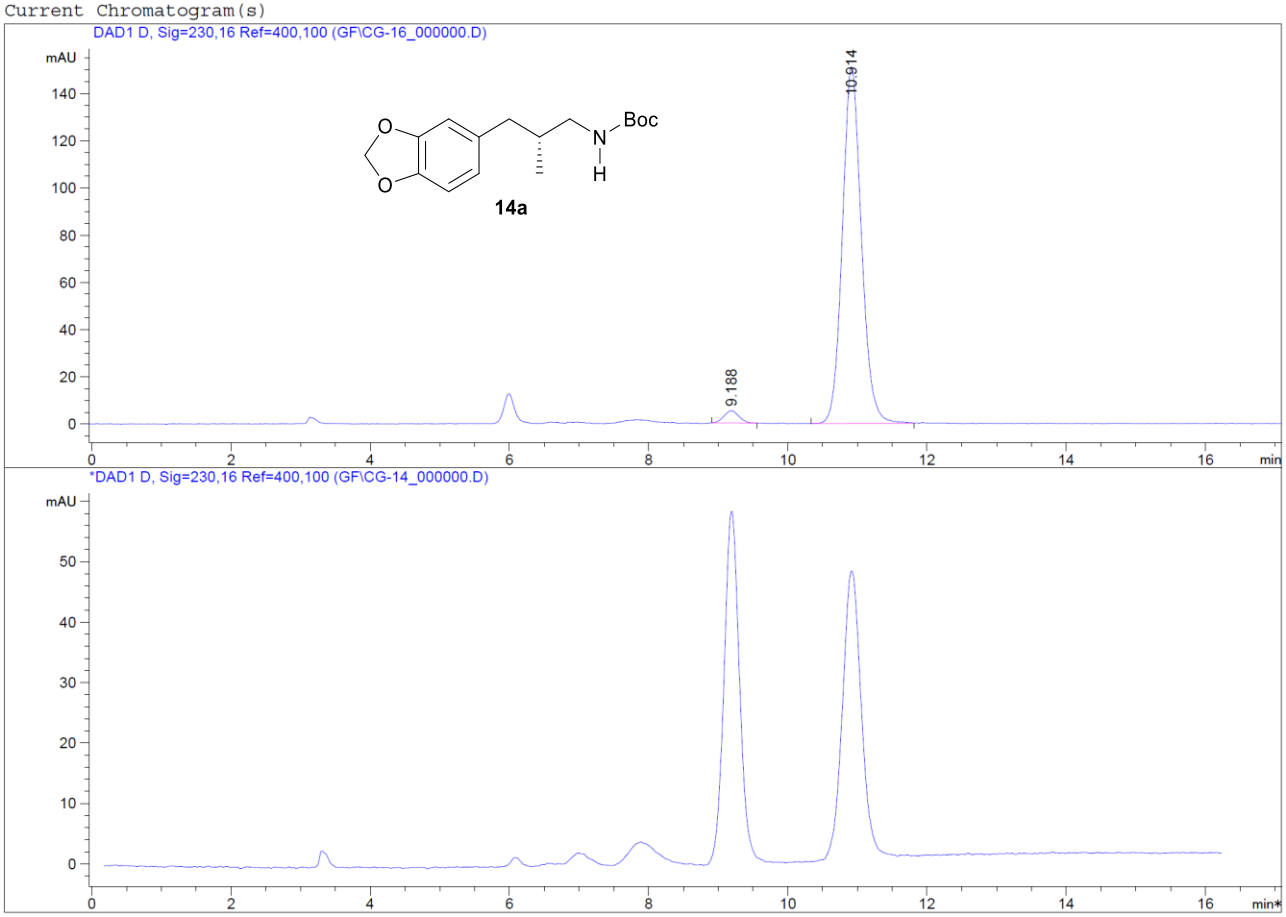

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.829 BB    0.3655 9634.39648  411.04367  97.1997
   2  14.073 BB    0.3682  277.56769   11.00733   2.8003

Totals :                  9911.96417  422.05100
```

Current Chromatogram(s)



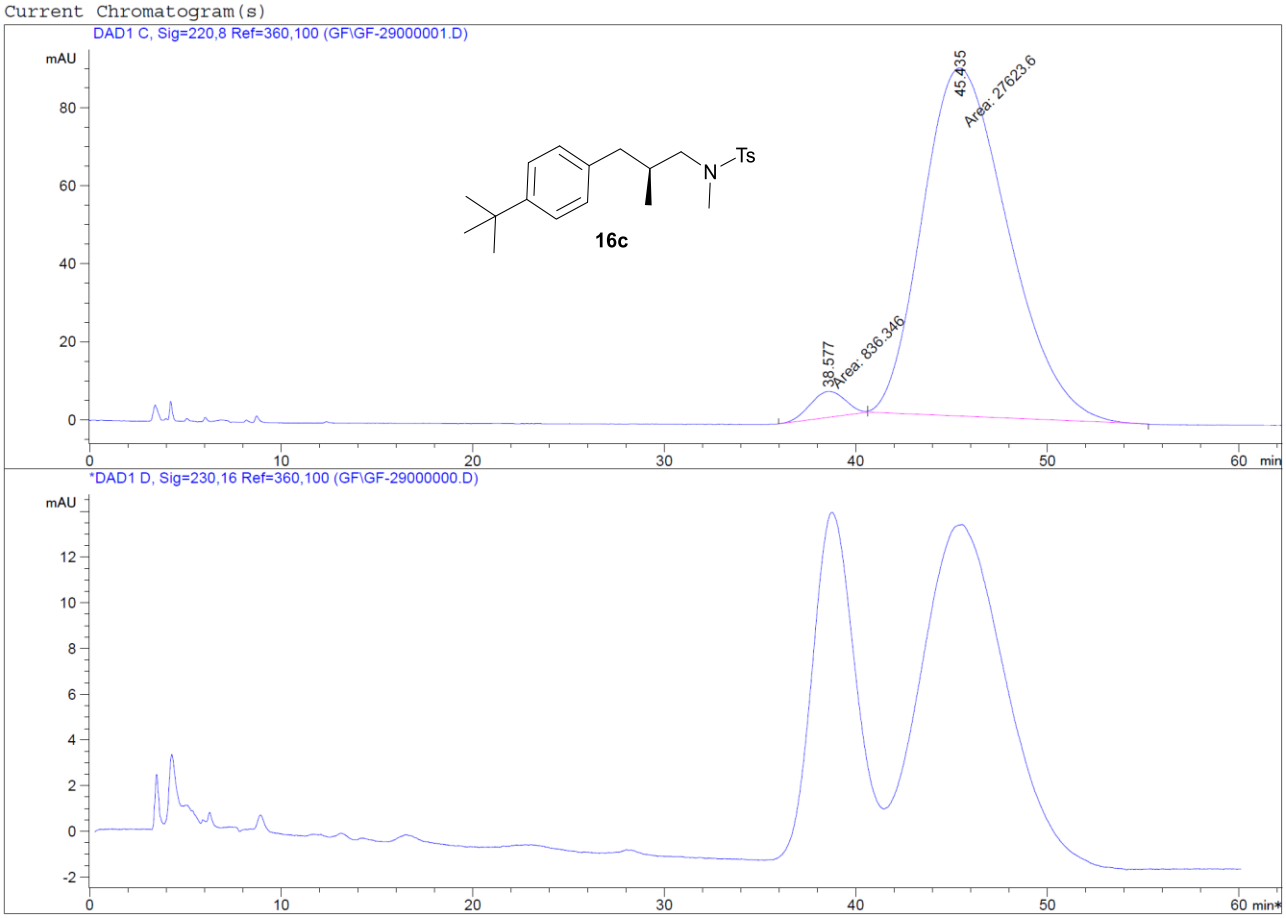

```
==================================================================================
                            Area Percent Report
==================================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.859 BB    0.8036 3052.41040   58.61059  96.5708
   2  27.152 MM    0.8778  108.38895    2.05786   3.4292

Totals :                  3160.79935   60.66845
```

Current Chromatogram(s)



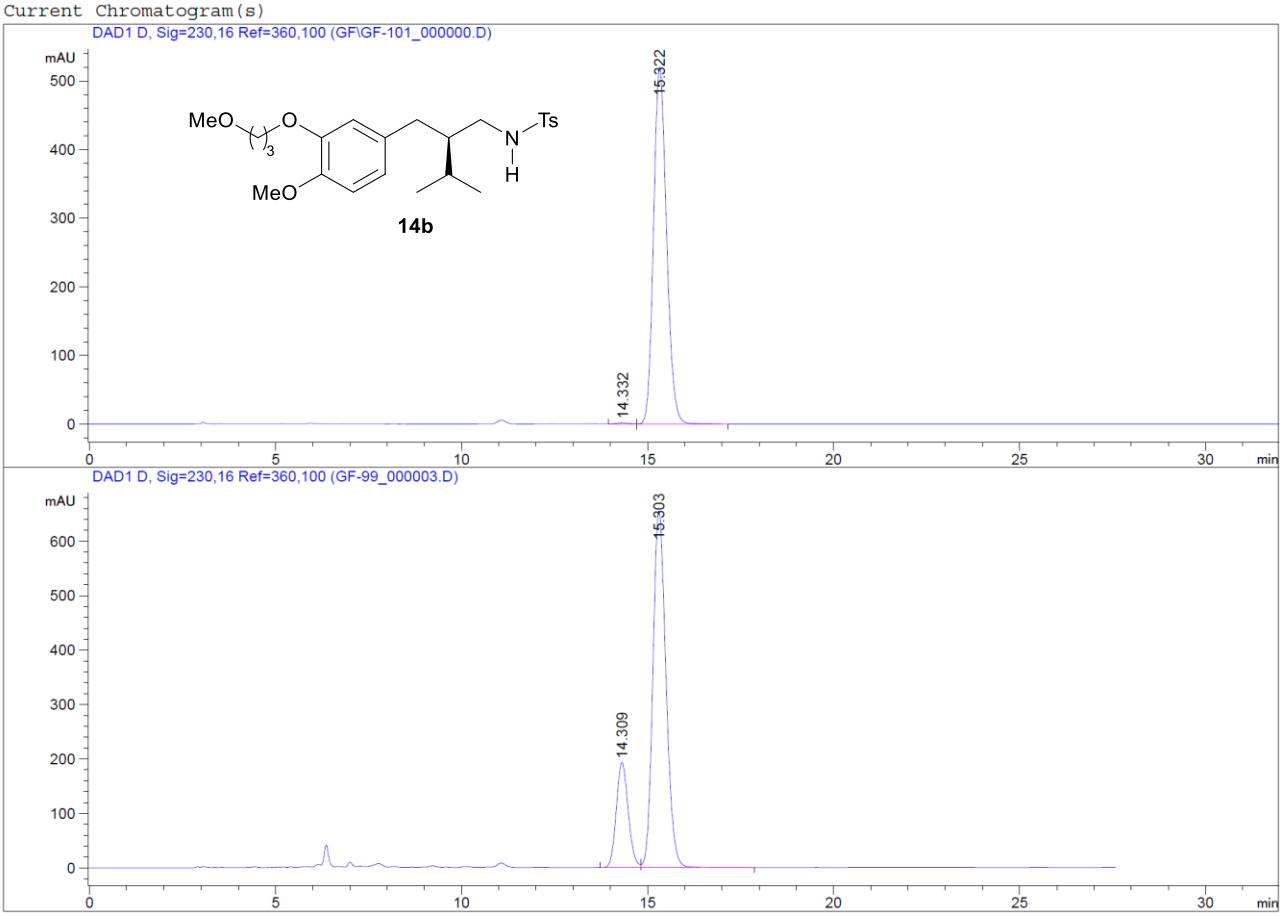

```
==================================================================================
                          Area Percent Report
==================================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,16 Ref=400,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.188 BB    0.1963   76.72138    5.19483   2.6073
   2  10.914 BV    0.2896 2865.85547  150.91365  97.3927

Totals :                  2942.57685  156.10848
```

Current Chromatogram(s)



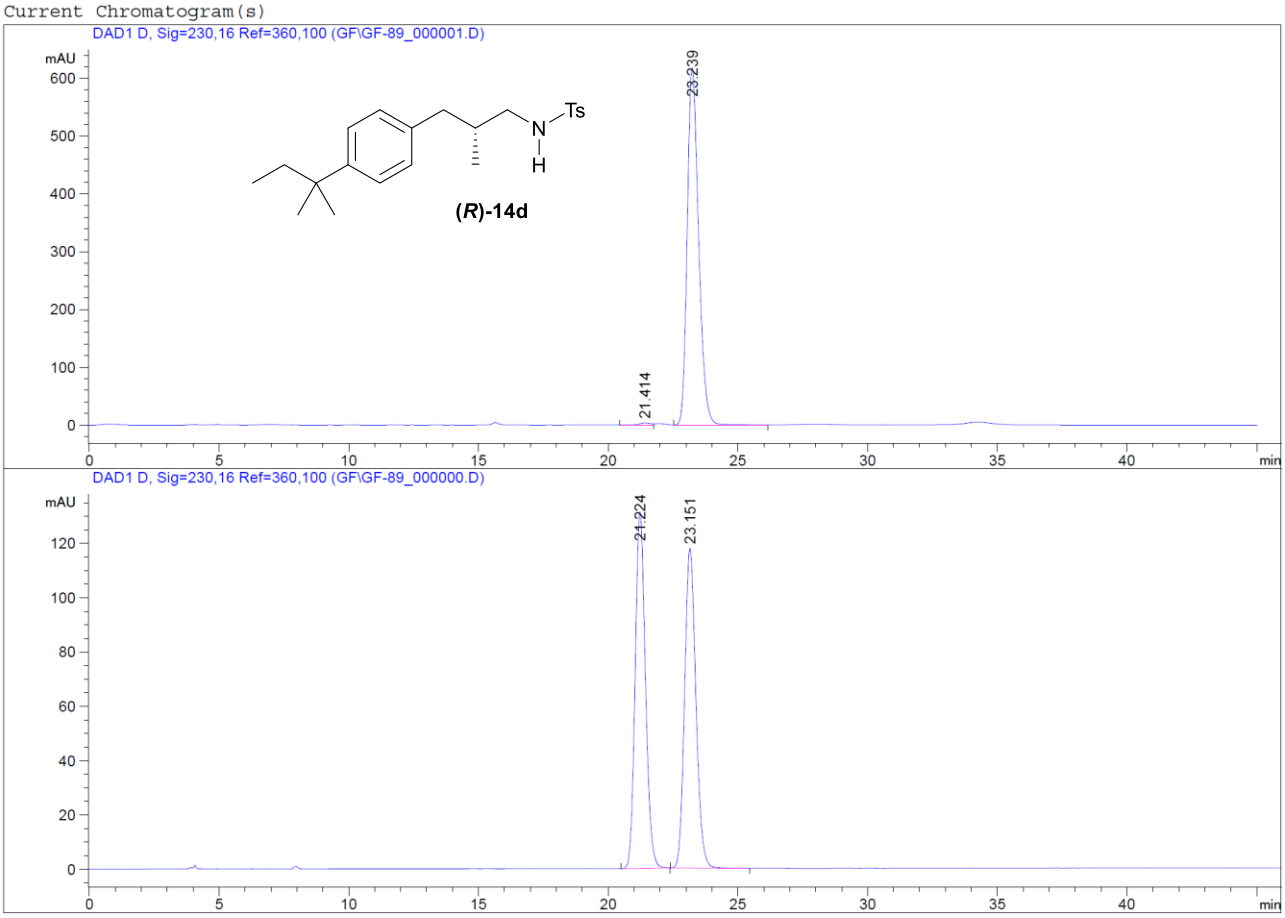

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  38.584 BV    1.7897  995.59662    6.56353   4.2036
   2  45.429 VB    3.7884 2.26888e4    71.22568  95.7964

Totals :                  2.36844e4    77.78921
```

Current Chromatogram(s)



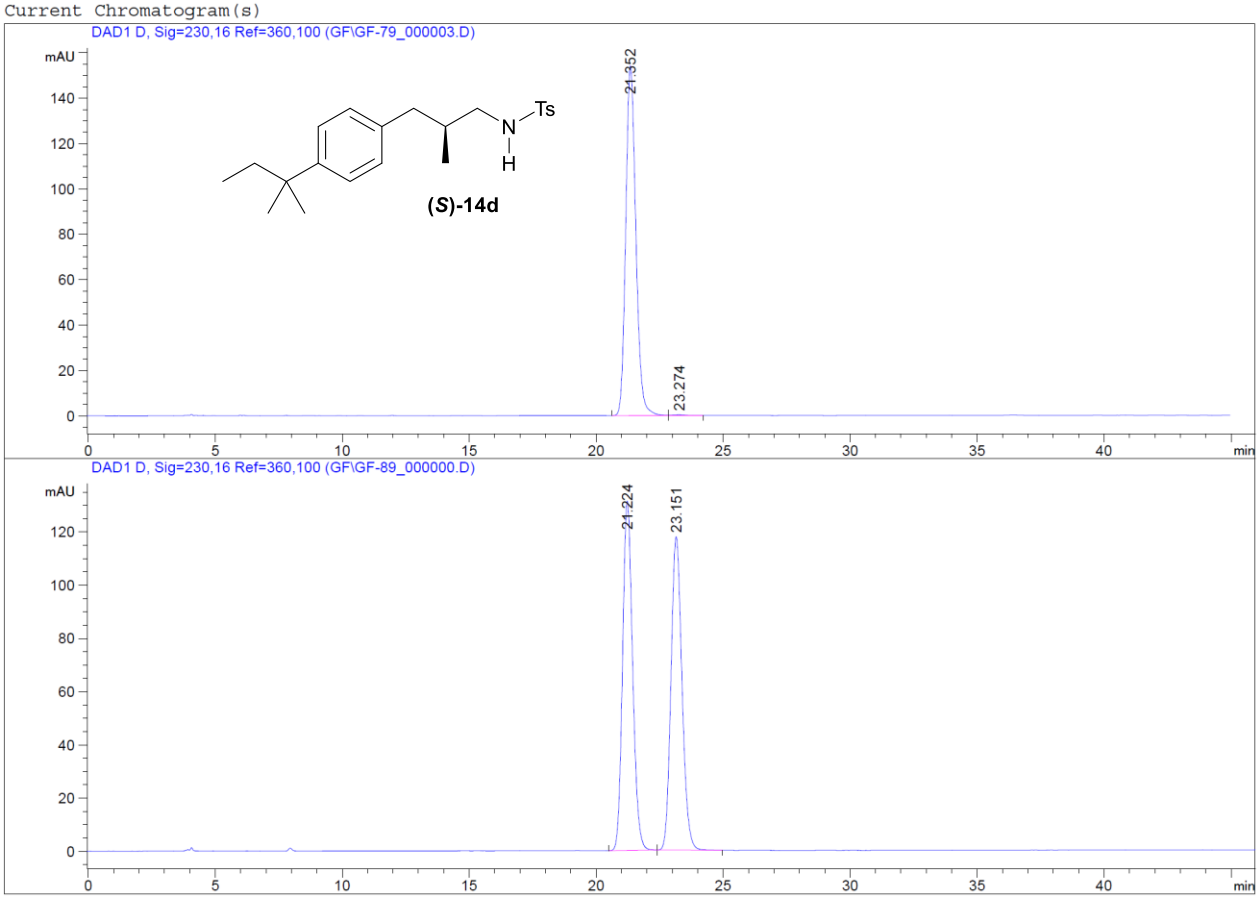

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.332 BB    0.3106   29.79396    1.46887   0.2362
   2  15.322 BB    0.3745 1.25859e4   519.82281  99.7638

Totals :                  1.26157e4   521.29169
```

Current Chromatogram(s)



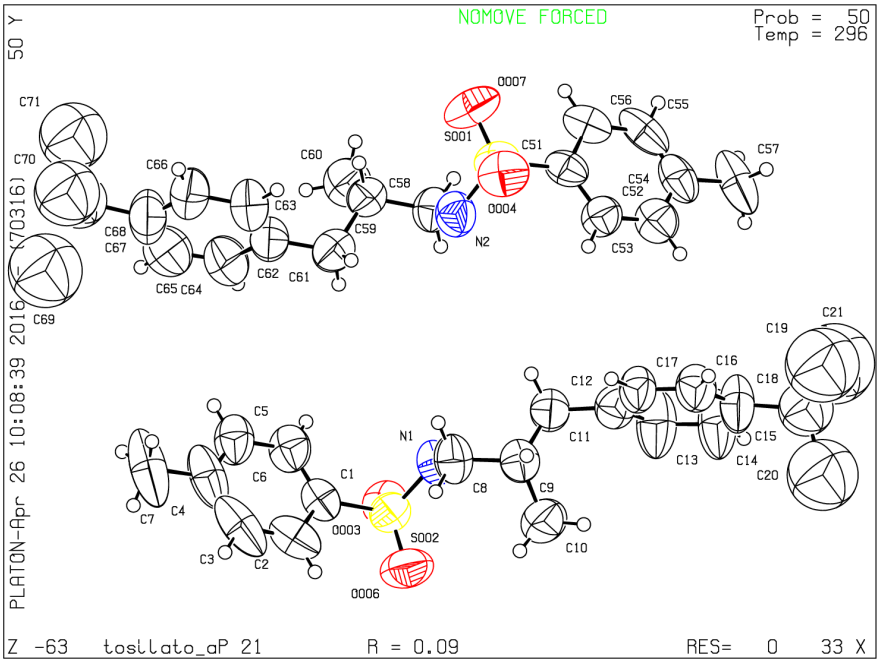

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  21.414 BV    0.4450  105.49149    3.56784   0.5594
   2  23.239 VB    0.4698 1.87529e4   618.36633  99.4406

Totals :                  1.88584e4   621.93417
```

Current Chromatogram(s)




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  21.352 BV    0.4256 4247.60547  154.10495  99.7440
   2  23.274 VB    0.4362   10.90308 3.05639e-1   0.2560

Totals :                  4258.50855  154.41059
```

Crystal data for compound (+)-(*S*)-14d



Molecular formula: $C_{21}H_{19}NO_2S$; M_r = 349.43, monoclinic, space group $P2_1$ (4), a = 7.1265(7), b = 28.922(3), c = 11.2917(10) Å, β = 106.2280(10); V = 2234.6(4) Å^3, T = 298(2) K, Z = 4, ρ_c = 1.039 g cm^{-3}, F(000) = 736, graphite-monochromated Mo$_{K\alpha}$ radiation (λ = 0.71073 Å), μ(Mo$_{K\alpha}$) = 0.156 mm^{-1}, colourless needle (0.45 × 0.20 × 0.20 mm^3), empirical absorption correction with SADABS (transmission factors: 0.933 – 0.970), 2400 frames, exposure time 15 s, 1.408 ≤ θ ≤ 25.50, –8≤ h ≤ 8, –35 ≤ k ≤ 35, –13 ≤ l ≤ 13, 22626 reflections collected, 8312 independent reflections (R_{int} = 0.0243), solution by intrinsic phasing method and subsequent Fourier syntheses, full-matrix least-squares on F_o^2 (SHELXL-2014/7), hydrogen atoms refined with a riding model, data / restraints / parameters = 8312/ 4/ 415, $S(F^2)$ = 0.879, $R(F)$ = 0.1279 and $wR(F^2)$ = 0.2878 on all data, $R(F)$ = 0.0933 and $wR(F^2)$ = 0.2460 for 5133 reflections with $I > 2\sigma(I)$, weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.1745P)^2 + 1.7294P]$ where $P = (F_o^2 + 2F_c^2)/3$, largest difference peak and hole 0.61 and –0.274 e Å^{-3}. Flack parameter: 0.09(2) for S absolute configuration (C9 and C58). The unit cell contains two independent molecules related by a pseudo-symmetry centre. The *t*-amyl groups were highly disordered and cannot be fully modelled. The terminal methyl of the ethyl group cannot be localized due to disorder. MS data confirmed the correct mass of the molecule. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1522373 (deposit@ccdc.cam.ac.uk).