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C$_3$-Symmetric Chiral Trisimidazoline-Catalyzed Friedel-Crafts (FC)-Type Reaction

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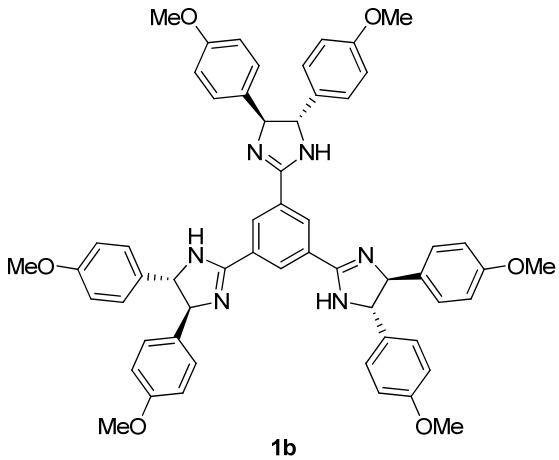
Contents of Electronic Supplementary Information

General information

^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded with JEOL JMN ECS400 FT NMR, JNM ECA600 FT NMR or Bruker AVANCE II (^{1}H-NMR 400, 500, 600 or 700 MHz, ^{13}C-NMR 100, 126, 150 or 175 MHz). ^{1}H-NMR spectra are reported as follows: chemical shift in ppm relative to the chemical shift of $CHCl_3$ at 7.26 ppm, ACETONE-D_6 at 2.09 ppm or DMSO-D_6 at 2.49 ppm, integration, multiplicities (s = singlet, d = doublet, q = quartet, t = triplet, m = multiplet), and coupling constants (Hz). ^{13}C-NMR spectra reported in ppm relative to the central line of triplet for $CDCl_3$ at 77 ppm, septet for ACETONE-D_6 at 30 ppm or septet for DMSO-D_6 at 40 ppm. FT-MS spectra were obtained with LTQ Orbitrap XL (Thermo Fisher Scientific). ESI-MS spectra were obtained with JMS-T100LC (JEOL). FAB-MS spectra were obtained with JMS-700 (JEOL). Optical rotations were measured with JASCO P-1030 polarimeter. HPLC analyses were performed on a JASCO HPLC system (JASCO PU 980 pump and UV-975 UV/Vis detector) using a mixture of hexane and 2-propanol as eluents. FT-IR spectra were recorded on a JASCO FT-IR system (FT/IR4100). Mp was measured with SHIMADZU DSC-60. Column chromatography on SiO_2 was performed with Kanto Silica Gel 60 (40-100 μm). Commercially available organic and inorganic compounds were used without further purification except for the solvent, which was distilled from sodium/benzophenone or CaH_2. *N*-4-Nosyl imines **2** were prepared following the reported procedures. [1] The products **4b**, **4d**, **4o** and **8** were identical in all respects with reported in the literature.[2,6] Absolute configurations were assigned by comparison of optical rotation reported in the literature.[2-6]

Preparation of trisimidazoline 1b

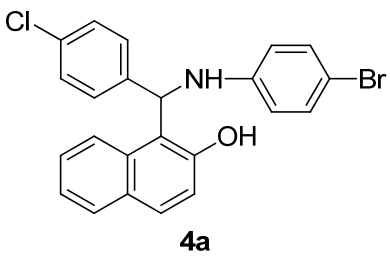


1b

1,3,5-Triformylbenzene (35.6 mg, 0.219 mmol) and (1*S*,2*S*)-1,2-bis(4-methoxyphenyl)ethane-1,2-diamine (185 mg, 0.680 mmol) was dissolved in dioxane (6.8 mL) and stirred for 2 h at rt under N_2. The resulting solution was added NBS (121 mg, 0.679 mmol) at 0 ^{o}C and stirred for 24 h at rt. After the reaction was completed, sat. $Na_2S_2O_5$ aq. and 5% NaOH aq. was added to the reaction mixture and the solution was extracted with CH_2Cl_2. Organic layer was dried over Na_2SO_4, and evaporated in vacuo. After the purification *via* SiO_2 column chromatography (hexane/AcOEt/TEA = 1/2/0.3), the desired product **1b** was obtained as pale yellow solid. Mp: >260 ^{o}C; $[\alpha]_D^{24}$ = -96.9 (*c* 1.2, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ: 8.61 (s, 3H), 7.16 (2H, d, *J* = 8.8 Hz), 6.82 (2H, d, *J* = 8.8 Hz), 4.80 (brs, 6H), 3.78 (s, 18H); ^{13}C-NMR ($CDCl_3$) δ: 161.6, 159.0, 135.1, 130.6, 128.5, 127.7, 114.0, 55.2; IR (KBr): ν 3130, 3001, 2955, 2835, 1612, 1514, 1248, 1173, 1034 cm^{-1}; HRMS (FAB) calcd for $C_{57}H_{55}N_6O_6$ m/z = 919.4183 [$(M+H^+)$], found m/z = 919.4175.

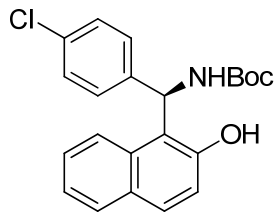
General procedure for enantioselective Friedel–Crafts (FC)-type reactions of aldimines (2) with 2-naphthols (3)

Under N_2 atmosphere, a test tube was charged with aldimine **2** (0.10 mmol), 2-naphthols **3** (0.15 mmol), and the catalyst **1** (0.005 mmol, 5 mol %) in toluene (0.4 mL). The reaction mixture was stirred at -5 °C. After the purification *via* SiO_2 column chromatography, the desired product **4** was obtained.



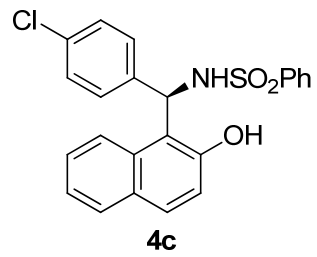
4a

4a: 82% yield; ^{1}H-NMR ($CDCl_3$) δ: 7.76 (2H, d, *J* = 8.5 Hz), 7.76 (2H, d, *J* = 8.5 Hz), 7.68 (2H, d, *J* = 7.3 Hz), 7.45-7.41 (2H, m), 7.35-7.31 (2H, m), 7.15 (2H, d, *J* = 2.3 Hz), 7.10 (2H, dd, *J* = 8.7, 2.3 Hz), 6.57 (1H, d, *J* = 8.7 Hz), 4.97 (2H, bs); ^{13}C-NMR ($CDCl_3$) δ: 155.7, 145.4, 139.0, 132.3, 132.0, 131.2, 130.4, 129.6, 129.4, 129.2, 128.8, 127.0, 123.1, 121.1, 119.9, 117.8, 114.2, 113.0, 61.5 ; HRMS (ESI) calcd for $C_{23}H_{16}BrClNO$, m/z = 436.0104 [$(M-H)^-$], found m/z = 436.0094; IR (KBr): ν 3569, 3339, 2345, 1719, 1625, 1490, 1233, 913, 815 cm^{-1}; enantiomeric excess: *Rac*, determined by HPLC (Chiralpak AS-H, hexane/2-propanol = 4/1, flow rate 1.0 mL/min, 25 °C, 330 nm) first peak: t_R = 6.7 min, second peak: t_R = 9.3 min.



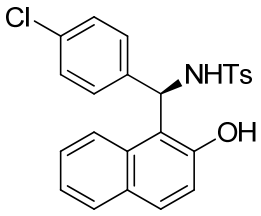
4b

4b[2b]: 17% yield; ^{1}H-NMR (ACETONE-D_6) δ: 9.30 (1H, bs), 8.14 (1H, d, *J* = 8.2 Hz), 7.89 (1H, d, *J* = 8.2 Hz), 7.85 (1H, d, *J* = 8.2 Hz), 7.53 (1H, t, *J* = 8.2 Hz), 7.39-7.30 (6H, m), 7.00 (1H, s), 3.27 (1H, bs), 1.47 (9H, s); ^{13}C-NMR ($CDCl_3$) δ: 156.5, 153.6, 143.0, 133.4, 132.5, 130.6, 130.0, 129.7, 128.9, 128.8, 128.0, 124.0, 123.4, 120.2, 119.3, 79.6, 50.8, 28.6; enantiomeric excess: 17%, determined by HPLC (Chiralpak IB, hexane/2-propanol = 95/5, flow rate 1.0 mL/min, 25 °C, 230 nm) minor peak: t_R = 7.6 min, major peak: t_R = 7.0 min.



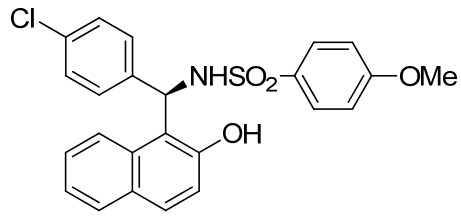
4c

4c: 88% yield; ^{1}H-NMR ($CDCl_3$) δ: 7.71 (1H, d, *J* = 8.2 Hz), 7.65 (1H, d, *J* = 8.2 Hz), 7.50 (1H, d, *J* = 8.7 Hz), 7.45-7.40 (3H, m), 7.30 (1H, t, *J* = 7.3 Hz), 7.22 (2H, d, *J* = 8.7 Hz), 7.15 (2H, t, *J* = 4.4 Hz), 7.07 (1H, t, *J* = 7.3 Hz), 6.89-6.82 (4H, m), 6.66 (1H, bs), 6.40 (1H, d, *J* = 10.1 Hz); ^{13}C-NMR ($CDCl_3$) δ:150.8, 139.2, 138.6, 133.1, 132.1, 130.2, 128.9, 128.6, 128.4 x 2, 128.1 x 2, 127.4, 126.4, 123.5, 121.6, 117.8, 116.9, 53.7; HRMS (ESI) calcd for $C_{23}H_{18}ClNO_3SNa$, m/z = 446.0594 [$(M+Na)^+$], found m/z = 446.0584; IR (KBr): ν 3319, 1701, 1630, 1518, 1490, 1439, 1328, 1156, 1091, 1014, 751 cm^{-1}; enantiomeric excess: 22%, determined by HPLC (Chiralcel OD-3, hexane/2-propanol = 19/1, flow rate 1.0 mL/min, 25 °C, 254 nm) minor peak: t_R = 12.0 min, major peak: t_R = 16.3 min.



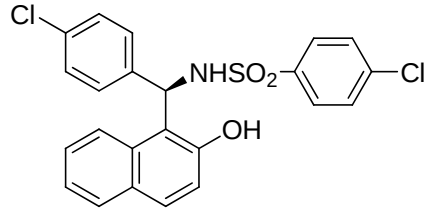
4d

4d[2a,3-5]: 70% yield; ^{1}H-NMR ($CDCl_3$) δ: 7.70 (1H, d, *J* = 9.2 Hz), 7.66 (1H, d, *J* = 8.7 Hz), 7.55 (1H, d, *J* = 8.7 Hz), 7.41 (1H, t, *J* = 7.8 Hz), 7.31 (2H, d, *J* = 8.2 Hz), 7.23 (2H, d, *J* = 8.7 Hz), 7.18 (2H, d, *J* = 8.2 Hz), 6.83 (1H, d, *J* = 8.7 Hz), 6.64 (2H, d, *J* = 7.8 Hz), 6.60 (1H, bs), 6.35 (1H, d, *J* = 10.1 Hz), 6.28 (1H, bs), 2.10 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 151.1, 142.8, 138.7, 135.9, 132.9, 132.1, 129.8, 128.7, 128.6, 128.4, 128.3, 128.2, 127.2, 126.4, 123.3, 121.6, 117.9, 116.9, 53.7, 21.1; enantiomeric excess: 27%, determined by HPLC (Chiralpak IC, hexane/2-propanol = 4/1, flow rate 1.0 mL/min, 25 °C, 254 nm) minor peak: t_R = 14.1 min, major peak: t_R = 16.1 min.



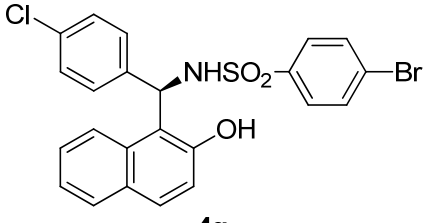
4e

4e: 65% yield; ^{1}H-NMR ($CDCl_3$) δ: 7.72 (1H, d, *J* = 8.7 Hz), 7.68 (1H, d, *J* = 8.1 Hz), 7.57 (1H, d, *J* = 8.7 Hz), 7.43 (1H, t, *J* = 7.3 Hz), 7.36-7.31 (3H, m), 7.23-7.18 (4H, m), 6.83 (1H, d, *J* = 8.7 Hz), 6.33 (3H, t, *J* = 8.1 Hz), 3.62 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 162.3, 150.8, 138.7, 133.1, 132.3, 130.8, 130.0, 129.0, 128.7, 128.5, 128.4, 128.2, 127.4, 123.6, 121.8, 118.0, 117.4, 113.3, 55.3, 53.7; HRMS (ESI) calcd for $C_{24}H_{20}ClNO_4SNa$, m/z = 476.0699 [$(M+Na)^+$], found m/z = 476.0689; IR (KBr): ν 3310, 2930, 1597, 1496, 1257, 1155, 1092, 910, 815, 731 cm^{-1}; enantiomeric excess: 30%, determined by HPLC (Chiralpak IA, hexane/2-propanol = 9/1, flow rate 1.0 mL/min, 25 °C, 335 nm) minor peak: t_R = 17.7 min, major peak: t_R = 22.6 min.



4f

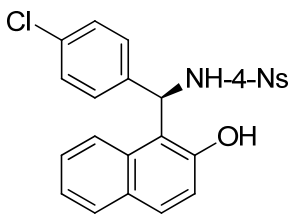
4f: 100% yield; ^{1}H-NMR ($CDCl_3$) δ: 7.74-7.71 (2H, m), 7.60 (1H, d, *J* = 8.7 Hz), 7.46 (1H, t, *J* = 7.5 Hz), 7.37 (1H, t, *J* = 7.5 Hz), 7.30-7.20 (8H, m), 6.77 (3H, d, *J* = 8.7 Hz), 6.40 (1H, s); ^{13}C-NMR ($CDCl_3$) δ: 150.7, 138.4, 138.3, 137.7, 133.2, 130.2, 129.4, 128.7, 128.5, 128.1 x 2, 127.9, 127.8, 127.6, 123.8, 121.5, 117.7, 117.0, 53.8; HRMS (ESI) calcd for $C_{23}H_{17}Cl_2NO_3SNa$, m/z = 480.0204 [$(M+Na)^+$], found m/z = 480.0193; IR (KBr): ν 3414, 3318, 2345, 1718, 1629, 1578, 1509, 1323, 1273, 1152, 1091, 812, 752 cm^{-1}; enantiomeric excess: 48%, determined by HPLC (Chiralcel OD-H, hexane/2-propanol = 19/1, flow rate 1.0 mL/min, 25 °C, 254 nm) minor peak: t_R = 21.1 min, major peak: t_R = 27.7 min.



4g

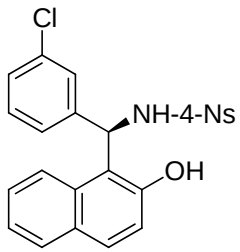
4g: 72% yield; ^{1}H-NMR ($CDCl_3$) δ: 7.73 (2H, d, *J* = 8.7 Hz), 7.61 (1H, d, *J* = 8.7 Hz), 7.46 (1H, t, *J* = 7.9 Hz), 7.37 (1H, t, *J* = 7.9 Hz), 7.27-7.20 (6H, m), 6.93 (2H, d, *J* = 8.7 Hz), 6.79 (1H, d, *J* = 8.7 Hz), 6.54 (1H, bs), 6.39 (1H, bs), 5.73 (1H, bs); ^{13}C-NMR ($CDCl_3$) δ: 150.5, 138.3 x 2, 133.3, 132.4, 131.1, 130.2, 128.8, 128.5, 128.1, 128.0, 127.9 x 2, 127.7, 126.9, 123.9, 117.6, 117.1, 53.7; HRMS (ESI) calcd for $C_{23}H_{17}BrClNO_3SNa$, m/z = 523.9699 [$(M+Na)^+$], found

m/z = 523.9687; IR (KBr): ν 3403, 3317, 3089, 2925, 2853, 2345, 1903, 1719, 1629, 1575, 1544, 1326, 1273, 1153, 1089 cm^{-1}; enantiomeric excess: 63%, determined by HPLC (Chiralcel OD-H, hexane/2-propanol = 19/1, flow rate 1.0 mL/min, 25 °C, 254 nm) minor peak: t_R = 16.2 min, major peak: t_R = 22.2 min.



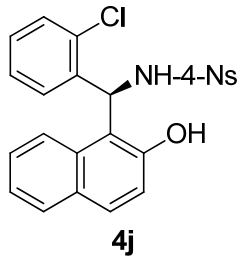
4h

4h: 89% yield; ^{1}H-NMR (DMSO-D_6) δ: 9.99 (1H, br s), 8.81 (1H, br s), 7.88 (2H, d, *J* = 8.7 Hz), 7.63 (2H, d, *J* = 8.7 Hz), 7.58 (2H, d, *J* = 8.2 Hz), 7.55 (1H, d, *J* = 9.2 Hz), 7.31 (2H, d, *J* = 8.7 Hz), 7.28-7.20 (3H, m), 7.16 (1H, t, *J* = 7.3 Hz), 6.96 (1H, d, *J* = 8.7 Hz), 6.52 (1H, s); ^{13}C-NMR (DMSO-D_6) δ:153.0, 148.6, 145.9, 139.9, 131.3, 131.2, 129.7, 128.2, 128.1, 128.0, 127.4, 126.3, 123.1, 122.4, 117.6, 116.1, 51.9; HRMS (ESI) calcd for $C_{23}H_{17}ClN_2O_5SNa$, m/z = 491.0444 [$(M+Na)^+$], found m/z = 491.0432; IR (KBr): ν 3432, 3315, 3112, 2548, 2375, 1730, 1628, 1586, 1521, 1320, 1280, 1154, 1080 cm^{-1};enantiomeric excess: 96%, determined by HPLC (Chiralcel OD-3, hexane/2-propanol = 9/1, flow rate 1.0 mL/min, 25 °C, 254 nm) minor peak: t_R = 8.9 min, major peak: t_R = 10.9 min; $[\alpha]_D^{22} = +16.9$ (*c* 1.8, $CHCl_3$).



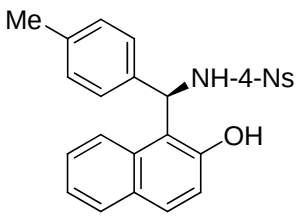
4i

4i: 92% yield; ^{1}H-NMR (DMSO-D_6) δ: 7.89 (2H, d, *J* = 9.2 Hz), 7.65 (2H, d, *J* = 9.2 Hz), 7.60 (2H, d, *J* = 7.8 Hz), 7.57 (1H, d, *J* = 8.7 Hz), 7.31-7.21 (4H, m), 7.17 (1H, t, *J* = 7.3 Hz), 7.13-7.09 (1H, m), 6.96 (1H, d, *J* = 8.7 Hz), 6.53 (1H, s); ^{13}C-NMR (DMSO-D_6) δ: 153.1, 148.7, 146.0, 143.5, 132.8, 131.3, 130.0, 129.8, 128.3, 128.1, 127.5, 126.6, 126.4, 125.9, 125.0, 123.2, 122.9, 122.4, 117.7, 116.1, 52.1; HRMS (ESI) HRMS (ESI) calcd for $C_{23}H_{17}ClN_2O_5SNa$, m/z = 491.0444 [$(M+Na)^+$], found m/z = 491.0436; IR (KBr): ν 3443, 3310, 3108, 2377, 1629, 1581, 1522, 1432, 1323, 1275, 1156, 1081 cm^{-1}; enantiomeric excess: 98%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 19/1, flow rate 1.0 mL/min, 25 °C, 254 nm) minor peak: t_R = 56.1 min, major peak: t_R = 44.9 min; $[\alpha]_D^{21} = +17.7$ (*c* 1.5, $CHCl_3$).



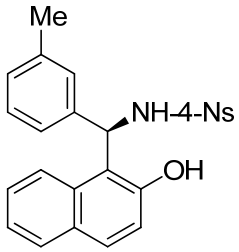
4j

4j: 90% yield; ^{1}H-NMR (DMSO-D_6) δ: 10.30 (1H, br s), 7.92 (2H, d, *J* = 8.7 Hz), 7.77 (1H, d, *J* = 8.7 Hz), 7.65-7.50 (5H, m), 7.30-7.22 (2H, m), 7.18-7.11 (3H, m), 6.91 (1H, d, *J* = 8.7 Hz), 6.60 (1H, s); ^{13}C-NMR (DMSO-D_6) δ: 154.8, 148.2, 139.3, 132.0, 131.9, 129.4, 129.1, 128.5, 128.3, 127.8, 127.4, 126.6, 126.1, 123.0, 122.2, 122.0, 118.8, 115.9, 53.1; HRMS (ESI) calcd for $C_{23}H_{17}ClN_2O_5SNa$, m/z = 491.0444 [$(M+Na)^+$], found m/z = 491.0435; IR (KBr): ν 3277, 3107, 3071, 2372, 1685, 1628, 1597, 1527, 1446, 1344, 1270, 1171, 1092 cm^{-1}; enantiomeric excess: 88%, determined by HPLC (Chiralpak IC-3, hexane/2-propanol = 19/1, flow rate 1.0 mL/min, 25 °C, 254 nm) minor peak: t_R = 77.6 min, major peak: t_R = 61.2 min; $[\alpha]_D^{22} = +92.7$ (*c* 1.8, MeOH).



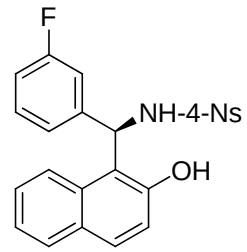
4k

4k: 100% yield; ^{1}H-NMR (ACETONE-D_6) δ: 7.85 (1H, d, *J* = 9.2 Hz), 7.78 (2H, d, *J* = 8.7 Hz), 7.69-7.66 (3H, m), 7.60 (1H, d, *J* = 8.7 Hz), 7.43 (1H, t, *J* = 7.6 Hz), 7.29 (3H, m), 7.11 (2H, d, *J* = 7.8 Hz), 7.04 (1H, d, *J* = 9.2 Hz), 6.58 (1H, s), 2.29 (3H, s); ^{13}C-NMR (ACETONE-D_6) δ: 153.8, 150.4, 147.5, 138.9, 137.7, 133.6, 131.0, 130.1, 130.0, 129.7, 129.0, 128.1, 127.9, 125.5, 124.3, 124.2, 119.2, 118.4, 55.1, 21.4; HRMS (ESI) calcd for $C_{24}H_{20}N_2O_5SNa$, m/z = 471.0991 [$(M+Na)^+$], found m/z = 471.0984; IR (KBr): ν 3432, 3313, 3111, 2375, 1629, 1520, 1431, 1321, 1277, 1153, 1078 cm^{-1}; enantiomeric excess: 90%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 4/1, flow rate 1.0 mL/min, 25 °C, 266 nm) minor peak: t_R = 16.2 min, major peak: t_R = 21.1 min; $[\alpha]_D^{23} = +42.4$ (*c* 1.2, $CHCl_3$).



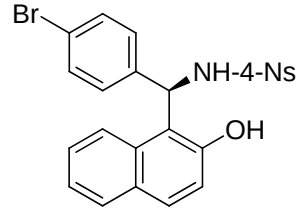
4l

4l: 95% yield; ^{1}H-NMR (ACETONE-D_6) δ: 7.86 (1H, d, *J* = 8.2 Hz), 7.79 (2H, d, *J* = 8.7 Hz), 7.70-7.66 (3H, m), 7.61 (1H, d, *J* = 8.7 Hz), 7.44 (1H, t, *J* = 8.0 Hz), 7.32-7.26 (2H, m), 7.20-7.14 (2H, m), 7.09-7.01 (2H, m), 6.59 (1H, s), 2.27 (3H, s); ^{13}C-NMR (ACETONE-D_6) δ: 153.3, 150.0, 147.1, 141.5, 138.4, 133.1, 130.6, 129.6, 129.2, 128.9, 128.6, 128.5, 128.0, 127.7, 124.6, 123.8, 123.8, 123.3, 118.7, 118.0, 54.7; HRMS (ESI) calcd for $C_{24}H_{20}N_2O_5SNa$, m/z = 471.0991 [$(M+Na)^+$], found m/z = 471.0980; IR (KBr): ν 3452, 3316, 3107, 1620, 1523, 1434, 1323, 1281, 1156, 1079 cm^{-1}; enantiomeric excess: 99%, determined by HPLC (Chiralpak IC-3, hexane/2-propanol = 19/1, flow rate 1.0 mL/min, 25 °C, 231 nm) minor peak: t_R = 36.9 min, major peak: t_R = 41.0 min; $[\alpha]_D^{24} = +29.5$ (*c* 2.0, $CHCl_3$).



4m

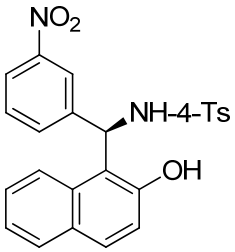
4m: 98% yield; ^{1}H-NMR ($CDCl_3$) δ: 7.75 (2H, d, *J* = 8.7 Hz), 7.65-7.47 (2H, m), 7.35 (2H, t, *J* = 7.8 Hz), 7.25 (1H, m), 7.12 (2H, d, *J* = 7.8 Hz), 7.03 (1H, d, *J* = 10.1 Hz), 6.94 (2H, t, *J* = 7.8 Hz), 6.76 (2H, d, *J* = 8.7 Hz), 6.70 (1H, s), 6.43 (1H, d, *J* = 10.1 Hz), 5.73 (1H, s); ^{13}C-NMR (ACETONE-D_6) δ: 164.8, 162.4, 153.4, 150.0, 147.0, 144.8, 133.0, 131.0, 130.9, 130.8, 129.6, 129.3, 128.7, 127.9, 123.9, 123.3, 118.6, 117.5, 114.6, 114.3, 114.1, 54.2; HRMS (ESI) calcd for $C_{23}H_{17}FN_2O_5SNa$, m/z = 475.0740 [$(M+Na)^+$], found m/z = 475.0736; IR (KBr): ν 3419, 3304, 2375, 1696, 1619, 1526, 1439, 1346, 1256, 1165, 1086 cm^{-1}; enantiomeric excess: 85%, determined by HPLC (Chiralpak IE, hexane/2-propanol = 7/1, flow rate 1.0 mL/min, 25 °C, 266 nm) minor peak: t_R = 11.4 min, major peak: t_R = 8.6 min; $[\alpha]_D^{14} = +12.6$ (*c* 1.5, $CHCl_3$).



4n

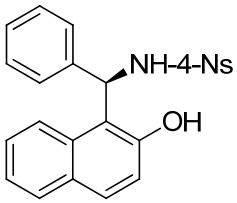
4n: 90% yield; ^{1}H-NMR (DMSO-D_6) δ: 9.96 (1H, br s), 8.81 (1H, br s), 7.88 (2H, d, *J* = 8.7 Hz), 7.64 (2H, d, *J* = 8.7 Hz), 7.58 (2H, d, *J* = 7.3 Hz), 7.55 (1H, d, *J* = 9.2 Hz), 7.44 (2H, d, *J* = 8.7 Hz), 7.25 (1H, t, *J* = 8.2 Hz), 7.19-7.13 (3H, m), 6.95 (1H, d, *J* = 9.2 Hz), 6.49 (1H, s); ^{13}C-NMR (DMSO-D_6) δ: 153.0, 148.6, 146.0, 140.4, 131.3, 131.0, 129.7, 128.4,

128.2, 127.4, 126.3, 123.1, 122.4, 119.7, 117.6, 116.1, 52.0; HRMS (ESI) calcd for $C_{23}H_{17}BrN_2O_5SNa$, m/z = 534.9939 [(M+Na)+], found m/z = 534.9926; IR (KBr): ν 3426, 3315, 3110, 2544, 2465, 2374, 1618, 1522, 1318, 1280, 1157, 1112 cm^{-1}; enantiomeric excess: 90%, determined by HPLC (Chiralcel OD-H, hexane/2-propanol = 19/1, flow rate 1.0 mL/min, 25 °C, 250 nm) minor peak: t_R = 47.5 min, major peak: t_R = 61.2 min; $[\alpha]_D^{20} = +21.8$ (*c* 1.6, $CHCl_3$).



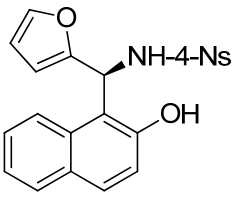
4o

4o[2a]: 80% yield; ^{1}H-NMR ($CDCl_3$) δ: 8.12 (1H, s), 8.06 (1H, d, *J* = 7.8 Hz), 7.75-7.67 (3H, m), 7.59 (1H, d, *J* = 8.6 Hz), 7.45 (1H, t, *J* = 7.1 Hz), 7.39 (1H, t, *J* = 7.1 Hz), 7.34 (3H, d, *J* = 8.6 Hz), 6.85 (1H, d, *J* = 8.6 Hz), 6.68 (3H, d, *J* = 7.8 Hz), 6.45 (1H, d, *J* = 10.1 Hz), 5.99 (1H, s), 2.11 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 151.2, 148.1, 143.0, 142.8, 135.8, 133.1, 132.0, 130.2, 129.1, 128.8, 128.7, 128.5, 127.5, 126.4, 123.5, 122.2, 121.6, 121.3, 117.8, 116.4, 53.5, 21.1; enantiomeric excess: 73%, determined by HPLC (Chiralpak IC-3, hexane/2-propanol = 4/1, flow rate 1.0 mL/min, 25 °C, 335 nm) minor peak: t_R = 12.4 min, major peak: t_R = 15.4 min.



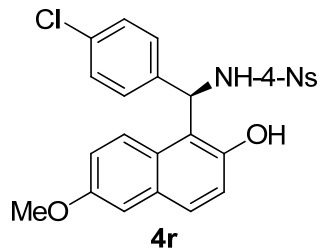
4p

4p: 100% yield; ^{1}H-NMR (ACETONE-D_6) δ: 7.87 (1H, d, *J* = 8.7 Hz), 7.81 (2H, d, *J* = 8.7 Hz), 7.70 (2H, d, *J* = 8.7 Hz), 7.69 (1H, d, *J* = 8.7 Hz), 7.63 (1H, d, *J* = 8.7 Hz), 7.46-7.41 (3H, m), 7.34-7.23 (4H, m), 7.04 (1H, d, *J* = 8.7 Hz), 6.64 (1H, s); ^{13}C-NMR (ACETONE-D_6) δ: 153.3, 150.0, 147.0, 141.5, 133.1, 130.7, 129.6, 129.2, 129.0 x 2, 128.6, 127.8, 127.4, 123.8, 123.3, 118.6, 117.9, 54.7; HRMS (ESI) calcd for $C_{23}H_{18}N_2O_5SNa$, m/z = 457.0834 [$(M+Na)^+$], found m/z = 457.0827; IR (KBr): ν 3305, 2359, 1698, 1528, 1430, 1348, 1312, 1162, 1090, 1028 cm^{-1}; enantiomeric excess: 73%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 7/1, flow rate 1.0 mL/min, 25 °C, 268 nm) minor peak: t_R = 18.3 min, major peak: t_R = 21.4 min; $[\alpha]_D^{20} = +22.4$ (*c* 2.3, $CHCl_3$).



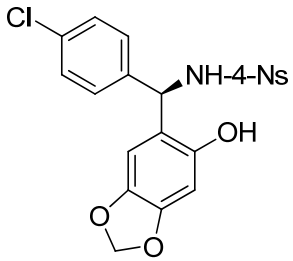
4q

4q: 100% yield; ^{1}H-NMR (ACETONE-D_6) δ: 7.99 (1H, d, *J* = 8.7 Hz), 7.86 (2H, d, *J* = 8.7 Hz), 7.72 (2H, d, *J* = 8.7 Hz), 7.68 (1H, d, *J* = 8.2 Hz), 7.62 (1H, d, *J* = 8.7 Hz), 7.48-7.42 (2H, m), 7.29 (1H, t, *J* = 7.5 Hz), 7.05 (1H, d, *J* = 8.7 Hz), 6.69 (1H, s), 6.34 (1H, dd, *J* = 3.2, 1.8 Hz), 6.23 (1H, d, *J* = 3.2 Hz); ^{13}C-NMR (ACETONE-D_6) δ: 153.8, 153.7, 150.0, 147.1, 143.0, 132.9, 130.9, 129.6, 129.2, 128.6, 127.6, 123.8, 123.2, 118.6, 115.7, 111.2, 108.4, 50.0; HRMS (ESI) calcd for $C_{21}H_{16}N_2O_6SNa$, m/z = 447.0627 [$(M+Na)^+$], found m/z = 447.0617; IR (KBr): ν 3396, 3324, 3162, 3104, 3067, 1702, 1614, 1525, 1411, 1345, 1310, 1281, 1160, 1078 cm^{-1}; enantiomeric excess: 72%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 7/1, flow rate 1.0 mL/min, 25 °C, 268 nm) minor peak: t_R = 45.3 min, major peak: t_R = 25.6 min; $[\alpha]_D^{20} = +37.0$ (*c* 3.9, $CHCl_3$).



4r

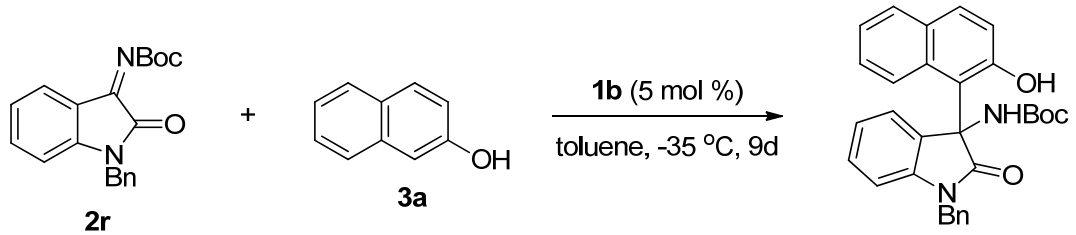
4r: 90% yield;[1]H-NMR (ACETONE-D_6) δ: 7.81 (2H, d, *J* = 9.2 Hz), 7.78-7.73 (1H, m), 7.69 (2H, d, *J* = 9.0 Hz), 7.50 (1H, d, *J* = 8.7 Hz), 7.38-7.34 (2H, m), 7.33-7.29 (2H, m), 7.13-7.08 (2H, m), 6.97 (1H, d, *J* = 9.2 Hz), 6.48 (1H, s), 3.85 (3H, s); ^{13}C-NMR (ACETONE-D_6) δ:156.8, 151.6, 150.1, 146.9, 140.7, 133.2, 130.8, 129.6, 129.3, 129.1, 128.6, 128.1, 124.7, 123.8, 120.3, 119.1, 117.9, 107.6, 55.6, 54.4; HRMS (ESI) calcd for $C_{24}H_{19}ClN_2O_6SNa$, m/z = 521.0550 [$(M+Na)^+$], found m/z = 521.0533; IR (KBr): ν 3453, 3268, 2371, 2350, 2336, 1609, 1523, 1432, 1341, 1234, 1162, 1083 cm^{-1}; enantiomeric excess: 77%, determined by HPLC (Chiralpak IC-3, hexane/2-propanol = 4/1, flow rate 1.0 mL/min, 25 °C, 369 nm) minor peak: t_R = 8.8 min, major peak: t_R = 11.7 min; $[\alpha]_D^{21} = +5.1$ (*c* 0.93, $CHCl_3$).



4s

4s: 96% yield; [1]H-NMR (ACETONE-D_6) δ: 8.55 (1H, br s), 8.25 (2H, d, *J* = 7.8 Hz), 7.97 (2H, d, *J* = 7.8 Hz), 7.63 (1H, br s), 7.40-7.25 (4H, m), 6.60 (1H, s), 6.32 (1H, s), 6.02 (1H, s), 5.83 (1H, s), 5.81 (1H, s); ^{13}C-NMR (ACETONE-D_6) δ: 150.5, 149.6, 148.3, 147.8, 141.6, 141.2, 133.2, 129.5, 129.2, 129.0, 124.5, 118.8, 108.3, 102.0, 98.3, 56.1; HRMS (ESI) calcd for $C_{20}H_{15}ClN_2O_7SNa$, m/z = 485.0186 [$(M+Na)^+$], found m/z = 485.0175; IR (KBr): ν 3286, 2924, 2371, 2350, 2336, 1695, 1531, 1447, 1346, 1168, 1087, 1038 cm^{-1}; enantiomeric excess: 84%, determined by HPLC (Chiralcel OD-3, hexane/2-propanol = 4/1, flow rate 1.0 mL/min, 25 °C, 260 nm) minor peak: t_R = 9.3 min, major peak: t_R = 12.6 min; $[\alpha]_D^{21} = -8.3$ (*c* 1.2, $CHCl_3$).

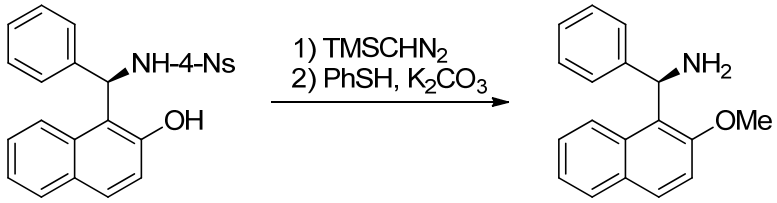
Procedure for enantioselective Friedel–Crafts (FC)-type reaction of ketimine (2r) with 2-naphthol (3a)



Under N_2 atmosphere, a test tube was charged with imine **2r** (0.10 mmol), 2-naphthol **3a** (0.15 mmol), and the catalyst **1b** (0.005 mmol, 5 mol %) in toluene (0.4 mL). The reaction mixture was stirred at -35 °C. After the purification *via* SiO_2 column chromatography (hexane/AcOEt = 3/1), the desired product **4** was obtained in 70% yield (33.6mg, 0.07 mmol) with 43% ee. **4t**: 70% yield; [1]H-NMR ($CDCl_3$) δ: 10.02 (1H, s), 7.68 (2H, dd, *J* = 7.8, 3.7 Hz), 7.34-7.16 (9H, m), 7.05 (1H, t, *J* = 7.8 Hz), 6.97 (1H, t, *J* = 7.8 Hz), 6.80 (2H, d, *J* = 7.8 Hz), 5.87 (1H, s), 5.18 (1H, d, *J* = 15.8 Hz), 4.87 (1H, d, *J* = 15.8 Hz), 1.31 (9H, s); ^{13}C-NMR ($CDCl_3$) δ: 179.7, 153.8, 143.0, 138.6, 138.2, 135.0, 131.9, 130.7, 130.2, 129.6, 128.8 x 2, 127.6, 127.1, 125.5 x 2, 124.3, 123.5, 122.8, 121.5,

114.2, 110.0, 80.7, 65.5, 44.6, 28.1; HRMS (ESI) calcd for $C_{30}H_{28}N_2O_4Na$, m/z = 503.1947 [$(M+Na)^+$], found m/z = 503.1932; IR (KBr): ν 3269, 1696, 1610, 1490, 1349, 1274, 1161, 1048, 818, 738 cm^{-1}; enantiomeric excess: 43%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 4/1, flow rate 1.0 mL/min, 25 °C, 231 nm) minor peak: t_R = 17.7 min, major peak: t_R = 36.9 min; $[\alpha]_D^{24} = +8.0$ (*c* 1.1, $CHCl_3$).

Procedures for the deprotection of sulfonamide group



4p (73% ee) **8** (73% ee)

To a solution of compound **4p** (50 mg, 0.12 mmol) in MeOH (0.2 mL) and DCM (0.2 mL), $TMSCHN_2$ (2N solution in Et_2O, 0.44 mL, 1.0 mmol) was added in 10 portions over 1 h at rt. The reaction mixture was then stirred at 45 ^oC for 0.5 h. The solvent was evaporated in vacuo. After the purification *via* SiO_2 column chromatography (hexane/AcOEt = 2/1), the methyl-capped product was obtained (18 mg, 0.04 mmol, 40% yield); ^{1}H-NMR ($CDCl_3$) δ: 7.78 (1H, d, *J* = 8.4 Hz), 7.64 (2H, d, *J* = 9.2 Hz), 7.56 (2H, d, *J* = 8.4 Hz), 7.49-7.42 (3H, m), 7.35 (1H, t, *J* = 7.5 Hz), 7.28-7.20 (4H, m), 6.99 (1H, d, *J* = 9.2 Hz), 6.62 (1H, bs), 6.47 (1H, d, *J* = 10.5 Hz), 3.67 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 154.3, 148.9, 145.4, 139.6, 132.0, 130.3, 128.8, 128.5, 128.3, 127.8, 127.6, 127.3, 126.3, 124.3, 122.7, 121.8, 120.4, 113.4, 56.5, 54.1; HRMS (ESI) calcd for $C_{24}H_{20}N_2O_5SNa$, m/z = 471.0991 [$(M+Na)^+$], found m/z = 471.0966; IR (KBr): ν 3435, 3302, 3104, 2917, 2352, 1523, 1348, 1156, 1022 cm^{-1}. Subsequently PhSH (44 μL, 0.43 mmol) was added to a solution of the methyl-capped product (10 mg, 0.022 mmol) and K_2CO_3 (55.2 mg, 0.040 mmol) in DMF (0.2 mL) and CH_3CN (0.2 mL). The mixture was stirred at 50 °C for 4 h. Water was added to the reaction mixture and the solution was extracted with AcOEt. The combined organic layer was back extracted with 1N HCl and then the aqueous layer was basified with NaOH and extracted with AcOEt. Organic layer was dried over Na_2SO_4, and evaporated in vacuo. After the purification *via* SiO_2 column chromatography (AcOEt), the desired product **8** was obtained (5.9 mg, 0.022 mmol, quant) without racemization. $[\alpha]_D^{23} = -145$ (73% ee, *c* 0.85, $CHCl_3$) (lit.[6] $[\alpha]_D^{25} = +196$ (> 99% ee, *c* 1.6, $CHCl_3$)); ^{1}H-NMR ($CDCl_3$) δ: 8.02 (1H, d, *J* = 8.7 Hz), 7.80 (2H, d, *J* = 8.7 Hz), 7.42-7.36 (3H, m), 7.34-7.22 (4H, m), 7.18-7.13 (1H, m), 6.13 (1H, s), 3.79 (3H, s), 2.15 (2H, br s) ; ^{13}C-NMR ($CDCl_3$) δ: 154.8, 145.4, 132.0, 129.6, 129.2, 128.7, 127.9, 126.8, 126.6, 126.0, 125.9, 123.5, 123.4, 114.2, 56.5, 50.9.

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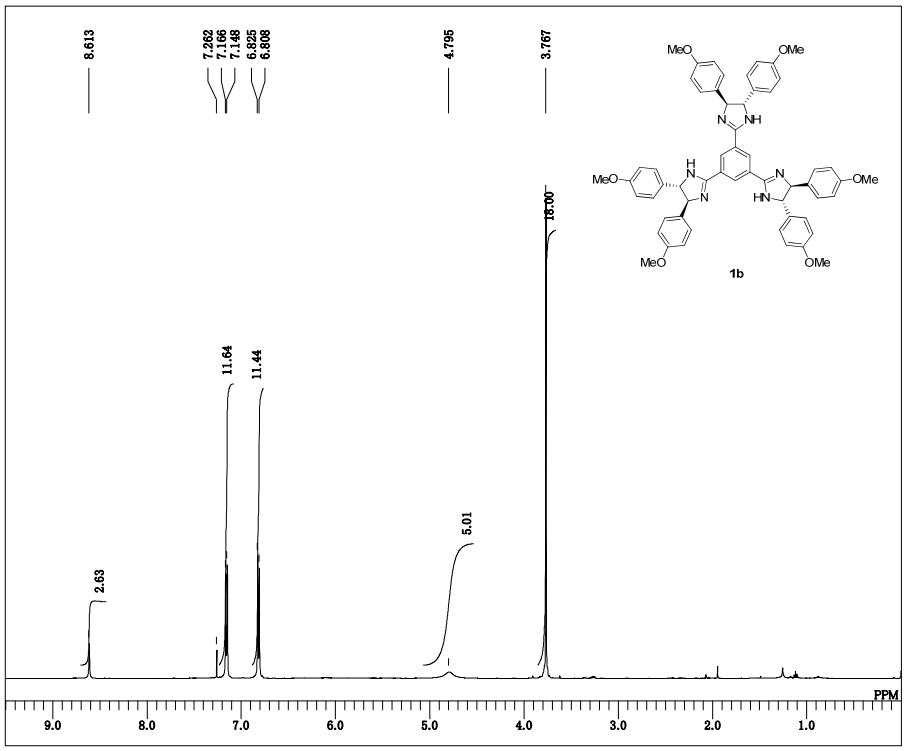
^{1}H-NMR and ^{13}C-NMR charts



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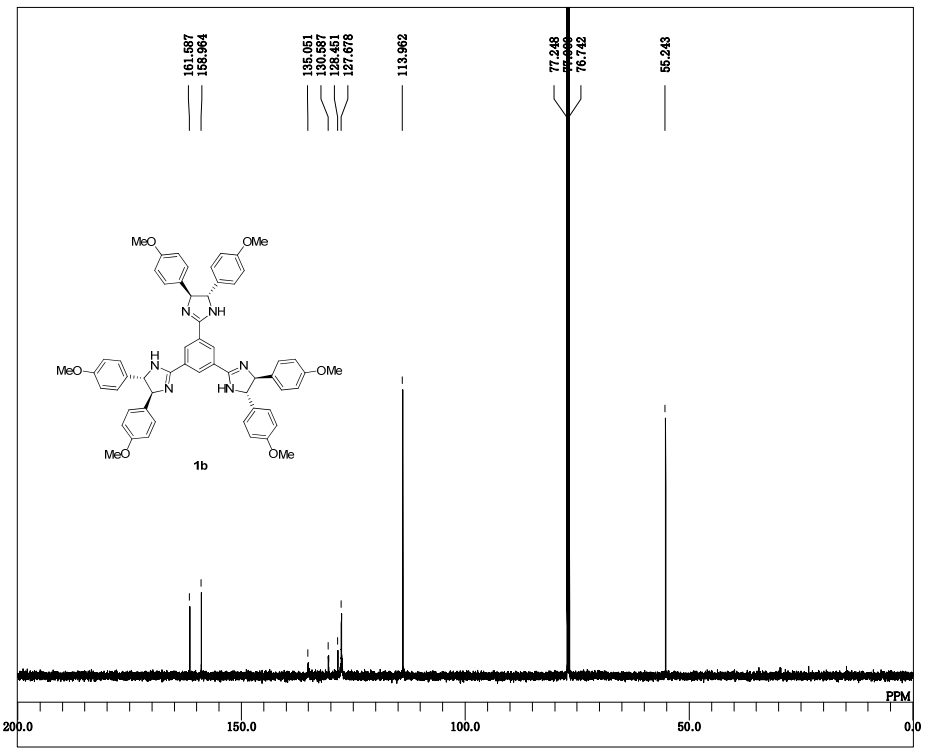

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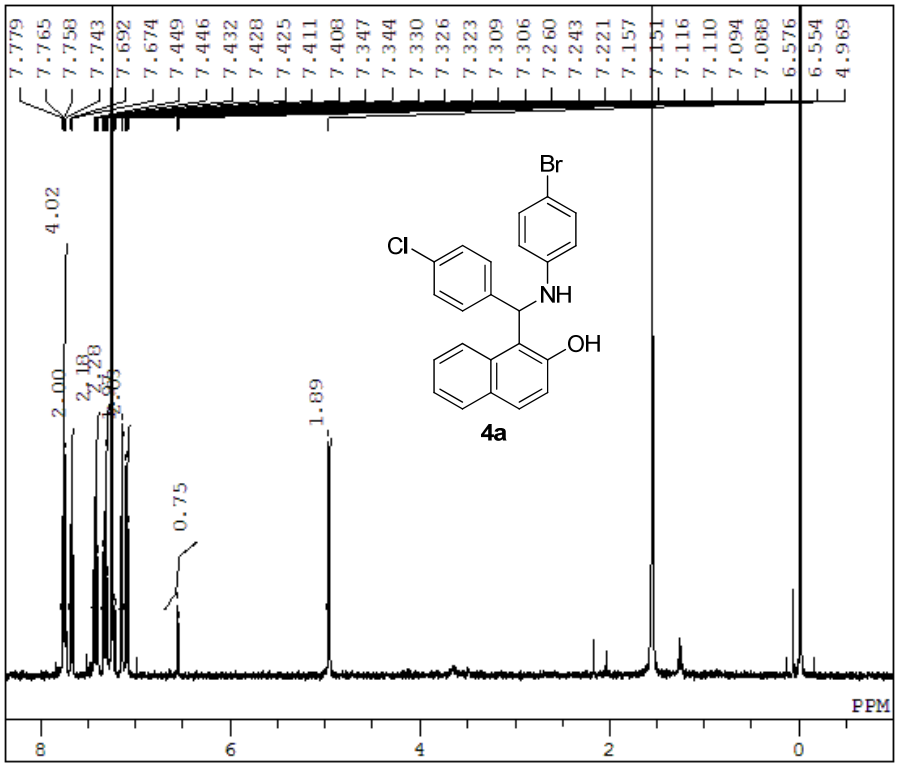
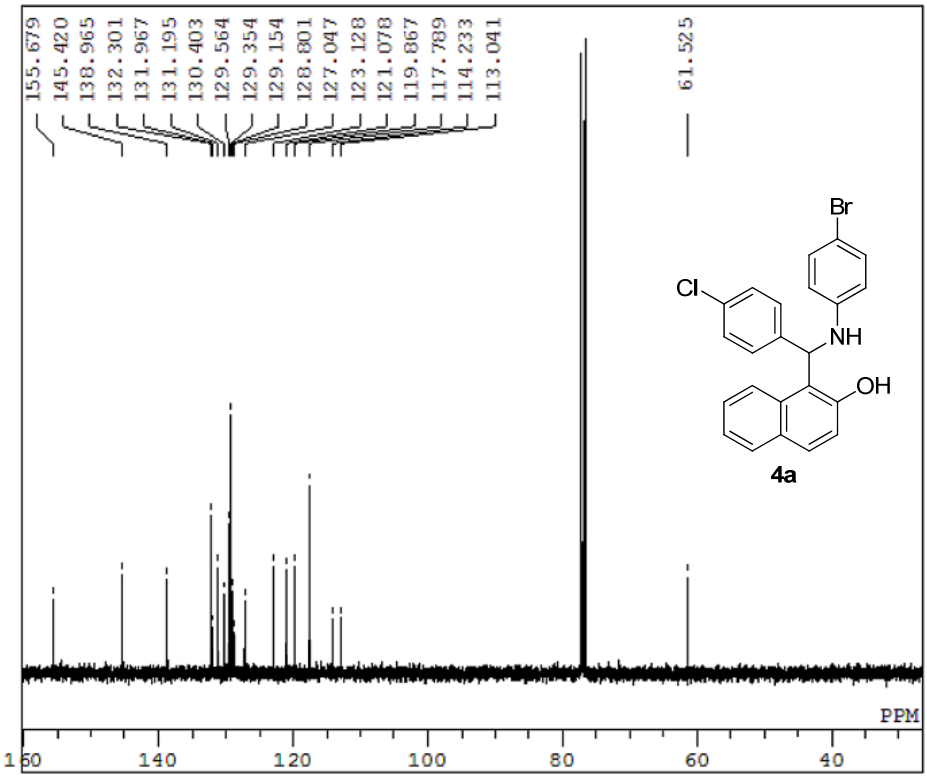
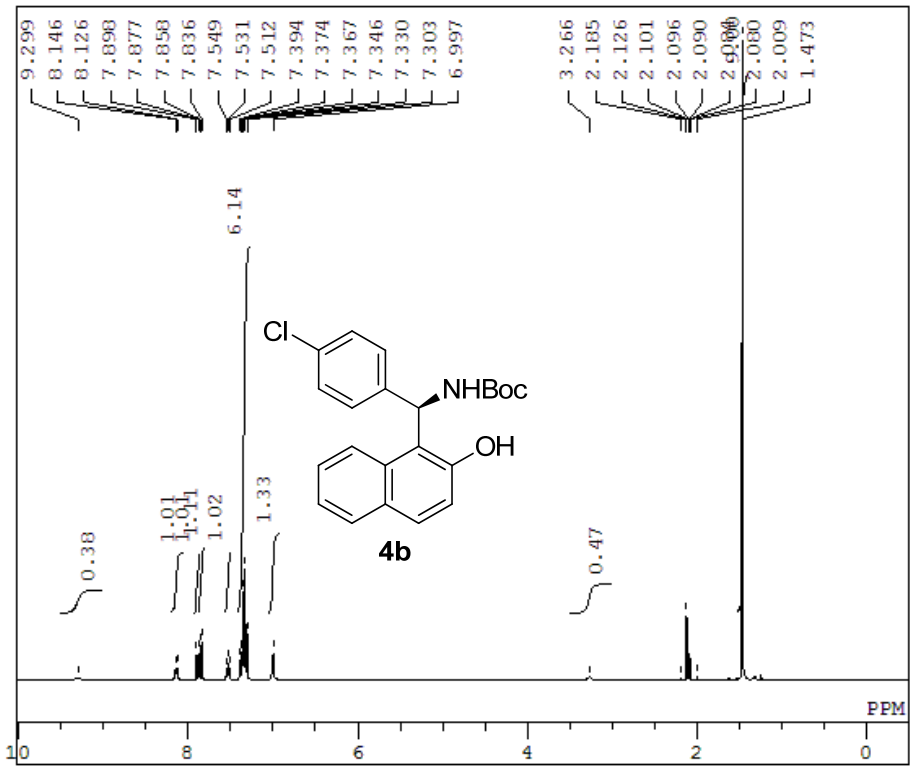
BF 0.12 Hz
RGAIN 60



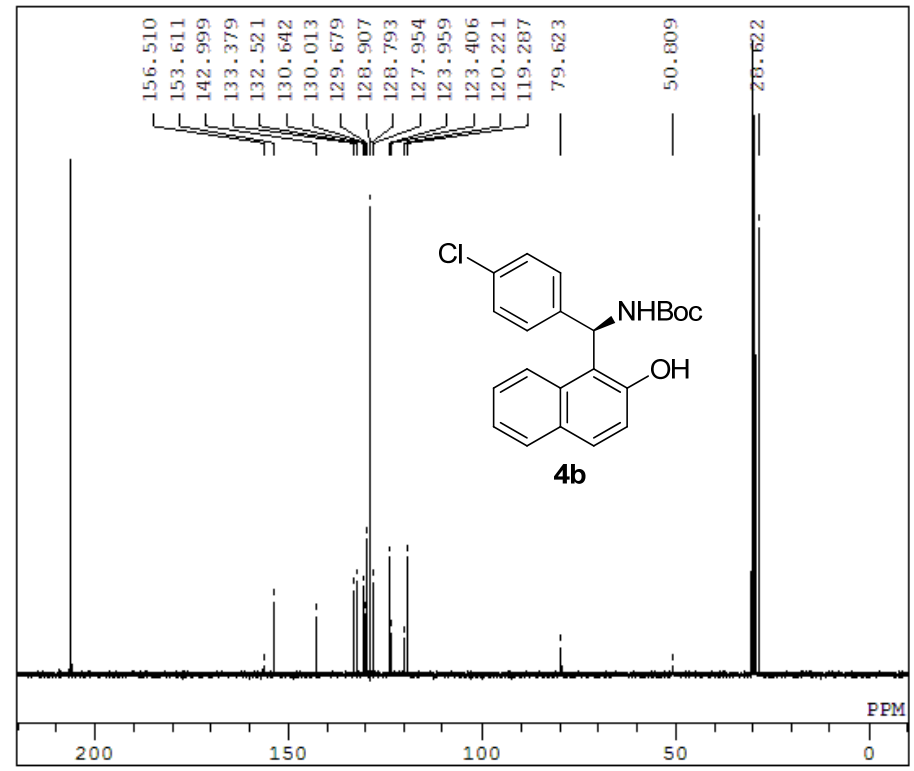

```
DFILE  8-21-3-rac.als
COMNT  single_pulse
DATIM  2012-09-20 21:11:
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         13107
FREQU       6002.40 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             6.05 usec
IRNUC  1H
CTEMP          22.1 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            58
```



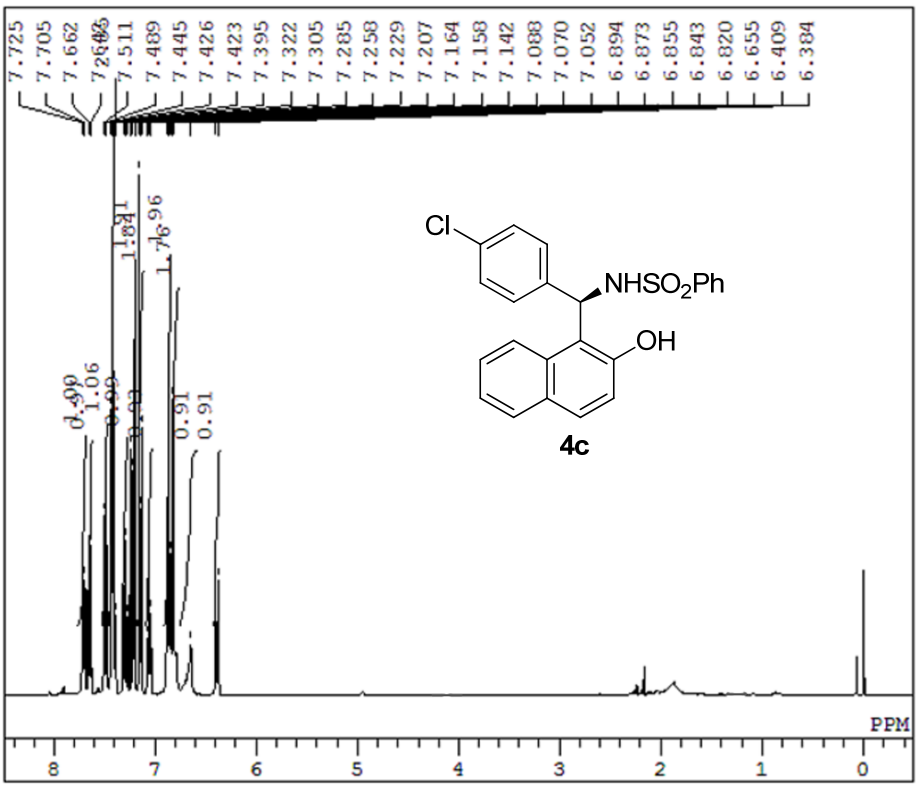

```
DFILE  8-21-2-check_Carb
COMNT  single pulse dec
DATIM  2014-05-22 13:27:
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32767
FREQU      31407.04 Hz
SCANS           256
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.20 usec
IRNUC  1H
CTEMP          18.6 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.10 Hz
RGAIN            50
```



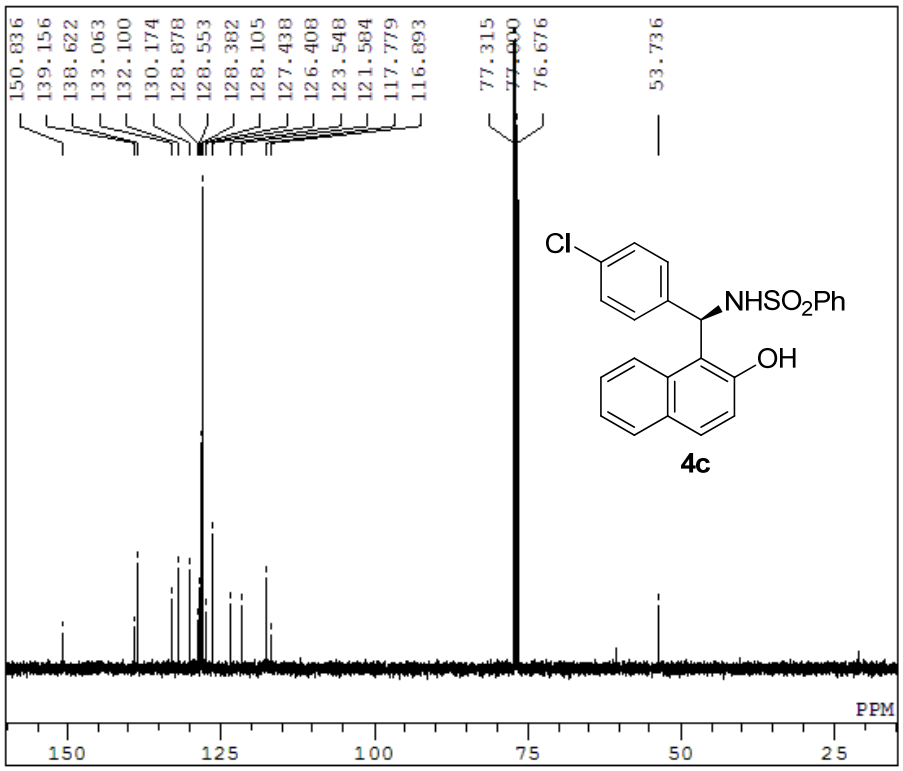

```
DFILE  8-168-Boc_Proton-
COMNT  single_pulse
DATIM  2014-06-16 12:39:
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         13107
FREQU       6002.40 Hz
SCANS             8
ACQTM        2.1837 sec
PD           5.0000 sec
PW1            6.05 usec
IRNUC  1H
CTEMP         20.8 c
SLVNT  ACETN
EXREF         2.09 ppm
BF            0.10 Hz
RGAIN           26
```



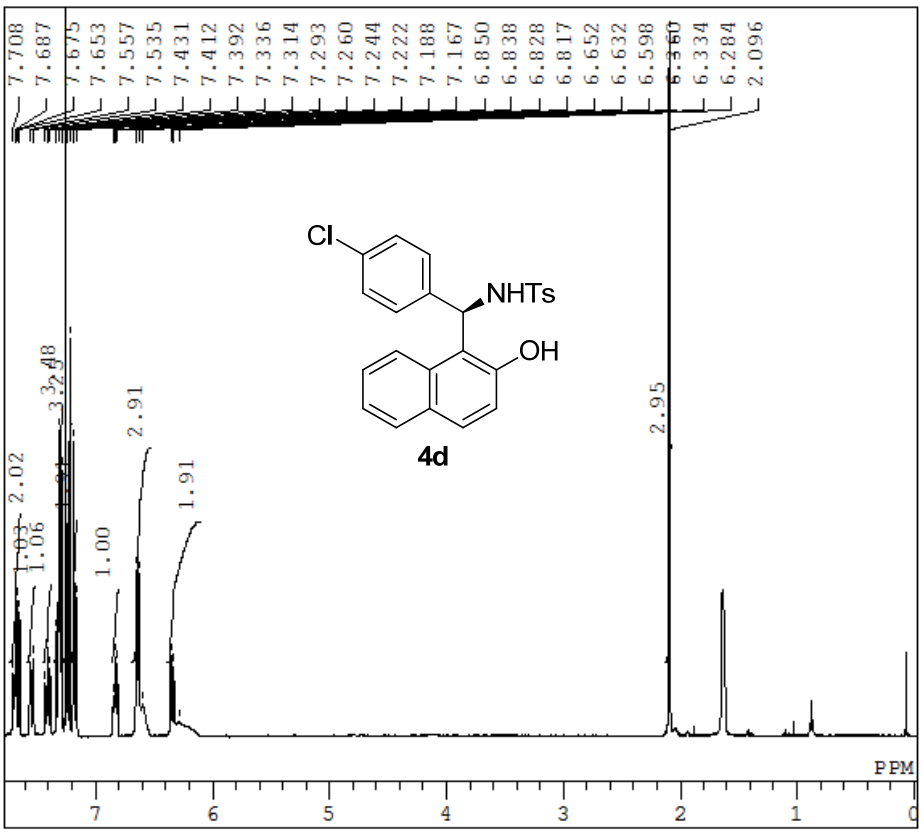

```
DFILE  8-168-Boc_Carbon-
COMNT  single pulse deco
DATIM  2014-06-16 12:41:
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32767
FREQU      31407.04 Hz
SCANS           250
ACQTM        1.0433 sec
PD           2.0000 sec
PW1            3.20 usec
IRNUC  1H
CTEMP         21.2 c
SLVNT  ACETN
EXREF         29.90 ppm
BF            0.10 Hz
RGAIN           60
```



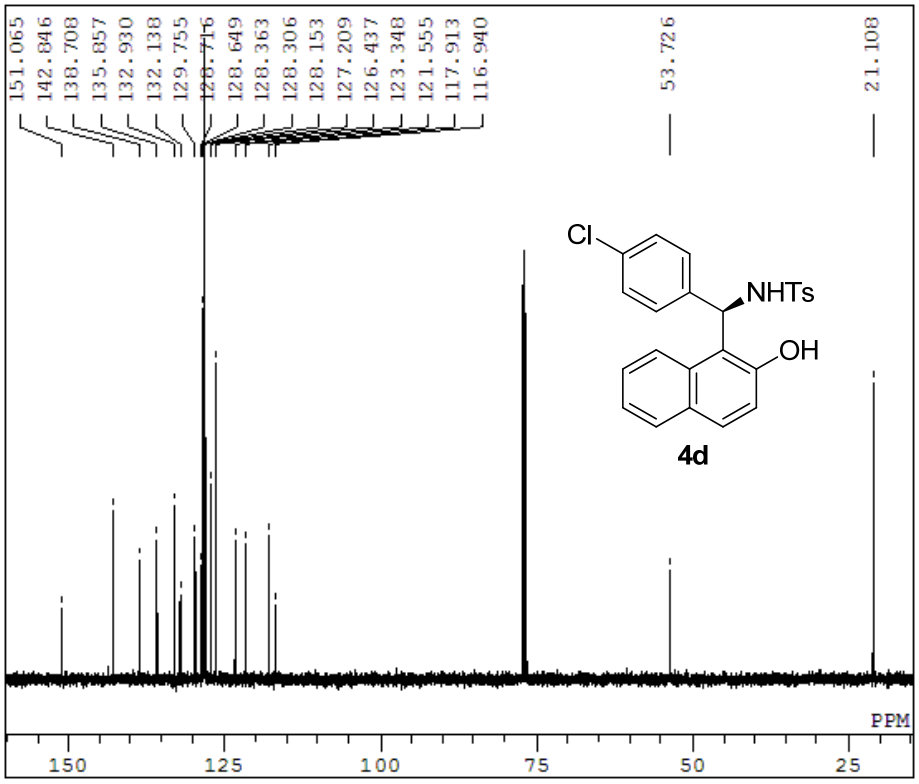

```
DFILE  8-51-2_Proton-1-1
COMNT  single_pulse
DATIM  2014-05-23 22:31:
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16384
FREQU       7503.00 Hz
SCANS             8
ACQTM        2.1837 sec
PD           5.0000 sec
PW1            6.05 usec
IRNUC  1H
CTEMP         18.8 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.10 Hz
RGAIN           40
```



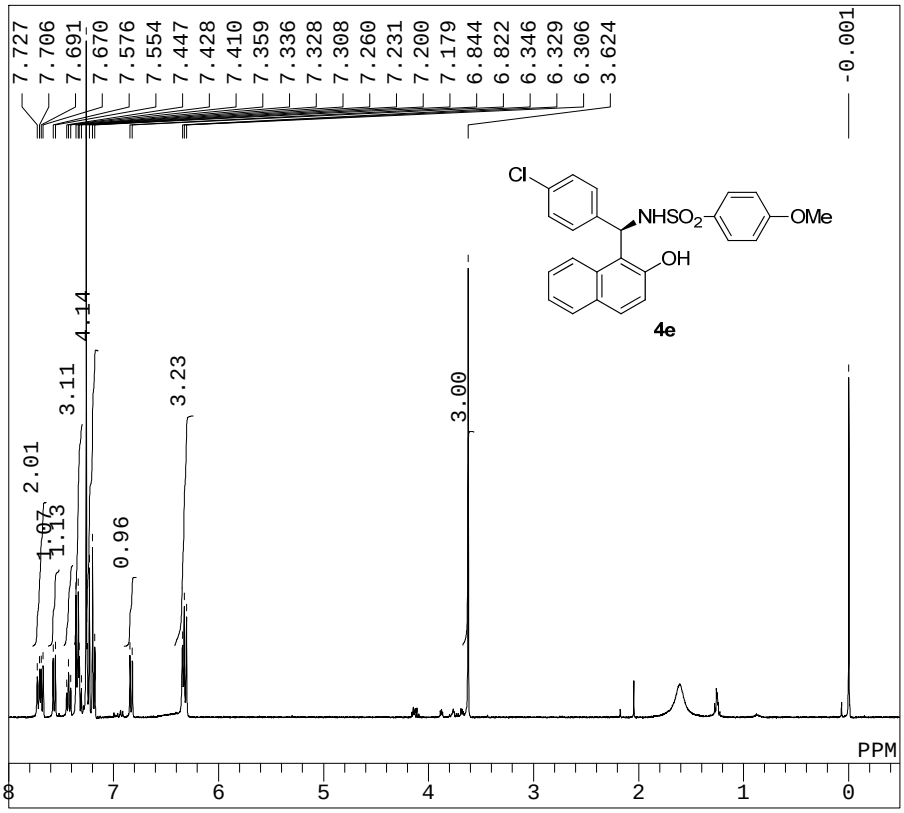

```
DFILE  8-51-2_Carbon-1-1
COMNT  single pulse deco
DATIM  2014-05-23 22:33:
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32767
FREQU      31407.04 Hz
SCANS           300
ACQTM        1.0433 sec
PD           2.0000 sec
PW1            3.20 usec
IRNUC  1H
CTEMP         19.5 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF            0.10 Hz
RGAIN           60
```



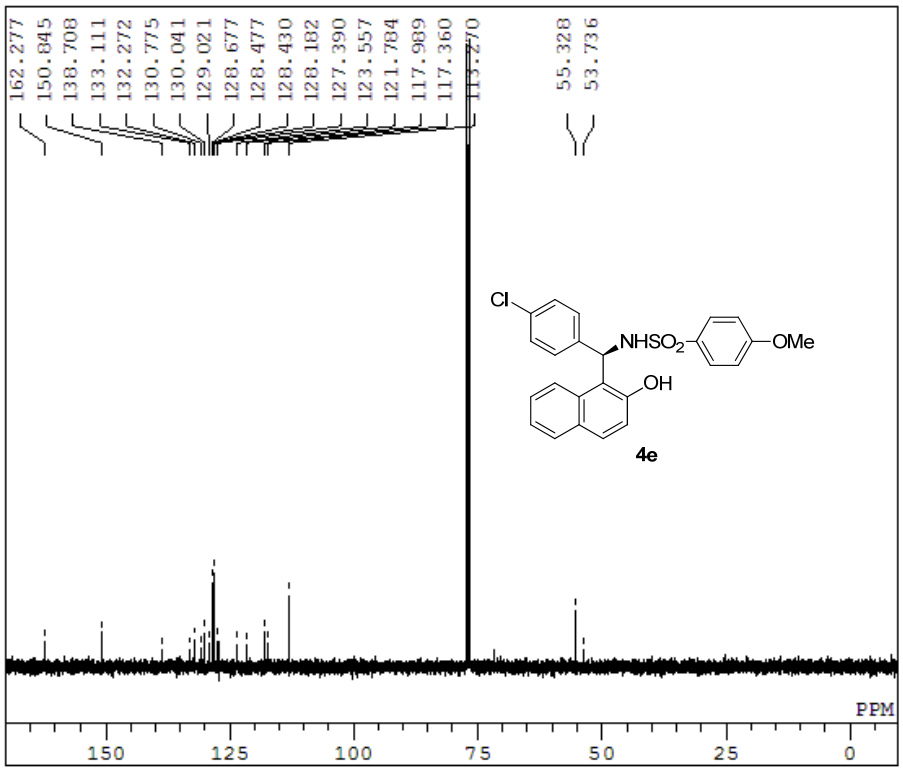

```
DFILE  7-54(pure).als
COMNT  single_pulse
DATIM  2011-03-05 15:39:
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         13107
FREQU       6002.40 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             6.00 usec
IRNUC  1H
CTEMP          21.7 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            46
```



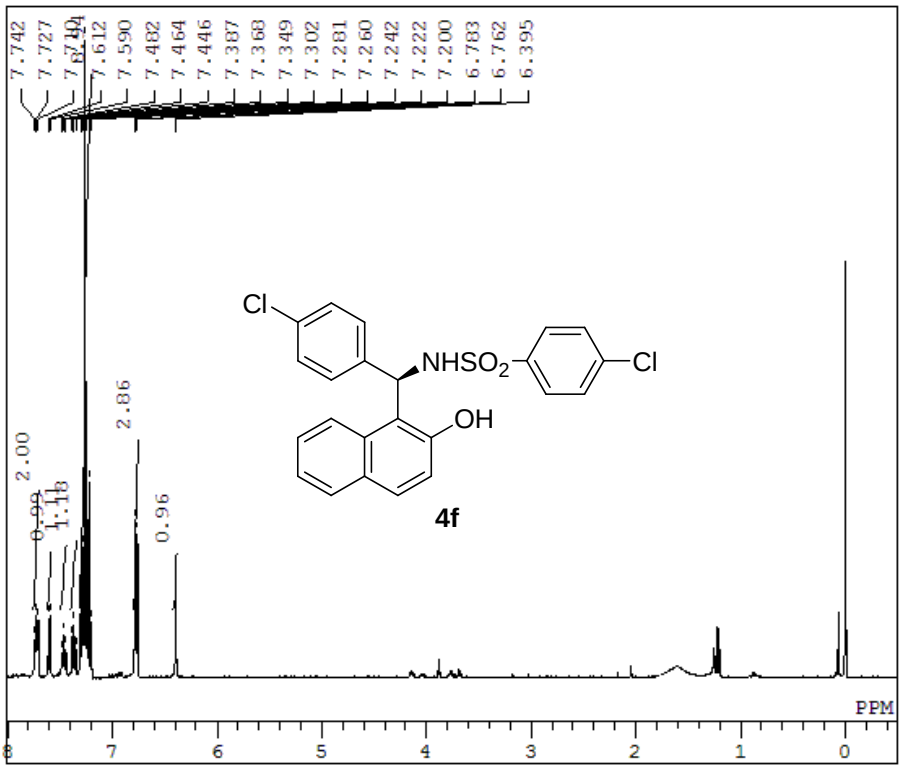

```
DFILE  8-166-2_Carbon-1-
COMNT  single pulse deco
DATIM  2014-06-13 23:16:
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32767
FREQU      31407.04 Hz
SCANS           200
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.20 usec
IRNUC  1H
CTEMP          20.0 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF             0.12 Hz
RGAIN            50
```



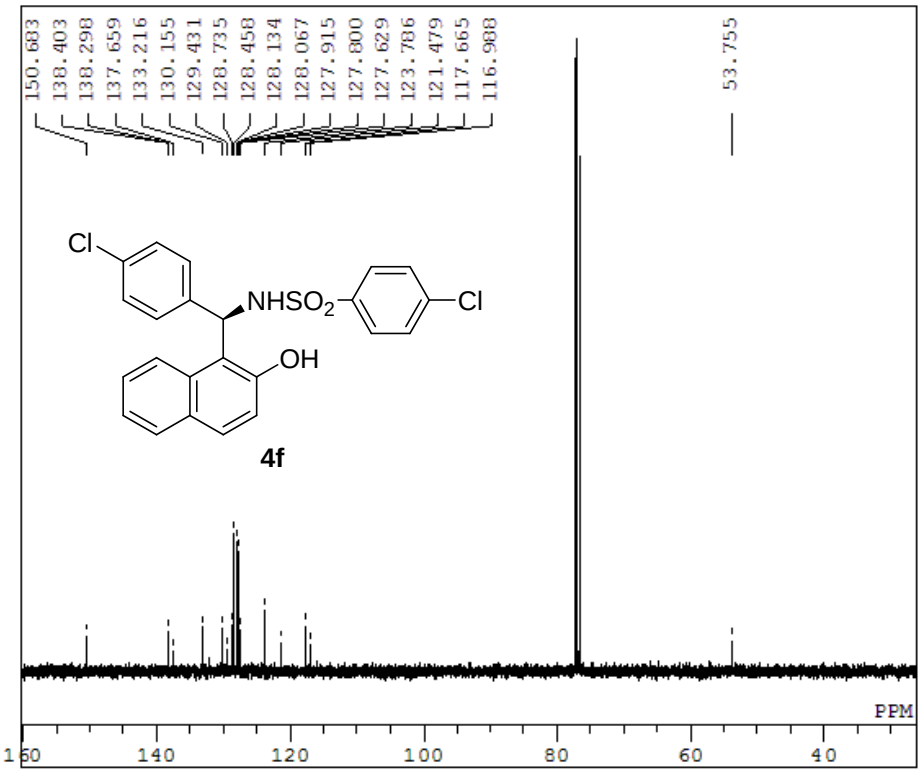

```
DFILE  sh4032-gpc3_Proto
COMNT  single_pulse
DATIM  2012-11-21 17:31:
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16384
FREQU       7503.00 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.50 usec
IRNUC  1H
CTEMP          20.3 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            46
```



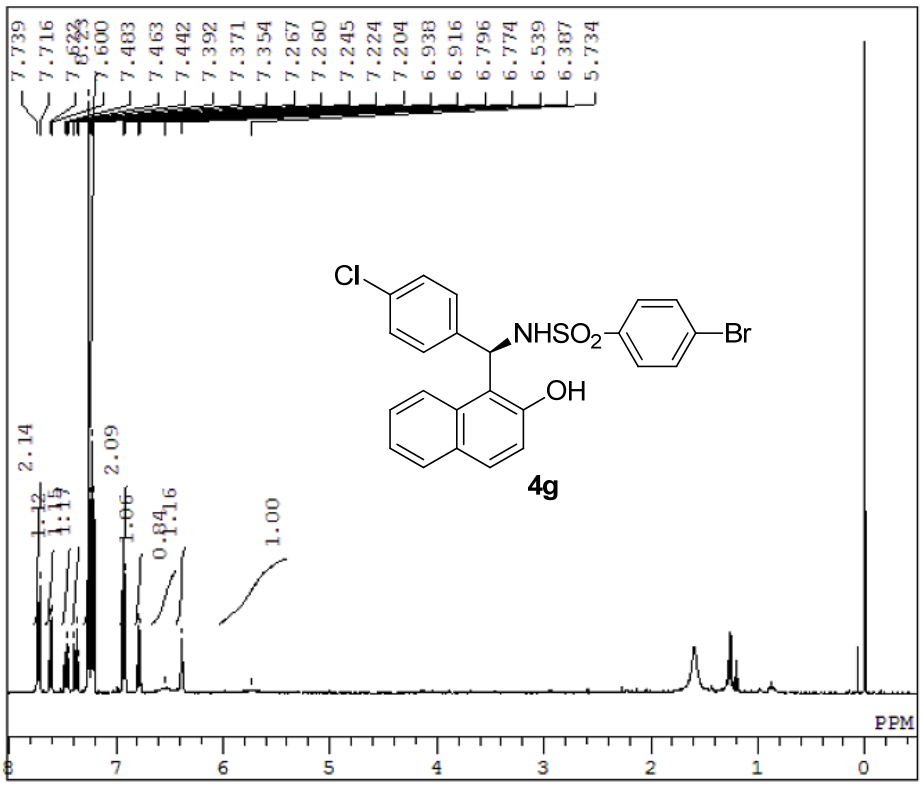

```
DFILE  8-54_Carbon-1-1.j
COMNT  single pulse deco
DATIM  2014-05-24 17:04:
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32767
FREQU      31407.04 Hz
SCANS           300
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.20 usec
IRNUC  1H
CTEMP          24.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.10 Hz
RGAIN            60
```



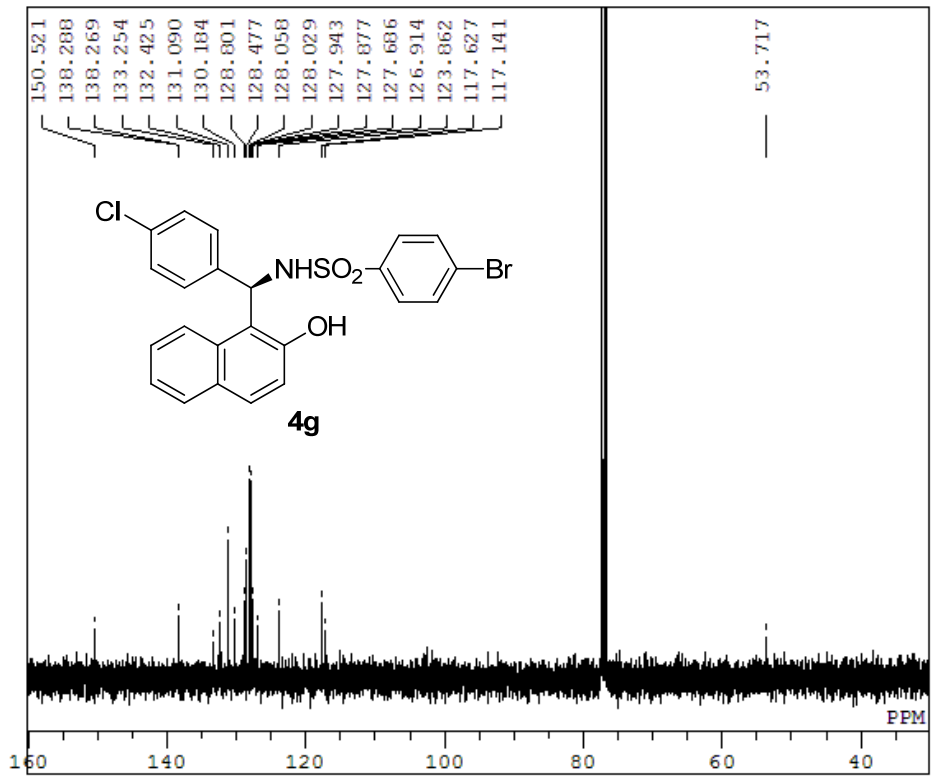

```
DFILE  sh4030a-gpc_Proto
COMNT  single_pulse
DATIM  2012-11-20 21:02:
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16384
FREQU       7503.00 Hz
SCANS             8
ACQTM        2.1837 sec
PD           5.0000 sec
PW1            5.50 usec
IRNUC  1H
CTEMP         20.6 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            48
```



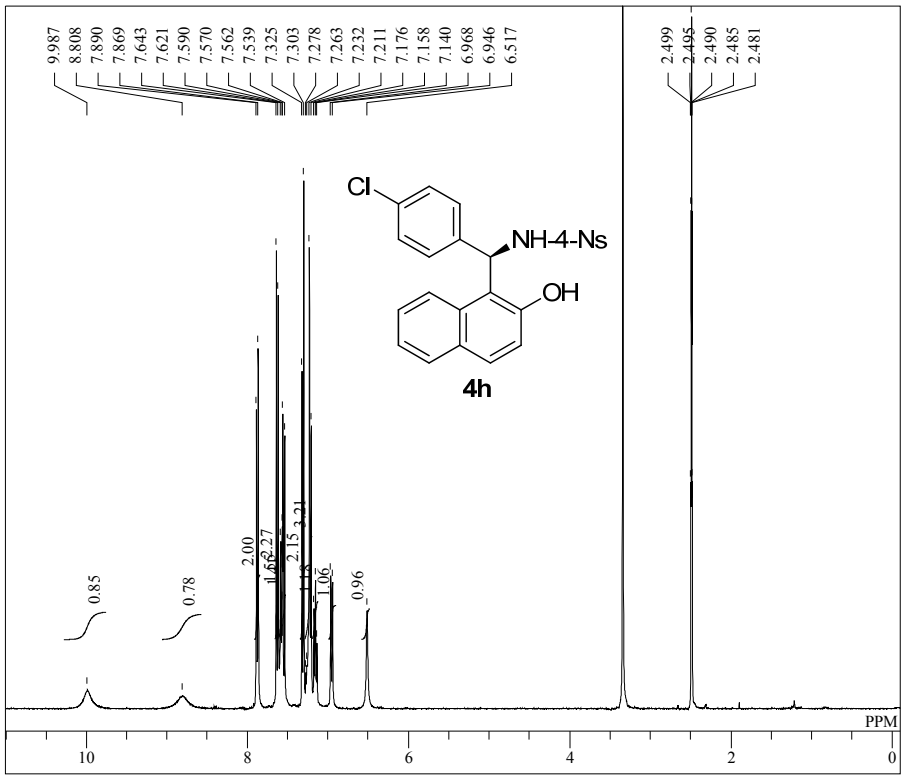

```
DFILE  8-53_Carbon-1-1.j
COMNT  single pulse deco
DATIM  2014-05-26 10:44:
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32767
FREQU      31407.04 Hz
SCANS           300
ACQTM        1.0433 sec
PD           2.0000 sec
PW1            3.20 usec
IRNUC  1H
CTEMP          19.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            60
```



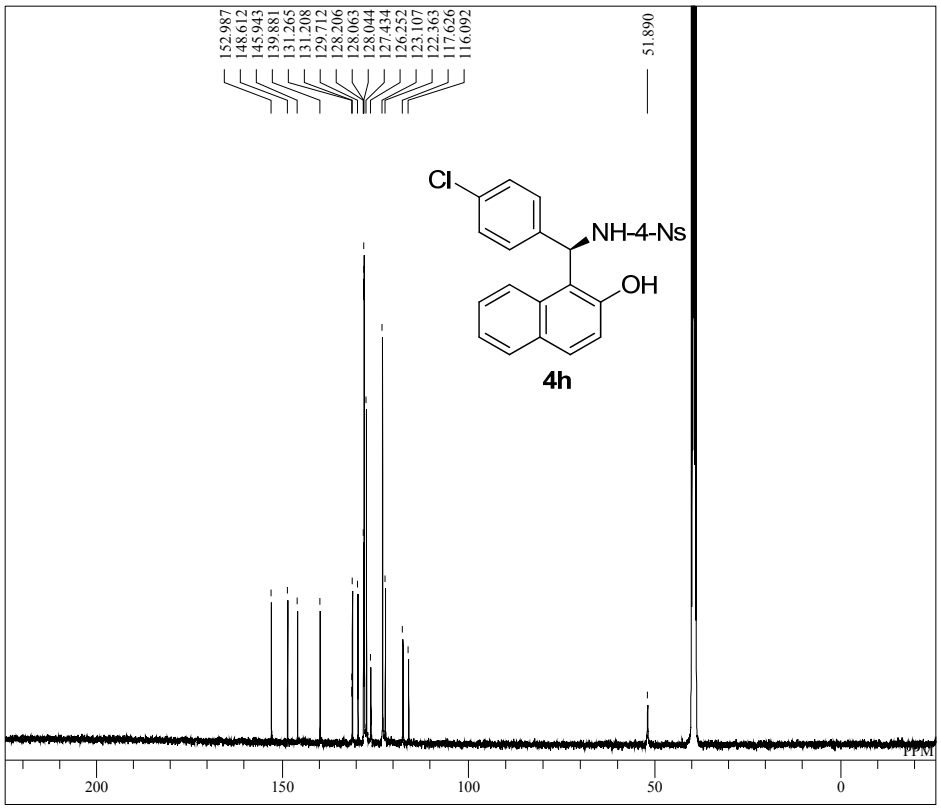

```
DFILE  sh4040-gpc22_Prot
COMNT  single_pulse
DATIM  2012-12-08 15:16:
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16384
FREQU       7503.00 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             6.05 usec
IRNUC  1H
CTEMP          23.0 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            50
```



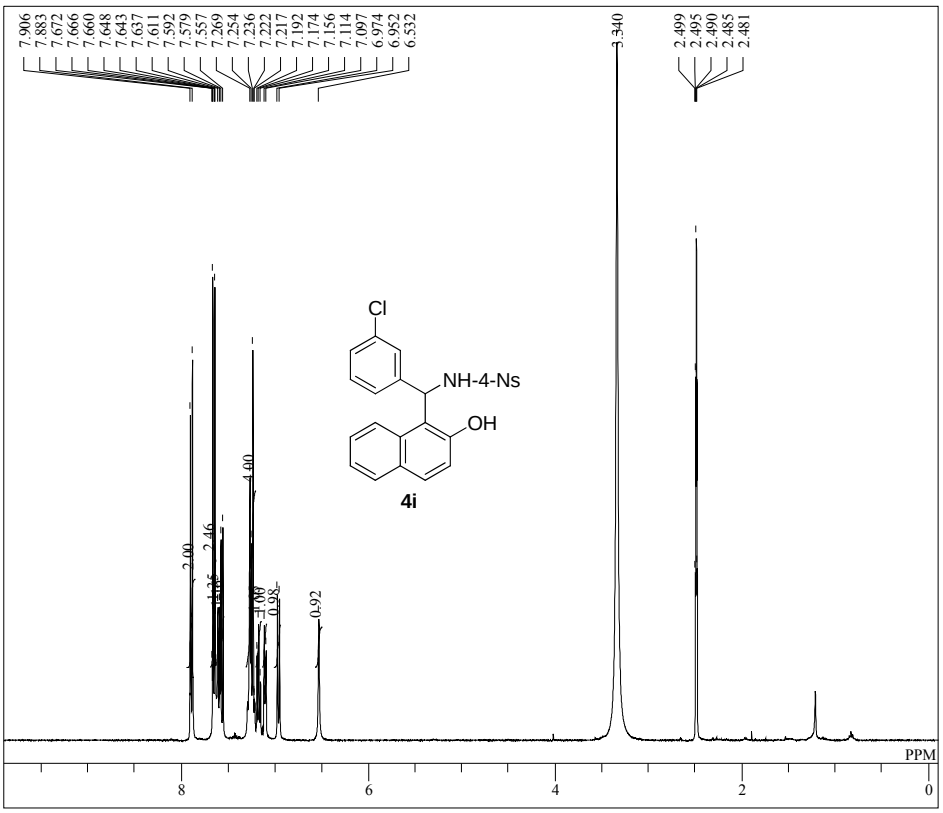

```
DFILE  8-58_Carbon-1-1.
COMNT  single pulse deco
DATIM  2014-05-26 11:09:
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32767
FREQU      31407.04 Hz
SCANS           350
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.20 usec
IRNUC  1H
CTEMP          19.4 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            50
```



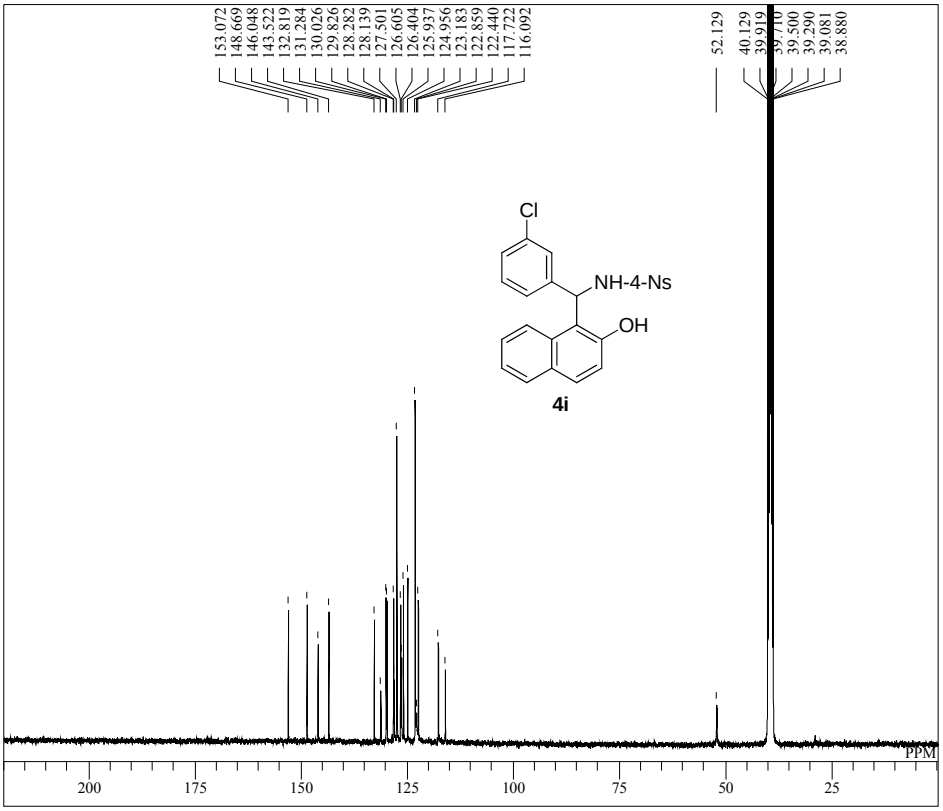
DFILE ba1001-dmso-4th_Proton-1-3.
COMNT single_pulse
DATIM 2014-03-04 10:33:37
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13120
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.10 Hz
RGAIN 44



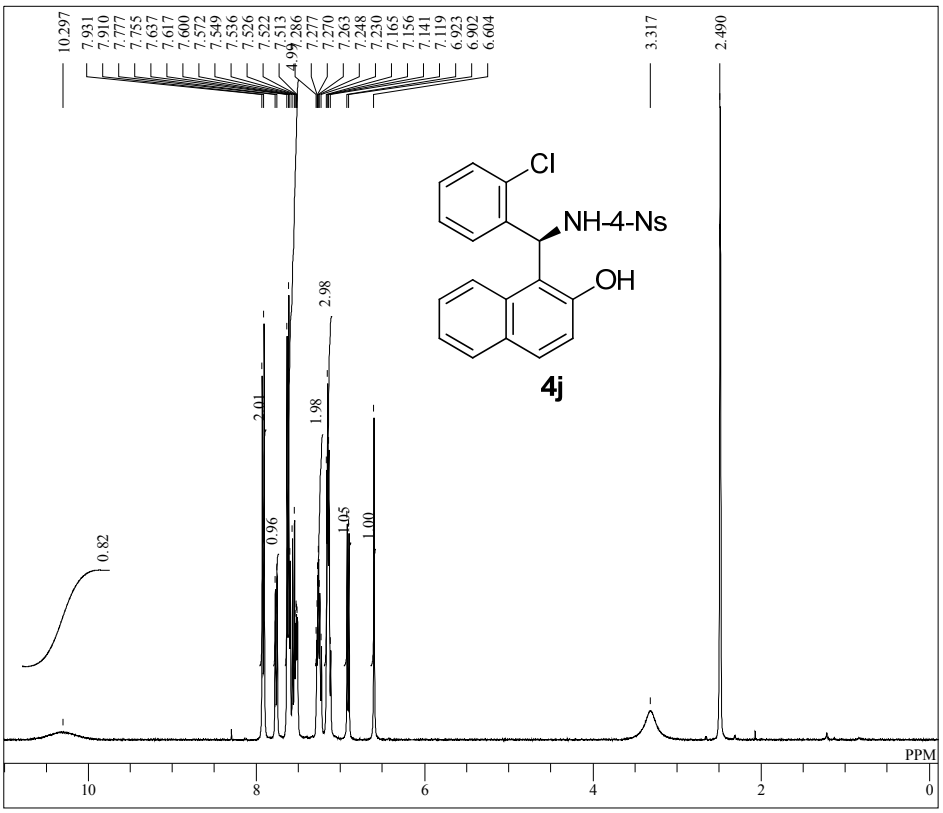
DFILE ba-1001-6th_Carbon-1-3.als
COMNT single pulse decoupled gated NOE
DATIM 2014-03-04 22:19:43
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26224
FREQU 25125.63 Hz
SCANS 13824
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.20 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT DMSO
EXREF 39.50 ppm
BF 0.10 Hz
RGAIN 60



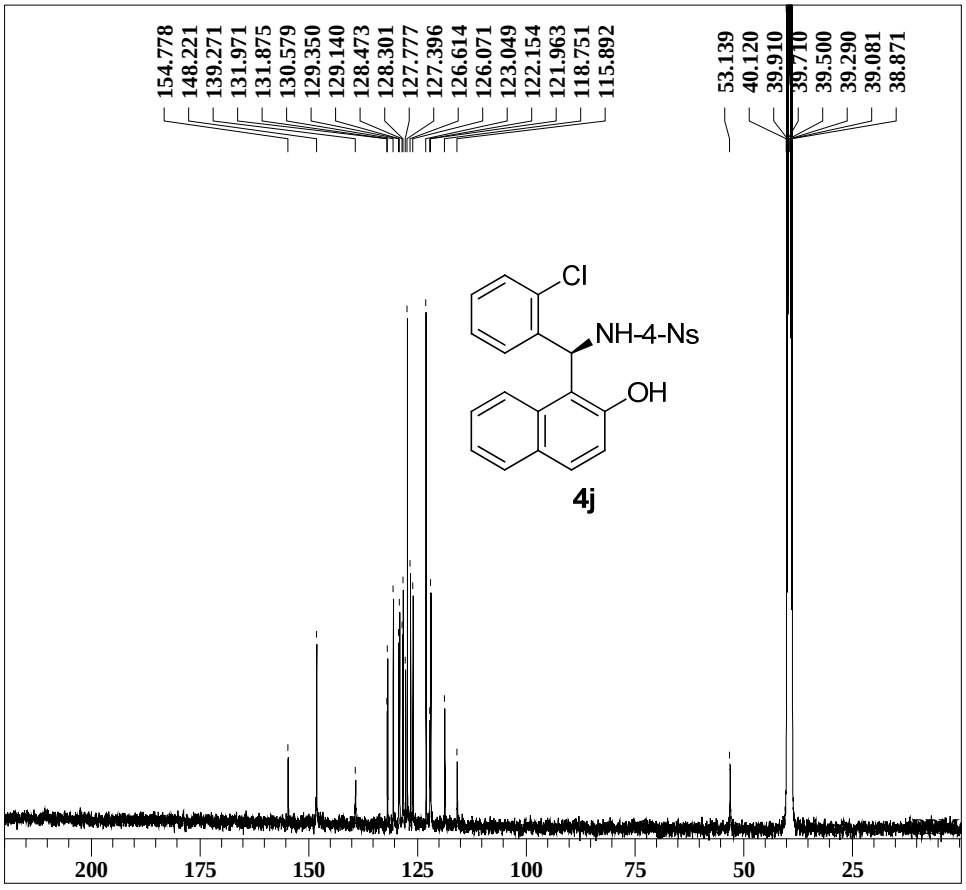
DFILE sh5104-3-cl-dmso-for-carbon_Proton
COMNT single_pulse
DATIM 2014-03-26 20:18:41
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13120
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.10 Hz
RGAIN 42



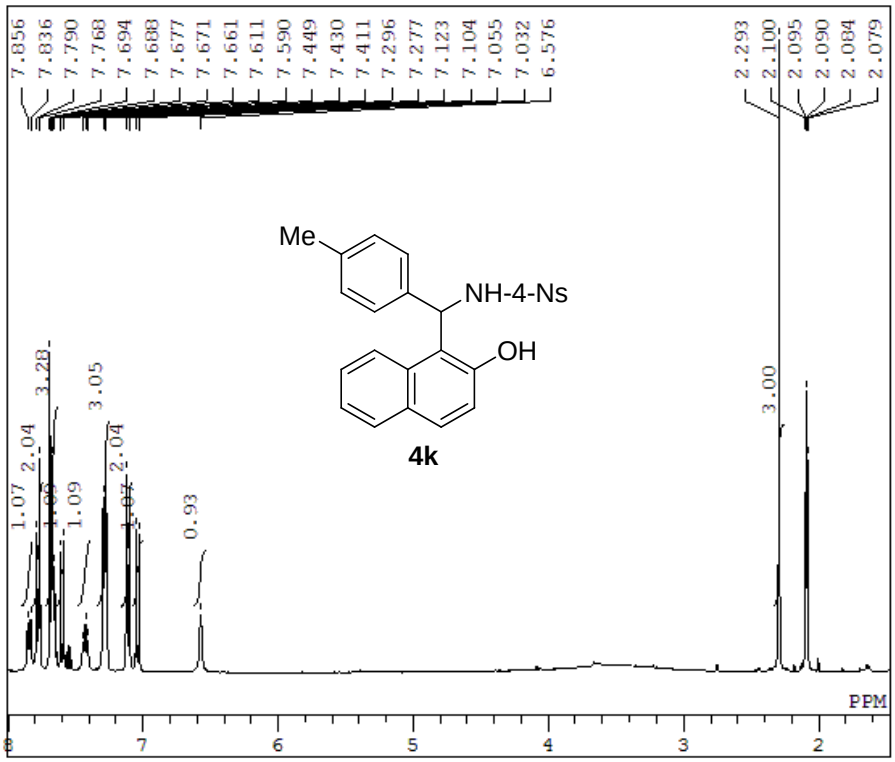
DFILE sh5104-3-cl-dmso-for-carbon_Carbon
COMNT single pulse decoupled gated NOE
DATIM 2014-03-26 20:21:38
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26224
FREQU 25125.63 Hz
SCANS 15360
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.20 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT DMSO
EXREF 39.50 ppm
BF 0.10 Hz
RGAIN 60



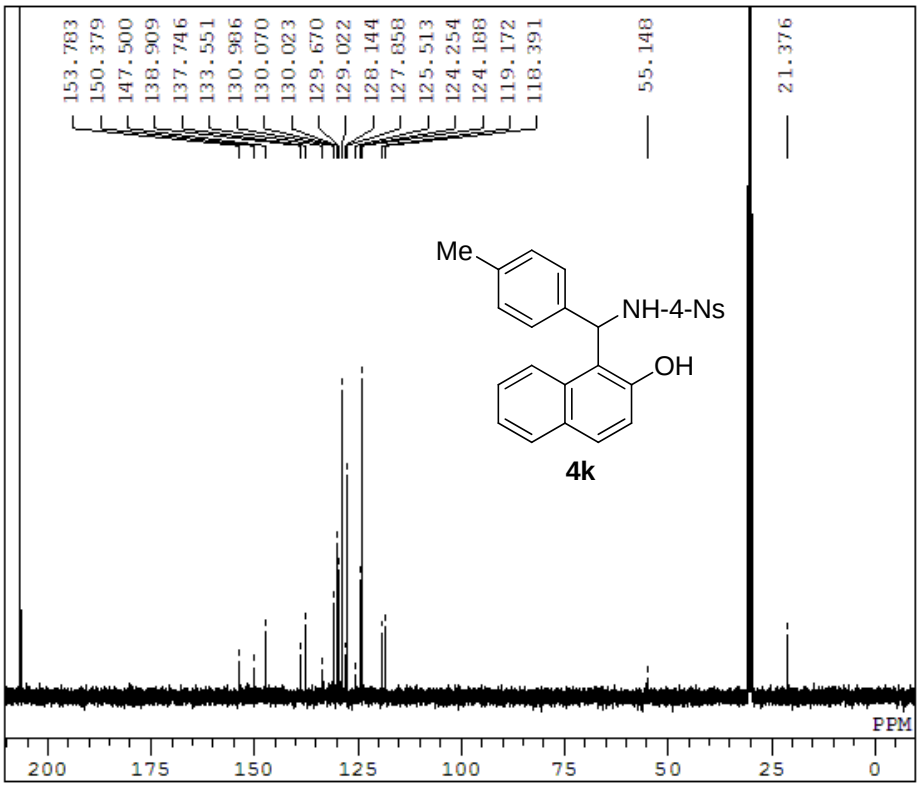
DFILE sh5127-3rd-dmso_Proton-1-3.jdf
COMNT single_pulse
DATIM 2014-04-19 18:36:44
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 24.8 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.10 Hz
RGAIN 44



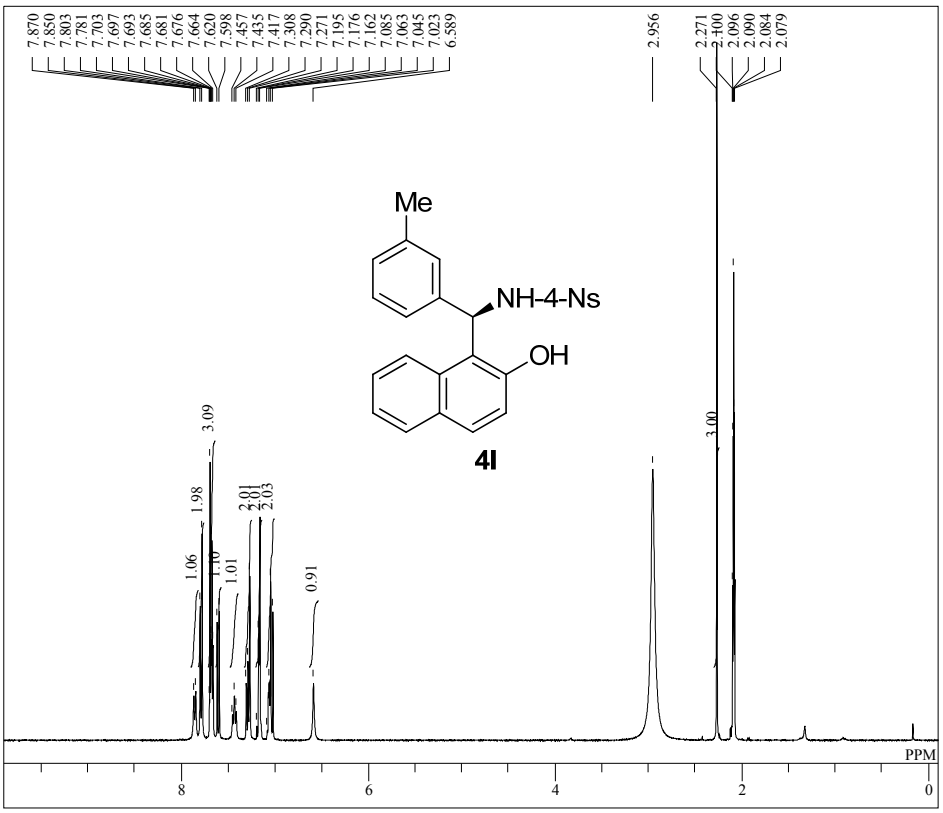
DFILE **sh5127-for_carbon_**
COMNT **single pulse decoupl**
DATIM **2014-04-23 22:14:01**
OBNUC **13C**
EXMOD **carbon.jxp**
OBFRQ **100.53 MHz**
OBSET **5.35 KHz**
OBFIN **5.86 Hz**
POINT **32780**
FREQU **31407.04 Hz**
SCANS **13312**
ACQTM **1.0433 sec**
PD **2.0000 sec**
PW1 **3.20 usec**
IRNUC **1H**
CTEMP **23.6 c**
SLVNT **DMSO**
EXREF **39.50 ppm**
BF **0.10 Hz**
RGAIN **50**



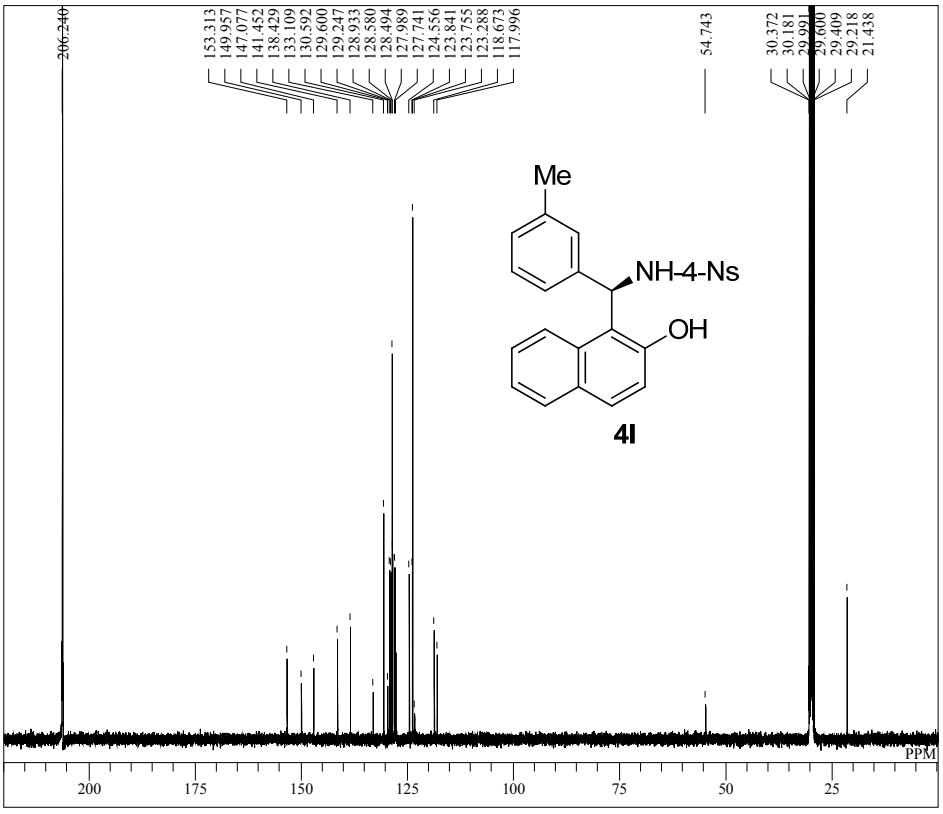

```
DFILE  8-141_Proton-1-1.
COMNT  single_pulse
DATIM  2014-04-19 18:00:
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16384
FREQU       7503.00 Hz
SCANS             8
ACQTM        2.1837 sec
PD           5.0000 sec
PW1            6.05 usec
IRNUC  1H
CTEMP          24.9 c
SLVNT  ACETN
EXREF          2.09 ppm
BF             0.12 Hz
RGAIN            36
```



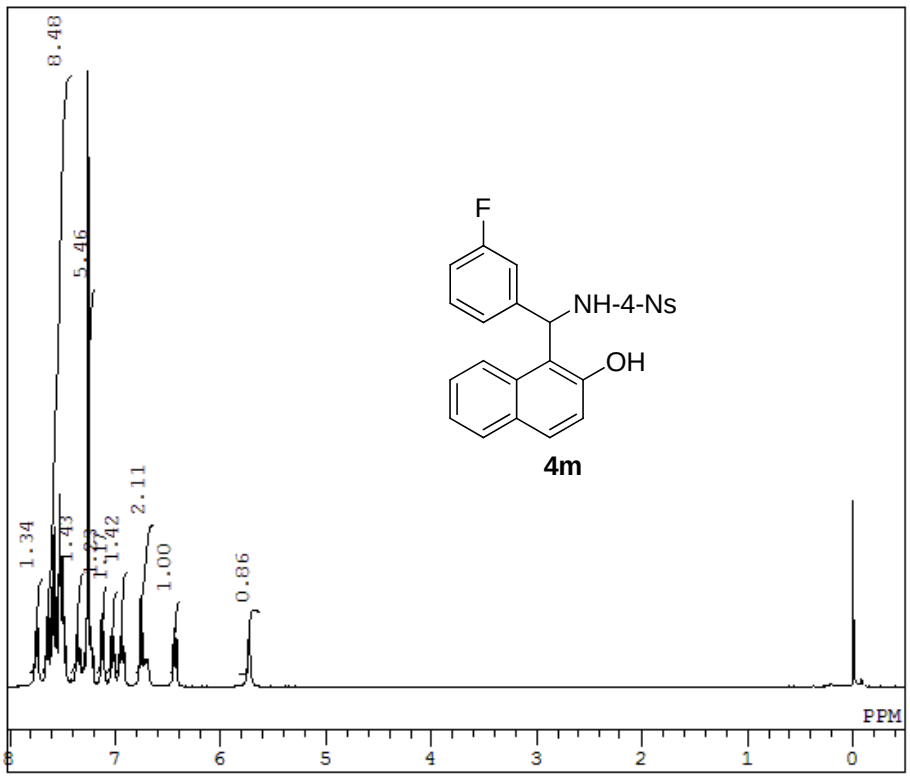

```
DFILE  8-141_Carbon-1-1.
COMNT  single pulse decc
DATIM  2014-04-19 18:02:
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32767
FREQU       31407.04 Hz
SCANS            512
ACQTM        1.0433 sec
PD           2.0000 sec
PW1            3.20 usec
IRNUC  1H
CTEMP          25.2 c
SLVNT  ACETN
EXREF        206.70 ppm
BF             0.12 Hz
RGAIN            60
```



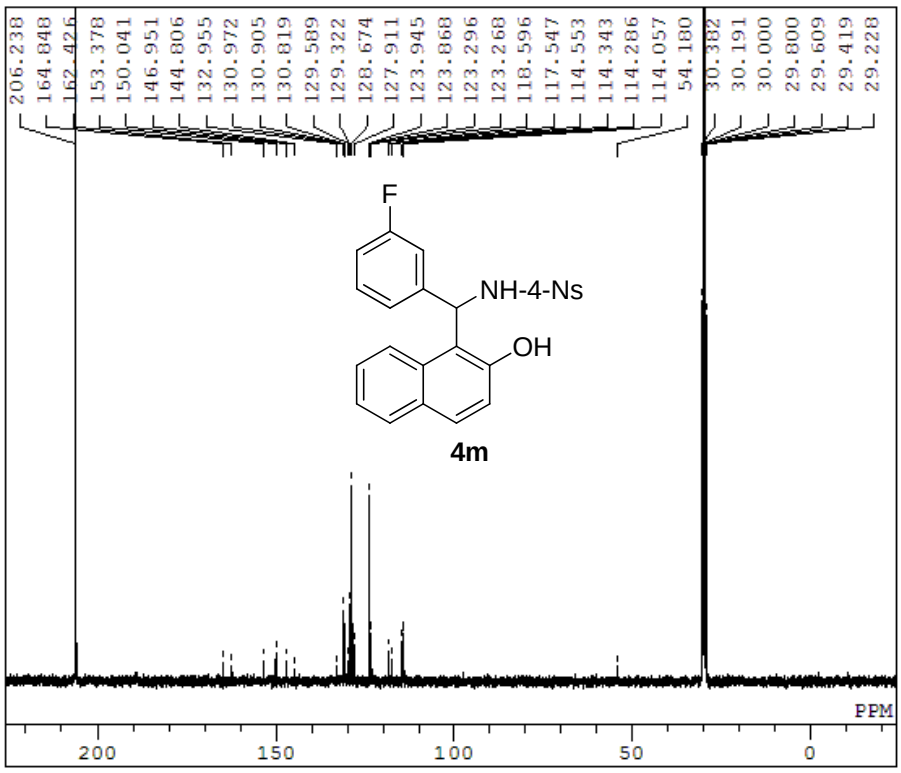
DFILE ba1008-acetone_Proton-2-3.als
COMNT single_pulse
DATIM 2014-04-22 22:34:45
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13120
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 24.2 c
SLVNT ACETN
EXREF 2.09 ppm
BF 0.10 Hz
RGAIN 40



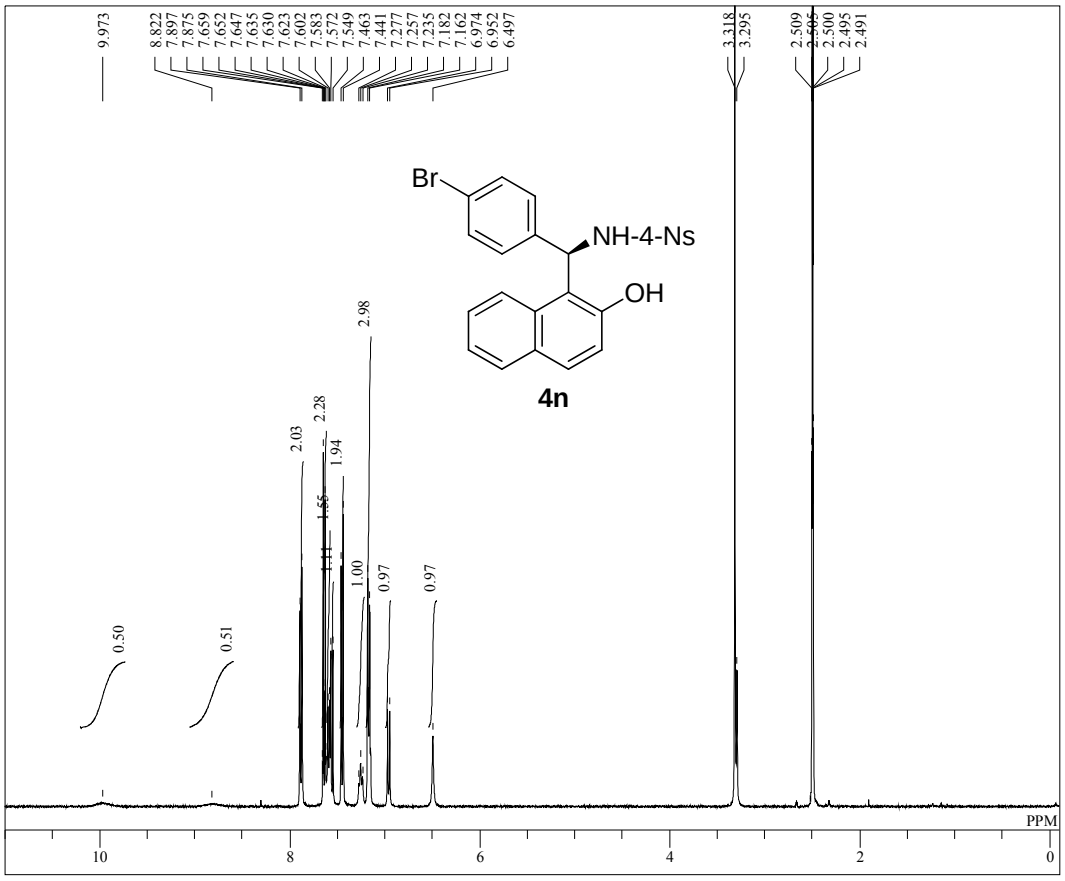
DFILE ba1008-acetone_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2014-04-22 22:36:39
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 13312
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.20 usec
IRNUC 1H
CTEMP 23.6 c
SLVNT ACETN
EXREF 29.80 ppm
BF 0.10 Hz
RGAIN 50



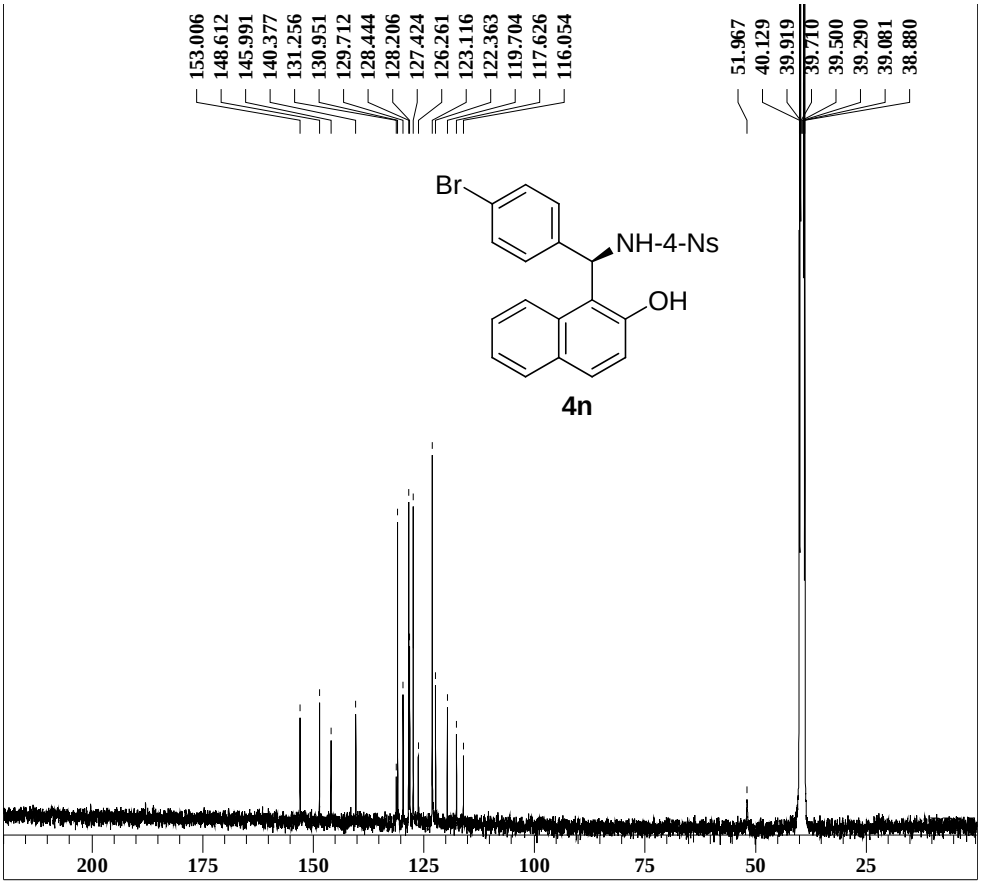

```
DFILE  3-F_Proton-2-1.j
COMNT  single_pulse
DATIM  2014-01-15 22:15
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16384
FREQU       7503.00 Hz
SCANS            32
ACQTM        2.1837 sec
PD           5.0000 sec
PW1            6.05 use
IRNUC  1H
CTEMP          25.0 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             1.20 Hz
RGAIN            58
```



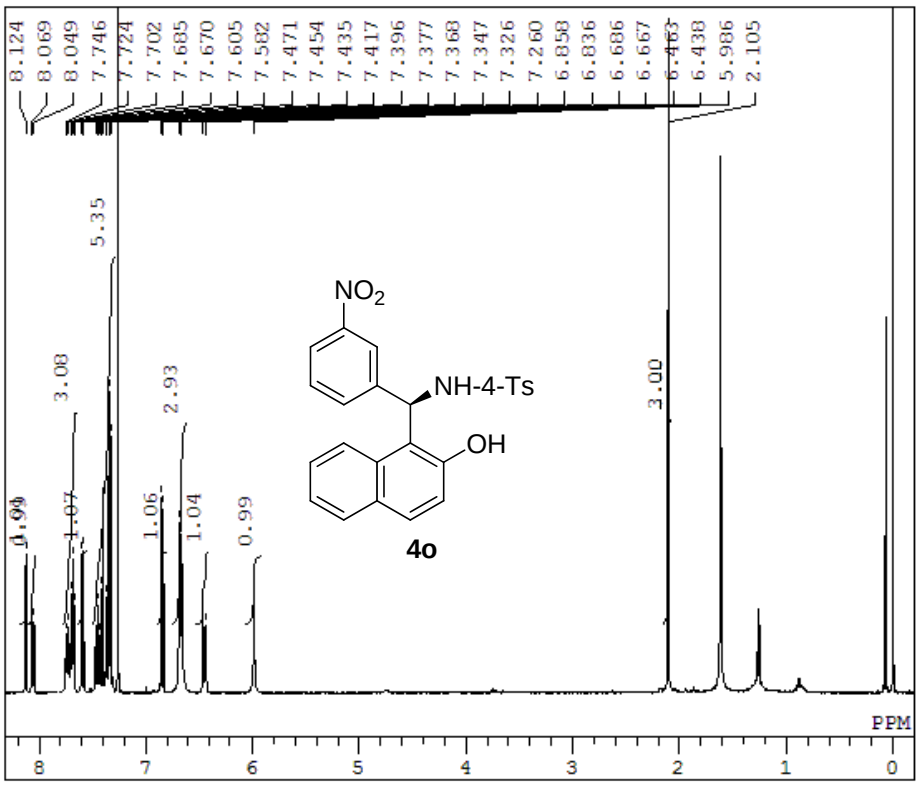

```
DFILE  8-121-3-F_Carbon
COMNT  single pulse dec
DATIM  2014-02-06 14:32
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32767
FREQU      31407.04 Hz
SCANS            512
ACQTM        1.0433 sec
PD           2.0000 sec
PW1            3.20 use
IRNUC  1H
CTEMP          21.0 c
SLVNT  ACETN
EXREF          29.80 ppm
BF             1.20 Hz
RGAIN            50
```



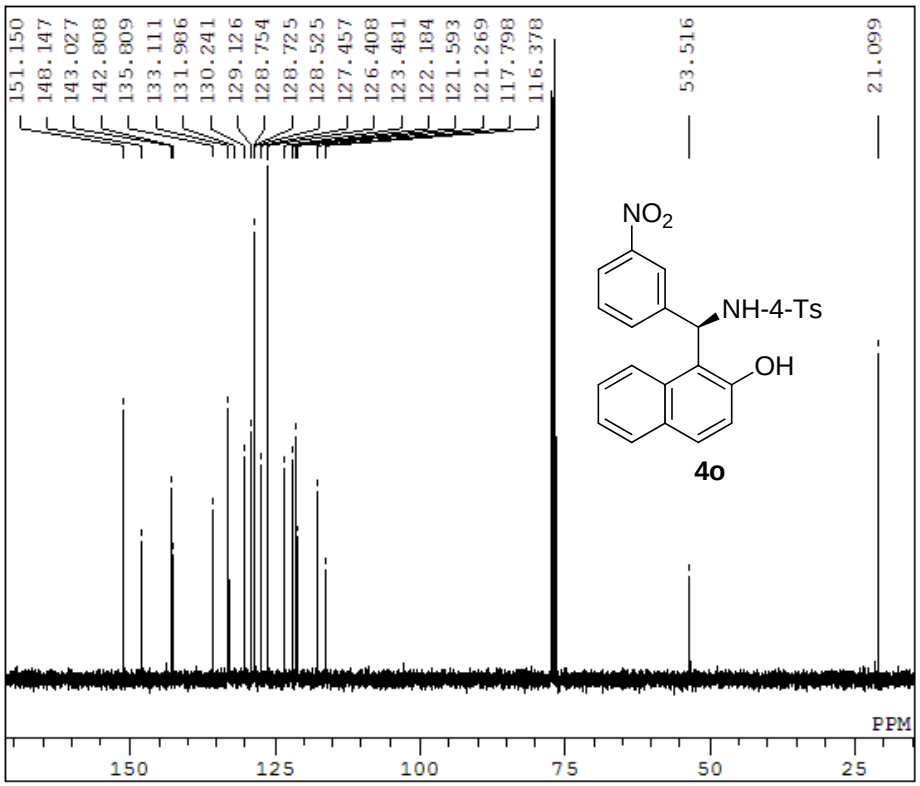
DFILE ba1002-dmso-1st_Proto
COMNT single_pulse
DATIM 2014-03-24 17:10:54
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13120
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT DMSO
EXREF 2.50 ppm
BF 0.10 Hz
RGAIN 54



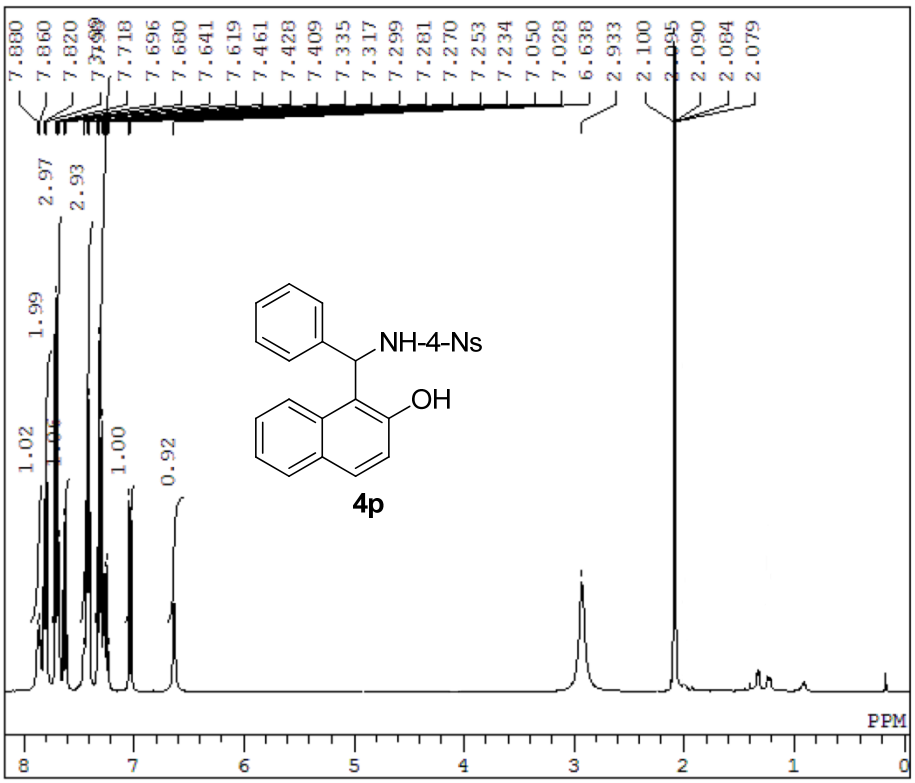
DFILE ba1002-for-carbon_C
COMNT single pulse decouple
DATIM 2014-03-25 22:24:13
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32780
FREQU 31407.04 Hz
SCANS 13312
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.20 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT DMSO
EXREF 39.50 ppm
BF 0.10 Hz
RGAIN 60



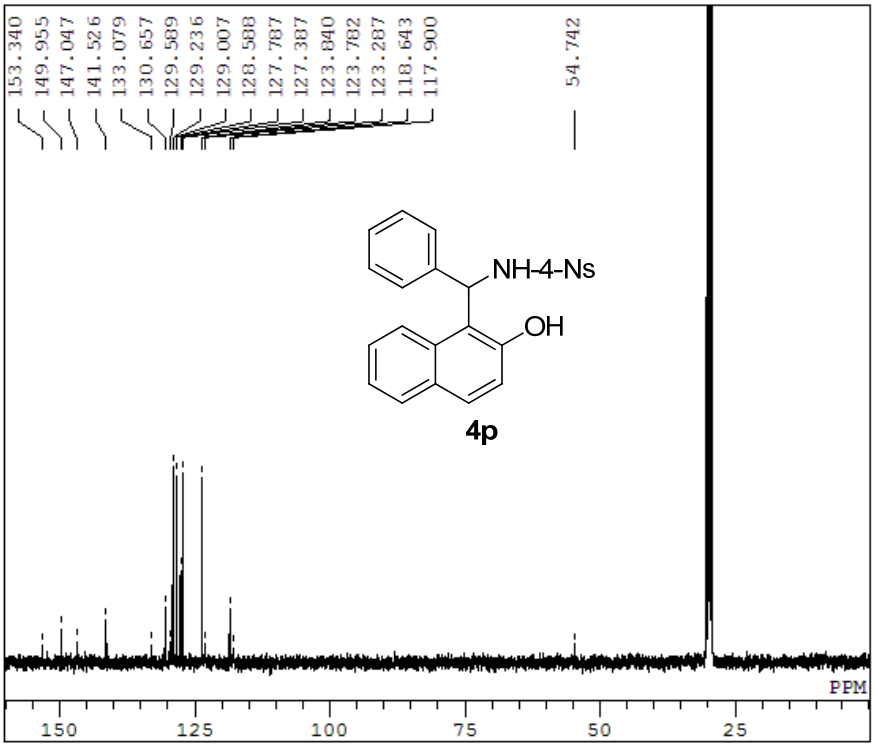

```
DFILE  8-100.als
COMNT  single_pulse
DATIM  2013-06-25 15:28:
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         13107
FREQU       6002.40 Hz
SCANS             8
ACQTM        2.1837 sec
PD           5.0000 sec
PW1            6.05 usec
IRNUC  1H
CTEMP          22.1 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            50
```



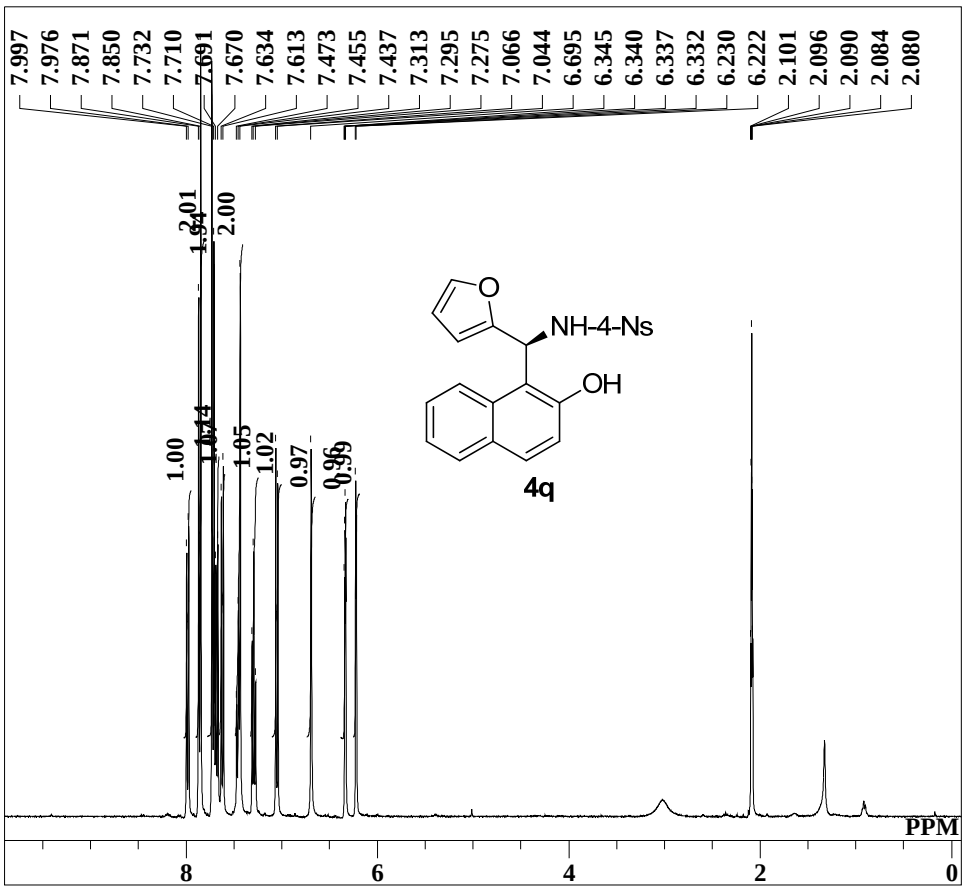

```
DFILE  8-166-1_Carbon-1-
COMNT  single pulse decc
DATIM  2014-06-13 16:23:
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32767
FREQU      31407.04 Hz
SCANS           200
ACQTM        1.0433 sec
PD           2.0000 sec
PW1            3.20 usec
IRNUC  1H
CTEMP          20.7 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            50
```



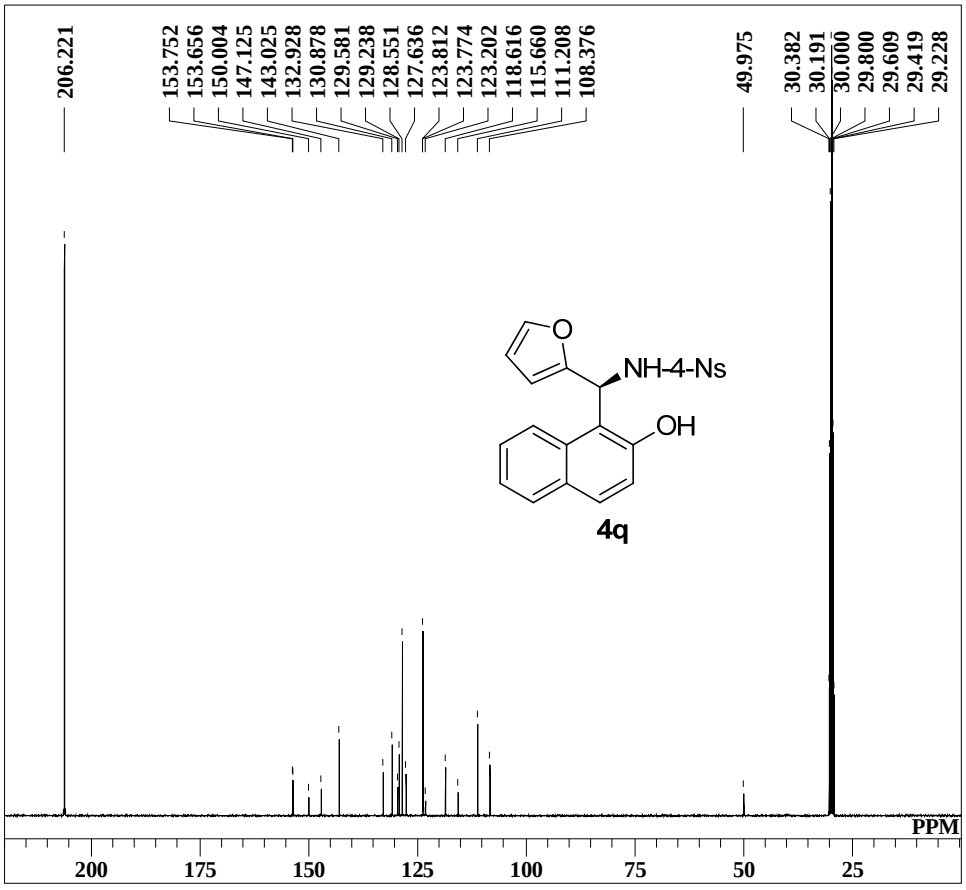

```
DFILE  Ph_Proton-1-1.jdi
COMNT  single_pulse
DATIM  2014-03-05 19:05:
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16384
FREQU       7503.00 Hz
SCANS            16
ACQTM        2.1837 sec
PD           5.0000 sec
PW1            6.05 usec
IRNUC  1H
CTEMP          21.7 c
SLVNT  ACETN
EXREF          2.09 ppm
BF             1.20 Hz
RGAIN            46
```



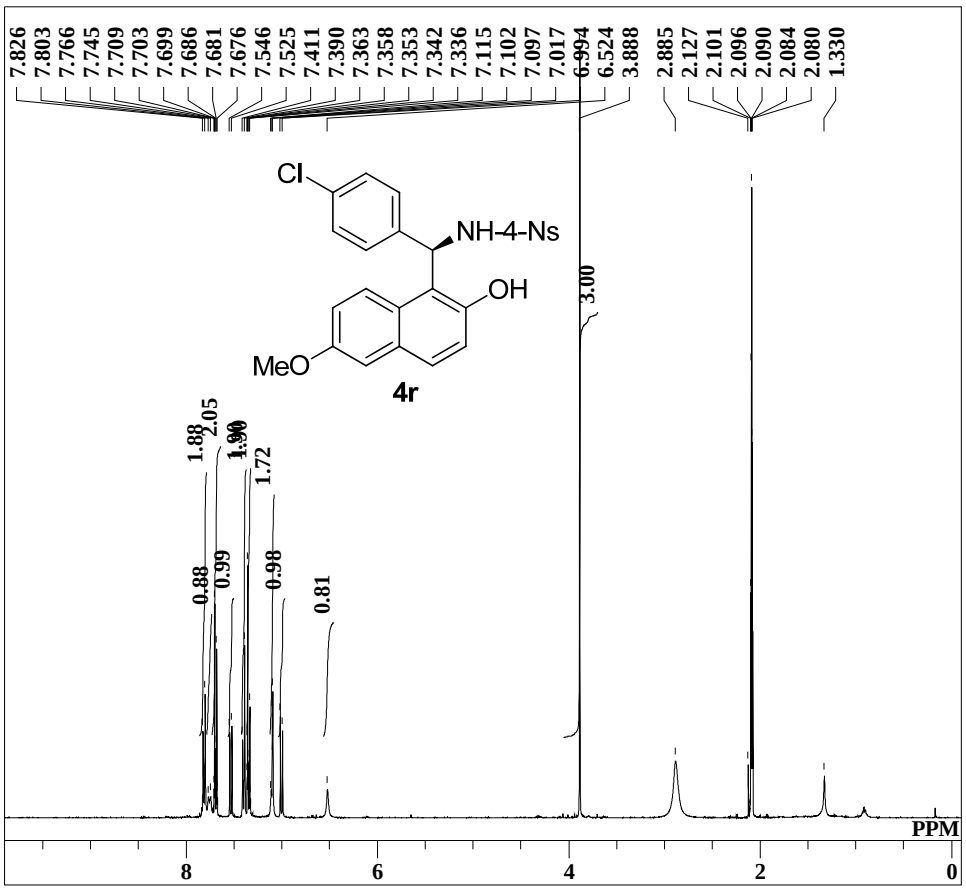

```
DFILE  8-127_Carbon-1-1.
COMNT  single pulse dec
DATIM  2014-03-14 11:56:
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32767
FREQU      31407.04 Hz
SCANS            512
ACQTM        1.0433 sec
PD           2.0000 sec
PW1            3.20 usec
IRNUC  1H
CTEMP          21.9 c
SLVNT  ACETN
EXREF          29.80 ppm
BF             1.20 Hz
RGAIN            60
```



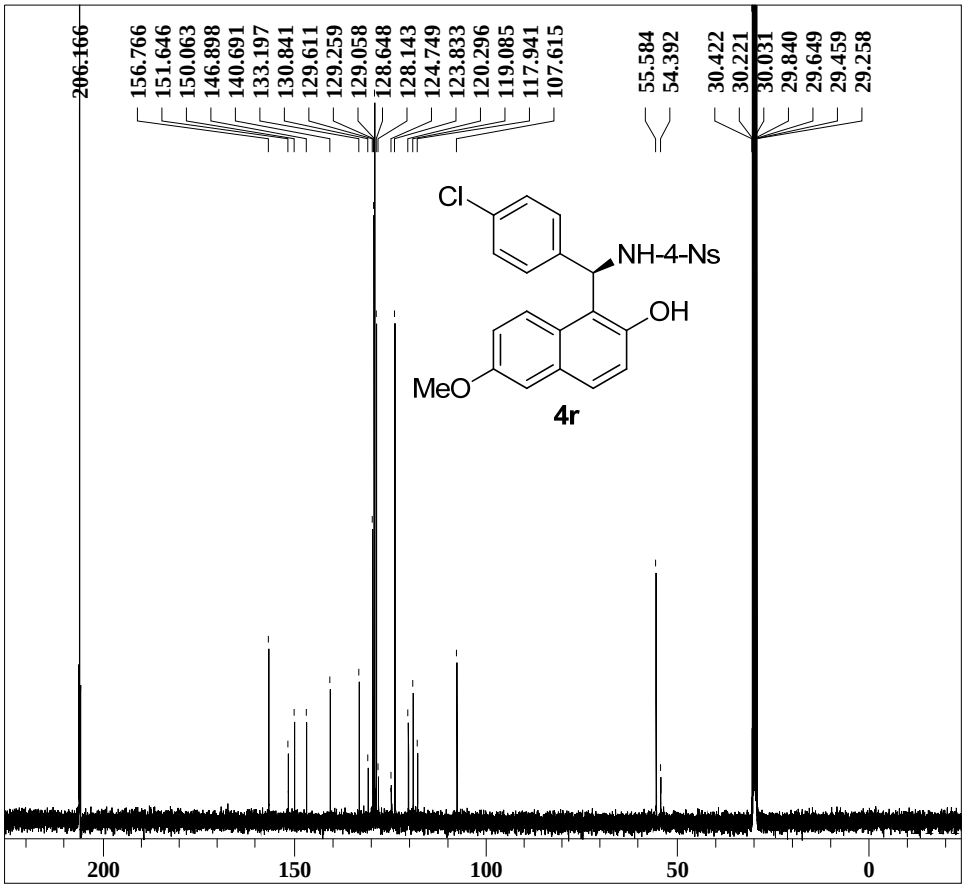
DFILE	ba1007-acetone
COMNT	single_pulse
DATIM	2014-04-14 21:5
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13120
FREQU	6002.40 Hz
SCANS	8
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	6.05 usec
IRNUC	1H
CTEMP	23.3 c
SLVNT	ACETN
EXREF	2.09 ppm
BF	0.10 Hz
RGAIN	40



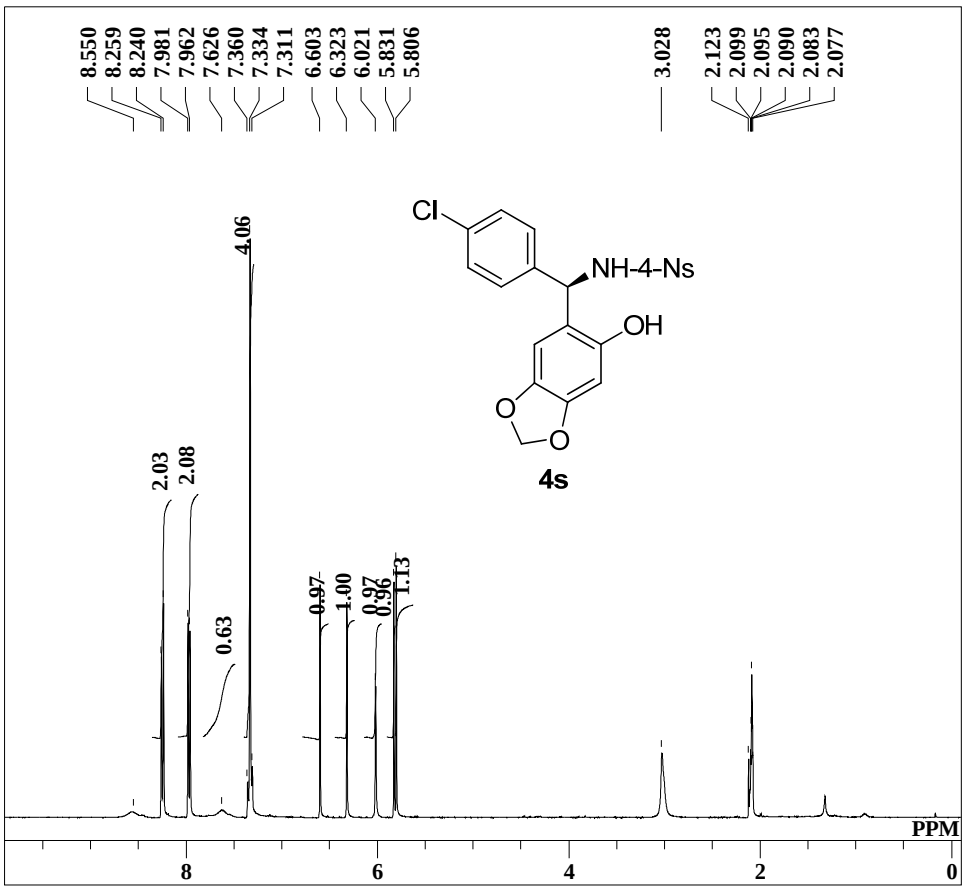
DFILE	ba1007-acetone3_Ca
COMNT	single pulse decoupl
DATIM	2014-04-14 21:57:51
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	13312
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	21.5 c
SLVNT	ACETN
EXREF	29.80 ppm
BF	0.10 Hz
RGAIN	50



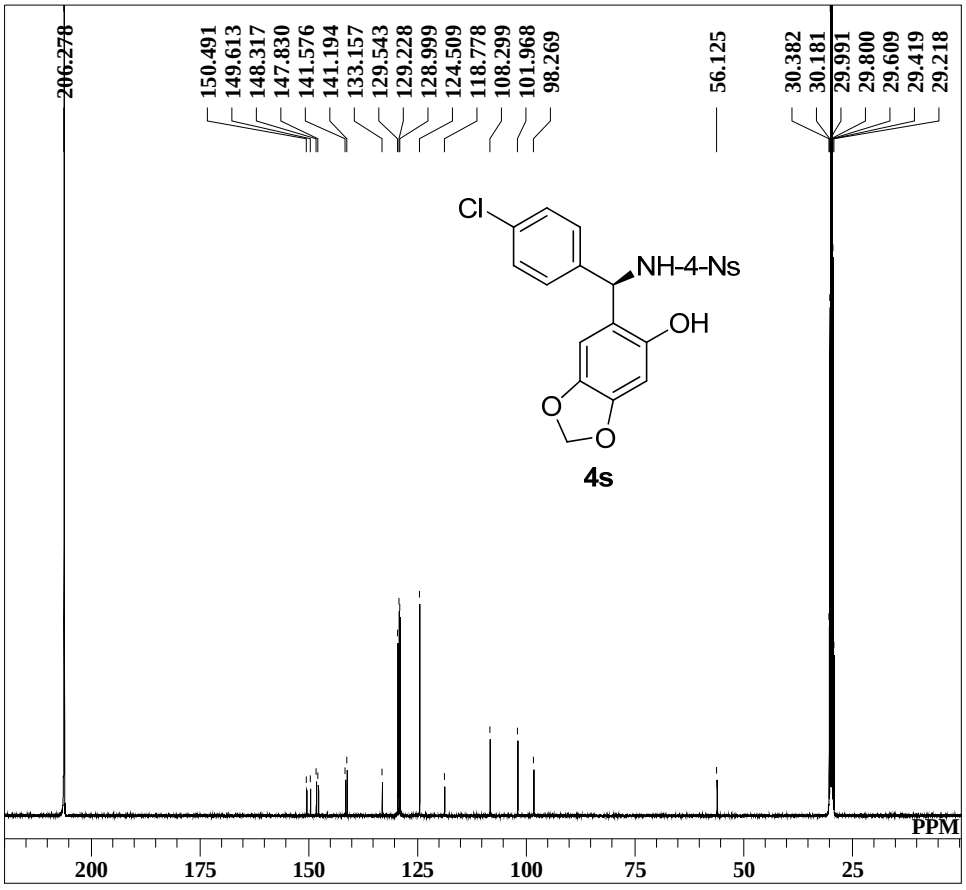
DFILE	ba1021_for-carbon_
COMNT	single_pulse
DATIM	2014-04-17 22:14:48
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13120
FREQU	6002.40 Hz
SCANS	8
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	6.05 usec
IRNUC	1H
CTEMP	25.8 c
SLVNT	ACETN
EXREF	2.09 ppm
BF	0.10 Hz
RGAIN	44



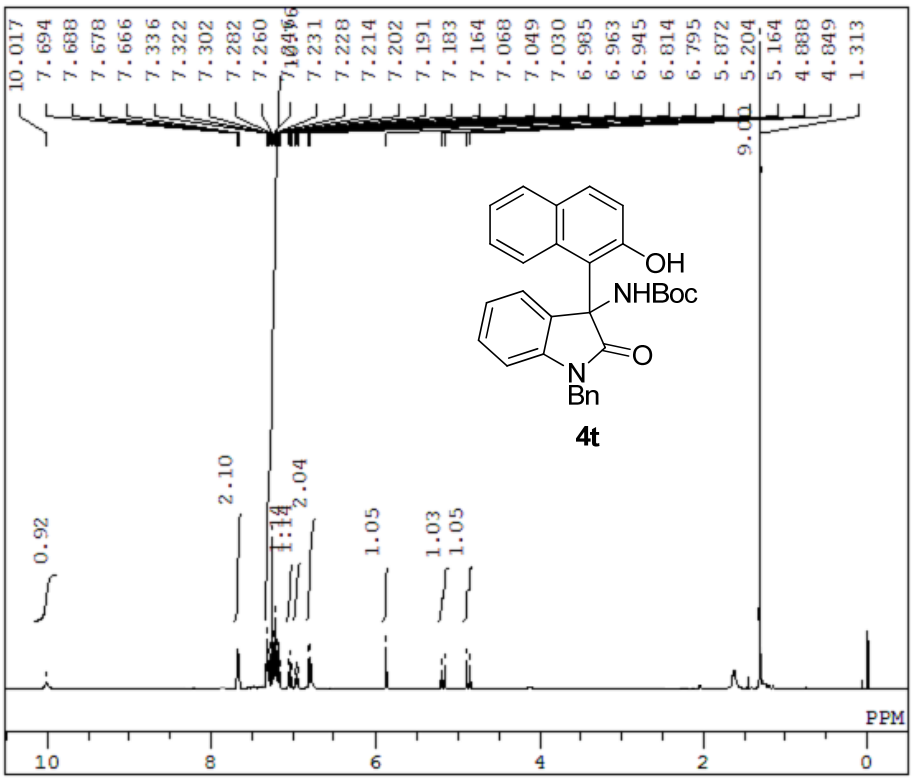
DFILE	ba1021_for-carbon_
COMNT	single pulse decoupl
DATIM	2014-04-17 22:17:02
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	13312
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	25.1 c
SLVNT	ACETN
EXREF	29.84 ppm
BF	0.10 Hz
RGAIN	50



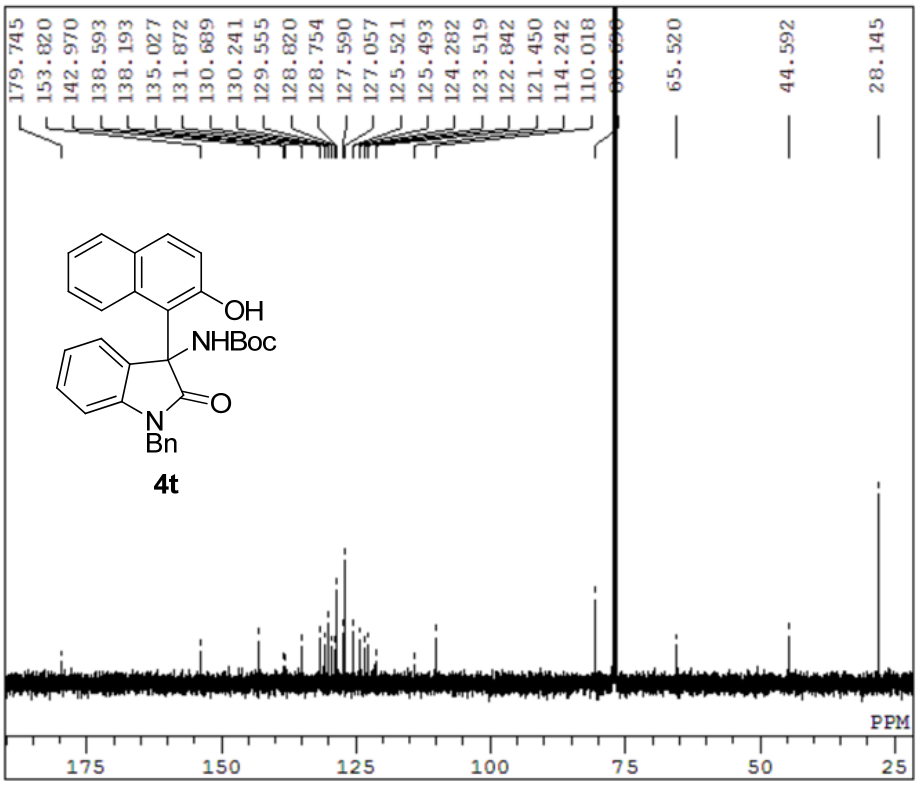
DFILE	ba1022-acetone_for_
COMNT	single_pulse
DATIM	2014-04-16 22:38:50
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13120
FREQU	6002.40 Hz
SCANS	8
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	6.05 usec
IRNUC	1H
CTEMP	24.3 c
SLVNT	ACETN
EXREF	2.09 ppm
BF	0.10 Hz
RGAIN	36



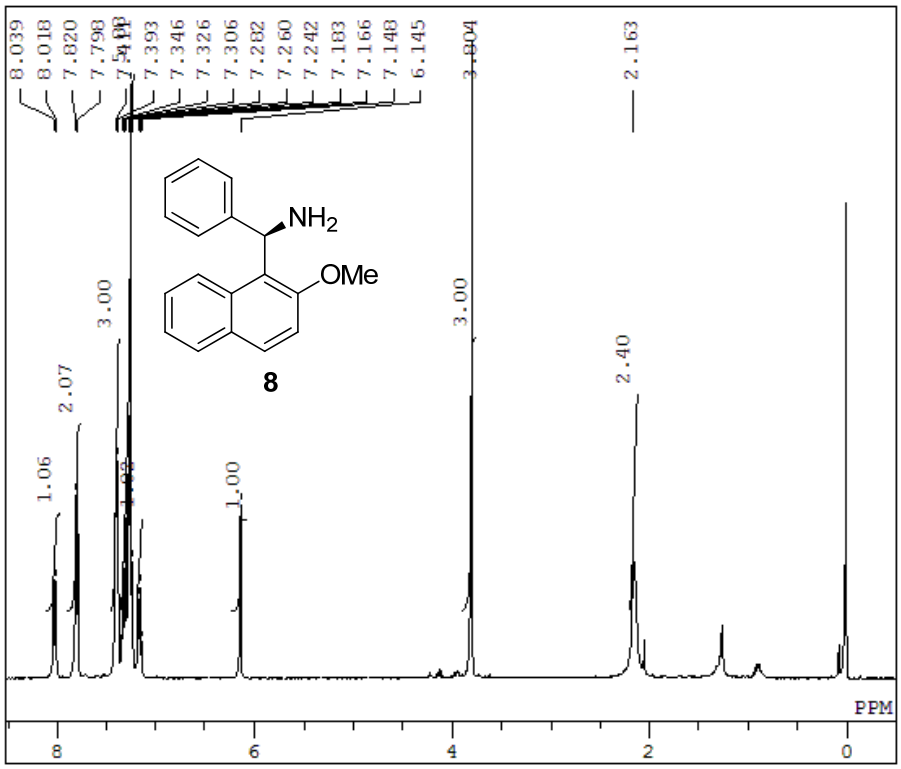
DFILE	ba1022-acetone_for_
COMNT	single pulse decoupl
DATIM	2014-04-16 22:43:27
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	12288
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	23.8 c
SLVNT	ACETN
EXREF	29.80 ppm
BF	0.10 Hz
RGAIN	50



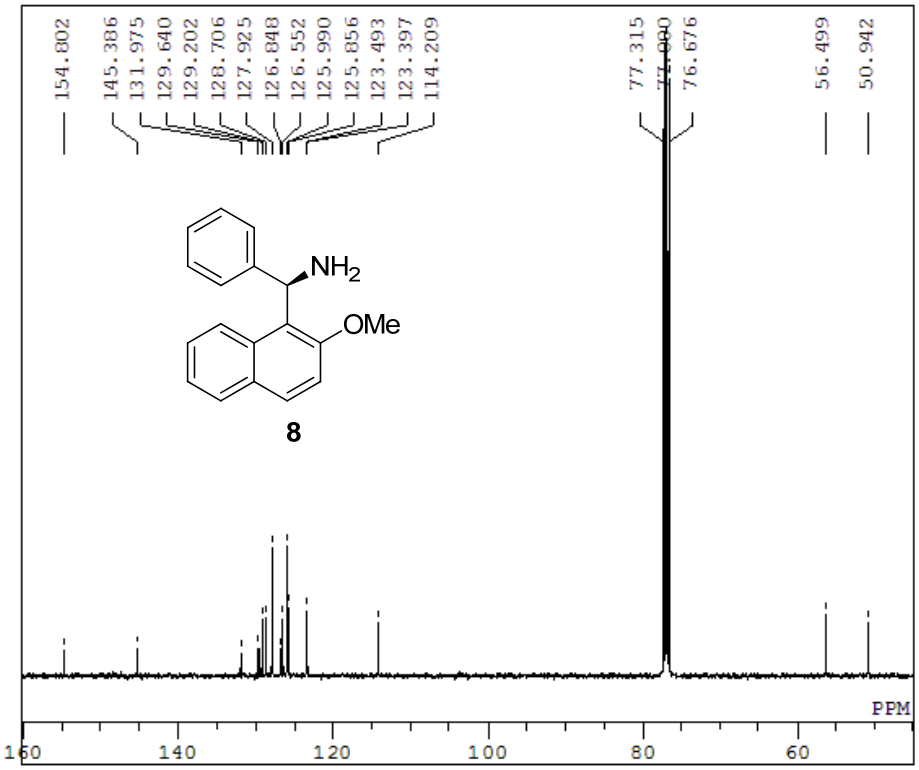

```
DFILE  8-158-A_Proton-1-
COMNT  single_pulse
DATIM  2014-05-27 15:11:
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16384
FREQU       7503.00 Hz
SCANS             8
ACQTM        2.1837 sec
PD           5.0000 sec
PW1            6.05 usec
IRNUC  1H
CTEMP         19.0 c
SLVNT  CDCL3
EXREF         7.26 ppm
BF            0.12 Hz
RGAIN           46
```




```
DFILE  8-158-A_Carbon-1-
COMNT  single_pulse_dec
DATIM  2014-05-27 15:14:
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32767
FREQU      31407.04 Hz
SCANS           400
ACQTM        1.0433 sec
PD           2.0000 sec
PW1            3.20 usec
IRNUC  1H
CTEMP         19.3 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF            0.12 Hz
RGAIN           60
```

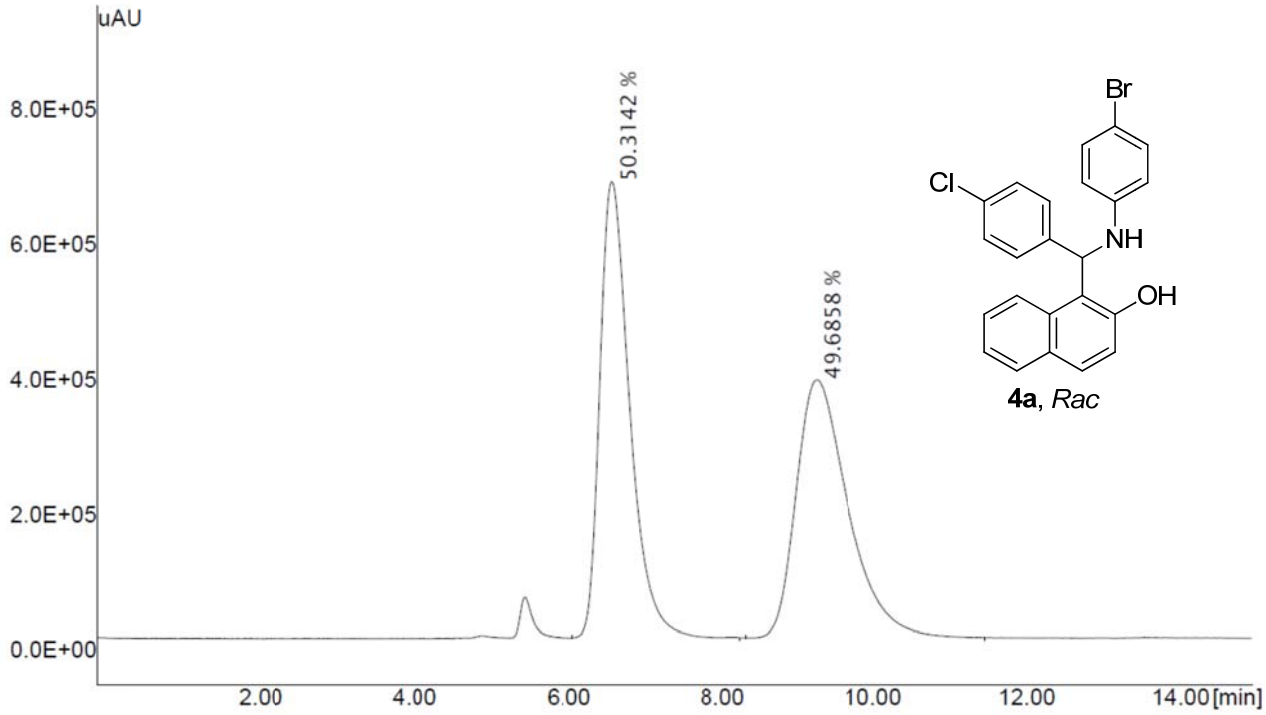



```
DFILE  sh5166-clomn_Prot
COMNT  single_pulse
DATIM  2014-06-14 15:56:
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16400
FREQU       7503.00 Hz
SCANS             8
ACQTM        2.1837 sec
PD           5.0000 sec
PW1            5.50 usec
IRNUC  1H
CTEMP         19.5 c
SLVNT  CDCL3
EXREF         7.26 ppm
BF            0.12 Hz
RGAIN           46
```



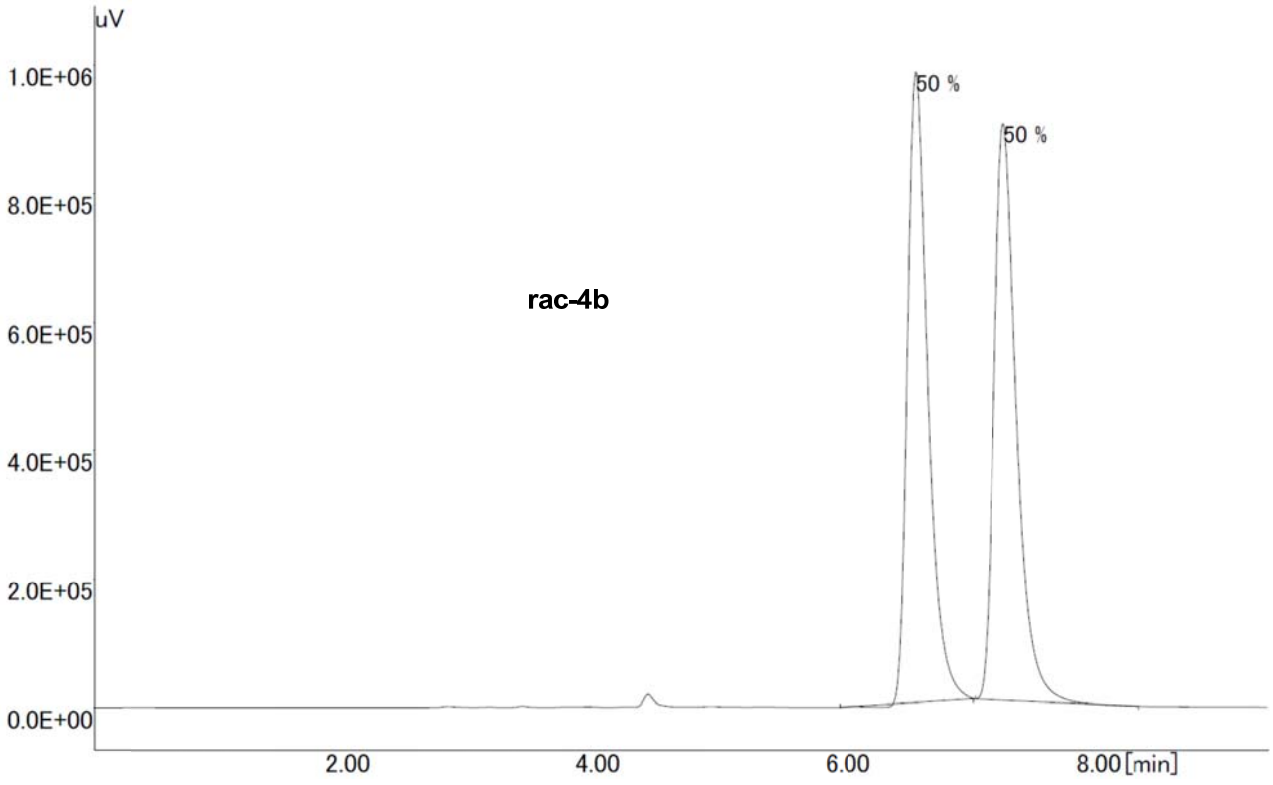

```
DFILE  sh5166-clomn-2_Ca
COMNT  single pulse deco
DATIM  2014-06-16 10:54:
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26224
FREQU      25125.63 Hz
SCANS           882
ACQTM        1.0433 sec
PD           2.0000 sec
PW1            3.20 usec
IRNUC  1H
CTEMP         20.9 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF            0.10 Hz
RGAIN           50
```

HPLC Chart

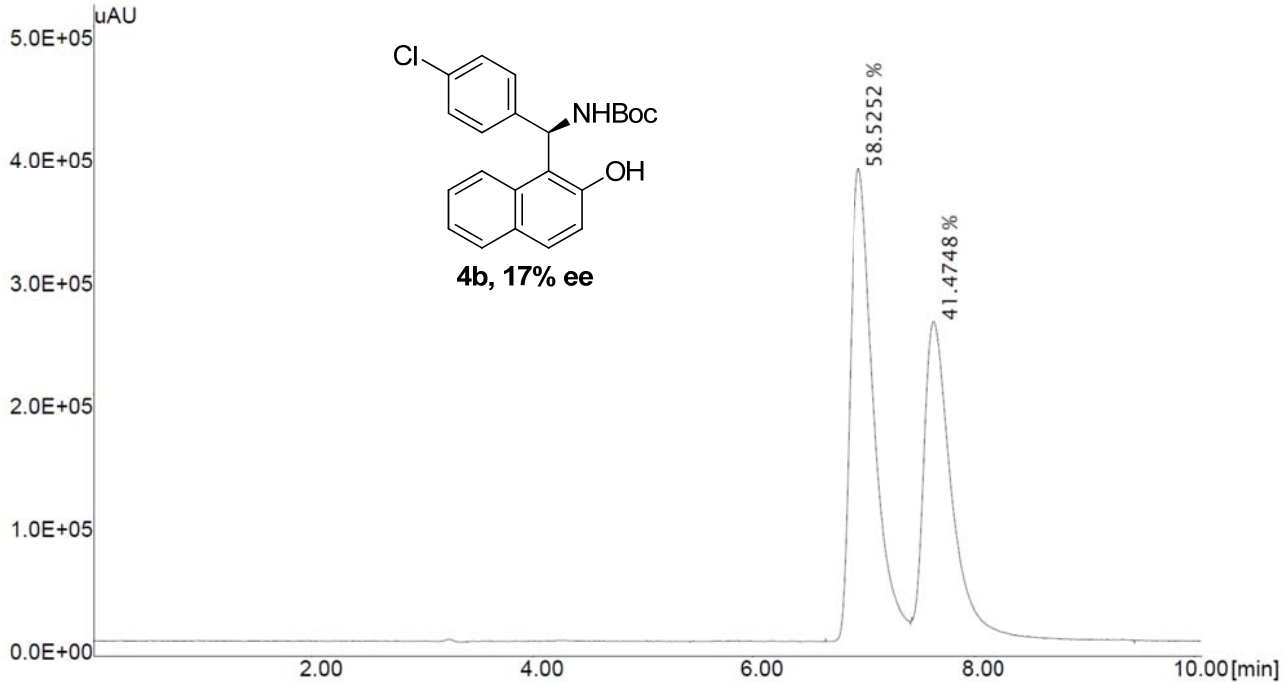


4a, *Rac*

#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		6.693	675953	18176759.071	50.31
2		9.347	381760	17949775.467	49.69

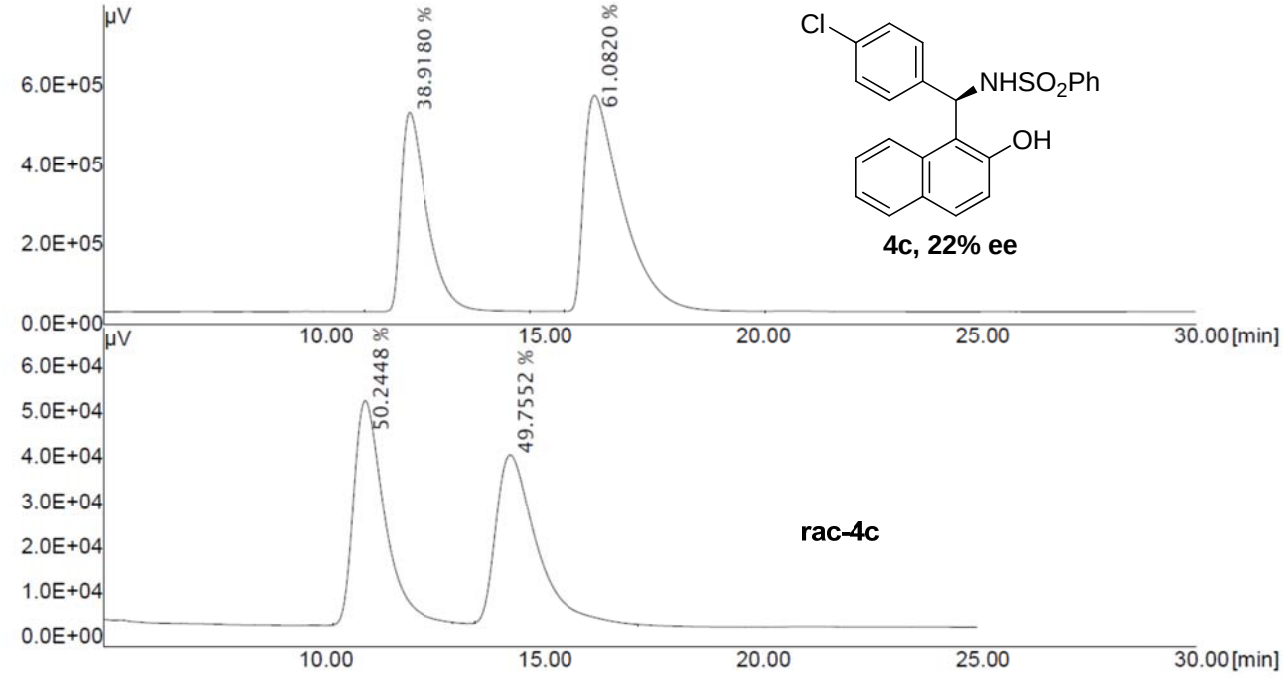


rac-4b



4b, 17% ee

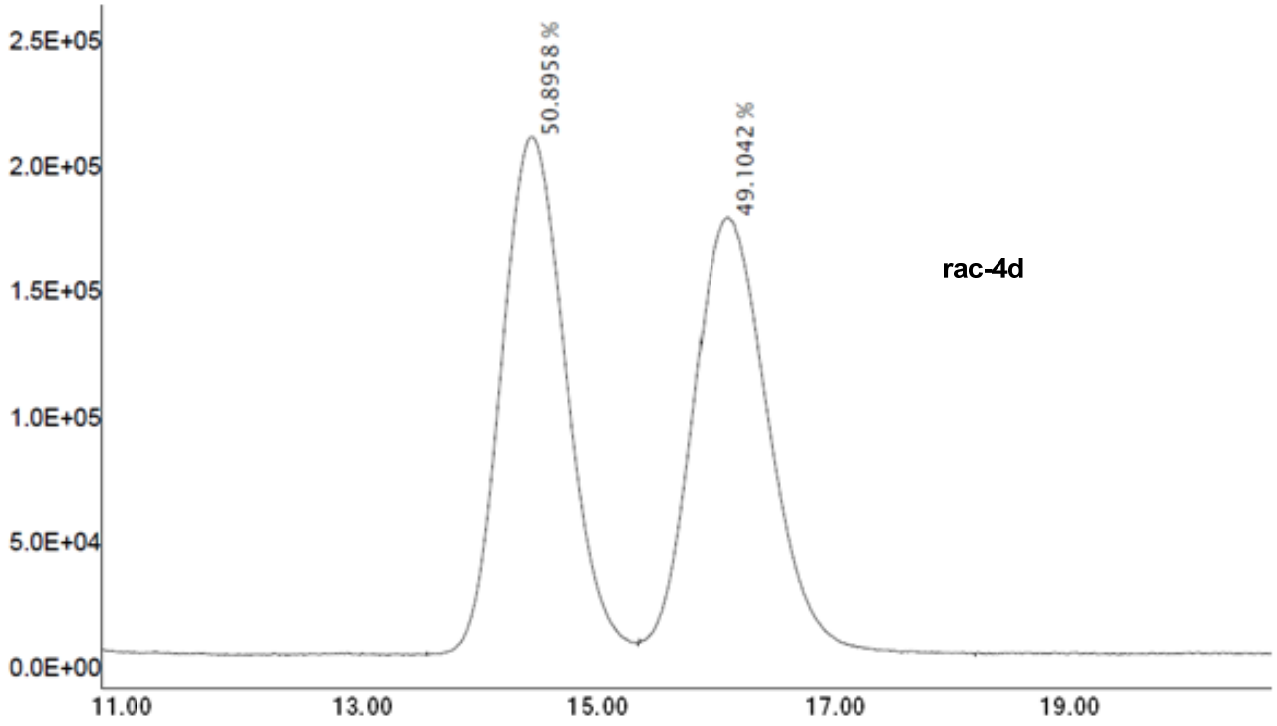
#	Name	RT	Area[uAU.Sec]	%Area
1		6.960	5357722.328	58.53
2		7.640	3796832.062	41.47

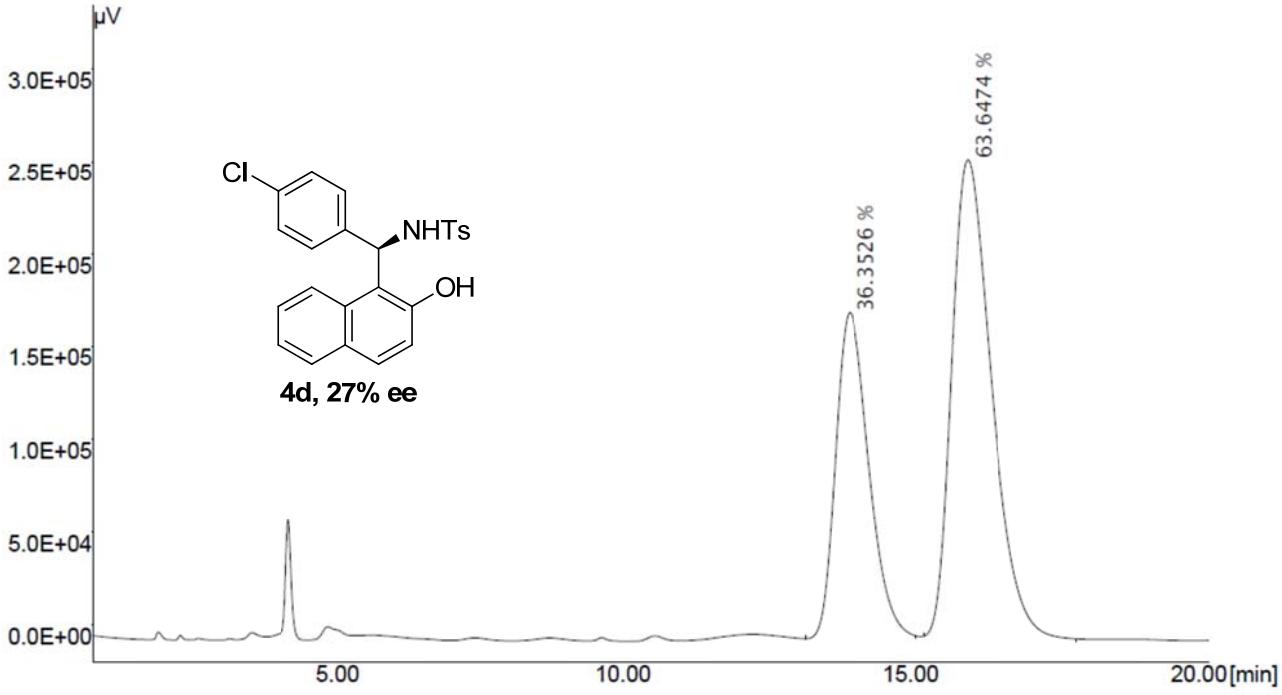


4c, 22% ee

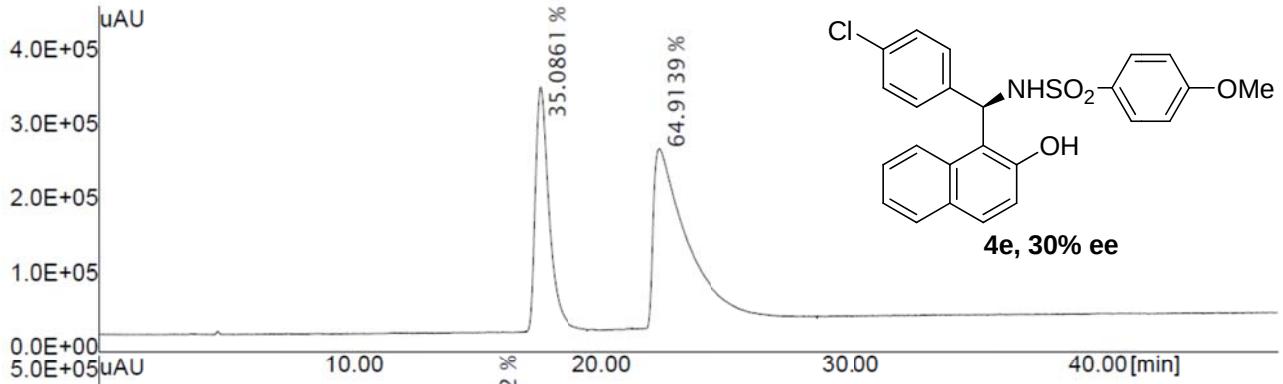
rac-4c

#	Name	RT	Area[μV.Sec]	%Area
1		12.033	21077599.000	38.92
2		16.267	33081388.502	61.08

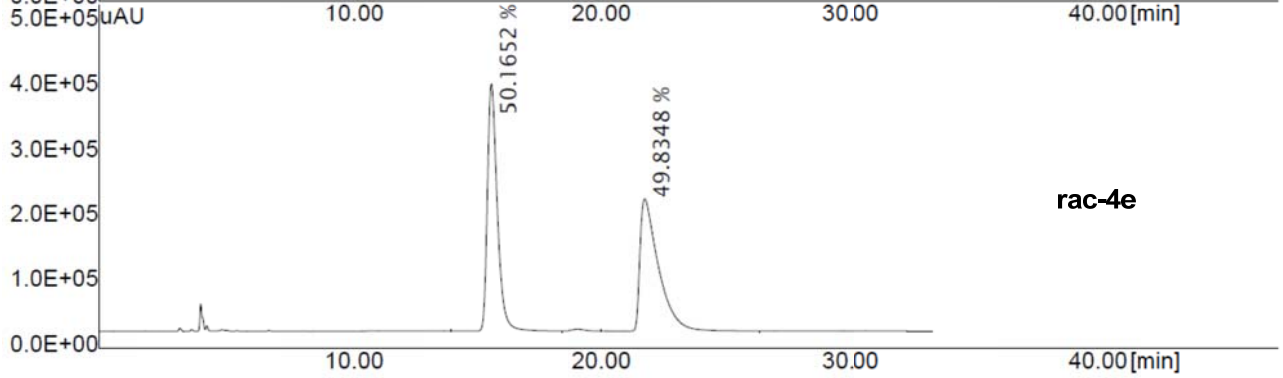




#	Name	RT	Area[μV.Sec]	%Area
1		14.058	7003414.437	36.35
2		16.092	12261830.500	63.65

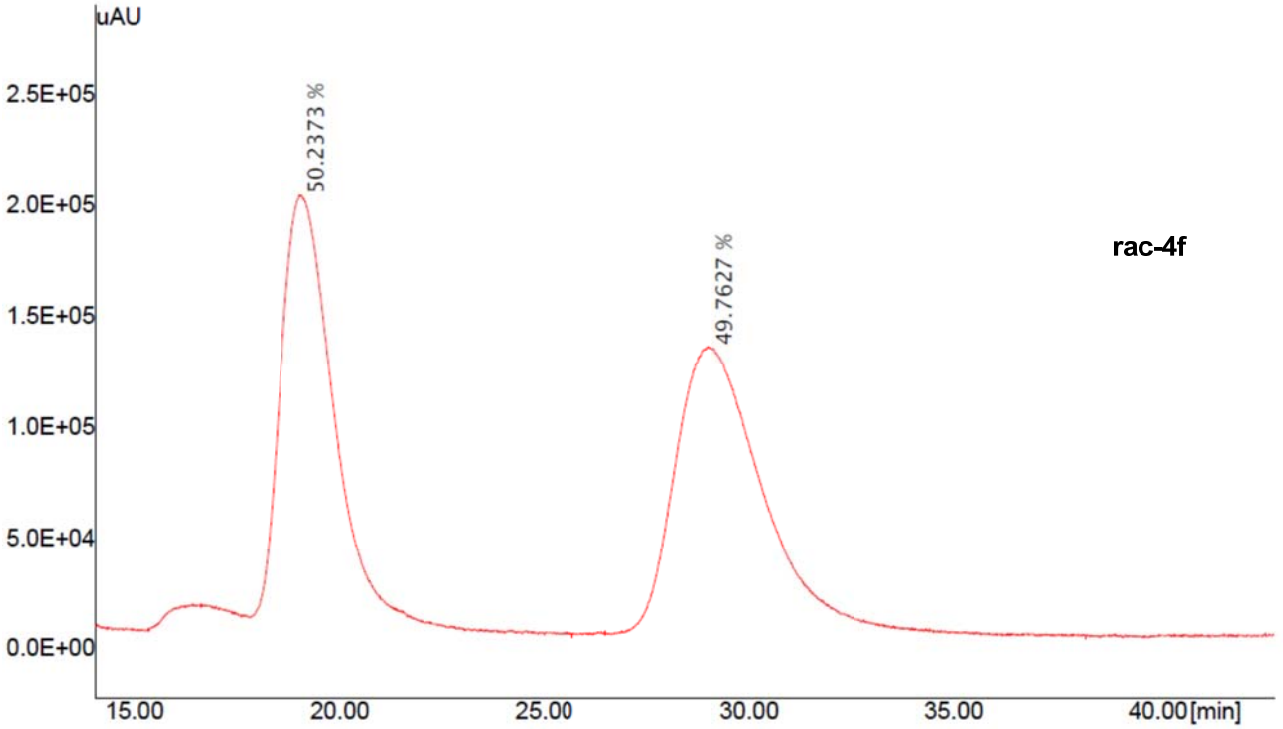


4e, 30% ee

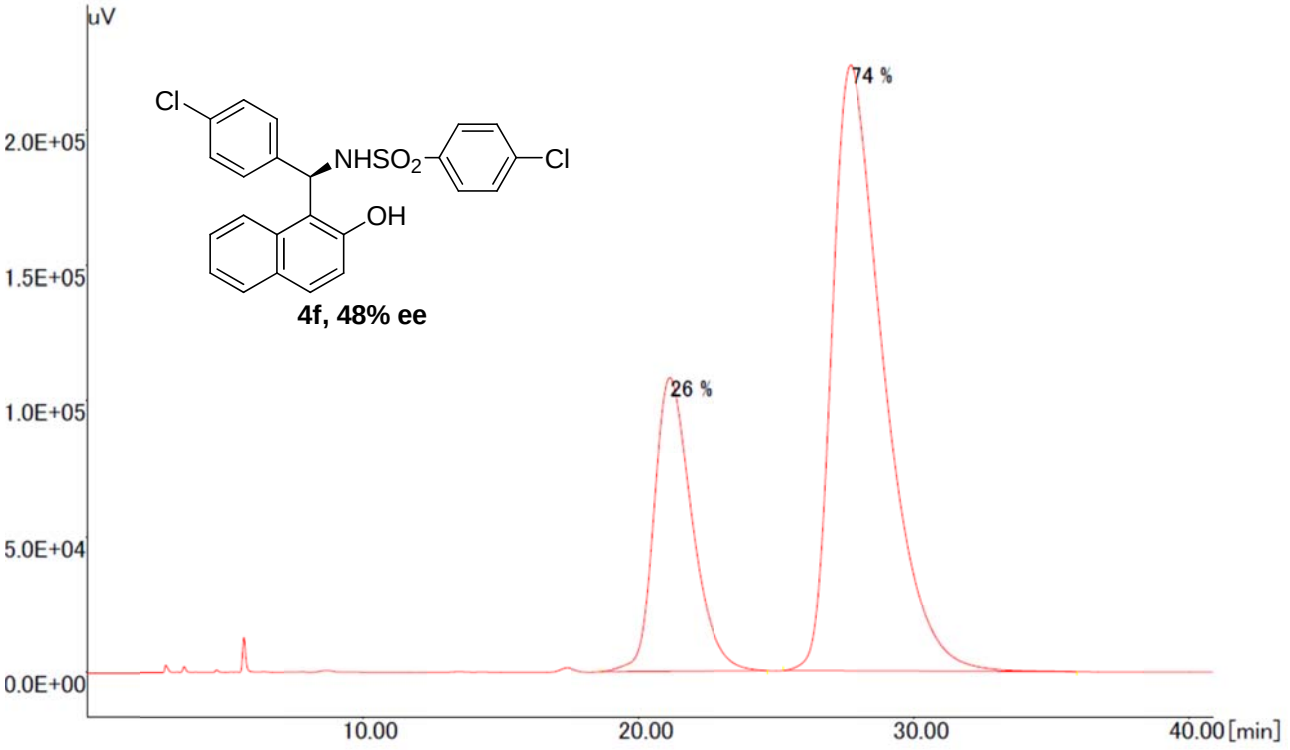


rac-4e

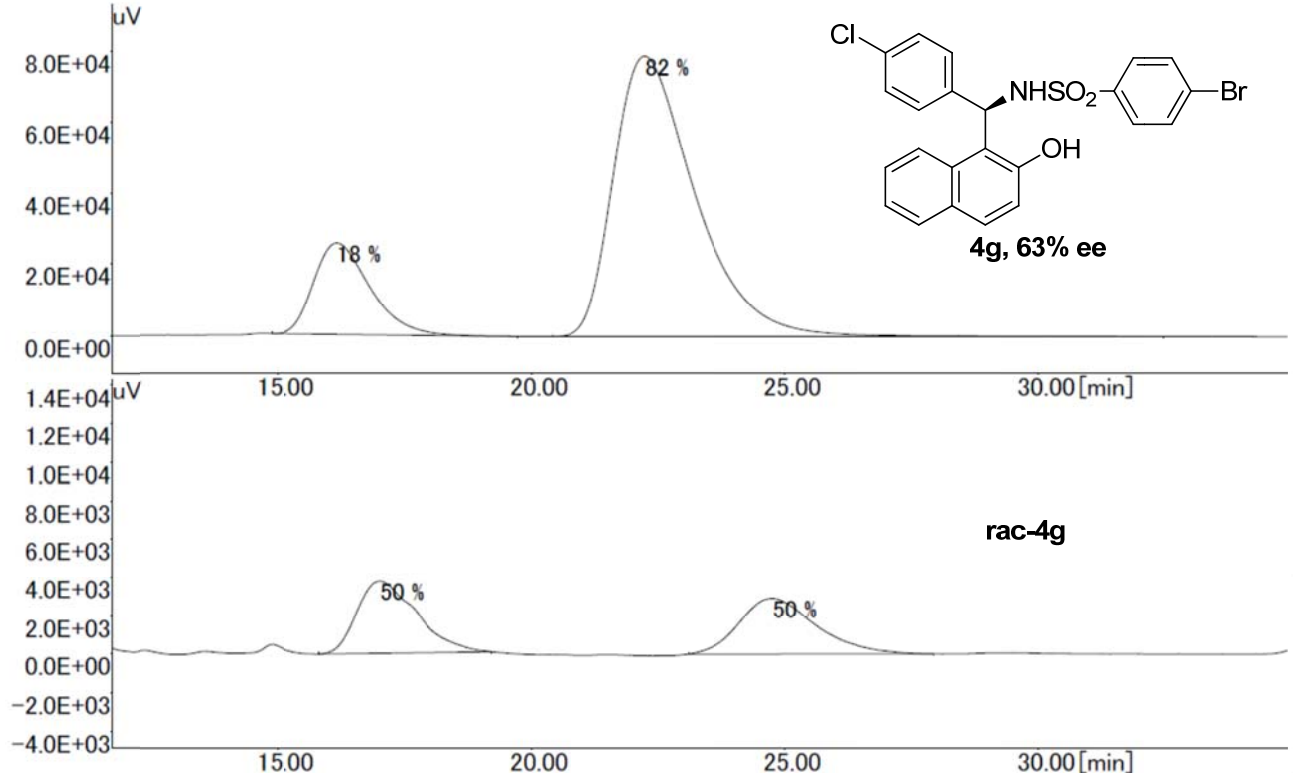
#	Name	RT	Area[uAU.Sec]	%Area
1		17.733	12585710.588	35.09
2		22.560	23285239.521	64.91



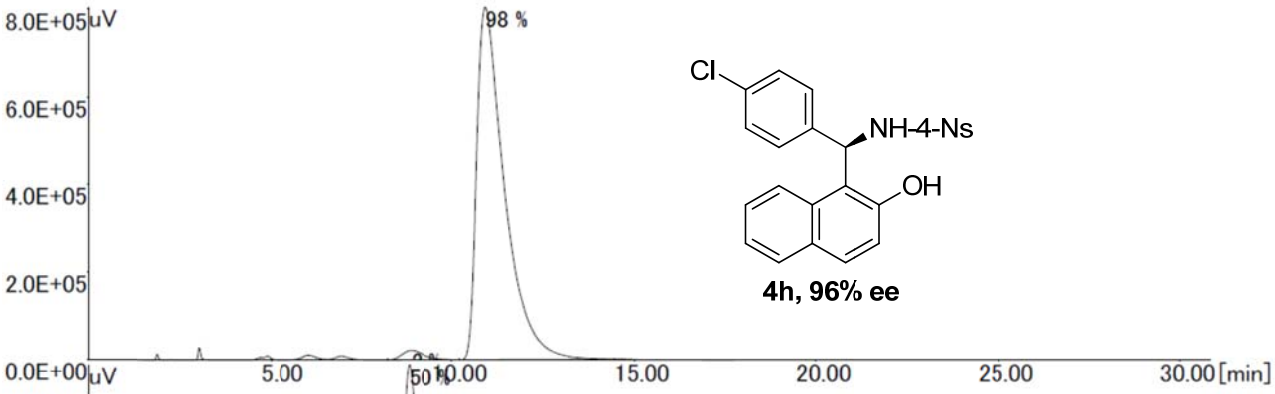
rac-4f



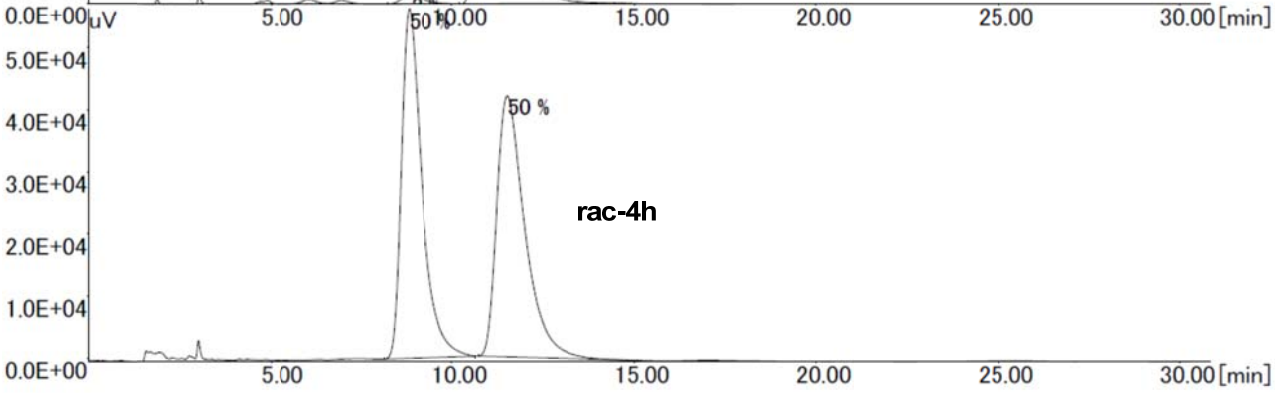
#	ピーク名	Rt	ピーク名	面積%
1		21.142		26.13
2		27.717		73.87



#	ピーク名	Rt	ピーク名	面積%	定量値
1		16.175		18.37	0.000
2		22.242		81.63	0.000

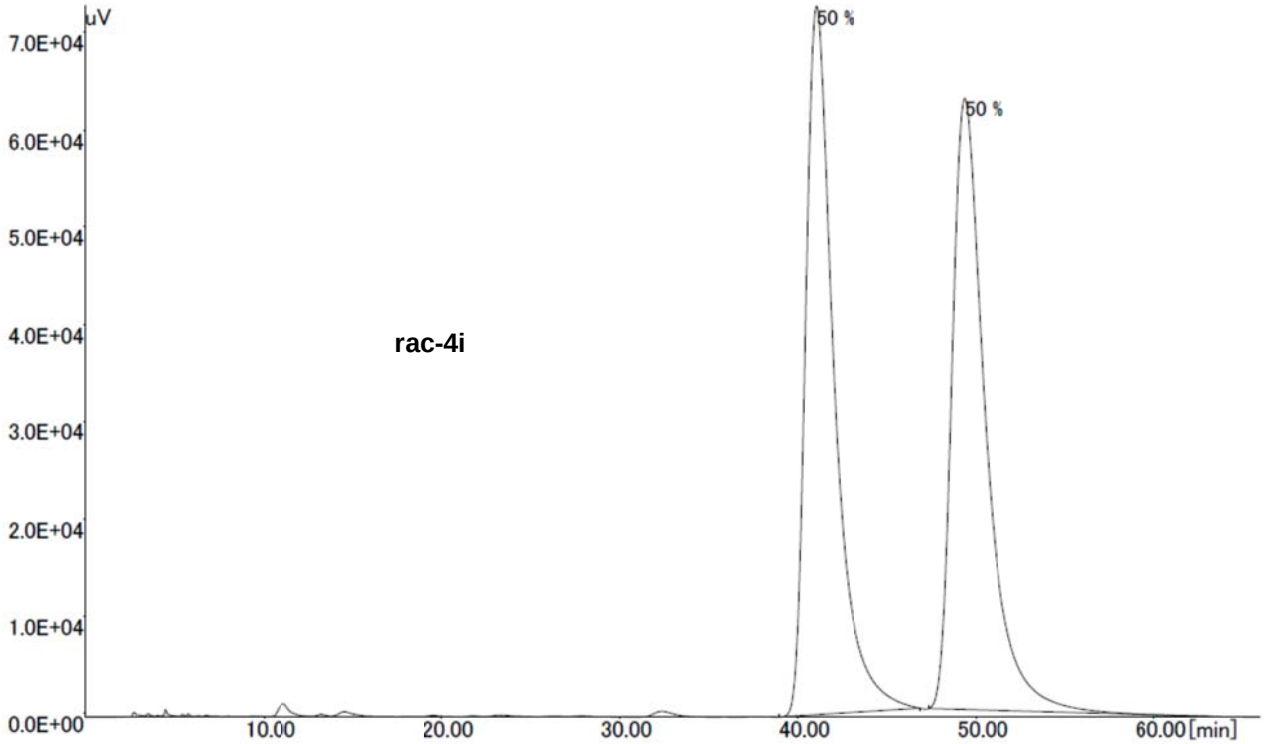


4h, 96% ee

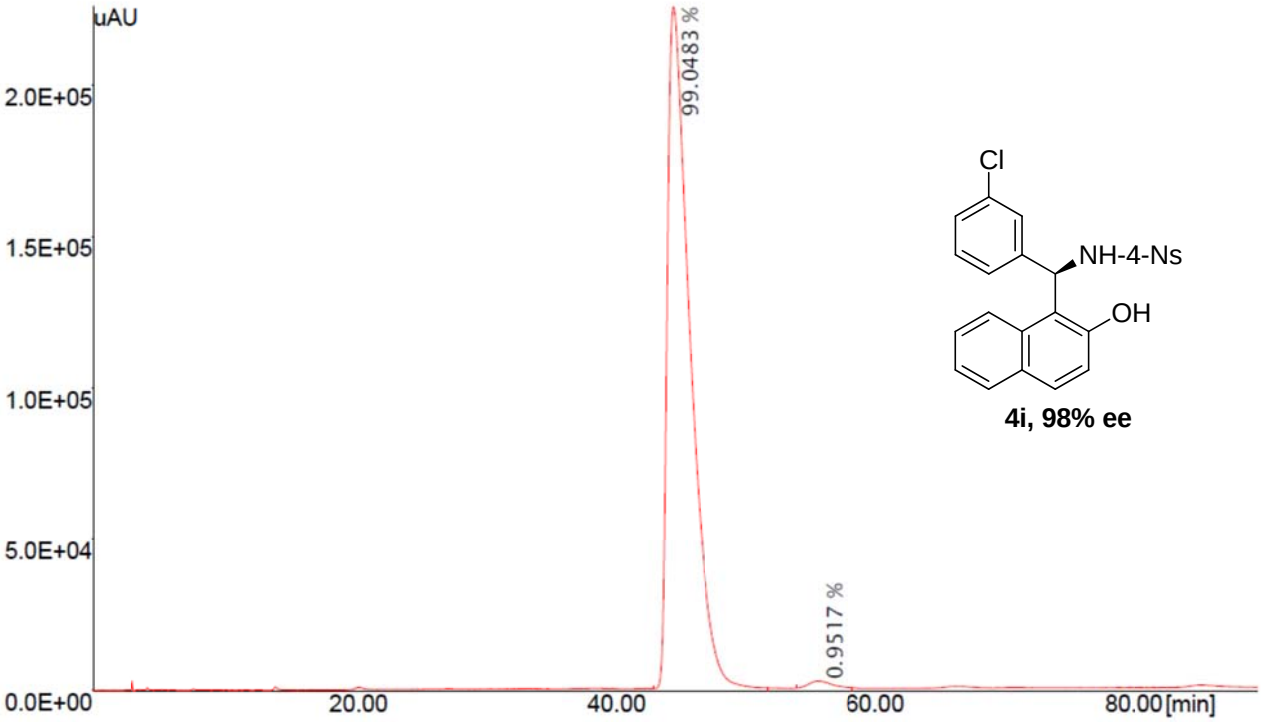


rac-4h

#	ピーク名	Rt	面積[uV.Sec]	面積%
1		8.858	919084.500	2.13
2		10.908	42229175.083	97.87

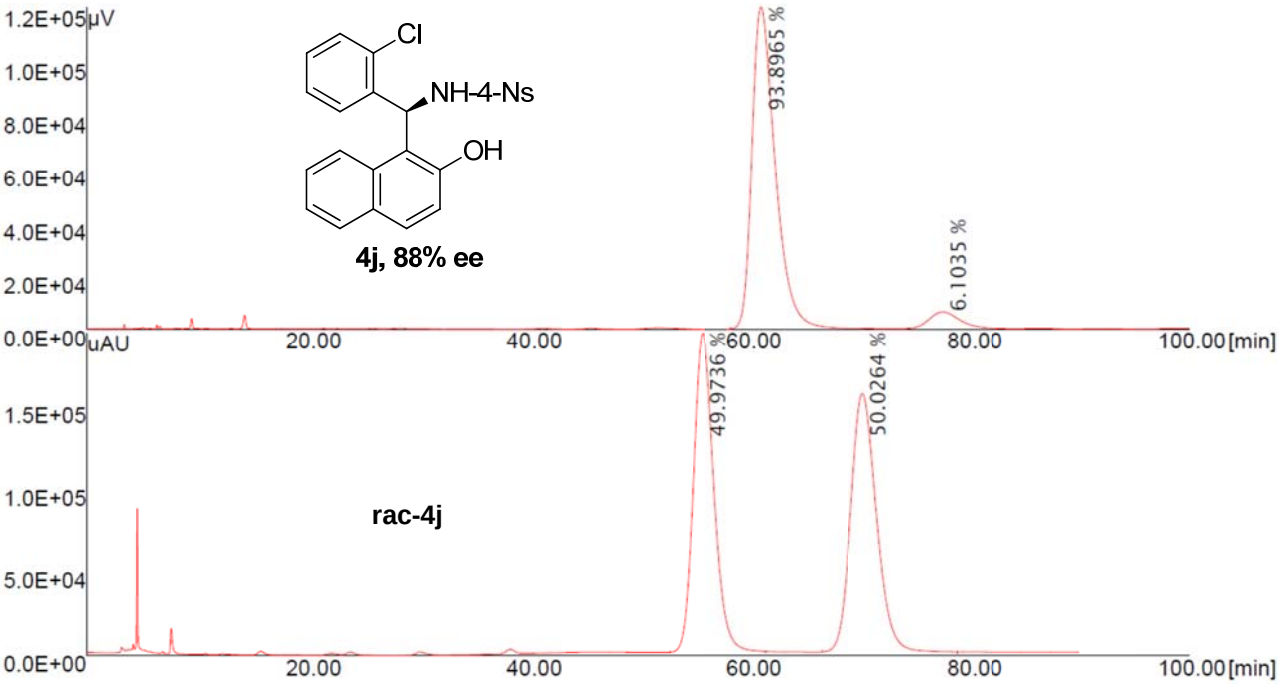


rac-4i



4i, 98% ee

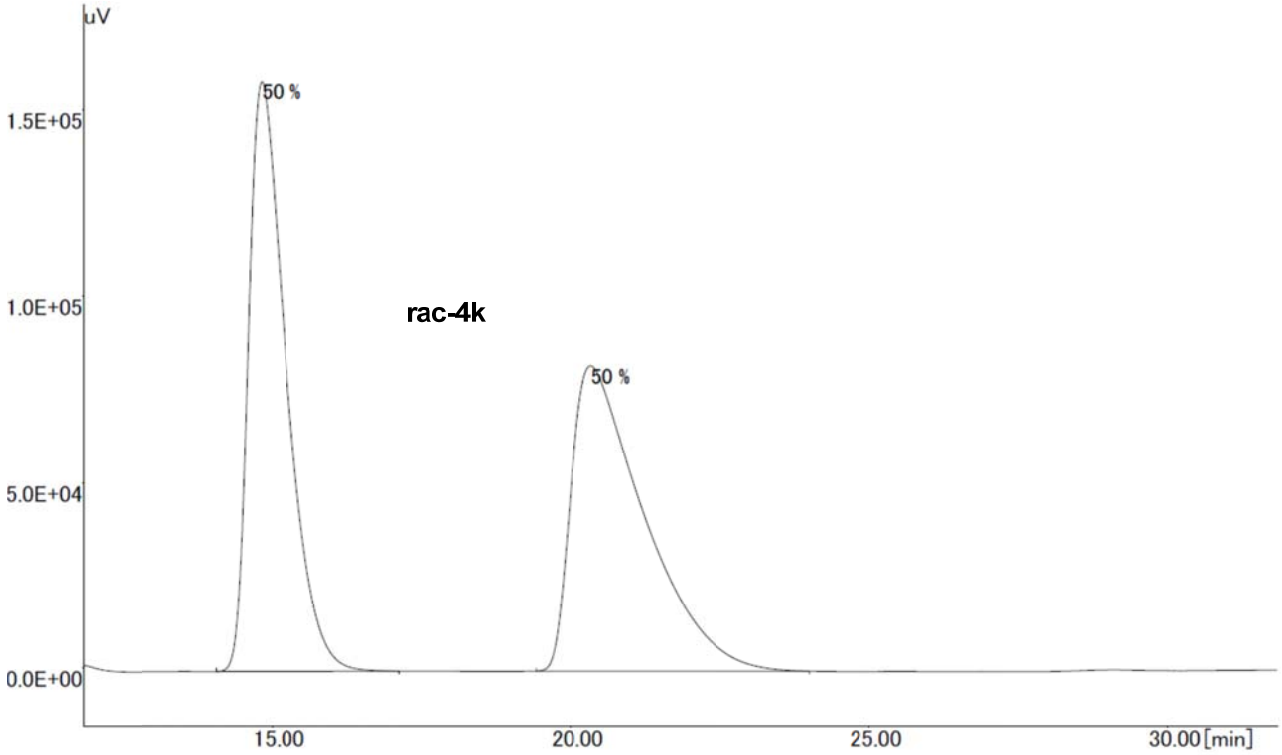
#	Name	RT	Area[uAU.Sec]	%Area
1		44.867	27565540.811	99.05
2		56.093	264856.804	0.95

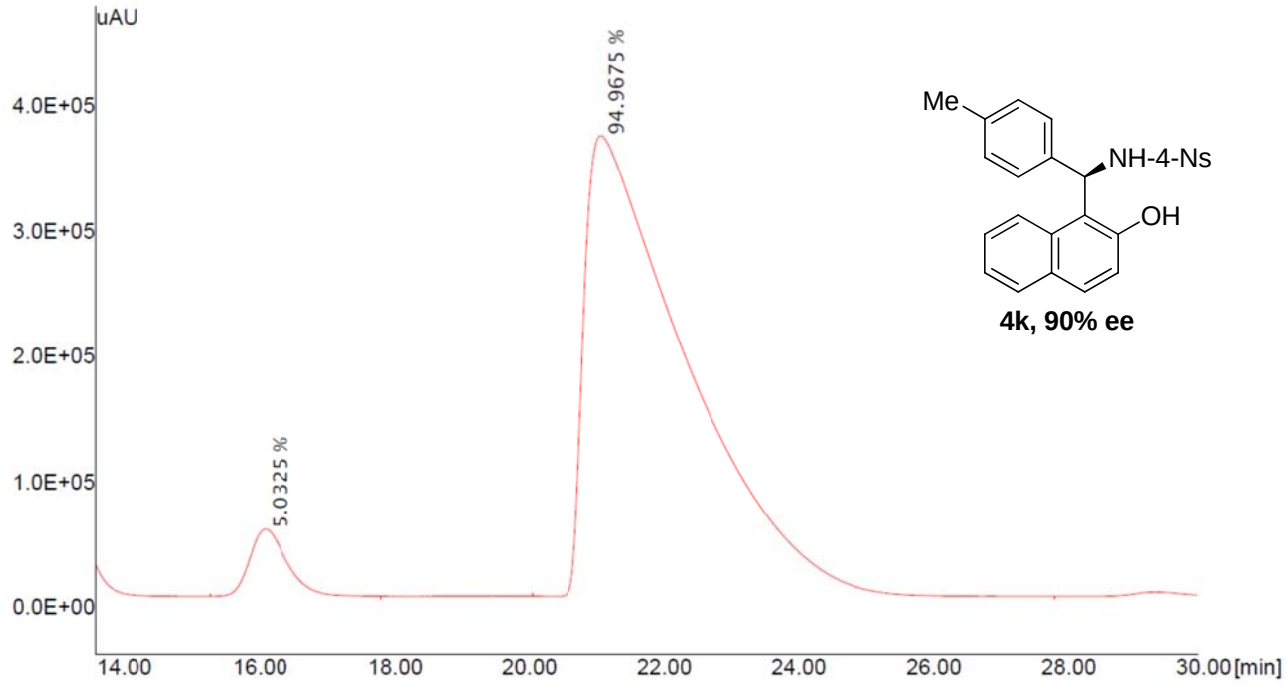


4j, 88% ee

rac-4j

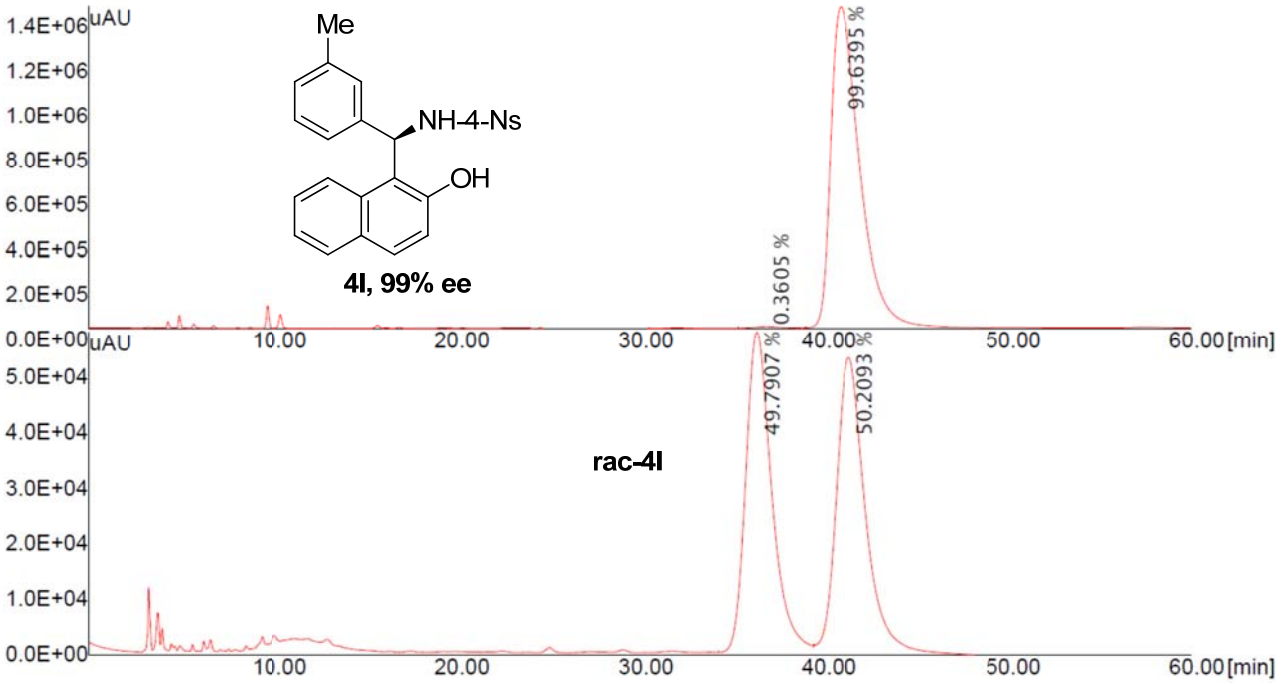
#	Name	RT	Area[μV.Sec]	%Area
1		61.175	17544115.000	93.90
2		77.633	1140415.500	6.10



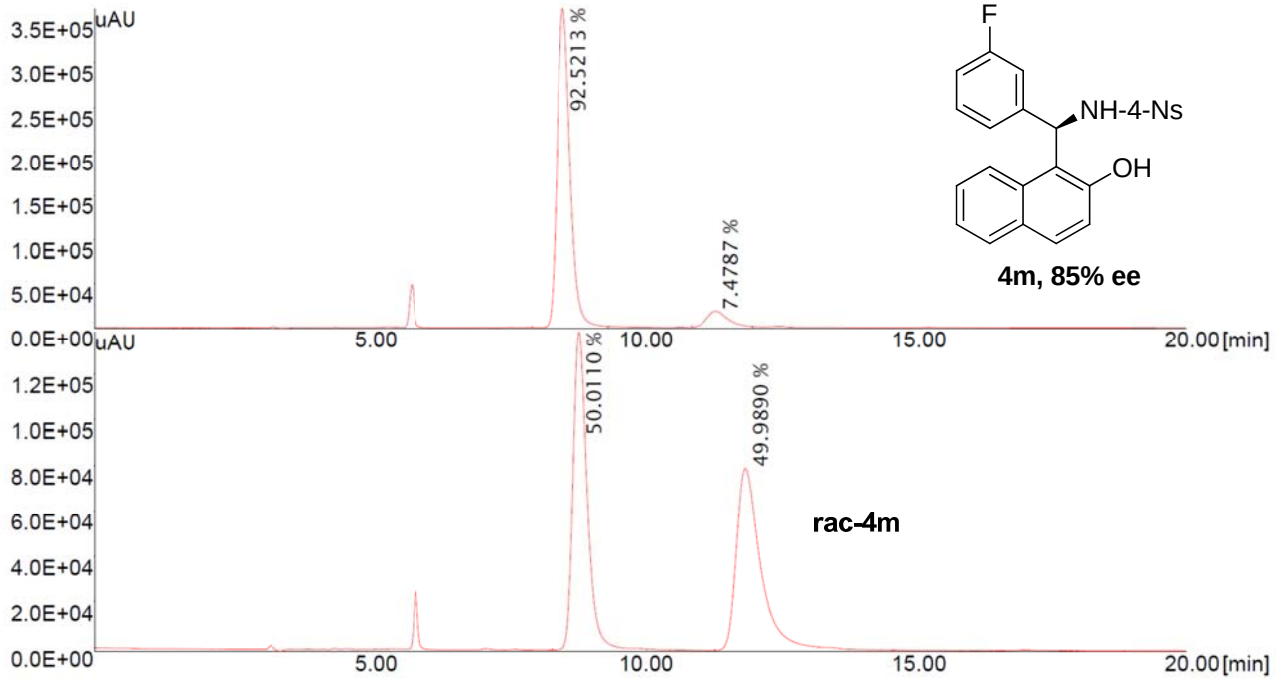


4k, 90% ee

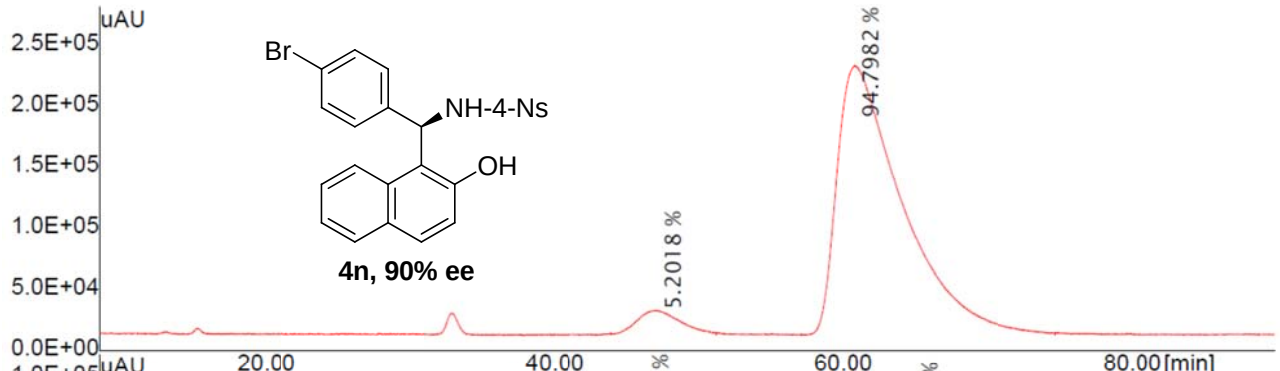
#	Name	RT	Area[uAU.Sec]	%Area
1		16.160	2062964.831	5.03
2		21.147	38929998.379	94.97

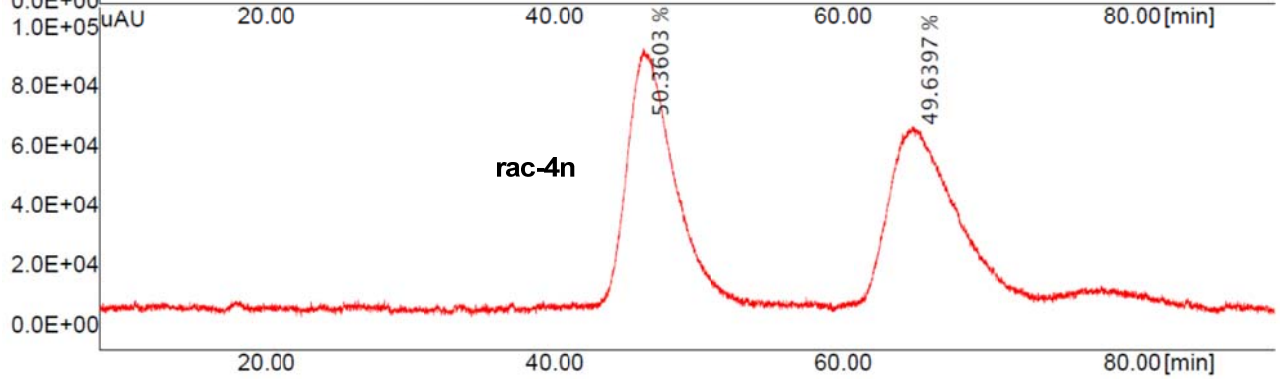


#	Name	RT	Area[uAU.Sec]	%Area
1		36.867	571956.009	0.36
2		40.973	158088692.760	99.64

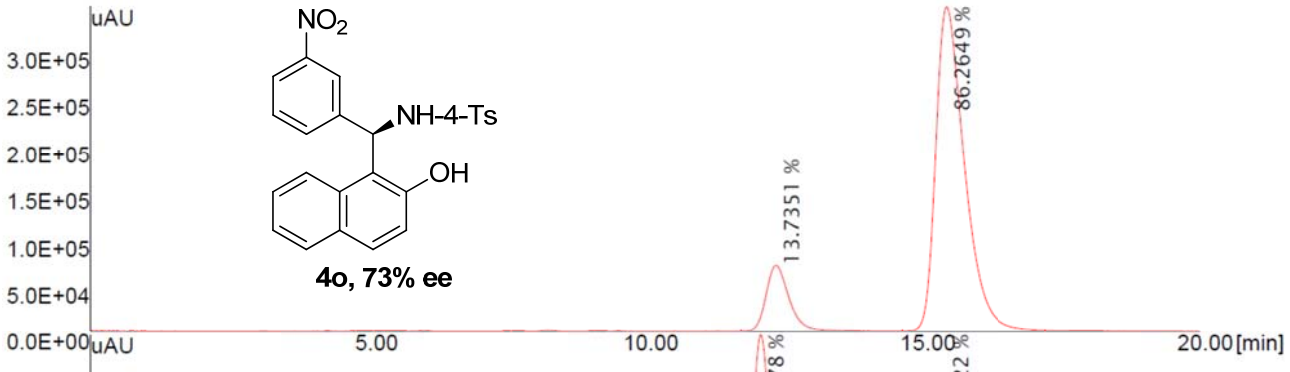


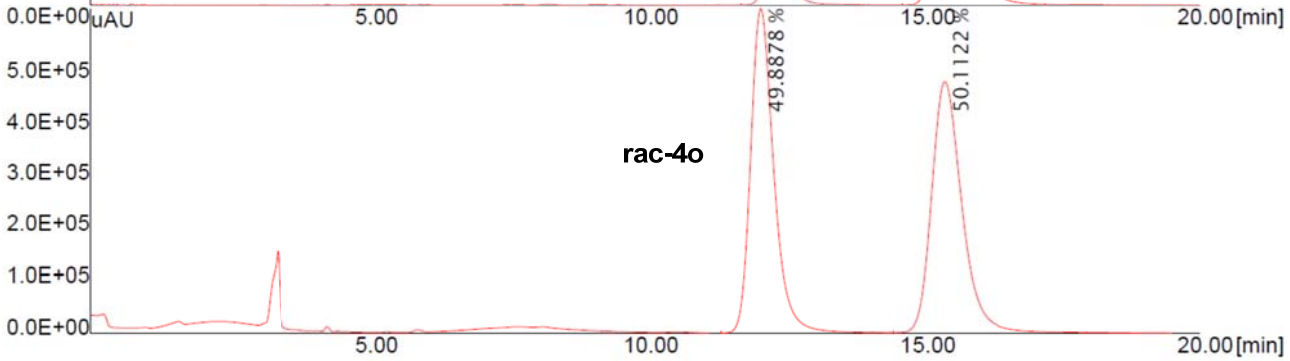
#	Name	RT	Area[uAU.Sec]	%Area
1		8.587	5839817.041	92.52
2		11.387	472047.207	7.48



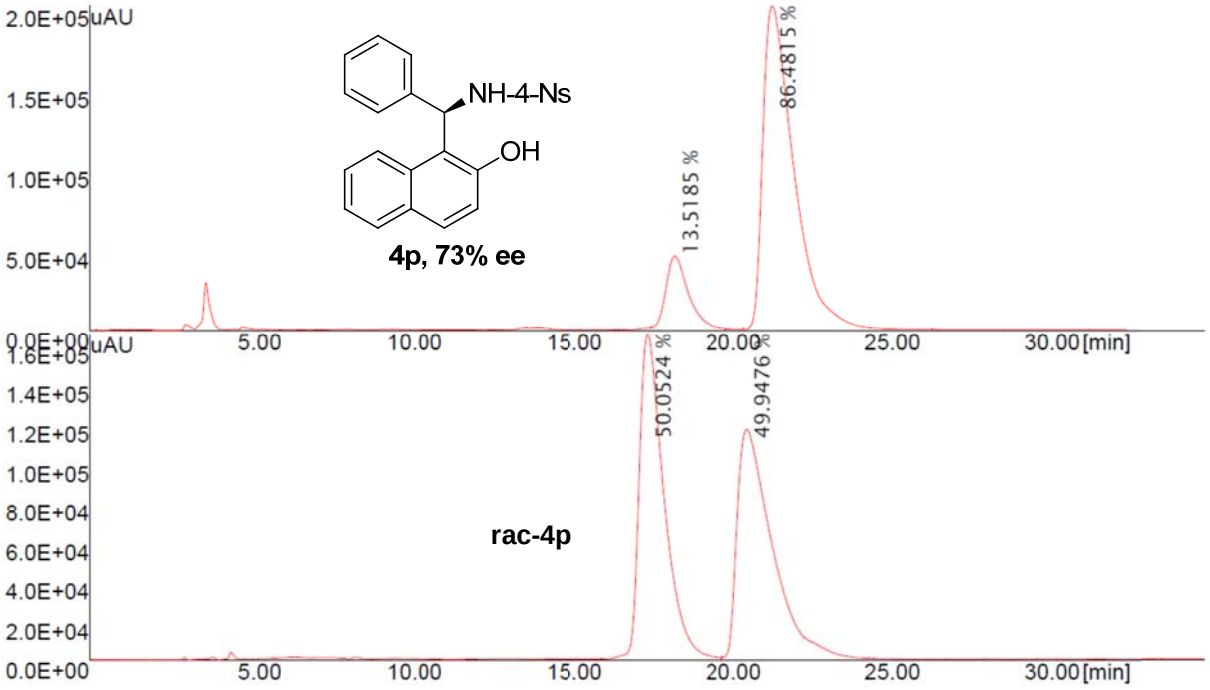


#	Name	RT	Area[uAU.Sec]	%Area
1		47.467	3798830.198	5.20
2		61.227	69230685.376	94.80

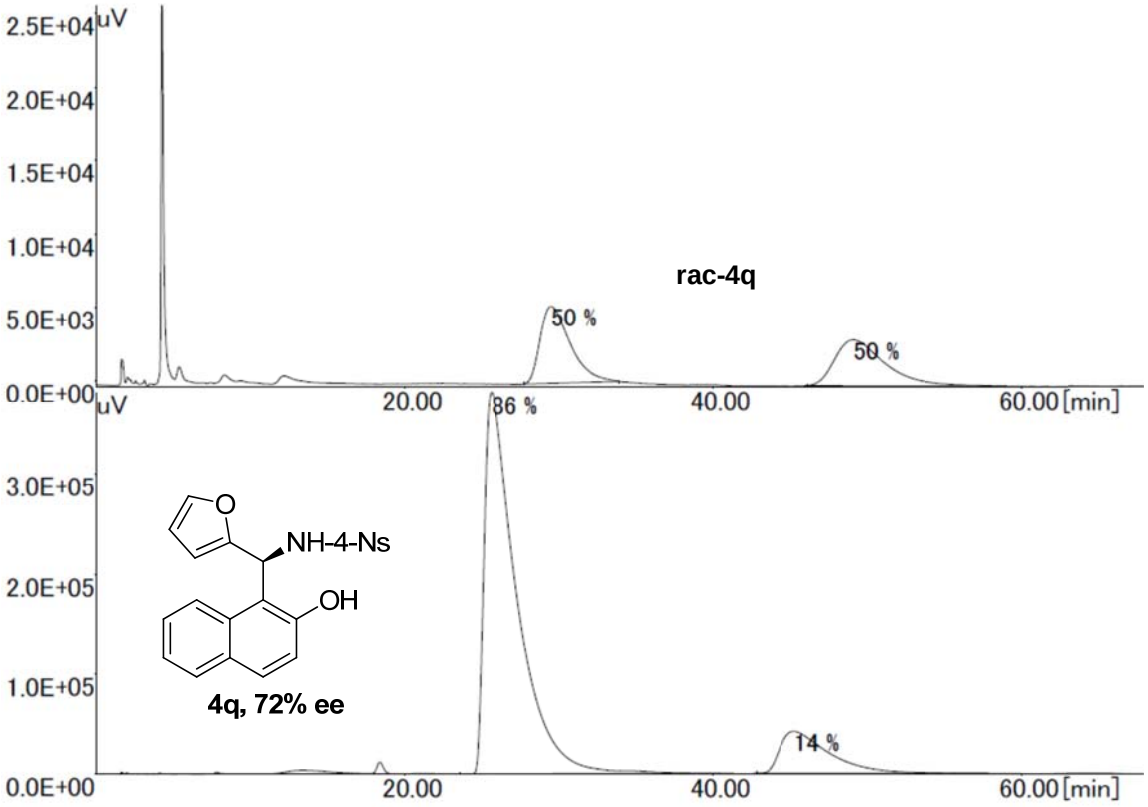




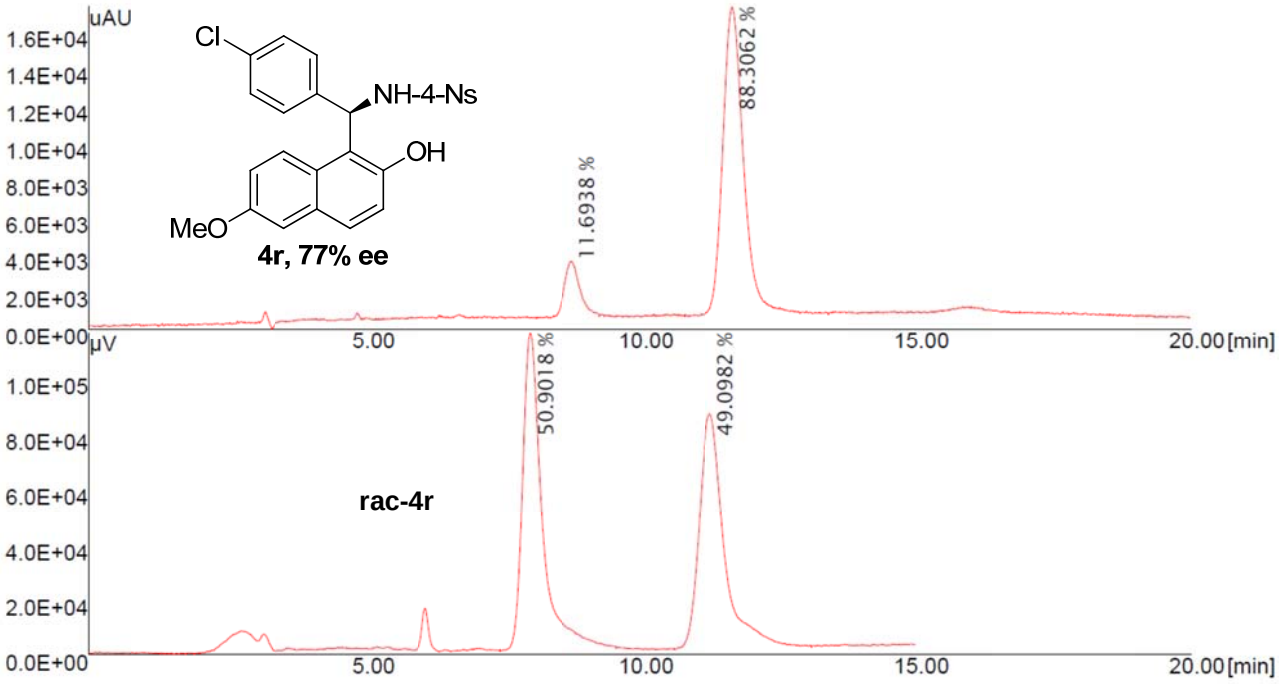
#	Name	RT	Area[uAU.Sec]	%Area
1		12.373	1950646.269	13.74
2		15.440	12251226.583	86.26



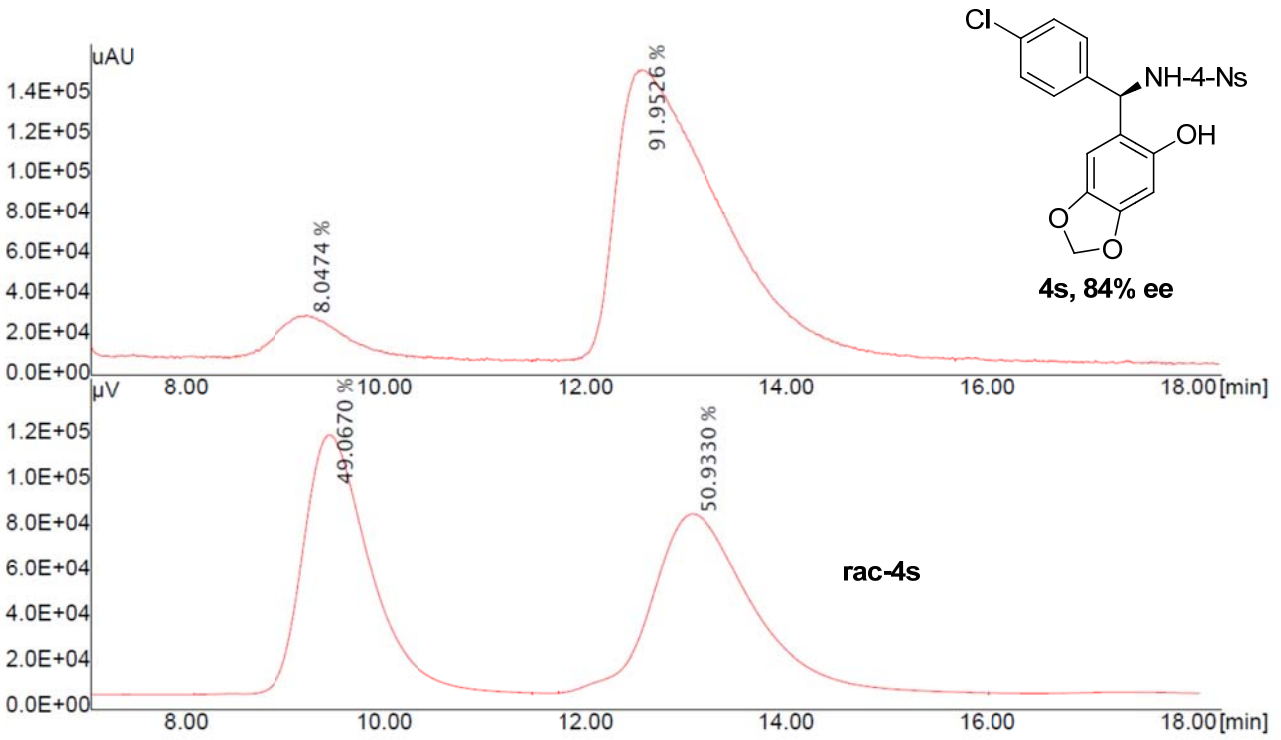
#	Name	RT	Area[uAU.Sec]	%Area
1		18.347	2100686.431	13.52
2		21.413	13438643.400	86.48



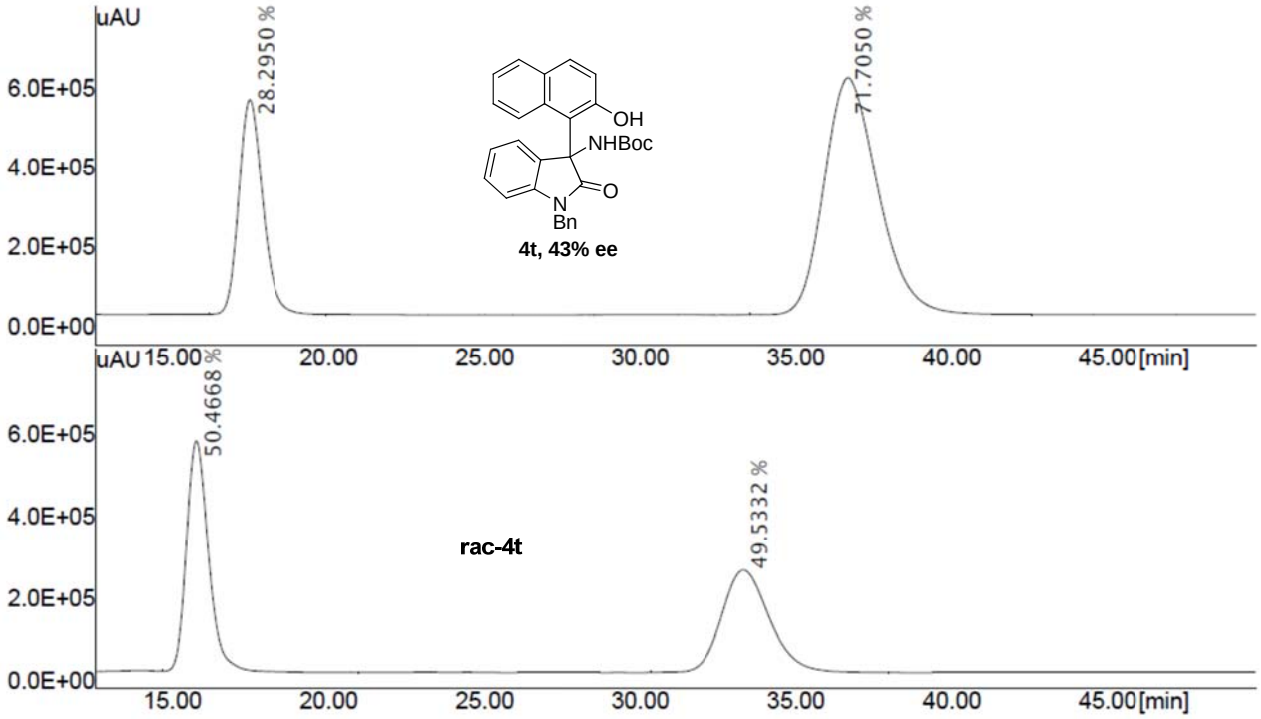
#	ピーク名	Rt	面積[uV.Sec]	面積%
1		25.633	56178788.909	85.88
2		45.292	9234136.780	14.12



#	Name	RT	Area[uAU.Sec]	%Area
1		8.760	57697.601	11.69
2		11.680	435706.770	88.31



#	Name	RT	Area[uAU.Sec]	%Area
1		9.293	915266.814	8.05
2		12.627	10458176.267	91.95



#	Name	RT	Area[uAU.Sec]	%Area
1		17.653	28493286.025	28.30
2		36.867	72207369.076	71.70