Supporting Information for

Iridium-catalyzed Regio- and Enantioselective Allylic Alkylation of Fluorobis(phenylsulfonyl)methane

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General: All manipulations were carried out under the argon atmosphere using standard Schlenk techniques. All glassware was oven or flame dried immediately prior to use. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

All reagents were obtained from commercial sources and used without further purification. ^{1}H NMR spectra were obtained at 300 MHz or 400 MHz and recorded relative to tetramethylsilane signal (0 ppm) or residual protio-solvent. ^{13}C NMR spectra were obtained at 75 MHz or 100 MHz, and chemical shifts were recorded relative to the solvent resonance ($CDCl_3$, 77.0 ppm). ^{19}F NMR spectra were obtained at 282 MHz or 376 MHz， and CF_3CO_2H was used as internal standard. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

The phosphoramidite ligands[1], substituted allylic carbonates[2], and fluorobis(phenylsulfonyl)methane (FBSM, **3**)[3] were prepared according to known procedures.

Reference:

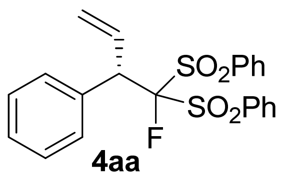
1. a) A. Alexakis, S. Rosset, J. Allamand, S. March, F. Guillen, C. Benhaim, *Synlett* **2001**, *9*, 1375; b) R. Naasz, L. A. Arnold, A. J. Minnaard, B. L. Feringa, *Angew. Chem. Int. Ed.* **2001**, *40*, 927; c) D. Polet, A. Alexakis, *Synthesis* **2004**, *15*, 2586.

2. P. G. M. Wuts, S. W. Ashford, A. M. Anderson,; J. R. Atkins, *Org. Lett.* **2003**, *5*, 1483.

3. a) G. K. S. Prakash, J. Hu, G. A. Olah, *J. Org. Chem.* **2003**, *68*, 4457; b) T. Fukuzumi, N. Shibata, M. Sugiura, H. Yasui, S. Nakamura, T. Toru, *Angew. Chem. Int. Ed.* **2006**, *45*, 4973.

General Procedure for the Iridium(I)-Catalyzed Enantioselective Allylic Alkylation of FBSM:

$[Ir(COD)Cl]_2$ (0.004 mmol, 2 mol%), phosphoramidite ligand **1a** [*O*,*O*'-(*S*)-(1,1'-dinaphthyl-2,2'-diyl)-*N*,*N*'-di-(*S*,*S*)-[phenylethylphosphoramidite] (0.008 mmol, 4 mol%) were dissolved in THF (0.5 mL) and propylamine (0.3 mL) in a dry Schlenk tube filled with argon. The reaction mixture was heated at 50°C for 30 min and then the volatile solvents were removed under vacuum to give a yellow solid. After that, allylic carbonate **2** (0.22 mmol, 110 mol%), FBSM **3** (0.20 mmol), cesium carbonate (0.44 mmol, 220 mol% or 0.50 mmol, 250 mol%), and DCM (2.0 mL) were added. The reaction was stirring at room temperature until the carbonate was fully consumed, monitored by TLC or ^{1}H NMR. Then the crude reaction mixture was filtrated with celite and the solvent was removed under reduced pressure. The ratio of regioisomers (branched to linear b/l) was determined by ^{1}H NMR of the crude reaction mixture. The crude residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to give the desired products.



4aa

4aa: white solid, mp. = 127-129 °C; R_f = 0.3 (petroleum ether/ethyl acetate: 5/1); b/l: >99/1, 89% yield (76.2 mg), 94% ee; 79% yield and >99% ee were obtained after recrystallization with hexane/2-propanol. [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 98/2; flow rate = 0.8 mL/min; detection wavelength = 214 nm; t_R = 42.92 (minor), 46.55 (major) min].

$[\alpha]_D^{20}$ = -39.4°(c 1.0, $CHCl_3$, >99% ee).

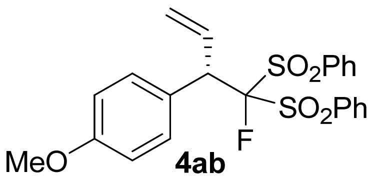
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86-7.84 (m, 2H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.55-7.45 (m, 5H), 7.31-7.15 (m, 7H), 6.86 (ddd, *J* = 17.2, 10.0, 9.6 Hz, 1H), 5.46 (d, *J* = 10.0 Hz, 1H), 5.31 (d, *J* = 17.2 Hz, 1H), 4.62 (dd, *J* = 13.6, 9.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.8 (d, *J* = 3.7 Hz), 135.9 (d, *J* = 3.7 Hz), 135.1, 134.8, 134.4, 131.7, 131.6, 131.0 (d, J = 2.3 Hz), 130.5 (d, J = 1.5 Hz), 130.4 (d, J = 1.5 Hz), 128.7, 128.4, 128.1, 127. 8, 121.5, 116.2 (d, J = 268.4 Hz), 52.2 (d, J = 17.1 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ = -129.18 (d, J = 12.7 Hz).

MS (EI, *m/z*, rel. intensity) 77 (100); HRMS (EI) calcd for $C_{22}H_{19}O_4FS_2$ (M^+): 430.0709, Found: 430.0706.

IR (KBr): ν_{max} (cm^{-1}) = 3095, 2993, 2910, 1585, 1496, 1478, 1450, 1417, 1349, 1335, 1291, 1163, 1147, 1080, 1071, 1018, 1004, 970, 936, 761, 746, 697, 688, 682.



4ab

4ab: white solid, 81-83 °C; R_f = 0.2 (petroleum ether/ethyl acetate: 5/1); b/l: >99/1, 95% yield (87.5 mg), 95% ee. [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 95/5; flow rate = 0.7 mL/min; detection wavelength = 214 nm; t_R = 38.38 (minor), 41.79 (major) min].

$[\alpha]_D^{20}$ = -43.2°(c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85-7.83 (m, 2H), 7.68-7.64 (m, 1H), 7.54-7.46 (m, 5H), 7.30 (dt, J = 7.6, 1.6 Hz, 2H), 7.13 (d, J = 7.6 Hz, 2H), 6.83 (ddd, J = 16.8, 10.0, 9.2 Hz, 1 H), 6.67 (dt, J = 9.6, 2.8 Hz, 2 H), 5.43 (d, J = 10.0 Hz, 1 H), 5.28 (d, J = 16.8 Hz, 1 H), 4.58 (dd, J = 13.6, 9.2 Hz, 1 H), 3.74 (s, 1H).

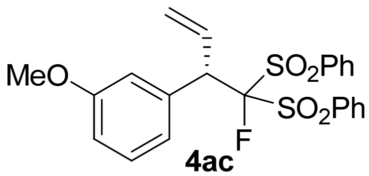
^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.1, 136.8, 136.0, 134.7, 134.3, 131.9, 131.8, 131.6, 130.9 (d, J = 2.2 Hz), 130.35 (d, J = 1.5 Hz), 128.6, 128.3, 126.8, 121.1, 116.2 (d, J = 268.5 Hz), 113.4, 55.1, 51.4 (d, J = 17.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -128.02 (d, J = 13.5 Hz).

MS (EI, *m/z*, rel. intensity) 460 (M^+, 1.6), 147 (100); HRMS (EI) calcd for

$C_{23}H_{21}O_5FS_2$ (M^+): 460.0814, Found: 460.0812.

IR (KBr): ν_{max} (cm^{-1}) = 3068, 2839, 1610, 1583, 1513, 1449, 1344, 1314, 1255, 1182, 1163, 1153, 1079, 1033, 1000, 913, 831, 755, 734, 685.



4ac

4ac: colorless oil, R_f = 0.3 (petroleum ether/ethyl acetate: 5/1); b/l: 95/5, 91% yield, 91% ee. [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 17.82 (minor), 19.49 (major) min].

$[\alpha]_D^{20}$ = -9.5°(c 0.5, $CHCl_3$).

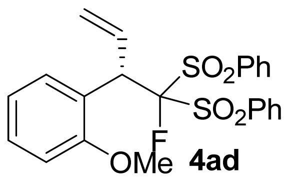
^1H NMR (300 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 7.8 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.56-7.47 (m, 5H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.88-6.70 (m, 4H), 5.47 (d, *J* = 10.8 Hz, 1H), 5.33 (d, *J* = 16.8 Hz, 1H), 4.61 (dd, *J* = 13.8, 9.3 Hz, 1H), 3.69 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.9, 136.7, 136.3, 135.8, 135.6, 135.14, 135.07, 134.7, 134.3, 131.4, 131.3, 130.84, 130.83. 130.76, 130.2, 130.0, 129.3, 128.9, 128.5, 128.2, 122.7, 121.4, 116.0 (d, *J* = 269.6 Hz), 115.9, 113.3, 54.9, 51.9 (d, *J* = 17.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ = -129.82 (d, *J* = 13.3 Hz).

MS (EI, *m/z*, rel. intensity) 460 (M^+, 6.3), 77 (100); HRMS (EI) calcd for $C_{23}H_{21}O_5FS_2$ (M^+): 460.0814, Found: 460.0816.

IR (KBr): ν_{max} (cm^{-1}) = 3069, 2838, 2258, 1601, 1585, 1492, 1466, 1449, 1418, 1348, 1315, 1291, 1264, 1157, 1079, 1050, 1000, 912, 782, 754, 733, 685.



4ad

4ad: white powder, mp. = 93-96 °C; R_f = 0.2 (petroleum ether/ethyl acetate: 5/1); b/l: >99/1, 86% yield, 70% ee. [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 21.58 (major), 27.90 (minor) min].

$[\alpha]_D^{20}$ = -10.1°(c 0.5, $CHCl_3$).

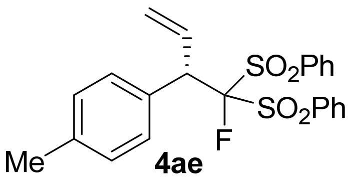
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86-7.84 (m, 2H), 7.77-7.75 (m, 2H), 7.65-7.59 (m, 3H), 7.47-7.42 (m, 4H), 7.18-7.14 (m, 1H), 6.89-6.74 (m, 2H), 6.65 (dd, *J* = 1.2, 8.4 Hz, 1H), 5.31 (dd, *J* = 12.0, 2.0 Hz, 1H), 5.19 (d, *J* = 17.2 Hz, 1H), 5.13 (dd, *J* = 10.4, 8.8 Hz, 1H), 3.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.1, 137.2, 136.0, 134.6, 132.28, 132.24, 131.8, 130.9, 130.8, 130.7, 128.9, 128.6, 128.3, 123.61, 123.58, 120.2, 119.8, 116.5 (d, *J* = 217.9 Hz), 110.2, 55.2, 44.3 (d, *J* = 18.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -133.03 (d, *J* = 7.90 Hz).

MS (EI, *m/z*, rel. intensity) 147 (100); HRMS (EI) calcd for $C_{23}H_{21}O_5FS_2$ (M^+): 460.0814, Found: 460.0817.

IR (KBr): ν_{max} (cm^{-1}) = 3067, 2841, 1600, 1585, 1493, 1464, 1449, 1349, 1314, 1291, 1267, 1250, 1168, 1153, 1080, 1029, 999, 931, 738, 704, 686.



4ae

4ae: white powder, mp. = 84-87 °C; R_f = 0.3 (petroleum ether/ethyl acetate: 5/1); b/l: 97/3, 94% yield, 94% ee. [Diacel CHIRALPAK AD-H (0.46 cm x 25 cm);

hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 17.71 (major), 19.07 (minor) min].

$[\alpha]_D^{20}$ = -73.5° (c 1.0, $CHCl_3$).

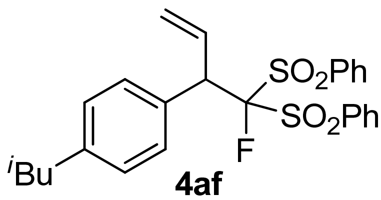
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 7.2 Hz, 2H), 7.69-7.64 (m, 1H), 7.55-7.45 (m, 5H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.95-6.78 (m, 3H), 5.44 (d, *J* = 10.2 Hz, 1H), 5.29 (d, *J* = 17.1 Hz, 1H), 4.59 (dd, *J* = 13.8, 9.3 Hz, 1H), 2.26 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.6, 136.7, 135.9, 134.7, 134.3, 132.0, 131.81, 131.73, 130.89, 130.87, 130.3, 128.9, 128.7, 128.6, 128.3, 126.3, 121.2, 116.2 (d, *J* = 268.5 Hz), 51.8 (d, *J* = 17.8 Hz), 20.9.

^{19}F NMR (282 MHz, $CDCl_3$) δ = -129.50 (d, *J* = 13.25 Hz).

MS (EI, *m/z*, rel. intensity) 131 (100); HRMS (EI) calcd for $C_{23}H_{21}O_4FS_2$ (M^+): 444.0865, Found: 444.0867.

IR (KBr): ν_{max} (cm^{-1}) = 1584, 1512, 1448, 1346, 1336, 1314, 1162, 1147, 1079, 1020, 1000, 930, 809, 764, 753, 714, 689, 682.



4af

4af: white solid, mp.: 129-131 °C; R_f = 0.3 (petroleum ether/ethyl acetate: 5/1); b/l: 97/3, 96% yield, 95% ee. [Diacel CHIRALPAK AD-H (0.46 cm x 25 cm); hexane/2-propanol = 98/2; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R = 51.54 (major), 57.80 (minor) min].

$[\alpha]_D^{20}$ = -41.6° (c 1.0, $CHCl_3$) for (*S*)-**4af** and $[\alpha]_D^{20}$ = +42.7° (c 1.10, $CHCl_3$, 94% ee) for (*R*)-**4af**.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 7.6 Hz, 2H), 7.67 (t, *J* = 6.8 Hz, 1H), 7.50-7.43 (m, 5H), 7.27 (t, *J* = 7.2 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 6.93-6.82

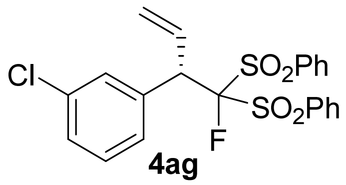
(m, 3H), 5.45 (d, *J* = 10.0 Hz, 1H), 5.31 (d, *J* = 16.8 Hz, 1H), 4.61 (dd, *J* = 12.4, 10.0 Hz, 1H), 2.38 (d, *J* = 6.8 Hz, 2H), 1.84-1.77 (m, 1H), 0.88 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.3, 136.8, 136.0, 134.7, 134.3, 132.2, 131.69, 131.63, 131.0, 130.2, 128.8, 128.6, 128.3, 121.3, 116.3 (d, *J* = 268.4 Hz), 51.8 (d, *J* = 17.9 Hz), 44.9, 30.0, 22.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -128.09 (d, *J* = 11.3 Hz).

MS (EI, *m/*z, rel. intensity) 344 (100); HRMS (EI) calcd for $C_{26}H_{26}O_4FS_2$ (M^+): 485.1257, Found: 485.1250.

IR (KBr): ν_{max} (cm^{-1}) = 2952, 2868, 1584, 1512, 1478, 1466, 1449, 1347, 1337, 1314, 1164, 1149, 1079, 1021, 999, 939, 914, 801, 755, 723, 685.



4ag

4ag: white solid, mp.: 109-113 °C; R_f = 0.3 (petroleum ether/ethyl acetate: 5/1); b/l: >99/1, 41% yield, 94% ee. [Diacel CHIRALPAK AD-H (0.46 cm x 25 cm); hexane/2-propanol = 98/2; flow rate = 0.8 mL/min; detection wavelength = 214 nm; t_R = 80.38 (major), 84.06 (minor) min].

$[\alpha]_D^{20}$ = -14.5° (c 0.5, $CHCl_3$).

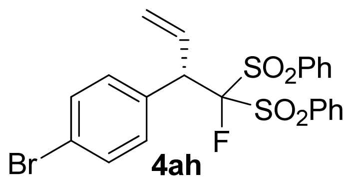
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 7.2 Hz, 2H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.57-7.48 (m, 5H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.17-7.09 (m, 4H), 6.80 (ddd, *J* = 17.1, 9.6, 7.5 Hz, 1H), 5.50 (d, *J* = 10.2 Hz, 1H), 5.33 (d, *J* = 16.8 Hz, 1H), 4.61 (dd, *J* = 13.5, 9.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.1, 136.5, 135.8, 135.0, 134.6, 133.8, 131.02, 130.99, 130.89, 130.80, 130.45, 130.30, 130.28, 129.2, 128.4, 128.0, 122.2, 115.7 (d, *J* = 269.1 Hz), 51.6 (d, *J* = 17.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ = -129.89 (d, J = 13.3 Hz).

MS (EI, *m/z*, rel. intensity) 77 (100); HRMS (EI) calcd for $C_{22}H_{19}O_4FClS_2$ (MH^+): 465.0397, Found: 465.0390.

IR (KBr): ν_{max} (cm^{-1}) = 2918, 1596, 1573, 1475, 1447, 1433, 1347, 1310, 1289, 1160, 1146, 1078, 999, 968, 950, 872, 844, 784, 753, 707, 683.



4ah

(*S*)-4ah: white solid, mp.: 163-165 °C; R_f = 0.3 (petroleum ether/ethyl acetate: 5/1); b/l: >99/1, 66% yield, 92% ee (54% yield and >99% ee after recrystallization with hexane/2-propanol). [Diacel CHIRALPAK IC (0.46 cm x 25 cm); hexane/2-propanol = 80/20; flow rate = 0.8 mL/min; detection wavelength = 214 nm; t_R = 35.98 (major), 60.54 (minor) min].

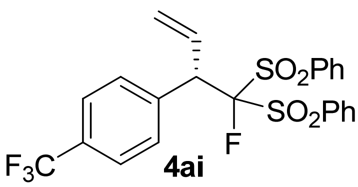
$[\alpha]_D^{20}$ = -44.1°(c 1.0, $CHCl_3$, >99% ee).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.84 (d, J = 7.8 Hz, 2H), 7.69 (t, J = 7.2 Hz, 1H), 7.59-7.46 (m, 5H), 7.35-7.24 (m, 4H), 7.09 (d, J = 8.1 Hz, 1H), 6.81 (ddd, J = 17.1, 9.6, 7.5 Hz, 1H), 5.47 (d, J = 9.9 Hz, 1H), 5.31 (d, J = 17.1 Hz, 1H), 4.59 (dd, J = 13.2, 9.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 136.4, 135.7, 134.9, 134.5, 134.2, 132.1, 131.10, 131.01, 130.93, 130.2, 128.7, 128.5, 122.2, 121.9, 115.8 (d, J = 268.5 Hz), 51.5 (d, J = 17.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ = -129.69 (d, J = 13.3 Hz).

MS (EI, *m/z*, rel. intensity) 77 (100); HRMS (EI) calcd for $C_{22}H_{18}O_4FBrS_2$ (M^+): 507.9814, Found: 507.9812. IR (KBr): ν_{max} (cm^{-1}) = 2923, 2852, 1583, 1488, 1448, 1314, 1162, 1147, 1079, 1011, 937, 815, 716, 684.



4ai

4ai: white solid, mp.: 127-129 °C; R_f = 0.3 (petroleum ether/ethyl acetate: 5/1); b/l: >99/1, 60% yield, 91% ee. [Diacel CHIRALPAK AD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 17.50 (minor), 20.80 (major) min].

$[\alpha]_D^{20}$ = -35.2°(c 0.5, $CHCl_3$).

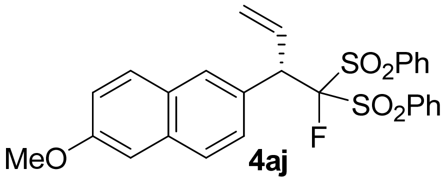
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 (d, *J* = 8.4 Hz, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.56-7.46 (m, 5H), 7.41-7.28 (m, 6H), 6.84 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.50 (d, *J* = 10.0 Hz, 1H), 5.33 (d, *J* = 16.8 Hz, 1H), 4.70 (dd, *J* = 13.6, 9.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.4, 136.5, 135.8, 135.0, 134.7, 131.02, 131.00, 130.90, 130.88, 130.30, 130.30, 128.8, 128.5, 124.9 (q, *J* = 3.7 Hz), 122.3, 115.8 (d, *J* = 269.2 Hz), 51.8 (d, *J* = 17.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.76 (s, 3F), -129.66 (d, *J* = 13.2 Hz, 1F).

MS (EI, *m/z*, rel. intensity) 77 (100); HRMS (EI) calcd for $C_{23}H_{18}O_4F_4S_2$ (M^+): 498.0583, Found: 498.0585.

IR (KBr): ν_{max} (cm^{-1}) = 2918, 2852, 1618, 1583, 1448, 1426, 1412, 1348, 1332, 1293, 1162, 1147, 1117, 1073, 1020, 951, 832, 819, 756, 745, 723, 707, 684.



4aj

4aj: white solid, mp.: 131-133 °C; R_f = 0.2 (petroleum ether/ethyl acetate: 4/1); b/l: >99/1, 94% yield, 93% ee. [Diacel CHIRALPAK AD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R = 26.76 (minor), 29.67 (major) min].

$[\alpha]_D^{20}$ = -73.9°(c 1.0, $CHCl_3$).

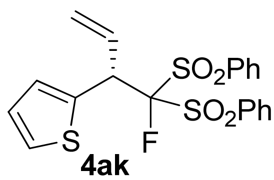
^1H NMR (400 MHz, $CDCl_3$) δ = 7.85 (d, *J* = 8.4 Hz, 2H), 7.63-7.54 (m, 3H), 7.45-7.34 (m, 6H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.11-7.07 (m, 3H), 7.01 (s, 1H), 6.94 (ddd, *J* = 16.8, 10.0, 6.8 Hz, 1H), 5.50 (d, *J* = 10.0 Hz, 1H), 5.36 (d, *J* = 16.8 Hz, 1H), 4.79 (dd, *J* = 14.8, 9.2 Hz, 1H), 3.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.0, 136.8, 136.2, 134.6, 134.1, 133.9, 131.75, 131.69, 131.0, 130.19, 130.10, 129.7, 129.5, 128.52, 128.39, 128.38, 128.1, 126.4, 121.5, 118.9, 116.5 (d, *J* = 268.5 Hz), 105.2, 55.3, 51.9 (d, *J* = 17.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -129.81 (d, *J* = 14.7 Hz).

MS (EI, *m/z*, rel. intensity) 510 (M^+, 10.8), 197 (100); HRMS (EI) calcd for $C_{27}H_{23}O_5FS_2$ (M^+): 510.0971, Found: 510.0975.

IR (KBr): ν_{max} (cm^{-1}) = 3071, 1632, 1599, 1582, 1506, 1483, 1447, 1411, 1396, 1345, 1314, 1264, 1227, 1170, 1160, 1150, 1078, 1027, 1010, 965, 905, 853, 812, 761, 753, 687.



4ak

4ak: yellow oil, R_f = 0.4 (petroleum ether/ethyl acetate: 4/1); b/l: >99/1, 28% yield, 96% ee. [Diacel CHIRALPAK AD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R = 20.43 (major), 21.64 (minor) min].

$[\alpha]_D^{20}$ = +13.3°(c 0.5, $CHCl_3$).

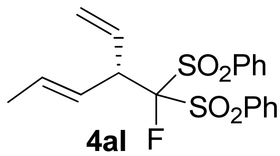
^1H NMR (300 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 7.8 Hz, 2H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.58-7.48 (m, 3H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 5.1 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.88-6.76 (m, 2H), 5.56 (d, *J* = 10.2 Hz, 1H), 5.46 (d, *J* = 16.8 Hz, 1H), 4.92 (t, *J* = 10.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.7, 136.6, 136.0, 134.9, 134.3, 131.31, 131.28, 131.24, 130.7, 130.6, 130.10, 130.08, 128.99, 128.70, 128.68, 128.63, 128.4, 126.5, 122.8, 115.1 (d, J = 267.7 Hz), 47.9 (d, J = 17.9 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ = -126.97 (d, J = 12.1 Hz).

MS (EI, *m/z*, rel. intensity) 123 (100); HRMS (EI) calcd for $C_{20}H_{17}O_4FS_3$ (M^+): 436.0273, Found: 436.0276.

IR (KBr): ν_{max} (cm^{-1}) = 3071, 2925, 1638, 1584, 1478, 1449, 1418, 1347, 1315, 1181, 1168, 1154, 1079, 999, 937, 912, 755, 734, 708, 685.



4al

4al: colorless oil, R_f = 0.4 (petroleum ether/ethyl acetate: 4/1); b/l: 84/16, 52% yield, 75% ee. [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 95/5; flow rate = 0.7 mL/min; detection wavelength = 230 nm; t_R = 26.34 (minor), 28.29 (major) min].

$[\alpha]_D^{20}$ = +13.7°(c 0.5, $CHCl_3$).

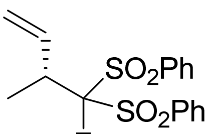
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.92-7.83 (m, 4H), 7.72-7.66 (m, 2H), 7.58-7.49 (m, 4H), 6.19 (ddd, J = 17.1, 10.2, 7.2 Hz, 1H), 5.66-5.46 (m, 2H), 5.24 (dd, J = 10.2, 1.2 Hz, 1H), 5.13 (d, J = 16.8 Hz, 1H), 3.88 (dd, J = 13.8, 6.9 Hz, 1H), 1.65 (d, J = 5.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 136.7, 136.2, 136.0, 135.22, 135.18, 134.99, 134.94, 132.0, 131.66, 131.59, 130.98, 130.91, 130.89, 130.4, 128.9, 128.8, 128.7, 123.47, 123.40, 119.9, 117.97, 117.88, 114.9 (d, J = 266.2 Hz), 50.5 (d, J = 18.3 Hz), 18.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ = -130.87 (d, J = 7.6 Hz).

MS (EI, *m/z*, rel. intensity) 77 (100); HRMS (EI) calcd for $C_{19}H_{19}O_4FS_2$ (M^+): 394.0709, Found: 394.0703.

IR (KBr): ν_{max} (cm^{-1}) = 3068, 2918, 2856, 1637, 1584, 1478, 1449, 1418, 1348, 1315, 1293, 1165, 1154, 1080, 998, 971, 930, 847, 755, 728, 686.



4am

4am: colorless oil, R_f = 0.3 (petroleum ether/ethyl acetate: 5/1); b/l: 87/13, 92% yield, 89% ee. [Diacel CHIRALPAK IC (0.46 cm x 25 cm); hexane/2-propanol = 80/20; flow rate = 0.7 mL/min; detection wavelength = 214 nm; t_R = 24.43 (major), 25.93 (minor) min].

$[\alpha]_D^{20}$ = +18.1°(c 1.0, $CHCl_3$).

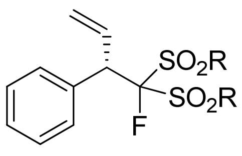
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88-7.84 (m, 4H), 7.71-7.65 (m, 2H), 7.53-7.47 (m, 4H), 6.09 (ddd, *J* = 17.6, 10.4, 3.6 Hz, 1H), 5.12 (d, *J* = 10.4 Hz, 1H), 5.01 (d, *J* = 17.2 Hz, 1H), 3.34-3.25 (m, 1H), 1.57 (dd, *J* = 7.2, 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.2, 135.7, 135.2, 135.1, 135.0, 134.9, 134.0, 133.9, 130.81, 130.79, 130.76, 128.94, 128.86, 128.81, 128.7, 118.7, 117.2, 114.6, 42.1 (d, *J* = 17.8 Hz), 14.5 (d, *J* = 5.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -130.81.

MS (EI, *m/z*, rel. intensity) 77 (100); HRMS (EI) calcd for $C_{17}H_{17}O_4FS_2$ (M^+): 368.0552, Found: 368.0546.

IR (KBr): ν_{max} (cm^{-1}) = 3069, 2950, 1639, 1584, 1478, 1449, 1419, 1347, 1315, 1292, 1163, 1153, 1079, 1046, 999, 931, 842, 755, 726, 685.



4ba R = 1-naphthyl

4ba: white powder, mp. = 93-97 °C; R_f = 0.4 (petroleum ether/ethyl acetate: 5/1); b/l: >99/1, 42% yield, 90% ee. [Diacel CHIRALPAK AD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm;

t_R = 34.22 (minor), 50.27 (major) min].

$[\alpha]_D^{20}$ = -50.3° (c 0.5, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.42-8.39 (m, 1H), 8.12 (d, *J* = 7.5 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.93-7.72 (m, 5H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.423-7.35 (m, 3H), 7.25-7.21 (m, 3H), 7.15-7.02 (m, 4H), 6.93 (ddd, *J* = 17.1, 9.9, 7.2 Hz, 1H), 5.46 (d, *J* = 10.2 Hz, 1H), 5.33 (d, *J* = 17.1 Hz, 1H), 4.82 (dd, *J* = 16.2, 9.3 Hz, 1H).

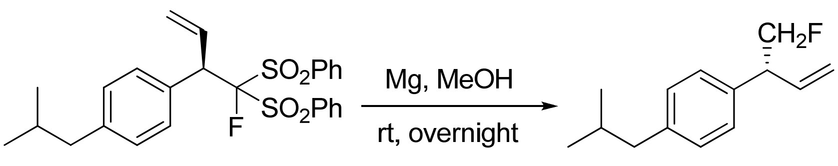
^{13}C NMR (75 MHz, $CDCl_3$) δ = 136.5, 136.2, 135.6, 134.8, 133.7, 133.5, 133.0, 132.1, 132.0, 131.9, 130.68, 130.65, 130.3, 130.15, 130.12, 128.54, 128.49, 128.42, 127.99, 127.93, 127.8, 126.8, 126.6, 125.4, 125.3, 124.9, 124.8, 124.0, 123.0, 121.0, 118.4 (d, *J* = 273.1 Hz), 52.4 (d, *J* = 16.7 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ = -131.23 (br).

MS (ESI, *m/z*, rel. intensity) 553 (MNa^+); HRMS (EI) calcd for $C_{30}H_{23}O_4FS_2Na$ (MNa^+): 553.0926, Found: 553.0914.

IR (KBr): ν_{max} (cm^{-1}) = 3060, 2924, 1593, 1565, 1506, 1453, 1337, 1198, 1164, 1129, 1028, 970, 932, 828, 806, 768, 697, 672.

Typical Procedure for the Reductive Desulfonylation of 4 with Mg/MeOH



(*R*)-**4af**
ee: 94%

(*R*)-**5af**
ee: 95%

Under argon atmosphere, Mg (360.8 mg, 15.0 mmol), (*R*)-**4af** (95% ee, 243.1 mg, 0.50 mmol) and MeOH (5.0 mL) was added in a dry Schlenk tube. The reaction mixture was stirred overnight at room temperature. When (*R*)-**4af** was fully consumed, monitored by TLC, the reaction was quenched with sat. NH_4Cl aq. and extracted with Et_2O (4 x 8 mL). The combined organic phase was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (Et_2O/*n*-hexane = 1/10) to give (*R*)-**5af** (91%

yield, 95% ee) as colorless liquid. The ee of the product was determined by HPLC. [Diacel CHIRALCEL OJ-H (0.46 cm x 25 cm); hexane/2-propanol = 1000/1; flow rate = 0.8 mL/min; detection wavelength = 214 nm; t_R = 10.32 (major), 11.37 (minor) min].

$[\alpha]_D^{20}$ = -41.2° (c = 1.0, $CHCl_3$) for (*R*)-**5af** and $[\alpha]_D^{20}$ = +41.8° (c = 1.3, $CHCl_3$, 95% ee) for (*S*)-**5af**.

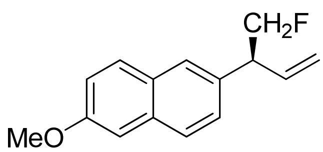
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.19 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.08 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.26 (d, *J* = 10.4 Hz, 1H), 5.23 (d, *J* = 16.8 Hz, 1H), 4.65 (dd, *J* = 47.2, 6.8 Hz, 2H), 3.75 (dt, *J* = 23.6, 6.8 Hz, 1H), 2.51 (d, *J* = 7.6 Hz, 2H), 1.97-1.84 (m, 1H), 0.96 (d, *J* = 6.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.5, 137.1 (d, *J* = 5.2 Hz), 136.5 (d, *J* = 6.0 Hz), 129.4, 127.7, 116.9, 85.6 (d, *J* = 174.0 Hz), 49.6 (d, *J* = 19.3 Hz), 45.0, 30.2, 22.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -216.96 (dt, *J* = 47.7, 16.9 Hz).

MS (EI, *m/z*, rel. intensity) 117 (100), 206 (M^+, 57); HRMS (EI) calcd for $C_{14}H_{19}F$ (M^+): 206.1471, Found: 206.1476.

IR(KBr): ν_{max} (cm^{-1}) = 3086, 2957, 2926, 2870, 1640, 1514, 1467, 1420, 1384, 1367, 1261, 1168, 1116, 1016, 996, 921, 845, 795.



(*S*)-**5aj**

(*S*)-**5aj** (90% yield, 95% ee) as colorless liquid. The ee of the product was determined by HPLC. [Diacel CHIRALCEL OJ-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R = 22.64 (minor), 24.01 (major) min].

$[\alpha]_D^{20}$ = +59.3° (c = 1.0, $CHCl_3$, 95% ee) for (*S*)-**5aj** and $[\alpha]_D^{20}$ = -59.2° (c = 1.0,

$CHCl_3$, 93% ee) for (*R*)-**5aj**.

[1]H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 5.6 Hz, 1H), 7.69 (d, *J* = 6.0 Hz, 1H), 7.61 (s, 1H), 7.32 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.15-7.11 (m, 2H), 6.10 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.25 (d, *J* = 11.2 Hz, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 4.70 (dd, *J* = 47.2, 6.4 Hz, 2H), 3.90 (s, 3H), 3.88-3.81 (m, 1H).

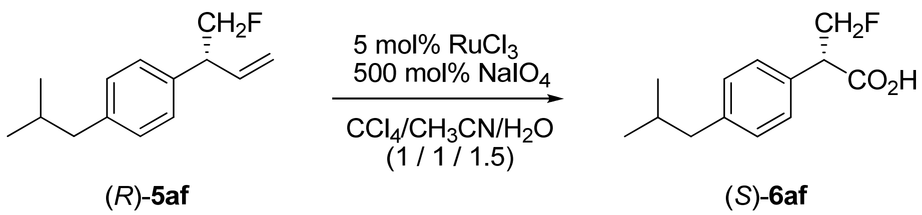
[13]C NMR (100 MHz, $CDCl_3$) δ = 157.6, 136.9 (d, *J* = 5.2 Hz), 134.4 (d, *J* = 5.2 Hz), 133.6, 129.2, 129.0, 127.2, 126.8, 126.6, 119.0, 117.2, 105.5, 85.6 (d, *J* = 173.2 Hz), 55.3, 49.8 (d, *J* = 19.3 Hz).

[19]F NMR (376 MHz, $CDCl_3$) δ = -216.96 (dt, *J* = 47.7, 16.9 Hz).

MS (EI, *m/z*, rel. intensity) 197 (100), 230 (M^+, 71); HRMS (EI) calcd for $C_{15}H_{15}OF$ (M^+): 230.1107, Found: 230.1104.

IR(KBr): ν_{max} (cm^{-1}) = 3061, 2963, 2851, 1637, 1608, 1508, 1484, 1392, 1262, 1214, 1176, 923, 854, 807.

Typical Procedure for $RuCl_3$ Catalyzed Oxidation of Alkene 5af to Carboxylic Acid 6af



The Sharpless procedure was followed: (*R*)-**5af** (95% ee, 41.7 mg, 0.2 mmol) and $NaIO_4$ (213.8 mg, 1.0 mmol) were mixed in a 1:1 mixture of CCl_4 and CH_3CN (2.0 mL). A solution of $RuCl_3$•(H_2O) (2.1 mg, 0.01 mmol) in H_2O (1.5 mL) was added to the flask and the reaction mixture was vigorously stirred. After the reaction was complete (1.5 h), Et_2O (5 mL) and sat. $NaHCO_3$(aq) (5 mL) was added. The organic phase was subsequently extracted with $NaHCO_3$(aq) (5 mL x 5). The aqueous phases were combined and concentrated HCl was carefully added at 0 °C until pH = 1. The product was extracted from the aqueous phase with CH_2Cl_2 (5 mL x 4) and the combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (EA/*n*-hexane = 1/1) to give (*S*)-**6af** in 91% yield as white solid.

$[\alpha]_D^{20}$ = +53.9° (c = 0.9, EtOH) for (*S*)-**6af** and $[\alpha]_D^{20}$ = -54.5° (c = 1.0, EtOH) for (*R*)-**6af**.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.11 (br s, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 4.93 (dt, *J* = 46.8, 9.2 Hz, 1H), 4.57 (ddd, *J* = 46.8, 9.2, 5.2 Hz, 1H), 4.01 (ddd, *J* = 17.6, 9.2, 5.2 Hz, 1H),2.45 (d, *J* = 7.2 Hz, 2H), 1.89-1.79 (m, 1H), 0.89 (d, *J* = 7.2 Hz, 6H).

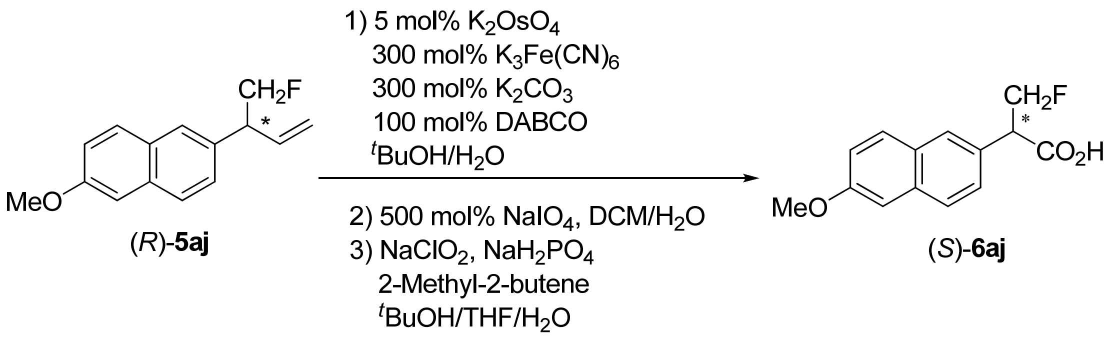
^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.7, 142.1, 130.2 (d, *J* = 8.2 Hz), 129.8, 127.9, 84.3 (d, *J* = 173.3 Hz), 51.7 (d, *J* = 20.9 Hz), 45.0, 30.1, 22.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -221.97 (dt, *J* = 46.2, 13.2 Hz).

MS (EI, *m/z*, rel. intensity) 117 (100), 224 (M^+, 32); HRMS (EI) calcd for $C_{13}H_{17}FO_2$ (M^+): 224.1213, Found: 224.1206.

IR(KBr): ν_{max} (cm^{-1}) = 2963, 1732, 1699, 1514, 1465, 1423, 1368, 1263, 1226, 1167, 1100, 1011, 801.

Typical Procedure for Oxidation of Alkene 5aj to Carboxylic Acid 6aj



A solution of (*R*)-**5aj** (63.1 mg, 0.27 mmol) in *tert*-butanol (2 mL) was added to an ice-cooled solution of potassium osmate(VI) dihydrate (4.9 mg, 0.013 mmol, 5 mol%), potassium hexacyanoferrate (III) (218.7 mg, 0.81 mmol, 300 mol%), potassium carbonate (111.8 mg, 0.81 mmol, 300 mol%) in water (2 mL). Then

DABCO (29.6 mg, 0.26 mmol, 100 mol%) was added and stirred at room temperature for 5 hours. After the reaction was complete, the mixture was extracted with CH_2Cl_2 (5 mL x 3). The combined organic phases were washed with water and brine, then dried over anhydrous Na_2SO_4. The sovents were removed under reduced pressure to give the crude mixture of *syn*- and *anti*-diols, which were used in the next step without purification.

The crude intermediate diols were dissolved in THF (3 mL) and a solution of sodium periodate (295.0 mg, 1.37 mmol, 500 mol%) in water (3 mL) was added at room temperature. After 30 min, water (5 mL) was added and extracted with CH_2Cl_2 (5 mL x 3). The combined organic phases were washed with water and brine, then dried over anhydrous Na_2SO_4. The sovents were removed under reduced pressure to give the crude product aldehyde, which was used in the next step without purification.

To an ice-cooled stirred solution of the above aldehyde in ^{t}BuOH/THF/H_2O (3:3:1), 2-methyl-2-butene (0.1 mL) was added. The solution of $NaClO_2$ (68.1 mg, 0.76 mmol) and NaH_2PO_4 (115.4 mg, 0.96 mmol) in water (1 mL) was dropped slowly. The reaction mixture was stirred for 4 h at rt. Then Et_2O (5 mL) was added, and the mixture was extracted with saturated aqueous $NaHCO_3$. The combined aqueous solution was slowly acidified with 2.0 M aqueous HCl at 0 °C to pH = 1, extracted with DCM (5 mL x 4). The combined organic layers were washed with water and brine, dried ($MgSO_4$), filtered and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (EA/PE = 4/1) to give (*S*)-**6aj** in 48% total yield over three steps as a white solid, mp.: 146-149 °C.

$[\alpha]_D^{20}$ = +65.9° (c = 0.5, $CHCl_3$) for (*S*)-**6aj**.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.74-7.69 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.17-7.11 (m, 2H), 5.03 (dt, *J* = 46.5, 9.0 Hz, 1H), 4.67 (ddd, *J* = 46.5, 9.3, 5.4 Hz, 1H), 4.22-4.13 (m, 1H), 3.91 (s, 3H).

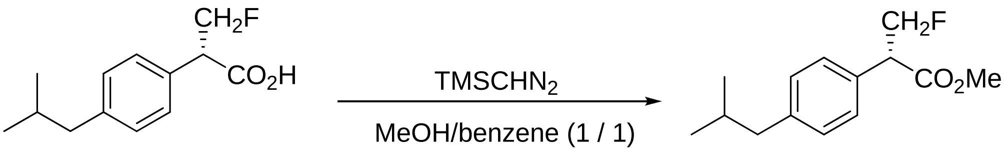
^{13}C NMR (75 MHz, $CDCl_3$) δ = 176.8, 158.0, 134.3, 129.4, 128.8, 128.1 (d, *J* = 8.0 Hz), 127.7, 127.3, 126.2, 119.4, 105.5, 83.3 (d, *J* = 173.3 Hz), 55.3, 51.9 (d, *J* = 21.0 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ = -216.50 (dt, *J* = 47.1, 13.5 Hz).

MS (EI, *m/z*, rel. intensity) 43 (100), 248 (M^+, 28); HRMS (EI) calcd for $C_{14}H_{13}O_3F$ (M^+): 253.0849, Found: 248.0853.

IR(KBr): ν_{max} (cm^{-1}) = 3066, 2962, 2850, 1731, 1686, 1605, 1057, 1485, 1394, 1267, 1227, 1175, 1159, 1027, 1016, 859, 818.

Procedure for Synthesis of Methyl Ester 7 Using Trimethylsilyldiazomethane



(*S*)-**6af** (*S*)-**7af**

Under argon atmosphere, (*S*)-**6af** (19.3 mg, 0.086 mmol) was dissolved in a 1:1 mixture of MeOH and benzene (2.0 mL). Trimethylsilyldiazomethane (0.10 mL, 2.0 M in diethyl ether, 0.20 mmol) was added slowly. Two drops of acetic acid was added after the reaction mixture was turned to yellow. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (R_f = 0.6, Et_2O/*n*-hexane = 1/10) to give (*S*)-**7af** (94% yield, 95% ee) as colorless liquid. The ee of the product was determined by HPLC. [Diacel CHIRALCEL OJ-H (0.46 cm x 25 cm); hexane/2-propanol = 95/5; flow rate = 0.6 mL/min; detection wavelength = 214 nm; t_R = 13.94 (minor), 14.78 (major) min].

$[\alpha]_D^{20}$ = +61.6° (c = 1.0, $CHCl_3$) for (*S*)-**7af** and $[\alpha]_D^{20}$ = -59.0° (c = 0.45, $CHCl_3$, 94% ee) for (*R*)-**7af**.

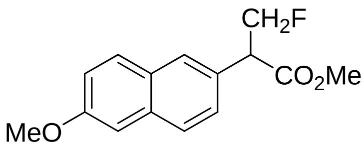
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.20 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 4.95 (dt, *J* = 46.5, 9.0 Hz, 1H), 4.55 (ddd, *J* = 46.5, 9.0, 5.4 Hz, 1H), 4.00 (ddd, *J* = 17.1, 9.3, 5.4 Hz, 1H), 3.73 (s, 3H), 2.45 (d, *J* = 6.9 Hz, 2H), 1.91-1.77 (m, 1H), 0.89 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 171.8 (d, *J* = 2.9 Hz), 141.8, 130.7 (d, *J* = 8.6 Hz), 129.7, 127.8, 83.7 (d, *J* = 173.5 Hz), 52.3, 51.7 (d, *J* = 21.2 Hz), 45.0, 30.1, 22.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ = -215.88 (dt, *J* = 46.0, 12.4 Hz).

MS (EI, *m/z*, rel. intensity) 43 (100), 238 (M^+, 32); HRMS (EI) calcd for $C_{14}H_{19}FO_2$ (M^+): 238.1369, Found: 238.1371.

IR(KBr): ν_{max} (cm^{-1}) = 2958, 2927, 2870, 1743, 1513, 1463, 1437, 1385, 1352, 1258, 1206, 1167, 1100, 1010, 796.



7aj

(*R*)-**7aj**: White solid, mp.: 83-86 °C; R_f = 0.6, EA/PE = 1/20; 97% yield. The ee of the product was determined by HPLC. [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 99/1; flow rate = 0.8 mL/min; detection wavelength = 254 nm; t_R = 19.54 (major), 30.31 (minor) min].

$[\alpha]_D^{20}$ = +43° (c = 0.1, $CHCl_3$, 93% ee) for (*S*)-**7aj** and $[\alpha]_D^{20}$ = -46° (c = 0.25, $CHCl_3$, 96% ee) for (*R*)-**7aj**.

^1H NMR (400 MHz, $CDCl_3$) δ = 7.73-7-69 (m, 2H), 7.37 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.18-7.11 (m, 2H), 5.04 (dt, *J* = 46.4, 8.4 Hz, 1H), 4.65 (ddd, *J* = 46.8, 9.2, 5.6 Hz, 1H), 4.15 (ddd, *J* = 14.0, 9.2, 5.6 Hz, 1H), 3.92 (s, 3H), 3.74 (s, 3H).

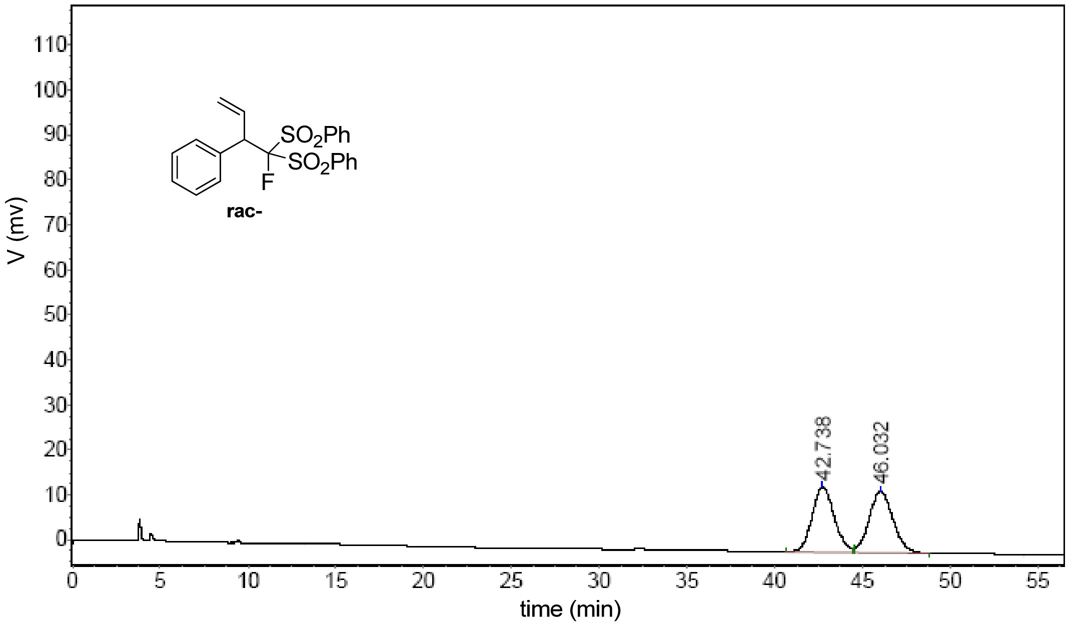
^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.8, 158.0, 134.2, 129.3, 128.7 (d, *J* = 9.1 Hz), 127.6, 127.1, 126.3, 119.4, 105.6, 83.7 (d, *J* = 173.7 Hz), 55.4, 52.4, 52.0 (d, *J* = 21.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -215.90 (dt, *J* = 46.2, 12.8 Hz).

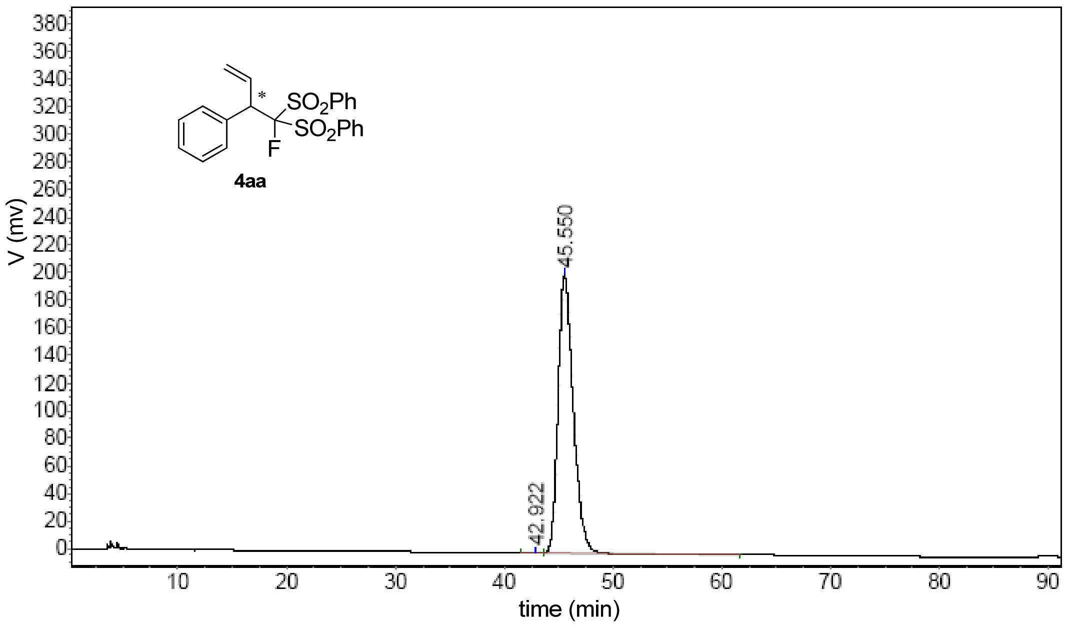
MS (EI, *m/z*, rel. intensity) 203 (100), 262 (M^+, 78); HRMS (EI) calcd for $C_{15}H_{15}FO_3$ (M^+): 262.1005, Found: 262.1002.

IR(KBr): ν_{max} (cm^{-1}) = 2964, 2852, 1733, 1631, 1605, 1504, 1485, 1448, 1391, 1352, 1317, 1262, 1222, 1200, 1174, 1099, 1021, 858, 821, 803.

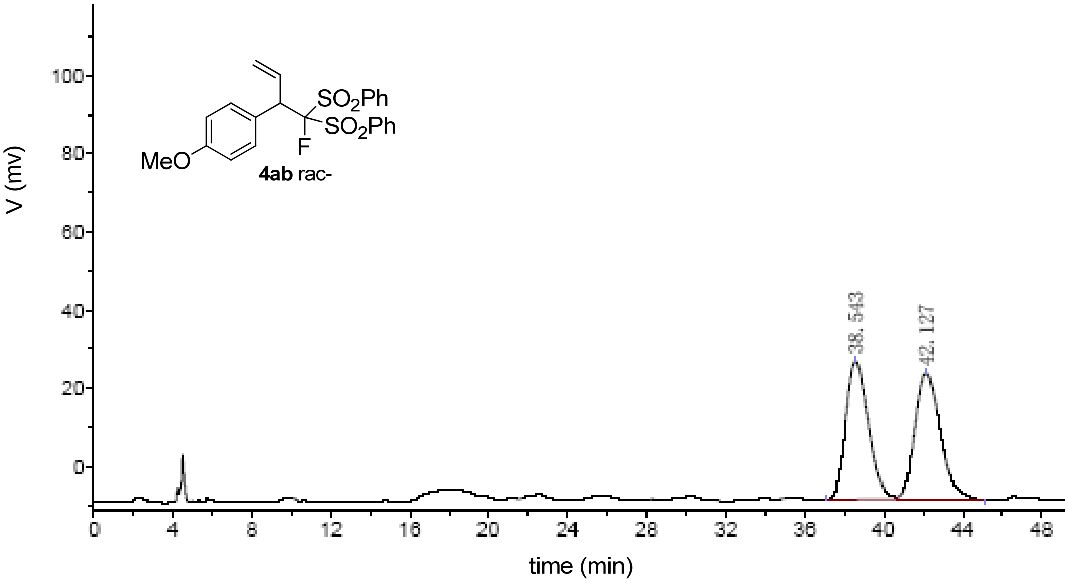
HPLC Spectra of the Chiral Compounds



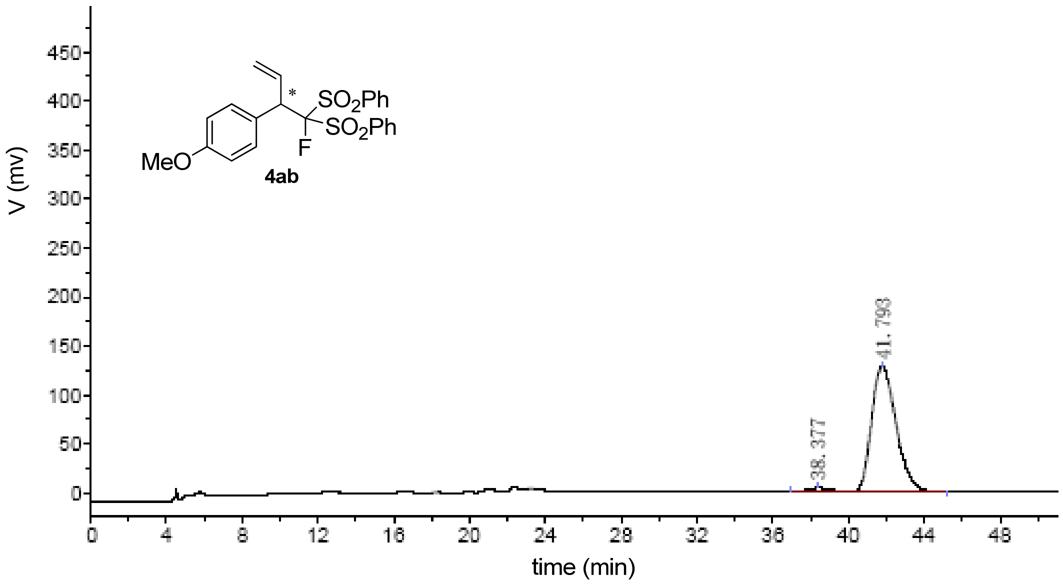
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	42.738	14508.560	1276202.625	49.6515
2	46.082	13659.488	1294116.250	50.3485
Total		28168.048	2570318.875	100.0000



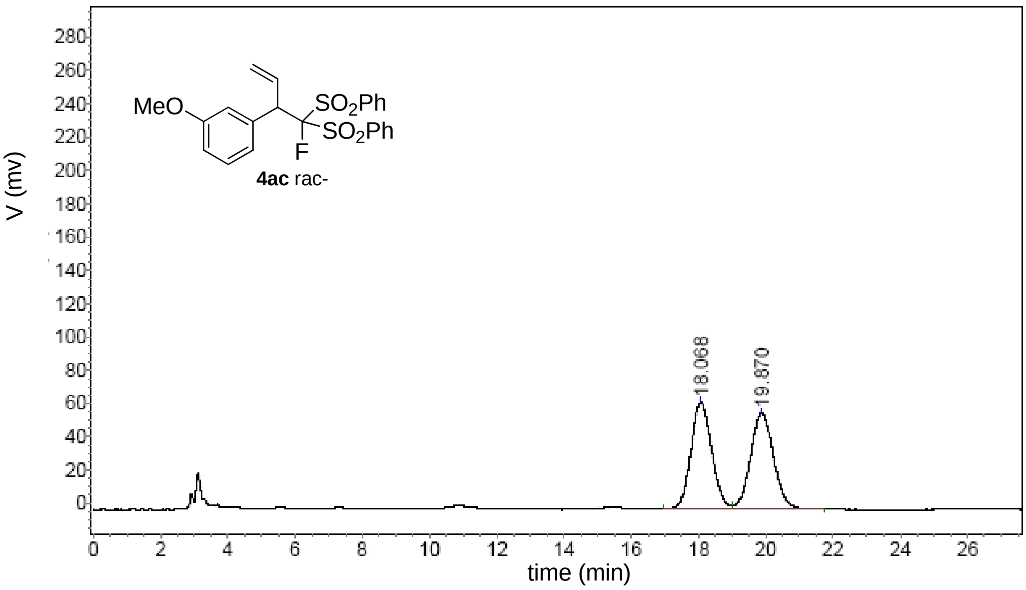
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	42.922	466.937	33664.262	0.1711
2	46.550	202022.797	19639490.000	99.8289
Total		202489.734	19673154.262	100.0000



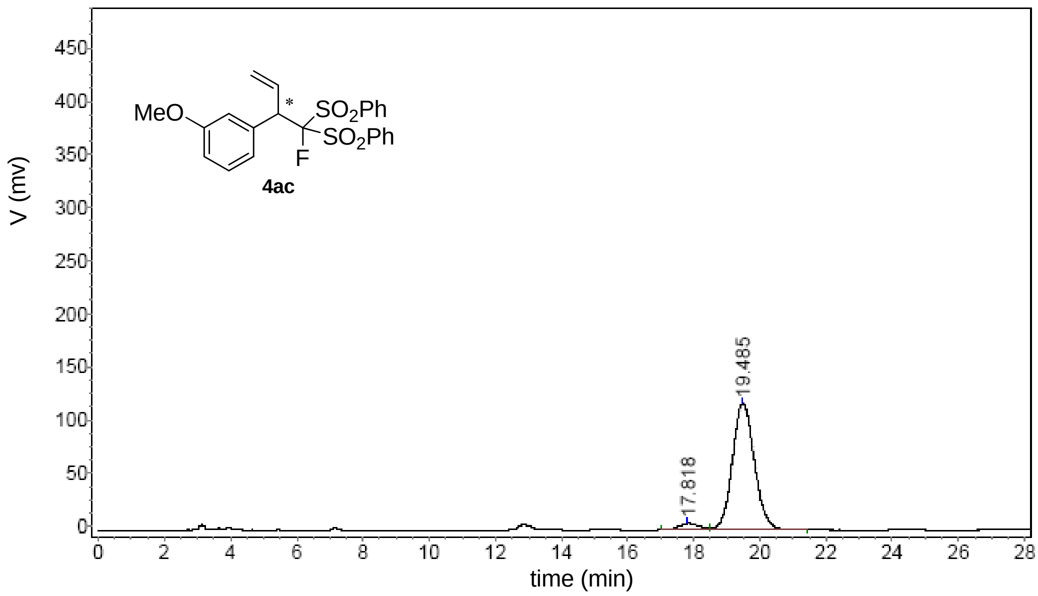
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	38.543	35406.3	2889574.9	49.9799
2	42.127	32124.2	2891903.5	50.0201
Total		67530.5	5781478.4	100.0000



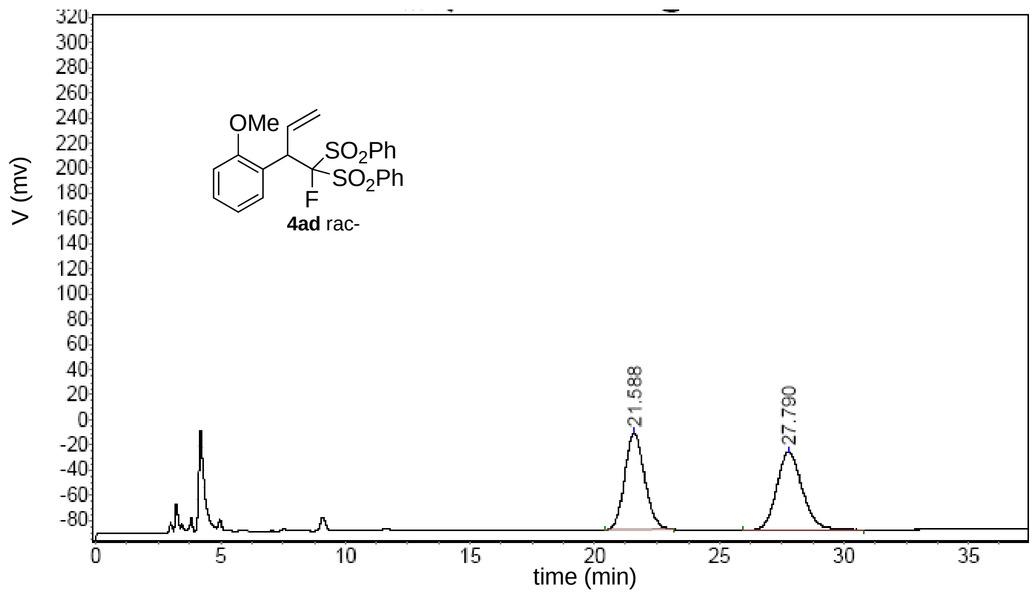
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	38.377	3476.7	299141.2	2.5459
2	41.793	127201.7	11450786.6	97.4541
Total		67530.5	11749928.8	100.0000



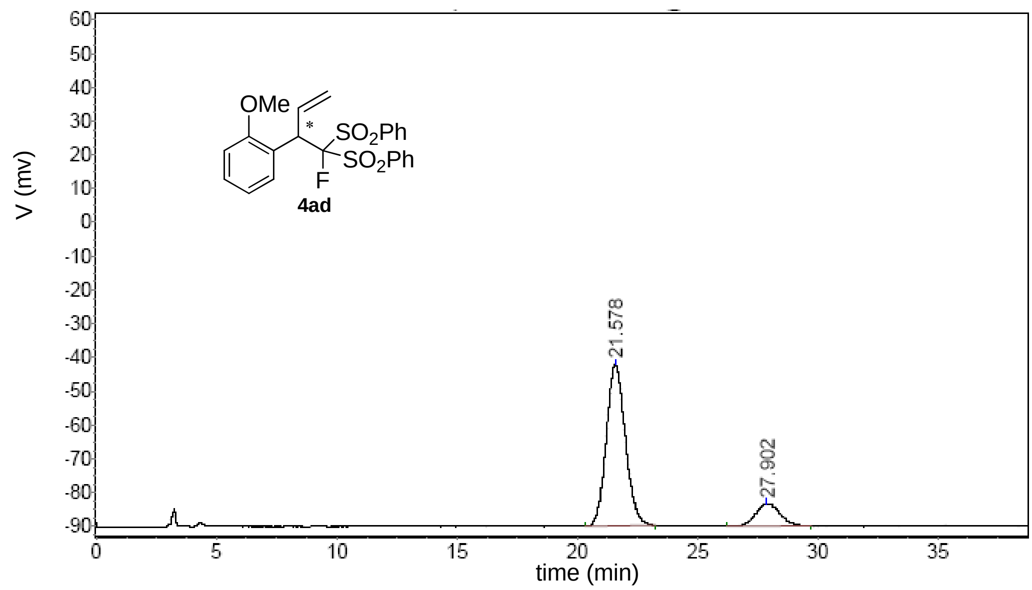
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	18.068	64342.137	2748665.750	50.1934
2	19.870	57482.431	2727480.250	49.8066
Total		121824.598	5476146.000	100.0000



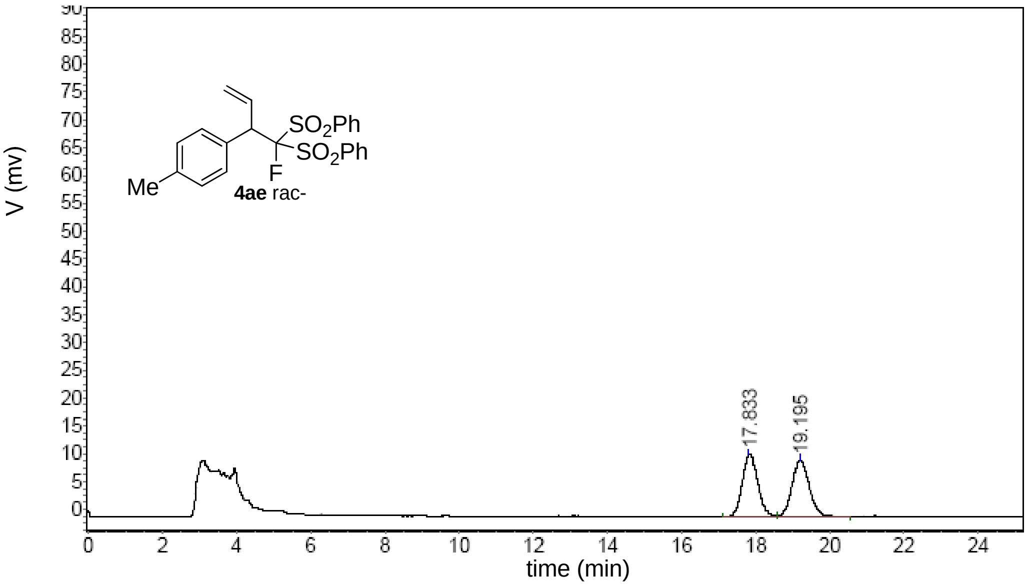
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	17.818	5747.666	268509.531	4.6441
2	19.485	118863.297	5513226.000	95.3559
Total		124610.962	5781735.531	100.0000



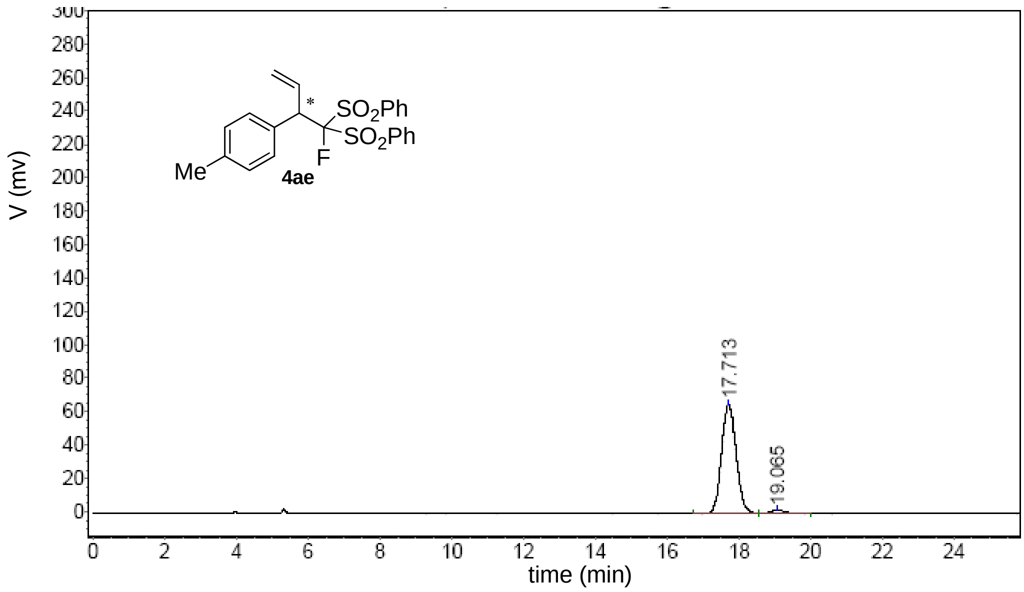
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	21.588	77178.898	4249509.000	49.3879
2	27.790	61728.926	4354850.000	50.6121
Total		138907.824	8604359.000	100.0000



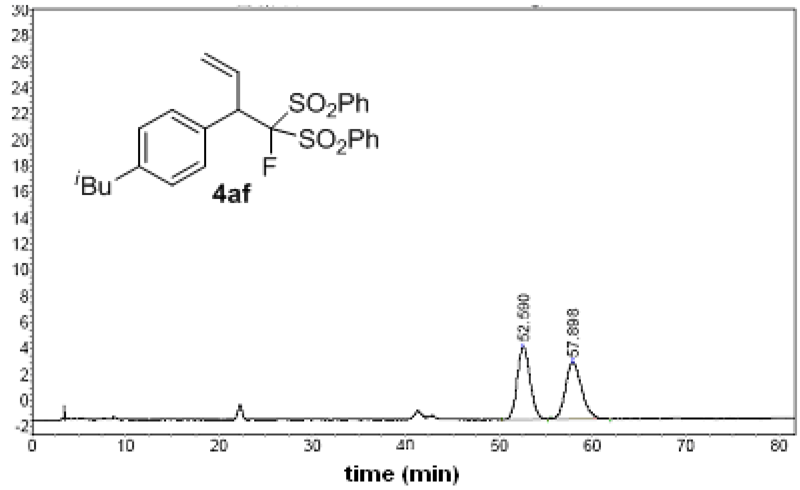
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	21.578	47841.074	2665587.000	84.6815
2	27.902	6682.854	482193.125	15.3185
Total		54523.928	3147780.125	100.0000



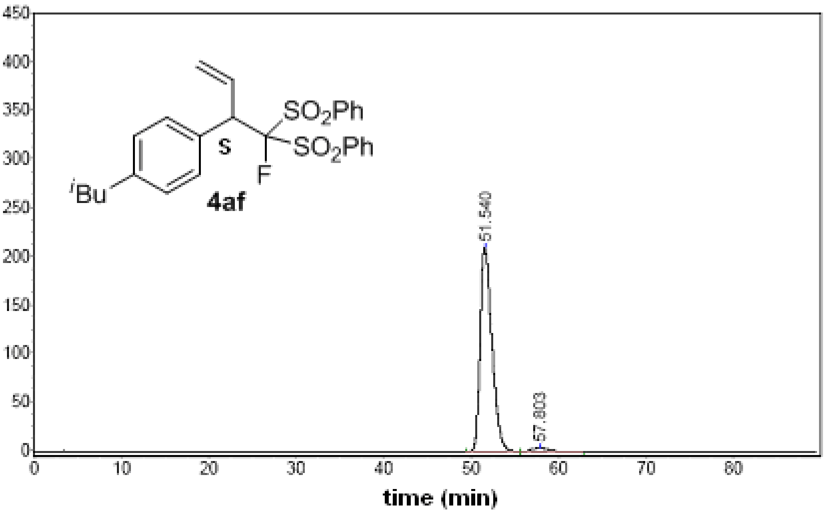
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	17.833	11233.765	324813.656	49.7130
2	19.195	10198.907	328563.781	50.2870
Total		138907.824	653377.438	100.0000



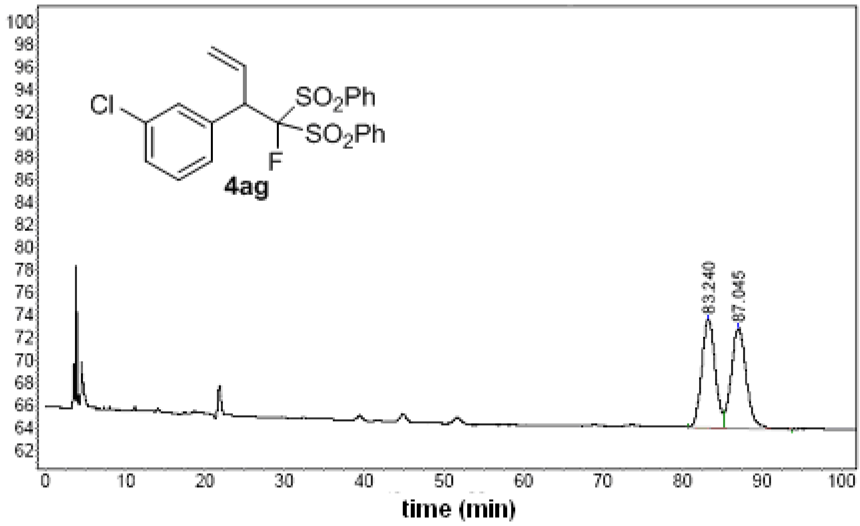
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	17.713	65508.227	1838586.000	96.8537
2	19.065	1847.718	59726.160	3.1463
Total		67355.944	1898312.160	100.0000



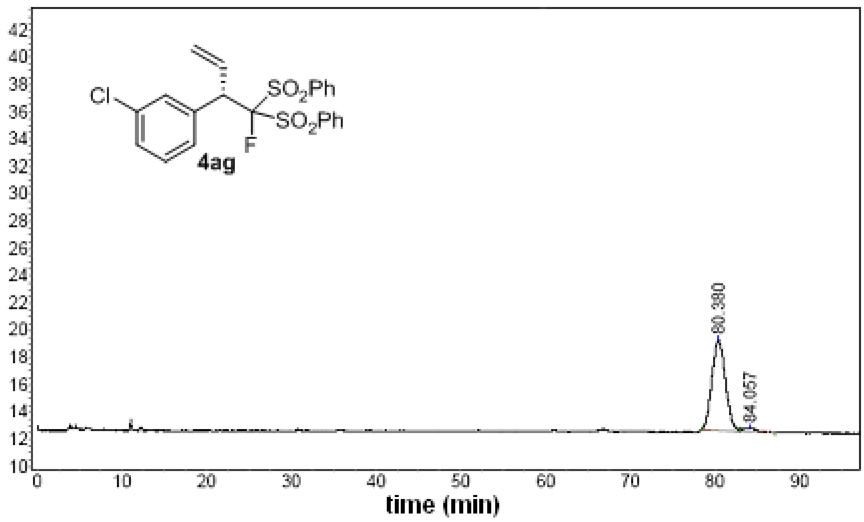
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	52.590	5592.430	537667.625	50.3741
2	57.898	4342.954	529681.750	49.6259
Total		9935.384	1067349.375	100.0000



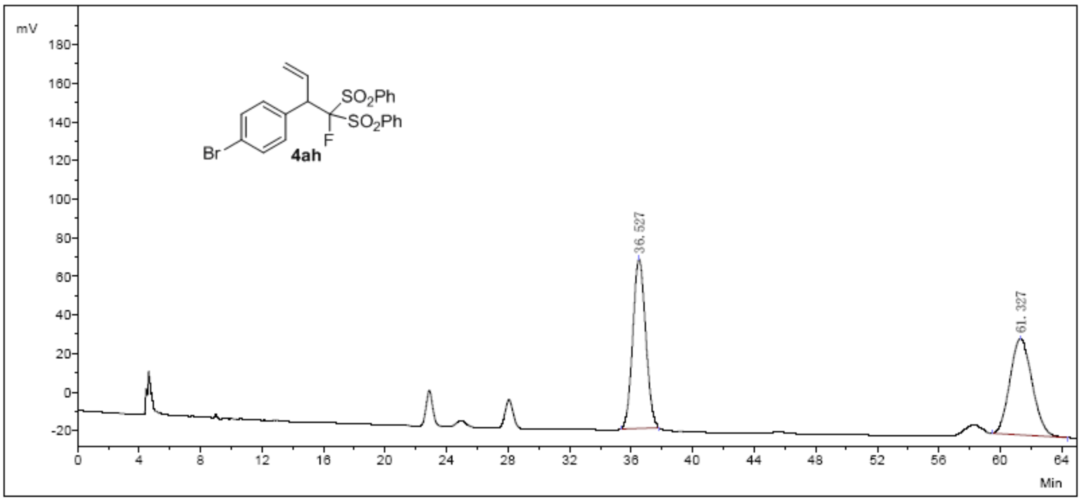
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	51.540	210701.891	19717642.000	97.4694
2	57.803	4054.494	511920.344	2.5306
Total		214756.385	20229562.344	100.0000



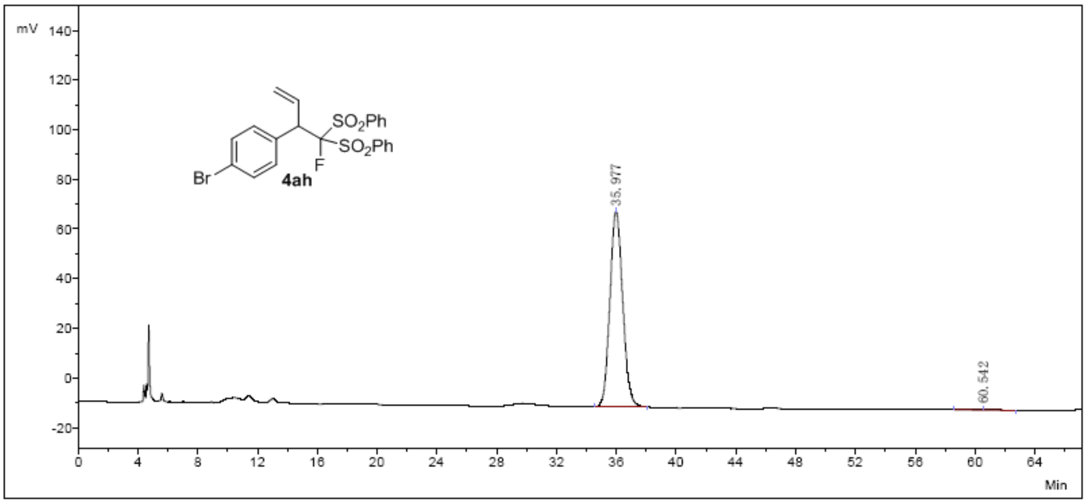
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	83.240	9612.902	1132713.750	49.3069
2	87.045	8889.600	1164560.250	50.6931
Total		18502.502	2297274.000	100.0000



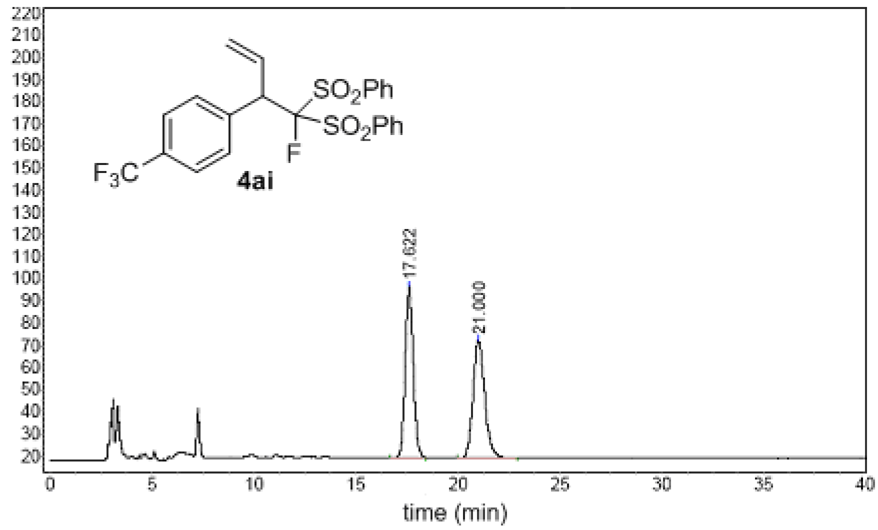
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	80.380	6616.428	731023.875	96.7865
2	84.057	228.847	24271.334	3.2135
Total		6845.275	755295.209	100.0000



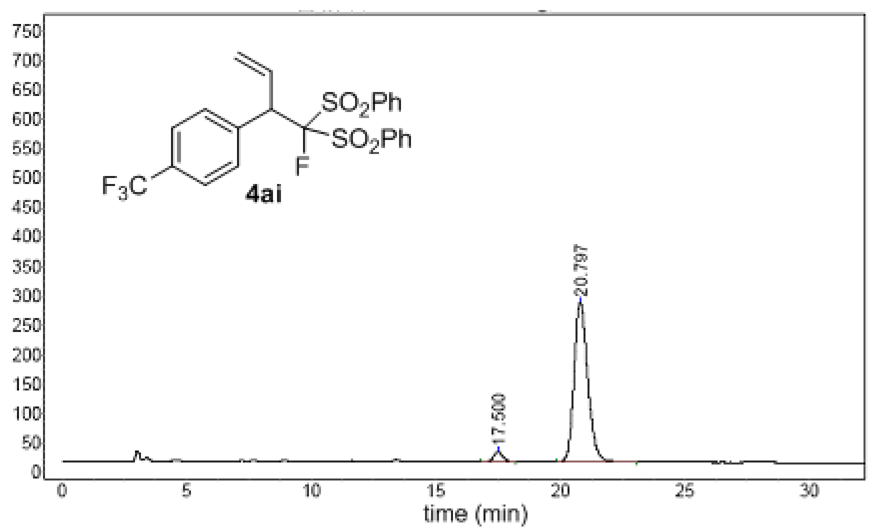
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	36.527	87627.4	5130990.9	50.5558
2	2	61.327	49891.3	5018165.2	49.4442
Total			137518.8	10149156.1	100.0000



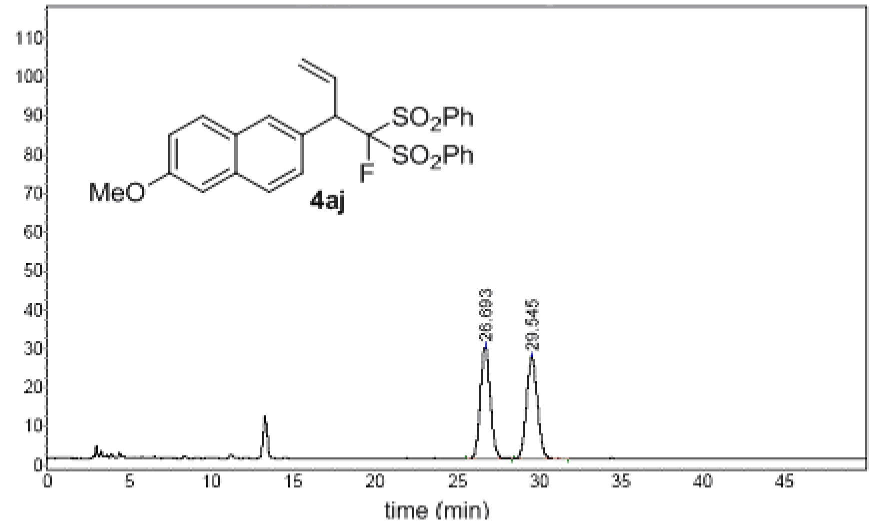
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	35.977	78773.4	4697376.0	99.5782
2	2	60.542	204.9	19895.4	0.4218
Total			78978.2	4717271.4	100.0000



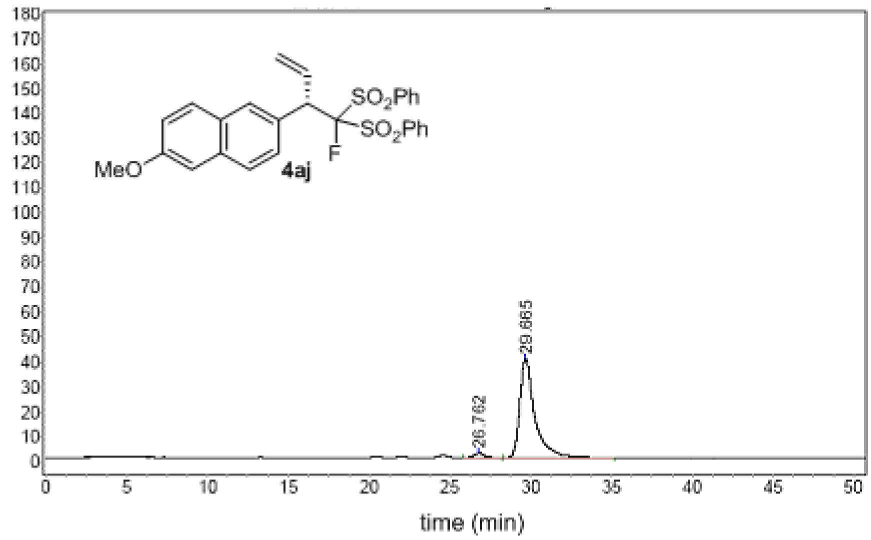
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	17.622	77478.117	2135268.000	50.1940
2	21.000	53082.602	2118764.000	49.8060
Total		130560.719	4254032.000	100.0000



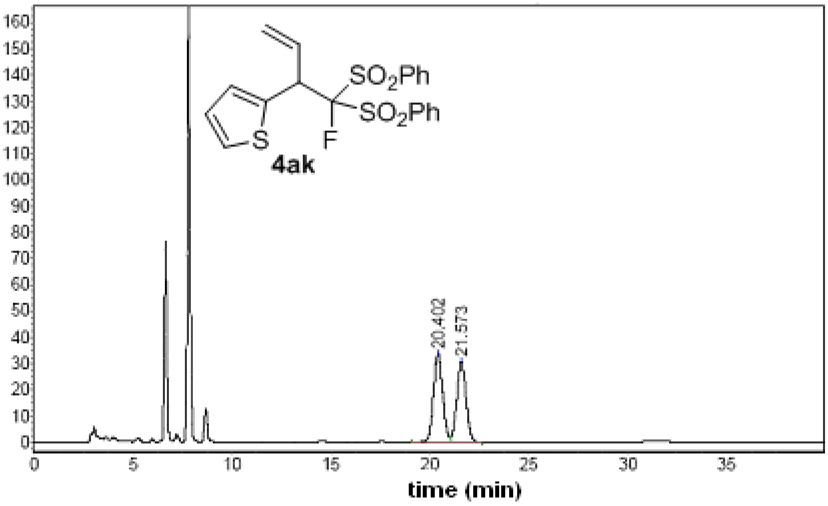
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	17.500	18438.518	500924.063	4.5930
2	20.797	271715.906	10405259.000	95.4070
Total		290154.424	10906183.063	100.0000



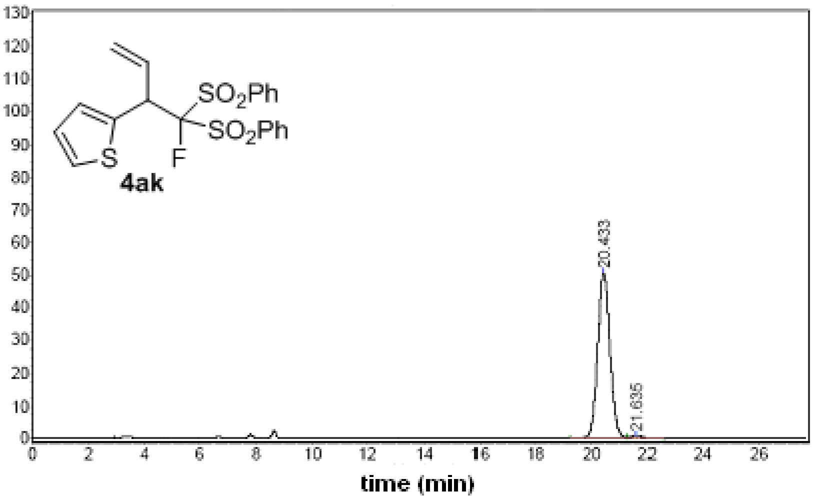
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	26.693	28896.637	1236599.875	50.0374
2	29.545	26301.602	1234752.875	49.9626
Total		55198.238	2471352.750	100.0000



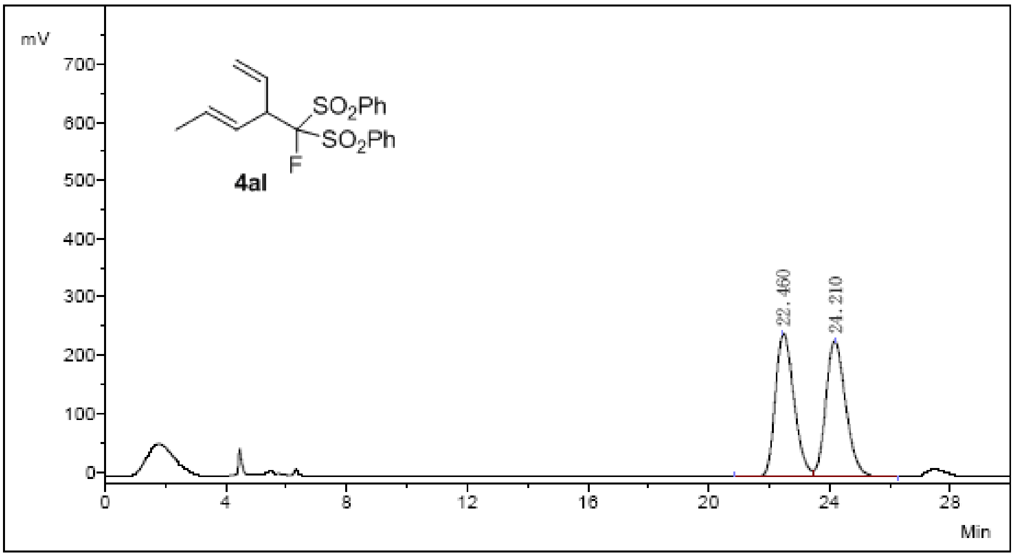
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	26.762	1973.397	88961.500	3.2937
2	29.665	39979.949	2612012.750	96.7063
Total		41953.346	2700974.250	100.0000



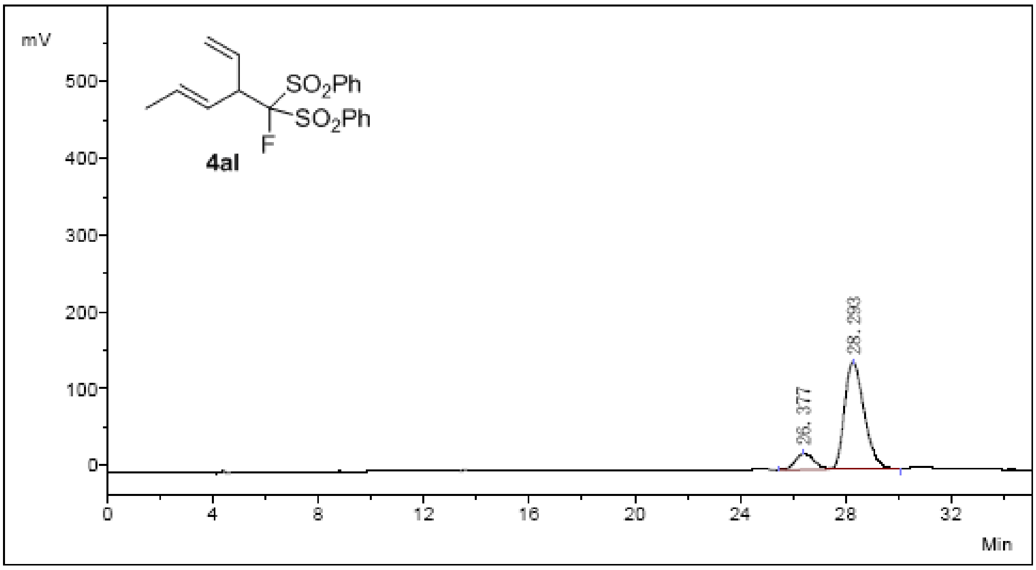
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	20.402	33605.395	1063947.750	51.2715
2	21.573	30841.543	1011177.938	48.7285
Total		64446.938	2075125.688	100.0000



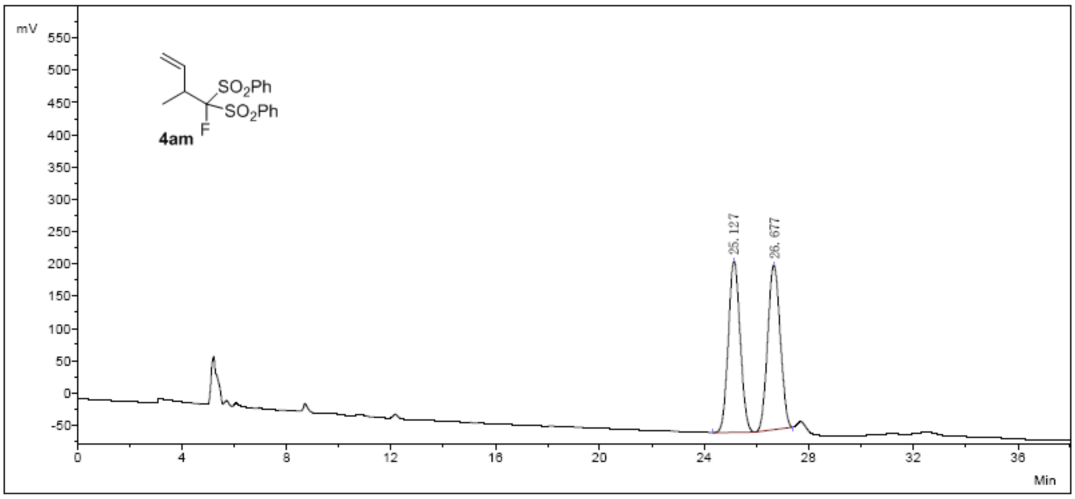
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	20.433	50673.953	1592095.000	98.2206
2	21.635	850.246	28843.459	1.7794
Total		51524.199	1620938.459	100.0000



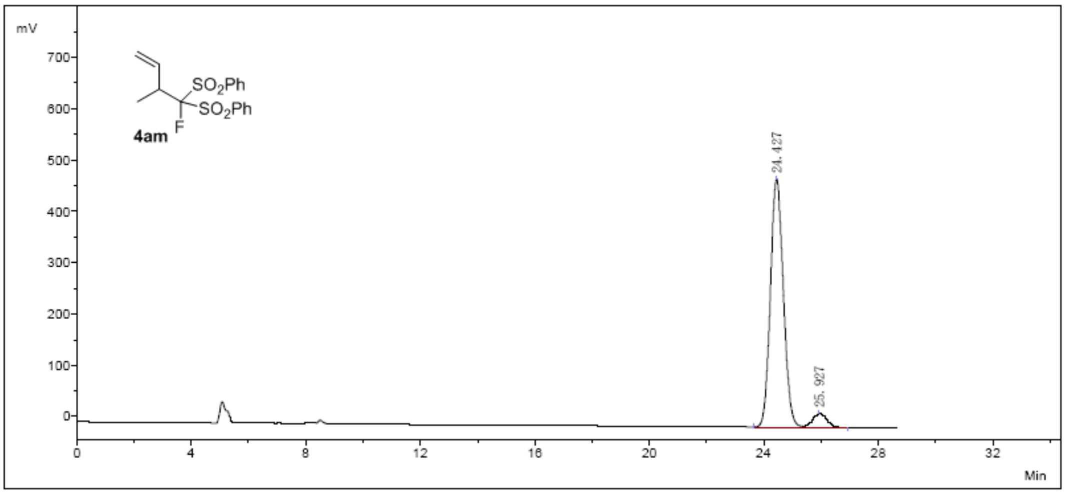
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	22.460	244112.6	10521258.4	49.7268
2	2	Unknown	24.210	231268.3	10636877.9	50.2732
Total				475380.9	21158136.3	100.0000



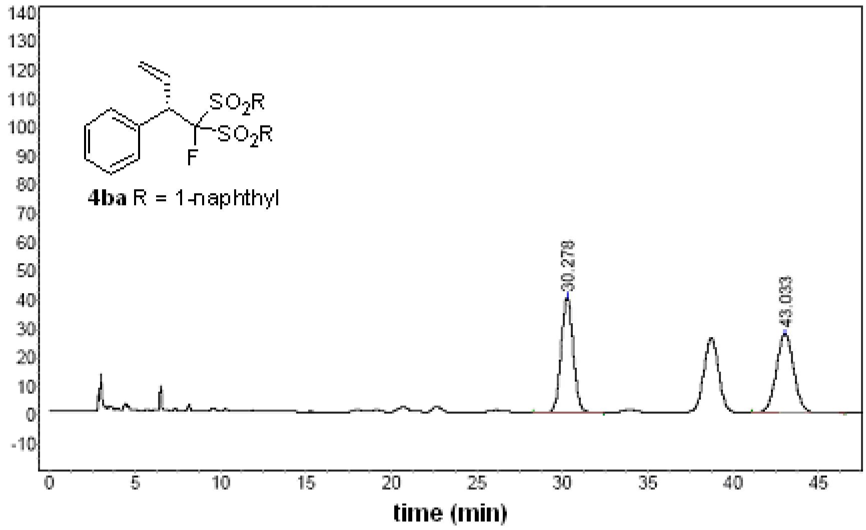
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	26.377	20794.5	1028813.1	12.4052
2	2	Unknown	28.293	139317.3	7264559.2	87.5948
Total				160111.8	8293372.3	100.0000



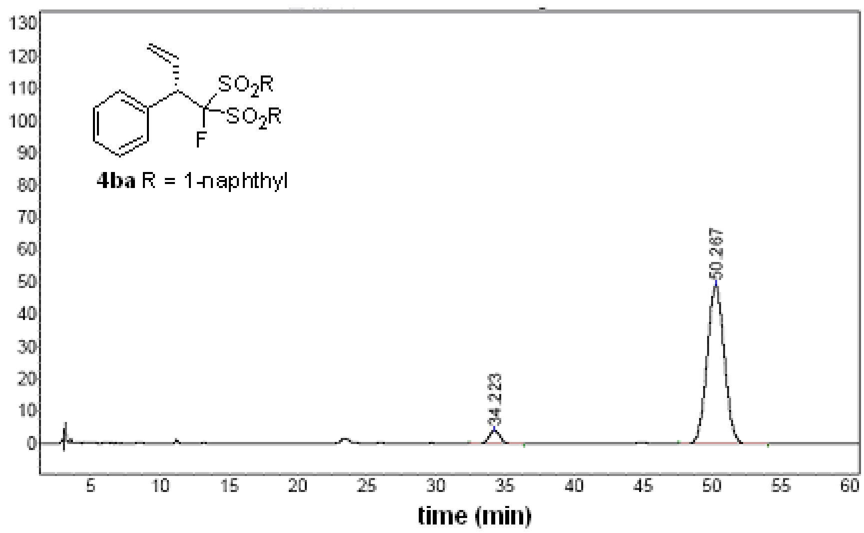
No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	25.127	265256.0	8389538.4	49.5343
2	2	26.677	254686.6	8547304.6	50.4657
Total			519942.6	16936843.0	100.0000



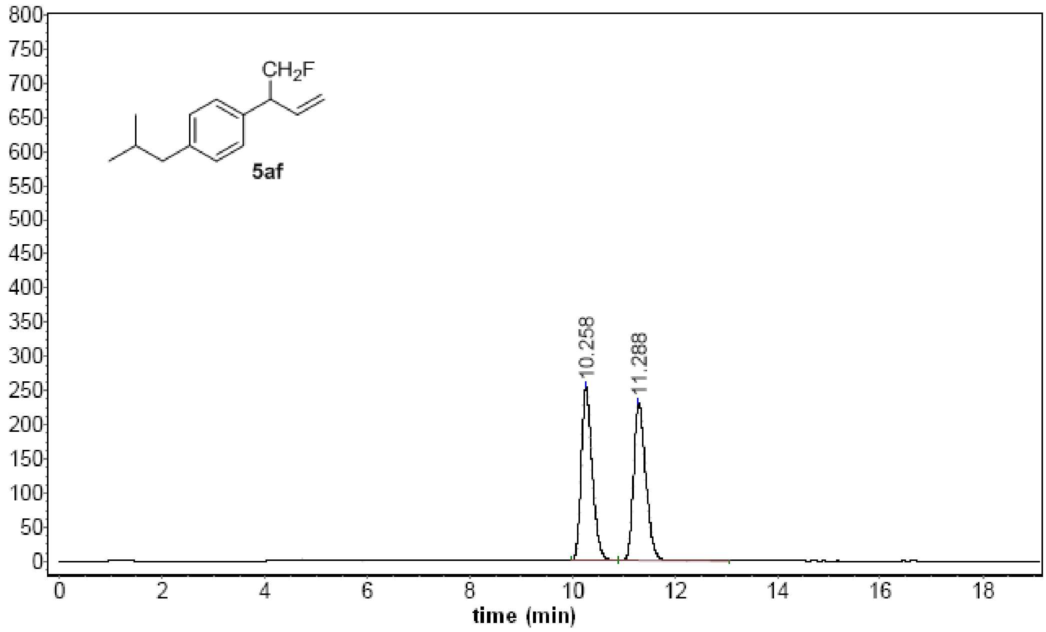
No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	24.427	482047.5	15159209.5	94.3206
2	2	25.927	26553.9	912787.2	5.6794
Total			508601.4	16071996.7	100.0000



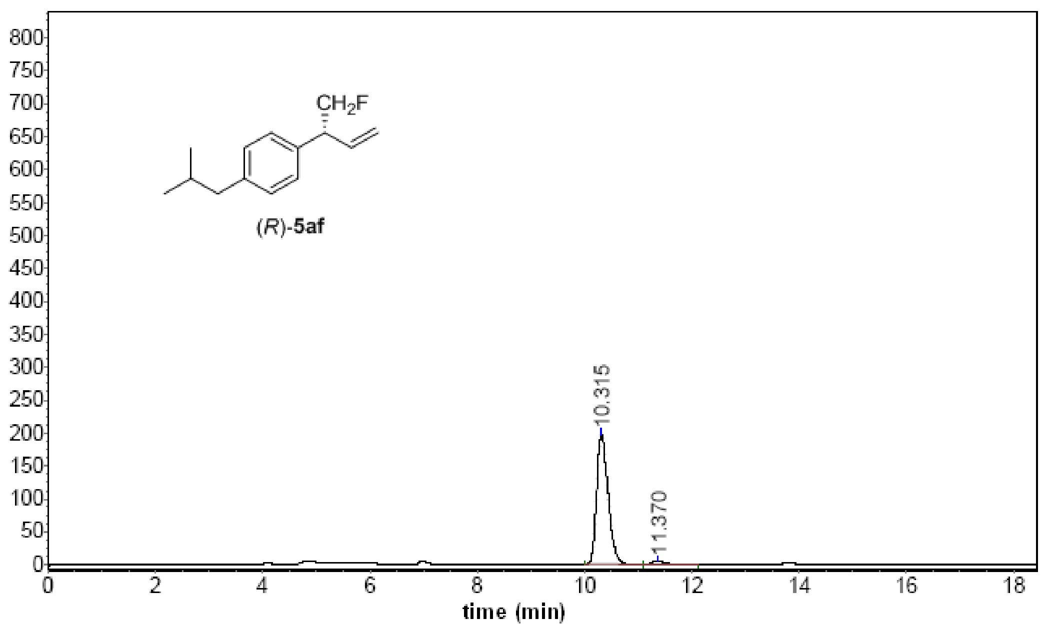
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	30. 278	39883. 387	1944295. 125	50. 0713
2	43. 033	27282. 225	1938758. 750	49. 9287
Total		67165. 611	3883053. 875	100. 0000



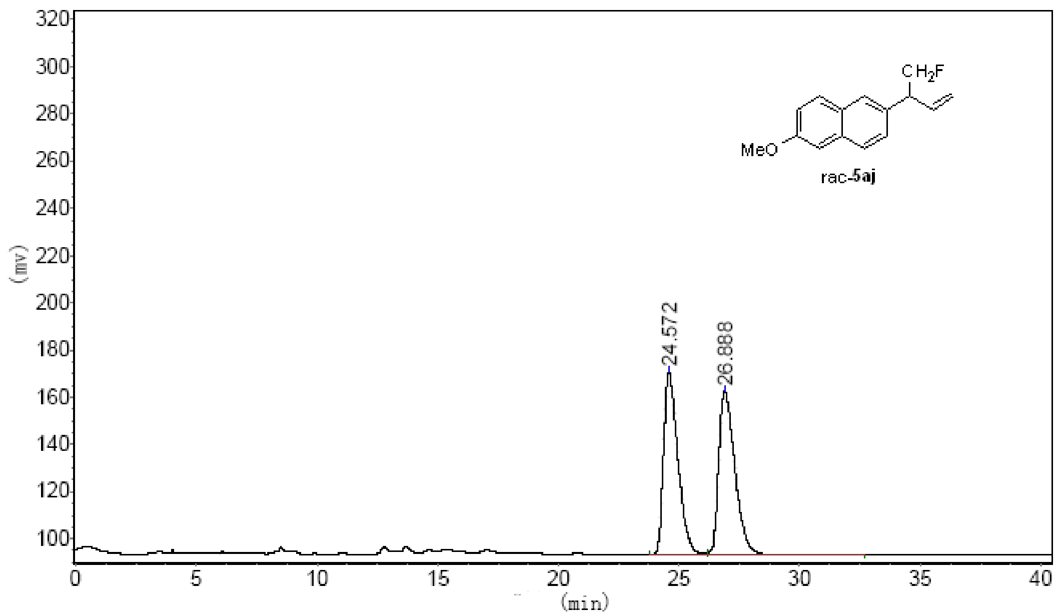
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	34. 223	4096. 642	235412. 797	5. 2082
2	50. 267	49288. 742	4284658. 500	94. 7918
Total		53385. 384	4520071. 297	100. 0000



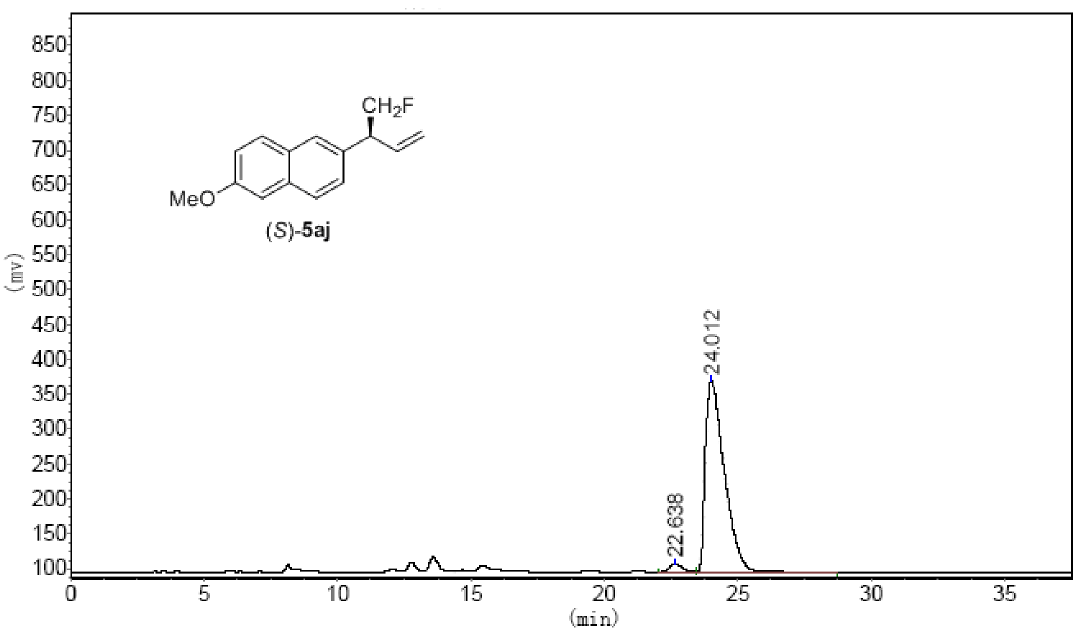
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	10. 258	254462. 484	3780591. 250	49. 9259
2	11. 288	230217. 672	3791809. 500	50. 0741
Total		484680. 156	7572400. 750	100. 0000



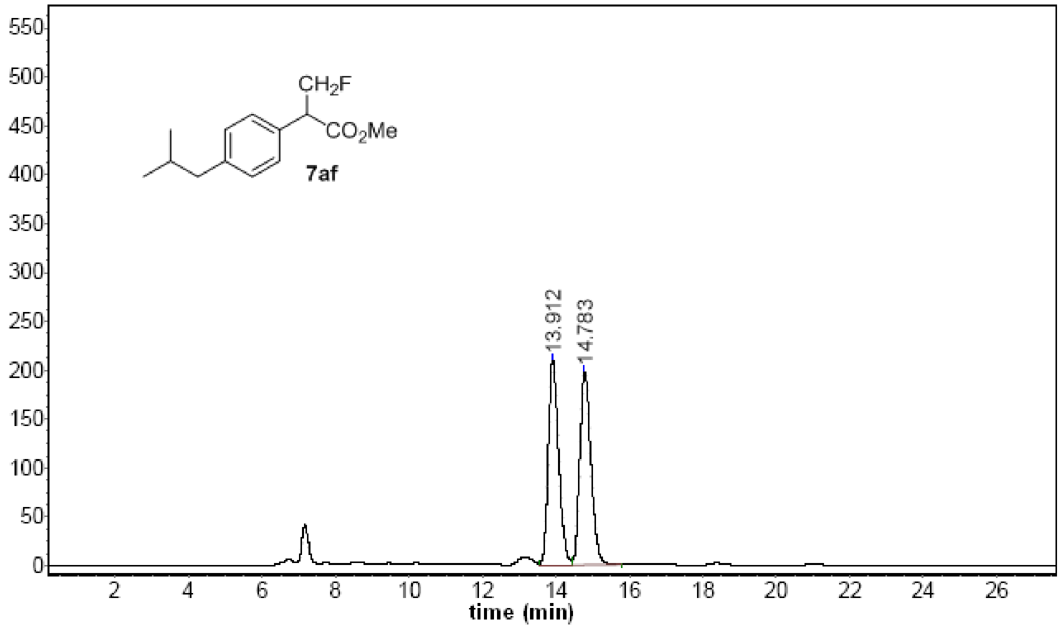
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	10. 315	197541. 828	2924663. 500	97. 4630
2	11. 370	4626. 288	76129. 477	2. 5370
Total		202168. 116	3000792. 977	100. 0000



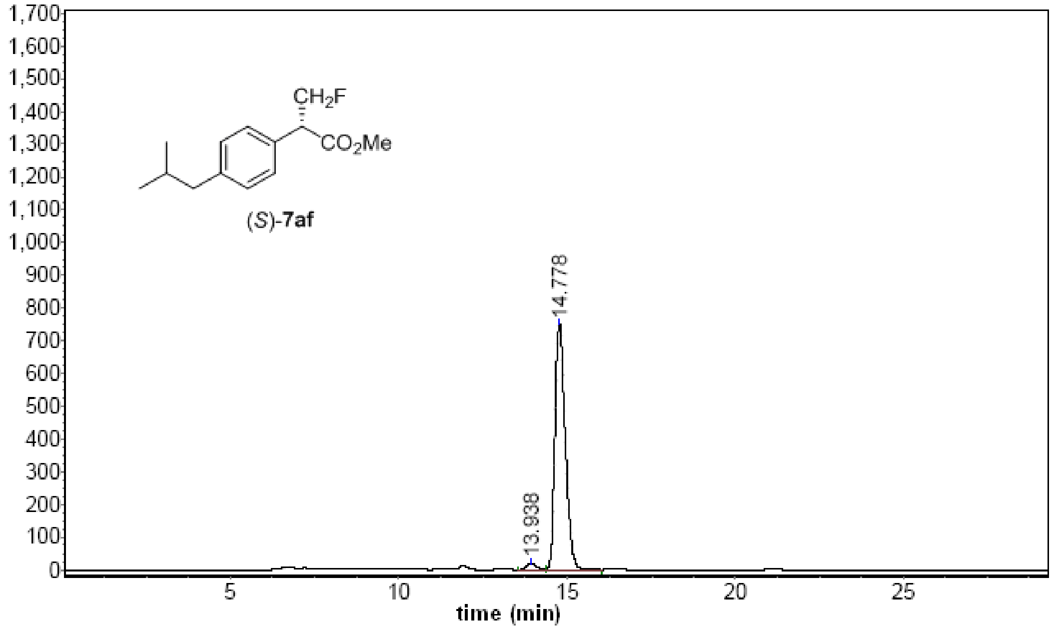
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	24. 572	77156. 242	3195651. 750	49. 8436
2	26. 888	69214. 492	3215711. 500	50. 1564
Total		146370. 734	6411363. 250	100. 0000



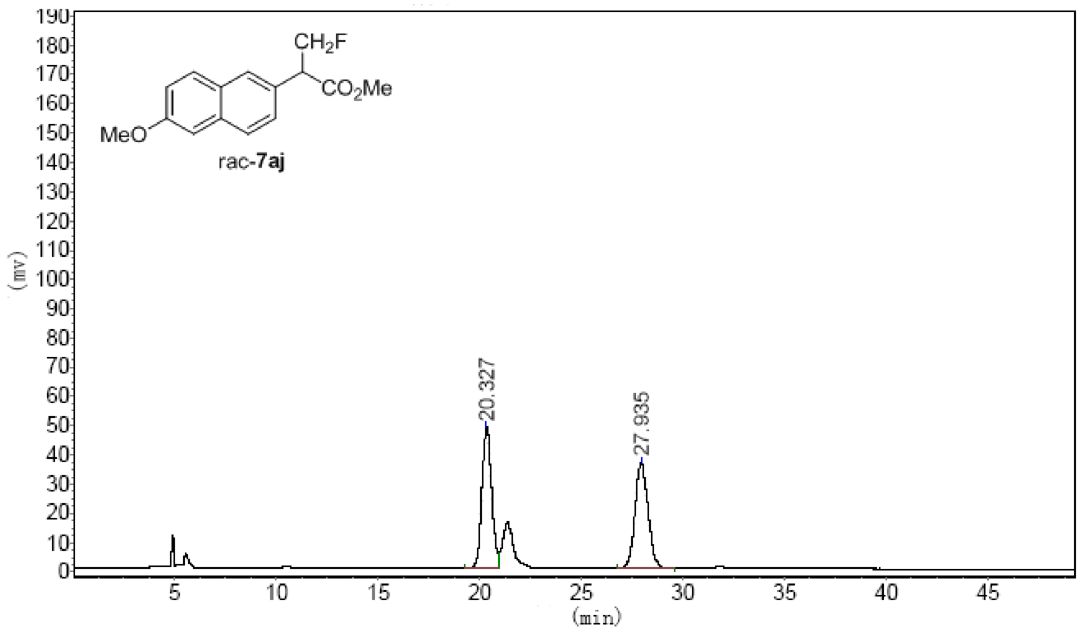
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	22. 638	10715. 069	347577. 688	2. 4989
2	24. 012	274551. 375	13561879. 000	97. 5011
Total		285266. 444	13909456. 688	100. 0000



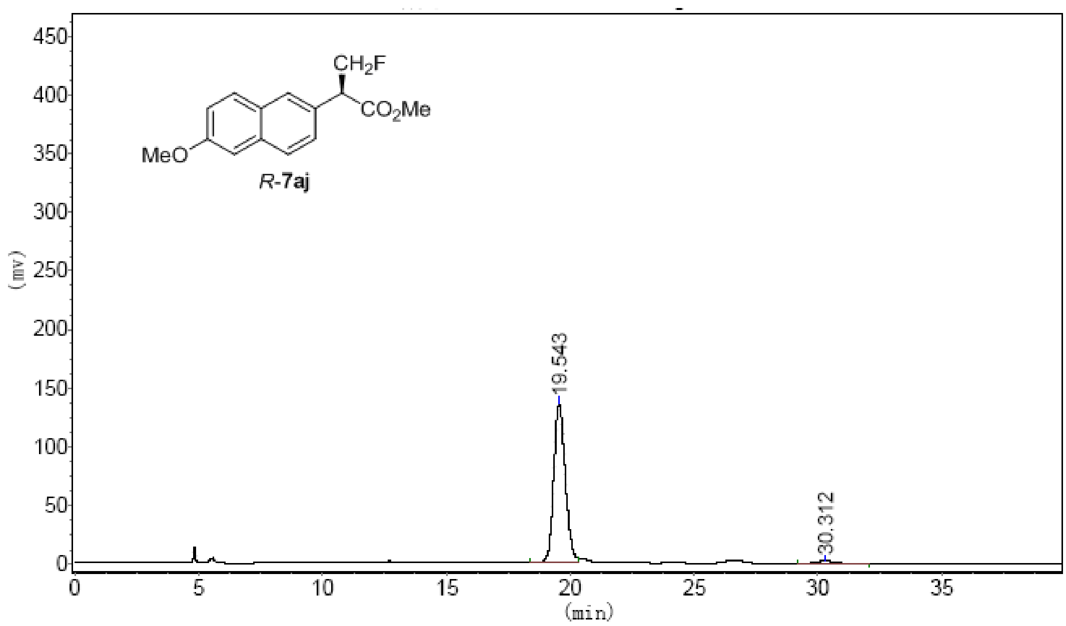
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13.912	209820.000	4133430.000	50.0530
2	14.783	198113.109	4124671.750	49.9470
Total		407933.109	8258101.750	100.0000



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13.938	20396.313	403829.531	2.4795
2	14.778	749562.375	15883202.000	97.5205
Total		769958.688	16287031.531	100.0000



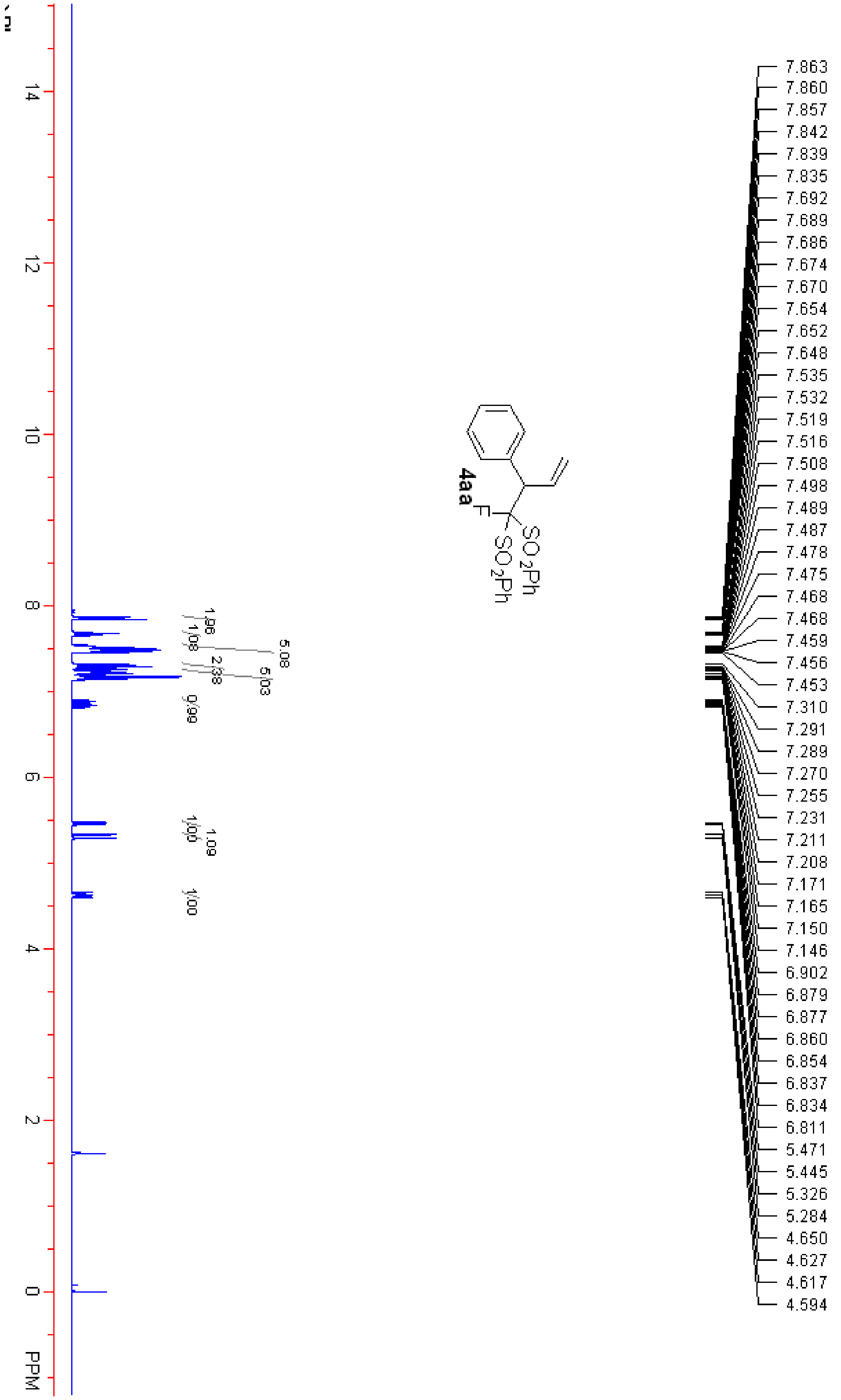
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	20.327	48213.105	1591737.250	49.7375
2	27.935	36243.254	1608539.750	50.2625
Total		84456.359	3200277.000	100.0000



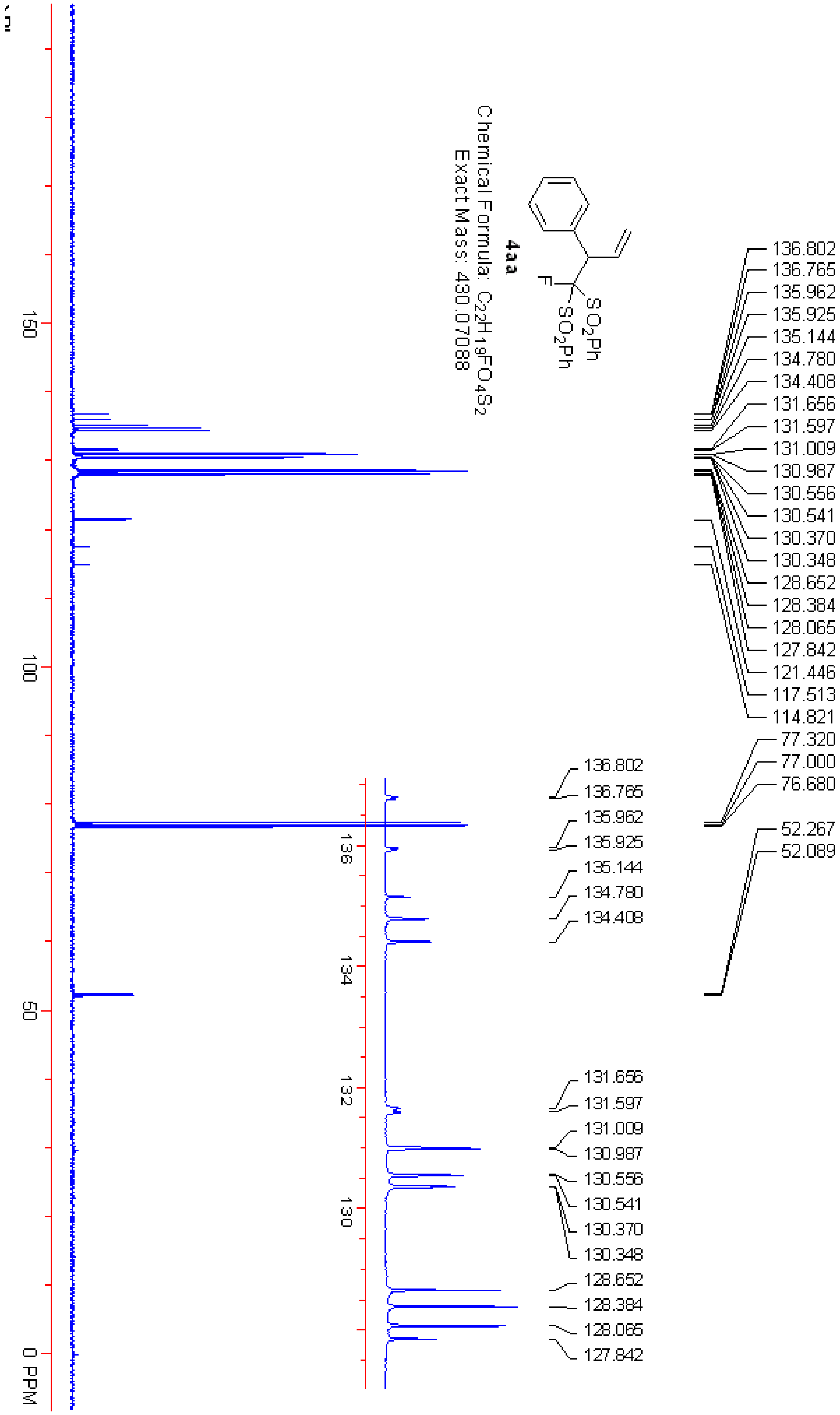
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	19.543	136554.516	4440641.000	98.1961
2	30.312	1715.960	81576.398	1.8039
Total		138270.476	4522217.398	100.0000

NMR Spectra of the compounds 4, 5, 6, and 7

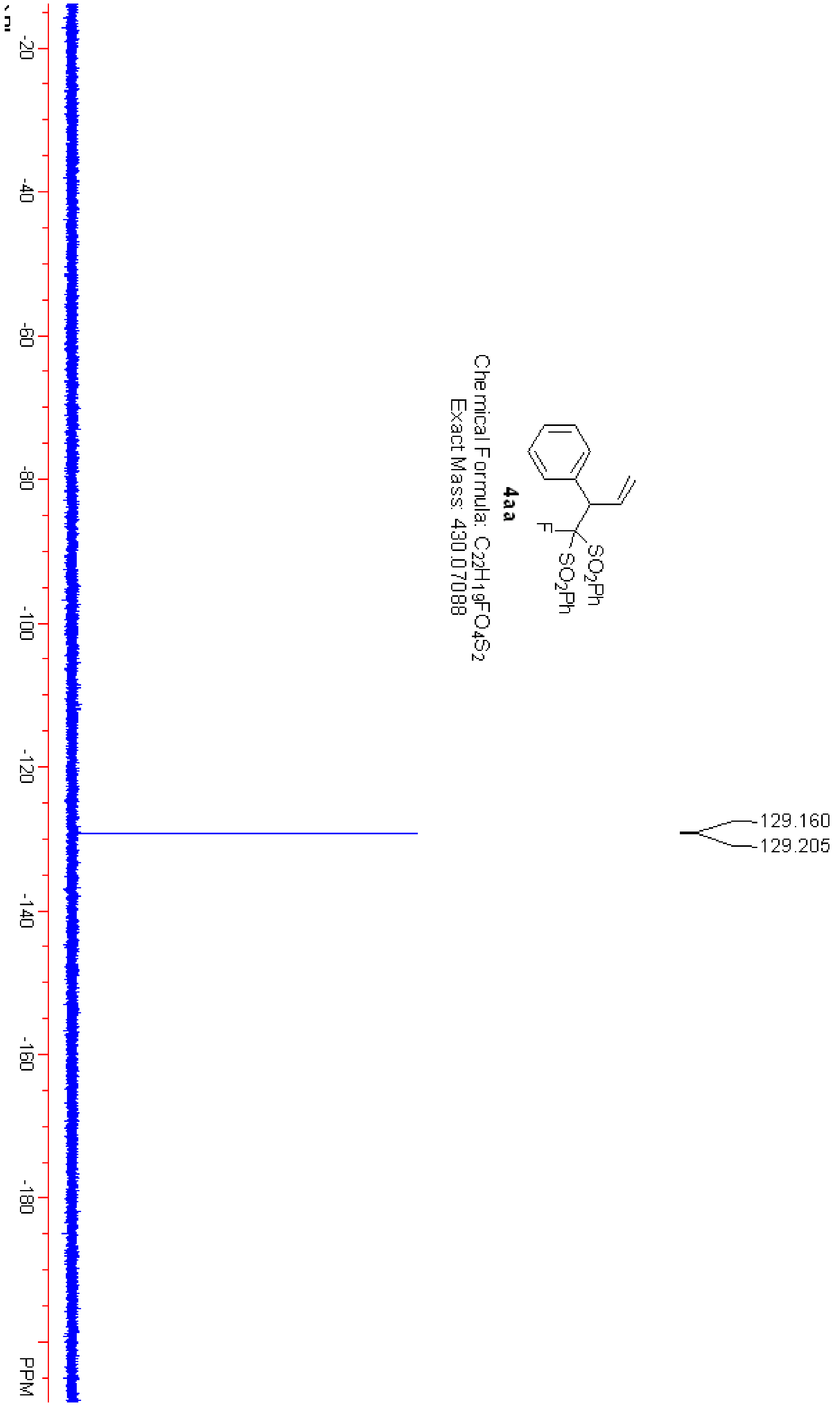
[1]H NMR (400 MHz, $CDCl_3$)



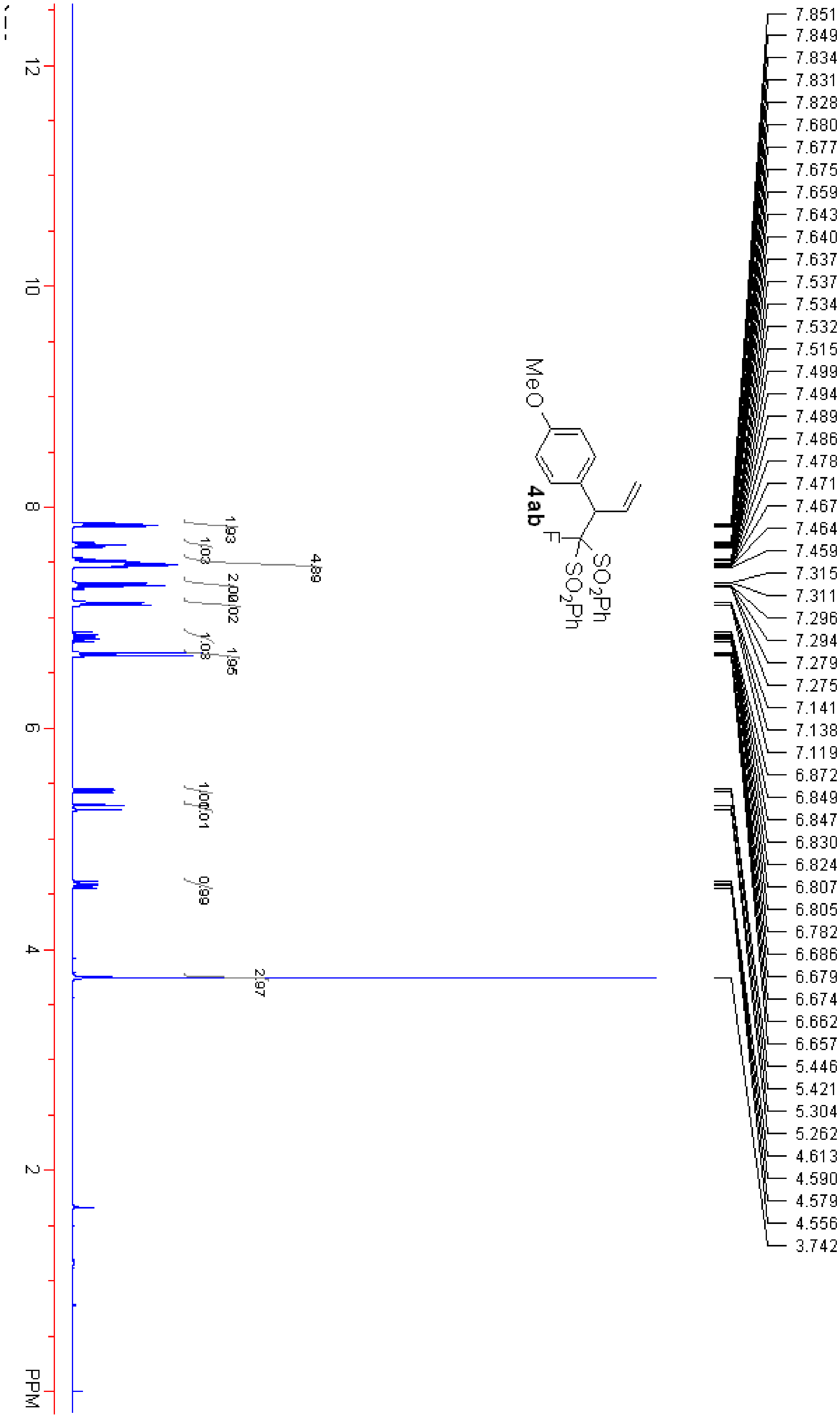
^{13}C NMR (100 MHz, $CDCl_3$)



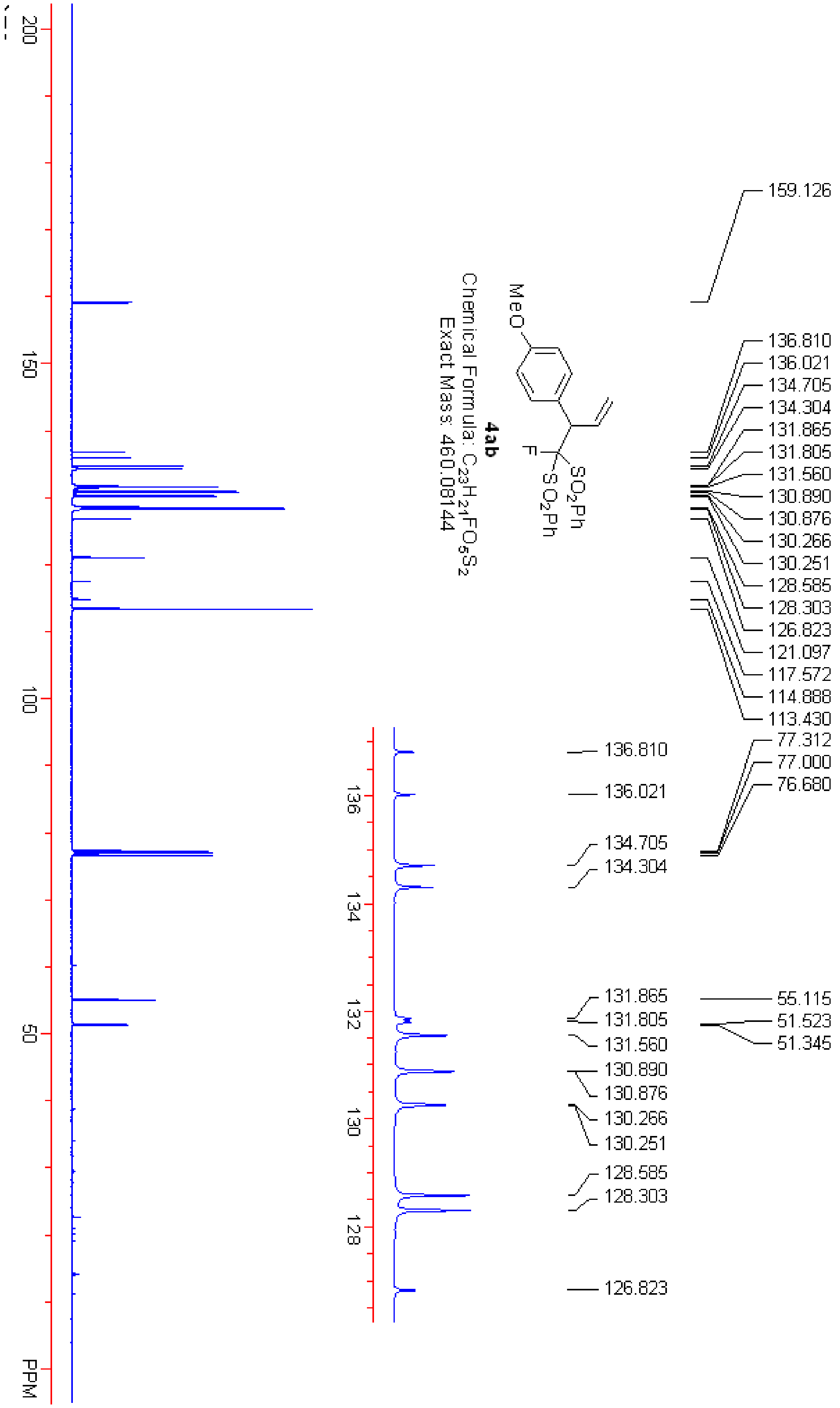
^{19}F NMR (282 MHz, $CDCl_3$)



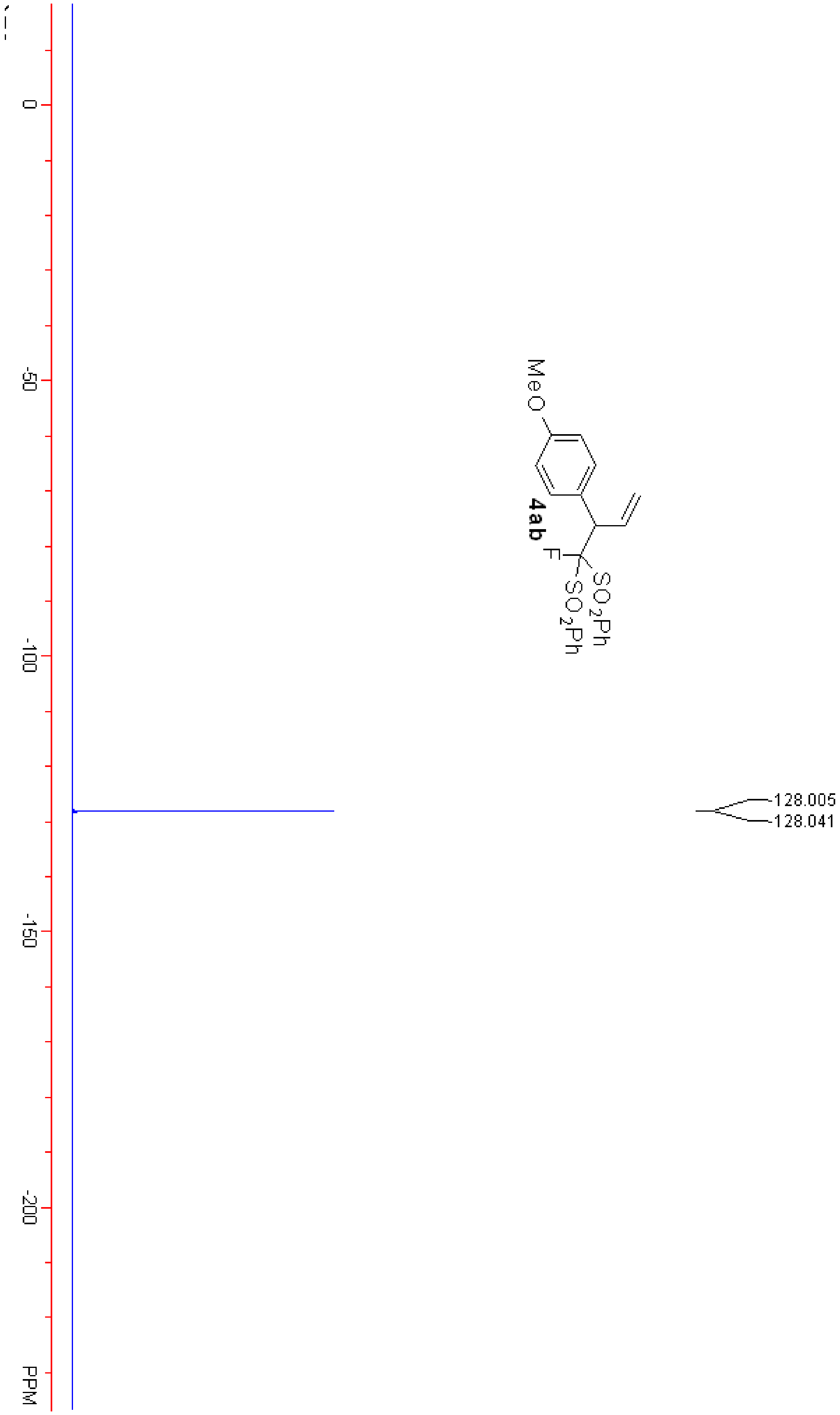
^{1}H NMR (400 MHz, $CDCl_3$)



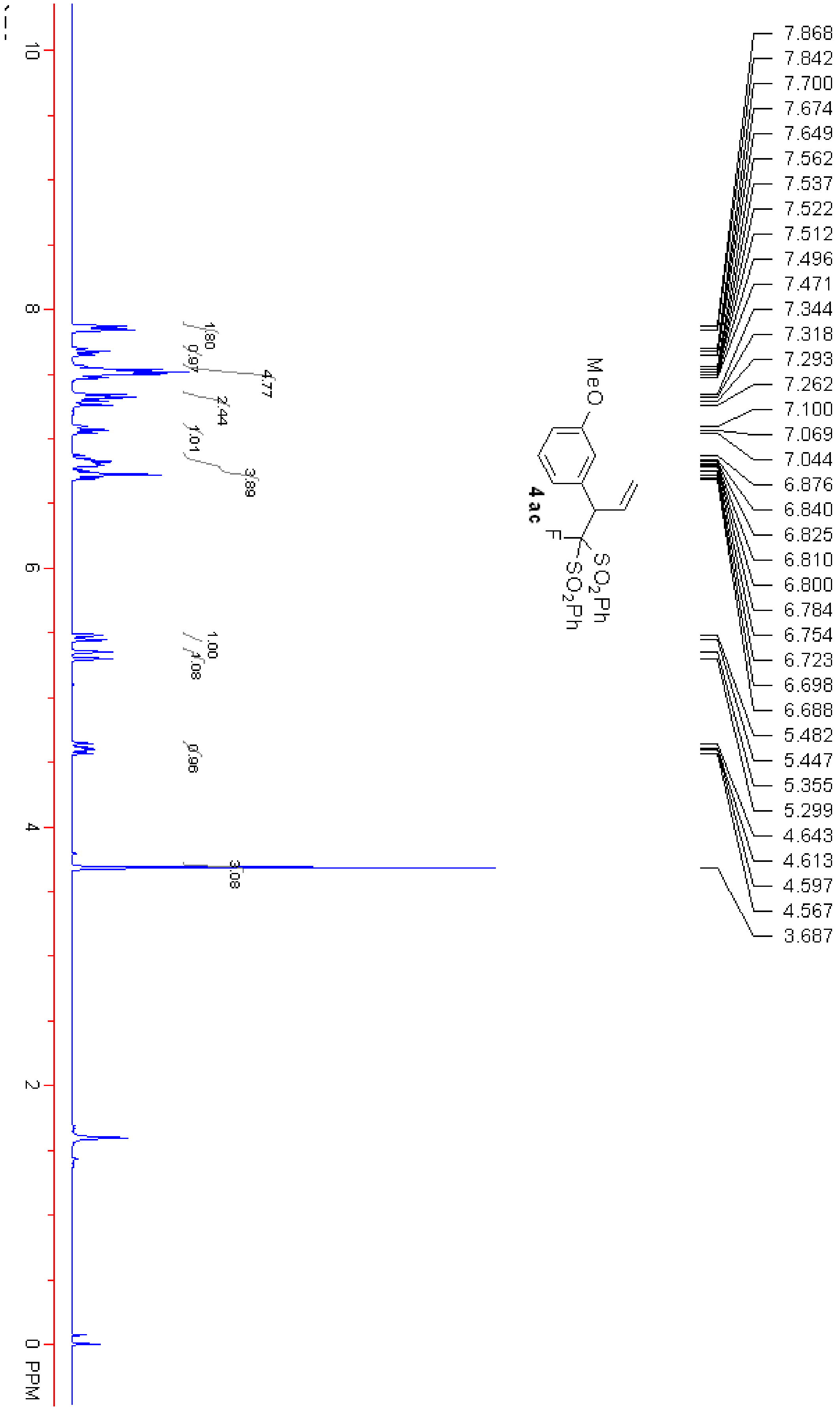
^{13}C NMR (100 MHz, $CDCl_3$)



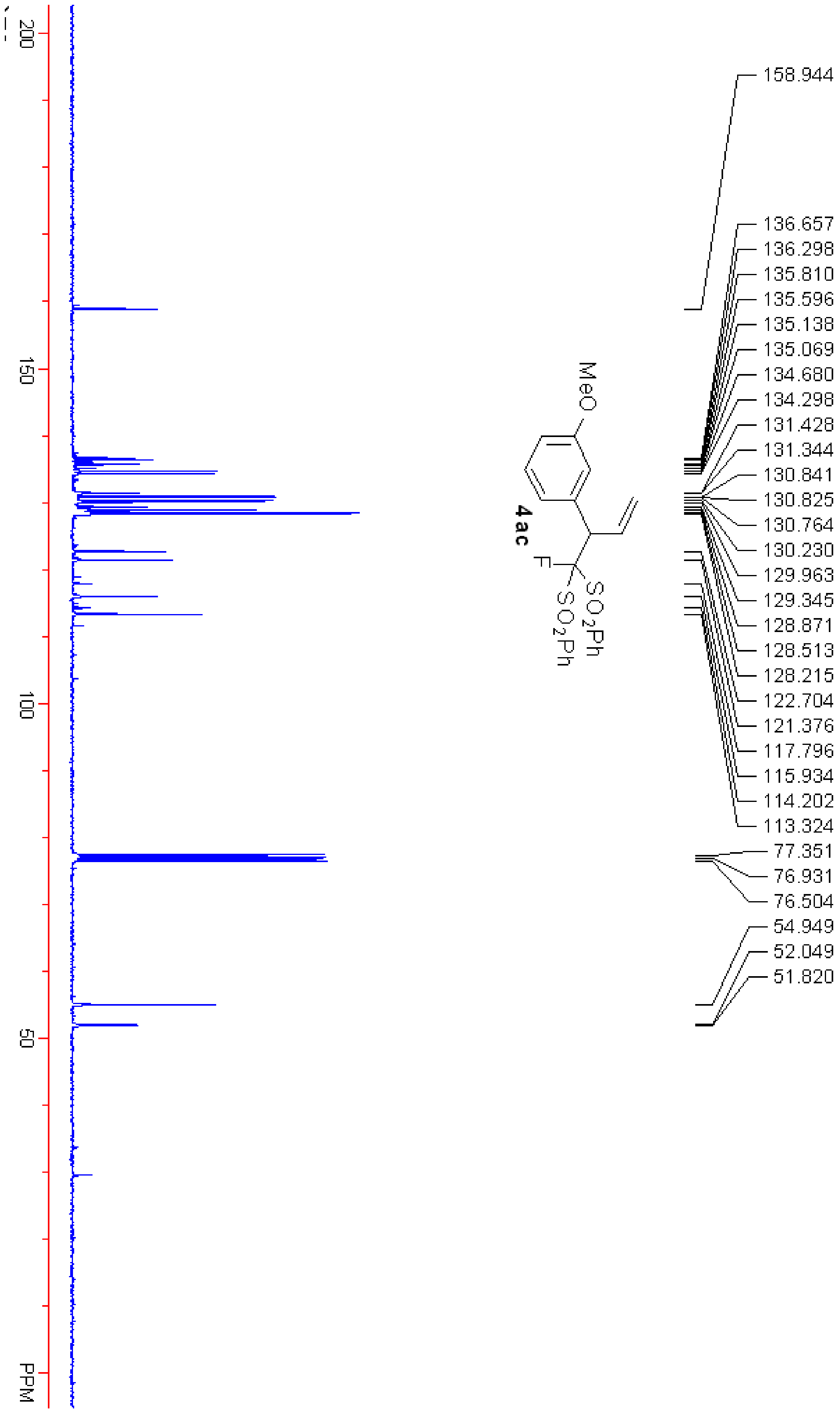
[19]F NMR (376 MHz, $CDCl_3$)



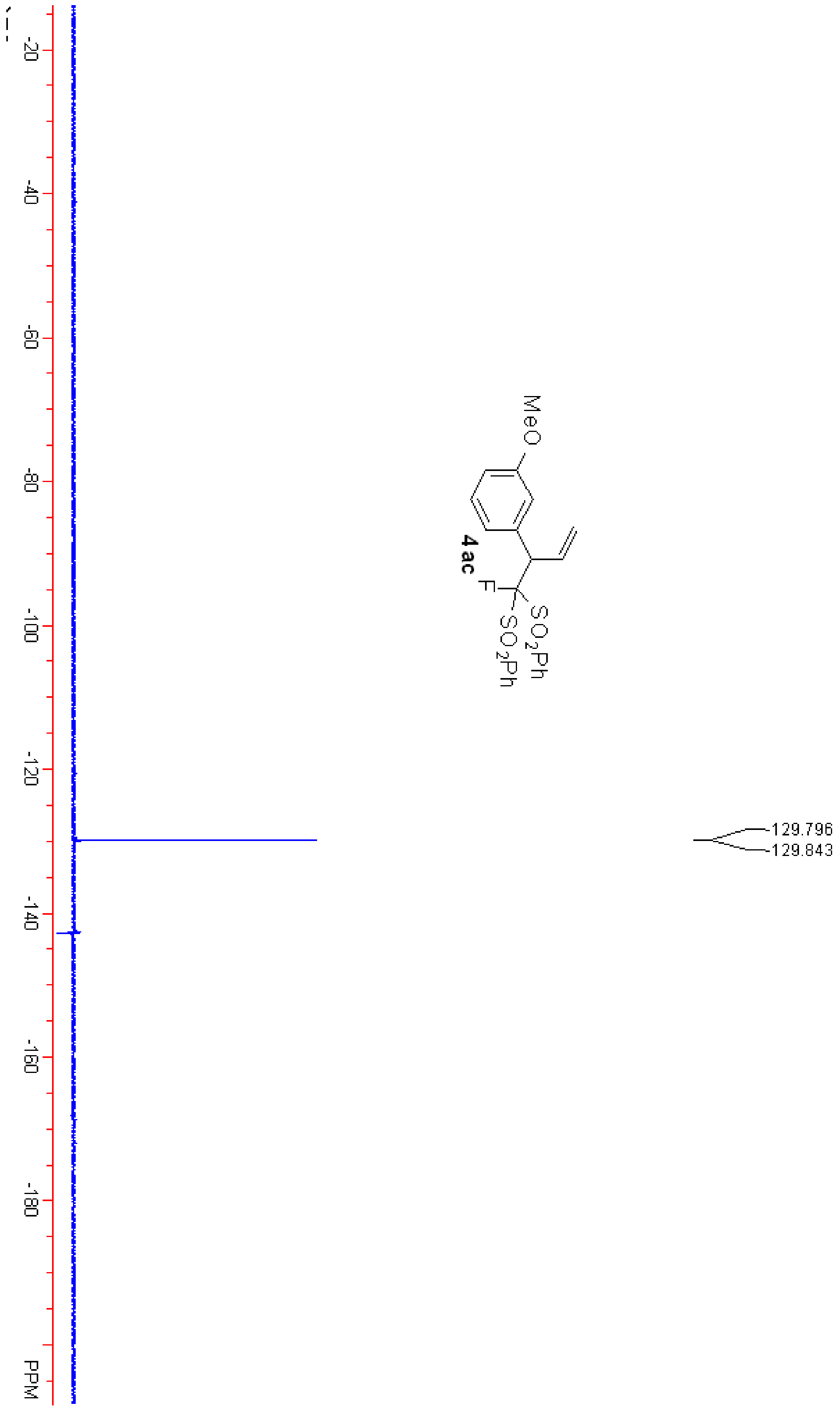
^1H NMR (300 MHz, $CDCl_3$)



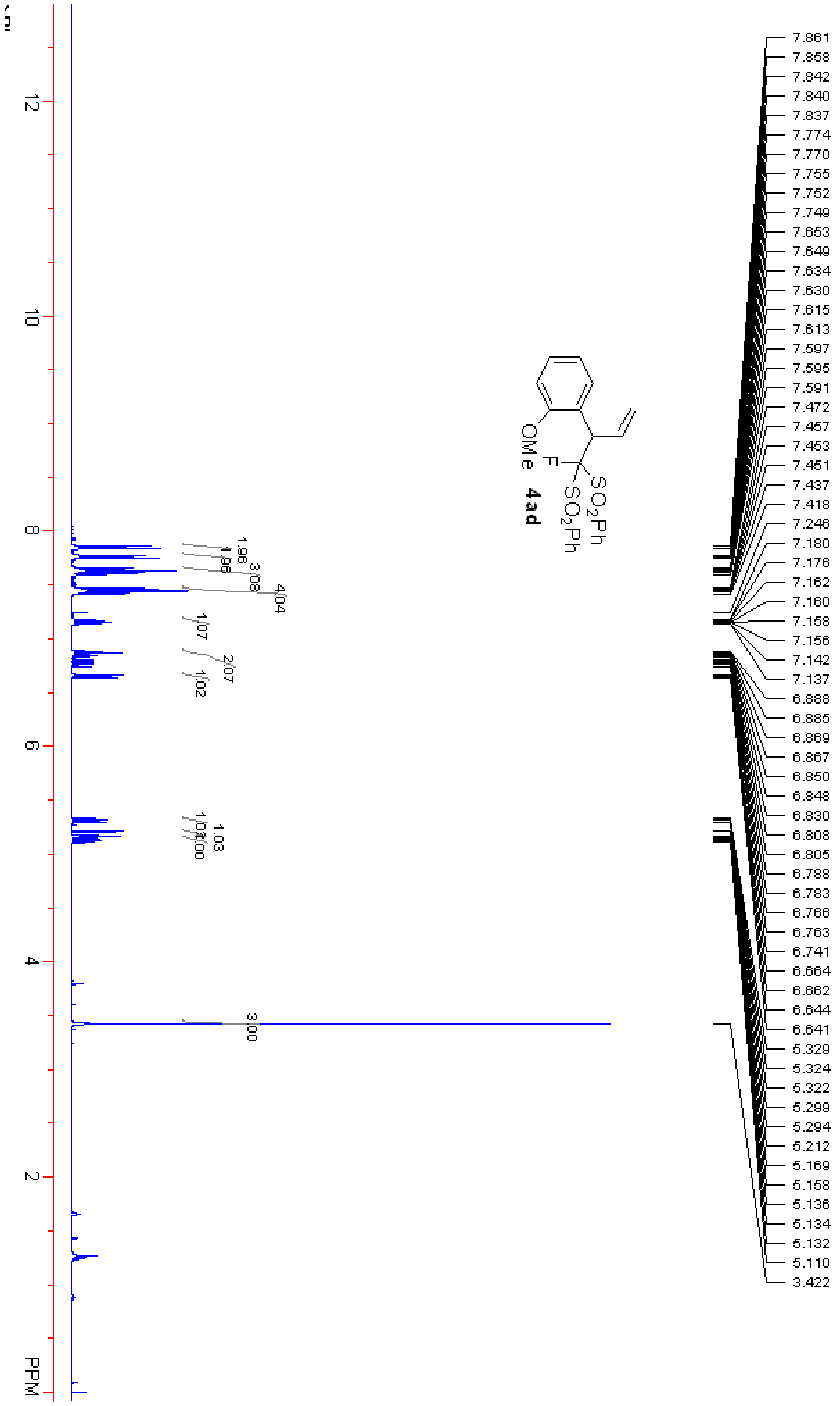
^{13}C NMR (75 MHz, $CDCl_3$)



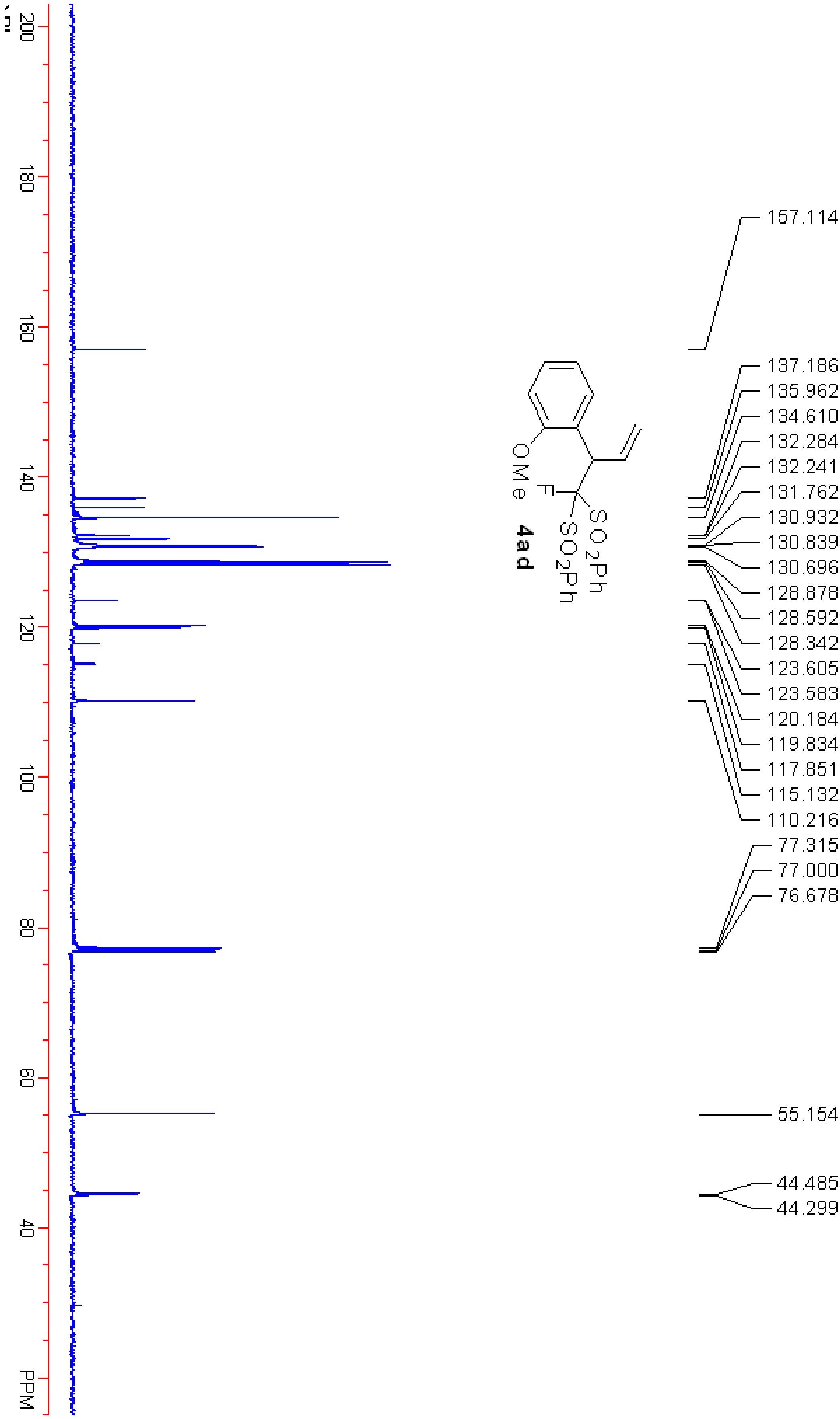
^{19}F NMR (282 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

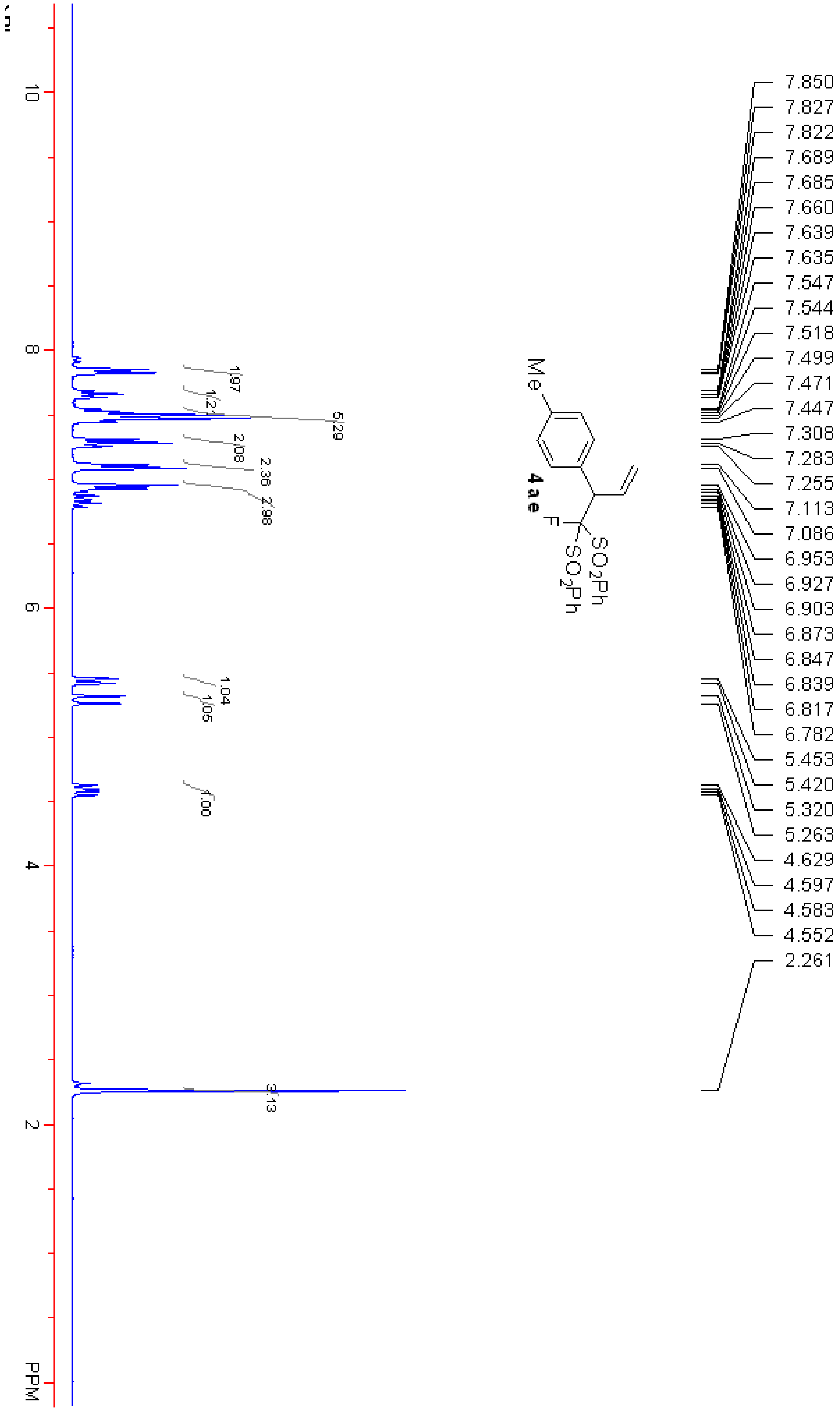


^{13}C NMR (100 MHz, $CDCl_3$)

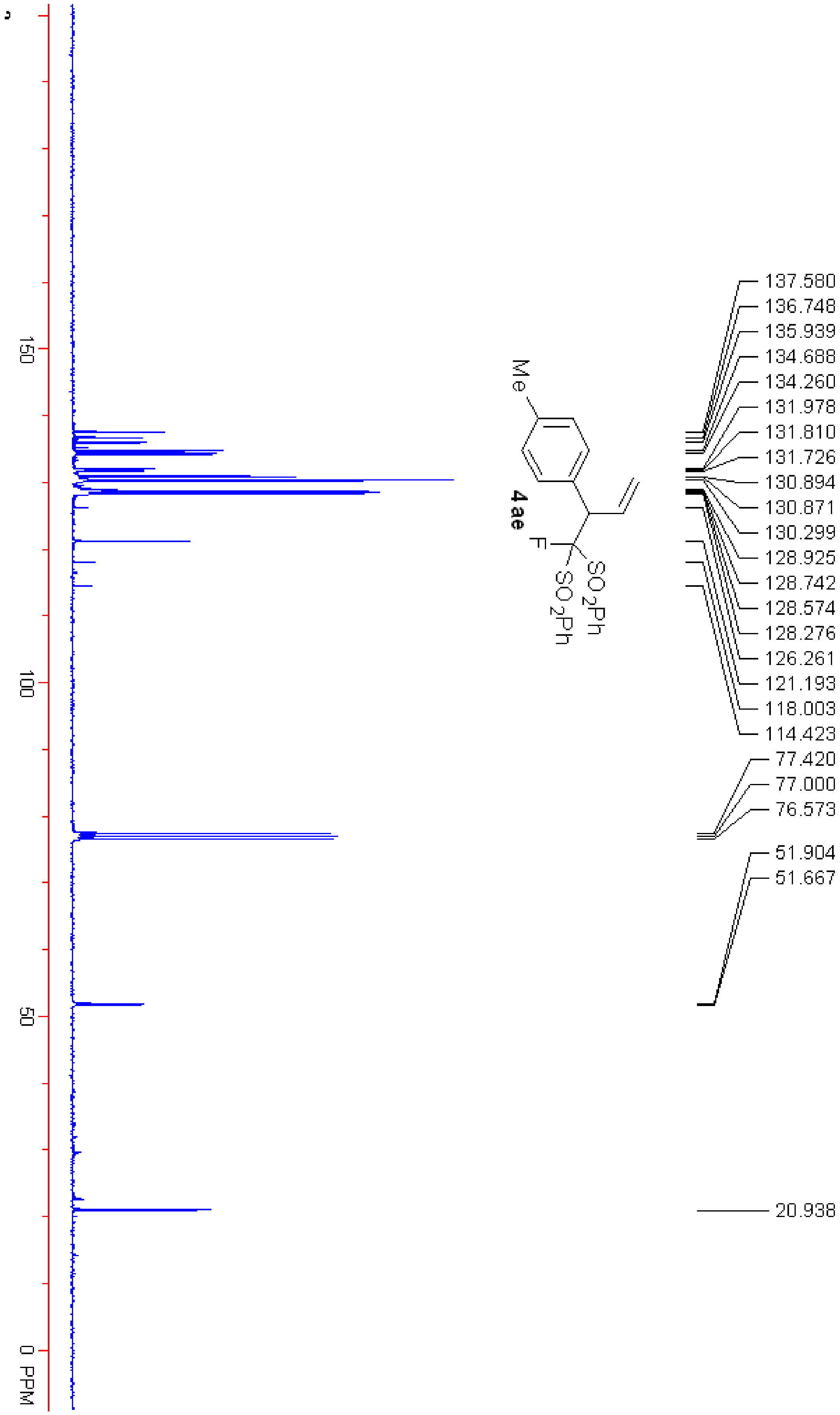


^{19}F NMR (376 MHz, $CDCl_3$)

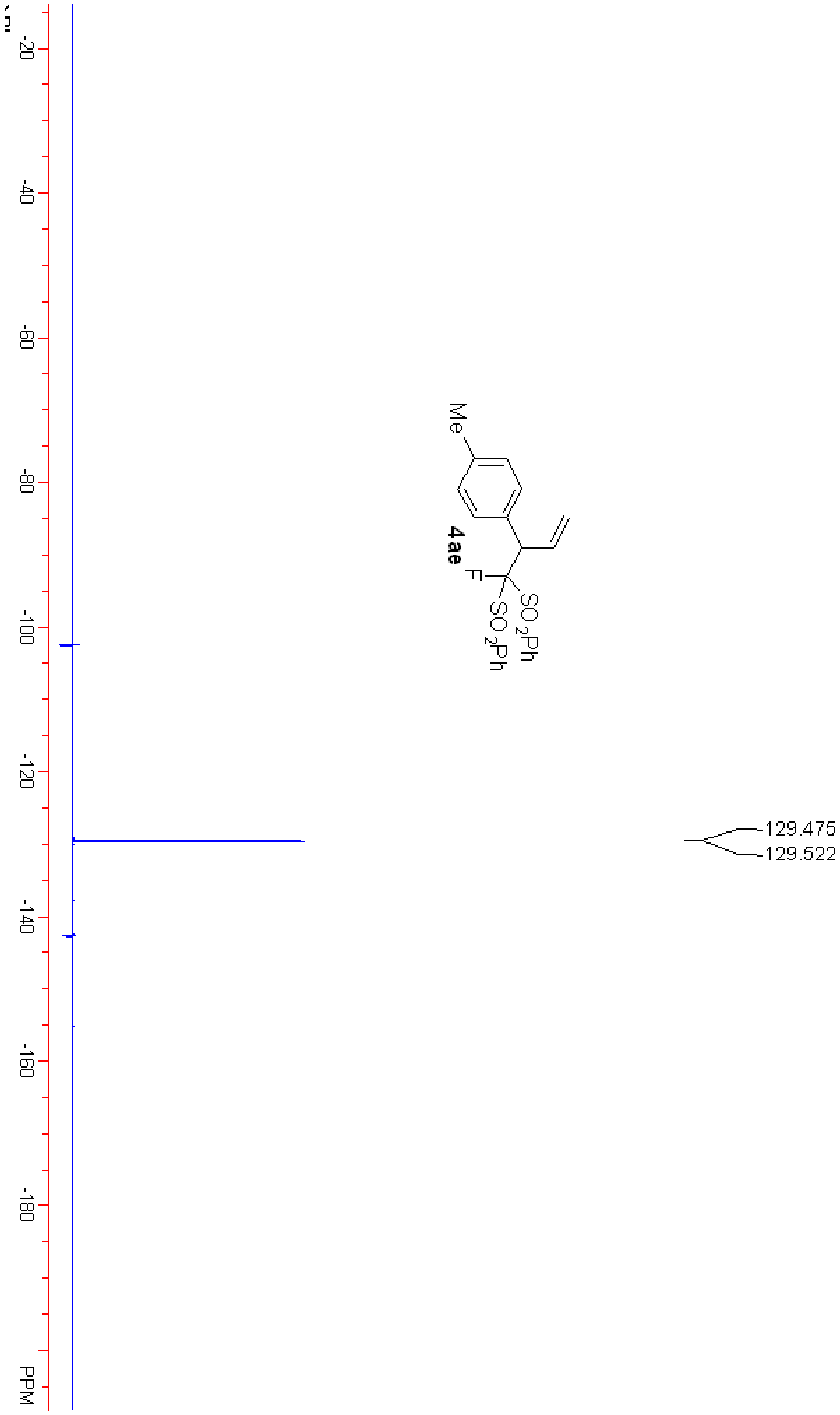
^{1}H NMR (300 MHz, $CDCl_3$)



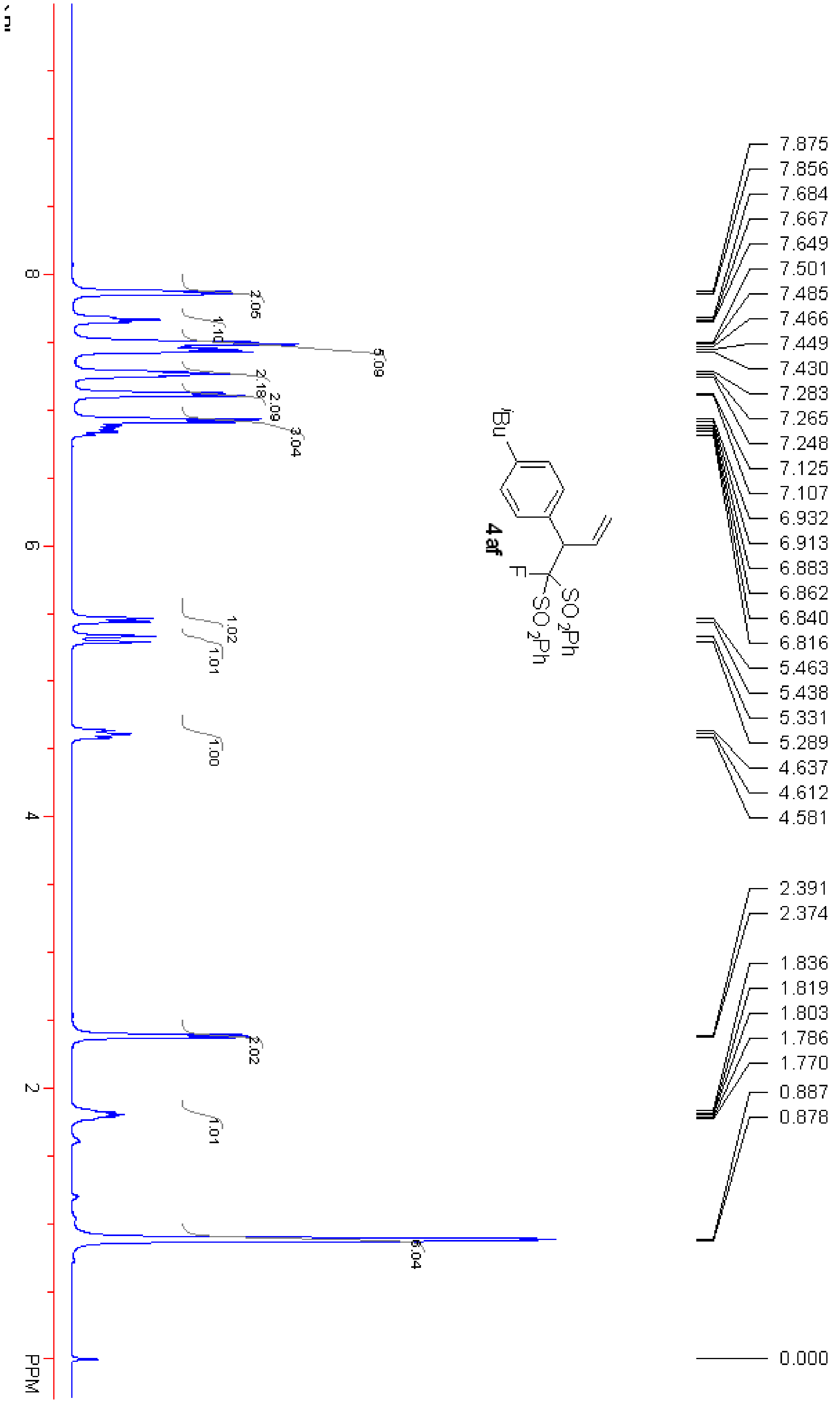
^{13}C NMR (75 MHz, $CDCl_3$)



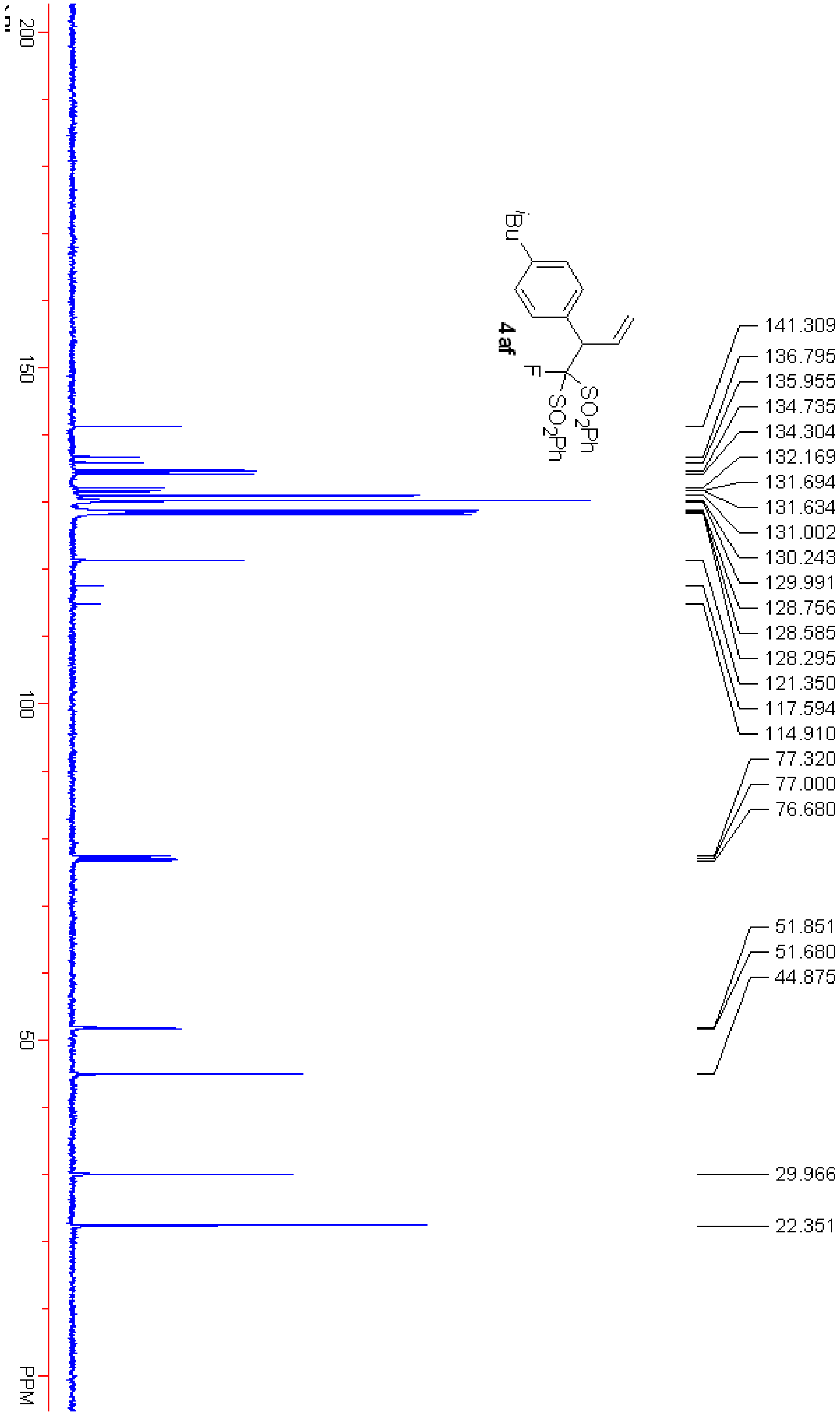
^{19}F NMR (282 MHz, $CDCl_3$)



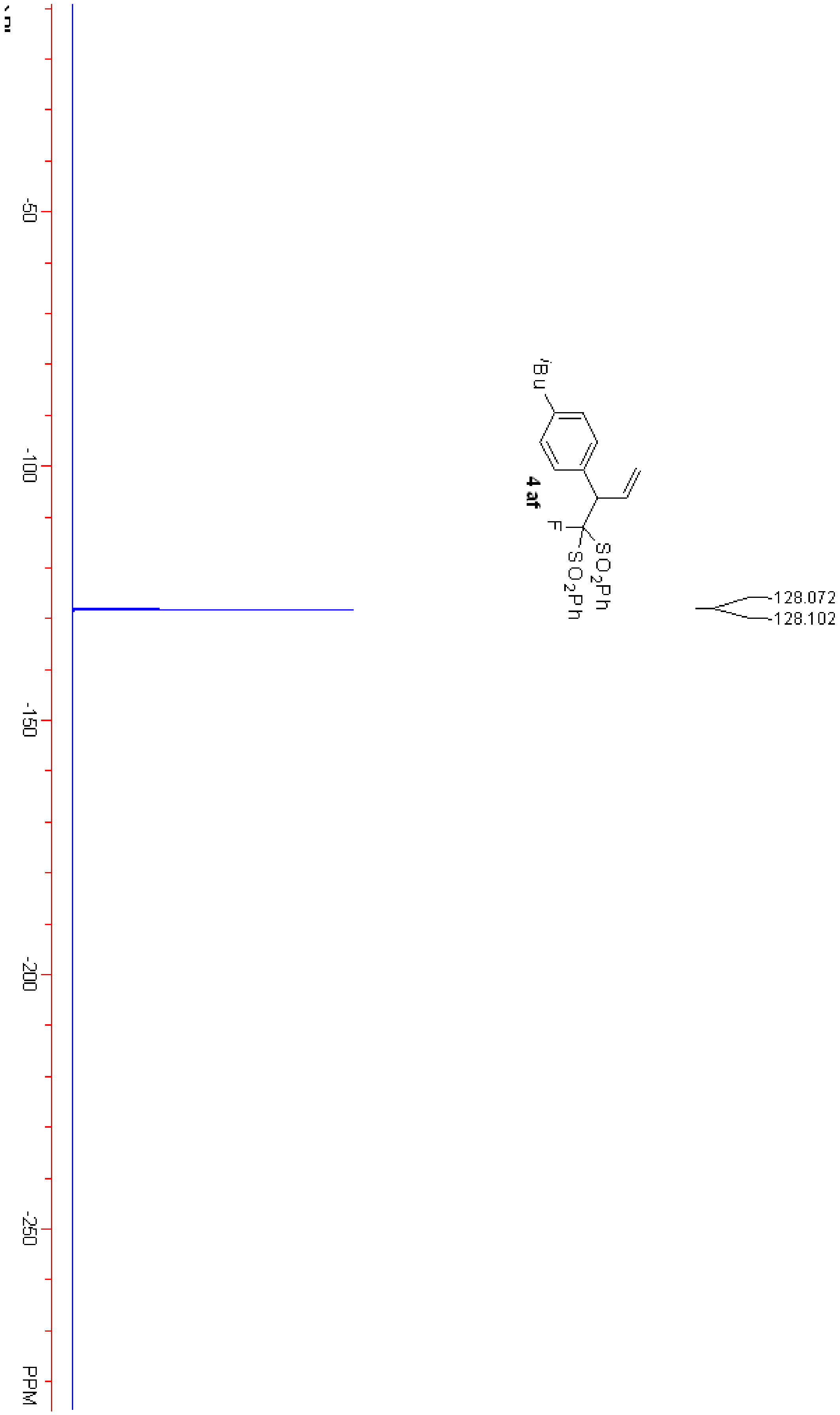
^{1}H NMR (400 MHz, $CDCl_3$)



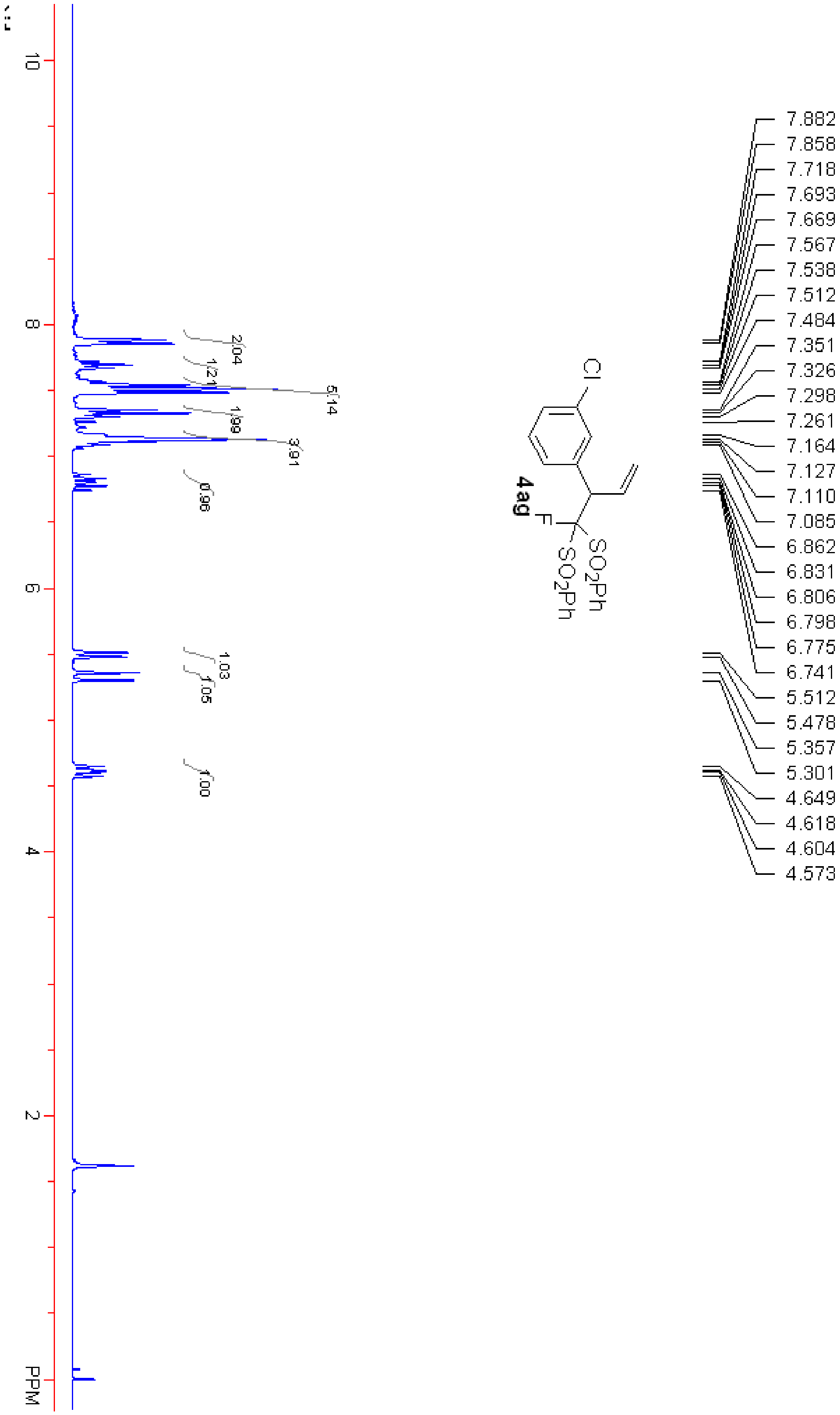
^{13}C NMR (100 MHz, $CDCl_3$)



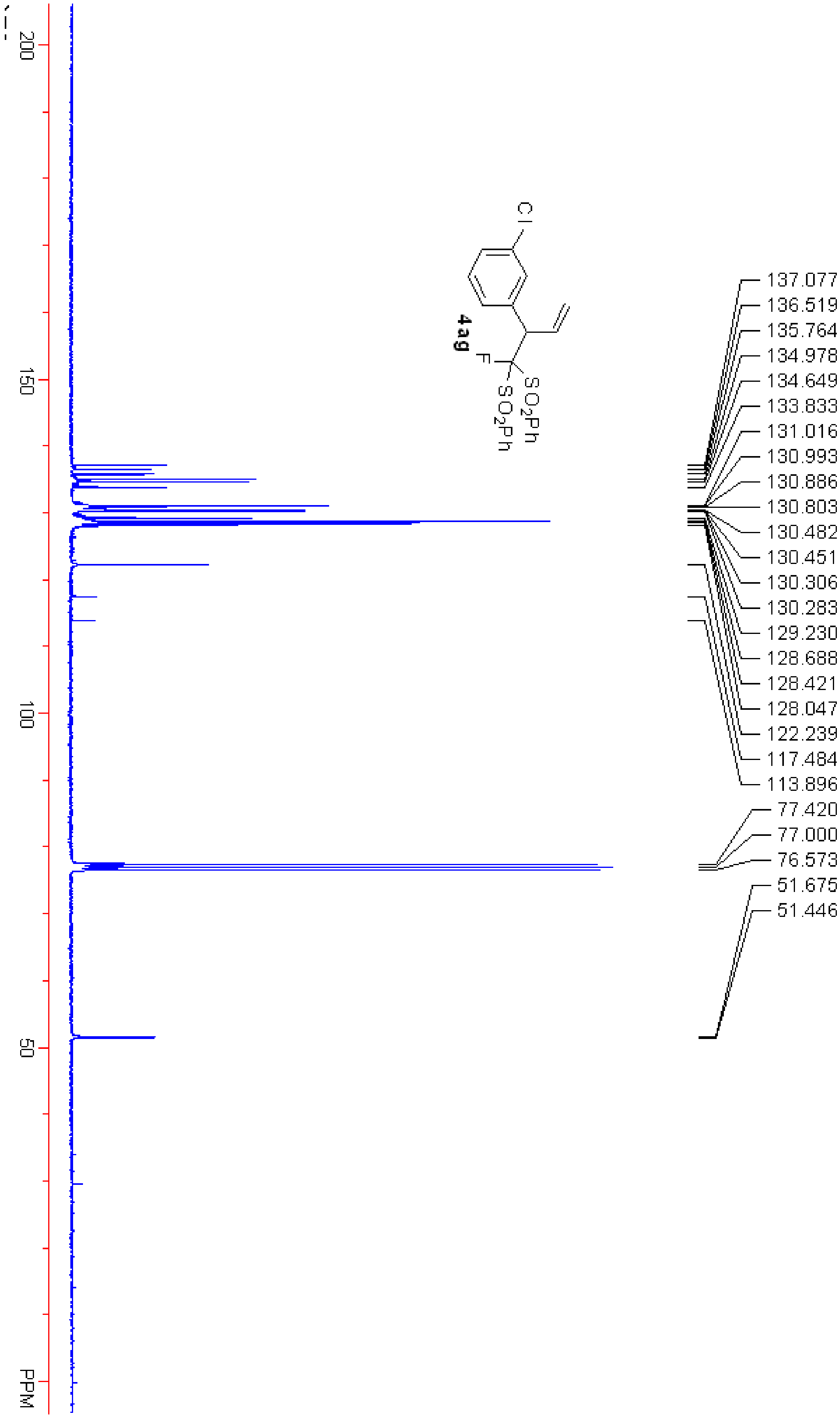
^{19}F NMR (376 MHz, $CDCl_3$)



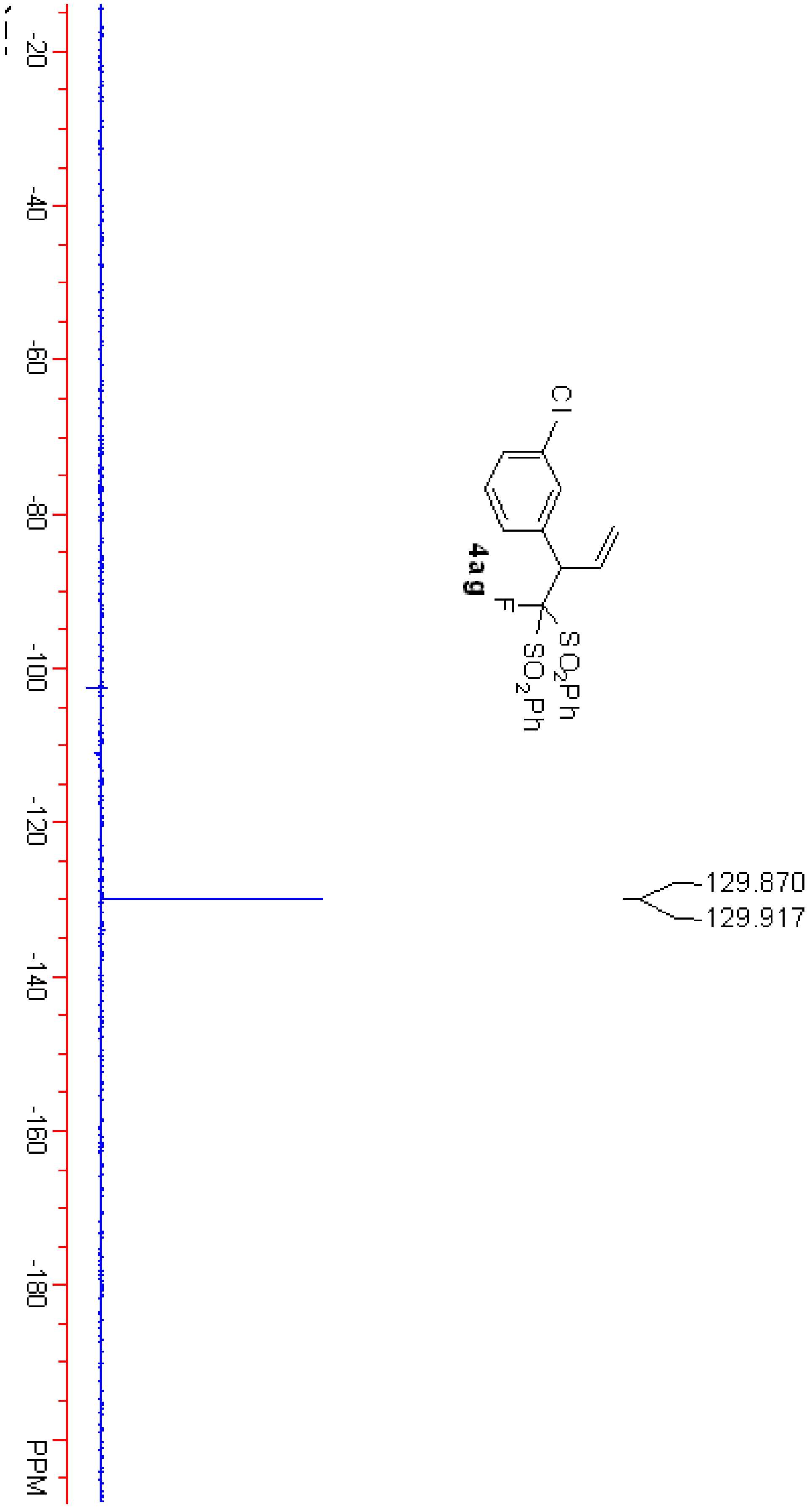
^{1}H NMR (300 MHz, $CDCl_3$)



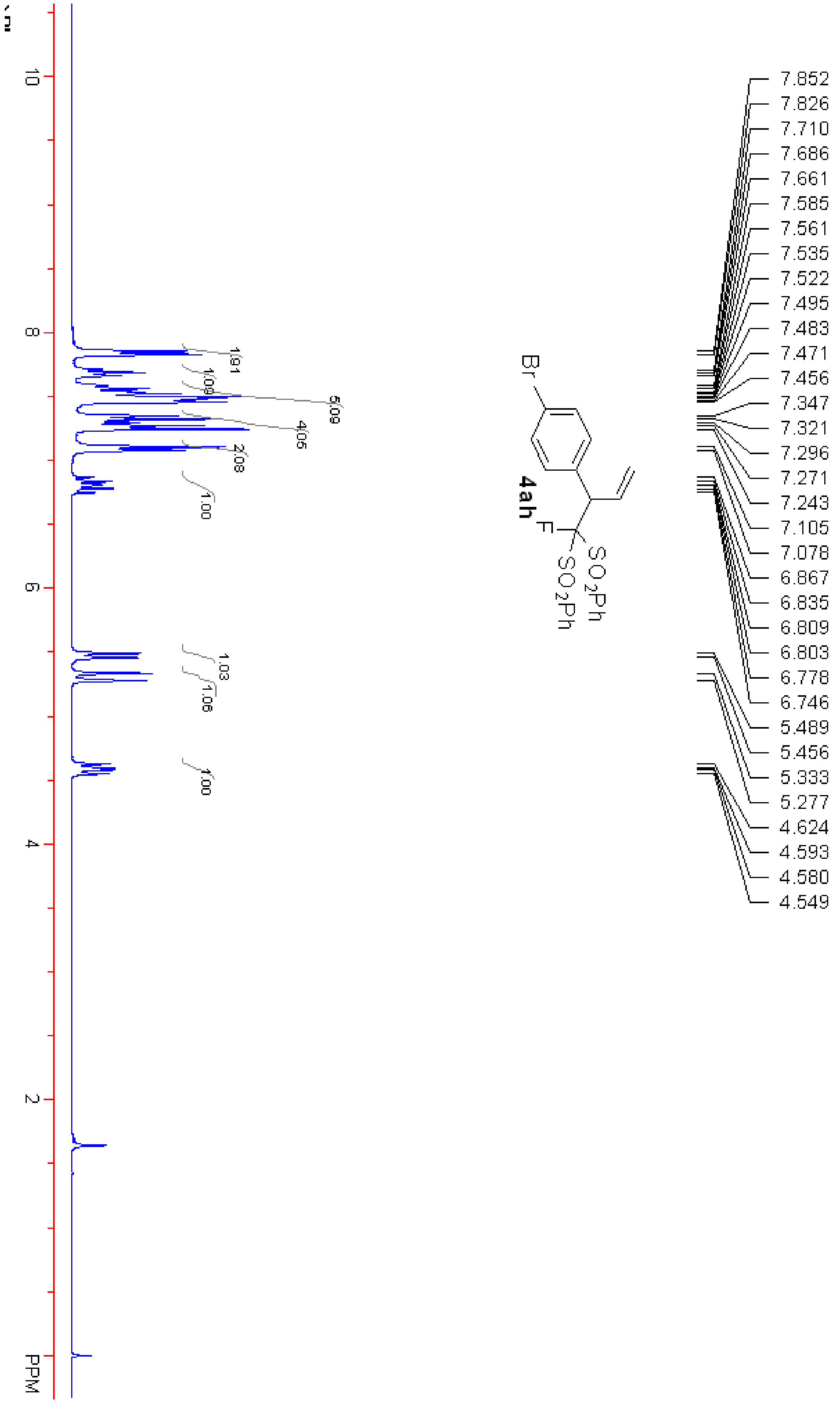
^{13}C NMR (75 MHz, $CDCl_3$)



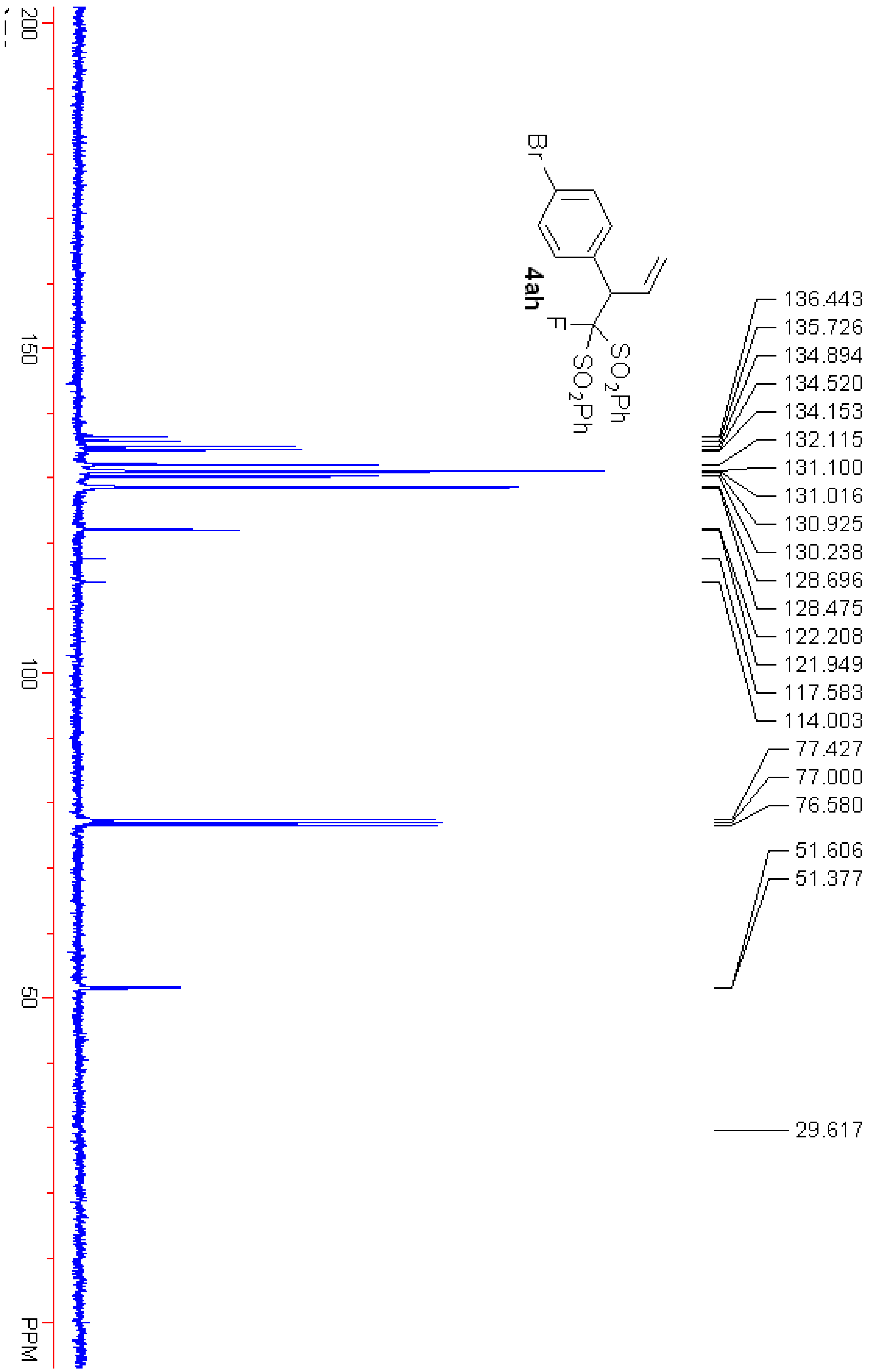
^{19}F NMR (282 MHz, $CDCl_3$)



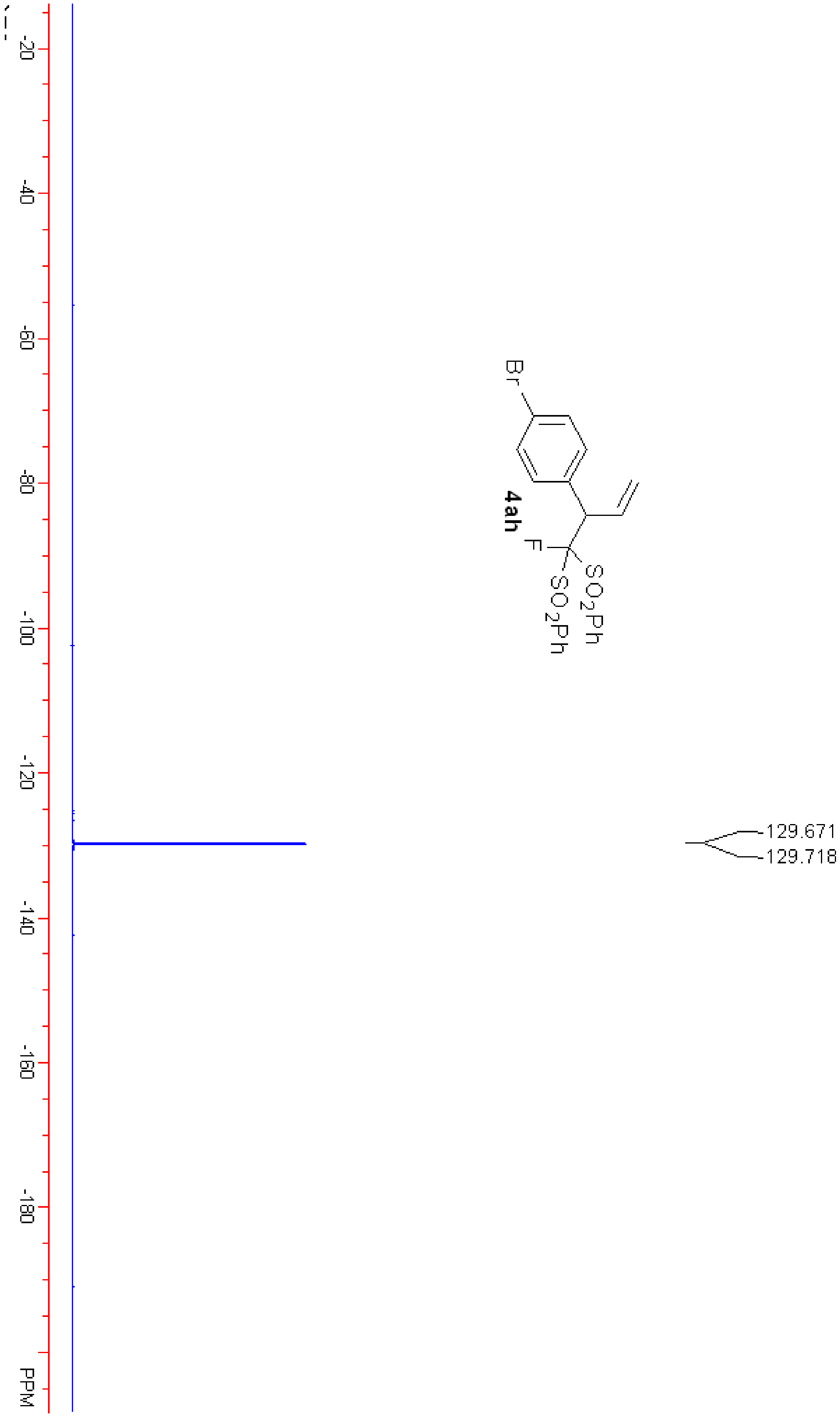
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

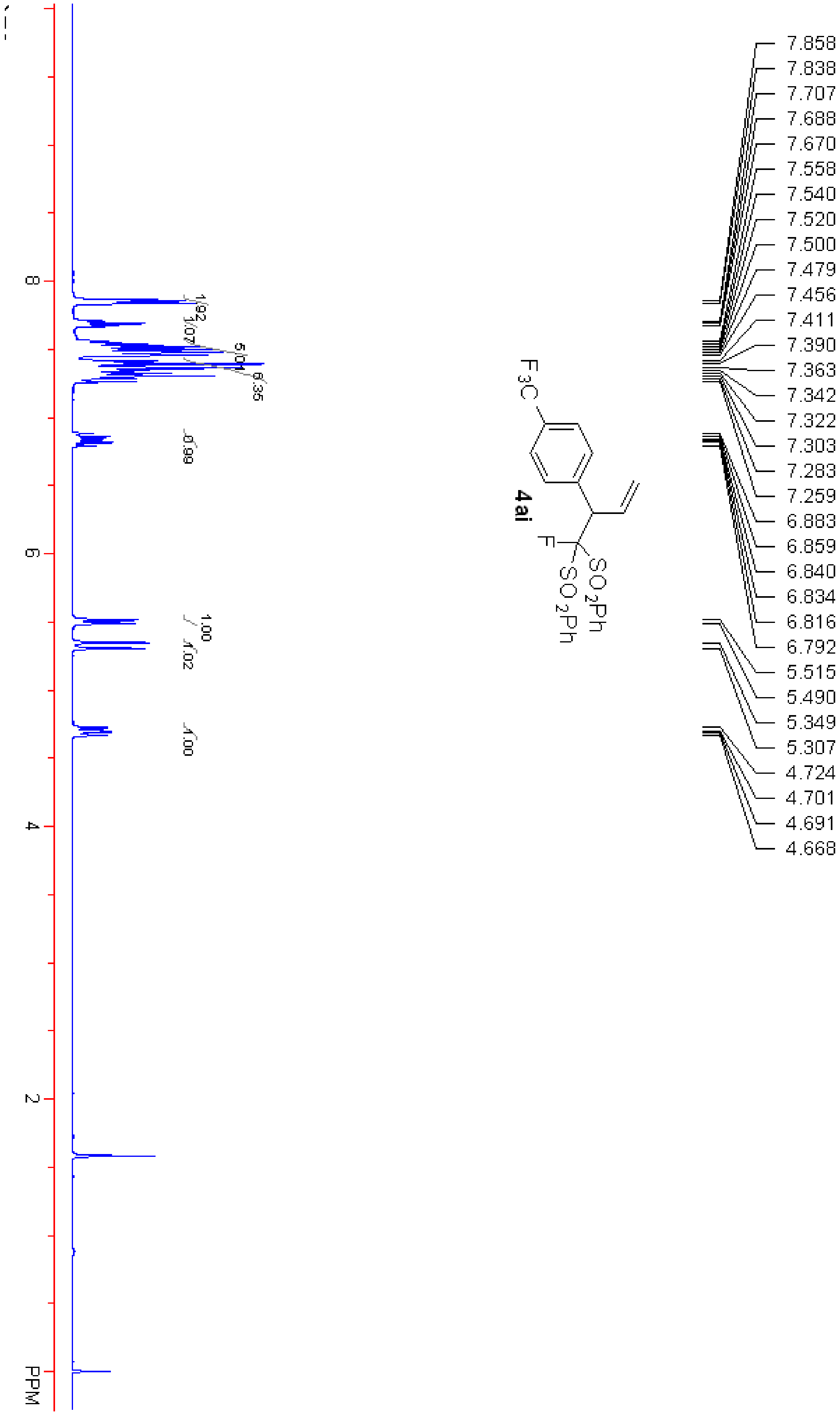


^{19}F NMR (282 MHz, $CDCl_3$)

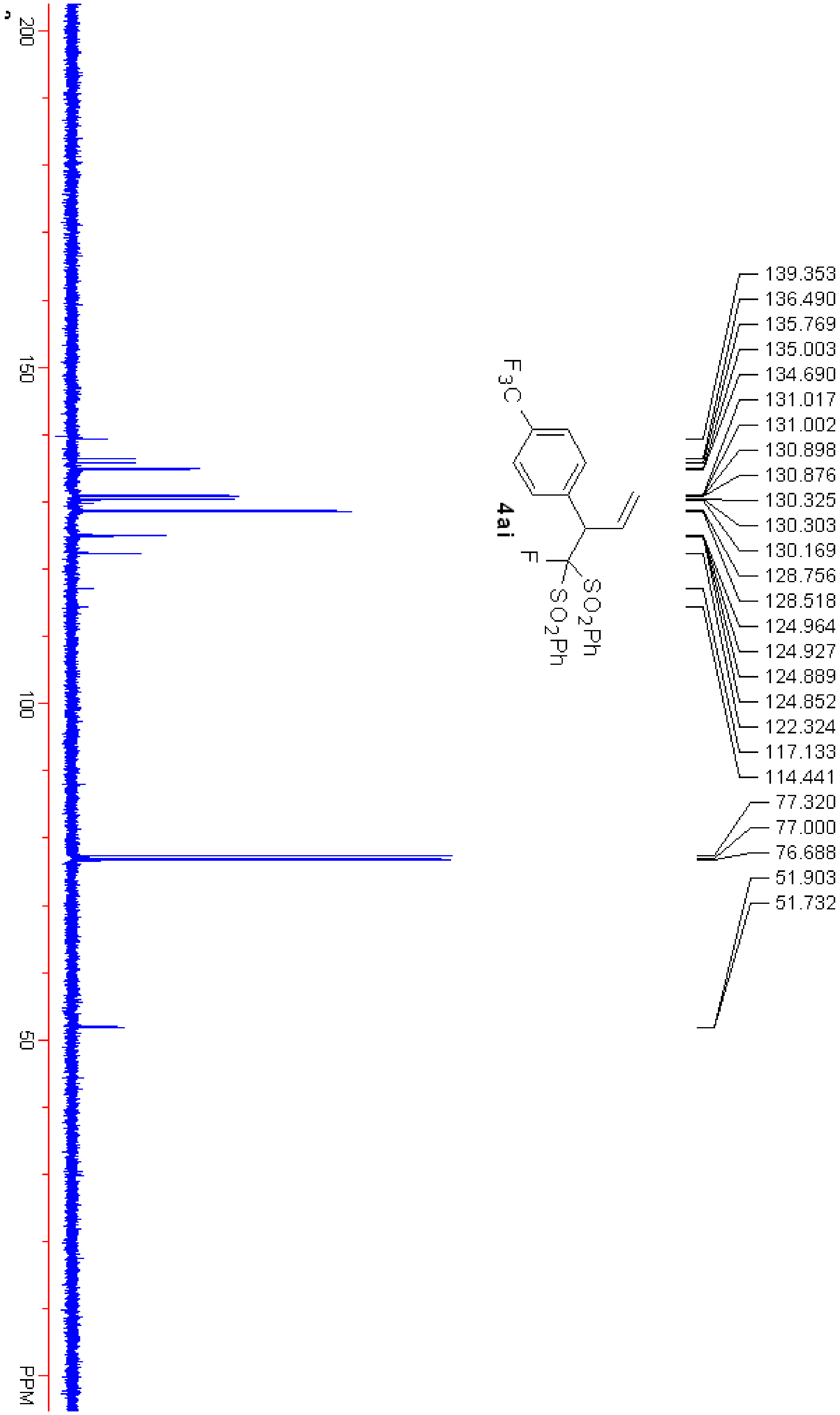


4ah

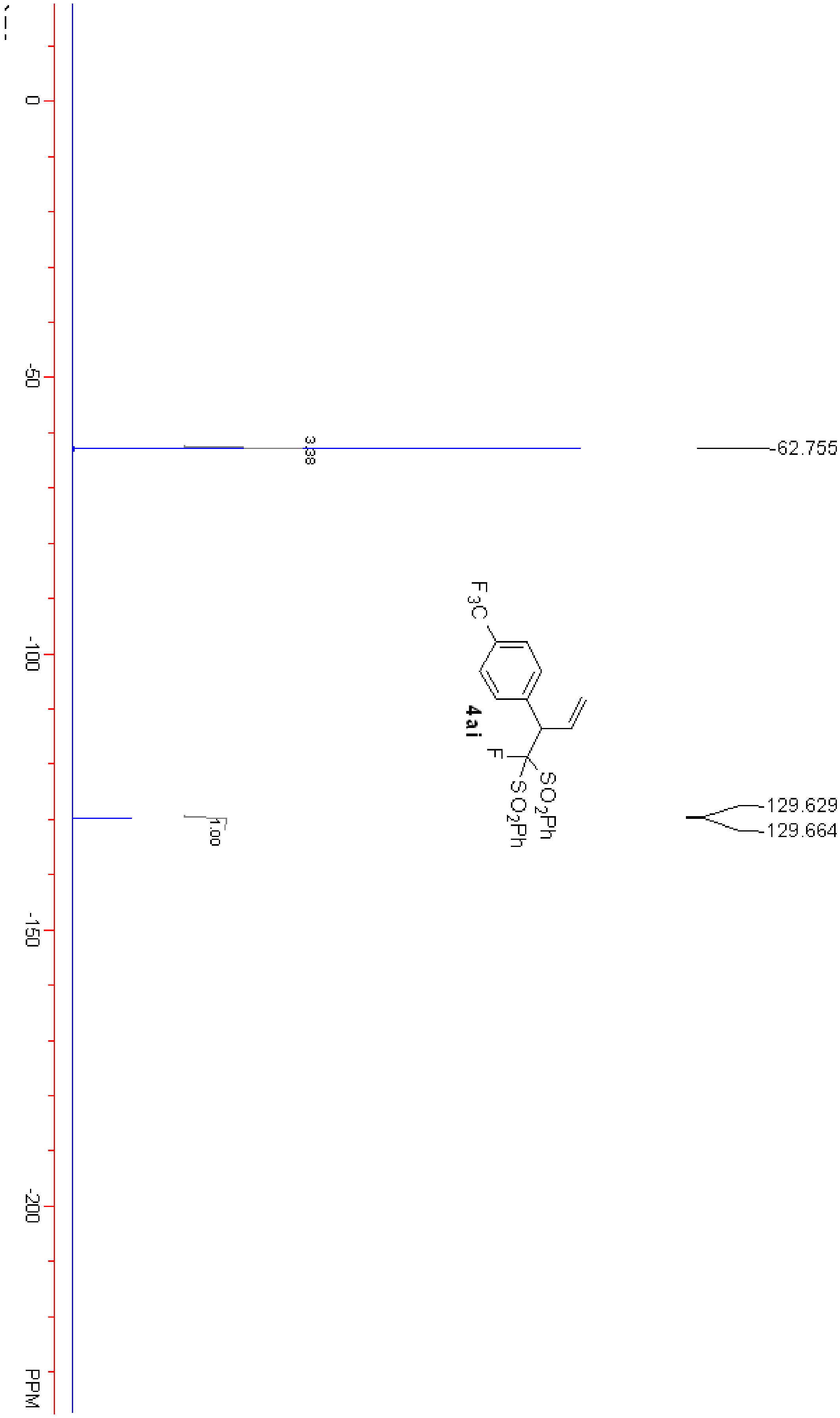
[1]H NMR (400 MHz, $CDCl_3$)



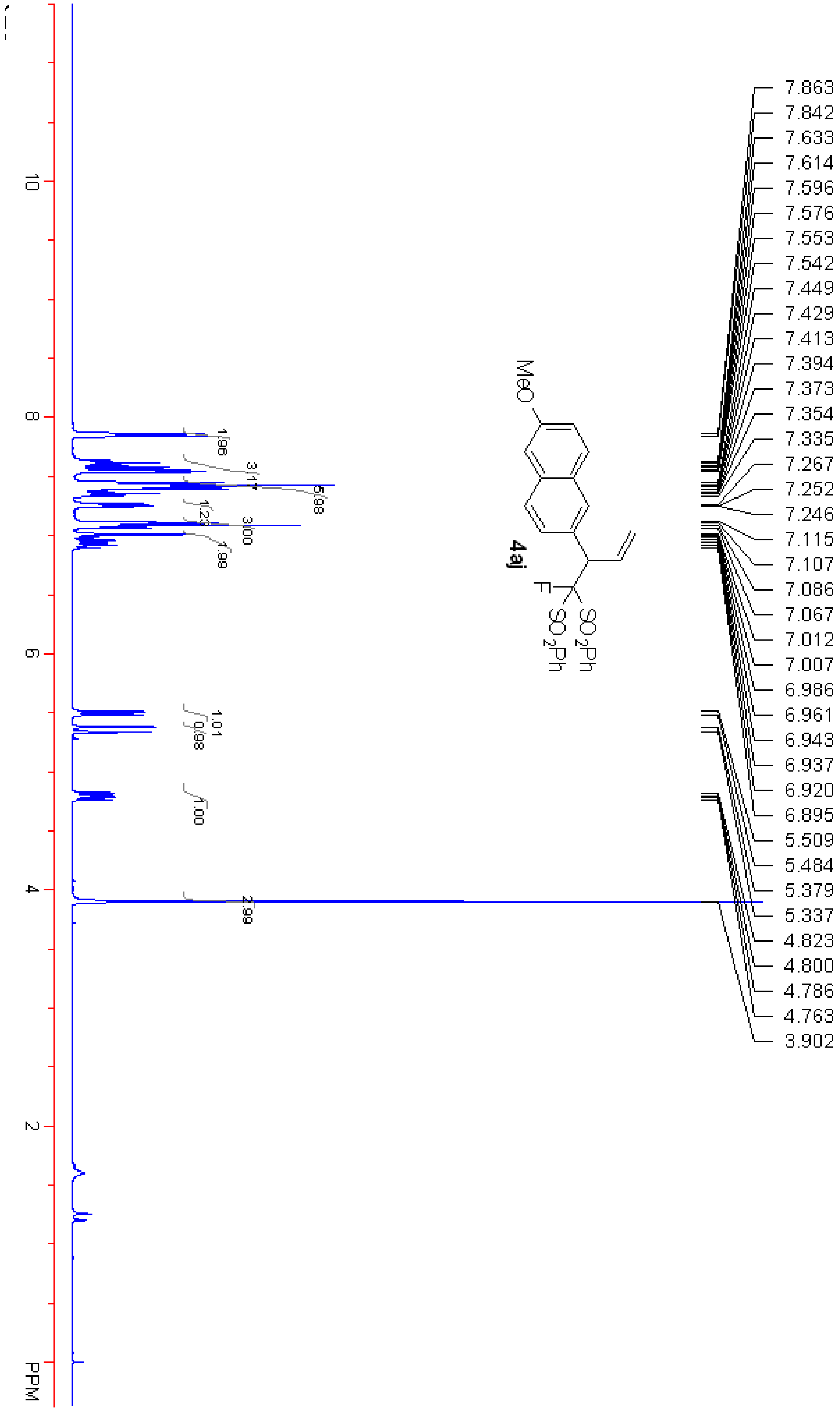
^{13}C NMR (100 MHz, $CDCl_3$)



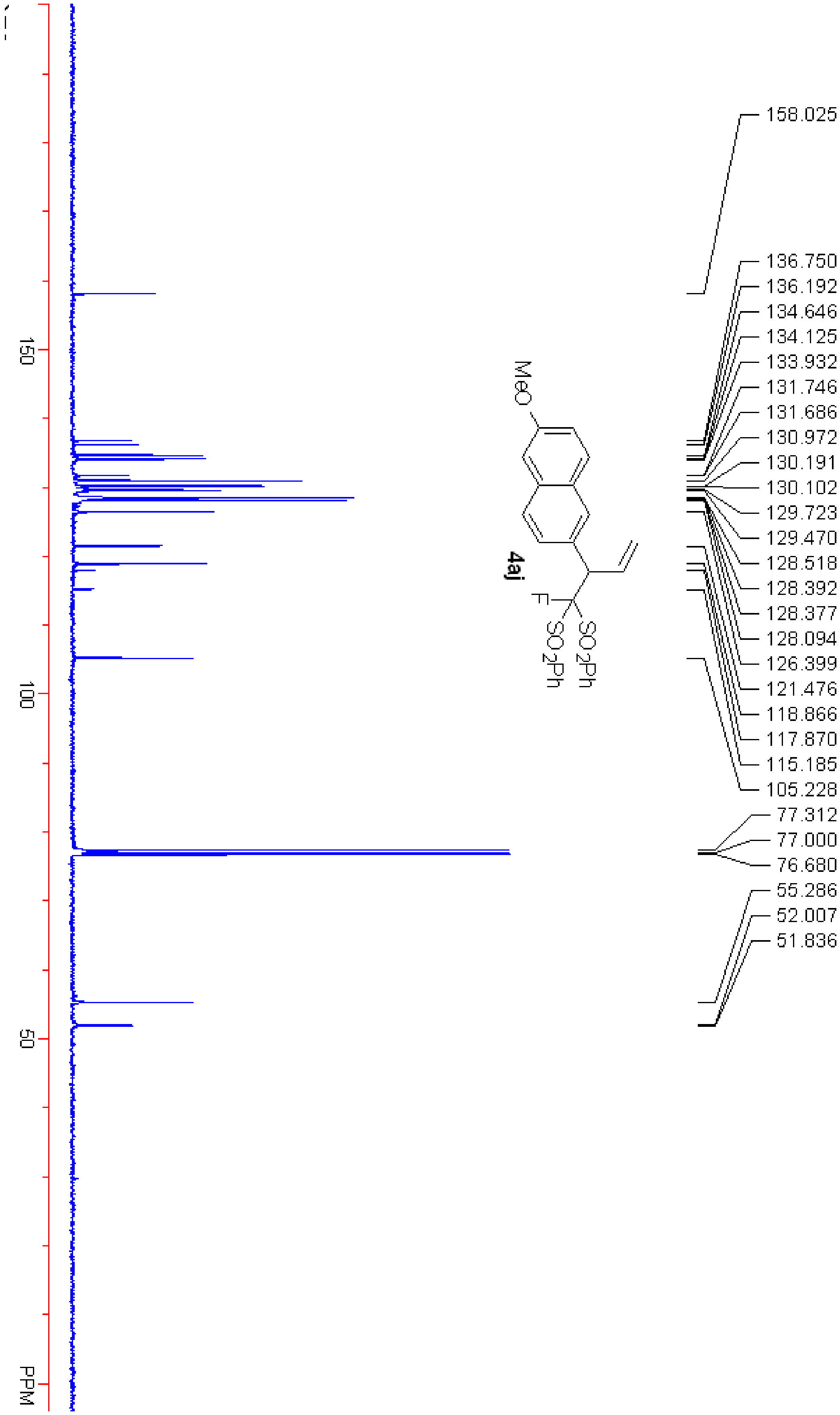
^{19}F NMR (376 MHz, $CDCl_3$)



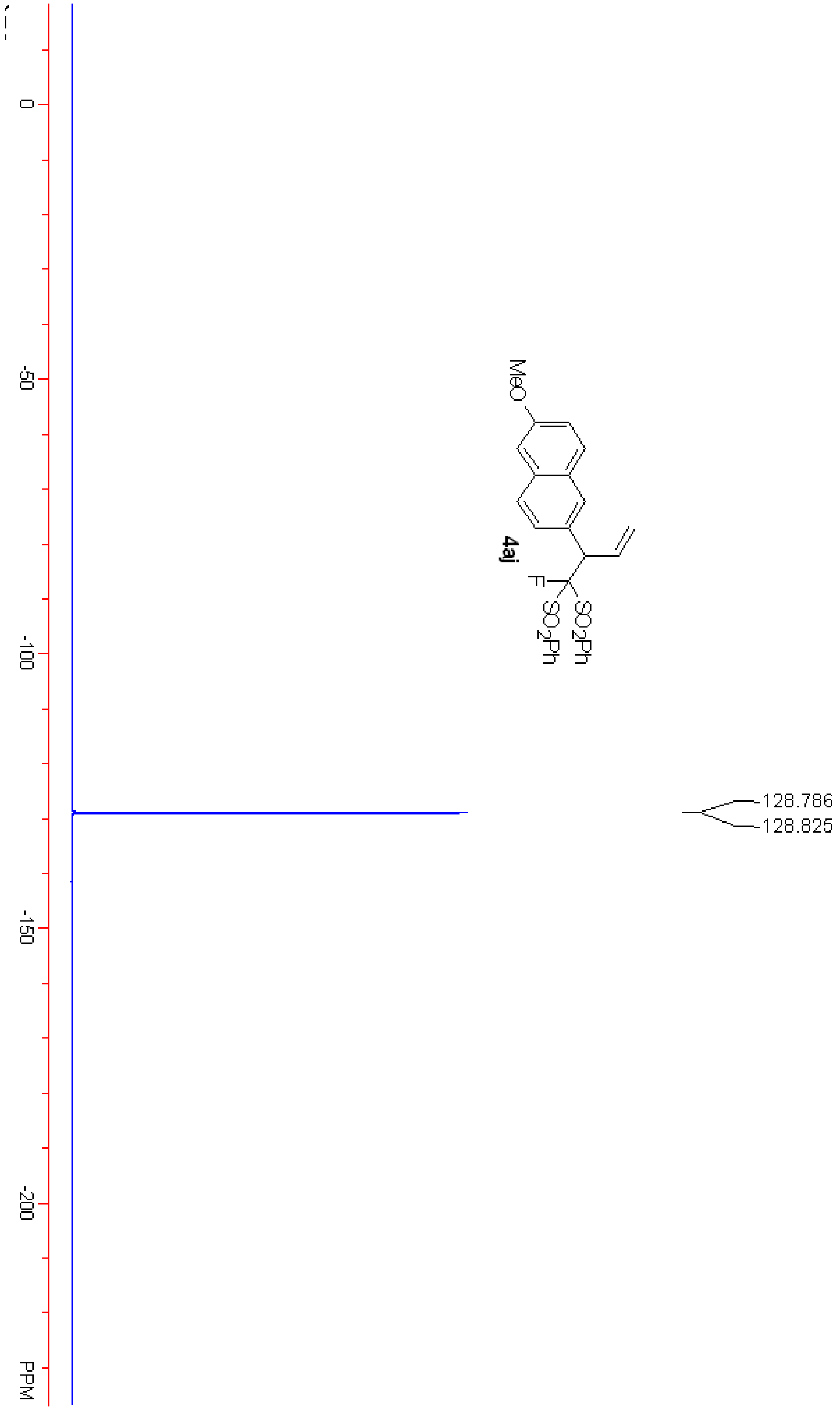
^{1}H NMR (400 MHz, $CDCl_3$)



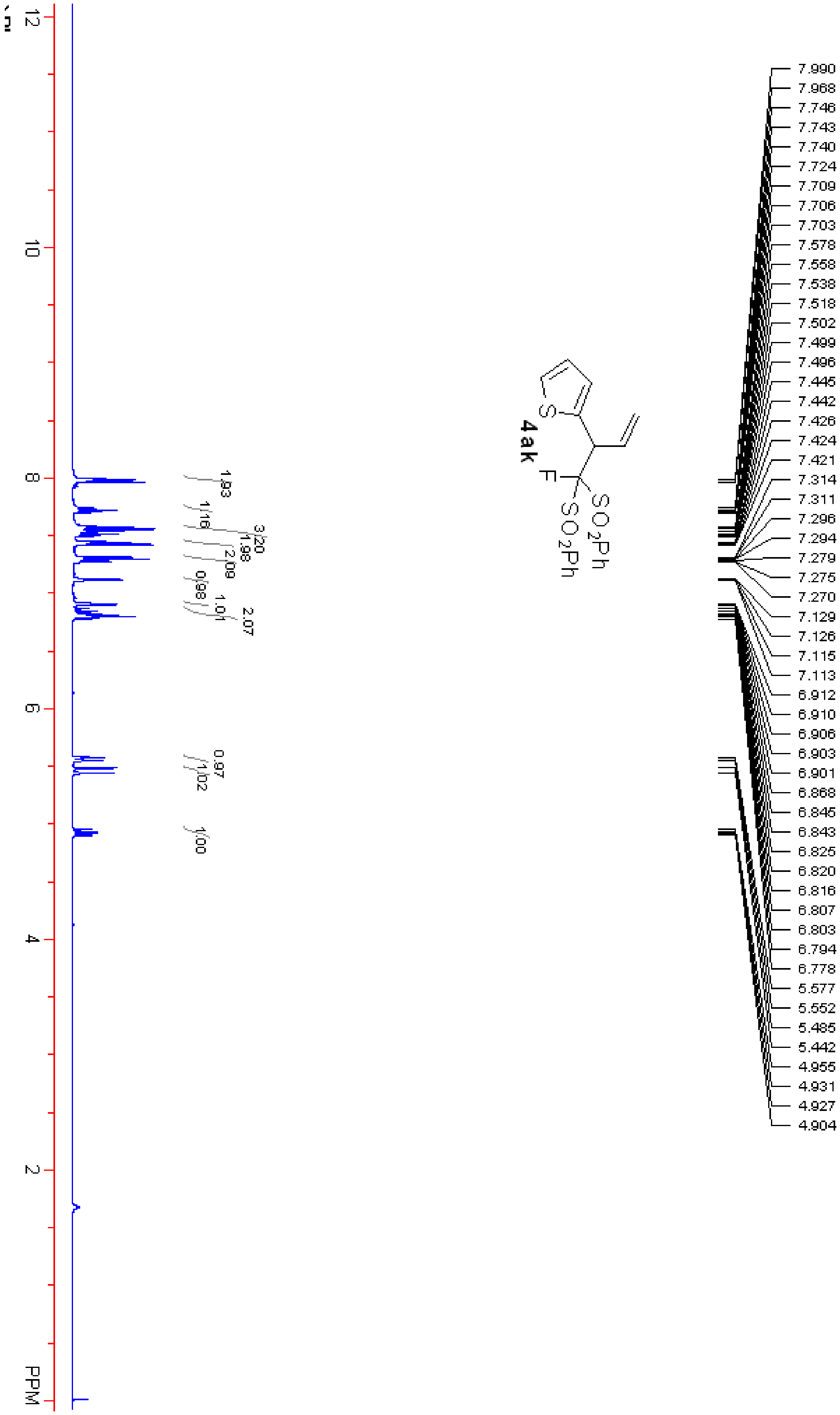
^{13}C NMR (100 MHz, $CDCl_3$)



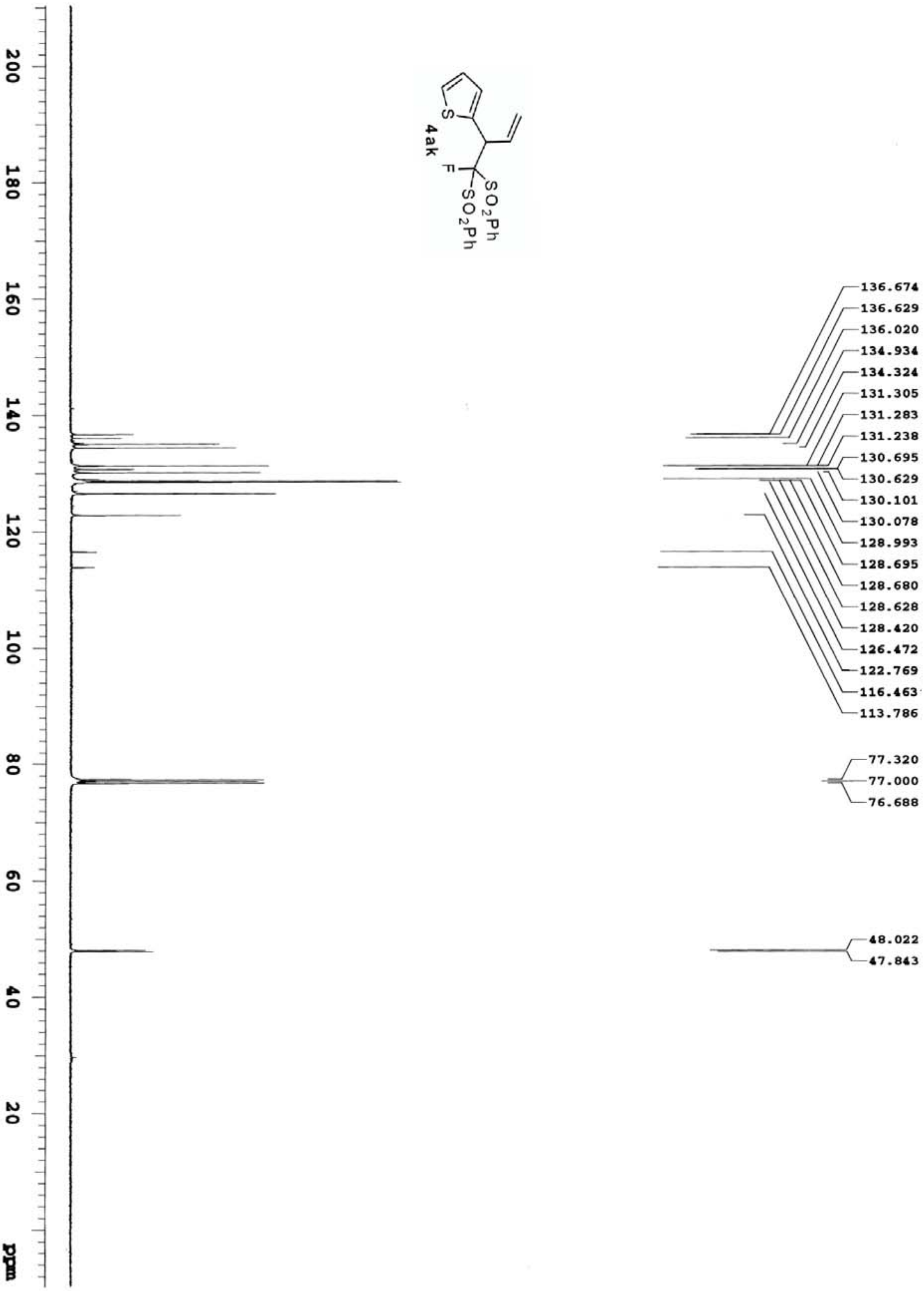
^{19}F NMR (376 MHz, $CDCl_3$)



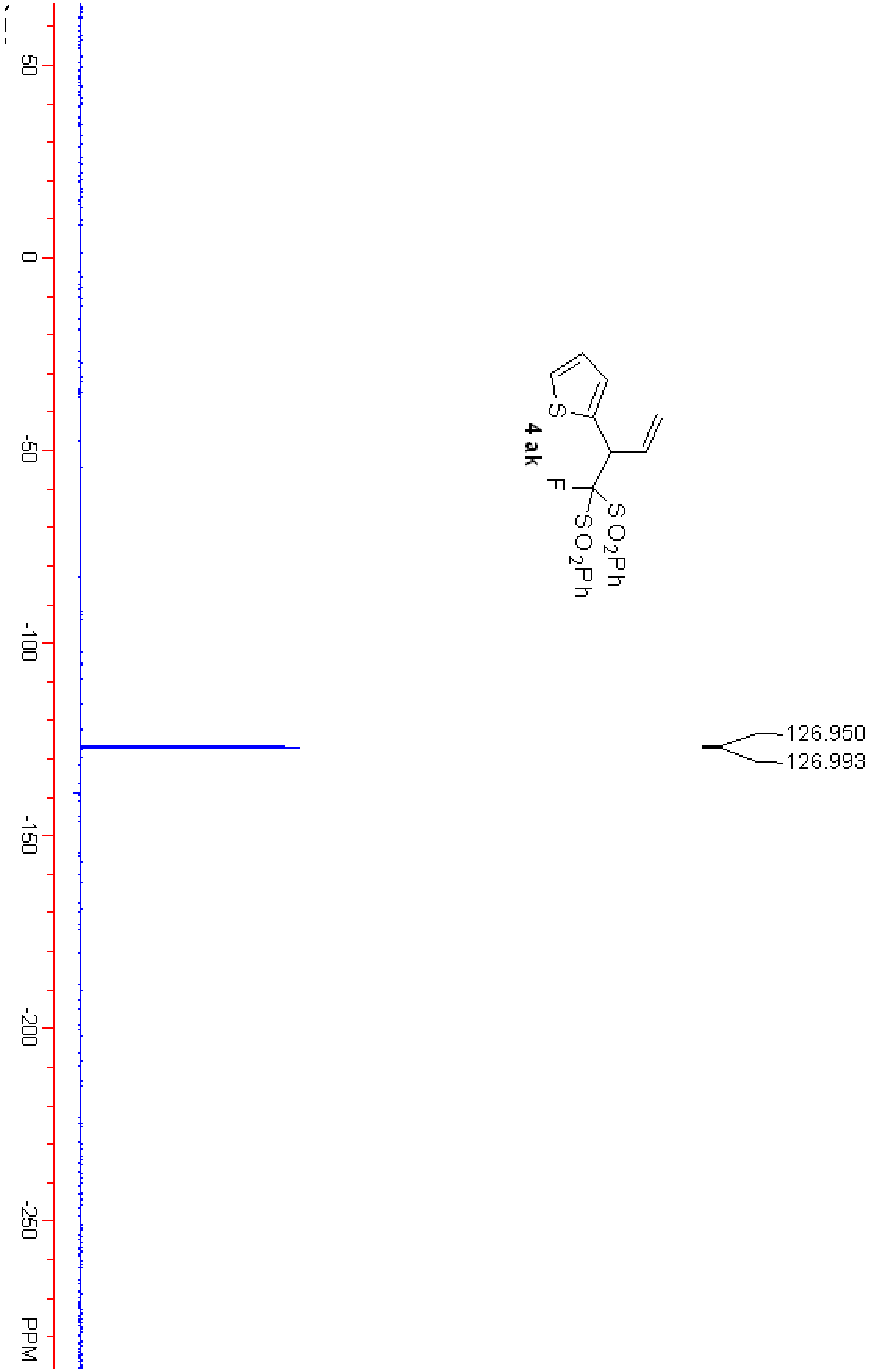
[1]H NMR (300 MHz, $CDCl_3$)



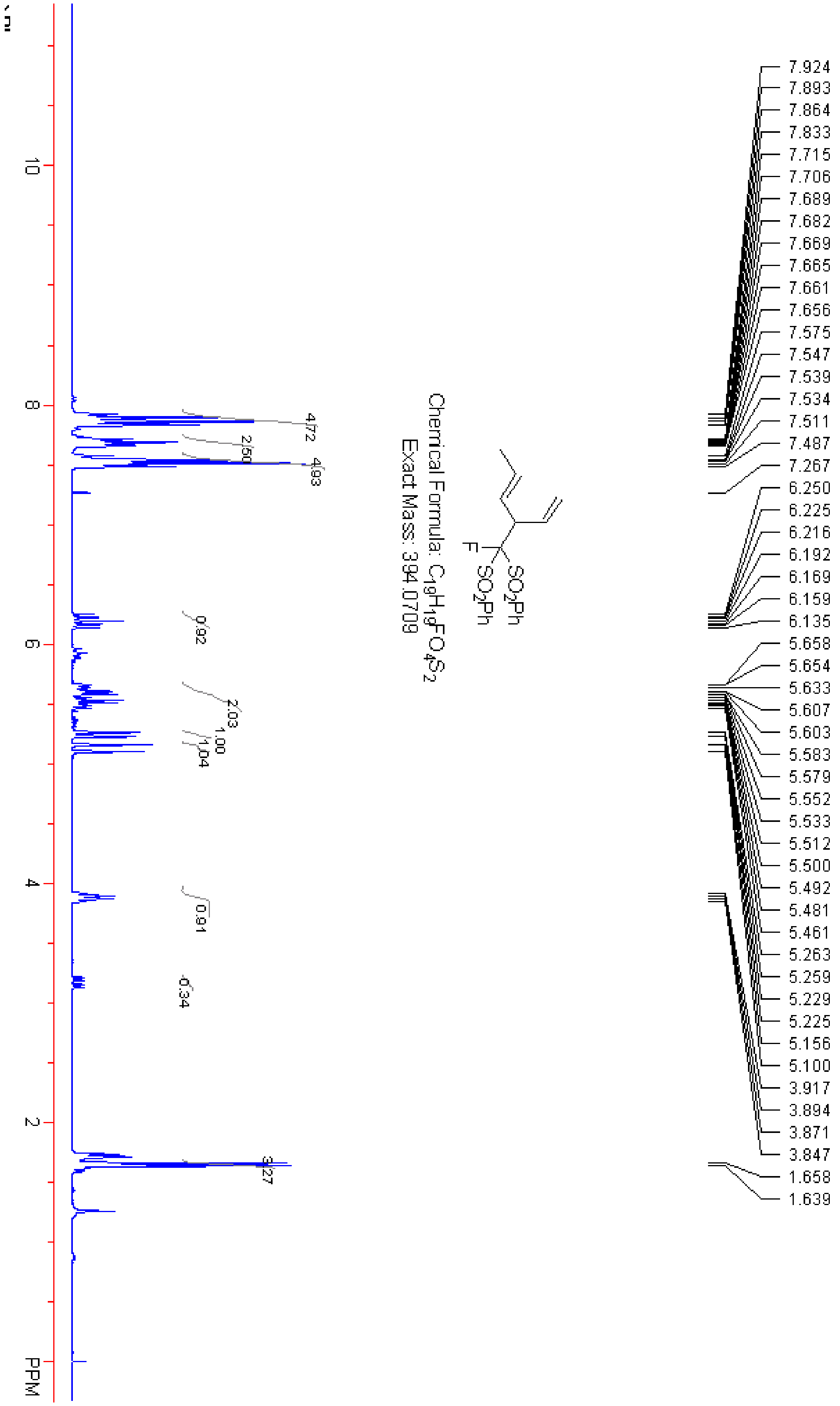
^{13}C NMR (100 MHz, $CDCl_3$)



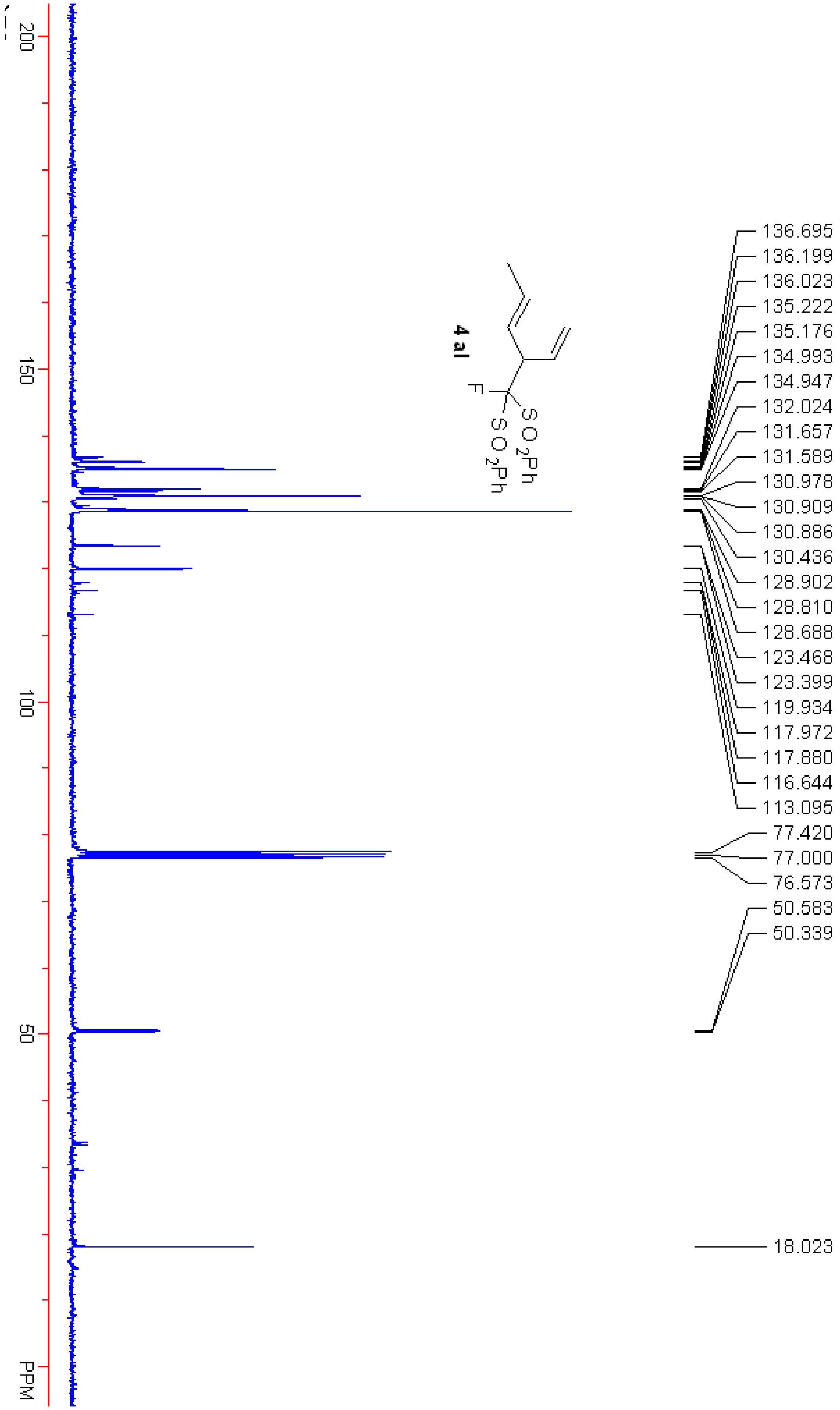
^{19}F NMR (282 MHz, $CDCl_3$)



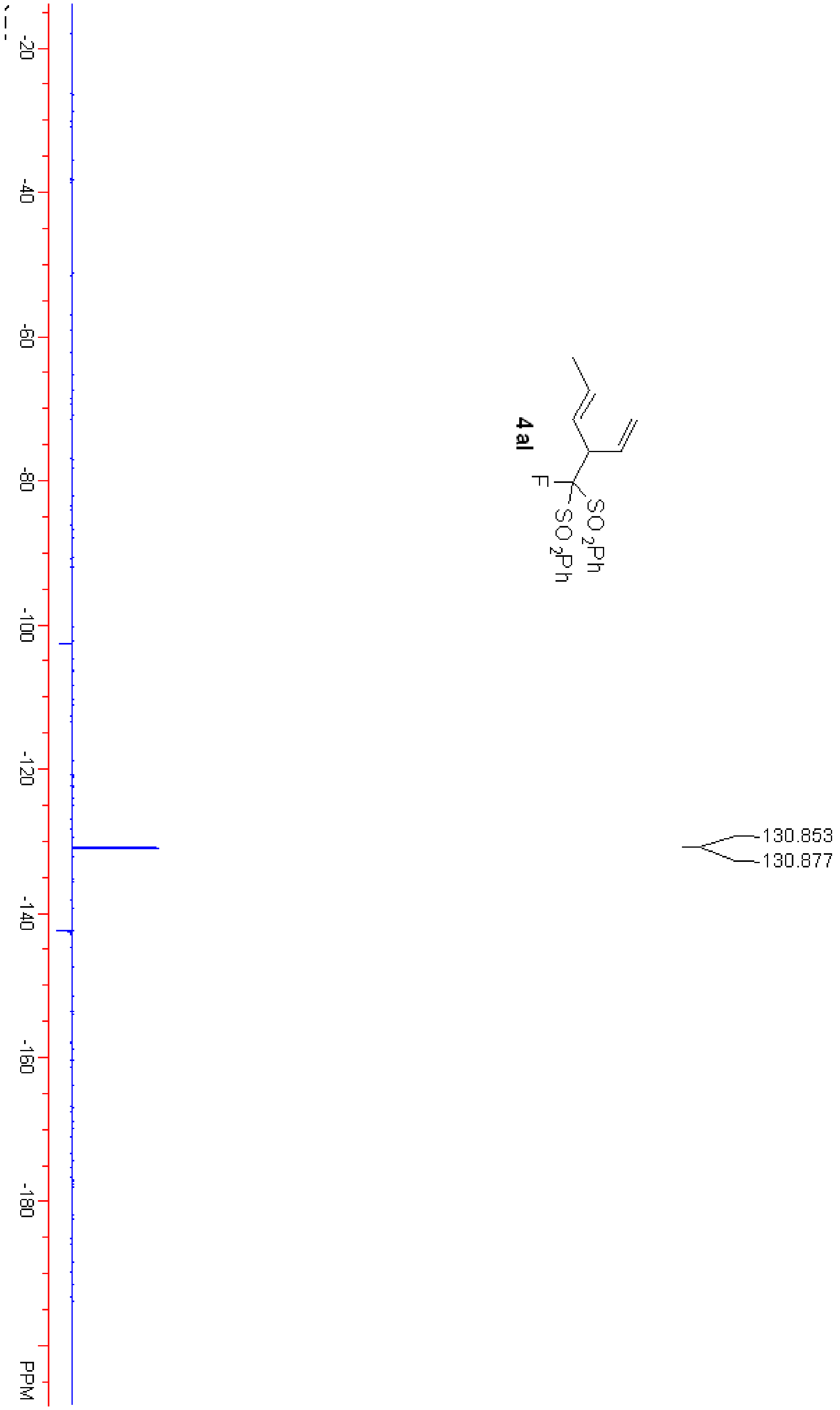
[1]H NMR (300 MHz, $CDCl_3$)



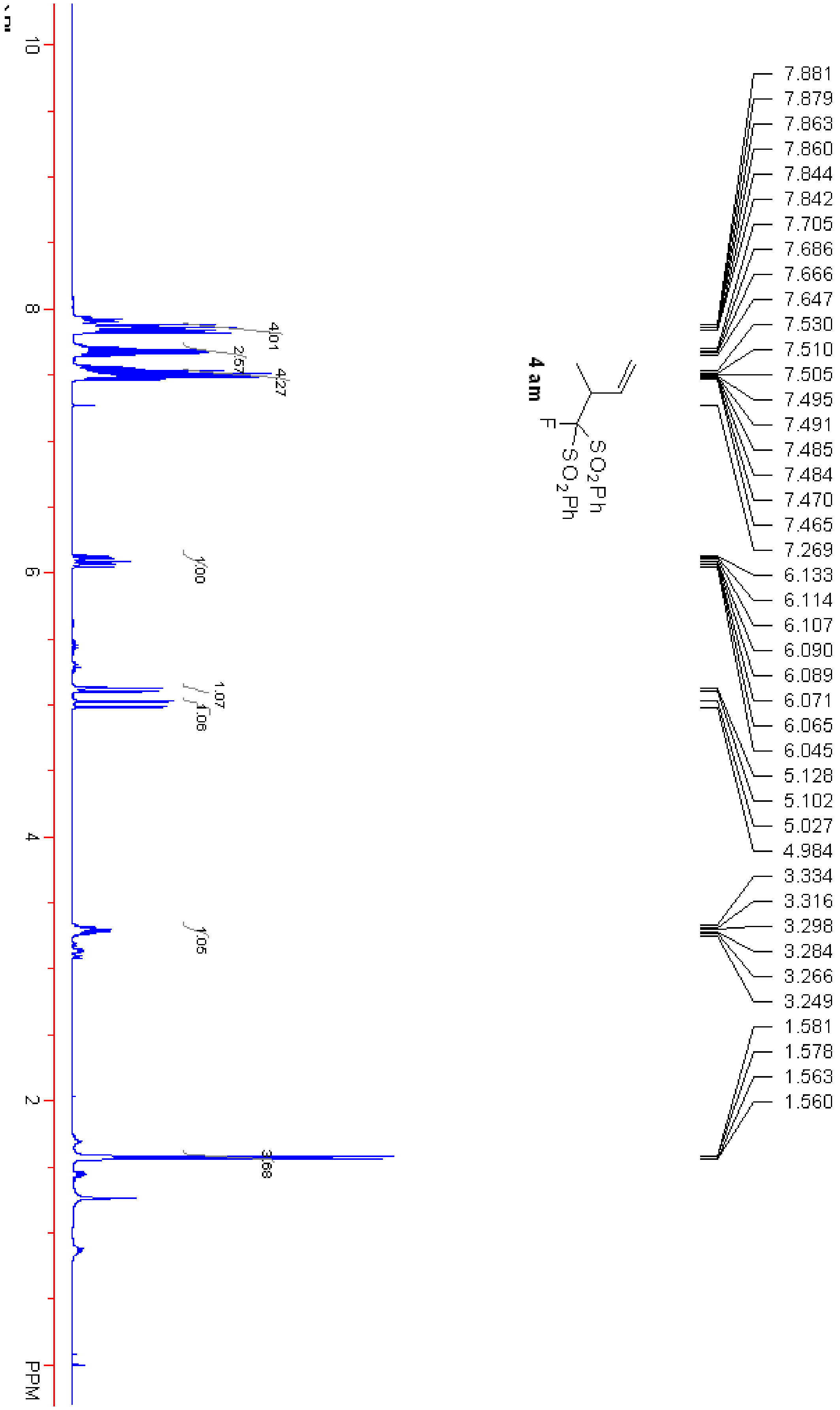
^{13}C NMR (75 MHz, $CDCl_3$)



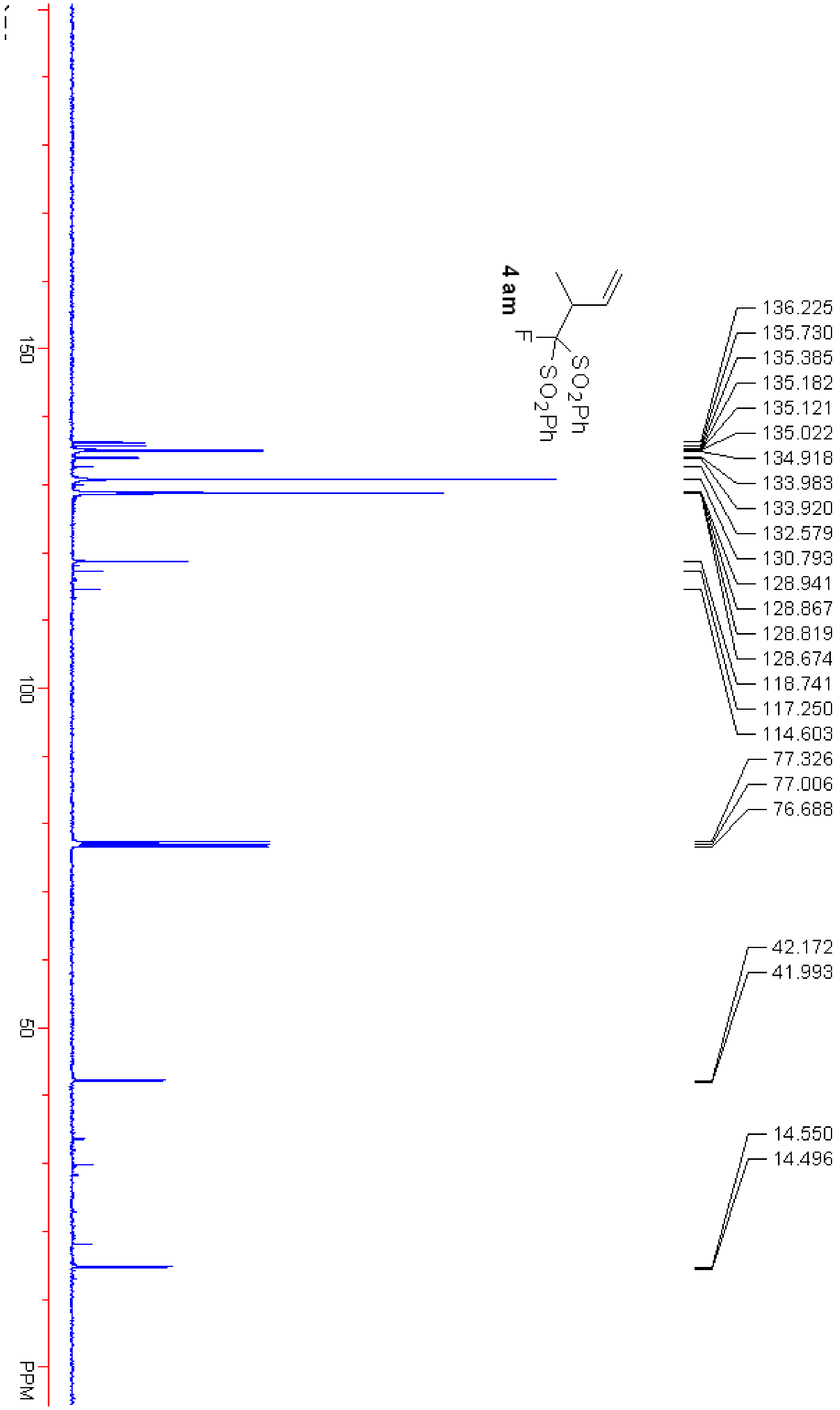
^{19}F NMR (282 MHz, $CDCl_3$)



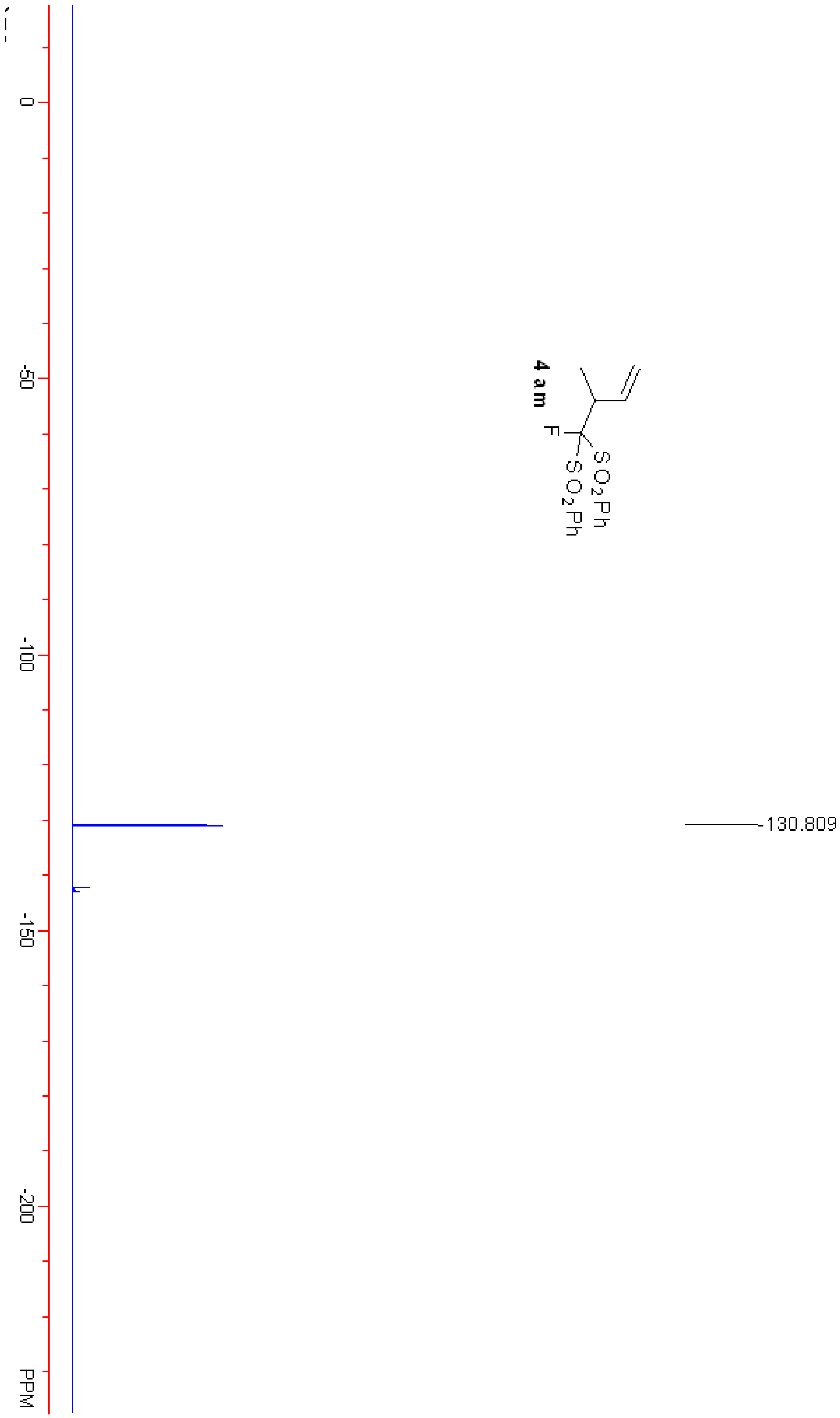
[1]H NMR (400 MHz, $CDCl_3$)



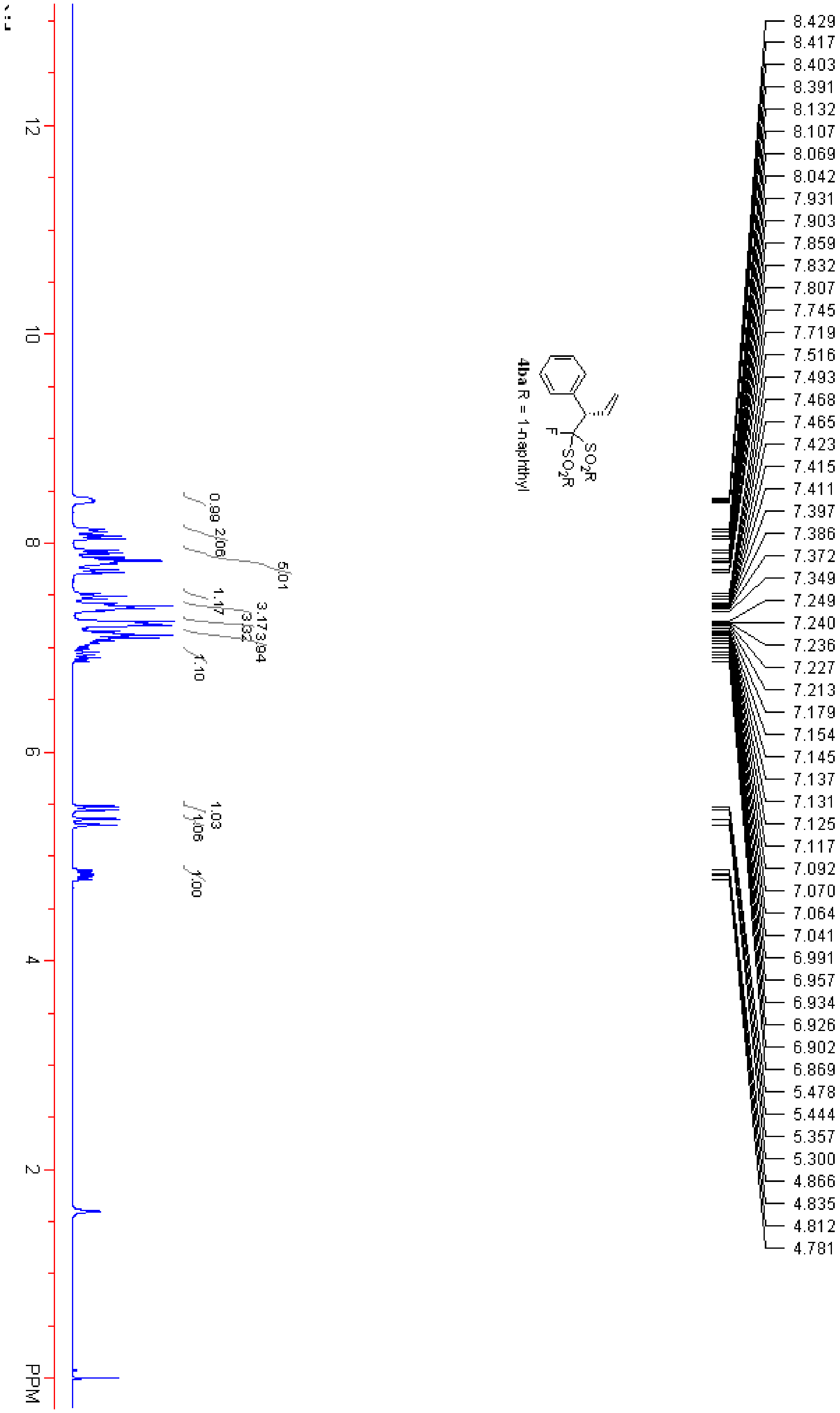
^{13}C NMR (100 MHz, $CDCl_3$)



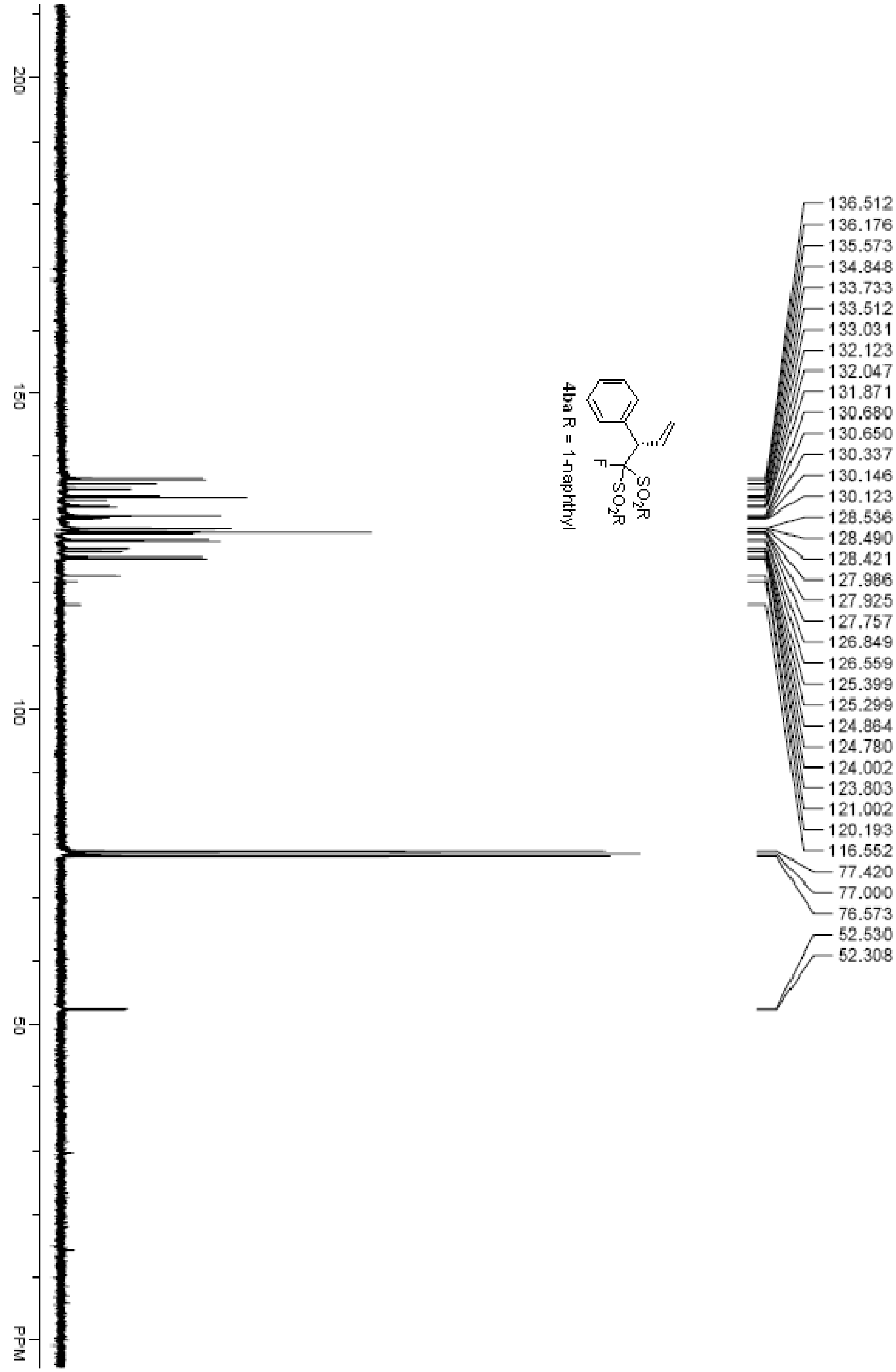
^{19}F NMR (376 MHz, $CDCl_3$)



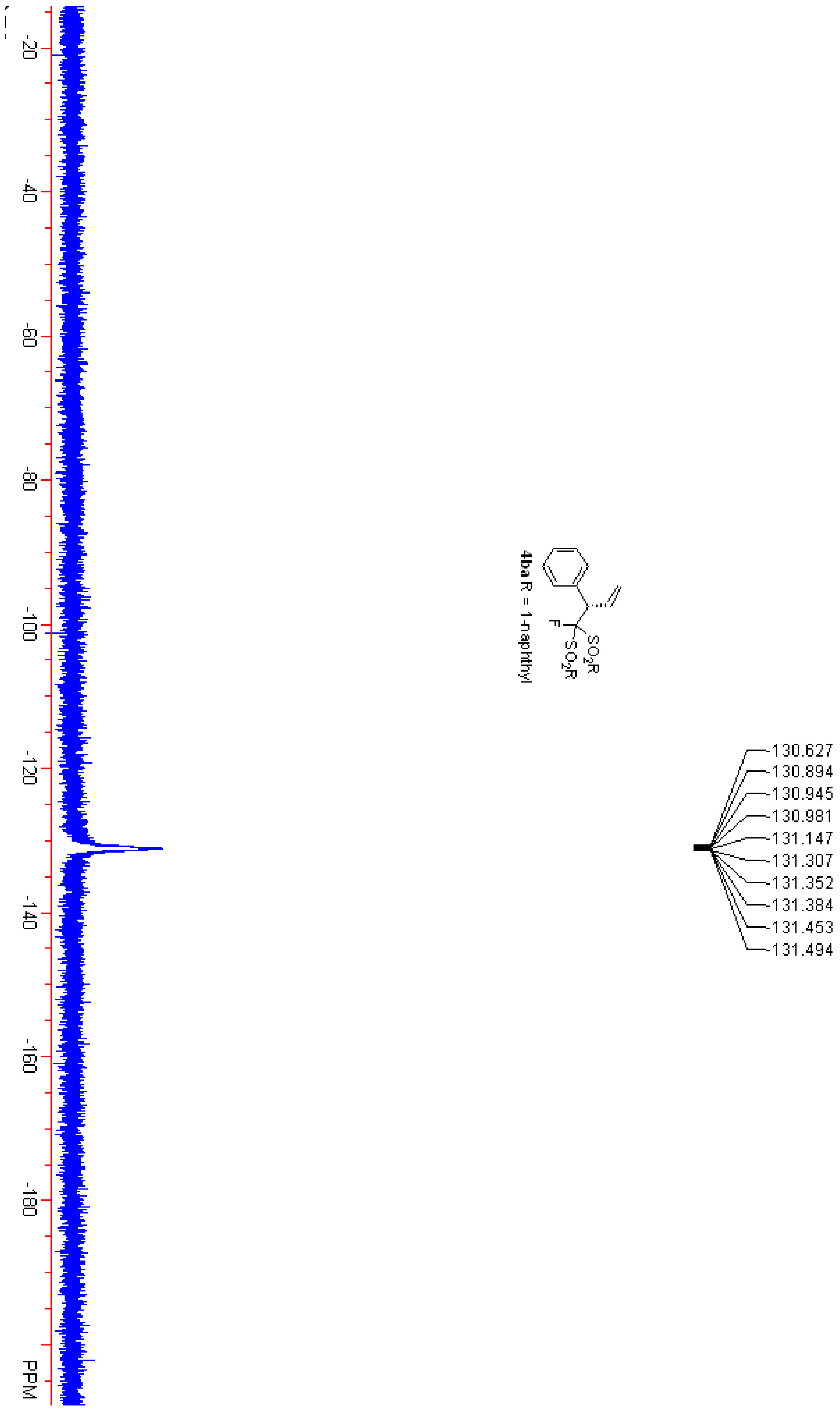
^{1}H NMR (300 MHz, $CDCl_3$)



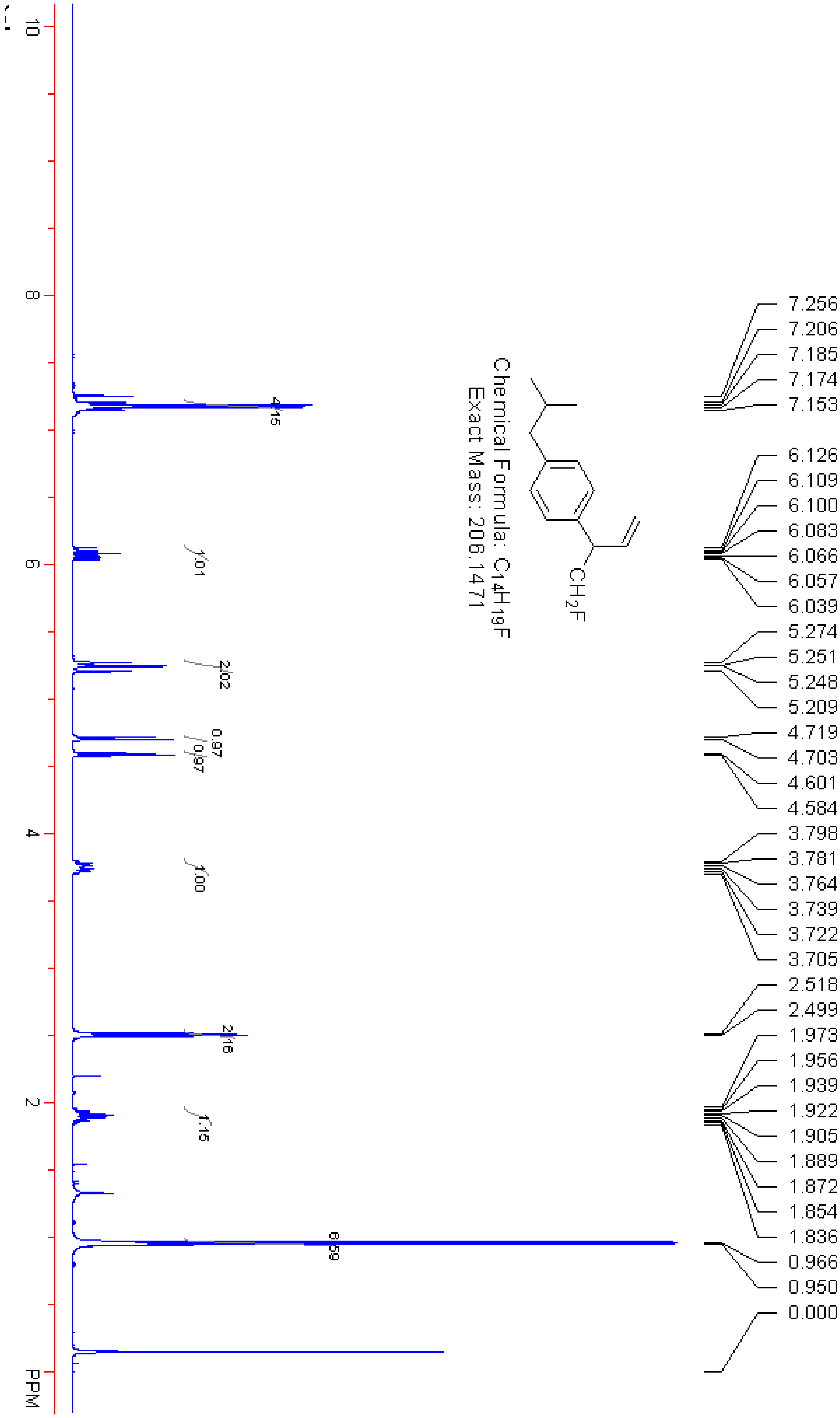
^{13}C NMR (75 MHz, $CDCl_3$)



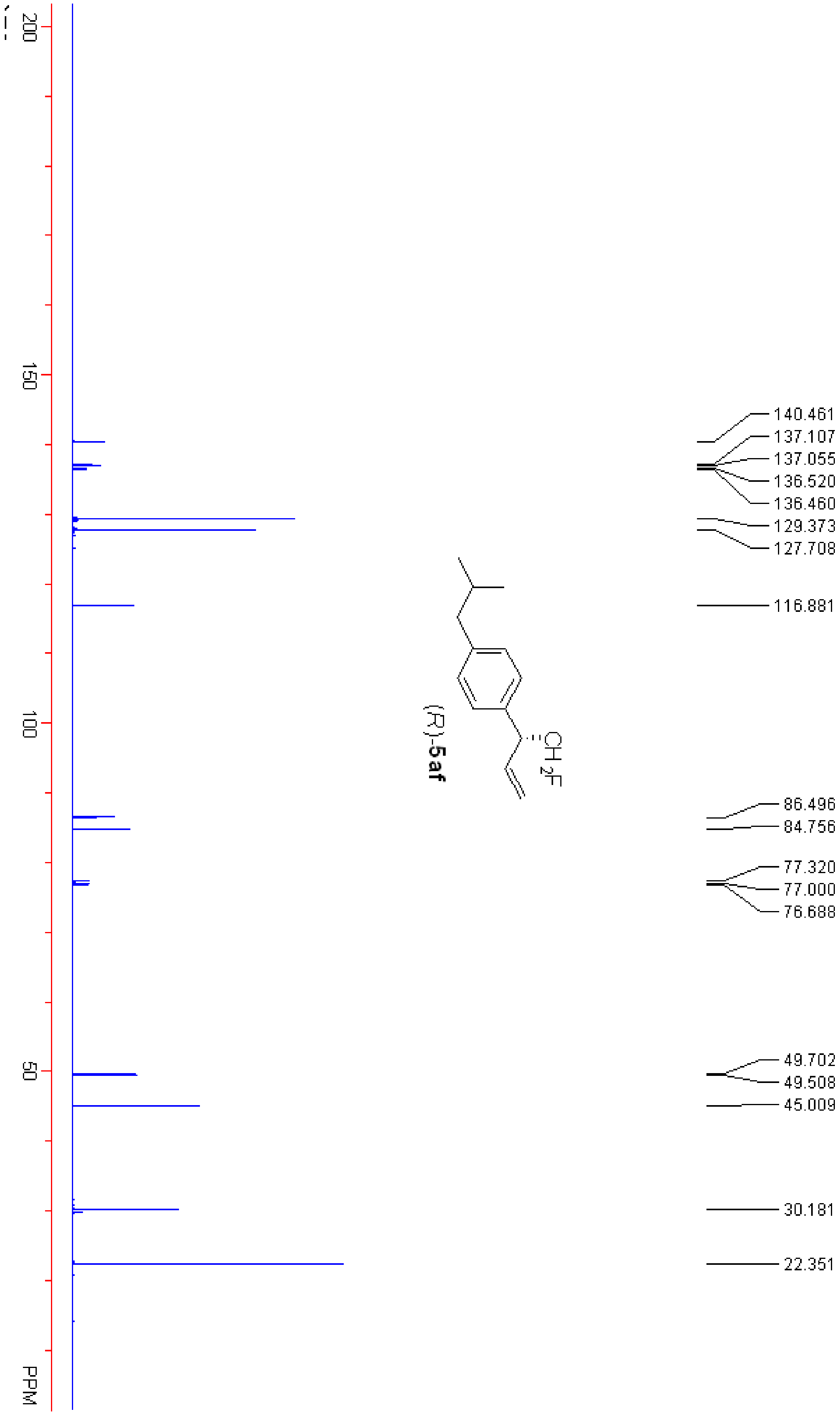
^{19}F NMR (282 MHz, $CDCl_3$)



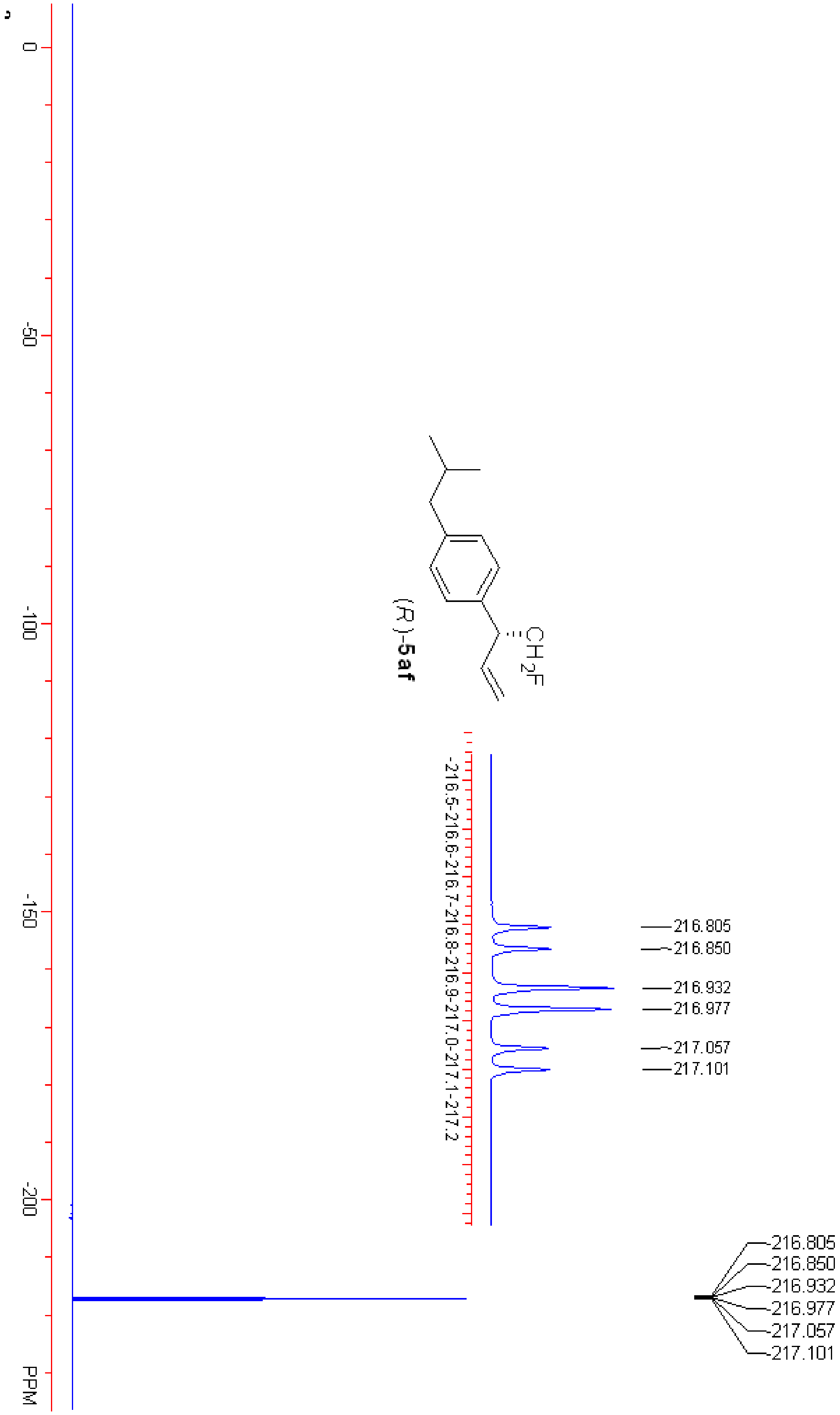
^{1}H NMR (400 MHz, $CDCl_3$)



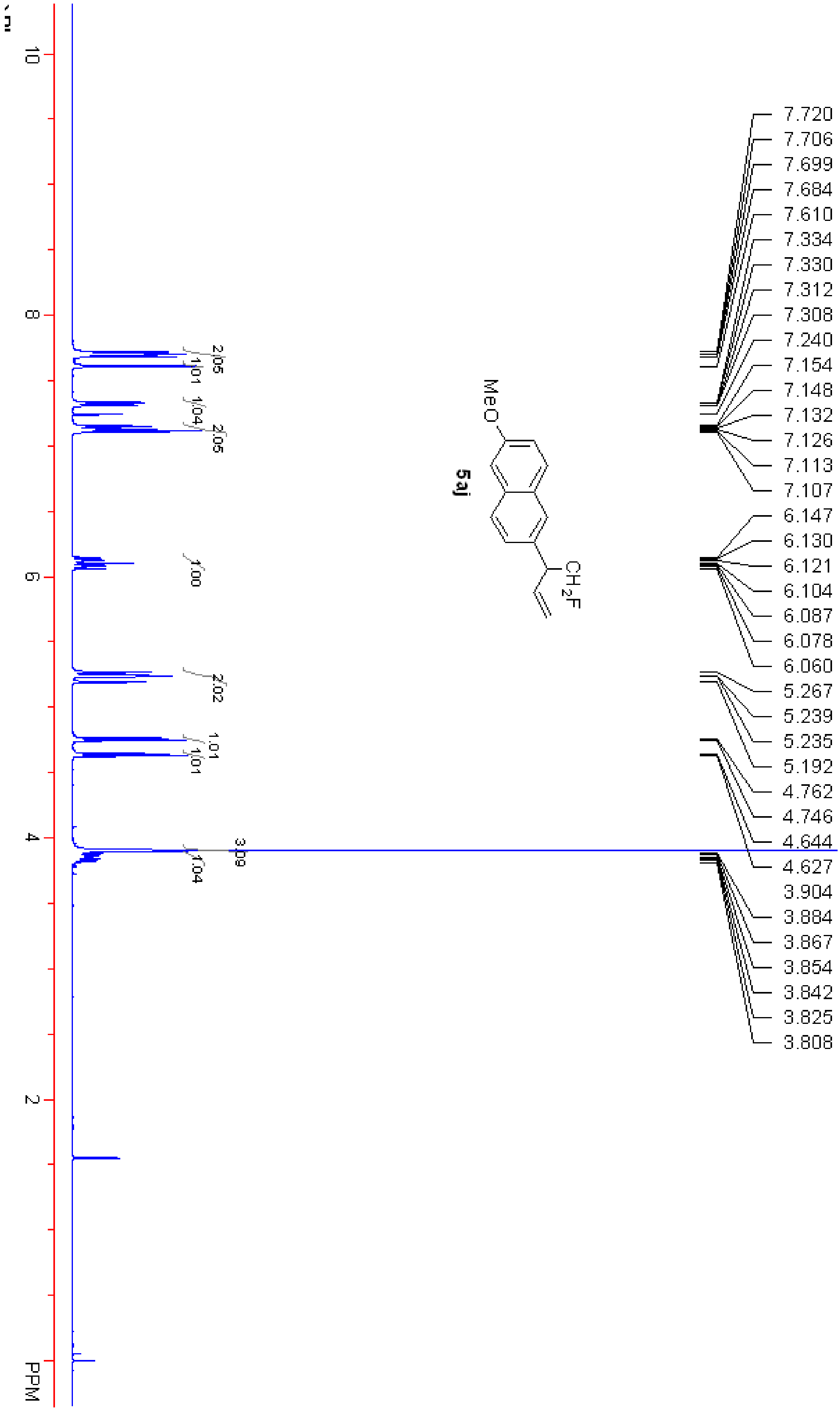
^{13}C NMR (100 MHz, $CDCl_3$)



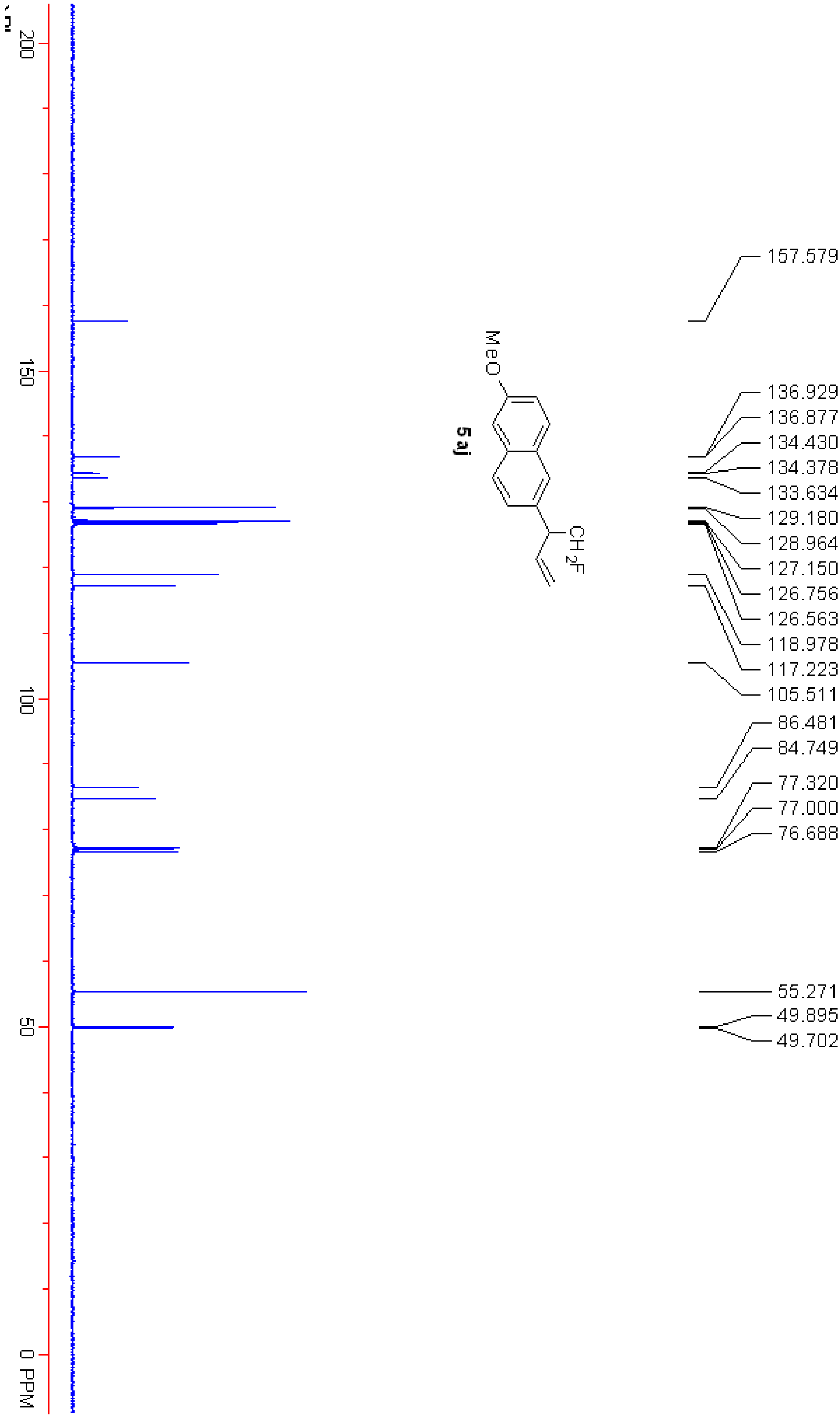
^{19}F NMR (376 MHz, $CDCl_3$)



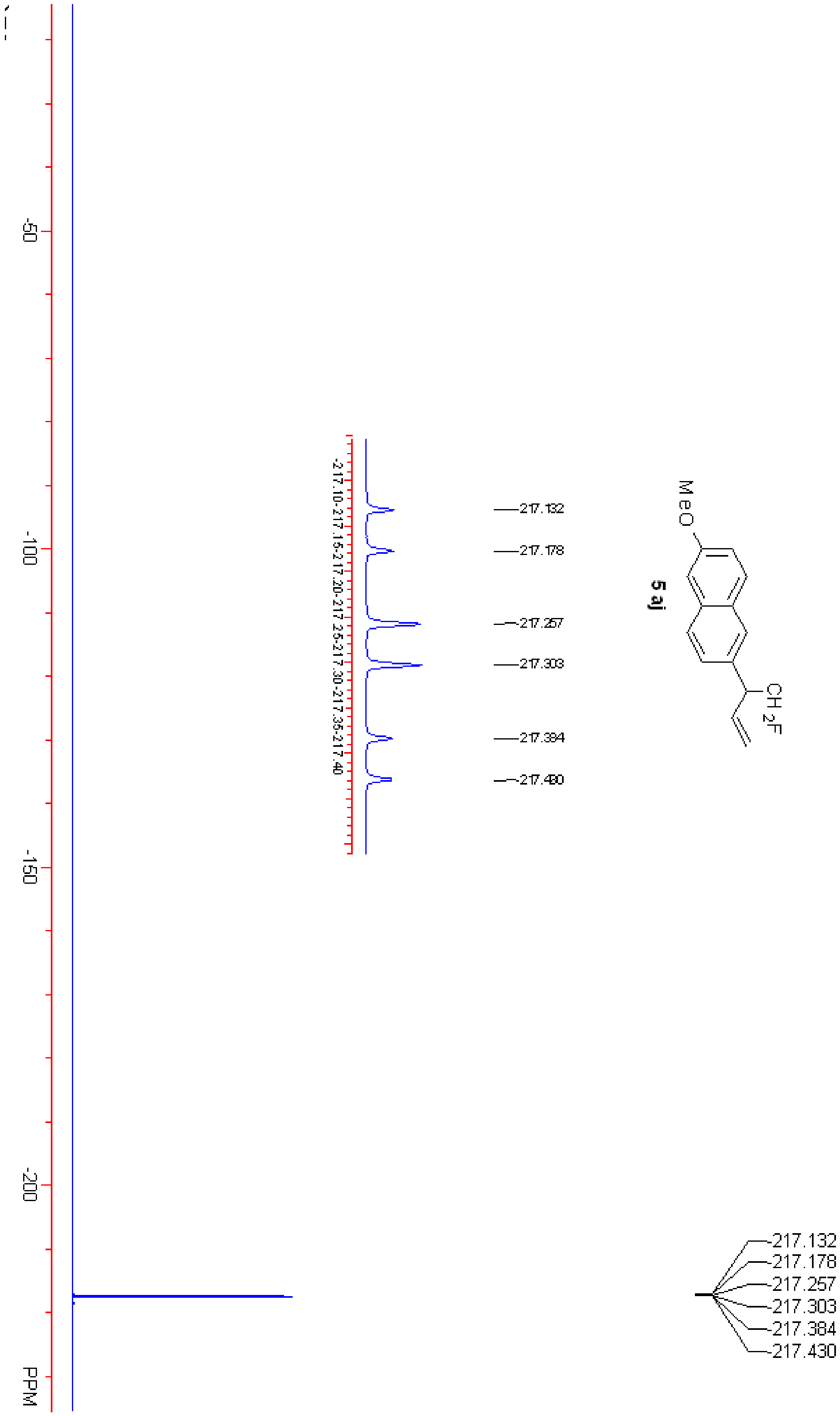
^{1}H NMR (400 MHz, $CDCl_3$)



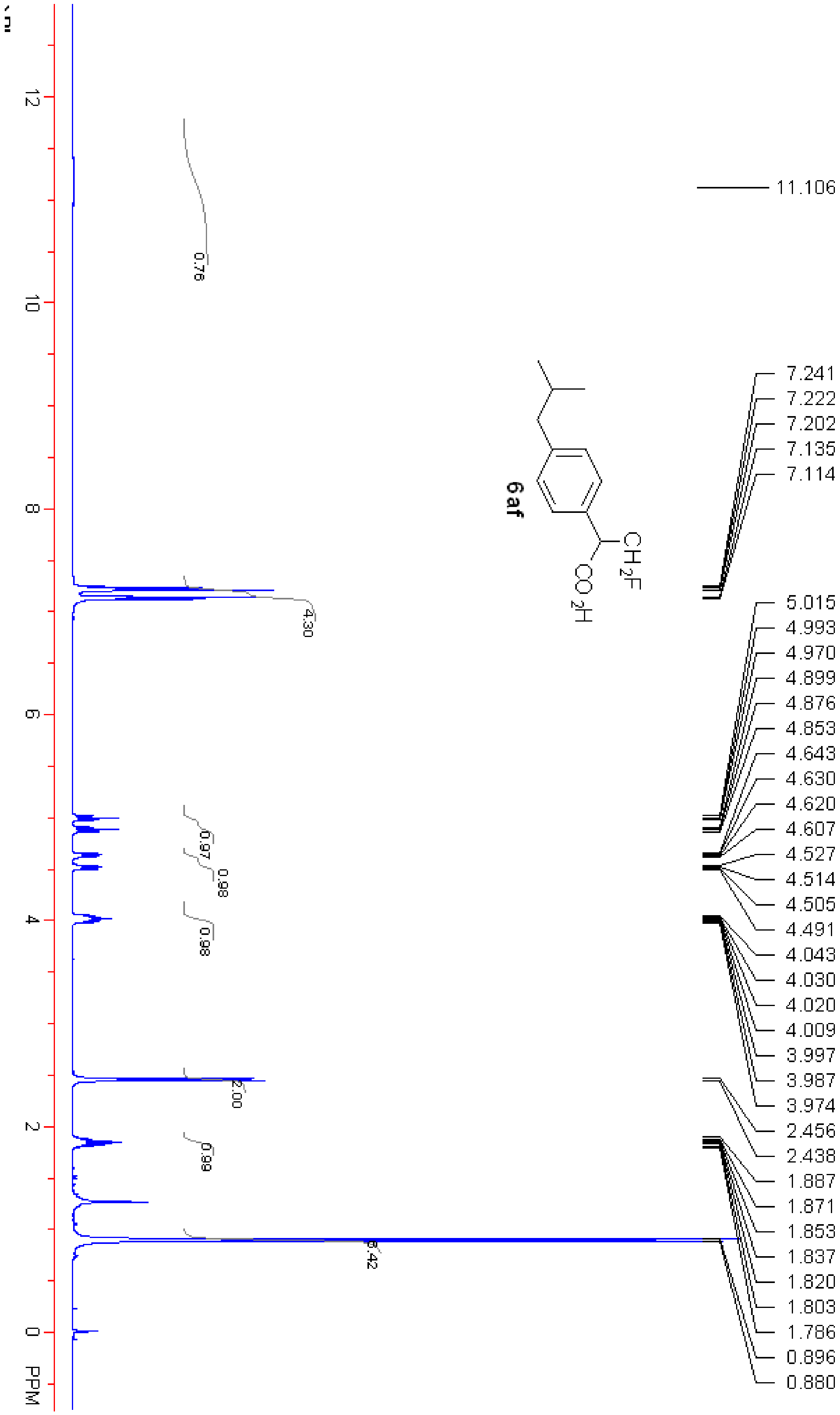
^{13}C NMR (100 MHz, $CDCl_3$)



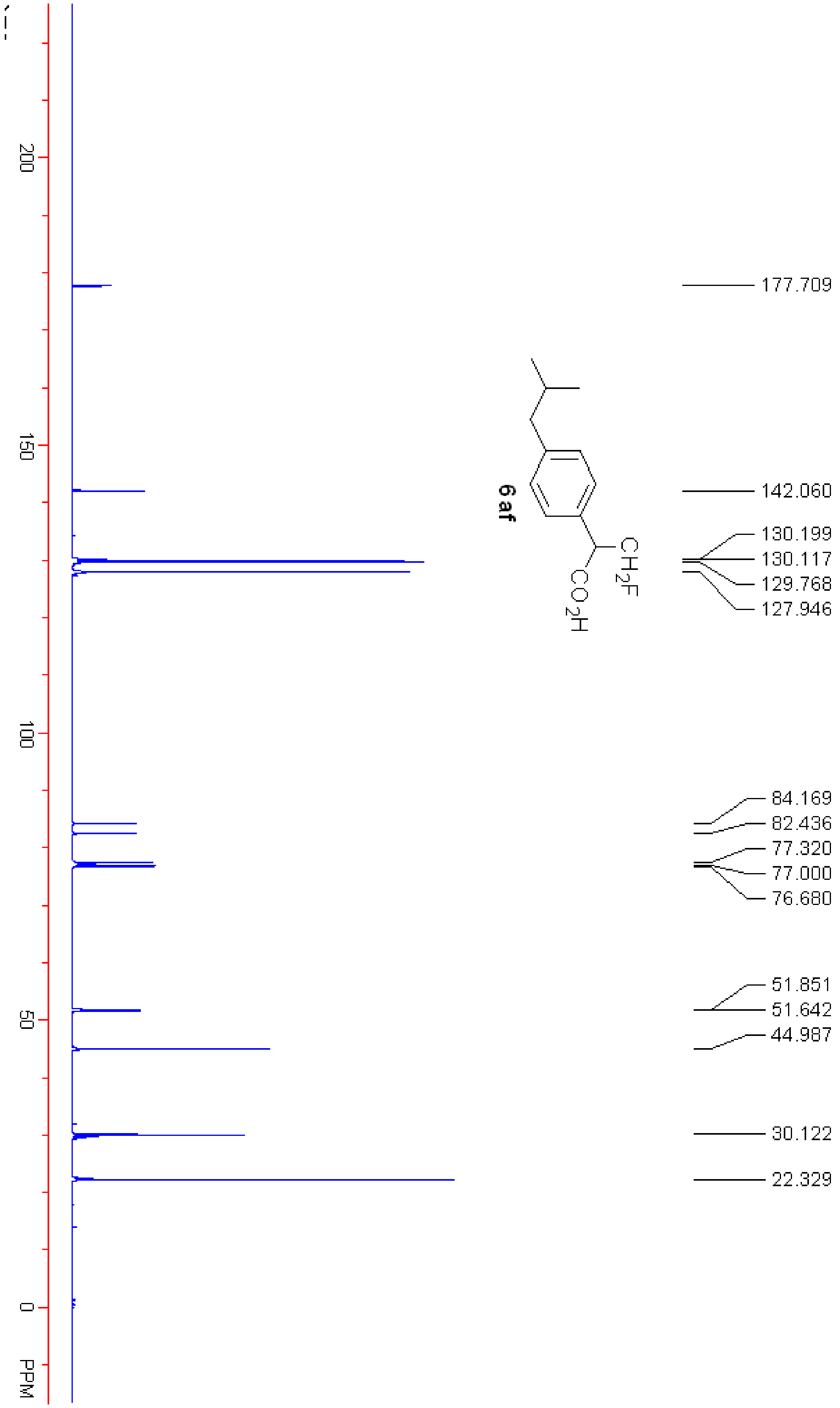
^{19}F NMR (383 MHz, $CDCl_3$)



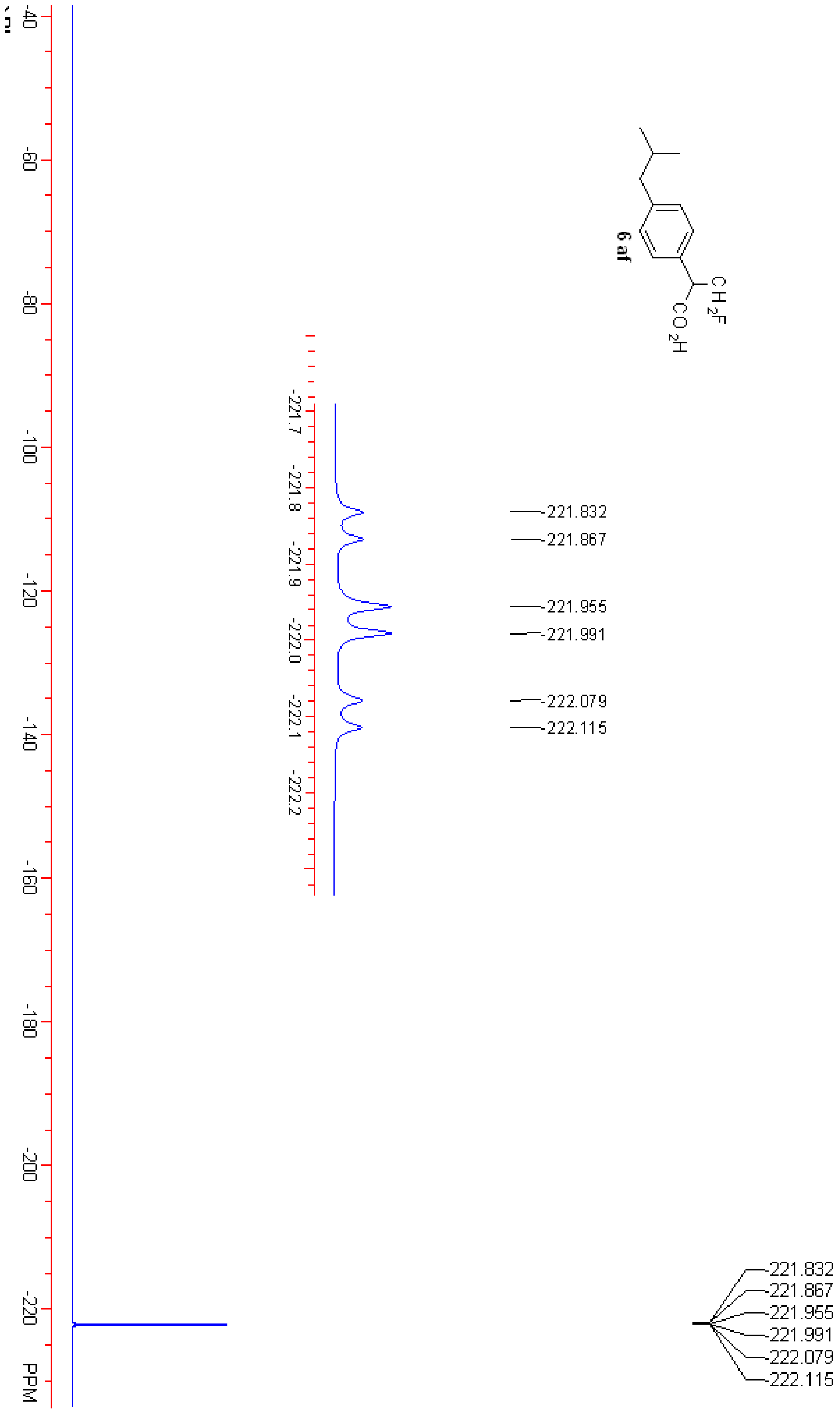
^{1}H NMR (400 MHz, $CDCl_3$)



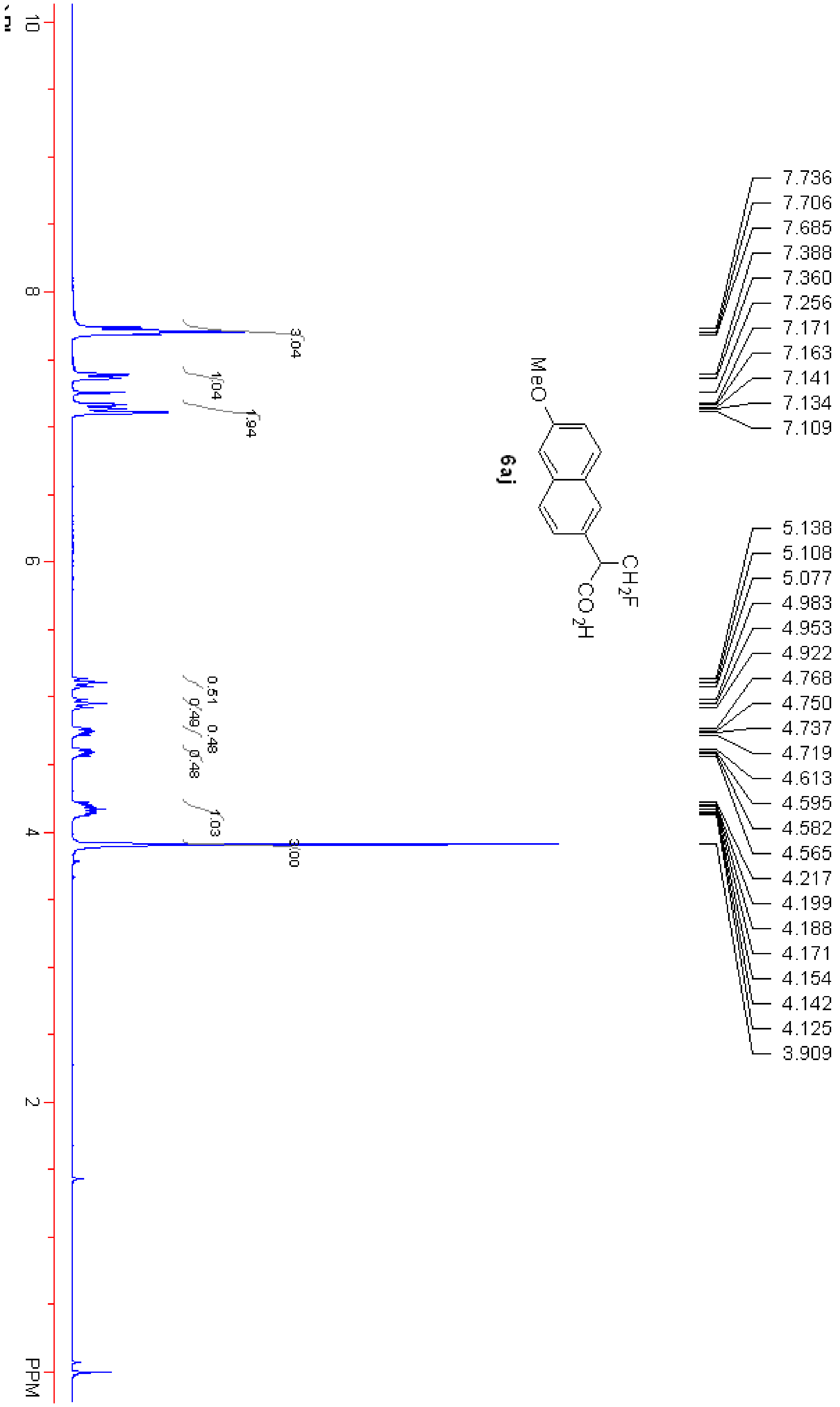
^{13}C NMR (100 MHz, $CDCl_3$)



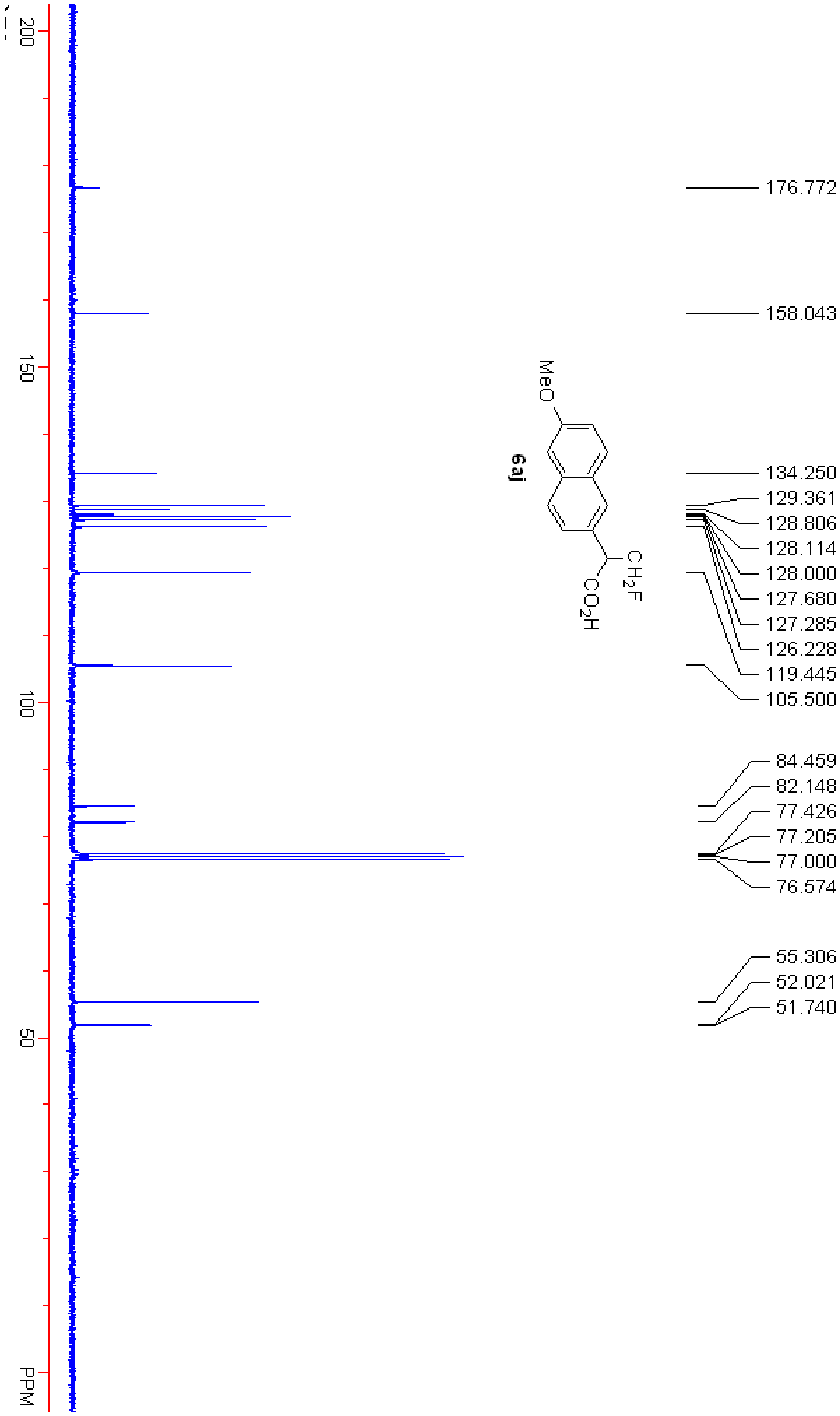
^{19}F NMR (376 MHz, $CDCl_3$)



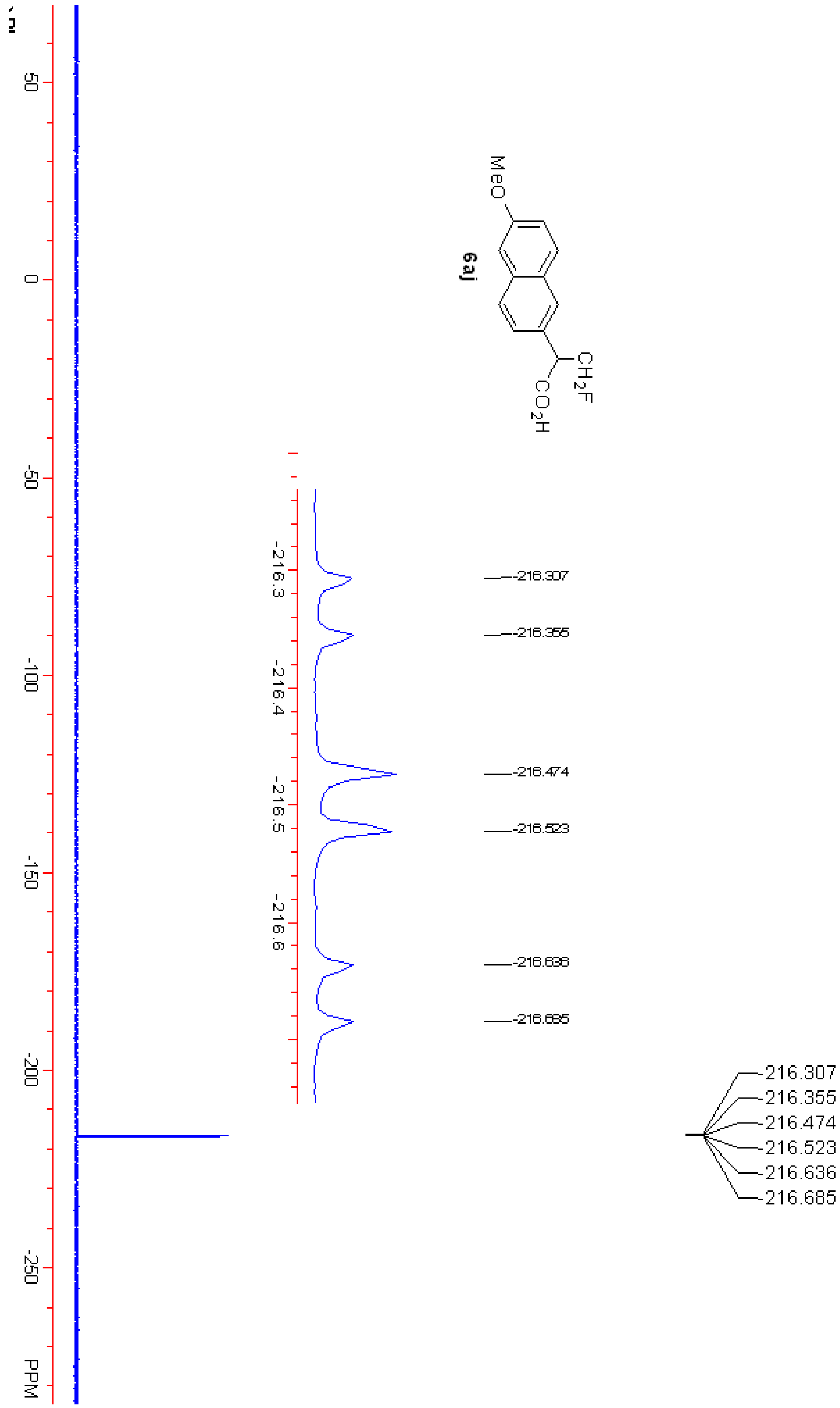
[1]H NMR (300 MHz, $CDCl_3$)



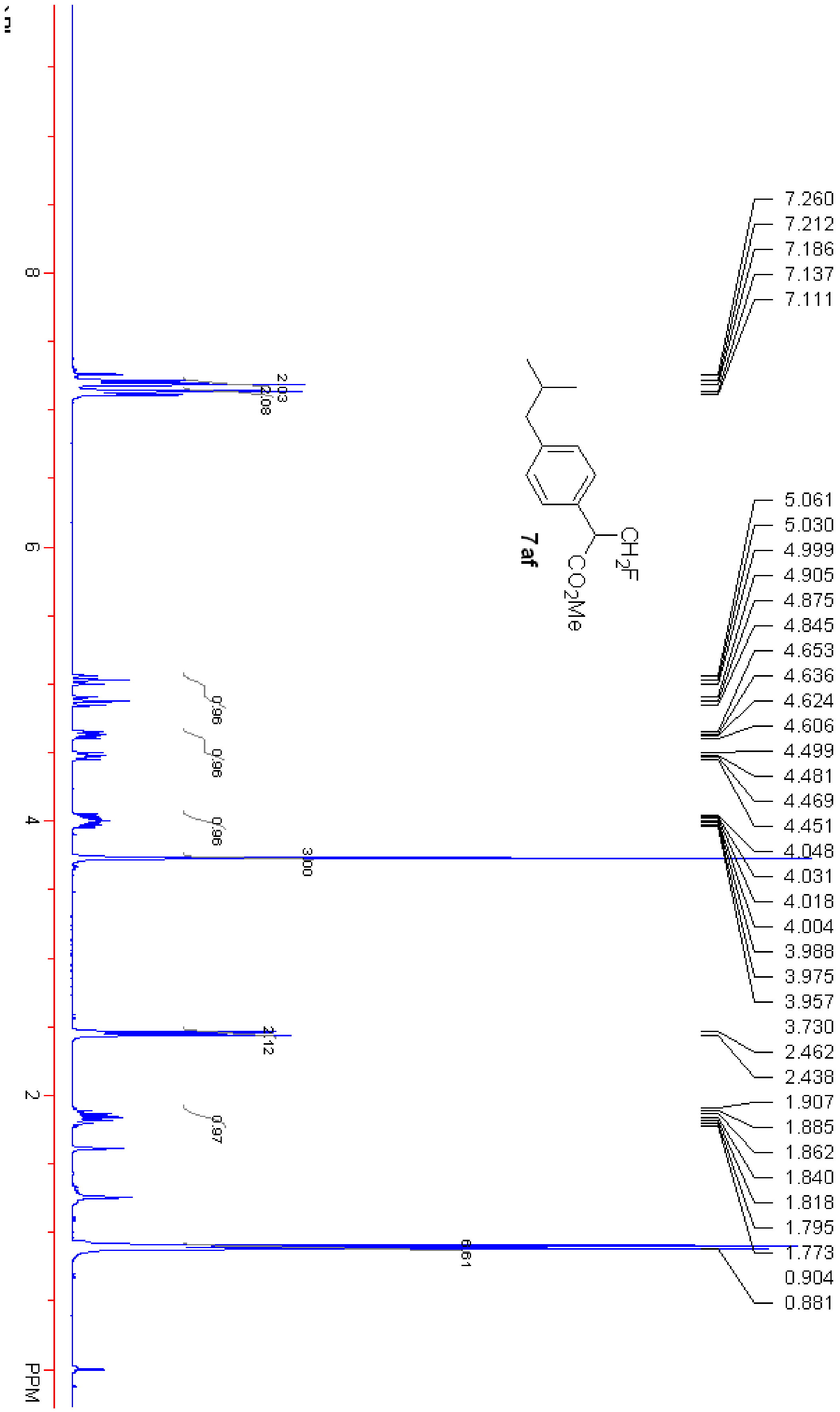
^{13}C NMR (75 MHz, $CDCl_3$)



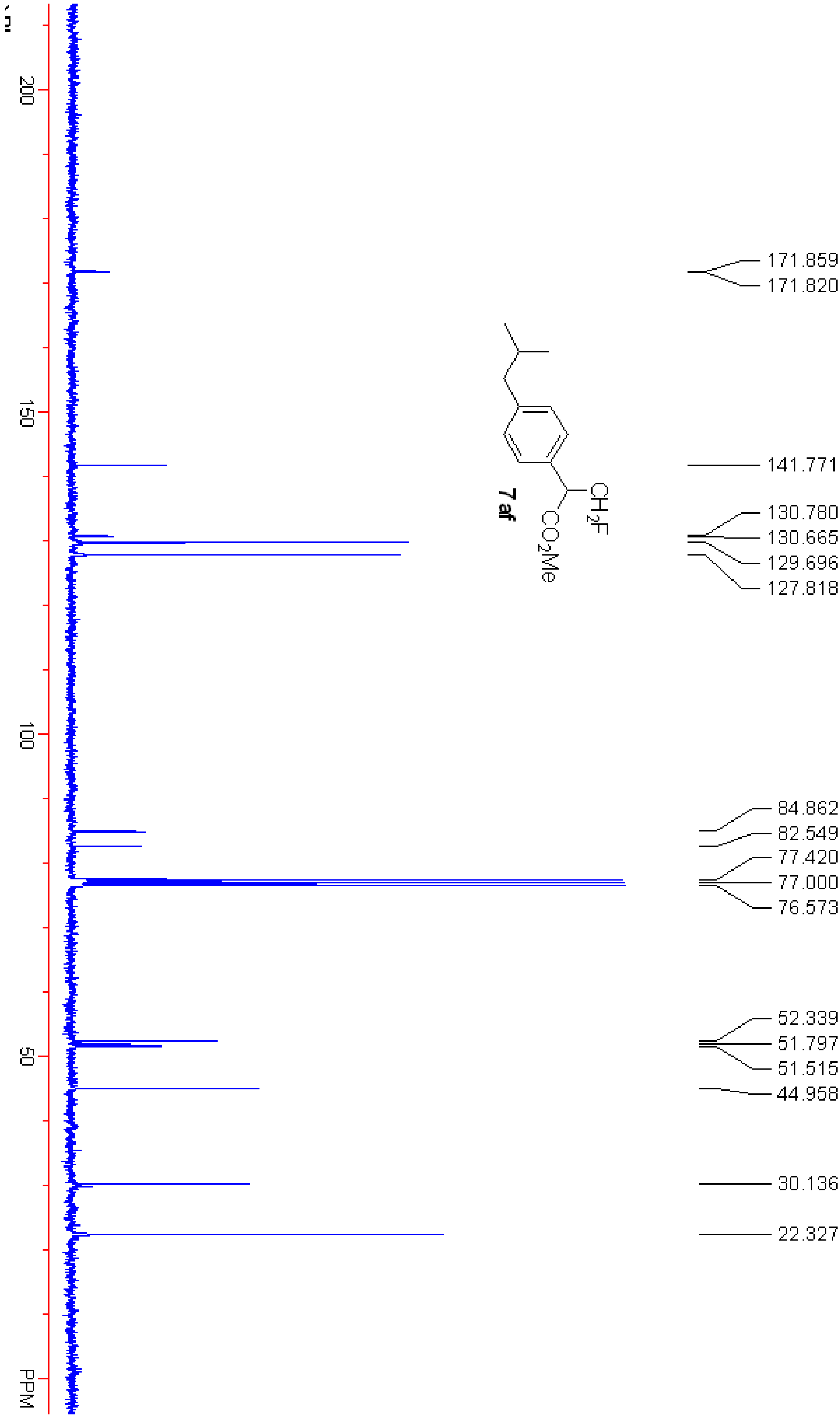
^{19}F NMR (282 MHz, $CDCl_3$)



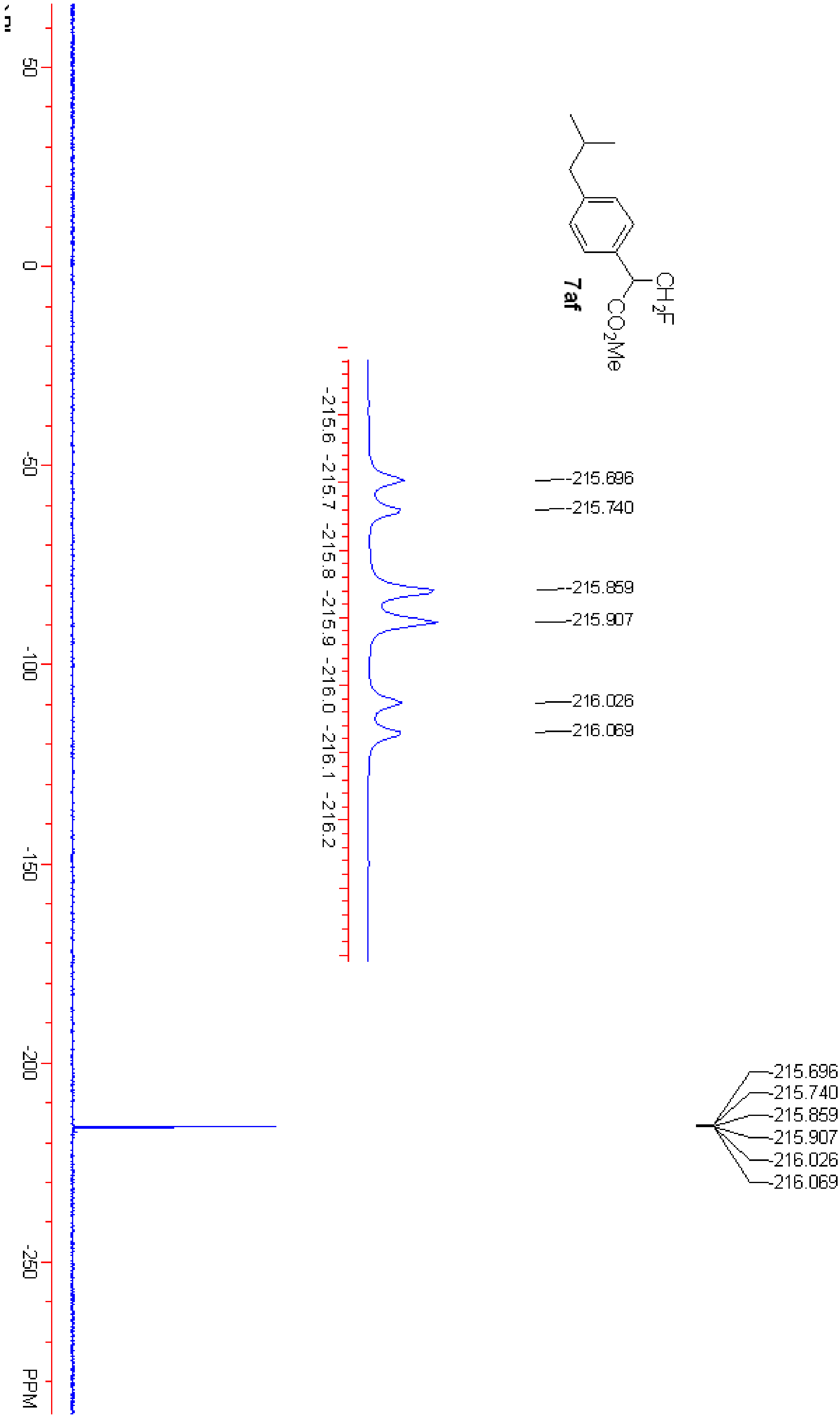
^{1}H NMR (300 MHz, $CDCl_3$)



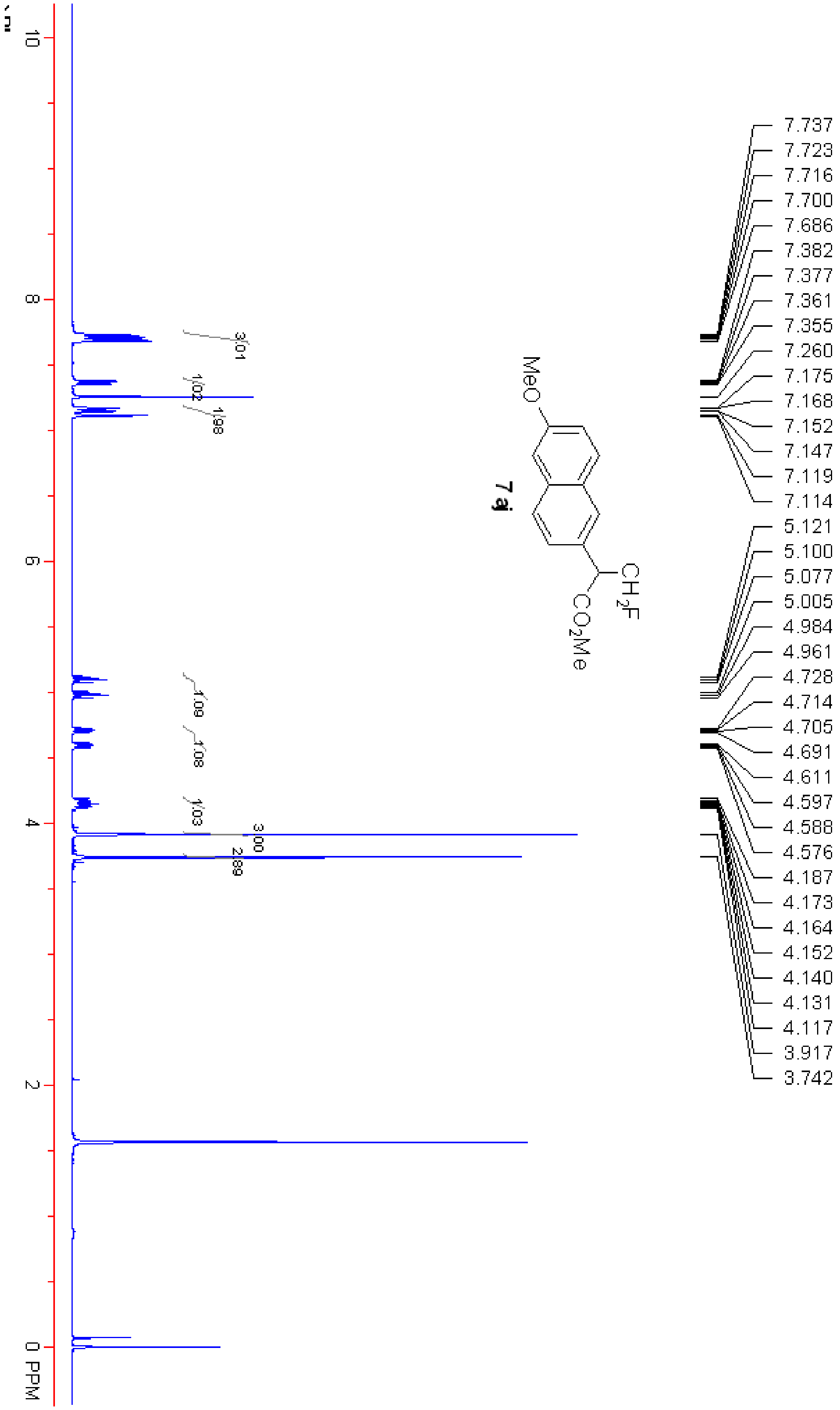
^{13}C NMR (75 MHz, $CDCl_3$)



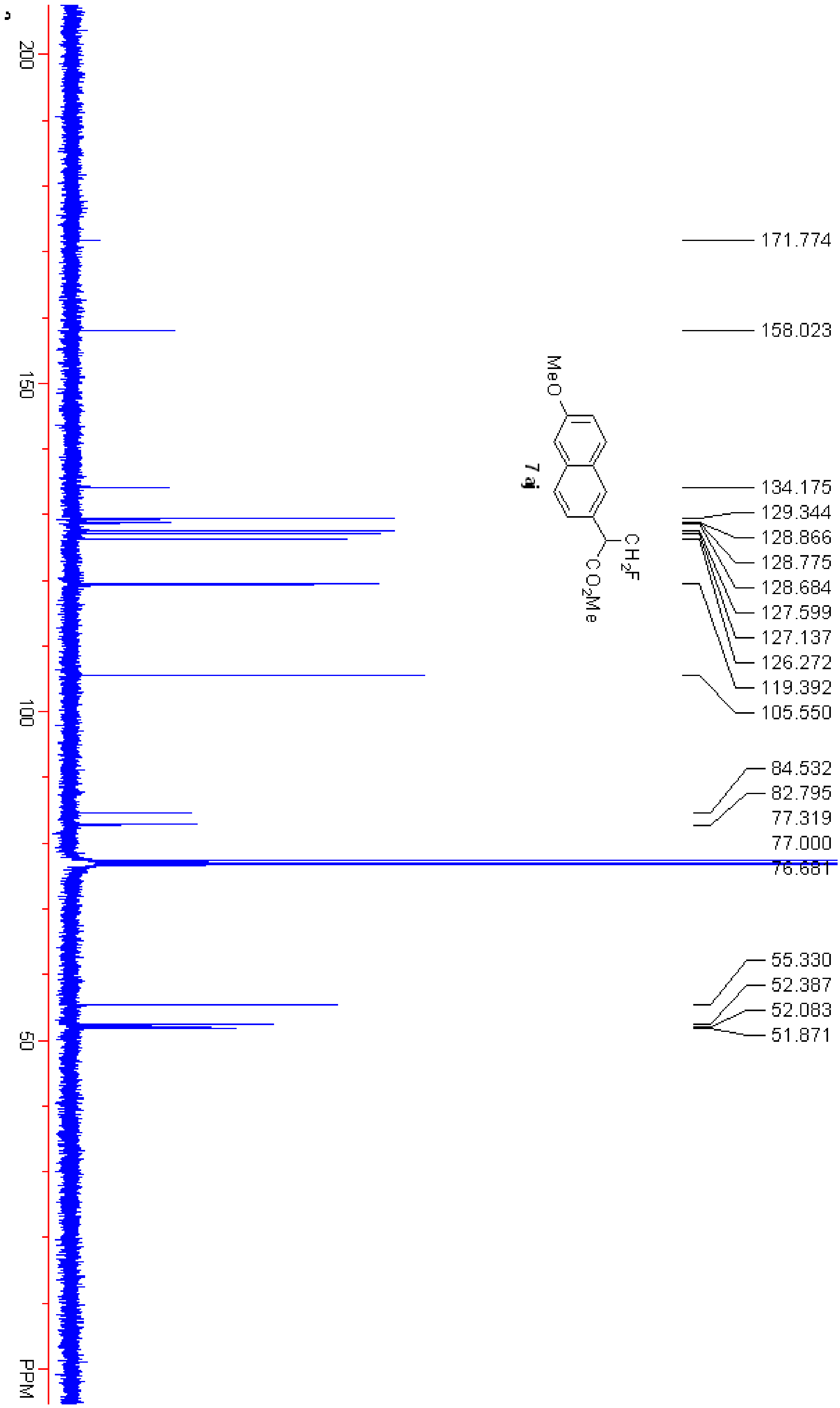
[19]F NMR (282 MHz, $CDCl_3$)



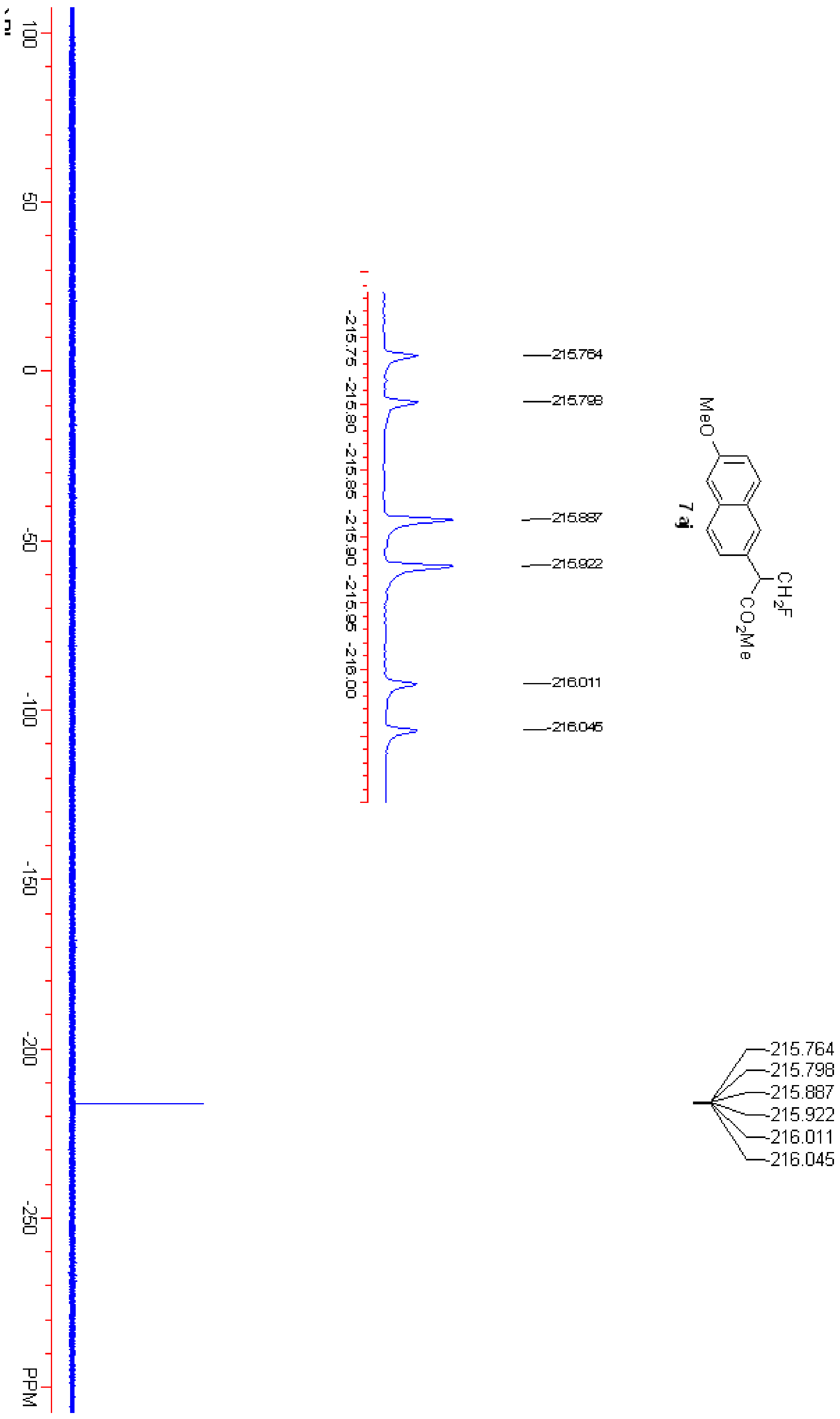
^{1}H NMR (400 MHz, $CDCl_3$)



^{19}C NMR (100 MHz, $CDCl_3$)



[19]F NMR (376 MHz, $CDCl_3$)



X-ray Crystallography of (*S*)-4ah

Single Crystal X-Ray Analysis. A representative crystal was surveyed on a Bruker APEX diffractometer. All crystallographic calculations were facilitated by the SHELXL-97 system.

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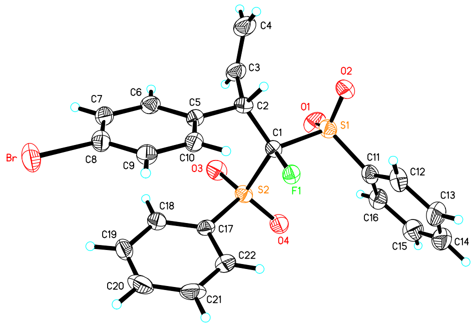
computing_cell_refinement	'Bruker SMART'
computing_data_reduction	'Bruker SHELXTL'
computing_structure_solution	'Bruker SHELXTL'
computing_structure_refinement	'Bruker SHELXTL'
computing_molecular_graphics	'Bruker SHELXTL'
computing_publication_material	'Bruker SHELXTL'



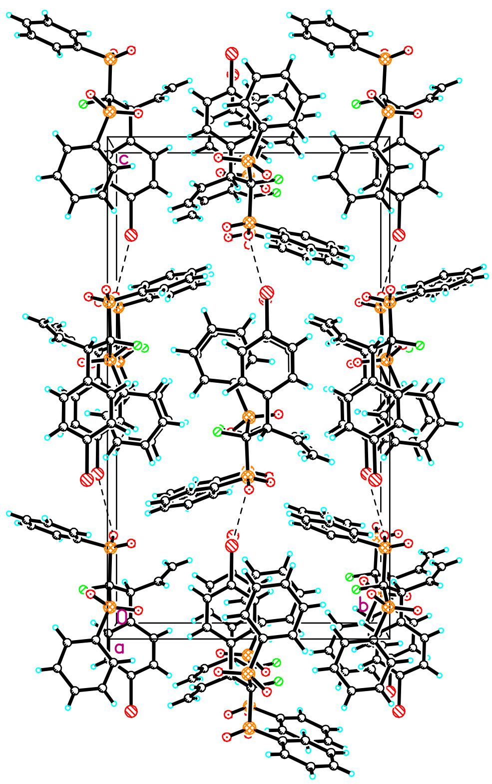


Table 1. Crystal data and structure refinement for cd28486.

Identification code	cd28486
Empirical formula	C22 H18 Br F O4 S2
Formula weight	509.39
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 6.7803(10) Å alpha = 90 deg.
	b = 13.3388(18) Å beta = 90 deg.
	c = 23.631(3) Å gamma = 90 deg.
Volume	2137.2(5) Å ^3
Z, Calculated density	4, 1.583 Mg/m^3
Absorption coefficient	2.154 mm^-1
F(000)	1032
Crystal size	0.403 x 0.140 x 0.127 mm
Theta range for data collection	1.72 to 27.00 deg.
Limiting indices	-8<=h<=8, -17<=k<=15, -26<=l<=30
Reflections collected / unique	12690 / 4655 [R(int) = 0.0871]
Completeness to theta = 27.00	99.8 %
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.7323
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4655 / 0 / 271
Goodness-of-fit on F^2	0.888
Final R indices [I>2sigma(I)]	R1 = 0.0526, wR2 = 0.0809
R indices (all data)	R1 = 0.0911, wR2 = 0.0912
Absolute structure parameter	-0.017(10)
Largest diff. peak and hole	0.514 and -0.357 e. Å^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for cd28486. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br	1973(1)	10610(1)	-1792(1)	71(1)
S(1)	5938(2)	9974(1)	1727(1)	47(1)
S(2)	7983(2)	10014(1)	577(1)	42(1)
F(1)	4954(4)	8942(2)	846(1)	41(1)
O(1)	7297(5)	10761(2)	1845(1)	65(1)
O(2)	3969(5)	10012(2)	1939(1)	57(1)
O(3)	8433(5)	11048(2)	521(1)	56(1)
O(4)	9313(4)	9374(2)	876(1)	54(1)
C(1)	5565(6)	9919(3)	945(2)	36(1)
C(2)	3934(6)	10640(3)	765(2)	39(1)
C(3)	4251(9)	11683(3)	996(2)	53(1)
C(4)	2870(11)	12165(4)	1268(2)	72(2)
C(5)	3512(6)	10638(3)	134(2)	35(1)
C(6)	3750(7)	11496(3)	-192(2)	47(1)
C(7)	3310(7)	11482(4)	-763(2)	49(1)
C(8)	2626(7)	10628(4)	-1010(2)	46(1)
C(9)	2332(7)	9777(3)	-692(2)	47(1)
C(10)	2772(7)	9792(3)	-126(2)	42(1)
C(11)	6971(9)	8811(3)	1938(2)	46(1)
C(12)	5707(9)	8003(4)	1985(2)	60(2)
C(13)	6464(10)	7116(4)	2196(3)	73(2)
C(14)	8402(11)	7057(5)	2347(2)	73(2)
C(15)	9607(10)	7871(4)	2308(2)	67(2)
C(16)	8893(9)	8758(4)	2098(2)	54(1)
C(17)	7608(6)	9499(3)	-99(2)	39(1)

C(18)	7551(6)	10130(4)	-561(2)	50(1)
C(19)	7297(8)	9727(4)	-1089(2)	58(2)
C(20)	7024(10)	8720(5)	-1153(2)	71(2)
C(21)	7110(9)	8089(4)	-690(2)	69(2)
C(22)	7437(8)	8464(3)	-162(2)	55(2)

Table 3. Bond lengths [Å] and angles [deg] for cd28486.

Br-C(8)	1.900(5)
S(1)-O(1)	1.424(3)
S(1)-O(2)	1.427(3)
S(1)-C(11)	1.772(5)
S(1)-C(1)	1.869(4)
S(2)-O(3)	1.419(3)
S(2)-O(4)	1.428(3)
S(2)-C(17)	1.759(4)
S(2)-C(1)	1.859(5)
F(1)-C(1)	1.387(4)
C(1)-C(2)	1.526(6)
C(2)-C(3)	1.511(6)
C(2)-C(5)	1.520(6)
C(2)-H(2)	0.9800
C(3)-C(4)	1.304(7)
C(3)-H(3)	0.9300
C(4)-H(4A)	0.9300
C(4)-H(4B)	0.9300
C(5)-C(10)	1.377(6)
C(5)-C(6)	1.389(6)
C(6)-C(7)	1.383(6)
C(6)-H(6)	0.9300
C(7)-C(8)	1.361(6)
C(7)-H(7)	0.9300
C(8)-C(9)	1.377(6)
C(9)-C(10)	1.371(6)

C(9)-H(9)	0.9300
C(10)-H(10)	0.9300
C(11)-C(16)	1.359(7)
C(11)-C(12)	1.382(7)
C(12)-C(13)	1.382(7)
C(12)-H(12)	0.9300
C(13)-C(14)	1.364(8)
C(13)-H(13)	0.9300
C(14)-C(15)	1.363(7)
C(14)-H(14)	0.9300
C(15)-C(16)	1.371(6)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(17)-C(18)	1.378(6)
C(17)-C(22)	1.394(6)
C(18)-C(19)	1.369(6)
C(18)-H(18)	0.9300
C(19)-C(20)	1.364(7)
C(19)-H(19)	0.9300
C(20)-C(21)	1.382(7)
C(20)-H(20)	0.9300
C(21)-C(22)	1.363(6)
C(21)-H(21)	0.9300
C(22)-H(22)	0.9300
O(1)-S(1)-O(2)	120.7(2)
O(1)-S(1)-C(11)	109.5(2)
O(2)-S(1)-C(11)	107.6(2)
O(1)-S(1)-C(1)	108.1(2)

O(2)-S(1)-C(1)	102.84(19)
C(11)-S(1)-C(1)	107.3(2)
O(3)-S(2)-O(4)	119.5(2)
O(3)-S(2)-C(17)	108.9(2)
O(4)-S(2)-C(17)	107.9(2)
O(3)-S(2)-C(1)	107.5(2)
O(4)-S(2)-C(1)	106.56(19)
C(17)-S(2)-C(1)	105.7(2)
F(1)-C(1)-C(2)	109.2(3)
F(1)-C(1)-S(2)	104.5(3)
C(2)-C(1)-S(2)	117.8(3)
F(1)-C(1)-S(1)	104.1(3)
C(2)-C(1)-S(1)	110.4(3)
S(2)-C(1)-S(1)	109.9(2)
C(3)-C(2)-C(5)	112.5(4)
C(3)-C(2)-C(1)	112.2(4)
C(5)-C(2)-C(1)	114.1(4)
C(3)-C(2)-H(2)	105.7
C(5)-C(2)-H(2)	105.7
C(1)-C(2)-H(2)	105.7
C(4)-C(3)-C(2)	122.0(5)
C(4)-C(3)-H(3)	119.0
C(2)-C(3)-H(3)	119.0
C(3)-C(4)-H(4A)	120.0
C(3)-C(4)-H(4B)	120.0
H(4A)-C(4)-H(4B)	120.0
C(10)-C(5)-C(6)	118.1(4)
C(10)-C(5)-C(2)	120.4(4)
C(6)-C(5)-C(2)	121.3(4)

C(7)-C(6)-C(5)	120.3(4)
C(7)-C(6)-H(6)	119.9
C(5)-C(6)-H(6)	119.9
C(8)-C(7)-C(6)	120.2(4)
C(8)-C(7)-H(7)	119.9
C(6)-C(7)-H(7)	119.9
C(7)-C(8)-C(9)	120.4(4)
C(7)-C(8)-Br	120.4(4)
C(9)-C(8)-Br	119.1(4)
C(10)-C(9)-C(8)	119.3(4)
C(10)-C(9)-H(9)	120.4
C(8)-C(9)-H(9)	120.4
C(9)-C(10)-C(5)	121.7(4)
C(9)-C(10)-H(10)	119.1
C(5)-C(10)-H(10)	119.1
C(16)-C(11)-C(12)	122.1(5)
C(16)-C(11)-S(1)	120.2(4)
C(12)-C(11)-S(1)	117.4(4)
C(13)-C(12)-C(11)	117.8(5)
C(13)-C(12)-H(12)	121.1
C(11)-C(12)-H(12)	121.1
C(14)-C(13)-C(12)	120.2(6)
C(14)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9
C(15)-C(14)-C(13)	120.8(6)
C(15)-C(14)-H(14)	119.6
C(13)-C(14)-H(14)	119.6
C(14)-C(15)-C(16)	120.1(6)
C(14)-C(15)-H(15)	120.0

C(16)-C(15)-H(15)	120.0
C(11)-C(16)-C(15)	119.0(5)
C(11)-C(16)-H(16)	120.5
C(15)-C(16)-H(16)	120.5
C(18)-C(17)-C(22)	121.3(4)
C(18)-C(17)-S(2)	119.0(3)
C(22)-C(17)-S(2)	119.7(3)
C(19)-C(18)-C(17)	119.0(5)
C(19)-C(18)-H(18)	120.5
C(17)-C(18)-H(18)	120.5
C(20)-C(19)-C(18)	120.4(5)
C(20)-C(19)-H(19)	119.8
C(18)-C(19)-H(19)	119.8
C(19)-C(20)-C(21)	120.3(5)
C(19)-C(20)-H(20)	119.8
C(21)-C(20)-H(20)	119.8
C(22)-C(21)-C(20)	120.6(5)
C(22)-C(21)-H(21)	119.7
C(20)-C(21)-H(21)	119.7
C(21)-C(22)-C(17)	118.2(5)
C(21)-C(22)-H(22)	120.9
C(17)-C(22)-H(22)	120.9

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^2 x 10^3) for cd28486. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br	85(1)	87(1)	41(1)	15(1)	1(1)	-1(1)
S(1)	60(1)	45(1)	37(1)	-6(1)	-1(1)	-1(1)
S(2)	37(1)	44(1)	44(1)	0(1)	6(1)	-4(1)
F(1)	50(2)	31(1)	41(2)	-1(1)	0(1)	-8(1)
O(1)	88(3)	42(2)	66(2)	-16(2)	-21(2)	-1(2)
O(2)	65(2)	68(2)	39(2)	0(2)	9(2)	13(2)
O(3)	59(3)	44(2)	66(2)	-3(2)	13(2)	-18(2)
O(4)	42(2)	70(2)	50(2)	5(2)	0(2)	7(2)
C(1)	38(3)	34(3)	36(3)	-3(2)	2(2)	-6(2)
C(2)	33(3)	38(3)	44(3)	-6(2)	2(2)	0(2)
C(3)	63(4)	39(3)	57(4)	-3(3)	-2(3)	7(3)
C(4)	101(5)	53(3)	63(4)	-11(3)	-7(4)	26(4)
C(5)	34(3)	32(2)	40(3)	0(2)	-1(2)	-2(2)
C(6)	52(3)	35(3)	54(3)	0(2)	4(3)	2(2)
C(7)	51(4)	44(3)	51(3)	13(2)	15(3)	6(3)
C(8)	40(3)	57(3)	43(3)	7(3)	-1(2)	-1(3)
C(9)	43(3)	51(3)	48(3)	2(2)	2(2)	3(2)
C(10)	39(3)	44(3)	43(3)	5(2)	0(2)	0(2)
C(11)	58(4)	47(3)	33(3)	-4(2)	-1(3)	-5(3)
C(12)	62(4)	68(4)	49(3)	12(3)	3(3)	-10(3)
C(13)	93(6)	52(4)	73(4)	14(3)	9(4)	-4(3)

C(14)	101(6)	68(4)	51(4)	7(3)	-4(4)	18(4)
C(15)	74(5)	72(4)	53(4)	-2(3)	-13(3)	3(4)
C(16)	64(4)	55(3)	42(3)	-3(3)	-12(3)	-5(3)
C(17)	33(3)	36(3)	46(3)	0(2)	3(2)	5(2)
C(18)	45(3)	57(3)	48(3)	3(3)	8(3)	8(2)
C(19)	52(4)	82(4)	39(3)	11(3)	8(3)	15(3)
C(20)	66(4)	95(5)	52(4)	-28(3)	0(3)	23(4)
C(21)	87(5)	50(3)	71(4)	-21(3)	4(4)	24(3)
C(22)	67(4)	40(3)	59(4)	2(2)	8(3)	10(3)

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Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for cd28486.

	x	y	z	U(eq)
H(2)	2728	10392	947	46
H(3)	5467	11992	943	64
H(4A)	1646	11866	1325	87
H(4B)	3109	12807	1406	87
H(6)	4208	12083	-25	57
H(7)	3482	12058	-980	58
H(9)	1840	9197	-859	57
H(10)	2567	9217	89	50
H(12)	4390	8054	1879	72
H(13)	5651	6559	2234	87
H(14)	8908	6452	2479	88
H(15)	10916	7826	2423	80
H(16)	9711	9315	2067	64
H(18)	7683	10819	-514	60
H(19)	7311	10141	-1405	69
H(20)	6778	8457	-1511	85
H(21)	6944	7402	-739	83
H(22)	7544	8039	149	66

Table 6. Torsion angles [deg] for cd28486.

O(3)-S(2)-C(1)-F(1)	163.7(3)
O(4)-S(2)-C(1)-F(1)	-67.1(3)
C(17)-S(2)-C(1)-F(1)	47.5(3)
O(3)-S(2)-C(1)-C(2)	42.4(4)
O(4)-S(2)-C(1)-C(2)	171.5(3)
C(17)-S(2)-C(1)-C(2)	-73.9(3)
O(3)-S(2)-C(1)-S(1)	-85.2(3)
O(4)-S(2)-C(1)-S(1)	44.0(3)
C(17)-S(2)-C(1)-S(1)	158.6(2)
O(1)-S(1)-C(1)-F(1)	156.1(3)
O(2)-S(1)-C(1)-F(1)	-75.2(3)
C(11)-S(1)-C(1)-F(1)	38.1(4)
O(1)-S(1)-C(1)-C(2)	-86.8(3)
O(2)-S(1)-C(1)-C(2)	41.9(3)
C(11)-S(1)-C(1)-C(2)	155.2(3)
O(1)-S(1)-C(1)-S(2)	44.7(3)
O(2)-S(1)-C(1)-S(2)	173.4(2)
C(11)-S(1)-C(1)-S(2)	-73.3(3)
F(1)-C(1)-C(2)-C(3)	165.0(4)
S(2)-C(1)-C(2)-C(3)	-76.1(4)
S(1)-C(1)-C(2)-C(3)	51.1(5)
F(1)-C(1)-C(2)-C(5)	-65.6(5)
S(2)-C(1)-C(2)-C(5)	53.3(4)
S(1)-C(1)-C(2)-C(5)	-179.4(3)
C(5)-C(2)-C(3)-C(4)	100.8(6)
C(1)-C(2)-C(3)-C(4)	-129.0(5)
C(3)-C(2)-C(5)-C(10)	-165.9(4)
C(1)-C(2)-C(5)-C(10)	64.8(5)

C(3)-C(2)-C(5)-C(6)	10.4(6)
C(1)-C(2)-C(5)-C(6)	-118.9(4)
C(10)-C(5)-C(6)-C(7)	-2.0(7)
C(2)-C(5)-C(6)-C(7)	-178.4(4)
C(5)-C(6)-C(7)-C(8)	0.5(7)
C(6)-C(7)-C(8)-C(9)	1.2(7)
C(6)-C(7)-C(8)-Br	178.9(4)
C(7)-C(8)-C(9)-C(10)	-1.3(7)
Br-C(8)-C(9)-C(10)	-179.0(4)
C(8)-C(9)-C(10)-C(5)	-0.3(7)
C(6)-C(5)-C(10)-C(9)	1.9(7)
C(2)-C(5)-C(10)-C(9)	178.3(4)
O(1)-S(1)-C(11)-C(16)	-9.1(5)
O(2)-S(1)-C(11)-C(16)	-142.0(4)
C(1)-S(1)-C(11)-C(16)	108.0(4)
O(1)-S(1)-C(11)-C(12)	164.6(3)
O(2)-S(1)-C(11)-C(12)	31.7(4)
C(1)-S(1)-C(11)-C(12)	-78.3(4)
C(16)-C(11)-C(12)-C(13)	-1.0(7)
S(1)-C(11)-C(12)-C(13)	-174.5(4)
C(11)-C(12)-C(13)-C(14)	-0.2(8)
C(12)-C(13)-C(14)-C(15)	1.7(9)
C(13)-C(14)-C(15)-C(16)	-1.9(9)
C(12)-C(11)-C(16)-C(15)	0.8(7)
S(1)-C(11)-C(16)-C(15)	174.1(4)
C(14)-C(15)-C(16)-C(11)	0.7(8)
O(3)-S(2)-C(17)-C(18)	-7.5(4)
O(4)-S(2)-C(17)-C(18)	-138.6(3)
C(1)-S(2)-C(17)-C(18)	107.7(4)
O(3)-S(2)-C(17)-C(22)	170.4(4)

O(4)-S(2)-C(17)-C(22)	39.3(4)
C(1)-S(2)-C(17)-C(22)	-74.4(4)
C(22)-C(17)-C(18)-C(19)	0.9(7)
S(2)-C(17)-C(18)-C(19)	178.7(4)
C(17)-C(18)-C(19)-C(20)	2.6(8)
C(18)-C(19)-C(20)-C(21)	-3.6(10)
C(19)-C(20)-C(21)-C(22)	1.1(10)
C(20)-C(21)-C(22)-C(17)	2.4(8)
C(18)-C(17)-C(22)-C(21)	-3.3(8)
S(2)-C(17)-C(22)-C(21)	178.8(4)

Symmetry transformations used to generate equivalent atoms: