Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Diversity-Oriented Derivatization of BODIPY Based on Regioselective Bromination

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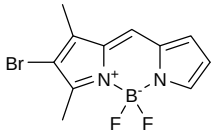
General: Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin layer chromatography using TLC Silica gel 60 F254 supplied by Qingdao Puke Seperation Meterial Corporation, Qingdao, P. R. China. Silica gel for column chromatography was 200-300 mesh and was supplied by Qingdao Marine Chemical Factory, Qingdao, P. R. China. Characterization of compounds was done using NMR spectroscopy and mass spectrometry. ^{1}H NMR, ^{13}C NMR and 2D NMR spectra were recorded on Bruker DPX-400 or Bruker DPX-500 Fourier transform spectrometer with *d*-$CHCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. All spectra were recorded at 25^{o}C and chemical shifts were given in ppm and coupling constants (*J*) in Hz. High-resolution mass data were obtained on a Waters GCT Premier^{TM} Micromass instrument. UV-vis spectra were acquired using a HITACHI U-3010 spectrophotometer with a 1 cm quartz cell. FT-IR spectra were taken on a Bruker Vector 22 spectrophotometer as KBr pellets. Fluorescence measurements were carried out on a JASCO FP 6500 spectrofluorimeter. Melting points were obtained on a BÜCHI Melting Point B-540 apparatus and were uncorrected.

Synthesis

General procedures for the synthesis of compounds 3-5

To a solution of **1** (200 mg, 0.91 mmol) in CH_2Cl_2 (50 mL) at 0^{o}C was added dropwise a solution of **2** (1 equiv. for **3**, 2 equiv. for **4**, and 3 equiv. for **5**) in CH_2Cl_2. Color change from bright green to reddish brown was instantly observed with the addition. After the addition, total consumption of **1** was observed by TLC, H_2O (15 mL) was added. The organic layer was separated and washed with H_2O (3 × 10 mL) and brine (1 × 10 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The products were purified by crystallisation from petroleum ether / CH_2Cl_2 (10 / 1) as red crystals (94% for **3**, 98% for **4**, and 96% for **5**).

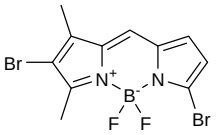
1,3-Dimethyl-2-bromo-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (3)



3

δ_H (400 MHz, $CDCl_3$): 7.71 (1 H, brs), 7.24 (1 H, s), 7.00 (1 H, brs), 6.47 (1H, brs), 2.61 (3 H, s), 2.24 (3 H, s); δ_C (101 MHz, $CDCl_3$): 159.13, 142.01, 141.31, 134.13, 133.10, 128.38, 125.47, 117.31, 111.12, 13.91, 11.15; IR (cm^{-1}): 3108, 2362, 1610, 1402, 1284, 1163; Mp: 156.6-157.8°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{11}H_{10}BN_2F_2Br$: 298.0088, found: 298.0089, Δ= 0.3 ppm.

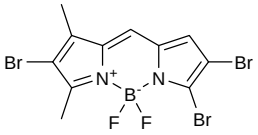
1,3-Dimethyl-2,5-dibromo-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (4)



4

δ_H (400 MHz, $CDCl_3$): 7.56 (1 H, brs), 7.16 (1 H, s), 6.92 (1 H, brs), 2.63 (3 H, s), 2.24 (3 H, s); δ_C (101 MHz, $CDCl_3$): 161.94, 143.52, 139.29, 135.08, 132.31, 127.06, 124.61, 112.44, 104.46, 14.18, 11.27; IR (cm^{-1}): 3129, 2362, 1609, 1398, 1358, 1161, 1090; Mp: 164.7-166.1°C. HRMS (TOF-EI): *m/z*: Calculated for $C_{11}H_9BN_2F_2Br_2$: 375.9194, found: 375.9197, Δ= 0.8 ppm.

1,3-Dimethyl-2,5,6-tribromo-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (5)



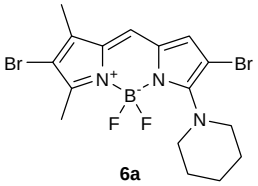
5

δ_H (400 MHz, $CDCl_3$): 7.05 (1 H, s), 6.94 (1 H, s), 2.64 (3 H, s), 2.24 (3 H, s); δ_C (101 MHz, $CDCl_3$): 162.40, 143.26, 134.97, 132.92, 127.91, 127.38, 122.90, 113.03, 108.47, 14.25, 11.26; IR (cm^{-1}): 3114, 1613, 1353, 1237, 1151, 1094; Mp: 201.6.7-203.9.1°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{11}H_8BN_2F_2Br_3$: 453.8299, found: 453.8291, Δ= -1.8 ppm.

General procedures for the synthesis of compounds 6a-6c and 7a-7b

To a solution of **5** (or **4**) (0.05 mmol) in benzene (10 mL) at 0°C was added the nucleophiles, namely, piperidine, diethylamine, or thiophenol. For *N* centred nucleophiles, two equivalents were added. While for *S* centred nucleophile, one equivalent in addition to one equivalent of Et_3N was added. Total transformation of the reactant to the corresponding product was observed in 5 minutes *via* TLC. H_2O (10 mL) was then added and the mixture was extracted with EtOAc (20 mL), the organic layer was washed with H_2O (3 × 10 mL) and brine (1 × 10 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The products were purified by column chromatography (silica gel) using petroleum ether / CH_2Cl_2 (8 / 1) as eluent and recovered as red powders.

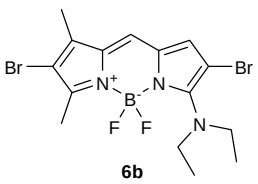
1,3-Dimethyl-2,6-dibromo-5-(piperidin-1-yl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (6a)



6a

δ_H (500 MHz, $CDCl_3$): 7.07 (1 H, s), 6.66 (1 H, s), 3.74-3.73 (4 H, m), 2.48 (3 H, s), 2.15 (3 H, s), 1.82-1.75 (4 H, m), 1.72-1.70 (2 H, m); IR (cm^{-1}): 3124, 2918, 2860, 2360, 1613, 1560, 1360, 1255, 1171, 1094; Mp: 171.6-173.1°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{16}H_{18}BN_3F_2Br_2$: 458.9929, found: 458.9923, Δ= -1.3 ppm.

1,3-Dimethyl-2,6-dibromo-5-(diethylamino)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (6b)

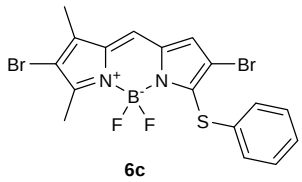


6b

δ_H (500 MHz, $CDCl_3$): 7.06 (1 H, brs), 6.70 (1 H, brs), 3.76 (4 H, q, *J* 7.1), 2.50 (3 H, s), 2.16 (3 H, s), 1.23 (6 H, t, *J* 7.1); IR (cm^{-1}): 3120, 3057, 2920, 2855, 2361, 1615,

1555, 1348, 1257, 1165, 1099; Mp: 169.6-161.3°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{15}H_{18}BN_3F_2Br_2$: 446.9929, found: 446.9934, Δ= 1.1 ppm.

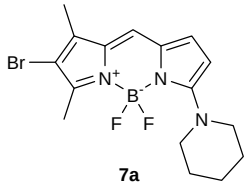
1,3-Dimethyl-2,6-dibromo-5-(phenylthio)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (6c)



6c

δ_H (400 MHz, $CDCl_3$): 7.35 (2 H, d, *J* 7.2), 7.29-7.24 (2 H, m), 7.20 (1 H, t, *J* 7.2), 7.09 (1 H, s), 6.99 (1 H, s), 2.66 (3 H, s), 2.26 (3 H, s); δ_C (101 MHz, $CDCl_3$): 162.96, 143.21, 135.51, 134.32, 133.19, 129.92, 129.87, 129.05, 129.03, 127.76, 127.01, 123.08, 113.15, 14.32, 11.27; IR (cm^{-1}): 3020, 2362, 1613, 1383, 1240, 1152, 1099, 1025; Mp: 158.6-151.3°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{17}H_{13}BN_2F_2SBr_2$: 483.9227, found: 483.9244, Δ= 3.5 ppm.

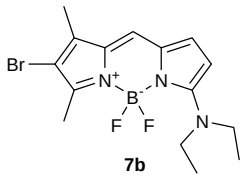
1,3-Dimethyl-2-bromo-5-(piperidin-1-yl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (7a)



7a

δ_H (500 MHz, $CDCl_3$): 6.97 (1 H, d, *J* 5.0), 6.57 (1 H, s), 6.23 (1 H, d, *J* 5.0), 3.89-3.83 (4 H, m), 2.46 (3 H, s), 2.13 (3 H, s), 1.81-1.70 (6 H, m); IR (cm^{-1}): 3134, 2932, 2860, 2360, 1624, 1574, 1364, 1261, 1095; Mp: 166.2-168.5°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{16}H_{19}BN_3F_2Br$: 381.0823, found: 381.0832, Δ= 2.4 ppm.

1,3-Dimethyl-2-bromo-5-(diethylamino)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (7b)



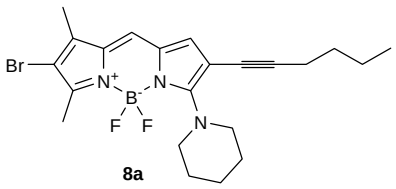
7b

δ_H (500 MHz, $CDCl_3$): 6.98 (1 H, d, *J* 5.0), 6.55 (1 H, s), 6.17 (1 H, d, *J* 5.0), 3.78 (4 H, q, *J* 7.1), 2.46 (3 H, s), 2.13 (3 H, s), 1.33 (5 H, t, *J* 7.1); δ_C (101 MHz, $CDCl_3$): 161.52, 140.62, 135.57, 134.62, 127.40, 126.73, 113.37, 112.87, 104.44, 46.66, 13.61, 12.64, 10.46; IR (cm^{-1}): 3040, 3025, 2920, 2850, 2361, 1620, 1574, 1281, 1090; Mp: 171.3-173.5°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{15}H_{19}BN_3F_2Br$: 369.0823, found: 369.0833, Δ= 2.7 ppm.

General procedures for the synthesis of compounds 8a-8d

To a carefully degassed solution of **5** (30 mg, 0.06 mmol) in a mixture of benzene / triethylamine (9 mL/1 mL) were added the nucleophile (piperidine or diethylamine, 1 equiv.), the alkyne (*p*-tolylacetylene, or hex-1-yne, 2 equiv., 0.13 mmol), CuI (10% mol, 0.006 mmol, 1 mg) and $Pd(PPh_3)_4$ (5% mol, 0.003 mmol, 4 mg). The mixture was heated at 60°C under N_2 atmosphere for 6 h, and then cooled to room temperature. H_2O was added (10 mL) to quench the reaction. The crude product was extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with H_2O (3 × 10 mL) and brine (1 × 10 mL) successively, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The products were purified using column chromatography (silica gel) eluted with petroleum ether / CH_2Cl_2 (5 / 1 to 2 / 1) as dark red powders.

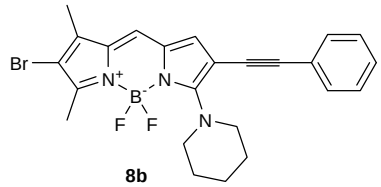
1,3-Dimethyl-2-bromo-5-(piperidin-1-yl)-6-(hex-1-ynyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (8a)



8a

δ_H (500 MHz, $CDCl_3$): 6.99 (1 H, s), 6.56 (1 H, s), 4.01-3.94 (4 H, m), 2.46 (3 H, s), 2.42 (2 H, t, *J* 7.1), 2.13 (3 H, s), 1.80-1.74 (4 H, m), 1.74-1.69 (2 H, m), 1.59-1.53 (2 H, m), 1.48-1.42 (2 H, m), 0.94 (3 H, t, *J* 7.3); δ_C (126 MHz, $CDCl_3$): 161.77, 143.27, 136.56, 132.57, 129.32, 128.70, 114.69, 110.36, 105.47, 97.43, 73.72, 51.71, 30.61, 26.51, 23.89, 22.12, 19.50, 13.62, 12.80, 10.62; IR (cm^{-1}): 3138, 3055, 2932, 2862, 2362, 2225, 1612, 1461, 1092; Mp: 109.1-110.9°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{22}H_{27}BN_3F_2Br$: 461.1449, found: 461.1440, Δ= -2.0 ppm.

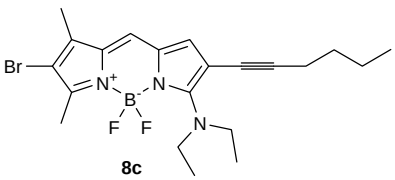
1,3-Dimethyl-2-bromo-5-(piperidin-1-yl)-6-(phenylethynyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (8b)



8b

δ_H (500 MHz, $CDCl_3$): 7.45 (2 H, dd, *J* 7.4, 2.0), 7.36-7.34 (3 H, m), 7.13 (1 H, s), 6.65 (1 H, s), 4.02-4.04 (4 H, m), 2.49 (3 H, s), 2.16 (3 H, s), 1.88-1.80 (4 H, m), 1.79-1.69 (2 H, m); δ_C (126 MHz, $CDCl_3$) 161.52, 144.53, 136.42, 132.53, 131.08 (2C), 130.45, 129.15, 128.52 (2C), 128.46, 122.90, 115.56, 108.94, 106.09, 95.75, 82.96, 51.90, 26.62, 23.92, 12.91, 10.69; IR (cm^{-1}): 3047, 2927, 2856, 2363, 2199, 1614, 1565, 1544, 1469, 1310, 1091; Mp: 196.7-198.3°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{24}H_{23}BN_3F_2Br$: 481.1136, found: 481.1155, Δ= 3.9 ppm.

1,3-Dimethyl-2-bromo-5-(diethylamino)-6-(hex-1-ynyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (8c)

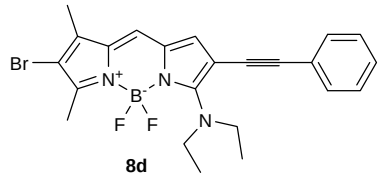


8c

δ_H (500 MHz, $CDCl_3$): 7.02 (1 H, s), 6.55 (1 H, s), 4.01 (4 H, q, *J* 7.0), 2.47 (3 H, s), 2.43 (2 H, t, *J* 7.1), 2.14 (3 H, s), 1.58-1.54 (2 H, m), 1.48-1.42 (2 H, m), 1.30 (6 H, t, *J* 7.0), 0.94 (3 H, t, *J* 7.3); δ_C (126 MHz, $CDCl_3$): 161.44, 143.28, 137.56, 132.86,

129.07, 128.54, 114.36, 110.14, 105.53, 96.48, 74.30, 46.22, 30.57, 22.10, 19.52, 14.15, 13.61, 12.81, 10.59; IR (cm^{-1}): 3140, 3025, 2930, 2858, 2361, 2226, 1617, 1458, 1090; Mp: 87.1-89.6°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{21}H_{27}BN_3F_2Br$: 449.1449, found: 449.1469, Δ= 4.5 ppm.

1,3-Dimethyl-2-bromo-5-(diethylamino)-6-(phenylethynyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (8d)



8d

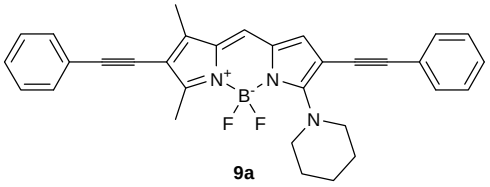
δ_H (500 MHz, $CDCl_3$): 7.51-7.41 (2 H, m), 7.39-7.32 (3 H, m), 7.15 (1 H, s), 6.62 (1 H, s), 4.07 (4 H, q, *J* 7.0), 2.49 (3 H, s), 2.15 (3 H, s), 1.36 (6 H, t, *J* 7.0); δ_C (126 MHz, $CDCl_3$): 161.05, 144.42 137.48, 132.82, 131.06 (2C), 130.12, 128.93, 128.50 (2C), 128.42, 122.97, 115.20, 108.60, 106.10, 94.70, 83.59, 46.44, 14.21, 12.91, 10.65; IR (cm^{-1}): 3057, 3025, 2927, 2856, 2363, 2200, 1619, 1566, 1544, 1468, 1312, 1092; Mp: 183.1-184.5°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{23}H_{23}BN_3F_2Br$: 469.1136, found: 469.1140, Δ= 0.9 ppm.

General procedures for the synthesis of compounds 9a-9c

To a carefully degassed solution of **5** (30 mg, 0.06 mmol) in a mixture of toluene / triethylamine (9 mL/1 mL) were added the nucleophile (piperidine, diethylamine, or EtONa, 1 equiv., 0.06 mmol), the alkyne (*p*-tolylacetylene, or hex-1-yne, 4 equiv., 0.26 mmol), CuI (10% mol, 0.006 mmol, 1 mg) and $Pd(PPh_3)_4$ (10% mol, 0.006 mmol, 8 mg). The mixture was heated at 90°C under N_2 atmosphere for 10 h. When cooled to room temperature, the reaction was quenched by the addition of H_2O (10 mL). The crude product was extracted with EtOAc (3 × 10 mL), the combined organic layer was washed with H_2O (3 × 10 mL) and brine (1 × 10 mL) successively, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The products were purified using column chromatography (silica gel) eluted with petroleum ether /

CH_2Cl_2 (5 / 1 to 2 / 1) as dark red powders.

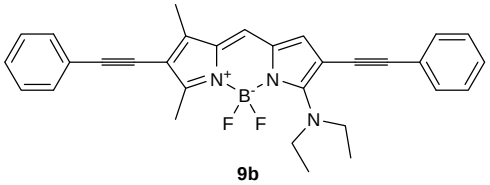
1,3-Dimethyl-2,6-bis(phenylethynyl)-5-(piperidin-1-yl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (9a)



9a

δ_H (500 MHz, $CDCl_3$): 7.53-7.51 (2 H, m), 7.47 (2 H, dd, *J* 6.5, 3.2), 7.38-7.31 (6 H, m), 7.15 (1 H, s), 6.69 (1 H, d, *J* 5.7), 4.08-4.00 (4 H, m), 2.62 (3 H, s), 2.31 (3 H, d, *J* 5.2), 1.90-1.82 (4 H, m), 1.82-1.73 (2 H, m); δ_C (126 MHz, $CDCl_3$): 161.48, 150.96, 136.13, 133.92, 132.83, 131.24 (2C), 131.09 (2C), 129.79, 128.52 (2C), 128.50, 128.28 (2C), 127.59, 124.08, 122.95, 115.88, 111.14, 108.79, 95.69, 94.42, 83.12, 83.05, 51.90, 26.64, 23.95, 13.25, 10.42; IR (cm^{-1}): 3057, 2928, 2854, 2363, 2200, 1612, 1565, 1545, 1469, 1309, 1253, 1197, 1090; Mp: 231.1-233.5°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{32}H_{28}BN_3F_2$: 503.2344, found: 503.2343, Δ= -0.2 ppm.

1,3-Dimethyl-2,6-bis(phenylethynyl)-5-(diethylamino)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (9b)

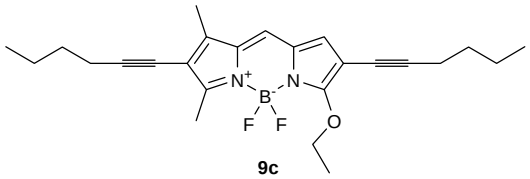


9b

δ_H (500 MHz, $CDCl_3$): 7.51 (2 H, d, *J* 6.7), 7.47-7.44 (2 H, m), 7.33-7.27 (6 H, m), 7.17 (1 H, s), 6.67 (1 H, s), 4.08 (4 H, q, *J* 6.9), 2.62 (3 H, s), 2.30 (3 H, s), 1.37 (6 H, t, *J* 6.9); δ_C (126 MHz, $CDCl_3$): 161.03, 150.94, 137.15, 133.63, 133.12, 131.23 (2C), 131.07 (2C), 129.62, 128.50 (2C), 128.48, 128.28 (2C), 127.58, 124.10, 123.03, 115.56, 111.18, 108.50, 94.66, 94.39, 83.67, 83.19, 46.43, 14.20, 13.24, 10.39; IR (cm^{-1}): 3049, 3020, 2926, 2852, 2363, 2200, 1611, 1567, 1548, 1467, 1308, 1255,

1197, 1091; Mp: 182.1-184.3°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{31}H_{28}BN_3F_2$: 491.2344, found: 491.2360, Δ= 3.3 ppm.

1,3-Dimethyl-2,6-bis(hex-1-ynyl)-5-ethoxy-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (9c)



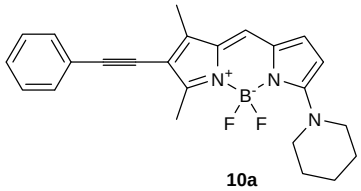
9c

δ_H (500 MHz, $CDCl_3$): 6.98 (1 H, s), 6.55 (1 H, s), 3.98 (2 H, q, *J* 7.2), 2.51 (3 H, s), 2.45 (2 H, t, *J* 7.1), 2.42 (2 H, t, *J* 7.1), 2.19 (3 H, s), 1.60-1.57 (4 H, m), 1.48-1.43 (4 H, m), 1.29 (3 H, t, *J* 6.9), 0.95 (3 H, t, *J* 7.2), 0.94 (3 H, t, *J* 7.2); δ_C (101 MHz, $CDCl_3$): 168.11, 150.18, 136.67, 133.24, 132.66, 129.18, 115.12, 111.31, 109.42, 96.04, 94.74, 74.42, 73.57, 46.09, 31.27, 30.63, 22.10, 21.96, 19.52, 19.44, 14.13, 13.67, 13.61, 13.02, 10.24; IR (cm^{-1}): 3130, 3028, 2922, 2861, 2361, 2225, 1619, 1458, 1120; Mp: 65.3-67.1°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{25}H_{31}BN_2OF_2$: 424.2498, found: 424.2501, Δ= 0.7 ppm.

General procedures for the synthesis of compounds 10a-10b

Similar procedures for the obtainment of **9a-9c** were employed for the preparation of **10a-10b**, except that **4** was employed as the reactant.

1,3-Dimethyl-2-(phenylethynyl)-5-(piperidin-1-yl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (10a)

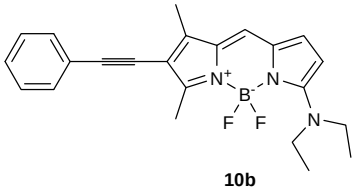


10a

δ_H (500 MHz, $CDCl_3$): 7.52 (2 H, d, *J* 7.0), 7.46 (1 H, t, *J* 8.0), 7.34 (2 H, t, *J* 7.5), 6.99 (1 H, d, *J* 5.0), 6.61 (1 H, s), 6.23 (1 H, d, *J* 5.0), 3.88 (4 H,m), 2.61 (3 H, s), 2.29 (3 H, s), 1.80 (6 H, m); δ_C (126 MHz, $CDCl_3$): 161.36, 148.47, 135.14, 134.24,

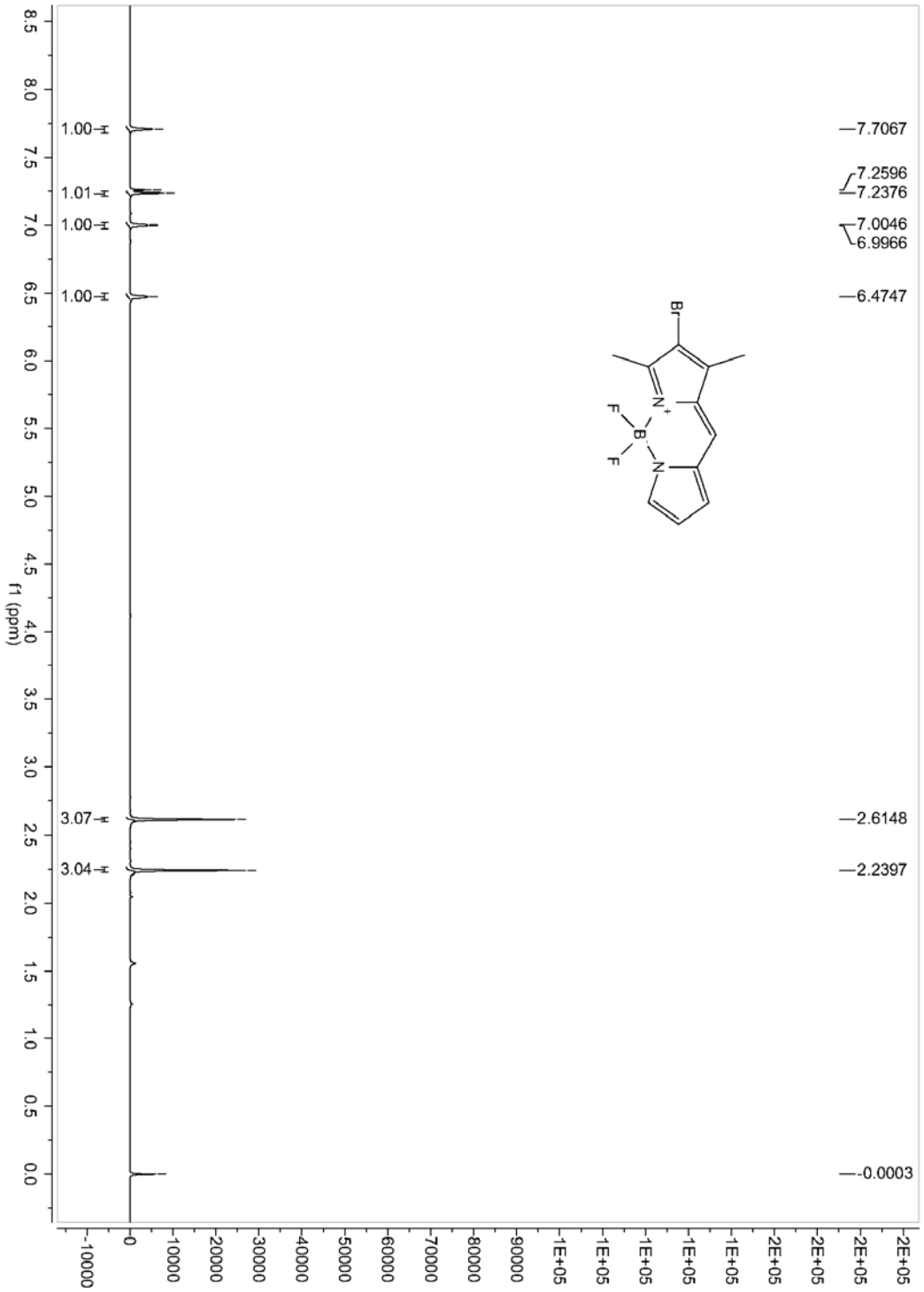
131.28, 131.18 (2C), 128.27, 128.23 (2C), 127.31, 124.42, 124.11, 113.96, 112.59, 93.61, 83.85, 51.66, 26.24, 24.20, 13.05, 10.22; IR (cm^{-1}): 3154, 2930, 2856, 2360, 2200, 1612, 1465, 1310, 1261, 1096; Mp: 163.6-166.3°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{24}H_{24}BN_3F_2$: 403.2031, found: 403.2040, Δ= 2.2 ppm.

1,3-Dimethyl-2-(phenylethynyl)-5-(diethylamino)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (10b)

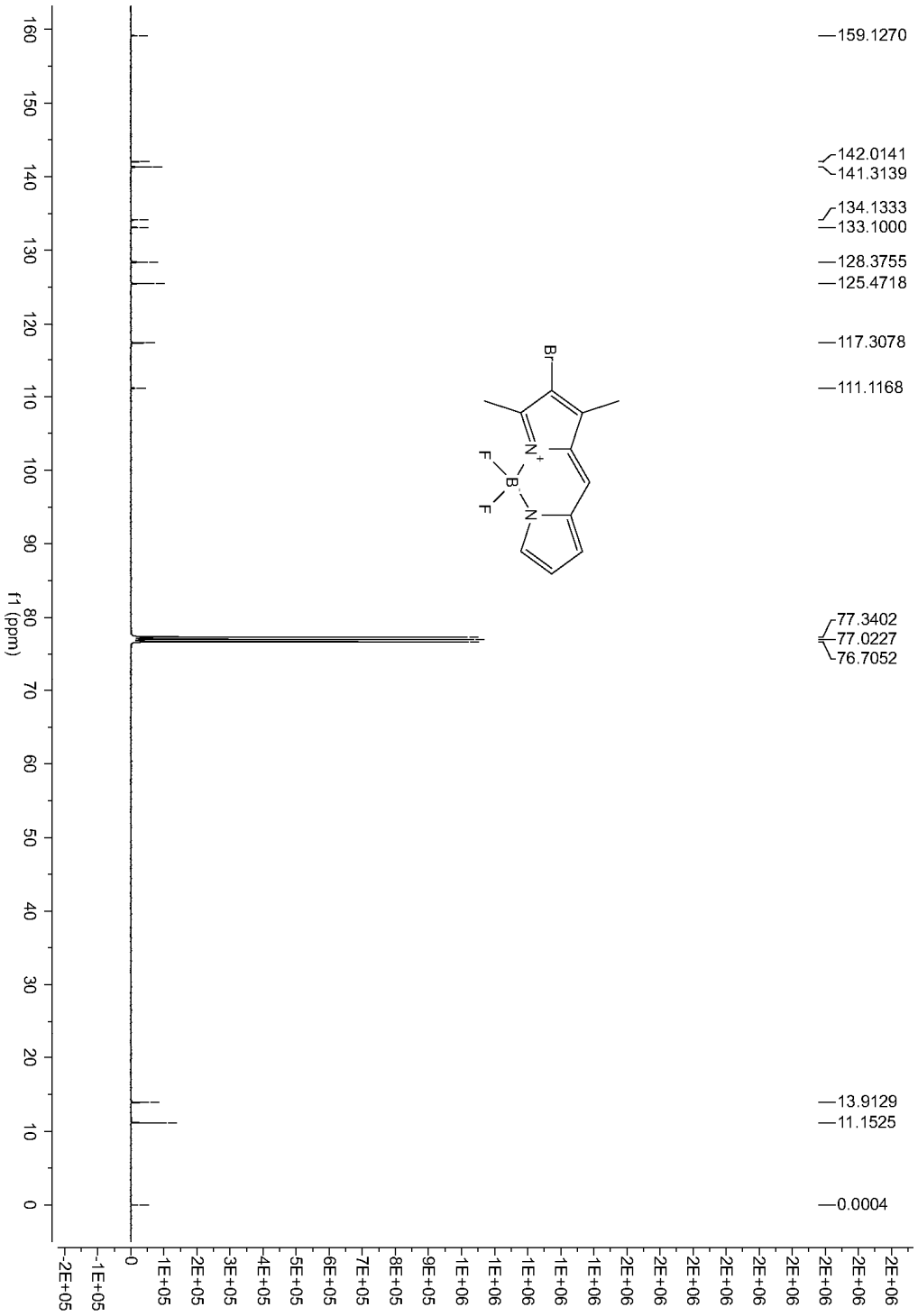


10b

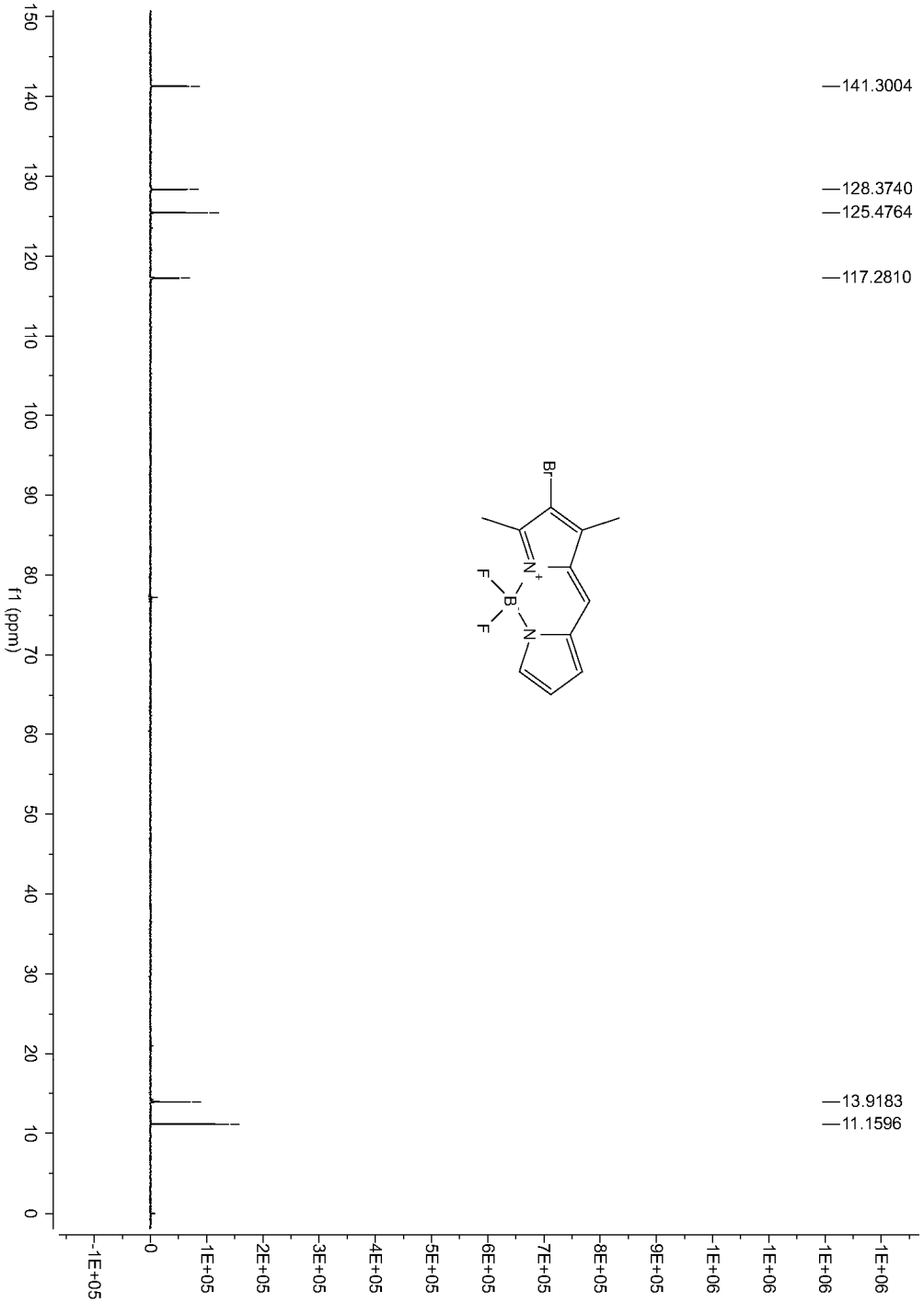
δ_H (500 MHz, $CDCl_3$): 7.51 (2 H, d, *J* 7.0), 7.45 (1 H, t, *J* 7.5), 7.32 (2 H, t, *J* 7.3), 7.00 (1 H, d, *J* 5.0), 6.59 (1 H, s), 6.17 (1 H, d, *J* 5.0), 3.80 (4 H, q, *J* 7.0), 2.60 (3 H, s), 2.27 (3 H, s), 1.34 (6 H, t, *J* 7.0); δ_C (126 MHz, $CDCl_3$): 160.77, 149.89, 135.78, 134.93, 131.17 (2C), 129.34, 128.33, 128.22 (2C), 127.31, 123.87, 121.52, 114.39, 113.57, 94.16, 82.28, 46.63, 14.20, 13.66, 13.48; IR (cm^{-1}): 3154, 3068, 2926, 2850, 2362, 2200, 1615, 1468, 1312, 1263, 1092; Mp: 141.4-144.3°C; HRMS (TOF-EI): *m/z*: Calculated for $C_{23}H_{24}BN_3F_2$: 391.2031, found: 391.2043, Δ= 3.1 ppm.



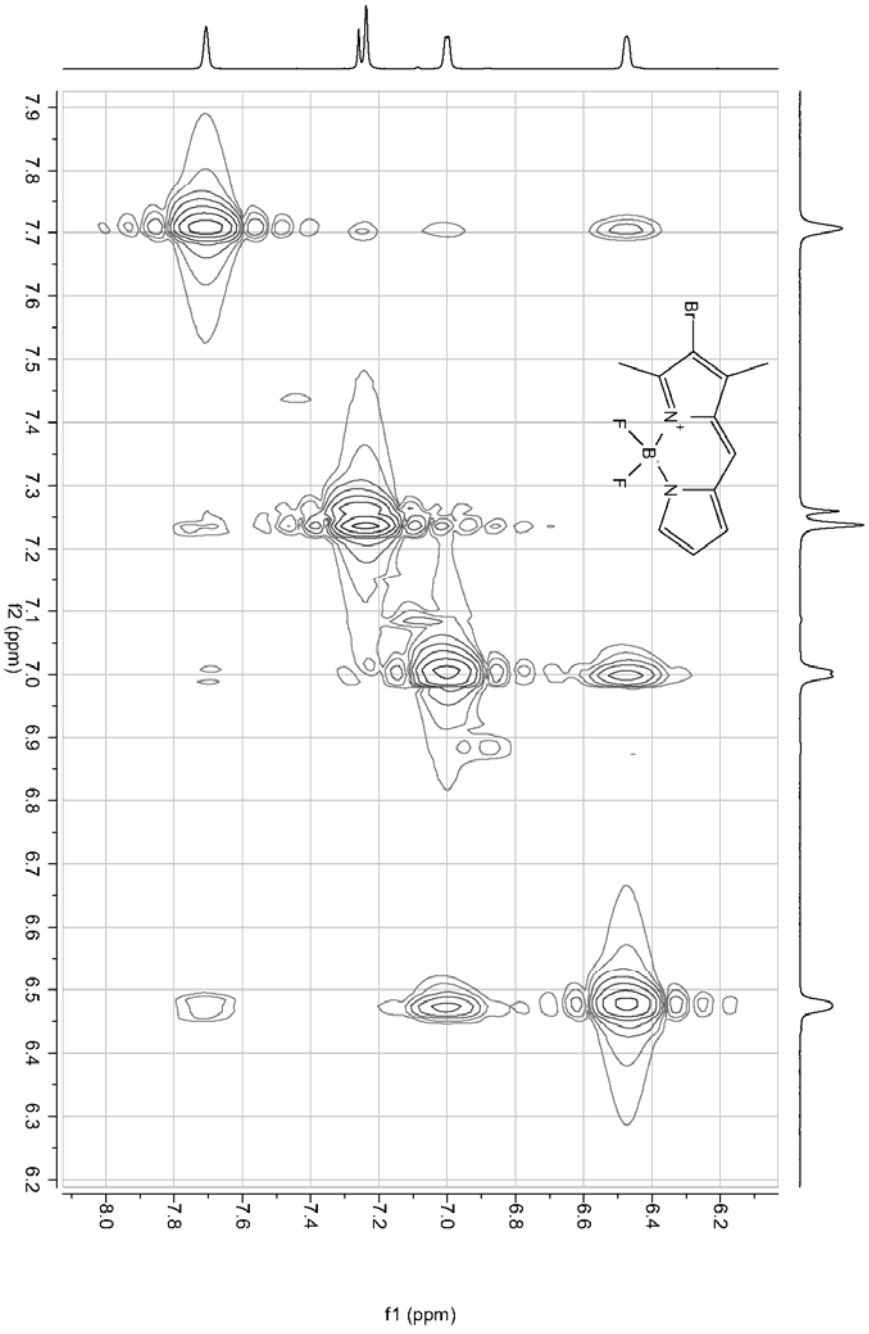
^{1}H NMR of Compound **3**



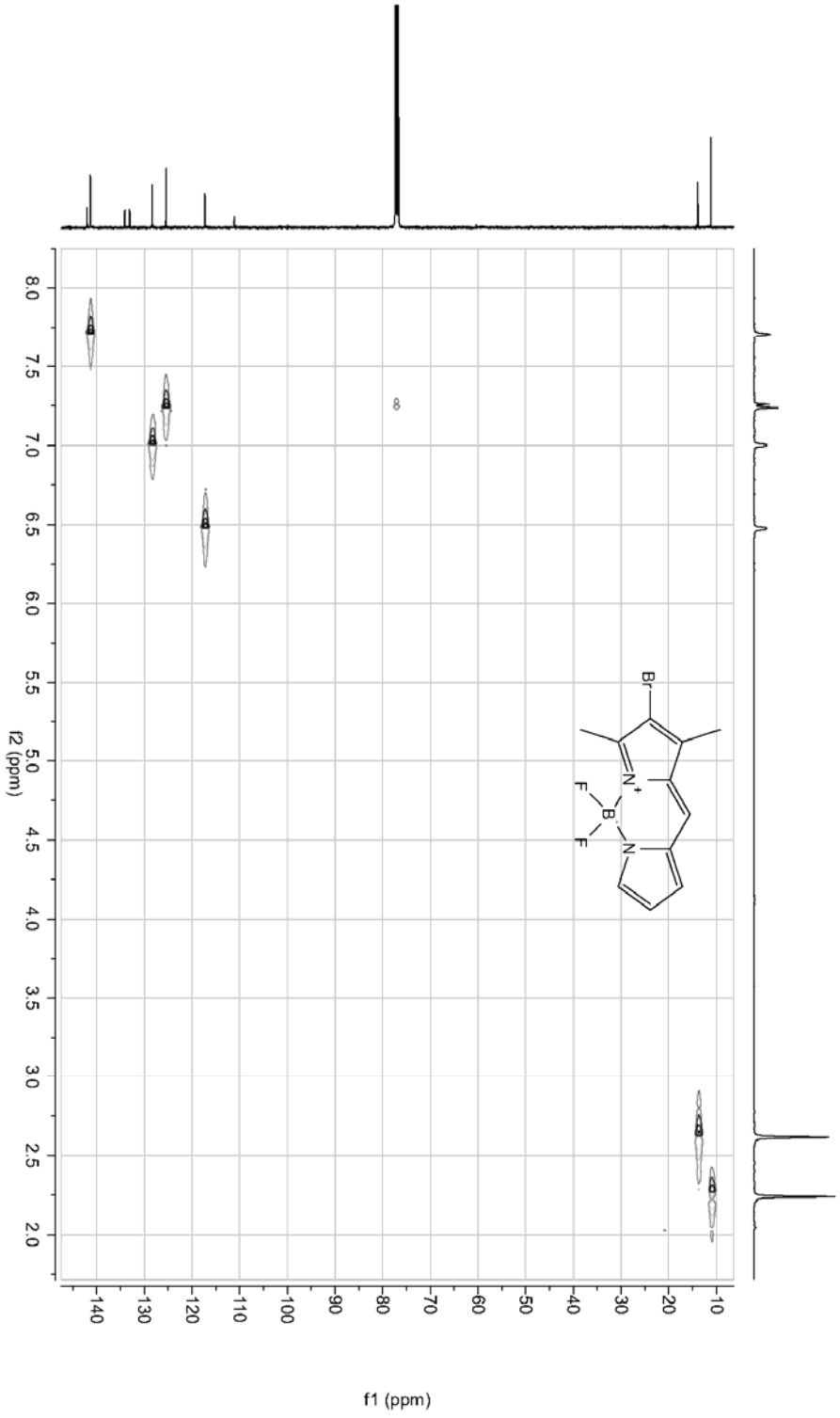
^{13}C NMR of Compound **3**



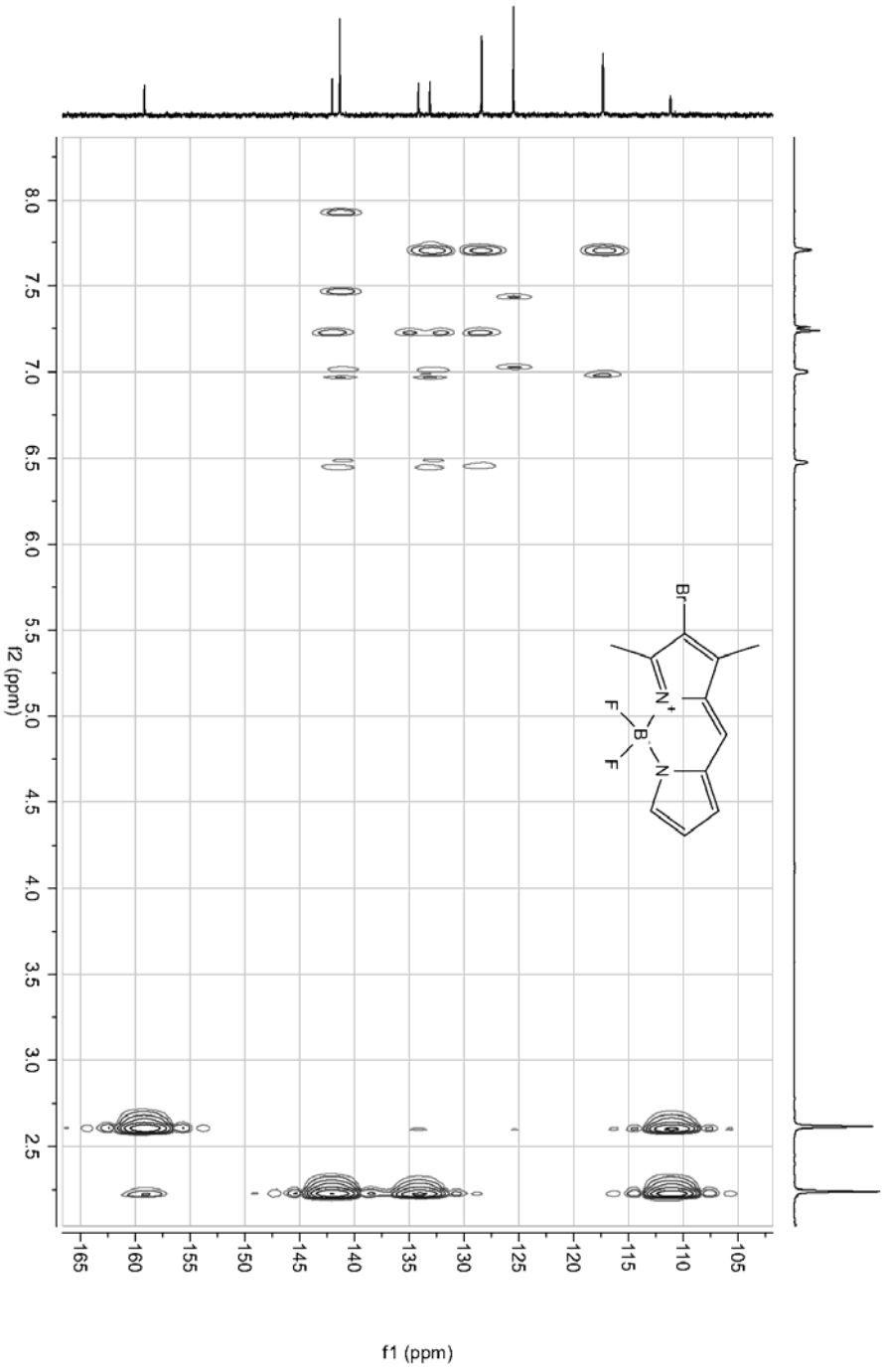
DEPT 135 of Compound **3**



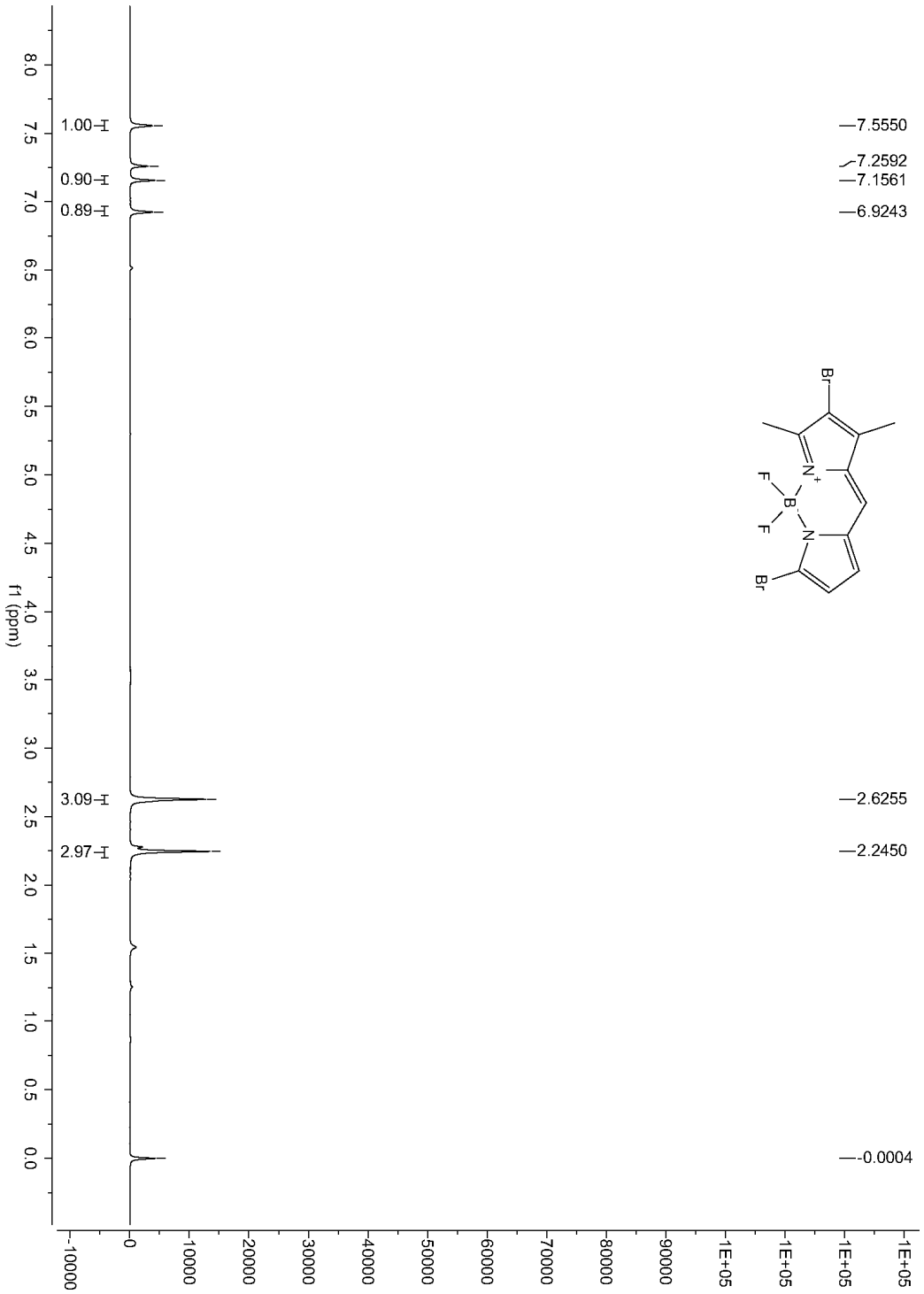
^{1}H-^{1}H COSY of Compound **3**



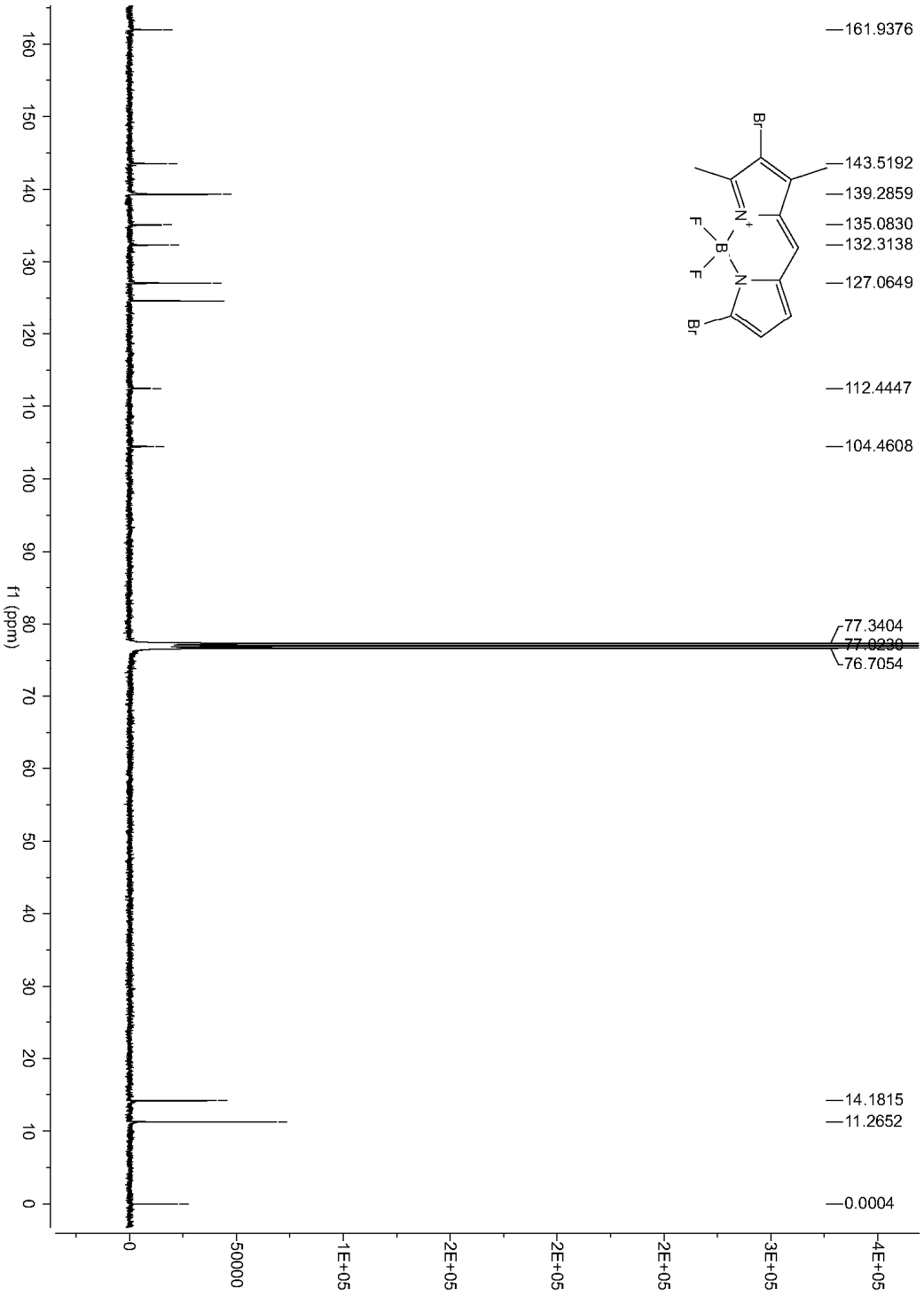
HMQC of Compound **3**



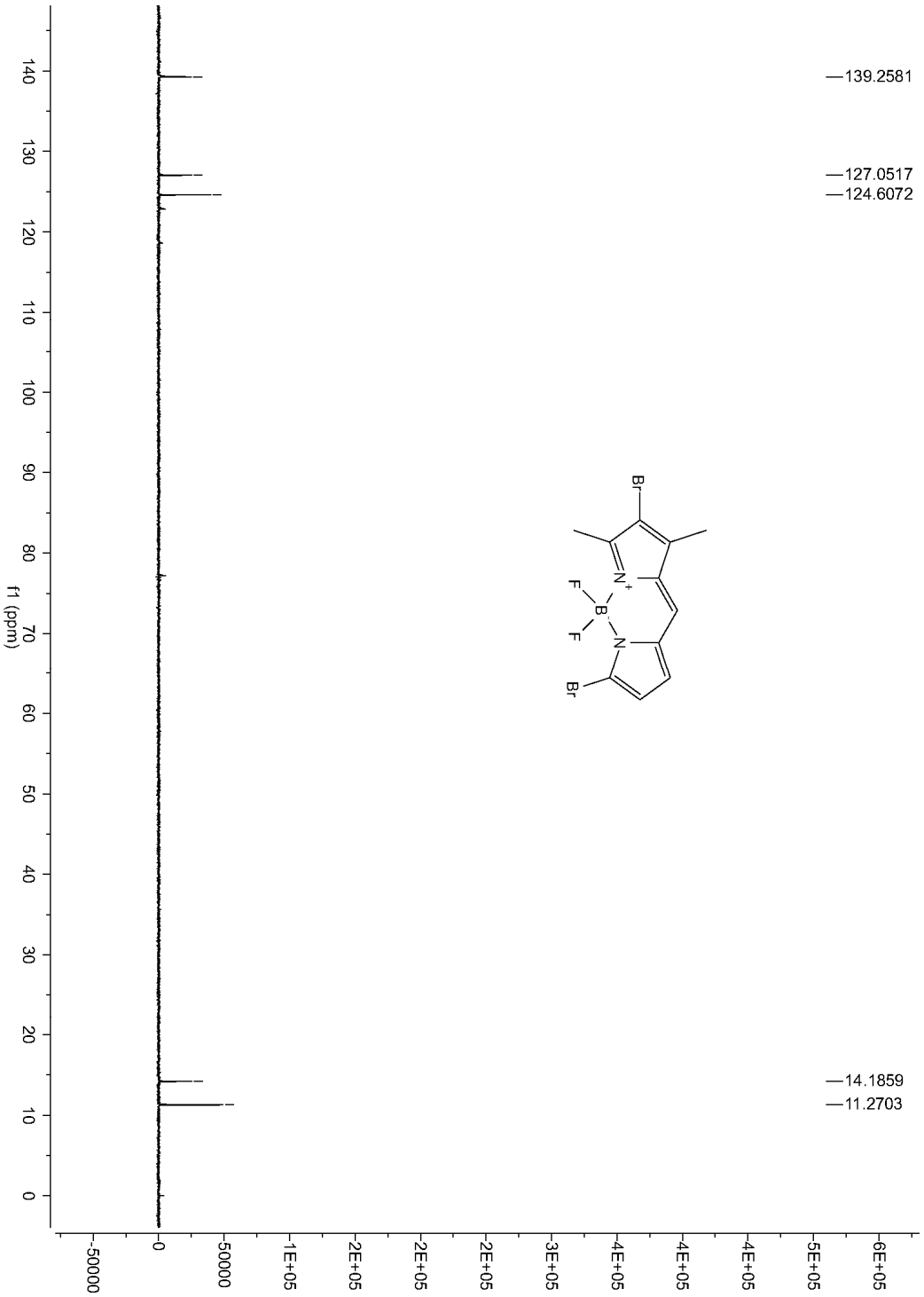
HMBC of Compound **3**



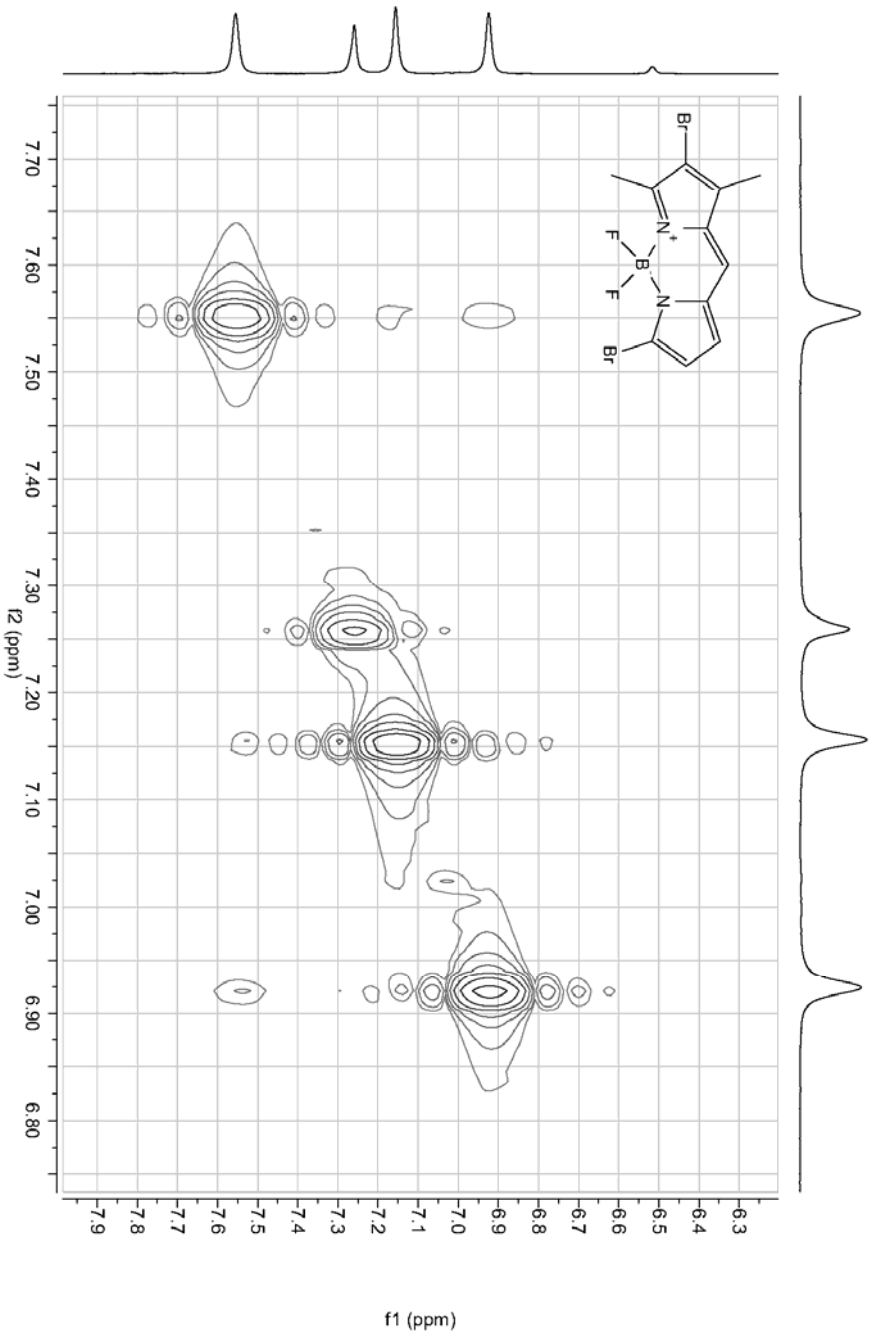
^{1}H NMR of Compound **4**



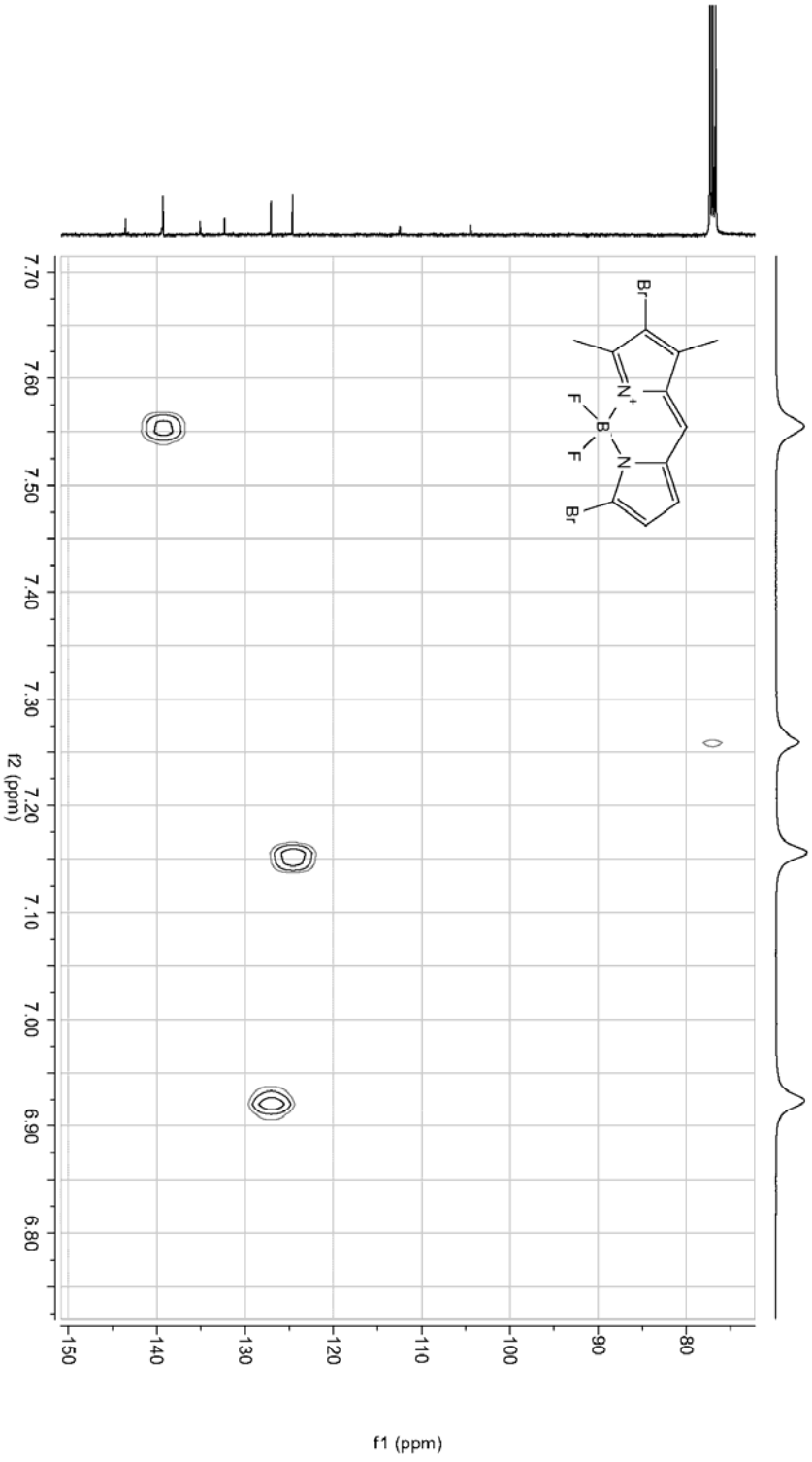
^{13}C NMR of Compound **4**



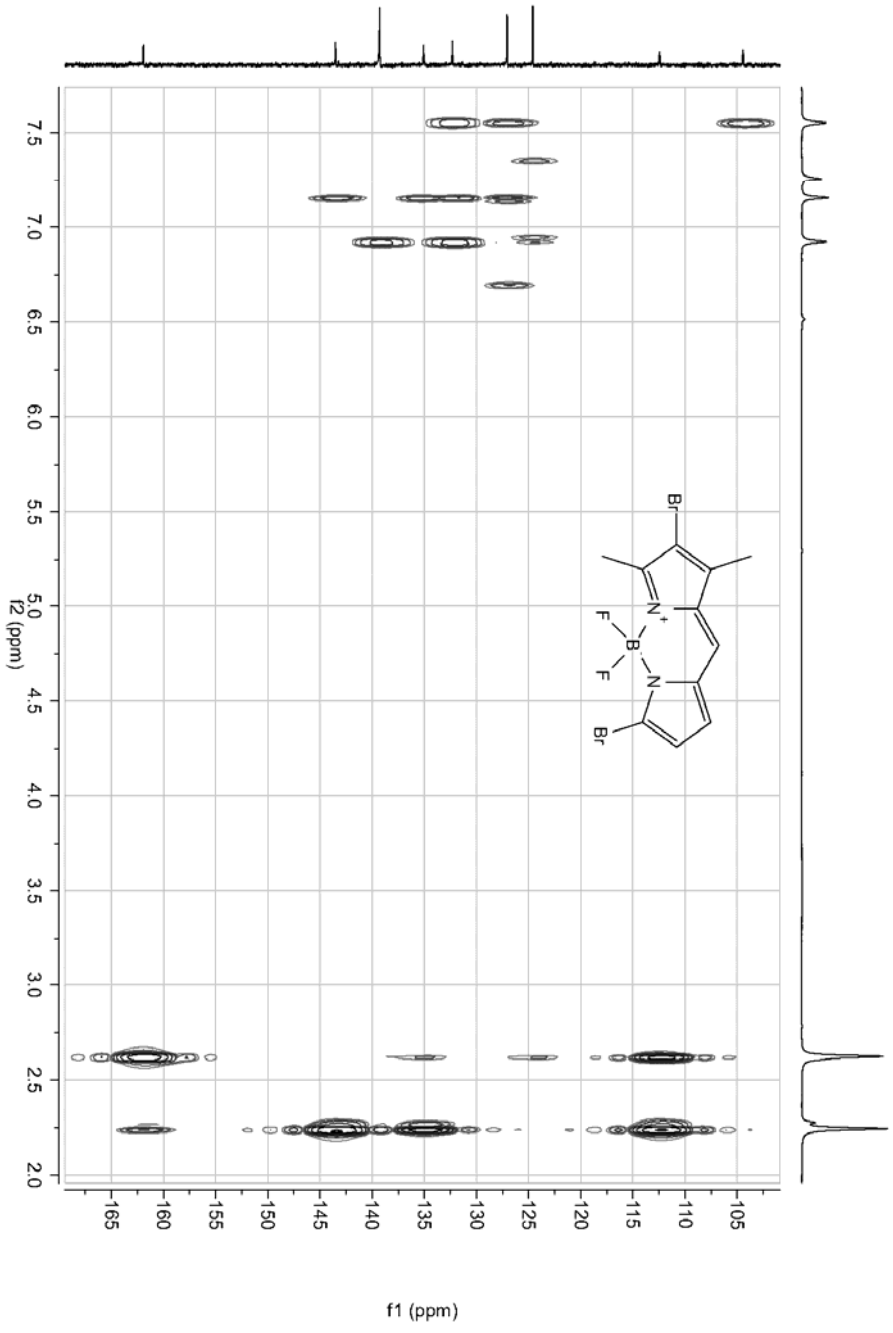
DEPT 135 of Compound **4**



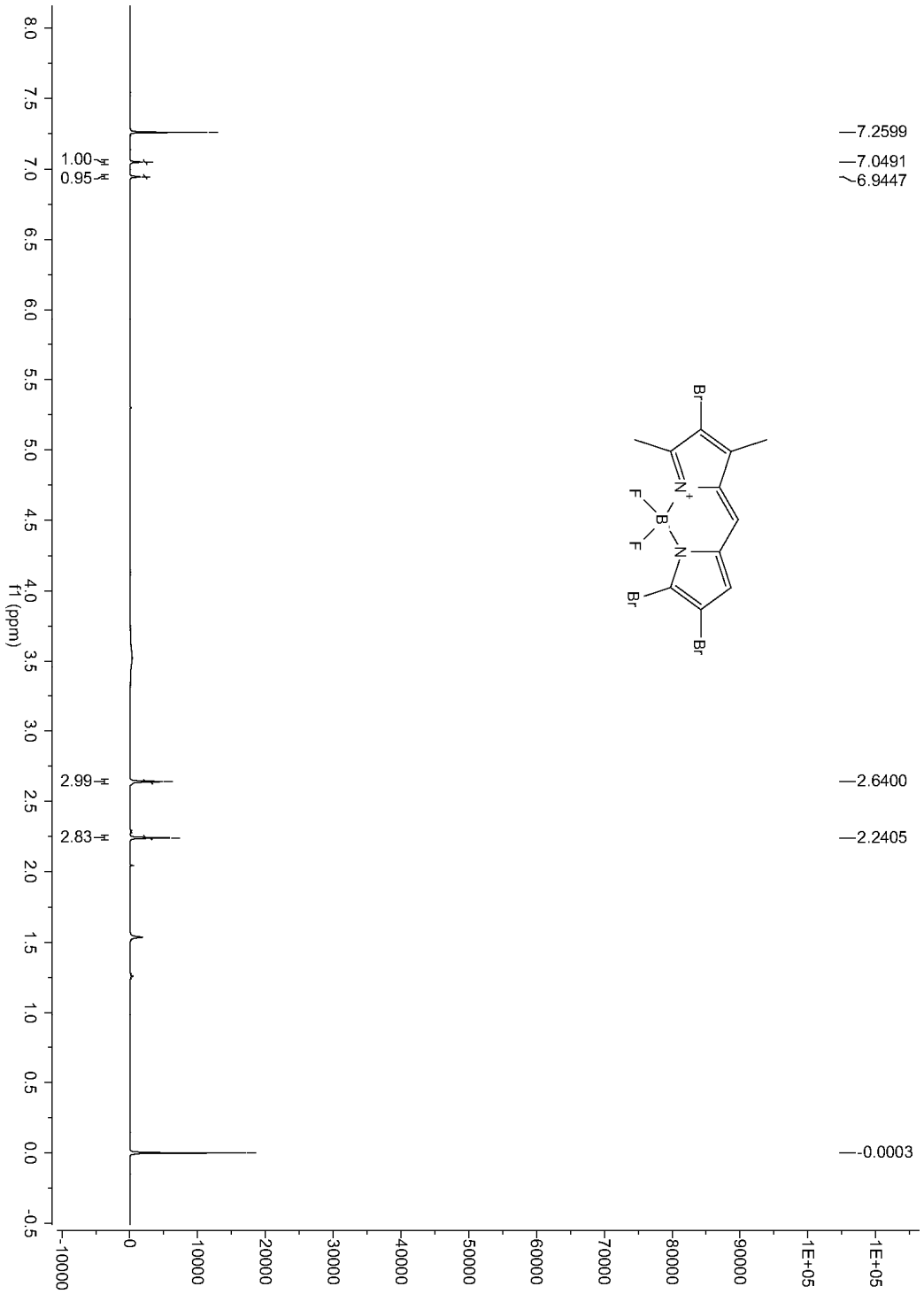
^{1}H-^{1}H COSY of Compound **4**



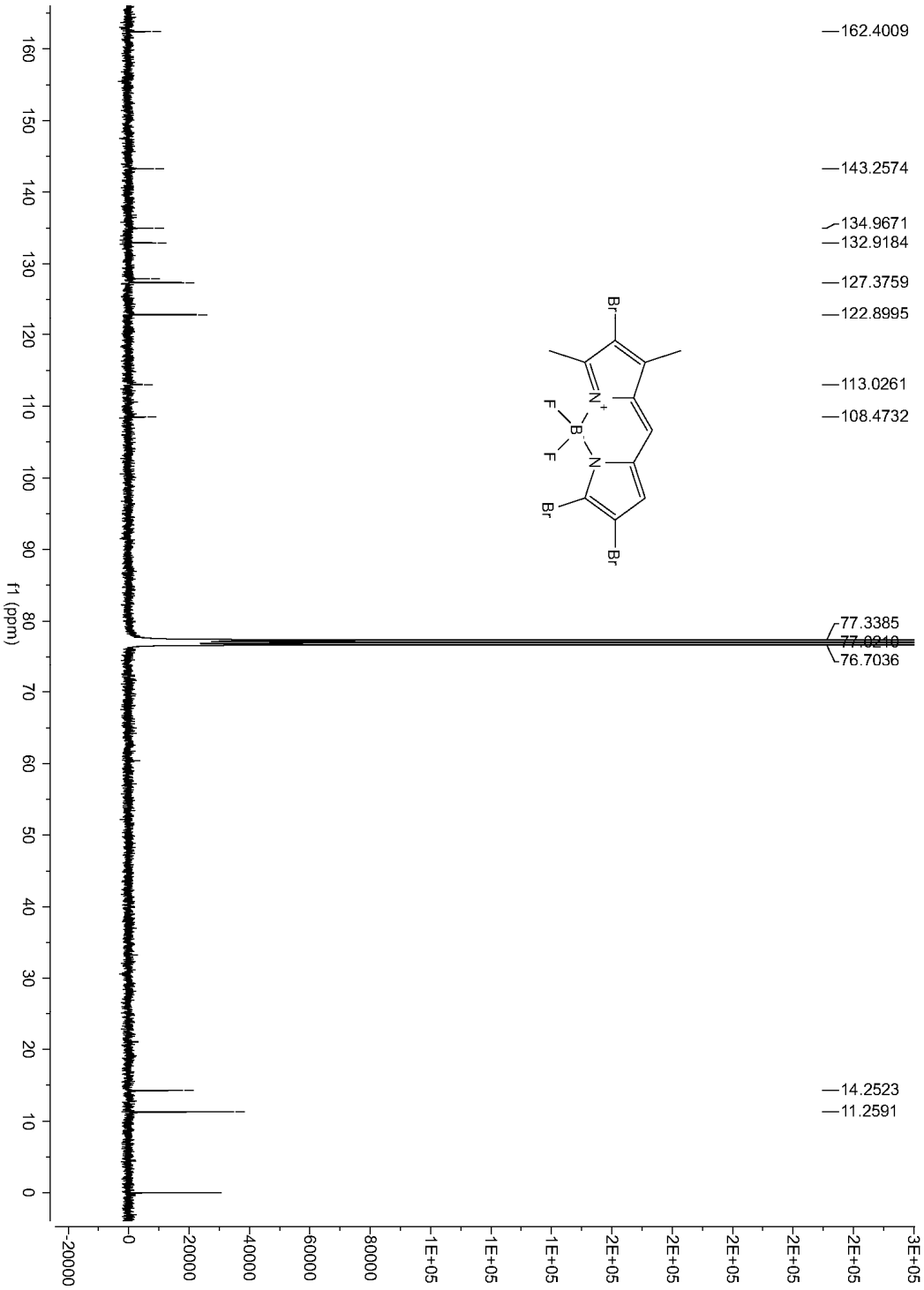
HMQC of Compound **4**



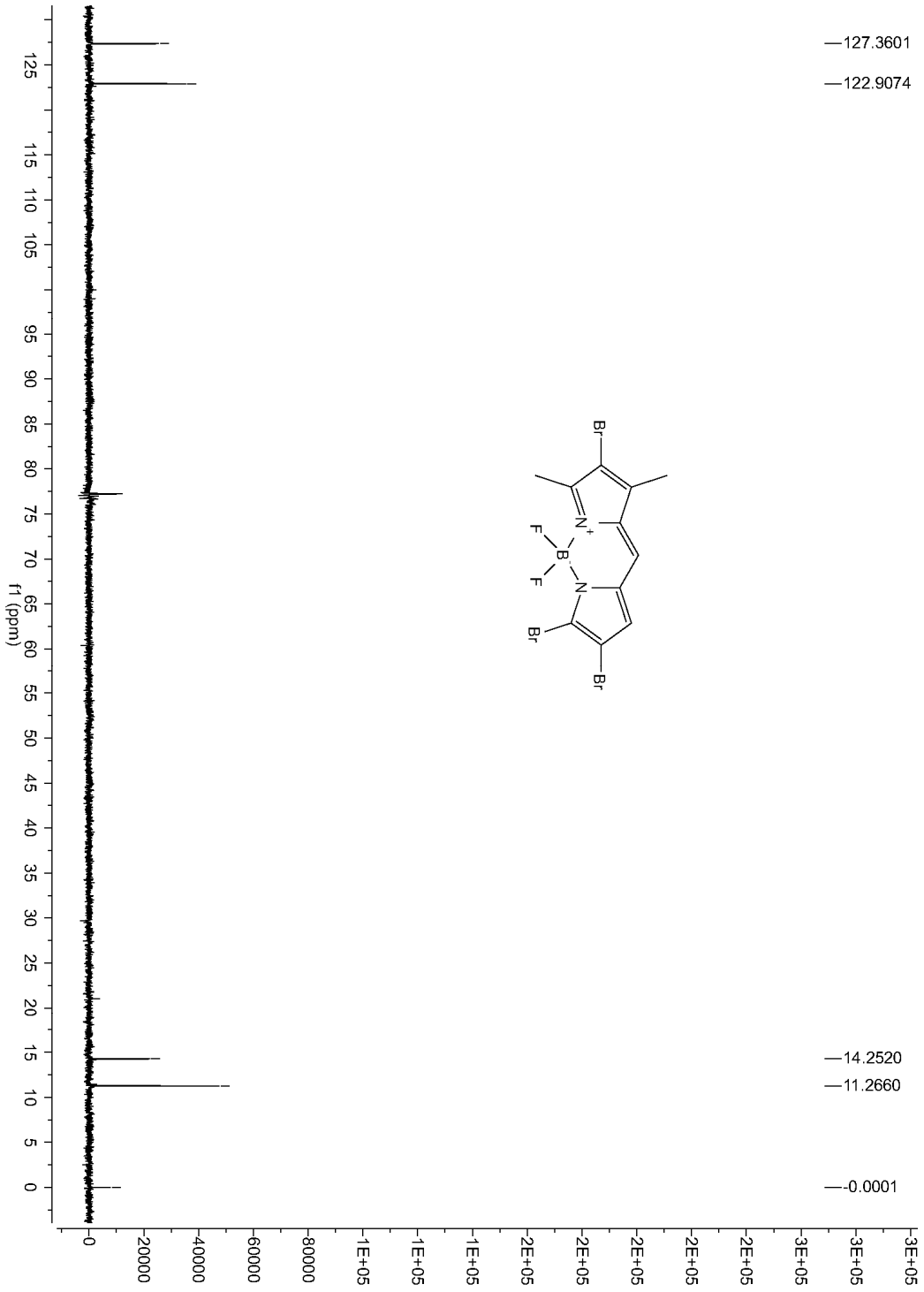
HMBC of Compound **4**



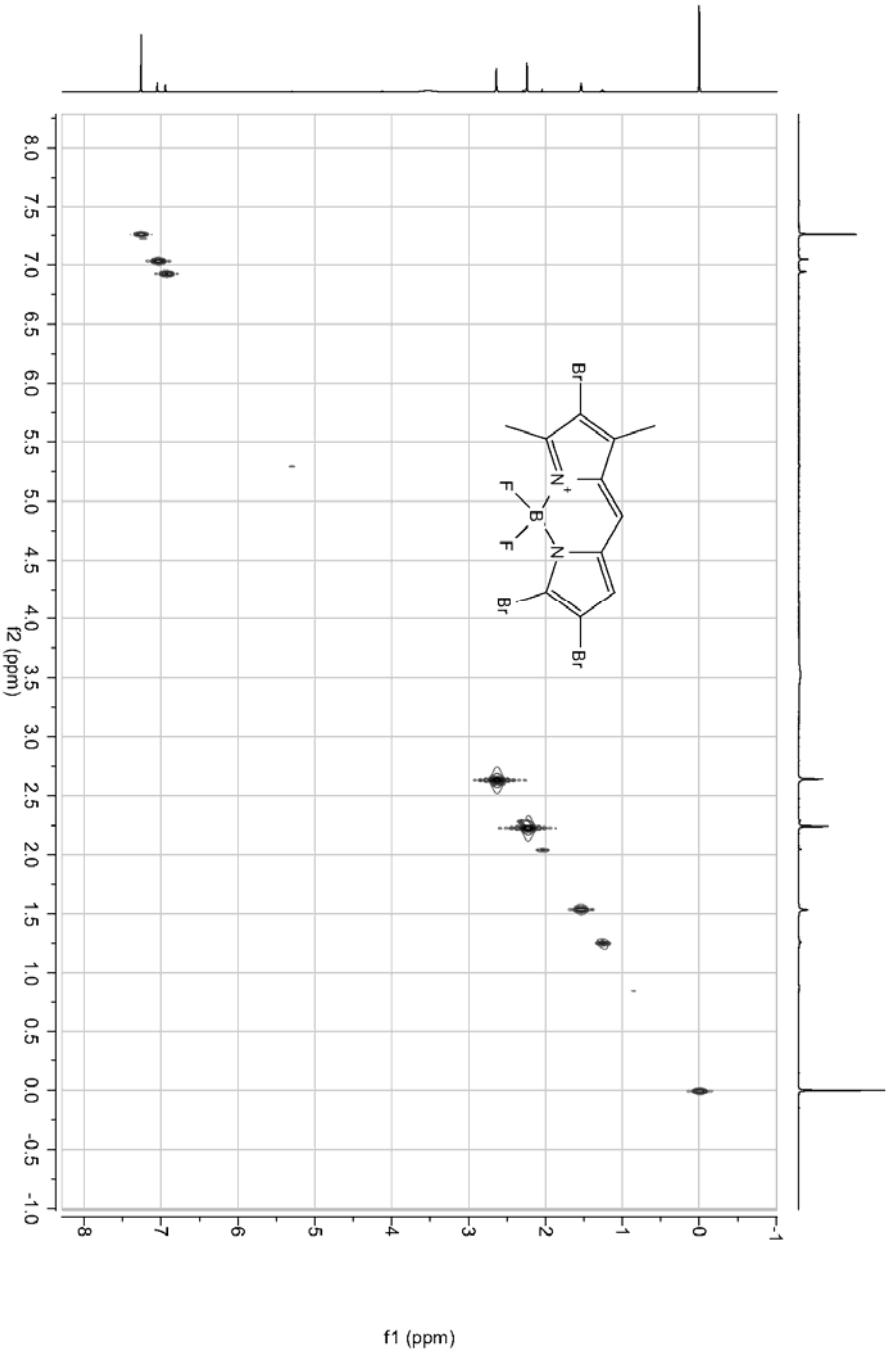
^{1}H NMR of Compound **5**



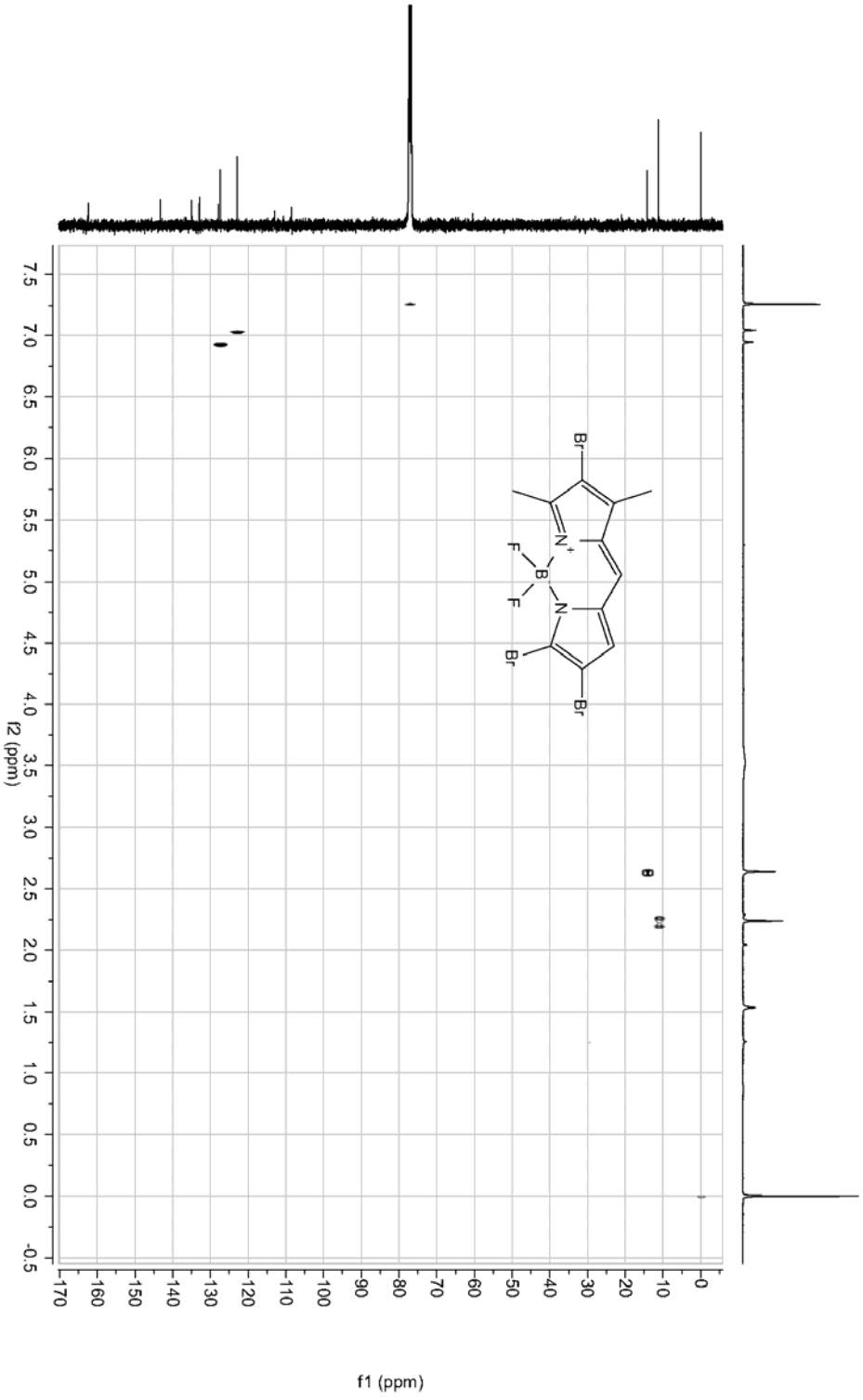
^{13}C NMR of Compound **5**



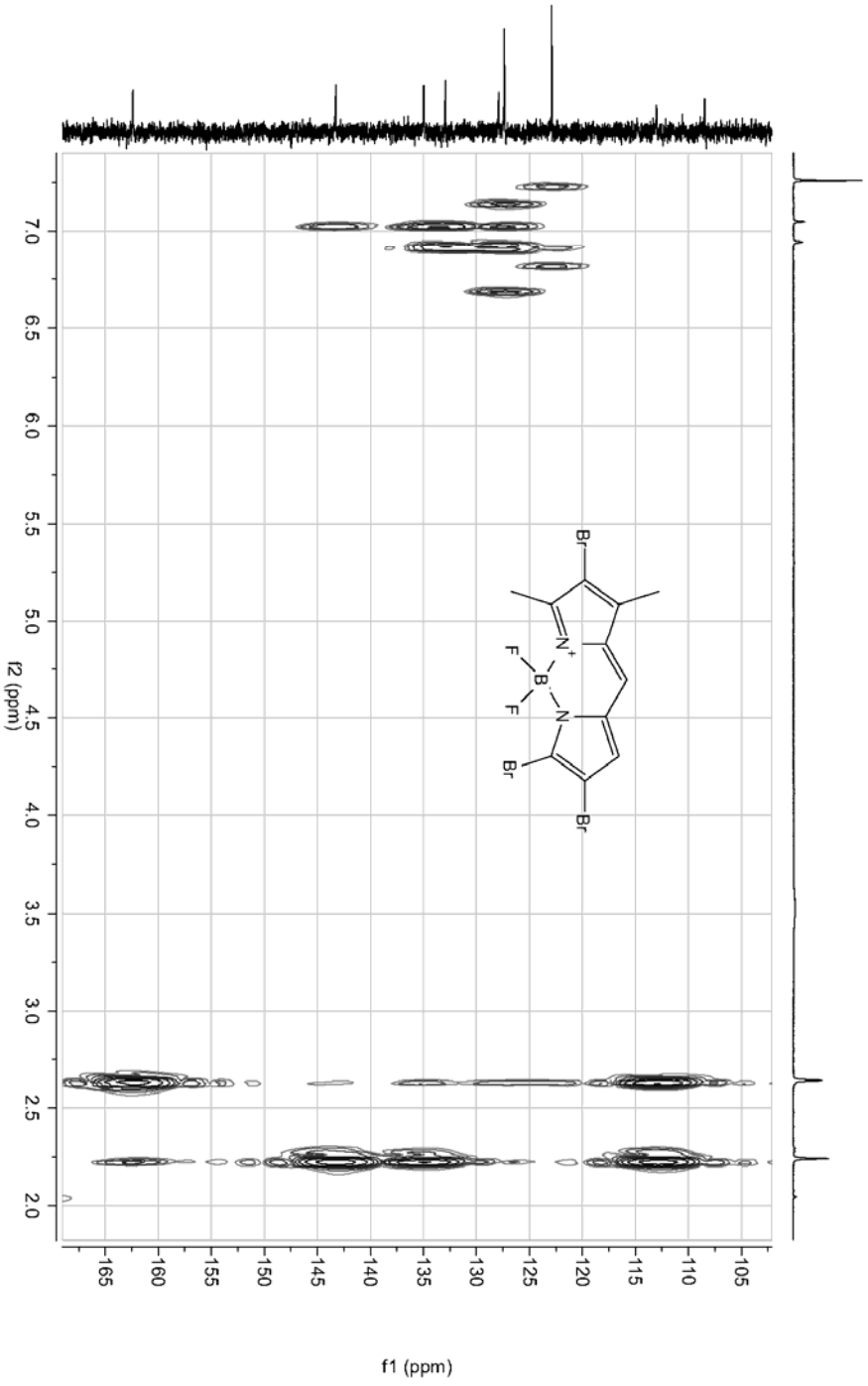
DEPT 135 of Compound **5**



^{1}H-^{1}H COSY of Compound **5**



HMQC of Compound **5**



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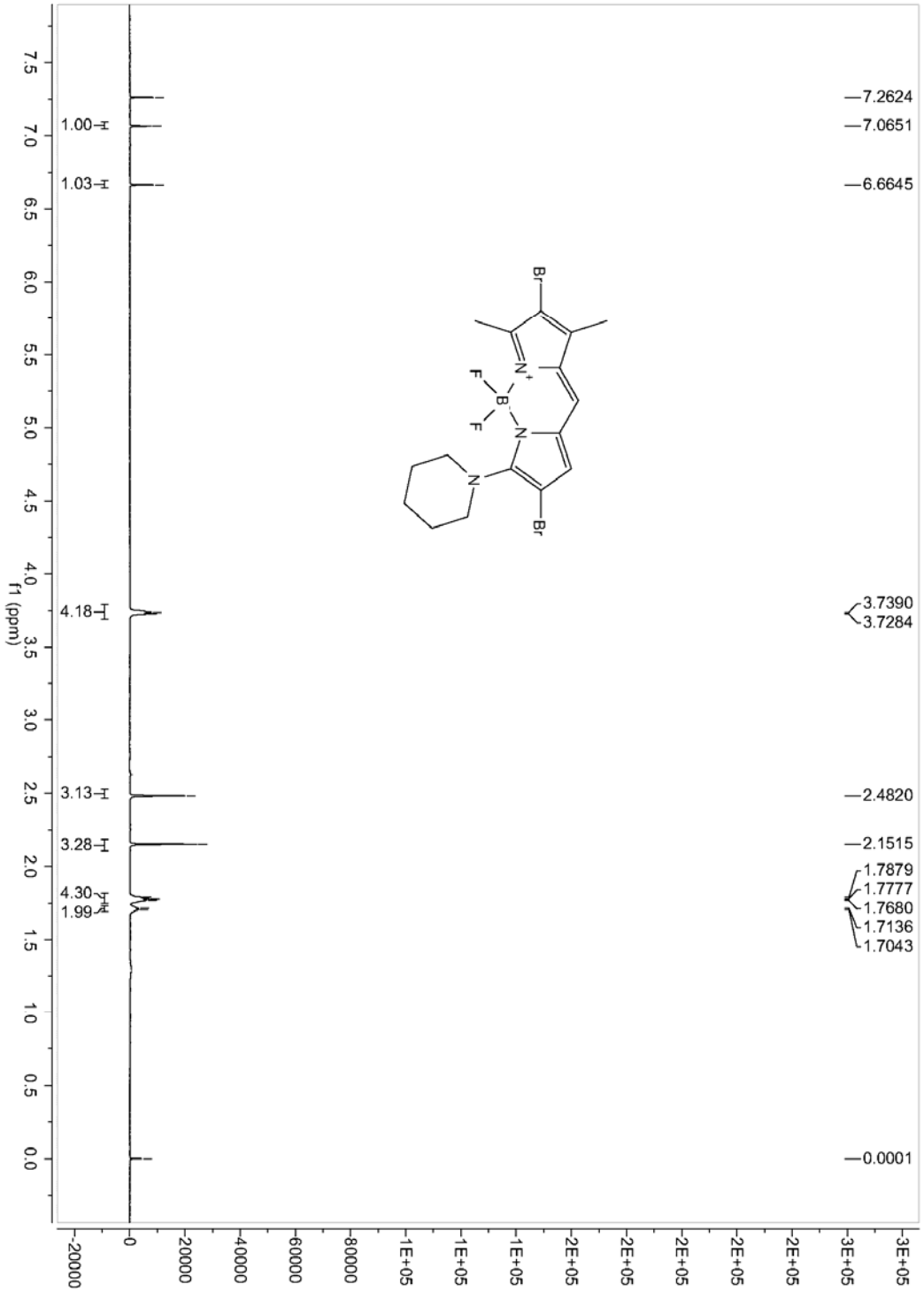
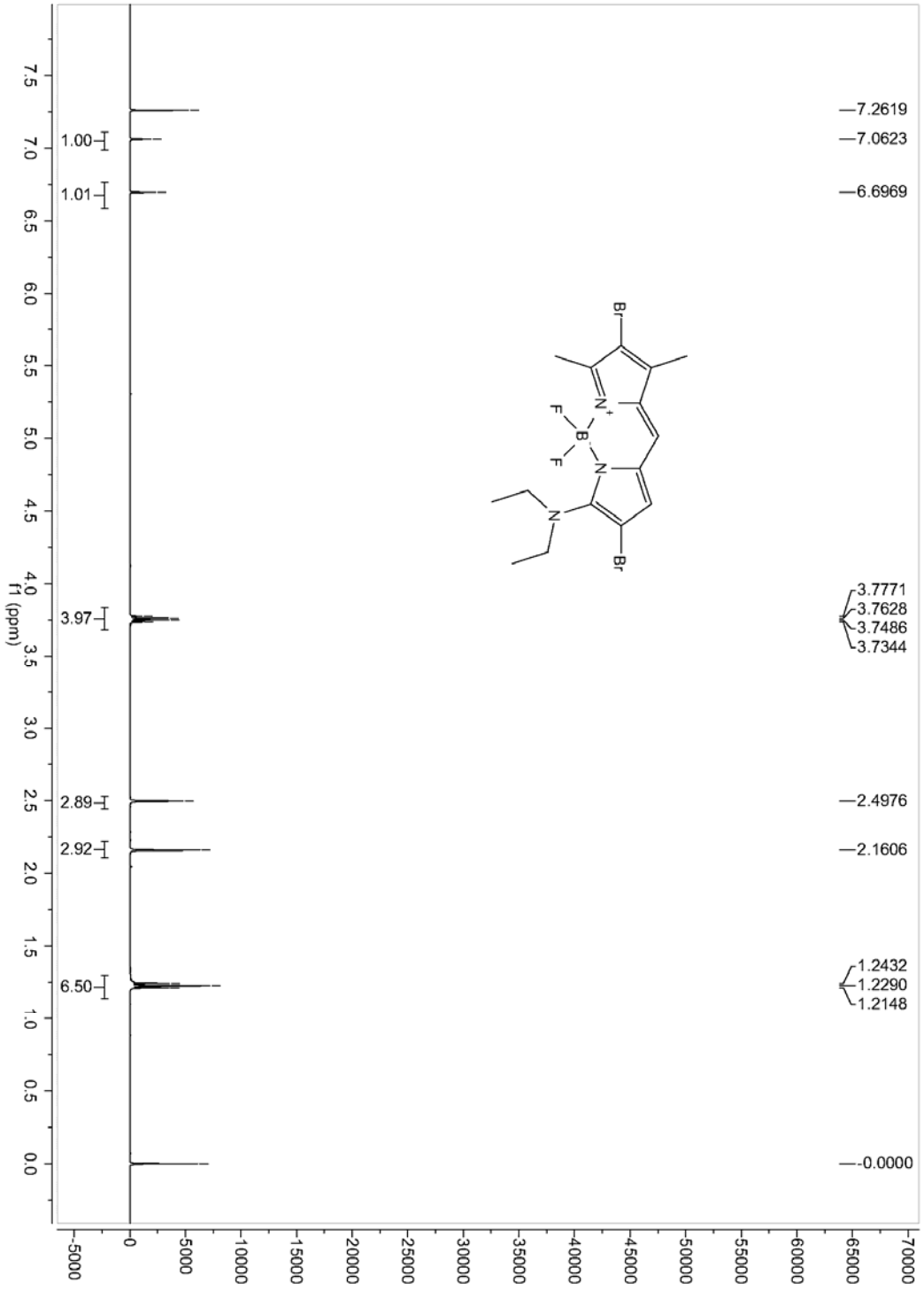
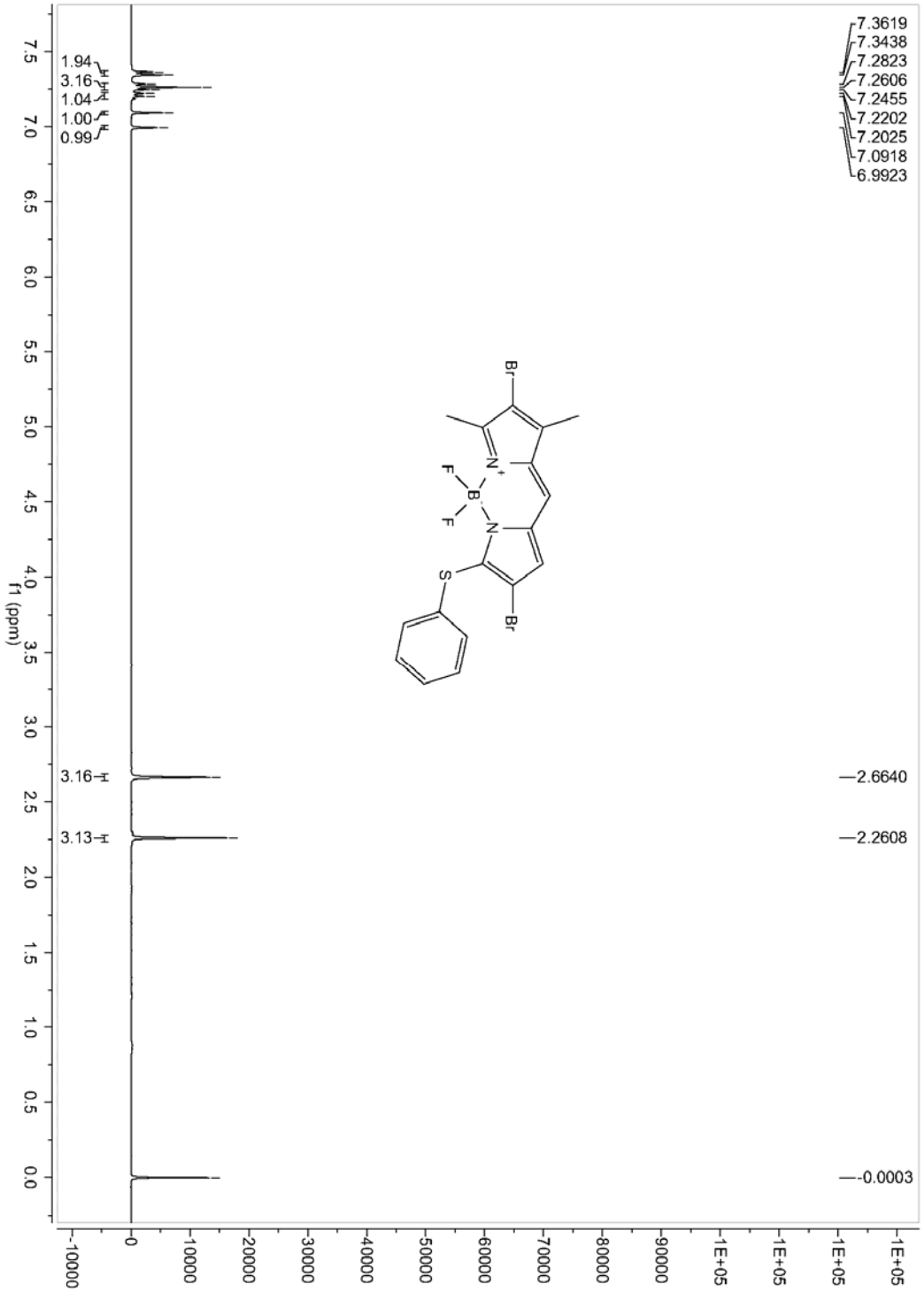


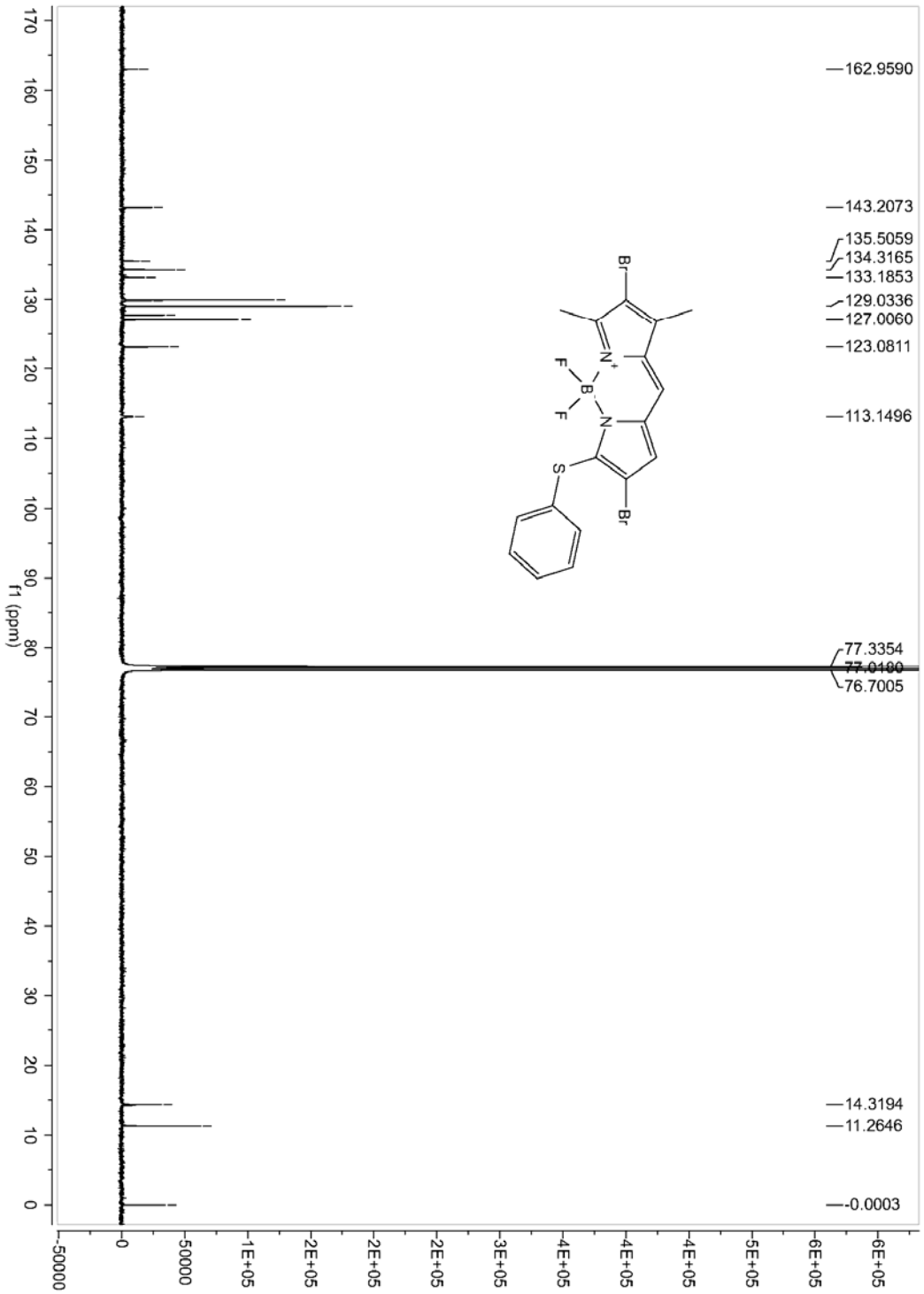
^{1}H NMR of Compound **6a**



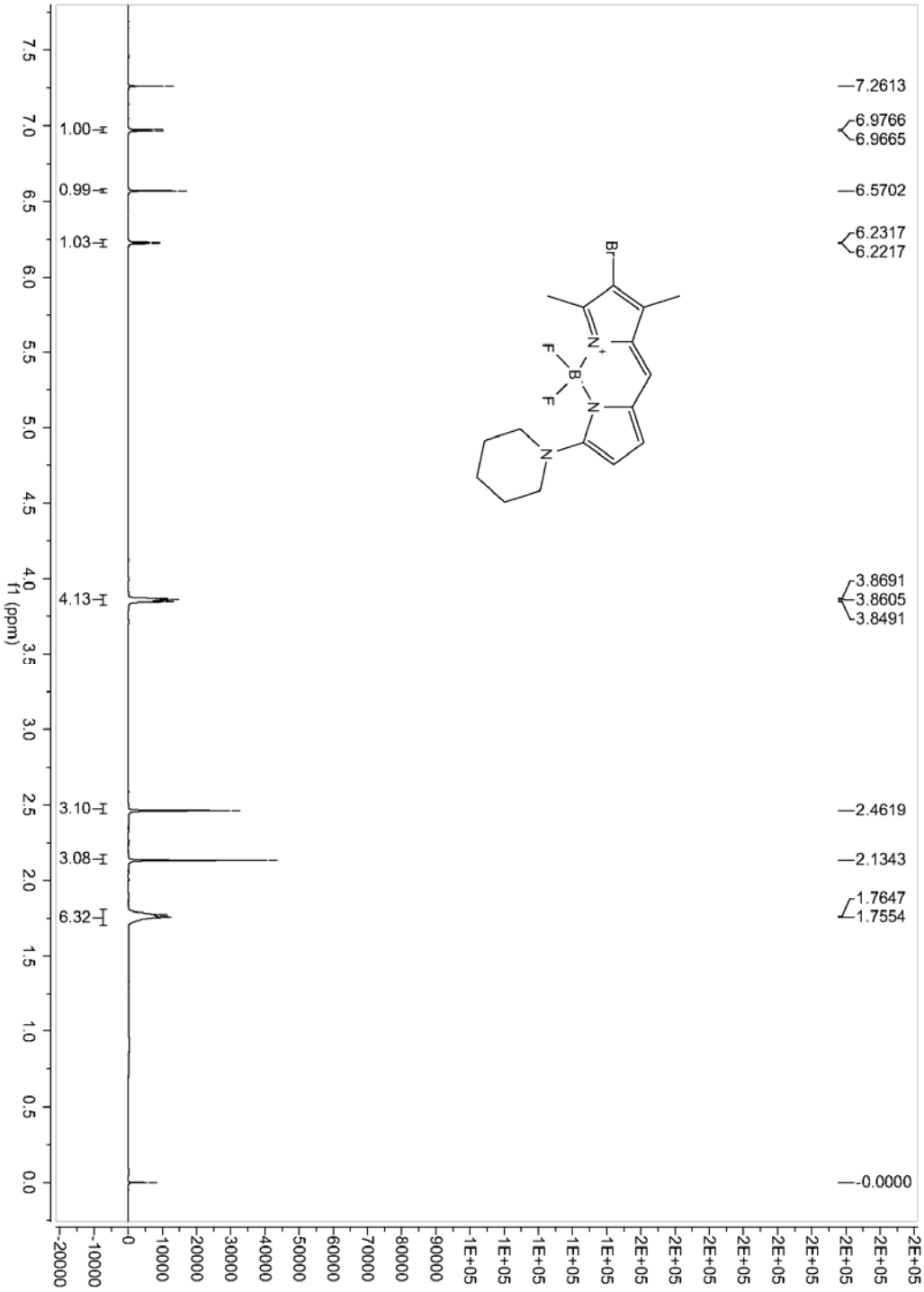
^{1}H NMR of Compound **6b**



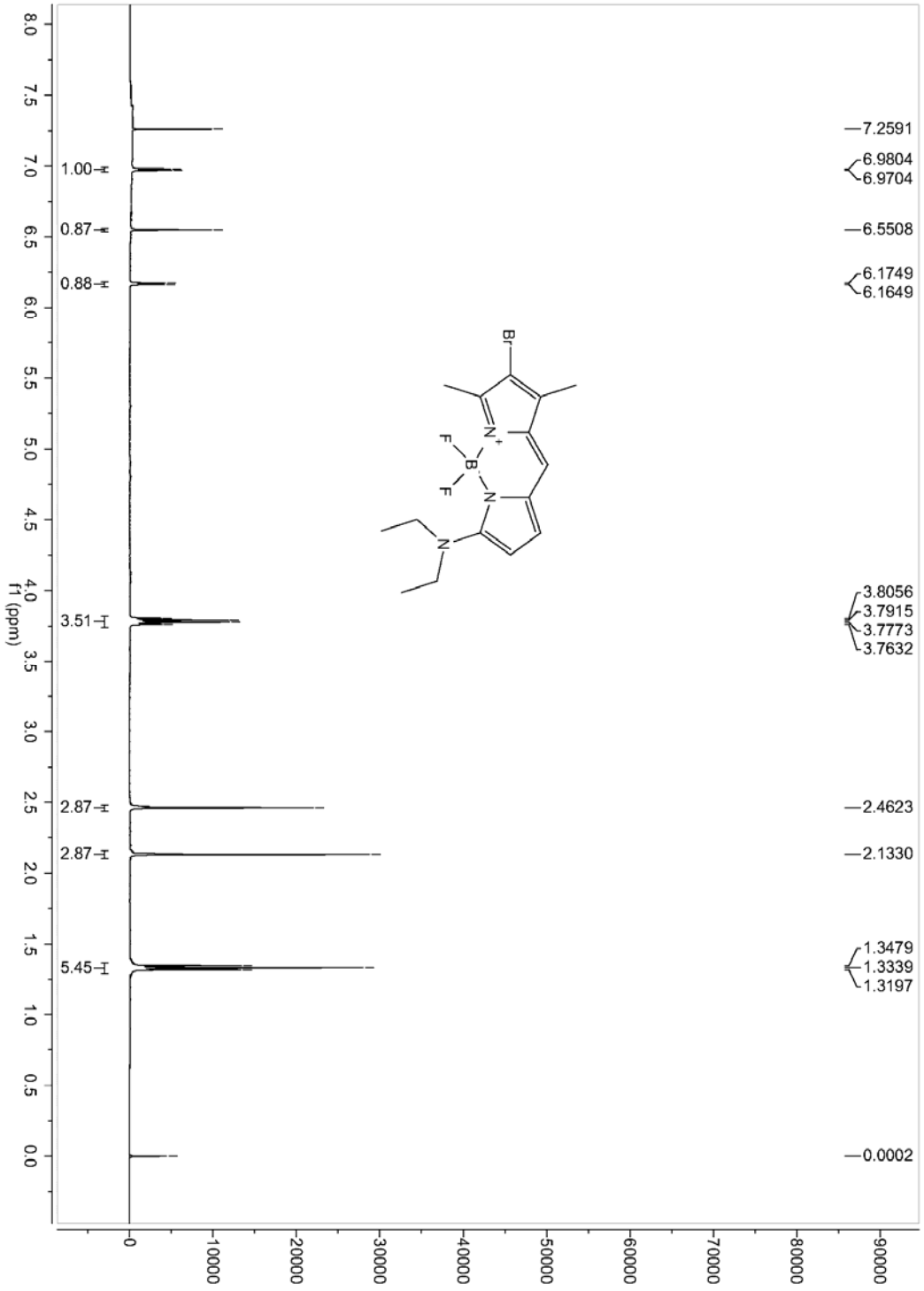
^{1}H NMR of Compound **6c**



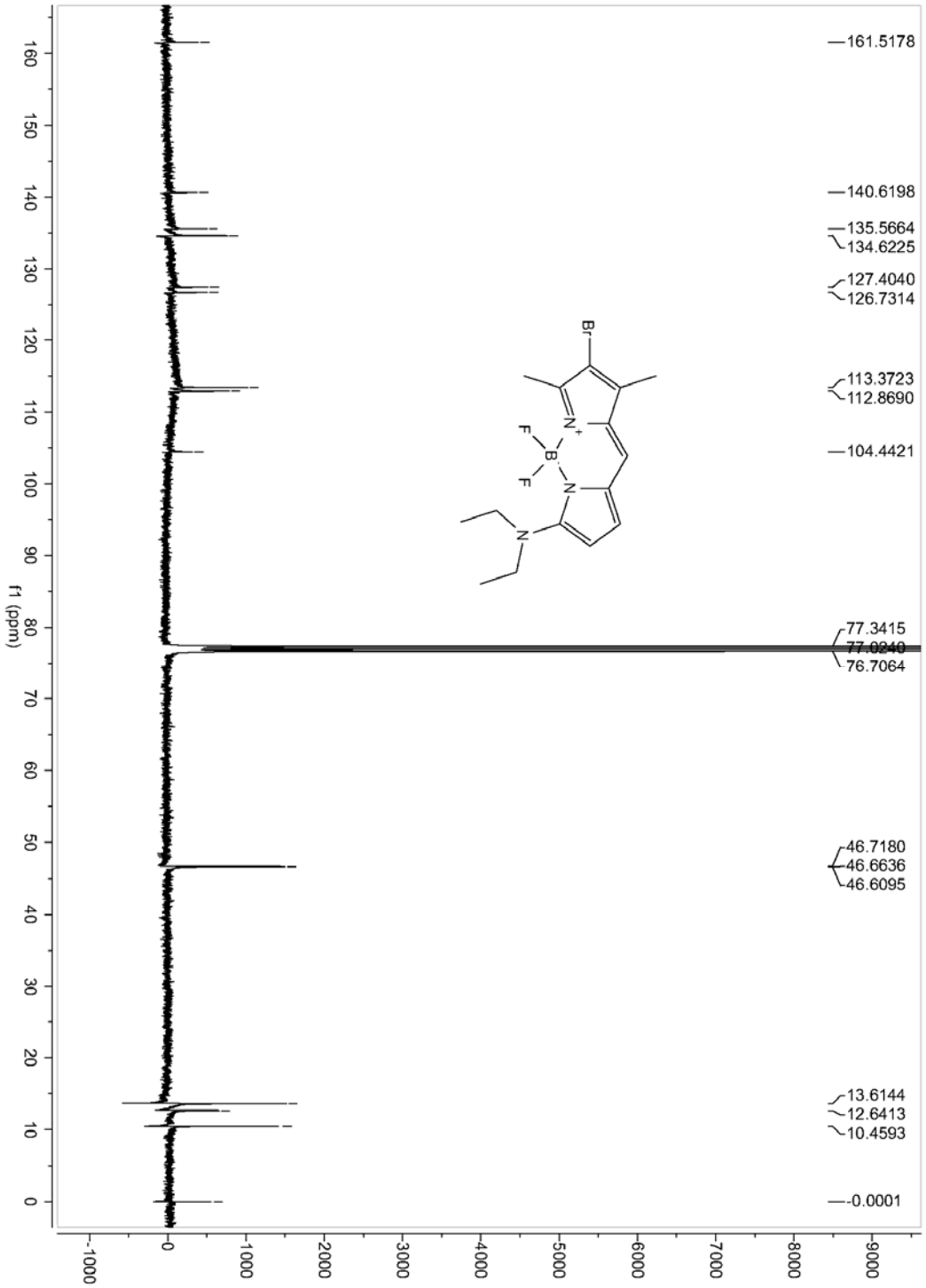
^{13}C NMR of Compound **6c**



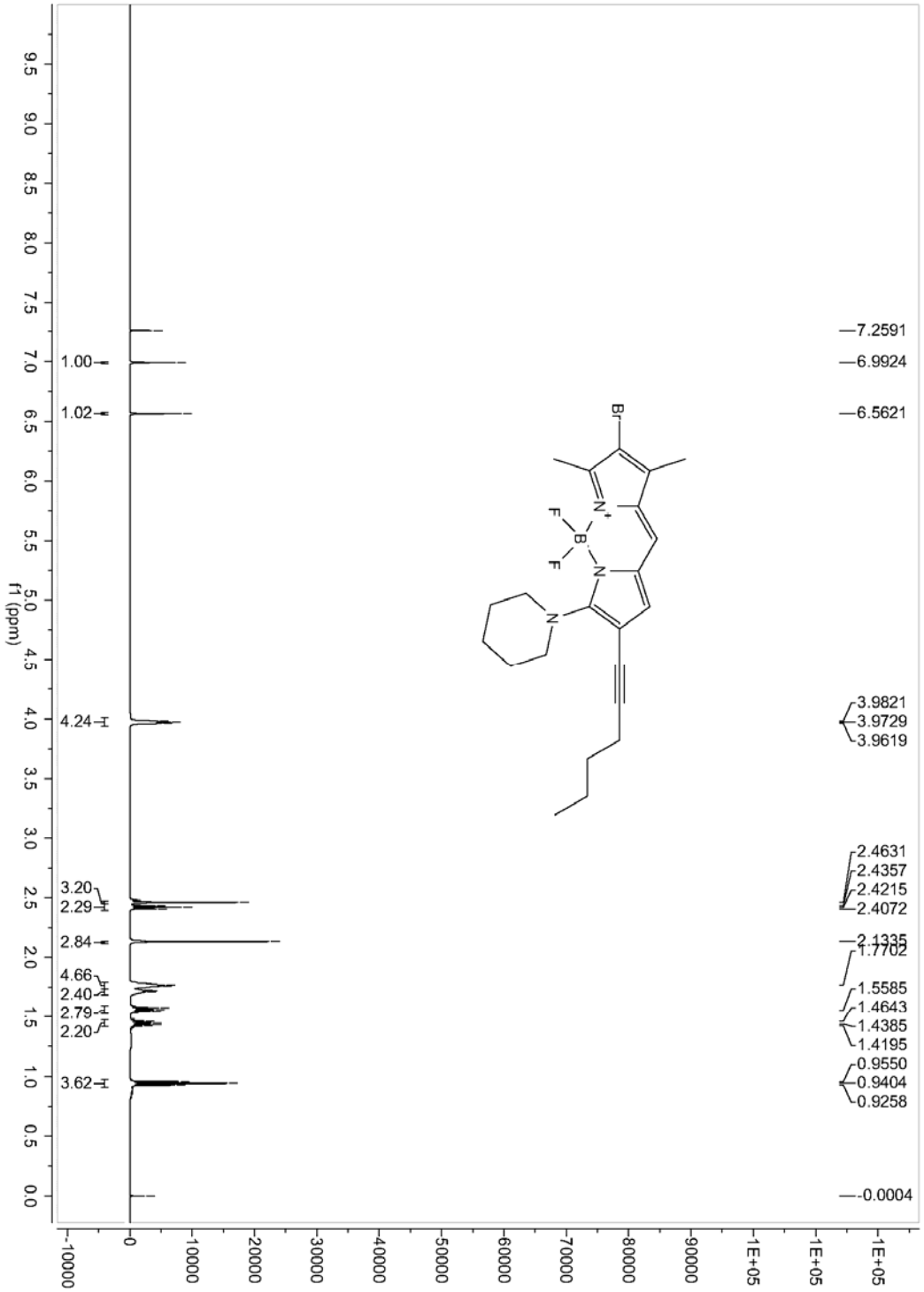
^{1}H NMR of Compound **7a**



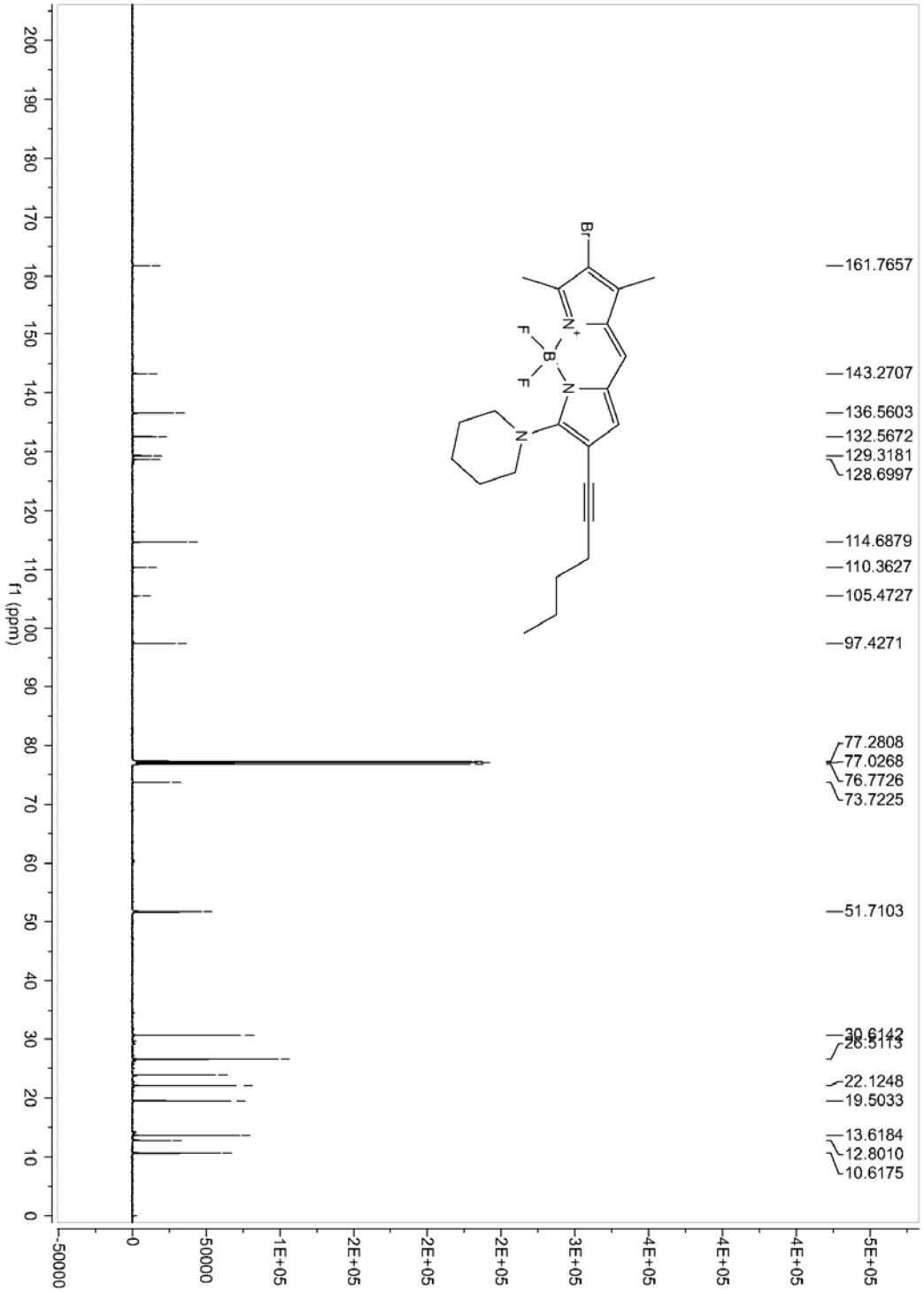
^{1}H NMR of Compound **7b**



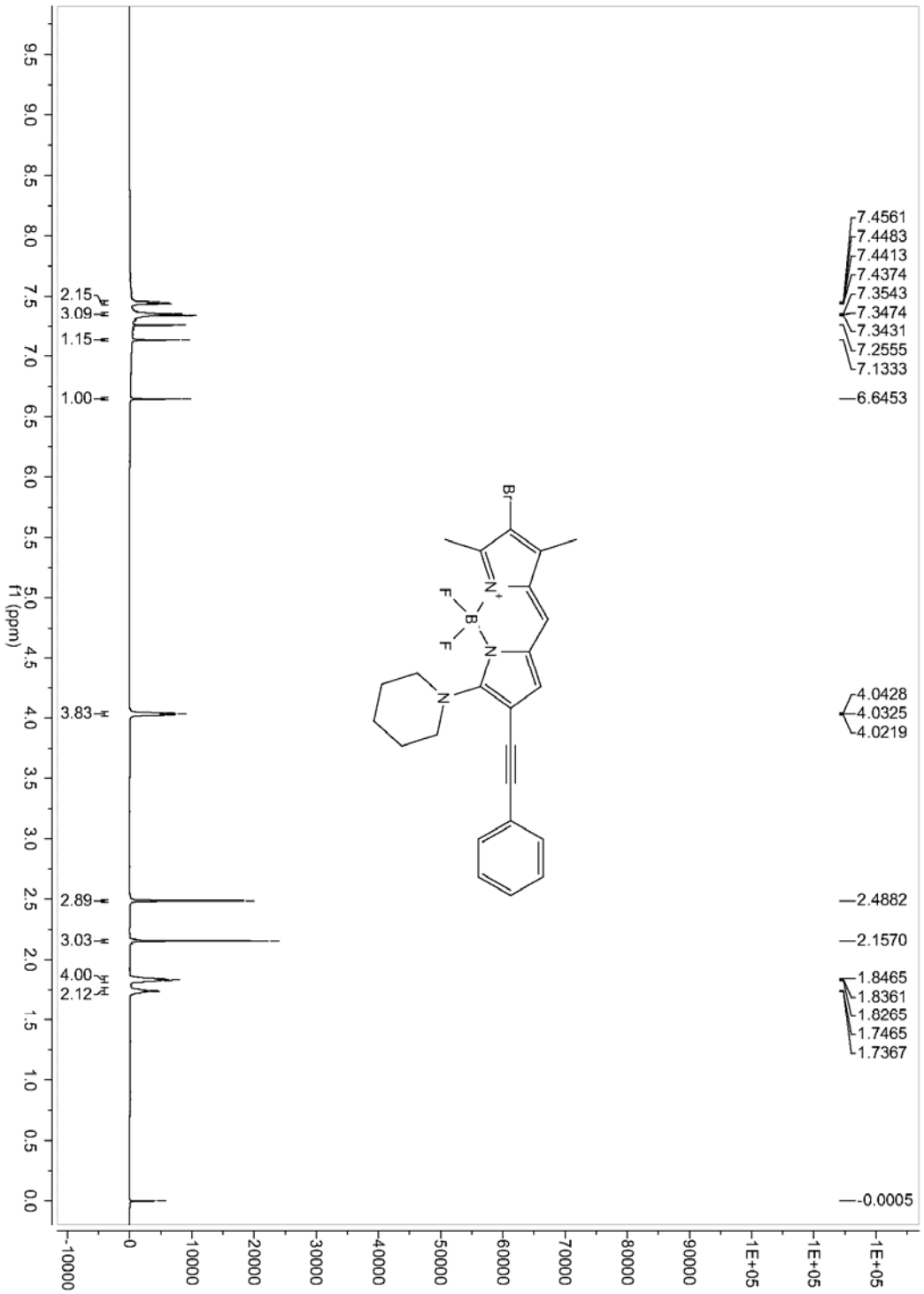
^{13}C NMR of Compound **7b**



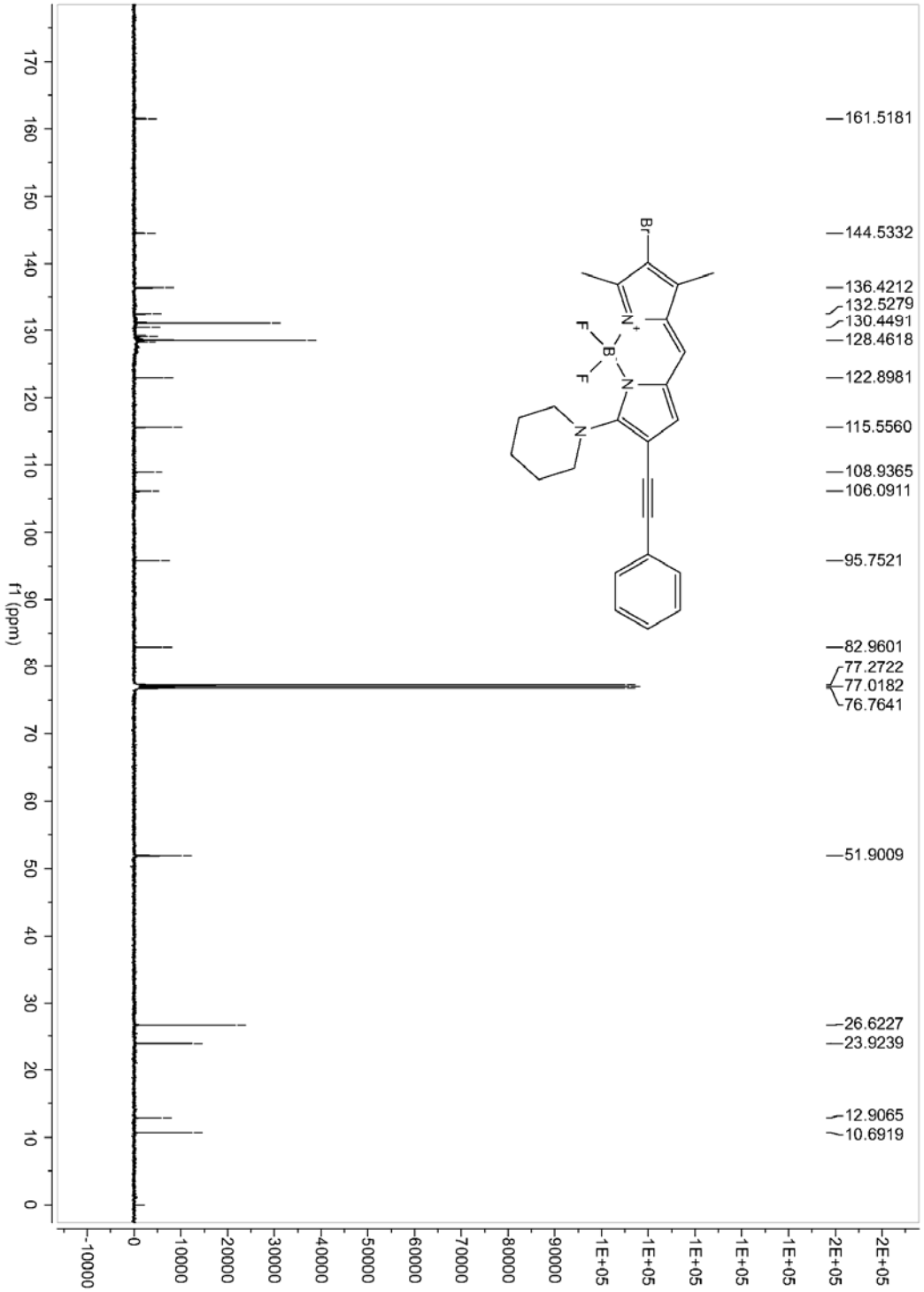
^{1}H NMR of Compound **8a**



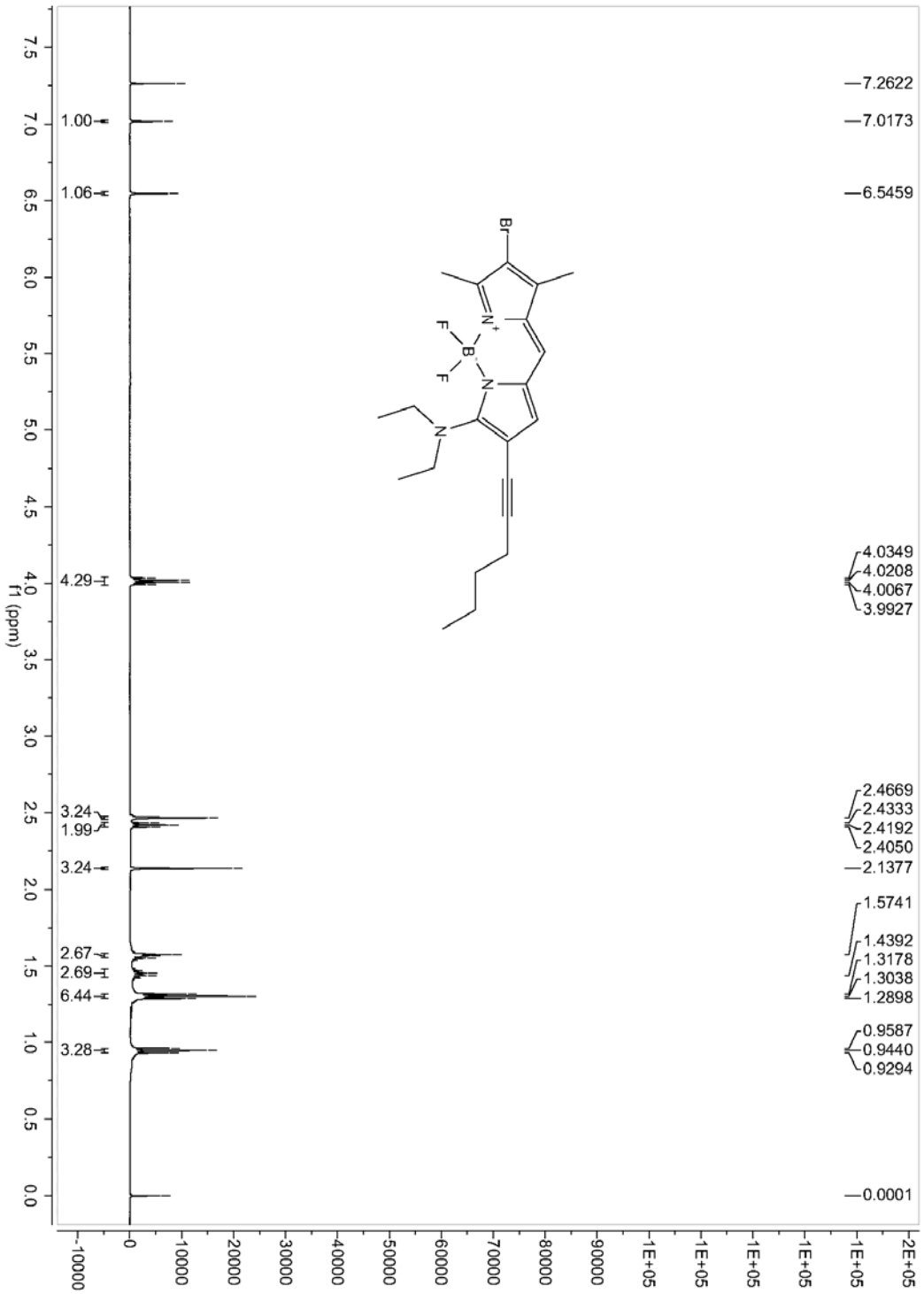
^{13}C NMR of Compound **8a**



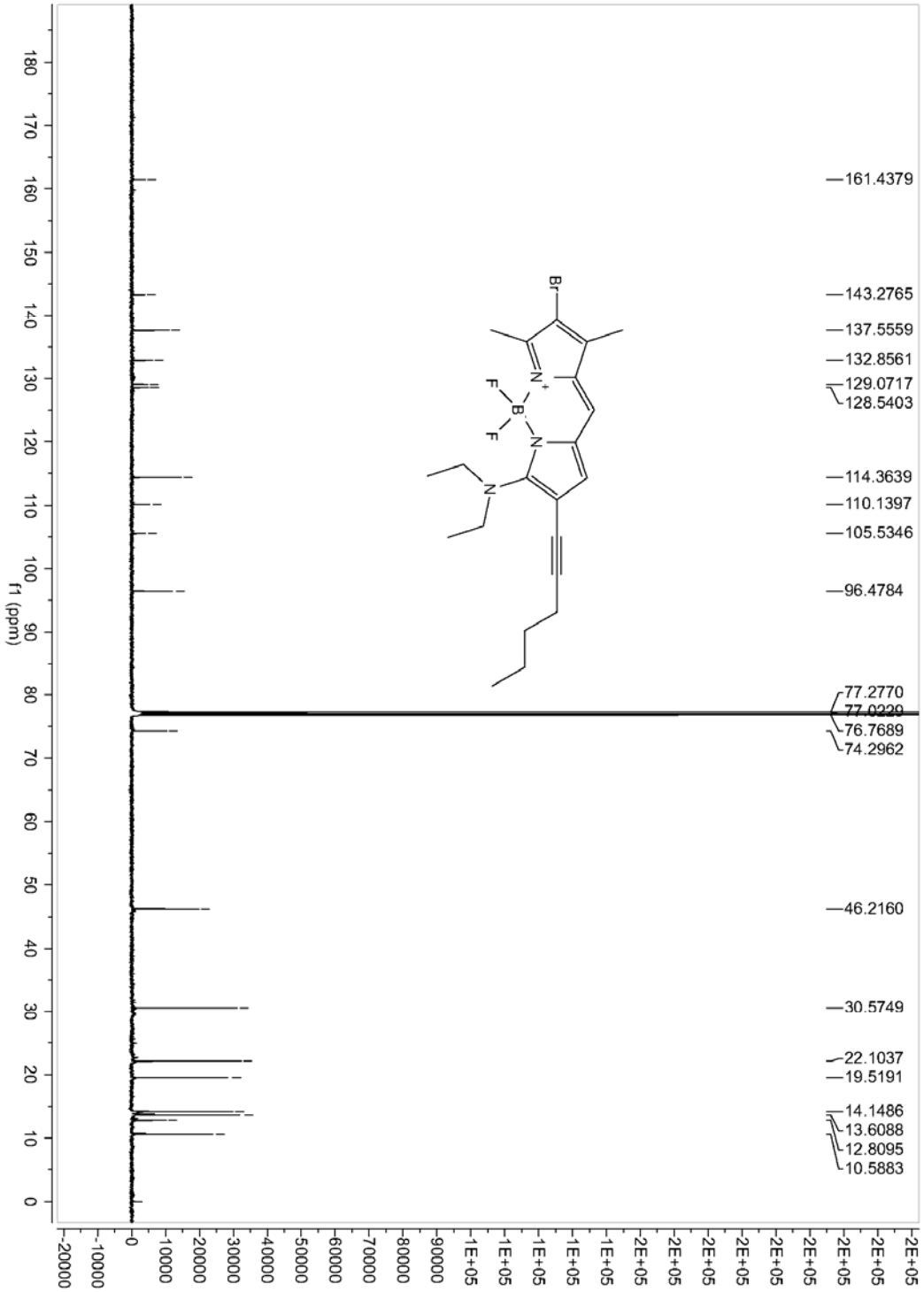
^{1}H NMR of Compound **8b**



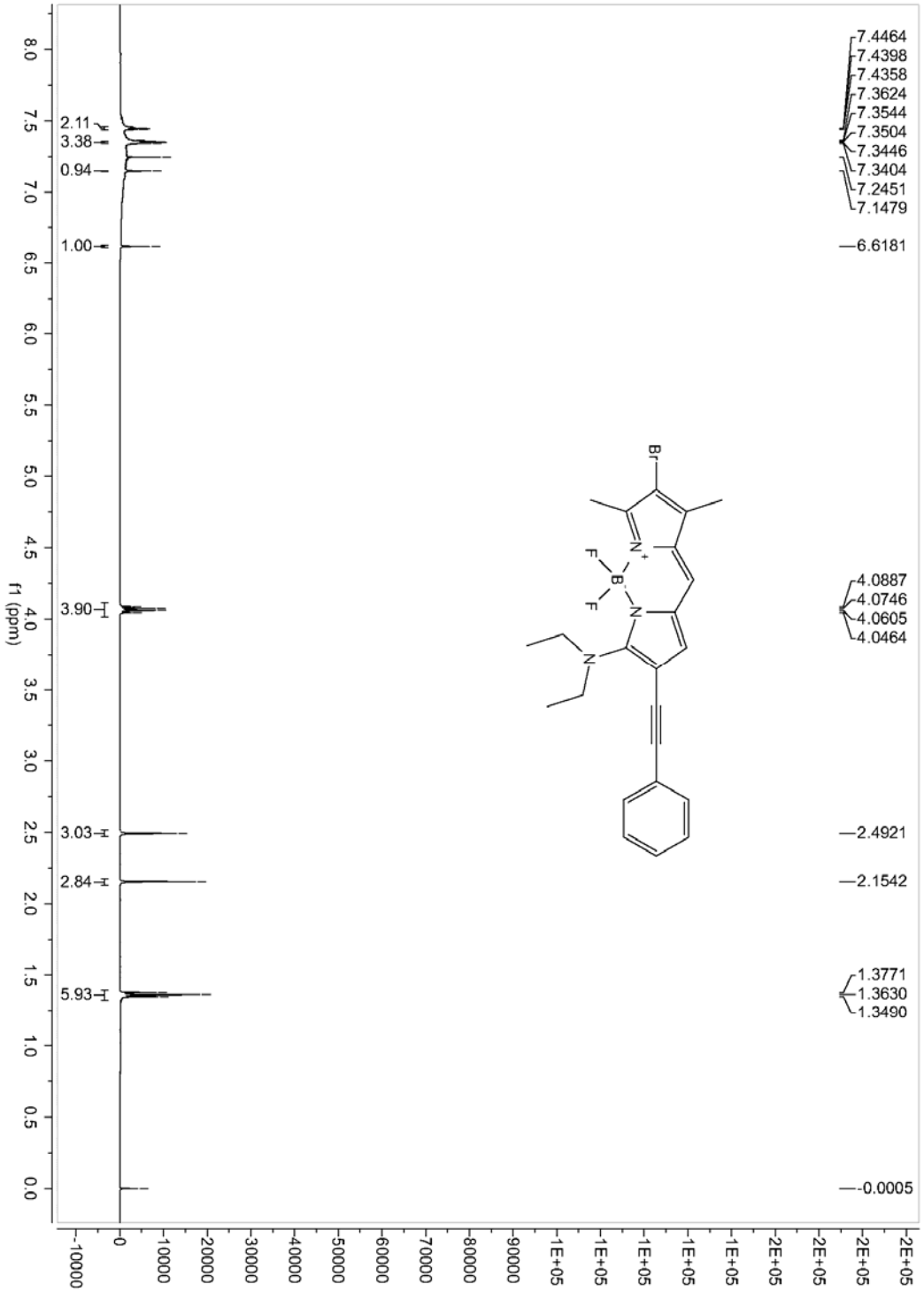
^{13}C NMR of Compound **8b**



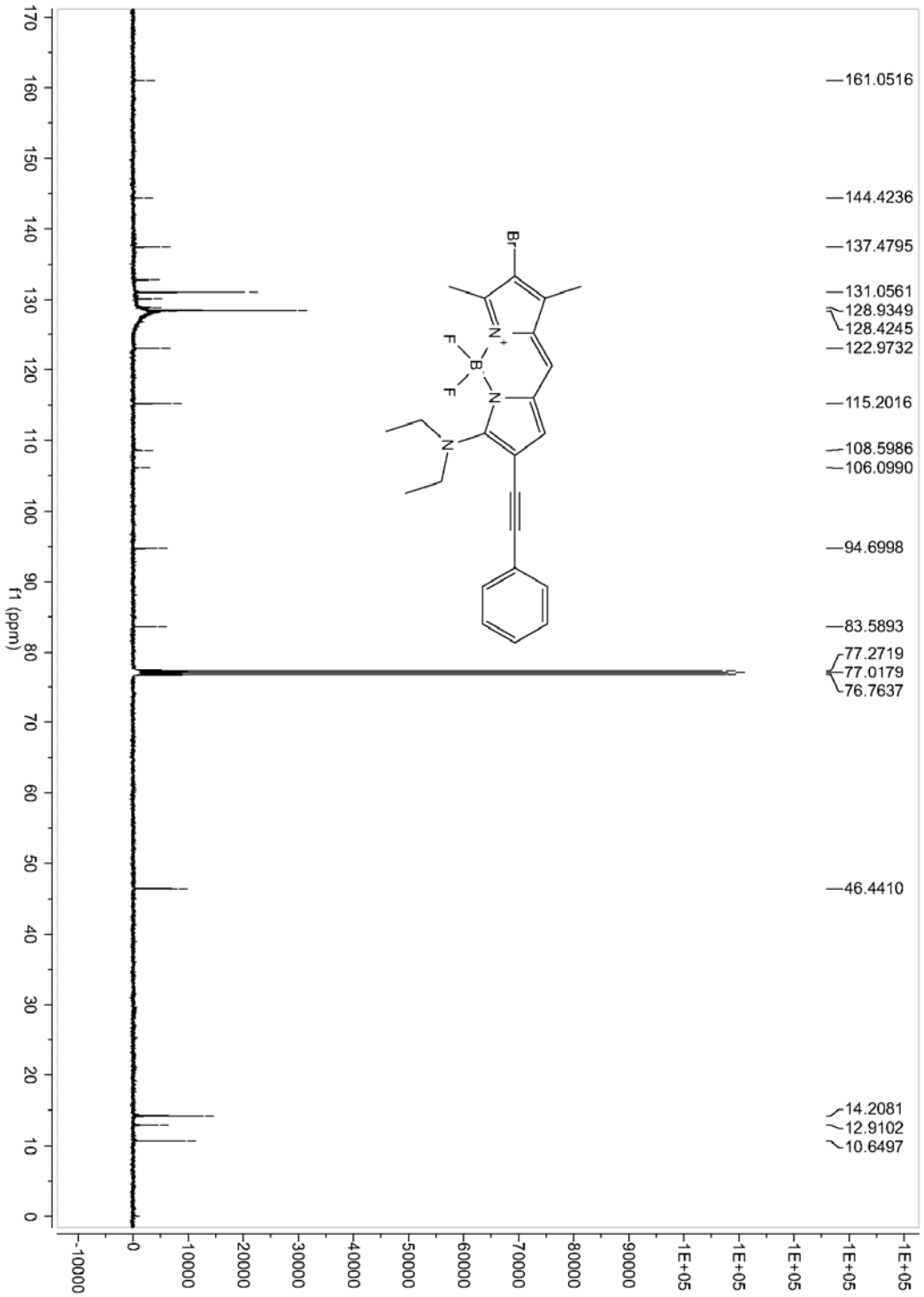
^{1}H NMR of Compound **8c**



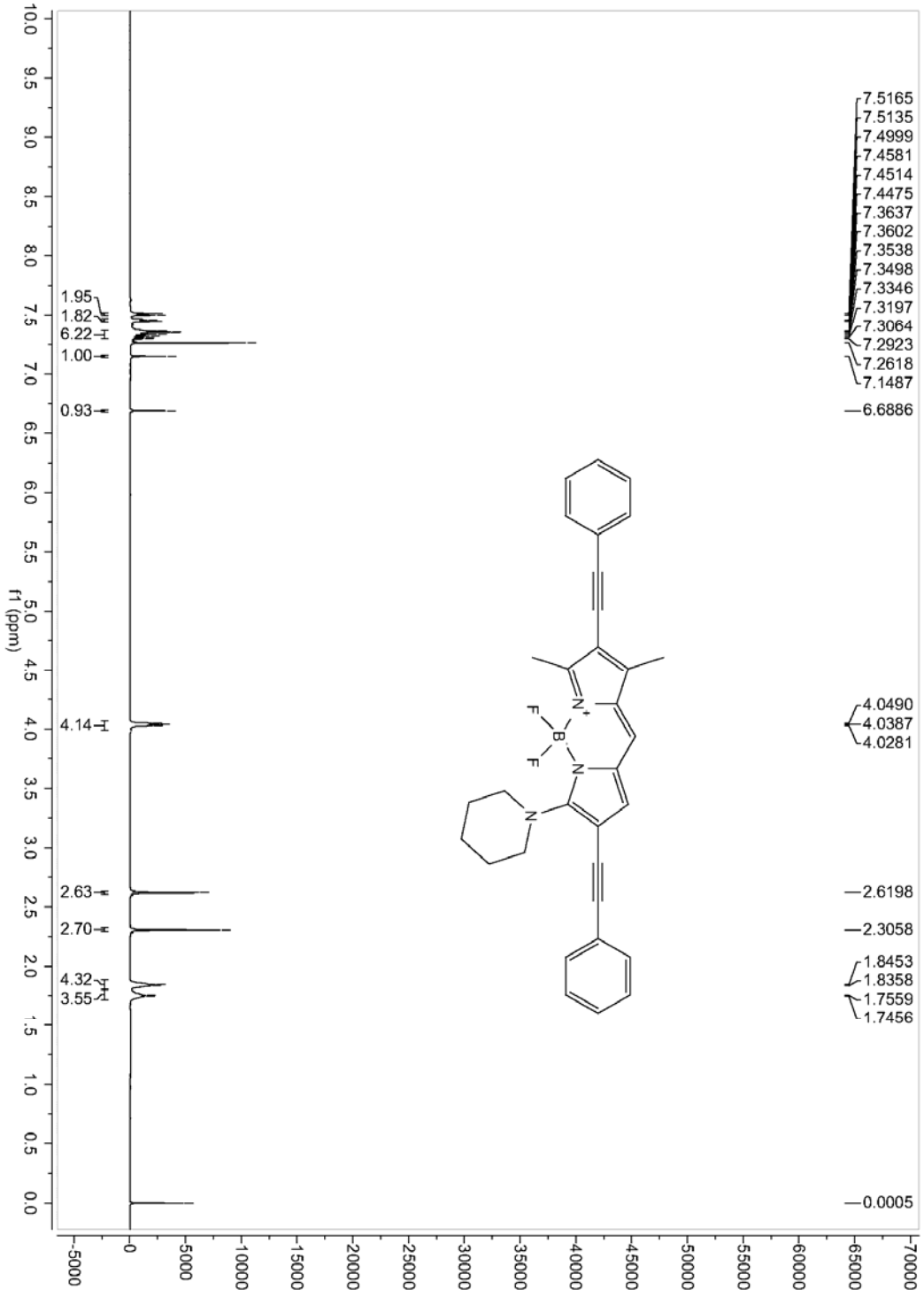
^{13}C NMR of Compound **8c**



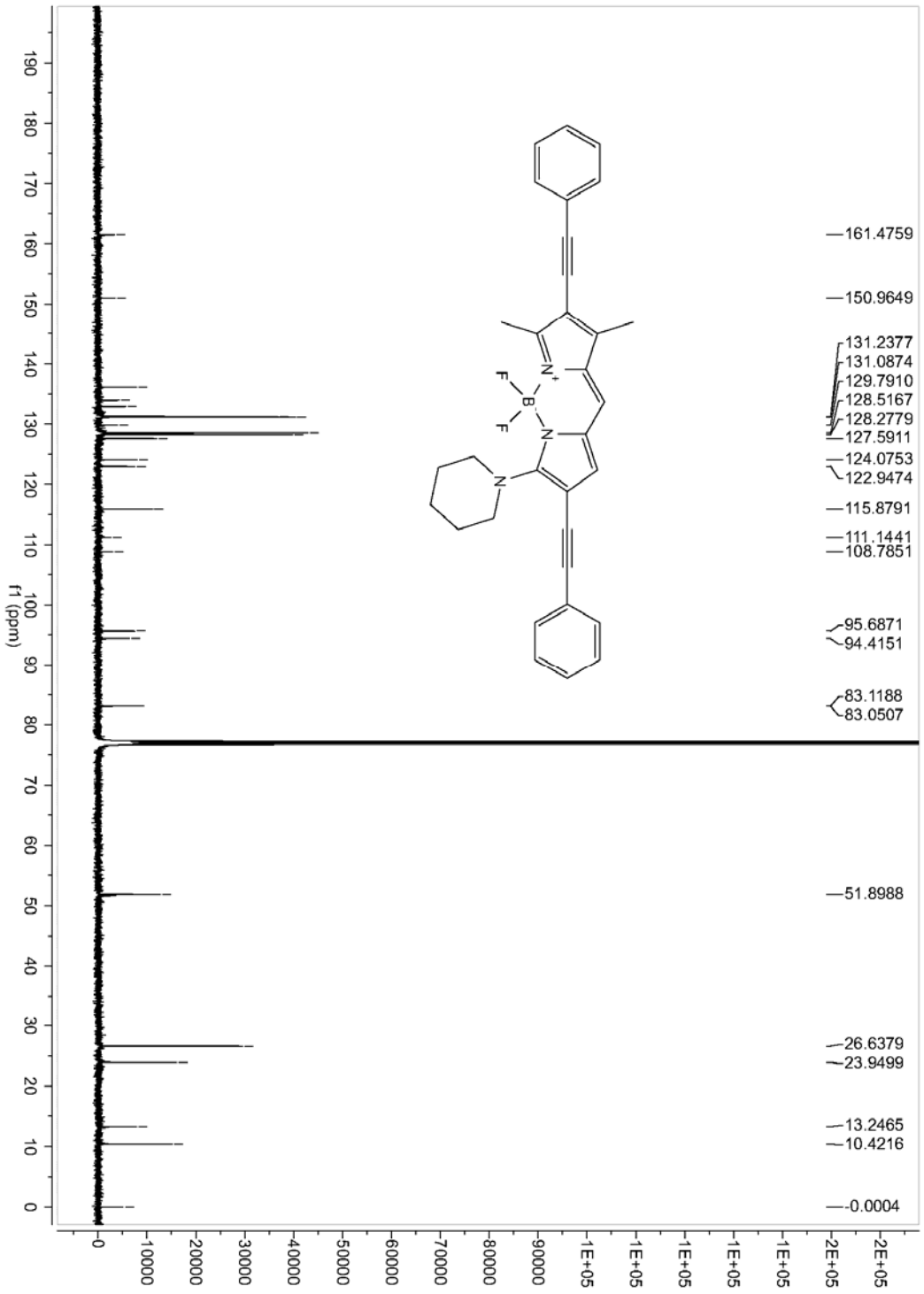
^{1}H NMR of Compound **8d**



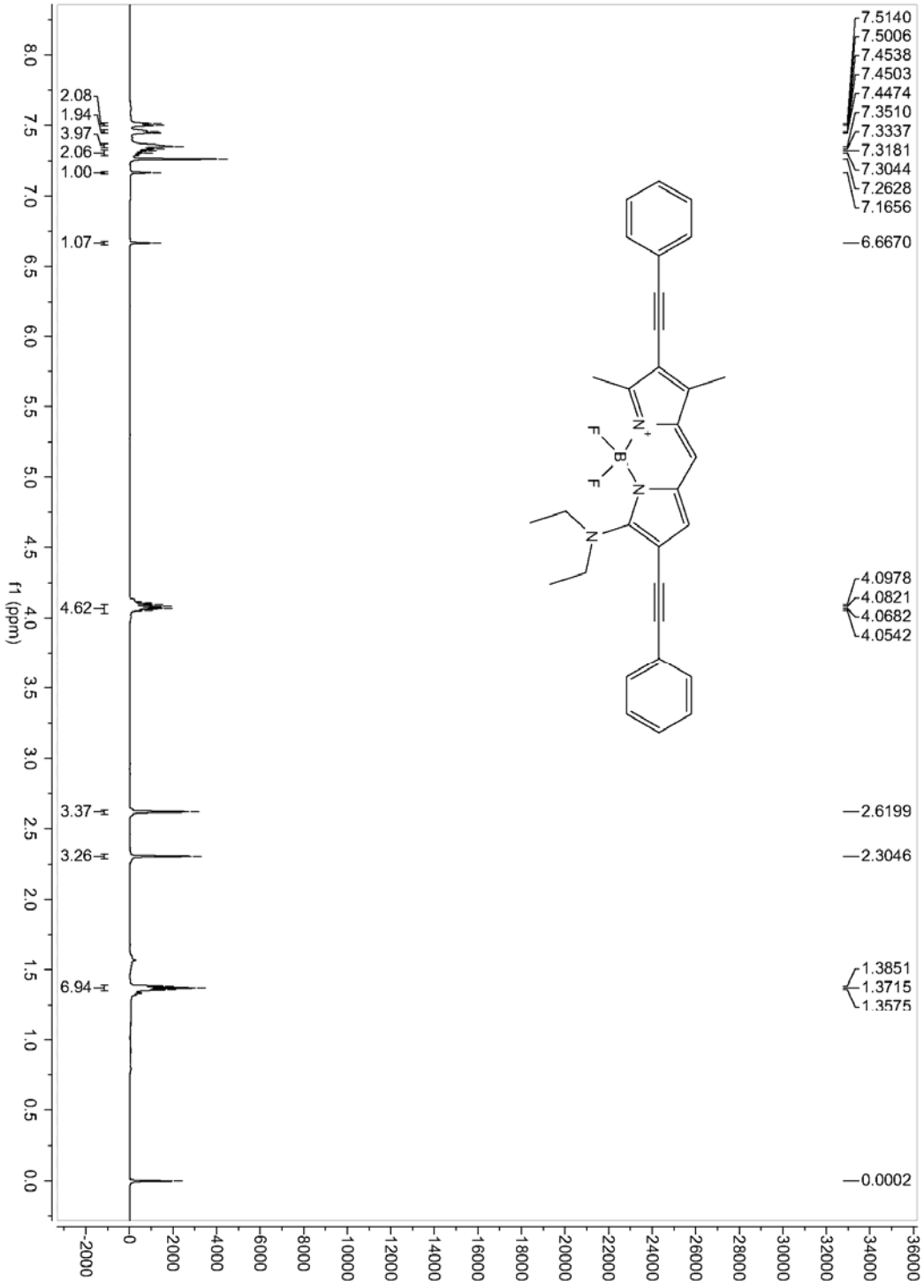
^{13}C NMR of Compound **8d**



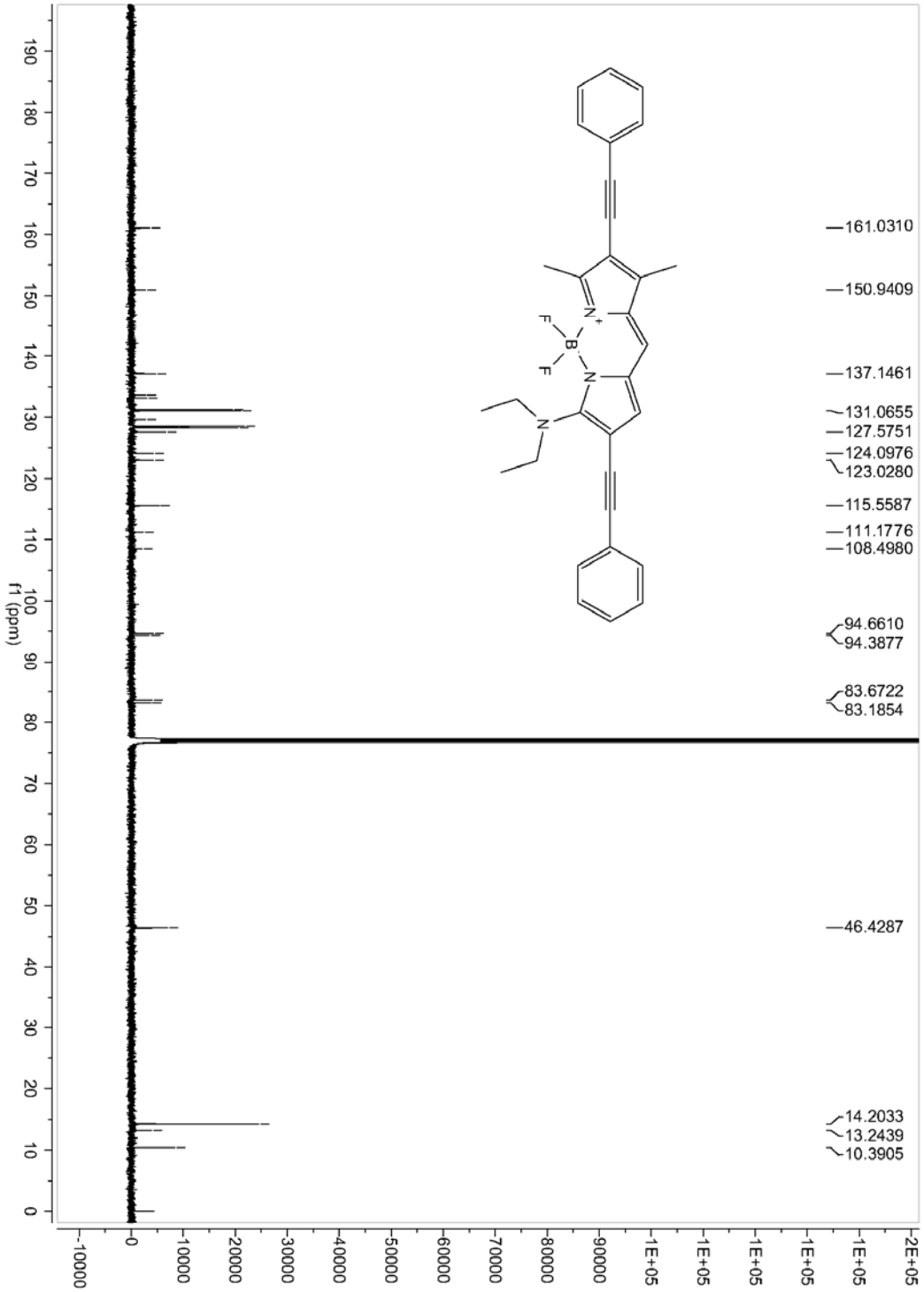
^{1}H NMR of Compound **9a**



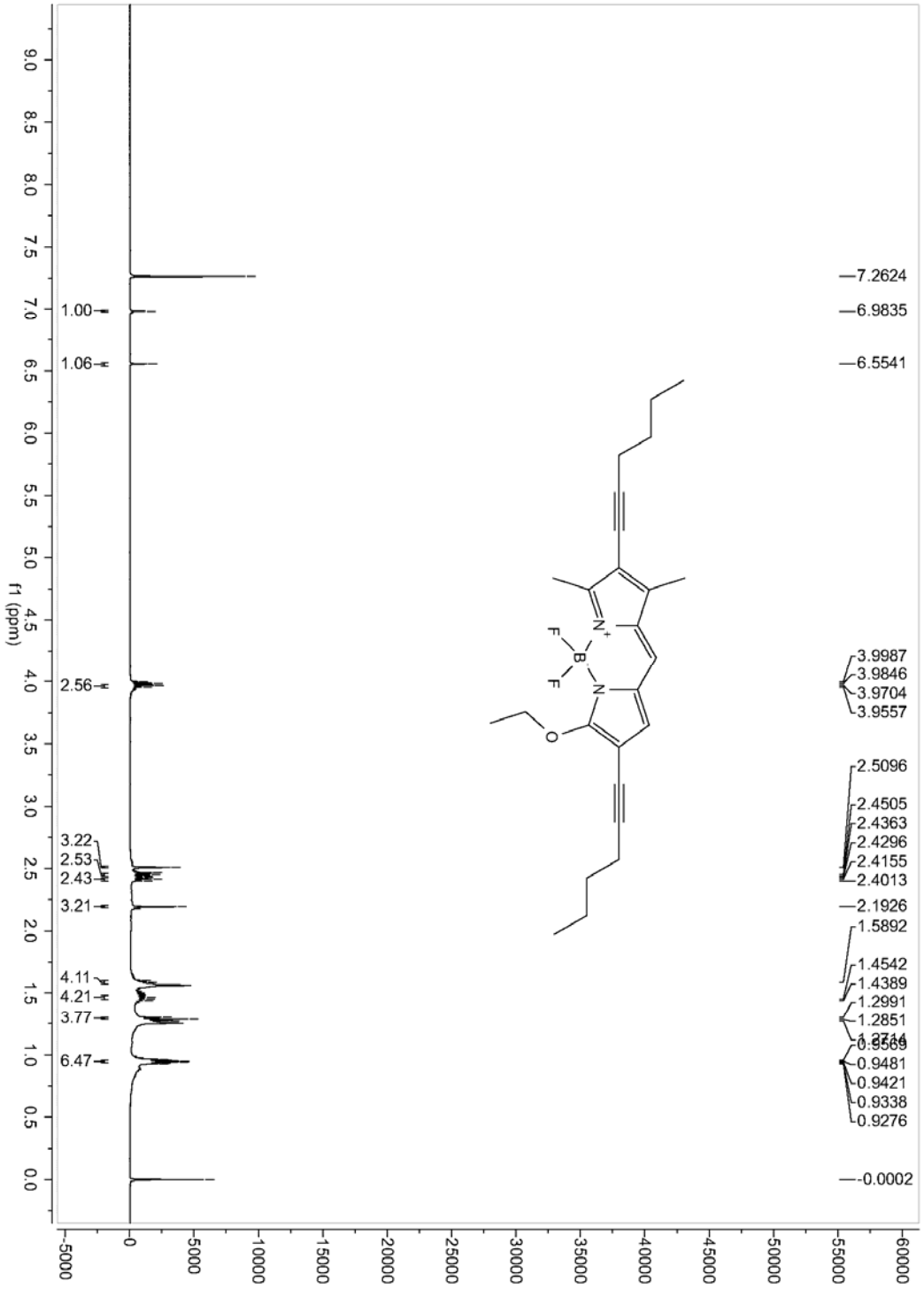
^{13}C NMR of Compound **9a**



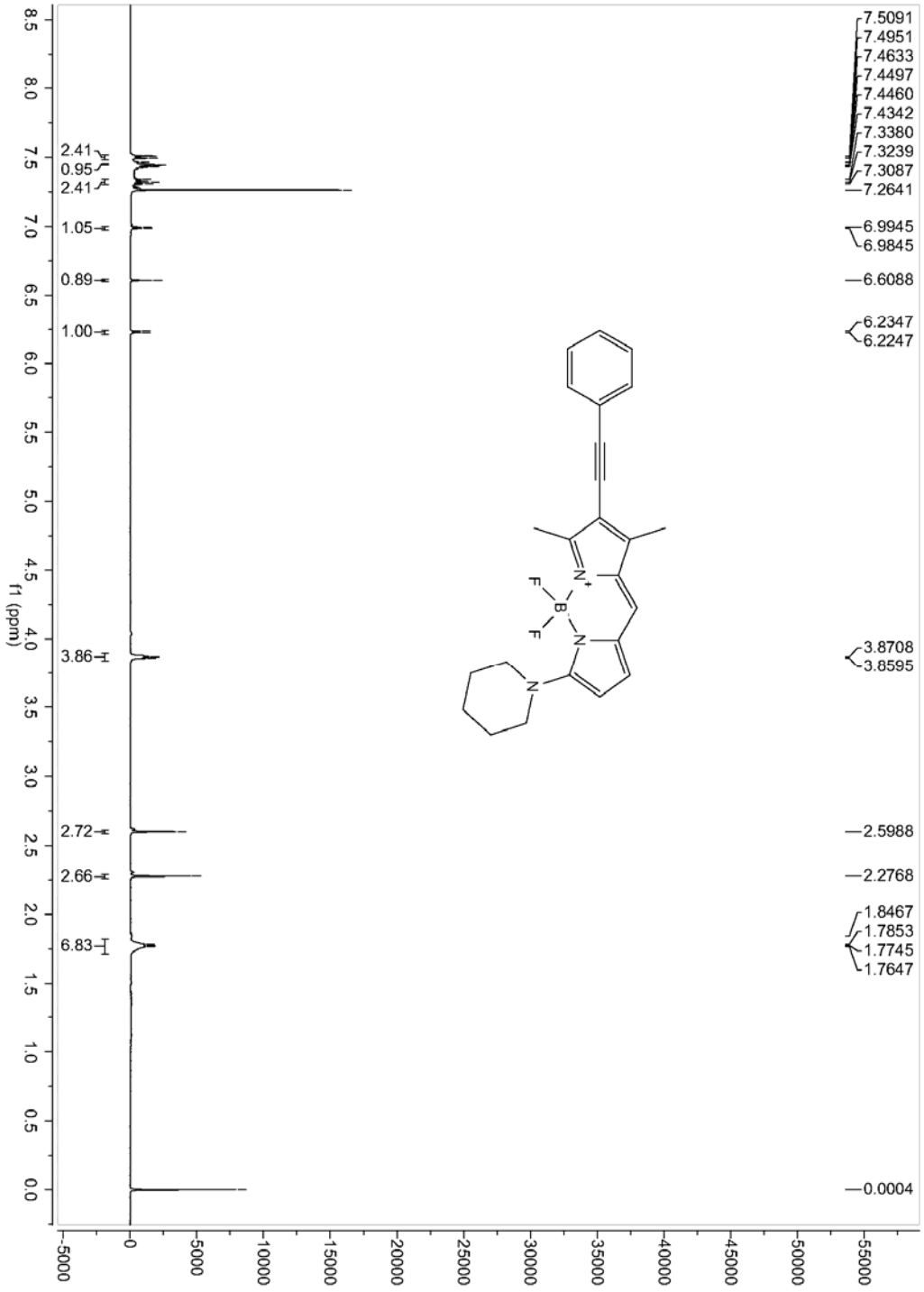
^{1}H NMR of Compound **9b**



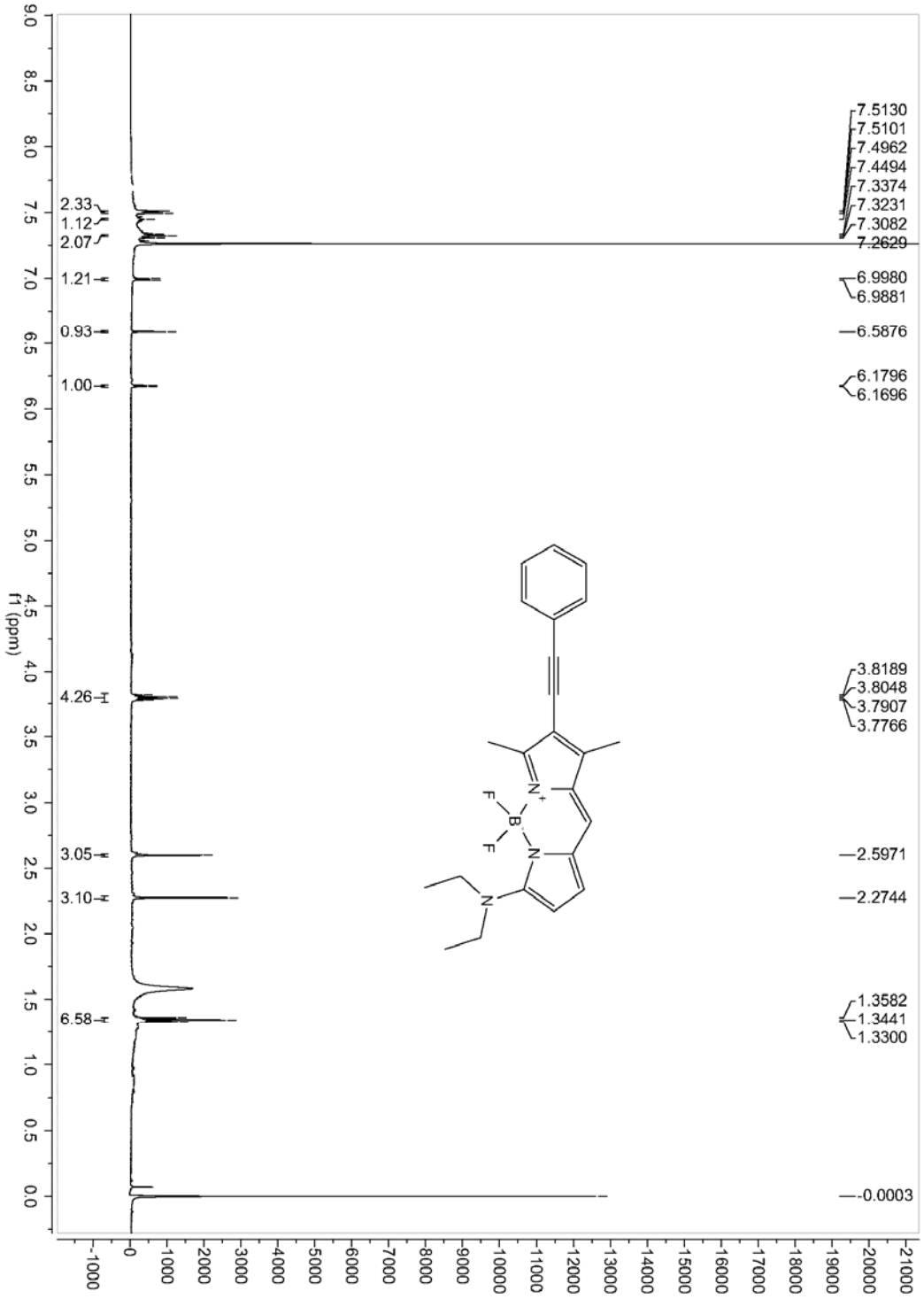
^{13}C NMR of Compound **9b**



^{1}H NMR of Compound **9c**



^{1}H NMR of Compound **10a**



^{1}H NMR of Compound **10b**

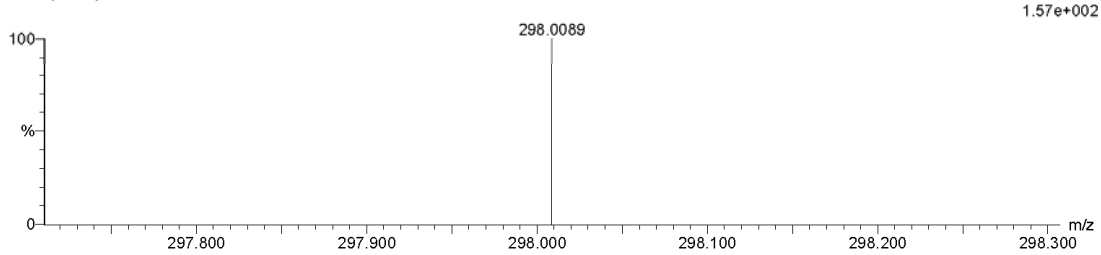
Elemental Composition Report **Page 1**

Tolerance = 0.3 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
219 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 0-2 Br: 0-2

12-Jul-2011GCT Premier ZJU
b 532 (1.951)

TOF MS EI+
1.57e+002



Minimum:				-1.5		
Maximum:		0.3	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
298.0089	298.0088	0.1	0.3	7.0	5546102.0	C11 H10 B N2 F2 Br

HRMS spectra of Compound **3**

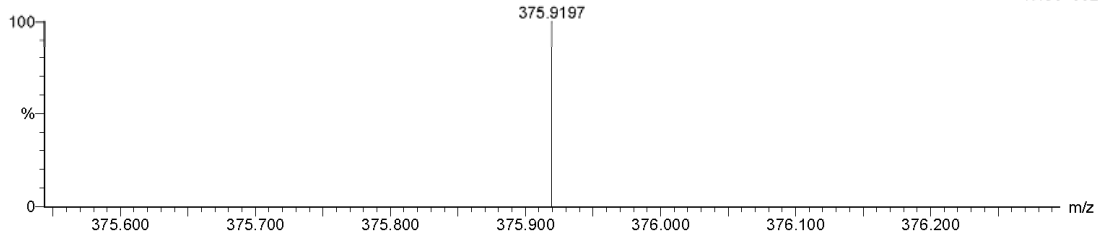
Elemental Composition Report **Page 1**

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
72 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 0-2 Br: 2-2

12-Jul-2011GCT Premier ZJU
c 654 (2.398)

TOF MS EI+
1.15e+002



Minimum:				-1.5		
Maximum:		1.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
375.9197	375.9194	0.3	0.8	7.0	5546082.0	C11 H9 B N2 F2 Br2

HRMS spectra of Compound **4**

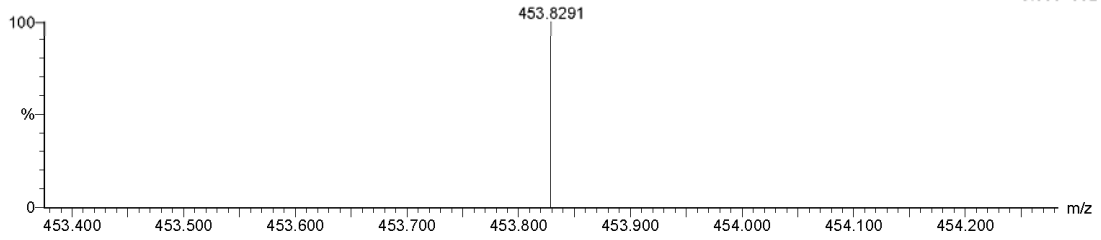
Elemental Composition Report **Page 1**

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
70 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 0-2 Br: 3-3

12-Jul-2011GCT Premier ZJU
d 484 (1.775) Cm (483:494)

TOF MS EI+
3.80e+002



Minimum:				-1.5		
Maximum:		1.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
453.8291	453.8299	-0.8	-1.8	7.0	5546214.5	C11 H8 B N2 F2 Br3

HRMS spectra of Compound **5**

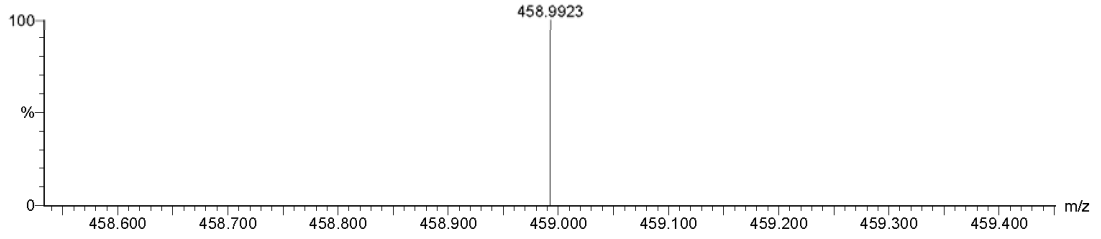
Elemental Composition Report **Page 1**

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
50 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 2-2 Br: 2-3

12-Jul-2011GCT Premier ZJU
f 771 (2.828)

TOF MS EI+
2.34e+003



Minimum:				-1.5		
Maximum:		3.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
458.9923	458.9929	-0.6	-1.3	8.0	5547193.5	C16 H18 B N3 F2 Br2

HRMS spectra of Compound **6a**

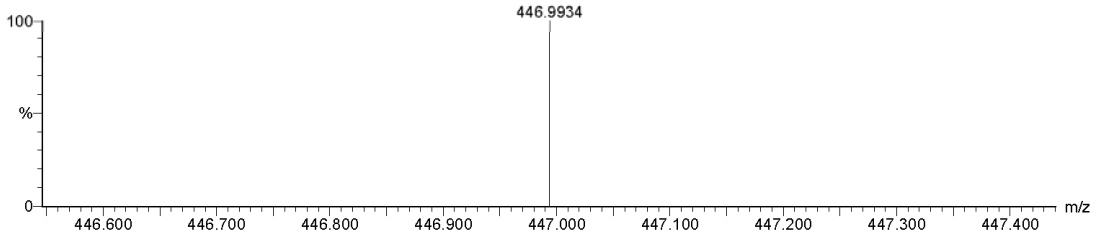
Elemental Composition Report **Page 1**

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
49 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 2-2 Br: 2-3

12-Jul-2011GCT Premier ZJU
e 481 (1.764) Cm (471:481)

TOF MS EI+
4.48e+002



Minimum:				-1.5		
Maximum:		3.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
446.9934	446.9929	0.5	1.1	7.0	5546248.5	C15 H18 B N3 F2 Br2

HRMS spectra of Compound **6b**

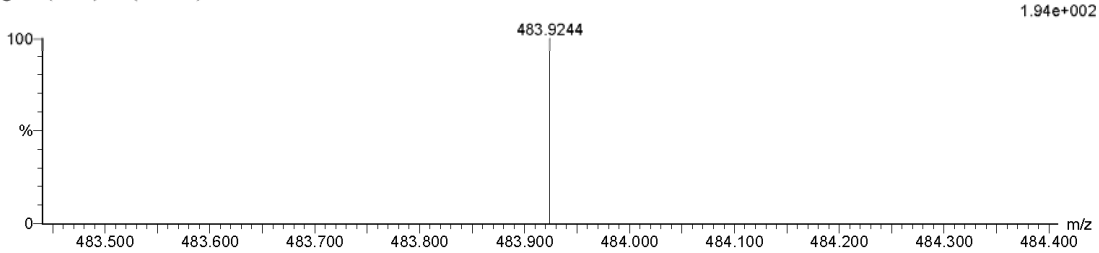
Elemental Composition Report **Page 1**

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
48 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 2-2 S: 1-1 Br: 2-3

12-Jul-2011GCT Premier ZJU
g 614 (2.252) Cm (614:623)

TOF MS EI+
1.94e+002



Minimum:				-1.5		
Maximum:		3.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
483.9244	483.9227	1.7	3.5	11.0	5546121.5	C17 H13 B N2 F2 S Br2

HRMS spectra of Compound **6c**

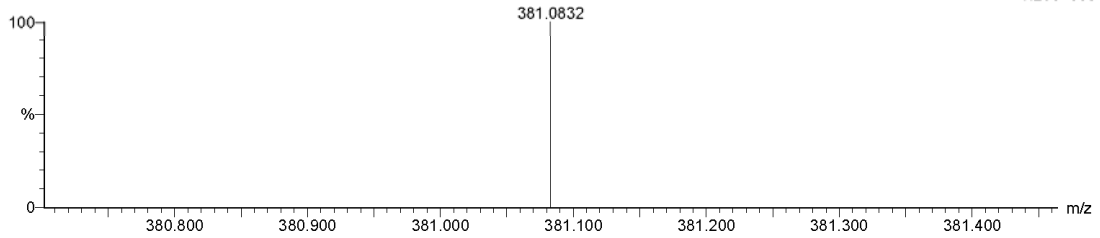
Elemental Composition Report **Page 1**

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
103 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 2-2 Br: 0-3

12-Jul-2011GCT Premier ZJU
i 1092 (4.011) Cm (1090:1114)

TOF MS EI+
1.20e+003



Minimum:				-1.5		
Maximum:		3.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
381.0832	381.0823	0.9	2.4	8.0	5546623.5	C16 H19 B N3 F2 Br

HRMS spectra of Compound **7a**

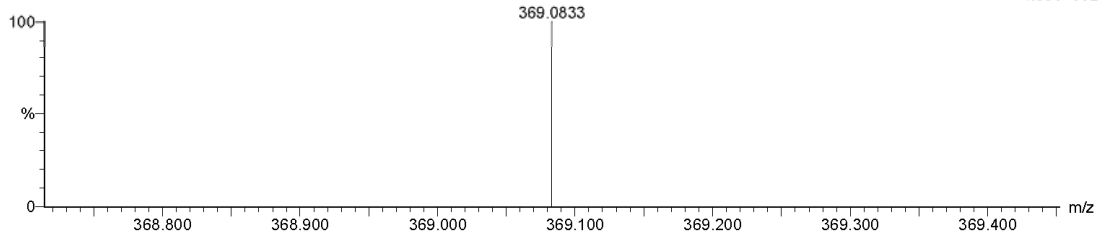
Elemental Composition Report **Page 1**

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
99 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 2-2 Br: 0-3

12-Jul-2011GCT Premier ZJU
h 424 (1.555) Cm (424:436)

TOF MS EI+
4.53e+002



Minimum:				-1.5		
Maximum:		3.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
369.0833	369.0823	1.0	2.7	7.0	5546250.0	C15 H19 B N3 F2 Br

HRMS spectra of Compound **7b**

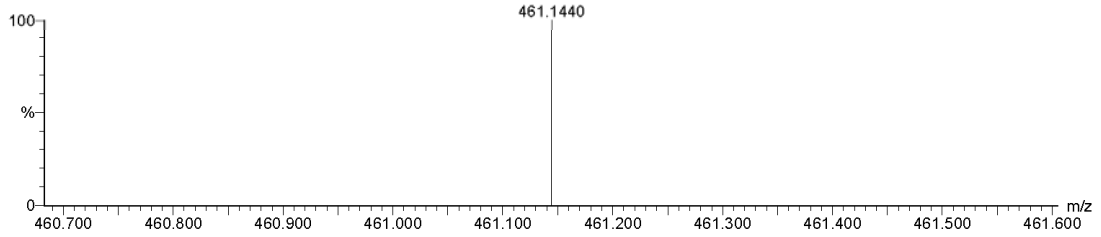
Elemental Composition Report **Page 1**

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
137 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 2-2 Br: 0-3

12-Jul-2011GCT Premier ZJU
k 855 (3.136) Cm (854:879)

TOF MS EI+
1.25e+002



Minimum:				-1.5		
Maximum:		3.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
461.1440	461.1449	-0.9	-2.0	10.0	5546086.0	C22 H27 B N3 F2 Br

HRMS spectra of Compound **8a**

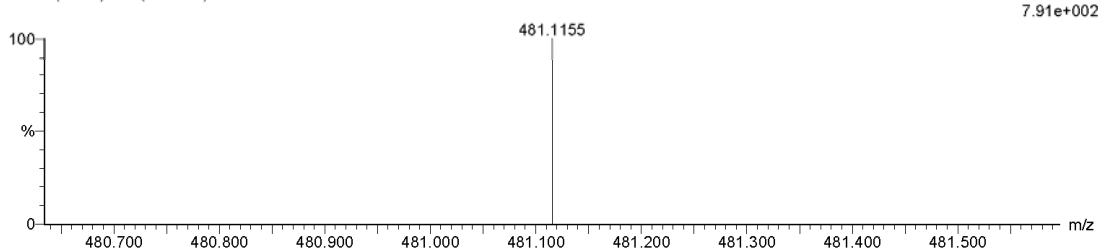
Elemental Composition Report **Page 1**

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
141 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 2-2 Br: 0-3

12-Jul-2011GCT Premier ZJU
m 365 (1.339) Cm (364:375)

TOF MS EI+
7.91e+002



Minimum:				-1.5		
Maximum:		3.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
481.1155	481.1136	1.9	3.9	14.0	5546419.0	C24 H23 B N3 F2 Br

HRMS spectra of Compound **8b**

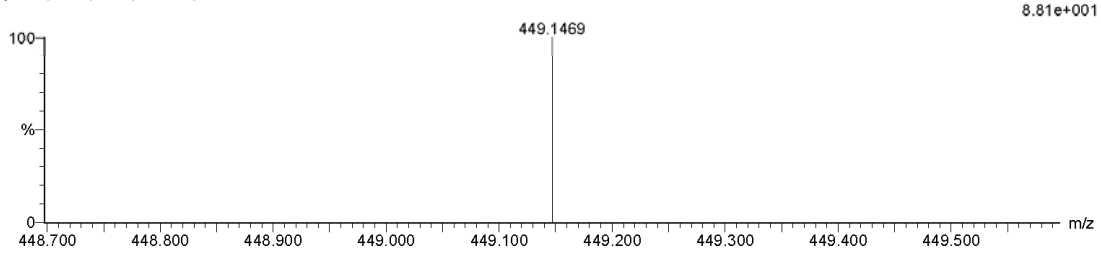
Elemental Composition Report **Page 1**

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
132 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 2-2 Br: 0-3

12-Jul-2011GCT Premier ZJU
j 369 (1.353) Cm (368:373)

TOF MS EI+
8.81e+001



Minimum:				-1.5		
Maximum:		3.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
449.1469	449.1449	2.0	4.5	9.0	5546067.5	C21 H27 B N3 F2 Br

HRMS spectra of Compound **8c**

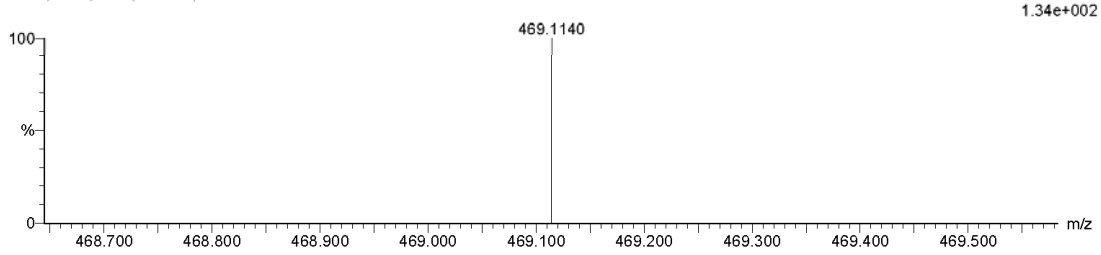
Elemental Composition Report **Page 1**

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
137 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 2-2 Br: 0-3

12-Jul-2011GCT Premier ZJU
I 429 (1.573) Cm (418:434)

TOF MS EI+
1.34e+002



Minimum:				-1.5		
Maximum:		3.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
469.1140	469.1136	0.4	0.9	13.0	5546090.5	C23 H23 B N3 F2 Br

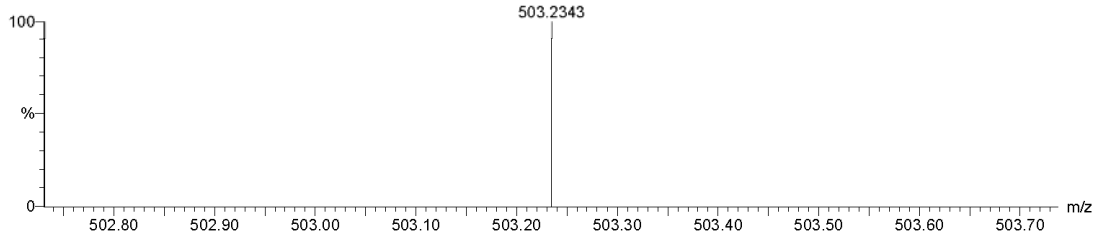
HRMS spectra of Compound **8d**

Elemental Composition Report **Page 1**

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
48 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 2-2
12-Jul-2011GCT Premier ZJU
n 529 (1.940)

TOF MS EI+
2.66e+003



Minimum:				-1.5		
Maximum:		3.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
503.2343	503.2344	-0.1	-0.2	20.0	5547350.5	C32 H28 B N3 F2

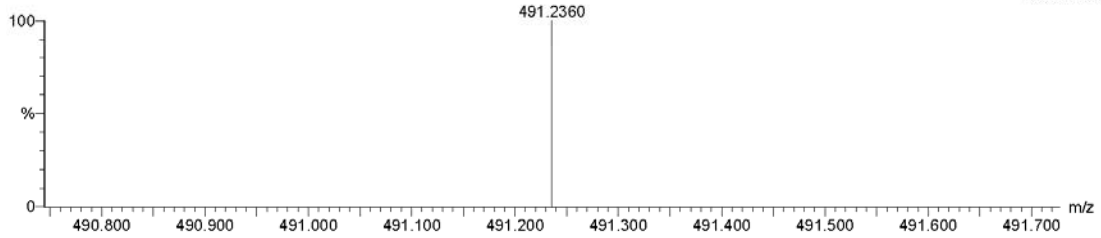
HRMS spectra of Compound **9a**

Elemental Composition Report **Page 1**

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
48 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 2-2
12-Jul-2011GCT Premier ZJU
o 468 (1.729) Cm (468:473)

TOF MS EI+
1.64e+002



Minimum:				-1.5		
Maximum:		3.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
491.2360	491.2344	1.6	3.3	19.0	5546100.5	C31 H28 B N3 F2

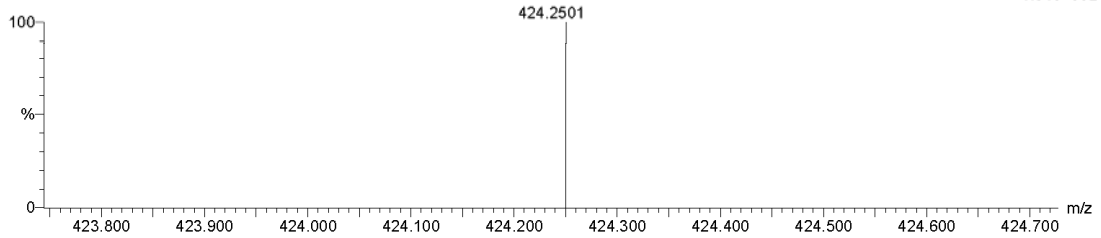
HRMS spectra of Compound **9b**

Elemental Composition Report **Page 1**

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
58 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 2-2 O: 0-1 F: 2-2
12-Jul-2011GCT Premier ZJU
r 456 (1.739)

TOF MS EI+
1.94e+002



Minimum:				-1.5		
Maximum:		3.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
424.2501	424.2498	1.4	0.7	18.0	5546129.1	C25 H31 B N2 O F2

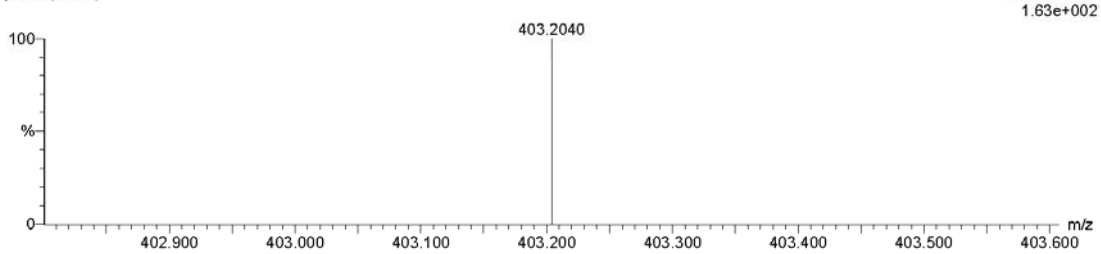
HRMS spectra of Compound **9c**

Elemental Composition Report **Page 1**

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
40 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 2-2
12-Jul-2011GCT Premier ZJU
p 418 (1.546)

TOF MS EI+
1.63e+002



Minimum:				-1.5		
Maximum:		3.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
403.2040	403.2031	0.9	2.2	14.0	5546097.0	C24 H24 B N3 F2

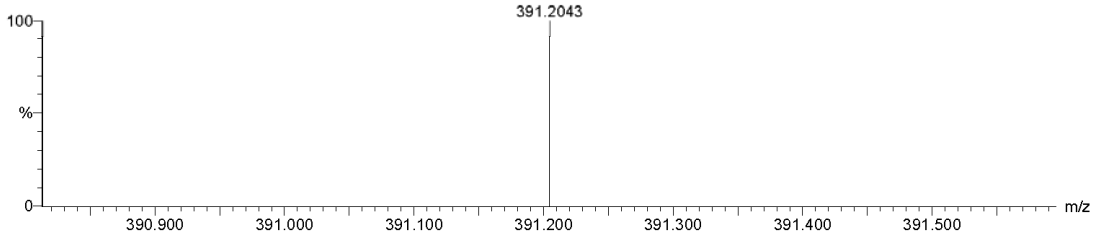
HRMS spectra of Compound **10a**

Elemental Composition Report **Page 1**

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
40 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-100 H: 0-300 B: 0-1 N: 0-3 F: 2-2
13-Jul-2011GCT Premier ZJU
q 380 (1.394) Cm (374:380)

TOF MS EI+
1.22e+002



Minimum:				-1.5		
Maximum:		3.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
391.2043	391.2031	1.2	3.1	13.0	5546076.0	C23 H24 B N3 F2

HRMS spectra of Compound **10b**