Supplementary Information

Synthesis of 3-aminoBODIPY dyes via copper-catalyzed vicarious nucleophilic substitution of 2-halogeno derivatives.

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Materials

8-(4-Methoxyphenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene 1. A flame dried Schlenk flask was charged with 4-methoxybenzaldehyde (2.7 mL, 22 mmol) and pyrrole (38.2 mL, 551 mmol) and the resulting solution was stirred at room temperature for 25 min. Thereafter, $BF_3.OEt_2$ (0.2 mL, 2 mmol) was added to the mixture and stirred for 4h. The solvent was removed under reduce pressure and the resulting material was portioned between CH_2Cl_2 (100 mL) and 0.1M NaOH (300 mL). The organic extract was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The resulting green oil was purified by column chromatography (CH_2Cl_2:petroleum ether 7:3) to give 2,2'-((4-methoxyphenyl)methylene)bis(1*H*-pyrrole) as a light grey solid (4.8 g, 87%), mp 97-98 °C (literature,[S1] 98-99 °C), R*f* = 0.4 (CH_2Cl_2/petrol 7:3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (s, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.61 (q, *J* = 2.6 Hz, 2H), 6.08 (q, *J* = 2.8 Hz, 2H), 5.84 (s, 2H), 5.36 (s, 1H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.34, 133.02, 129.51, 117.28, 114.08, 108.47, 107.19, 55.42, 43.21. IR (neat): υ_{max}/cm^{-1}: 3341, 2922, 2853, 1610, 1511, 1461, 1252, 1176, 1032, 842, 723. HRMS-ES Calcd for $C_{16}H_{16}N_2O + Na^+$: 275.1160. Found: 275.1167.
2,2'-((4-methoxyphenyl)methylene)bis(1*H*-pyrrole) (4.30 g, 17.3 mmol) was taken in dry CH_2Cl_2 (200 mL) and cooled to 0 °C. A solution of DDQ (3.92 g, 17.3 mmol) in CH_2Cl_2 (70 mL) was added to the mixture dropwise over 30 min. The mixture was then neutralized with *N*,*N*-diisopropylethylamine (25.7 g, 199 mmol) and treated with $BF_3.OEt_2$ (39.7 g, 280 mmol). The mixture was stirred at room temperature for 2 h and then washed with 0.1 M NaOH (150 mL) and water (100 mL). The aqueous layer was back extracted with CH_2Cl_2 (2 × 150 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under pressure. The resulting orange crude product was purified by column chromatography (CH_2Cl_2:petroleum ether 4:1) to give the title compound **1** as an orange solid (4.0 g, 78%), mp 135-136 °C (literature,[S2] mp 137-138 °C). Rf = 0.6 (CH_2Cl_2/petrol, 4:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 4.2 Hz, 2H), 6.54 (d, J = 5.5 Hz, 2H), 3.90 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.17, 147.51, 143.49, 134.92, 132.52, 131.45, 126.40, 118.38, 114.15, 55.63.^{11}B NMR (128 MHz, $CDCl_3$) δ -0.67 (t, J_{BF} = 29.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.00 (q, J_{FB} = 29.0 Hz). IR (neat): υ_{max}/cm^{-1}: 3017, 2841, 1601, 1574, 1537, 1473, 1384, 1256, 1220, 1112, 1065, 977, 844, 779. HRMS-ES Calcd for $C_{16}H_{13}BN_2OF_2 + Na^+$: 321.0987. Found: 321.0975.

2-Bromo-8-(4-methoxyphenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene 6. 8-(4-Methoxyphenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene **1** (0.300 g, 1.01 mmol) was taken in dry CH_2Cl_2/MeCN (1:1, 50 mL). A solution of NBS (0.250 g, 1.20 mmol) in CH_2Cl_2 (10 mL) was added to the mixture dropwise. The mixture was stirred at room temperature for 90 min and then the solvent was removed under reduced pressure. The crude product was dissolved in CH_2Cl_2 (60 mL) and washed with H_2O (3 x 100 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The resulting orange crude product was purified by column chromatography (CH_2Cl_2:petroleum ether 1:1) to give the title compound **6** as an orange solid (0.28 g, 73%), mp 246-248 °C. Rf = 0.5 (CH_2Cl_2/petrol, 1:1). IR (neat): υ_{max}/cm^{-1}: 3227, 1603, 1573, 1536, 1474, 1400, 1356, 1246, 1060, 981. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.75 (s, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 3H), 6.91 (s, 1H), 6.59 (d, *J* = 4.3 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.55, 147.30, 145.45, 141.46, 135.24, 134.22, 133.05, 132.58, 130.20, 125.87, 119.41, 114.38, 105.77, 55.70. ^{11}B NMR (128 MHz, $CDCl_3$) δ -0.96 (t, J_{BF} = 28.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.91 (q, J_{FB} = 28.1 Hz). HRMS-ES Calcd for $C_{16}H_{12}BN_2OF_2Br + Na^+$: 398.0128. Found: 398.0136. This ^{1}H and ^{13}C NMR data agrees with that in the literature.[S3]

S1. R. Naik, P. Joshi, S.P. Kaiwar, and R.K. Deshpande, *Tetrahedron*, 2003, **59**, 2207.
S2. E. Pena-Cabrera, A. Aguilar-Aguilar, M. Gonzalez-Dominguez, E. Lager, R. Zamudio-Vazquez, J. Godoy-Vargas, and F. Villanueva-Garcia, *Org. Lett.*, 2007, **9**, 3985.
S3. L. Jiao, W. Pang, J. Zhou, Y. Wei, X. Mu, G. Bai, and E. Hao, *J. Org. Chem.*, 2011, **76**, 9988.

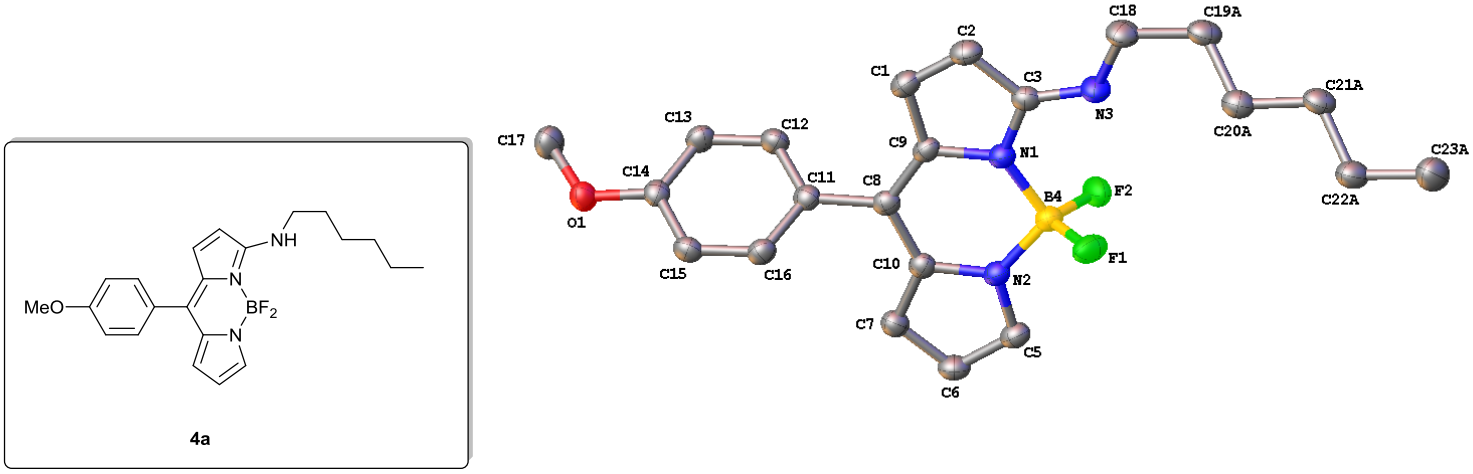
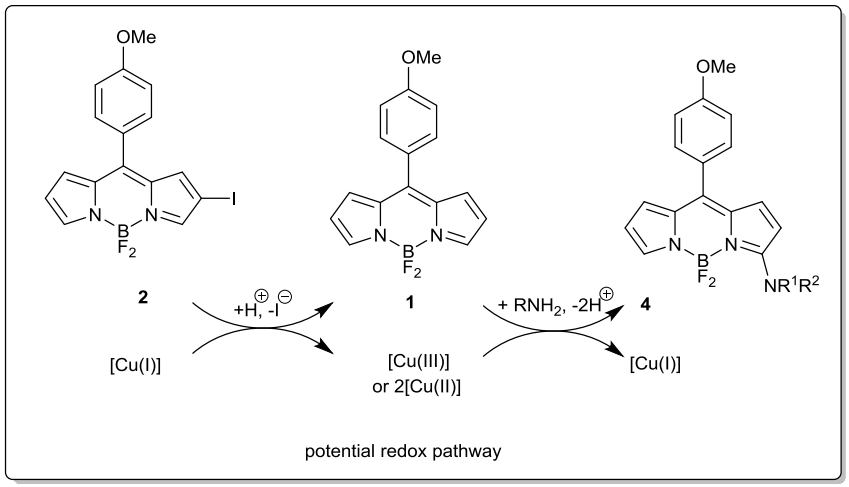
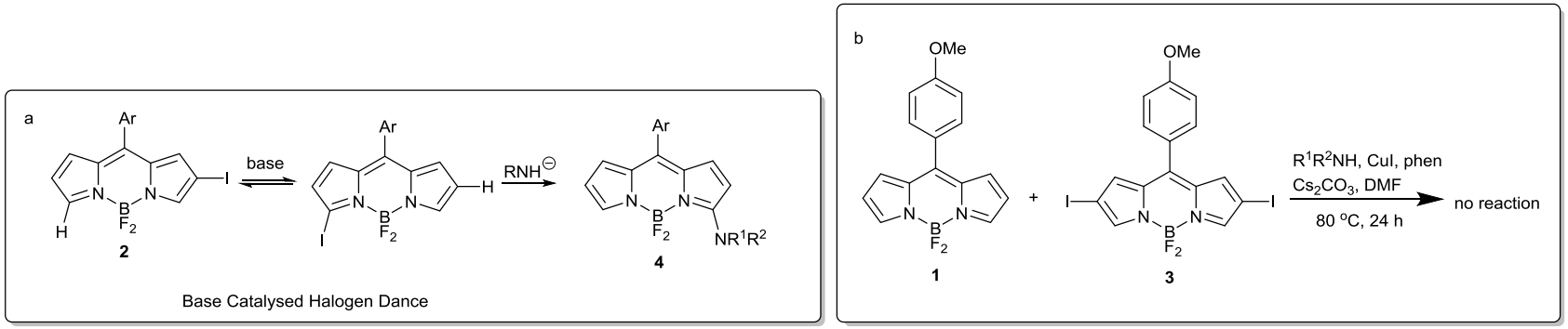


Figure S1. Molecular structure of **4a**. Hydrogen atoms have been omitted for clarity. There is a two-fold disorder of the hexyl chain; the figure shows the predominant orientation.

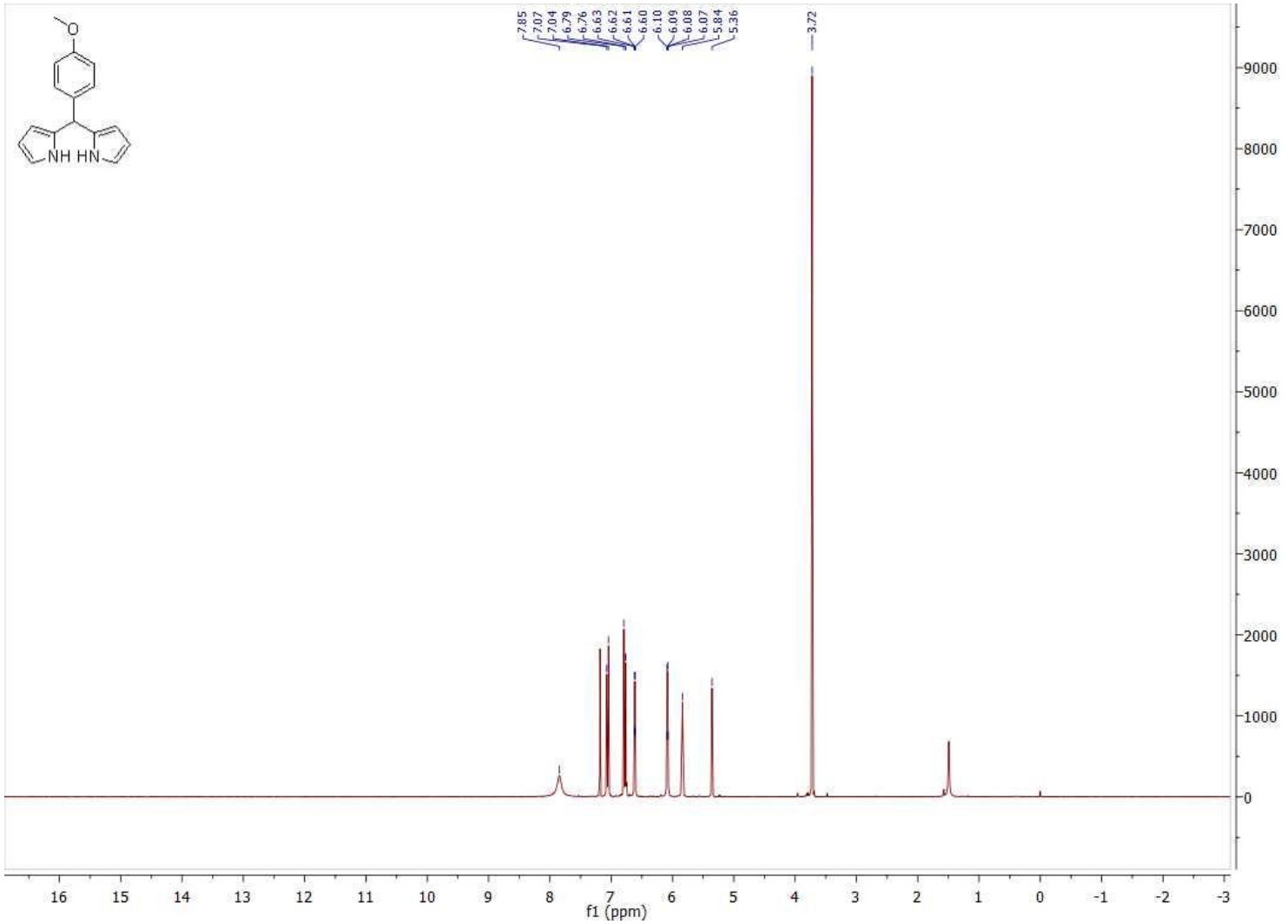


Scheme S2. Possible mechanistic pathway involving a copper redox cycle, discounted by isotopic labelling.

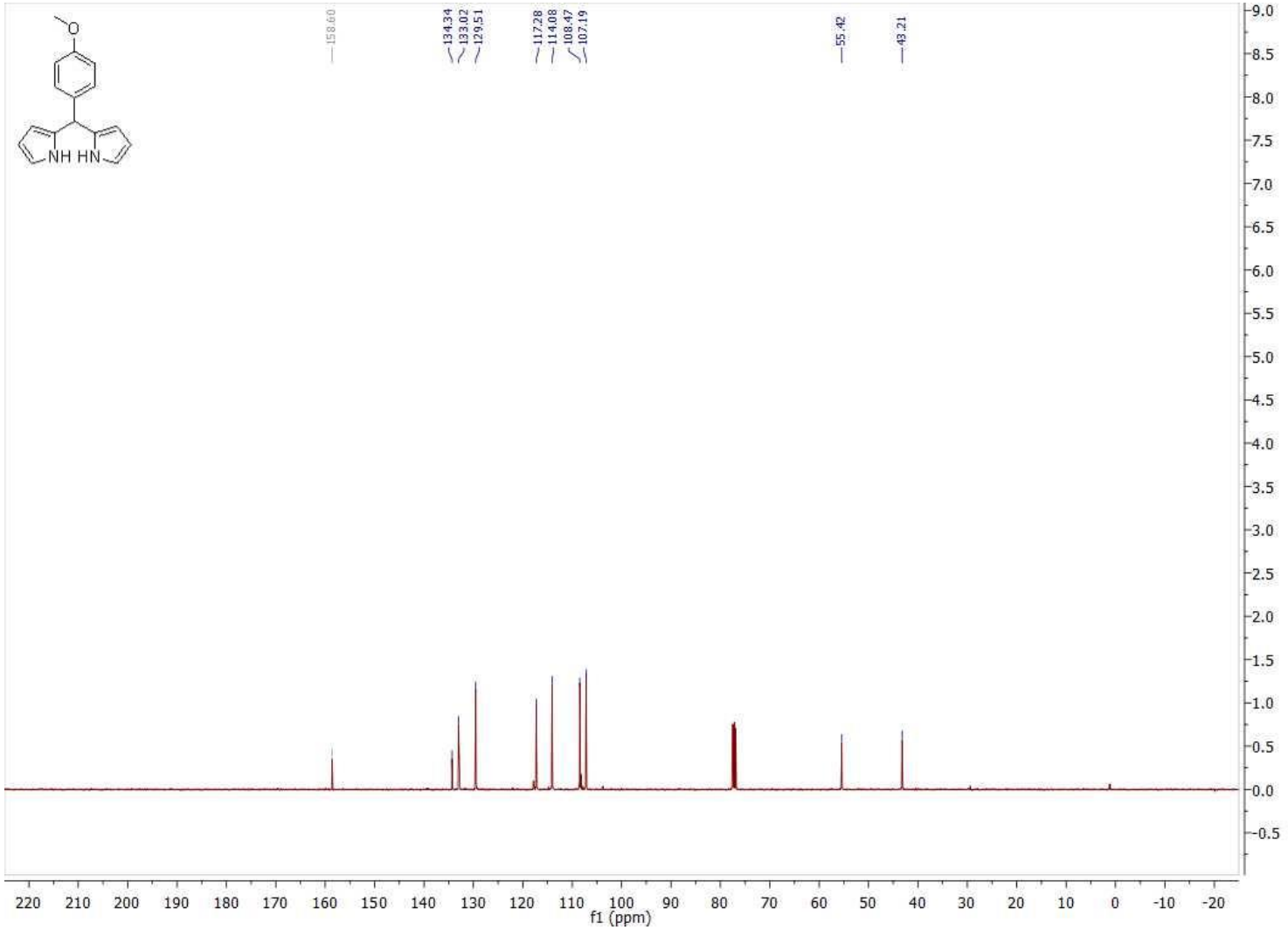


Scheme S3. Possible mechanistic pathway involving Base Catalysed Halogen Dance (a), discounted by failure of reaction of a 1:1 mixture of the diiodide **3** and unhalogenated BODIPY **1** (b).

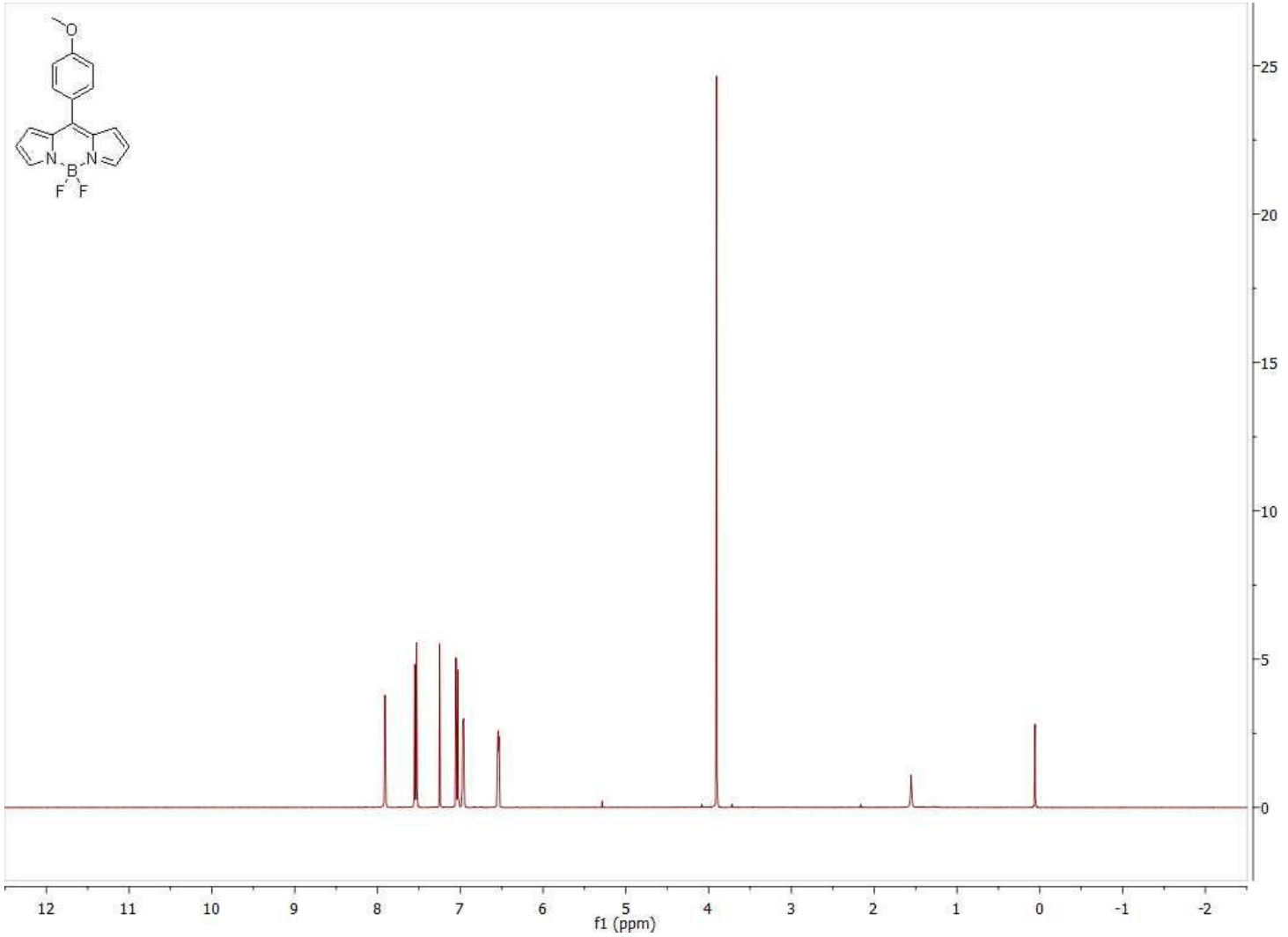
^{1}H NMR (300 MHz, Chloroform-*d*)



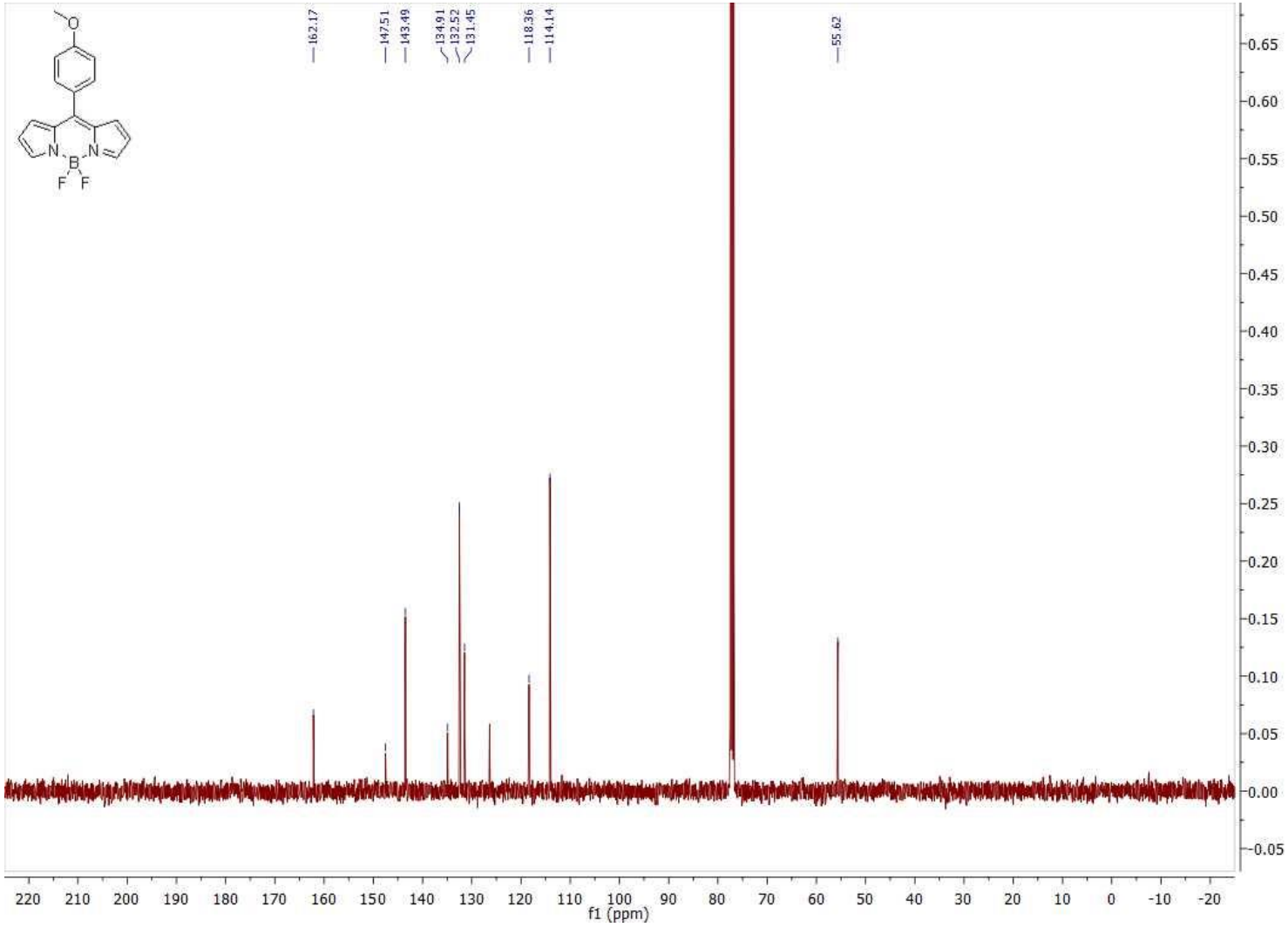
^{13}C NMR (101 MHz, Chloroform-*d*)



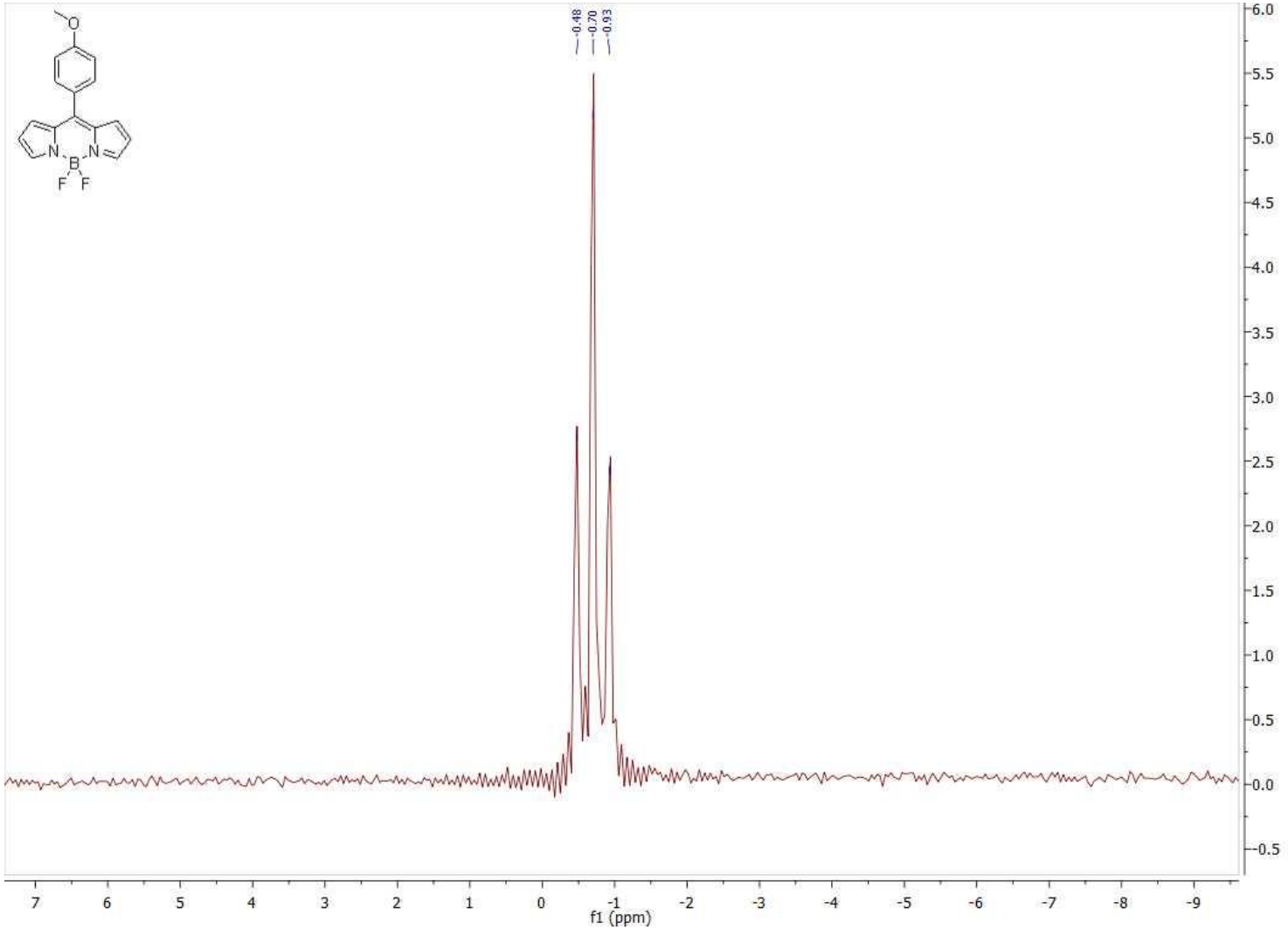
^{1}H NMR (400 MHz, Chloroform-d) 1



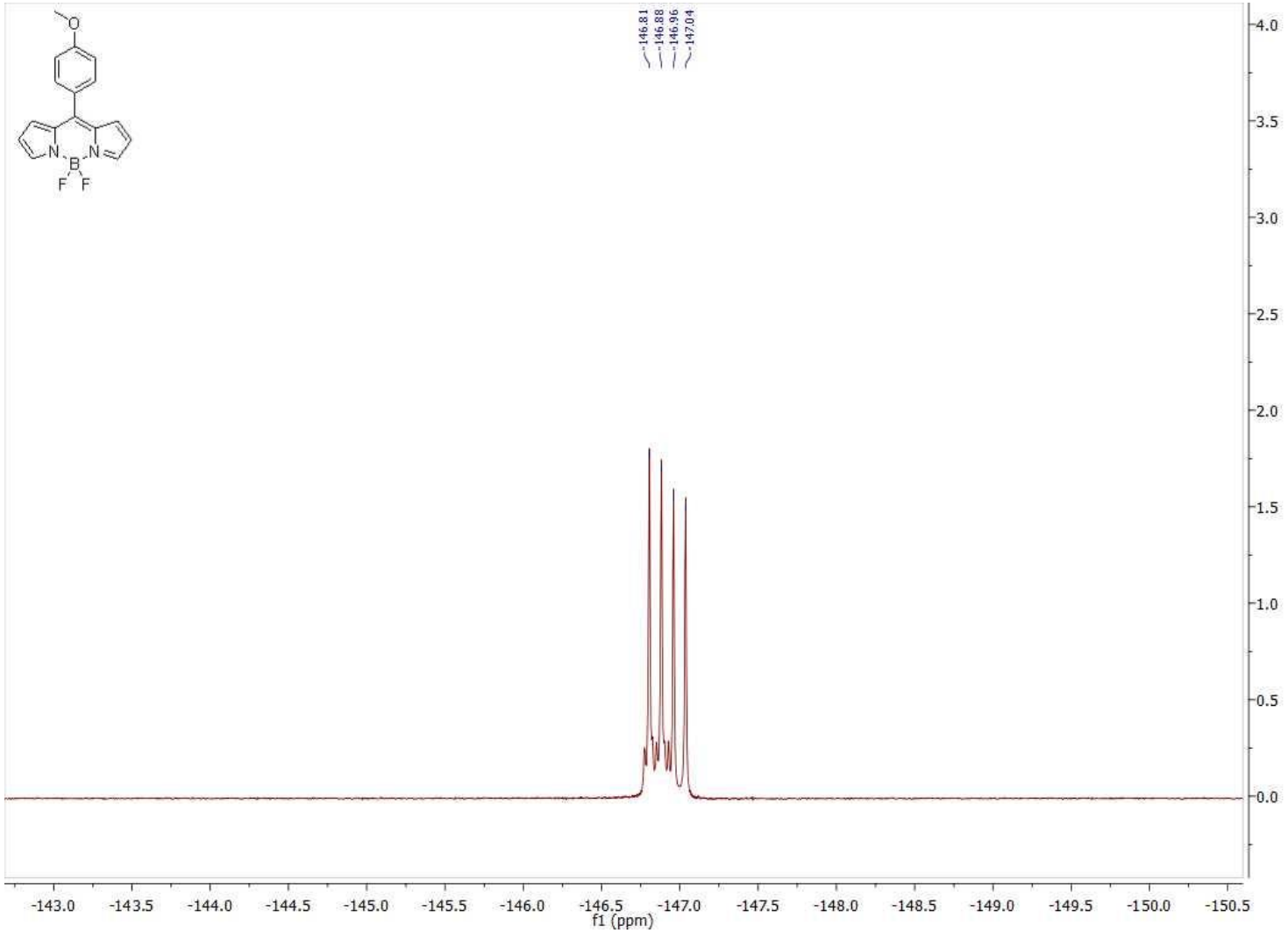
^{13}C NMR (101 MHz, Chloroform-d) 1



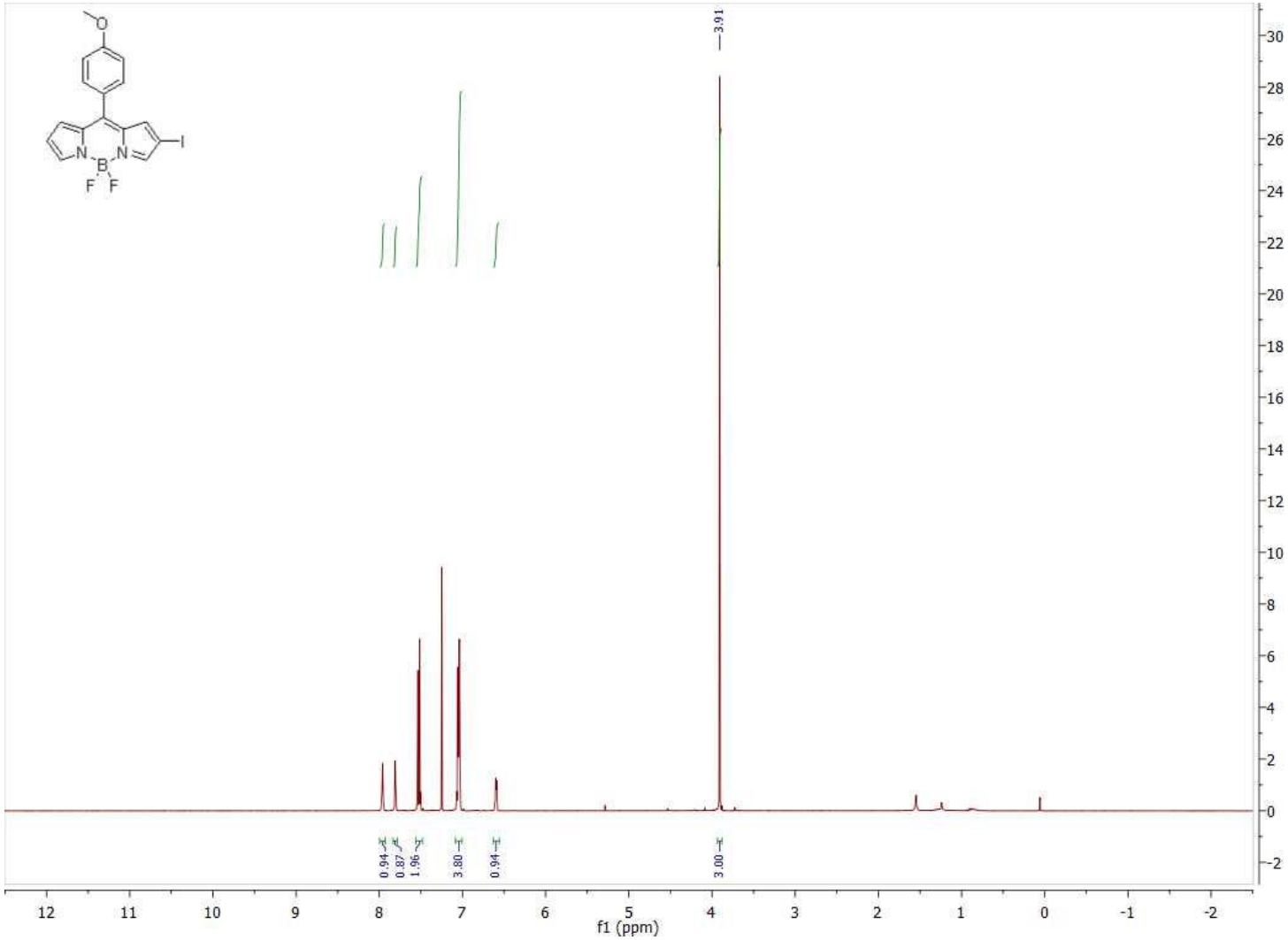
^{11}B NMR (128 MHz, Chloroform-d) 1



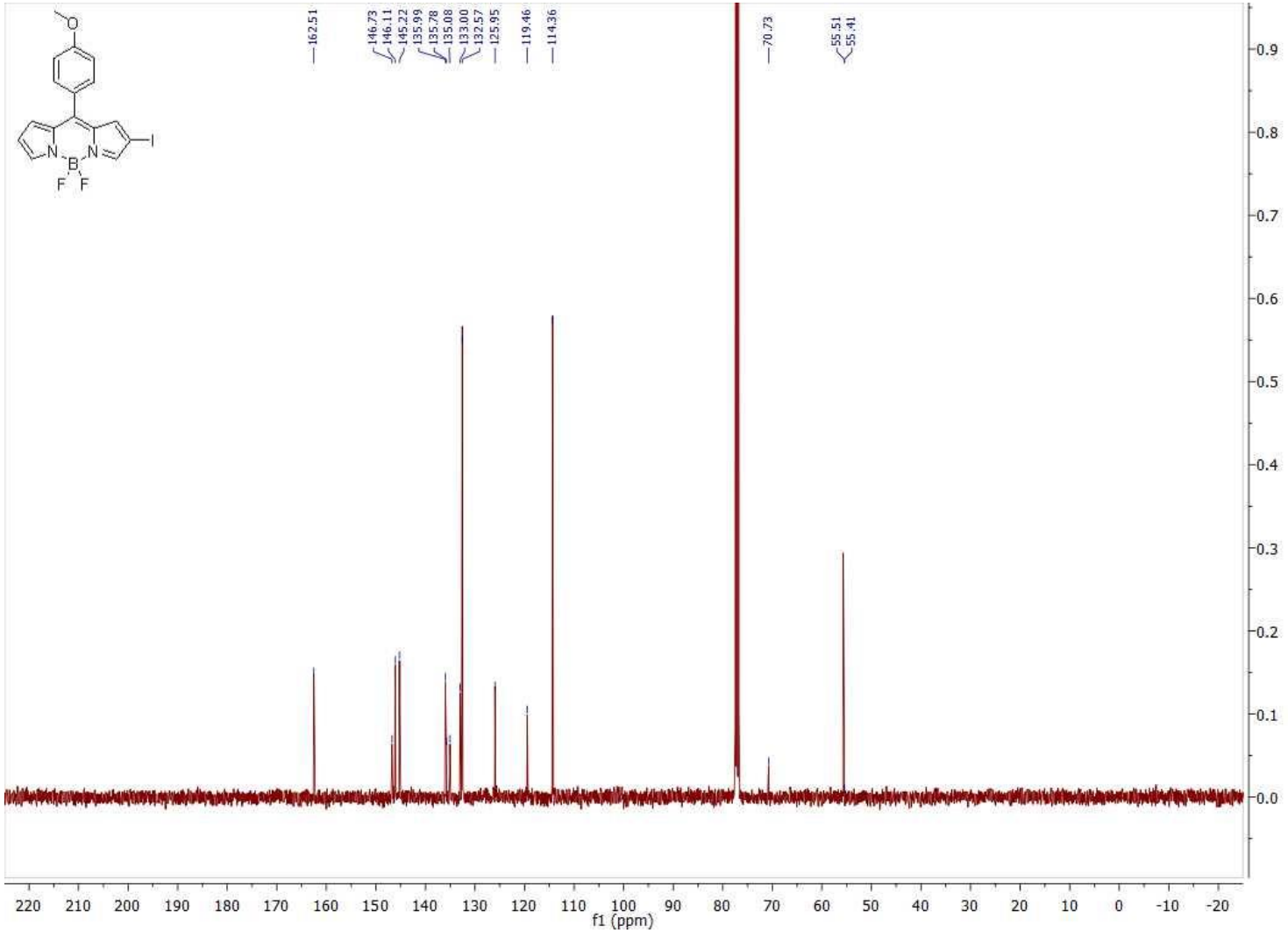
^{19}F NMR (376 MHz, Chloroform-d) 1



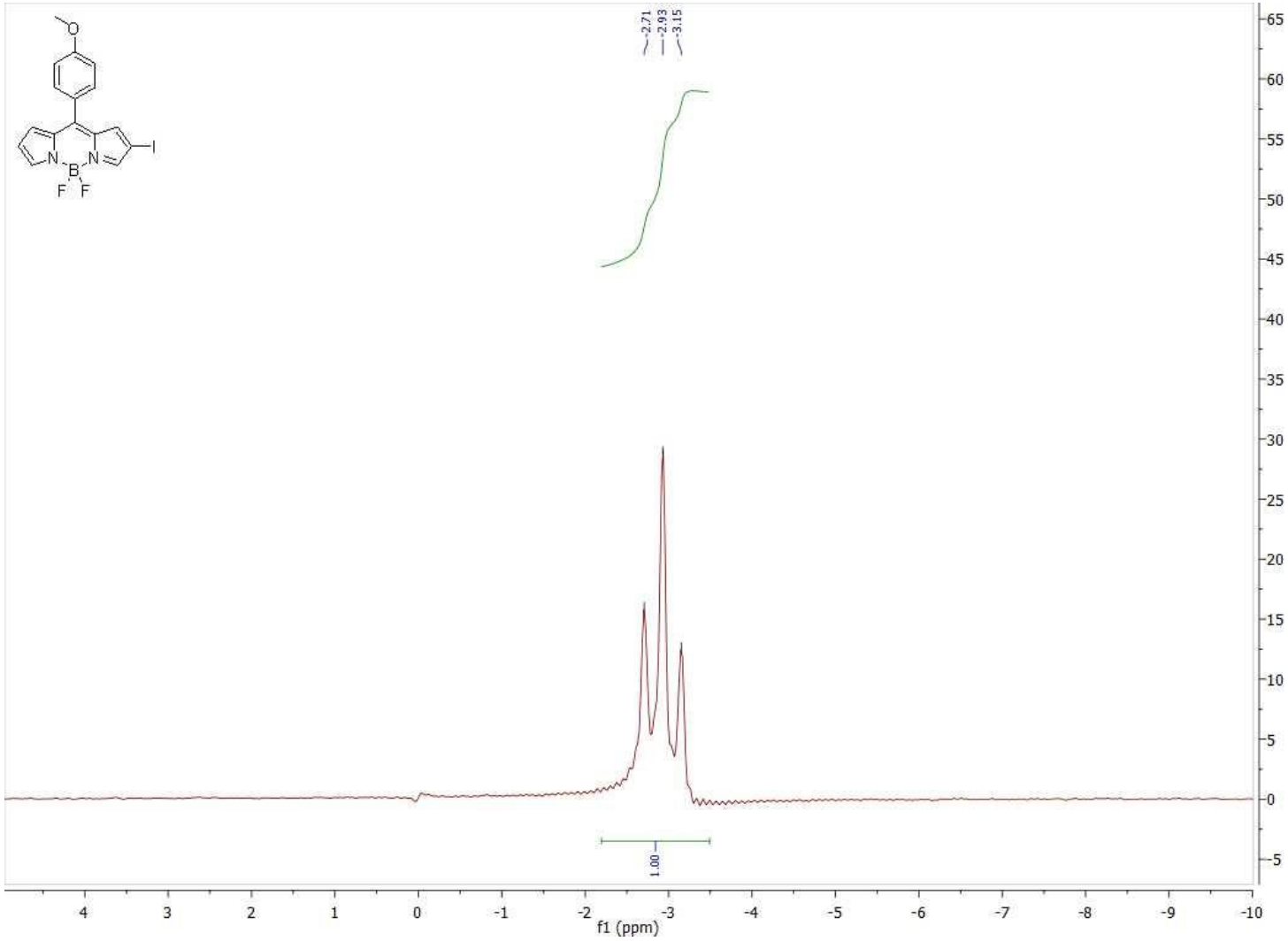
^{1}H NMR (400 MHz, Chloroform-d) 2



^{13}C NMR (101 MHz, Chloroform-d) 2



^{11}B NMR (128 MHz, Chloroform-d) 2



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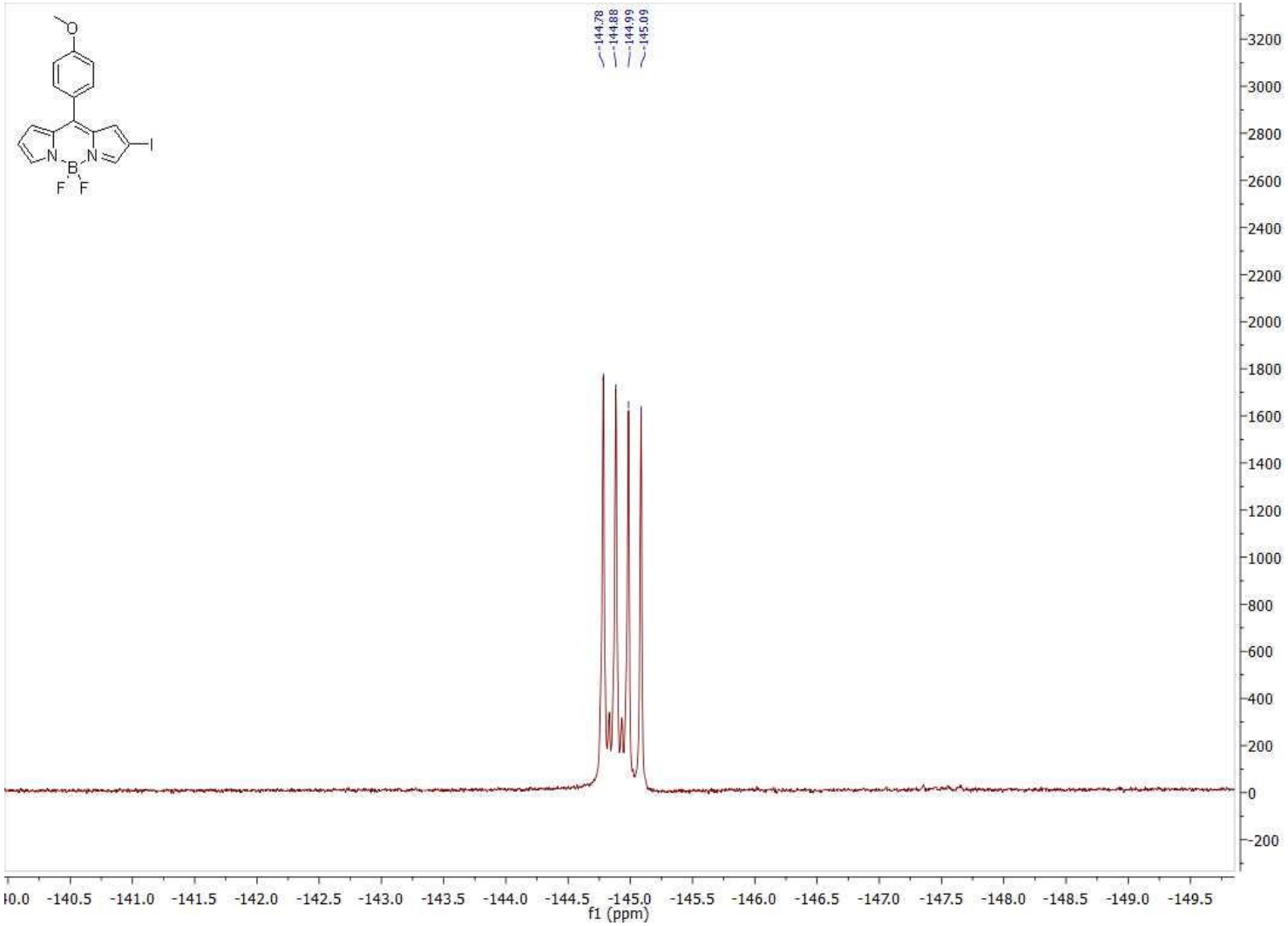
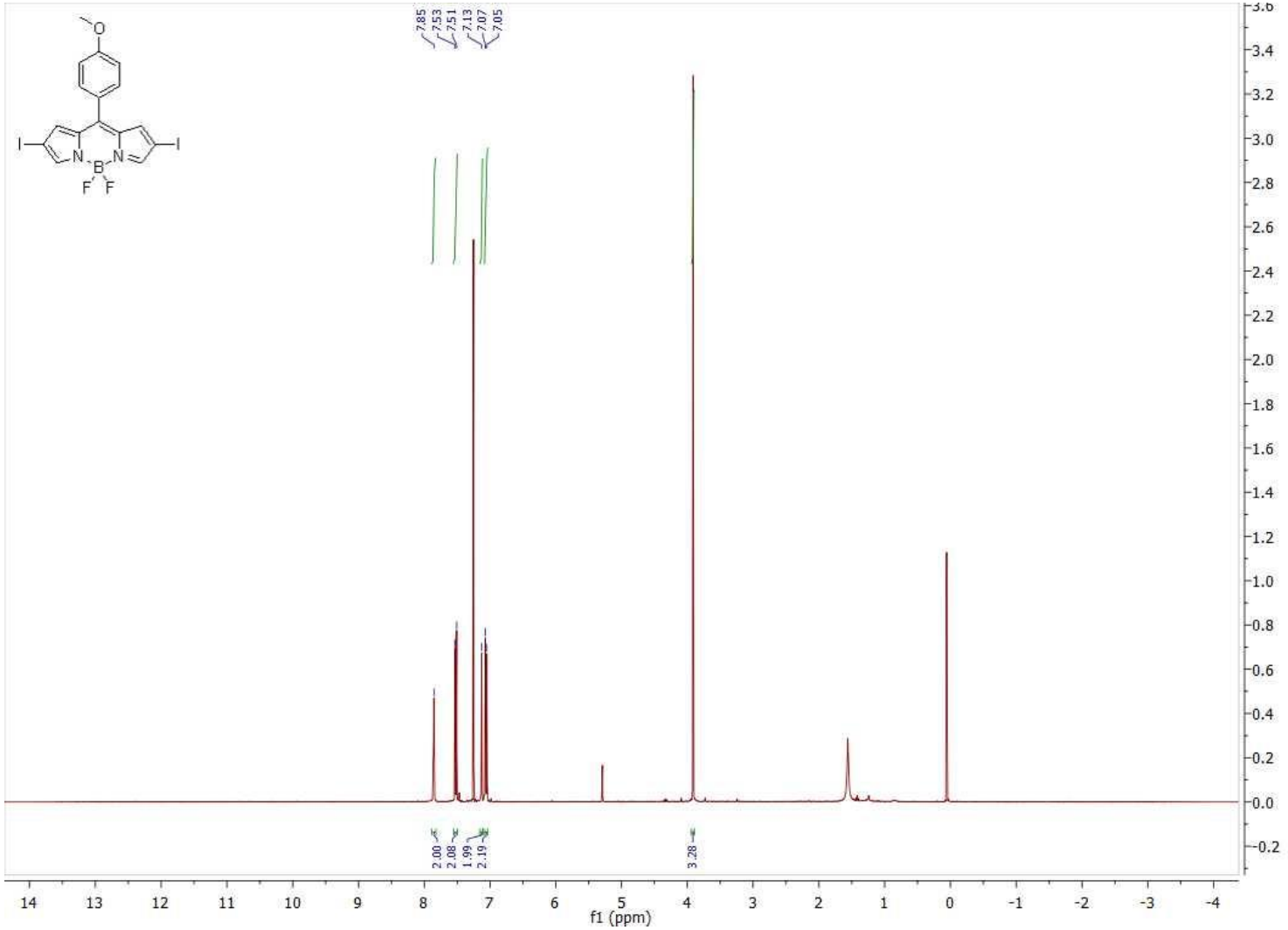
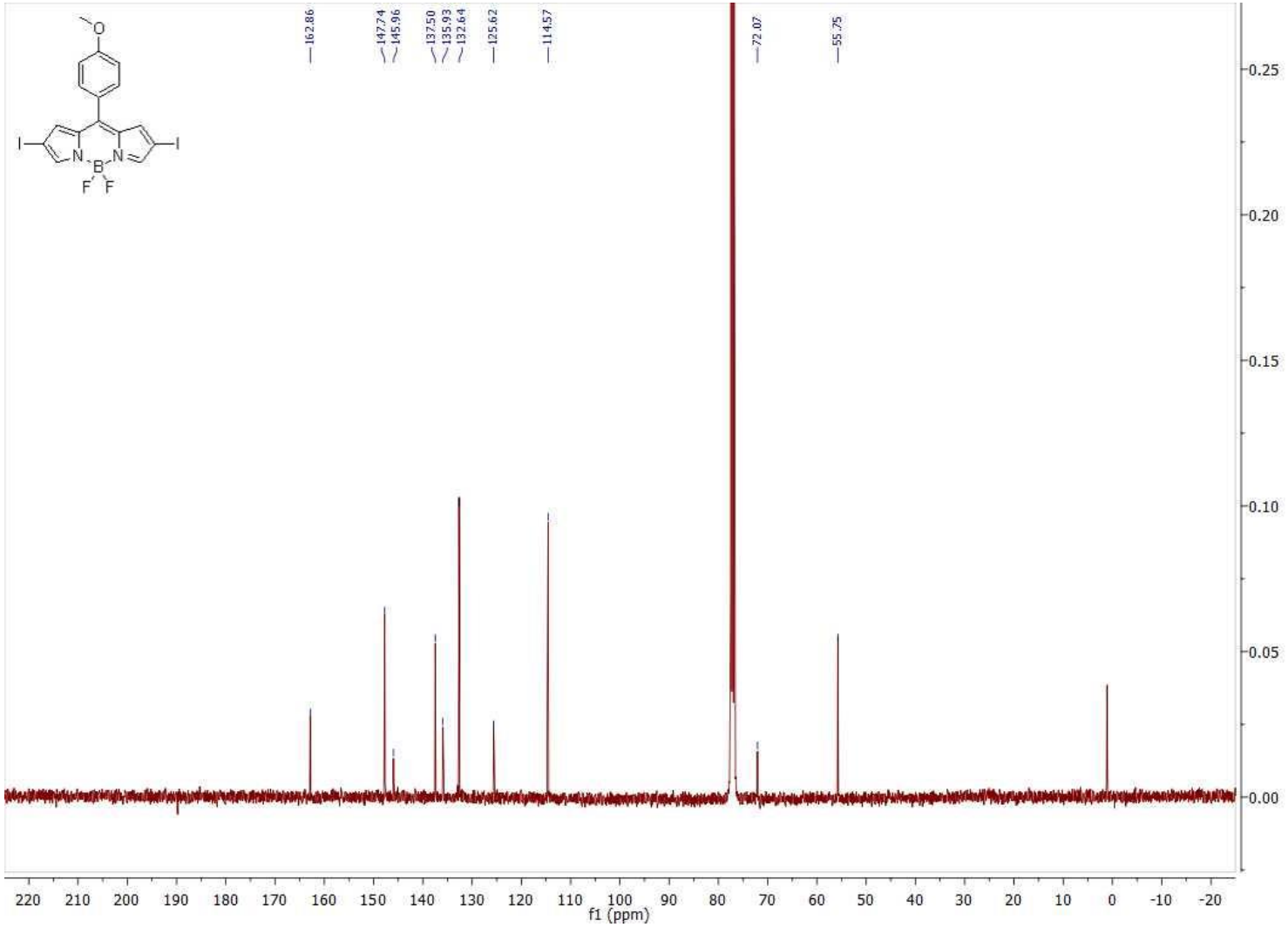


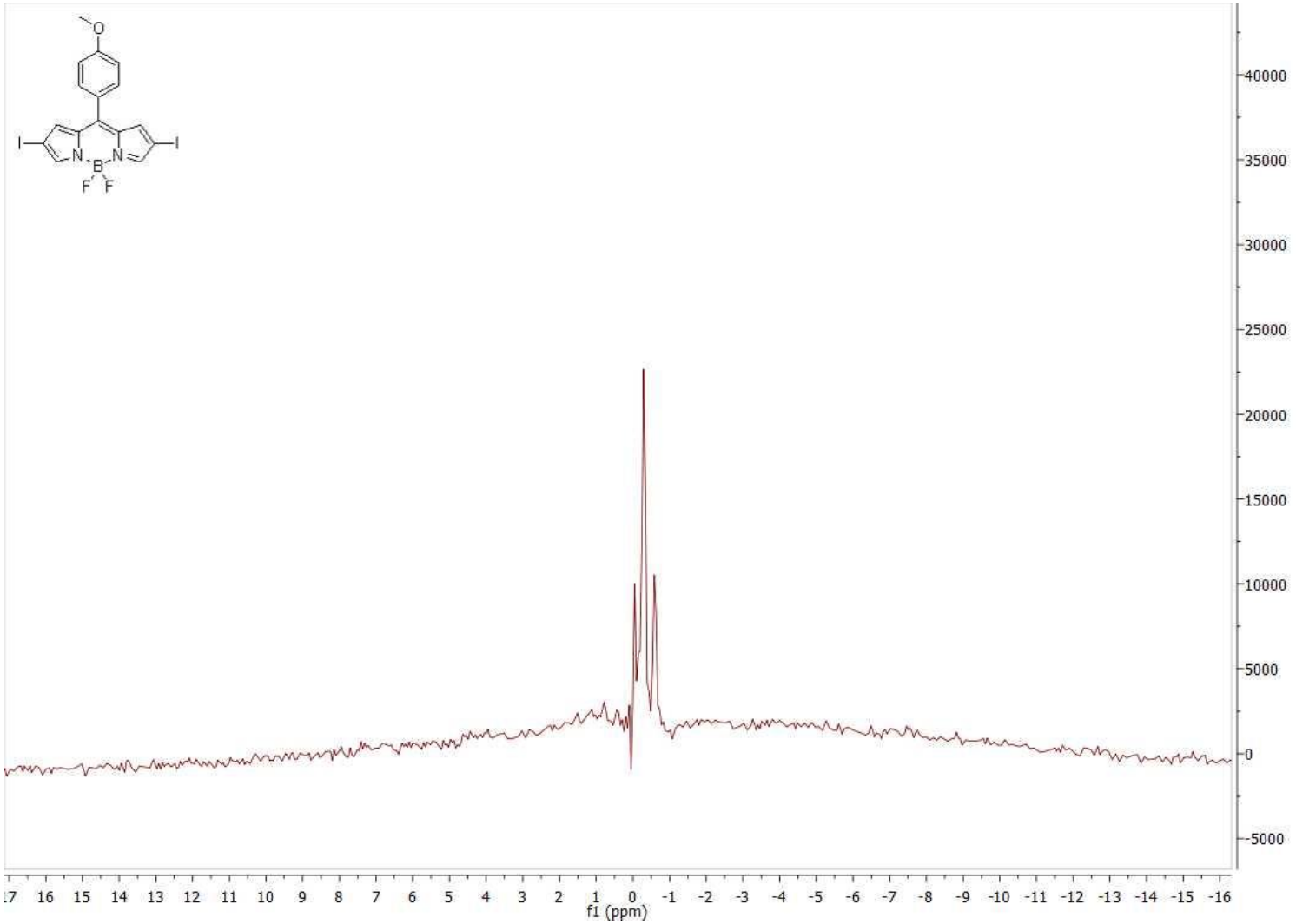
^{1}H NMR (400 MHz, Chloroform-d) 3



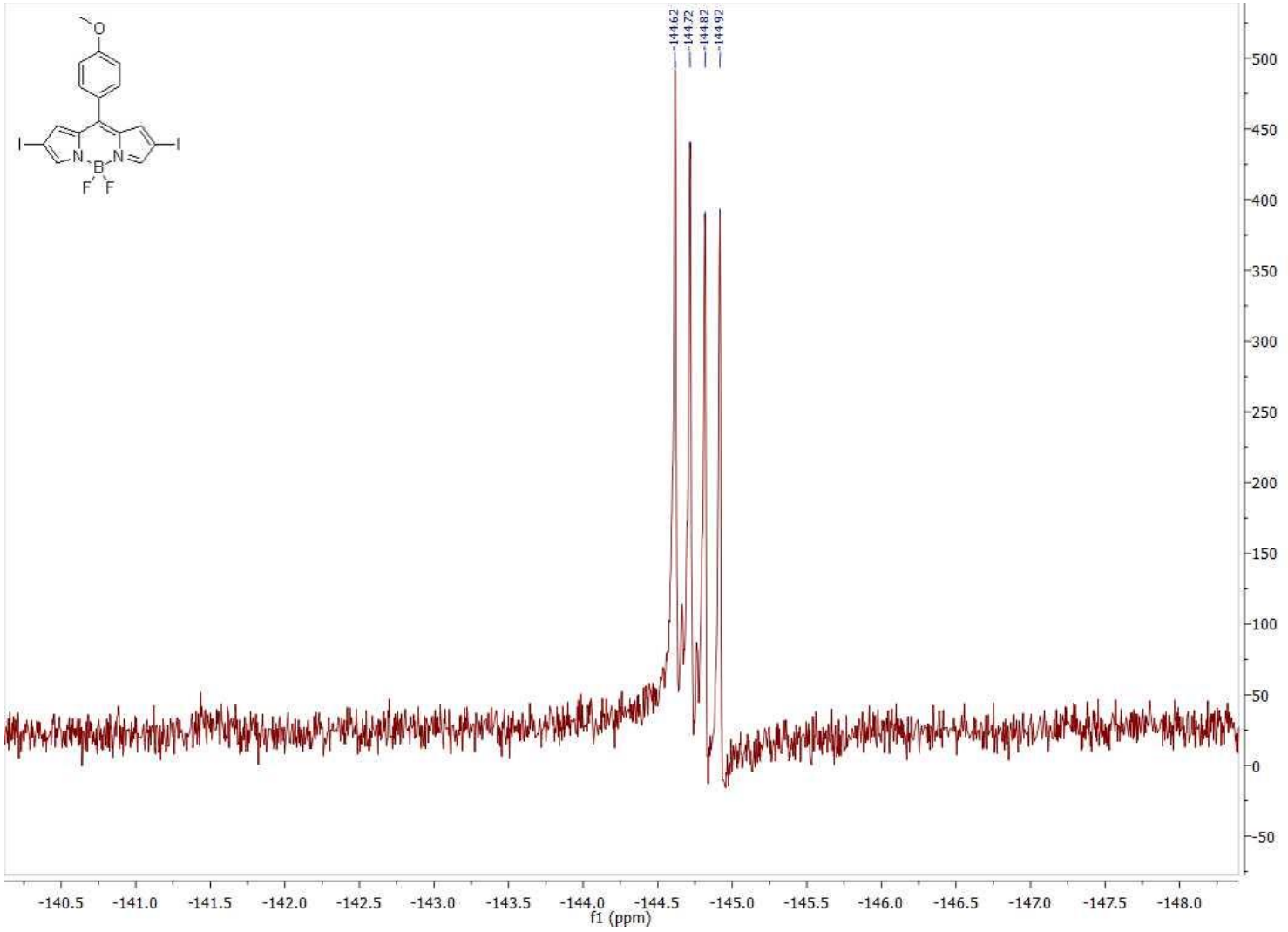
^{13}C NMR (101 MHz, Chloroform-d) 3



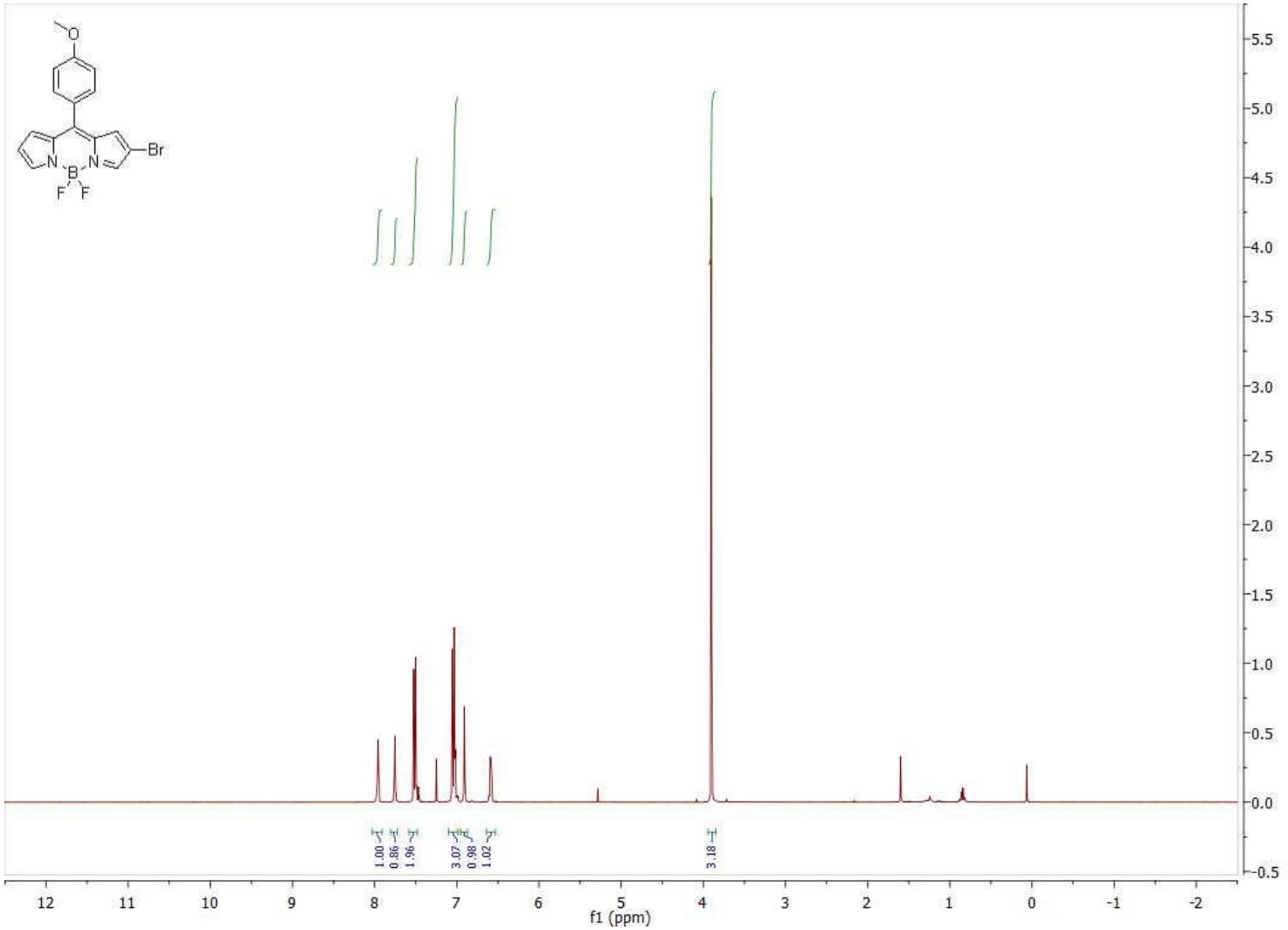
^{11}B NMR (128 MHz, Chloroform-d) 3



^{19}F NMR (376 MHz, Chloroform-d) 3



^{1}H NMR (400 MHz, Chloroform-*d*) 10



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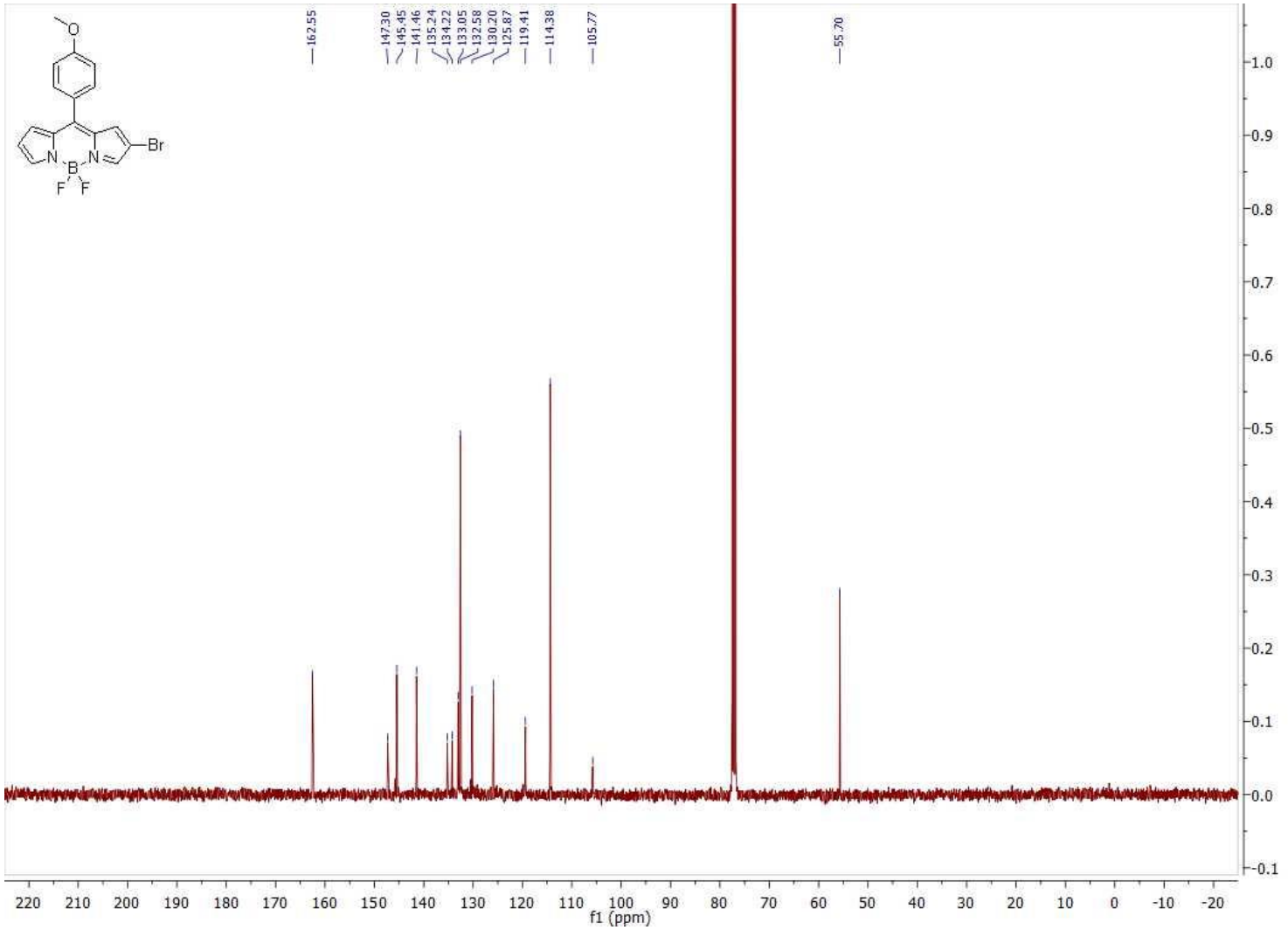

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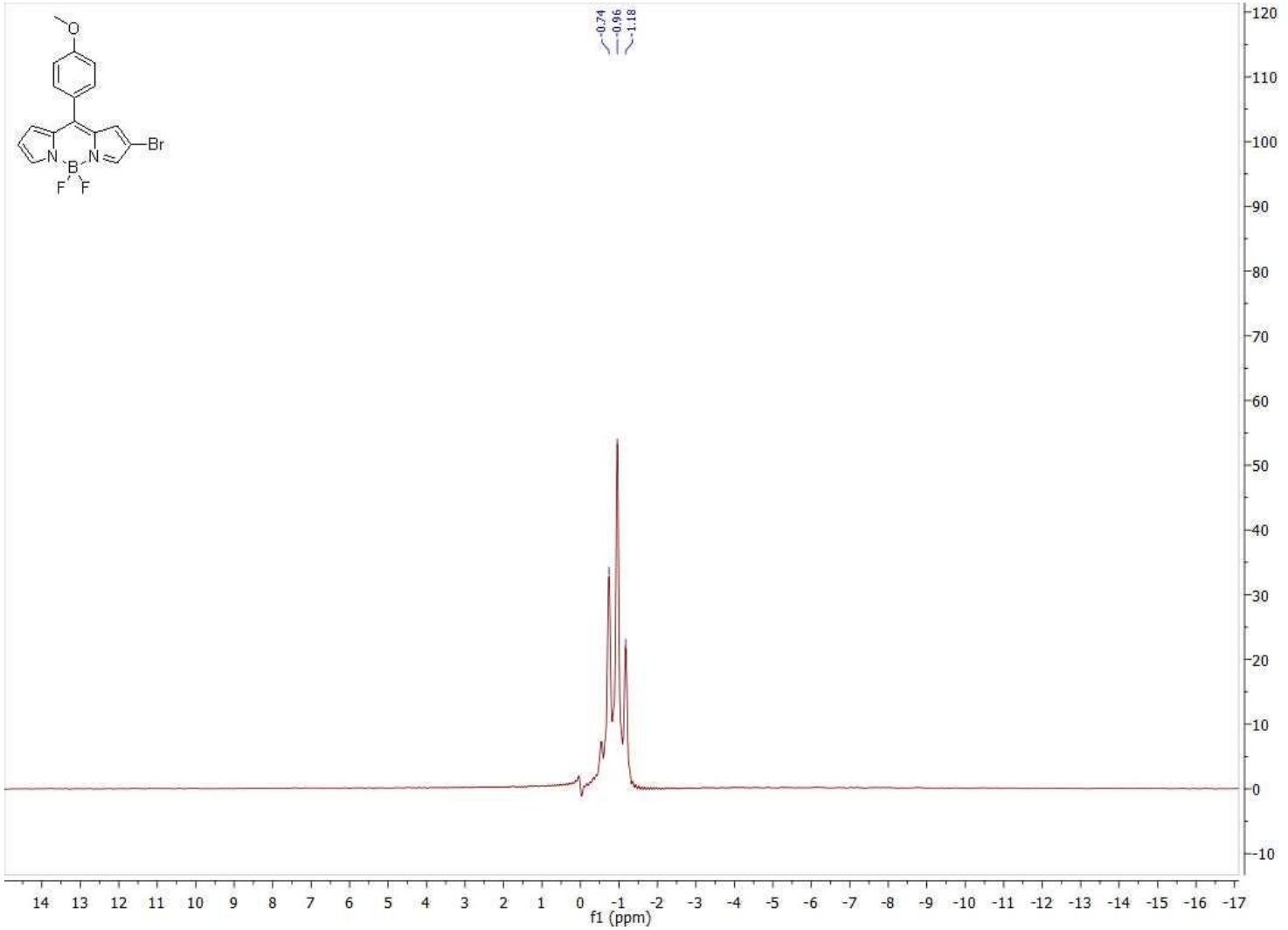
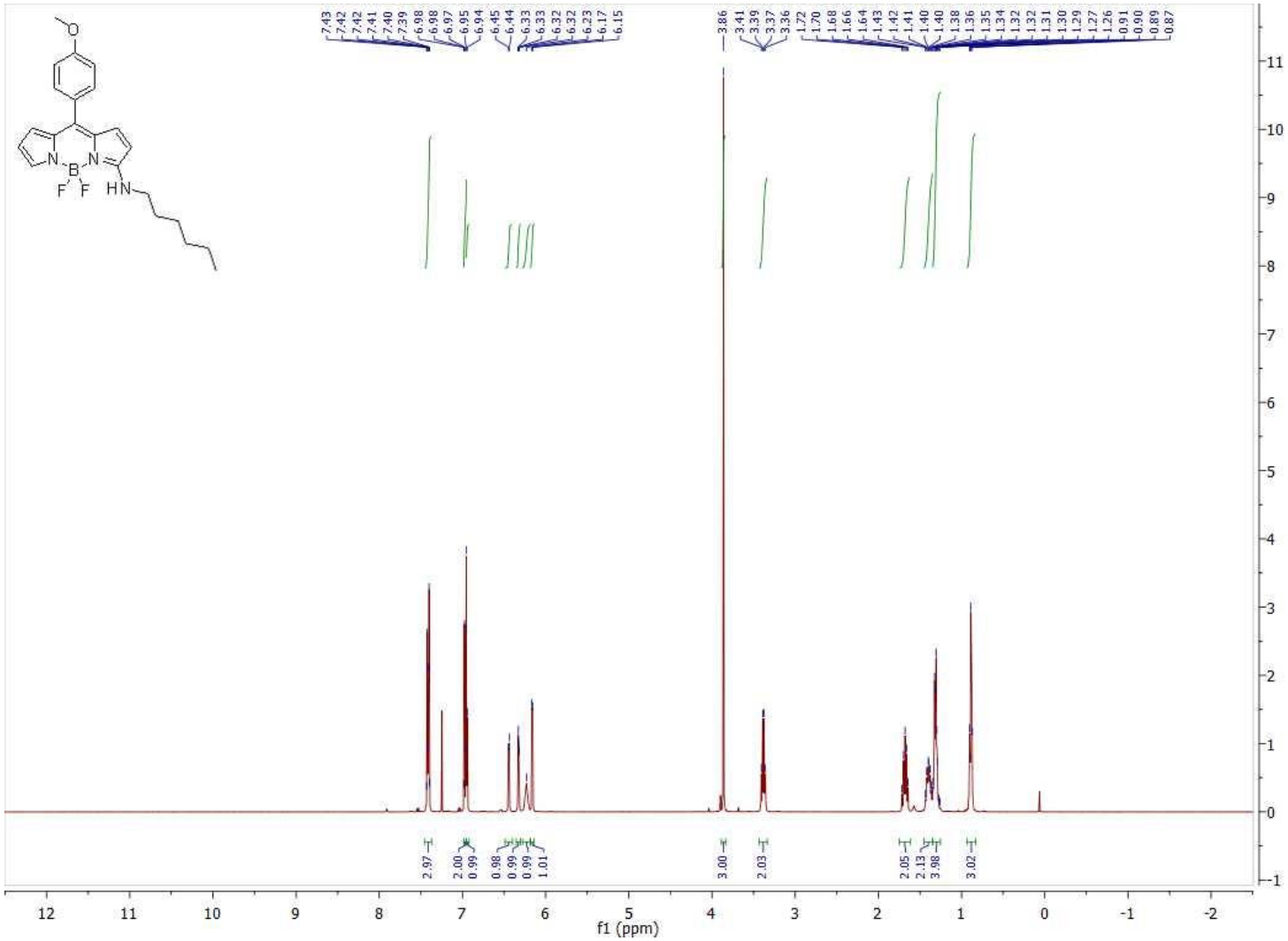
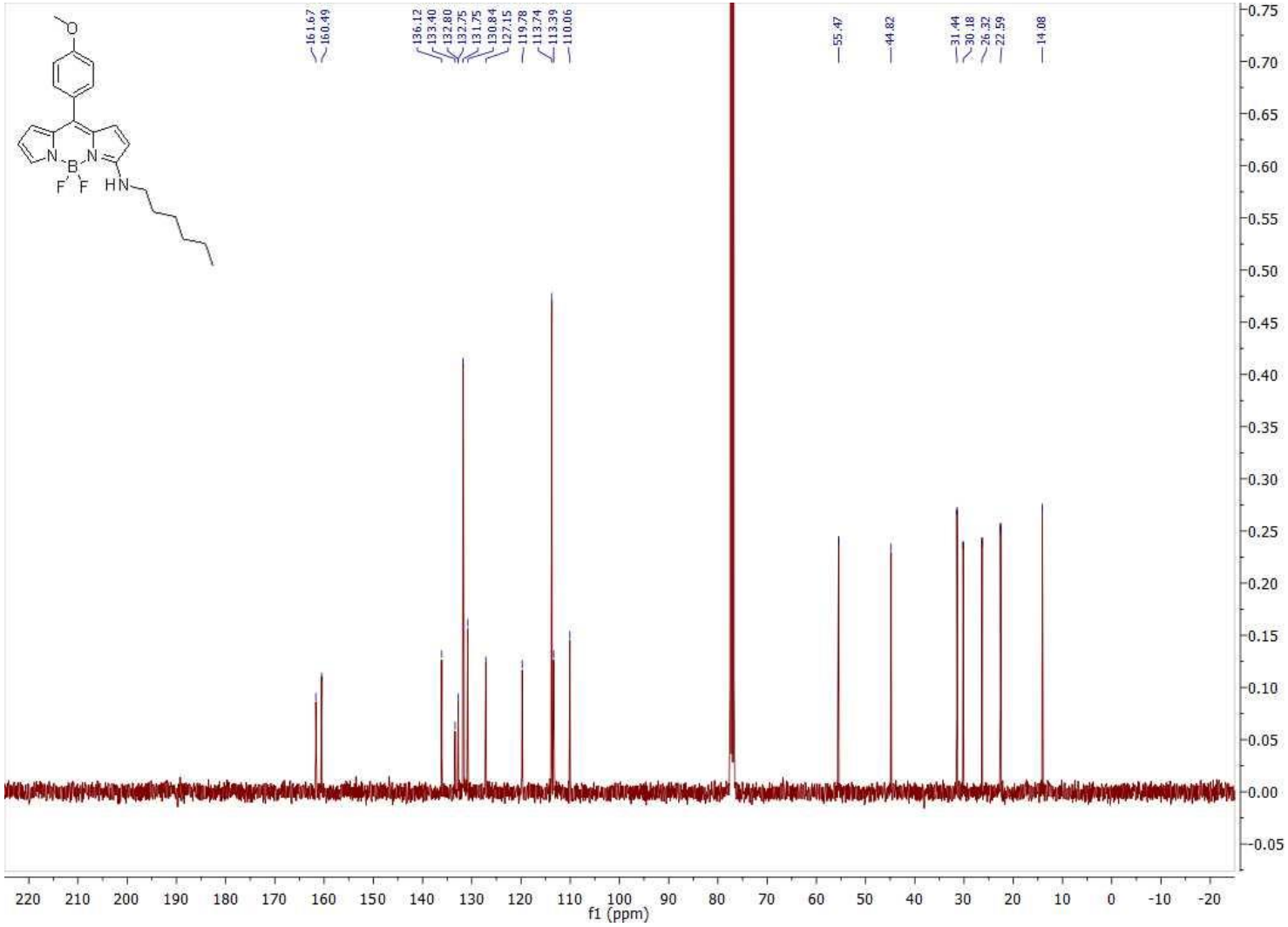


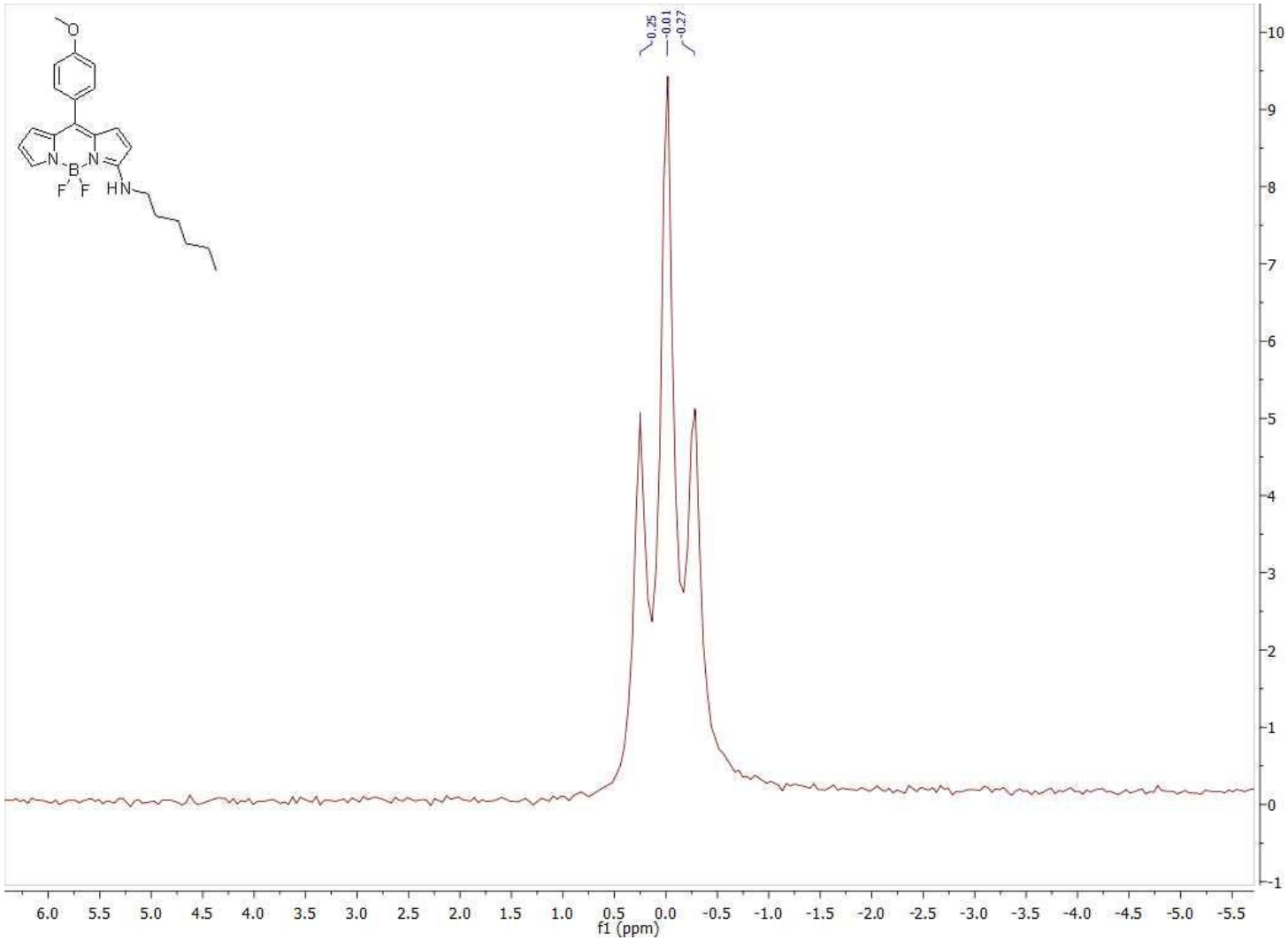
^{1}H NMR (400 MHz, Chloroform-*d*) 4a



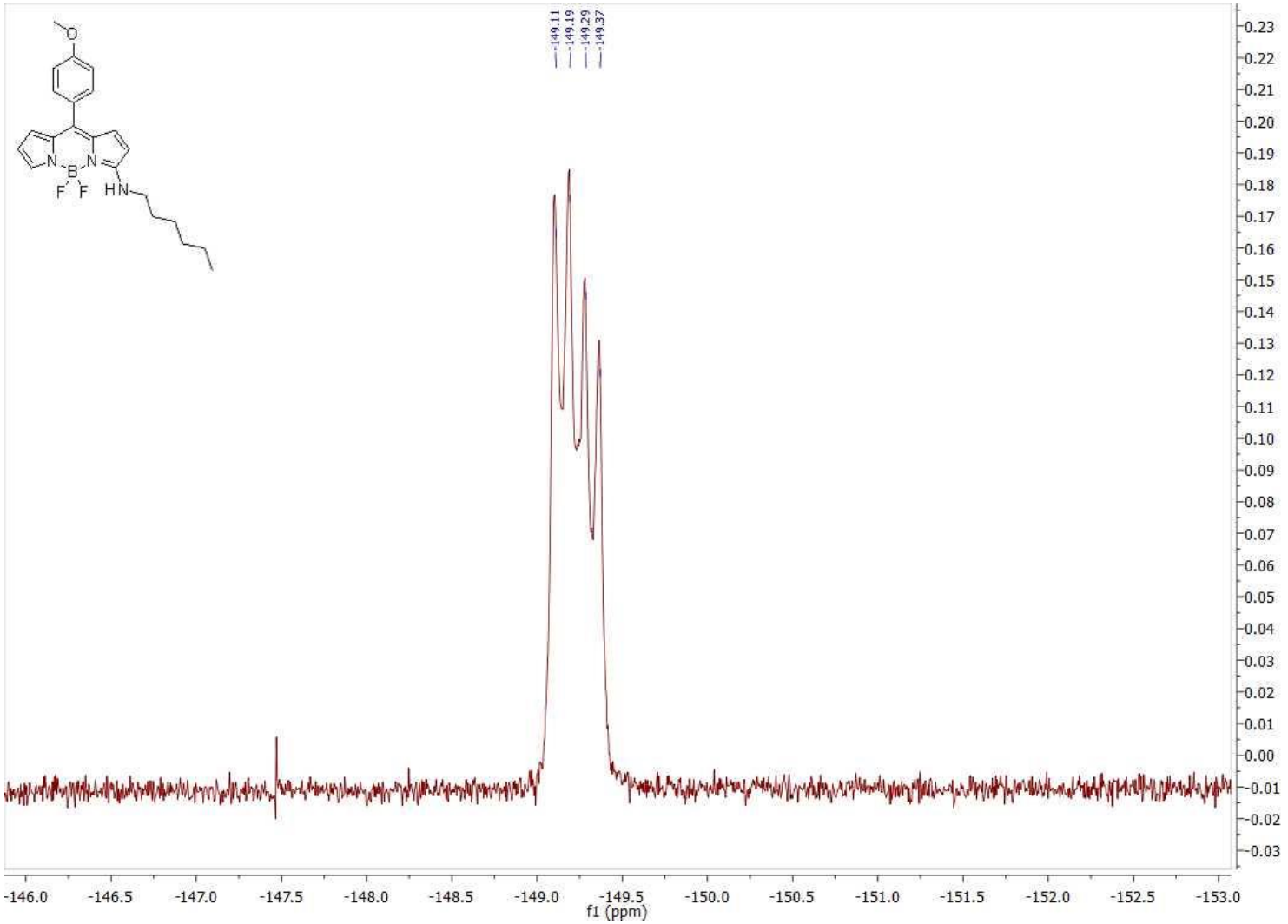
^{13}C NMR (101 MHz, Chloroform-*d*) 4a



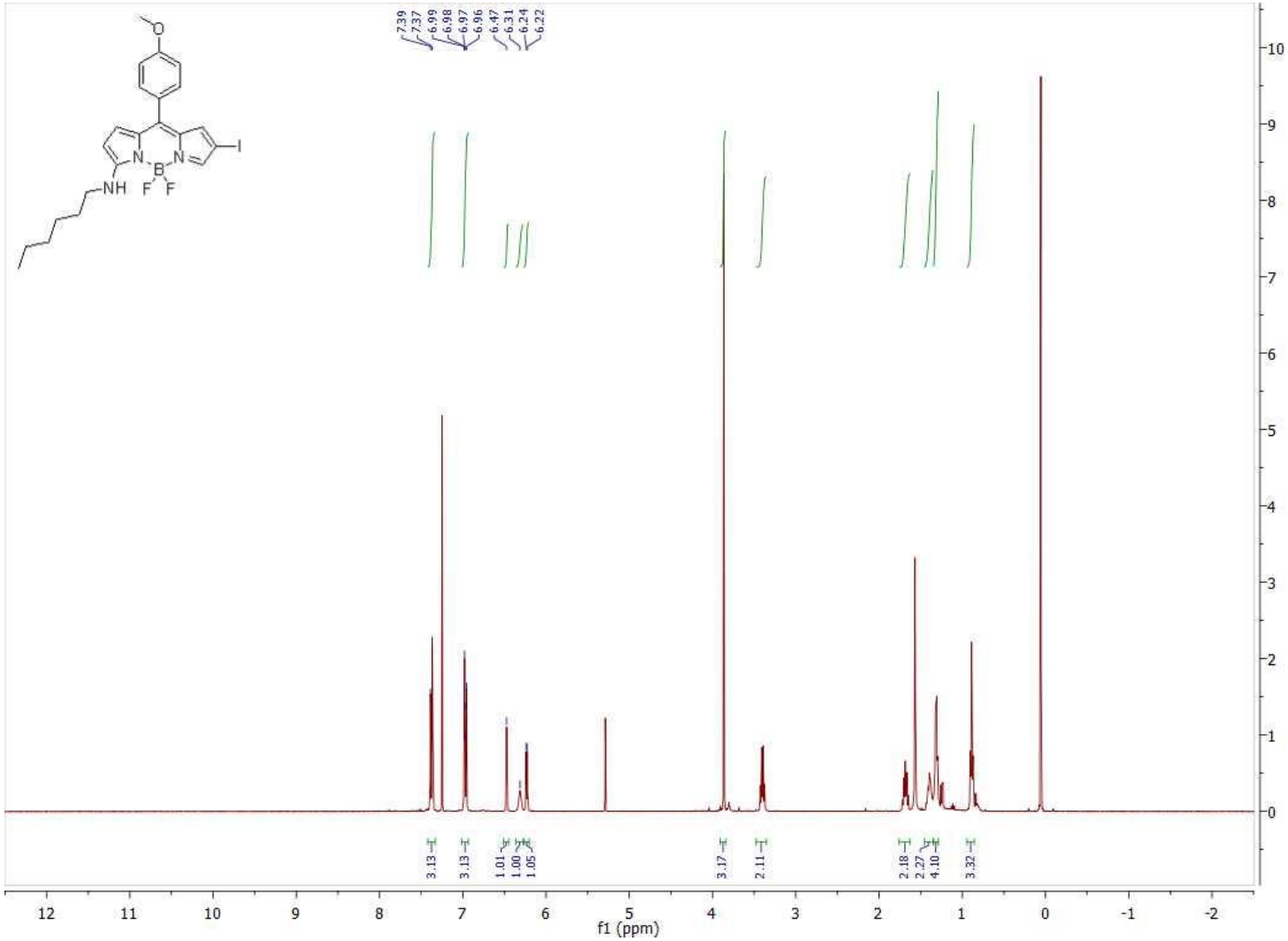
^{11}B NMR (128 MHz, Chloroform-*d*) 4a



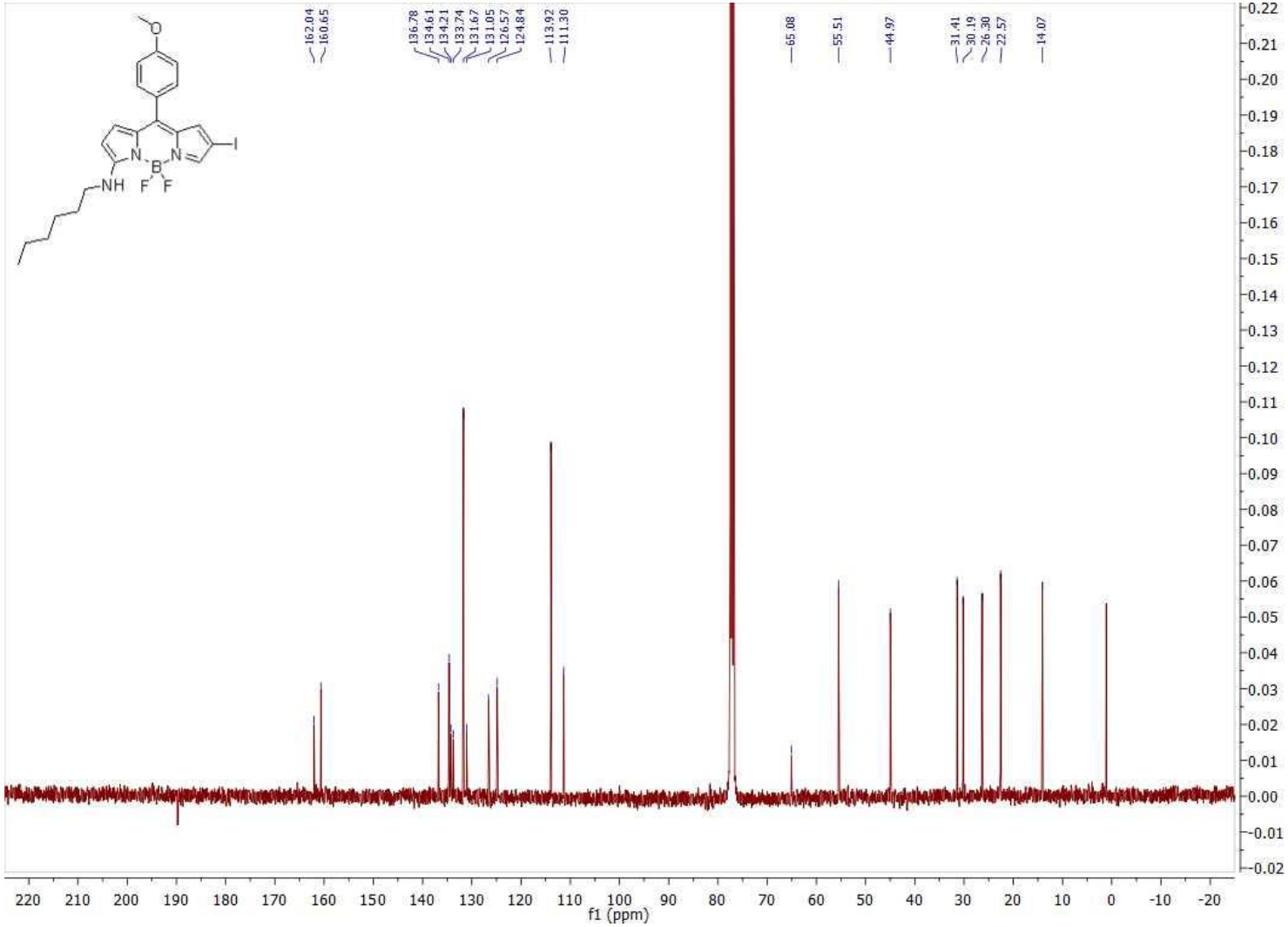
^{19}F NMR (376 MHz, Chloroform-*d*) 4a



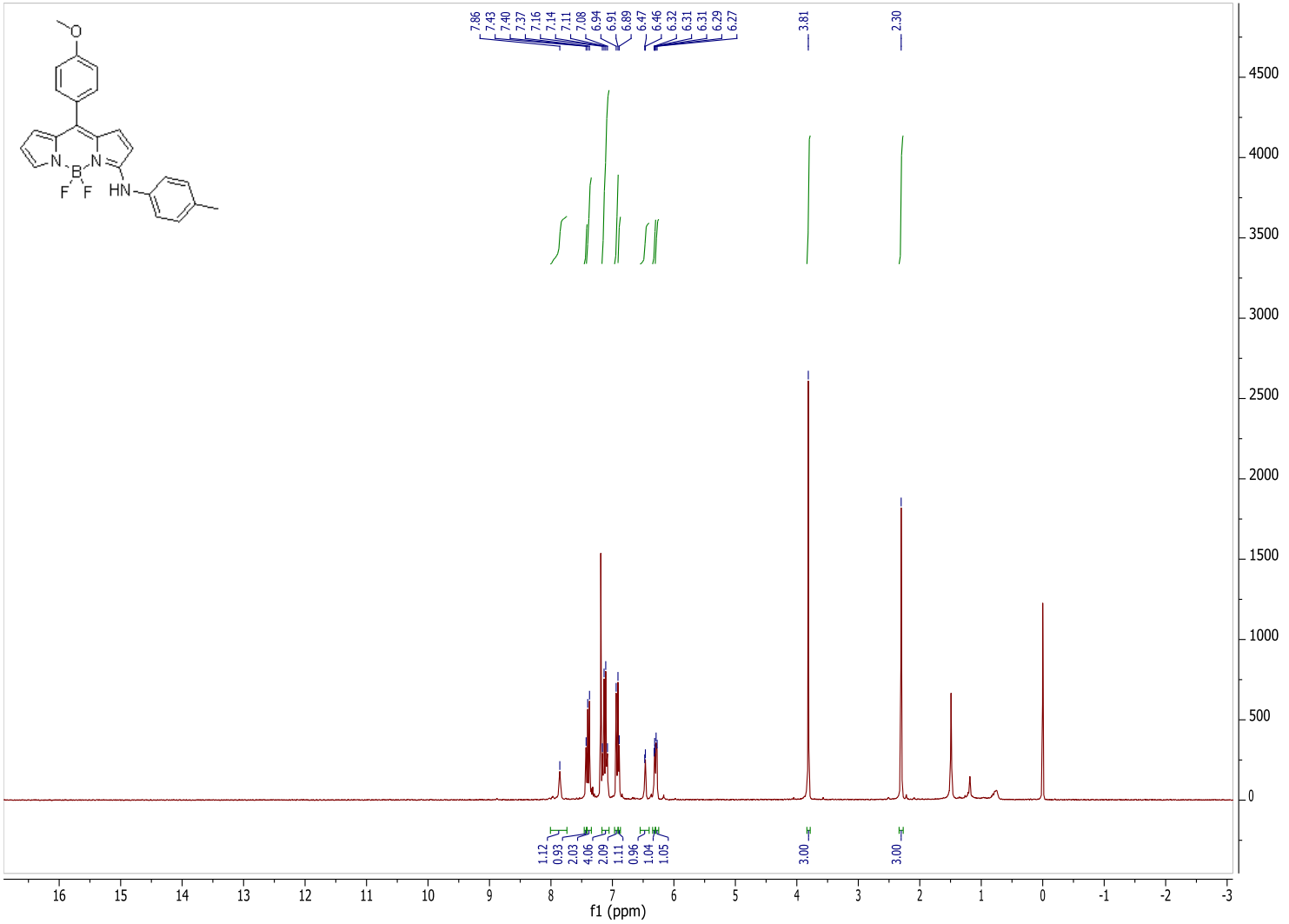
^{1}H NMR (400 MHz, Chloroform-*d*) 5a



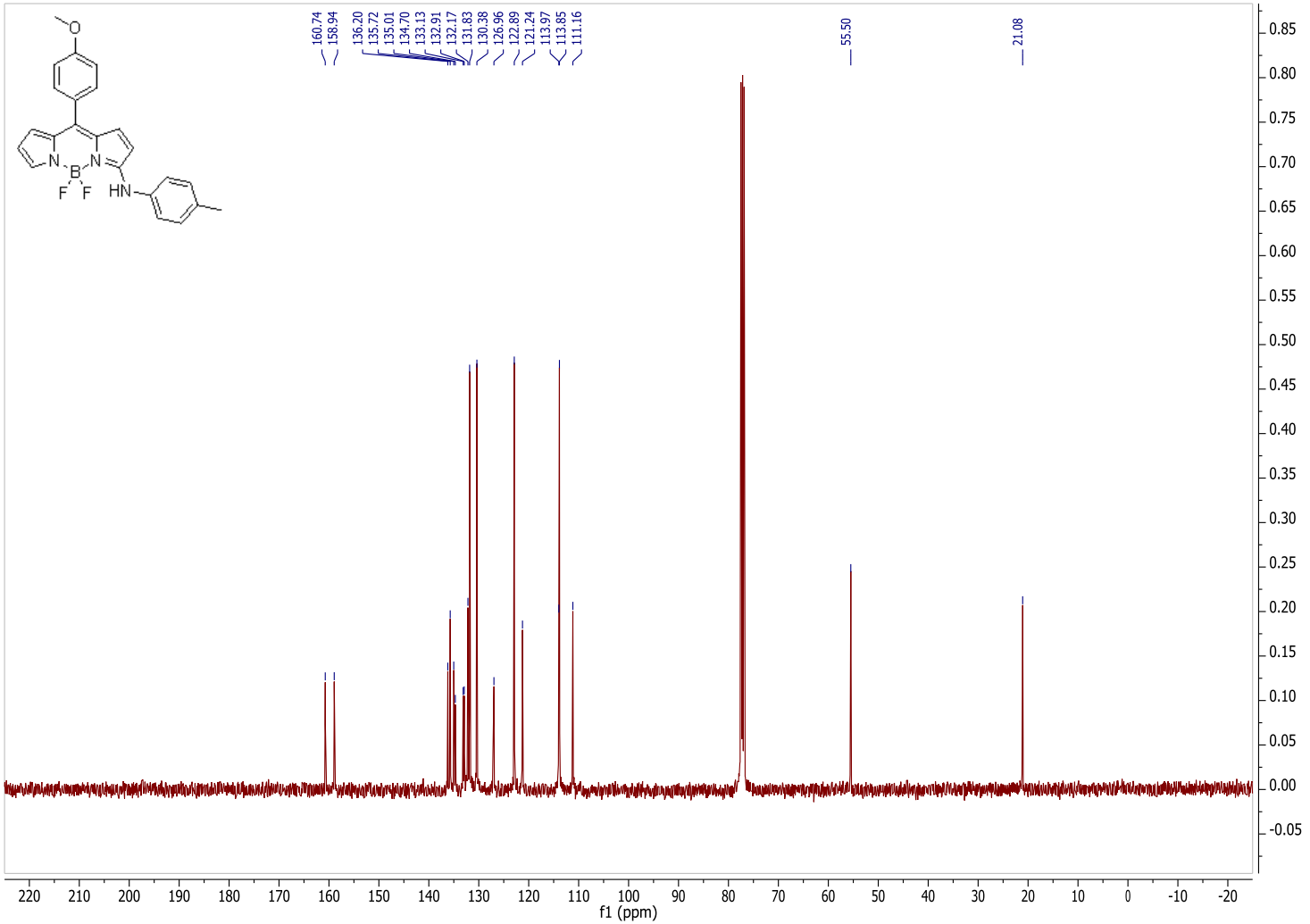
^{13}C NMR (101 MHz, Chloroform-*d*) 5a



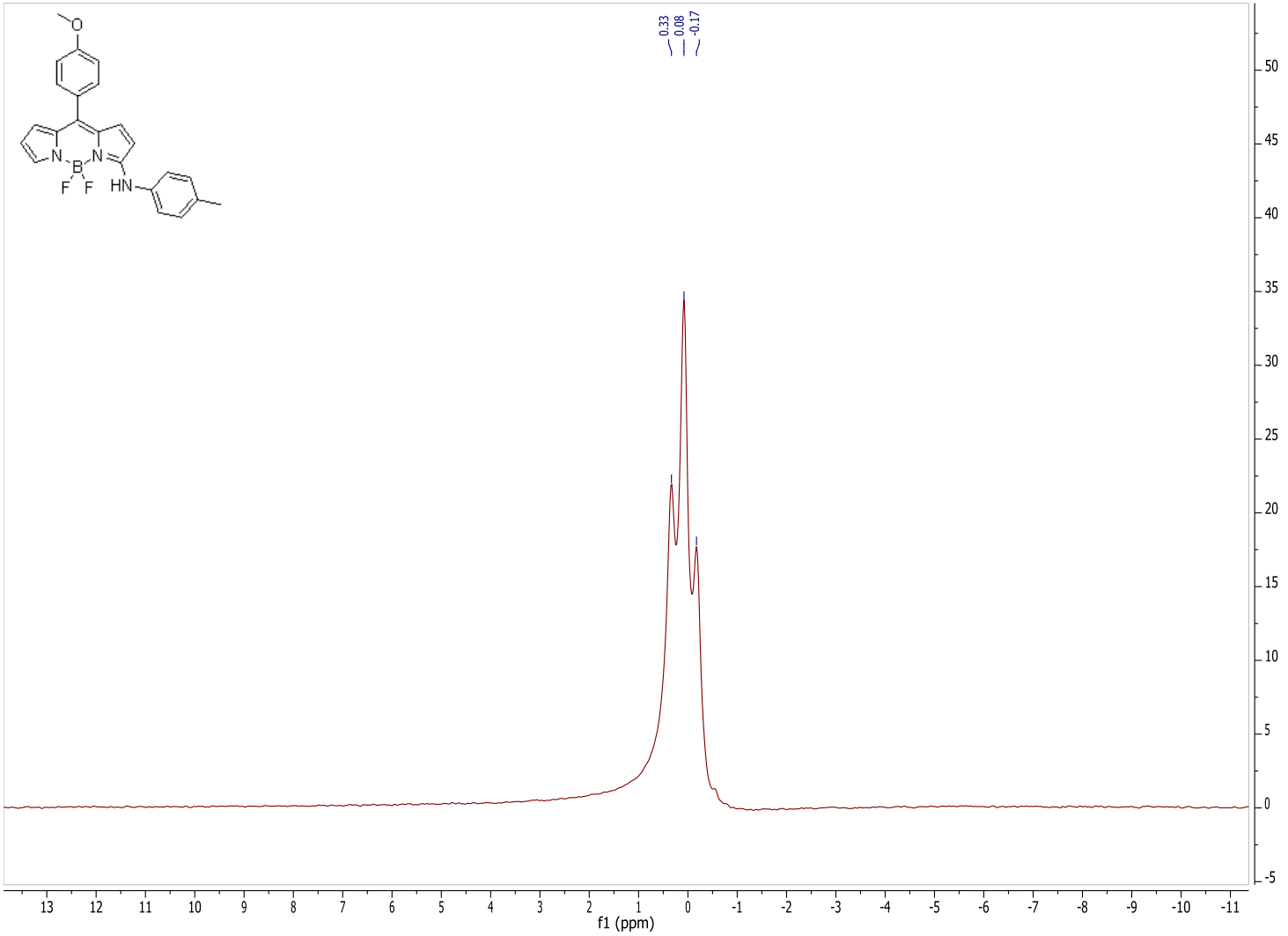
^{1}H NMR (300 MHz, Chloroform-d) 4b



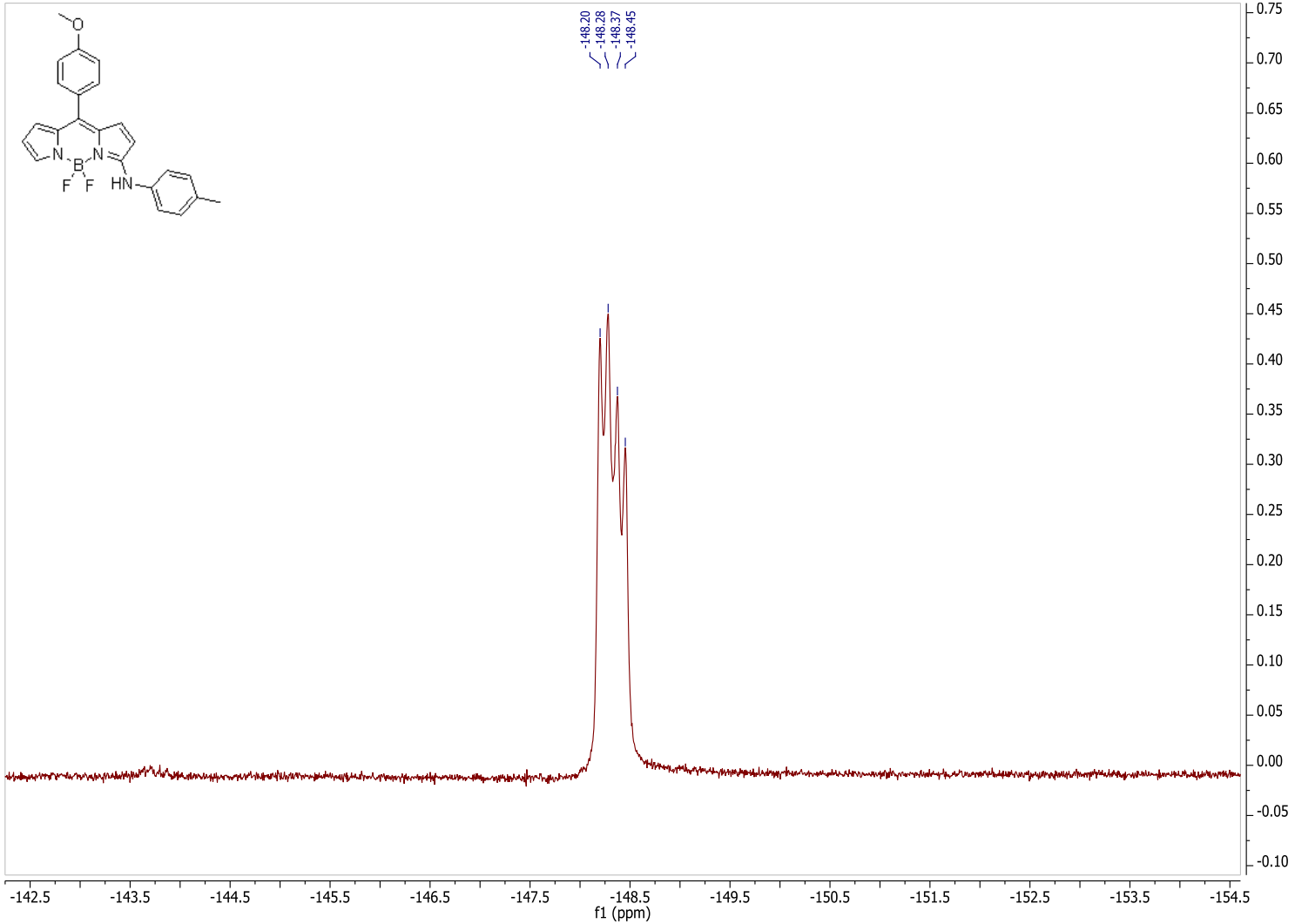
^{13}C NMR (101 MHz, Chloroform-*d*) 4b



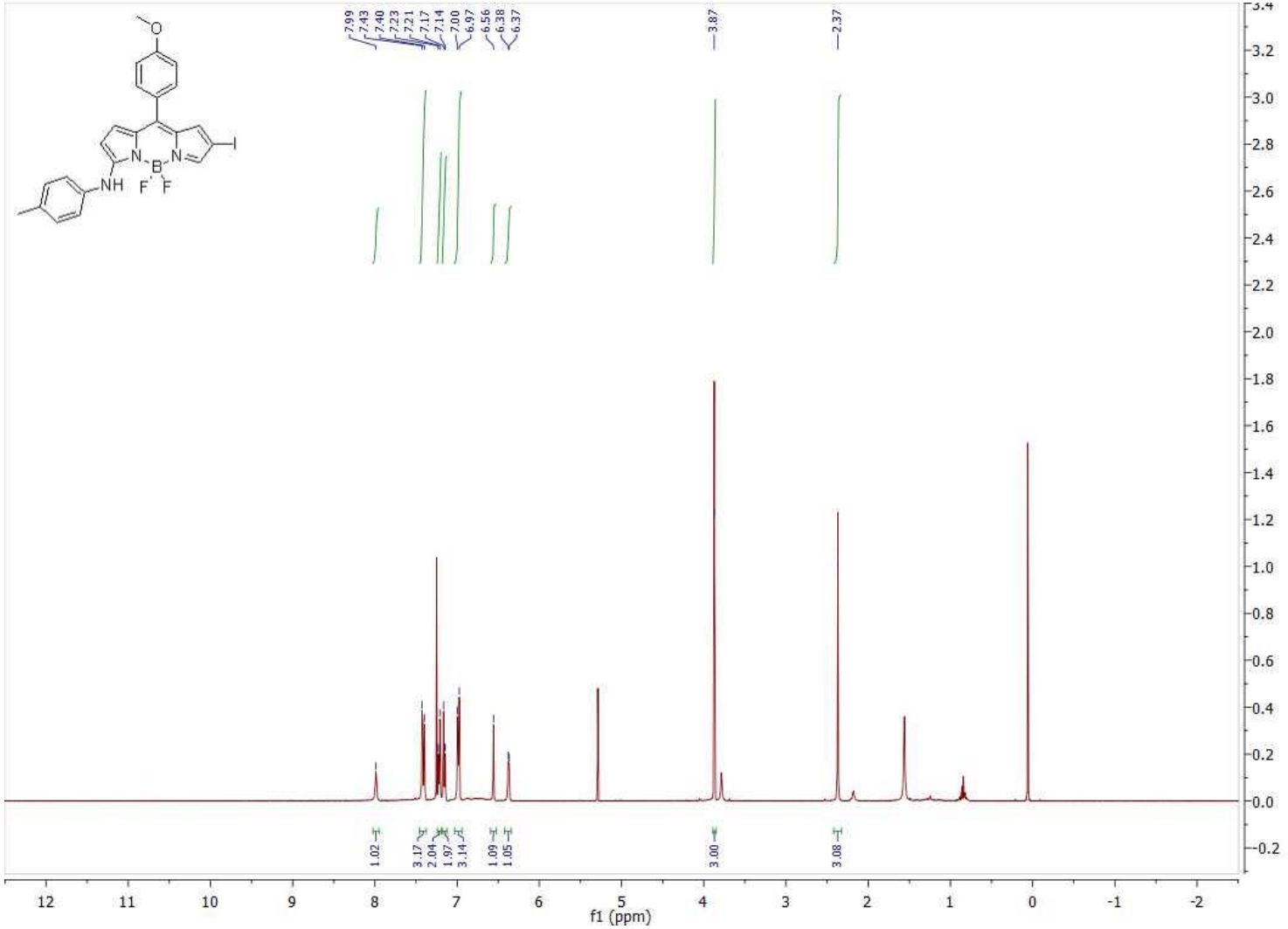
^{11}B NMR (128 MHz, Chloroform-*d*) 4b



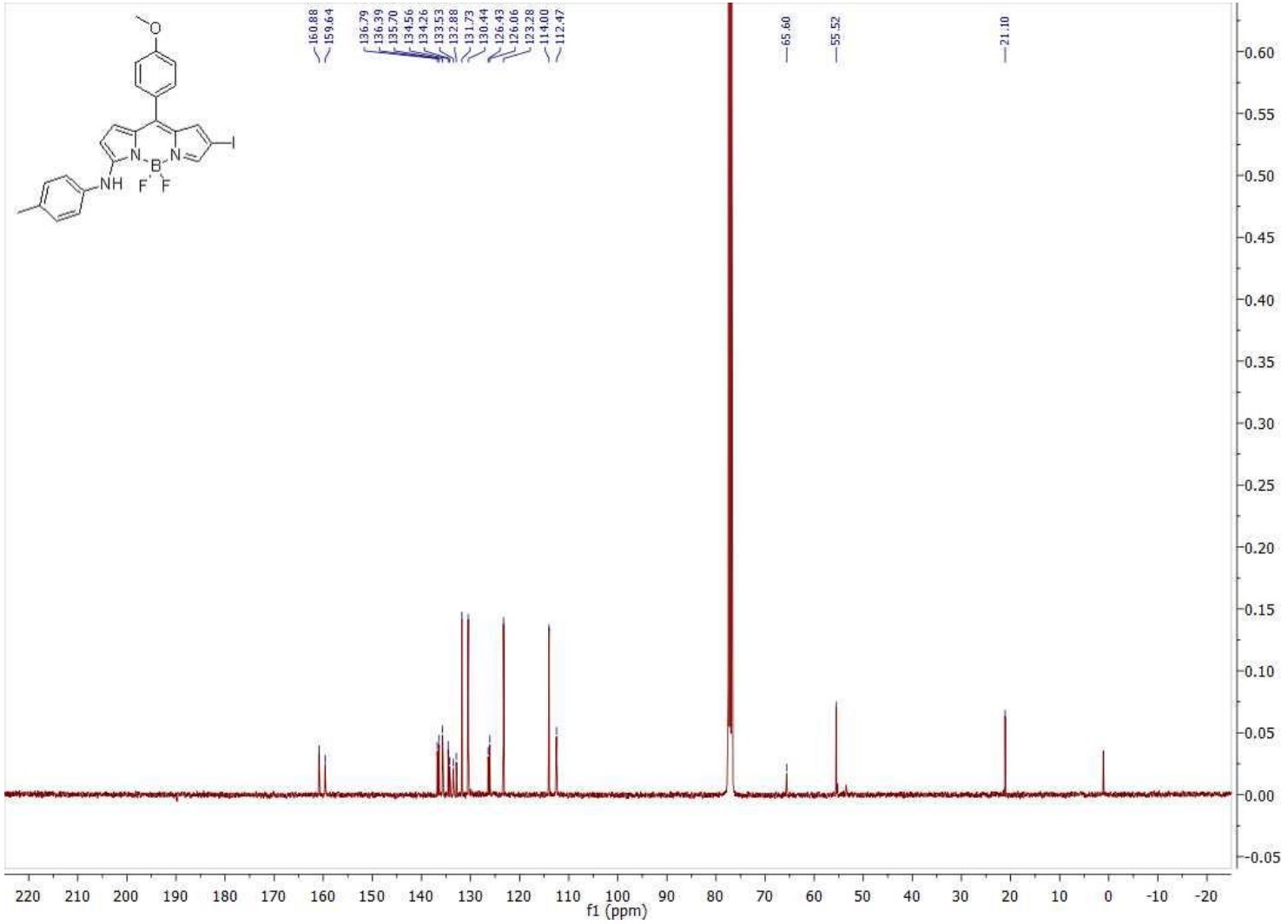
^{19}F NMR (376 MHz, Chloroform-*d*) 4b



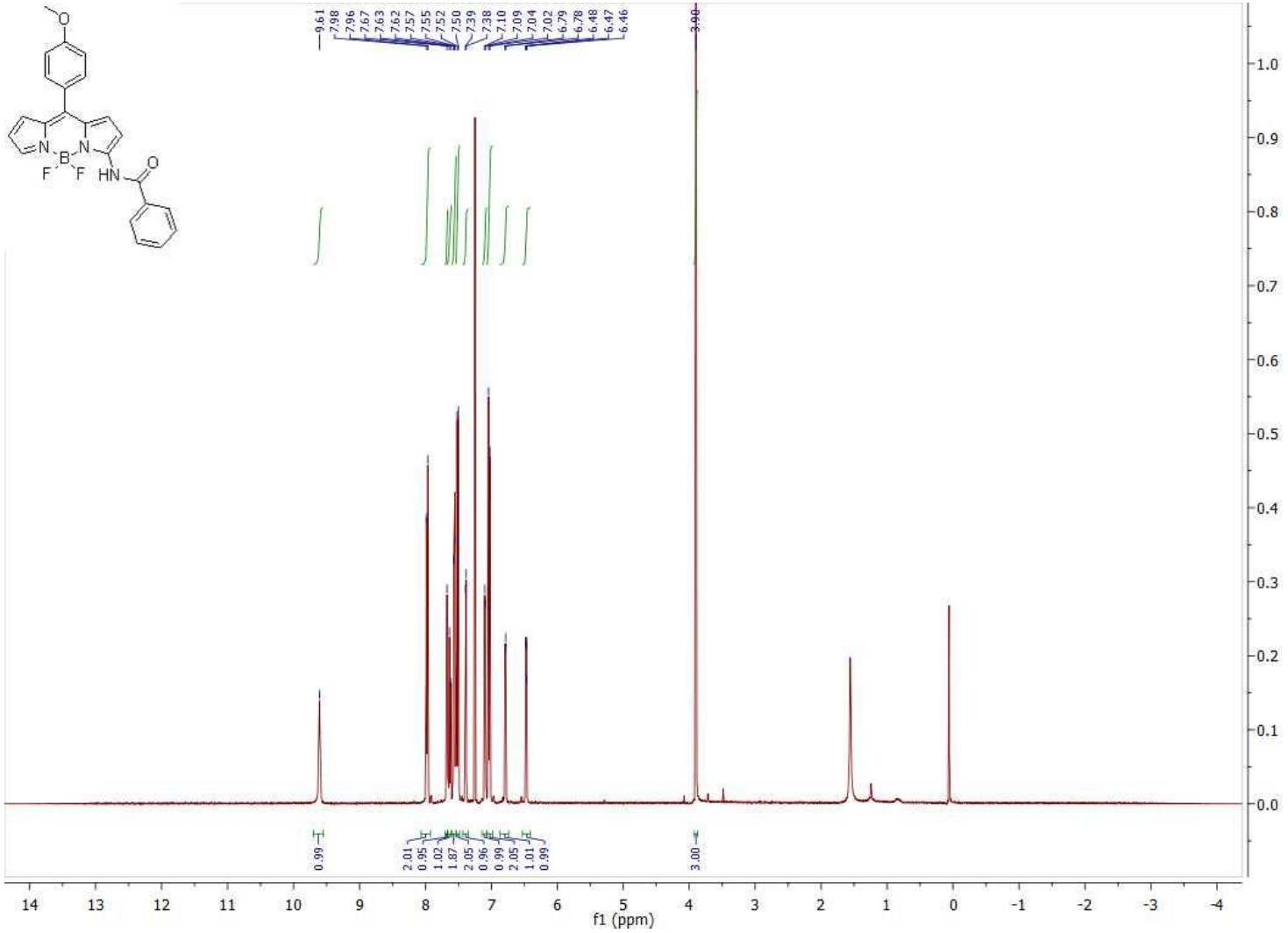
^{1}H NMR (400 MHz, Chloroform-*d*) 5b



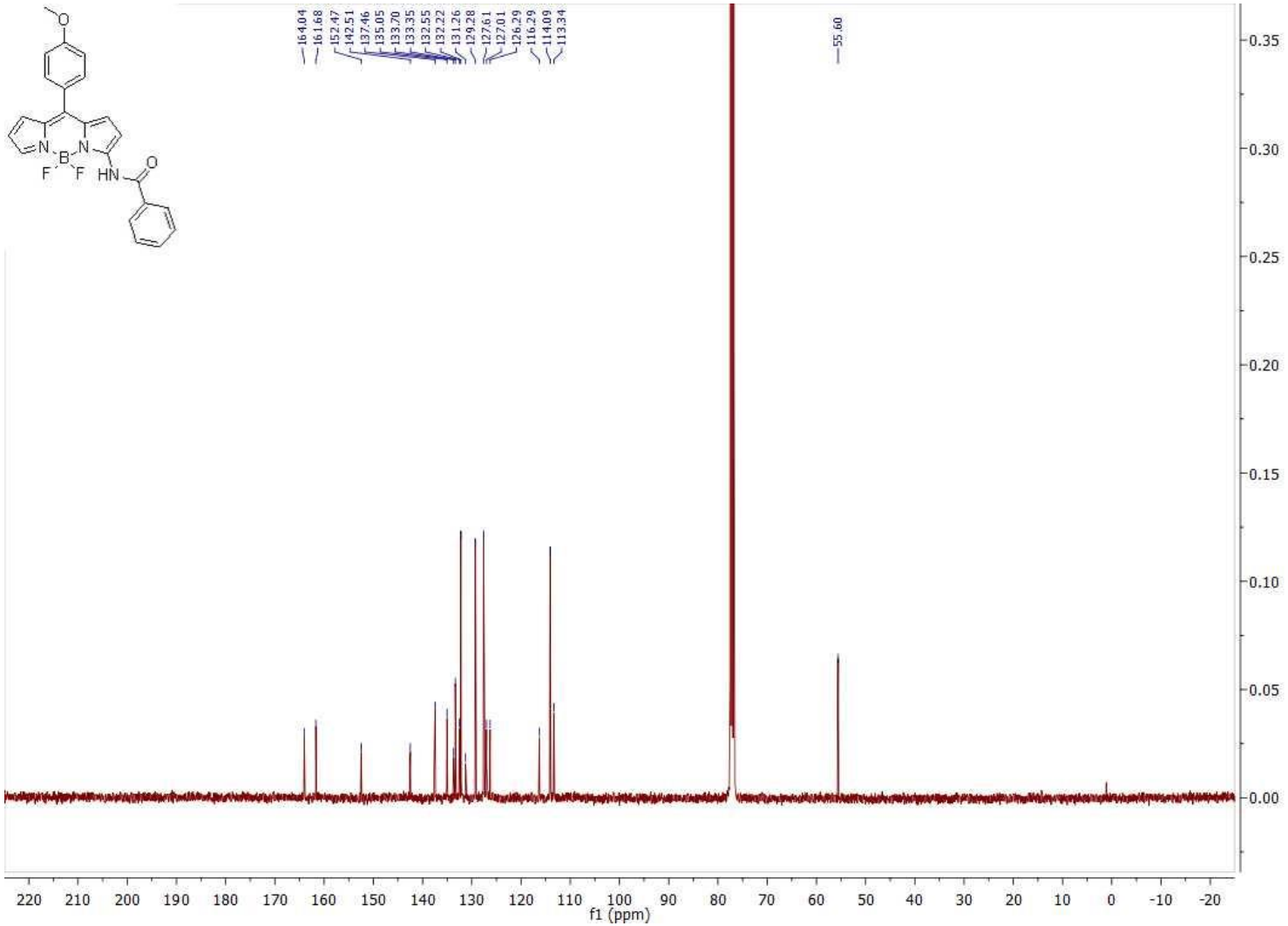
^{13}C NMR (101 MHz, Chloroform-*d*) 5b



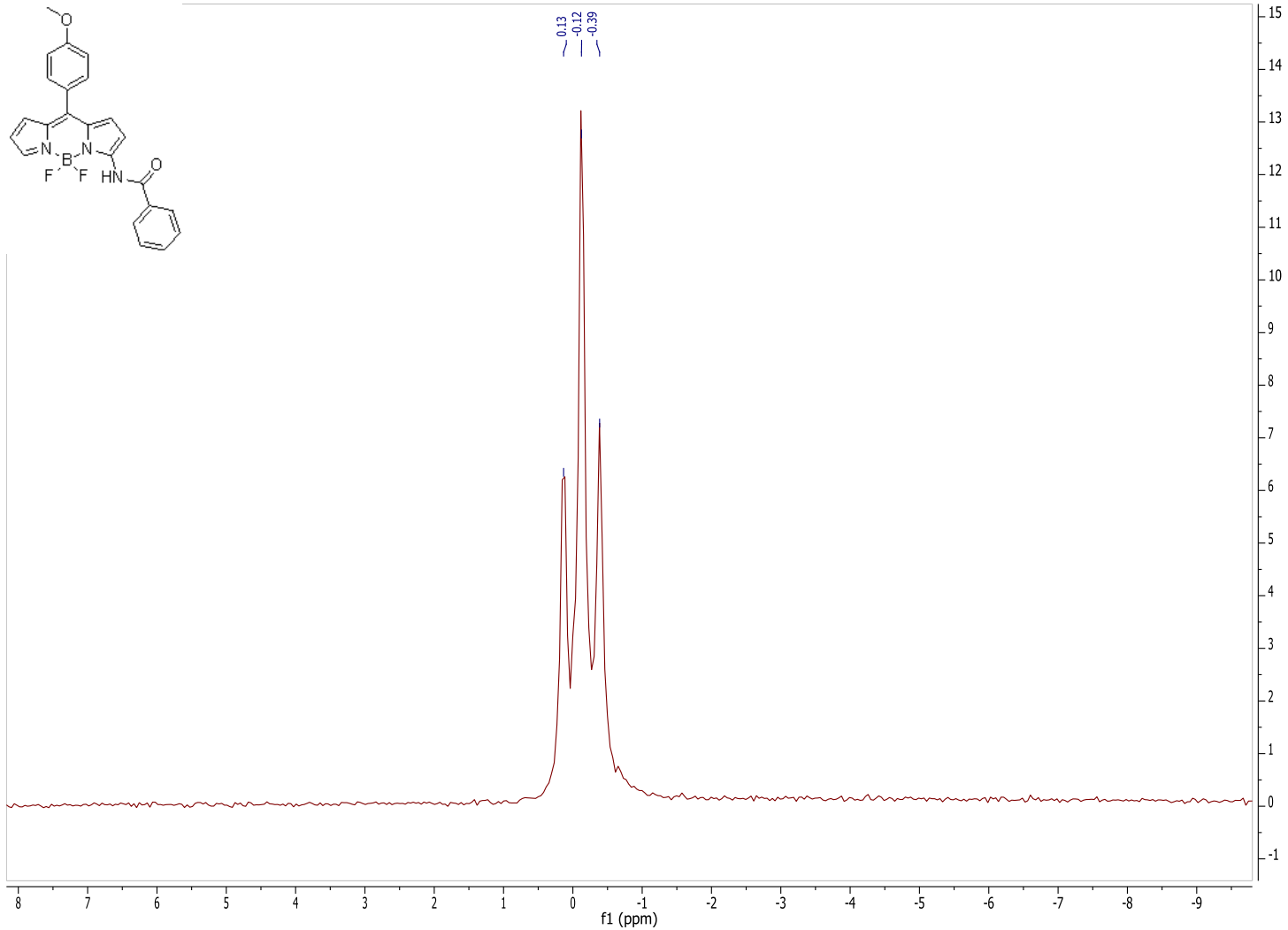
^{1}H NMR (400 MHz, Chloroform-d) 4c



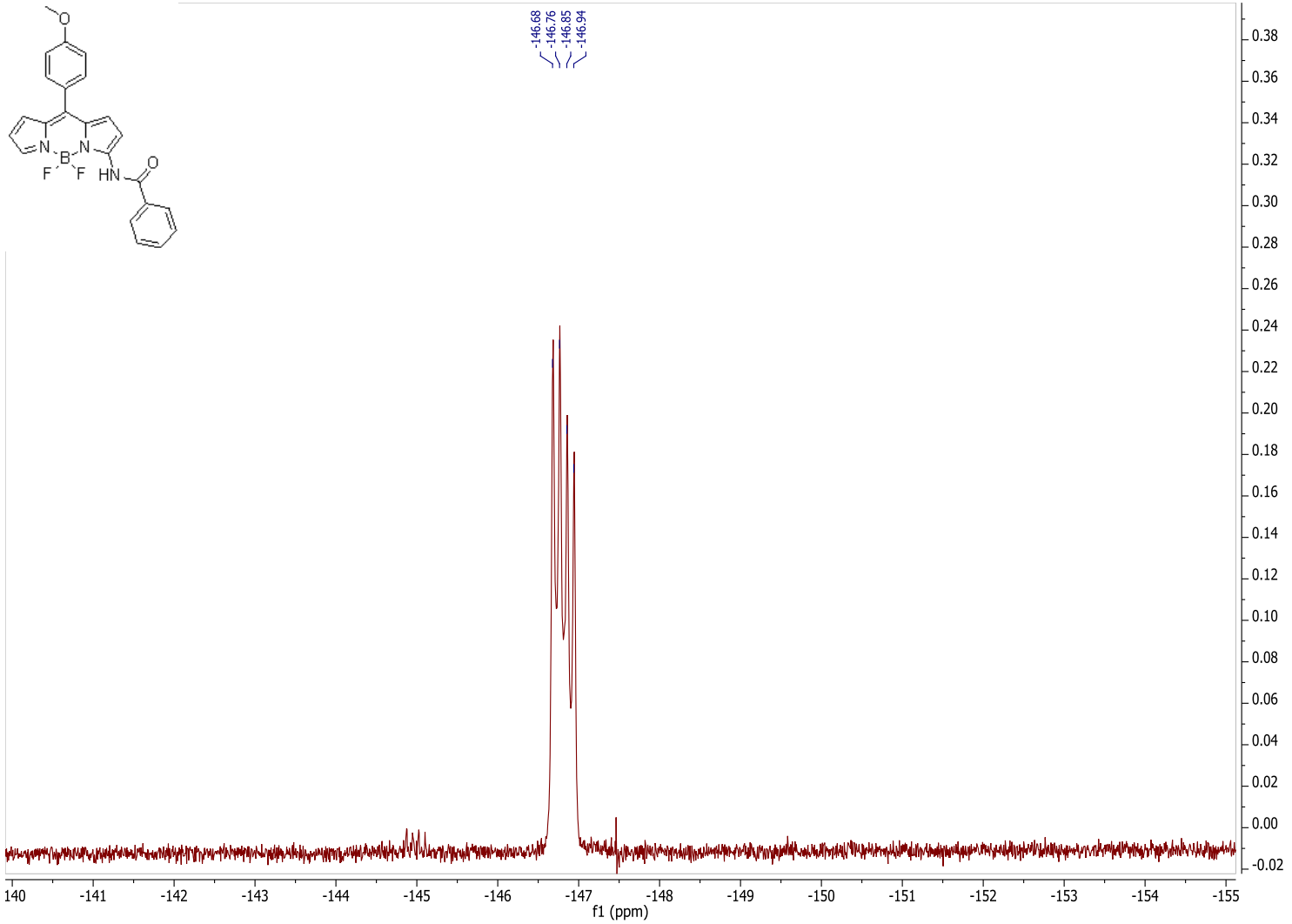
^{13}C NMR (101 MHz, Chloroform-d) 4c



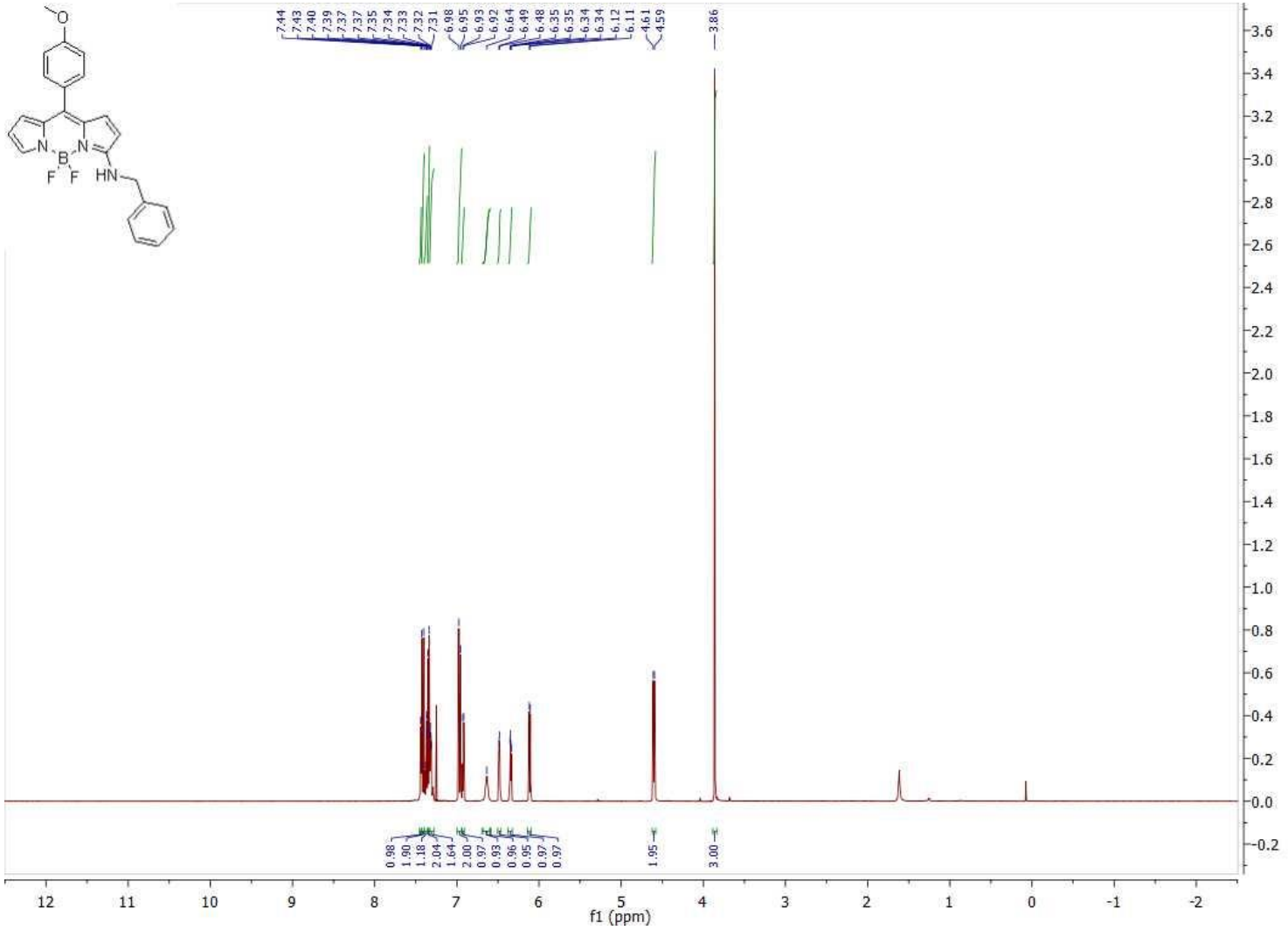
^{11}B NMR (128 MHz, Chloroform-d) 4c



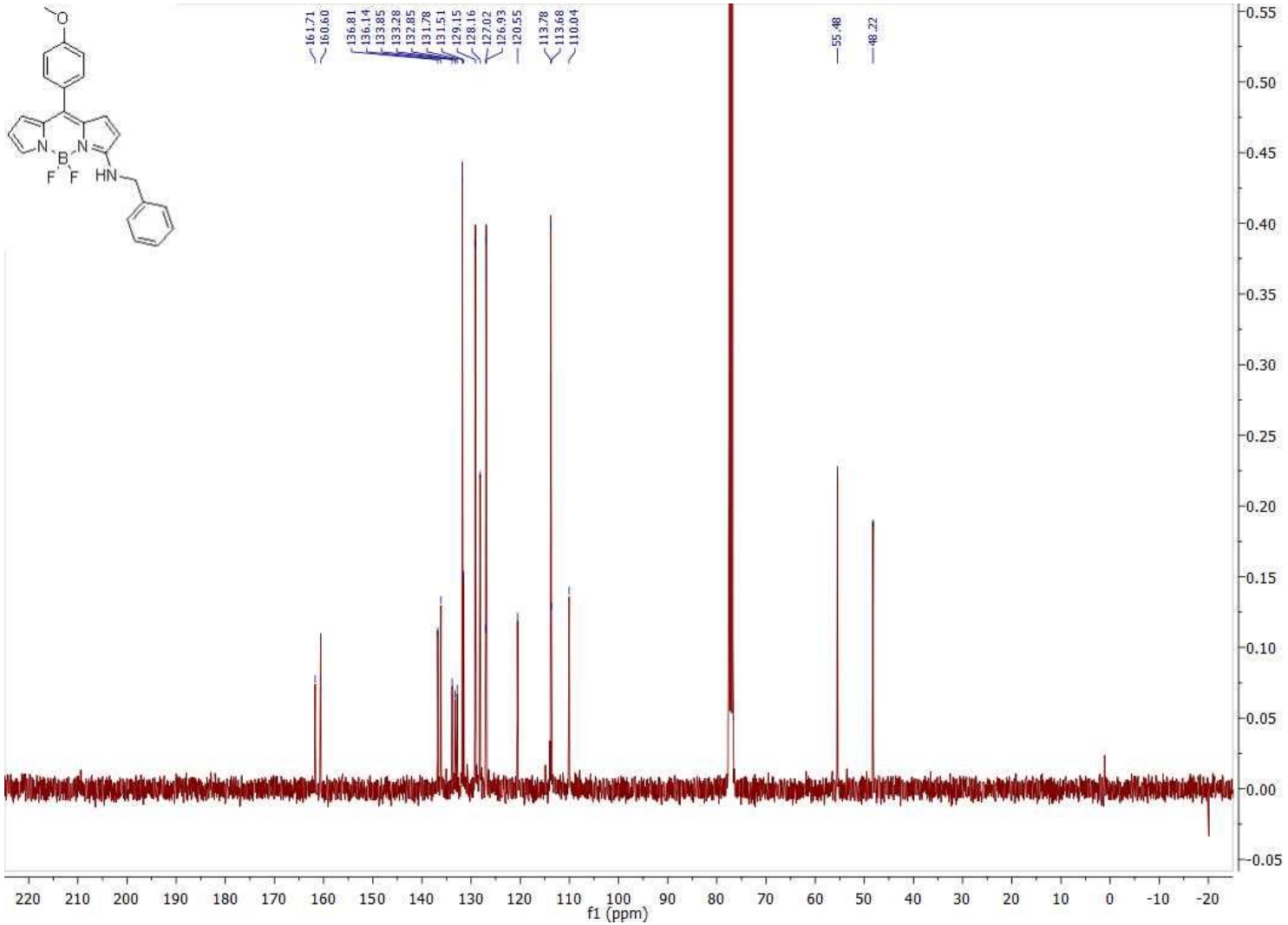
^{19}F NMR (376 MHz, Chloroform-d) 4c



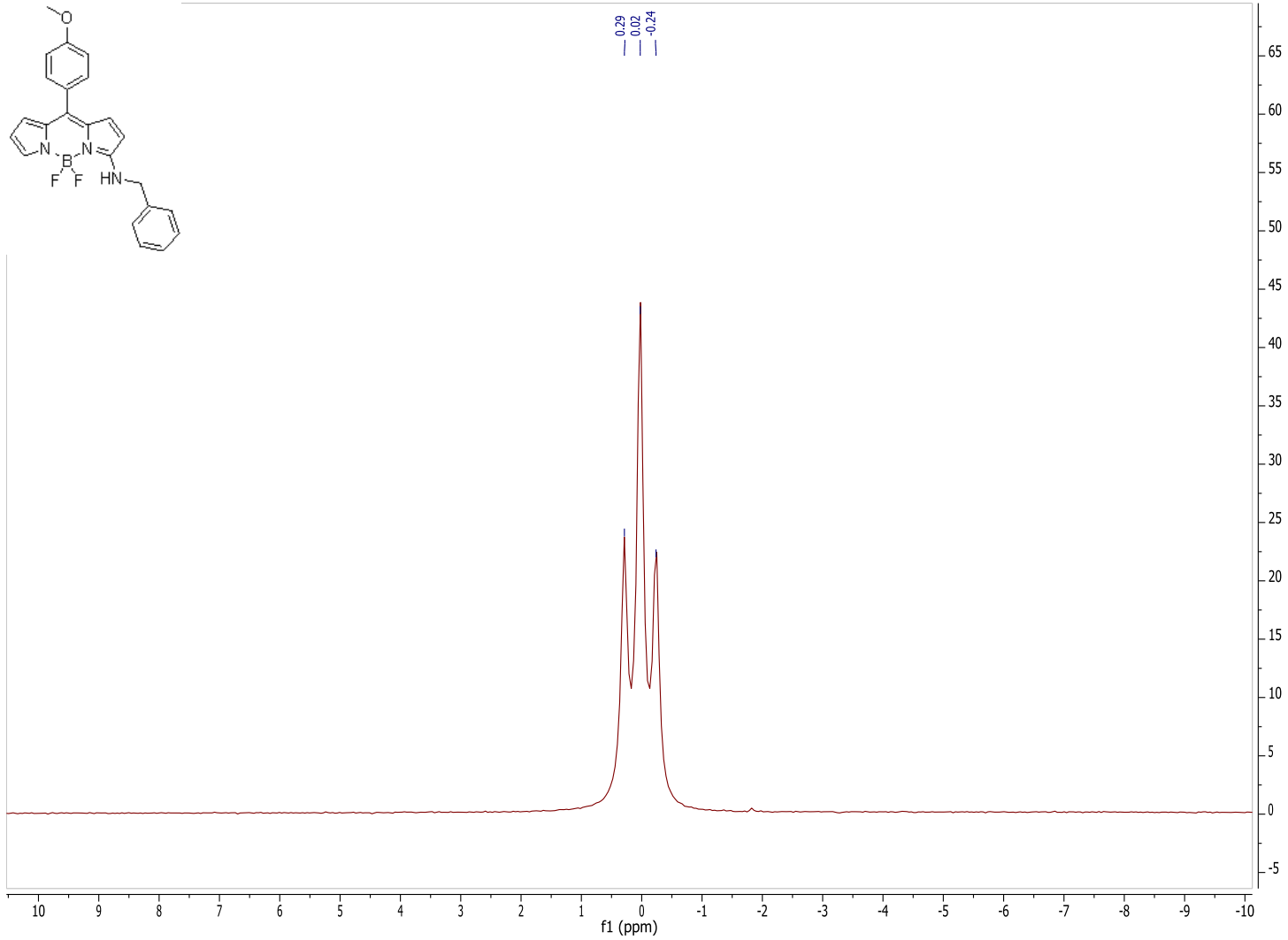
^{1}H NMR (400 MHz, Chloroform-d) 4d



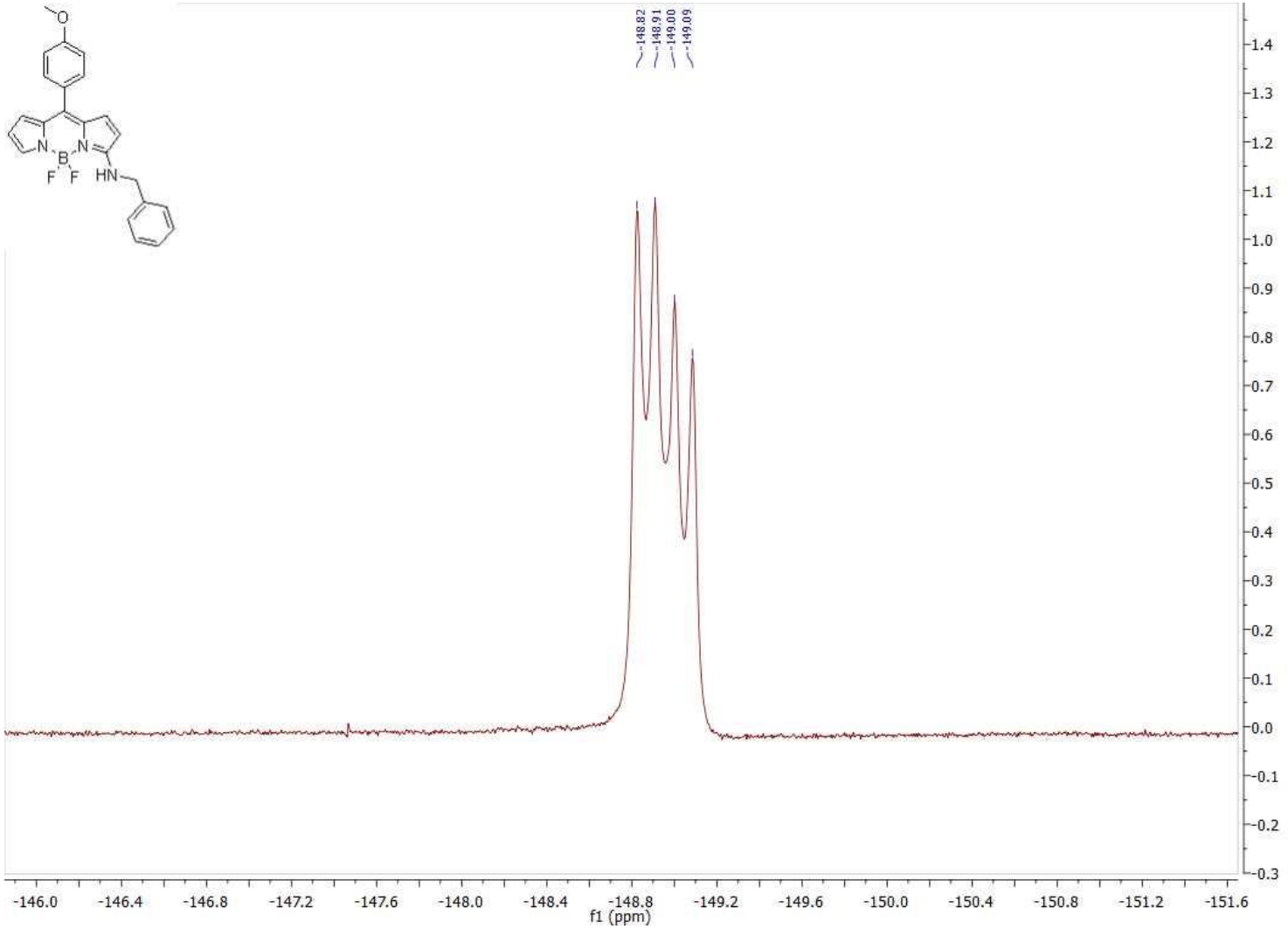
^{13}C NMR (101 MHz, Chloroform-d) 4d



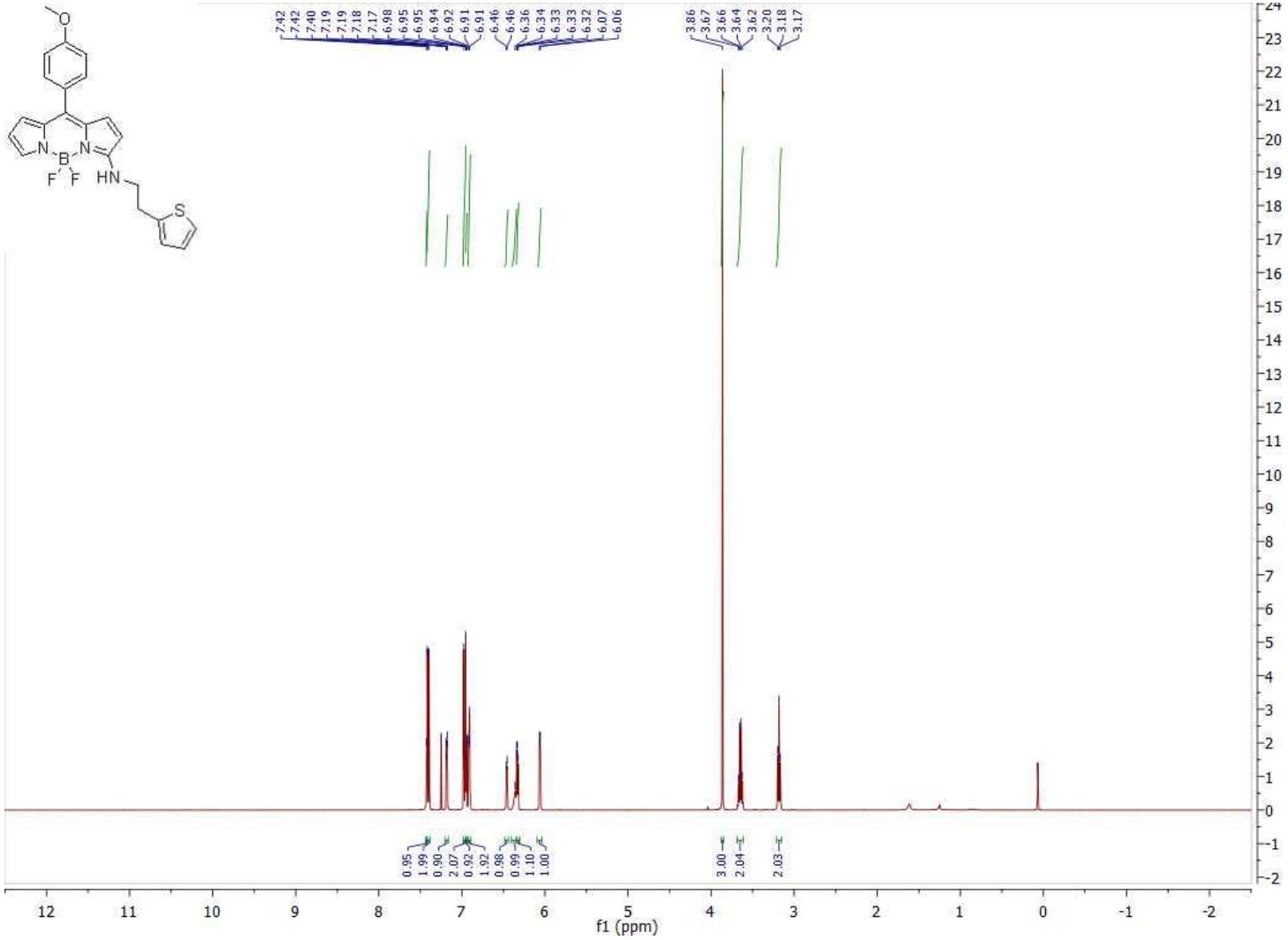
^{11}B NMR (128 MHz, Chloroform-d) 4d



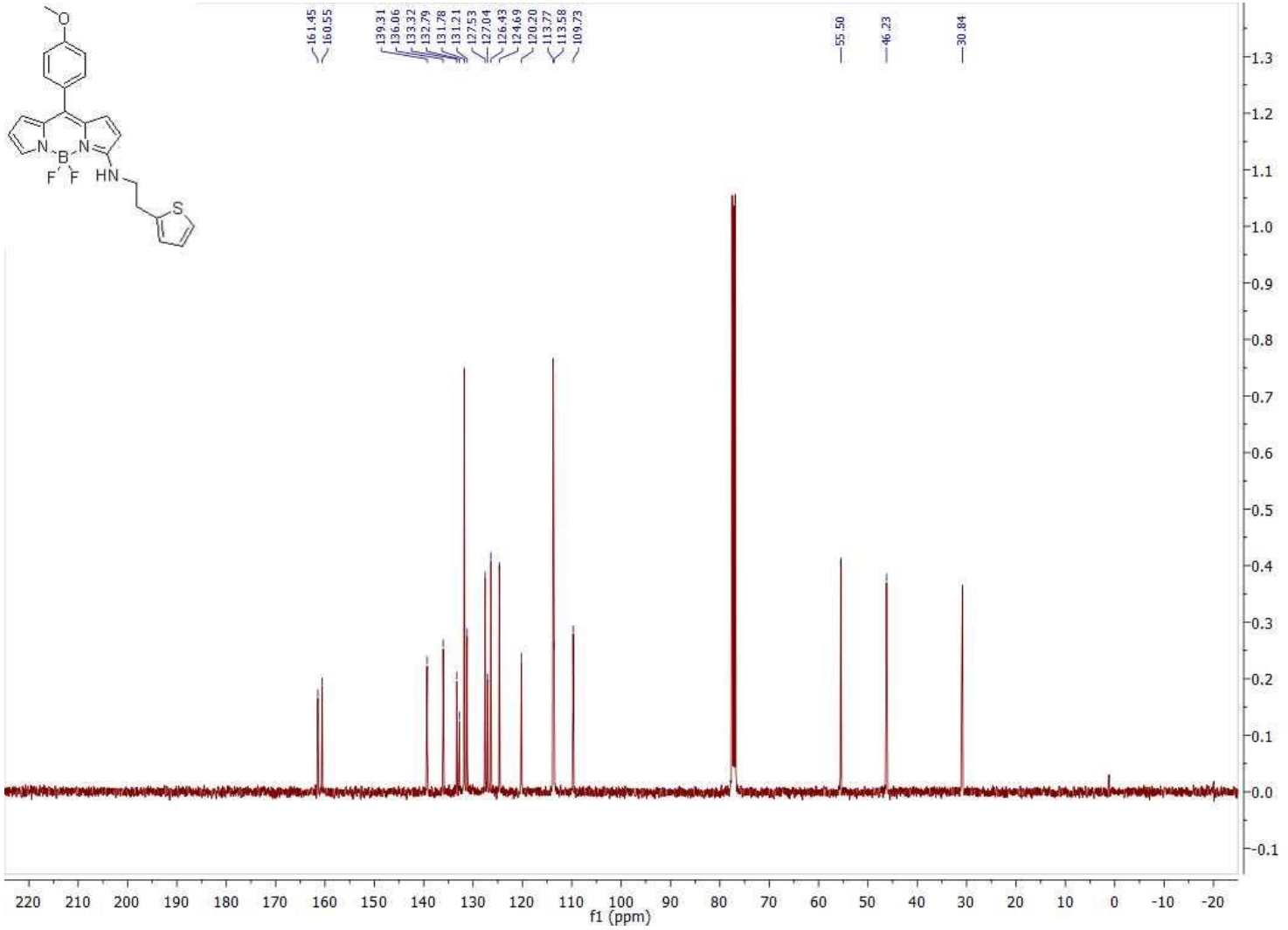
^{19}F NMR (376 MHz, Chloroform-d) 4d



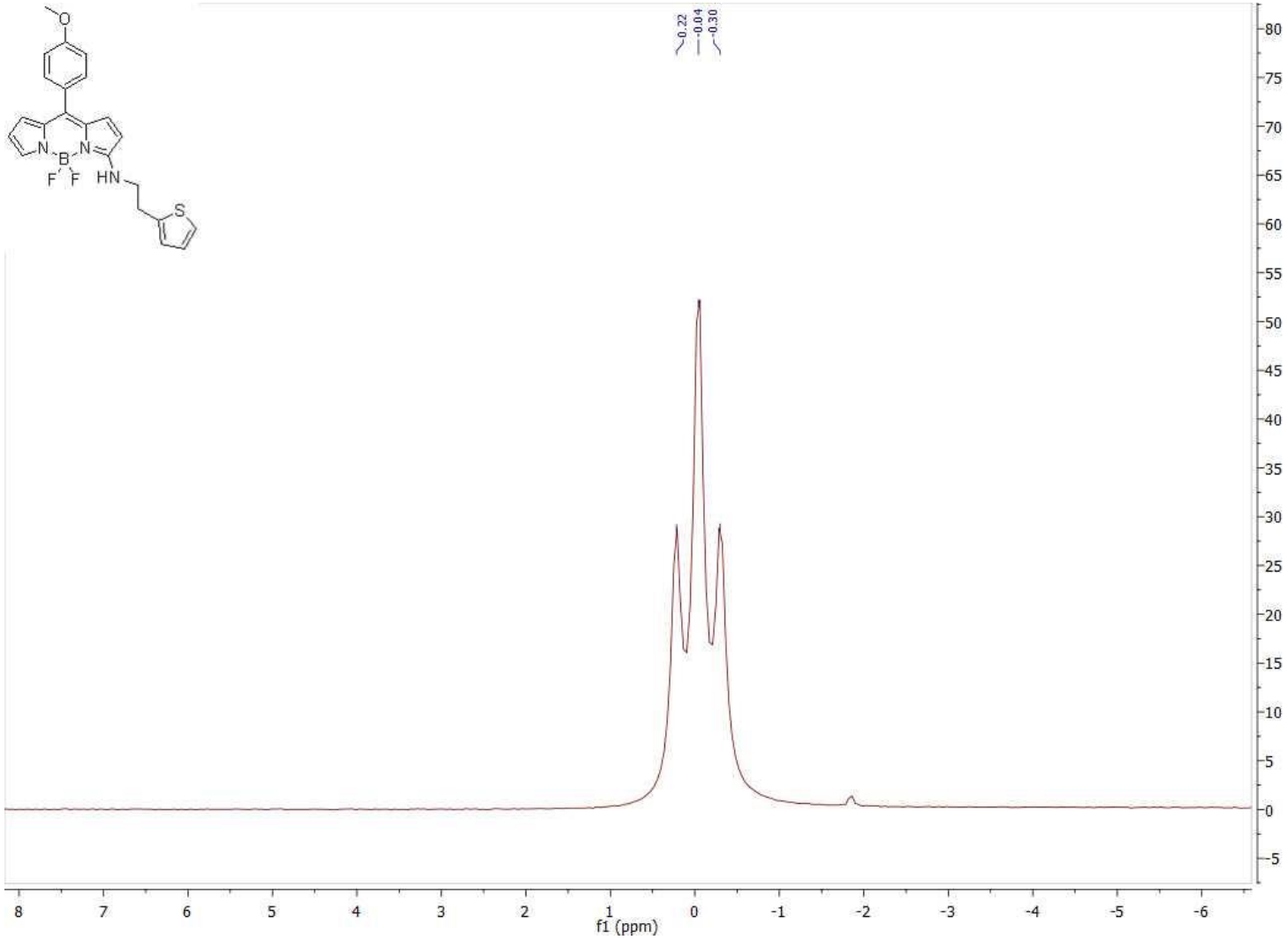
^{1}H NMR (400 MHz, Chloroform-d) 4e



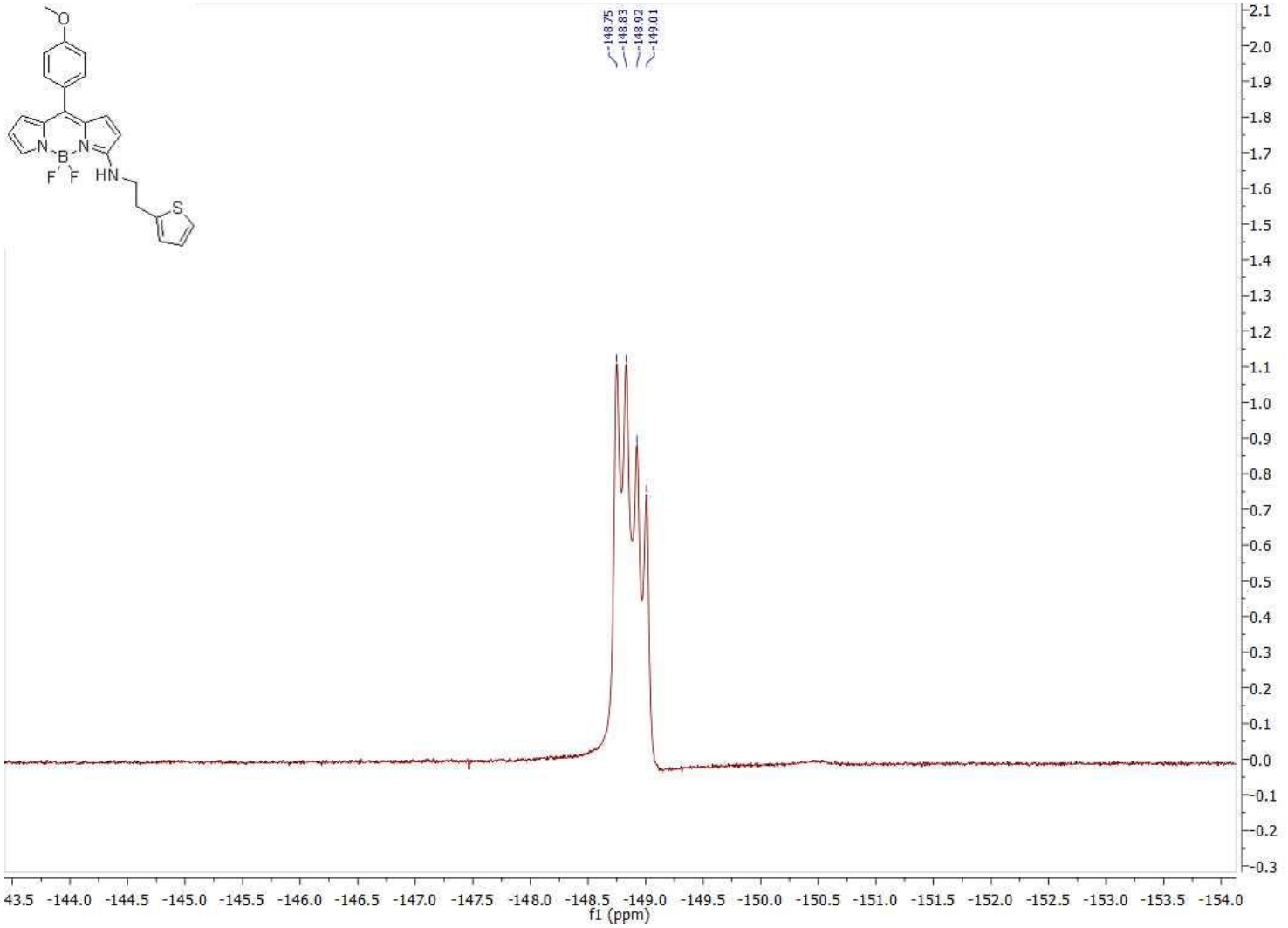
^{13}C NMR (101 MHz, Chloroform-d) 4e



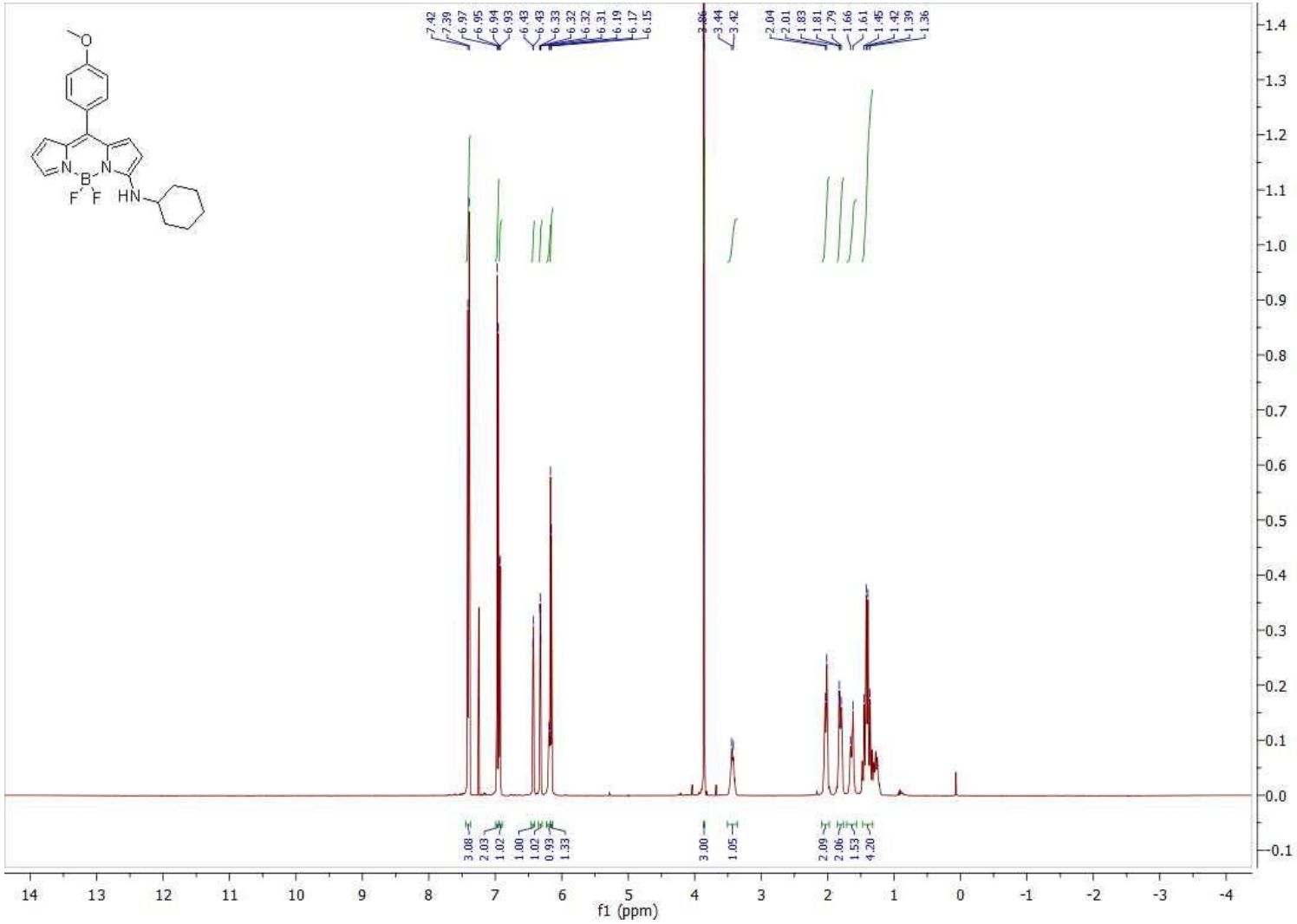
^{11}B NMR (128 MHz, Chloroform-d) 4e



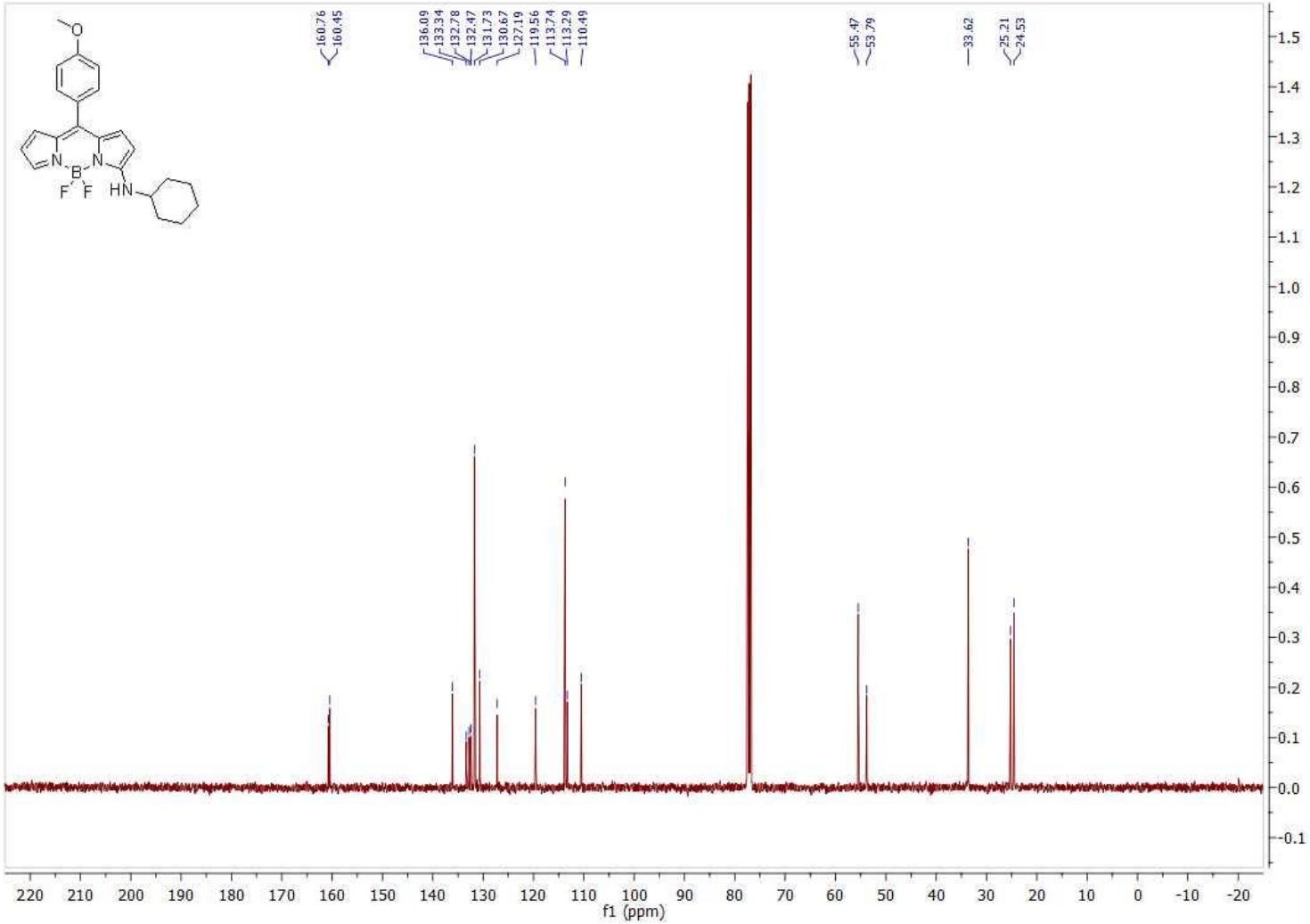
^{19}F NMR (376 MHz, Chloroform-d) 4e



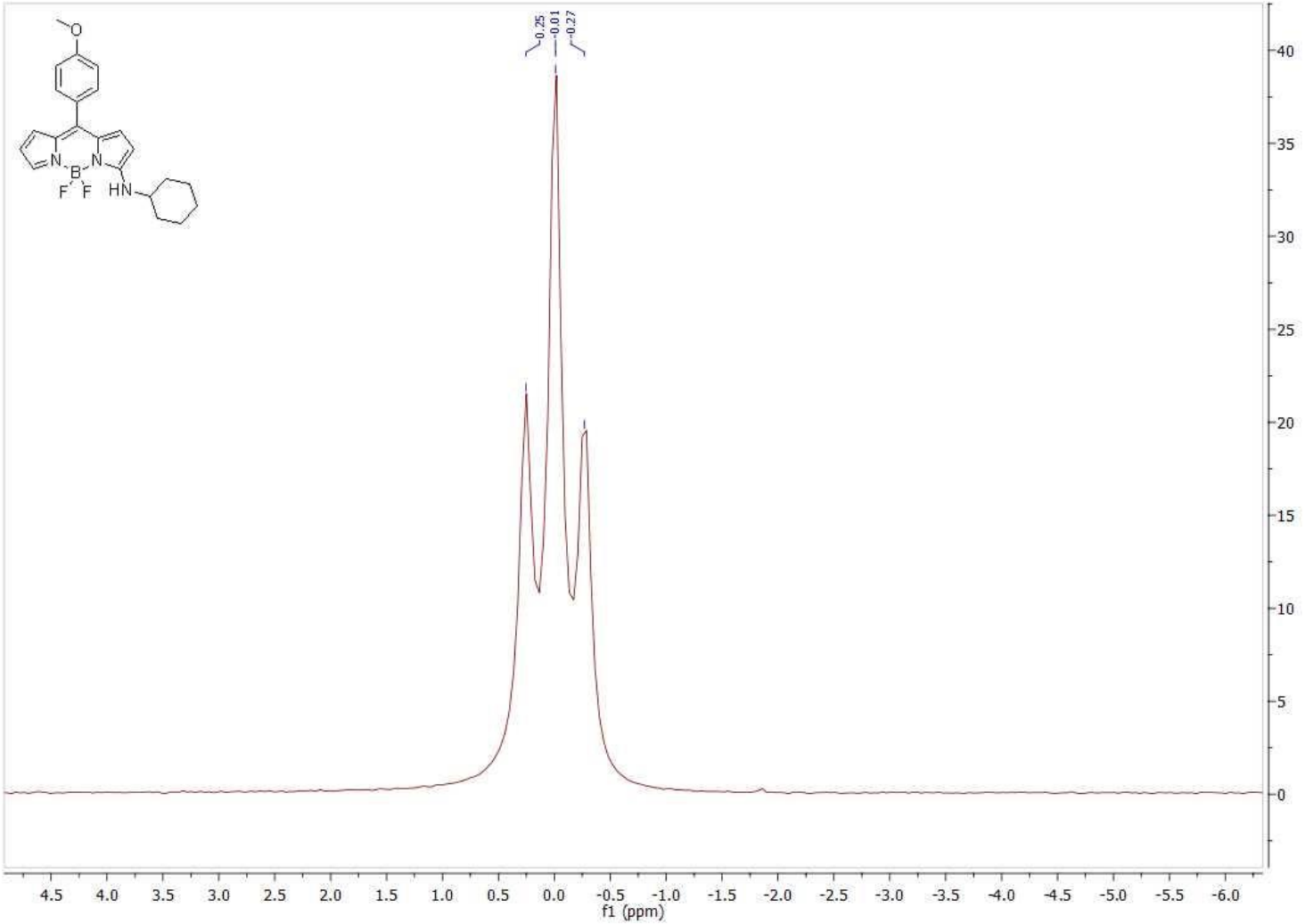
^{1}H NMR (400 MHz, Chloroform-d) 4f



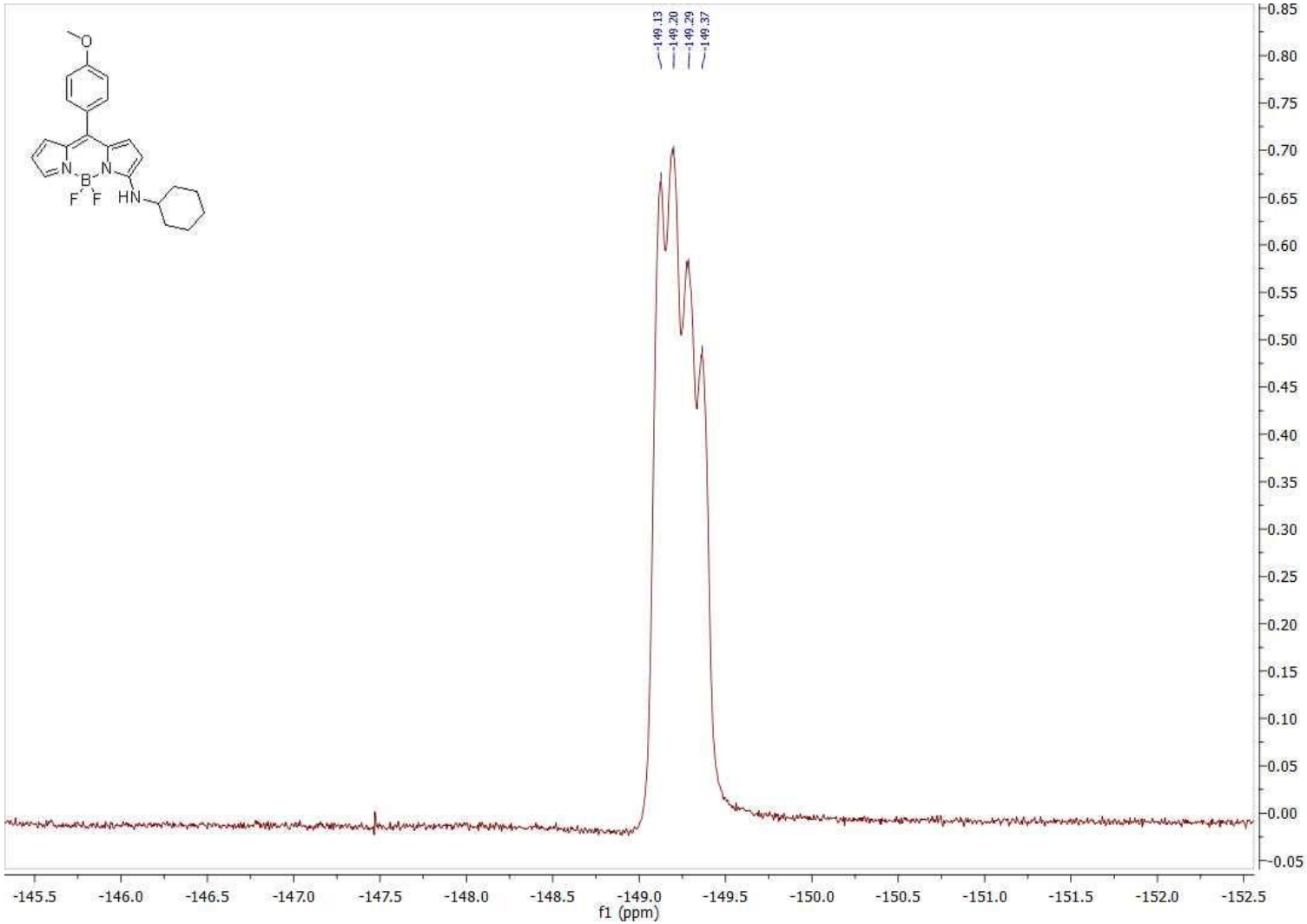
^{13}C NMR (101 MHz, Chloroform-d) 4f



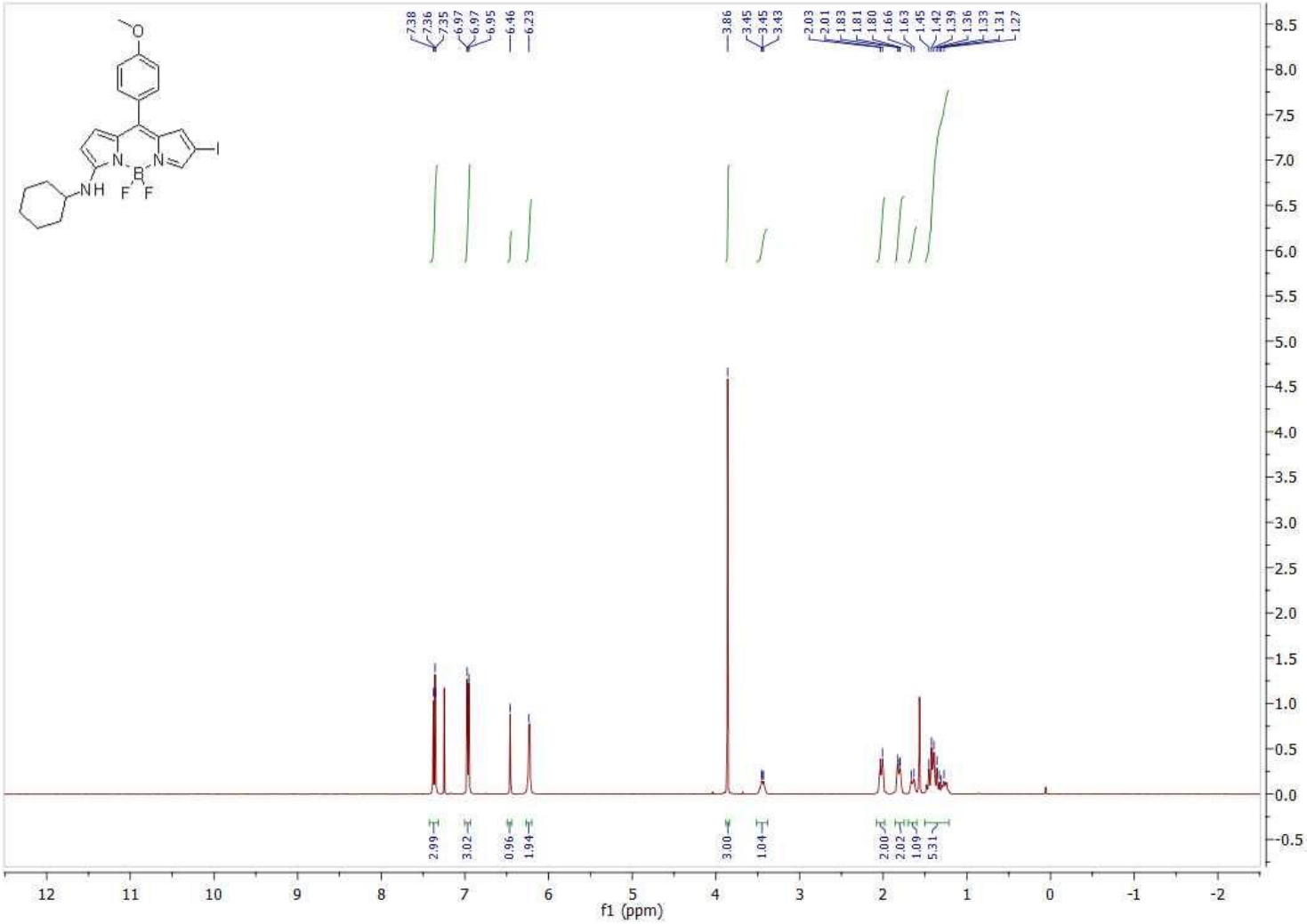
^{11}B NMR (128 MHz, Chloroform-d) 4f



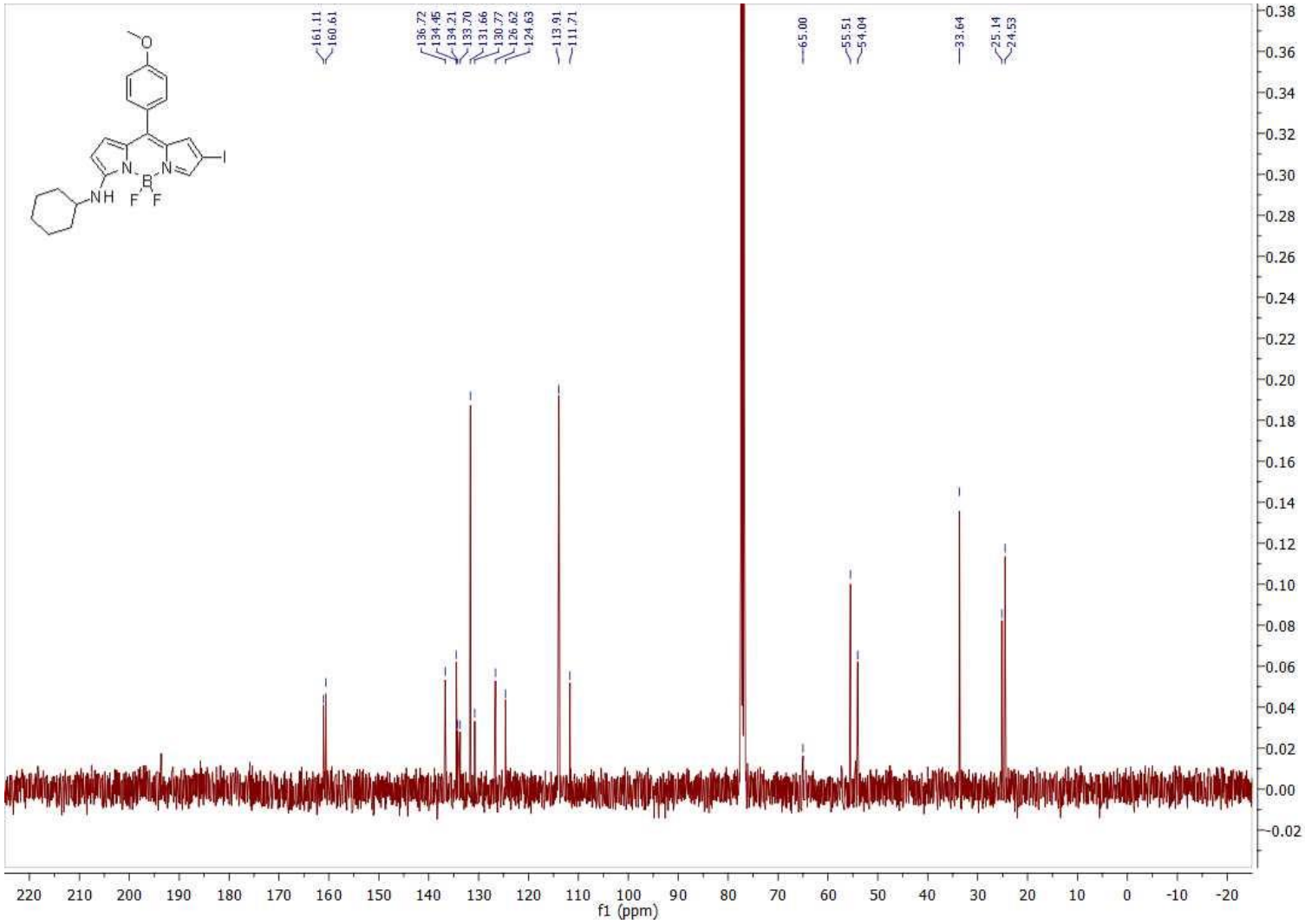
^{19}F NMR (376 MHz, Chloroform-d) 4f



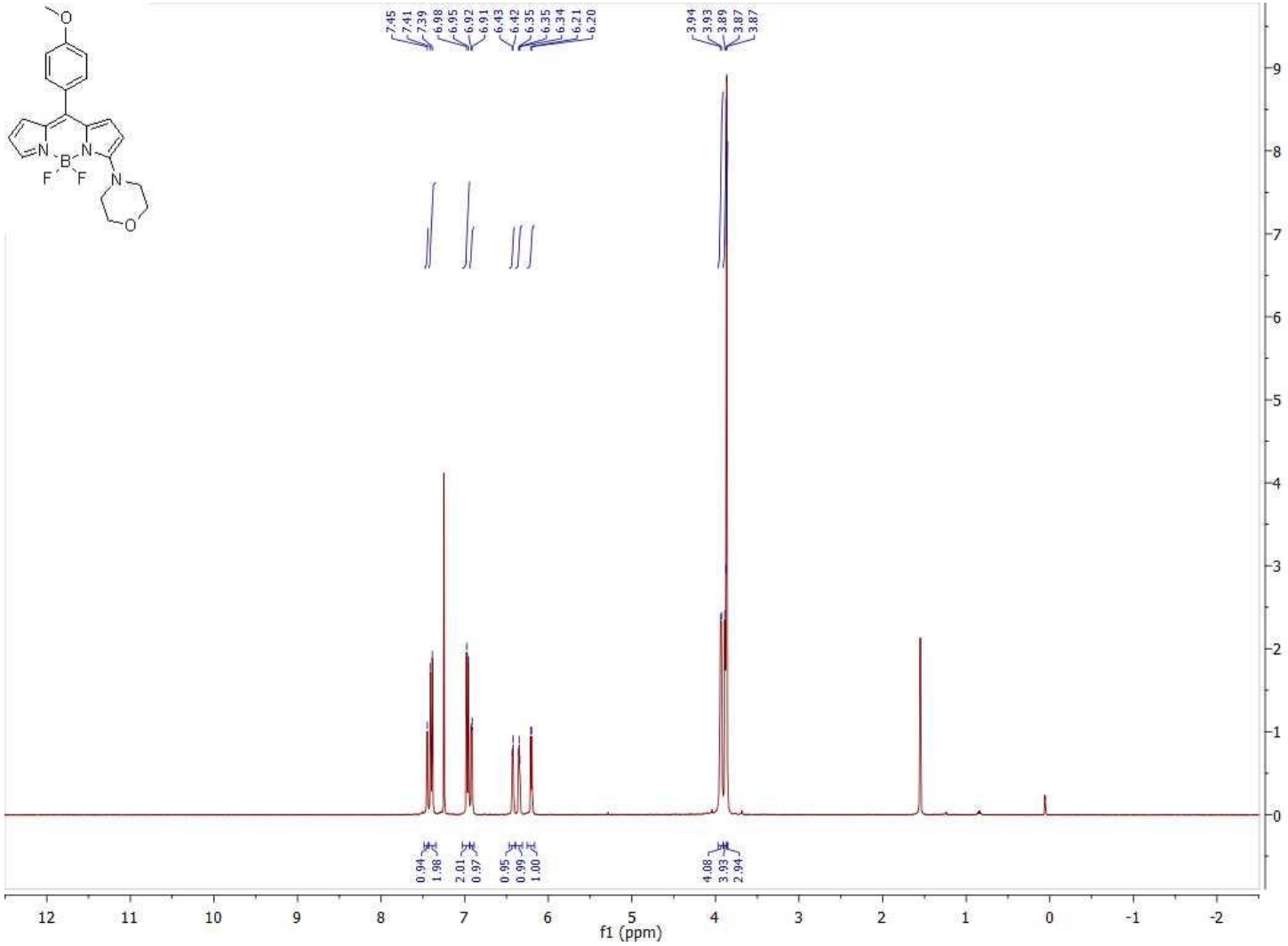
^{1}H NMR (400 MHz, Chloroform-d) 5f



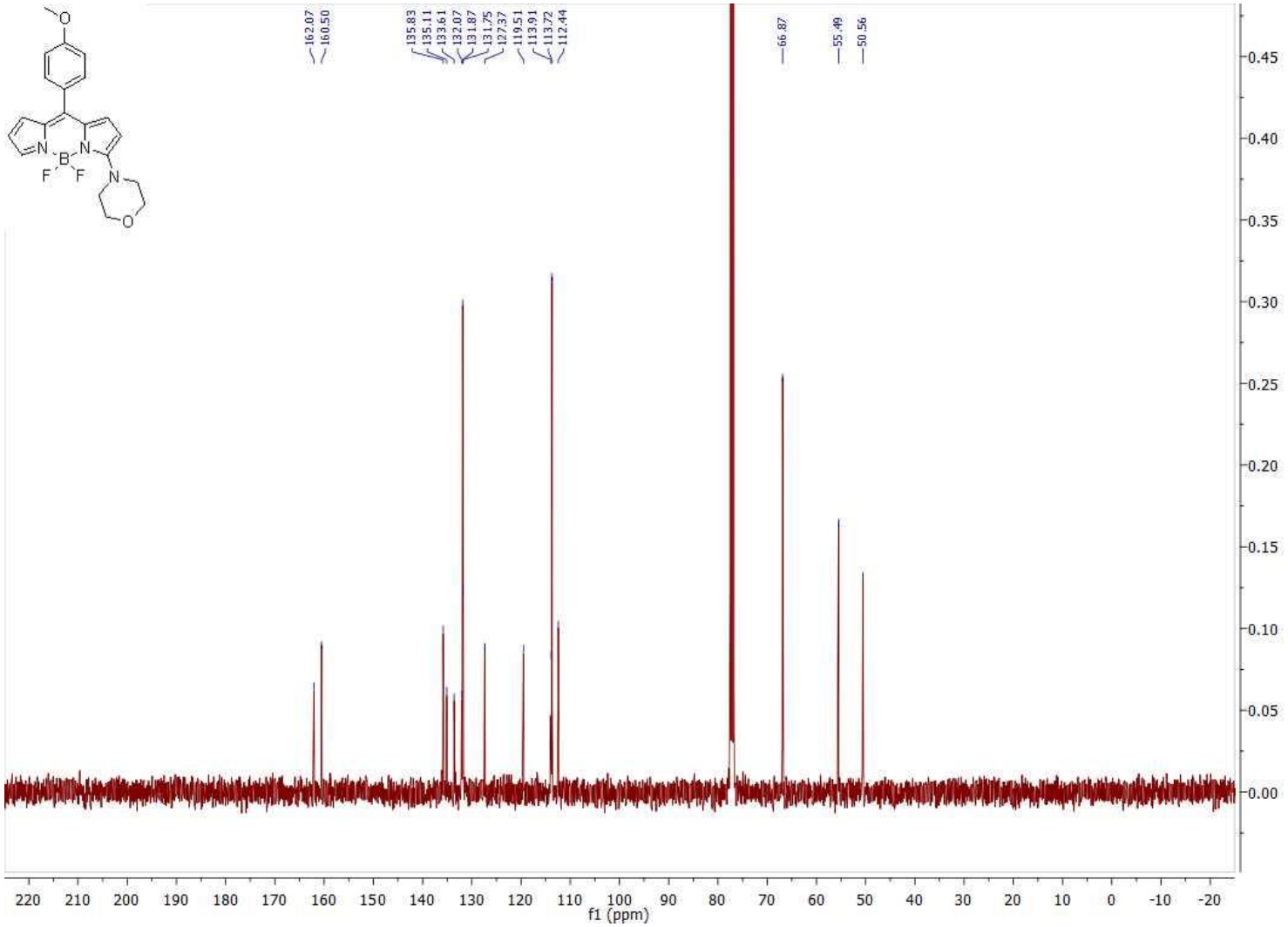
^{13}C NMR (101 MHz, Chloroform-d) 5f



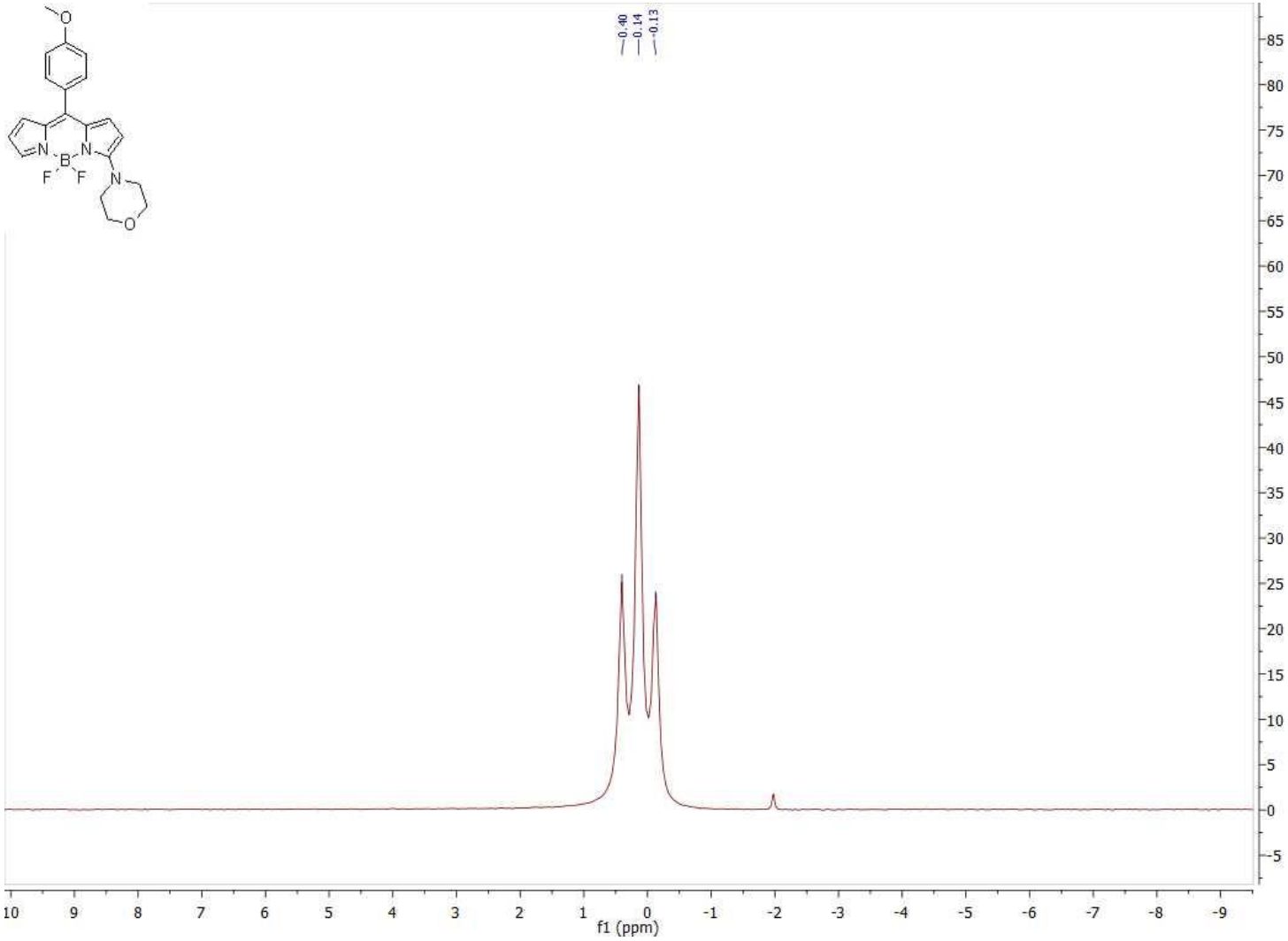
^{1}H NMR (400 MHz, Chloroform-d) 4g



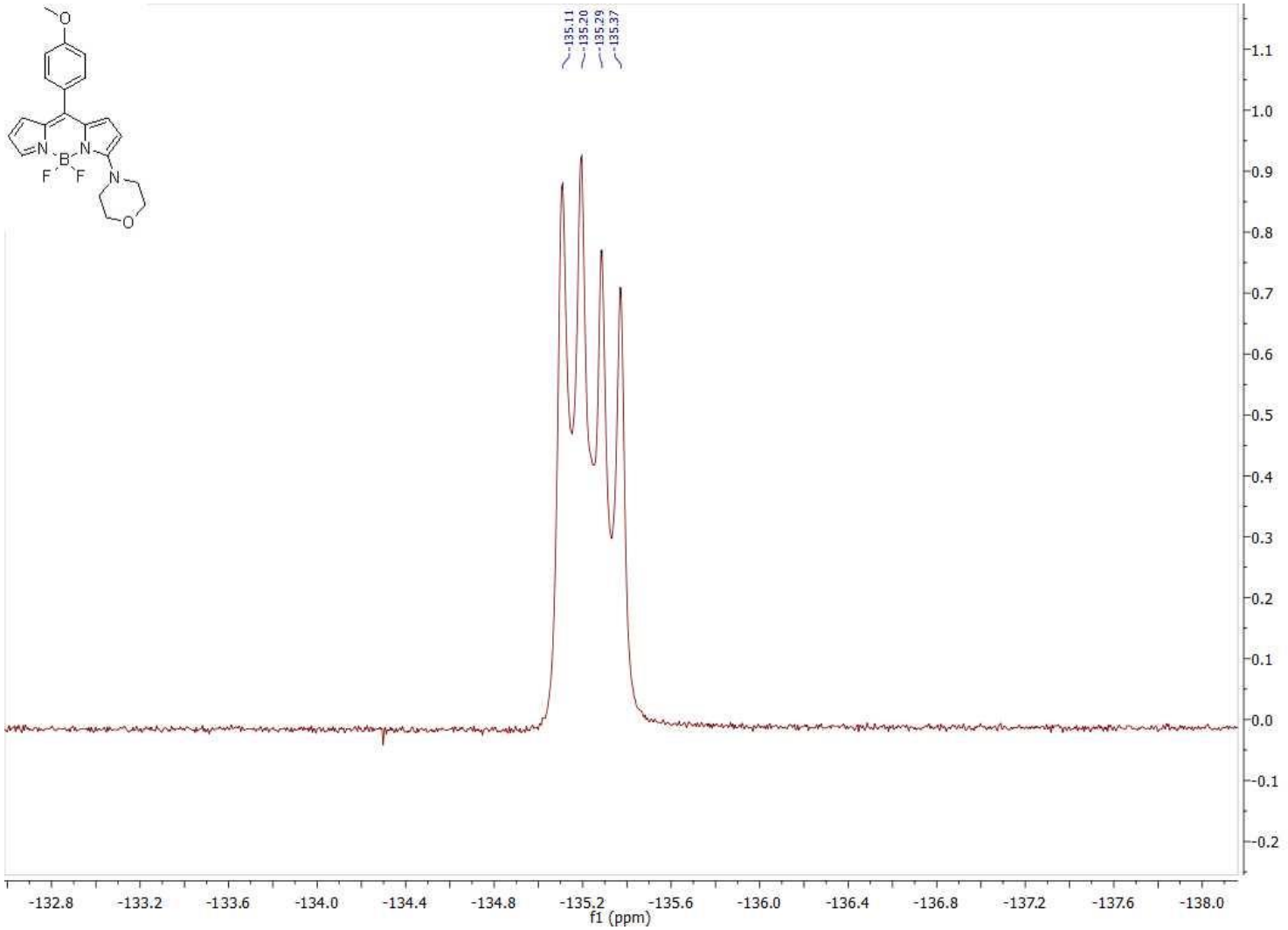
^{13}C NMR (101 MHz, Chloroform-d) 4g



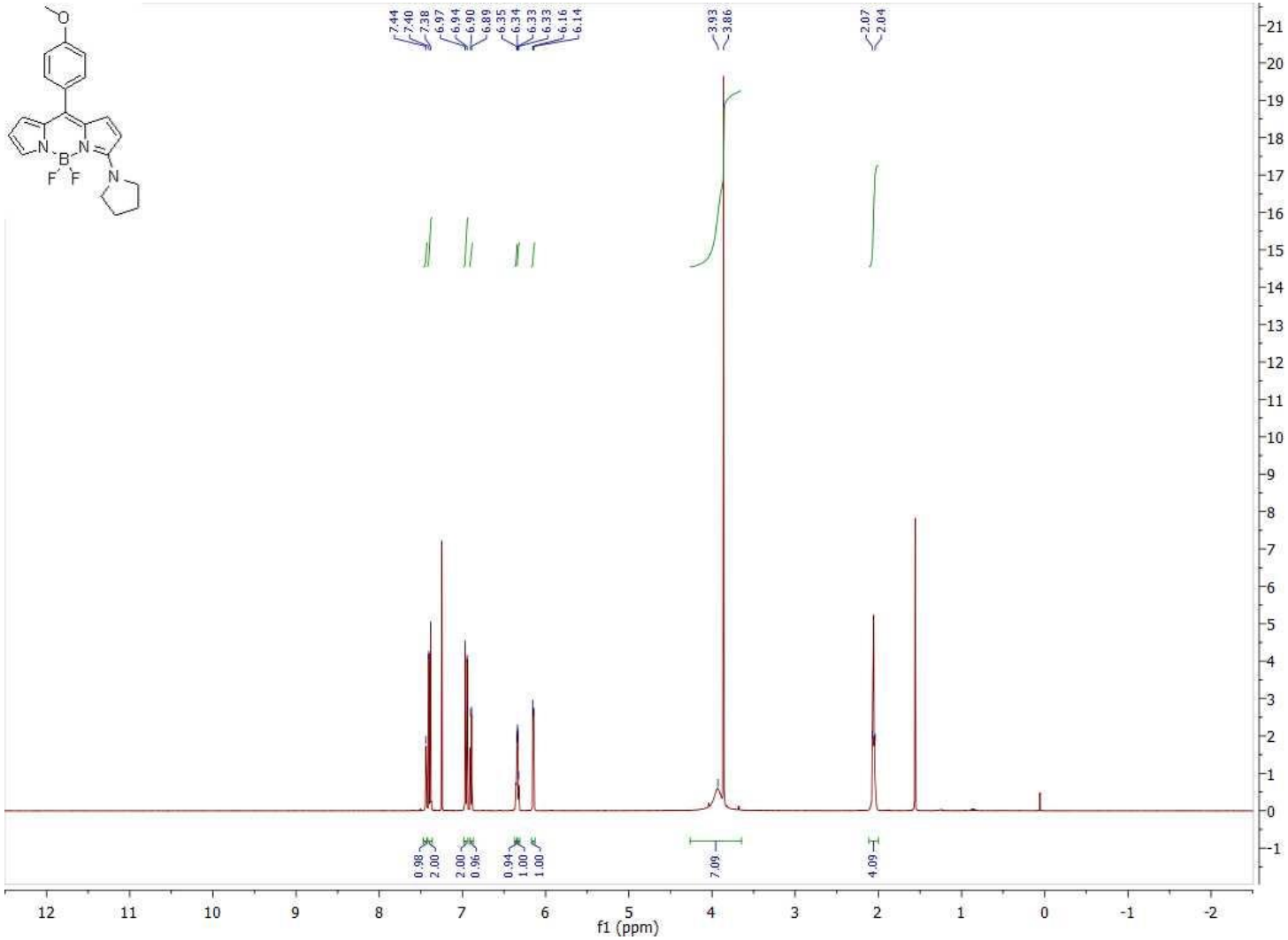
^{11}B NMR (128 MHz, Chloroform-d) 4g



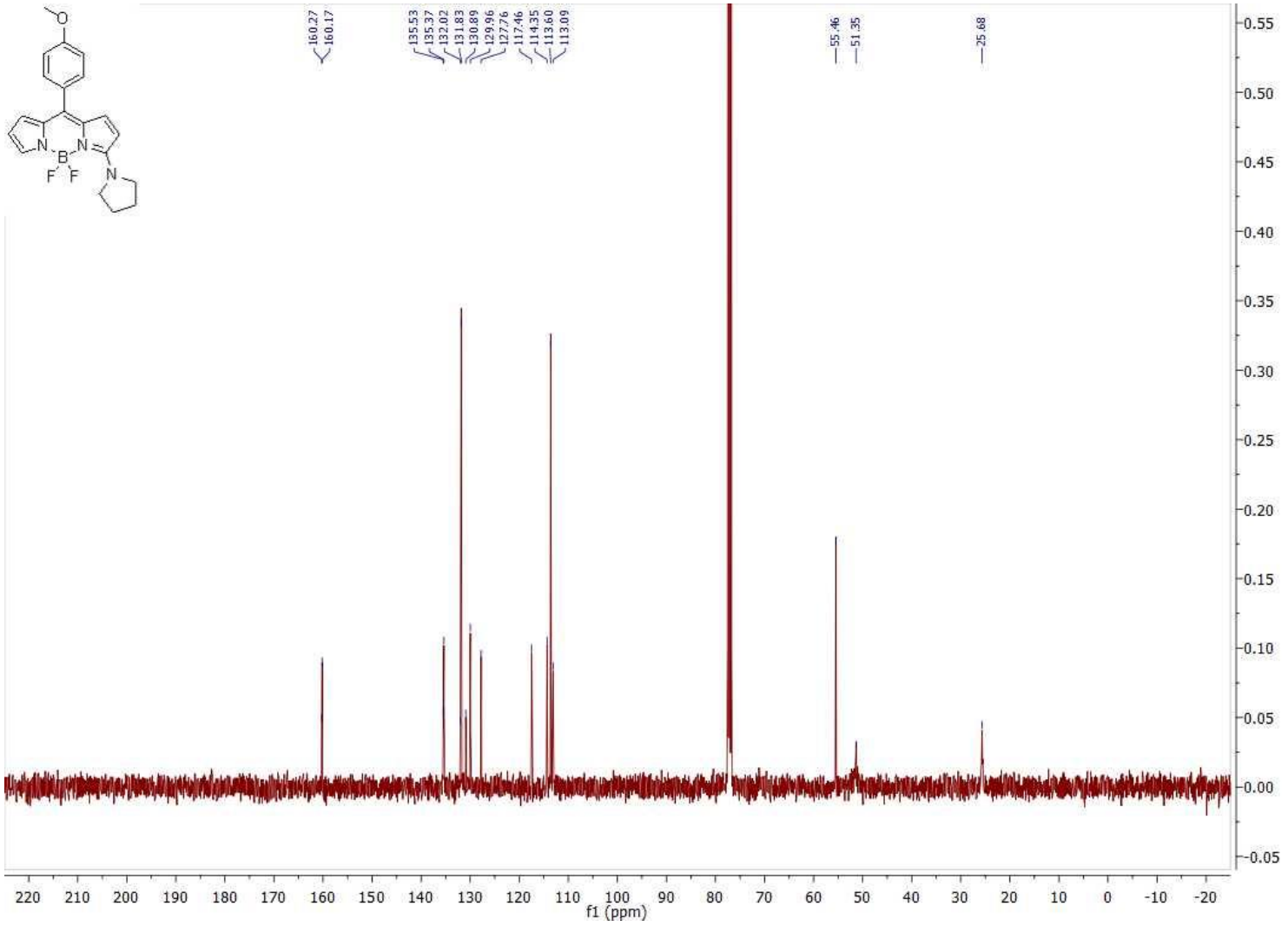
^{19}F NMR (376 MHz, Chloroform-d) 4g



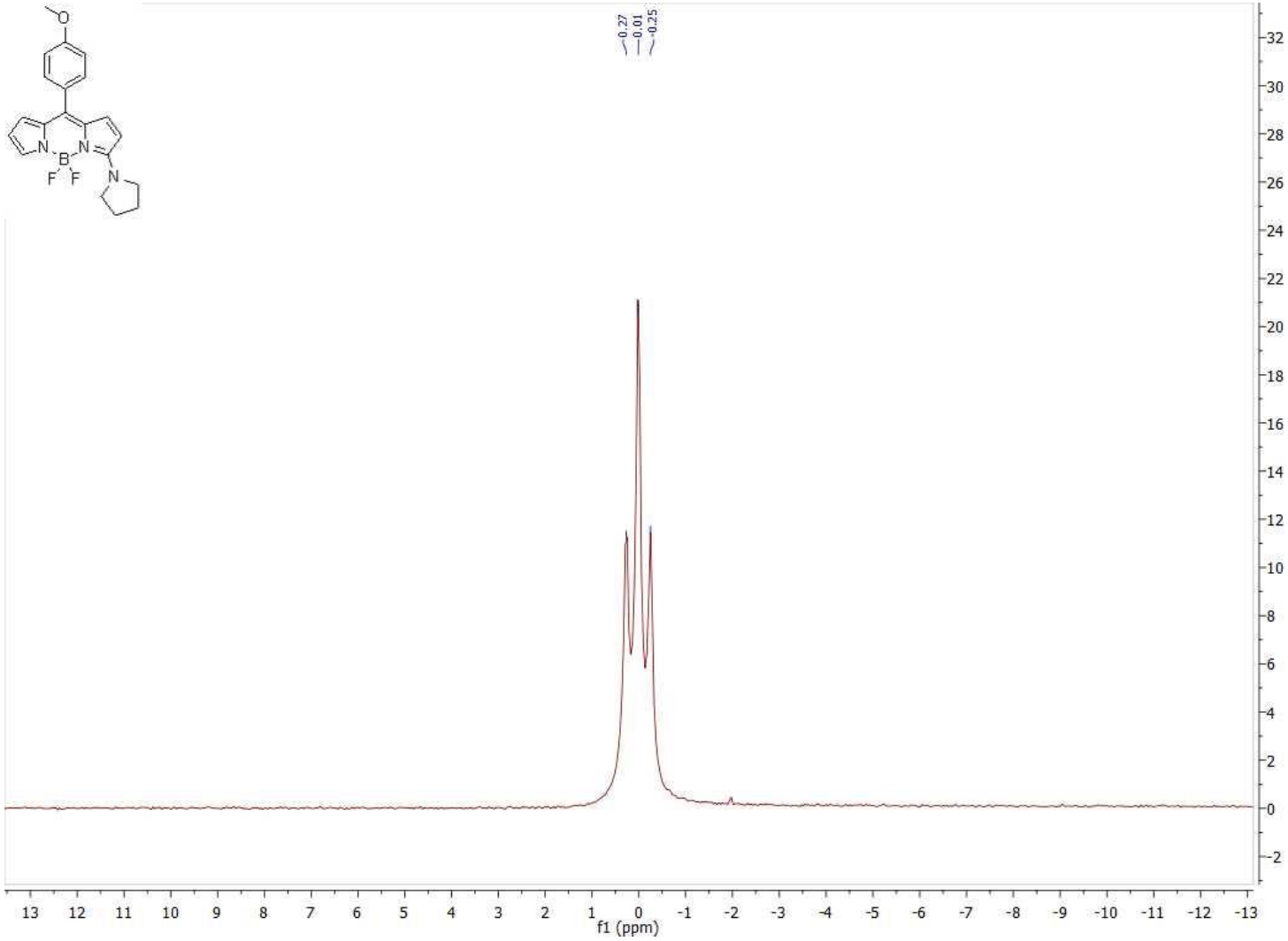
^{1}H NMR (400 MH, Chloroform-d) 4h



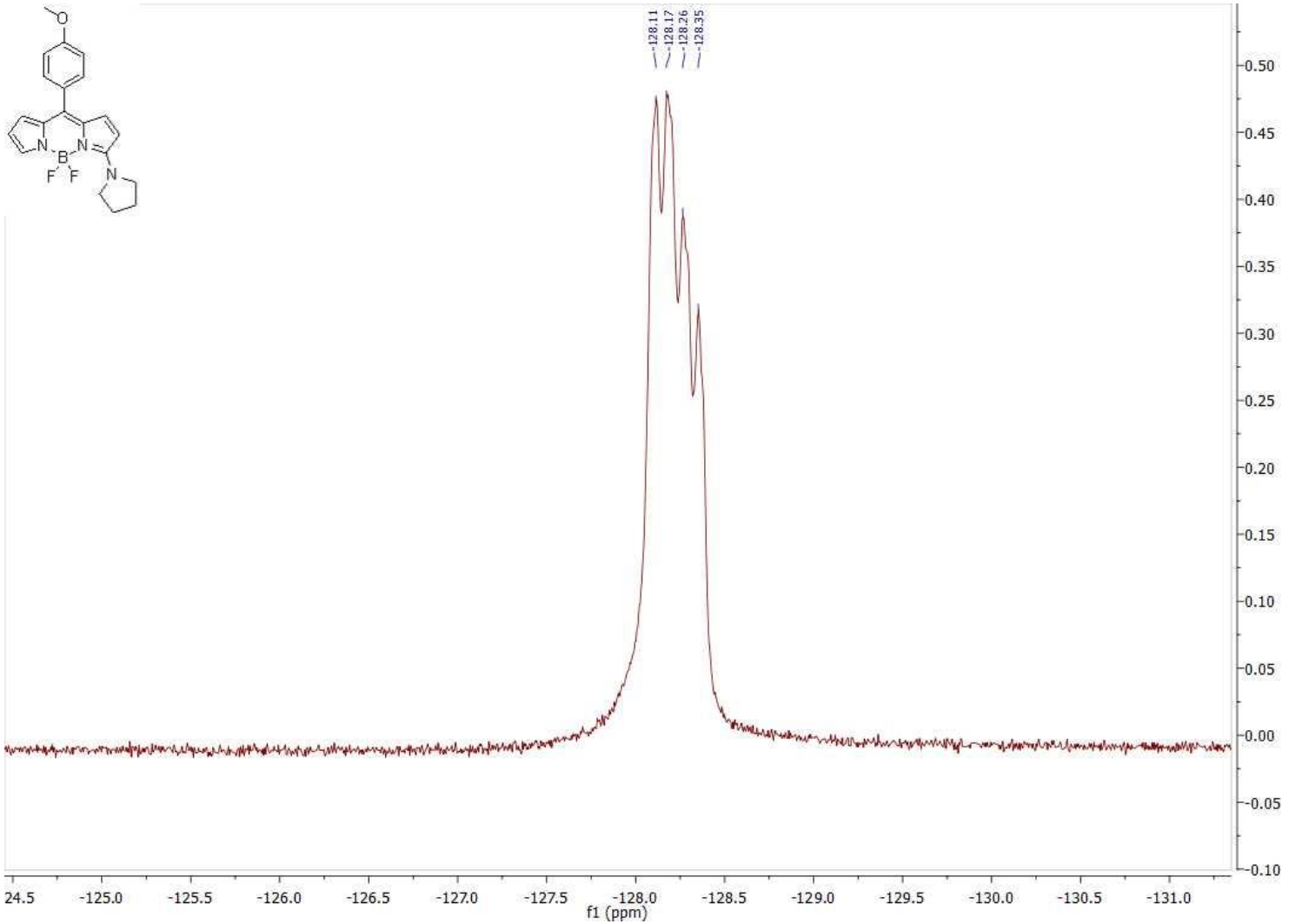
^{13}C NMR (101 MHz, Chloroform-d) 4h



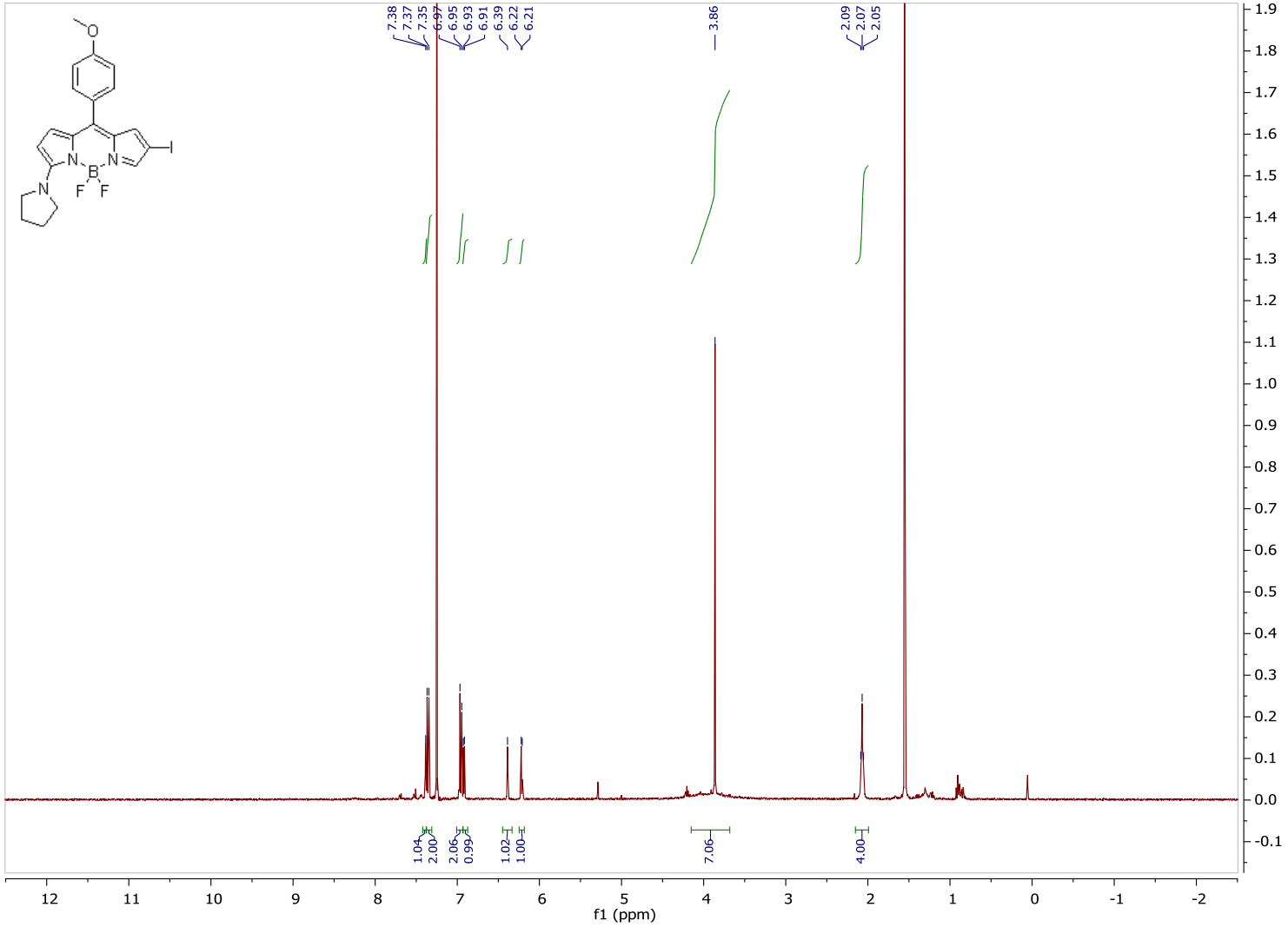
^{1}B NMR (128 MHz, Chloroform-d) 4h



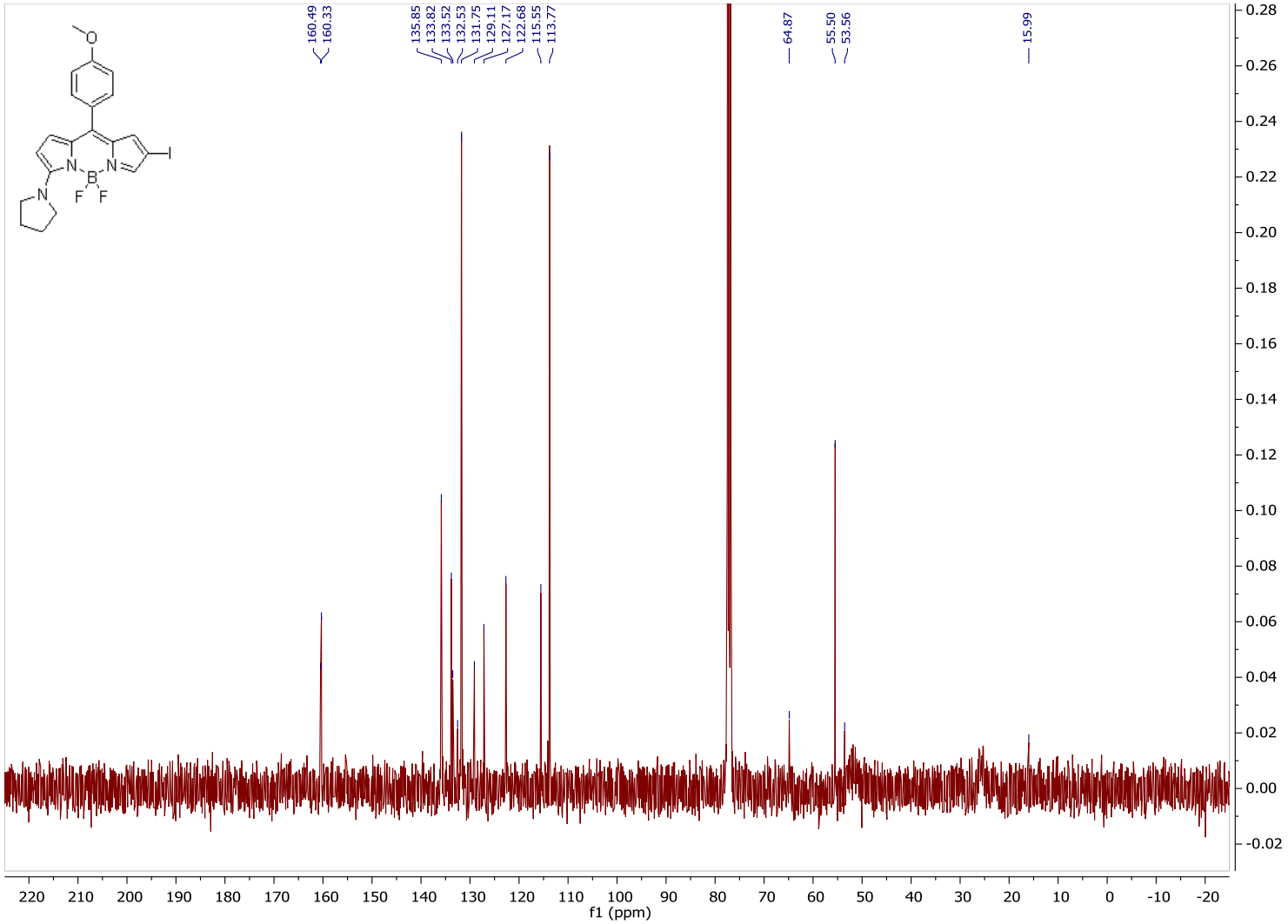
^{19}F NMR (376 MHz, Chloroform-d) 4h



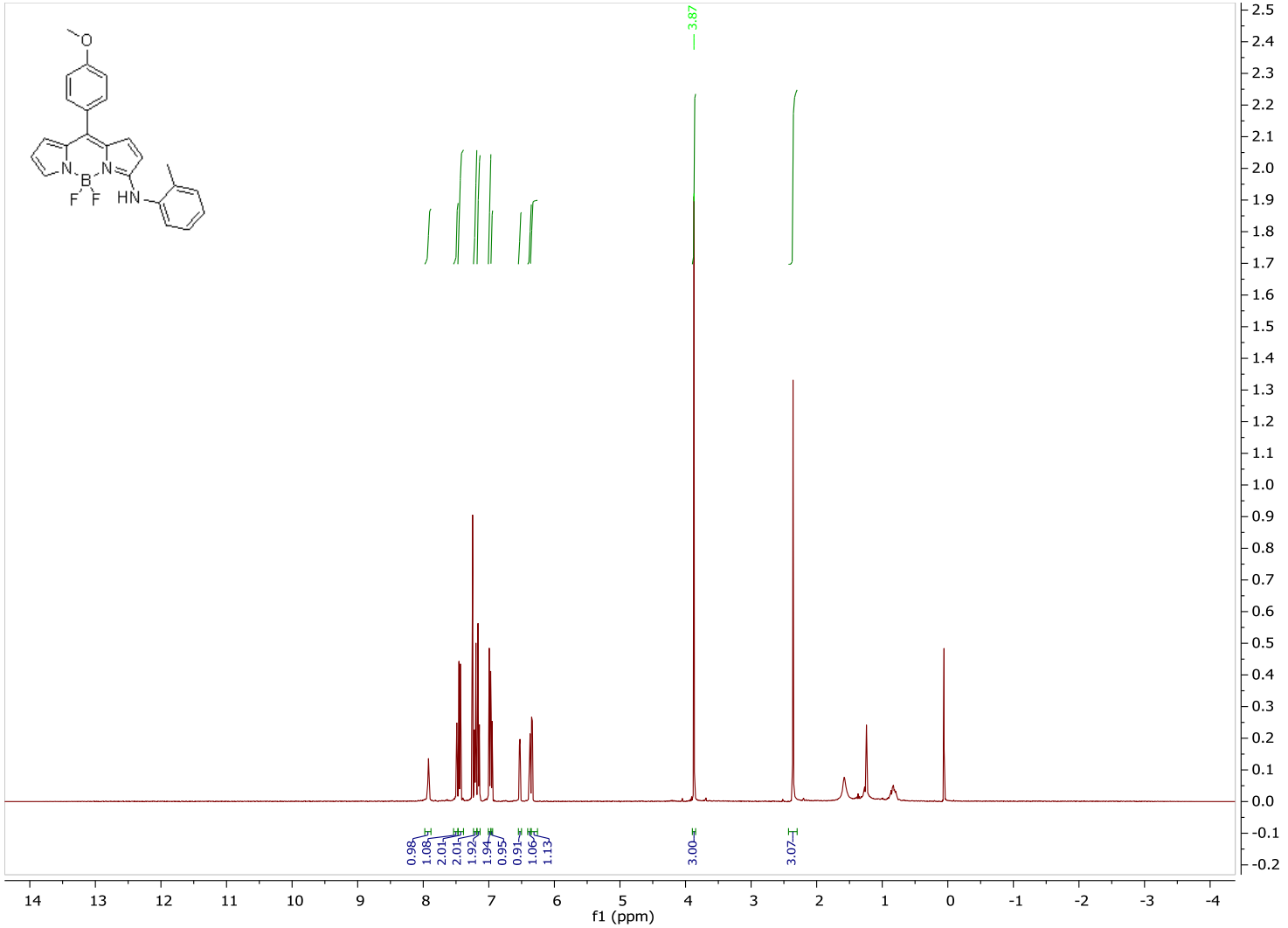
^{1}H NMR (400 MHz, Chloroform-d) 5h



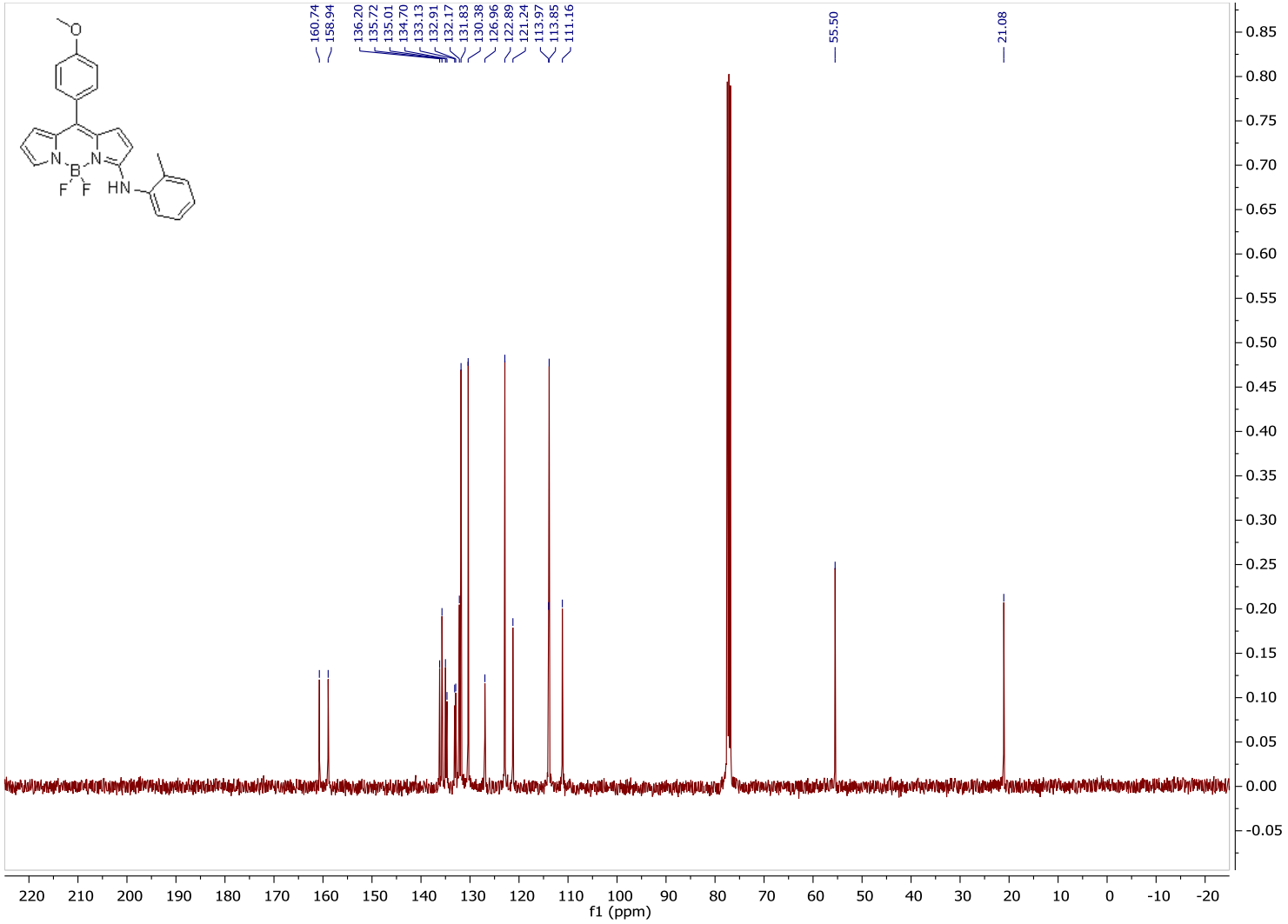
^{13}C NMR (101 MHz, Chloroform-d) 5h



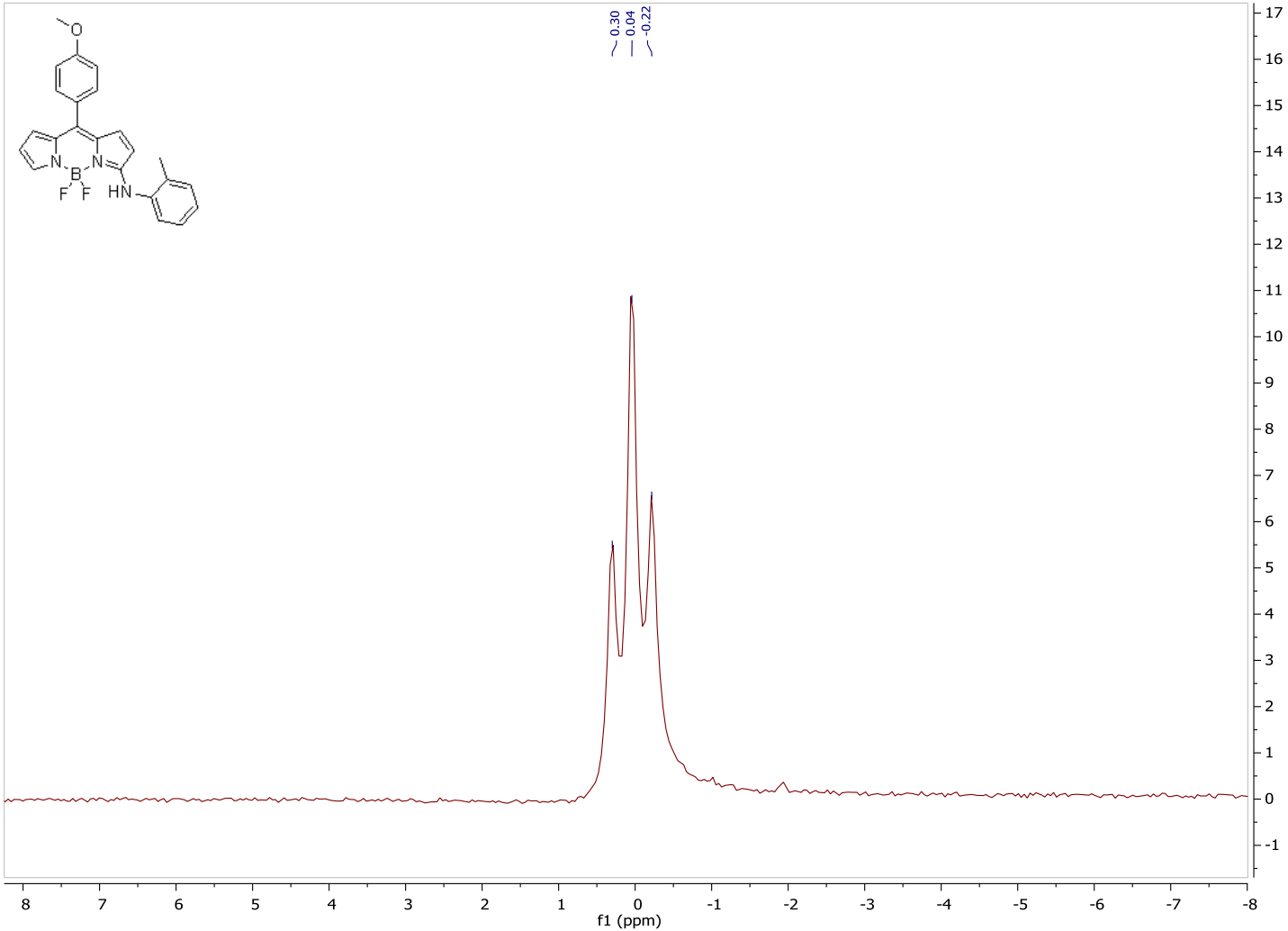
^{1}H NMR (400 MH, Chloroform-d) 4i



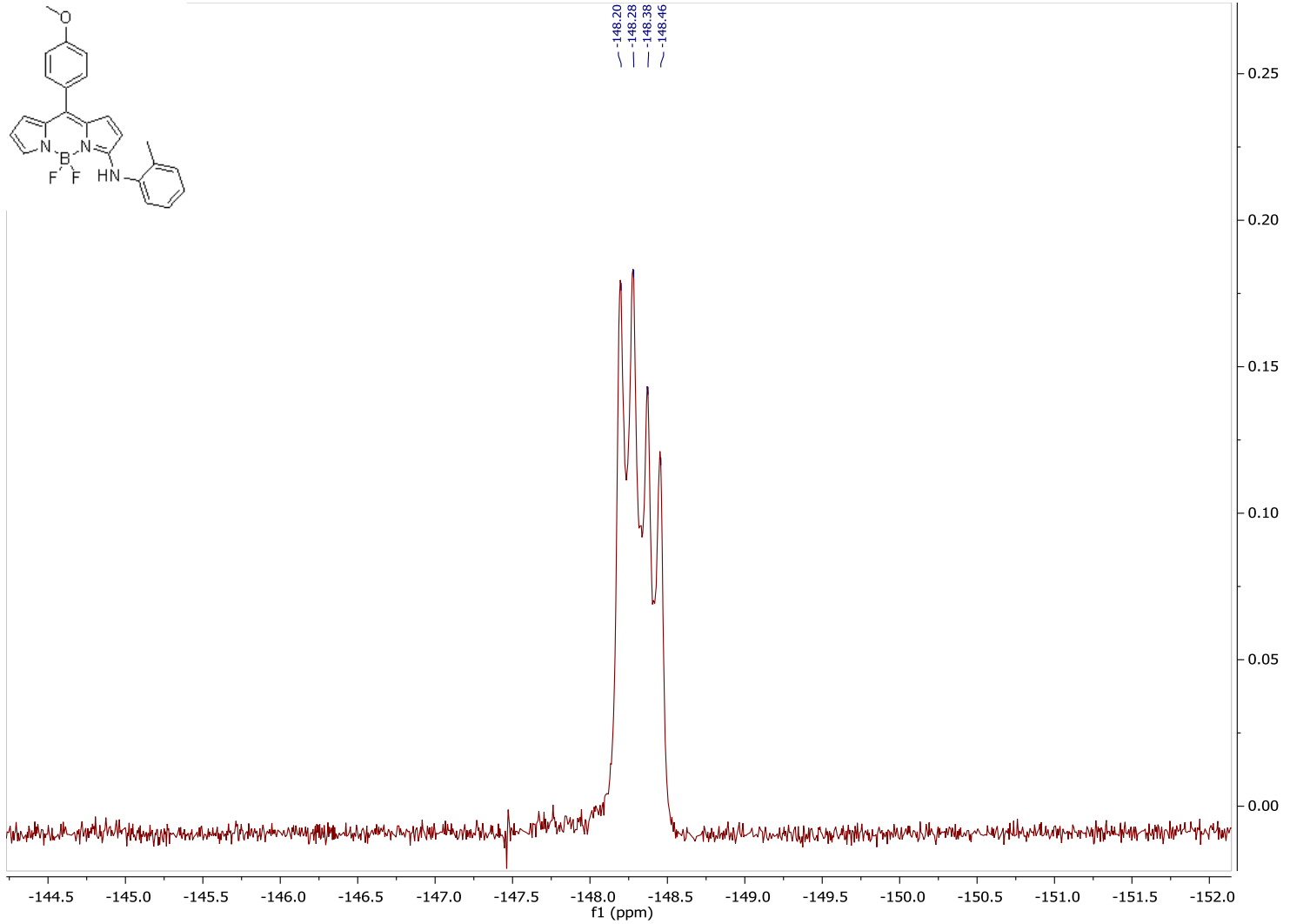
^{13}C NMR (101 MHz, Chloroform-d) 4i



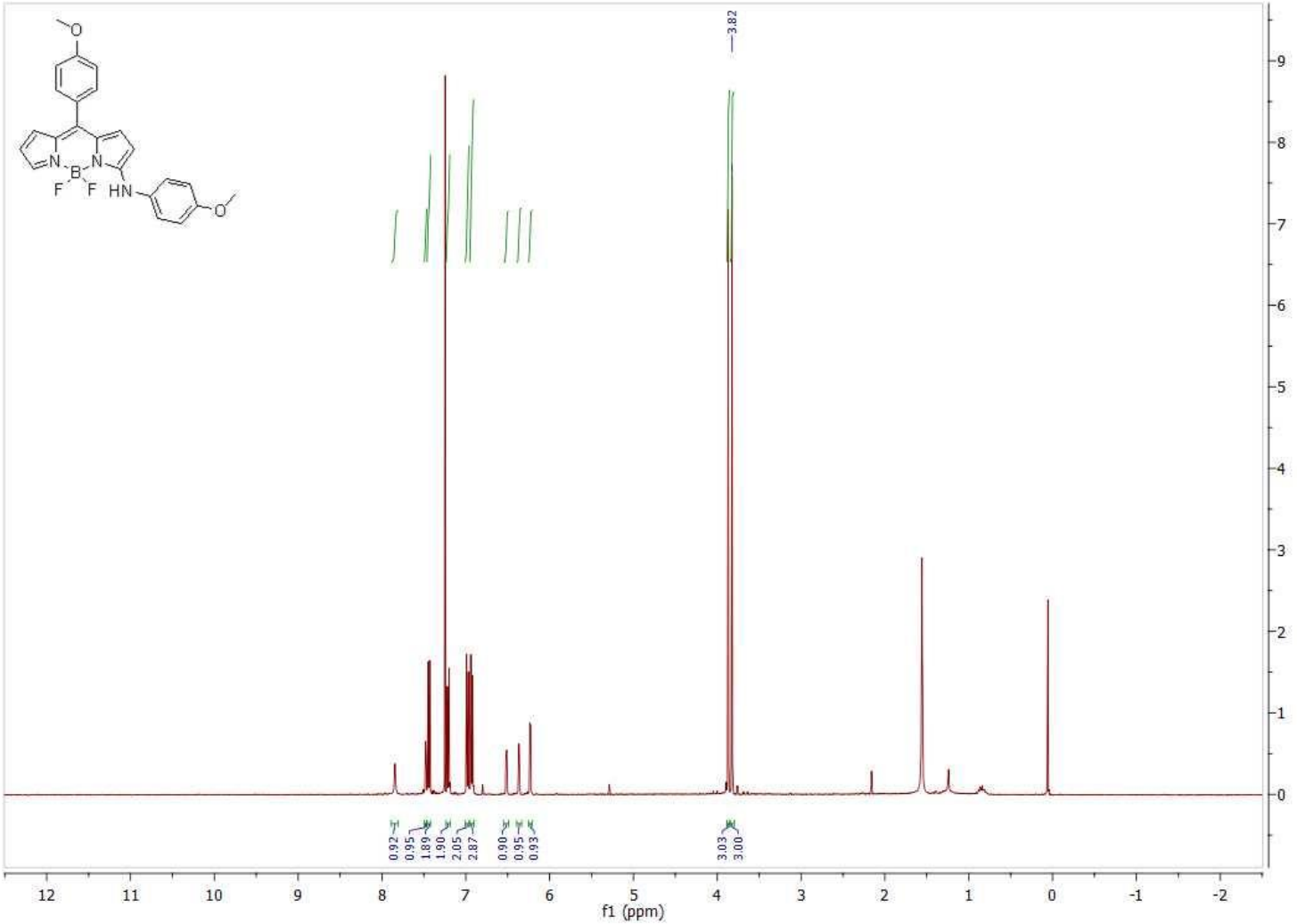
^{1}B NMR (128 MHz, Chloroform-d) 4i



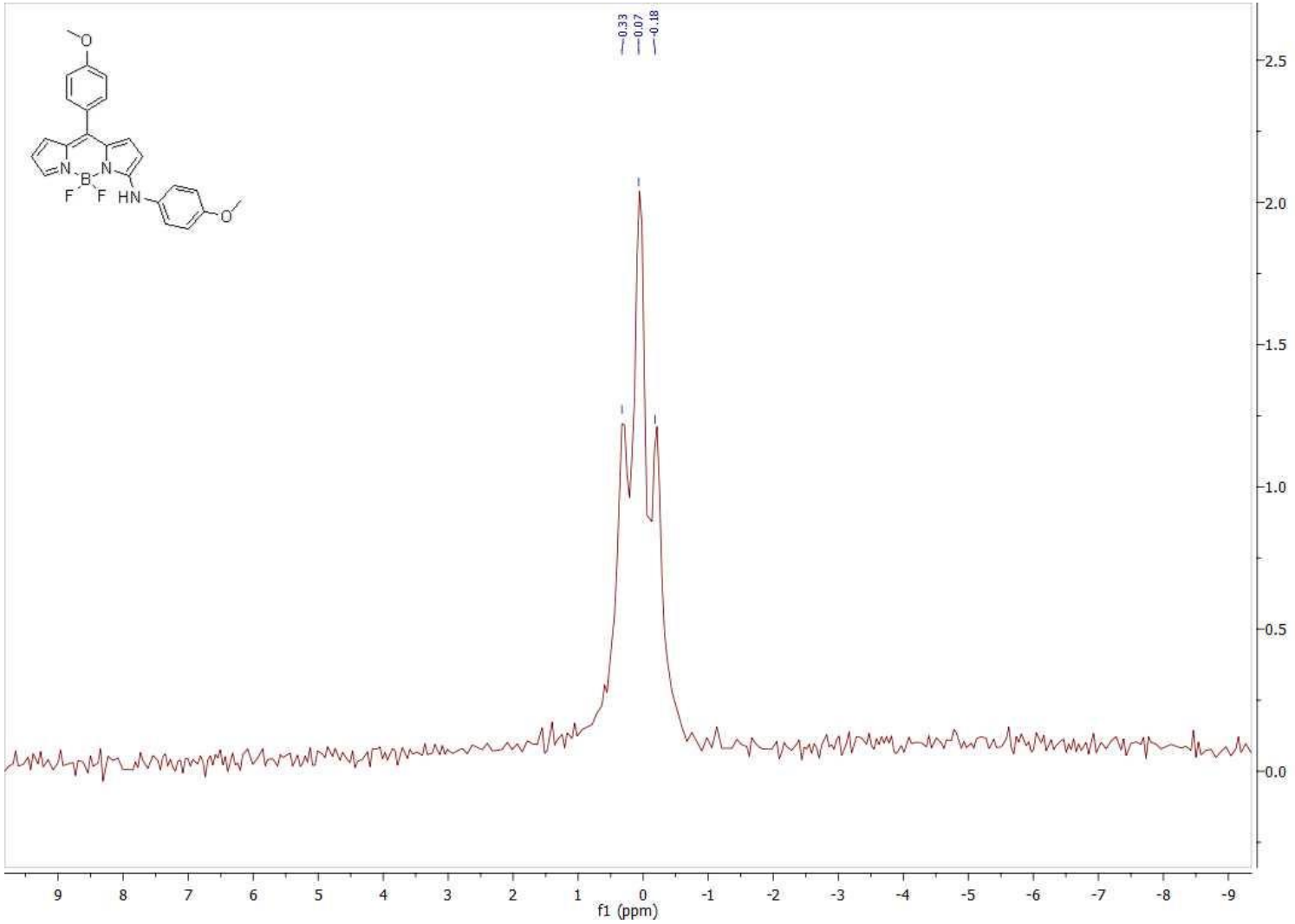
^{19}F NMR (376 MHz, Chloroform-d) 4i



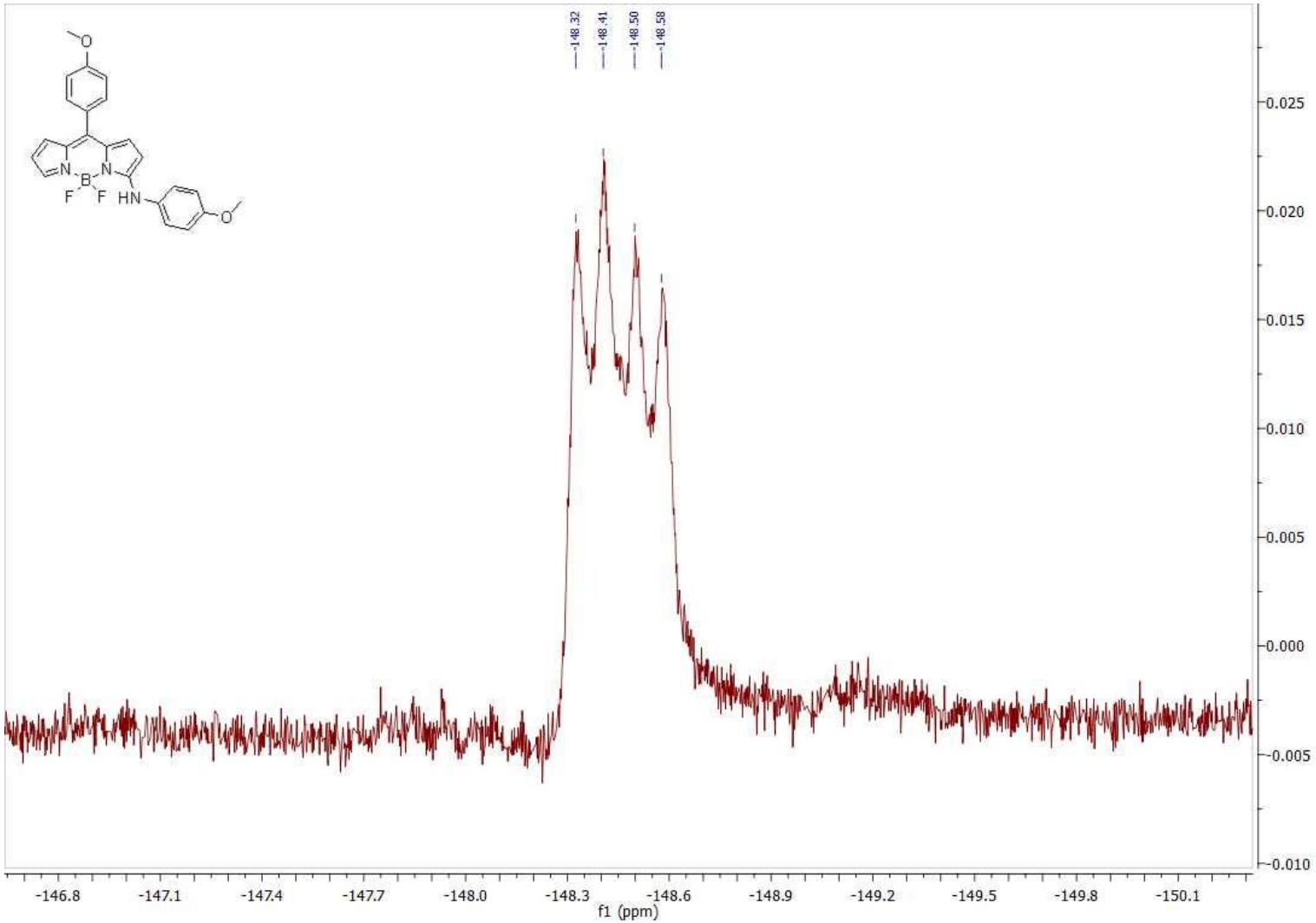
^{1}H NMR (400 MH, Chloroform-d) 4j



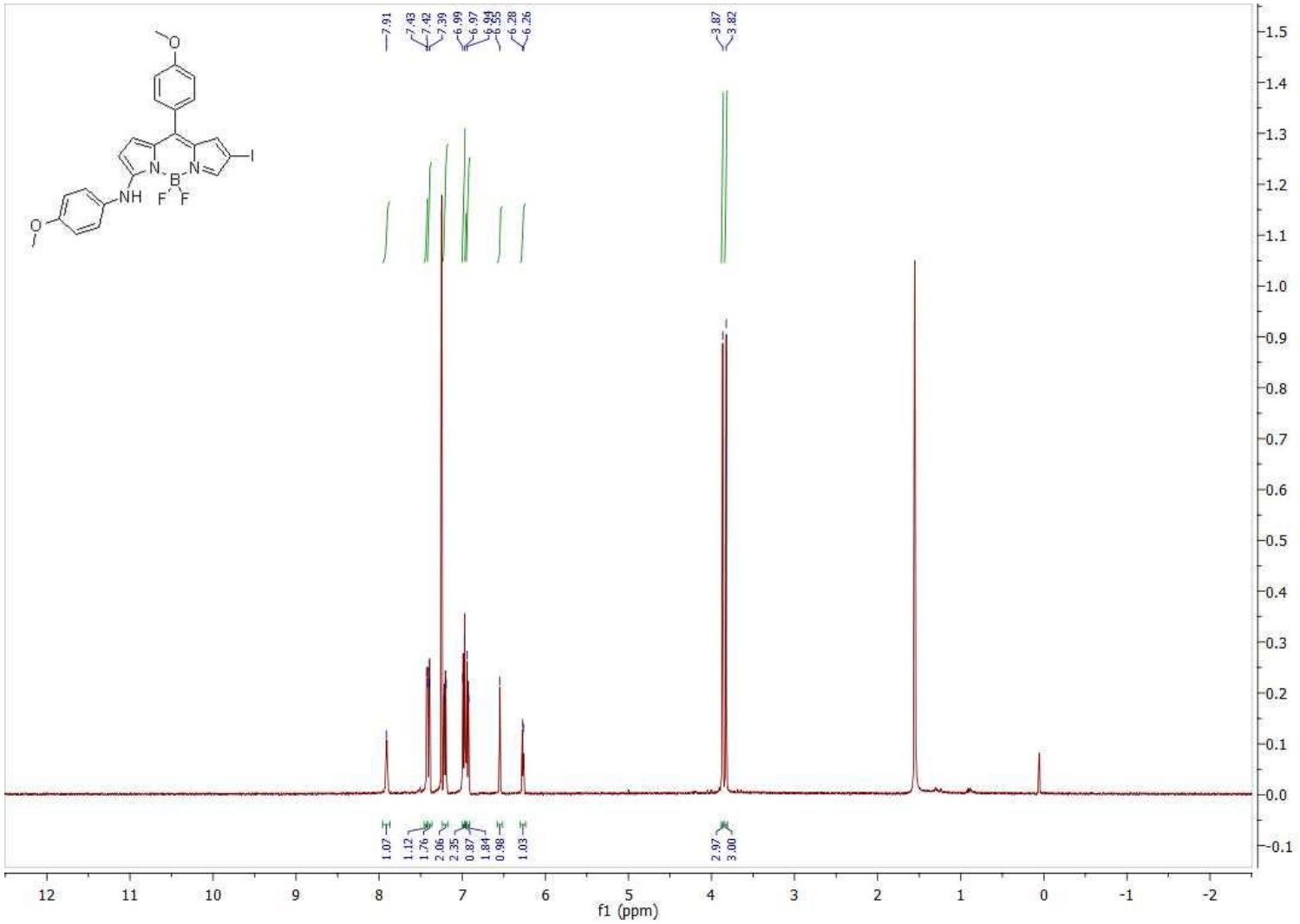
^{1}B NMR (128 MHz, Chloroform-d) 4j



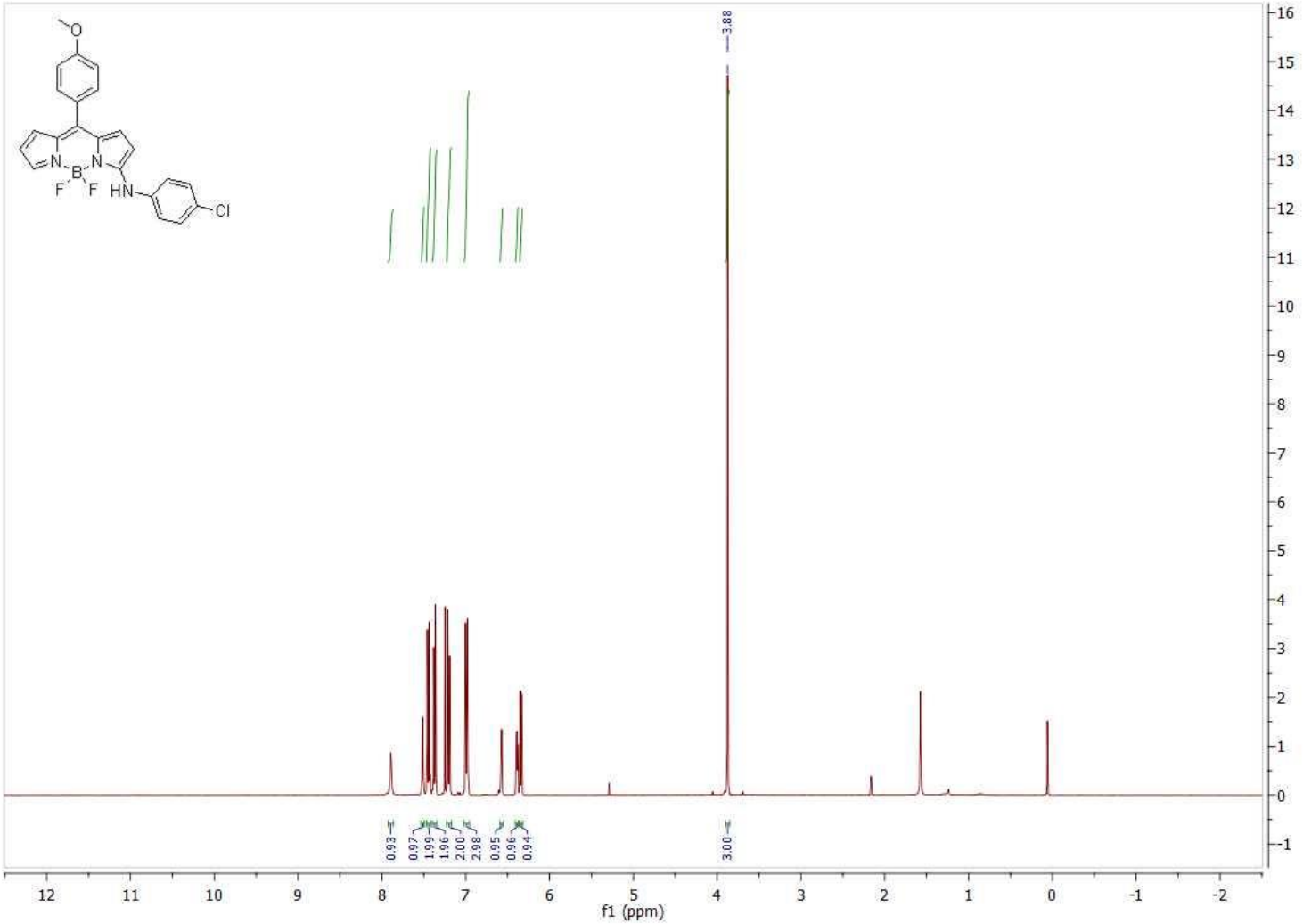
^{19}F NMR (376 MHz, Chloroform-d) 4j



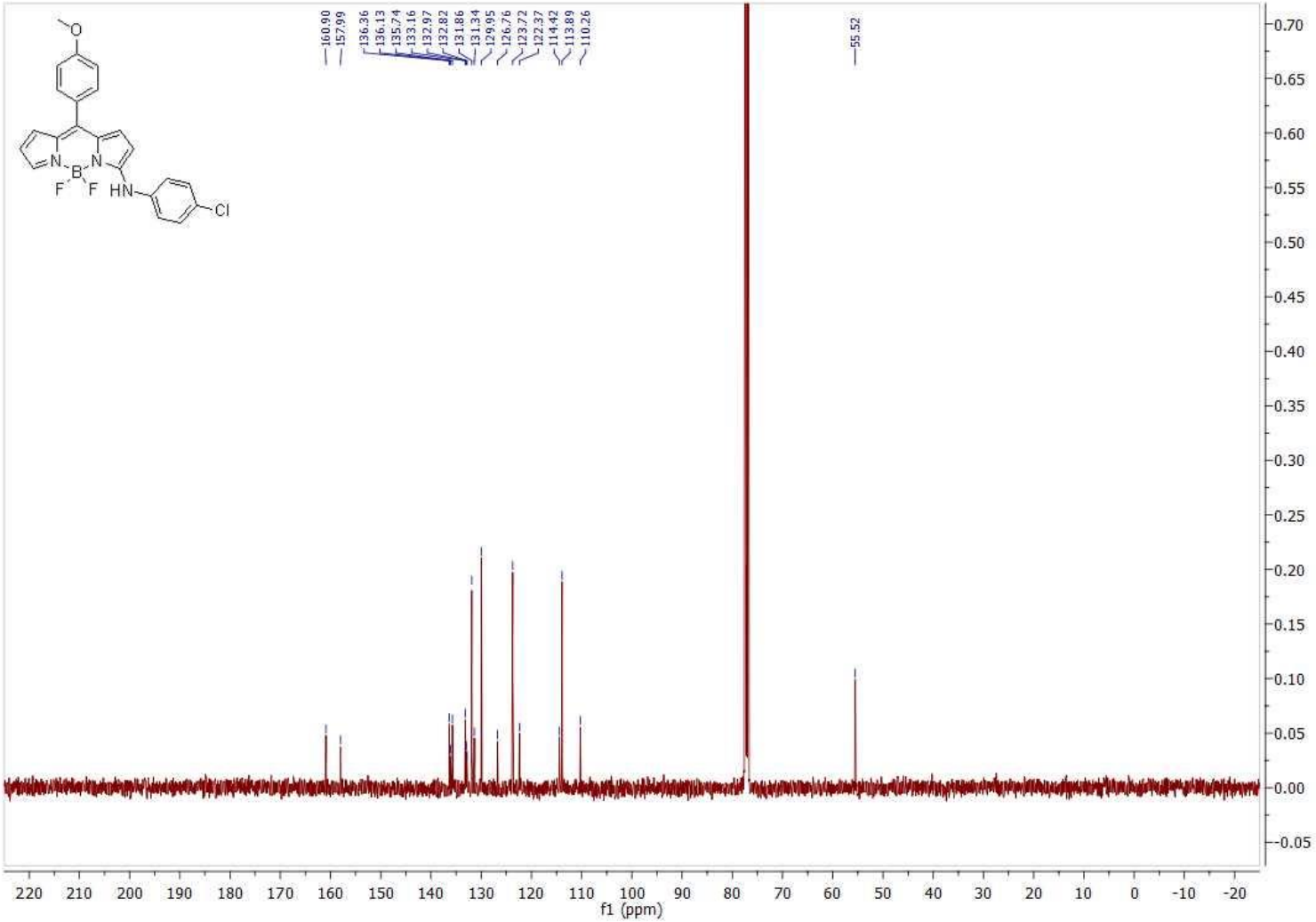
^{1}H NMR (400 MH, Chloroform-d) 5j



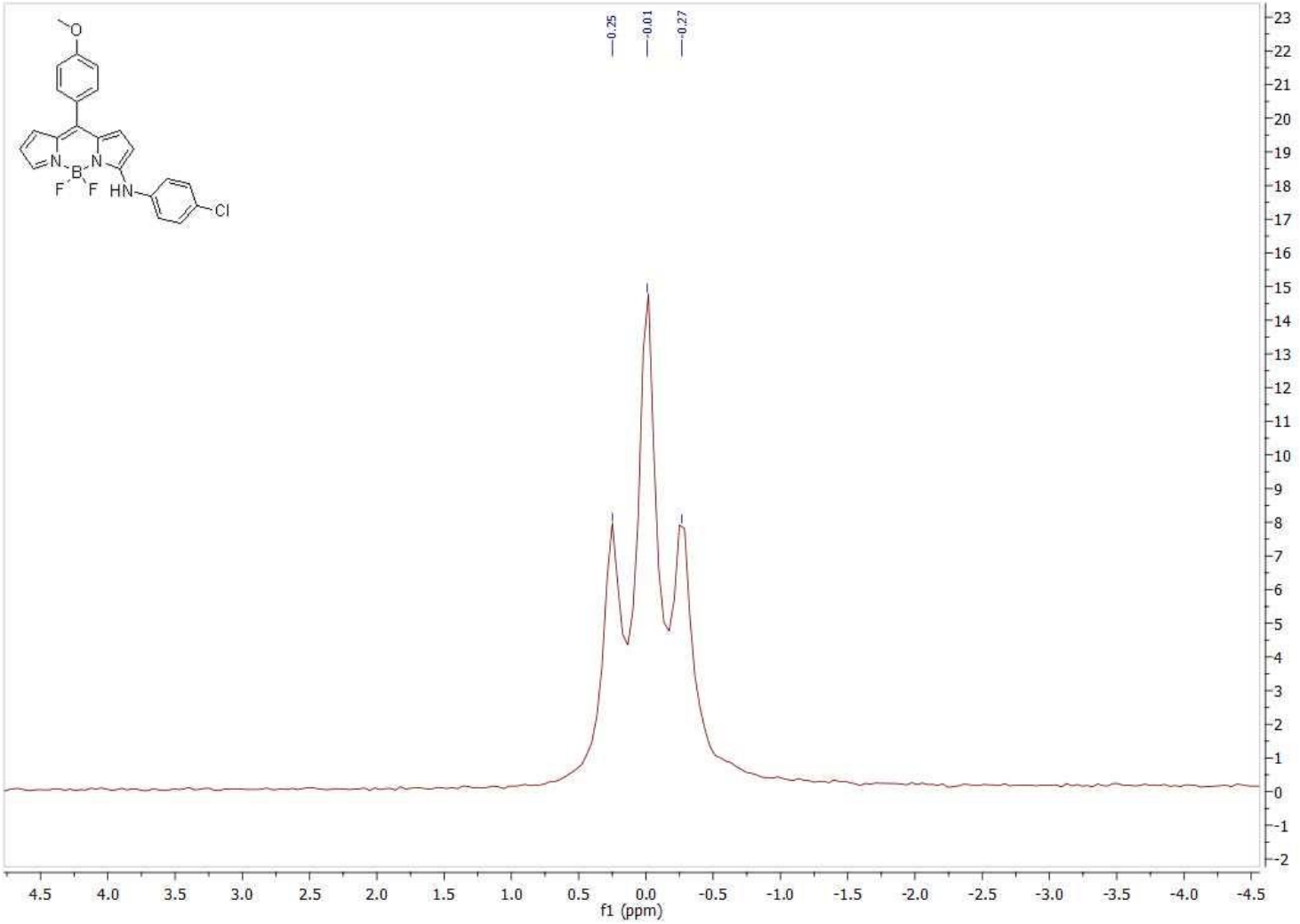
^{1}H NMR (400 MH, Chloroform-d) 4k



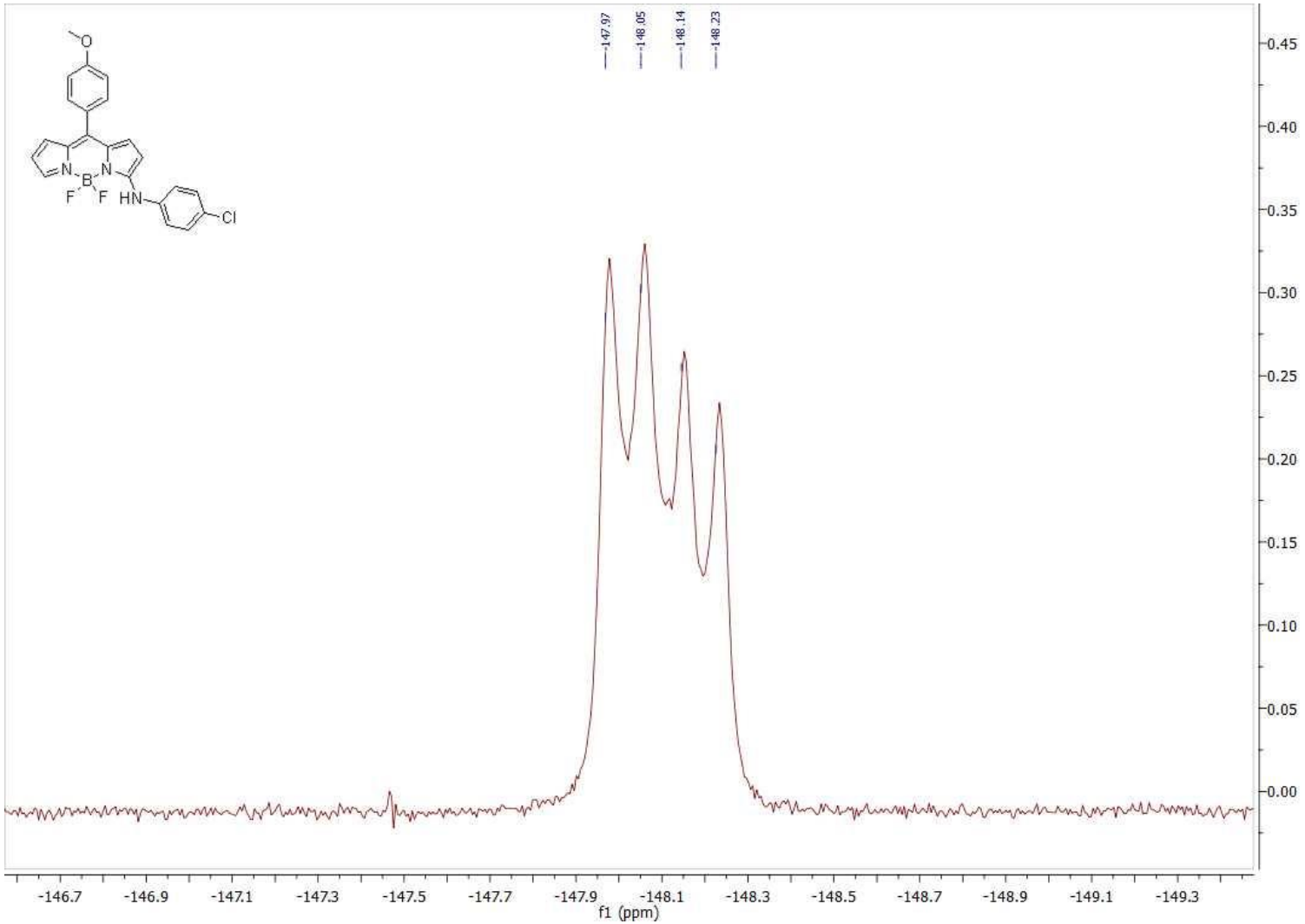
^{13}C NMR (101 MHz, Chloroform-d) 4k



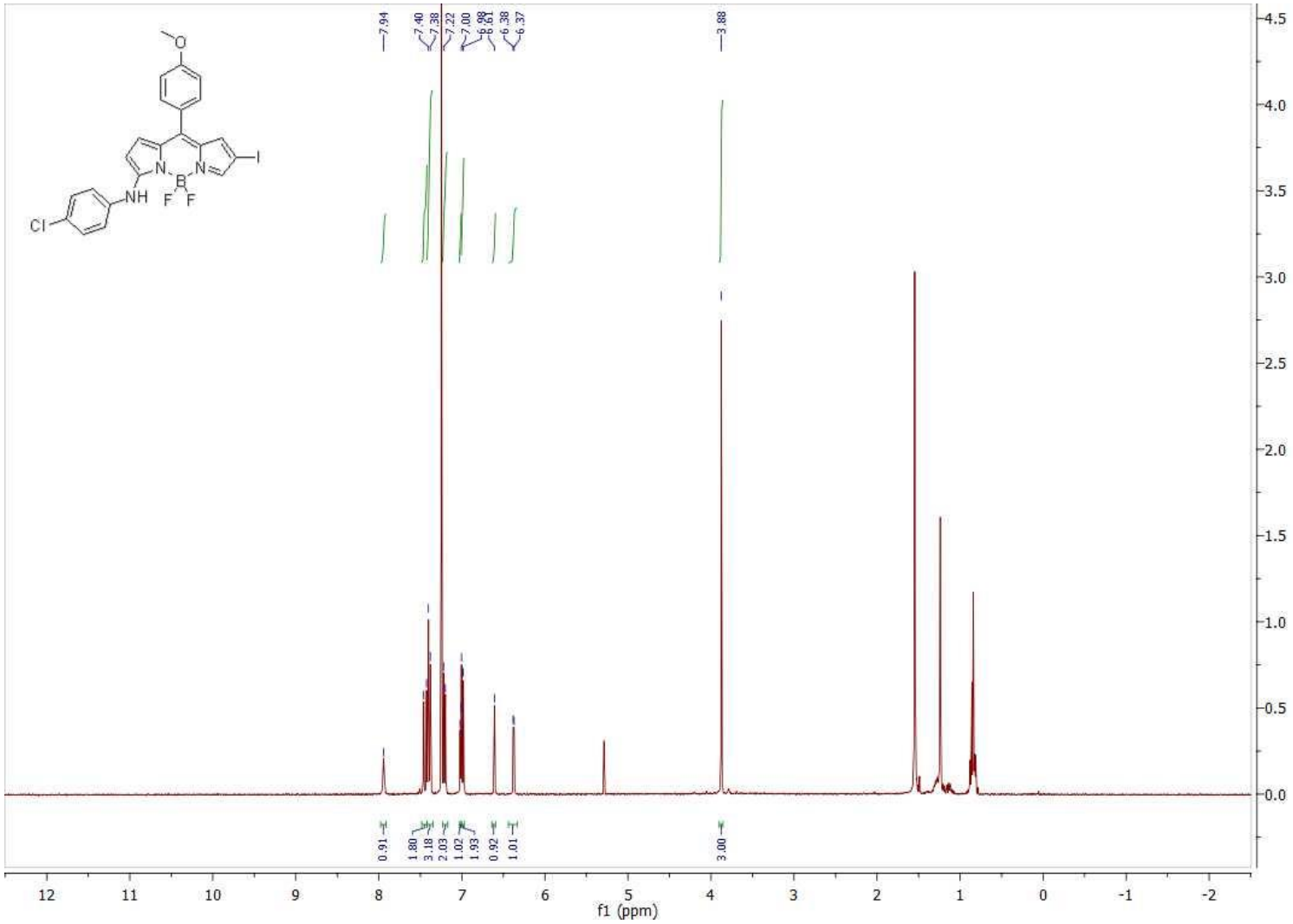
^{1}B NMR (128 MHz, Chloroform-d) 4k



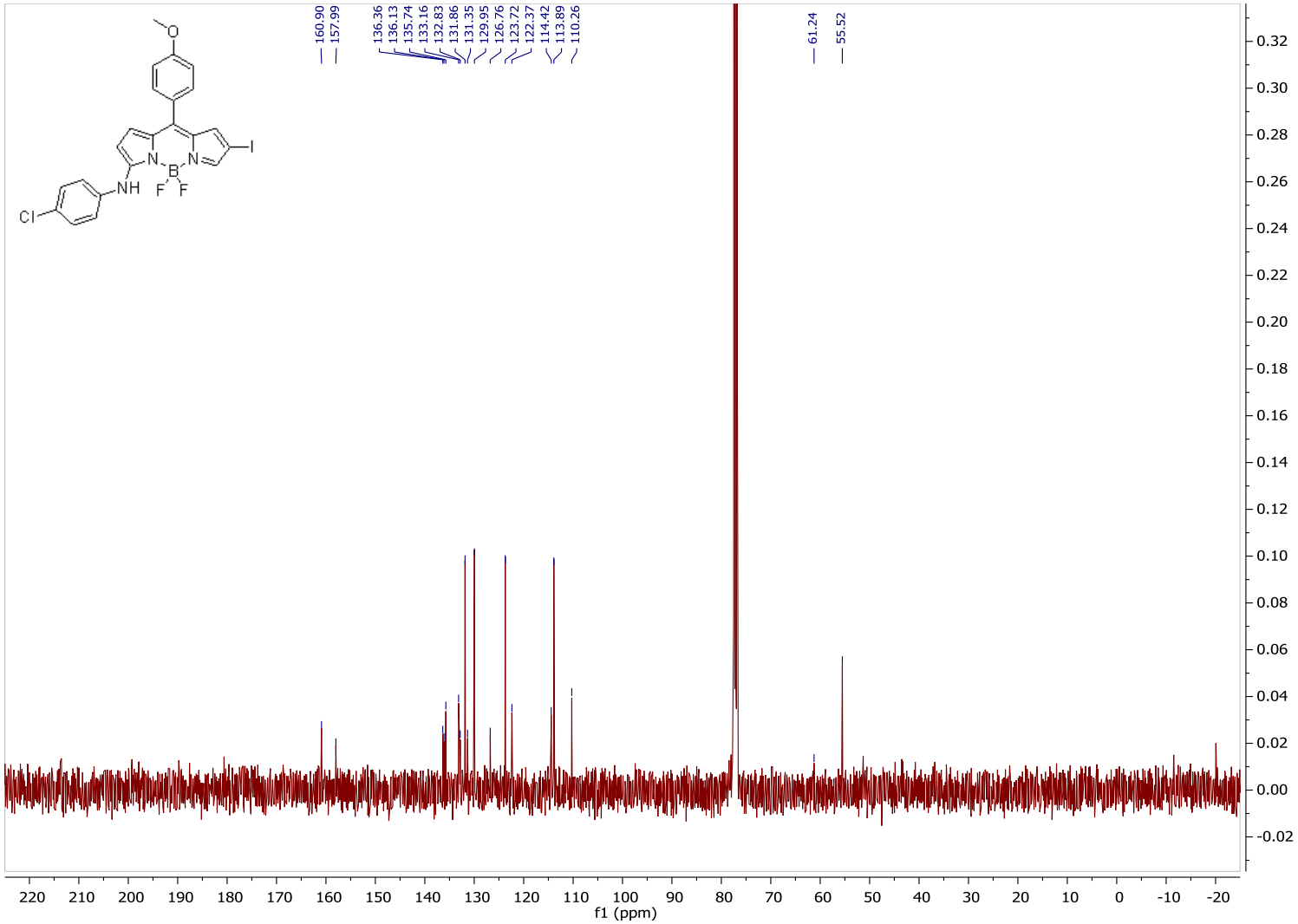
^{19}F NMR (376 MHz, Chloroform-d) 4k



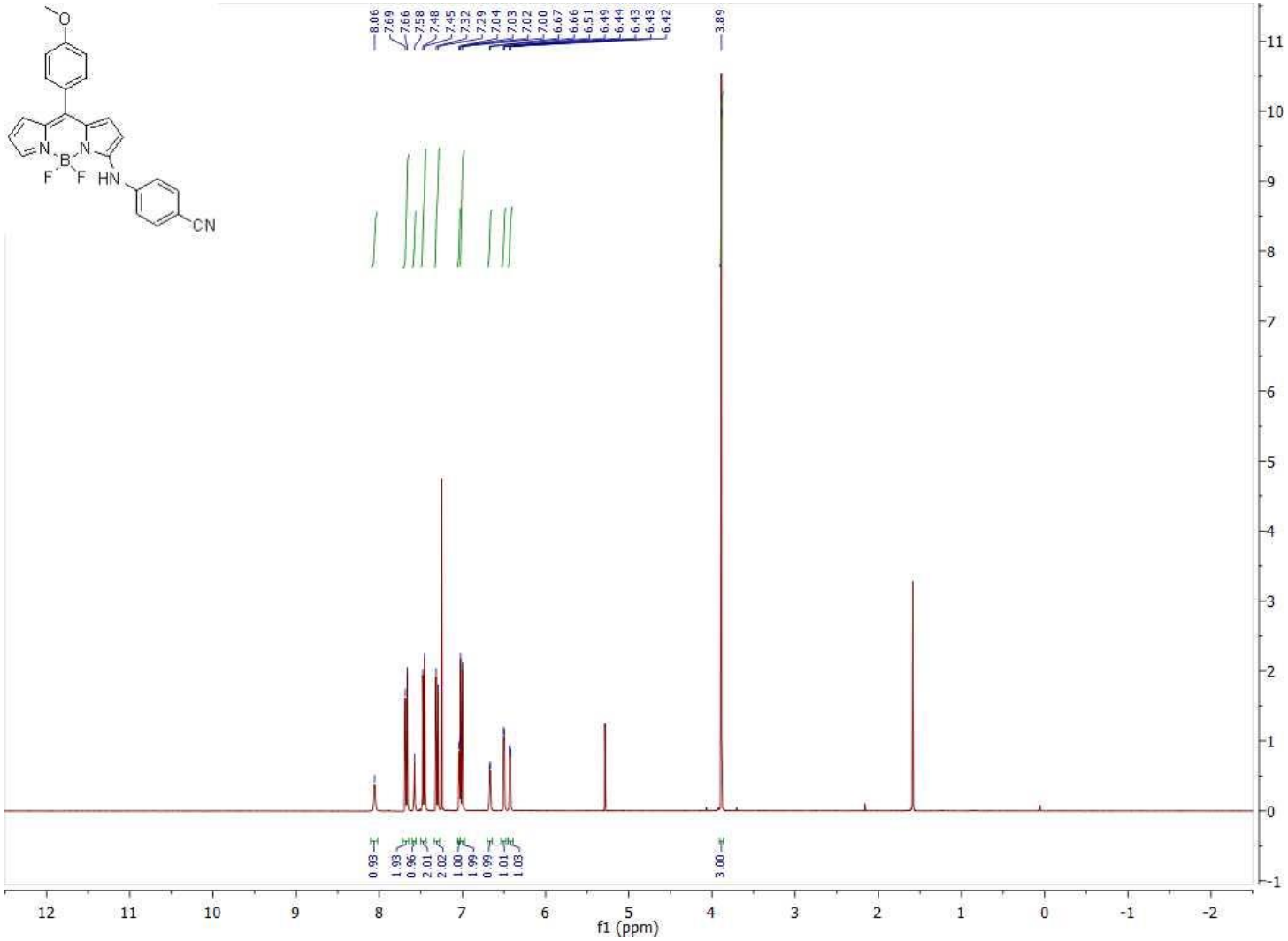
^{1}H NMR (400 MH, Chloroform-d) 5k



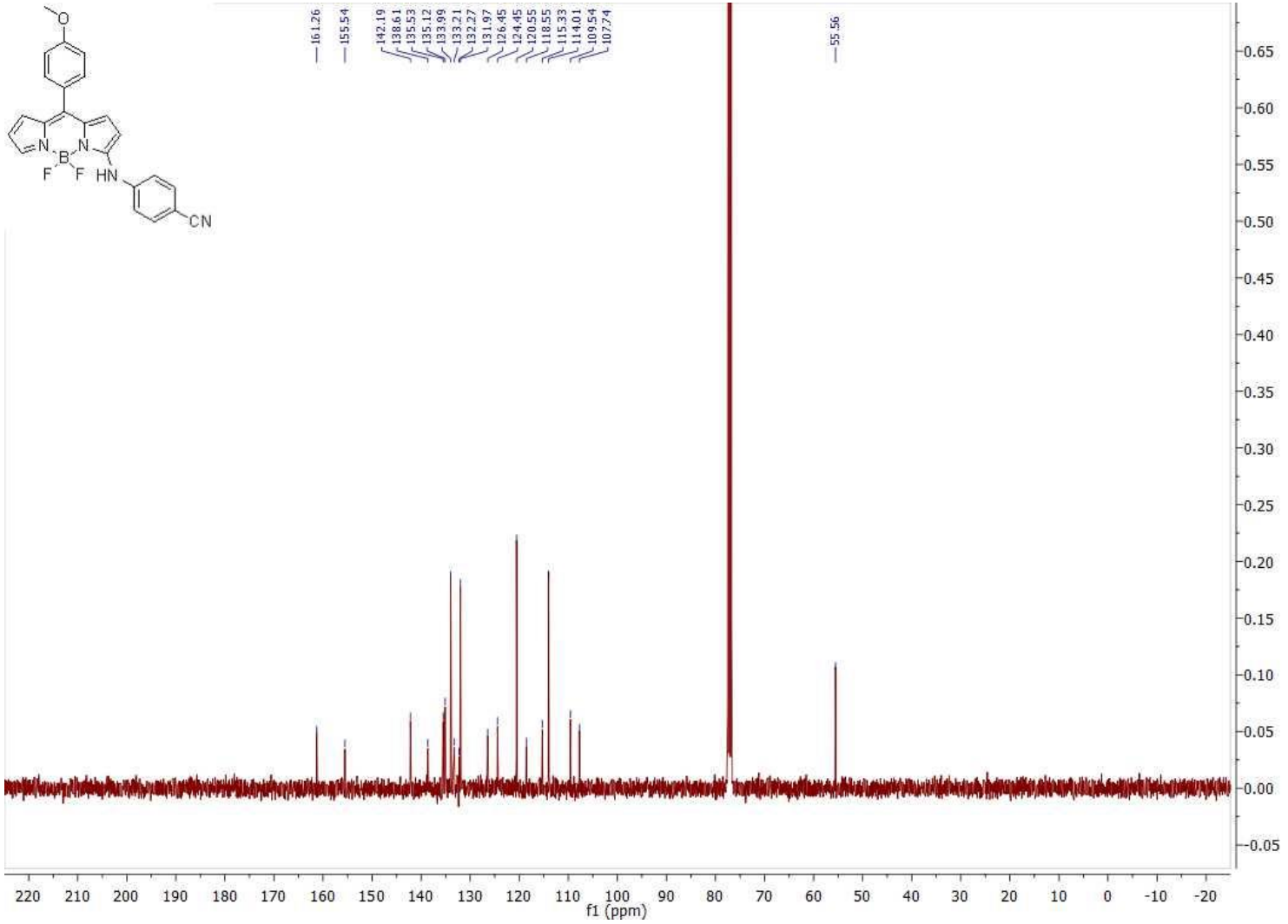
^{13}C NMR (101 MHz, Chloroform-d) 5k



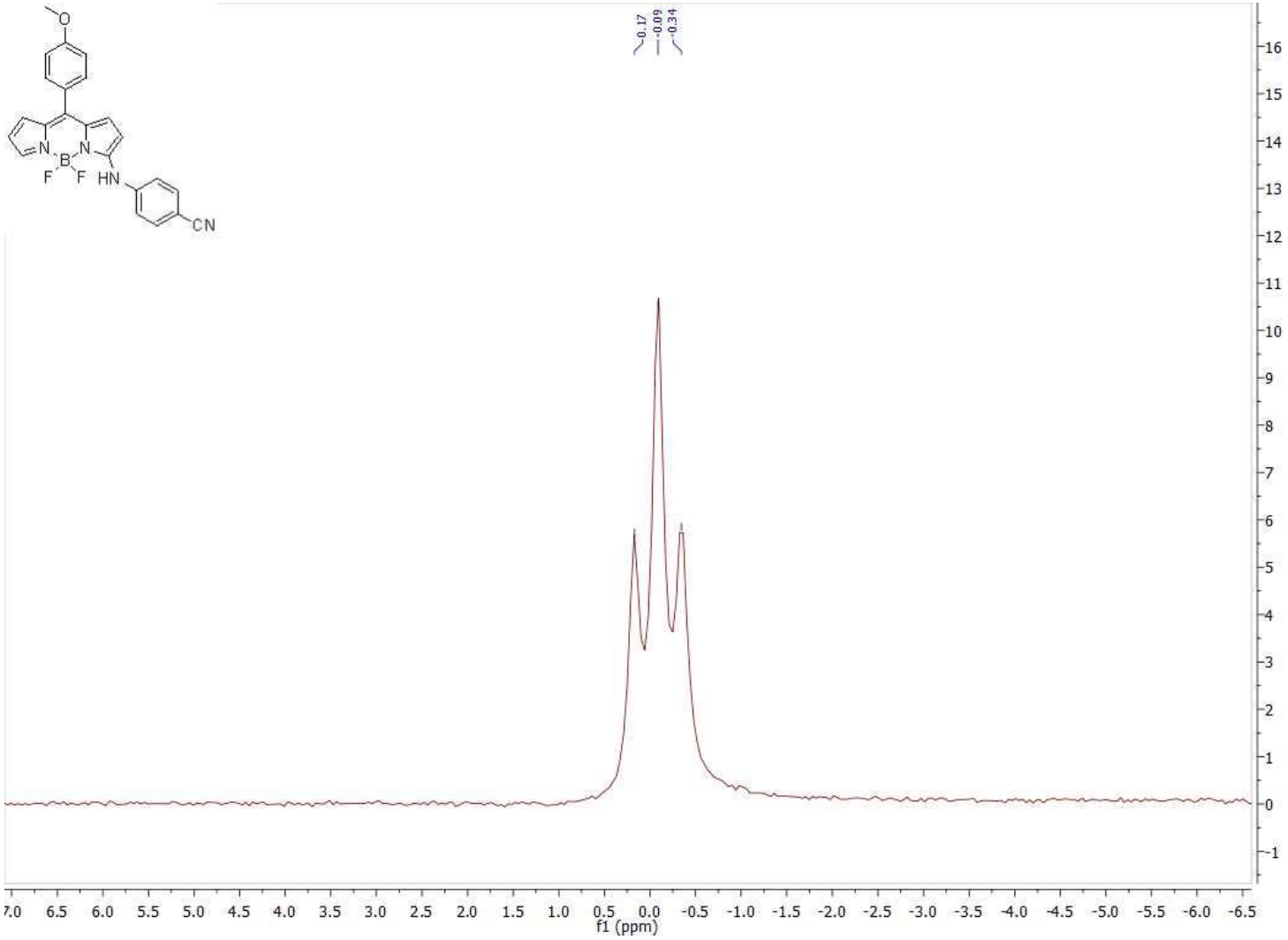
^{1}H NMR (400 MH, Chloroform-d) 4l



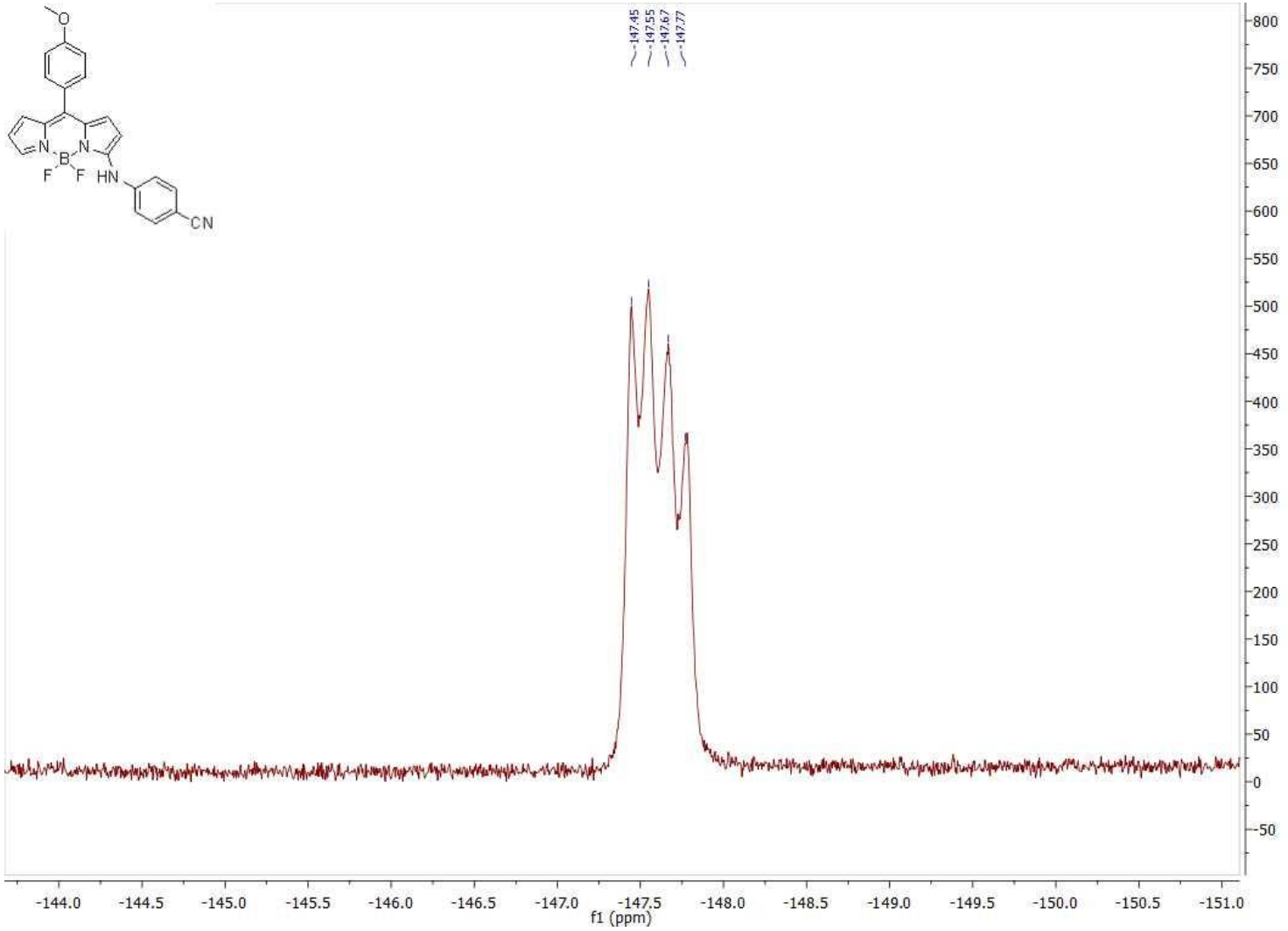
^{13}C NMR (101 MHz, Chloroform-d) 4l



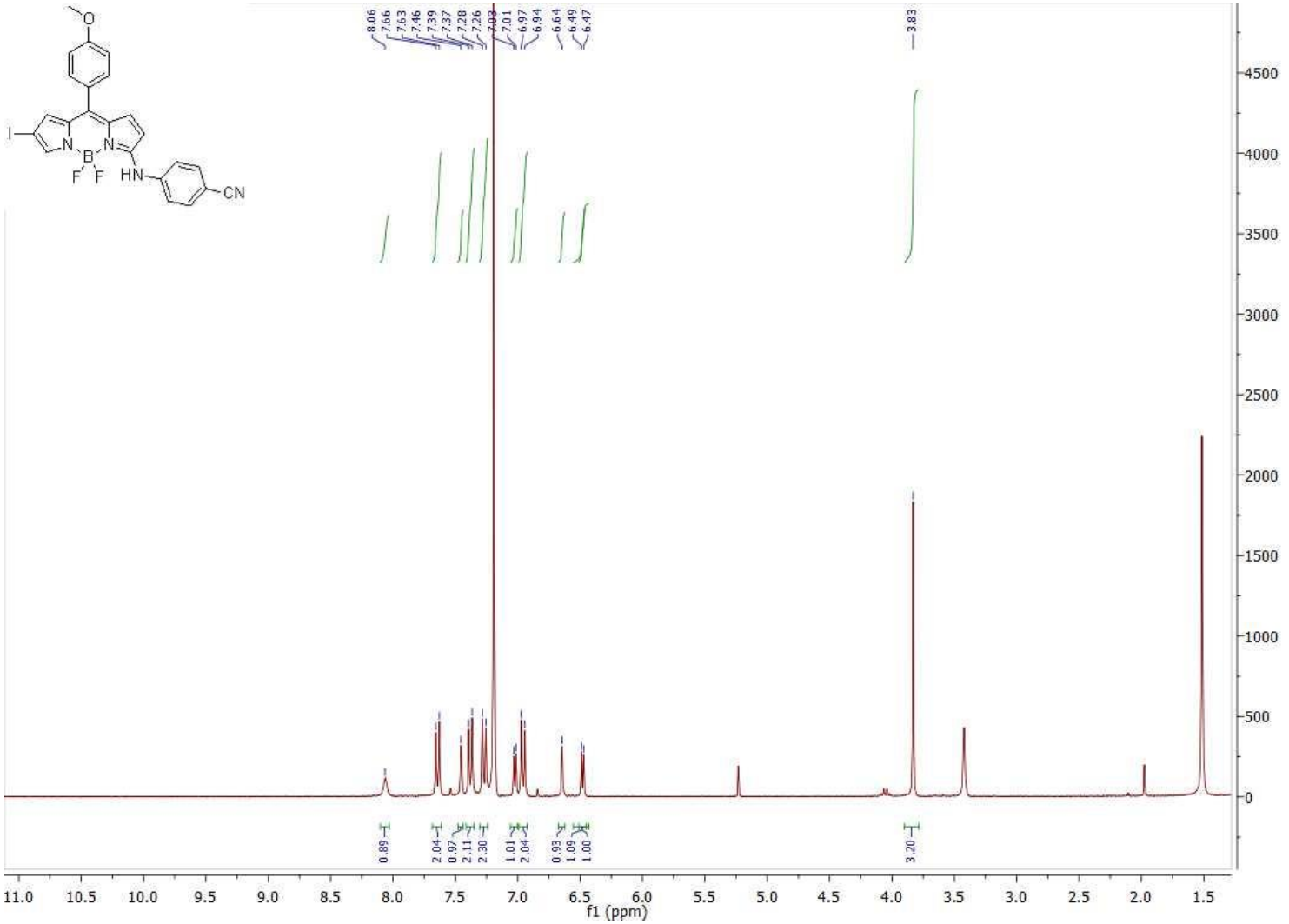
^{1}B NMR (128 MHz, Chloroform-d) 4l



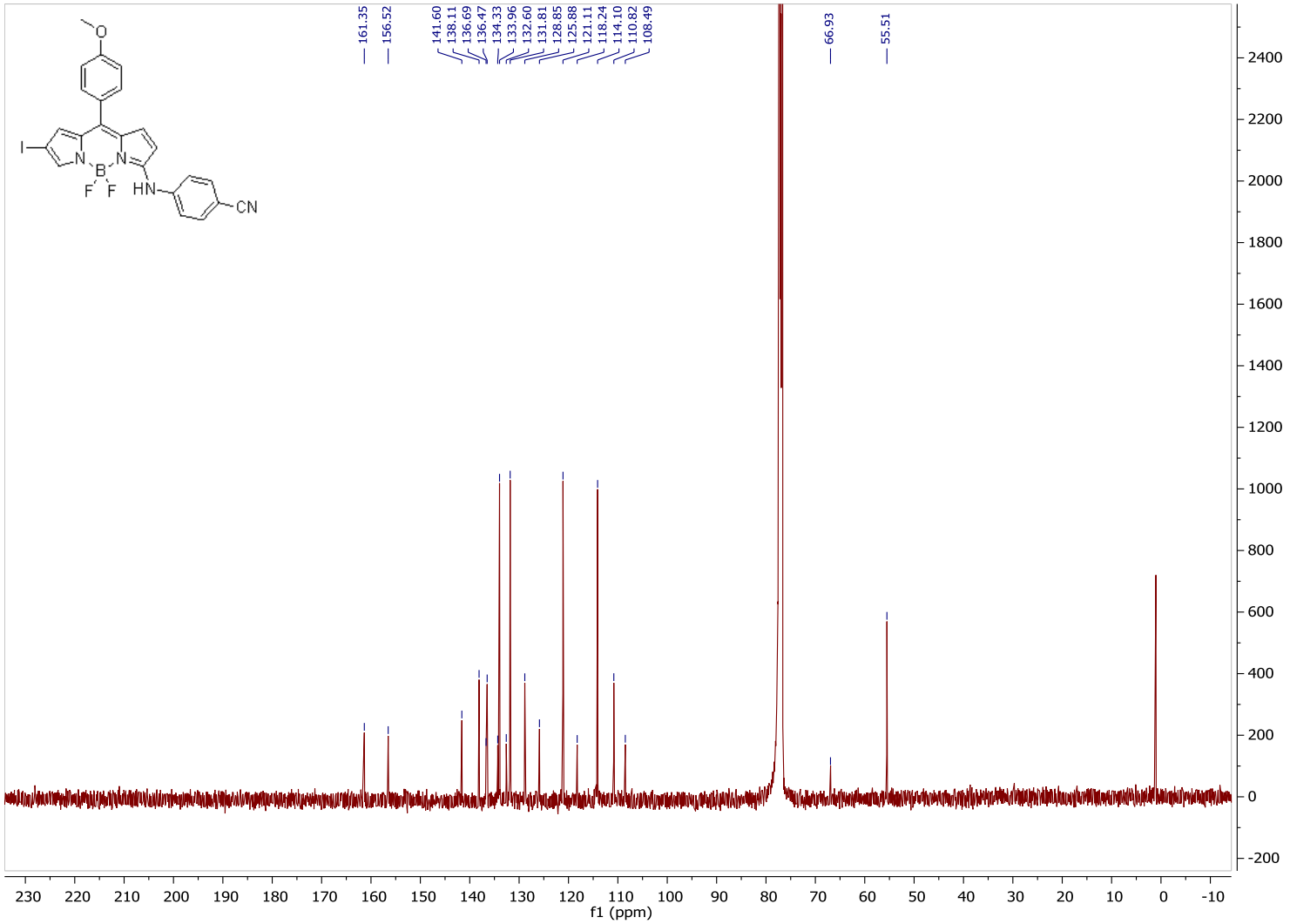
^{19}F NMR (376 MHz, Chloroform-d) 4l



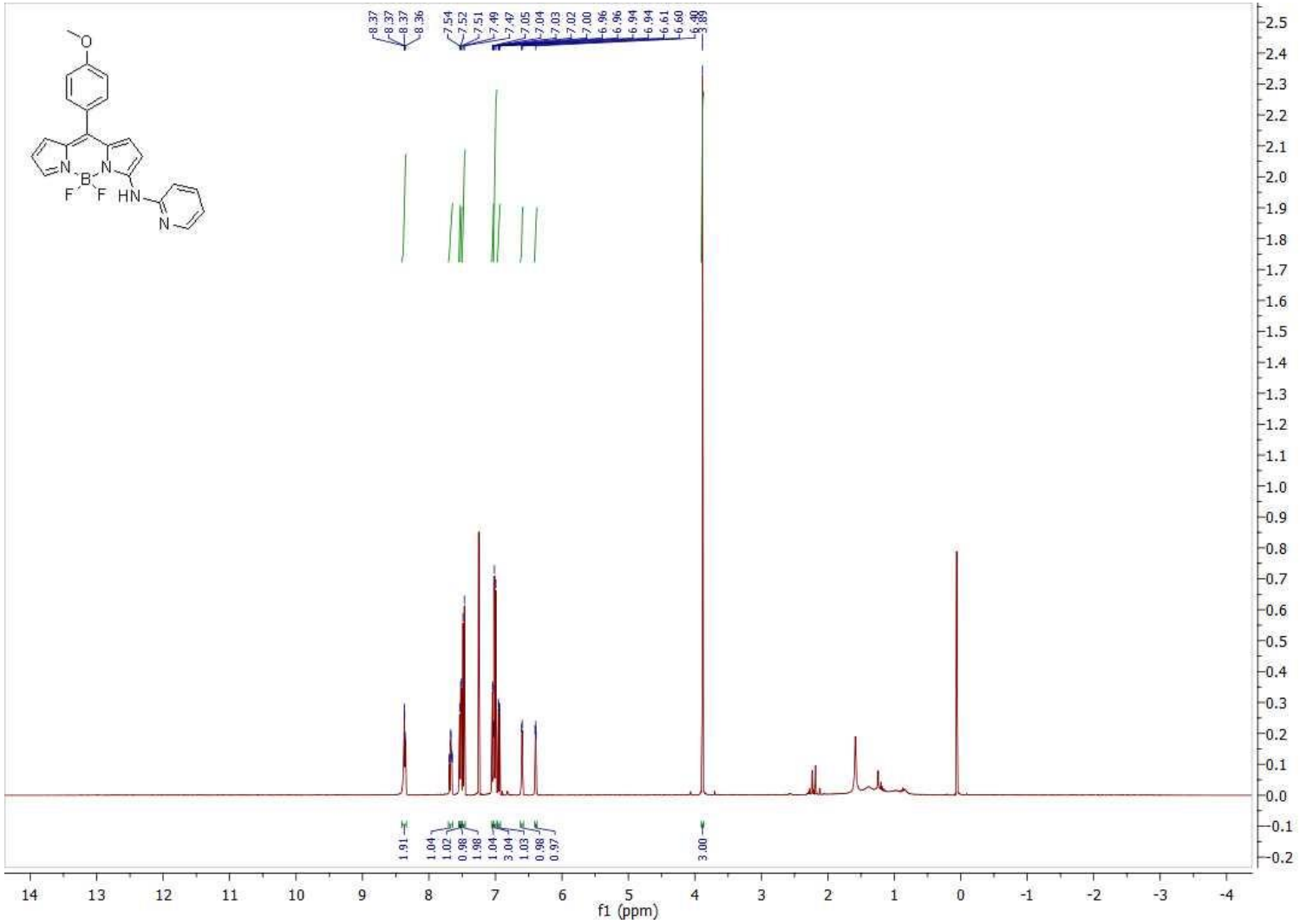
^{1}H NMR (300 MH, Chloroform-d) 5l



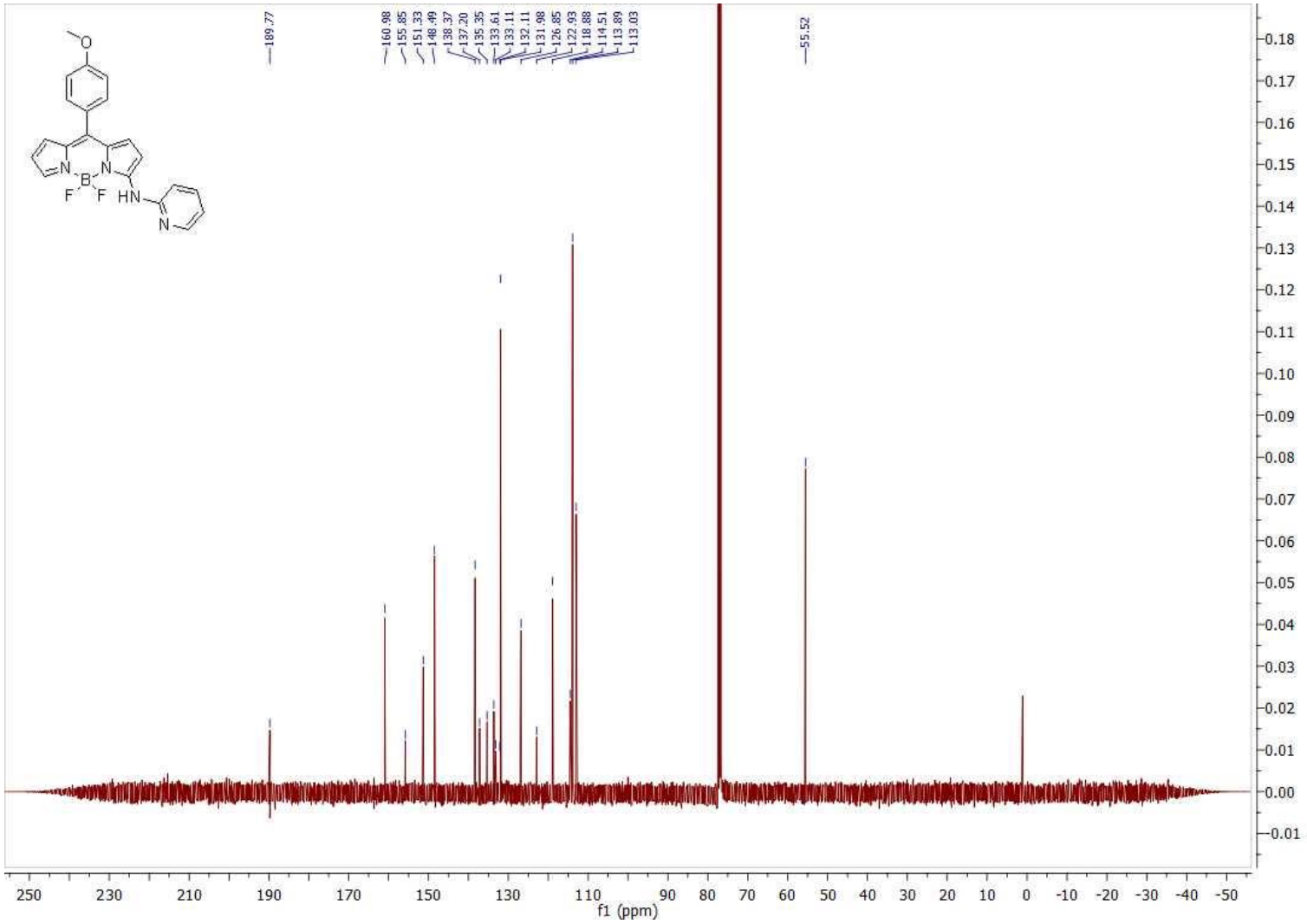
^{13}C NMR (126 MHz, Chloroform-d) 5l



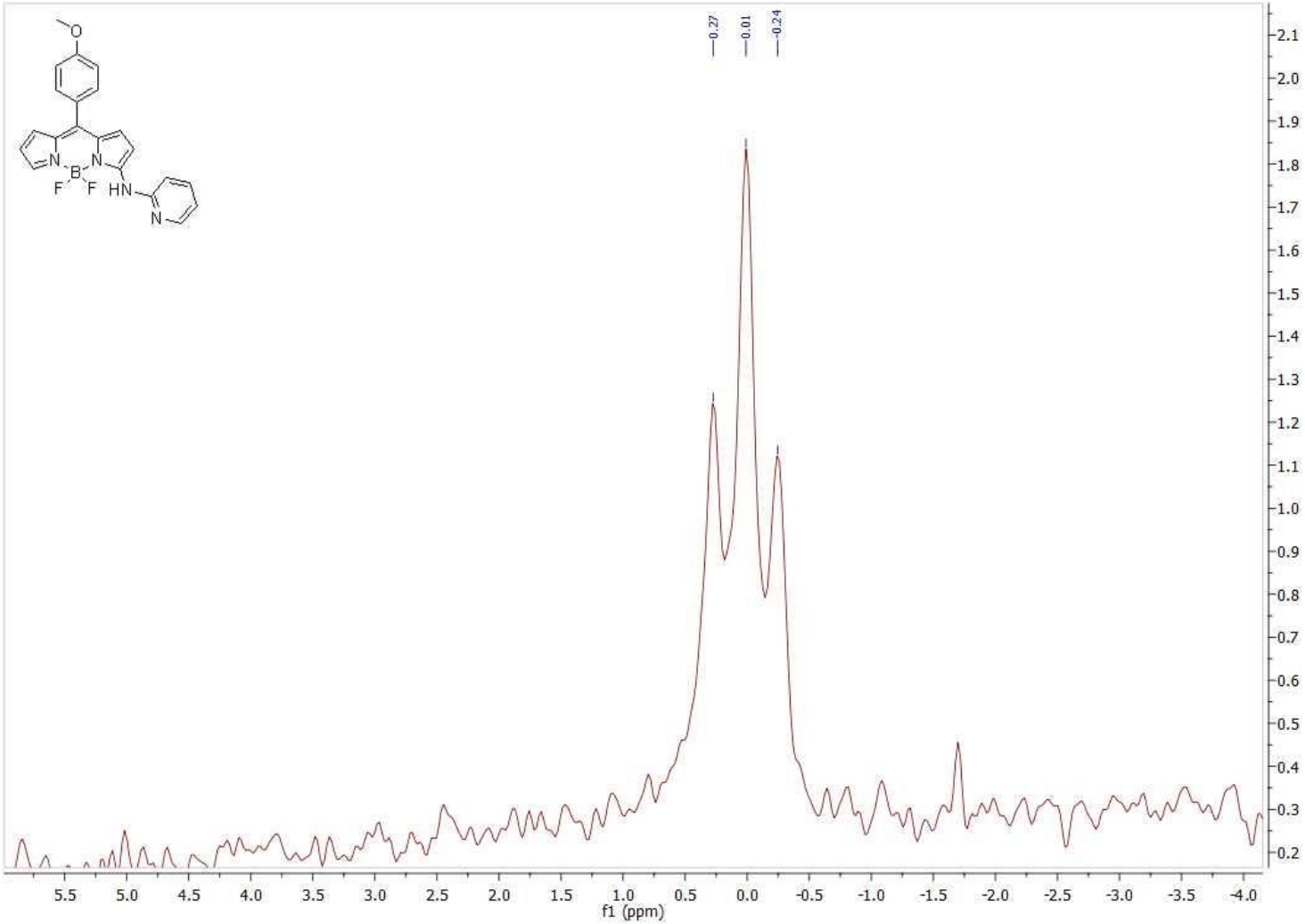
^{1}H NMR (400 MH, Chloroform-d) 4m



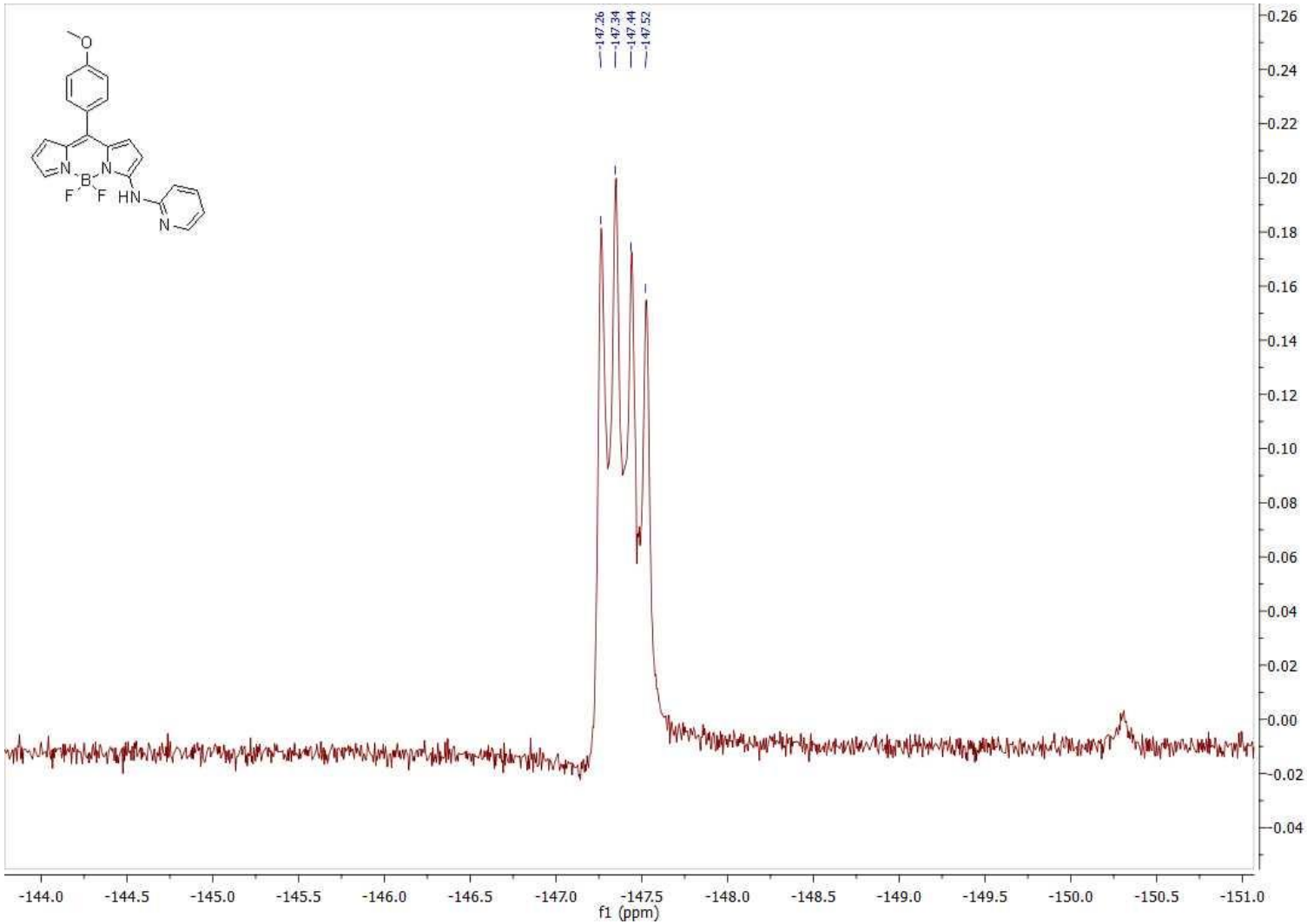
^{13}C NMR (101 MHz, Chloroform-d) 4m



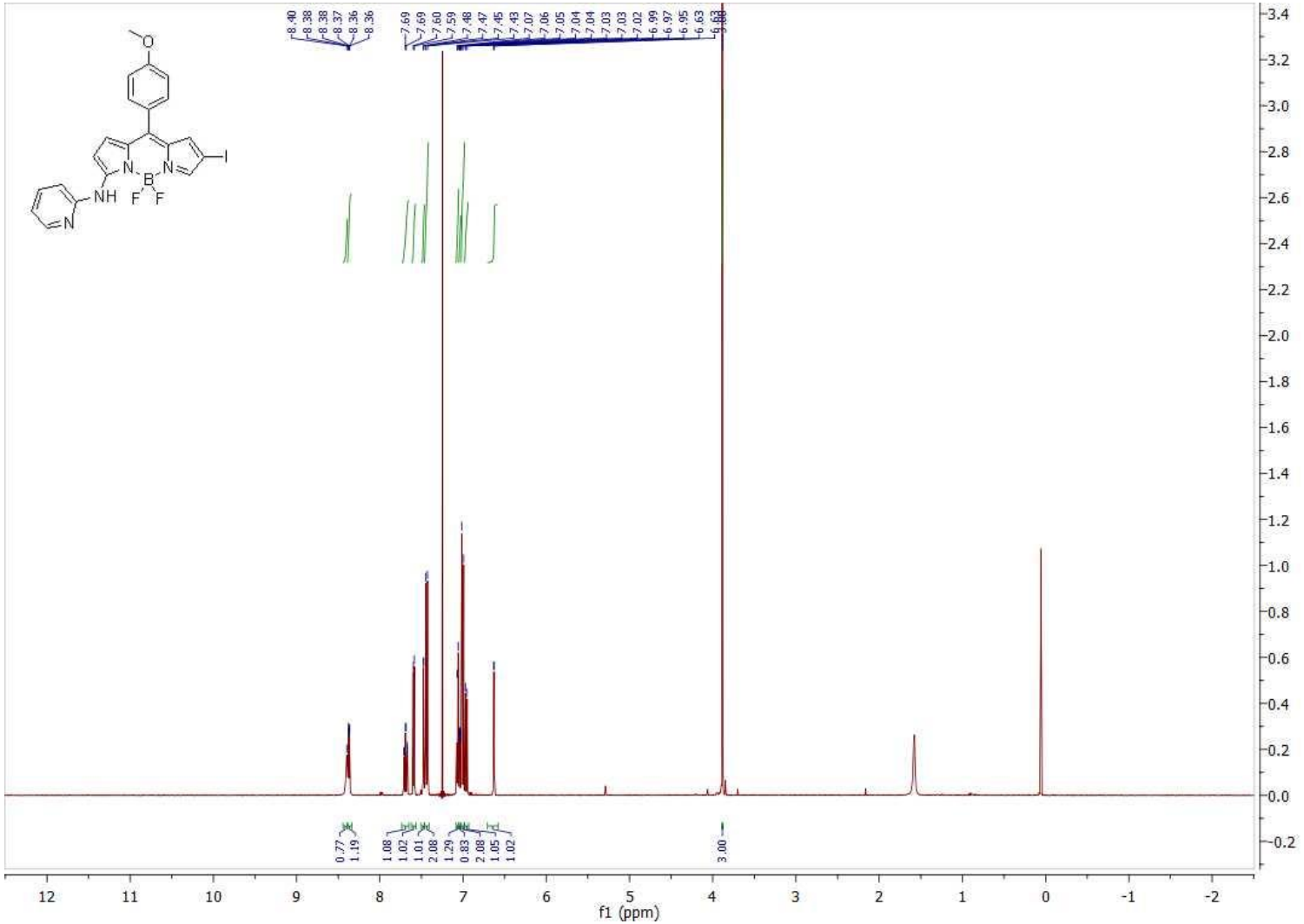
^{1}B NMR (128 MHz, Chloroform-d) 4m



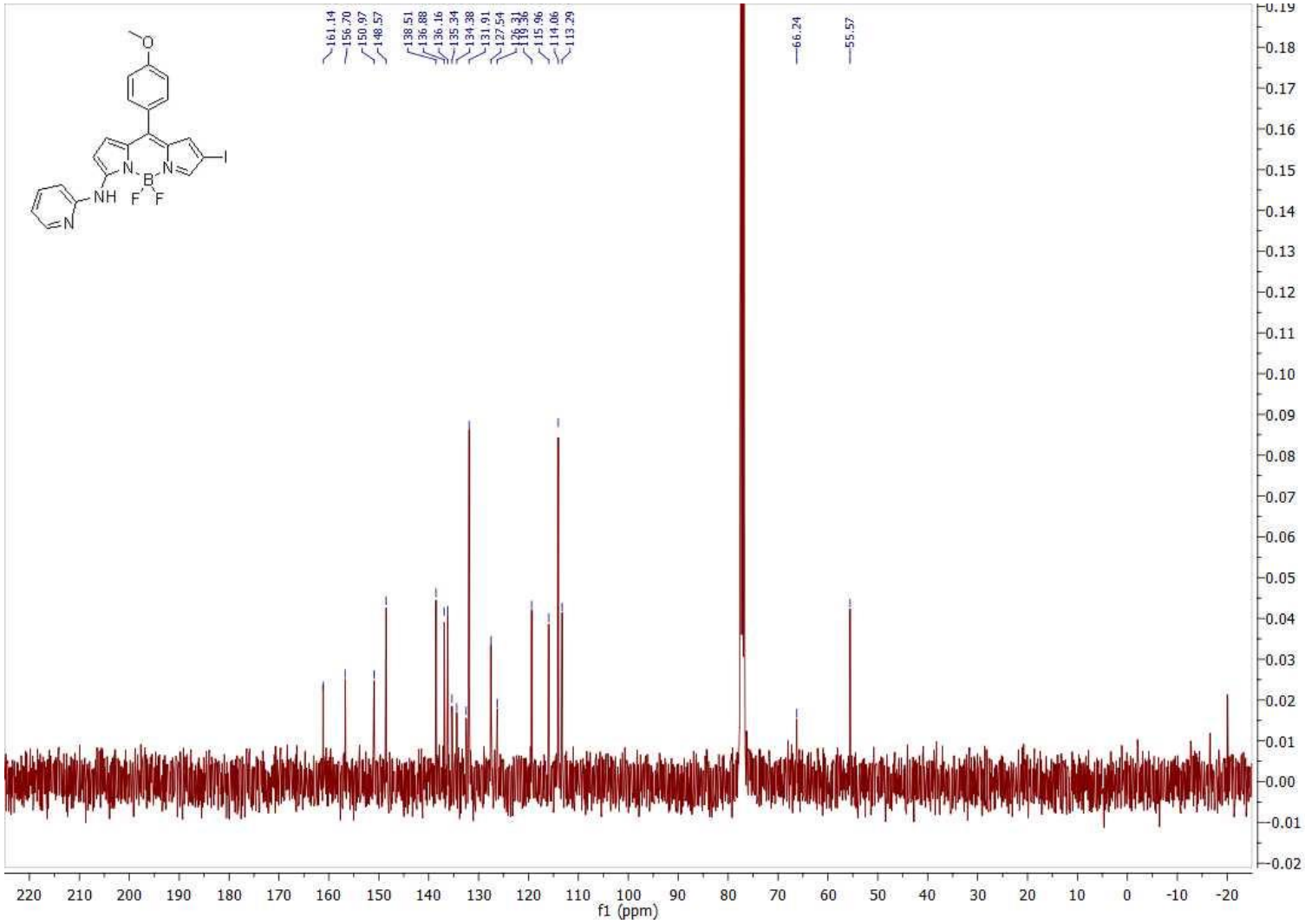
^{19}F NMR (376 MHz, Chloroform-d) 4m



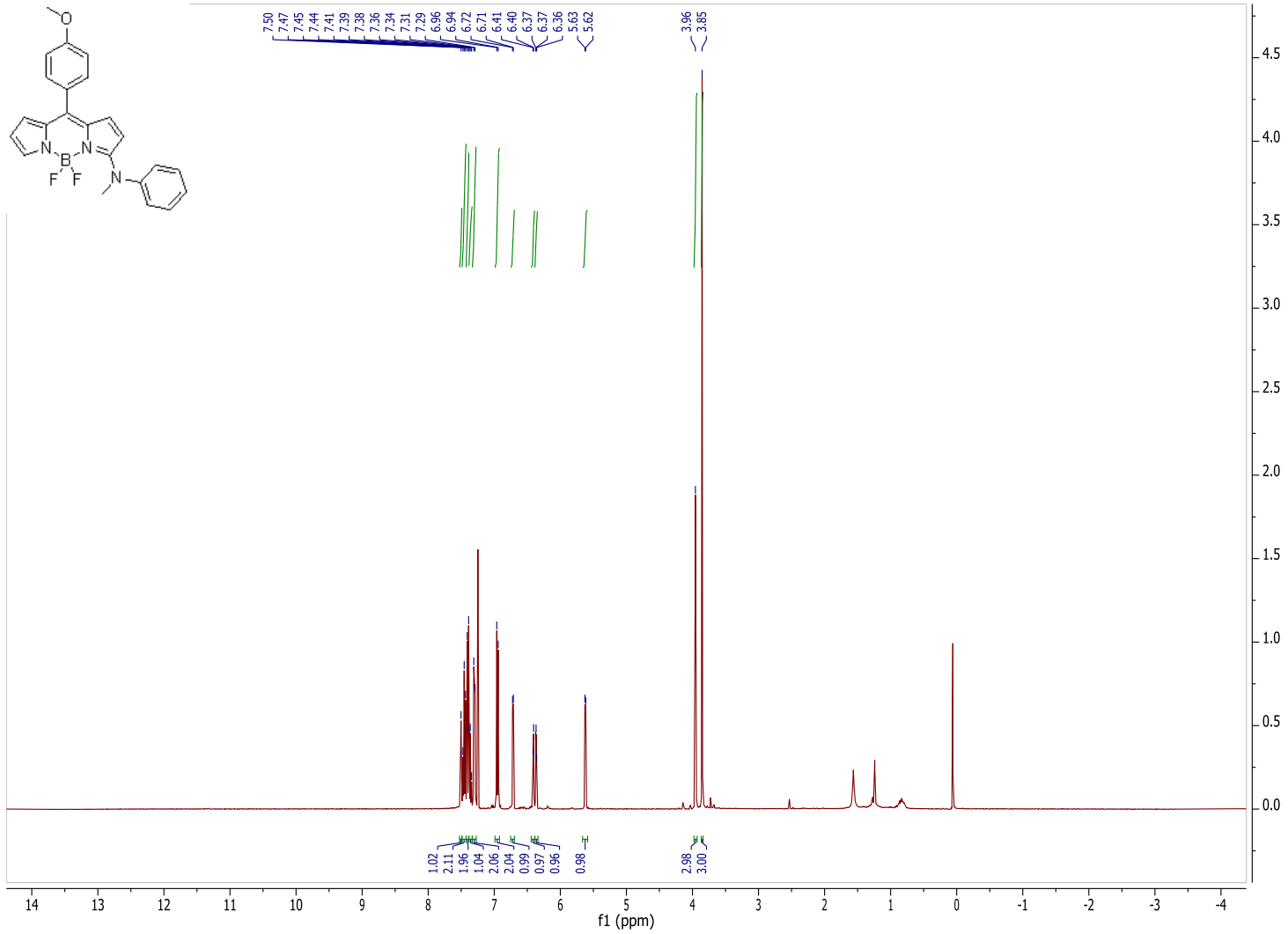
^{1}H NMR (400 MH, Chloroform-d) 5m



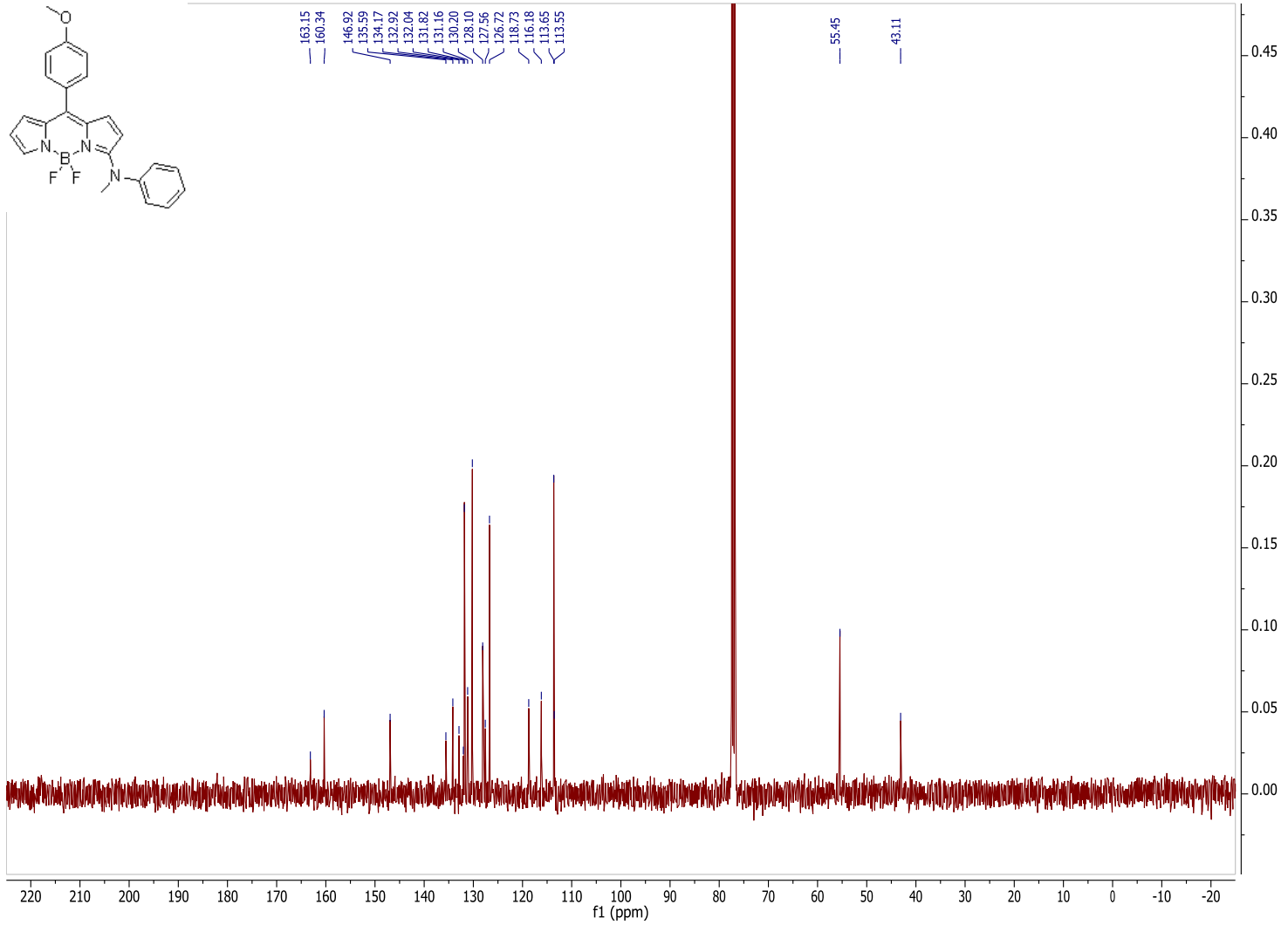
^{13}C NMR (101 MHz, Chloroform-d) 5m



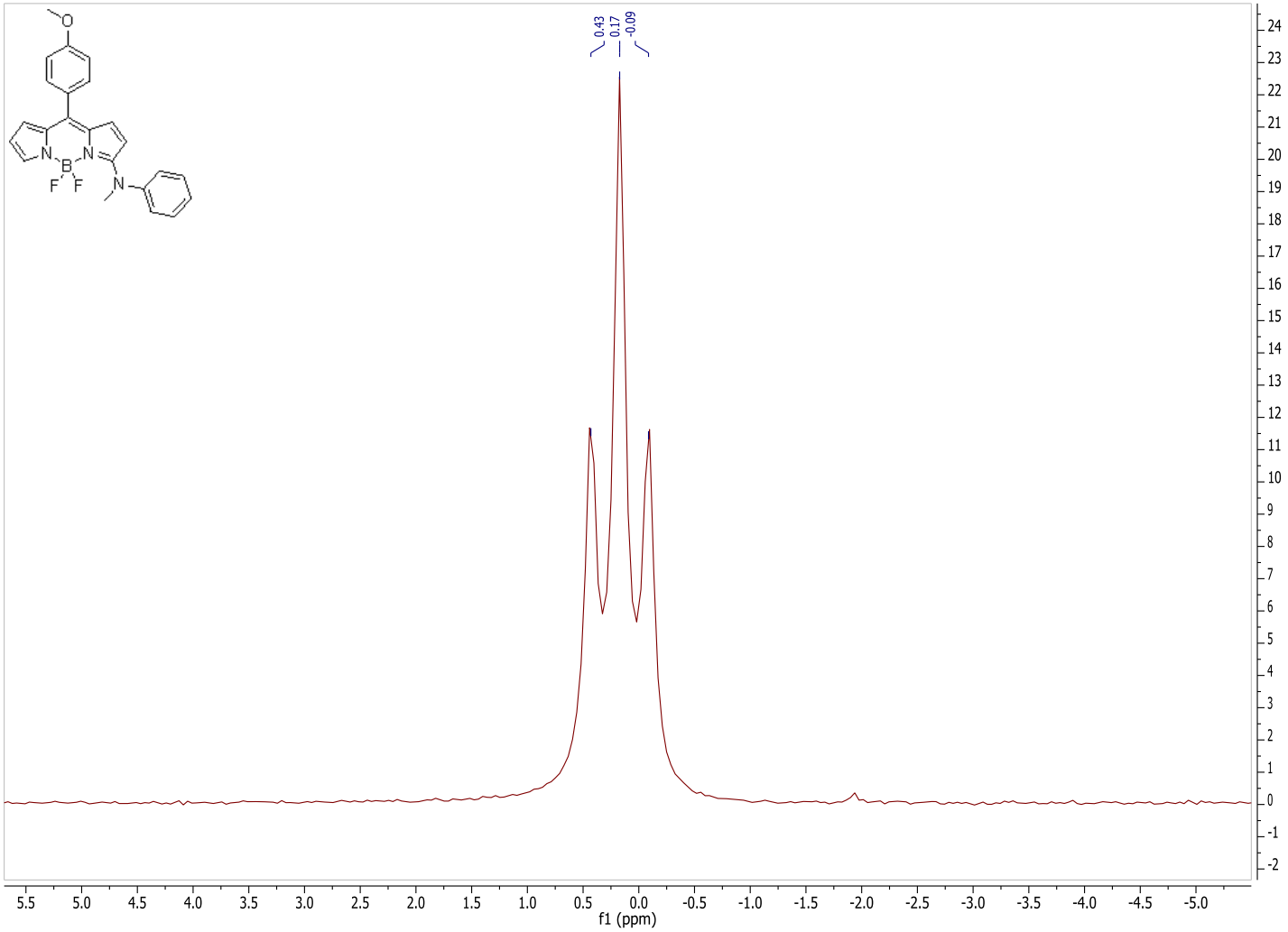
^{1}H NMR (400 MH, Chloroform-d) 4n



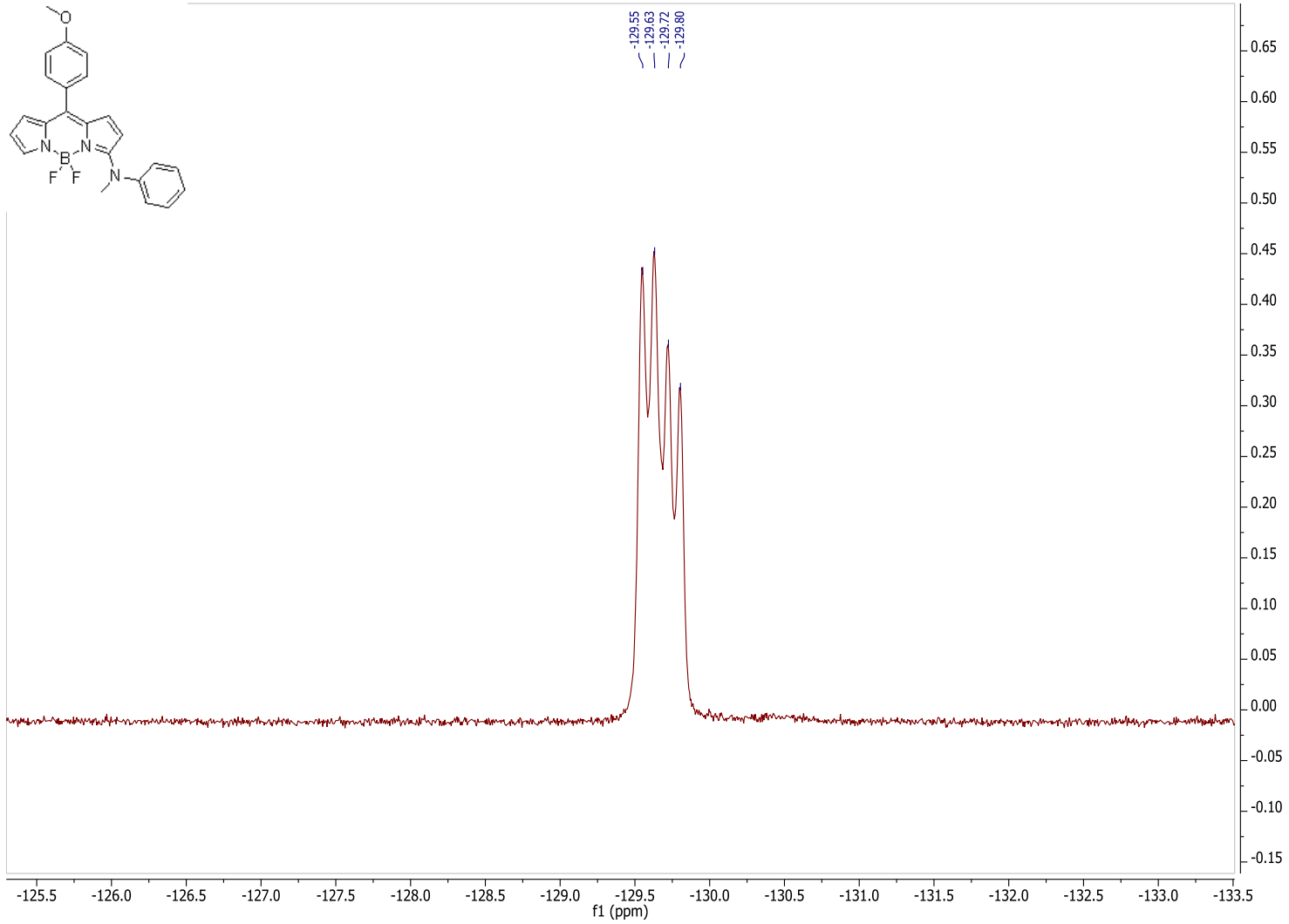
^{13}C NMR (101 MHz, Chloroform-d) 4n



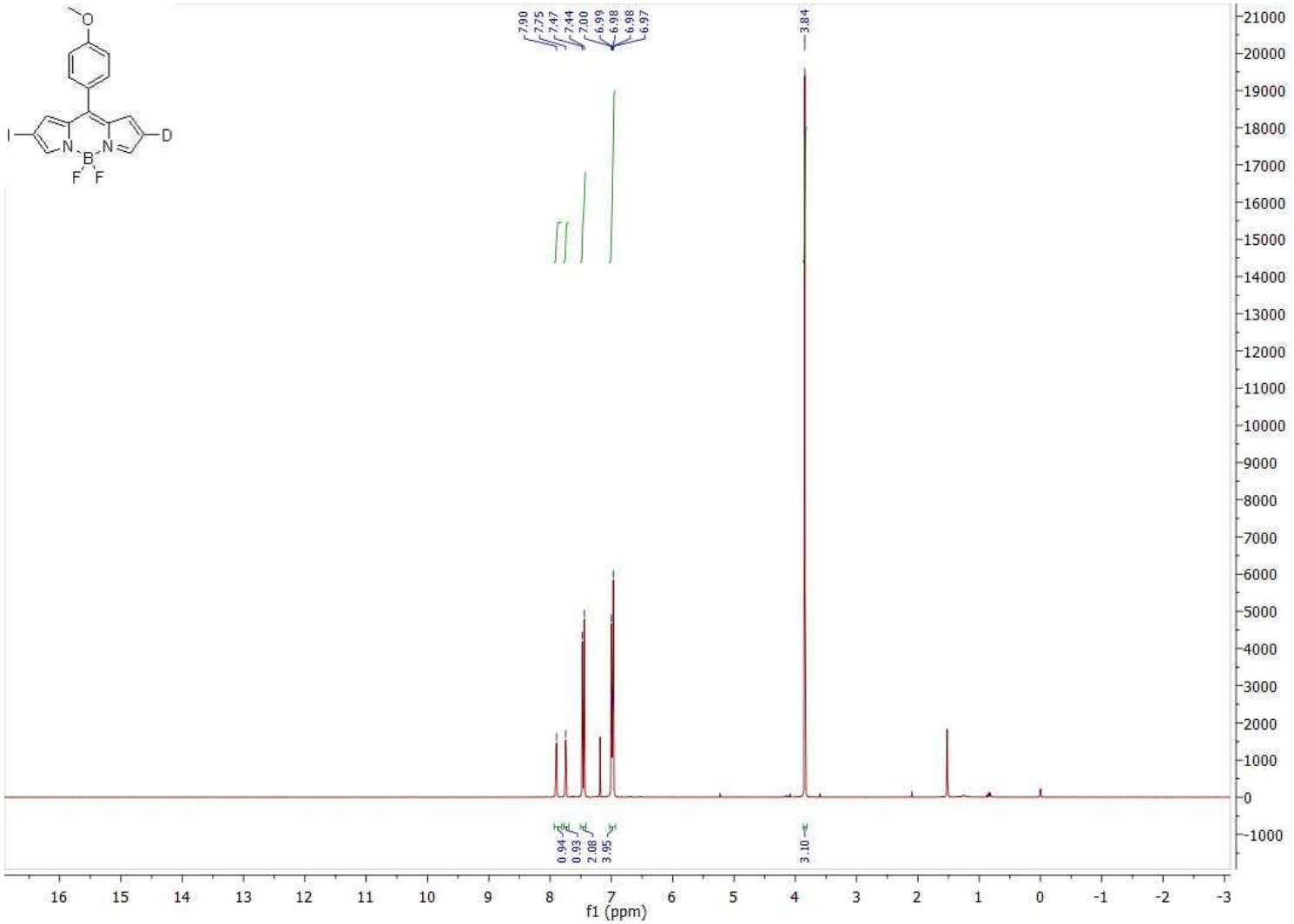
^{1}B NMR (128 MHz, Chloroform-d) 4n



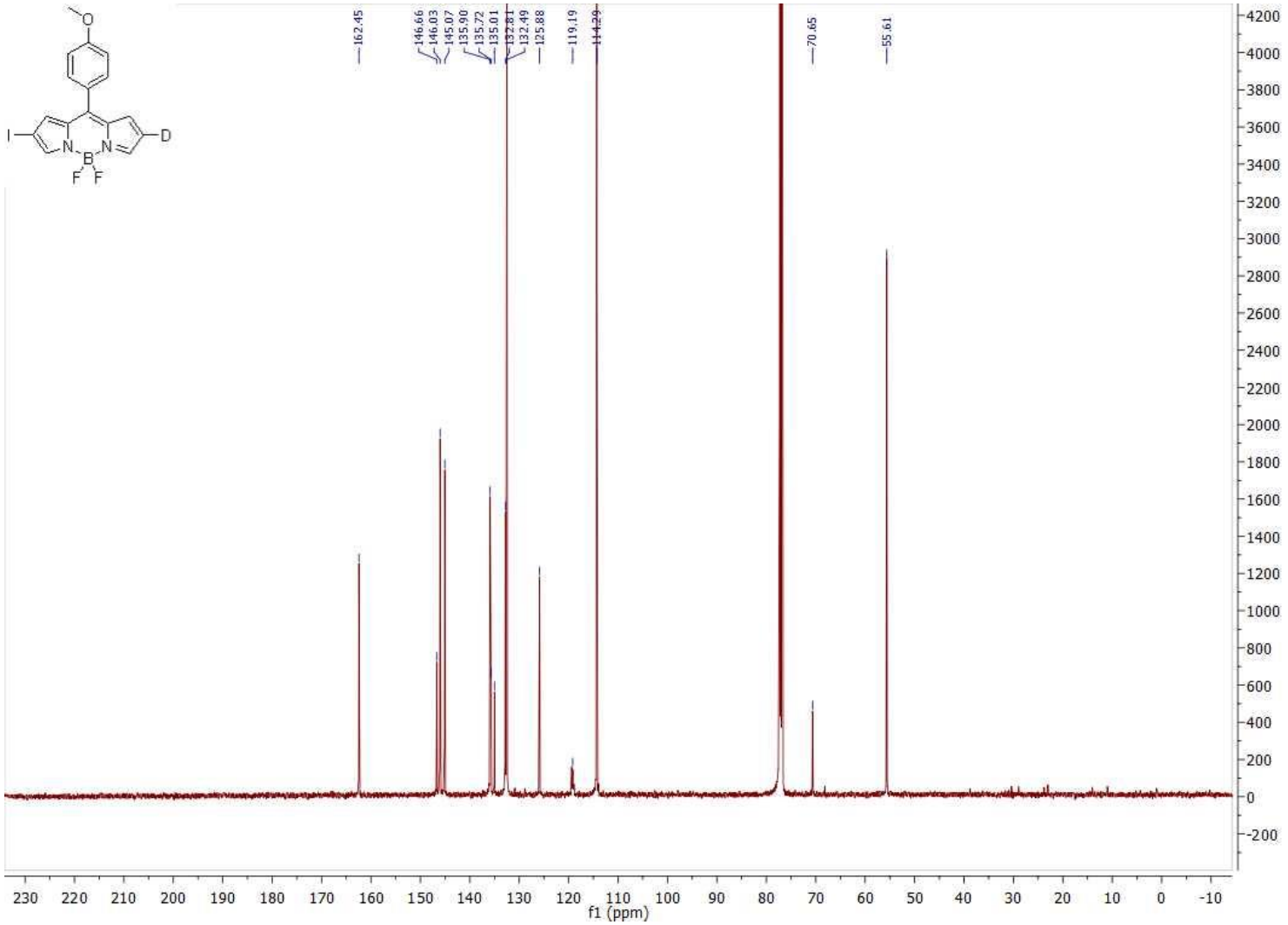
^{19}F NMR (376 MHz, Chloroform-d) 4n



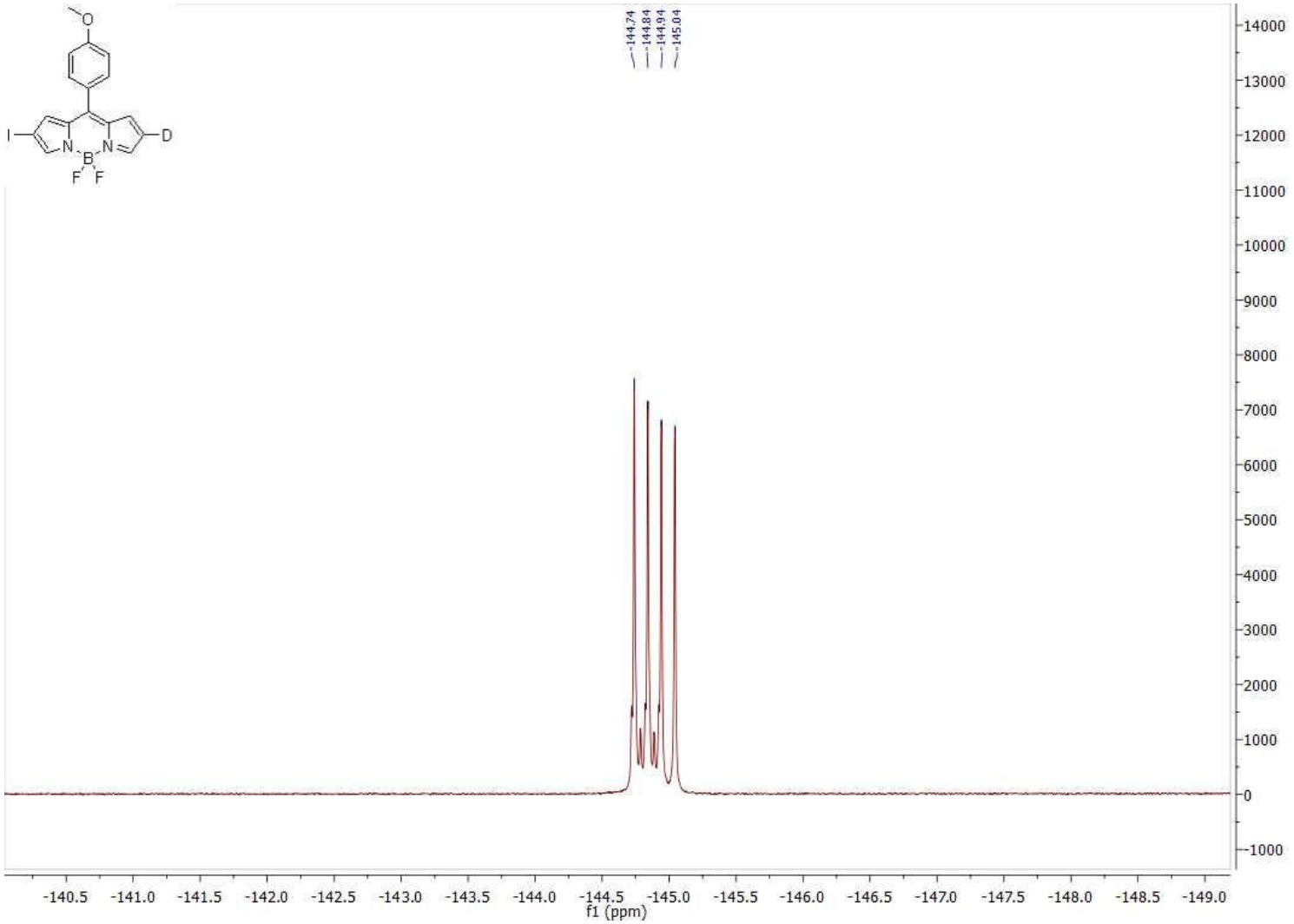
^{1}H NMR (300 MH, Chloroform-d) 12



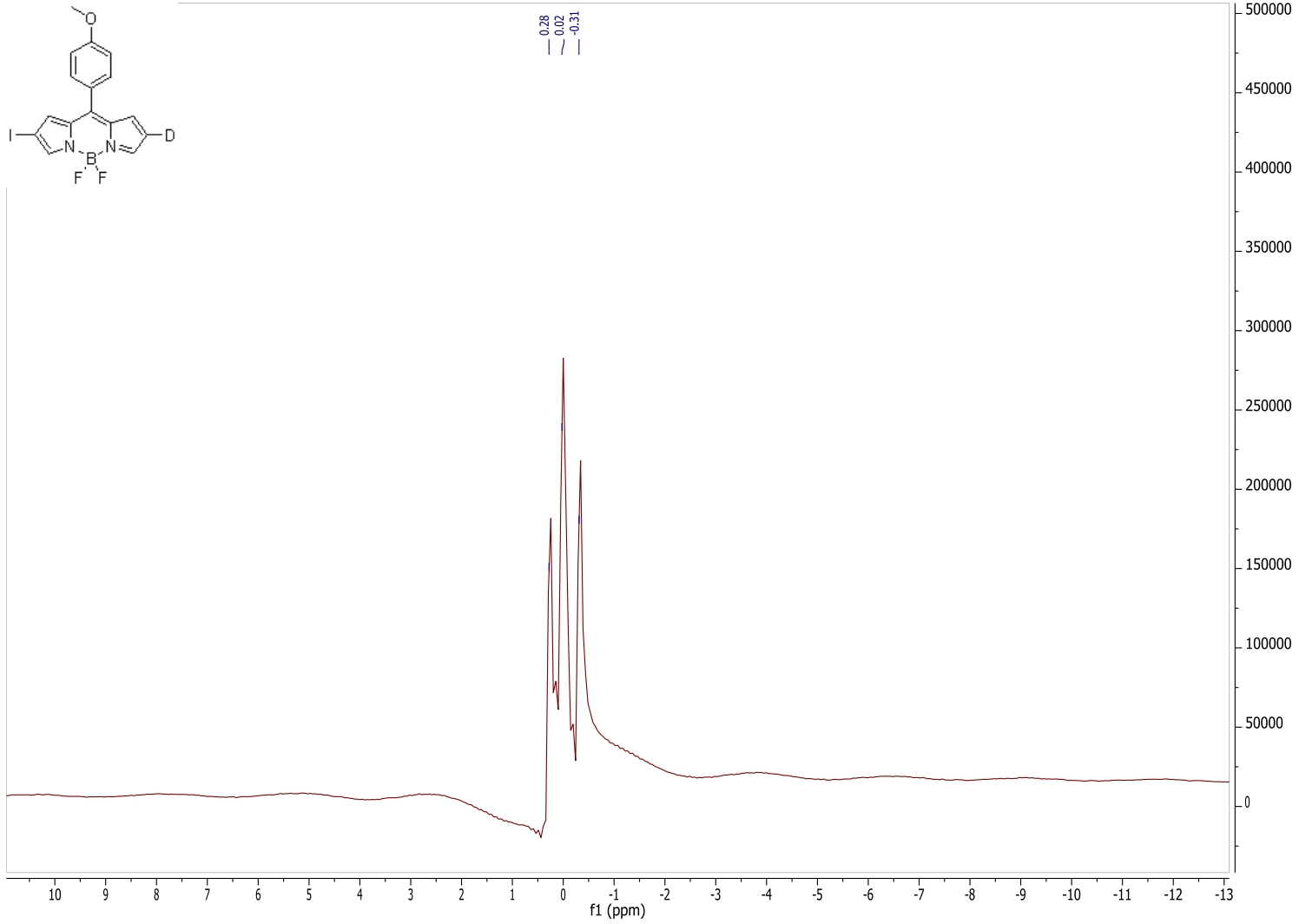
^{13}C NMR (126 MHz, Chloroform-d) 12



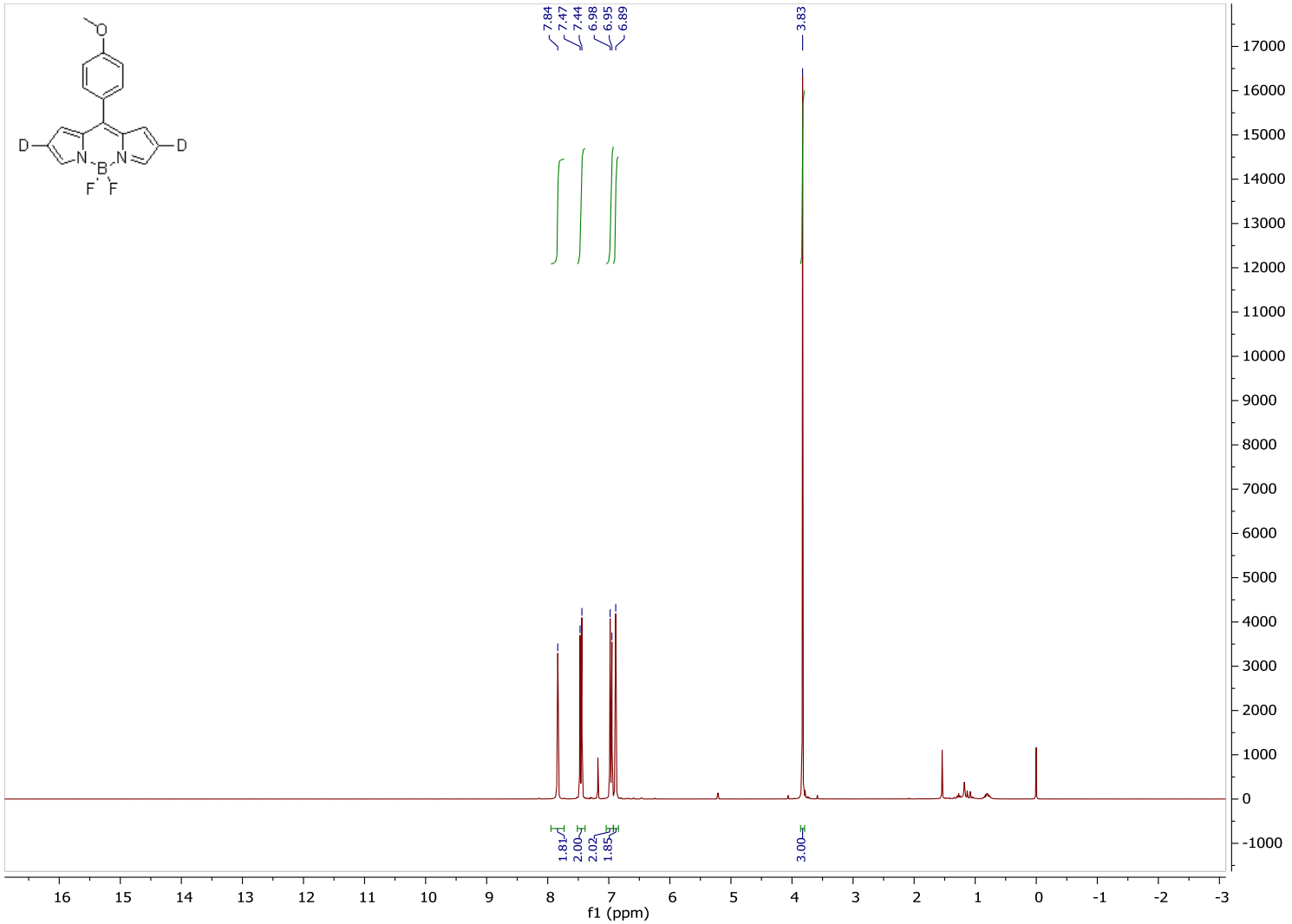
^{19}F NMR (282 MHz, Chloroform-*d*) 12



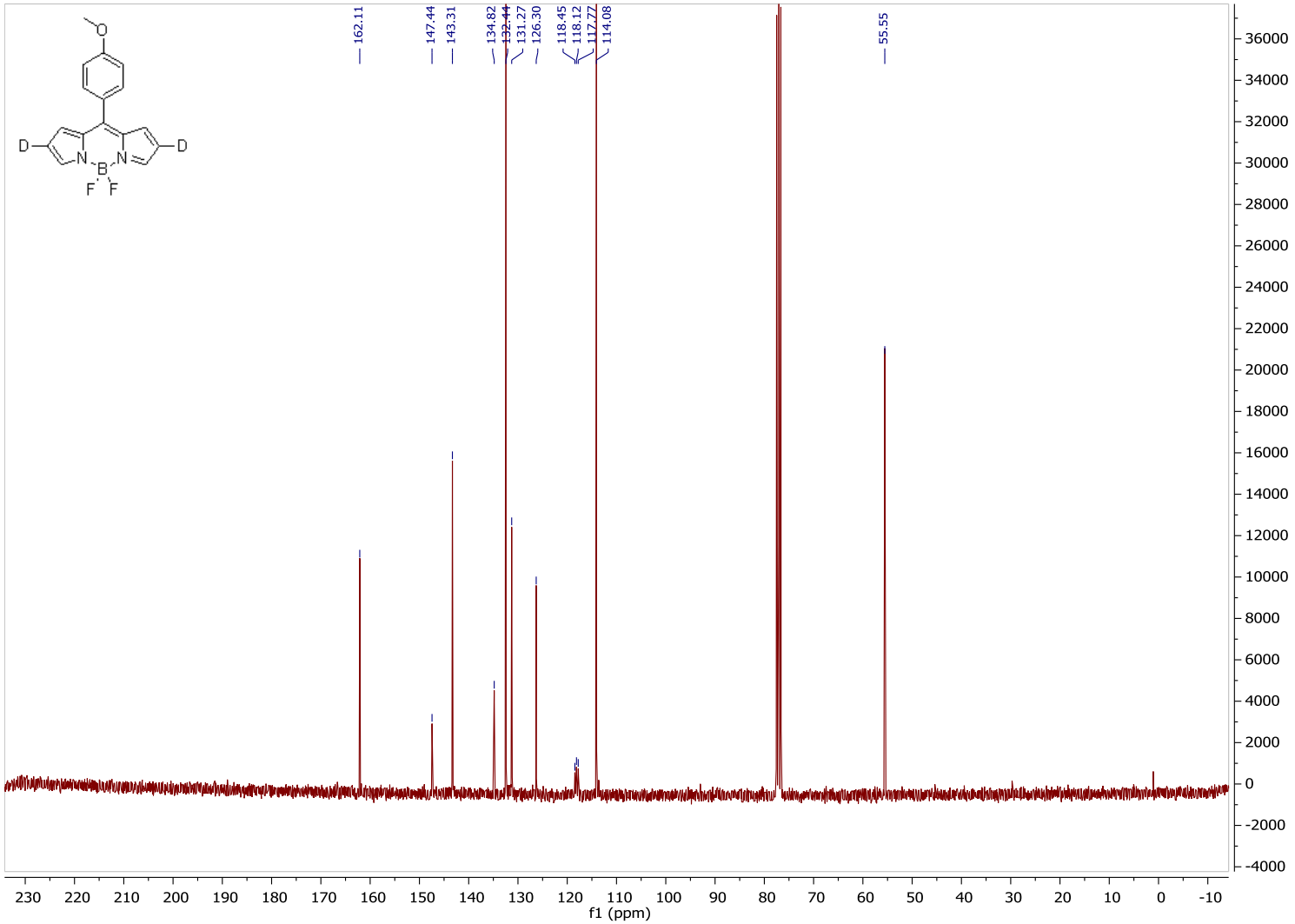
^{11}B NMR (96 MHz, Chloroform-*d*) 12



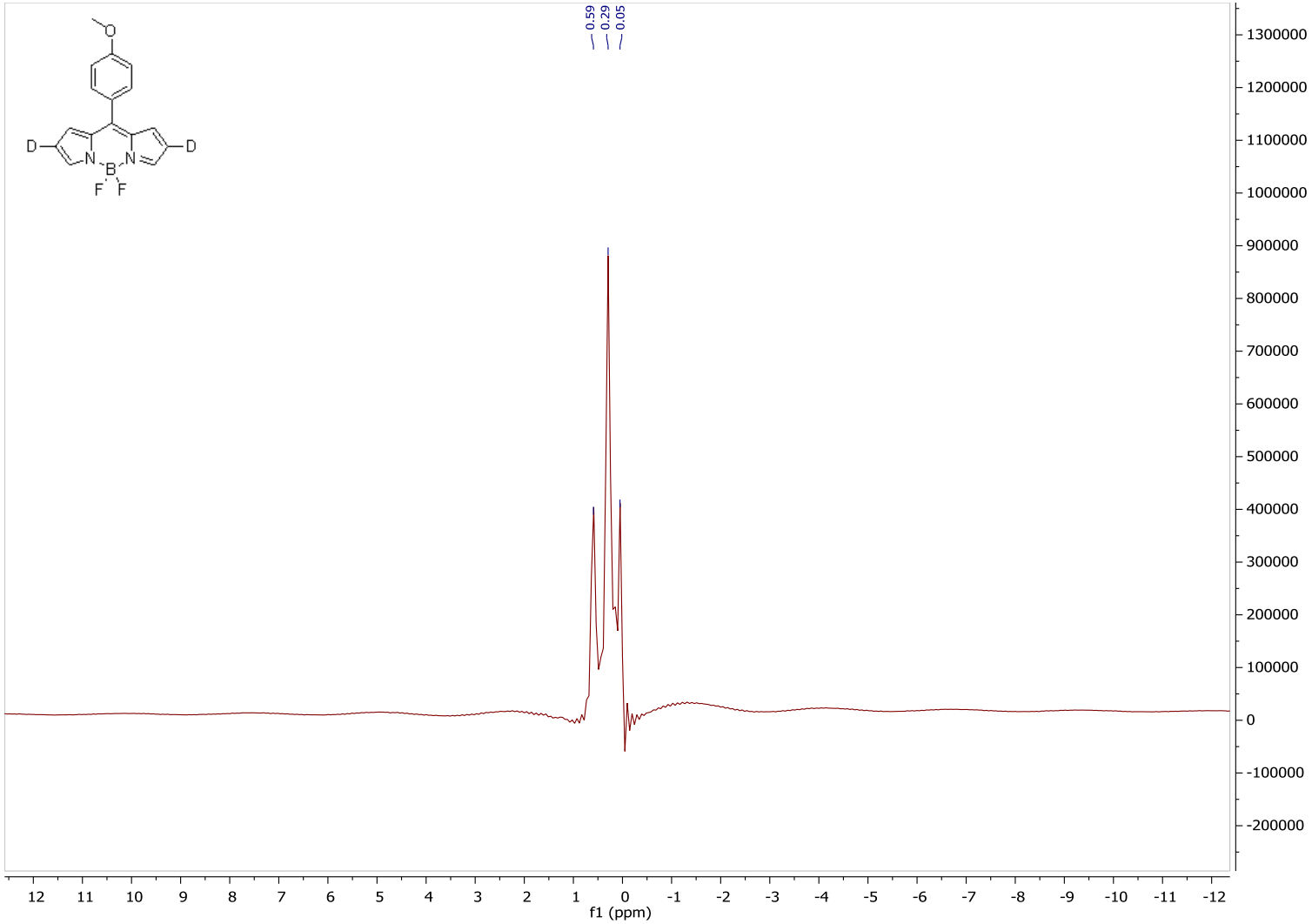
^{1}H NMR (300 MH, Chloroform-d) (2,6-$^{2}H_2$-1)



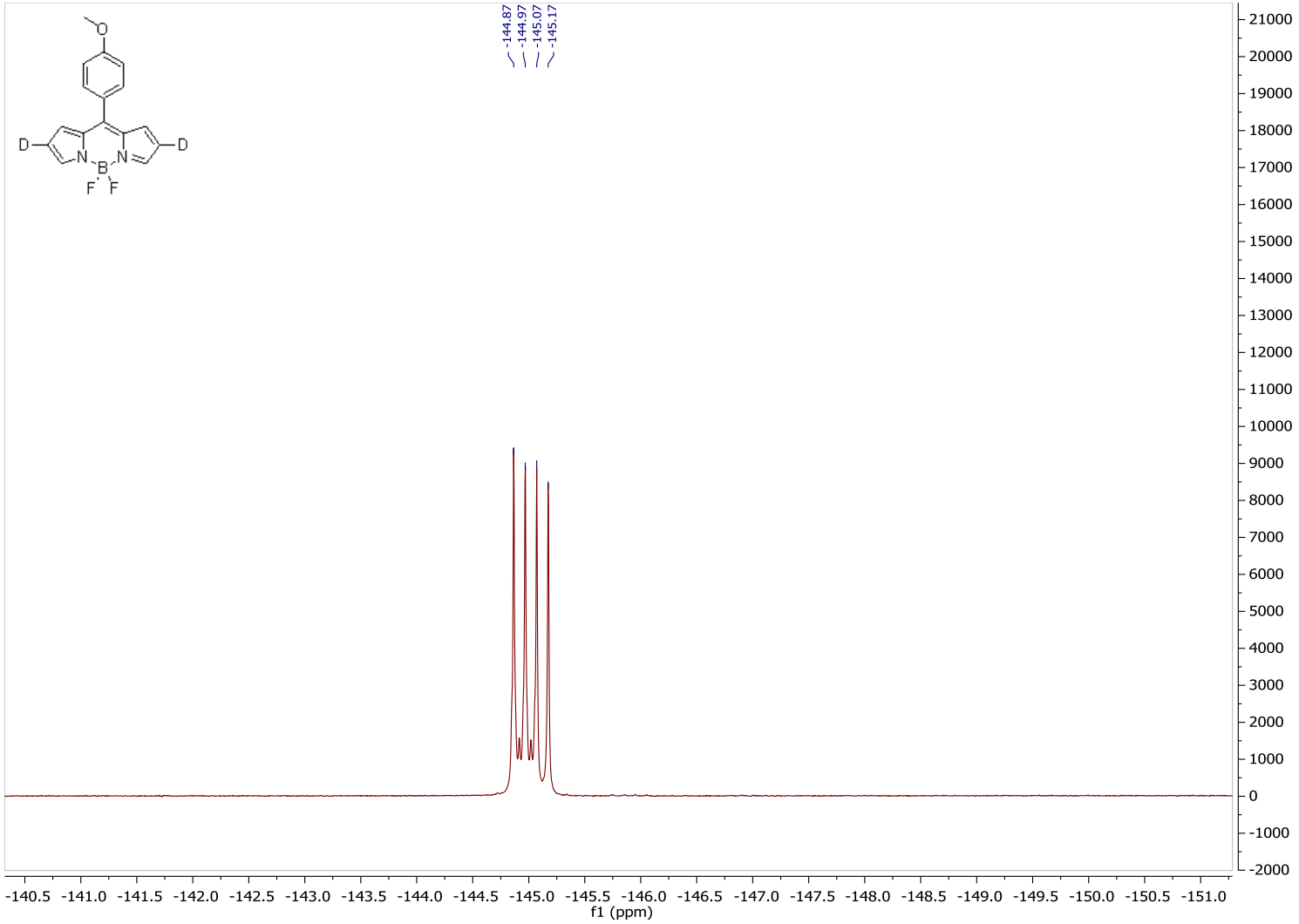
^{13}C NMR (75 MHz, $CDCl_3$) (2,6-$^{2}H_2$-1)



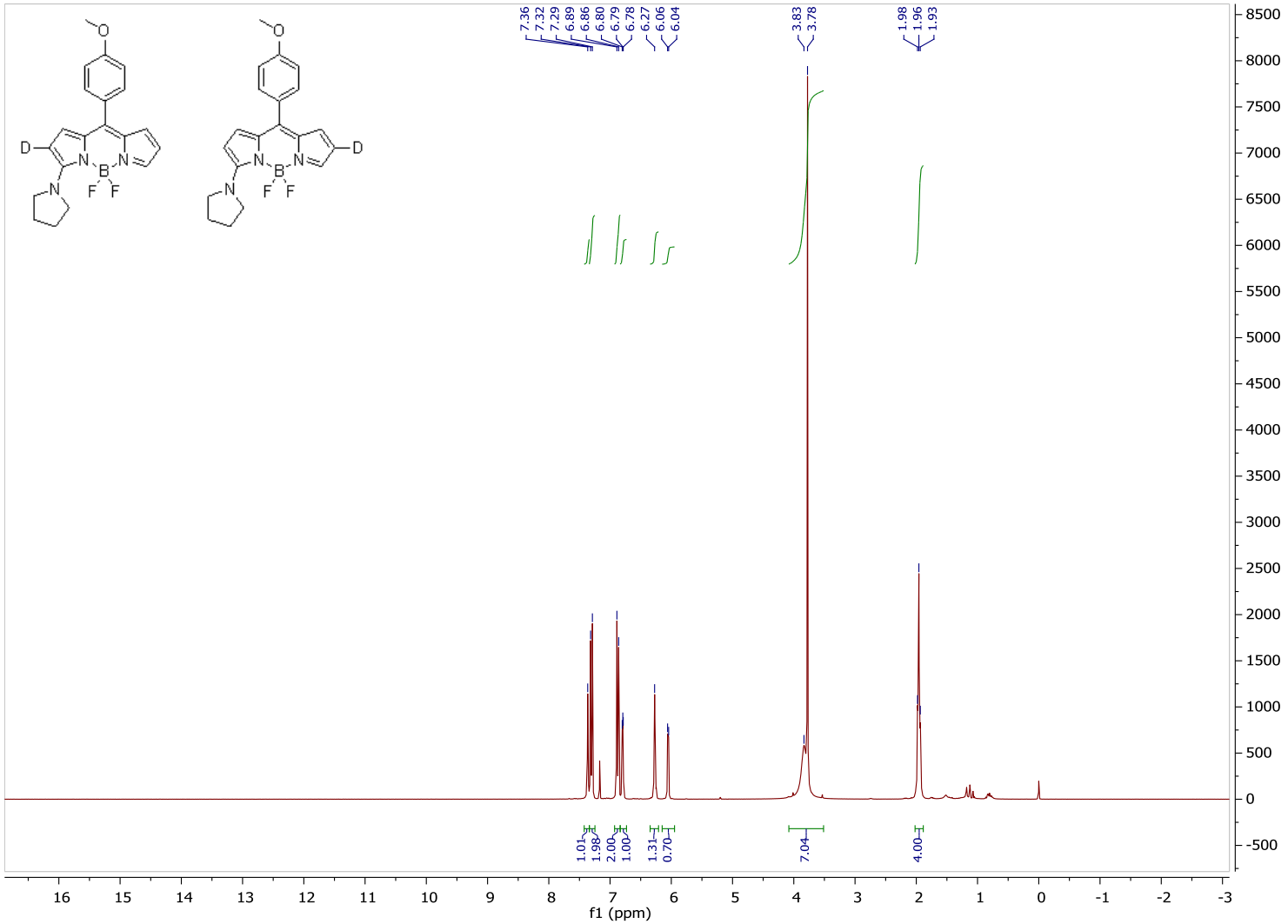
^{11}B NMR (96 MHz, Chloroform-*d*) (2,6-$^{2}H_2$-1)



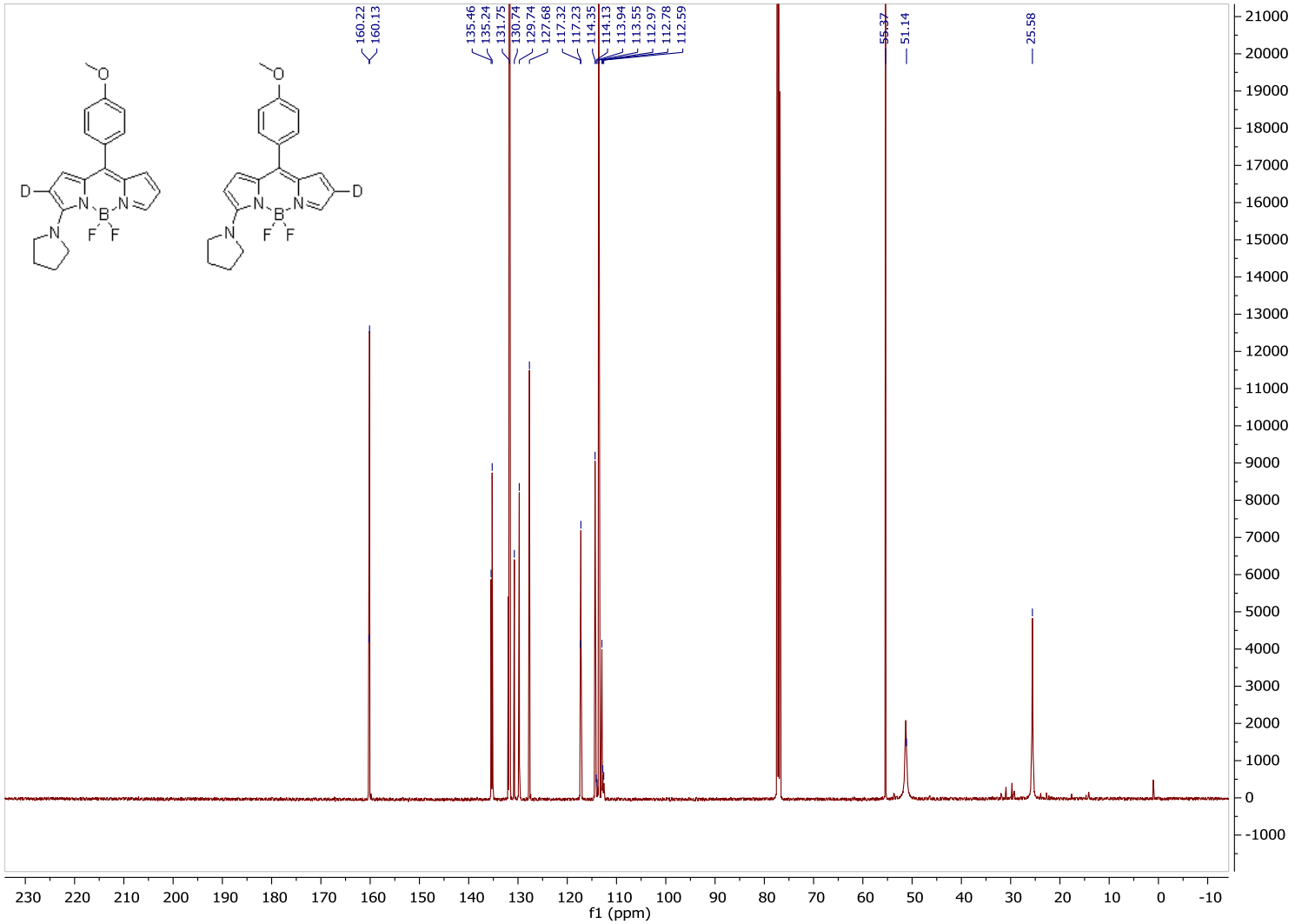
^{19}F NMR (282 MHz, Chloroform-*d*) (2,6-$^{2}H_2$-1)



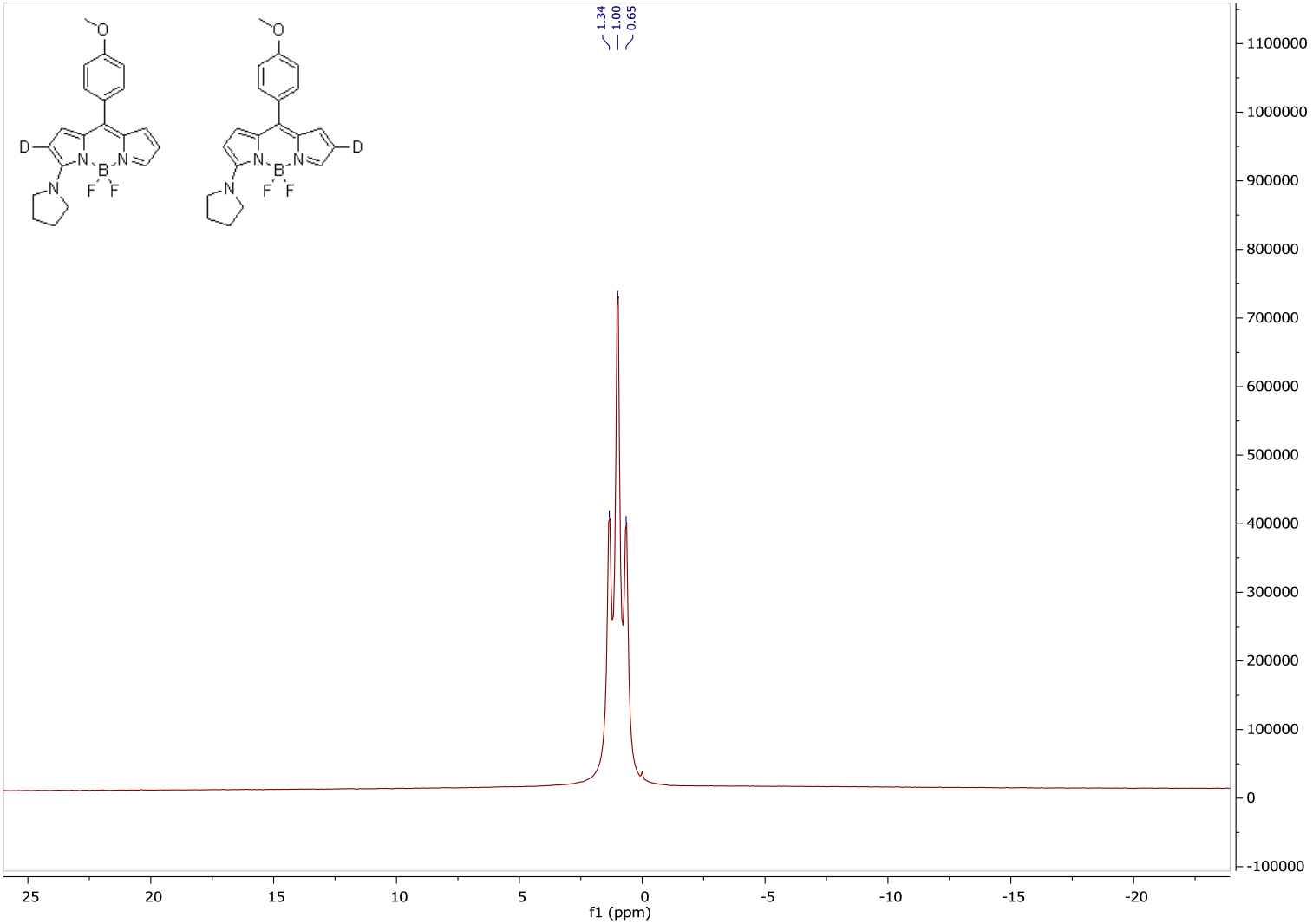
^{1}H NMR (300 MHz, Chloroform-*d*) 13 + 14



^{13}C NMR (126 MHz, Chloroform-*d*)) 13 + 14



^{11}B NMR (96 MHz, Chloroform-*d*) 13 + 14



^{19}F NMR (282 MHz, Chloroform-*d*) 13 + 14