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Synthesis of BODIPY derivatives with iodinated cobalt bis(dicarbollide)

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Experimental

General. The acetylenic iodine derivatives of cobalt bis(dicarbollide) Cs[8-$OCH_2C{\equiv}CH$-8′-I-3,3′-Co(1,2-$C_2B_9H_{10})_2$] **1a** and Cs[8-$O(CH_2)_2C{\equiv}CH$-8′-I-3,3′-Co(1,2-$C_2B_9H_{10})_2$] **1b** [S1] and azido derivative BODIPY **2** [S2] were prepared according to the literature procedures. Other chemicals were commercial reagent grade. The reaction progress was monitored by TLC (Merck F254 silica gel on aluminum plates). Acros Organics silica gel (0.060-0.200 mm) was used for column chromatography. NMR spectra were recorded on a Bruker Avance-400 spectrometer at 400.1 MHz (^{1}H), 128.4 MHz (^{11}B, ^{11}B{^{1}H}) and 100.0 MHz (^{13}C{^{1}H}), 364.0 MHz (^{19}F{^{1}H}). The residual signal of the NMR solvent relative to TMS was taken as the internal reference for ^{1}H and ^{13}C NMR spectra. ^{11}B NMR spectra were referenced to $BF_3{\times}Et_2O$ as external standard. ^{19}F NMR spectra were referenced to $CHCl_2F$ as external standard. Infrared spectra were recorded on an IR Prestige-21 (SHIMADZU) instrument. UV spectra were recorded on Spectra SF 2000 (Russia) instrument. High-resolution mass spectra (HRMS) were measured on a mictOTOF II (Bruker Daltonic, Bremen, Germany) instrument using electrospray ionization (ESI). The measurements were performed in a negative ion mode (interface capillary voltage 4000 V), mass range from m/z 50 to m/z 1800, external or internal calibration was carried out with ESI Tuning Mix, Agilent. A syringe injection was used for solutions in acetonitrile (flow rate 3 μL/min). Nitrogen was applied as a dry gas; the interface temperature was set at 180 °C.

Synthesis of conjugate 3a. Copper(I) iodide (6 mg, 0.003 mmol) and DIPEA (1 mL) were added to a solution of alkyne **1a** (100 mg, 0.17 mmol) and azido derivative BODIPY **2** (68 mg, 0.17 mmol) in ethanol (25 mL). The mixture was refluxed for 3 h. Then the reaction mixture was cooled to room temperature, and the inorganic precipitate was filtered. Then, the organic solvent was removed *in vacuo*. The residue was extracted using CH_2Cl_2 (100 mL) and washed with 1M HCl (4 × 50 mL) and brine (2 × 50 mL) and dried (Na_2SO_4). Then the CH_2Cl_2 was evaporated. The crude product was purified on a silica column using CH_2Cl_2-CH_3CN (2/1) as an eluent to obtain 127 mg (73%) of the desired product **3a**. ^{1}H NMR (acetone-d_6, ppm) δ 7.90 (s,

1H, CH_{triaz}), 7.30 (2H, d, J = 8.6 Hz, CH_{ar}), 7.20 (d, 2H, J = 8.7 Hz, CH_{ar}), 6.11 (s, 2H, CH_{pyr}), 4.88 (t, 2H, J = 5.1 Hz, -OCH$_2$CH_2N$_{triaz}$), 4.56 (m, 4H, -OCH_2CH$_2$-N$_{triaz}$, -OC$\underline{H_2}$-triazole), 4.43 (s, 2H, CH_{carb}), 4.23 (s, 2H, CH_{carb}), 2.50 (s, 6H, CH_{3pyr}), 1.46 (s, 6H, CH_{3pyr}). ^{13}C NMR (acetone-d_6, ppm) δ 159.1 (C_{arc}), 155.0 (C_{pyr}(CH$_3$)), 147.6 (C_{triaz}), 143.2 (C_{pyr}(CH$_3$)), 142.3 (–C=), 131.6 (C_{pyr}), 129.4 (CH$_{ar}$), 127.4 (C_{ar}), 122.7 (CH$_{triaz}$), 121.1 (CH$_{pyr}$), 115.4 (CH$_{ar}$), 66.7 (-OCH$_2$CH$_2$N$_{triaz}$), 63.4 (B-OCH$_2$-triazole), 56.6 (C_{carb}), 54.5 (C_{carb}), 49.2 (-OCH$_2$$CH_2N_{triaz}$), 13.9 ($CH_{3pyr}$), 13.6 ($CH_{3pyr}$). ^{11}B NMR (acetone-$d_6$, ppm) δ 21.8 (1B, s, B-O), 0.7 (1B, t, J = 33 Hz, -BF$_2$), -0.3 (m, 2B), -5.5 (m, 9B), -17.8 (2B, d, J = 146 Hz), -19.8 (2B, d, J = 143 Hz), -23.1 (1B, d, J = 168 Hz), -26.9 (1B, d, J = 174 Hz). ^{19}F NMR (acetone-d_6, ppm) δ -145.79 (q, J = 32.6 Hz). IR (ν/cm^{-1}): 2574 (BH), 1562 (triazole). UV (acetone, λ_{max}/нм): 498 (4.4). ESI-HRMS, *m/z* for $C_{28}H_{45}B_{19}CoF_2IN_5O_2$: calcd. 913.3820 [M]$^-$, found 913.3835 [M]$^-$.

Synthesis of conjugate 3b was similarly to **3a** using CuI (6 mg, 0.003 mmol), and DIPEA (1 mL), alkyne **1b** (100 mg, 0.16 mmol) and azido derivative BODIPY **2** (67 mg, (0.16 mmol) and ethanol (25 mL). Yield 122 mg (71%) of the desired product **3b**. ^{1}H NMR (acetone-d_6, ppm) δ 7.83 (s, 1H, CH_{triaz}), 7.30 (2H, d, J = 8.6 Hz, CH_{ar}), 7.20 (2H, d, J = 8.6 Hz, CH_{ar}), 6.11 (s, 2H, CH_{pyr}), 4.84 (t, 2H, J = 5.2 Hz, -OCH$_2$CH_2N$_{triaz}$), 4.56 (t, 2H, J = 5.2 Hz, -OCH_2CH$_2$-N$_{triaz}$), 4.30 (s, 2H, CH_{carb}), 4.21 (s, 2H, CH_{carb}), 3.70 (t, 2H, J = 6.6 Hz, -OCH$_2$CH$_2$-triazole), 2.84 (2H, t, J = 6.6 Hz, -OCH$_2$CH$_2$-triazole), 2.50 (s, 6H, CH_{3pyr}), 1.45 (s, 6H, CH_{3pyr}). ^{13}C NMR (acetone-d_6, ppm) δ 159.1 (C_{ar}), 155.0 (C_{pyr}(CH$_3$)), 145.2 (C_{triaz}), 143.1 (C_{pyr}(CH$_3$)), 142.3 (–C=), 131.6 (C_{pyr}), 129.4 (CH$_{ar}$), 127.3 (C_{ar}), 122.5 (CH$_{triaz}$), 121.1 (CH$_{pyr}$), 115.4 (CH$_{ar}$), 68.0 (B-OCH$_2$CH$_2$-triazole), 66.7 (-OCH$_2$CH$_2$N$_{triaz}$), 56.5 (C_{carb}), 54.5 (C_{carb}), 49.1 (-OCH$_2$$CH_2N_{triaz}$), 28.3 (B-OCH$_2$$CH_2$-triazole) 14.0 ($CH_{3pyr}$), 13.6 ($CH_{3pyr}$). ^{11}B NMR (acetone-$d_6$, ppm) δ 21.6 (1B, s, B-O,), 0.7 (1B, t, J = 32 Hz, -BF$_2$,), -0.5 (2B, d, J = 113 Hz,), -4.6 (m, 1B), -5.6 (d, 2B, J = 169 Hz), -7.3 (d, 2B, J = 148 Hz), -17.9 (d, 2B, J = 158 Hz), -19.8 (d, 2B, J = 162 Hz), -23.2 (d, 1B, J = 155 Hz), -27.2 (d, 1B, J = 147 Hz). ^{19}F NMR (acetone-d_6, ppm) δ -145.86 (q, J = 32.7 Hz). IR (ν/cm^{-1}): 2567 (BH), 1546 (triazole). UV (acetone, λ_{max}/нм): 498 (4.4). ESI-HRMS, *m/z* for $C_{29}H_{47}B_{19}CoF_2IN_5O_2$: calcd. 926.3996 [M]$^-$, found 926.3996 [M]$^-$.

References

[S1] I. D. Kosenko, I. A. Lobanova, I. A. Godovikov, Z. A. Starikova, I. B. Sivaev and V. I. Bregadze, *J. Organomet. Chem*., 2014, **769**, 72; https://doi.org/10.1016/j.jorganchem.2014.07.005.

[S2] X. Wu, W. Wu, X. Cui, J. Zhao and M. Wu, *J. Mater. Chem. C*., 2016, **4**, 2843; https://doi.org/10.1039/c5tc01222h.

Display Report

Analysis Info

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Sample Name	DA-74_neg	Instrument / Ser#	maXis 43
Comment			

Acquisition Parameter

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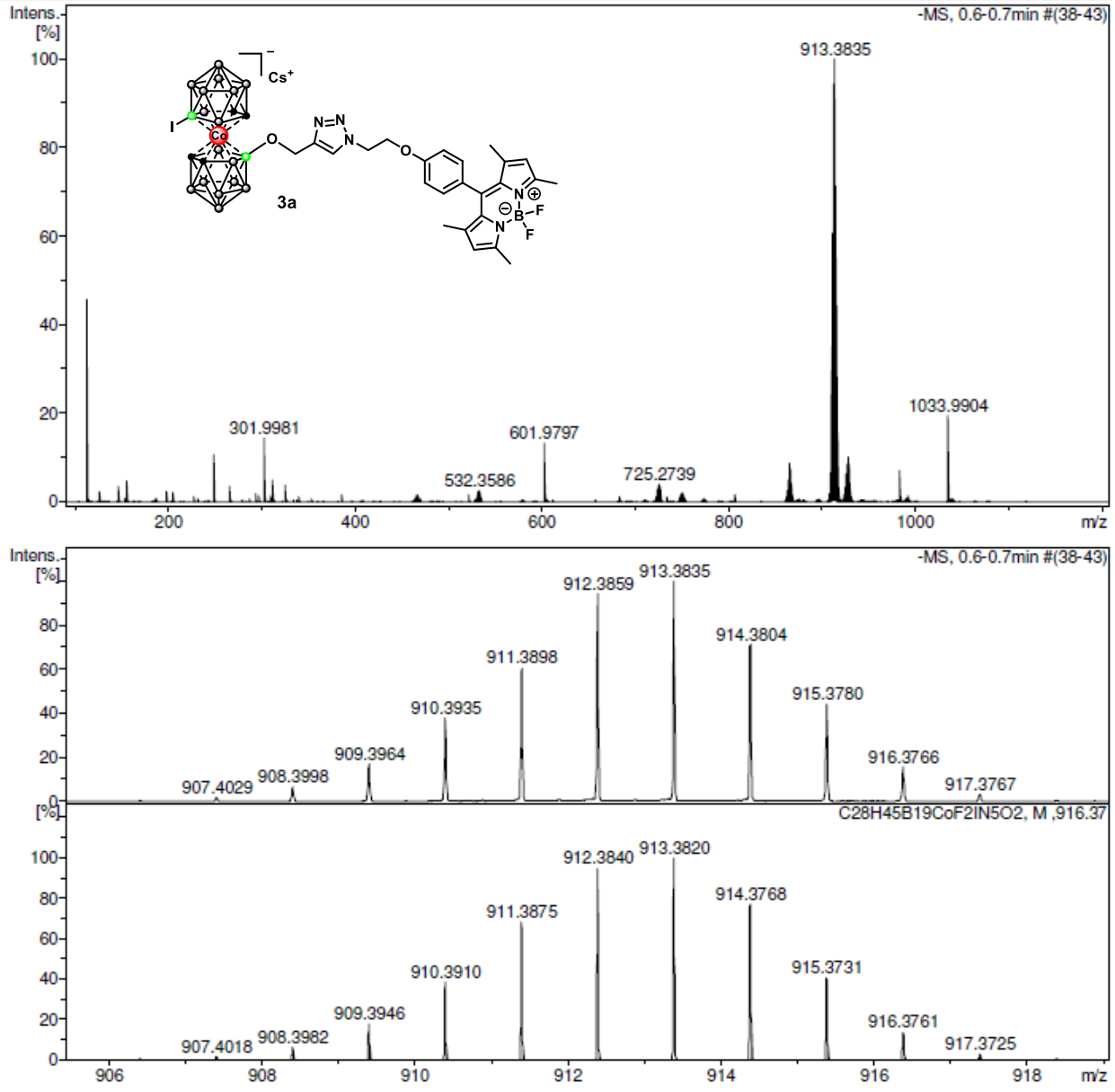

Figure S1. ESI-HRMS of conjugate **3a**

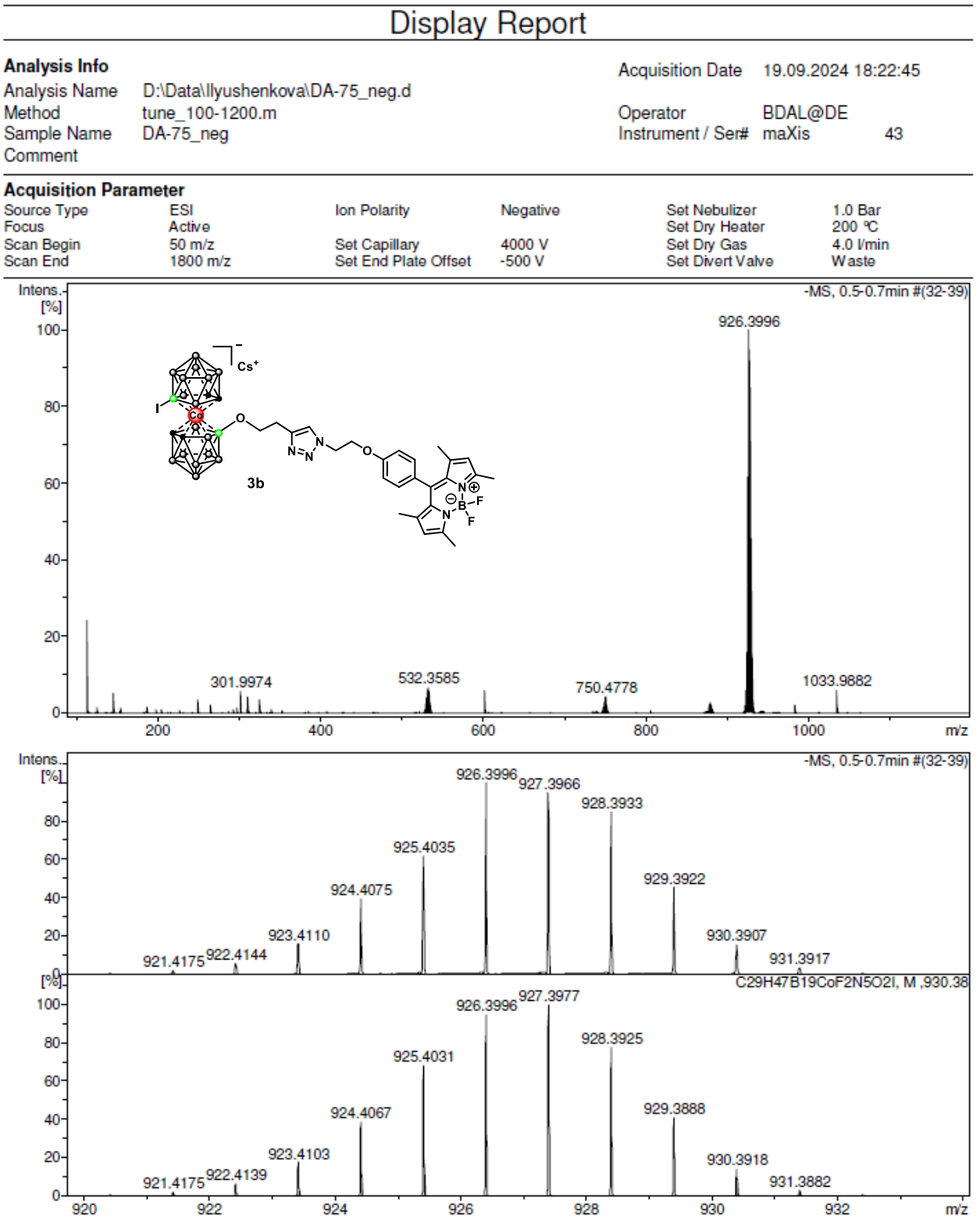

Figure S2. ESI-HRMS spectrum of conjugate **3b**

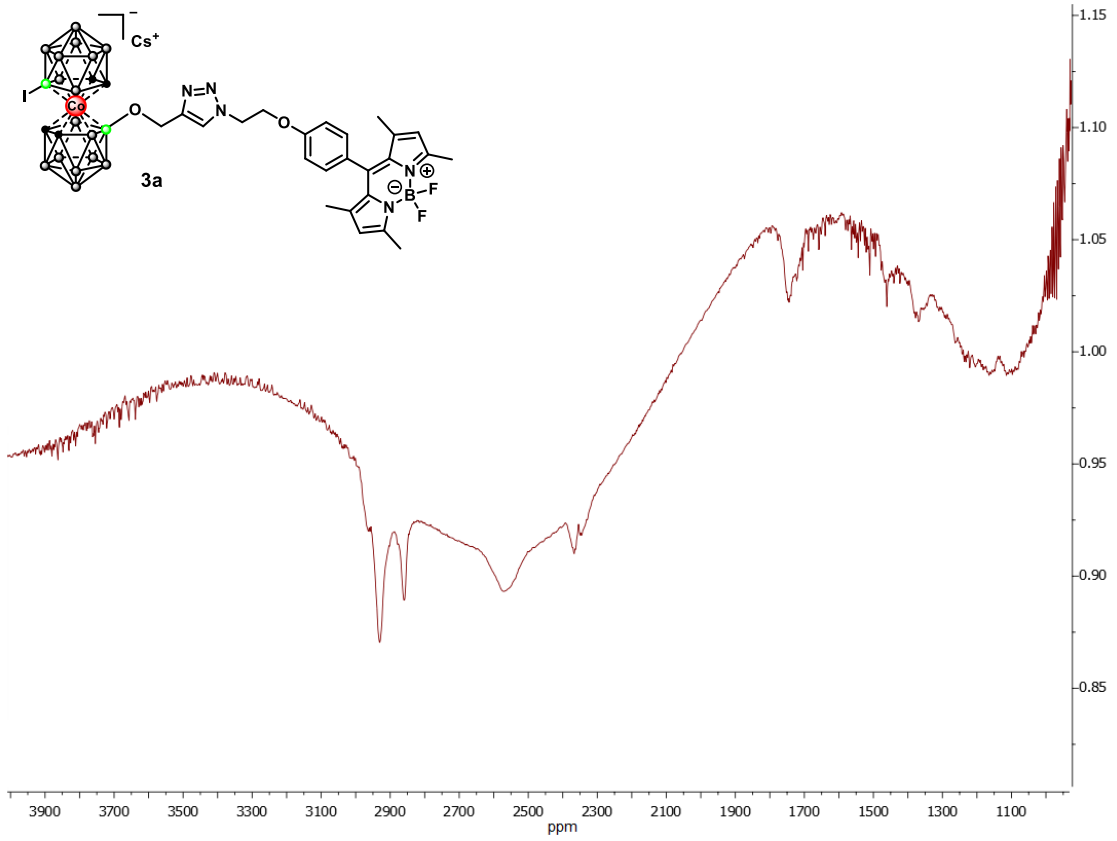

Figure S3. IR spectrum of conjugate **3a**

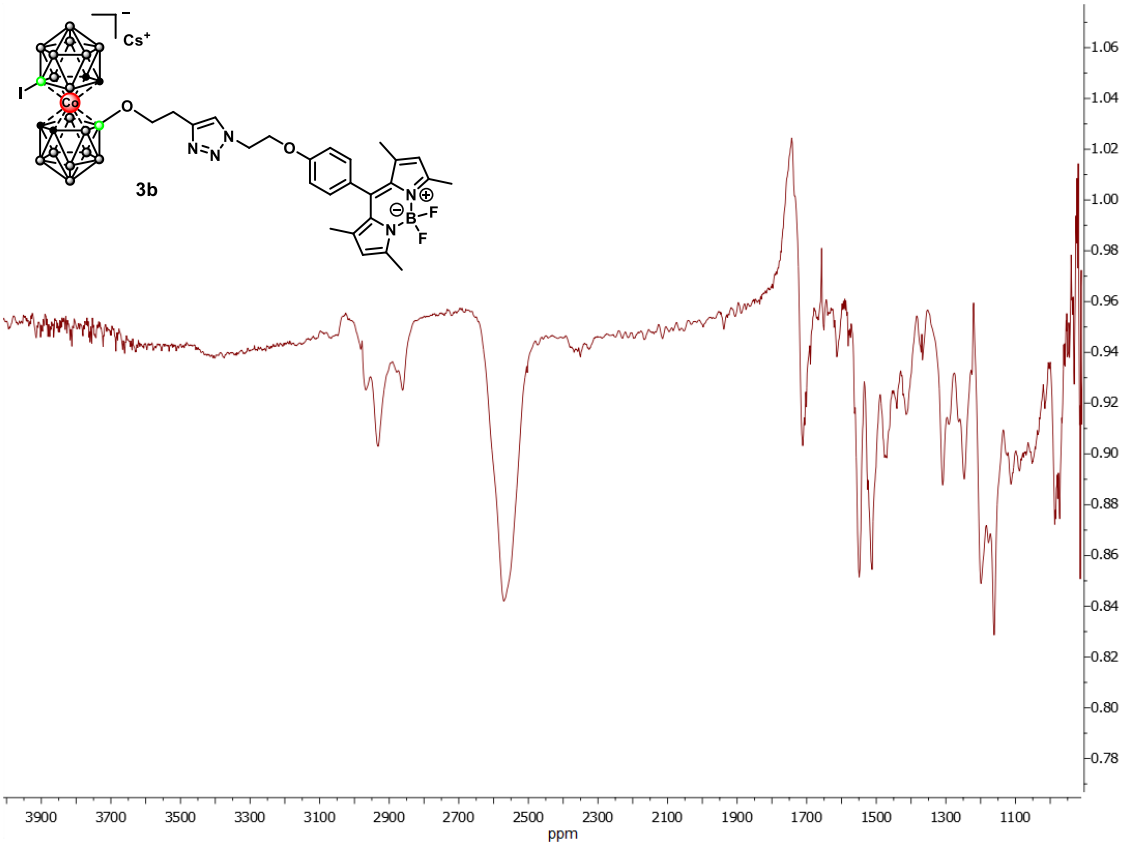

Figure S4. IR spectrum of conjugate **3b**

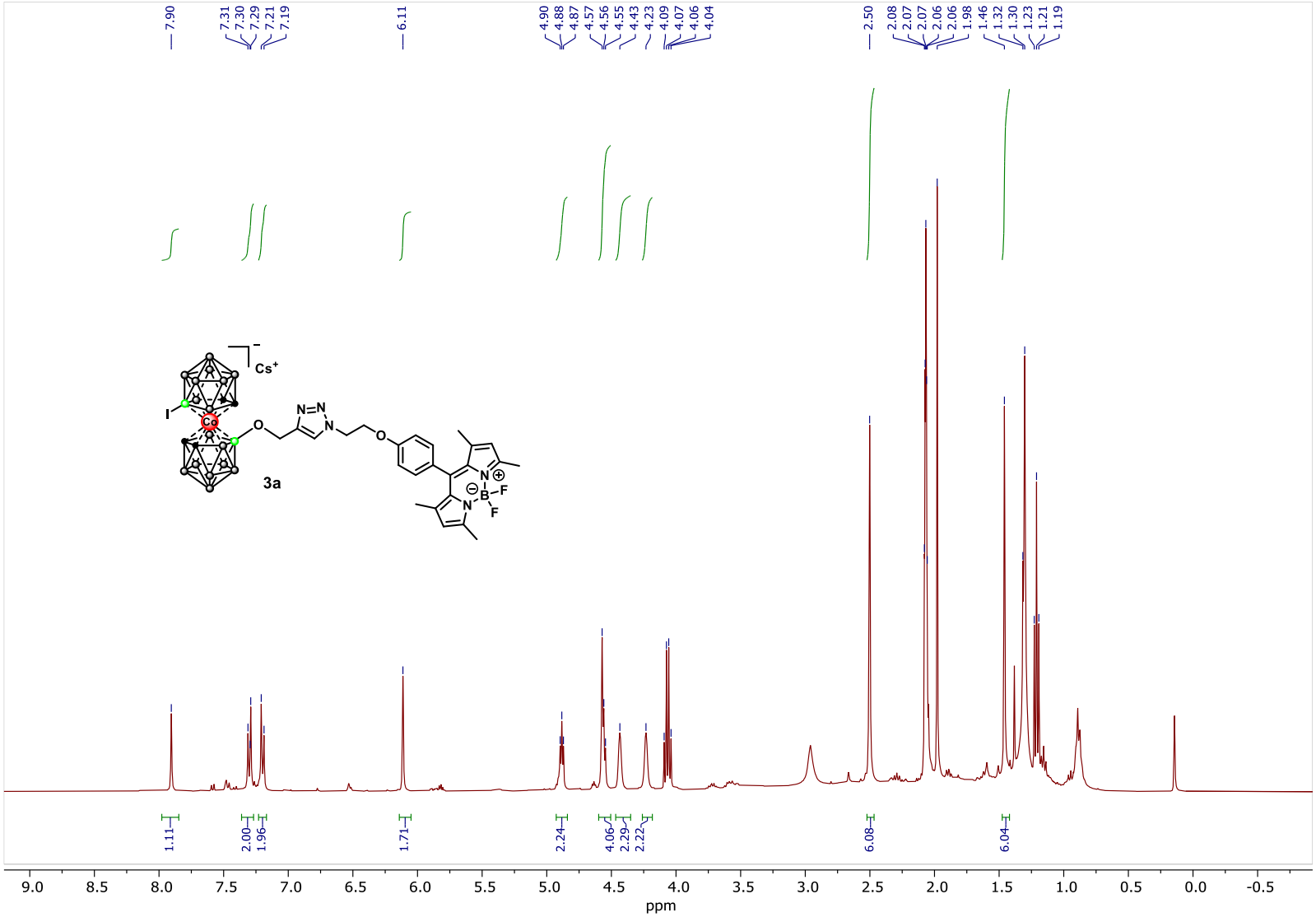

Figure S5. ^{1}H NMR spectrum of conjugate **3a**

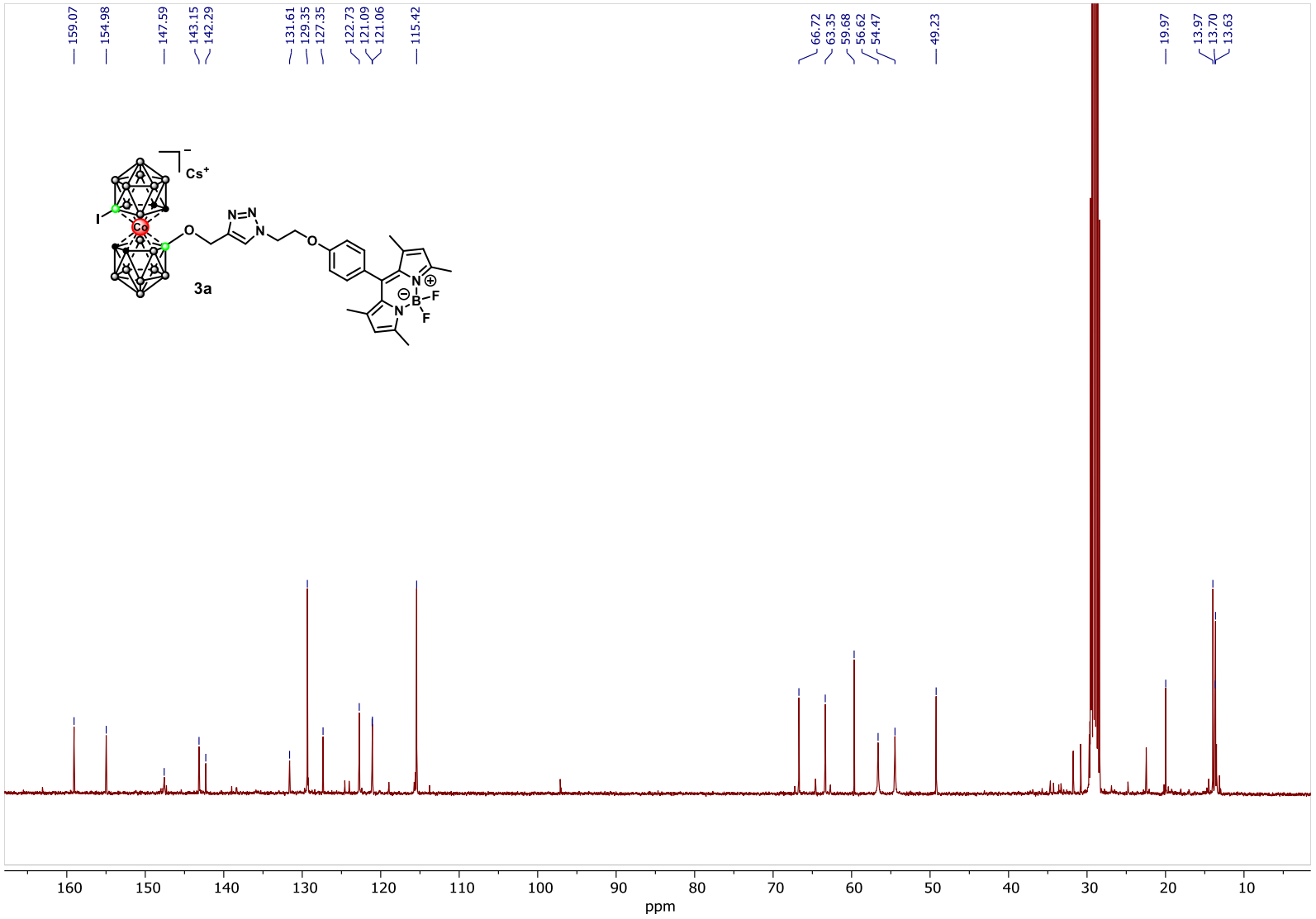

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of conjugate **3a**

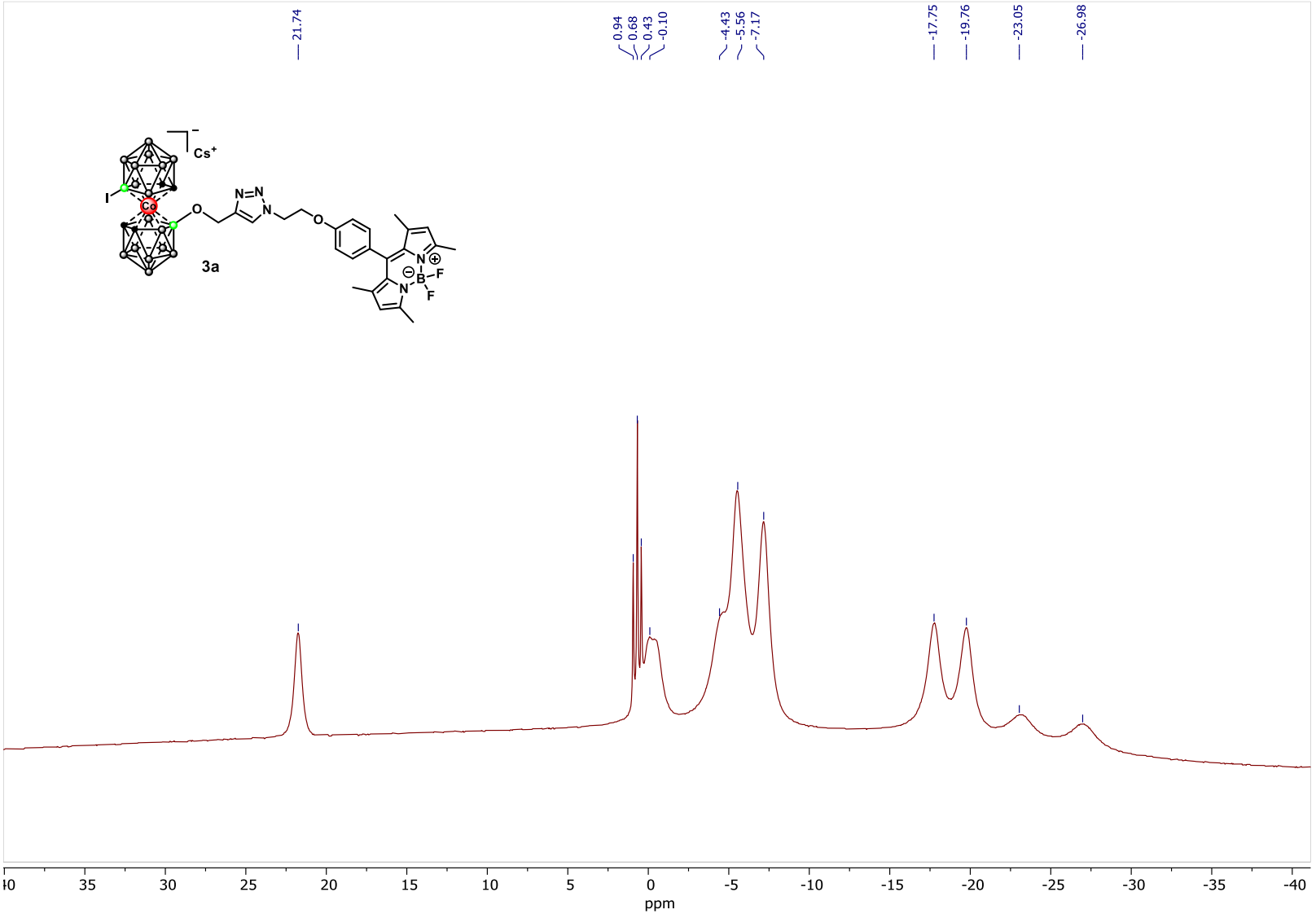

Figure S7. NMR $^{11}B\{^{1}H\}$ spectrum of conjugate **3a**

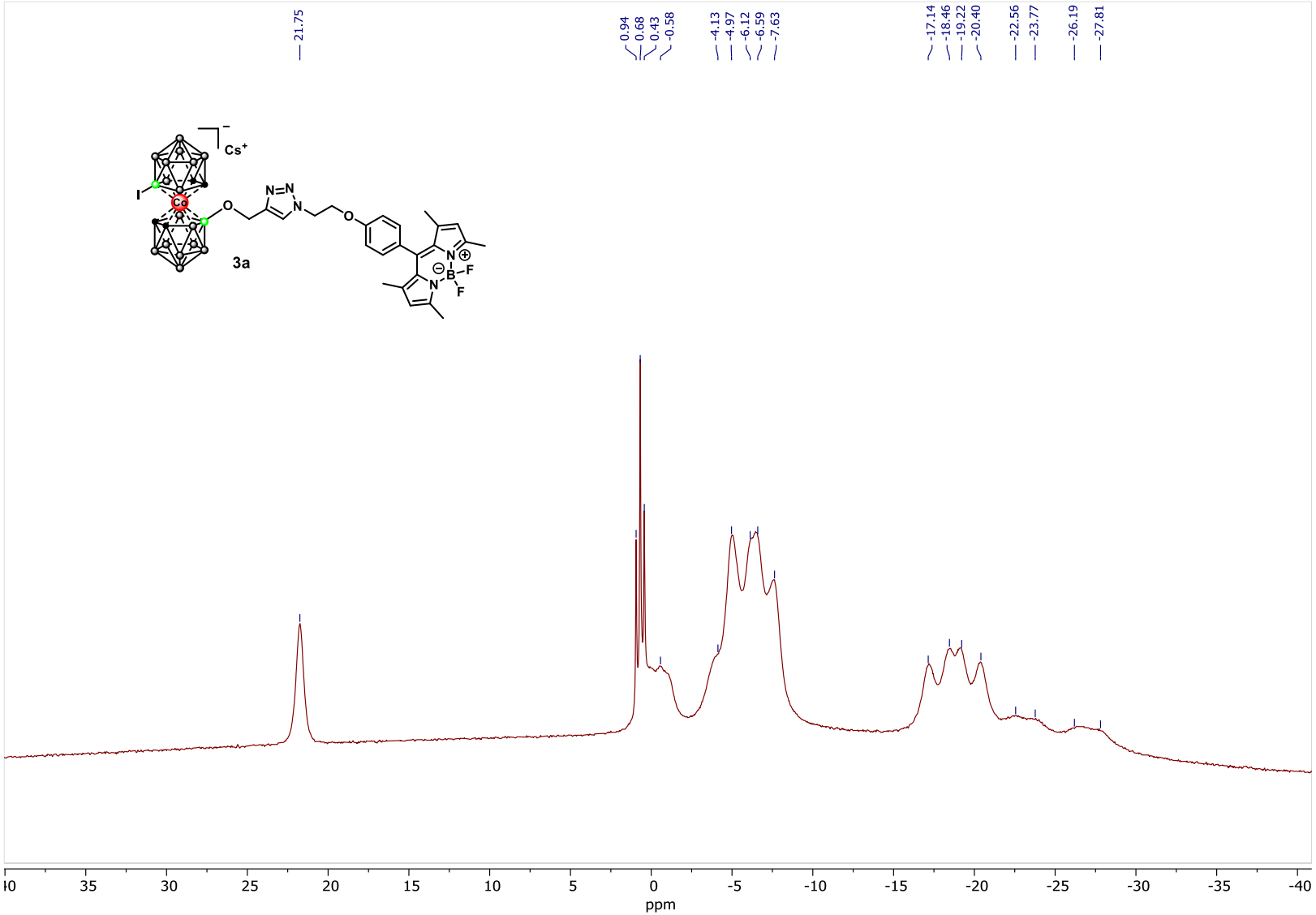

Figure S8. NMR ^{11}B spectrum of conjugate **3a**

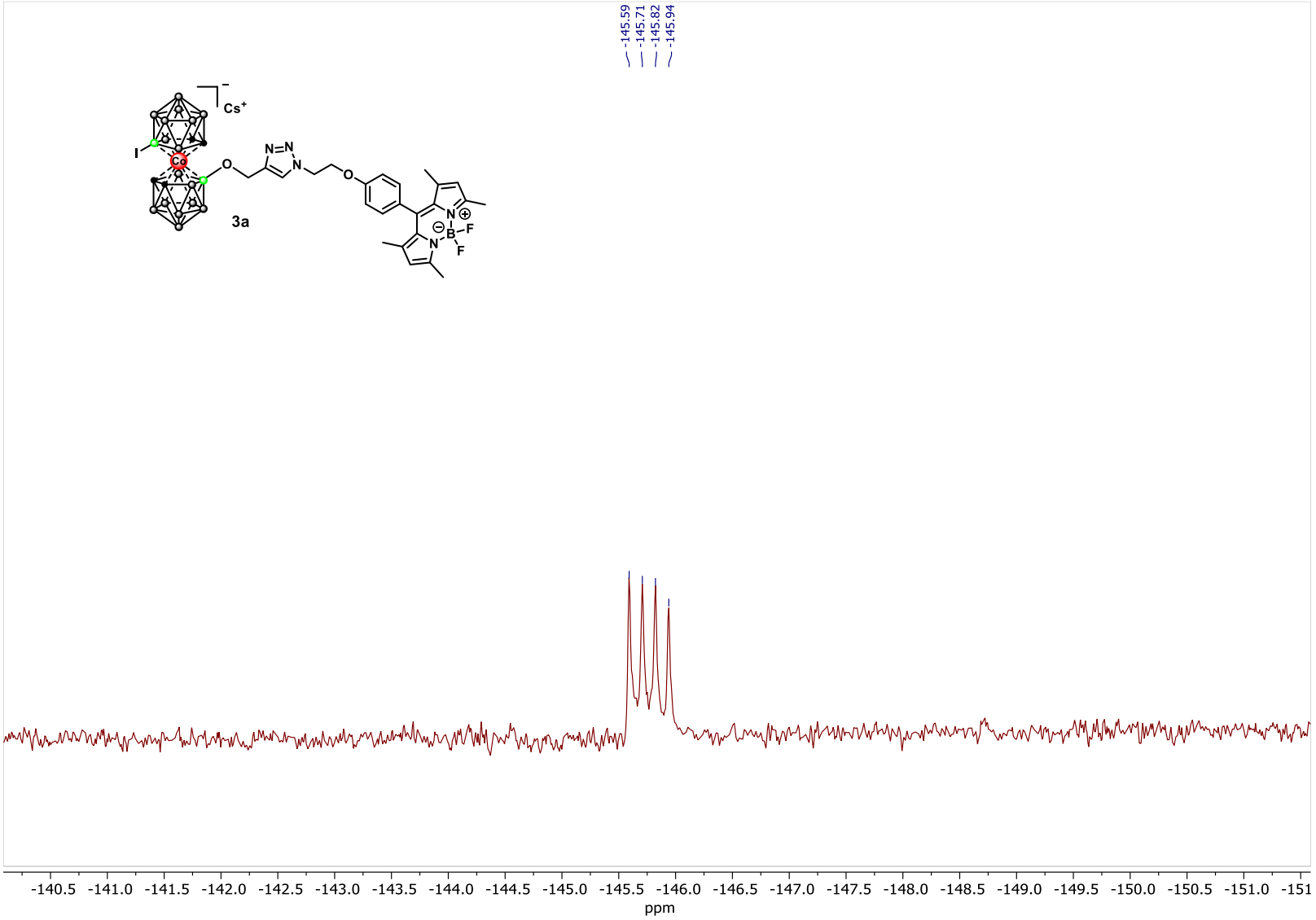

Figure S9. NMR $^{19}F\{^{1}H\}$ spectrum of conjugate **3a**

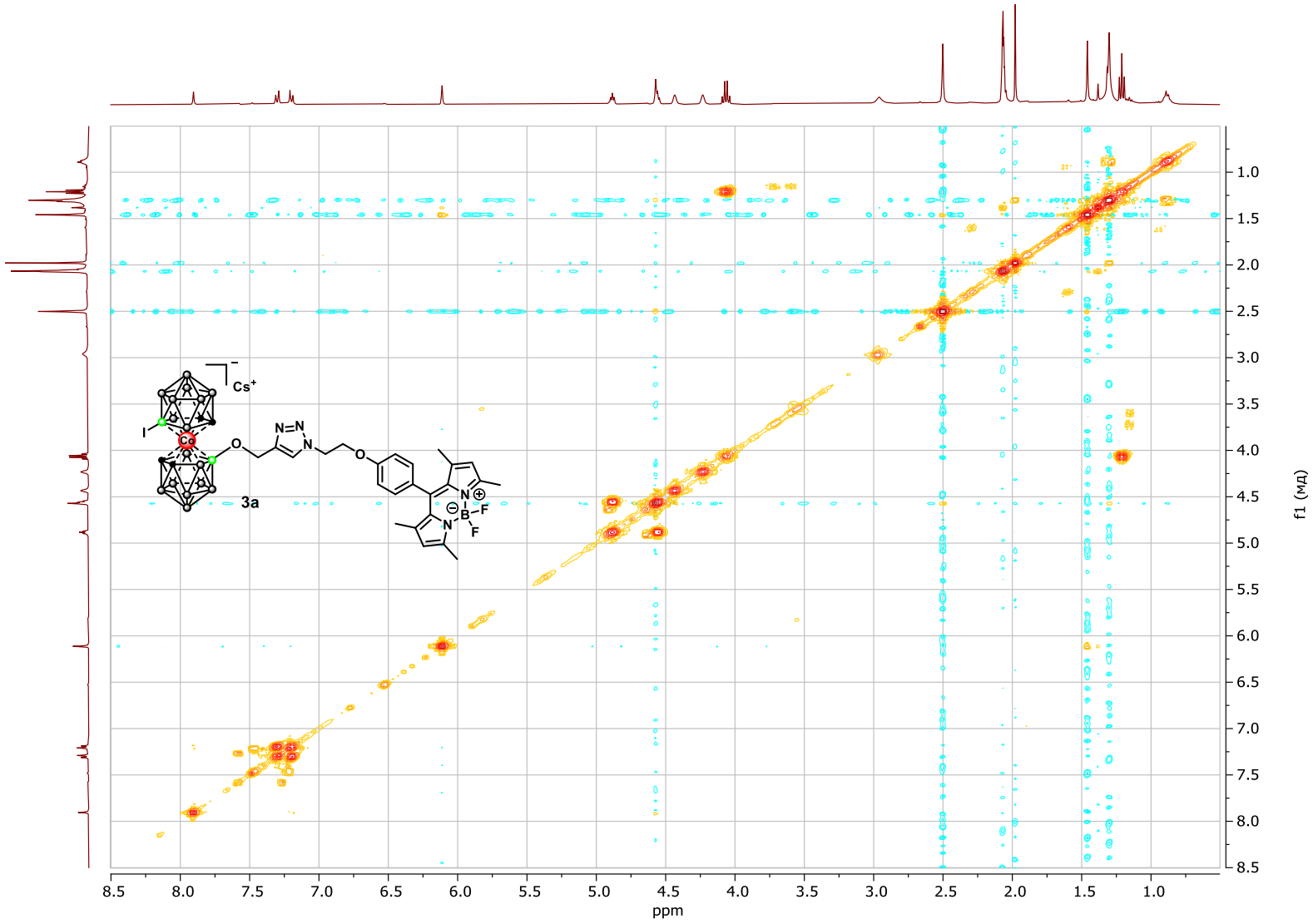

Figure S10. NMR ^{1}H-^{1}H COSY spectrum of conjugate **3a**

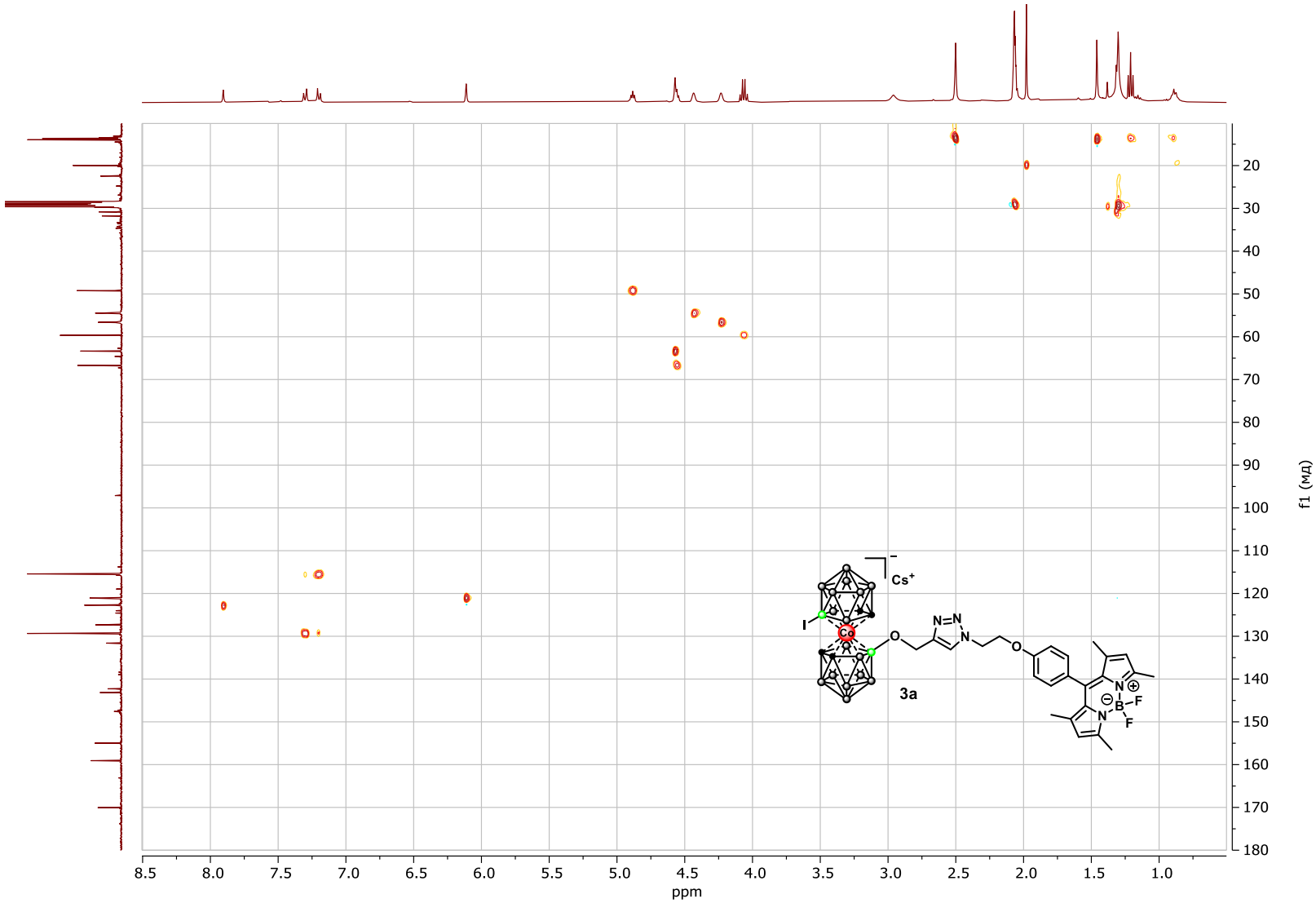

Figure S11. NMR ^{1}H-^{13}C HSQC spectrum of conjugate **3a**

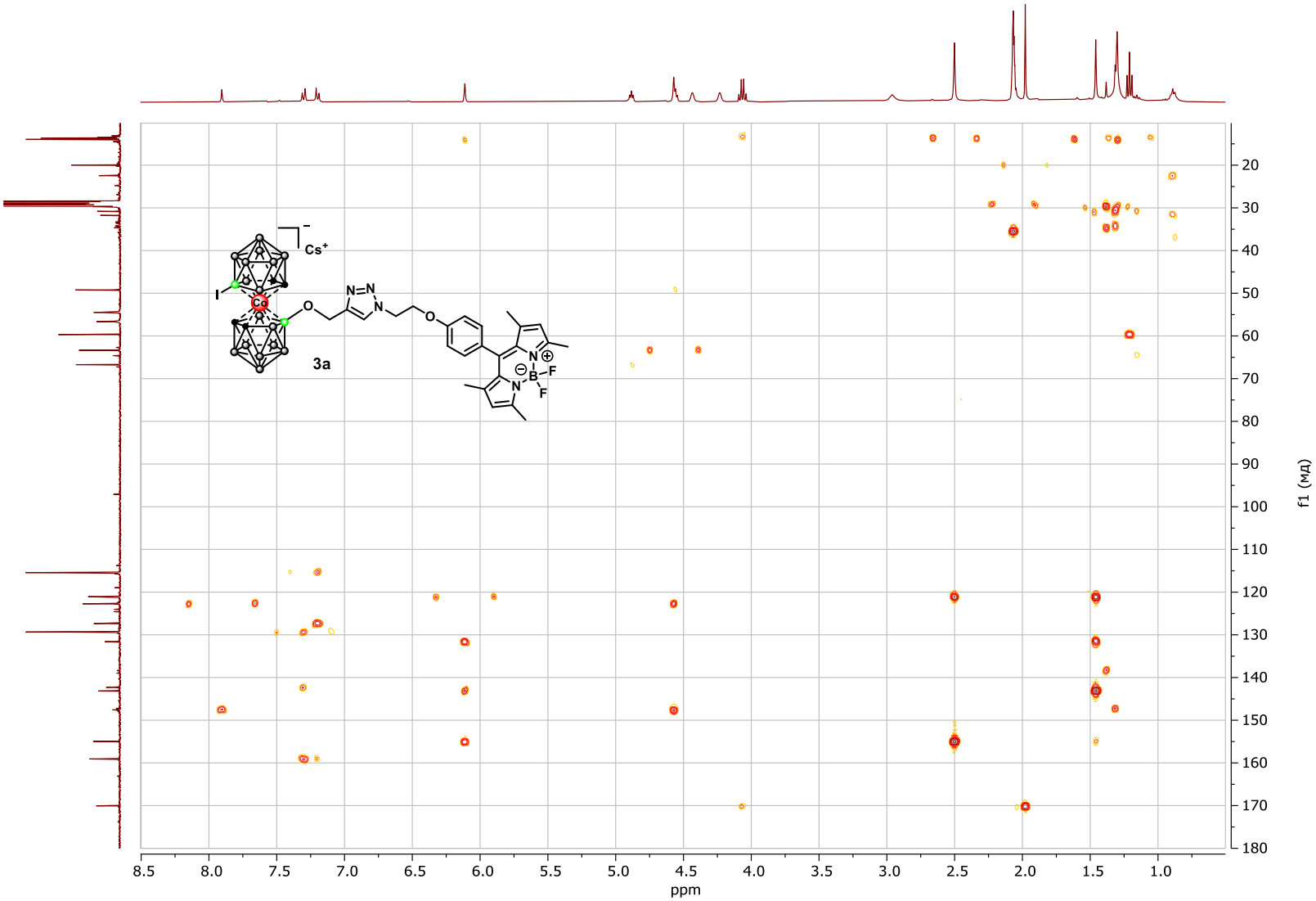

Figure S12. NMR ^{1}H-^{13}C HMBC spectrum of conjugate **3a**

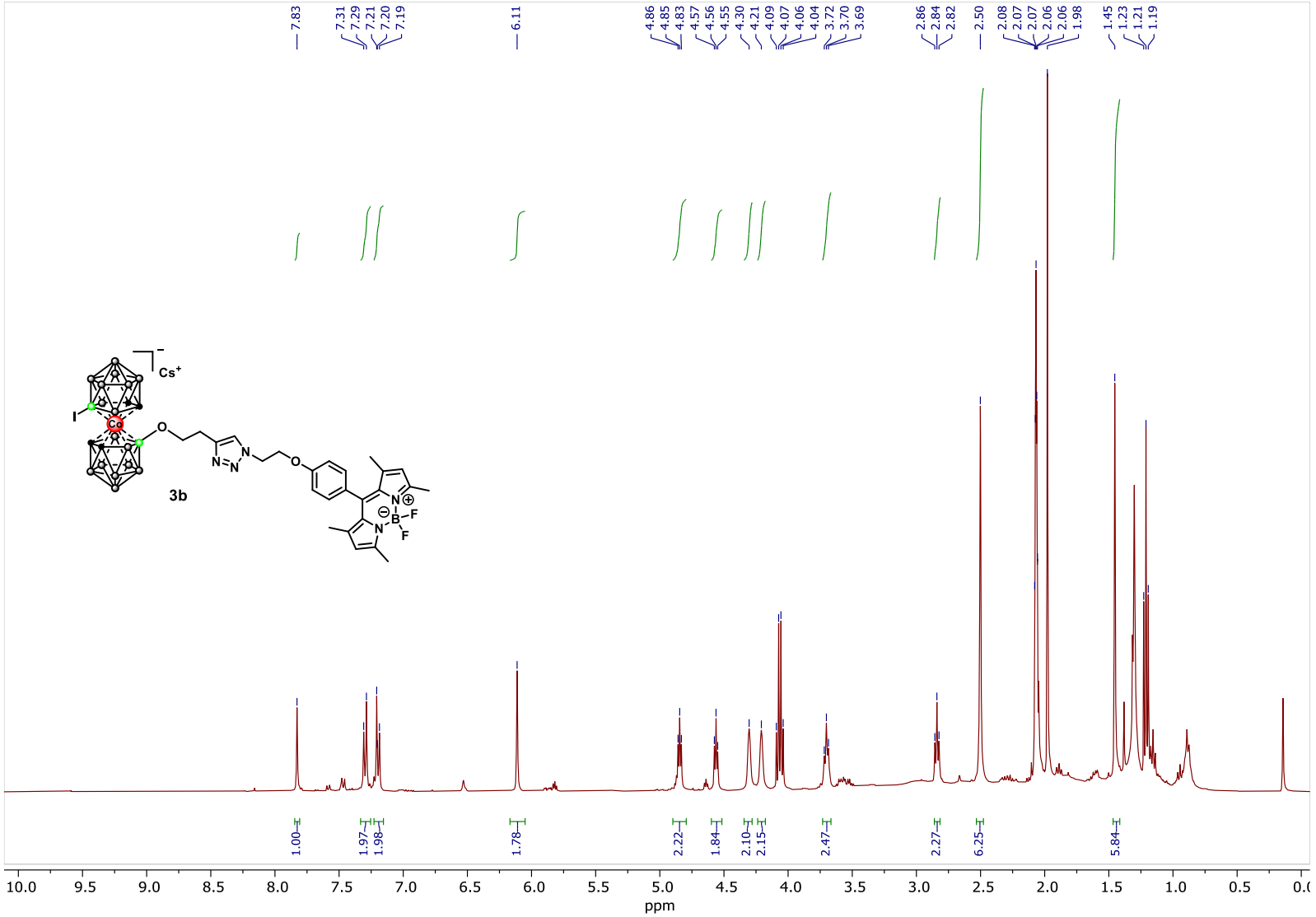

Figure S13. ^{1}H NMR spectrum of conjugate **3b**

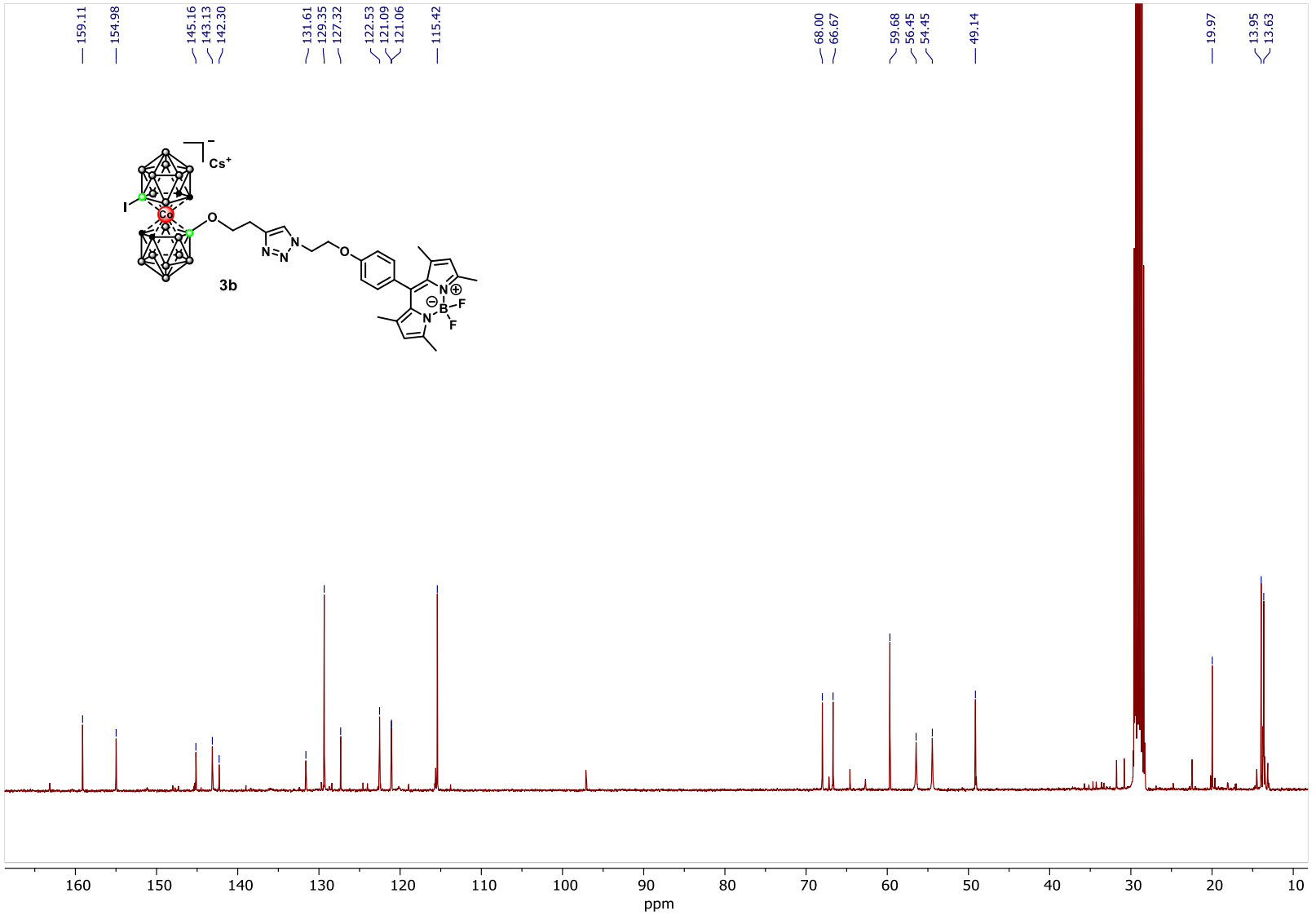

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of conjugate **3b**

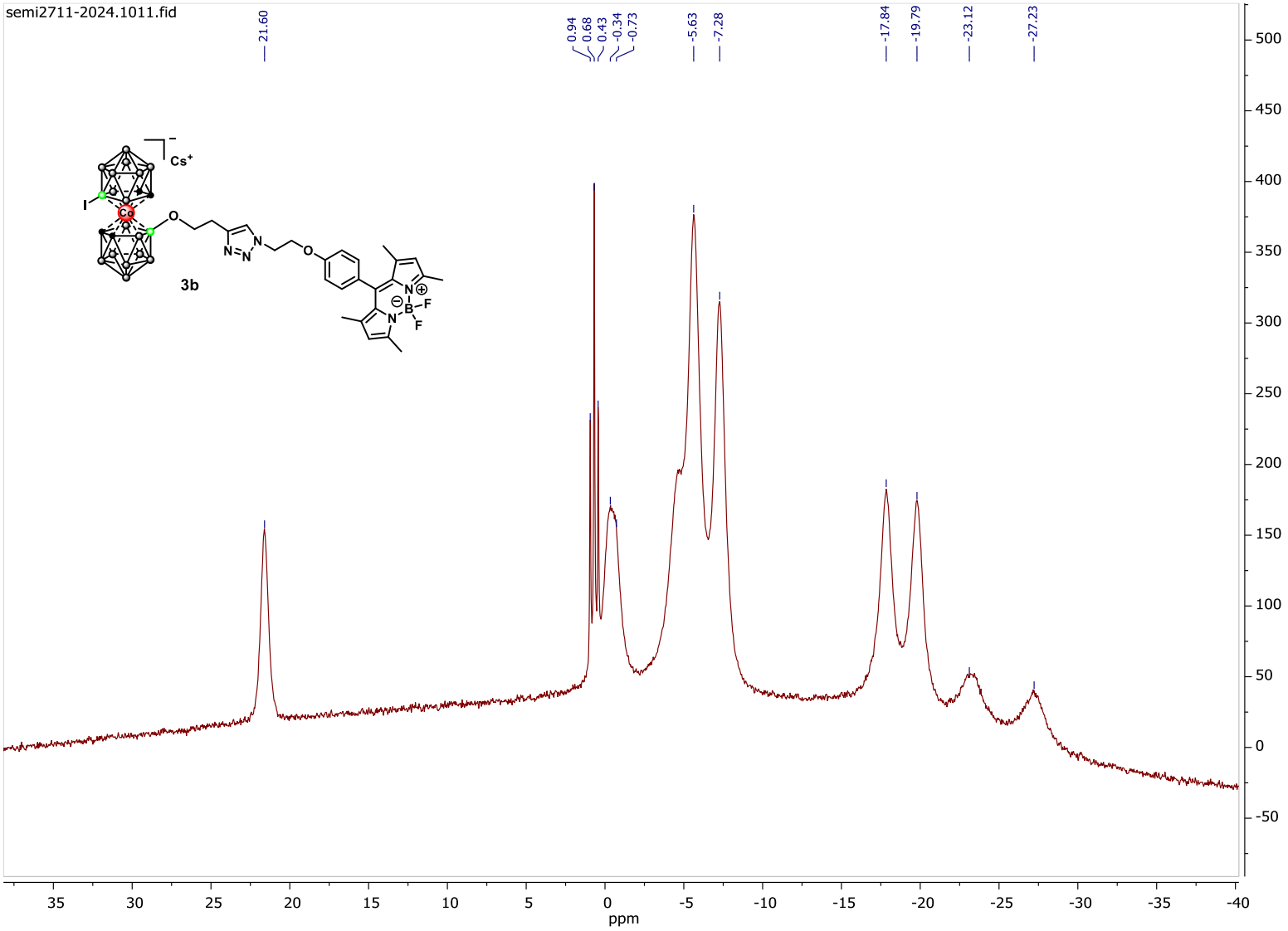

Figure S15. NMR $^{11}B\{^{1}H\}$ spectrum of conjugate **3b**

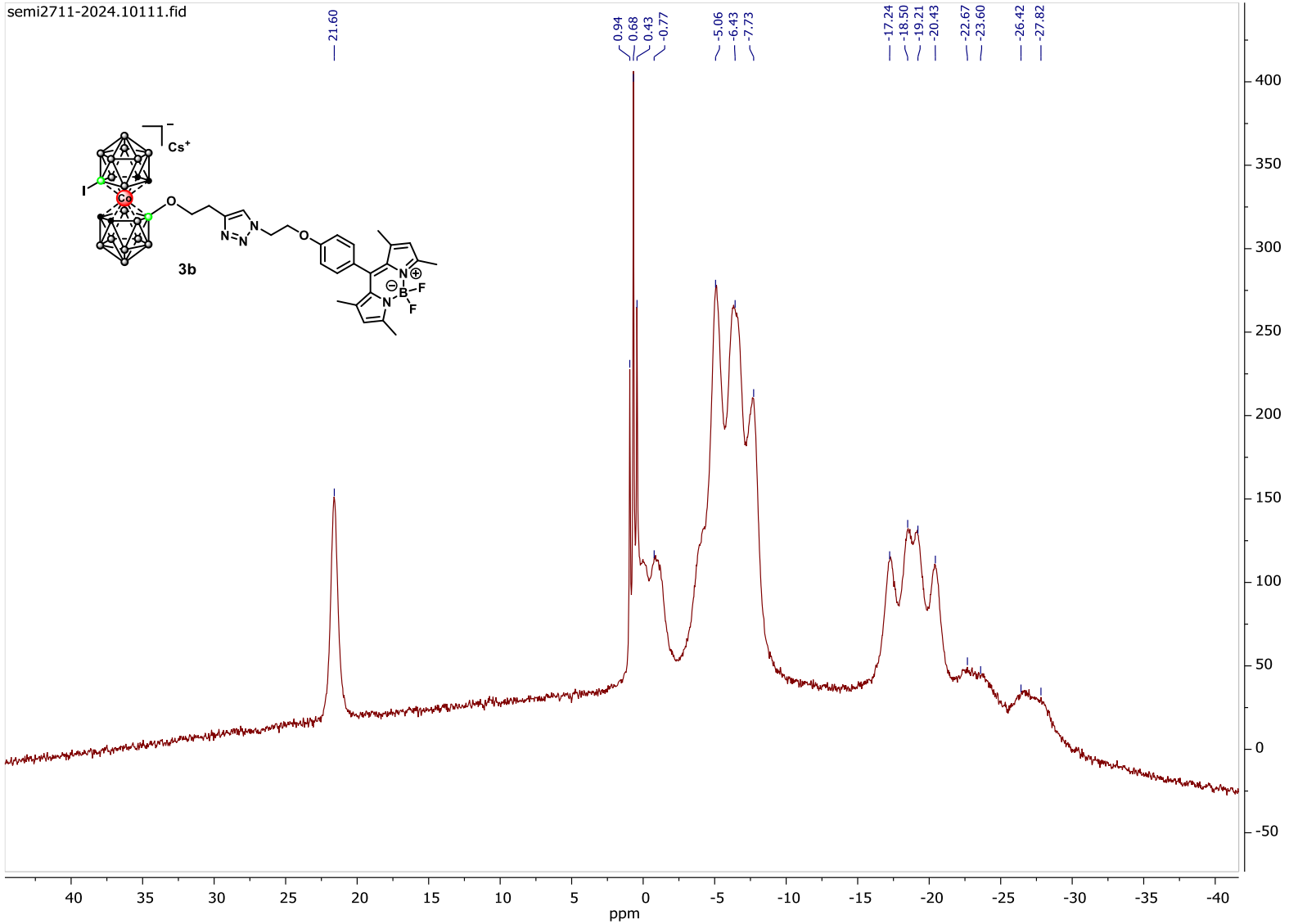

Figure S16. NMR ^{11}B spectrum of conjugate **3b**

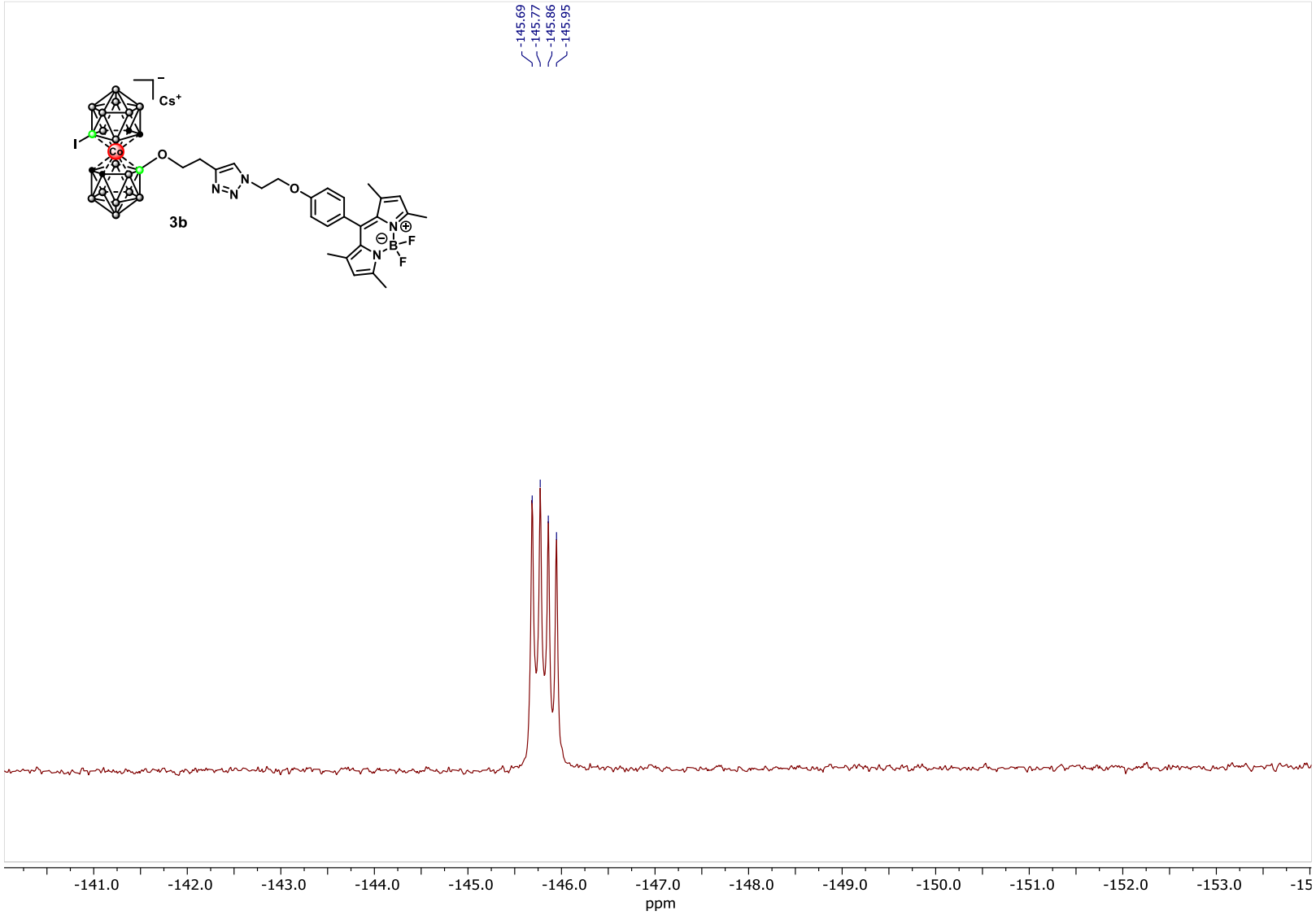

Figure S17. NMR $^{19}F\{^{1}H\}$ spectrum of conjugate **3b**

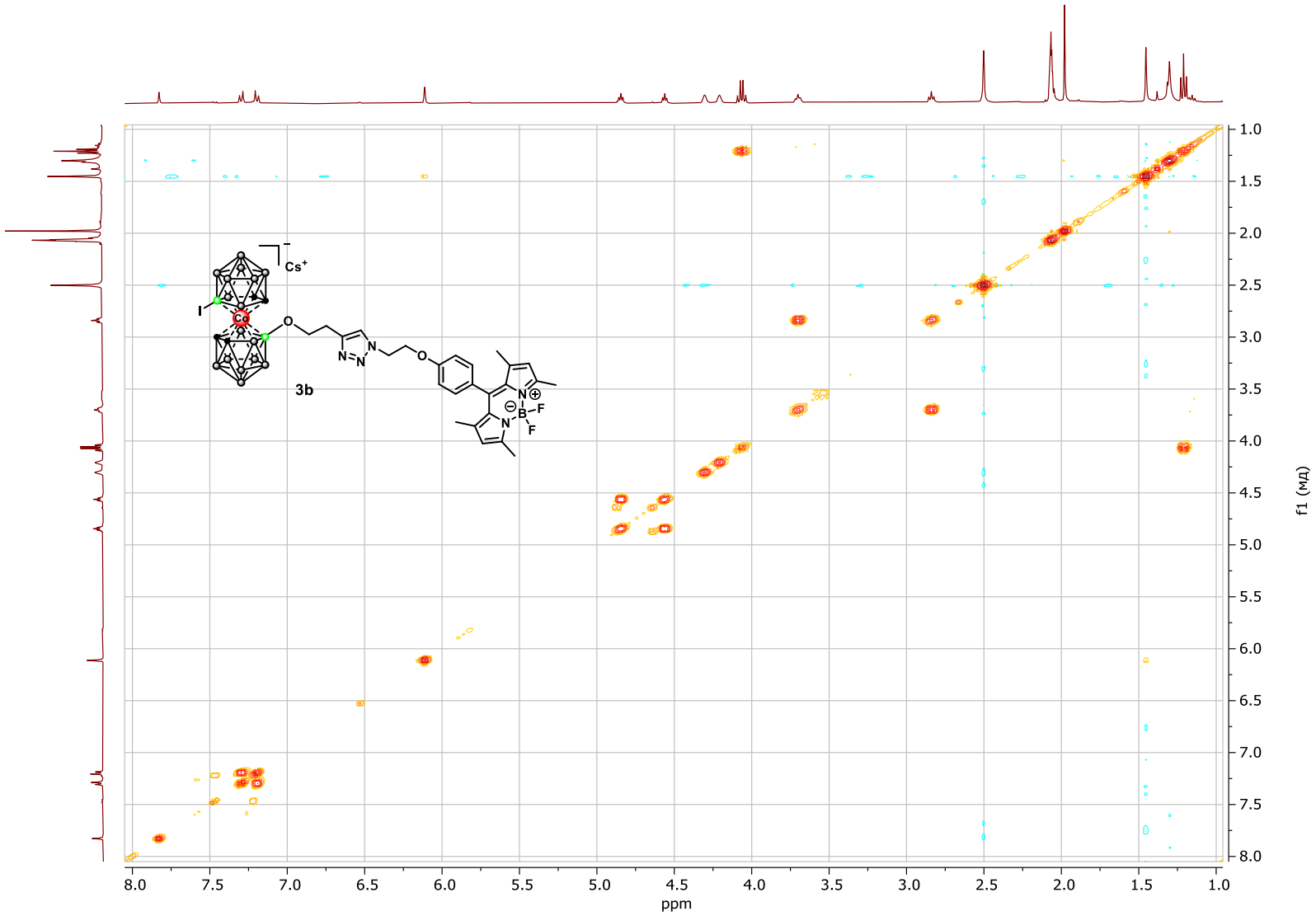

Figure S18. NMR ^{1}H-^{1}H COSY spectrum of conjugate **3b**

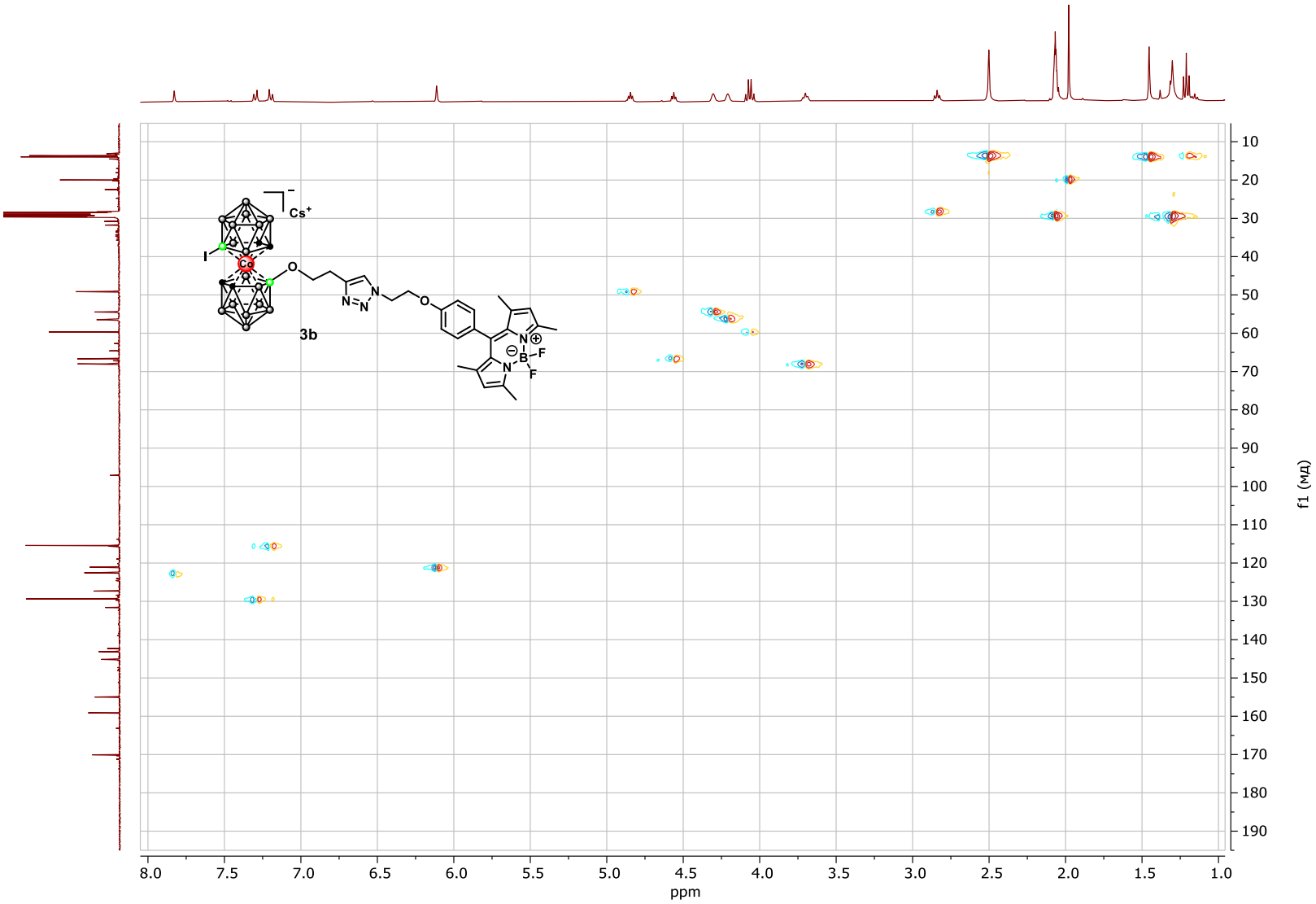

Figure S19. NMR ^{1}H-^{13}C HSQC spectrum of conjugate **3b**

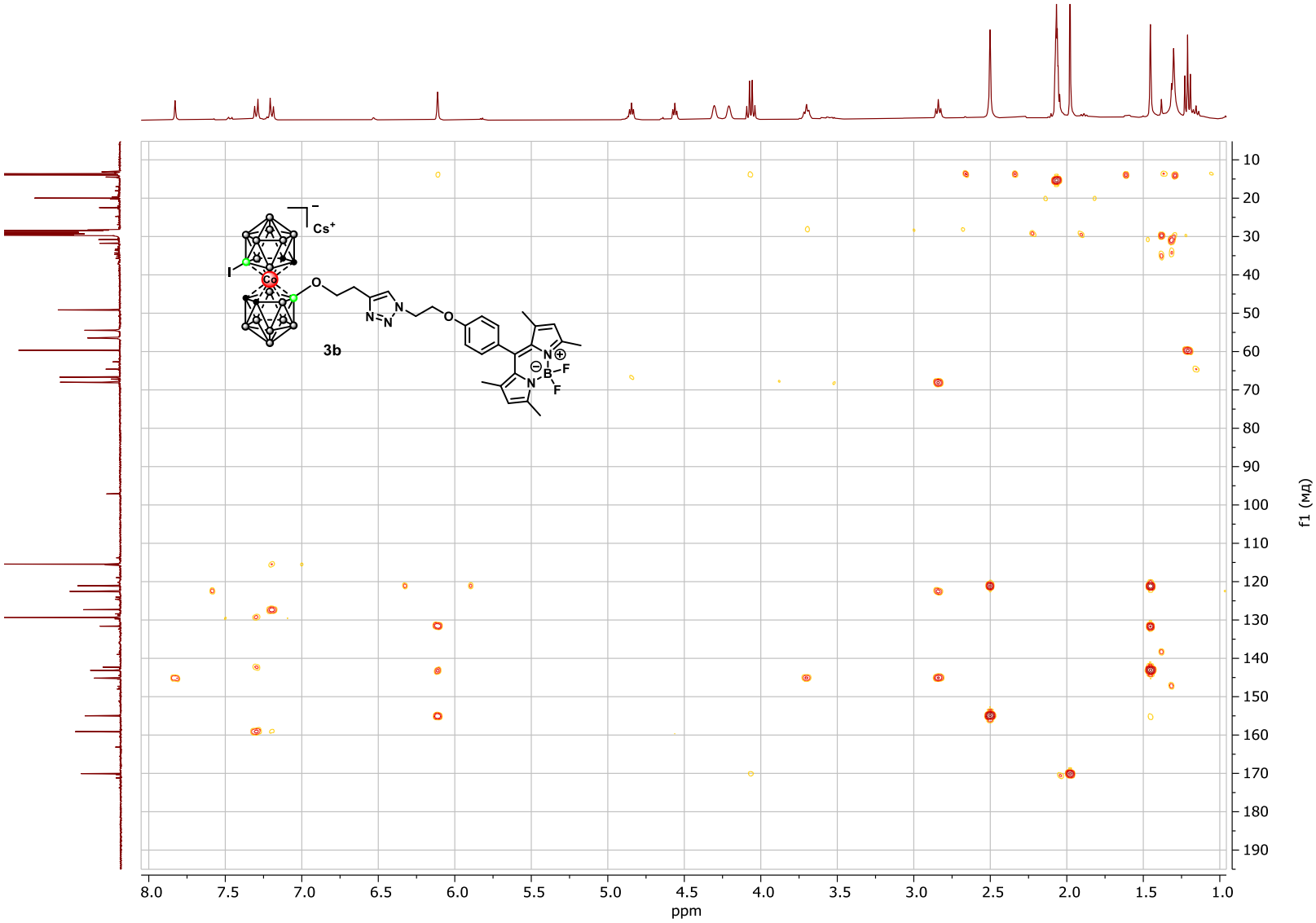

Figure S20. NMR ^{1}H-^{13}C HMBC spectrum of conjugate **3b**

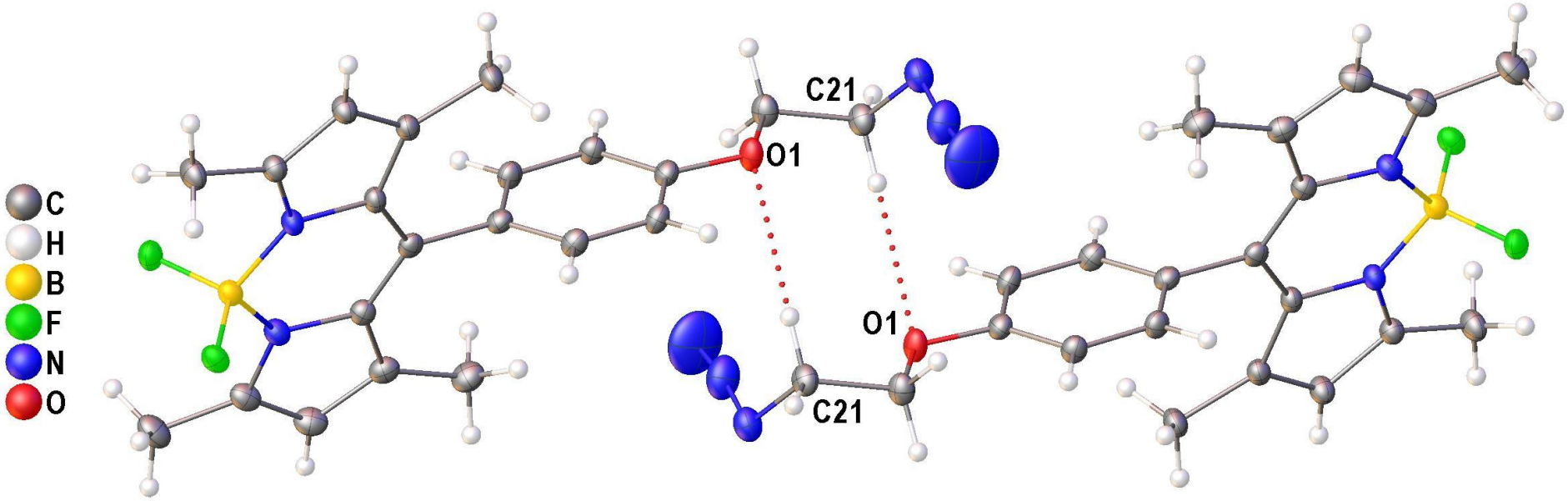

Figure S21. The centrosymmetric dimer of azido derivative BODIPY **2** in its crystal stabilized by the C-H…O H-bonds (dotted lines).

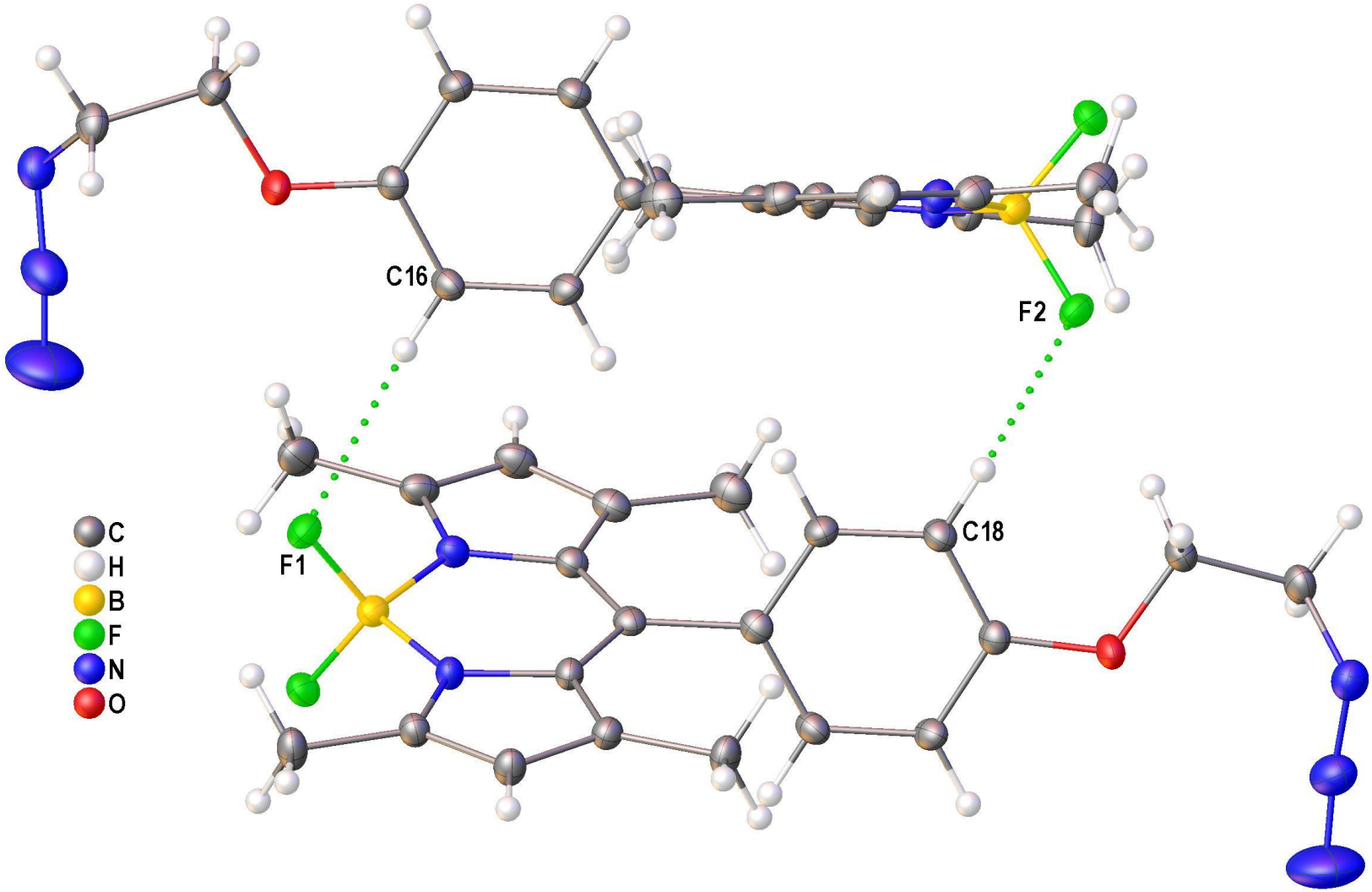

Figure S22. The intermolecular CH…F hydrogen bonds (dotted lines) in the crystal of azido derivative BODIPY **2**.

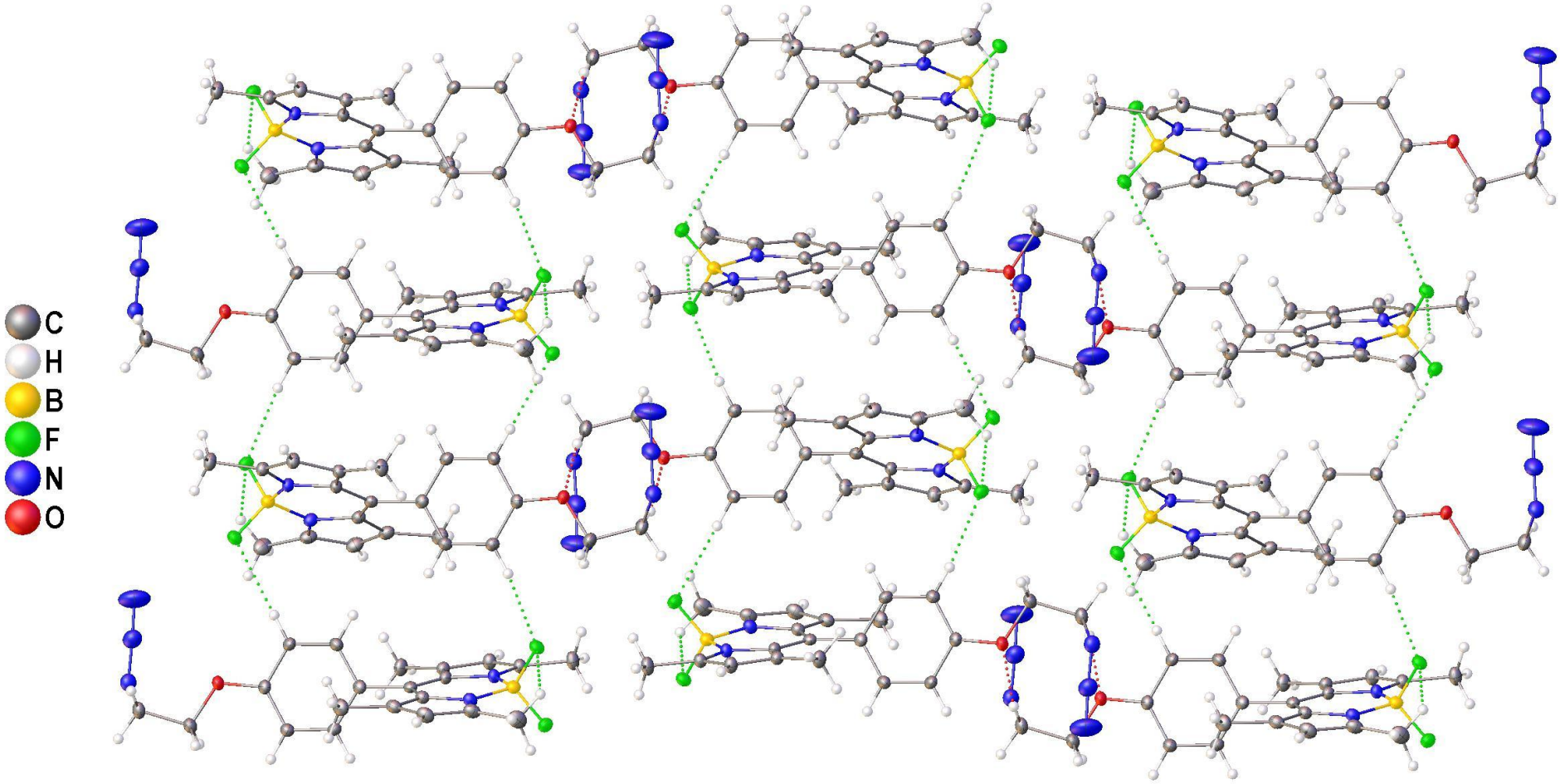

Figure S23. A fragment of infinite layer of molecules in the crystal of azido derivative BODIPY **2**. The CH…F and CH…O interactions are given by dotted lines.