Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 717–718

Deep blue luminescent cyclometallated 1,2,3-triazol-5-ylidene iridium(III) complexes

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Experimental part

General information. All reactions were performed under argon atmosphere. The solvents were distilled from appropriate drying agents prior to use. All reagents were purchased from commercial sources and were used as received. Triethyloxonium tetrafluoroborate was synthesized using literature procedure.[S1] Dichloromethane, 1,2-dichloroethane and DMSO were distilled over CaH_2; *o*-xylene was distilled over sodium.

NMR spectra were obtained on a Bruker "Avance 600" (600 MHz ^{1}H, 151 MHz ^{13}C). Chemical shifts (δ) in ppm are reported with the use of the residual undeuterated solvent (^{1}H NMR) or deuterated solvent peaks (^{13}C NMR) as internal references.[S2] Coupling constants *J* are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as ''s", ''d", "t" or ''m" for singlet, doublet, triplet or multiplet, respectively. The abbreviation ''br" is given for broadened signals.

Photoluminescence spectra

Photoluminescence spectra were measured using a "Fluoromax-4" (Horiba) fluorescence spectrometer at slit widths of 5 nm. All optical spectra were recorded using a cell with optical path length of 1 cm. Quantum yields were determined using Coumarin-460 (Coumarin 1, CAS No.: 91-44-1) as a standard (excitation wavelength 360 nm, Φ_{PL} 73 %, λ_{max} 451 nm).[S3,S4]

Quantum yields measurements were performed using solutions of complexes and Coumarin-460 with equal optical density. Luminescence λ_{max} of Coumarin-460 was close to the luminescence λ_{max} of iridium complexes. At the same experimental conditions (e.g. optical density, concentration, temperature, solvent, cuvettes) quantum yields ratios of new compounds to the standard one were equal to the ratios of the areas under corresponding photoluminescence curves of new compounds to the standard ones: ${S_1}/{S_2} = {\Phi_1}/{\Phi_2}$. Thus, quantum yields of new compounds can be derived as: $\Phi_x = \Phi_s \cdot \frac{S_x}{S_s}$ (Φ_s-quantum yield of standard compound, S_x and S_S – areas under corresponding photoluminescence curves of new compounds and the standard ones).

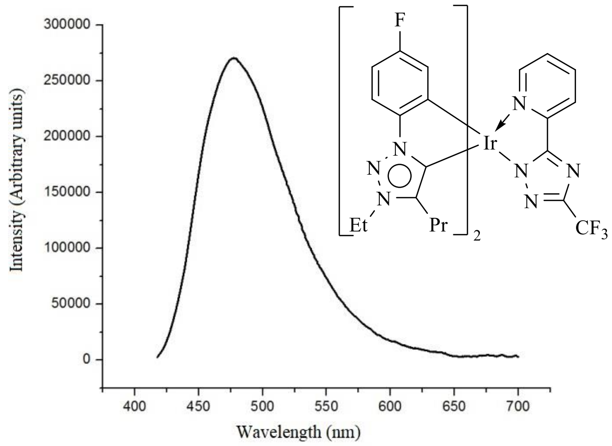


Figure S1 Photoluminescence spectrum of **3a** (λ_{max} 477 nm, Φ_{PL} 10.9%)

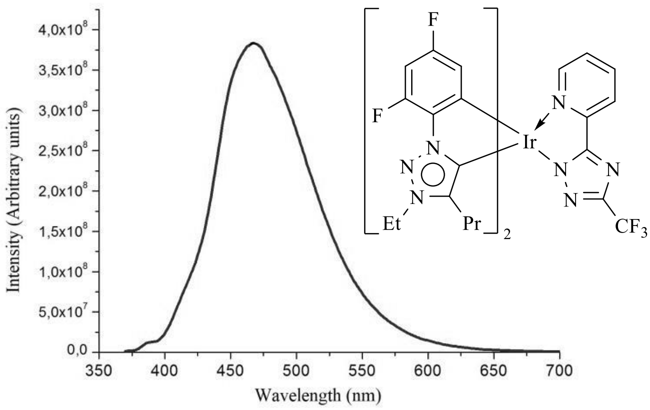


Figure S2 Photoluminescence spectrum of **3b** (λ_{max} 468 nm, Φ_{PL} 40%)

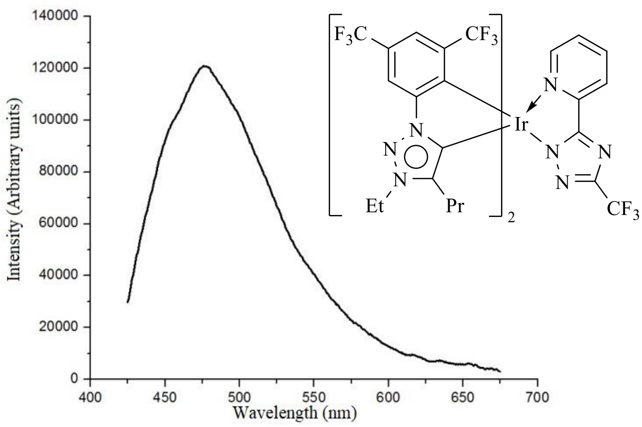


Figure S3 Photoluminescence spectrum of **3c** (λ_{max} 476 nm, Φ_{PL} 5.6%)

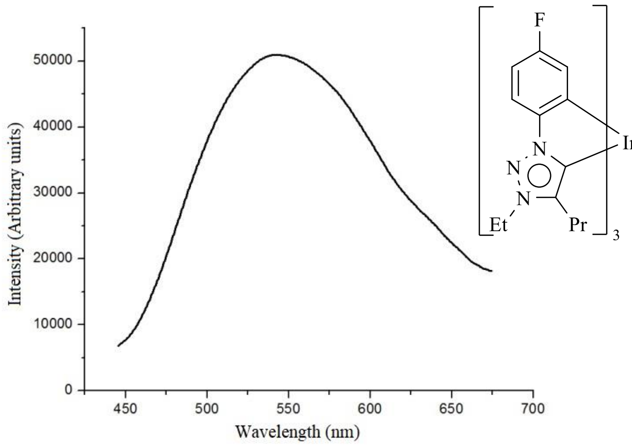


Figure S4 Photoluminescence spectrum of **4a** (λ_{max} 543 nm, Φ_{PL} 4%)

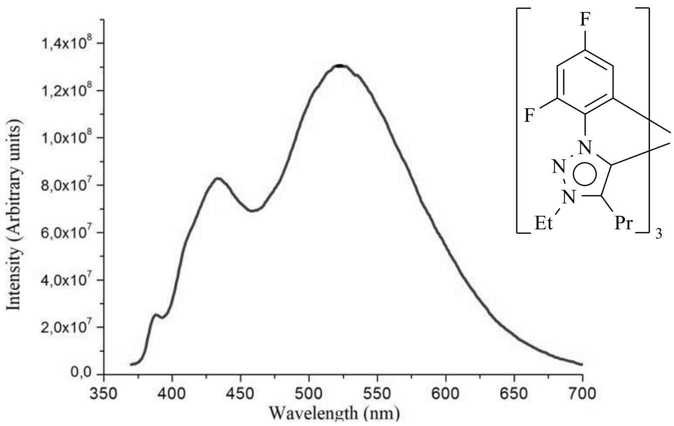


Figure S5 Photoluminescence spectrum of **4b** (λ_{max} 522 nm, Φ_{PL} 23%)

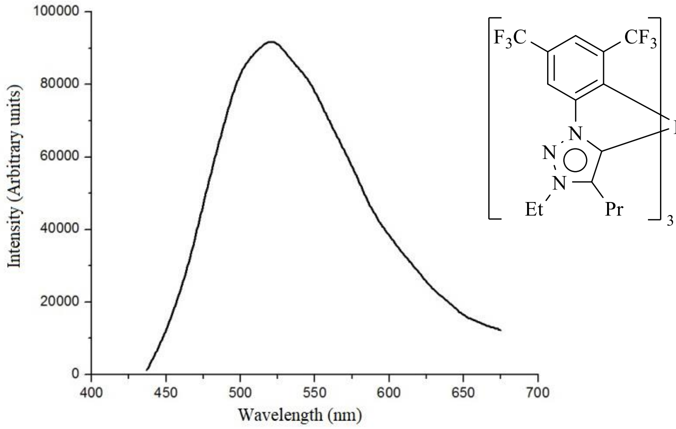


Figure S6 Photoluminescence spectrum of **4c** (λ_{max} 521 nm, Φ_{PL} 6%)

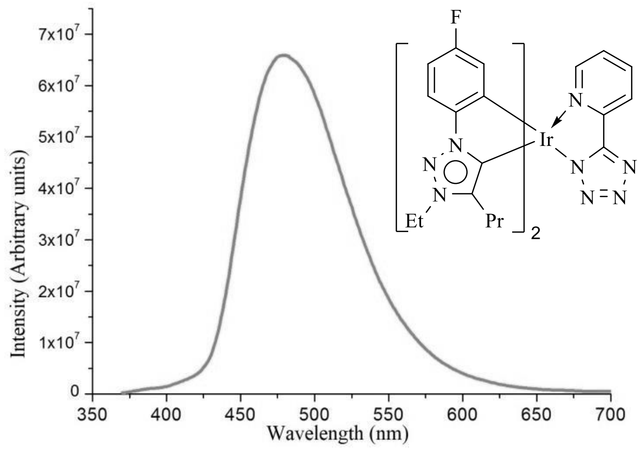


Figure S7 Photoluminescence spectrum of **5a** (λ_{max} 480 nm, Φ_{PL} 7%)

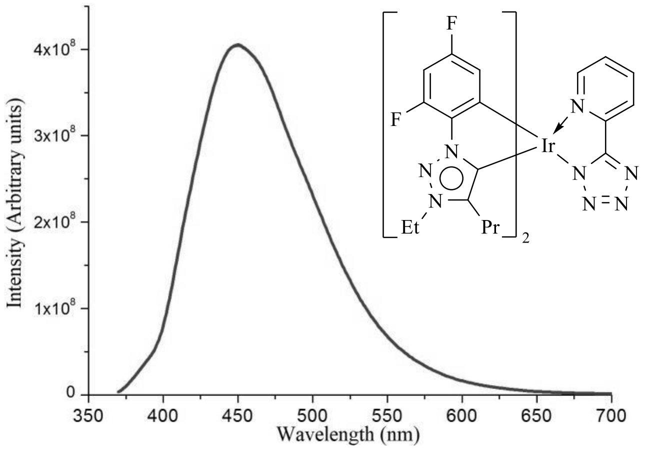
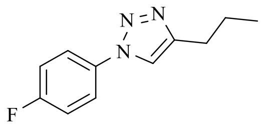


Figure S8 Photoluminescence spectrum of **5b** (λ_{max} 450 nm, Φ_{PL} 46%)

Preparation of starting materials

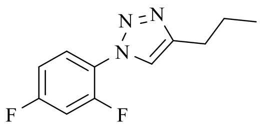
1-(4-Fluoro-phenyl)-4-propyl-1*H*-1,2,3-triazole



^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.63 (m, 3H), 7.23 – 7.16 (m, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 1.75 (h, *J* = 7.4 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.3 (d, *J* = 248.5 Hz), 149.2, 133.7 (d, *J* = 2.8 Hz), 122.5 (d, *J* = 8.7 Hz), 119.2, 116.7 (d, *J* = 23.2 Hz), 27.8, 22.8, 13.9.

1-(2,4-Difluorophenyl)-4-propyl-1*H*-1,2,3-triazole

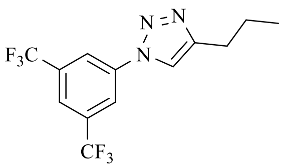


^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (td, *J* = 8.9, 5.8 Hz, 1H), 7.73 (d, *J* = 2.9 Hz, 1H), 7.06 – 6.97 (m, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 1.74 (h, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.3 (dd, *J* = 263.0, 11.1 Hz), 155.6 (dd, *J* = 289.3, 12.4 Hz), 150.0 , 148.9 , 126.2 (d, *J* = 10.2 Hz), 122.0 (d, *J* = 6.9 Hz), 112.6 (dd, *J* = 22.6, 3.7 Hz), 105.4 (dd, *J* = 26.6, 23.9 Hz), 27.7 , 22.7 , 13.9 .

HRMS (ESI) calc. for $C_{11}H_{12}F_2N_3$ $[M+H]^+$: 224.0994, 225.1027; found: 224.0999, 225.1027.

1-[3,5-Bis(trifluoromethyl)phenyl]-4-propyl-1*H*-1,2,3-triazole

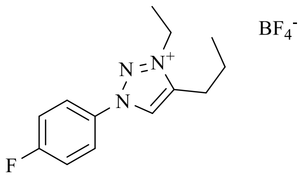


^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 (s, 2H), 7.91 (s, 1H), 7.88 (s, 1H), 2.79 (t, *J* = 7.6 Hz, 2H), 1.78 (h, *J* = 7.4 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.2, 138.4, 133.6 (q, *J* = 34.3 Hz), 122.7 (q, *J* = 273.5 Hz), 121.9 – 121.7 (m), 120.3 – 120.2 (m), 118.8, 27.7, 22.7, 13.8.

HRMS (ESI) calc. for $C_{13}H_{12}F_6N_3$ $[M+H]^+$: 324.0929, 325.0963; found: 324.0935, 325.0964.

*1-(4-Fluorophenyl)-3-ethyl-4-propyl-1H-1,2,3-triazolium tetrafluoroborate (**1a**)*



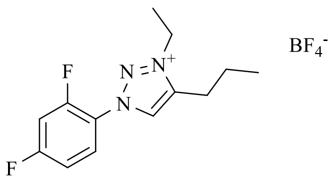
To a solution of 1-(4-fluorophenyl)-4-propyl-1*H*-1,2,3-triazole (2.05 g, 10 mmol, 1 eq.) in dichloromethane (10 ml), triethyloxonium tetrafluoroborate (2.1 g, 11 mmol, 1.1 eq.) was added. The mixture was stirred at room temperature for 24 h, then of methanol (1 ml) was added, and the mixture was evaporated. The resulting viscous oily residue was dissolved in dichloromethane and concentrated again. Prolonged drying in vacuum gave 3.21 g (99%) of salt **1a** as a white solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.70 (s, 1H), 7.94 – 7.83 (m, 2H), 7.25 – 7.20 (m, 2H), 4.58 (q, *J* = 7.3 Hz, 2H), 2.84 (t, *J* = 7.8 Hz, 2H), 1.80 (h, *J* = 7.3 Hz, 2H), 1.67 (t, *J* = 7.3 Hz, 3H), 1.01 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.2 (d, *J* = 253.6 Hz), 145.5 , 131.3 (d, *J* = 3.1 Hz), 126.6 , 124.2 (d, *J* = 9.1 Hz), 117.5 (d, *J* = 23.5 Hz), 47.1 , 25.1 , 20.6 , 13.9 , 13.6 .

HRMS (ESI) calc. for $C_{13}H_{17}FN_3$ [M-BF_4^-]$^+$: 234.1407, 235.1440; found: 234.1404, 235.1431.

*1-(2,4-Difluorophenyl)-3-ethyl-4-propyl-1H-1,2,3-triazolium tetrafluoroborate (**1b**)*



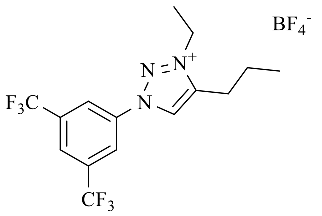
To a solution of 1-(2,4-difluorophenyl)-4-propyl-1*H*-1,2,3-triazole (2.22 g, 10 mmol, 1 eq.) in dichloromethane (10 ml), triethyloxonium tetrafluoroborate (2.1 g, 11 mmol, 1.1 eq.) was added. The mixture was stirred at room temperature for 24 h, then methanol (1 ml) was added, and the mixture was evaporated. The obyained viscous oily residue was dissolved in dichloromethane and concentrated again. Prolonged drying in vacuum gave 3.39 g (99 %) of salt **2b** as a white solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 8.03 – 7.89 (m, 2H), 7.17 – 7.04 (m, 3H), 4.62 (q, *J* = 7.3 Hz, 2H), 2.88 (t, *J* = 7.9 Hz, 2H), 1.83 (h, *J* = 7.4 Hz, 2H), 1.69 (t, *J* = 7.3 Hz, 3H), 1.06 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.5 (dd, *J* = 256.9, 11.0 Hz), 155.4 (dd, *J* = 258.7, 12.7 Hz), 145.2 , 129.3 (d, *J* = 4.4 Hz), 128.7 (d, *J* = 10.7 Hz), 119.9 (dd, *J* = 10.6, 4.1 Hz), 113.5 (dd, *J* = 23.1, 3.6 Hz), 105.9 (dd, *J* = 27.0, 22.6 Hz), 47.4 , 25.1 , 20.5 , 13.6 (2C).

HRMS (ESI) calc. for $C_{13}H_{16}F_2N_3$ [M-BF_4^-]$^+$: 252.1312, 253.1346; found: 252.1309, 253.1339.

*1-[3,5-Bis(trifluoromethyl)phenyl]-3-ethyl-4-propyl-1H-1,2,3-triazolium tetrafluoroborate (**1c**)*

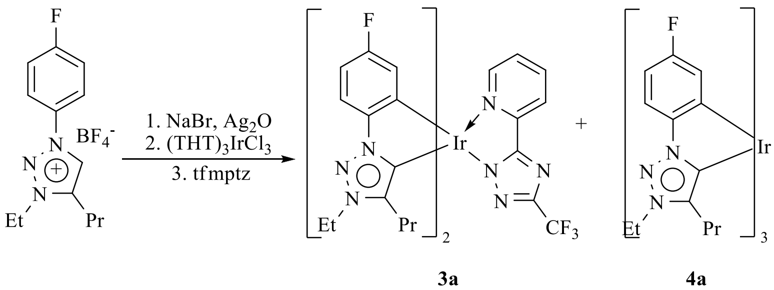


To a solution of 1-(3,5-bis(trifluoromethyl)phenyl)-4-propyl-1*H*-1,2,3-triazole (3.23 g, 10 mmol, 1 eq.) in dichloromethane (10 ml), triethyloxonium tetrafluoroborate (2.1 g, 11 mmol, 1.1 eq.) was added. The mixture was stirred at room temperature for 24 h, then methanol (1 ml) was added, and the mixture was evaporated. The obtained viscous oily residue was dissolved in dichloromethane and concentrated again. Prolonged drying in vacuum afforded 4.38 g (99%) of salt **1c** as a white solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.81 (s, 1H), 8.40 (s, 2H), 8.04 (s, 1H), 4.60 (q, *J* = 7.3 Hz, 2H), 2.83 (t, *J* = 7.8 Hz, 2H), 1.84 – 1.74 (m, 2H), 1.68 (t, *J* = 7.3 Hz, 3H), 0.99 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.2 , 136.4 , 134.0 (q, *J* = 34.5 Hz), 127.4 , 125.3 – 125.0 (m), 123.2 – 122.9 (m), 122.3 (q, *J* = 273.2 Hz), 47.5 , 25.2 , 20.4 , 13.6 , 13.5 .
HRMS (ESI) calc. for $C_{15}H_{16}F_6N_3$ [M-BF_4^-]$^+$: 252.1312, 253.1346; found: 252.1309, 253.1339.

*Bis[2-(5-carbeno-3-ethyl-4-propyl-1H-1,2,3-triazol-1-yl)-5-fluorophenyl][5-(pyridin-2-yl)-3-trifluoromethyl-1H-1,2,4-triazol-1-yl]iridium(III) (**3a**) and tris[2-(5-carbeno-3-ethyl-4-propyl-1H-1,2,3-triazol-1-yl)-5-fluorophenyl]iridium(III) (**4a**)*



To a solution of salt **1a** (0.706 g, 2.2 mmol) in dry dichloromethane (20 ml), a solution of anhydrous sodium iodide in acetonitrile (10 ml, 0.5 M, 5 mmol, 2.3 eq.) was added. The mixture was stirred for 0.5 h and evaporated to dryness. The solid residue was suspended in dichloromethane (40 ml) followed by addition of silver(I) oxide (0.281 g, 1.22 mmol, 0.55 eq.). The mixture was protected from light and stirred at room temperature for 24 h under inert atmosphere. The mixture was evaporated to dryness followed by addition of *o*-xylene (40 ml) and iridium tris(tetrahydrothiophene) trichloride (0.563 g, 1 mmol, 0.45 eq.). The reaction mixture was refluxed for 48 h and cooled to room temperature. To the mixture, 2-(5-trifluoromethyl-2*H*-1,2,4-triazol-3-yl)pyridine (0.214 g, 1 mmol, 0.45 eq.) and finely powdered anhydrous sodium carbonate (0.265 g, 2.5 mmol, 1.2 eq.) were added, and the mixture was refluxed for more 24 h. The mixture was cooled and evaporated to dryness. The solid residue was extracted with dichloromethane, filtered, the filtrate was collected and evaporated again. The solid residue was purified by column chromatography with gradual elution to give 105 mg (11%) of complex **4a** and 239 mg (27%) of complex **3a**.

Complex **3a**. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.17 (dt, *J* = 8.0, 1.1 Hz, 1H), 8.00 (dt, *J* = 5.6, 1.1 Hz, 1H), 7.75 (td, *J* = 7.7, 1.6 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.44 (dd, *J* = 8.6, 5.2 Hz, 1H), 7.01 (ddd, *J* = 7.3, 5.5, 1.5 Hz, 1H), 6.62 (td, *J* = 8.6, 2.8 Hz, 1H), 6.50 (td, *J* = 8.7, 2.7 Hz, 1H), 6.34 – 6.27 (m, 1H), 6.18 (dd, *J* = 10.0, 2.7 Hz, 1H), 4.35 – 4.16 (m, 4H), 2.18 – 2.07 (m, 1H), 1.94 – 1.85 (m, 1H), 1.85 – 1.71 (m, 2H), 1.65 – 1.55 (m, 6H), 1.44 – 1.33 (m, 1H), 1.23 – 1.13 (m, 1H), 1.04 – 0.90 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H), 0.51 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.21, 163.12, 162.68, 161.57, 161.04, 156.18, 155.07, 152.00, 150.96, 144.34, 143.10, 142.87, 142.24, 142.14, 142.11, 136.85, 136.67, 123.74, 123.51, 123.48, 123.37, 121.14, 115.35, 115.29, 115.00, 114.93, 108.15, 107.99, 107.76, 107.60, 71.96, 59.22, 44.35, 44.25, 26.40, 26.00, 24.07, 23.81, 15.27, 15.23, 14.06, 13.88.

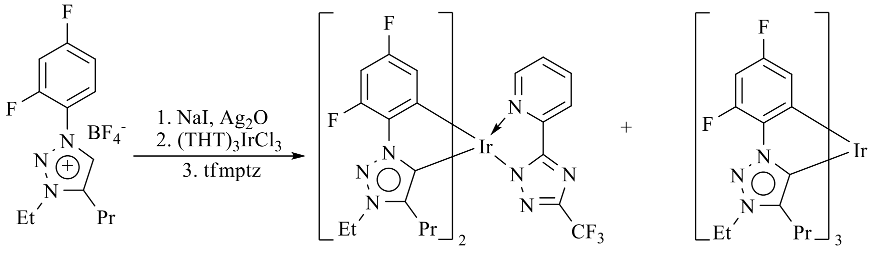
HRMS (ESI) calc. for $C_{34}H_{35}F_5IrN_{10}$ $[M+H]^+$: 869.2567, 870.2595, 871.2592, 872.2619; found: 869.2567, 870.2592, 871.2591, 872.2616.

Complex **4a.** ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.53 – 7.45 (m, 3H), 6.66 – 6.57 (m, 2H), 6.56 – 6.41 (m, 4H), 4.27 – 4.14 (m, 6H), 2.20 – 2.11 (m, 2H), 2.08 – 1.98 (m, 2H), 1.97 – 1.90 (m, 1H), 1.84 – 1.77 (m, 1H), 1.58 – 1.52 (m, 9H), 0.95 – 0.79 (m, 4H), 0.73 – 0.63 (m, 1H), 0.58 (t, *J* = 7.3 Hz, 3H), 0.50 (t, *J* = 7.3 Hz, 3H), 0.45 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.67, 163.37, 163.31, 162.04, 161.73, 161.68, 158.25, 156.88, 156.85, 156.61, 156.54, 156.26, 156.20, 154.60, 144.63, 143.60, 143.16, 142.81, 142.47, 141.99, 124.71, 124.60, 124.19, 124.09, 122.70, 122.59, 114.38, 114.32, 114.23, 114.17, 113.82, 113.77, 113.71, 105.98, 105.88, 105.81, 105.72, 105.66, 53.59, 43.87, 43.74, 43.64, 29.84, 26.98, 26.46, 26.32, 23.62, 23.52, 23.39, 15.54, 15.44, 15.33, 14.15, 13.75, 13.71.

HRMS (ESI) calc. for $C_{39}H_{46}F_3IrN_9$ $[M+H]^+$: 888.3429, 889.3458, 890.3454, 891.3482; found: 888.3424, 889.3413, 890.3450, 891.3482.

*Bis[2-(5-carbeno-3-ethyl-4-propyl-1H-1,2,3-triazol-1-yl)-3,5-difluorophenyl][5-(pyridin-2-yl)-3-trifluoromethyl-1H-1,2,4-triazol-1-yl]iridium(III) (**3b**) and tris[2-(5-carbeno-3-ethyl-4-propyl-1H-1,2,3-triazol-1-yl)-3,5-difluorophenyl]iridium(III) (**4b**)*



3b **4b**

To a solution of salt **1b** (0.746 g, 2.2 mmol) in dry dichloromethane (20 ml), a solution of anhydrous sodium iodide in acetonitrile (10 ml, 0.5 M, 5 mmol, 2.3 eq.) was added. The mixture was stirred for 0.5 h and evaporated to dryness. The solid residue was suspended in dichloromethane (40 ml) followed by addition of silver(I) oxide (0.281 g, 1.22 mmol, 0.55 eq.). The reaction mixture was protected from light and stirred at room temperature for 24 h under inert atmosphere. The mixture was evaporated to dryness followed by addition of *o*-xylene (40 ml) and iridium tris(tetrahydrothiophene) trichloride (0.563 g, 1 mmol, 0.45 eq.). The reaction mixture was refluxed for 48 h and cooled to room temperature. To the reaction mixture, 2-(5-trifluoromethyl-2*H*-1,2,4-triazol-3-yl)pyridine (0.214 g, 1 mmol, 0.45 eq.) and finely powdered anhydrous sodium carbonate (0.265 g, 2.5 mmol, 1.2 eq.) were added, and the mixture was refluxed for more 24 h. The mixture was cooled and evaporated to dryness. The solid residue was extracted with dichloromethane, filtered, the filtrate was collected and evaporated again. The solid residue was purified by column chromatography with gradual elution to give 133 mg (14%) of iridium complex **4b** and 258 mg (28%) of iridium complex **3b**.

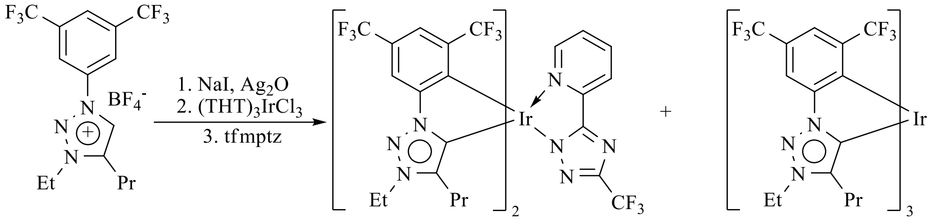
Complex **3b**. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 5.4 Hz, 1H), 7.11 – 7.06 (m, 1H), 7.06 – 6.99 (m, 1H), 6.41 (t, *J* = 9.1 Hz, 0H), 6.13 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.10 (dd, *J* = 8.7, 2.5 Hz, 1H), 5.95 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.75 (dd, *J* = 8.1, 2.4 Hz, 1H), 4.38 – 4.24 (m, 6H), 1.81 – 1.71 (m, 2H), 1.62 – 1.57 (m, 9H), 0.74 – 0.61 (m, 6H), 0.51 (t, *J* = 7.3 Hz, 3H). HRMS (ESI) calc. for $C_{34}H_{34}F_7IrN_{10}$ $[M+H]^+$: 905.2378, 906.2407, 907.2403, 908.2431; found: 905.2380, 906.2406, 907.2406, 908.2429.

Complex **4b**. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.43 – 6.35 (m, 4H), 6.27 – 6.11 (m, 2H), 4.35 – 4.18 (m, 6H), 2.22 – 1.94 (m, 6H), 1.62 – 1.55 (m, 9H), 1.20 – 1.10 (m, 2H), 0.93 – 0.84 (m, 2H), 0.83 – 0.75 (m, 2H), 0.61 – 0.56 (m, 6H), 0.55 – 0.48 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.05, 172.91, 161.46, 160.98, 142.78, 142.63, 120.95, 120.91, 119.76, 119.21, 118.71, 118.69, 118.67, 117.93, 117.91, 117.81, 96.27, 96.24, 96.09, 96.05, 95.93, 95.89, 95.83, 95.64, 44.14, 44.11, 44.01, 43.03, 29.85, 27.13, 26.79, 26.36, 26.25, 23.71, 23.58, 23.38, 23.31, 15.42, 14.11, 14.08, 13.67, 13.64.

HRMS (ESI) calc. for $C_{39}H_{43}F_6IrN_9$ $[M+H]^+$: 942.3146, 943.3176, 944.3172, 945.3200; found: 942.3140, 943.3139, 944.3164, 945.3196.

*Bis[2-(5-carbeno-3-ethyl-4-propyl-1H-1,2,3-triazol-1-yl)-4,6-bis(trifluoromethyl)phenyl]-[5-(pyridin-2-yl)-3-trifluoromethyl-1H-1,2,4-triazol-1-yl]iridium(III) (**3c**) and tris[2-(5-carbeno-3-ethyl-4-propyl-1H-1,2,3-triazol-1-yl)-4,6-bis(trifluoromethyl)phenyl]iridium(III) (**4c**)*



3c **4c**

To a solution of salt **1c** (0.746 g, 2.2 mmol) in dry dichloromethane (20 ml), a solution of anhydrous sodium iodide in acetonitrile (10 ml, 0.5 M, 5 mmol, 2.3 eq.) was added. The mixture was stirred for 0.5 h and evaporated to dryness. The solid residue was suspended in dichloromethane (40 ml) followed by addition of silver(I) oxide (0.281 g, 1.22 mmol, 0.55 eq.). The mixture was protected from light and stirred at room temperature for 24 h under inert atmosphere. The mixture was evaporated to dryness followed by addition of *o*-xylene (40 ml) and iridium tris(tetrahydrothiophene) trichloride (0.563 g, 1 mmol, 0.45 eq.). The mixture was refluxed for 48 h and cooled to room temperature. To the mixture, 2-(5-trifluoromethyl-2*H*-1,2,4-triazol-3-yl)pyridine (0.214 g, 1 mmol, 0.45 eq.) and finely powdered anhydrous sodium carbonate (0.265 g, 2.5 mmol, 1.2 eq.) were added, and the mixture was refluxed for more 24 h. The reaction mixture was cooled and evaporated to dryness. The solid residue was extracted with dichloromethane, filtered, the filtrate was collected and evaporated again. The solid residue was purified by column chromatography with gradual elution to give 99 mg (8%) of iridium complex **4c** and 263 mg (23%) of iridium complex **3c**.

Complex **3c**. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 8.03 (s, 1H), 7.99 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.70 (tt, *J* = 7.8, 1.1 Hz, 1H), 7.65 (s, 1H), 7.61 (d, *J* = 5.6 Hz, 1H), 7.50 (s, 1H), 6.98 (t, *J* = 6.7 Hz, 1H), 4.28 – 4.16 (m, 4H), 2.01 – 1.91 (m, 2H), 1.83 – 1.72 (m, 2H), 1.58 – 1.55 (m, 3H), 1.55 – 1.52 (m, 3H), 1.48 – 1.39 (m, 2H), 0.85 – 0.76 (m, 2H), 0.68 (t, *J* = 7.2 Hz, 3H), 0.38 (t, *J* = 7.3 Hz, 3H).

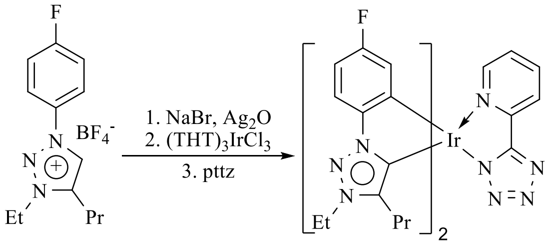
HRMS (ESI) calc. for $C_{38}H_{33}F_{15}IrN_{10}$ $[M+H]^+$: 1105.2251, 1106.2279, 1107.2276, 1108.2303; found: 1105.2252, 1106.2278, 1107.2279, 1108.2302.

Complex **4c**. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.57 – 7.47 (m, 5H), 4.31 – 4.21 (m, 6H), 2.53 – 2.39 (m, 2H), 1.95 – 1.86 (m, 2H), 1.80 – 1.70 (m, 2H), 1.65 – 1.51 (m, 9H), 1.44 – 1.39 (m, 2H), 1.12 – 0.95 (m, 4H), 0.47 – 0.41 (m, 6H), 0.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.08, 154.13, 150.96, 150.65, 150.45, 150.15, 150.02, 149.99, 149.43, 148.68, 147.55, 147.49, 145.94, 145.65, 145.58, 145.39, 143.99, 143.15, 142.36, 129.73, 125.94, 123.61, 121.50, 121.16, 117.25, 113.49, 112.72, 112.60, 112.44, 112.31, 110.89, 44.71, 44.55, 44.48, 44.30, 44.14, 29.88, 27.52, 26.62, 26.37, 25.90, 25.69, 23.52, 23.47, 22.95, 22.83, 22.31, 19.86, 15.43, 15.39, 15.37, 15.15, 14.98, 14.33, 14.28, 13.99, 13.58, 13.37, 12.91.

HRMS (ESI) calc. for $C_{45}H_{43}F_{18}IrN_9$ $[M+H]^+$: 1242.2955, 1243.2984, 1244.2981, 1245.3009; found: 1242.2955, 1243.2944, 1244.2975, 1245.3008.

*Bis[2-(5-carbeno-3-ethyl-4-propyl-1H-1,2,3-triazol-1-yl)-5-fluorophenyl][5-(pyridin-2-yl)-1H-tetrazol-1-yl]iridium(III) (**5a**)*



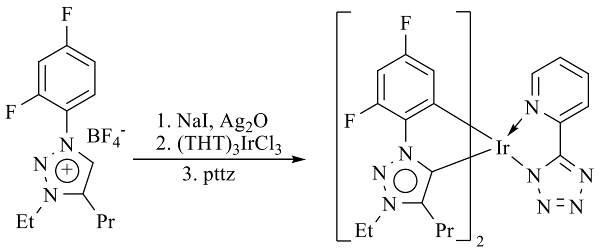
An oven-dried 100 ml Schlenk flask equipped with magnetic stirring bar was charged with dry DMSO (35 ml), salt **1a** (0.6422 g, 2 mmol) and sodium bromide (0.206 g, 2 mmol). The flask deaerated by evacuation and filling with argon. Silver(I) oxide (0.255 g, 1.1 mmol) was added followed by $IrCl_3(THT)_3$ (0.563 g, 1 mmol). The resulting mixture was protected from light and stirred at ambient temperature for 6 h and then heated at 140 °C for 24 h. 2-(1*H*-Tetrazol-5-yl)pyridine (0.1471 g, 1 mmol) and finely powdered anhydrous sodium carbonate (0.265 g, 2.5 mmol) were added, and the mixture was refluxed for more 24 h. The mixture cooled, treated with water and dichloromethane. This was filtered through Celite, the organic phase was collected, dried over sodium sulfate and evaporated. The residue was subjected to column chromatography (gradual eluting) to afford 60 mg (6%) of tris(carbene) complex **4a** and 267 mg (33%) of bis(carbene) complex **5a**.

Complex **5a**. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.31 (dt, *J* = 7.9, 1.1 Hz, 1H), 8.04 (dt, *J* = 5.6, 1.2 Hz, 1H), 7.81 (td, *J* = 7.7, 1.6 Hz, 1H), 7.55 (dd, *J* = 8.6, 5.1 Hz, 1H), 7.48 (dd, *J* = 8.6, 5.2 Hz, 1H), 7.07 (ddd, *J* = 7.1, 5.5, 1.4 Hz, 1H), 6.63 (td, *J* = 8.6, 2.7 Hz, 1H), 6.54 (td, *J* = 8.7, 2.7 Hz, 1H), 6.37 (dd, *J* = 9.6, 2.8 Hz, 1H), 6.21 (dd, *J* = 9.9, 2.7 Hz, 1H), 4.26 (ddp, *J* = 27.8, 21.0, 7.1 Hz, 4H), 2.10 – 1.96 (m, 1H), 1.90 – 1.79 (m, 1H), 1.76 – 1.66 (m, 2H), 1.62 – 1.54 (m, 6H), 1.39 – 1.28 (m, 1H), 1.23 – 1.13 (m, 1H), 0.99 – 0.82 (m, 2H), 0.66 (t, *J* = 7.3 Hz, 3H), 0.51 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.19, 162.69, 161.55, 161.06, 155.88, 154.74, 151.21, 150.52, 144.43, 143.12, 142.81, 142.31, 141.39, 141.36, 136.90, 135.52, 135.48, 124.37, 123.68, 123.60, 123.56, 123.47, 122.06, 115.43, 115.37, 115.06, 115.00, 108.23, 108.10, 108.07, 107.94, 59.19, 44.35, 44.26, 26.33, 25.89, 24.07, 23.76, 15.23, 14.09, 13.96.

HRMS (ESI) calc. for $C_{32}H_{35}F_2IrN_{11}$ $[M+H]^+$: 802.2646, 803.2673, 804.2670, 805.2697; found: 802.2645, 803.2668, 804.2672, 805.2698.

*Bis[2-(5-carbeno-3-ethyl-4-propyl-1H-1,2,3-triazol-1-yl)-3,5-difluorophenyl][5-(pyridin-2-yl)-1H-tetrazol-1-yl]iridium(III) (**5b**)*



An oven dried 100 ml Schlenk flask equipped with magnetic stirring bar was charged with dry DMSO (35 ml), salt **1b** (0.6422 g, 2 mmol) and sodium bromide (0.206 g, 2 mmol). The flask was deaerated by evacuation and filling with argon. Silver oxide (0.255 g, 1.1 mmol) was added followed by $IrCl_3(THT)_3$ (0.563 g, 1 mmol). The flask was protected from light, and the mixture was stirred at ambient temperature for 6 h and then heated at 140 °C for 24 h. 2-(1*H*-Tetrazol-5-yl)pyridine (0.1471 g, 1 mmol) and finely powdered anhydrous sodium carbonate (0.265 g, 2.5 mmol) were added, and the mixture was refluxed for more 24 h. Then mixture was cooled to RT, treated with water and dichloromethane and filtered through Celite. The organic phase was collected, dried over sodium sulfate and evaporated. The residue was subjected to column chromatography (gradual eluting) to afford 82 mg (8%) of tris(carbene) complex **4b** and 262 mg (31%) of bis(carbene) complex **5b**.

Complex **5b**. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 8.0 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.15 (ddt, *J* = 7.1, 5.6, 1.3 Hz, 1H), 6.50 (dd, *J* = 14.0, 6.0 Hz, 2H), 6.17 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.71 (dd, *J* = 8.0, 2.3 Hz, 1H), 4.34 – 4.18 (m, 4H), 2.15 – 2.09 (m, 2H), 2.04 – 1.94 (m, 2H), 1.78 – 1.75 (m, 2H), 1.64 – 1.52 (m, 6H), 0.94 – 0.84 (m, 2H), 0.66 – 0.61 (m, 8H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.68, 150.51, 149.80, 146.40, 146.38, 145.74, 144.89, 142.28, 137.57, 131.16, 131.12, 125.33, 122.47, 119.94, 119.92, 119.82, 119.24, 118.20, 116.29, 116.28, 114.39, 114.37, 114.28, 114.26, 114.24, 98.28, 46.41, 44.75, 44.55, 41.19, 31.58, 30.34, 29.84, 26.55, 25.80, 25.60, 24.22, 23.52, 15.30, 14.93, 14.20, 13.93.

HRMS (ESI) calc. for $C_{32}H_{33}F_4IrN_{11}$ $[M+H]^+$: 838.2457, 839.2484, 840.2482, 841.2508; found: 838.2453, 839.2479, 840.2479, 841.2504.

References

S1. H. Meerwein,*Organic Syntheses*, 1966, **46**, 113.
S2. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176.
S3. K. H. Drexhage, *J. Res. Natl. Bur. Stand., Sect. A*, 1976, **80A**, 421.
S4. G. Jones II, W. R. Jackson, C. Y. Choi and W. R. Bergmark, *J. Phys. Chem.*, 1985, **89**, 294.

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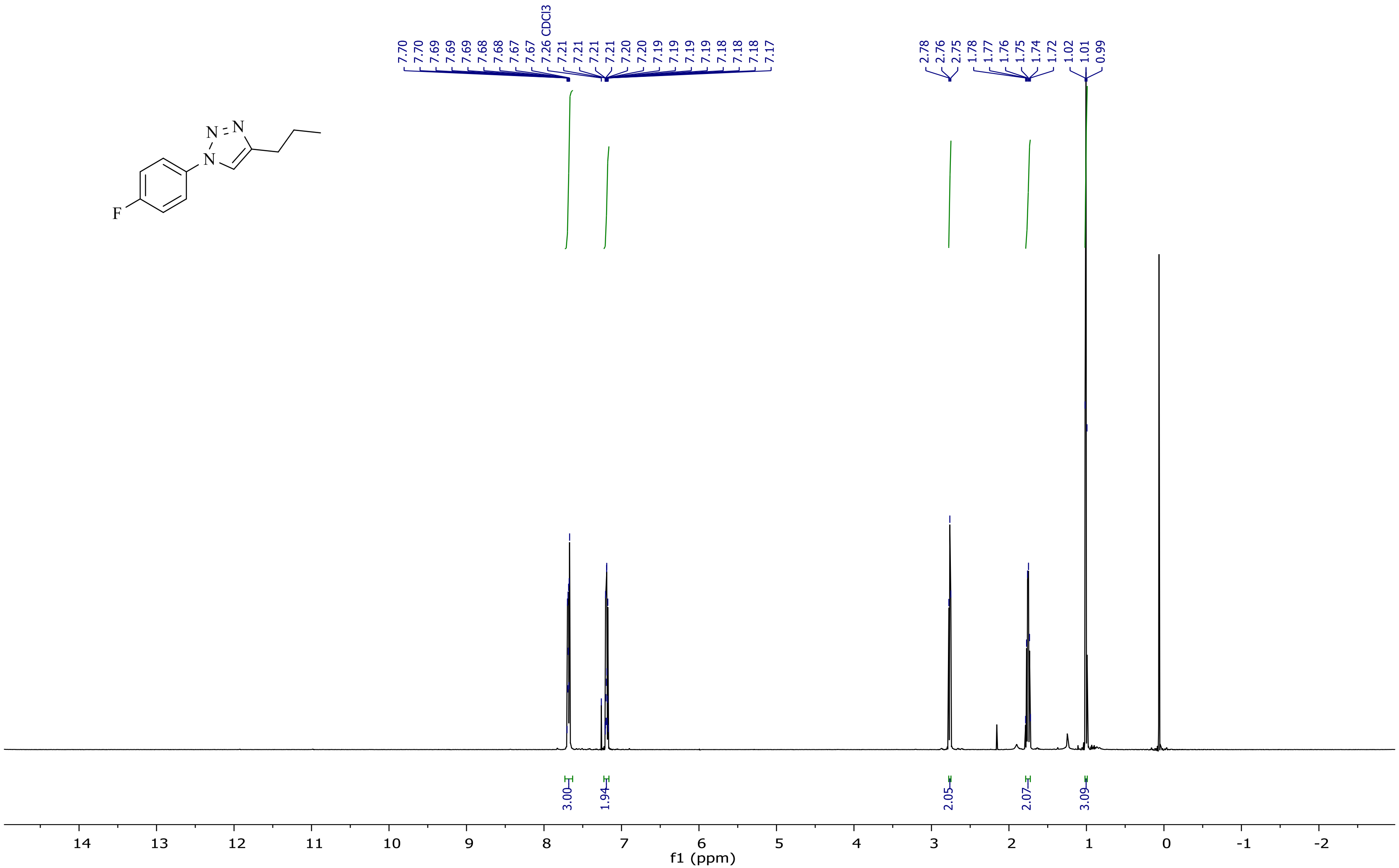

Figure S9. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-(4-fluorophenyl)-4-propyl-1*H*-1,2,3-triazole

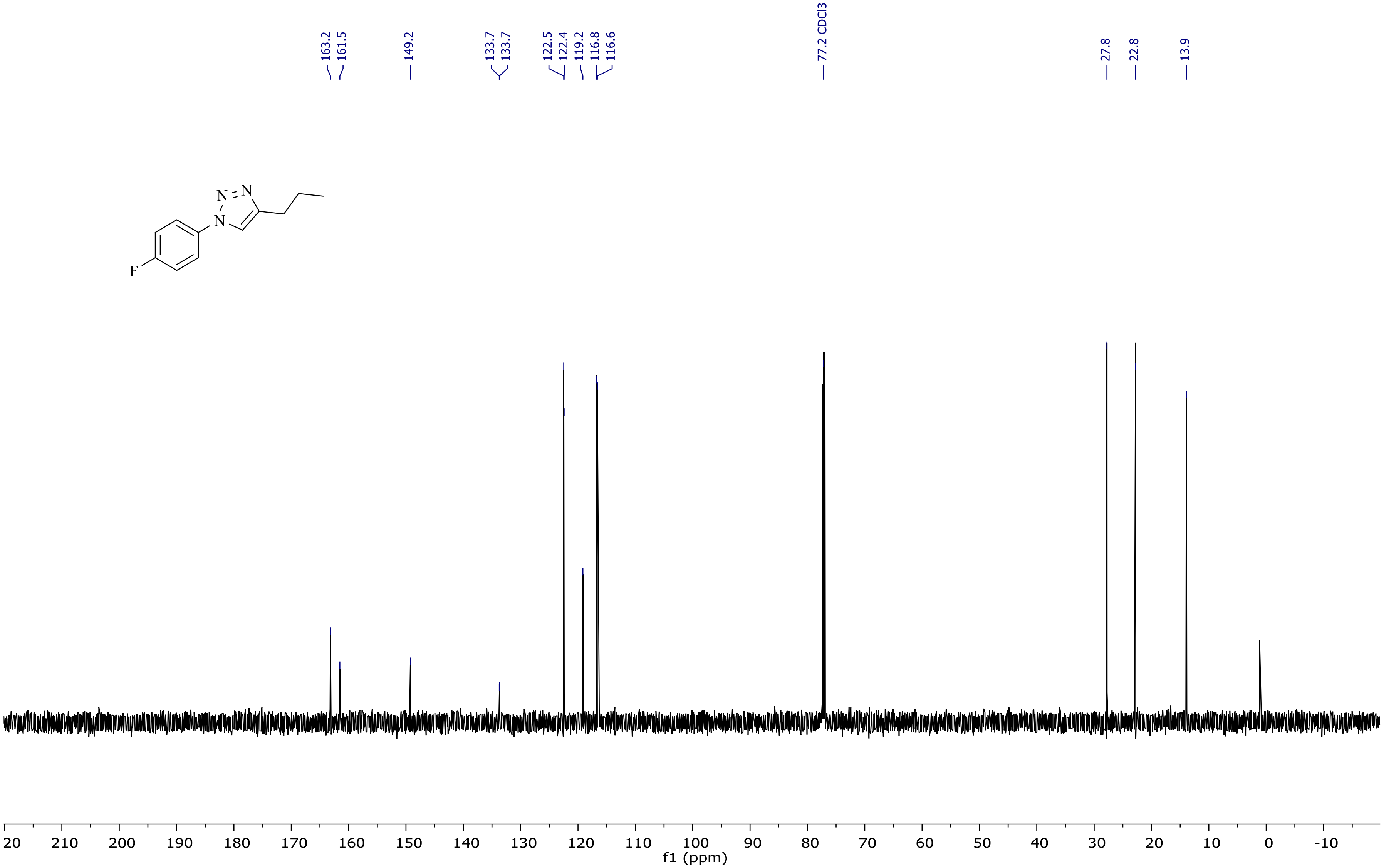

Figure S10. ^{13}C NMR (151 MHz, Chloroform-d) of 1-(4-fluorophenyl)-4-propyl-1*H*-1,2,3-triazole

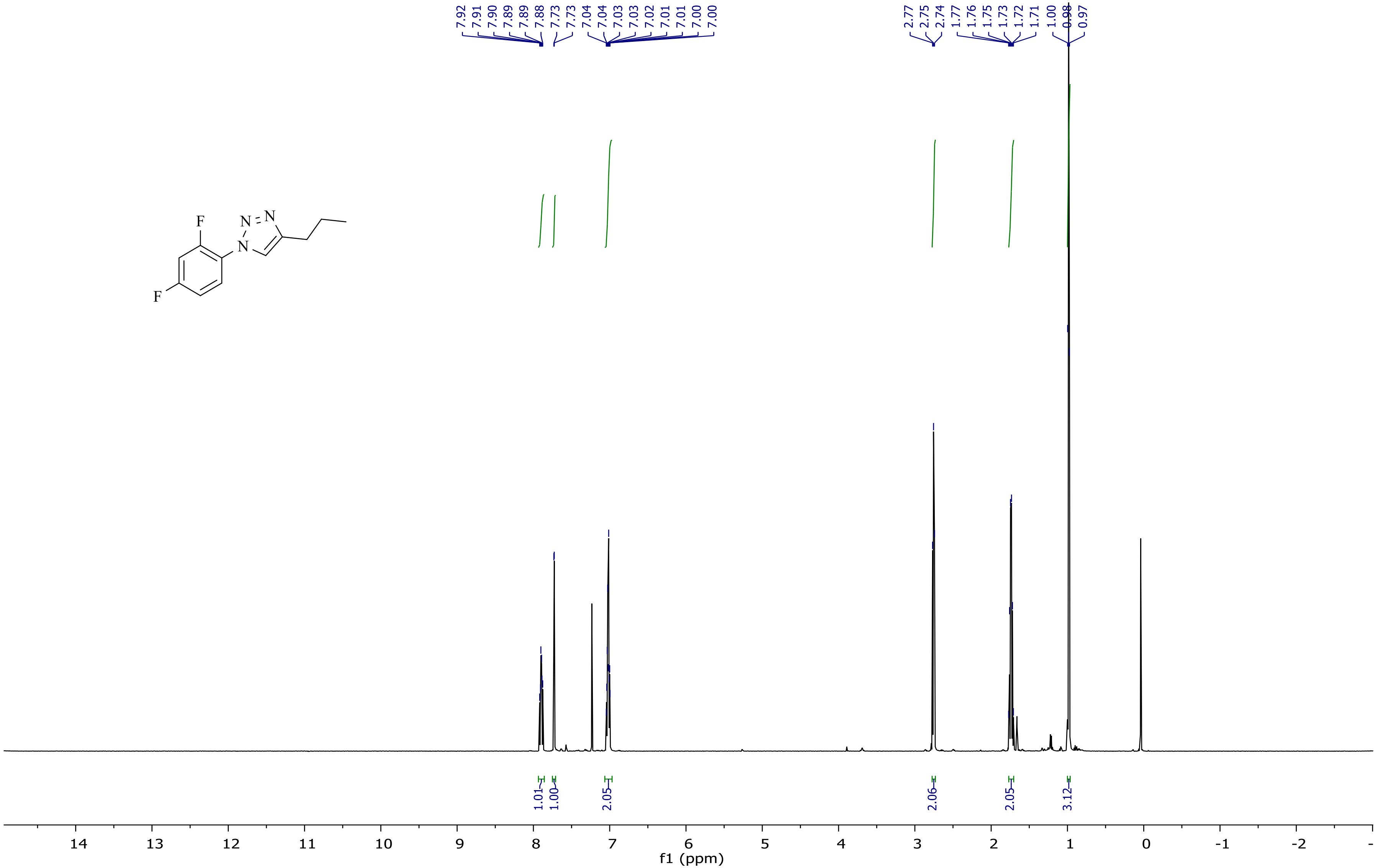

Figure S11. ¹H NMR (600 MHz, Chloroform-*d*) of 1-(2,4-difluorophenyl)-4-propyl-1*H*-1,2,3-triazole

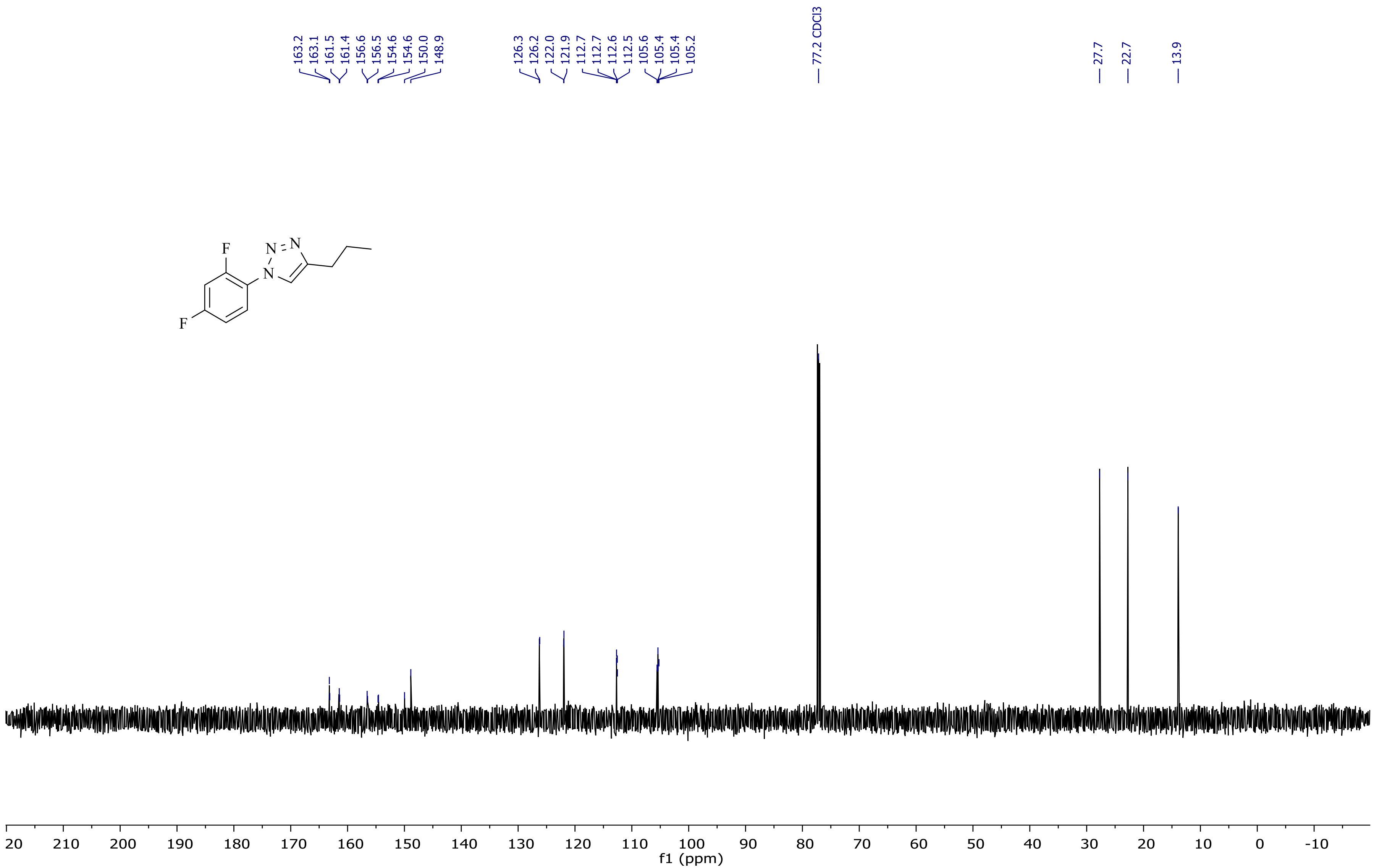

Figure S12. ^{13}**C NMR (151 MHz, Chloroform-d) of 1-(2,4-difluorophenyl)-4-propyl-1*H*-1,2,3-triazole**

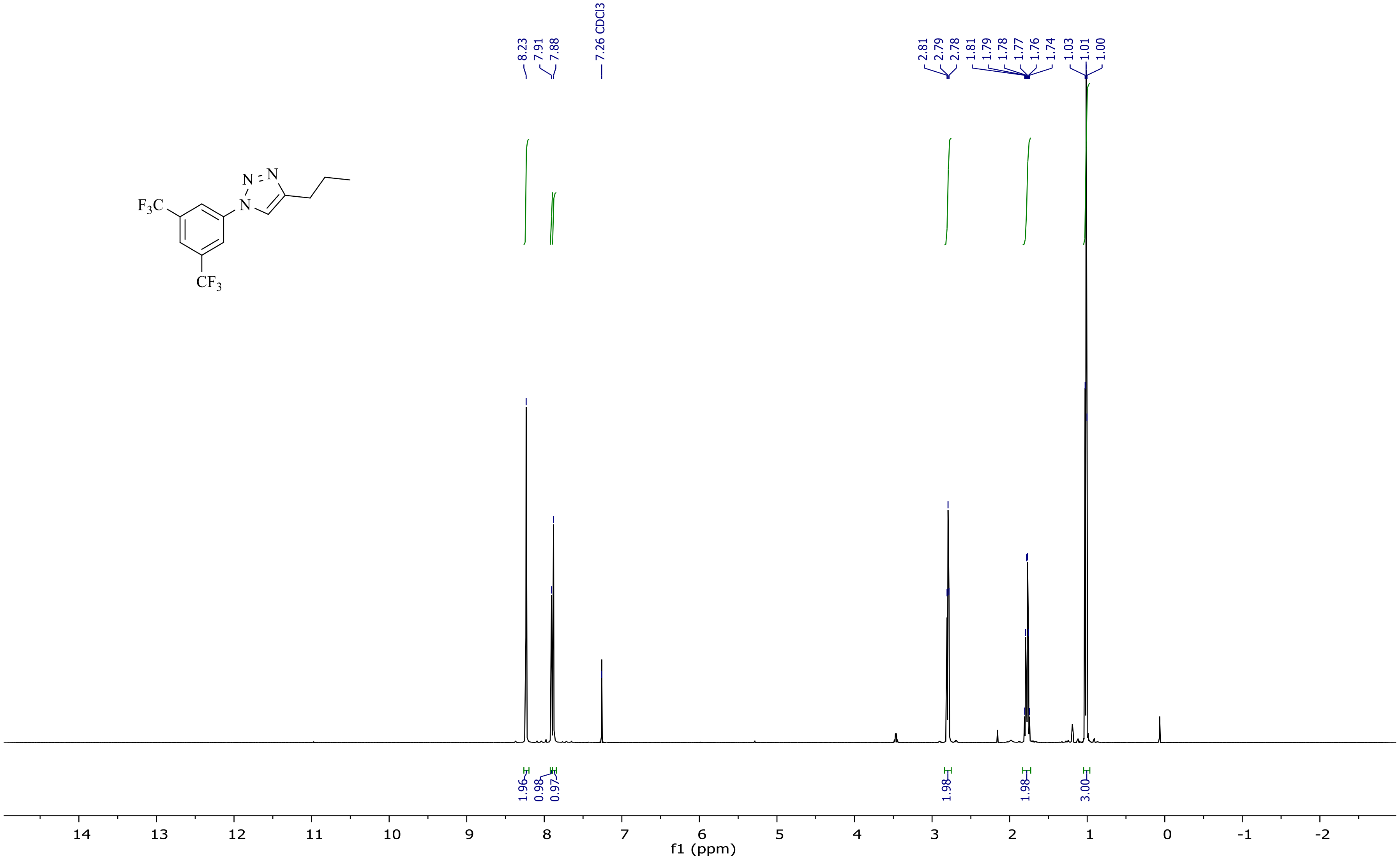

Figure S13. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-[3,5-bis(trifluoromethyl)phenyl]-4-propyl-1*H*-1,2,3-triazole

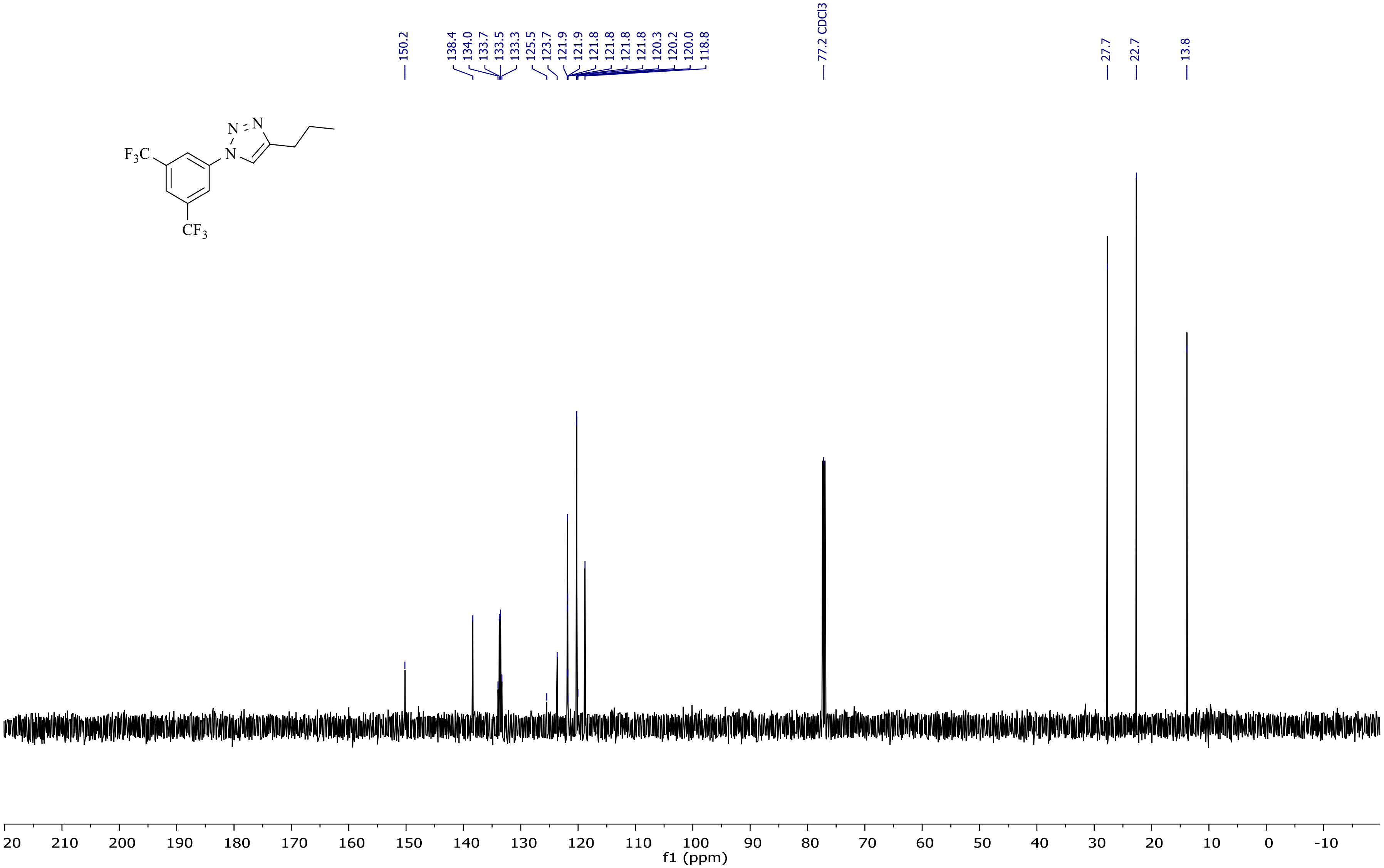

Figure S14. **^{13}C NMR (151 MHz, Chloroform-d) of 1-[3,5-bis(trifluoromethyl)phenyl]-4-propyl-1*H*-1,2,3-triazole**

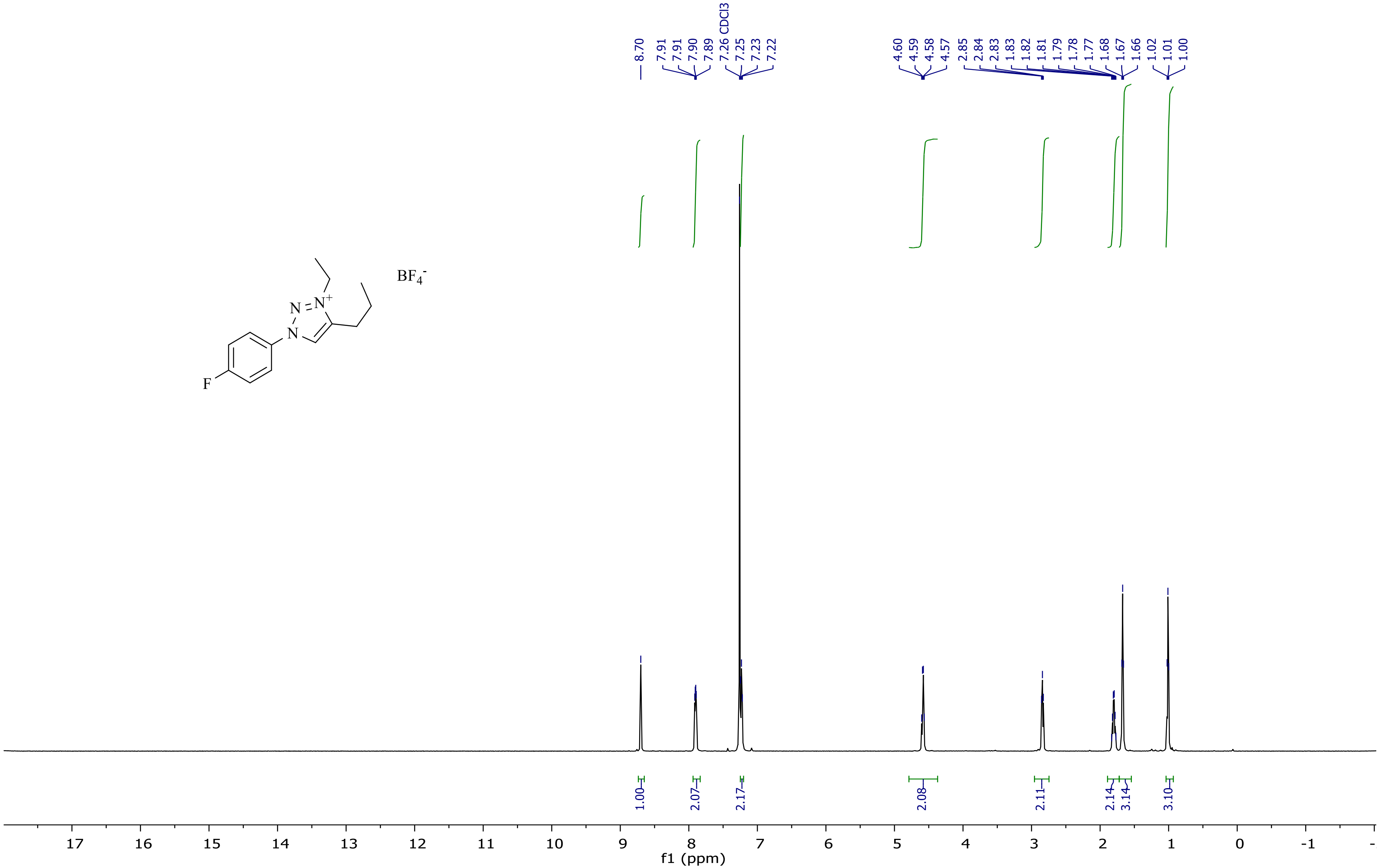

Figure S15. [1]**H NMR (600 MHz, Chloroform-*d*) of 1-(4-fluorophenyl)-3-ethyl-4-propyl-1*H*-1,2,3-triazolium tetrafluoroborate (1a)**

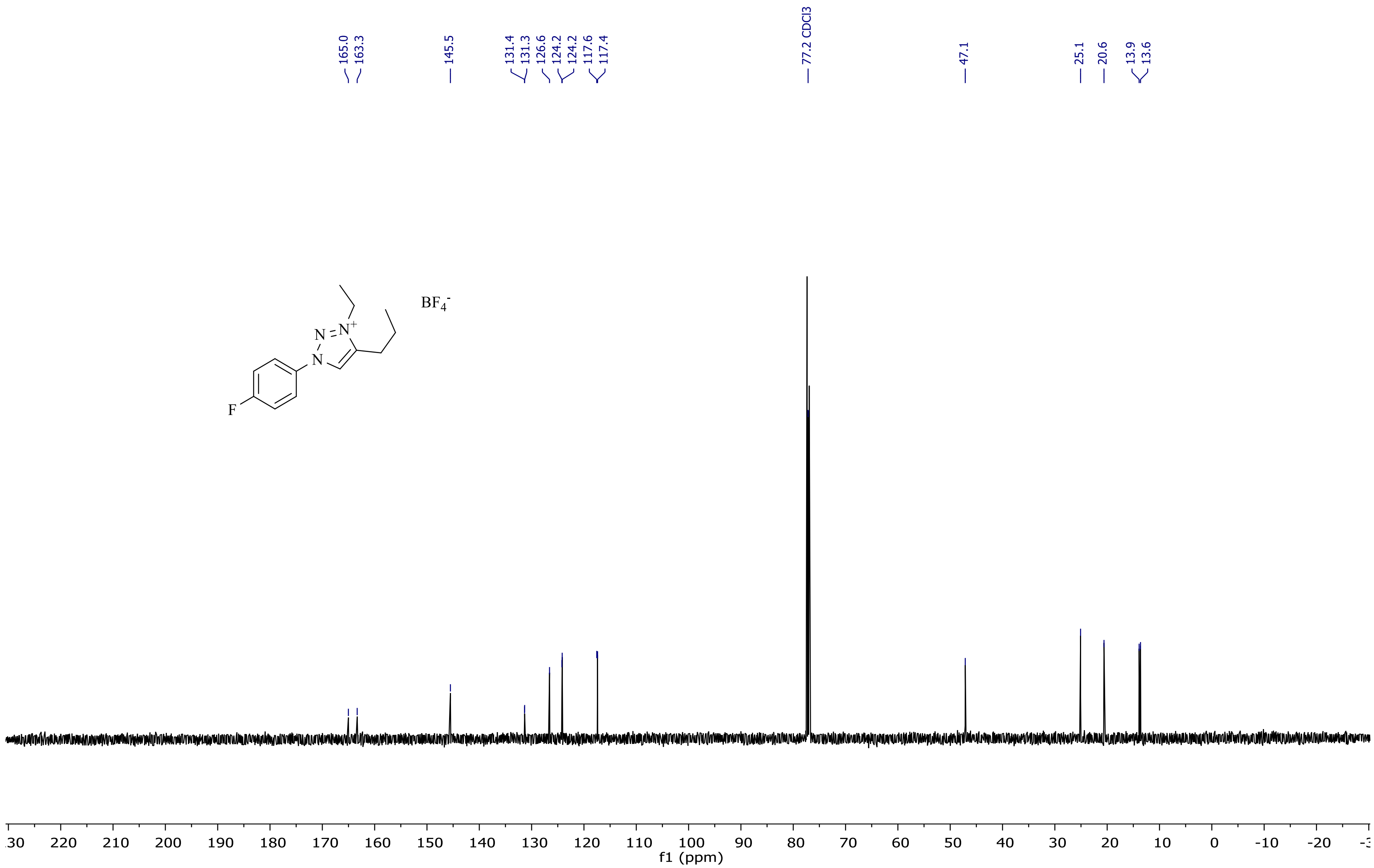

Figure S16. **^{13}C NMR (151 MHz, Chloroform-d) of 1-(4-fluorophenyl)-3-ethyl-4-propyl-1*H*-1,2,3-triazolium tetrafluoroborate (1a)**

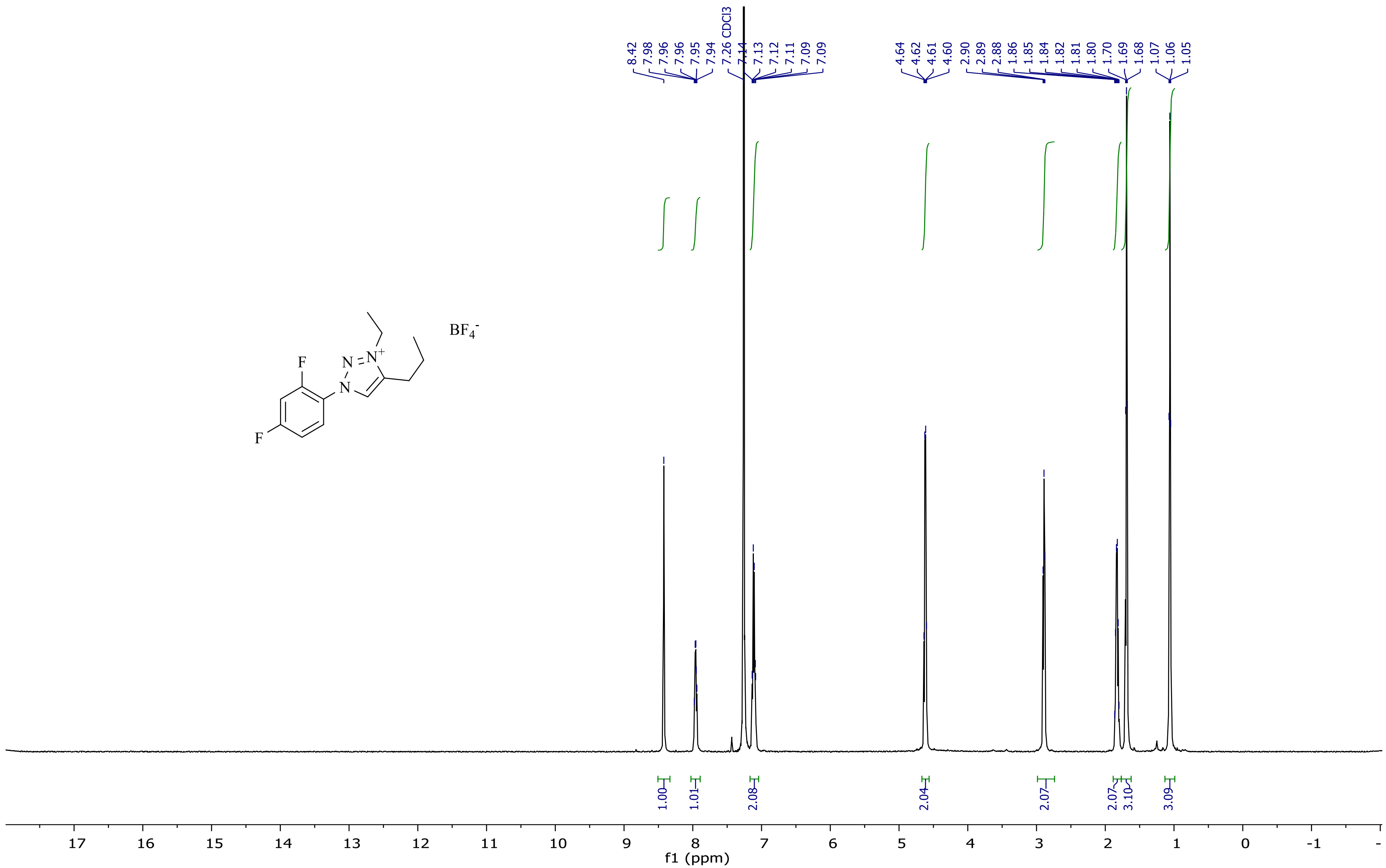

Figure S17. [1]**H NMR (600 MHz, Chloroform-*d*) of 1-(2,4-difluorophenyl)-3-ethyl-4-propyl-1*H*-1,2,3-triazolium tetrafluoroborate (1b)**

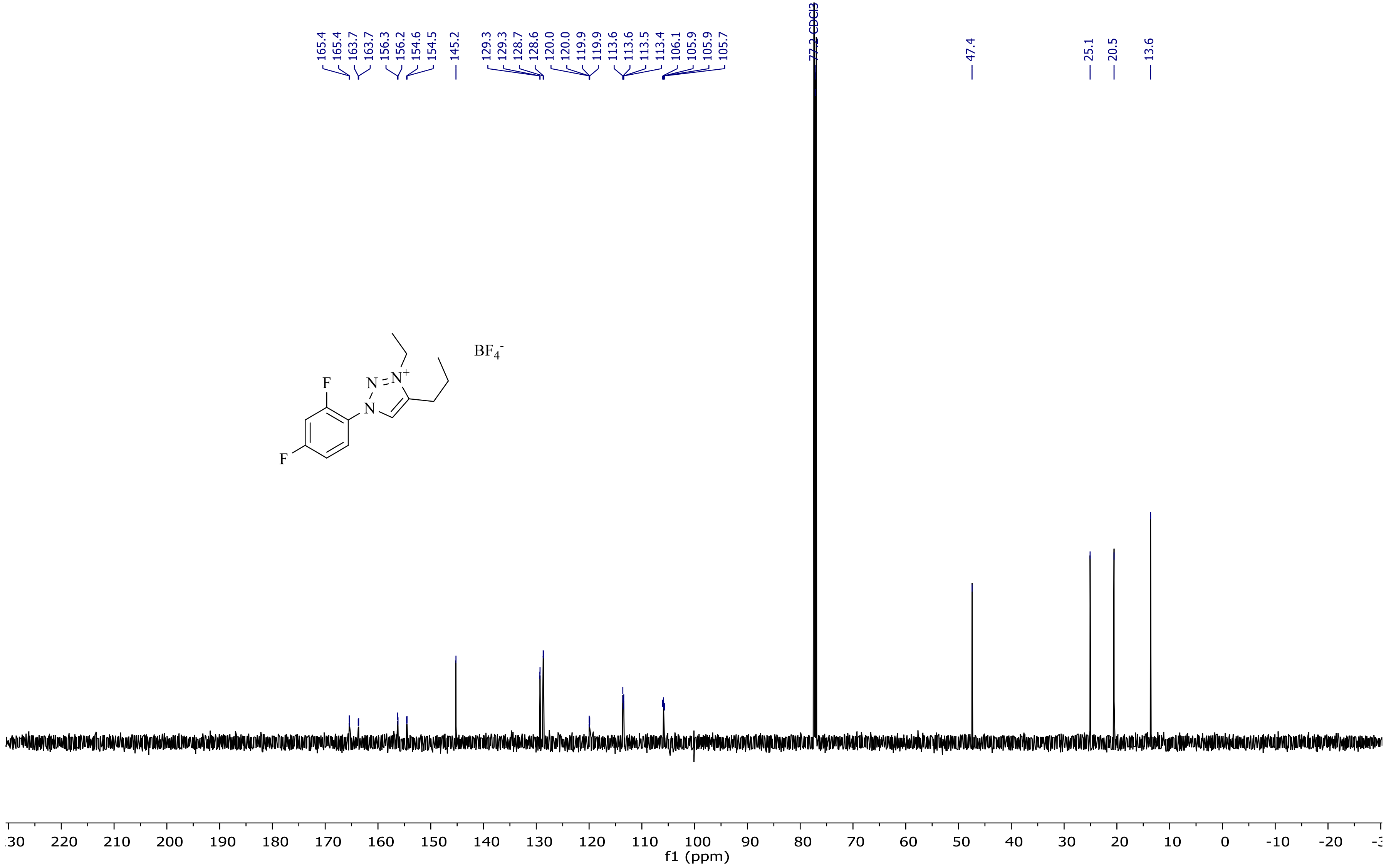

Figure S18. ^{13}**C NMR (151 MHz, Chloroform-d) of 1-(2,4-difluorophenyl)-3-ethyl-4-propyl-1*H*-1,2,3-triazolium tetrafluoroborate (1b)**

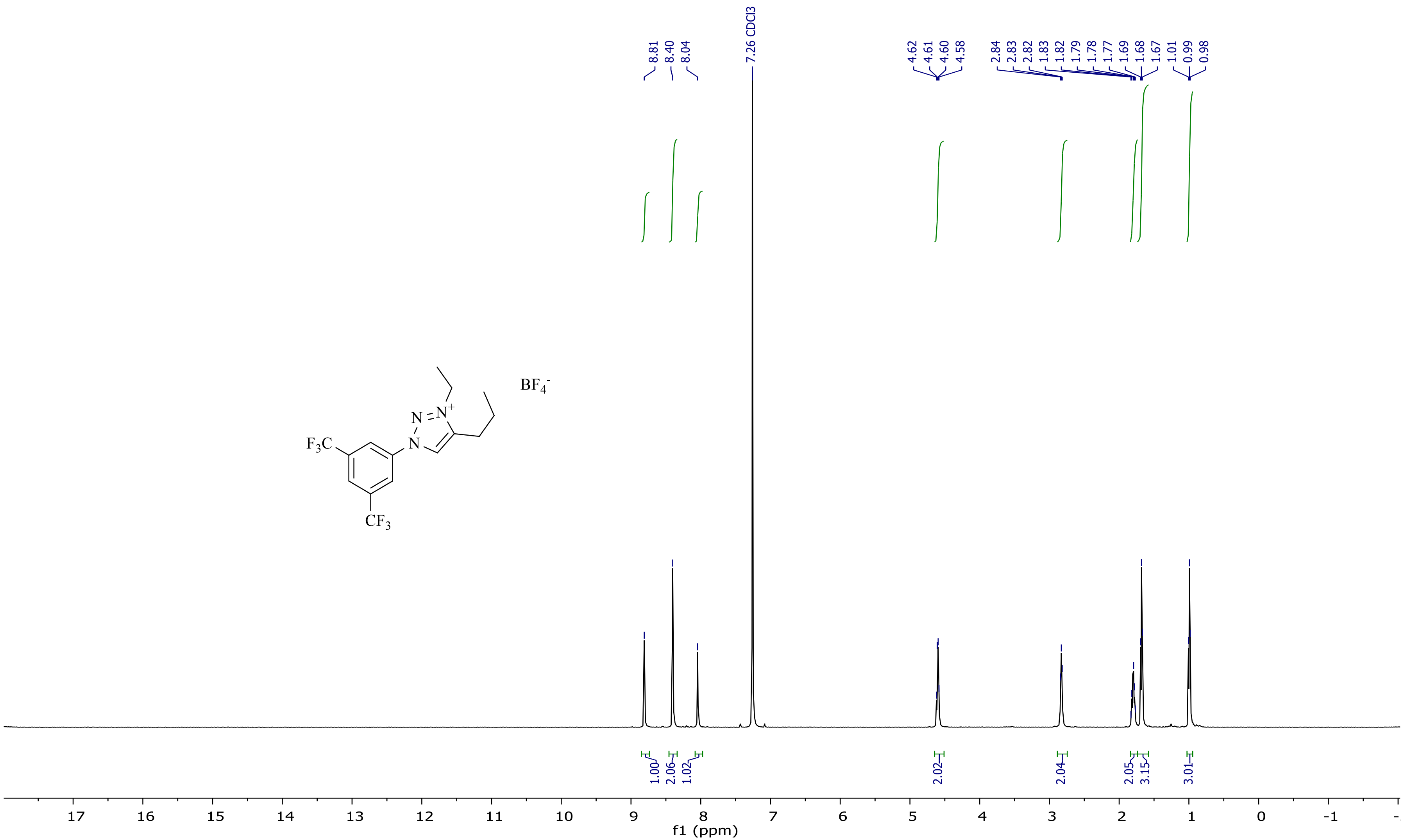

Figure S19. [1]H NMR (600 MHz, $CDCl_3$) of 1-[3,5-bis(trifluoromethyl)phenyl]-3-ethyl-4-propyl-1*H*-1,2,3-triazolium tetrafluoroborate (1c)

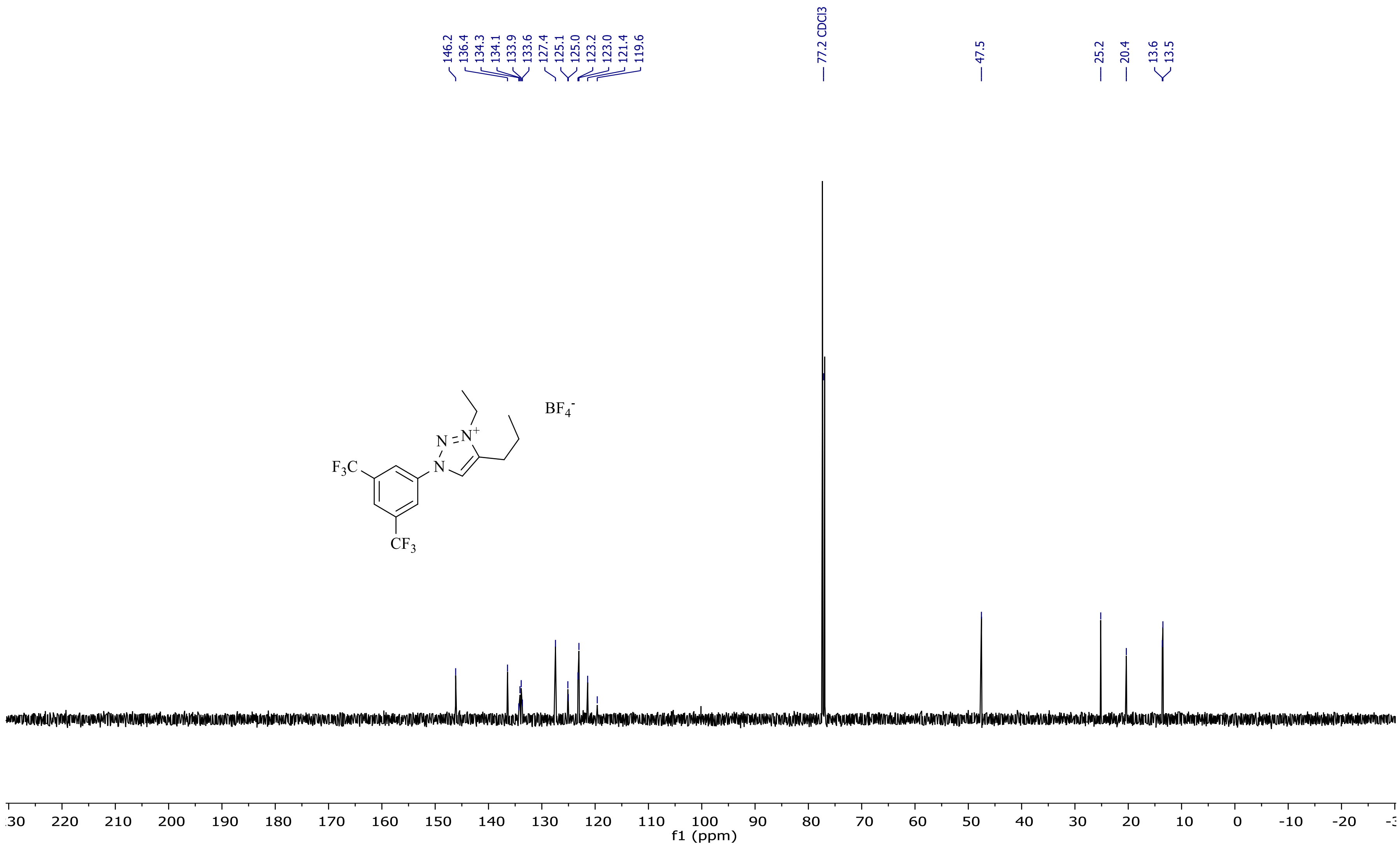

Figure S20. ^{13}C NMR (151 MHz, $CDCl_3$) of 1-[3,5-bis(trifluoromethyl)phenyl]-3-ethyl-4-propyl-1*H*-1,2,3-triazolium tetrafluoroborate (1c)

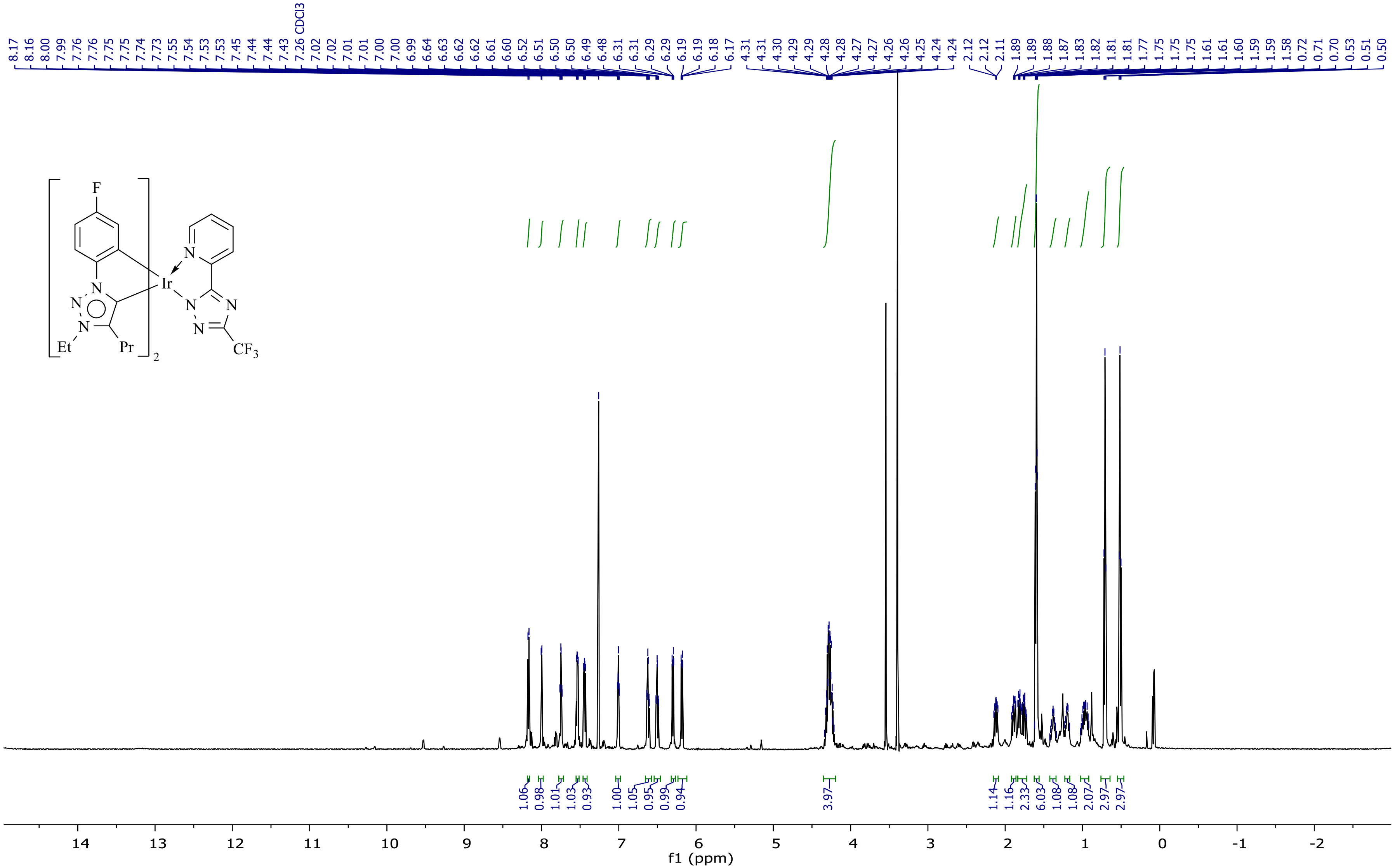

Figure S21. ^{1}H **NMR (600 MHz, Chloroform-*d*) of iridium complex 3a**

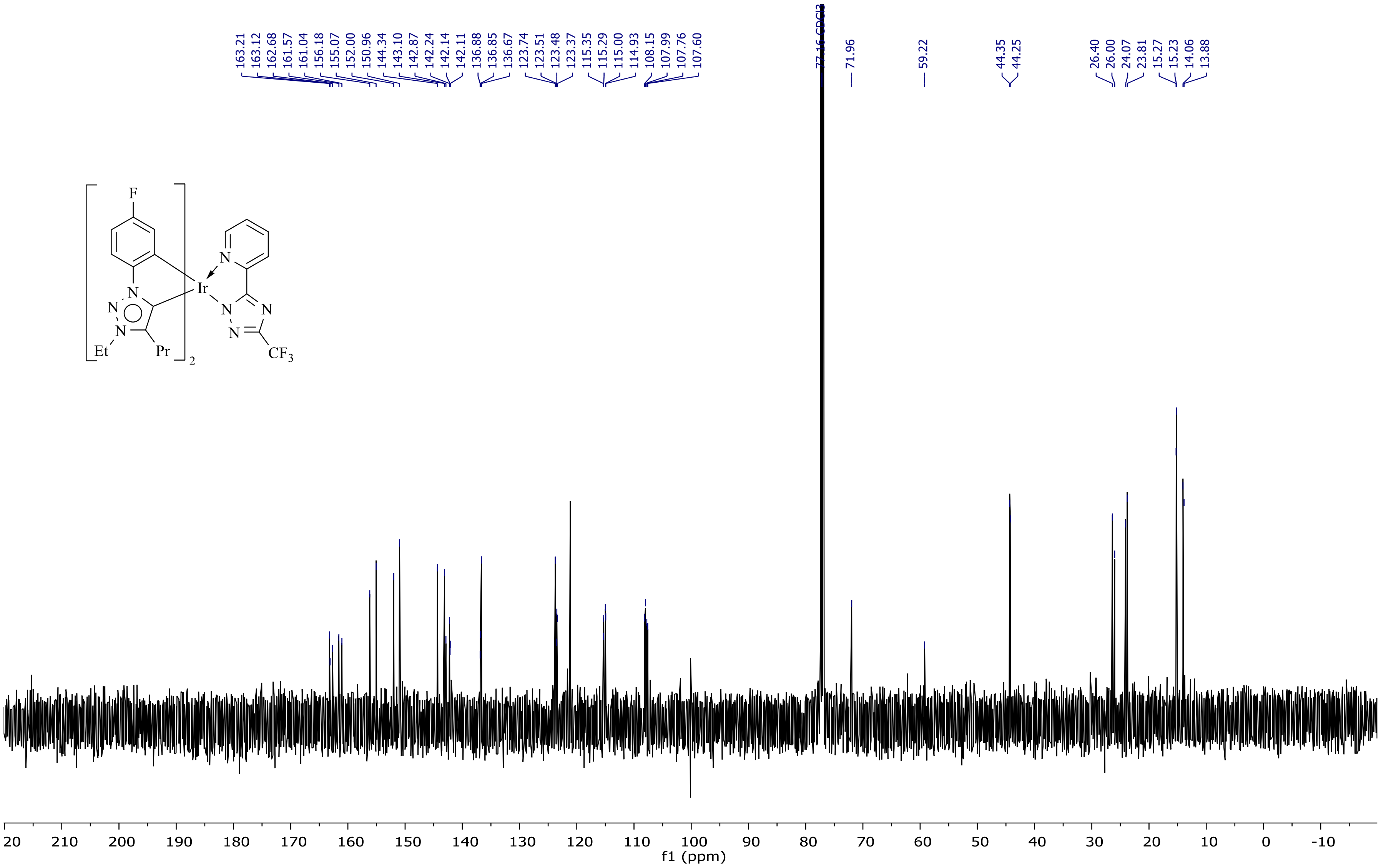

Figure S22. ^{13}C NMR (151 MHz, Chloroform-d) of iridium complex 3a

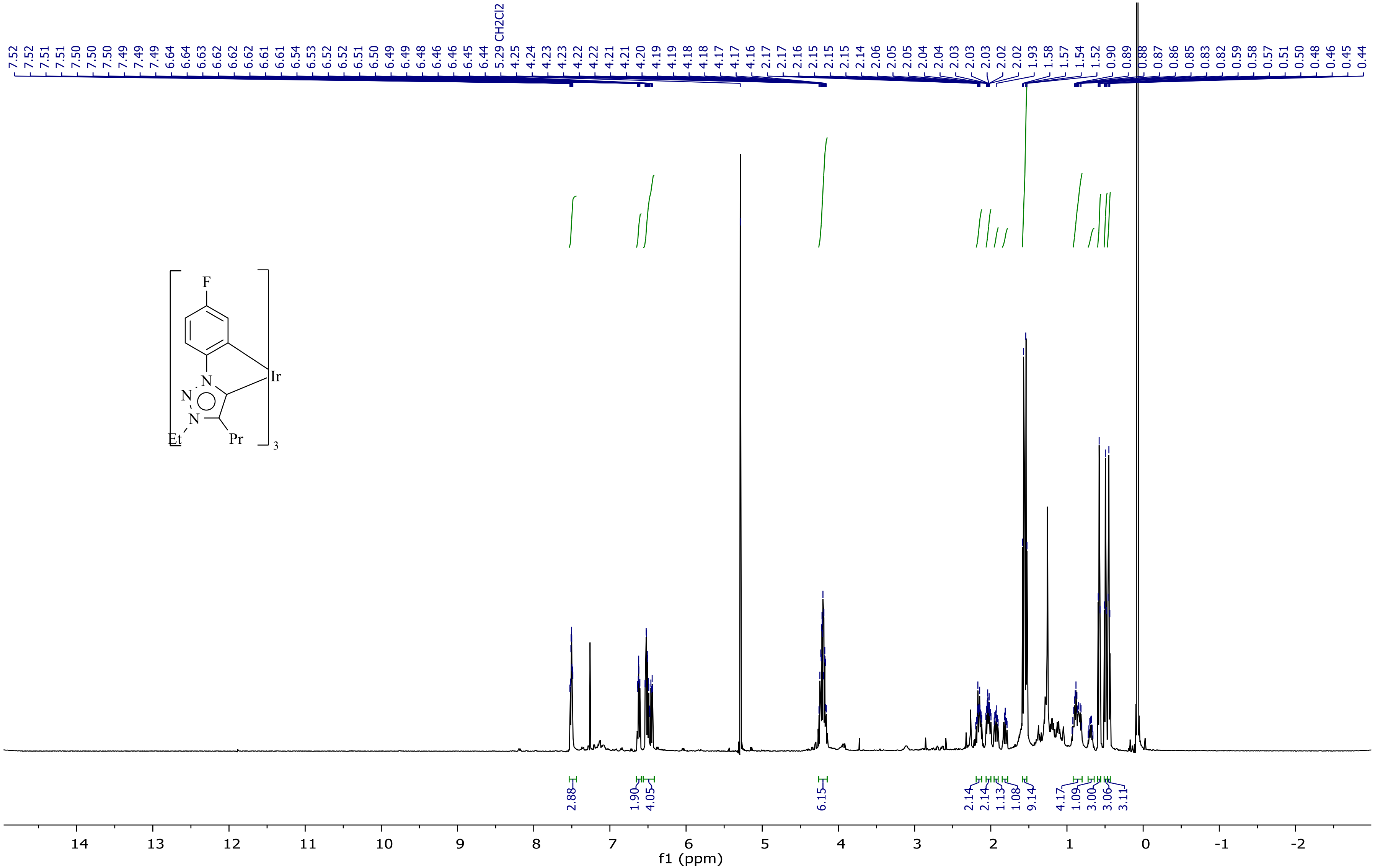

Figure S23. [1]H NMR (600 MHz, Chloroform-*d*) of iridium complex 4a

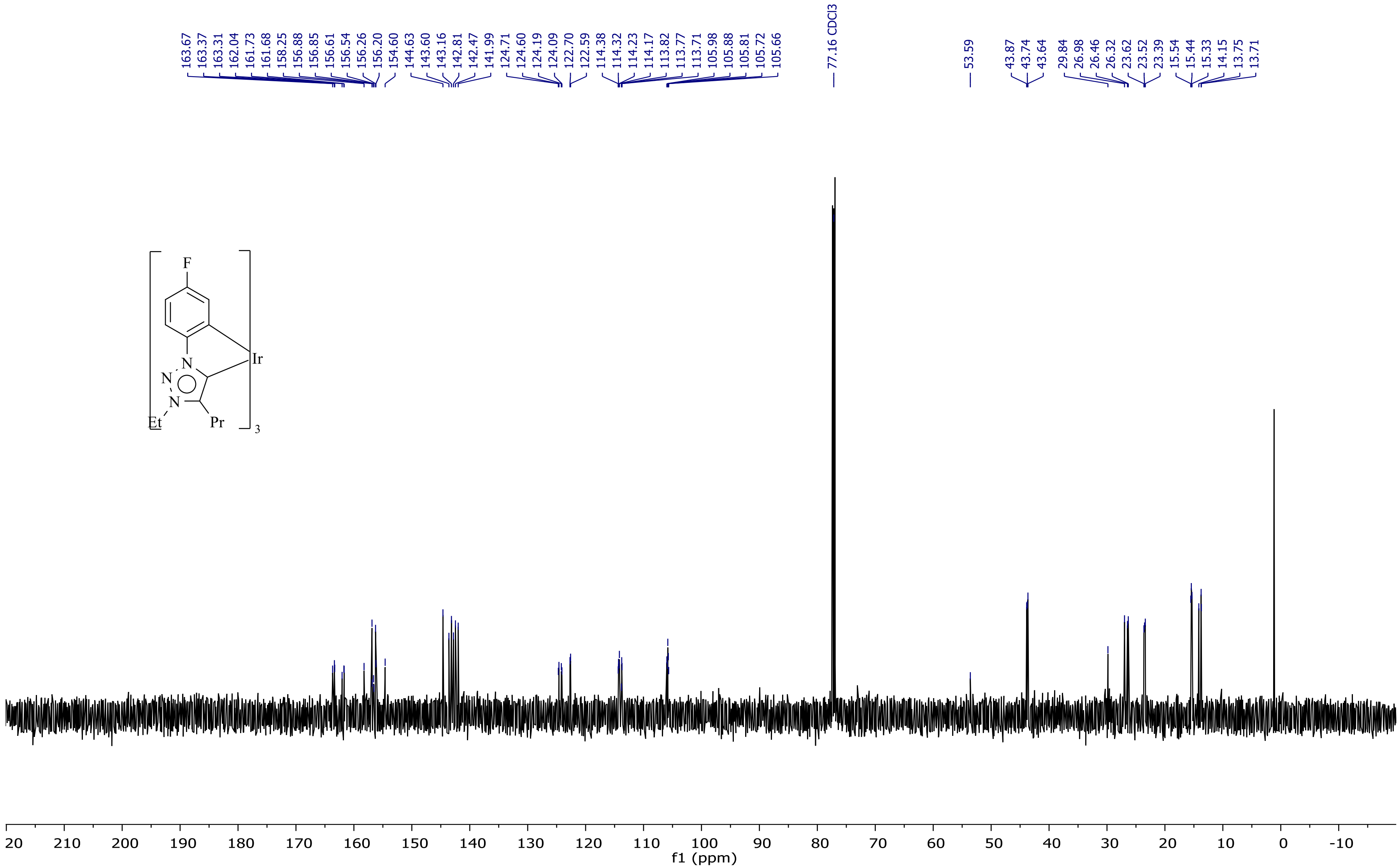

Figure S24. ^{13}C NMR (151 MHz, Chloroform-d) of iridium complex 4a

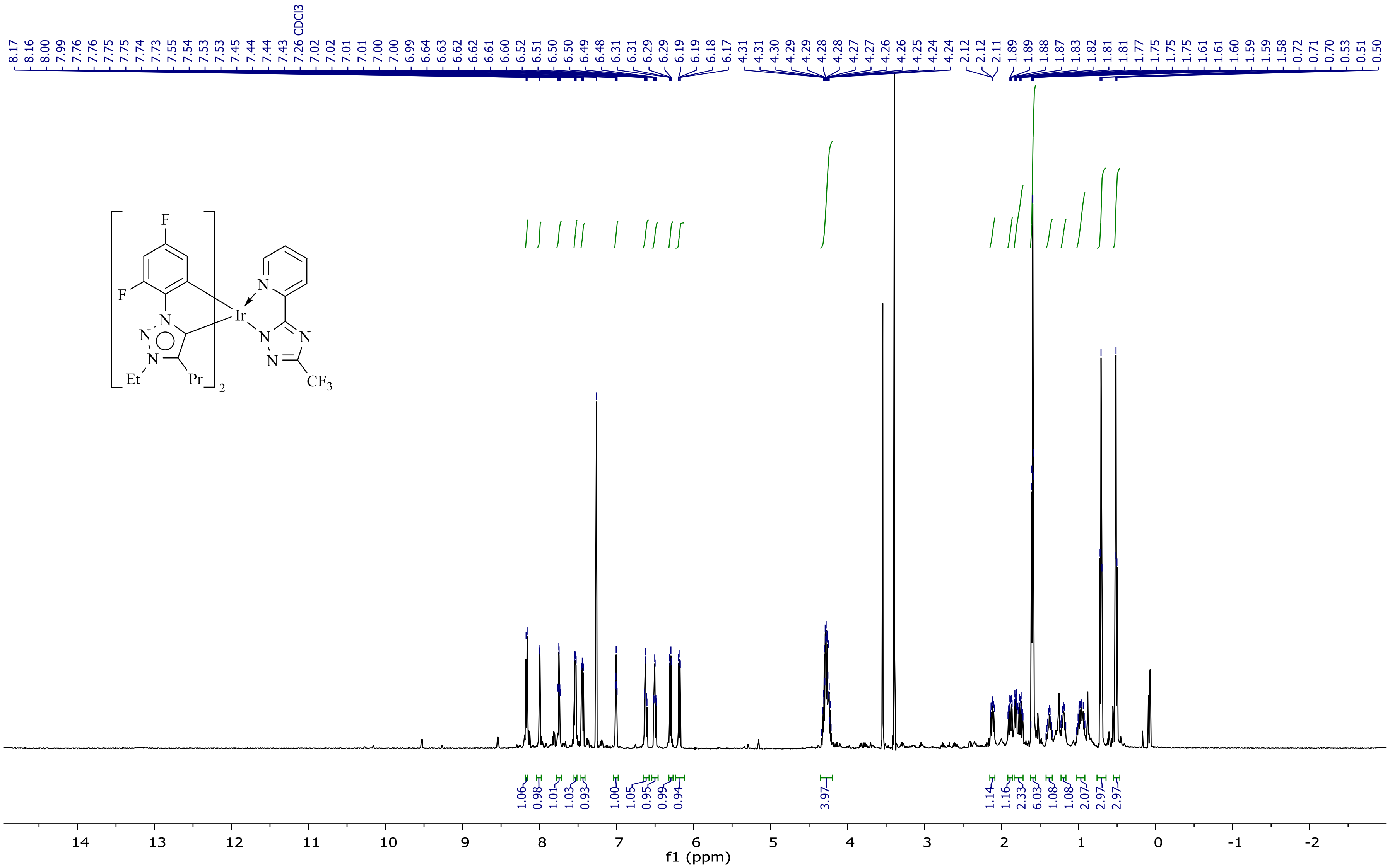

Figure S25. [1]H NMR (600 MHz, Chloroform-*d*) of iridium complex 3b

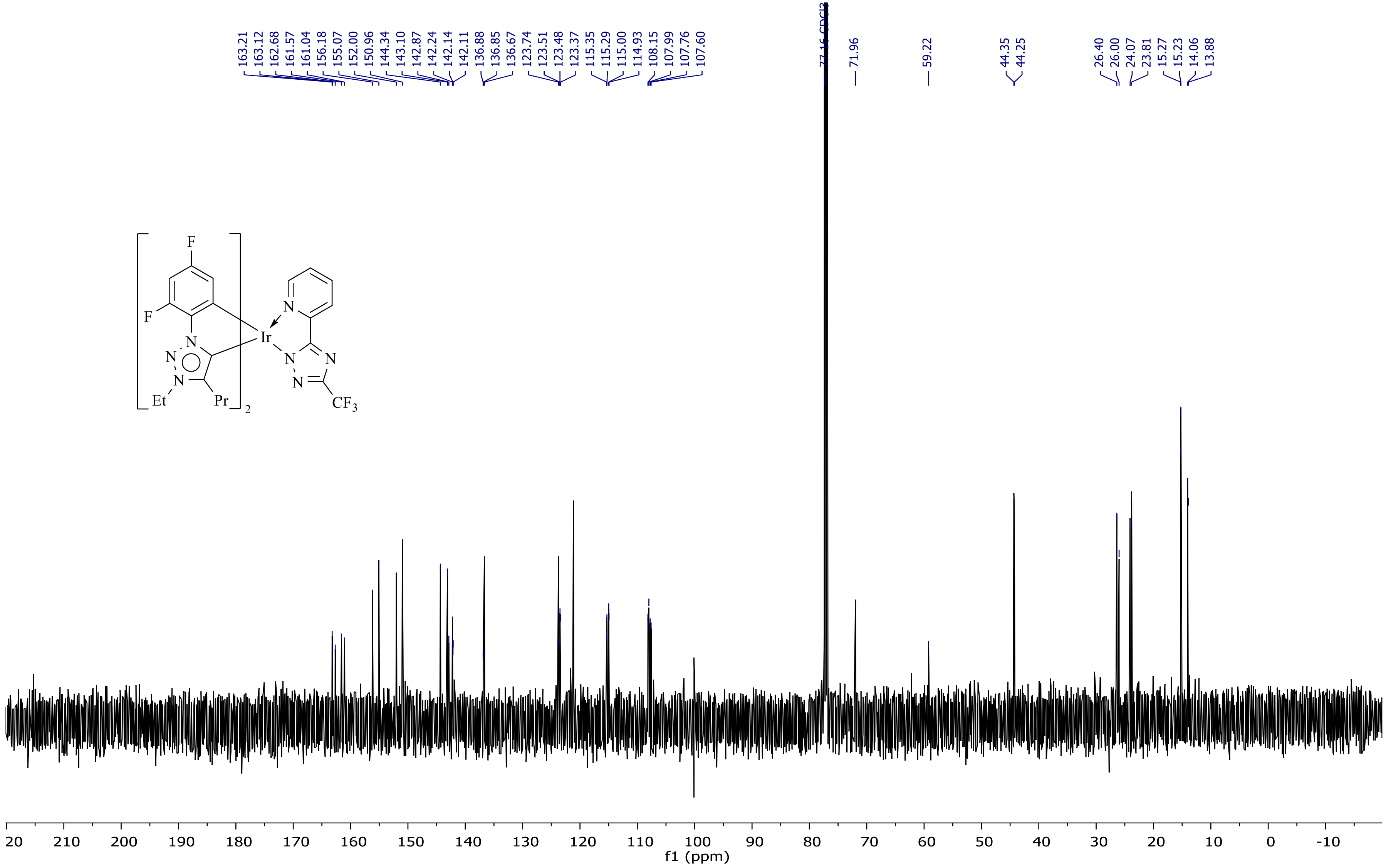

Figure S26. ^{13}C NMR (151 MHz, Chloroform-d) of iridium complex 3b

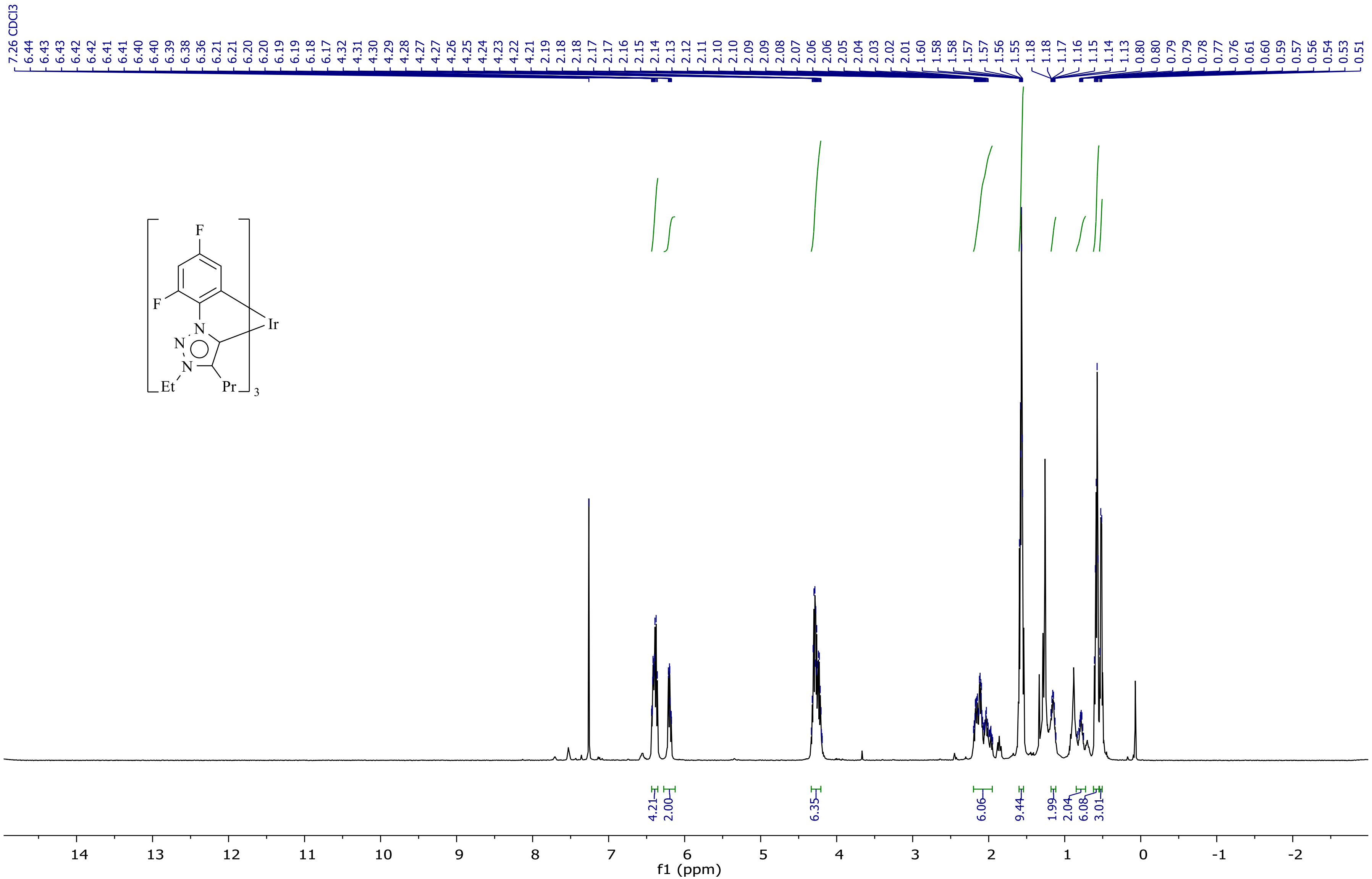

Figure S27. ^{1}H NMR (600 MHz, Chloroform-*d*) of iridium complex 4b

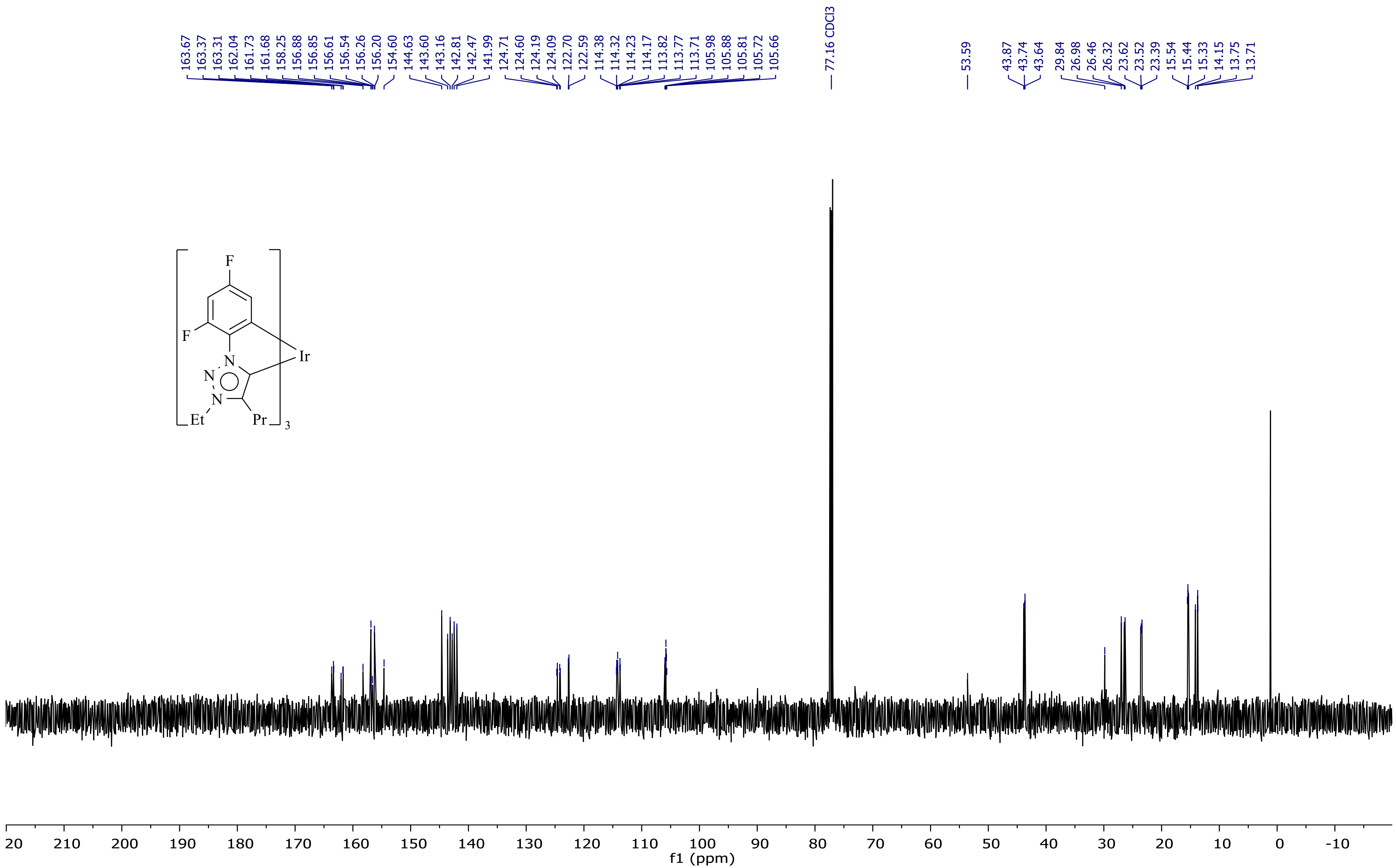

Figure S28. ^{13}**C NMR (151 MHz, Chloroform-d) of iridium complex 4b**

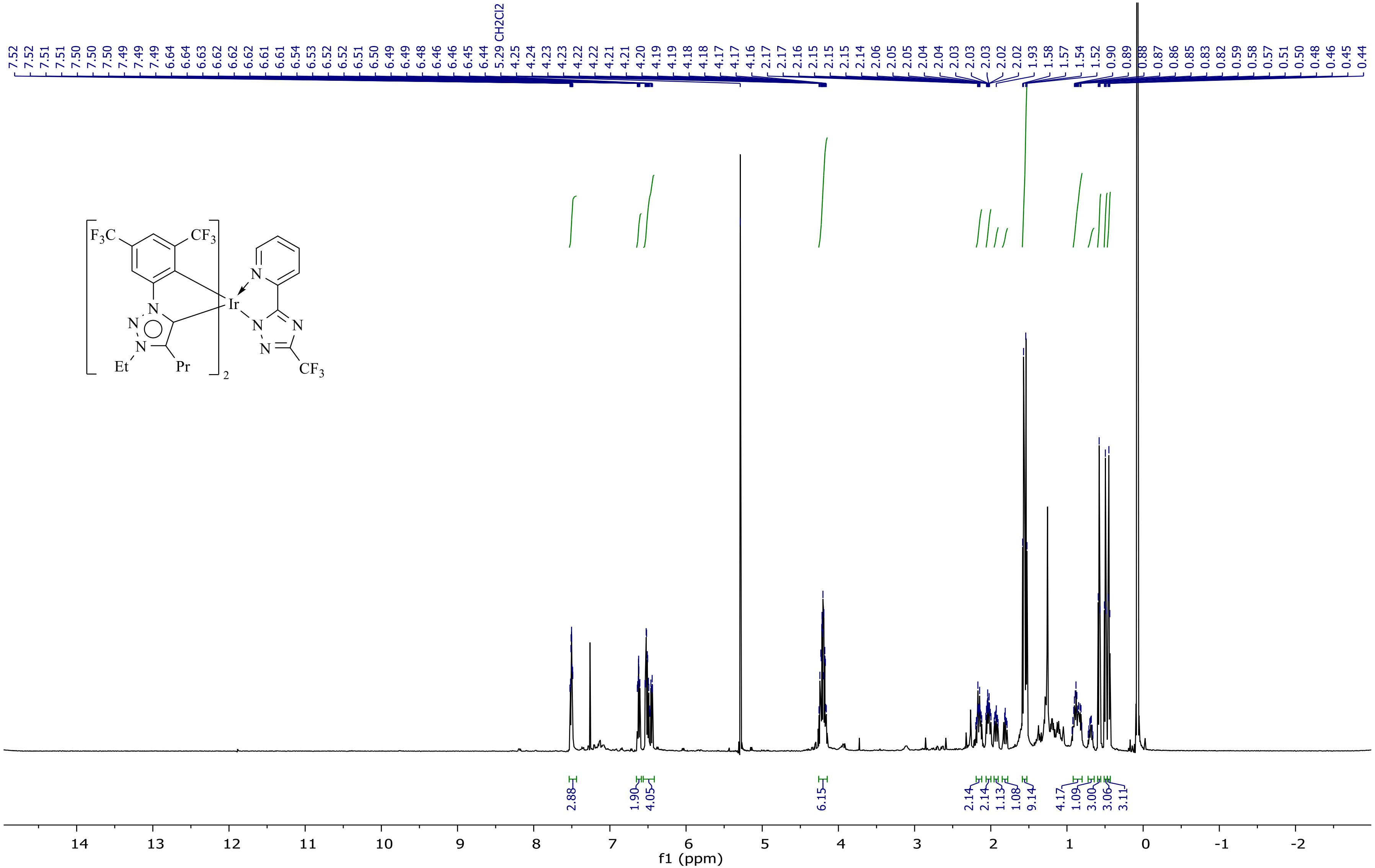

Figure S29. ^{1}H NMR (600 MHz, Chloroform-*d*) of iridium complex 3c

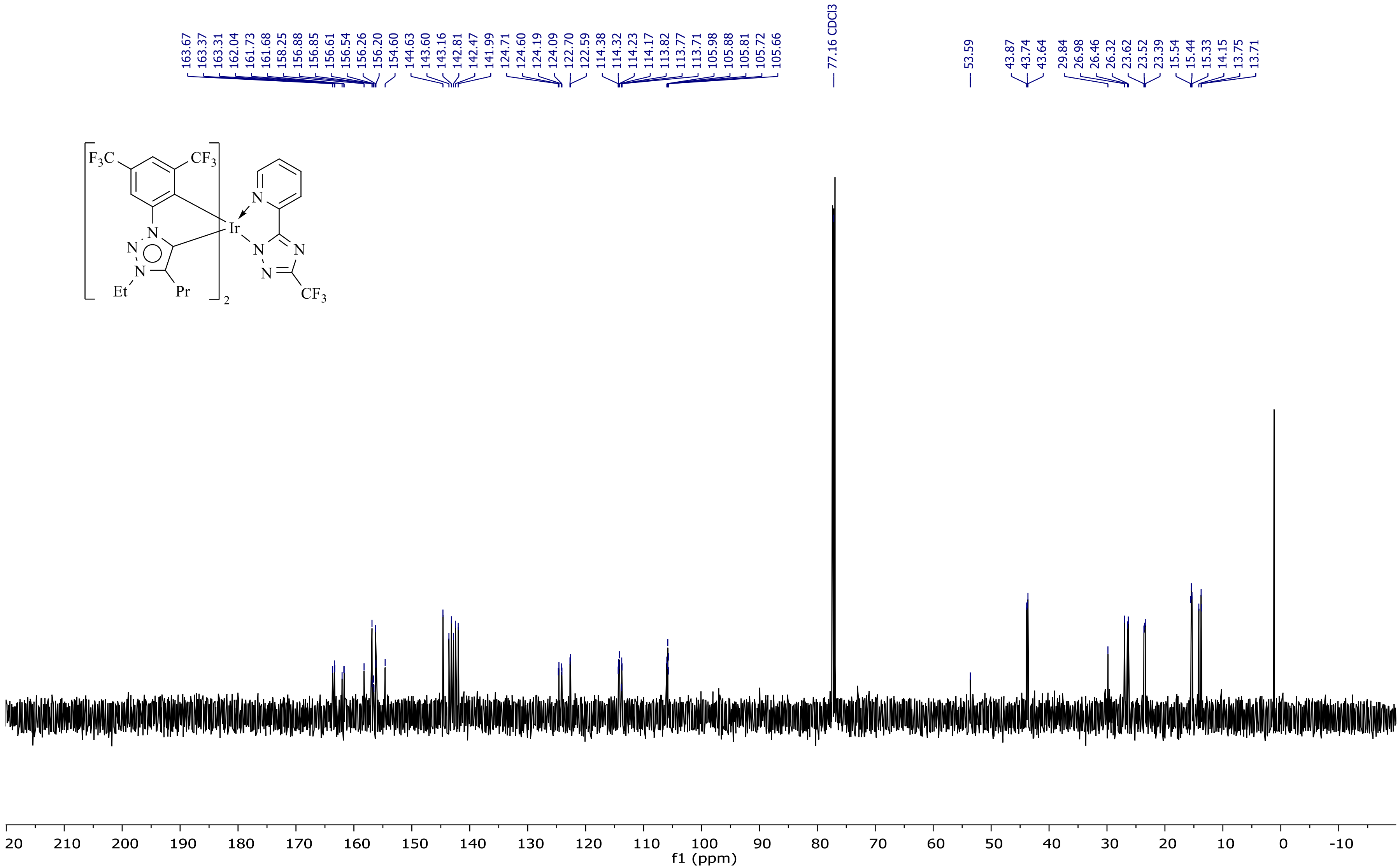

Figure S30. ^{13}C NMR (151 MHz, Chloroform-d) of iridium complex 3c

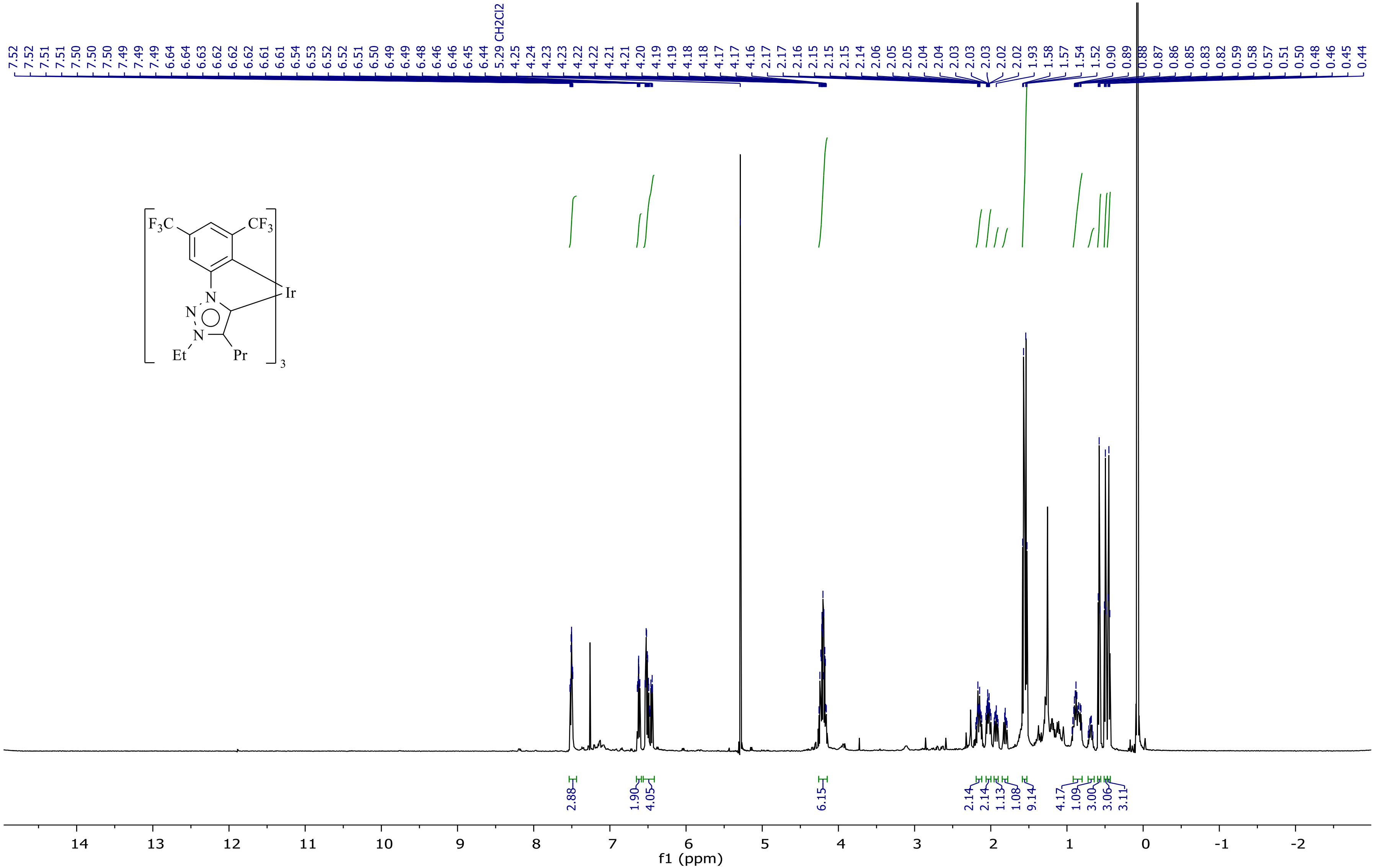

Figure S31. ^{1}H NMR (600 MHz, Chloroform-*d*) of iridium complex 4c

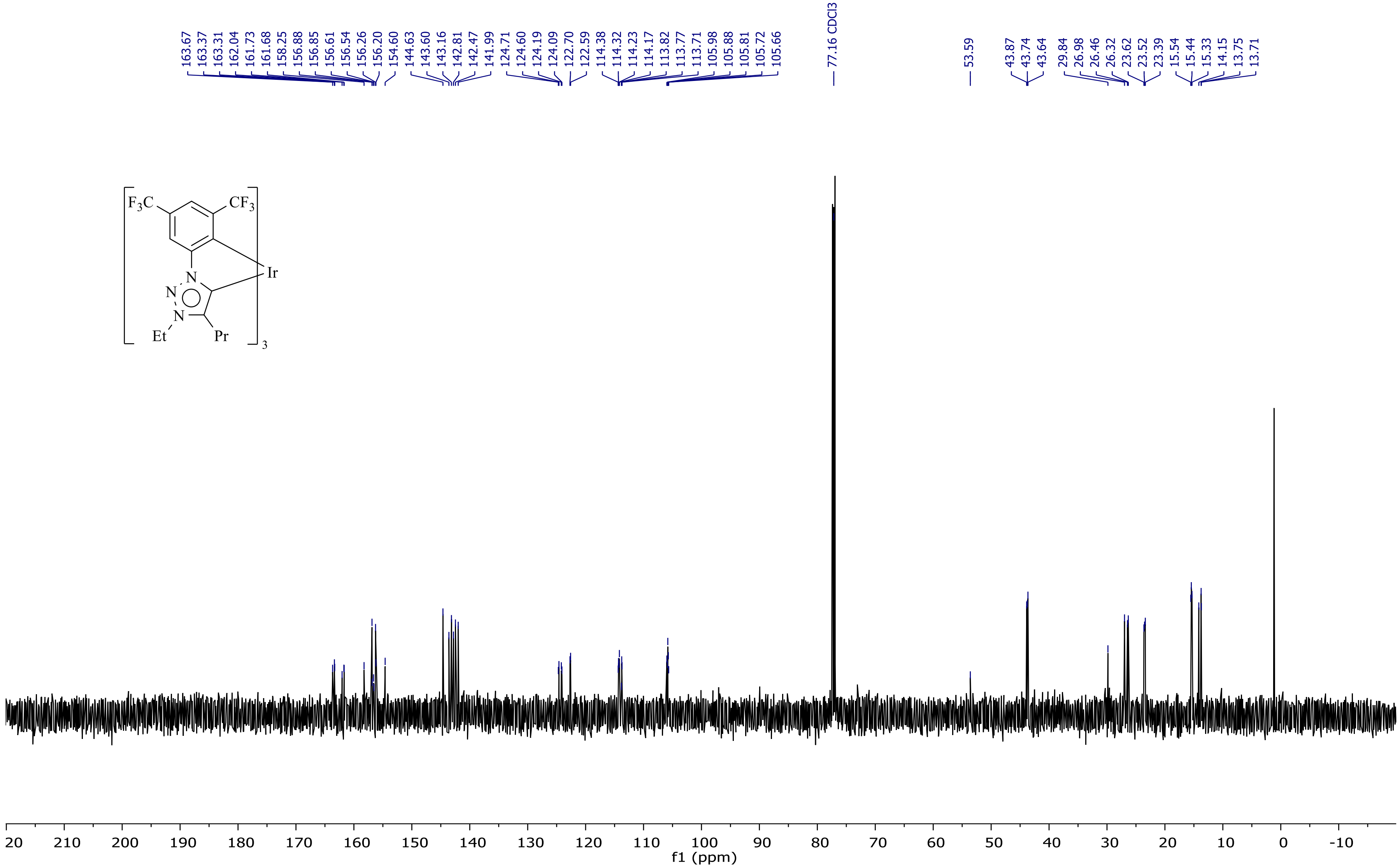

Figure S32. ^{13}C NMR (151 MHz, Chloroform-d) of iridium complex 4c

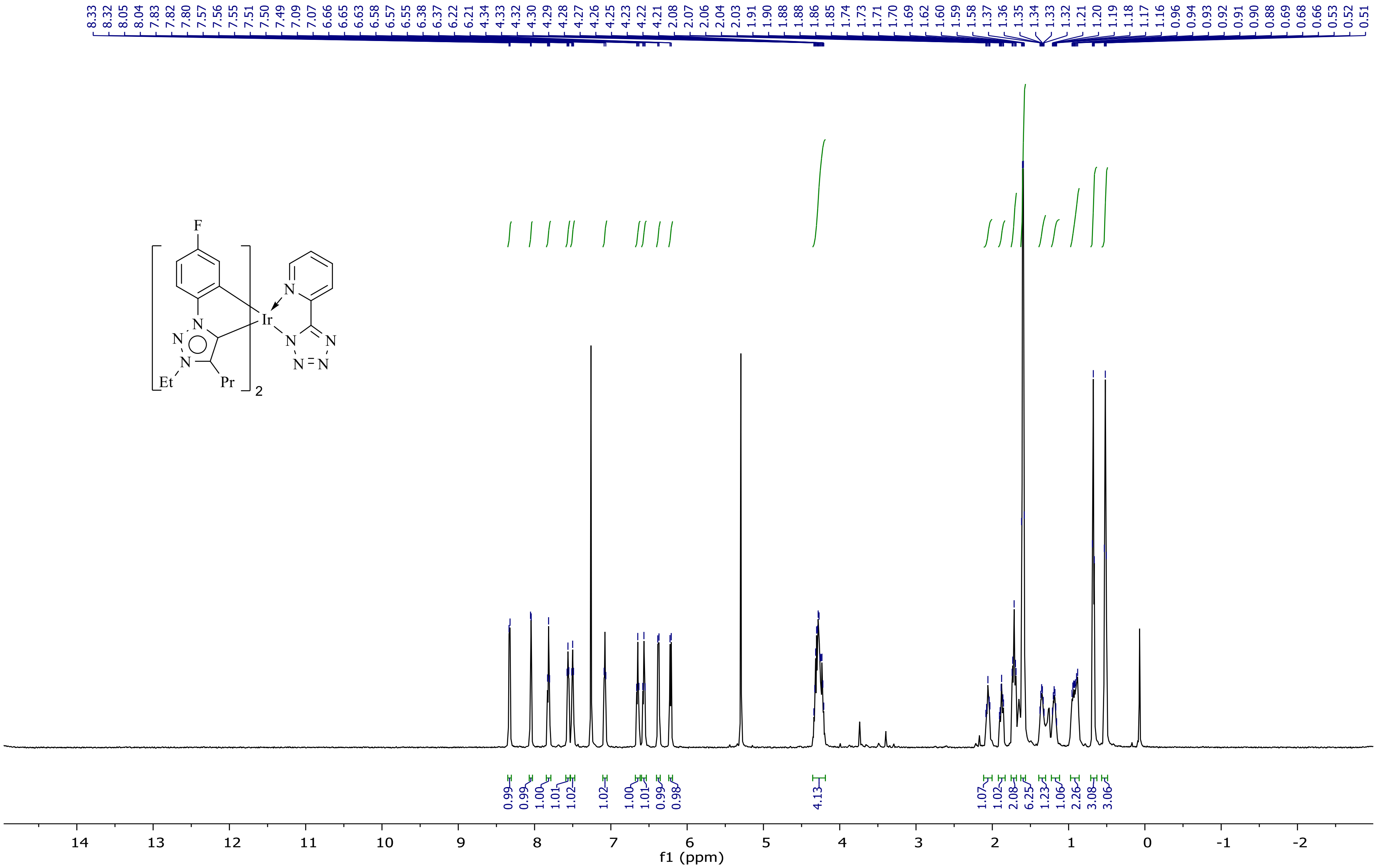

Figure S33. ¹H NMR (600 MHz, Chloroform-*d*) of iridium complex 5a

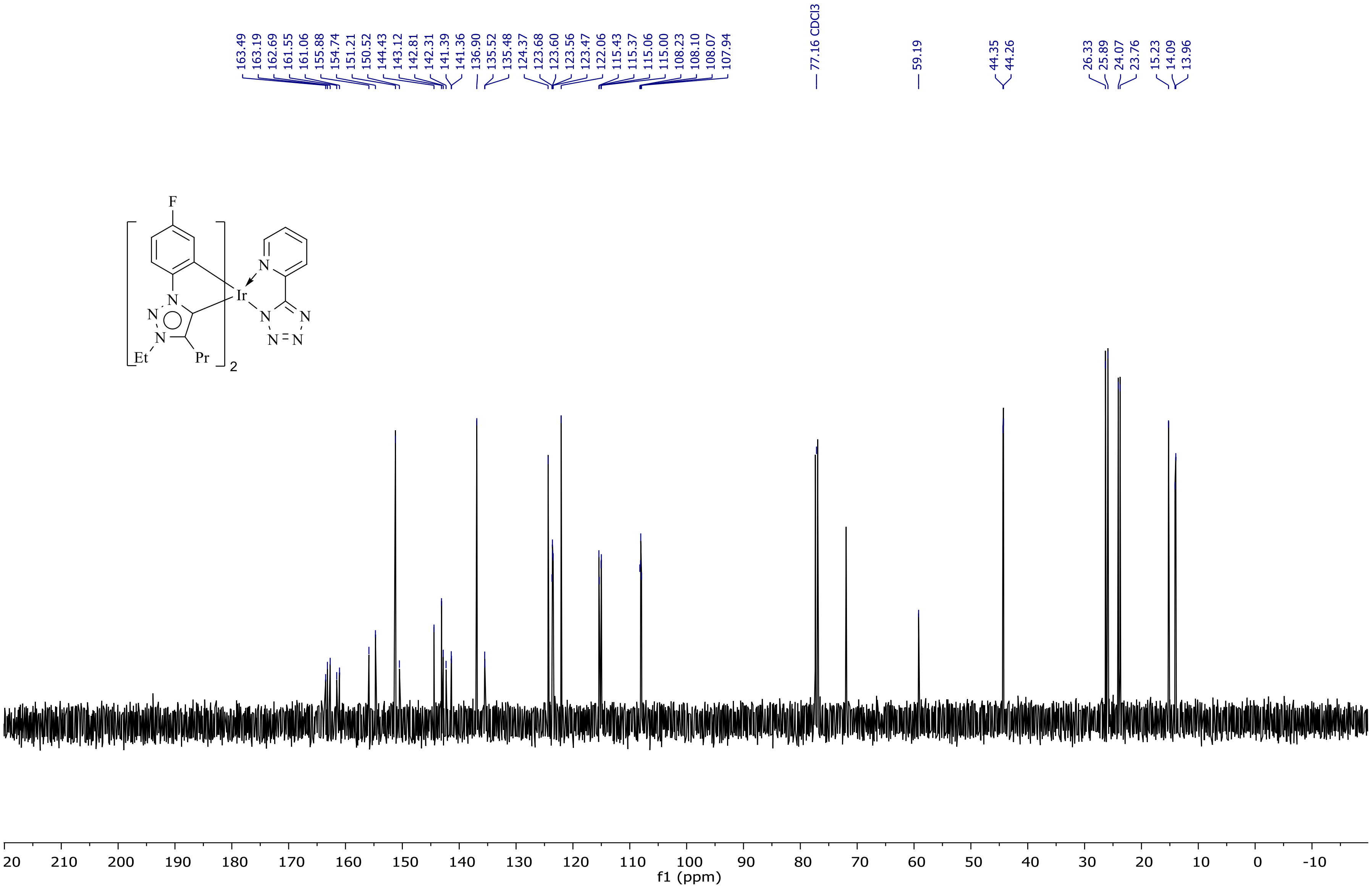

Figure S34. ^{13}C NMR (151 MHz, Chloroform-d) of iridium complex 5a

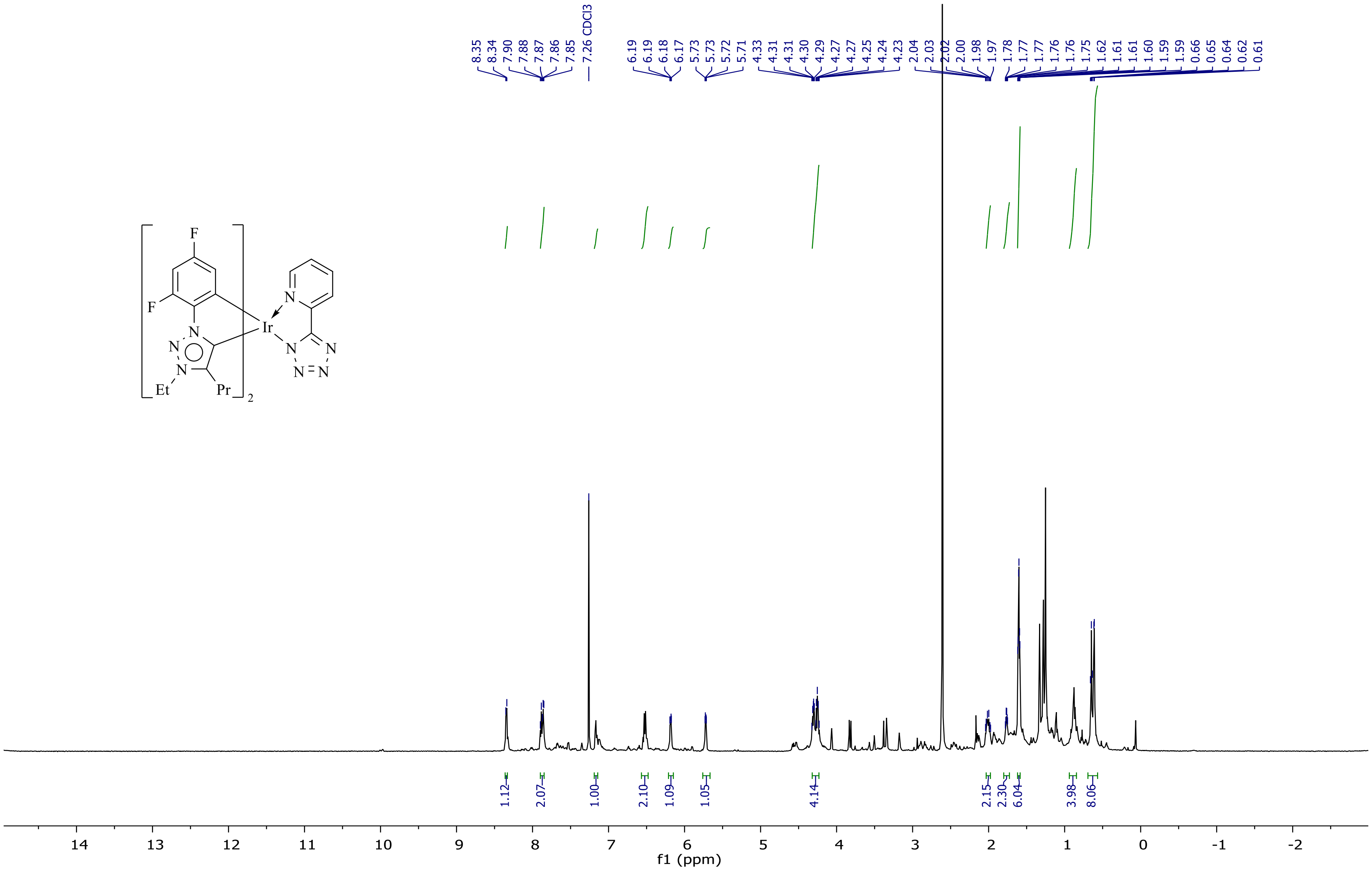

Figure S35. ^{1}H NMR (600 MHz, Chloroform-*d*) of iridium complex 5b

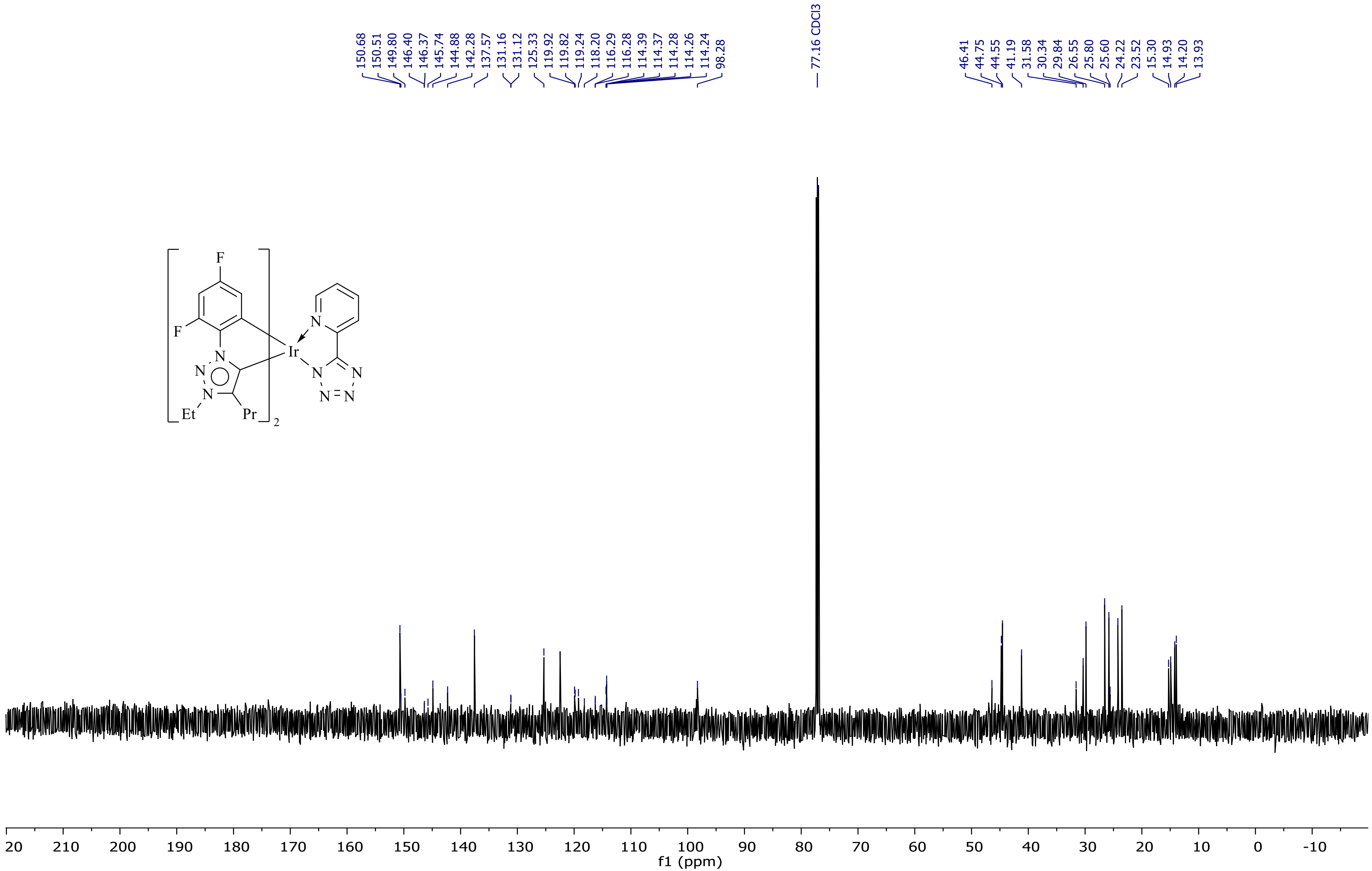

Figure S36. 13C NMR (151 MHz, Chloroform-d) of iridium complex 5b

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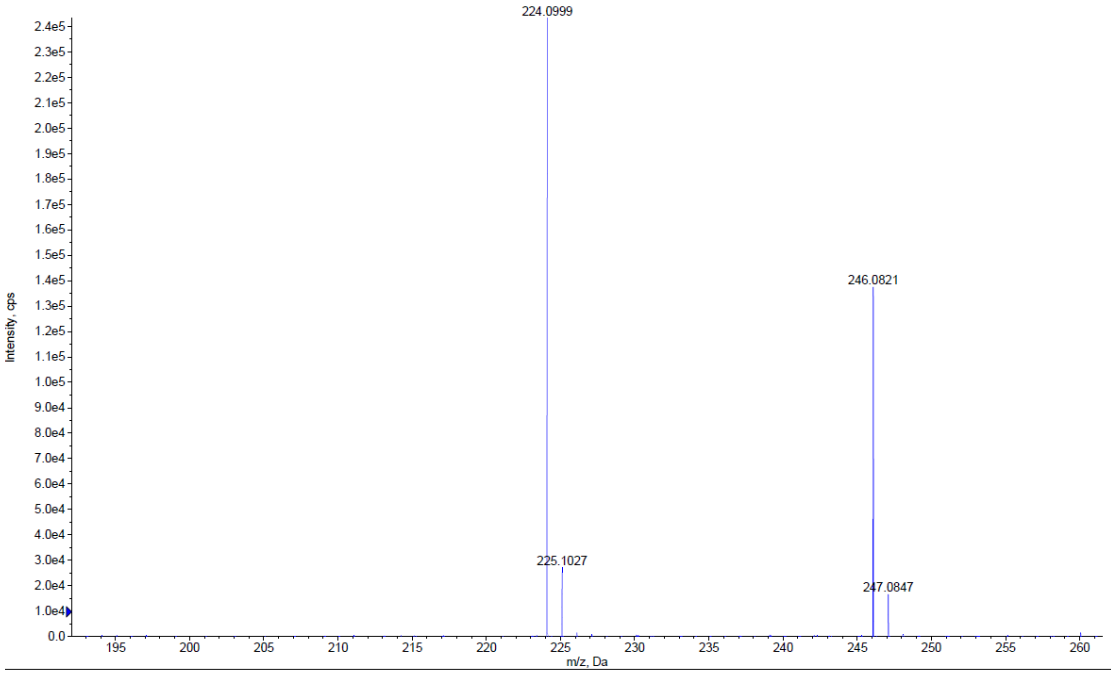

Figure S37. HRMS of 1-(2,4-difluorophenyl)-4-propyl-1*H*-1,2,3-triazole

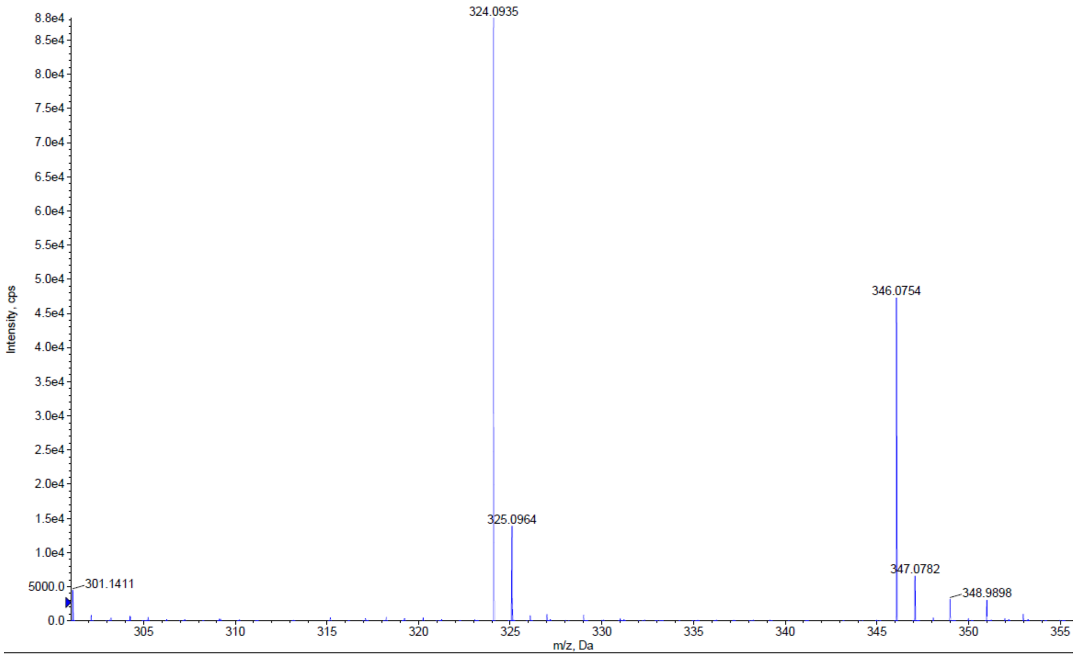

Figure S38. HRMS of 1-[3,5-bis(trifluoromethyl)phenyl]-4-propyl-1*H*-1,2,3-triazole

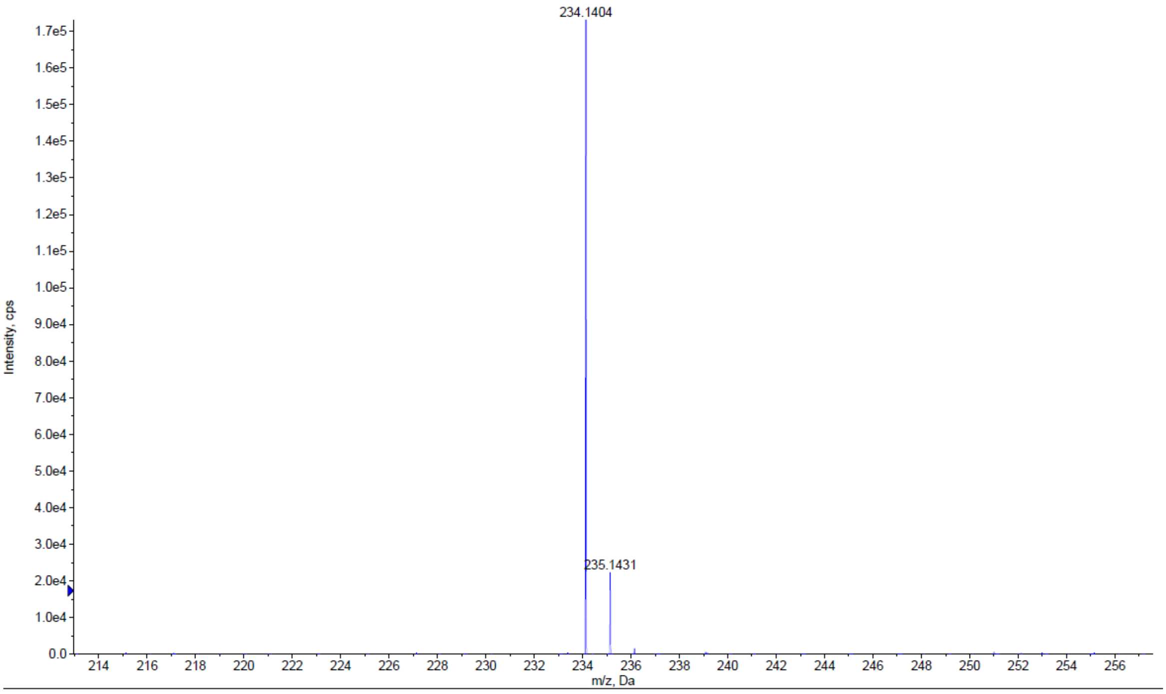

Figure S39. HRMS of 1-(4-fluorophenyl)-3-ethyl-4-propyl-1*H*-1,2,3-triazolium tetrafluoroborate (1a)

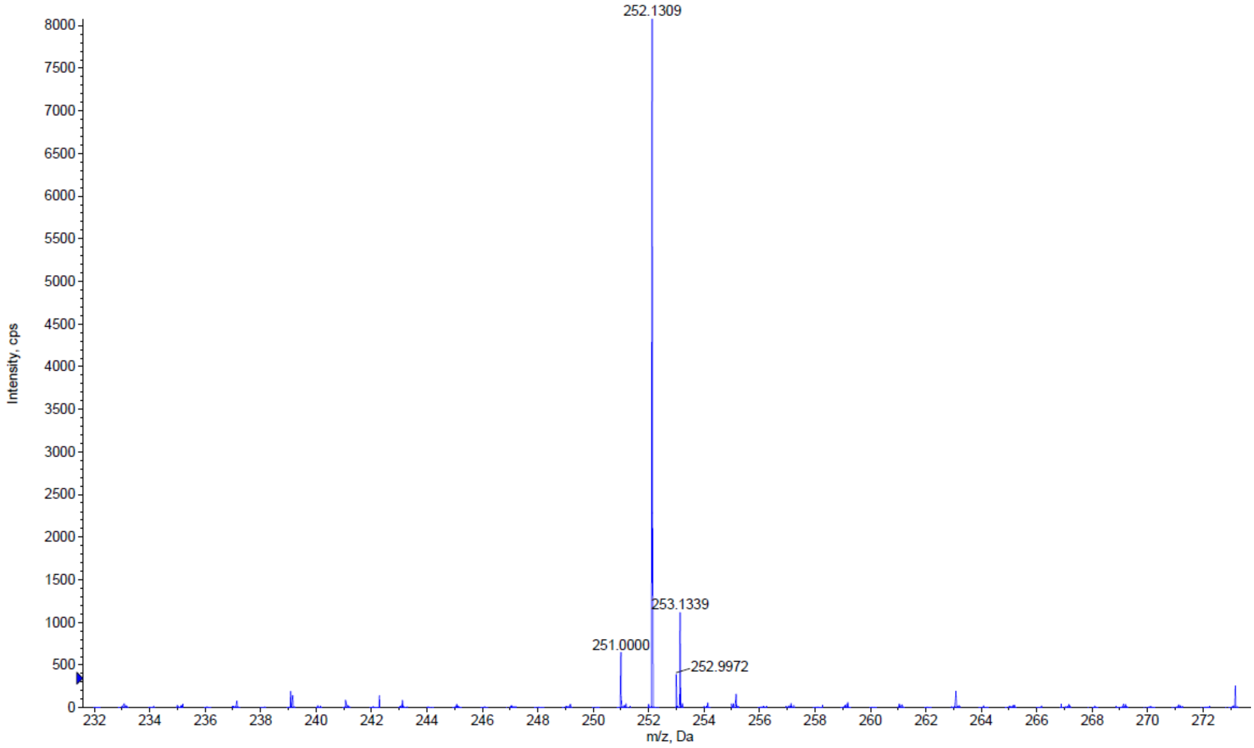

Figure S40. HRMS of 1-(2,4-difluorophenyl)-3-ethyl-4-propyl-1*H*-1,2,3-triazolium tetrafluoroborate (1b)

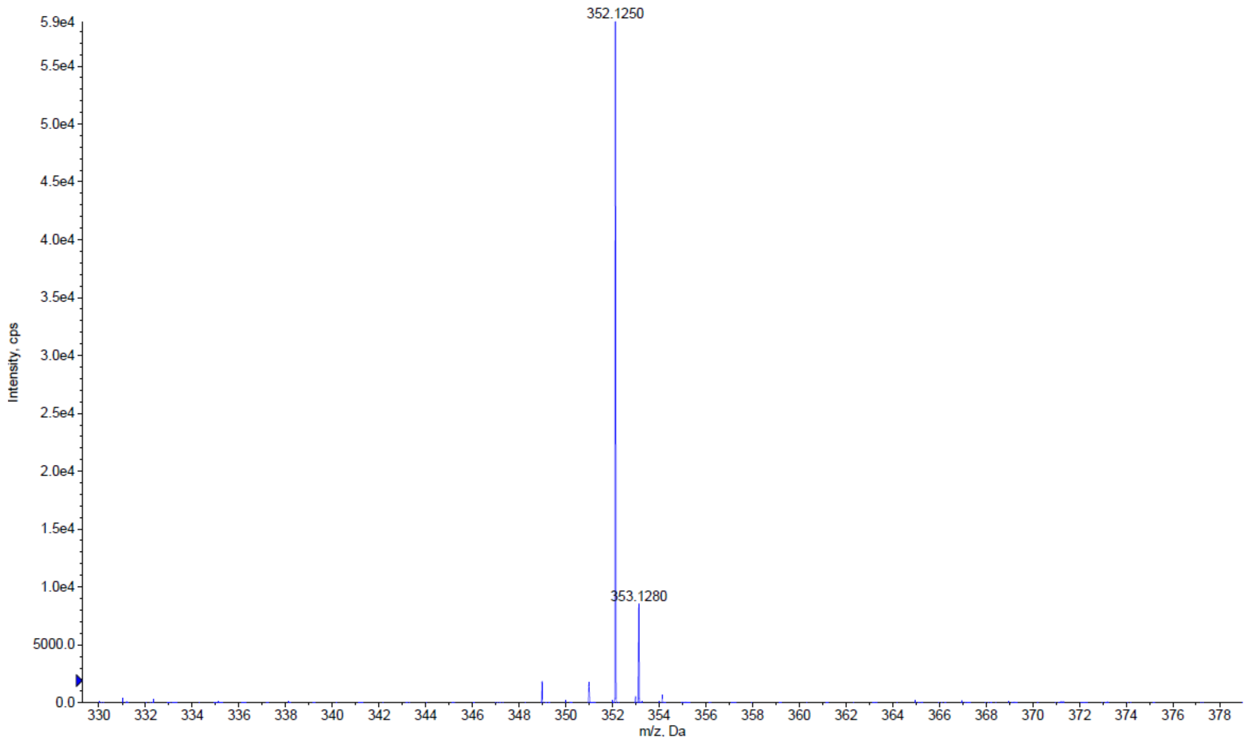

Figure S41. HRMS of 1-[3,5-bis(trifluoromethyl)phenyl]-3-ethyl-4-propyl-1*H*-1,2,3-triazolium tetrafluoroborate (1c)

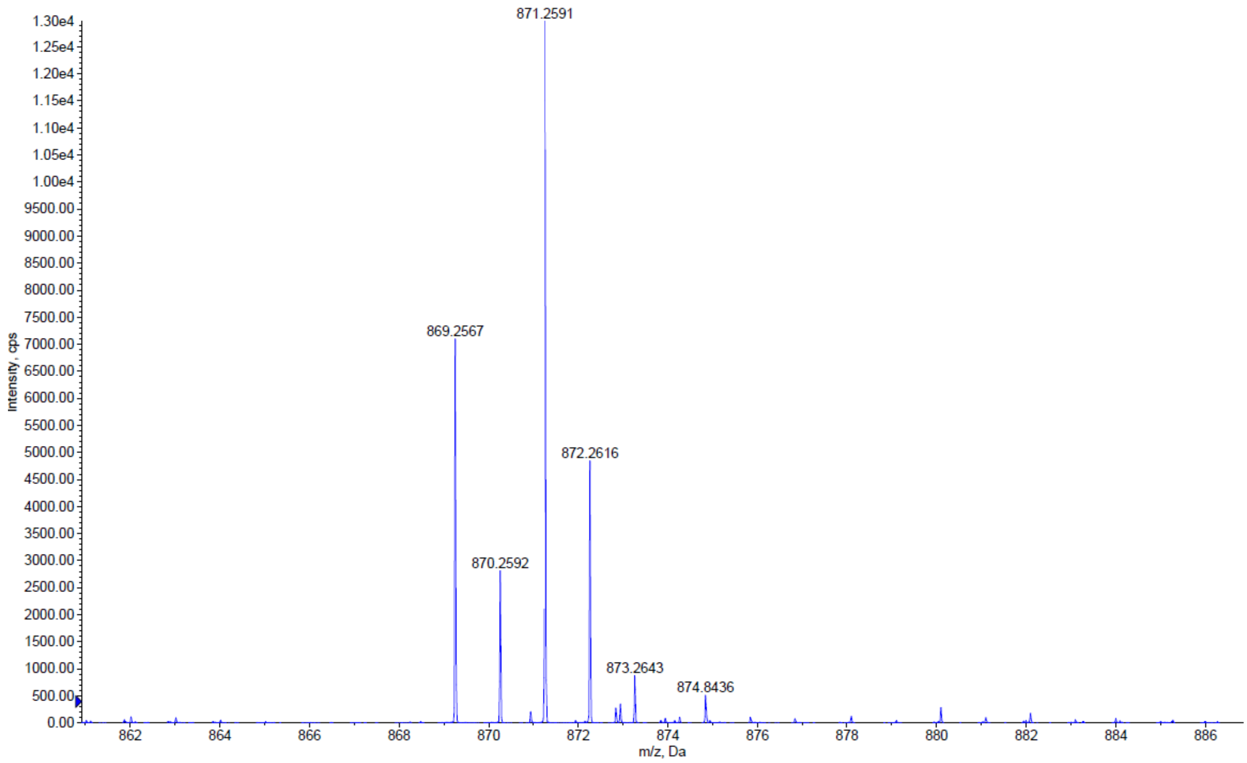

Figure S42. HRMS of complex 3a

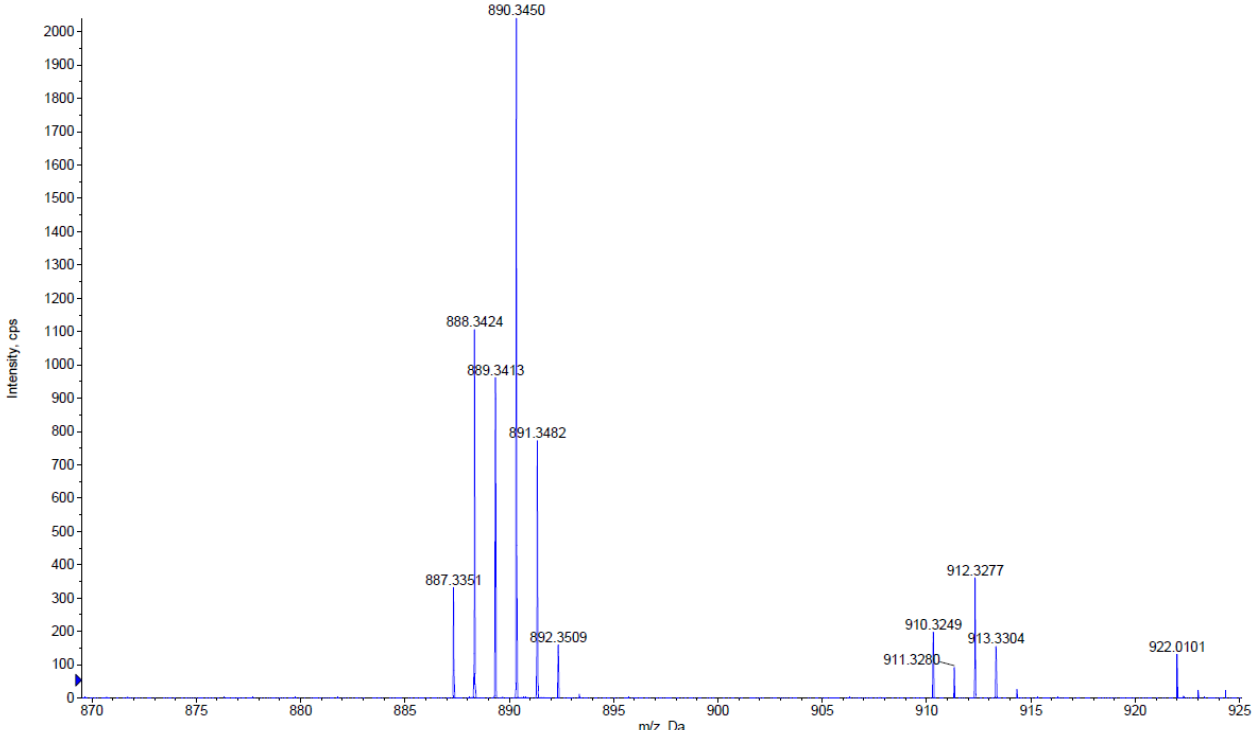

Figure S43. HRMS of complex 4a

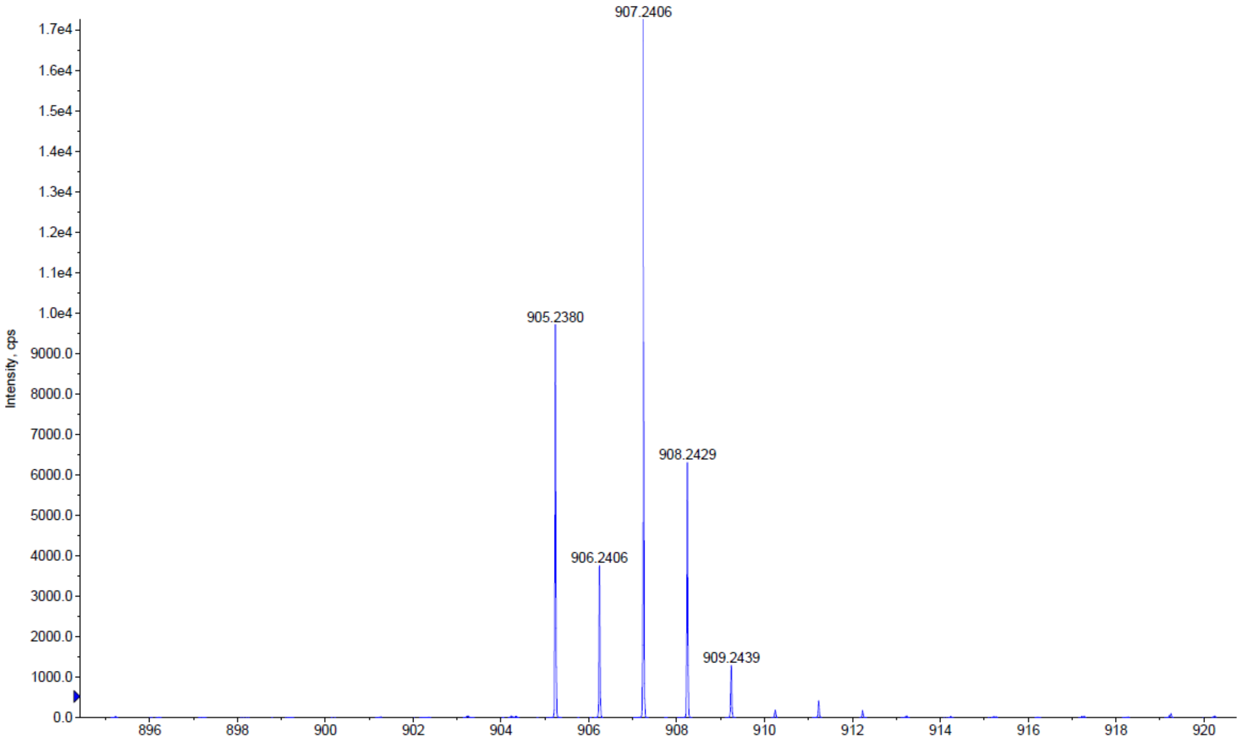

Figure S44. HRMS of complex 3b

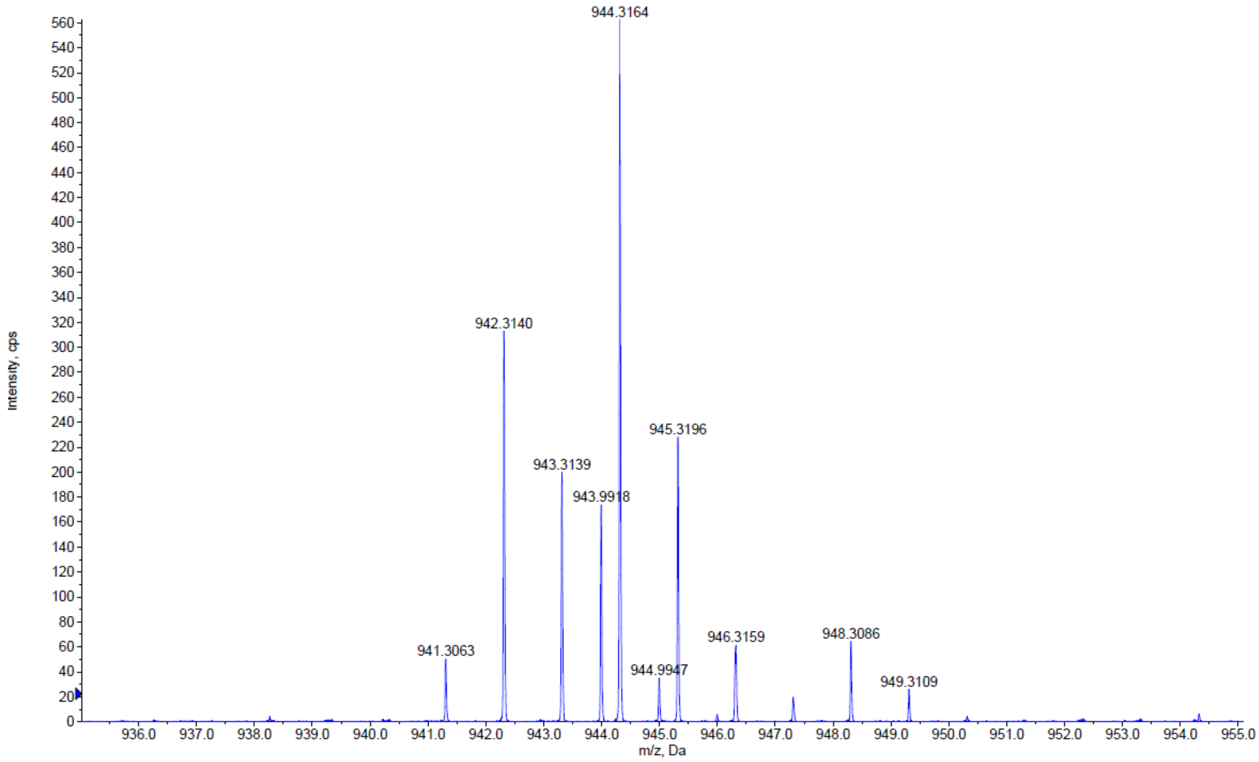

Figure S45. HRMS of complex 4b

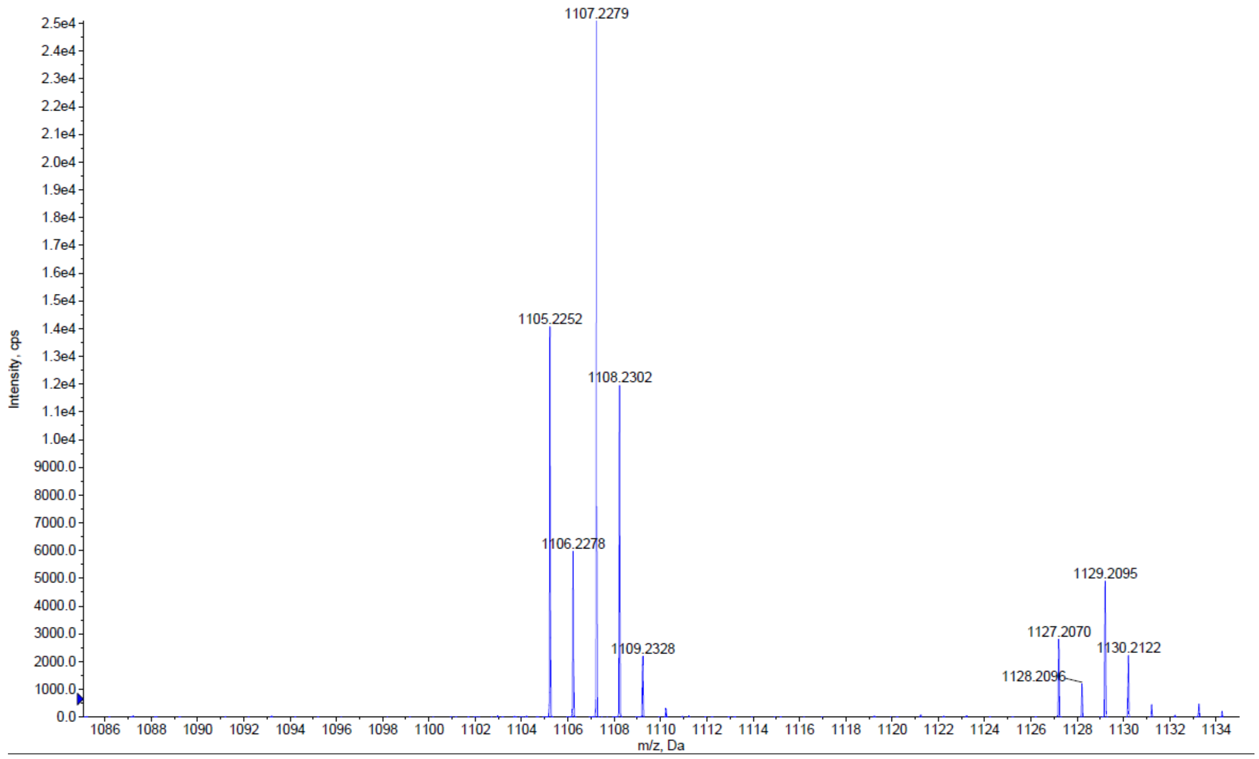

Figure S46. HRMS of complex 3c

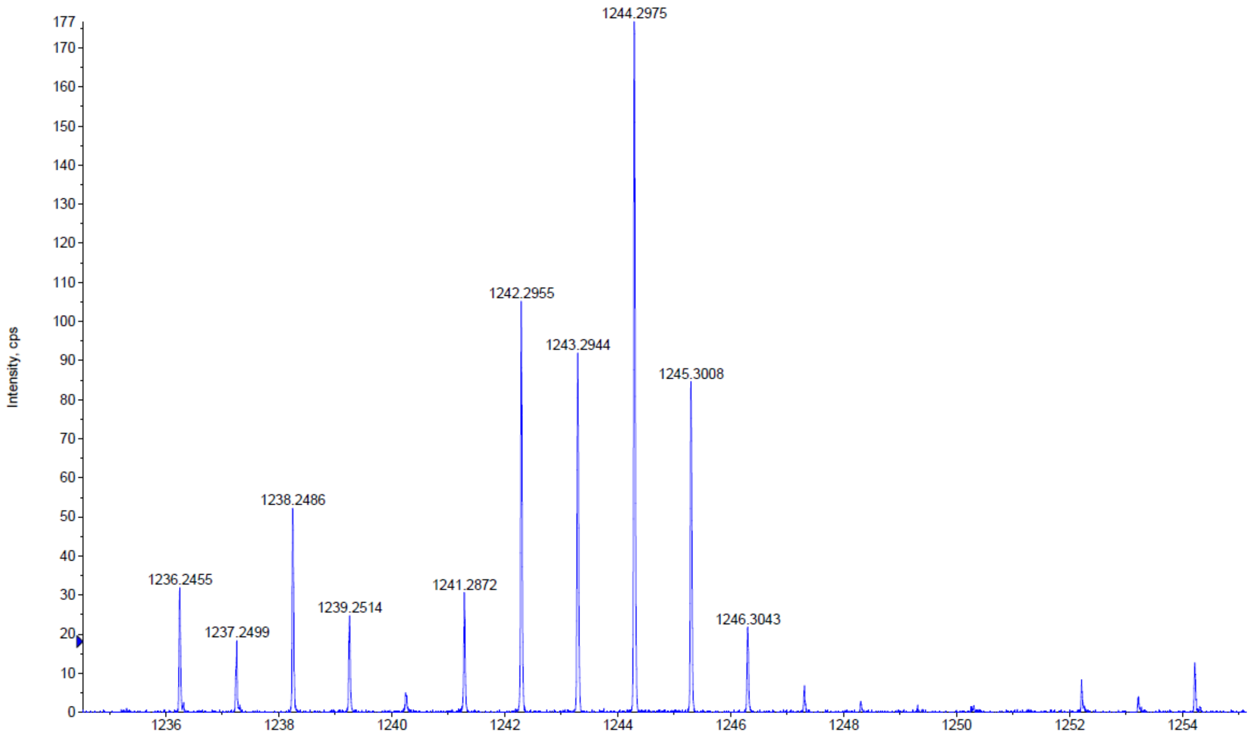

Figure S47. HRMS of complex 4c

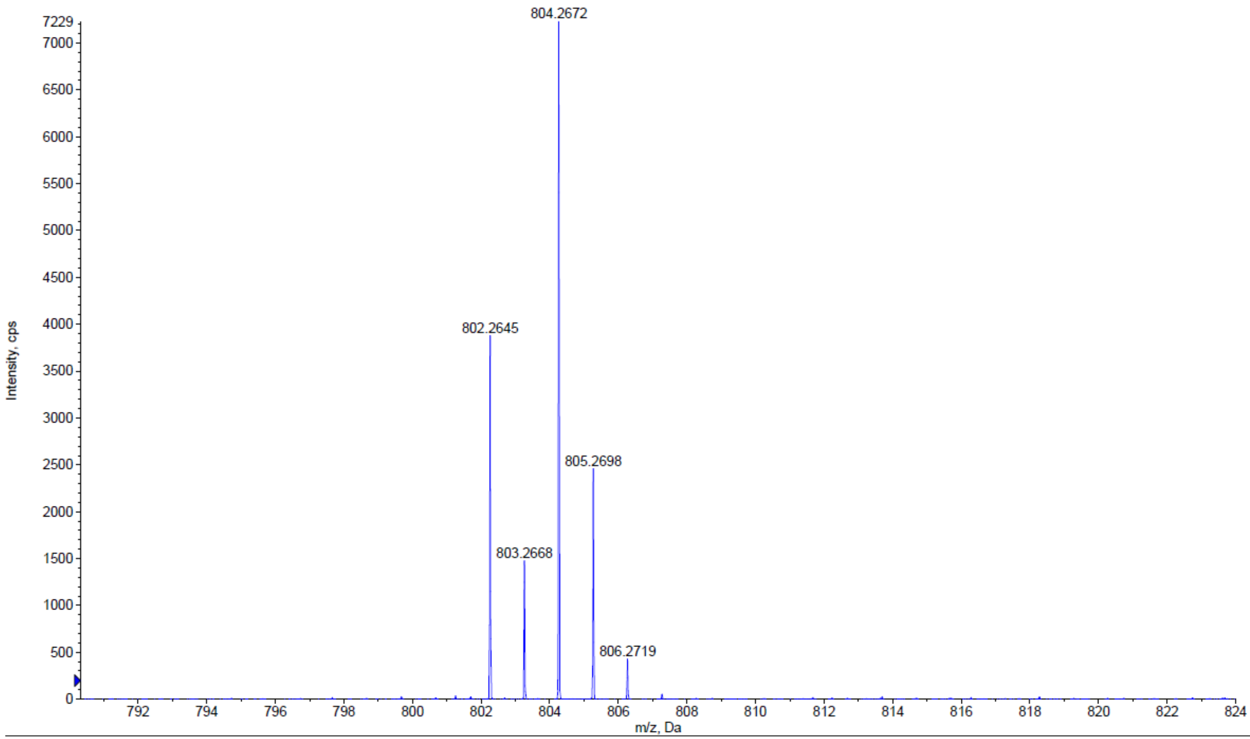

Figure S48. HRMS of complex 5a

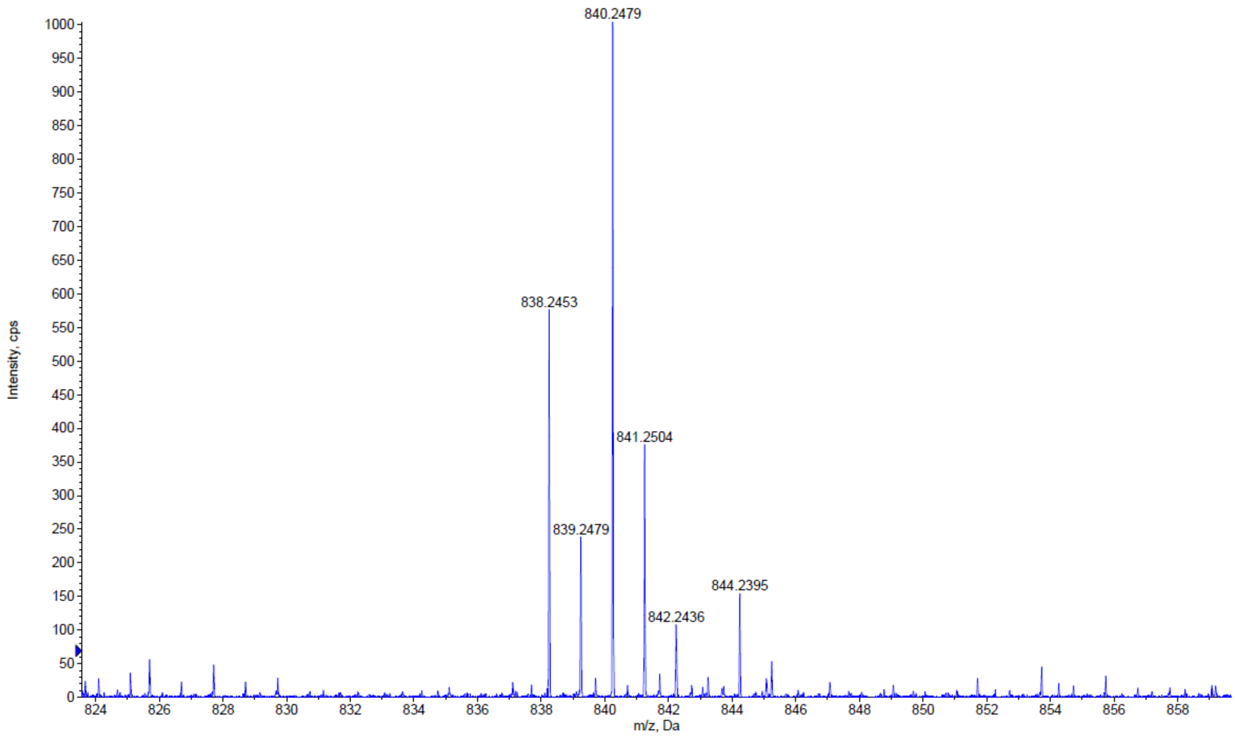

Figure S49. HRMS of complex 5b