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Cyclometallated 1,2,3-triazol-5-ylidene iridium(III) complexes: synthesis, structure, and photoluminescence properties

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Experimental part

General information

All reactions were carried out under argon atmosphere, and 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 according to the known procedure.[S1] Dichloromethane, 1,2-dichloroethane, and DMSO were distilled over CaH_2; *o*-xylene was distilled over sodium.

NMR spectra were recorded on a Bruker Avance 600 instrument (600 MHz ^{1}H, 151 MHz ^{13}C). Chemical shifts (δ) in ppm are reported using the residual undeuterated (^{1}H NMR) or deuterated solvent peaks (^{13}C NMR) as the internal standards.[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.

DFT calculations

All calculations were conducted at the DFT level using the PBE functional.[S3–5] Valence electrons were treated using a TZ2P basis set. Innermost electrons of Ir, F, C, N and O atoms were emulated using effective core potentials ECP-SBKJC.[S6–8] Stationary points were characterized as minima by calculations of normal modes of vibrations. All calculations were performed using the PRIRODA software.[S9,10]

PL (Photoluminescence spectra)

PL spectra were recorded 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 the standard (excitation wavelength of 360 nm, Φ_{PL} = 73 %, λ_{max} = 451 nm).[S11,12]

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. Under the same experimental conditions (*e.g.*, optical density, concentration, temperature, solvent, cuvettes, *etc.*) 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 one's: $S_1/S_2 = \Phi_1/\Phi_2$. 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 one's)

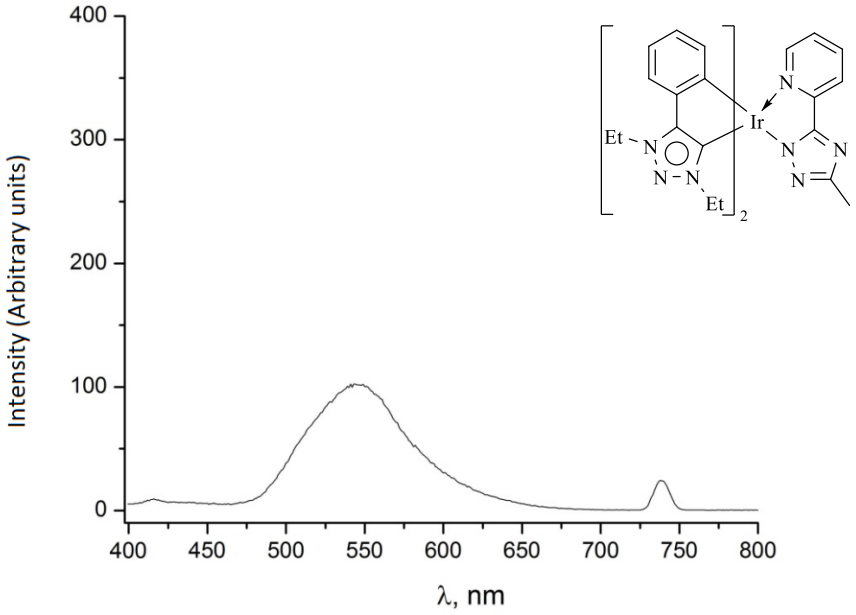


Figure S1 Photoluminescence spectrum of compound **4** (λ_{max} = 550 nm, Φ_{PL} = 3.1 %).

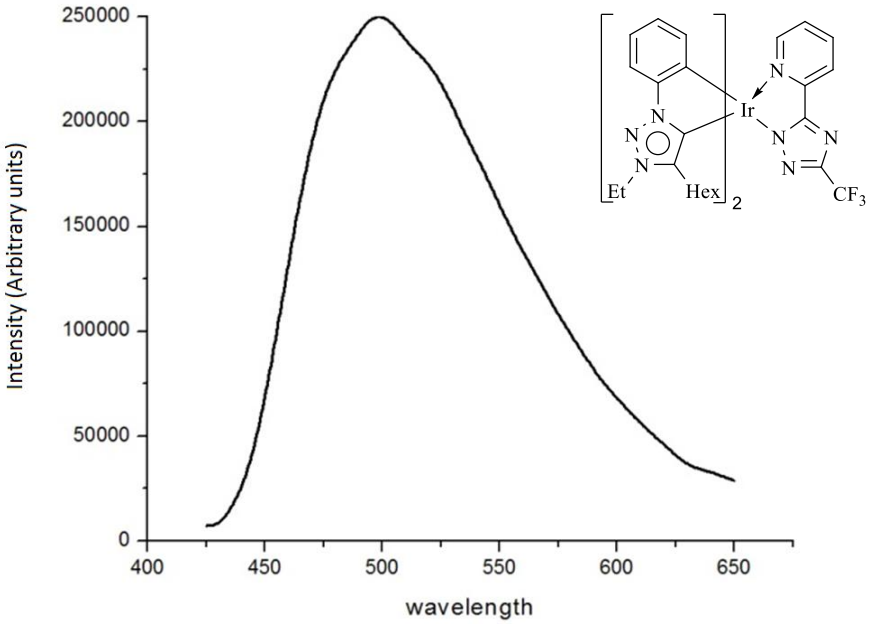


Figure S2 Photoluminescence spectrum of **6** (λ_{max} = 499 nm, Φ_{PL} = 13.3 %).

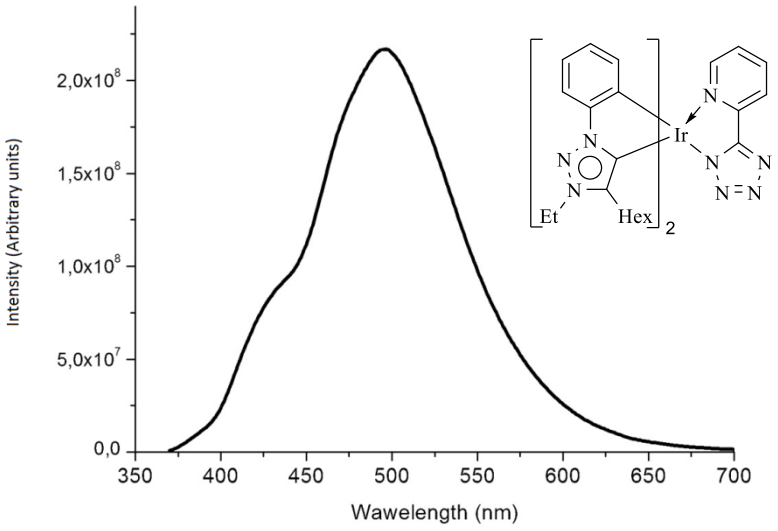


Figure S3 Photoluminescence spectrum of **7** (λ_{max} = 496 nm, Φ_{PL} = 28.0 %).

X-ray crystal structure determination.

Data were collected using a Bruker APEX-II CCD diffractometer (λ(MoK$_\alpha$)-radiation, graphite monochromator, ω and φ scanning mode) and corrected for absorption using the *SADABS* program.[S13] The details are given in Table S1. The crystal structures of **4** and **6** were solved by direct methods and refined by a full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The crystal of **4** contained a solvate chloroform molecule. The trifluoromethyl and two *n*-hexyl substituents in the molecule of **6** were disordered over two sites each with the occupancies of 0.5 : 0.5, 0.5 : 0.5, and 0.6 : 04, respectively. The hydrogen atoms in both compounds were placed in calculated positions and included in the refinement within the riding model with fixed isotropic displacement parameters (U_{iso}(H) = 1.5U_{eq}(C) for the CH_3-groups and 1.2U_{eq}(C) for the other groups). All calculations were carried out using the *SHELXTL* program.[S14] Crystallographic data for **4 • CHCl$_3$** and **6** have been deposited with the Cambridge Crystallographic Data Center. CCDC 1861632 and CCDC 1861633 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

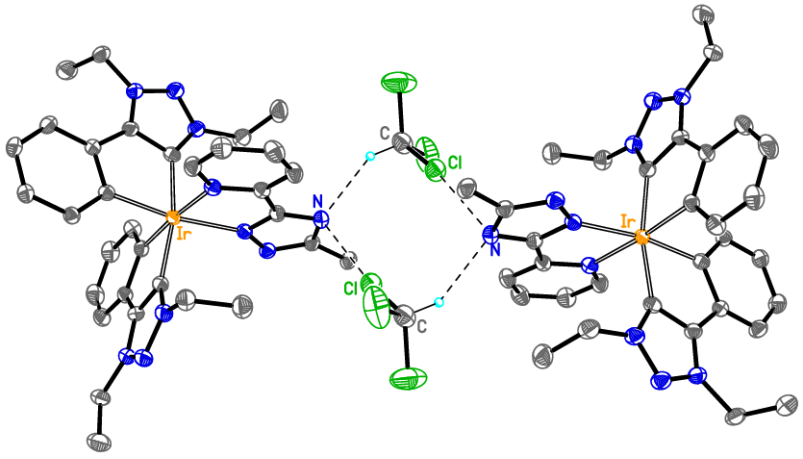


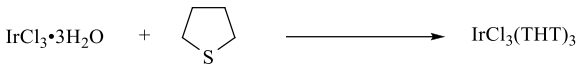
Figure S4 The centrosymmetric dimeric complex [**4 • CHCl$_3$**]$_2$. Dashed lines indicate the C─H…N hydrogen bonds and non-valent N…Cl interactions.

Table S1 Crystallographic data for **4 • CHCl$_3$** and **6**.

compound	**4 • CHCl$_3$**	**6**
empirical formula	$C_{33}H_{36}N_{10}Cl_3Ir$	$C_{40}H_{48}N_{10}F_3Ir$
fw	871.29	918.10
T, K	100(2)	100(2)
crystal size, mm	0.06×0.24×0.30	0.12×0.12×0.15
crystal system	triclinic	monoclinic
space group	*P*-1	*C*2/c
a, Å	9.4486(5)	38.125(2)
b, Å	10.4030(5)	9.4410(6)
c, Å	18.0132(9)	25.3081(16)
α, deg.	95.182(1)	90
β, deg.	90.063(1)	122.880(1)
γ, deg.	103.991(1)	90
V, Å^3	1710.56(15)	7650.1(8)
Z	2	8
d_c, g cm^{-3}	1.692	1.594
F(000)	864	3696
μ, mm^{-1}	4.178	3.549
θ_{max}, deg.	32.80	32.78
index range	-14 < = h < = 14 -15 < = k < = 15 -27 < = l < = 27	-58 < = h < = 57 -14 < = k < = 14 -38 < = l < = 38
no. of rflns collected	26581	57267
no. of unique rflns, R_{int}	12534, 0.0242	14114. 0.0651
no. of rflns with $I > 2\sigma(I)$	11643	8973
data/restraints/parameters	12534 / 0 / 430	14114 / 37 / 478
R_1; wR_2 ($I > 2\sigma(I)$)	0.0320; 0.0802	0.0511; 0.1145
R_1; wR_2 (all data)	0.0352; 0.0819	0.0934; 0.1368
GOF on F^2	1.050	1.003
T_{min}; T_{max}	0.300; 0.777	0.590; 0.642

Preparation of supporting ligands and starting materials

Trichlorotris(tetrahydrothiophene)iridium(III) ($IrCl_3(THT)_3$)

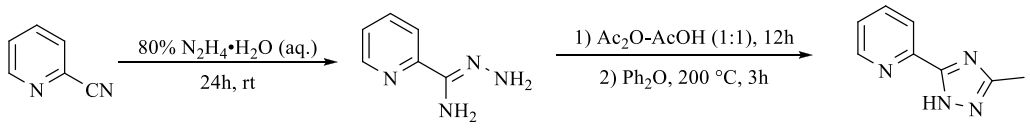


The title compound was synthesized with a minor modification of a literature procedure.[S15] A 500 ml round-bottomed flask, equipped with a reflux condenser and a magnetic stir bar, was charged with $IrCl_3 \cdot 3H_2O$ (4.0 g, 11.34 mmol) and freshly distilled 2-methoxyethanol (200 ml). Tetrahydrothiophene (5.0 ml, 5.0 g, 56.7 mmol) was added to the resulting suspension. The reaction mixture was refluxed for 12h, cooled to room temperature, and evaporated *in vacuo* to a half of volume. The reaction mixture was diluted with deionized water (300 ml) and filtered. The yellow precipitate was washed with water, dried, dissolved in a minimal amount of dichloromethane, and filtered through a Celite® pad to remove any insoluble material. Evaporation of the filtrate afforded $IrCl_3(THT)_3$ (5.69 g, 89%) as a yellow microcrystalline solid.

^{1}H NMR (600 MHz, $CDCl_3$), δ: 3.70–3.57 (m, 2H), 3.27–3.16 (m, 1H), 2.96–2.80 (m, 3H), 2.39–2.27 (m, 2H), 2.21 (m, 1H), 2.17–1.99 (m, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$), δ: 36.7 , 36.5 , 30.4 , 30.3.

2-(3-methyl-1H-1,2,4-triazol-5-yl)pyridine (mptz)



The title compound was synthesized with a minor modification of the known procedure.[S16] A mixture of 2-pyridinecarbonitrile (104 g, 1 mol, 1 equiv.), aqueous (80 %) hydrazine monohydrate (62.5 g, 1 mol, 1 equiv.) and ethanol (40 ml) was allowed staying overnight. The colorless crystals of (pyridine-2-yl)amidrazone were filtered off, washed with minimal amount of cold diethyl ether, and air dried to give (pyridine-2-yl)amidrazone (77.7 g, 57 %) as a white solid.

A mixture of glacial acetic acid and acetic anhydride (1 : 1, 300 ml) was cooled to 0 °C followed by addition of (pyridine-2-yl)amidrazone (35 g). The reaction mixture was slowly warmed to room temperature and stirred overnight. The solution was then concentrated *in vacuo*,

and the resulting oil heated at 130 °C for 3h. TLC (CH_2Cl_2-acetone 5 : 1) showed only partial conversion to product, the solid was dissolved in melted diphenyl ether (400 ml) and the mixture was stirred at 200 °C for 3h. Then the solution was diluted with hexane (500 ml) and then extracted with concentrated hydrochloric acid (3×50 ml). Acidic aqueous layer was collected, evaporated to dryness, and neutralized with saturated solution of sodium hydrogencarbonate. Extraction of the solution with dichloromethate (4×50 ml) followed by flash chromatography purification (eluent CH_2Cl_2, then CH_2Cl_2 : triethylamine = 100 : 1) afforded pure 2-(3-methyl-2*H*-1,2,4-triazol-5-yl)pyridine (11.7g, 41%) as off-white solid.

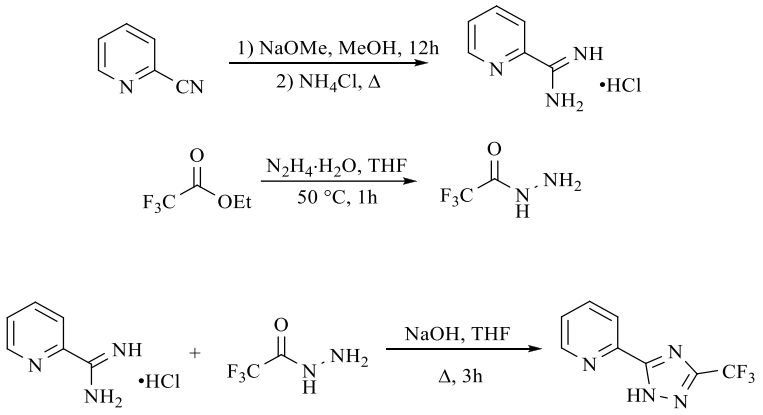
m.p. 164–165 °C (Lit. data[S17]: m.p. 163–165 °C)

^{1}H NMR (600 MHz, $CDCl_3$), δ: 13.56 (s, 1H), 8.73 (s, 1H), 8.19 (d, *J* 7.7 Hz, 1H), 7.81 (t, *J* 7.0 Hz, 1H), 7.38–7.30 (m, 1H), 2.52 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$), δ: 159.6, 156.2, 149.5, 147.3, 137.7, 124.7, 121.9, 13.5.

The NMR data are in agreement with those reported previously.[S16]

2-(3-(trifluoromethyl)-1H-1,2,4-triazol-5-yl)pyridine (tfmptz)



The title compound was synthesized according to the known procedure.[S18] A solution of 2-pyridinecarbonitrile (5.2 g, 50 mmol, 1 equiv.) and sodium methoxide (0.27 g, 5 mmol, 0.1 equiv.) in methanol (100 ml) was stirred at room temperature for 12h followed by the addition of ammonium chloride (2.68 g, 50 mmol, 1 equiv.). The reaction mixture was refluxed for 6h, and then cooled to room temperature. Addition of diethyl ether and filtration of precipitate afforded crude pyridine-2-carboximidamide hydrochloride that was used without further purification.

A solution of ethyl trifluoroacetate (7.1 g, 50 mmol) and hydrazine monohydrate (2.76 g, 55 mmol, 1.1 equiv.) in THF (35 ml) was refluxed for 1 h and then stirred at room temperature

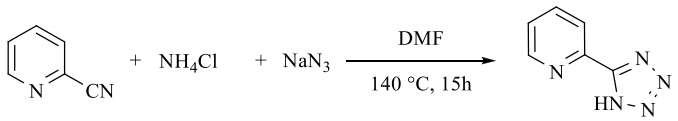
for 12h under Ar. Crude pyridine-2-carboximidamide hydrochloride and powdered NaOH (2.0 g) were added to the reaction mixture, and this mixture was refluxed for 12h. The mixture was cooled to room temperature and evaporated to dryness. The solid residue was dissolved in ethyl acetate–water mixture. The water layer was extracted with ethyl acetate, the combined organic extracts were dried over Na_2SO_4, and evaporated under reduced pressure. The crude residue was purified by chromatography (petroleum ether–ethyl acetate, 5 : 1) to give 2-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)pyridine (8.25 g, 77 %) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$), δ: 14.80 (s, 1H), 8.88 (dd, *J* 5.1, 1.5 Hz, 1H), 8.37 (d, *J* 7.5 Hz, 1H), 8.00 (t, *J* 7.7 Hz, 1H), 7.68–7.45 (m, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$), δ: 155.4, 155.2 (q, *J* 39.6 Hz), 149.6, 145.0, 138.9, 126.4, 123.1, 119.3 (q, *J* 269.9 Hz).

The NMR data were consistent with those reported previously.[S19]

2-(1H-tetrazol-5-yl)pyridine (pttz)



A round-bottom flask equipped with a magnetic stir bar and a reflux condenser was charged with 2-pyridinecarbonitrile (10.4 g, 100 mmol, 1 equiv.), sodium azide (8.45 g, 130 mmol, 1.3 equiv.), ammonium chloride (6.97 g, 130 mmol, 1.3 equiv.), and DMF (60 ml). The reaction mixture was heated at 140 °C for 15h, cooled to room temperature, and poured into cold water (500 ml). The pH of the mixture was adjusted to 6 using HCl (10 % aq.); the precipitate was filtered, washed with water, dried, and recrystallized from ethanol-water mixture (1.1 : 1), and then dried *in vacuo* to give the disered product (9.7 g, 66 %) as the light gray needles.

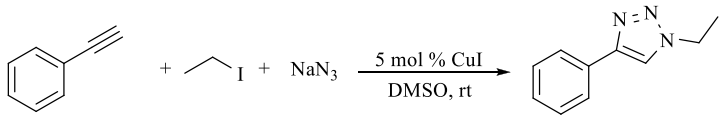
m.p. 212 °C (Lit. data[S20]: m.p. 210–213 °C)

^{1}H NMR (600 MHz, DMSO-d_6), δ: 8.78 (d, *J* 4.7 Hz, 1H), 8.22 (d, *J* 7.8 Hz, 1H), 8.07 (td, *J* 7.7, 1.7 Hz, 1H), 7.62 (ddd, *J* 7.6, 4.8, 1.0 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6), δ: 154.8, 150.1, 143.7, 138.2, 126.1, 122.6 .

The NMR data are in agreement with those reported previously.[S20]

1-ethyl-4-phenyl-1H-1,2,3-triazole



A round-bottom flask equipped with a magnetic stir bar was charged with dry DMSO (180 ml) and then, fine powdered sodium azide (5.6 g, 86 mmol)) was added under vigorous stirring. The reaction flask was sealed with septum, placed in cold water bath, and ethyl iodide (6.8 ml, 13.2 g, 84.6 mmol) was then slowly added to the reaction mixture. The mixture was stirred at room temperature for 12h, and phenylacetylene (9.3 ml, 8.63 g, 84.6 mmol) and copper(I) iodide (0.806 g, 4.23 mmol, 5 mol%) were then added. The reaction mixture was stirred at room temperature for 24h and diluted with cold water (800 ml); the formed precipitate was filtered off, dried, and then purified by flash-chromatography (in ethyl acetate : hexane = 1 : 1) to give 1-ethyl-4-phenyl-1*H*-1,2,3-triazole (9.4 g, 64 %) as a white solid.

m.p. 60–61 °C (Lit. data[S21]: m.p. 61–62 °C)

^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.83 (d, *J* 7.1 Hz, 2H), 7.77 (br.s, 1H), 7.41 (t, *J* 7.4 Hz, 2H), 7.32 (t, *J* 7.3 Hz, 1H), 4.44 (q, *J* 7.3 Hz, 2H), 1.58 (t, *J* 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$), δ: 147.9, 130.8, 128.9, 128.2, 125.8, 119.1, 45.5, 15.6.

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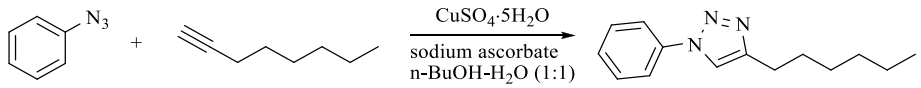
The NMR data are in agreement with those reported previously.[S22]

4-hexyl-1-phenyl-1H-1,2,3-triazole



A round-bottom flask equipped with a magnetic stir bar was charged with a water/*n*-butanol mixture (1 : 1, 30 ml), phenyl azide (4.83 g, 40.5 mmol, 1 equiv.), and 1-octyne (5.97 ml, 4.46 g, 40.5 mmol, 1 equiv.). Sodium ascorbate (8.1 ml of 1M freshly prepared solution in water, 0.2 equiv.) was added, followed by the addition of copper(II) sulfate pentahydrate (1.25 g, 4.05 mmol, 0.1 eq.) solution in water (10 ml). The heterogeneous mixture was stirred vigorously overnight. TLC monitoring (CH_2Cl_2) indicated complete consumption of the reactants. The reaction mixture was diluted with water (100 ml), extracted with hexane–EtOAc (1 : 1) mixture (3×100 ml). The organic extracts were washed with water, dried over Na_2SO_4, and evaporated to dryness. The residue was purified by flash chromatography (CH_2Cl_2) to give 4-hexyl-1-phenyl-1*H*-1,2,3-triazole (7.8 g, 83 %) as a white solid.

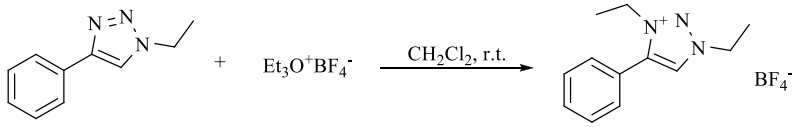
m.p. 42 °C (Lit. data[S23]: m.p. 41 °C)

^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.73–7.69 (m, 3H), 7.51–7.47 (m, 2H), 7.42–7.37 (m, 1H), 2.81–2.75 (m, 2H), 1.72 (p, *J* 7.6 Hz, 2H), 1.42–1.36 (m, 2H), 1.34–1.28 (m, 4H), 0.90–0.87 (m, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$), δ: 149.3, 137.4, 129.8, 128.5, 120.5, 118.9, 31.7, 29.5, 29.0, 25.8, 22.7, 14.2 .

The NMR data are in agreement with those reported previously.[S23]

1,3-diethyl-4-phenyl-1H-1,2,3-triazolium tetrafluoroborate (1)



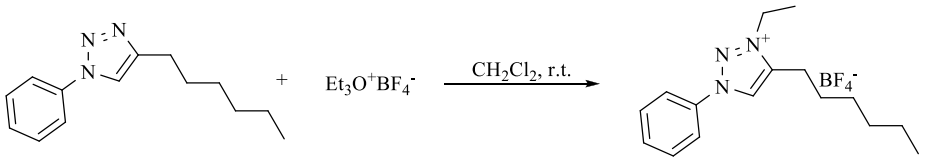
Triethyloxonium tetrafluoroborate (2.1 g, 11 mmol, 1.1 equiv.) was added to a solution of 1-ethyl-4-phenyl-1*H*-1,2,3-triazole (1.73 g, 10 mmol, 1 equiv.) in dichloromethane (10 ml). The reaction mixture was stirred for 24h at room temperature, methanol (1 ml) was then added, and the reaction mixture was evaporated to give viscous oily residue, which was dissolved in dichloromethane and concentrated again. Prolonged drying *in vacuo* provided 1,3-diethyl-4-phenyl-1*H*-1,2,3-triazolium tetrafluoroborate (2.89 g, 99 %) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$), δ: 8.49 (s, 1H), 7.61–7.53 (m, 3H), 7.51 (d, *J* 7.1 Hz, 2H), 4.63 (q, *J* 7.0 Hz, 2H), 4.52 (q, *J* 7.0 Hz, 2H), 1.63 (t, *J* 7.2 Hz, 3H), 1.52 (t, *J* 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$), δ: 142.7, 131.8, 129.7, 129.6, 128.5, 122.3, 49.8, 47.3, 14.2, 14.1 .

The NMR data are in agreement with those reported previously.[S22]

3-ethyl-4-hexyl-1-phenyl-1H-1,2,3-triazolium tetrafluoroborate (5)



3-ethyl-4-hexyl-1-phenyl-1*H*-1,2,3-triazolium tetrafluoroborate was synthesized using the same procedure given for 1,3-diethyl-4-phenyl-1*H*-1,2,3-triazolium tetrafluoroborate (**1**). Alkylation of 4-hexyl-1-phenyl-1*H*-1,2,3-triazole (2.75 g, 12 mmol) with triethyloxonium tetrafluoroborate (2.5 g, 13 mmol, 1.1 equiv.) in dichloromethane (40 ml) afforded 3-ethyl-4-

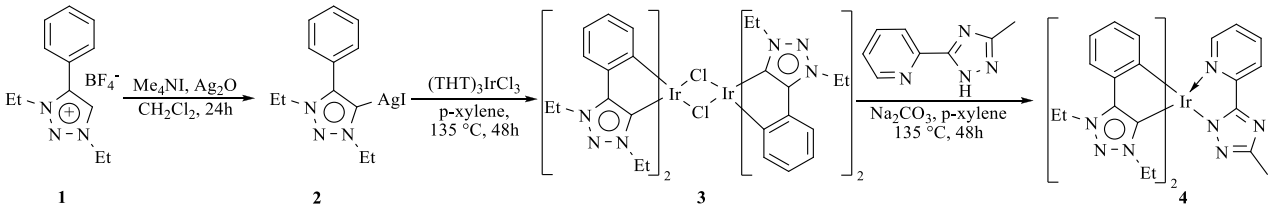
hexyl-1-phenyl-1*H*-1,2,3-triazolium tetrafluoroborate (**2**) an off-white solid in a virtually quantitative yield (99 %).

^{1}H NMR (600 MHz, $CDCl_3$), δ: 8.73 (s, 1H), 7.90–7.84 (m, 2H), 7.59–7.53 (m, 3H), 4.61 (q, *J* 7.3 Hz, 2H), 2.94–2.84 (m, 2H), 1.81–1.72 (m, 2H), 1.69 (t, *J* 7.3 Hz, 3H), 1.39 (q, *J* 7.2 Hz, 2H), 1.32–1.22 (m, 4H), 0.88–0.80 (m, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$), δ: 145.7, 135.1, 131.8, 130.4, 126.3, 121.6, 47.1, 31.3, 28.9, 27.3, 23.3, 22.5, 14.1, 14.0.

Synthesis of iridium complexes

Complex 4



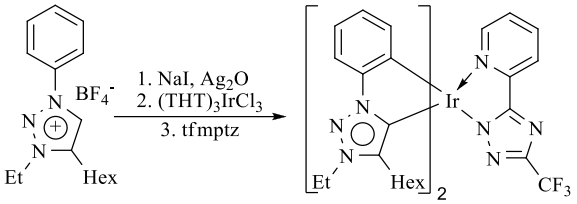
A mixture of 1,3-diethyl-4-phenyl-1*H*-1,2,3-triazolium tetrafluoroborate (1.45 g, 5 mmol) and tetramethylammonium iodide (5.03 g, 25 mmol, dried *in vacuo* at 80 °C for 1h) in dichloromethane (50 ml) was stirred for 30 min at room temperature under inert atmosphere followed by the addition of silver(I) oxide (0.87 g, 3.8 mmol). The resulting suspension was protected from light and stirred for 24h at room temperature. Dry *o*-xylene (30 ml) and iridium tris(tetrahydrothiophene) trichloride (1.17 g, 2.1 mmol) were then added to the reaction mixture, dichloromethane was distilled off, and the reaction flask was heated to 135 °C under inert atmosphere. The mixture was stirred at 135 °C for 48h, cooled to room temperature, and 2-(5-methyl-2*H*-1,2,4-triazol-3-yl)pyridine (0.33 g, 2.1 mmol) and fine powdered anhydrous sodium carbonate (1.77 g) were then added. The reaction mixture was heated to 135 °C and stirred for another 48h, then cooled to room temperature, and evaporated to dryness. The solid residue was extracted with dichloromethane; the solution was filtered and concentrated. Purification of the residue by column chromatography afforded target iridium complex **4** (67 mg, 9%) as a light yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.92 (d, *J* 7.9 Hz, 1H), 7.78 (d, *J* 5.4 Hz, 1H), 7.56 (td, *J* 7.8, 1.4 Hz, 2H), 7.13 (d, *J* 7.1 Hz, 1H), 7.10 (d, *J* 7.9 Hz, 2H), 6.79 (ddd, *J* 7.2, 5.6, 1.3 Hz, 1H), 6.73 (td, *J* 7.5, 1.1 Hz, 1H), 6.66 (td, *J* 7.4, 1.4 Hz, 1H), 6.55 (td, *J* 7.4, 1.1 Hz, 1H), 6.53–6.46

(m, 3H), 4.49–4.44 (m, 4H), 3.69 (dq, *J* 14.5, 7.3 Hz, 1H), 3.55 (dq, *J* 14.4, 7.2 Hz, 1H), 3.39 (qt, *J* 13.3, 6.2 Hz, 2H), 2.32 (s, 3H), 1.53–.49 (m, 6H), 0.94 (t, *J* 7.3 Hz, 3H), 0.89 (t, *J* 7.3 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), δ: 163.0, 162.6, 161.9, 161.8, 155.6, 155.3, 153.6, 152.7, 150.4, 148.5, 138.4, 138.2, 137.7, 136.9, 136.1, 127.6, 127.2, 122.5, 120.7, 120.59, 120.63, 120.1, 119.8, 47.1, 46.7, 45.2, 31.8, 29.6, 29.2, 22.6, 16.0, 15.8, 14.5, 14.3, 14.1

Complex 6



5 **6**

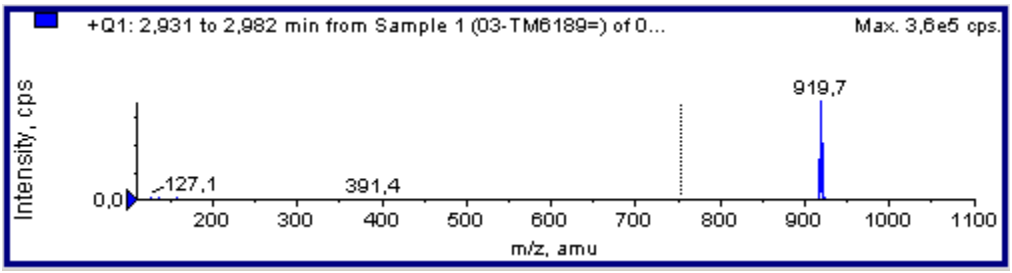
A solution of anhydrous sodium iodide in acetonitrile (10 ml of 0.5M solution, 5 mmol, 2.3 equiv.) was added to a solution of 3-ethyl-4-hexyl-1-phenyl-1*H*-1,2,3-triazolium tetrafluoroborate (0.767 g, 2.2 mmol) in dichloromethane (20 ml). The mixture was stirred for 30 min, evaporated to dryness, and dried *in vacuo*. The residue was dissolved in dichloromethane (40 ml) followed by the addition of silver(I) oxide (0.281 g, 1.22 mmol, 0.55 equiv.). The reaction mixture was protected from light and stirred for 24h at room temperature under inert atmosphere. The reaction mixture was evaporated to dryness followed by the addition of *o*-xylene (40 ml) and iridium tris(tetrahydrothiophene) trichloride (0.563 g, 1 mmol, 0.45 equiv.). The reaction mixture was refluxed for 48h and cooled to room temperature. 2-(5-Trifluoromethyl-2*H*-1,2,4-triazol-3-yl)pyridine (0.214 g, 1 mmol, 0.45 equiv.) and fine powdered anhydrous sodium carbonate (0.265 g, 2.5 mmol, 1.2 equiv.) were added to the reaction mixture, and it was refluxed for another 24h. Then the reaction mixture was cooled and evaporated to dryness. The solid residue was extracted with dichloromethane, the solution was collected and evaporated again. The solid residue was purified by column chromatography with gradual elution to give crude iridium complex **6** (224 mg). Crystallization from DMSO afforded the analytically pure complex (204 mg, 22%) as a yellow crystals, while the obtained crystals were suitable for the single crystal X-ray analysis.

^{1}H NMR (600 MHz, $CDCl_3$), δ: 8.15 (d, *J* 7.9 Hz, 1H), 8.00 (d, *J* 5.4 Hz, 1H), 7.70 (td, *J* 7.8, 1.5 Hz, 1H), 7.55 (dd, *J* 7.8, 1.1 Hz, 1H), 7.51 (dd, *J* 7.8, 1.2 Hz, 1H), 6.95 (ddd, *J* 7.2, 5.6, 1.4 Hz, 1H), 6.90 (td, *J* 7.6, 1.3 Hz, 1H), 6.83 (td, *J* 7.7, 1.2 Hz, 1H), 6.77 (td, *J* 7.4, 1.2 Hz, 1H),

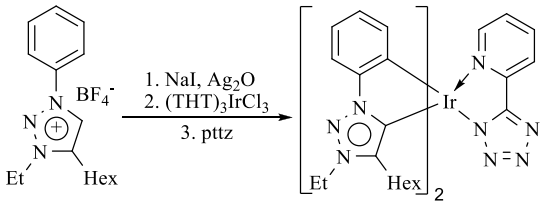
6.70 (td, *J* 7.4, 1.3 Hz, 1H), 6.68 (dd, *J* 7.4, 1.1 Hz, 1H), 6.62–6.55 (m, 1H), 4.32–4.21 (m, 4H), 2.19–2.12 (m, 1H), 2.00–1.92 (m, 1H), 1.92–1.88 (m, 1H), 1.83–1.75 (m, 1H), 1.61–1.58 (m, 6H), 0.90–0.76 (m, 26H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$), δ: 163.2, 157.5, 156.4, 152.1, 151.0, 146.7, 146.1, 144.3, 143.0, 139.0, 137.8, 137.7, 136.3, 134.2, 128.1, 127.4, 123.6, 121.3, 120.9, 120.8, 114.14, 114.09, , 44.2, 44.1, 32.1, 31.7, 31.5, 30.7, 29.2, 24.6, 24.2, 22.8, 22.7, 22.6, 15.4, 14.3, 14.2.

MS calc.for $C_{40}H_{49}F_3IrN_{10}$ $[M+H]^+$: 919,4; found: 919.7.



Complex 7



5 **7**

A solution of anhydrous sodium iodide in acetonitrile (10 ml of 0.5M solution, 5 mmol, 2.3 equiv.) was added to a solution of 3-ethyl-4-hexyl-1-phenyl-1*H*-1,2,3-triazolium tetrafluoroborate (0.767 g, 2.2 mmol) in dichloromethane (20 ml). The mixture was stirred for 30 min, evaporated to dryness, and dried *in vacuo*. The residue was dissolved in dichloromethane (40 ml) followed by the addition of silver(I) oxide (0.281 g, 1.22 mmol, 0.55 equiv.). The reaction mixture was protected from light and stirred for 24h at room temperature under inert atmosphere. The reaction mixture was evaporated to dryness followed by the addition of *o*-xylene (40 ml) and iridium tris(tetrahydrothiophene) trichloride (0.563 g, 1 mmol, 0.45 equiv.). The reaction mixture was refluxed for 48h and cooled to room temperature. 2-(1*H*-Tetrazol-5-yl)pyridine (0.1471 g, 1 mmol, 0.45 equiv.) and fine powdered anhydrous sodium carbonate (0.265 g, 2.5 mmol, 1.2 equiv.) were added to the reaction mixture and it was refluxed for another 24h. Then the reaction mixture was cooled and evaporated to dryness. The solid residue was extracted with dichloromethane, the solution was collected and evaporated again. The solid

residue was purified by column chromatography with gradual elution to give crude iridium complex **7** (167 mg, 19%).

^{1}H NMR (600 MHz, $CDCl_3$), δ: 8.30 (d, *J* 7.9 Hz, 1H), 8.06–8.01 (m, 1H), 7.76 (td, *J* 7.8, 1.4 Hz, 1H), 7.57 (d, *J* 7.4 Hz, 1H), 7.52 (d, *J* 7.8 Hz, 1H), 7.01 (ddd, *J* 7.0, 5.6, 1.2 Hz, 1H), 6.92 (td, *J* 7.7, 1.4 Hz, 1H), 6.85–6.81 (m, 1H), 6.81–6.77 (m, 1H), 6.75 (dd, *J* 7.4, 1.2 Hz, 1H), 6.74–6.69 (m, 1H), 6.59 (d, *J* 7.0 Hz, 1H), 4.33–4.19 (m, 4H), 2.14–2.07 (m, 1H), 1.97–1.90 (m, 1H), 1.87–1.81 (m, 1H), 1.78–1.71 (m, 1H), 1.62–1.57 (m, 9H), 1.34–0.91 (m, 24H), 0.85–0.80 (m, 9H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$), δ: 151.3, 144.4, 138.0, 137.7, 136.4, 132.7, 128.1, 127.5, 124.1, 121.9, 121.3, 121.2, 114.3, 114.1, 44.1, 31.7, 31.5, 30.7, 30.5, 29.5, 29.0, 24.6, 24.1, 22.7, 22.6, 15.3, 14.3, 14.2.

Copies of NMR spectra

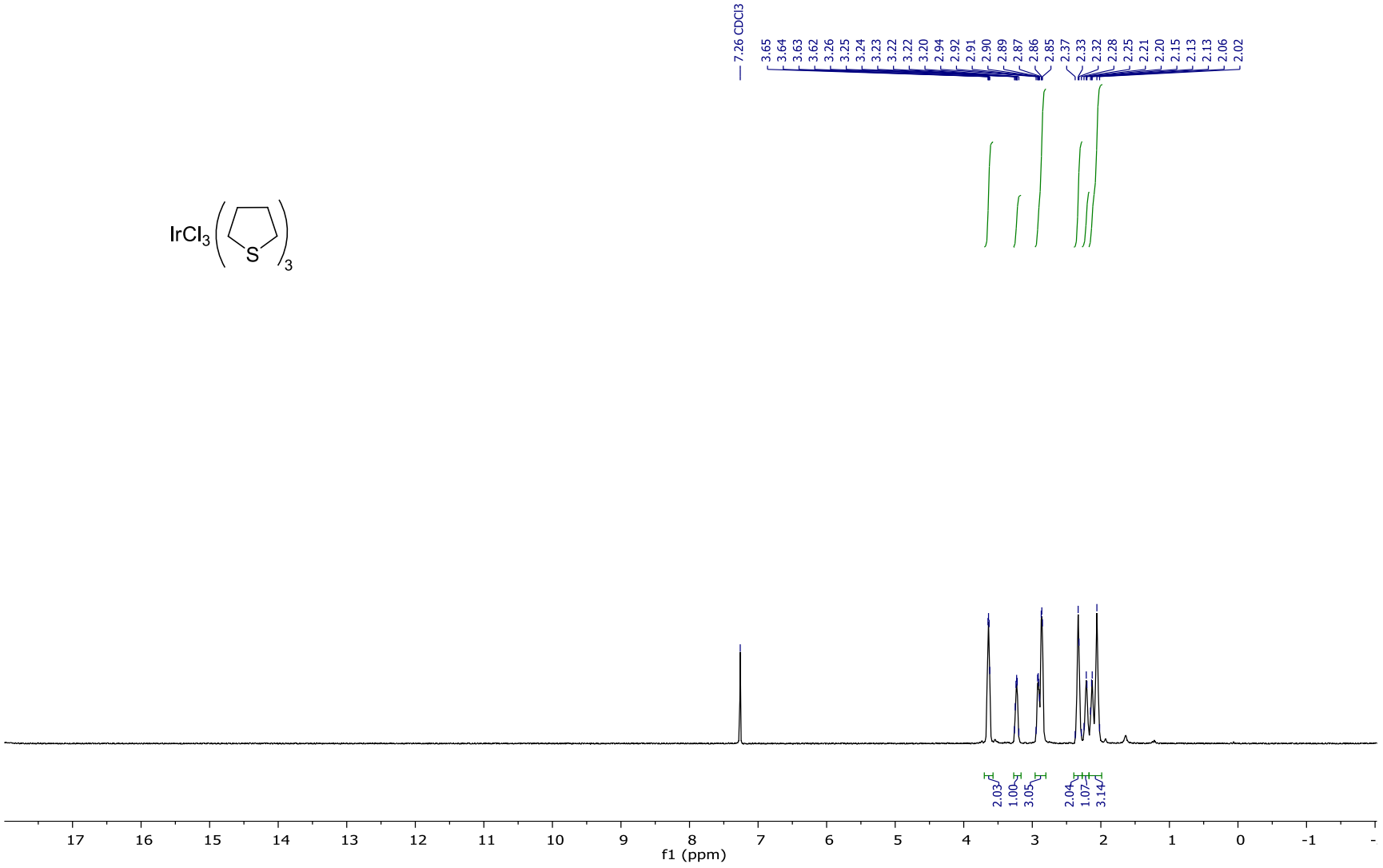


Figure S5 ^{1}H NMR (600 MHz, $CDCl_3$) of trichlorotris(tetrahydrothiophene)iridium(III).

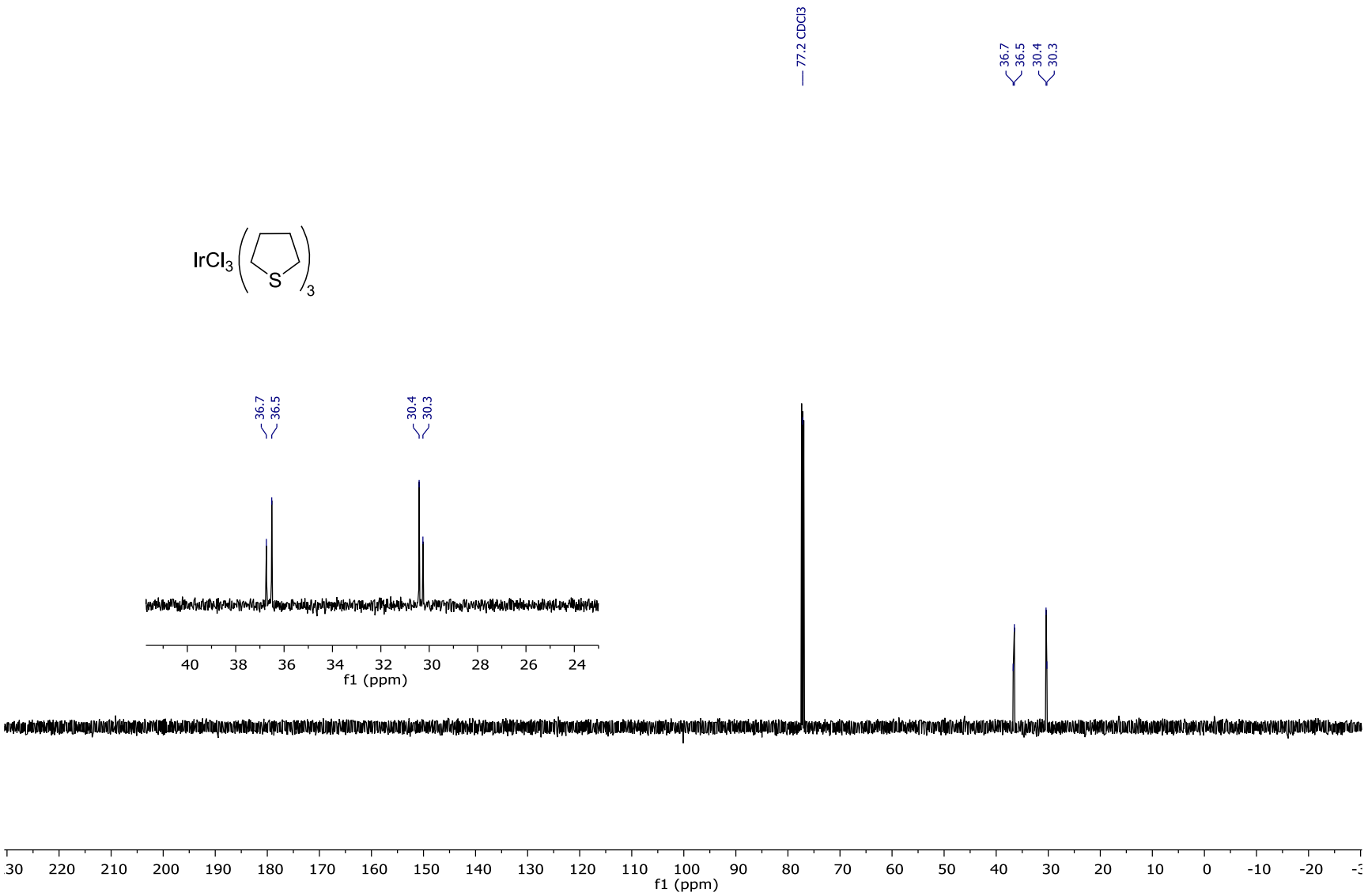


Figure S6 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of trichlorotris(tetrahydrothiophene)iridium(III).

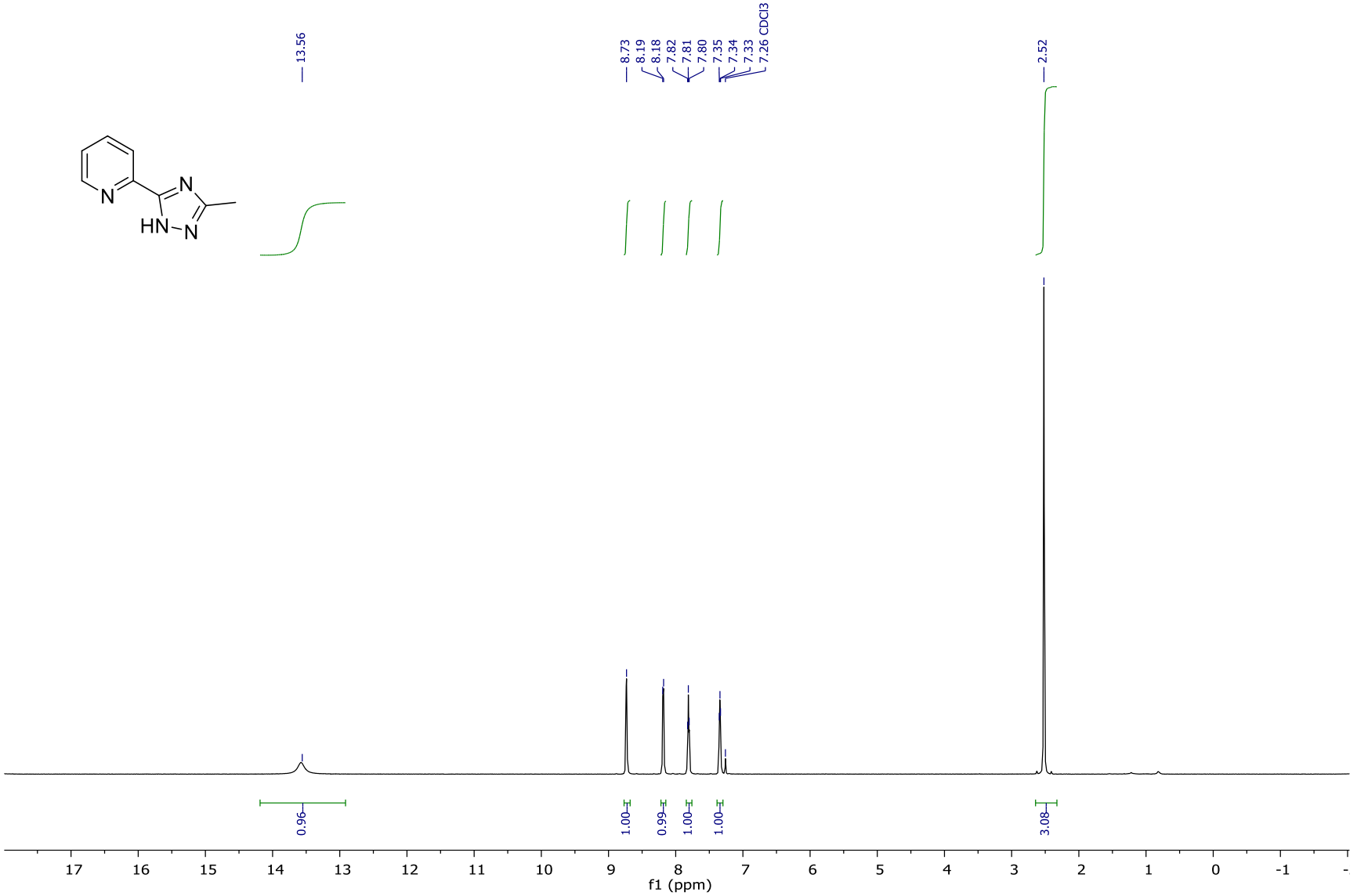


Figure S7 ^{1}H NMR (600 MHz, $CDCl_3$) of 2-(3-methyl-1*H*-1,2,4-triazol-5-yl)pyridine (**mptz**).

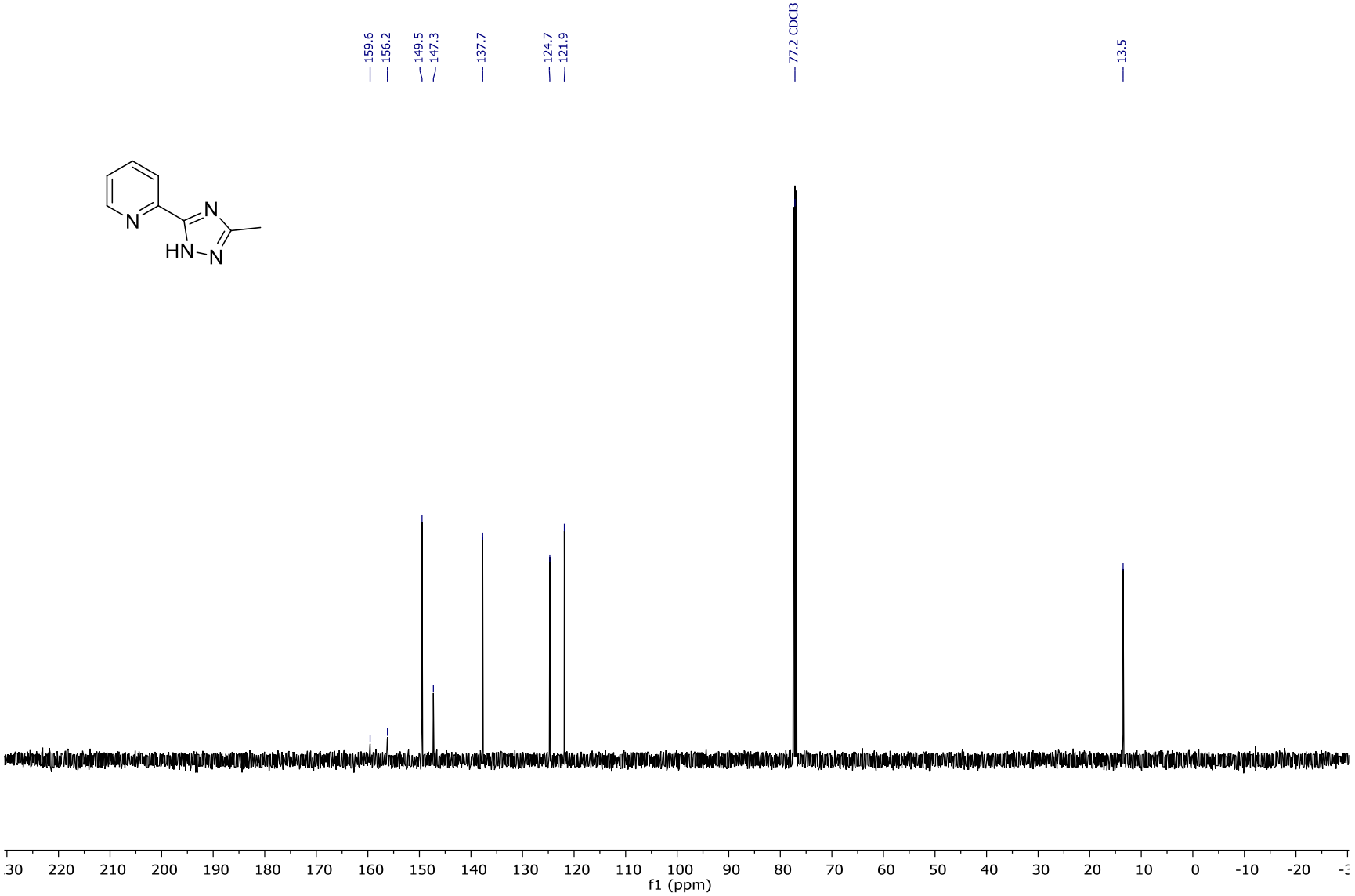


Figure S8 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of 2-(3-methyl-1*H*-1,2,4-triazol-5-yl)pyridine (**mptz**).

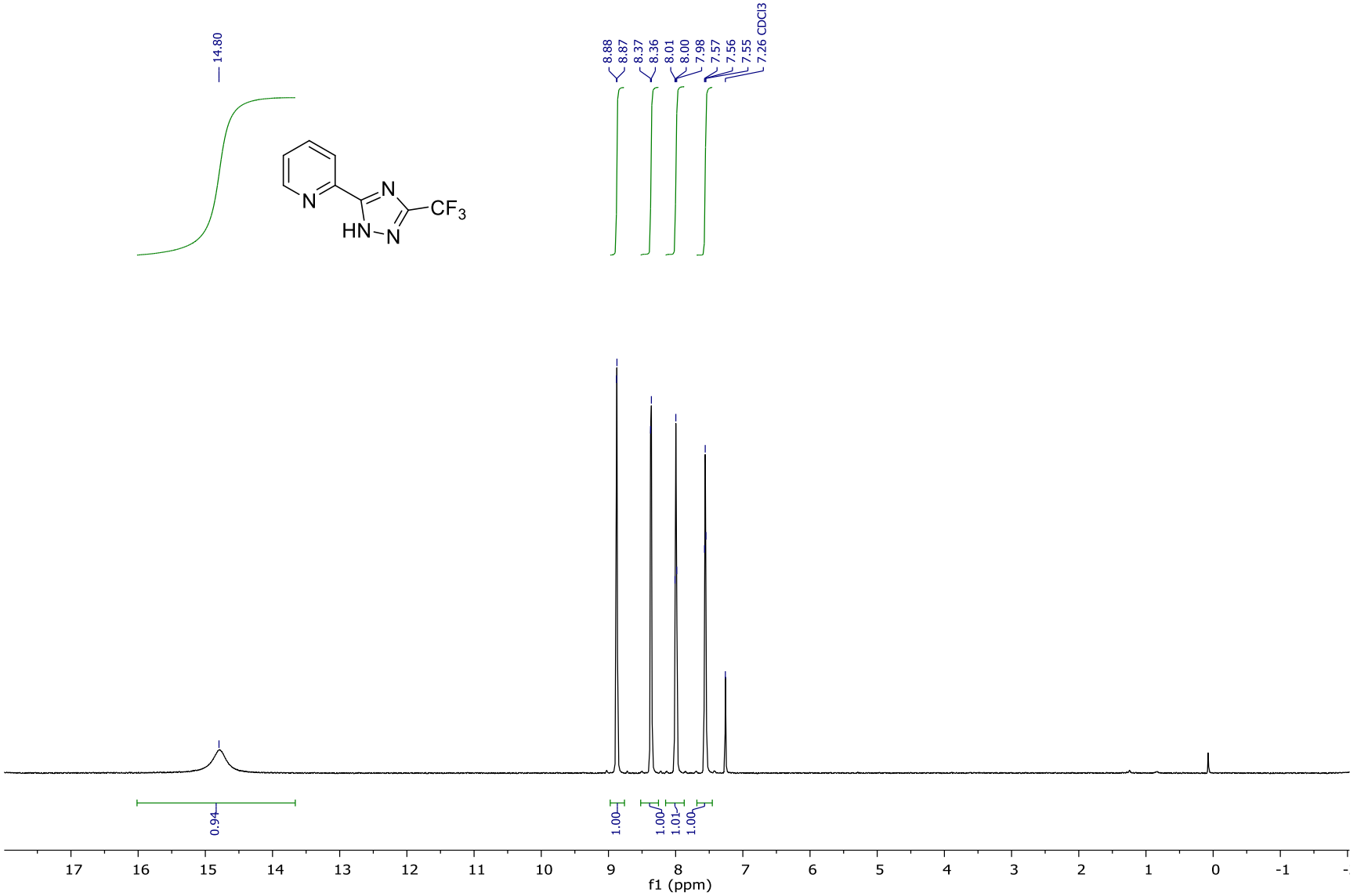


Figure S9 ^{1}H NMR (600 MHz, $CDCl_3$) of 2-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)pyridine (**tfmptz**).

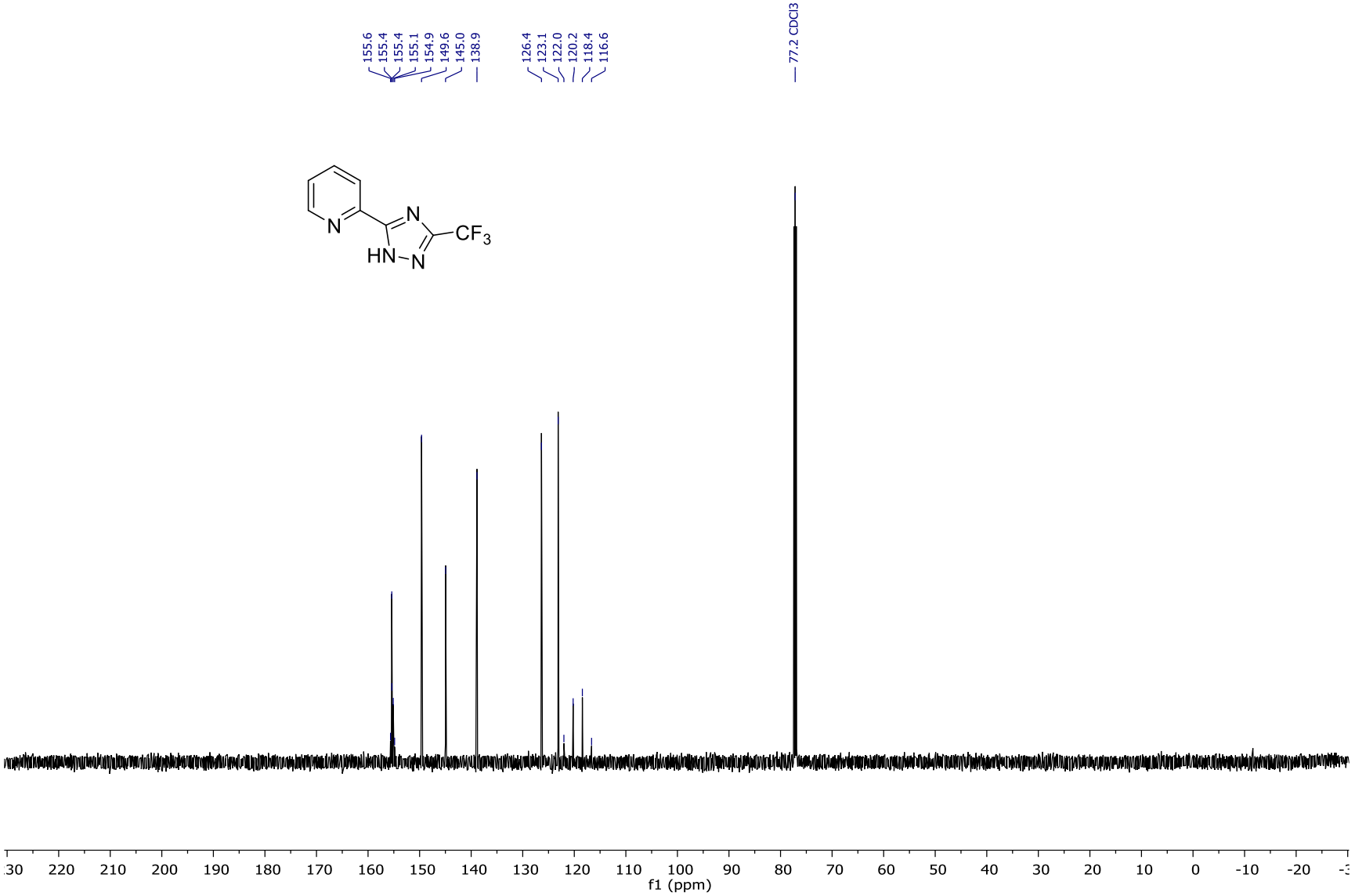


Figure S10 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of 2-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)pyridine (**tfmptz**).

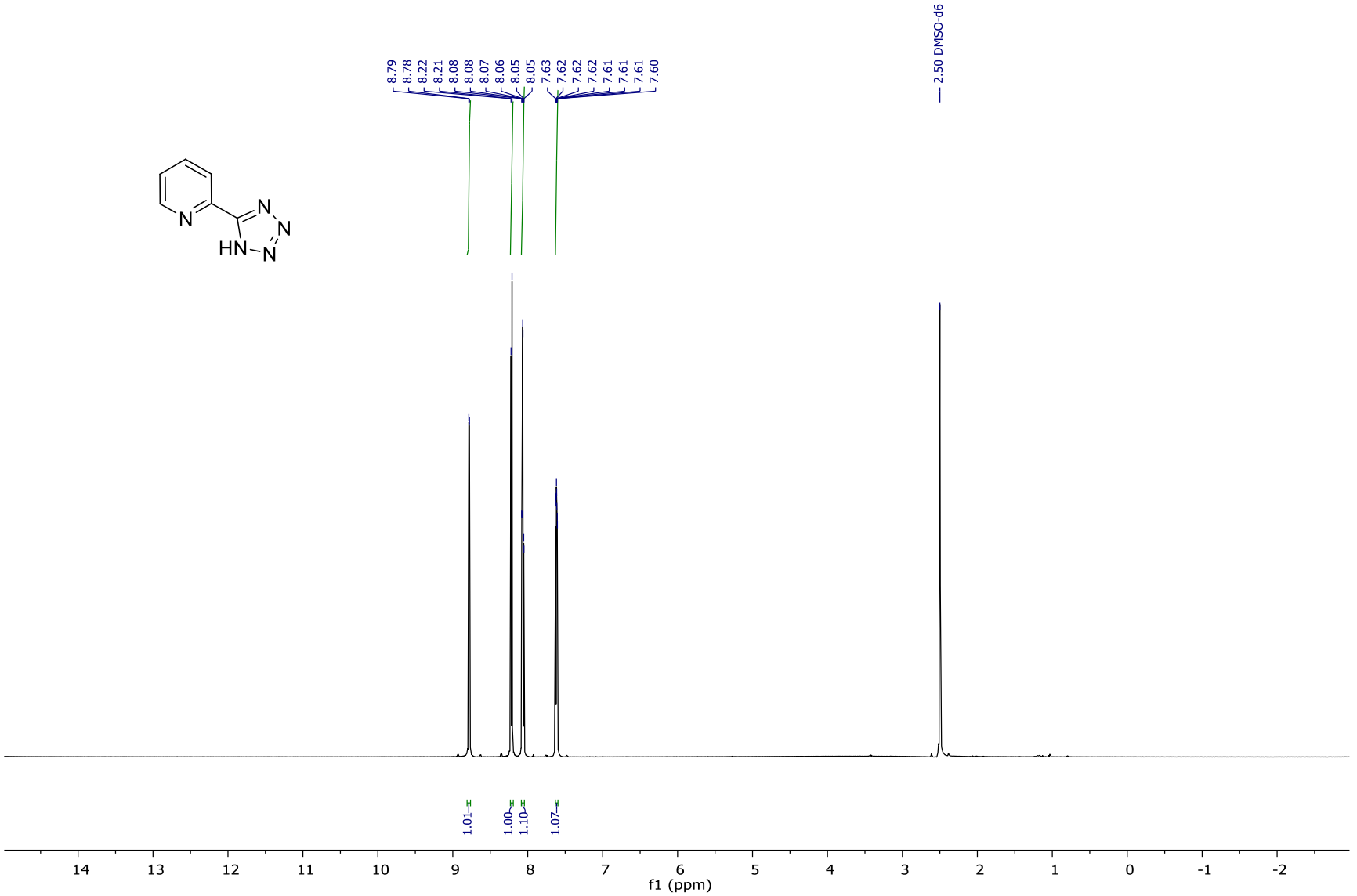


Figure S11 ^{1}H NMR (600 MHz, DMSO-d_6) of 2-(1*H*-tetrazol-5-yl)pyridine (**pttz**).

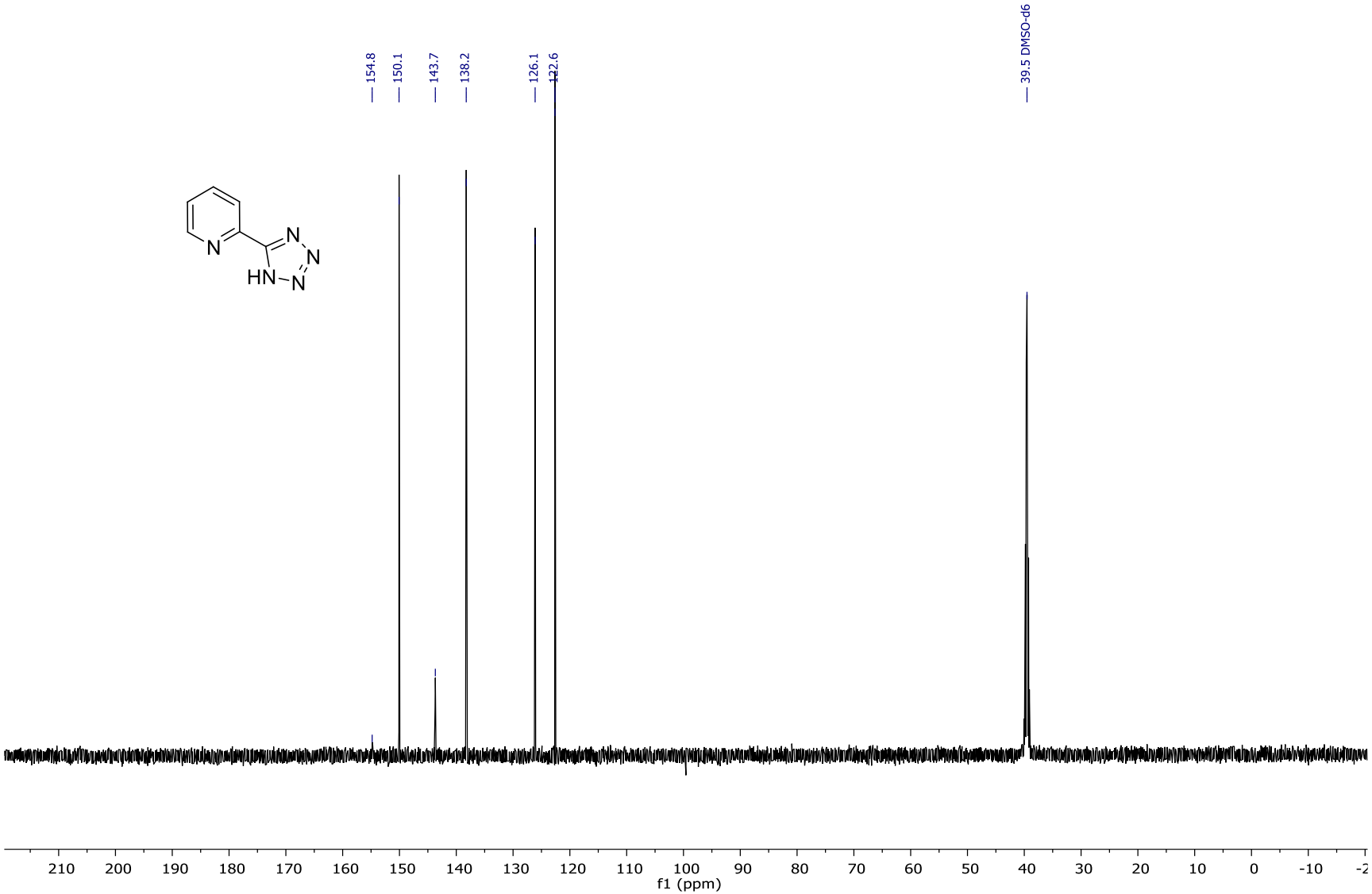


Figure S12 $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6) of 2-(1*H*-tetrazol-5-yl)pyridine (**pttz**).

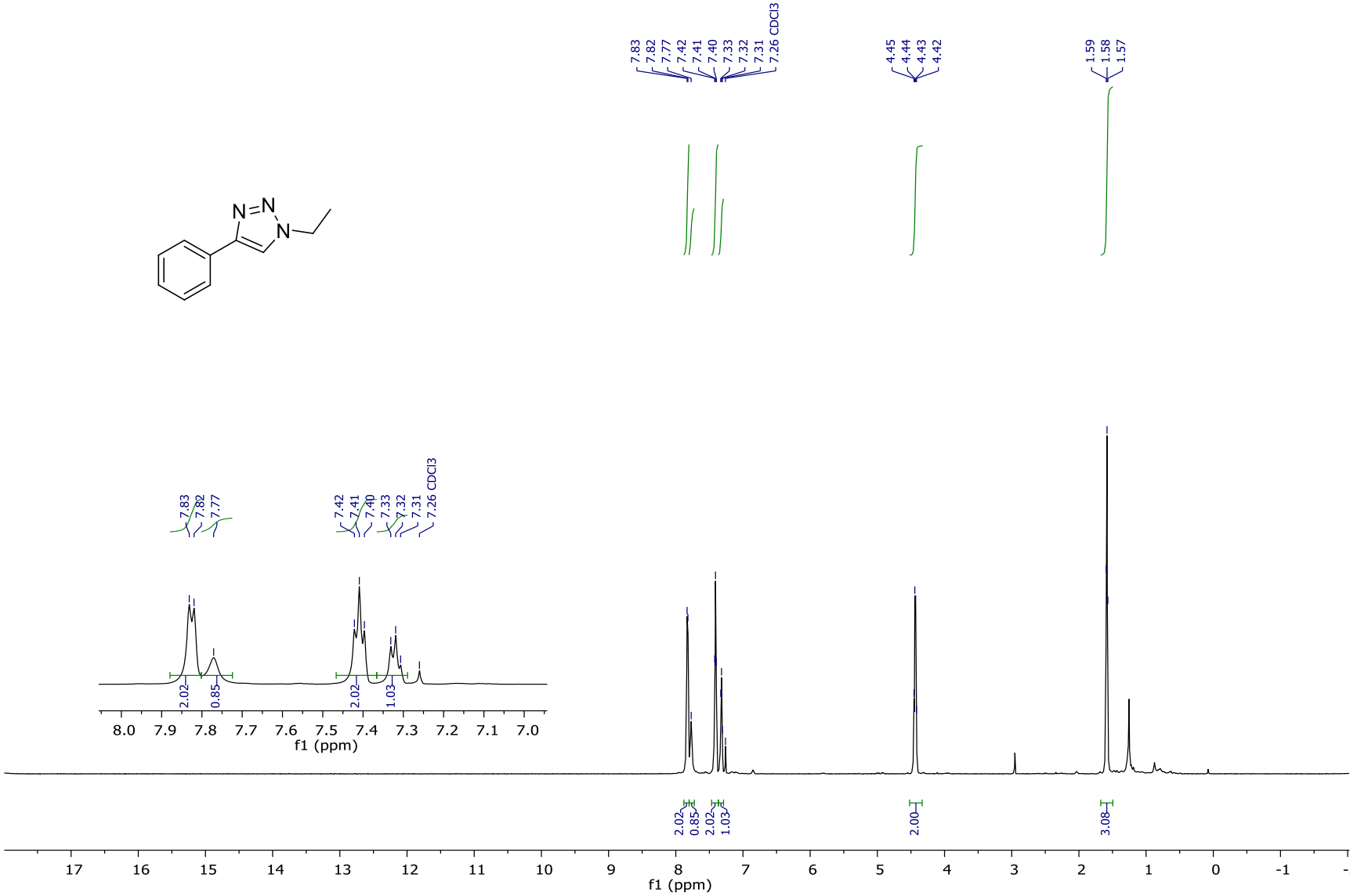


Figure S13 ^{1}H NMR (600 MHz, $CDCl_3$) of 1-ethyl-4-phenyl-1*H*-1,2,3-triazole.

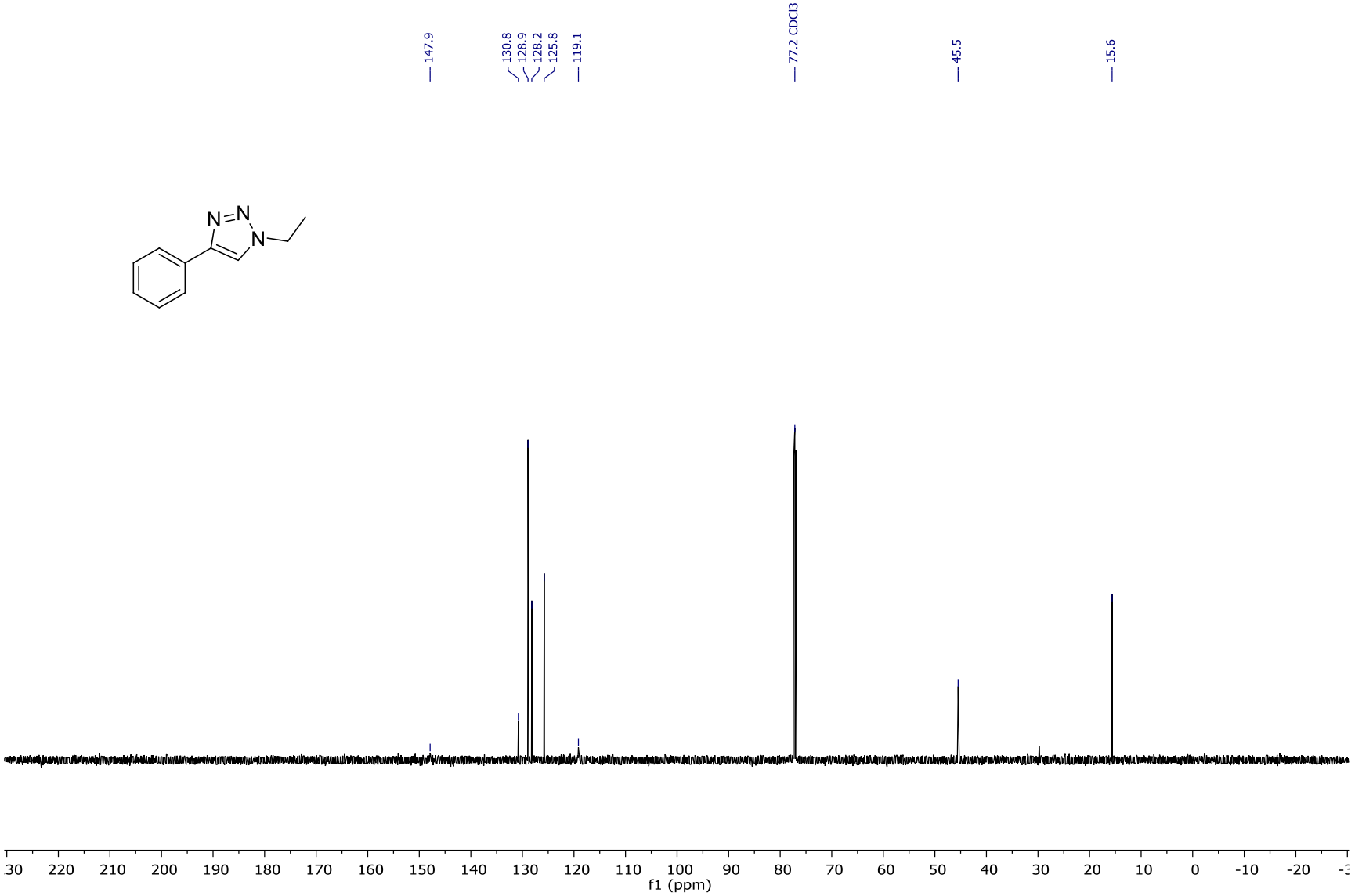


Figure S14 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of 1-ethyl-4-phenyl-1*H*-1,2,3-triazole.

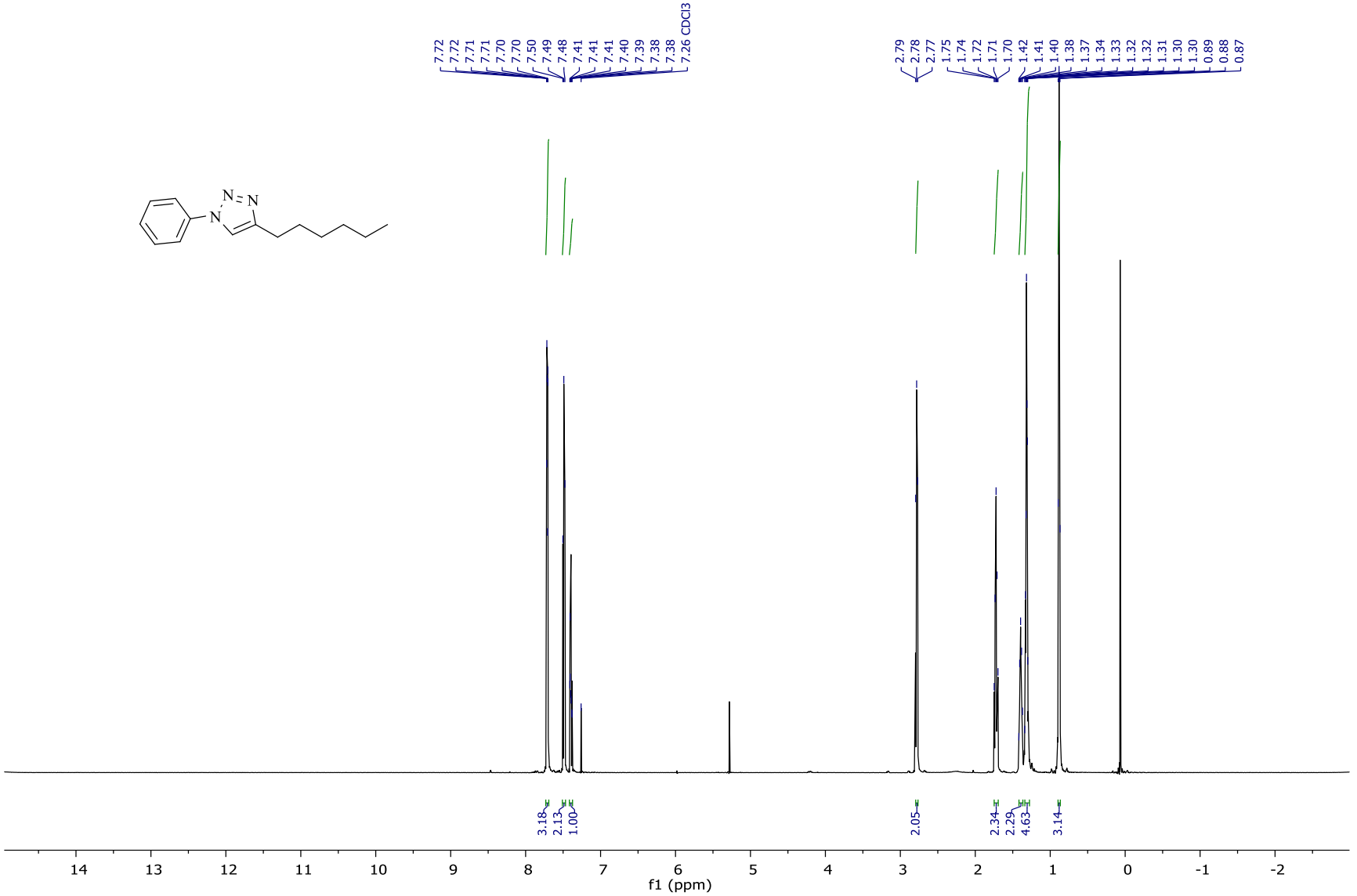


Figure S15 ^{1}H NMR (600 MHz, $CDCl_3$) of 4-hexyl-1-phenyl-1*H*-1,2,3-triazole.

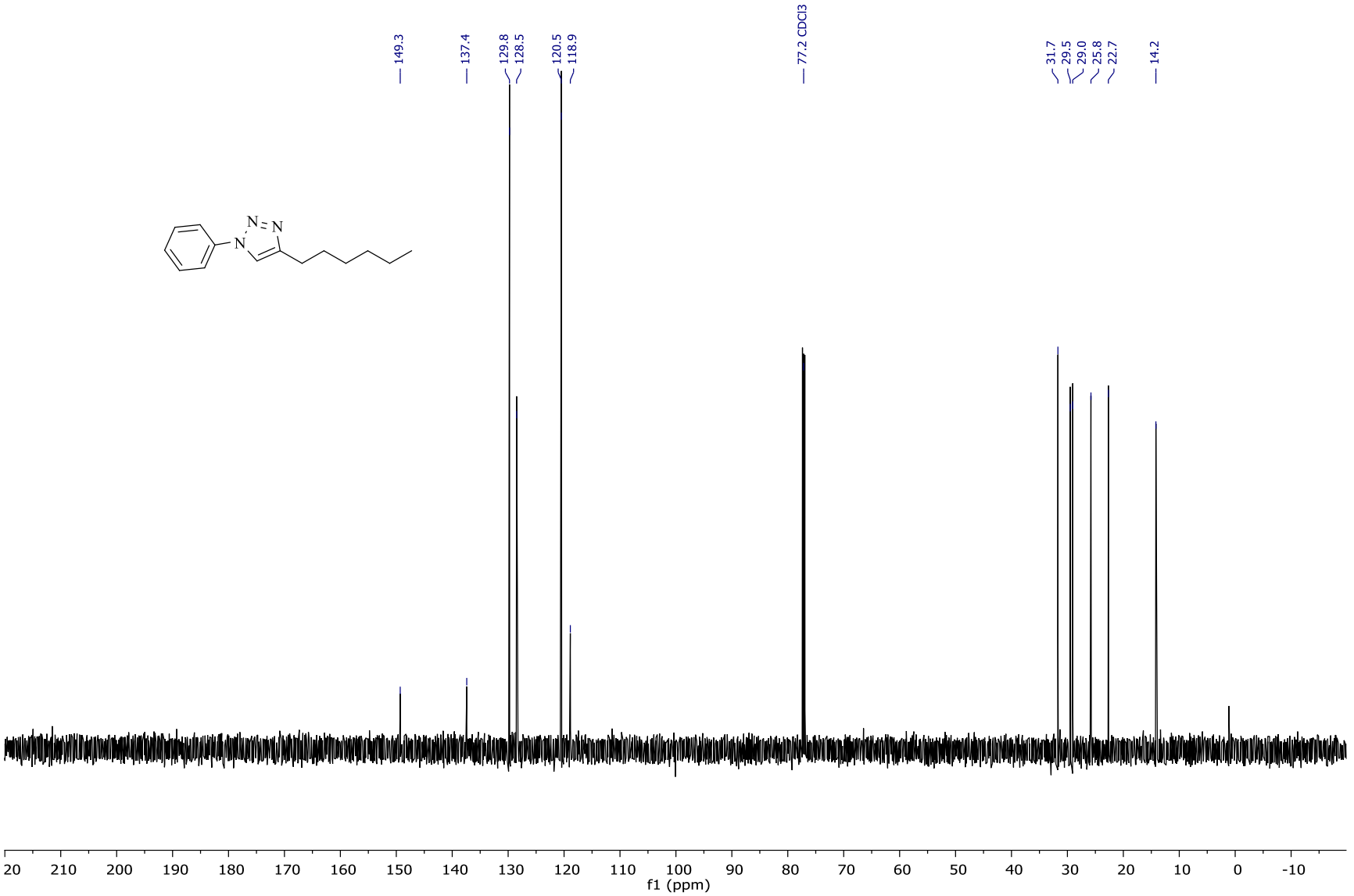


Figure S16 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of 4-hexyl-1-phenyl-1*H*-1,2,3-triazole.

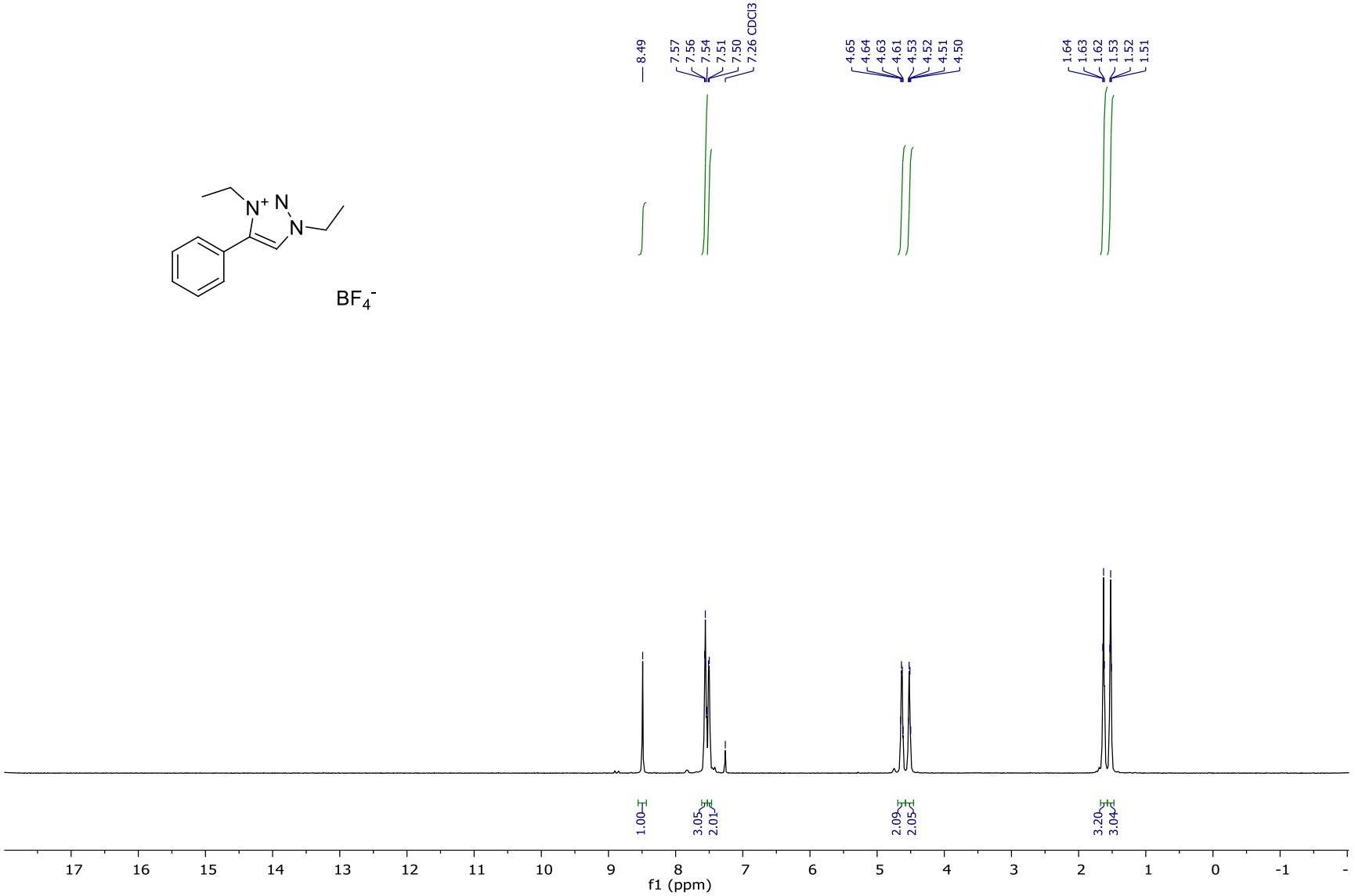


Figure S17 ^{1}H NMR (600 MHz, $CDCl_3$) of 1,3-diethyl-4-phenyl-1*H*-1,2,3-triazolium tetrafluoroborate (**1**).

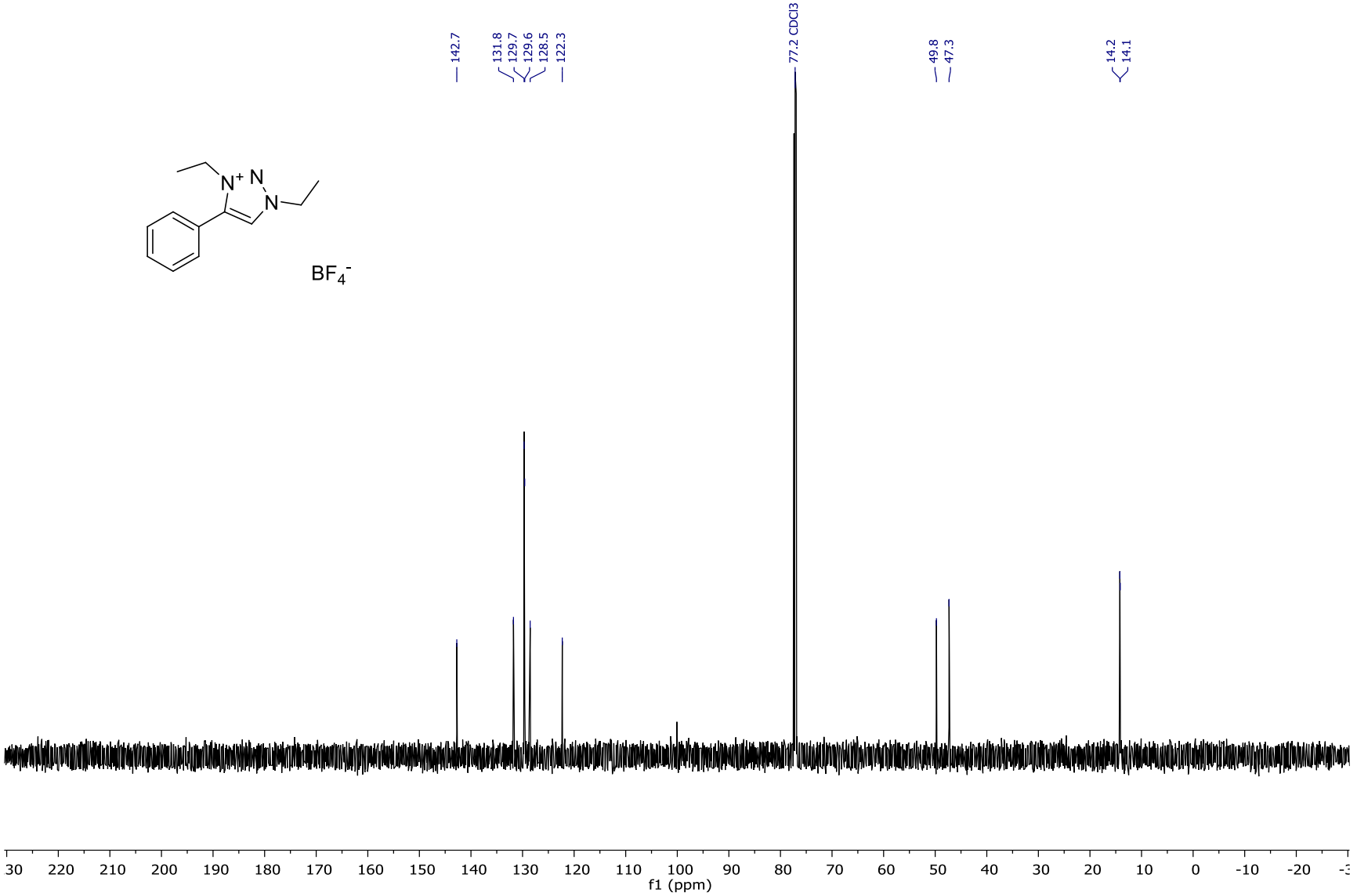


Figure S18 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of 1,3-diethyl-4-phenyl-1*H*-1,2,3-triazolium tetrafluoroborate (**1**).

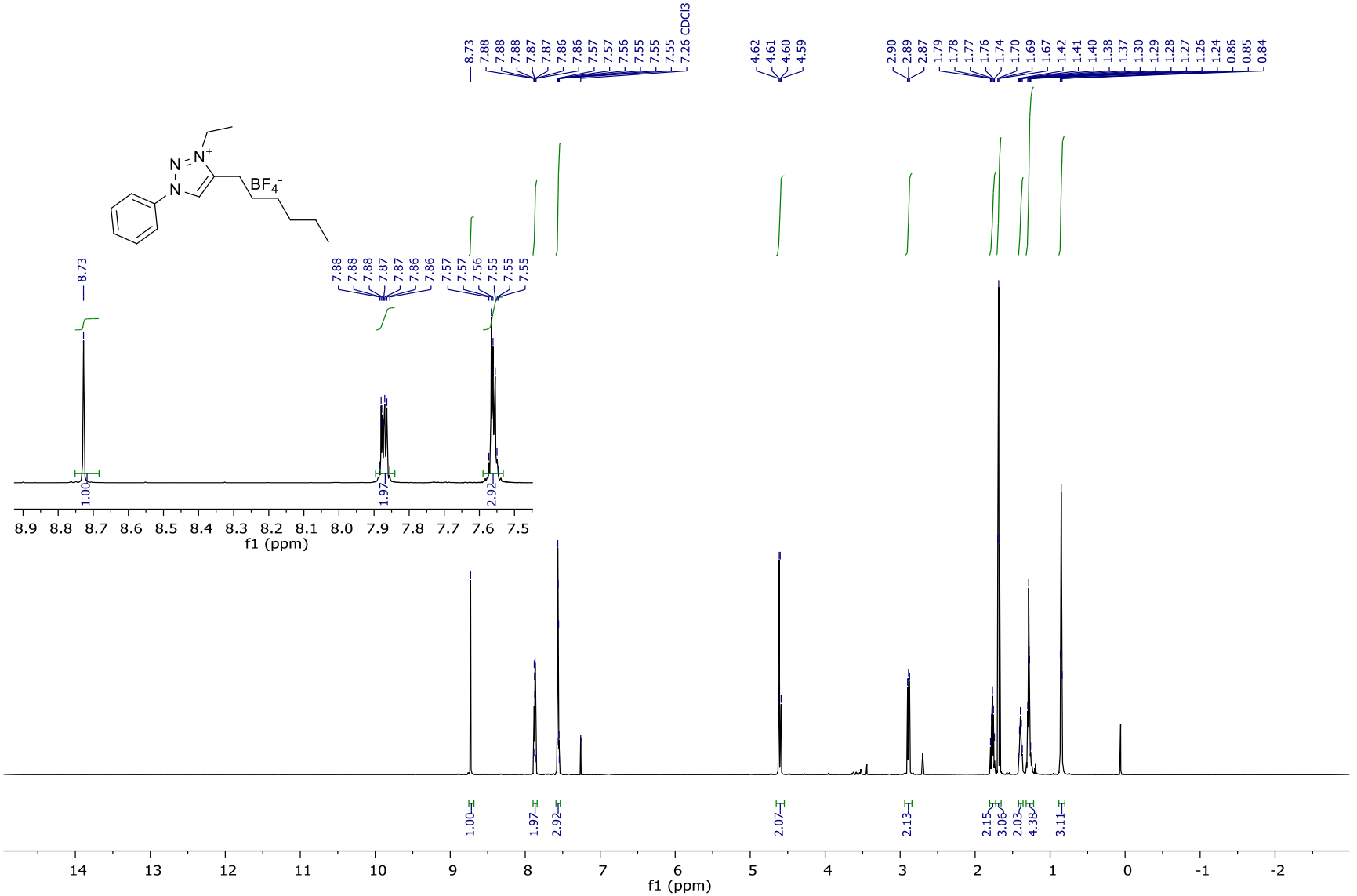


Figure S19 1H NMR (600 MHz, $CDCl_3$) of 3-ethyl-4-hexyl-1-phenyl-1*H*-1,2,3-triazolium tetrafluoroborate (**5**).

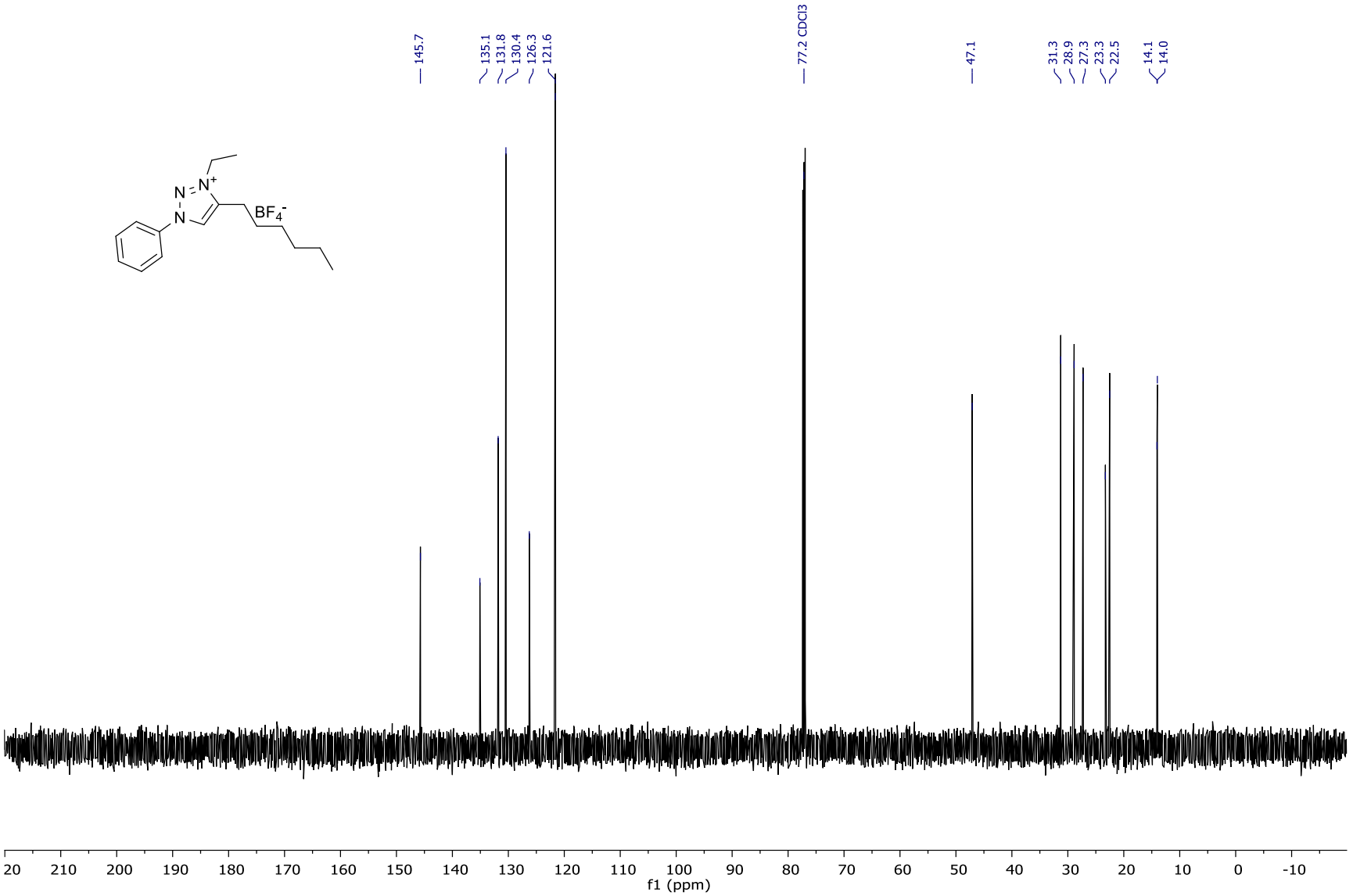


Figure S20 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of 3-ethyl-4-hexyl-1-phenyl-1*H*-1,2,3-triazolium tetrafluoroborate (**5**).

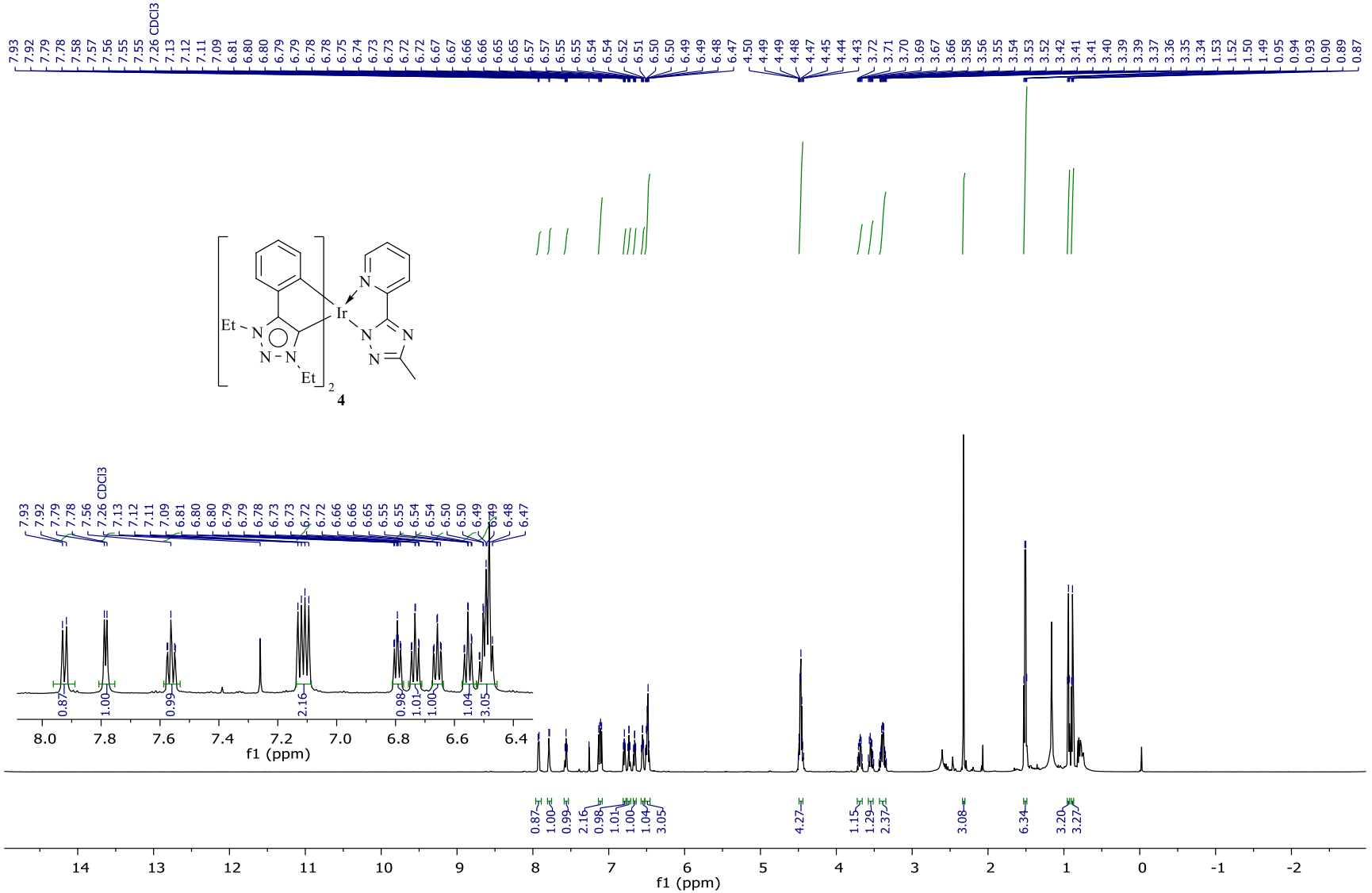


Figure S21 ^{1}H NMR (600 MHz, $CDCl_3$) of complex **4**.

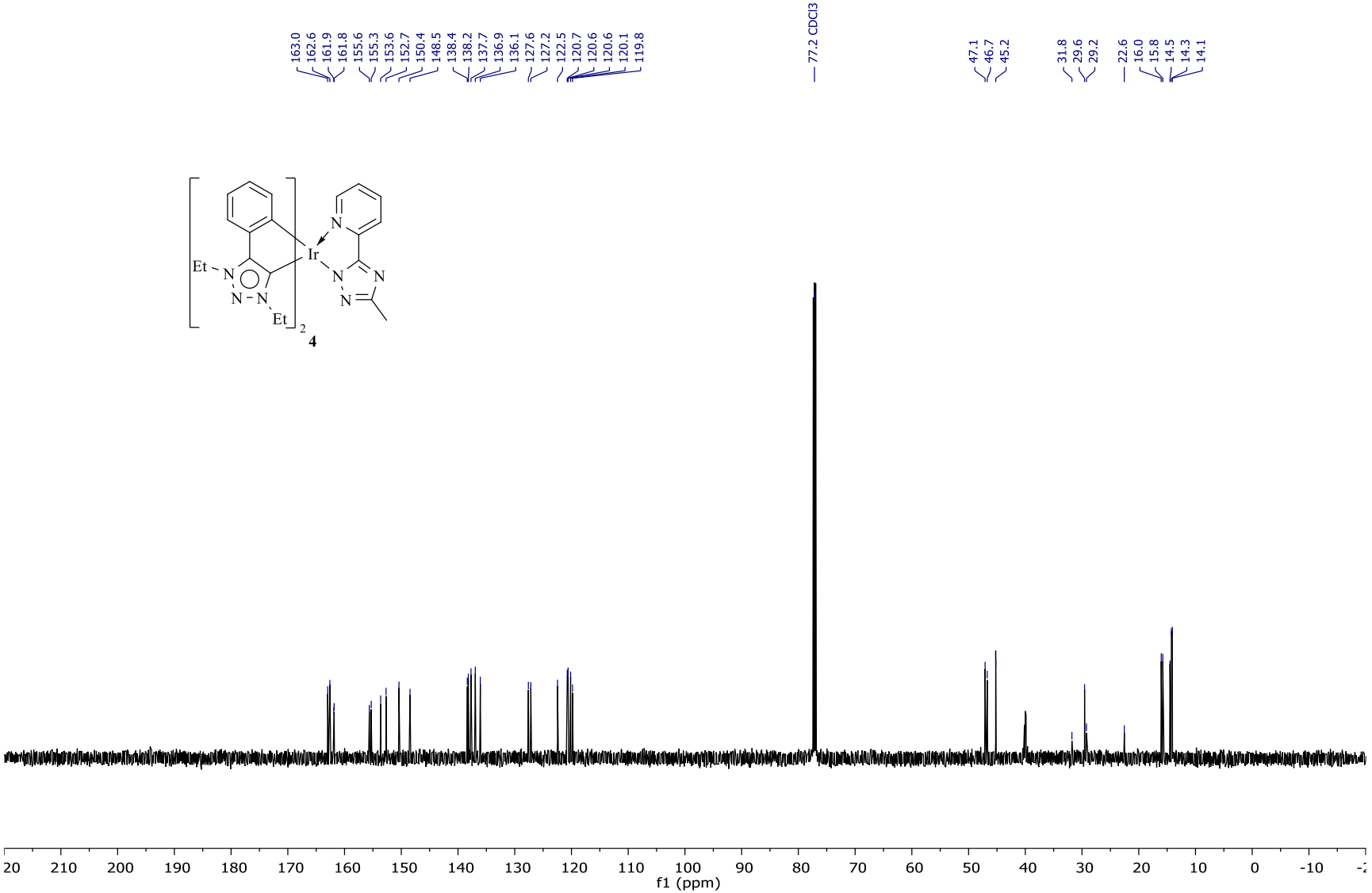


Figure S22 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of complex **4**.

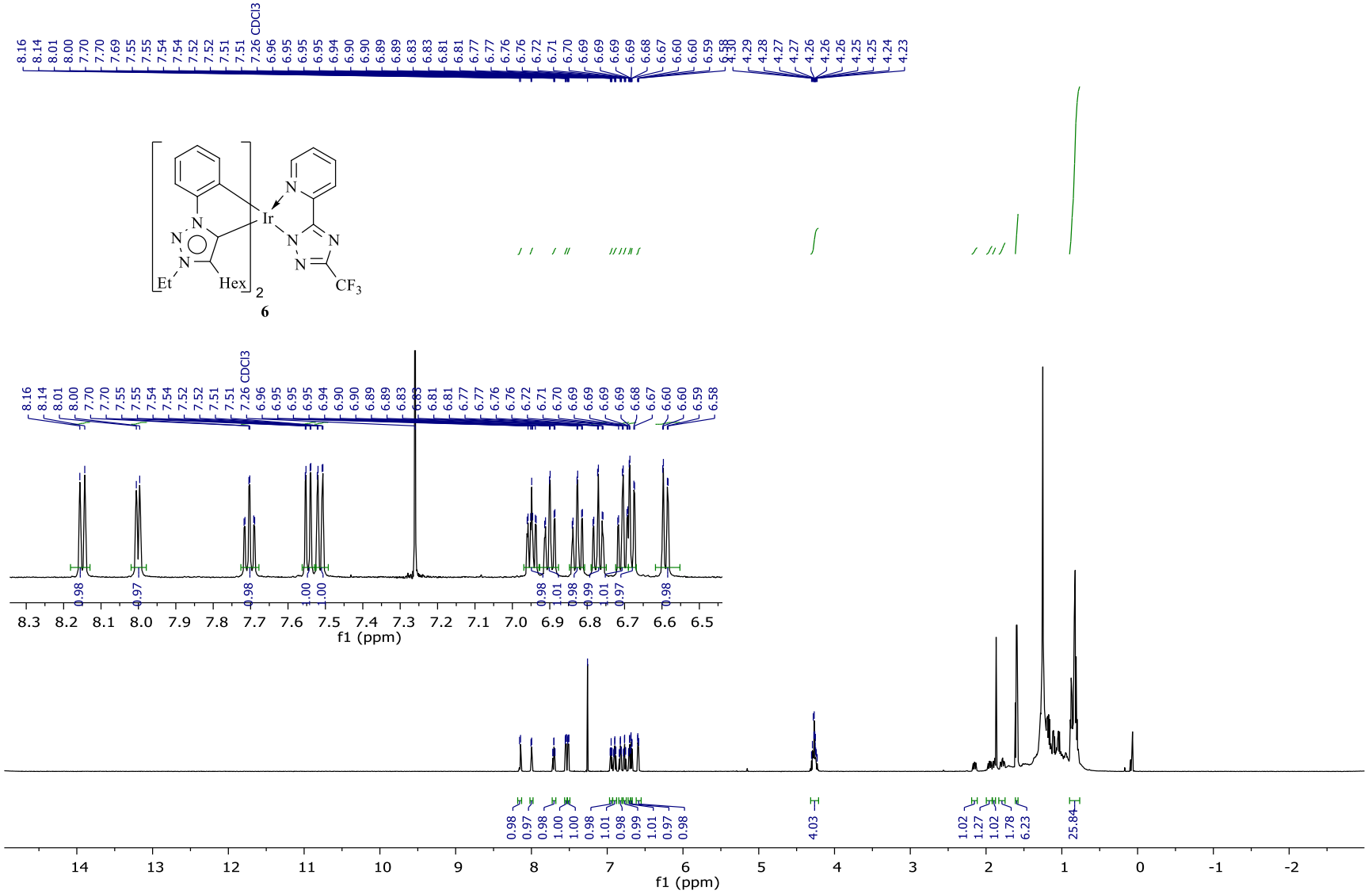


Figure S23 ^{1}H NMR (600 MHz, $CDCl_3$) of complex **6**.

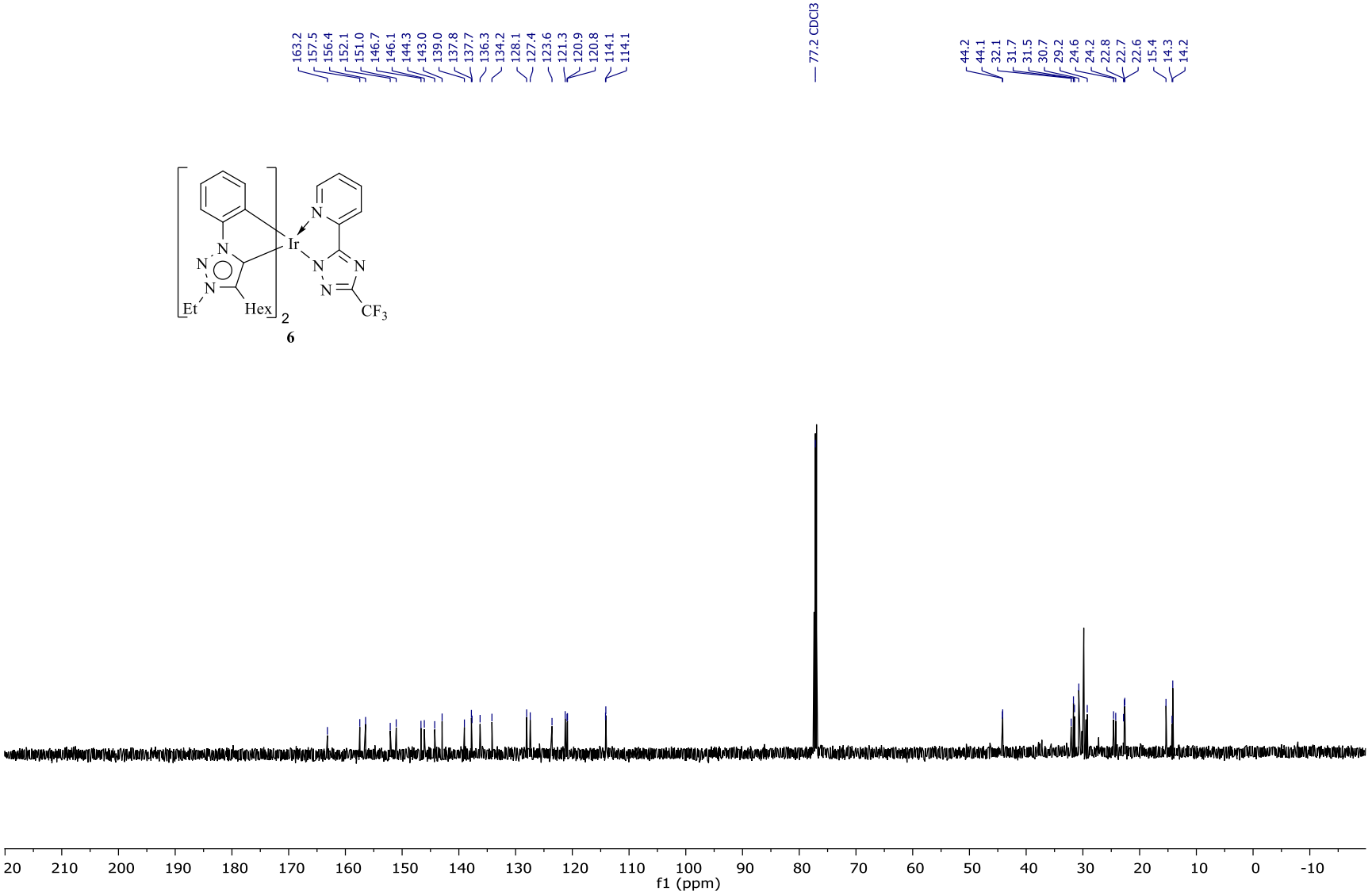


Figure S24 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of complex **6**.

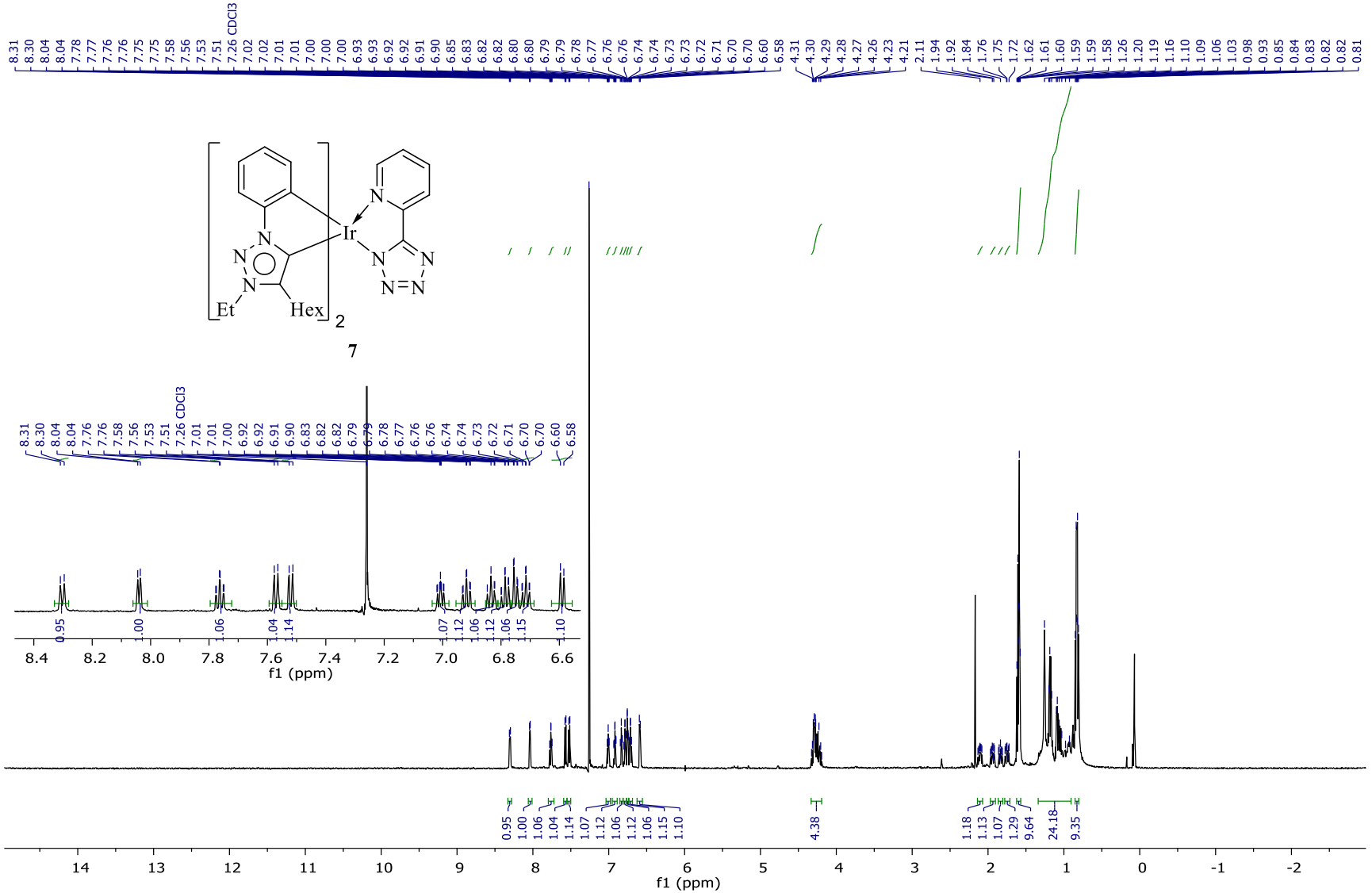


Figure S25 ^{1}H NMR (600 MHz, $CDCl_3$) of complex **7**.

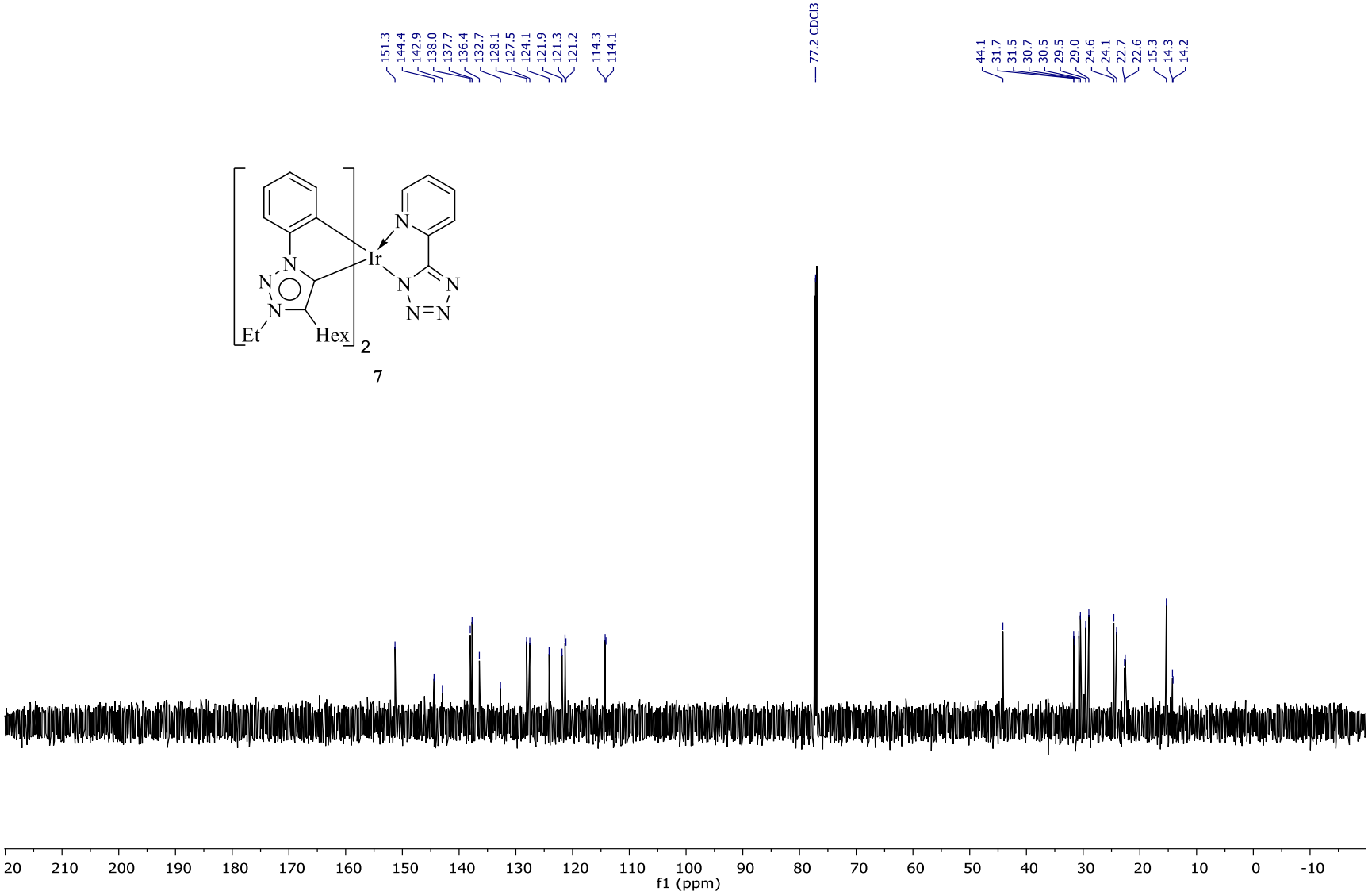


Figure S26 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of complex **7**.

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