Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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General Information

All chemical reagents obtained from commercial suppliers were used without further purification. All solvents were anhydrous grade and used as received. *trans*-6-Azido-5,6-dihydro-1,10-phenanthrolin-5-yl acetate **2**,[1] $[Ir(ppy)_2(phen–NH_2)][PF_6]$ **4a**,[2] $[Ir(ppy)_2(NCMe)_2][PF_6]$,[3] ppy-COOH,[4] phen-$NH_2$,[5] peg **S2**,[6] alkyne-tagged BSA,[7] and Yes-MBP[8] were prepared according to literature procedures. Triazole ligand THPTA (#1010) and TAMRA-NHS ester (#1074) were purchased from Click Chemistry Tools. Amino-DBCO (#761540), amino-BCN (#745073), and BCN NHS carbonate (#744867) were purchased from Sigma-Aldrich. Phosphate buffered saline (Hyclone, 1X, 0.0067 M phosphate, pH = 7.4, #SH30256.01) was purchased from Thermo Scientific.

NMR

NMR spectra were obtained on Bruker AVANCE 400 or AVANCE 500 spectrometers. Chemical shift are calibrated to residual solvent or tetramethylsilane (TMS).

MS spectrometry

ESI-MS was performed on a Bruker Daltonics MicroToF spectrometer.

Optical spectroscopy

Absorption spectra were recorded on a Shimadzu UV-2450 UV-Vis spectrometer. Steady-state photoluminescence spectra were recorded on a Horiba-Jovin Yvon Fluorolog 3. Samples were excited at 420 nm and emission was measured from 450 to 830 nm. Compounds on blot membrane were excited at 370 nm. Quantum yield was determined using a standard of known quantum yield ($[Ru(bpy)_3]Cl_2$ in water, $\Phi = 0.04$).[9] The photoluminescence lifetime measurement for both solution sample and blot membrane was performed on an Edinburgh Instruments OD470 single-photon counting spectrometer equipped with a high speed red detector and a 370 nm picosecond pulse diode laser.

Imaging of blot membrane and SDS-PAGE

SDS-PAGE was performed following a protocol from Life Technologies (https://tools.lifetechnologies.com/content/sfs/manuals/MAN0007891_NuPAGE_BisTris_MiniGels.pdf). Protein solution was loaded to polyacrylamide gel (NuPage Novex 4-12% Bis-Tris Protein Gels, LieTechnologies) with loading buffer (NuPage, 4X LDS sample buffer, LifeTechnologies). The mixture was separated by gel electrophoresis (1X MOPS buffer, 200V, 50-60 min) and transferred to a membrane (Low-Fluorescence poly(vinyledene) fluoride (PVDF) Transfer Membrane, pore size 0.2 μm, 7 cm × 8.4 cm, Thermo Scientific) under 24 mV for 30 min. Imaging was performed on a Fujifilm LAS-4000 instrument using an epi-UV light source (370 nm LED) and a long pass filter at 515 nm (Y515) for fluorescence imaging.

Plate-Reader Fluorescence Experiment

Reactions were conducted in a 96-well microtiter plate and measurements were made using BioTek Synergy 4 Hybrid Plate Reader. For copper-catalyzed reaction, 2 mM sodium ascorbate, 500 μM THPTA, 1 mM pentynoic acid, 100 μM Ir complex, and 1 mM $CuSO_4$ were mixed in each well. For copper-free reactions, a 10 mM stock solution of cyclooctynes in DMSO was put into a mixture of PBS buffer and ^{t}BuOH and then the bisulfate azido complex **5d** (2 μL, 200 μmol of 10 mM stock solution in DMSO) was added for a final concentration of 100 μM (PBS/^{t}BuOH/DMSO = 75:18:7). Total reaction volume in each well was 200 μL of solution. The plate was continuously shaken during reactions. Compounds were excited at 370 nm and emission was collected at 600 nm.

Click chemistry of alkyne-tagged BSA with 5b

Alkyne-tagged BSA (7 μM) was incubated with sodium ascorbate (2 mM), THPTA (500 μM), carboxyazido Ir complex **5b** (100 μM), and copper sulfate (1 mM) in PBS buffer/DMSO (95:5) at rt overnight. Specifically, alkyne-tagged BSA (5 μL, 0.65 nmol of 130 μM aqueous solution) was mixed with 2 μL of 100 mM sodium ascorbate (2 μL, 0.2 μmol of 100 mM aqueous solution), THPTA (0.5 μL, 0.05 μmol of 100 mM aqueous solution), carboxyazido Ir complex **5b** (1 μL, 10 nmol of 10 mM DMSO solution), PBS buffer (86.5 μL), and DMSO (4 μL). the reaction mixture (1.2 μL) was mixed with 4X loading buffer (2.5 μL) and water (6.3 μL), loaded to acrylamide gel, and separated by electrophoresis (55 min, 200 V) and visualized by Coomassie staining or fluorescence imaging after transfer to blot membrane.

Preparation of MBP-TAMRA

Yes-MBP (130 μL, 8.1 nmol of 62.5 μM aqueous solution) was mixed with TAMRA-NHS ester (8 μL, 80.0 nmol of 10 mM aqueous solution) in PBS buffer at 4 °C overnight. The reaction mixture was diluted with Tris buffer and concentrated using Amicon Ultra-0.5 mL centrifugal filter (MWCO: 3kDa). The dilution and filtration were repeated four times. The concentration of the solution was determined by NanoDrop UV-vis spectroscopy based on absorbance of TAMRA (544 nm).

Preparation of the membrane with BSA-Ir and MBP-TAMRA

BSA-Ir (1.2 μL, 8.4 nmol of 7 μM aqueous solution) and MBP-TAMRA (2.25 μL, 0.084 nmol of 37.3 μM aqueous solution) were mixed with loading buffer (2.5 μL), water (3.55 μL), and XT reducing agent 20X (0.5 μL , Bio-Rad). After heating in boiling water for 2 min., the mixture was loaded to SDS-PAGE, separated by gel electrophoresis (55 min. 200 V), transferred to blot membrane, and imaged using an LAS-4000 imager.

Mammalian cell imaging

Human bone osteosarcoma epithelial (U2OS) cells were grown in DMEM (Life Technologies #11995065) supplemented with 10% fetal bovine serum (Life Technologies #10082147), penicillin-streptomycin (1,000 U/mL, Life Technologies #15140122), and non-essential amino acids (Life Technologies #11140050). The cells were washed with PBS buffer (3 × 1 mL) and incubated with BCN-NHS carbonate (500 μM) in PBS buffer (pH = 8.0) at 4 °C for 30 min. Specifically, freshly prepared BCN-NHS carbonate solution in (50 μL, 0.5 μmol of 10 mM DMSO solution) was added to the well filled with the PBS buffer (1 mL). The cells were washed with PBS buffer (3 × 1 mL), and then fixed with 4% paraformaldehyde in PBS buffer for 15 min at rt. The fixed cells were washed with PBS buffer (3 × 1 mL) and incubated with iridium complex (50 μM) in PBS buffer (500 μL) for 30 min at rt

in the dark. Specifically, iridium complex **5a**, **5b**, or **5d** (2.5 μL, 25 nmol of 10 mM DMSO solution) was added to the well filled with the PBS buffer. The cells were washed with PBS buffer (3 × 1 mL) and mounted onto a cover slide with ProLong Gold Antifade Mountant (Life Technologies #P36934), covered with CoverGrip (Biotium #23005), and imaged with confocal microscopy.

Fluorescence microscopy

Mammalian cell imaging was performed on a Nikon A1Rsi Confocal microscope (Nikon, Tokyo, Japan) using a Nikon CFI Apo Lambda 40X (NA 1.15) water-immersion objective lens (Nikon, Tokyo, Japan). A 405 nm laser was used for excitation, and emission was detected after passage through a band-pass filter, 561 nm to 640 nm (Chroma Technologies, Bellow Falls, VT). Pinhole size was set at 1 AU. Imaging under two-photon excitation was performed on a Nikon Eclipse FN1 Multiphoton microscope using Nikon 25X water-dipping objective lens with NA 1.15 (Nikon, Tokyo, Japan). Samples were excited using pulsed 860 nm laser and emission was detected after passage through a band-pass filter from 601 nm to 657 nm (Chroma Technologies, Bellow Falls, VT).

Supplementary figures

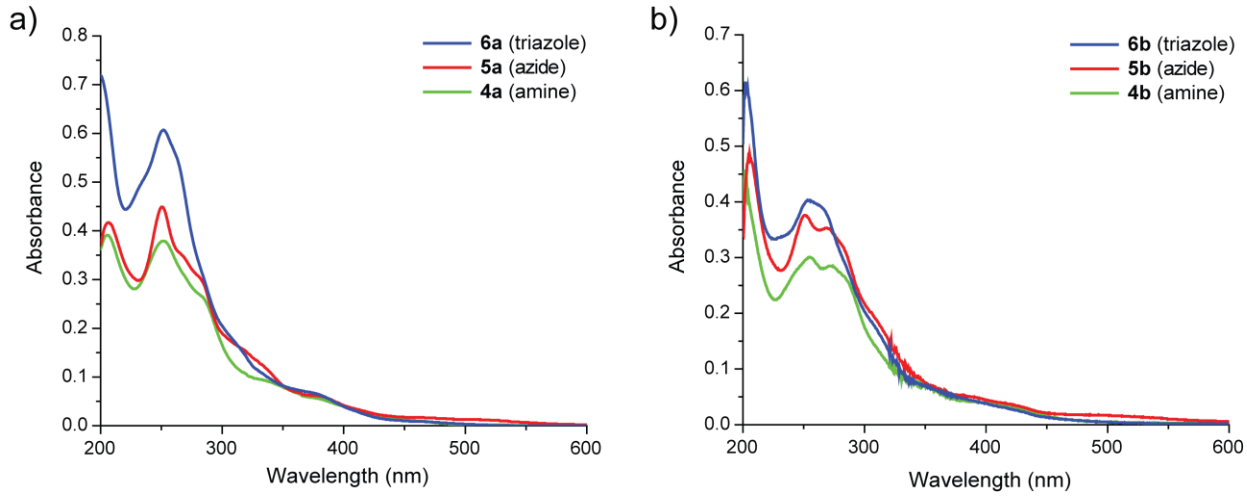


Figure S1. Absorption spectra of a) complexes **4a**, **5a**, and **6a** in PBS buffer/MeOH (4:1) b) carboxylate-containing complexes **4b**, **5b**, and **6c** in PBS buffer/MeOH (95:5).

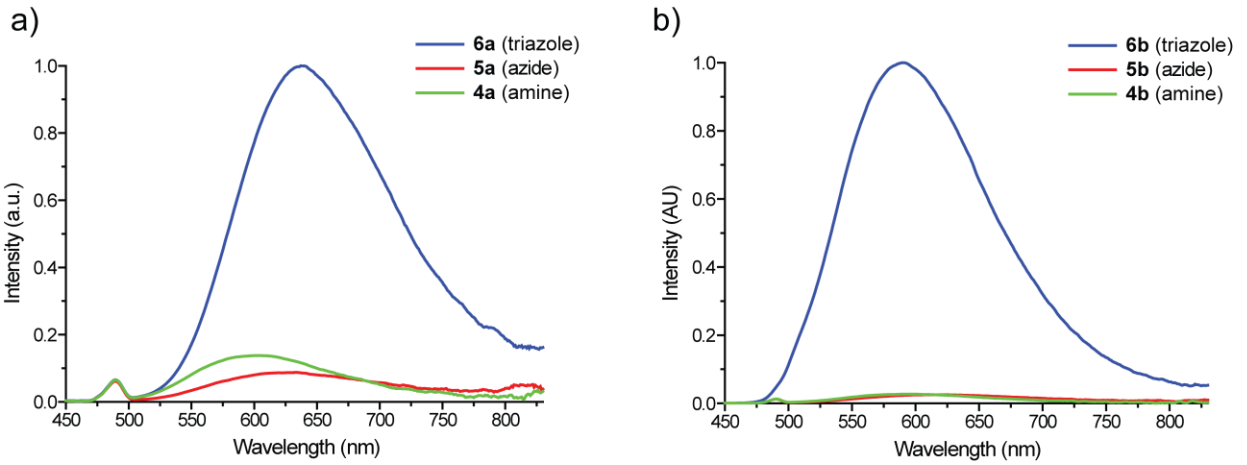


Figure S2. Emission spectra of a) complexes **4a**, **5a**, and **6a** in PBS buffer/MeOH (4:1) b) carboxylate-containing complexes **4b**, **5b**, and **6c** in PBS buffer/MeOH (95:5). All complexes were excited at 420 nm.

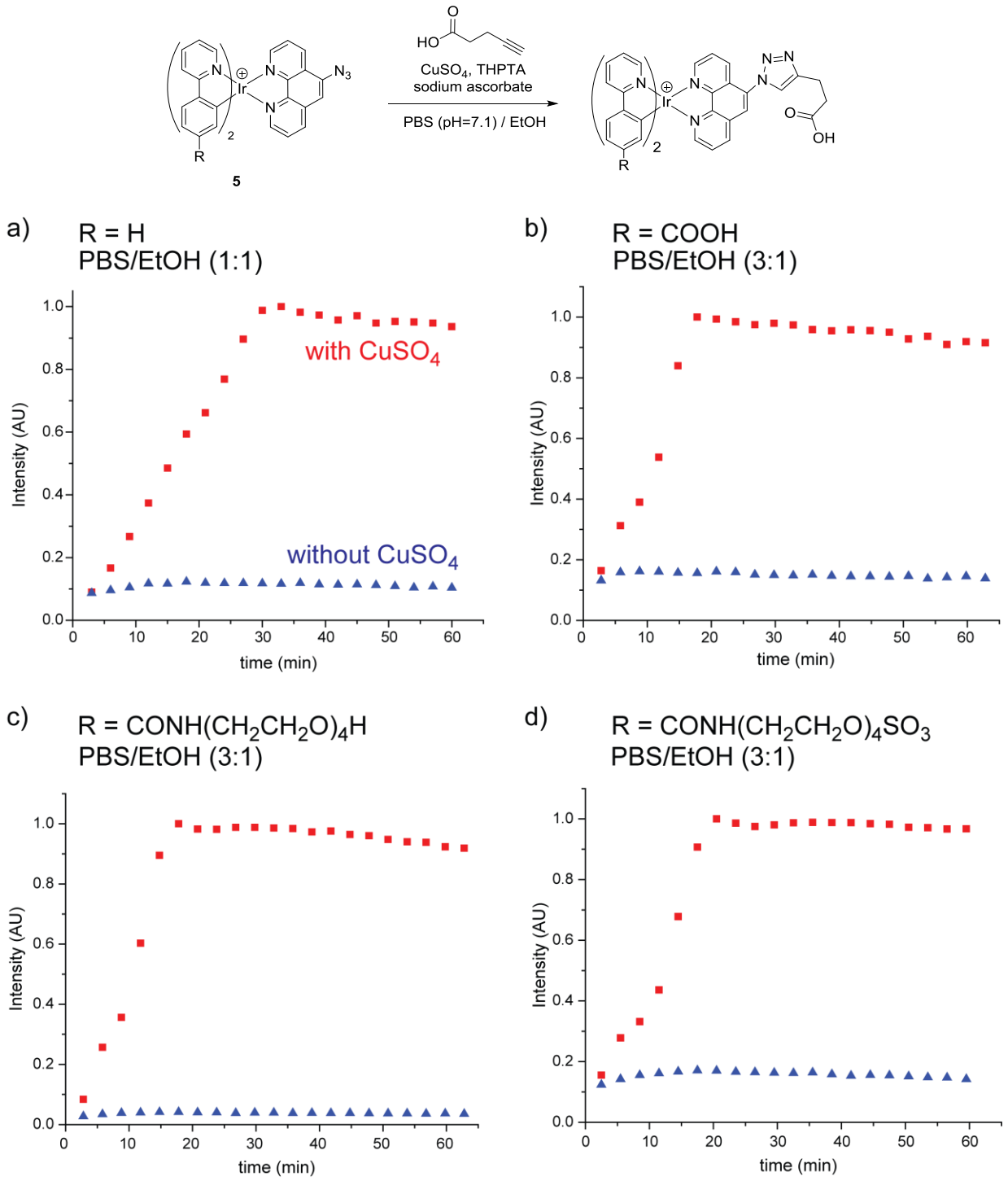


Figure S3. Kinetics of azide-alkyne cycloaddition between complexes **5a-5d** and pentynoic acid with (red rectangular) and without (blue triangle) a copper catalyst ($CuSO_4$). The photoluminescence enhancement was measured by microplate reader. The solution was excited at 370 nm and emission was measured at 600 nm every 3 min.

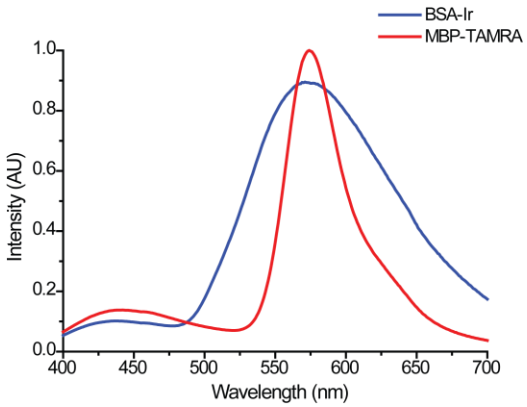


Figure S4. Steady-state emission curves of BSA-Ir (blue line) and MBP-TAMRA (red line) on blot membrane. Both compounds were excited at 370 nm. The broad, weak emission near 450 nm was observed even for blank membrane.

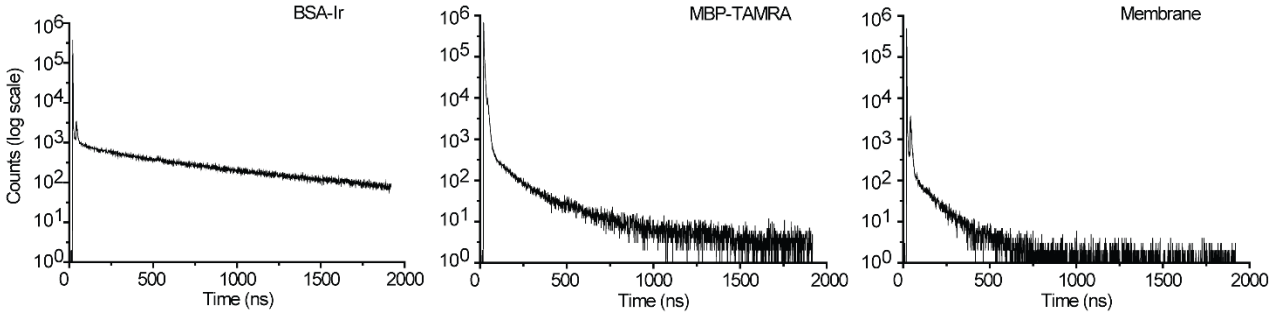


Figure S5. Lifetime decay curves of BSA-Ir, MBP-TAMRA, and a negative-control membrane (no emitter) on PVDF membrane. A 370 nm laser was used for excitation and the emission was collected at 570 nm.

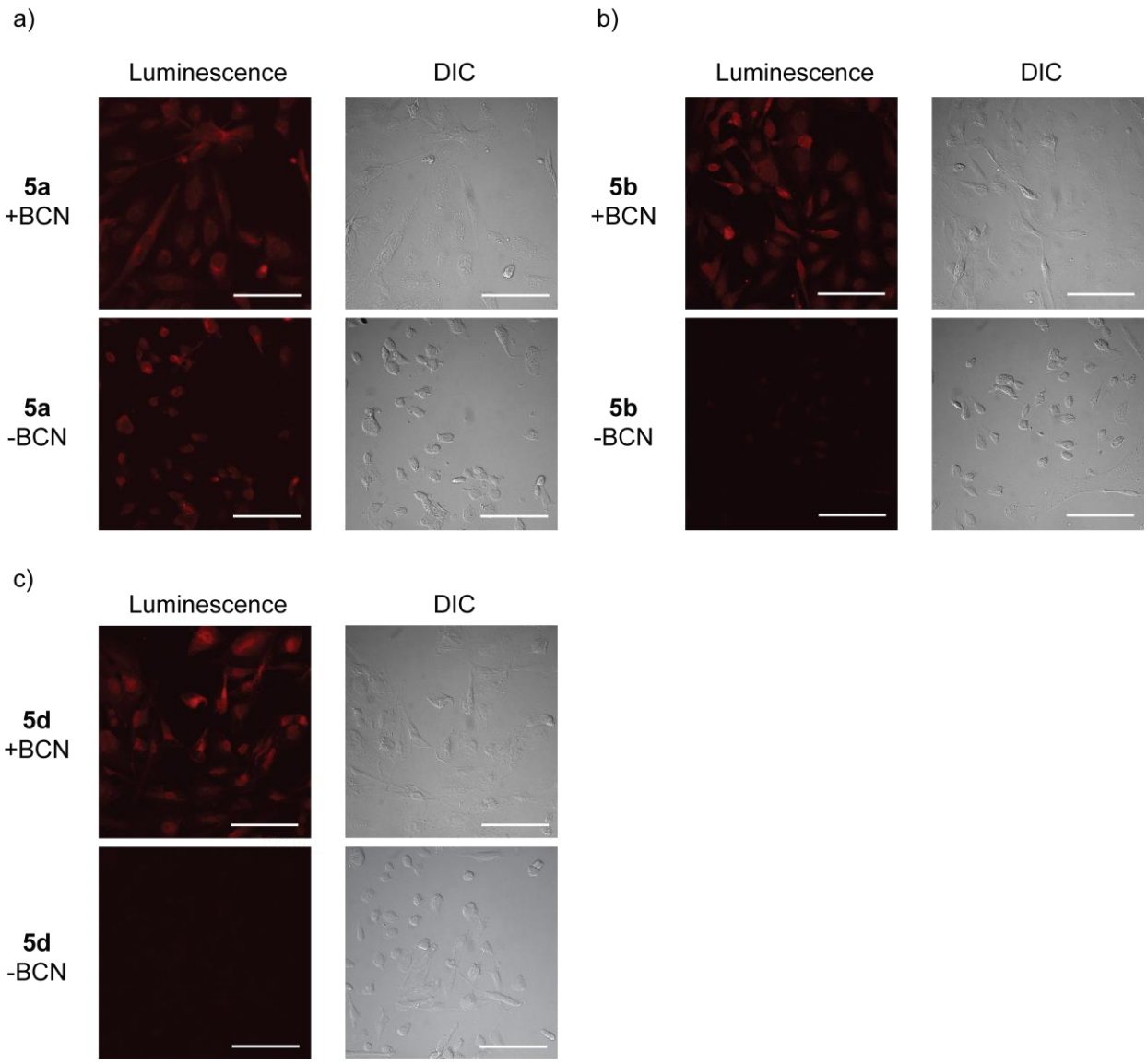
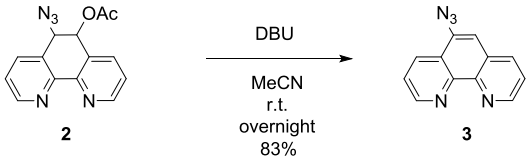


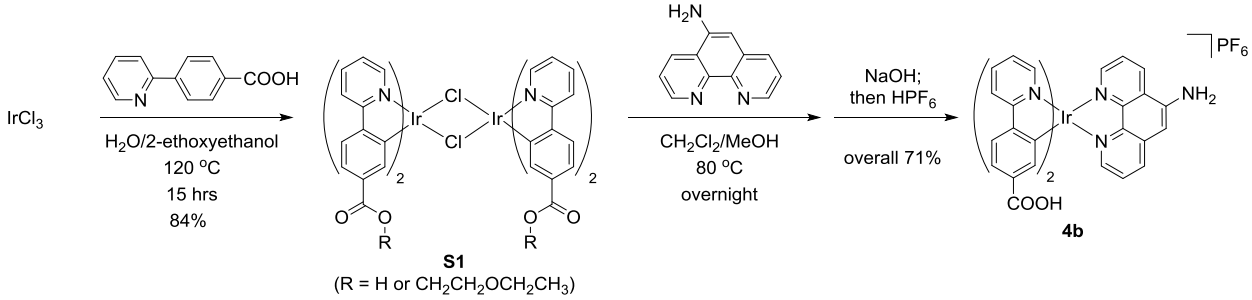
Figure S6. Photoluminescence and bright-field images of U2OS cells treated with a) parent azide complex **5a**, b) carboxyazido complex **5b**, and c) bisulfate complex **5d** by using single-photon excitation. Scale bar: 100 μm.

Synthesis of compounds



5-azido-1,10-phenanthroline 3

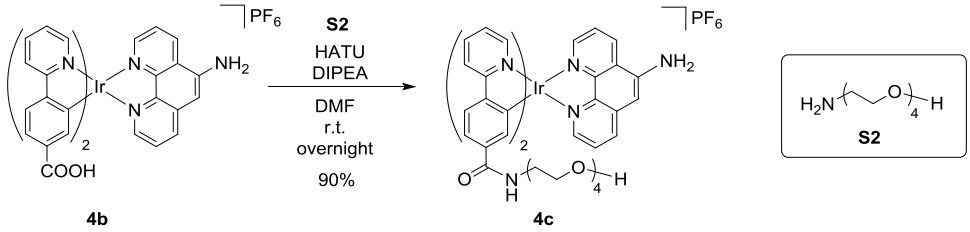
Azido-acetate **2** (95.0 mg, 0.338 mmol) was placed in a 10-mL round bottom flask capped with a rubber septum. Dry acetonitrile (2 mL) and 1,8-diazabicycloundec-7-ene (75 μL, 0.492 mmol) were added and the reaction mixture stirred overnight at rt. The mixture was diluted with water and product extracted with ethyl acetate. Extracts were combined and washed with brine. All volatiles were removed under reduced pressure to obtain a yellow solid (62.0 mg, 83%). IR (neat, cm^{-1}): 2111; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.23 (dd, *J* = 4.2, 1.7 Hz, 1H), 9.12 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.54 (dd, *J* = 8.2, 1.7 Hz, 1H), 8.17 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.65 (m, 2H), 7.48 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 151.4, 149.8, 146.7, 144.3, 135.5, 134.8, 131.5, 128.4, 123.7, 123.4, 123.2, 112.4. ESI-MS: *m/z* calcd for $C_{12}H_8N_5$ $[M+H]^+$ 222.1, found 222.0.



[Ir(ppy-COOH)$_2$(phen-NH$_2$)][PF$_6$] 4b

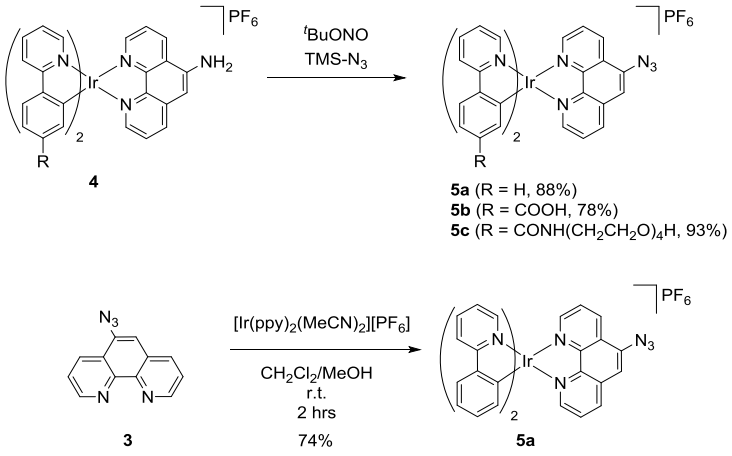
Iridium chloride hydrate (165 mg, 0.467 mmol) and ppy-COOH (185 mg, 0.931 mmol) were suspended in a mixture of water (1.5 mL) and 2-ethoxyethanol (5.5mL). The mixture was stirred at 120 °C for 15 h. After cooling to rt, the precipitate was separated by centrifugation and the residue was washed with H_2O (3 × 14 mL) and ethanol (7 mL). The solid obtained was transferred to a round bottom flask with chloroform and solvent was removed in vacuo to afford an orange solid of **S1** as mixture of 2-ethoxyethyl ester and carboxylic acid (299 mg, 84%). The ratio of ester to carboxylic acid was determined by ^{1}H NMR in acetone-d_6. Additional product could be obtained from the ethanol soln produced from the washing step after dryin under vacuum and washing the solid thus obtained with water and ethanol, giving an orange solid. Dimer **S1** (359 mg, 0.258 mmol) and phen-NH_2 (102 mg, 0.522 mmol) were dissolved in CH_2Cl_2/MeOH (1:1, total 40 mL). The reaction mixture was stirred at reflux overnight under N_2 atmosphere in the dark. After cooling to rt, solvent was removed under vacuum. To the dark yellow suspension of the crude mixture in MeOH/H_2O (2:1, total 6 mL), aq NaOH (2 N, 2 mL) was added and stirred for 24 h at rt. The dark yellow suspension was concentrated to ~5 mL under vacuum and aq HPF_6 (15 mL, 6% by wt) was added to form yellow precipitate. The precipitate was collected by centrifugation and washed with the HPF_6 soln (total 30 mL). The solid was dissolved in MeOH (50 mL), dried over Na_2SO_4, filtered, and concentrated to ~5 mL under vacuum. Upon addition of ether (50 mL), a dark green precipitate formed, was filtered, was washed with ether (2 × 50 mL), and was dried in vacuo. The solid was dissolved in MeCN (50 mL) and passed through Celite to remove a black residue. Drying under vacuum afforded **4b** as a yellow powder (342 mg, 71%). ^{1}H NMR (500 MHz, CD_3CN): δ 9.22 (br, 2H), 8.69 (dd, *J* = 8.6, 1.3 Hz, 1H), 8.27 (m, 2H), 8.16 (d, *J* = 8.3 Hz, 2H), 7.89 (m, 5H), 7.79 (m, 1H), 7.69 (m, 2H), 7.58 (m, 1H), 7.52-7.47 (m, 2H), 7.19 (s, 1H), 6.96 (m,

4H), 5.56 (br, 2H). ^{1}H NMR (500 MHz, CD_3OD/D_2O (3:1)): δ 8.89 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.25 (m, 4H), 7.91 (m, 5H), 7.81 (m, 1H), 7.64 (m, 2H), 7.57 (m, 1H), 7.50 (m, 2H), 7.21 (s, 1H), 7.05 (m, 4H), 7.05 (m, 3H). ^{13}C{^{1}H} NMR (125 MHz, CD_3OD/D_2O (3:1)): δ 170.27, 170.25, 167.70, 167.63, 151.8, 150.7, 150.27, 150.24, 150.20, 150.1, 148.7, 147.2, 146.3, 142.0, 140.1, 136.8, 134.9, 133.6, 133.5, 132.3, 132.2, 127.6, 126.6, 125.84, 125.78, 125.69, 125.62, 125.5, 125.4, 122.27, 122.24, 104.7. ESI-MS: *m/z* calcd for $C_{36}H_{25}IrN_5$ $[M]^+$ 784.2, found 784.2.



[Ir(ppy-CONH(CH$_2$CH$_2$O)$_4$H)$_2$(phen-NH$_2$)][PF$_6$] 4c

To a soln of [Ir(ppy-COOH)$_2$(phen-NH$_2$)][PF$_6$] (**4b**) (80.0 mg, 0.086 mmol) and peg **S2** (50.7 mg, 0.263 mmol) in DMF (1 mL), HATU (83.0 mg, 0.218 mmol) and *i*-Pr$_2$EtN (45 μL, 0.258 mmol) were added at 0 °C and stirred for 10 min at the same temperature. Then, the mixture was stirred overnight at rt. All volatiles were removed in vacuo and the residue was dissolved in CH_2Cl_2 (10 mL). The soln was washed with sat aq $NaHCO_3$ (2 × 5 mL) and brine (5 mL), dried over Na_2SO_4, and filtered through a pad of Celite. After removal of the volatiles, the solid was reprecipitated with MeOH/ether (1 mL/40 mL) and the precipitate was collected by centrifugation. The reprecipitation and centrifugation were repeated with MeCN/ether (1 mL/40 mL) and the resulting solid was transferred to round bottom flask with MeCN. Removal of the solvent under vacuum afforded **4c** as a yellow oil (98 mg, 90%). ^{1}H NMR (500 MHz, CD_3CN): δ 8.69 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.26 (m, 2H), 8.09 (d, *J* = 8.1 Hz, 2H), 7.85 (m, 6H), 7.56 (m, 1H), 7.50 (m, 1H), 7.45 (m, 1H), 7.40 (m, 2H), 7.18 (s, 1H), 7.07 (m, 2H), 6.93 (m, 2H), 6.74 (m, 2H), 5.59 (br, 2H), 3.50 (m, 24H), 3.39 (m, 8H), 3.02 (br, 2H). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN): δ 168.19, 168.17, 167.37, 168.32, 152.1, 151.0, 150.6, 148.5, 148.2, 148.1, 147.6, 145.5, 142.1, 139.6, 136.88, 136.84, 136.4, 134.3, 134.2, 131.3, 131.1, 127.5, 126.5, 125.60, 125.54, 125.52, 125.19, 125.12, 122.3, 122.2, 121.6, 104.5, 73.2, 71.14, 71.09, 70.83, 70.80, 70.18, 61.9, 40.3. ESI-MS: *m/z* calcd for $C_{52}H_{59}IrN_7O_{10}$ $[M]^+$ 1134.4, found 1134.0.



[Ir(ppy)$_2$(phen-N$_3$)][PF$_6$] 5a

$[Ir(ppy)_2(phen\text{-}NH_2)][PF_6]$ (**4a**) (147 mg, 0.175 mmol) was dissolved in MeCN (2 mL). *tert*-Butyl nitrite (25 μL, 0.210 mmol) and trimethylsilyl azide (28 μL, 0.210 mmol) were added at –40 °C. The soln was stirred at the same temperature for 60 min in the dark. Ether (30 mL) was added to form red precipitate. The precipitate was filtered and washed with ether (3 × 5 mL). Drying in vacuo afforded **5a** as a dark red powder (133 mg, 88%).

Alternatively, **5a** can be prepared from azidophenanthroline **3** and $[Ir(ppy)_2(NCMe)_2][PF_6]$. Briefly, $[Ir(ppy)_2(NCMe)_2][PF_6]$ (28.5 mg, 0.039 mmol) was dissolved in $MeOH/CH_2Cl_2$ (1:1, total 2 mL) and **3** (8.6 mg, 0.039 mmol) was added. The reaction was stirred at rt for 2 h in the dark and then concentrated under reduced pressure. The concentrated soln was added dropwise into ether to form precipitate. The precipitate was separated by centrifugation and then washed with ether (3 × 5 mL). Drying in vacuo afforded **3** as a dark orange solid (25.1 mg, 74%). ^{1}H NMR was identical to the product obtained via the diazotization route. ^{1}H NMR (500 MHz, CD_3CN): δ 8.74 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.57 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.33 (dd, *J* = 5.0, 1.4 Hz, 1H), 8.20 (dd, *J* = 5.0, 1.4 Hz, 1H), 8.05 (m, 3H), 7.80 (m, 6H), 7.44 (m, 2H), 7.06 (m, 2H), 6.96 (m, 2H), 6.88 (m, 2H), 6.37 (m, 2H). $^{13}C\{^1H\}$

NMR (125 MHz, CD_3CN): δ 168.38, 168.36, 153.0, 151.2, 150.6, 150.47, 150.46, 150.41, 148.4, 145.6, 145.26, 145.23, 139.5, 139.1, 138.0, 134.6, 132.7, 132.6, 132.1, 131.32, 131.31, 128.2, 127.9, 127.1, 125.84, 125.82, 124.4, 124.3, 123.64, 123.62, 120.8, 115.0. ESI-MS: *m/z* calcd for $C_{34}H_{23}IrN_7$ $[M]^+$ 722.2, found 721.9.

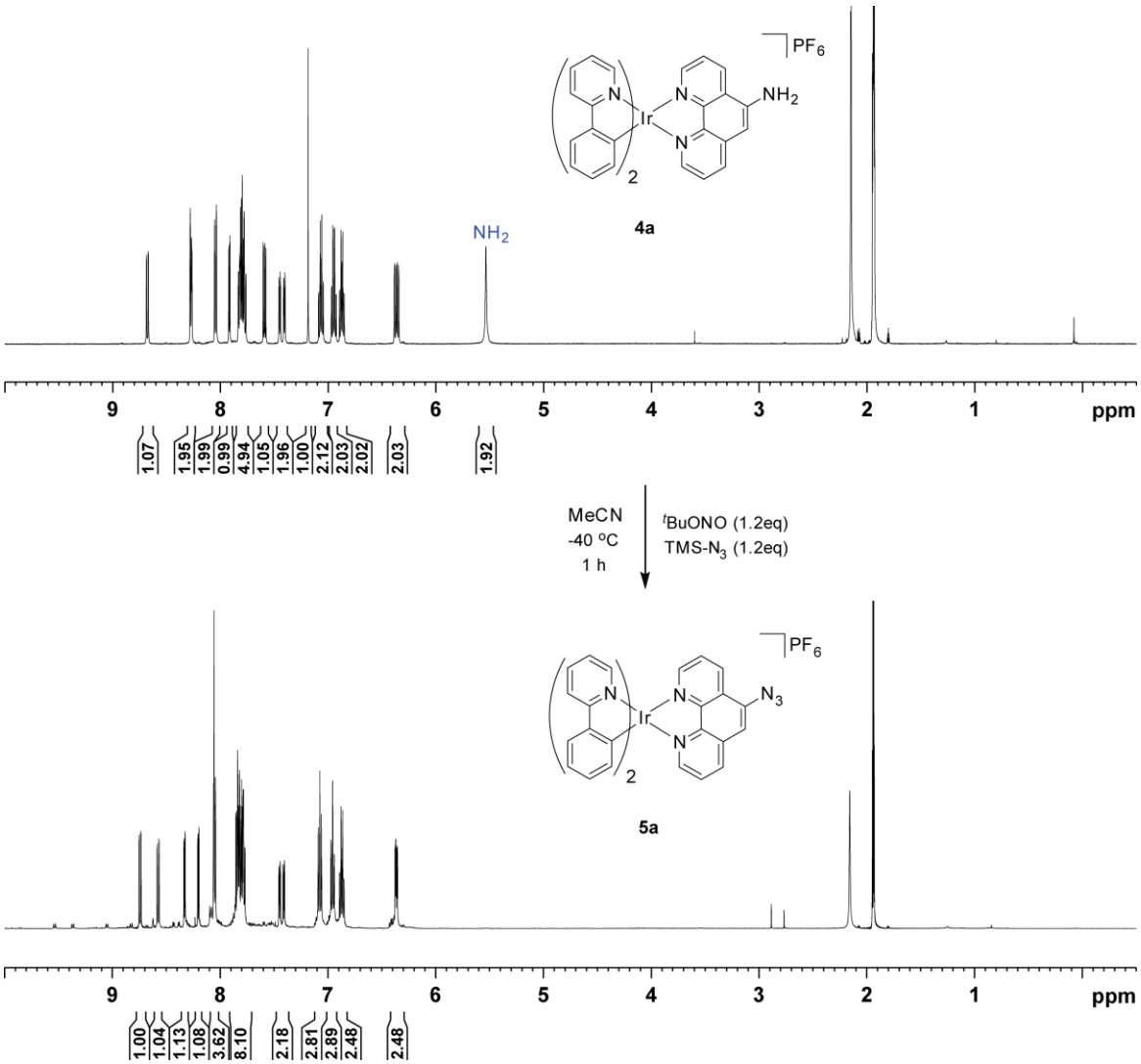


Figure S7. ^{1}H NMR spectra of parent amine complex **4a** and azide complex **5a** in CD_3CN. Upon conversion of amine to azide group, a broad peak at 5.5 ppm disappeared.

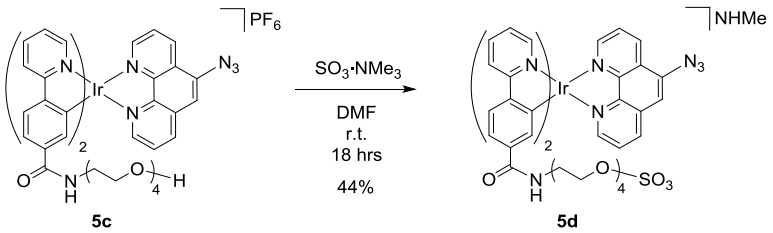
[Ir(ppy-COOH)$_2$(phen-N$_3$)][PF$_6$] 5b

[Ir(ppy-COOH)$_2$(phen-NH$_2$)][PF$_6$] (**4b**) (50.9 mg, 0.055 mmol) was dissolved in MeCN/DMF (9:1, total 600 μL). *tert*-Butyl nitrite (26 μL, 0.220 mmol) and trimethylsilyl azide (15 μL, 0.110 mmol) were added at –40 °C. The soln was stirred with warming to 0 °C for 80 min in the dark. Upon addition of ether (20 mL) to the reaction mixture, a red precipitate formed. The precipitate was filtered, reprecipitated with MeOH/ether (1 mL/20 mL), and washed with ether (2 × 20 mL). Drying in vacuo afforded **5b** as a red powder (40.6 mg, 78%). ^{1}H NMR (500 MHz, CD_3CN): δ 9.25 (br, 2H), 8.76 (dd, *J* = 8.5, 1.4 Hz, 1H), 8.59 (dd, *J* = 8.4, 1.3 Hz, 1H), 8.32 (dd, *J* = 5.0, 1.4 Hz, 1H), 8.18 (m, 3H), 8.07 (s, 1H), 7.84 (m, 6H), 7.70 (m, 2H), 7.49 (m, 2H), 6.97 (m, 4H). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.82 (d, *J* = 8.3 Hz, 2H), 8.40 (m, 3H), 8.26 (d, *J* = 4.6 Hz, 1H), 8.04 (m, 7H), 7.59 (m, 4H), 7.11 (m, 2H), 6.89 (d, *J* = 2.0 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ 167.3, 165.51, 165.46, 151.9, 149.9, 149.8, 149.7, 148.8, 148.6, 148.50, 148.47, 146.7, 143.9, 139.3, 137.6, 137.4, 134.0, 131.82, 131.76, 131.3,

130.9, 127.7, 127.6, 125.6, 125.1, 125.0, 124.0, 121.3, 114.8. ESI-MS: *m/z* calcd for $C_{36}H_{23}IrN_7$ $[M]^+$ 810.1, found 810.2.

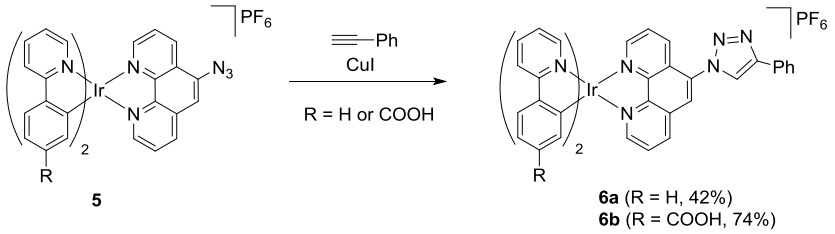
[Ir(ppy-CONH(CH_2CH_2O)$_4$H)$_2$(phen-N_3)][PF_6] 5c

[Ir(ppy-CONH(CH_2CH_2O)$_4$H)$_2$(phen-NH_2)][PF_6] (**4c**) (44.2 mg, 0.035 mmol) was dissolved in MeCN (600 μL). *tert*-Butyl nitrite (17 μL, 0.140 mmol) and trimethylsilyl azide (9 μL, 0.070 mmol) were added at –40 °C and the soln was stirred for 60 min with warming to 0 °C in the dark. Ether (10 mL) was added to form a red precipitate. The precipitate was filtered, washed with ether (10 mL), reprecipitated with MeOH/ether (1 mL/10 mL), and washed with ether (10 mL). Drying under vacuum afforded **5c** as red powder (41.0 mg, 90%). ^{1}H NMR (500 MHz, CD_3CN): δ 8.74 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.58 (dd, *J* = 8.4, 1.3 Hz, 1H), 8.32 (dd, *J* = 5.0, 1.3 Hz, 1H), 8.19 (dd, *J* = 5.0, 1.3 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 2H), 8.06 (s, 1H), 7.83 (m, 6H), 7.49 (m, 1H), 7.46 (m, 1H), 7.41 (m, 2H), 7.09 (m, 2H), 6.95 (m, 2H), 6.75 (m, 2H), 3.50 (m, 24H), 3.38 (m, 8H), 3.04 (br, 2H). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN): δ 168.1, 167.27, 167.25, 153.3, 151.4, 150.80, 150.75, 150.1, 150.0, 148.3, 148.20, 148.17, 145.5, 139.8, 139.1, 138.1, 136.91, 136.89, 134.8, 132.2, 131.23, 131.18, 128.3, 127.9, 127.2, 125.64, 125.61, 125.21, 125.18, 122.40, 122.36, 121.7, 115.1, 73.2, 71.14, 71.08, 70.83, 70.80, 70.2, 61.8, 40.3. ESI-MS: *m/z* calcd for $C_{52}H_{57}IrN_9O_{10}$ $[M]^+$ 1160.4, found 1160.0.



[Ir(ppy-CONH(CH_2CH_2O)$_4$$SO_3$)$_2$(phen-$N_3$)][$Me_3NH$] 5d

[Ir(ppy-CONH(CH_2CH_2O)$_4$H)$_2$(phen-N_3)][PF_6] (**5c**) (35.5 mg, 0.027 mmol) was placed in a 10-mL round bottom flask capped with a rubber septum, and dry DMF (500 μL) was added under nitrogen atmosphere. Shortly after the septum was removed, sulfur trioxide trimethylamine complex (18.2 mg, 0.131 mmol) was added to the soln in one portion. The flask was recapped and nitrogen gas was flowed through the flask for 1 min, and the reaction mixture stirred for 18 h at rt in the dark. The reaction mixture was put dropwise into acetone (12 mL), and the resulting red precipitate was collected by centrifugation. The obtained solid was dissolved in MeOH/MeCN (1:1, total 500 μL) and reprecipitated with acetone/ether (1:1, total 50 mL). The precipitate was collected by centrifugation, redissolved in MeOH/MeCN (1:1, 10 mL), filtered, dried in vacuo, affording the trimethylammonium salt of **5d** as a dark red solid (16.1 mg, 44%). ^{1}H NMR (500 MHz, CD_3OD/CD_3CN (95:5)): δ 8.80 (dd, *J* = 8.5, 1.4 Hz, 1H), 8.66 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.37 (dd, *J* = 5.1, 1.3 Hz, 1H), 8.24 (m, 3H), 8.11 (s, 1H), 7.95 (dd, *J* = 8.2, 2.2 Hz, 2H), 7.87 (m, 4H), 7.55 (m, 2H), 7.44 (m, 2H), 7.02 (m, 2H), 6.84 (dd, *J* = 4.8, 1.7 Hz, 2H), 4.04 (m, 4H), 3.59 (m, 24H), 3.41 (m, 4H), 2.87 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, CD_3OD/ CD_3CN (95:5)): δ 170.7, 167.75, 167.70, 153.3, 151.4, 150.69, 150.66, 150.3, 150.1, 148.90, 148.87, 148.6, 145.7, 140.0, 139.6, 138.7, 136.96, 136.95, 135.3, 132.6, 131.74, 131.68, 128.4, 128.0, 127.5, 125.91, 125.89, 125.6, 122.9, 122.11, 122.08, 115.3, 71.45, 71.44, 71.38, 71.37, 71.2, 70.5, 70.4, 68.0, 45.5, 40.8. ESI-MS: *m/z* calcd for $C_{52}H_{55}IrN_9O_{16}S_2$ $[M]^-$ 1318.3, found 1317.7.



[Ir(ppy)$_2$(phen-triazole-Ph)][PF$_6$] 6a

[Ir(ppy)$_2$(phen-N$_3$)][PF$_6$] (**5a**) (61.0 mg, 0.071 mmol) and CuI (6.4 mg, 0.033 mmol) were dissolved in MeCN (0.8 mL) and *i*-Pr$_2$EtN (0.3 mL). Phenylacetylene (7.7 μL, 0.071 mmol) was added and the reaction mixture was stirred at rt overnight in the dark. All volatiles were removed in vacuo and obtained solid was dissolved in EtOAc. The mixture was filtered through Celite and the residue was washed with EtOAc (total 100 mL). After drying with MgSO$_4$, the soln was concentrated under vacuum. Upon addition of ether, a yellow precipitate was formed, filtered, and washed with ether to give a yellow solid (29 mg, 42%). ^{1}H NMR (500 MHz, CD$_3$CN): δ 8.76 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.71 (s, 1H), 8.65 (dd, *J* = 8.6, 1.2 Hz, 1H), 8.54 (s, 1H), 8.41 (m, 2H), 8.05 (m, 4H), 7.90 (m, 6H), 7.51 (m, 5H), 7.08 (m, 2H), 6.97 (m, 2H), 6.91 (m, 2H), 6.39 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, CD$_3$CN): δ 168.34, 168.31, 153.5, 153.3, 150.65, 150.61, 150.5, 150.2, 148.9, 148.5, 147.9, 145.27, 145.26, 140.0, 139.6, 135.9, 134.6, 132.68, 132.66, 132.3, 131.36, 131.35, 131.07, 131.02, 130.1, 129.74, 129.69, 128.6, 128.52, 128.45, 126.7, 125.89, 125.87, 125.6, 124.44, 124.41, 123.7, 120.83, 120.82. ESI-MS: *m/z* calcd for C$_{42}$H$_{29}$IrN$_7$ [M]$^+$ 824.2, found 823.9.

[Ir(ppy-COOH)$_2$(phen-triazole-Ph)][PF$_6$] 6b

[Ir(ppy-COOH)$_2$(phen-N$_3$)][PF$_6$] (**5b**) (36.8 mg, 0.039 mmol) and CuI (12.8 mg, 0.067 mmol) were suspended in MeCN (300 μL), MeOH (300 μL) and *i*-Pr$_2$EtN (300 μL). Phenylacetylene (5.2 μL, 0.047 mmol) was added and the reaction mixture was stirred at rt overnight in the dark. The reaction mixture was precipitated with aq HPF$_6$ (40 mL, 6% by wt) and the precipitate was collected by centrifugation and washed with the aq HPF$_6$ (40 mL). The residue was dissolved in MeOH (50 mL), dried over Na$_2$SO$_4$, filtered, and dried under vacuum. The solid obtained was dissolved in acetone (70 mL), and the mixture was passed through Celite and dried in vacuo. The residue was reprecipitated with MeOH/ether (1 mL/40 mL), filtered, and washed with ether (40 mL) and CH$_2$Cl$_2$ (2 × 2mL), giving **6b** as a yellow solid (30.4 mg, 74%). ^{1}H NMR (500 MHz, CD$_3$CN/ DMSO-*d*$_6$ (95:5)): δ 12.25 (br, 2H), 8.82 (s, 1H), 8.79 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.68 (dd, *J* = 8.6, 1.3 Hz, 1H), 8.59 (s, 1H), 8.39 (m, 2H), 8.20 (m, 2H), 8.03 (m, 2H), 7.92 (m, 7H), 7.72 (m, 2H), 7.54 (m, 4H), 7.44 (m, 1H), 6.99 (m, 4H). ^{1}H NMR (500 MHz, CD$_3$OD/ DMSO-*d*$_6$ (95:5)): δ 9.01 (s, 1H), 8.81 (d, *J* = 8.0 Hz, 1H), 8.71 (dd, *J* = 8.6, 1.0 Hz, 1H), 8.62 (s, 1H), 8.45 (m, 2H), 8.29 (m, 2H), 7.97 (m, 9H), 7.70 (m, 4H), 7.53 (m, 2H), 7.45 (m, 1H), 7.10 (m, 4H).). ^{13}C{^{1}H} NMR (125 MHz, CD$_3$OD/ DMSO-*d*$_6$ (95:5)): δ 169.5, 167.63, 167.60, 153.6, 153.4, 150.9, 150.8, 150.1, 149.7, 149.5, 149.4, 148.6, 148.0, 140.8, 140.3, 136.6, 134.9, 133.7, 133.0, 132.4, 131.5, 131.2, 130.3, 129.99, 129.95, 128.85, 127.0, 126.1, 126.0, 125.9, 125.7, 124.9, 122.4, 118.3. ESI-MS: *m/z* calcd for C$_{44}$H$_{29}$IrN$_7$O$_4$ [M]$^+$ 912.2, found 912.0.

IR-spectrum

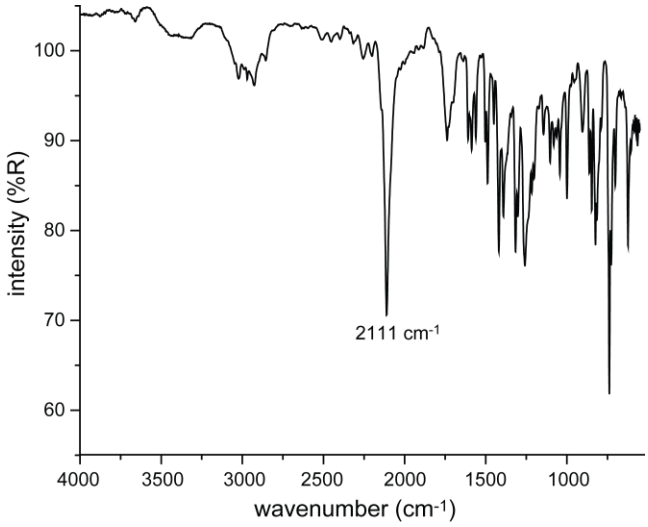


Figure S8. IR spectrum of 5-azidophenanthroline **3**. An azide stretch was observed at 2111 cm^{-1}.

ESI-MS

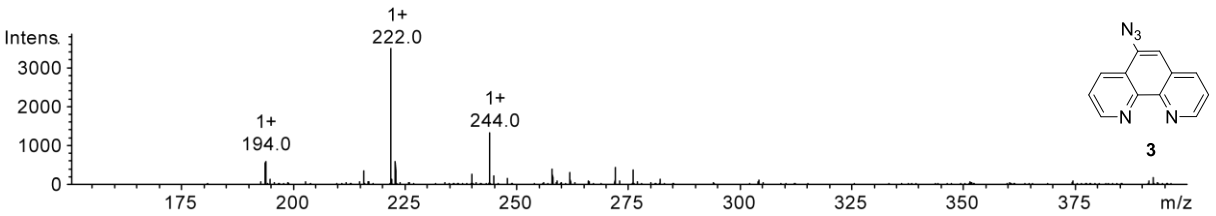


Figure S9. Azidophenanthroline **3** (positive mode). *m/z* 244.0, 222.0, and 194.0 correspond to $[M+Na]^+$, $[M+H]^+$,and $[M+H–N_2]^+$, respectively.

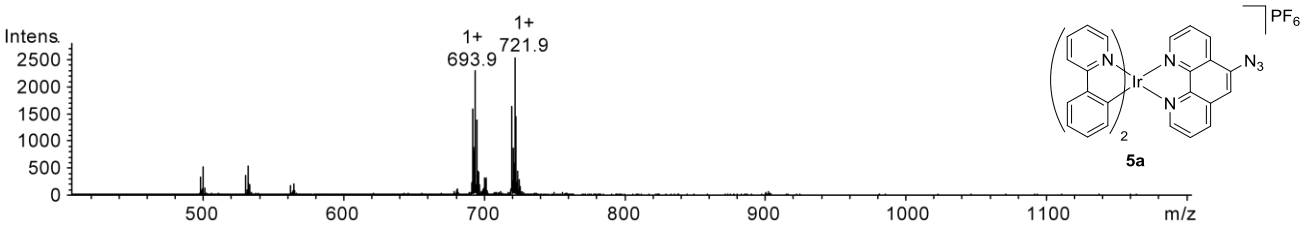


Figure S10. Parent azide complex **5a** (positive mode). *m/z* 721.9 and 693.9 correspond to $[M]^+$ and $[M–N_2]^+$, respectively.

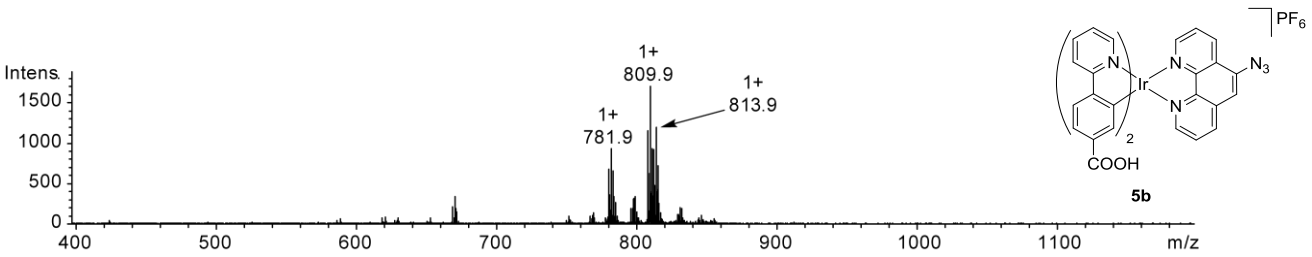


Figure S11. Carboxyazide complex **5b** (positive mode). *m/z* 813.9, 809.9, and 781.9 correspond to $[M–N_2+O_2]^+$, $[M]^+$, and $[M–N_2]^+$, respectively.

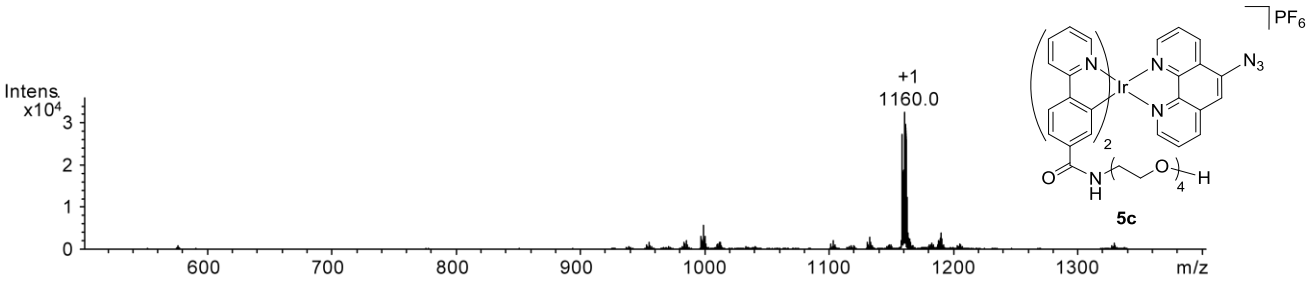


Figure S12. PEGylated azide complex **5c** (positive mode). *m/z* 1160.0 corresponds to $[M]^+$.

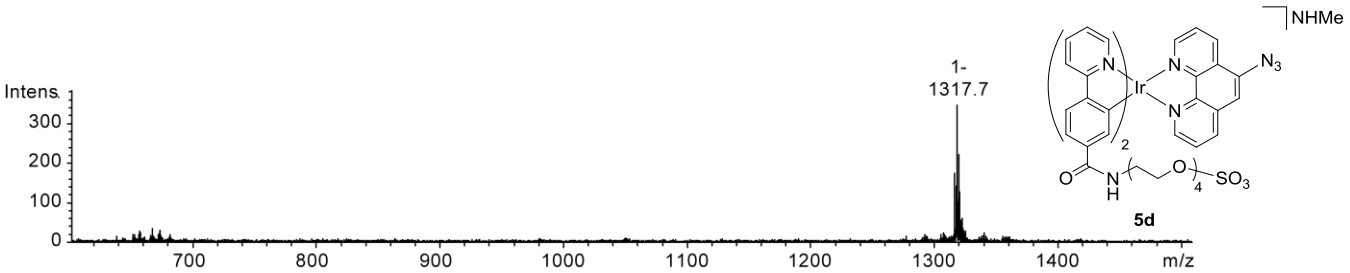


Figure S13 Bisulfate azide complex **5d** (negative mode). *m/z* 1317.7 corresponds to $[M]^-$.

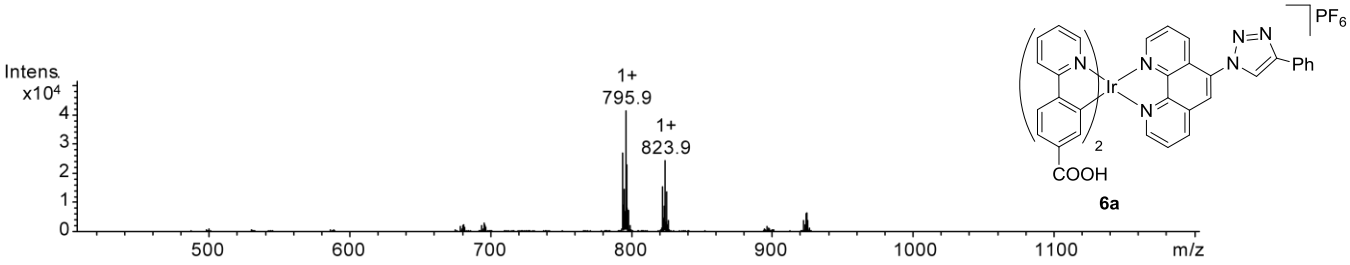


Figure S14. Parent triazole complex **6a** (positive mode). *m/z* 823.9 and 795.9 correspond to $[M]^+$ and $[M–N_2]^+$, respectively.

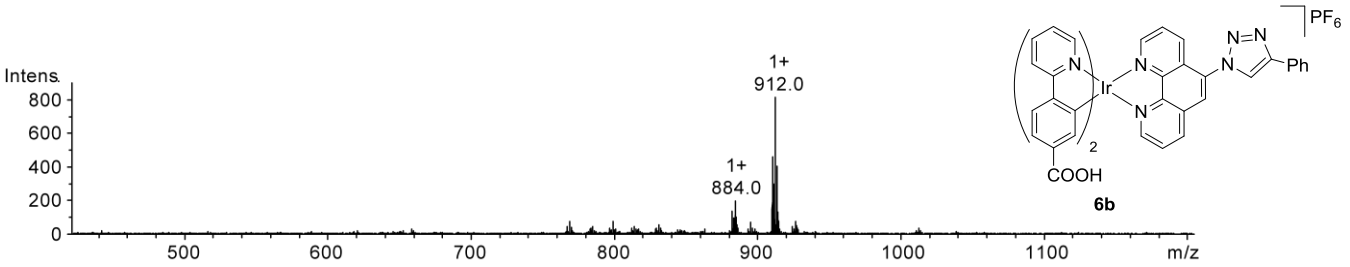


Figure S15. Carboxytriazole complex **6b** (positive mode). *m/z* 912.0 and 884.0 correspond to $[M]^+$ and $[M–N_2]^+$, respectively.

NMR spectra

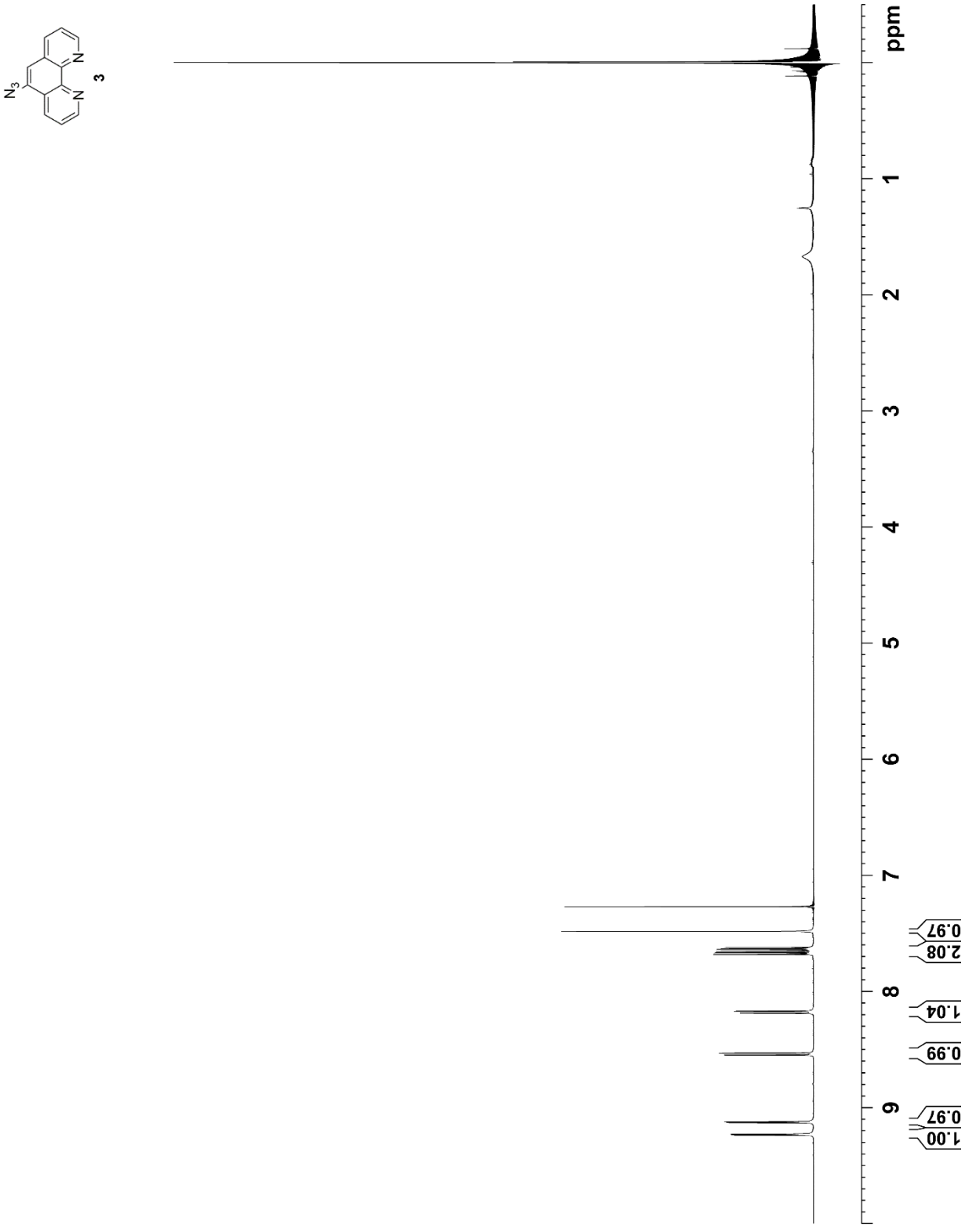


Figure S16. ^{1}H NMR spectrum of azidophenanthroline **3** in $CDCl_3$.

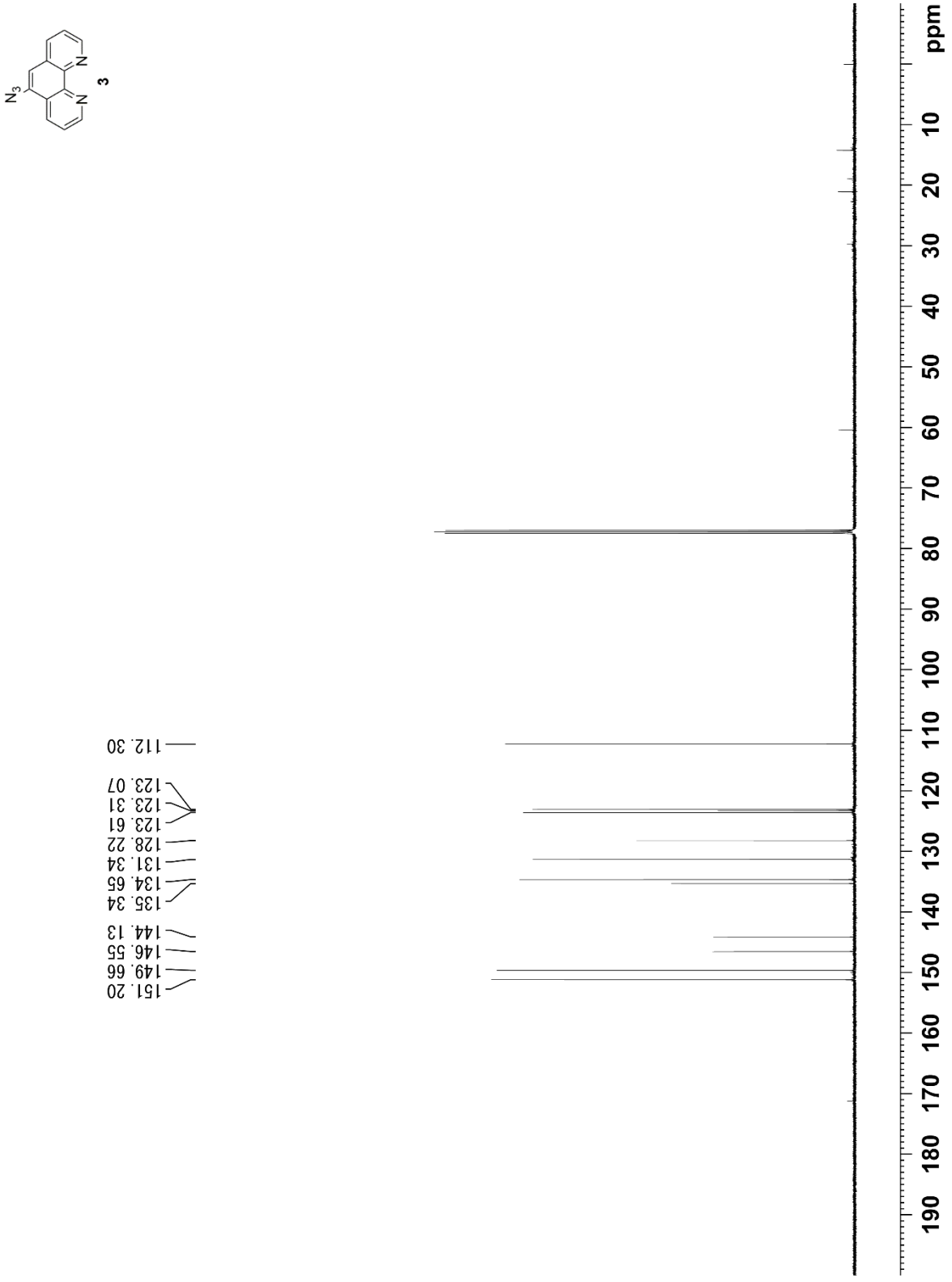


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of azidophenanthroline **3** in $CDCl_3$.

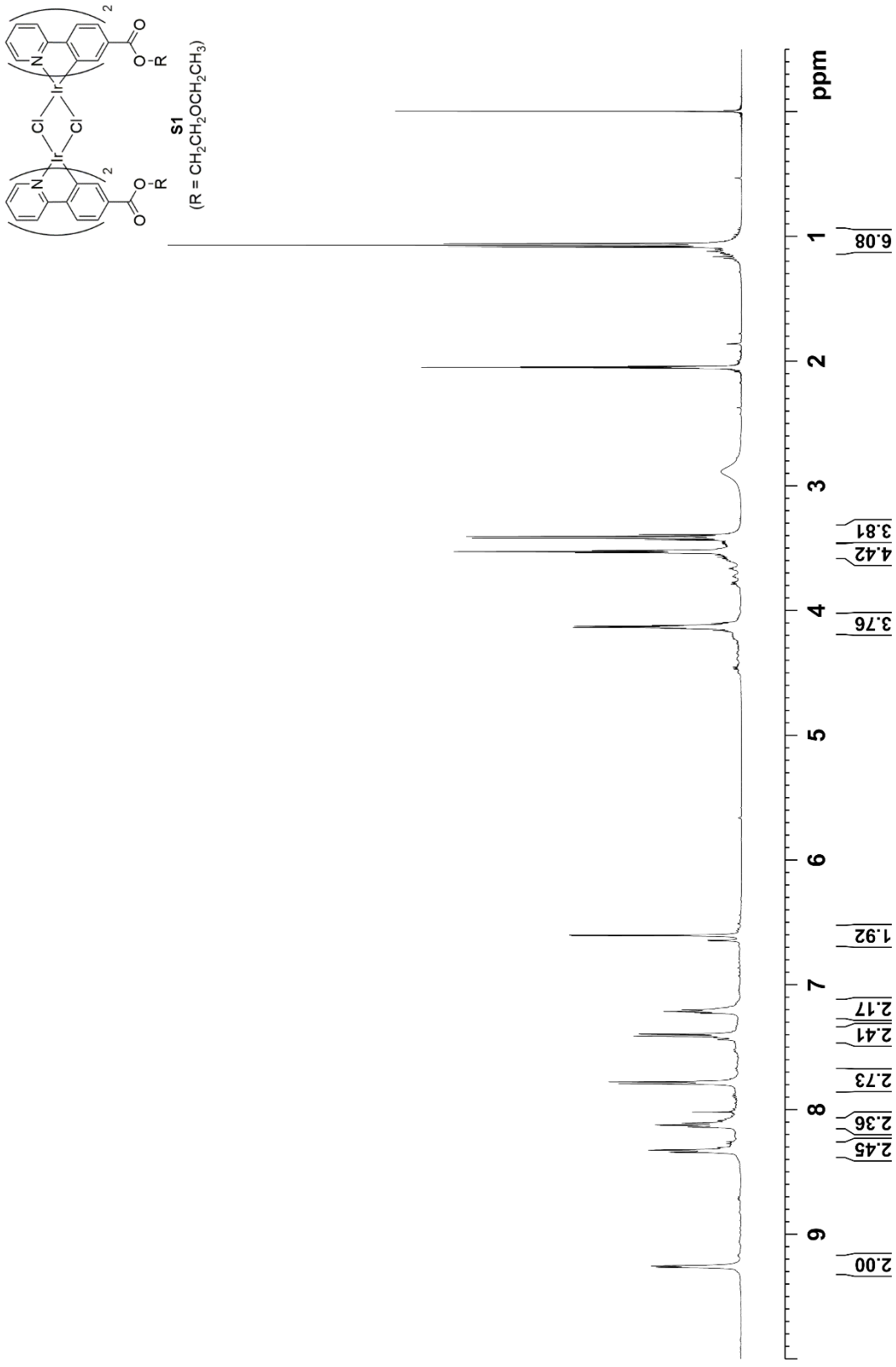


Figure S18. ^{1}H NMR spectrum of 2-ethoxyethyl ester of dimer complex **S1** in acetone–d_6.

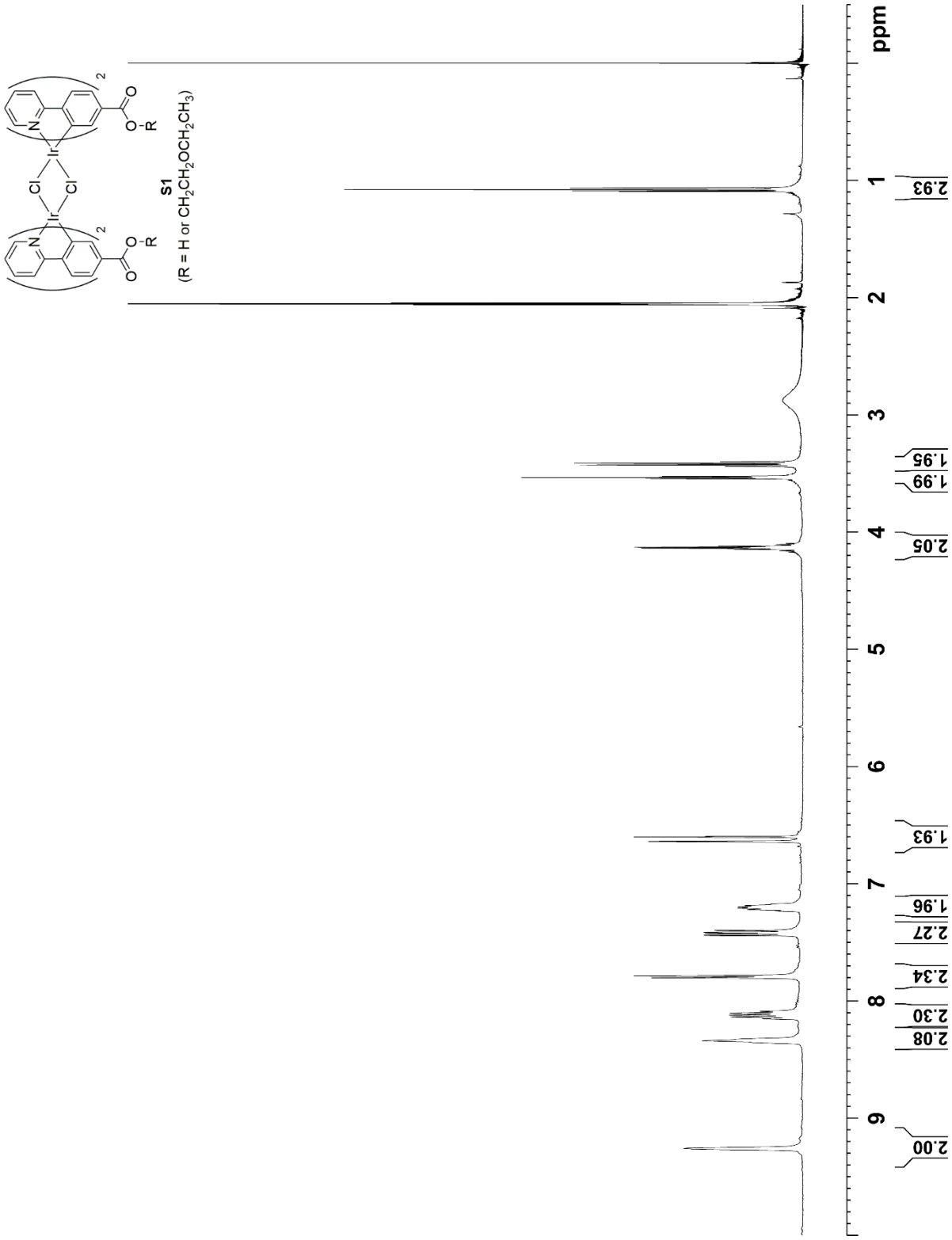


Figure S19. ^{1}H NMR spectrum of mixture of carboxylic acid and ester of dimer complex **S1** in acetone–d_6.

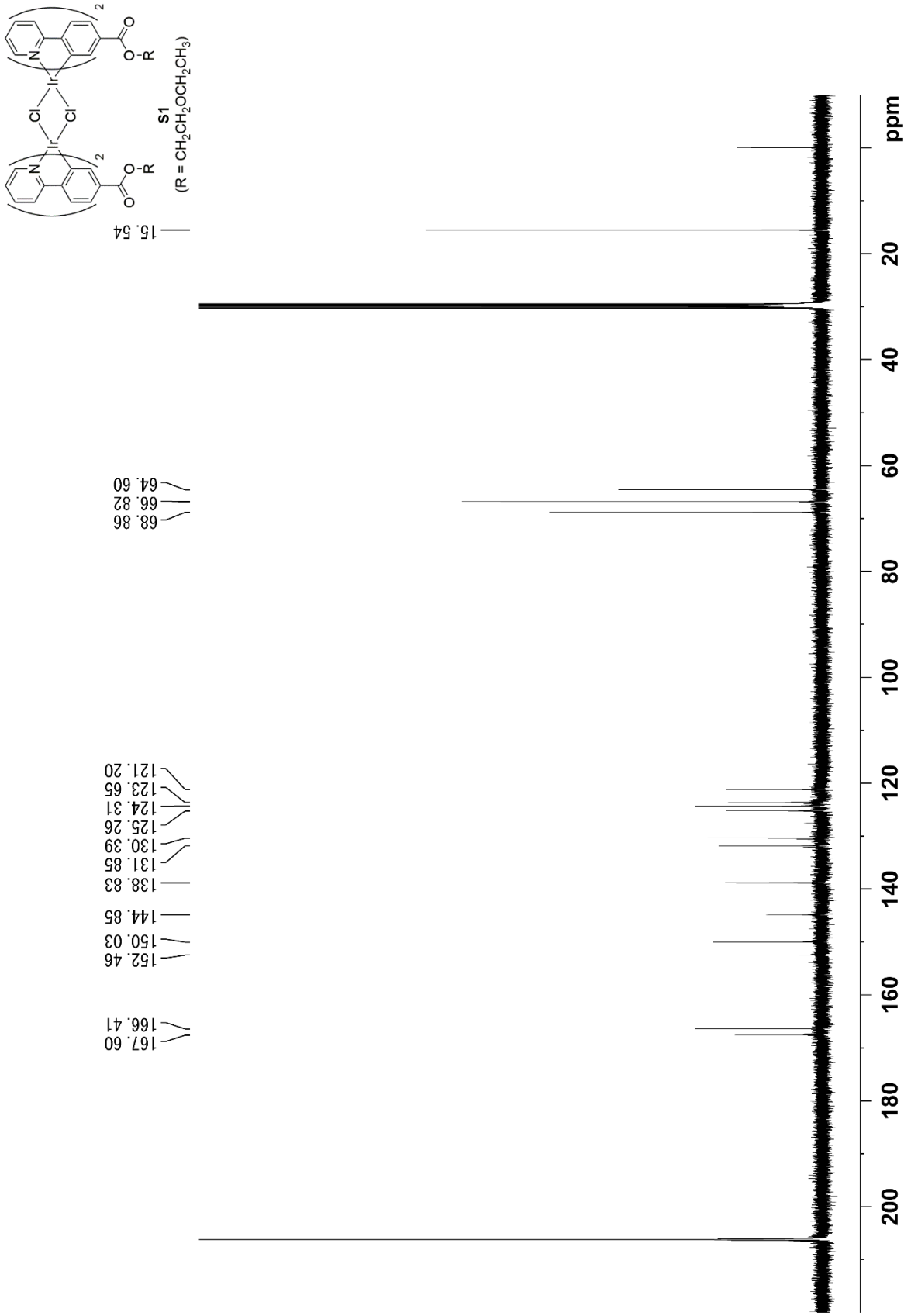


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of 2-ethoxyethyl ester of dimer complex **S1** in acetone–d_6.

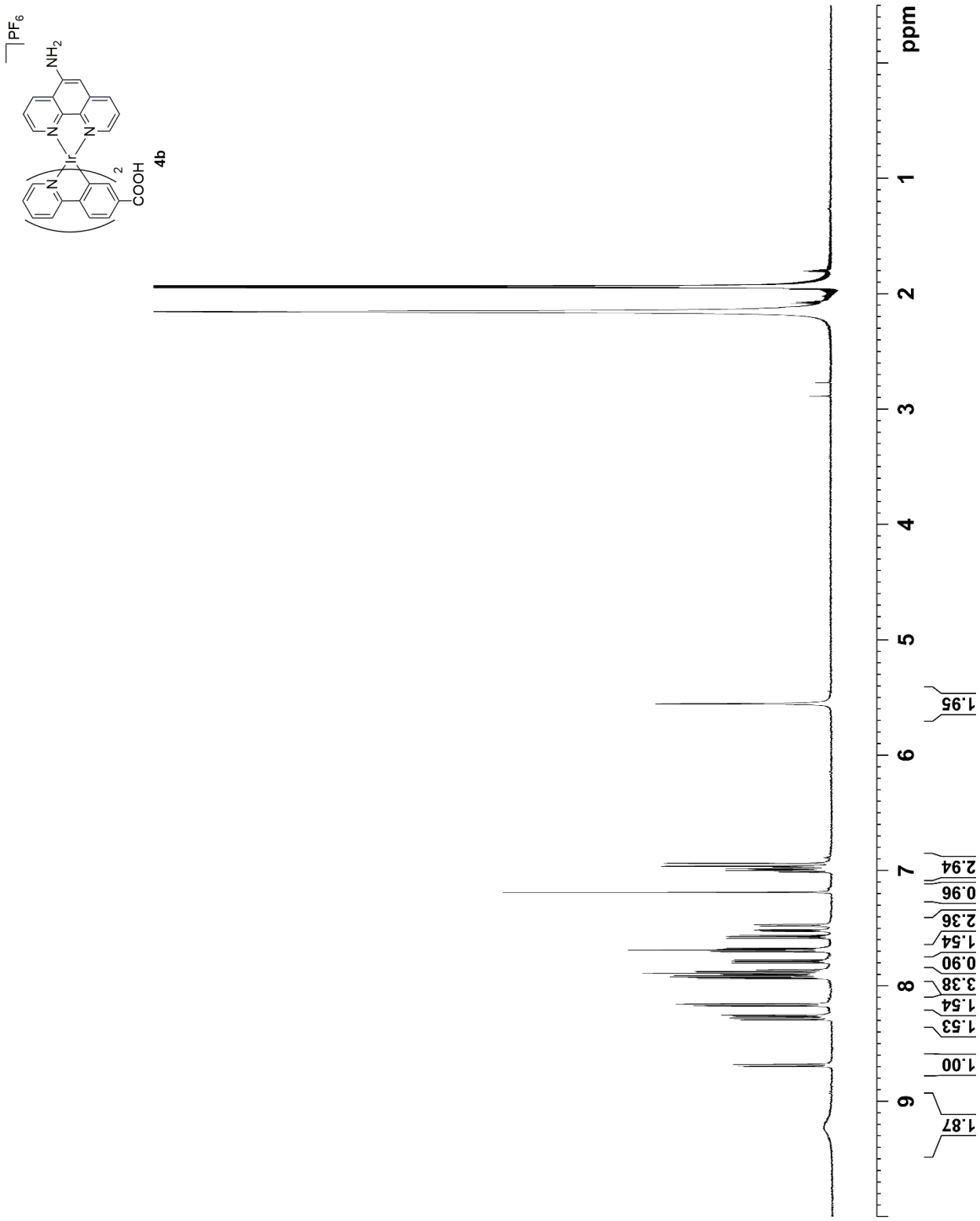


Figure S21. ^{1}H NMR spectrum of carboxyamino complex **4b** in CD_3CN.

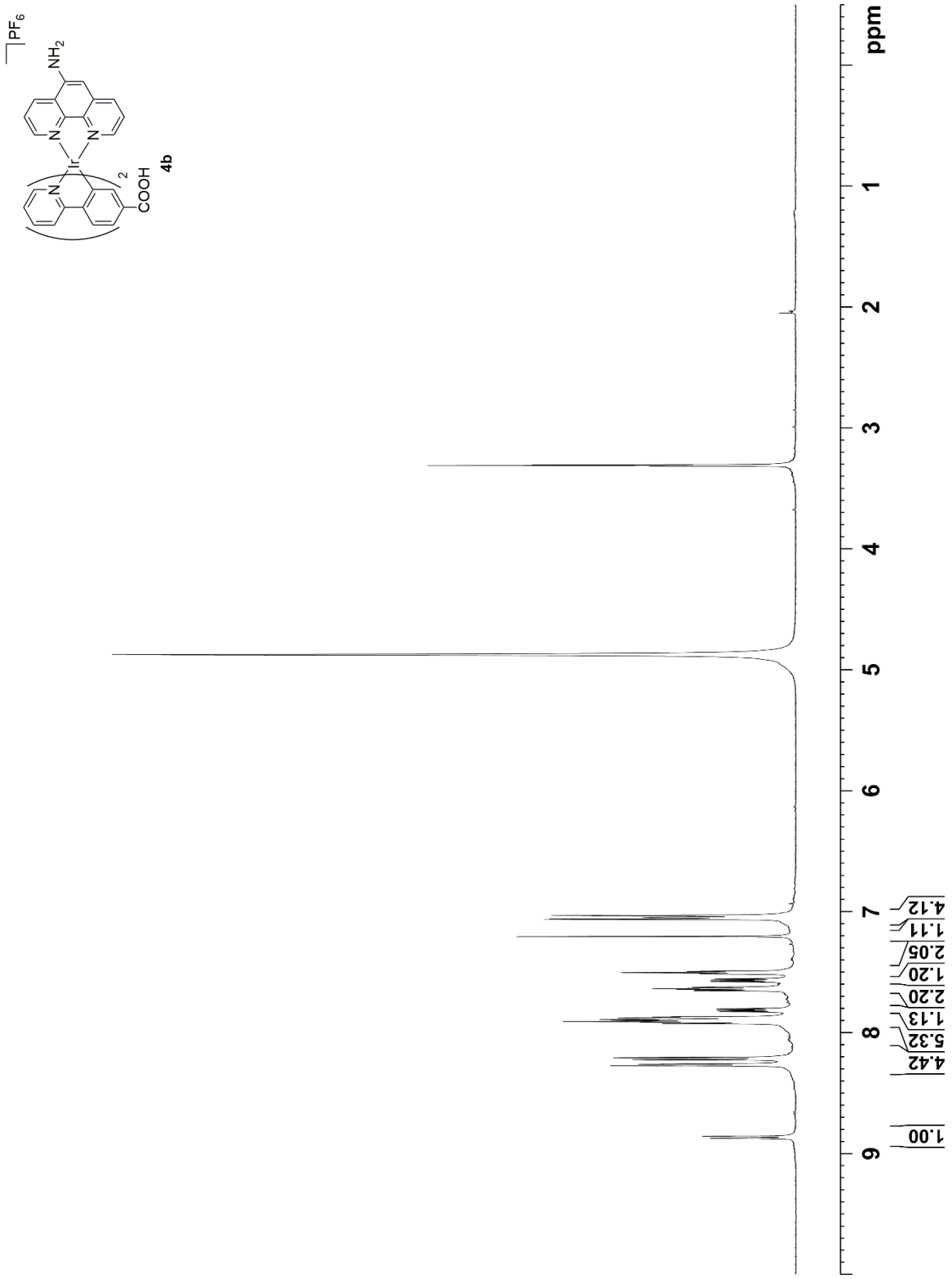


Figure S22. ^{1}H NMR spectrum of carboxyamino complex **4b** in CD_3OD/D_2O (3:1).

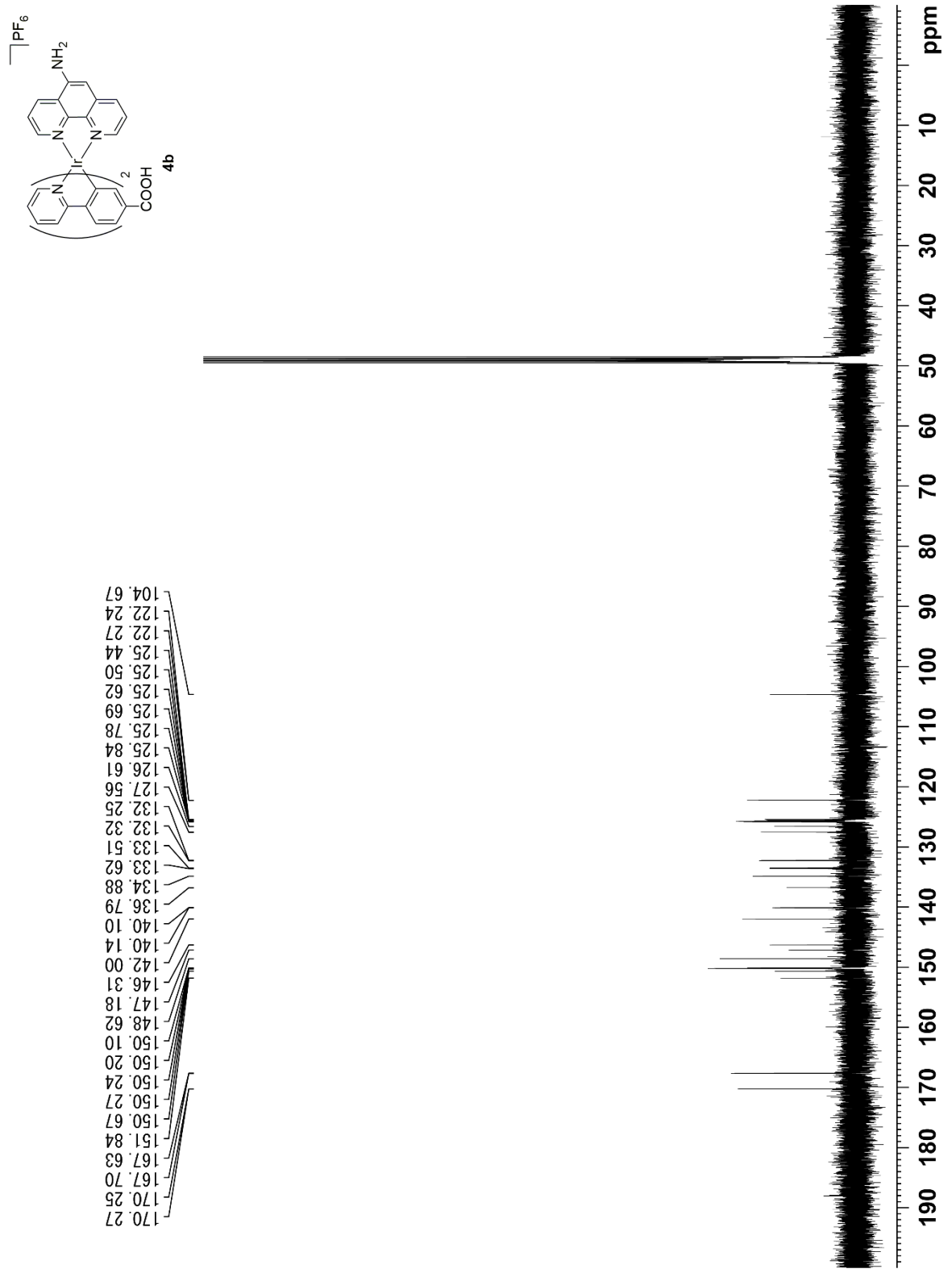


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of carboxyamino complex **4b** in CD_3OD/D_2O (3:1).

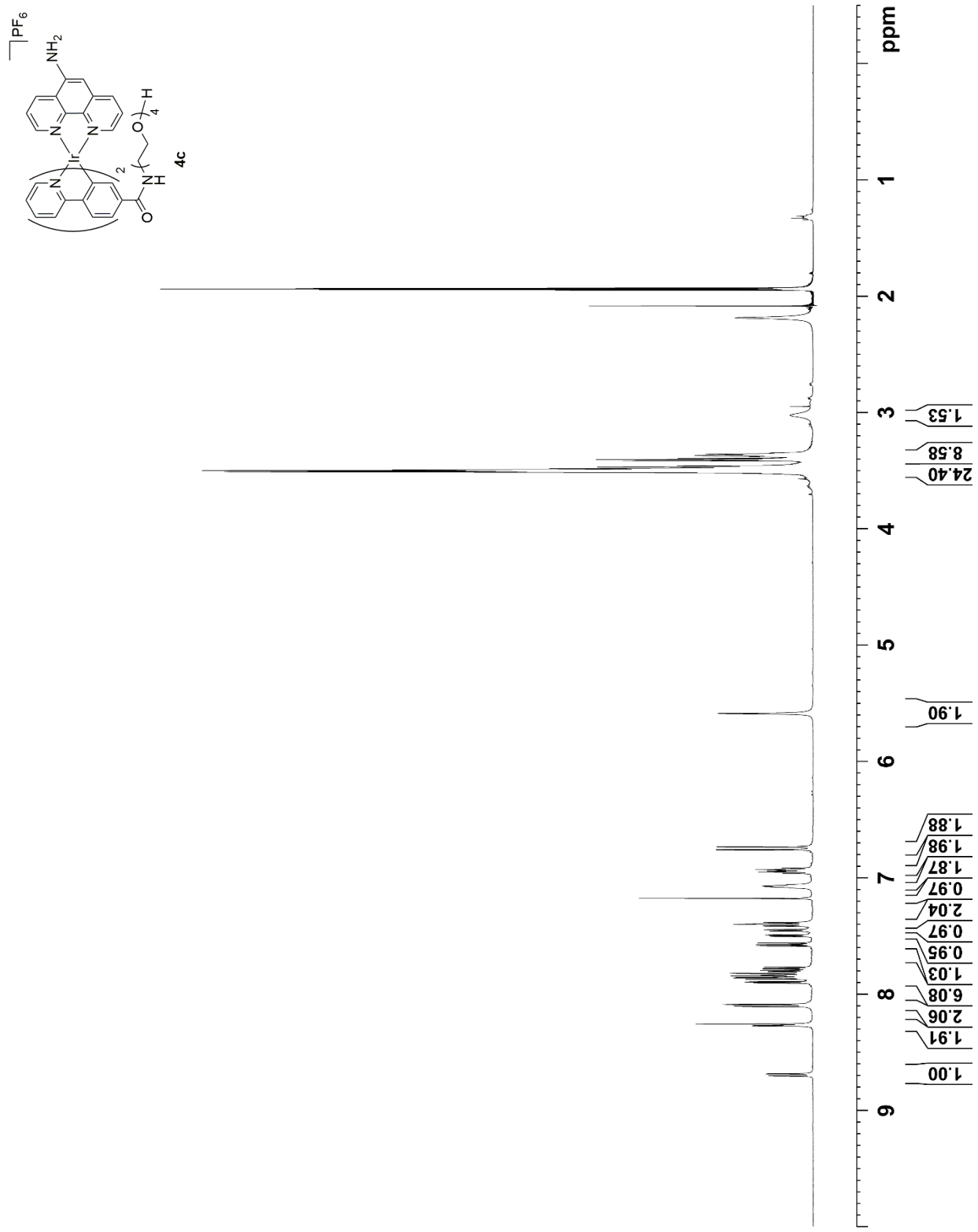


Figure S24. ^{1}H NMR spectrum of PEGylated amine complex **4c** in CD_3CN.

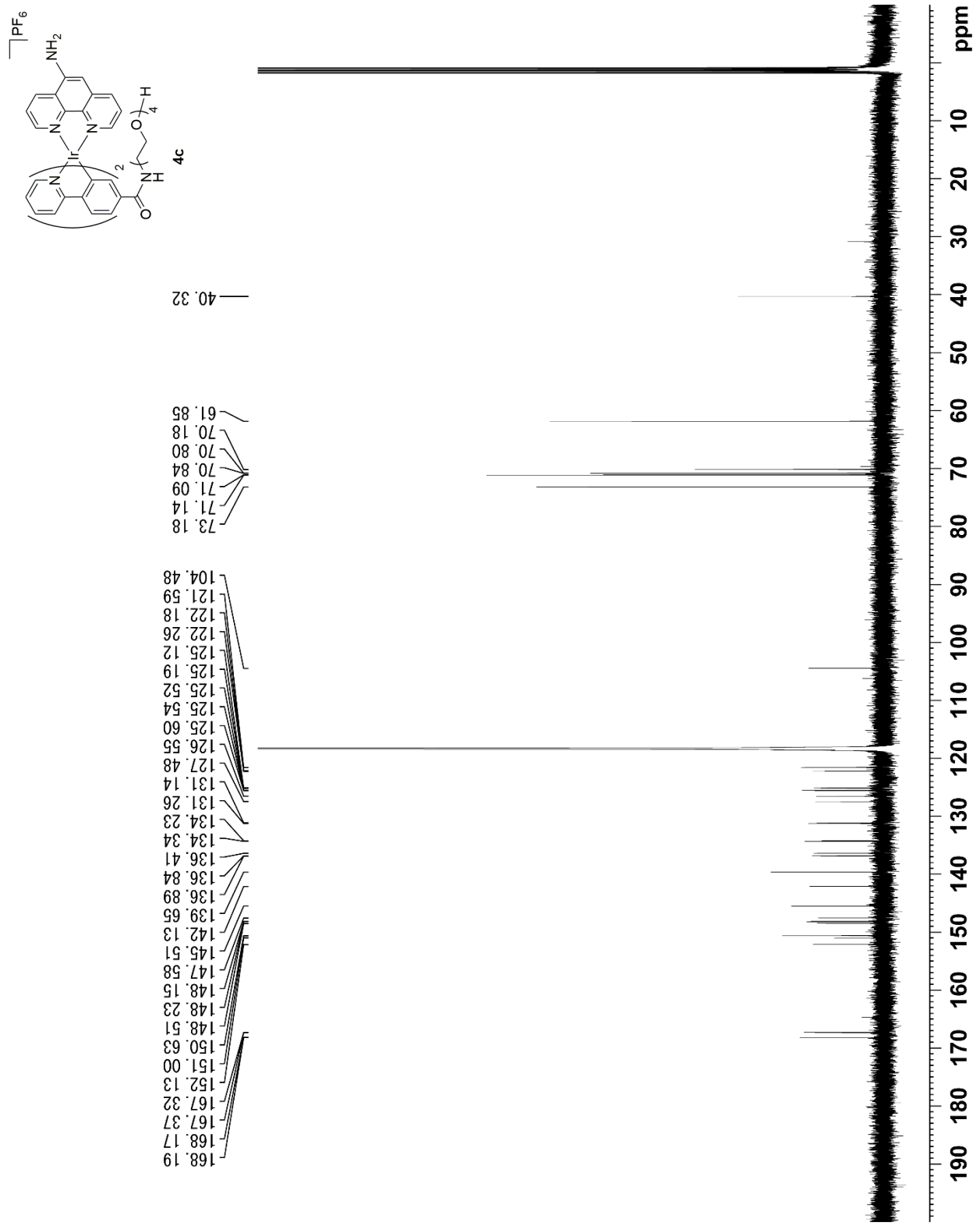


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of PEGylated amine complex **4c** in CD_3CN.

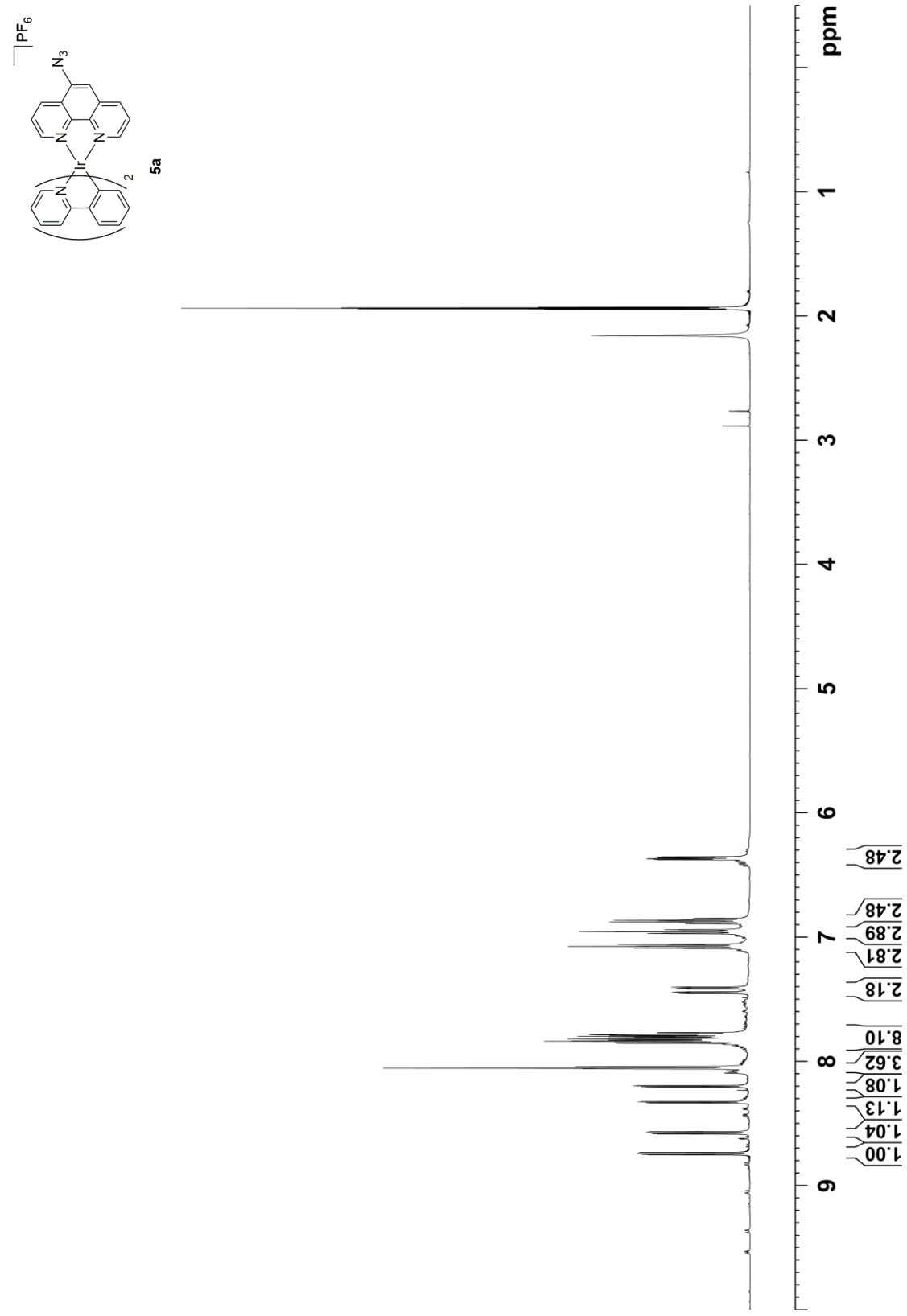


Figure S 26. ^{1}H NMR spectrum of parent azide complex **5a** in CD_3CN.

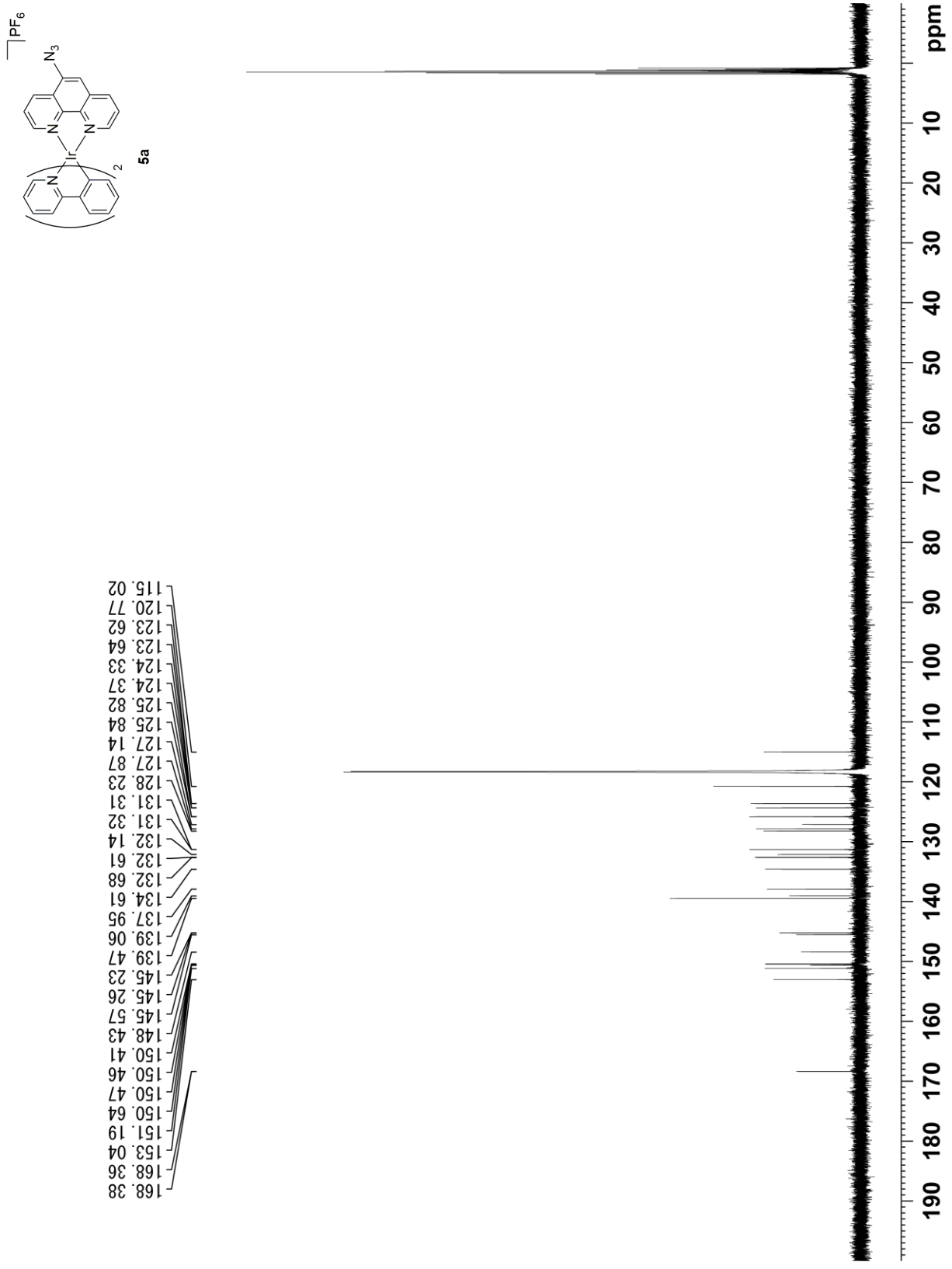


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of parent azide complex **5a** in CD_3CN.

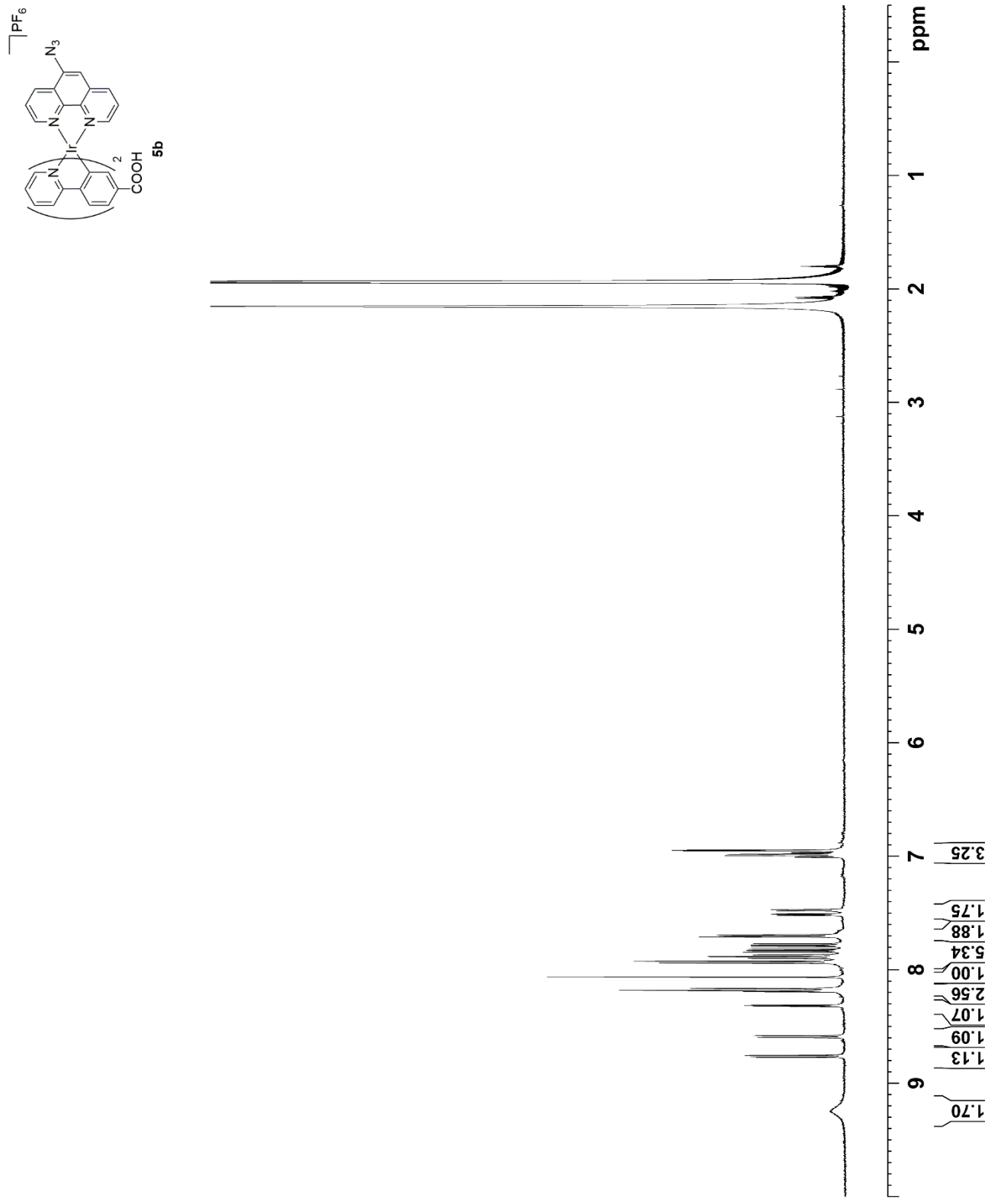


Figure S28. ^{1}H NMR spectrum of carboxyazido complex **5b** in CD_3CN.

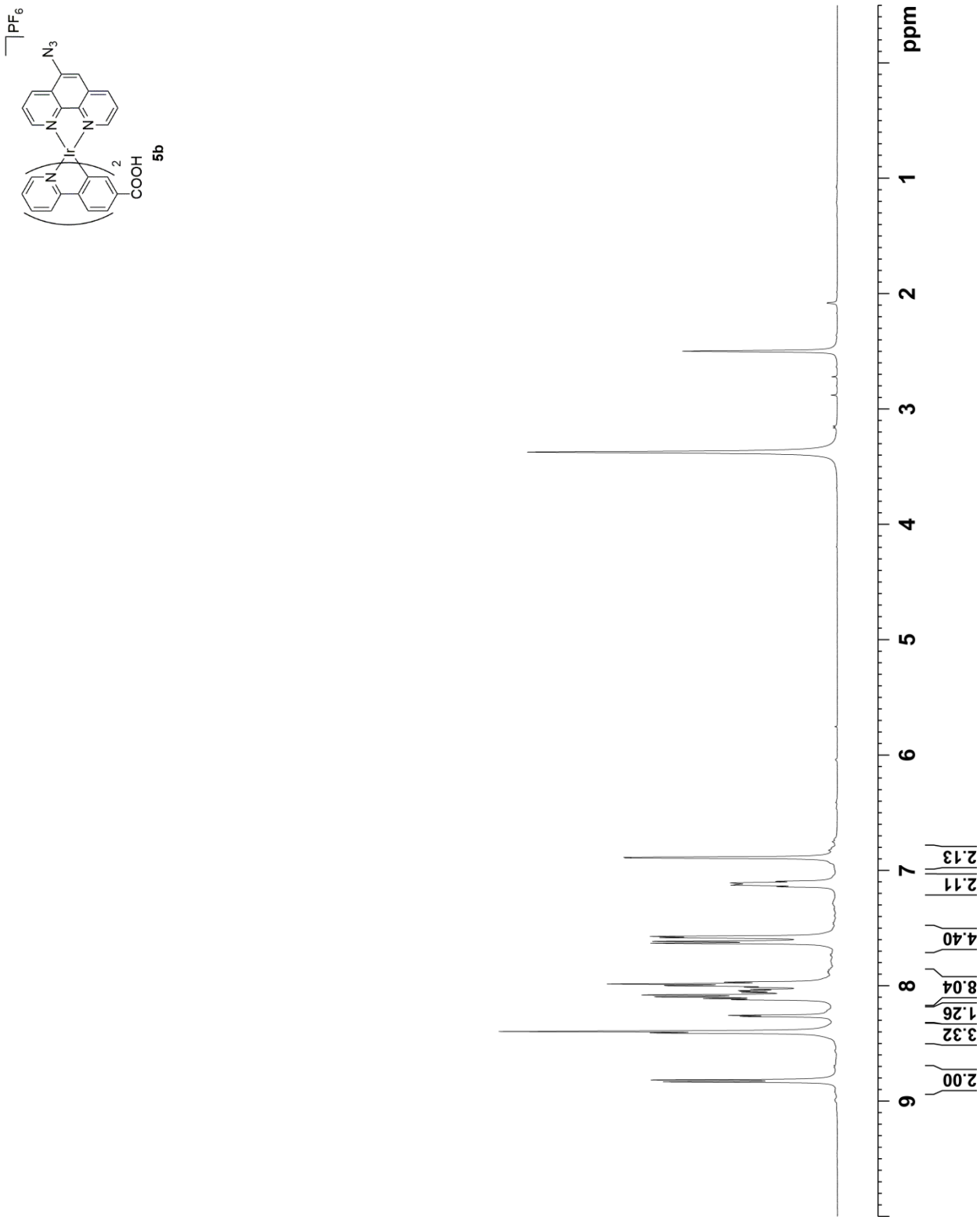


Figure S29. ^{1}H NMR spectrum of carboxyazido complex **5b** in DMSO–d_6.

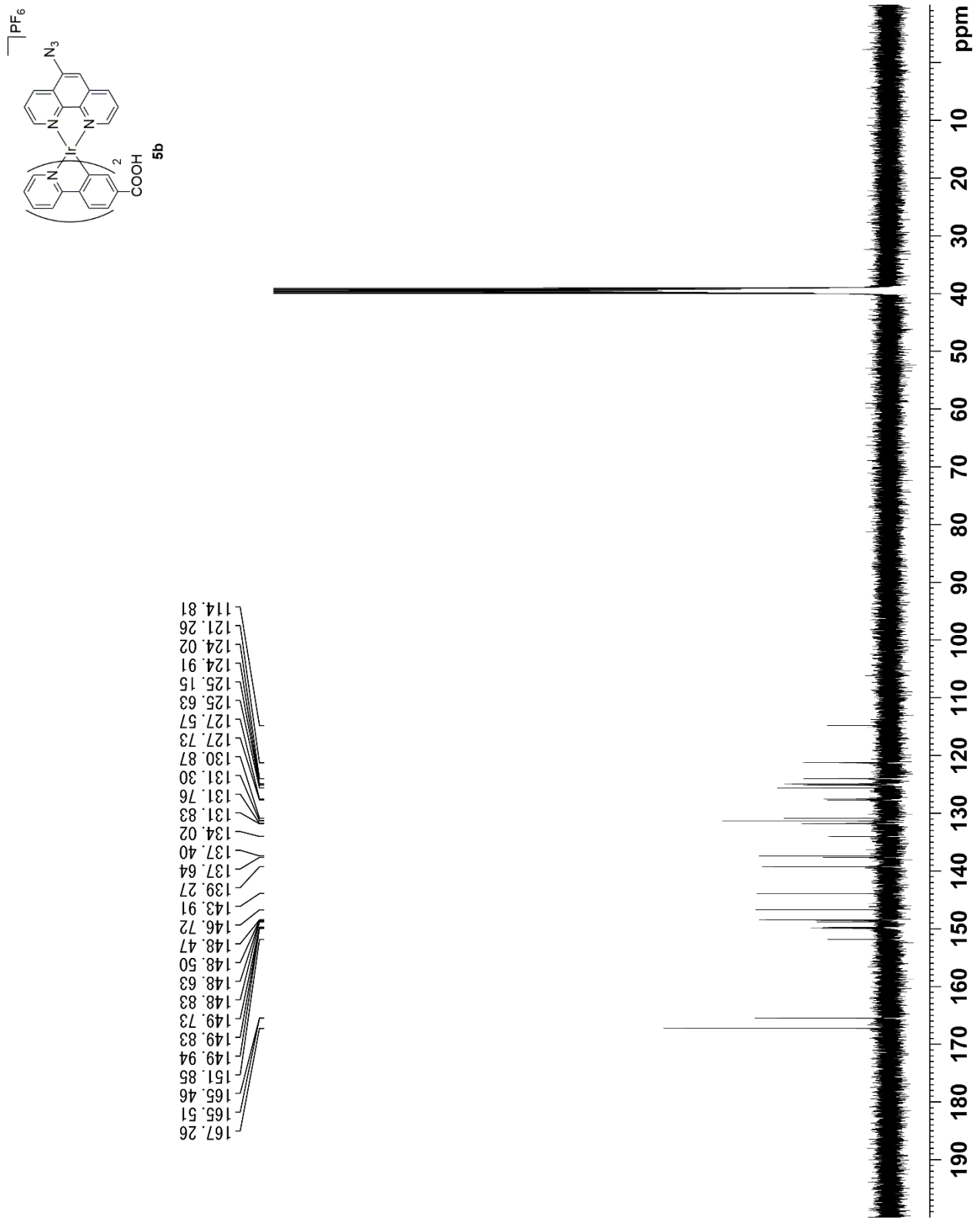


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of carboxyazido complex **5b** in DMSO–d_6.

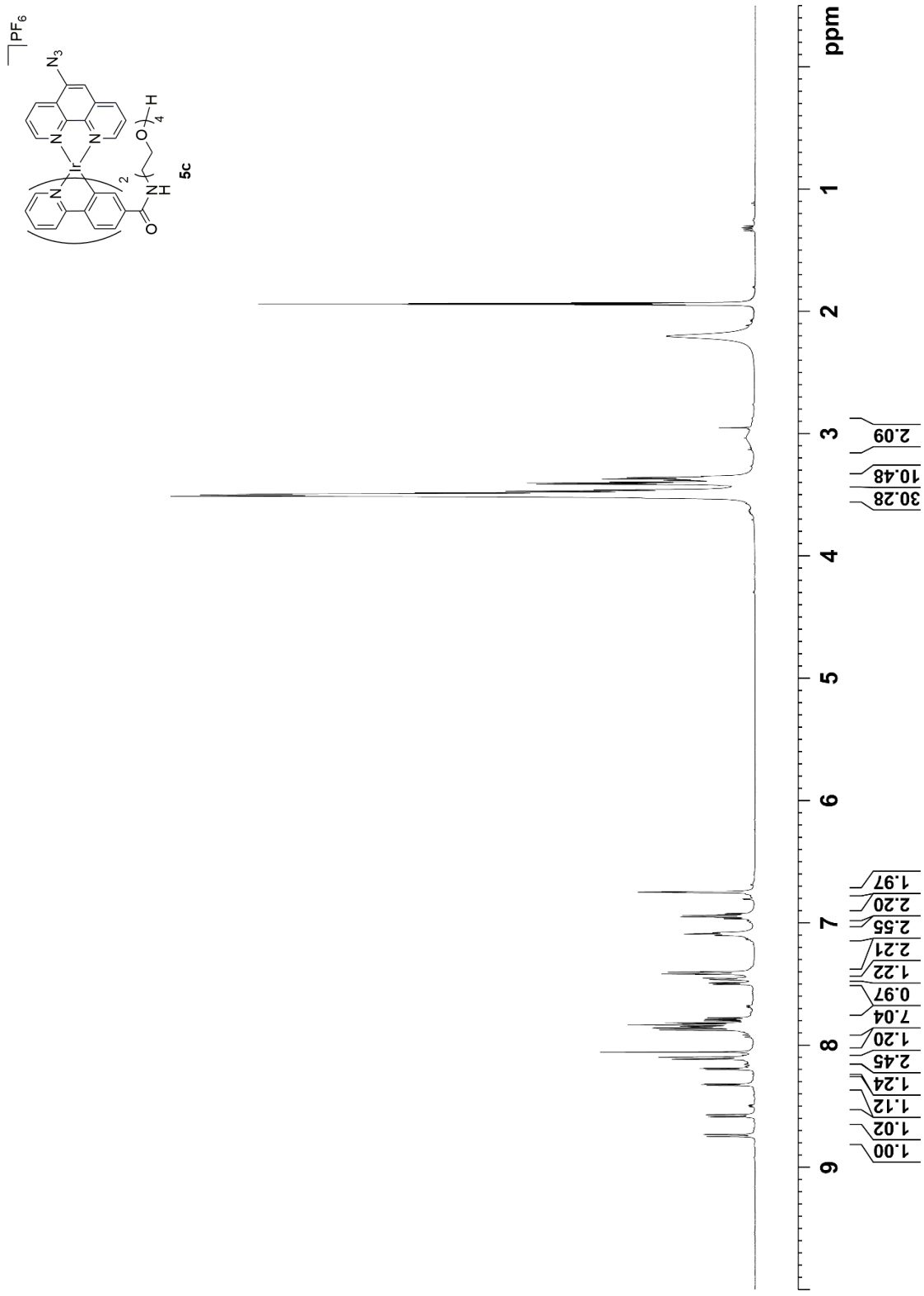


Figure S31. ^{1}H NMR spectrum of PEGylated azido complex **5c** in CD_3CN.

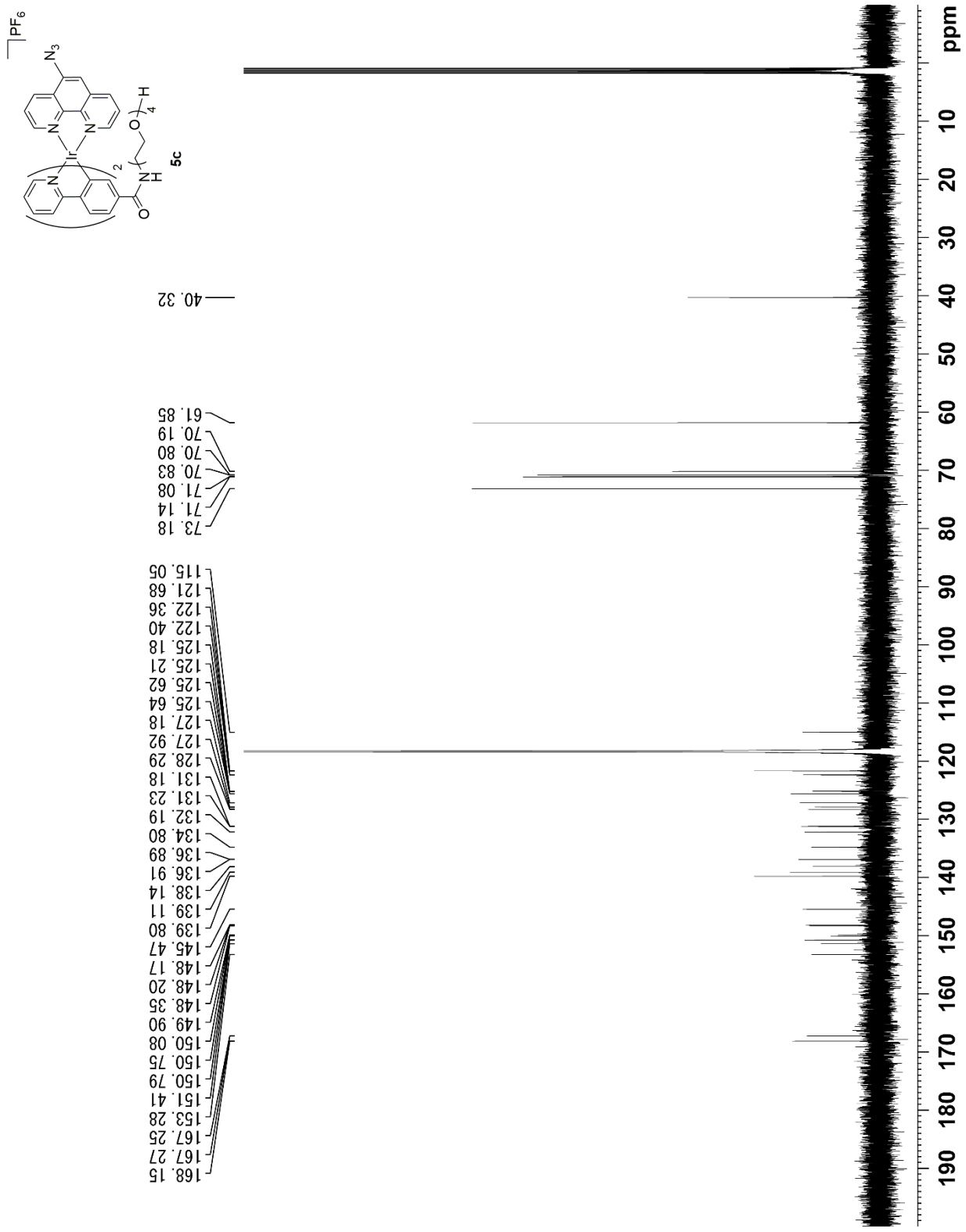


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of PEGylated azido complex **5c** in CD_3CN.

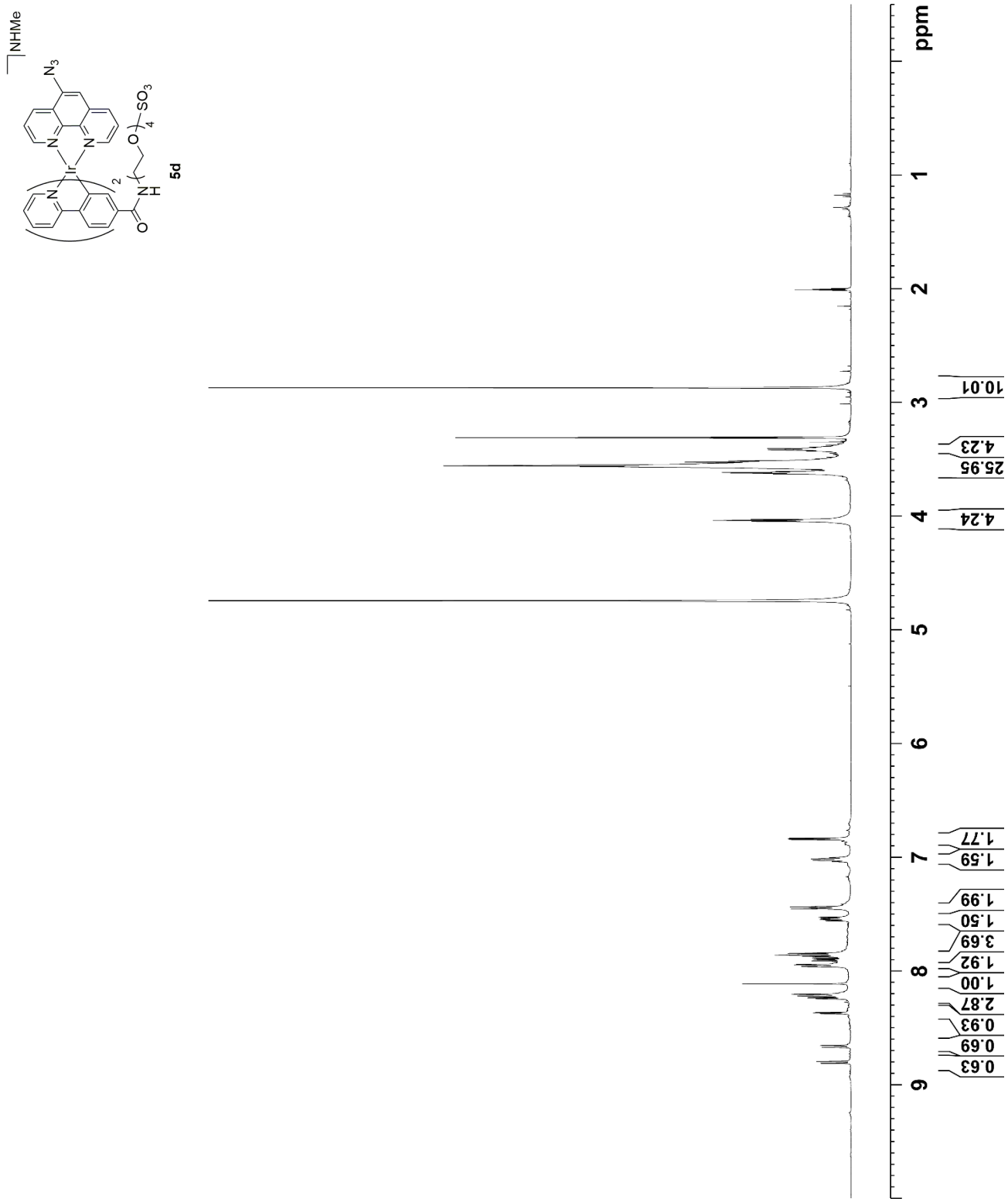


Figure S33. ^{1}H NMR spectrum of bisulfate azido complex **5d** in CD_3OD/CD_3CN (95:5).

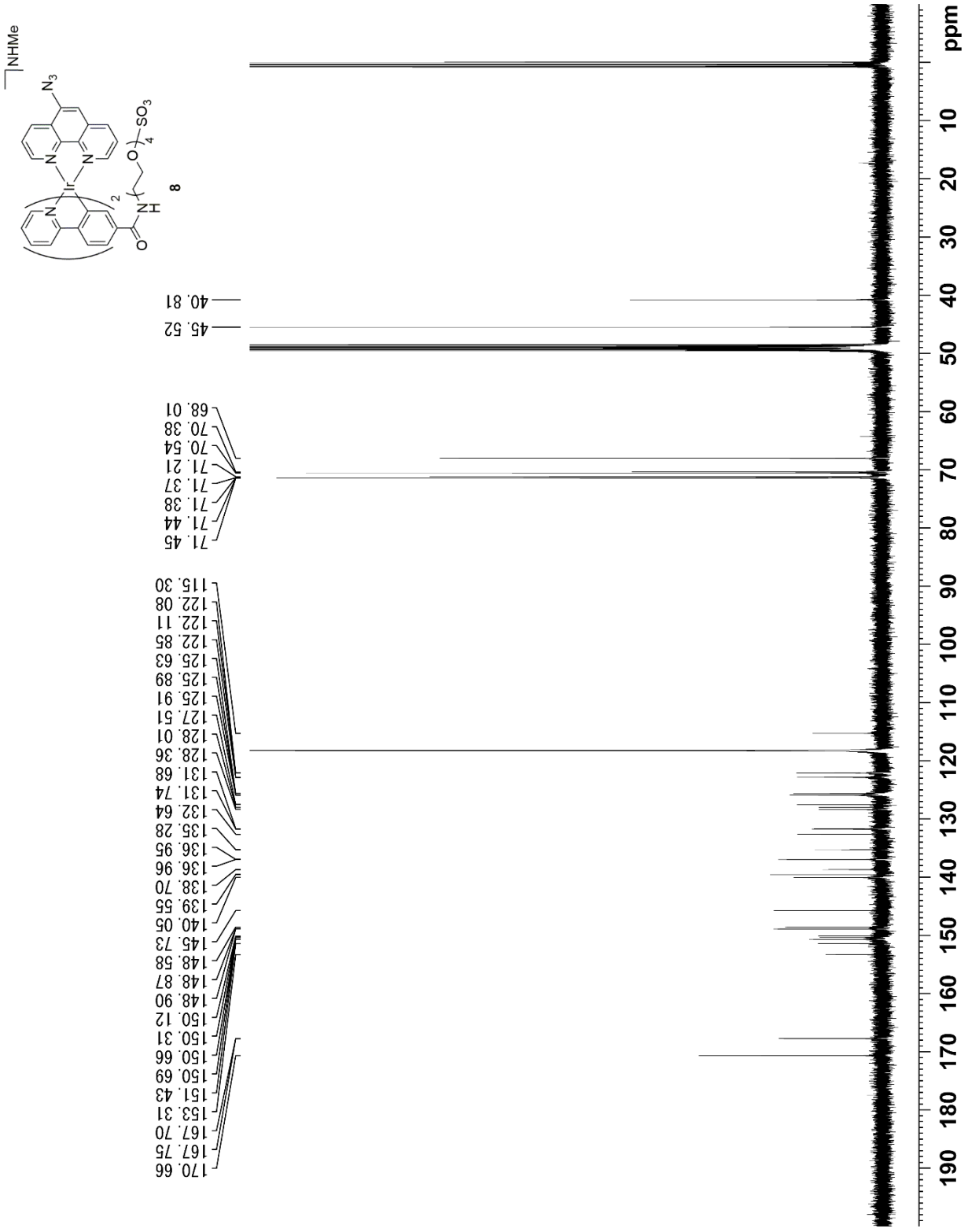


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of bisulfate azido complex **5d** in CD_3OD/CD_3CN (95:5).

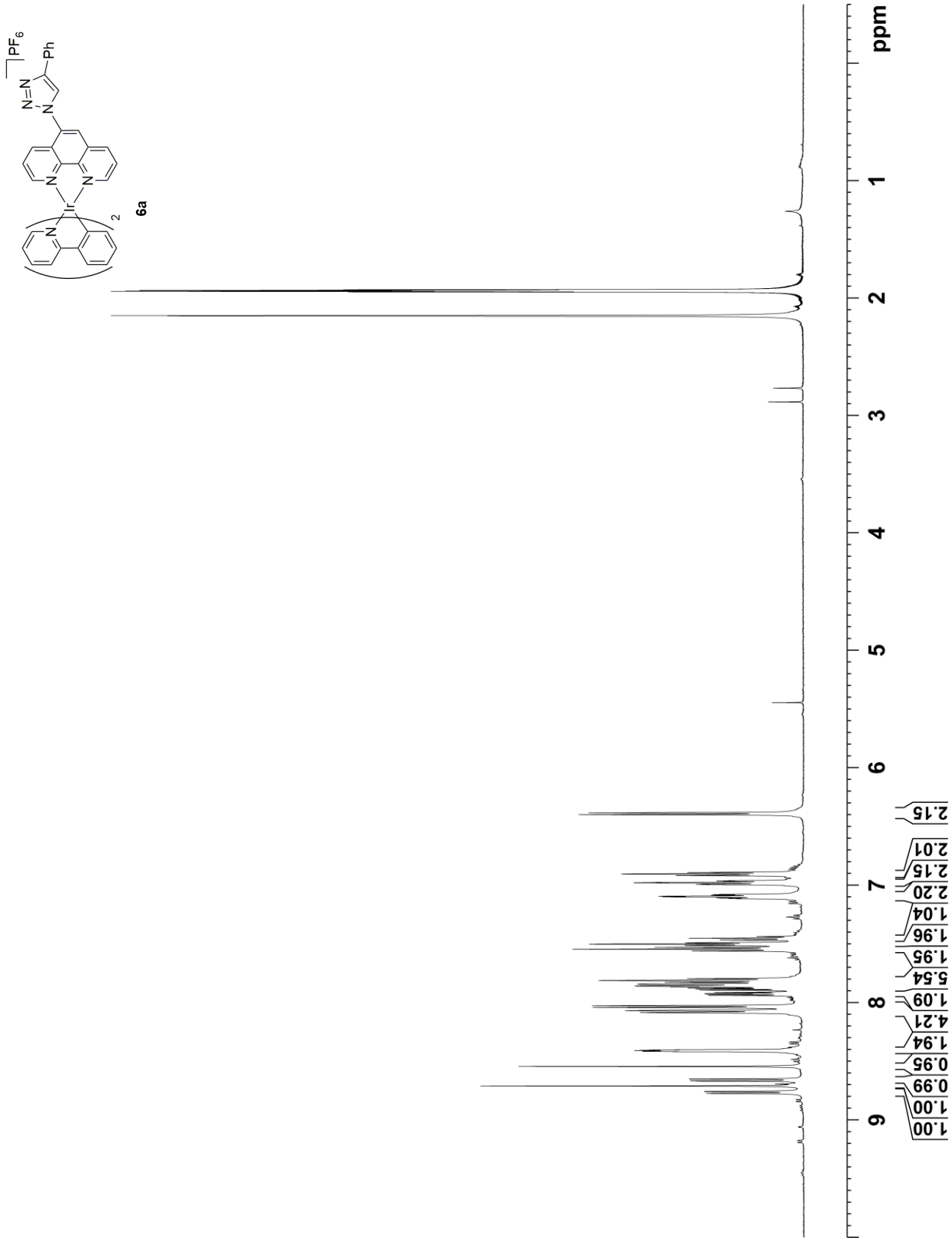


Figure S35. ^{1}H NMR spectrum of parent triazole complex **6a** in CD_3CN.

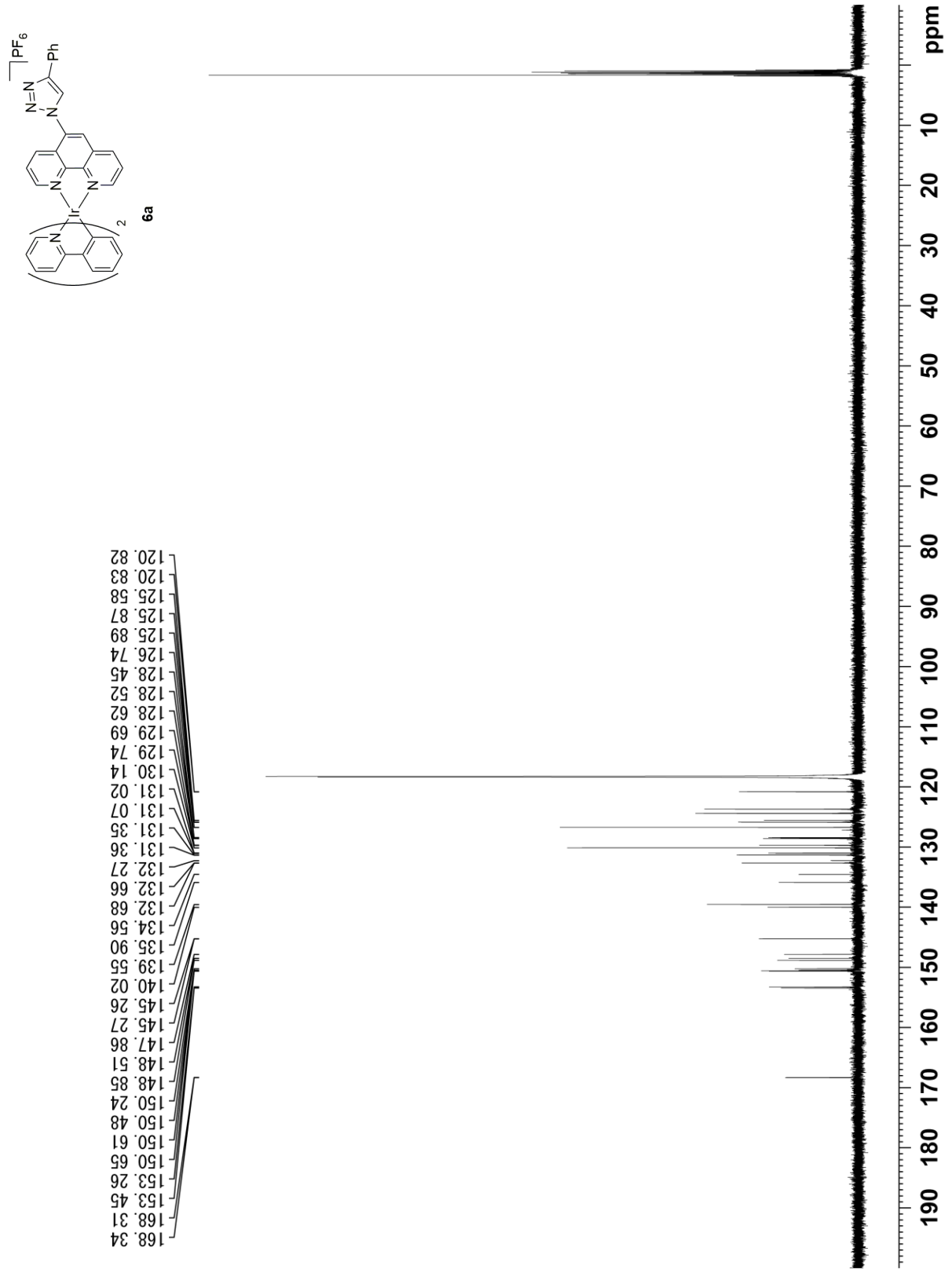


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of parent triazole complex **6a** in CD_3CN.

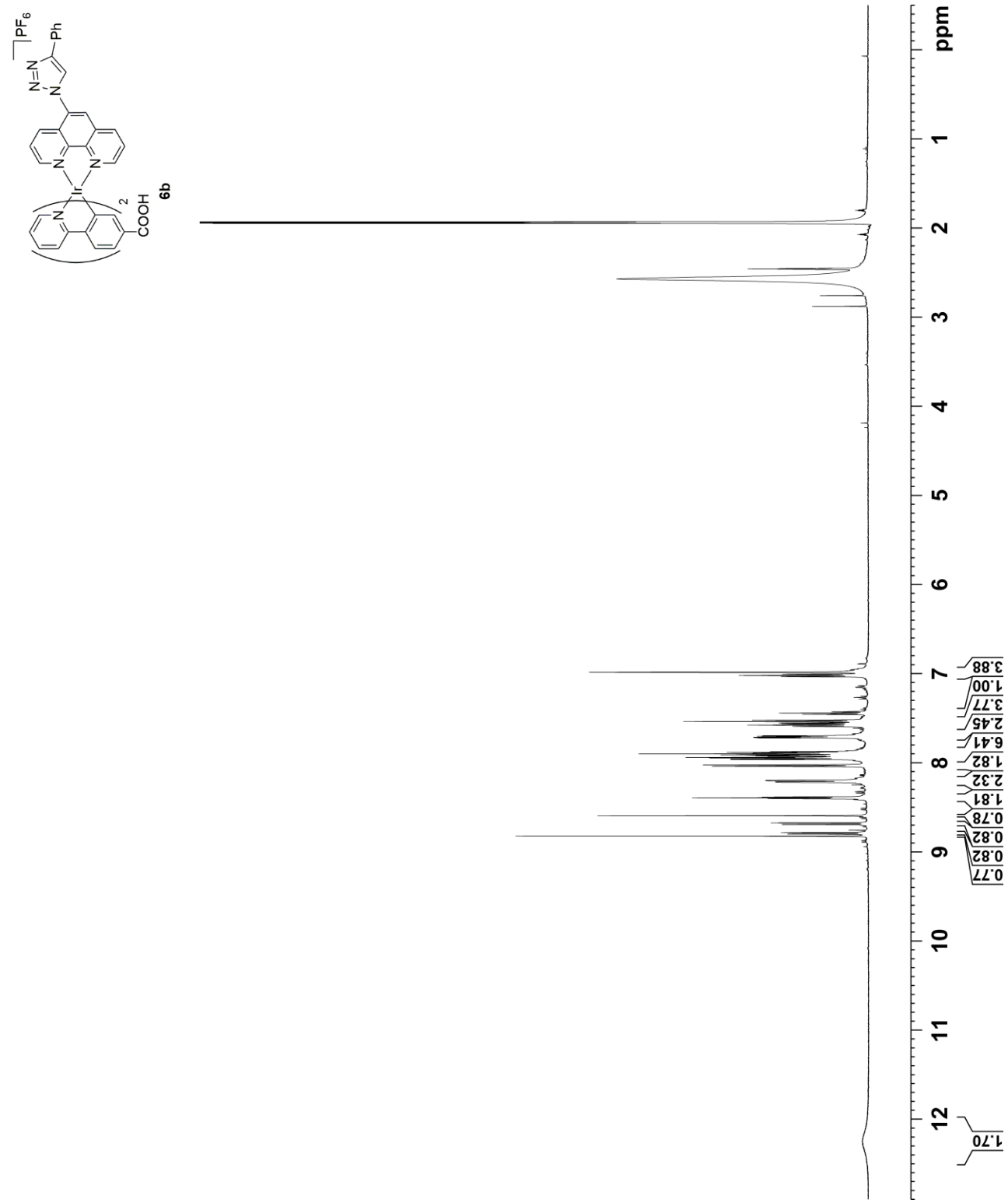


Figure S37. ^{1}H NMR spectrum of carboxytriazole complex **6b** in CD_3CN/DMSO–d_6 (95:5).

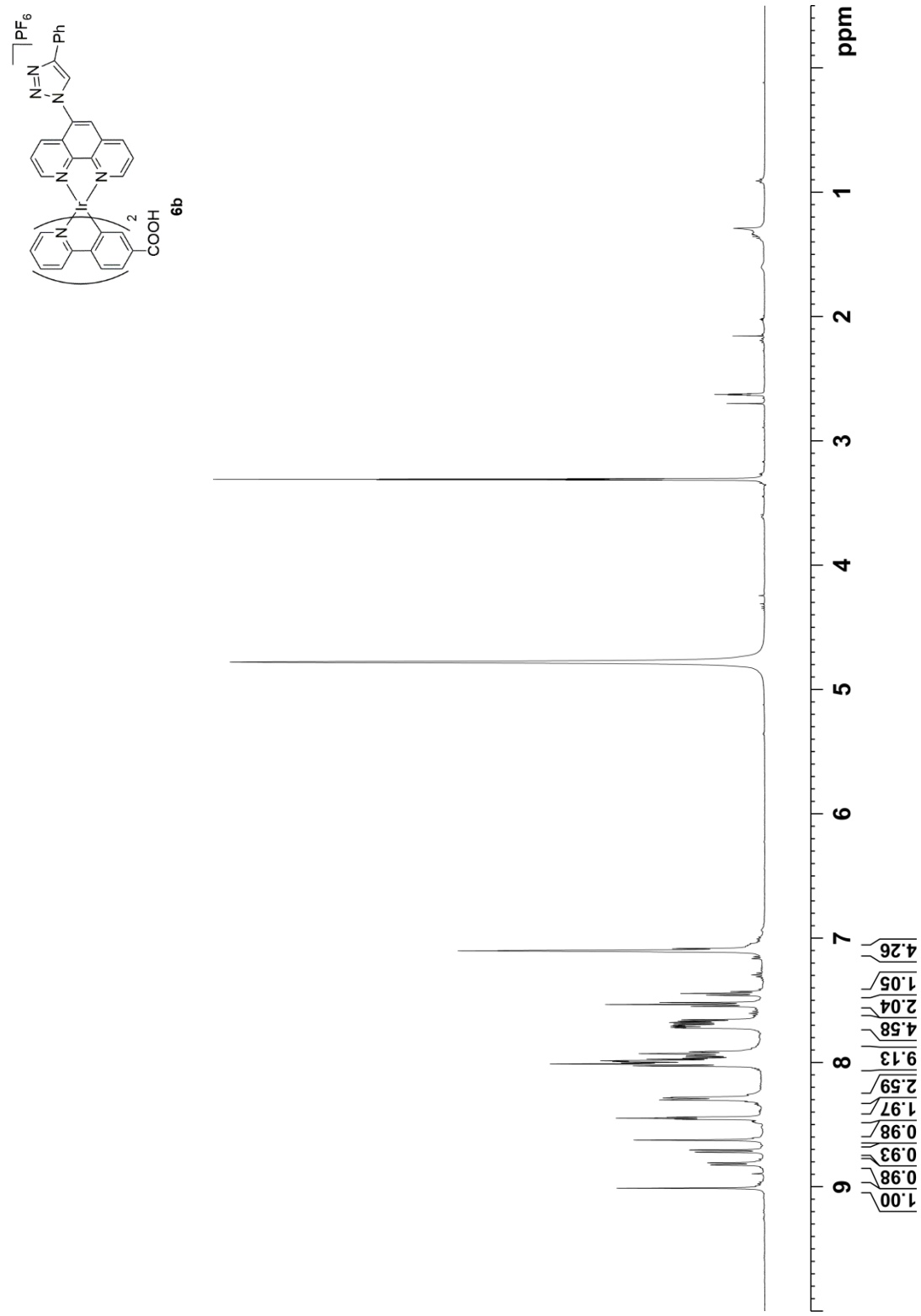


Figure S38. ^{1}H NMR spectrum of carboxytriazole complex **6b** in CD_3OD/DMSO–d_6 (95:5).

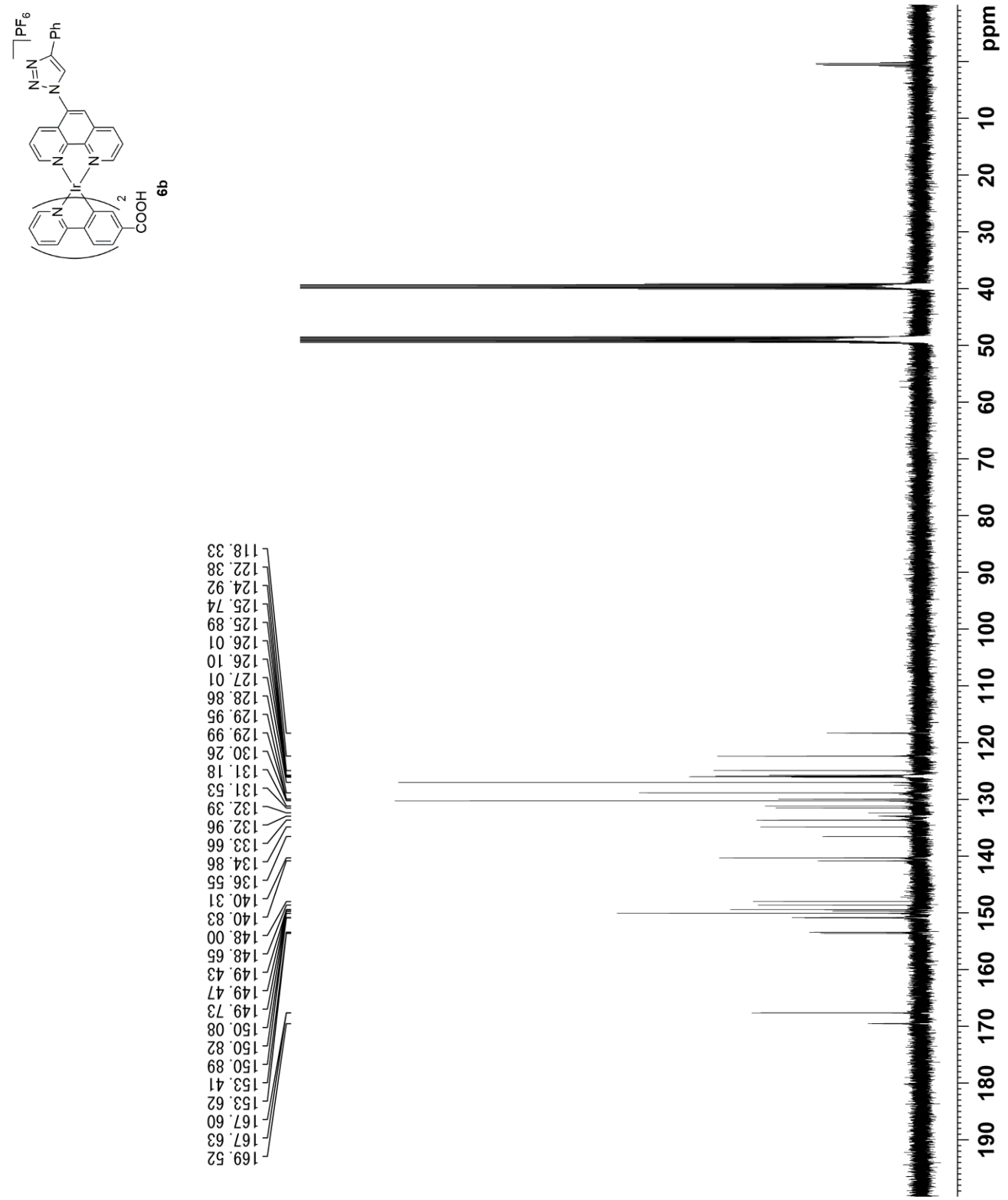


Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of carboxytriazole complex **6b** in CD_3OD/DMSO–d_6 (95:5).

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