Electronic Supplementary Information

Ir(III)-Catalysed Electrooxidative Intramolecular Dehydrogenative C−H/N−H Coupling for the Synthesis of N−H Indoles

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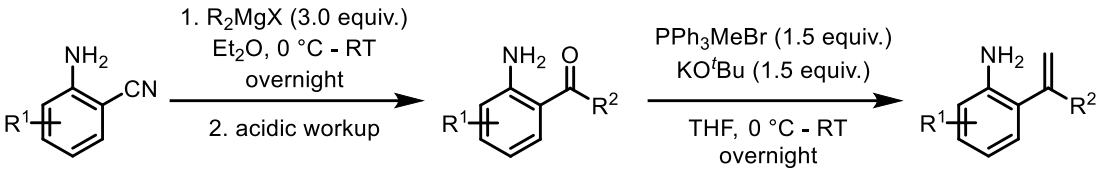
I. General Methods

Unless otherwise stated, all commercial reagents were used without additional purification. All the chemical reaction was performed under Ar atmosphere, using glove box or Schlenk technique. Solvents were sparged with N_2 and dried over activated 4Å molecular sieves before use. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F_{254} plates. Visualization on TLC was achieved by the use of UV light (254 nm) or treatment with acidic anisaldehyde, 10% ninhydrin in ethanol, 5% phosphormolybdic acid in ethanol, or ceric ammonium molybdate stain followed by heating. Column chromatography was undertaken on silica gel (400-630 mesh) using ethyl acetate/hexane as eluent. Electrochemical analyses and electrolysis were conducted using Biologic Multichannel Potentiostat VSP-127 or Single Potentiostat SP-150. Electrolysis was conducted under constant current mode. ^{1}H NMR was recorded on Agilent Technologies DD2 (600 MHz), Bruker Avance 500 (500 MHz), Bruker Avance 400 (400 MHz) or Bruker Avance 300 (300 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak. The following abbreviations were used to describe peak splitting patterns when appropriate: brs (broad singlet), s (singlet), d (doublet), t (triplet), hept (heptet), dd (doublet of doublet), td (triplet of doublet), m (multiplet). Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on Agilent Technologies DD2 (150 MHz), Avance 500 (125 MHz), Bruker Avance 400 (100 MHz) or Bruker Avance 300 (75 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the appropriate solvent peak. ^{19}F NMR was recorded on Agilent Technologies DD2 (564 MHz), Bruker Avance 400 (376 MHz). Infrared (IR) spectra were recorded on Bruker Alpha FT-IR Spectrometer. Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported. High resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using EI method or from KAIST Research Analysis Center by using ESI method. Single crystal X-ray diffraction experiments with synchrotron radiation (BL2D-SMC) were performed at the Pohang Accelerator Laboratory. X-ray diffraction data operating by APEX3 software was collected on a Bruker D8 QUEST coated with Parabar oil under a stream of N_2 (g) at 173 K. Melting point was measured with Buchi Melting Point M-565.

II. Procedures for the Preparation of Starting Materials

Following 2-alkenyl anilines were purchased from Sigma-Aldrich, TCI, Alfa aesar, Azepine and Enamine chemical company and used without further purification; 2-(prop-1-en-2-yl)aniline (**1a**), 2-(1-phenylvinyl)aniline (**1e**), 2-bromo-6-(prop-1-en-2-yl)aniline (**1l**) and 2-vinyl aniline (**1p**).

General Procedure 1 (GP1): Starting materials **1b-1d**, **1f**, **1i-1j** and **1m** were prepared according to a modified literature procedure.[1]



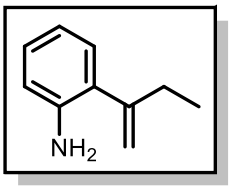
Procedure for the preparation of 2'-aminoacetophenones and 2'-aminobenzophenones

To a solution of 2-aminobenzonitrile (5.0 mmol) in Et_2O (15 mL) was added Grignard reagent (15 mmol, 3.0 equiv.) dropwise at 0 °C. Then, the reaction mixture was allowed to warm up to room temperature and stirred for overnight. After complete conversion of the nitrile, the suspension was cooled to 0 °C and 1M HCl aqueous solution (20 mL) was added. The resulting mixture was vigorously stirred until complete hydrolysis of the corresponding imine. After saturated $NaHCO_3$ aqueous solution (20 mL) and EtOAc (20 mL) were added, the phases were separated and the aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (*n*-hexane/EtOAc as an eluent) to give the desired 2'-aminoacetophenone and 2'-aminobenzophenone.

Procedure for the preparation of 2-alkenyl anilines

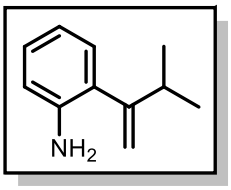
To a suspension of PPh_3MeBr (1.5 equiv.) in dry THF (2.0 mL/mmol) at 0 °C was added KO^{t}Bu (1.5 equiv.) in two portions. The resulting yellow mixture was allowed to stir for 30 minutes at room temperature before it was cooled to 0 °C again and the corresponding 2'-aminoacetophenone or 2'-aminobenzophenone (1 equiv.) was added. Then, the reaction mixture was allowed to warm up to room temperature and stirred for overnight. After completion of the reaction, the mixture was diluted with EtOAc (2.0 mL/mmol) and saturated $NaHCO_3$ aqueous solution (2.0 mL/mmol). The phases were separated and the aqueous phase was extracted with EtOAc (2 x 4.0 mL/mmol). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (*n*-hexane/EtOAc as an eluent) to give the desired 2-alkenyl anilines.

2-(But-1-en-2-yl)aniline (1b)[1]



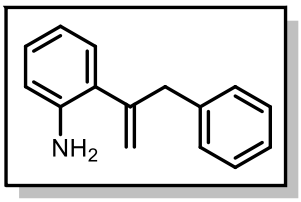
Pale yellow liquid (65%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.15 – 7.06 (m, 1H), 7.05 – 6.99 (m, 1H), 6.79 – 6.75 (m, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 5.30 (d, *J* = 3.9 Hz, 1H), 5.08 (d, *J* = 4.0 Hz, 1H), 3.77 (s, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 1.10 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.6, 143.2, 129.1, 128.6, 127.9, 118.2, 115.5, 113.4, 30.3, 12.7. The spectroscopic and physical data are in accordance to that reported in the literature.[1]

2-(3-Methylbut-1-en-2-yl)aniline (1c)[1]



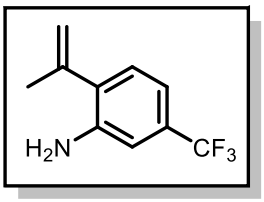
Pale yellow liquid (80%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.12 – 7.04 (m, 1H), 7.00 – 6.94 (m, 1H), 6.78 – 6.70 (m, 2H), 5.30 – 5.26 (m, 1H), 5.05 – 5.02 (m, 1H), 3.73 (s, 2H), 2.63 (hept, *J* = 7.2 Hz, 1H), 1.17 – 1.04 (m, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.1, 143.4, 129.5, 129.0, 127.8, 118.0, 115.4, 112.2, 34.6, 21.7 (2C). The spectroscopic and physical data are in accordance to that reported in the literature.[1]

2-(3-Phenylprop-1-en-2-yl)aniline (1d)[2]



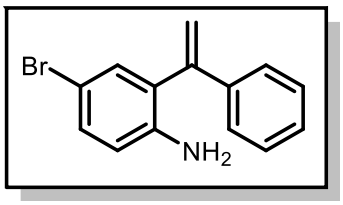
Pale yellow liquid (85%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.18 (m, 3H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.02 – 6.96 (m, 1H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 5.24 (s, 1H), 5.20 (s, 1H), 3.91 – 3.57 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.3, 143.2, 139.2, 129.3 (2C), 128.8, 128.5, 128.4 (2C), 128.1, 126.3, 118.2, 116.3, 115.6, 43.9. The spectroscopic and physical data are in accordance to that reported in the literature.[2]

2-(Prop-1-en-2-yl)-5-(trifluoromethyl)aniline (1f)[3]



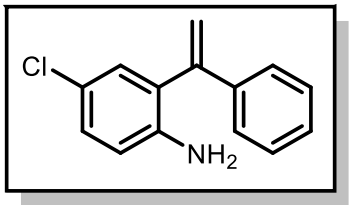
Yellow liquid (80%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.98 (s, 1H), 5.41 (s, 1H), 5.15 (s, 1H), 4.10 (s, 2H), 2.13 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.3, 142.6, 132.5, 130.2 (q, *J* = 32.0 Hz), 128.8, 124.3 (q, *J* = 272.0 Hz), 116.4, 114.7 (q, *J* = 3.9 Hz), 111.9 (q, *J* = 3.9 Hz), 23.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.8. The spectroscopic and physical data are in accordance to that reported in the literature.[3]

4-Bromo-2-(1-phenylvinyl)aniline (1i)[4]



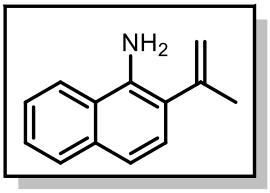
Yellow liquid (55%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 5H), 7.26 (d, *J* = 3.3 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 1H), 5.82 (s, 1H), 5.37 (s, 1H), 3.58 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.1, 143.1, 139.0, 133.2, 131.5, 129.2, 128.8 (2C), 128.5, 126.7 (2C), 117.3, 117.0, 110.1. The spectroscopic and physical data are in accordance to that reported in the literature.[4]

4-Chloro-2-(1-phenylvinyl)aniline (1j)[4]



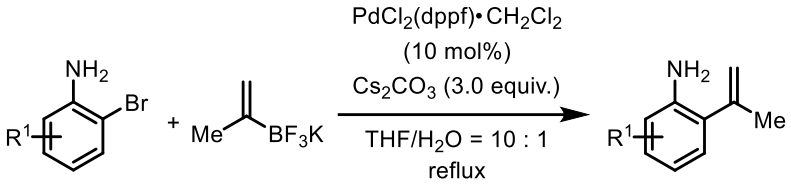
Yellow liquid (60%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H), 7.16 – 7.11 (m, 2H), 6.64 (d, *J* = 9.1 Hz, 1H), 5.83 (s, 1H), 5.38 (s, 1H), 3.65 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.2, 142.5, 139.0, 130.4, 128.8 (2C), 128.6, 128.5, 126.7 (2C), 123.1, 116.9. The spectroscopic and physical data are in accordance to that reported in the literature.[4]

2-(Prop-1-en-2-yl)naphthalen-1-amine (1m)[5]



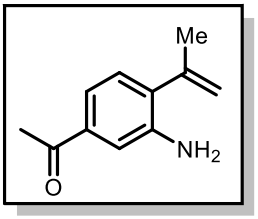
Brown liquid (50%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 4.6 Hz, 1H), 7.50 (dd, *J* = 7.7, 3.7 Hz, 2H), 7.40 – 7.31 (m, 1H), 7.30 – 7.24 (m, 1H), 5.49 (s, 1H), 5.22 (s, 1H), 4.41 (s, 2H), 2.21 (d, *J* = 3.8 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.0, 137.7, 133.4, 128.5, 126.4, 125.6, 125.2, 123.8, 123.8, 121.3, 118.2, 116.1, 24.3. The spectroscopic and physical data are in accordance to that reported in the literature.[5]

General Procedure 2 (GP2): Starting materials **1g-1h**, and **1k** were prepared according to a modified literature procedure.[3]



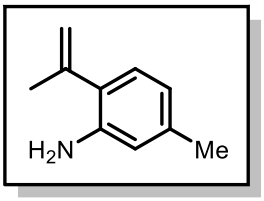
To a suspension of potassium isopropenyltrifluoroborate (5.5 mmol, 1.1 equiv), Cs_2CO_3 (3.0 equiv), $PdCl_2(dppf)•CH_2Cl_2$ (10 mol%) in a solvent mixture (THF/H_2O = 75 mL/7.5 mL) was added 2-bromoaniline (5.0 mmol, 1.0 equiv). The reaction mixture was stirred at reflux for 16 h, then cooled to room temperature and diluted with water (30 mL) followed by extraction with EtOAc (50 mL x 3). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (petroleum ether/EtOAc as an eluent) to give the desired products.

1-(3-Amino-4-(prop-1-en-2-yl)phenyl)ethan-1-one (1g)



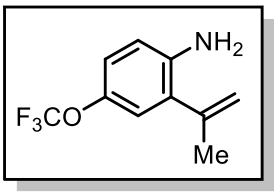
Orange solid (70%); **m.p.** 59 – 61 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 5.34 (s, 1H), 5.09 (s, 1H), 3.85 (brs, 2H), 2.55 (s, 3H), 2.07 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.2, 143.3, 142.8, 136.9, 134.1, 128.5, 118.7, 116.2, 114.8, 26.7, 23.6; **IR** (cm^{-1}) 3441, 3358, 1671, 1616, 1421, 1268, 1230, 1113, 893, 750; **High Resolution MS** (EI): Calculated for $C_{11}H_{13}NO$ $[M]^+$: 175.0997, Found: 175.0996.

5-Methyl-2-(prop-1-en-2-yl)aniline (1h)[1]



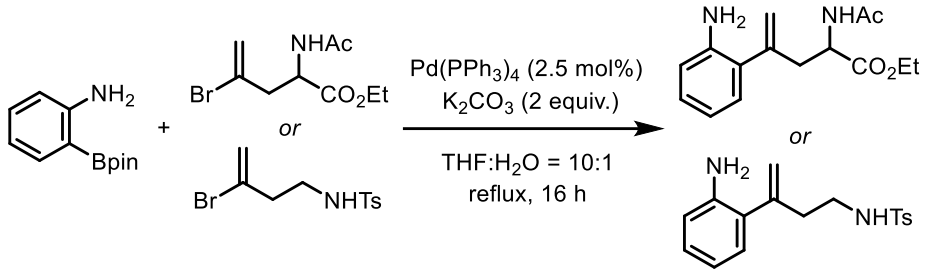
Yellow liquid (73%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.99 (d, *J* = 7.6 Hz, 1H), 6.63 – 6.60 (m, 1H), 6.58 (d, *J* = 1.9 Hz, 1H), 5.32 (dd, *J* = 2.3, 1.5 Hz, 1H), 5.10 (dd, *J* = 2.3, 1.1 Hz, 1H), 3.78 (s, 2H), 2.31 (s, 3H), 2.13 – 2.10 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.4, 142.8, 137.8, 128.2, 126.5, 119.2, 116.3, 115.1, 24.1, 21.2. The spectroscopic and physical data are in accordance to that reported in the literature.[1]

2-(Prop-1-en-2-yl)-4-(trifluoromethoxy)aniline (1k)



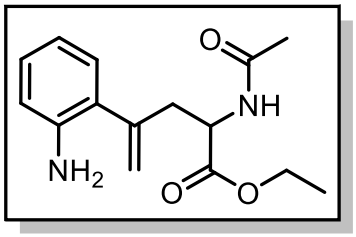
Brown Oil (52%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.96 – 6.88 (m, 2H), 6.67 (d, *J* = 8.5 Hz, 1H), 5.34 (s, 1H), 5.09 (d, *J* = 1.9 Hz, 1H), 3.91 (brs, 2H), 2.06 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.4, 141.9, 141.1 (q, *J* = 2.0 Hz), 130.0, 121.4, 121.0, 120.8 (q, *J* = 255.4 Hz), 116.4, 116.0, 23.7; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -58.4; **IR** (cm^{-1}) 3402, 3338, 1621, 1499, 1248, 1216, 1142, 1088, 606; **High Resolution MS** (EI): Calculated for $C_{10}H_{10}F_3NO$ $[M+H]^+$: 218.0787, Found: 218.0789.

General Procedure 3 (GP3): Starting material **1n** and **1o** were prepared according to a modified literature procedure.[6-8]



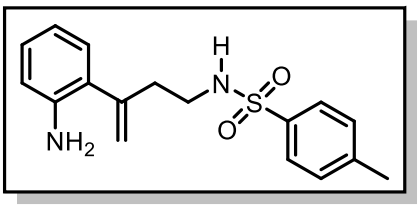
To a solution of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (5.0 mmol, 1.0 equiv), K_2CO_3 (2.0 equiv.), $Pd(PPh_3)_4$ (2.5 mol%) in a solvent mixture (THF/H_2O = 75 mL/7.5 mL) was added ethyl 2-acetamido-4-bromopent-4-enoate[7] or *N*-(3-Bromobut-3-en-1-yl)-4-methylbenzenesulfonamide[8] (5.0 mmol, 1.0 equiv.). The reaction mixture was stirred at reflux for 16 h, then cooled to room temperature and diluted with water (30 mL) followed by extraction with EtOAc (50 mL x 3). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (petroleum ether/EtOAc as an eluent) to give the desired product.

Ethyl 2-acetamido-4-(2-aminophenyl)pent-4-enoate (1n)



Pale yellow liquid (82%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.05 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.77 – 6.69 (m, 2H), 6.35 (t, *J* = 7.7 Hz, 1H), 5.30 (s, 1H), 5.19 (s, 1H), 4.73 – 4.61 (m, 1H), 4.06 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.97 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.65 (s, 2H), 3.02 (dd, *J* = 13.9, 4.8 Hz, 1H), 2.88 (dd, *J* = 14.1, 5.5 Hz, 1H), 1.79 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 169.8, 142.7, 142.5, 128.9, 128.5, 127.8, 119.1, 119.0, 116.3, 61.6, 52.0, 39.4, 23.0, 14.2; **IR** (cm^{-1}) 3307, 3066, 1733, 1655, 1535, 1212, 1026, 751; **High Resolution MS** (ESI): Calculated for $C_{15}H_{20}N_2O_3$ $[M]^+$: 276.1474, Found: 276.1477.

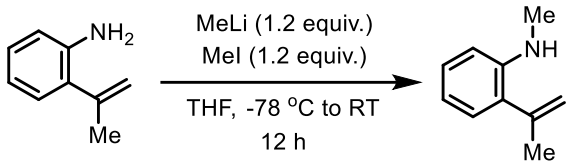
***N*-(3-(2-Aminophenyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (1o)**



Yellow liquid (68%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.03 (td, *J* = 7.6, 1.6 Hz, 1H), 6.87 – 6.77 (m, 1H), 6.68 (t, *J* = 7.5 Hz, 2H), 5.47 (t, *J* = 6.3 Hz, 1H), 5.25 (d, *J* = 1.8 Hz, 1H), 5.09 (d, *J* = 1.8 Hz, 1H), 3.73 (s, 2H), 2.92 (q, *J* = 6.1 Hz, 2H), 2.53 (t, *J* = 6.3 Hz, 2H),

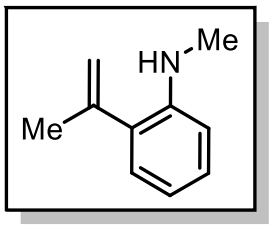
2.40 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.0, 143.2, 142.8, 137.1, 129.7 (2C), 128.3, 128.3, 127.4, 127.0 (2C), 118.8, 117.8, 116.2, 41.3, 37.6, 21.5; **IR** (cm^{-1}) 3450, 3278, 1614, 1493, 1320, 1155, 1093, 814; **High Resolution MS** (EI): Calculated for $C_{17}H_{20}N_2O_2S$ $[M]^+$: 316.1245, Found: 361.1244.

General Procedure 4 (GP4): Starting material **S1** was prepared according to a modified literature procedure.[9]



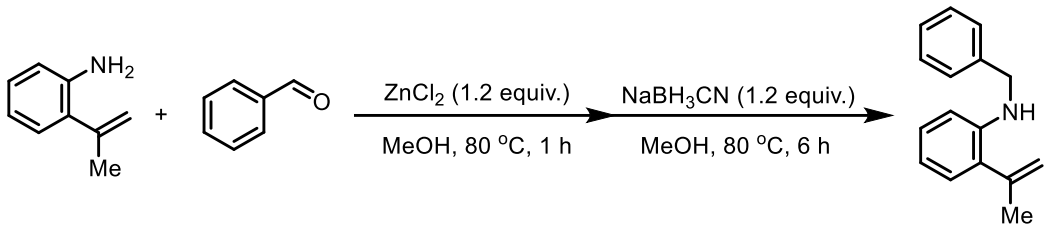
2-(Prop-1-en-2-yl)aniline (5.0 mmol, 1.0 equiv.) was dissolved in THF (17 mL) and cooled to -78 °C. Then methyllithium (1.2 equiv, 1.6 M in Et_2O) was added dropwise. The reaction was stirred for 1 h. Then iodomethane (1.2 equiv) was added and the reaction was warmed to room temperature and stirred for 12 h. The reaction was quenched with water (30 mL) then diluted with EtOAc (50 mL x 3). The organic layer was separated, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc as an eluent) to give the desired product.

***N*-Methyl-2-(prop-1-en-2-yl)aniline (S1)**[10]



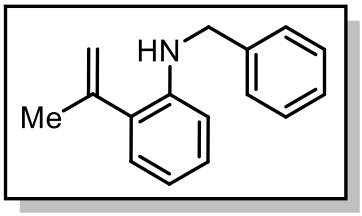
Brown Oil (45%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (ddd, *J* = 8.0, 7.3, 1.6 Hz, 1H), 7.02 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.70 (td, *J* = 7.4, 1.2 Hz, 1H), 6.65 (dd, *J* = 8.1, 1.1 Hz, 1H), 5.29 (dq, *J* = 3.0, 1.6 Hz, 1H), 5.07 – 4.99 (m, 1H), 4.32 (brs, 1H), 2.84 (s, 3H), 2.06 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.6, 143.7, 129.4, 128.3, 127.8, 116.5, 115.7, 109.8, 30.9, 24.2. The spectroscopic and physical data are in accordance to that reported in the literature.[10]

General Procedure 5 (GP5): Starting material **S2** was prepared according to a modified literature procedure.[11]



To a solution of 2-(prop-1-en-2-yl)aniline (5 mmol, 1.0 equiv.) in methanol (10 mL) were added benzaldehyde (6 mmol, 1.2 equiv.) and zinc chloride (6 mmol, 1.2 equiv.) and stirred at 80 °C for 1 hour. To the mixture was added sodium cyanoborohydride (6 mmol, 1.2 equiv.) and continuously stirred for 6 hours. After completion of the reaction, the mixture was diluted with EtOAc (20 mL) and saturated $NaHCO_3$ aqueous solution (20 mL). The phases were separated and the aqueous phase was extracted with EtOAc (20 mL x 2). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (*n*-hexane/EtOAc as an eluent) to give the desired product.

***N*-Benzyl-2-(prop-1-en-2-yl)aniline (S2)**[11]

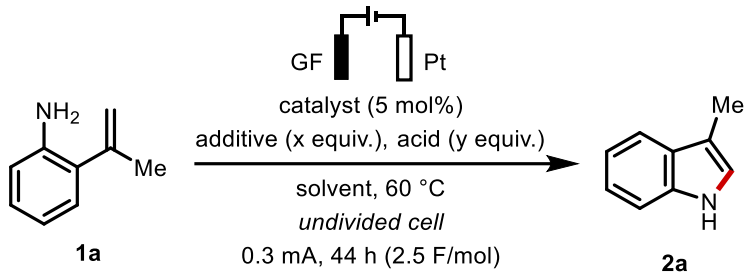


Colorless Oil (80%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 4H), 7.37 – 7.31 (m, 1H), 7.22 – 7.17 (m, 1H), 7.13 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 1H), 5.38 (s, 1H), 5.17 (s, 1H), 4.67 (s, 1H), 4.42 (s, 2H), 2.16 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.2, 143.7, 139.7, 129.5, 128.7 (2C), 128.2, 128.0, 127.4 (2C), 127.2, 117.0, 115.9, 110.8, 48.4, 24.2. The spectroscopic and physical data are in accordance to that reported in the literature.[11]

III. Procedure for the Optimization Study

An oven-dried, 10 mL two-neck glass tube was equipped with a magnetic stir bar, a threaded Teflon cap fitted with electrical feed-throughs, a graphite felt anode (0.6 cm × 1.2 cm × 0.7 cm) (connected to the electrical feed-through via a 9 cm in length, 2 mm in diameter graphite rod), and a platinum plate cathode. Inside a glove box, to pre-stirred mixture of 2-isopropenylaniline (27 mg, 0.20 mmol), catalyst (5.0 mol%) and additives in solvent (3.0 mL) was added carboxylic acid (3.0 equiv.). After the reaction tube was sealed with a rubber septum, the electrolysis was performed at 60 °C under constant current (I = 0.30 mA) with stirring for 44 h. The reaction mixture was cooled to room temperature, filtered through a pad of silica and then washed with EtOAc (10 mL x 3). The solvents were removed under reduced pressure and the crude yield was measured by ^{1}H NMR using 1,1,2,2-tetrachloroehtane or dibromomethane as an internal standard.

Table S1. Optimization of Reaction condition[a]

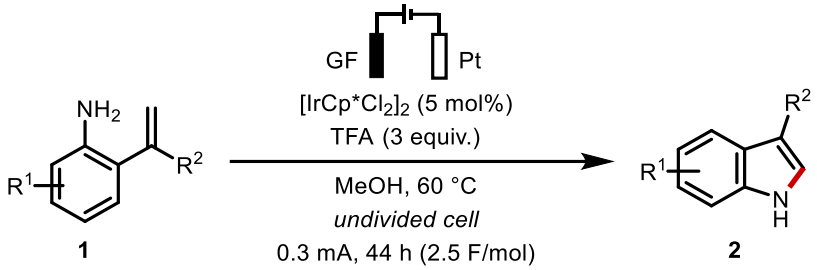


entry	catalyst	additive (x mmol)	acid (y mmol)	solvent	yield (%)[a]
1	$[IrCp^*Cl_2]_2$	$TBAPF_6$ (0.2)	PivOH (0.6)	MeCN	39
2[b]	$[IrCp^*Cl_2]_2$	$TBAPF_6$ (0.2)	PivOH (0.6)	MeCN	n.d.
3[c]	$[IrCp^*Cl_2]_2$	$TBAPF_6$ (0.2)	PivOH (0.6)	MeCN	16
4	$[IrCp^*Cl_2]_2$	TBAOAc (0.6)	-	MeCN	n.d.
5	$[IrCp^*Cl_2]_2$	$TBAPF_6$ (0.2)	PivOH (0.6)	DMF	9
6	$[IrCp^*Cl_2]_2$	$TBAPF_6$ (0.2)	PivOH (0.6)	DCE	43
7	$[IrCp^*Cl_2]_2$	$TBAPF_6$ (0.2)	PivOH (0.6)	MeOH	47
8	$[IrCp^*Cl_2]_2$	$TBABF_4$ (0.2)	PivOH (0.6)	MeOH	43
8	$[IrCp^*Cl_2]_2$	$TBAPF_6$ (0.2)	1-$AdCO_2H$ (0.6)	MeOH	55
9	$[IrCp^*Cl_2]_2$	$TBAPF_6$ (0.2)	AcOH (0.6)	MeOH	47
10	$[IrCp^*Cl_2]_2$	$TBAPF_6$ (0.2)	$C_6F_5CO_2H$ (0.6)	MeOH	56
11	$[IrCp^*Cl_2]_2$	$TBAPF_6$ (0.2)	TFA (0.6)	MeOH	60
12	$[IrCp^*Cl_2]_2$	KPF_6 (0.2)	TFA (0.6)	MeOH	45
13	**$[IrCp^*Cl_2]_2$**	**-**	**TFA (0.6)**	**MeOH**	**61**

14	$[IrCp^*Cl_2]_2$	-	TFA (0.6)	MeOH	n.d.
15[d]	-	-	TFA (0.6)	MeOH	n.d.
16	$[IrCp^*Cl_2]_2$	-	-	MeOH	19
17	$[RhCp^*Cl_2]_2$	-	TFA (0.6)	MeOH	7
18	$[CoCp^*Cl_2]_2$	-	TFA (0.6)	MeOH	n.d.
19	$[Ru(p\text{-cymene})Cl]_2$	-	TFA (0.6)	MeOH	9
20[e]	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2$ (0.08)	PivOH (0.4)	NMP	n.d.
21[f]	$[IrCp^*Cl_2]_2$	-	TFA (0.6)	MeOH	5
22[g]	$[IrCp^*Cl_2]_2$	-	TFA (0.6)	MeOH	n.d.

[a]n.d.= not detected. [b]Pt anode was used. [c]Reticulated vitreous carbon (RVC) anode was used. [d]Reaction without electricity. [e]Reaction at 120 °C for 12 h without electricity. [f]*N*-methyl-2-(prop-1-en-2-yl)aniline (**S1**) was used as a starting material in place of **1a**; yield of *N*-methyl-3-methylindole was indicated. [g]*N*-benzyl-2-(prop-1-en-2-yl)aniline (**S2**) was used as a starting material in place of **1a**; yield of *N*-benzyl-3-methylindole was indicated.

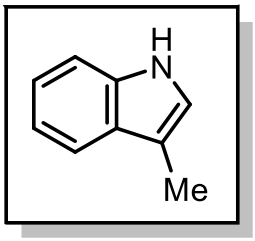
IV. Procedure for the Ir-Catalyzed Electrooxidative Dehydrogenative C–H/N–H coupling



An oven-dried, 10 mL two-neck glass tube was equipped with a magnetic stir bar, a threaded Teflon cap fitted with electrical feed-throughs, a graphite felt anode (0.6 cm × 1.2 cm × 0.7 cm) (connected to the electrical feed-through via a 9 cm in length, 2 mm in diameter graphite rod), and a platinum plate cathode. Inside a glove box, to a pre-stirred mixture of substrate (0.20 mmol) and $[IrCp^*Cl_2]_2$ (7.9 mg, 5.0 mol%) in methanol (3.0 mL) was added TFA (46 uL, 3.0 equiv.). After the reaction tube was sealed with a rubber septum, the electrolysis was performed at 60 °C under constant current (I = 0.30 mA) with stirring for 44 h. The reaction mixture was filtered through a pad of silica and then washed with EtOAc (10 mL x 3). Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc) to give the desired products.

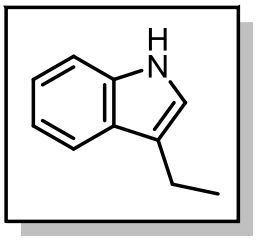
Figure S1. Setup for electrochemical intramolecular dehydrogenative C–H/N–H coupling

3-Methyl-1*H*-indole (2a)[12]



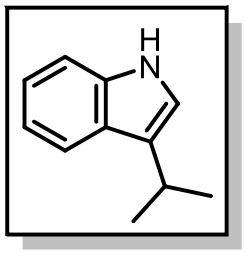
Colorless solid (61%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.98 (s, 1H), 2.37 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 136.4, 128.4, 122.0, 121.7, 119.2, 119.0, 111.9, 111.1, 9.8. The spectroscopic and physical data are in accordance to that reported in the literature.[12]

3-Ethyl-1*H*-indole (2b)[12]



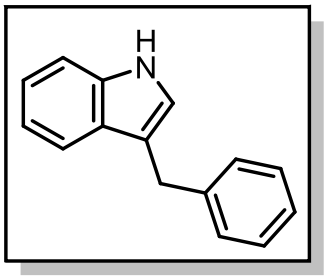
Colorless solid (50%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 1H), 6.98 (s, 1H), 2.81 (q, *J* = 7.9, 7.5 Hz, 2H), 1.35 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 136.5, 127.6, 122.0, 120.5, 119.2, 119.1, 119.0, 111.2, 18.5, 14.6. The spectroscopic and physical data are in accordance to that reported in the literature.[12]

3-Isopropyl-1*H*-indole (2c)[13]



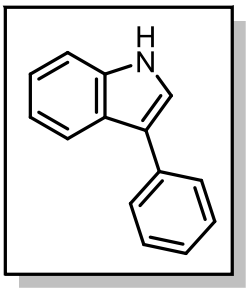
Colorless oil (60%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 3.23 (p, *J* = 6.9 Hz, 1H), 1.38 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 136.7, 126.9, 124.2, 122.0, 119.5, 119.3, 119.1, 111.2, 25.6, 23.5 (2C). The spectroscopic and physical data are in accordance to that reported in the literature.[13]

3-Benzyl-1*H*-indole (2d)[13]



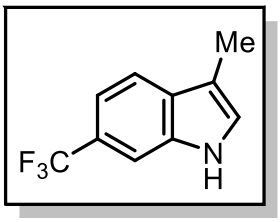
Colorless solid (68%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.27 (m, 4H), 7.22 – 7.18 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.92 (s, 1H), 4.13 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.3, 136.6, 128.8 (2C), 128.5 (2C), 127.6, 126.0, 122.4, 122.2, 119.5, 119.3, 116.0, 111.2, 31.7. The spectroscopic and physical data are in accordance to that reported in the literature.[13]

3-Phenyl-1*H*-indole (2e)[14]



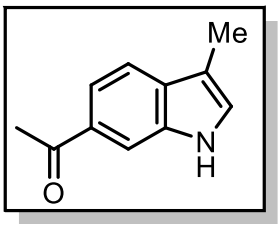
Colorless solid (60%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.45 (q, *J* = 7.9 Hz, 3H), 7.37 (d, *J* = 2.4 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.20 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 136.8, 135.7, 128.9 (2C), 127.6 (2C), 126.1, 125.9, 122.6, 121.9, 120.5, 120.0, 118.5, 111.5. The spectroscopic and physical data are in accordance to that reported in the literature.[14]

3-Methyl-6-(trifluoromethyl)-1*H*-indole (2f)[15]



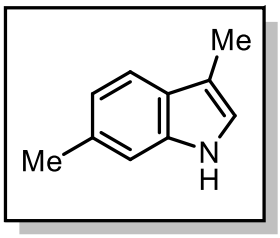
Pale yellow solid (45%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.63 (s, 1H), 7.36 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.12 (s, 1H), 2.36 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 135.1, 130.5, 125.5 (q, *J* = 271.5 Hz), 124.4, 124.1 (q, *J* = 31.7 Hz), 119.4, 116.0 (q, *J* = 3.5 Hz), 112.3, 108.6 (q, *J* = 4.4 Hz), 9.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -60.5. The spectroscopic and physical data are in accordance to that reported in the literature.[15]

1-(3-Methyl-1*H*-indol-6-yl)ethan-1-one (2g)



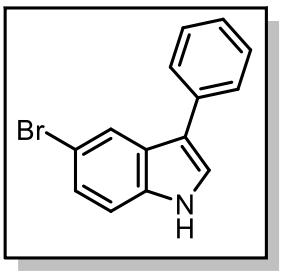
Yellow solid (65%); **m.p.** 162 – 164 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.05 (d, *J* = 1.5 Hz, 1H), 7.75 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.17 (d, *J* = 2.2 Hz, 1H), 2.66 (s, 3H), 2.35 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.8, 135.8, 132.1, 131.4, 126.0, 119.7, 118.6, 112.3, 112.2, 27.0, 9.7; **IR** (cm^{-1}) 3374, 2961, 2922, 2851, 1657, 1612, 1439, 1354, 1264, 1094, 883, 823; **High Resolution MS** (EI): Calculated for $C_{11}H_{11}NO$ $[M]^+$: 173.0841, Found: 173.0839.

3,6-Dimethyl-1*H*-indole (2h)[16]



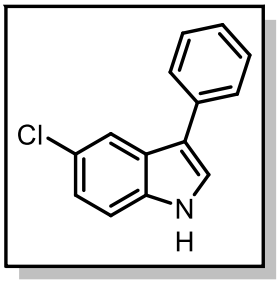
Yellow solid (45%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.37 (s, 1H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.02 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.93 (s, 1H), 2.47 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 134.7, 128.6, 128.5, 123.6, 121.8, 118.6, 111.4, 110.7, 21.6, 9.8. The spectroscopic and physical data are in accordance to that reported in the literature.[16]

5-Bromo-3-phenyl-1*H*-indole (2i)[17]



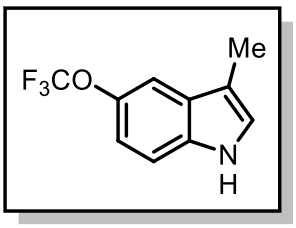
Orange solid (45%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.06 (d, *J* = 1.7 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.51 – 7.42 (m, 2H), 7.36 (dd, *J* = 3.8, 2.2 Hz, 1H), 7.34 – 7.28 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 135.4, 134.9, 129.0 (2C), 127.7, 127.6 (2C), 126.5, 125.4, 122.9, 122.5, 118.3, 113.8, 113.0. The spectroscopic and physical data are in accordance to that reported in the literature.[17]

5-Chloro-3-phenyl-1*H*-indole (2j)[17]



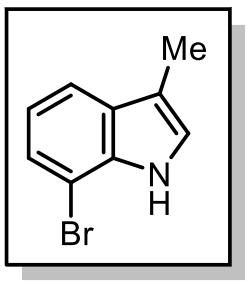
Brown solid (50%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.90 (d, *J* = 2.0 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.51 – 7.43 (m, 2H), 7.39 (d, *J* = 2.1 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.21 (dd, *J* = 8.6, 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.1, 134.9, 129.0 (2C), 127.6 (2C), 127.0, 126.5, 126.3, 123.1, 122.9, 119.5, 118.4, 112.5. The spectroscopic and physical data are in accordance to that reported in the literature.[17]

3-Methyl-5-(trifluoromethoxy)-1*H*-indole (2k)[15]



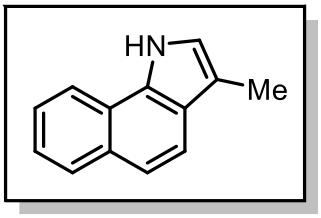
Colorless solid (56%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.42 (s, 1H), 7.31 (d, *J* = 8.7 Hz, 1H), 7.09 – 7.01 (m, 2H), 2.32 (d, *J* = 1.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.9 (q, *J* = 1.7 Hz), 134.6, 128.7, 123.6, 121.0 (q, *J* = 255.1 Hz) 116.0, 112.4, 111.6, 111.5, 9.7; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -58.1. The spectroscopic and physical data are in accordance to that reported in the literature.[15]

7-Bromo-3-methyl-1*H*-indole (2l)[18]



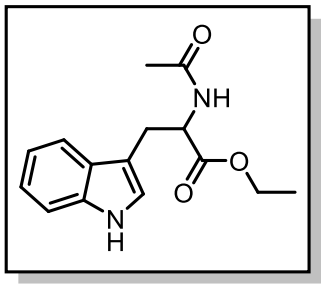
Colorless solid (41%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.03 (s, 1H), 7.00 (t, *J* = 7.7 Hz, 1H), 2.33 (d, *J* = 1.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 135.1, 129.6, 124.3, 122.3, 120.4, 118.2, 113.2, 104.7, 10.0. The spectroscopic and physical data are in accordance to that reported in the literature.[18]

3-Methyl-1*H*-benzo[*g*]indole (2m)



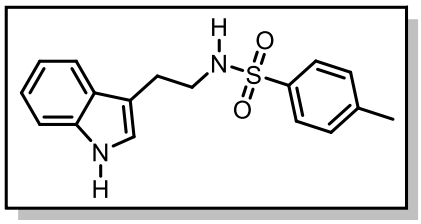
Colorless solid (35%); **m.p.** 190 – 192 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 1H), 2.44 (d, *J* = 1.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 130.9, 130.6, 129.0, 125.5, 124.1, 123.9, 121.9, 120.2, 119.9, 119.5, 119.2, 113.6, 9.9; **IR** (cm^{-1}) 3415, 3050, 2915, 2849, 1541, 1523, 1391, 1377, 1218, 787; **High Resolution MS** (EI): Calculated for $C_{13}H_{11}N$ $[M]^+$: 181.0891, Found: 181.1889.

***N*-Acetyltryptophan ethyl ester (2n)**



Pale yellow solid (45%); **m.p.** 124 – 126 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.98 (s, 1H), 6.02 (d, *J* = 7.8 Hz, 1H), 4.94 (dt, *J* = 7.8, 5.2 Hz, 1H), 4.24 – 4.05 (m, 2H), 3.32 (qd, *J* = 14.8, 5.3 Hz, 2H), 1.96 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.0, 169.8, 136.1, 127.8, 122.7, 122.2, 119.7, 118.6, 111.3, 110.2, 61.5, 53.2, 27.6, 23.3, 14.1; **IR** (cm^{-1}) 3355, 3300, 2924, 2849, 1714, 1659, 1530, 1227, 1017, 736; **High Resolution MS** (EI): Calculated for $C_{15}H_{18}N_2O_3$ $[M]^+$: 274.1317, Found: 274.1320.

***N*-(2-(1*H*-Indol-3-yl)ethyl)-4-methylbenzenesulfonamide (2o)**[19]



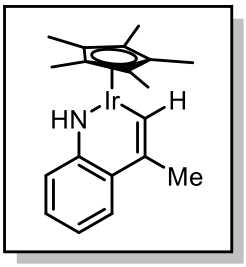
Colorless regin (58%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.42 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.37 – 7.27 (m, 1H), 7.19 (dd, *J* = 8.3, 7.1 Hz, 3H), 7.07 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 4.75 (t, *J* = 6.1 Hz, 1H), 3.26 (q, *J* = 6.6 Hz, 2H), 2.91 (t, *J* = 6.7 Hz, 2H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 136.6, 136.3, 129.6 (2C), 126.9 (2C), 126.8, 122.7, 122.0, 119.3, 118.4, 111.4, 111.3, 43.1, 25.4, 21.4. The spectroscopic and physical data are in accordance to that reported in the literature.[19]

V. Experimental Procedures of Mechanistic Studies

1. Preparation of iridium complex

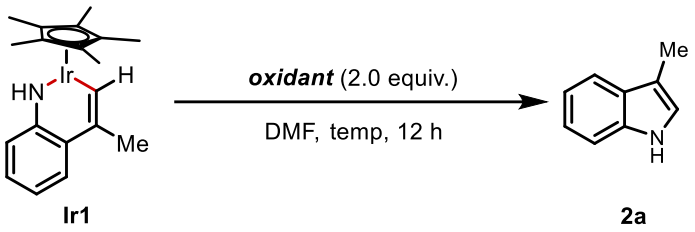
A solution of 2-isopropenylaniline (**1a**, 0.13 g, 1.0 mmol), $[IrCp^*Cl_2]_2$ (0.40 g, 0.50 mmol), and cesium pivalate (0.47 g, 2.0 mmol) in 1,2-dichloroethane (5.0 mL) was stirred for 12 h at room temperature under argon atmosphere. The resulting crude mixture was filtered through a pad of celite washing with 1,2-dichloroethane (15 mL), and concentrated under reduced pressure. The crude mixture was reconstituted in methylene chloride (0.5 mL) and then pentane (10 mL) was added for the recrystallization. The precipitant was collected by filtration and washed with pentane to obtain the product as purple solid. Single crystal of **Ir1** was obtained by slow diffusion of pentane into a saturated dichloromethane solution at -20 °C.

Iridium complex **Ir1**



Purple solid (79%); Decomposed at 210 °C; **^{1}H NMR** (600 MHz, CD_2Cl_2) δ 12.04 (s, 1H), 10.62 (s, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.32 – 7.19 (m, 2H), 2.69 (s, 3H), 2.00 (s, 15H); **^{13}C NMR** (150 MHz, CD_2Cl_2) 167.8, 147.3, 131.6, 128.0, 125.3, 124.7, 120.6, 117.9, 91.4 (5C), 26.2, 10.1 (5C); **IR** (cm^{-1}) 3063, 2951, 2903, 2863, 1501, 1440, 1337, 1026, 754; **High Resolution MS** (EI): Calculated for $C_{19}H_{24}IrN$ $[M]^+$: 459.1538, Found: 459.1536.

2. Chemical oxidation of Ir1 for the C–N bond-forming reductive elimination



Ir1 **2a**

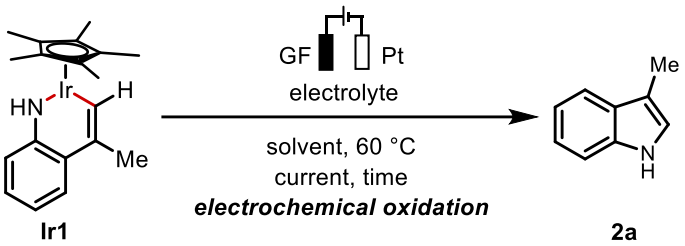
To an oven-dried screw capped vial equipped with a spinvane triangular-shaped Teflon stirbar were added **Ir1** (23 mg, 0.050 mmol), chemical oxidant (2.0 equiv.) and DMF (0.5 mL) under argon atmosphere. The reaction mixture was stirred in a pre-heated oil bath or a heating block at the indiciated temperature for 12 h. The reaction mixture was cooled to room temperature, filtered through a pad of silica and then washed with EtOAc (10 mL x 3). The solvents were removed under reduced pressure and the crude yield was measured by ^{1}H NMR using dibromomethane as an internal standard.

Table S2. Reductive elimination from **Ir1** using chemical oxidant system

entry	oxidant	temp (^{o}C)	conversion (%)	yield (%)[a]
1	-	120	0	n.d.
2	$AgNTf_2$	60	>95	n.d.
3	AgOTFA	60	>95	n.d.
4	AgOAc	60	90	n.d.
5	$Mn(OAc)_3$	60	75	n.d.
6	$AcFcBF_4$	60	84	n.d.
7	$(NH_4)_2Ce(NO_3)_6$	60	>95	n.d.
9	$Cu(OAc)_2$	60	30	10

[a]n.d.= not detected.

3. Electrochemical oxidation of Ir1 for the C–N bond-forming reductive elimination



The electrolysis was carried out in an undivided cell with a graphite felt anode and a Pt cathode. **Ir1** (23 mg, 0.050 mmol) and electrolyte were dissolved in the indicated solvent (3.0 mL). The electrolysis was performed with an indicated constant current and time with stirring at 60 °C. The solution was concentrated under reduced pressure and the crude yield was determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroehtane or dibromomethane as the internal standard. For entry 7, the reaction was repeated five times in separated reaction vials and the average ± standard deviation is depicted.

Table S3. Reductive elimination from **Ir1** using electrolytic oxidation

entry	electrolyte (x mmol)	solvent	current	time	yield (%)[a]
1	$TBAPF_6$ (0.3)	MeOH	4 mA	3 h	n.d
2	KPF_6 (0.3)	MeOH	4 mA	3 h	trace
3	KPF_6 (0.3)	MeCN	4 mA	3 h	8
4	KPF_6 (0.3)	DMF	4 mA	3 h	28
5	KOPiv (0.3)	DMF	4 mA	3 h	n.d.
6	KBF_4 (0.3)	DMF	4 mA	3 h	20
7	**KPF_6 (0.9)**	**DMF**	**4 mA**	**3 h**	**30 ± 2.6**
8	KPF_6 (0.9)	DMF	2 mA	6 h	15
9	$TBAPF_6$ (0.9)	DMF	4 mA	3 h	n.d.
10	KPF_6 (0.9)	DMF	-	12 h	n.d.

[a]n.d.= not detected.

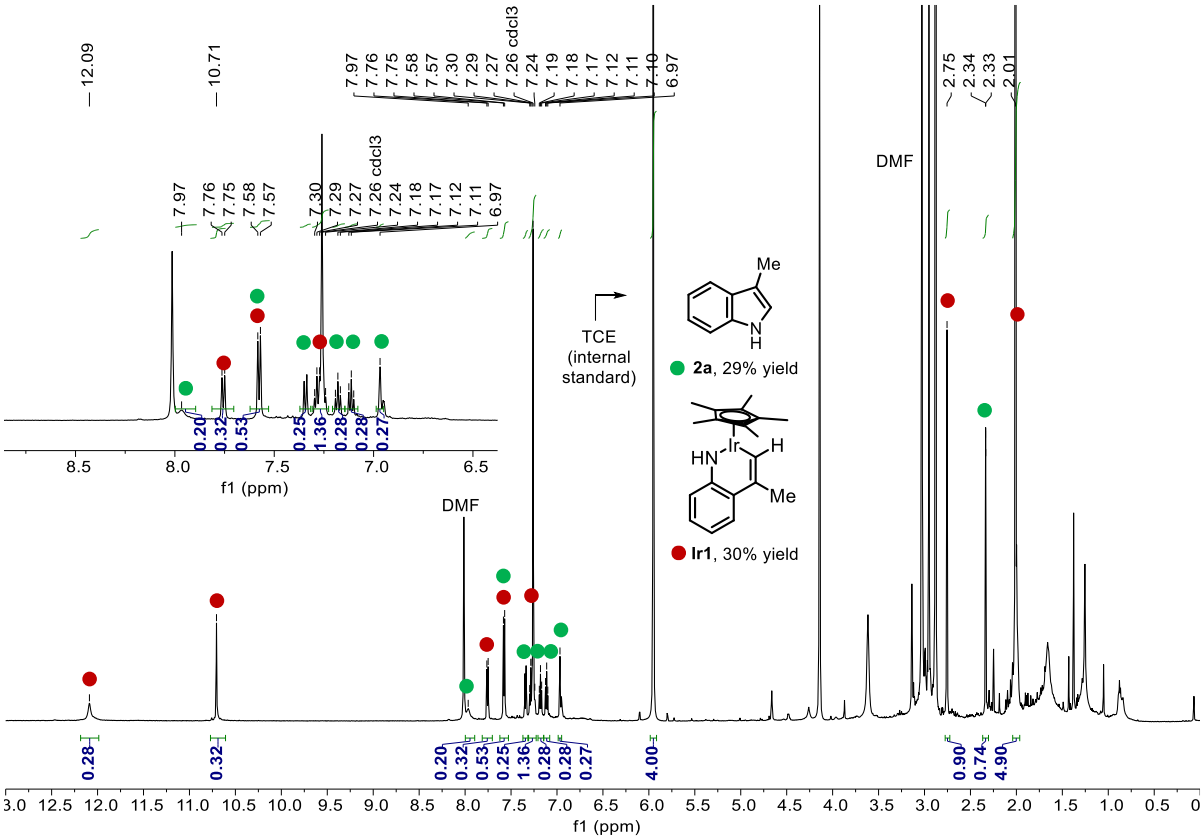


Figure S2. ^{1}H NMR spectrum of the crude reaction mixture

VI. DFT Calculations

1. Computational details

All DFT calculations were carried out with Gaussian09 quantum chemical package.[20] Geometry optimizations were performed with B3LYP functional[21,22] along with Grimme's D3 dispersion correction[23] and the 6-31G** basis set. Iridium was represented using the Los Alamos LANL2DZ basis set which includes relativistic effective core potentials.[24] For those structures having various conformations, the most stable conformer was searched and utilized. Vibrational frequency calculations were carried out at the same calculating theory level as the geometry optimization calculations. The single-point calculations of the optimized geometries were performed with M06[25] functional along with Grimme's D3 dispersion correction[23] and triple-zeta quality of basis set including Stuttgart/Dresden basis set (SDD)[26] for iridium and 6-311+G** basis set for other atoms. Standard approximation was used to obtain zero-point vibrational energy and entropy corrections. We obtained solvation energies using the optimized gas phase structures with SMD model.[27] Solvation calculations were carried out with the same level of single-point calculations employing the dielectric constants of ε = 37.219 for N,N-dimethylformamide. Graphical structures are visualized with Chemcraft.

2. Kohn-Sham orbital plot of Ir1

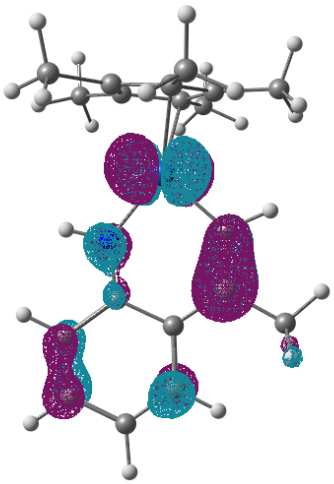


Figure S3. HOMO of **Ir(III)**. Isovalue=0.05

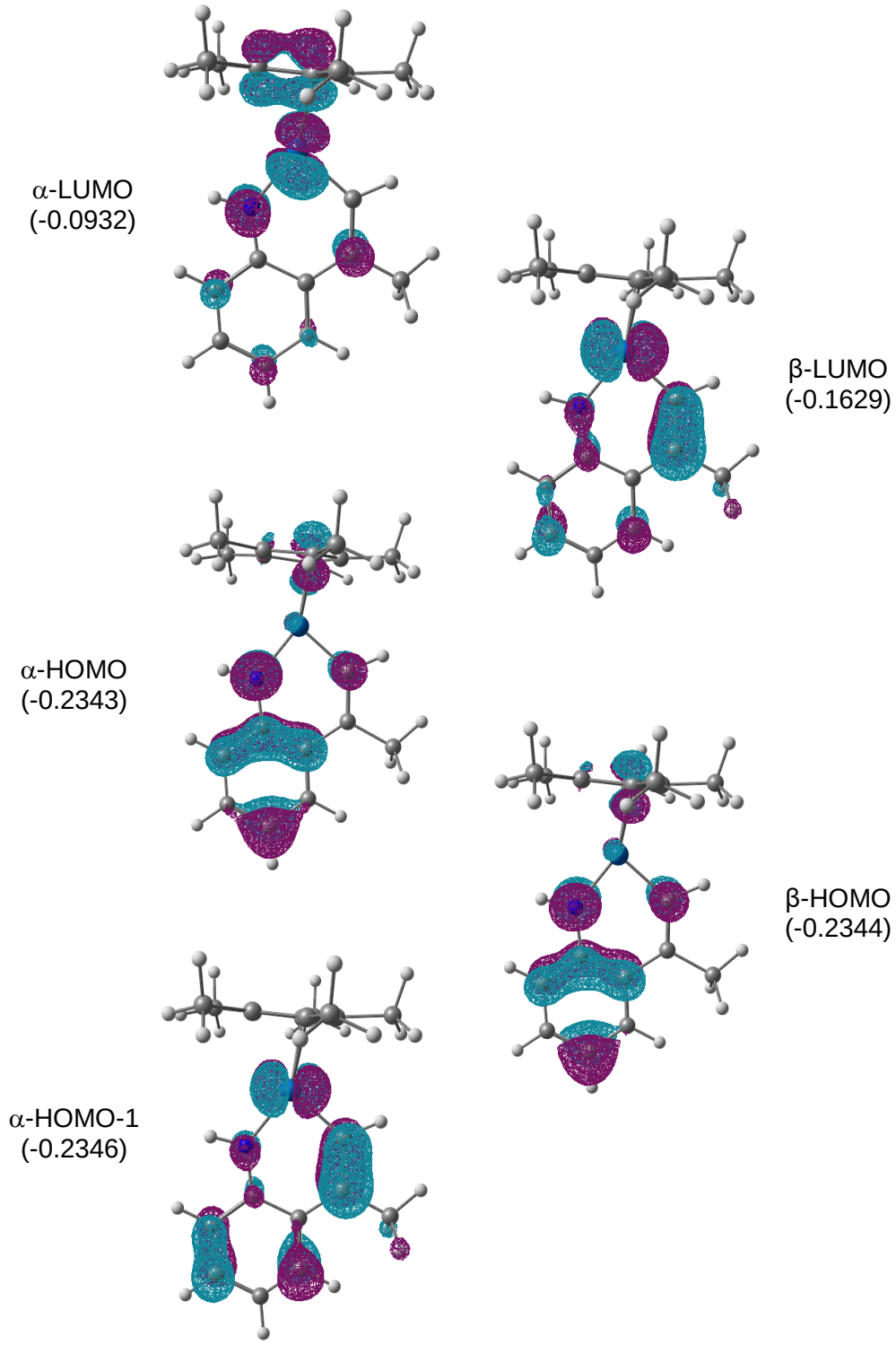


Figure S4. Frontier orbitals of **Ir(IV)**. Isovalue=0.05

3. Reaction energy profiles for reductive eliminations from Ir1 with various oxidation states

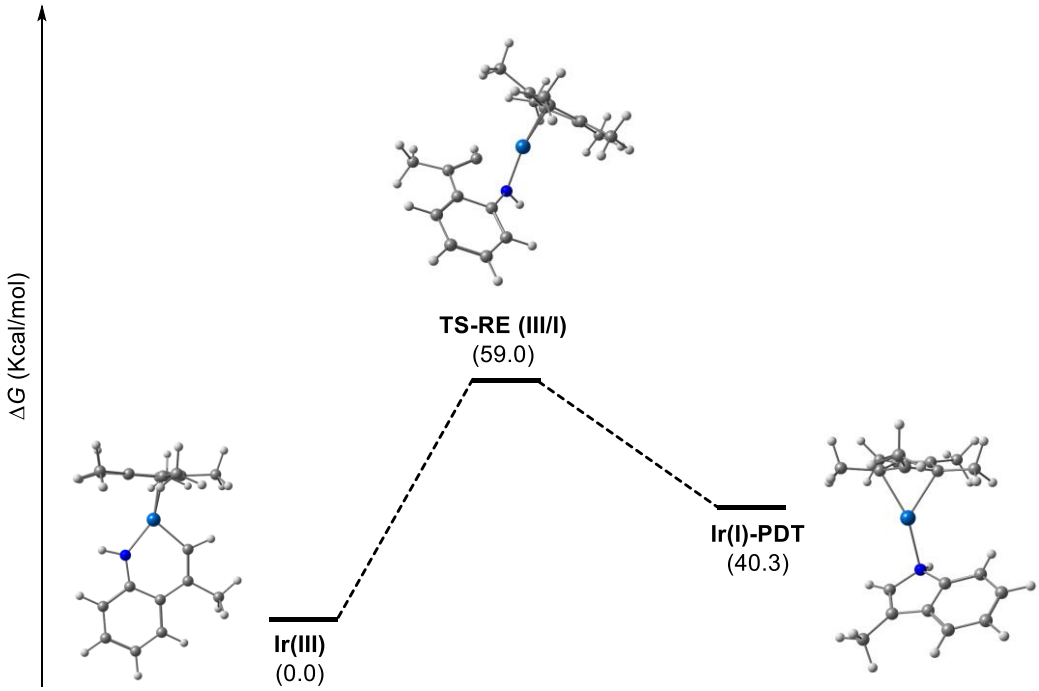


Figure S5. Reductive elimination from **Ir(III)**

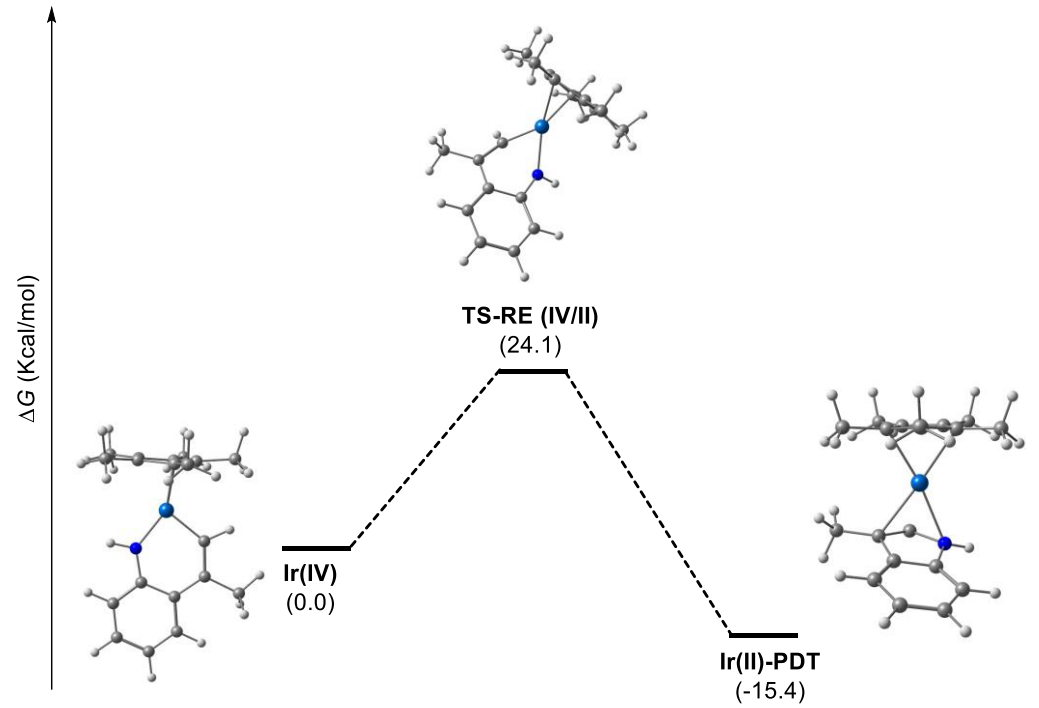


Figure S6. Reductive elimination from **Ir(IV)**

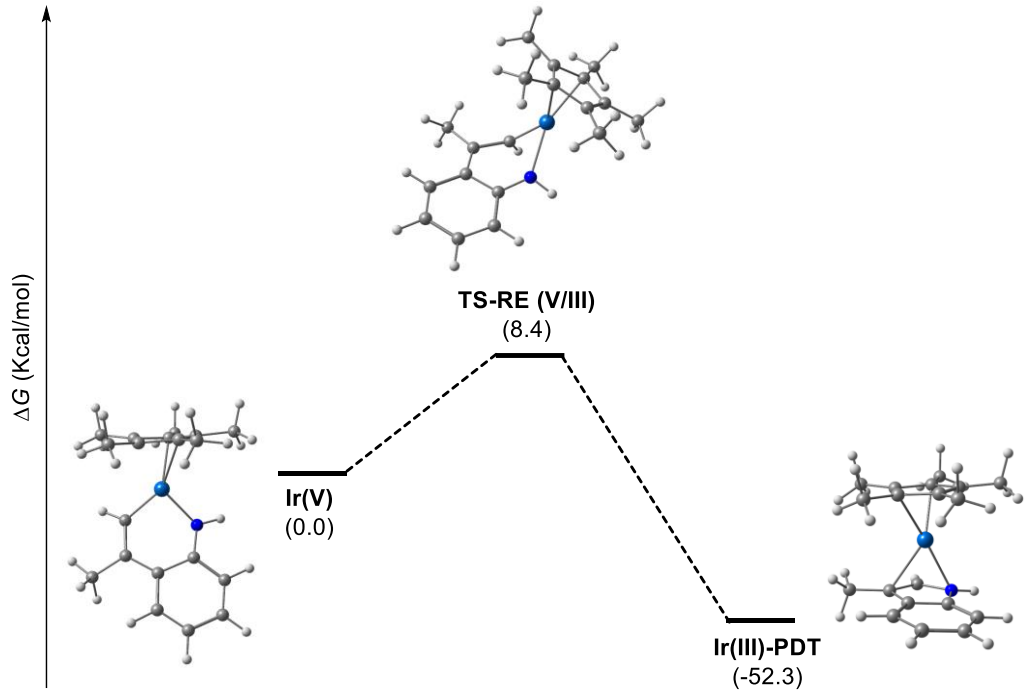


Figure S7. Reductive elimination from **Ir(V)**

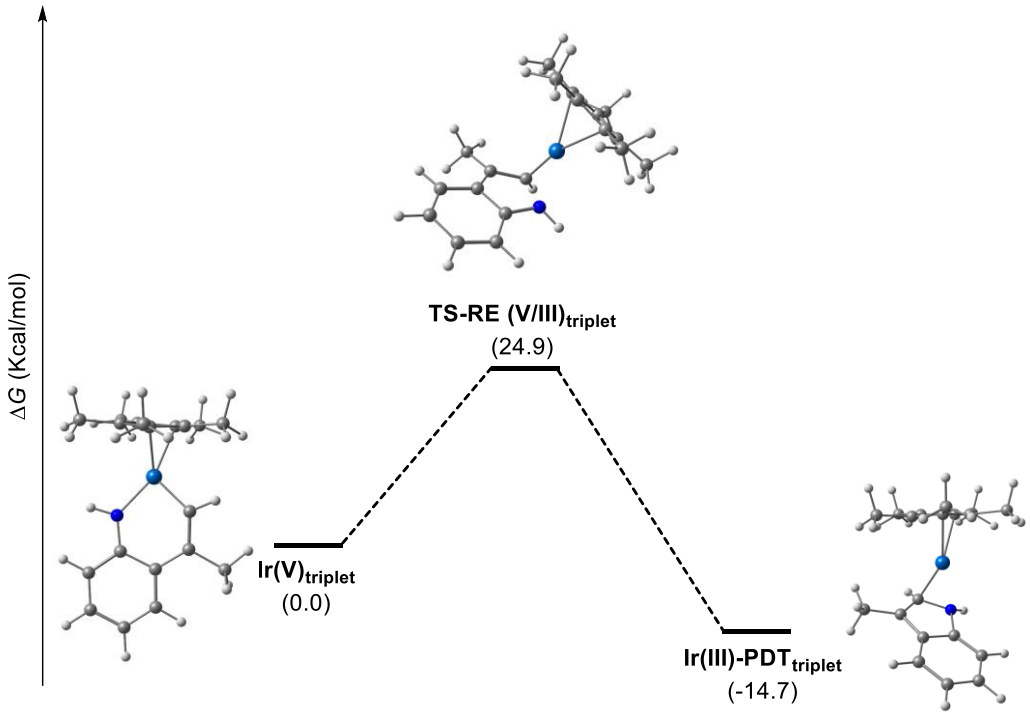


Figure S8. Reductive elimination from **Ir(V)** at the triplet state

4. Absolute energies of the optimized structures

Table S4. Absolute energies of the optimized structures

Name	Charge	Multiplicity	Electronic energy (Hartree)	Thermal correction (Hartree)	Gibbs free energy (Hartree)
Ir(III)	0	1	-897.242	0.330	-896.912
TS-RE(III/I)	0	1	-897.141	0.324	-896.818
Ir(I)-PDT	0	1	-897.173	0.326	-896.848
Ir(IV)	1	2	-897.055	0.329	-896.727
TS-RE(IV/II)	1	2	-897.012	0.323	-896.688
Ir(II)-PDT	1	2	-897.080	0.329	-896.751
Ir(V)	2	1	-896.860	0.328	-896.532
TS-RE(V/III)	2	1	-896.843	0.324	-896.519
Ir(III)-PDT	2	1	-896.947	0.331	-896.616
Ir(V)$_{triplet}$	2	3	-896.857	0.326	-896.531
TS-RE(V/III)$_{triplet}$	2	3	-896.812	0.322	-896.490
Ir(III)-PDT$_{triplet}$	2	3	-896.879	0.326	-896.553

VII. Electrochemical Analysis

1. General procedure for cyclic voltammetry experiments

Cyclic voltammetry analysis was performed in a 3-electrode cell consisting of a 3 mm glassy carbon disc working electrode, a Pt wire counter electrode, and Ag/Ag^+ reference electrode with Ag wire in a fritted chamber containing a solution of $AgNO_3$ (0.010 M) and KPF_6 (0.30 M) in N,N-dimethylformamide. A solution of each compound (0.0030 M) and KPF_6 (0.30 M) in N,N-dimethylformamide was added to the electrochemical cell. Cyclic voltammetry scans were taken at selected scan rates (from 200 to 800 mV/s) and in the selected potential window. The cyclic voltammogram of each compound was referenced to Fc/Fc^+ redox couple as an external standard.

2. Cyclic voltammograms of Ir1

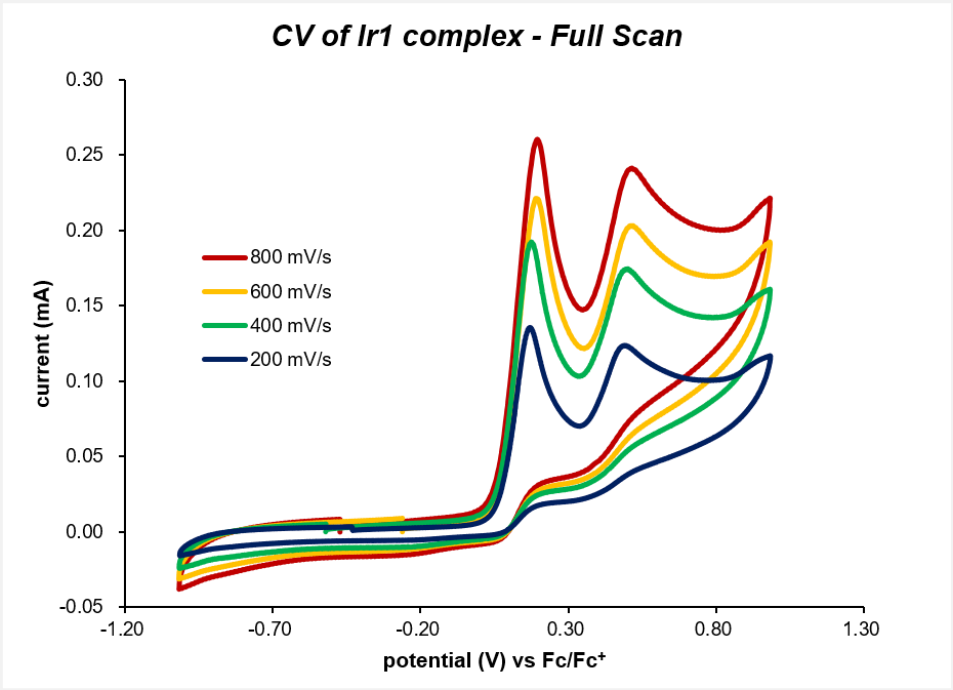


Figure S9. Full potential window CVs of **Ir1** at various scan rates

Table S5. Peak potentials of full potential window CVs at various scan rates

Scan rate (mV/s)	E_{pa} ($Ir^{III/IV}$)	E_{pa} ($Ir^{IV/V}$)
200	170 mV	490 mV
400	176 mV	503 mV
600	193 mV	519 mV
800	196 mV	516 mV

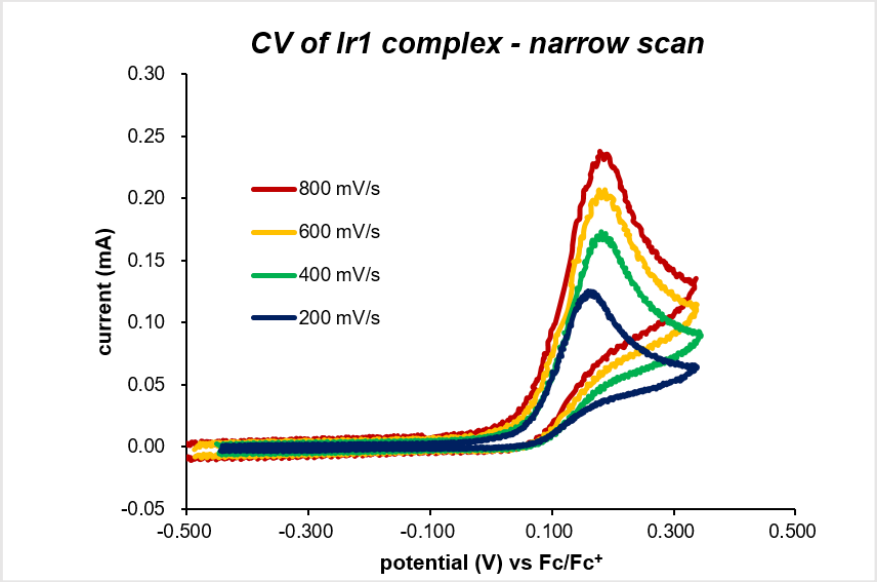


Figure S10. Narrow potential window CVs of **Ir1** at various scan rates

Table S6. Peak potentials of narrow potential window CVs at various scan rates

Scan rate (mV/s)	E_{pa} ($Ir^{III/IV}$)
200	159 mV
400	173 mV
600	177 mV
800	179 mV

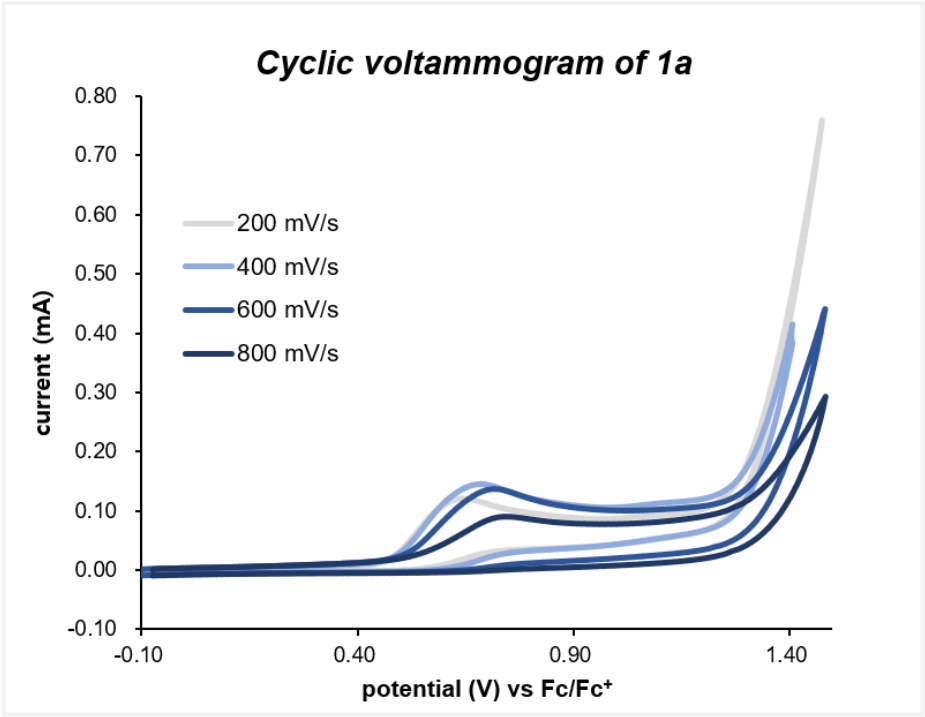


Figure S11. CVs of **1a** at various scan rates

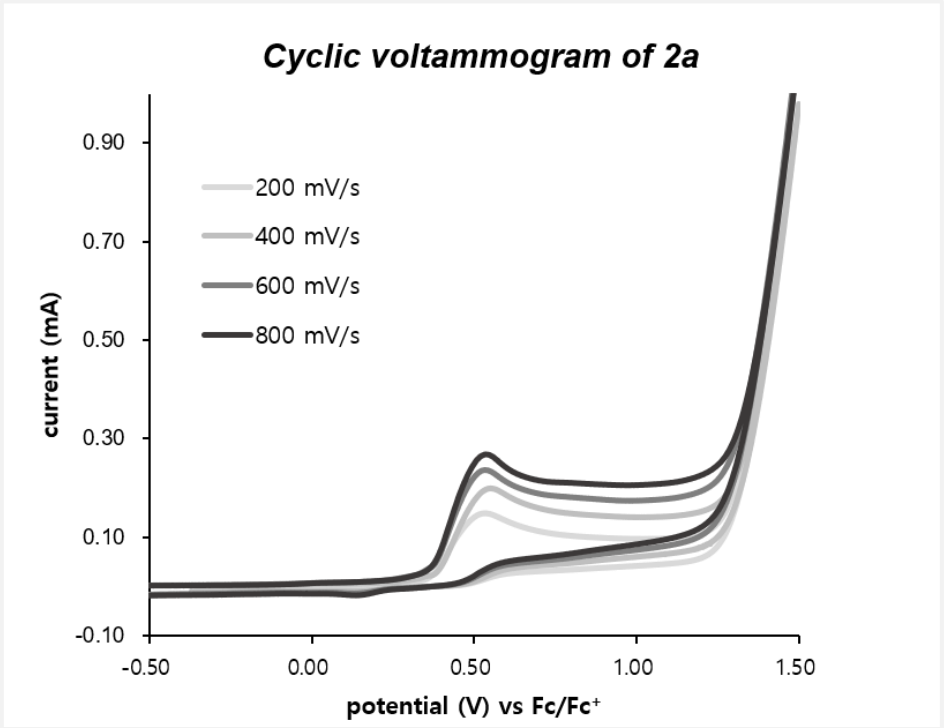


Figure S12. CVs of **2a** at various scan rates

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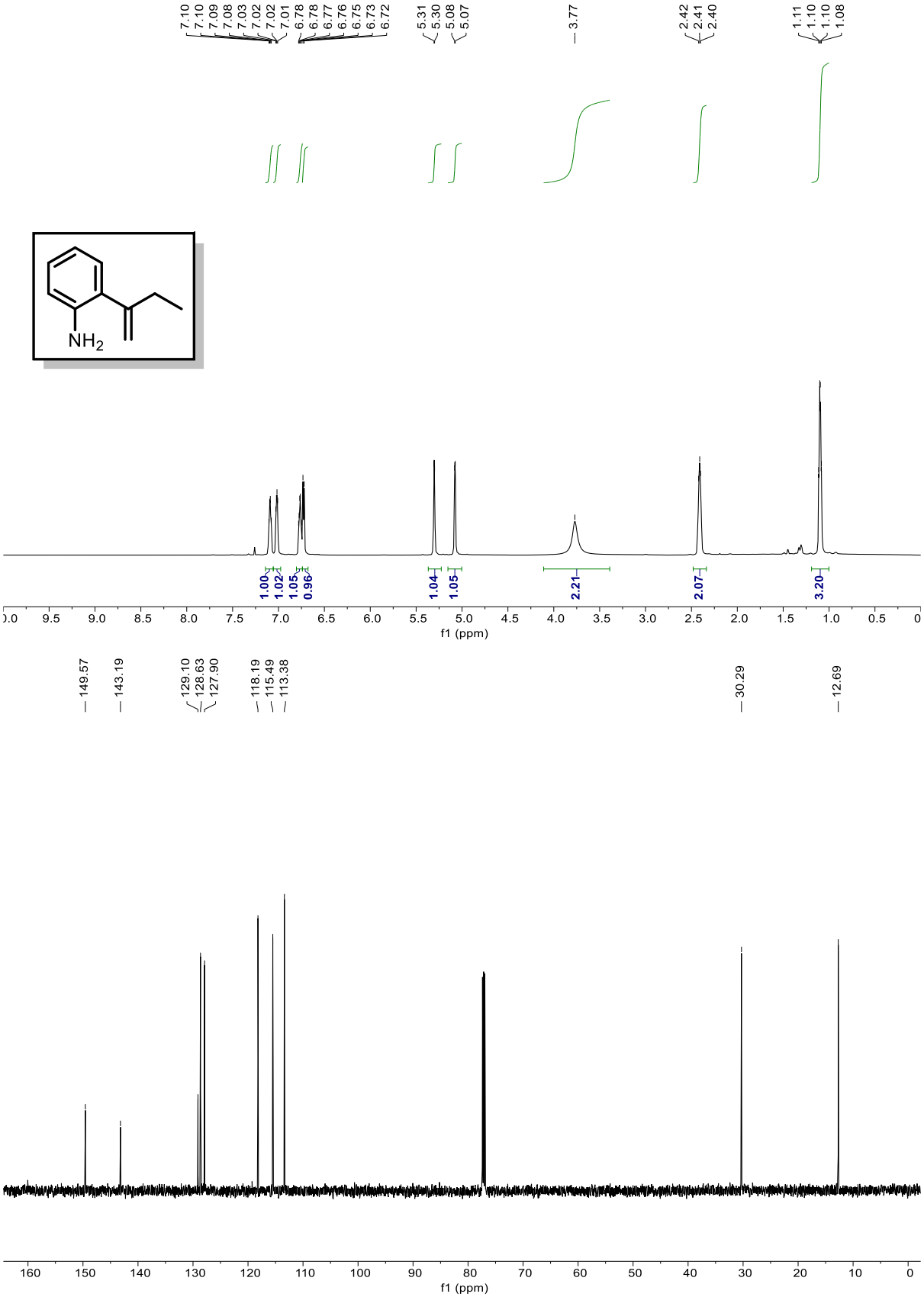
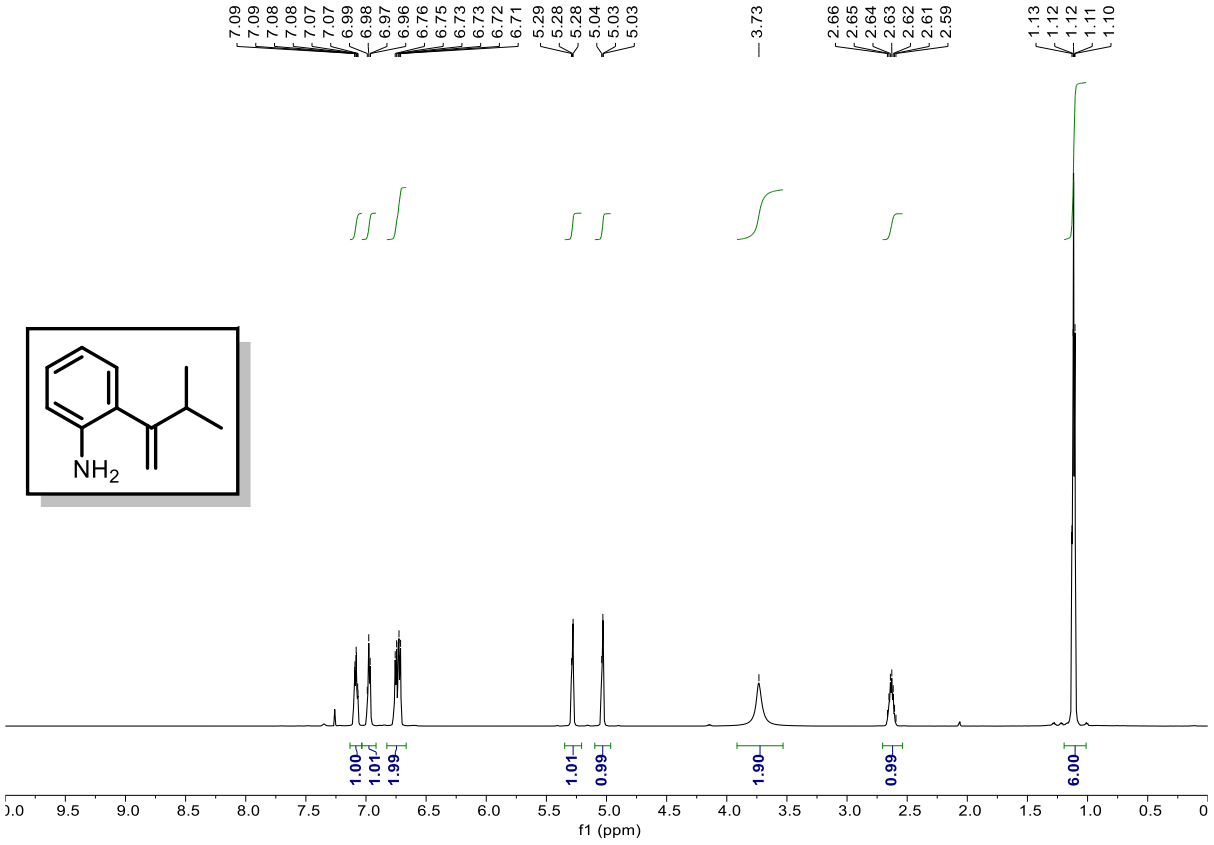
Appendix I

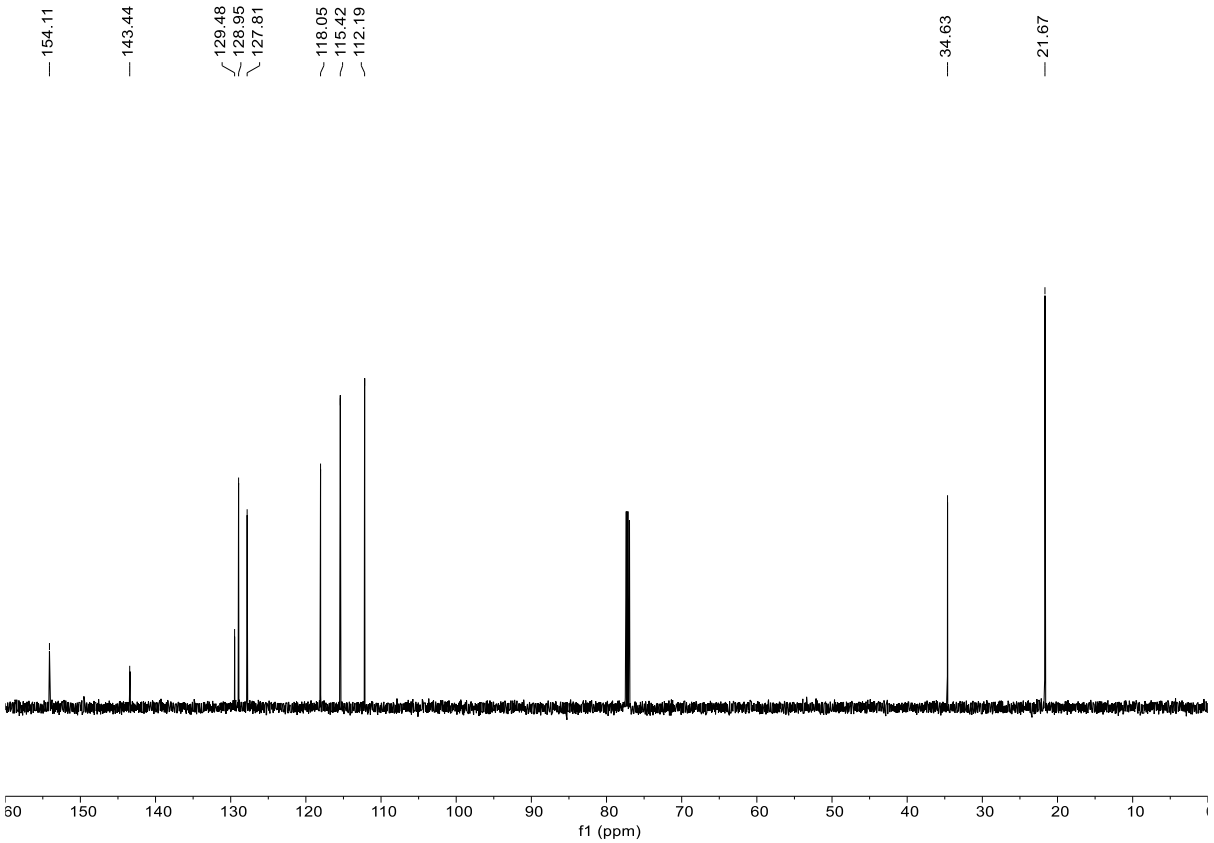
Spectral Copies of ^{1}H, ^{13}C and ^{19}F NMR of Compounds Obtained in this Study

2-(But-1-en-2-yl)aniline (1b)

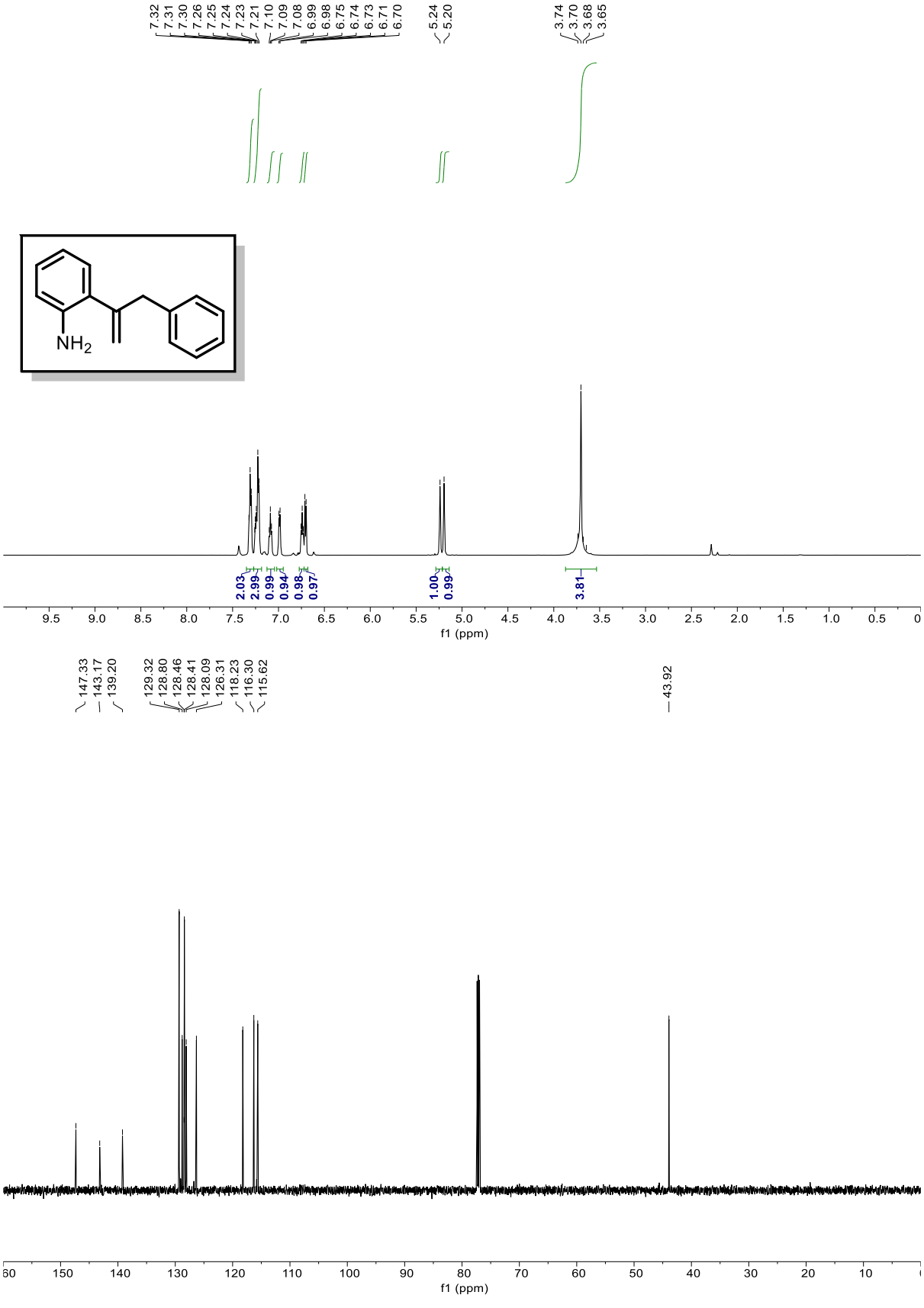


2-(3-Methylbut-1-en-2-yl)aniline (1c)

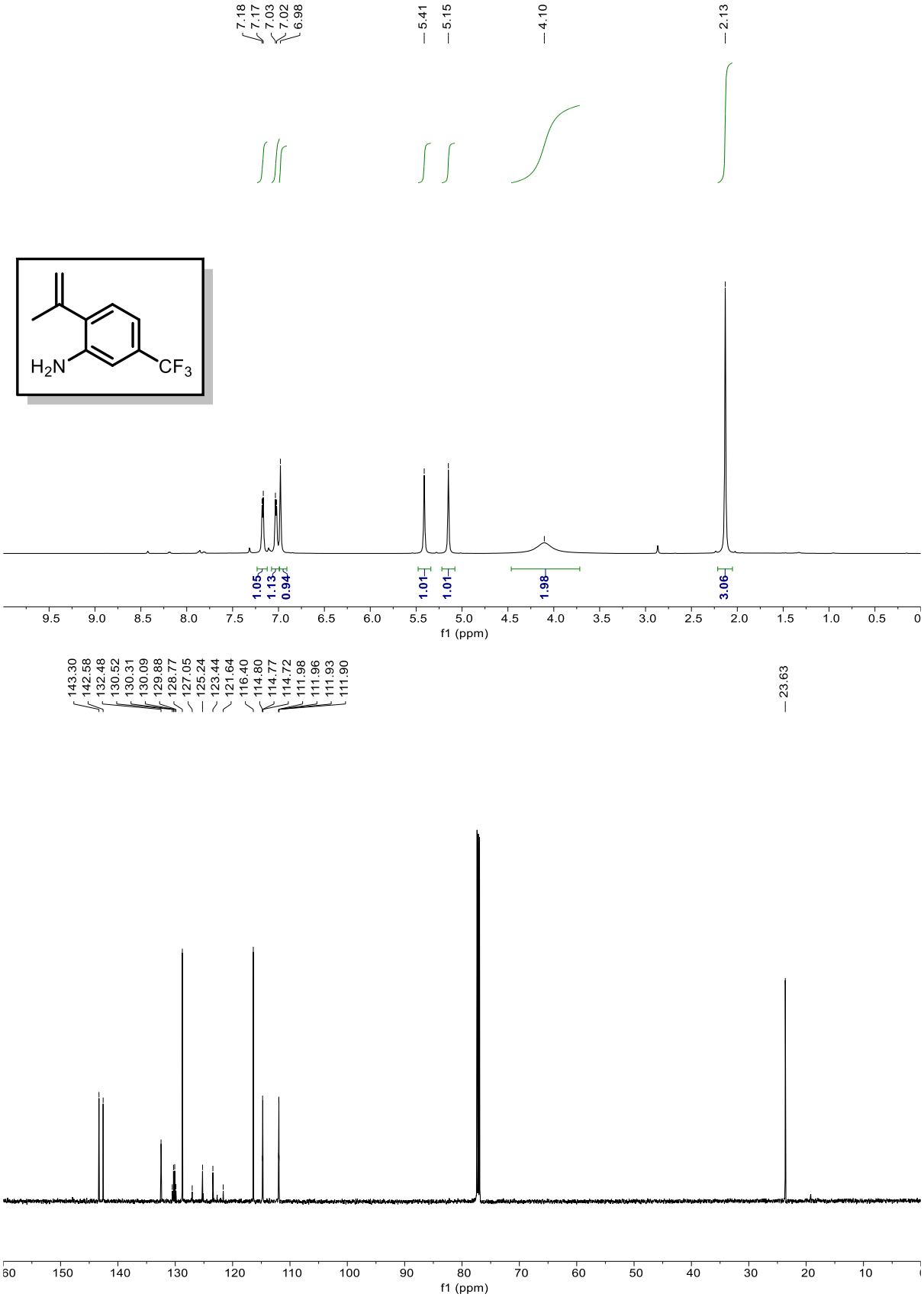


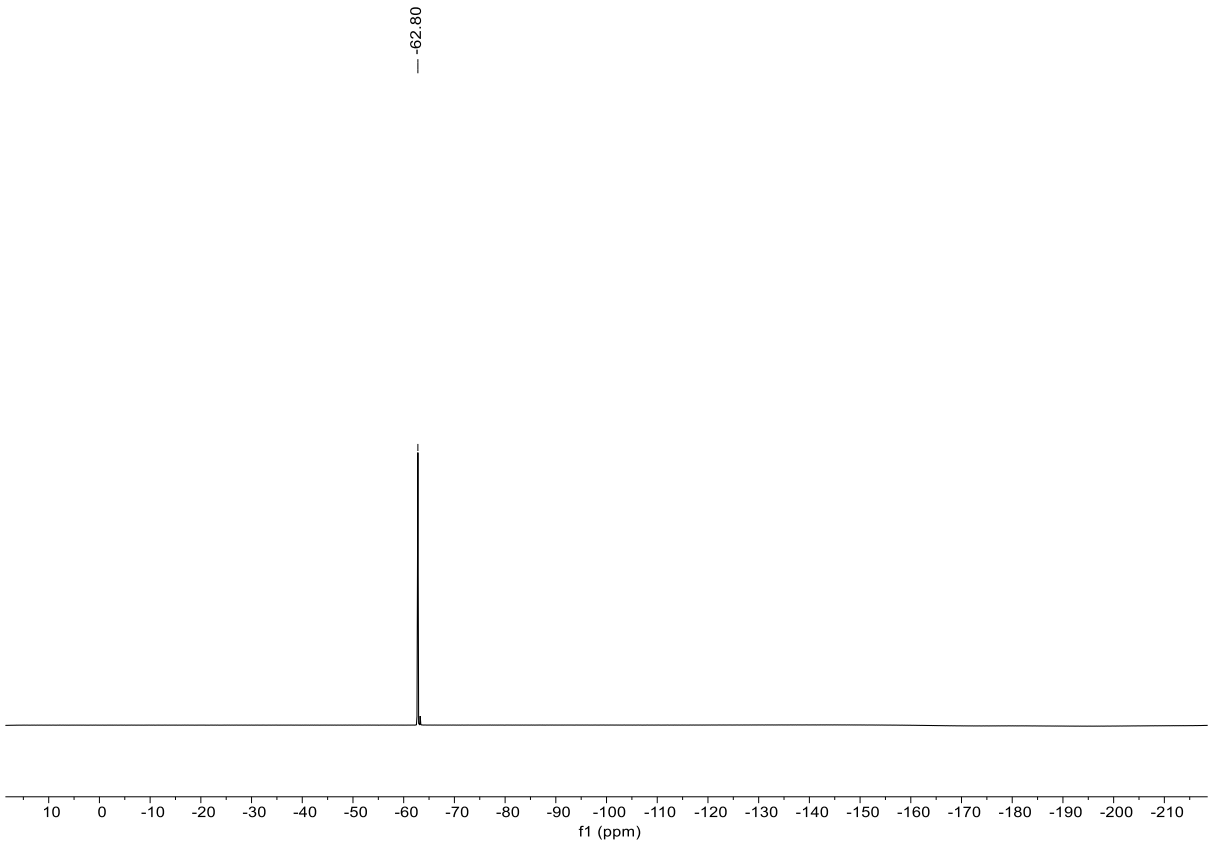


2-(3-Phenylprop-1-en-2-yl)aniline (1d)



2-(Prop-1-en-2-yl)-5-(trifluoromethyl)aniline (1f)

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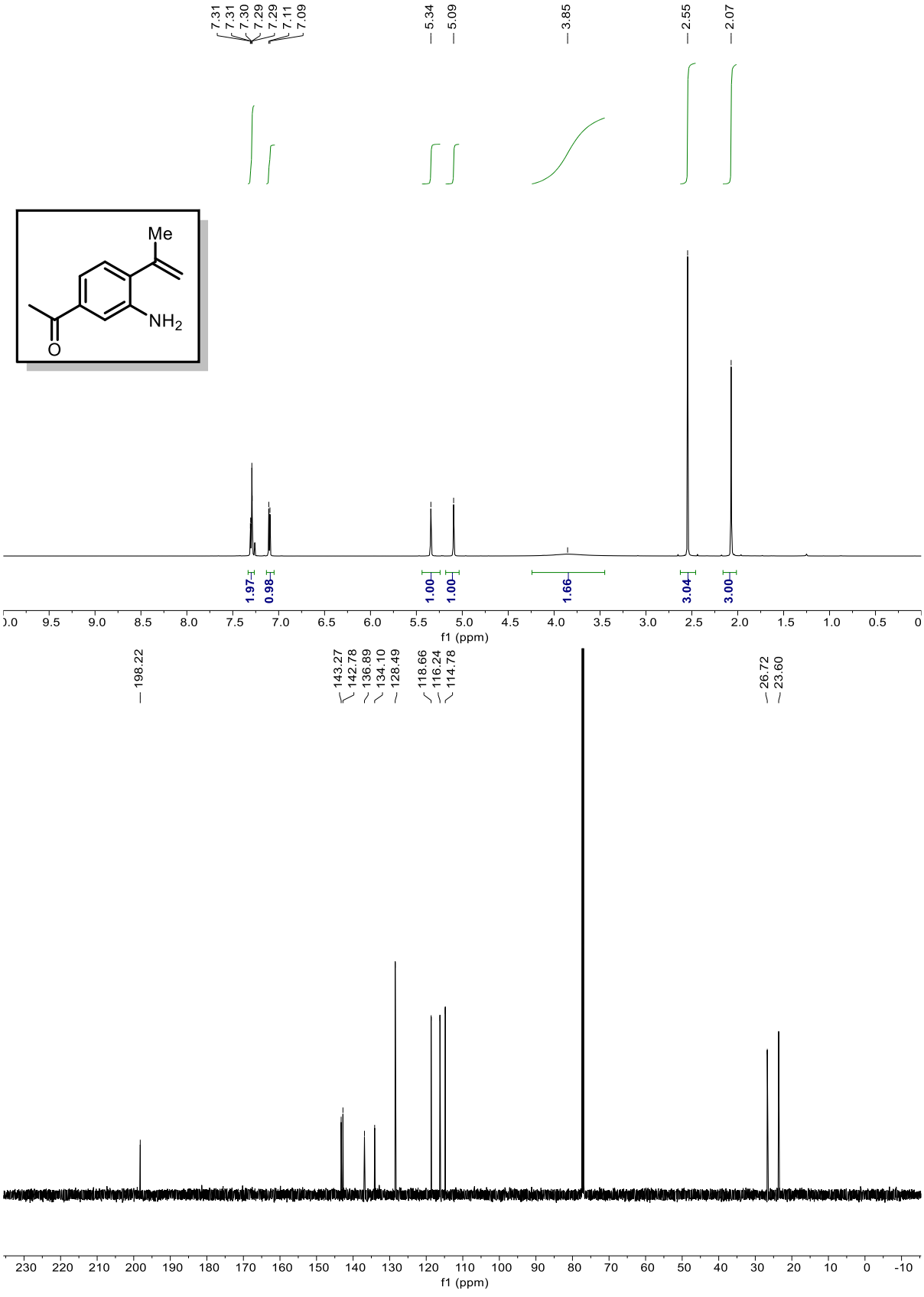
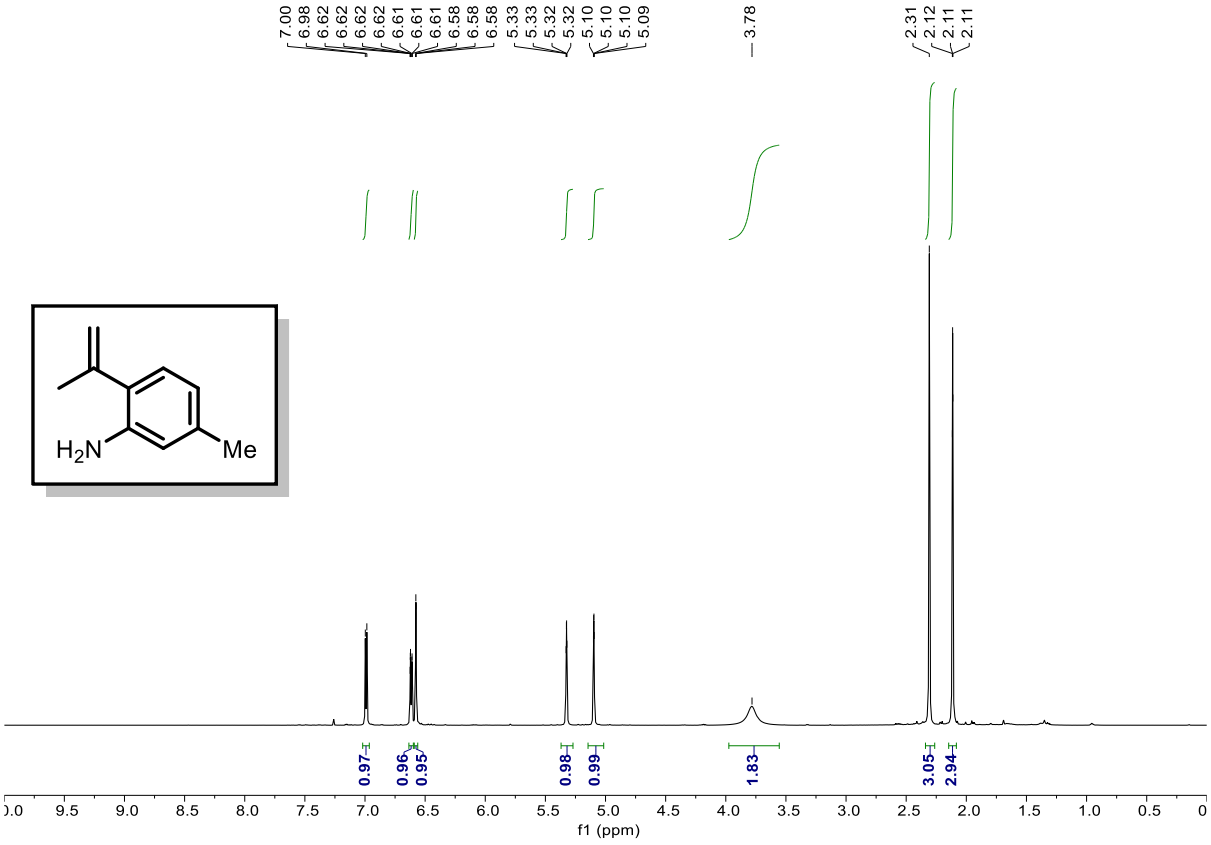
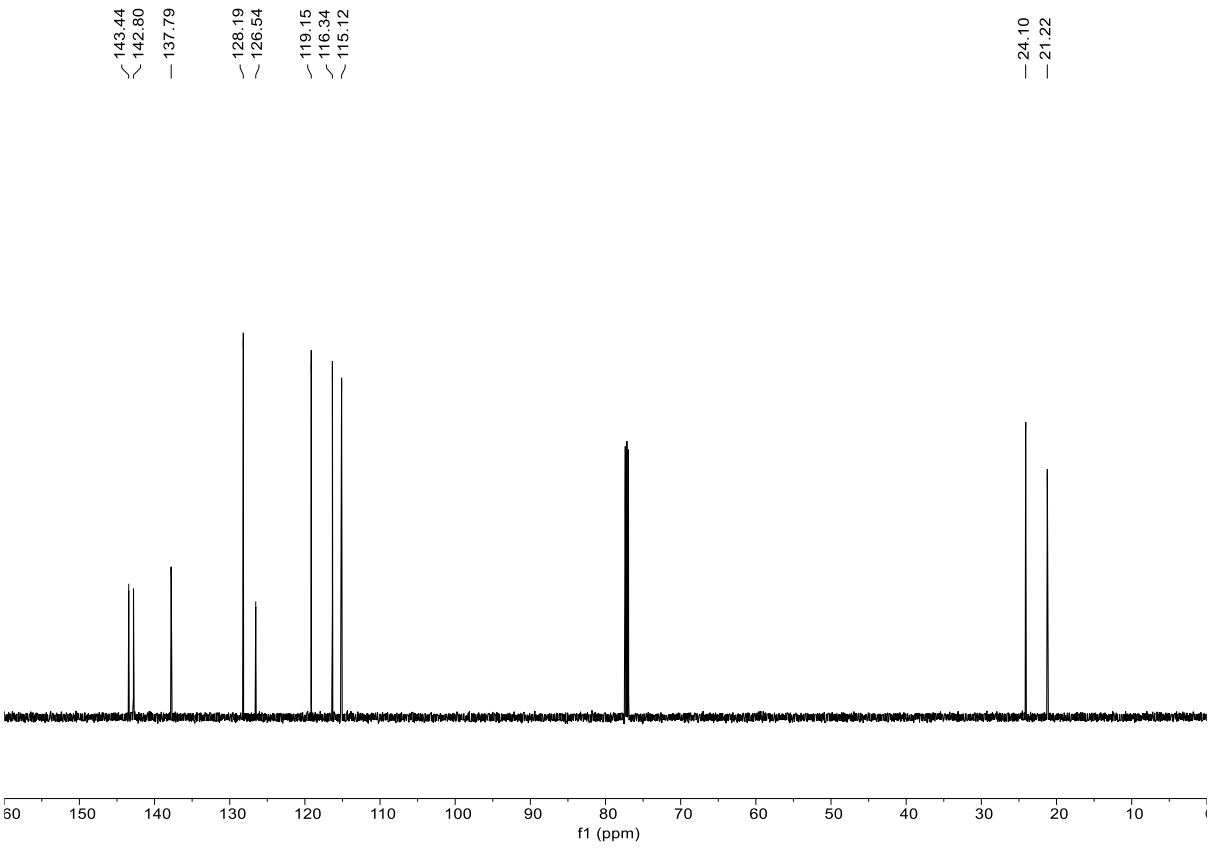
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

1-(3-Amino-4-(prop-1-en-2-yl)phenyl)ethan-1-one (1g)

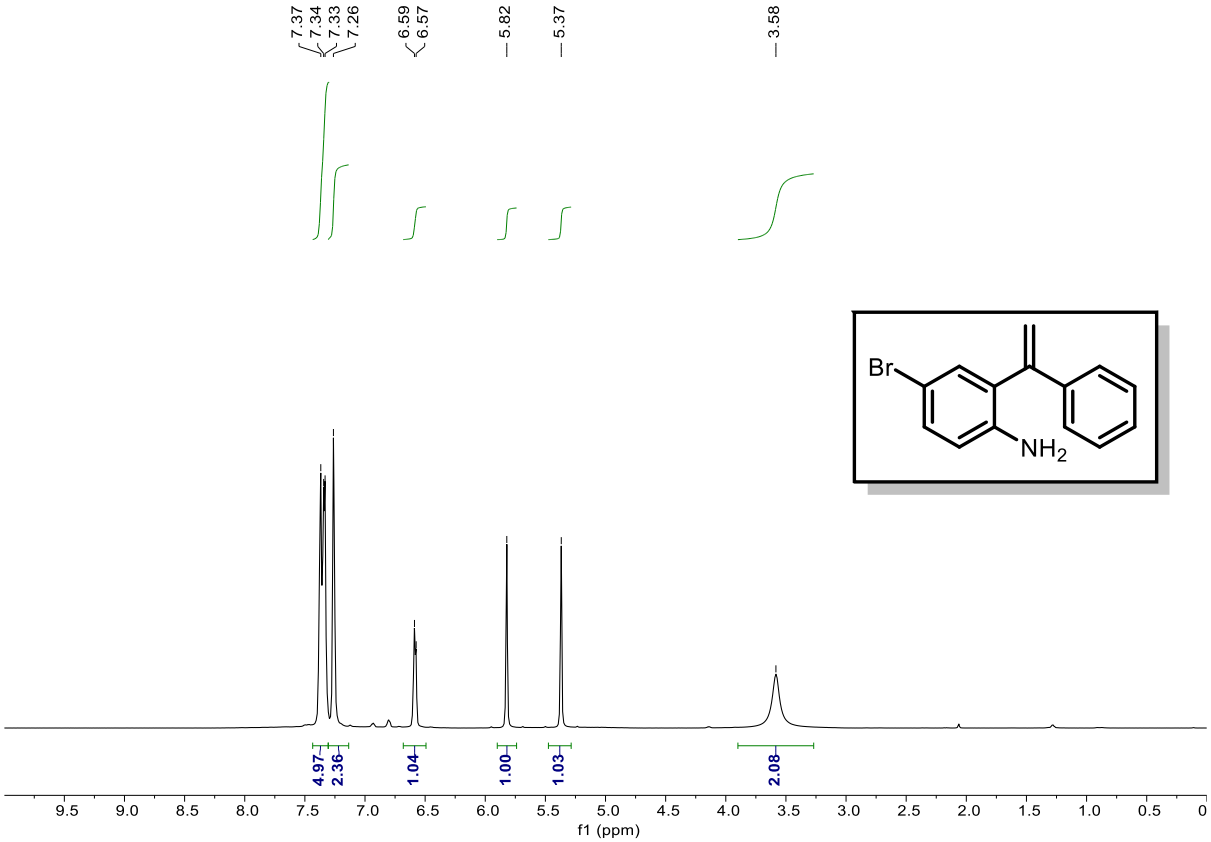


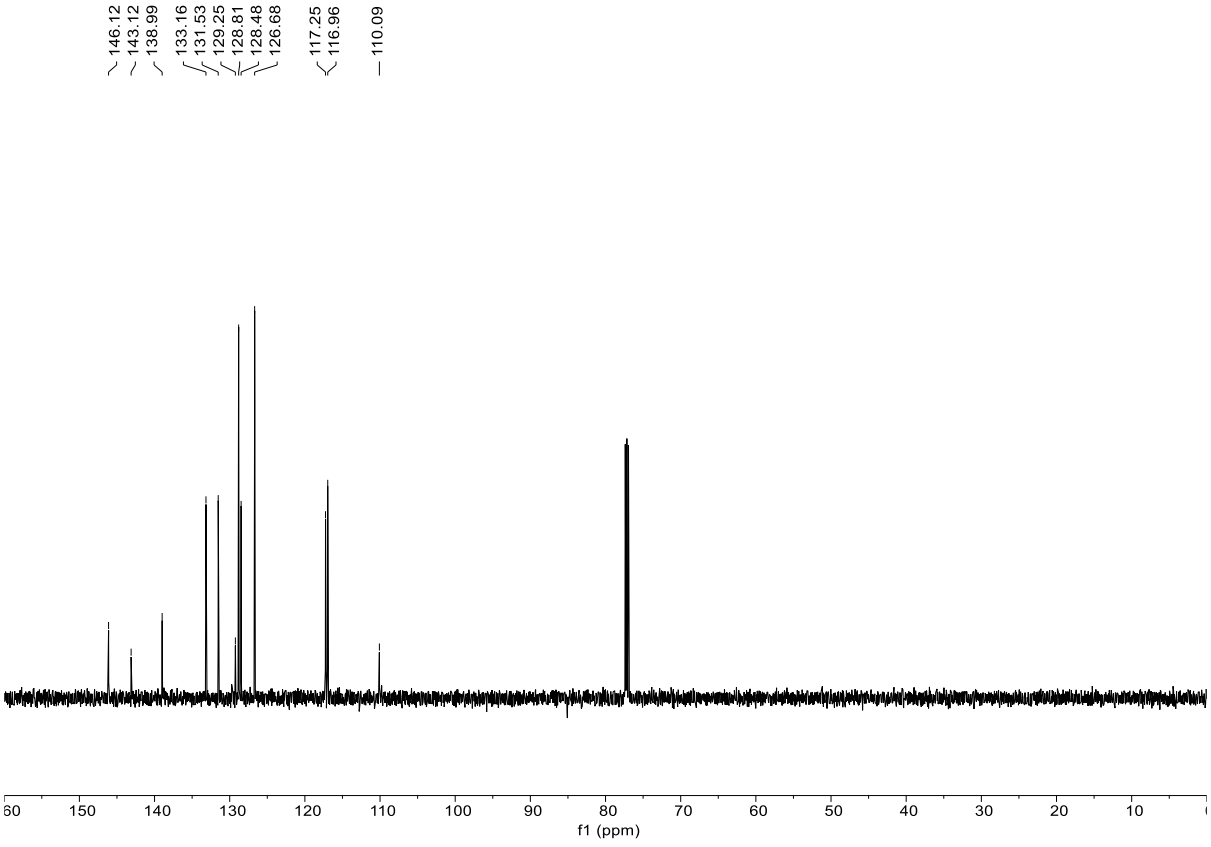
5-Methyl-2-(prop-1-en-2-yl)aniline (1h)



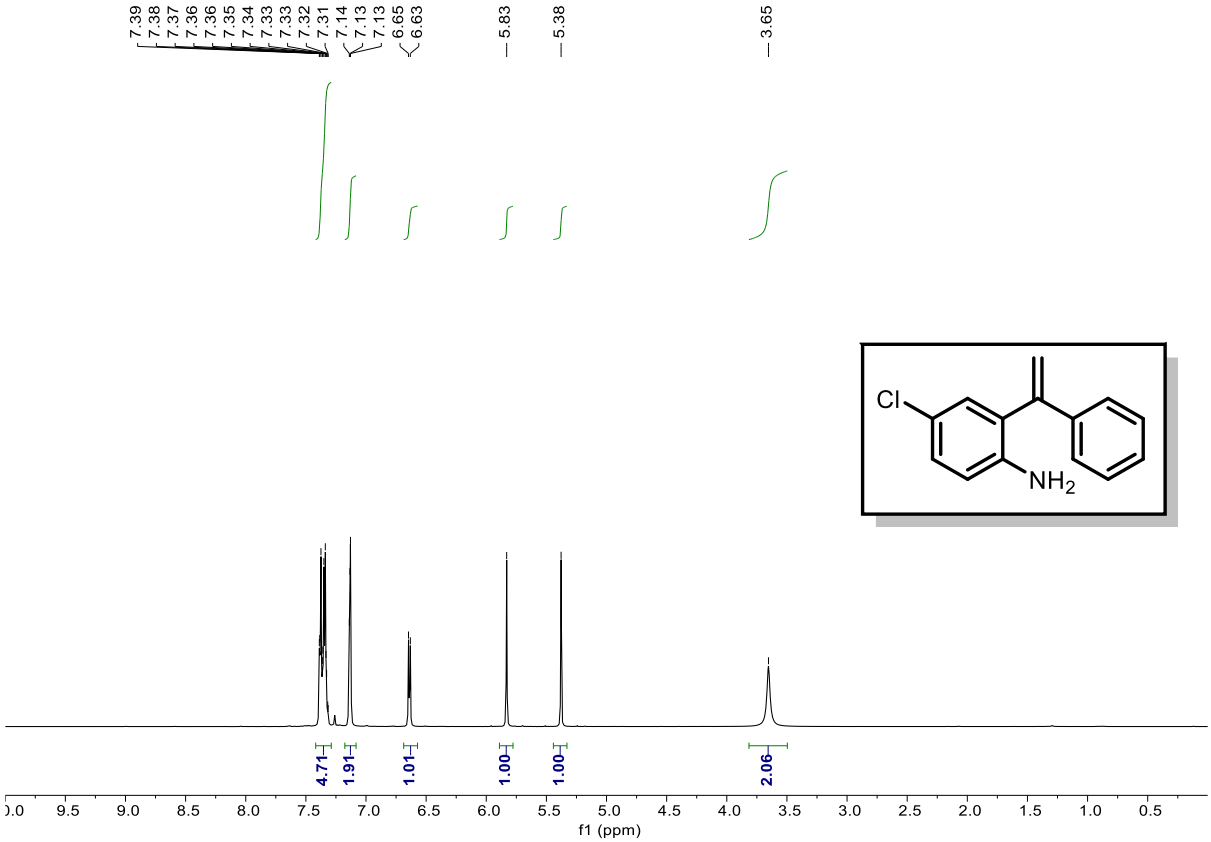


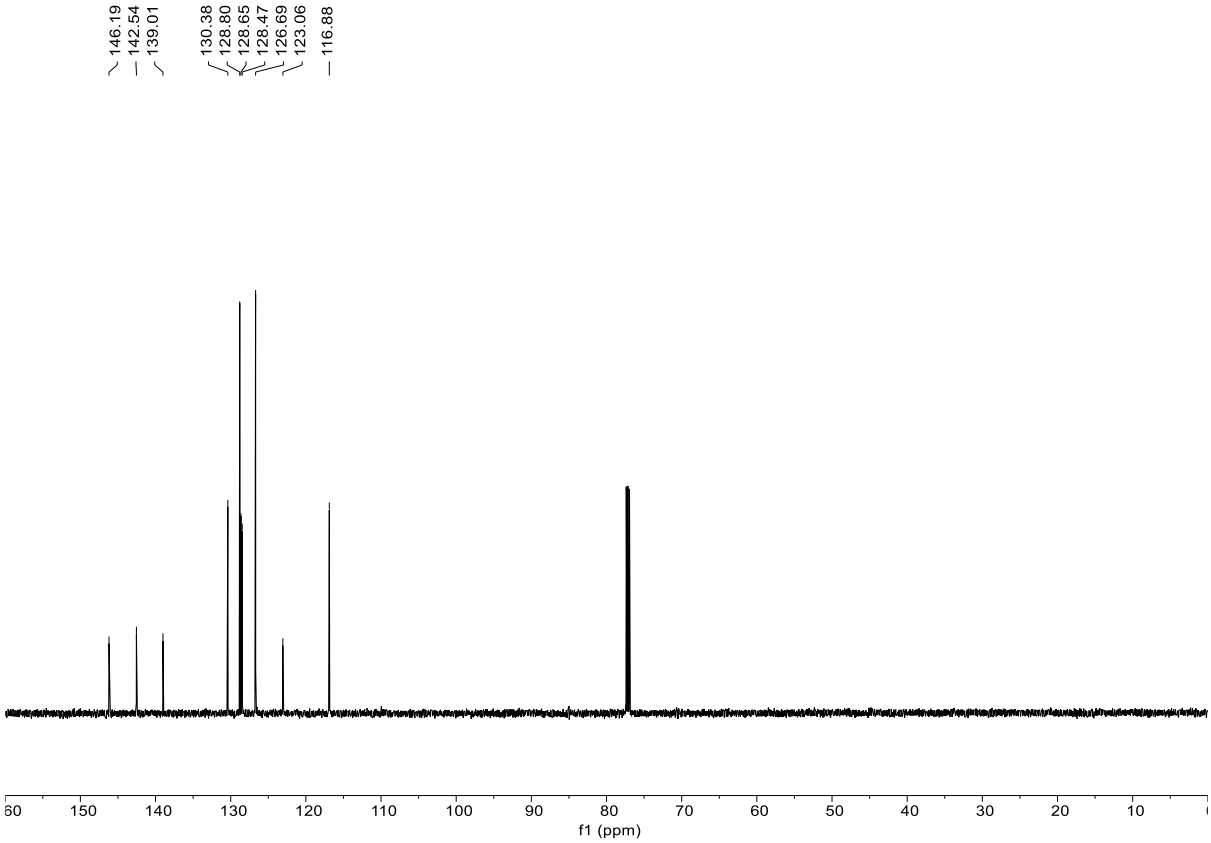
4-Bromo-2-(1-phenylvinyl)aniline (1i)



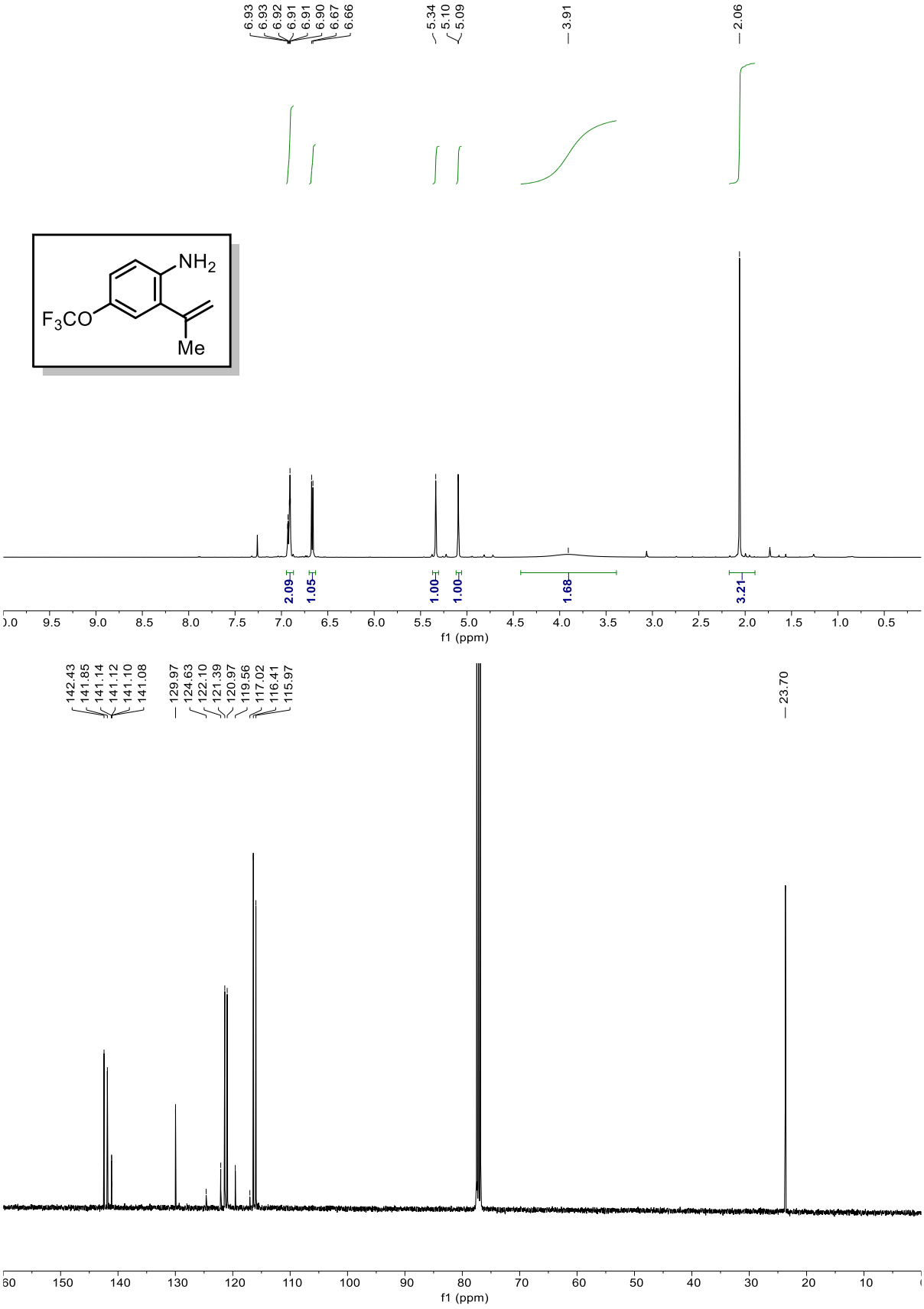


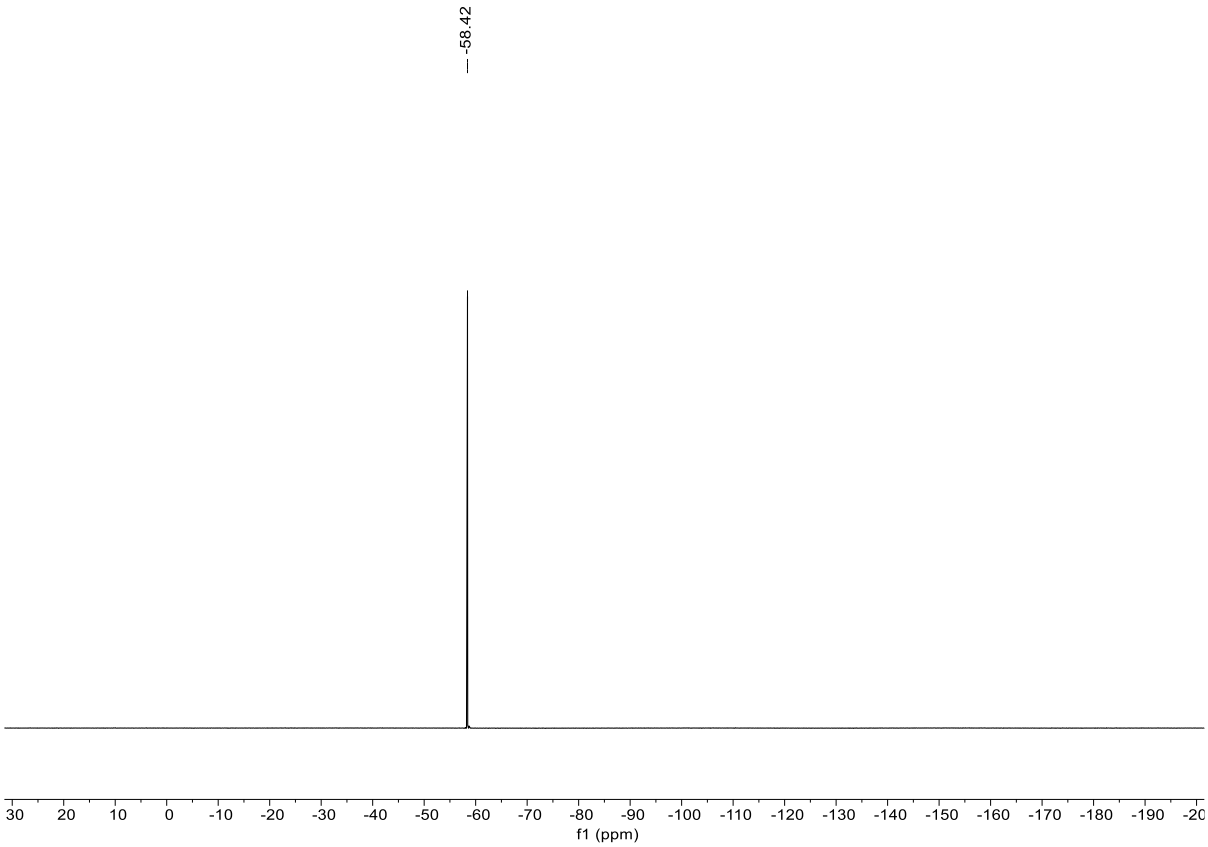
4-Chloro-2-(1-phenylvinyl)aniline (1j)



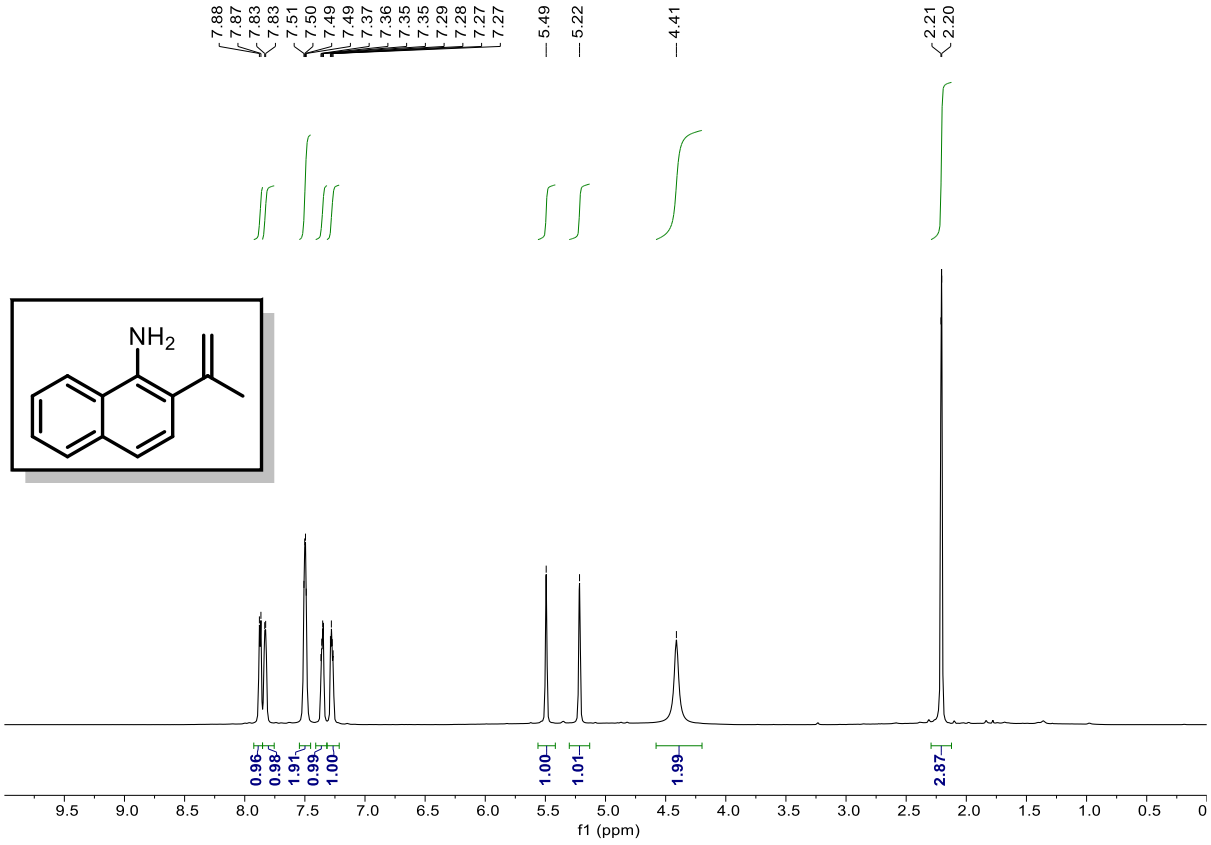


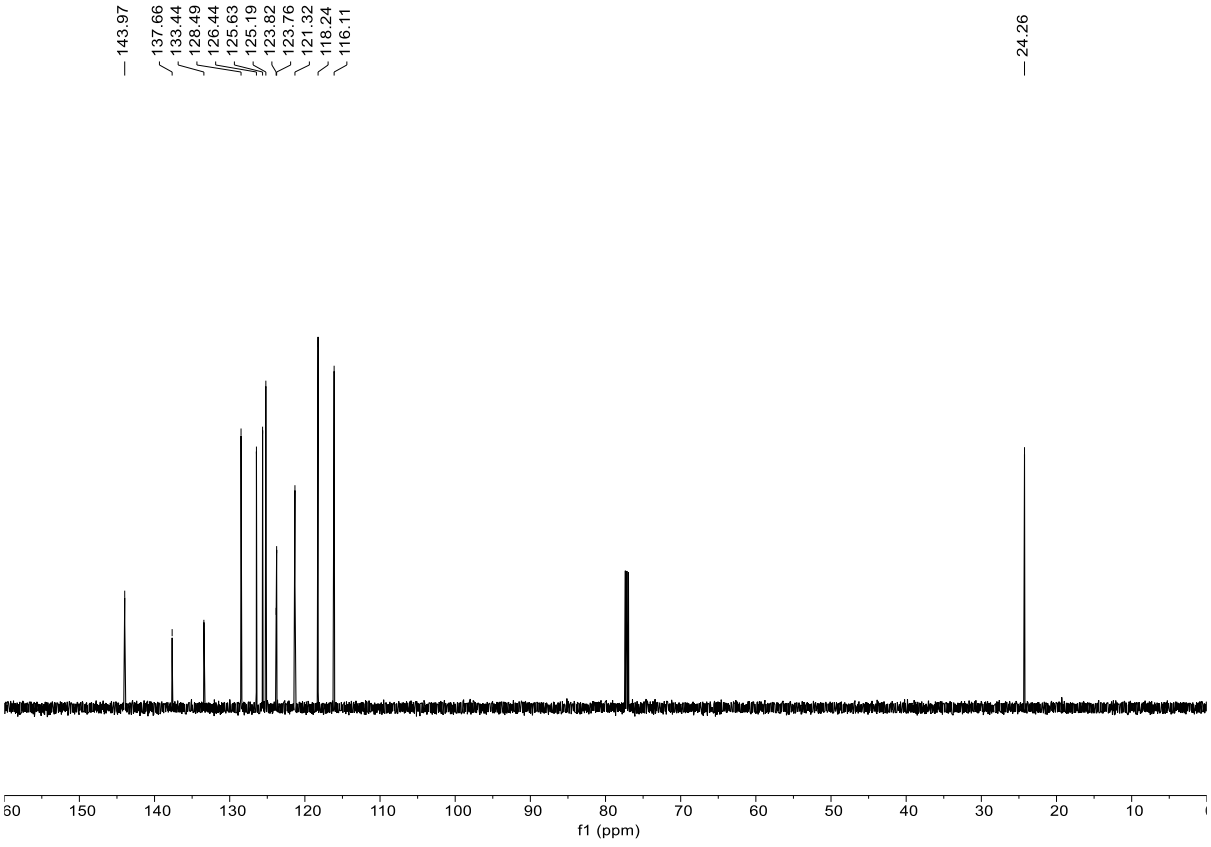
2-(Prop-1-en-2-yl)-4-(trifluoromethoxy)aniline (1k)



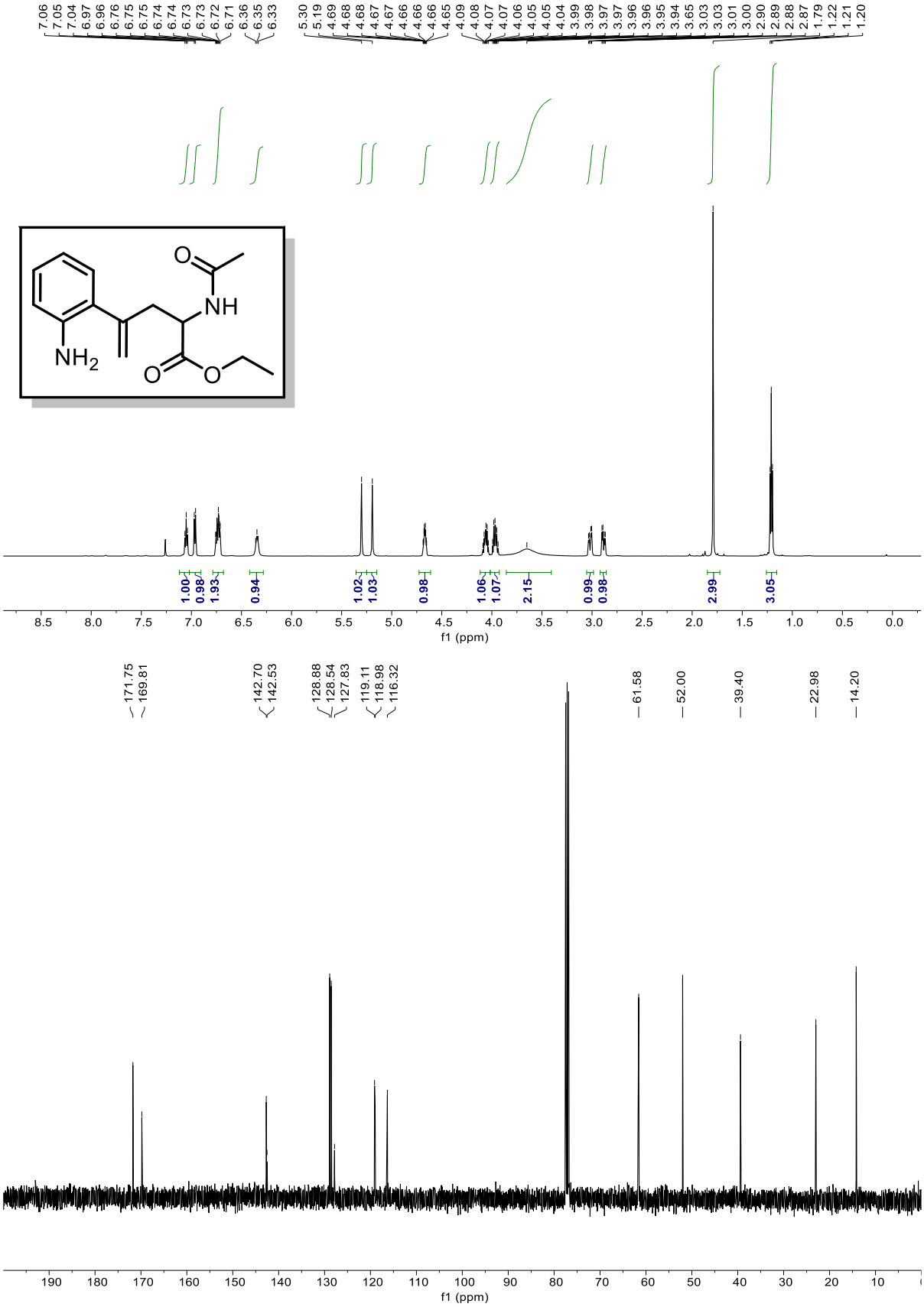

-58.42
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

2-(Prop-1-en-2-yl)naphthalen-1-amine (1m)

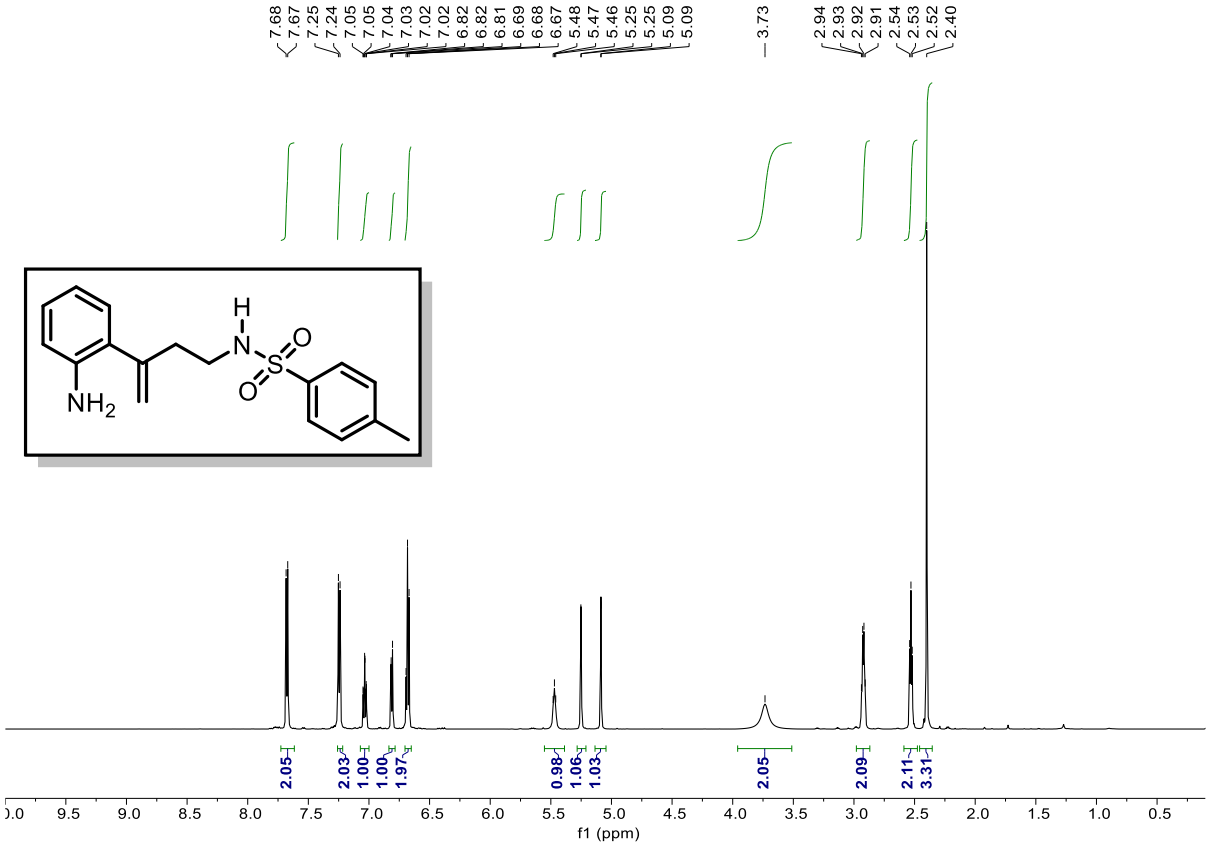


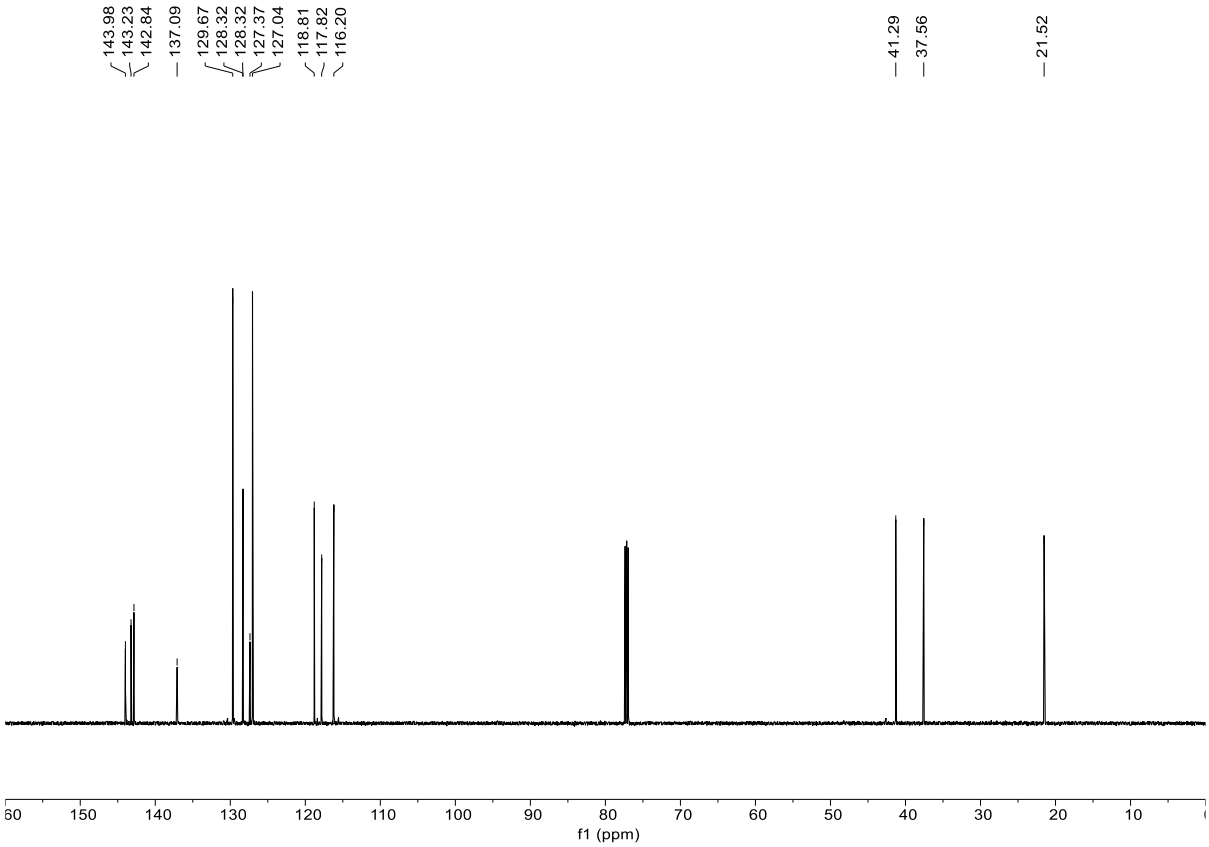


Ethyl 2-acetamido-4-(2-aminophenyl)pent-4-enoate (1n)

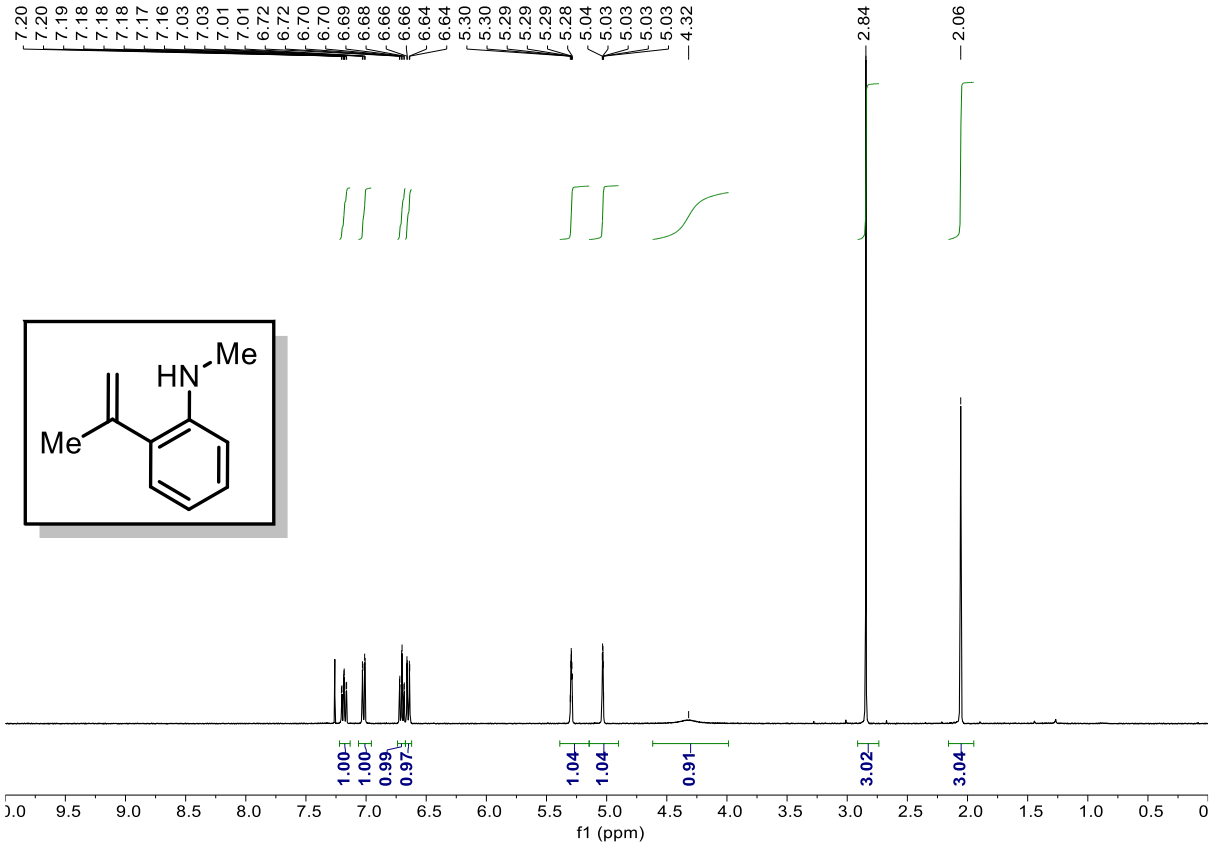


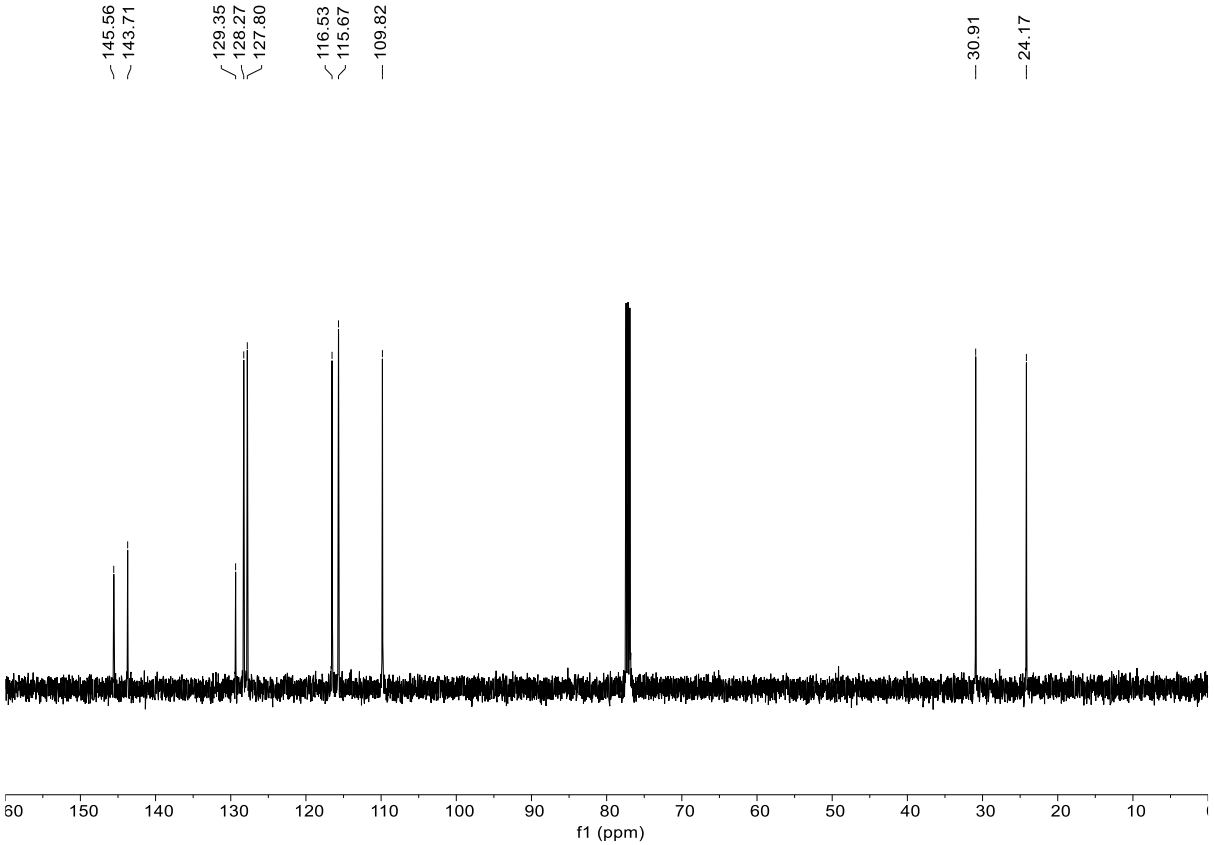
_N_-(3-(2-Aminophenyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (1o)



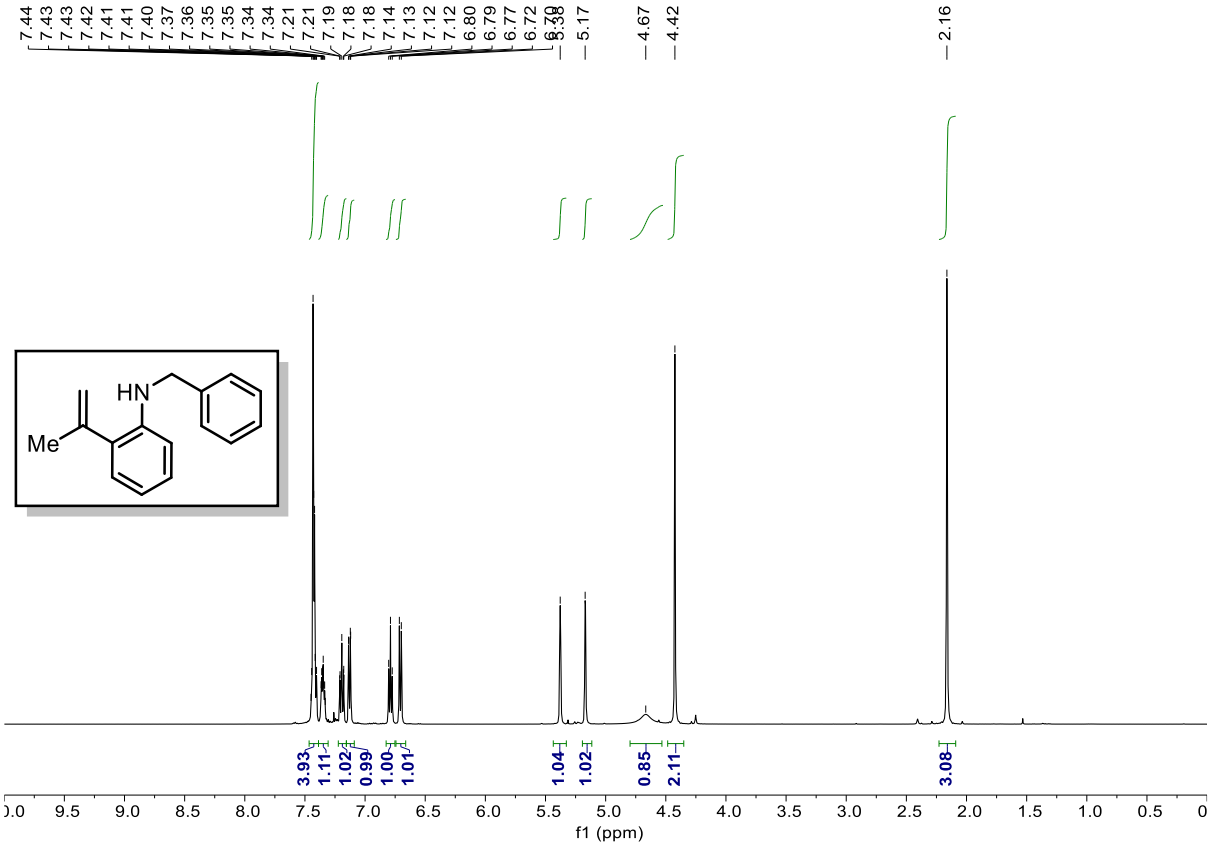


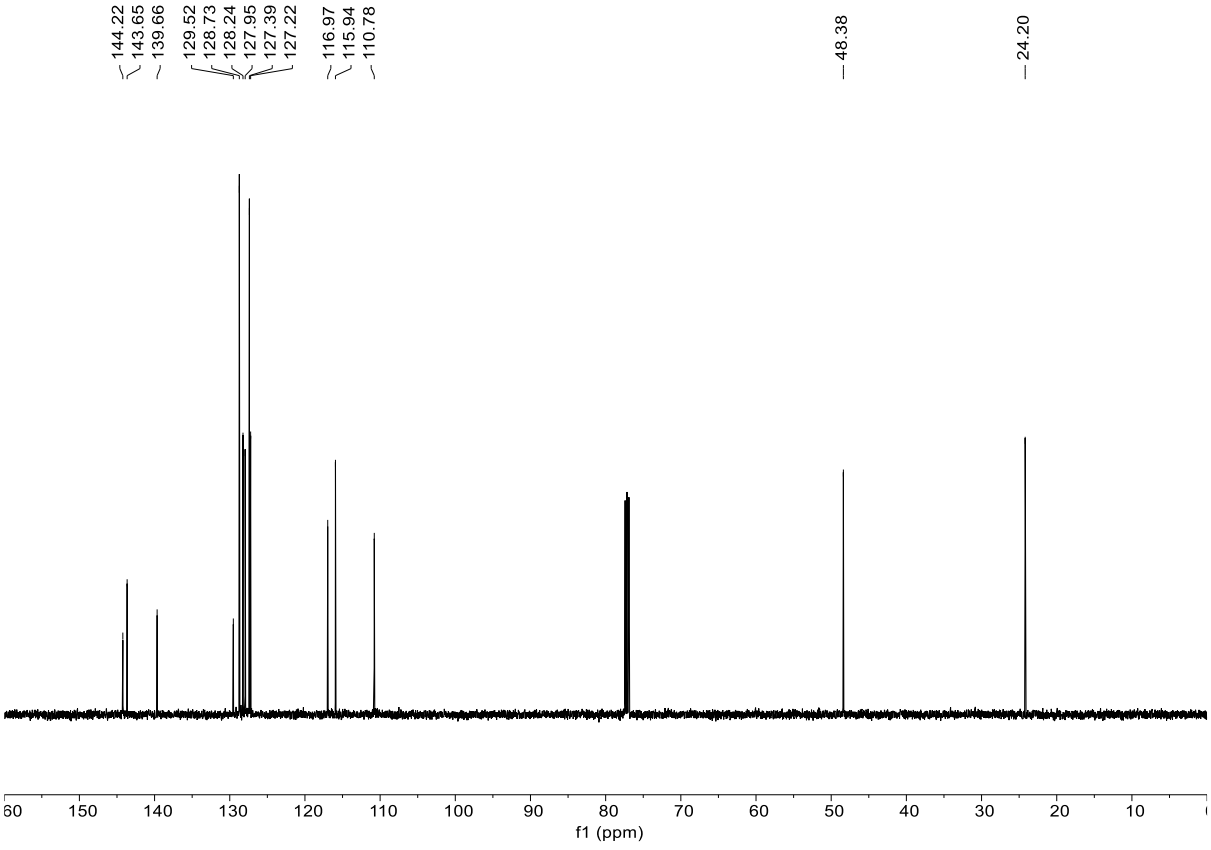
_N_-Methyl-2-(prop-1-en-2-yl)aniline (S1)



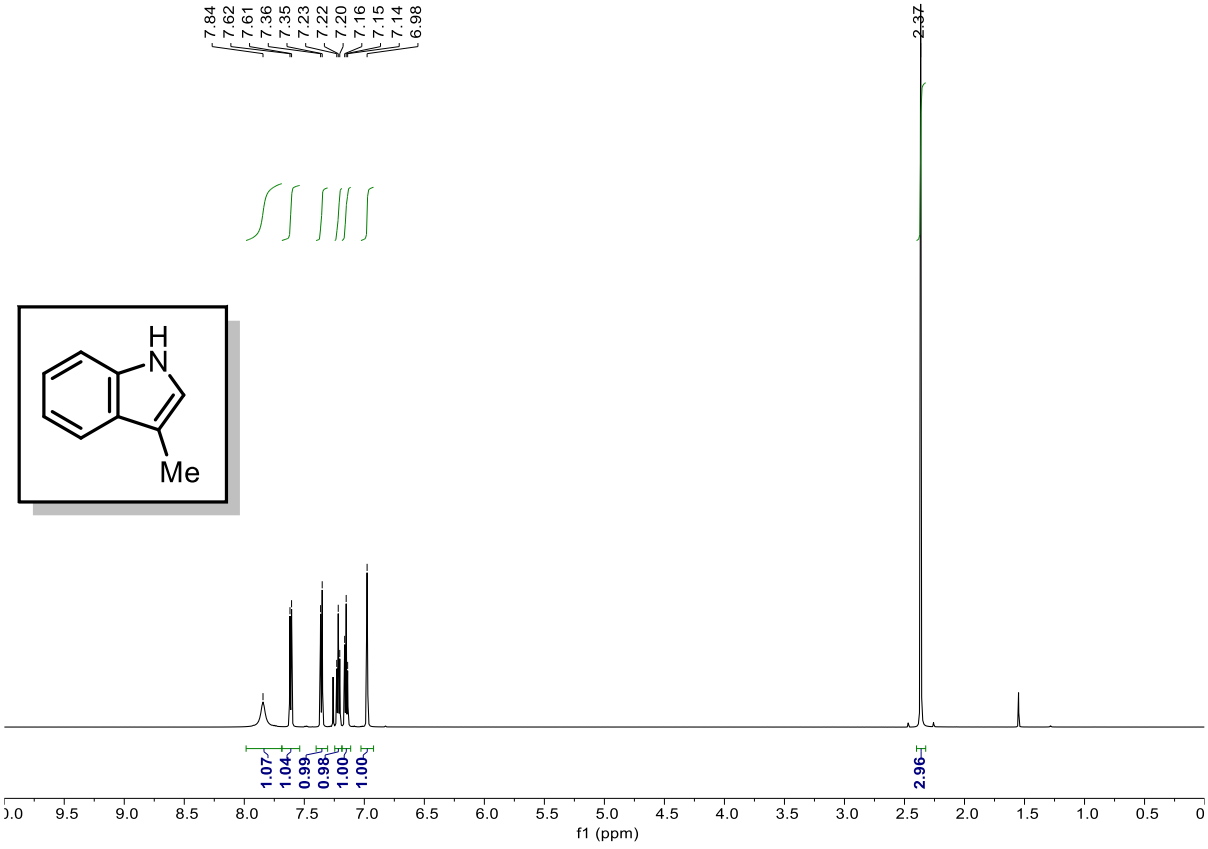


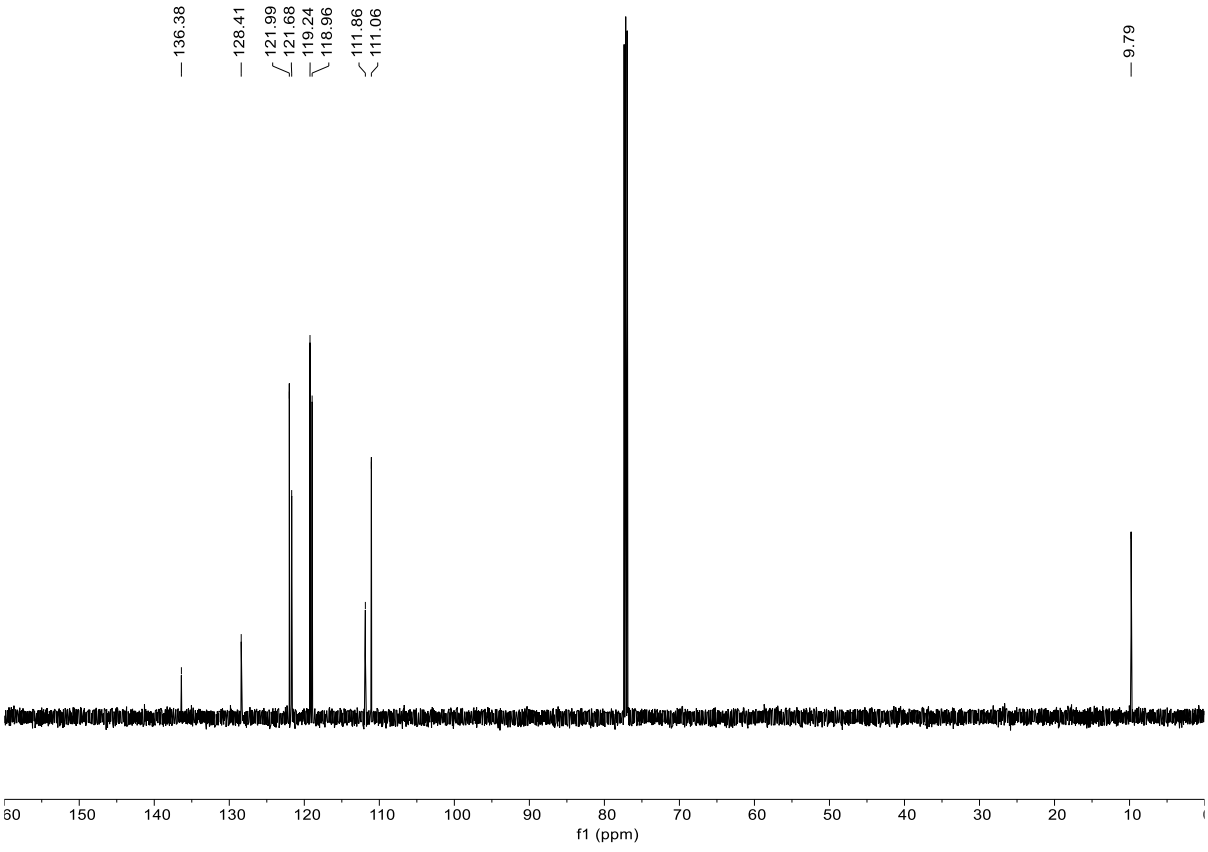
_N_-Benzyl-2-(prop-1-en-2-yl)aniline (S2)



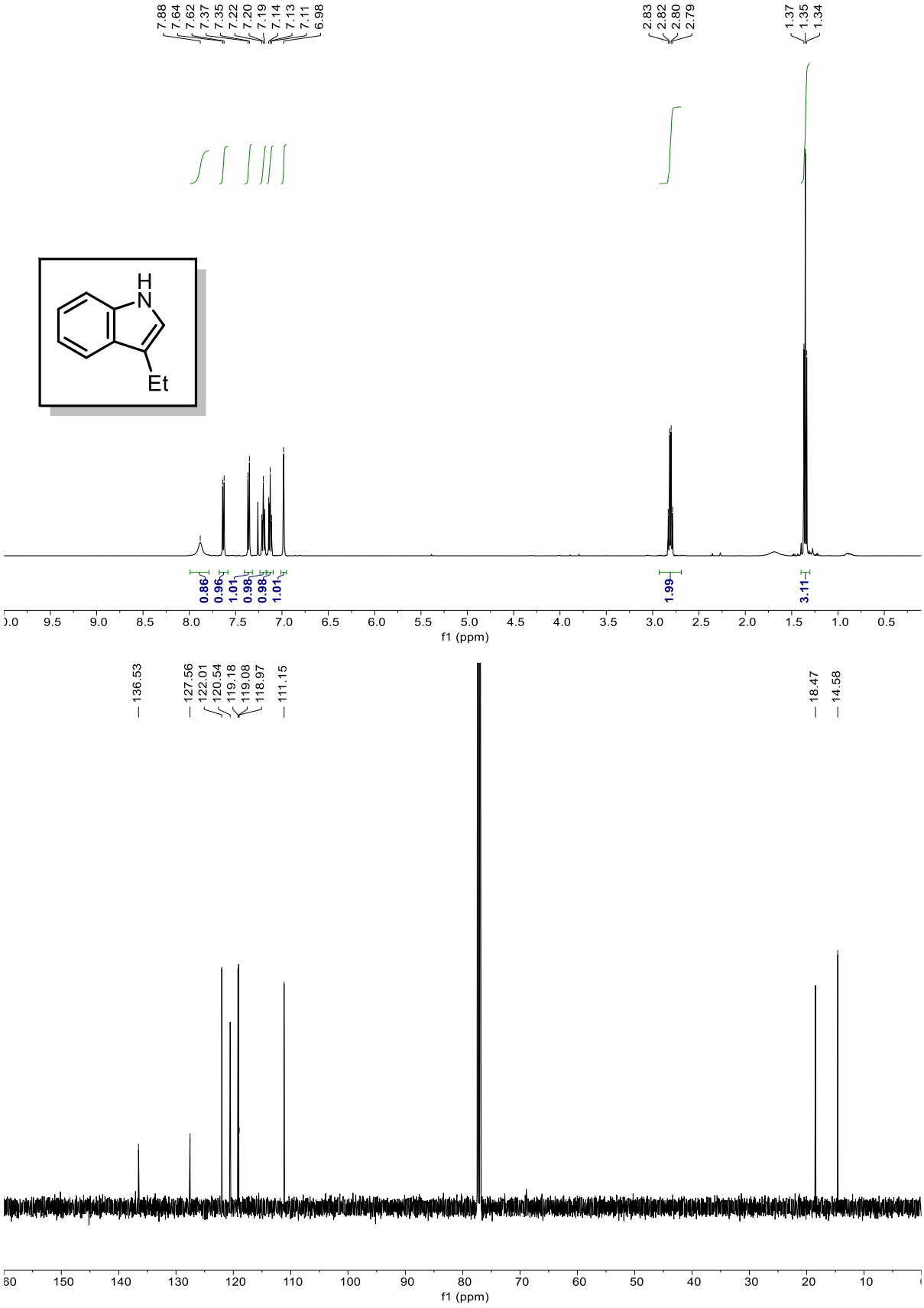


3-Methyl-1*H*-indole (2a)

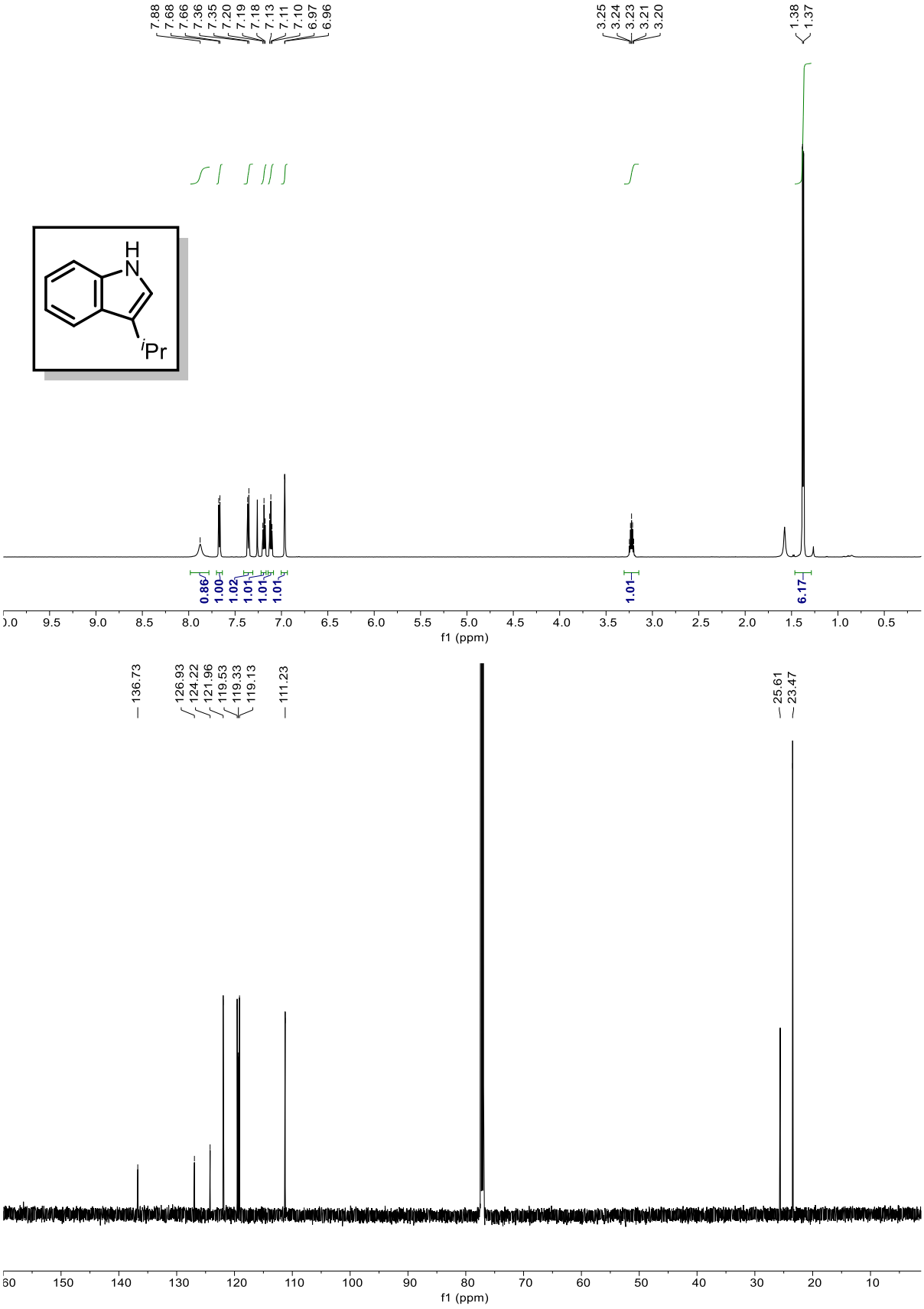




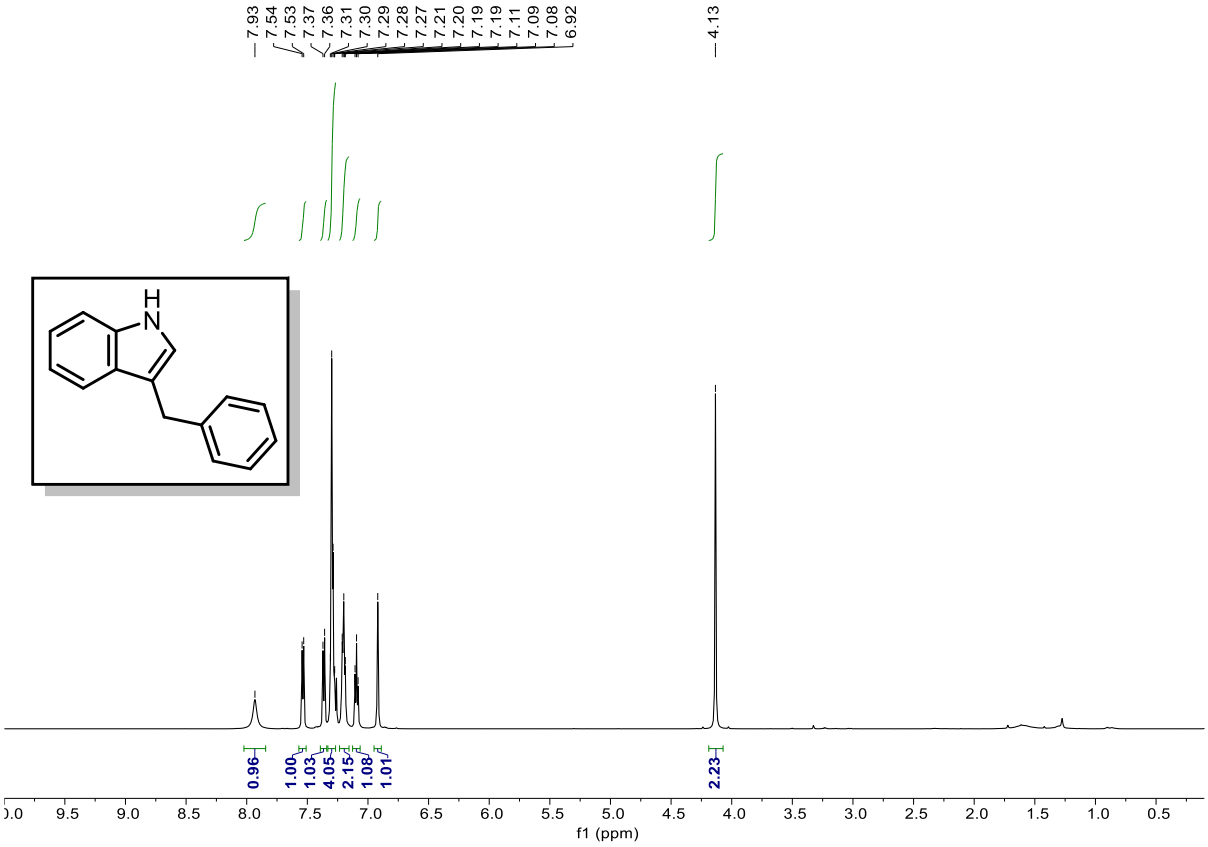
3-Ethyl-1*H*-indole (2b)

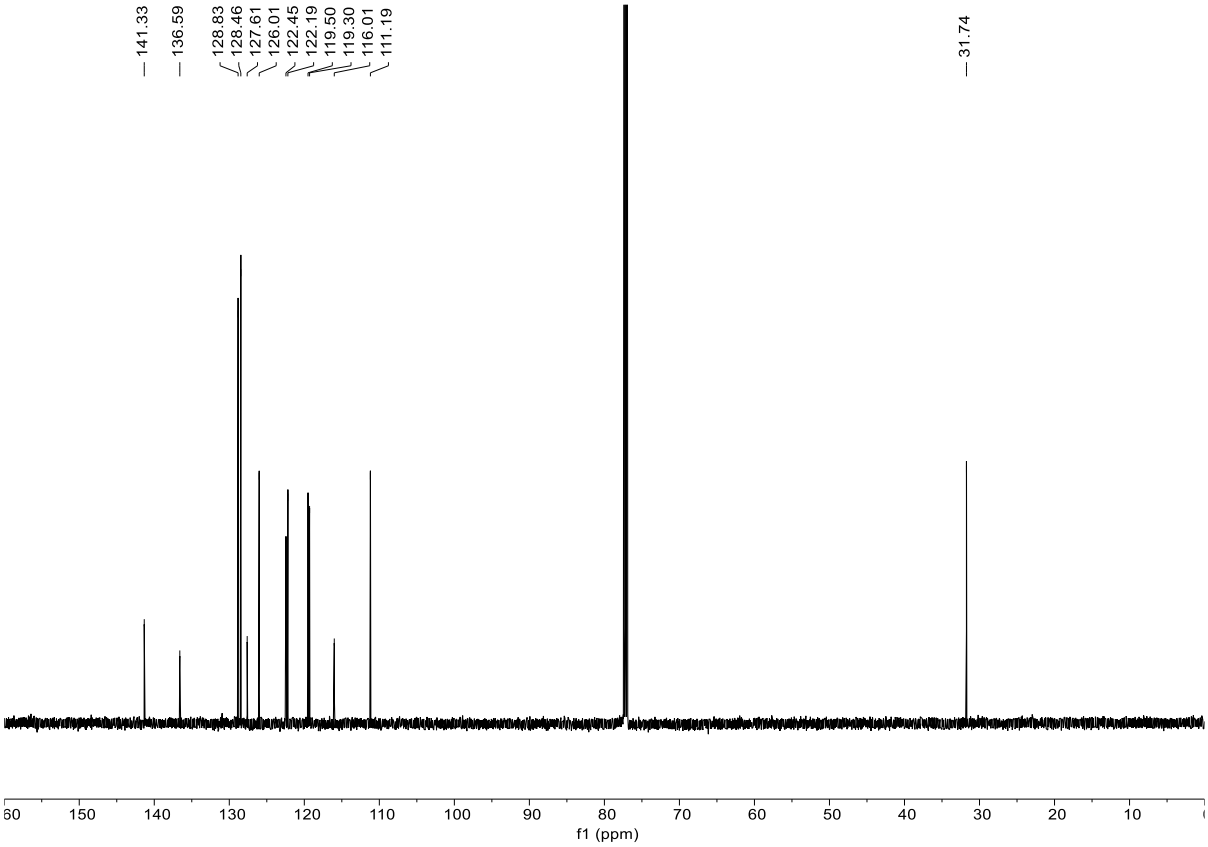


3-Isopropyl-1*H*-indole (2c)

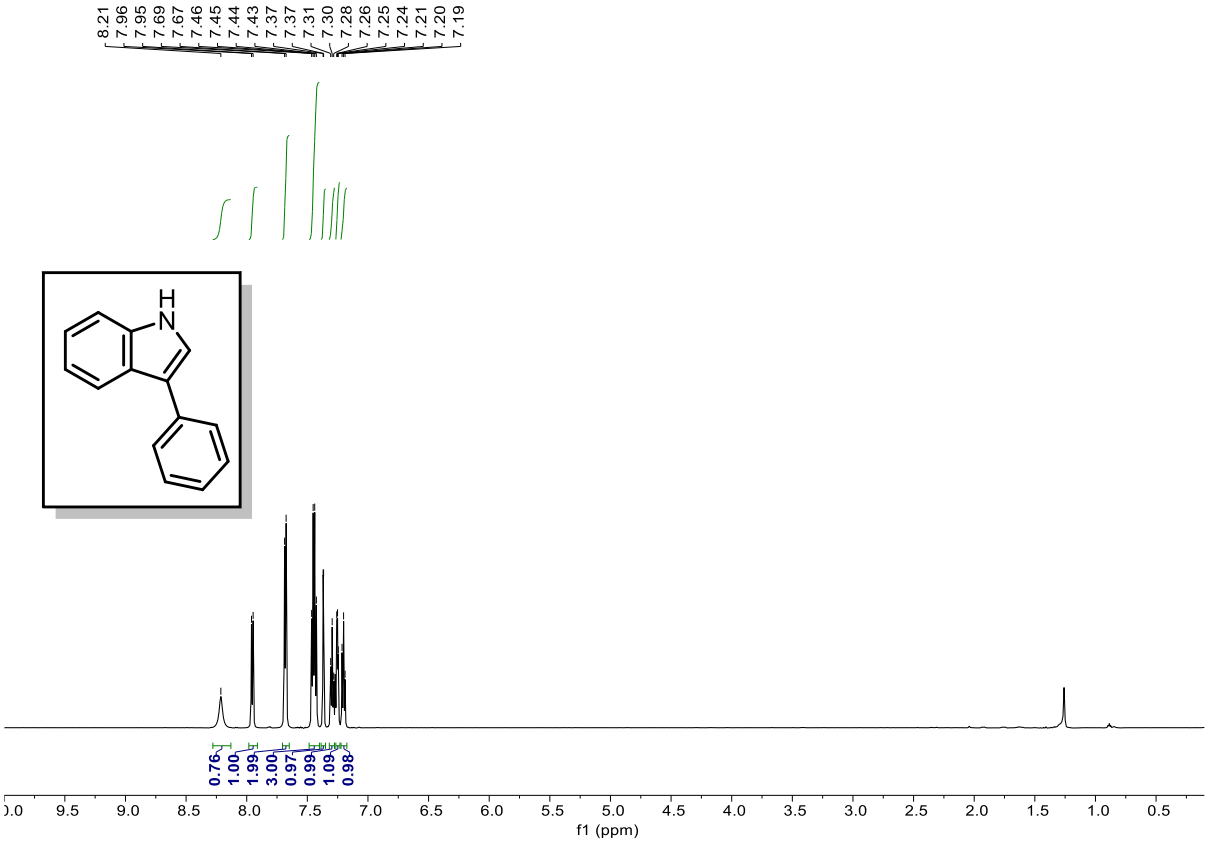


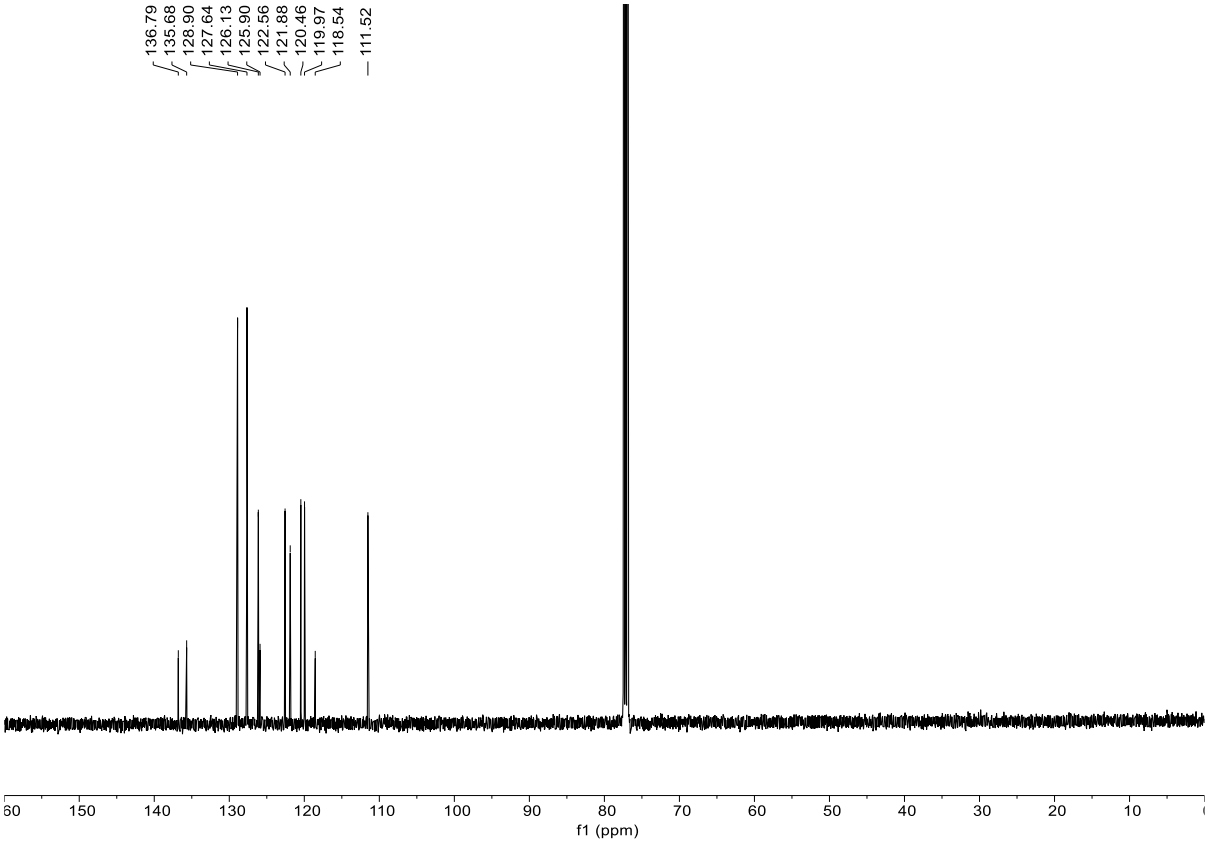
3-Benzyl-1*H*-indole (2d)



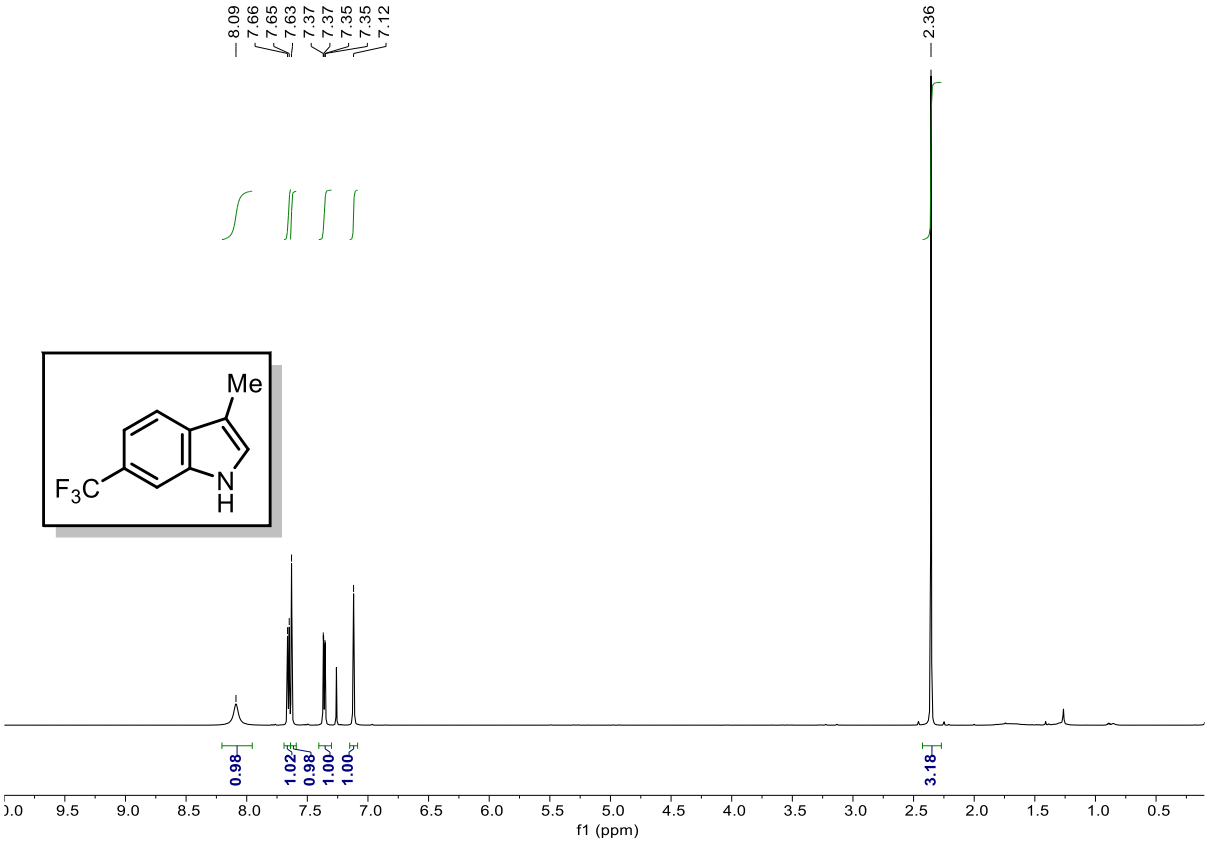


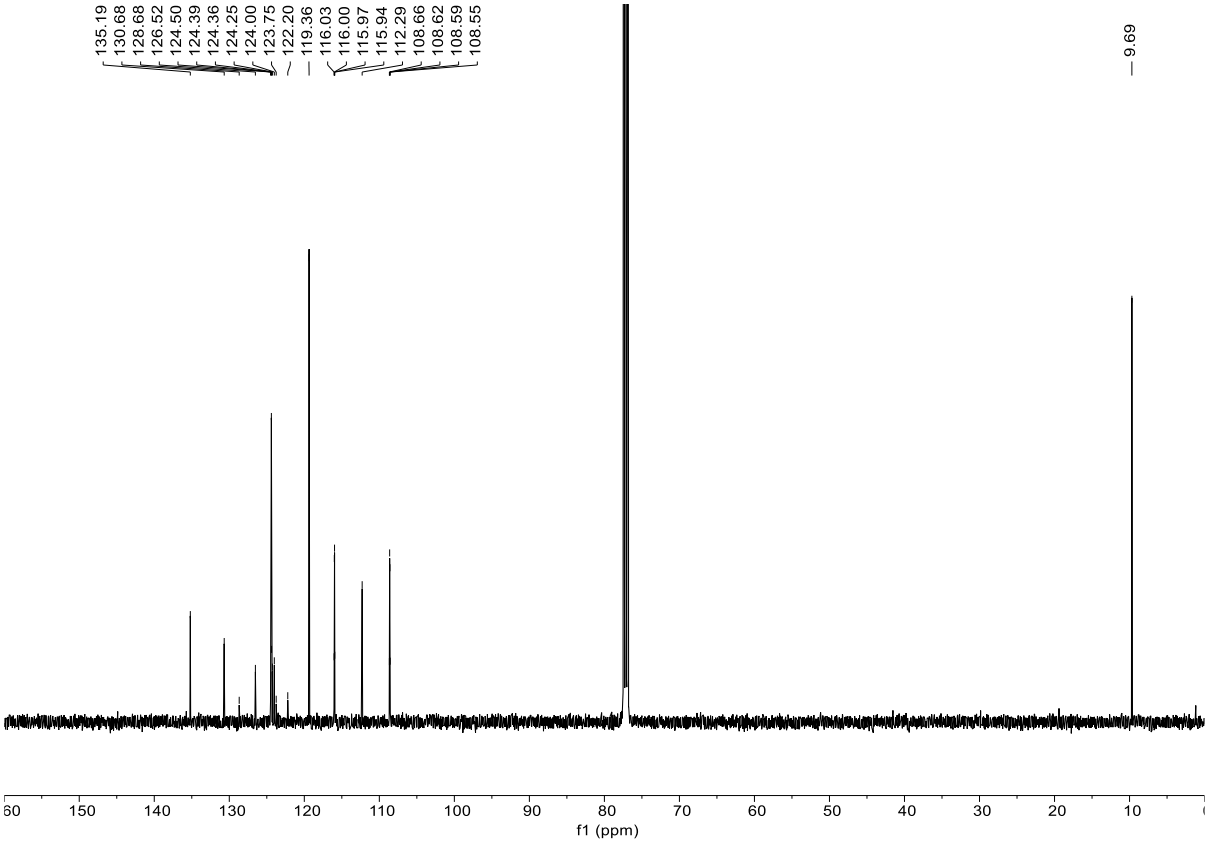
3-Phenyl-1*H*-indole (2e)

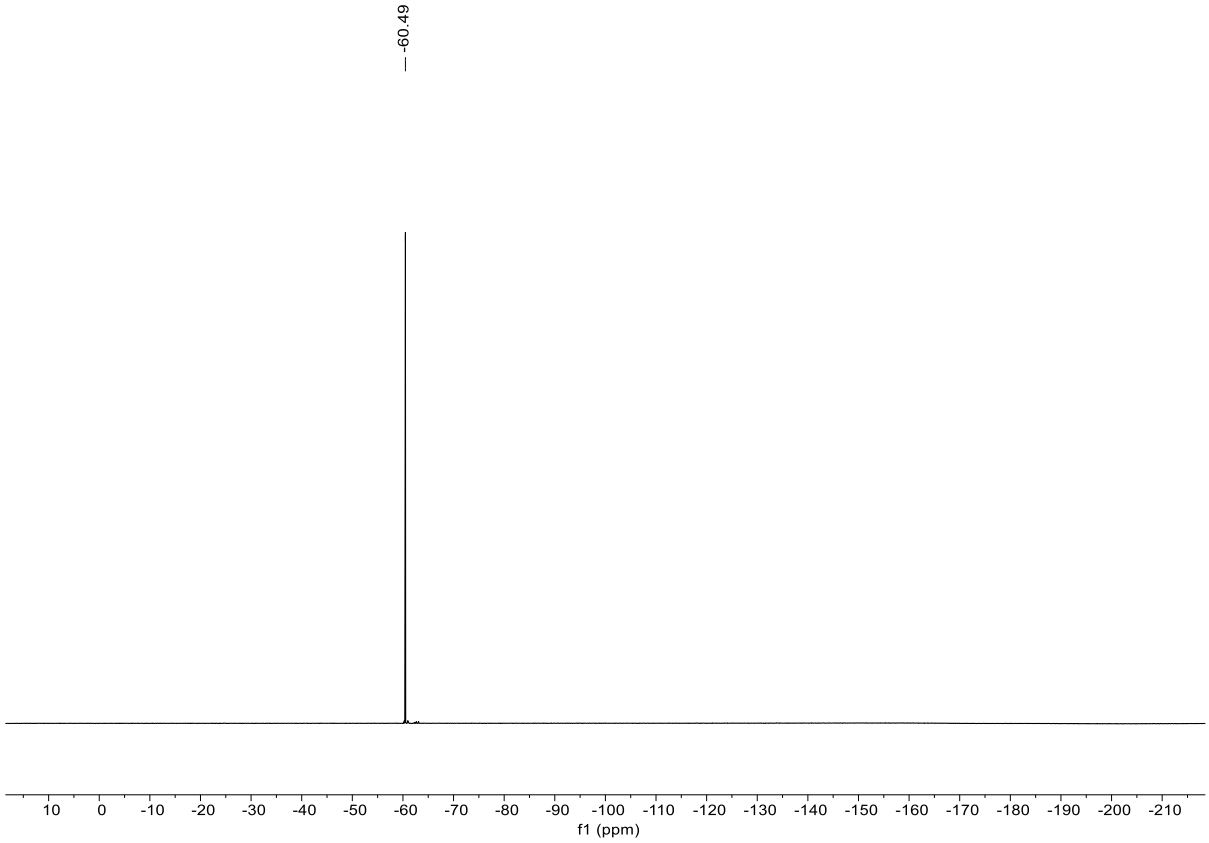




3-Methyl-6-(trifluoromethyl)-1*H*-indole (2f)



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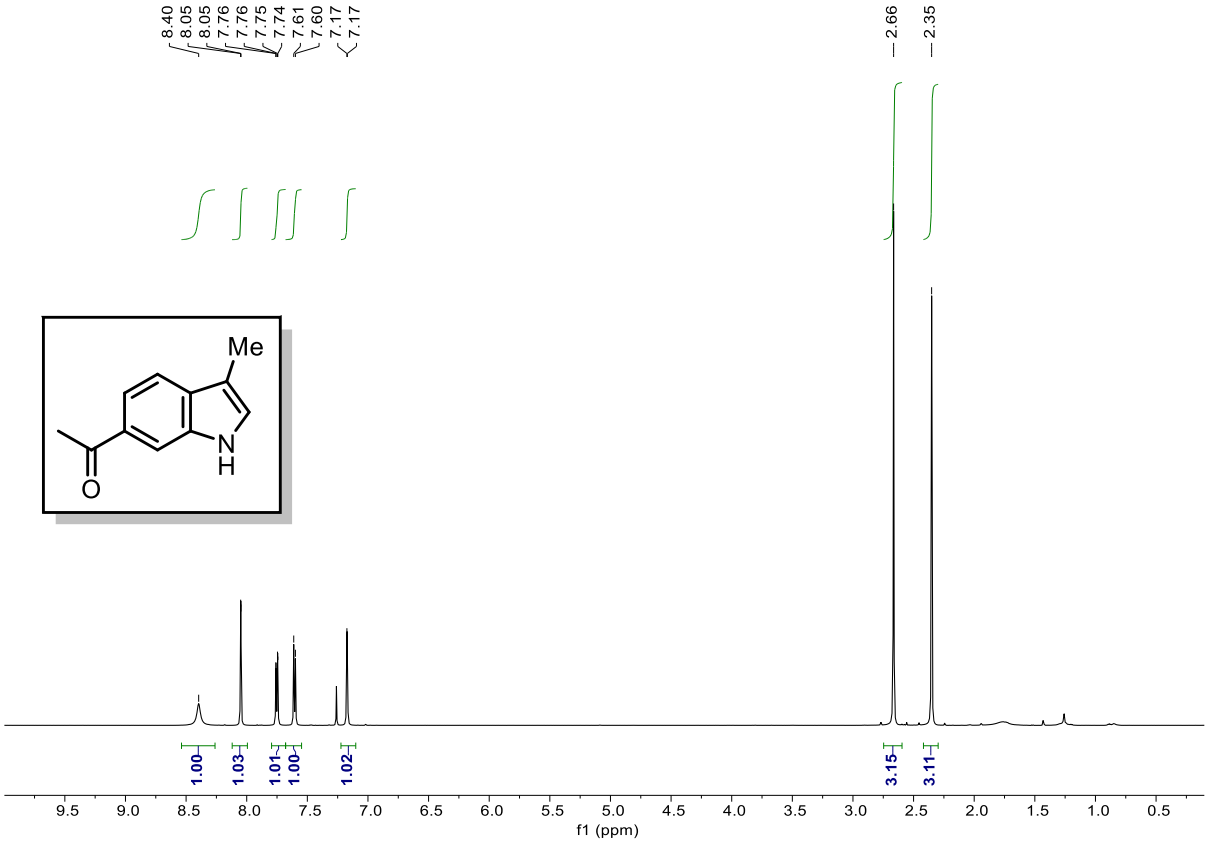
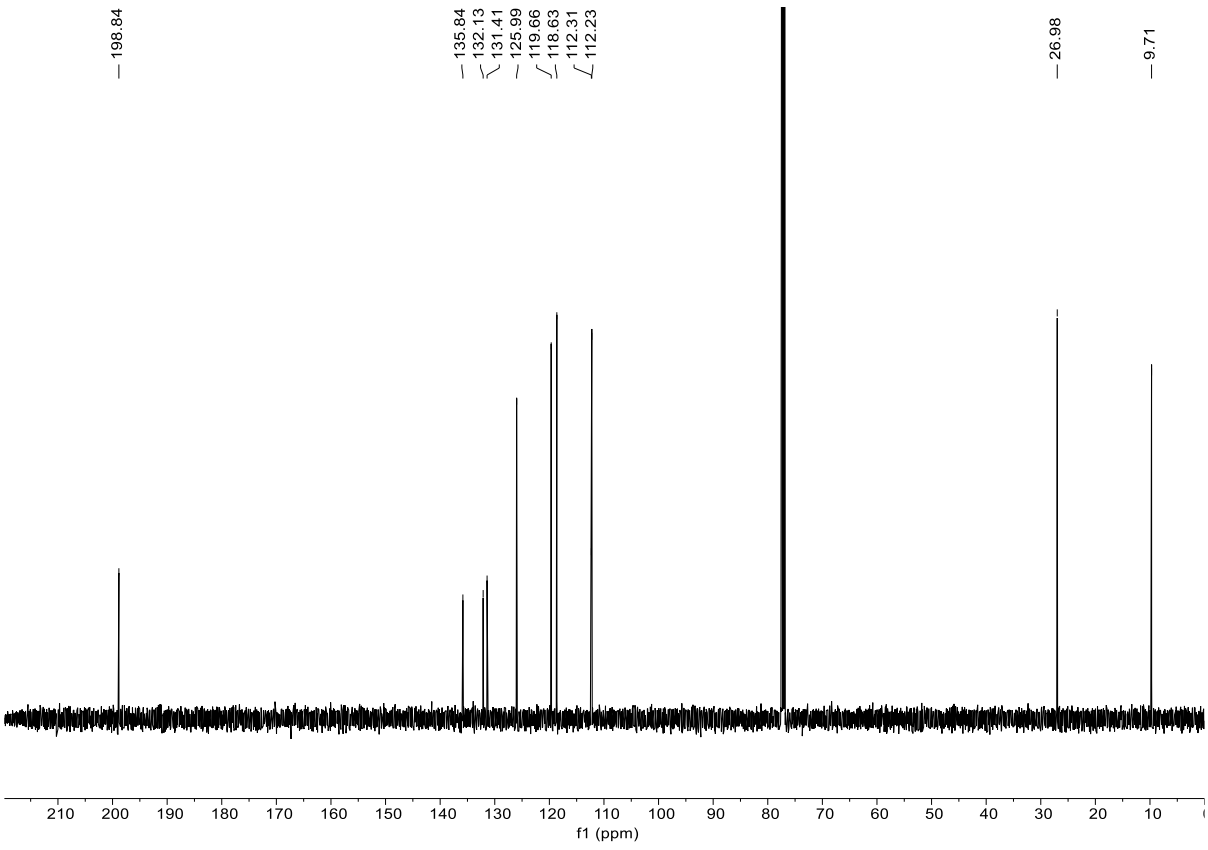
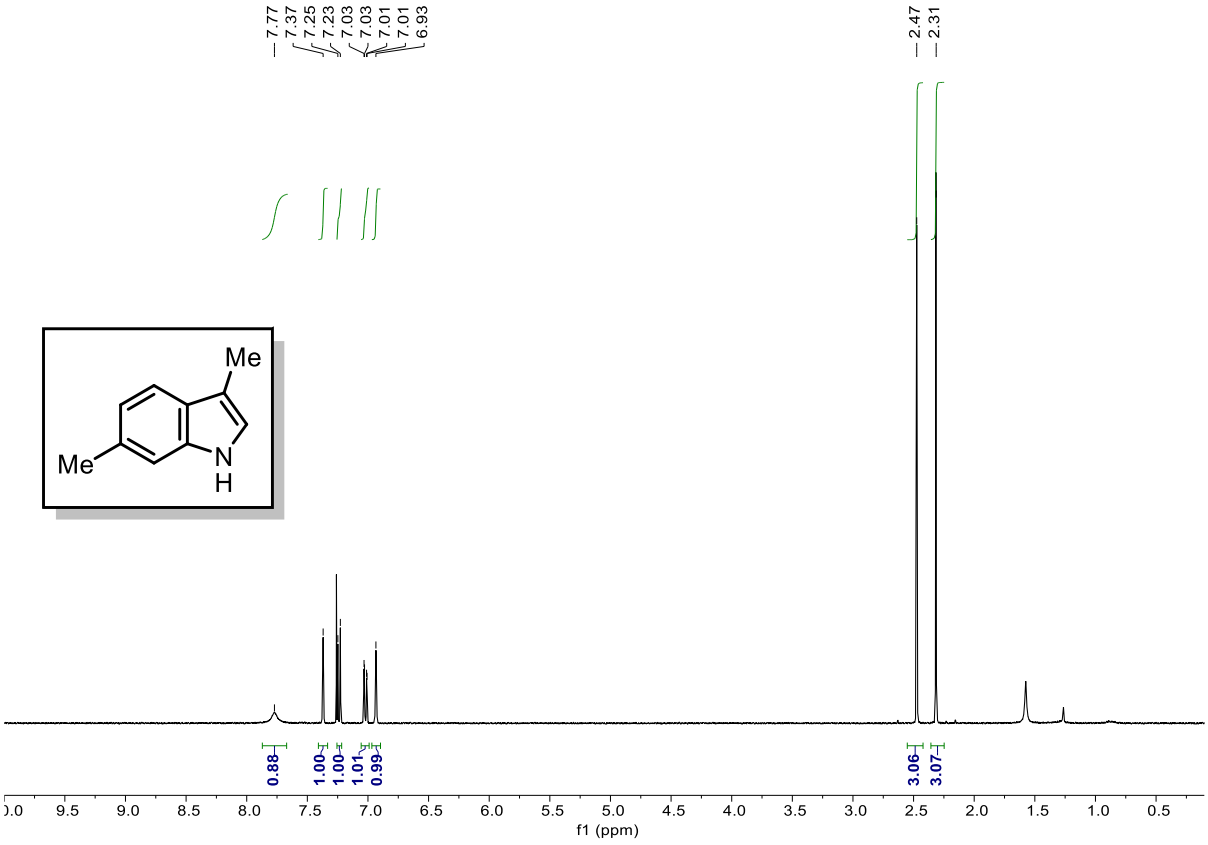
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

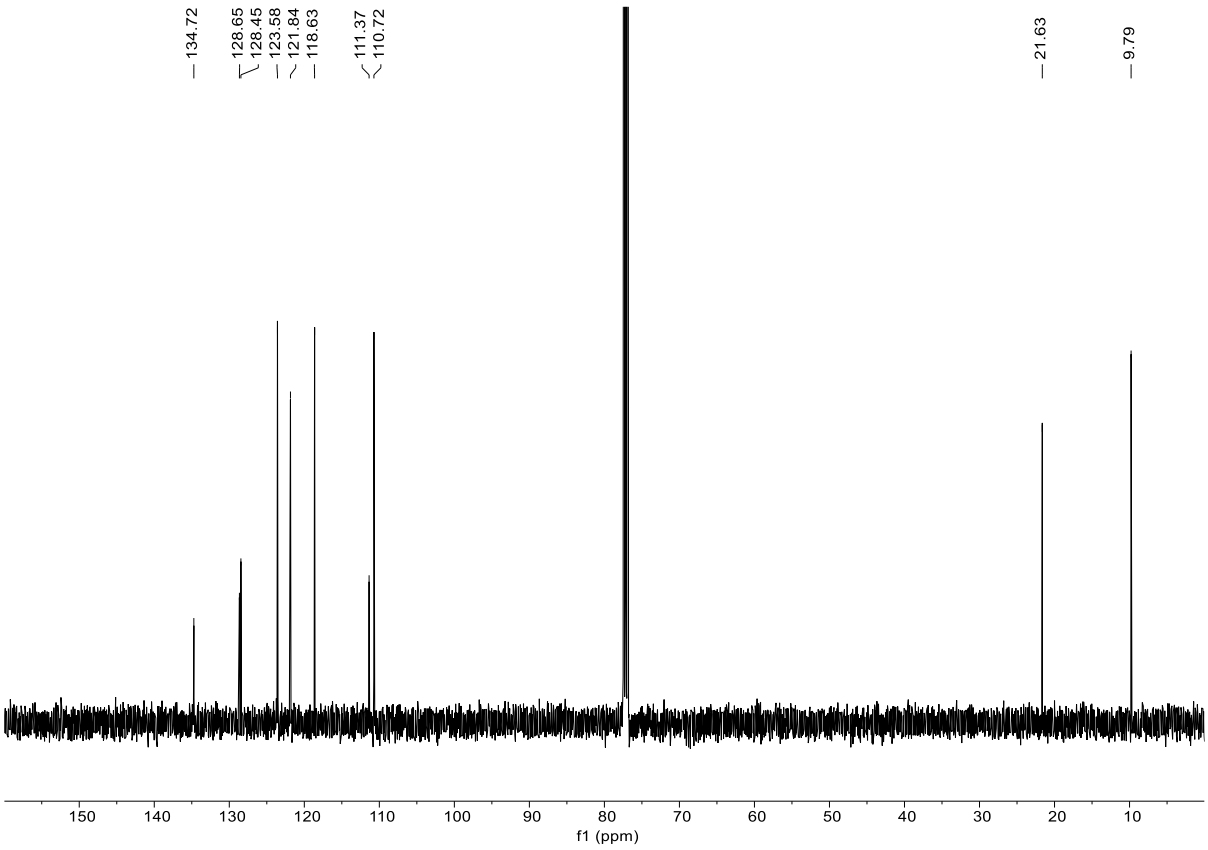
1-(3-Methyl-1*H*-indol-6-yl)ethan-1-one (2g)



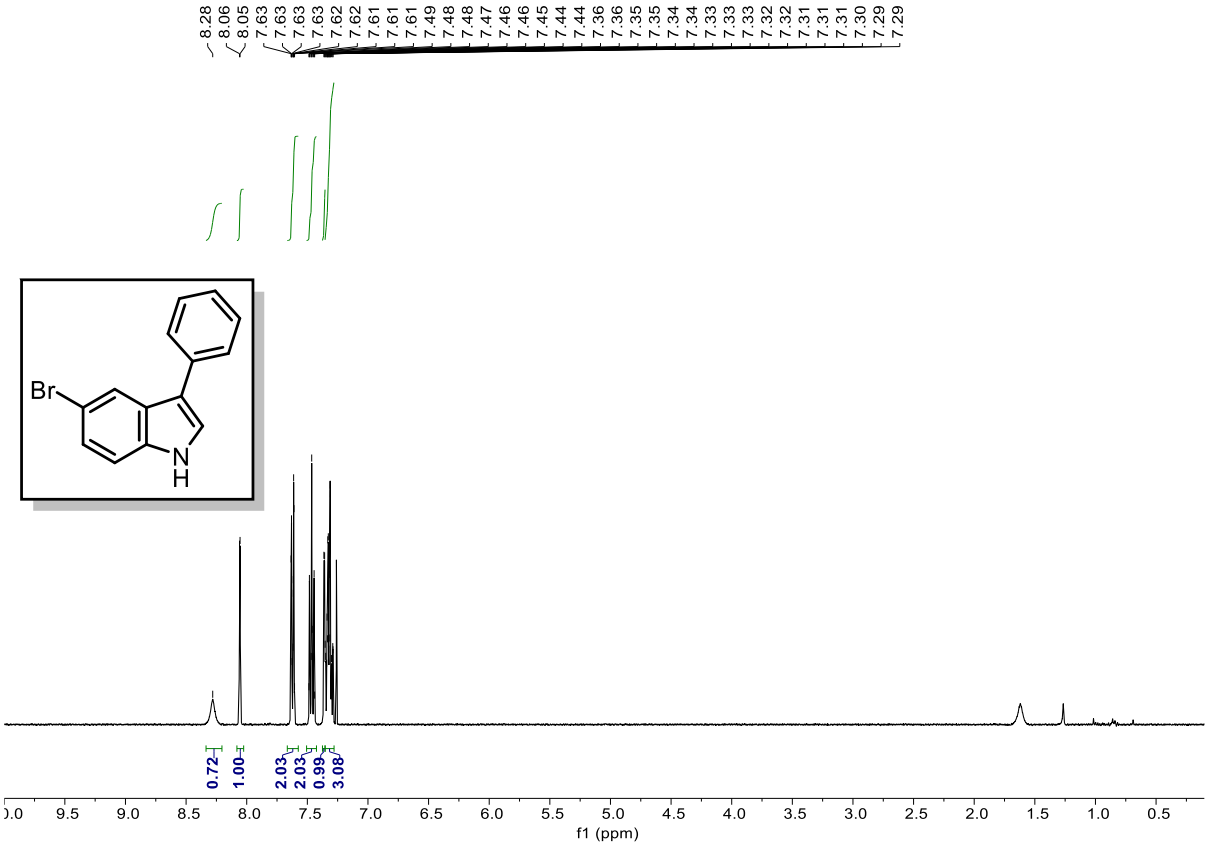


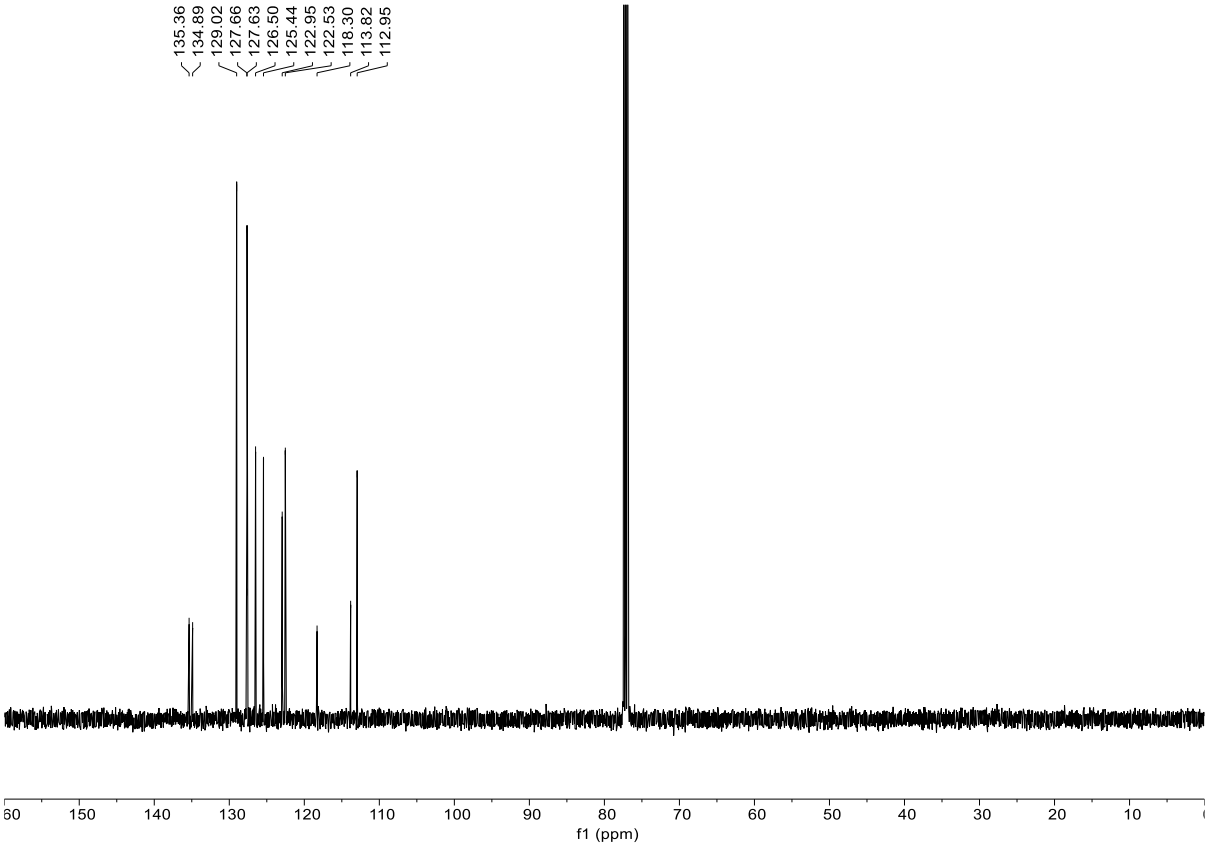
3,6-Dimethyl-1*H*-indole (2h)



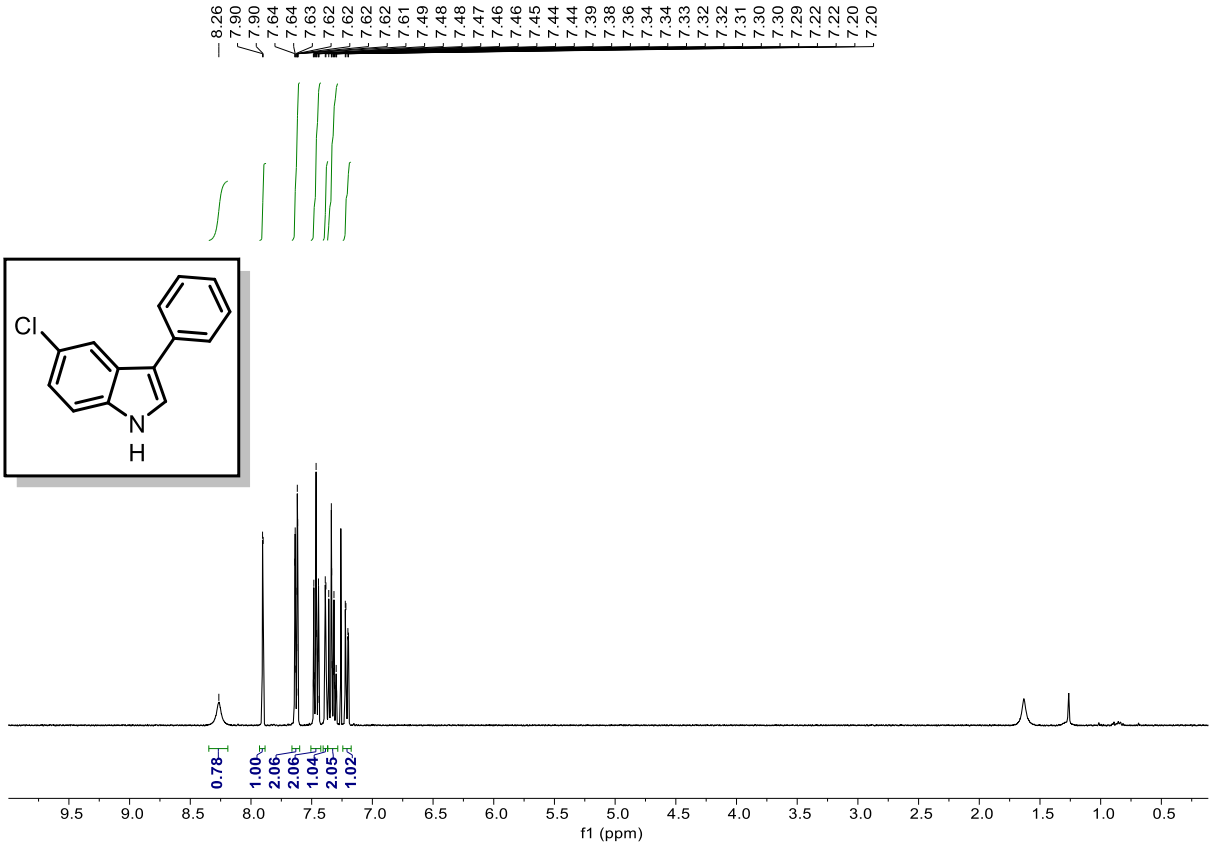


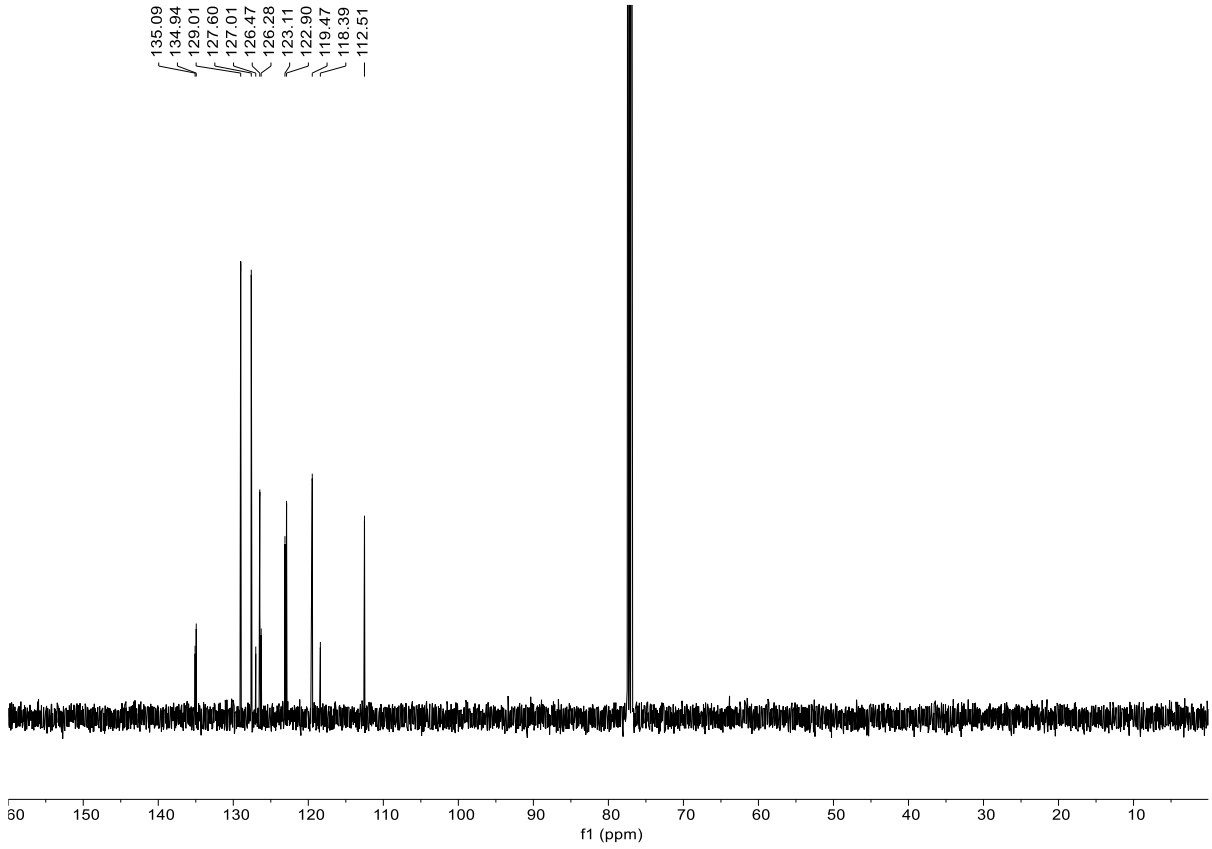
5-Bromo-3-phenyl-1*H*-indole (2i)



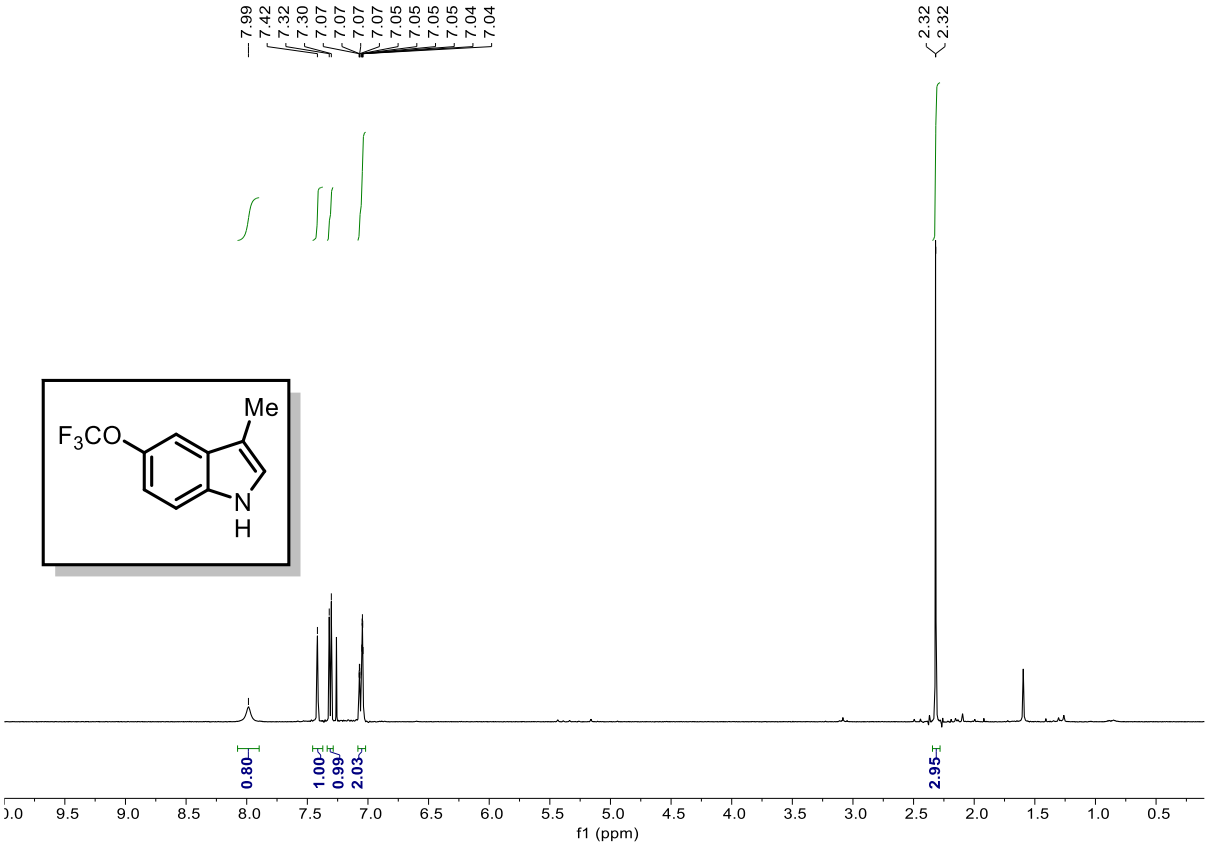


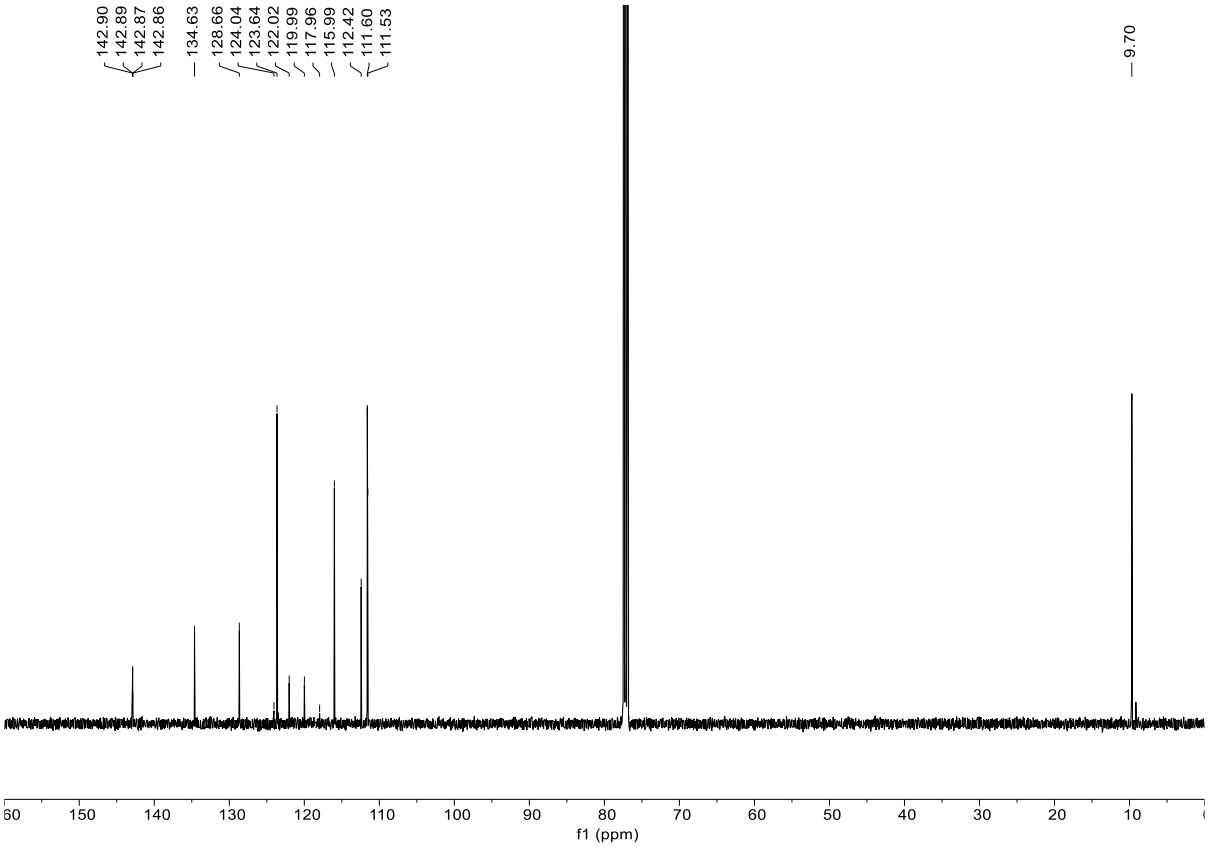
5-Chloro-3-phenyl-1*H*-indole (2j)

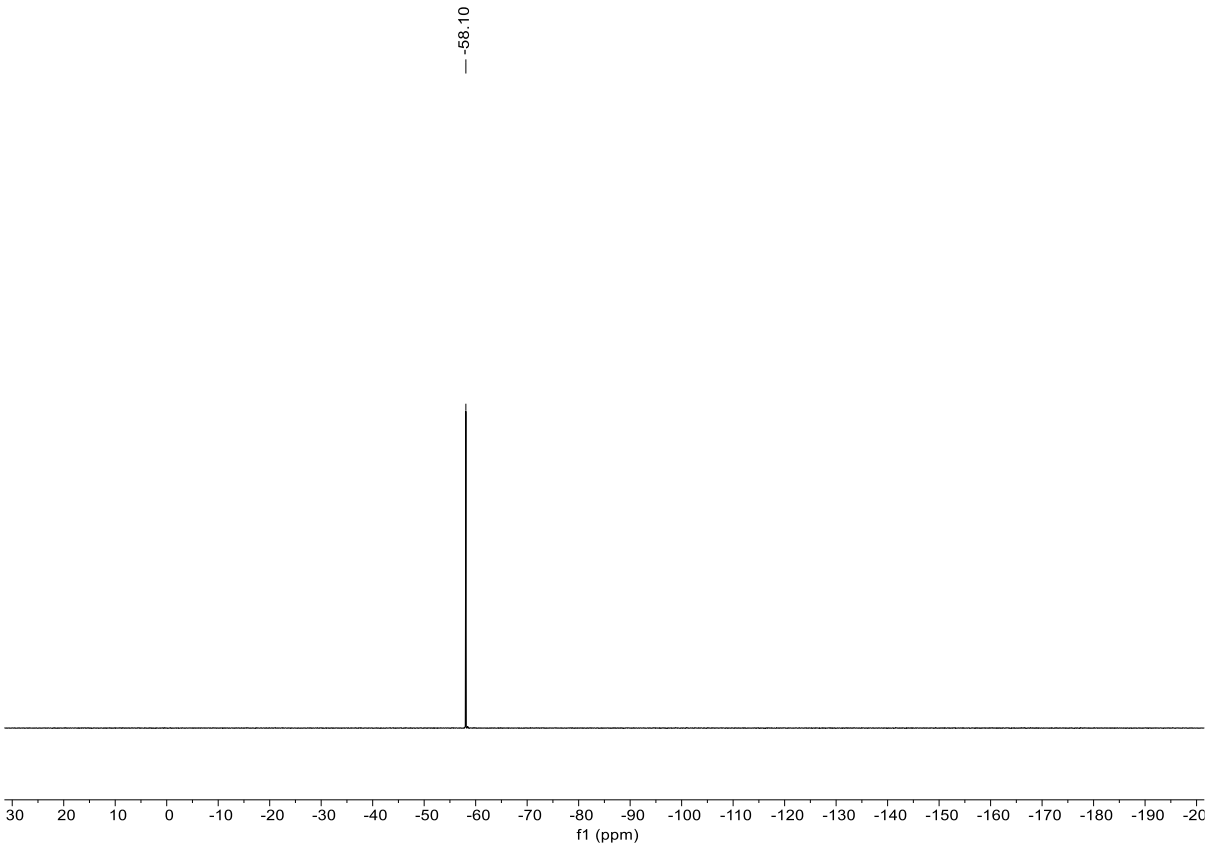




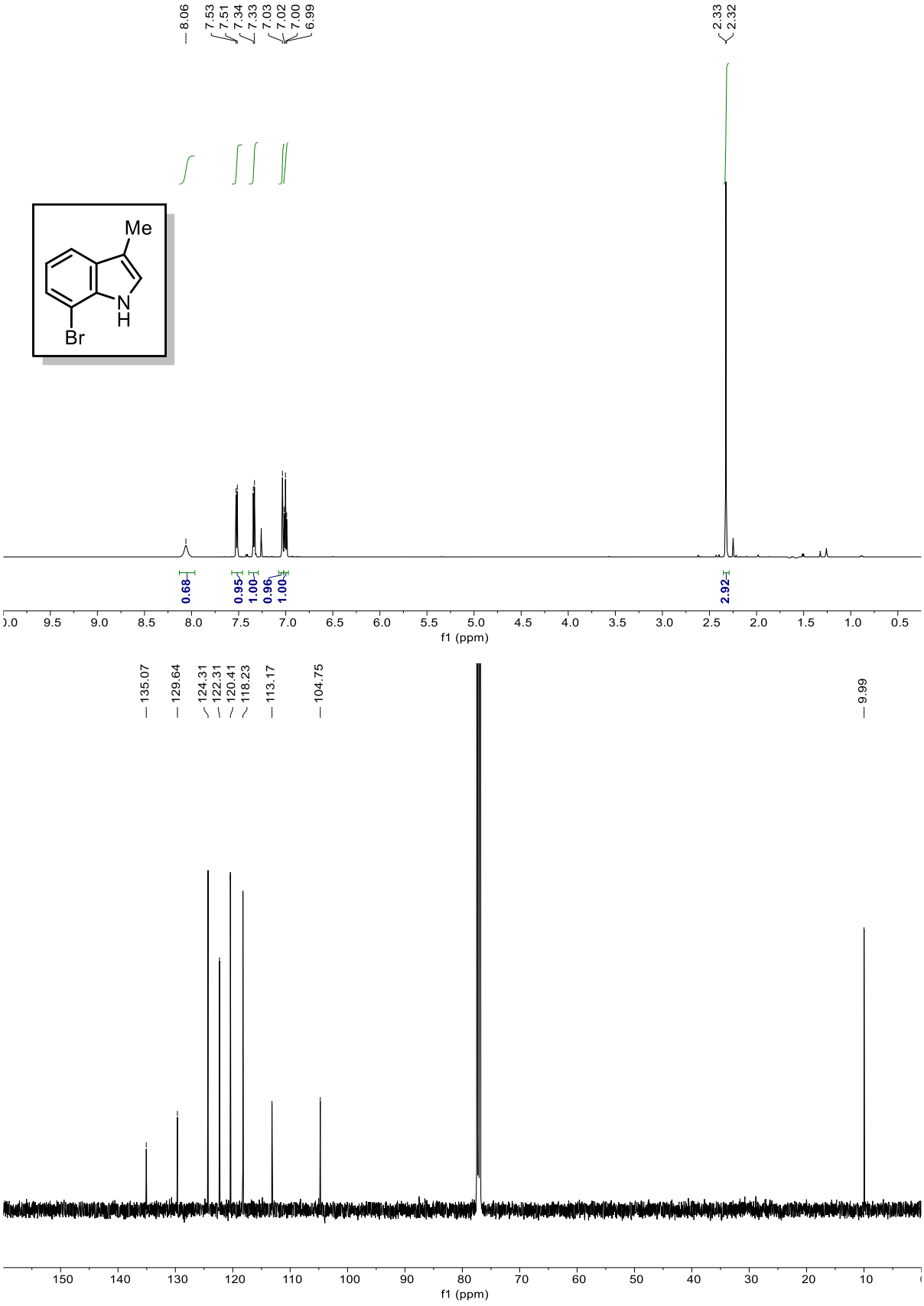
3-Methyl-5-(trifluoromethoxy)-1*H*-indole (2k)



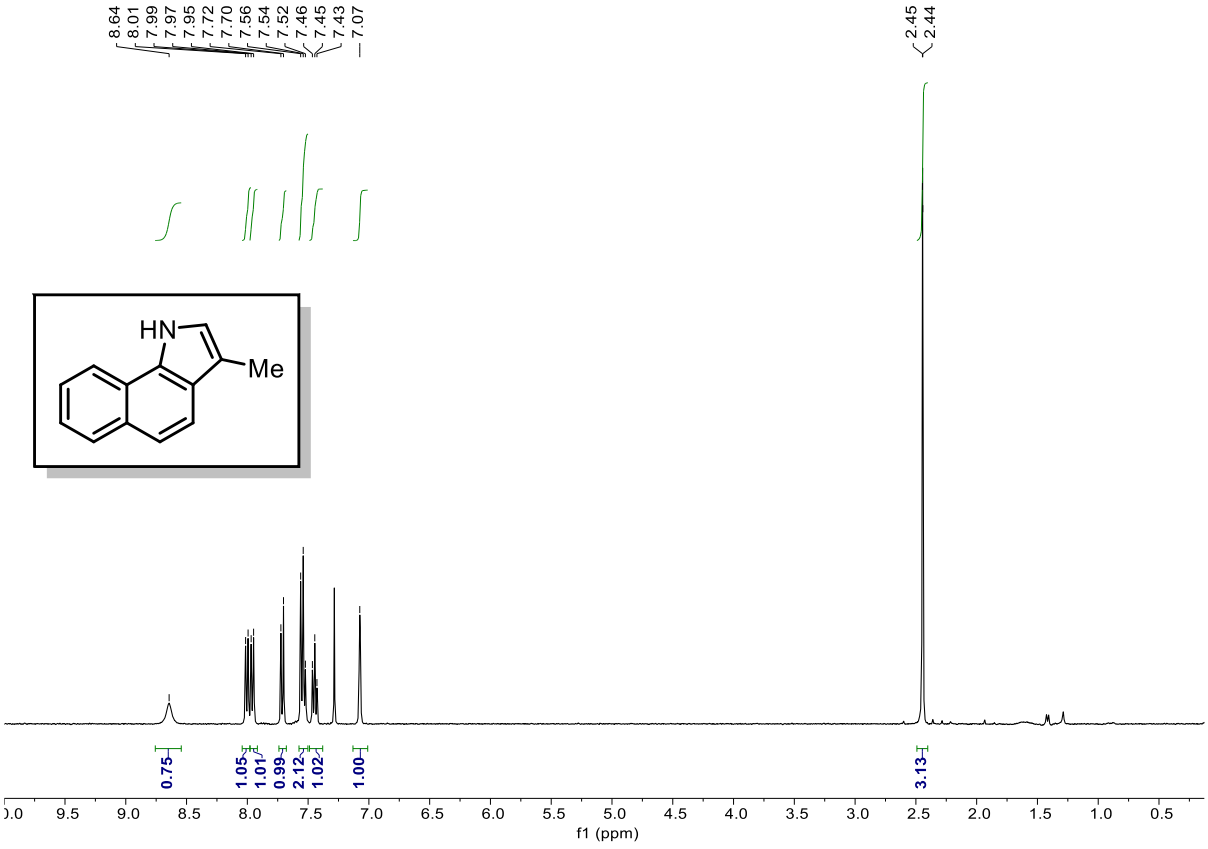


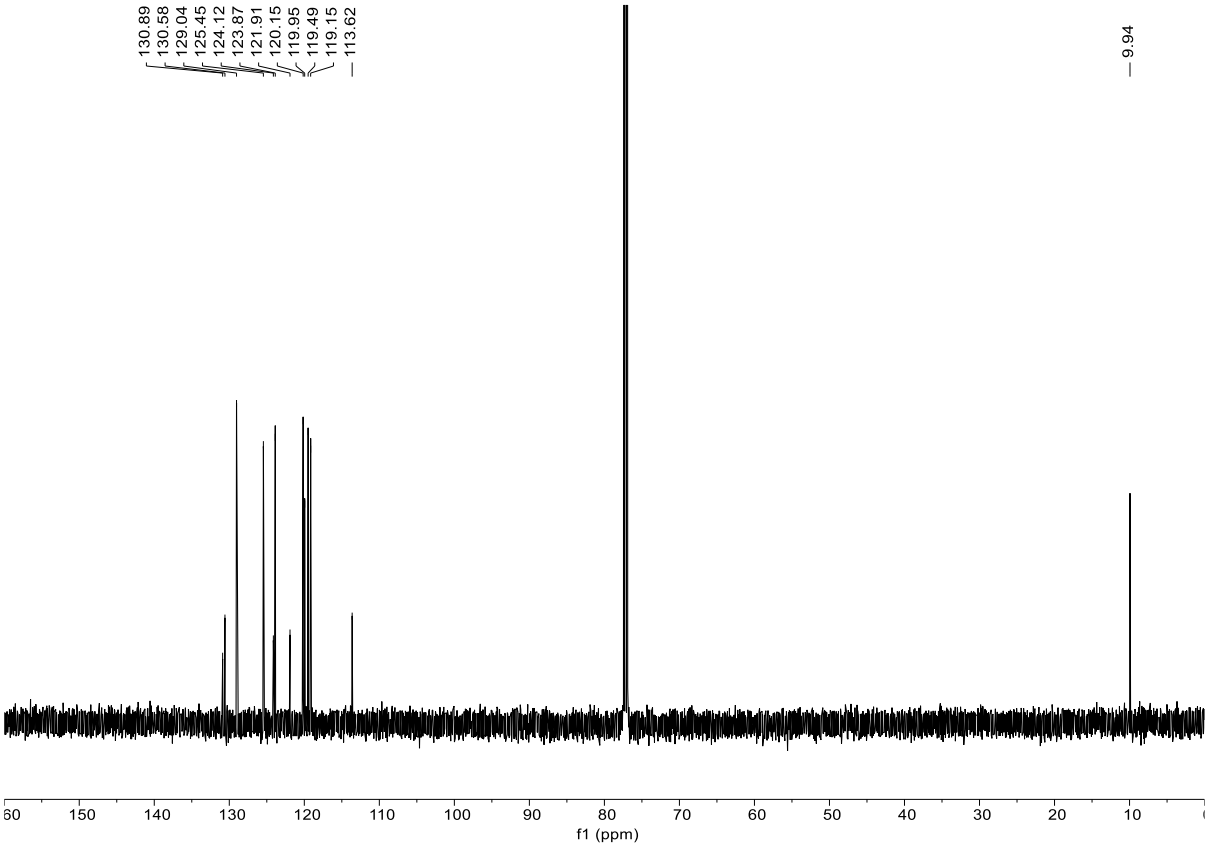

-58.10
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

7-Bromo-3-methyl-1*H*-indole (2l)

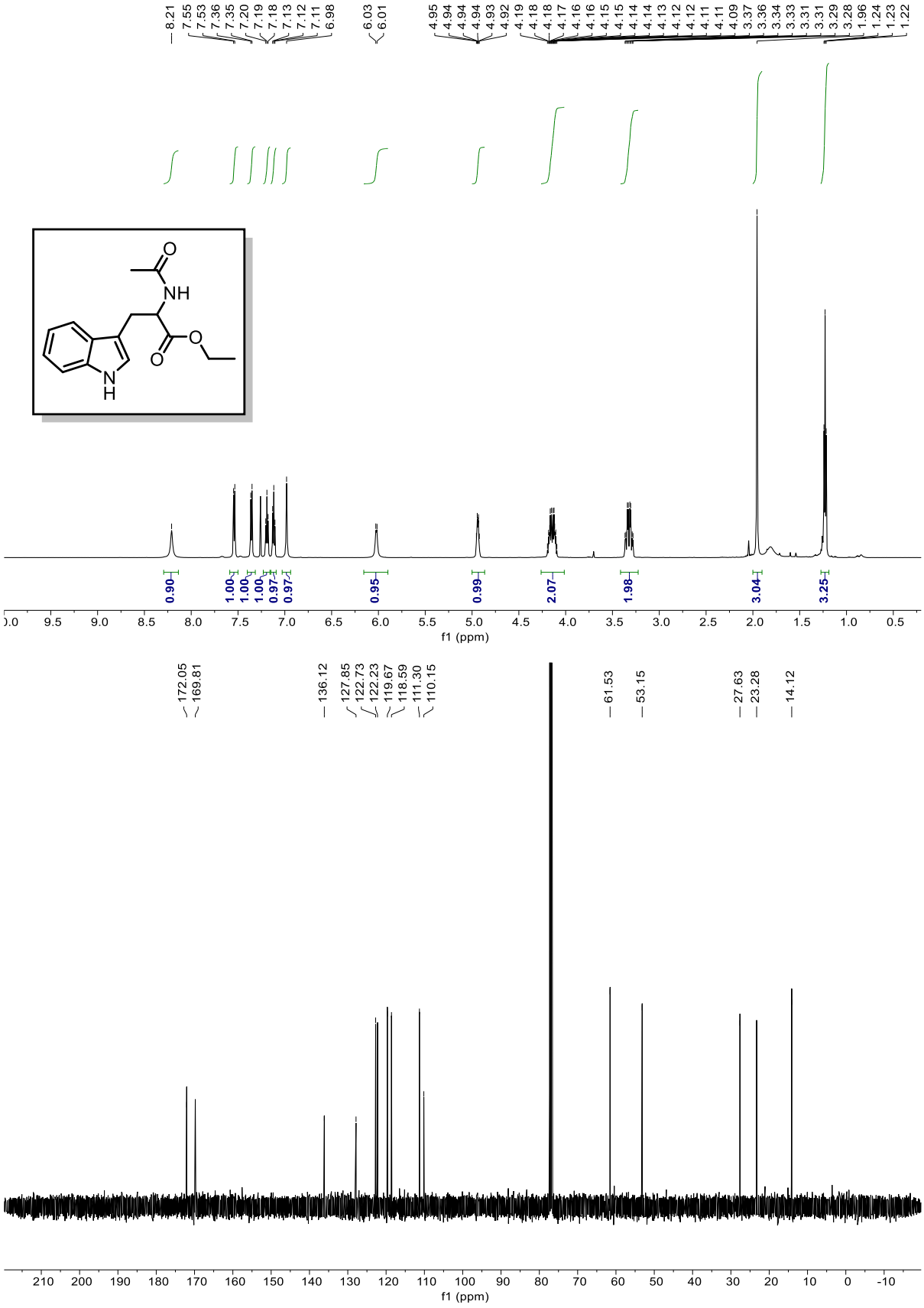


3-Methyl-1*H*-benzo[*g*]indole (2m)

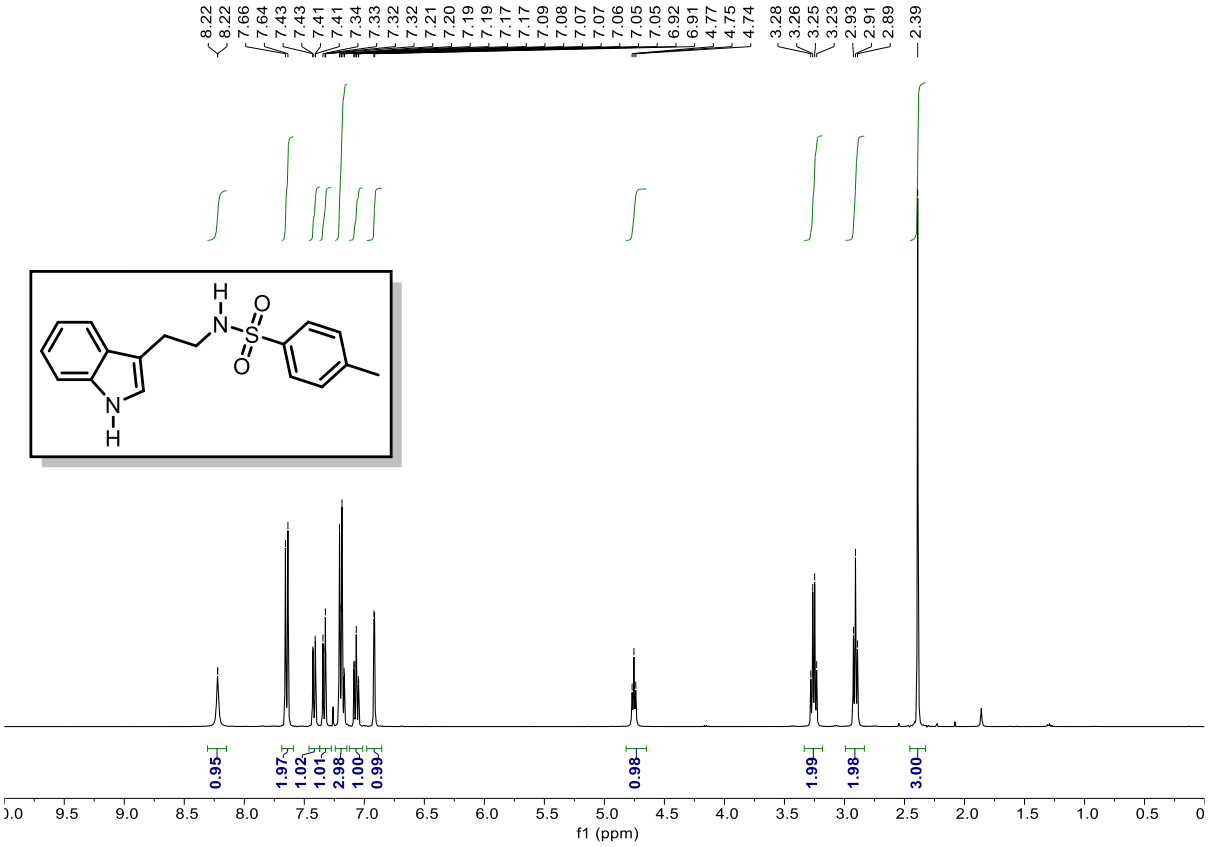


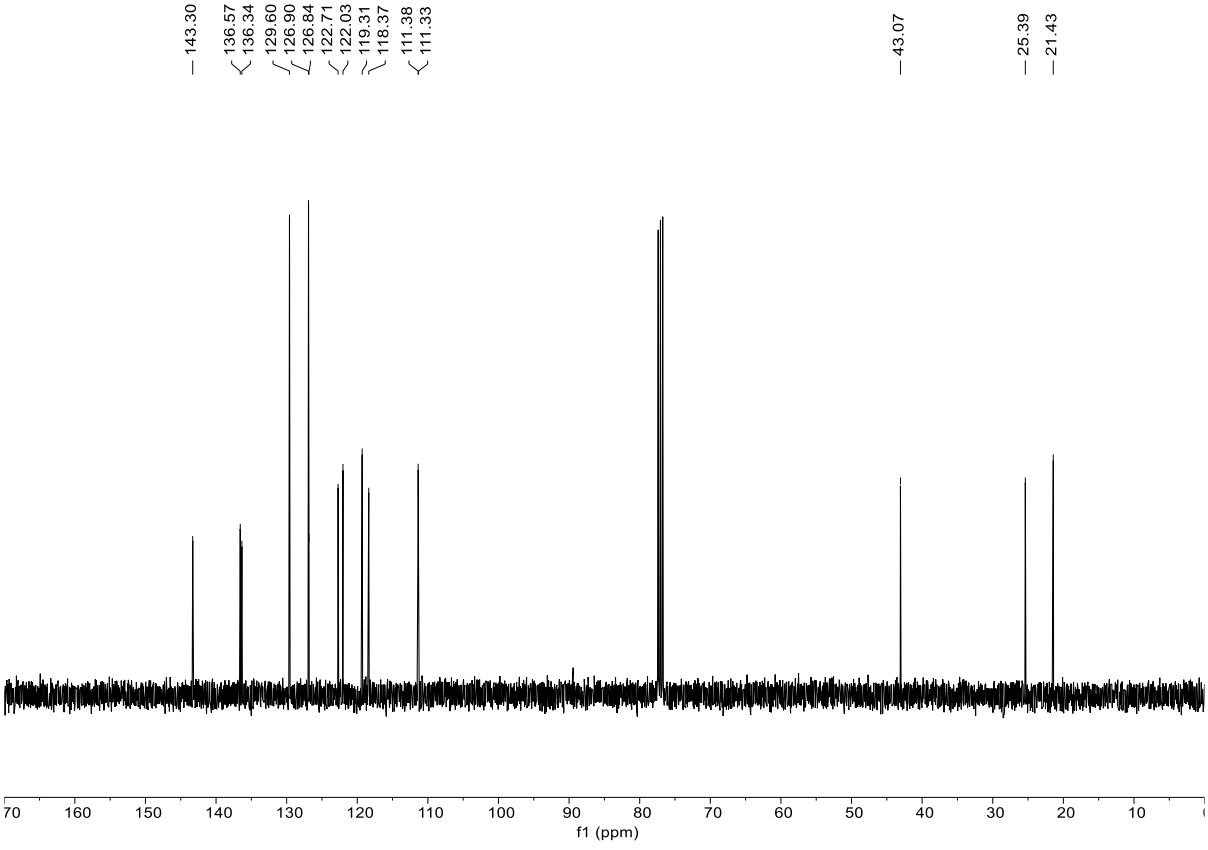


N-Acetyltryptophan ethyl ester (2n)

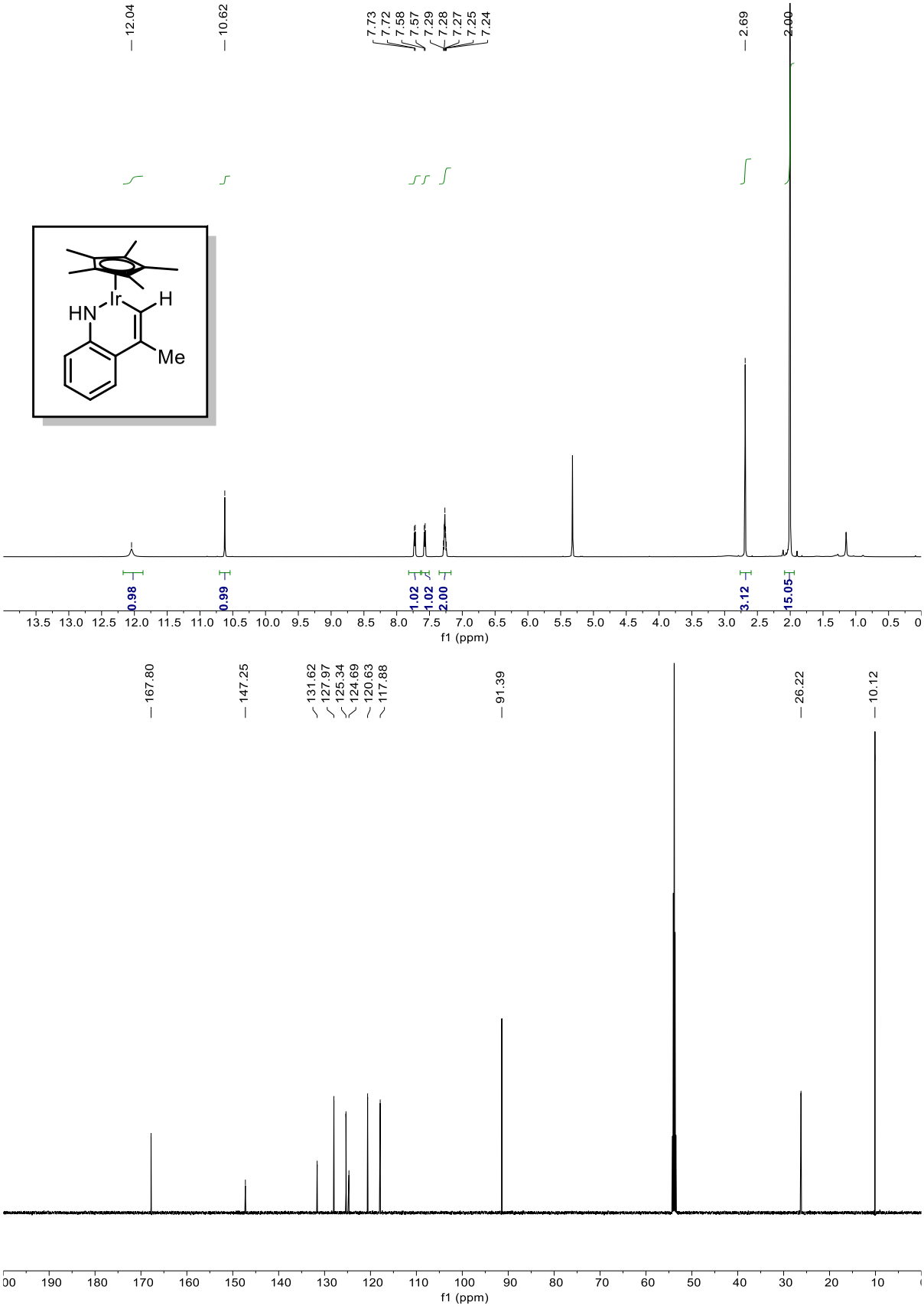


_N_-(2-(1_H_-Indol-3-yl)ethyl)-4-methylbenzenesulfonamide (2o)





Iridium complex **Ir1**



Appendix II

Crystallographic Data for 2g and Ir1

Crystallographic data of 2g (Scheme 2)

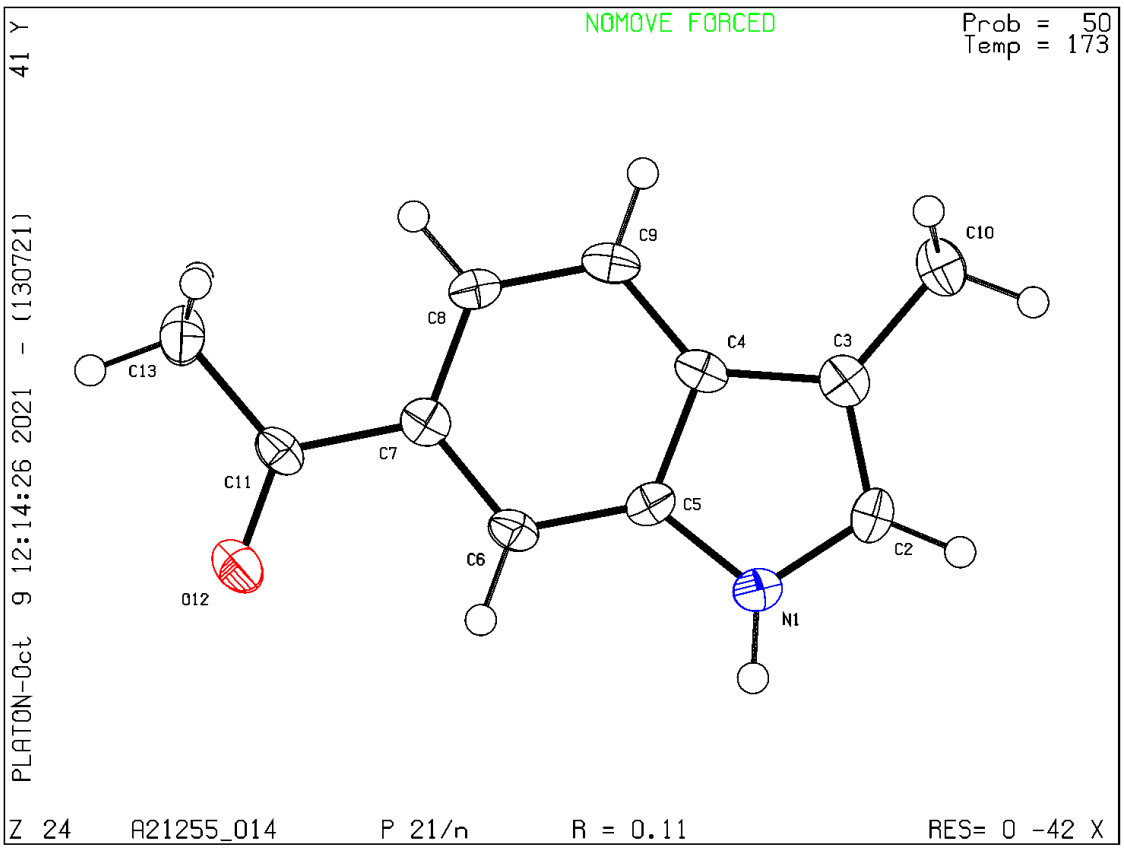


Figure S13. Crystallographic data of **2g** (CCDC 2115124).

Table S7. Crystal data and structure refinement for **2g** (CCDC 2115124).

Empirical formula	C_{11} H_{11} N O	
Formula weight	173.21	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.9622(9) Å	α = 90°
	b = 5.7301(4) Å	β = 106.083(3)°
	c = 15.9848(13) Å	γ = 90°
Volume	876.77(12) Å^3	
Z	4	
Density (calculated)	1.312 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	368	
Crystal size	0.158 x 0.087 x 0.024 mm^3	
Theta range for data collection	2.652 to 25.497°.	
Index ranges	–12<=h<=12, –6<=k<=6, –19<=l<=19	
Reflections collected	9045	
Independent reflections	1590 [R(int) = 0.1088]	
Completeness to theta = 25.242°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.3951	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1590 / 0 / 121	
Goodness-of-fit on F^2	1.162	
Final R indices [I>2sigma(I)]	R1 = 0.1139, wR2 = 0.2674	
R indices (all data)	R1 = 0.1289, wR2 = 0.2778	
Extinction coefficient	0.46(8)	
Largest diff. peak and hole	0.613 and –0.413 e·Å^{-3}	

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	5832(3)	972(6)	3085(2)	26(1)
C(2)	6095(4)	1905(7)	2362(3)	24(1)
C(3)	5368(4)	3934(7)	2121(3)	23(1)
C(4)	4618(4)	4317(6)	2750(2)	21(1)
C(5)	4928(4)	2419(6)	3342(2)	21(1)
C(6)	4355(4)	2241(7)	4041(3)	22(1)
C(7)	3480(4)	4022(7)	4163(2)	21(1)
C(8)	3174(4)	5932(6)	3584(3)	23(1)
C(9)	3723(4)	6083(7)	2882(3)	23(1)
C(10)	5337(5)	5445(8)	1355(3)	31(1)
C(11)	2901(4)	3850(7)	4922(2)	23(1)
O(12)	3154(3)	2173(6)	5412(2)	36(1)
C(13)	1964(5)	5766(8)	5074(3)	35(1)

Table S9. Bond lengths [Å] and angles [°].

N(1)-C(2)	1.364(5)
N(1)-C(5)	1.368(5)
N(1)-H(1)	0.8800
C(2)-C(3)	1.367(6)
C(2)-H(2)	0.9500
C(3)-C(4)	1.426(6)
C(3)-C(10)	1.493(6)
C(4)-C(9)	1.403(5)
C(4)-C(5)	1.418(5)
C(5)-C(6)	1.392(6)
C(6)-C(7)	1.390(5)
C(6)-H(6)	0.9500
C(7)-C(8)	1.412(5)
C(7)-C(11)	1.484(5)
C(8)-C(9)	1.380(6)
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-O(12)	1.221(5)
C(11)-C(13)	1.503(6)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(2)-N(1)-C(5)	108.3(3)
C(2)-N(1)-H(1)	125.8
C(5)-N(1)-H(1)	125.8
N(1)-C(2)-C(3)	111.1(3)
N(1)-C(2)-H(2)	124.4
C(3)-C(2)-H(2)	124.4
C(2)-C(3)-C(4)	105.8(3)
C(2)-C(3)-C(10)	127.8(4)
C(4)-C(3)-C(10)	126.4(4)
C(9)-C(4)-C(5)	118.9(4)

C(9)-C(4)-C(3)	134.1(4)
C(5)-C(4)-C(3)	107.0(3)
N(1)-C(5)-C(6)	130.3(4)
N(1)-C(5)-C(4)	107.7(3)
C(6)-C(5)-C(4)	122.0(3)
C(7)-C(6)-C(5)	118.1(3)
C(7)-C(6)-H(6)	120.9
C(5)-C(6)-H(6)	120.9
C(6)-C(7)-C(8)	120.5(4)
C(6)-C(7)-C(11)	117.8(3)
C(8)-C(7)-C(11)	121.7(4)
C(9)-C(8)-C(7)	121.3(4)
C(9)-C(8)-H(8)	119.3
C(7)-C(8)-H(8)	119.3
C(8)-C(9)-C(4)	119.2(4)
C(8)-C(9)-H(9)	120.4
C(4)-C(9)-H(9)	120.4
C(3)-C(10)-H(10A)	109.5
C(3)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(3)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(12)-C(11)-C(7)	121.2(4)
O(12)-C(11)-C(13)	119.9(4)
C(7)-C(11)-C(13)	118.9(3)
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters ($Å^2$ x 10^3). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	30(2)	23(2)	26(2)	3(1)	9(1)	7(1)
C(2)	24(2)	28(2)	24(2)	-6(2)	10(2)	0(2)
C(3)	19(2)	25(2)	23(2)	-2(2)	3(2)	-6(2)
C(4)	18(2)	20(2)	21(2)	4(2)	-1(2)	-5(1)
C(5)	19(2)	19(2)	22(2)	-3(2)	2(2)	1(1)
C(6)	22(2)	23(2)	20(2)	5(2)	2(2)	1(2)
C(7)	17(2)	24(2)	20(2)	-1(2)	0(2)	-3(1)
C(8)	20(2)	18(2)	27(2)	1(2)	3(2)	3(1)
C(9)	23(2)	18(2)	24(2)	3(2)	-2(2)	-2(2)
C(10)	32(2)	34(2)	30(2)	3(2)	13(2)	-4(2)
C(11)	21(2)	27(2)	18(2)	5(2)	3(2)	-3(2)
O(12)	39(2)	41(2)	30(2)	13(2)	15(1)	7(1)
C(13)	35(2)	44(3)	30(2)	3(2)	17(2)	7(2)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3).

	x	y	z	U(eq)
H(1)	6183	-336	3342	31
H(2)	6703	1233	2064	29
H(6)	4556	940	4424	27
H(8)	2578	7138	3678	27
H(9)	3497	7368	2492	28
H(10A)	5693	7000	1558	47
H(10B)	4375	5577	986	47
H(10C)	5924	4752	1020	47
H(13A)	2482	7240	5175	52
H(13B)	1641	5386	5584	52
H(13C)	1156	5920	4561	52

Table S12. Hydrogen bonds [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(12)#1	0.88	2.19	2.949(4)	144.8

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1

Crystallographic data of Ir1 (Scheme 3)

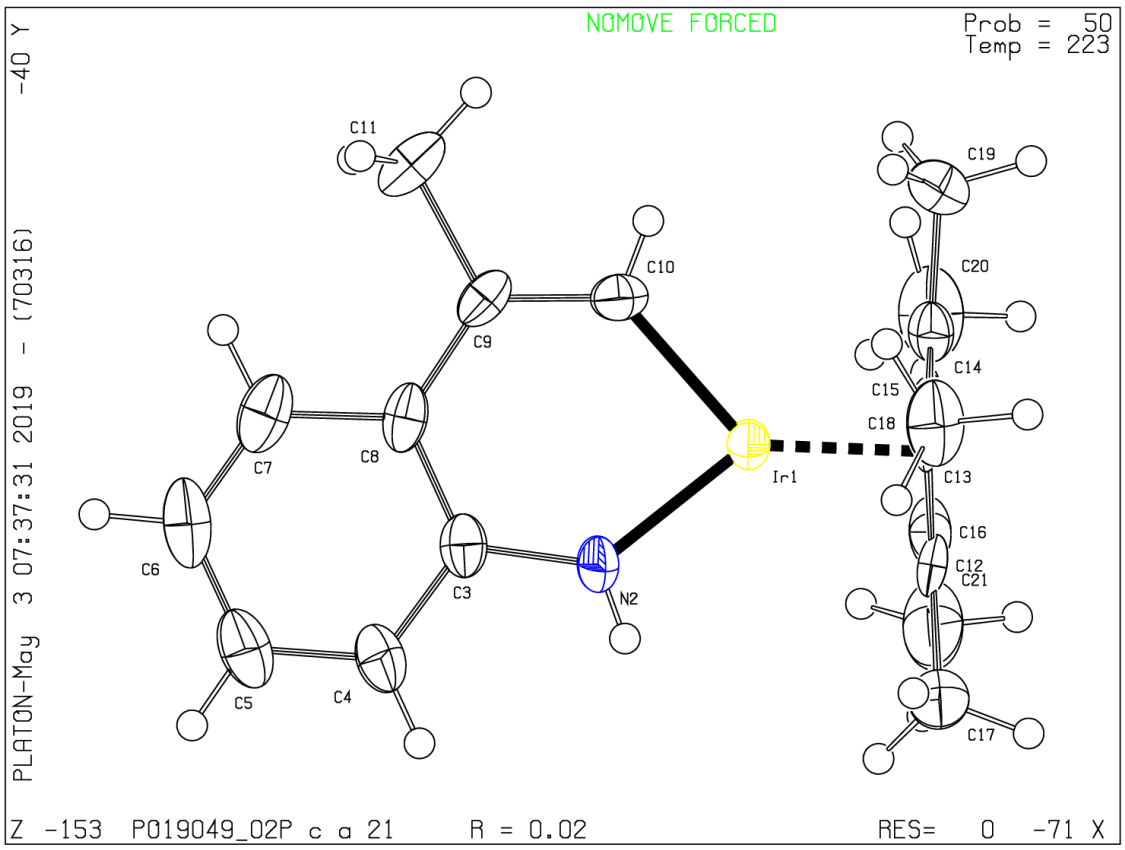


Figure S14. Crystallographic data of **Ir1** (CCDC 2113438).

Table S13. Crystal data and structure refinement for **Ir1** (CCDC 2113438).

Empirical formula	$C_{19}H_{24}NIr$	
Formula weight	458.59	
Temperature	223(2) K	
Wavelength	0.650 Å	
Crystal system	Orthorhombic	
Space group	*Pca*2_1	
Unit cell dimensions	a = 14.834(3) Å	α = 90°
	b = 8.0960(16) Å	β = 90°
	c = 14.131(3) Å	γ = 90°
Volume	1697.1(6) $Å^3$	
Z	4	
Density (calculated)	1.795 Mg/m^3	
Absorption coefficient	6.224 mm^{-1}	
F(000)	888	
Crystal size	0.042 x 0.035 x 0.031 mm^3	
Theta range for data collection	2.301 to 23.996°.	
Index ranges	–18<=h<=18, –10<=k<=10, –17<=l<=17	
Reflections collected	12196	
Independent reflections	3480 [R(int) = 0.0379]	
Completeness to theta = 22.955°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.940	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3480 / 2 / 202	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0193, wR2 = 0.0492	
R indices (all data)	R1 = 0.0209, wR2 = 0.0497	
Absolute structure parameter	0.002(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.241 and –1.126 $e \cdot Å^{-3}$	

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	2067(1)	5484(1)	4911(1)	26(1)
N(2)	2456(4)	6855(6)	3864(4)	31(1)
C(3)	3131(4)	7986(7)	3752(5)	30(1)
C(4)	3256(5)	8708(7)	2854(5)	38(1)
C(5)	3935(5)	9811(9)	2676(6)	48(2)
C(6)	4519(5)	10245(7)	3407(7)	50(2)
C(7)	4403(5)	9588(7)	4277(7)	43(2)
C(8)	3715(4)	8435(7)	4503(5)	31(1)
C(9)	3625(4)	7747(7)	5437(5)	30(1)
C(10)	3010(4)	6570(9)	5672(5)	30(1)
C(11)	4273(4)	8355(8)	6210(5)	44(2)
C(12)	744(6)	4310(9)	4495(7)	42(2)
C(13)	744(5)	4986(8)	5455(6)	30(2)
C(14)	1395(4)	4085(7)	6016(4)	27(1)
C(15)	1841(5)	2978(7)	5394(5)	28(1)
C(16)	1426(5)	3108(9)	4473(6)	41(2)
C(17)	129(7)	4834(12)	3722(7)	69(3)
C(18)	100(4)	6238(8)	5845(6)	46(2)
C(19)	1564(6)	4267(8)	7049(5)	41(2)
C(20)	2571(5)	1757(8)	5673(6)	55(2)
C(21)	1703(7)	2057(11)	3646(6)	72(3)

Table S15. Bond lengths [Å] and angles [°]

Ir(1)-N(2)	1.937(5)
Ir(1)-C(10)	1.972(6)
Ir(1)-C(13)	2.147(7)
Ir(1)-C(15)	2.167(6)
Ir(1)-C(14)	2.171(6)
Ir(1)-C(16)	2.233(7)
Ir(1)-C(12)	2.259(8)
N(2)-C(3)	1.366(7)
N(2)-H(2)	0.79(3)
C(3)-C(4)	1.409(9)
C(3)-C(8)	1.418(9)
C(4)-C(5)	1.369(9)
C(4)-H(4)	0.9400
C(5)-C(6)	1.395(13)
C(5)-H(5)	0.9400
C(6)-C(7)	1.350(13)
C(6)-H(6)	0.9400
C(7)-C(8)	1.419(9)
C(7)-H(7)	0.9400
C(8)-C(9)	1.439(8)
C(9)-C(10)	1.360(9)
C(9)-C(11)	1.537(8)
C(10)-H(10)	0.83(9)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(11)-H(11C)	0.9700
C(12)-C(16)	1.405(12)
C(12)-C(13)	1.462(10)
C(12)-C(17)	1.485(13)
C(13)-C(14)	1.447(9)
C(13)-C(18)	1.498(9)
C(14)-C(15)	1.419(9)
C(14)-C(19)	1.490(9)
C(15)-C(16)	1.443(9)
C(15)-C(20)	1.518(10)
C(16)-C(21)	1.503(10)

C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(17)-H(17C)	0.9700
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(18)-H(18C)	0.9700
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(19)-H(19C)	0.9700
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(20)-H(20C)	0.9700
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(21)-H(21C)	0.9700

N(2)-Ir(1)-C(10)	87.1(3)
N(2)-Ir(1)-C(13)	130.8(3)
C(10)-Ir(1)-C(13)	122.5(3)
N(2)-Ir(1)-C(15)	145.4(2)
C(10)-Ir(1)-C(15)	110.8(3)
C(13)-Ir(1)-C(15)	64.5(3)
N(2)-Ir(1)-C(14)	170.0(2)
C(10)-Ir(1)-C(14)	99.6(3)
C(13)-Ir(1)-C(14)	39.2(2)
C(15)-Ir(1)-C(14)	38.2(2)
N(2)-Ir(1)-C(16)	114.1(3)
C(10)-Ir(1)-C(16)	146.8(3)
C(13)-Ir(1)-C(16)	63.1(3)
C(15)-Ir(1)-C(16)	38.2(2)
C(14)-Ir(1)-C(16)	63.5(3)
N(2)-Ir(1)-C(12)	107.5(3)
C(10)-Ir(1)-C(12)	161.1(3)
C(13)-Ir(1)-C(12)	38.7(3)
C(15)-Ir(1)-C(12)	63.5(3)
C(14)-Ir(1)-C(12)	64.4(3)
C(16)-Ir(1)-C(12)	36.4(3)
C(3)-N(2)-Ir(1)	133.7(5)

C(3)-N(2)-H(2)	118(6)
Ir(1)-N(2)-H(2)	108(6)
N(2)-C(3)-C(4)	118.6(6)
N(2)-C(3)-C(8)	122.2(6)
C(4)-C(3)-C(8)	119.1(5)
C(5)-C(4)-C(3)	122.2(7)
C(5)-C(4)-H(4)	118.9
C(3)-C(4)-H(4)	118.9
C(4)-C(5)-C(6)	119.0(7)
C(4)-C(5)-H(5)	120.5
C(6)-C(5)-H(5)	120.5
C(7)-C(6)-C(5)	119.8(6)
C(7)-C(6)-H(6)	120.1
C(5)-C(6)-H(6)	120.1
C(6)-C(7)-C(8)	123.8(8)
C(6)-C(7)-H(7)	118.1
C(8)-C(7)-H(7)	118.1
C(3)-C(8)-C(7)	116.1(7)
C(3)-C(8)-C(9)	122.0(5)
C(7)-C(8)-C(9)	121.9(6)
C(10)-C(9)-C(8)	123.9(5)
C(10)-C(9)-C(11)	118.1(6)
C(8)-C(9)-C(11)	118.0(5)
C(9)-C(10)-Ir(1)	130.9(5)
C(9)-C(10)-H(10)	111(5)
Ir(1)-C(10)-H(10)	118(5)
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(16)-C(12)-C(13)	106.3(7)
C(16)-C(12)-C(17)	128.7(9)
C(13)-C(12)-C(17)	125.1(9)
C(16)-C(12)-Ir(1)	70.8(4)
C(13)-C(12)-Ir(1)	66.5(4)
C(17)-C(12)-Ir(1)	127.2(5)

C(14)-C(13)-C(12)	108.6(7)
C(14)-C(13)-C(18)	124.4(7)
C(12)-C(13)-C(18)	126.5(8)
C(14)-C(13)-Ir(1)	71.3(4)
C(12)-C(13)-Ir(1)	74.8(5)
C(18)-C(13)-Ir(1)	126.0(5)
C(15)-C(14)-C(13)	106.9(6)
C(15)-C(14)-C(19)	126.3(6)
C(13)-C(14)-C(19)	126.8(6)
C(15)-C(14)-Ir(1)	70.7(3)
C(13)-C(14)-Ir(1)	69.5(4)
C(19)-C(14)-Ir(1)	125.2(4)
C(14)-C(15)-C(16)	108.3(6)
C(14)-C(15)-C(20)	125.7(7)
C(16)-C(15)-C(20)	125.9(7)
C(14)-C(15)-Ir(1)	71.1(3)
C(16)-C(15)-Ir(1)	73.4(4)
C(20)-C(15)-Ir(1)	125.5(5)
C(12)-C(16)-C(15)	109.7(6)
C(12)-C(16)-C(21)	127.3(9)
C(15)-C(16)-C(21)	122.9(8)
C(12)-C(16)-Ir(1)	72.8(4)
C(15)-C(16)-Ir(1)	68.4(4)
C(21)-C(16)-Ir(1)	125.9(5)
C(12)-C(17)-H(17A)	109.5
C(12)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(12)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(13)-C(18)-H(18A)	109.5
C(13)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(13)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(14)-C(19)-H(19A)	109.5
C(14)-C(19)-H(19B)	109.5

H(19A)-C(19)-H(19B)	109.5
C(14)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(15)-C(20)-H(20A)	109.5
C(15)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(15)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(16)-C(21)-H(21A)	109.5
C(16)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(16)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters ($Å^2$ x 10^3). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	26(1)	25(1)	26(1)	0(1)	2(1)	-6(1)
N(2)	36(3)	24(2)	33(3)	3(2)	1(2)	-11(2)
C(3)	29(3)	20(3)	40(4)	-1(2)	7(3)	0(2)
C(4)	44(3)	26(3)	44(4)	6(3)	9(3)	-3(3)
C(5)	52(5)	32(3)	60(5)	16(3)	12(4)	0(3)
C(6)	41(4)	30(3)	79(7)	8(3)	19(4)	-5(3)
C(7)	31(3)	29(3)	69(5)	-9(3)	1(3)	-2(2)
C(8)	24(3)	16(3)	51(4)	-5(3)	5(2)	0(2)
C(9)	23(3)	27(3)	38(4)	-12(3)	-4(3)	0(2)
C(10)	30(3)	37(3)	24(3)	-2(3)	-3(2)	1(2)
C(11)	33(3)	43(3)	55(4)	-17(3)	-14(3)	-2(3)
C(12)	35(4)	46(5)	44(4)	8(4)	-3(3)	-31(4)
C(13)	18(3)	29(3)	44(4)	8(3)	4(3)	-14(3)
C(14)	25(3)	19(2)	39(3)	4(2)	2(2)	1(2)
C(15)	35(3)	17(2)	33(4)	7(2)	9(3)	-10(3)
C(16)	48(4)	33(3)	41(4)	-7(3)	16(4)	-20(3)
C(17)	68(6)	84(6)	54(6)	30(5)	-27(5)	-37(5)
C(18)	25(3)	37(3)	77(5)	6(3)	13(3)	8(3)
C(19)	49(4)	46(4)	29(4)	5(3)	1(3)	-5(3)
C(20)	45(4)	30(3)	91(7)	0(3)	18(4)	11(3)
C(21)	95(6)	67(5)	55(5)	-30(4)	35(5)	-42(5)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3)

	x	y	z	U(eq)
H(2)	2140(40)	6670(110)	3420(40)	46
H(4)	2861	8422	2361	46
H(5)	4005	10270	2069	58
H(6)	4993	10992	3295	60
H(7)	4800	9914	4760	52
H(10)	3040(40)	6340(100)	6240(60)	36
H(11A)	4163	7748	6791	66
H(11B)	4175	9524	6320	66
H(11C)	4890	8177	6008	66
H(17A)	468	4952	3140	103
H(17B)	-145	5884	3886	103
H(17C)	-338	4009	3637	103
H(18A)	-422	5679	6108	70
H(18B)	-92	6974	5342	70
H(18C)	396	6873	6337	70
H(19A)	1163	3542	7397	62
H(19B)	1455	5403	7237	62
H(19C)	2184	3977	7188	62
H(20A)	2308	667	5745	83
H(20B)	2840	2098	6267	83
H(20C)	3030	1725	5185	83
H(21A)	1536	918	3765	108
H(21B)	2351	2131	3559	108
H(21C)	1401	2445	3079	108

Appendix III

Cartesian Coordinates of DFT-Optimized Structures

Ir(III)

7	-1.128130000	-1.131632000	0.045903000
6	-0.778154000	1.541676000	-0.055475000
6	2.304532000	0.204729000	-1.172392000
77	0.447751000	0.010282000	-0.002265000
6	2.311440000	0.296565000	1.137123000
6	2.348120000	-1.167776000	-0.667712000
6	2.352076000	-1.111731000	0.742589000
6	2.379252000	-2.393137000	-1.530590000
6	2.384461000	1.102782000	-0.051724000
6	2.382570000	0.586532000	-2.619522000
6	2.503574000	2.594908000	-0.111203000
6	2.397295000	0.792501000	2.548761000
6	2.387909000	-2.264771000	1.699770000
1	3.423717000	0.570223000	-2.967773000
1	1.807316000	-0.104270000	-3.240291000
1	1.984684000	1.589708000	-2.784378000
1	3.554496000	2.907723000	-0.127032000
1	2.019906000	2.993888000	-1.006586000
1	2.025905000	3.063433000	0.753181000
1	3.440608000	0.807374000	2.890518000
1	1.996451000	1.804274000	2.635603000
1	1.828427000	0.151509000	3.226228000
1	3.395902000	-2.592006000	-1.893113000
1	1.733300000	-2.275452000	-2.404664000
1	2.043834000	-3.278647000	-0.984926000
1	2.050166000	-3.190754000	1.227675000
1	3.406376000	-2.434165000	2.072018000
1	1.746045000	-2.077956000	2.564773000
1	-0.290531000	2.521898000	-0.094497000
6	-2.153531000	1.602178000	-0.052168000
6	-3.007934000	0.438491000	-0.004507000
6	-4.423282000	0.561965000	-0.002493000
6	-2.471637000	-0.889360000	0.042939000
1	-0.943841000	-2.130383000	0.082793000
6	-3.360762000	-1.997574000	0.088919000
1	-2.934273000	-2.998723000	0.124718000
6	-4.728578000	-1.829667000	0.089163000
1	-2.065577000	3.761110000	-0.134418000
6	-2.817065000	2.968479000	-0.100920000
1	-3.449470000	3.147440000	0.777727000
1	-3.457567000	3.080619000	-0.984744000
6	-5.268670000	-0.529765000	0.042716000
1	-4.861952000	1.552245000	-0.037692000
1	-6.344942000	-0.384638000	0.042447000
1	-5.383098000	-2.695993000	0.125077000

TS-RE(III/I)

7	-1.174553000	-0.166661000	-1.459824000
6	-1.059606000	1.483991000	-0.711460000
6	2.338957000	0.772935000	-0.417843000
77	0.349364000	0.029751000	-0.159791000
6	1.797535000	-0.411320000	1.462461000
6	2.754446000	-0.629361000	-0.645868000
6	2.382510000	-1.351317000	0.473280000
6	3.317057000	-1.125555000	-1.939362000
6	1.960349000	0.920811000	0.985399000
6	2.682524000	1.900400000	-1.345009000
6	1.805844000	2.202581000	1.747290000
6	1.390173000	-0.816462000	2.847913000
6	2.456509000	-2.829813000	0.695377000
1	3.741654000	2.173743000	-1.247364000
1	2.502671000	1.619712000	-2.386594000
1	2.084086000	2.787555000	-1.125440000
1	2.768755000	2.537709000	2.154998000
1	1.415586000	2.997978000	1.106853000
1	1.108184000	2.082685000	2.579675000
1	2.269659000	-0.967512000	3.488411000
1	0.759319000	-0.054313000	3.310687000
1	0.824132000	-1.751963000	2.833238000
1	4.301020000	-0.683084000	-2.140172000
1	2.665989000	-0.855544000	-2.779065000
1	3.431655000	-2.211939000	-1.942832000
1	2.787150000	-3.360580000	-0.200310000
1	3.151268000	-3.072801000	1.509272000
1	1.477195000	-3.229843000	0.978854000
1	-0.622610000	2.268115000	-1.330823000
6	-2.311136000	1.645325000	-0.122034000
6	-2.938985000	0.379929000	0.055260000
6	-4.130995000	0.041709000	0.735241000
6	-2.282375000	-0.641292000	-0.708464000
1	-1.046586000	-0.543045000	-2.399659000
6	-2.811421000	-1.938461000	-0.791747000
1	-2.305248000	-2.692825000	-1.388357000
6	-3.984133000	-2.236424000	-0.109705000
1	-2.460966000	3.769619000	-0.436538000
6	-2.991293000	2.968735000	0.090578000
1	-3.025051000	3.255344000	1.151070000
1	-4.029193000	2.958049000	-0.268979000
6	-4.636124000	-1.246176000	0.657283000
1	-4.646045000	0.801668000	1.316337000
1	-5.546939000	-1.500931000	1.192488000
1	-4.397340000	-3.239479000	-0.160472000

Ir(I)-PDT

7	-1.392354000	-0.271498000	-1.248046000
6	-1.821767000	0.928343000	-1.912724000
6	2.502917000	0.864754000	-0.156567000
77	0.421549000	0.254410000	-0.175486000
6	1.760581000	-0.887274000	1.062346000
6	3.085172000	-0.383020000	-0.749126000
6	2.646667000	-1.436740000	-0.007659000
6	3.855693000	-0.385457000	-2.029683000
6	1.978008000	0.552911000	1.153792000
6	2.928151000	2.233129000	-0.610099000
6	1.893106000	1.429730000	2.368146000
6	1.225850000	-1.740543000	2.177889000

6	2.798210000	-2.901596000	-0.264698000
1	3.977308000	2.428001000	-0.344768000
1	2.837805000	2.332260000	-1.696693000
1	2.311329000	3.008610000	-0.149389000
1	2.829520000	1.398403000	2.944576000
1	1.701757000	2.469442000	2.089014000
1	1.079918000	1.111186000	3.026451000
1	2.029780000	-2.037153000	2.866877000
1	0.465477000	-1.204908000	2.751903000
1	0.770857000	-2.657304000	1.788100000
1	4.748145000	0.250354000	-1.966913000
1	3.244562000	0.011682000	-2.851378000
1	4.179657000	-1.390779000	-2.312279000
1	3.465692000	-3.102838000	-1.107021000
1	3.195320000	-3.430247000	0.611412000
1	1.826712000	-3.361202000	-0.494553000
1	-1.259371000	1.283219000	-2.763603000
6	-2.920100000	1.452429000	-1.304653000
6	-3.291541000	0.548905000	-0.234019000
6	-4.332102000	0.552573000	0.706032000
6	-2.367857000	-0.515651000	-0.228165000
1	-1.148306000	-1.059248000	-1.846881000
6	-2.466288000	-1.600117000	0.640312000
1	-1.730723000	-2.397367000	0.622739000
6	-3.520005000	-1.587565000	1.551126000
1	-3.189100000	3.197076000	-2.534645000
6	-3.611786000	2.735697000	-1.638223000
1	-3.521548000	3.453532000	-0.814212000
1	-4.682117000	2.572495000	-1.809425000
6	-4.436439000	-0.518423000	1.588827000
1	-5.045113000	1.371050000	0.737326000
1	-5.238905000	-0.534209000	2.320369000
1	-3.628605000	-2.409705000	2.251828000

Ir(IV)

7	1.115495000	-1.150976000	-0.025092000
6	0.764171000	1.525571000	0.028994000
6	-2.308578000	0.243627000	1.171154000
77	-0.419694000	0.010496000	0.004128000
6	-2.316689000	0.290709000	-1.138683000
6	-2.399842000	-1.141088000	0.690732000
6	-2.404748000	-1.112464000	-0.714378000
6	-2.477645000	-2.339869000	1.584366000
6	-2.358957000	1.122920000	0.033837000
6	-2.380965000	0.648718000	2.610076000
6	-2.473074000	2.616525000	0.064656000
6	-2.398849000	0.754113000	-2.559374000
6	-2.488787000	-2.273809000	-1.655623000
1	-3.426040000	0.646366000	2.943415000
1	-1.824167000	-0.041642000	3.247046000
1	-1.979855000	1.651699000	2.763629000
1	-3.526073000	2.917603000	0.076230000
1	-1.997187000	3.035448000	0.954451000
1	-2.006538000	3.071089000	-0.812496000
1	-3.446122000	0.765081000	-2.885544000
1	-1.998681000	1.762610000	-2.674525000
1	-1.846276000	0.090489000	-3.227651000
1	-3.491205000	-2.441210000	1.990174000
1	-1.794268000	-2.249229000	2.432573000
1	-2.240965000	-3.262140000	1.050489000
1	-2.249824000	-3.217236000	-1.161185000
1	-3.504765000	-2.357839000	-2.059337000
1	-1.810236000	-2.149080000	-2.503382000
1	0.287347000	2.508421000	0.050211000
6	2.175511000	1.584826000	0.024705000
6	3.016246000	0.417149000	-0.002664000
6	4.429524000	0.545828000	-0.006862000
6	2.475057000	-0.910101000	-0.026799000
1	0.926425000	-2.150522000	-0.044264000
6	3.348369000	-2.009381000	-0.053255000
1	2.931691000	-3.013337000	-0.071510000
6	4.732913000	-1.839531000	-0.056628000
1	2.060132000	3.740701000	0.070386000
6	2.814242000	2.952915000	0.050298000
1	3.445028000	3.113128000	-0.831618000
1	3.453551000	3.076234000	0.931980000
6	5.278481000	-0.553565000	-0.033266000
1	4.870297000	1.534814000	0.010910000
1	6.353367000	-0.410759000	-0.035676000
1	5.379533000	-2.710908000	-0.077477000

TS-RE(IV/II)

7	-1.170494000	-0.514195000	-1.280538000
6	-0.871859000	1.449078000	-0.837487000
6	2.454246000	0.072133000	-0.810320000
77	0.435404000	0.121533000	-0.111235000
6	2.000358000	0.231675000	1.446301000
6	2.233427000	-1.292324000	-0.296386000
6	1.965824000	-1.191313000	1.081228000
6	2.293422000	-2.534145000	-1.128857000
6	2.414811000	0.998376000	0.313484000
6	2.890904000	0.404644000	-2.199329000
6	2.765639000	2.452886000	0.274256000
6	1.779893000	0.747971000	2.833157000
6	1.642506000	-2.298804000	2.031791000
1	3.981050000	0.302679000	-2.273368000
1	2.441959000	-0.267841000	-2.933058000
1	2.630581000	1.431035000	-2.464333000
1	3.843437000	2.585860000	0.423901000
1	2.503892000	2.900386000	-0.687143000
1	2.246678000	3.009186000	1.057091000
1	2.685576000	0.601761000	3.434049000
1	1.543883000	1.813347000	2.830882000
1	0.963428000	0.217634000	3.329150000
1	3.335004000	-2.846742000	-1.266484000
1	1.867760000	-2.367481000	-2.121708000
1	1.752635000	-3.358885000	-0.661710000
1	1.373720000	-3.217590000	1.508346000

1	2.509691000	-2.513036000	2.668124000
1	0.813471000	-2.027006000	2.690495000
1	-0.559050000	2.191972000	-1.574955000
6	-2.127046000	1.613976000	-0.193294000
6	-2.918855000	0.446724000	0.013843000
6	-4.161963000	0.370110000	0.679065000
6	-2.422321000	-0.688457000	-0.690286000
1	-0.971163000	-1.100976000	-2.084060000
6	-3.188593000	-1.851282000	-0.773147000
1	-2.825375000	-2.709741000	-1.330145000
6	-4.421639000	-1.898603000	-0.117035000
1	-1.952211000	3.768764000	-0.250483000
6	-2.604163000	2.994488000	0.160128000
1	-2.634129000	3.125162000	1.248254000
1	-3.621627000	3.154192000	-0.214191000
6	-4.902094000	-0.801225000	0.619063000
1	-4.537921000	1.231943000	1.221256000
1	-5.858315000	-0.868608000	1.126384000
1	-5.016311000	-2.804953000	-0.176284000

Ir(II)-PDT

7	-1.303679000	-0.189752000	-1.866266000
6	-0.775008000	1.127487000	-1.637780000
6	2.489306000	-0.559744000	-0.441264000
77	0.303153000	0.049602000	-0.235512000
6	1.603257000	0.489768000	1.449950000
6	1.790072000	-1.547068000	0.366190000
6	1.339083000	-0.926349000	1.577553000
6	1.696508000	-3.007908000	0.044846000
6	2.366030000	0.706627000	0.223634000
6	3.246456000	-0.834106000	-1.701811000
6	2.987100000	2.000319000	-0.200021000
6	1.329892000	1.528214000	2.493858000
6	0.670207000	-1.598233000	2.734499000
1	4.274404000	-1.137671000	-1.467379000
1	2.789624000	-1.642370000	-2.277350000
1	3.299425000	0.050776000	-2.339681000
1	3.985555000	2.100371000	0.242601000
1	3.093968000	2.057870000	-1.285210000
1	2.392232000	2.854733000	0.129660000
1	2.171016000	1.590815000	3.194075000
1	1.193263000	2.514620000	2.046267000
1	0.431782000	1.288112000	3.066941000
1	2.582053000	-3.534100000	0.420063000
1	1.642917000	-3.176822000	-1.032867000
1	0.816838000	-3.463164000	0.504273000
1	0.144473000	-2.504011000	2.425636000
1	1.415771000	-1.885959000	3.486531000
1	-0.051001000	-0.937029000	3.219885000
1	-0.329437000	1.697276000	-2.444014000
6	-1.379470000	1.583599000	-0.418712000
6	-2.471159000	0.662251000	-0.098506000
6	-3.445665000	0.660630000	0.904457000
6	-2.433588000	-0.406640000	-1.029127000
1	-1.182104000	-0.672201000	-2.748249000
6	-3.319791000	-1.470924000	-0.997247000
1	-3.269349000	-2.281228000	-1.717018000
6	-4.296744000	-1.443194000	0.005404000
1	-0.312691000	3.434529000	-0.181279000
6	-1.238321000	2.961554000	0.154960000
1	-1.226883000	2.928485000	1.247821000
1	-2.080018000	3.592779000	-0.152533000
6	-4.356171000	-0.396416000	0.940548000
1	-3.498510000	1.469347000	1.625694000
1	-5.131033000	-0.408656000	1.699993000
1	-5.025518000	-2.245367000	0.055774000

Ir(V)

7	1.106709000	-1.126448000	0.778027000
6	0.685079000	1.602363000	0.608716000
6	-2.393982000	-0.335765000	0.815512000
77	-0.359821000	0.053940000	0.108395000
6	-2.030043000	0.659812000	-1.248098000
6	-2.239313000	-1.418250000	-0.165736000
6	-1.989192000	-0.823932000	-1.410139000
6	-2.313079000	-2.876364000	0.159546000
6	-2.395504000	0.946449000	0.093706000
6	-2.767526000	-0.517377000	2.244274000
6	-2.738812000	2.274024000	0.685871000
6	-1.925930000	1.625477000	-2.383960000
6	-1.729623000	-1.496779000	-2.713114000
1	-3.860250000	-0.620604000	2.306186000
1	-2.327475000	-1.420306000	2.670956000
1	-2.480729000	0.341326000	2.853157000
1	-3.828861000	2.395123000	0.682870000
1	-2.402609000	2.356876000	1.721763000
1	-2.311550000	3.096978000	0.110826000
1	-2.873735000	1.644046000	-2.935736000
1	-1.722844000	2.639024000	-2.034793000
1	-1.141542000	1.335728000	-3.086664000
1	-3.363086000	-3.186747000	0.220415000
1	-1.860350000	-3.098885000	1.129590000
1	-1.829405000	-3.491045000	-0.601013000
1	-1.530793000	-2.562584000	-2.597284000
1	-2.610690000	-1.386201000	-3.358667000
1	-0.891052000	-1.033251000	-3.240787000
1	0.234434000	2.499805000	1.033704000
6	2.048429000	1.662694000	0.281079000
6	2.810650000	0.475006000	0.027638000
6	4.160406000	0.583157000	-0.406498000
6	2.349916000	-0.905941000	0.393862000
1	0.932375000	-2.045408000	1.183286000
6	3.302792000	-1.996122000	0.398077000
1	2.954056000	-2.978622000	0.703093000
6	4.583862000	-1.802149000	-0.009689000
1	2.082695000	3.784619000	0.662986000
6	2.748252000	3.004281000	0.291265000
1	3.050910000	3.292658000	-0.722672000

1	3.645793000	2.991299000	0.917040000
6	5.007461000	-0.499235000	-0.445286000
1	4.536719000	1.548943000	-0.717950000
1	6.025181000	-0.369869000	-0.801057000
1	5.289302000	-2.626479000	-0.025276000

TS-RE(V/III)

7	-1.268842000	-0.869432000	-0.993425000
6	-0.896476000	1.198625000	-1.040683000
6	2.746607000	0.471945000	-0.193353000
77	0.563120000	0.134488000	-0.372602000
6	1.444827000	-0.352753000	1.556102000
6	2.584602000	-0.981849000	-0.370535000
6	1.801642000	-1.481582000	0.700207000
6	3.163714000	-1.754302000	-1.505342000
6	2.091983000	0.848119000	1.022585000
6	3.571825000	1.348373000	-1.074566000
6	2.107996000	2.190626000	1.676735000
6	0.693775000	-0.437899000	2.836992000
6	1.381072000	-2.896777000	0.934646000
1	4.628377000	1.239592000	-0.797163000
1	3.477748000	1.068280000	-2.125884000
1	3.304443000	2.400276000	-0.966871000
1	2.934367000	2.225414000	2.397515000
1	2.262045000	2.991079000	0.951948000
1	1.182958000	2.385415000	2.222262000
1	1.406538000	-0.646923000	3.646891000
1	0.190964000	0.501056000	3.074590000
1	-0.039481000	-1.245943000	2.825201000
1	4.234428000	-1.910200000	-1.319385000
1	3.077556000	-1.208389000	-2.448219000
1	2.699424000	-2.734269000	-1.619334000
1	1.439558000	-3.495204000	0.024478000
1	2.043132000	-3.355927000	1.678153000
1	0.361692000	-2.951666000	1.323301000
1	-0.830082000	1.439411000	-2.114053000
6	-2.126423000	1.561102000	-0.375044000
6	-2.995266000	0.528545000	-0.078633000
6	-4.297976000	0.672822000	0.509737000
6	-2.540386000	-0.774363000	-0.534326000
1	-1.071730000	-1.698867000	-1.547052000
6	-3.445033000	-1.856609000	-0.509910000
1	-3.146350000	-2.829960000	-0.885719000
6	-4.702644000	-1.665162000	0.032497000
1	-1.417149000	3.596350000	-0.166467000
6	-2.344663000	3.022834000	-0.109729000
1	-2.796568000	3.174918000	0.873863000
1	-3.035054000	3.423273000	-0.863833000
6	-5.131889000	-0.408629000	0.560746000
1	-4.617492000	1.641364000	0.878489000
1	-6.126597000	-0.321493000	0.983079000
1	-5.389034000	-2.506349000	0.068732000

Ir(III)-PDT

7	-1.604075000	-0.896004000	-1.748983000
6	-1.047575000	0.323920000	-2.195568000
6	1.946494000	0.641419000	0.193629000
77	-0.026862000	-0.179312000	-0.266951000
6	0.867459000	-0.842960000	1.667192000
6	2.111341000	-0.708340000	-0.314842000
6	1.459039000	-1.619701000	0.613205000
6	2.927495000	-1.103886000	-1.501336000
6	1.149083000	0.561467000	1.403156000
6	2.545584000	1.880547000	-0.384915000
6	0.770603000	1.702279000	2.290103000
6	0.108740000	-1.363310000	2.843592000
6	1.448292000	-3.108786000	0.501135000
1	3.530546000	2.045040000	0.069151000
1	2.687234000	1.797731000	-1.463704000
1	1.935555000	2.761366000	-0.177087000
1	1.517537000	1.804219000	3.086580000
1	0.738100000	2.646196000	1.743525000
1	-0.199557000	1.536311000	2.762709000
1	0.782134000	-1.435892000	3.706298000
1	-0.709865000	-0.694540000	3.118774000
1	-0.301456000	-2.356461000	2.655939000
1	3.961510000	-1.281640000	-1.180499000
1	2.946862000	-0.319491000	-2.259715000
1	2.561604000	-2.024643000	-1.958924000
1	1.485776000	-3.439366000	-0.538362000
1	2.336892000	-3.508836000	1.005257000
1	0.571929000	-3.548490000	0.980085000
1	-0.540046000	0.386724000	-3.148305000
6	-1.420726000	1.351324000	-1.294732000
6	-2.259444000	0.728347000	-0.282000000
6	-2.943953000	1.241144000	0.853781000
6	-2.400304000	-0.663952000	-0.607387000
1	-1.600070000	-1.757171000	-2.288592000
6	-3.204362000	-1.546827000	0.134862000
1	-3.314919000	-2.589291000	-0.142937000
6	-3.863383000	-1.000503000	1.219889000
1	-0.254215000	2.979303000	-2.072924000
6	-1.130275000	2.810513000	-1.443732000
1	-0.961903000	3.278231000	-0.470989000
1	-1.986747000	3.307935000	-1.912211000
6	-3.731308000	0.374187000	1.578448000
1	-2.870257000	2.292418000	1.109129000
1	-4.286464000	0.742734000	2.434839000
1	-4.512965000	-1.634331000	1.815164000

Ir(V)$_{\text{triplet}}$

7	1.191729000	-1.174417000	-0.116469000
6	0.727859000	1.490409000	0.363063000
6	-2.218359000	-0.229039000	0.783709000
77	-0.363362000	0.042029000	-0.340983000
6	-2.312577000	0.621580000	-1.368481000

6	-2.231466000	-1.372339000	-0.150057000
6	-2.302953000	-0.853916000	-1.457538000
6	-2.226381000	-2.808445000	0.266882000
6	-2.359587000	0.997128000	0.007691000
6	-2.303310000	-0.338489000	2.266737000
6	-2.585396000	2.367716000	0.562002000
6	-2.423723000	1.530222000	-2.546595000
6	-2.352676000	-1.609686000	-2.740926000
1	-3.357453000	-0.466646000	2.548357000
1	-1.753342000	-1.202905000	2.642829000
1	-1.933563000	0.559997000	2.762759000
1	-3.660825000	2.534860000	0.690887000
1	-2.116786000	2.492025000	1.540692000
1	-2.207550000	3.143100000	-0.107118000
1	-3.466382000	1.545467000	-2.890491000
1	-2.139223000	2.553825000	-2.299929000
1	-1.809738000	1.185693000	-3.381909000
1	-3.240353000	-3.111339000	0.554743000
1	-1.584226000	-2.973683000	1.135822000
1	-1.903046000	-3.467906000	-0.540392000
1	-2.107763000	-2.664282000	-2.610540000
1	-3.367393000	-1.551047000	-3.156346000
1	-1.679657000	-1.178728000	-3.487692000
1	0.207642000	2.373394000	0.739509000
6	2.130433000	1.591253000	0.355282000
6	3.002365000	0.442065000	0.241031000
6	4.393167000	0.593332000	0.370236000
6	2.498817000	-0.914755000	0.060205000
1	0.999317000	-2.174337000	-0.168265000
6	3.417310000	-2.010418000	0.046629000
1	3.028116000	-3.016400000	-0.085676000
6	4.777325000	-1.806289000	0.180448000
1	1.955751000	3.740445000	0.458059000
6	2.726286000	2.969245000	0.481541000
1	3.439275000	3.175401000	-0.322908000
1	3.264448000	3.066374000	1.434342000
6	5.271431000	-0.497323000	0.337044000
1	4.815208000	1.579802000	0.515534000
1	6.338374000	-0.327784000	0.439531000
1	5.459460000	-2.649924000	0.164169000

TS-RE(V/III)$_{\text{triplet}}$

7	-1.280040000	-0.824020000	-1.298802000
6	-0.816824000	1.065264000	-1.465241000
6	2.513522000	0.523921000	-0.112404000
77	0.350415000	0.083408000	-0.227342000
6	1.485925000	-0.460228000	1.772393000
6	2.338013000	-0.906159000	-0.348154000
6	1.730884000	-1.498623000	0.838338000
6	2.857522000	-1.657388000	-1.525718000
6	1.901154000	0.808070000	1.160324000
6	3.270627000	1.473770000	-0.980824000
6	1.876437000	2.135521000	1.847122000
6	0.893611000	-0.596103000	3.133150000
6	1.456860000	-2.956164000	1.026894000
1	4.331973000	1.446880000	-0.703443000
1	3.197110000	1.206249000	-2.036529000
1	2.921557000	2.500070000	-0.856425000
1	2.762949000	2.229159000	2.486724000
1	1.892744000	2.959454000	1.131980000
1	0.997262000	2.243578000	2.485555000
1	1.701074000	-0.619823000	3.876996000
1	0.253492000	0.253392000	3.381908000
1	0.317383000	-1.516117000	3.241135000
1	3.894351000	-1.958800000	-1.322994000
1	2.864864000	-1.043666000	-2.428329000
1	2.286313000	-2.567818000	-1.716347000
1	1.199420000	-3.445636000	0.085320000
1	2.357566000	-3.448563000	1.413292000
1	0.651338000	-3.130486000	1.741934000
1	-0.583595000	1.457978000	-2.457113000
6	-1.874019000	1.523431000	-0.631154000
6	-2.812731000	0.519915000	-0.180479000
6	-3.995572000	0.707377000	0.525916000
6	-2.521024000	-0.774952000	-0.738634000
1	-1.081650000	-1.561683000	-1.973540000
6	-3.451965000	-1.832584000	-0.670032000
1	-3.234568000	-2.792468000	-1.127865000
6	-4.627604000	-1.621741000	0.041281000
1	-1.276944000	3.588526000	-0.862104000
6	-2.080598000	2.994134000	-0.424644000
1	-2.142014000	3.228086000	0.643442000
1	-3.029663000	3.298116000	-0.884351000
6	-4.893494000	-0.373022000	0.643466000
1	-4.250537000	1.674923000	0.944942000
1	-5.824455000	-0.231691000	1.183378000
1	-5.351809000	-2.424130000	0.133599000

Ir(III)-PDT$_{\text{triplet}}$

7	-1.780497000	-1.216645000	-0.733196000
6	-1.025190000	-0.280600000	-1.506877000
6	1.938366000	0.697620000	0.392547000
77	-0.056653000	-0.324194000	0.385299000
6	1.501924000	-1.108560000	1.787624000
6	2.323417000	-0.517246000	-0.323292000
6	2.011199000	-1.622685000	0.512511000
6	2.894710000	-0.569747000	-1.698871000
6	1.515255000	0.341074000	1.738599000
6	2.168380000	2.092747000	-0.085562000
6	1.324928000	1.281892000	2.889032000
6	1.205644000	-1.940676000	2.991376000
6	2.211875000	-3.065488000	0.198220000
1	3.179746000	2.405935000	0.204745000
1	2.100319000	2.172586000	-1.171985000
1	1.465962000	2.794314000	0.368133000
1	2.284372000	1.435925000	3.397475000
1	0.963320000	2.256722000	2.557074000
1	0.619223000	0.885934000	3.621519000

1	2.141783000	-2.123317000	3.537297000
1	0.520485000	-1.437257000	3.675451000
1	0.788636000	-2.913930000	2.724755000
1	3.988659000	-0.491798000	-1.644924000
1	2.548484000	0.260886000	-2.318110000
1	2.663040000	-1.508491000	-2.206085000
1	2.233816000	-3.255518000	-0.876022000
1	3.175695000	-3.391869000	0.611231000
1	1.441481000	-3.691313000	0.654342000
1	-0.453374000	-0.608598000	-2.368084000
6	-1.631347000	1.008934000	-1.330650000
6	-2.821291000	0.831399000	-0.560466000
6	-3.812497000	1.741623000	-0.133098000
6	-2.955833000	-0.552493000	-0.251405000
1	-1.808851000	-2.201257000	-0.986630000
6	-4.023238000	-1.063706000	0.450433000
1	-4.118626000	-2.118272000	0.686332000
6	-5.013510000	-0.137688000	0.841768000
1	-0.128485000	2.171516000	-2.334172000
6	-1.148592000	2.266791000	-1.959155000
1	-1.201138000	3.108012000	-1.262411000
1	-1.798614000	2.512255000	-2.809957000
6	-4.906514000	1.238507000	0.560268000
1	-3.729744000	2.799278000	-0.359857000
1	-5.694549000	1.908482000	0.886427000
1	-5.883099000	-0.501462000	1.380098000