Electronic Supplementary Information

Organocatalytic Atroposelective Synthesis of Axially Chiral *N*, *N*'-Pyrrolylindoles by *De Novo* Indole Formation

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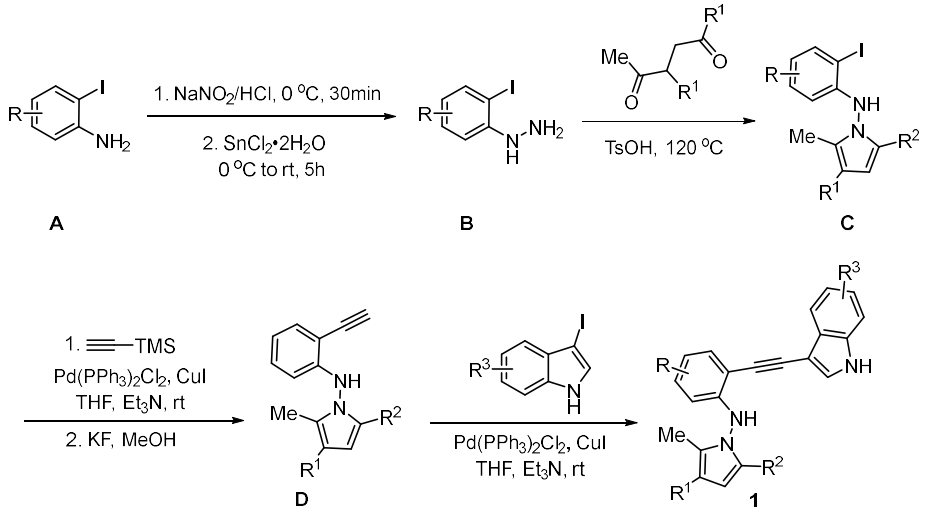
1. General remarks

^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. ^{13}C NMR spectra were recorded on a Bruker 100 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. ^{19}F NMR spectra were recorded on a Bruker 376 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal CF_3COOH signal at -76.55 ppm. The data are reported as follows: (s = single, d = double, t = triple, q = quartet, m = multiple or unresolved, brs = broad single, coupling constant(s) in Hz, integration). High resolution mass spectra (HR-MS) were recorded on a LTQ-Orbitrap Elite mass spectrometer with MeOH as solvent mixture for the measurements. Commercially obtained reagents were used without further purification. Solvents were purified prior to use according to the standard methods. Enantiomeric ratios were determined by chiral-phase HPLC analysis in comparison with authentic racemic materials. Optical rotations were measured on an Rudolph Research Analytical Autopol VI polarimeter with $[\alpha]_D$ values reported in degrees; concentration (c) is in g/100 mL. UV-Vis absorption spectra were recorded on a Shimadzu UV-2501 recording spectrophotometer with the baseline correction.

2. General procedure for synthesis of 2-alkynylanilines 1



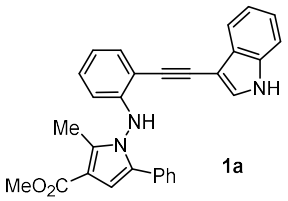
General procedure for synthesis of **B**:[1] To a stirred solution of 2-Iodoaniline **A** (17.4 mmol) in concentrated aq. HCl (34 mL) at 0 °C a solution of sodium nitrite (1.20 g, 17.4 mmol) in

H_2O (12 mL) was added over a period of 30 minutes. The reaction mixture was stirred for a further 30 minutes then added dropwise to a solution of tin chloride hydrate (5.90 g, 26.1 mmol) in concentrated aq. HCl (30 mL) at 0 °C. After the addition is complete, the reaction was stirred at room temperature for 5 hours. Then the reaction was basified with 40% aqueous NaOH at 0 °C until the pH was 13. The mixture was then extracted with DCM (100 mL × 3) and water (100 mL). The organic phase was separated and dried over Na_2SO_4 and concentrated in vacuo. The crude product was further purified by column chromatography to afford the compounds **B**.

General procedure for synthesis of **C**:[2] To a solution of 1, 4-diketone (15 mmol) in toluene (80 mL) was added the (2-iodophenyl)hydrazine **B** (15 mmol) and *p*-toluenesulfonic acid (TsOH, 5 mol%). The resulting mixture was heated at 120 ℃ for 12 h. The solvent was evaporated under reduced pressure and the residue purified by silica gel column chromatography to afford the compounds **C**.

General procedure for synthesis of **D**:[3] To a solution of $(Ph_3P)_2PdCl_2$ (0.36 g, 0.5mmol) and CuI (0.19 g, 1.0 mmol) in Et_3N (30 mL) were added *N*-(2-iodophenyl)-1H-pyrrol-1-amine **C** (10 mmol) and trimethylsilylacetylene (1.41 mL, 10 mmol) at room temperature. After stirring for 12 h at room temperature, the mixture was poured into saturated NH_4Cl aq. and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, then concentrated under reduced pressure to afford crude product. The crude product is dissolved in MeOH (50 mL), $KF·2H_2O$ (1.13 g, 12 mmol) was added and mixture was stirred for 12 h at room temperature. After the completion of the reaction which was indicated by TLC, the solvent was evaporated and the residue was diluted with Et_2O and brine. The organic layer was separated, dried over Na_2SO_4, and concentrated under reduced pressure to give a crude product, which was purified by column chromatography to afford the compounds **D**.

General procedure for synthesis of **1**:[3] To a solution of $(Ph_3P)_2PdCl_2$ (70 mg, 0.1 mmol) and CuI (38 mg, 0.2 mmol) in Et_3N (102 mL) were added 3-iodoindole[4] (5.0 mmol) and *N*-(2-ethynylphenyl)-1H-pyrrol-1-amine **D** (5.0 mmol) at room temperature. After being stirred for 12 h at room temperature, the mixture was poured into saturated NH_4Cl aq. and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over Na_2SO_4, then concentrated under reduced pressure to afford product **1**.



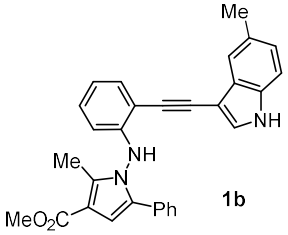
1a

methyl 1-((2-((1*H*-indol-3-yl)ethynyl)phenyl)amino)-2-methyl-5-phenyl-1*H*-pyrr-ole-3-carboxylate (**1a**): 50% yield (1.11 g); Brown solid; m.p. 183-185 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.29 (m, 6H), 7.25 – 7.18 (m, 3H), 7.17 – 7.10 (m, 2H), 7.10 – 7.01 (m, 1H), 6.86 – 6.75 (m, 1H), 6.71 (s, 1H), 6.11 (d, *J* = 8.2 Hz, 1H), 3.78 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 146.9, 138.5, 135.2, 133.3, 132.0, 130.9, 129.6, 128.4, 128.2, 128.0, 127.7, 127.3, 123.3, 121.0, 120.6, 119.7, 111.5, 111.4, 110.6, 108.3, 107.7, 98.1, 90.0, 85.4, 51.0, 10.8.

HRMS (ESI+) Calcd. For $C_{29}H_{24}N_3O_2^+$ ($[M+H]^+$): 446.1863, found: 446.1867.



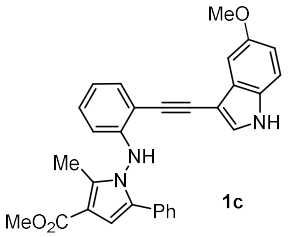
1b

methyl 2-methyl-1-((2-((5-methyl-1*H*-indol-3-yl)ethynyl)phenyl)amino)-5-phenyl-1*H*-pyrrole-3-carboxylate (**1b**): 53% yield (1.21 g); Brown solid; m.p. 189-191 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.56 – 7.37 (m, 6H), 7.34 – 7.26 (m, 3H), 7.24 – 7.18 (m, 1H), 7.17 – 7.06 (m, 2H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.79 (s, 1H), 6.17 (d, *J* = 8.2 Hz, 1H), 3.85 (s, 3H), 2.50 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 146.9, 138.5, 133.5, 133.3, 132.0, 130.9, 130.5, 129.5, 128.5, 128.4, 128.1, 127.6, 127.3, 125.0, 120.6, 119.3, 111.3, 111.2, 110.6, 108.4, 107.7, 97.5, 90.3, 85.3, 51.0, 21.5, 10.8.

HRMS (ESI+) Calcd. For $C_{30}H_{26}N_3O_2^+$ ($[M+H]^+$): 460.2019, found: 460.2016.



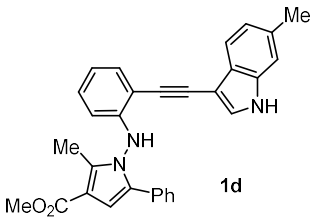
1c

methyl 1-((2-((5-methoxy-1*H*-indol-3-yl)ethynyl)phenyl)amino)-2-methyl-5-phen-yl-1*H*-pyrrole-3-carboxylate (**1c**): 47% yield (1.12 g); Brown solid; m.p. 168-170 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.44 – 7.33 (m, 5H), 7.25 – 7.18 (m, 3H), 7.16 – 7.12 (m, 1H), 7.09 – 7.02 (m, 2H), 6.86 – 6.76 (m, 2H), 6.71 (s, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 155.2, 146.9, 138.4, 133.3, 132.0, 130.9, 130.2, 129.6, 128.9, 128.5, 128.4, 127.6, 127.2, 120.6, 113.8, 112.4, 111.4, 110.7, 108.4, 107.7, 101.0, 97.7, 90.2, 85.5, 55.7, 51.0, 10.7.

HRMS (ESI+) Calcd. For $C_{30}H_{26}N_3O_3^+$ ($[M+H]^+$): 476.1968, found: 476.1969.



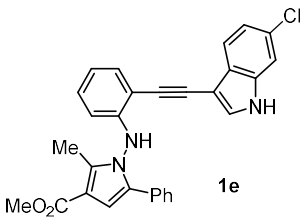
1d

methyl 2-methyl-1-((2-((6-methyl-1*H*-indol-3-yl)ethynyl)phenyl)amino)-5-phenyl-1*H*-pyrrole-3-carboxylate (**1d**): 50% yield (1.15 g); Brown solid; m.p. 189-191 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.49 – 7.37 (m, 5H), 7.33 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.17 (s, 1H), 7.15 – 7.08 (m, 1H), 7.06 – 6.99 (m, 1H), 6.89 – 6.82 (m, 1H), 6.78 (s, 1H), 3.85 (s, 3H), 2.50 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 146.9, 138.5, 135.6, 133.29, 133.27, 131.9, 130.8, 129.5, 129.4, 127.7, 127.5, 127.3, 126.1, 122.8, 120.6, 119.3, 111.4, 111.3, 110.6, 108.4, 107.7, 97.8, 90.3, 85.2, 51.0, 21.7, 10.8.

HRMS (ESI+) Calcd. For $C_{30}H_{26}N_3O_2^+$ ($[M+H]^+$): 460.2019, found: 460.2018.



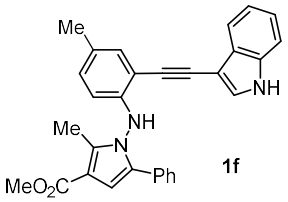
1e

methyl 1-((2-((6-chloro-1*H*-indol-3-yl)ethynyl)phenyl)amino)-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (**1e**): 52% yield (1.25 g); Brown solid; m.p. 193-195 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.47 – 7.42 (m, 4H), 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.21 (m, 1H), 7.19 – 7.11 (m, 2H), 6.93 – 6.83 (m, 1H), 6.78 (s, 1H), 3.85 (s, 3H), 2.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 147.0, 138.4, 135.5, 133.3, 132.1, 130.9, 129.8, 129.3, 128.6, 128.5, 127.7, 127.4, 126.8, 121.8, 120.7, 120.6, 111.5, 111.4, 110.7, 108.0, 107.8, 98.4, 89.3, 85.8, 51.0, 10.8.

HRMS (ESI+) Calcd. For $C_{29}H_{22}N_3O_2ClNa^+$ ($[M+Na]^+$): 502.1299, found: 502.1295.



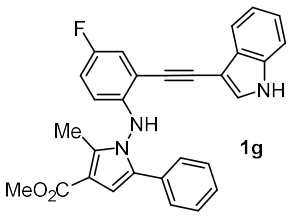
1f

methyl 1-((2-((1*H*-indol-3-yl)ethynyl)-4-methylphenyl)amino)-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (**1f**): 49% yield (1.12 g); Brown solid; m.p. 137-139 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.25 (m, 5H), 7.22 – 7.16 (m, 2H), 6.97 – 6.90 (m, 1H), 6.78 (s, 1H), 6.10 (d, *J* = 8.3 Hz, 1H), 3.85 (s, 3H), 2.49 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 144.7, 138.5, 135.2, 133.3, 132.3, 131.0, 130.3, 130.0, 128.4, 128.3, 128.0, 127.7, 127.3, 123.3, 121.0, 119.7, 111.5, 110.5, 108.2, 107.6, 98.1, 89.7, 85.6, 51.0, 20.4, 10.8.

HRMS (ESI+) Calcd. For $C_{30}H_{26}N_3O_2^+$ ($[M+H]^+$): 460.2019, found: 460.2018.



1g

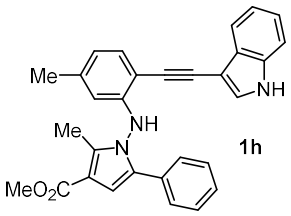
methyl 1-((2-((1*H*-indol-3-yl)ethynyl)-4-fluorophenyl)amino)-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (**1g**): 55% yield (1.27 g); Brown solid; m.p. 123-125 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.57 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.42 (d, *J* = 2.7 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.26 – 7.19 (m, 4H), 7.16 – 7.12 (m, 2H), 7.07 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.81 – 6.72 (m, 1H), 6.70 (s, 1H), 6.01 (dd, *J* = 9.0, 4.7 Hz, 1H), 3.78 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 156.8 (d, *J* = 239.5 Hz), 143.4, 138.3, 135.2, 133.2, 130.8, 128.5, 128.4, 128.2, 127.7, 127.4, 123.4, 121.2, 119.6, 118.1 (d, *J* = 24.1 Hz), 116.5 (d, *J* = 22.8 Hz), 112.7, 111.6, 110.7, 109.4 (d, *J* = 9.5 Hz), 107.8, 97.6, 91.1, 84.6, 51.0, 10.8.

^{19}F NMR (376 MHz, CDCl3) δ -123.4 – -123.5 (m, 1F).

HRMS (ESI+) Calcd. For $C_{29}H_{22}N_3O_2FNa^+$ ($[M+Na]^+$): 486.1588, found: 486.1592.



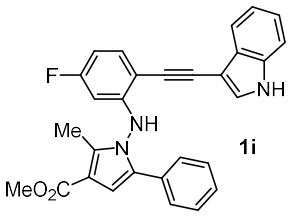
1h

methyl 1-((2-((1*H*-indol-3-yl)ethynyl)-5-methylphenyl)amino)-2-methyl-5-phenyl-1H-pyrrole-3-carboxylate (**1h**): 50% yield (1.15 g); Brown solid; m.p. 143-145 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.57 – 7.52 (m, 1H), 7.43 – 7.38 (m, 2H), 7.36 (d, *J* = 2.7 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.26 – 7.19 (m, 3H), 7.19 – 7.13 (m, 3H), 7.12 – 7.07 (m, 1H), 6.71 (s, 1H), 6.64 – 6.58 (m, 1H), 5.96 – 5.90 (m, 1H), 3.78 (s, 3H), 2.42 (s, 3H), 2.13 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 146.9, 138.4, 134.8, 133.3, 131.9, 130.9, 129.5, 128.4, 127.9, 127.7, 127.3, 123.9, 121.2, 120.8, 120.6, 117.3, 111.3, 110.6, 108.4, 107.7, 98.5, 90.2, 85.4, 51.0, 16.5, 10.8.

HRMS (ESI+) Calcd. For $C_{30}H_{26}N_3O_2^+$ ($[M+H]^+$): 460.2019, found: 460.2016.



1i

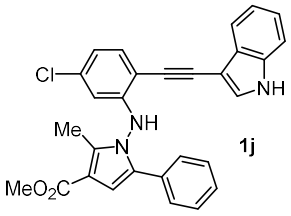
methyl 1-((2-((1*H*-indol-3-yl)ethynyl)-5-fluorophenyl)amino)-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (**1i**): 47% yield (1.09 g); Brown solid; m.p. 121-123 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.56 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.41 – 7.35 (m, 4H), 7.35 – 7.30 (m, 2H), 7.23 – 7.21 (m, 1H), 7.20 – 7.16 (m, 3H), 7.16 – 7.10 (m, 1H), 6.71 (s, 1H), 6.52 – 6.45 (m, 1H), 5.79 (dd, *J* = 10.3, 2.5 Hz, 1H), 3.78 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 163.7 (d, *J* = 248.7 Hz), 148.8 (d, *J* = 10.5 Hz), 138.1, 135.2, 133.6 (d, *J* = 9.7 Hz), 133.1, 130.7, 128.5, 128.1, 127.7, 127.5, 123.4, 121.1, 119.6, 111.6, 110.9, 108.0, 107.7 (d, *J* = 22.3 Hz), 104.2 (d, *J* = 2.9 Hz), 99.1 (d, *J* = 27.5 Hz), 97.9, 89.6, 84.4, 51.1, 10.7.

^{19}F NMR (376 MHz, CDCl3) δ -108.1 – -108.3 (m, 1F).

HRMS (ESI+) Calcd. For $C_{29}H_{22}N_3O_2FNa^+$ ([M+Na]$^+$): 486.1588, found: 486.1590.



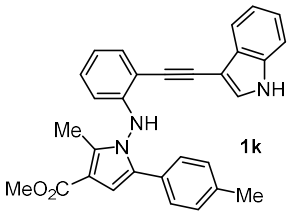
1j

methyl 1-((2-((1*H*-indol-3-yl)ethynyl)-5-chlorophenyl)amino)-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (**1j**): 43% yield (1.03 g); Brown solid; m.p. 172-174 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.59 – 7.52 (m, 1H), 7.40 (d, *J* = 2.7 Hz, 1H), 7.39 – 7.31 (m, 4H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.20 – 7.10 (m, 4H), 6.76 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.71 (s, 1H), 6.07 (d, *J* = 2.1 Hz, 1H), 3.79 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 147.8, 138.1, 135.5, 135.2, 133.0, 132.9, 130.6, 128.5, 128.20, 128.16, 127.7, 127.5, 123.4, 121.1, 120.9, 119.6, 111.6, 111.3, 110.9, 108.0, 106.8, 97.8, 91.0, 84.5, 51.1, 10.8.

HRMS (ESI+) Calcd. For $C_{29}H_{22}N_3O_2ClNa^+$ ([M+Na]$^+$): 502.1292, found: 502.1295.

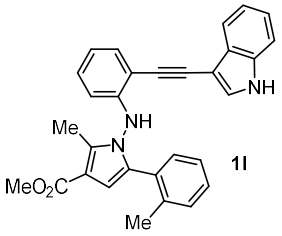


methyl 1-((2-((1*H*-indol-3-yl)ethynyl)phenyl)amino)-2-methyl-5-(p-tolyl)-1*H*-pyr-role-3-carboxylate (**1k**): 50% yield (1.15 g); Brown solid; m.p. 113-115 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.41 – 7.33 (m, 4H), 7.29 – 7.25 (m, 1H), 7.22 – 7.17 (m, 1H), 7.15 – 7.08 (m, 3H), 6.91 – 6.82 (m, 1H), 6.74 (s, 1H), 6.25 – 6.11 (m, 1H), 3.85 (s, 3H), 2.49 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 147.0, 138.2, 137.1, 135.2, 133.4, 131.9, 129.6, 129.2, 128.3, 128.03, 128.00, 127.6, 123.3, 121.0, 120.6, 119.7, 111.5, 111.3, 110.5, 108.2, 107.2, 98.1, 90.0, 85.5, 51.0, 21.1, 10.8.

HRMS (ESI+) Calcd. For $C_{30}H_{26}N_3O_2^+$ ([M+H]$^+$): 460.2019, found: 460.2020.

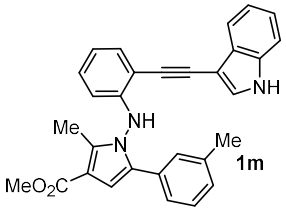


methyl 1-((2-((1*H*-indol-3-yl)ethynyl)phenyl)amino)-2-methyl-5-(*o*-tolyl)-1*H*-pyrrole-3-carboxylate (**1l**): 51% yield (1.17 g); Brown solid; m.p. 103-105 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.69 – 7.56 (m, 1H), 7.39 (d, *J* = 2.7 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.21 – 7.16 (m, 4H), 7.11 – 6.92 (m, 5H), 6.76 – 6.68 (m, 1H), 6.52 (s, 1H), 6.03 – 5.97 (m, 1H), 3.78 (s, 3H), 2.50 (s, 3H), 2.13 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 147.2, 137.6, 135.2, 132.0, 131.5, 130.8, 130.2, 130.0, 129.1, 128.3, 128.2, 127.9, 125.4, 123.3, 120.9, 120.6, 119.7, 111.6, 109.8, 108.8, 108.4, 98.2, 89.6, 85.2, 51.0, 20.2, 10.9.

HRMS (ESI+) Calcd. For $C_{30}H_{26}N_3O_2^+$ ([M+H]$^+$): 460.2019, found: 460.2017.

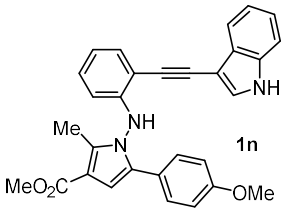


methyl 1-((2-((1*H*-indol-3-yl)ethynyl)phenyl)amino)-2-methyl-5-(*m*-tolyl)-1*H*-pyrrole-3-carboxylate (**1m**): 52% yield (1.19 g); Brown solid; m.p. 117-119 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.66 – 7.59 (m, 1H), 7.49 – 7.35 (m, 4H), 7.26 – 7.23 (m, 3H), 7.22 – 7.16 (m, 2H), 7.16 – 7.09 (m, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.91 – 6.81 (m, 1H), 6.77 (s, 1H), 6.19 – 6.13 (m, 1H), 3.85 (s, 3H), 2.52 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 147.0, 138.5, 138.0, 135.2, 133.3, 131.9, 130.7, 129.5, 128.5, 128.3, 128.2, 128.1, 128.0, 124.8, 123.3, 121.0, 120.6, 119.7, 111.5, 111.4, 110.4, 108.3, 107.7, 98.1, 90.0, 85.4, 51.0, 21.4, 10.8.

HRMS (ESI+) Calcd. For $C_{30}H_{26}N_3O_2^+$ ($[M+H]^+$): 460.2019, found: 460.2022.

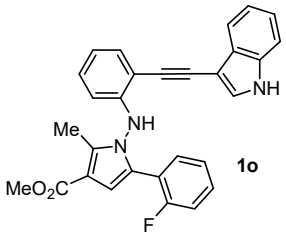


methyl 1-((2-((1*H*-indol-3-yl)ethynyl)phenyl)amino)-5-(4-methoxyphenyl)-2-met-hyl-1*H*-pyrrole-3-carboxylate (**1n**): 57% yield (1.35 g); Brown solid; m.p.114-116 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.67 – 7.61 (m, 1H), 7.48 – 7.43 (m, 2H), 7.42 – 7.34 (m, 4H), 7.30 – 7.25 (m, 1H), 7.23 – 7.17 (m, 1H), 7.17 – 7.10 (m, 1H), 6.92 – 6.79 (m, 3H), 6.69 (s, 1H), 6.18 (d, *J* = 8.1 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 2.49 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 159.0, 147.0, 137.9, 135.2, 133.2, 132.0, 129.6, 129.1, 128.3, 128.0, 123.5, 123.3, 121.0, 120.6, 119.7, 113.9, 111.5, 111.3, 110.4, 108.3, 106.8, 98.1, 90.0, 85.5, 55.2, 51.0, 10.8.

HRMS (ESI+) Calcd. For $C_{30}H_{26}N_3O_3^+$ ($[M+H]^+$): 476.1968, found: 476.1970.



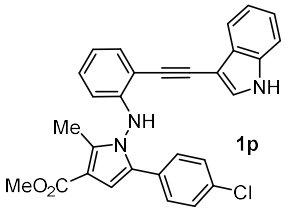
methyl 1-((2-((1*H*-indol-3-yl)ethynyl)phenyl)amino)-5-(2-fluorophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (**1o**): 49% yield (1.13 g); Brown solid; m.p. 123-125 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.84 – 7.77 (m, 1H), 7.60 (d, *J* = 4.2 Hz, 1H), 7.54 (d, *J* = 2.6 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.33 – 7.27 (m, 3H), 7.25 – 7.16 (m, 2H), 7.08 – 6.96 (m, 3H), 6.79 – 6.71 (m, 2H), 5.93 (dd, *J* = 8.3, 1.1 Hz, 1H), 3.86 (s, 3H), 2.57 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 159.8 (d, *J* = 245.7 Hz), 146.9, 139.2, 135.3, 131.5, 131.3 (d, *J* = 3.0 Hz), 129.7 (d, *J* = 8.6 Hz), 129.1, 128.2, 128.1, 127.6, 124.3 (d, *J* = 3.5 Hz), 123.3, 121.0, 120.4, 119.9, 119.0 (d, *J* = 14.0 Hz), 115.7 (d, *J* = 22.7 Hz), 111.5, 110.9, 110.5, 109.6, 108.2, 98.3, 89.8, 85.2, 51.0, 10.9.

^{19}F NMR (376 MHz, CDCl3) δ -113.8 – -114.0 (m, 1F).

HRMS (ESI+) Calcd. For $C_{29}H_{22}N_3O_2FNa^+$ ([M+Na]$^+$): 486.1588, found: 486.1591.

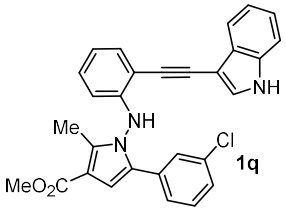


methyl 1-((2-((1*H*-indol-3-yl)ethynyl)phenyl)amino)-5-(4-chlorophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (**1p**): 45% yield (1.08 g); Brown solid; m.p. 123-125 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.44 – 7.36 (m, 4H), 7.27 – 7.19 (m, 4H), 7.17 – 7.07 (m, 1H), 6.93 – 6.84 (m, 1H), 6.77 (s, 1H), 6.20 – 6.10 (m, 1H), 3.85 (s, 3H), 2.49 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 146.7, 138.7, 135.2, 133.2, 132.13, 132.10, 129.6, 129.4, 128.8, 128.6, 128.2, 128.1, 123.4, 121.1, 120.8, 119.6, 111.6, 111.3, 110.8, 108.4, 107.9, 98.0, 90.2, 85.3, 51.1, 10.8.

HRMS (ESI+) Calcd. For $C_{29}H_{23}N_3O_2^+$ ([M+H]$^+$): 481.1551, found: 484.1554.

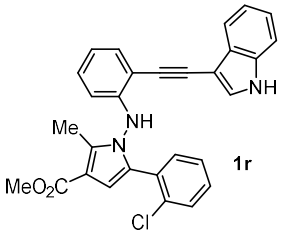


methyl 1-((2-((1*H*-indol-3-yl)ethynyl)phenyl)amino)-5-(3-chlorophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (**1q**): 42% yield (1.01 g); Brown solid; m.p. 119-121 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.73 – 7.64 (m, 1H), 7.50 (d, *J* = 2.6 Hz, 2H), 7.47 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.43 – 7.34 (m, 3H), 7.30 – 7.27 (m, 1H), 7.24 – 7.17 (m, 3H), 7.16 – 7.11 (m, 1H), 6.94 – 6.85 (m, 1H), 6.80 (s, 1H), 6.19 – 6.06 (m, 1H), 3.85 (s, 3H), 2.49 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 146.7, 139.0, 135.2, 134.2, 132.6, 132.1, 131.8, 129.7, 129.6, 128.2, 128.1, 127.6, 127.3, 125.5, 123.4, 121.1, 120.9, 119.7, 111.5, 111.3, 110.9, 108.5, 108.4, 98.0, 90.2, 85.3, 51.1, 10.8.

HRMS (ESI+) Calcd. For $C_{29}H_{22}N_3O_2ClNa^+$ ($[M+Na]^+$): 502.1292, found: 502.1290.

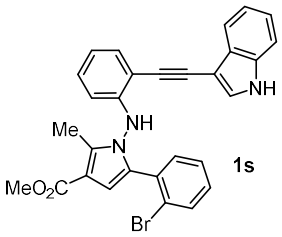


methyl 1-((2-((1*H*-indol-3-yl)ethynyl)phenyl)amino)-5-(2-chlorophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (**1r**): 40% yield (0.96 g); Brown solid; m.p. 107-109 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.78 (dd, *J* = 7.0, 1.9 Hz, 1H), 7.64 - 7.47 (m, 2H), 7.44 - 7.38 (m, 1H), 7.35 - 7.25 (m, 4H), 7.20 - 7.12 (m, 2H), 7.10 - 6.98 (m, 2H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.69 (s, 1H), 5.96 (d, *J* = 8.2 Hz, 1H), 3.86 (s, 3H), 2.59 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 147.1, 138.7, 135.2, 134.0, 132.6, 131.5, 130.5, 130.2, 129.7, 129.4, 129.0, 128.2, 128.1, 126.6, 123.2, 120.9, 120.4, 119.9, 111.5, 111.1, 110.0, 109.3, 108.4, 98.3, 89.8, 85.1, 51.0, 10.9.

HRMS (ESI+) Calcd. For $C_{29}H_{22}N_3O_2ClNa^+$ ($[M+Na]^+$): 502.1292, found: 502.1294.

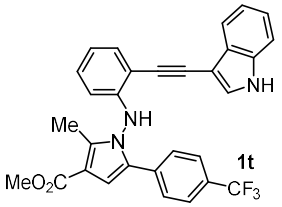


methyl 1-((2-((1*H*-indol-3-yl)ethynyl)phenyl)amino)-5-(2-bromophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (**1s**): 43% yield (1.12 g); Brown solid; m.p. 129-131 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.81 - 7.67 (m, 1H), 7.51 (s, 1H), 7.48 (d, *J* = 2.7 Hz, 1H), 7.45 - 7.40 (m, 1H), 7.37 - 7.32 (m, 1H), 7.24 - 7.19 (m, 1H), 7.18 - 7.15 (m, 2H), 7.07 - 6.92 (m, 4H), 6.72 - 6.65 (m, 1H), 6.59 (s, 1H), 5.93 - 5.88 (m, 1H), 3.79 (s, 3H), 2.52 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 147.1, 138.5, 135.2, 132.8, 132.4, 132.2, 131.9, 131.5, 129.9, 129.0, 128.2, 128.1, 127.1, 124.7, 123.2, 120.8, 120.4, 119.9, 111.5, 111.3, 109.8, 109.1, 108.3, 98.3, 89.8, 85.1, 51.0, 10.9.

HRMS (ESI+) Calcd. For $C_{29}H_{22}N_3O_2BrNa^+$ ([M+Na]$^+$): 546.0787, found: 546.0791.



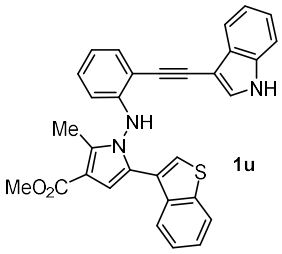
Methyl 1-((2-((1*H*-indol-3-yl)ethynyl)phenyl)amino)-2-methyl-5-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole-3-carboxylate (**1t**): 90% yield (1.53 g); Brown solid; m.p. 112-114 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.62 (m, 2H), 7.57 – 7.54 (m, 2H), 7.51 – 7.49 (m, 2H), 7.43 – 7.41 (m, 2H), 7.30 – 7.28 (m, 1H), 7.24 – 7.20 (m, 1H), 7.17 – 7.13 (m, 1H), 6.93 – 6.89 (m, 2H), 6.17 (d, *J* = 8.2 Hz, 1H), 3.86 (s, 3H), 2.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 146.5, 139.3, 135.2, 132.2, 130.0 (q, *J* = 253.0 Hz), 129.7, 128.1, 127.4, 125.4 (q, *J* = 4.0 Hz), 123.4, 121.1, 121.0, 119.6, 111.6, 111.3, 108.9, 108.5, 98.0, 90.3, 85.2, 51.1, 10.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.5.

HRMS (ESI+) Calcd. For $C_{30}H_{22}F_3N_3O_2Na^+$ ([M+Na]$^+$): 535.1484, found: 535.1490.



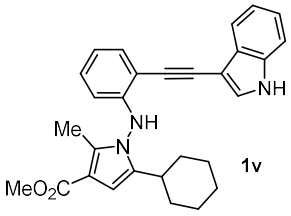
1u

methyl 1-((2-((1*H*-indol-3-yl)ethynyl)phenyl)amino)-5-(benzo[*b*]thiophen-3-yl)-2-methyl-1*H*-pyrrole-3-carboxylate (**1u**): 60% yield (1.50 g); Brown solid; m.p. 125-127 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.83 – 7.64 (m, 1H), 7.62 – 7.58 (m, 1H), 7.56 – 7.52 (m, 1H), 7.45 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.43 (s, 1H), 7.40 (d, *J* = 2.7 Hz, 1H), 7.35 (s, 1H), 7.30 – 7.26 (m, 1H), 7.20 – 7.14 (m, 2H), 7.14 – 7.08 (m, 2H), 7.06 – 7.00 (m, 1H), 6.92 (s, 1H), 6.86 – 6.76 (m, 1H), 6.17 – 6.03 (m, 1H), 3.76 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 146.2, 139.9, 139.1, 138.9, 135.2, 132.3, 132.1, 129.7, 128.2, 127.3, 124.3, 124.1, 123.3, 121.8, 121.04, 121.01, 119.7, 119.4, 111.6, 111.4, 111.2, 108.7, 108.2, 97.9, 90.5, 85.5, 51.1, 10.6.

HRMS (ESI+) Calcd. For $C_{31}H_{23}N_3O_2SNa^+$ ([M+Na]$^+$): 524.1403, found: 524.1407.



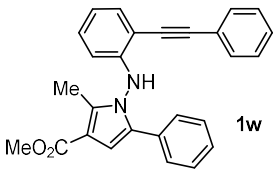
1v

methyl 1-((2-((1*H*-indol-3-yl)ethynyl)phenyl)amino)-5-cyclohexyl-2-methyl-1*H*-pyrrole-3-carboxylate (**1v**): 57% yield (1.29 g); Brown solid; m.p. 126-128 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.51 (dd, *J* = 8.9, 2.1 Hz, 2H), 7.45 – 7.38 (m, 1H), 7.31 – 7.25 (m, 1H), 7.24 (m, 2H), 7.18 – 7.07 (m, 1H), 6.90 (td, *J* = 7.5, 1.2 Hz, 1H), 6.32 (s, 1H), 6.04 (d, *J* = 8.2 Hz, 1H), 3.82 (s, 3H), 2.57 – 2.45 (m, 1H), 2.41 (s, 3H), 2.09 – 1.95 (m, 1H), 1.73 (d, *J* = 11.8 Hz, 3H), 1.45 – 1.10 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 147.2, 139.3, 136.2, 135.2, 131.9, 129.6, 128.3, 128.1, 123.3, 121.0, 120.6, 119.6, 111.6, 111.3, 109.5, 108.2, 103.0, 98.0, 90.1, 85.4, 50.8, 34.6, 26.4, 26.0, 10.6.

HRMS (ESI+) Calcd. For $C_{29}H_{29}N_3O_2Na^+$ ([M+Na]$^+$): 474.2151, found: 474.2154.

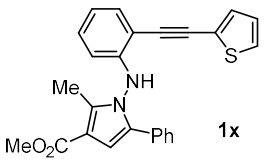


methyl 2-methyl-5-phenyl-1-((2-(phenylethynyl)phenyl)amino)-1*H*-pyrrole-3-carboxylate (**1w**): 90% yield (1.82 g); Brown solid; m.p. 117-119 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.47 – 7.39 (m, 3H), 7.39 – 7.35 (m, 3H), 7.33 – 7.26 (m, 3H), 7.25 – 7.19 (m, 1H), 7.17 – 7.09 (m, 1H), 6.93 – 6.82 (m, 1H), 6.78 (s, 1H), 6.20 – 6.13 (m, 1H), 3.85 (s, 3H), 2.49 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 147.2, 138.4, 133.2, 132.2, 131.5, 130.8, 130.2, 128.8, 128.5, 128.4, 127.7, 127.3, 122.5, 120.7, 111.5, 110.7, 107.8, 107.3, 96.2, 83.9, 51.0, 10.7.

HRMS (ESI+) Calcd. For $C_{27}H_{23}N_2O_2^+$ ($[M+H]^+$): 407.1754, found: 407.1750.

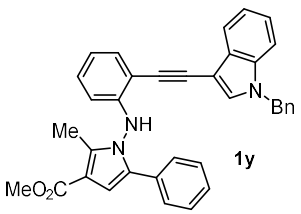


Methyl 2-methyl-5-phenyl-1-((2-(thiophen-2-ylethynyl)phenyl)amino)-1*H*-pyrrole-3-carboxylate (**1x**): 78% yield (980 mg); yellow solid; m.p. 134-136 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.1 Hz, 2H), 7.38 (d, J = 7.7 Hz, 1H), 7.34 (d, J = 5.2 Hz, 1H), 7.31 – 7.21 (m, 5H), 7.17 – 7.13 (m, 1H), 7.05 – 7.03 (m, 1H), 6.87 – 6.84 (m, 1H), 6.78 (s, 1H), 6.15 (d, J = 8.2 Hz, 1H), 3.83 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 147.1, 138.3, 133.2, 132.3, 132.2, 130.8, 130.4, 128.4, 127.9, 127.6, 127.3, 127.2, 122.4, 120.7, 111.6, 110.7, 107.8, 107.0, 89.2, 87.5, 51.01, 10.8.

HRMS (ESI+) Calcd. For $C_{25}H_{20}N_2O_2SNa^+$ ($[M+Na]^+$): 434.1065, found: 434.1069.



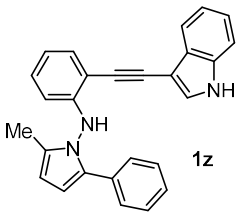
***N*-(2-((1*H*-indol-3-yl)ethynyl)phenyl)-2-methyl-5-phenyl-1*H*-pyrrol-1-amine** (**1y**): 59% yi

eld (1.58 g); Brown solid; m.p. 130-132 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 1H), 7.43 – 7.34 (m, 3H), 7.32 – 7.31 (m, 2H), 7.27 – 7.18 (m, 7H), 7.16 – 7.01 (m, 5H), 6.82 – 6.75 (m, 1H), 6.70 (s, 1H), 6.14 – 6.05 (m, 1H), 5.23 (s, 2H), 3.77 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 146.9, 138.4, 136.3, 135.8, 133.3, 131.9, 131.7, 130.9, 129.5, 129.1, 128.9, 128.4, 128.0, 127.7, 127.3, 127.0, 123.1, 120.9, 120.6, 119.9, 111.3, 110.6, 110.2, 108.4, 107.7, 97.0, 90.1, 85.6, 51.0, 50.4, 10.8.

HRMS (ESI+) Calcd. For $C_{36}H_{29}N_3O_2Na^+$ ($[M+Na]^+$): 558.2151, found: 558.2154.



1z

***N*-(2-((1*H*-indol-3-yl)ethynyl)phenyl)-2-methyl-5-phenyl-1*H*-pyrrol-1-amine** (**1z**): 50% yi eld (0.97 g); Brown solid; m.p. 99-101 ºC.

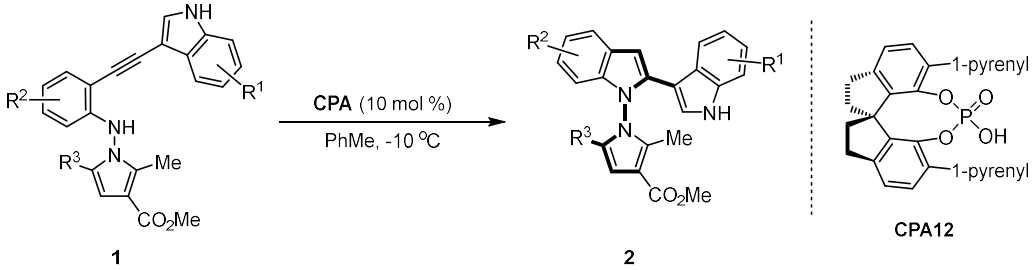
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.70 – 7.57 (m, 1H), 7.47 – 7.42 (m, 2H), 7.41 – 7.38 (m, 1H), 7.37 (d, *J* = 1.5 Hz, 1H), 7.34 – 7.32 (m, 0H), 7.32 – 7.28 (m, 2H), 7.22 – 7.17 (m, 4H), 7.15 – 7.03 (m, 3H), 6.78 - 6.74 (m, 1H), 6.26 (d, *J* = 3.9 Hz, 1H), 6.18 – 6.10 (m, 1H), 5.96 (dd, *J* = 3.9, 1.0 Hz, 1H), 2.11 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 135.2, 133.1, 132.1, 131.8, 131.2, 129.6, 128.32, 128.26, 127.9, 127.2, 126.4, 123.3, 121.0, 120.0, 119.8, 111.5, 107.9, 106.2, 105.5, 98.3, 89.6, 85.8, 11.4.

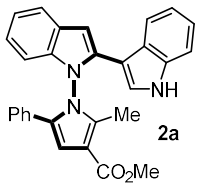
HRMS (ESI+) Calcd. For $C_{27}H_{22}N_3^+$ ($[M+H]^+$): 388.1808, found: 388.1809.

3. Procedure for the synthesis of products 2 and characterization data

General Procedure for the Synthesis of Products 2:



Following the general procedure, *o*-alkynylanilines **1** (0.2mmol), chiral phosphoric acid (*S*)-**CPA 12** (14.4 mg, 0.02 mmol) were added to a dried tube. Then, toluene (2 mL) was added to the reaction mixture, which was stirred at -10 °C for 12 h. After the completion of the reaction indicated by TLC, the reaction mixture was further purified through flash chromatography (petroleum ether/EtOAc) to afford pure product **2**.



methyl (*S*)-1-(1*H*,1'*H*-[2,3'-biindol]-1-yl)-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (2a):

Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 90% yield (80.1 mg); white solid; m.p. = 119-121 ºC; $[\alpha]_D^{30}$ = -26.0 (*c* 1.22, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 95:5 er (Chiralcel OD-H, *i*-propanol/hexane = 95/5, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 23.5 min (minor), t_R = 27.6 min (major).

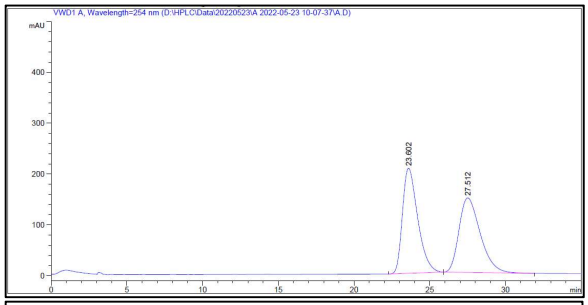
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.06 – 7.97 (m, 1H), 7.71 – 7.62 (m, 1H), 7.43 – 7.34 (m, 1H), 7.29 – 7.26 (m, 1H), 7.24 (d, *J* = 2.3 Hz, 1H), 7.21 – 7.12 (m, 2H), 7.10 – 7.01 (m, 6H), 6.99 (s, 1H), 6.96 – 6.88 (m, 1H), 6.35 (d, *J* = 2.7 Hz, 1H), 3.86 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 138.8, 136.6, 135.9, 134.4, 133.4, 129.9, 128.6, 127.4, 126.5, 126.2, 125.8, 123.04, 122.95, 121.6, 121.5, 120.9, 120.4, 120.0, 111.6, 111.4, 108.6,

108.0, 106.2, 100.1, 51.2, 10.1.

HRMS (ESI-TOF) Calcd. For $C_{29}H_{24}N_3O_2^+$ ([M+H]$^+$): 446.1863, found: 446.1867;

HPLC chromatogram of compound 2a



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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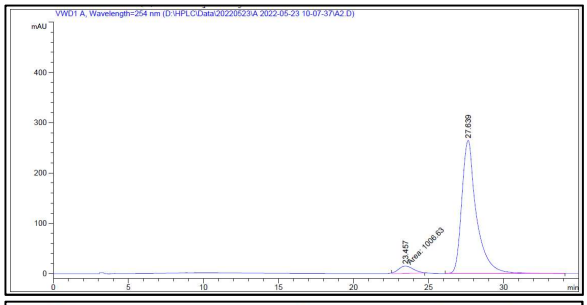
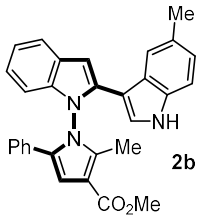
2	27.512	BB	1.4991	1.43002e4	146.58736	49.6582



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.457	MM	1.1404	1006.63269	14.71116	5.3366
2	27.639	BB	0.9861	1.78563e4	264.66461	94.6634



2b

methyl (*S*)-2-methyl-1-(5'-methyl-1*H*,1'*H*-[2,3'-biindol]-1-yl)-5-phenyl-1*H*-pyrrole-3-carboxylate (2b):

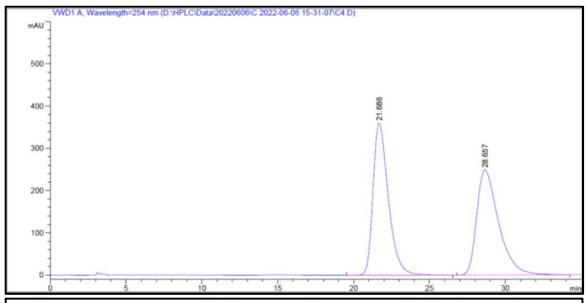
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 87% yield (79.9 mg); white solid; m.p. = 114-126 ºC; $[\alpha]_D^{30}$ = -18.7 (*c* 0.85, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 95:5 er (Chiralcel OD-H, *i*-propanol/hexane = 95/5, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 21.6 min (minor), t_R = 28.2 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.78 (s, 1H), 7.71 – 7.65 (m, 1H), 7.29 – 7.25 (m, 1H), 7.22 – 7.12 (m, 2H), 7.12 – 7.02 (m, 7H), 6.98 (s, 1H), 6.95 – 6.90 (m, 1H), 6.33 (d, *J* = 2.8 Hz, 1H), 3.86 (s, 3H), 2.52 (s, 3H), 2.04 (s, 3H).

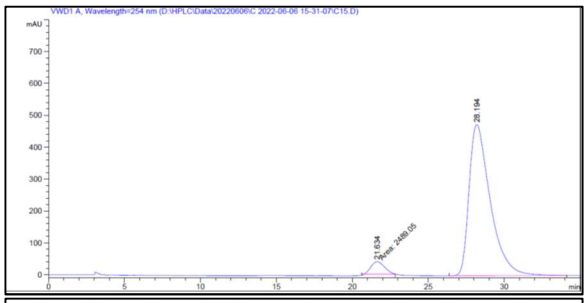
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 138.9, 136.6, 134.7, 134.2, 133.4, 130.3, 129.9, 128.6, 127.4, 126.5, 126.3, 126.0, 124.5, 123.0, 121.6, 120.4, 119.7, 111.6, 111.0, 108.5, 108.0, 105.7, 100.0, 51.2, 21.7, 10.1.

HRMS (ESI-TOF) Calcd. For $C_{30}H_{26}N_3O_2^+$ ([M+H]$^+$): 460.2019, found: 460.2014.

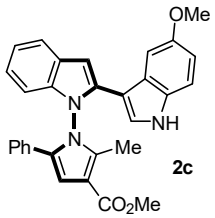
HPLC chromatogram of compound 2b



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.686	BB	1.0758	2.53123e4	360.21555	50.3963
2	28.657	BB	1.5394	2.49142e4	248.76514	49.6037



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.634	MM	1.0456	2489.04810	39.67683	5.1407
2	28.194	BB	1.4709	4.59291e4	474.23444	94.8593



2c

methyl (*S*)-1-(5'-methoxy-1*H*,1'*H*-[2,3'-biindol]-1-yl)-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (2c):

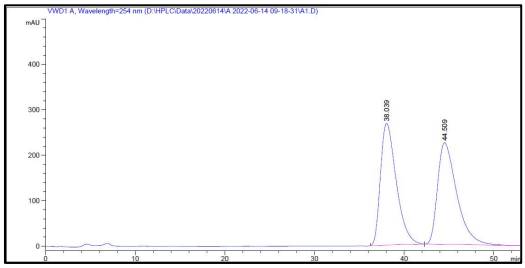
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 97% yield (90.3 mg); white solid; m.p. = 103-105 ºC; $[\alpha]_D^{30}$ = -18.5 (*c* 1.25, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 93:7 er (Chiralcel OD-H, *i*-propanol/hexane = 95/5, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 34.5 min (minor), t_R = 40.5 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.75 – 7.61 (m, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.22 – 7.11 (m, 2H), 7.09 – 6.98 (m, 6H), 6.96 (s, 1H), 6.95 – 6.88 (m, 2H), 6.34 (d, *J* = 2.9 Hz, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 2.05 (s, 3H).

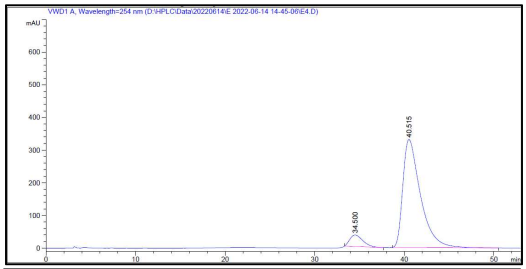
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 155.0, 138.8, 136.6, 134.6, 133.4, 130.9, 129.9, 128.5, 127.4, 126.5, 126.3, 126.2, 123.0, 122.2, 121.6, 120.4, 113.0, 112.0, 111.5, 108.6, 107.9, 105.8, 102.0, 99.8, 56.0, 51.2, 10.1.

HRMS (ESI-TOF) Calcd. For $C_{30}H_{26}N_3O_3^+$ ($[M+H]^+$): 476.1968, found: 476.1960.

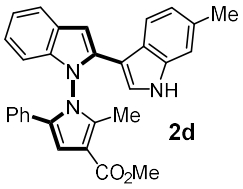
HPLC chromatogram of compound 2c



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.039	BB	1.7553	3.28165e4	267.86853	49.5680
2	44.509	BBA	2.1578	3.33885e4	223.64177	50.4320



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.500	BB	1.4010	3540.34839	35.24367	7.2563
2	40.515	BB	1.9062	4.52497e4	330.94589	92.7437



2d

methyl (*S*)-2-methyl-1-(6'-methyl-1*H*,1'*H*-[2,3'-biindol]-1-yl)-5-phenyl-1*H*-pyrrole-3-carboxylate (2d):

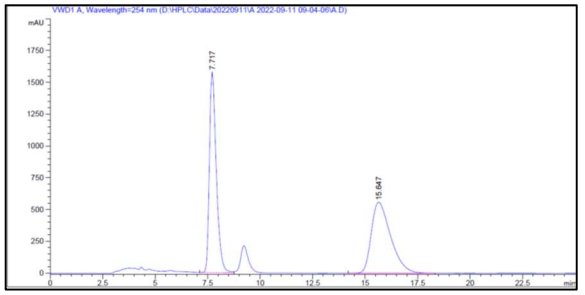
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 90% yield (82.6 mg); white solid; m.p. = 107-109 ºC; $[\alpha]_D^{30}$ = -18.5 (*c* 1.25, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 91:9 er (Chiralcel OD-H, *i*-propanol/hexane = 95/5, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 7.8 min (minor), t_R = 16.1 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (m, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.73 – 7.61 (m, 1H), 7.21 – 7.11 (m, 3H), 7.11 – 7.06 (m, 4H), 7.05 – 7.01 (m, 3H), 6.99 (s, 1H), 6.94 – 6.88 (m, 1H), 6.28 (d, *J* = 2.7 Hz, 1H), 3.86 (s, 3H), 2.47 (s, 3H), 2.03 (s, 3H).

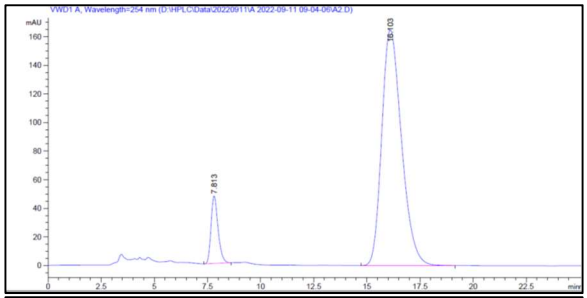
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 138.9, 136.6, 136.4, 134.7, 133.4, 132.9, 130.0, 128.6, 127.4, 126.6, 126.3, 123.6, 123.0, 122.7, 121.6, 120.9, 120.4, 119.7, 111.6, 111.3, 108.5, 108.0, 106.1, 100.1, 51.2, 21.6, 10.1.

HRMS (ESI-TOF) Calcd. For $C_{30}H_{26}N_3O_2^+$ ($[M+H]^+$): 460.2019, found: 460.2015;

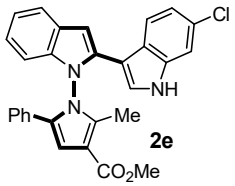
HPLC chromatogram of compound 2d



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.717	BV	0.3465	3.60345e4	1577.44910	50.3111
2	15.647	BB	0.9759	3.55888e4	557.36206	49.6889



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.813	BB	0.3480	1079.76245	47.18141	9.2183
2	16.103	BB	0.9943	1.06335e4	164.68082	90.7817



methyl (*S*)-1-(6'-chloro-1*H*,1'*H*-[2,3'-biindol]-1-yl)-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (2e):

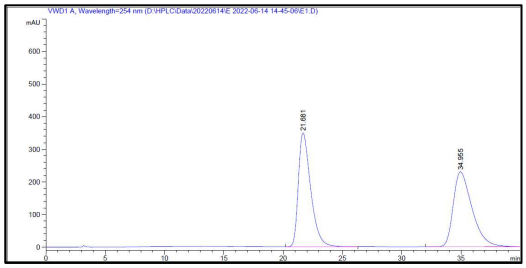
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 95% yield (91.0 mg); white solid; m.p. = 100-102 ºC; $[\alpha]_D^{30}$ = -29.17 (*c* 0.79, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 93:7 er (Chiralcel OD-H, *i*-propanol/hexane = 95/5, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 22.4 min (minor), t_R = 33.9 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.14 (m, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.72 – 7.62 (m, 1H), 7.34 (d, *J* = 1.8 Hz, 1H), 7.22 – 7.13 (m, 3H), 7.08 – 7.00 (m, 6H), 6.98 – 6.88 (m, 2H), 6.32 (d, *J* = 2.7 Hz, 1H), 3.86 (s, 3H), 2.05 (s, 3H).

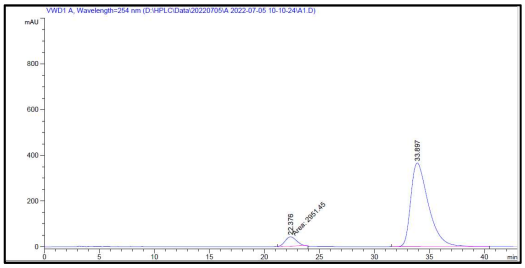
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 138.7, 136.7, 136.2, 133.8, 133.5, 129.8, 128.8, 128.6, 127.5, 126.3, 126.2, 124.4, 123.3, 122.0, 121.8, 121.5, 120.8, 120.6, 111.6, 111.3, 108.6, 108.0, 106.3, 100.4, 51.3, 10.1.

HRMS (ESI-TOF) Calcd. For $C_{29}H_{23}N_3O_2Cl^+$ ($[M+H]^+$): 481.1551, found: 481.1560.

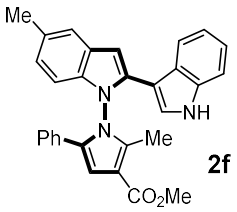
HPLC chromatogram of compound 2e



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.681	BB	1.1055	2.52580e4	349.36789	49.9606
2	34.955	BBA	1.6614	2.52979e4	229.79028	50.0394



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.376	MM	1.1978	2951.44507	41.06851	6.7640
2	33.897	BB	1.6857	4.06834e4	365.47772	93.2360



2f

methyl (*S*)-2-methyl-1-(5-methyl-1*H*,1'*H*-[2,3'-biindol]-1-yl)-5-phenyl-1*H*-pyrrole-3-carboxylate (2f):

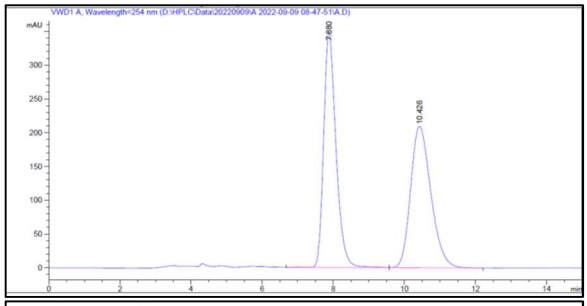
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 88% yield (80.8 mg); white solid; m.p. = 103-105 ºC; $[\alpha]_D^{30}$ = -26.44 (*c* 1.18, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 91:9 er (Chiralcel AD-H, *i*-propanol/hexane =70/30, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 10.5 min (minor), t_R = 7.9 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.96 – 7.90 (m, 1H), 7.43 – 7.35 (m, 1H), 7.32 – 7.25 (m, 1H), 7.21 – 7.18 (m, 1H), 7.17 – 7.13 (m, 1H), 7.05 – 6.87 (m, 8H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.26 (d, *J* = 2.8 Hz, 1H), 3.78 (s, 3H), 2.38 (s, 3H), 1.95 (s, 3H).

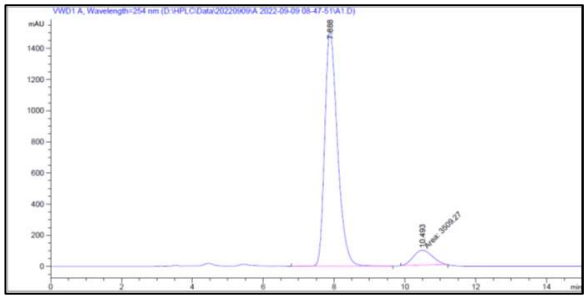
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 138.9, 135.9, 135.0, 134.5, 133.4, 131.0, 130.0, 128.6, 127.4, 126.8, 126.2, 125.8, 124.5, 122.9, 121.4, 120.8, 120.3, 120.0, 111.5, 111.3, 108.3, 107.9, 106.3, 99.8, 51.2, 21.5, 10.1.

HRMS (ESI-TOF) Calcd. For $C_{30}H_{26}N_3O_2^+$ ($[M+H]^+$): 460.2019, found: 460.2016.

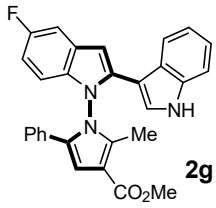
HPLC chromatogram of compound 2f



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.880	VB R	0.3664	8353.26855	347.53036	50.2919
2	10.426	BB	0.6083	8256.31641	209.24464	49.7081



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.888	VB R	0.3818	3.75988e4	1508.18848	91.4633
2	10.493	MM	0.6113	3509.27246	95.68404	8.5367



methyl (*S*)-1-(5-fluoro-1*H*,1'*H*-[2,3'-biindol]-1-yl)-2-methyl-5-phenyl-1*H*-pyrrole-3-carb oxylate (2g):

Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 90% yield (83.3 mg); white solid; m.p. = 107-109 ºC; $[\alpha]_D^{30}$ = -43.6 (*c* 1.05, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 91:9 er (Chiralcel AD-H, *i*-propanol/hexane =70/30, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 6.1 min (minor), t_R = 8.7 min (major).

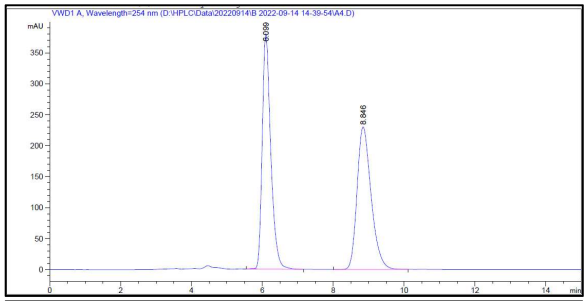
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.95 – 7.89 (m, 1H), 7.35 – 7.28 (m, 1H), 7.27 – 7.21 (m, 1H), 7.21 – 7.18 (m, 1H), 7.17 (d, *J* = 5.3 Hz, 1H), 7.00 – 6.94 (m, 6H), 6.91 (s, 1H), 6.85 – 6.71 (m, 2H), 6.28 (d, *J* = 2.8 Hz, 1H), 3.79 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 159.0 (d, *J* = 237.0 Hz), 138.6, 136.0 (d, *J* = 33.2 Hz), 133.2 (d, *J* = 26.7 Hz), 129.8, 128.6, 127.5, 127.0 (d, *J* = 10.6 Hz), 126.2, 125.6, 123.1, 121.7, 121.0, 120.0, 111.8, 111.4, 111.1 (d, *J* = 26.4 Hz), 109.2 (d, *J* = 9.7 Hz), 108.1, 106.0, 105.7 (d, *J* = 24.3 Hz), 99.9 (d, *J* = 4.4 Hz), 51.2, 10.1.

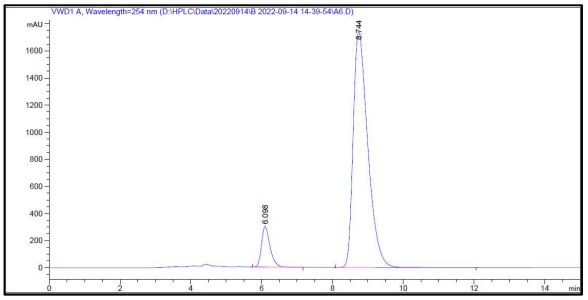
^{19}F NMR (376 MHz, CDCl3) δ -119.99 – -125.38 (m, 1F).

HRMS (ESI-TOF) Calcd. For $C_{29}H_{22}N_3O_2FNa^+$ ($[M+Na]^+$): 486.1588, found: 486.1582.

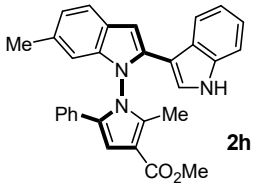
HPLC chromatogram of compound 2g



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.099	VB R	0.2523	6360.30176	380.03842	50.1223
2	8.846	BB	0.4210	6329.25537	230.03984	49.8777



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.098	BB	0.2514	5007.17529	300.53271	9.1445
2	8.744	BV R	0.4354	4.97490e4	1738.43750	90.8555



2h

methyl (*S*)-2-methyl-1-(6-methyl-1*H*,1'*H*-[2,3'-biindol]-1-yl)-5-phenyl-1*H*-pyrrole-3-carboxylate (2h):

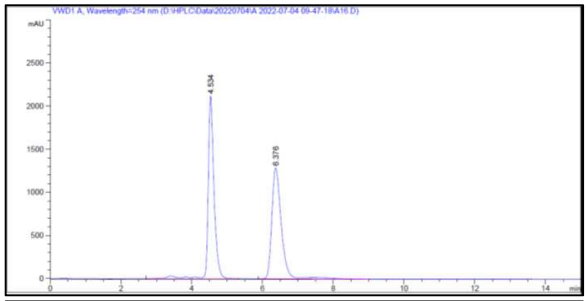
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 96% yield (88.1 mg); white solid; m.p. = 170-172 ºC; $[\alpha]_D^{30}$ = -28.4 (*c* 1.07, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 95:5 er (Chiralcel AD-H, *i*-propanol/hexane =70/30, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 4.5 min (minor), t_R = 6.1 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.03 – 7.92 (m, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.25 – 7.19 (m, 2H), 7.12 – 7.06 (m, 2H), 7.06 – 7.01 (m, 5H), 7.00 (d, *J* = 4.4 Hz, 1H), 6.71 (dd, *J* = 1.6, 0.9 Hz, 1H), 6.32 (d, *J* = 2.7 Hz, 1H), 3.86 (s, 3H), 2.38 (s, 3H), 2.04 (s, 3H).

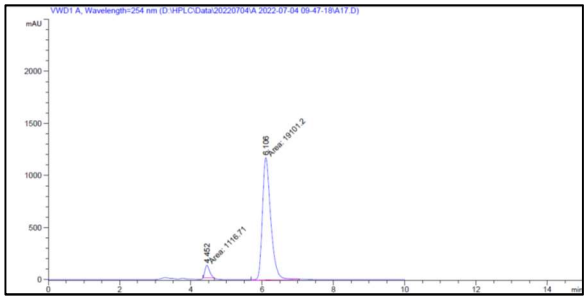
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 139.0, 137.1, 135.8, 133.8, 133.3, 133.2, 129.9, 128.6, 127.3, 126.2, 125.8, 124.3, 123.4, 122.9, 121.2, 120.8, 120.1, 120.0, 111.5, 111.3, 108.5, 107.9, 106.3, 100.1, 51.2, 21.8, 10.1.

HRMS (ESI-TOF) Calcd. For $C_{30}H_{26}N_3O_2^+$ ($[M+H]^+$): 460.2019, found: 460.2020.

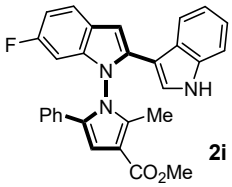
HPLC chromatogram of compound 2h



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.534	VB R	0.1647	2.45041e4	2116.29907	50.1659
2	6.376	BV R	0.2753	2.43420e4	1285.66895	49.8341



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.452	PM	0.1524	1116.70898	122.16109	5.5234
2	6.106	MM	0.2711	1.91012e4	1174.20044	94.4766



2i

methyl (S)-1-(6-fluoro-1*H*,1'*H*-[2,3'-biindol]-1-yl)-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (2i):

Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 97% yield (89.8 mg); white solid; m.p. = 100-102 ºC; $[\alpha]_D^{30}$= -33.8 (*c* 1.03, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 95:5 er (Chiralcel AD-H, *i*-propanol/hexane =70/30, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 4.8 min (minor), t_R = 5.7 min (major).

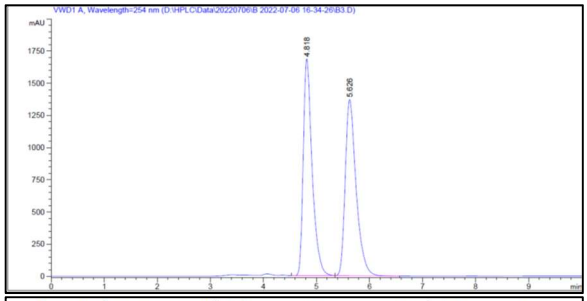
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.12 (m, 1H), 8.07 – 7.94 (m, 1H), 7.57 (dd, *J* = 8.6, 5.0 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.30 – 7.25 (m, 2H), 7.10 – 7.02 (m, 6H), 6.98 (s, 1H), 6.96 – 6.88 (m, 1H), 6.61 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.35 (d, *J* = 2.8 Hz, 1H), 3.87 (s, 3H), 2.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 160.4 (d, *J* = 240.8 Hz), 138.5, 136.8 (d, *J* = 12.2 Hz), 135.9, 135.2, 133.2, 129.7, 128.6, 127.5, 126.3, 125.6, 123.0, 122.8, 121.4, 121.3, 121.0, 119.9, 111.8, 111.4, 110.2 (d, *J* = 24.2 Hz), 108.2, 106.0, 99.9, 95.5 (d, *J* = 27.4 Hz), 51.3, 10.1.

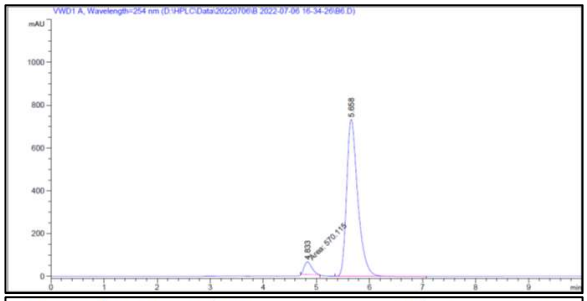
^{19}F NMR (376 MHz, CDCl3) δ -111.82 – -125.10 (m, 1F).

HRMS (ESI-TOF) Calcd. For $C_{29}H_{22}N_3O_2FNa^+$ ($[M+Na]^+$): 486.1588, found: 486.1592.

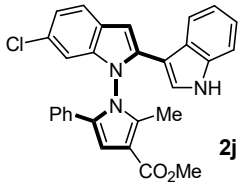
HPLC chromatogram of compound 2i



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.818	BB	0.1720	1.94869e4	1684.49866	50.0042
2	5.626	BB	0.2142	1.94836e4	1367.72961	49.9958



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.833	MM	0.1637	570.11536	58.05790	5.0594
2	5.658	BB	0.2193	1.06983e4	732.98492	94.9406



2j

methyl (*S*)-1-(6-chloro-1*H*,1'*H*-[2,3'-biindol]-1-yl)-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (2j):

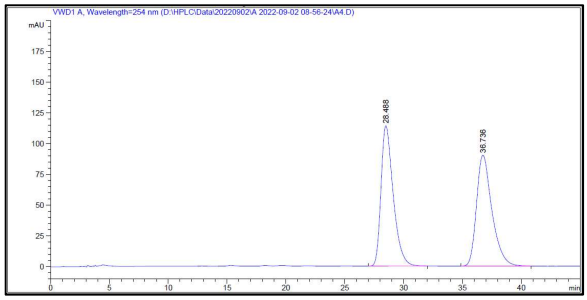
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 81% yield (77.6 mg); white solid; m.p. = 167-167 ºC; $[\alpha]_D^{30}$= -29.7 (*c* 1.17, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 95:5 er (Chiralcel AD-H, *i*-propanol/hexane =95/5, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 27.7 min (minor), t_R = 35.6 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.98 – 7.83 (m, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.23 – 7.19 (m, 1H), 7.08 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.01 – 6.96 (m, 6H), 6.92 (s, 1H), 6.83 (d, *J* = 1.8 Hz, 1H), 6.28 (d, *J* = 2.8 Hz, 1H), 3.80 (s, 3H), 1.99 (s, 3H).

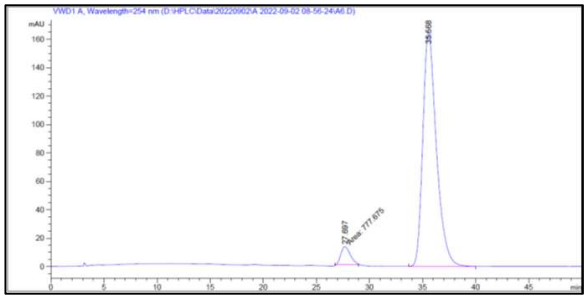
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 138.5, 137.0, 135.9, 135.4, 133.2, 129.7, 128.9, 128.6, 127.6, 126.2, 125.6, 125.0, 123.1, 122.5, 121.6, 121.4, 121.0, 119.9, 111.9, 111.4, 108.5, 108.2, 105.8, 99.9, 51.3, 10.1.

HRMS (ESI-TOF) Calcd. For $C_{29}H_{23}N_3O_2Cl^+$ ($[M+H]^+$): 481.1551, found: 481.1547.

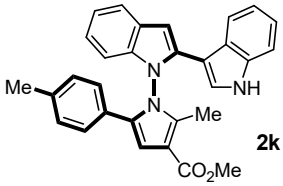
HPLC chromatogram of compound 2j



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.488	BB	1.0845	8201.87500	113.97959	49.9942
2	36.736	BB	1.3592	8203.78711	90.10354	50.0058



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.697	MM	1.0242	777.67511	12.65445	5.0407
2	35.568	BB	1.3287	1.46504e4	165.02550	94.9593



2k

methyl (*S*)-1-(1*H*,1'*H*-[2,3'-biindol]-1-yl)-2-methyl-5-(*p*-tolyl)-1*H*-pyrrole-3-carboxylate (2k):

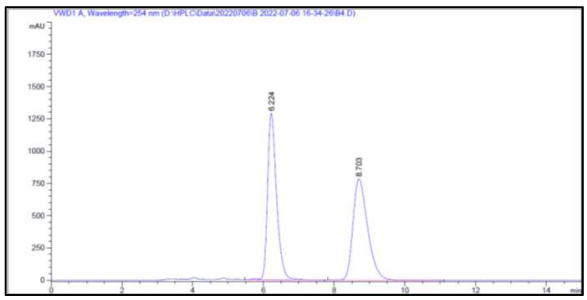
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 95% yield (87.2 mg); white solid; m.p. = 106-108 ºC; $[\alpha]_D^{30}$ = -44.5 (*c* 1.16, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 94:6 er (Chiralcel AD-H, *i*-propanol/hexane =70/30, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 6.2 min (minor), t_R = 8.7 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.09 – 7.96 (m, 1H), 7.75 – 7.63 (m, 1H), 7.40 – 7.32 (m, 1H), 7.29 – 7.26 (m, 1H), 7.25 – 7.22 (m, 1H), 7.21 – 7.11 (m, 2H), 7.08 (d, *J* = 0.9 Hz, 1H), 7.00 – 6.89 (m, 4H), 6.87 – 6.80 (m, 2H), 6.35 (d, *J* = 2.7 Hz, 1H), 3.85 (s, 3H), 2.13 (s, 3H), 2.02 (s, 3H).

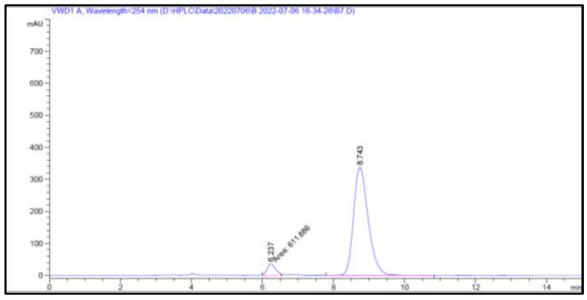
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 138.6, 137.2, 136.6, 135.9, 134.5, 133.5, 129.3, 127.0, 126.5, 126.1, 125.8, 123.0, 122.9, 121.6, 121.5, 120.8, 120.4, 120.0, 111.5, 111.4, 108.6, 107.5, 106.2, 100.0, 51.2, 21.0, 10.1.

HRMS (ESI-TOF) Calcd. For $C_{30}H_{26}N_3O_2^+$ ($[M+H]^+$): 460.2019, found: 460.2020.

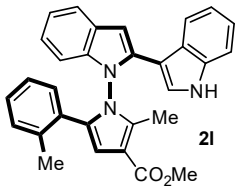
HPLC chromatogram of compound 2k



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.224	VB R	0.2657	2.27696e4	1290.28625	50.1949
2	8.703	BB	0.4419	2.25928e4	782.29688	49.8051



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.237	MM	0.2793	611.88605	36.50825	5.9409
2	8.743	BB	0.4401	9687.69336	337.29596	94.0591



2l

methyl (*S*)-1-(1*H*,1'*H*-[2,3'-biindol]-1-yl)-2-methyl-5-(*o*-tolyl)-1*H*-pyrrole-3-carboxylate (2l):

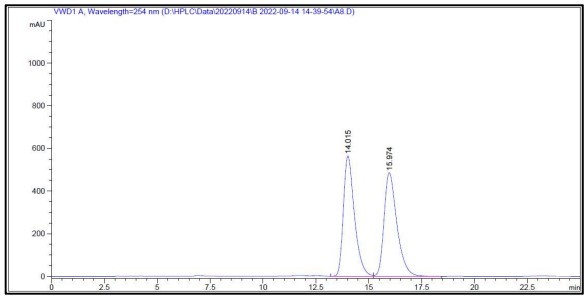
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 92% yield (84.5 mg); white solid; m.p. = 173-175 ºC; $[\alpha]_D^{30}$ = -33.8 (*c* 1.02, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 91:9 er (Chiralcel AD-H, *i*-propanol/hexane =90/10, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 16.2 min (minor), t_R = 14.2 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 6.51 – 6.42 (m, 1H), 6.36 – 6.29 (m, 1H), 6.20 – 6.08 (m, 1H), 6.06 – 6.00 (m, 1H), 5.97 – 5.84 (m, 3H), 5.80 – 5.73 (m, 1H), 5.69 – 5.60 (m, 1H), 5.60 – 5.55 (m, 2H), 5.40 (s, 1H), 5.34 – 5.28 (m, 2H), 5.11 (d, *J* = 2.7 Hz, 1H), 2.64 (s, 3H), 1.06 (s, 3H), 0.62 (s, 3H).

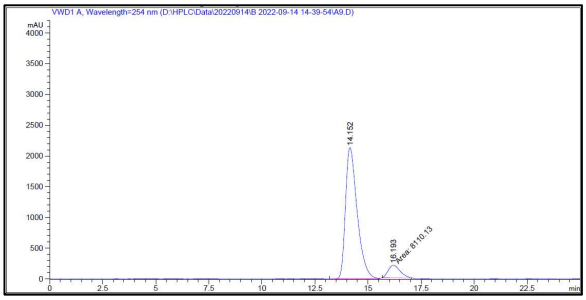
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 137.32, 137.30, 137.1, 135.8, 134.4, 131.9, 130.0, 129.4, 128.7, 127.9, 126.4, 125.9, 124.9, 122.9, 122.7, 121.4, 121.3, 120.8, 120.5, 120.1, 111.2, 110.8, 109.9, 108.5, 106.7, 100.2, 51.2, 19.9, 10.7.

HRMS (ESI-TOF) Calcd. For $C_{30}H_{26}N_3O_2^+$ ($[M+H]^+$): 460.2019, found: 460.2015.

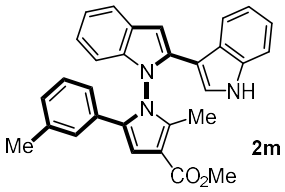
HPLC chromatogram of compound 2l



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.015	BV	0.5480	2.04562e4	564.19141	49.9722
2	15.974	VB	0.6369	2.04789e4	485.68735	50.0278



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.152	BV	0.5800	8.16116e4	2134.60791	90.9608
2	16.193	MM	0.6533	8110.12695	206.88649	9.0392



2m

methyl (*S*)-1-(1*H*,1'*H*-[2,3'-biindol]-1-yl)-2-methyl-5-(m-tolyl)-1*H*-pyrrole-3-carboxylate (2m):

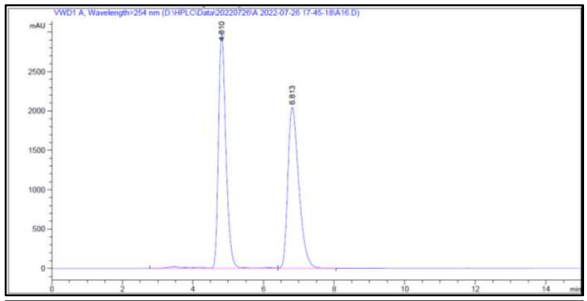
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 93% yield (85.4 mg); white solid; m.p. = 176-178 ºC; $[\alpha]_D^{30}$ = -32.1 (*c* 1.17, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 95:5 er (Chiralcel AD-H, *i*-propanol/hexane = 70/30, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 4.8 min (minor), t_R = 6.8 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.05 – 7.95 (m, 1H), 7.75 – 7.62 (m, 1H), 7.42 – 7.32 (m, 1H), 7.28 – 7.25 (m, 1H), 7.24 – 7.20 (m, 1H), 7.19 – 7.12 (m, 2H), 7.07 (s, 1H), 6.96 (s, 1H), 6.95 – 6.91 (m, 1H), 6.90 – 6.82 (m, 3H), 6.81 – 6.77 (m, 1H), 6.36 (d, *J* = 2.8 Hz, 1H), 3.86 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H).

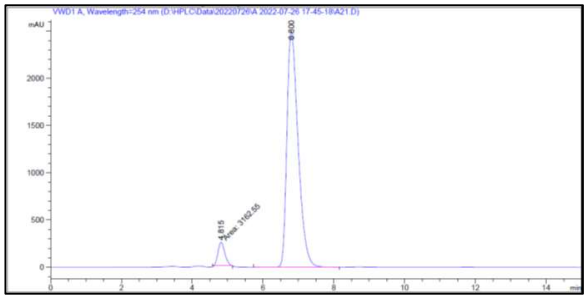
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 138.7, 138.0, 136.7, 135.9, 134.5, 133.6, 129.7, 128.4, 128.2, 127.3, 126.5, 125.8, 123.1, 123.0, 122.9, 121.6, 121.5, 120.8, 120.4, 120.0, 111.5, 111.3, 108.6, 107.8, 106.2, 100.1, 51.2, 21.2, 10.1.

HRMS (ESI-TOF) Calcd. For $C_{30}H_{26}N_3O_2^+$ ($[M+H]^+$): 460.2019, found: 460.2016.

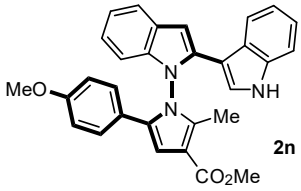
HPLC chromatogram of compound 2m



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.810	VV R	0.2219	4.49142e4	2989.41431	50.3683
2	6.813	VB	0.3311	4.42574e4	2047.75098	49.6317



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.815	MM	0.2159	3162.54956	244.08194	5.4612
2	6.800	BB	0.3376	5.47472e4	2489.05615	94.5388



2n

methyl (*S*)-1-(1*H*,1'*H*-[2,3'-biindol]-1-yl)-5-(4-methoxyphenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (2n):

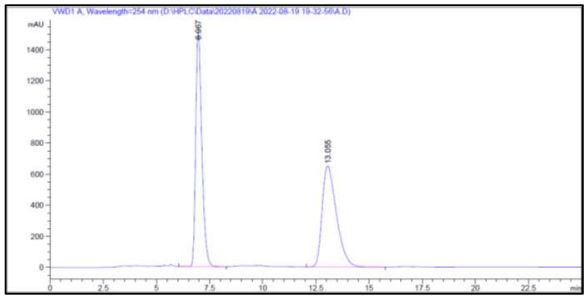
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 96% yield (91.2 mg); white solid; m.p. = 100-102 ºC; $[\alpha]_D^{30}$ = -37.5 (*c* 1.26, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 95:5 er (Chiralcel AD-H, *i*-propanol/hexane =70/30, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 7.0 min (minor), t_R = 12.9 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.07 – 7.98 (m, 1H), 7.72 – 7.61 (m, 1H), 7.42 – 7.32 (m, 1H), 7.30 – 7.25 (m, 2H), 7.23 – 7.13 (m, 2H), 7.10 – 7.05 (m, 1H), 7.00 – 6.91 (m, 3H), 6.88 (s, 1H), 6.58 – 6.49 (m, 2H), 6.34 (d, *J* = 2.7 Hz, 1H), 3.86 (s, 3H), 3.61 (s, 3H), 2.04 (s, 3H).

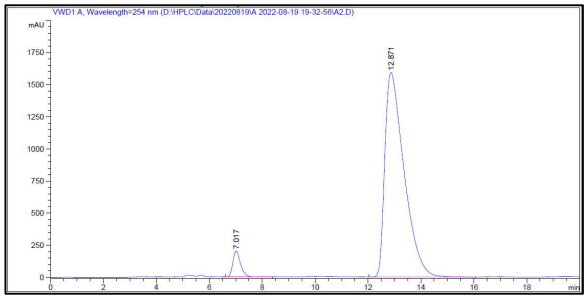
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 158.9, 138.2, 136.6, 135.9, 134.5, 133.4, 127.7, 126.5, 125.7, 123.0, 122.9, 122.5, 121.6, 121.5, 120.9, 120.4, 120.0, 114.0, 111.39, 111.36, 108.6, 107.0, 106.2, 100.0, 55.0, 51.2, 10.1.

HRMS (ESI-TOF) Calcd. For $C_{30}H_{26}N_3O_3^+$ ($[M+H]^+$): 476.1968, found: 476.1960.

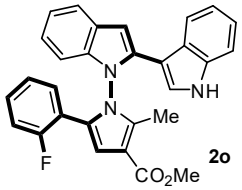
HPLC chromatogram of compound 2n



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.967	VB R	0.3060	3.04100e4	1510.03516	50.0220
2	13.055	BB	0.7162	3.03834e4	650.19830	49.9780



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.017	BV R	0.3047	4084.81763	201.65883	4.8351
2	12.871	BB	0.7615	8.03983e4	1593.76489	95.1649



methyl (*S*)-1-(1*H*,1'*H*-[2,3'-biindol]-1-yl)-5-(2-fluorophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (2o):

Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 87% yield (80.6 mg); white solid; m.p. = 137-139 ºC; $[\alpha]_D^{30}$ = -31.6 (*c* 0.68, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 92:8 er (Chiralcel AD-H, *i*-propanol/hexane =95/5, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 52.2 min (minor), t_R = 44.8 min (major).

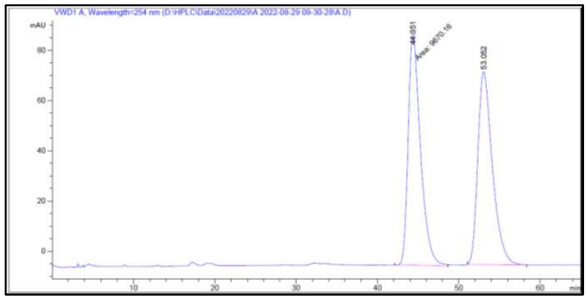
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.84 (d, *J* = 7.7, 1.1 Hz, 1H), 7.64 – 7.51 (m, 1H), 7.40 – 7.25 (m, 1H), 7.19 – 7.15 (m, 1H), 7.15 – 7.08 (m, 3H), 6.96 (d, *J* = 2.7 Hz, 1H), 6.95 – 6.88 (m, 3H), 6.81 – 6.72 (m, 1H), 6.66 – 6.58 (m, 1H), 6.57 – 6.51 (m, 1H), 6.25 (d, *J* = 2.8 Hz, 1H), 3.80 (s, 3H), 2.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 159.6 (d, *J* = 249.1 Hz), 138.7, 136.8, 135.9, 134.5, 129.2 (d, *J* = 8.4 Hz), 128.9, 126.4, 126.1, 125.7, 123.9 (d, *J* = 3.8 Hz), 123.0, 122.9, 121.6, 121.4, 120.8, 120.4, 120.0, 117.7 (d, *J* = 13.2 Hz), 115.6 (d, *J* = 22.7 Hz), 111.6, 111.4, 111.3, 108.5, 106.1, 100.1, 51.2, 10.2.

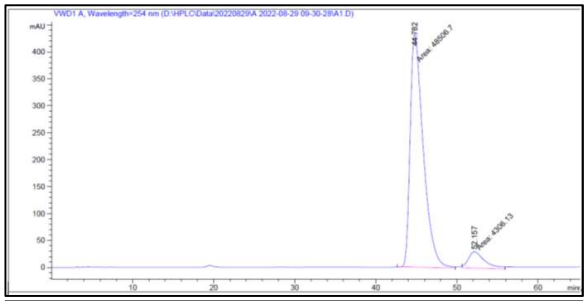
^{19}F NMR (376 MHz, CDCl3) δ -109.55 – -119.42 (m, 1F);

HRMS (ESI-TOF) Calcd. For $C_{29}H_{22}N_3O_2FNa^+$ ($[M+Na]^+$): 486.1588, found: 486.1591.

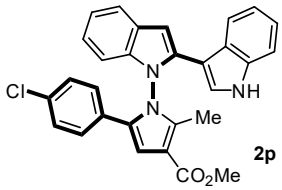
HPLC chromatogram of compound 2o



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.351	MM	1.7403	9670.15625	92.61250	50.3123
2	53.052	BB	1.7499	9550.11133	76.73753	49.6877



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.782	MM	1.8672	4.85067e4	432.96356	91.8464
2	52.157	MM	2.3585	4306.12842	30.43014	8.1536



methyl (*S*)-1-(1*H*,1'*H*-[2,3'-biindol]-1-yl)-5-(4-chlorophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (2p):

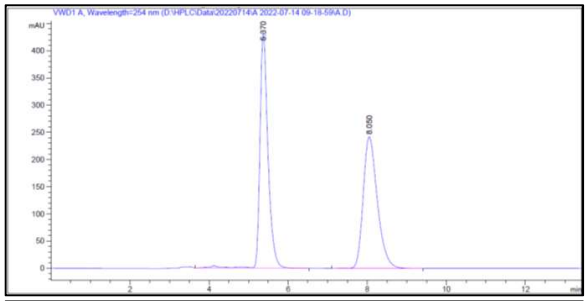
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 95% yield (91.0 mg); white solid; m.p. = 100-102 ºC; $[\alpha]_D^{30}$ = -37.5 (*c* 1.26, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 92:8 er (Chiralcel AD-H, *i*-propanol/hexane = 70/30, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 5.4 min (minor), t_R = 8.1 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.03 – 7.94 (m, 1H), 7.71 – 7.63 (m, 1H), 7.43 – 7.32 (m, 1H), 7.30 – 7.26 (m, 1H), 7.25 – 7.22 (m, 1H), 7.21 – 7.16 (m, 2H), 7.08 (d, *J* = 0.8 Hz, 1H), 7.00 – 6.87 (m, 6H), 6.31 (d, *J* = 2.8 Hz, 1H), 3.86 (s, 3H), 2.08 (s, 3H).

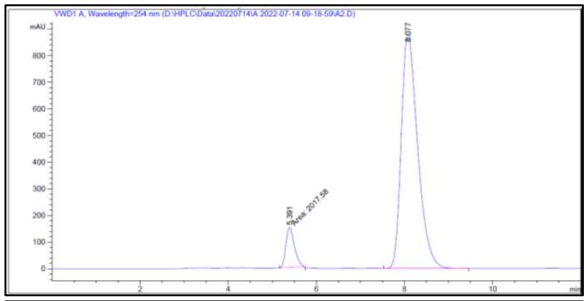
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 139.1, 136.5, 135.9, 134.3, 133.3, 132.2, 128.8, 128.3, 127.4, 126.5, 125.7, 123.2, 123.1, 121.8, 121.2, 121.0, 120.6, 120.0, 111.7, 111.4, 108.4, 108.2, 106.1, 100.4, 51.3, 10.1.

HRMS (ESI-TOF) Calcd. For $C_{29}H_{22}N_3O_2ClNa^+$ ($[M+Na]^+$): 486.1588, found: 486.1592.

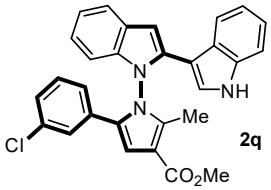
HPLC chromatogram of compound 2p



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.370	VB R	0.2096	6154.37451	432.63812	50.5887
2	8.050	VB R	0.3787	6011.14209	242.08504	49.4113



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.391	MM	0.2234	2017.58179	150.49478	8.1626
2	8.077	VB	0.3951	2.26999e4	879.60834	91.8374



methyl (*S*)-1-(1*H*,1'*H*-[2,3'-biindol]-1-yl)-5-(3-chlorophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (2q):

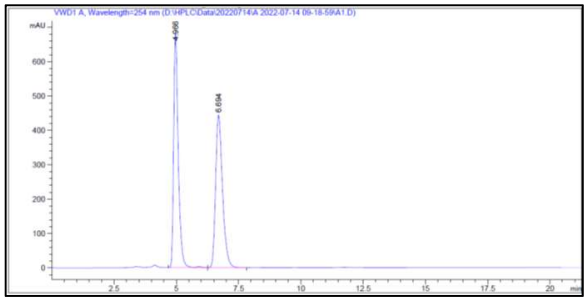
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 93% yield (89.1 mg); white solid; m.p. = 100-102 ºC; $[\alpha]_D^{30}$ = -39.9 (*c* 1.11, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 94:6 er (Chiralcel AD-H, *i*-propanol/hexane = 70/30, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 5.0 min (minor), t_R = 6.7 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.05 – 7.94 (m, 1H), 7.73 – 7.64 (m, 1H), 7.41 – 7.34 (m, 1H), 7.29 – 7.26 (m, 1H), 7.24 – 7.14 (m, 3H), 7.10 – 7.07 (m, 2H), 7.03 – 6.97 (m, 2H), 6.94 – 6.85 (m, 2H), 6.80 – 6.75 (m, 1H), 6.32 (d, *J* = 2.8 Hz, 1H), 3.87 (s, 3H), 2.09 (s, 3H).

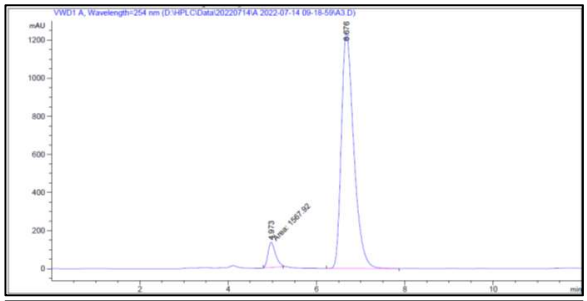
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 139.4, 136.5, 135.9, 134.33, 134.30, 132.0, 131.5, 129.8, 127.4, 126.54, 126.52, 125.7, 123.8, 123.2, 123.1, 121.8, 121.2, 121.0, 120.6, 120.0, 111.8, 111.4, 108.7, 108.4, 106.1, 100.5, 51.3, 10.1.

HRMS (ESI-TOF) Calcd. For $C_{29}H_{23}N_3O_2Cl^+$ ($[M+H]^+$): 481.1551, found: 481.1547.

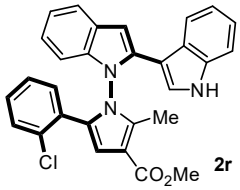
HPLC chromatogram of compound 2q



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.966	BV R	0.1901	8707.61426	682.79266	50.3348
2	6.694	VB	0.2937	8591.76465	444.14667	49.6652



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.973	MM	0.1980	1567.92346	131.97272	6.0859
2	6.676	BB	0.2975	2.41952e4	1235.54834	93.9141



2r

methyl (*S*)-1-(1*H*,1'*H*-[2,3'-biindol]-1-yl)-5-(2-chlorophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (2r):

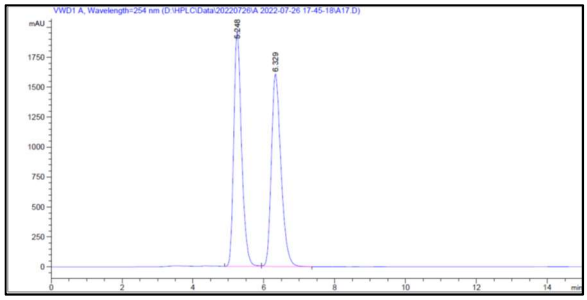
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 95% yield (91.0 mg); white solid; m.p. = 115-117 ºC; $[\alpha]_D^{30}$ = -14.7 (*c* 0.79, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 92:8 er (Chiralcel AD-H, *i*-propanol/hexane = 70/30, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 6.3 min (minor), t_R = 5.2 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.93 – 7.80 (m, 1H), 7.67 – 7.55 (m, 1H), 7.47 – 7.35 (m, 1H), 7.31 – 7.27 (m, 1H), 7.24 – 7.15 (m, 3H), 7.13 – 7.09 (m, 1H), 7.08 – 7.04 (m, 1H), 6.98 – 6.90 (m, 3H), 6.73 – 6.64 (m, 2H), 6.36 (d, *J* = 2.8 Hz, 1H), 3.89 (s, 3H), 2.22 (s, 3H).

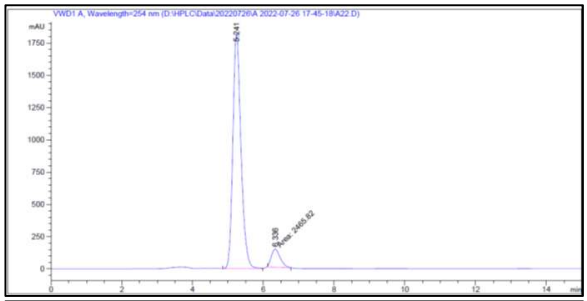
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 137.8, 137.0, 135.9, 134.5, 133.9, 130.7, 129.7, 129.3, 129.1, 128.2, 126.4, 126.1, 125.8, 122.94, 122.89, 121.53, 121.48, 120.8, 120.4, 120.0, 111.6, 111.3, 111.2, 108.6, 106.3, 100.1, 51.2, 10.5.

HRMS (ESI-TOF) Calcd. For $C_{29}H_{22}N_3O_2ClNa^+$ ($[M+Na]^+$): 502.1292, found: 502.1299.

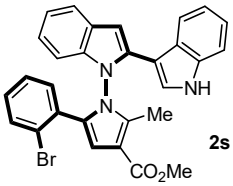
HPLC chromatogram of compound 2r



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.248	BV	0.2318	3.01191e4	1965.60242	49.9142
2	6.329	VB	0.2865	3.02226e4	1606.30322	50.0858



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.241	BV	0.2423	2.90334e4	1817.78638	92.1718
2	6.336	MM	0.2923	2465.82251	140.58836	7.8282



methyl (*S*)-1-(1*H*,1'*H*-[2,3'-biindol]-1-yl)-5-(2-bromophenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (2s):

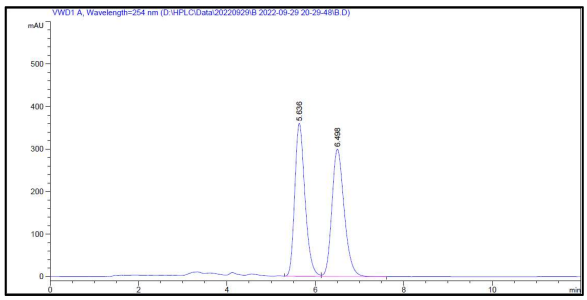
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 90% yield (94.1 mg); white solid; m.p. = 120-122 ºC; $[\alpha]_D^{30}$ = +12.07 (*c* 1.06, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 93:7 er (Chiralcel AD-H, *i*-propanol/hexane =70/30, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 6.7 min (minor), t_R = 5.8 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.83 – 7.75 (m, 1H), 7.56 – 7.49 (m, 1H), 7.37 – 7.31 (m, 1H), 7.27 – 7.19 (m, 2H), 7.17 – 7.07 (m, 3H), 7.05 – 6.99 (m, 1H), 6.89 (s, 1H), 6.85 (s, 1H), 6.82 – 6.75 (m, 1H), 6.66 – 6.60 (m, 2H), 6.29 (d, *J* = 2.8 Hz, 1H), 3.82 (s, 3H), 2.15 (s, 3H).

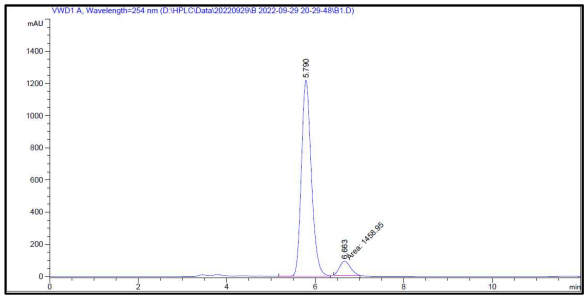
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 137.6, 136.9, 135.9, 134.5, 133.0, 131.0, 130.9, 130.1, 129.4, 126.7, 126.3, 125.7, 124.5, 122.95, 122.9, 121.52, 121.49, 120.8, 120.3, 120.0, 111.6, 111.4, 111.0, 108.7, 106.3, 100.0, 51.3, 10.5.

HRMS (ESI-TOF) Calcd. For $C_{29}H_{22}N_3O_2BrNa^+$ ($[M+Na]^+$): 546.0787, found: 546.0785.

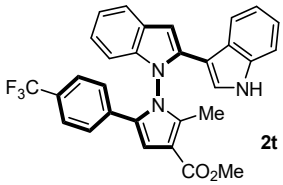
HPLC chromatogram of compound 2s



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.636	BV	0.2451	5766.66357	359.55365	49.9090
2	6.498	VB	0.2966	5787.69629	299.34909	50.0910



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.790	VV R	0.2405	1.90589e4	1218.44055	92.8894
2	6.663	MM	0.2810	1458.95093	86.54406	7.1106



2t

Methyl (*S*)-1-(1*H*,1'*H*-[2,3'-biindol]-1-yl)-2-methyl-5-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole-3-carboxylate (2t):

Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 90% yield (92.3 mg); white solid; m.p. = 99-101 ºC; $[\alpha]_D^{30}$ = -42.0 (*c* 1.49, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 87:13 er (Chiralcel OD-H, *i*-propanol/hexane =95/5, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 14.8 min (minor), t_R = 20.7 min (major).

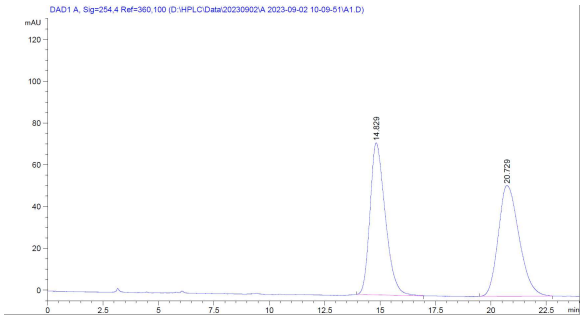
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.27 – 7.17 (m, 6H), 7.14 – 7.02 (m, 4H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.33 (d, *J* = 2.7 Hz, 1H), 3.88 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 139.8, 136.5, 135.9, 134.3, 133.2, 131.9, 126.6, 126.0, 125.7, 125.6 (q, *J* = 4.0 Hz), 123.4, 123.1, 122.0, 121.2, 121.1, 120.7, 119.9, 112.0, 111.4, 109.3, 108.4, 106.1, 100.6, 51.3, 10.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.8.

HRMS (ESI-TOF) Calcd. For $C_{30}H_{21}F_3N_3O_2^+$ ($[M+H]^+$): 514.1742, found: 514.1750.

HPLC chromatogram of compound 2t



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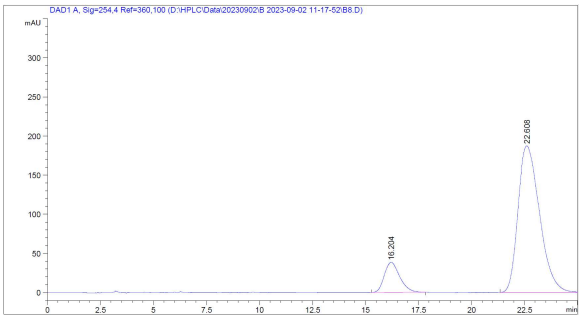
2	20.729	BB	0.7787	3462.17969	52.96048	49.8896



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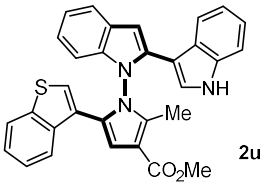
2	22.608	BB	0.8460	1.32139e4	187.31456	87.1199



2u

methyl (*S*)-1-(1*H*,1'*H*-[2,3'-biindol]-1-yl)-5-(benzo[*b*]thiophen-3-yl)-2-methyl-1*H*-pyrrole -3-carboxylate (2u):

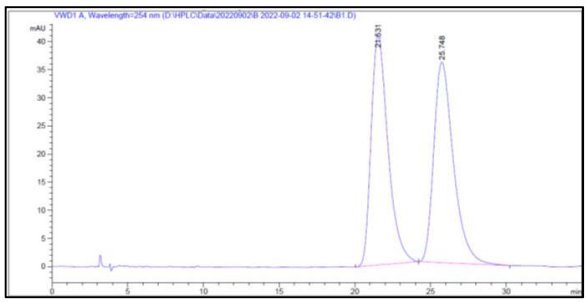
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 90% yield (90.2 mg); white solid; m.p. = 109-111 ºC; $[\alpha]_D^{30}$ = -43.7 (*c* 1.20, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 90:10 er (Chiralcel AD-H, *i*-propanol/hexane =95/5, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 21.5 min (minor), t_R = 25.3 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.04 – 7.95 (m, 1H), 7.72 – 7.62 (m, 1H), 7.54 – 7.47 (m, 1H), 7.36 – 7.31 (m, 1H), 7.30 – 7.25 (m, 1H), 7.21 – 7.18 (m, 1H), 7.17 – 7.14 (m, 2H), 7.12 – 7.04 (m, 5H), 6.91 – 6.85 (m, 1H), 6.58 (s, 1H), 6.38 (d, *J* = 2.8 Hz, 1H), 3.78 (s, 3H), 1.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 140.0, 139.7, 138.5, 136.5, 135.9, 134.4, 131.2, 127.7, 126.8, 125.8, 124.3, 123.5, 123.3, 123.0, 122.0, 121.7, 121.6, 121.0, 120.6, 119.9, 119.0, 112.0, 111.4, 108.8, 108.6, 105.9, 100.7, 51.3, 10.0.

HRMS (ESI-TOF) Calcd. For $C_{31}H_{23}N_3O_2SNa^+$ ($[M+Na]^+$): 524.1403, found: 524.1410.

HPLC chromatogram of compound 2u



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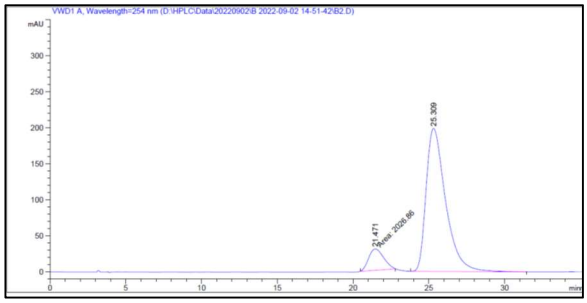

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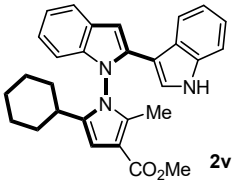
2	25.309	BB	1.3558	1.77241e4	198.47865	89.7379



2v

methyl (*S*)-1-(1*H*,1'*H*-[2,3'-biindol]-1-yl)-5-cyclohexyl-2-methyl-1*H*-pyrrole-3-carboxylate (2v):

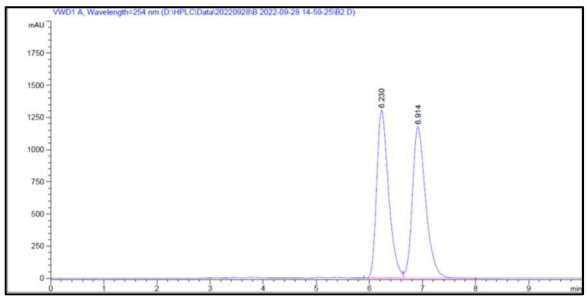
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 97% yield (87.5 mg); white solid; m.p. = 103-105 ºC; $[\alpha]_D^{30}$ = +8.12 (*c* 1.49, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 95:5 er (Chiralcel AD-H, *i*-propanol/hexane =90/10, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 6.3 min (minor), t_R = 6.9 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.08 – 8.02 (m, 1H), 7.75 – 7.58 (m, 1H), 7.40 – 7.27 (m, 1H), 7.24 – 7.20 (m, 2H), 7.17 – 7.10 (m, 2H), 7.07 (s, 1H), 6.89 – 6.81 (m, 1H), 6.41 (s, 1H), 5.94 (d, *J* = 2.8 Hz, 1H), 3.78 (s, 3H), 1.95 (s, 3H), 1.93 – 1.84 (m, 2H), 1.70 – 1.48 (m, 3H), 1.16 – 0.93 (m, 3H), 0.90 – 0.72 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 139.9, 136.8, 136.1, 135.8, 134.6, 126.5, 125.7, 122.9, 122.8, 121.5, 121.4, 120.9, 120.4, 120.2, 111.4, 110.7, 108.4, 106.1, 104.2, 99.7, 51.1, 34.3, 34.0, 33.0, 26.1, 25.7, 10.0.

HRMS (ESI-TOF) Calcd. For $C_{29}H_{30}N_2O_2^+$ ($[M+H]^+$): 452.2332, found: 452.2330.

HPLC chromatogram of compound 2v



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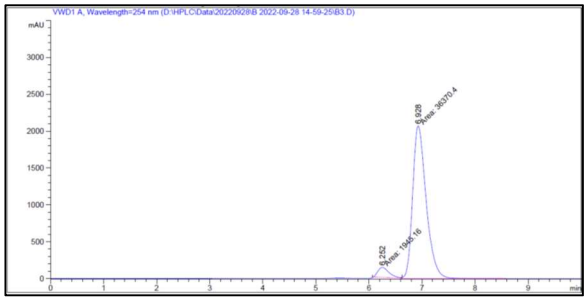
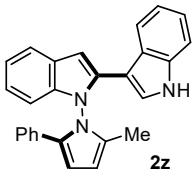
1	6.230	BV	0.2340	2.01444e4	1305.58325	49.7359
2	6.914	VB	0.2617	2.03583e4	1177.43066	50.2641



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.252	MM	0.2407	1945.16199	134.69331	5.0767
2	6.928	FM	0.2928	3.63704e4	2070.05542	94.9233



2z

(*S*)-1-(2-methyl-5-phenyl-1*H*-pyrrol-1-yl)-1H,1'*H*-2,3'-biindole (2z):

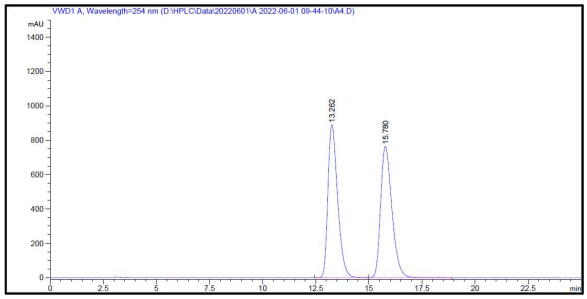
Flash column chromatography eluent (petroleum ether/ ethyl acetate = 20/1); 79% yield (61.1 mg); white solid; m.p. = 95-97 ºC; $[\alpha]_D^{30}$ = -62.0 (*c* 1.49, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 86:14 er (Chiralcel OD-H, *i*-propanol/hexane =95/5, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 13.4 min (minor), t_R = 15.8 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.95 (m, 1H), 7.73 – 7.50 (m, 1H), 7.41 – 7.23 (m, 1H), 7.19 (d, *J* = 6.2 Hz, 4H), 7.14 – 6.86 (m, 8H), 6.47 (d, *J* = 4.0 Hz, 1H), 6.23 (d, *J* = 2.8 Hz, 1H), 6.11 – 5.98 (m, 1H), 1.77 – 1.63 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 135.9, 134.9, 132.7, 131.9, 131.1, 128.5, 126.5, 126.4, 125.8, 125.7, 122.73, 122.66, 122.0, 121.2, 120.8, 120.2, 111.3, 108.8, 106.9, 106.5, 106.3, 99.4, 10.7.

HRMS (ESI-TOF) Calcd. For $C_{27}H_{21}N_3^+$ ($[M+H]^+$): 388.1808, found: 388.1806.

HPLC chromatogram of compound 2z



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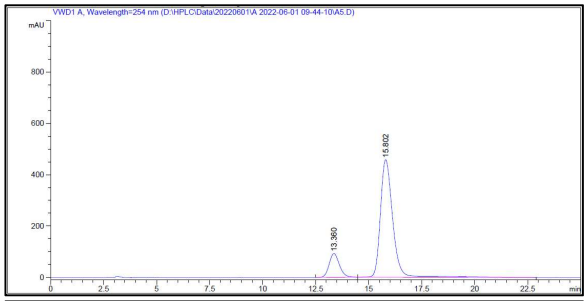
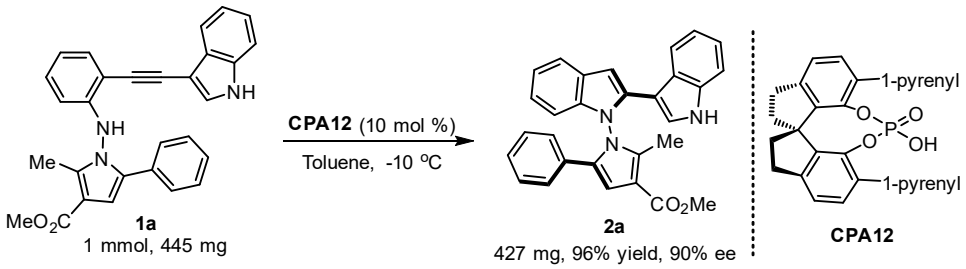
2	15.780	BB	0.5686	2.81305e4	764.00580	49.9502

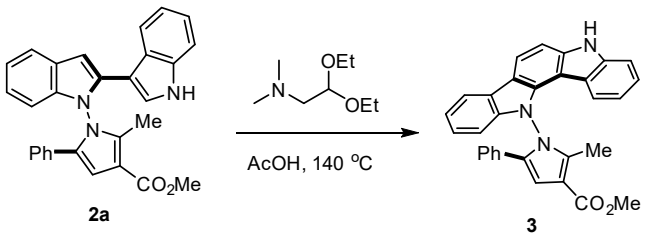


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.360	BB	0.5155	3092.16968	92.62021	14.3790
2	15.802	BB	0.6167	1.84126e4	457.36935	85.6210

4. Procedure for one-mmol-scale reaction and synthesis of compound 3



o-alkynylanilines **1** (445 mg, 1mmol), chiral phosphoric acid (*S*)-**CPA 12** (72 mg, 0.1 mmol) were added to a dried tube. Then, toluene (10 mL) was added to the reaction mixture, which was stirred at -10 °C for 12 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was further purified through preparative thin-layer chromatography on silica gel (petroleum ether/EtOAc = 8:1) to afford pure product **2a** in 96% yield (427 mg), 95:5 er.



Following a reported procedure,[5] in a flame dried vial under nitrogen atmosphere, *N*,*N*'-pyrrolylindole **2a** (89.0 mg, 0.2 mmol, 1.00 equiv.) was dissolved in AcOH (2mL, 0.1 M); commercially available 2,2-diethoxy-*N*,*N*-dimethylethanamine (40.0 µL, 0.2 mmol, 1.00 equiv.) **3** was added under vigorous stirring. The reaction mixture was heated up to reflux (140 °C) and monitored via TLC (3:1 hexane/EtOAc). Upon complete consumption of the

starting material (12 hour), the reaction was cooled to room temperature and the solvent removed under reduced pressure. The crude product was purified via flash chromatography to afford pure product **3** in 80% yield (84.4 mg), 95:5 er.

methyl (*S*)-1-(indolo[3,2-a]carbazol-12(5*H*)-yl)-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxy late (3):

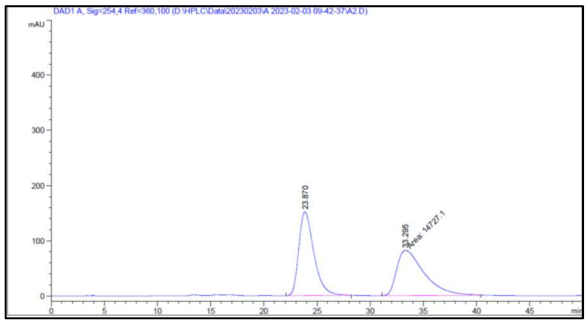
Flash column chromatography eluent (gradient 8:1-3:1 hexane:EtOAc); 80% yield (84.4 mg); white solid; m.p. = 113-115 ºC; $[\alpha]_D^{30}$ = -12.8 (*c* 0.75, acetone); The product was analyzed by HPLC to determine the enantiomeric excess: 95:5 er (Chiralcel OD-H, *i*-propanol/hexane = 90/10, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 23.8 min (minor), t_R = 33.5 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.07 – 7.99 (m, 1H), 7.51 – 7.42 (m, 2H), 7.37 – 7.25 (m, 5H), 7.13 (s, 1H), 7.04 – 6.90 (m, 4H), 6.87 – 6.79 (m, 1H), 6.49 – 6.34 (m, 1H), 3.90 (s, 3H), 2.00 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 140.4, 140.1, 139.3, 138.8, 135.6, 135.5, 130.2, 128.4, 127.4, 127.1, 125.10, 125.05, 122.6, 122.3, 121.6, 120.9, 120.8, 119.1, 118.7, 114.3, 111.7, 110.3, 108.6, 108.4, 107.2, 105.4, 51.3, 10.2;

HRMS (ESI-TOF) Calcd. For $C_{31}H_{24}N_3O_2^+$ ($[M+H]^+$): 470.1863, found: 470.1858.

HPLC chromatogram of compound 3



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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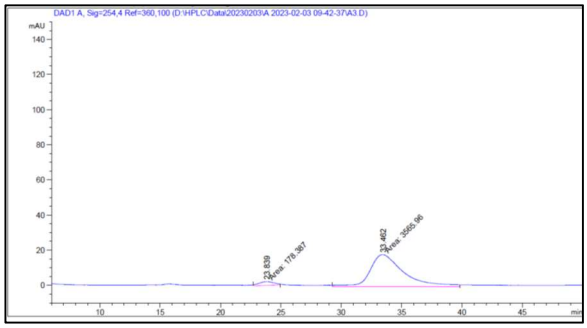
2	33.295	MM	2.9883	1.47271e4	82.13849	49.5892



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.839	MM	1.4466	178.38739	2.05519	4.7642
2	33.462	MM	3.2443	3565.96411	18.31938	95.2358

5. Non-linear effect study

The reactions were carried out following general procedure with **1a** (0.2 mmol), using **CPA-**

12 of varying ee under standard conditions until complete consumption of starting material (detected by TLC). After filtration and evaporation, the residue was purified by a flash column chromatography, and analyzed by chiral HPLC.

CPA12 (ee %)	**2a** (ee %)[a]	**CPA12** (ee %)	**2a** (ee %)[a]
21.74	25.44	81.06	79.22
41.08	42.80	99.00	90.00
62.34	65.08		

[a]The ee was determined by HPLC (Chiralcel OD-H, *i*-propanol/hexane = 95/5, flow rate 1.0 mL/min, T = 20 °C, λ = 254 nm); t_R = 23.457 min (minor), t_R = 27.639 min (major).

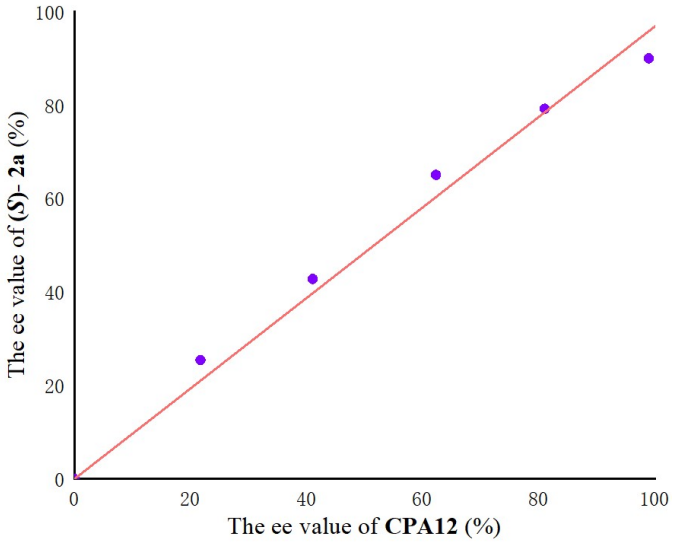


Figure S1. The study on the relationship between ee value of the phosphoric acid (*S*)-**CPA12** and that of the product (*S*)-**2a**

6. Absolute configuration determination

To a 4 mL oven-dried glass sample bottle was added 30 mg pure **2b** with 3 mL ethyl ether to get clear solution. The mixture solution was sealed with filter paper to slowly grow crystals at room temperature. Crystal data for (*S*)-**2b**: $C_{30}H_{25}N_3O_2$, M_r = 459.53, T = 293 K, orthorhombic, space group P 21 21 21, a= 7.3836(2), b= 17.6933(6), c= 18.4913(6) Å, V = 2415.71(13) Å^3, Z = 4, 9959 unique reflections, final R_1 = 0.0317 for 3854 and wR_2 = 0.0924 for 4262 observed [I>2σ(I)] reflections, Flack χ = -0.04(10). CCDC 2279386 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge

via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

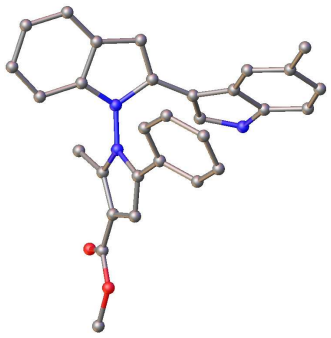


Figure S2. ORTEP representation of (*S*)-**2b** (CCDC 2279386).

7. Reference

[1] N. Kim, J. T. Han, D. H. Ryu, J. Yun, *Org. Lett.* **2017**, *19*, 6144-6147.

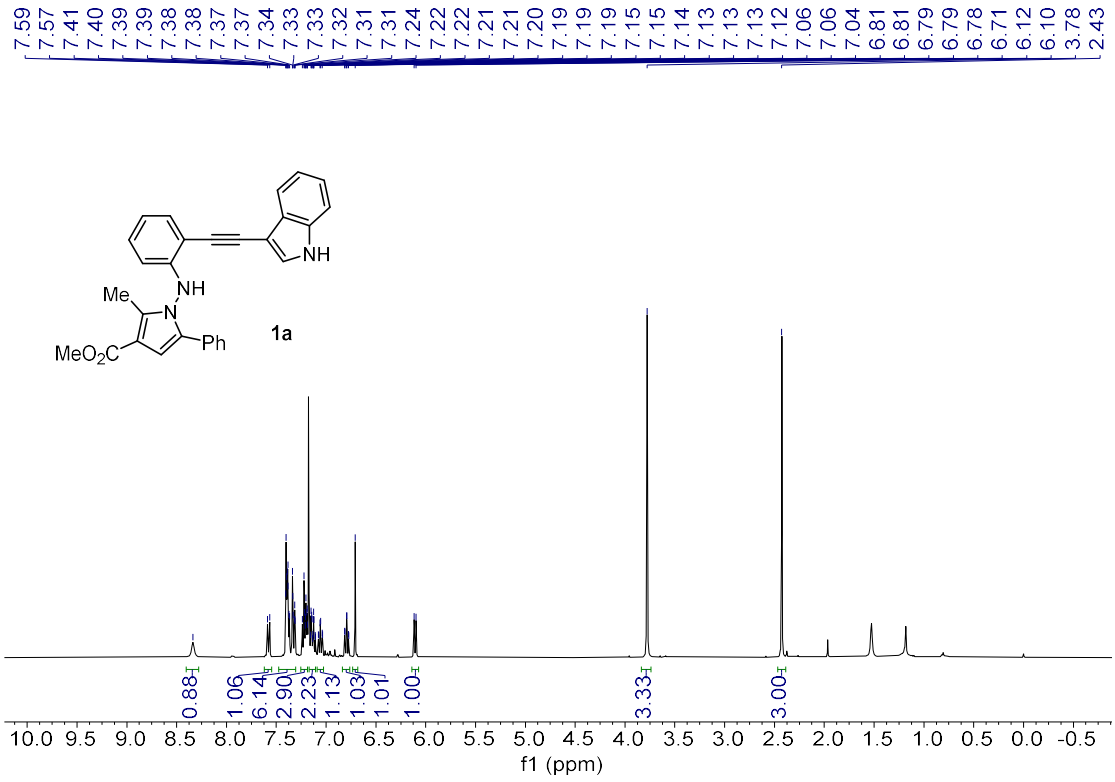
[2] Y. Gao, L.-Y. Wang, T. Zhang, B.-M. Yang, Y. Zhao, *Angew. Chem. Int. Ed.* **2022**, *61*, e202200371.

[3] M. Hatano, K. Mikami, *J. Am. Chem. Soc.* **2003**, *125*, 4704-4705

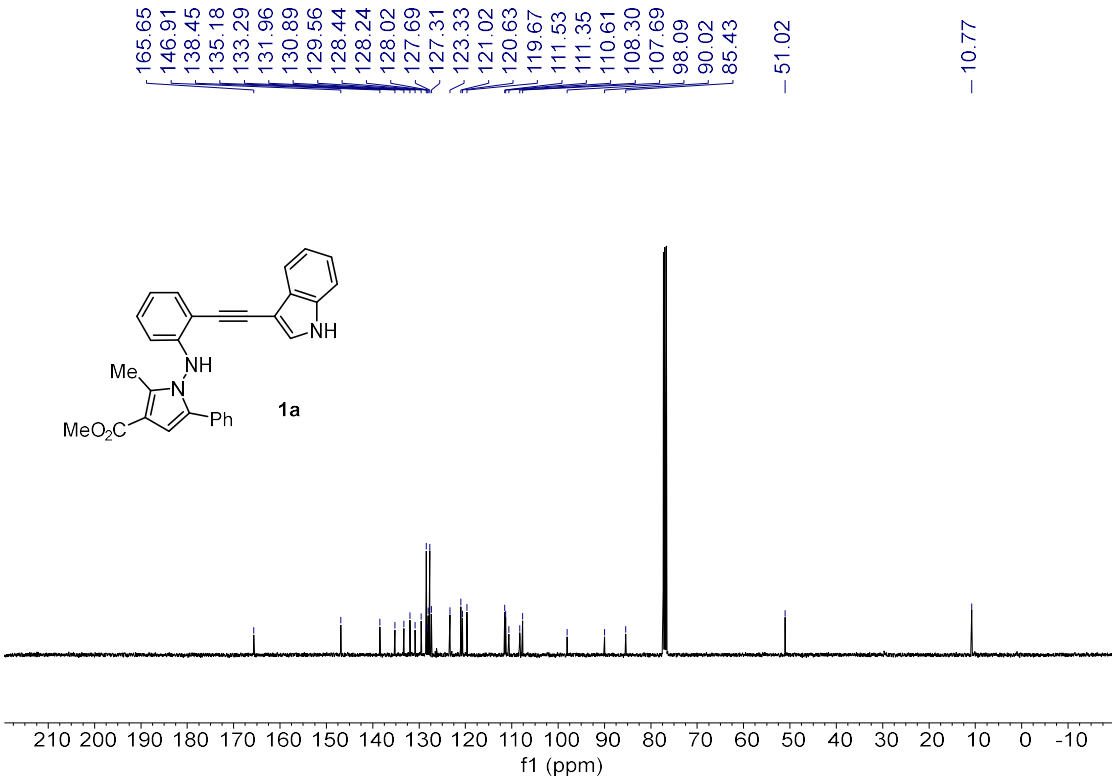
[4] J. S. Oakdale, D. L. Boger, *Org. Lett.* **2010**, *12*, 1132-1134.

[5] J. Bergman, E. Desarbre, E. Koch, *Tetrahedron* **1999**, *55*, 2363-2370.

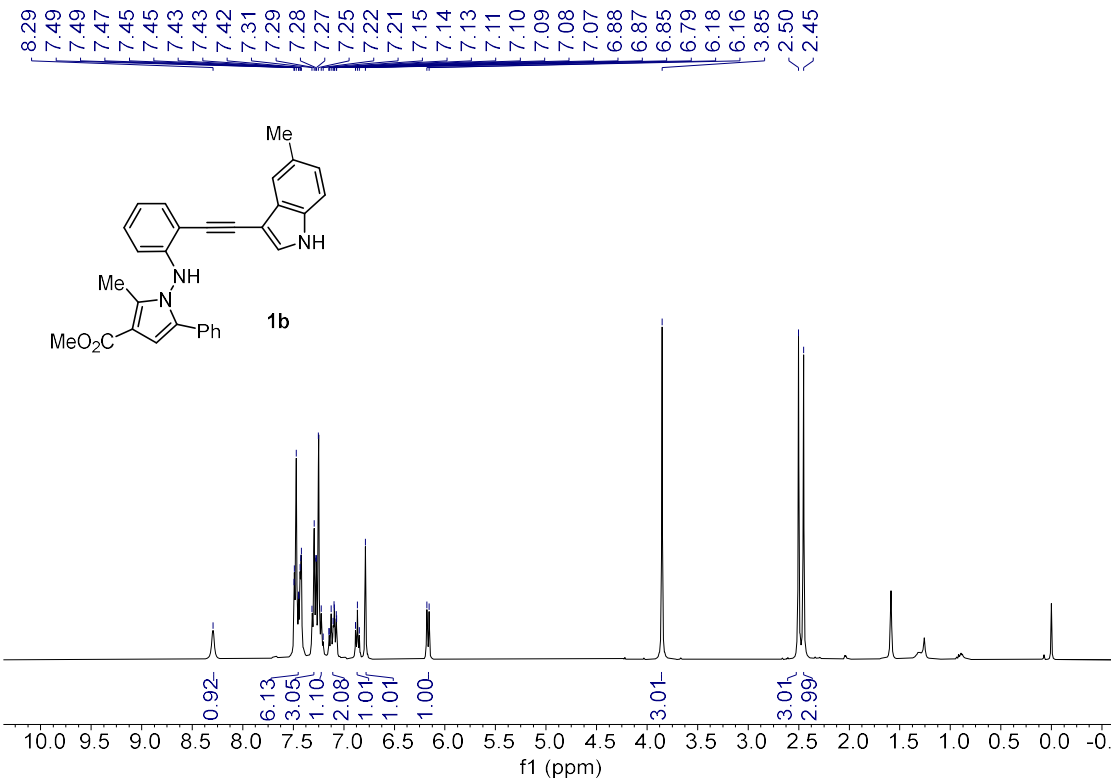
8. NMR spectra



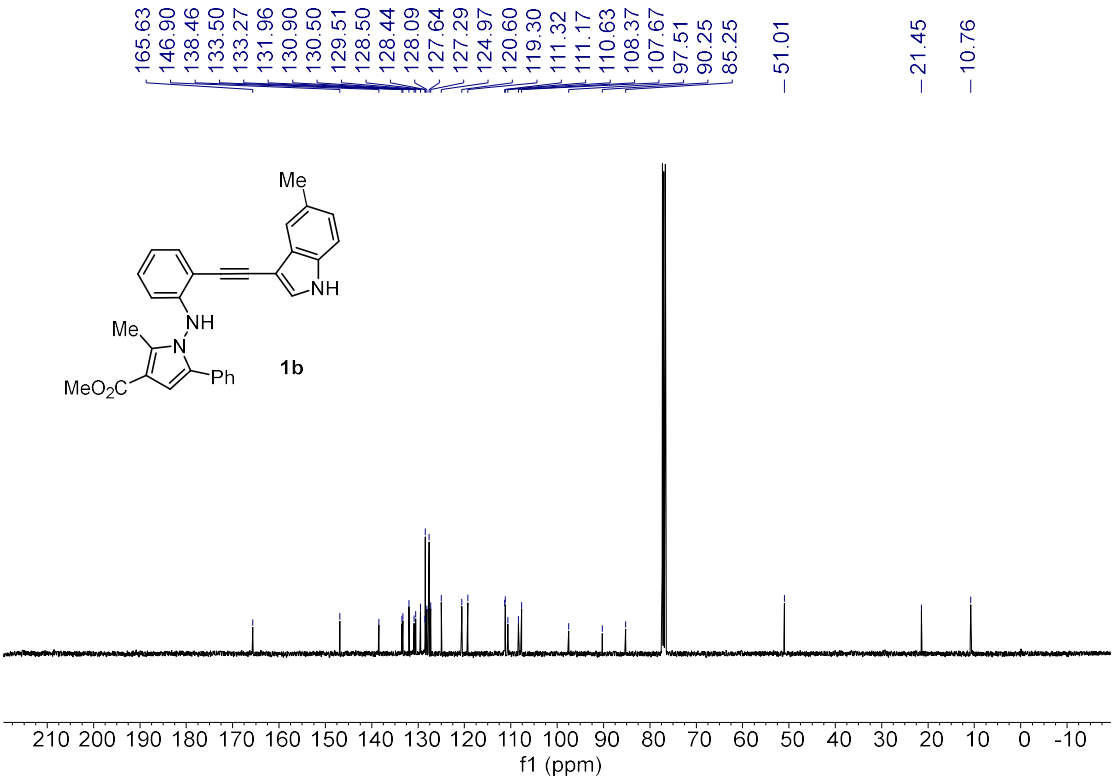
^{1}H NMR (400 MHz, $CDCl_3$) of **1a**



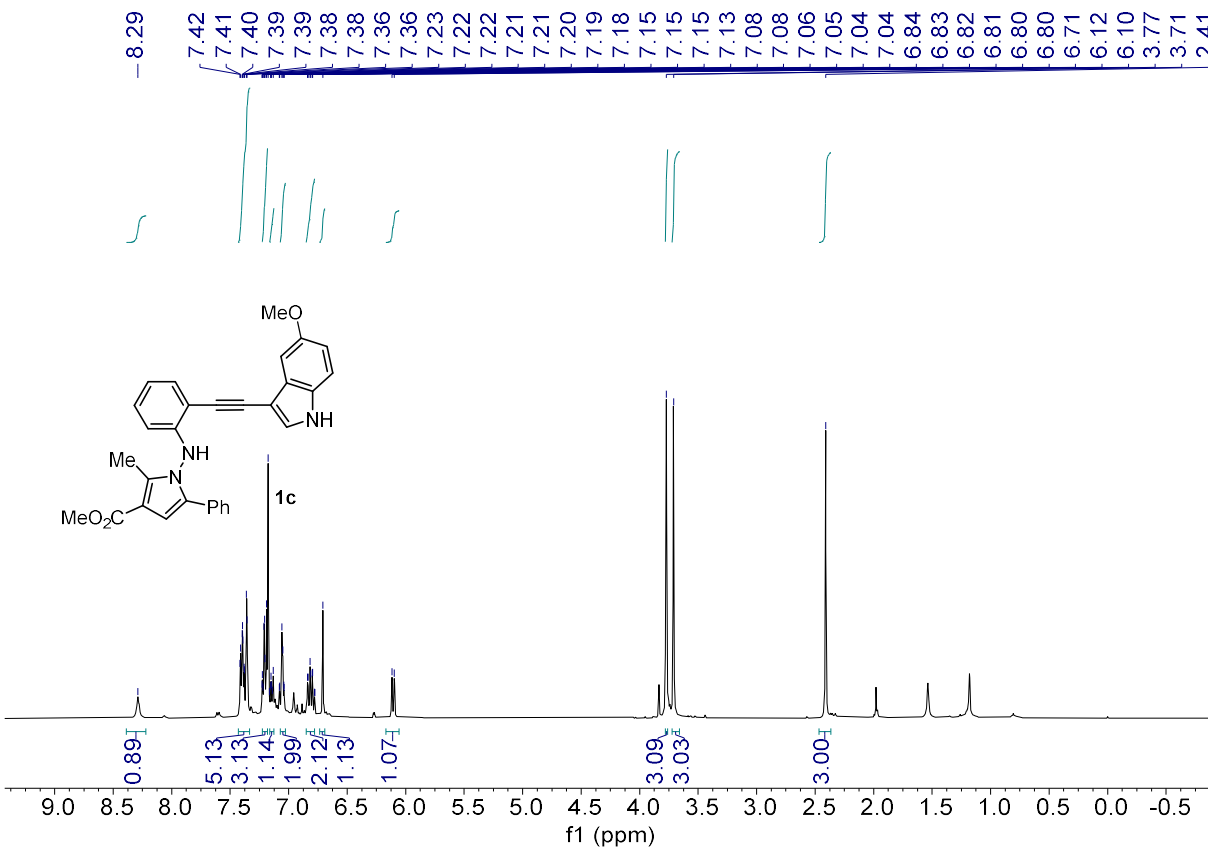
^{13}C NMR (101 MHz, $CDCl_3$) of **1a**



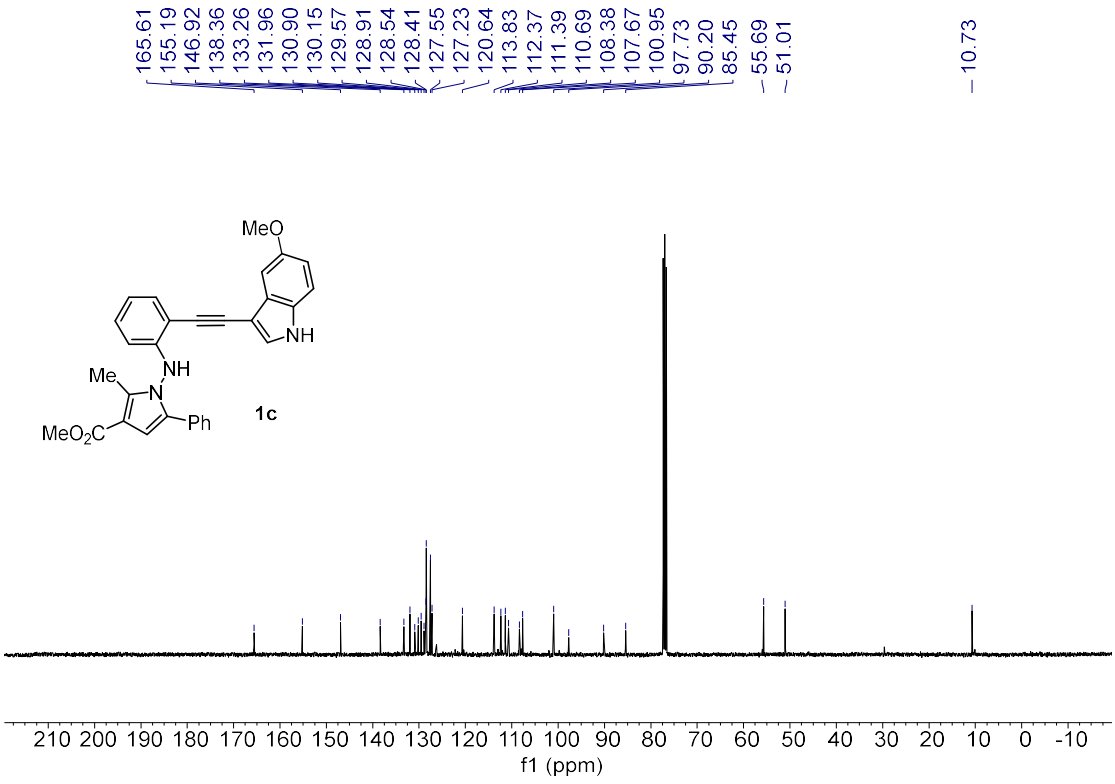
^{1}H NMR (400 MHz, $CDCl_3$) of **1b**



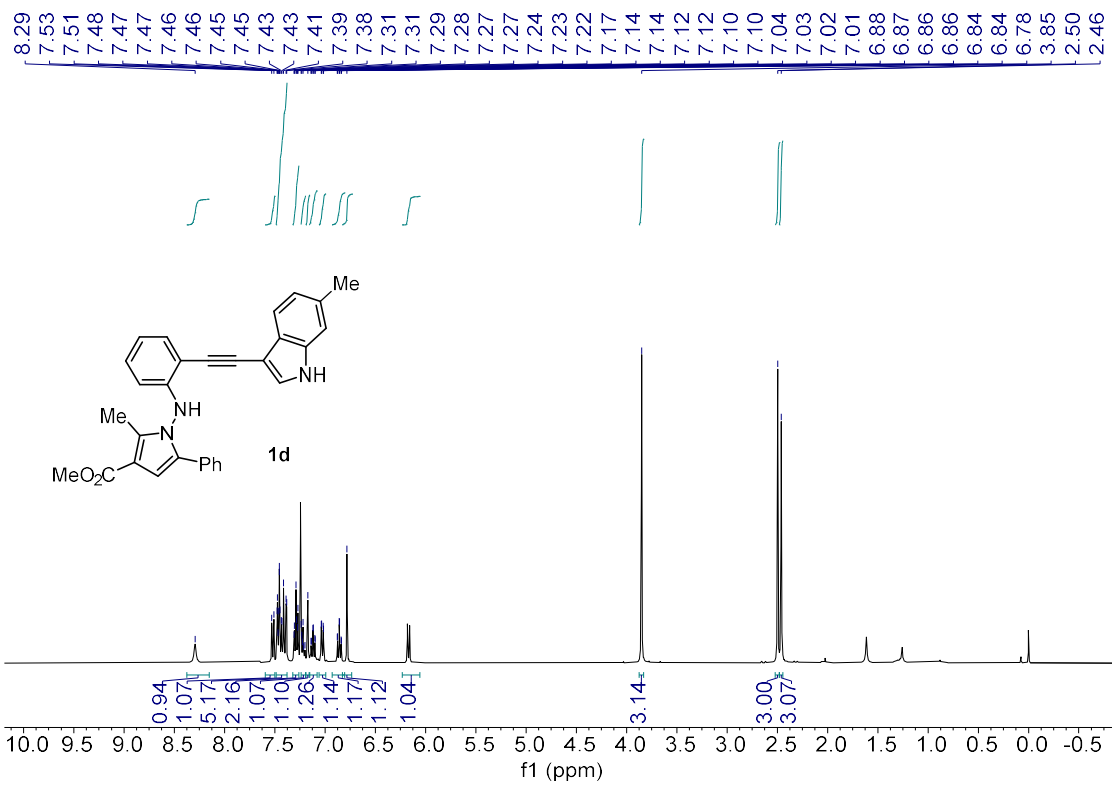
^{13}C NMR (101 MHz, $CDCl_3$) of **1b**



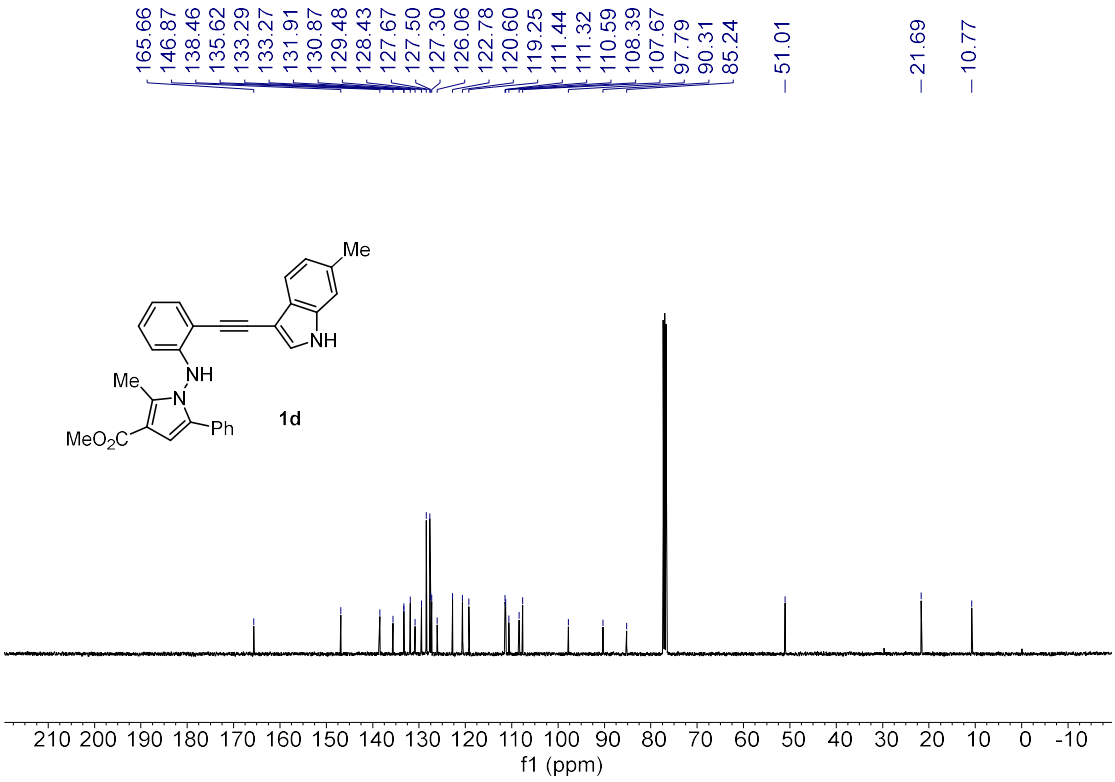
^{1}H NMR (400 MHz, $CDCl_3$) of **1c**



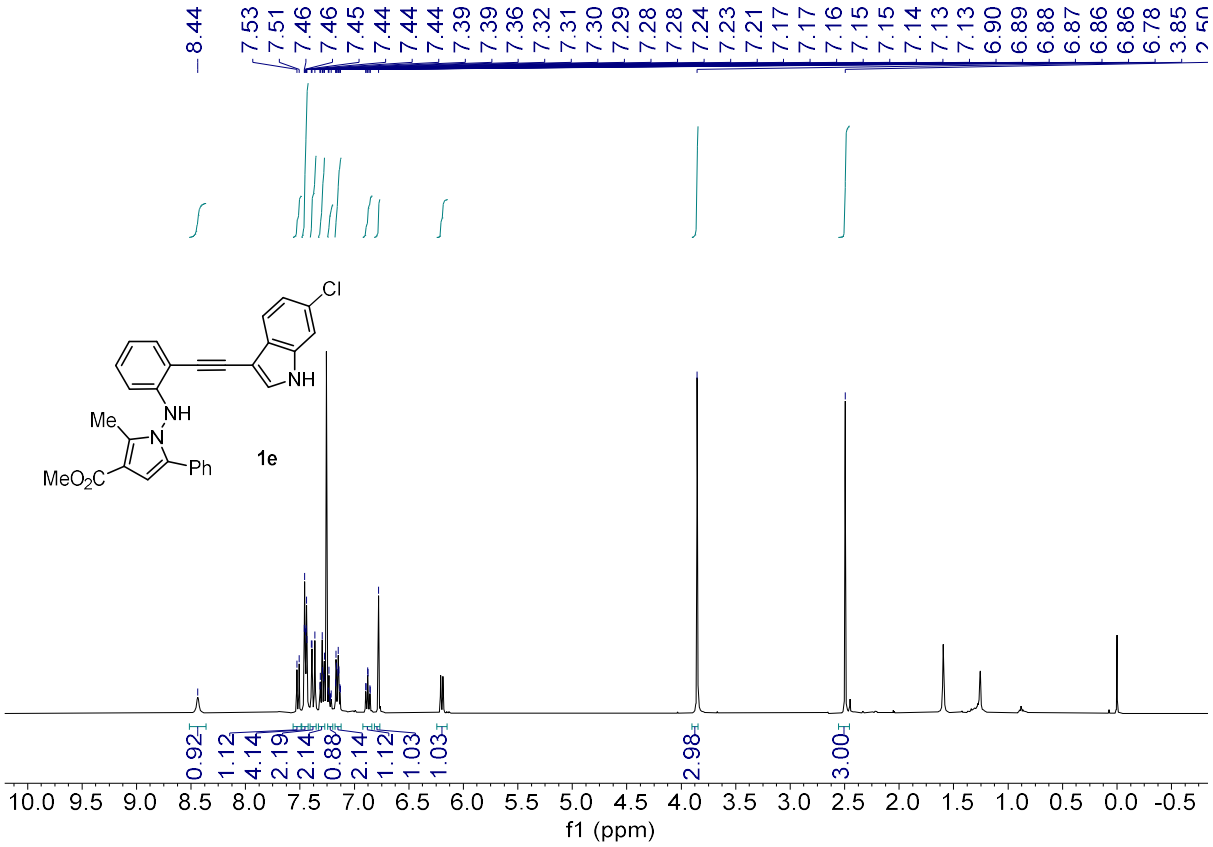
^{13}C NMR (101 MHz, $CDCl_3$) of **1c**



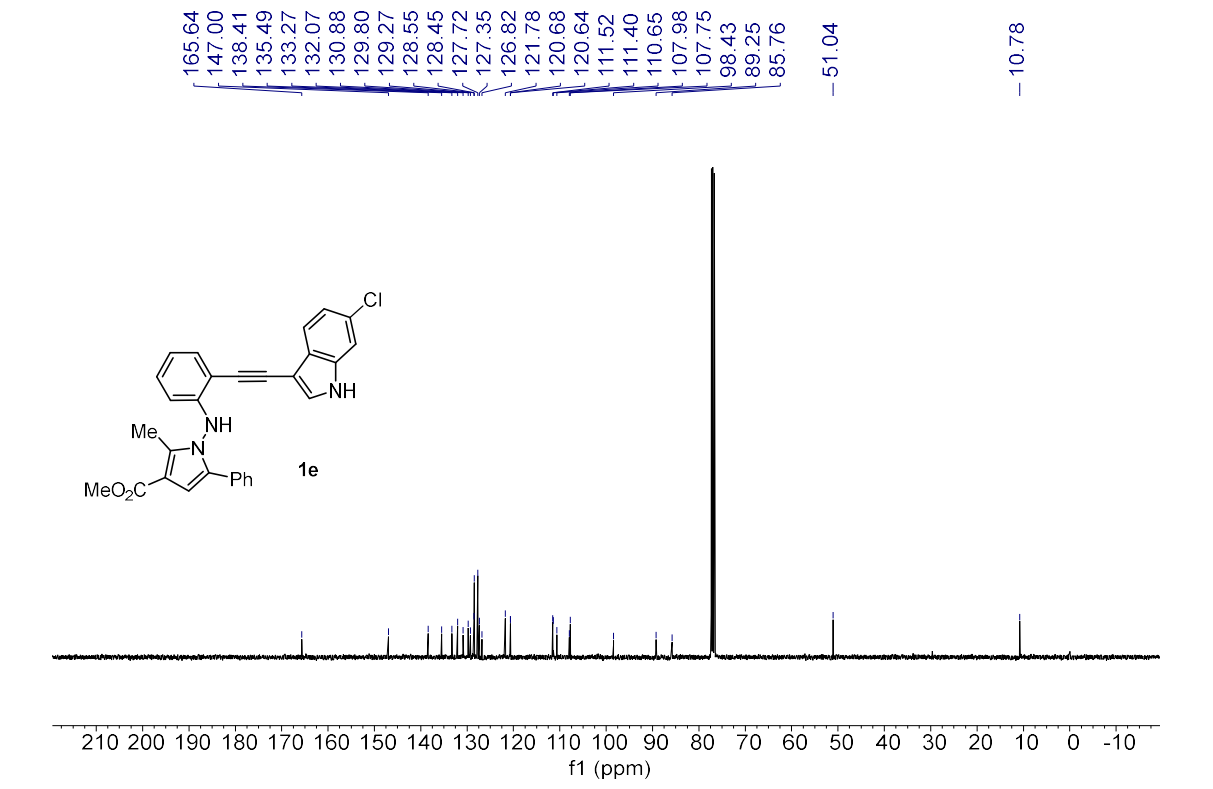
^{1}H NMR (400 MHz, $CDCl_3$) of **1d**



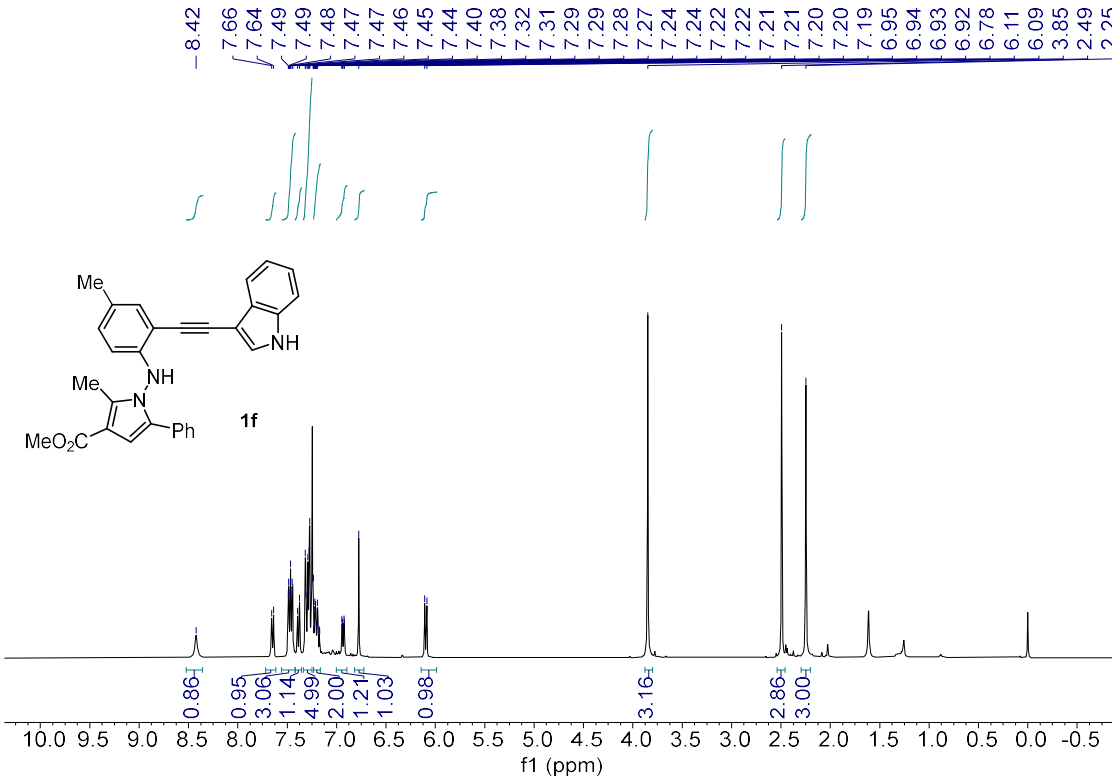
^{13}C NMR (101 MHz, $CDCl_3$) of **1d**



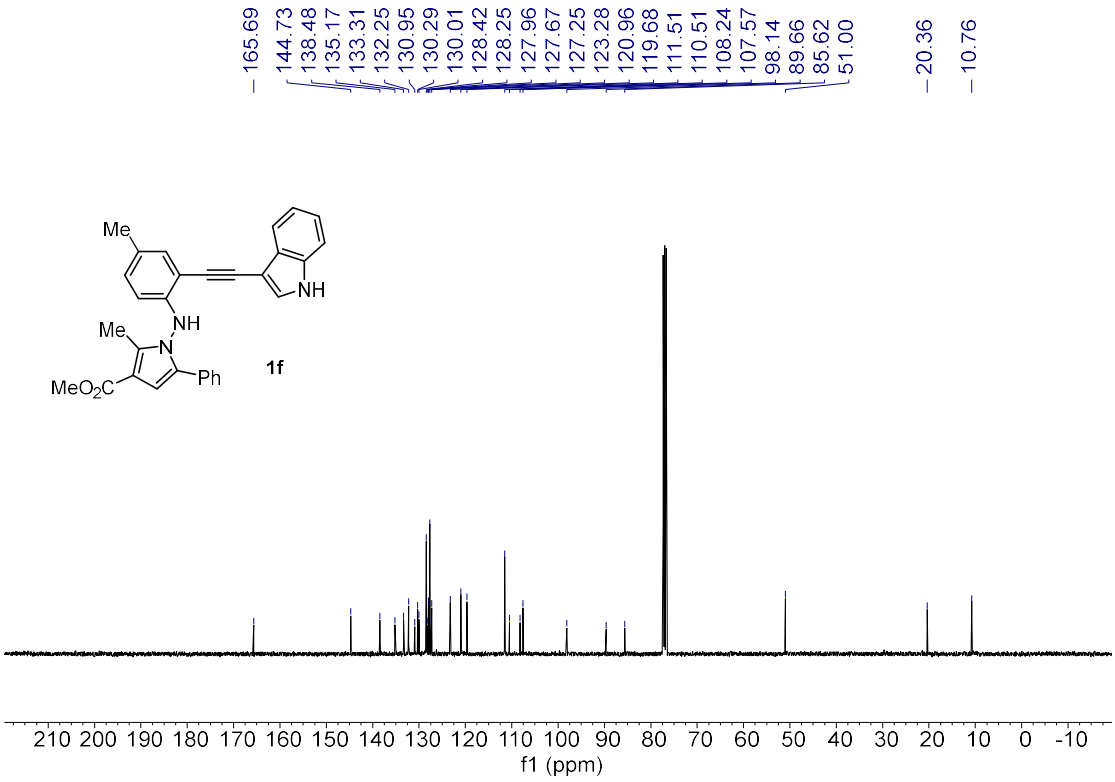
^{1}H NMR (400 MHz, $CDCl_3$) of **1e**



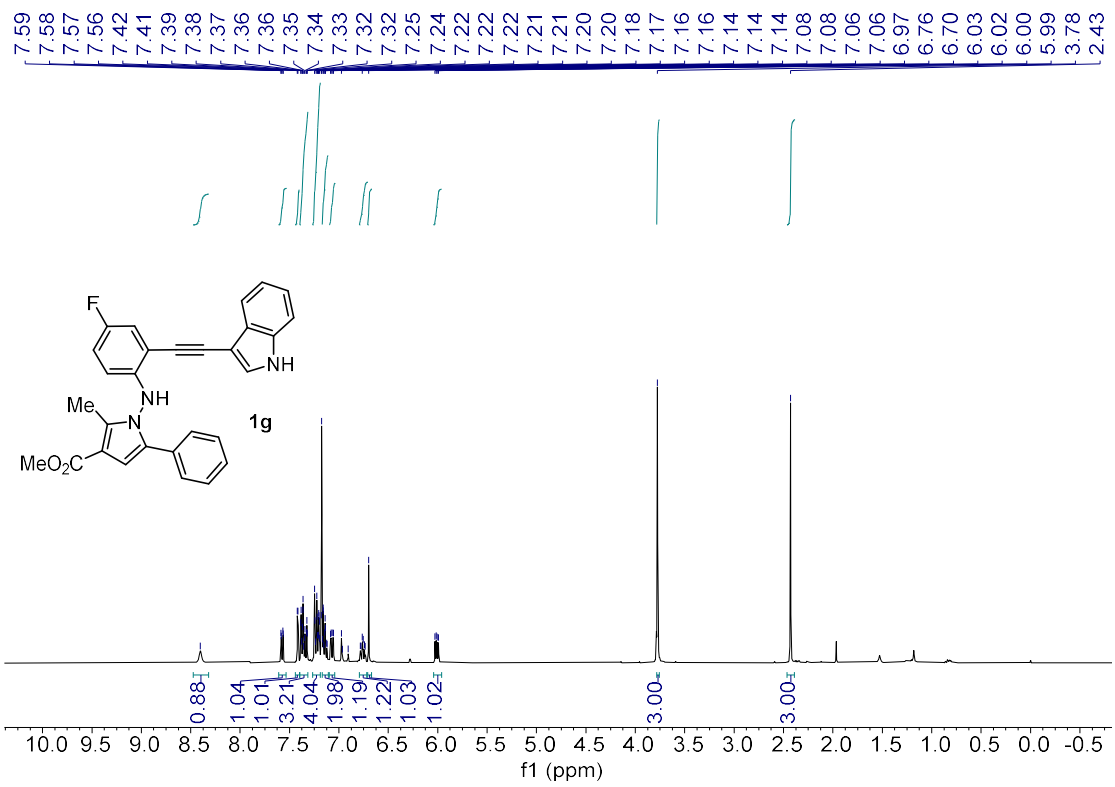
^{13}C NMR (101 MHz, $CDCl_3$) of **1e**



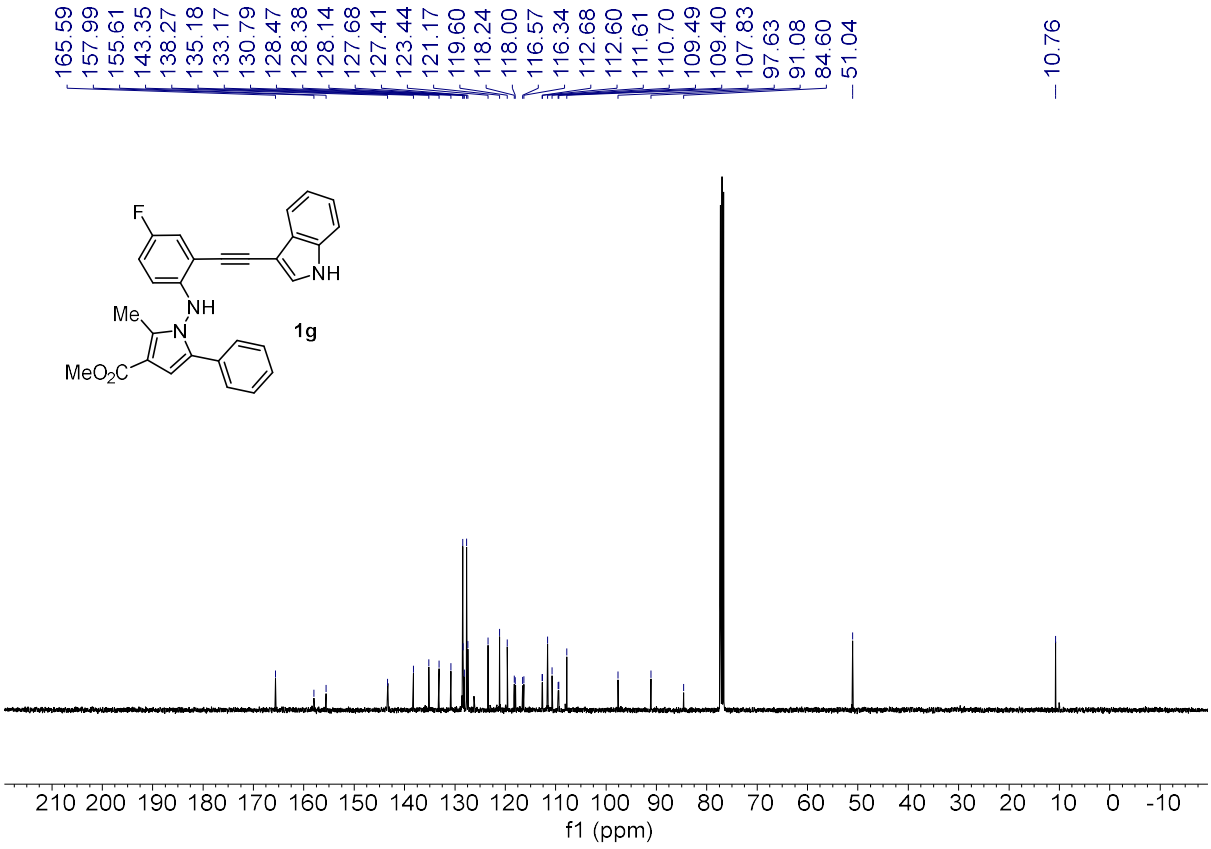
^{1}H NMR (400 MHz, $CDCl_3$) of **1f**



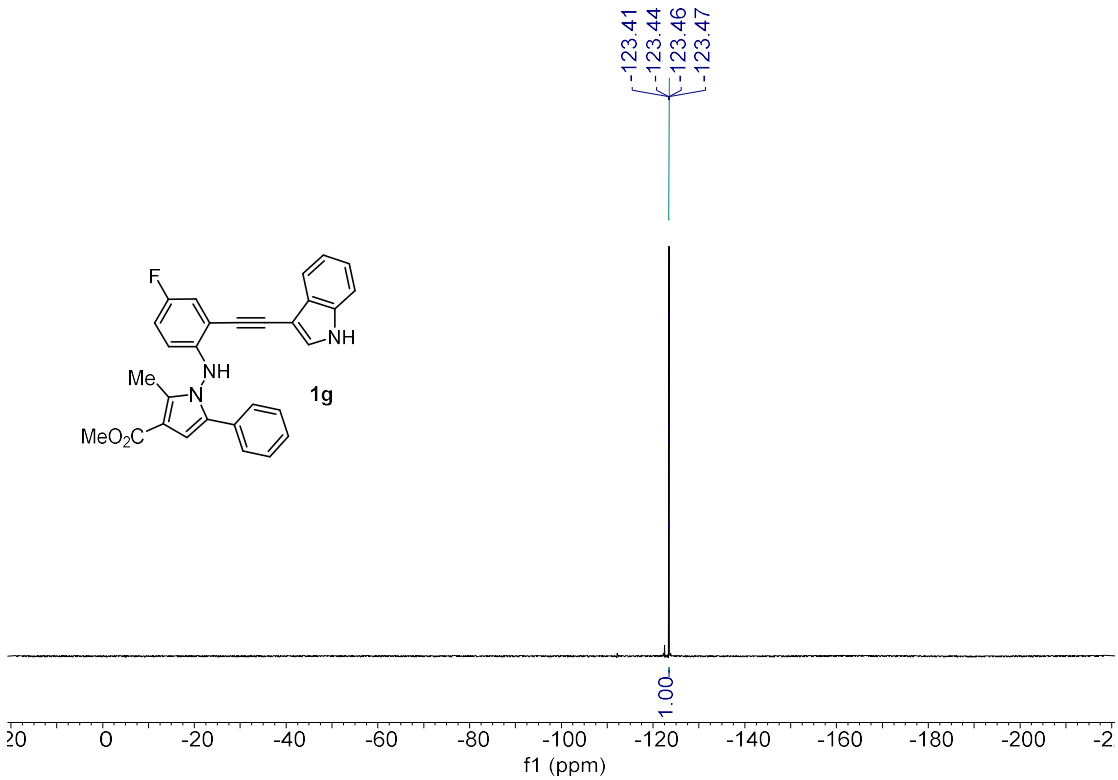
^{13}C NMR (101 MHz, $CDCl_3$) of **1f**



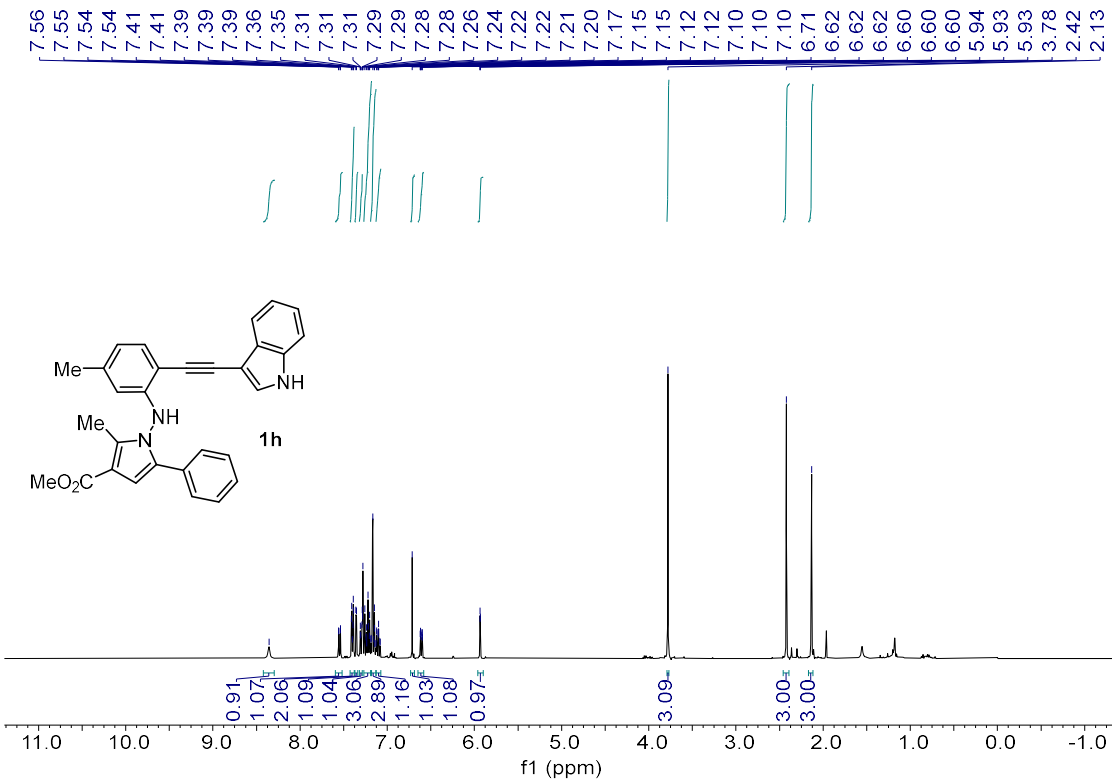
^{1}H NMR (400 MHz, $CDCl_3$) of **1g**



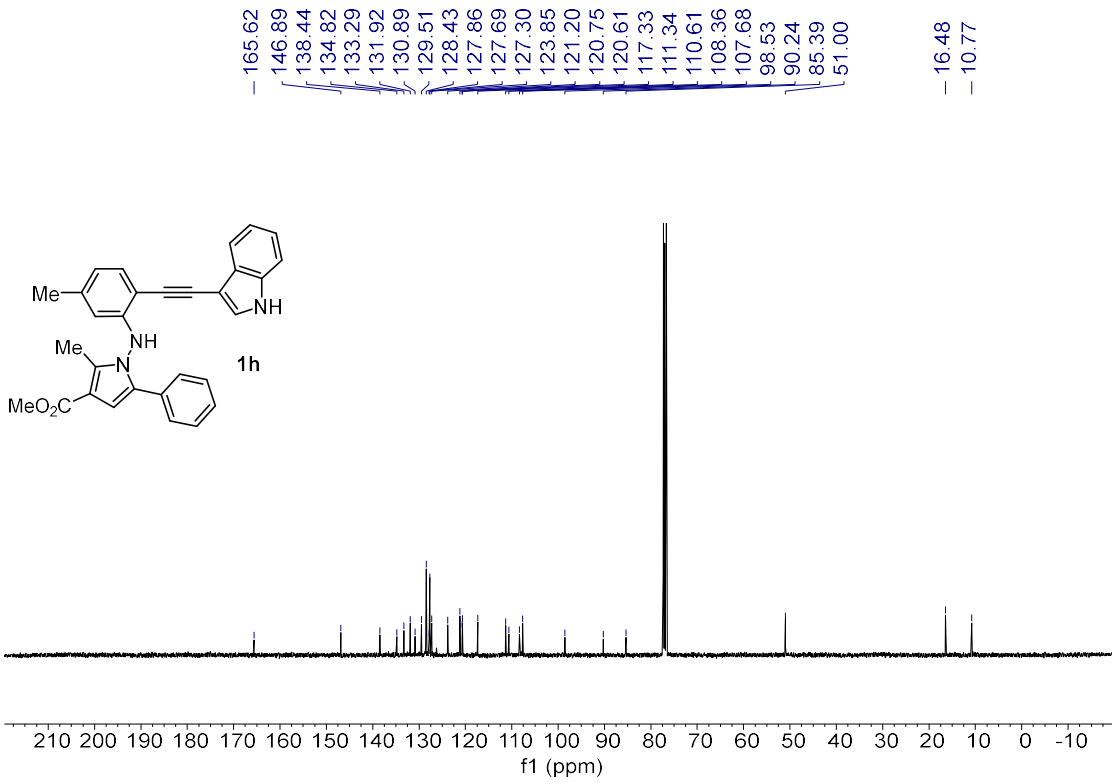
^{13}C NMR (101 MHz, $CDCl_3$) of **1g**



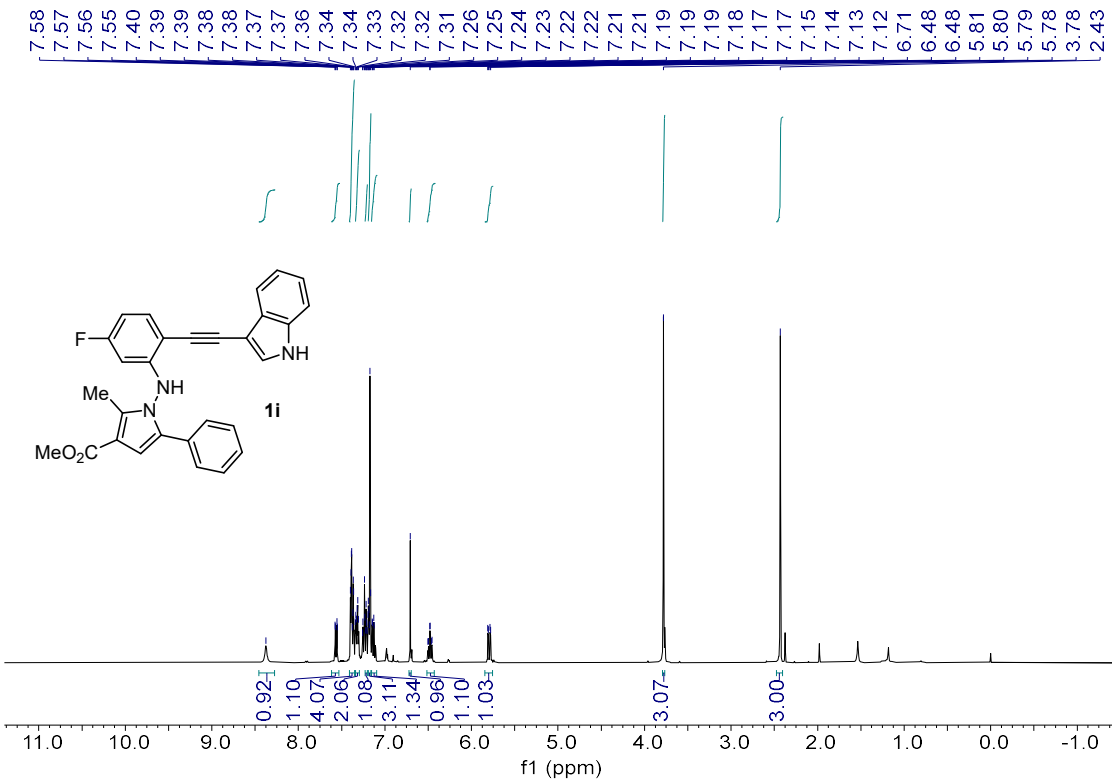
^{19}F NMR (376 MHz, $CDCl_3$) of **1g**



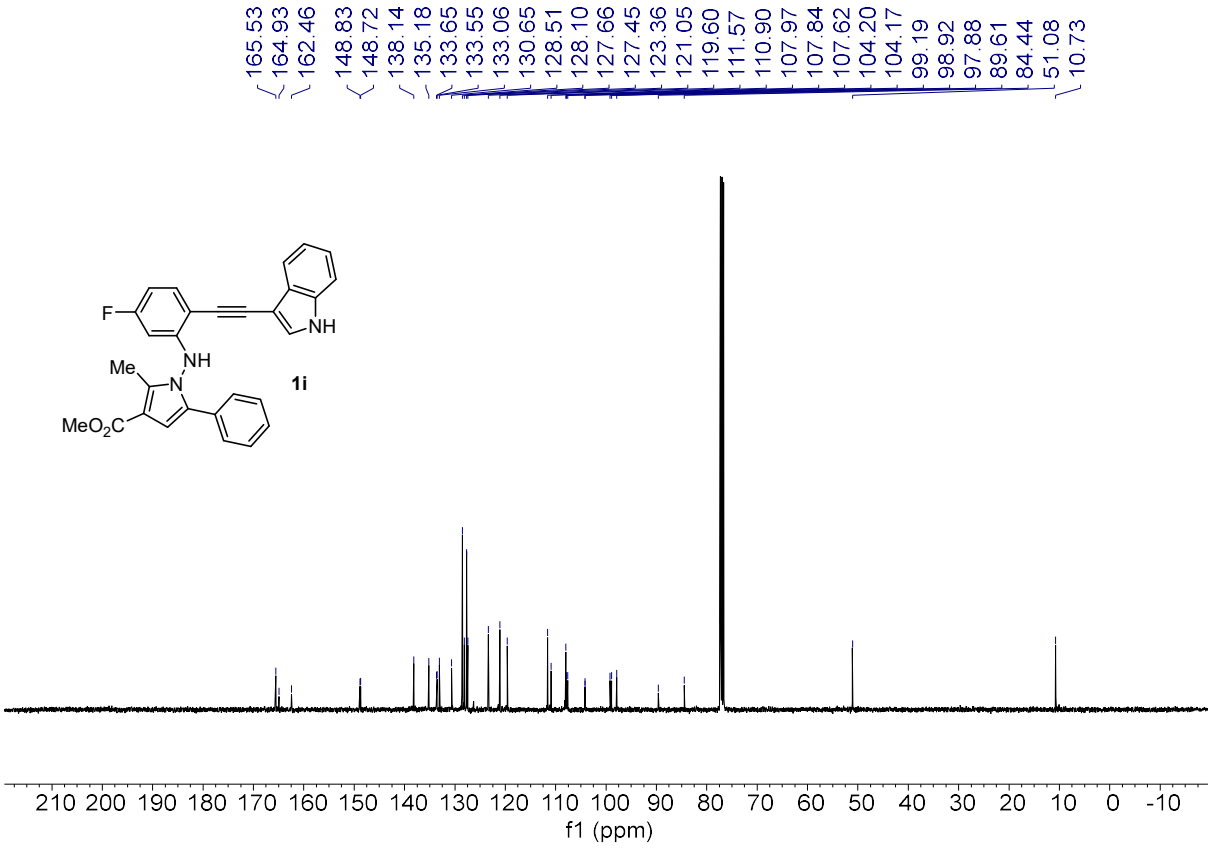
^{1}H NMR (400 MHz, $CDCl_3$) of **1h**



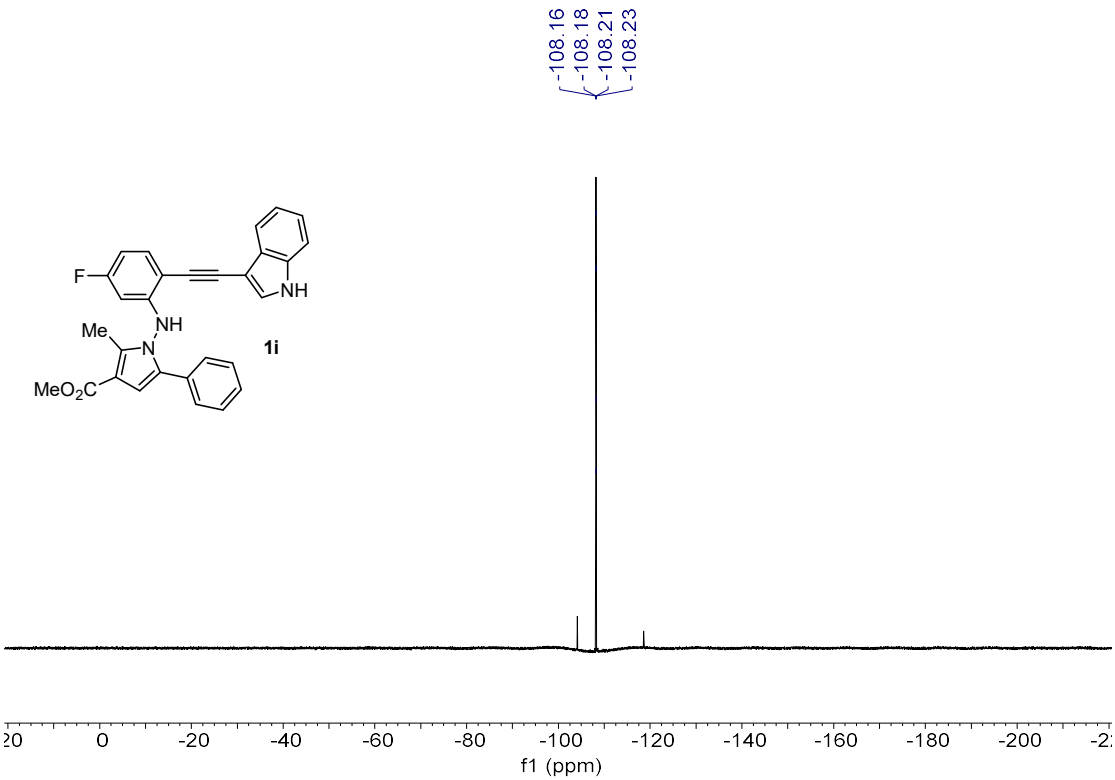
^{13}C NMR (101 MHz, $CDCl_3$) of **1h**



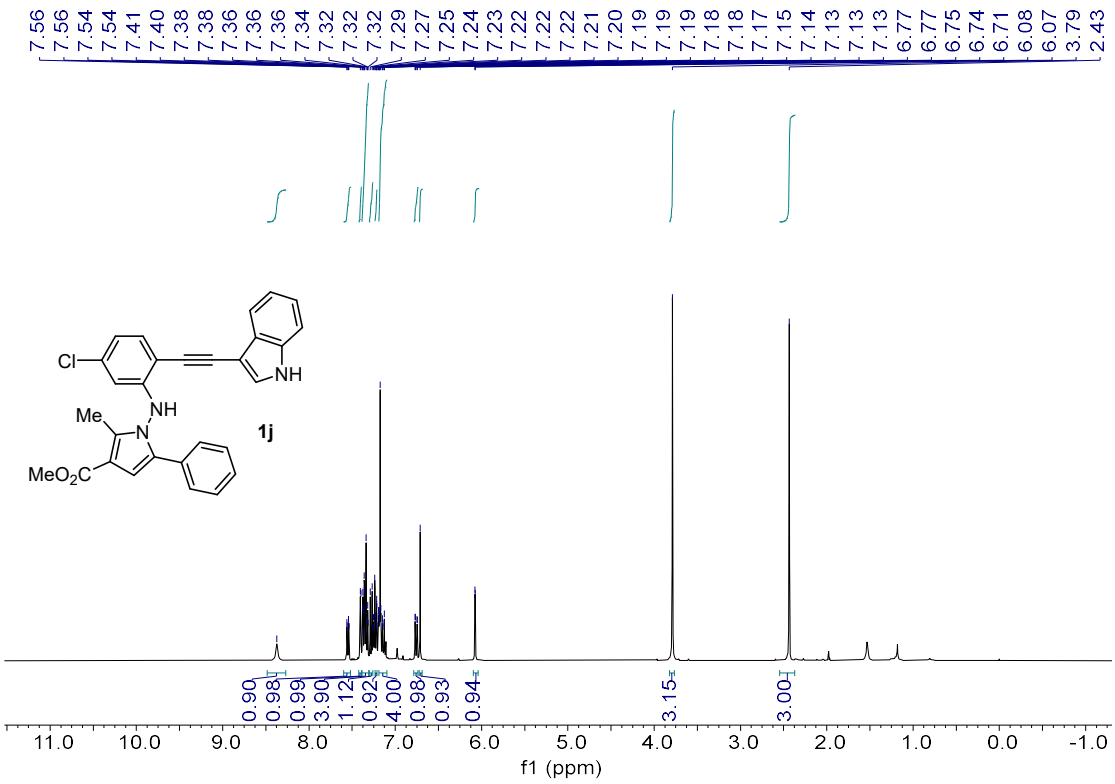
^{1}H NMR (400 MHz, $CDCl_3$) of **1i**



^{13}C NMR (101 MHz, $CDCl_3$) of **1i**



^{19}F NMR (376 MHz, $CDCl_3$) of **1i**



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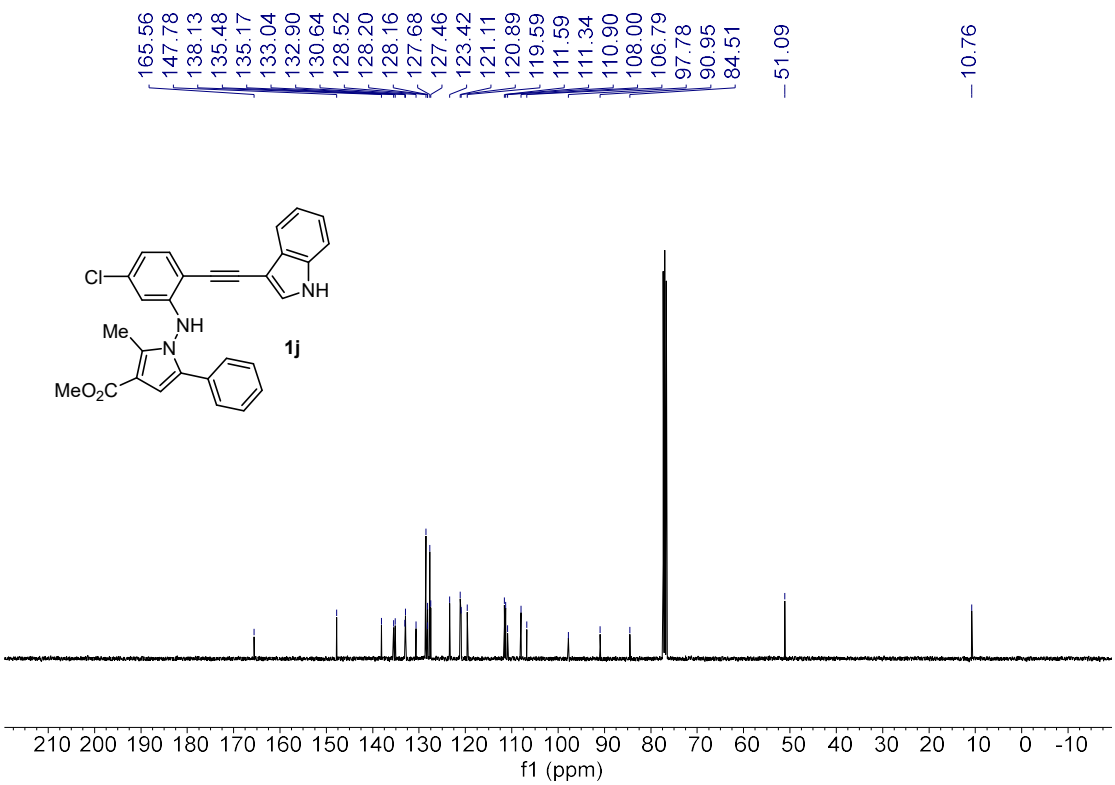
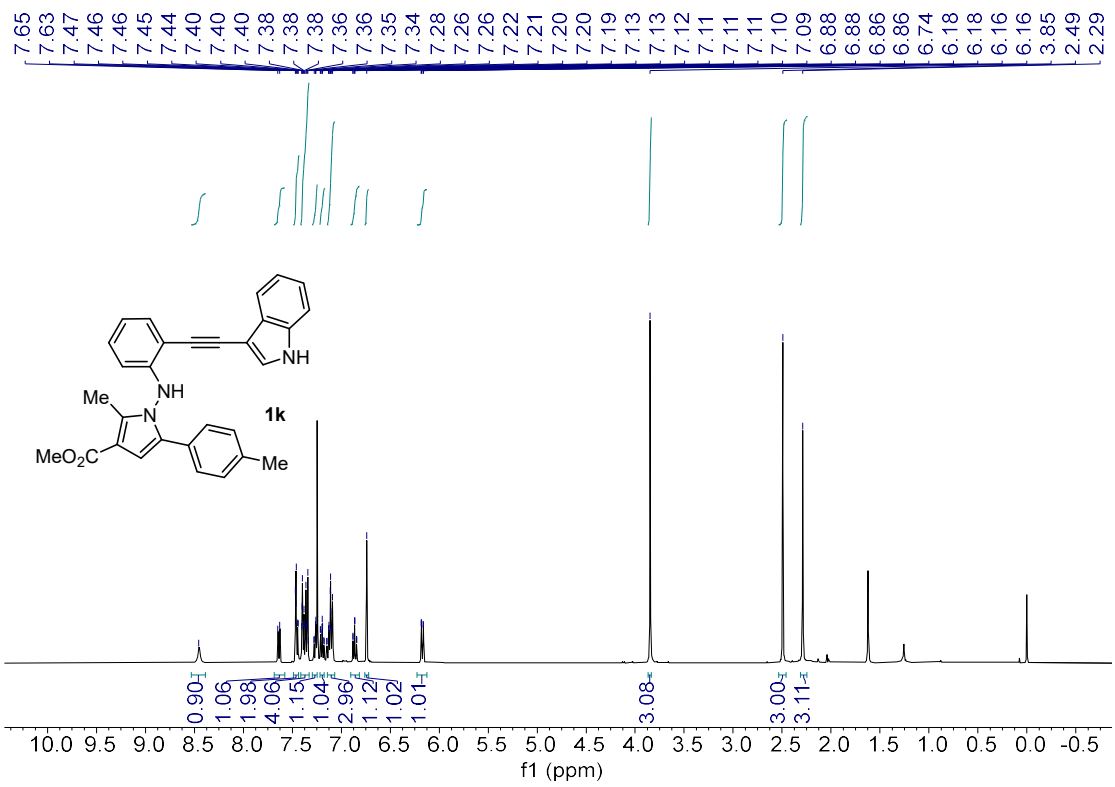
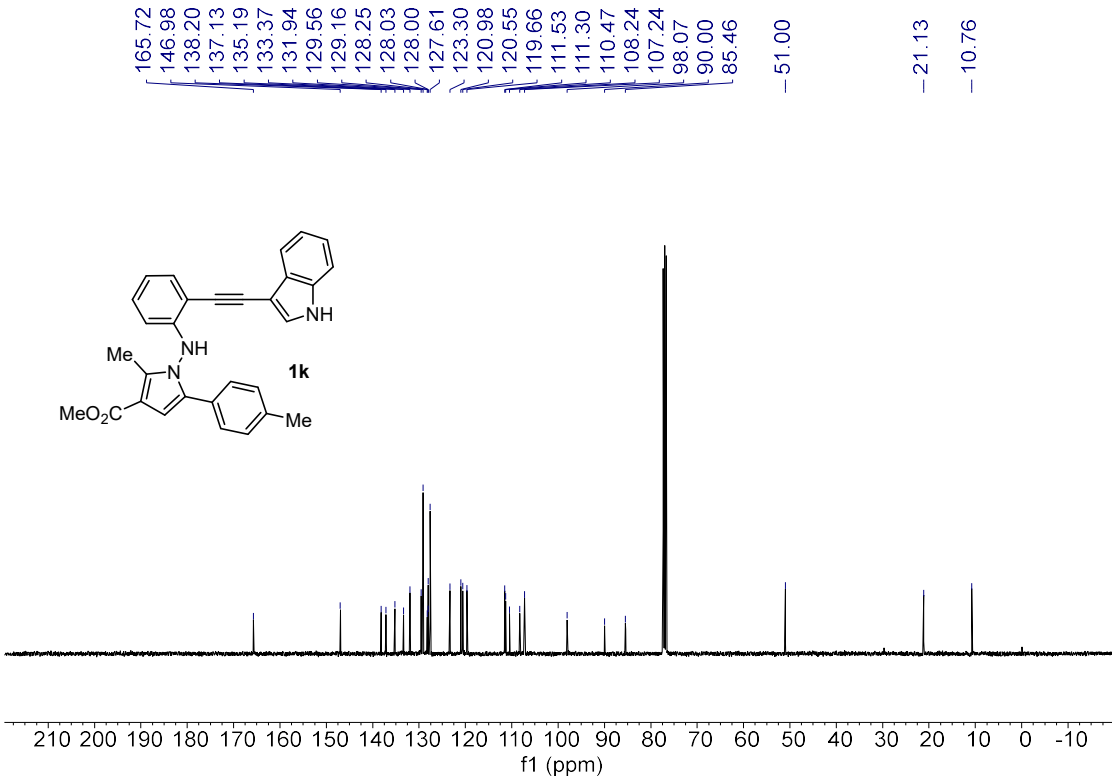


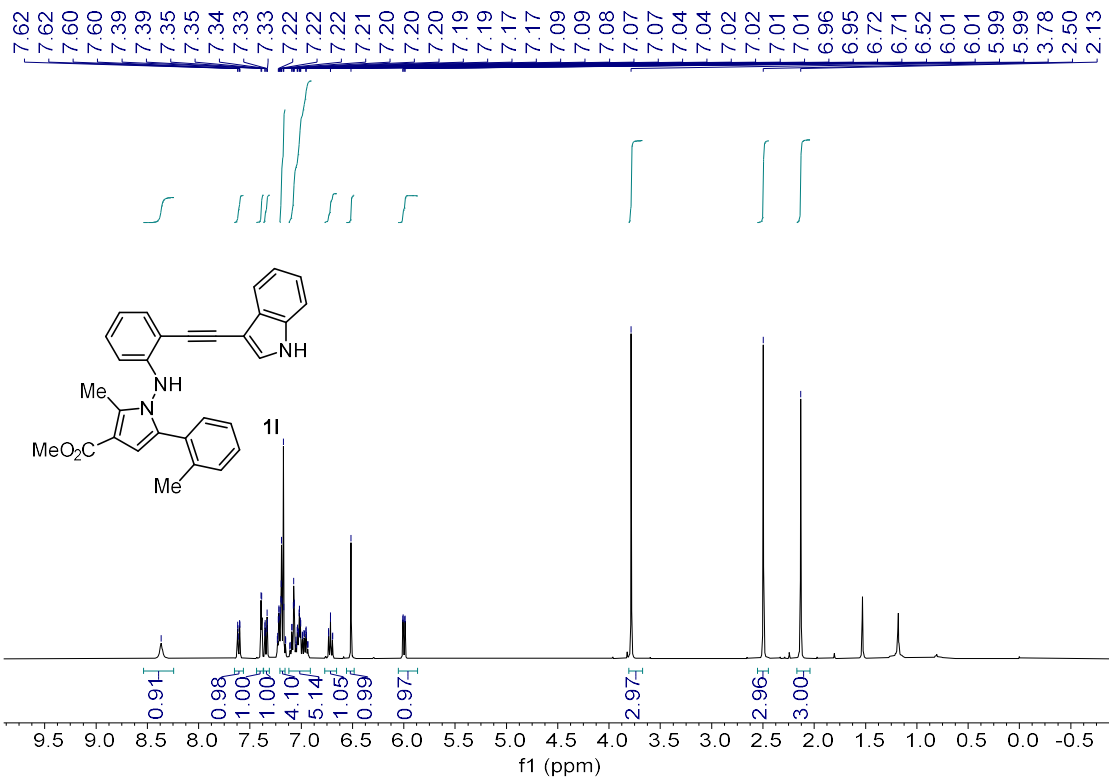
^{13}C NMR (101 MHz, $CDCl_3$) of **1j**



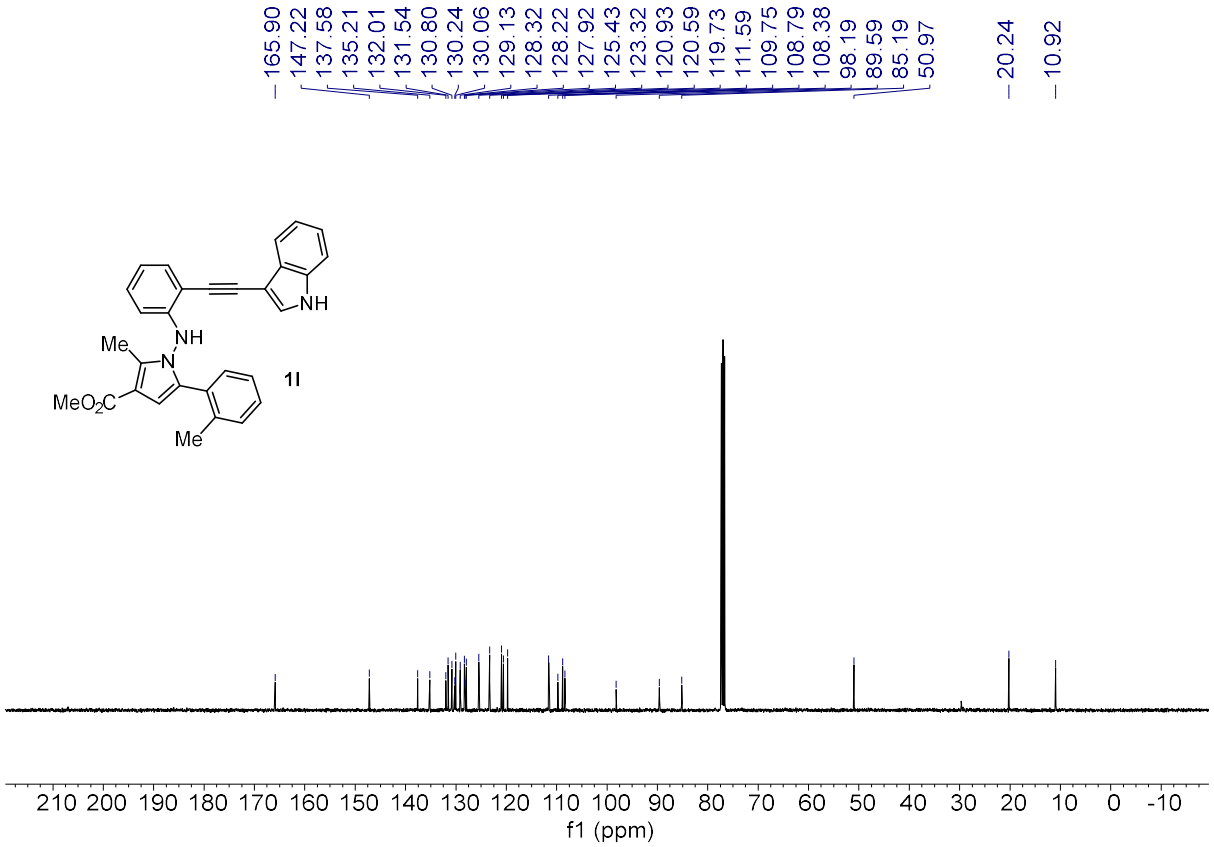
^{1}H NMR (400 MHz, $CDCl_3$) of **1k**



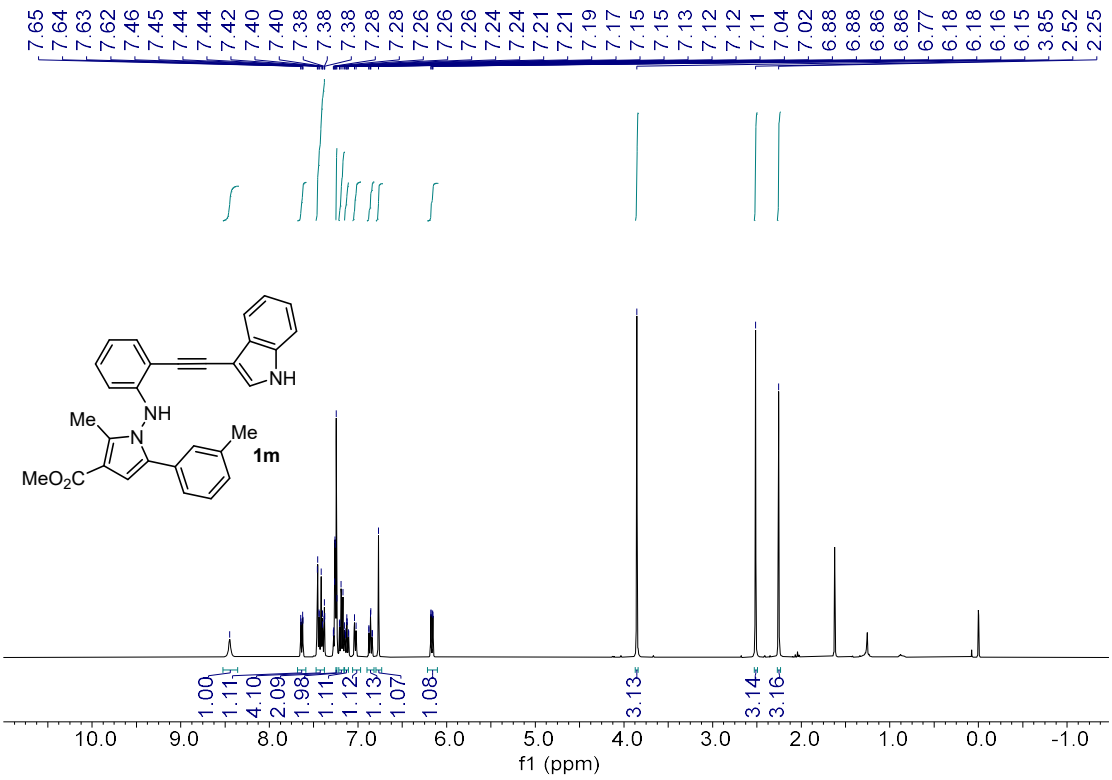
^{13}C NMR (101 MHz, $CDCl_3$) of **1k**



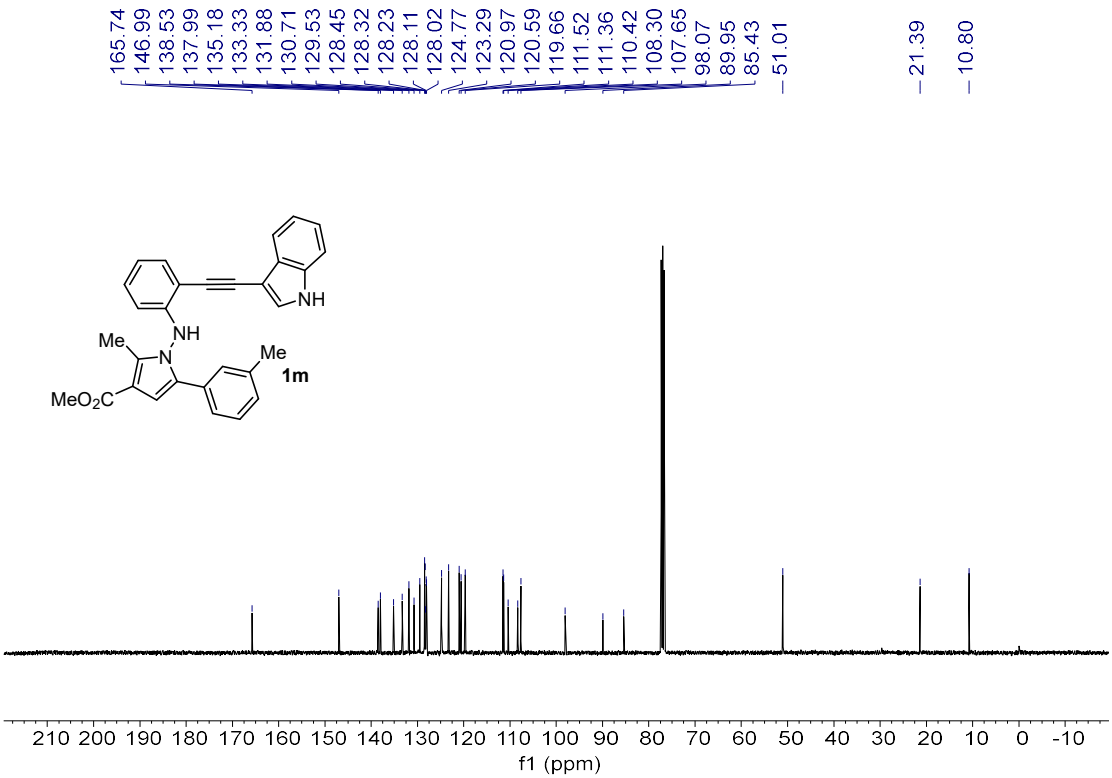
^{1}H NMR (400 MHz, $CDCl_3$) of **1l**



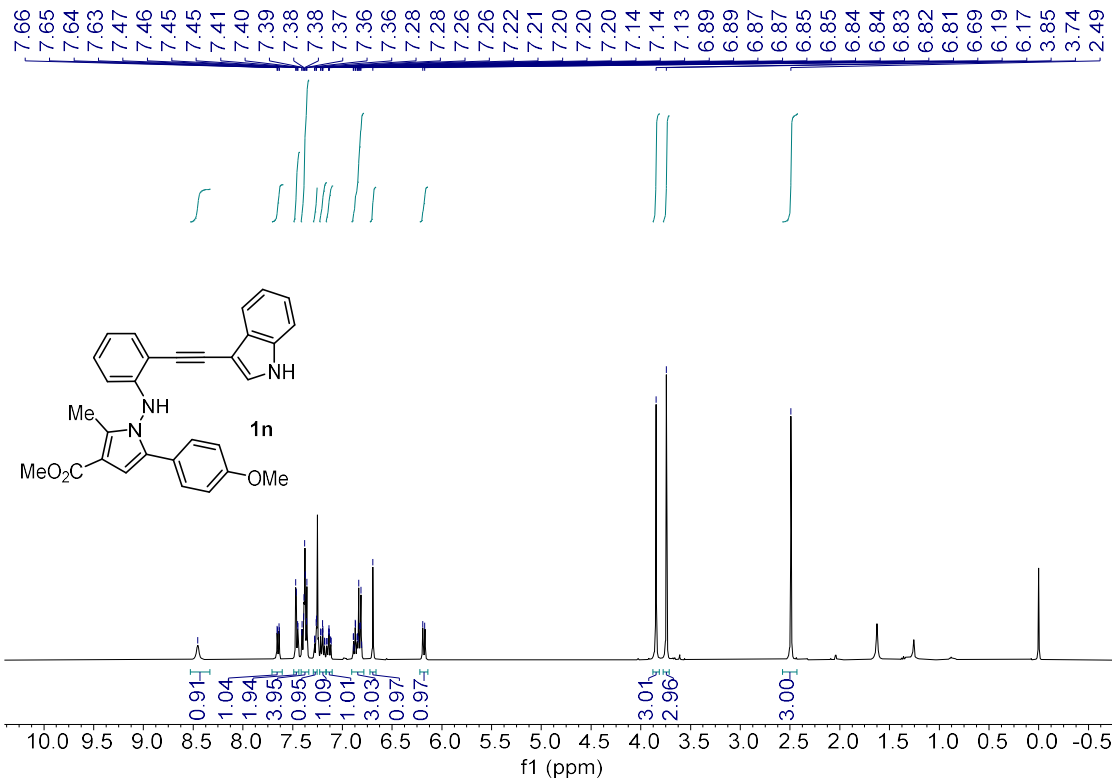
^{13}C NMR (101 MHz, $CDCl_3$) of **1l**



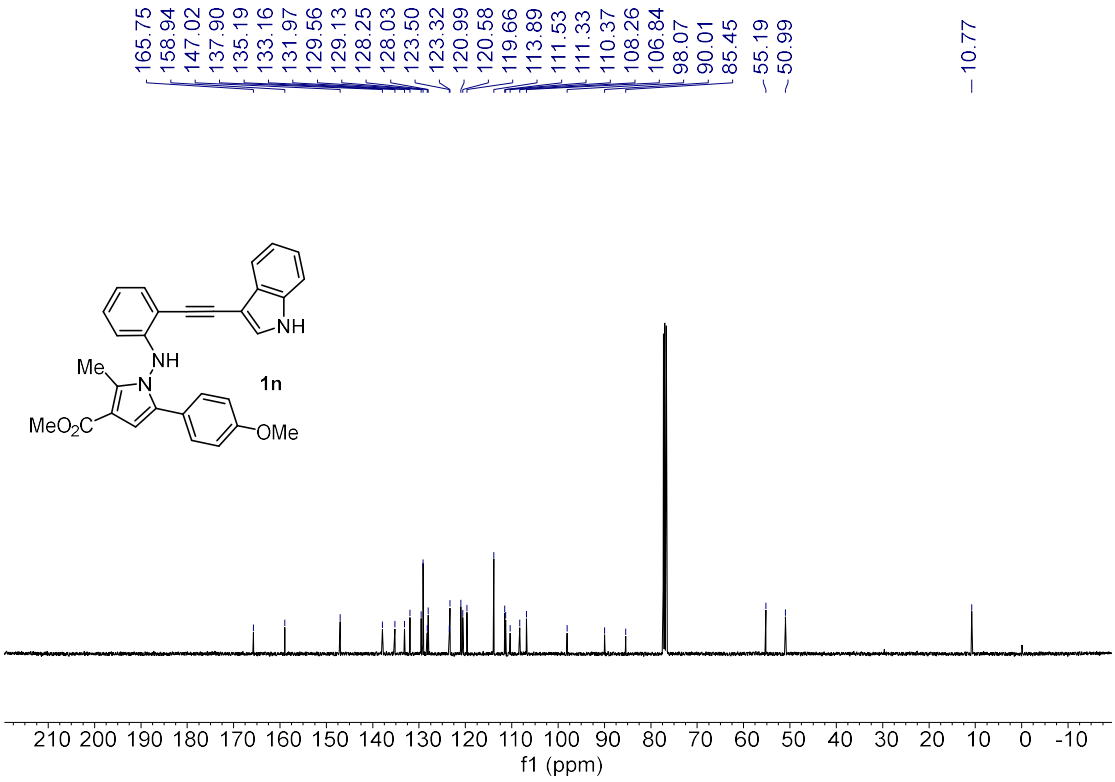
^{1}H NMR (400 MHz, $CDCl_3$) of **1m**



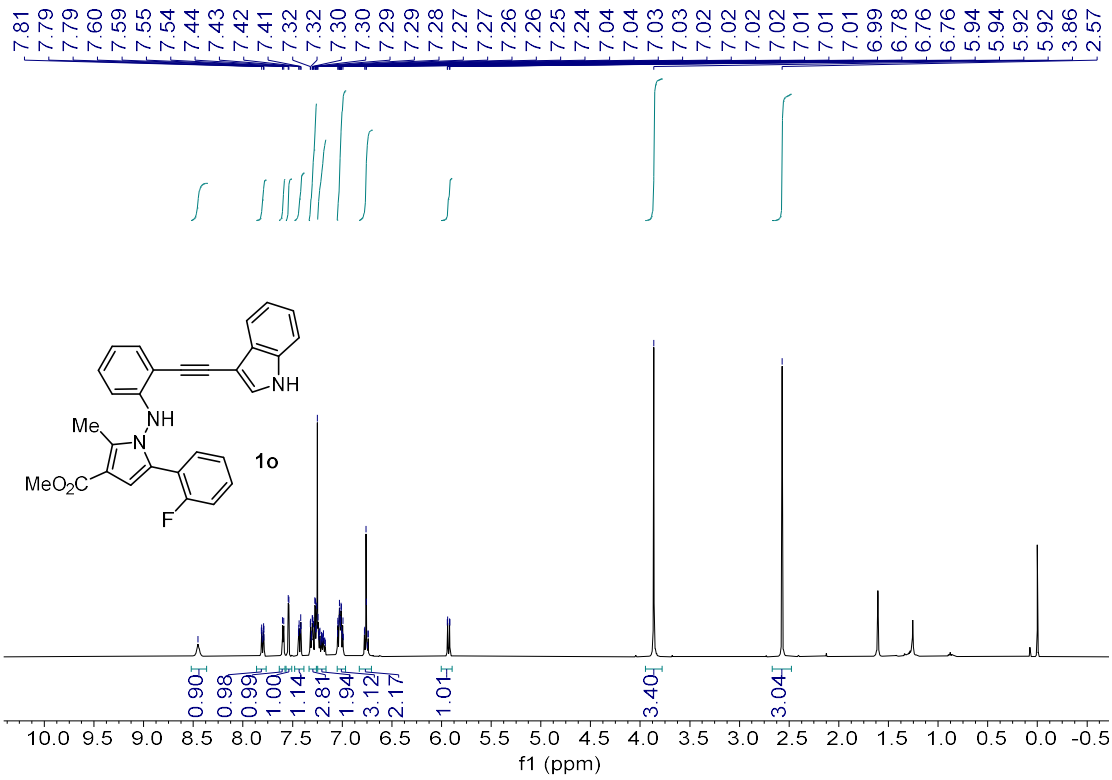
^{13}C NMR (101 MHz, $CDCl_3$) of **1m**



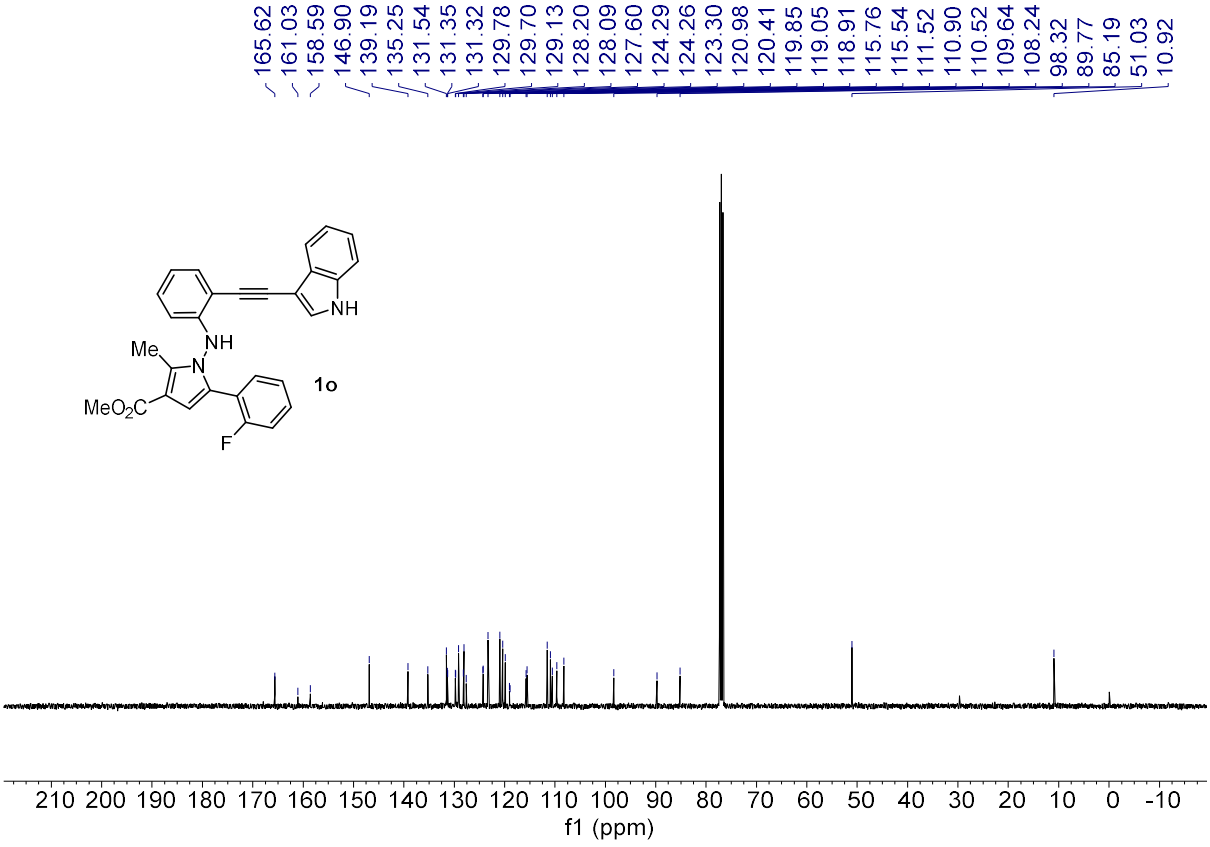
^{1}H NMR (400 MHz, $CDCl_3$) of **1n**



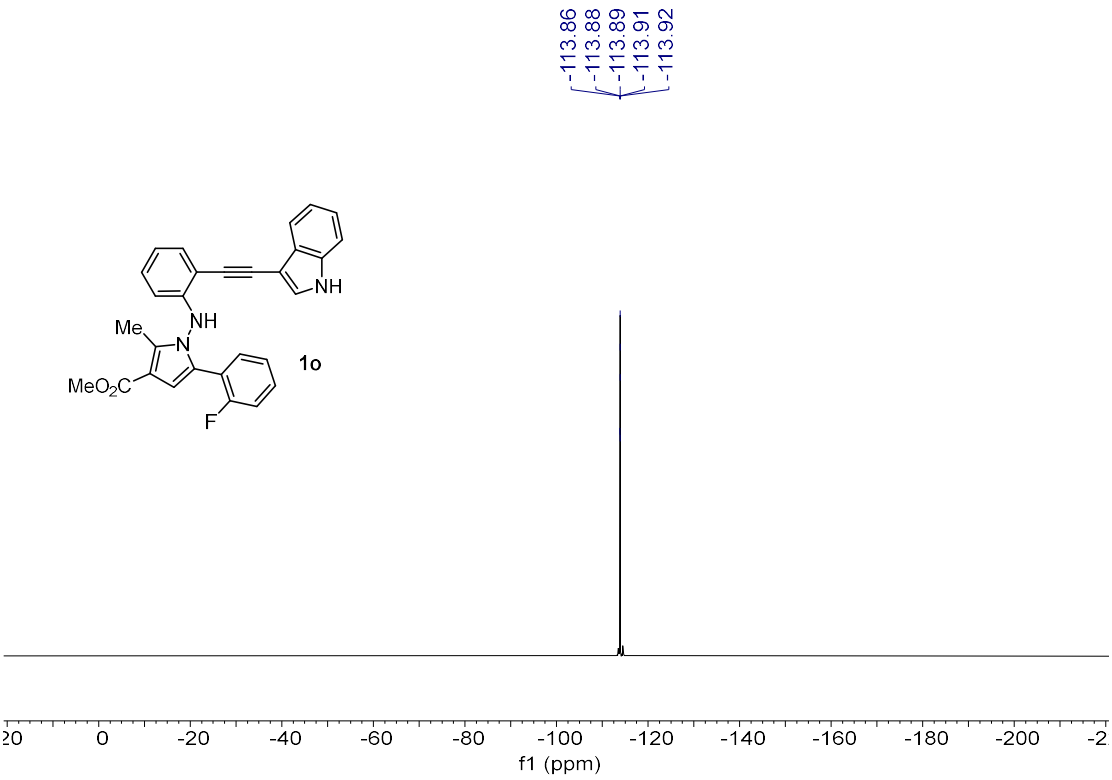
^{13}C NMR (101 MHz, $CDCl_3$) of **1n**



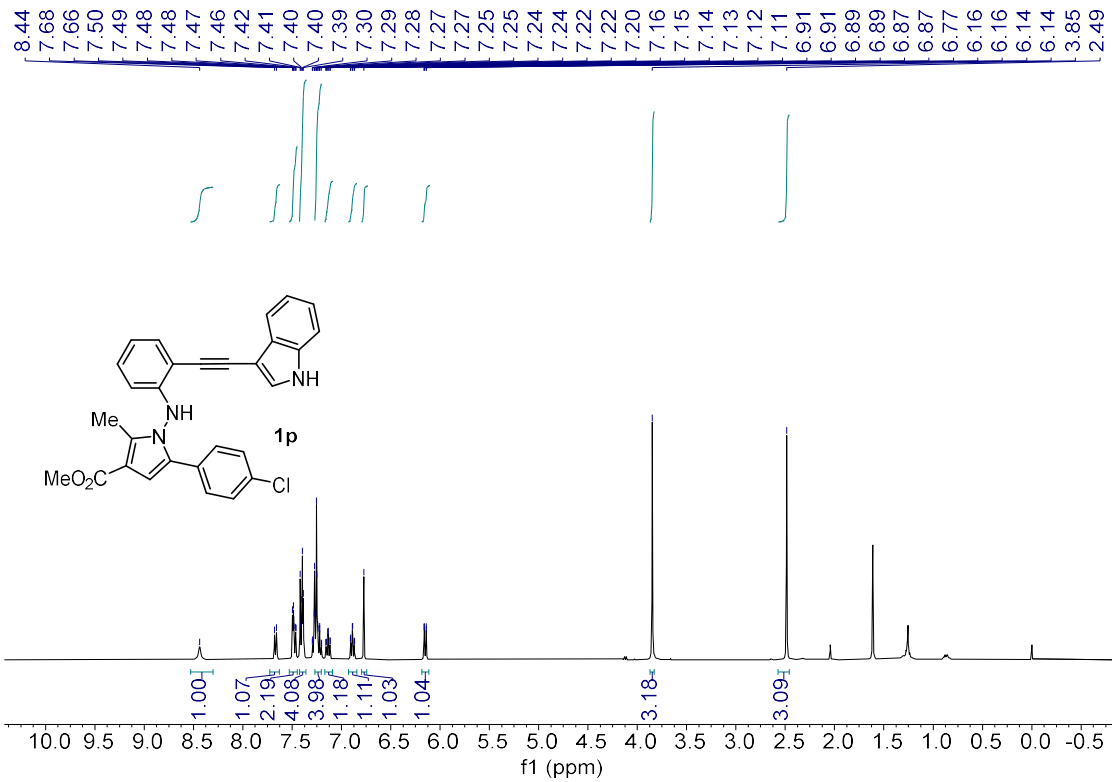
^{1}H NMR (400 MHz, $CDCl_3$) of **1o**



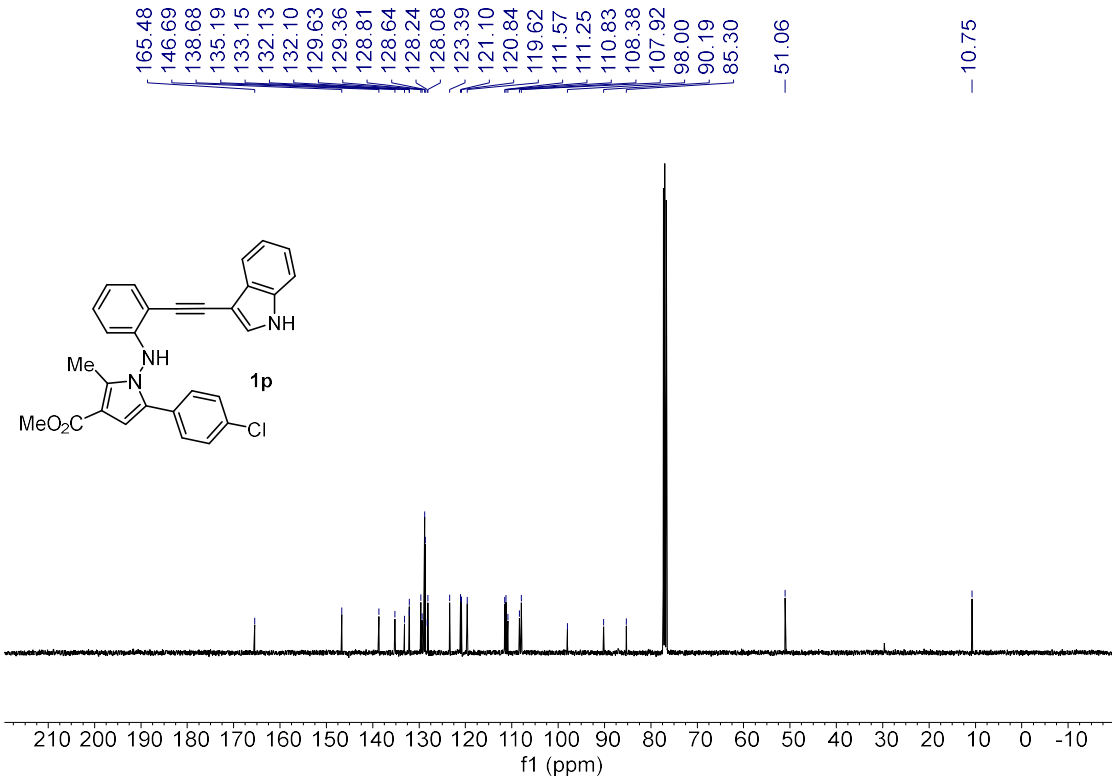
^{13}C NMR (101 MHz, $CDCl_3$) of **1o**



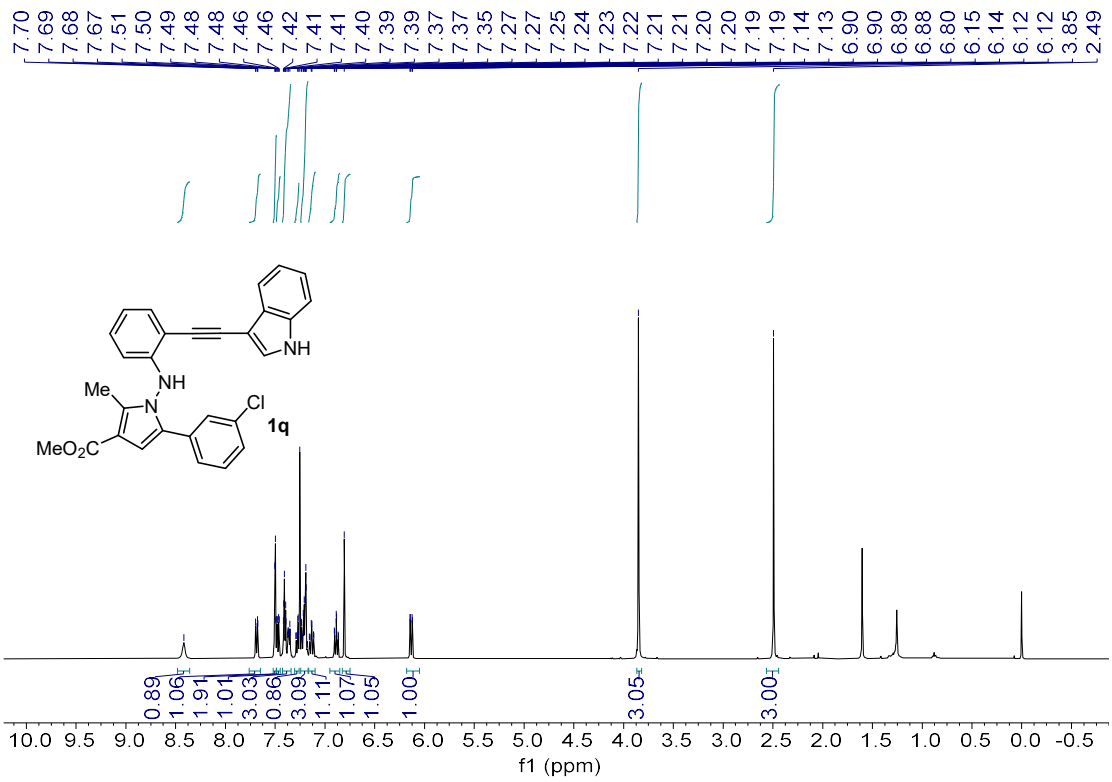
^{19}F NMR (376 MHz, $CDCl_3$) of **1o**



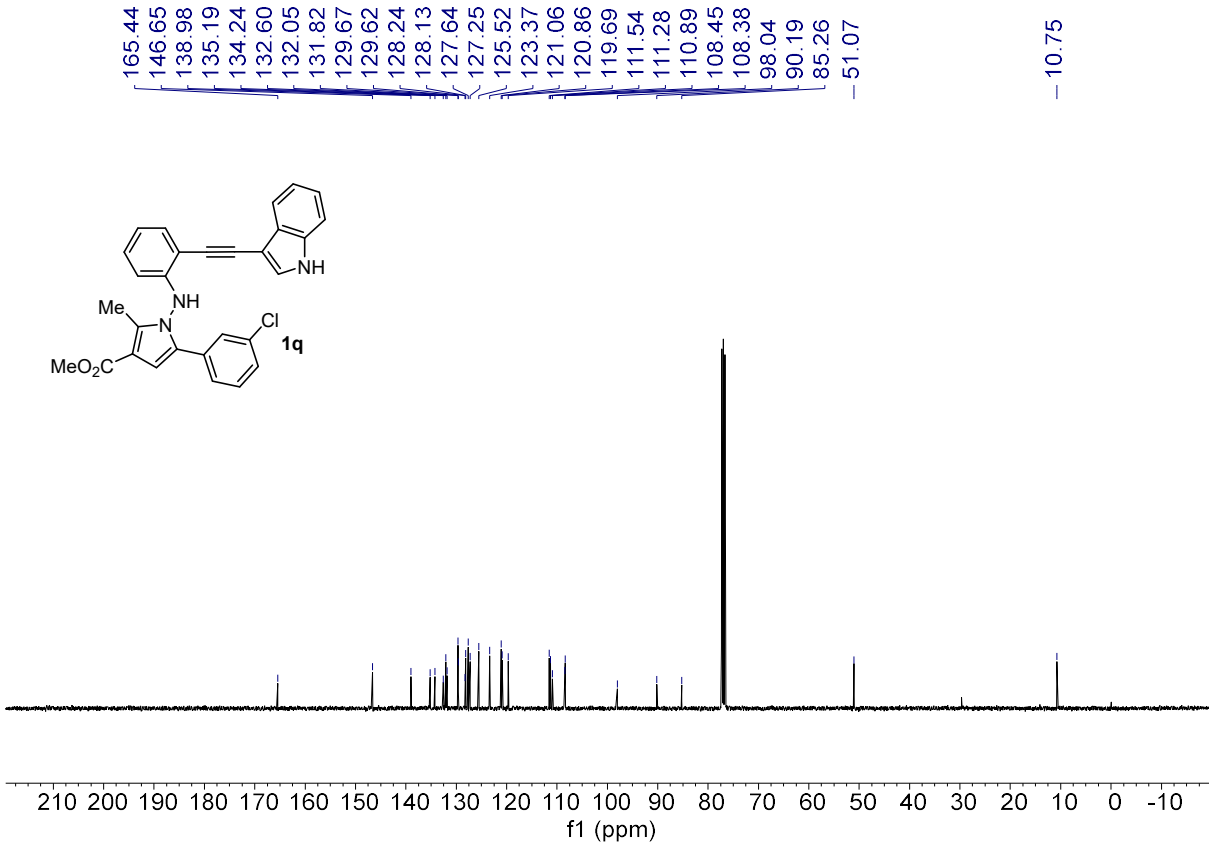
^{1}H NMR (400 MHz, $CDCl_3$) of **1p**



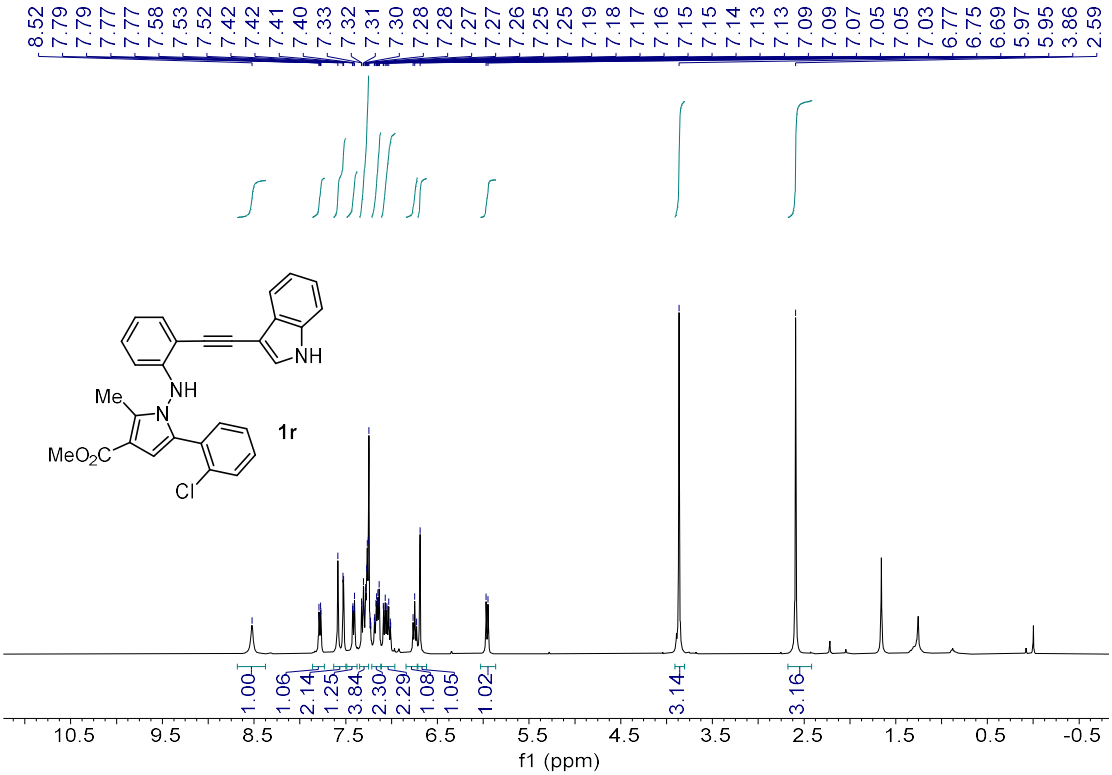
^{13}C NMR (101 MHz, $CDCl_3$) of **1p**



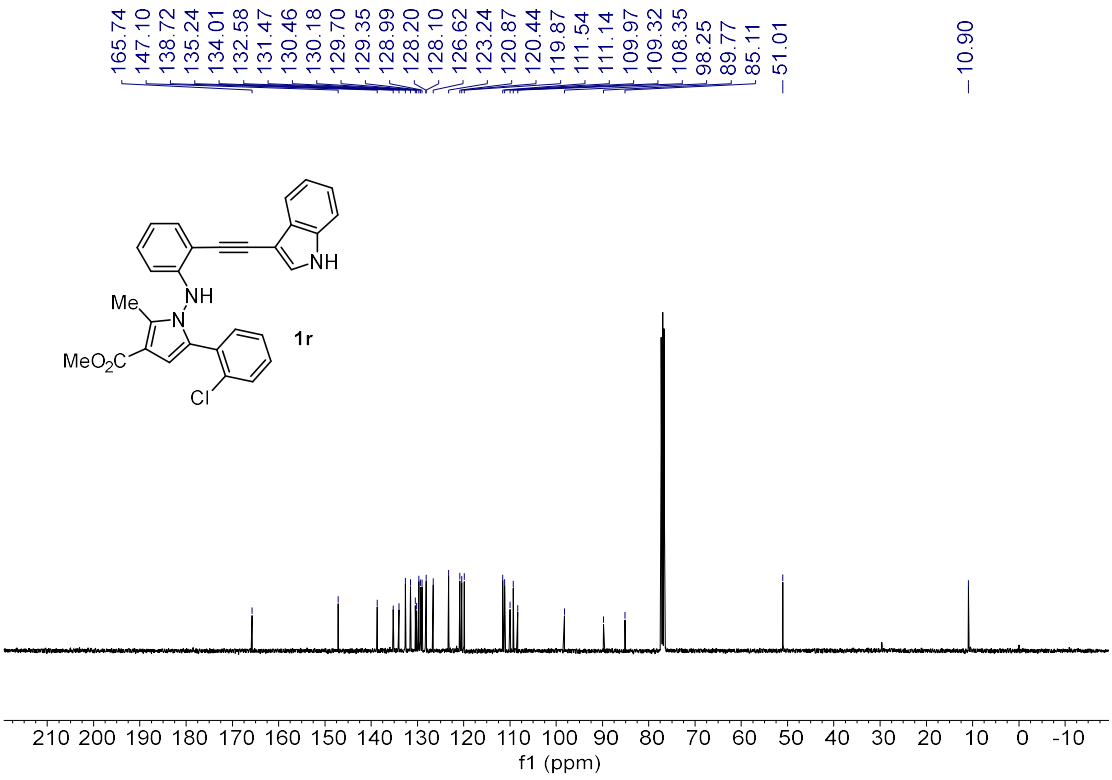
^{1}H NMR (400 MHz, $CDCl_3$) of **1q**



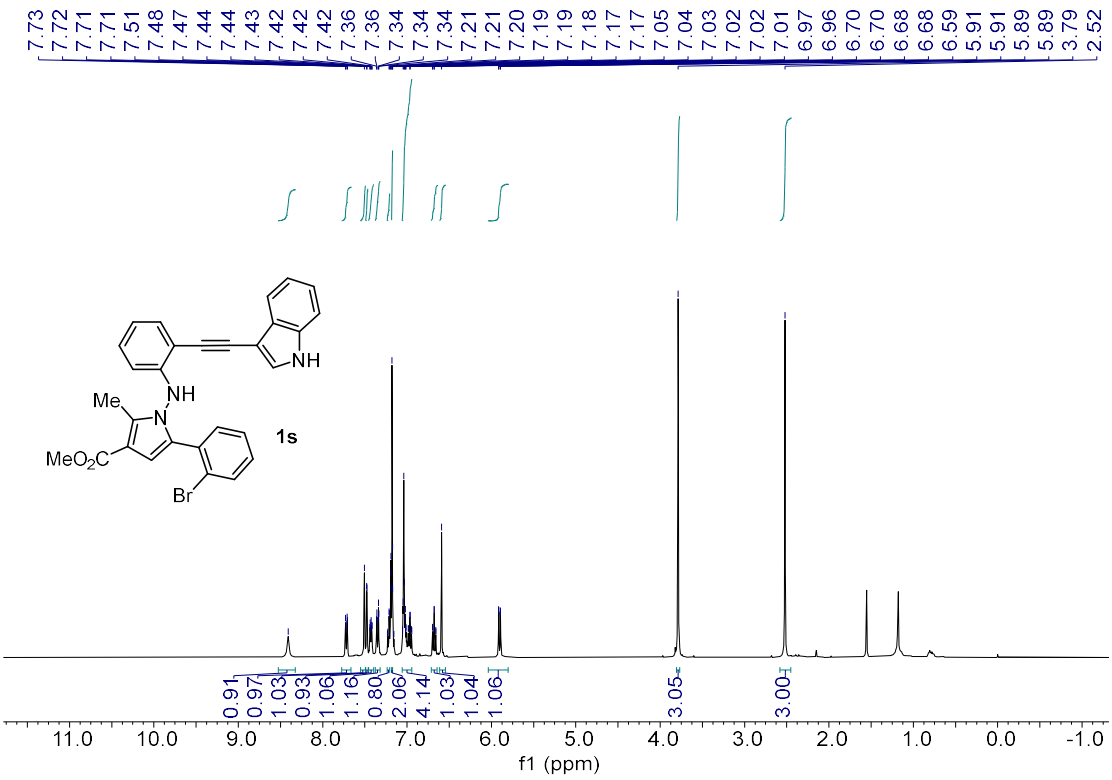
^{13}C NMR (101 MHz, $CDCl_3$) of **1q**



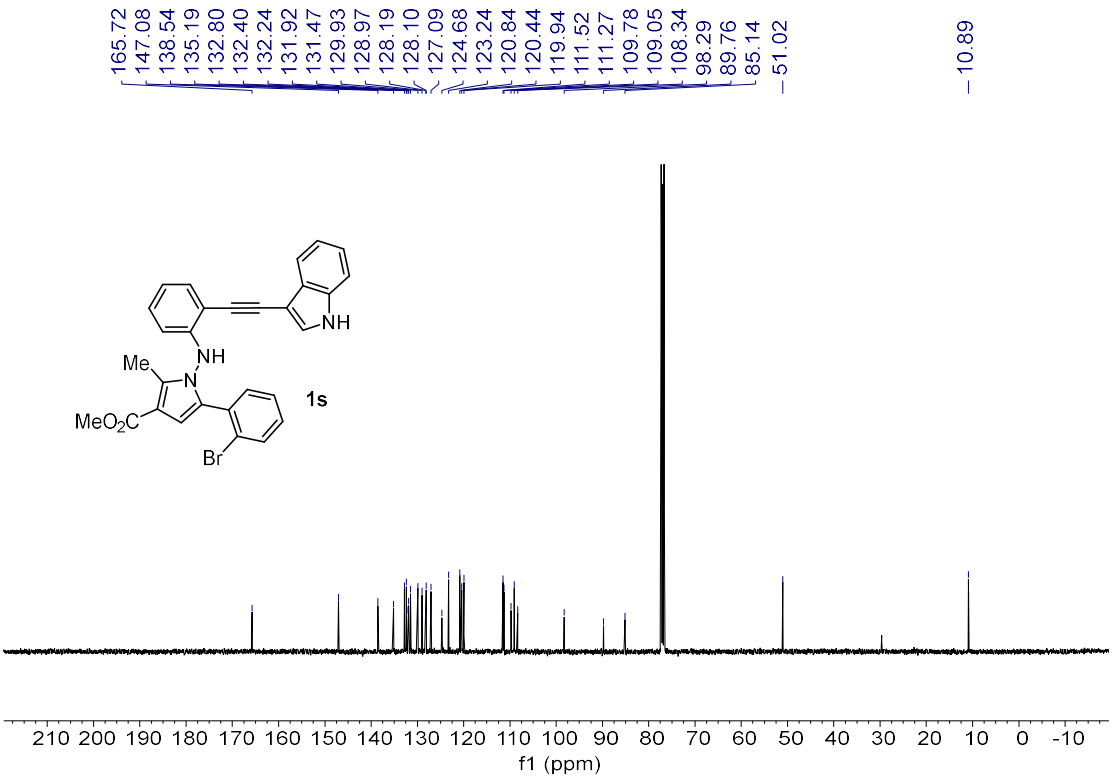
^{1}H NMR (400 MHz, $CDCl_3$) of **1r**



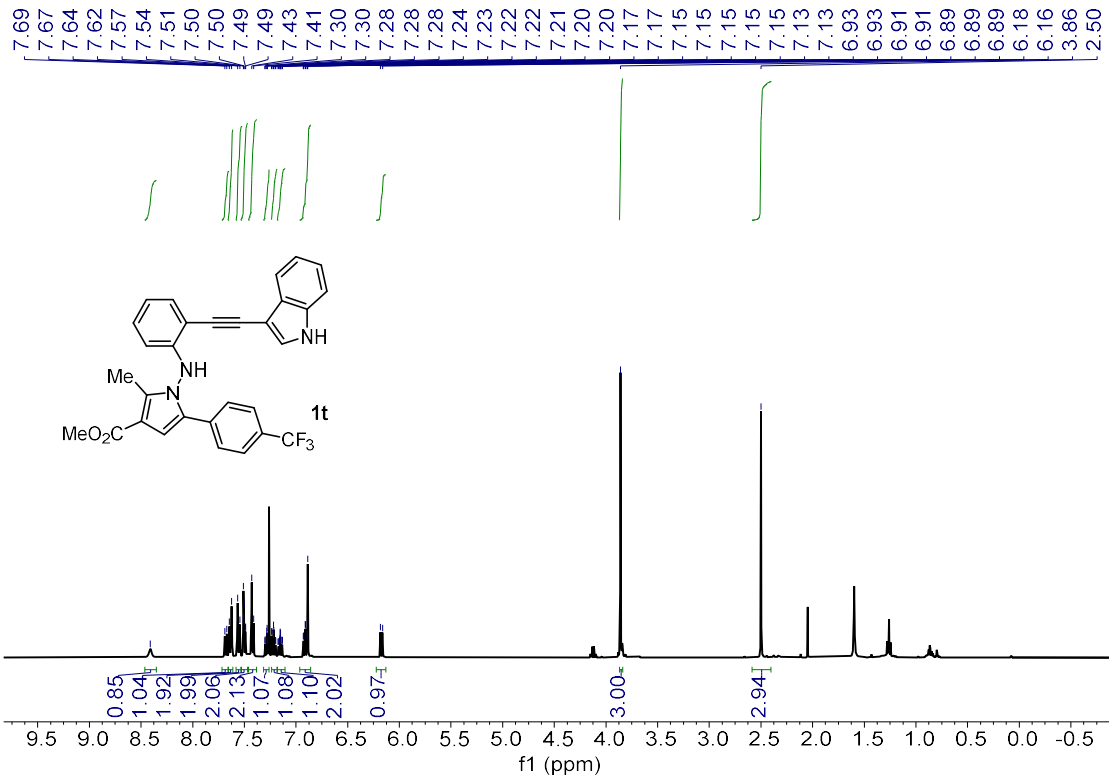
^{13}C NMR (101 MHz, $CDCl_3$) of **1r**



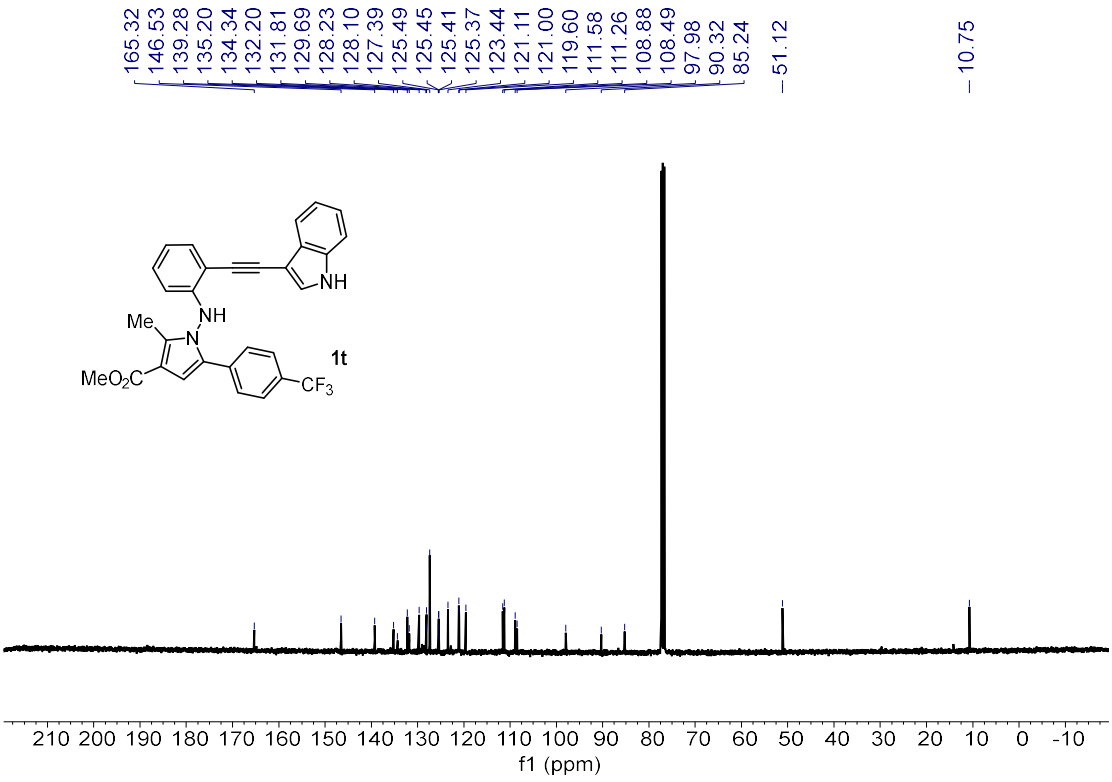
^{1}H NMR (400 MHz, $CDCl_3$) of **1s**



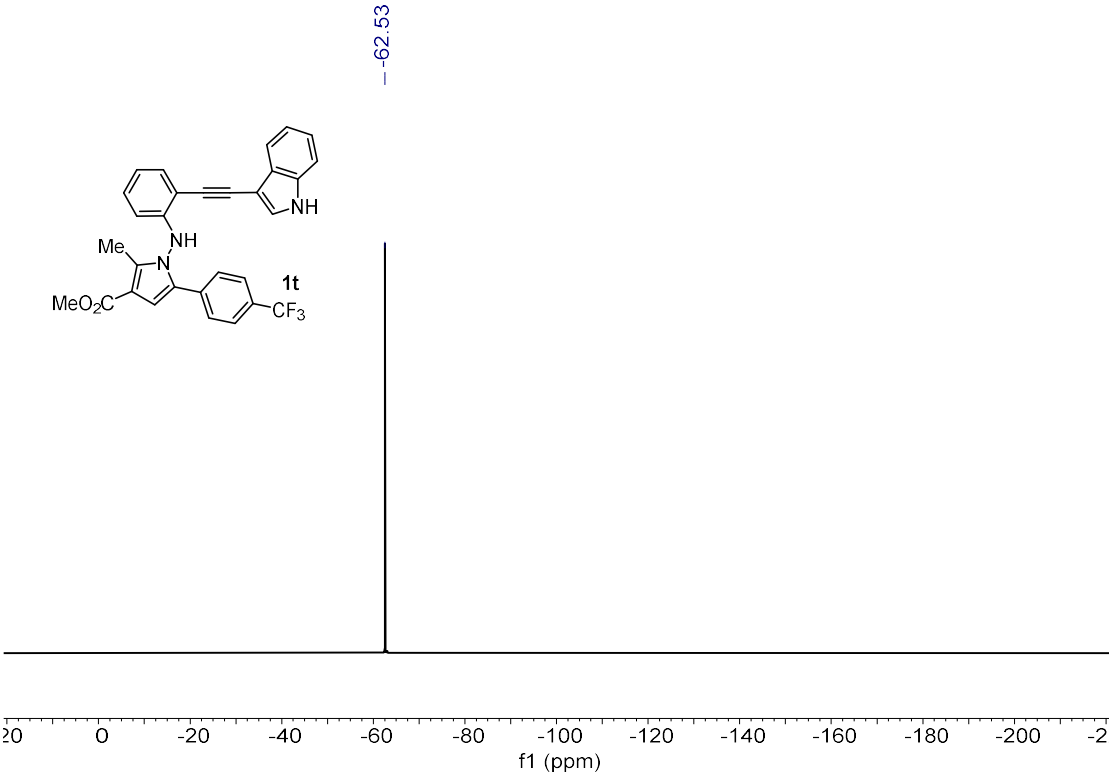
^{13}C NMR (101 MHz, $CDCl_3$) of **1s**



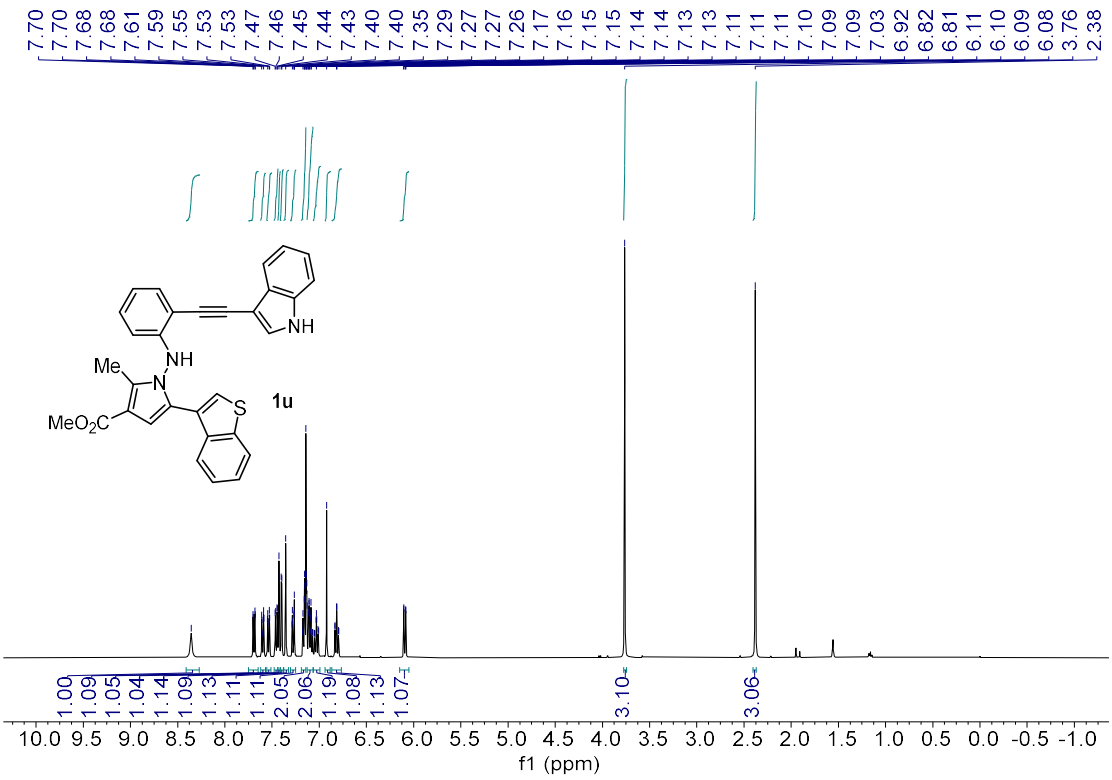
^{1}H NMR (400 MHz, $CDCl_3$) of **1t**



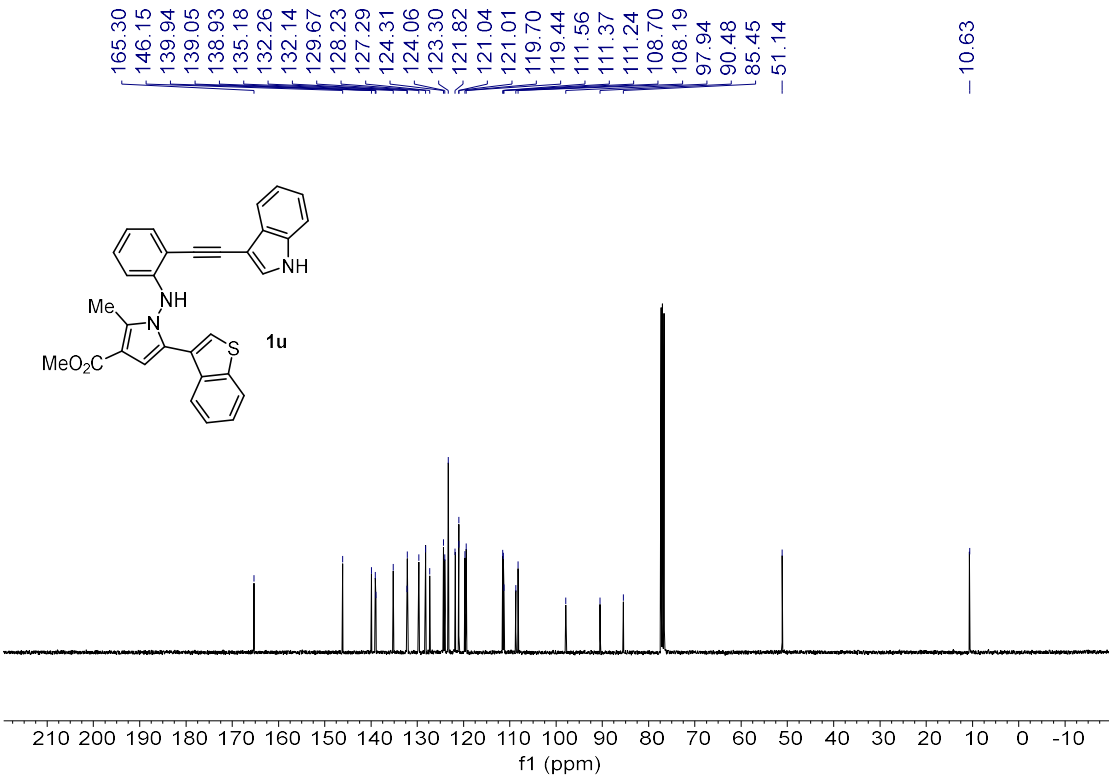
^{13}C NMR (101 MHz, $CDCl_3$) of **1t**



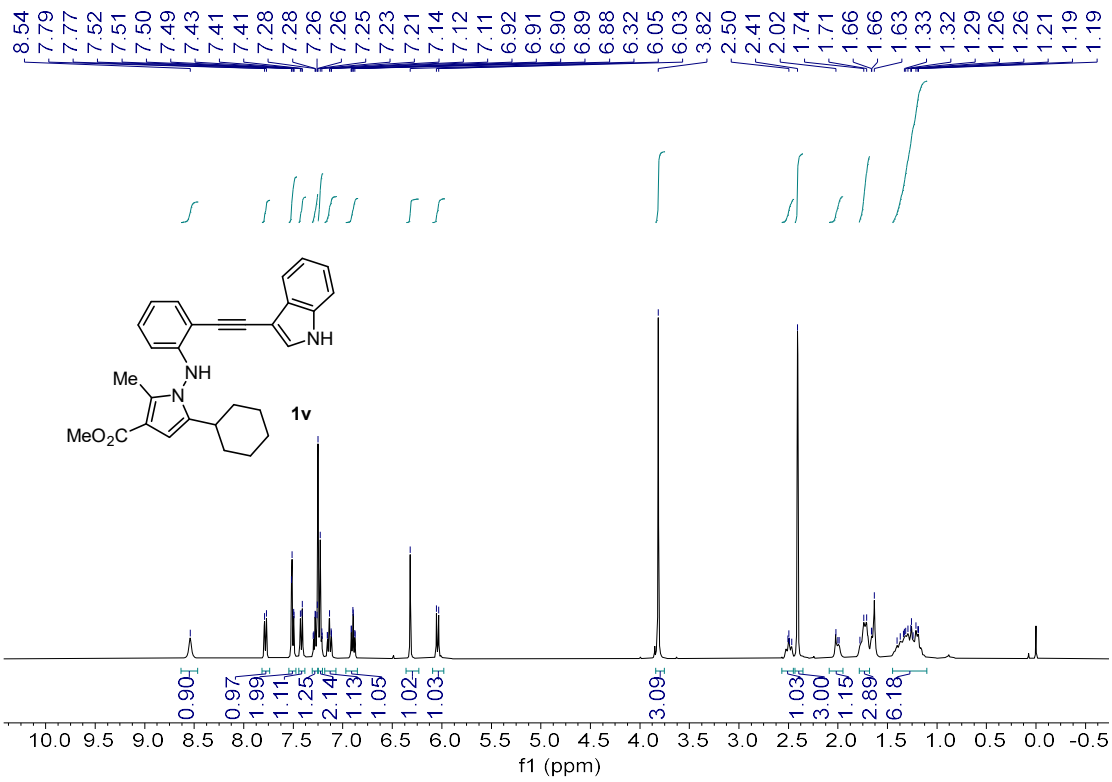
^{19}F NMR (376 MHz, $CDCl_3$) of **1t**



^{1}H NMR (400 MHz, $CDCl_3$) of **1u**



^{13}C NMR (101 MHz, $CDCl_3$) of **1u**



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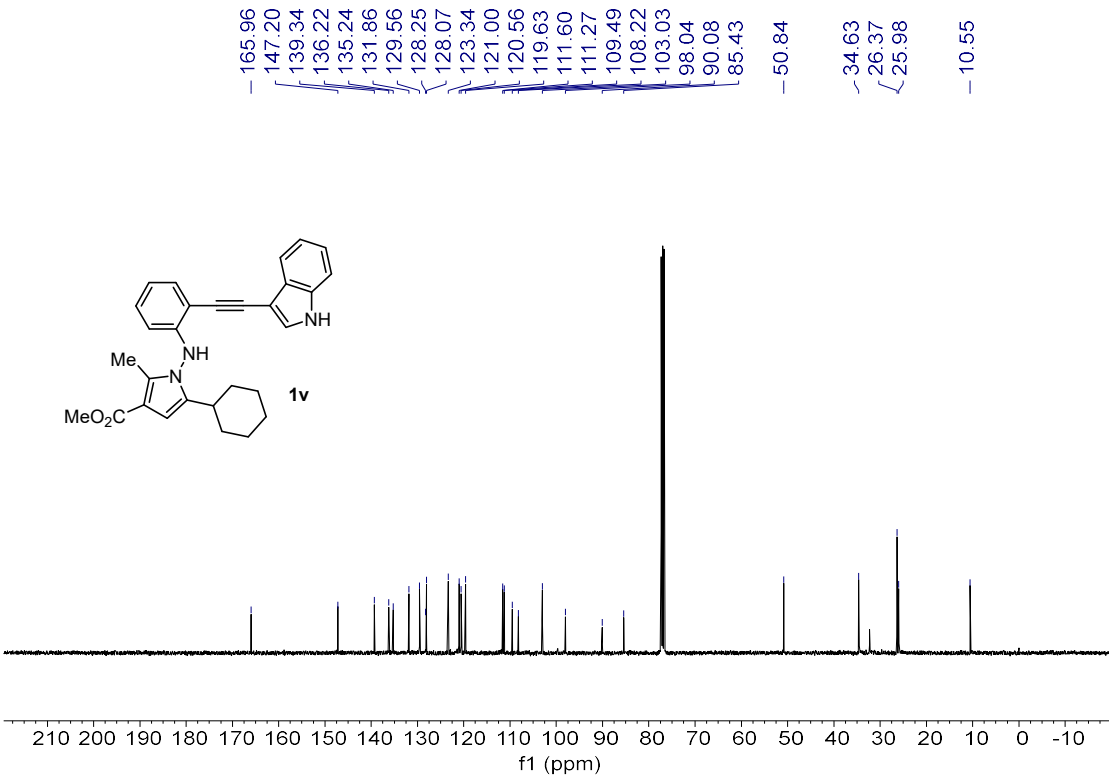
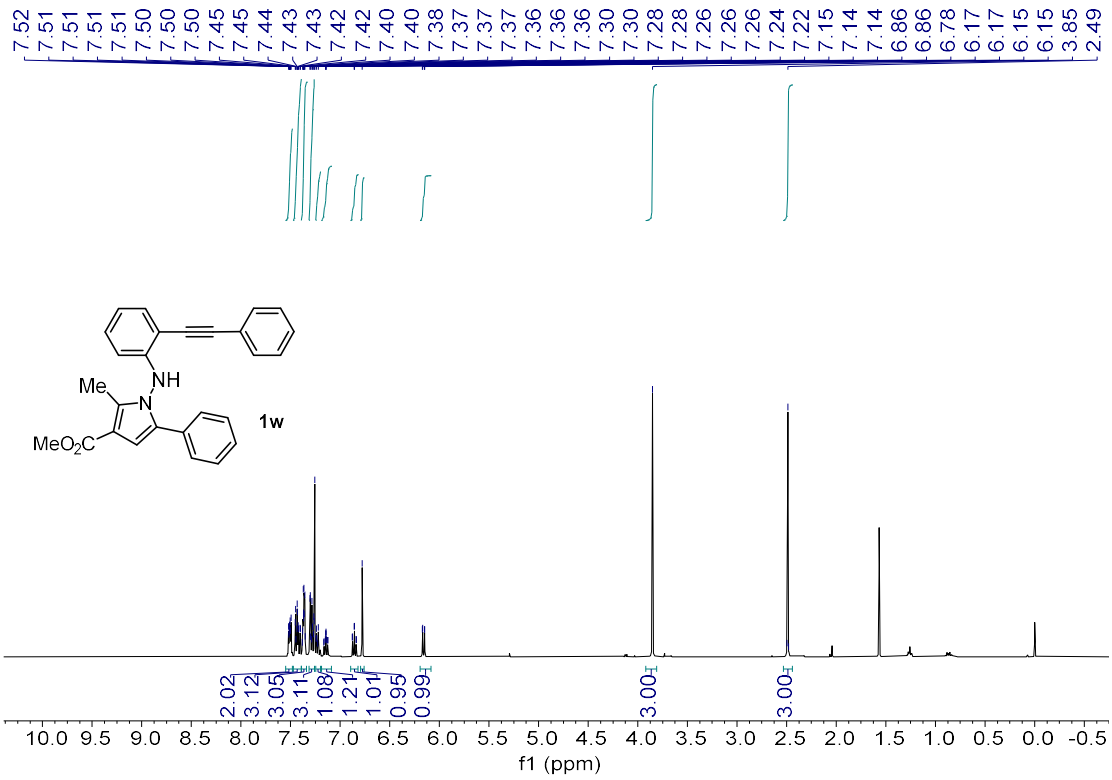
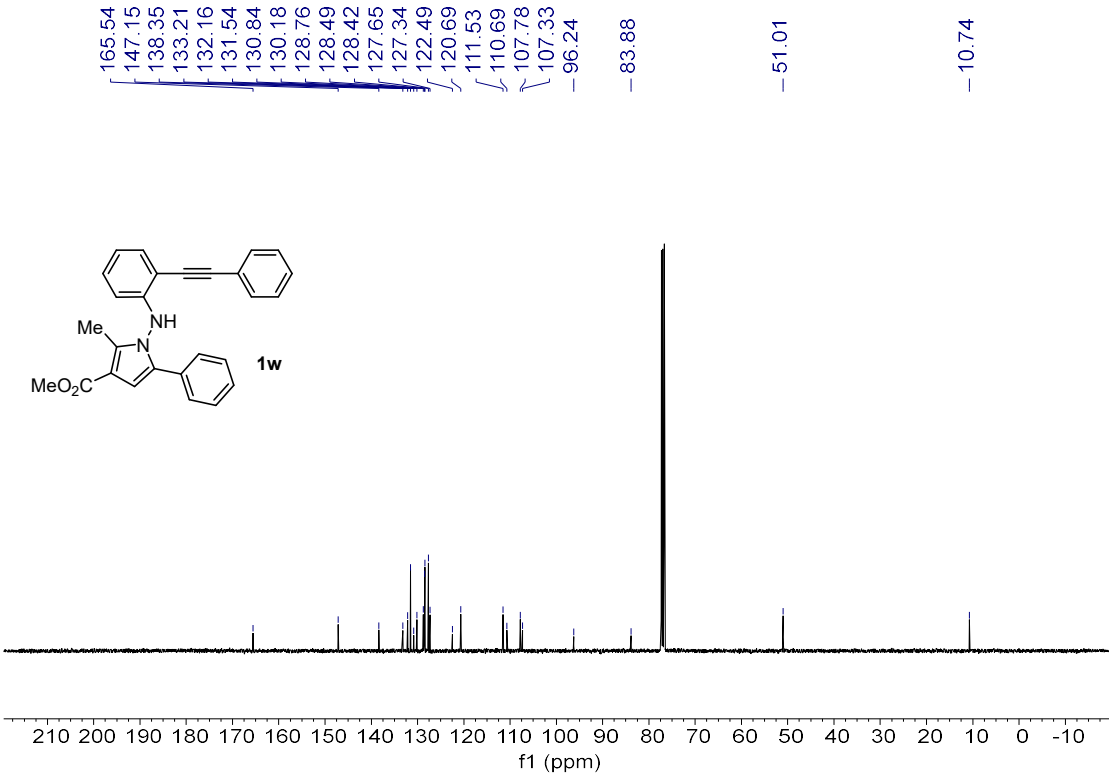


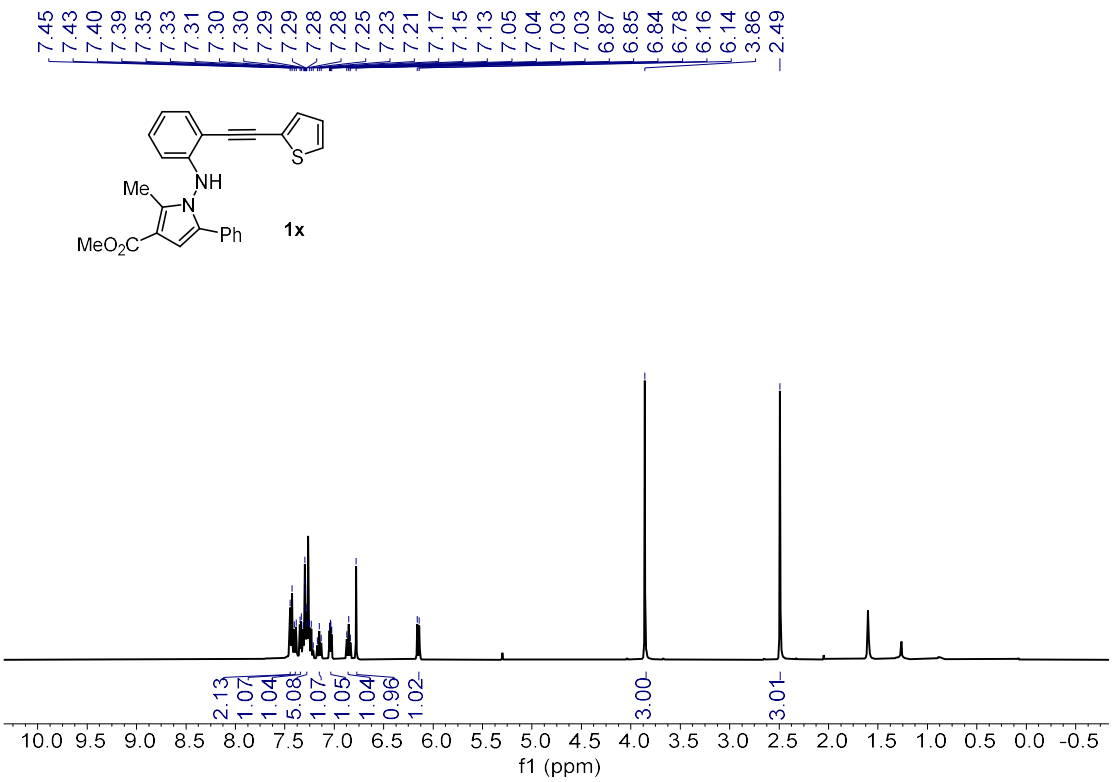
^{13}C NMR (101 MHz, $CDCl_3$) of **1v**



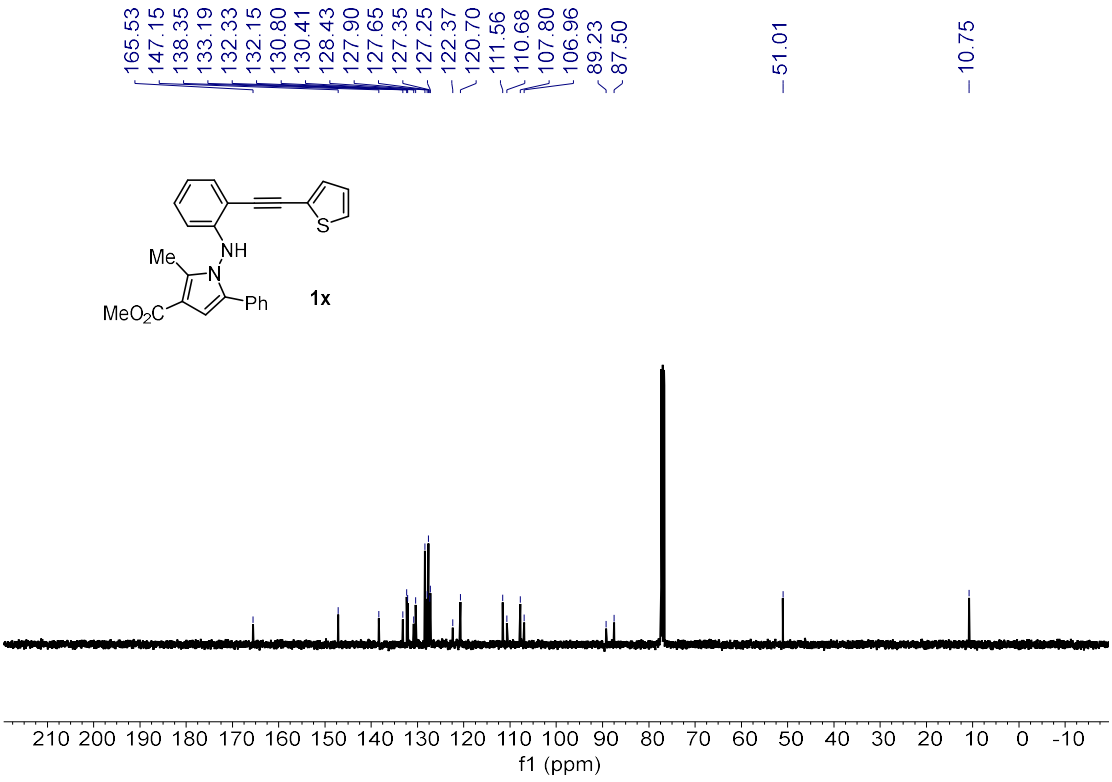
^{1}H NMR (400 MHz, $CDCl_3$) of **1w**



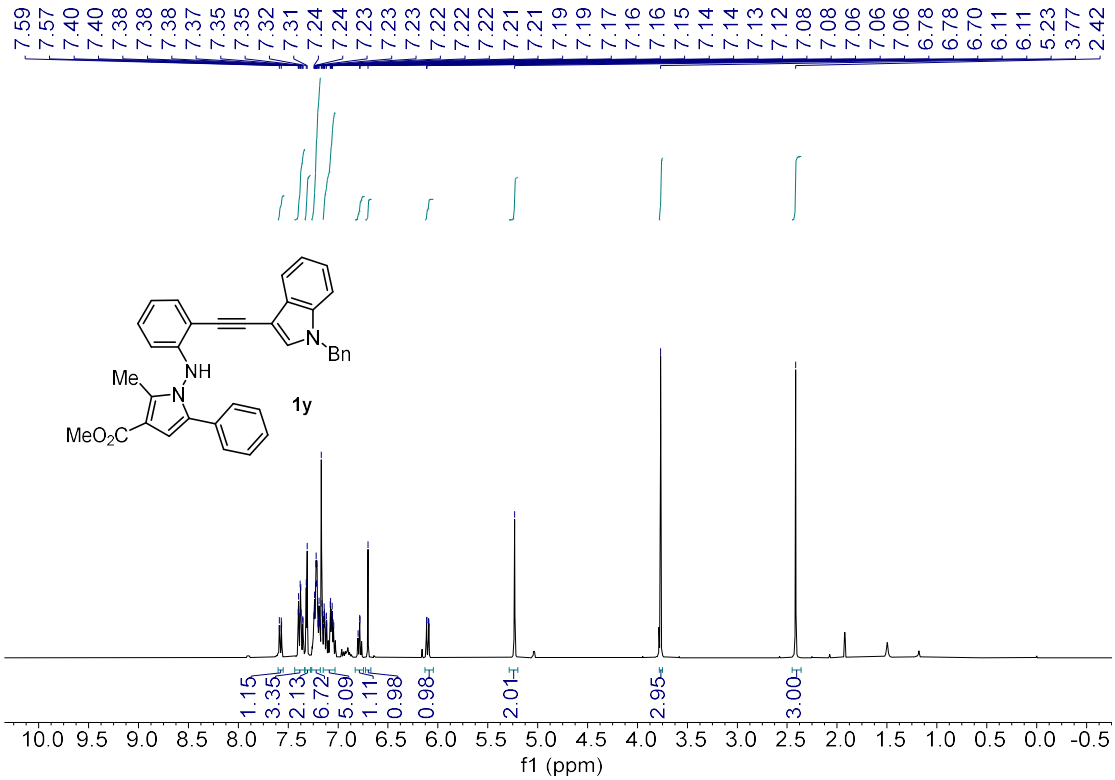
^{13}C NMR (101 MHz, $CDCl_3$) of **1w**



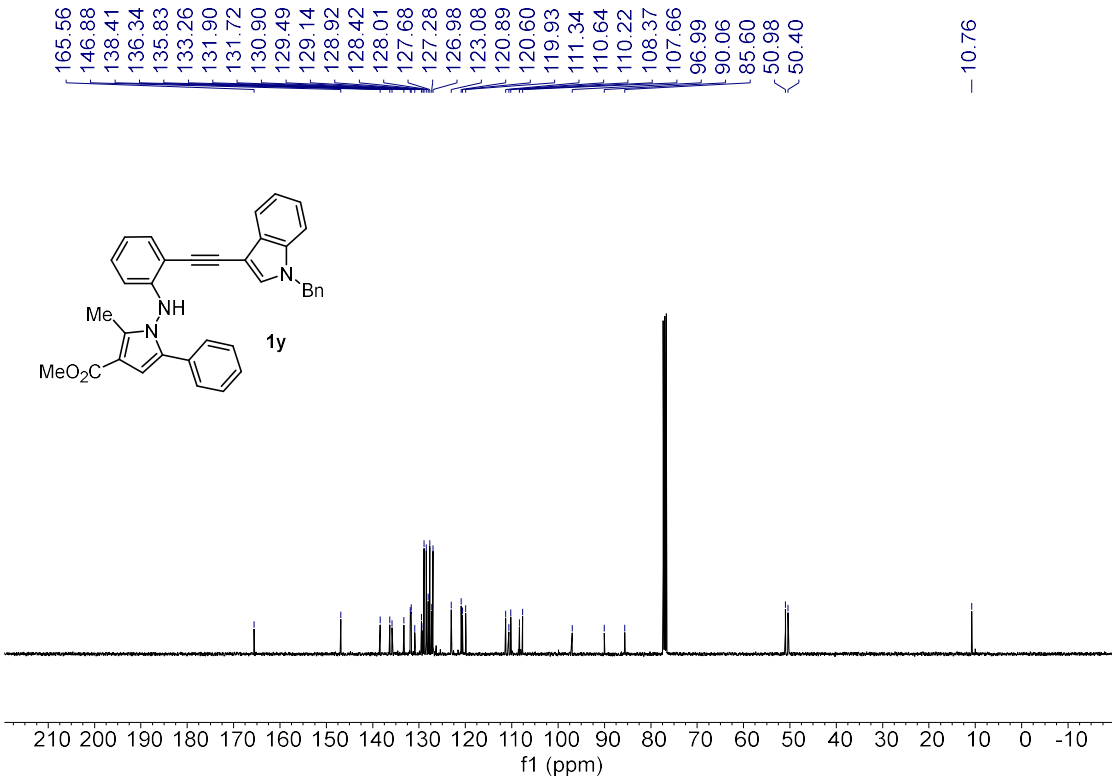
^{1}H NMR (400 MHz, $CDCl_3$) of **1x**



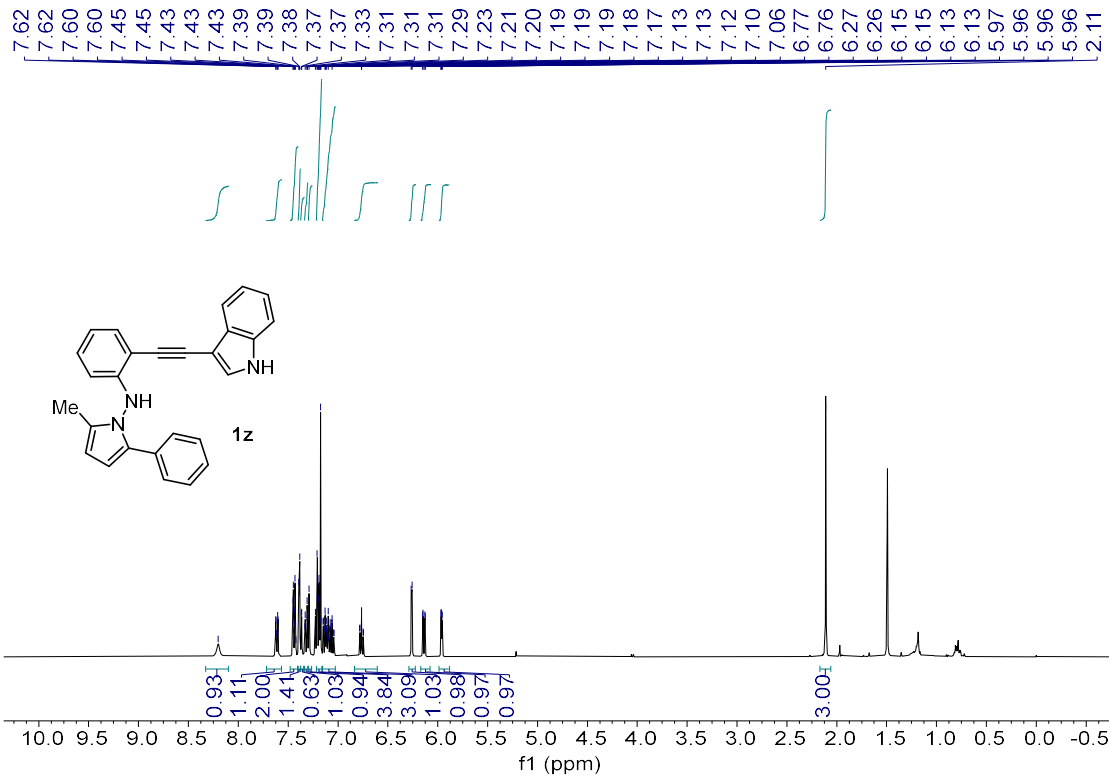
^{13}C NMR (101 MHz, $CDCl_3$) of **1x**



^{1}H NMR (400 MHz, $CDCl_3$) of **1y**



^{13}C NMR (101 MHz, $CDCl_3$) of **1y**



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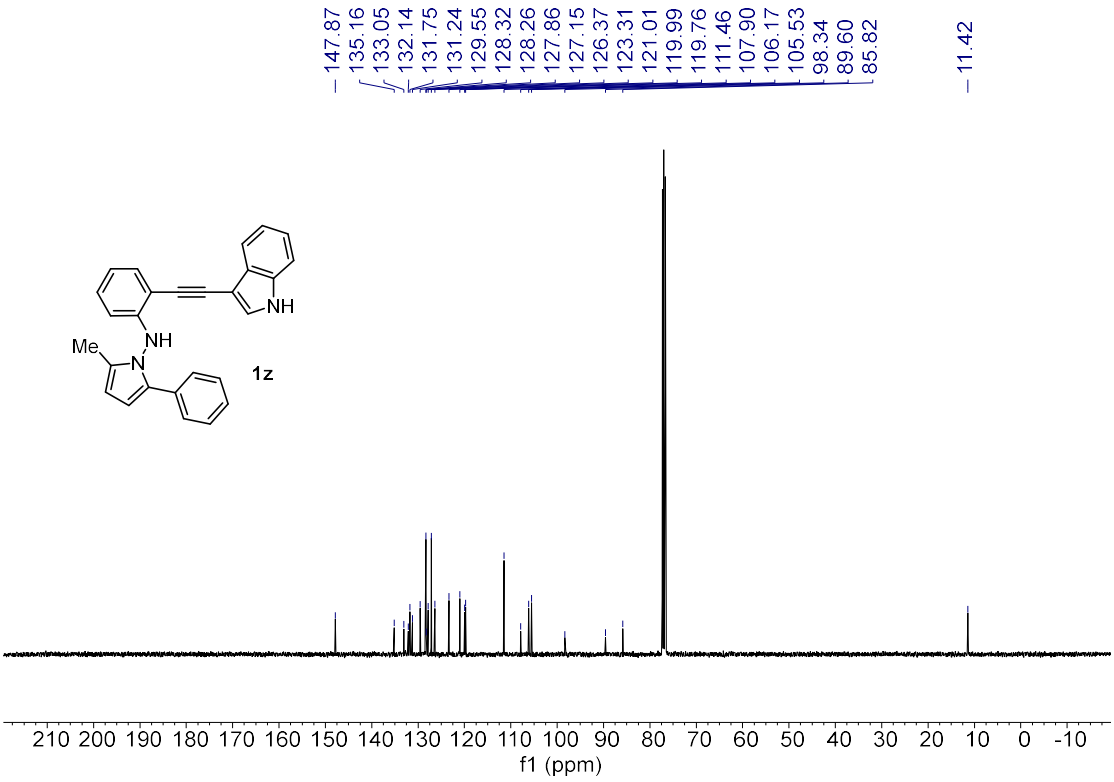
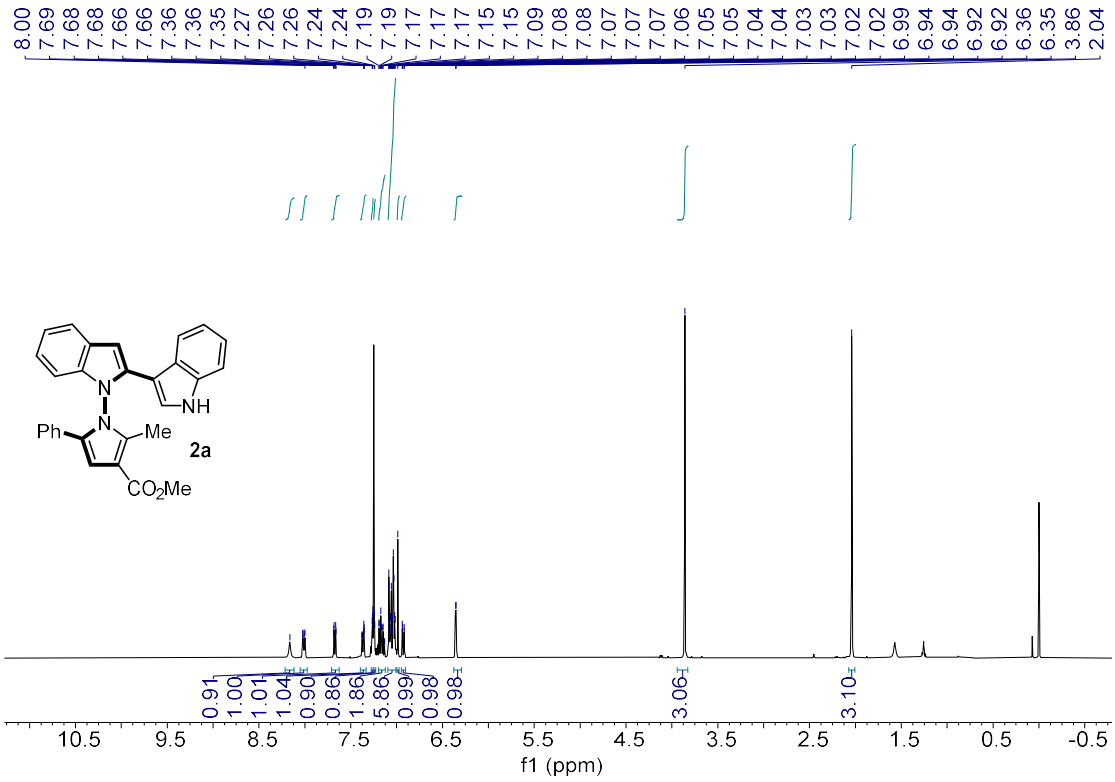
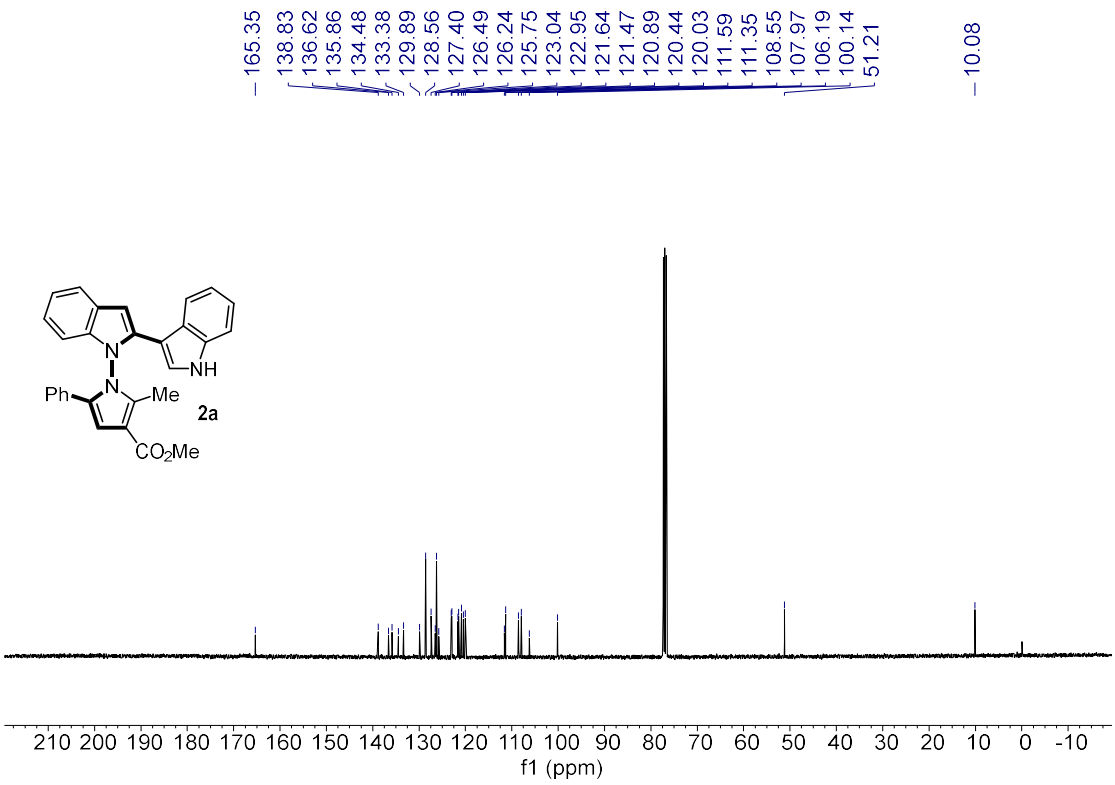


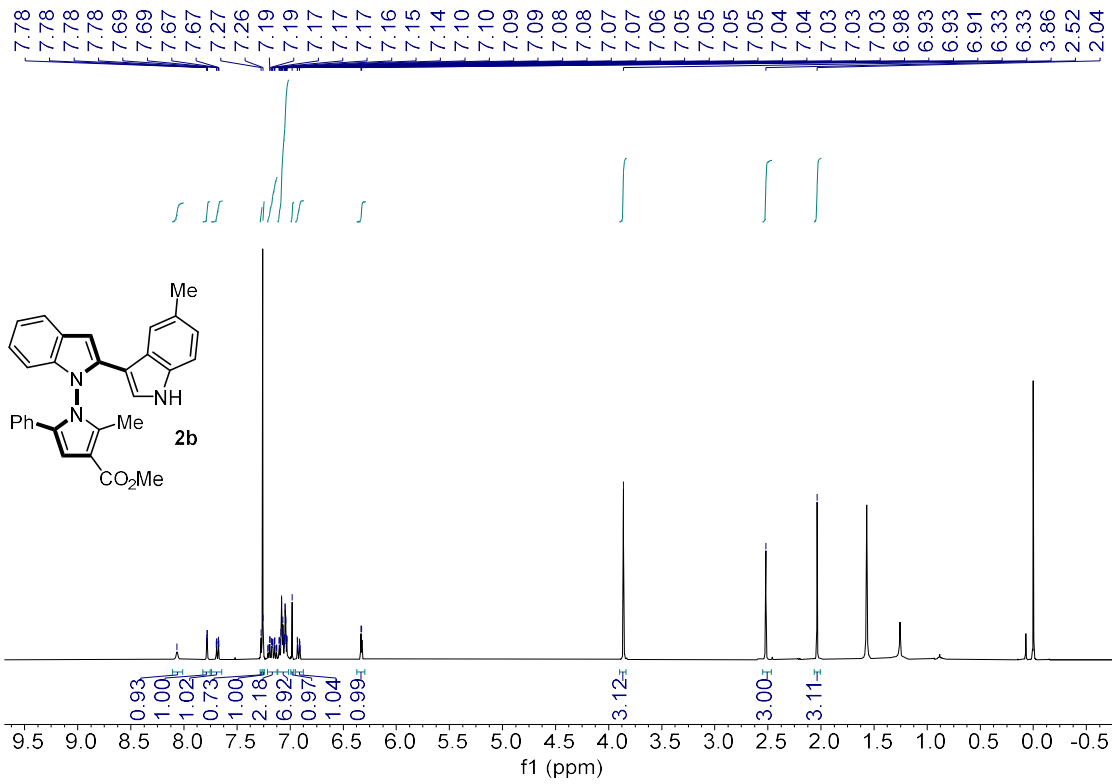
^{13}C NMR (101 MHz, $CDCl_3$) of **1z**



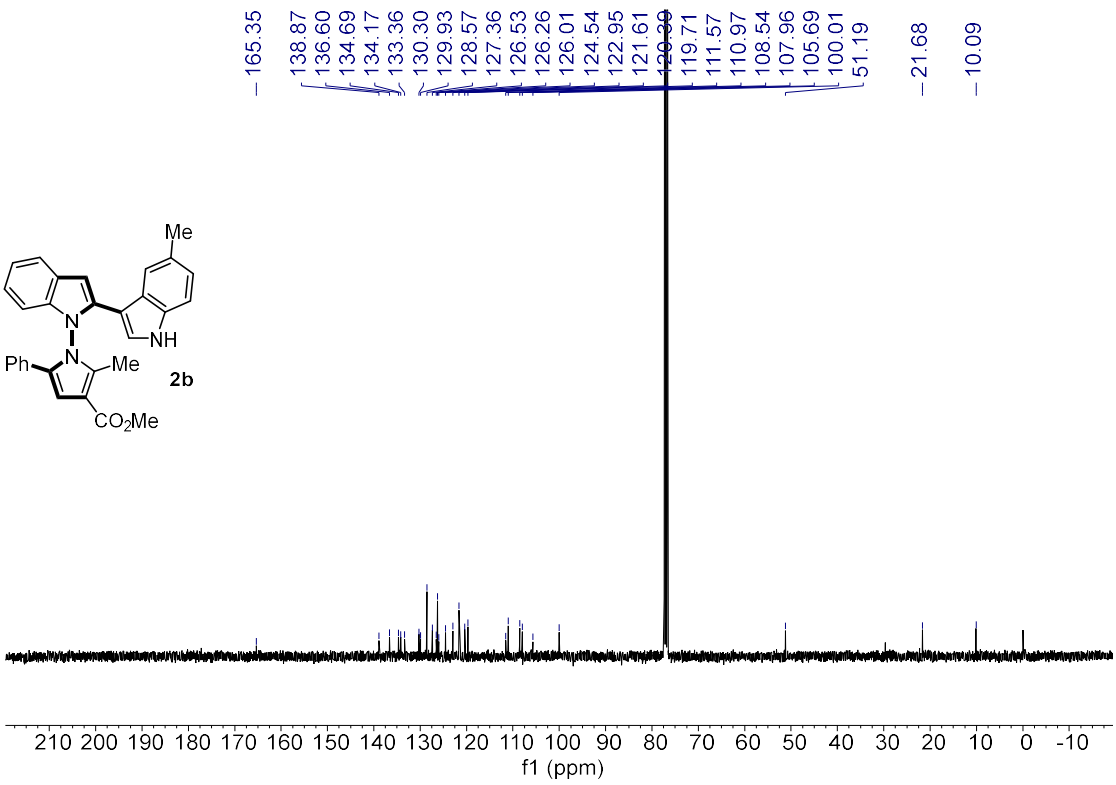
^{1}H NMR (400 MHz, $CDCl_3$) of **2a**



^{13}C NMR (101 MHz, $CDCl_3$) of **2a**



^{1}H NMR (400 MHz, $CDCl_3$) of **2b**



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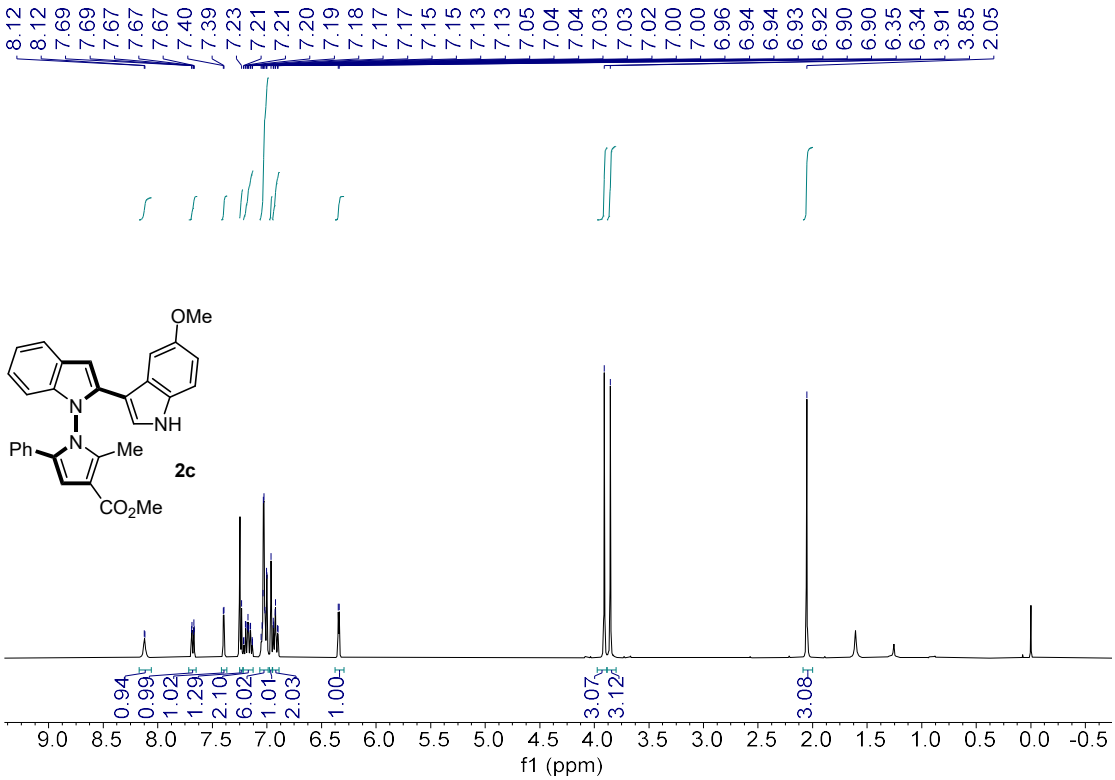
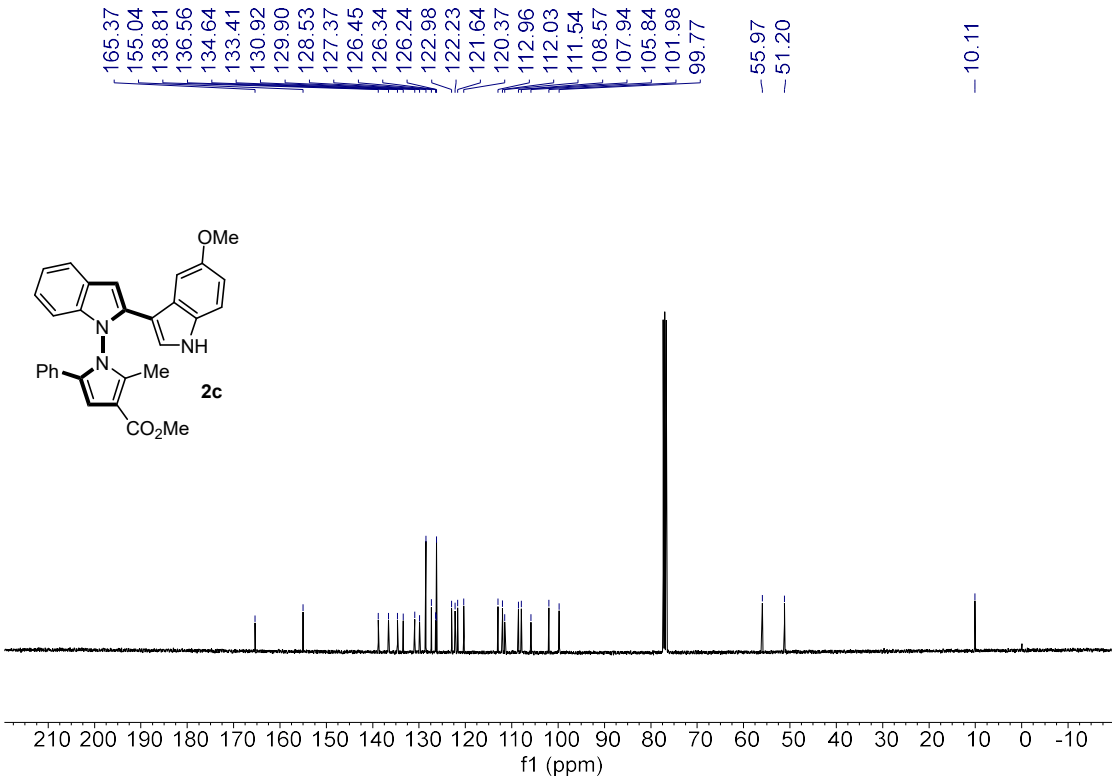
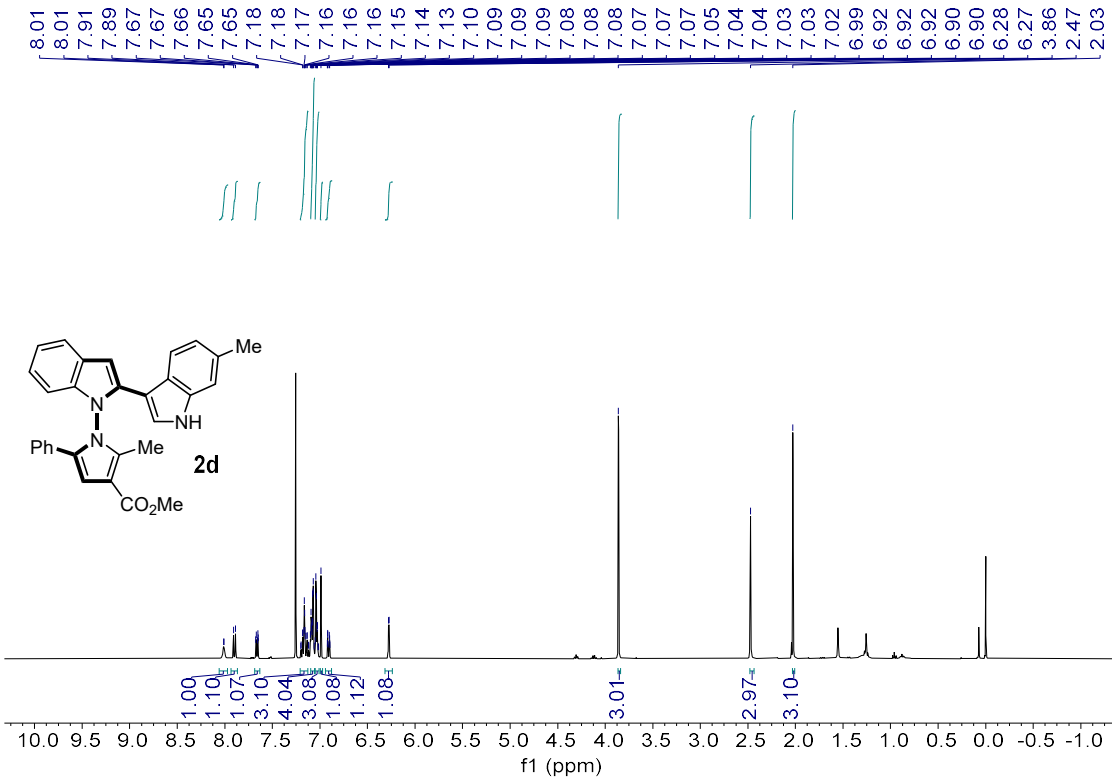


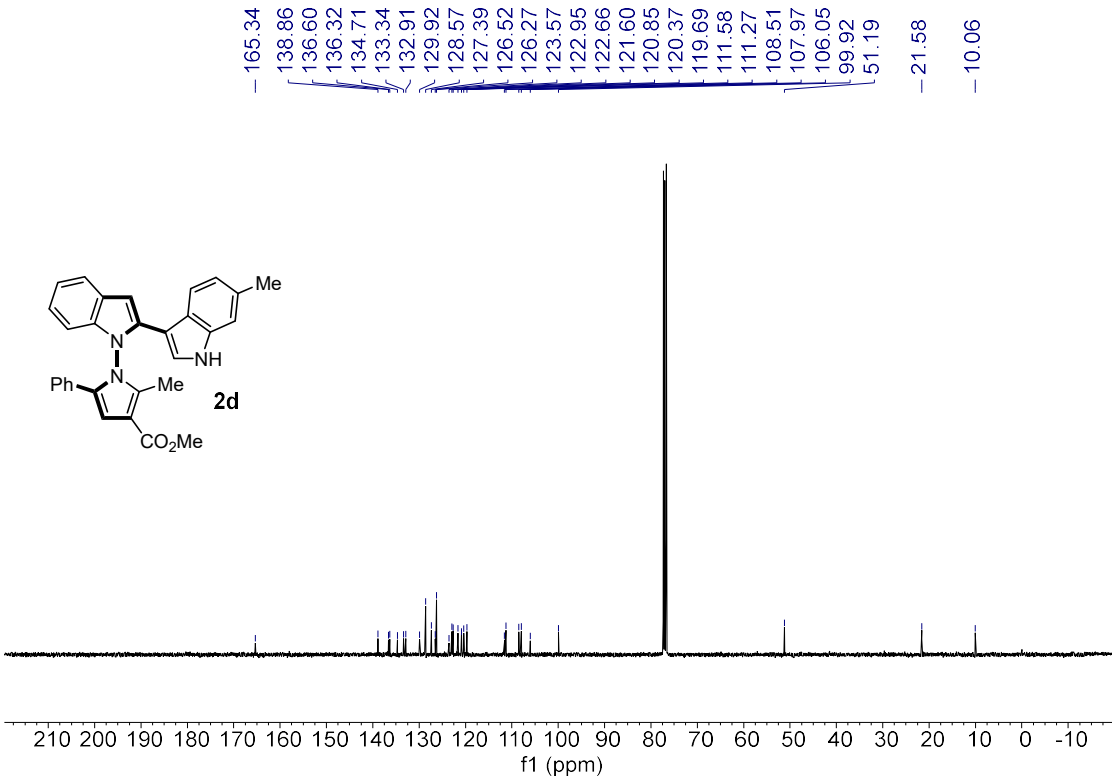
^{1}H NMR (400 MHz, $CDCl_3$) of **2c**



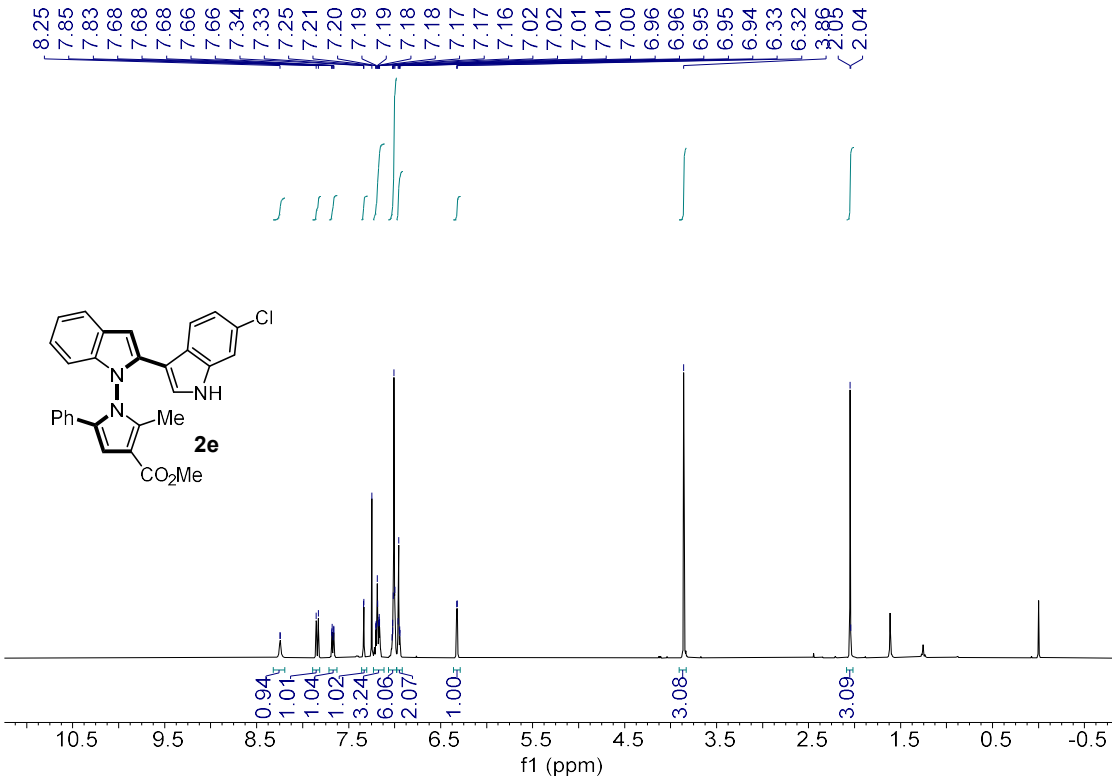
^{13}C NMR (101 MHz, $CDCl_3$) of **2c**



^{1}H NMR (400 MHz, $CDCl_3$) of **2d**



^{13}C NMR (101 MHz, $CDCl_3$) of **2d**



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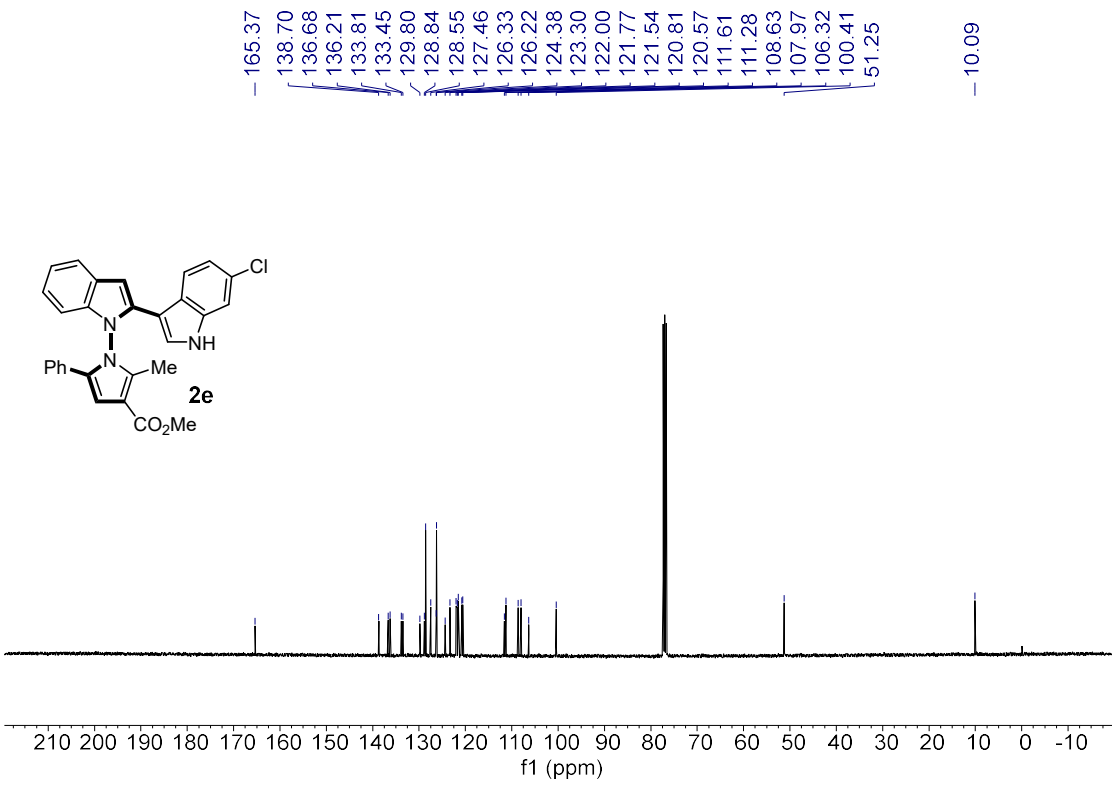

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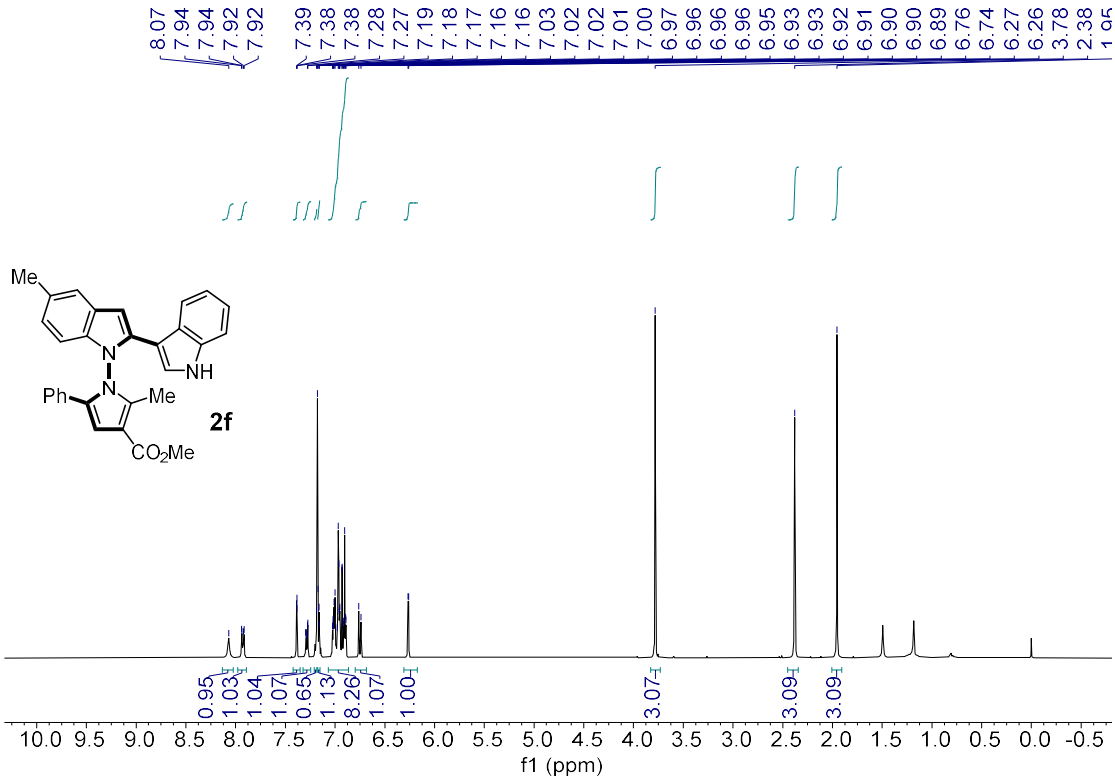
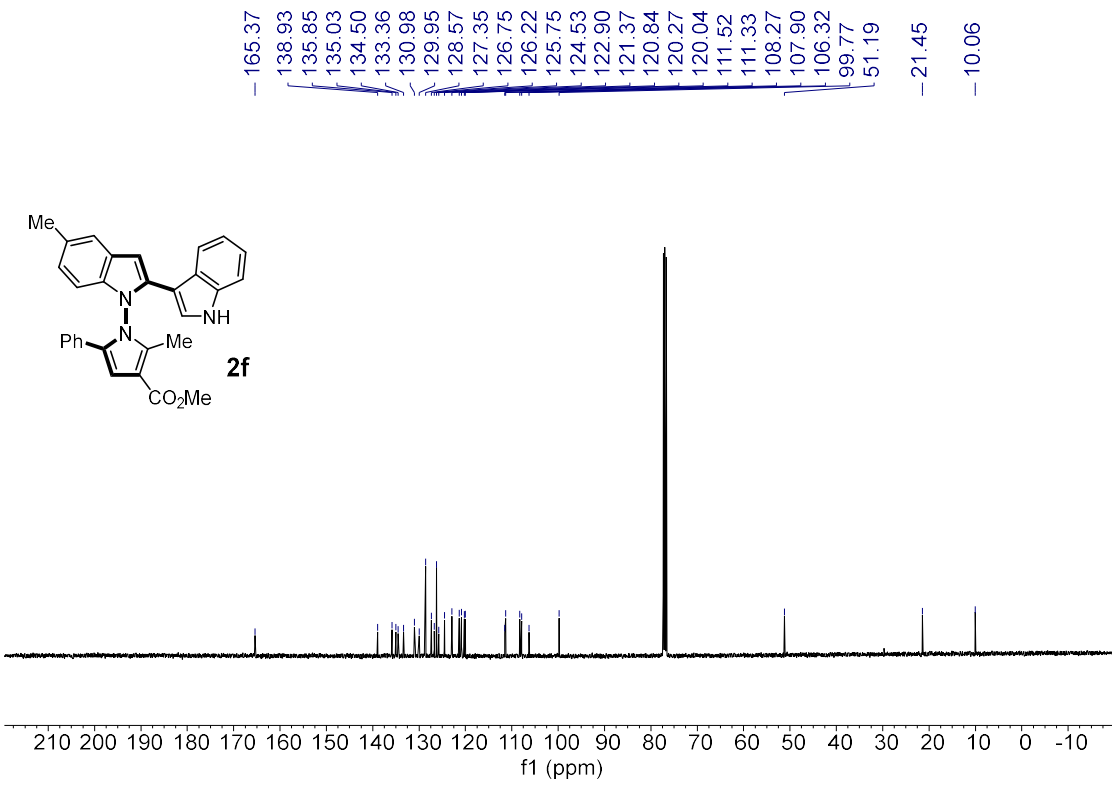
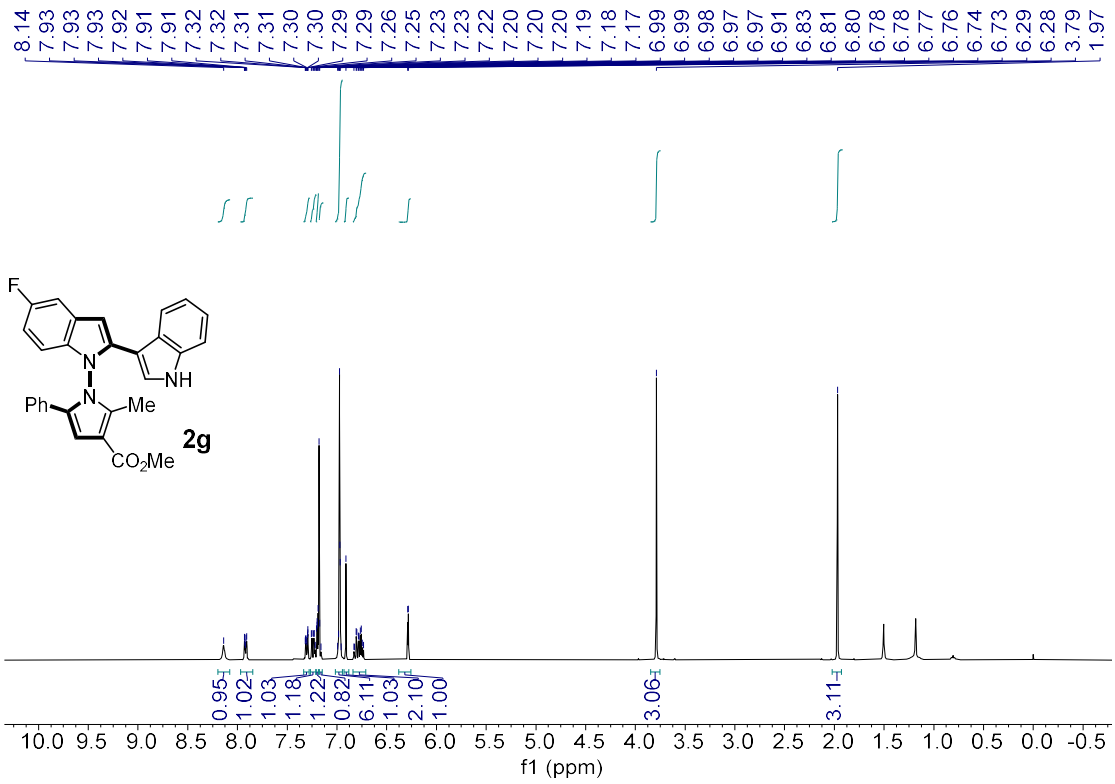


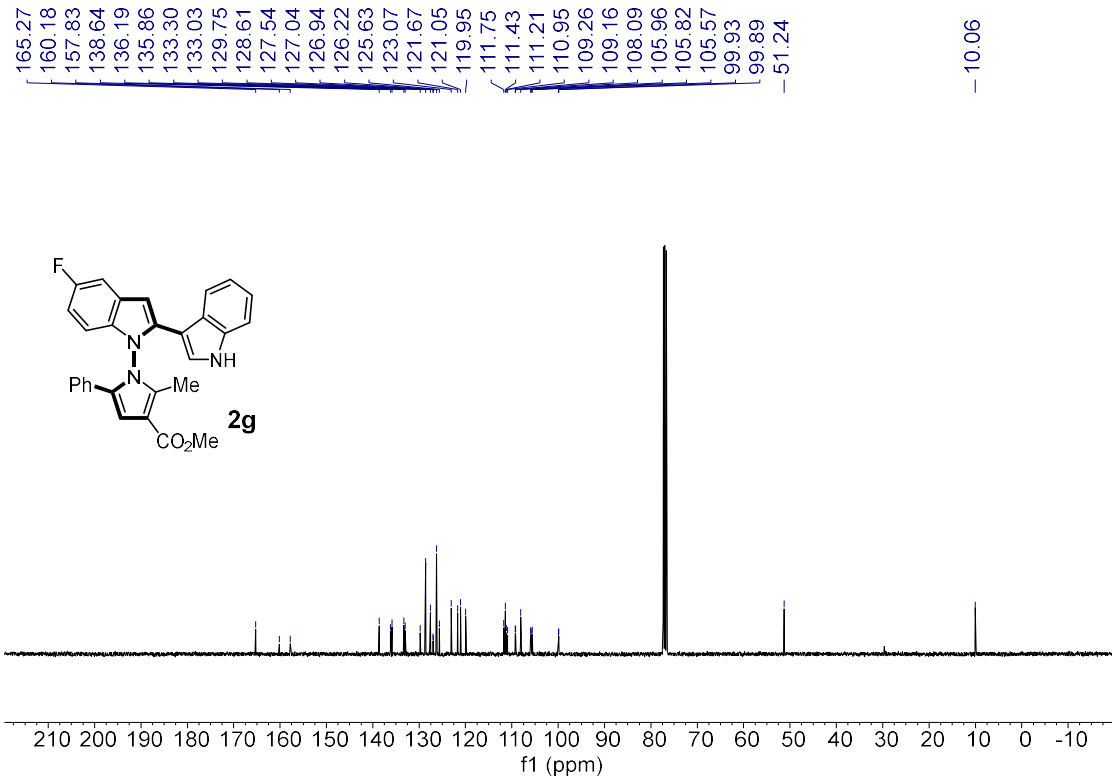
^{1}H NMR (400 MHz, $CDCl_3$) of **2f**



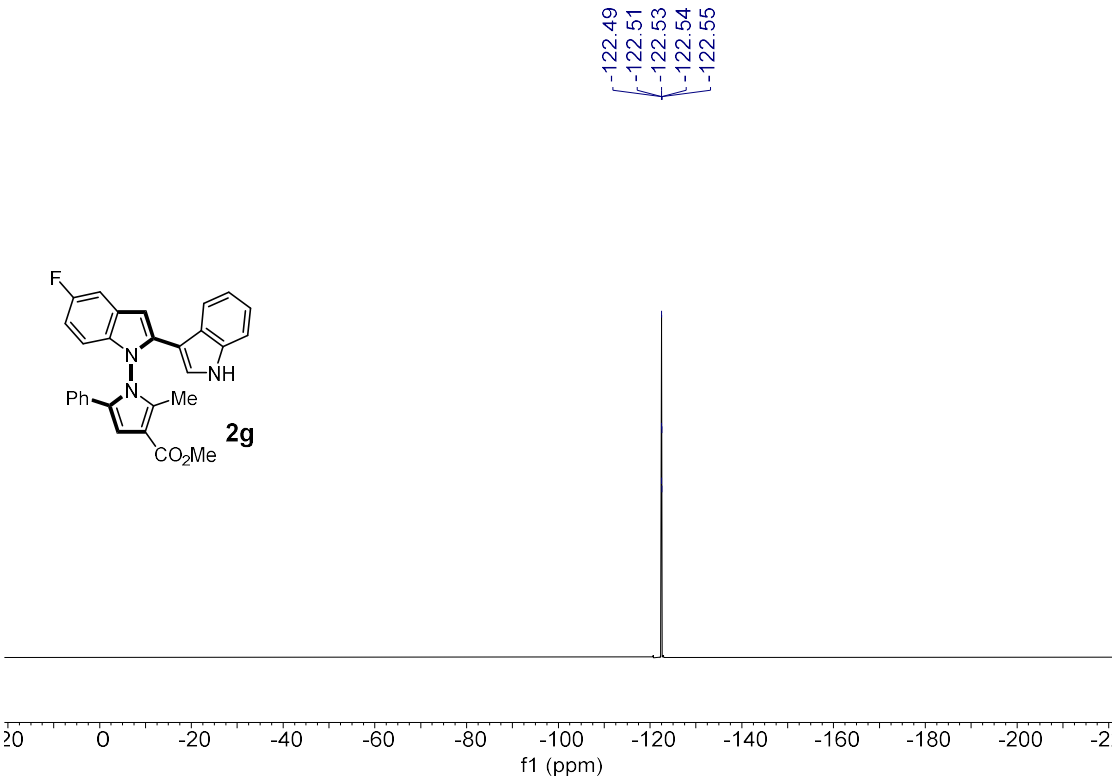
^{13}C NMR (101 MHz, $CDCl_3$) of **2f**



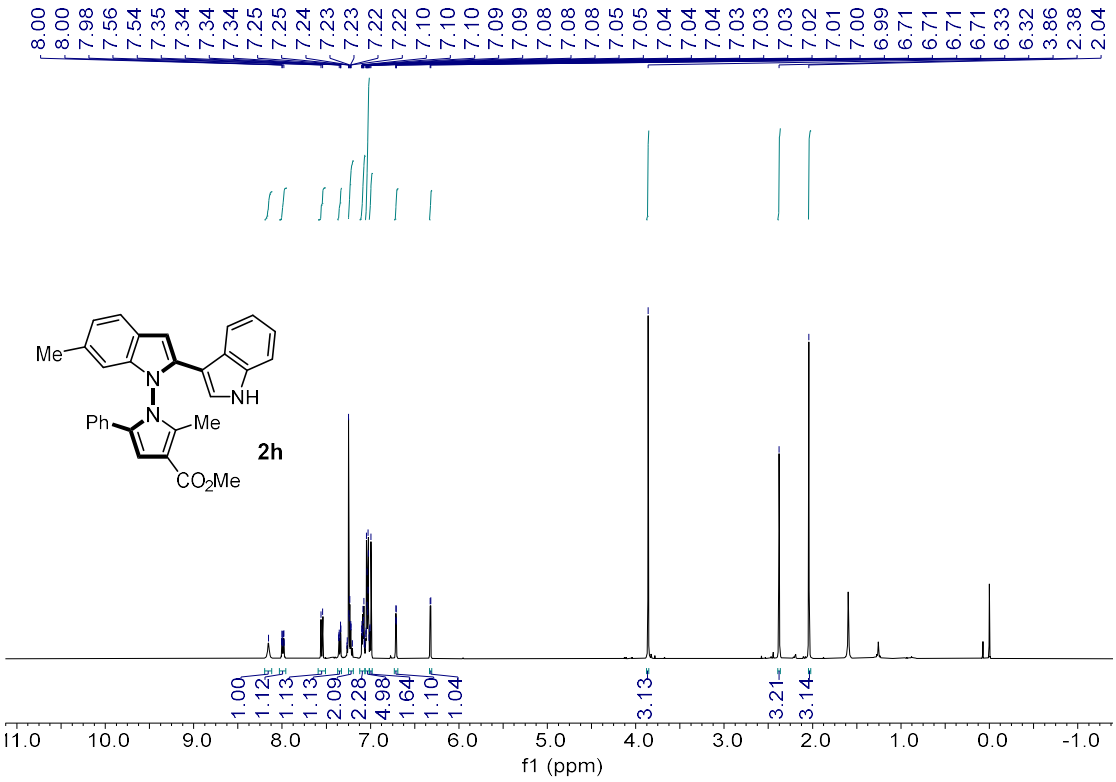
^{1}H NMR (400 MHz, $CDCl_3$) of **2g**



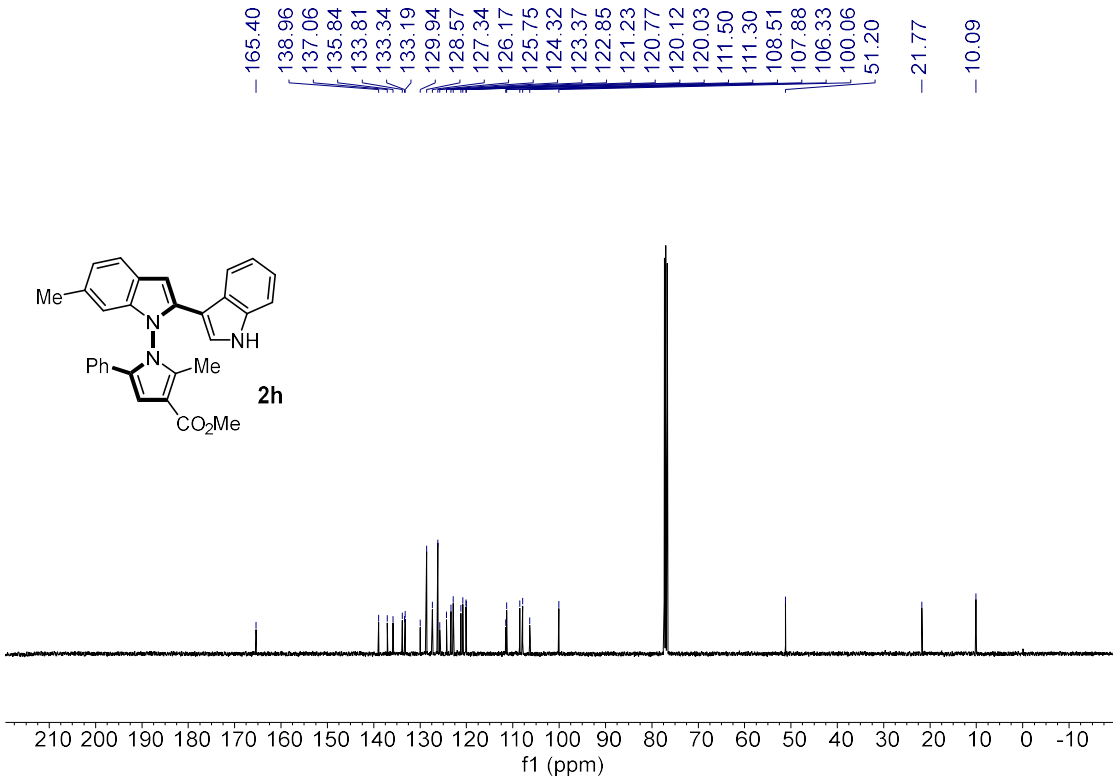
^{13}C NMR (101 MHz, $CDCl_3$) of **2g**



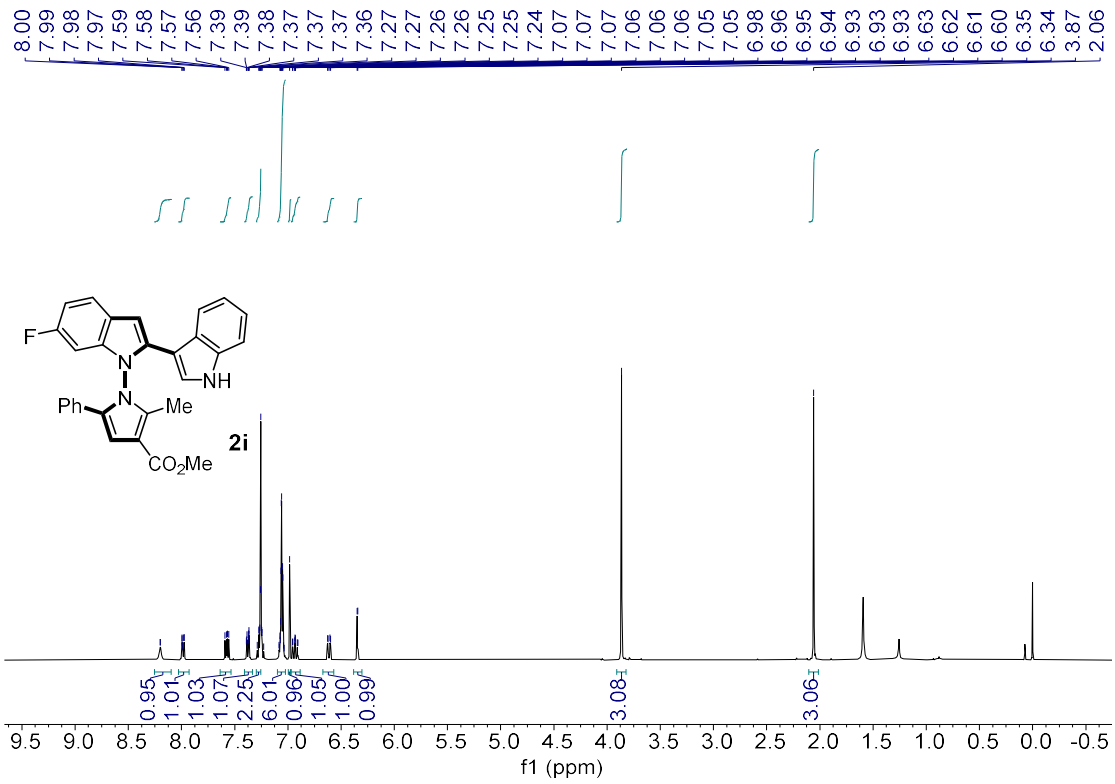
^{19}F NMR (376 MHz, $CDCl_3$) of **2g**



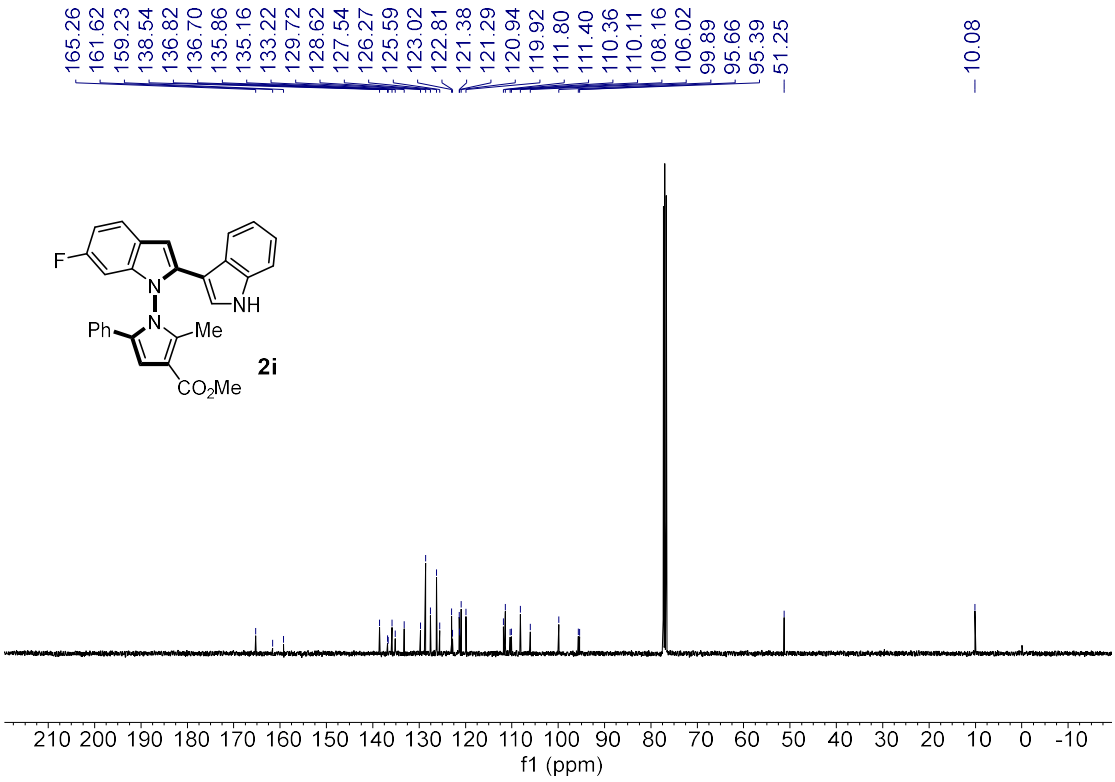
^{1}H NMR (400 MHz, $CDCl_3$) of **2h**



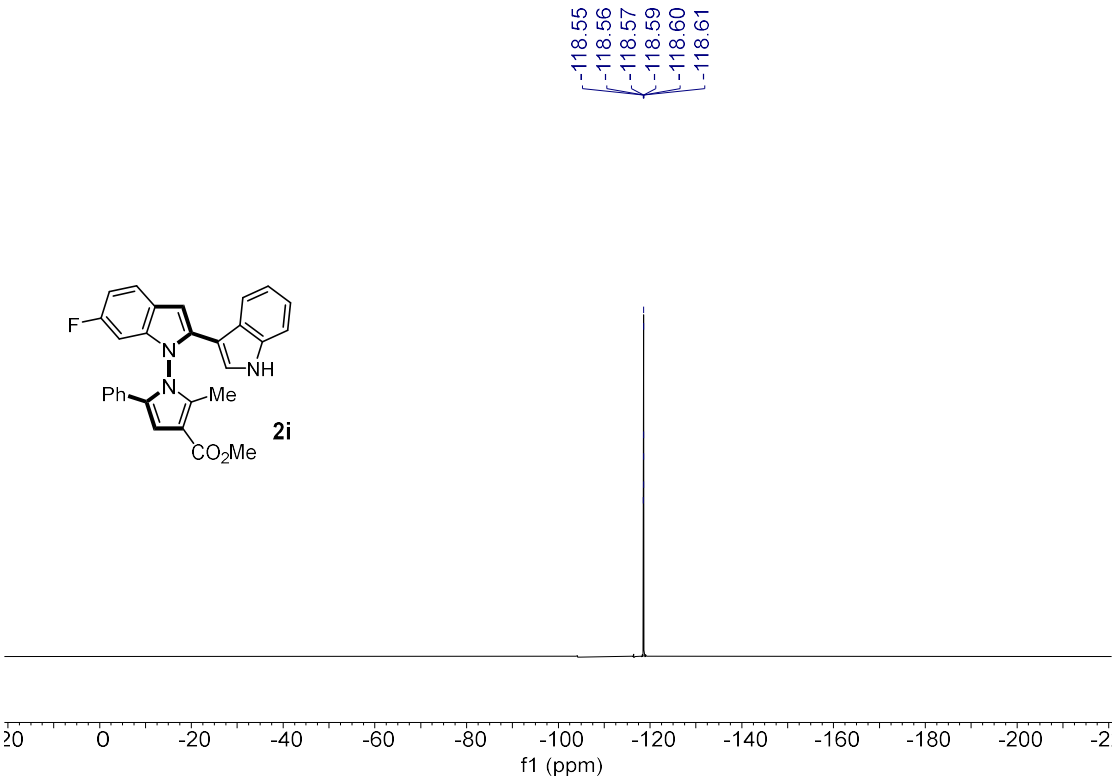
^{13}C NMR (101 MHz, $CDCl_3$) of **2h**



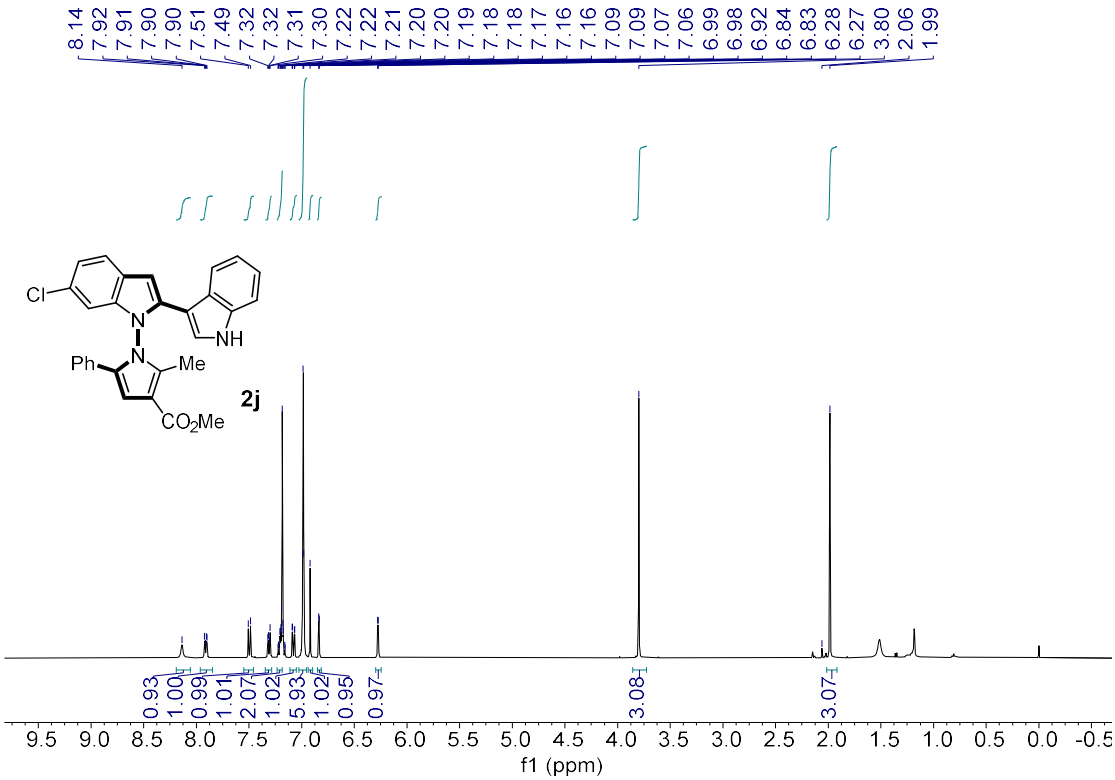
^{1}H NMR (400 MHz, $CDCl_3$) of **2i**



^{13}C NMR (101 MHz, $CDCl_3$) of **2i**



^{19}F NMR (376 MHz, $CDCl_3$) of **2i**



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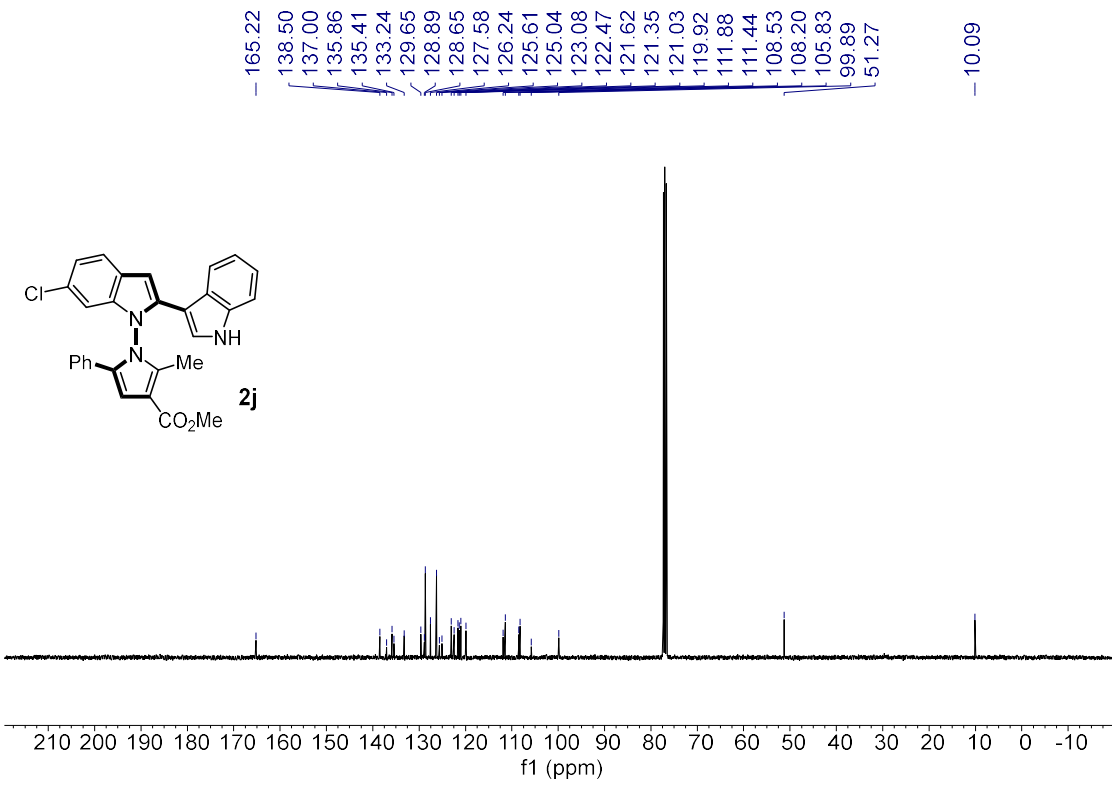

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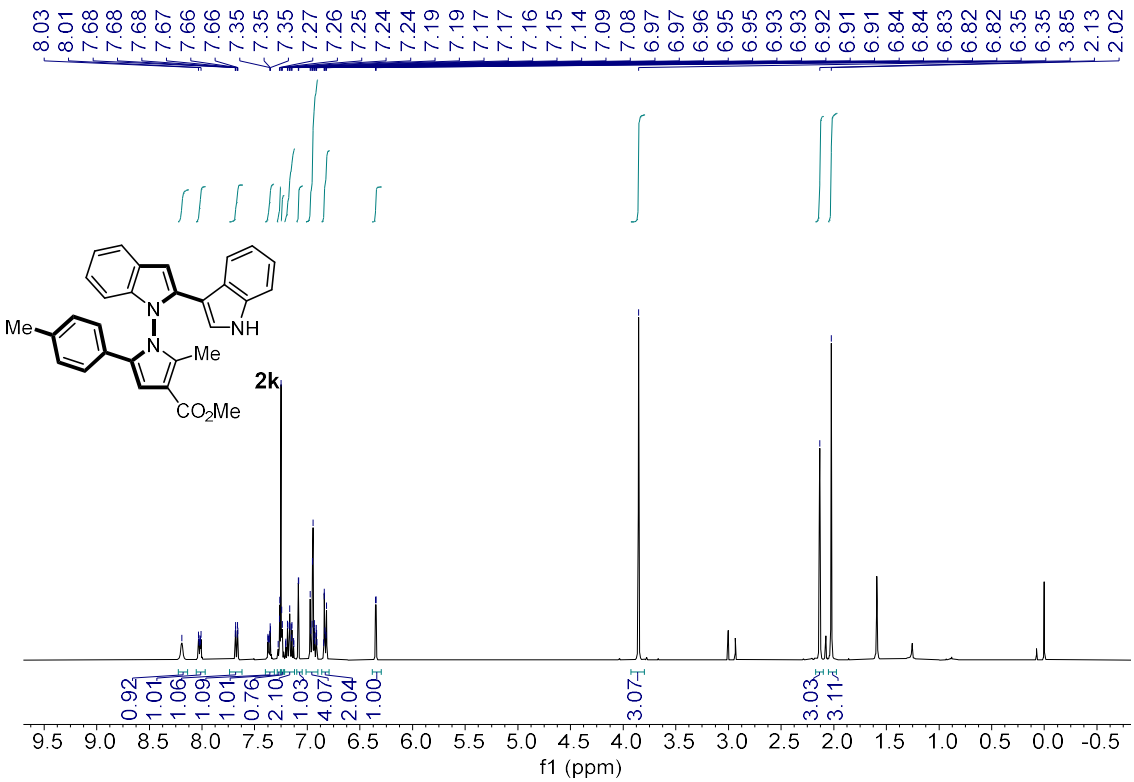
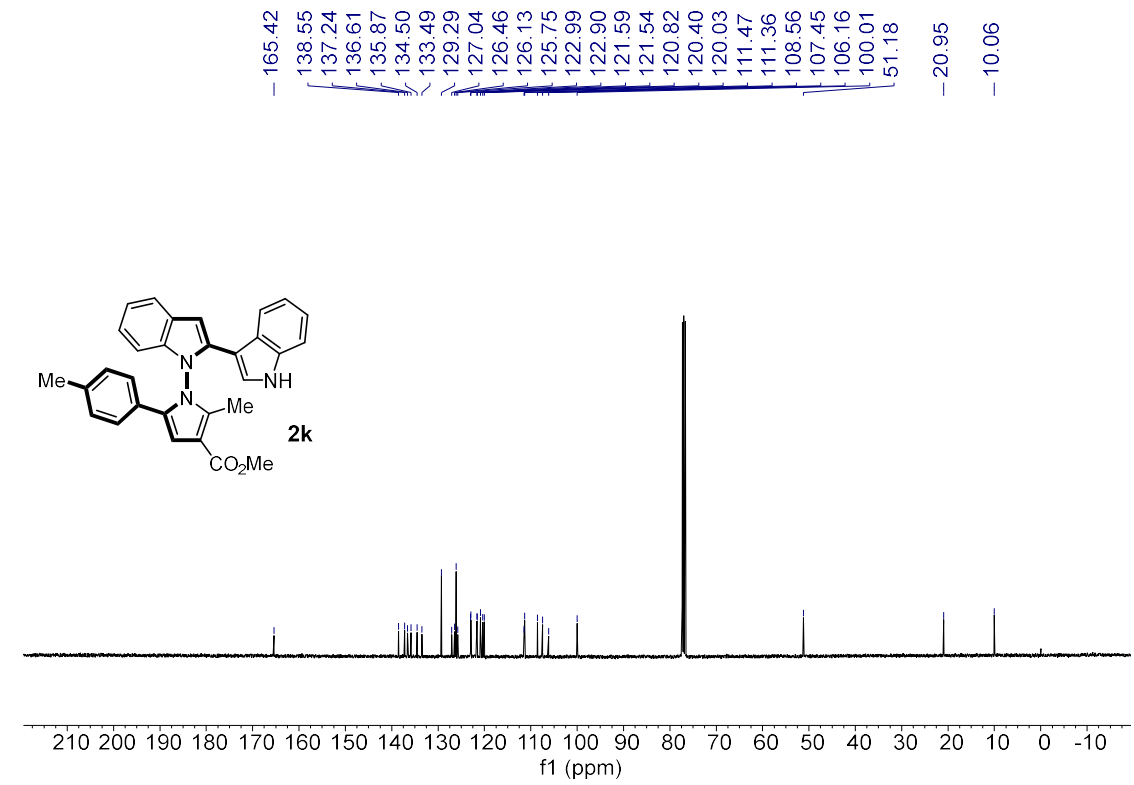
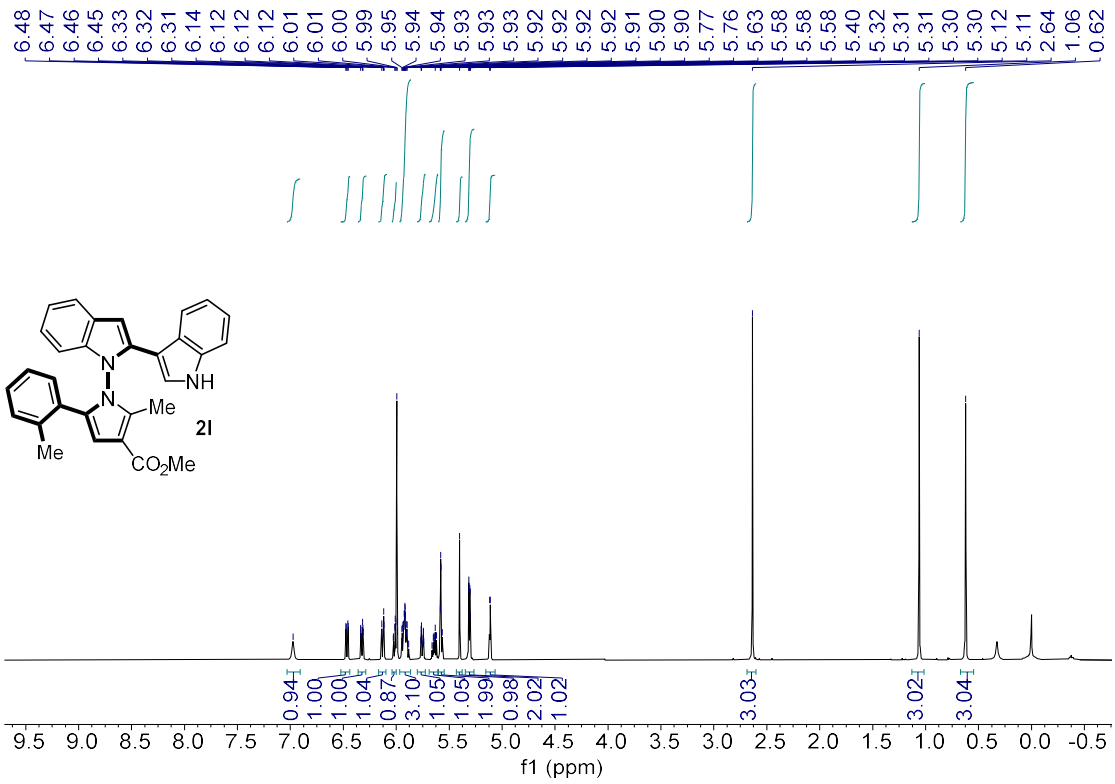


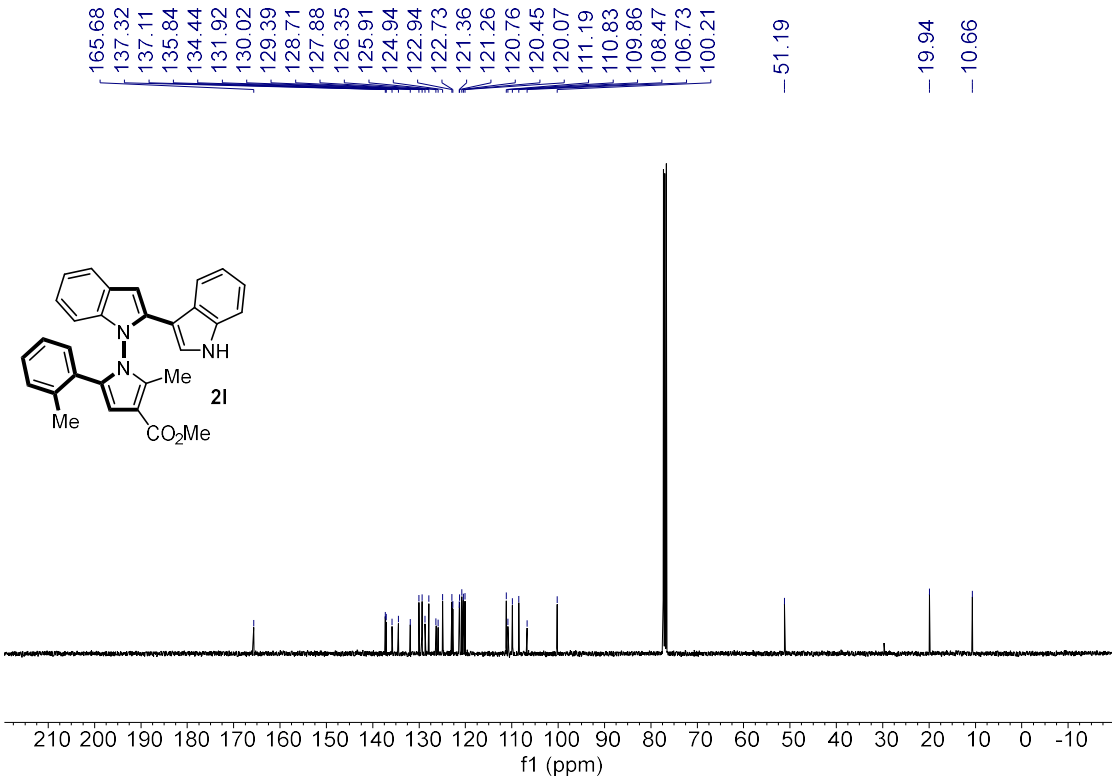
^{1}H NMR (400 MHz, $CDCl_3$) of **2k**



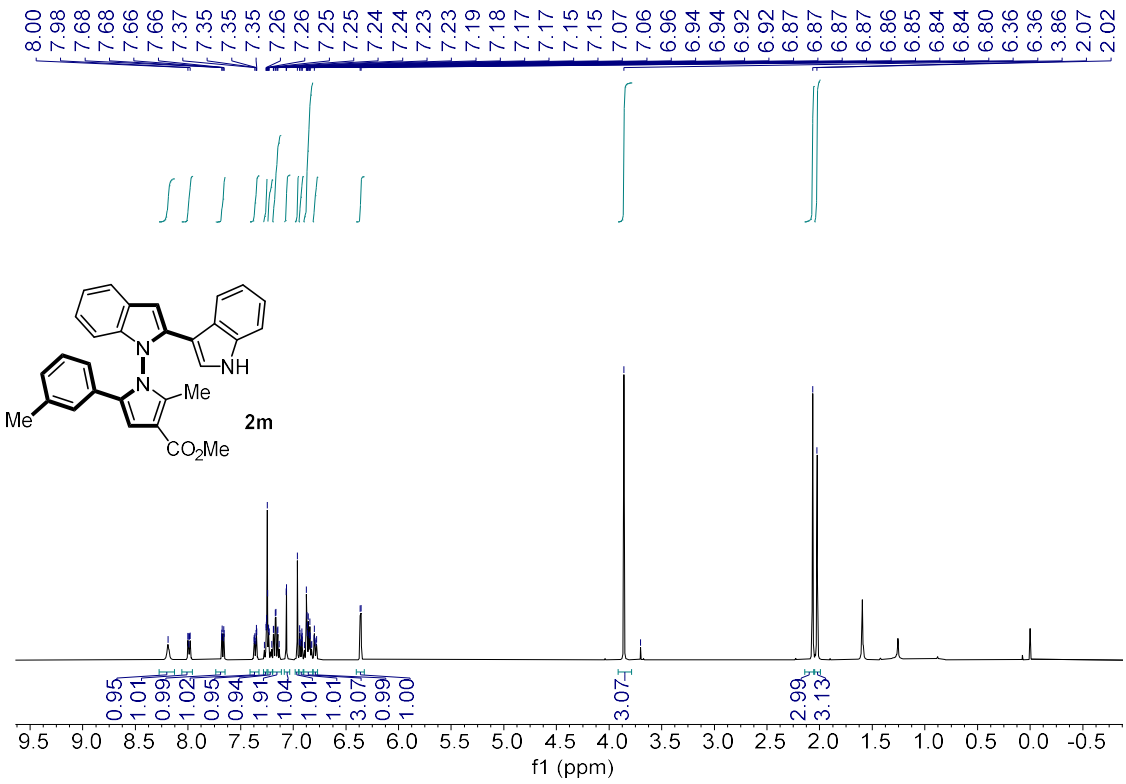
^{13}C NMR (101 MHz, $CDCl_3$) of **2k**



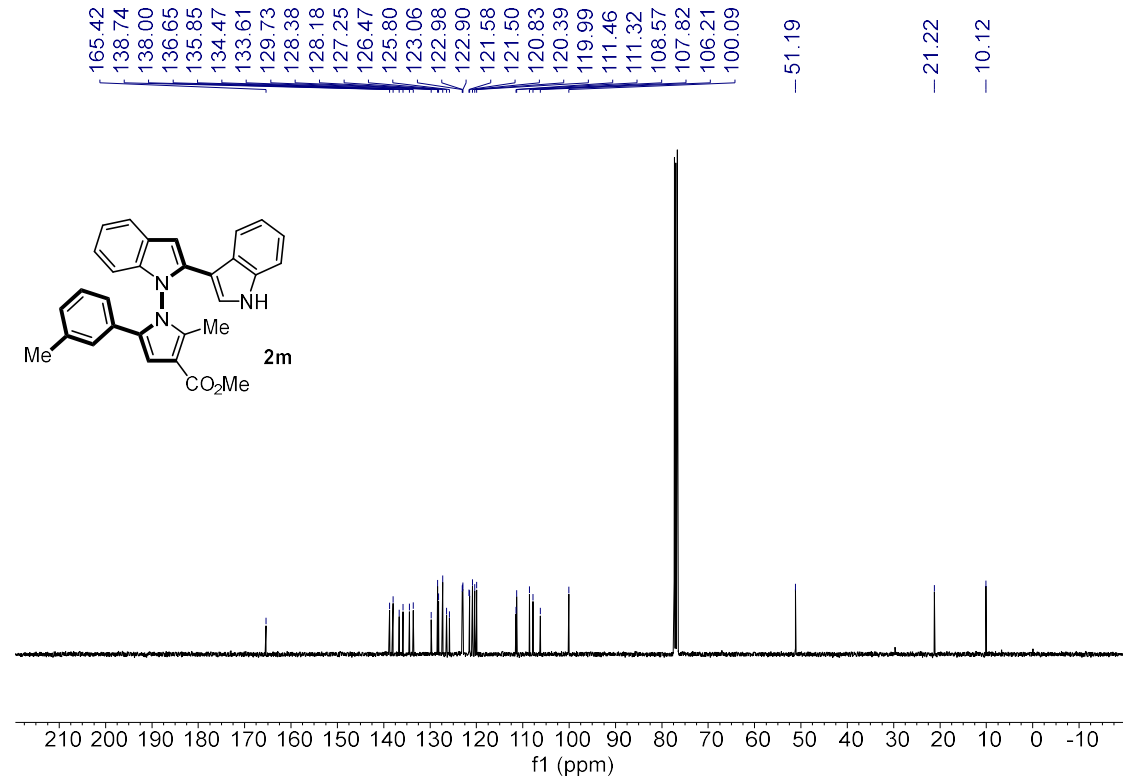
^{1}H NMR (400 MHz, $CDCl_3$) of **2l**



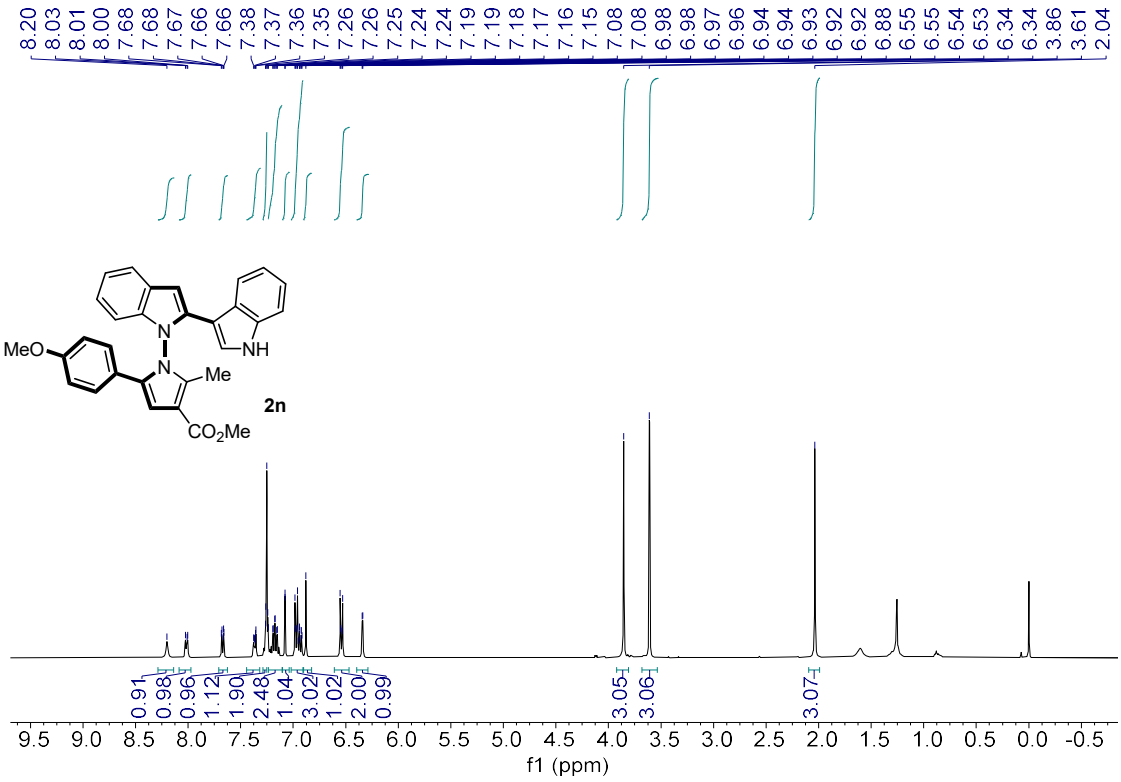
^{13}C NMR (101 MHz, $CDCl_3$) of **2l**



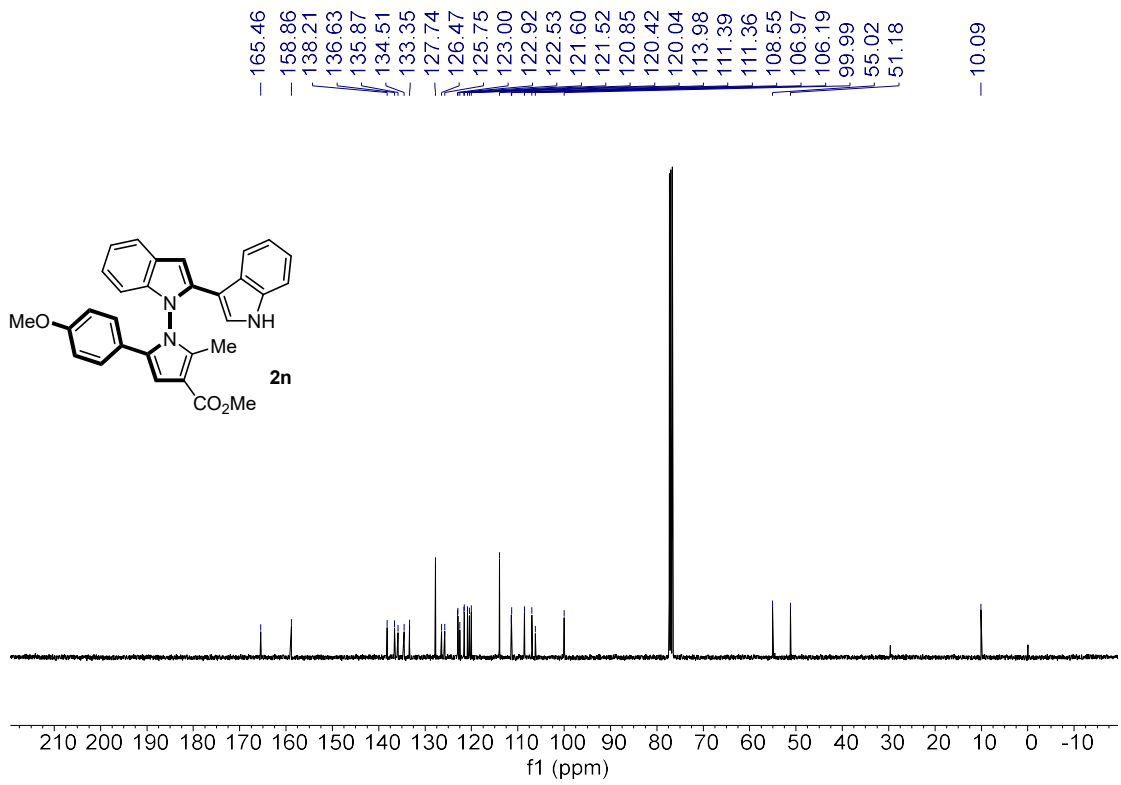
^{1}H NMR (400 MHz, $CDCl_3$) of **2m**



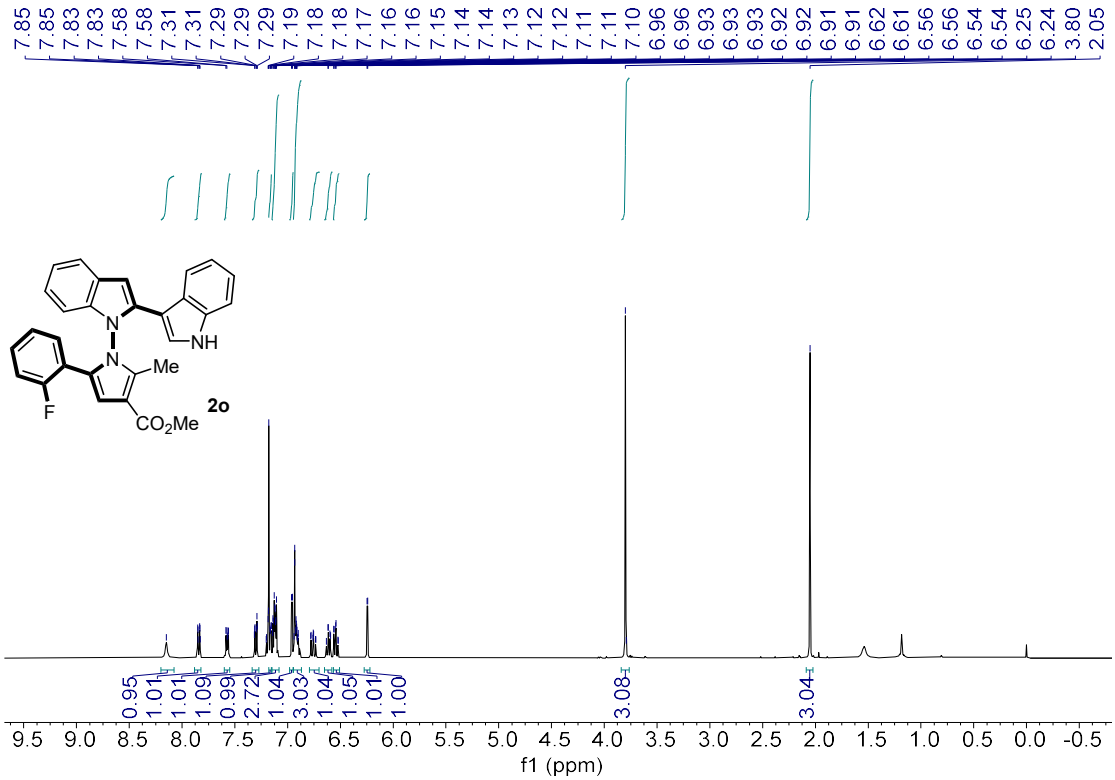
^{13}C NMR (101 MHz, $CDCl_3$) of **2m**



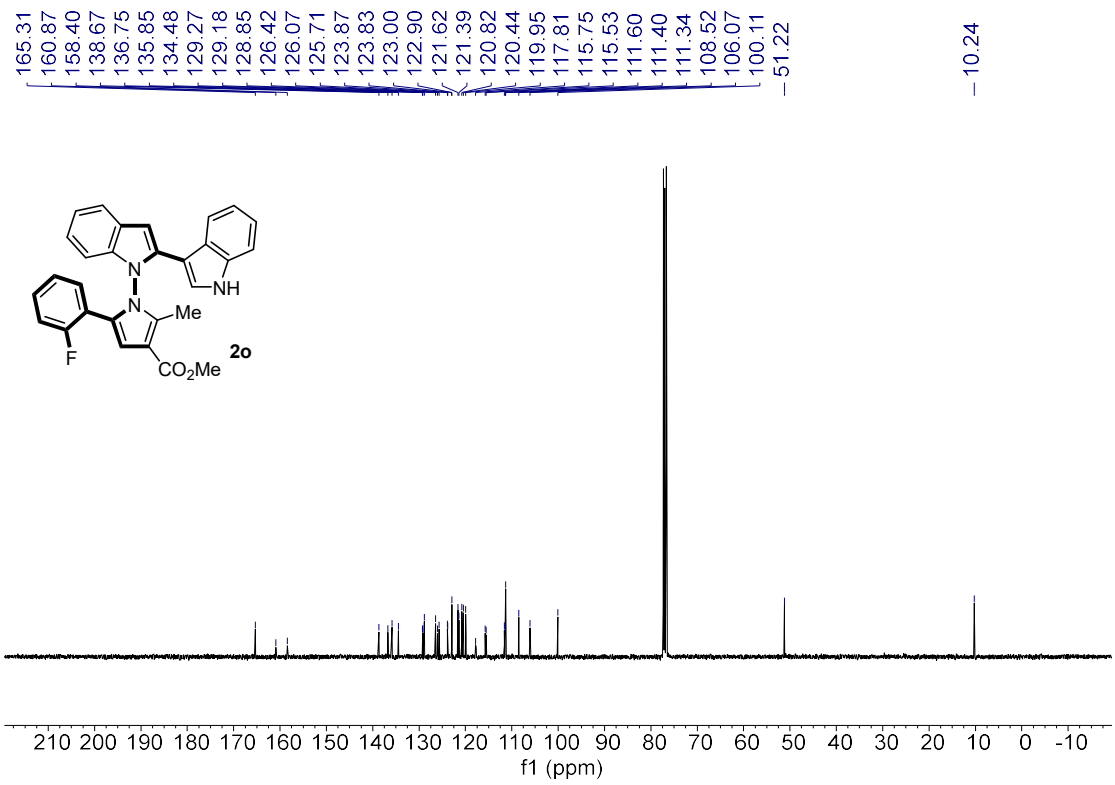
^{1}H NMR (400 MHz, $CDCl_3$) of **2n**



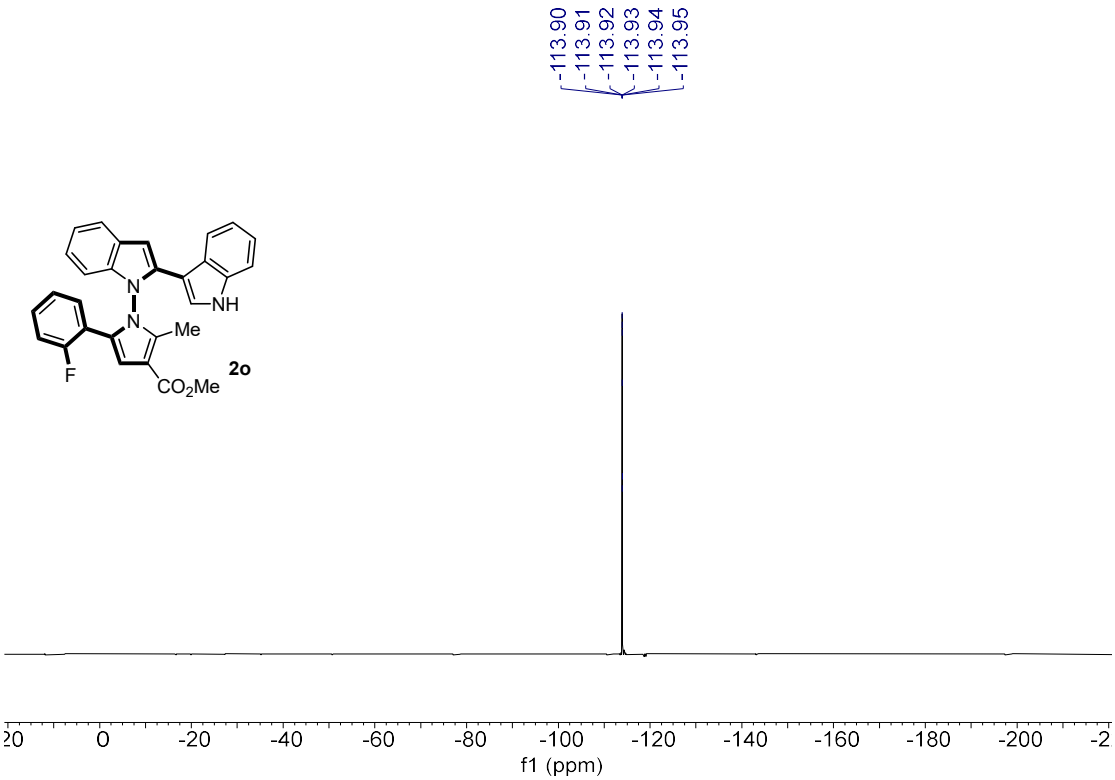
^{13}C NMR (101 MHz, $CDCl_3$) of **2n**



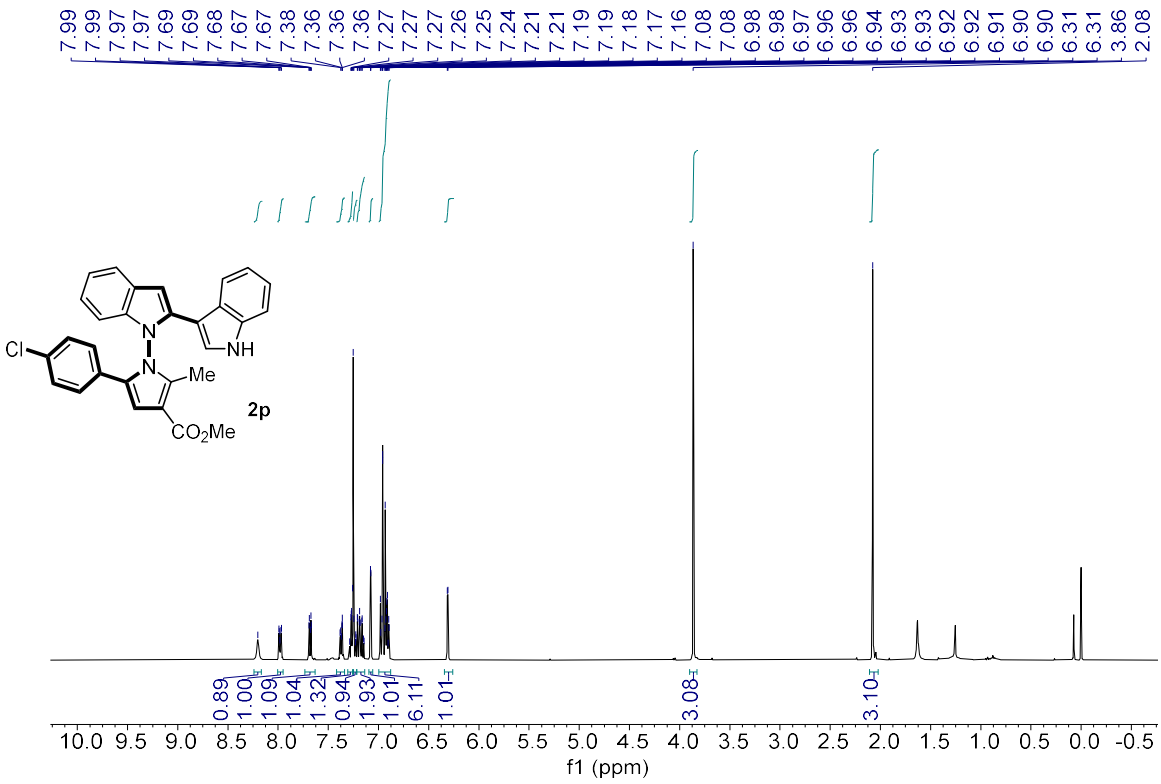
^{1}H NMR (400 MHz, $CDCl_3$) of **2o**



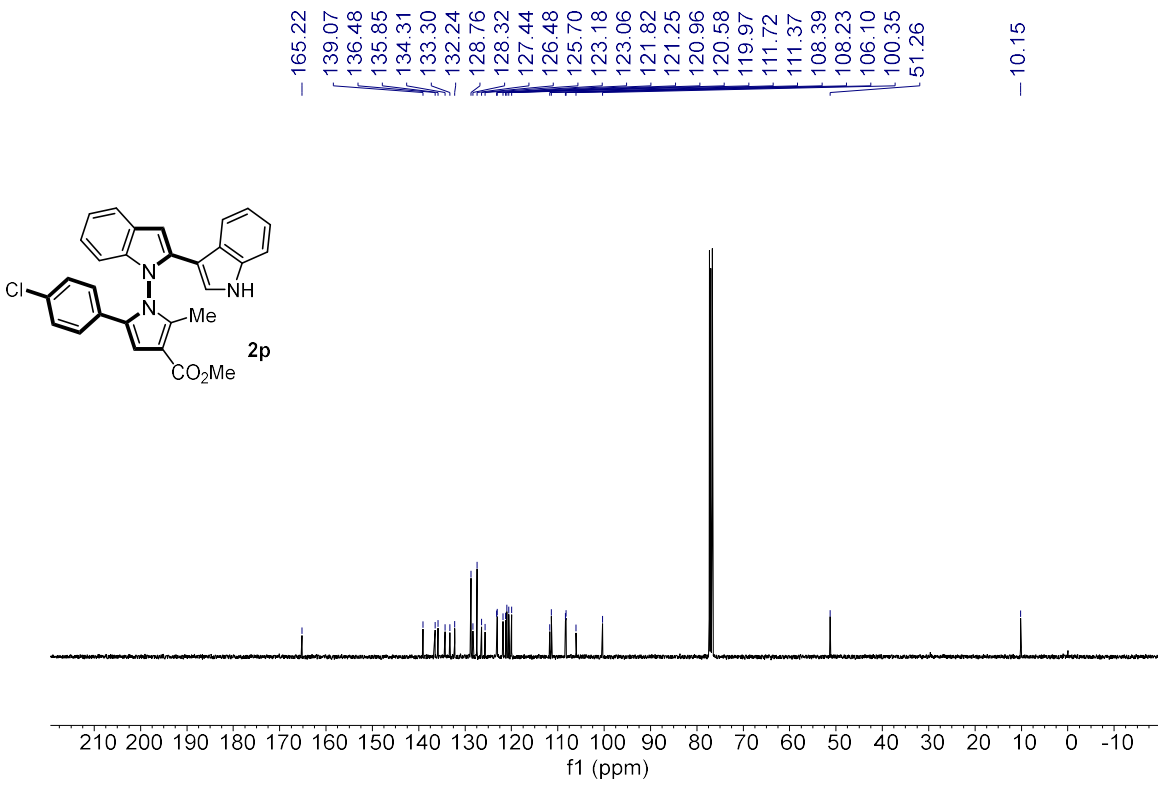
^{13}C NMR (101 MHz, $CDCl_3$) of **2o**



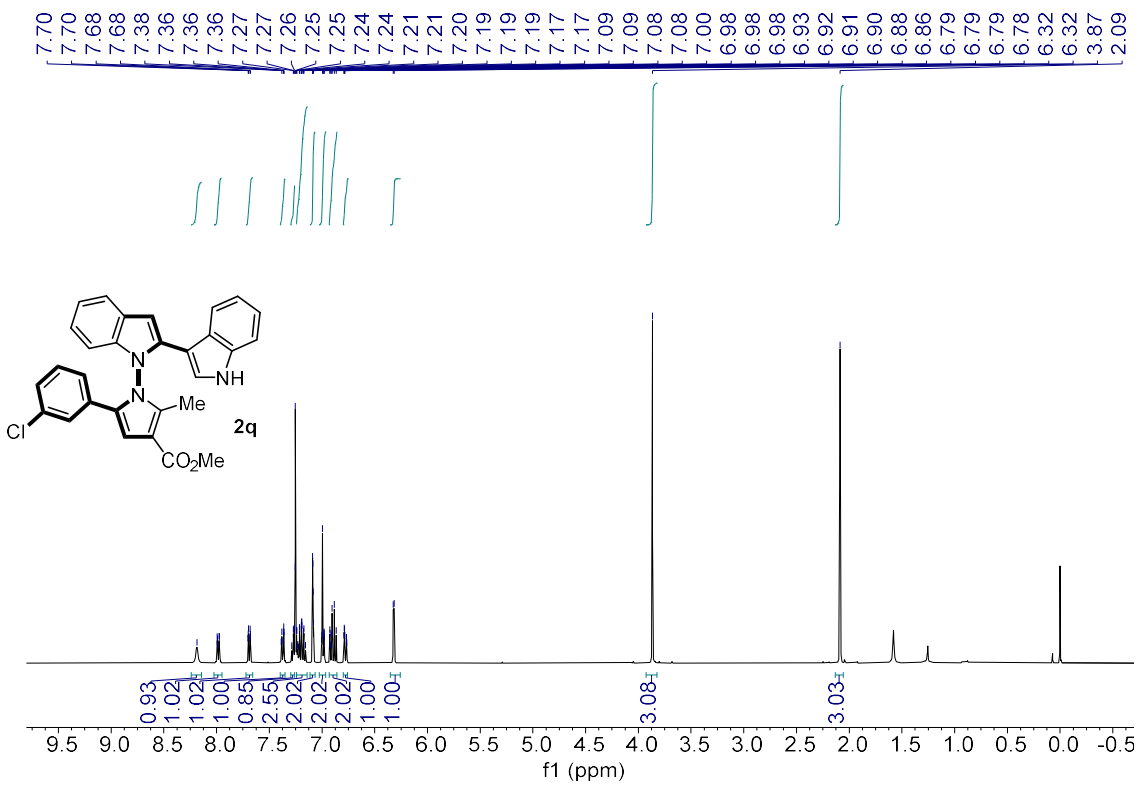
^{19}F NMR (376 MHz, $CDCl_3$) of **2o**



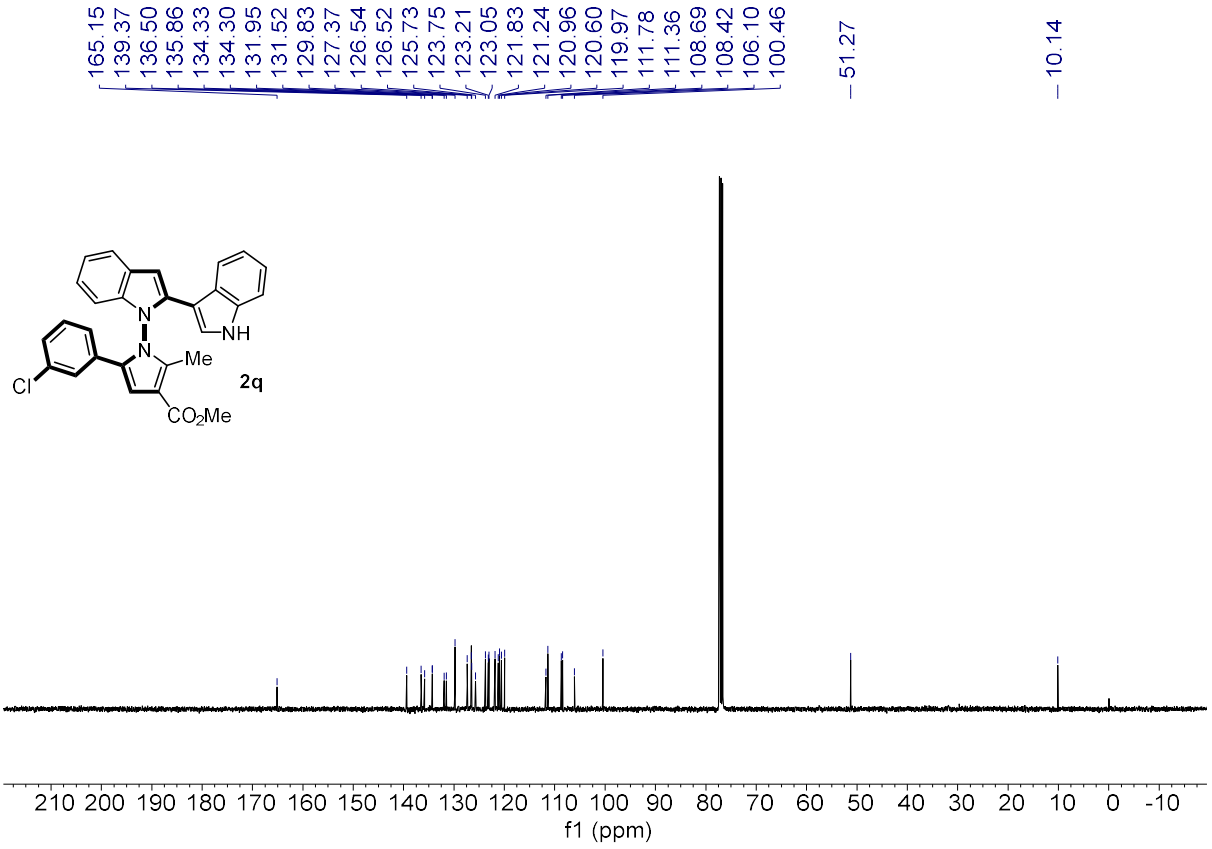
^{1}H NMR (400 MHz, $CDCl_3$) of **2p**



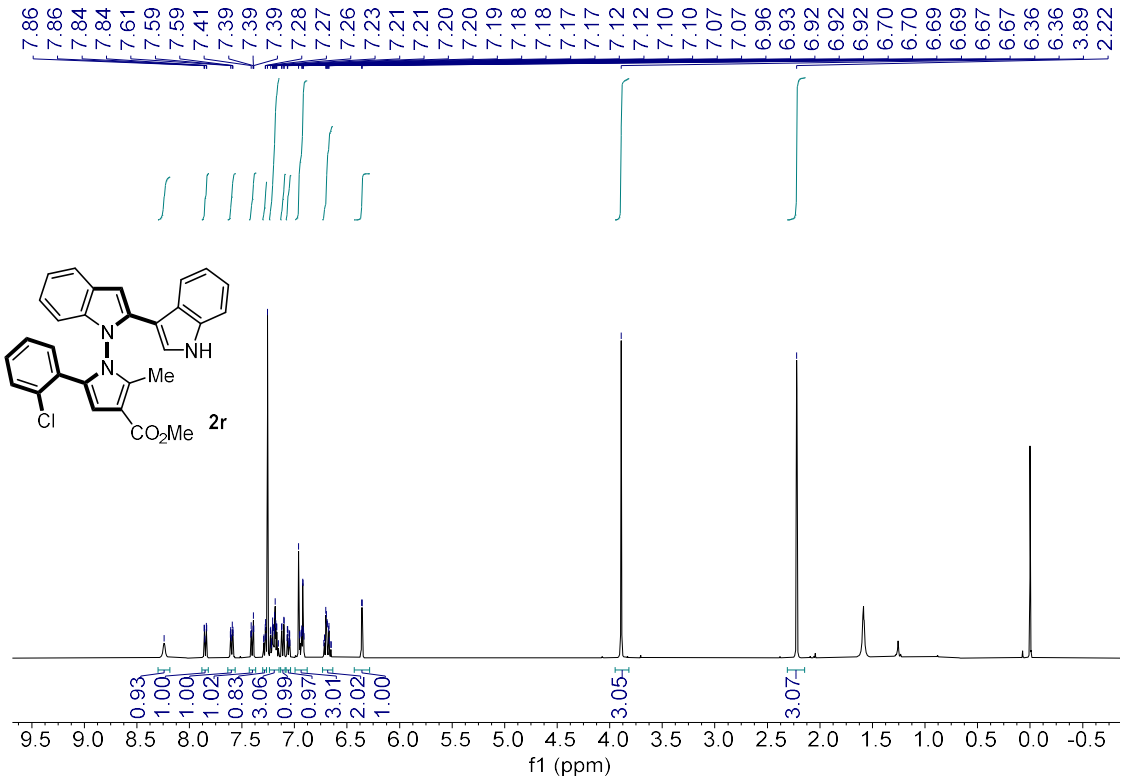
^{13}C NMR (101 MHz, $CDCl_3$) of **2p**



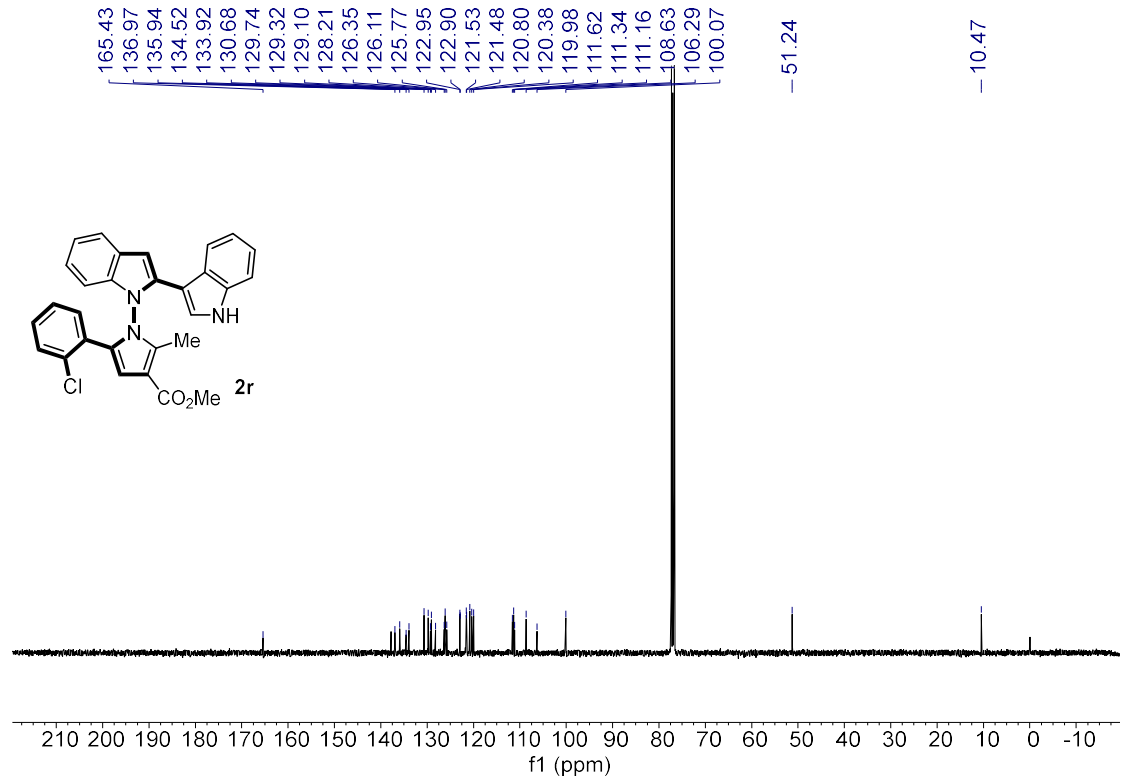
^{1}H NMR (400 MHz, $CDCl_3$) of **2q**



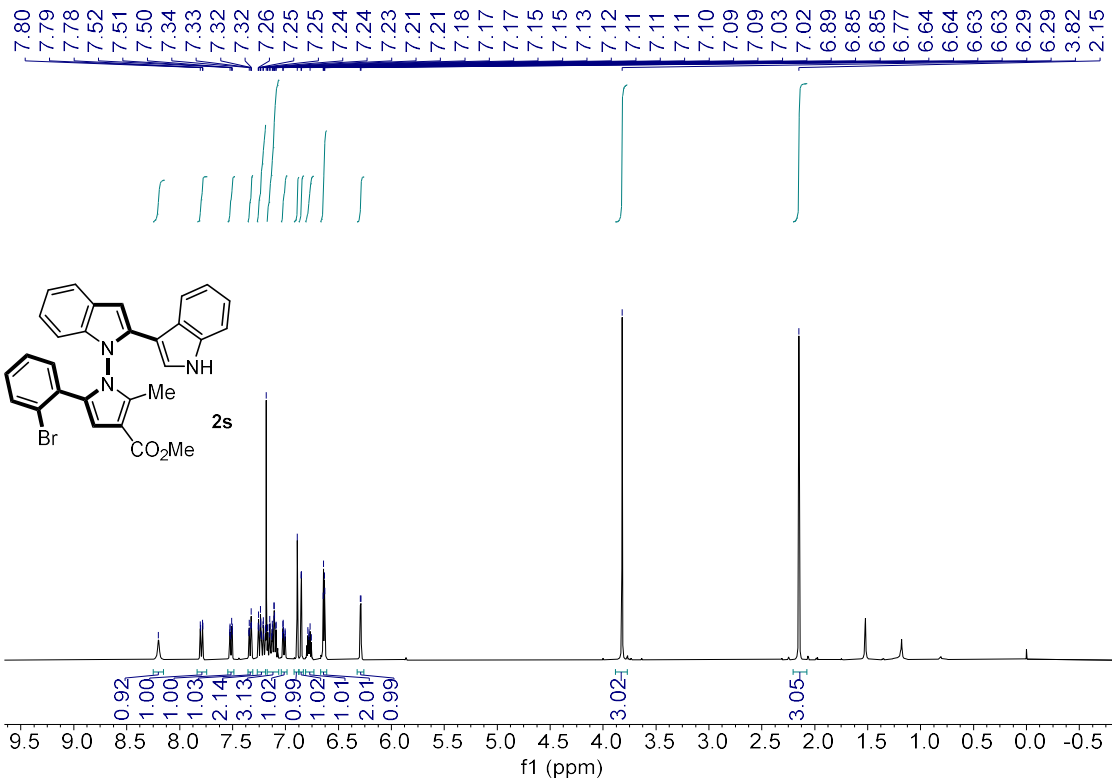
^{13}C NMR (101 MHz, $CDCl_3$) of **2q**



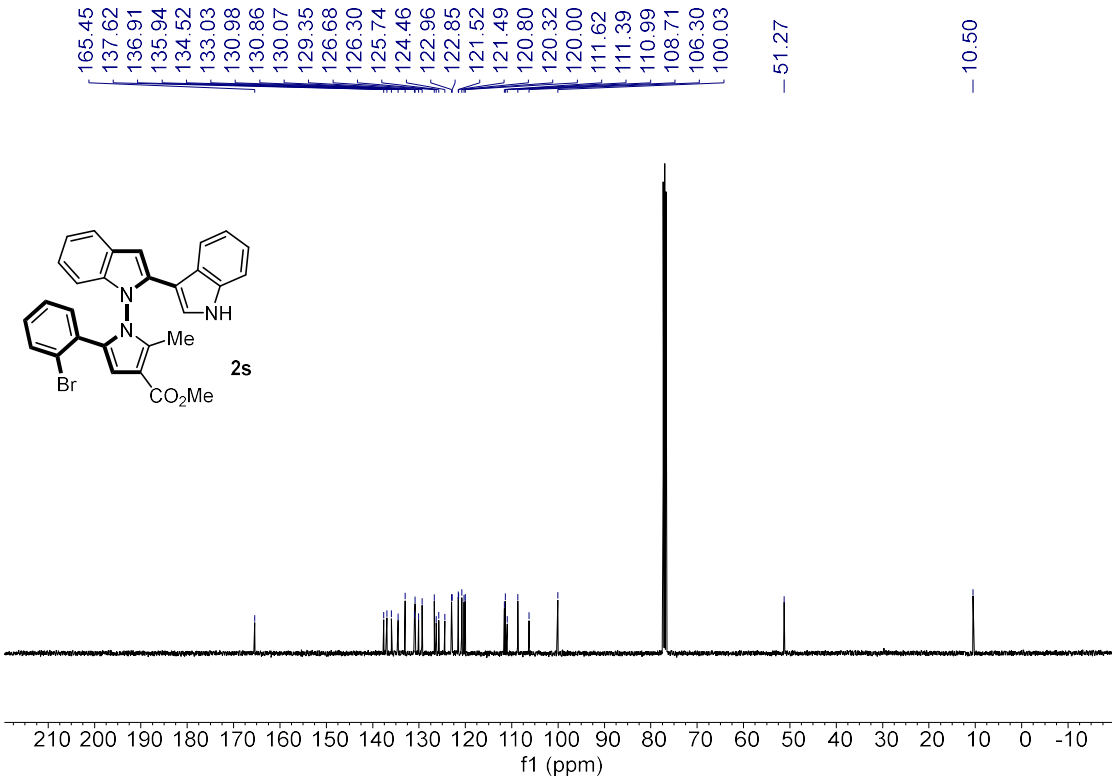
^{1}H NMR (400 MHz, $CDCl_3$) of **2r**



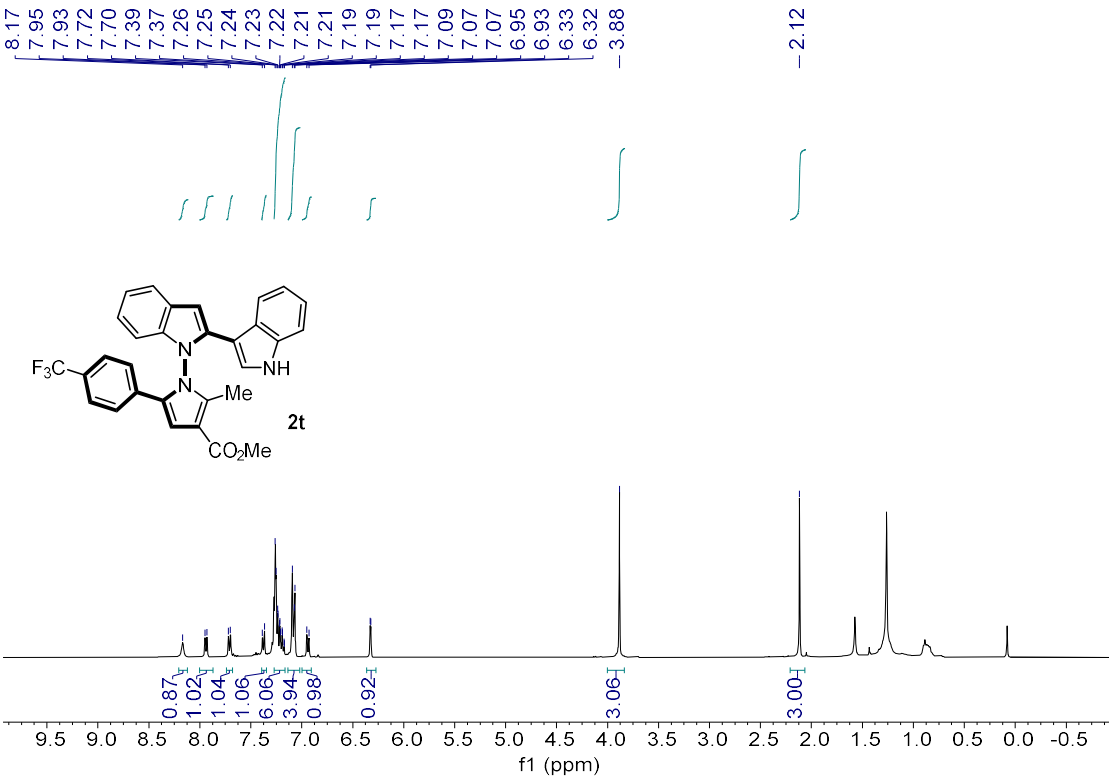
^{13}C NMR (101 MHz, $CDCl_3$) of **2r**



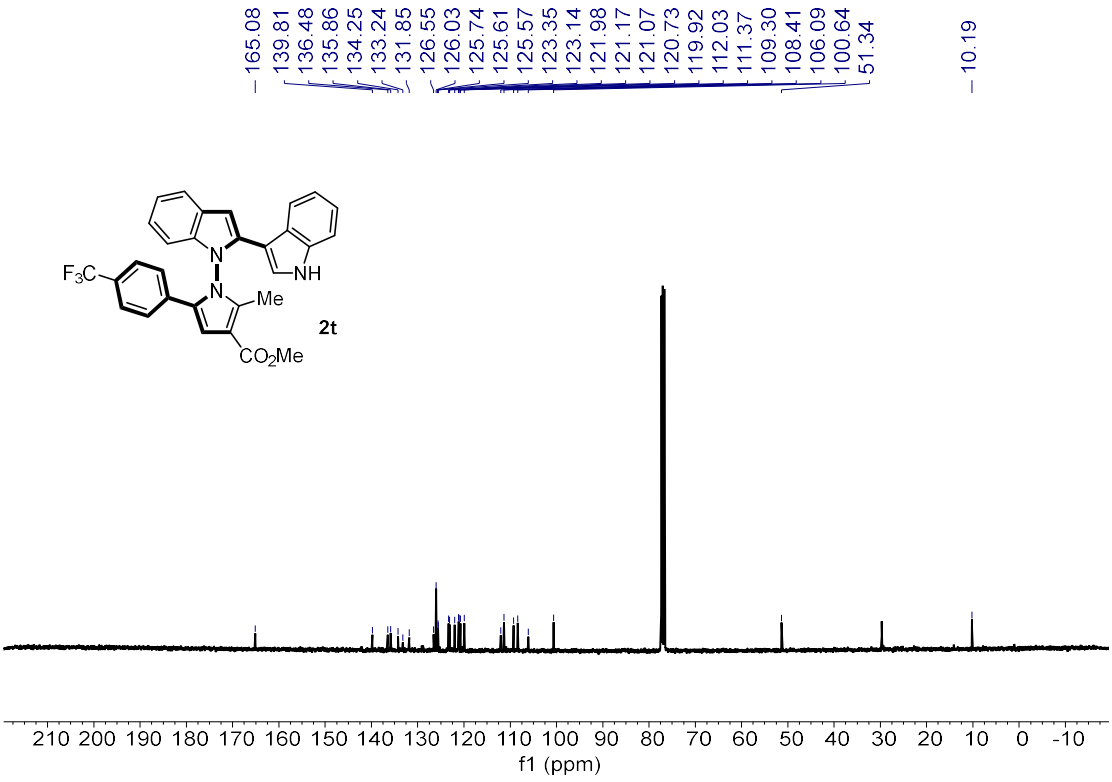
^{1}H NMR (400 MHz, $CDCl_3$) of **2s**



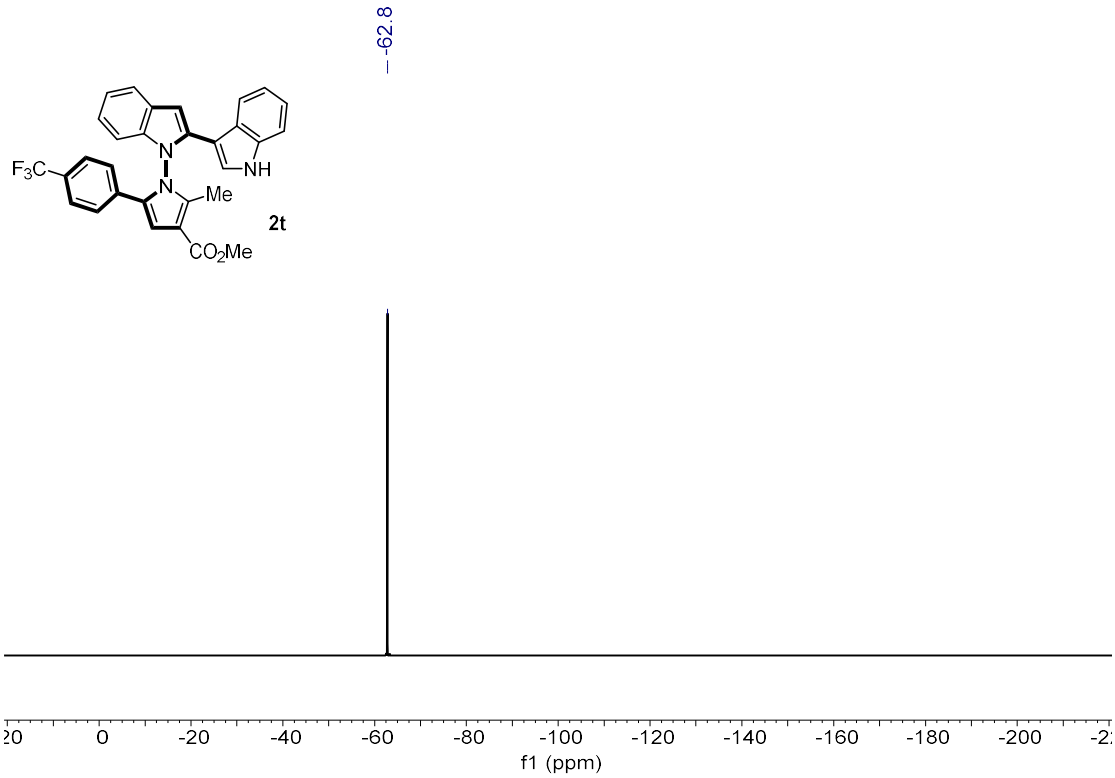
^{13}C NMR (101 MHz, $CDCl_3$) of **2s**



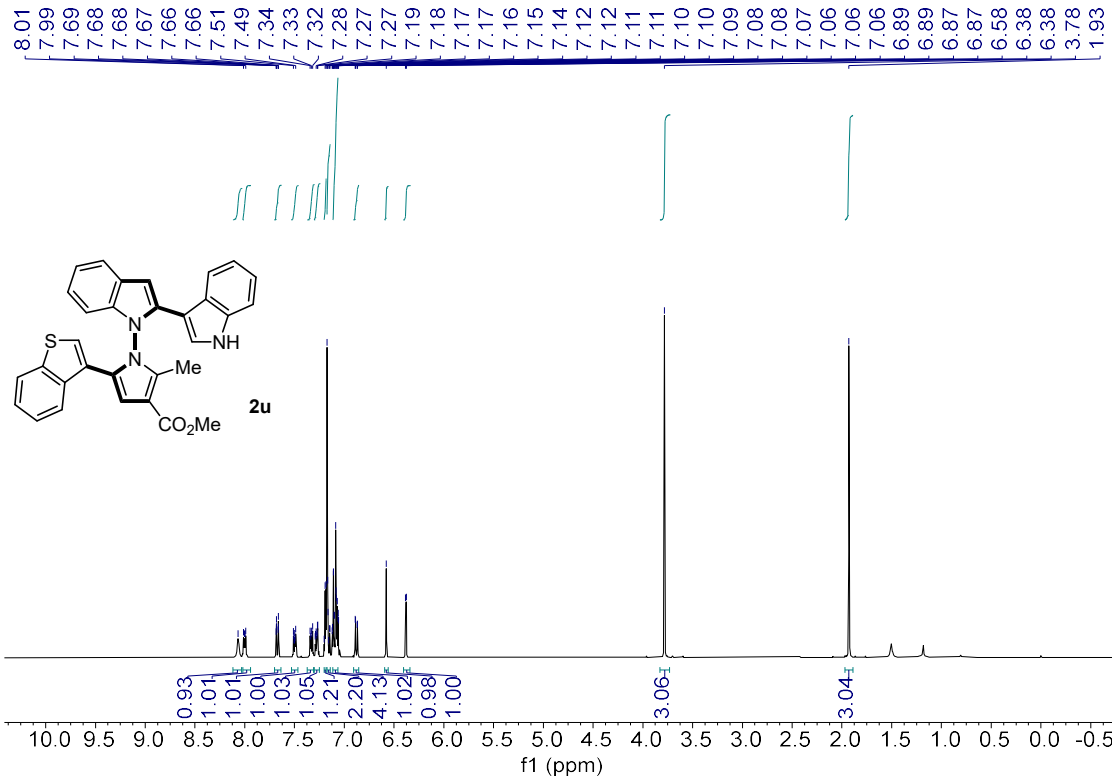
^{1}H NMR (400 MHz, $CDCl_3$) of **2t**



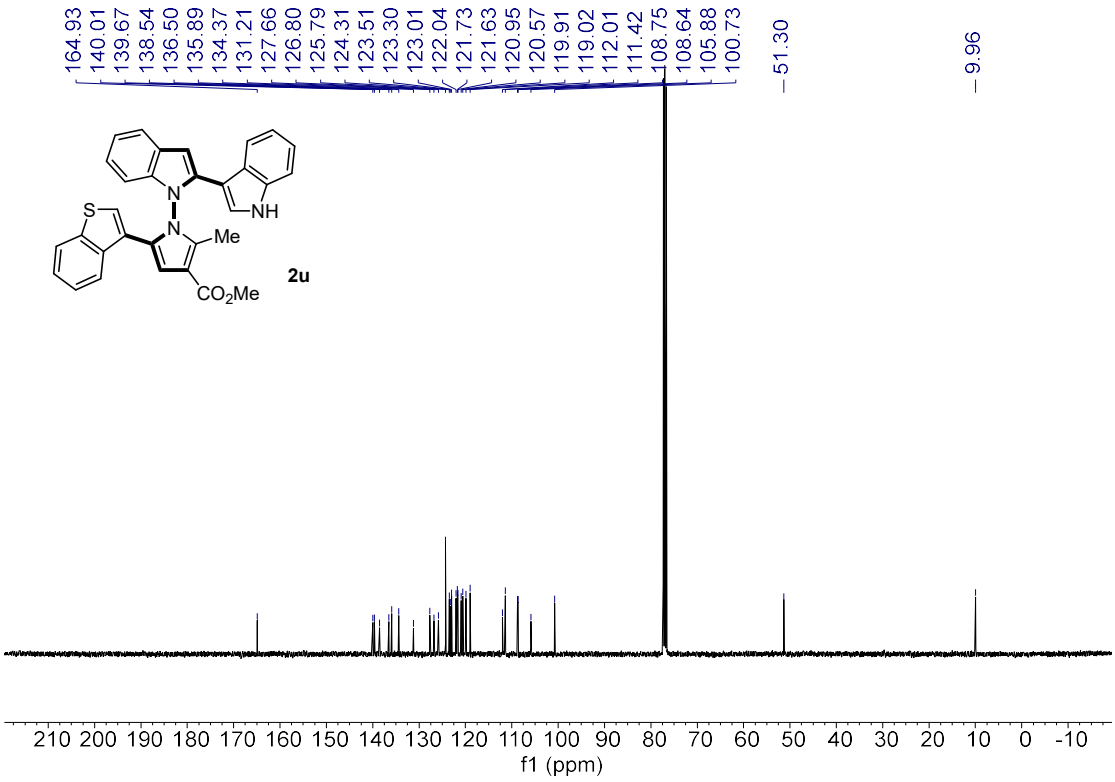
^{13}C NMR (101 MHz, $CDCl_3$) of **2t**



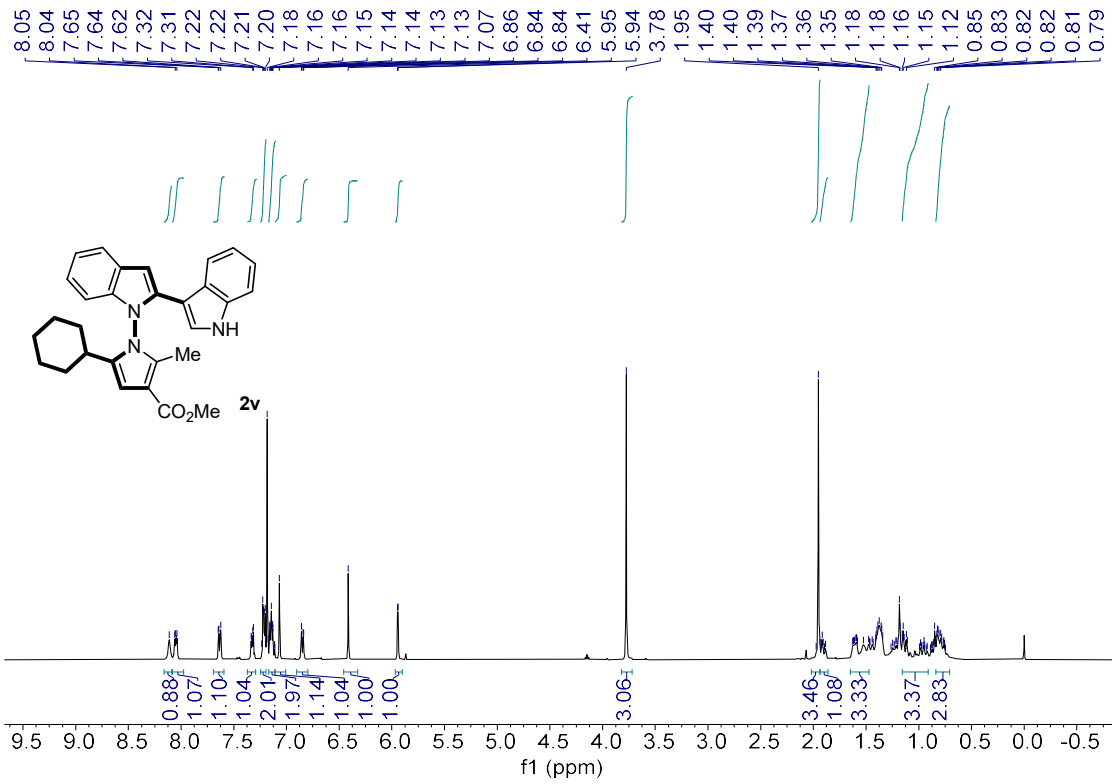
^{19}F NMR (376 MHz, $CDCl_3$) of **2t**



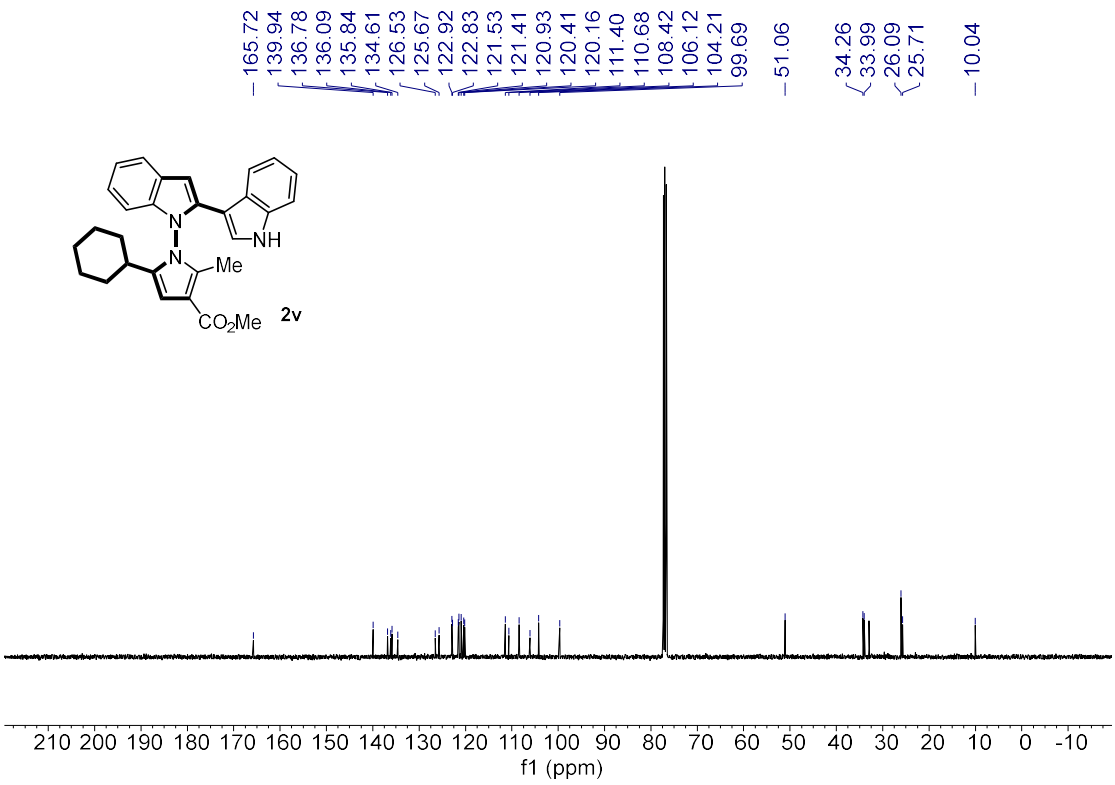
^{1}H NMR (400 MHz, $CDCl_3$) of **2u**



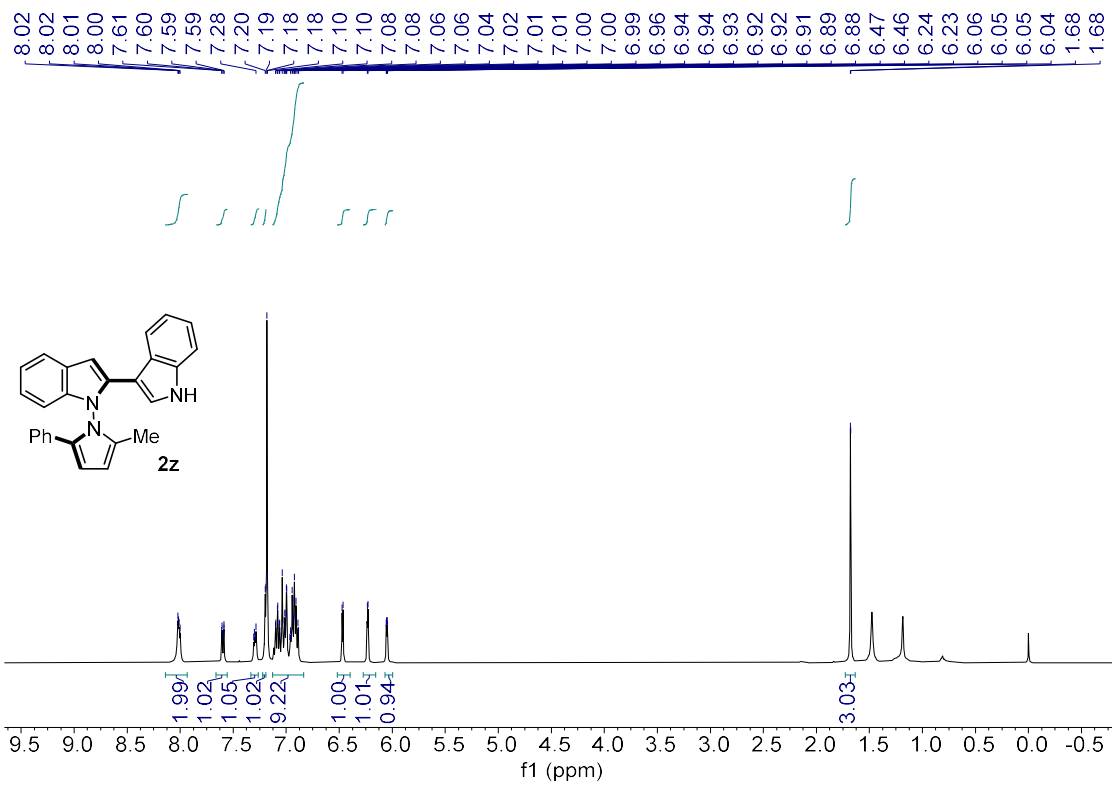
^{13}C NMR (101 MHz, $CDCl_3$) of **2u**



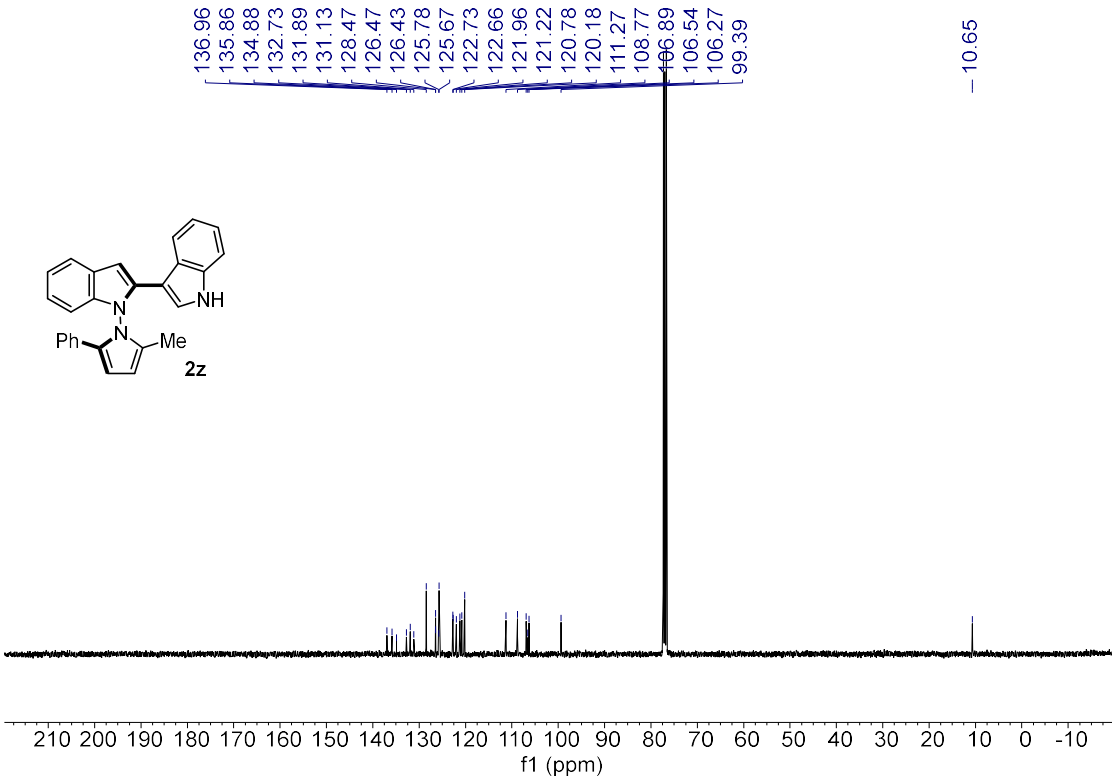
^{1}H NMR (400 MHz, $CDCl_3$) of **2v**



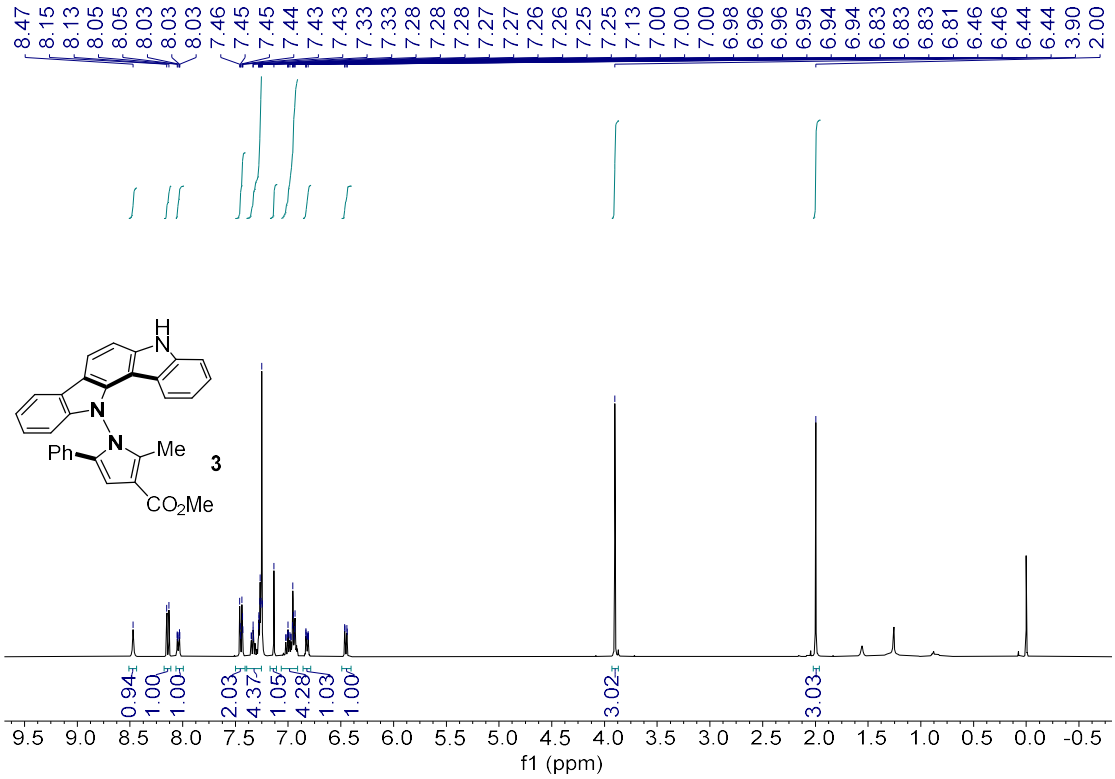
^{13}C NMR (101 MHz, $CDCl_3$) of **2v**



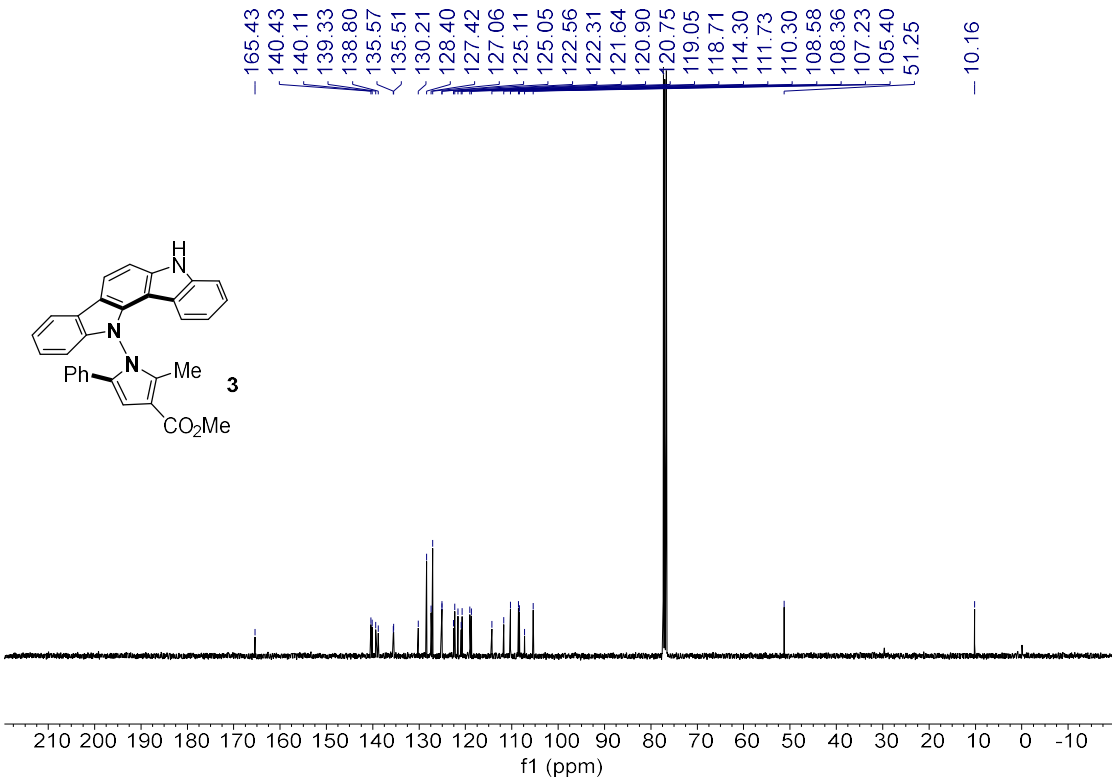
^{1}H NMR (400 MHz, $CDCl_3$) of **2z**



^{13}C NMR (101 MHz, $CDCl_3$) of **2z**



^{1}H NMR (400 MHz, $CDCl_3$) of **3**



^{13}C NMR (101 MHz, $CDCl_3$) of **3**

Computational Mechanistic studies.

Computational Methods: All DFT calculations were performed with the Gaussian 09.[1] Geometry optimizations were computed at the M06-2X/6-31G** level of theory.[2] Frequency analysis was performed at the same level to provide correction to thermodynamic functions and confirm the nature of optimized structures (minima and transition states featured zero or one imaginary frequency, respectively). Single-point energies were then calculated at the M06-2X/def2-TZVP[3] level of theory with the Truhlar-Cramer universal solvation model based on density (SMD)[4] for toluene (ε: 2.3741). Multiwfn[5] was utilized to analyze noncovalent interactions (NCIs) with the independent gradient model based on Hirshfeld partition (IGMH)[6]. Molecular visualizations were performed with PyMOL.[7]

Much efforts have been made to locate the hypothetical transition state of proton transfer **TS3**, but regrettably we can only locate transition state **TS3'** where the proton oscillates between two oxygen atoms in CPA. That is, pre- and post- intermediates are convergent to the product-CPA adduct, which indicates the high tendency of proton transferring from ammonium to phosphate anion without a barrier in the free energy profile.

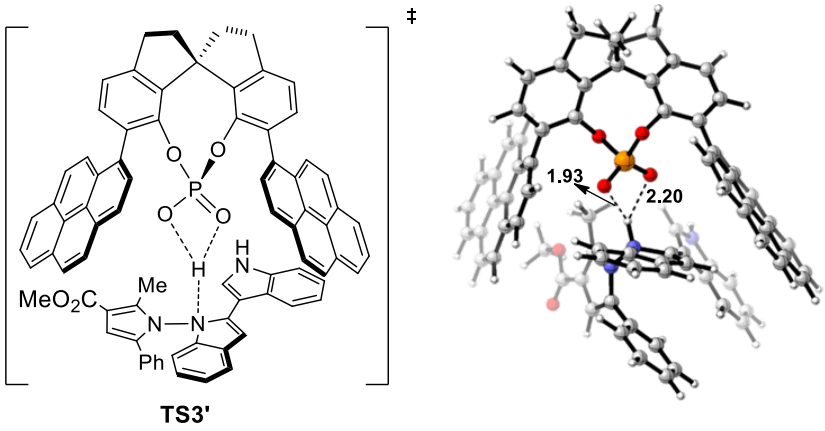


Figure S1. Optimized structure for H-oscillation transition state **TS3'**.

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[1] Frisch, M. J. et al. Gaussian 09; Gaussian, Inc.: Wallingford, CT, 2009.
[2] Y. Zhao and D. G. Truhlar, *J. Chem. Phys.* **2006**, *125*, 194101−194118.
[3] F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys*. **2005**, *7*, 3297-3305.
[4] A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378-6396.
[5] T. Lu and F. Chen, *J. Comput. Chem.* **2012**, *33*, 580-592.
[6] T. Lu and Q. Chen, *J. Comput. Chem.* **2022**, 43, 539-555.
[7] Delano, W. L. The PyMOL Molecular Graphics System; Delano Scientific, 2002.

Energies and Cartesian Coordinates (Å) for the Optimized Structures

IM1

M06-2X SCF energy in Solvent: -3961.951716 a.u.

M06-2X Free energy in Solvent: -3960.919271 a.u.

P	2.909471	-0.600147	-0.249457
O	2.560387	0.651323	0.431811
O	3.713918	-1.578212	0.744664
O	3.895636	-0.500501	-1.526845
C	1.846377	-3.812941	0.929462
C	1.410138	-3.051792	2.034933
C	0.892427	-4.422728	0.102830
C	0.011953	-2.846687	2.223710
C	2.315960	-2.468860	2.993751
C	-0.466675	-4.277715	0.322472
C	-0.454054	-1.982602	3.262231
C	-0.931148	-3.471279	1.364677
C	1.870561	-1.662801	3.985986
H	3.373914	-2.687373	2.902461
H	-1.182037	-4.739552	-0.352896
C	0.472765	-1.359146	4.137993
C	-1.844865	-1.730944	3.413038
C	-2.334039	-3.221359	1.553984
H	2.571009	-1.225949	4.692100
C	0.001638	-0.486926	5.124401
C	-2.274658	-0.851386	4.412922
C	-2.770645	-2.384878	2.525434
H	-3.034508	-3.700714	0.875150
C	-1.358965	-0.229894	5.253639
H	0.715210	-0.008111	5.789241
H	-3.336340	-0.644676	4.514225
H	-3.833596	-2.190443	2.649407
H	-1.709996	0.459142	6.014892
H	1.234344	-4.981115	-0.763194
C	5.744717	-4.218772	-0.786716
C	4.114271	-2.839414	0.322477
C	3.265644	-3.945199	0.502471
C	3.736427	-5.195135	0.073704
C	4.957455	-5.341533	-0.574931
H	3.098618	-6.060176	0.227415
H	5.272846	-6.316097	-0.935125
C	7.296903	0.270914	-0.364562
C	6.176519	-0.467125	-0.763897
C	5.068432	0.206873	-1.259259

C	5.069948	1.601196	-1.404534
C	6.238175	2.297891	-1.077061
C	7.346285	1.646343	-0.543505
H	8.223174	2.212653	-0.244550
C	6.443696	-1.949045	-0.561359
C	5.349991	-2.970165	-0.297988
H	6.245684	3.376763	-1.201598
C	8.309685	-0.630958	0.301268
H	8.737821	-0.179074	1.200011
C	7.472635	-1.887085	0.602296
H	6.928352	-1.751698	1.542792
H	8.065288	-2.802745	0.679390
C	7.036983	-4.098565	-1.559227
H	7.024960	-4.683899	-2.482476
H	7.888451	-4.450886	-0.964180
C	7.118580	-2.583074	-1.811493
H	6.527090	-2.323621	-2.695594
H	8.137064	-2.214953	-1.962926
C	3.846346	2.330809	-1.832142
C	3.250205	3.287001	-0.983151
C	3.271117	2.059779	-3.074889
C	2.093796	3.984162	-1.427719
C	3.727076	3.541597	0.354182
C	2.138293	2.734672	-3.508443
H	3.727219	1.304483	-3.707341
C	1.464712	4.948365	-0.579032
C	1.536017	3.706221	-2.704512
C	3.138855	4.463020	1.152994
H	4.555377	2.952097	0.728320
H	1.710393	2.511977	-4.481751
C	1.994610	5.214959	0.712787
C	0.292882	5.626202	-1.012410
C	0.359415	4.421898	-3.125556
H	3.508458	4.630349	2.160689
C	1.354168	6.150835	1.537699
C	-0.327407	6.540461	-0.152332
C	-0.233256	5.336891	-2.322261
H	-0.050917	4.202489	-4.107519
C	0.200041	6.800953	1.108919
H	1.766385	6.354626	2.522300
H	-1.229276	7.048050	-0.483663
H	-1.127165	5.862731	-2.646333
H	-0.289541	7.517300	1.761000
H	9.142871	-0.857990	-0.374934

C	-1.058372	0.050985	0.171543
C	-1.279602	-0.880744	-0.583167
H	0.880453	-1.256199	-0.471522
O	1.740681	-1.437276	-0.905182
C	-1.797381	-1.804292	-1.546964
C	-3.200016	-1.977315	-1.616409
C	-0.979115	-2.464914	-2.471724
N	-4.004180	-1.405917	-0.611114
C	-3.746856	-2.757650	-2.635075
C	-1.532021	-3.261879	-3.465404
H	0.095906	-2.330476	-2.407960
C	-2.916083	-3.392201	-3.552253
H	-4.824085	-2.852449	-2.713852
H	-0.886677	-3.763613	-4.177925
H	-3.359212	-3.993621	-4.339385
N	-5.284170	-0.997634	-0.949041
C	-5.654480	0.310764	-1.264653
C	-6.380419	-1.814510	-0.865043
C	-7.017307	0.301052	-1.413192
C	-7.475251	-1.025386	-1.185156
H	-7.640170	1.145708	-1.668577
C	-6.264913	-3.247105	-0.461617
H	-5.269170	-3.437109	-0.055154
H	-6.436583	-3.920413	-1.306845
H	-7.018892	-3.482020	0.290810
C	-4.709372	1.438782	-1.219712
C	-5.072296	2.583830	-0.497381
C	-3.448455	1.395068	-1.827515
C	-4.187143	3.645546	-0.362434
H	-6.037935	2.608402	-0.001509
C	-2.560693	2.458060	-1.684827
H	-3.160141	0.526430	-2.413440
C	-2.923239	3.579663	-0.944391
H	-4.467823	4.507092	0.235140
H	-1.571469	2.398969	-2.130238
H	-2.209015	4.383952	-0.794742
C	-8.878159	-1.426915	-1.281479
O	-9.796858	-0.682112	-1.537649
C	-3.357725	1.239522	2.101157
C	-2.098386	1.733313	1.744266
C	-4.202523	2.040330	2.852312
C	-1.726894	3.030524	2.157341
C	-0.992471	1.217984	0.969202
C	-3.813289	3.332526	3.252564

H	-5.182756	1.669717	3.135094
C	-2.572168	3.845825	2.912649
C	-0.023129	2.200081	0.952708
H	-4.497524	3.936509	3.839827
H	-2.265941	4.842481	3.215171
H	-3.657256	0.233646	1.815873
N	-0.463877	3.275938	1.663773
H	0.063325	4.127570	1.795823
H	0.956670	2.179507	0.493590
O	-9.057286	-2.749441	-1.052389
C	-10.411390	-3.181984	-1.132811
H	-10.399124	-4.248401	-0.911409
H	-10.813784	-3.002025	-2.132352
H	-11.029861	-2.646137	-0.409195
H	-3.523422	-0.687815	-0.076180

TS1

M06-2X SCF energy in Solvent: -3961.91928 a.u.

M06-2X Free energy in Solvent: -3960.892374 a.u.

P	2.752476	-0.621304	-0.508391
O	2.220600	0.527373	0.260096
O	3.344200	-1.711019	0.573551
O	4.122435	-0.257851	-1.344000
C	1.645023	-3.954970	-0.179165
C	0.900296	-3.660818	0.978926
C	0.971200	-4.245733	-1.372944
C	-0.523441	-3.679643	0.908909
C	1.515301	-3.368943	2.250136
C	-0.409297	-4.251314	-1.449144
C	-1.306551	-3.410624	2.074342
C	-1.177969	-3.977417	-0.313820
C	0.771995	-3.102114	3.349901
H	2.597658	-3.365399	2.308487
H	-0.906559	-4.451055	-2.394464
C	-0.667013	-3.115561	3.308035
C	-2.727586	-3.455572	2.011801
C	-2.613279	-3.980970	-0.360313
H	1.254695	-2.882607	4.297884
C	-1.449547	-2.874522	4.442133
C	-3.474437	-3.226220	3.174988
C	-3.357811	-3.730620	0.746945
H	-3.087354	-4.215611	-1.309921
C	-2.838157	-2.938119	4.376776
H	-0.957016	-2.644720	5.382643

H	-4.559084	-3.270692	3.123552
H	-4.443912	-3.751056	0.704787
H	-3.427469	-2.758054	5.270577
H	1.562212	-4.427156	-2.264946
C	5.875610	-3.989849	-0.781919
C	3.922852	-2.853737	0.064571
C	3.131784	-3.974104	-0.241735
C	3.761188	-5.104641	-0.778028
C	5.123659	-5.123226	-1.056013
H	3.148282	-5.970365	-1.011374
H	5.579834	-5.997312	-1.510968
C	6.950315	0.339200	0.913938
C	6.050290	-0.323881	0.074124
C	5.082713	0.404465	-0.606705
C	5.031285	1.802915	-0.491487
C	6.000674	2.445002	0.287565
C	6.950360	1.724330	1.005926
H	7.662044	2.239081	1.644489
C	6.350450	-1.811739	0.072224
C	5.290446	-2.868219	-0.187354
H	5.974188	3.528929	0.355135
C	7.794163	-0.660096	1.671115
H	7.915211	-0.388242	2.723361
C	7.001454	-1.965215	1.475265
H	6.202797	-2.027486	2.221939
H	7.613804	-2.868406	1.552144
C	7.326530	-3.719291	-1.102475
H	7.616333	-4.109313	-2.082011
H	7.988979	-4.182486	-0.360527
C	7.388045	-2.184055	-1.025214
H	7.054151	-1.754975	-1.975753
H	8.385611	-1.792830	-0.805250
C	3.953779	2.581421	-1.153975
C	3.134824	3.462593	-0.415942
C	3.744800	2.446151	-2.528869
C	2.158618	4.243346	-1.095604
C	3.205652	3.566993	1.021159
C	2.773554	3.183691	-3.189367
H	4.359567	1.743101	-3.080961
C	1.344455	5.171487	-0.371961
C	1.975705	4.098987	-2.496723
C	2.446285	4.457606	1.705582
H	3.866498	2.893729	1.553755
H	2.631225	3.059874	-4.259220

C	1.504225	5.315339	1.033942
C	0.378322	5.960766	-1.054551
C	0.974626	4.893203	-3.157695
H	2.523896	4.523719	2.788307
C	0.714840	6.246818	1.722989
C	-0.387142	6.883229	-0.329901
C	0.215536	5.784154	-2.474923
H	0.843334	4.762494	-4.228285
C	-0.214420	7.028659	1.042728
H	0.851699	6.365882	2.795219
H	-1.123349	7.485384	-0.854780
H	-0.534587	6.381386	-2.985220
H	-0.811317	7.753448	1.587374
H	8.799845	-0.735824	1.239484
C	-0.773725	-0.040532	-0.071988
C	-0.614214	-0.806785	-1.073950
H	0.569101	-1.218638	-1.154842
O	1.891156	-1.356707	-1.522578
C	-1.426396	-0.995775	-2.282982
C	-2.824059	-0.804159	-2.261178
C	-0.792147	-1.312191	-3.484560
N	-3.423043	-0.578413	-1.003949
C	-3.537391	-0.816927	-3.458650
C	-1.513700	-1.353849	-4.674013
H	0.280664	-1.483978	-3.464447
C	-2.877687	-1.080342	-4.657749
H	-4.604968	-0.623931	-3.448459
H	-1.009780	-1.578571	-5.607573
H	-3.446301	-1.085109	-5.582098
N	-4.771174	-0.285227	-0.935257
C	-5.233930	0.926882	-0.426719
C	-5.816938	-1.159955	-1.135031
C	-6.595105	0.819036	-0.323068
C	-6.965004	-0.479570	-0.768650
H	-7.279427	1.589240	0.000648
C	-5.628665	-2.540631	-1.670162
H	-4.569351	-2.766541	-1.784153
H	-6.114187	-2.644090	-2.644541
H	-6.090853	-3.275997	-1.007632
C	-4.366687	2.061420	-0.087213
C	-4.676191	2.818421	1.049908
C	-3.280734	2.445549	-0.883977
C	-3.924881	3.940669	1.377912
H	-5.499436	2.504760	1.684455

C	-2.526091	3.565302	-0.548118
H	-3.035923	1.875668	-1.775137
C	-2.845277	4.316728	0.581584
H	-4.173769	4.511712	2.267162
H	-1.683697	3.855354	-1.171724
H	-2.244847	5.184373	0.839658
C	-8.349768	-0.952489	-0.817083
O	-9.311764	-0.308862	-0.465027
C	-2.636456	0.091363	2.654875
C	-1.651911	0.922554	2.128413
C	-3.313150	0.512476	3.790943
C	-1.371864	2.149858	2.750879
C	-0.815982	0.867584	0.939632
C	-3.022997	1.744022	4.398582
H	-4.078768	-0.127428	4.217587
C	-2.041077	2.584351	3.889472
C	-0.064749	2.060774	0.926713
H	-3.574871	2.045210	5.282720
H	-1.818705	3.542092	4.348763
H	-2.857426	-0.866639	2.195144
N	-0.378499	2.784156	1.997995
H	0.011314	3.700298	2.183254
H	0.703723	2.350881	0.221554
O	-8.454502	-2.210971	-1.303569
C	-9.786986	-2.711719	-1.358826
H	-9.712475	-3.713625	-1.779233
H	-10.410392	-2.074856	-1.989935
H	-10.226332	-2.745930	-0.359177
H	-3.132294	-1.244688	-0.290060

IM2

M06-2X SCF energy in Solvent: -3961.928493 a.u.

M06-2X Free energy in Solvent: -3960.899445 a.u.

P	2.753913	-0.648921	-0.816499
O	2.128769	0.507649	-0.114815
O	3.299792	-1.644053	0.406405
O	4.216855	-0.204299	-1.466784
C	1.672774	-3.984512	-0.132335
C	0.963960	-3.655831	1.042504
C	0.957018	-4.383398	-1.270456
C	-0.460037	-3.738792	1.043249
C	1.619855	-3.238545	2.257542
C	-0.424371	-4.474177	-1.271496
C	-1.204412	-3.381008	2.210709

C	-1.155159	-4.154974	-0.122484
C	0.913588	-2.902449	3.362592
H	2.702430	-3.190291	2.266596
H	-0.953611	-4.760571	-2.176192
C	-0.524704	-2.957438	3.384290
C	-2.626071	-3.453026	2.208806
C	-2.591799	-4.189612	-0.109948
H	1.427553	-2.587006	4.266064
C	-1.268405	-2.629319	4.523559
C	-3.332083	-3.134488	3.376765
C	-3.298365	-3.851849	0.998758
H	-3.099465	-4.508981	-1.016878
C	-2.656323	-2.727572	4.521946
H	-0.744600	-2.305010	5.418292
H	-4.416540	-3.206104	3.374089
H	-4.385044	-3.893302	0.999046
H	-3.214877	-2.481877	5.419717
H	1.513783	-4.583519	-2.180002
C	5.900515	-3.939834	-0.767783
C	3.915308	-2.800231	0.001483
C	3.156125	-3.957597	-0.245462
C	3.808874	-5.096642	-0.732170
C	5.171746	-5.095284	-1.011325
H	3.217994	-5.988004	-0.923039
H	5.646908	-5.975456	-1.434031
C	6.888494	0.396311	0.961142
C	6.032004	-0.261173	0.074512
C	5.082264	0.461195	-0.639633
C	4.995457	1.856403	-0.482217
C	5.926207	2.496909	0.345545
C	6.865505	1.779559	1.079635
H	7.549549	2.293226	1.748634
C	6.339314	-1.747181	0.061487
C	5.289670	-2.809494	-0.217542
H	5.882081	3.579026	0.432897
C	7.724258	-0.605500	1.723104
H	7.816083	-0.352342	2.783098
C	6.952127	-1.914403	1.481733
H	6.132374	-1.995208	2.203571
H	7.570244	-2.813188	1.564589
C	7.352610	-3.656442	-1.075343
H	7.654420	-4.050826	-2.049658
H	8.012638	-4.109938	-0.325255
C	7.402734	-2.119045	-1.009100

H	7.086618	-1.698137	-1.969235
H	8.393517	-1.721277	-0.769638
C	3.921919	2.633341	-1.150771
C	3.093263	3.510995	-0.417019
C	3.716291	2.496660	-2.526935
C	2.109149	4.281144	-1.099320
C	3.157795	3.624407	1.019899
C	2.736921	3.221004	-3.188259
H	4.336114	1.796894	-3.076553
C	1.290518	5.210726	-0.382107
C	1.927112	4.129301	-2.499415
C	2.397292	4.518649	1.700047
H	3.823557	2.961460	1.559209
H	2.596582	3.092427	-4.257849
C	1.451982	5.369443	1.022943
C	0.320248	5.991816	-1.069761
C	0.920227	4.911733	-3.164406
H	2.475795	4.592693	2.782151
C	0.654730	6.298183	1.707023
C	-0.445881	6.919085	-0.351179
C	0.155839	5.803573	-2.487958
H	0.789661	4.773121	-4.234125
C	-0.276335	7.072848	1.020868
H	0.788957	6.422119	2.778827
H	-1.182501	7.516542	-0.880922
H	-0.597705	6.393140	-3.001972
H	-0.876178	7.798970	1.560444
H	8.741072	-0.661811	1.314808
C	-0.795246	-0.277419	0.061020
C	-0.648017	-1.161059	-0.874240
H	0.225318	-1.817778	-0.805121
O	2.077068	-1.464416	-1.862152
C	-1.451922	-1.243833	-2.112245
C	-2.829170	-0.959989	-2.123543
C	-0.794631	-1.580084	-3.295623
N	-3.447186	-0.684821	-0.880153
C	-3.514217	-0.934026	-3.337049
C	-1.488988	-1.574051	-4.502139
H	0.271967	-1.788267	-3.238930
C	-2.837774	-1.232904	-4.518684
H	-4.570258	-0.685169	-3.353304
H	-0.972926	-1.815030	-5.424923
H	-3.381819	-1.206235	-5.457479
N	-4.790052	-0.365637	-0.868336

C	-5.250817	0.886047	-0.470090
C	-5.838746	-1.233960	-1.067490
C	-6.618352	0.808153	-0.432266
C	-6.990992	-0.511716	-0.808814
H	-7.303330	1.609869	-0.198942
C	-5.637438	-2.651575	-1.489110
H	-4.578456	-2.910317	-1.473451
H	-6.019285	-2.811651	-2.501420
H	-6.188813	-3.326189	-0.830481
C	-4.378000	2.026846	-0.164626
C	-4.728017	2.859148	0.905927
C	-3.251270	2.349012	-0.933778
C	-3.980467	3.994831	1.194273
H	-5.584992	2.596123	1.518539
C	-2.501714	3.484230	-0.638164
H	-2.976096	1.723510	-1.777630
C	-2.862828	4.310615	0.425134
H	-4.262991	4.624829	2.032275
H	-1.634522	3.732614	-1.246238
H	-2.266479	5.189803	0.652592
C	-8.380441	-0.965297	-0.896417
O	-9.345660	-0.287455	-0.627480
C	-2.714295	0.239084	2.723765
C	-1.703397	0.961937	2.103001
C	-3.354942	0.816995	3.815388
C	-1.367551	2.234378	2.579891
C	-0.854114	0.728302	0.934697
C	-3.002125	2.091082	4.278893
H	-4.142123	0.265780	4.319505
C	-1.992795	2.826900	3.665725
C	-0.037806	1.901277	0.794382
H	-3.524448	2.513550	5.130607
H	-1.719900	3.820093	4.006848
H	-2.983040	-0.753712	2.377501
N	-0.341675	2.742485	1.757413
H	0.088072	3.658390	1.853710
H	0.751746	2.055832	0.066099
O	-8.484152	-2.247370	-1.316037
C	-9.821807	-2.728703	-1.411174
H	-9.746045	-3.754735	-1.768270
H	-10.399672	-2.119706	-2.109769
H	-10.311875	-2.695930	-0.435386
H	-3.206325	-1.359390	-0.155260

TS2

M06-2X SCF energy in Solvent: -3961.916776 a.u.

M06-2X Free energy in Solvent: -3960.885287 a.u.

C	-1.705326	-4.014953	0.418968
C	-0.896750	-3.827224	-0.723194
C	-1.104949	-4.469663	1.602300
C	0.507353	-4.057271	-0.628273
C	-1.435484	-3.449132	-2.006201
C	0.251655	-4.731654	1.686661
C	1.350297	-3.849402	-1.765097
C	1.085245	-4.510035	0.587198
C	-0.635955	-3.253325	-3.081207
H	-2.505409	-3.315207	-2.098135
H	0.684410	-5.090293	2.616980
C	0.787458	-3.433253	-3.001304
C	2.753892	-4.069590	-1.671123
C	2.507914	-4.704142	0.666578
H	-1.062958	-2.958215	-4.035032
C	1.626458	-3.232580	-4.103367
C	3.557078	-3.869892	-2.802256
C	3.307588	-4.494430	-0.409933
H	2.928549	-5.026453	1.617042
C	2.996300	-3.451161	-4.004798
H	1.191332	-2.903380	-5.042694
H	4.625292	-4.059817	-2.732552
H	4.378321	-4.672771	-0.349804
H	3.631509	-3.301405	-4.872515
H	-1.732394	-4.597563	2.478568
C	-5.941878	-3.545272	0.808457
C	-3.836883	-2.671299	-0.006989
C	-3.181622	-3.832851	0.445234
C	-3.951631	-4.841697	1.043940
C	-5.319167	-4.705496	1.246672
H	-3.447254	-5.745581	1.372963
H	-5.881070	-5.486114	1.750770
C	-6.502572	0.558883	-1.554824
C	-5.748788	-0.031018	-0.536737
C	-4.792209	0.712791	0.143342
C	-4.620776	2.073710	-0.158785
C	-5.437249	2.657445	-1.134361
C	-6.367229	1.908383	-1.849536
H	-6.959189	2.370522	-2.633943
C	-6.165940	-1.475881	-0.352021
C	-5.217789	-2.554846	0.141039

H	-5.311142	3.715081	-1.348999
C	-7.361483	-0.479822	-2.238461
H	-7.366766	-0.366423	-3.326164
C	-6.708216	-1.794200	-1.774367
H	-5.857494	-2.030890	-2.422245
H	-7.389505	-2.650294	-1.778431
C	-7.382854	-3.123814	0.978978
H	-7.765731	-3.347999	1.978714
H	-8.032596	-3.640527	0.261414
C	-7.313272	-1.615069	0.686865
H	-7.021436	-1.076910	1.594656
H	-8.255429	-1.192152	0.325710
C	-3.607570	2.901121	0.541910
C	-2.680605	3.684102	-0.179329
C	-3.617577	2.974701	1.937720
C	-1.865506	4.621156	0.515670
C	-2.495086	3.541087	-1.603609
C	-2.800213	3.863769	2.621680
H	-4.299374	2.332063	2.484717
C	-0.969403	5.472789	-0.207435
C	-1.943211	4.726154	1.930805
C	-1.632494	4.336345	-2.286231
H	-3.022557	2.738836	-2.106156
H	-2.848077	3.920789	3.705946
C	-0.852390	5.348854	-1.619818
C	-0.192079	6.444342	0.482863
C	-1.156027	5.727556	2.600619
H	-1.493644	4.200820	-3.355683
C	0.044247	6.177626	-2.305992
C	0.687190	7.255689	-0.243095
C	-0.329905	6.553776	1.913392
H	-1.250853	5.815464	3.680234
C	0.804686	7.119634	-1.622630
H	0.134635	6.077800	-3.384506
H	1.279333	7.997420	0.285550
H	0.252762	7.311388	2.430189
H	1.493602	7.754888	-2.169924
H	-8.403747	-0.413042	-1.901630
C	1.338886	-0.756942	0.927011
N	3.372234	-1.122332	1.016636
C	1.043986	-1.591703	1.897508
H	-0.020814	-1.828632	2.009235
O	-1.976143	0.581401	-0.504390
C	2.121997	-2.125724	2.732806

C	3.408989	-1.851177	2.258675
H	3.330575	-1.787794	0.234889
C	1.978388	-2.858989	3.905673
C	4.549366	-2.257100	2.926299
P	-2.531562	-0.452190	0.409489
C	3.118622	-3.281688	4.591040
H	0.984702	-3.075866	4.284781
C	4.391536	-2.977324	4.113751
H	5.533071	-1.994207	2.548056
O	-3.140232	-1.645834	-0.584123
O	-3.973356	0.096825	1.053035
O	-1.789683	-1.067144	1.544422
H	3.011885	-3.838144	5.516239
H	5.268452	-3.293624	4.668090
N	4.389247	-0.208326	0.761986
C	4.356280	1.155829	1.058725
C	5.489878	-0.522568	-0.005323
C	5.477798	1.693116	0.485082
C	6.187675	0.657313	-0.181699
H	5.794305	2.723505	0.550658
C	5.687250	-1.906766	-0.522674
H	6.694284	-2.003540	-0.921956
H	5.540484	-2.653759	0.264864
H	4.979096	-2.127120	-1.332465
C	3.311992	1.842232	1.829129
C	2.748065	1.309642	2.993555
C	2.884265	3.098632	1.380928
C	1.747392	2.001727	3.669154
H	3.100297	0.360197	3.383568
C	1.899172	3.797127	2.068830
H	3.302039	3.502022	0.463311
C	1.318222	3.244823	3.208869
H	1.306817	1.568219	4.561118
H	1.561867	4.760540	1.700461
H	0.532051	3.782600	3.729531
C	7.441894	0.909544	-0.903571
O	7.970316	1.994001	-0.979307
O	7.959006	-0.192477	-1.488868
C	9.171743	0.034878	-2.204284
H	9.452881	-0.927501	-2.629206
H	9.016761	0.774294	-2.992456
H	9.949953	0.400669	-1.531057
C	2.286412	-0.374098	-2.237677
C	1.533885	0.398772	-1.353982

C	2.566446	0.146670	-3.494743
C	1.084666	1.670986	-1.753831
C	1.094694	0.235976	0.019649
C	2.113108	1.418791	-3.873625
H	3.138411	-0.450967	-4.197126
C	1.363056	2.204344	-3.006385
C	0.385852	1.403407	0.354750
H	2.351839	1.796776	-4.862110
H	1.014162	3.193936	-3.283214
H	2.618473	-1.375370	-1.971893
N	0.396532	2.234007	-0.680965
H	-0.155034	3.080653	-0.731865
H	-0.124322	1.634309	1.280070

IM3

M06-2X SCF energy in Solvent: -3961.94041 a.u.

M06-2X Free energy in Solvent: -3960.903085 a.u.

C	-1.423437	-3.856684	0.414126
C	-0.610391	-3.526369	-0.694936
C	-0.799532	-4.285589	1.597092
C	0.807228	-3.661314	-0.586232
C	-1.148163	-3.088960	-1.959703
C	0.570333	-4.452251	1.695534
C	1.652916	-3.315434	-1.687425
C	1.396207	-4.153945	0.609247
C	-0.342424	-2.717855	-2.983348
H	-2.221156	-3.039557	-2.077907
H	1.014855	-4.804703	2.623114
C	1.087774	-2.809146	-2.887330
C	3.064013	-3.488611	-1.600348
C	2.822629	-4.312551	0.682976
H	-0.771638	-2.366446	-3.917207
C	1.928120	-2.462184	-3.951805
C	3.866104	-3.168616	-2.703586
C	3.621436	-4.011597	-0.376000
H	3.247373	-4.706439	1.604048
C	3.301435	-2.649890	-3.863798
H	1.490112	-2.052071	-4.857159
H	4.938002	-3.345371	-2.650368
H	4.691167	-4.204286	-0.333068
H	3.936629	-2.383101	-4.702080
H	-1.424478	-4.491658	2.459474
C	-5.694185	-4.000425	0.809031
C	-3.745214	-2.827698	-0.016847

C	-2.915100	-3.876599	0.422033
C	-3.532700	-4.996270	1.006041
C	-4.903663	-5.066336	1.216765
H	-2.903491	-5.824931	1.316104
H	-5.340780	-5.932287	1.704815
C	-6.862660	0.029234	-1.461691
C	-6.012155	-0.464199	-0.466877
C	-5.163744	0.406117	0.207498
C	-5.213250	1.784090	-0.054849
C	-6.114952	2.257486	-1.012918
C	-6.929371	1.388174	-1.734522
H	-7.590778	1.768159	-2.507556
C	-6.216844	-1.960543	-0.310761
C	-5.125314	-2.908896	0.153397
H	-6.145276	3.325621	-1.209768
C	-7.570311	-1.110043	-2.159174
H	-7.609550	-0.974630	-3.243701
C	-6.722159	-2.322453	-1.735759
H	-5.852870	-2.411064	-2.396084
H	-7.266801	-3.271180	-1.756743
C	-7.178391	-3.791320	0.994551
H	-7.519414	-4.087402	1.990613
H	-7.752020	-4.380986	0.268276
C	-7.325443	-2.281826	0.731524
H	-7.107121	-1.725151	1.648735
H	-8.320491	-1.989902	0.383386
C	-4.328991	2.732762	0.674094
C	-3.375607	3.519646	-0.000180
C	-4.482997	2.874984	2.055854
C	-2.627001	4.483256	0.730052
C	-3.095760	3.354024	-1.405936
C	-3.754545	3.812551	2.772389
H	-5.199789	2.238466	2.565162
C	-1.647426	5.286023	0.066187
C	-2.831853	4.641539	2.127101
C	-2.161319	4.109045	-2.031015
H	-3.623035	2.570818	-1.937472
H	-3.902619	3.915840	3.843900
C	-1.404587	5.107965	-1.322552
C	-0.897098	6.249528	0.795519
C	-2.068739	5.634178	2.837901
H	-1.953193	3.963979	-3.088190
C	-0.424738	5.885706	-1.949381
C	0.072848	7.008498	0.129709

C	-1.148338	6.401717	2.205380
H	-2.245483	5.748869	3.904059
C	0.305876	6.826200	-1.229006
H	-0.236748	5.742213	-3.009905
H	0.647180	7.740301	0.690813
H	-0.573828	7.143623	2.752912
H	1.064942	7.418332	-1.730275
H	-8.605476	-1.206767	-1.807834
C	2.180051	-0.800485	0.736139
N	3.650935	-1.032736	1.034337
C	1.471850	-1.313450	1.765691
H	0.383018	-1.365529	1.782831
O	-2.421831	0.641023	-0.638593
C	2.362488	-1.749896	2.821973
C	3.680460	-1.530271	2.429659
H	3.877755	-1.845891	0.423740
C	2.140607	-2.298564	4.084345
C	4.792573	-1.762904	3.205843
P	-2.764498	-0.432739	0.339559
C	3.243993	-2.566849	4.895095
H	1.129259	-2.494037	4.424221
C	4.548478	-2.294871	4.476782
H	5.795306	-1.518698	2.870314
O	-3.236053	-1.710767	-0.615221
O	-4.213842	-0.091257	1.070698
O	-1.829141	-0.909645	1.397554
H	3.085175	-2.983710	5.884258
H	5.381821	-2.489053	5.141982
N	4.584029	-0.017794	0.734566
C	4.404743	1.364531	0.858911
C	5.857395	-0.338488	0.298902
C	5.596303	1.913282	0.474324
C	6.501763	0.869767	0.132656
H	5.818305	2.969501	0.443949
C	6.247554	-1.746264	-0.009987
H	7.319852	-1.783561	-0.187767
H	6.004911	-2.439937	0.803054
H	5.739828	-2.094717	-0.918577
C	3.143902	2.027931	1.226279
C	2.476759	1.752361	2.421507
C	2.600546	2.947357	0.320679
C	1.247448	2.349533	2.680083
H	2.913130	1.062703	3.140197
C	1.383505	3.558736	0.592747

H	3.118112	3.133414	-0.616160
C	0.696695	3.244462	1.765526
H	0.713428	2.112454	3.594163
H	0.956120	4.259445	-0.118281
H	-0.268792	3.697442	1.964854
C	7.877757	1.146460	-0.315087
O	8.333857	2.258999	-0.421679
O	8.588916	0.034715	-0.592237
C	9.929800	0.282705	-1.017732
H	10.370130	-0.695899	-1.200712
H	9.934362	0.885392	-1.927822
H	10.481819	0.815616	-0.241115
C	3.605488	0.266714	-2.291538
C	2.328508	0.271264	-1.713170
C	3.780966	0.808044	-3.555389
C	1.258044	0.854729	-2.448297
C	1.745758	-0.163837	-0.464107
C	2.704401	1.359417	-4.269598
H	4.770436	0.804970	-4.001317
C	1.430924	1.391144	-3.724032
C	0.408946	0.193879	-0.505297
H	2.874012	1.776766	-5.256759
H	0.593604	1.827855	-4.258748
H	4.457532	-0.161850	-1.774751
N	0.119550	0.784056	-1.673585
H	-0.839324	1.077697	-1.854211
H	-0.340755	0.073852	0.262215

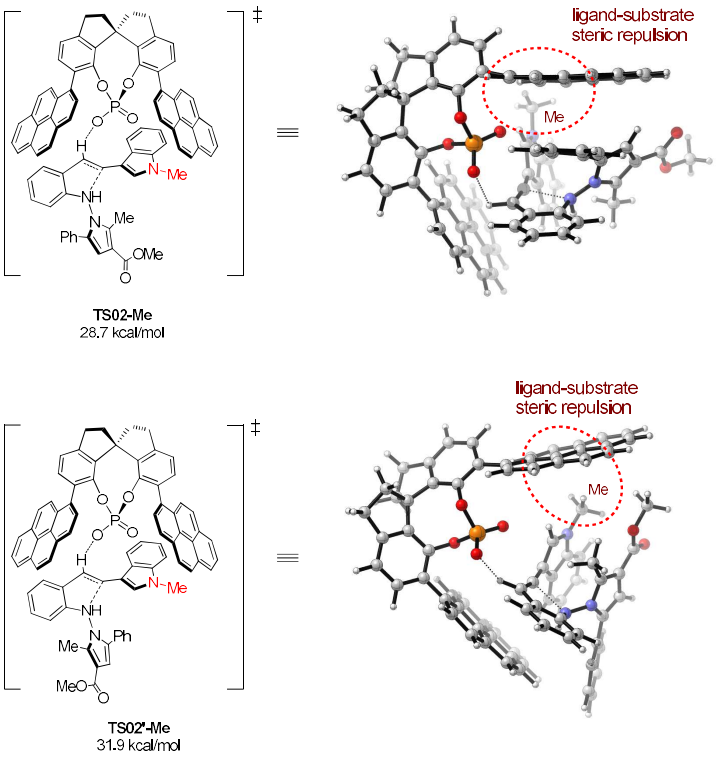

Figure S2. Nucleophilic cyclization transition states with indole N-Me group involved substrate.

IM1-Me

M062X SCF energy in Solvent: -4001.264442 a.u.

M062X Free energy in Solvent: -4000.206905 a.u.

P	-1.897778	-1.421359	-0.399230
O	-1.089938	-1.008958	0.756188
O	-3.469587	-1.273464	-0.051361
O	-1.755632	-2.944942	-0.897447
C	-4.348772	0.873738	-1.728655
C	-4.703648	1.619747	-0.586271
C	-3.615753	1.488132	-2.748663
C	-4.350267	2.997481	-0.520184
C	-5.453701	1.054305	0.508516
C	-3.237427	2.820493	-2.668920
C	-4.756564	3.790267	0.598062
C	-3.613937	3.603063	-1.573042
C	-5.822284	1.803455	1.574944
H	-5.729748	0.006425	0.462296
H	-2.656918	3.272242	-3.468425
C	-5.494368	3.202038	1.660078
C	-4.432538	5.173674	0.646432
C	-3.300217	5.006311	-1.497886
H	-6.388711	1.357912	2.388274

C	-5.874372	3.990905	2.752235
C	-4.823678	5.925951	1.760752
C	-3.703635	5.759349	-0.448805
H	-2.725874	5.448627	-2.306790
C	-5.536384	5.339574	2.802877
H	-6.436489	3.535304	3.562779
H	-4.566118	6.981107	1.798448
H	-3.457189	6.815568	-0.398163
H	-5.834206	5.939048	3.657209
H	-3.328501	0.891059	-3.609133
C	-5.565751	-3.187971	-2.377578
C	-4.365826	-1.569988	-1.073811
C	-4.788055	-0.536952	-1.919477
C	-5.613059	-0.871676	-2.998317
C	-5.991817	-2.189907	-3.243005
H	-5.941649	-0.076330	-3.660532
H	-6.601452	-2.432203	-4.108246
C	-3.484943	-5.153475	1.459141
C	-3.240049	-4.335803	0.353696
C	-1.953153	-3.880698	0.120442
C	-0.869191	-4.274050	0.918843
C	-1.140222	-5.151651	1.977145
C	-2.436437	-5.572279	2.268094
H	-2.620564	-6.216711	3.122615
C	-4.515165	-4.130852	-0.442604
C	-4.773345	-2.881254	-1.266437
H	-0.309904	-5.487430	2.590985
C	-4.968055	-5.414129	1.592347
H	-5.314607	-5.336351	2.626382
C	-5.575554	-4.333239	0.676884
H	-5.677196	-3.394836	1.232620
H	-6.557004	-4.599850	0.274226
C	-5.785615	-4.680253	-2.463853
H	-5.704022	-5.056775	-3.486933
H	-6.784447	-4.949093	-2.098529
C	-4.684517	-5.224736	-1.536347
H	-3.744500	-5.306899	-2.091940
H	-4.913223	-6.204652	-1.107831
C	0.513326	-3.822358	0.606656
C	1.385546	-3.299541	1.587570
C	0.970008	-3.968601	-0.707626
C	2.732299	-3.001310	1.227788
C	0.970493	-3.012869	2.939207
C	2.267178	-3.641037	-1.066930

H	0.288885	-4.358647	-1.457117
C	3.653019	-2.514807	2.207872
C	3.170942	-3.167464	-0.112440
C	1.844902	-2.546181	3.863747
H	-0.073831	-3.147506	3.198211
H	2.595611	-3.761036	-2.094606
C	3.224650	-2.299276	3.542340
C	4.995321	-2.218129	1.845001
C	4.529129	-2.837606	-0.457575
H	1.506711	-2.324234	4.872705
C	4.138451	-1.821126	4.488257
C	5.881086	-1.750988	2.821545
C	5.400895	-2.385896	0.474355
H	4.835031	-2.962833	-1.492366
C	5.456280	-1.558777	4.131907
H	3.801358	-1.650546	5.507193
H	6.908412	-1.535208	2.540026
H	6.421236	-2.126944	0.205178
H	6.154679	-1.190303	4.876534
H	-5.222505	-6.422015	1.242065
C	0.183777	1.771670	-1.107673
C	0.790869	1.058394	-1.888214
H	-1.105519	0.114951	-1.680625
O	-1.665170	-0.685525	-1.776791
C	1.650572	0.179512	-2.626957
C	3.050455	0.289377	-2.459502
C	1.133296	-0.836911	-3.440178
N	3.567316	1.392190	-1.759614
C	3.886594	-0.654831	-3.057624
C	1.975579	-1.744507	-4.067031
H	0.057350	-0.917201	-3.551845
C	3.349950	-1.656919	-3.857609
H	4.955675	-0.605812	-2.884706
H	1.561713	-2.525206	-4.695669
H	4.018822	-2.376961	-4.320055
N	4.789322	1.243683	-1.124508
C	4.967717	0.976763	0.233061
C	5.989371	1.458753	-1.750240
C	6.321730	0.993539	0.452890
C	6.966079	1.273458	-0.782527
H	6.816988	0.818065	1.396728
C	6.072120	1.836762	-3.192063
H	6.497865	1.028516	-3.794221
H	6.728576	2.700242	-3.310116

H	5.077909	2.077379	-3.572996
C	3.860445	0.883740	1.193878
C	4.031477	1.461902	2.460078
C	2.645698	0.251328	0.901830
C	3.012033	1.418598	3.402595
H	4.967600	1.962264	2.688306
C	1.616524	0.228790	1.838423
H	2.511241	-0.275539	-0.039301
C	1.796571	0.815985	3.087306
H	3.164550	1.868911	4.378807
H	0.686763	-0.271673	1.591872
H	0.993428	0.786059	3.818407
C	8.417437	1.346461	-0.940608
O	9.221189	1.178974	-0.050816
C	0.153866	5.036676	-0.848629
C	-0.415313	4.028156	-0.062323
C	0.029362	6.351626	-0.431411
C	-1.110669	4.376109	1.115660
C	-0.479955	2.591373	-0.162667
C	-0.640871	6.676778	0.764047
H	0.468008	7.147035	-1.025206
C	-1.217176	5.697235	1.556249
C	-1.212861	2.151557	0.923957
H	-0.704088	7.715926	1.071372
H	-1.743004	5.946787	2.472606
H	0.685512	4.783979	-1.761367
N	-1.602493	3.216001	1.678030
H	-1.456160	1.135261	1.210303
O	8.789810	1.622982	-2.212707
C	10.197387	1.710279	-2.407810
H	10.339762	1.952448	-3.460185
H	10.679093	0.760300	-2.164445
H	10.626469	2.488504	-1.772639
H	2.892187	1.852815	-1.155205
C	-2.347225	3.146661	2.917443
H	-1.676014	3.203111	3.780367
H	-3.065793	3.969780	2.957740
H	-2.900284	2.206382	2.943540

TS02-Me

M062X SCF energy in Solvent: -4001.217499 a.u.

M062X Free energy in Solvent: -4000.161138 a.u.

C	4.232414	1.276662	1.412209
C	3.843603	2.230030	0.444881

C	4.015497	1.557343	2.767416
C	3.277006	3.467679	0.872175
C	4.027031	2.022169	-0.971371
C	3.450284	2.753382	3.185649
C	2.923194	4.468862	-0.086706
C	3.084533	3.731559	2.255122
C	3.661084	2.959386	-1.877746
H	4.467397	1.090469	-1.304147
H	3.286212	2.938776	4.243846
C	3.107141	4.223710	-1.473380
C	2.417467	5.727415	0.342855
C	2.521825	4.992601	2.659316
H	3.810941	2.781013	-2.939188
C	2.782389	5.224795	-2.395895
C	2.132017	6.711750	-0.610106
C	2.212512	5.948682	1.750836
H	2.368792	5.166987	3.720883
C	2.312728	6.460596	-1.965706
H	2.921553	5.030714	-3.455860
H	1.761515	7.677307	-0.275481
H	1.810928	6.906900	2.069597
H	2.079233	7.231572	-2.693645
H	4.280919	0.796276	3.494808
C	6.311172	-2.369098	0.557020
C	4.411362	-0.929957	0.174960
C	4.939321	0.014378	1.069226
C	6.159342	-0.269317	1.695670
C	6.840877	-1.461076	1.464549
H	6.566106	0.461206	2.389179
H	7.765767	-1.674993	1.991724
C	3.416358	-3.928079	-2.912194
C	3.425122	-3.522028	-1.575341
C	2.242220	-3.503681	-0.844066
C	1.047573	-3.955979	-1.425840
C	1.074565	-4.389445	-2.757050
C	2.243654	-4.363578	-3.513218
H	2.233175	-4.676302	-4.553400
C	4.834903	-3.164454	-1.144373
C	5.121544	-2.087727	-0.116931
H	0.146486	-4.741608	-3.199061
C	4.790223	-3.760170	-3.518945
H	4.755956	-3.358340	-4.535706
C	5.469207	-2.808035	-2.519429
H	5.203311	-1.773144	-2.761686

H	6.560649	-2.884619	-2.506612
C	6.820230	-3.738087	0.165857
H	7.174097	-4.313338	1.026005
H	7.659439	-3.657253	-0.536607
C	5.585445	-4.367135	-0.508294
H	4.936813	-4.812674	0.252991
H	5.831802	-5.139090	-1.243707
C	-0.224947	-4.070524	-0.660651
C	-1.403056	-3.416146	-1.070824
C	-0.281767	-4.975420	0.403470
C	-2.641643	-3.758482	-0.460966
C	-1.404733	-2.397358	-2.092253
C	-1.484701	-5.297765	1.013310
H	0.637948	-5.453962	0.726375
C	-3.858496	-3.159939	-0.914984
C	-2.683086	-4.723156	0.578817
C	-2.555340	-1.803292	-2.492856
H	-0.442981	-2.108503	-2.506174
H	-1.507795	-6.017757	1.827268
C	-3.832056	-2.181231	-1.943521
C	-5.103692	-3.560126	-0.357700
C	-3.954229	-5.087239	1.145759
H	-2.545625	-1.031696	-3.260402
C	-5.034910	-1.626009	-2.392665
C	-6.286608	-2.994814	-0.852175
C	-5.109087	-4.543112	0.694029
H	-3.963691	-5.820496	1.948219
C	-6.252402	-2.036208	-1.859039
H	-5.009734	-0.864268	-3.167686
H	-7.237431	-3.308811	-0.429980
H	-6.065139	-4.834402	1.120651
H	-7.173755	-1.581130	-2.204755
H	5.315179	-4.722556	-3.569645
C	0.064012	1.842907	0.552555
N	-2.074710	1.841664	1.608581
C	0.558779	1.534720	1.717056
H	1.644269	1.431247	1.762394
O	0.705361	-1.089037	-0.383189
C	-0.207665	1.229497	2.925149
C	-1.593676	1.404736	2.884286
H	-2.093634	2.856579	1.537229
C	0.396200	0.708963	4.066703
C	-2.389327	1.073124	3.970438
P	1.891213	-1.352878	0.485577

C	-0.399260	0.354845	5.151024
H	1.463173	0.512551	4.049131
C	-1.781289	0.536340	5.102613
H	-3.468067	1.177195	3.904949
O	3.175198	-0.738899	-0.386839
O	2.246524	-2.973569	0.425855
O	1.997128	-0.936158	1.908696
H	0.055012	-0.090894	6.029294
H	-2.395369	0.241144	5.946849
N	-3.312947	1.365151	1.167956
C	-3.742100	0.035709	1.177500
C	-4.217598	2.175426	0.533396
C	-4.965340	0.031375	0.560356
C	-5.265821	1.353303	0.138071
H	-5.582747	-0.840234	0.402001
C	-3.966148	3.639501	0.376766
H	-4.827116	4.098879	-0.102399
H	-3.821926	4.130068	1.348169
H	-3.083928	3.841210	-0.244125
C	-3.043134	-1.067677	1.858383
C	-3.765626	-1.851981	2.763686
C	-1.676317	-1.306642	1.678994
C	-3.118452	-2.823361	3.520866
H	-4.829399	-1.670839	2.890551
C	-1.025916	-2.256839	2.458370
H	-1.106300	-0.752722	0.936669
C	-1.744978	-3.005403	3.389460
H	-3.686999	-3.423629	4.225207
H	0.044437	-2.398351	2.342304
H	-1.233259	-3.745874	3.997384
C	-6.488014	1.678479	-0.598399
O	-7.336375	0.872624	-0.910293
O	-6.600292	2.991557	-0.916473
C	-7.789198	3.327023	-1.624631
H	-7.745857	4.402884	-1.789369
H	-7.832902	2.794824	-2.577654
H	-8.672834	3.062914	-1.039922
C	-0.565758	4.721247	-0.949410
C	-0.441296	3.409163	-1.397399
C	-0.902337	5.701616	-1.876959
C	-0.654799	3.116680	-2.753743
C	-0.163779	2.131937	-0.749572
C	-1.101920	5.390904	-3.228491
H	-0.992073	6.732629	-1.551006

C	-0.978792	4.085627	-3.693798
C	-0.239508	1.144486	-1.765448
H	-1.358114	6.181765	-3.925186
H	-1.139461	3.839943	-4.738425
H	-0.380279	4.969304	0.092000
N	-0.503860	1.728046	-2.927501
H	-0.063852	0.077978	-1.623915
C	-0.617053	1.054092	-4.208288
H	-1.623358	1.191049	-4.612030
H	0.114779	1.466252	-4.906858
H	-0.422055	-0.007945	-4.060594

TS02'-Me

M062X SCF energy in Solvent: -4001.217656 a.u.

M062X Free energy in Solvent: -4000.156030 a.u.

C	-1.169265	-4.274796	0.698854
C	-0.208811	-4.118498	-0.319806
C	-0.741518	-4.440306	2.021962
C	1.174049	-4.104583	0.023403
C	-0.566973	-3.995027	-1.711043
C	0.601414	-4.429185	2.358913
C	2.166722	-3.948807	-0.993077
C	1.578705	-4.239122	1.376442
C	0.376585	-3.888023	-2.676815
H	-1.619982	-3.997998	-1.970201
H	0.907593	-4.534373	3.396405
C	1.780872	-3.868190	-2.358347
C	3.545592	-3.881745	-0.645175
C	2.973680	-4.126611	1.708305
H	0.087056	-3.809091	-3.720766
C	2.772326	-3.769825	-3.342349
C	4.506262	-3.760630	-1.658478
C	3.914005	-3.945710	0.747303
H	3.255547	-4.185362	2.757319
C	4.119612	-3.725222	-2.994585
H	2.474730	-3.718067	-4.385886
H	5.556270	-3.696888	-1.386063
H	4.967828	-3.874217	1.001566
H	4.875221	-3.646814	-3.770700
H	-1.497638	-4.535575	2.794263
C	-5.414805	-4.460546	0.279970
C	-3.353781	-3.255578	-0.097618
C	-2.634306	-4.332903	0.448988
C	-3.333768	-5.465380	0.880920

C	-4.721350	-5.535238	0.816252
H	-2.767212	-6.289517	1.305266
H	-5.248413	-6.403597	1.200355
C	-6.190178	-0.368257	-2.033035
C	-5.516789	-0.886516	-0.924470
C	-4.818539	-0.040066	-0.070505
C	-4.815213	1.348849	-0.301778
C	-5.595356	1.844730	-1.356857
C	-6.264688	1.002232	-2.237609
H	-6.821790	1.413245	-3.074390
C	-5.733839	-2.385477	-0.848424
C	-4.738080	-3.343153	-0.219257
H	-5.651074	2.920002	-1.496688
C	-6.741314	-1.487128	-2.885667
H	-6.580167	-1.314166	-3.953524
C	-5.970778	-2.707481	-2.351176
H	-4.996336	-2.774561	-2.846676
H	-6.494075	-3.657017	-2.496646
C	-6.909232	-4.255588	0.192535
H	-7.426823	-4.586998	1.097177
H	-7.337791	-4.815523	-0.648366
C	-7.011663	-2.737785	-0.036006
H	-6.961535	-2.215964	0.925354
H	-7.929000	-2.429247	-0.546173
C	-4.034209	2.285663	0.545870
C	-3.289187	3.344376	-0.023675
C	-4.082039	2.167464	1.940652
C	-2.694428	4.321019	0.826727
C	-3.085599	3.487271	-1.446789
C	-3.450953	3.081301	2.768086
H	-4.631096	1.339094	2.372944
C	-2.042918	5.467967	0.269289
C	-2.770236	4.181948	2.237303
C	-2.486607	4.582168	-1.975593
H	-3.417929	2.687134	-2.096938
H	-3.507293	2.963314	3.846724
C	-1.966905	5.632480	-1.140970
C	-1.486073	6.461840	1.122164
C	-2.166391	5.182668	3.074811
H	-2.362684	4.672193	-3.052207
C	-1.344479	6.769631	-1.668852
C	-0.891666	7.596145	0.553497
C	-1.557234	6.272178	2.547165
H	-2.223213	5.048915	4.151742

C	-0.821401	7.747253	-0.826873
H	-1.286424	6.887174	-2.747760
H	-0.483374	8.360525	1.209679
H	-1.119009	7.029888	3.191031
H	-0.356276	8.631783	-1.250713
H	-7.822386	-1.601344	-2.736751
C	1.195509	-0.582013	0.440336
N	3.238098	-0.430468	1.266177
C	0.779483	-1.223542	1.500774
H	-0.219400	-1.683848	1.519614
O	-1.815815	0.187984	0.118195
C	1.587929	-1.235885	2.728401
C	2.902872	-0.769805	2.616418
H	3.694551	-1.198447	0.766024
C	1.094715	-1.623051	3.969986
C	3.731426	-0.663581	3.721346
P	-2.534297	-0.956166	0.742834
C	1.924748	-1.527327	5.086916
H	0.063234	-1.956692	4.042832
C	3.227583	-1.046170	4.966971
H	4.734000	-0.258602	3.619321
O	-2.706418	-2.102771	-0.463606
O	-4.133381	-0.583109	0.984542
O	-2.085341	-1.632948	1.995552
H	1.545269	-1.810306	6.063162
H	3.855153	-0.958567	5.847564
N	3.890582	0.768114	0.987897
C	4.938837	0.840421	0.064868
C	3.221017	1.973469	1.060713
C	4.931460	2.112461	-0.440912
C	3.870671	2.828102	0.184941
H	5.638852	2.532516	-1.140738
C	2.101032	2.189650	2.025768
H	1.549903	3.088278	1.755559
H	1.411592	1.344778	2.052797
H	2.498185	2.324429	3.037909
C	5.866061	-0.267762	-0.188411
C	6.490614	-0.367193	-1.440858
C	6.214127	-1.191385	0.807025
C	7.443285	-1.348341	-1.682455
H	6.209691	0.331673	-2.222012
C	7.164010	-2.179164	0.558297
H	5.765068	-1.122476	1.794099
C	7.786545	-2.259218	-0.683549

H	7.919570	-1.405389	-2.656236
H	7.429247	-2.876459	1.347333
H	8.532771	-3.024148	-0.871909
C	3.523047	4.206230	-0.176165
O	3.977512	4.792290	-1.135645
O	2.607906	4.755996	0.645423
C	2.224177	6.095586	0.338707
H	1.607476	6.423027	1.173925
H	3.106811	6.727893	0.225591
H	1.636200	6.133378	-0.582987
C	3.076201	-0.582138	-2.275533
C	2.152235	0.315102	-1.750213
C	3.830833	-0.179421	-3.369891
C	2.029061	1.596088	-2.310805
C	1.236763	0.271050	-0.624691
C	3.702591	1.108577	-3.911695
H	4.539513	-0.879421	-3.802458
C	2.798990	2.025800	-3.385289
C	0.580001	1.523603	-0.606746
H	4.315011	1.395694	-4.760017
H	2.706505	3.027331	-3.791223
H	3.195099	-1.569179	-1.844599
N	1.052983	2.293392	-1.582646
H	-0.226122	1.827562	0.052011
C	0.675540	3.670411	-1.847329
H	1.585349	4.261195	-1.988881
H	0.050239	3.729570	-2.741030
H	0.116895	4.052754	-0.992276