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Supporting Information

Microwave-assisted Synthesis of 7-Azaindoles *via* Iron-catalyzed Cyclization of *o*-Haloaromatic Amine with Terminal Alkynes

Yi Le [a,b,c], Zhisong Yang [b], Yumei Chen [b], Dongmei Chen [b], Longjia Yan [b,c,*] Zhenchao Wang [b,c,] and Guiping Ouyang [a,b,c,*]

[a] State Key Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering, Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, State-Local Joint Laboratory for Comprehensive Utilization of Biomass, Center for Research and Development of Fine Chemicals, Guizhou University, Guiyang 550025

[b] School of Pharmaceutical Sciences, GuizhouUniversity, Guiyang 550025,

[c] Guizhou Engineering Laboratory for Synthetic Drugs, Guiyang 550025

*corresponding author: ylj1089@163.com; oygp710@163.com

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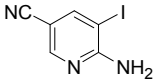
Experimental section

All commercial materials were used without further purification. Melting points were determined on a Kofler apparatus as uncorrected values. Analytical thin-layer chromatography was performed on precoated 250 μm layer thickness silica gel 60 F254 plates and visualized with UV light. Column chromatography was performed using silica gel 300-400 mesh. ^{1}H NMR and ^{13}C NMR spectra were measured on 400 MHz spectrometer in DMSO-d_6 or $CDCl_3$ with chemical shift (δ) given in parts per million (ppm) relative to TMS as internal standard and recorded at 23 °C. The high resolution mass spectra (HRMS) were obtained with an electrospray ionization (ESI) using the mass spectrometer QStar Elite (Applied Biosystems SCIEX). The microwave-assisted reaction was performed on a Discover SP microwave reactor-CEM.

*General method for preparation of compounds **1c-d***

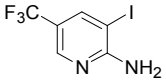
A mixture of corresponding pyridine (10 mmol), iodine (5 mmol) and silver sulphate (10 mmol) in ethanol (20 mL), was stirred at room temperature for 12 h. The mixture was filtered off and washed with ethanol. Combined organic layers were concentrated in vacuum to dryness and purified via chromatography on silica gel (n-Hexane: EtOAc = 2:1) to give the product.

*6-Amino-5-iodo-nicotinonitrile (**1c**)*[1]



1.22 g (50%); Brown solid; ^{1}H NMR (400 MHz, DMSO) δ 8.35 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 7.16 (s, 2H). Spectral properties were in accordance with the literature. [1]

*3-Iodo-5-trifluoromethyl-pyridin-2-ylamine (**1d**)* [1]

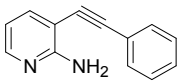


1.38 g (48%); Brown solid; ^{1}H NMR (400 MHz, DMSO) δ 8.26 (d, *J* = 2.0 Hz, 1H), 8.15 (d, *J* = 2.0 Hz, 1H), 6.88 (s, 2H). Spectral properties were in accordance with the literature. [1]

*Preparation of compound **3aa***

A mixture of 3-iodo-pyridin-2-ylamine (**1a**, 1 mmol), ethynyl-benzene (**2a**, 2 mmol), $Pd(PPh_3)_2Cl_2$ (0.1 mmol), CuI (0.1 mmol) and K_3PO_4 (1.5 mmol) were dissolved in DMF (2 mL) in a 5 mL microwave reaction vial. The microwave vial was then sealed under Ar atmosphere and irradiated in the microwave reactor at 100 °C for 30 min with the absorbance set to "very high". After cooling, the reaction mixture was extracted with EtOAc (3 × 20 mL). The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure and the crude residue purified by flash chromatography on silica gel.

*3-Phenylethynyl-pyridin-2-ylamine (**3aa**)* [2]

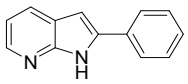


68 mg (35%); Yellow solid; m.p = 123-124 ℃; ^{1}H NMR (400 MHz, DMSO) δ 7.97 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.65 – 7.58 (m, 3H), 7.48 – 7.34 (m, 3H), 6.57 (dd, *J* = 7.2, 4.8 Hz, 1H), 6.30 (s, 2H)； ^{13}C NMR (100 MHz, DMSO) δ 159.9, 148.8, 140.3, 131.9, 129.1, 129.0, 123.0, 112.5, 101.5, 94.9, 85.9 HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{13}H_{10}N_2$, 195.0916; found, 195.0919. Spectral properties were in accordance with the literature. [2]

*General method for preparation of compounds **3a-p***

A mixture of compound **1** (1 mmol), compound **2** (3 mmol), $Fe(acac)_3$ (0.1 mmol), CuI (0.1 mmol) and KO^tBu (1.5 mmol) were dissolved in NMP (2 mL) in a 5 mL microwave reaction vial. The microwave vial was then sealed under Ar atmosphere and irradiated in the microwave reactor at 130 °C for 60 min with the absorbance set to "very high". After cooling, the reaction mixture was extracted with EtOAc (3 × 20 mL). The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure and the crude residue purified by flash chromatography on silica gel.

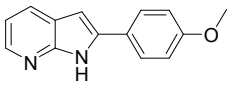
*2-Phenyl-1H-pyrrolo[2,3-b]pyridine (**3a**)* [3]



140 mg (72%); Yellow solid; m.p = 207-208 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.12 (s, 1H), 8.21 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.03 – 7.86 (m, 3H), 7.49 – 7.45 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.06 (dd, *J*

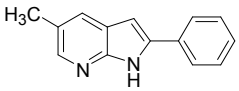
= 7.6, 4.8 Hz, 1H), 6.92 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 150.1, 143.3, 138.7, 132.1, 129.4, 128.4, 128.2, 125.8, 121.4, 116.5, 97.6; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{13}H_{10}N_2$, 195.0916; found, 195.0921. Spectral properties were in accordance with the literature. [3]

*2-(4-Methoxy-phenyl)-1H-pyrrolo[2,3-b]pyridine (**3b**)* [3]



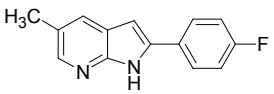
163 mg (73%); Yellow solid; m.p = 202-203 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.01 (s, 1H), 8.16 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.90 – 7.85 (m, 3H), 7.62 – 7.54 (m, 1H), 7.06 – 7.01 (m, 3H), 6.79 (d, *J* = 2.0 Hz, 1H), 3.81 (s, 3H);^{13}C NMR (100 MHz, DMSO) δ 159.7, 150.1, 142.6, 138.9, 133.5, 127.7, 127.2, 124.7, 121.6, 114.8, 96.1, 55.7; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{14}H_{12}N_2O$, 225.1022; found, 225.1029. Spectral properties were in accordance with the literature. [3]

*5-Methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridine (**3c**)* [3]



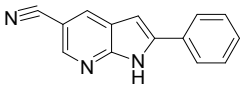
152 mg (73%); Yellow solid; m.p = 248-249 ℃; ^{1}H NMR (400 MHz, DMSO) δ 11.98 (s, 1H), 8.06 (d, *J* = 1.6 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.72 (d, *J* = 2.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 2.4 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 148.8, 144.1, 138.7, 132.2, 129.3, 128.3, 128.1, 125.7, 124.9, 121.2, 97.0, 18.6; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{14}H_{12}N_2$, 209.1072; found, 209.1077. Spectral properties were in accordance with the literature. [3]

*2-(4-Fluoro-phenyl)-5-methyl-1H-pyrrolo[2,3-b]pyridine (**3d**)*



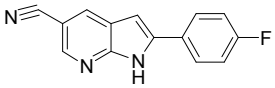
154 mg (68%); Yellow solid; m.p = 283-284 ℃; ^{1}H NMR (400 MHz, DMSO) δ 11.98 (s, 1H), 8.05 (d, *J* = 1.6 Hz, 1H), 7.99 – 7.93 (m, 2H), 7.72 (d, *J* = 2.0 Hz, 1H), 7.34 – 7.27 (m, 2H), 6.81 (d, *J* = 2.0 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 163.5, 148.8, 144.1, 137.8, 128.8, 128.1, 127.8, 127.7, 124.9, 121.2, 97.0, 18.6; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{14}H_{11}FN_2$, 227.0978; found, 227.0982.

*2-Phenyl-1H-pyrrolo[2,3-b]pyridine-5-carbonitrile (**3e**)* [4]



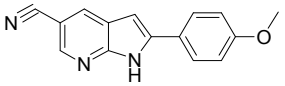
142 mg (65%); Yellow solid; m.p = 266-268 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.79 (s, 1H), 8.60 (d, *J* = 2.0 Hz, 1H), 8.48 (d, *J* = 2.0 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 150.8, 145.9, 141.5, 132.5, 131.1, 129.5, 129.3, 126.2, 120.7, 119.4, 100.7, 98.4; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{14}H_9N_3$, 220.0868; found, 220.0871. Spectral properties were in accordance with the literature. [4]

*2-(4-Fluoro-phenyl)-1H-pyrrolo[2,3-b]pyridine-5-carbonitrile (**3f**)* [5]



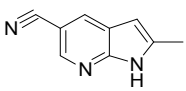
144 mg (61%); Yellow solid; m.p = 280-281 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.80 (s, 1H), 8.60 (s, 1H), 8.49 (s, 1H), 8.04 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.06 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 164.1, 150.8, 145.9, 140.6, 132.6, 128.5, 128.4, 127.7, 120.7, 119.4, 100.8, 98.4; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{14}H_8FN_3$, 238.0774; found, 238.0779. Spectral properties were in accordance with the literature. [5]

*2-(4-Methoxy-phenyl)-1H-pyrrolo[2,3-b]pyridine-5-carbonitrile (**3g**)*



164 mg (66%); Yellow solid; m.p = 275-276 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.68 (s, 1H), 8.55 (d, *J* = 2.0 Hz, 1H), 8.42 (d, *J* = 2.0 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 2.0 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 160.3, 150.8, 145.4, 141.7, 131.8, 127.7, 123.6, 121.0, 119.5, 114.9, 100.6, 96.9, 55.8; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{15}H_{11}N_3O$, 250.0974; found, 250.0977.

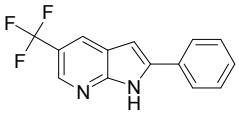
*2-Methyl-1H-pyrrolo[2,3-b]pyridine-5-carbonitrile (**3h**)*



68 mg (43%); Yellow solid; m.p = 233-234 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.13 (s, 1H), 8.47 (d, *J* = 2.0 Hz, 1H), 8.32 – 8.27 (m, 1H), 6.30 (s, 1H), 2.43 (s, 4H); ^{13}C NMR (100 MHz, DMSO) δ 152.8,

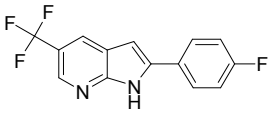
149.1, 140.5, 131.0, 120.7, 117.7, 99.1, 97.0, 14.0; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_9H_7N_3$, 158.0712; found, 158.0713.

*2-Phenyl-5-trifluoromethyl-1H-pyrrolo[2,3-b]pyridine (**3i**)* [6]



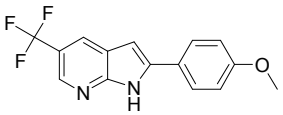
162 mg (62%); Yellow solid; m.p = 276-277 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.68 (s, 1H), 8.56 (s, 1H), 8.35 (s, 1H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 161.6, 151.4, 141.4, 139.8, 131.3, 129.5, 129.2, 126.2, 125.8 (*J* = 3.6 Hz), 120.5, 118.2, 98.4; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{14}H_9F_3N_2$, 263.0790; found, 263.0799. Spectral properties were in accordance with the literature. [6]

*2-(4-Fluoro-phenyl)-5-trifluoromethyl-1H-pyrrolo[2,3-b]pyridine (**3j**)* [5]



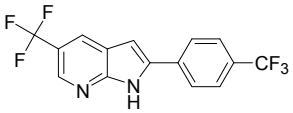
157 mg (56%); Yellow solid; m.p = 243-244 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.68 (s, 1H), 8.55 (s, 1H), 8.35 (s, 1H), 8.04 (dd, *J* = 8.4, 5.2 Hz, 2H), 7.36 (t, *J* = 8.8 Hz, 2H), 7.07 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 164.0, 161.5, 151.4, 140.4, 139.8, 128.4 (*J* = 8.4 Hz), 127.9 (*J* = 3.2 Hz), 125.8 (*J* = 3.6 Hz), 120.5, 116.6, 116.4, 98.4; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{14}H_8F_4N_2$, 281.0696; found, 281.0702. Spectral properties were in accordance with the literature. [5]

*2-(4-Methoxy-phenyl)-5-trifluoromethyl-1H-pyrrolo[2,3-b]pyridine (**3k**)*



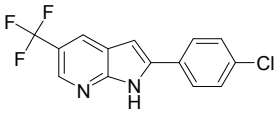
231 mg (79%); Yellow solid; m.p = 268-269 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.56 (s, 1H), 8.51 (s, 1H), 8.29 (s, 1H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 2.0 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 160.2, 151.4, 141.6, 139.2, 133.8, 127.6, 125.1 (*J* = 3.6 Hz), 124.4, 123.8, 120.8, 114.9, 96.9, 55.7; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{15}H_{11}F_3N_2O$, 293.0895; found, 293.0902.

*5-Trifluoromethyl-2-(4-trifluoromethyl-phenyl)-1H-pyrrolo[2,3-b]pyridine (**3l**)*



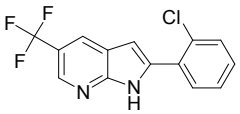
148 mg (45%); Yellow solid; m.p = 264-265 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.87 (s, 1H), 8.62 (d, *J* = 1.6 Hz, 1H), 8.42 (d, *J* = 1.6 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 151.5, 140.6, 139.5, 135.2, 129.0, 126.7, 126.5, 126.3, 124.2, 123.2, 120.2, 118.4, 100.4; HRMS-ESI (*m/z*): [M + H]$^{+}$ calcd for $C_{15}H_8F_6N_2$, 331.0664; found, 331.0667.

*2-(4-Chloro-phenyl)-5-trifluoromethyl-1H-pyrrolo[2,3-b]pyridine (**3m**)*



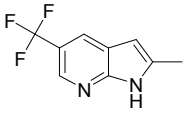
172 mg (58%); Yellow solid; m.p = 262-263 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.72 (s, 1H), 8.57 (s, 1H), 8.37 (s, 1H), 8.01 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.13 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 151.5, 140.1, 133.7, 130.2, 129.5, 127.8, 126.9, 126.05 (*J* = 3.6 Hz), 124.2, 120.4, 118.4, 99.1; HRMS-ESI (*m/z*): [M + H]$^{+}$ calcd for $C_{15}H_8F_6N_2$, 297.0400; found, 297.0409.

*2-(2-Chloro-phenyl)-5-trifluoromethyl-1H-pyrrolo[2,3-b]pyridine (**3n**)*



95 mg (32%); Yellow solid; m.p = 258-259 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.59 (s, 1H), 8.61 (d, *J* = 2.0 Hz, 1H), 8.44 (d, *J* = 2.0 Hz, 1H), 7.77 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.65 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.02 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 161.8, 150.6, 140.3, 138.1, 134.2, 131.8, 128.0, 127.7, 126.5 (*J* = 3.6 Hz), 122.2, 119.7, 117.9, 102.9, 92.5; HRMS-ESI (*m/z*): [M + H]$^{+}$ calcd for $C_{15}H_8F_6N_2$, 297.0400; found, 297.0408.

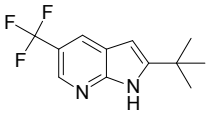
*2-Methyl-5-trifluoromethyl-1H-pyrrolo[2,3-b]pyridine (**3o**)*



66 mg (33%); White solid; m.p = 209-210 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.00 (s, 1H), 8.43 (d, *J*

= 1.6 Hz, 1H), 8.18 (d, *J* = 2.0 Hz, 1H), 6.34 – 6.31 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 150.6, 140.2, 138.2, 127.2, 124.31 (*J* = 3.6 Hz), 120.4, 117.4, 99.1, 14.1; HRMS-ESI (*m/z*): [M + H]$^+$ calcd for $C_9H_7F_3N_2$, 201.0633; found, 201.0638.

*2-tert-Butyl-5-trifluoromethyl-1H-pyrrolo[2,3-b]pyridine (**3p**)*

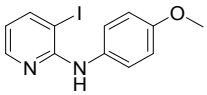


116 mg (48%); White solid; m.p = 202-203 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.06 (s, 1H), 8.46 (d, *J* = 1.6 Hz, 1H), 8.21 (d, *J* = 2.0 Hz, 1H), 6.31 (d, *J* = 2.0 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, DMSO) δ 153.4, 150.9, 138.6, 127.2, 124.9 (d, *J* = 3.6 Hz), 119.7, 117.4, 95.6, 32.5, 29.8; HRMS-ESI (*m/z*): [M + H]$^+$ calcd for $C_{12}H_{13}F_3N_2$, 243.1103; found, 243.1110.

*General method for preparation of compounds **4a-b***

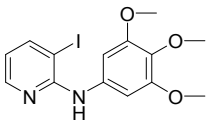
A mixture of 2-fluoro-3-iodo-pyridine (6 mmol), corresponding amine (18 mmol) and 3 N HCl (2 mL) were dissolved in dioxane (20 mL) in a 100 mL flask. The reaction mixture was then heated at 100 °C for overnight under Ar atmosphere. After cooling, the solution was added saturated $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 50 mL). The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure and the crude residue purified by flash chromatography on silica gel.

*(3-Iodo-pyridin-2-yl)-(4-methoxy-phenyl)-amine (**4a**)*



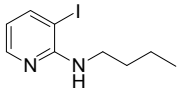
1 g (52%); Yellow oil; ^{1}H NMR (400 MHz, DMSO) δ 8.12 – 7.95 (m, 2H), 7.58 (s, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.53 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 155.4, 155.2, 148.0, 147.3, 134.2, 123.6, 116.4, 114.0, 81.2, 55.6; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{12}H_{11}IN_2O$, 326.9988; found, 326.9992.

*(3-Iodo-pyridin-2-yl)-(3,4,5-trimethoxy-phenyl)-amine (**4b**)*



1.274 g (55%); Yellow solid; m.p = 112-113 ℃; ^{1}H NMR (400 MHz, DMSO) δ 8.16 – 8.03 (m, 2H), 7.63 (s, 1H), 7.00 (s, 2H), 6.59 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.74 (s, 6H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 154.7, 153.0, 148.3, 147.3, 137.3, 133.2, 117.0, 98.9, 81.9, 60.6, 56.2; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{14}H_{15}IN_2O_3$, 387.0199; found, 387.0206.

*Butyl-(3-iodo-pyridin-2-yl)-amine (**4c**)*

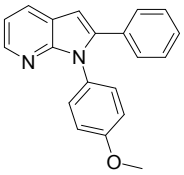


580 mg (35%); Yellow oil; ^{1}H NMR (400 MHz, DMSO) δ 8.00 (d, *J* = 4.4 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 6.31 (dd, *J* = 7.6, 4.4 Hz, 1H), 5.80 (t, *J* = 5.2 Hz, 1H), 3.35 – 3.30 (m, 2H), 1.59 – 1.45 (m, 2H), 1.40 – 1.21 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 157.0, 147.8, 146.9, 113.8, 80.1, 41.7, 31.5, 20.2, 14.3; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_9H_{13}IN_2$, 277.0195; found, 277.0201.

*General method for preparation of compounds **5a-m***

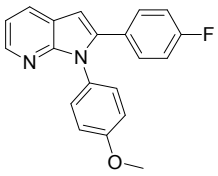
A mixture of compound **4** (1 mmol), compound **2** (3 mmol), $Fe(acac)_3$ (0.1 mmol), CuI (0.1 mmol) and KO^tBu (1.5 mmol) were dissolved in NMP (2 mL) in a 5 mL microwave reaction vial. The microwave vial was then sealed under Ar atmosphere and irradiated in the microwave reactor at 130 °C for 60 min with the absorbance set to "very high". After cooling, the reaction mixture was extracted with EtOAc (3 × 20 mL). The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure and the crude residue purified by flash chromatography on silica gel.

*1-(4-Methoxy-phenyl)-2-phenyl-1H-pyrrolo[2,3-b]pyridine (**5a**)* [7]



222 mg (74%); White solid; m.p = 187-188 ℃; ^{1}H NMR (400 MHz, DMSO) δ 8.21 (d, *J* = 6.4 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.27 (m, 5H), 7.22 – 7.17 (m, 3H), 7.01 – 6.97 (m, 2H), 6.85 (s, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 150.2, 143.6, 141.2, 132.2, 131.1, 129.9, 129.4, 128.9, 128.3, 127.7, 120.7, 116.8, 114.4, 100.9, 55.4; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{20}H_{16}N_2O$, 301.1335; found, 301.1338. Spectral properties were in accordance with the literature. [7]

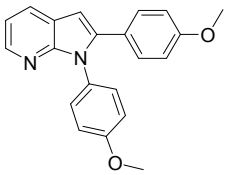
*2-(4-Fluoro-phenyl)-1-(4-methoxy-phenyl)-1H-pyrrolo[2,3-b]pyridine (**5b**)* [7]



210 mg (66%); White solid; m.p = 171-172 ℃; ^{1}H NMR (400 MHz, DMSO) δ 8.21 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.06 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.23 – 7.16 (m, 5H), 7.02 – 6.98 (m, 2H), 6.84 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 163.5, 158.8, 150.2, 143.7, 140.1, 131.2 (d, *J* = 8.4 Hz), 130.1, 129.8, 128.9, 128.7 (d, *J* = 3.2 Hz), 120.5, 117.6, 115.5 (d, *J* = 21.7 Hz), 114.6, 101.4, 55.8; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{20}H_{15}FN_2O$, 319.1240; found,

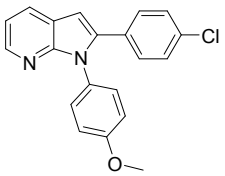
319.1244. Spectral properties were in accordance with the literature. [7]

*1,2-Bis-(4-methoxy-phenyl)-1H-pyrrolo[2,3-b]pyridine (**5c**)* [7]



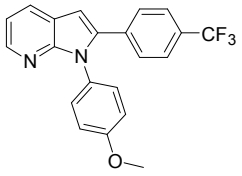
257 mg (78%); White solid; m.p = 145-146 ℃; ^{1}H NMR (400 MHz, DMSO) δ 8.17 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.02 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.26 – 7.12 (m, 5H), 7.02 – 6.97 (m, 2H), 6.92 – 6.86 (m, 2H), 6.75 (s, 1H), 3.80 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 159.5, 158.7, 150.2, 143.1, 141.2, 130.4, 130.1, 130.0, 128.5, 124.4, 120.7, 117.4, 114.6, 114.4, 100.4, 55.8, 55.6; HRMS-ESI (*m/z*): [M + H]$^+$ calcd for $C_{21}H_{18}N_2O_2$, 331.1440; found, 331.1444. Spectral properties were in accordance with the literature. [7]

*2-(4-Chloro-phenyl)-1-(4-methoxy-phenyl)-1H-pyrrolo[2,3-b]pyridine (**5d**)*



207 mg (62%); Yellow solid; m.p = 157-158 ℃; ^{1}H NMR (400 MHz, DMSO) δ 8.22 (d, *J* = 3.6 Hz, 1H), 8.07 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.41 (d, *J* = 8.4Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.18 (m, 3H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.89 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 158.8, 150.3, 143.9, 139.8, 133.2, 131.0, 130.7, 130.1, 129.7, 129.1, 128.9, 120.5, 117.7, 114.7, 101.9, 55.8; HRMS-ESI (*m/z*): [M + H]$^+$ calcd for $C_{20}H_{15}ClN_2O$, 335.0945; found, 335.0950.

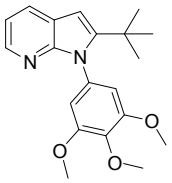
*1-(4-Methoxy-phenyl)-2-(4-trifluoromethyl-phenyl)-1H-pyrrolo[2,3-b]pyridine (**5e**)* [7]



221 mg (60%); Yellow solid; m.p = 156-157 ℃; ^{1}H NMR (400 MHz, DMSO) δ 8.26 (dd, *J* = 4.6, 1.6 Hz, 1H), 8.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.26

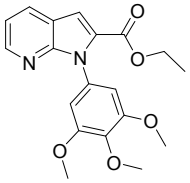
– 7.21 (m, 3H), 7.04 – 7.00 (m, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 158.9, 150.4, 144.4, 139.3, 136.2, 130.1, 129.6, 129.4, 128.3, 125.8 (d, *J* = 3.6 Hz), 123.5, 120.4, 117.8, 114.7, 114.0, 103.0, 55.8; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{21}H_{15}F_3N_2O$, 369.1208; found, 369.1211. Spectral properties were in accordance with the literature. [7]

*2-tert-Butyl-1-(3,4,5-trimethoxy-phenyl)-1H-pyrrolo[2,3-b]pyridine (**5f**)*



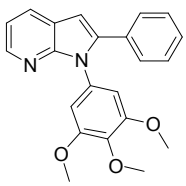
143 mg (42%); White solid; m.p = 157-158 ℃; ^{1}H NMR (400 MHz, DMSO) δ 8.07 (d, *J* = 4.4 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.07 (dd, *J* = 7.6, 4.4 Hz, 1H), 6.72 (s, 2H), 6.45 (s, 1H), 3.77 (s, 3H), 3.74 (s, 6H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, DMSO) δ 152.0, 149.9, 146.3, 141.4, 137.0, 133.5, 126.7, 118.3, 115.5, 108.2, 96.3, 59.6, 55.6, 32.6, 29.9; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{20}H_{24}N_2O_3$, 341.1859; found, 341.1866.

*1-(3,4,5-Trimethoxy-phenyl)-1H-pyrrolo[2,3-b]pyridine-2-carboxylic acid ethyl ester (**5g**)*



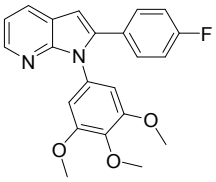
117 mg (33%); Yellow solid; m.p = 228-229 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.4 Hz, 1H), 8.07 (d, *J* = 6.8 Hz, 1H), 7.40 (s, 1H), 7.18 (dd, *J* = 8.0, 4.4 Hz, 1H), 6.60 (s, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 3H), 3.84 (s, 6H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 153.2, 150.4, 147.6, 137.9, 132.9, 130.9, 129.8, 118.7, 117.6, 109.2, 105.9, 60.9, 56.1, 29.7, 14.1; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{19}H_{20}N_2O_5$, 357.1444; found, 357.1449.

*2-Phenyl-1-(3,4,5-trimethoxy-phenyl)-1H-pyrrolo[2,3-b]pyridine (**5h**)*



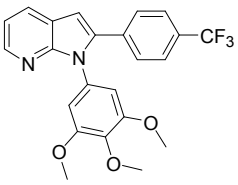
274 mg (76%); Yellow solid; m.p = 148-149 ℃; ^{1}H NMR (400 MHz, DMSO) δ 8.25 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.07 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.38 – 7.33 (m, 5H), 7.22 – 7.19 (m, 1H), 6.86 (s, 1H), 6.61 (s, 2H), 3.70 (s, 3H), 3.61 (s, 6H); ^{13}C NMR (100 MHz, DMSO) δ 153.1, 150.0, 143.7, 141.2, 137.1, 132.8, 132.3, 129.1, 128.9, 128.8, 128.4, 120.7, 117.6, 107.0, 101.5, 60.6, 56.4; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{22}H_{20}N_2O_3$, 361.1546; found, 361.1550.

*2-(4-Fluoro-phenyl)-1-(3,4,5-trimethoxy-phenyl)-1H-pyrrolo[2,3-b]pyridine (**5i**)*



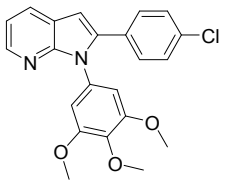
257 mg (68%); White solid; m.p = 179-180 ℃; ^{1}H NMR (400 MHz, DMSO) δ 8.25 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.07 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.25 – 7.19 (m, 3H), 6.85 (s, 1H), 6.61 (s, 2H), 3.71 (s, 3H), 3.63 (s, 6H); ^{13}C NMR (100 MHz, DMSO) δ 163.5, 161.1, 153.2, 150.0, 143.7, 140.2, 137.2, 132.7, 131.2 (d, *J* = 8.4 Hz), 128.9, 128.7(d, *J* = 3.6 Hz), 120.6, 117.7, 115.9, 115.7, 107.1, 101.5, 60.6, 56.5; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{22}H_{19}FN_2O_3$, 379.1452; found, 379.1455.

*2-(4-Trifluoromethyl-phenyl)-1-(3,4,5-trimethoxy-phenyl)-1H-pyrrolo[2,3-b]pyridine (**5j**)*



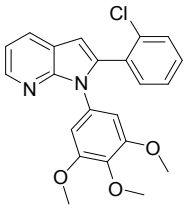
248 mg (58%); White solid; m.p = 218-219 ℃; ^{1}H NMR (400 MHz, DMSO) δ 8.30 (d, *J* = 3.6 Hz, 1H), 8.12 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.19 (m, 1H), 7.03 (s, 1H), 6.65 (s, 2H), 3.72 (s, 3H), 3.63 (s, 6H); ^{13}C NMR (100 MHz, DMSO) δ 153.3, 150.3, 144.5, 139.4, 137.3, 136.3, 132.5, 129.54 (d, *J* = 12.0 Hz), 128.7, 128.3, 125.70 (d, *J* = 3.6 Hz), 120.5, 117.8, 107.1, 103.0, 60.6, 56.5; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{22}H_{19}FN_2O_3$, 379.1452; found, 379.1455.

*2-(4-Chloro-phenyl)-1-(3,4,5-trimethoxy-phenyl)-1H-pyrrolo[2,3-b]pyridine (**5k**)*



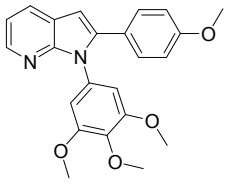
244 mg (62%); White solid; m.p = 214-215 ℃; ^{1}H NMR (400 MHz, DMSO) δ 8.26 (d, *J* = 4.0 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 1H), 7.45 – 7.37 (m, 4H), 7.21 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.91 (s, 1H), 6.63 (s, 2H), 3.71 (s, 3H), 3.64 (s, 6H); ^{13}C NMR (100 MHz, DMSO) δ 153.2, 150.1, 144.0, 139.9, 137.3, 133.2, 132.6, 131.1, 130.7, 129.1, 128.9, 120.5, 117.7, 107.1, 101.9, 60.6, 56.5; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{22}H_{19}ClN_2O_3$, 395.1156; found, 395.1159.

*2-(2-Chloro-phenyl)-1-(3,4,5-trimethoxy-phenyl)-1H-pyrrolo[2,3-b]pyridine (**5l**)*



217 mg (55%); White solid; m.p = 210-211 ℃; ^{1}H NMR (400 MHz, DMSO) δ 8.30 (d, *J* = 4.4 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.45 – 7.37 (m, 2H), 7.24 (dd, *J* = 7.6, 4.4 Hz, 1H), 6.77 (s, 1H), 6.58 (s, 2H), 3.65 (s, 3H), 3.59 (s, 6H); ^{13}C NMR (100 MHz, DMSO) δ 152.8, 148.8, 144.0, 138.2, 136.8, 134.0, 133.6, 132.2, 131.9, 131.1, 129.8, 129.3, 127.4, 120.3, 117.6, 106.2, 102.9, 60.5, 56.3; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{22}H_{19}ClN_2O_3$, 395.1156; found, 395.1160.

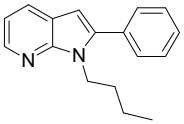
*2-(4-Methoxy-phenyl)-1-(3,4,5-trimethoxy-phenyl)-1H-pyrrolo[2,3-b]pyridine (**5m**)*



304 mg (78%); White solid; m.p = 174-175 ℃; ^{1}H NMR (400 MHz, DMSO) δ 8.21 (d, *J* = 4.4 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.18 (dd, *J* = 7.6, 4.4 Hz, 1H), 6.92 (d, *J* = 8.8Hz, 2H), 6.76 (s, 1H), 6.61 (s, 2H), 3.75 (s, 3H), 3.71 (s, 3H), 3.63 (s, 6H); ^{13}C NMR (100 MHz, DMSO) δ 159.5, 153.2, 150.0, 143.2, 141.2, 137.1, 133.0, 130.3, 128.5, 124.5, 120.8, 117.5,

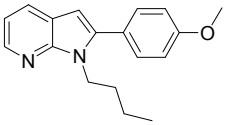
114.3, 107.1, 100.6, 60.6, 56.5, 55.6; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{23}H_{22}N_2O_4$, 391.1652; found, 391.1658.

*1-Butyl-2-phenyl-1H-pyrrolo[2,3-b]pyridine (**5n**)*



85 mg (34%); White solid; m.p = 156-157 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 6.4 Hz, 1H), 7.56 – 7.50 (m, 3H), 7.40 – 7.35 (m, 3H), 6.52 (dd, *J* = 7.2, 5.2 Hz, 1H), 5.24 (s, 1H), 3.50 (dd, *J* = 12.8, 7.2 Hz, 2H), 1.65 (d, *J* = 7.2 Hz, 2H), 1.46 (dd, *J* = 15.2, 7.2 Hz, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 148.0, 139.3, 131.5, 128.6, 128.5, 122.8, 111.6, 103.1, 95.8, 84.7, 41.2, 31.9, 20.3, 13.9; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{17}H_{18}N_2$, 251.1542; found, 251.1548.

*1-Butyl-2-(4-methoxy-phenyl)-1H-pyrrolo[2,3-b]pyridine (**5o**)*



106 mg (38%); White solid; m.p = 159-160 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.51 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.44 (dd, *J* = 6.0, 3.6 Hz, 2H), 6.91 – 6.88 (m, 2H), 6.51 (dd, *J* = 7.2, 5.2 Hz, 1H), 5.23 (s, 1H), 3.84 (s, 3H), 3.48 (dd, *J* = 10.8, 3.6 Hz, 2H), 1.63 (s, 2H), 1.46 (dd, *J* = 15.2, 7.2 Hz, 2H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 147.6, 139.1, 130.5, 127.8, 125.3, 120.7, 111.6, 103.5, 95.8, 83.3, 55.3, 41.2, 31.9, 20.3, 13.9; HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{18}H_{20}N_2O$, 281.1648; found, 281.1655.

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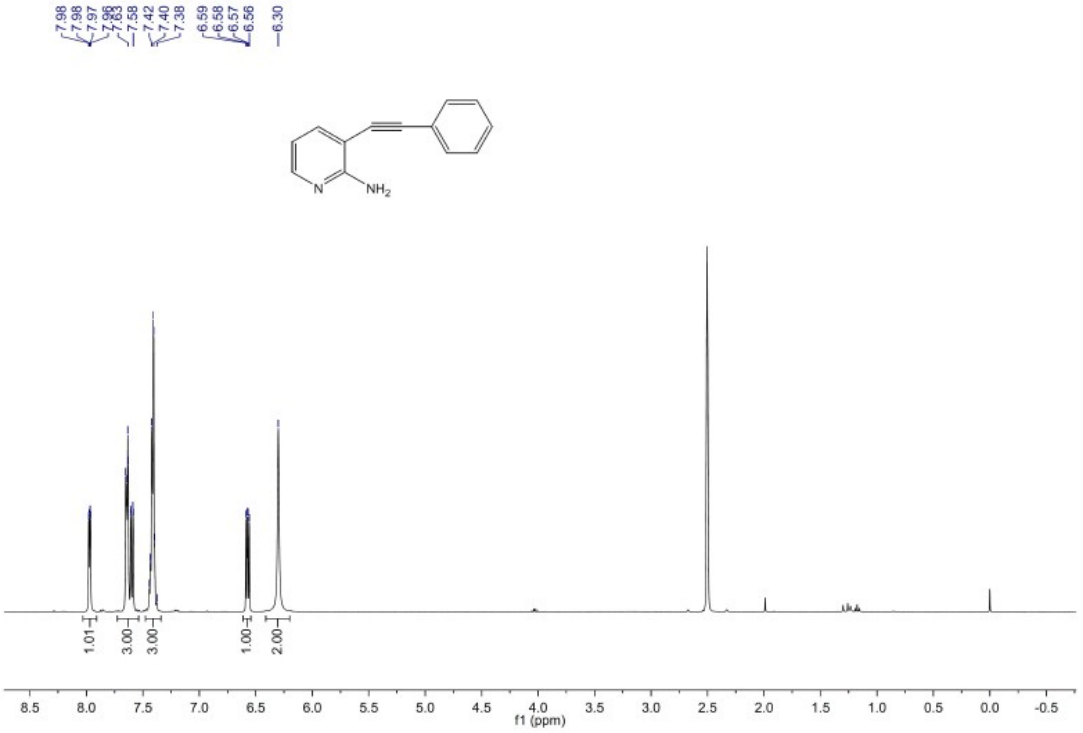
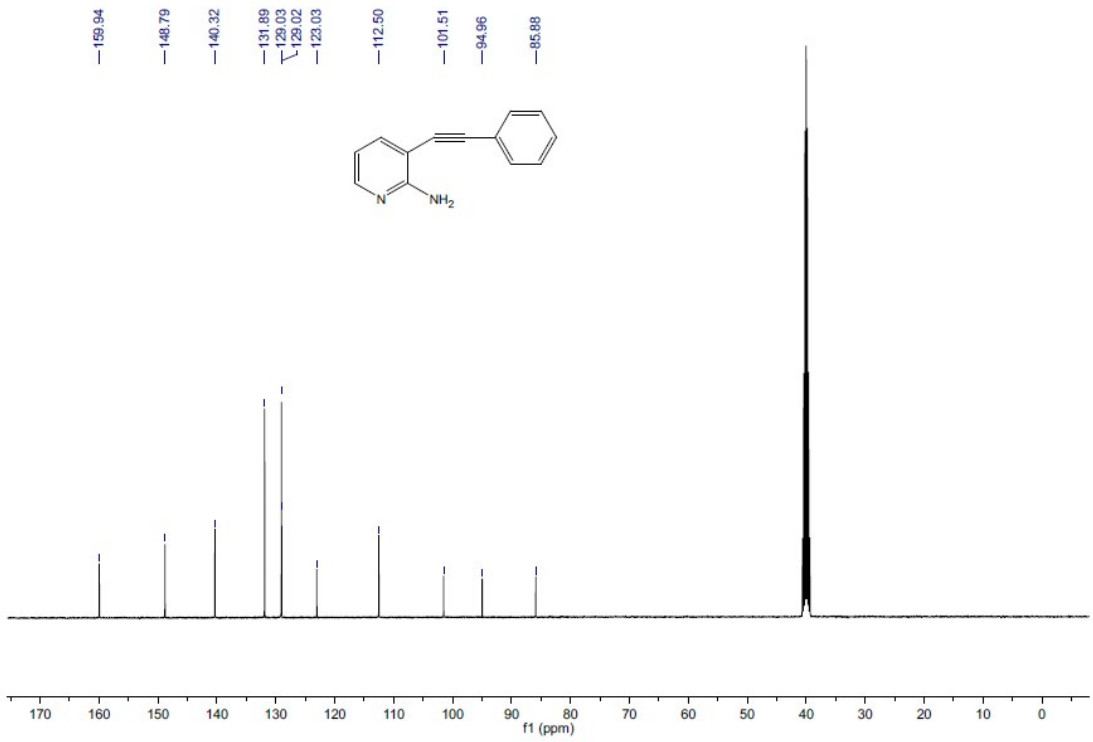
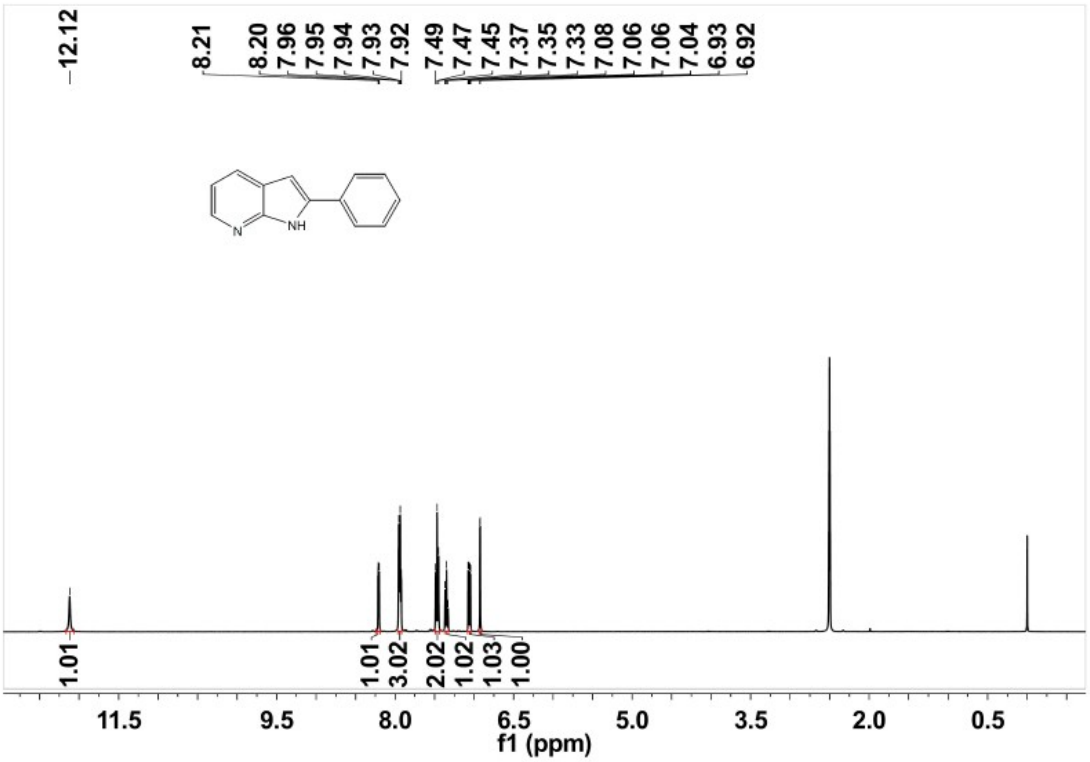
^{1}H NMR spectrum of compound **3aa**



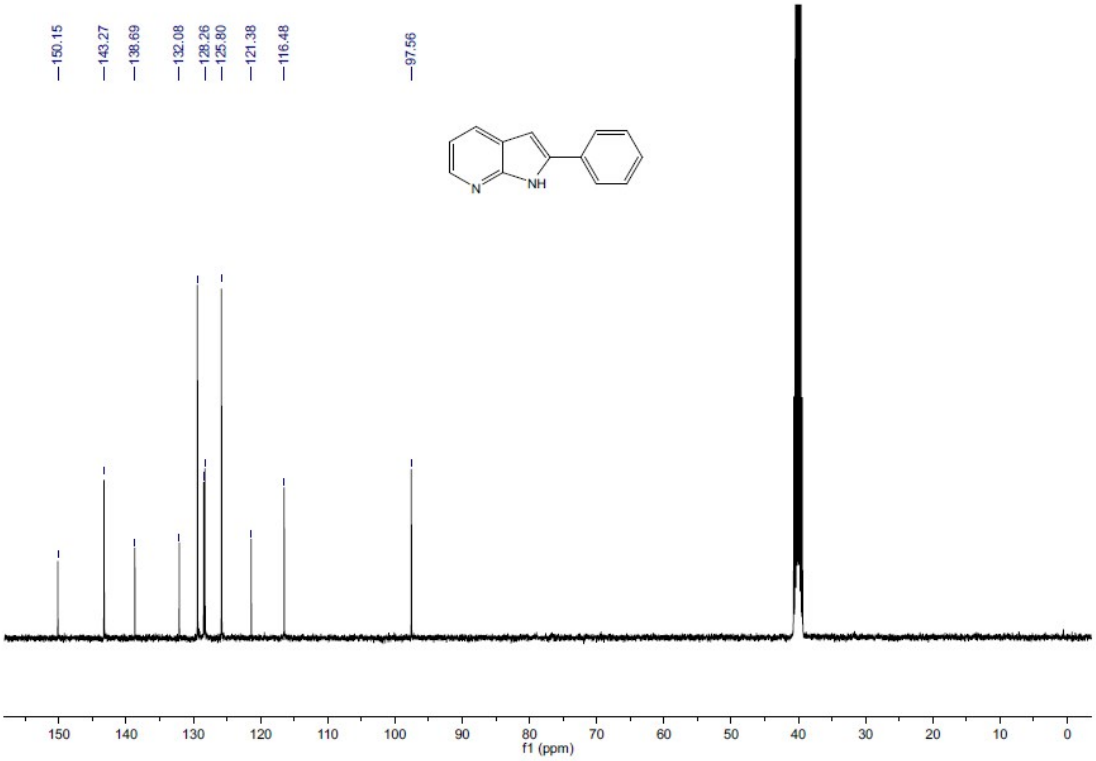
^{13}C NMR spectrum of compound **3aa**



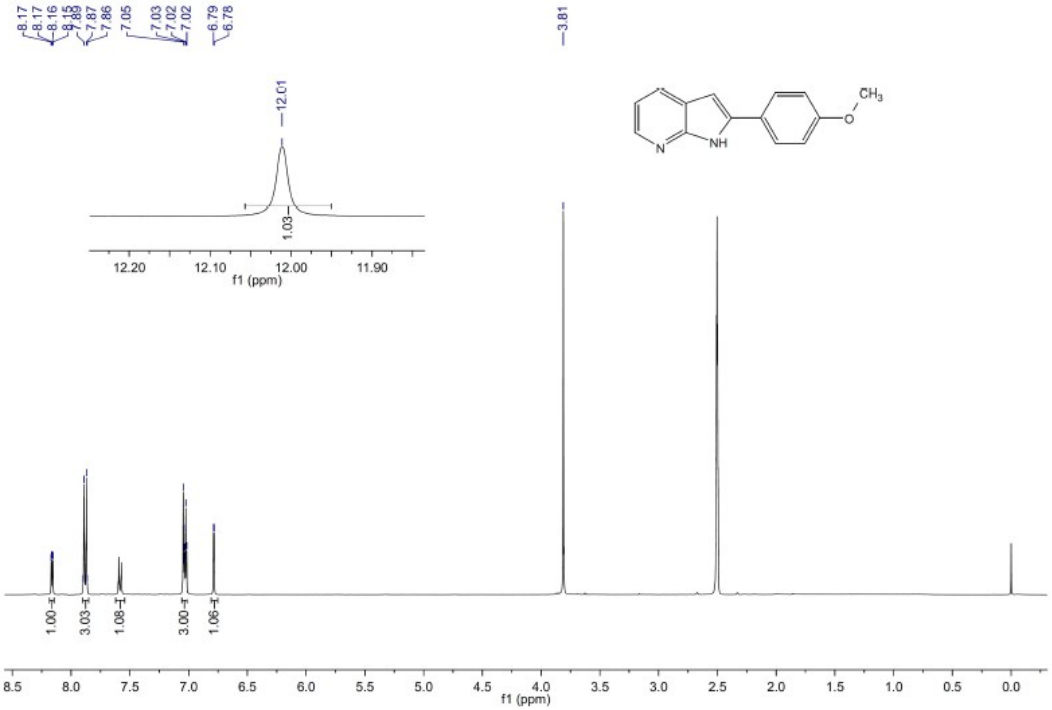
^{1}H NMR spectrum of compound **3a**



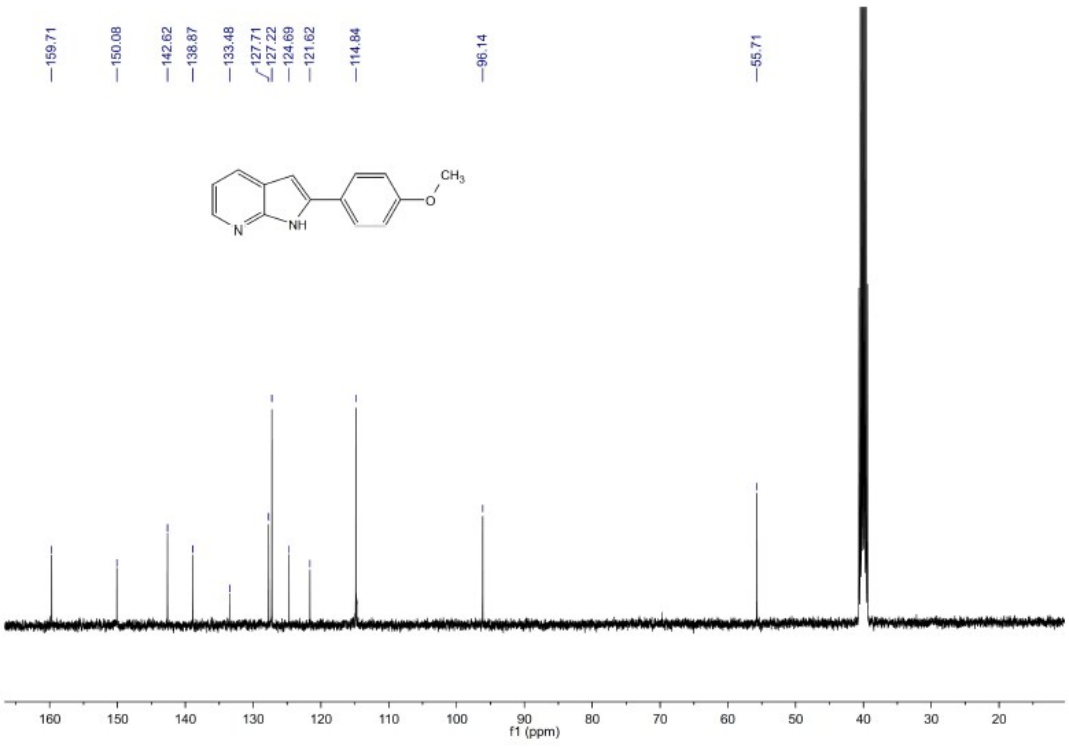
^{13}C NMR spectrum of compound **3a**



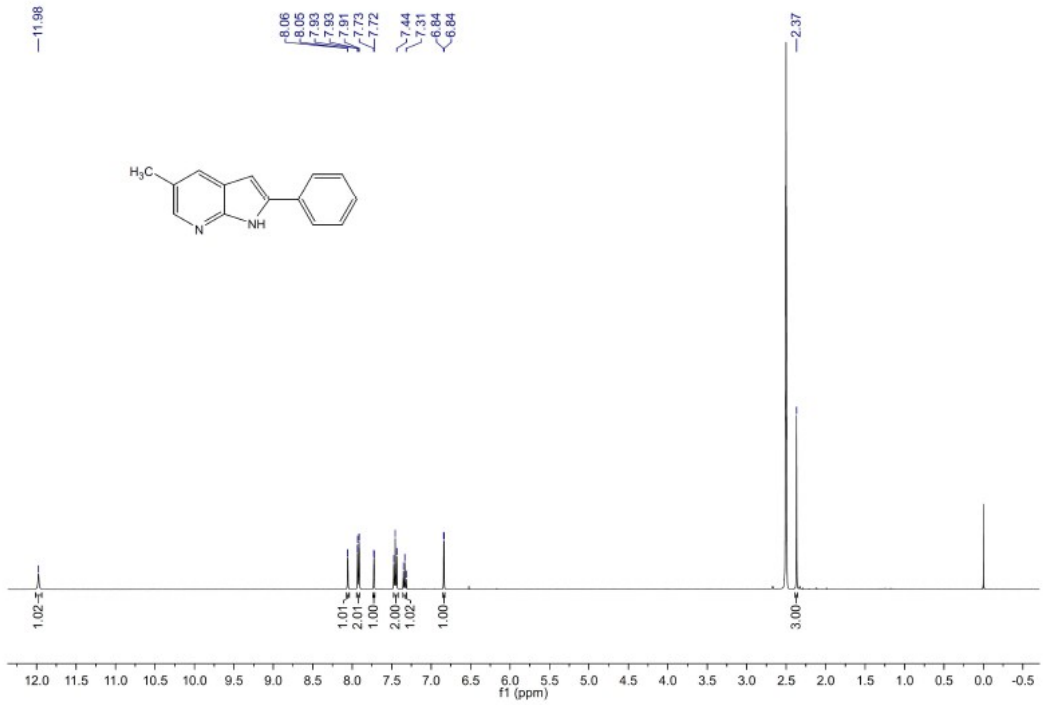
^{1}H NMR spectrum of compound **3b**



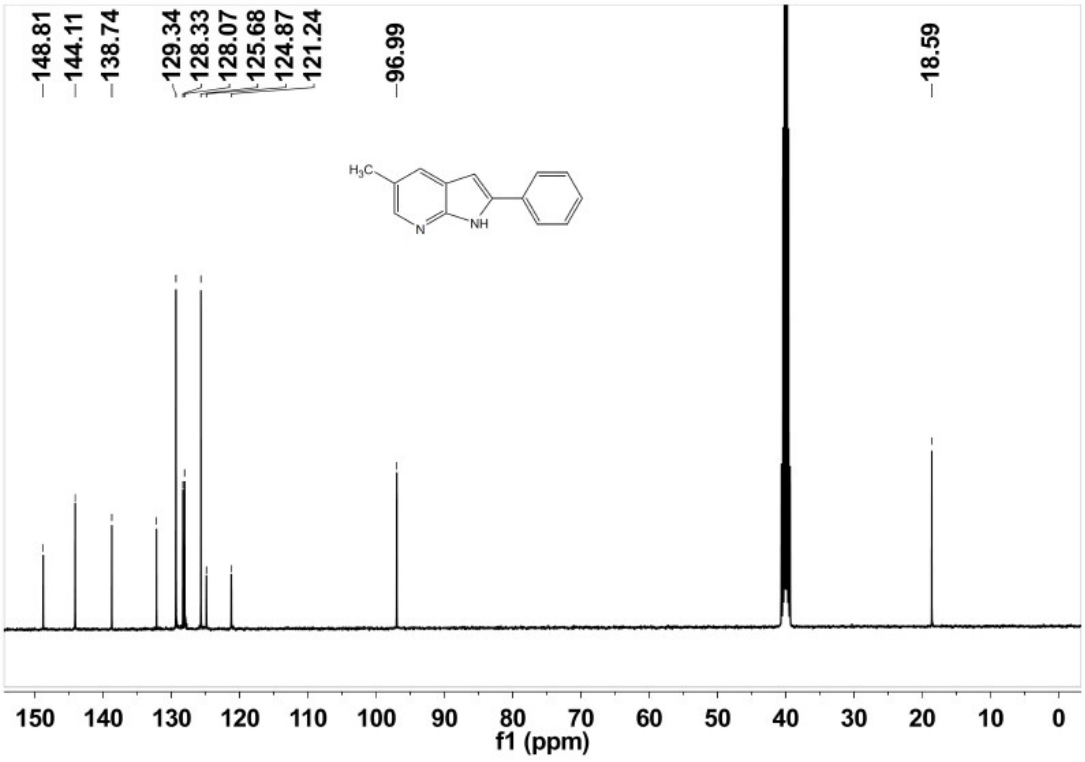
^{13}C NMR spectrum of compound **3b**



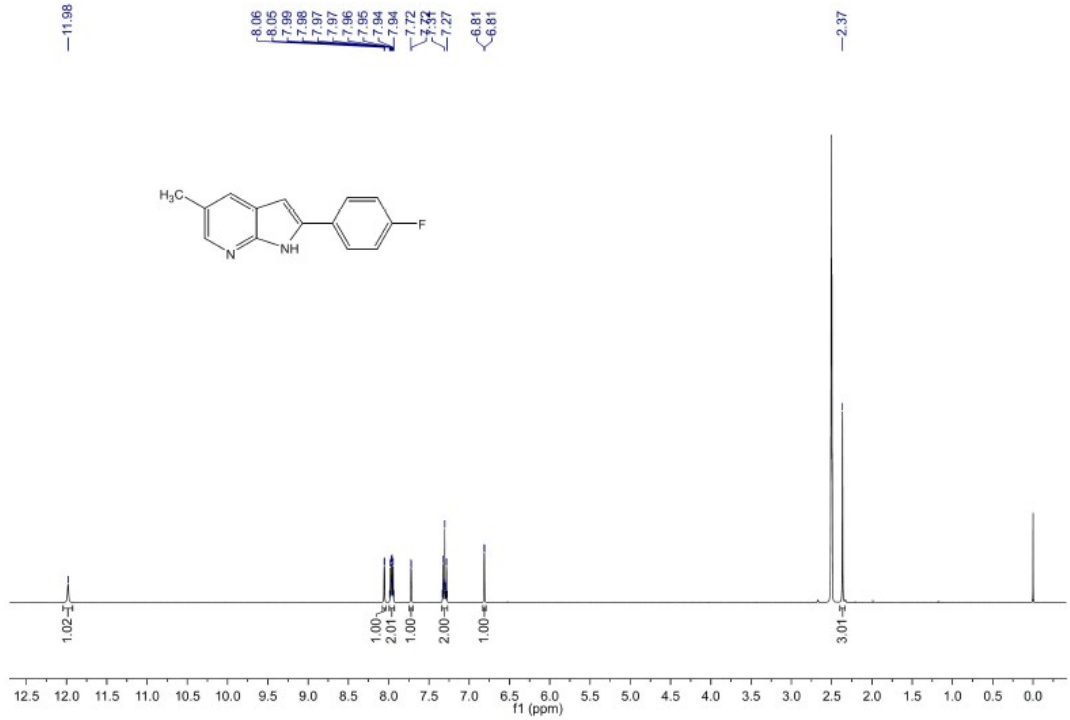
^{1}H NMR spectrum of compound **3c**



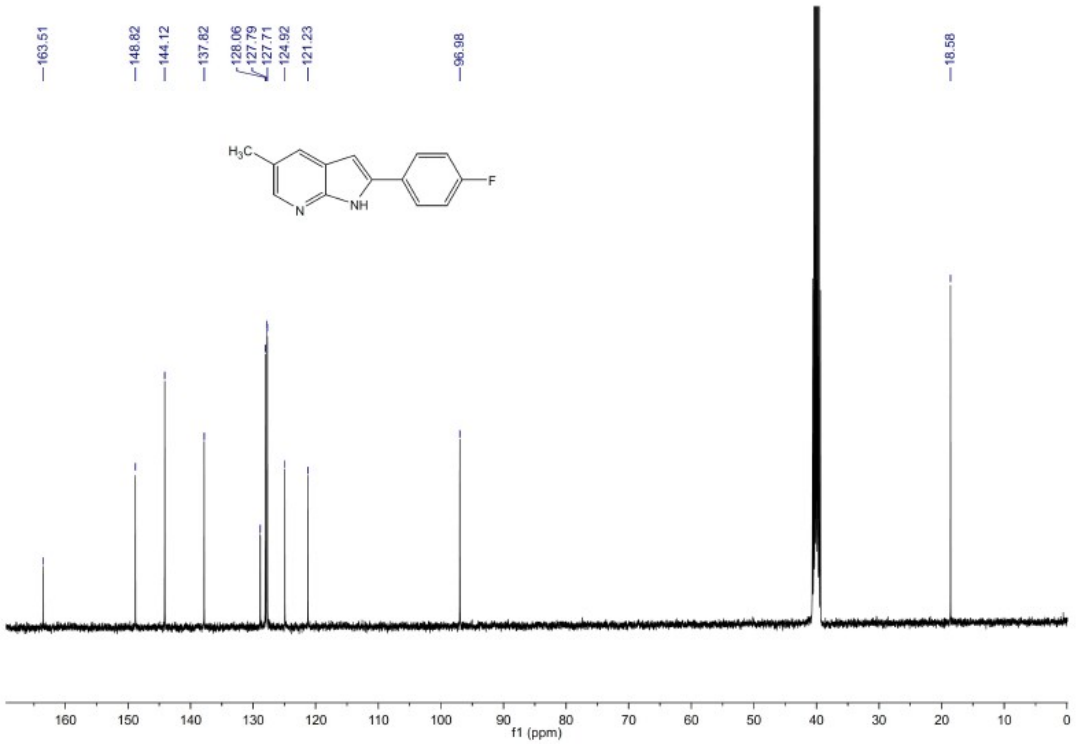
^{13}C NMR spectrum of compound **3c**



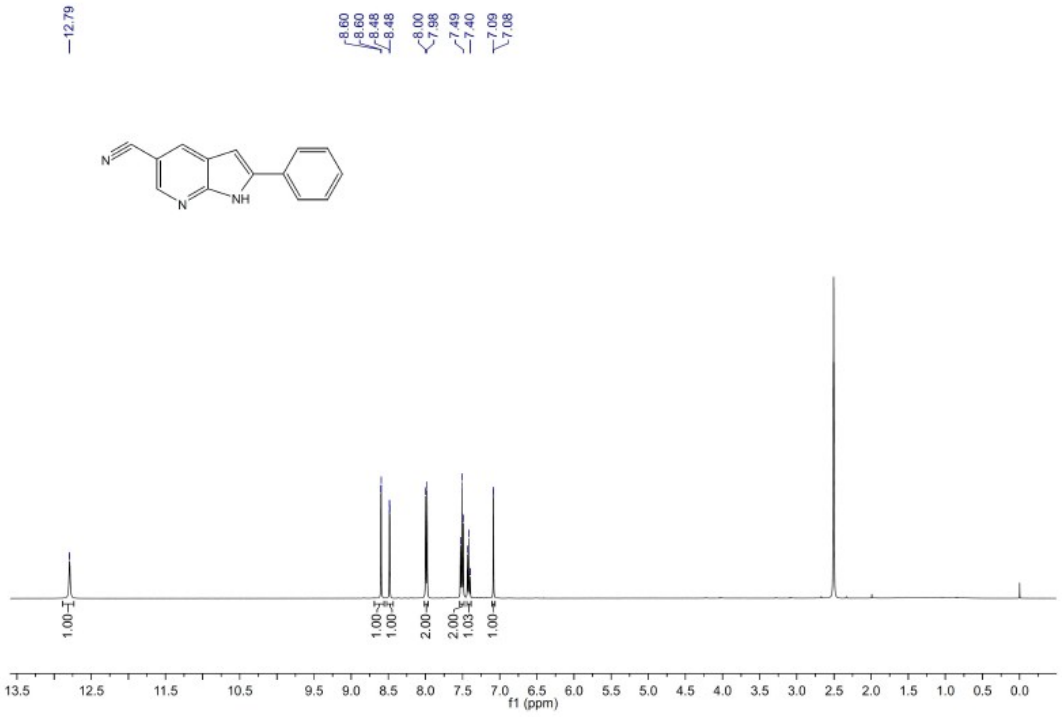
^{1}H NMR spectrum of compound **3d**



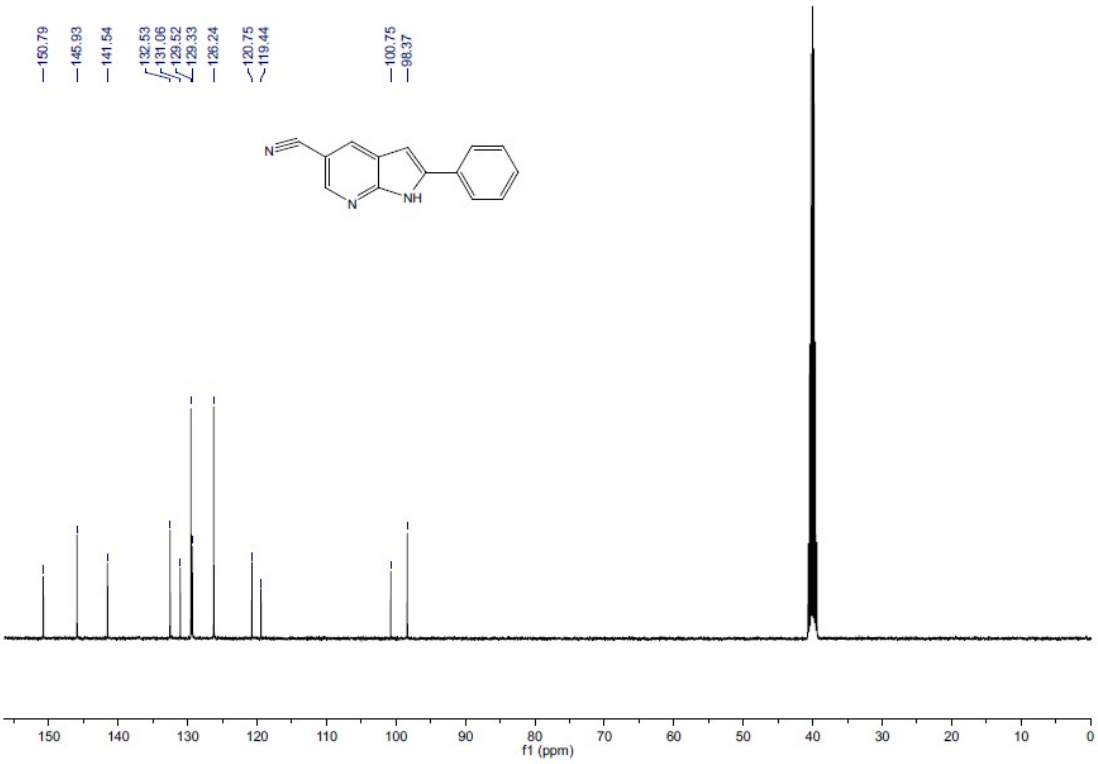
^{13}C NMR spectrum of compound **3d**



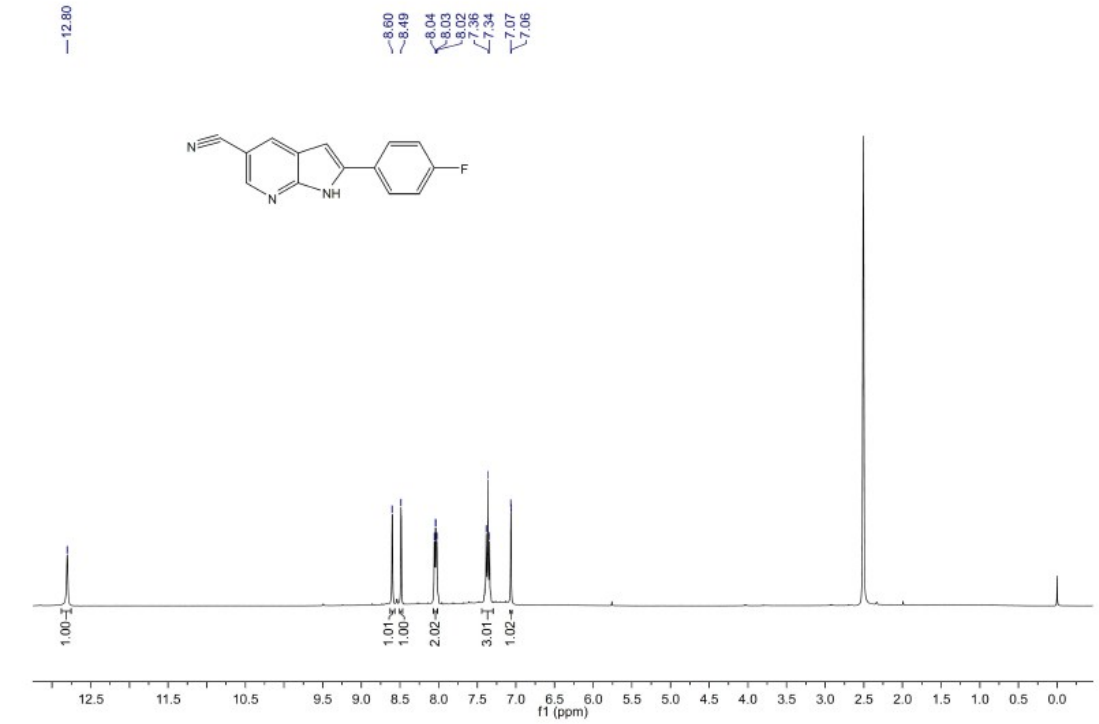
^{1}H NMR spectrum of compound **3e**



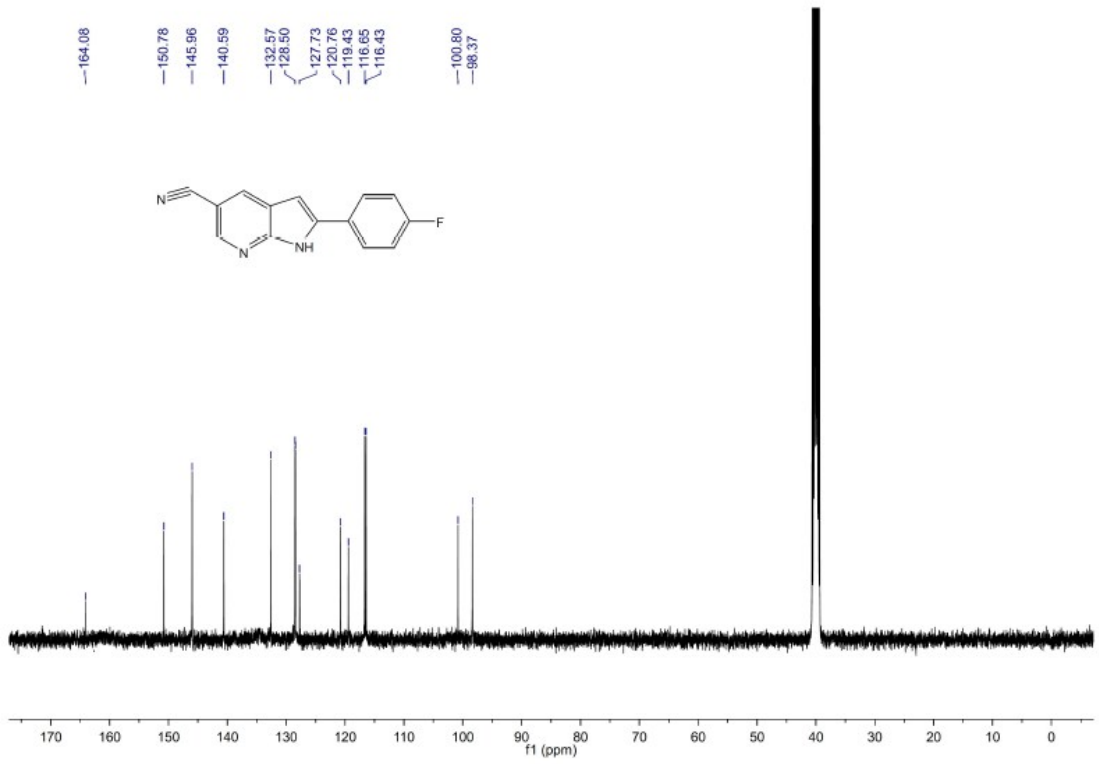
^{13}C NMR spectrum of compound **3e**



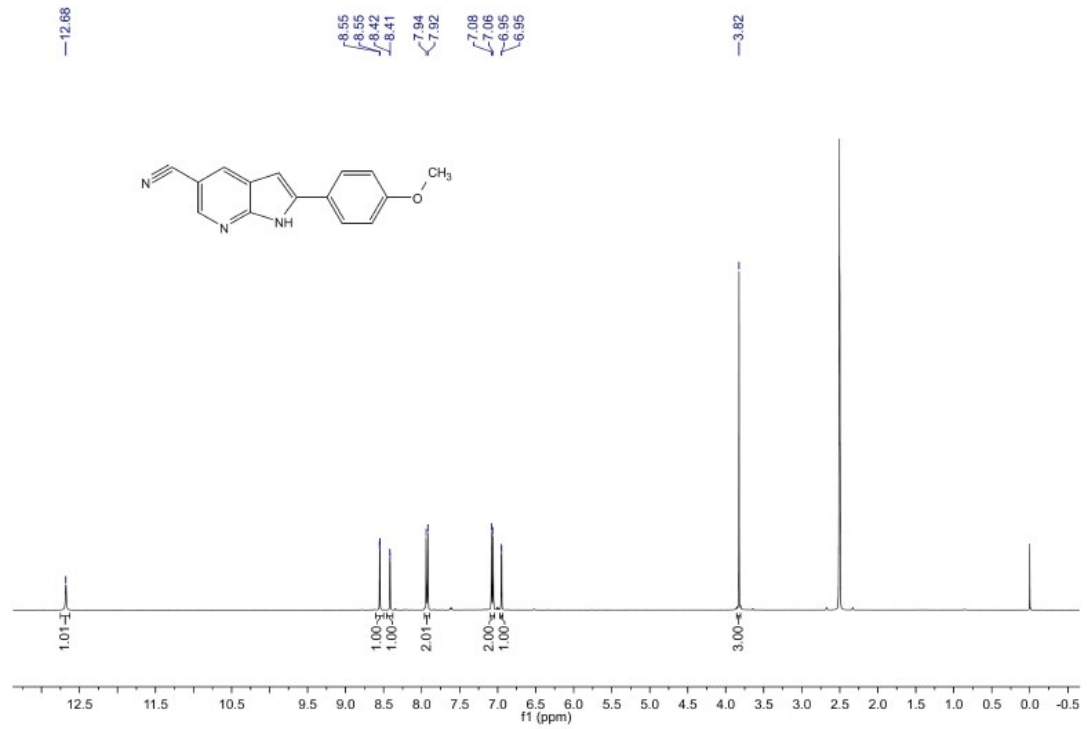
^{1}H NMR spectrum of compound **3f**



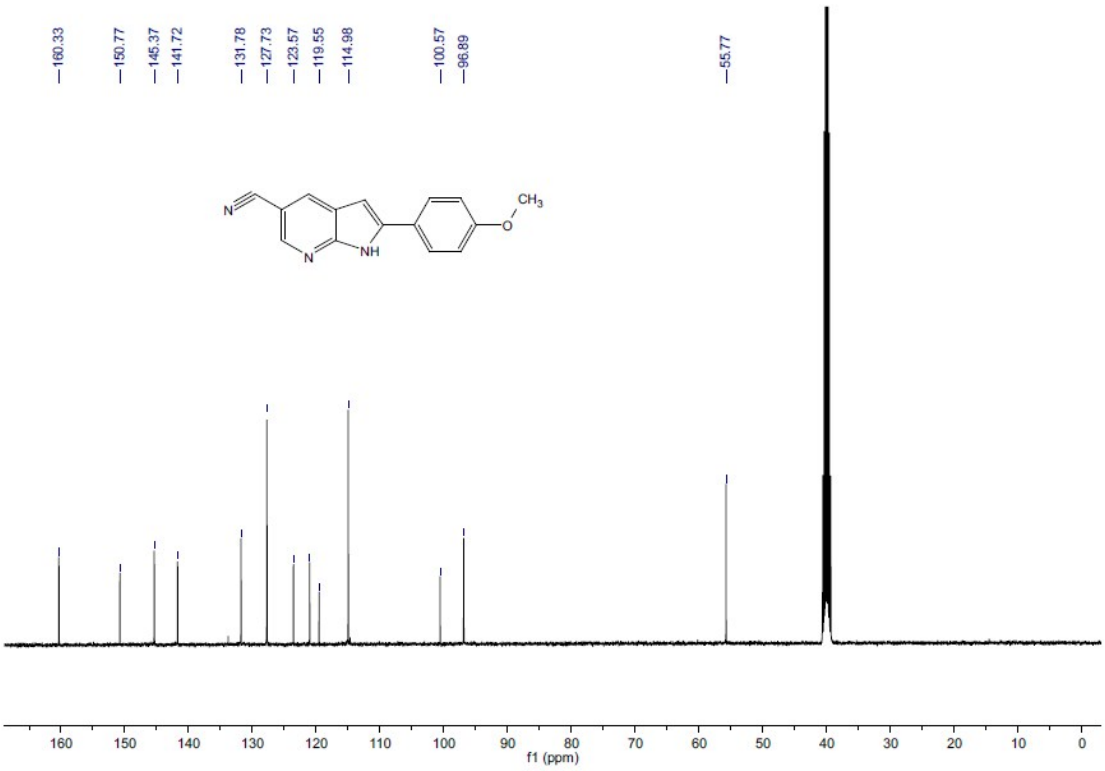
^{13}C NMR spectrum of compound **3f**



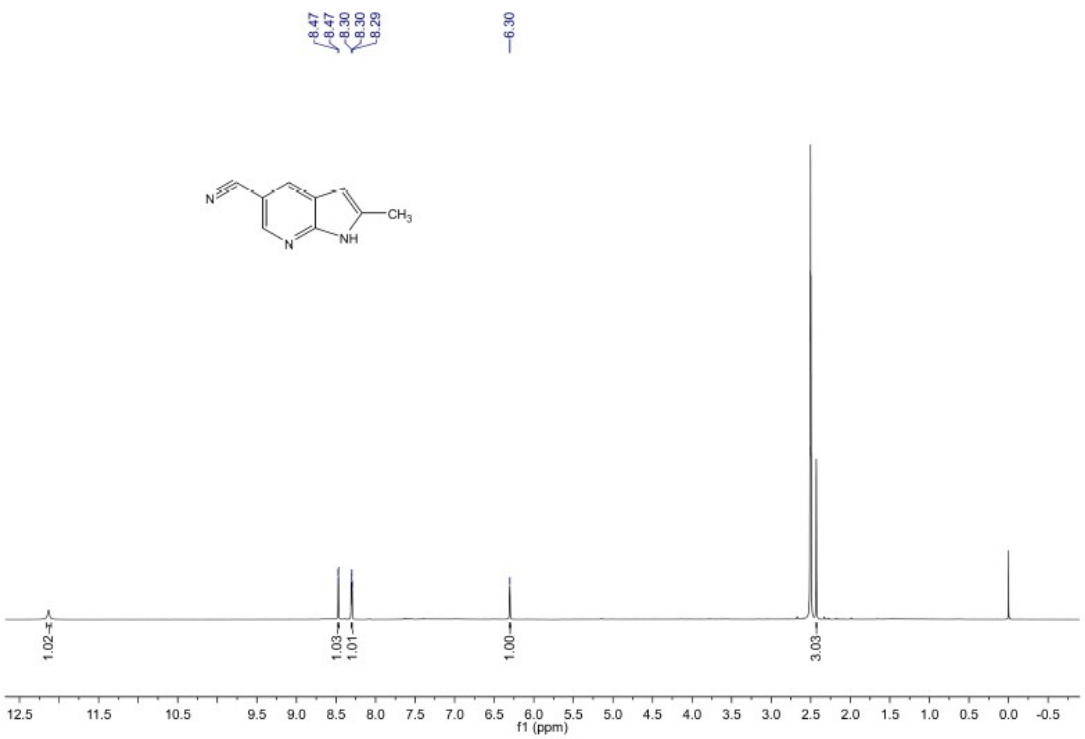
^{1}H NMR spectrum of compound **3g**



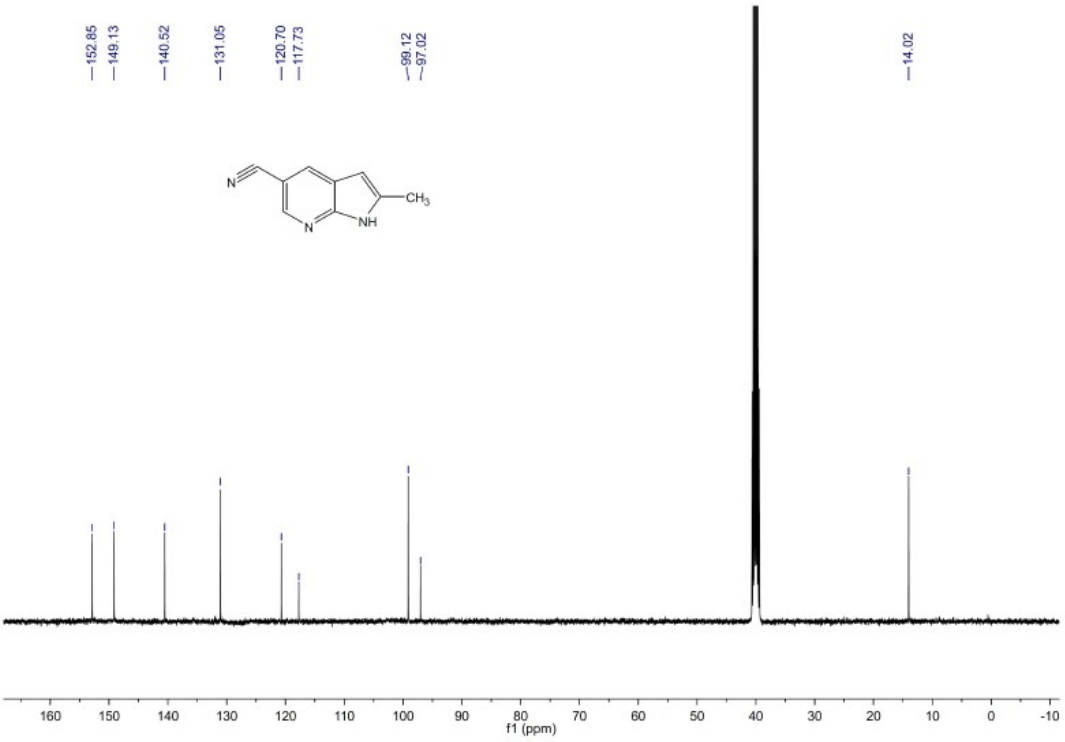
^{13}C NMR spectrum of compound **3g**



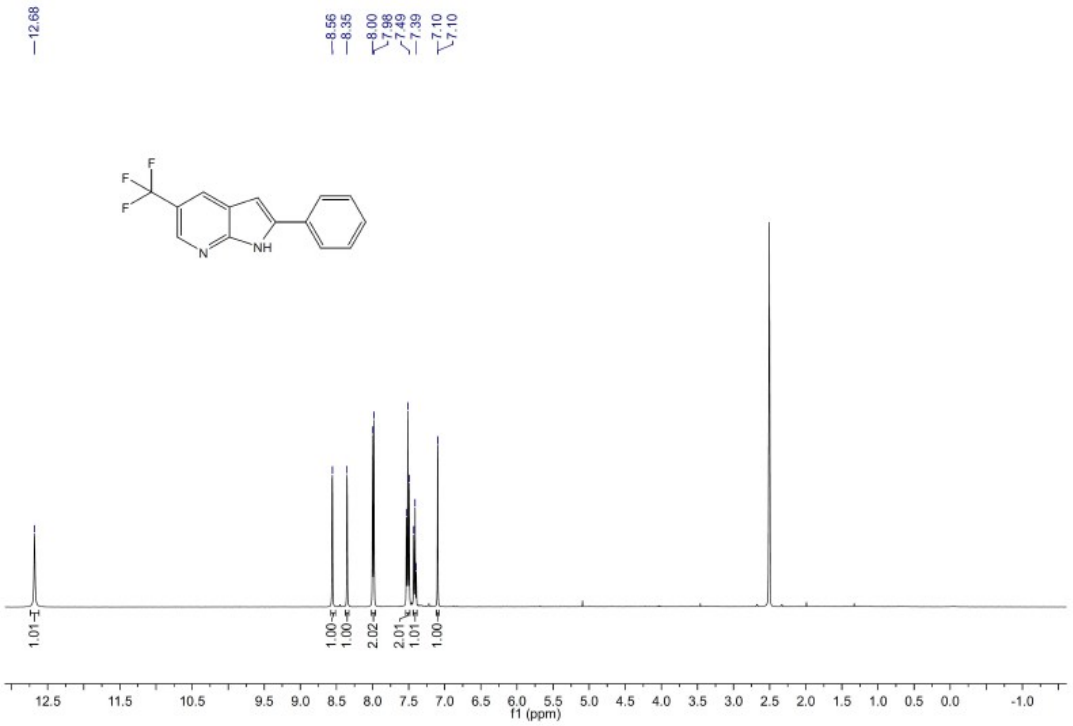
^{1}H NMR spectrum of compound **3h**



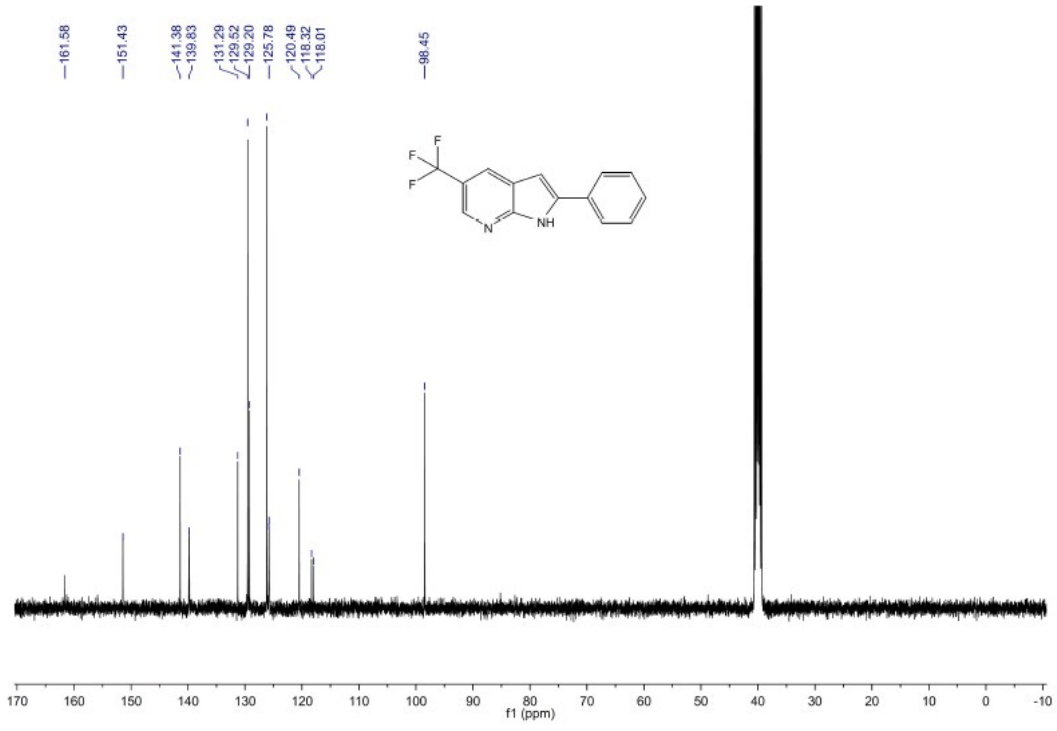
^{13}C NMR spectrum of compound **3h**



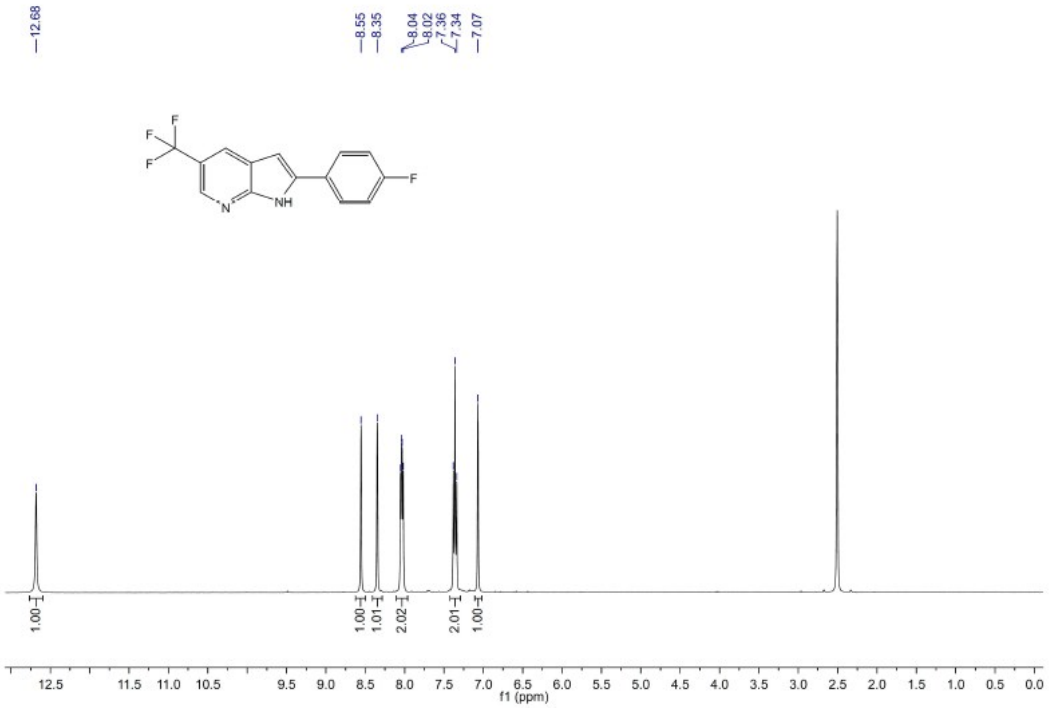
^{1}H NMR spectrum of compound **3i**



^{13}C NMR spectrum of compound **3i**



^{1}H NMR spectrum of compound **3j**



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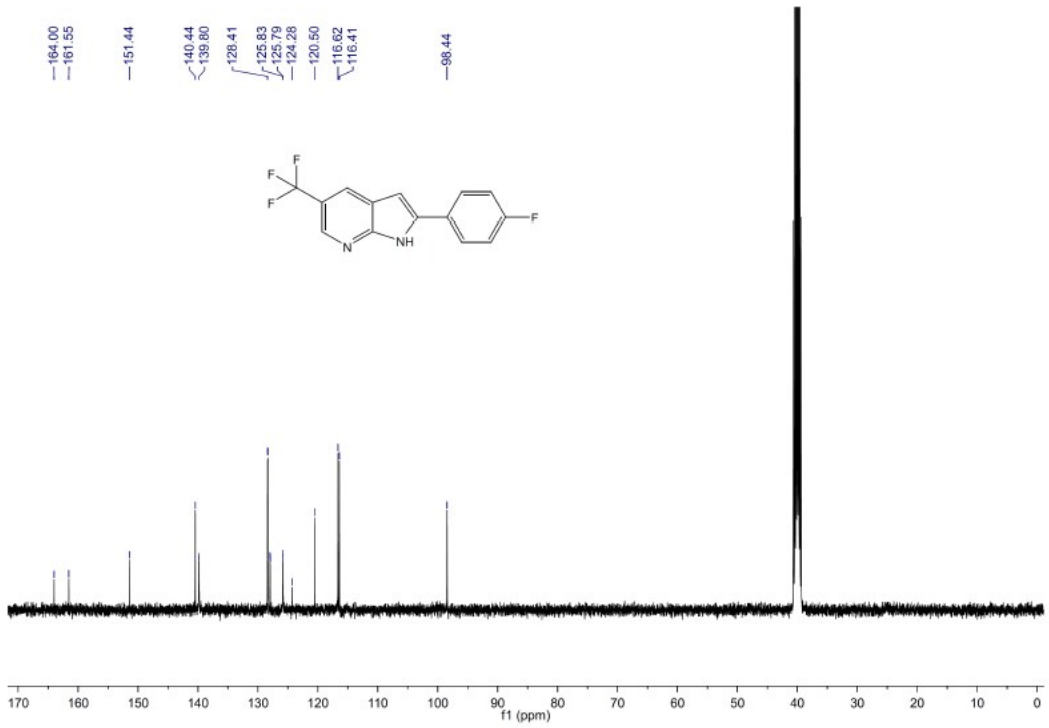
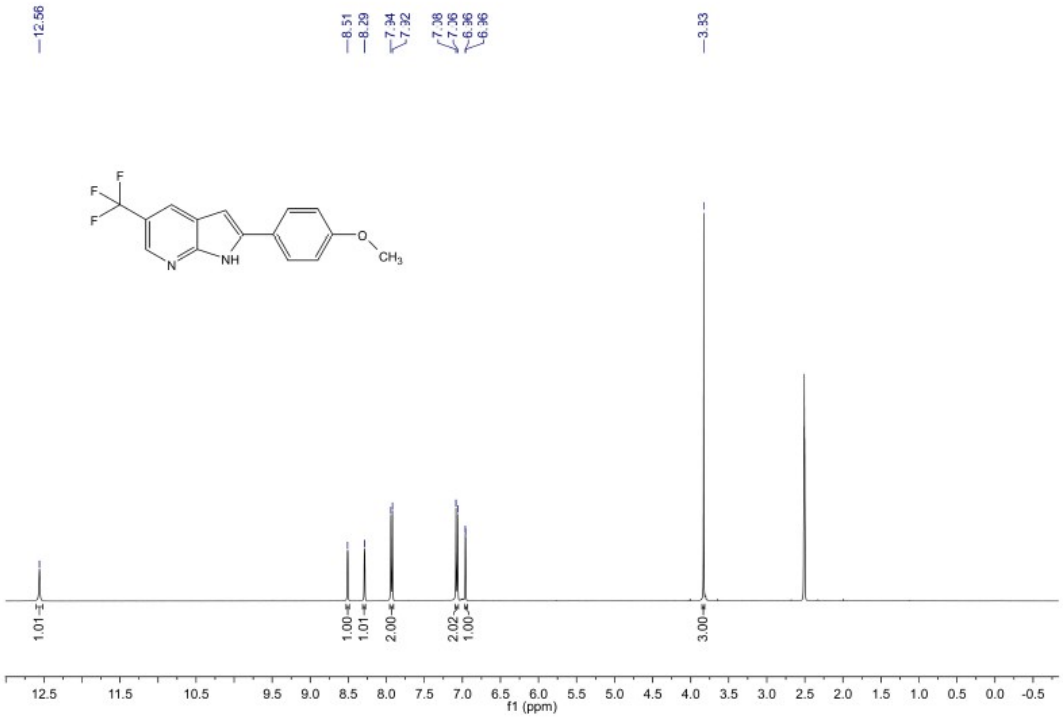


^{1}H NMR spectrum of compound **3k**



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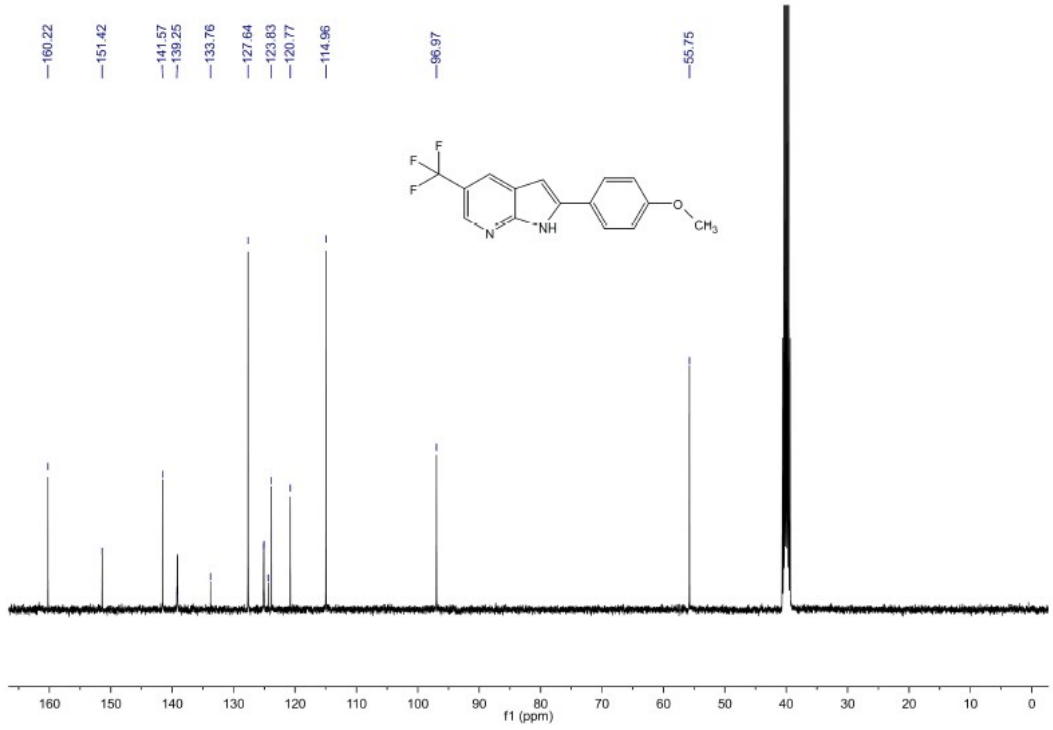
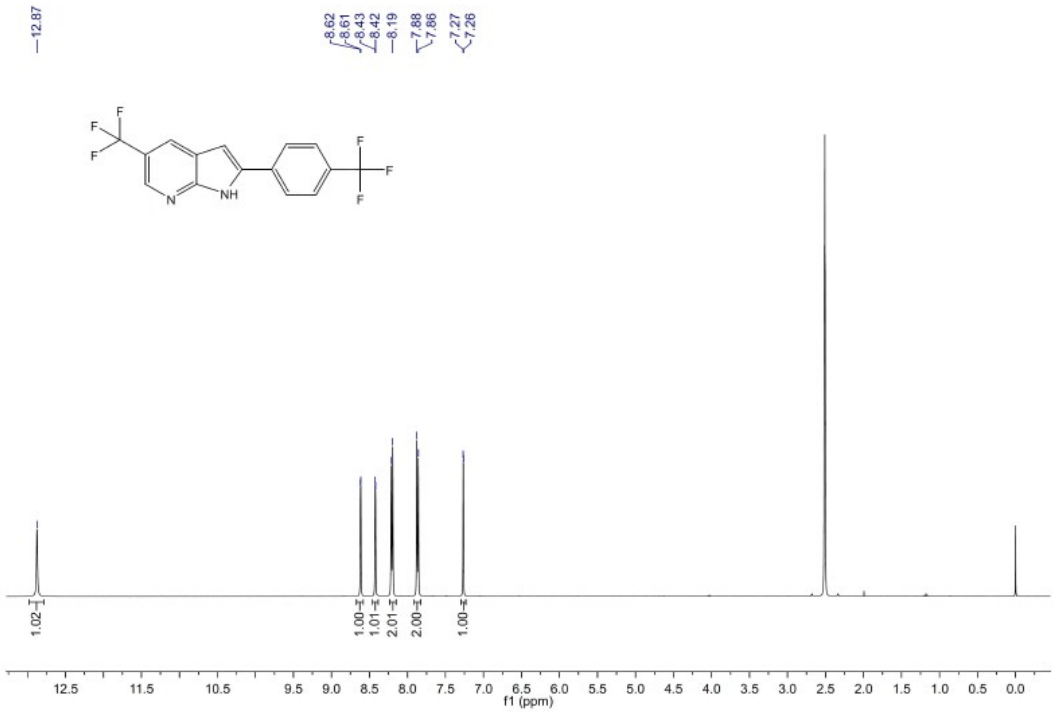
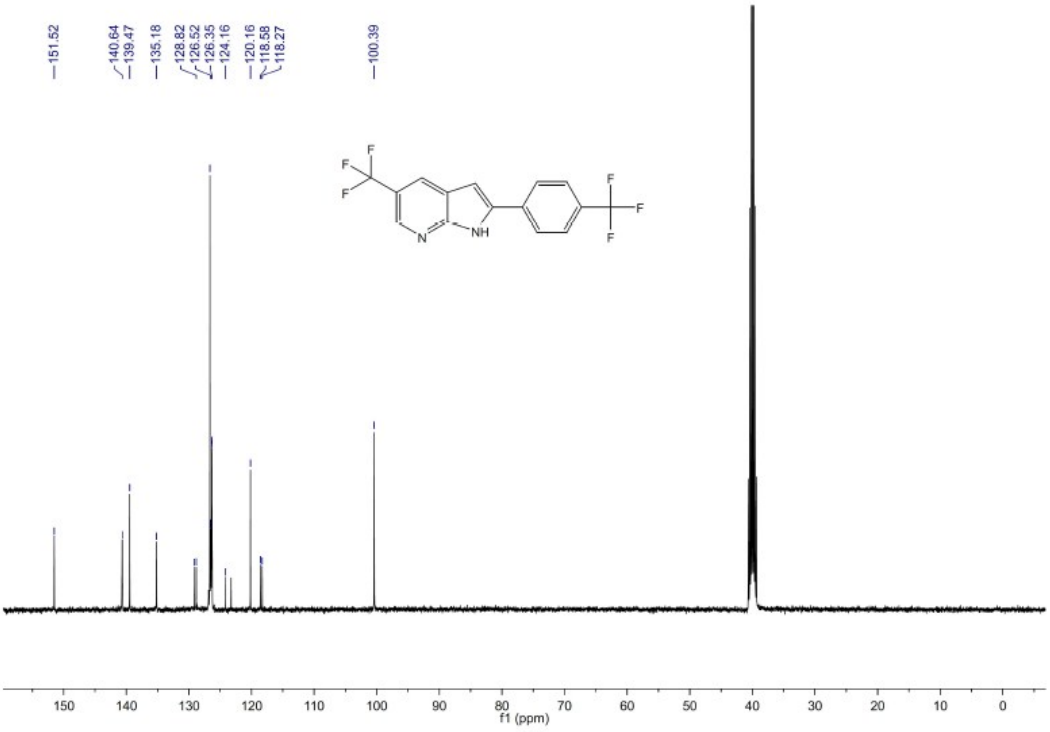


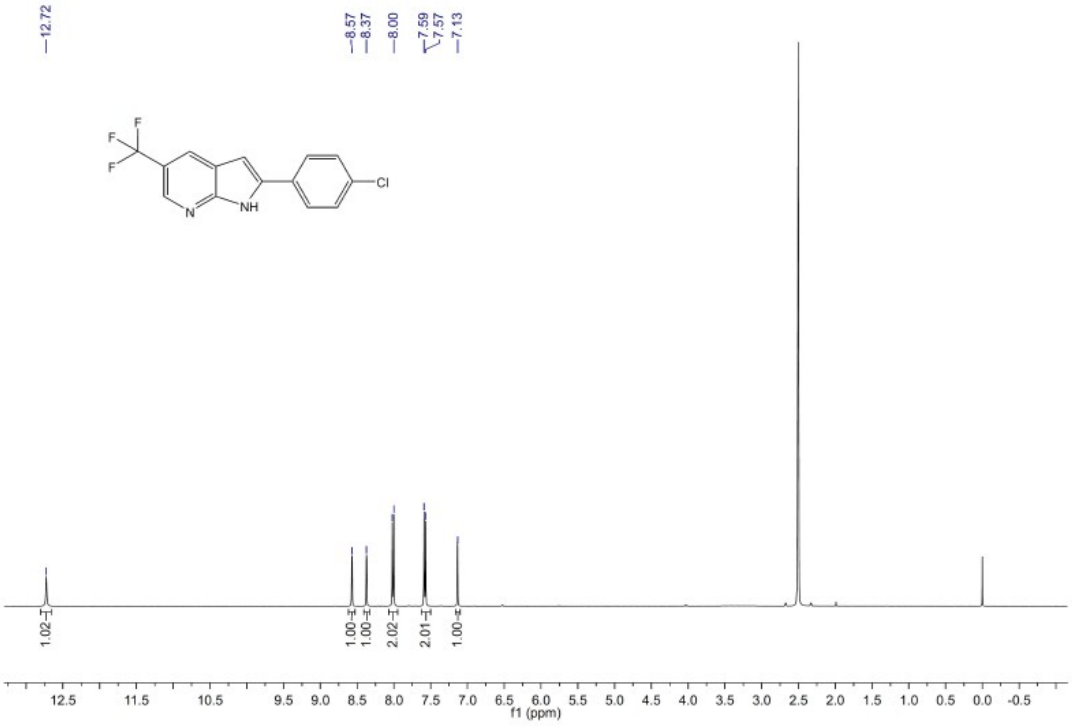
^{1}H NMR spectrum of compound **3l**



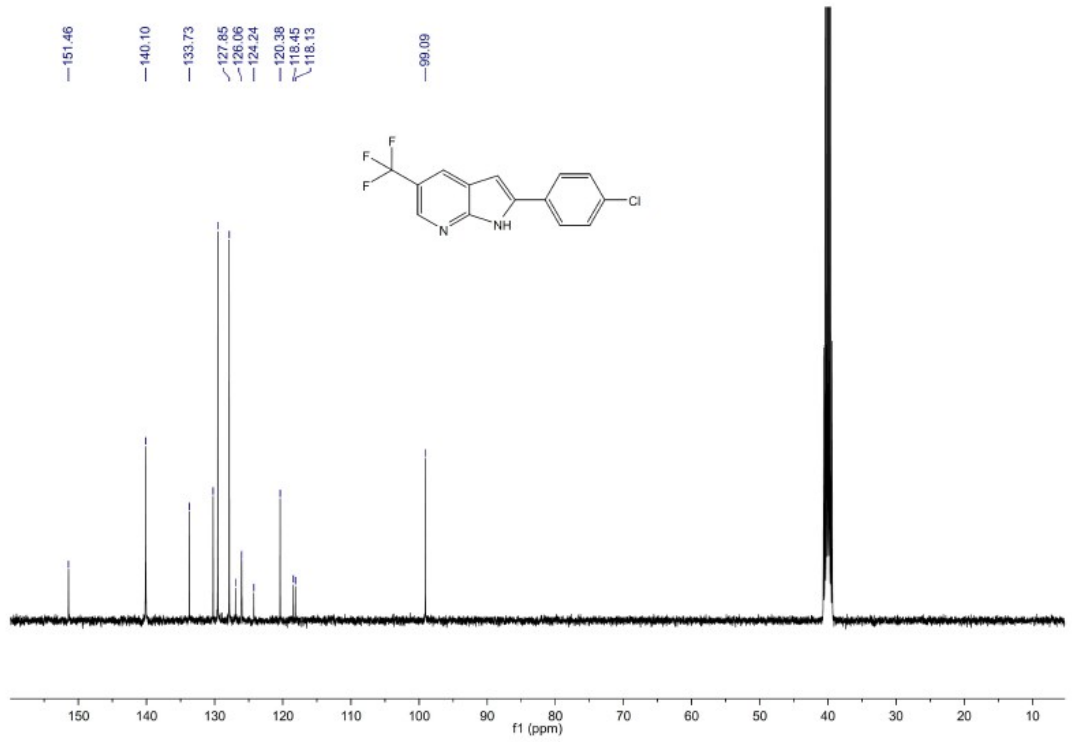
^{13}C NMR spectrum of compound **3l**



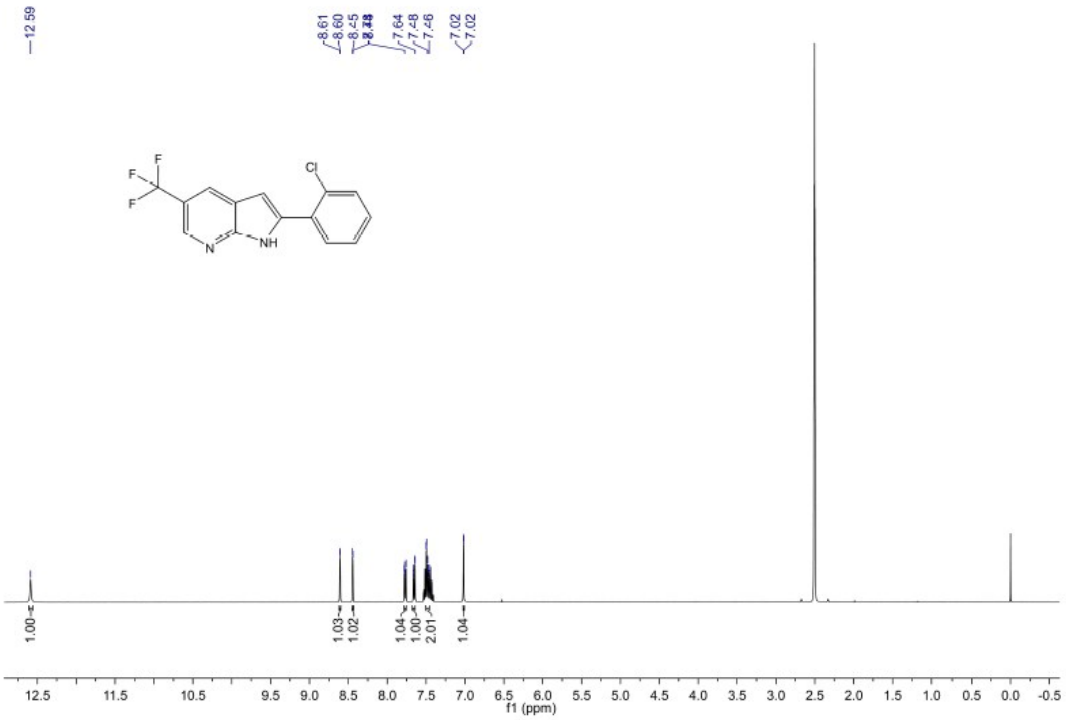
^{1}H NMR spectrum of compound **3m**



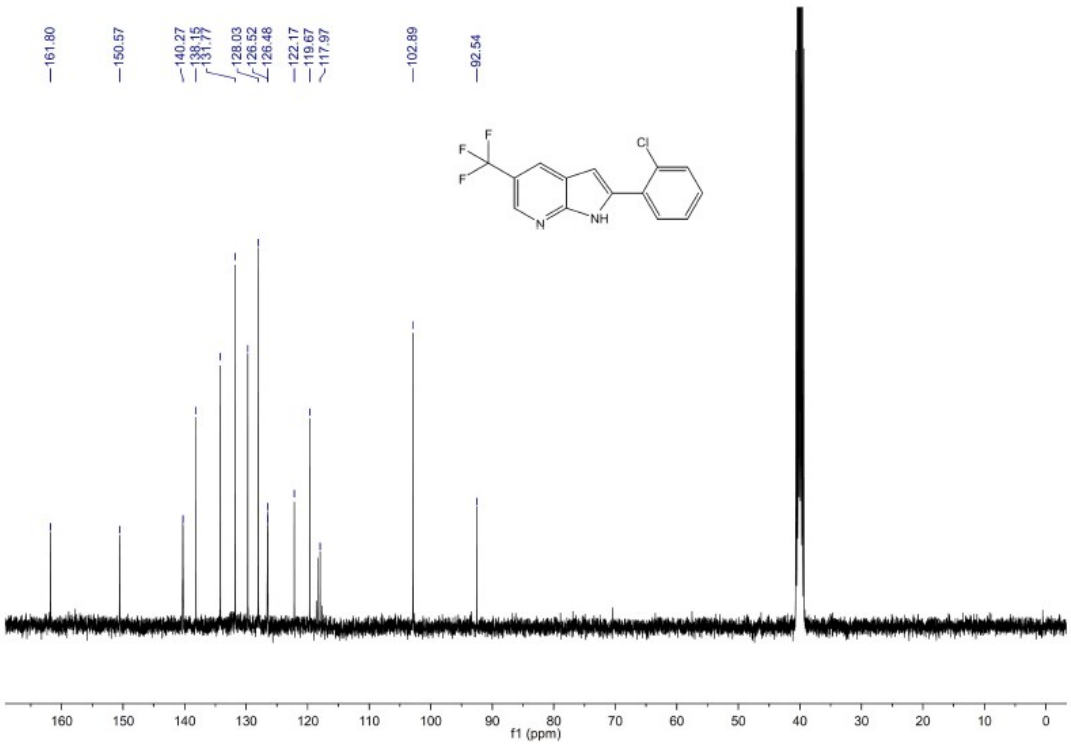
^{13}C NMR spectrum of compound **3m**



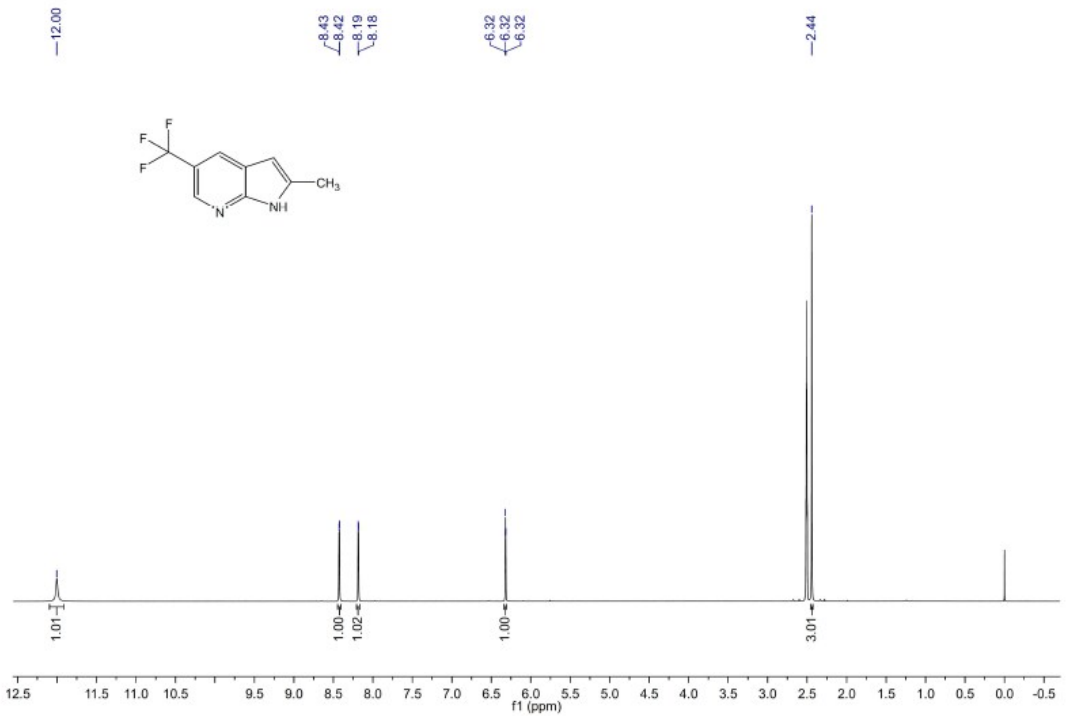
^{1}H NMR spectrum of compound **3n**



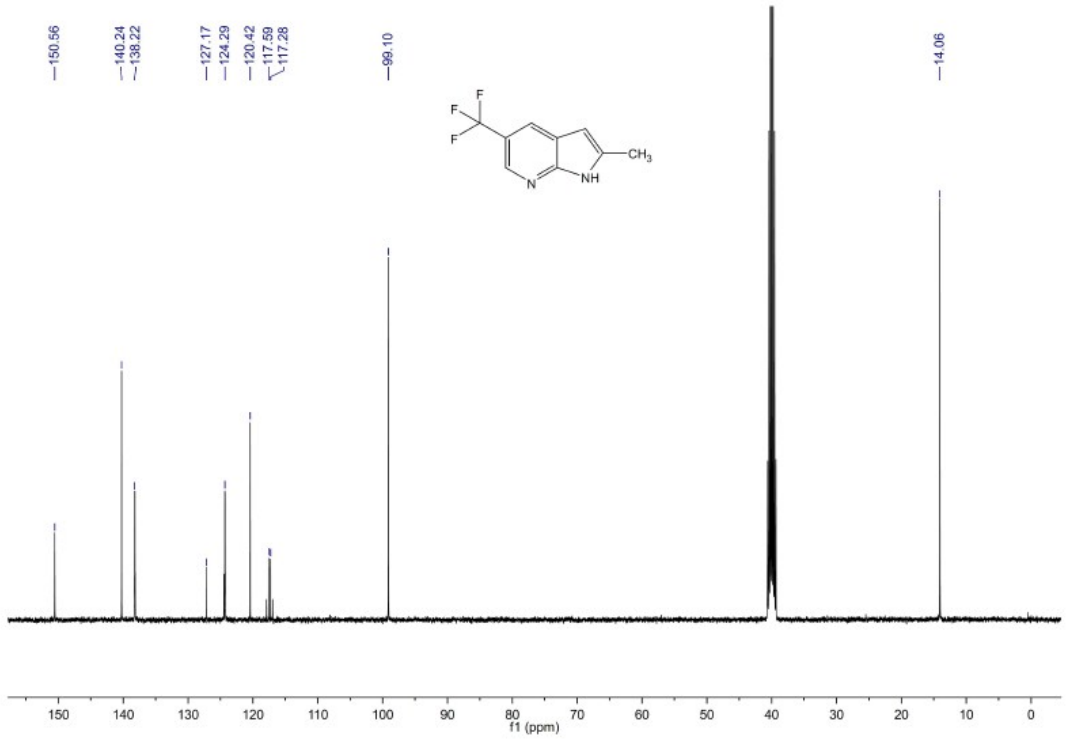
^{13}C NMR spectrum of compound **3n**



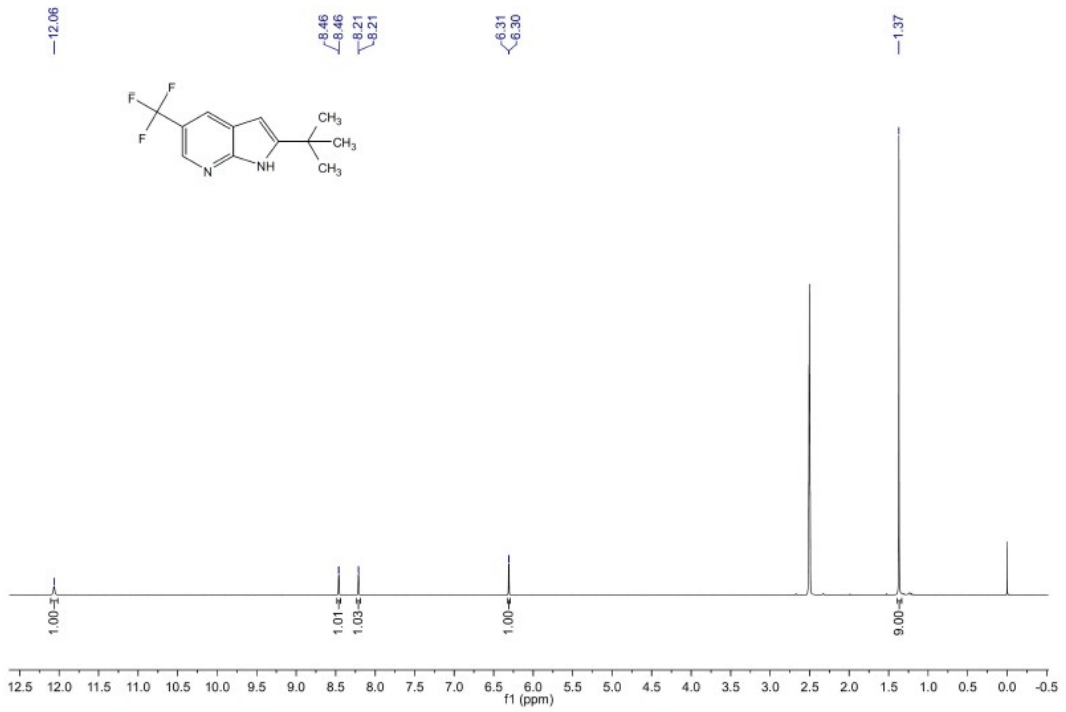
^{1}H NMR spectrum of compound **3o**



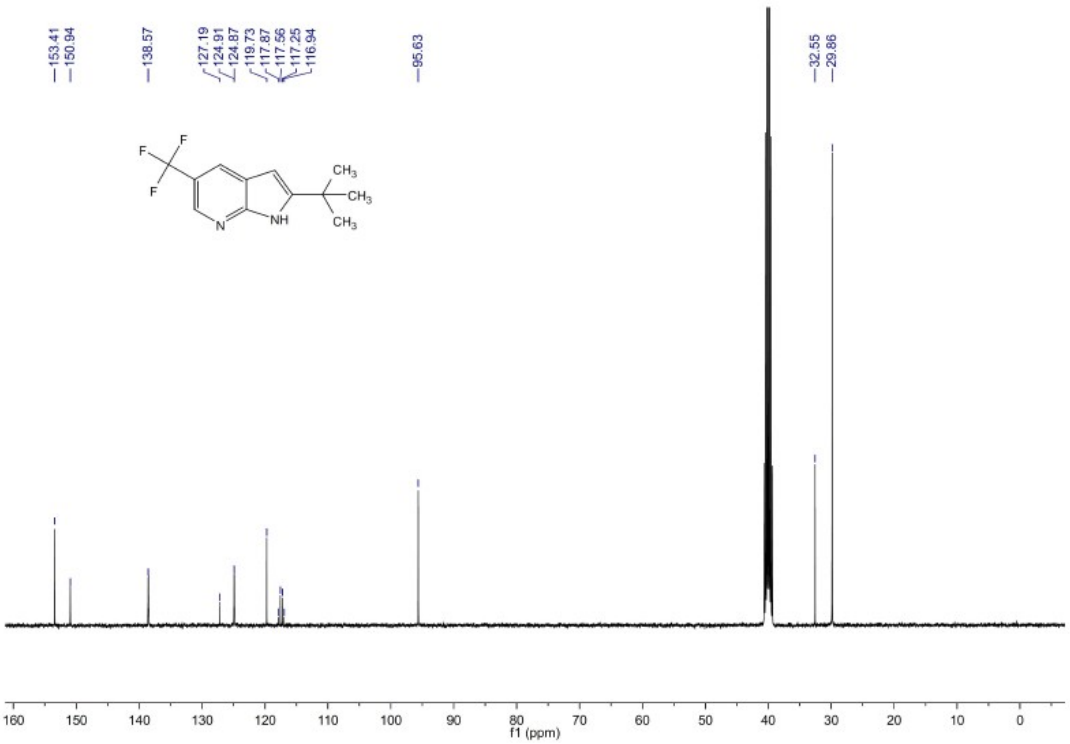
^{13}C NMR spectrum of compound **3o**



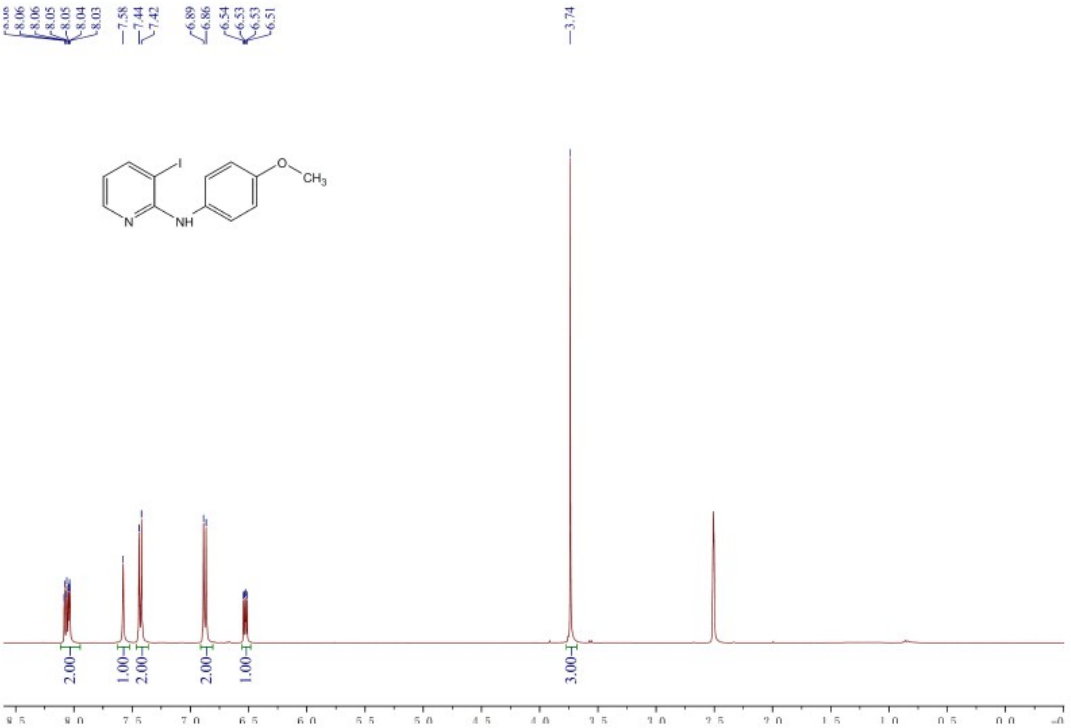
^{1}H NMR spectrum of compound **3p**



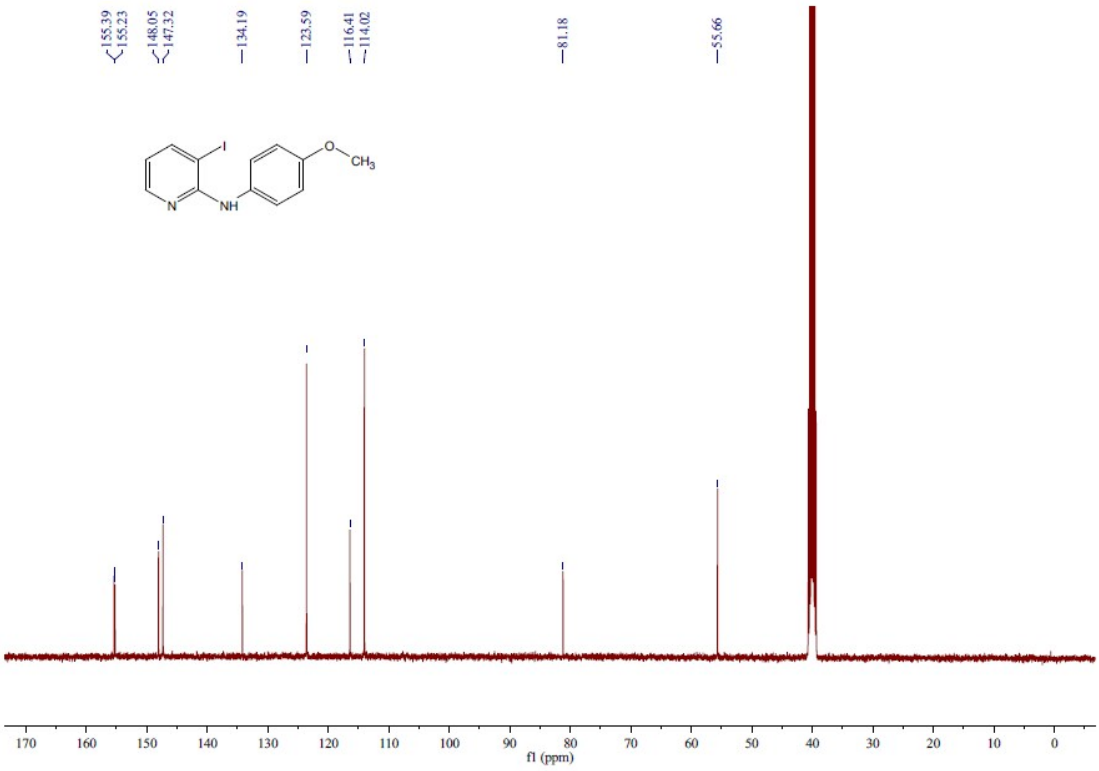
^{13}C NMR spectrum of compound **3p**



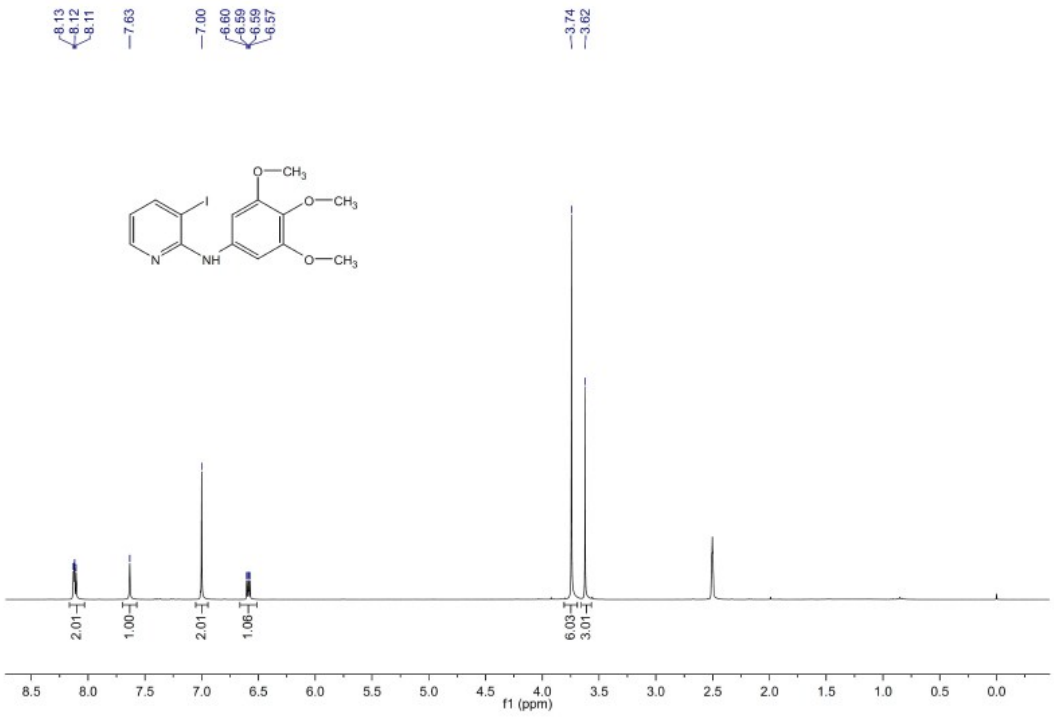
^{1}H NMR spectrum of compound **4a**



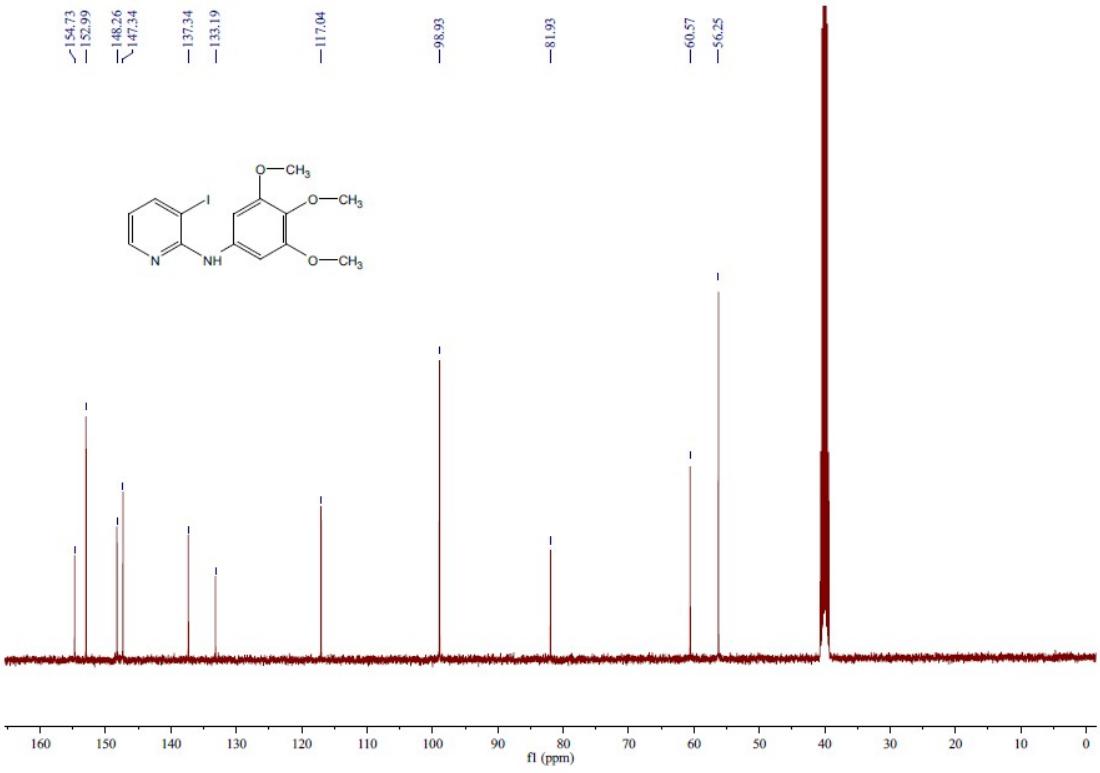
^{13}C NMR spectrum of compound **4a**



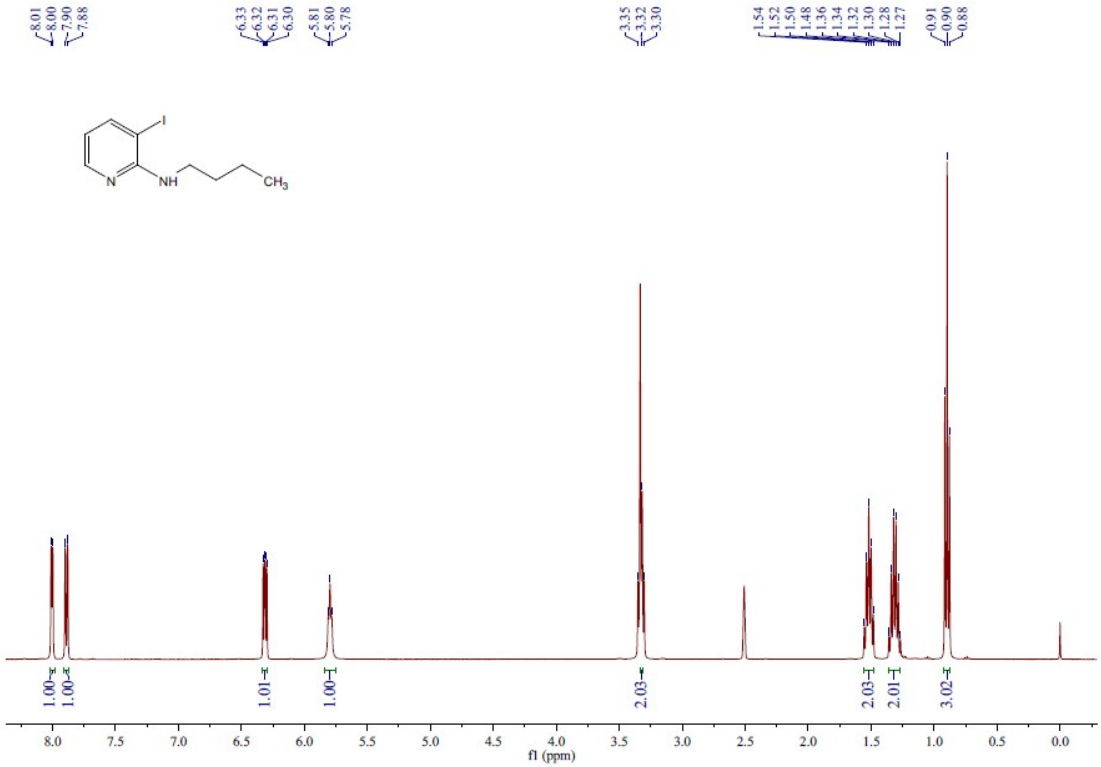
^{1}H NMR spectrum of compound **4b**



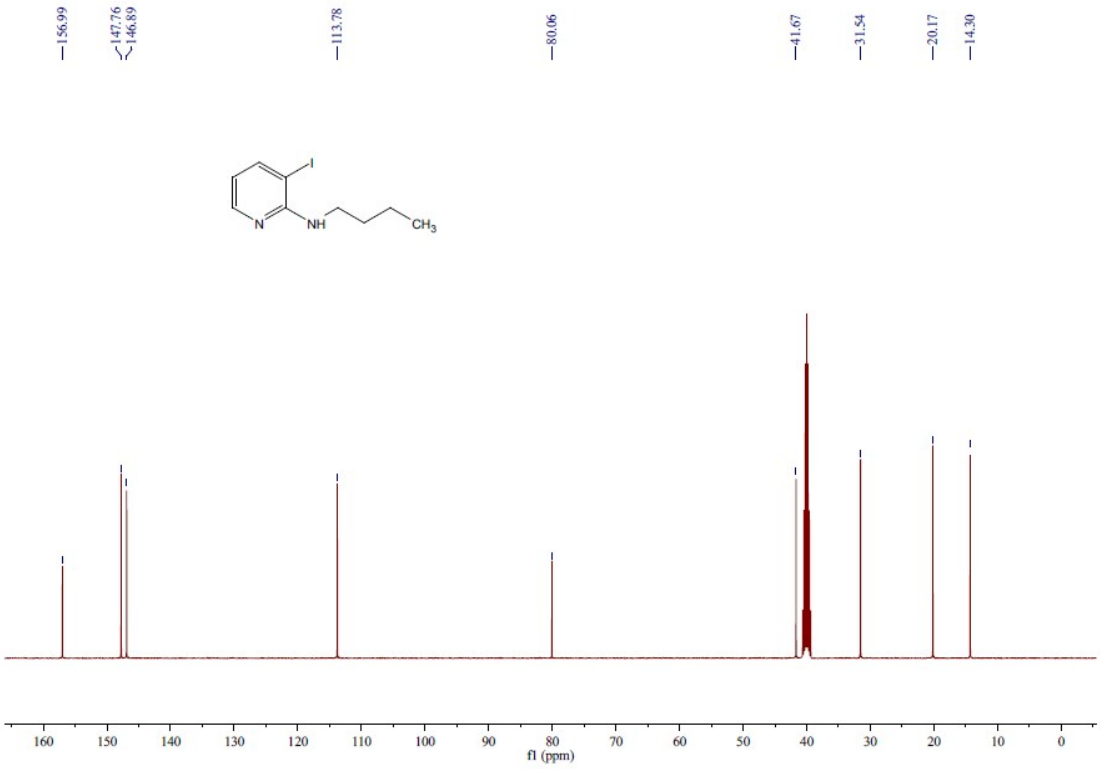
^{13}C NMR spectrum of compound **4b**



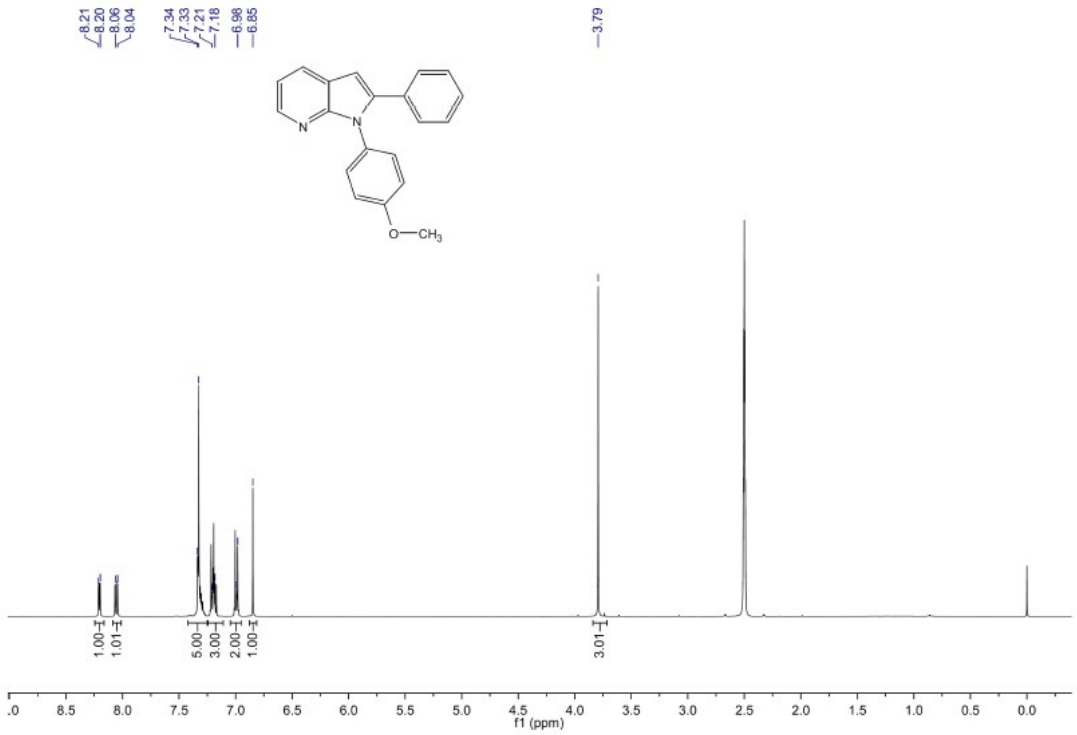
^{1}H NMR spectrum of compound **4c**



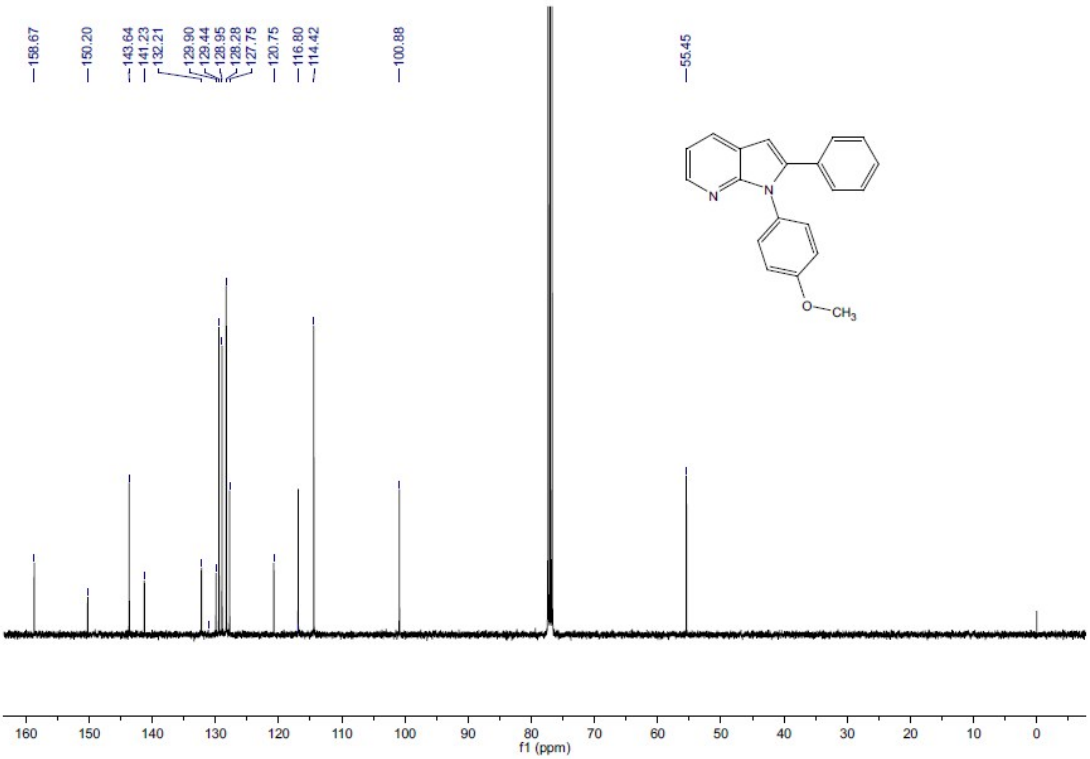
^{13}C NMR spectrum of compound **4c**



^{1}H NMR spectrum of compound **5a**



^{13}C NMR spectrum of compound **5a**



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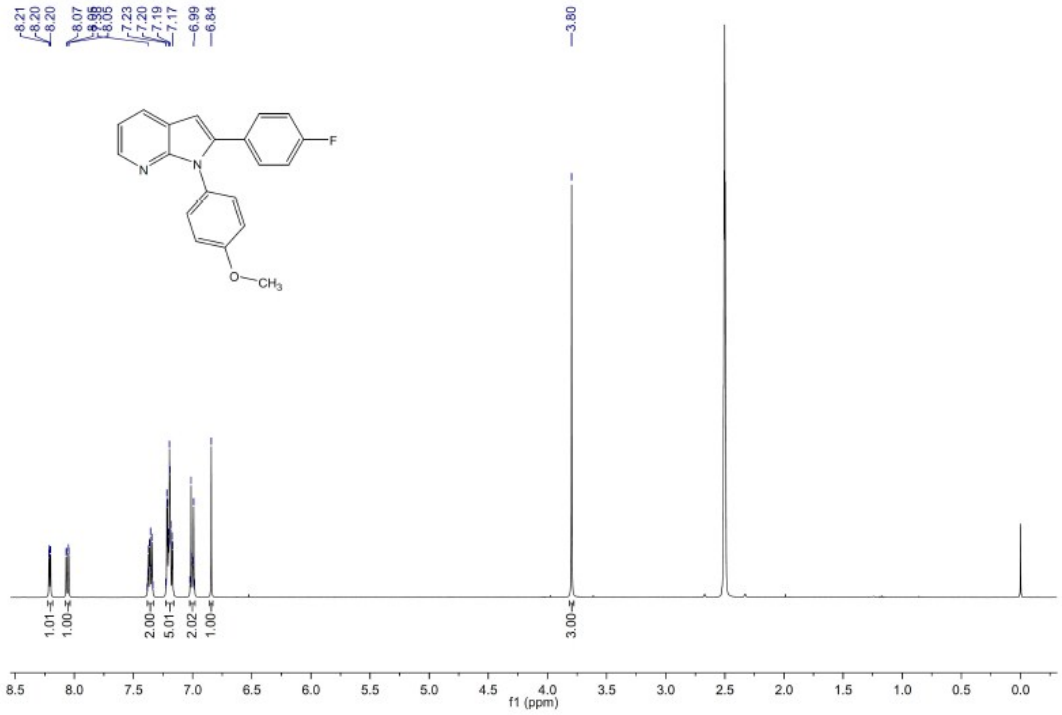
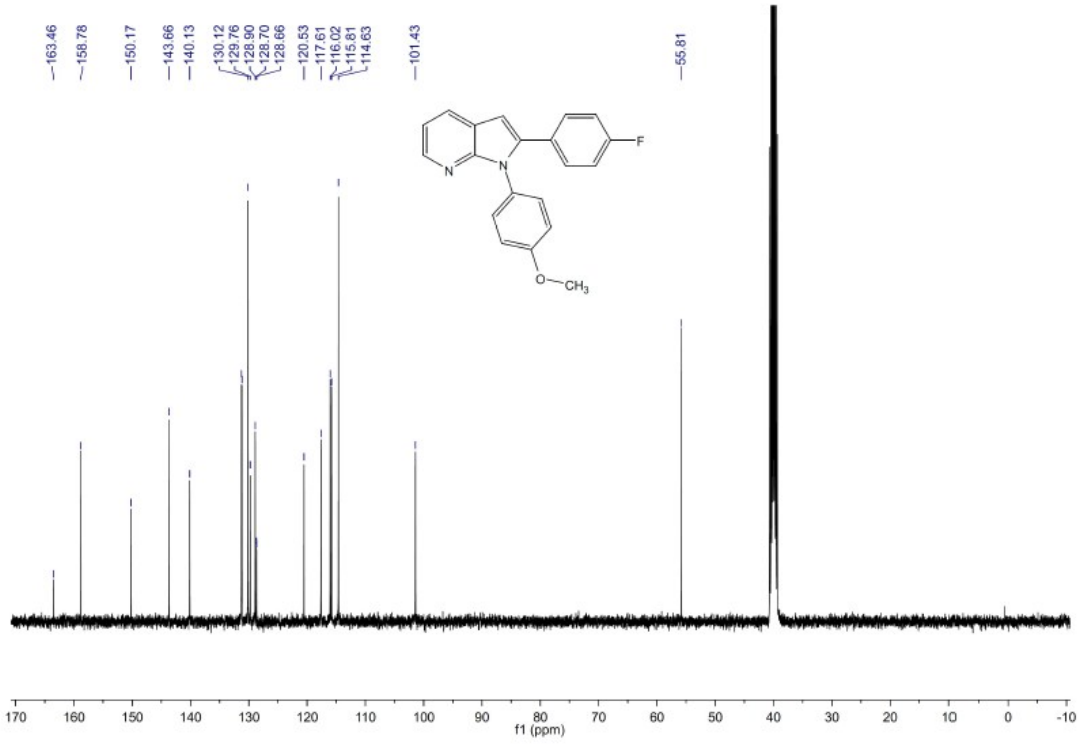
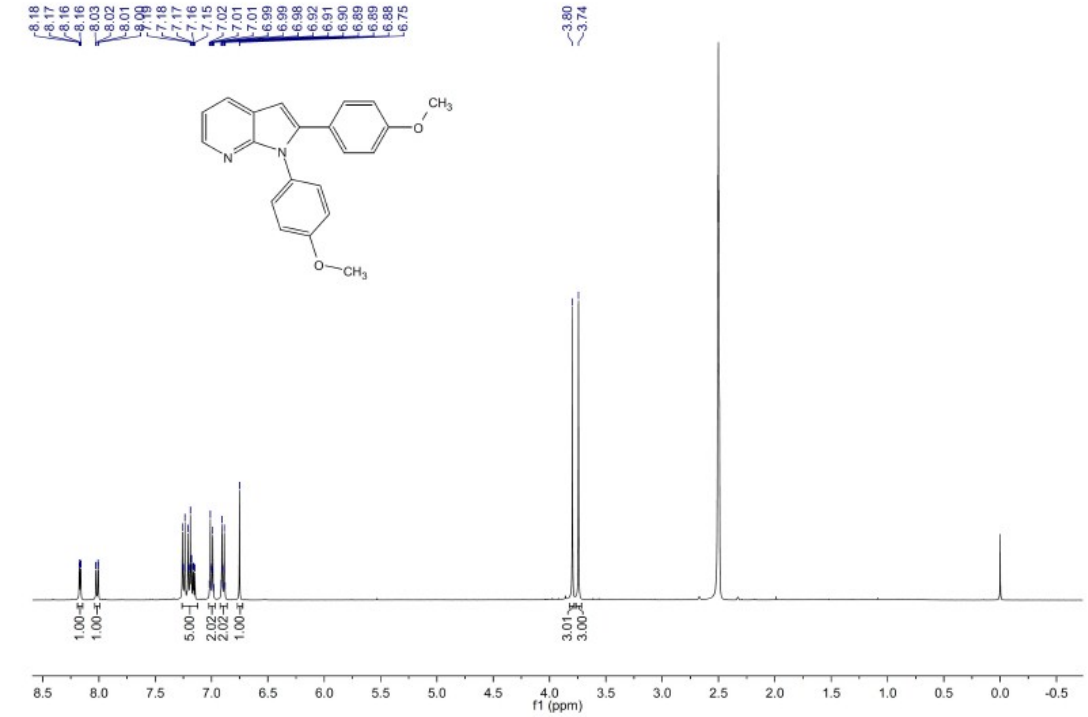


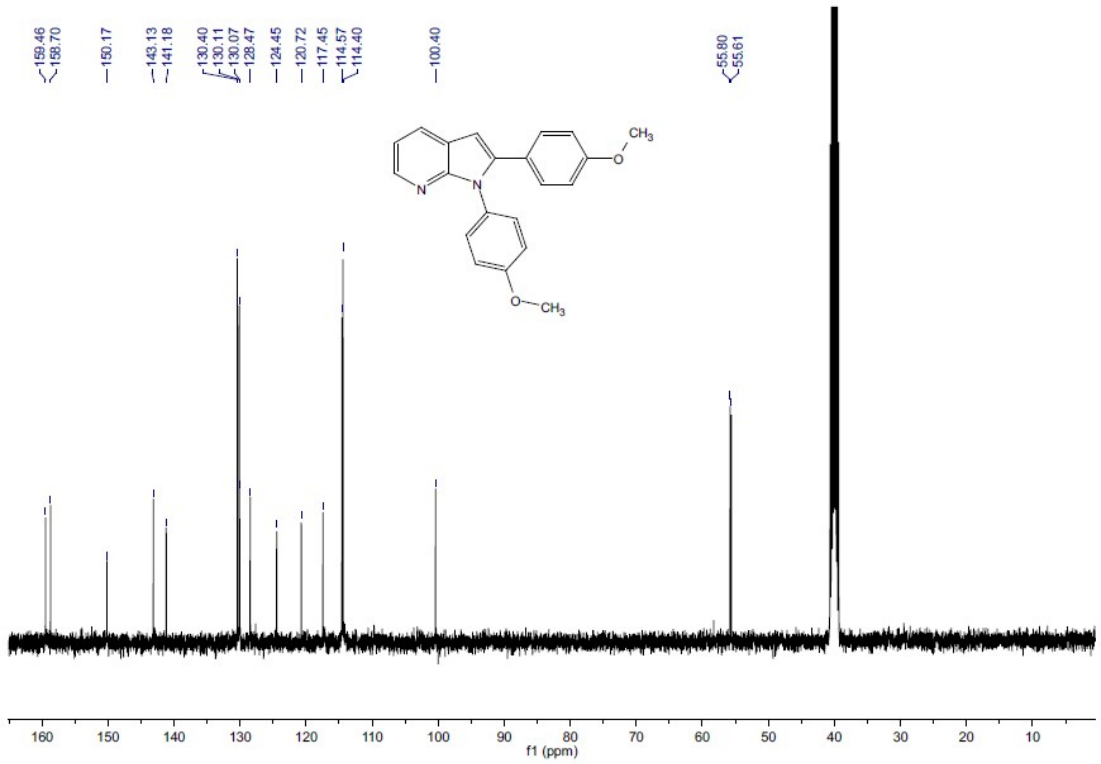
^{13}C NMR spectrum of compound **5b**



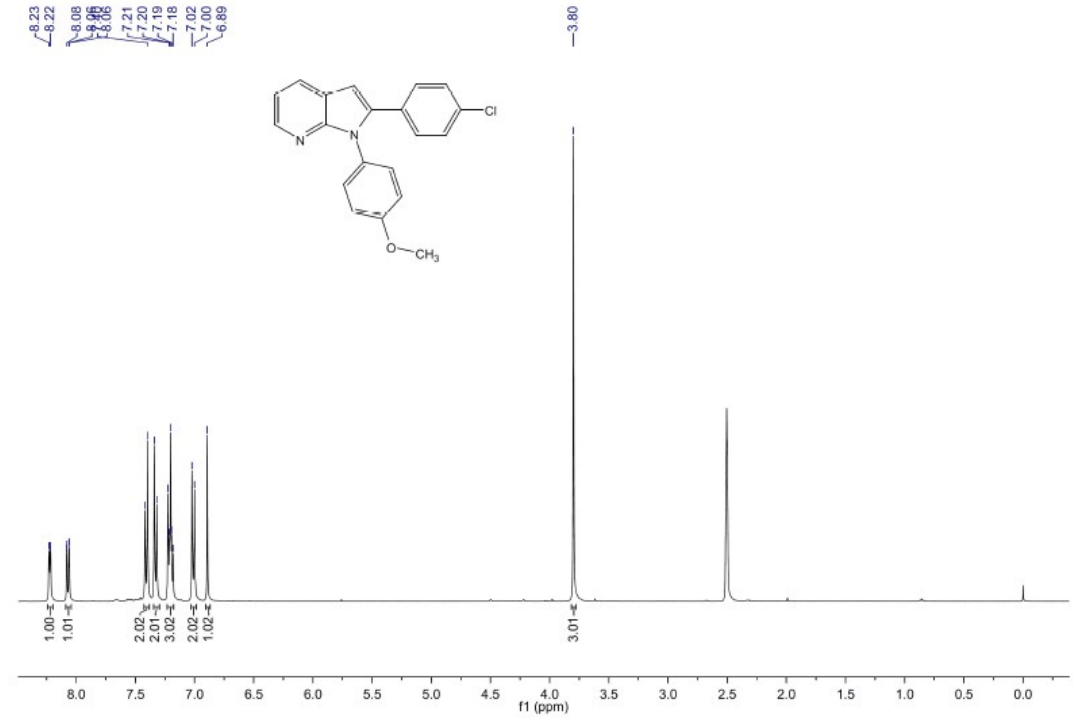
^{1}H NMR spectrum of compound **5c**



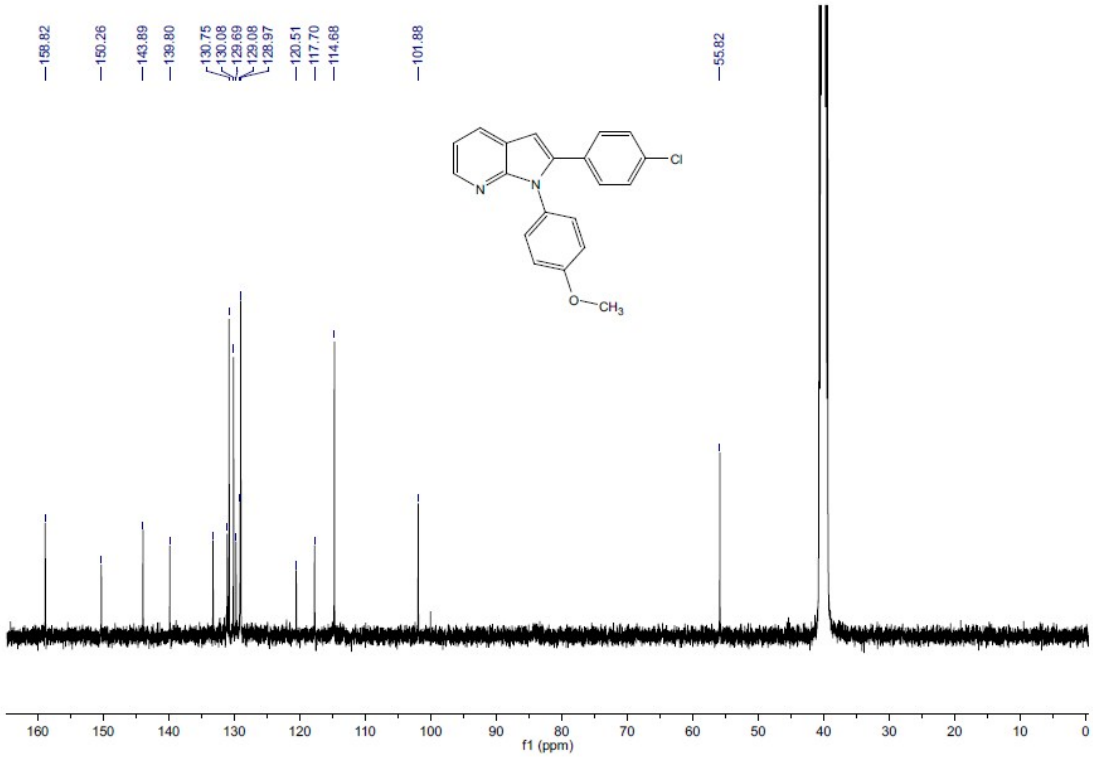
^{13}C NMR spectrum of compound **5c**



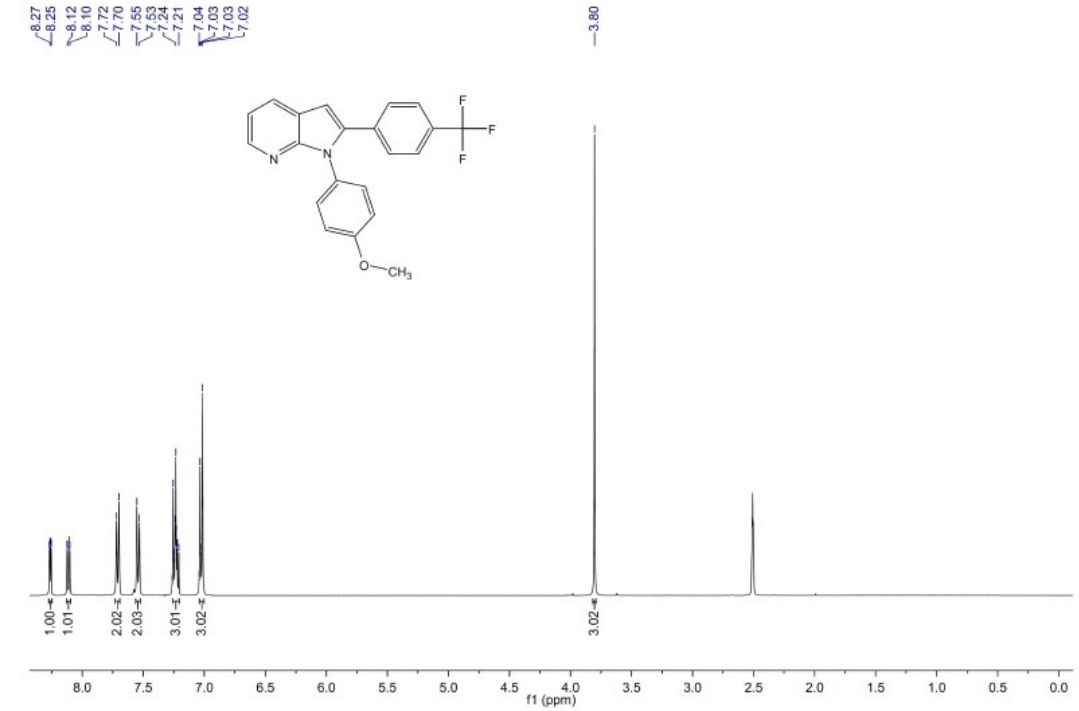
^{1}H NMR spectrum of compound **5d**



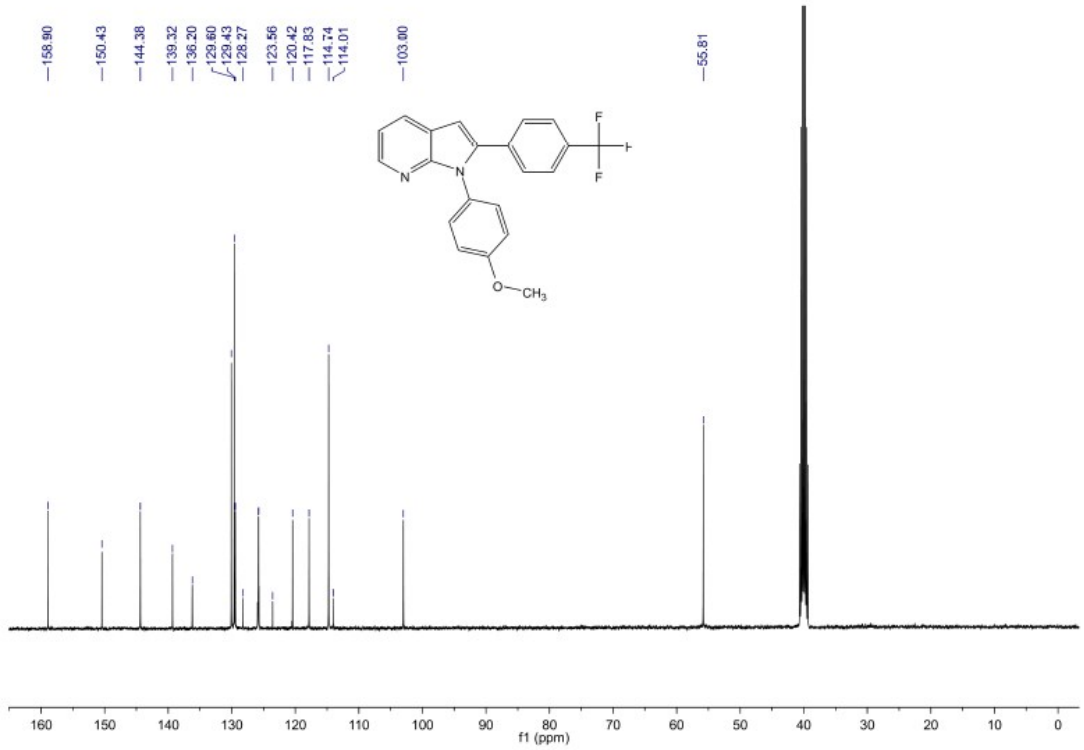
^{13}C NMR spectrum of compound **5d**



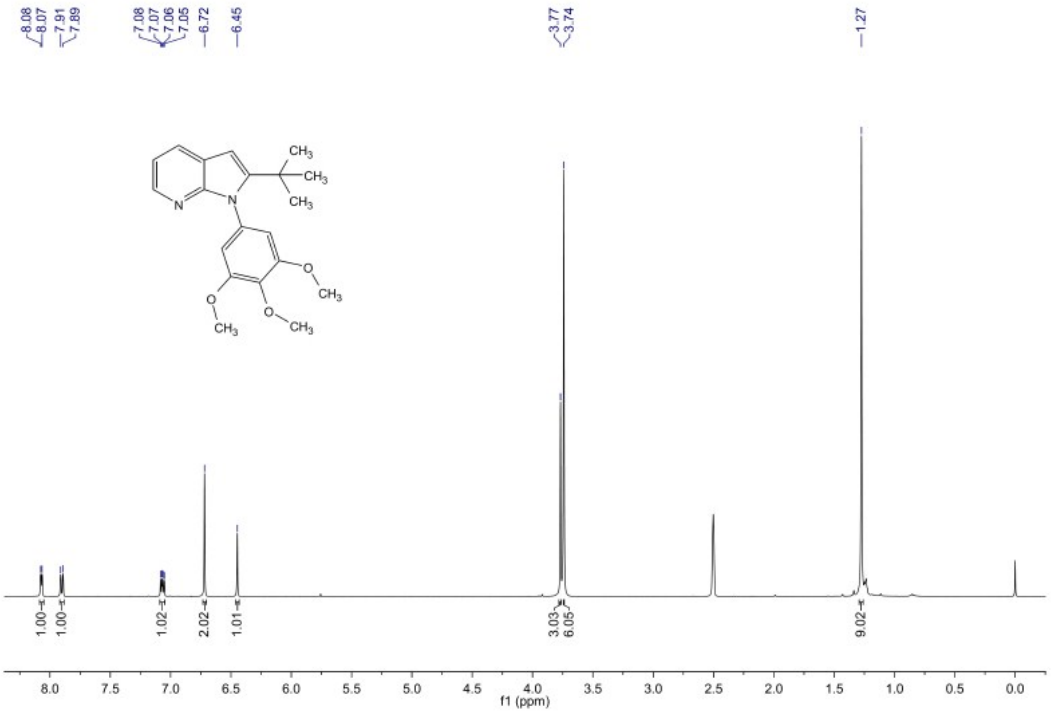
^{1}H NMR spectrum of compound **5e**



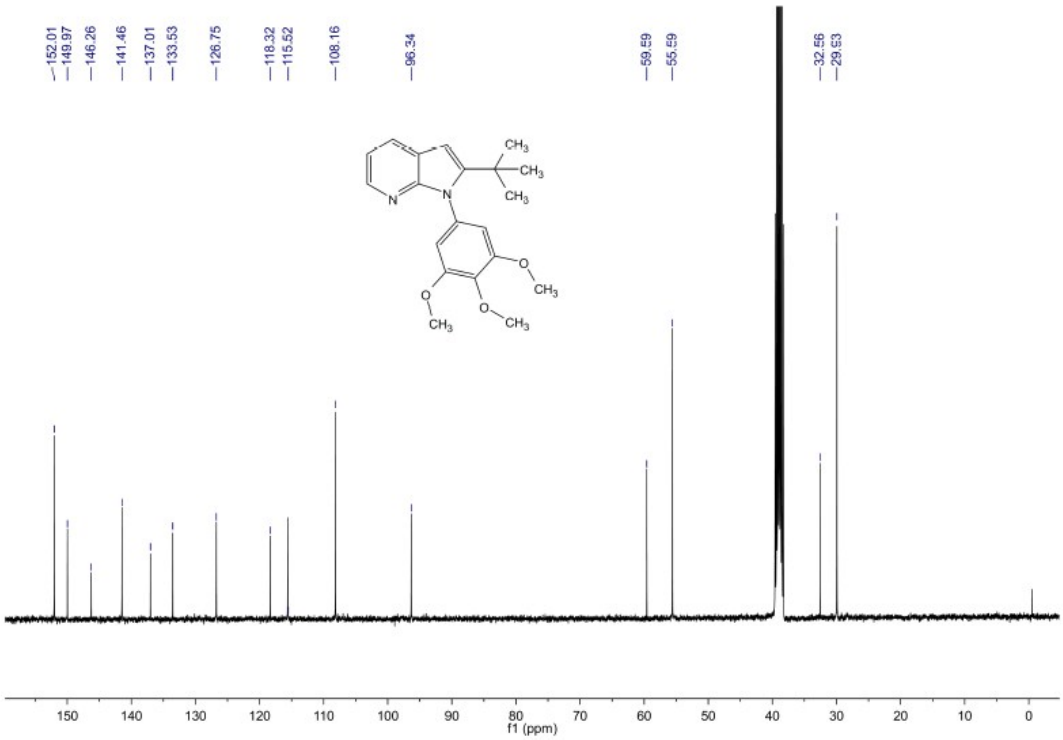
^{13}C NMR spectrum of compound **5e**



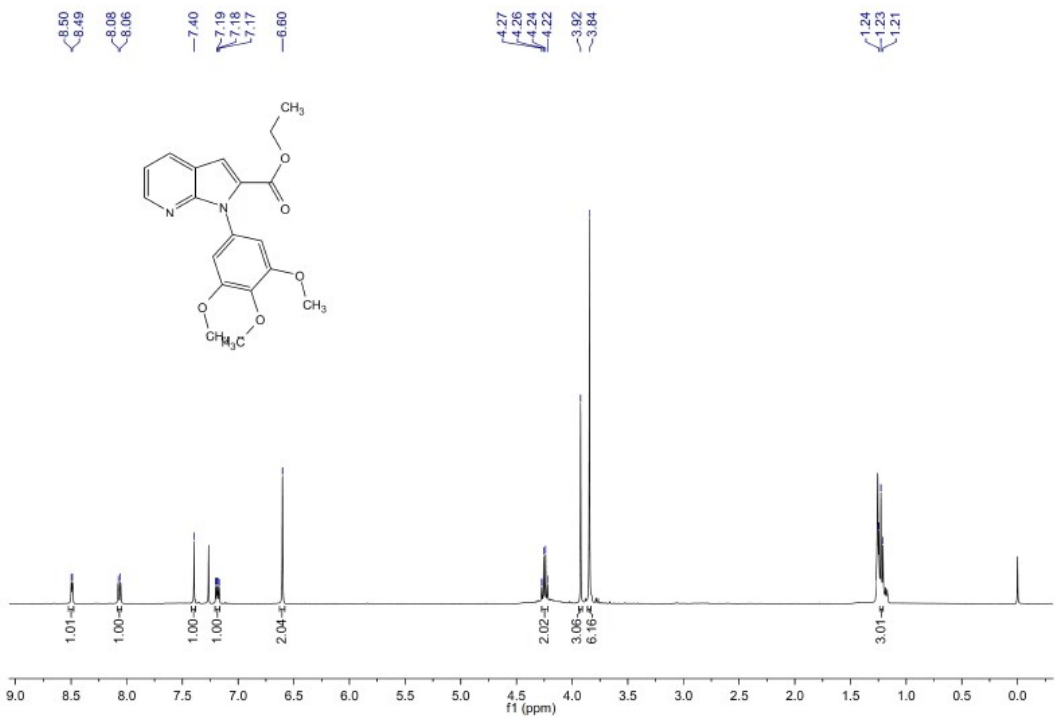
^{1}H NMR spectrum of compound **5f**



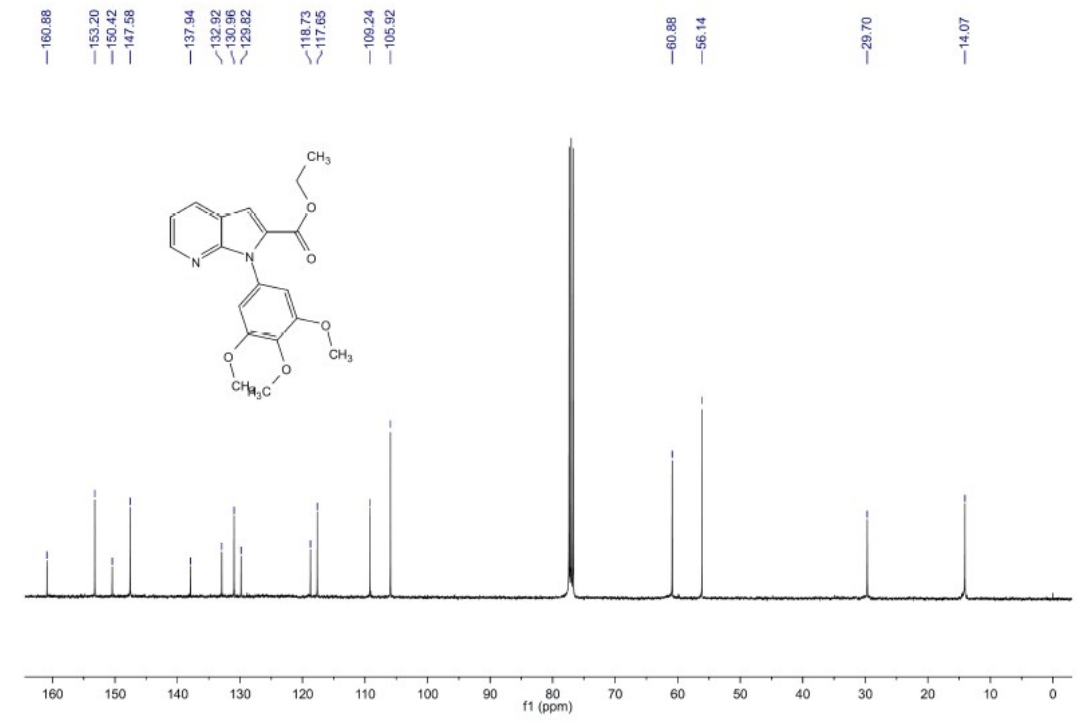
^{13}C NMR spectrum of compound **5f**



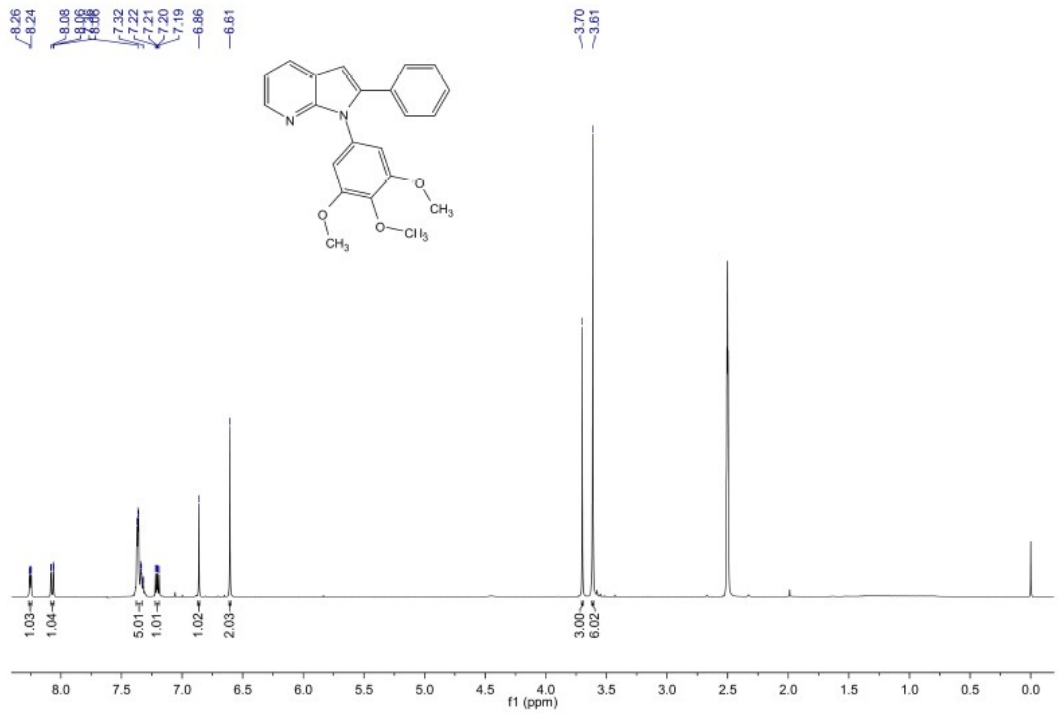
^{1}H NMR spectrum of compound **5g**



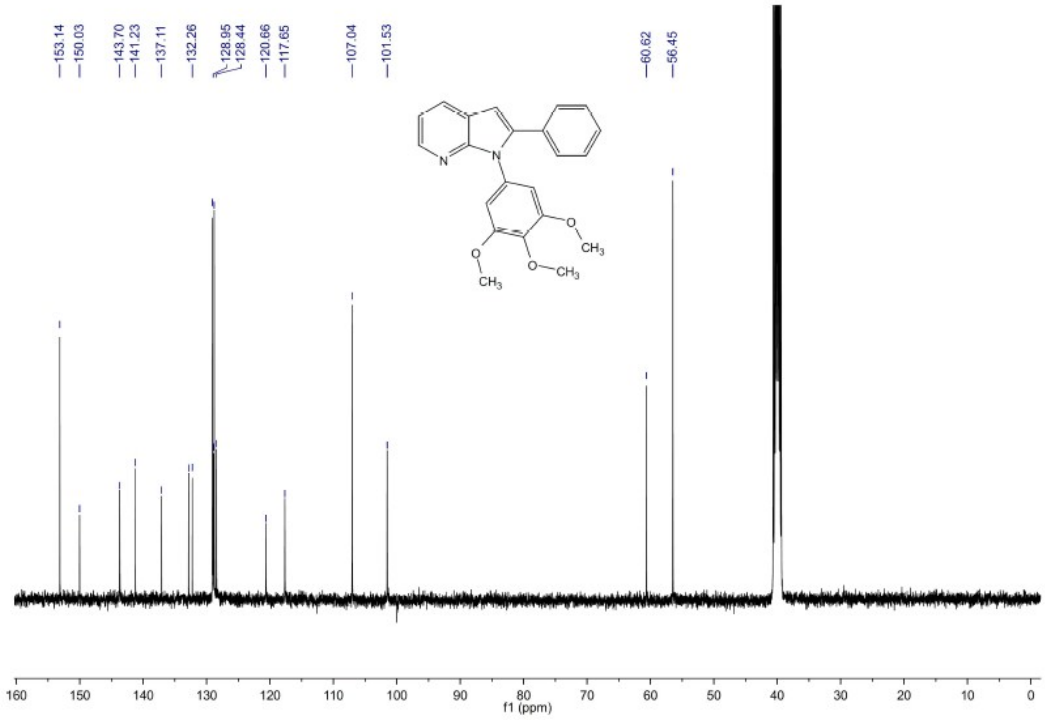
^{13}C NMR spectrum of compound **5g**



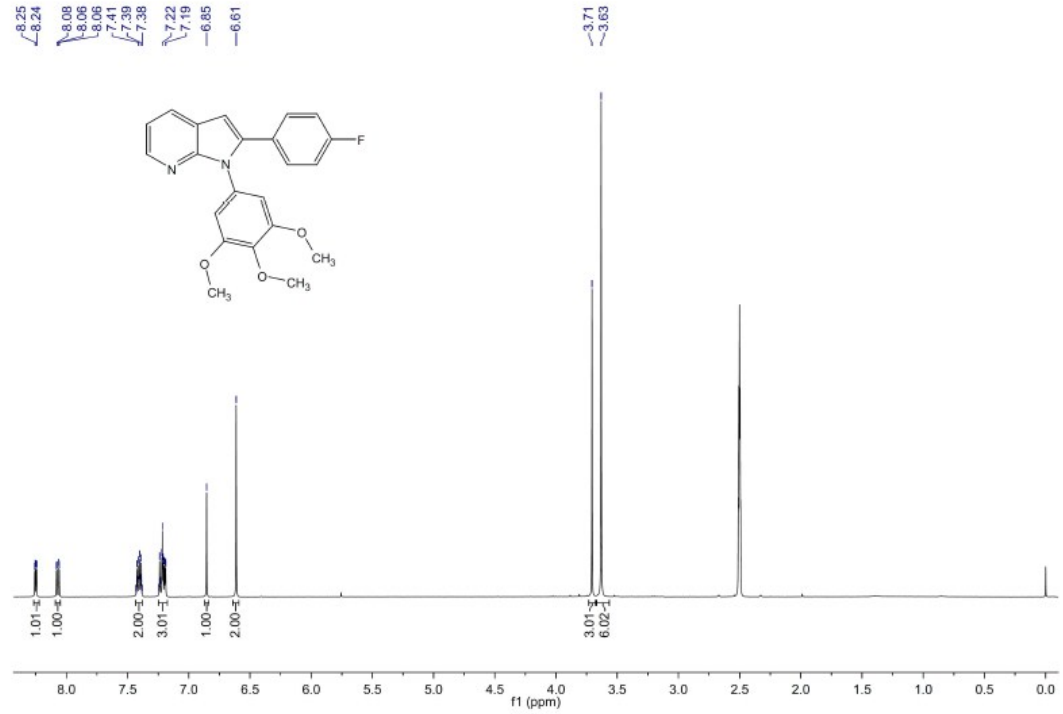
^{1}H NMR spectrum of compound **5h**



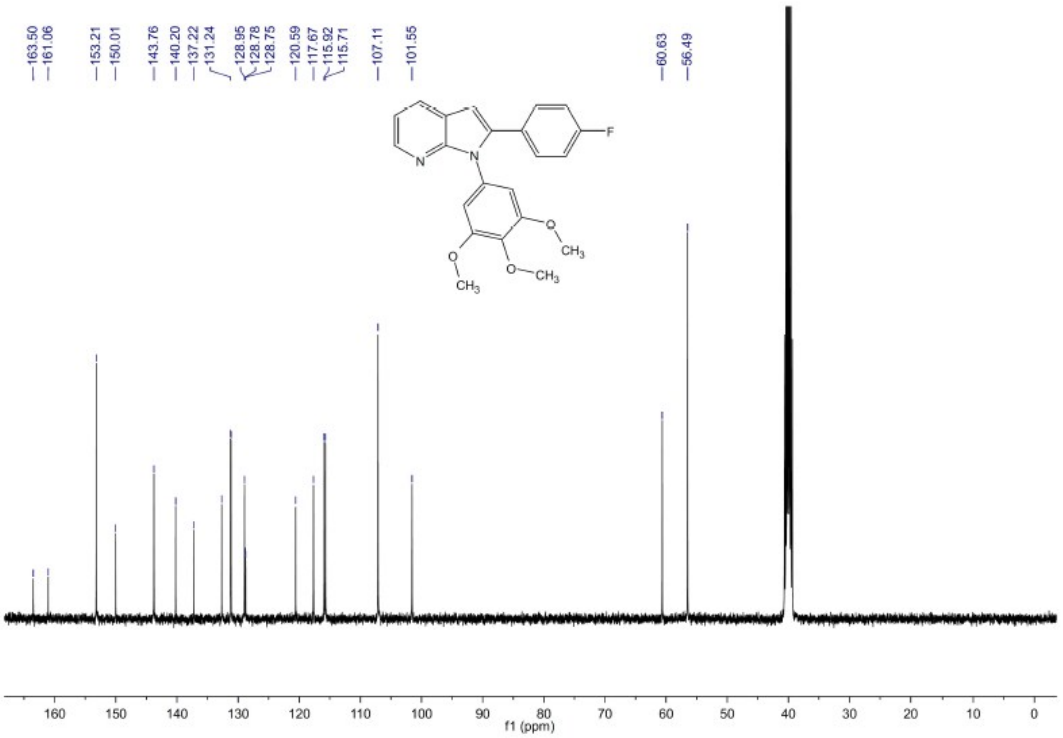
^{13}C NMR spectrum of compound **5h**



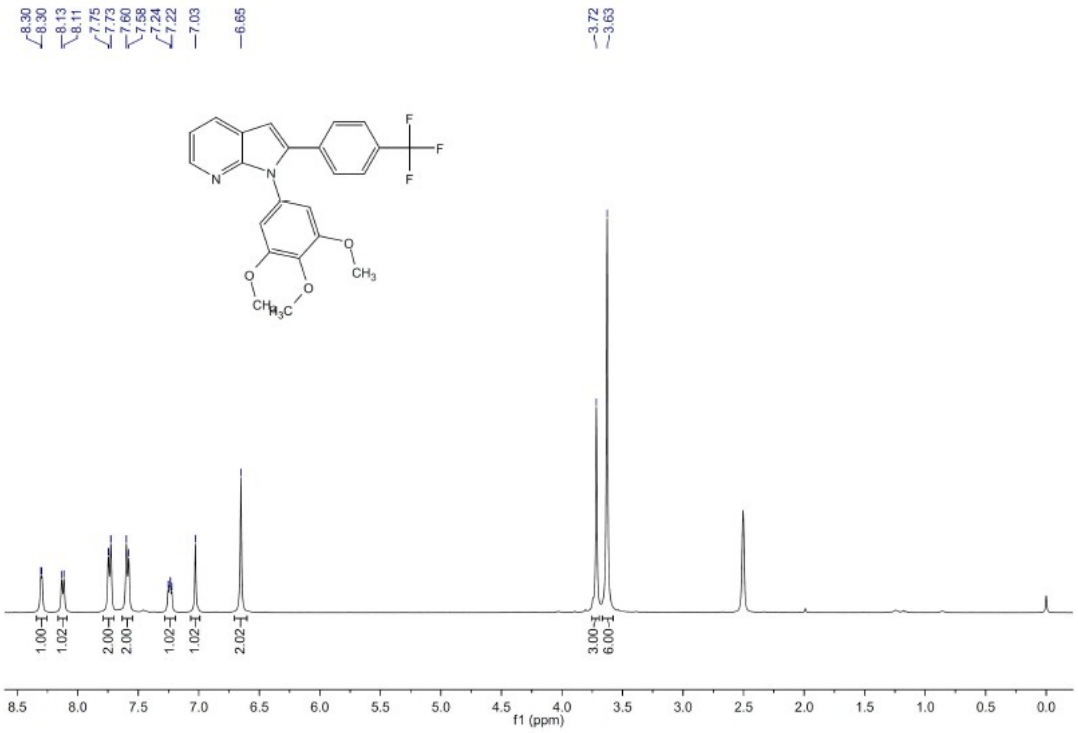
^{1}H NMR spectrum of compound **5i**



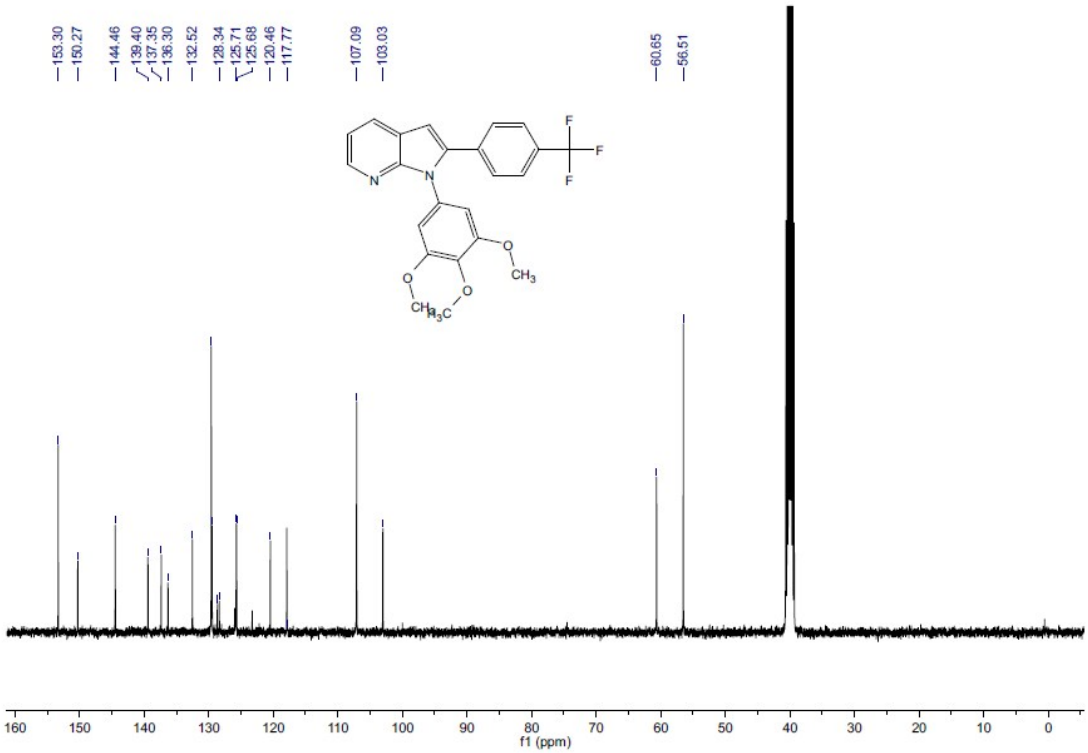
^{13}C NMR spectrum of compound **5i**



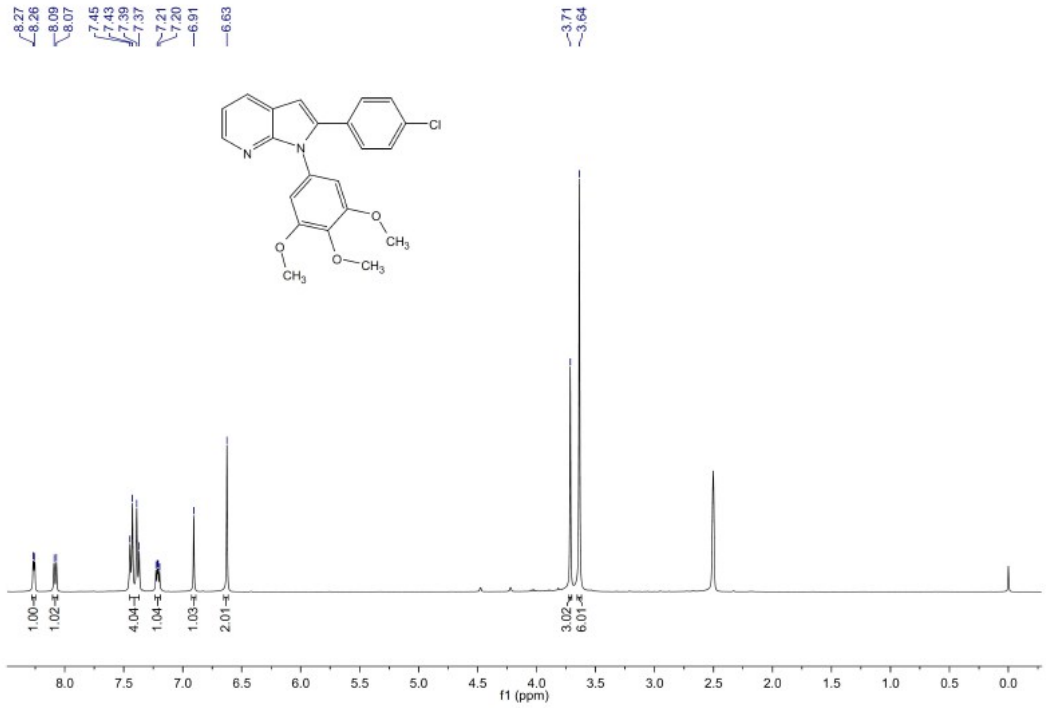
^{1}H NMR spectrum of compound **5j**



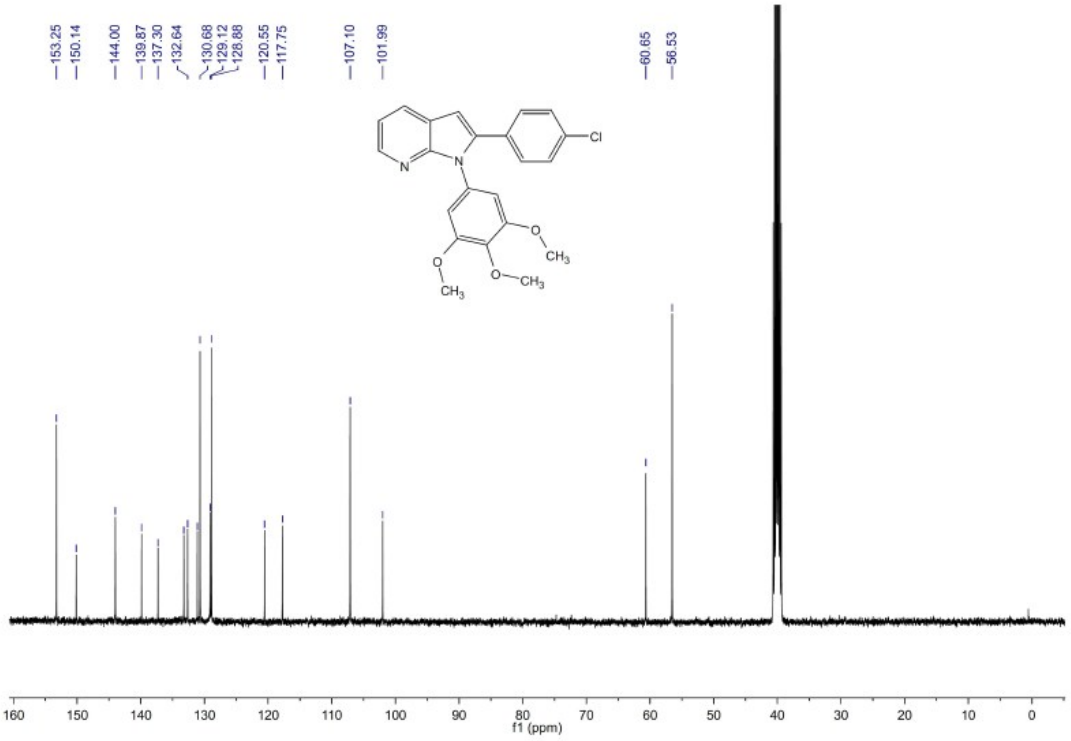
^{13}C NMR spectrum of compound **5j**



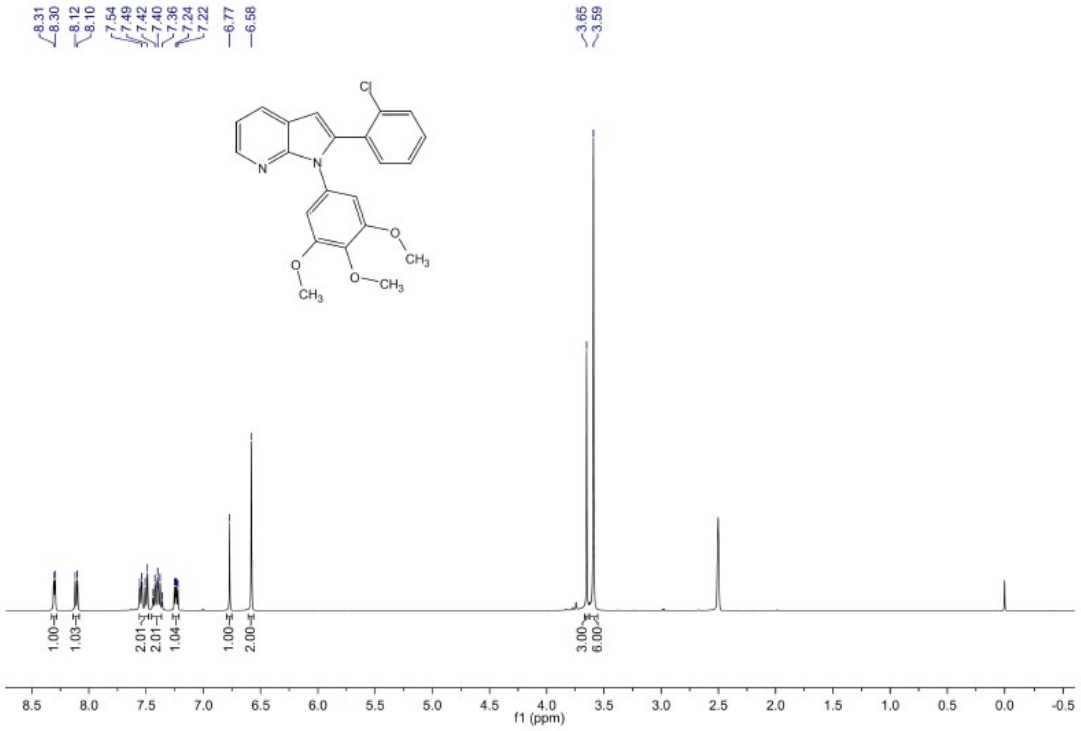
^{1}H NMR spectrum of compound **5k**



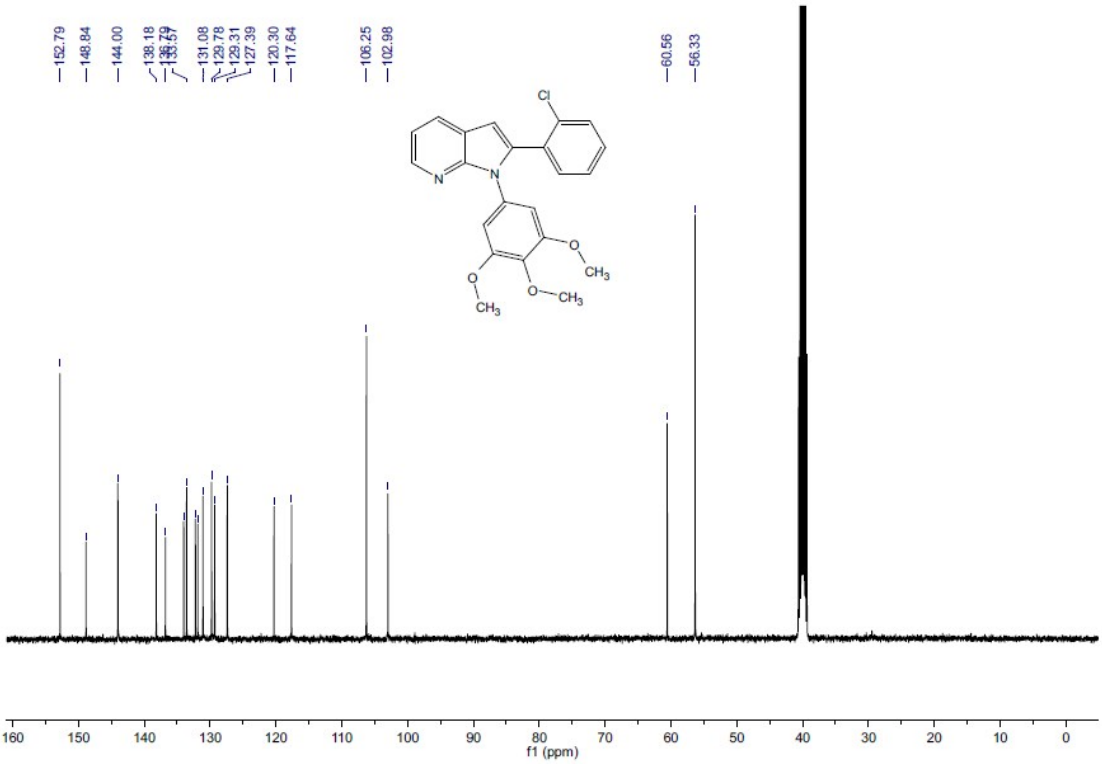
^{13}C NMR spectrum of compound **5k**



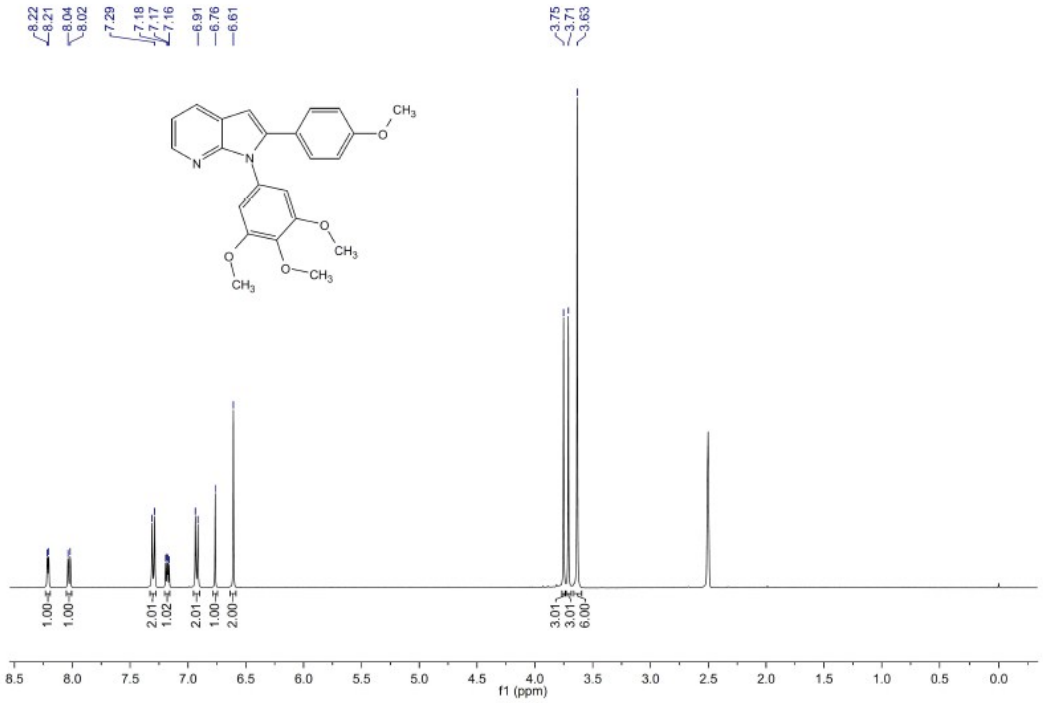
^{1}H NMR spectrum of compound **5l**



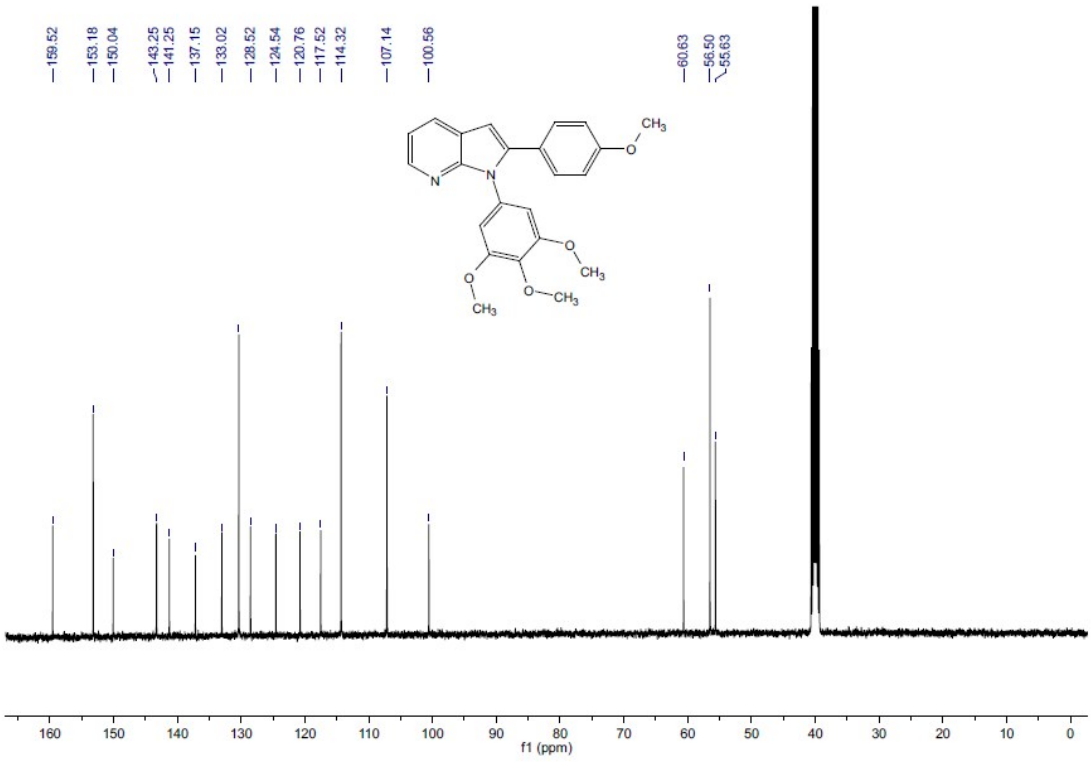
^{13}C NMR spectrum of compound **5l**



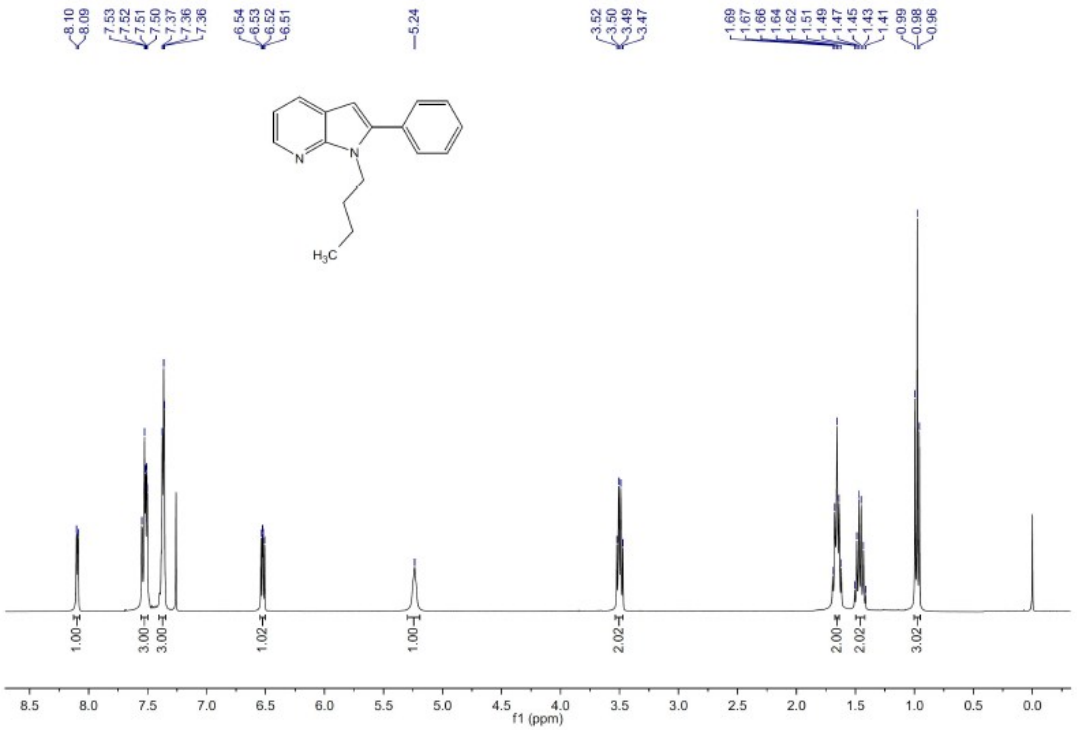
^{1}H NMR spectrum of compound **5m**



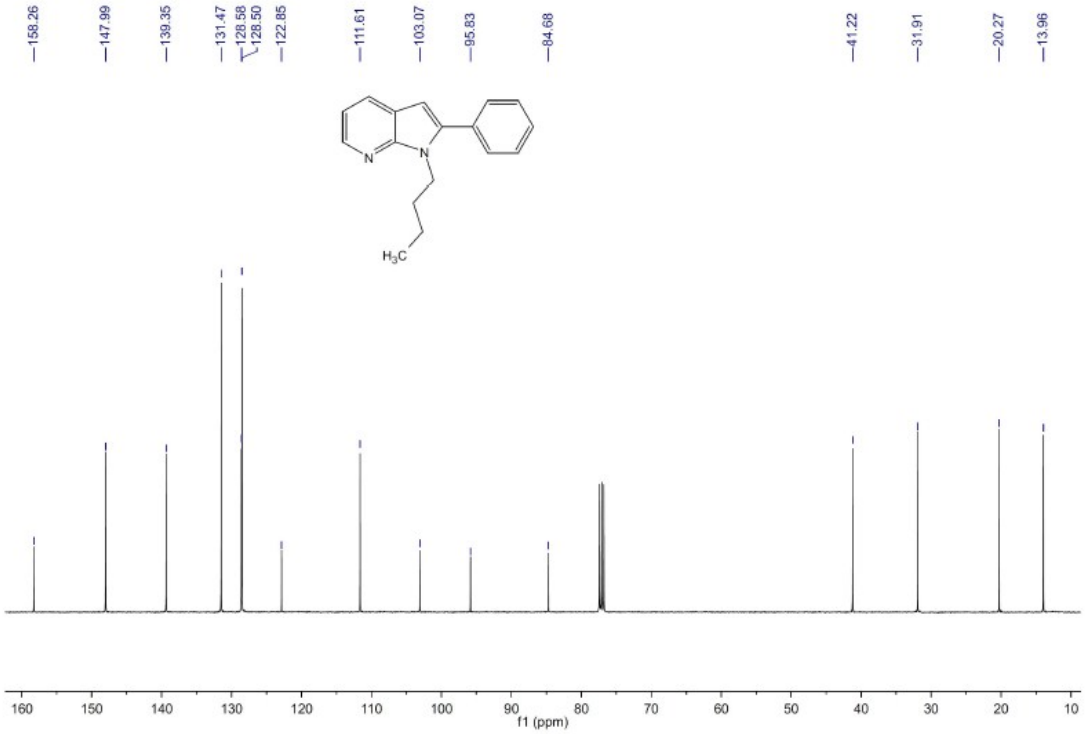
^{13}C NMR spectrum of compound **5m**



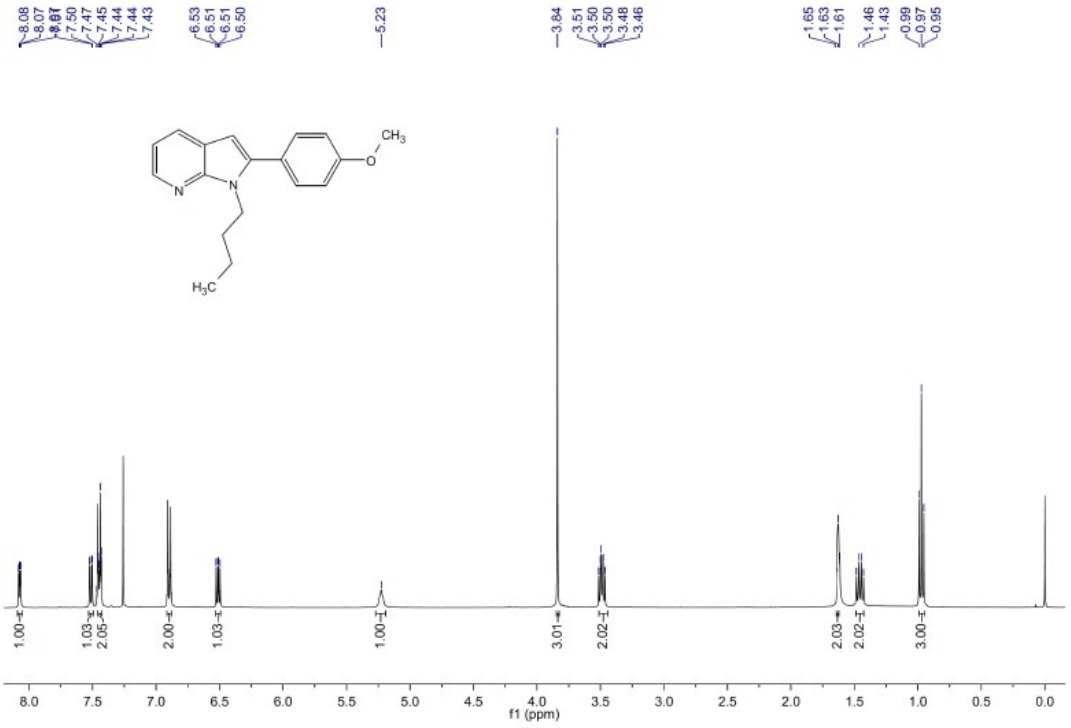
^{1}H NMR spectrum of compound **5n**



^{13}C NMR spectrum of compound **5n**



^{1}H NMR spectrum of compound **5o**



^{13}C NMR spectrum of compound **5o**