Supporting Information

Palladium-catalyzed denitrative *N*-arylation of nitroarenes with pyrroles, indoles, and carbazoles

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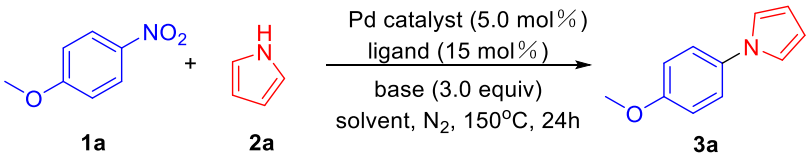
1. General Information

^{1}H NMR spectra were recorded on Bruker 500 or 600 MHz spectrometer and the chemical shifts were reported in parts per million (δ) relative to internal solvent signal (7.261 ppm in $CDCl_3$). The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet. The coupling constants, J, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained at Bruker 125 or 150 MHz and referenced to the internal solvent signals (central peak is 77.000 ppm in $CDCl_3$). $CDCl_3$ was used as the NMR solvent. APEX II (Bruker Inc.) was used for HR-MS and APCI-MS.

Unless otherwise noted, all reagents were purchased from commercial suppliers (Energy-Chemical, Bidepharm, Heowns, or TCI) and used without further purification. Flash column chromatography was performed over silica gel 200-300. The reagents were weighed and handled in a glove box. All reactions were heated by metal sand bath (WATTCAS, LAB-500, https://www.wattcas.com).

2. Optimization of the Reaction Conditions

Table S1. Optimization of the reaction conditions[a,b]



1a **2a** **3a**

entry	catalyst	ligand	base	solvent	**3a**/yield/%
1	$Ni(cod)_2$	BrettPhos	K_3PO_4	1,4-dioxane	n.d.
2	$NiBr_2$	BrettPhos	K_3PO_4	1,4-dioxane	n.d.
3	NiF_2	BrettPhos	K_3PO_4	1,4-dioxane	n.d.
4	$Ni(acac)_2$	BrettPhos	K_3PO_4	1,4-dioxane	n.d.
5	$NiCl_2$·dme	BrettPhos	K_3PO_4	1,4-dioxane	n.d.
6	$Cu(OAc)_2$	BrettPhos	K_3PO_4	1,4-dioxane	n.d.
7	$Co(acac)_3$	BrettPhos	K_3PO_4	1,4-dioxane	n.d.
8	$Pd(PPh_3)_4$	BrettPhos	K_3PO_4	1,4-dioxane	trace
9	$Pd_2(dba)_3$	BrettPhos	K_3PO_4	1,4-dioxane	27
10	$PdCl_2$	BrettPhos	K_3PO_4	1,4-dioxane	18
11	$PdCl_2$·dppf	BrettPhos	K_3PO_4	1,4-dioxane	<10
12	$Pd(OAc)_2$	BrettPhos	K_3PO_4	1,4-dioxane	trace
13	$Pd(P^tBu_3)_2$	BrettPhos	K_3PO_4	1,4-dioxane	trace
14	$[Pd(allyl)Cl]_2$	BrettPhos	K_3PO_4	1,4-dioxane	trace
15	$Pd(acac)_2$	BrettPhos	K_3PO_4	1,4-dioxane	37
16	$Pd(acac)_2$	XantPhos	K_3PO_4	1,4-dioxane	n.d.
17	$Pd(acac)_2$	NixantPhos	K_3PO_4	1,4-dioxane	n.d.
18	$Pd(acac)_2$	DPEPhos	K_3PO_4	1,4-dioxane	n.d.
19	$Pd(acac)_2$	DPPF	K_3PO_4	1,4-dioxane	n.d.
20	$Pd(acac)_2$	BINAP	K_3PO_4	1,4-dioxane	n.d.
21	$Pd(acac)_2$	P^tBu_3	K_3PO_4	1,4-dioxane	n.d.

22	$Pd(acac)_2$	JohnPhos	K_3PO_4	1,4-dioxane	n.d.
23	$Pd(acac)_2$	^{t}BuXPhos	K_3PO_4	1,4-dioxane	n.d.
24	$Pd(acac)_2$	^{t}BuBrettPhos	K_3PO_4	1,4-dioxane	trace
25	$Pd(acac)_2$	Me_4-^{t}BuXPhos	K_3PO_4	1,4-dioxane	n.d.
26	$Pd(acac)_2$	DavePhos	K_3PO_4	1,4-dioxane	n.d.
27	$Pd(acac)_2$	XPhos	K_3PO_4	1,4-dioxane	n.d.
28	$Pd(acac)_2$	SPhos	K_3PO_4	1,4-dioxane	n.d.
29	$Pd(acac)_2$	RuPhos	K_3PO_4	1,4-dioxane	trace
30	$Pd(acac)_2$	BrettPhos	K_3PO_4 $3H_2O$	1,4-dioxane	18
31	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	1,4-dioxane	n.d.
32	$Pd(acac)_2$	BrettPhos	NaOH	1,4-dioxane	n.d.
33	$Pd(acac)_2$	BrettPhos	^{t}BuOLi	1,4-dioxane	n.d.
34	$Pd(acac)_2$	BrettPhos	^{t}BuOK	1,4-dioxane	n.d.
35	$Pd(acac)_2$	BrettPhos	KF	1,4-dioxane	n.d.
36	$Pd(acac)_2$	BrettPhos	K_2CO_3	1,4-dioxane	25
37	$Pd(acac)_2$	BrettPhos	DBU	1,4-dioxane	trace
38	$Pd(acac)_2$	BrettPhos	TMG	1,4-dioxane	trace
39	$Pd(acac)_2$	BrettPhos	K_3PO_4	*n*-heptane	<10
40	$Pd(acac)_2$	BrettPhos	K_3PO_4	$PhCF_3$	trace
41	$Pd(acac)_2$	BrettPhos	K_3PO_4	*o*-xylene	31
42	$Pd(acac)_2$	BrettPhos	K_3PO_4	*m*-xylene	<10
43	$Pd(acac)_2$	BrettPhos	K_3PO_4	*p*-xylene	36
44	$Pd(acac)_2$	BrettPhos	K_3PO_4	toluene	16
45	$Pd(acac)_2$	BrettPhos	K_3PO_4	pyridine	n.d.
46	$Pd(acac)_2$	BrettPhos	K_3PO_4	NMP	n.d.
47	$Pd(acac)_2$	BrettPhos	K_3PO_4	DMF	n.d.
48	$Pd(acac)_2$	BrettPhos	K_3PO_4	1,4-dioxane	45[c]
49	$Pd(acac)_2$	BrettPhos	K_3PO_4	1,4-dioxane	65[d]
50	$Pd(acac)_2$	BrettPhos	K_3PO_4	1,4-dioxane	69[e]
51	$Pd(acac)_2$	BrettPhos	K_3PO_4	1,4-dioxane	95[f]
52	-	BrettPhos	K_3PO_4	1,4-dioxane	n.d.
53	$Pd(acac)_2$	-	K_3PO_4	1,4-dioxane	n.d.
54	$Pd(acac)_2$	BrettPhos	-	1,4-dioxane	n.d.

[a] Reaction conditions: 4-nitroanisole **1a** (0.30 mmol), pyrrole **2a** (0.60 mmol), catalyst (5.0 mol%), ligand (15 mol%) and base (3.0 equiv) in solvent (3.0 mL) at 150 °C for 24 hr under N_2; [b] The yields of **3a** were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard; [c] solvent (2.0 mL); [d] $Pd(acac)_2$ (10 mol%), BrettPhos (20 mol%); [e] 4-nitroanisole **1a** (0.60 mmol), pyrrole **2a** (0.30 mmol); [f] 4-nitroanisole **1a** (0.60 mmol), pyrrole **2a** (0.30 mmol), $Pd(acac)_2$ (10 mol%), BrettPhos (20 mol%) and solvent (2.0 mL).

3. General Procedure for *N*-Arylation Product 3 or 4

In a glovebox, a sealed tube (35 mL) equipped with a magnetic stir bar was charged with $Pd(acac)_2$ (9.2 mg, 10 mol%), BrettPhos (32 mg, 20 mol%), nitroarenes **1** (0.60 mmol), N–H

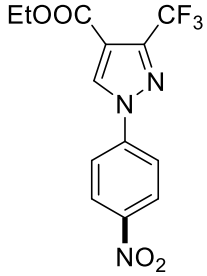
heteroarenes **2** (0.30 mmol), K_3PO_4 (191.0 mg, 0.90 mmol) and 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 150 °C for 24 hours. After the mixture was cooled to room temperature, the resulting solution was directly filtered through a pad of silica by EtOAc (10 mL). The solvent was evaporated in vacuo to give the crude products. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired product **3** or **4**.

4. Procedure for 1 mmol Scale Reaction of 1a with Indole

In a glovebox, a sealed tube (35 mL) equipped with a magnetic stir bar was charged with 4-nitroanisole **1a** (306.3 mg, 2.0 mmol), $Pd(acac)_2$ (30.5 mg, 0.10 mmol), BrettPhos (107.4 mg, 0.20 mmol), K_3PO_4 (636.8 mg, 3.0 mmol), indole (117.2 mg, 1.0 mmol). Then 1,4-dioxane (6.7 mL) was added and the mixture stirred at 150 °C for 24 hours. After the reaction cooled to room temperature, the resulting solution was directly filtered through a pad of silica by EtOAc. Concentration in vacuo followed by silica gel column purification gave the desired product **4a** in 95% yield (212.7 mg)

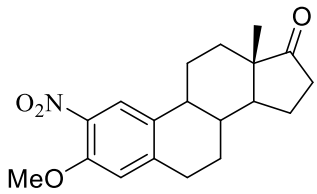
5. Characterization Data of Starting Materials and Products

ethyl 1-(4-nitrophenyl)-3-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate (5a)



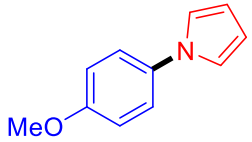
The title compound was prepared according to previously reported literature procedure[1]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.41-8.35 (m, 2H), 8.16 (s, 1H), 7.68-7.62 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.5, 148.2, 143.9, 143.2, 132.7 (q, J_{C-F} = 40.6 Hz), 126.8 (d, J_{C-F} = 0.9 Hz), 124.6, 118.9 (q, J_{C-F} = 272.2 Hz), 117.9 (d, J_{C-F} = 1.3 Hz), 61.6, 14.0; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -54.95.

(13S)-3-methoxy-13-methyl-2-nitro-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (6a)



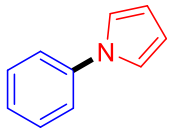
The title compound was prepared according to previously reported literature procedure[1]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (s, 1H), 6.76 (s, 1H), 3.88 (s, 3H), 3.00-2.84 (m, 2H), 2.48 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.35 (dd, *J* = 17.0, 3.6 Hz, 1H), 2.21 (td, *J* = 10.8, 4.0 Hz, 1H), 2.10 (dd, *J* = 18.9, 9.0 Hz, 1H), 2.06-1.99 (m, 2H), 1.97-1.90 (m, 1H), 1.64-1.40 (m, 6H), 0.88 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.0, 144.4, 137.1, 132.3, 122.9, 113.5, 56.3, 50.1, 47.7, 43.3, 37.7, 35.6, 31.2, 29.6, 25.9, 25.6, 21.4, 13.7.

1-(4-methoxyphenyl)-1*H*-pyrrole (3a)



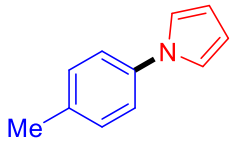
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 100:1) as a white crystal in 88 % (46.0 mg) yield; The spectral data were in accordance with those reported in the literature[2]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.9 Hz, 2H), 7.03 (t, *J* = 2.0 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.36 (t, *J* = 2.0 Hz, 2H), 3.85 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.6, 134.4, 122.1, 119.6, 114.6, 109.8, 55.5; **FT-IR** (KBr) ν/cm^{-1}: 3141, 2961, 2936, 2838, 1635, 1519, 1307, 1260, 1245, 1030, 827, 721, 610, 526.

1-phenyl-1*H*-pyrrole (3b)



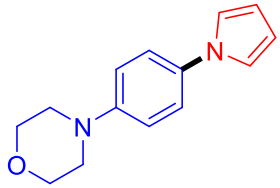
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 200:1) as a light brown solid in 71 % (30.5 mg) yield; The spectral data were in accordance with those reported in the literature[3]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48-7.37 (m, 4H), 7.30-7.22 (m, 1H), 7.11 (t, *J* = 2.2 Hz, 2H), 6.37 (t, *J* = 2.2 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.7, 129.5, 125.6, 120.5, 119.3, 110.4. The **FT-IR** data refers the literature[2].

1-(*p*-tolyl)-1*H*-pyrrole (3c)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE) as a white crystal in 75 % (35.3 mg) yield; The spectral data were in accordance with those reported in the literature[2]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.31-7.25 (m, 2H), 7.13 (dd, *J* = 3.7, 1.9 Hz, 2H), 6.42 (dd, *J* = 3.8, 1.9 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.4, 135.3, 130.0, 120.4, 119.3, 110.0, 20.8; **FT-IR** (KBr) ν/cm^{-1}: 3141, 3105, 2921, 2855, 1612, 1525, 1479, 1400, 1379, 1326 , 1126, 813, 717, 611, 515.

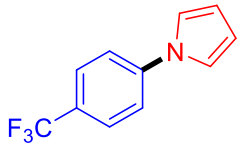
4-(4-(1*H*-pyrrol-1-yl) phenyl) morpholine (3d)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 10:1) as a light yellow solid in 77 % (52.7 mg) yield; The spectral data were in accordance with those reported in the literature[13]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37-7.28 (m, 2H), 7.04 (t, *J* = 2.2

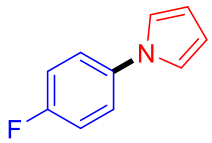
Hz, 2H), 7.00-6.93 (m, 2H), 6.35 (t, *J* = 2.2 Hz, 2H), 3.93-3.87 (m, 4H), 3.18 (dd, *J* = 5.7, 4.0 Hz, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.3, 133.7, 121.7, 119.4, 116.4, 109.7, 66.8, 49.4; **FT-IR** (KBr) ν/cm^{-1}: 3134, 3104, 3050, 2965, 2913, 2895, 2860, 2837, 1523, 1322, 1237, 1124, 1072, 923, 822, 728, 665.

1-(4-(trifluoromethyl) phenyl)-1*H*-pyrrole (3e)



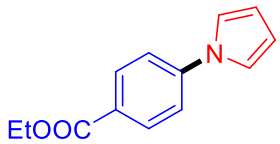
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 200:1) as a white crystal in 76 % (48.1 mg) yield; The spectral data were in accordance with those reported in the literature[4]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.15 (t, *J* = 2.1 Hz, 2H), 6.46-6.38 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.2, 127.4 (q, $J_{C\text{-}F}$ = 32.8 Hz), 126.8 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.0 (q, $J_{C\text{-}F}$ = 270.1 Hz), 119.9, 119.0, 111.5; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.21; **FT-IR** (KBr) ν/cm^{-1}: 3145, 3086, 1620, 1530, 1475, 1432, 1326, 1116, 1063, 834, 723, 607, 473.

1-(4-fluorophenyl)-1*H*-pyrrole (3f)



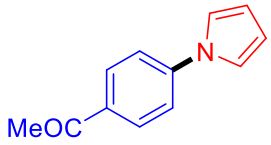
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 200:1) as a light yellow solid in 45 % (21.7 mg) yield; The spectral data were in accordance with those reported in the literature[5]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41-7.31 (m, 2H), 7.18-7.08 (m, 2H), 7.03 (t, *J* = 1.9 Hz, 2H), 6.36 (dd, *J* = 2.9, 1.3 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.6 (d, $J_{C\text{-}F}$ = 243.4 Hz), 137.1 (d, $J_{C\text{-}F}$ = 2.8 Hz), 122..2 (d, $J_{C\text{-}F}$ = 8.3 Hz), 119.6, 116.2 (d, $J_{C\text{-}F}$ = 22.6 Hz), 110.4; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -117.16; **FT-IR** (KBr) ν/cm^{-1}: 3139, 3108, 1621, 1518, 1341 1331, 1234, 1116 , 1072, 836, 725, 607, 527.

ethyl 4-(1*H*-pyrrol-1-yl) benzoate (3g)



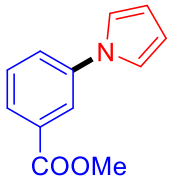
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 60:1) as a light yellow crystal in 74 % (47.8 mg) yield; The spectral data were in accordance with those reported in the literature[6]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18-8.03 (m, 2H), 7.53-7.36 (m, 2H), 7.22-7.09 (m, 2H), 6.48-6.29 (m, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.9, 143.9, 131.2, 127.2, 119.2, 119.0, 111.4, 61.0, 14.3; **FT-IR** (KBr) ν/cm^{-1}: 3141, 3105, 3080, 2981, 2904, 2873, 1716, 1609, 1521, 1478, 1333, 1278, 1183, 1067, 922, 852, 770, 696, 610, 512.

1-(4-(1*H*-pyrrol-1-yl) phenyl) ethan-1-one (3h)



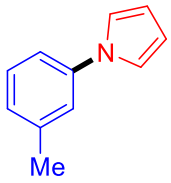
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 20:1→16:1) as a yellow solid in 20 % (11.1 mg) yield; The spectral data were in accordance with those reported in the literature[5]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.19-7.15 (m, 2H), 6.42-6.37 (m, 2H), 2.61 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.7, 144.0, 133.93, 130.1, 119.3, 118.9, 111.6, 26.5; **FT-IR** (KBr) ν/cm^{-1}: 3141, 3105, 3062, 2960, 2923, 2855, 1682, 1522, 1472, 1361, 1278, 1198, 1077, 919, 823, 736, 615, 588, 515.

methyl 3-(1*H*-pyrrol-1-yl) benzoate (3i)



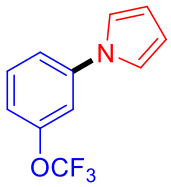
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 200:1→100:1) as a yellow oil in 79 % (47.7 mg) yield; The spectral data were in accordance with those reported in the literature[7]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10-8.05 (m, 1H), 7.94-7.88 (m, 1H), 7.58 (ddd, *J* = 8.1, 2.4, 1.1 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.17-7.12 (m, 2H), 6.39 (t, *J* = 2.2 Hz, 2H), 3.95 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.2, 140.7, 131.5, 129.5, 126.3, 124.3, 121.0, 119.0, 110.8, 52.2; **FT-IR** (KBr) ν/cm^{-1}: 3139, 3104, 3073, 2951, 2842, 1725, 1592, 1500 , 1453, 1340 , 1264, 1110, 1069, 937, 755, 724, 684, 554.

1-(*m*-tolyl)-1*H*-pyrrole (3j)



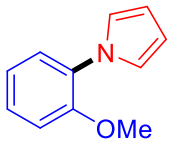
Following the general procedure, the title compound was isolated by Flash column chromatography (PE) as a yellow oil in 71 % (33.5 mg) yield; The spectral data were in accordance with those reported in the literature[8]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.7 Hz, 1H), 7.30-7.22 (m, 2H), 7.15 (t, *J* = 2.0 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.41 (s, 2H), 2.46 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.7, 139.4, 129.2, 126.3, 121.2, 119.2, 117.6, 110.2, 21.4; **FT-IR** (KBr) ν/cm^{-1}: 3136, 3103, 3040, 2920, 2856, 1610, 1501, 1481, 1336, 1072, 945, 829, 780, 724, 692, 620.

1-(3-(trifluoromethoxy) phenyl)-1*H*-pyrrole (3k)



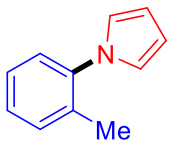
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 40:1) as a colorless oil in 63 % (42.9 mg) yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (t, *J* = 8.2 Hz, 1H), 7.38-7.32 (m, 1H), 7.26 (d, *J* = 3.7 Hz, 1H), 7.15-7.08 (m, 3H), 6.39 (t, *J* = 2.2 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.0 (q, $J_{C\text{-}F}$ = 1.8 Hz), 142.0, 130.7, 120.4 (q, $J_{C\text{-}F}$ = 256.3 Hz), 119.2, 118.4, 117.5, 113.1, 111.2; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -57.80; **FT-IR** (KBr) ν/cm^{-1}: 3139, 3108, 3082, 1613, 1505, 1340, 1260, 1068, 968, 870, 783, 724, 634, 587; **HRMS** (APCI) calcd for $C_{11}H_8F_3NO$ [M+H$^+$], 228.0631; found: 228.0621.

1-(2-methoxyphenyl)-1*H*-pyrrole (3l)



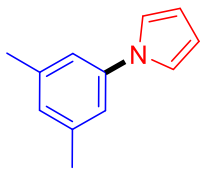
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 300:1) as a light brown oil in 70 % (36.3 mg) yield; The spectral data were in accordance with those reported in the literature[2]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.12-7.01 (m, 4H), 6.37 (t, *J* = 2.1 Hz, 2H), 3.87 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.7, 130.2, 127.4, 125.7, 122.0, 120.9, 112.3, 108.7, 55.7; **FT-IR** (KBr) ν/cm^{-1}: 3101, 3070, 2959, 2936, 2837, 1598, 1511, 1479, 1320, 1280, 1250, 1071, 1025, 923, 752, 726, 626.

1-(*o*-tolyl)-1*H*-pyrrole (3m)



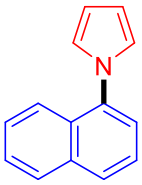
Following the general procedure, the title compound was isolated by Flash column chromatography (PE) as a yellow oil in 69 % (32.5 mg) yield; The spectral data were in accordance with those reported in the literature[8]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (m, 4H), 6.85 (d, *J* = 1.8 Hz, 2H), 6.44-6.31 (m, 2H), 2.27 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.6, 133.8, 131.0, 127.4, 126.6, 126.5, 122.0, 108.7, 17.8; **FT-IR** (KBr) ν/cm^{-1}: 3102, 3068, 3029, 2956, 2925, 2856, 1505, 1325, 1100, 1072, 925, 762, 725, 634, 550.

1-(3,5-dimethylphenyl)-1*H*-pyrrole (3n)



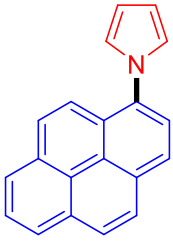
Following the general procedure, the title compound was isolated by Flash column chromatography (PE) as a light brown oil in 77 % (39.5 mg) yield; The spectral data were in accordance with those reported in the literature[9]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12 (t, *J* = 1.9 Hz, 2H), 7.09-7.04 (m, 2H), 6.94 (d, *J* = 0.6 Hz, 1H), 6.38 (t, *J* = 1.9 Hz, 2H), 2.41 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.7, 139.2, 127.2, 119.3, 118.4, 110.0, 21.3; **FT-IR** (KBr) ν/cm^{-1}: 3103, 2919, 2855, 1611, 1493, 1346, 1228, 1075, 951, 843, 723, 622.

1-(naphthalen-1-yl)-1*H*-pyrrole (3o)



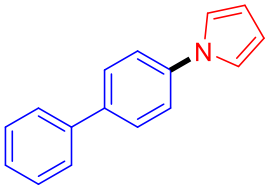
Following the general procedure, the title compound was isolated by Flash column chromatography (PE) as a yellow oil in 87 % (50.4 mg) yield; The spectral data were in accordance with those reported in the literature[2]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.60-7.47 (m, 4H), 7.05 (t, *J* = 2.1 Hz, 2H), 6.47 (t, *J* = 2.1 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.2, 134.2, 129.8, 128.0, 127.8, 126.9, 126.5, 125.2, 123.2, 123.2, 123.2, 109.0; **FT-IR** (KBr) ν/cm^{-1}: 3100, 3051, 1597, 1505, 1488, 1325, 1234, 1086, 990, 917, 801, 726, 631.

1-(pyren-1-yl)-1*H*-pyrrole (3p)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE) as a light-yellow oil in 82 % (65.7 mg) yield; The spectral data were in accordance with those reported in the literature[10]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15-8.22 (m 3H), 8.11-7.98 (m, 6H), 7.21 (t, *J* = 2.1 Hz, 2H), 6.61 (t, *J* = 2.1 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.2, 131.1, 130.8, 130.3, 128.4, 127.6, 126.9, 126.4, 126.2, 125.5, 125.2, 125.0, 124.7, 124.3, 123.9, 123.6, 122.1, 109.3; **FT-IR** (KBr) ν/cm^{-1}: 3133, 3098, 3041, 1602, 1512, 1482, 1302, 1095, 844, 718, 680.

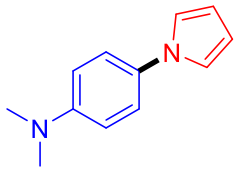
1-([1,1'-biphenyl]-4-yl)-1*H*-pyrrole (3q)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 100:1) as a white crystal in 78 % (51.3 mg) yield; The spectral data were in accordance with those reported in the literature[11]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72-7.62 (m, 4H), 7.49 (dt, *J* = 7.8, 3.3 Hz, 4H), 7.44-7.36 (m, 1H), 7.17 (t, *J* = 2.2 Hz, 2H), 6.42 (t, *J* = 2.2 Hz, 2H); **^{13}C NMR** (126

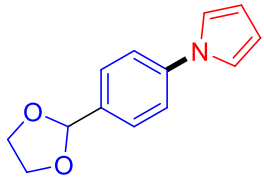
MHz, $CDCl_3$) δ 140.1, 139.9, 138.5, 128.8, 128.1, 127.4, 126.9, 120.6, 119.2, 110.5; **FT-IR** (KBr) ν/cm^{-1}: 3139, 3101, 3035, 1606, 1533, 1495, 1332, 1249, 1068, 830, 763, 721, 609.

N, N-dimethyl-4-(1*H*-pyrrol-1-yl) aniline (3r)



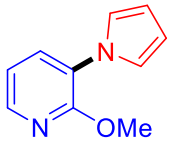
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 40:1) as a white crystal in 67 % (37.4 mg) yield; The spectral data were in accordance with those reported in the literature[12]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.01 (t, *J* = 2.1 Hz, 2H), 6.81-6.76 (m, 2H), 6.33 (t, *J* = 2.1 Hz, 2H), 2.99 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.9, 131.2, 122.2, 119.7, 113.1, 109.3, 40.8; **FT-IR** (KBr) ν/cm^{-1}: 3133, 3099, 2954, 2923, 2849, 2803, 1533, 1323, 1225, 1073, 1020, 811, 721, 615, 524.

1-(4-(1,3-dioxolan-2-yl) phenyl)-1*H*-pyrrole (3s)



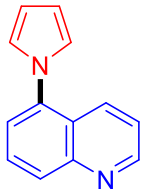
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 20:1) as a white crystal in 74 % (47.8 mg) yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59-7.52 (m, 2H), 7.46-7.38 (m, 2H), 7.12 (t, *J* = 2.2 Hz, 2H), 6.40-6.35 (m, 2H), 5.85 (s, 1H), 4.20-4.11 (m, 2H), 4.11-4.02 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.3, 135.1, 127.8, 120.2, 119.2, 110.5, 103.2, 65.3; **FT-IR** (KBr) ν/cm^{-1}: 3141, 3104, 3076, 2959, 2924, 2884, 1698, 1603, 1527, 1329, 1083, 967, 825, 723, 612, 545; **HRMS** (APCI) calcd for $C_{13}H_{13}NO_2$ [M+H^+], 216.1019; found: 216.1018.

2-methoxy-3-(1*H*-pyrrol-1-yl) pyridine (3t)



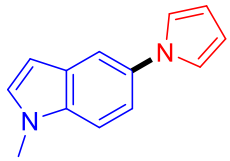
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 60:1) as a yellow oil in 81 % (42.3 mg) yield; The spectral data were in accordance with those reported in the literature[14]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 5.0, 1.7 Hz, 1H), 7.56 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.06 (t, *J* = 2.2 Hz, 2H), 6.97 (dd, *J* = 7.6, 5.0 Hz, 1H), 6.35 (t, *J* = 2.2 Hz, 2H), 4.03 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.9, 143.9, 132.3, 125.1, 121.6, 116.9, 109.5, 53.7; **FT-IR** (KBr) ν/cm^{-1}: 3135, 3103, 3062, 2986, 2949, 2859, 1592, 1496, 1309, 1226, 1107, 1011, 923, 795, 726, 624.

5-(1*H*-pyrrol-1-yl) quinoline (3u)



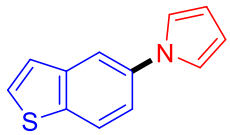
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 20:1) as a yellow solid in 73 % (42.5 mg) yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.94 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 8.10 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.73 (dd, *J* = 8.5, 7.4 Hz, 1H), 7.52 (dd, *J* = 7.3, 0.9 Hz, 1H), 7.39 (dd, *J* = 8.6, 4.2 Hz, 1H), 6.96 (t, *J* = 2.1 Hz, 2H), 6.42 (t, *J* = 2.1 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.8, 148.5, 137.9, 131.8, 129.1, 128.7, 124.9, 123.4, 123.0, 121.7, 109.5; **FT-IR** (KBr) ν/cm^{-1}: 3111, 3096, 3060, 1616, 1569, 1490, 1308, 1087, 919, 801, 747, 633; **HRMS** (APCI) calcd for $C_{13}H_{10}N_2$ [M+H$^+$], 195.0917; found: 195.0916.

5-(1*H*-pyrrol-1-yl) quinoline (3v)



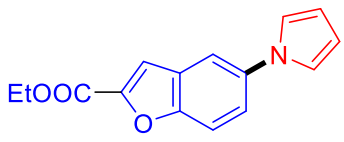
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 200:1) as a light yellow crystal in 79 % (46.5 mg) yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75-7.67 (m, 1H), 7.37 (m , 2H), 7.22-7.13 (m, 3H), 6.58 (dd, *J* = 2.3, 1.4 Hz, 1H), 6.49-6.40 (m, 2H), 3.84 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.0, 134.0, 130.2, 128.7, 120.3, 116.2, 113.2, 109.7, 109.4, 101.1, 32.9; **FT-IR** (KBr) ν/cm^{-1}: 3119, 3098, 2926, 2908 2824, 1575, 1501, 1304, 1278, 1073, 853, 738, 623; **HRMS** (APCI) calcd for $C_{13}H_{12}N_2$ [M+H$^+$], 197.1073; found: 197.1072.

1-(benzo[*b*]thiophen-5-yl)-1*H*-pyrrole (3w)



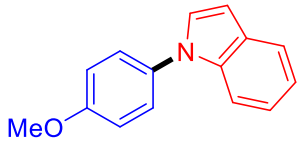
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 100:1→40:1) as a white solid in 50 % (29.9 mg) yield; The spectral data were in accordance with those reported in the literature[15]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 1H), 7.84 (d, *J* = 2.1 Hz, 1H), 7.55 (d, *J* = 5.4 Hz, 1H), 7.45 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.38 (d, *J* = 5.4 Hz, 1H), 7.18 (d, *J* = 1.0 Hz, 2H), 6.44 (d, *J* = 2.0 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.4, 138.0, 137.0, 128.3, 123.7, 123.3, 119.8, 118.2, 115.1, 110.3; **FT-IR** (KBr) ν/cm^{-1}: 3130, 3096, 1600, 1507, 1478, 1302, 1188, 863, 728, 626.

ethyl 5-(1*H*-pyrrol-1-yl) benzofuran-2-carboxylate (3x)



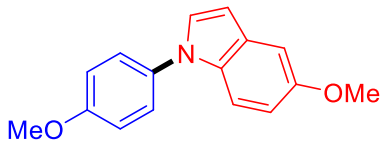
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 100:1→40:1) as a colourless oil in 78 % (59.7 mg) yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66-7.59 (m, 2H), 7.53 (d, *J* = 0.9 Hz, 1H), 7.49 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.10-7.05 (t, *J* = 2.2 Hz, 2H), 6.37 (t, *J* = 2.2 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.2, 153.6, 147.0, 137.4, 127.7, 121.5, 120.0, 114.3, 113.6, 113.1, 110.4, 61.6, 14.3; **FT-IR** (KBr) ν/cm^{-1}: 3102, 2979, 2928, 1728, 1564, 1496, 1303, 1260, 1177, 949, 866, 720, 684; **HRMS** (APCI) calcd for $C_{15}H_{13}NO_3$ [M+H$^+$], 256.0968; found: 256.0964.

1-(4-methoxyphenyl)-1*H*-indole (4a)



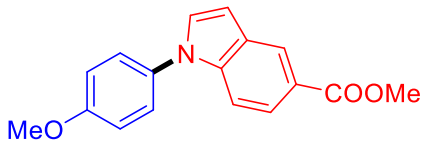
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 200:1) as a yellow oil in 95 % (63.6 mg) yield; The spectral data were in accordance with those reported in the literature[15]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.74 (m, 1H), 7.59-7.51 (m, 1H), 7.50-7.43 (m, 2H), 7.35 (t, *J* = 2.6 Hz, 1H), 7.32-7.22 (m, 2H), 7.13-7.05 (m, 2H), 6.74 (dd, *J* = 3.1, 0.8 Hz, 1H), 3.92 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.1, 136.2, 132.7, 128.9, 128.2, 125.9, 122.1, 121.0, 120.0, 114.6, 110.3, 102.8, 55.5; **FT-IR** (KBr) ν/cm^{-1}: 3049, 2956, 2933, 2836, 1611, 1518, 1458, 1250, 1231, 1033, 834, 742, 660, 584.

5-methoxy-1-(4-methoxyphenyl)-1*H*-indole (4b)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 200:1→100:1) as a light yellow oil in 85 % (64.5 mg) yield; The spectral data were in accordance with those reported in the literature[16]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (m, 3H), 7.34-7.28 (m, 1H), 7.22 (d, *J* = 2.3 Hz, 1H), 7.09-7.02 (m, 2H), 6.95 (dt, *J* = 8.9, 2.4 Hz, 1H), 6.69-6.61 (m, 1H), 3.93 (s, 3H), 3.90 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.0, 154.3, 132.8, 131.5, 129.4, 128.6, 125.5, 114.6, 112.3, 111.1, 102.5, 102.5, 55.7, 55.4; **FT-IR** (KBr) ν/cm^{-1}: 3100, 3045, 2953, 2932, 2833, 1616, 1511, 1447, 1247, 1218, 1155, 1030, 832, 715.

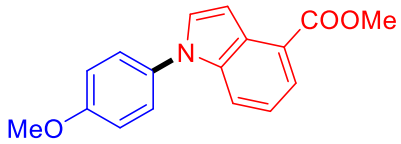
methyl 1-(4-methoxyphenyl)-1*H*-indole-5-carboxylate (4c)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 20:1) as a light brown oil in 76 % (64.1 mg) yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 1.5 Hz, 1H), 7.89 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 1H), 7.40-7.34 (m, 2H), 7.32 (d, *J* = 3.2 Hz, 1H), 7.09-6.99 (m, 2H), 6.74 (d, *J* = 3.2 Hz, 1H), 3.94 (s, 3H), 3.89 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.9, 158.5, 138.6, 132.0, 129.7, 128.4, 125.9, 123.9, 123.4, 122.0, 114.7, 109.9,

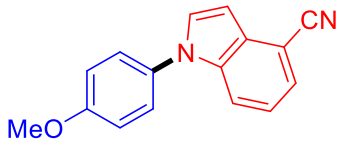
104.1, 55.5, 51.7; **FT-IR** (KBr) ν/cm^{-1}: 3104, 3045, 2998, 2949, 2837, 1712, 1611, 1515, 1337, 1270, 1032, 835, 754, 597; **HRMS** (APCI) calcd for $C_{17}H_{15}NO_3$ [M+H$^+$], 282.1125; found: 282.1123.

methyl 1-(4-methoxyphenyl)-1*H*-indole-4-carboxylate (4d)



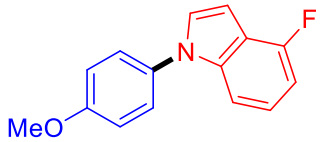
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 40:1) as a light yellow crystal in 75 % (63.2 mg) yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.5, 0.7 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.41 (d, *J* = 3.2 Hz, 1H), 7.39-7.34 (m, 2H), 7.34-7.31 (m, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.07-6.99 (m, 2H), 4.02 (s, 3H), 3.87 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.8, 158.5, 137.2, 132.1, 130.3, 128.3, 126.2, 123.6, 121.6, 121.2, 115.1, 114.7, 103.9, 55.5, 51.7; **FT-IR** (KBr) ν/cm^{-1}: 3120, 3093, 2959, 2940, 2837, 1705, 1604, 1515, 1331, 1286, 1029, 834, 768, 620; **HRMS** (APCI) calcd for $C_{17}H_{15}NO_3$ [M+H$^+$], 282.1125; found: 282.1122.

1-(4-methoxyphenyl)-1*H*-indole-4-carbonitrile (4e)



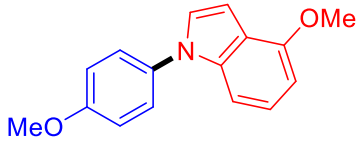
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 40:1) as a white crystal in 9 % (6.7 mg) yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 1H), 7.51 (dd, *J* = 7.4, 0.7 Hz, 1H), 7.44 (d, *J* = 3.2 Hz, 1H), 7.40-7.34 (m, 2H), 7.23 (dd, *J* = 8.3, 7.5 Hz, 1H), 7.09-7.02 (m, 2H), 6.87 (dd, *J* = 3.2, 0.7 Hz, 1H), 3.89 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.9, 136.2, 131.5, 131.0, 130.1, 126.3, 125.5, 121.7, 118.6, 115.2, 114.9, 103.3, 101.7, 55.6; **FT-IR** (KBr) ν/cm^{-1}: 3121, 3099, 3016, 2929, 2854, 2221, 1600, 1519, 1299, 1250, 1028, 830, 754, 611; **HRMS** (APCI) calcd for $C_{16}H_{12}N_2O$ [M+H$^+$], 249.1022; found: 249.1022.

4-fluoro-1-(4-methoxyphenyl)-1*H*-indole (4f)



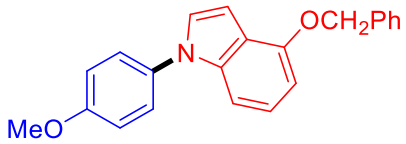
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 40:1) as a light yellow oil in 82 % (59.3 mg) yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45-7.36 (m, 2H), 7.28-7.21 (m, 2H), 7.13 (td, *J* = 8.0, 5.2 Hz, 1H), 7.09-7.01 (m, 2H), 6.86 (ddd, *J* = 10.2, 7.8, 0.6 Hz, 1H), 6.77 (dd, *J* = 3.2, 0.8 Hz, 1H), 3.90 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.5, 156.3, (d, $J_{C\text{-}F}$ = 245.6 Hz), 138.9 (d, $J_{C\text{-}F}$ = 11.0 Hz), 132.4, 128.2, 126.0, 122.6 (d, $J_{C\text{-}F}$ = 7.8 Hz), 117.9 (d, $J_{C\text{-}F}$ = 7.8 Hz), 114.7, 106.5 (d, $J_{C\text{-}F}$ = 3.6 Hz), 104.7 (d, $J_{C\text{-}F}$ = 18.9 Hz), 98.8, 55.5; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -122.03; **FT-IR** (KBr) ν/cm^{-1}: 3112, 3043, 2958, 2837, 1627, 1518, 1297, 1250, 1213, 1033, 833, 742, 652; **HRMS** (APCI) calcd for $C_{15}H_{12}FNO$ [M+H$^+$], 242.0976; found: 242.0973.

4-methoxy-1-(4-methoxyphenyl)-1*H*-indole (4g)



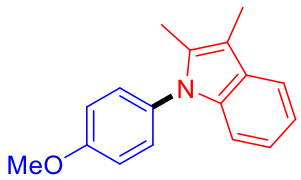
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 200:1) as a light yellow oil in 93 % (70.6 mg) yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53-7.44 (m, 2H), 7.31-7.18 (m, 3H), 7.12-7.04 (m, 2H), 6.90 (dd, *J* = 5.0, 2.4 Hz, 1H), 6.68 (dd, *J* = 7.0, 3.8 Hz, 1H), 4.07 (s, 3H), 3.92 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.1, 153.3, 137.6, 132.8, 126.7, 125.8, 122.9, 119.4, 114.5, 103.7, 100.1, 99.8, 55.4, 55.2; **FT-IR** (KBr) ν/cm^{-1}: 3076, 3045, 2953, 2935, 2906, 2837, 1610, 1517, 1297, 1247, 1092, 832, 736, 608; **HRMS** (APCI) calcd for $C_{16}H_{15}NO_2$ [M+H$^+$], 254.1176; found: 254.1172.

4-(benzyloxy)-1-(4-methoxyphenyl)-1*H*-indole (4h)



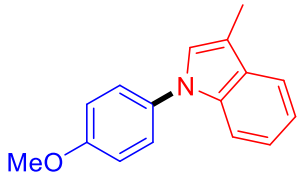
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 200:1) as a light yellow oil in 80 % (79.0 mg) yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63-7.57 (m, 2H), 7.51-7.36 (m, 5H), 7.26-7.25 (m, 1H), 7.20-7.15 (m, 2H), 7.12-7.03 (m, 2H), 6.91 (d, *J* = 3.2 Hz, 1H), 6.74-6.66 (m, 1H), 5.33 (s, 2H), 3.91 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.2, 152.5, 137.8, 137.6, 132.9, 128.4, 127.7, 127.3, 126.8, 125.9, 122.9, 119.8, 114.6, 104.0, 101.4, 100.4, 69.9, 55.5; **FT-IR** (KBr) ν/cm^{-1}: 3061, 3032, 2932, 2836, 1610, 1518, 1297, 1248, 1089, 838, 738, 615; **HRMS** (APCI) calcd for $C_{22}H_{19}NO_2$ [M+H$^+$], 330.1489; found: 330.1485.

1-(4-methoxyphenyl)-2,3-dimethyl-1*H*-indole (4i)



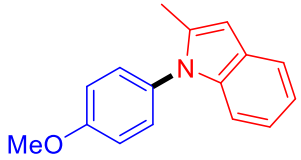
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 40:1) as a white solid in 51 % (38.4 mg) yield; The spectral data were in accordance with those reported in the literature[17]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.2 Hz, 1H), 7.37-7.29 (m, 2H), 7.26-7.16 (m, 3H), 7.14-7.06 (m, 2H), 3.96 (s, 3H), 2.45 (s, 3H), 2.32 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.7, 137.6, 133.1, 131.0, 129.1, 128.6, 120.9, 119.2, 117.7, 114.5, 109.6, 107.3, 55.4, 10.8, 8.8; **FT-IR** (KBr) ν/cm^{-1}: 3068, 3051, 2964, 2911, 2854, 1611, 1511, 1297, 1238, 1031, 833, 744, 607.

1-(4-methoxyphenyl)-3-methyl-1*H*-indole (4j)



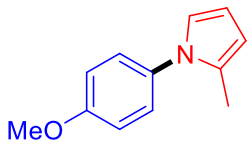
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 200:1) as a light yellow oil in 92 % (65.4 mg) yield; The spectral data were in accordance with those reported in the literature[18]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.49-7.41 (m, 2H), 7.34-7.22 (m, 2H), 7.15 (s, 1H), 7.11-7.04 (m, 2H), 3.92 (s, 3H), 2.49 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.8, 136.3, 133.0, 129.3, 125.8, 125.5, 122.1, 119.4, 119.0, 114.6, 112.0, 110.1, 55.5, 9.5; **FT-IR** (KBr) ν/cm^{-1}: 3047, 2956, 2932, 2917, 2860, 2836, 1612, 1514, 1459, 1299, 1248, 1034 , 834, 740, 606.

1-(4-methoxyphenyl)-2-methyl-1*H*-indole (4k)



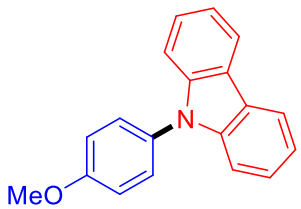
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 40:1) as a light brown oil in 29 % (20.6 mg) yield; The spectral data were in accordance with those reported in the literature[19]; **^{1}H NMR** (600 MHz, CDCl3) δ 7.57 (dd, *J* = 6.7, 1.7 Hz, 1H), 7.30-7.24 (m, 2H), 7.13-7.02 (m, 5H), 6.39 (s, 1H), 3.90 (s, 3H), 2.29 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.0, 138.5, 137.3, 130.6, 129.2, 128.0, 120.9, 119.8, 119.5, 114.6, 110.0, 100.7, 55.5, 13.2; **FT-IR** (KBr) ν/cm^{-1}: 3049, 2957, 2932, 2836, 1610, 1514, 1323, 1248, 1035, 828, 747, 608.

1-(4-methoxyphenyl)-2-methyl-1*H*-pyrrole (4l)



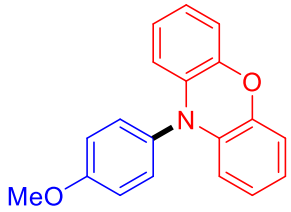
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 200:1) as a light brown oil in 42 % (23.6 mg) yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30-7.22 (m, 2H), 7.02-6.94 (m, 2H), 6.76 (dd, *J* = 2.7, 1.9 Hz, 1H), 6.21 (t, *J* = 3.1 Hz, 1H), 6.06 (ddd, *J* = 3.3, 1.7, 0.8 Hz, 1H), 3.88 (s, 3H), 2.21 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.4, 133.4, 129.2, 127.0, 121.5, 114.1, 107.6, 107.5, 55.4, 12.7; **FT-IR** (KBr) ν/cm^{-1}: 3072, 3049, 2934, 2835, 1609, 1515, 1289, 1247, 1037, 835, 704, 607; **HRMS** (APCI) calcd for $C_{12}H_{13}NO$ [M+H^+], 188.1070; found: 188.1069.

9-(4-methoxyphenyl)-9*H*-carbazole (4m)



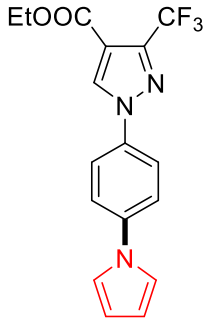
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 200:1→100:1) as a white crystal in 82 % (67.2 mg) yield; The spectral data were in accordance with those reported in the literature[20]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.25-8.16 (m, 2H), 7.57-7.28 (m, 8H), 7.19-7.11 (m, 2H), 3.95 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.8, 141.3, 130.2, 128.5, 125.8, 123.0, 120.2, 119.6, 115.0, 109.6, 55.5; **FT-IR** (KBr) ν/cm^{-1}: 3043, 3015, 2958, 2931, 2837, 1593, 1514, 1319, 1248, 1029, 830, 750, 622.

10-(4-methoxyphenyl)-10*H*-phenoxazine (4n)



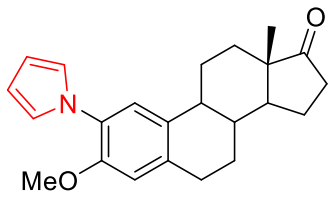
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 40:1) as a white crystal in 71 % (61.6 mg) yield; The spectral data were in accordance with those reported in the literature[21]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.67 (m, 6H), 5.98 (d, *J* = 7.6 Hz, 2H), 3.92 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.3, 143.9, 134.7, 131.7, 131.2, 123.2, 121.0, 116.1, 115.2, 113.1, 55.4; **FT-IR** (KBr) ν/cm^{-1}: 3059, 3005, 2948, 2927, 2829, 1606, 1510, 1459, 1299, 1248, 1032, 828, 743, 616.

ethyl 1-(4-(1*H*-pyrrol-1-yl)phenyl)-3-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate (5)



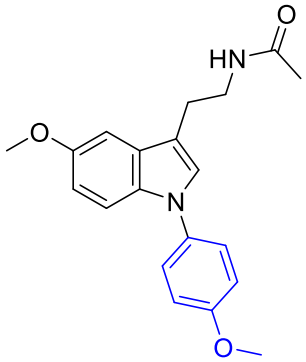
Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 10:1) as a white solid in 72 % (75.4 mg) yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.57-7.43 (m, 4H), 7.14 (t, *J* = 2.2 Hz, 2H), 6.39 (t, *J* = 2.2 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.9, 142.5, 141.6, 136.3, 132.5 (q, $J_{C\text{-}F}$ = 40.2 Hz), 127.1, 120.3, 119.1, 119.1 (q, $J_{C\text{-}F}$ = 272.0 Hz), 116.8 (d, $J_{C\text{-}F}$ = 1.1 Hz), 111.4, 61.3, 14.0; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -55.30; **FT-IR** (KBr) ν/cm^{-1}: 3133, 3103, 2983, 2927, 2871, 1724, 1607, 1526, 1299, 1253, 1133, 1041, 845, 723, 608; **HRMS** (APCI) calcd for $C_{17}H_{14}F_3N_3O_2$ [M+H$^+$], 350.1111; found: 350.1108.

(13S)-3-methoxy-13-methyl-2-(1*H*-pyrrol-1-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (6)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 40:1) as a white crystal in 50 % (52.4 mg) yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 (s, 1H), 6.95 (t, *J* = 2.0 Hz, 2H), 6.75 (s, 1H), 6.30 (t, *J* = 2.1 Hz, 2H), 3.80 (s, 3H), 2.96 (dd, *J* = 8.6, 3.7 Hz, 2H), 2.52 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.41-2.34 (m, 1H), 2.29 (d, *J* = 3.7 Hz, 1H), 2.21-2.03 (m, 3H), 1.99-1.93 (m, 1H), 1.66-1.46 (m, 6H), 0.93 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.7, 135.8, 132.2, 128.1, 123.1, 122.1, 112.6, 108.5, 55.8, 50.3, 47.9, 43.8, 38.2, 35.8, 31.5, 29.4, 26.5, 25.9, 21.5, 13.8; **FT-IR** (KBr) ν/cm^{-1}: 3099, 3043, 2930, 2858, 1739, 1613, 1515, 1317, 1236, 1068, 887, 726, 633; **HRMS** (APCI) calcd for $C_{23}H_{27}NO_2$ [M+H$^+$], 350.2115; found: 350.2112.

N-(2-(5-methoxy-1-(4-methoxyphenyl)-1*H*-indol-3-yl)ethyl)acetamide (7)



Following the general procedure, the title compound was isolated by Flash column chromatography (PE:EtOAc 1:1) as a gray solid in 90 % (91.3 mg) yield **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37-7.29 (m, 3H), 7.09 (d, *J* = 2.5 Hz, 2H), 7.01-6.95 (m, 2H), 6.86 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.09 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.59 (q, *J* = 6.8 Hz, 2H), 2.97 (t, *J* = 6.9 Hz, 2H), 1.94 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.1, 157.7, 154.1, 132.6, 131.6, 128.8, 126.3, 125.1, 114.6, 113.0, 112.3, 111.2, 100.6, 55.7, 55.4, 39.7, 25.1, 23.1; **FT-IR** (KBr) ν/cm^{-1}: 3250, 3073, 3000, 2951, 2936, 2852, 1636, 1518, 1301, 1251, 1035, 831, 788, 635; **HRMS** (APCI) calcd for $C_{20}H_{22}N_2O_3$ [M+H$^+$], 339.1703; found: 339.1699.

6. References

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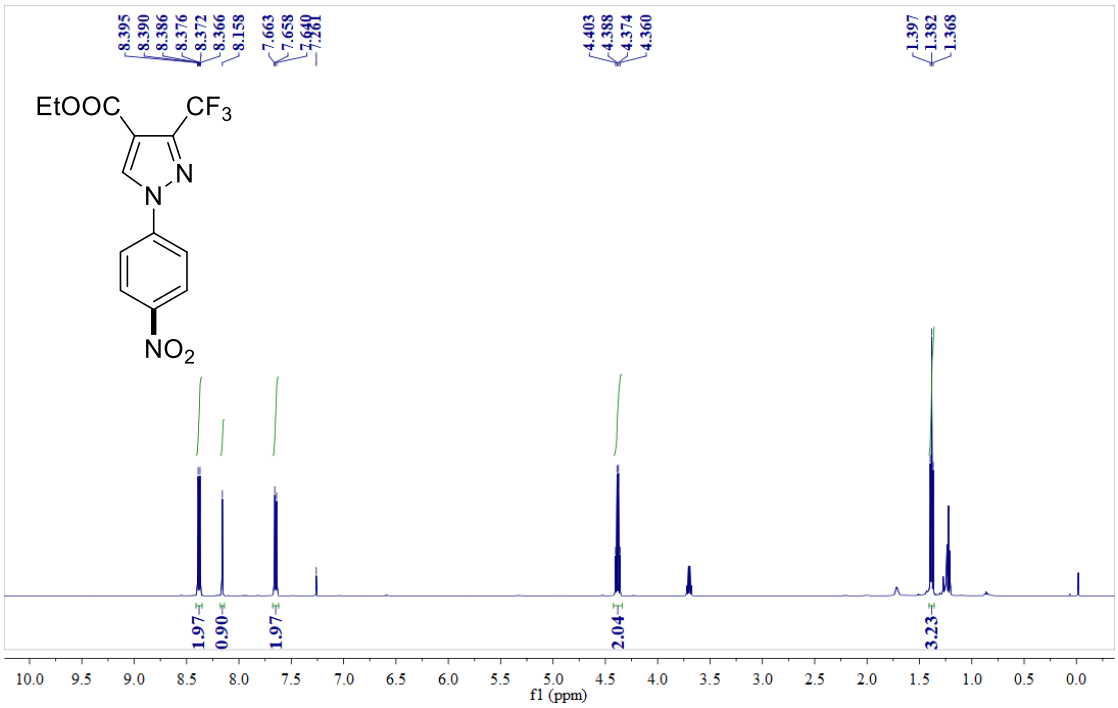
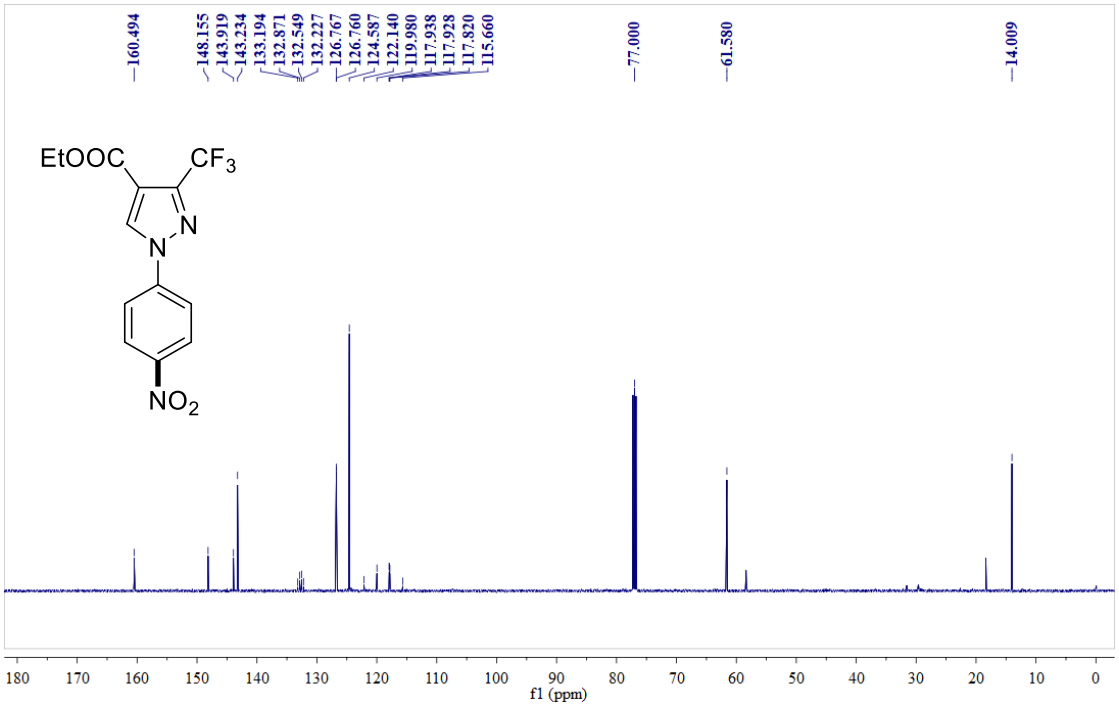
7. NMR Spectra of Starting Materials and Products

^{1}H NMR Spectrum of **5a**



^{13}C NMR Spectrum of **5a**



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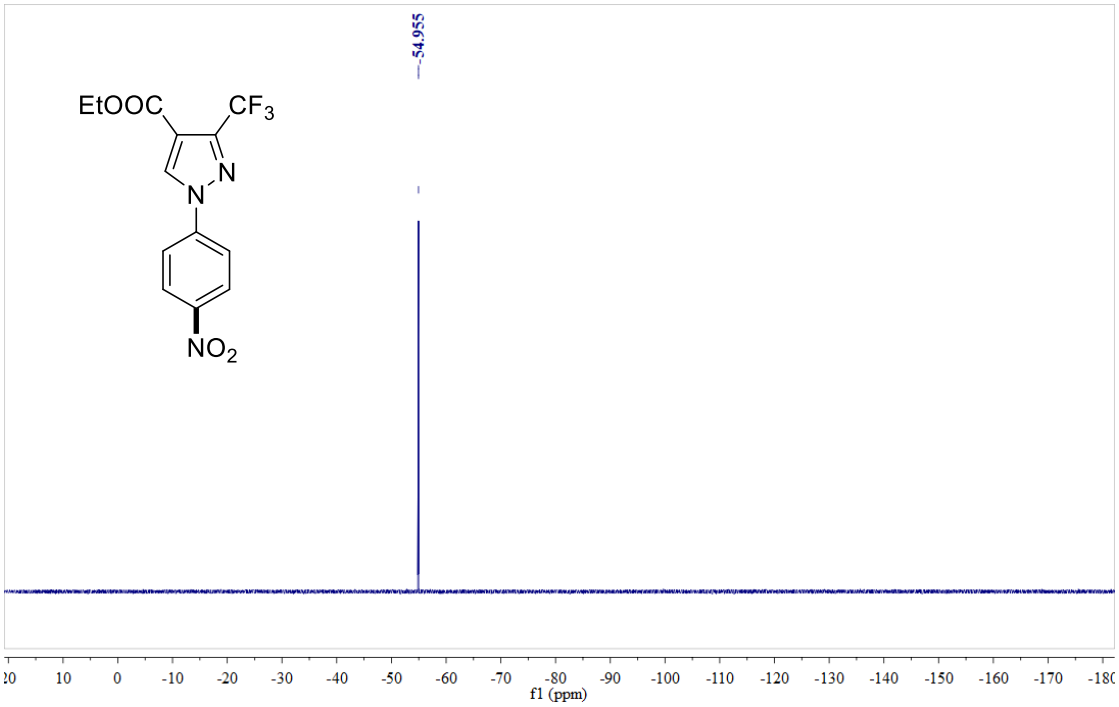

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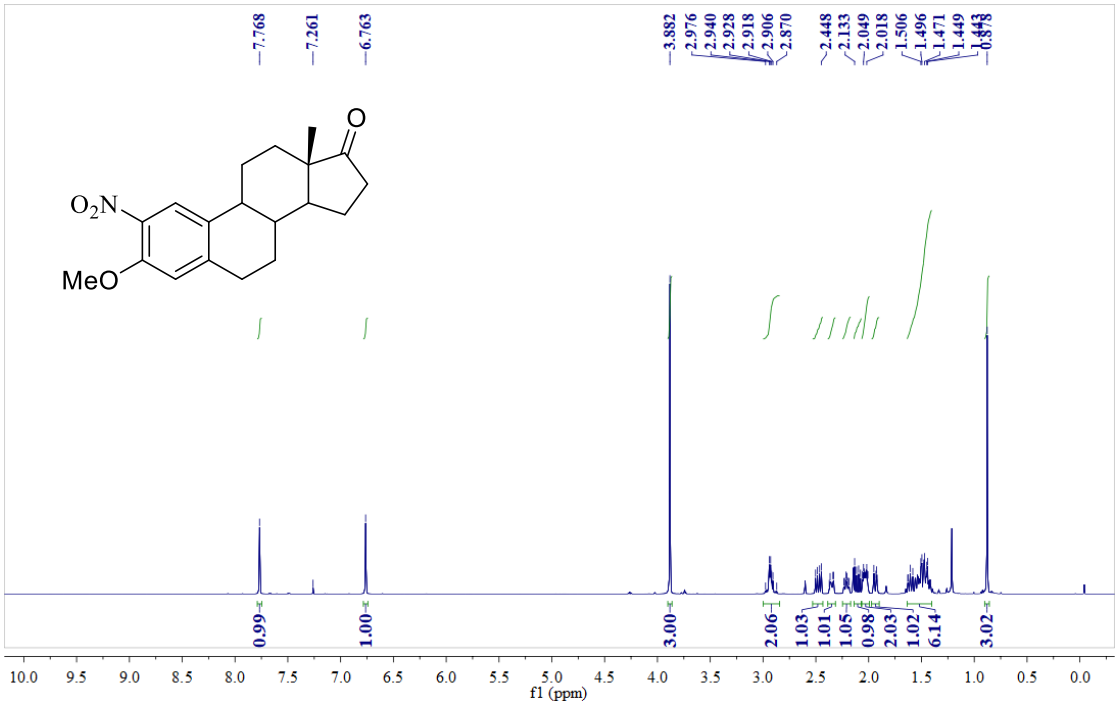

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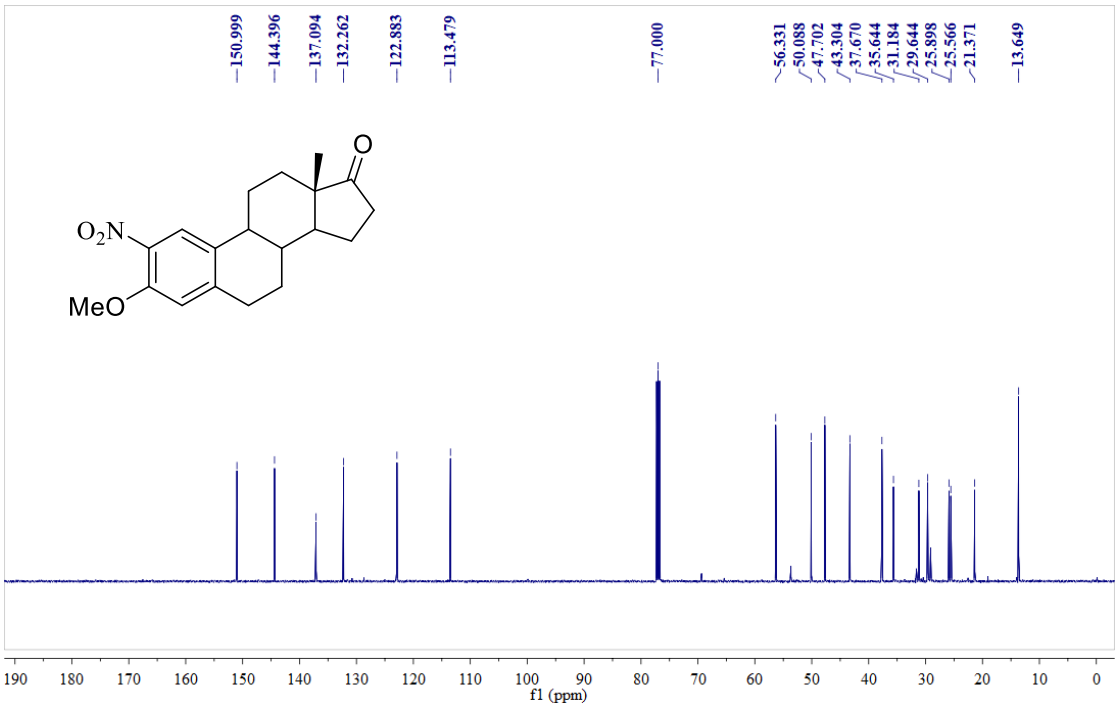

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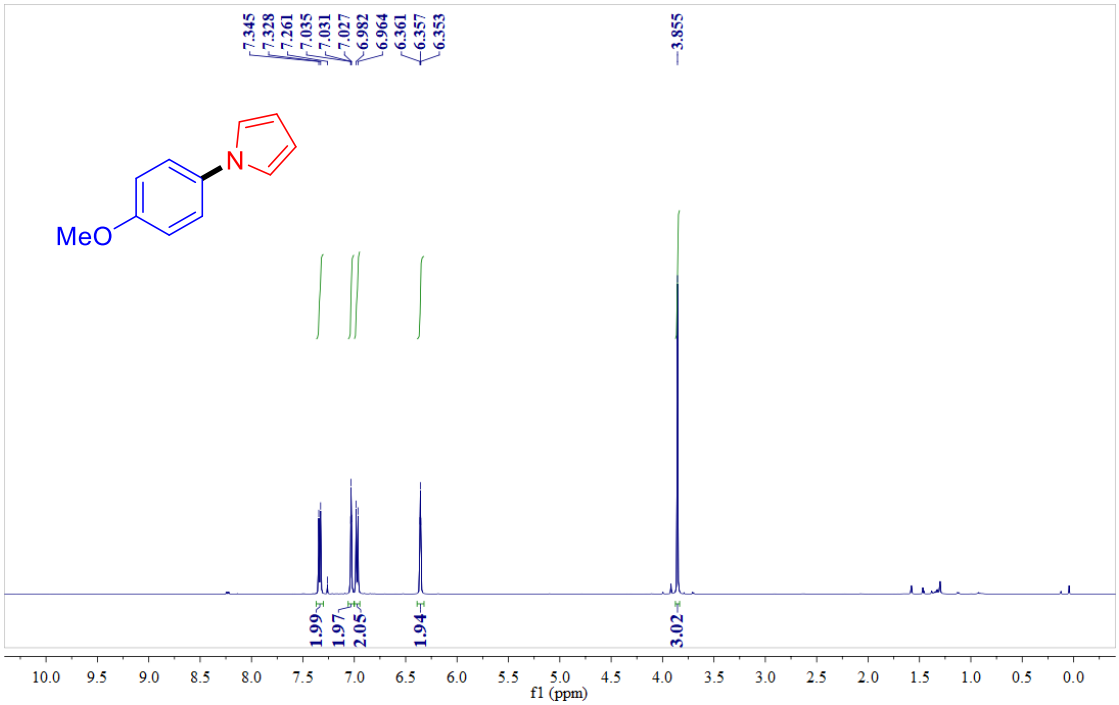
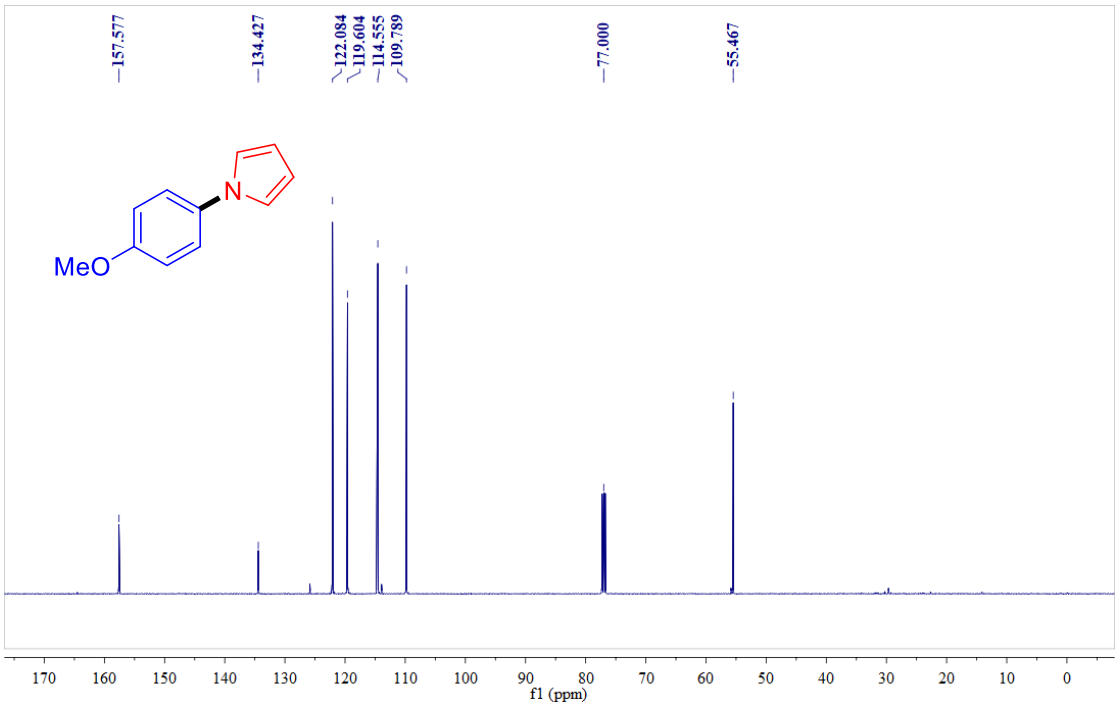


^{13}C NMR Spectrum of **3a**



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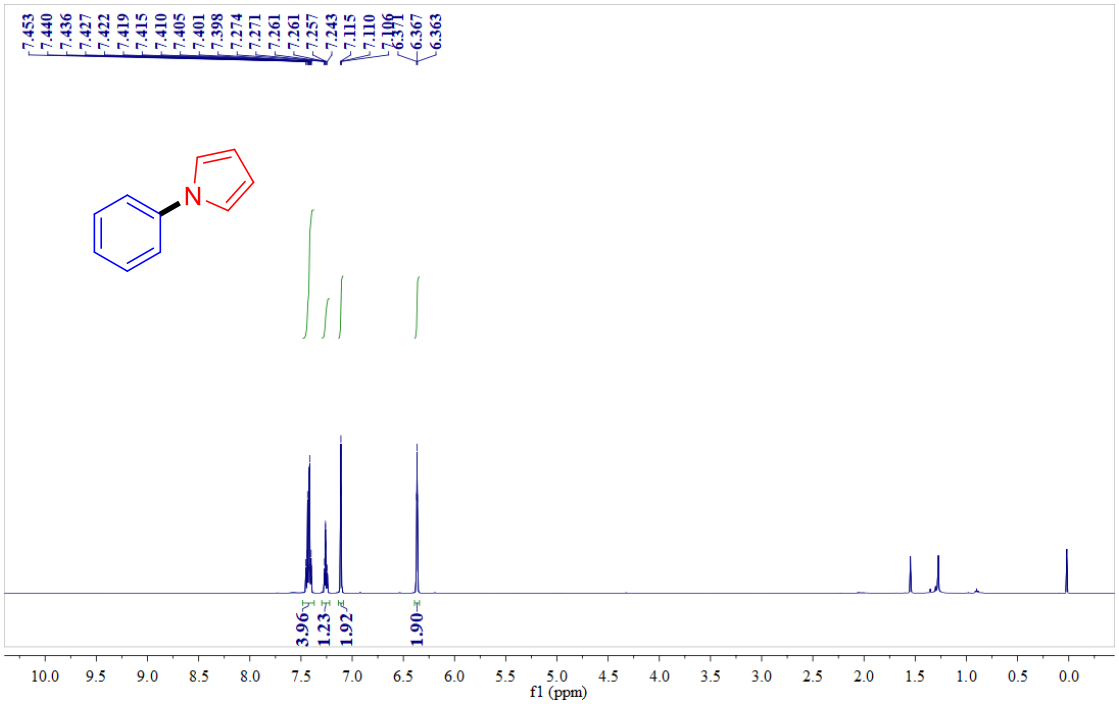
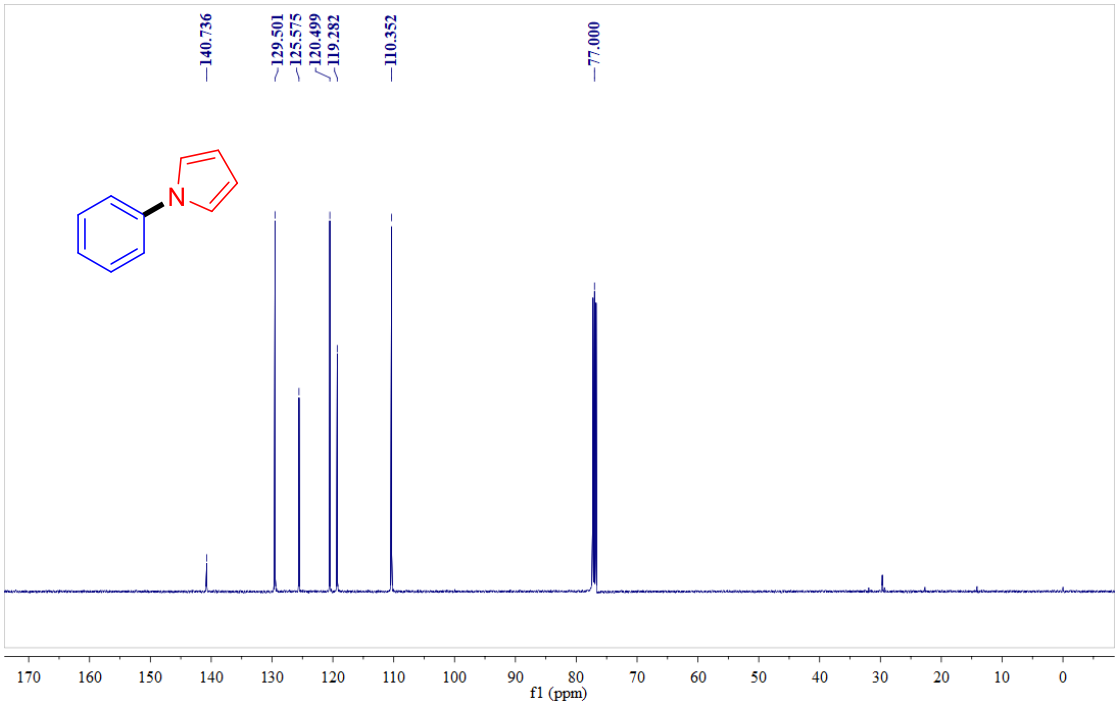
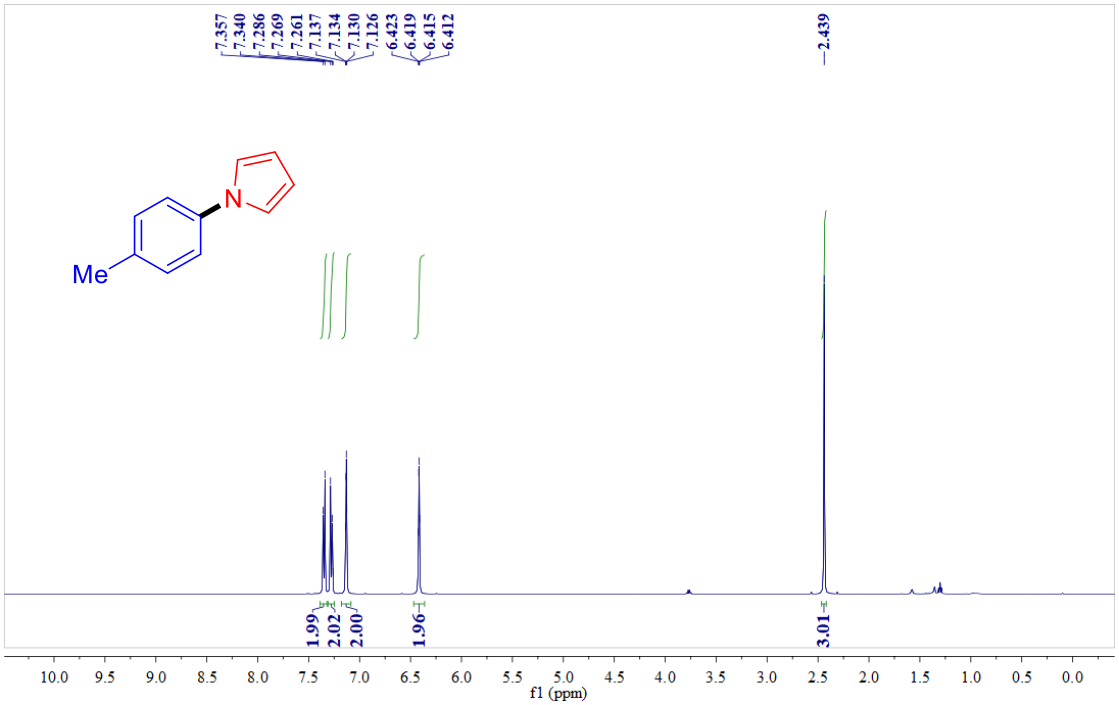


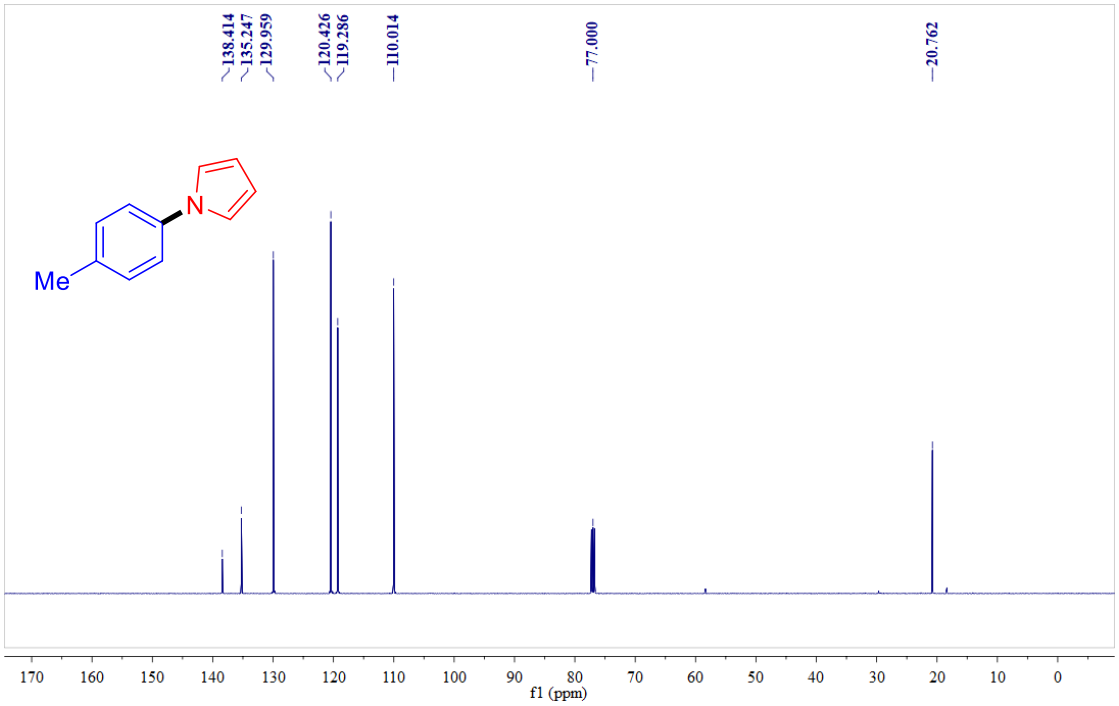
^{13}C NMR Spectrum of **3b**



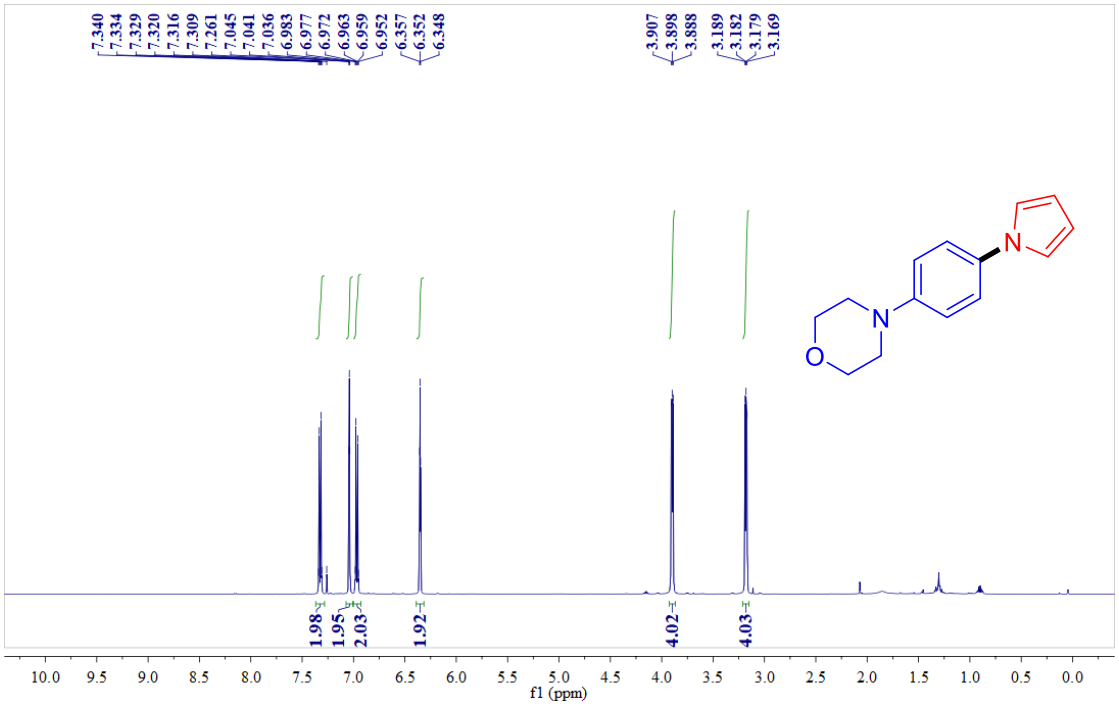
^{1}H NMR Spectrum of **3c**



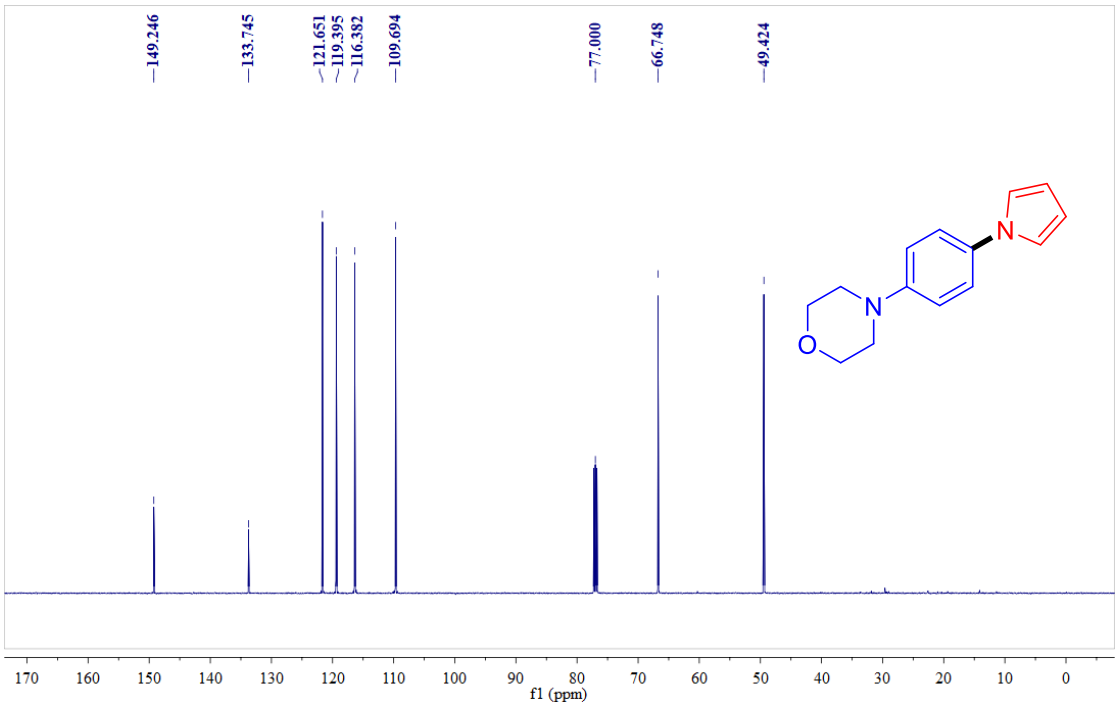
^{13}C NMR Spectrum of **3c**



^{1}H NMR Spectrum of **3d**



^{13}C NMR Spectrum of **3d**



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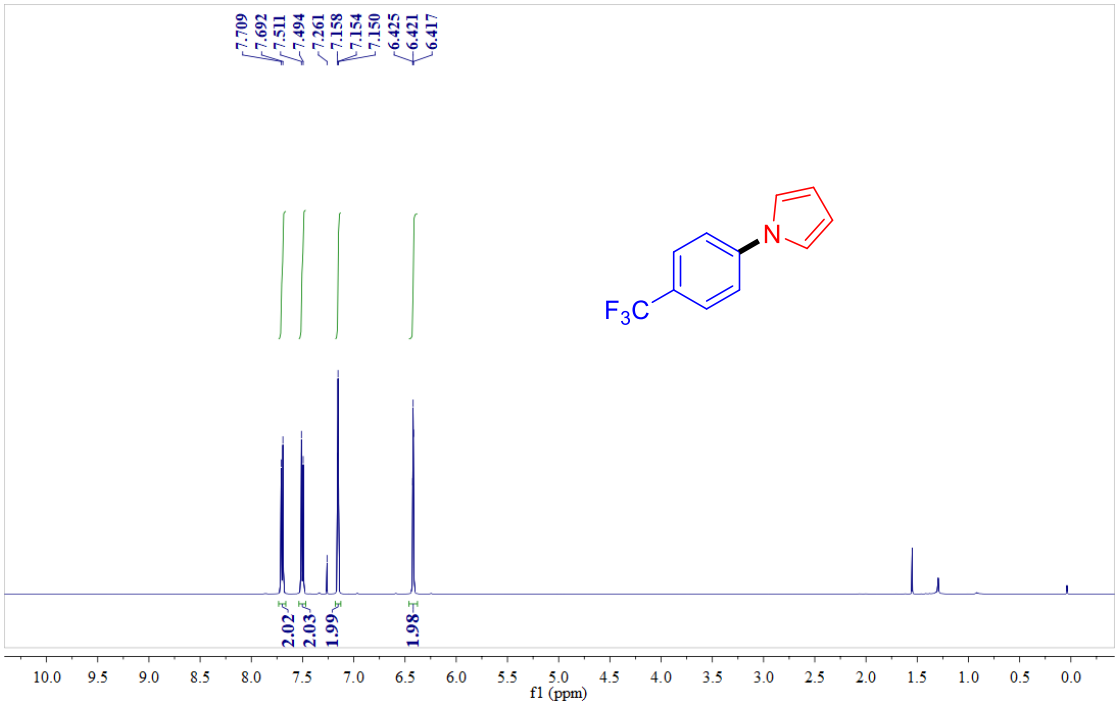
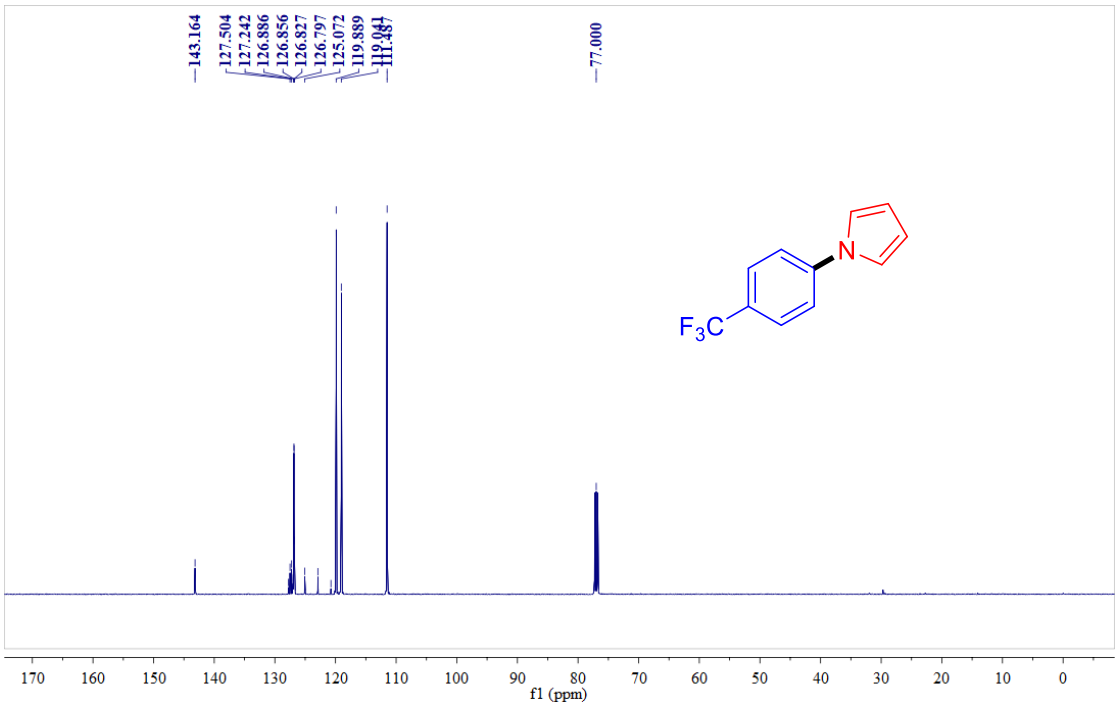
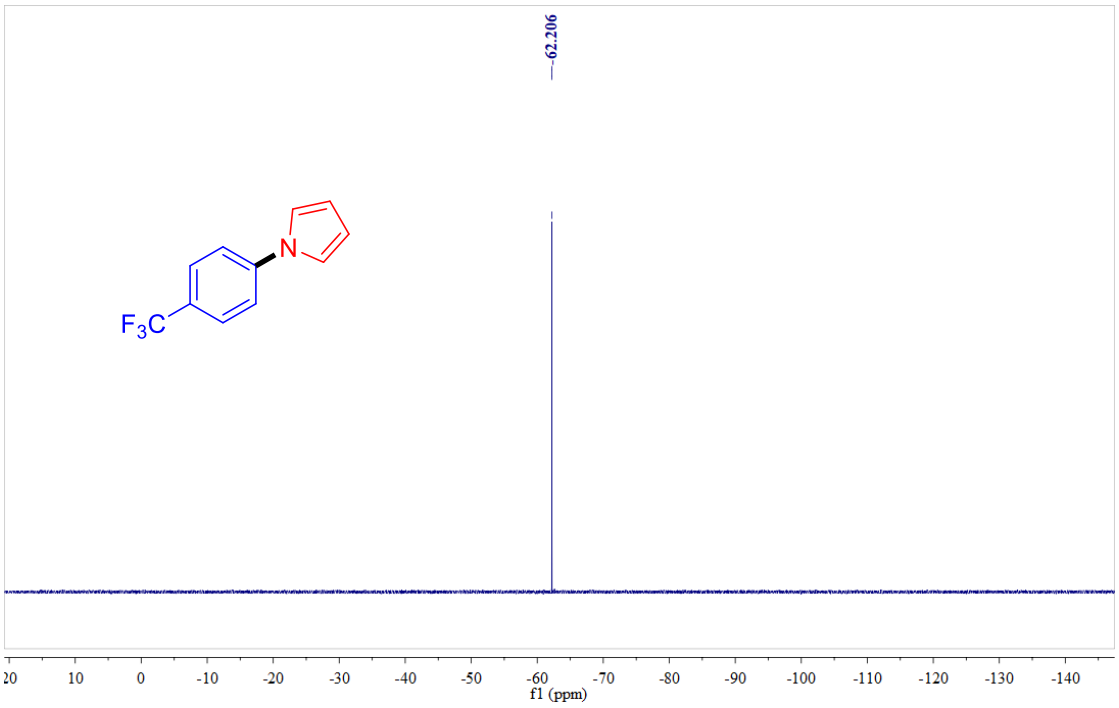


^{13}C NMR Spectrum of **3e**



^{19}F NMR Spectrum of **3e**



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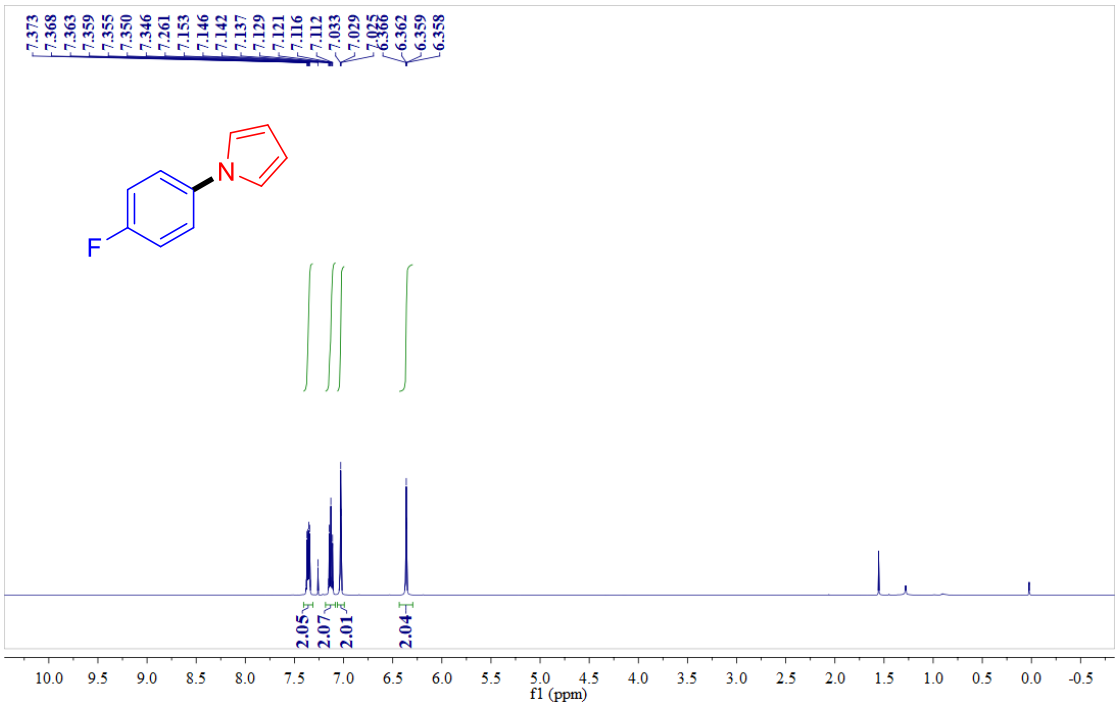

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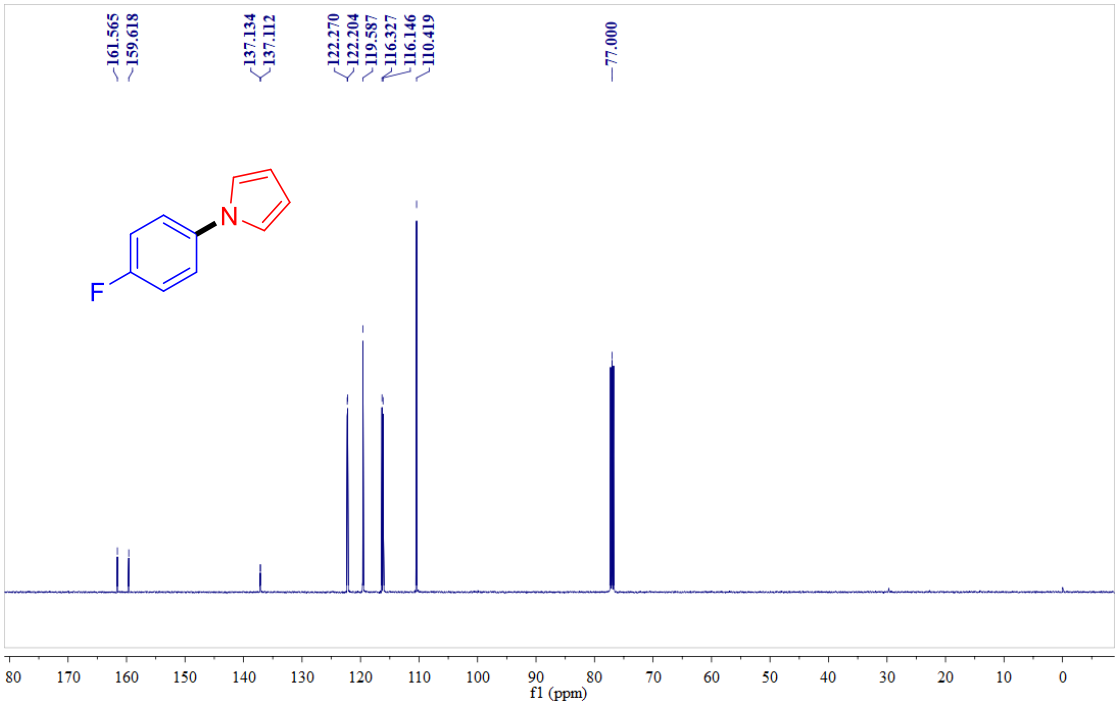
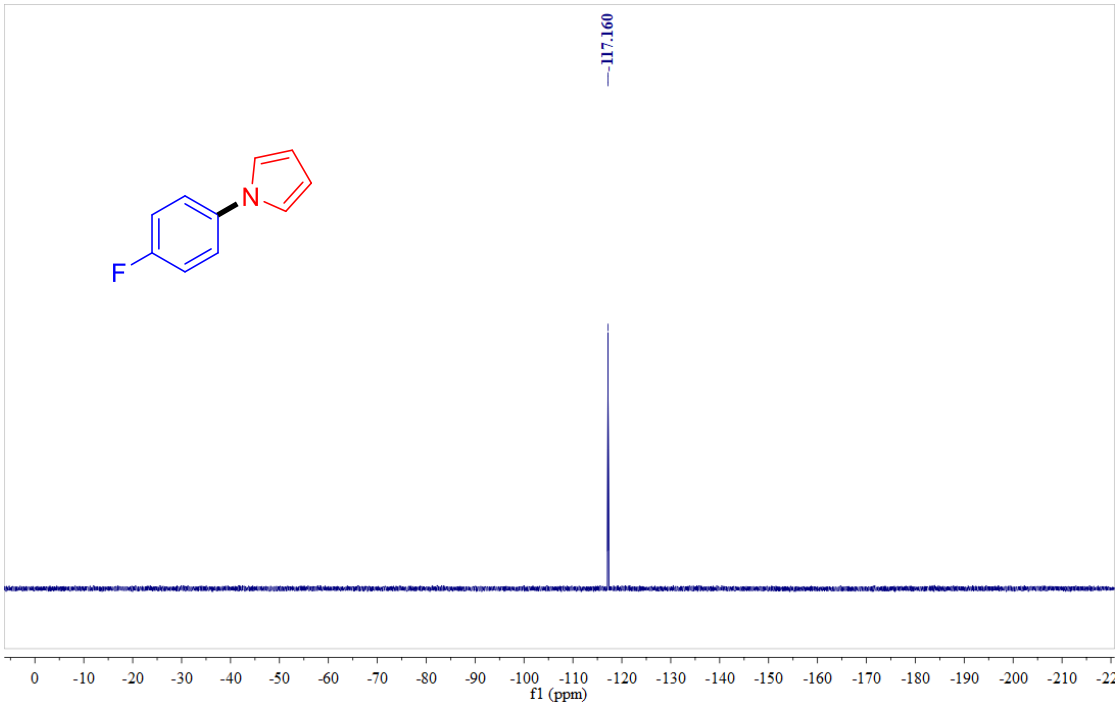
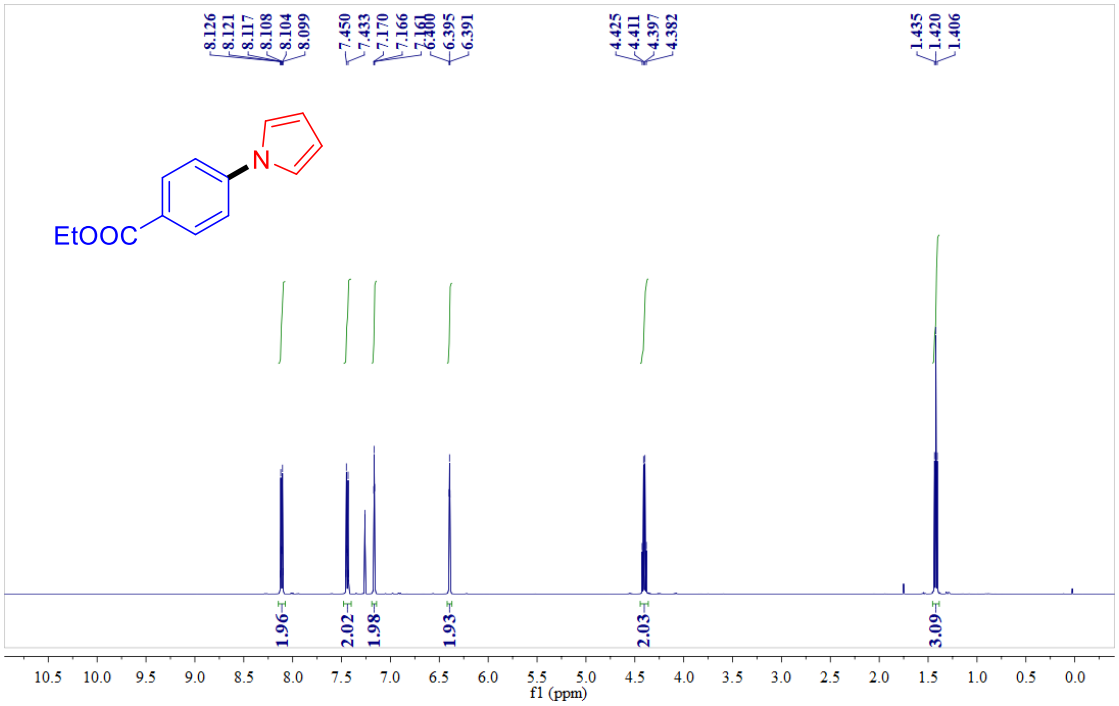


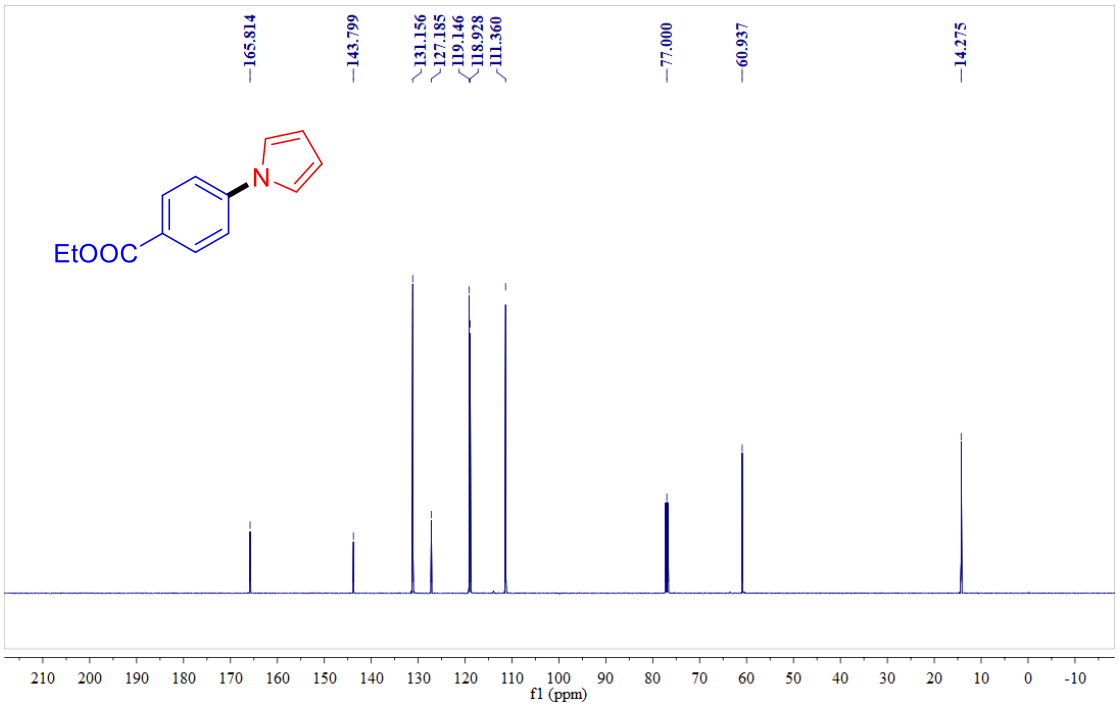
^{19}F NMR Spectrum of **3f**



^{1}H NMR Spectrum of **3g**



^{13}C NMR Spectrum of **3g**



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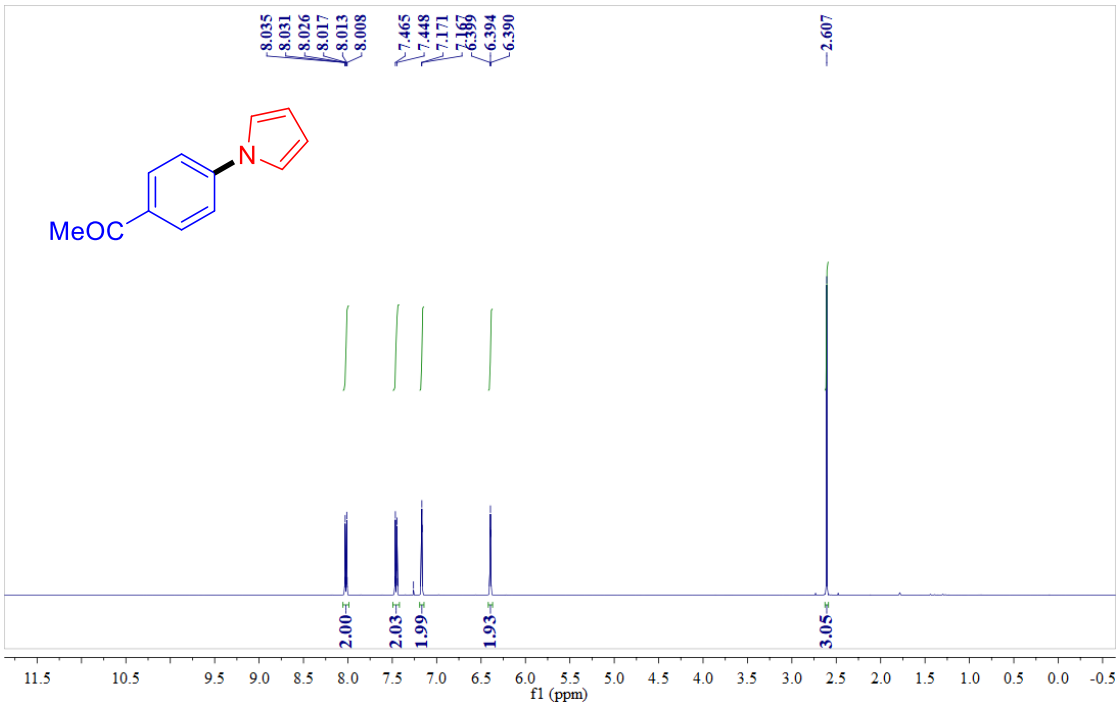
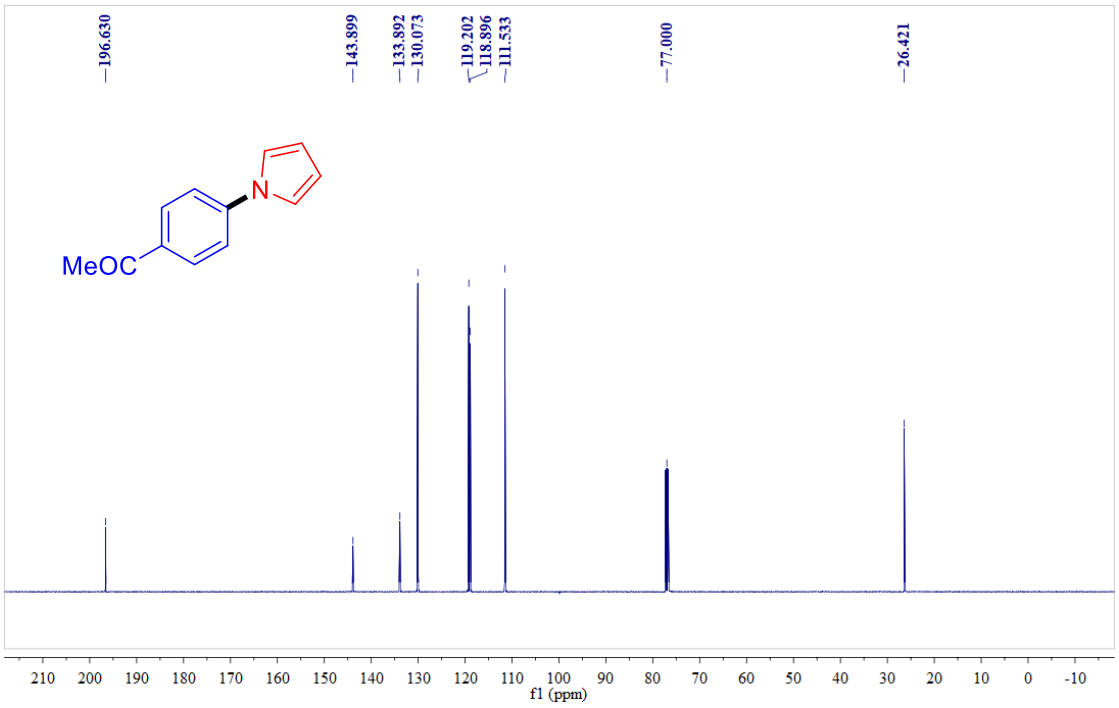
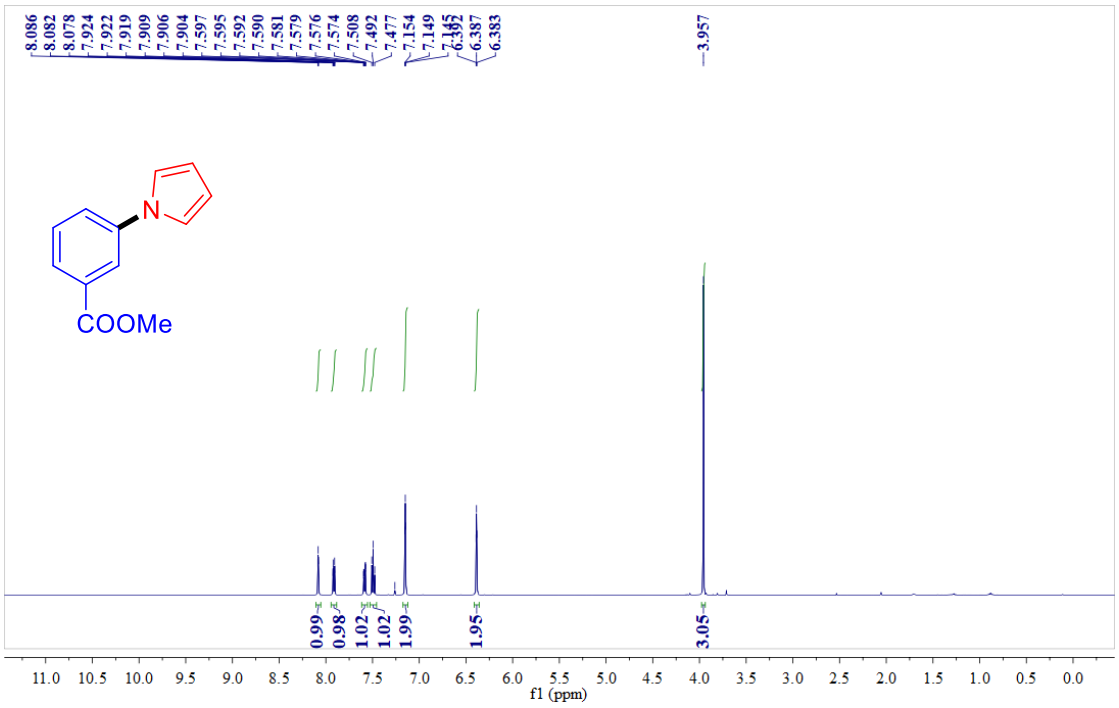


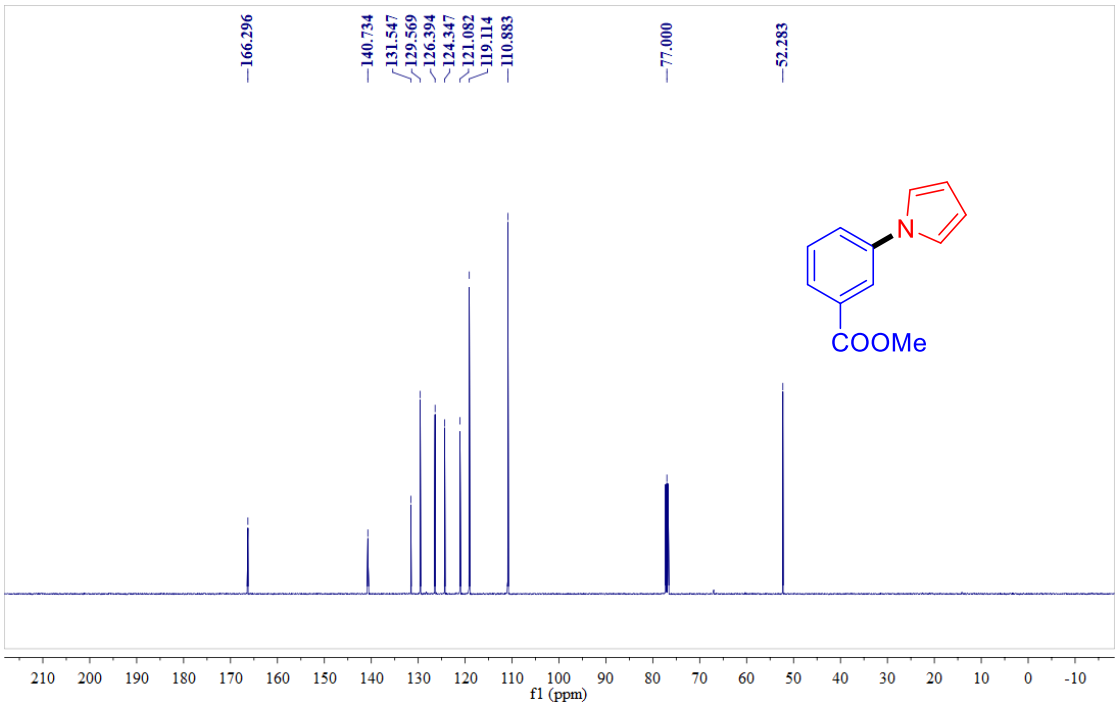
^{13}C NMR Spectrum of **3h**



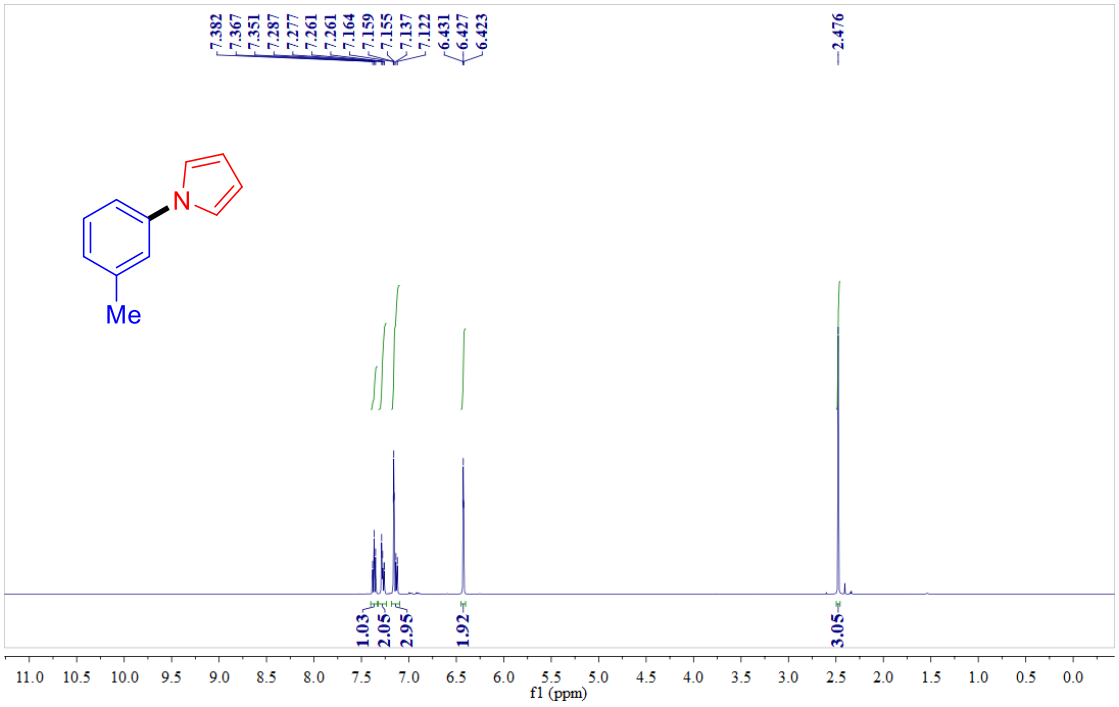
^{1}H NMR Spectrum of **3i**



^{13}C NMR Spectrum of **3i**



^{1}H NMR Spectrum of **3j**



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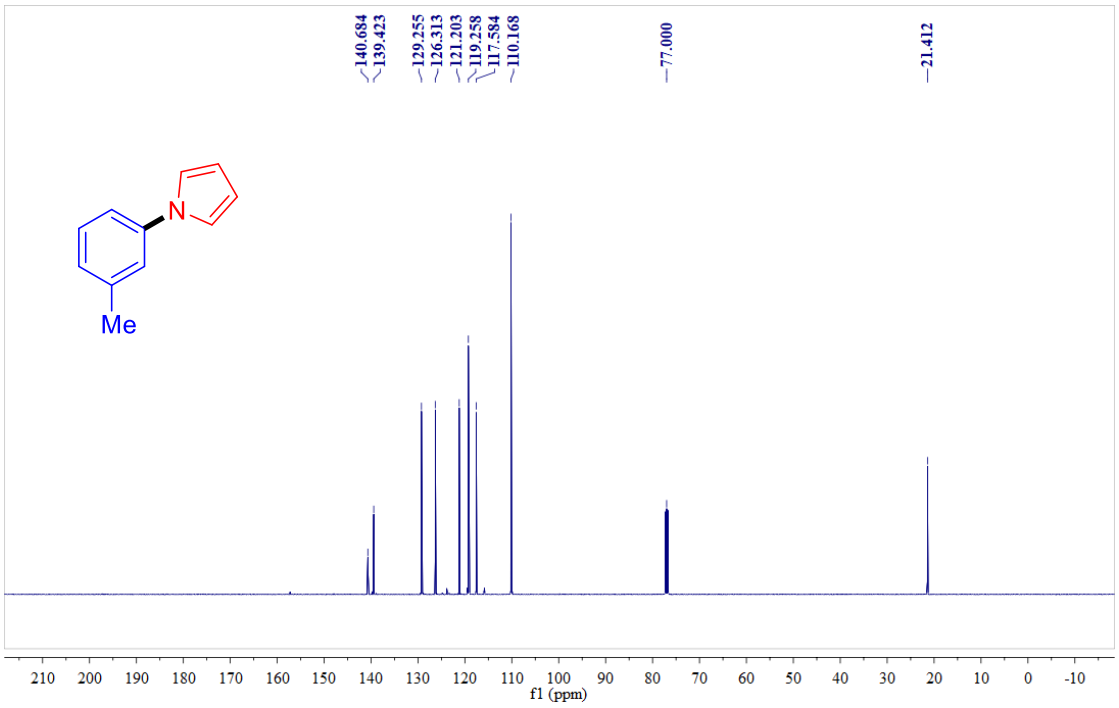

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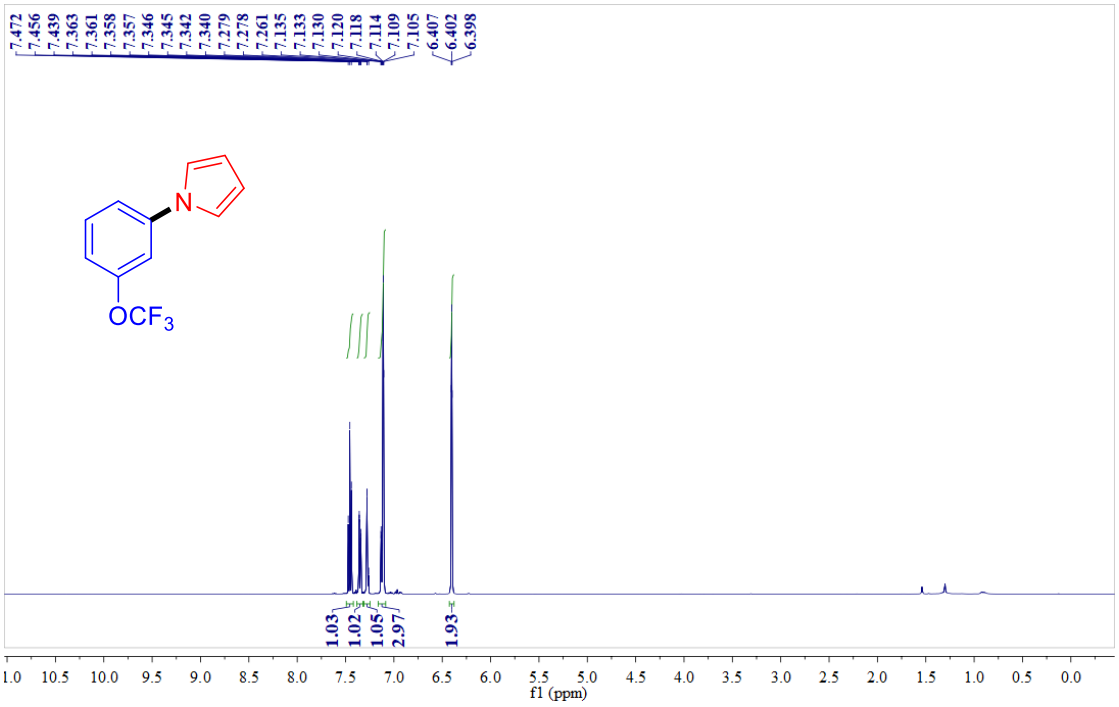

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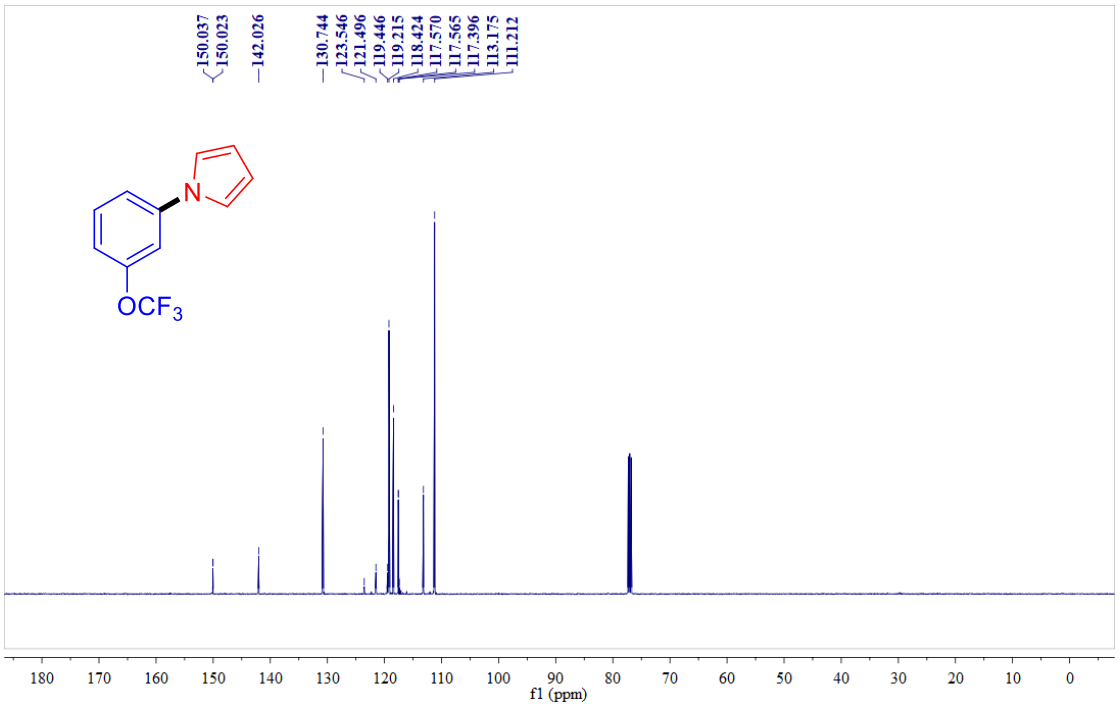
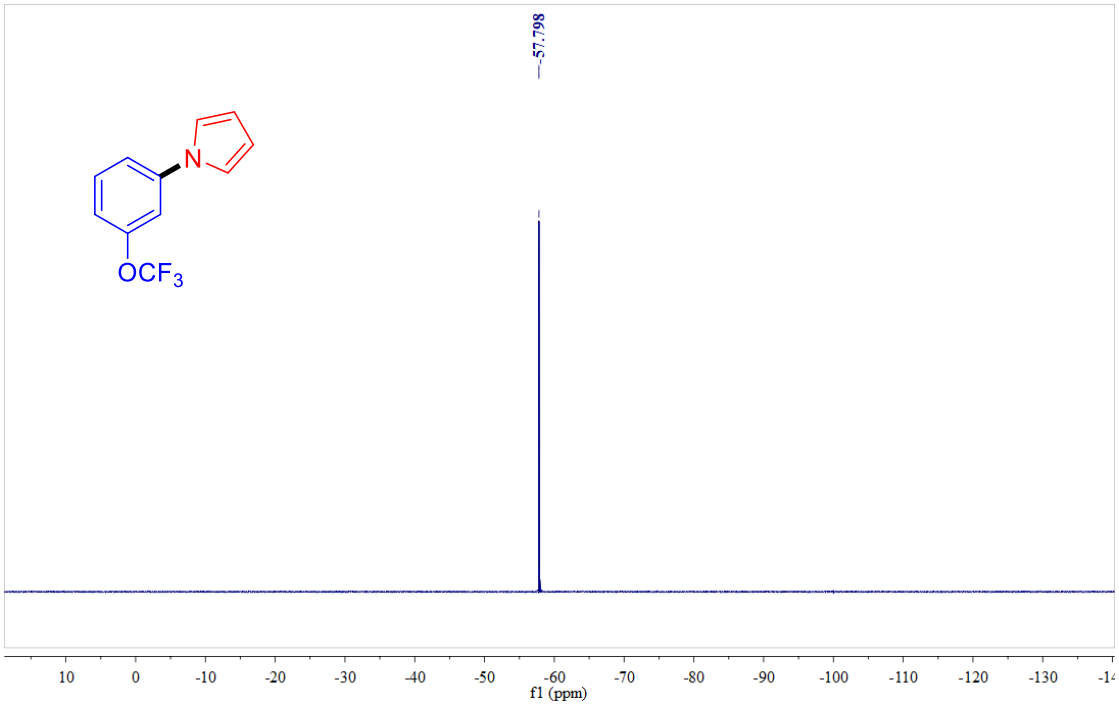


^{19}F NMR Spectrum of **3k**



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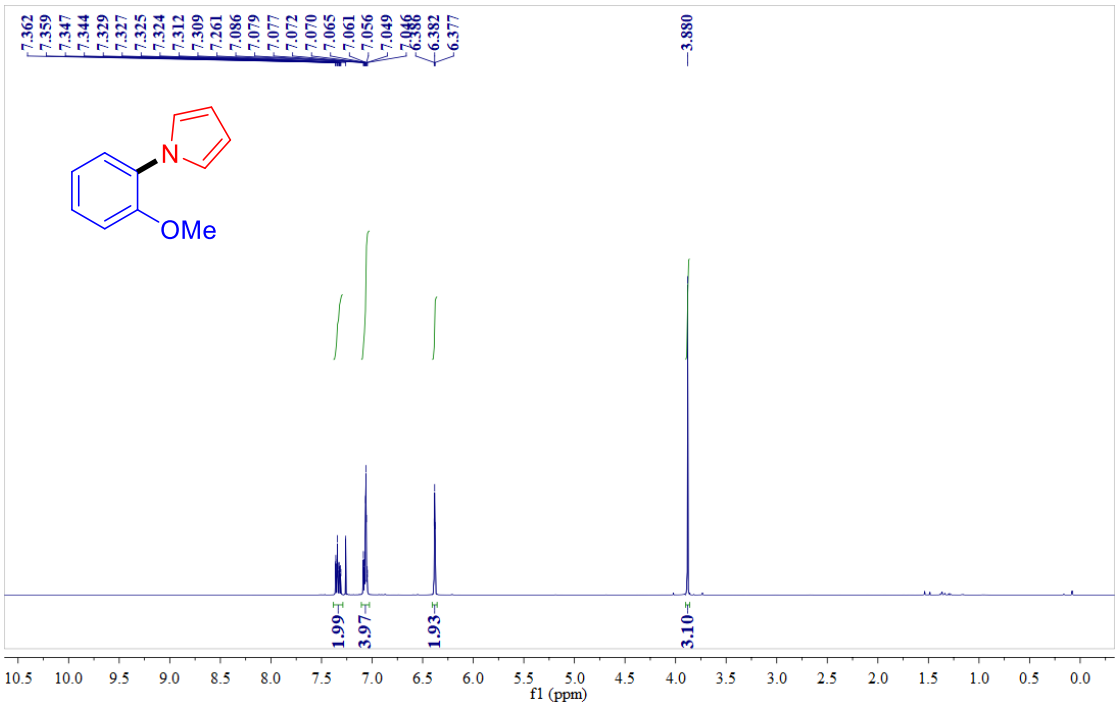
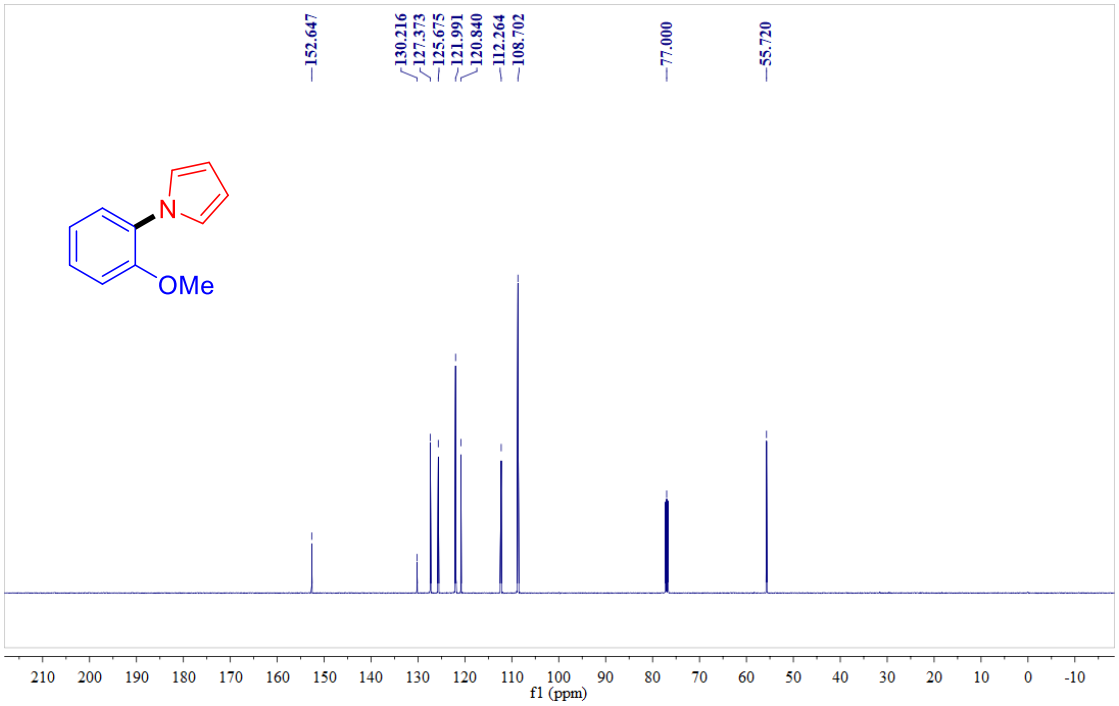


^{13}C NMR Spectrum of **3l**



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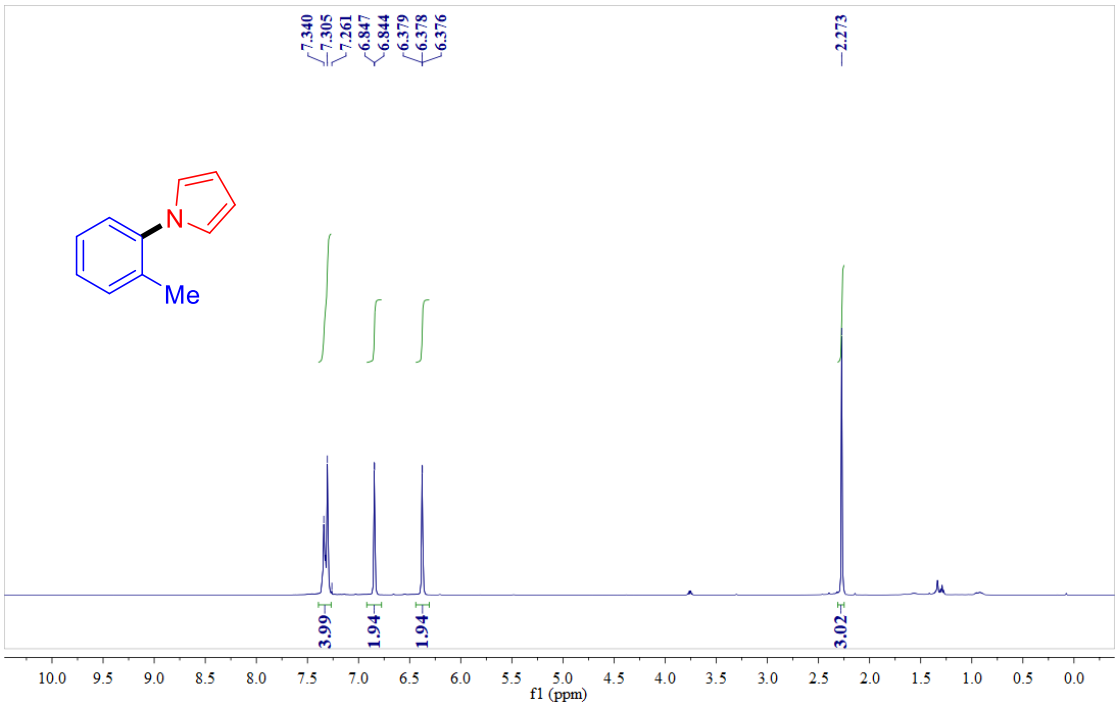
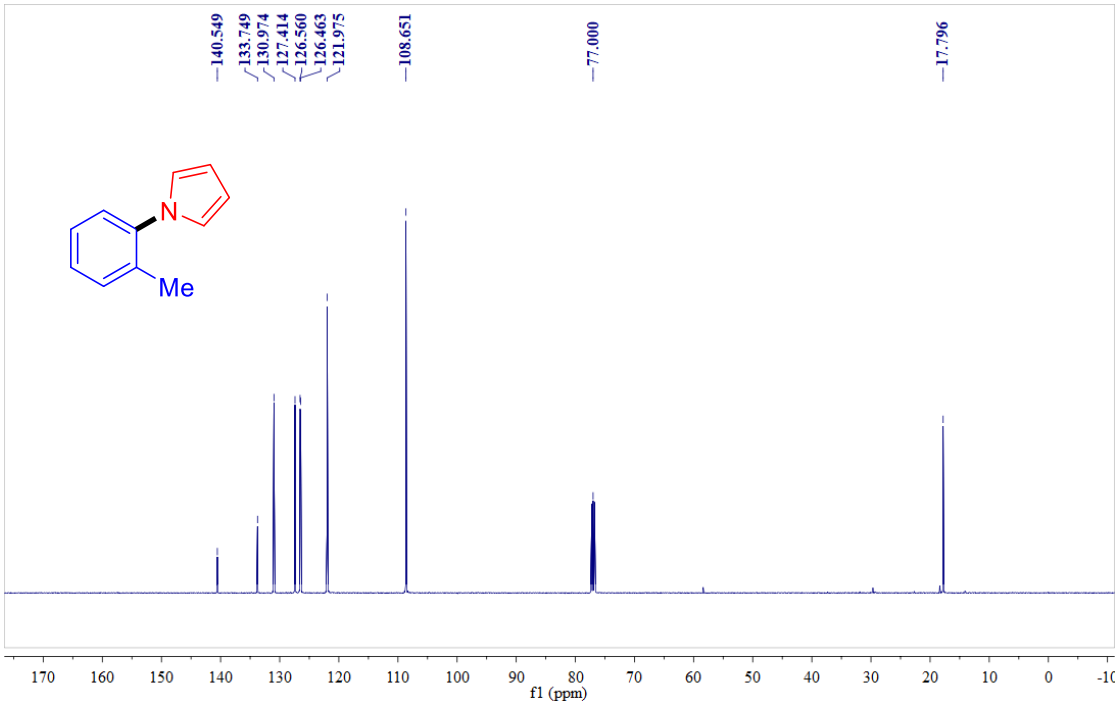
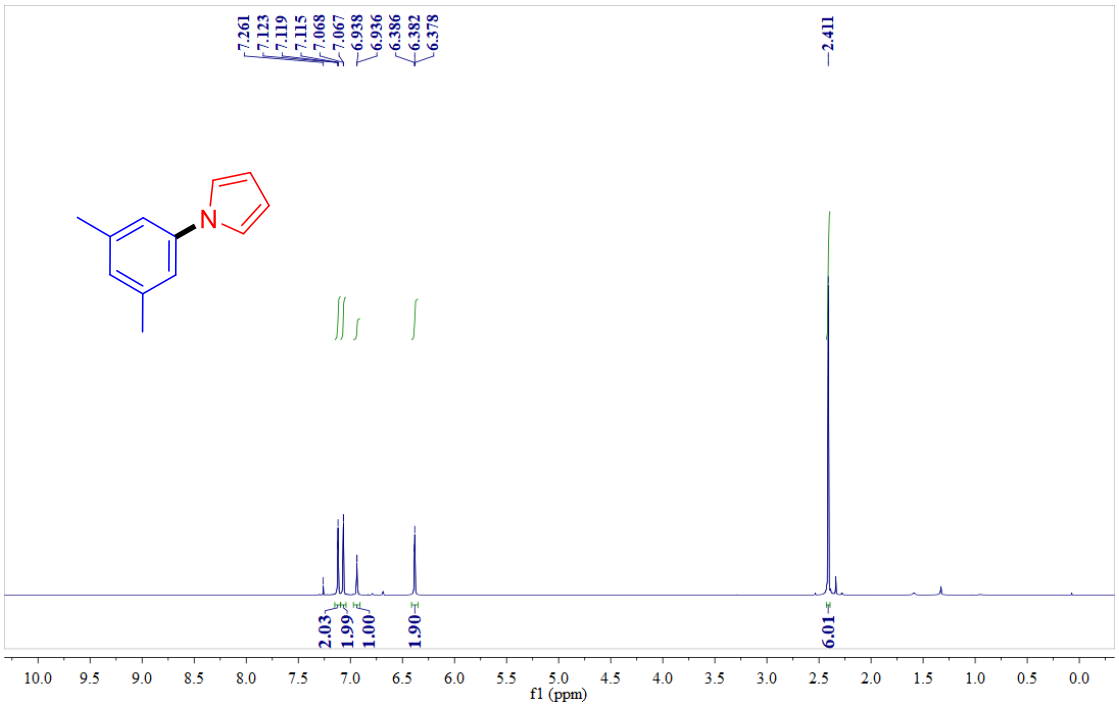


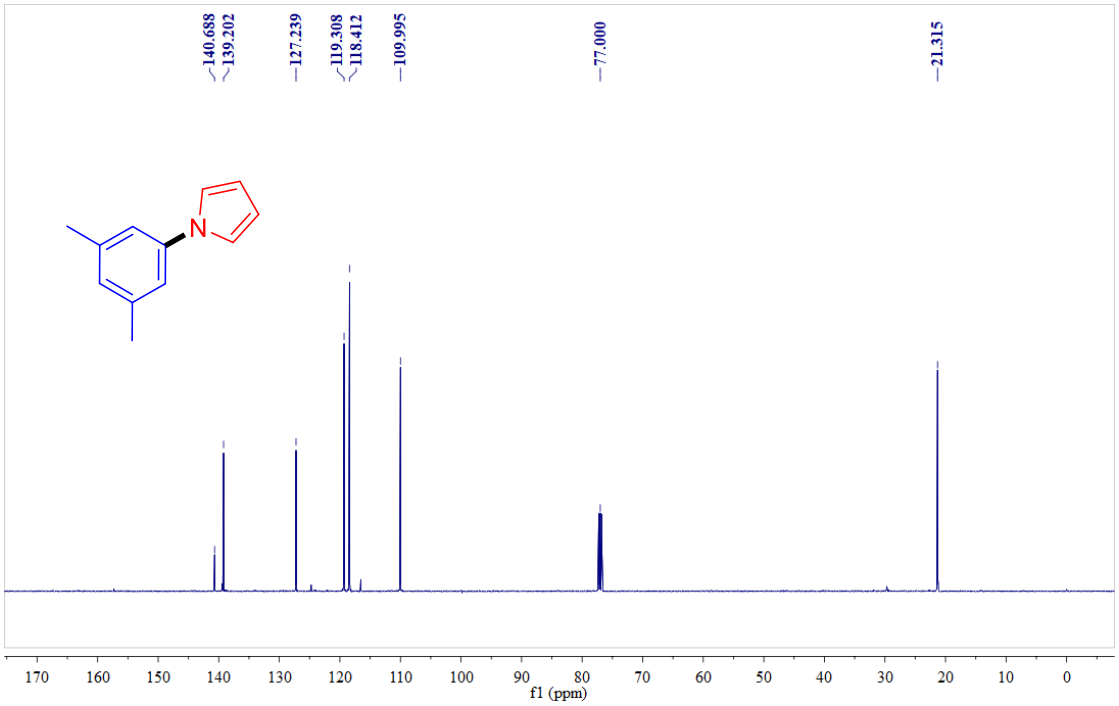
^{13}C NMR Spectrum of **3m**



^{1}H NMR Spectrum of **3n**



^{13}C NMR Spectrum of **3n**



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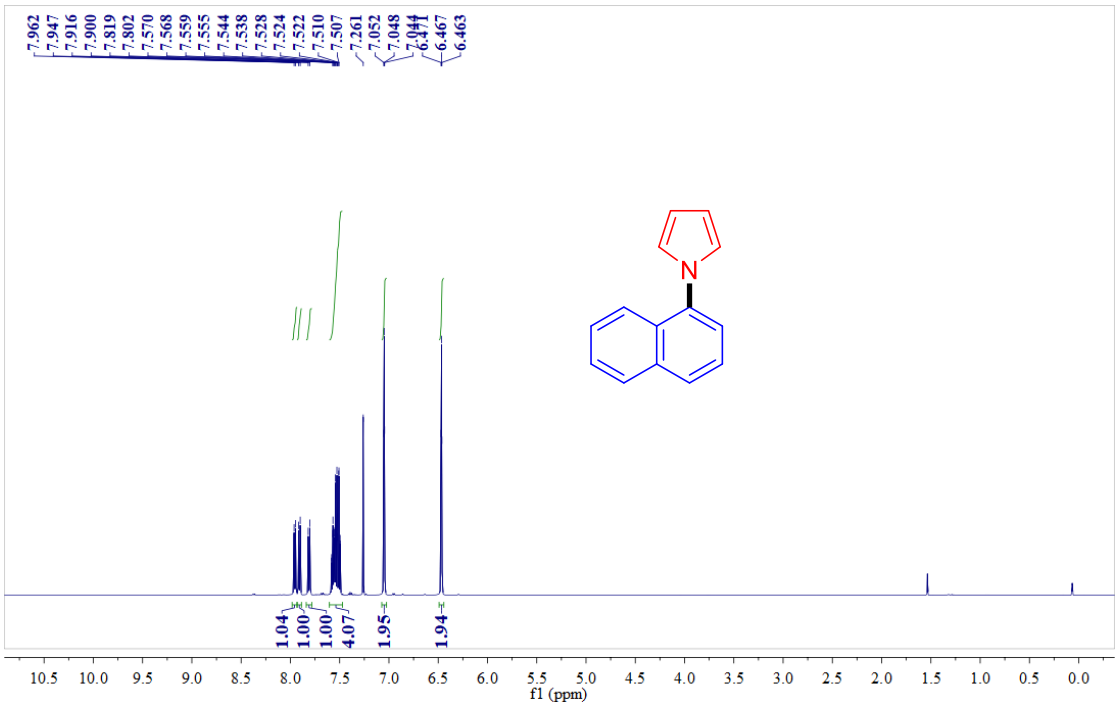
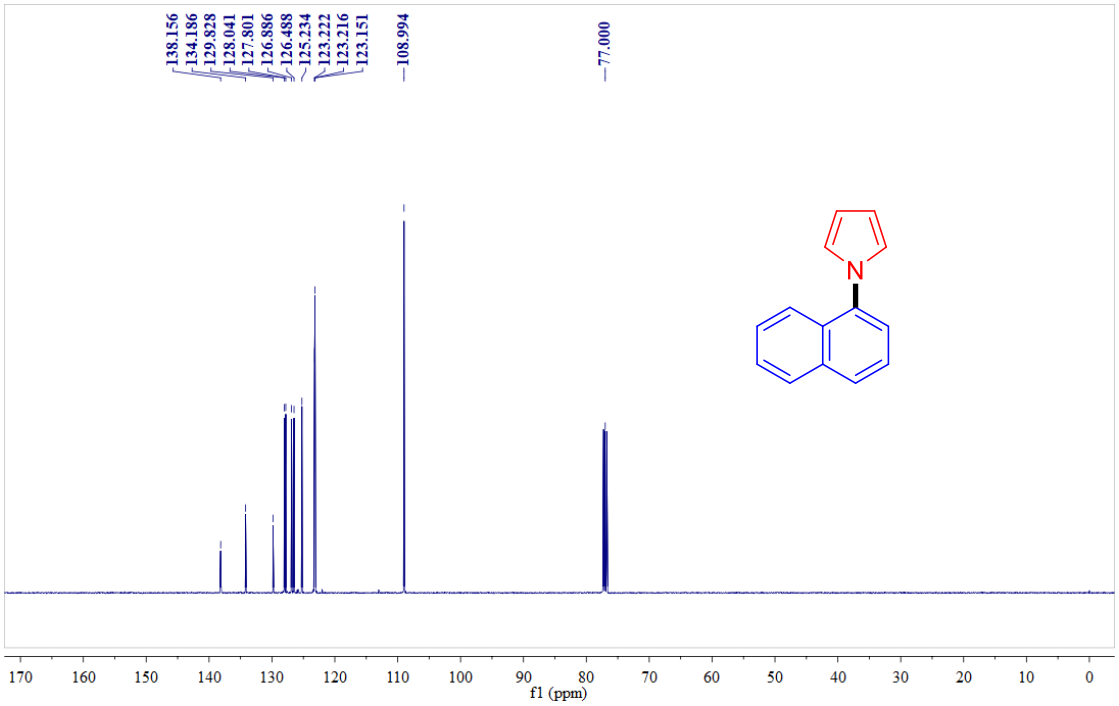


^{13}C NMR Spectrum of **3o**



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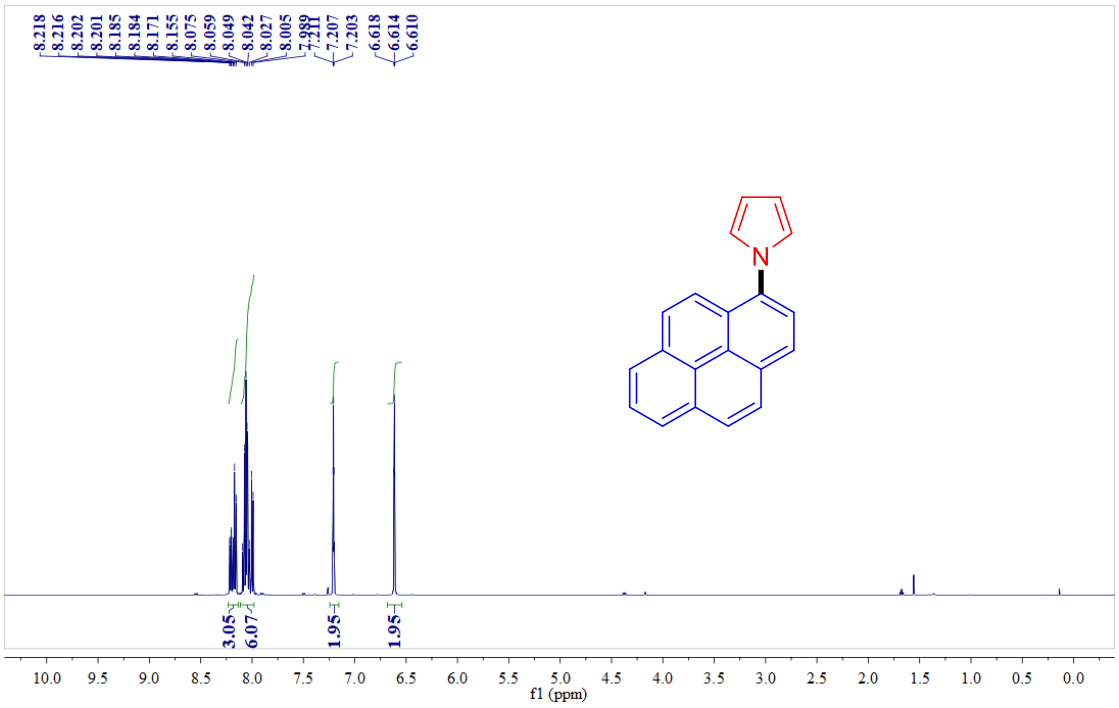
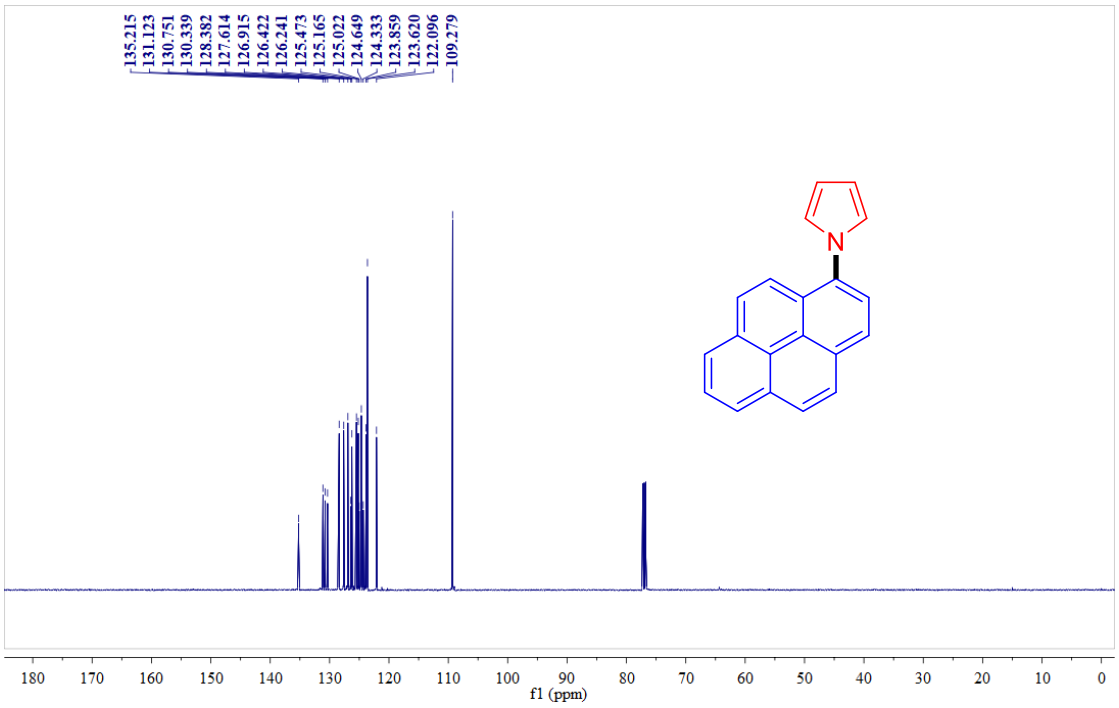
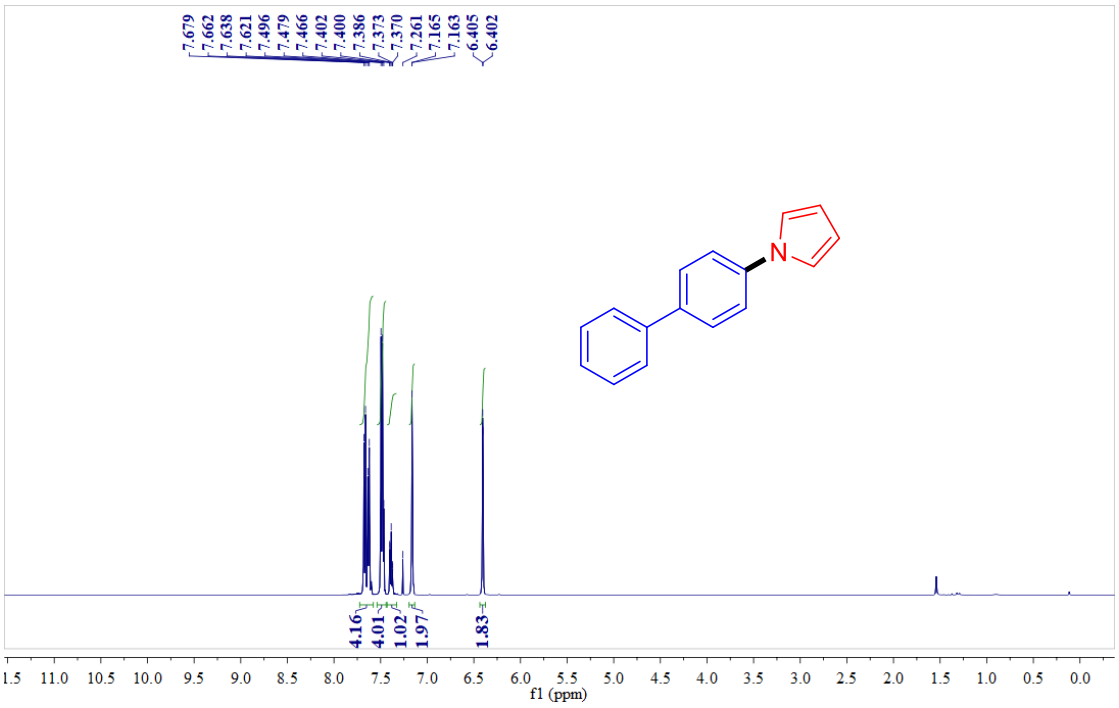


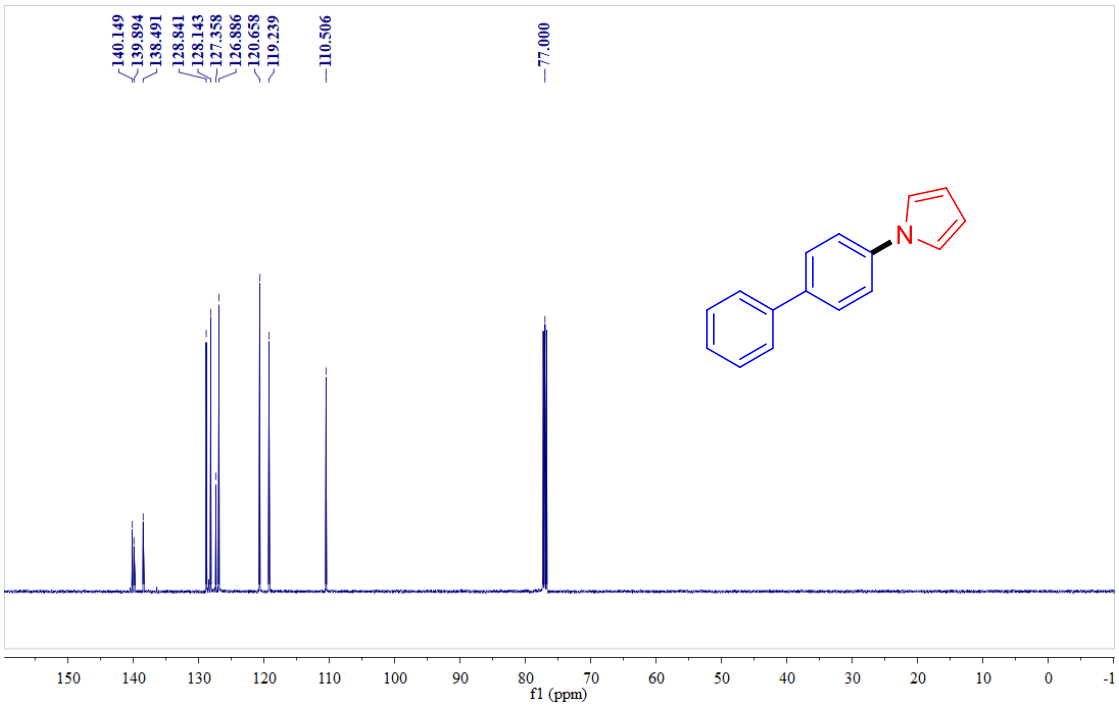
^{13}C NMR Spectrum of **3p**



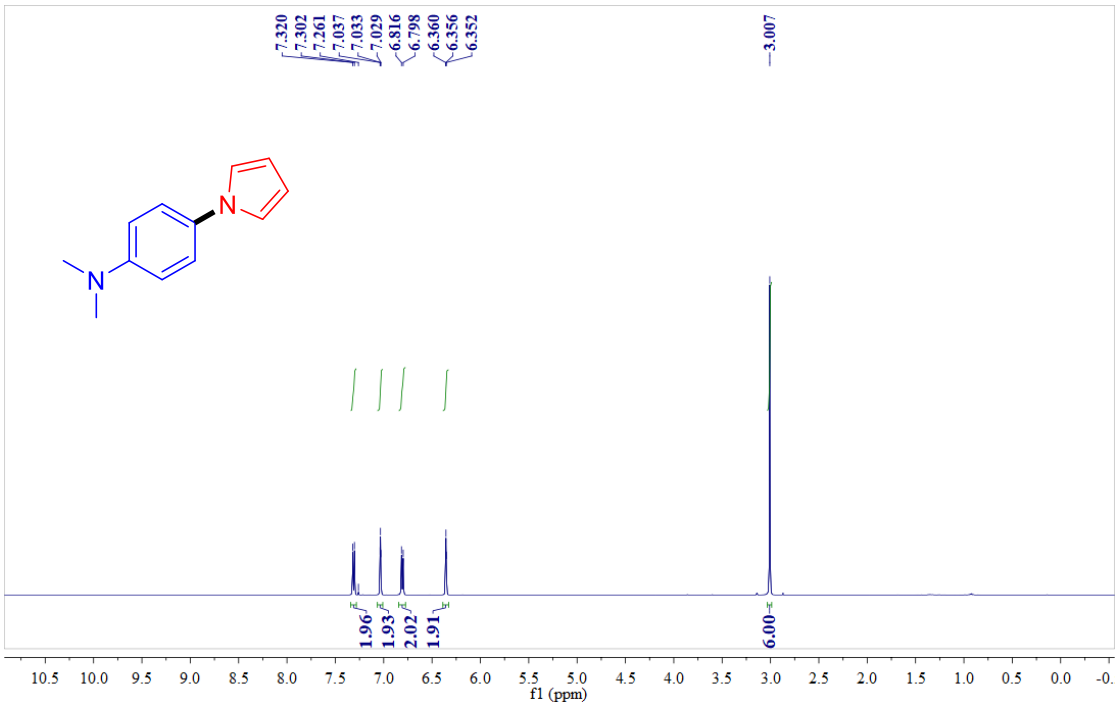
^{1}H NMR Spectrum of **3q**



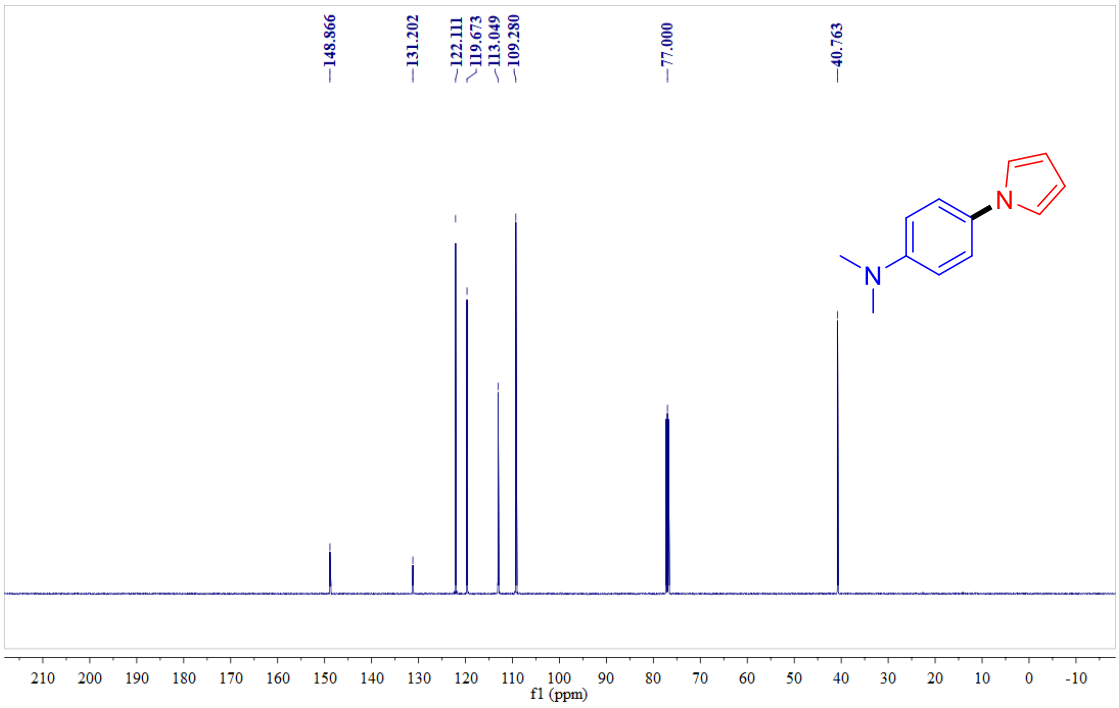
^{13}C NMR Spectrum of **3q**



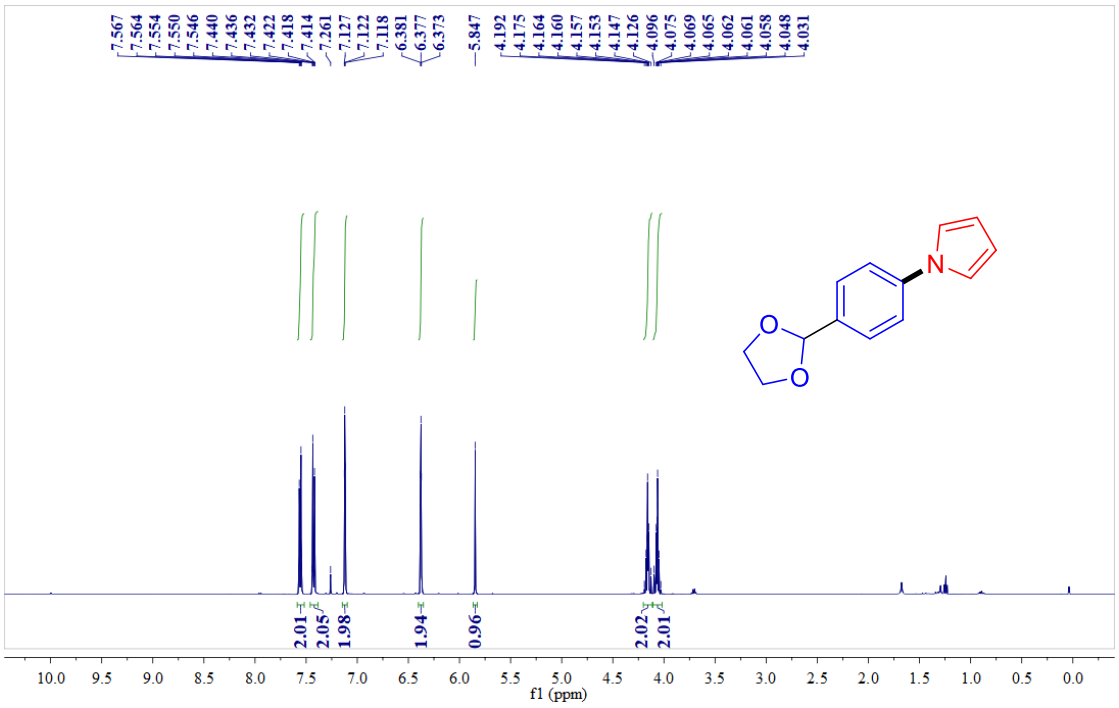
^{1}H NMR Spectrum of **3r**



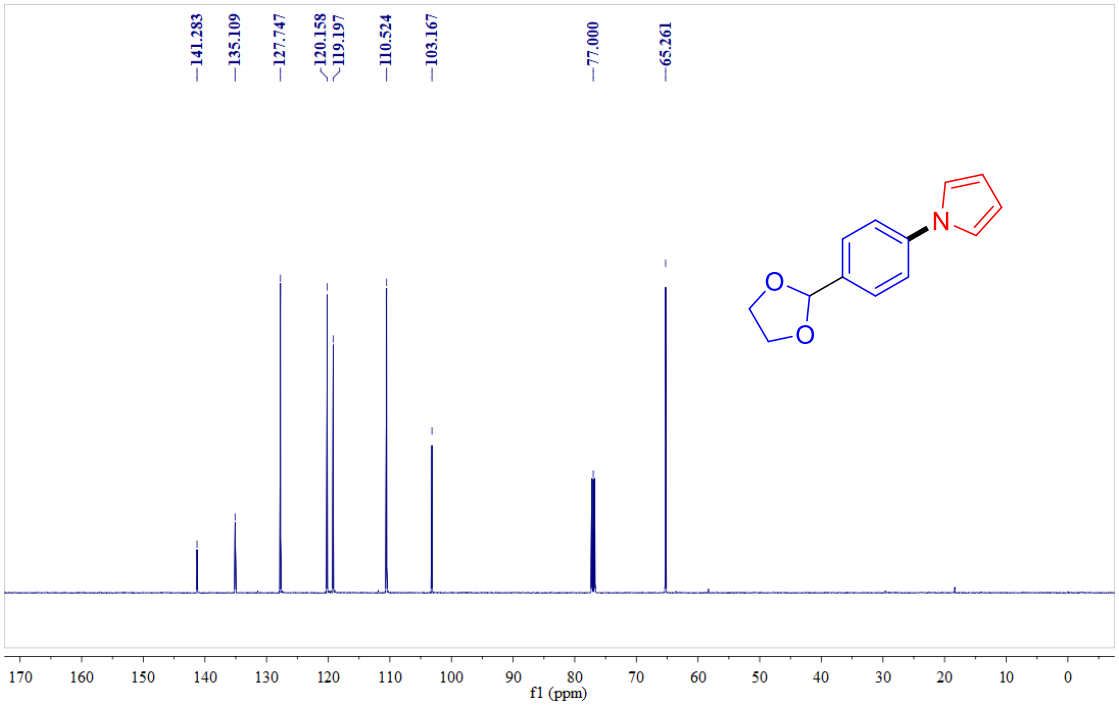
^{13}C NMR Spectrum of **3r**



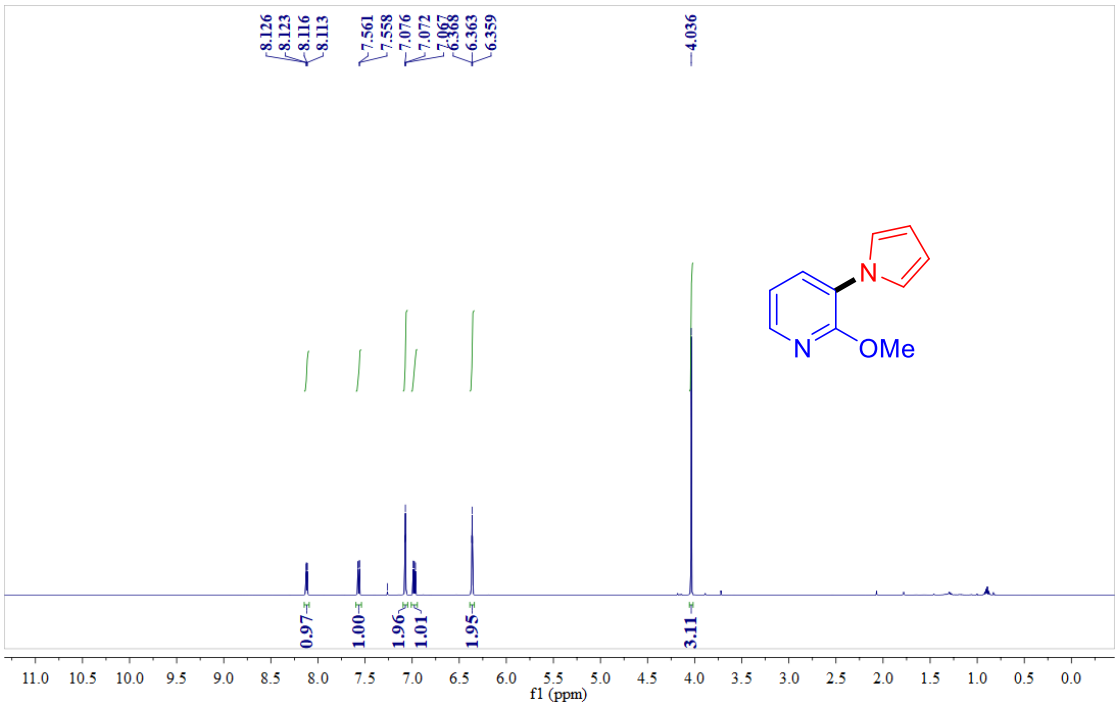
^{1}H NMR Spectrum of **3s**



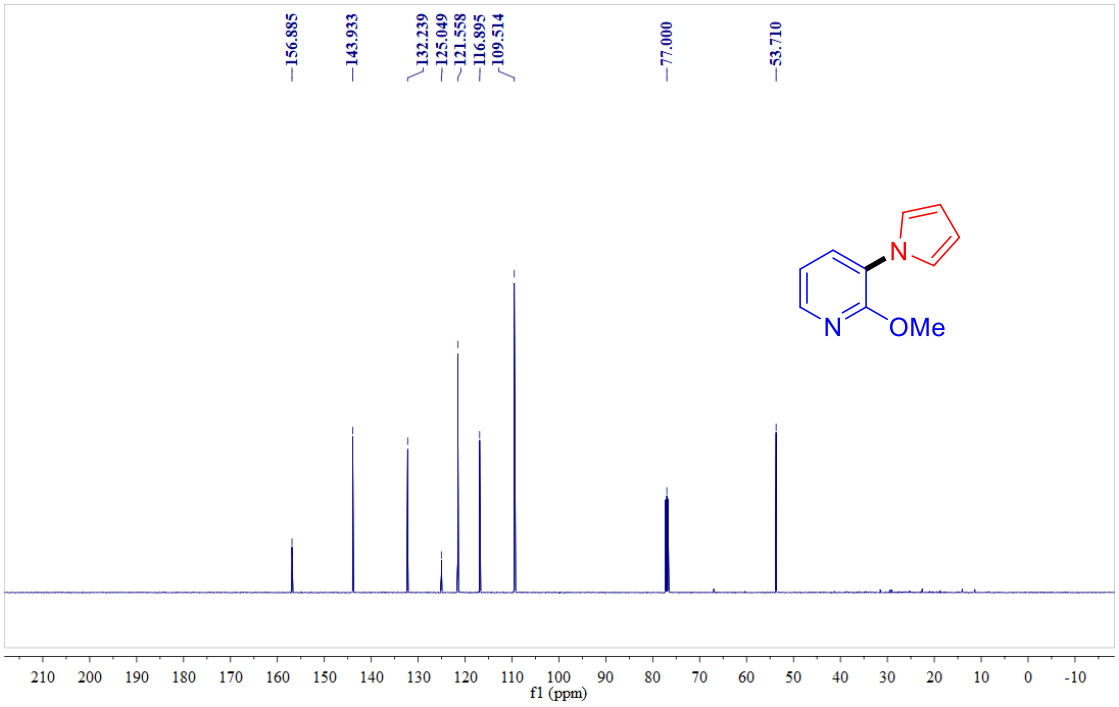
^{13}C NMR Spectrum of **3s**



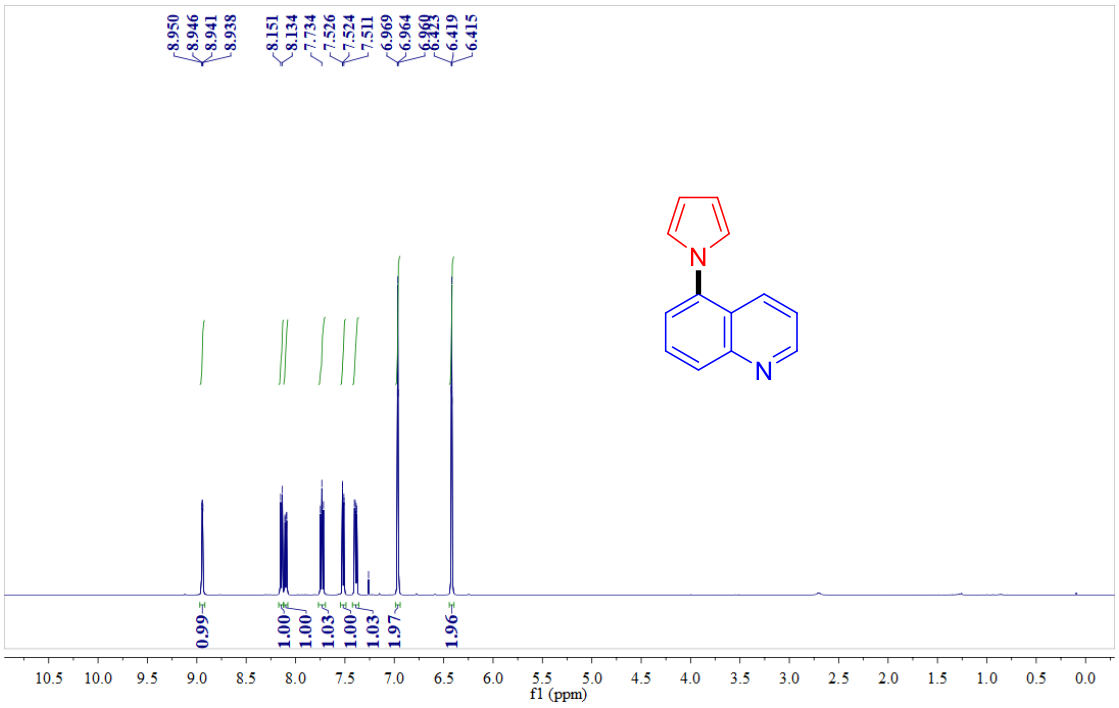
^{1}H NMR Spectrum of **3t**



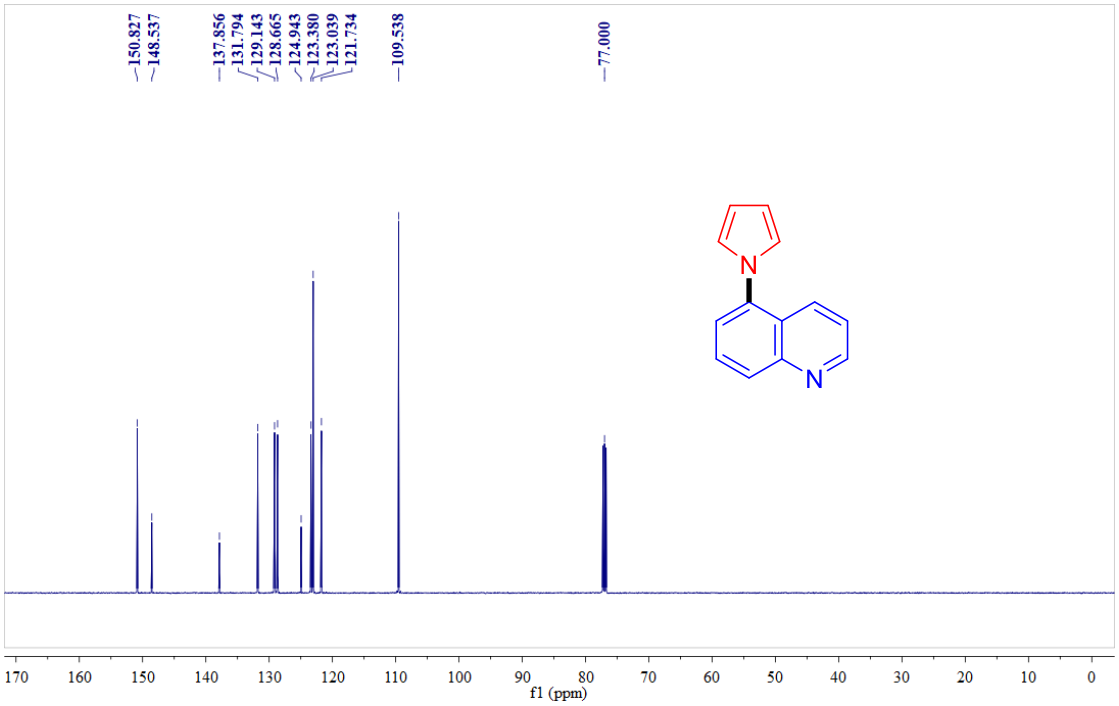
^{13}C NMR Spectrum of **3t**



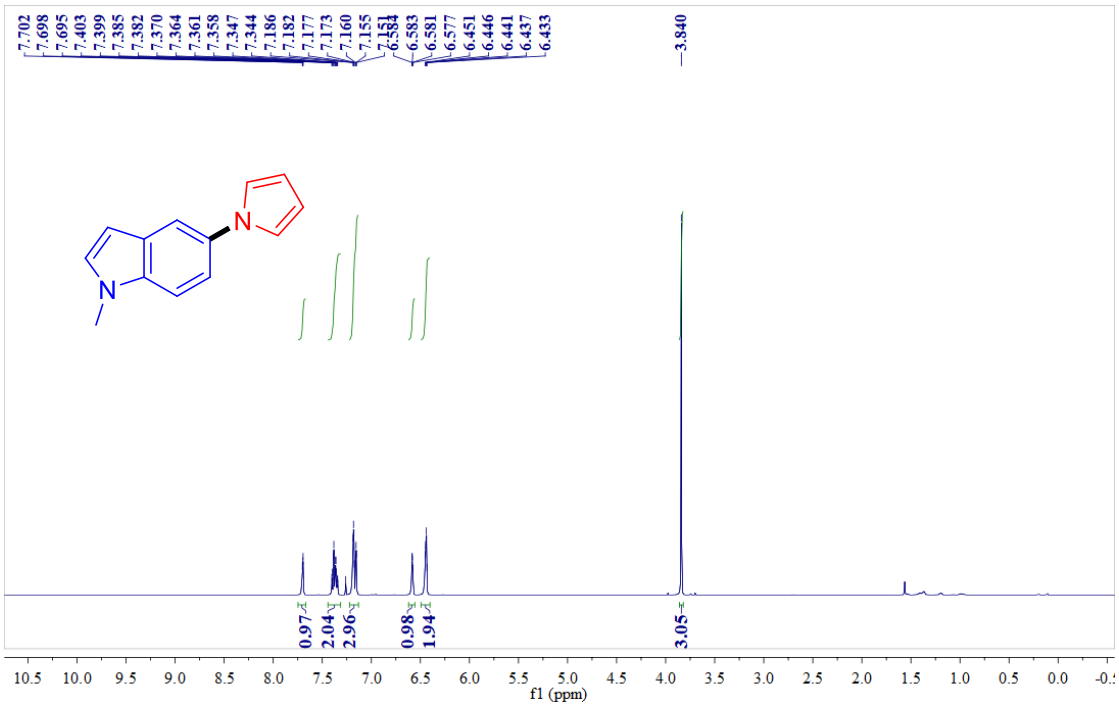
^{1}H NMR Spectrum of **3u**



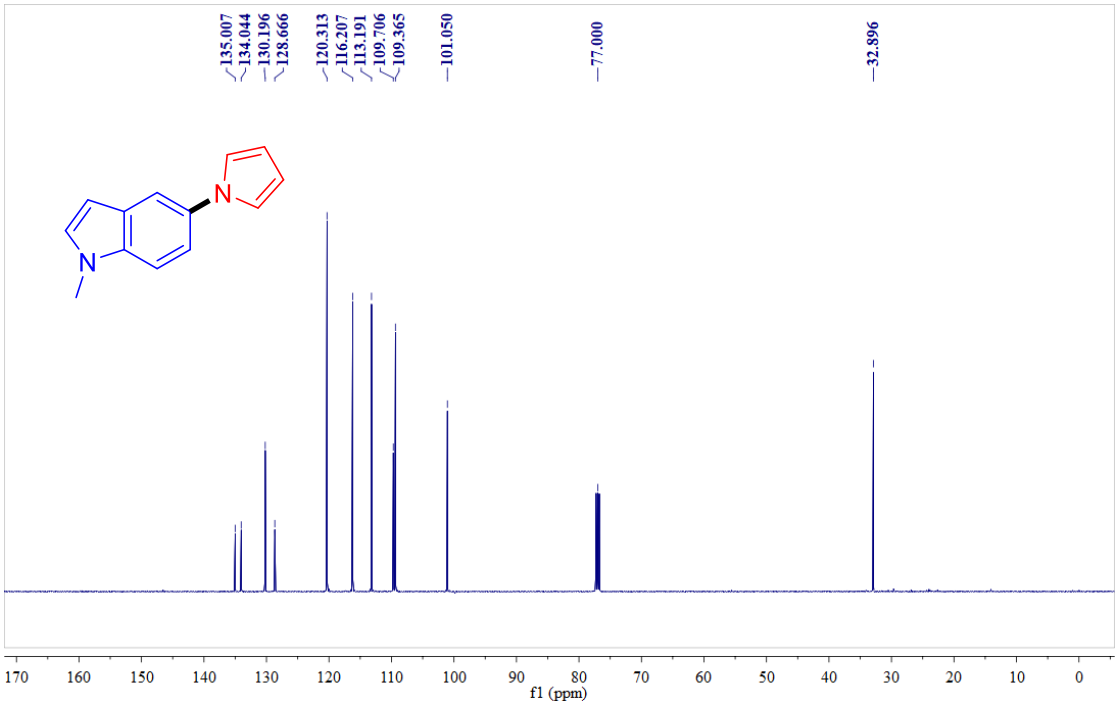
^{13}C NMR Spectrum of **3u**



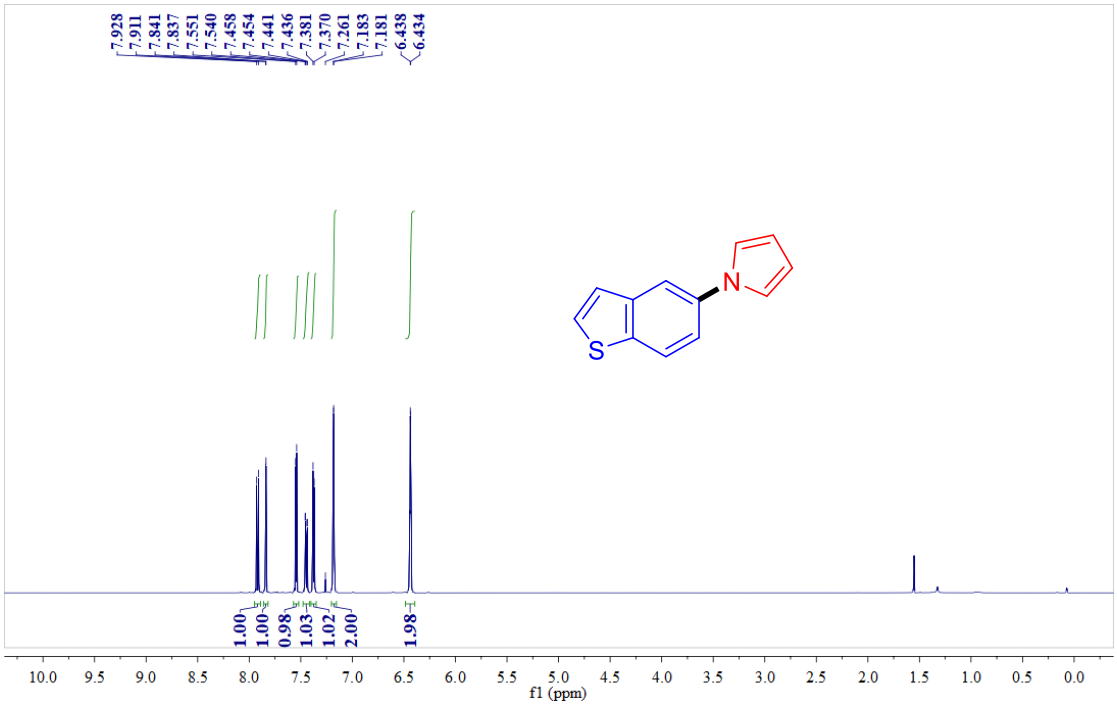
^{1}H NMR Spectrum of **3v**



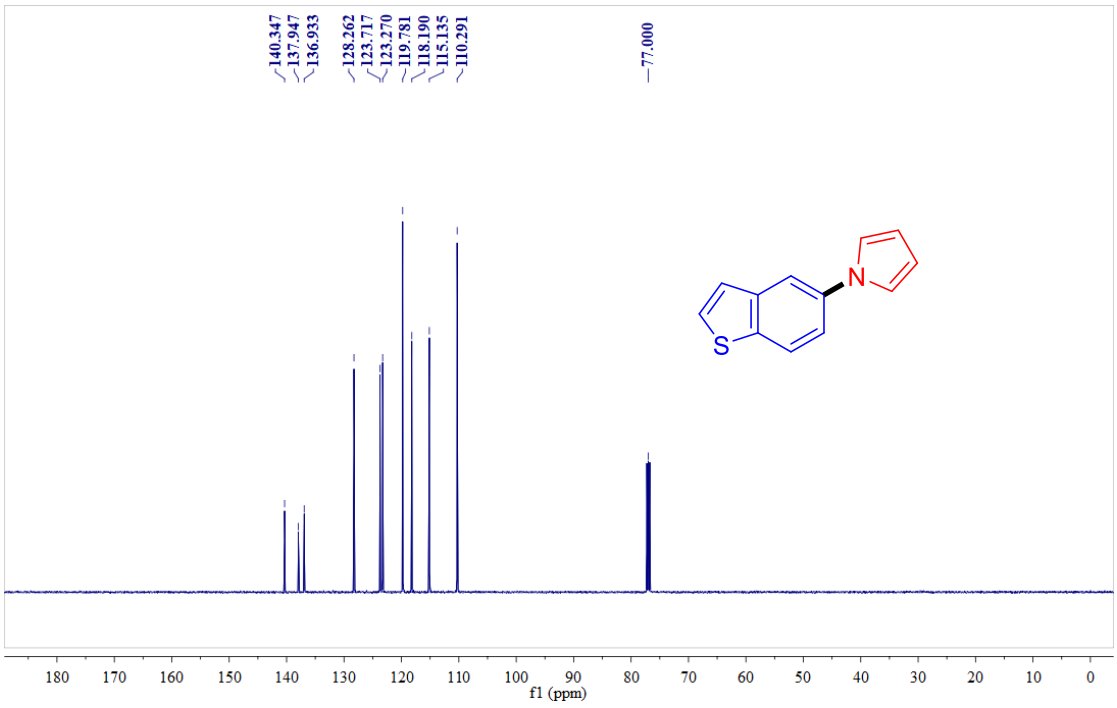
^{13}C NMR Spectrum of **3v**



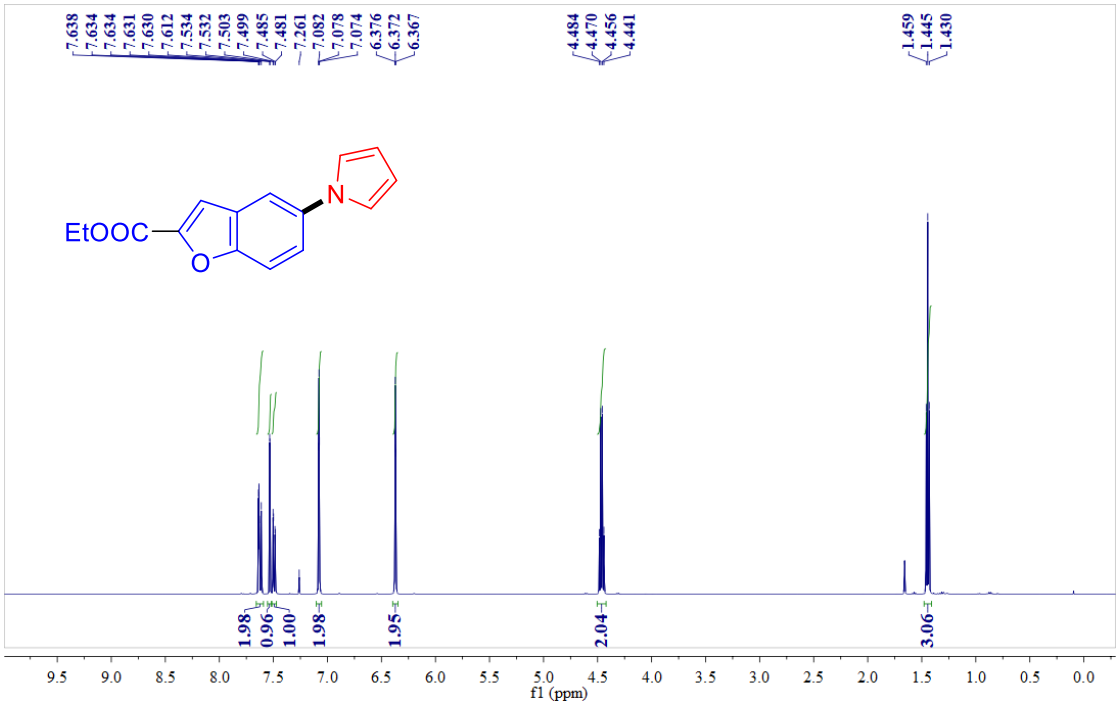
^{1}H NMR Spectrum of **3w**



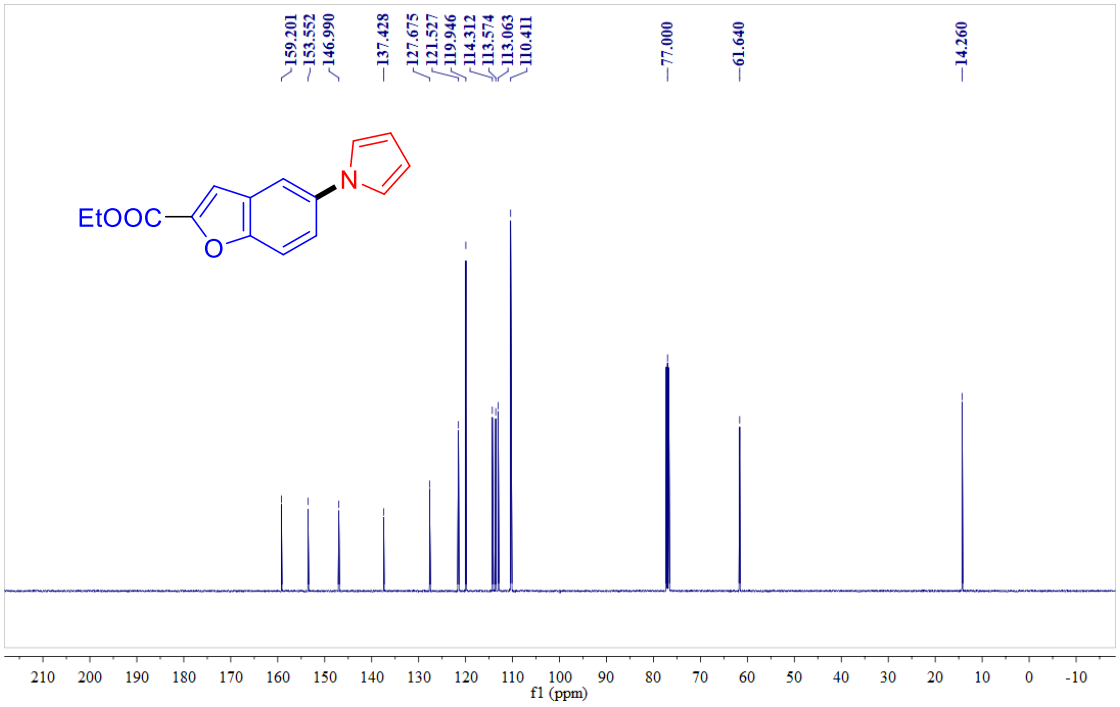
^{13}C NMR Spectrum of **3w**



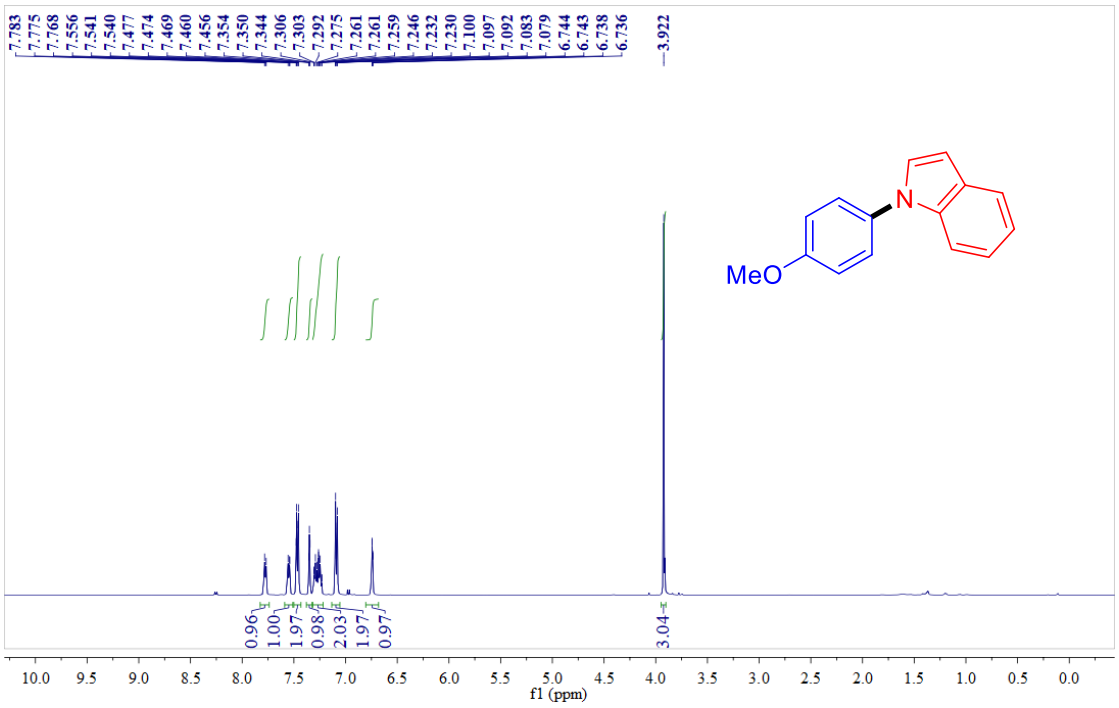
^{1}H NMR Spectrum of **3x**



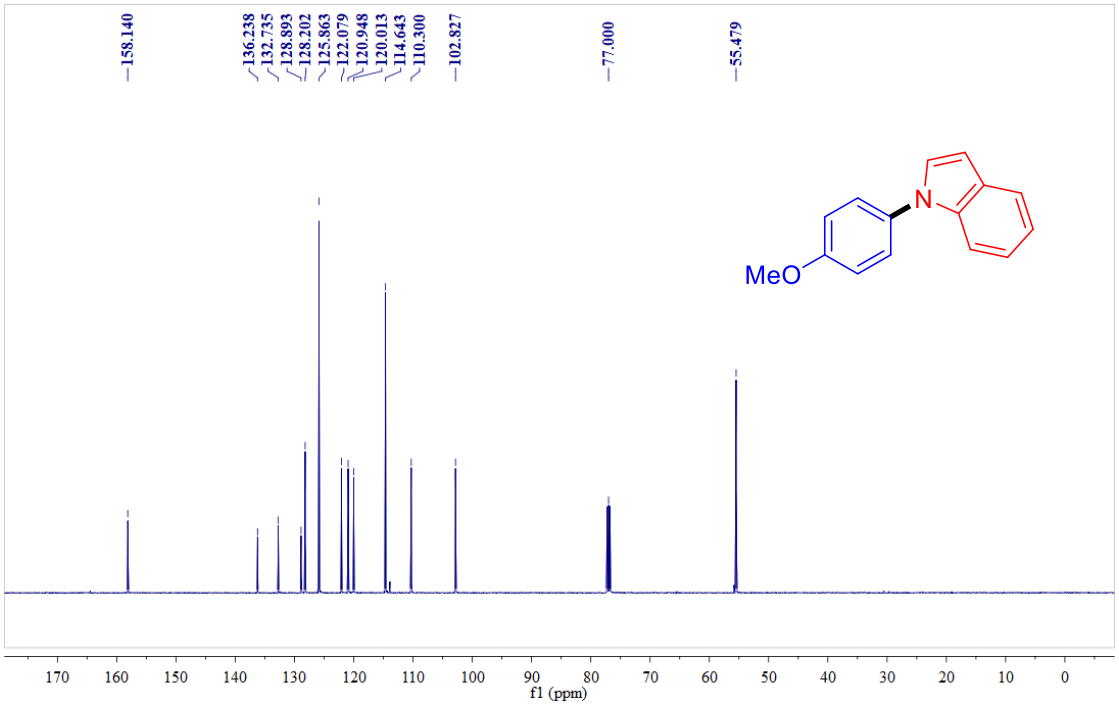
^{13}C NMR Spectrum of **3x**



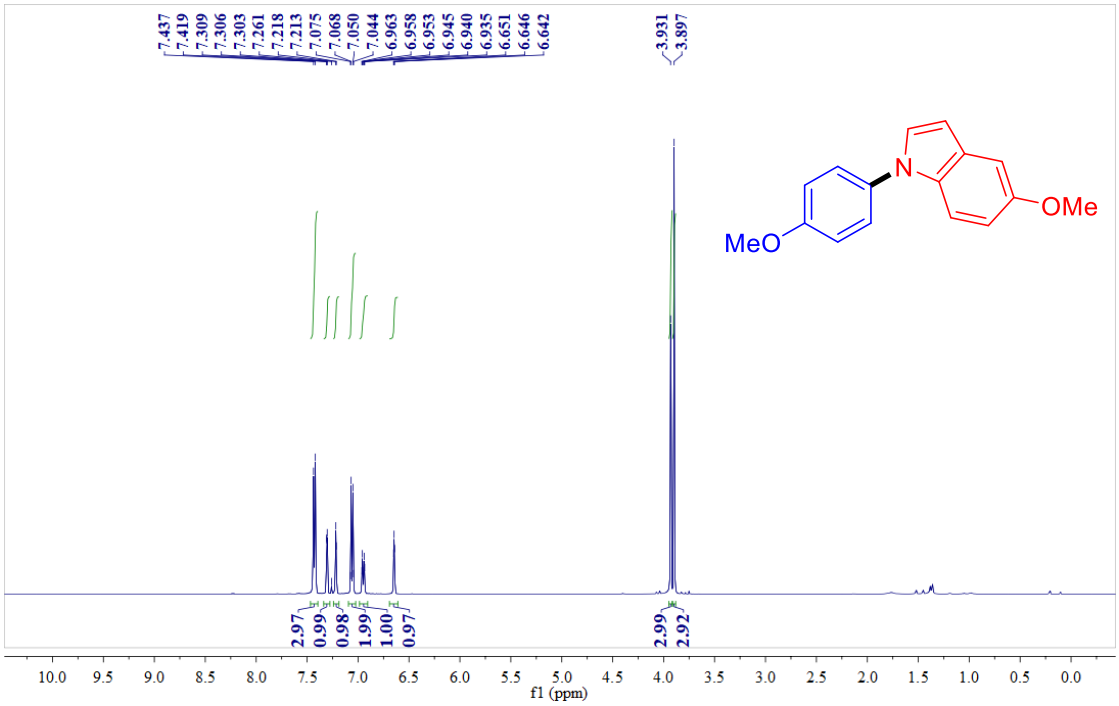
^{1}H NMR Spectrum of **4a**



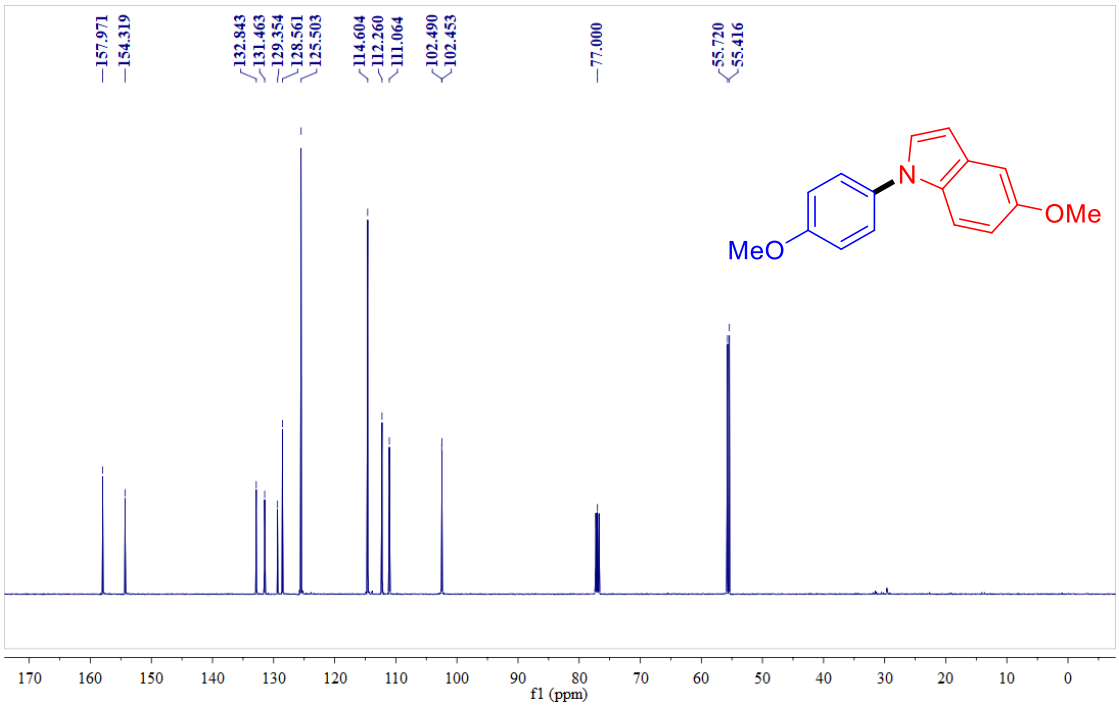
^{13}C NMR Spectrum of **4a**



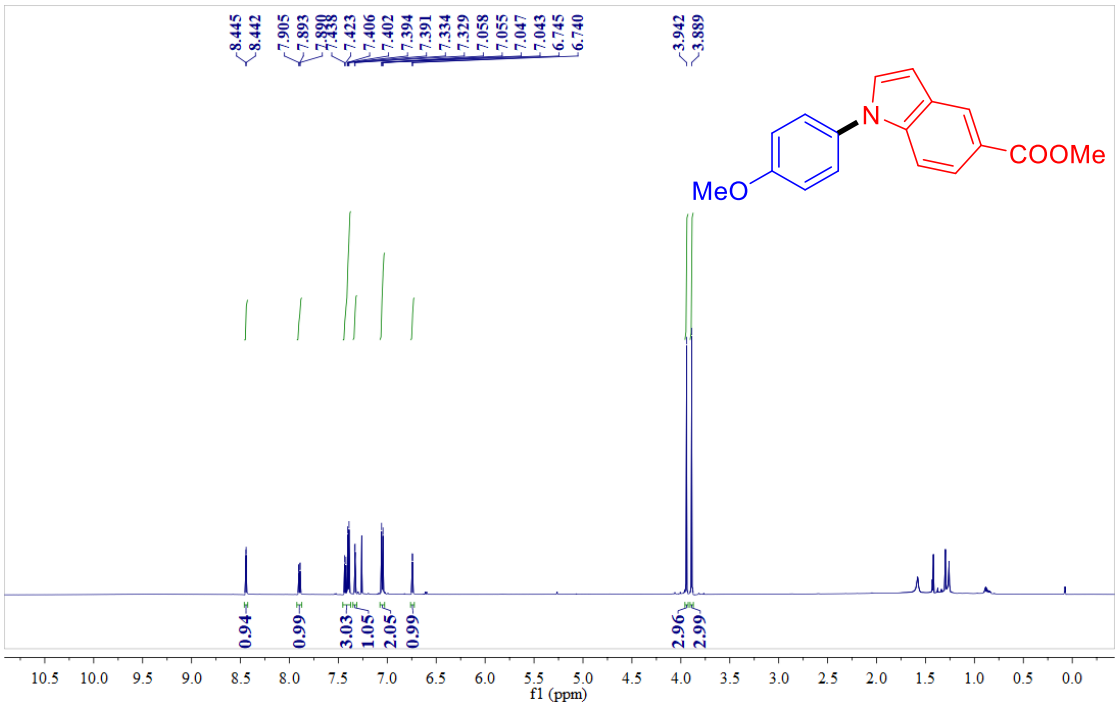
^{1}H NMR Spectrum of **4b**



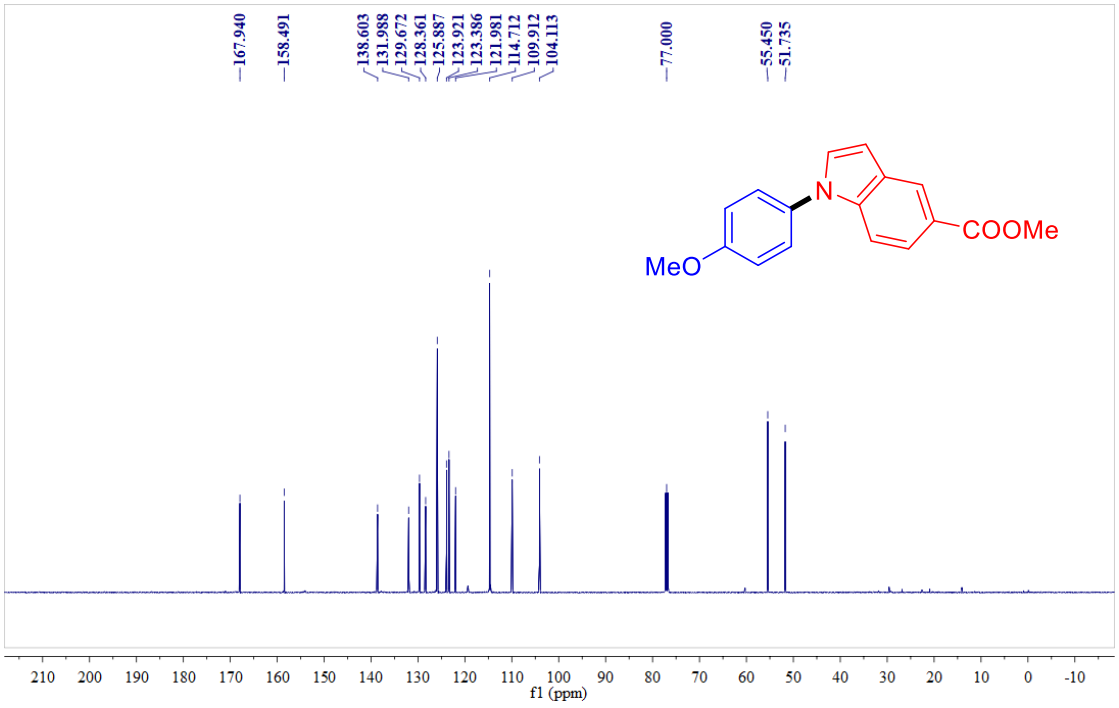
^{13}C NMR Spectrum of **4b**



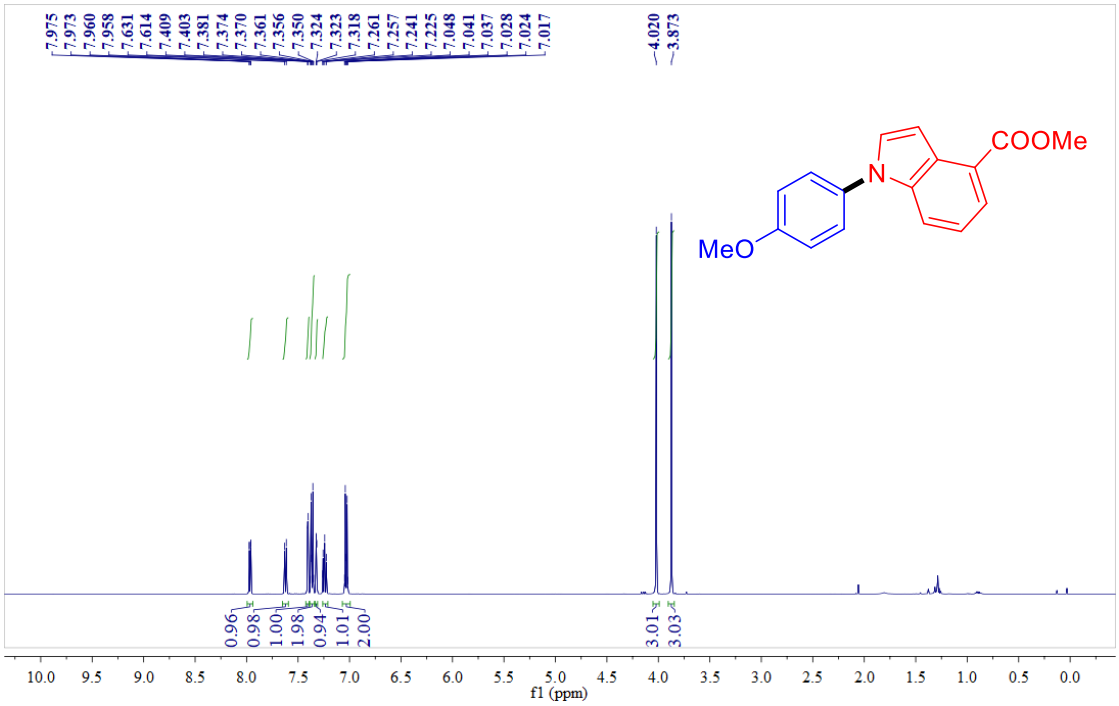
^{1}H NMR Spectrum of **4c**



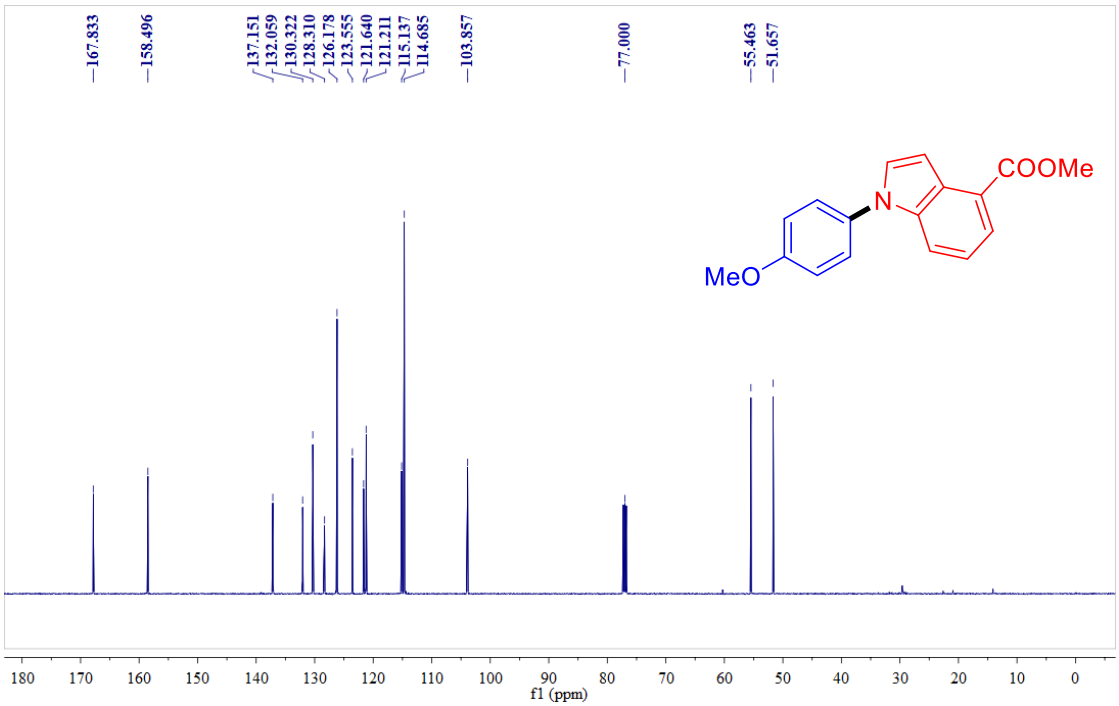
^{13}C NMR Spectrum of **4c**



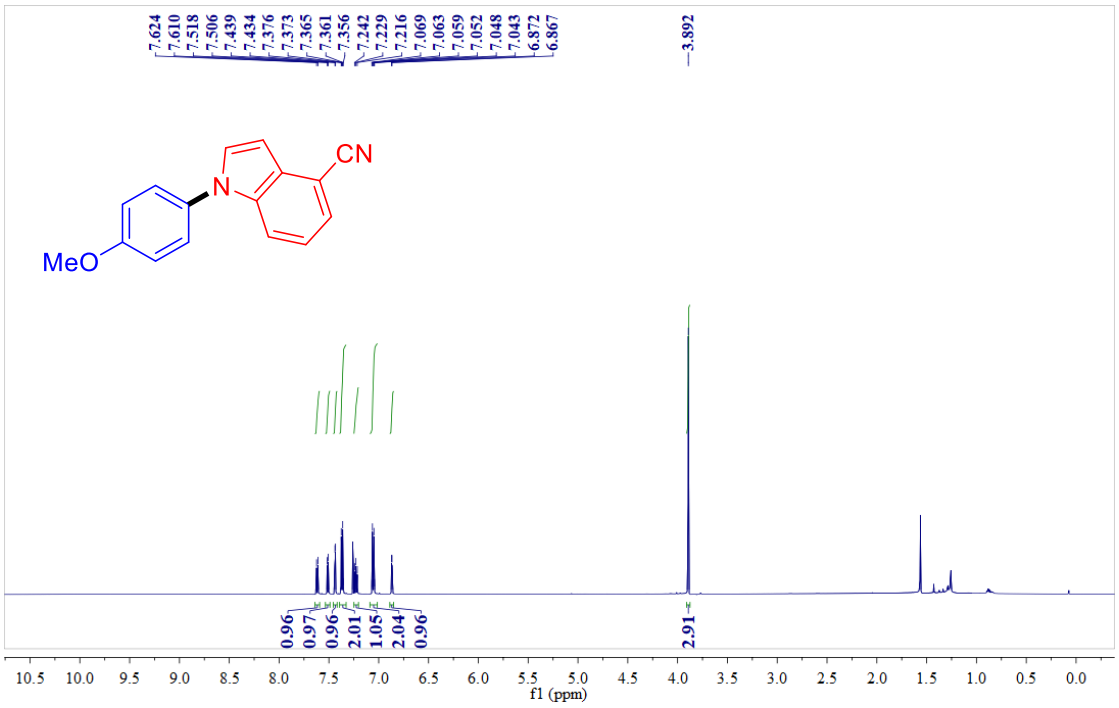
^{1}H NMR Spectrum of **4d**



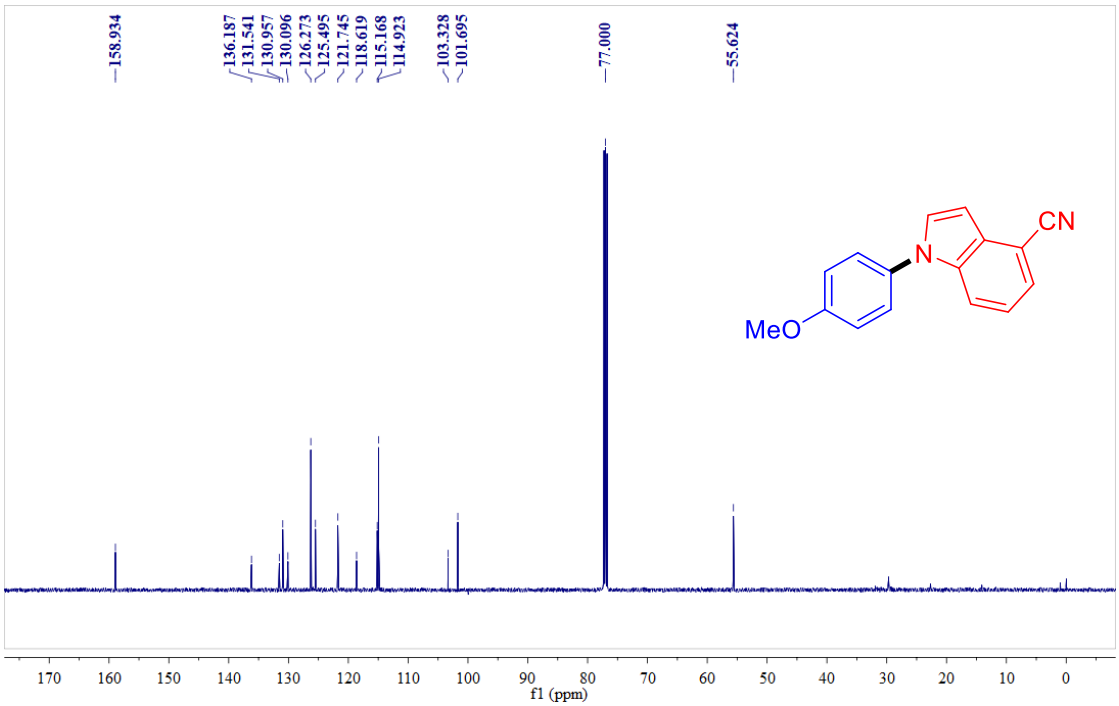
^{13}C NMR Spectrum of **4d**



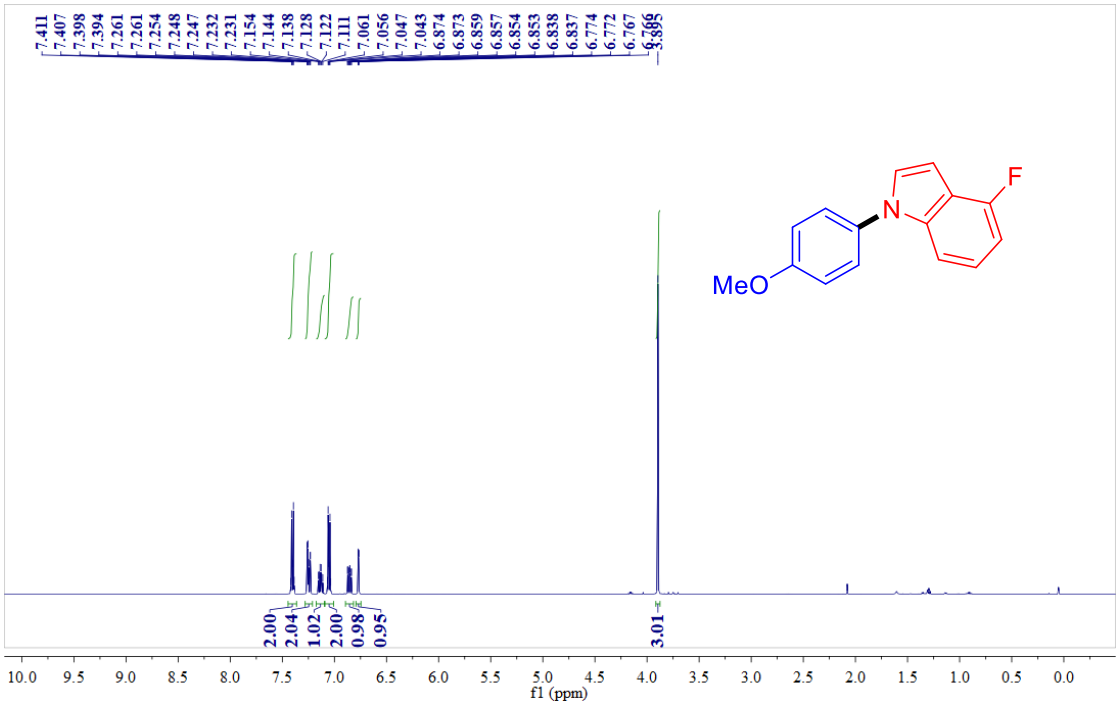
^{1}H NMR Spectrum of **4e**



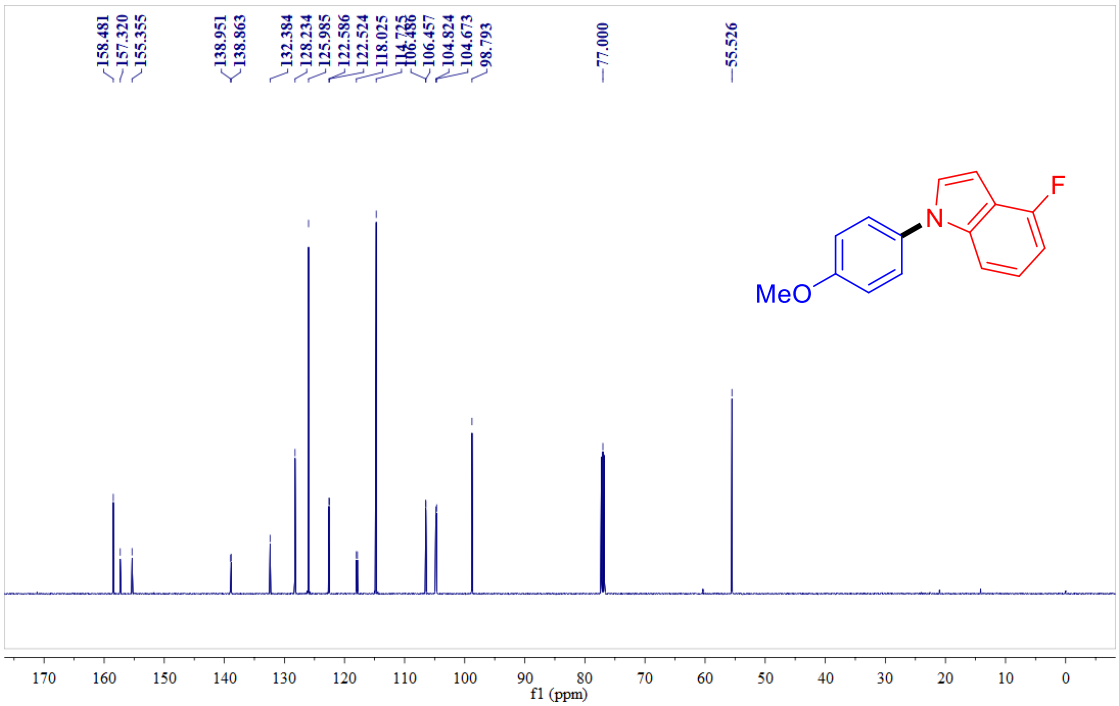
^{13}C NMR Spectrum of **4e**



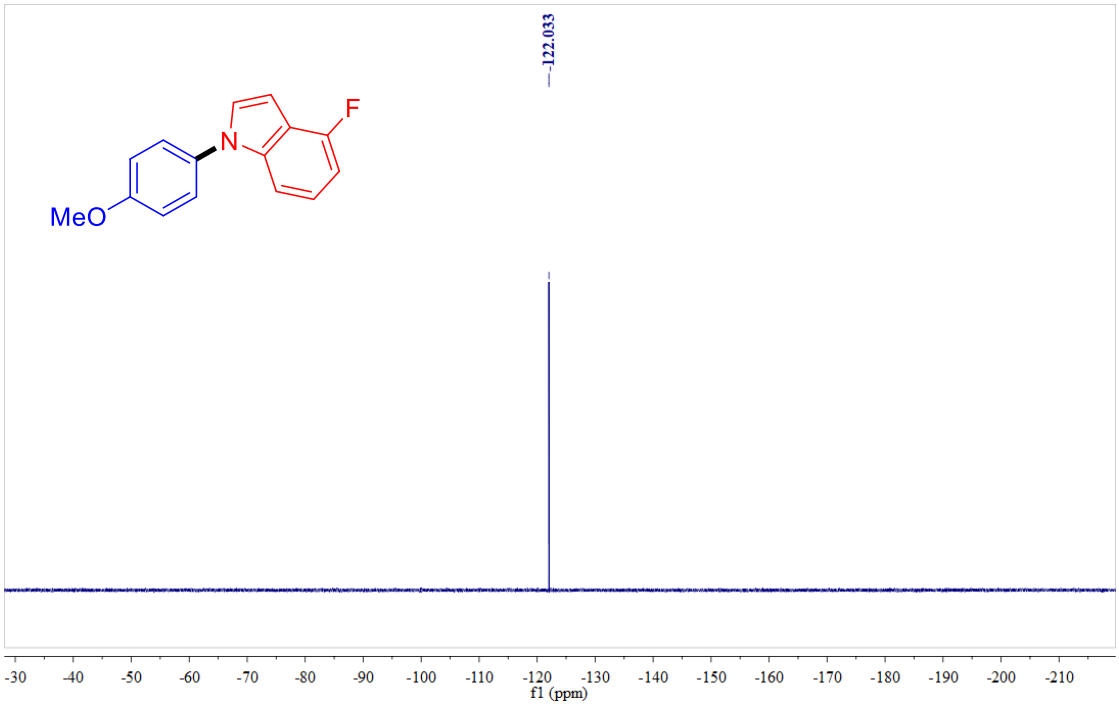
^{1}H NMR Spectrum of **4f**



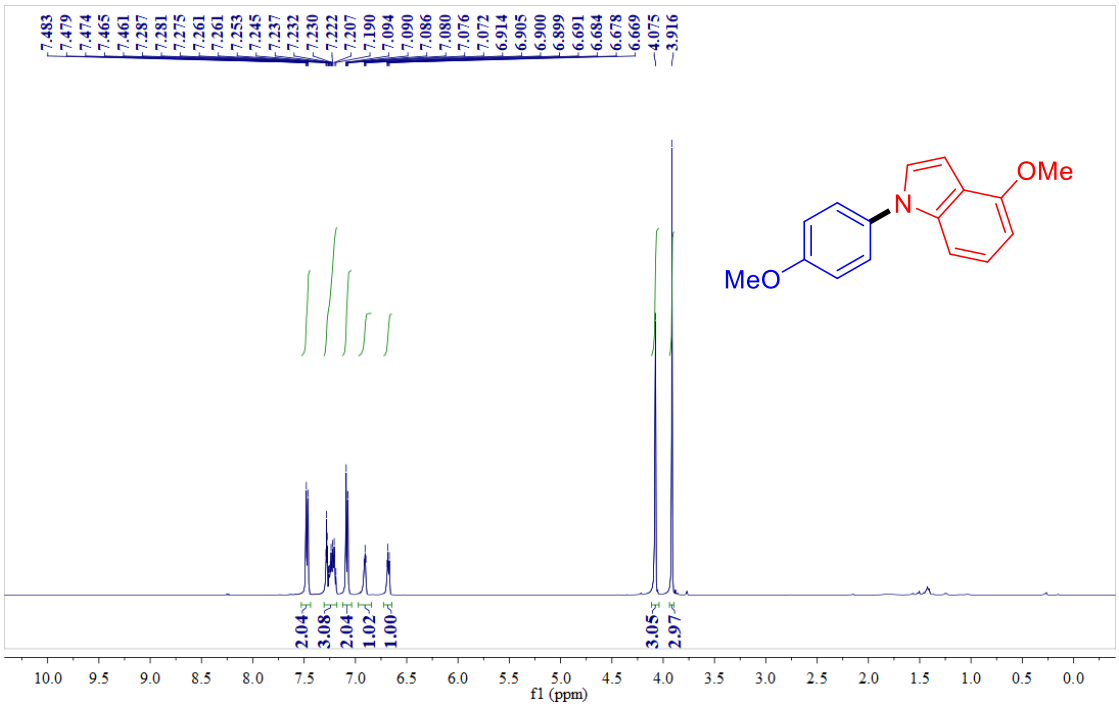
^{13}C NMR Spectrum of **4f**



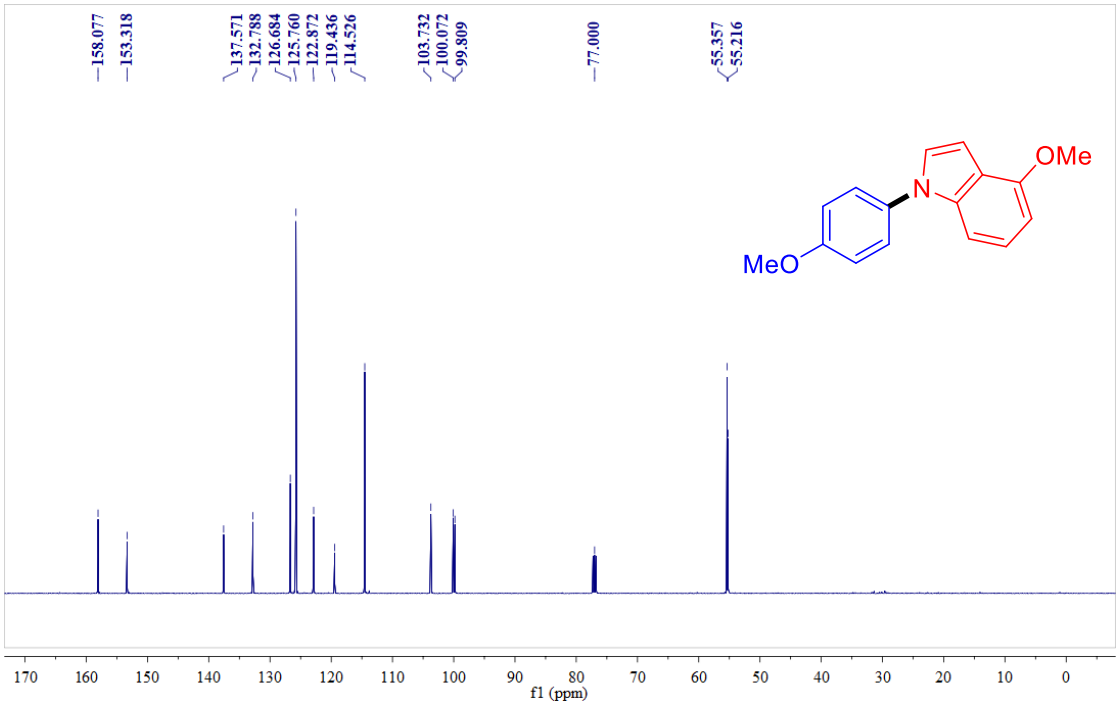
^{19}F NMR Spectrum of **4f**



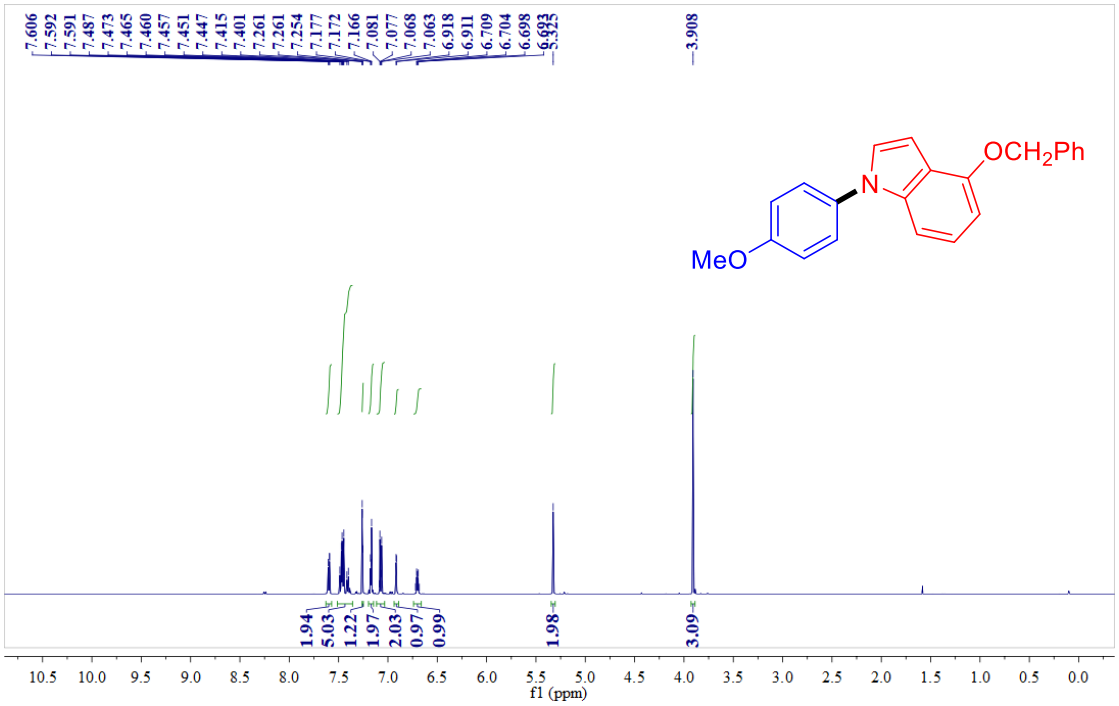
^{1}H NMR Spectrum of **4g**



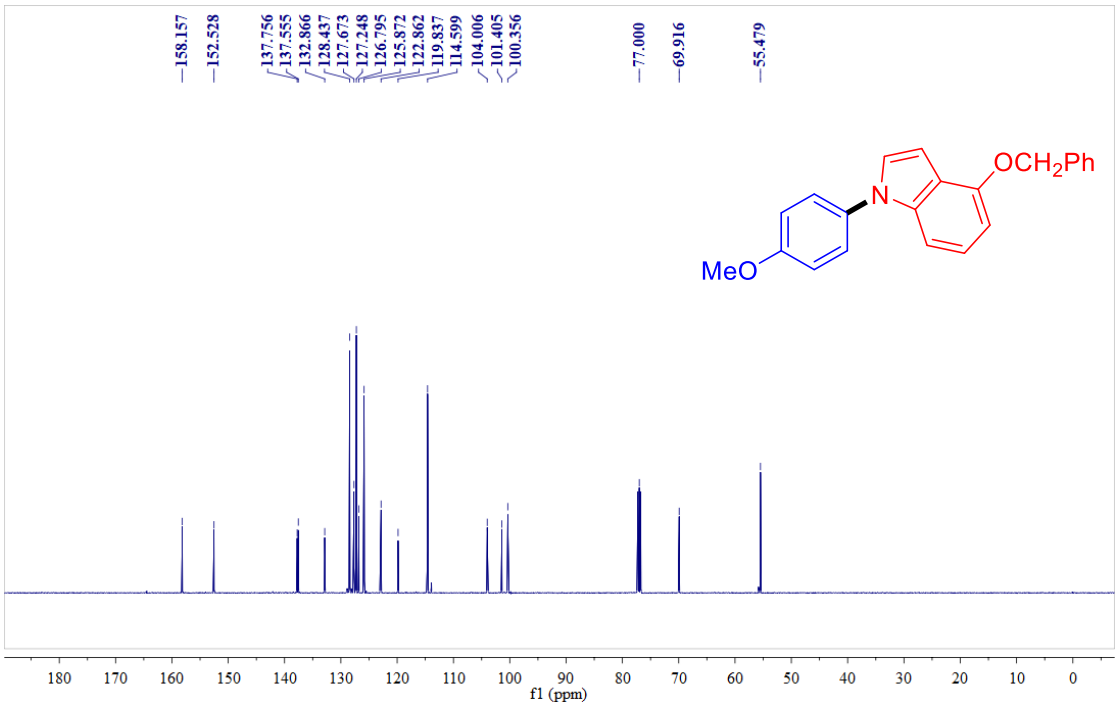
^{13}C NMR Spectrum of **4g**



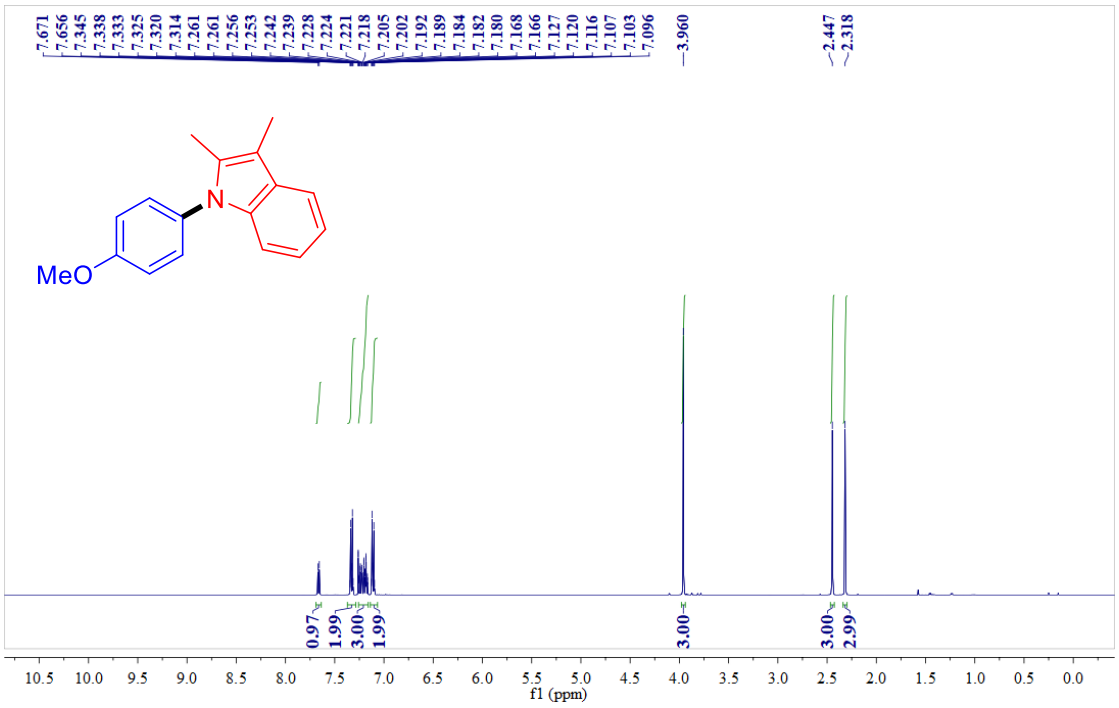
^{1}H NMR Spectrum of **4h**



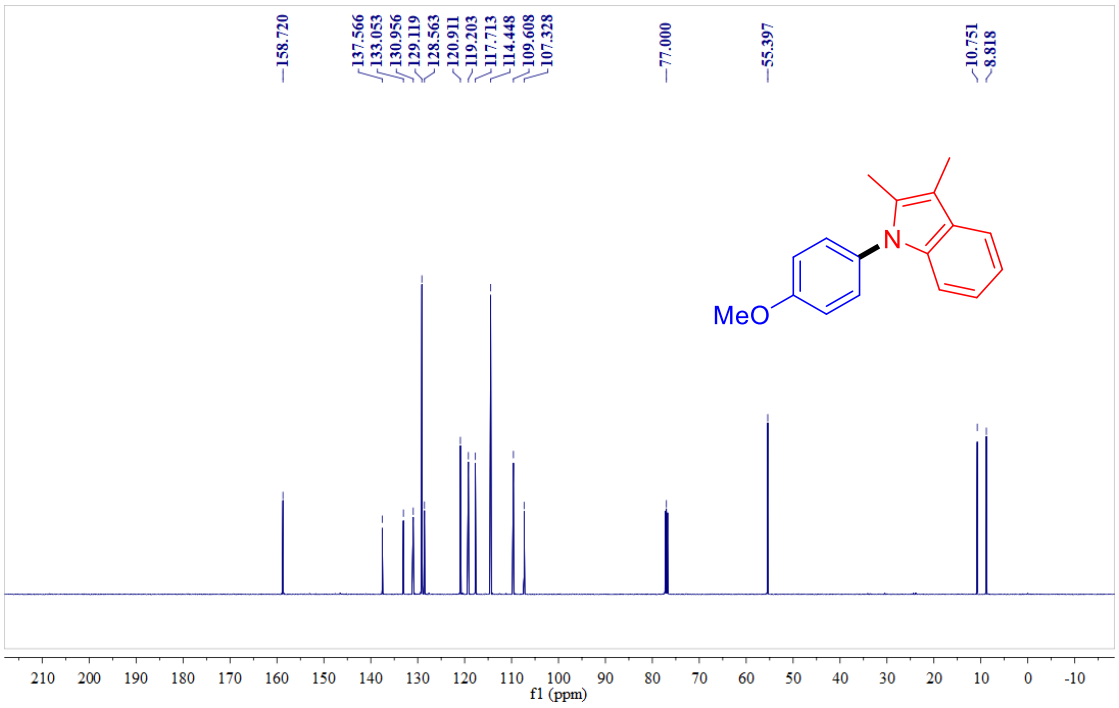
^{13}C NMR Spectrum of **4h**



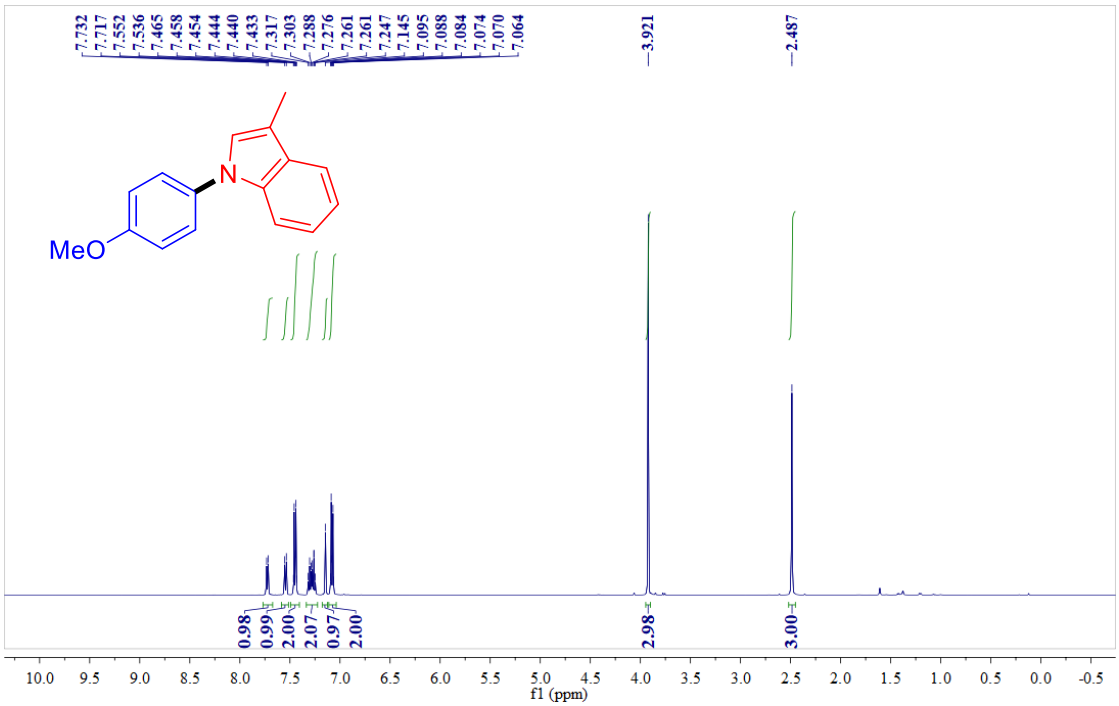
^{1}H NMR Spectrum of **4i**



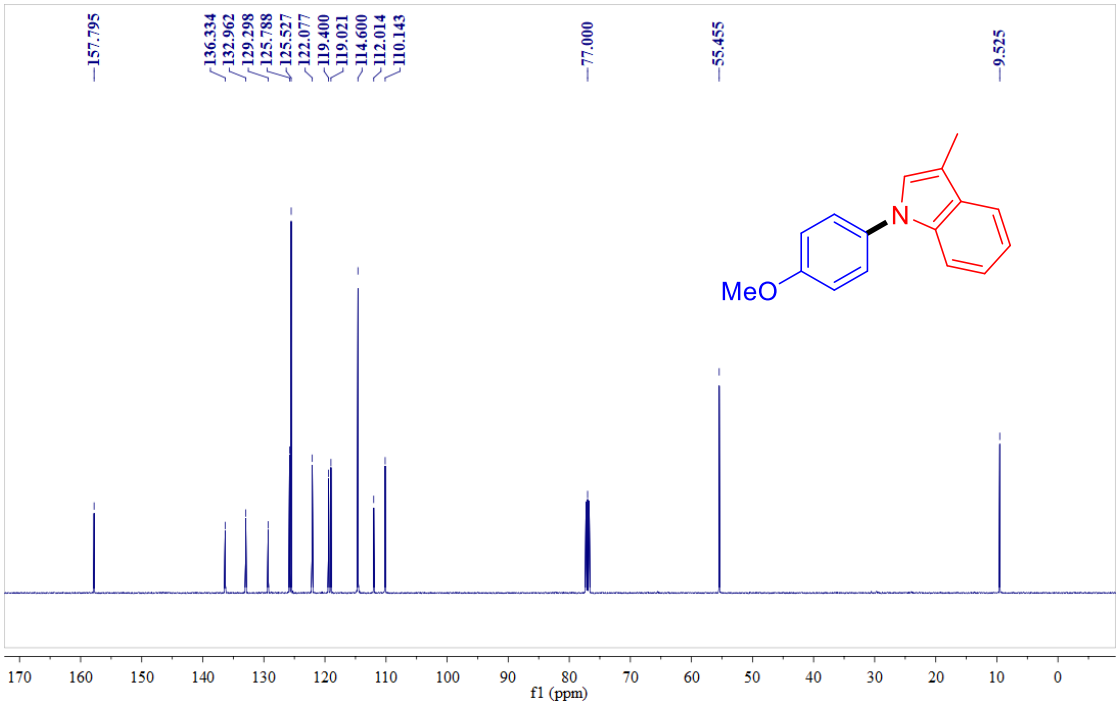
^{13}C NMR Spectrum of **4i**



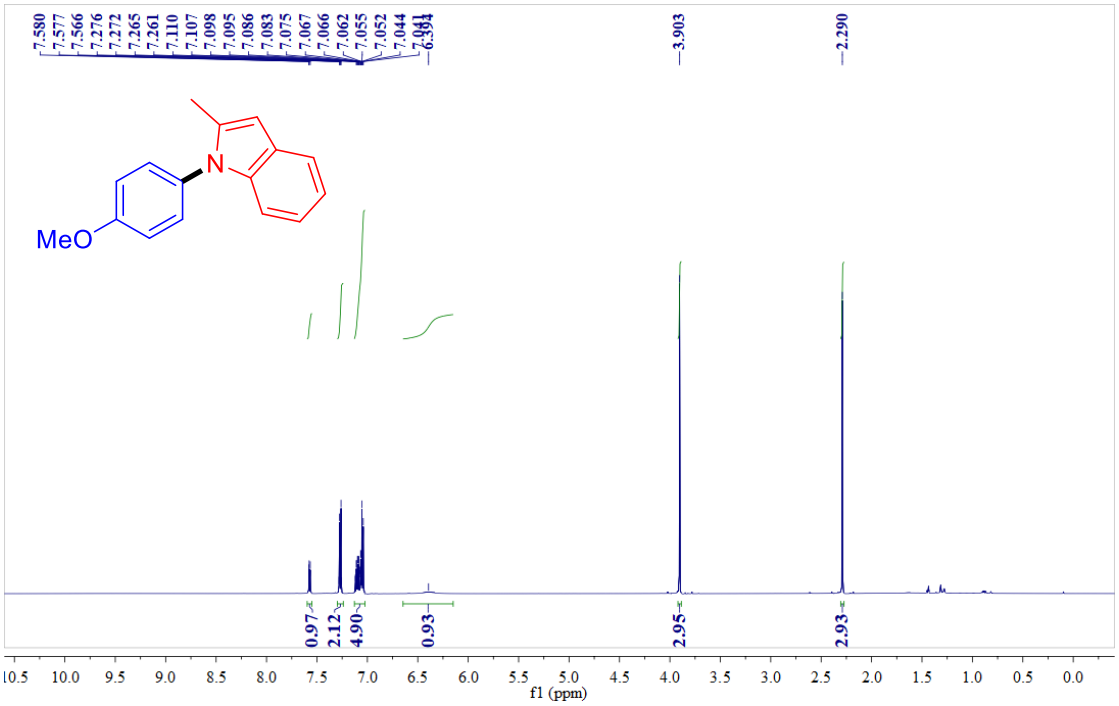
^{1}H NMR Spectrum of **4j**



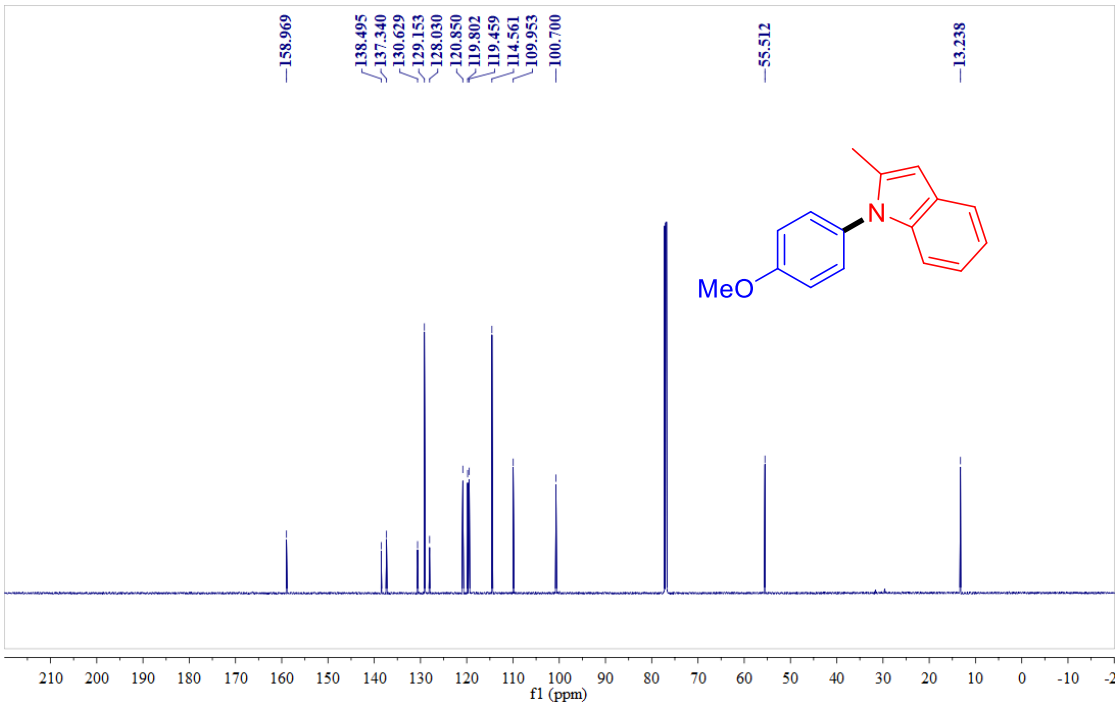
^{13}C NMR Spectrum of **4j**



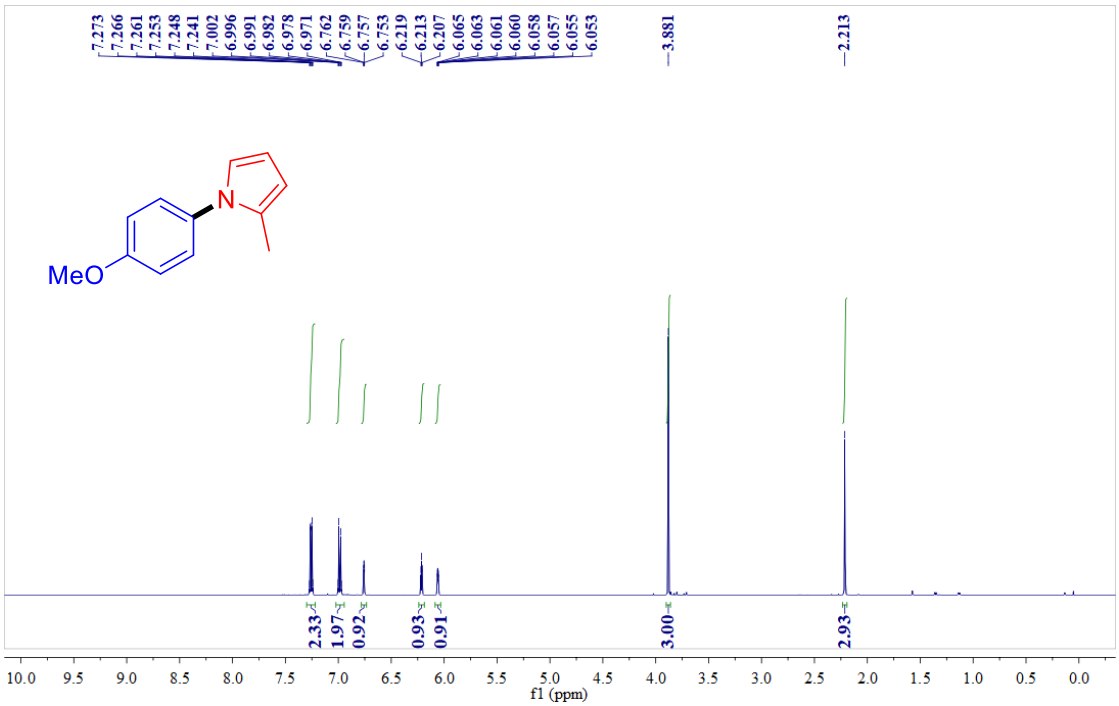
^{1}H NMR Spectrum of **4k**



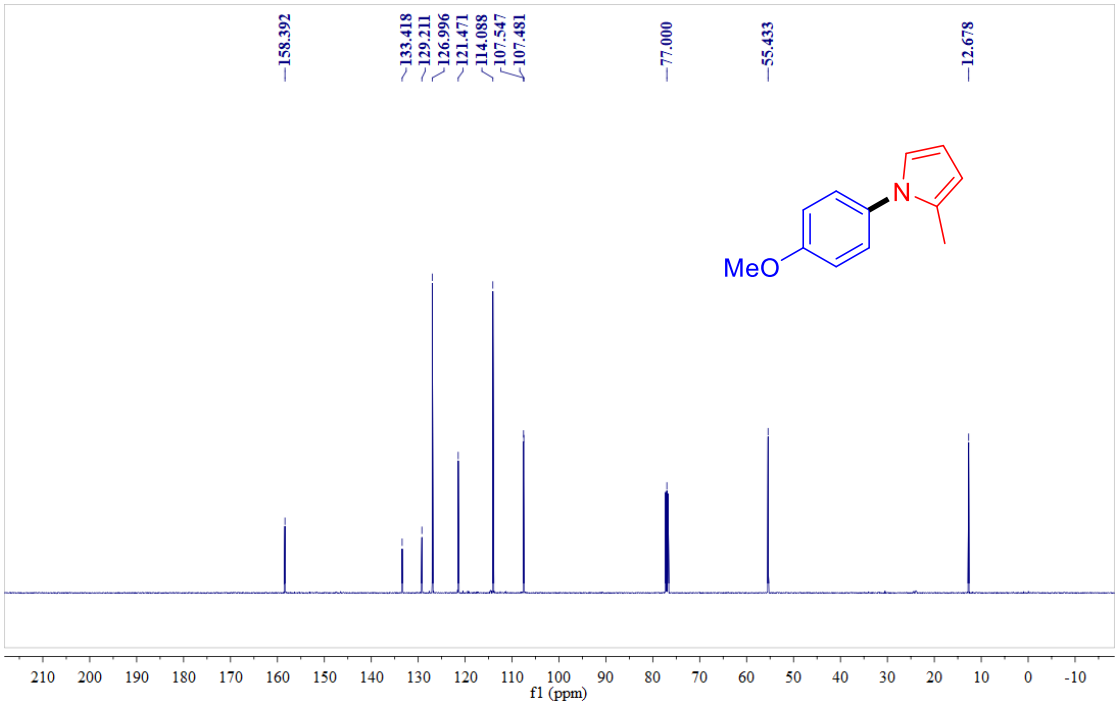
^{13}C NMR Spectrum of **4k**



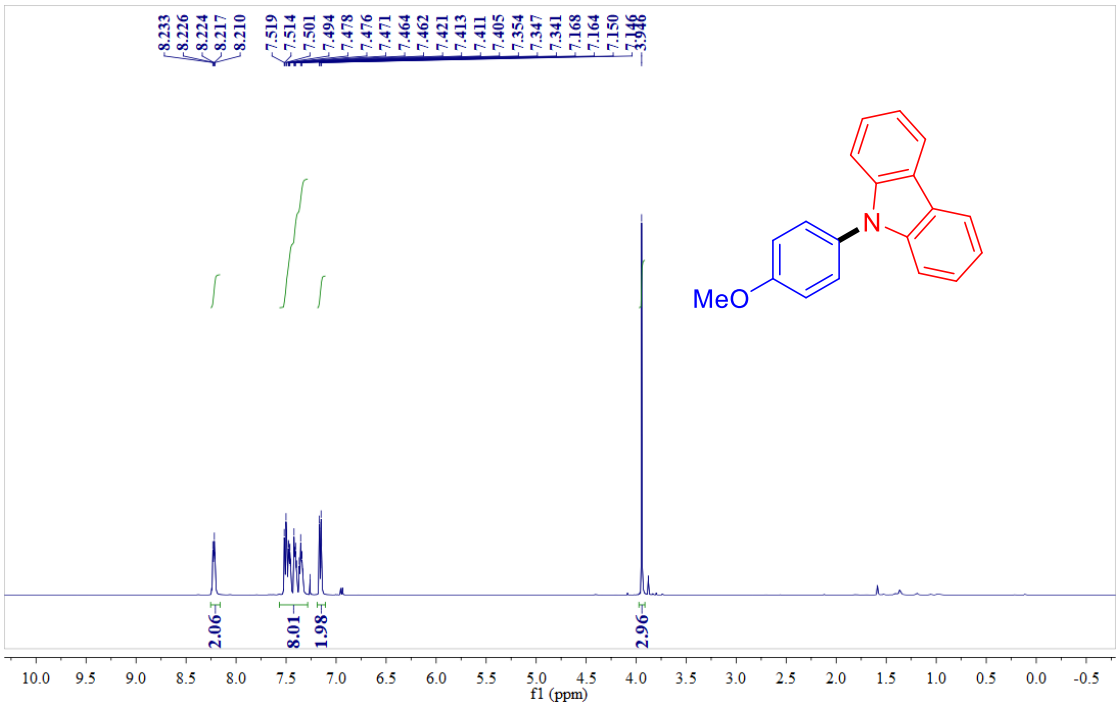
^{1}H NMR Spectrum of **4l**



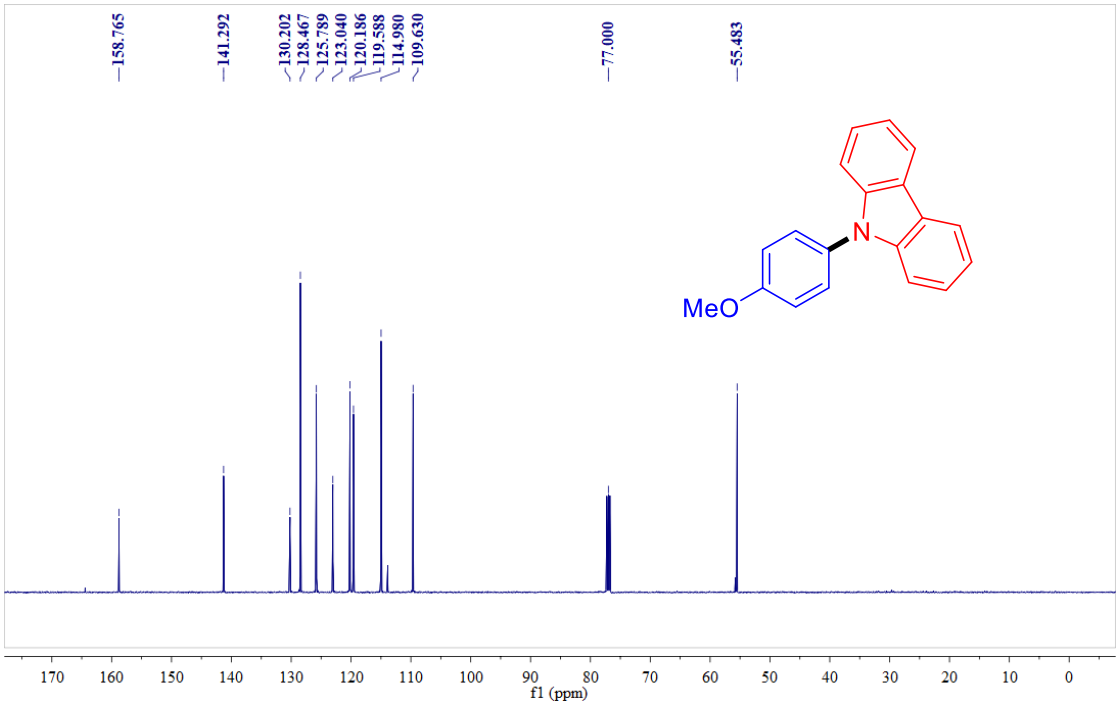
^{13}C NMR Spectrum of **4l**



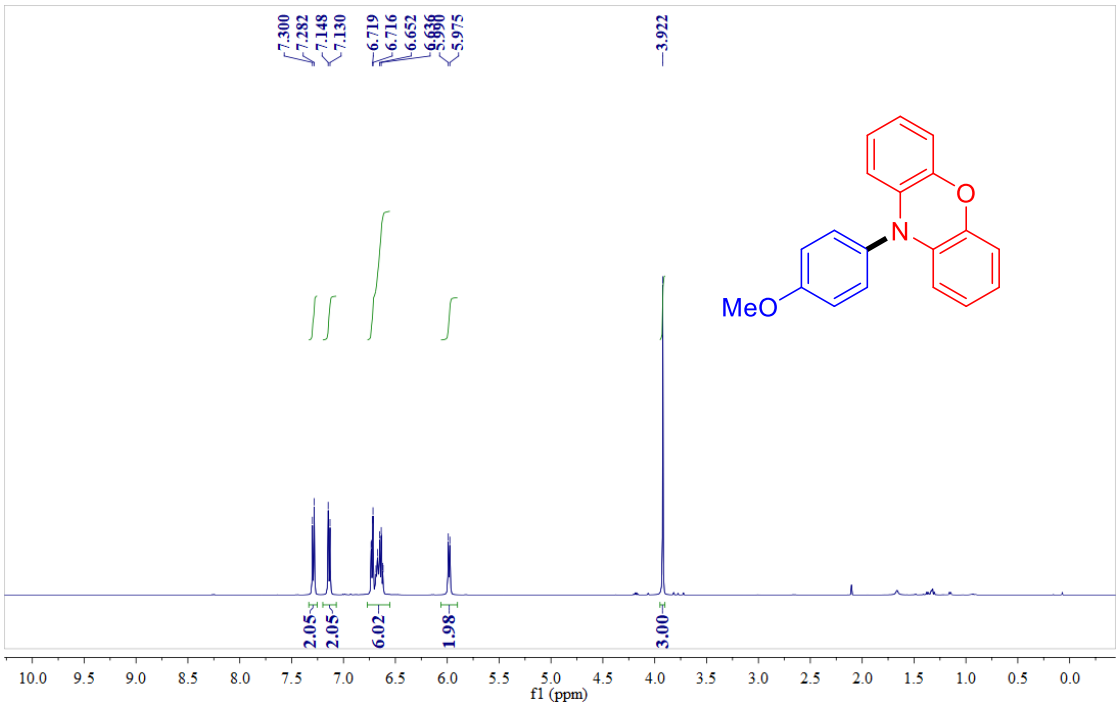
^{1}H NMR Spectrum of **4m**



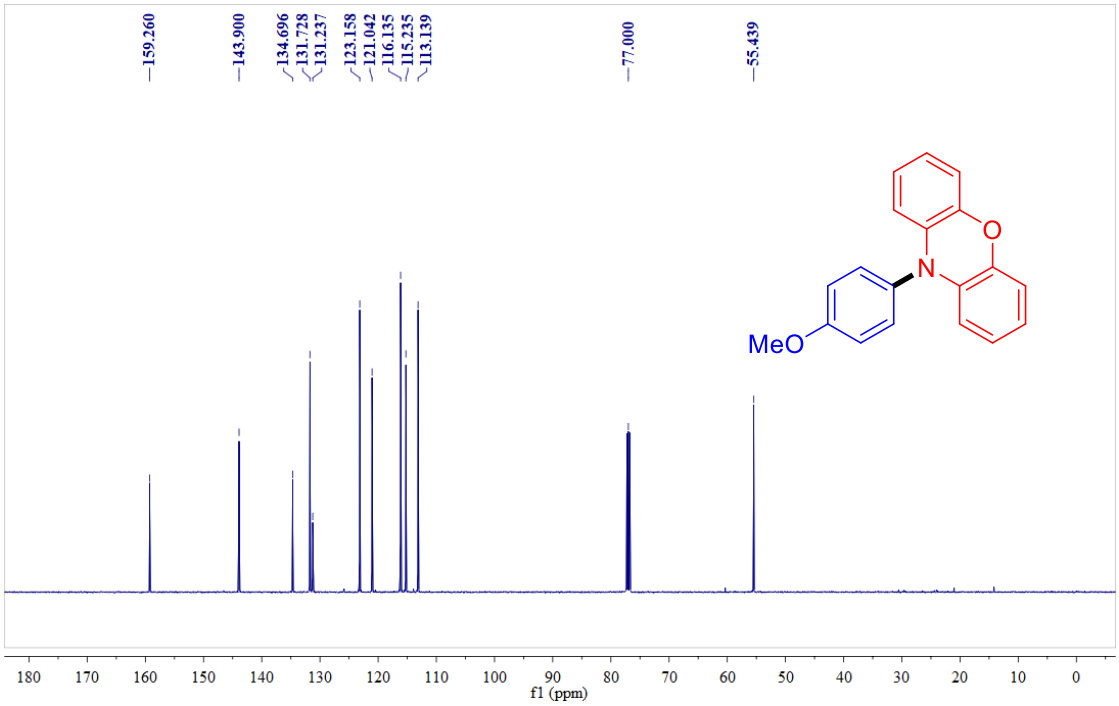
^{13}C NMR Spectrum of **4m**



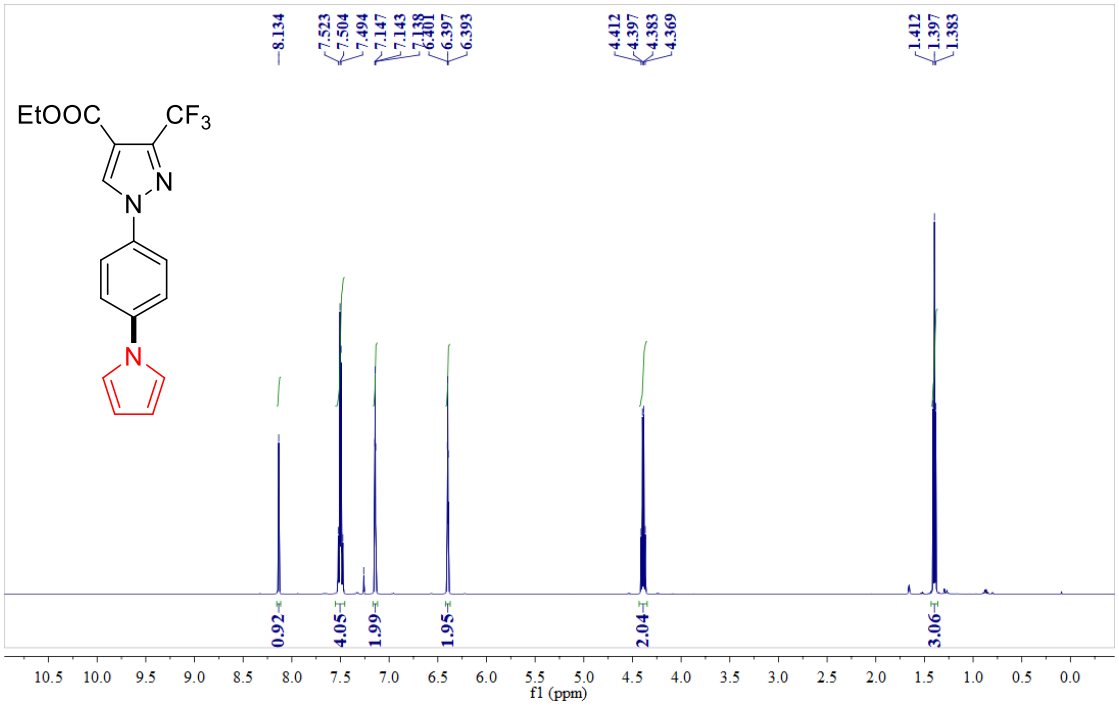
^{1}H NMR Spectrum of **4n**



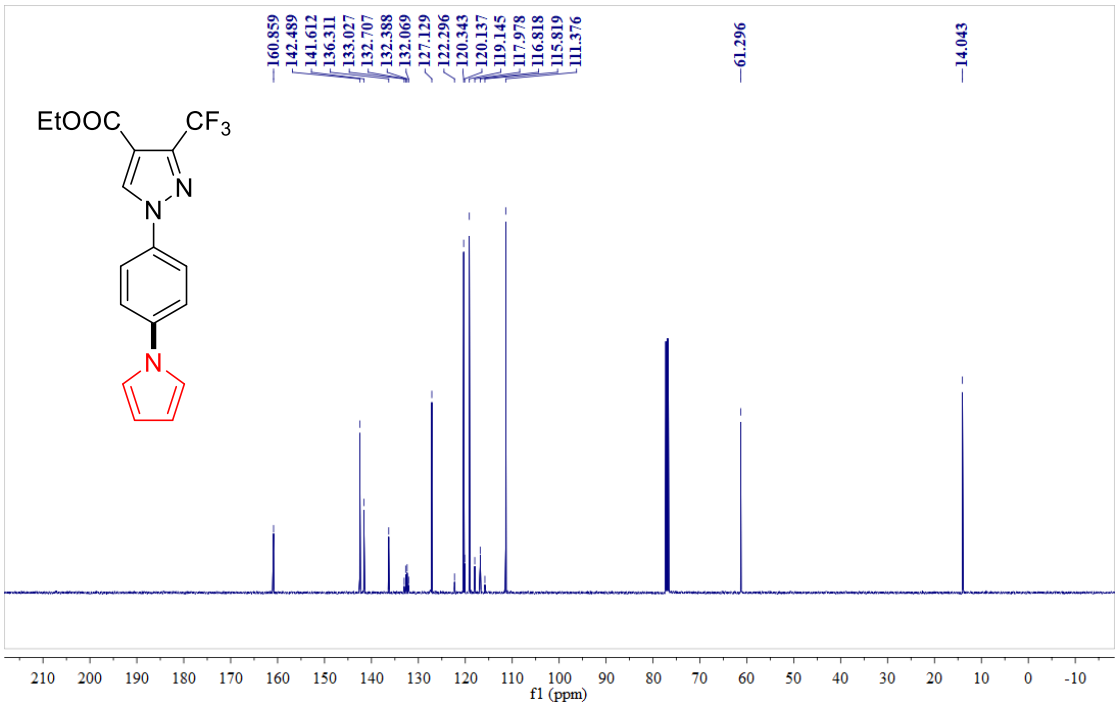
^{13}C NMR Spectrum of **4n**



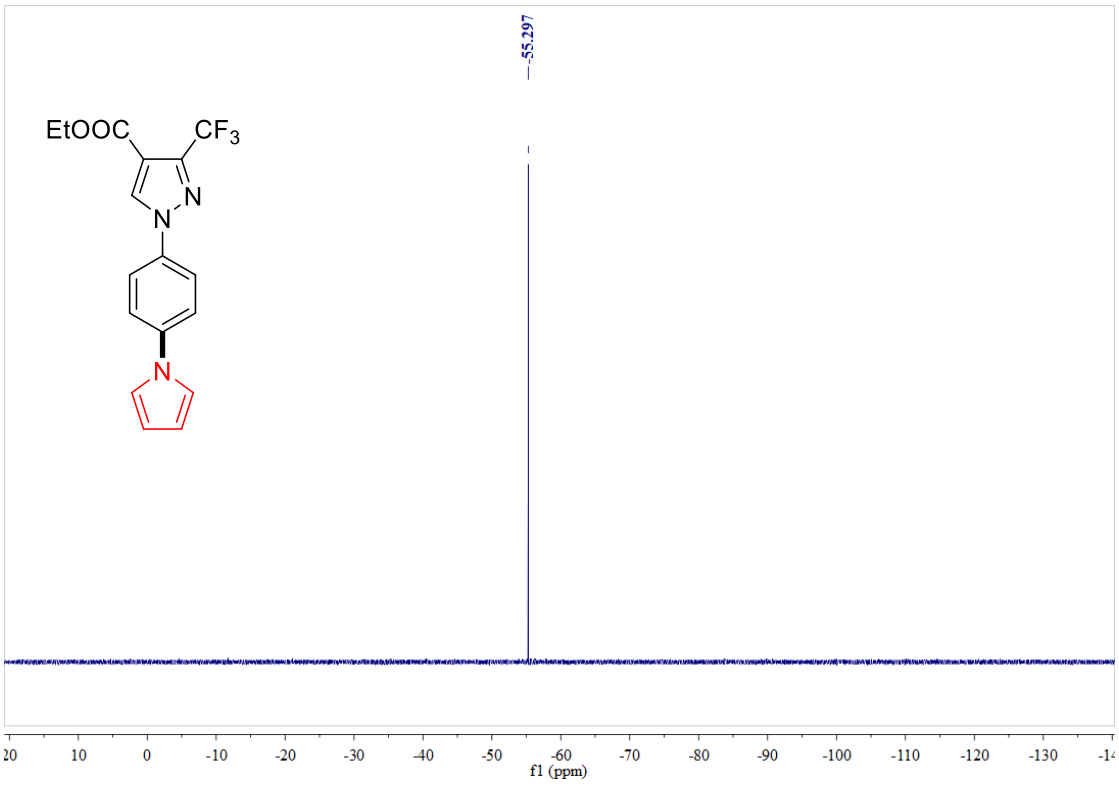
^{1}H NMR Spectrum of **5**



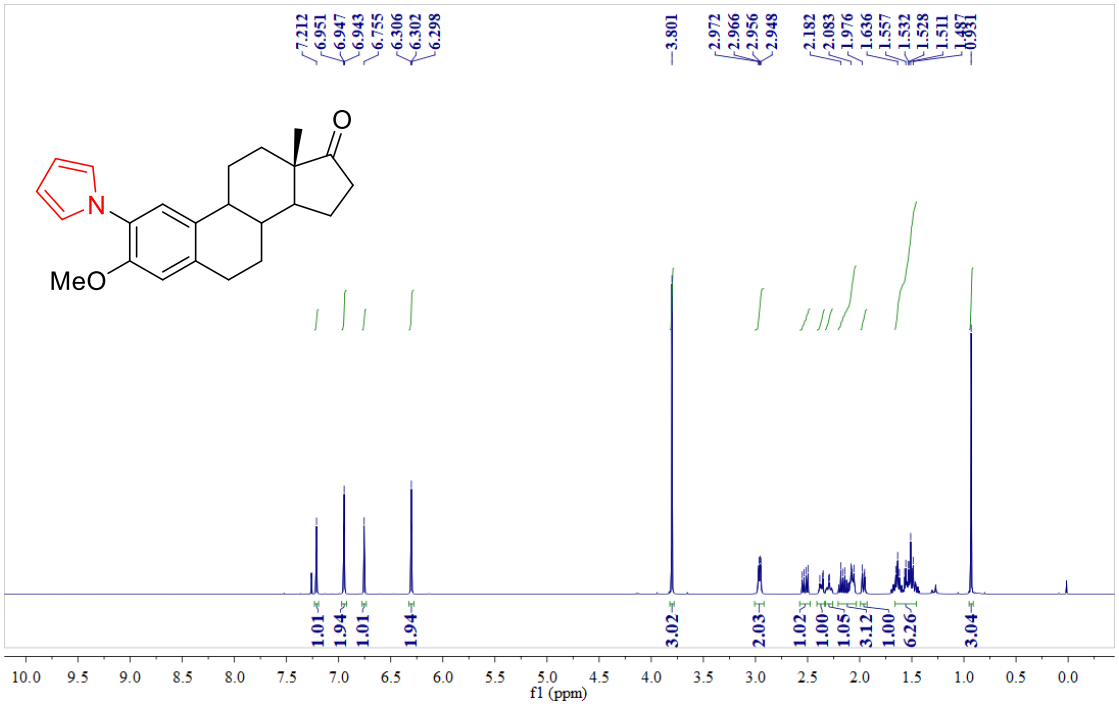
^{13}C NMR Spectrum of **5**



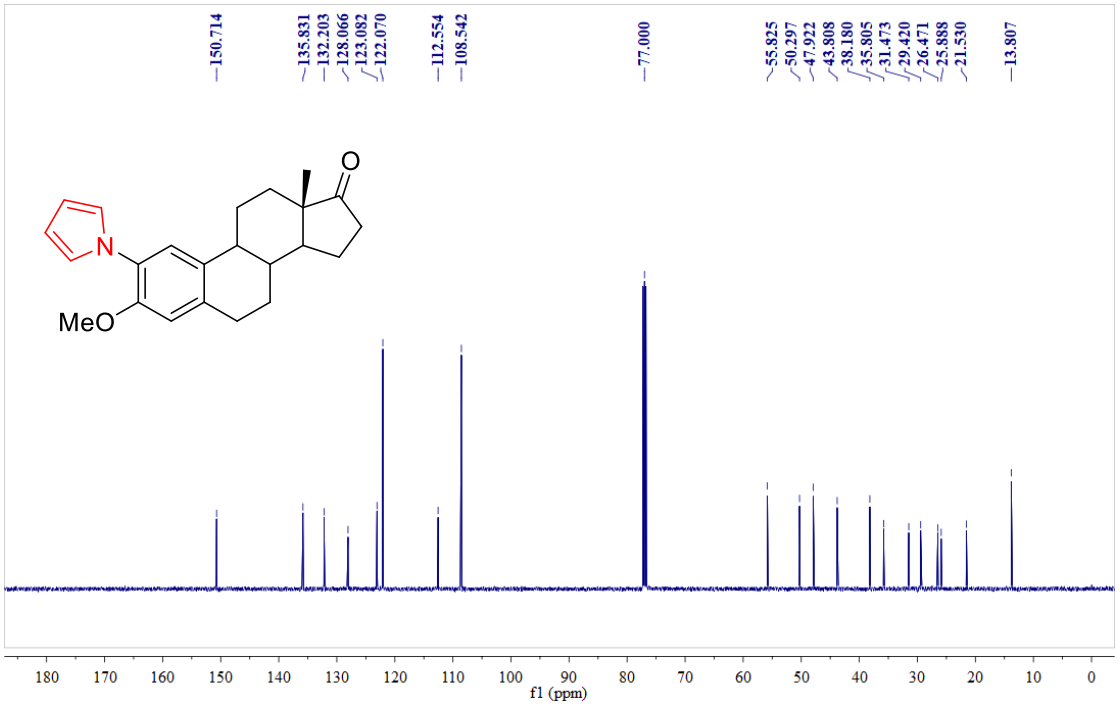
^{19}F NMR Spectrum of **5**



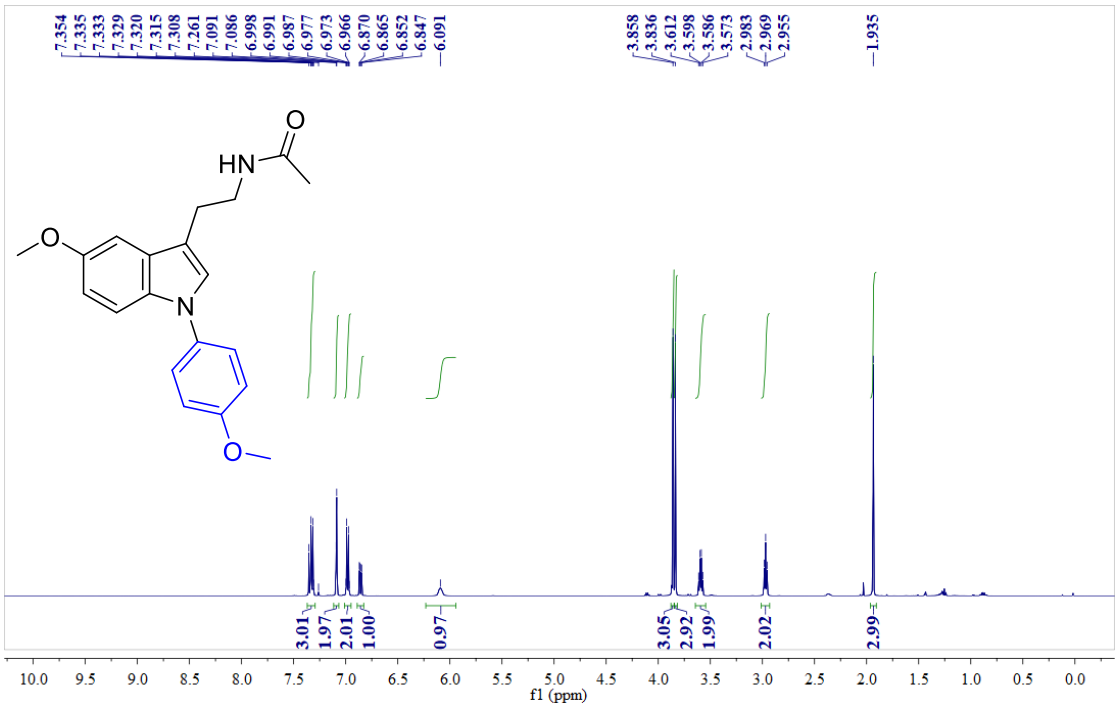
^{1}H NMR Spectrum of **6**



^{13}C NMR Spectrum of **6**



^{1}H NMR Spectrum of **7**



^{13}C NMR Spectrum of **7**