Supplementary Materials

Synthesis of 2-Substituted Benzo[b]furans/furo-Pyridines Catalyzed by $NiCl_2$

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Supporting Information

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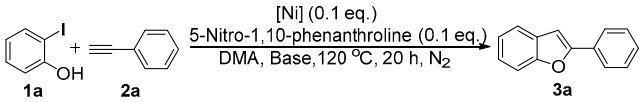
Materials and Methods: All chemicals were purchased from commercial suppliers. Except for some liquid reagents being sensitive to light and moisture (DMA) was redistilled prior to use, there is no further treatment. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a VARIAN 400-MR. Mass spectrosopy data of the products were collected with a MS-EI instrument. All products were isolated by short chromatography on a silica gel (300-400 mesh) using petroleum ether (60-90 ℃), unless otherwise noted. Compouds described in the literature were characterized by ^{1}H NMR spectroscopy and compared to the reported data.

General Procedure for the Synthesis of 2-Substituted Benzo[b]furans/furo-pyridines: $NiCl_2$ (0.1 mmol), Ligand (0.1 mmol), 2-halophenol (1 mmol), terminal alkynes (1.2 mmol), NaOH (2 mmol) and degassed DMA (2 mL) were added successively into a dried Schlenk tube with a magnetic bar under nitrogen. The reaction was performed at 120 ℃. At the end of reaction, the solution was cooled to room temperature and water (3 mL) was added into it. The mixture solution was extracted with ethyl acetate (3×3 mL). The organic layer was dried over $MgSO_4$, filtered and purified with silica gel chromatography (petroleum ether) to give a corresponding product.

Table S1. Optimization of reaction conditions[a]

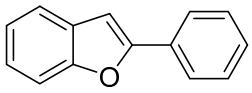


1a **2a** **3a**

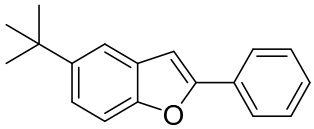
Entry	[Ni]	Base	Solvent	Yeild (%)
1	$NiCl_2$	NaOH	DMA	80
2	$NiCl_2$	NaOH	DMA	47[b]
3	--	NaOH	DMA	0.8
4	$Ni(dppe)Cl_2$	NaOH	DMA	26
5	$Ni(dppp)Cl_2$	NaOH	DMA	16
6	$Ni(PPh_3)_2Cl_2$	NaOH	DMA	41
7	$Ni(PCy_3)_2Cl_2$	NaOH	DMA	13
8	$Ni(COD)_2Cl_2$	NaOH	DMA	28
9	$NiSO_4$	NaOH	DMA	75
10	$NiCl_2$	$NaHCO_3$	DMA	0.6
11	$NiCl_2$	$KHCO_3$	DMA	0.7
12	$NiCl_2$	Na_2CO_3	DMA	2
13	$NiCl_2$	Cs_2CO_3	DMA	1
14	$NiCl_2$	K_3PO_4	DMA	26
15	$NiCl_2$	NaOH	DMA	80
16	$NiCl_2$	KOH	DMA	74
17	$NiCl_2$	Et_3N	DMA	0.1
18	$NiCl_2$	pyridine	DMA	0.1
19	$NiCl_2$	NaOH	DMF	56
20	$NiCl_2$	NaOH	1,4-Dioxane	0.2[c]
21	$NiCl_2$	NaOH	Toluene	0.6[c]
22	$NiCl_2$	NaOH	H_2O	--[c]
23	$NiCl_2$	NaOH	n-BuOH	0.1[c]
24	$NiCl_2$	NaOH	t-BuOH	--[d]

[a] Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), NaOH (2 mmol), [Ni] (0.1 mmol), 5-Nitro-1,10-phenanthroline (0.1 mmol), DMA (2 mL), 120 ℃, 20 h, N_2; [b]: in air; [c]: 100 ℃; [d]: 115 ℃; [e]: 80 ℃.

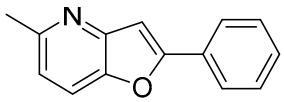
Characterization Data:



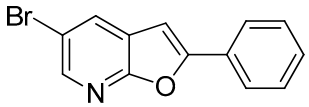
3a[1]:[1]H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J*=8.3 Hz, 2H), 7.47 (dd, *J*=22.6, 7.8 Hz, 2H), 7.36 (t, *J*=7.7 Hz, 2H), 7.30-7.12 (m, 3H), 6.94 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.85, 154.82, 130.42, 129.17, 128.76, 128.52, 124.88, 124.23, 122.90, 120.88, 111.15, 101.27.



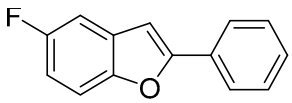
3b[2]: [1]H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J*=7.6 Hz, 2H), 7.62 (s, 1H), 7.47 (t, *J*=7.9 Hz, 3H), 7.41-7.33 (m, 2H), 7.02 (s, 1H), 1.43 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.77, 152.89, 145.71, 130.44, 128.56, 128.48, 128.10, 124.59, 121.99, 116.83, 110.18, 101.43, 34.38, 31.76.



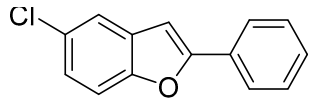
3c: [1]H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, *J*=7.3 Hz, 2H), 7.62 (d, *J*=8.4 Hz, 1H), 7.45 (t, *J*=7.5 Hz, 2H), 7.38 (t, *J*=7.3 Hz, 1H), 7.13 (s, 1H), 7.03 (d, *J*=8.4 Hz, 1H), 2.65 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.36, 154.65, 148.32, 146.50, 129.84, 129.32, 128.84, 125.15, 118.69, 117.97, 102.14, 77.42, 24.3.
MS (ACPI): Calc'd for $C_{15}H_{13}NO^+$, 210.0919; found, 210.0912.



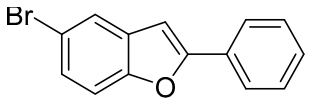
3d: [1]H NMR (400 MHz, $CDCl_3$) δ: 8.33 (d, *J*=2.1 Hz, 1H), 8.01 (d, *J*=2.1 Hz, 1H), 7.89 (d, *J*=7.3 Hz, 2H), 7.45 (dt, *J*=24.3, 7.2 Hz, 3H), 6.95 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.40, 156.26, 143.33, 130.56, 128.78, 128.02, 124.34, 122.33, 114.31, 98.38.
MS (ACPI): Calc'd for $C_{15}H_{13}NO^+$, 275.1245; found, 275.1240.



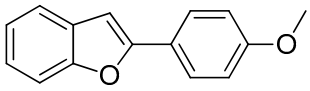
3e[3]: [1]H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, *J*=7.3 Hz, 2H), 7.45 (dd, *J*=14.6, 6.9 Hz, 3H), 7.38 (t, *J*=7.4 Hz, 1H), 7.24 (dd, *J*=8.5, 2.6 Hz, 1H), 7.01 (dt, *J*=9.0, 2.9 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.49, 149.97, 129.07, 127.85, 127.79, 123.97, 110.94, 110.73, 110.68, 110.63, 105.41, 105.16, 100.38, 100.36.



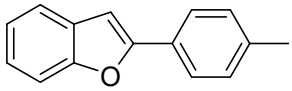
3f[4]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, *J*=7.2 Hz, 2H), 7.53 (d, *J*=2.1 Hz, 1H), 7.48-7.34 (m, 4H), 7.23 (dd, *J*=8.7, 2.1 Hz, 1H), 6.95 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.33, 153.19, 130.53, 129.90, 128.97, 128.90, 128.43, 125.04, 124.36, 120.39, 112.09, 100.76.



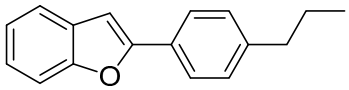
3g[3]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, *J*=7.3 Hz, 2H), 7.70 (d, *J*=1.6 Hz, 1H), 7.54-7.33 (m, 5H), 6.96 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.19, 153.57, 132.52, 131.22, 129.88, 128.85, 127.06, 125.04, 123.45, 115.93, 112.60, 100.61.



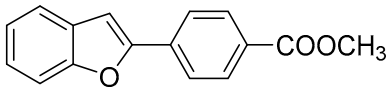
3h[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, *J*=8.8 Hz, 2H), 7.52 (dd, *J*=21.9, 8.1 Hz, 2H), 7.28-7.18 (m, 2H), 6.98 (d, *J*=8.8 Hz, 2H), 6.89 (s, 1H), 3.86 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.96, 155.03, 153.67, 128.46, 125.40, 122.70, 122.33, 121.79, 119.53, 113.23, 109.95, 98.65, 54.35.



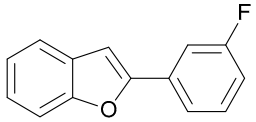
3i[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (d, *J*=8.2 Hz, 2H), 7.53 (dd, *J*=22.4, 7.6 Hz, 2H), 7.29-7.19 (m, 4H), 6.96 (s, 1H), 2.39 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.16, 153.73, 137.55, 128.45, 128.31, 126.72, 123.85, 122.95, 121.81, 119.69, 110.05, 99.52, 20.35.



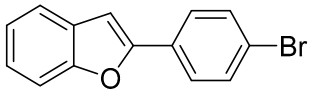
3j[6]: 1H NMR (400 MHz, $CDCl_3$) δ: 7.76 (t, *J*=12.6 Hz, 2H), 7.62-7.40 (m, 2H), 7.32-7.09 (m, 4H), 6.97 (d, *J*=0.8 Hz, 1H), 2.67-2.54 (m, 2H), 1.74-1.59 (m, 2H), 0.99-0.90 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.22, 154.74, 143.45, 132.38, 129.35, 128.89, 128.60, 127.95, 124.86, 123.96, 122.82, 120.72, 111.07, 100.55, 37.88, 24.46, 13.86.



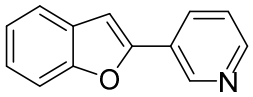
3k[7]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J*=8.5 Hz, 2H), 7.93 (d, *J*=8.4 Hz, 2H), 7.62 (d, *J*=7.7 Hz, 1H), 7.54 (d, *J*=8.3 Hz, 1H), 7.33 (t, *J*=7.7 Hz, 1H), 7.28-7.23 (m, 1H), 7.16 (s, 1H), 3.95 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.70, 155.13, 154.62, 134.47, 130.12, 129.65, 128.88, 125.06, 124.60, 123.20, 121.28, 111.34, 103.44, 52.22.



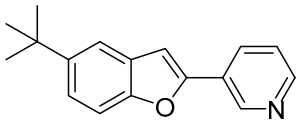
3l[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66-7.50 (m, 4H), 7.40 (dd, *J*=13.9, 8.0 Hz, 1H), 7.31 (t, *J*=7.1 Hz, 1H), 7.25 (d, *J*=8.2 Hz, 1H), 7.08-6.99 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.36, 161.92, 154.88, 132.57, 130.42, 128.91, 124.72, 123.10, 121.11, 120.55, 115.21, 111.89, 111.25, 102.32.



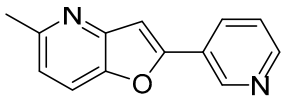
3m[8]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (d, *J*=8.6 Hz, 2H), 7.51 (dd, *J*=7.6, 5.6 Hz, 3H), 7.44 (d, *J*=8.1 Hz, 1H), 7.25-7.14 (m, 2H), 6.95 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.84, 154.74, 131.94, 129.00, 126.33, 124.59, 123.09, 122.47, 121.00, 111.19, 101.83.



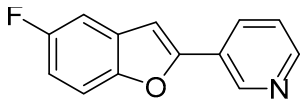
3n[3]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.12 (d, *J*=2.1 Hz, 1H), 8.58 (dd, *J*=4.8, 1.5 Hz, 1H), 8.14 (dt, *J*=8.0, 1.9 Hz, 1H), 7.62 (d, *J*=7.6 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.39 (dd, *J*=8.0, 4.9 Hz, 1H), 7.33 (t, *J*=7.1 Hz, 1H), 7.28 (s, 1H), 7.13 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.05, 152.85, 149.24, 146.36, 131.89, 128.72, 126.62, 124.95, 123.63, 123.25, 121.21, 111.31, 102.75.



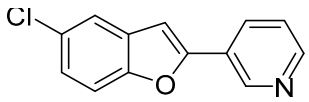
3o: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.10 (s, 1H), 8.57 (d, *J* = 4.3 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 1.8 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.39 (dd, *J* = 8.6, 2.1 Hz, 2H), 7.09 (s, 1H), 1.39 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 153.34, 152.83, 148.83, 146.37, 146.11, 131.89, 128.40, 126.88, 123.63, 123.01, 117.34, 110.57, 103.02, 34.73, 31.78.
MS (ACPI): Calc'd for $C_{17}H_{18}NO^+$, 252.1388; found, 252.1383.



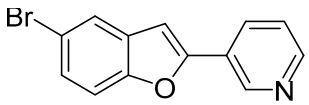
3p: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.12 (d, *J* = 1.9 Hz, 1H), 8.61 (d, *J* = 4.8 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.39 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.22 (s, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 2.66 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.40, 155.24, 150.04, 147.79, 146.84, 146.59, 132.19, 126.08, 123.64, 119.41, 118.30, 103.62, 24.34.
MS (ACPI): Calc'd for $C_{13}H_{11}N_2O^+$, 211.0871; found, 211.0868.



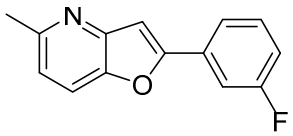
3q: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.08 (s, 1H), 8.58 (d, *J* = 3.4 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.44 (dd, *J* = 8.9, 4.1 Hz, 1H), 7.36 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.23 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.05 (s, 1H), 7.04 – 6.98 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.56, 158.19, 154.59, 151.25, 149.50, 146.34, 131.90, 129.47, 126.21, 123.58, 112.61, 111.90, 106.56, 102.78.
MS (ACPI): Calc'd for $C_{13}H_9NFO^+$, 214.0668; found, 214.0658.



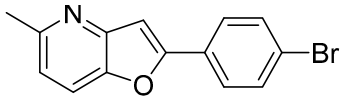
3r: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.05 (s, 1H), 8.57 (d, *J* = 4.8 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 2.1 Hz, 1H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.34 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.23 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.98 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.27, 153.33, 149.57, 146.34, 131.92, 130.00, 128.78, 126.03, 125.05, 123.57, 120.64, 112.20, 102.13.
MS (ACPI): Calc'd for $C_{13}H_9NClO^+$, 230.0373; found, 230.0366.



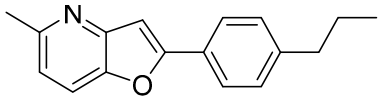
3s: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.06 (s, 1H), 8.58 (d, *J* = 4.8 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.68 (s, 1H), 7.39 – 7.32 (m, 3H), 7.00 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 153.11, 152.70, 148.59, 145.36, 130.95, 129.62, 126.74, 124.99, 122.70, 122.57, 115.28, 111.68, 100.97.
MS (ACPI): Calc'd for $C_{13}H_9NBrO^+$, 273.9868; found, 273.9860.



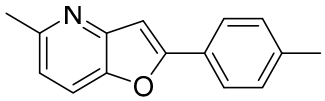
3t: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (dd, *J* = 8.1, 4.1 Hz, 2H), 7.59 – 7.55 (m, 1H), 7.43 (td, *J* = 8.0, 5.8 Hz, 1H), 7.16 (s, 1H), 7.11 – 7.06 (m, 2H), 2.66 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.28, 161.83, 157.99, 154.91, 147.86, 146.66, 130.45, 120.92, 119.17, 118.26, 116.07, 111.92, 103.08, 24.21.
MS (ACPI): Calc'd for $C_{14}H_{11}NFO^{+}$, 228.0825; found, 228.0821.



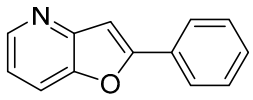
3u: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.15 (s, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 2.67 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.33, 154.81, 147.94, 146.64, 138.00, 132.07, 128.73, 126.60, 123.52, 119.04, 118.22, 102.54, 24.18.
MS (ACPI): Calc'd for $C_{14}H_{11}NBrO^{+}$, 288.0024; found, 288.0022.



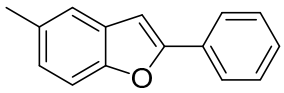
3v: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.08 (s, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 2.65 – 2.59 (m, 5H), 1.71 – 1.61 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.93, 154.31, 151.58, 148.32, 146.44, 144.43, 128.97, 127.30, 125.17, 119.97, 118.41, 118.00, 101.30, 37.92, 24.32, 24.13, 13.74.
MS (ACPI): Calc'd for $C_{17}H_{18}NO^{+}$, 252.1388; found, 252.1384.



3w: ^{1}H NMR (400 MHz, $CDCl_3$) δ: δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.11 (s, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 2.67 (s, 3H), 2.41 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.01, 154.29, 148.28, 146.52, 139.72, 129.61, 127.08, 125.23, 118.47, 118.14, 101.26, 24.11, 21.47.
MS (ACPI): Calc'd for $C_{15}H_{14}NO^{+}$, 244.1075; found, 244.1068.



3x[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.12 (d, *J*=2.1 Hz, 1H), 8.58 (dd, *J*=4.8, 1.5 Hz, 1H), 8.14 (dt, *J*=8.0, 1.9 Hz, 1H), 7.62 (d, *J*=7.6 Hz, 1H), 7.55 (d, *J*=8.1 Hz, 1H), 7.39 (dd, *J*=8.0, 4.9 Hz, 1H), 7.33 (t, *J*=7.1 Hz, 1H), 7.28 (s, 1H), 7.13 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.05, 152.85, 149.24, 146.36, 131.89, 128.72, 126.62, 124.95, 123.63, 123.25, 121.21, 111.31, 102.75.



3y[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, *J*=7.2 Hz, 2H), 7.39 (ddd, *J*=27.0, 16.6, 8.3 Hz, 5H), 7.09 (d, *J*=8.3 Hz, 1H), 6.95 (s, 1H), 2.45 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.98, 152.33, 131.31, 129.63, 128.30, 127.72, 127.38, 124.50, 123.84, 119.69, 109.63, 100.05, 76.30, 75.98, 75.66, 28.68.

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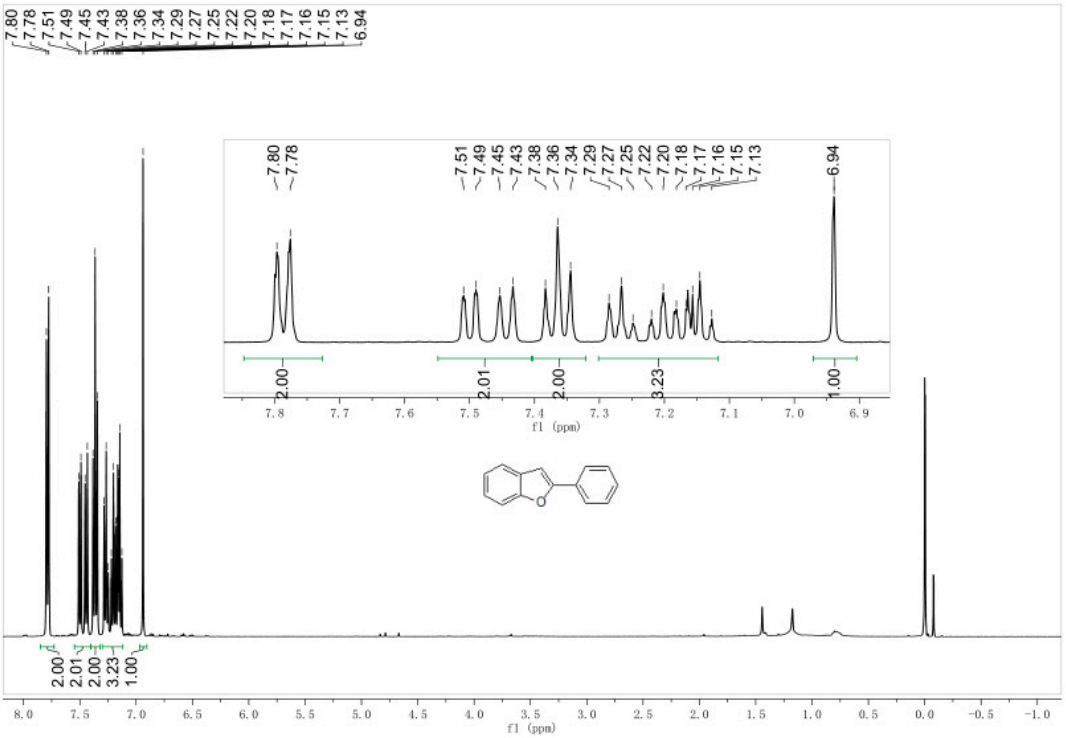
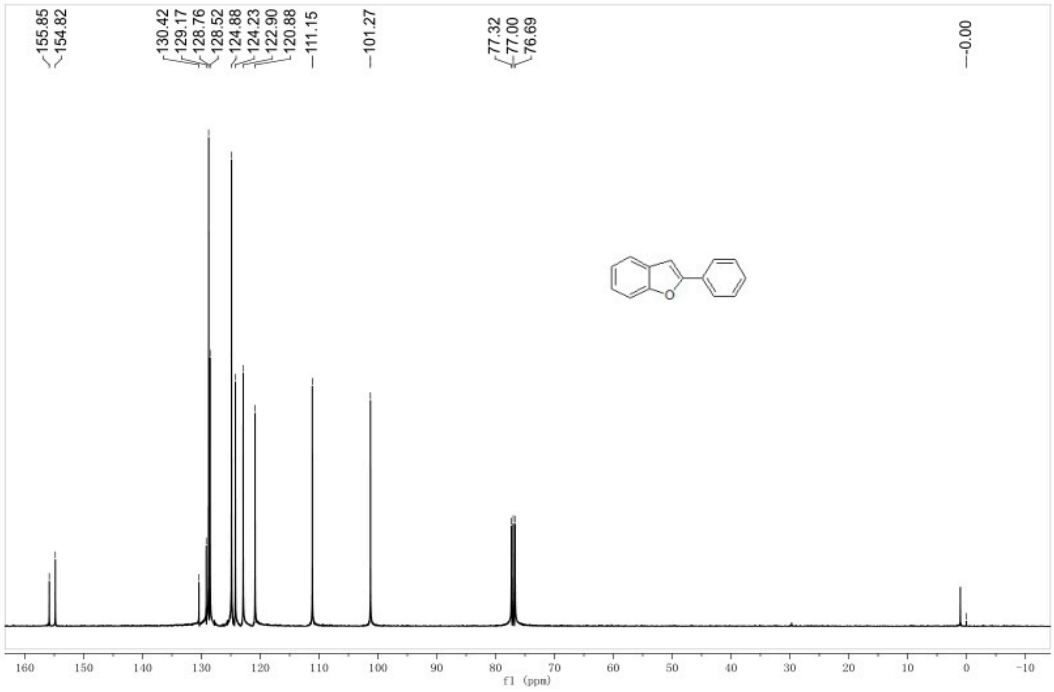
NMR spectra of compounds

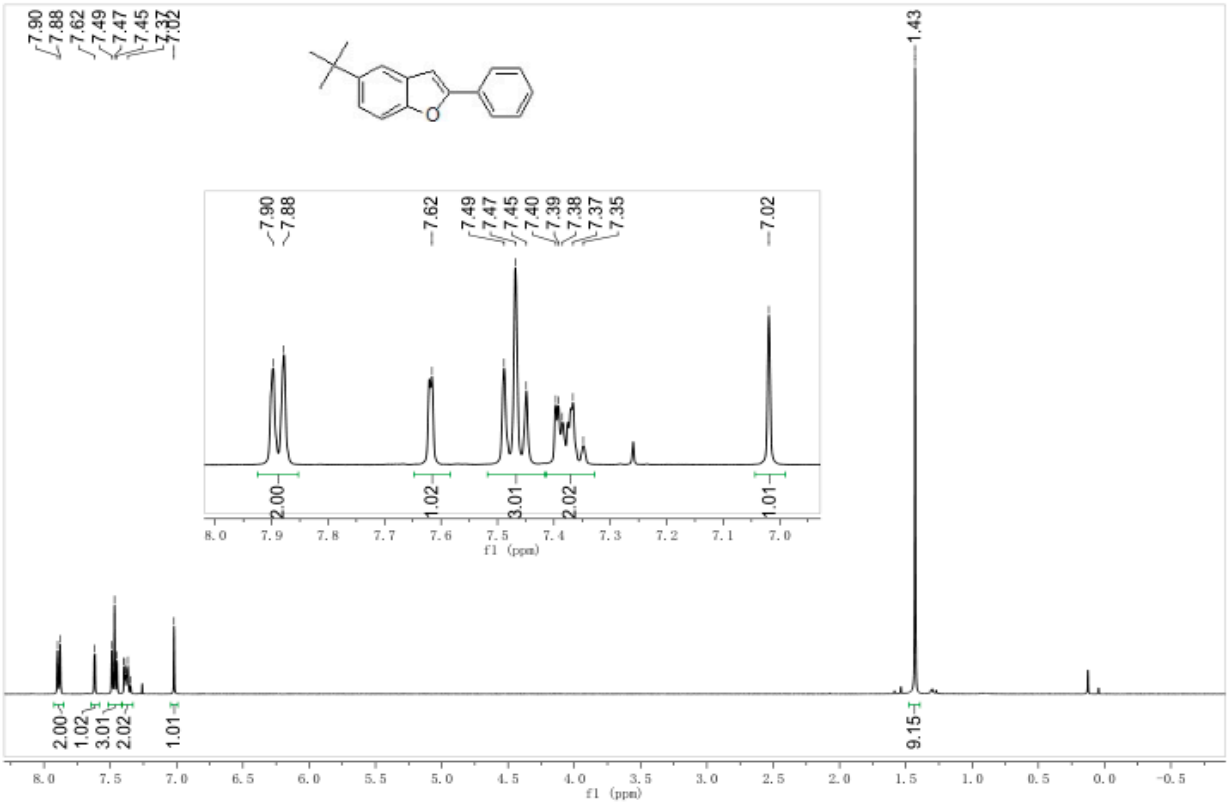
^{1}H NMR of ligand **3a:**



^{13}C NMR of ligand **3a:**



^{1}H NMR of **3b:**



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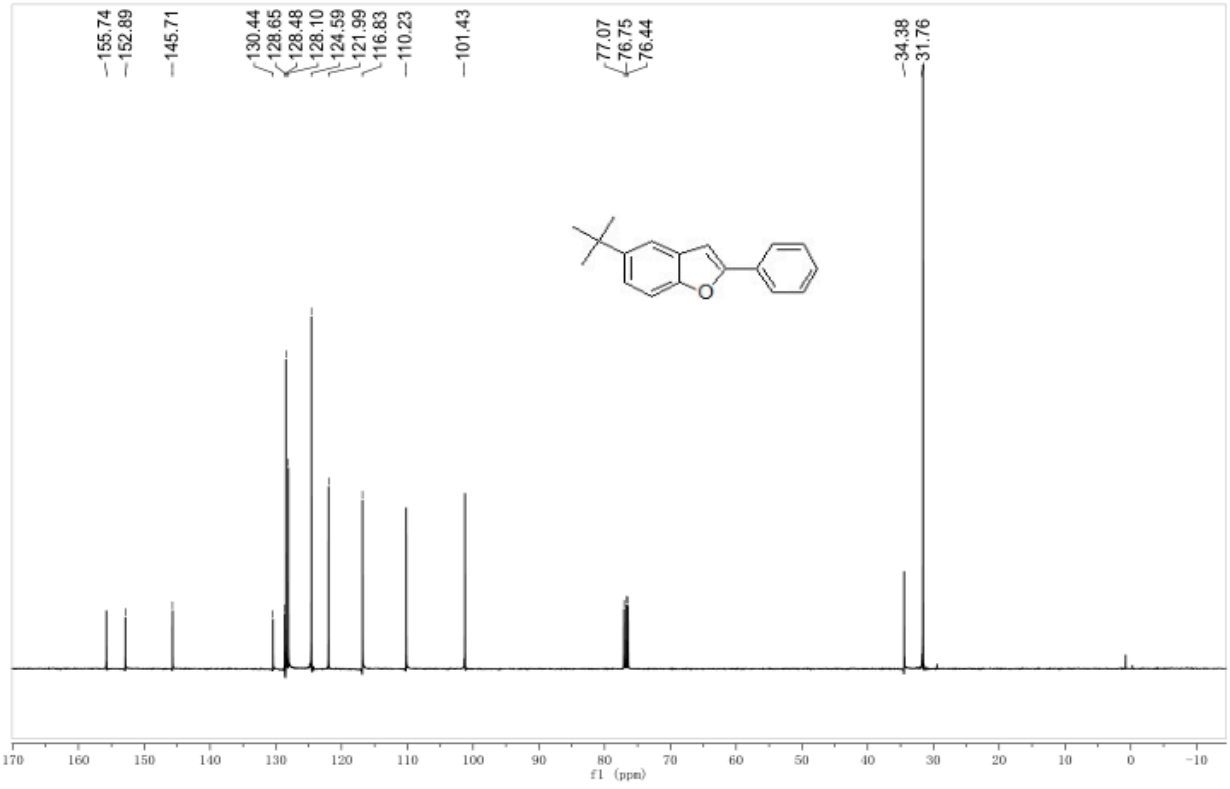

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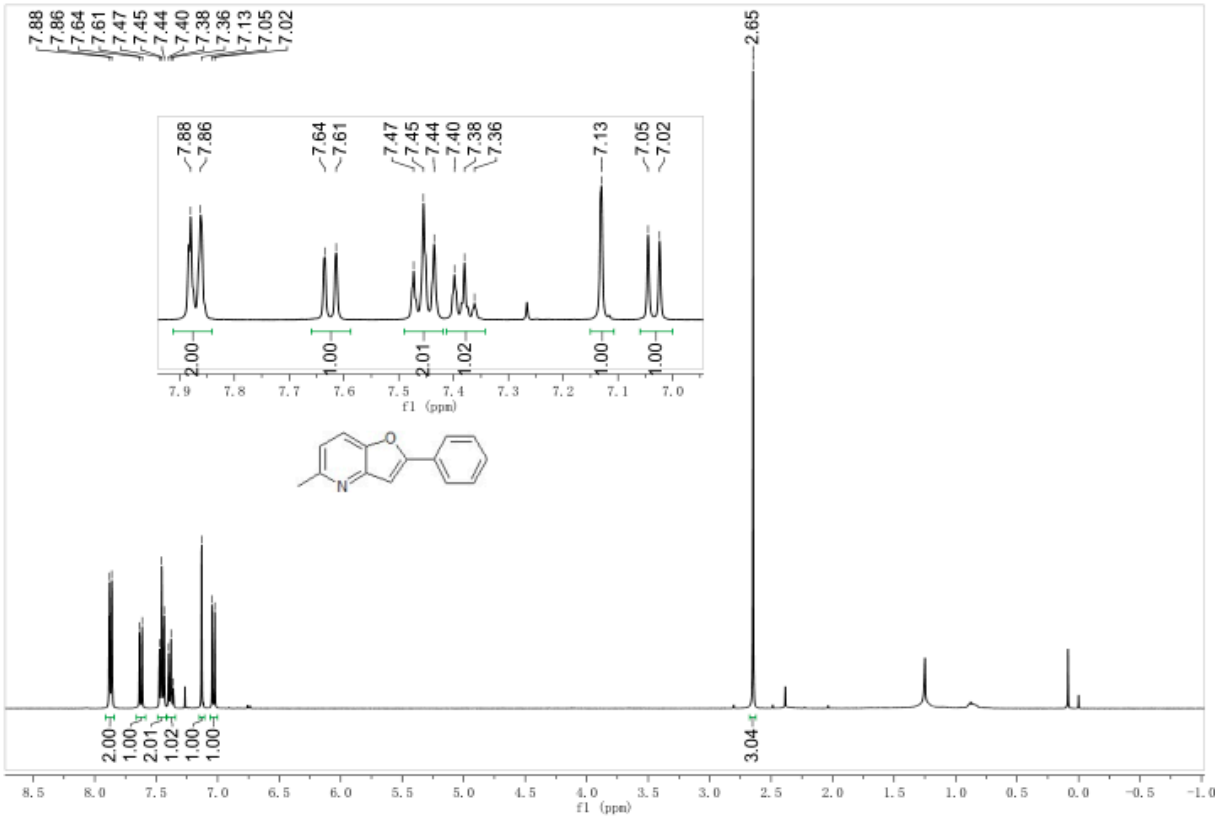

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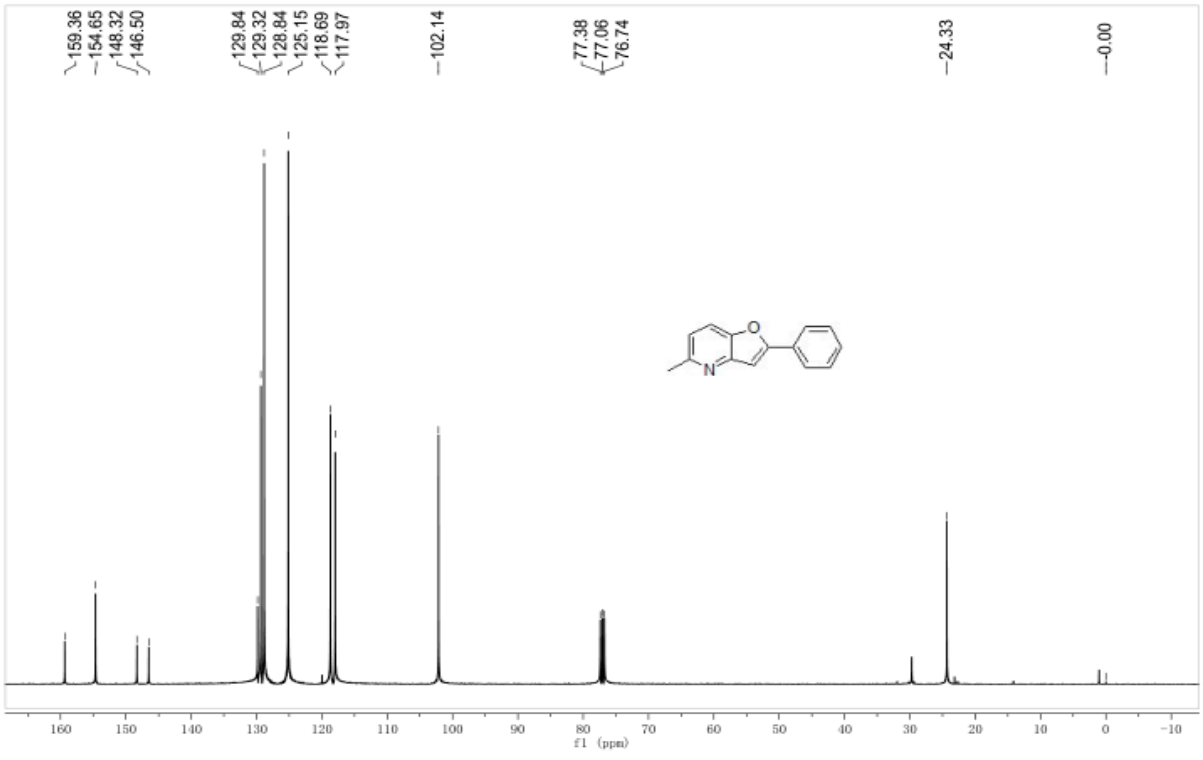

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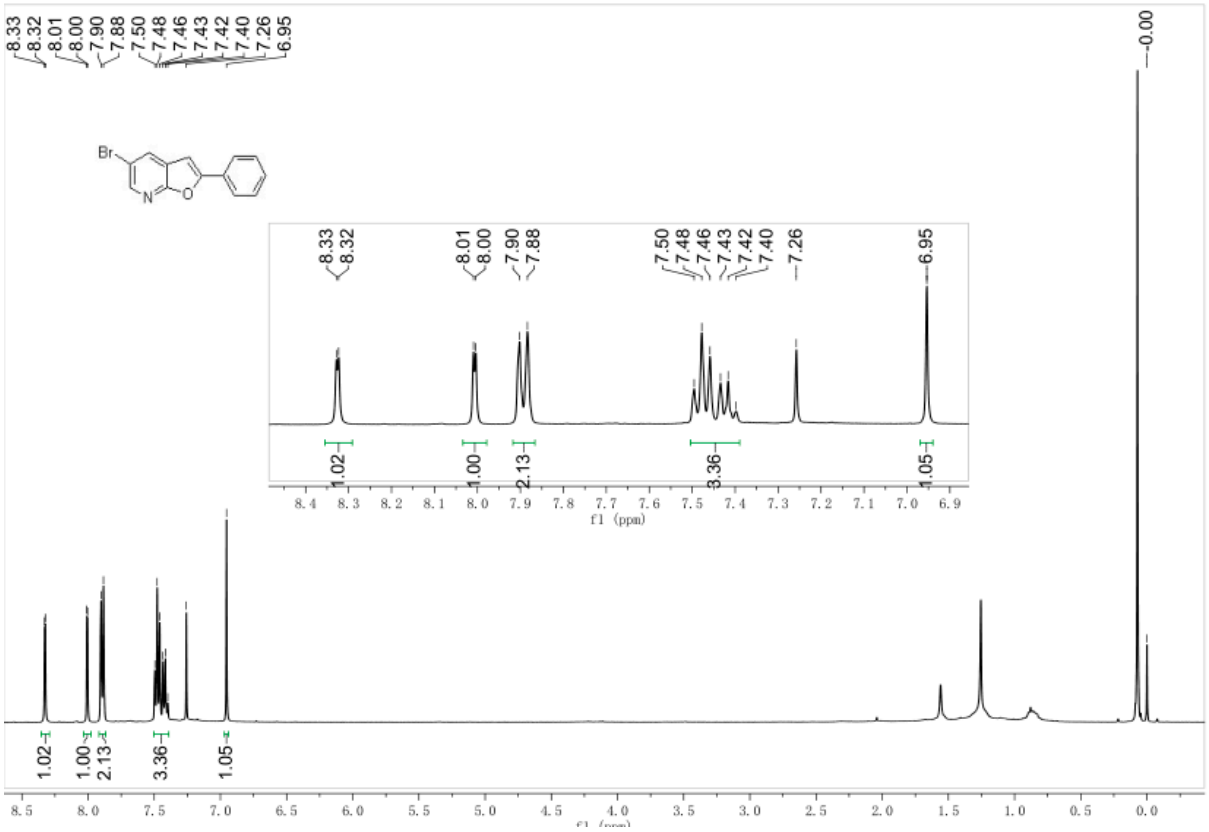

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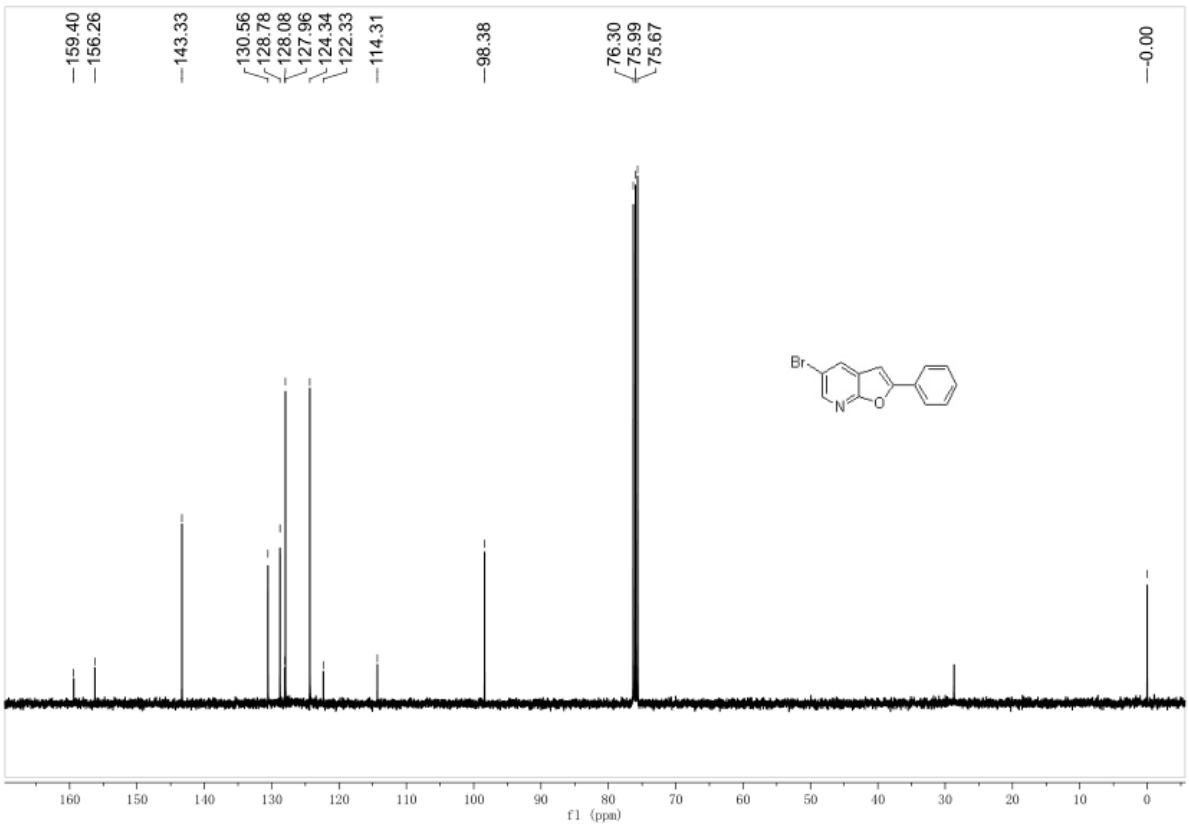

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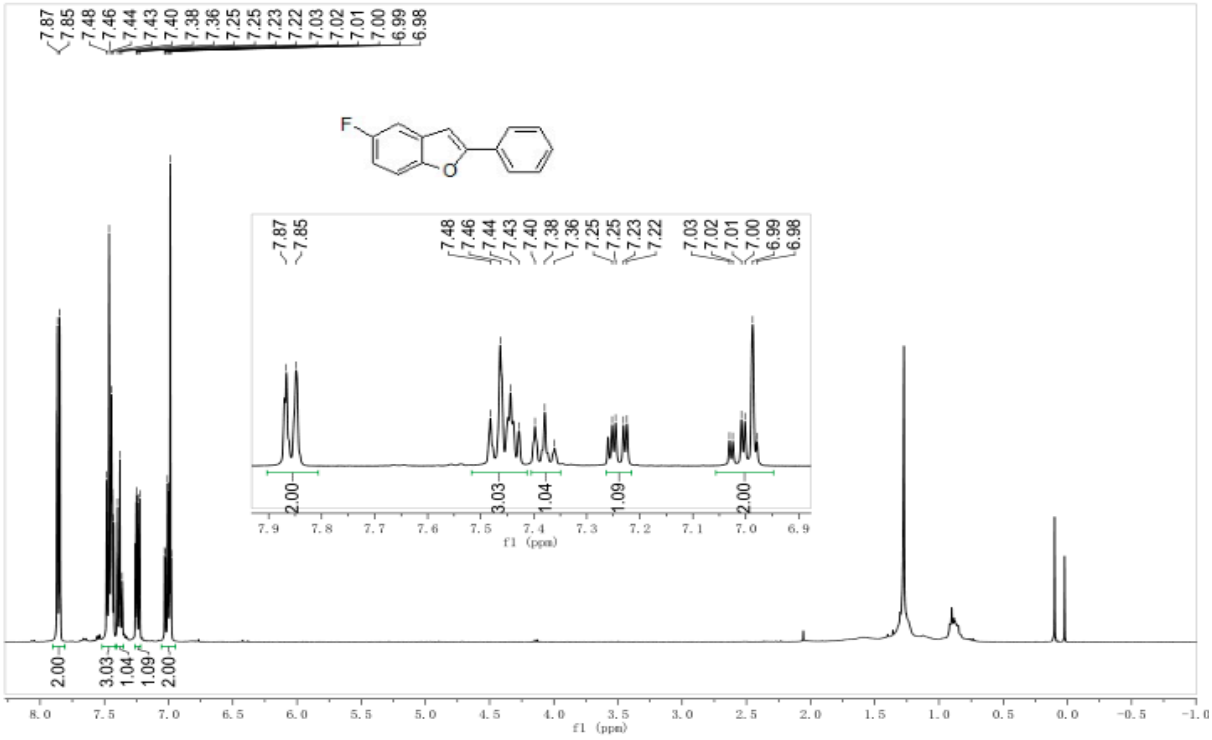

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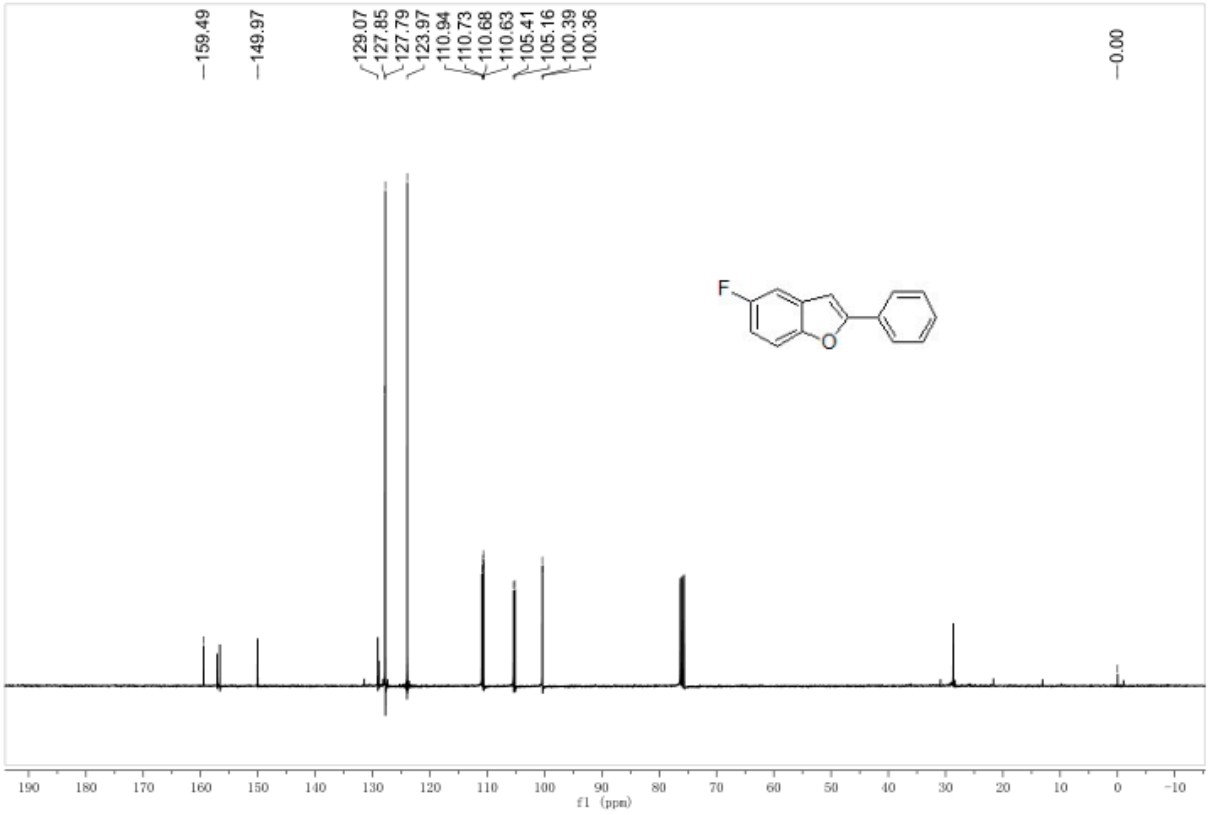
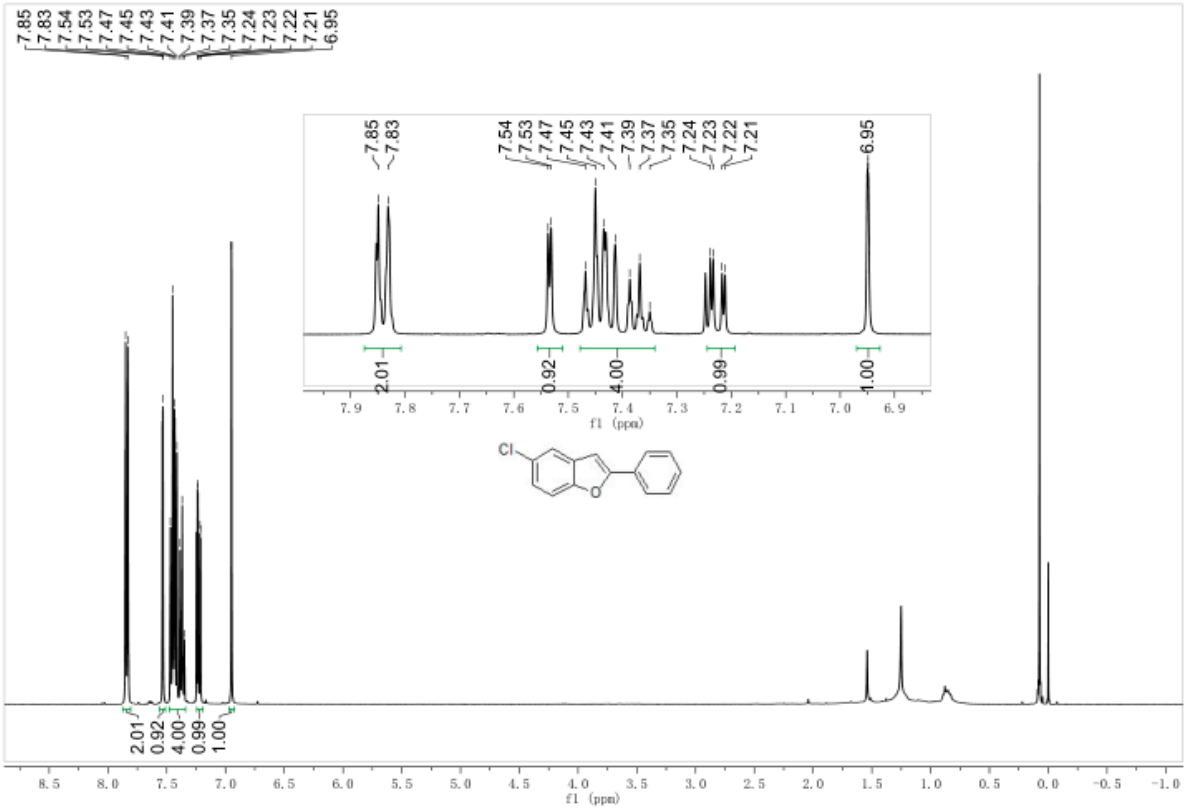
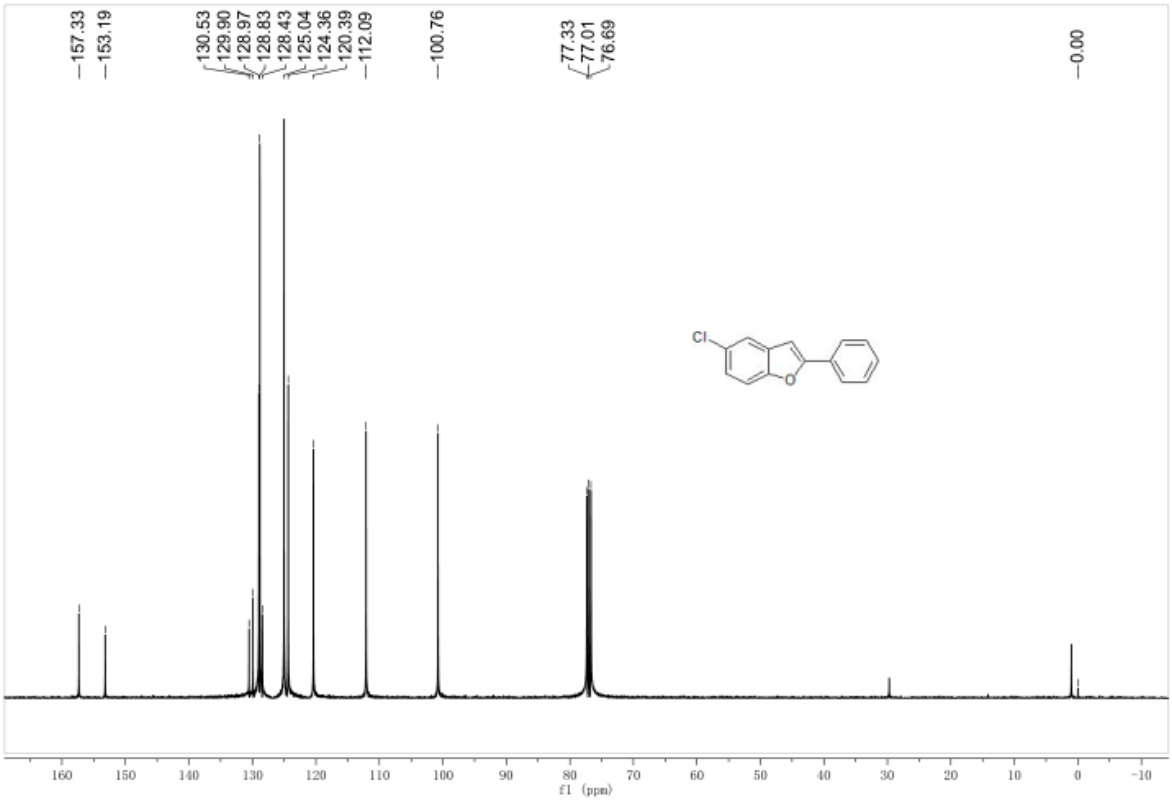


^{1}H NMR of **3f:**



^{13}C NMR of ligand **3f:**



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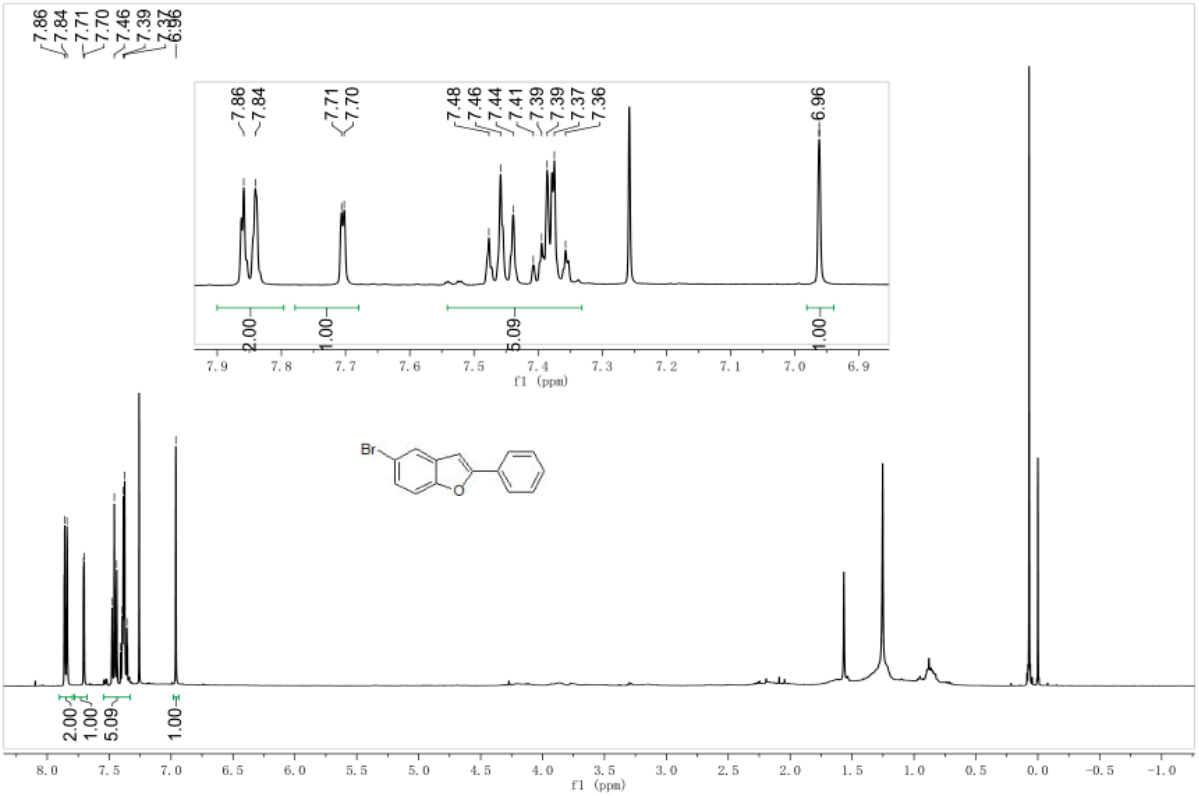
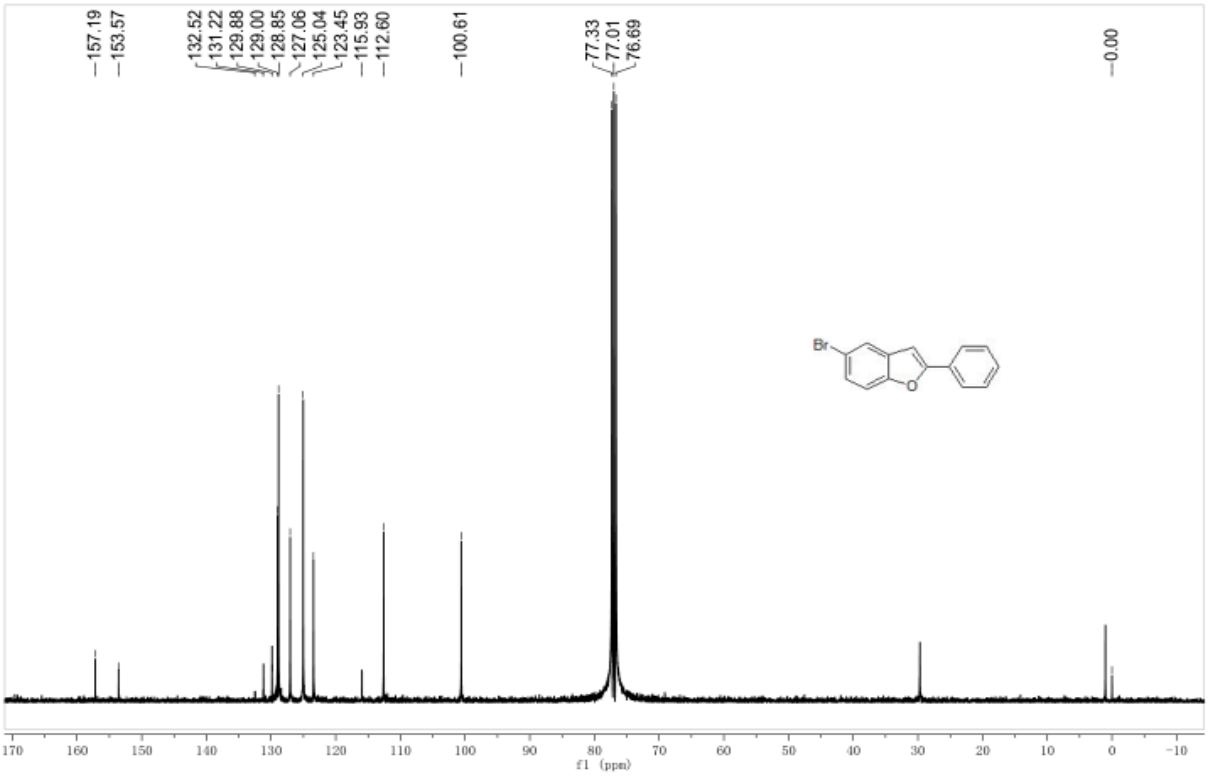
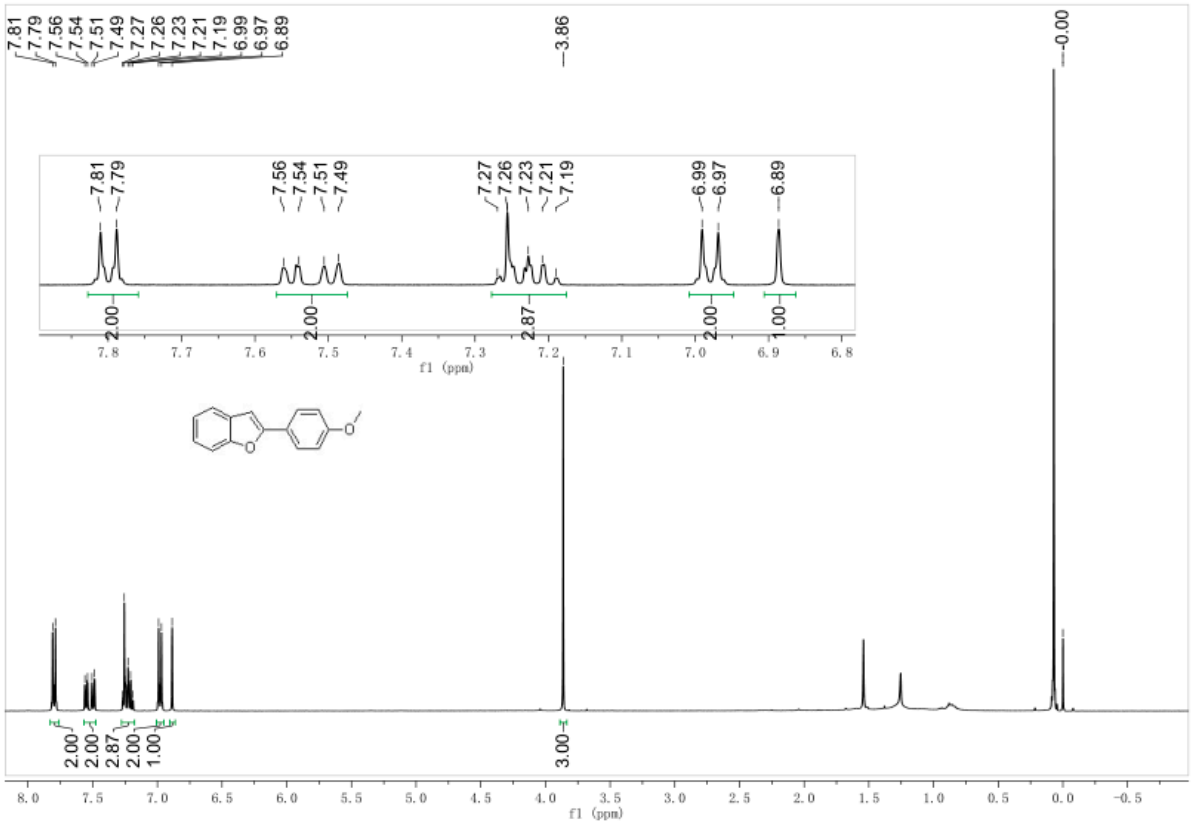


^{13}C NMR of ligand **3g:**



^{1}H NMR of **3h:**



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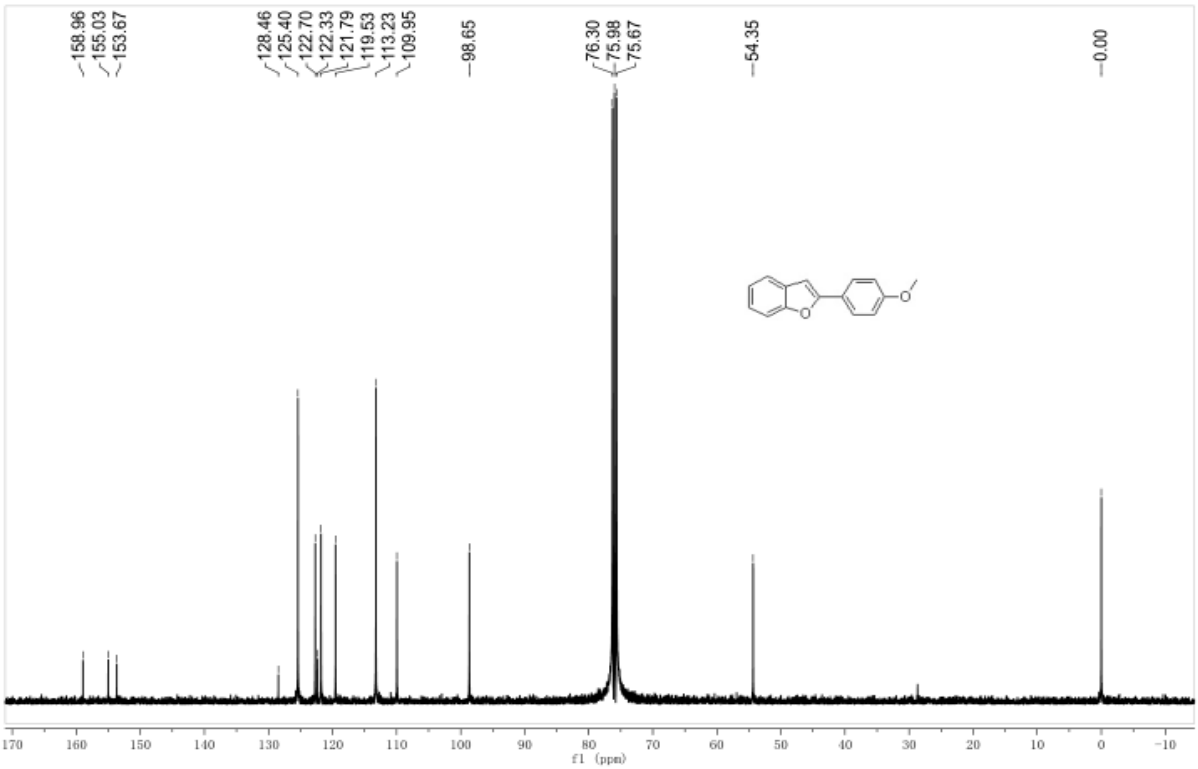
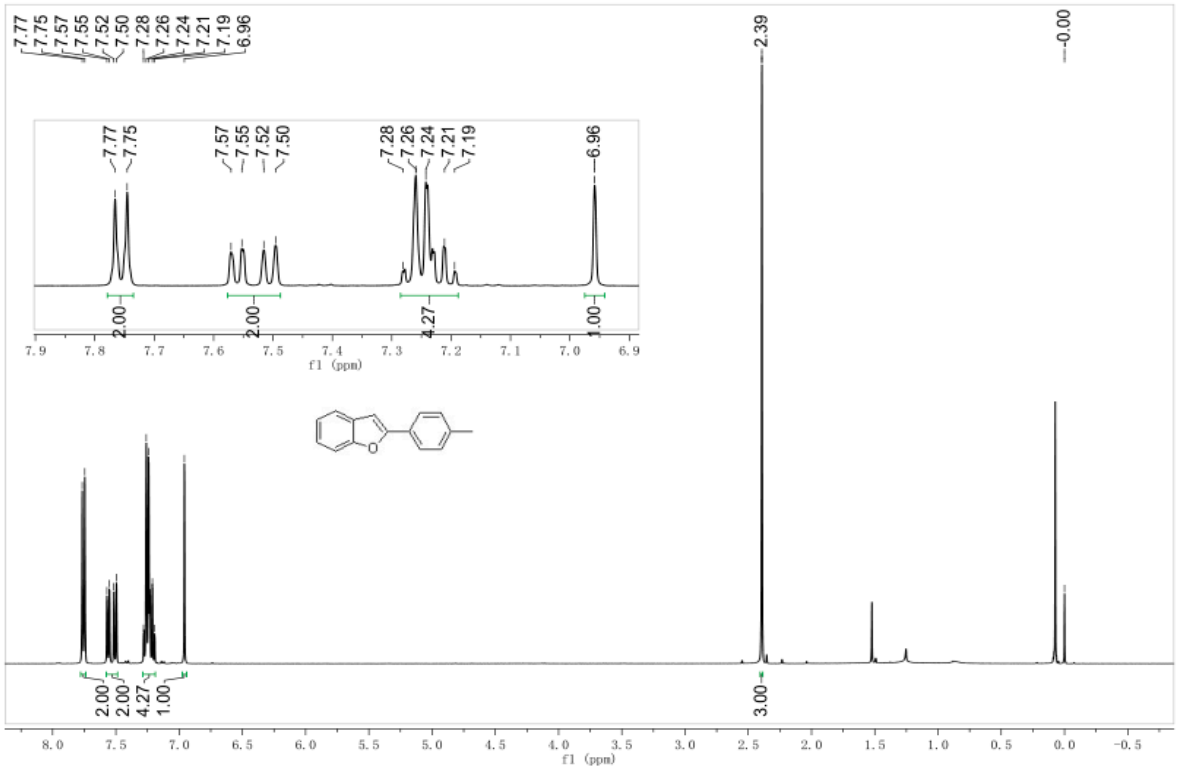


^{1}H NMR of **3i:**



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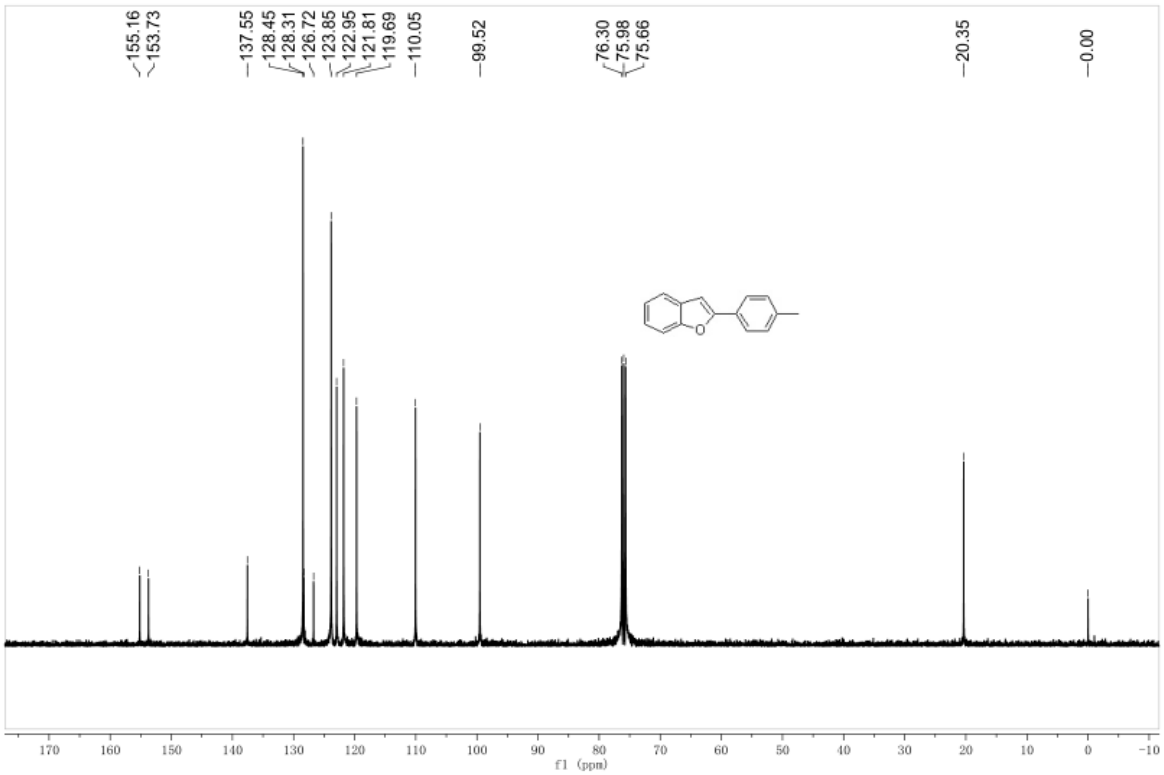

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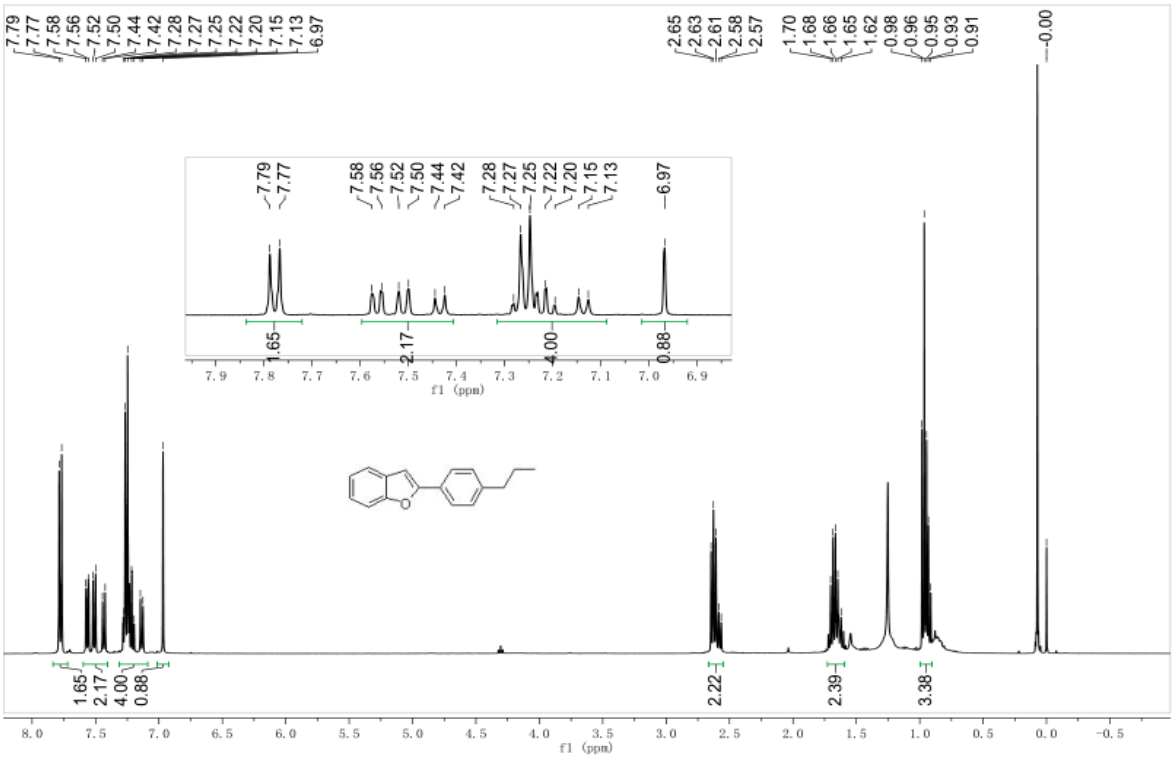
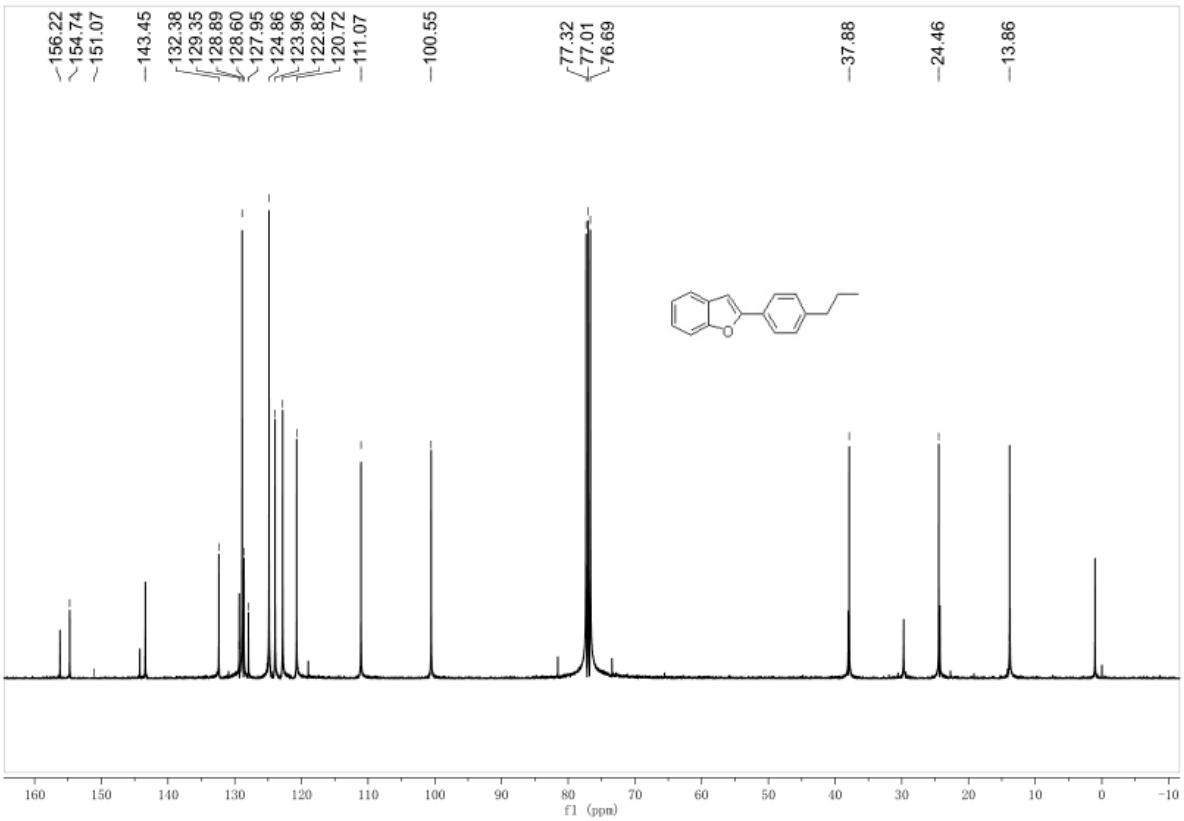


^{13}C NMR of ligand **3j:**



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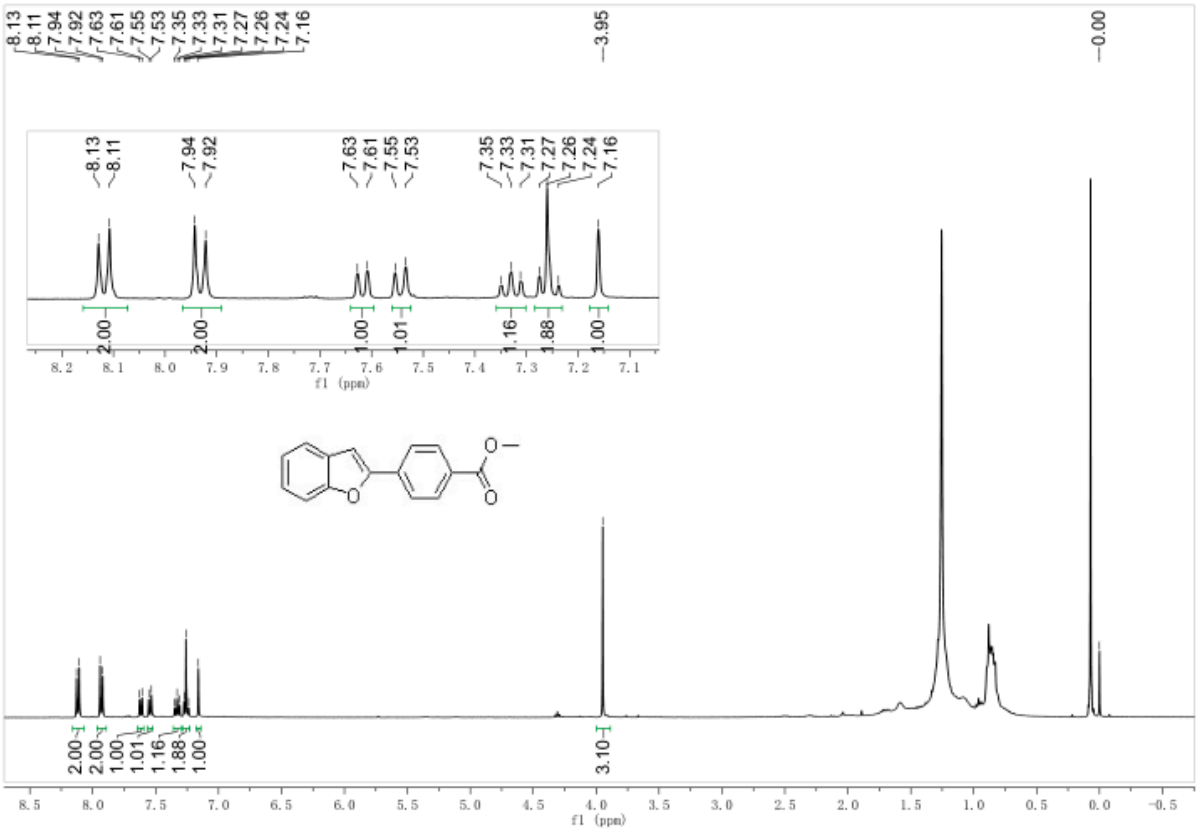

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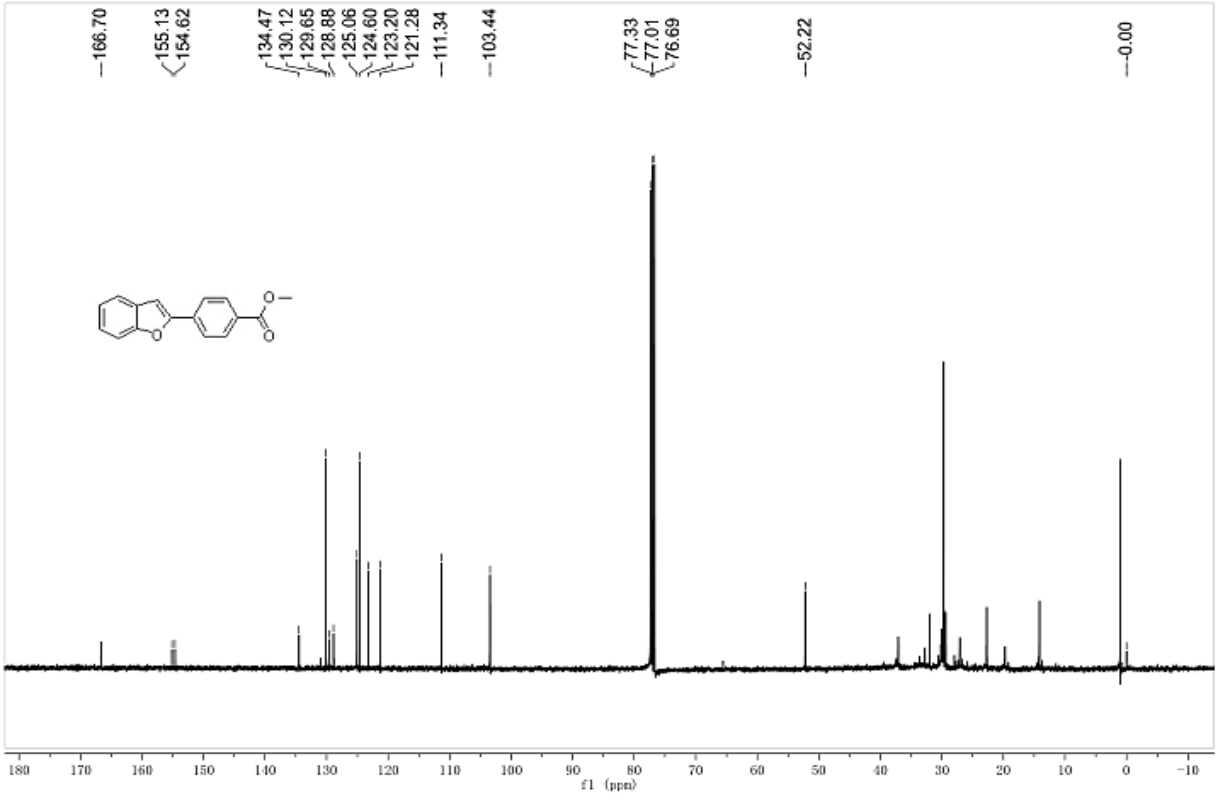

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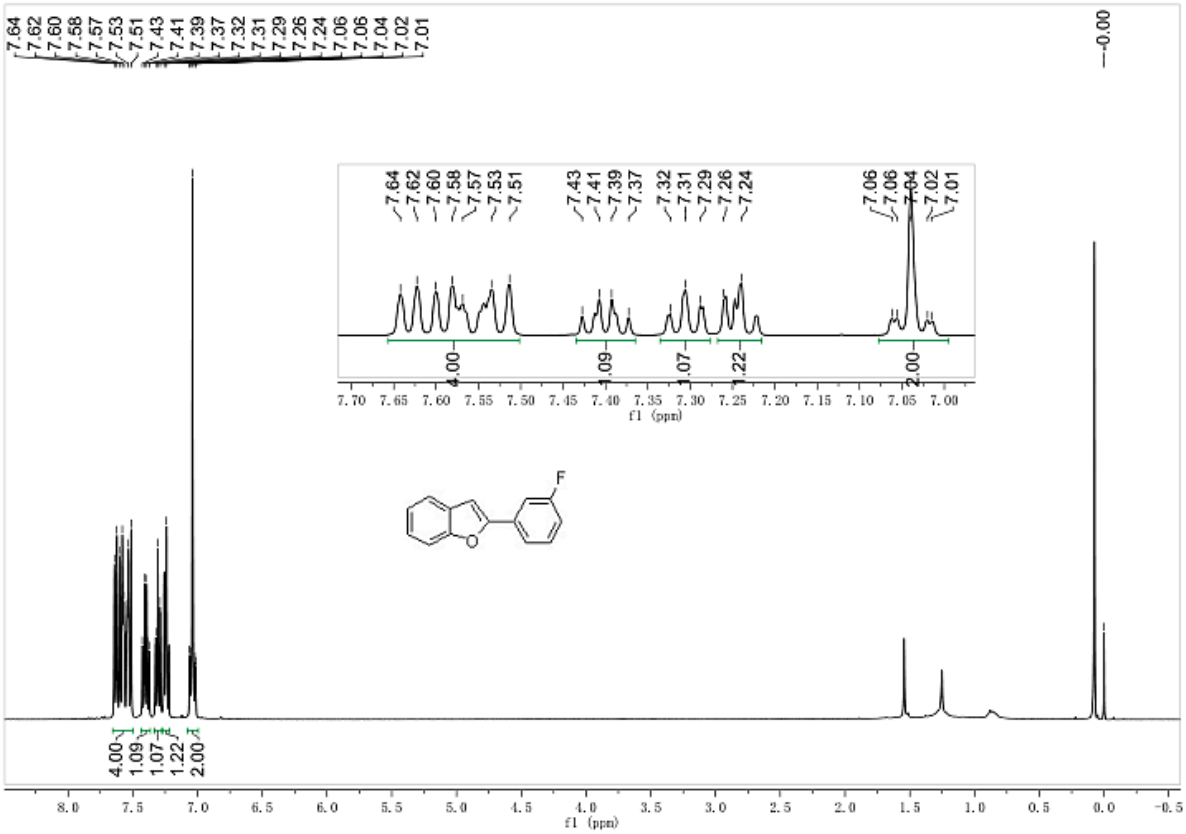

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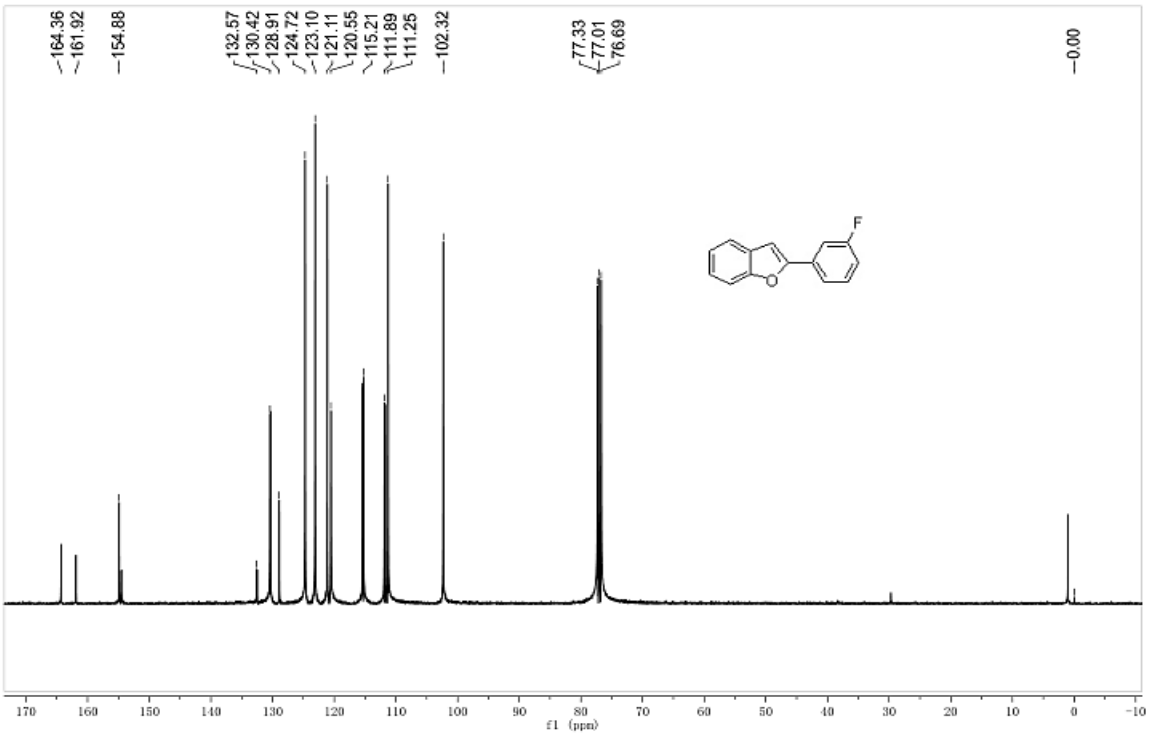

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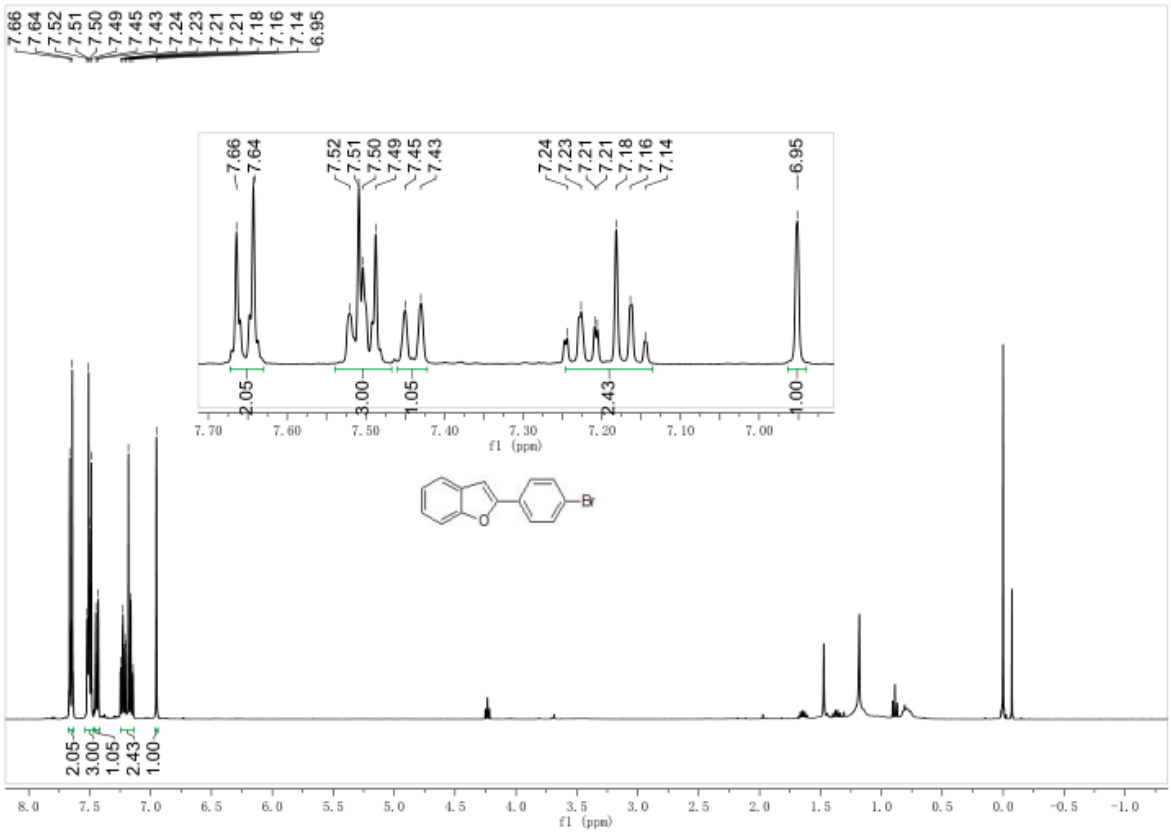
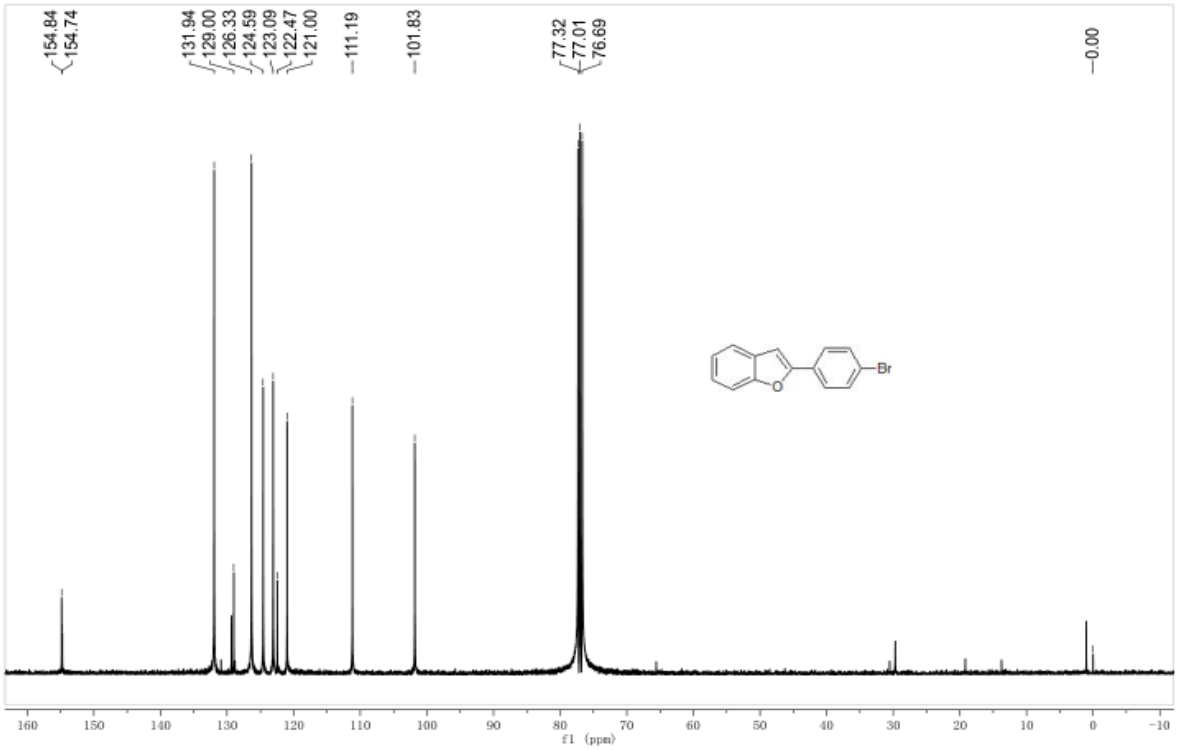


^{13}C NMR of ligand **3m:**



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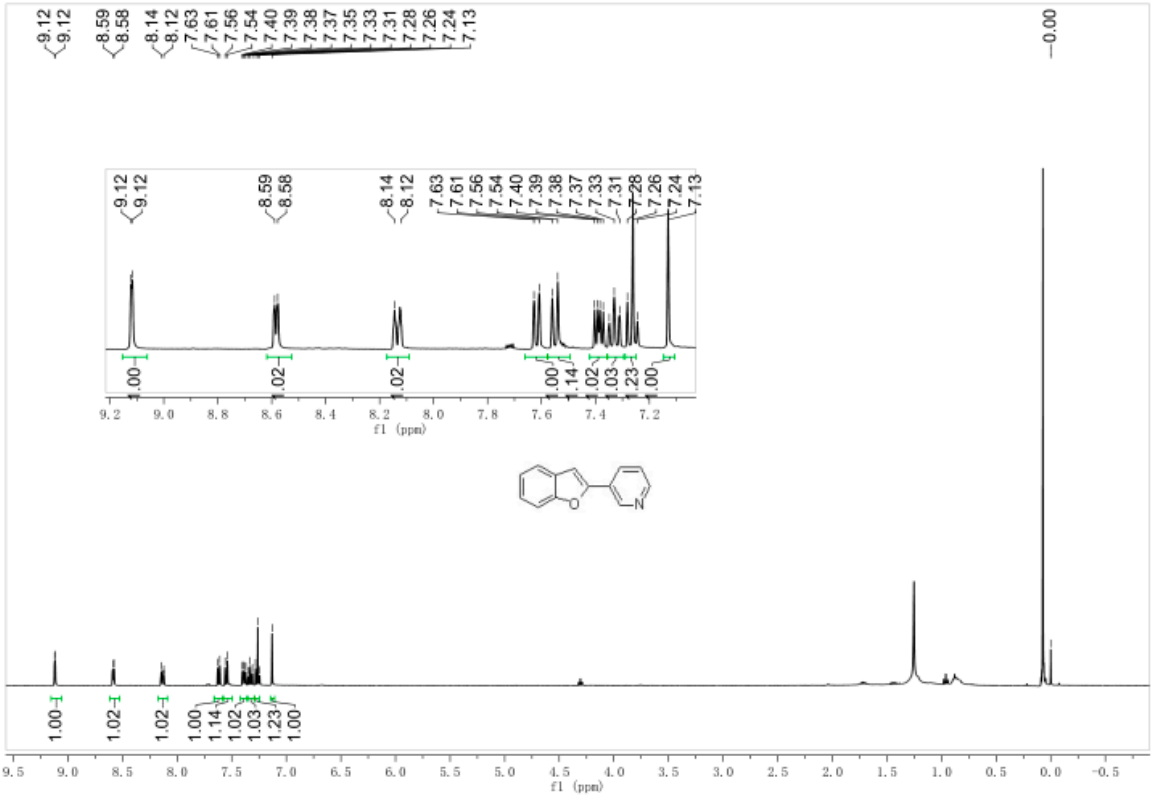
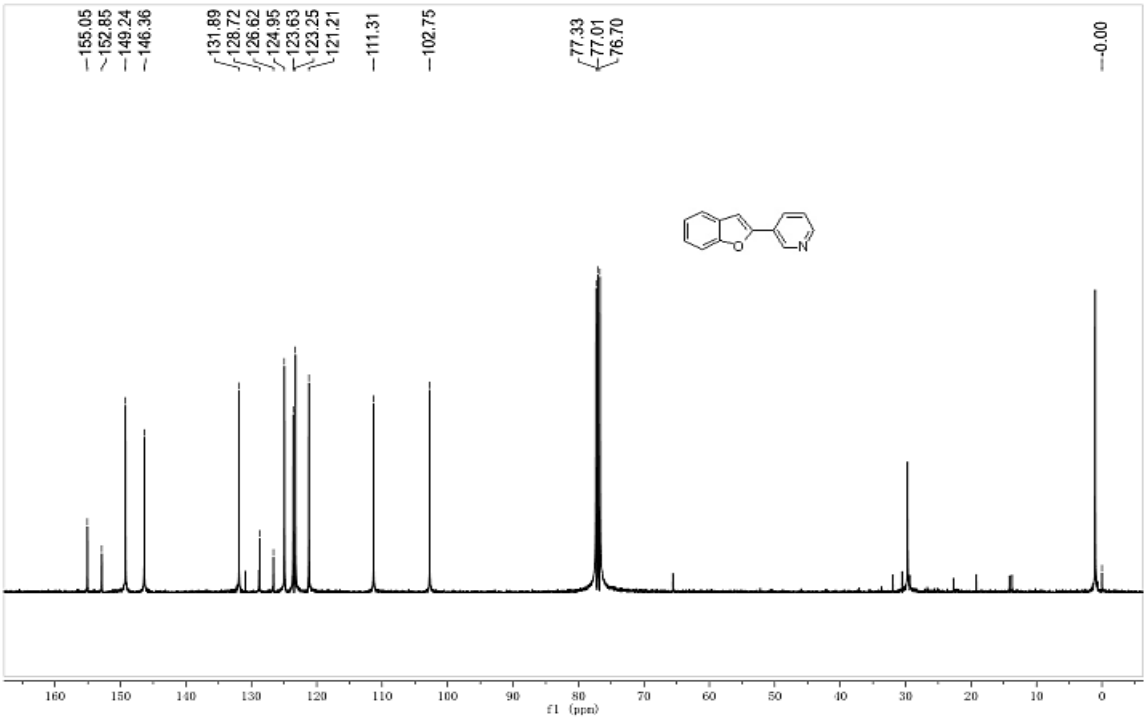


^{13}C NMR of ligand **3n:**



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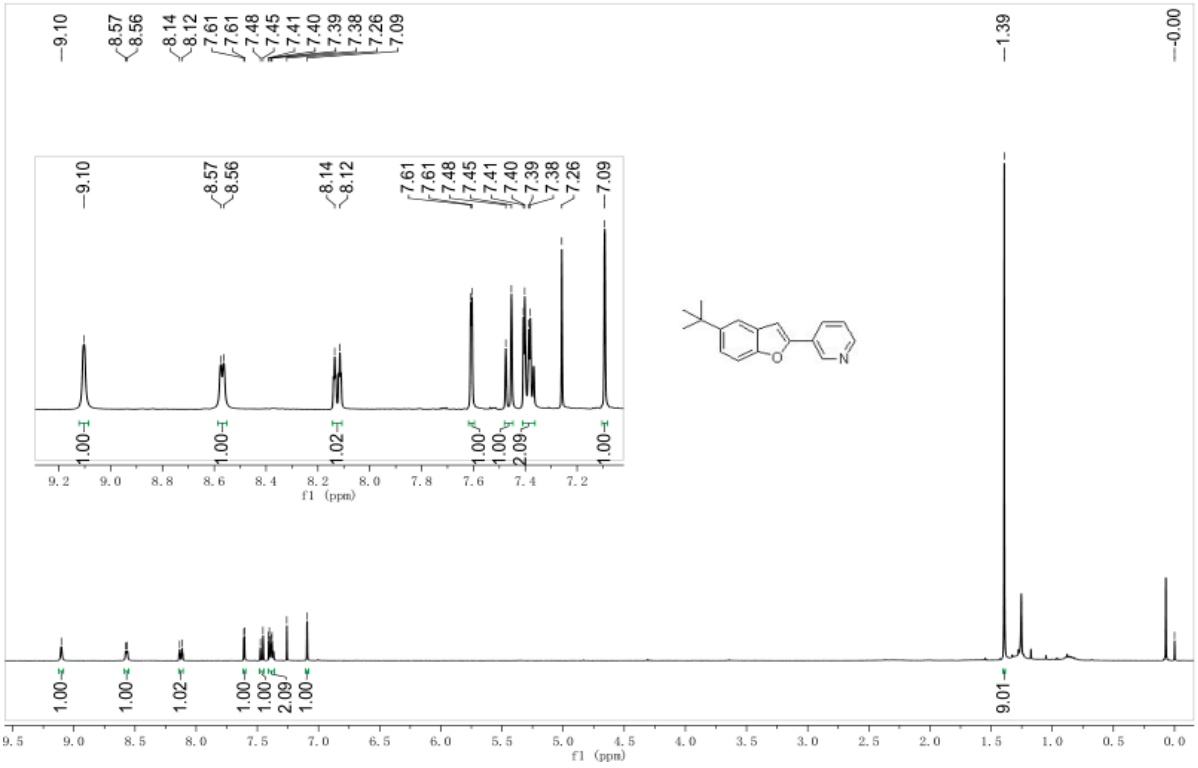

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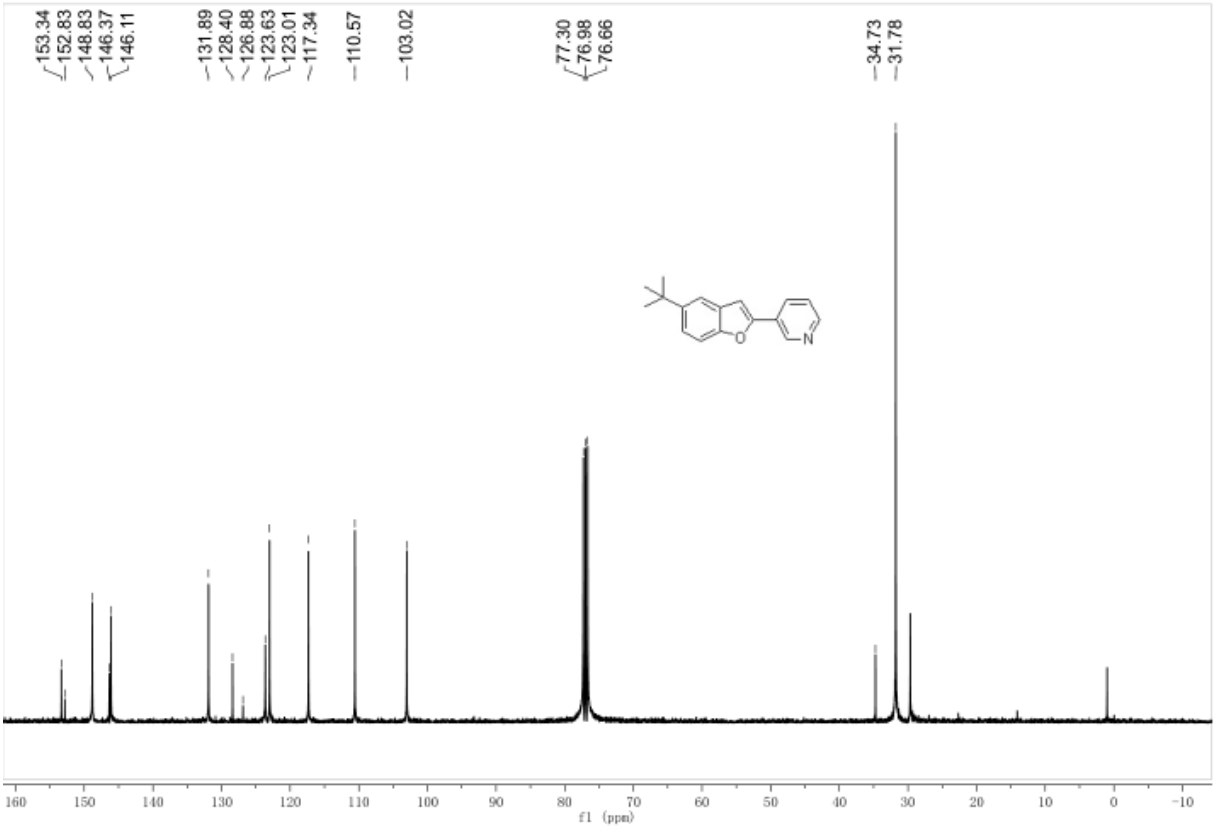

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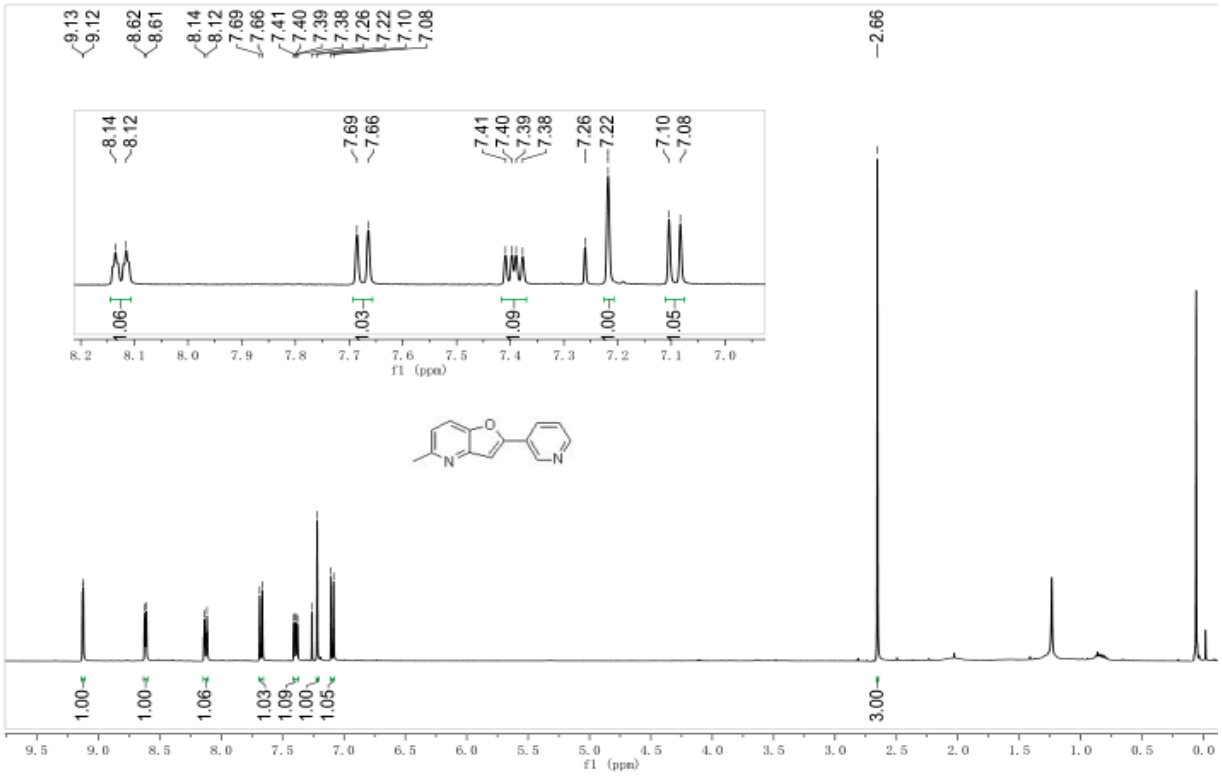

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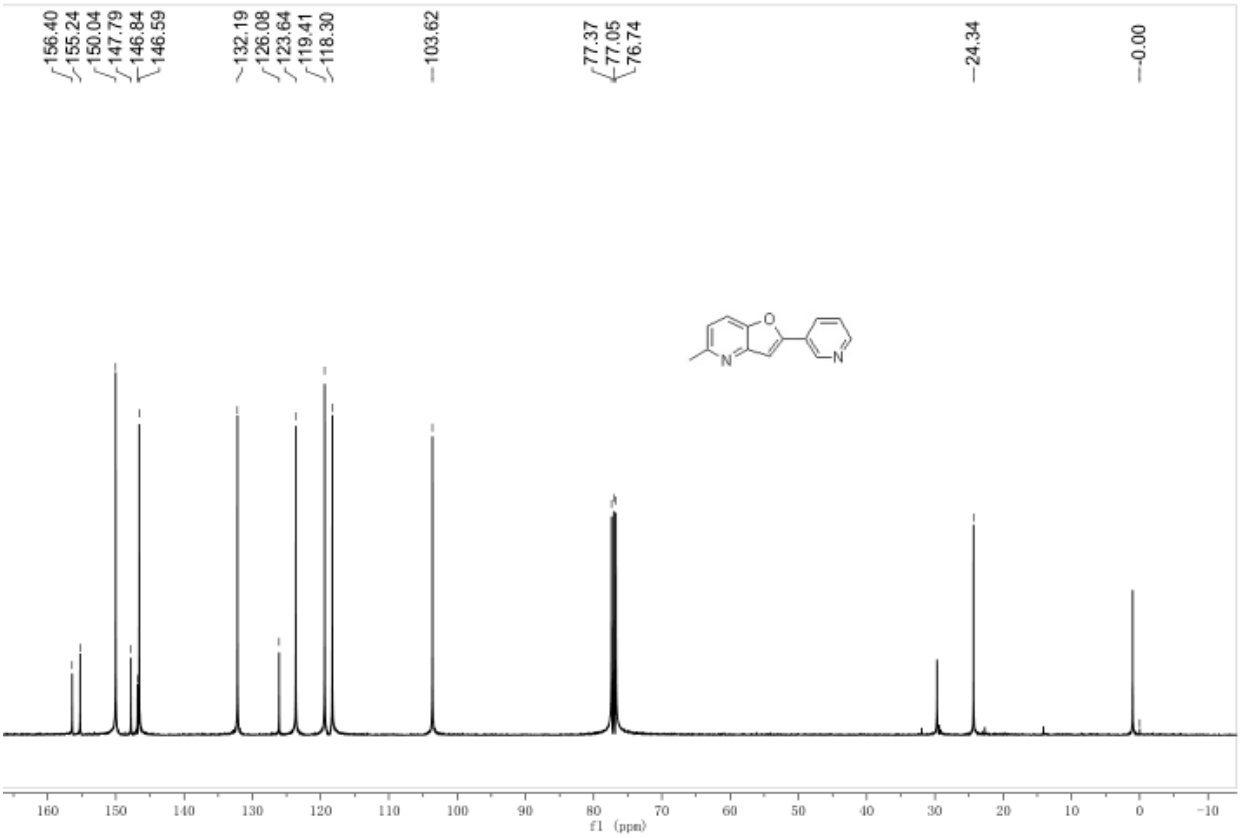

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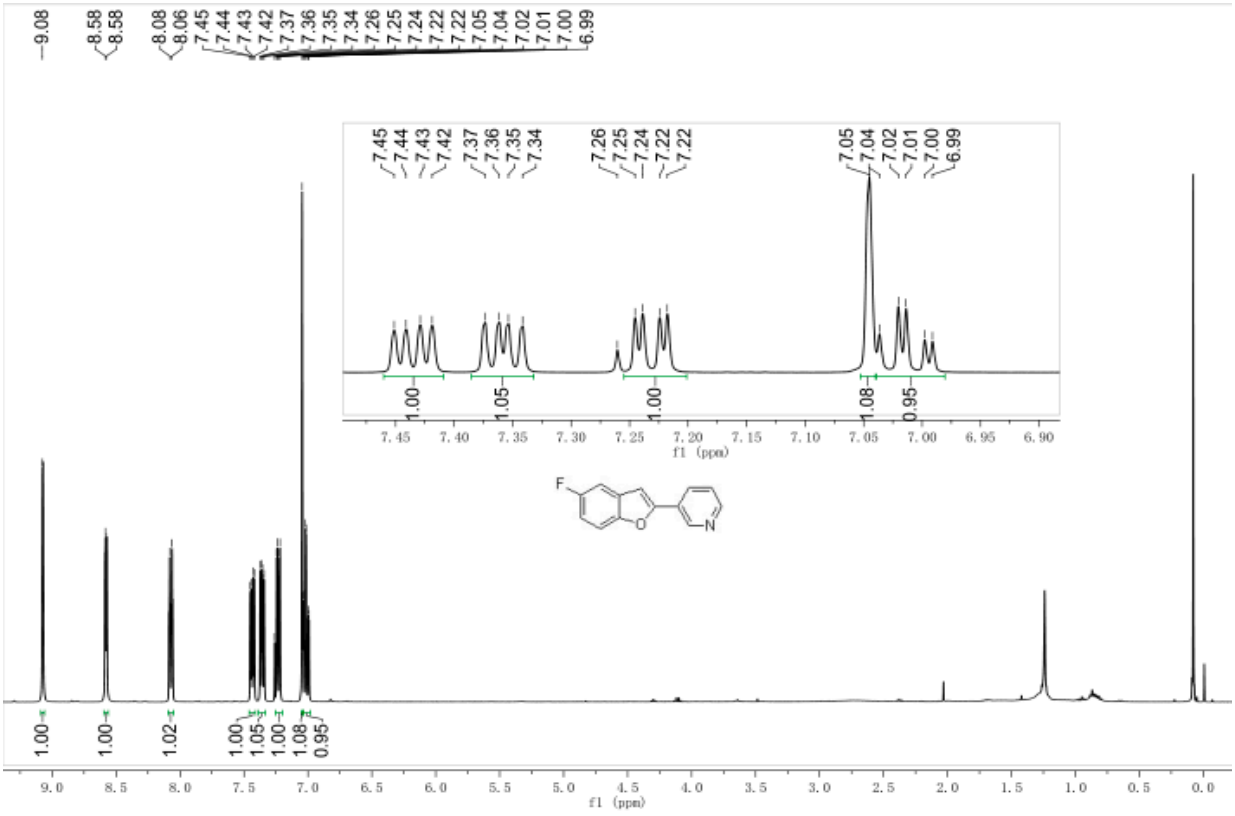

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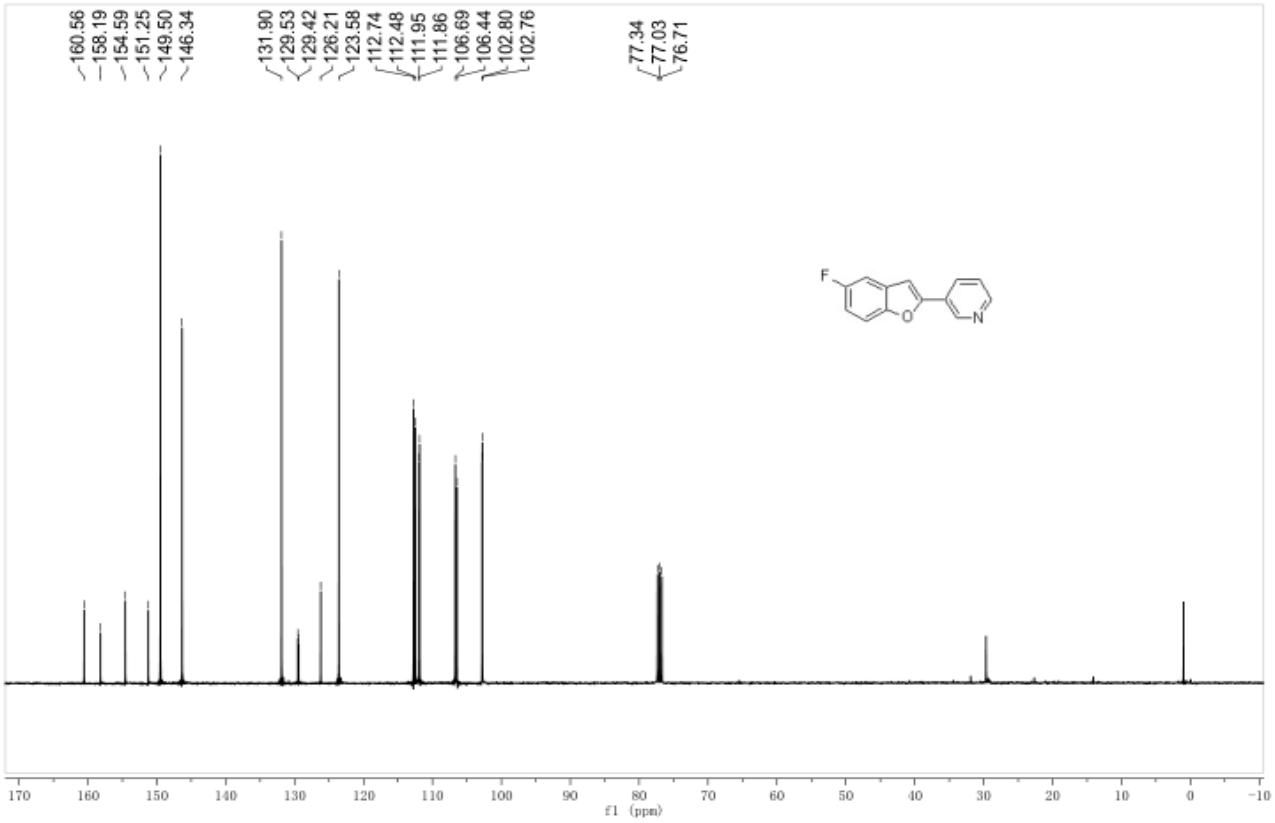

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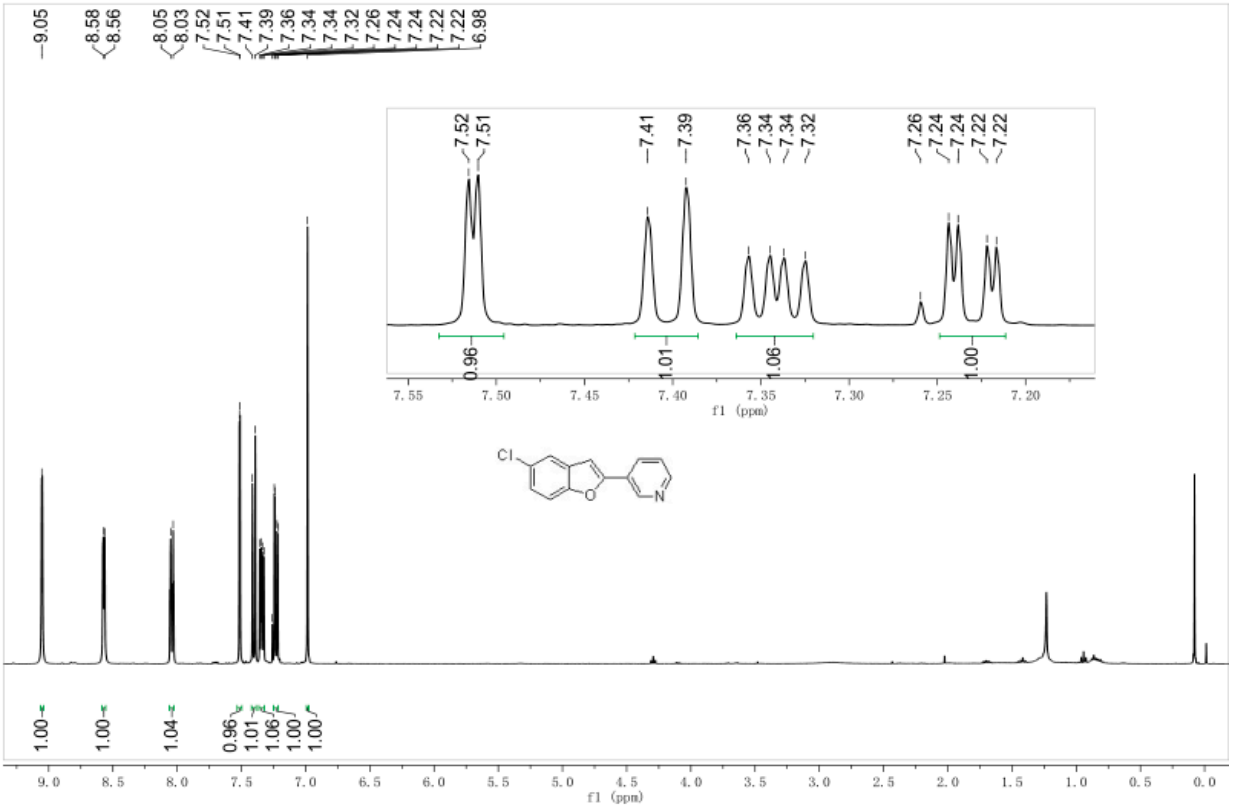

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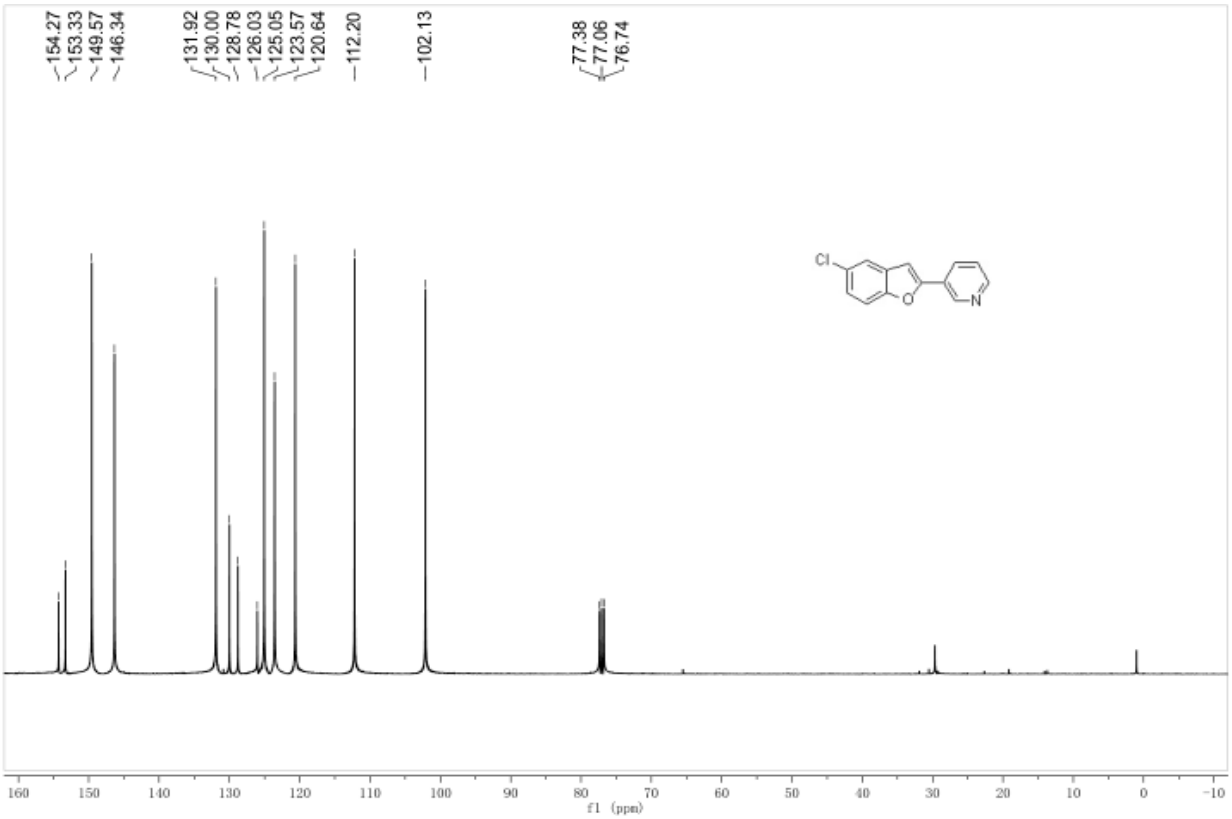

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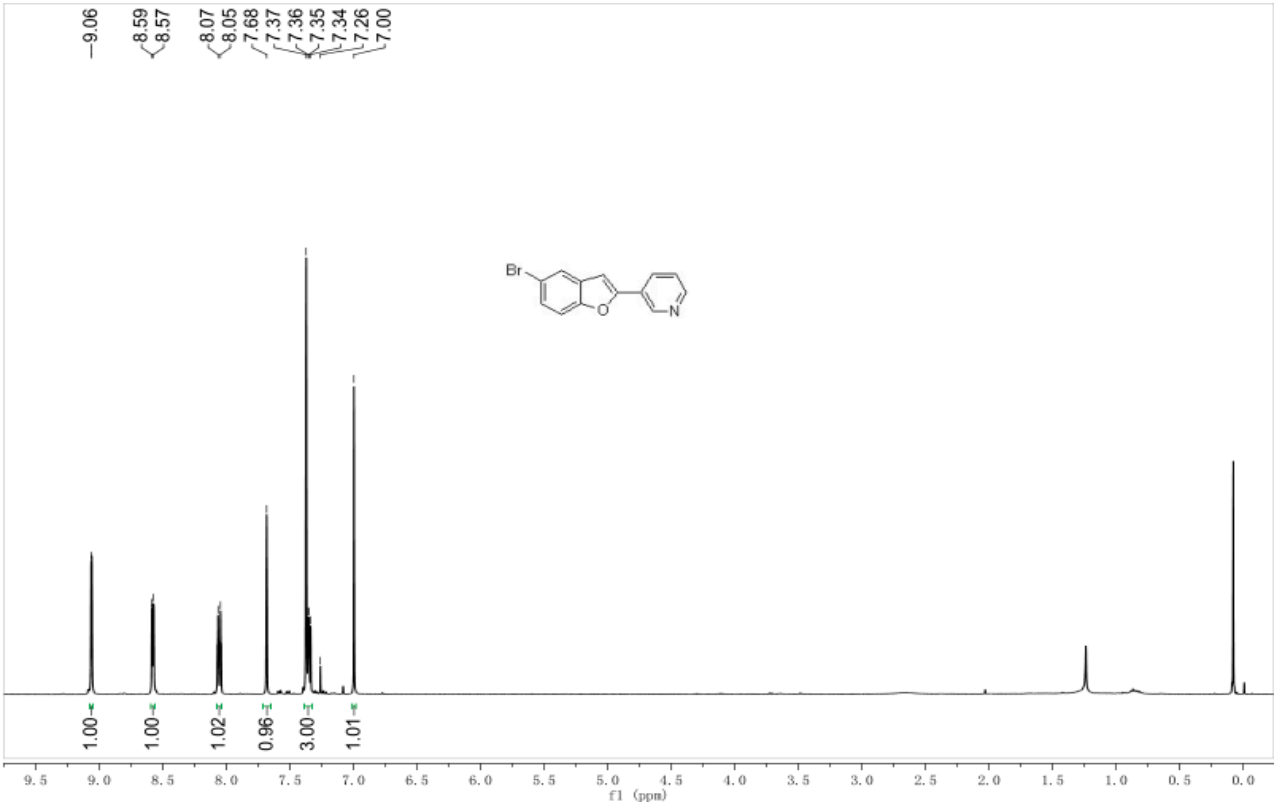

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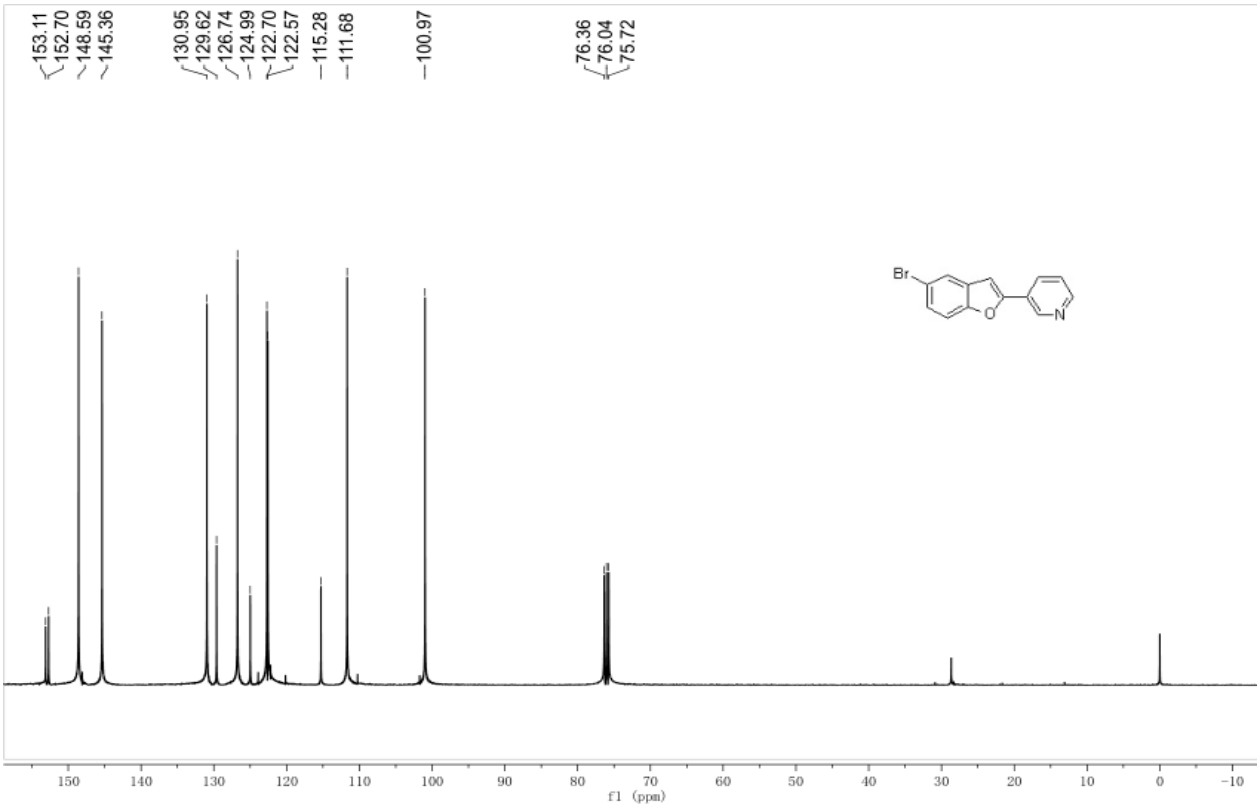

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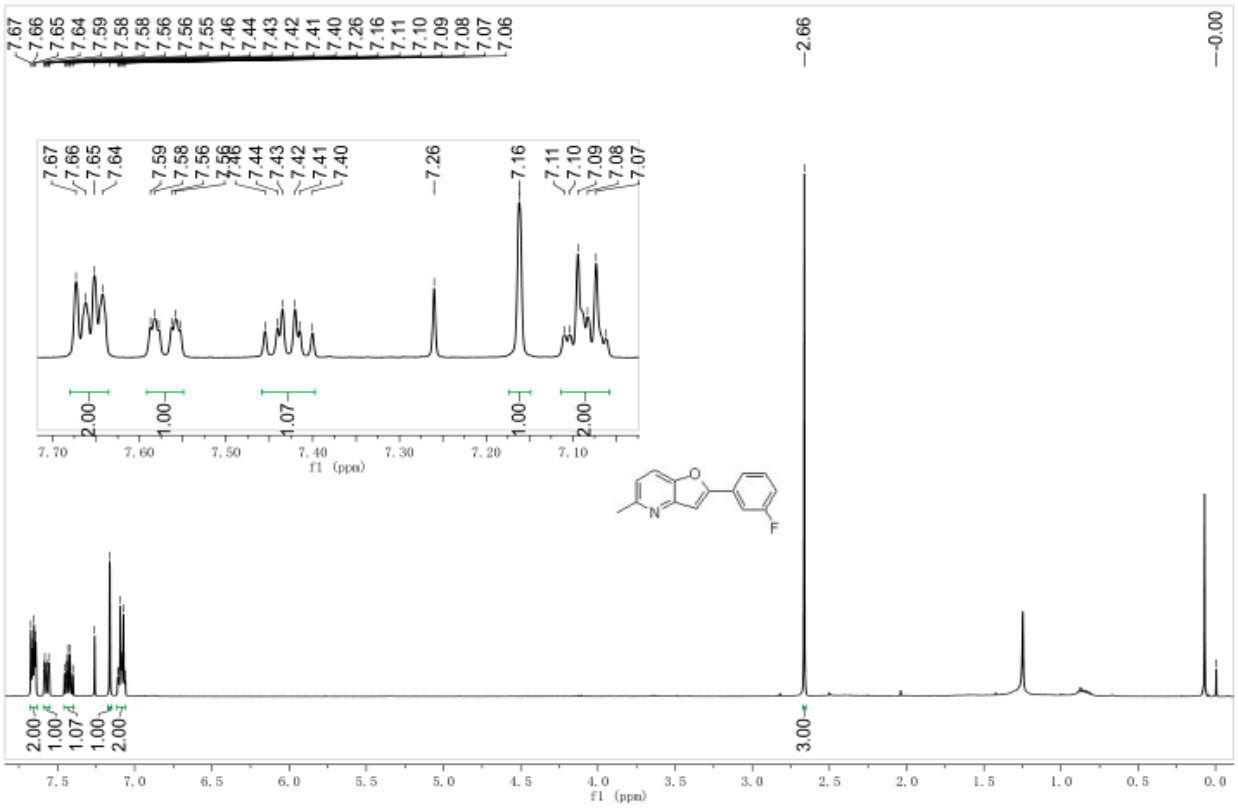

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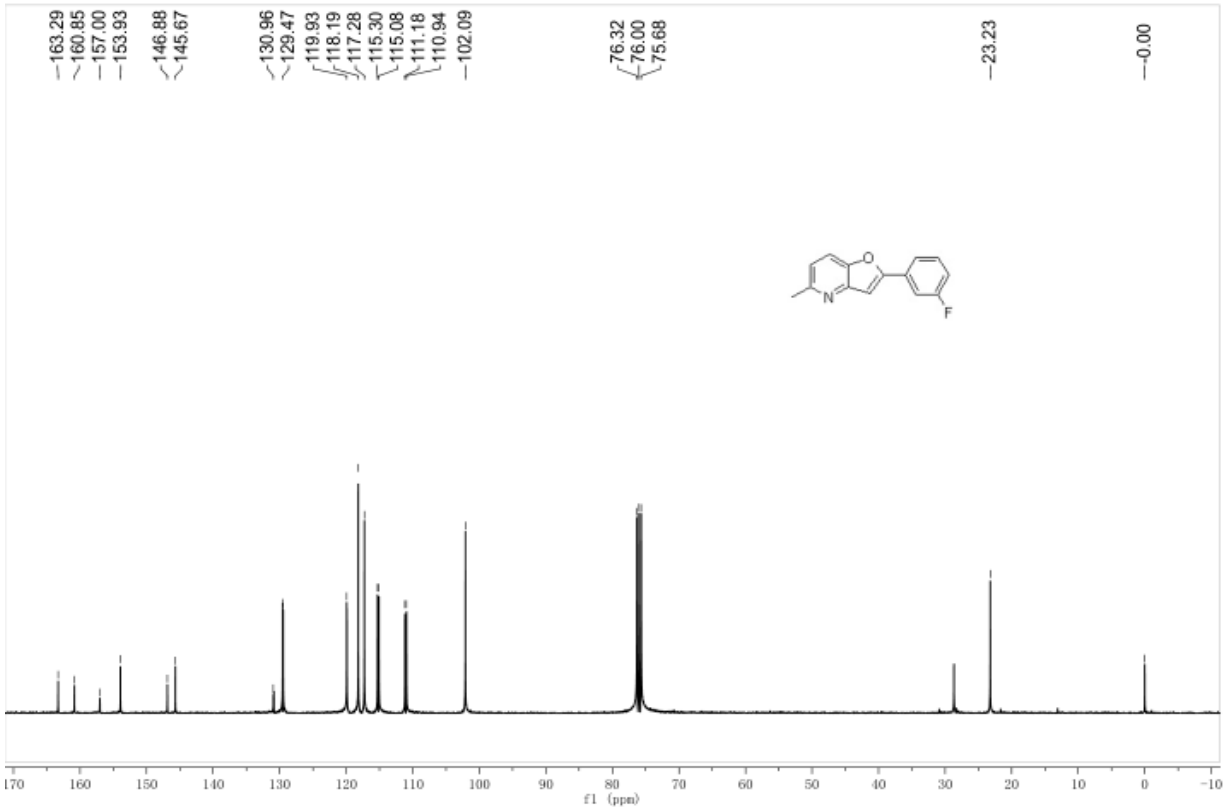

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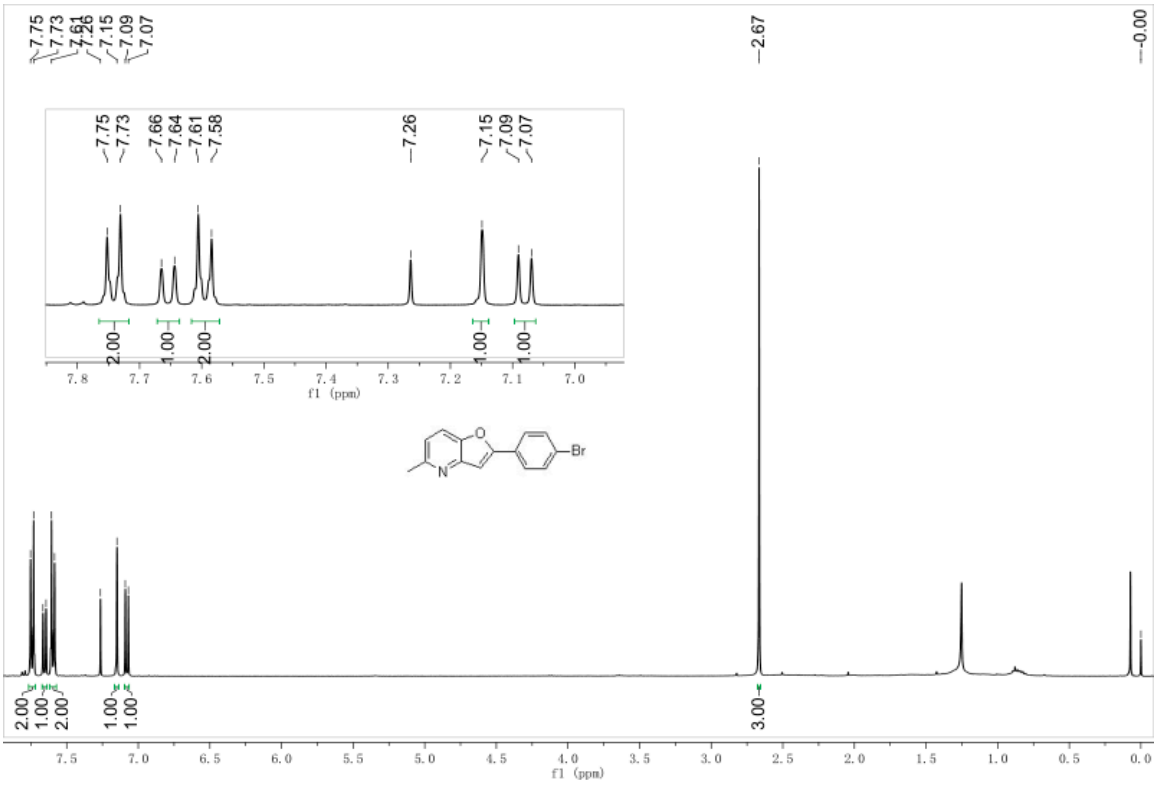
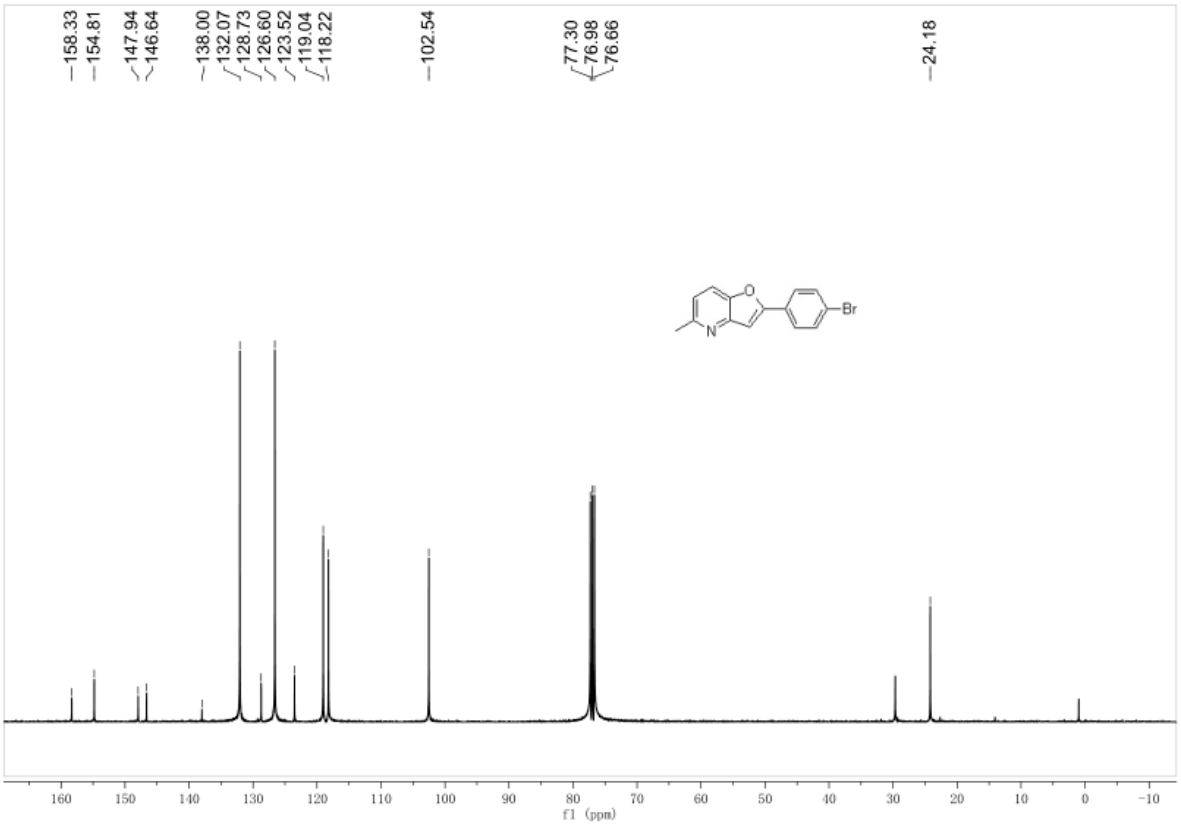
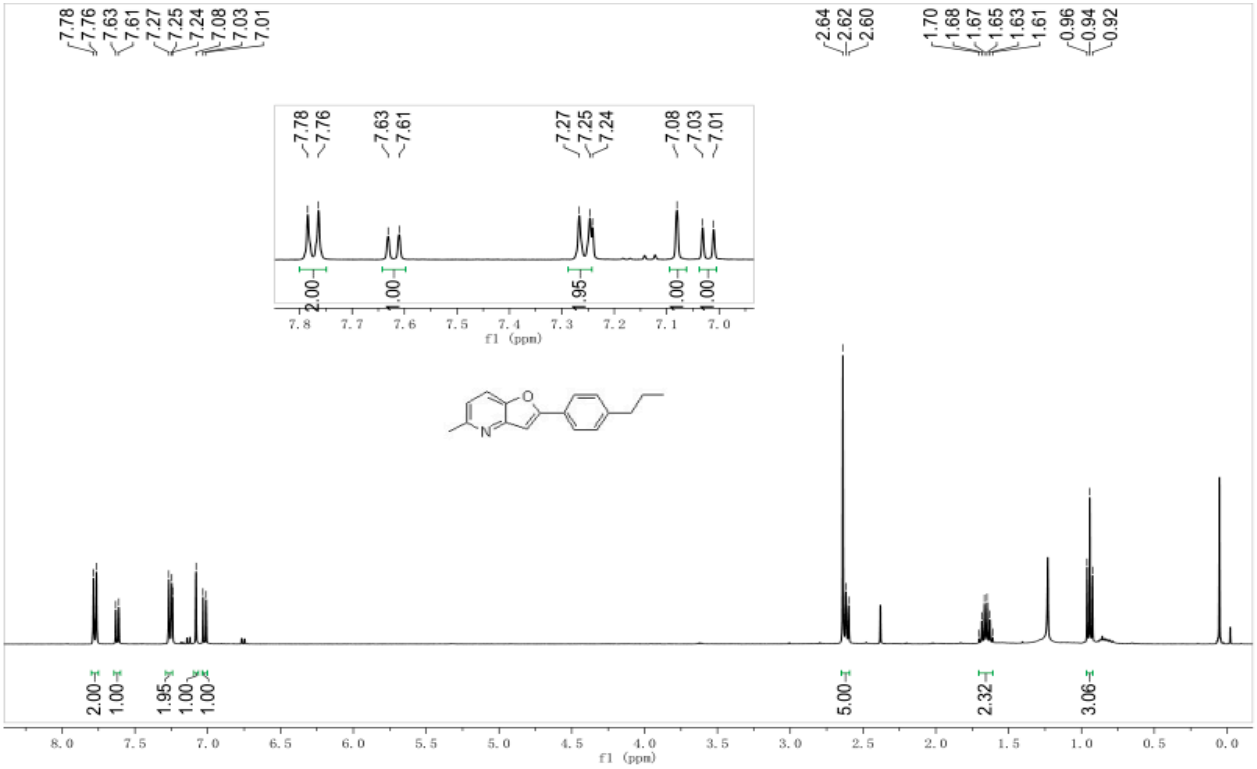


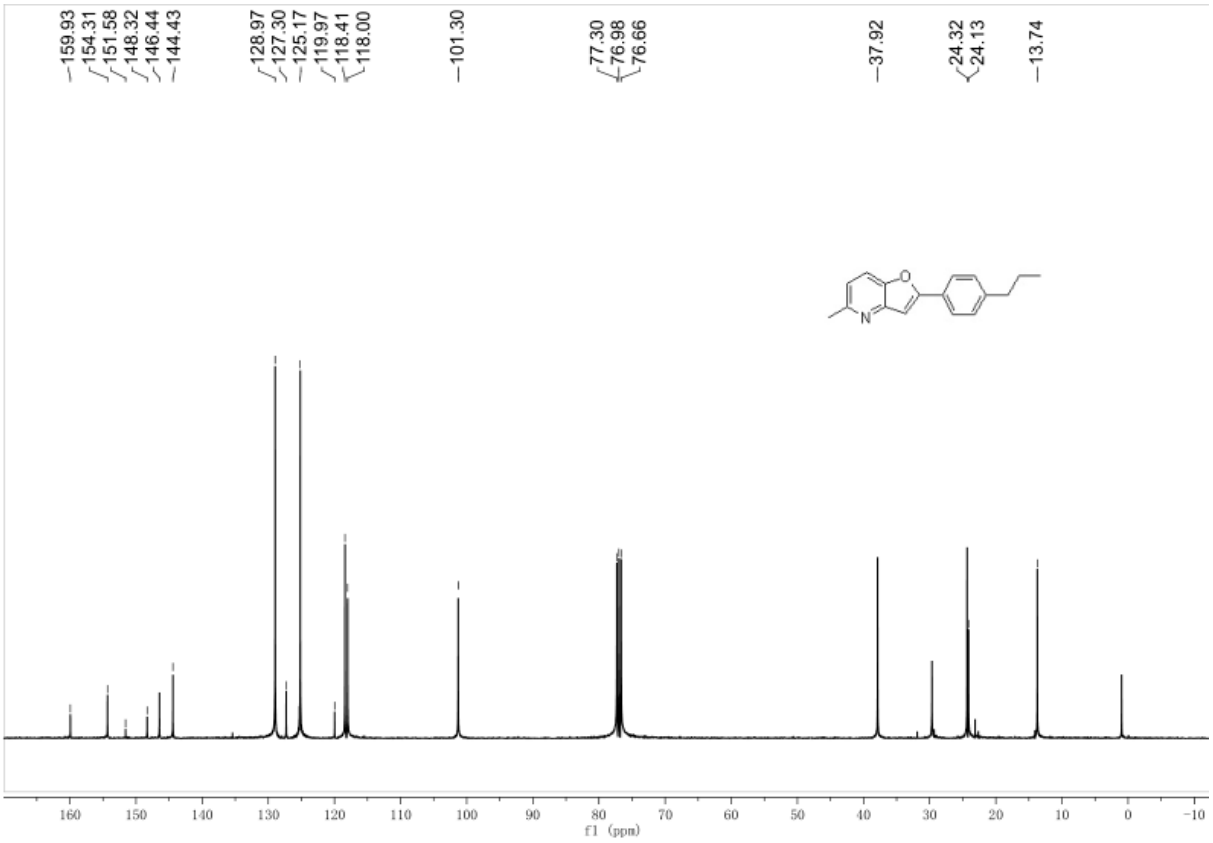
^{13}C NMR of ligand **3u:**



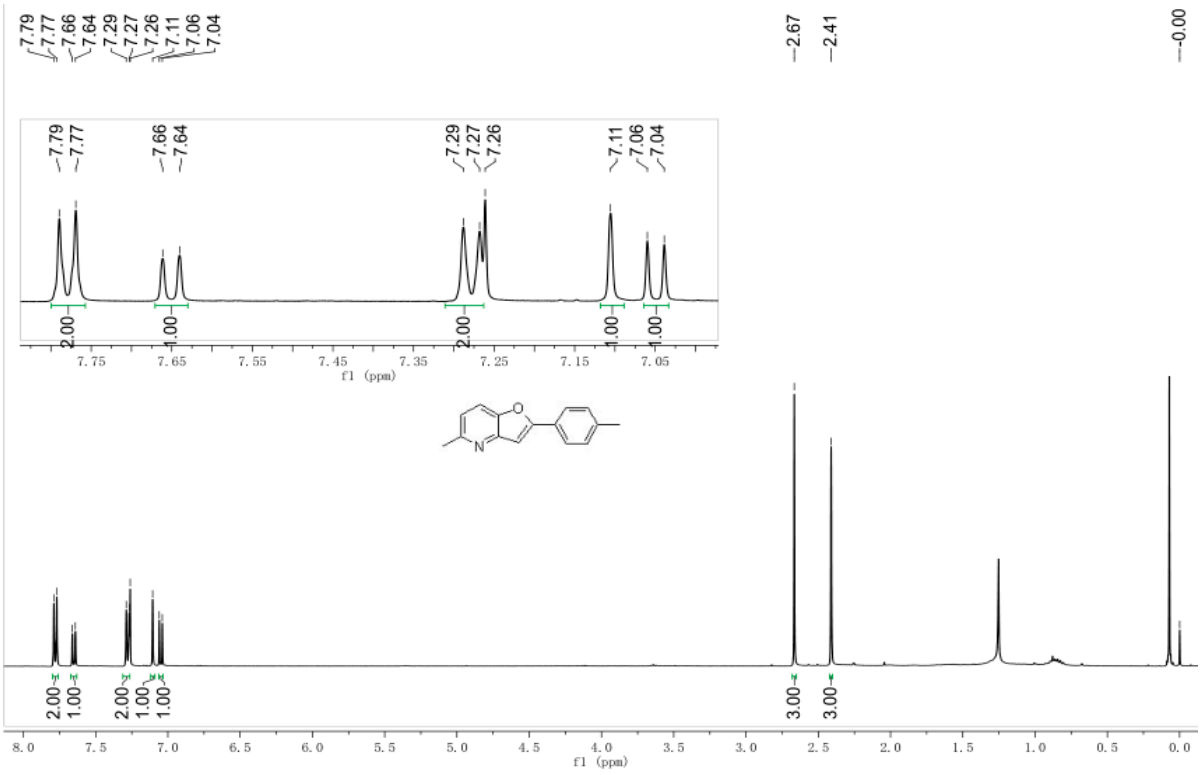
^{1}H NMR of **3v:**



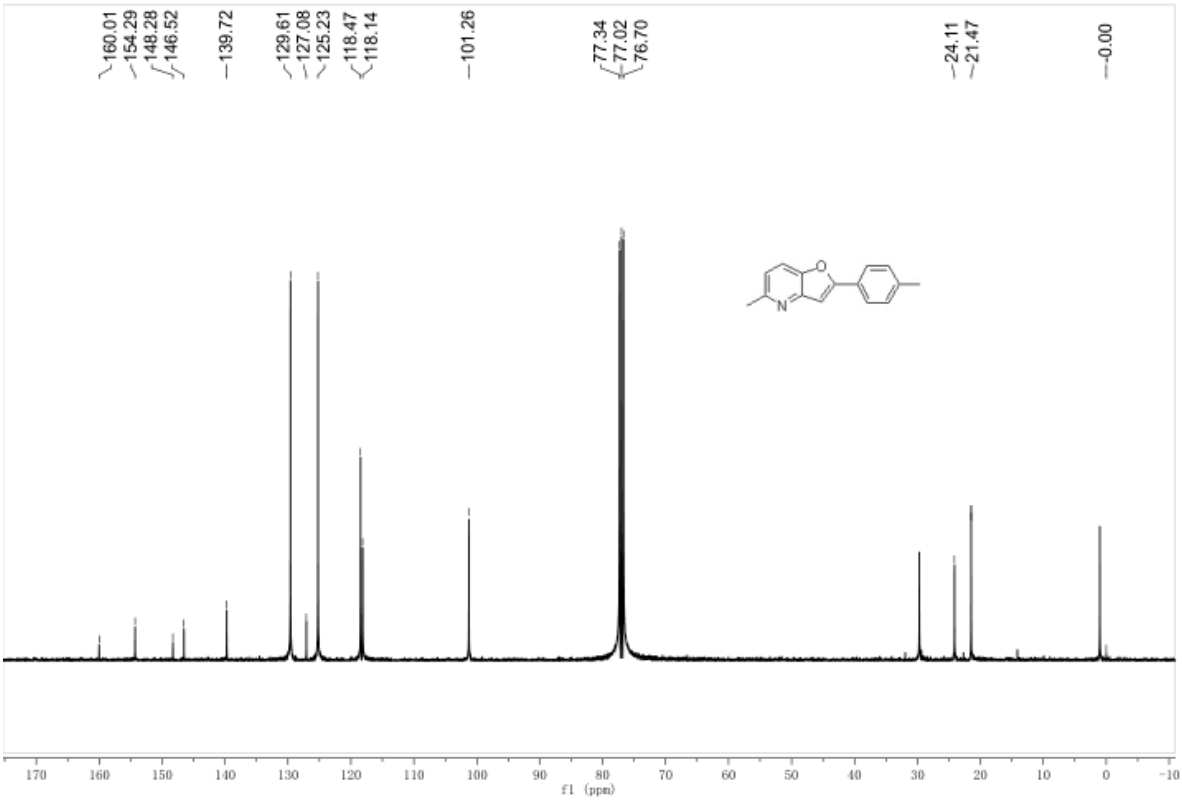
^{13}C NMR of ligand **3v:**



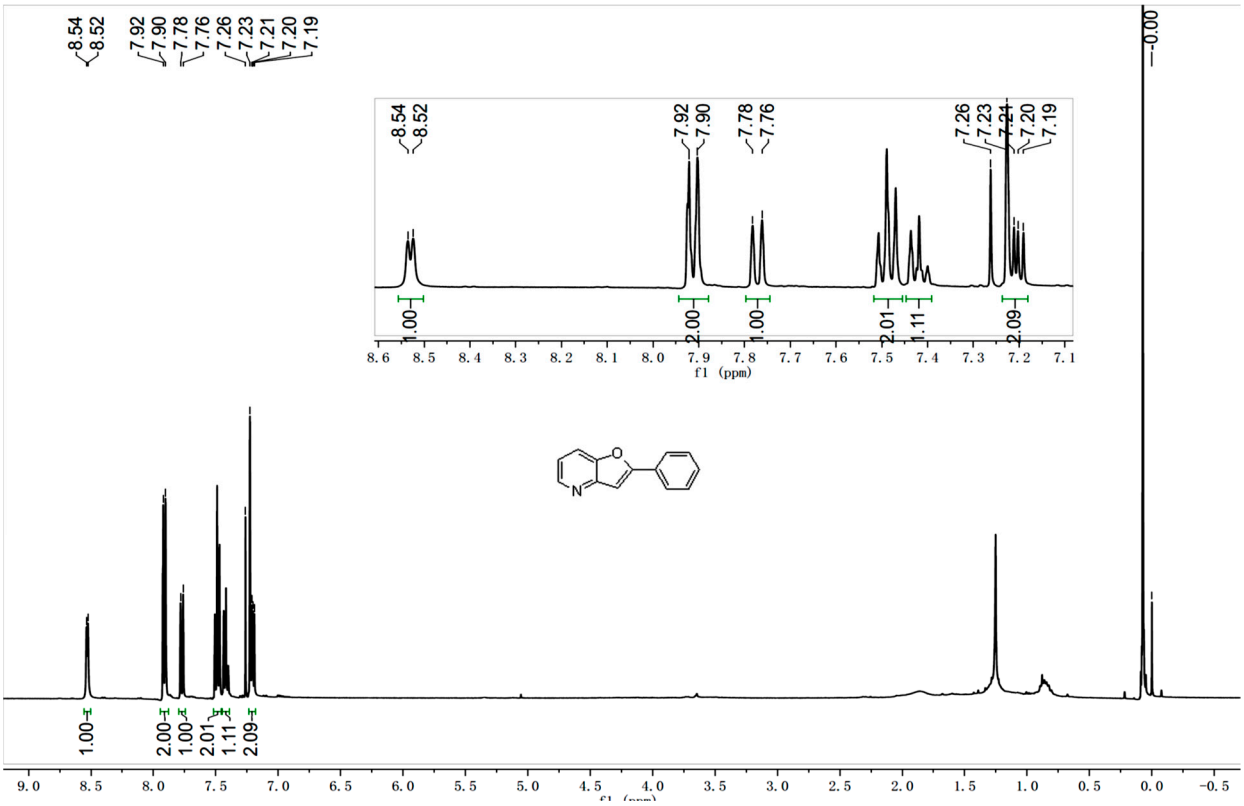
^{1}H NMR of **3w:**



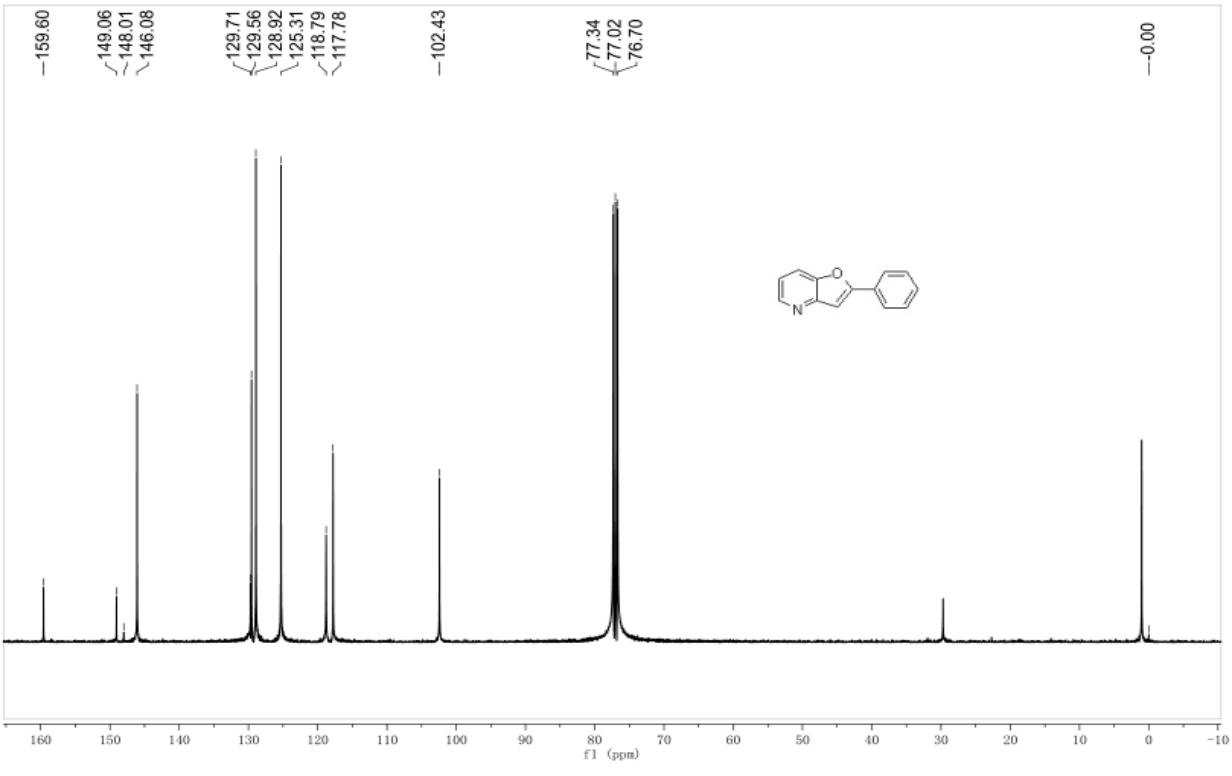
^{13}C NMR of ligand **3w:**



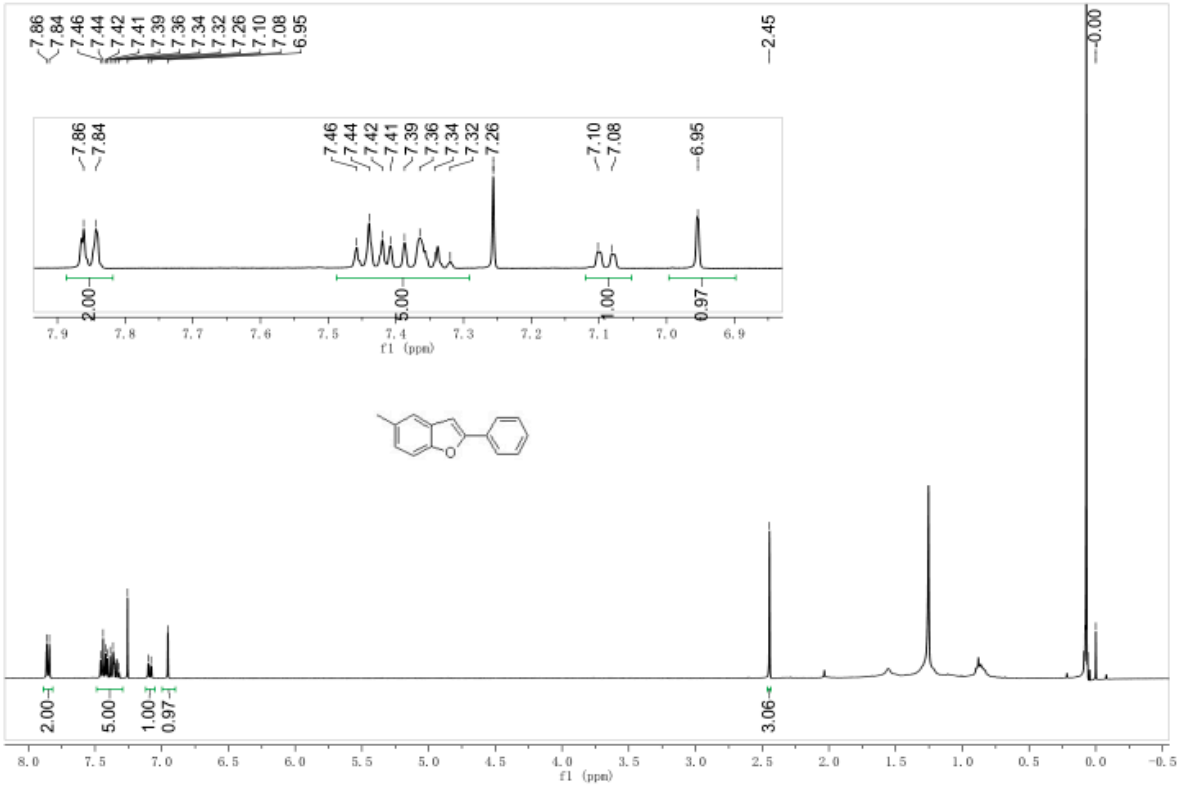
^{1}H NMR of **3x:**



^{13}C NMR of ligand **3x:**



^{1}H NMR of **3y:**



^{13}C NMR of ligand **3y:**