

Visible light-driven C–H arylation of heteroarenes with aryl diazonium salts in water catalyzed by Z-scheme CuInS₂/K-C₃N₄ heterojunction

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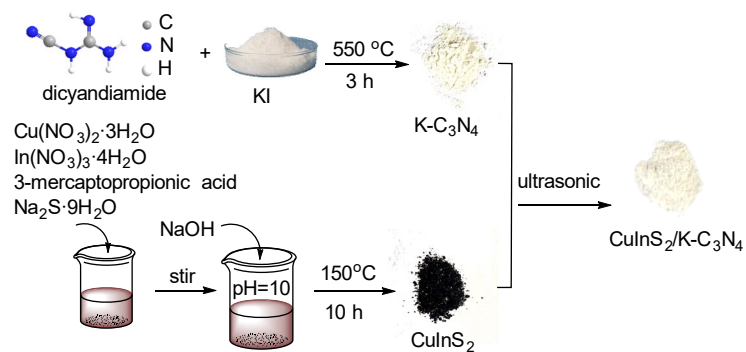
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General information

Unless otherwise noted, all reagents including the starting materials were obtained from commercial suppliers and used as purchased without further purification. The melting points were observed using a X-5 electrothermal melting and are uncorrected. IR spectra were obtained on a Bruker Tensor 27 Fourier transform infrared spectroscope. ^1H NMR and ^{13}C NMR spectra were acquired on a Zhongke Niujin AS 400 instrument in CDCl_3 and using TMS as an internal reference with chemical shift values reported in ppm. Mass spectra analysis was conducted, and the results were recorded on a 3200 Qtrap instrument with an electrospray ionization (ESI) source. Power X-ray diffraction data were obtained from a PANalytical X'Pert Pro X-ray diffractometer, $\text{Cu-K}\alpha$ ray was used as the X-ray source, and the scanning rate was 0.05 o/s between 20° and 80° . Surface morphology was investigated using a Hitachi S-4800 SEM instrument. Mass spectra analysis was conducted, and the results were recorded on a 3200 Qtrap instrument with an electrospray ionization (ESI) source. The reactions were performed on photocatalytic parallel reactor (WATTCAS: WP-TEC-1020LC manufactured by Xi'an huataikesi chemical technology co., ltd. Co.) and maintaining a relatively constant temperature by regulating the condensed water.



Scheme S1 Synthesis process of CuInS₂/K-C₃N₄

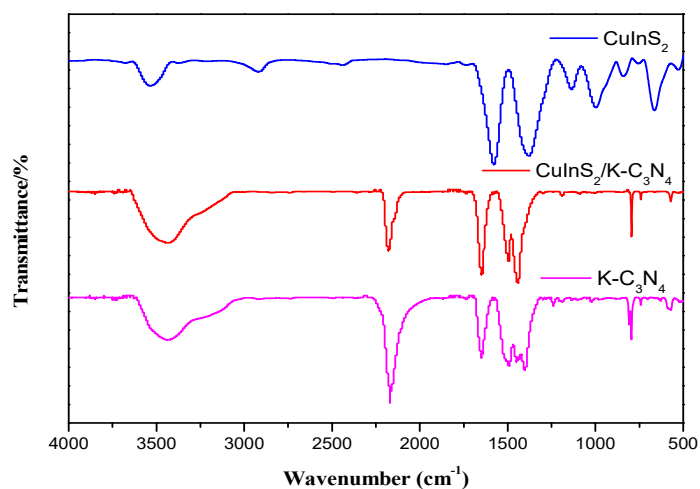


Fig. S1 FTIR spectra of CuInS₂, K-C₃N₄, and CuInS₂/K-C₃N₄.

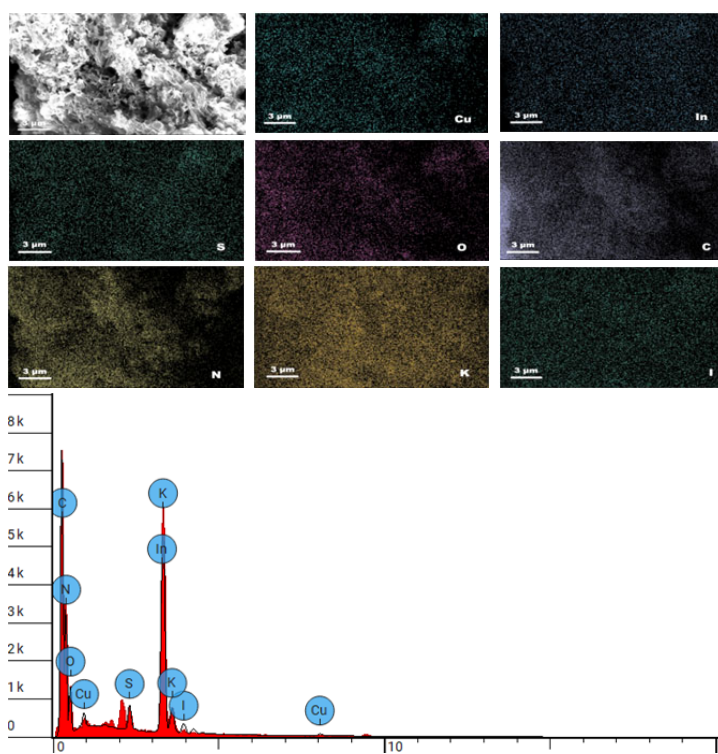


Fig. S2 The elemental mapping and EDX spectrum of CuInS₂/K-C₃N₄.

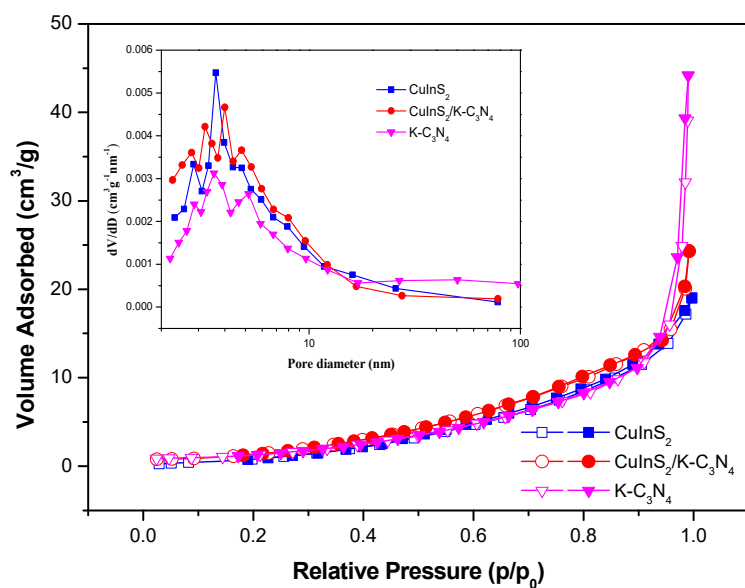


Fig.S3 N₂ adsorption–desorption isotherm of CuInS₂, K-C₃N₄ and CuInS₂/K-C₃N₄.

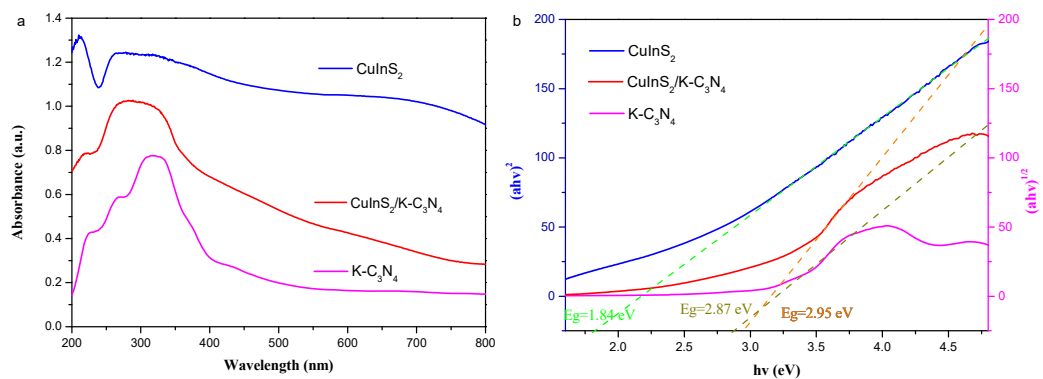
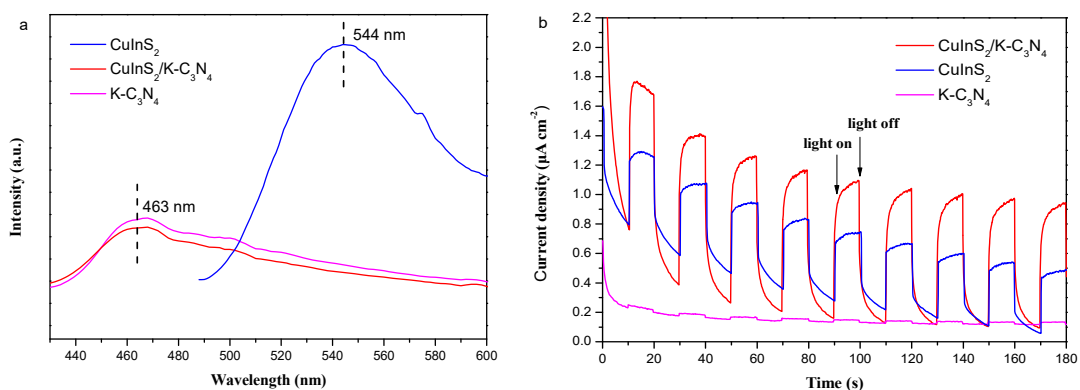


Fig. S4 (a) UV–vis DRS and (b) of Nyquist plots of CuInS₂, K-C₃N₄, and CuInS₂/K-C₃N₄.



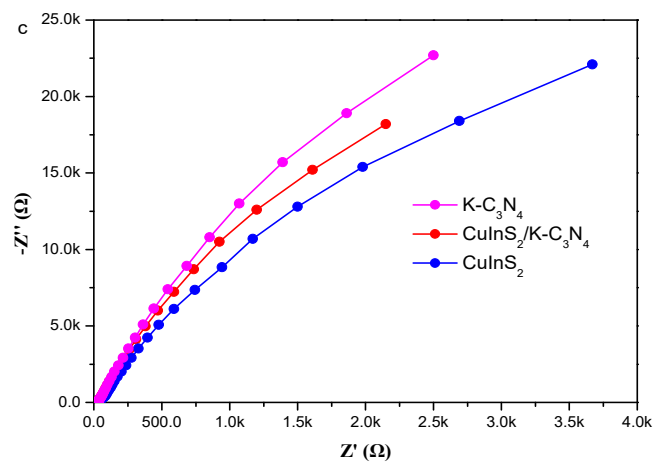


Fig. S5 (a) PL emission spectra; (b) Photocurrent responses; (c) electrochemical impedance spectra (EIS) Nyquist plots

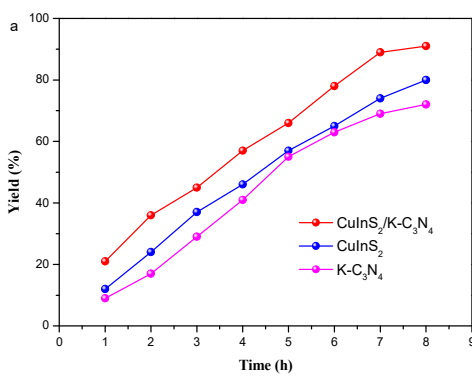
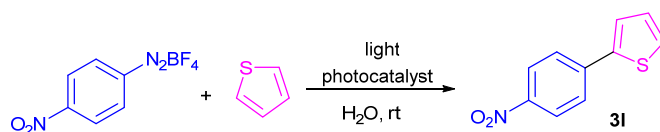
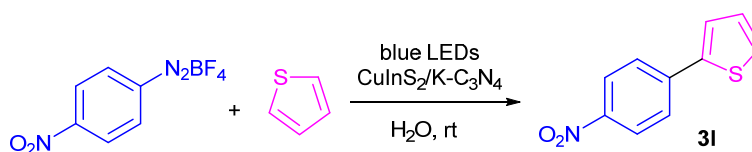


Fig. S6 Kinetic profile of the photocatalytic C–H arylation of 4-nitrobenzenediazonium tetrafluoroborate salt with thiophen

Table S1 Optimization of the reaction condition for synthesis of **31**^a.

Entry	Photocatalyst	Light source	Time (h)	Yield/% ^b
1	CuInS ₂ /K-C ₃ N ₄	red	8.0	trace
2	CuInS ₂ /K-C ₃ N ₄	yellow	8.0	trace
3	CuInS ₂ /K-C ₃ N ₄	green	8.0	51
4	CuInS ₂ /K-C ₃ N ₄	white	8.0	73
5	CuInS ₂ /K-C ₃ N ₄	blue	6.0	74
6	CuInS ₂ /K-C ₃ N ₄	blue	10.0	91
7	rhodamine B	blue	8.0	77
8	rose bengal	blue	8.0	56
9	eosin Y	blue	8.0	53
10	fluorescein	blue	8.0	50
11	4-CzIPN	blue	8.0	42
12	Ru(bpy) ₂ Cl ₂	blue	8.0	75
13	CuFe ₂ O ₄ /PDA/MoS ₂	blue	8.0	33

Reaction conditions: 4-nitrobenzenediazonium tetrafluoroborate salt (1 mmol), thiophene (10.0 mmol), photocatalyst (20 mg), room temperature, 10 W LEDs, air, room temperature.^b Isolated yields.

Table S2 Effects of different amounts of thiophene on the coupling of 4-nitrobenzenediazonium tetrafluoroborate salt and thiophene^a.

Entry	Thiophene (eq.)	Time (h)	Yield/% ^b
1	1.0	12.0	23
2	3.0	8.0	36
3	5.0	8.0	69
4	7.0	8.0	83
5	10.0	8.0	91
6	15.0	8.0	91
7	20.0	8.0	91

Table S3 Representation of previous and present works for synthesis **31**

Entry	Reaction conditions	Time (h)	Yield (%)	Ref.
1	eosin Y, thiophene (10. equiv.), DMSO, 20 °C, 530 nm LED	4.0	70	18
2	AcrH ₂ , thiophene (20. equiv.), CH ₃ CN, rt, blue LED	12.0	79	20
3	Bismuthene, thiophene (20. equiv.), DMSO, 25 °C, indoor light	5.0	90	22
4	pnictogen bismuth, thiophene (20. equiv.), CH ₃ CN, rt, blue LED	2.0	65	23
5	black phosphorus, thiophene (20. equiv.), DMSO, 25 °C, 150 W metal halide lamp	2.0	75	24
6	CuInS ₂ /K-C ₃ N ₄ , thiophene (20. equiv.), H ₂ O, rt, blue LED	8.0	91	This work



Photocatalytic parallel reactor

Experimental

Preparation of CuInS₂ QDs:

In brief, Cu(NO₃)₂·3H₂O (12 mg, 0.05 mmol), In(NO₃)₃·4H₂O (37 mg, 0.1 mmol), and 3-mercaptopropionic acid (127 mg, 1.2 mmol) were dissolved in deionized water (60 mL). The mixture were stirred for 30 min to make a homogeneous solution. After that, 0.8 mmol Na₂S·9H₂O (192 mg, 0.8 mmol) was added in the above reaction mixture. The above solution was adjusted to pH = 10 with 1 mol/L NaOH and stirred at room temperature for 30 min. After, the well-mixed homogeneous solution was transferred into Teflon-lined stainless-steel autoclave and kept at 150 °C for 10 h. After cooling to room temperature, ethanol was added, the precipitates were collected by centrifugation and washed three times with deionized water and absolute ethanol to remove any possible remnants. The obtained black green precipitates were dried in a vacuum oven under 60 °C for 12 h to give the desired CuInS₂ QDs.

Preparation of K-C₃N₄:

A mixture of dicyandiamide (10.0 g) and KI (1.0 g) was grounded in an agate mortar and then transferred to a covered alumina crucible, and heated to 500 °C with a ramp rate of 0.5 °C/min, and maintained at this temperature for 3 h.. The temperature was raised to 550 °C in a muffle furnace at After cooling to room temperature, the obtained bright yellow solid was ground into a powder with an agate mortar. The powder was washed with a large amount of distilled water to remove unreacted KI and dried overnight at 80 °C.

Synthesis of CuInS₂/K-C₃N₄ heterostructures:

Briefly, CuInS₂ QDs (20 mg) and K-C₃N₄ (600 mg) were dispersed in 100 mL deionized water. The mixture was sonicated for 4 h. The precipitate was collected by centrifugation and washed three times with deionized and ethanol, and dried at 60 °C for 10 h.

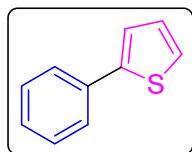
General procedure for C–H arylation of heteroarenes:

Heteroarene (10 mmol), aryl diazonium salt (1 mmol), CuInS₂/K-C₃N₄ (20 mg) and water (2 ml) were added to a 10 ml quartz tube, and reaction tube was placed in a

photocatalytic parallel reactor with a magnetic stir bar. The reaction mixture was stirred under the irradiation of 10 W blue LEDs (455–460 nm) at room temperature. After completion of the reaction (monitored by TLC), the catalyst was separated by centrifugation, washed with ethanol (2 mL × 3), and dried in vacuum for subsequent cycles without further purification. The reaction mixture was diluted with brine (2 mL), and extracted with EtOAc (2 mL × 3). Then, the organic layer was separated, dried over Na₂SO₄, and filtered. The solvent was removed under reduced pressure to obtain a crude product, which was purified by column chromatography on silica gel using EtOAc/hexanes as eluent to deliver the pure product.

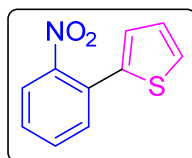
Spectra data of all products

2-Phenylthiophene (**3a**)



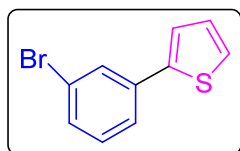
White solid (101 mg, 0.63 mmol, 63%); m.p.: 33 - 35 °C; IR (KBr): 3098.4, 1617.9, 1446.5, 1384.1, 1073.3, 850.6, 749.7, 689.6 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 3.4 Hz, 1H), 7.29 (m, 2H), 7.09 (t, *J* = 4.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 144.47, 134.44, 128.95, 128.20, 128.08, 127.53, 126.01, 124.88, 123.14 ppm; ESI-MS: *m/z* = 161.2 (*M* + 1)⁺.

2-(2-Nitrophenyl)thiophene (**3b**)



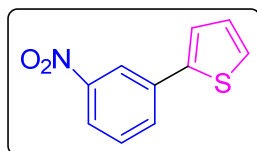
Yellow oil (160 mg, 0.78 mmol, 78%); IR (KBr): 2863.7, 1605.3, 1524.2, 1357.9, 1261.3, 908.5, 850.5, 777.1, 742.3, 703.6 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.49 – 7.43 (m, 1H), 7.42 (dd, *J* = 4.8, 0.5 Hz, 1H), 7.09 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 149.49, 137.17, 132.31, 131.96, 128.66, 128.39, 127.82, 127.20, 123.88 ppm; ESI-MS: *m/z* = 206.2 (*M* + 1)⁺.

2-(3-Bromophenyl)thiophene (**3c**)



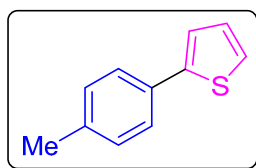
Colorless oil (191 mg, 0.80 mmol, 80%); IR (KBr): 2924.6, 1590.8, 1560.9, 1471.9, 1400.5, 852.4, 774.1, 696.8 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.35 (d, *J* = 4.4 Hz, 2H), 7.29 (d, *J* = 6.8 Hz, 1H), 7.14 – 7.11 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 142.64, 136.45, 130.40, 130.32, 128.81, 128.18, 125.67, 124.56, 123.92, 123.01 ppm; ESI-MS: *m/z* = 240.1 (*M* + 1)⁺.

2-(3-Nitrophenyl)thiophene (**3d**)



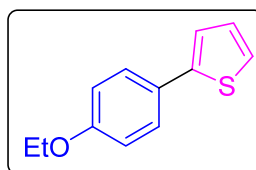
Yellow oil (172 mg, 0.84 mmol, 84%); IR (KBr): 1651.1, 1637.2, 1536.6, 1521.8, 1400.8, 1348.6, 735.77, 673.94 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.45 (t, *J* = 1.9 Hz, 1H), 8.12 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.39 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.14 (dd, *J* = 5.1, 3.7 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 148.77, 141.55, 136.12, 131.58, 129.90, 128.49, 126.56, 124.83, 121.93, 120.49 ppm; ESI-MS: *m/z* = 206.2 (*M* + 1)⁺.

2-(4-Methylphenyl)thiophene (**3e**)



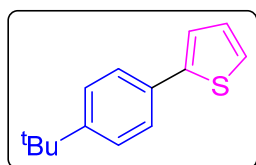
White solid (87 mg, 0.50 mmol, 50%); m.p.: 61 - 63 °C; IR (KBr): 3073.7, 3020.6, 2910.7, 2845.3, 1539.4, 1500.5, 1432.7, 850.6, 806.7 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 3.7 Hz, 1H), 7.24 (s, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.07 (dd, *J* = 4.9, 3.7 Hz, 1H), 2.37 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 137.36, 131.66, 129.58, 127.96, 125.90, 124.30, 122.60, 21.22 ppm; ESI-MS: *m/z* = 175.3 (*M* + 1)⁺.

2-(4-Ethoxyphenyl)thiophene (**3f**)



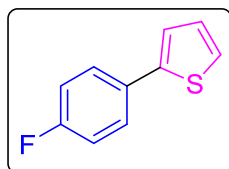
White solid (149 mg, 0.73 mmol, 73%); m.p.: 80 - 82 °C; IR (KBr): 2973.7, 1608.8, 1499.8, 1250.1, 1181.3, 1120.8, 1049.2, 819.7, 690.5, 601.4, 535.5 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 8.7 Hz, 2H), 7.21 (t, *J* = 4.5 Hz, 2H), 7.05 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 4.12 - 4.02 (m, 2H), 1.44 (dd, *J* = 8.8, 5.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.58, 144.44, 127.94, 127.23, 123.79, 122.03, 114.83, 63.57, 14.87 ppm; ESI-MS: *m/z* = 205.3 (*M* + 1)⁺.

2-(4-(Tert-butyl)phenyl)thiophene (**3g**)



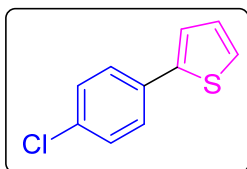
Colorless oil (158 mg, 0.73 mmol, 73%); IR (KBr): 2963.3, 1649.8, 1405.3, 1266.1, 1118.2, 819.6, 692.0, 556.7 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.56 (t, *J* = 6.8 Hz, 2H), 7.45 - 7.39 (m, 2H), 7.31 - 7.25 (m, 2H), 7.09 (dd, *J* = 5.0, 3.7 Hz, 1H), 1.36 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 150.61, 144.51, 131.69, 127.96, 126.20, 125.84, 125.76, 124.38, 122.71, 119.82, 34.64, 31.33 ppm; ESI-MS: *m/z* = 217.3 (*M* + 1)⁺.

2-(4-Fluorophenyl)thiophene (**3h**)



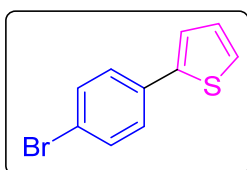
Colorless oil (152 mg, 0.86 mmol, 86%); IR (KBr): 1636.9, 1500.1, 1400.4, 820.1, 696.9 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.60 - 7.54 (m, 2H), 7.29 - 7.22 (m, 2H), 7.10 - 7.04 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 163.55, 161.09 (d, *J*_{C-F} = 229.4 Hz), 143.34, 130.70 (d, *J*_{C-F} = 3.6 Hz), 128.09, 127.67 (d, *J*_{C-F} = 8.5 Hz), 124.81, 123.11, 115.95, 115.73 (d, *J*_{C-F} = 22.0 Hz) ppm; ESI-MS: *m/z* = 178.2 (*M* + 1)⁺.

2-(4-Chlorophenyl)thiophene (**3i**)



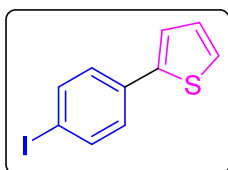
Colourless solid (171 mg, 0.88 mmol, 88%); m.p.: 78 - 80 °C; IR (KBr): 1647.9, 1401.4, 1096.9, 815.7, 696.8 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.28 (m, 2H), 7.09 – 7.06 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 143.12, 133.23, 132.96, 129.06, 128.18, 127.14, 125.23, 123.48 ppm; ESI-MS: *m/z* = 195.7 (M + 1)⁺.

2-(4-Bromophenyl)thiophene (**3j**)



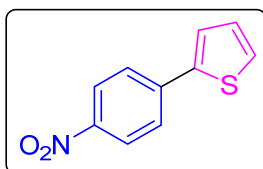
Colourless solid (208 mg, 0.87 mmol, 87%); m.p.: 89 - 91 °C; IR (KBr): 1684.4, 1651.4, 1483.3, 1426.9, 1399.5, 1007.2, 852.6, 813.2, 779.8, 694.2 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.45 (m, 4H), 7.30 (d, *J* = 4.4 Hz, 2H), 7.10 – 7.06 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 143.12, 133.40, 132.00, 128.73, 128.21, 127.44, 125.30, 123.52, 121.30 ppm; ESI-MS: *m/z* = 240.1 (M + 1)⁺.

2-(4-Iodophenyl)thiophene (**3k**)



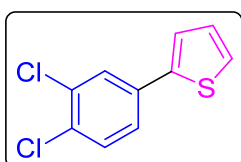
Colourless solid (243 mg, 0.85 mmol, 85%); m.p.: 108 - 110 °C; IR (KBr): 2925.2, 1646.3, 1481.9, 1258.6, 812.9, 692.2 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.34 (m, 2H), 7.12 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 143.19, 137.94, 133.95, 128.20, 127.63, 125.34, 123.53, 92.61 ppm; ESI-MS: *m/z* = 287.1 (M + 1)⁺.

2-(4-Nitrophenyl)thiophene (**3l**)



Yellow solid (187 mg, 0.91 mmol, 91%); m.p.: 197 - 199 °C; IR (KBr): 3107.3, 1587.9, 1509.7, 1418.8, 1339.6, 1111.5, 851.4, 836.9, 750.0 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 3.6 Hz, 1H), 7.44 (d, *J* = 4.9 Hz, 1H), 7.15 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 146.64, 141.62, 140.60, 128.73, 127.72, 126.85, 126.05, 125.75, 124.45 ppm; ESI-MS: *m/z* = 206.2 (M + 1)⁺.

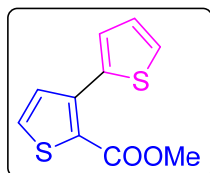
2-(3,4-Dichlorophenyl)thiophene (**3m**)



Colorless oil (192 mg, 0.84 mmol, 84%); IR (KBr): 1648.9,

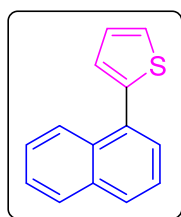
1398.1, 1032.9, 852.2, 820.2, 708.7 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (s, 1H), 7.43 (m, 2H), 7.31 (m, 2H), 7.09 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 141.68, 134.46, 133.00, 131.23, 130.79, 128.31, 127.54, 125.94, 125.12, 124.18 ppm; ESI-MS: $m/z = 230.1$ ($M + 1$) $^+$.

Methyl [2,3'-bithiophene]-2'-carboxylate (**3n**)



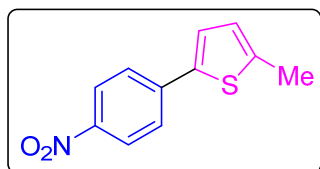
Colorless oil (163.7 mg, 0.73 mmol, 73%); IR (KBr): 3109.7, 2949.9, 1713.9, 1435.3, 1403.5, 1260.4, 1235.9, 1070.6, 910.4, 770.1, 733.2 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (dd, $J = 3.6$, 0.9 Hz, 1H), 7.48 (d, $J = 5.1$ Hz, 1H), 7.38 (d, $J = 5.1$, 0.9 Hz, 1H), 7.25 (d, $J = 5.2$ Hz, 1H), 7.10 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 162.40, 140.18, 136.33, 131.52, 130.26, 128.93, 127.20, 126.60, 52.12 ppm; ESI-MS: $m/z = 225.3$ ($M + 1$) $^+$.

2-(Naphthalen-1-yl)thiophene (**3o**)



Colorless oil (141 mg, 0.67 mmol, 67%); IR (KBr): 3104.2, 1932.1, 1813.6, 1675.9, 1638.4, 1589.7, 1505.7, 1326.6, 1270.3, 1244.1, 1218.9, 930.9, 900.4, 850.0, 835.7, 638.9, 605.7 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.35 – 8.28 (m, 1H), 8.00 – 7.90 (m, 2H), 7.66 (m, 1H), 7.61 – 7.55 (m, 3H), 7.50 (m, 1H), 7.33 (d, $J = 3.4$, 1H), 7.26 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 141.83, 133.91, 132.50, 131.94, 128.46, 128.39, 128.27, 127.45, 127.34, 126.50, 126.07, 125.82, 125.69, 125.31 ppm; ESI-MS: $m/z = 211.3$ ($M + 1$) $^+$.

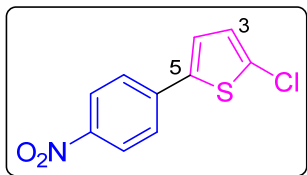
2-Methyl-5-(4-nitrophenyl)thiophene (**3p**)



Yellow solid (164 mg, 0.75 mmol, 75%); m.p.: 132 – 134 $^{\circ}\text{C}$; IR (KBr): 2975.7, 1630.6, 1508.7, 1400.3, 1050.7, 1020.3, 852.9 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.9$ Hz, 2H), 7.66 (d, $J = 8.9$ Hz, 2H), 7.29 (d, $J = 3.6$ Hz, 1H), 6.80 (dd, $J = 3.6$, 0.9 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 143.03, 140.91, 127.07, 125.83, 125.41, 124.44, 15.66 ppm; ESI-MS: $m/z = 220.3$ ($M + 1$) $^+$.

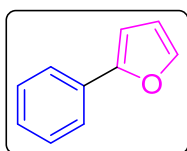
Major isomer: 2-chloro-5-(4-nitrophenyl)thiophene; minor isomer:

2-chloro-3-(4-nitrophenyl)thiophene (**3q**)



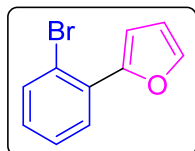
Yellow oil (175 mg, 0.73 mmol, 73%); IR (KBr): (mixture of 3- and 5-substituted) 3103.5, 2923.1, 1591.8, 1508.6, 1432.7, 1374.3, 1336.9, 1211.2, 1110.3, 1007.8, 952.3, 851.5, 747.2, 725.4 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ (5-substituted, major regioisomer) 8.22 (d, $J = 8.8$ Hz, 2H), 7.63 (d, $J = 8.8$ Hz, 2H), 7.25 (d, $J = 4.0$ Hz, 1H), 6.96 (d, $J = 3.9$ Hz, 1H); (3-substituted, minor regioisomer) 8.28 (d, $J = 8.8$ Hz, 2H), 7.74 (d, $J = 8.8$ Hz, 2H), 7.23 (d, $J = 5.9$ Hz, 1H), 7.10 (d, $J = 5.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ (mixture of 3- and 5-substituted) 146.90, 146.78, 140.60, 139.96, 139.69, 129.24, 127.89, 125.65, 125.07, 124.57, 123.85 ppm; ESI-MS: $m/z = 241.7$ ($M + 1$) $^+$.

2-Phenylfuran (**3r**)



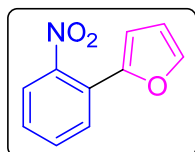
Red oil (111 mg, 0.77 mmol, 77%); IR (KBr): 1646.3, 1515.7, 1397.9, 1156.2 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 7.8$ Hz, 2H), 7.48 (s, 1H), 7.39 (t, $J = 7.7$ Hz, 2H), 7.26 (t, $J = 7.9$ Hz, 2H), 6.66 (d, $J = 3.2$ Hz, 1H), 6.48 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 142.09, 128.70, 127.36, 123.82, 111.66, 104.98 ppm; ESI-MS: $m/z = 145.2$ ($M + 1$) $^+$.

2-(2-Bromophenyl)furan (**3s**)



Colorless oil (167 mg, 0.75 mmol, 75%); IR (KBr): 2920.0, 1654.0, 1637.1, 1630.0, 1617.7, 1466.8, 1401.0, 1026.9, 1006.0, 753.8 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.80 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.53 (d, $J = 1.1$ Hz, 1H), 7.40 – 7.32 (m, 1H), 7.17 (d, $J = 3.4$ Hz, 1H), 7.13 (td, $J = 8.0, 1.5$ Hz, 1H), 6.53 (dd, $J = 3.3, 1.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.34, 142.25, 134.12, 131.28, 128.83, 128.45, 127.43, 119.67, 111.45, 110.59 ppm; ESI-MS: $m/z = 224.1$ ($M + 1$) $^+$.

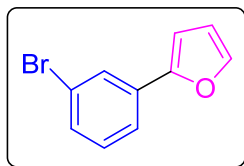
2-(2-Nitrophenyl)furan (**3t**)



Colorless oil (136 mg, 0.72 mmol, 72%); IR (KBr): 2920.7, 1617.9, 1530.9, 1364.7, 1160.8, 1009.9, 907.5, 850.5, 744.2 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.77 – 7.64 (m, 2H), 7.57 (t, $J = 7.8$ Hz, 1H), 7.52 (d, $J = 1.4$ Hz, 1H), 7.45 – 7.37 (m, 1H), 6.67 (d, $J = 3.4$ Hz, 1H), 6.50 (dd, $J = 3.3, 1.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.40, 147.54, 143.82, 131.89,

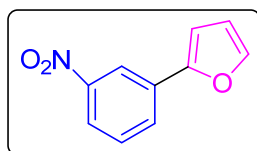
128.90, 128.29, 124.15, 123.87, 111.90, 109.73 ppm; ESI-MS: $m/z = 190.2 (M + 1)^+$.

2-(3-Bromophenyl)furan (**3u**)



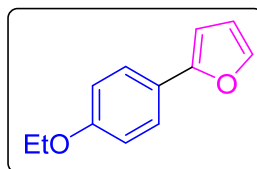
Colorless oil (178 mg, 0.80 mmol, 80%); IR (KBr): 2923.6, 1599.5, 1560.9, 1470.0, 1218.8, 1157.9, 1008.1, 911.4, 778.0, 731.6 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.86 (s, 1H), 7.63 (d, $J = 7.8$ Hz, 1H), 7.52 (d, $J = 1.1$ Hz, 1H), 7.44 – 7.39 (m, 1H), 7.29 (d, $J = 7.8$ Hz, 1H), 6.71 (d, $J = 3.1$ Hz, 1H), 6.52 (dd, $J = 3.4, 1.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 152.40, 142.67, 132.79, 130.26, 130.16, 126.74, 122.90, 122.30, 111.86, 106.14 ppm; ESI-MS: $m/z = 224.1 (M + 1)^+$.

2-(3-Nitrophenyl)furan (**3v**)



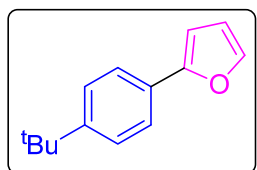
Yellow oil (149 mg, 0.79 mmol, 79%); IR (KBr): 1622.7, 1528.0, 1352.1, 1013.9, 741.3, 728.7 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.48 (s, 1H), 8.13 – 8.05 (m, 1H), 7.95 (d, $J = 7.8$ Hz, 1H), 7.58 – 7.51 (m, 2H), 6.81 (d, $J = 3.4$ Hz, 1H), 6.53 (dd, $J = 3.4, 1.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.53, 148.74, 143.34, 132.39, 129.73, 129.25, 121.72, 118.54, 112.13, 107.32 ppm; ESI-MS: $m/z = 190.1 (M + 1)^+$.

2-(4-Ethoxyphenyl)furan (**3w**)



White solid (150 mg, 0.80 mmol, 80%); m.p.: 58 - 60 $^\circ\text{C}$; IR (KBr): 2924.6, 1613.1, 1400.5, 1247.7, 1120.2, 1050.6, 901.7, 802.9, 730.7 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 8.7$ Hz, 2H), 7.42 (m, 1H), 6.91 (d, $J = 8.8$ Hz, 2H), 6.51 (d, $J = 3.3$ Hz, 1H), 6.44 (dd, $J = 3.2, 1.8$ Hz, 1H), 4.06 (q, $J = 6.9$ Hz, 2H), 1.43 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.41, 154.13, 141.36, 125.24, 123.91, 114.68, 111.55, 103.31, 63.52, 14.87 ppm; ESI-MS: $m/z = 189.2 (M + 1)^+$.

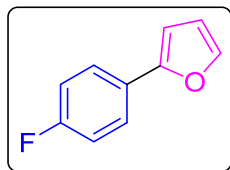
2-(4-(Tert-butyl)phenyl)furan (**3x**)



Colorless oil (138 mg, 0.69 mmol, 69%); IR (KBr): 2967.1, 1650.8, 1402.4, 837.9, 728.7 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 8.5$ Hz, 2H), 7.46 – 7.38 (m, 3H), 6.60 (d, $J = 3.3$ Hz, 1H), 6.46 (m, 1H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 154.19, 150.42, 141.76, 128.25, 125.61, 123.61, 111.55, 104.36, 100.00, 34.65, 31.31 ppm; ESI-MS:

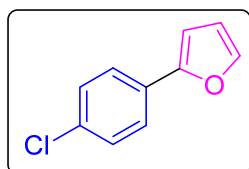
$m/z = 201.3 (M + 1)^+$.

2-(4-Fluorophenyl)furan (**3y**)



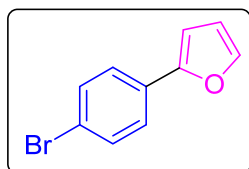
Colourless solid (130 mg, 0.80 mmol, 80%); m.p.: 82 - 84 °C; IR (KBr): 1647.9, 1557.9, 1402.4, 1238.1, 735.5 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.68 – 7.61 (m, 2H), 7.45 (s, 1H), 7.08 (t, $J = 8.7$ Hz, 2H), 6.58 (d, $J = 3.3$ Hz, 1H), 6.47 (dd, $J = 3.2, 1.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 163.36 (d, $J_{\text{C-F}} = 248.3$ Hz), 160.91, 153.18, 142.06, 127.31 (d, $J_{\text{C-F}} = 3.5$ Hz), 125.60 (d, $J_{\text{C-F}} = 8.1$ Hz), 115.81, 115.59 (d, $J_{\text{C-F}} = 21.5$ Hz), 111.70, 104.64 ppm; ESI-MS: $m/z = 163.2 (M + 1)^+$.

2-(4-Chlorophenyl)furan (**3z**)



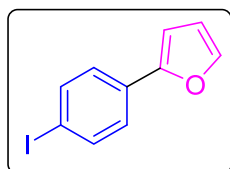
Colourless solid (144 mg, 0.81 mmol, 81%); m.p.: 68 - 70 °C; IR (KBr): 1653.9, 1400.9, 1094.1, 1009.2, 902.8, 833.1, 804.2, 735.8 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.58 (m, 2H), 7.47 (d, $J = 1.2$ Hz, 1H), 7.35 (d, $J = 8.6$ Hz, 2H), 6.64 (d, $J = 3.3$ Hz, 1H), 6.48 (dd, $J = 3.3, 1.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 152.96, 142.36, 132.98, 129.40, 128.91, 125.05, 111.82, 105.46 ppm; ESI-MS: $m/z = 179.6 (M + 1)^+$.

2-(4-Bromophenyl)furan (**3aa**)



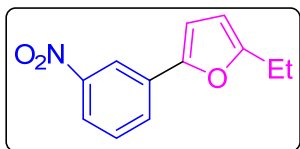
Colourless solid (185 mg, 0.83 mmol, 83%); m.p.: 83 - 85 °C; IR (KBr): 1654.1, 1400.8, 1012.5, 903.7, 830.7, 801.8, 733.9 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.50 (m, 4H), 6.65 (d, $J = 3.3$ Hz, 2H), 6.49 – 6.46 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 152.96, 142.42, 131.83, 129.81, 125.31, 121.09, 111.83, 105.56 ppm; ESI-MS: $m/z = 224.1 (M + 1)^+$.

2-(4-Iodophenyl)furan (**3ab**)



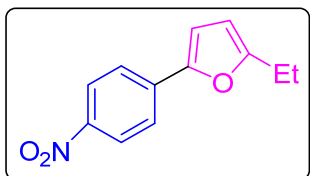
Colourless solid (221 mg, 0.82 mmol, 82%); m.p.: 99 - 101 °C; IR (KBr): 2924.6, 1647.9, 1500.0, 1401.4, 1011.9, 902.7, 828.3, 803.2, 731.6 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 8.5$ Hz, 2H), 7.47 (d, $J = 1.0$ Hz, 1H), 7.41 (d, $J = 8.5$ Hz, 2H), 6.66 (d, $J = 3.3$ Hz, 1H), 6.48 (dd, $J = 3.3, 1.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 153.01, 142.47, 137.75, 130.34, 125.49, 111.84, 105.71, 92.48 ppm; ESI-MS: $m/z = 271.1 (M + 1)^+$.

2-Ethyl-5-(3-nitrophenyl)furan (**3ac**)



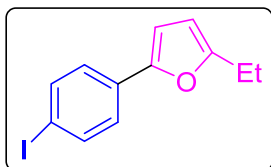
Yellow oil (163 mg, 0.75 mmol, 75%); IR (KBr): 2974.8, 1619.1, 1550.2, 1524.5, 1350.3, 1019.6, 863.6, 798.1, 740.2, 678.3, 532.8 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.44 (s, 1H), 8.08 – 8.01 (m, 1H), 7.91 (d, $J = 7.8$ Hz, 1H), 7.51 (t, $J = 8.0$ Hz, 1H), 6.71 (d, $J = 3.2$ Hz, 1H), 6.12 (dd, $J = 3.2, 0.8$ Hz, 1H), 2.74 (q, $J = 7.5$ Hz, 2H), 1.30 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.21, 149.70, 148.76, 132.75, 129.60, 128.77, 121.07, 117.99, 108.14, 106.71, 21.57, 12.17 ppm; ESI-MS: $m/z = 218.2$ ($M + 1$) $^+$.

2-Ethyl-5-(4-nitrophenyl)furan (**3ad**)



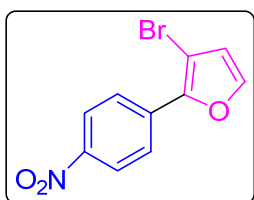
Colorless oil (163 mg, 0.75 mmol, 75%); IR (KBr): 2975.8, 1605.3, 1511.6, 1330.9, 1112.4, 1017.7, 851.5, 751.9, 693.9 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, $J = 8.9$ Hz, 2H), 7.73 (d, $J = 8.9$ Hz, 2H), 6.79 (d, $J = 3.3$ Hz, 1H), 6.15 (d, $J = 3.3$ Hz, 1H), 2.75 (q, $J = 7.5$ Hz, 2H), 1.31 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 160.30, 149.99, 145.90, 136.83, 124.37, 123.31, 110.14, 107.27, 21.64, 12.09 ppm; ESI-MS: $m/z = 218.2$ ($M + 1$) $^+$.

2-Ethyl-5-(4-iodophenyl)furan (**3ae**)



Colorless oil (217 mg, 0.73 mmol, 73%); IR (KBr): 2970.0, 1648.8, 1471.9, 1398.5, 1000.3, 821.5, 777.1 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 8.5$ Hz, 2H), 7.36 (d, $J = 8.5$ Hz, 2H), 6.56 (d, $J = 3.2$ Hz, 1H), 6.06 (d, $J = 3.2$ Hz, 1H), 2.71 (q, $J = 7.5$ Hz, 2H), 1.28 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.19, 151.13, 137.63, 130.69, 125.04, 106.46, 106.33, 91.59, 21.55, 12.20 ppm; ESI-MS: $m/z = 299.1$ ($M + 1$) $^+$.

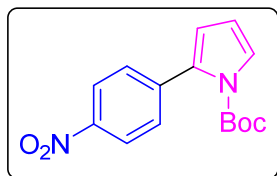
3-Bromo-2-(4-nitrophenyl)furan (**3af**)



Yellow oil (217 mg, 0.81 mmol, 81%); IR (KBr): 1596.9, 1518.1, 1503.4, 1334.8, 1110.6, 849.3, 757.3, 690.2 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, $J = 9.0$ Hz, 2H), 8.12 (d, $J = 9.0$ Hz, 2H), 7.51 (d, $J = 1.7$ Hz, 1H), 6.61 (d, $J = 1.7$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 146.67, 146.57, 143.60, 135.44, 125.49, 123.99,

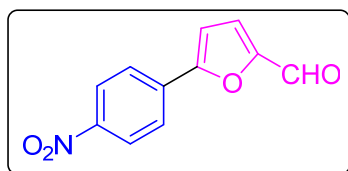
117.21, 99.96 ppm; ESI-MS: $m/z = 269.1 (M + 1)^+$.

Tert-butyl 2-(4-nitrophenyl)-1H-pyrrole-1-carboxylate (3ag)



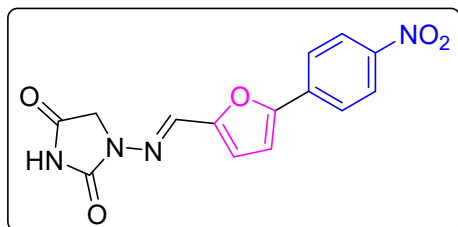
Yellow solid (239 mg, 0.83 mmol, 83%); m.p.: 123 - 125 °C; IR (KBr): 1730.7, 1744.8, 1595.5, 1514.3, 1341.1, 1309.7, 1054.6, 600.7 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, $J = 8.9$ Hz, 2H), 7.54 – 7.48 (m, 2H), 7.40 (m, 1H), 6.32 (m, 1H), 6.27 (m, 1H), 1.43 (s, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.93, 146.62, 140.72, 132.80, 129.58, 124.34, 122.98, 116.57, 111.19, 84.58, 27.76 ppm; ESI-MS: $m/z = 289.3 (M + 1)^+$.

5-(4-Nitrophenyl)furan-2-carbaldehyde (3al)



Yellow solid (145 mg, 0.67 mmol, 67%); m.p.: 204 - 206 °C; IR (KBr): 2923.8, 2851.6, 1684.9, 1667.2, 1600.3, 1515.5, 1344.4, 1105.4, 1042.0, 996.2, 809.3 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ 9.69 (s, 1H), 8.36 (d, $J = 9.0$ Hz, 2H), 8.14 (d, $J = 9.0$ Hz, 2H), 7.73 (d, $J = 3.8$ Hz, 1H), 7.61 (d, $J = 3.8$ Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 179.05, 155.96, 153.14, 147.83, 134.82, 126.40, 125.42, 125.02, 112.68 ppm; ESI-MS: $m/z = 218.2 (M + 1)^+$.

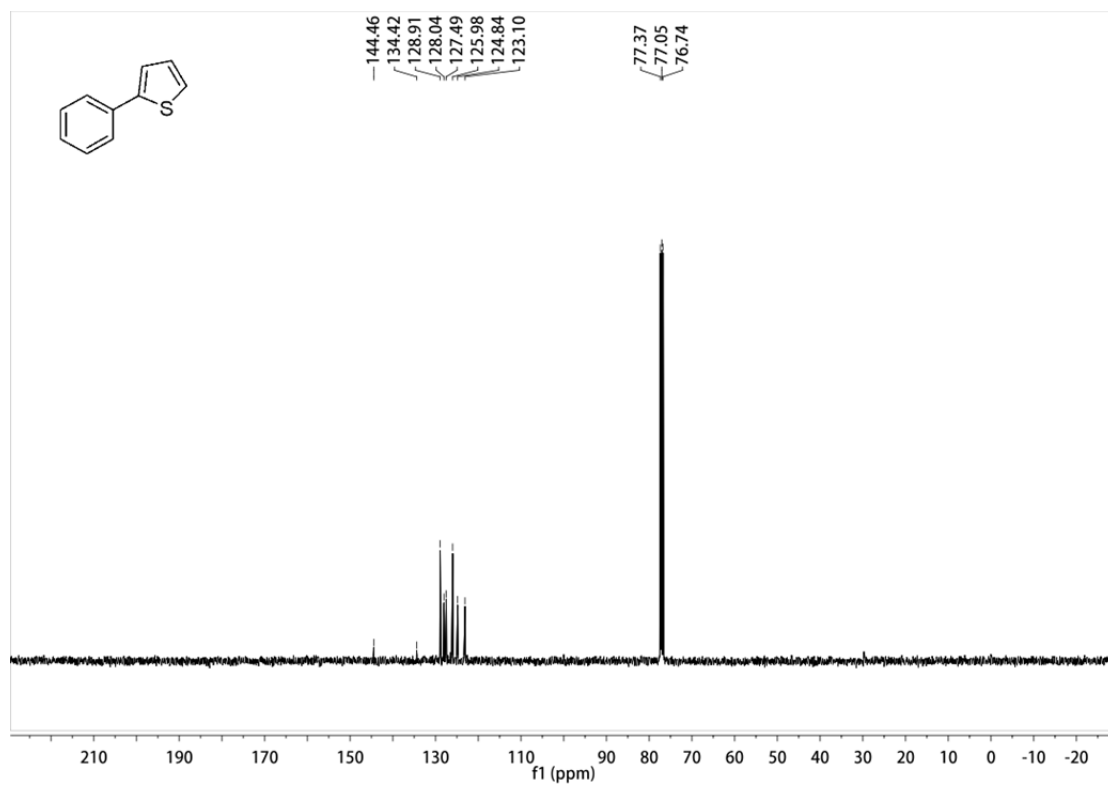
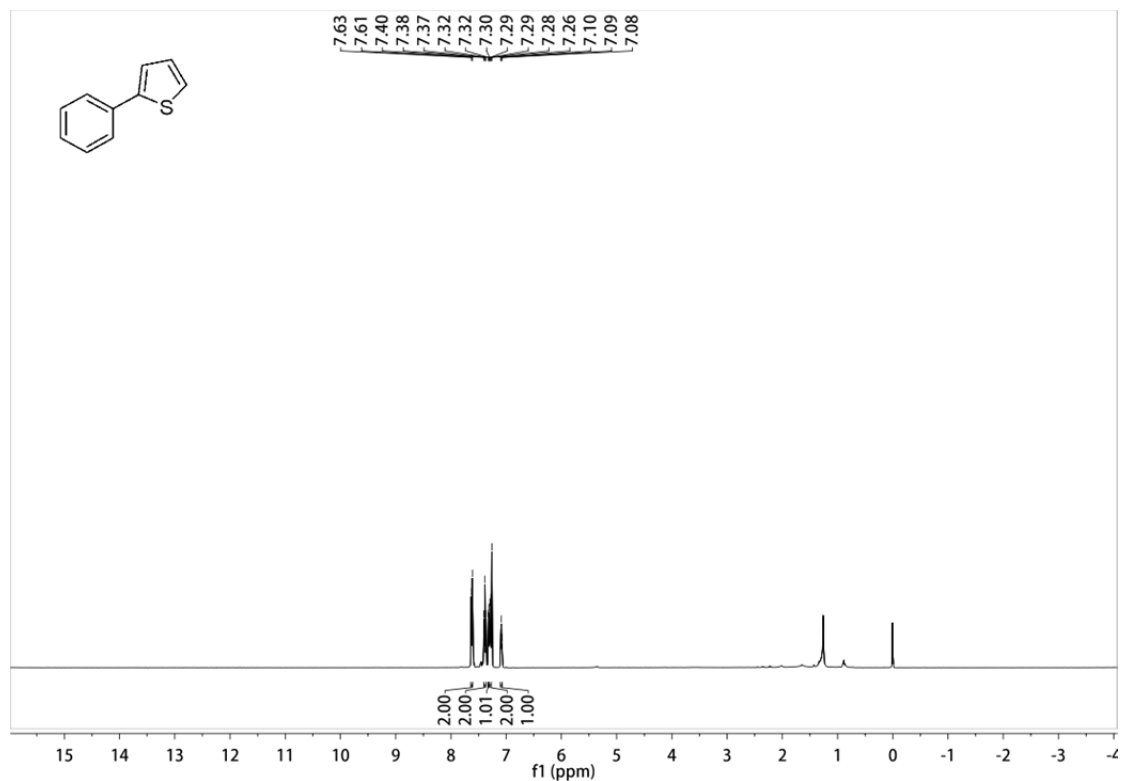
Dantrolene (4)



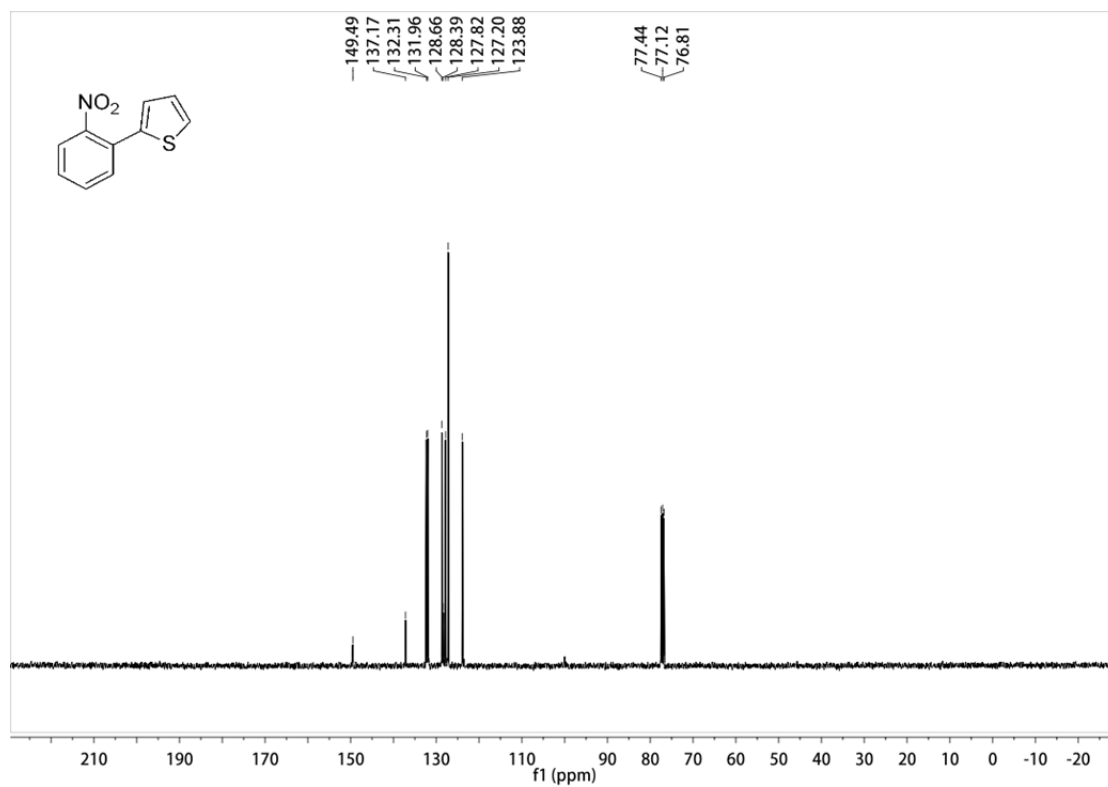
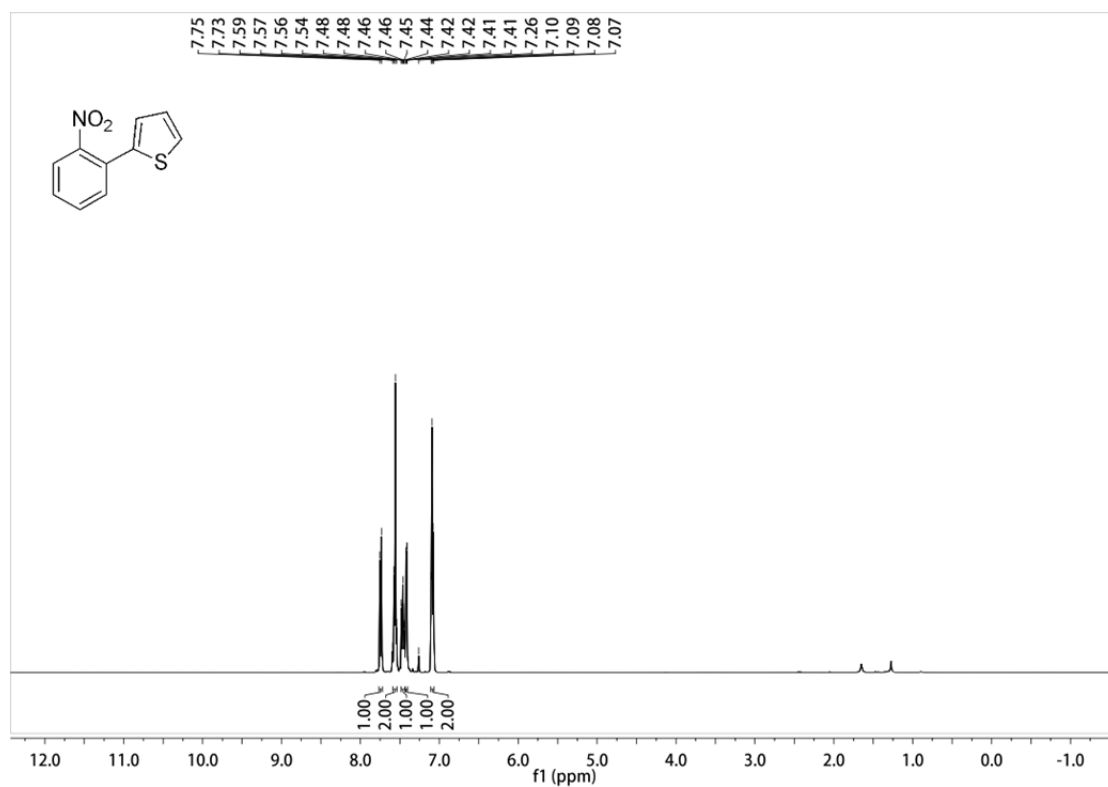
Yellow solid (285 mg, 0.91 mmol, 91%); m.p.: 240 - 242 °C; IR (KBr): 2763.2, 1773.5, 1598.8, 1537.8, 1517.2, 1436.4, 1407.4, 1339.7, 1213.6, 1108.3, 853.6, 799.6 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ 11.35 (s, 1H), 8.31 (d, $J = 8.8$ Hz, 2H), 8.00 (d, $J = 8.7$ Hz, 2H), 7.76 (s, 1H), 7.46 (d, $J = 3.5$ Hz, 1H), 7.04 (d, $J = 3.5$ Hz, 1H), 4.36 (s, 2H); ^{13}C NMR (101 MHz, DMSO) δ 169.37, 153.76, 152.55, 151.50, 146.66, 135.63, 133.05, 125.01, 124.94, 116.08, 112.90, 49.43 ppm; ESI-MS: $m/z = 315.1 (M + 1)^+$.

Copies of NMR spectra for products

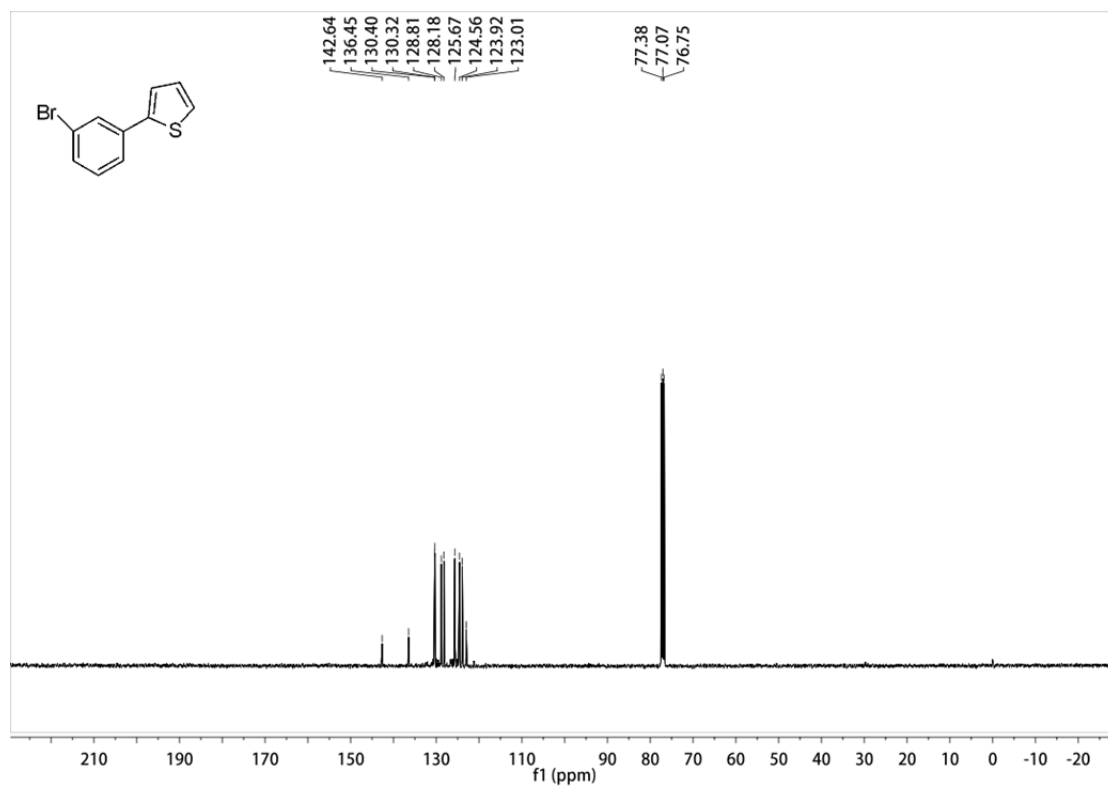
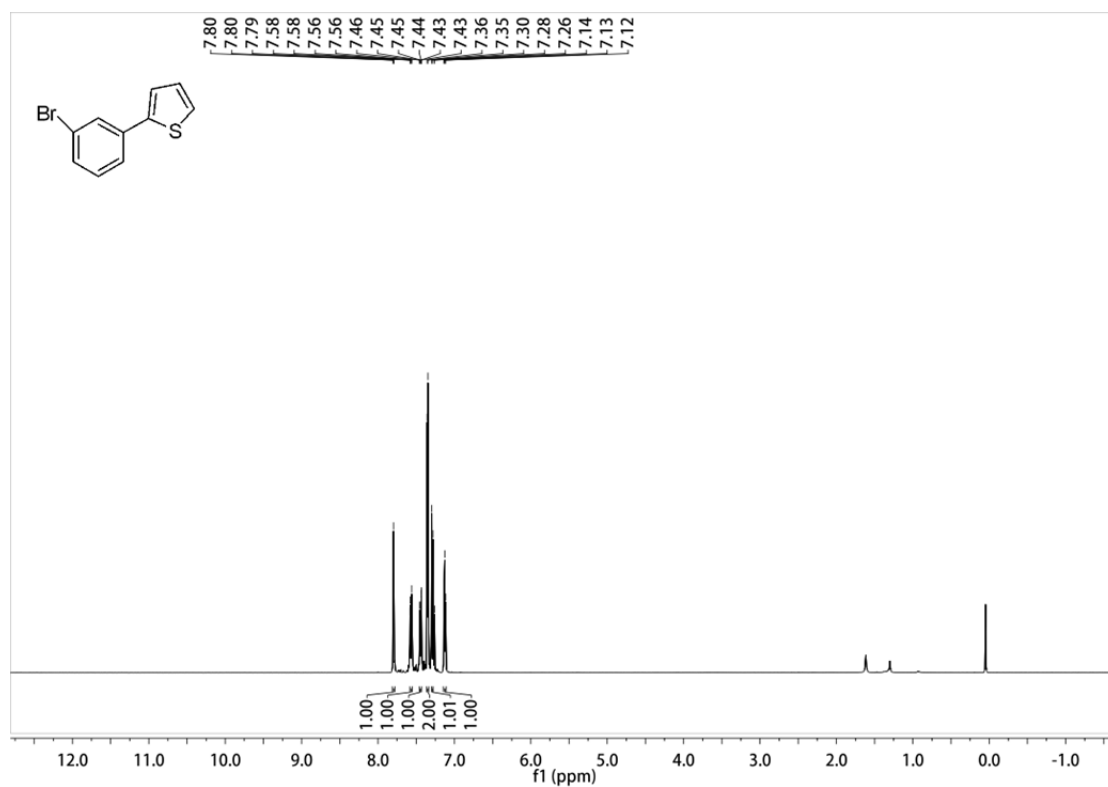
^1H NMR and ^{13}C NMR of compound **3a**



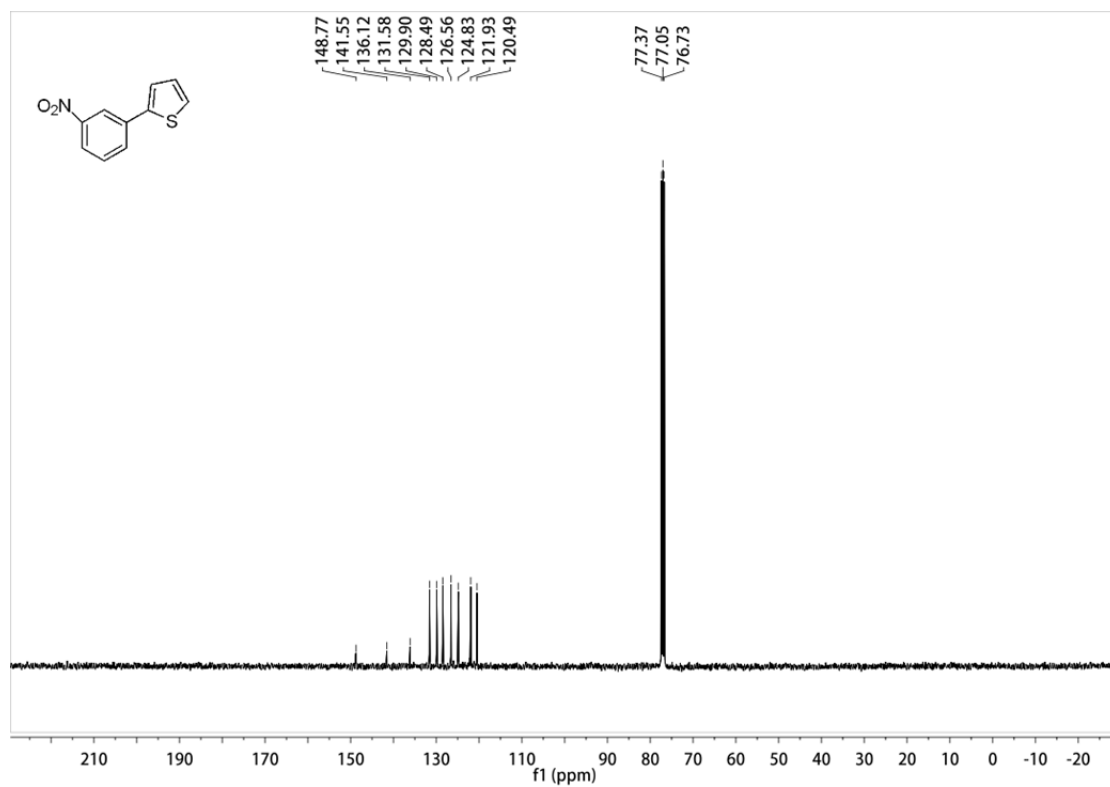
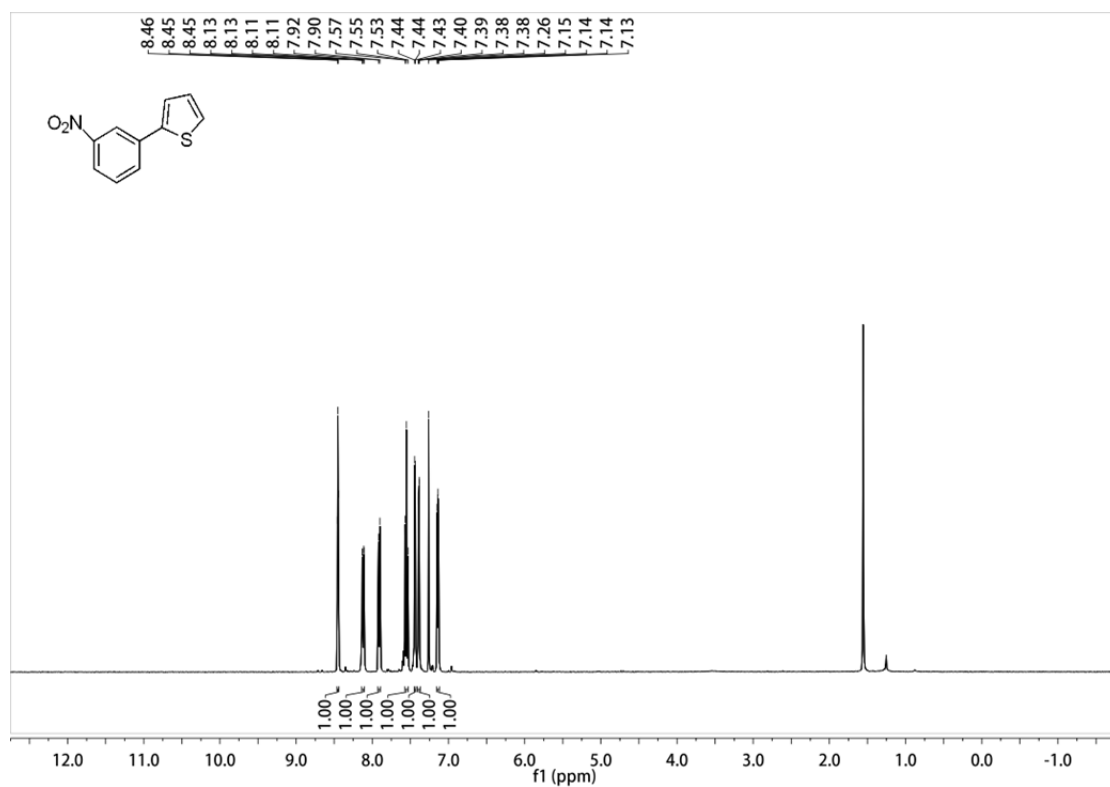
^1H NMR and ^{13}C NMR of compound **3b**



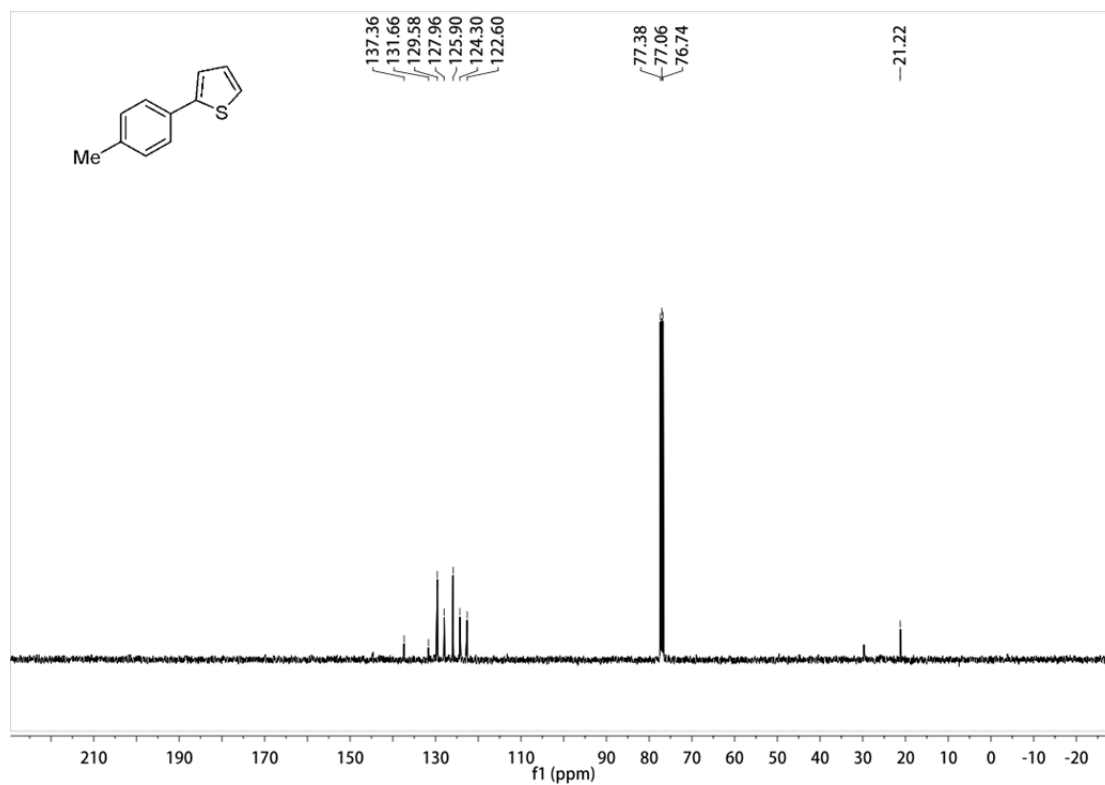
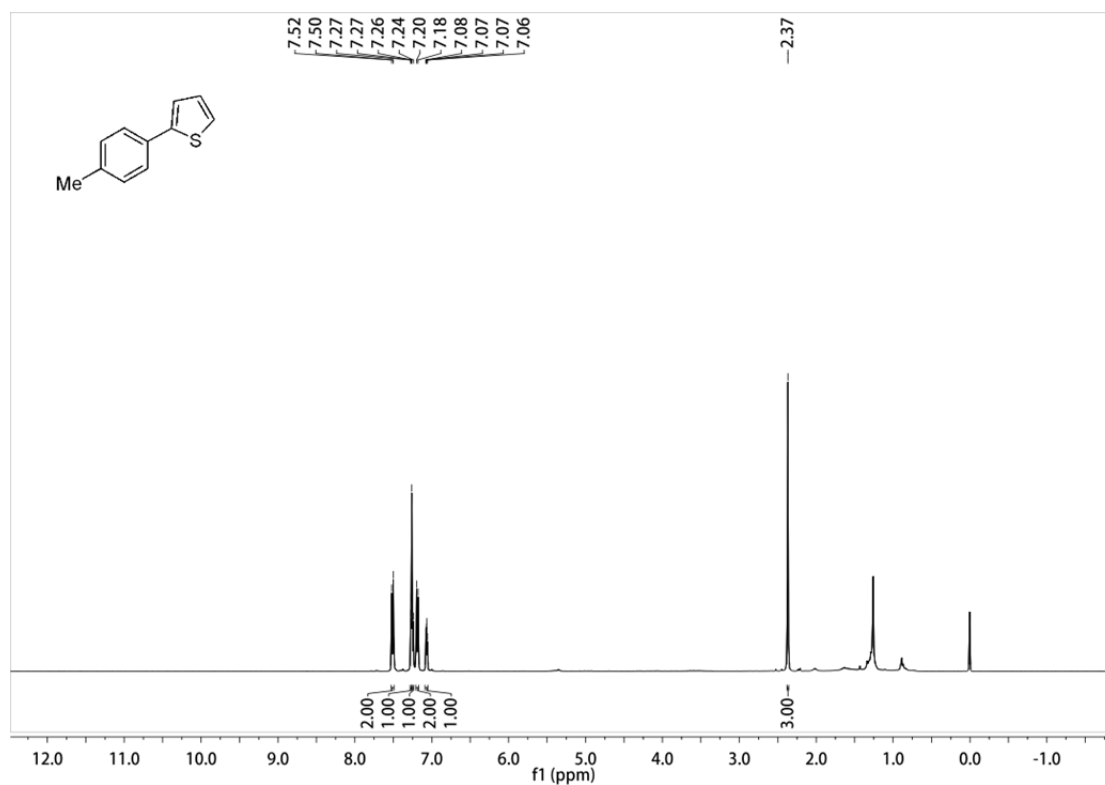
^1H NMR and ^{13}C NMR of compound **3c**



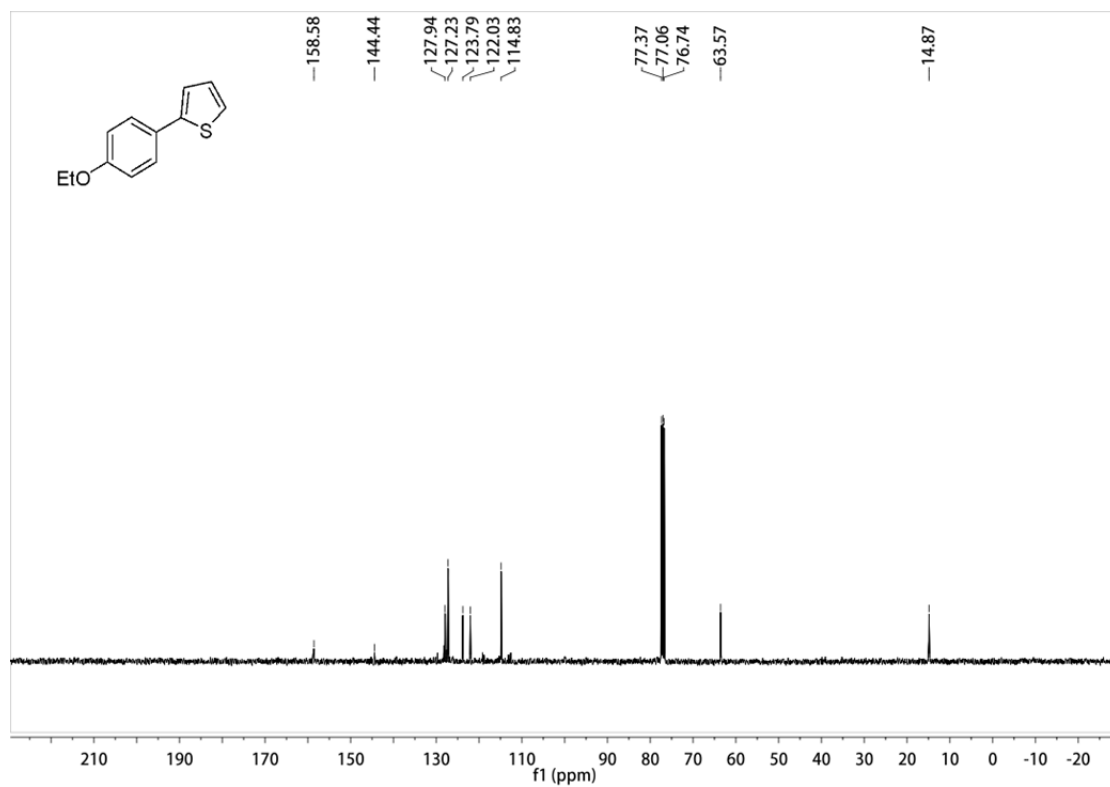
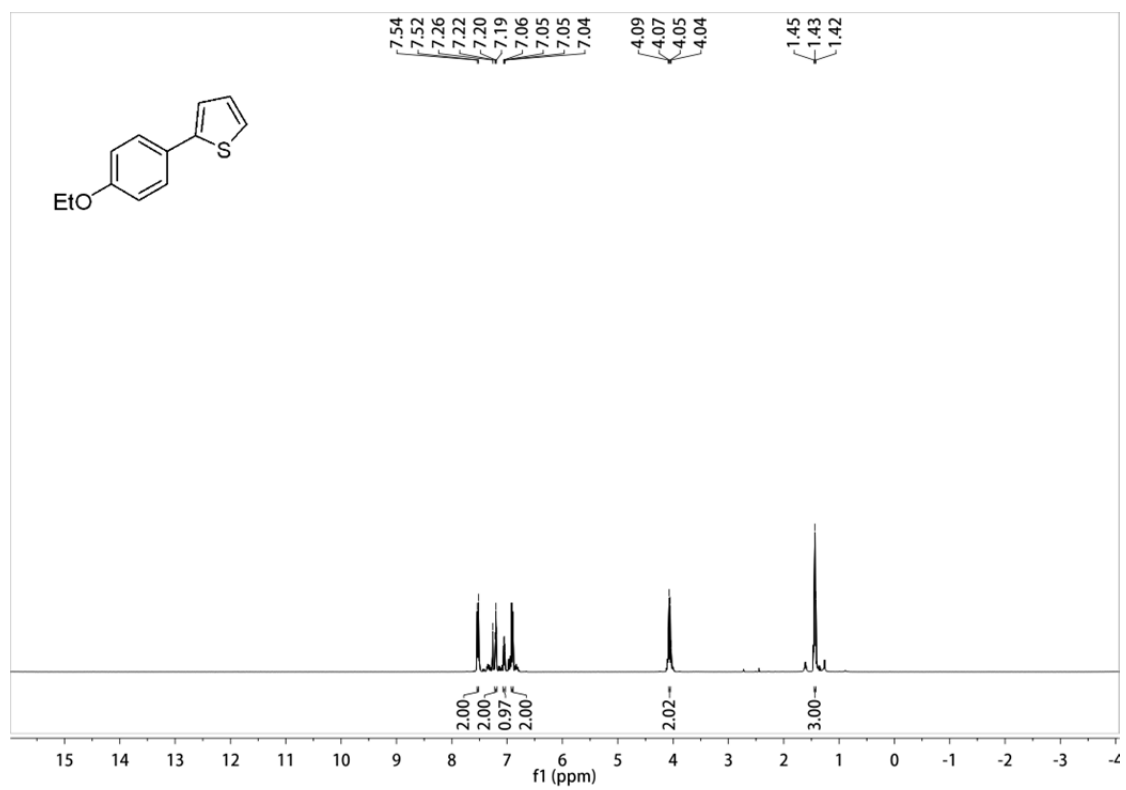
^1H NMR and ^{13}C NMR of compound **3d**



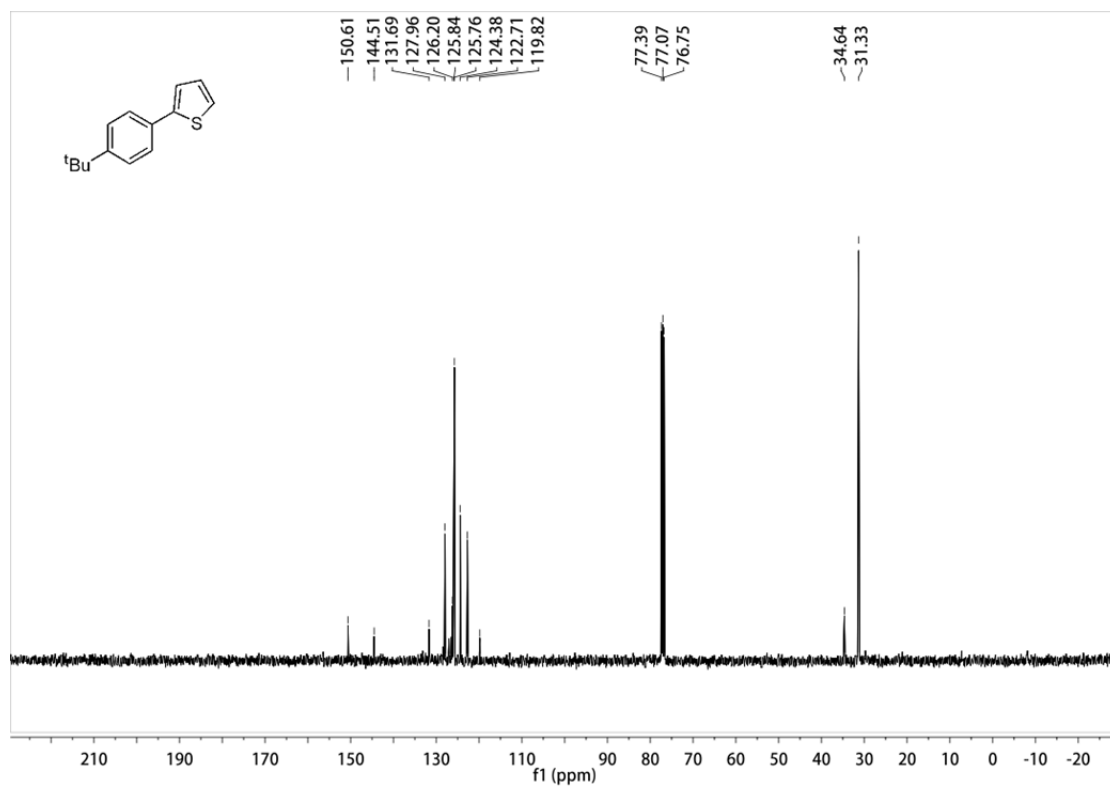
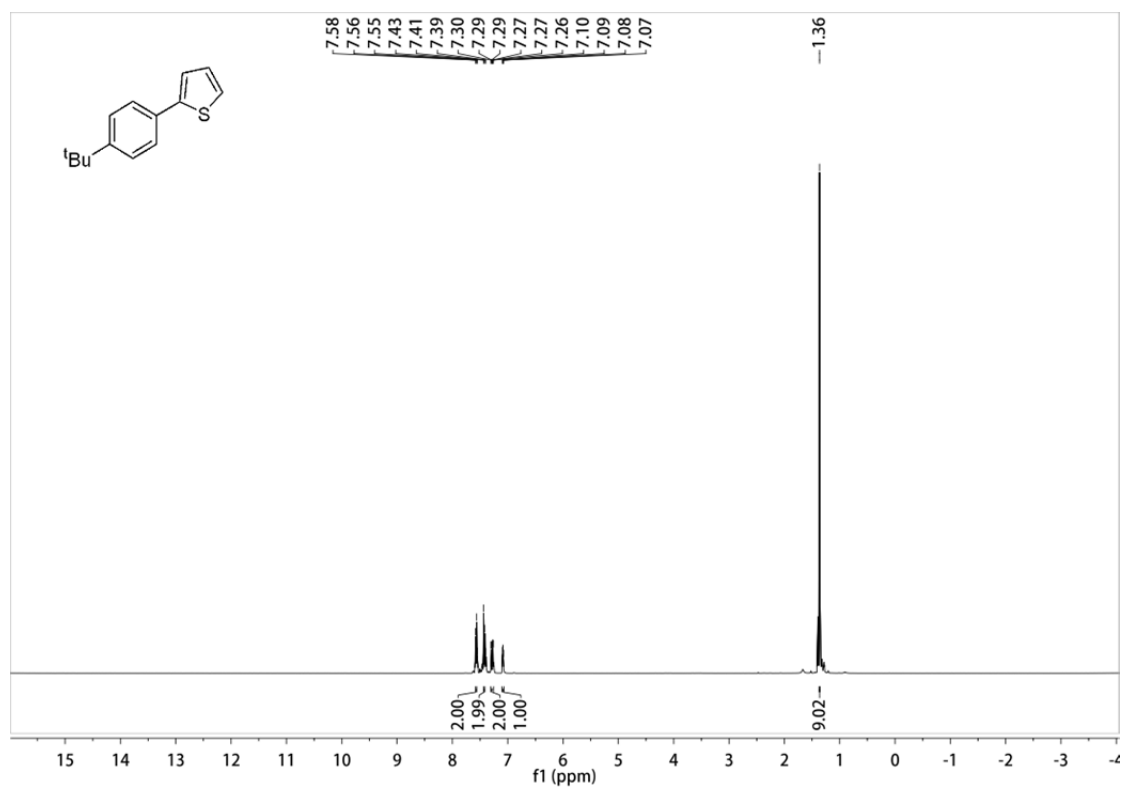
^1H NMR and ^{13}C NMR of compound **3e**



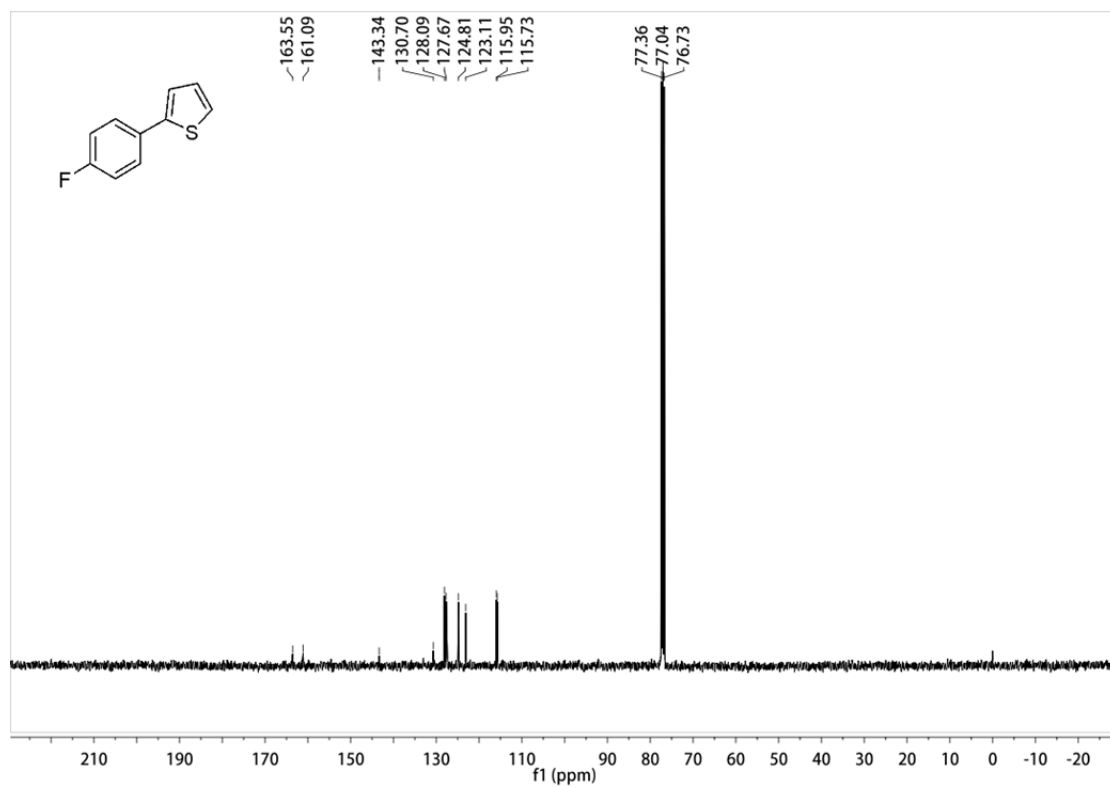
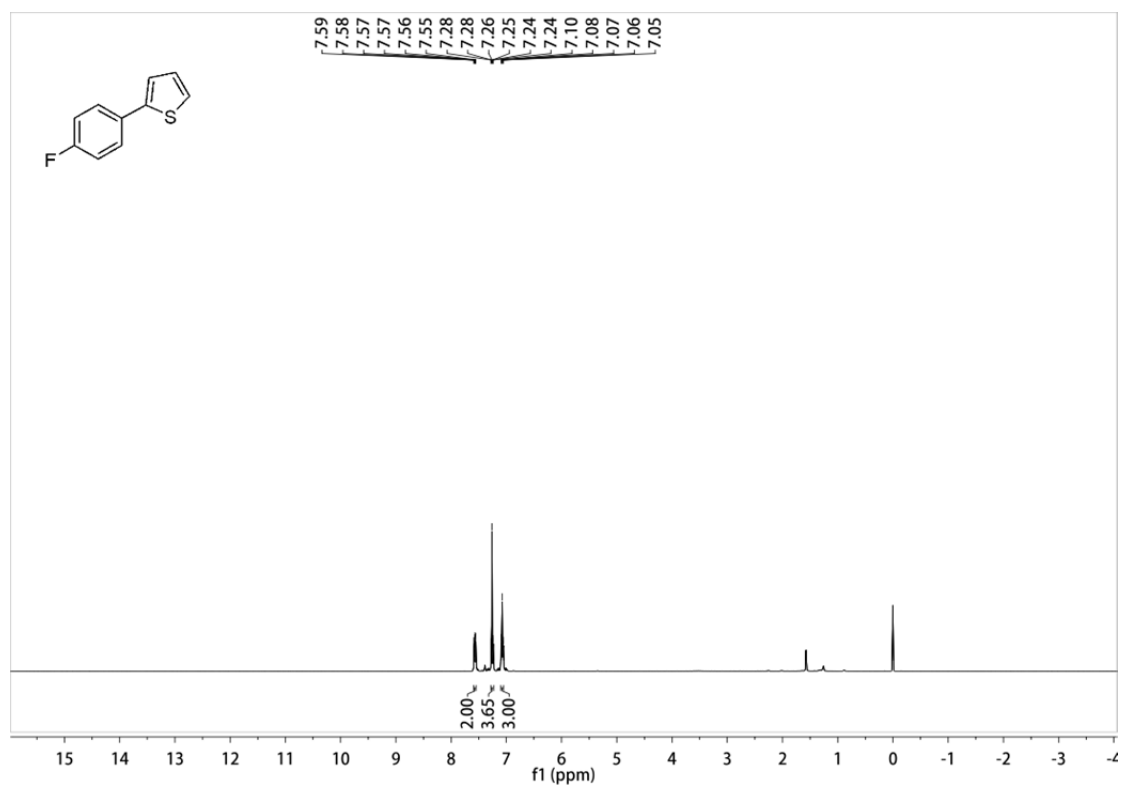
^1H NMR and ^{13}C NMR of compound **3f**



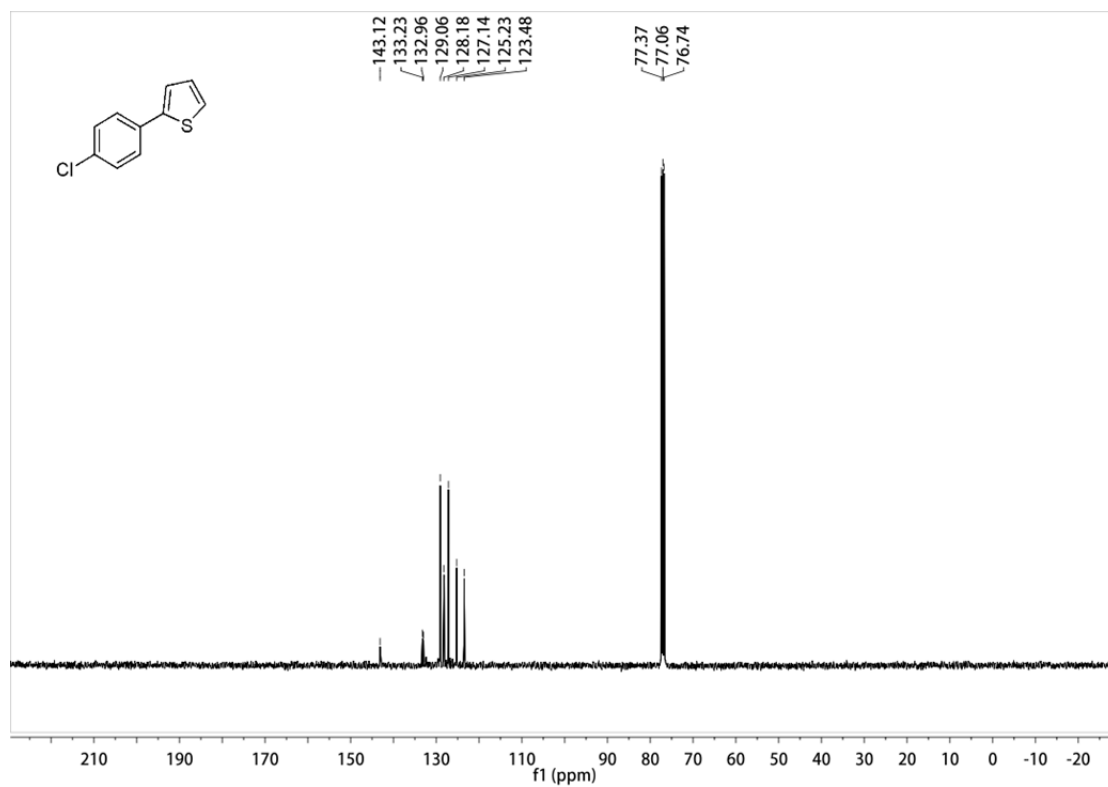
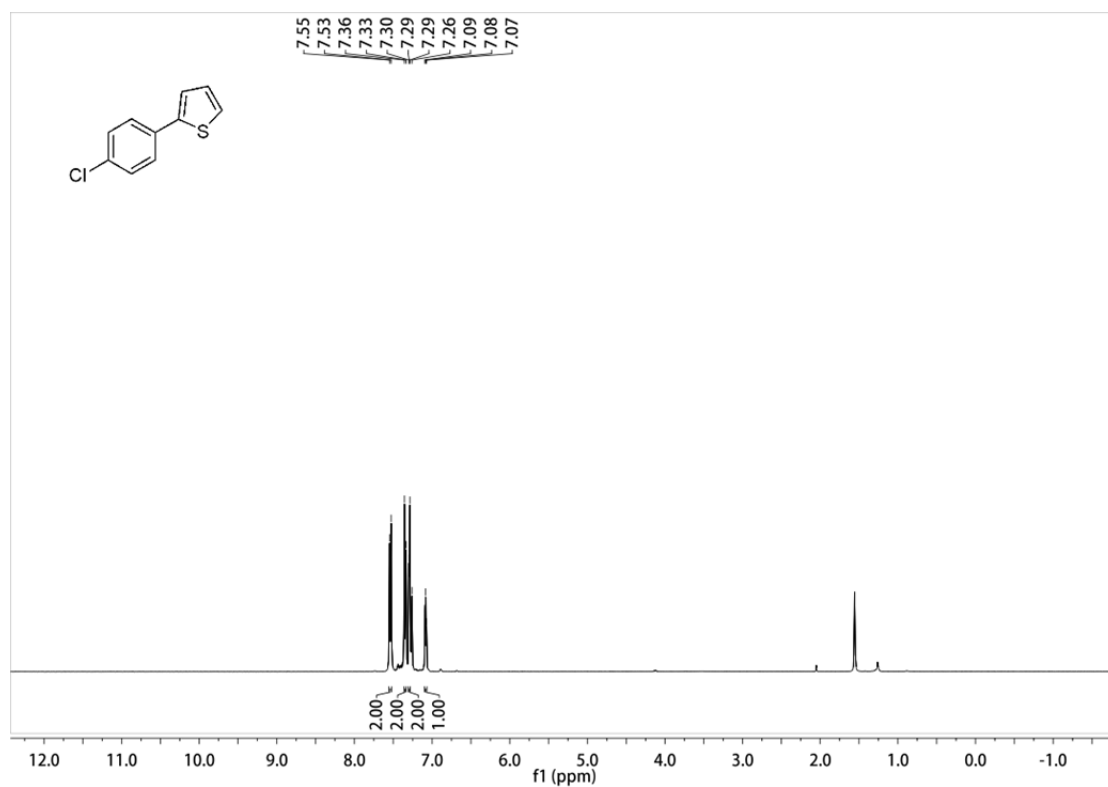
^1H NMR and ^{13}C NMR of compound **3g**



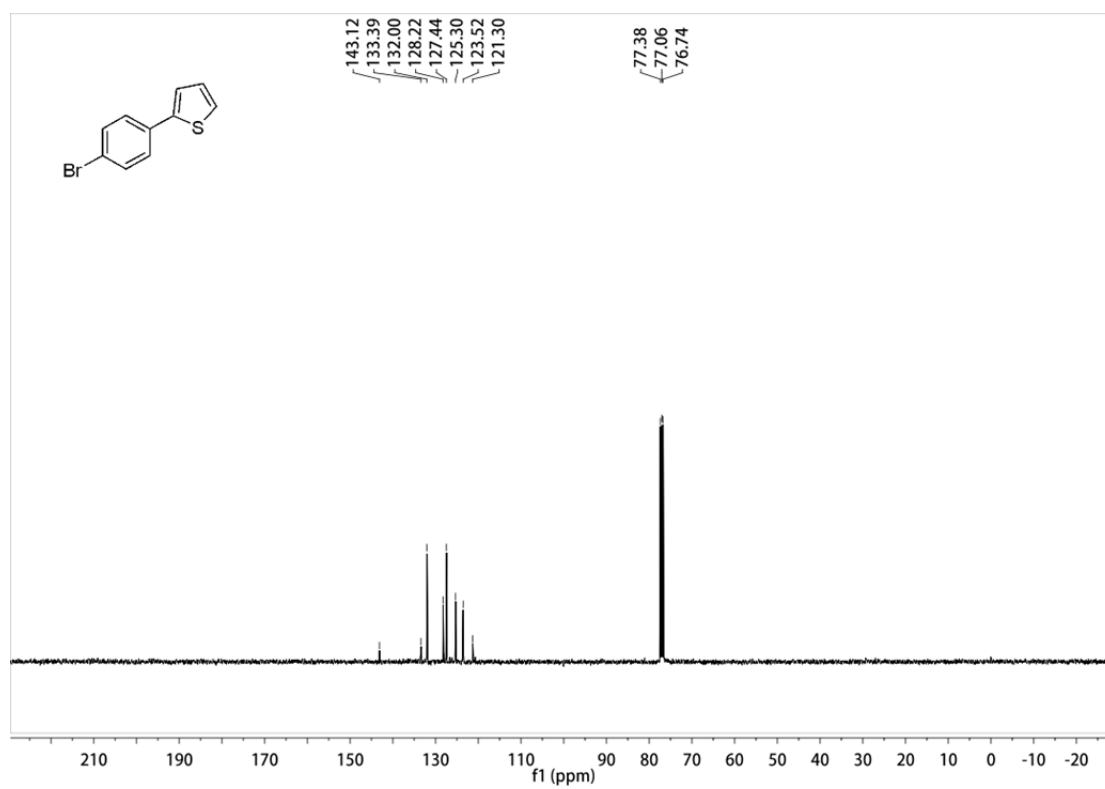
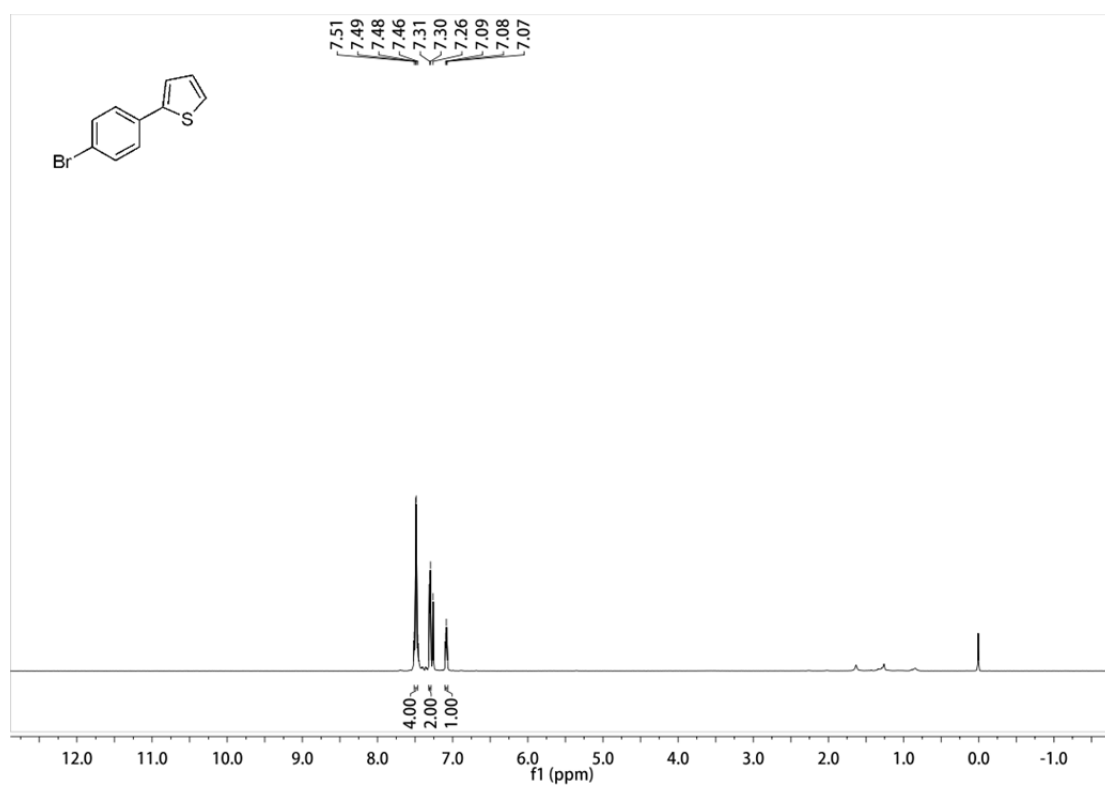
^1H NMR and ^{13}C NMR of compound **3h**



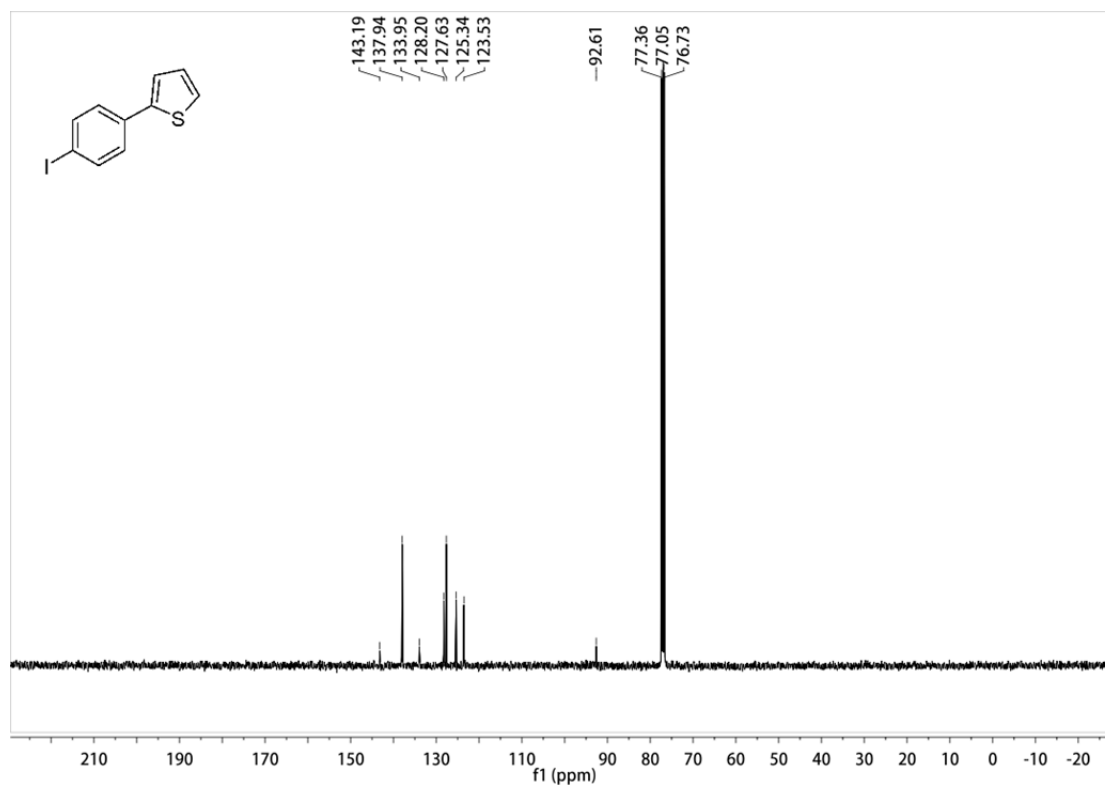
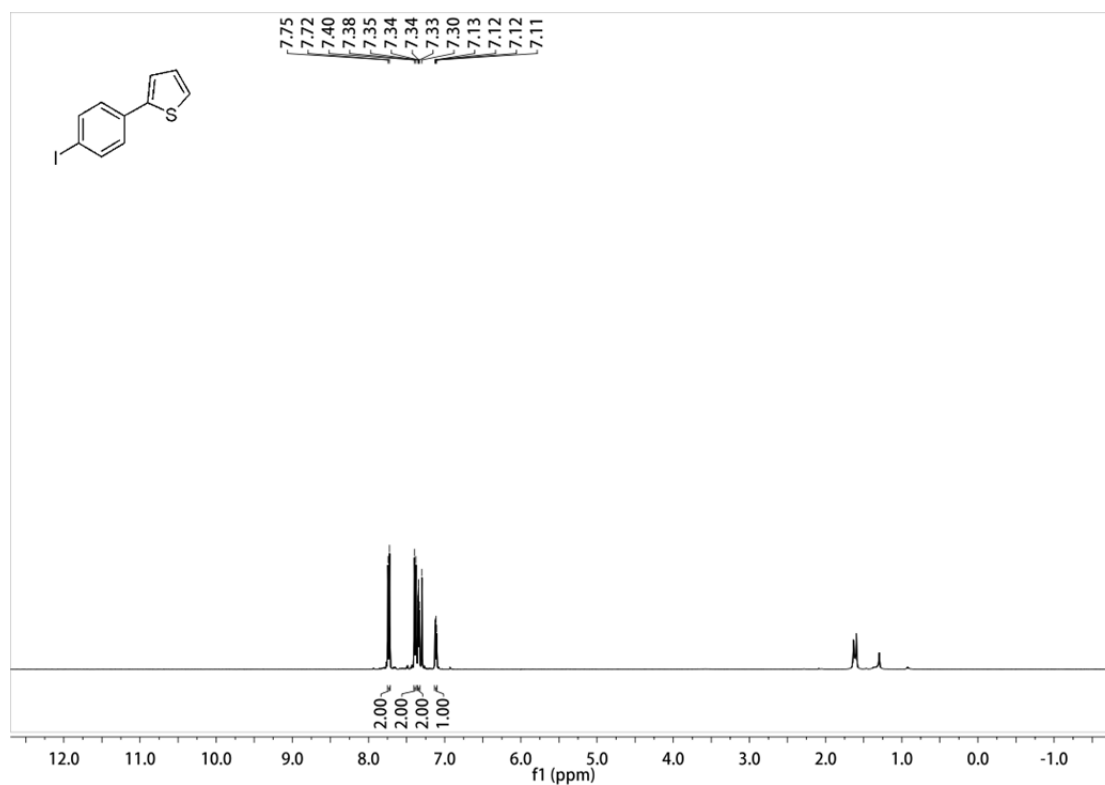
^1H NMR and ^{13}C NMR of compound **3i**



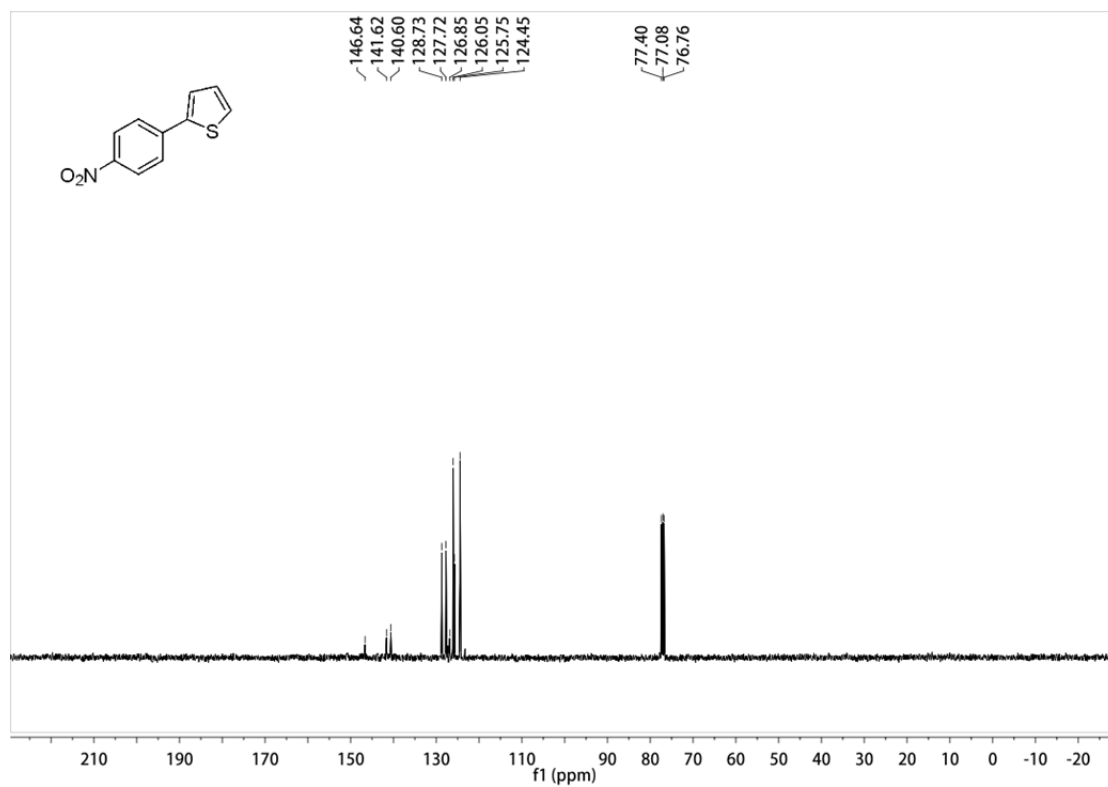
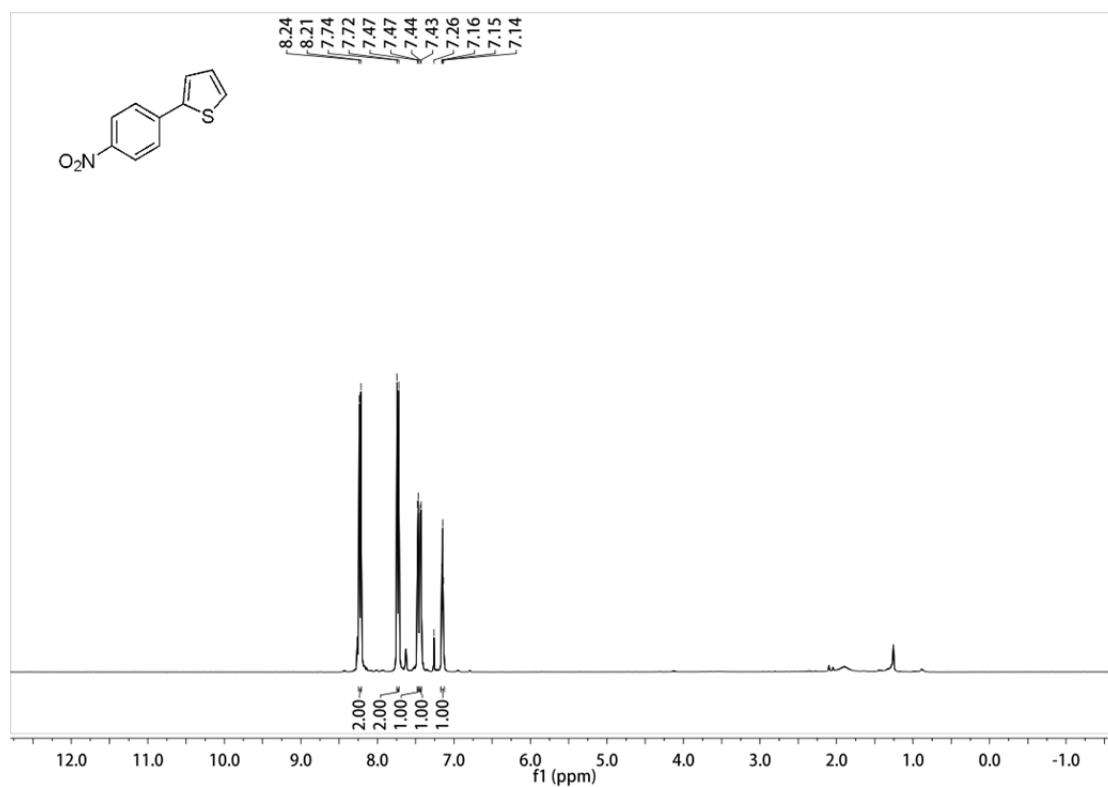
^1H NMR and ^{13}C NMR of compound **3j**



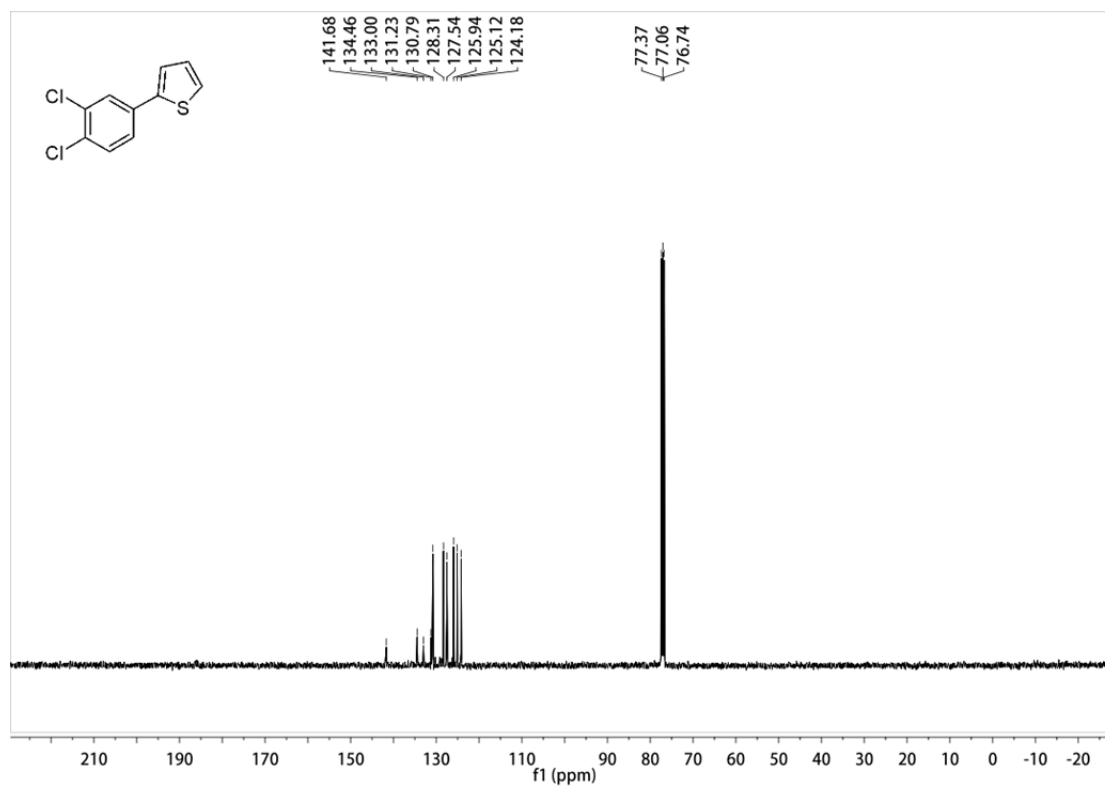
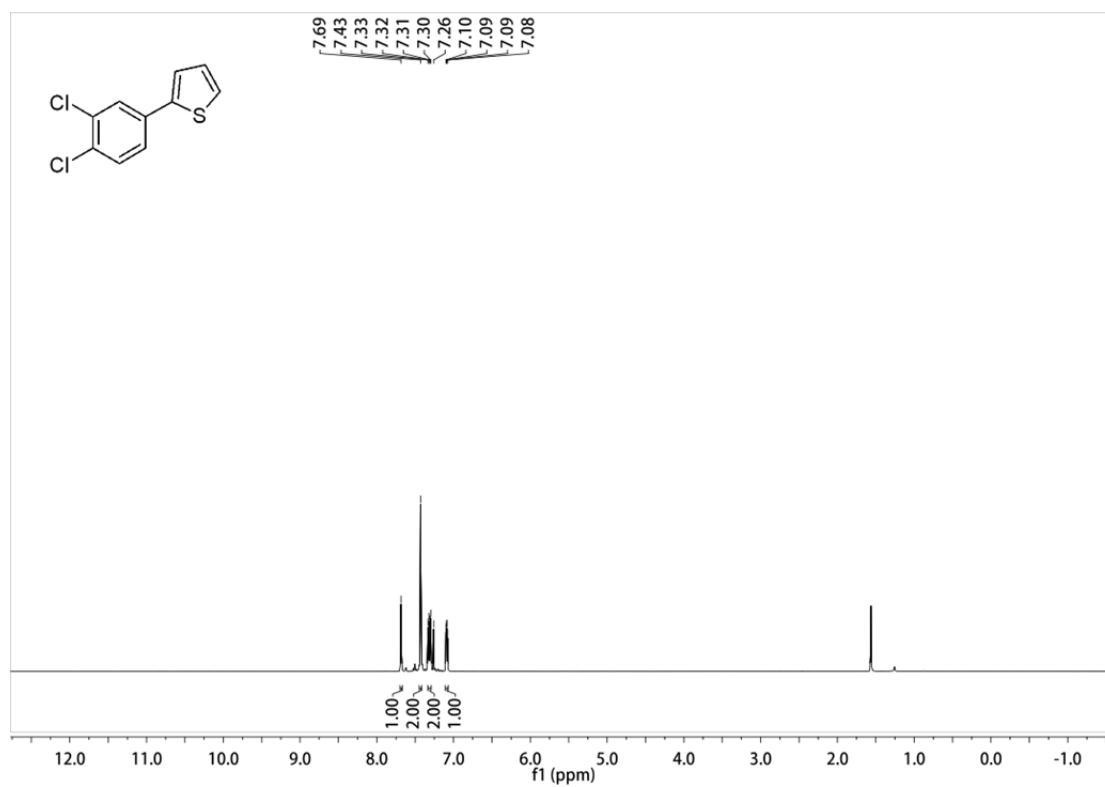
^1H NMR and ^{13}C NMR of compound **3k**



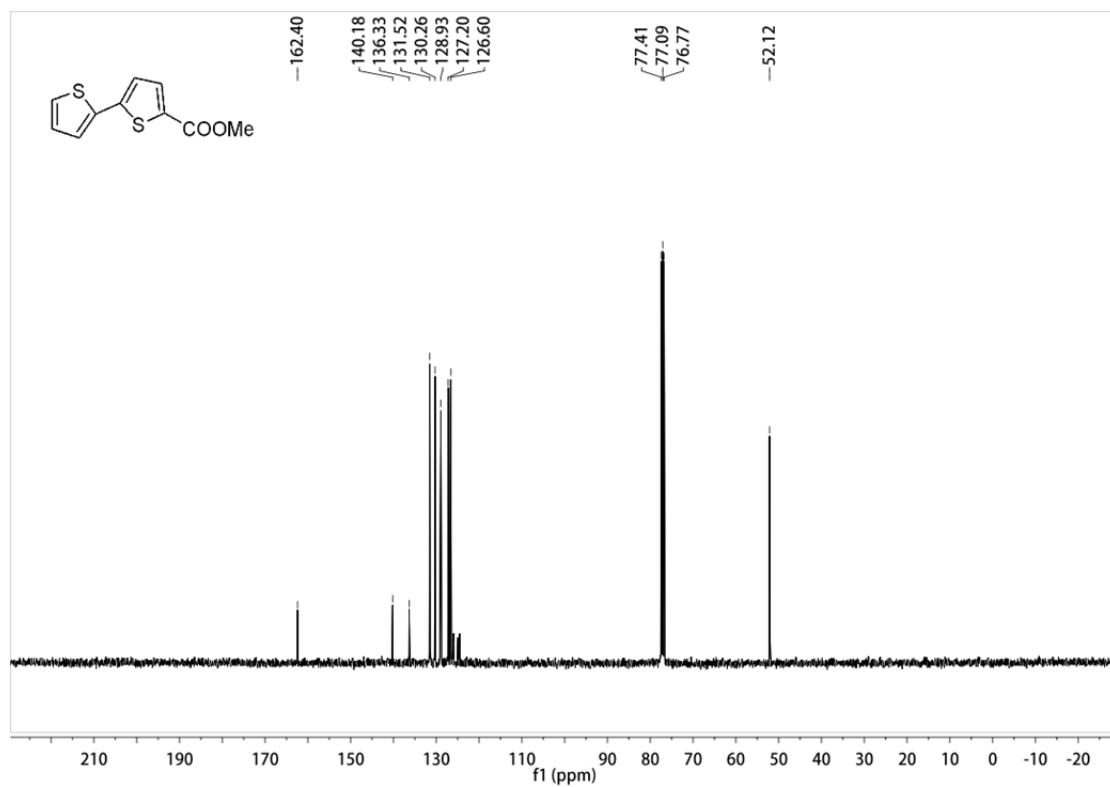
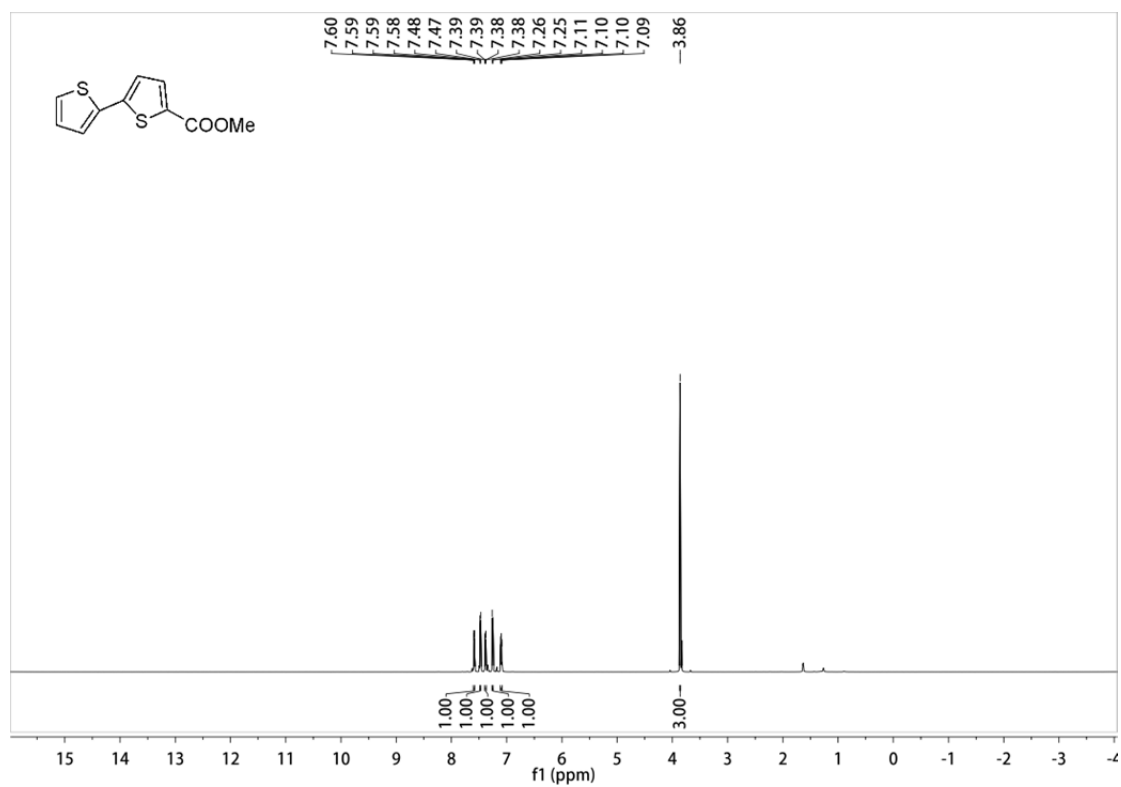
^1H NMR and ^{13}C NMR of compound **31**



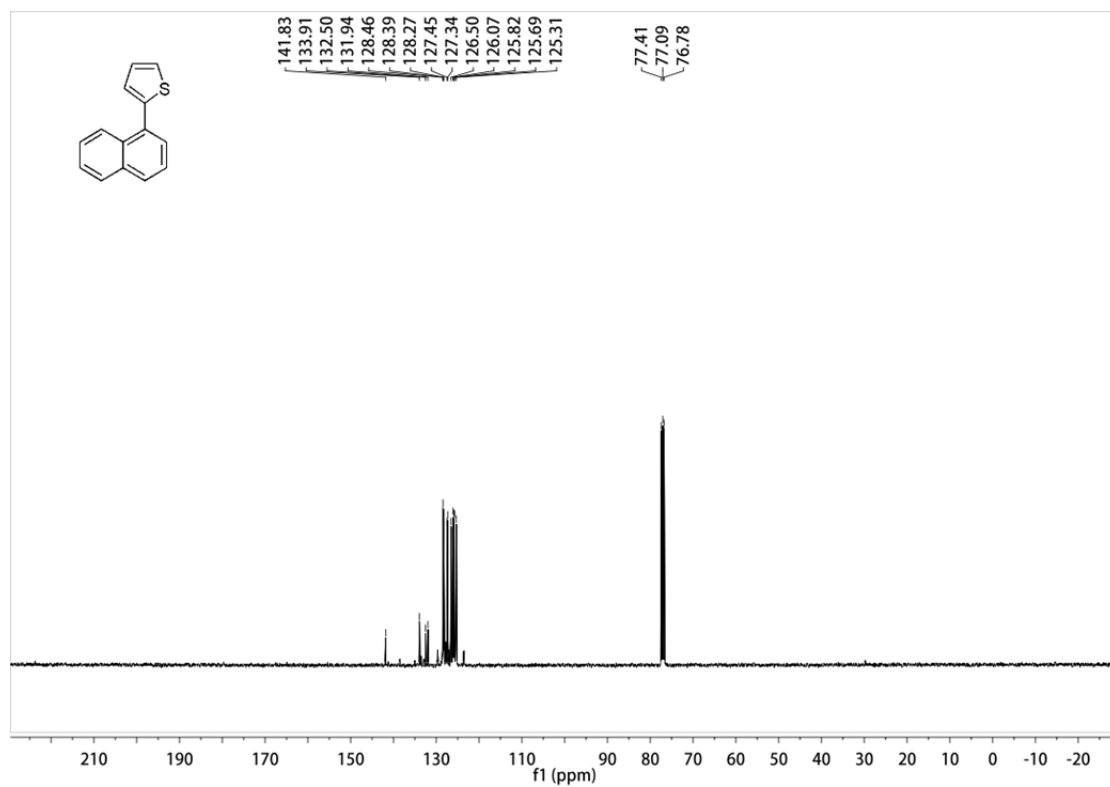
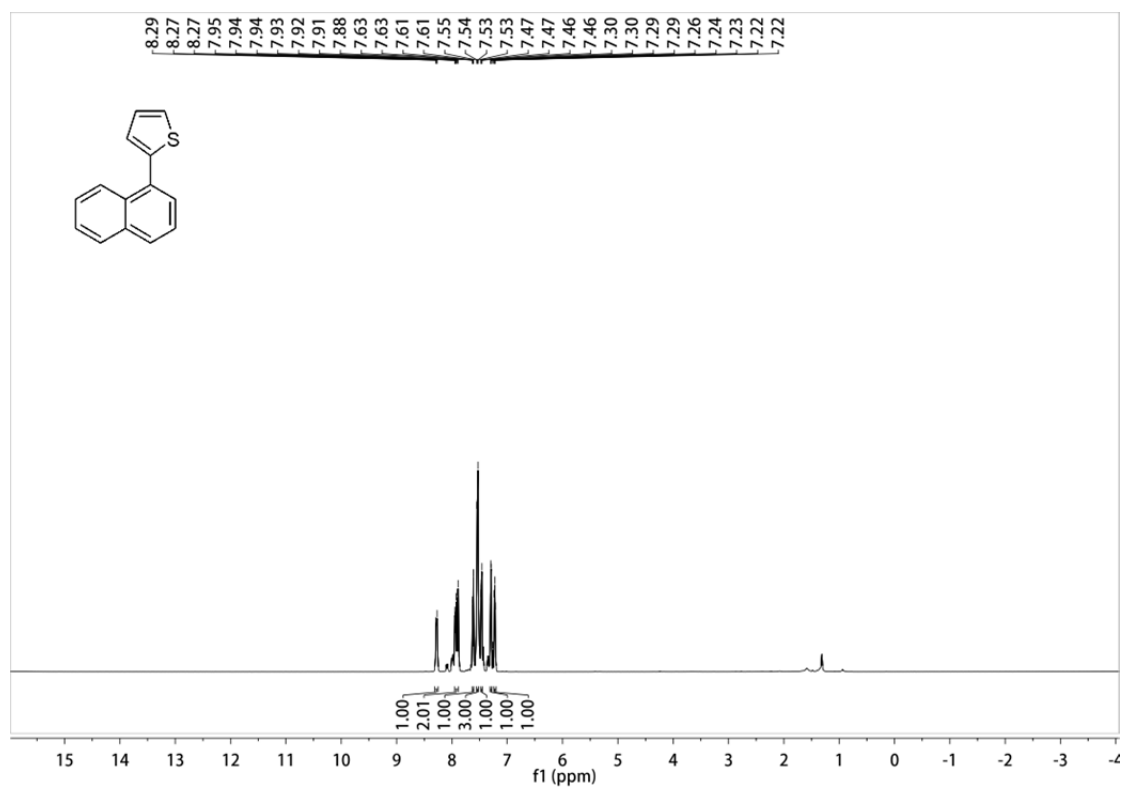
^1H NMR and ^{13}C NMR of compound **3m**



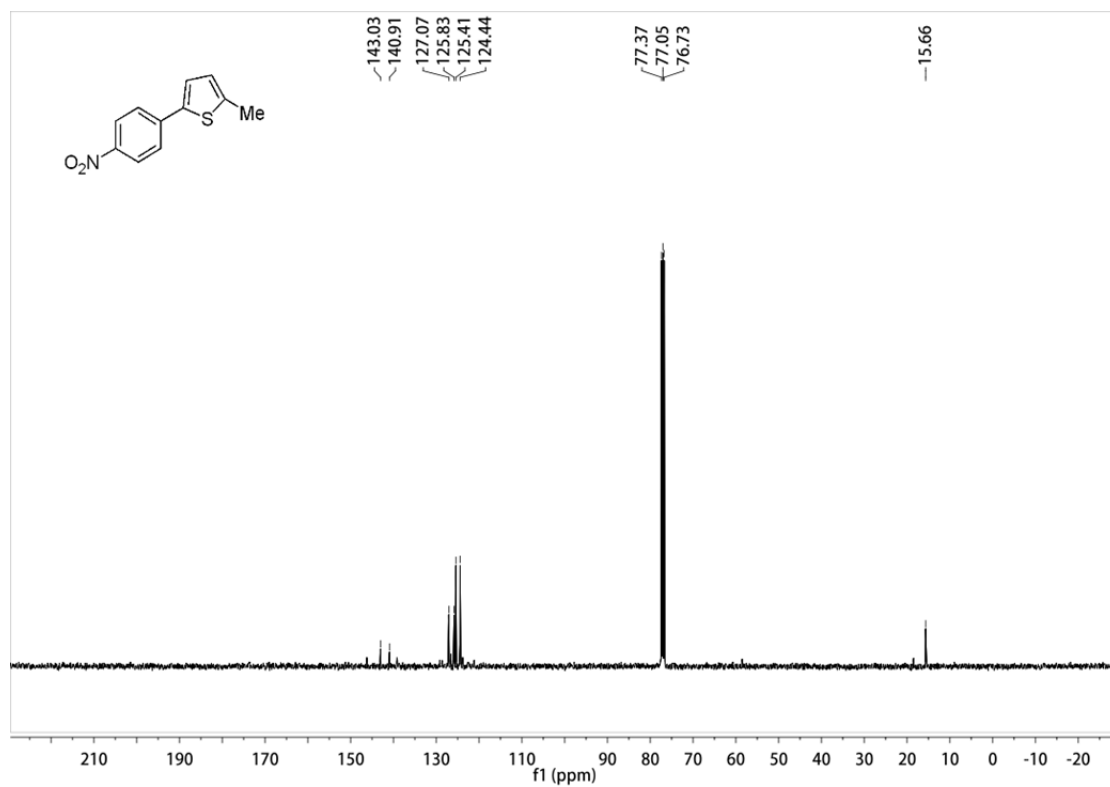
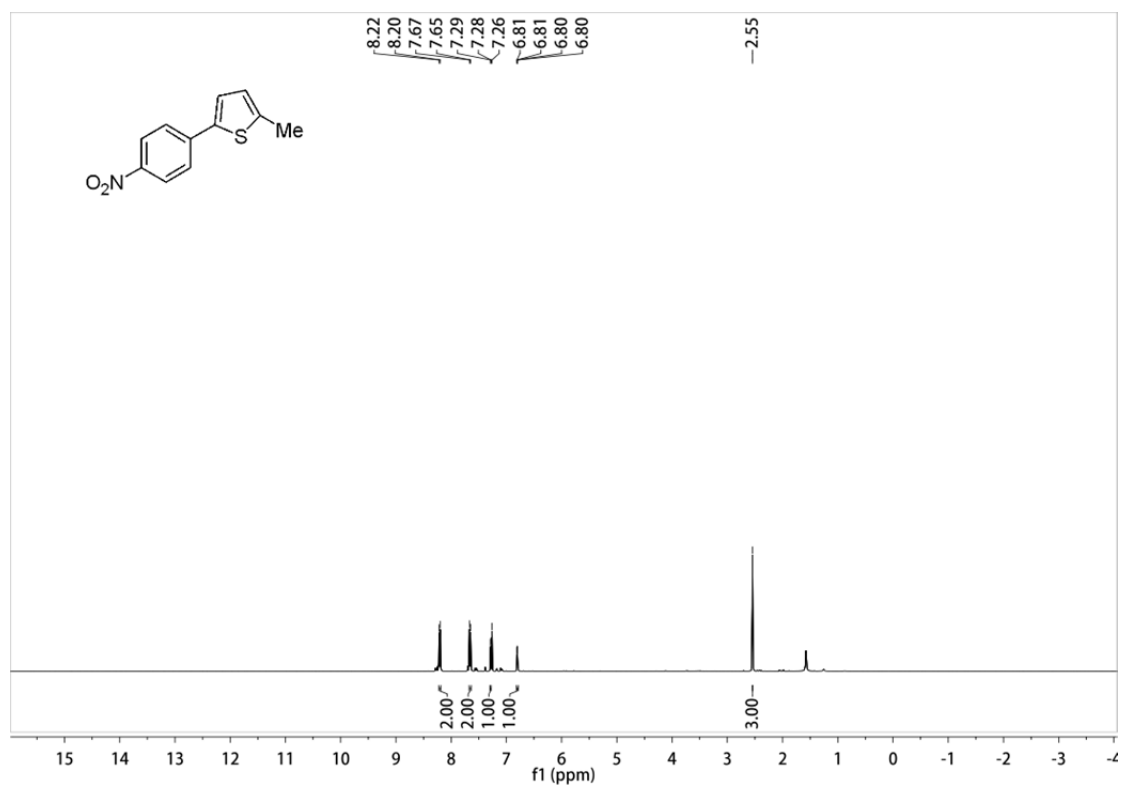
^1H NMR and ^{13}C NMR of compound **3n**



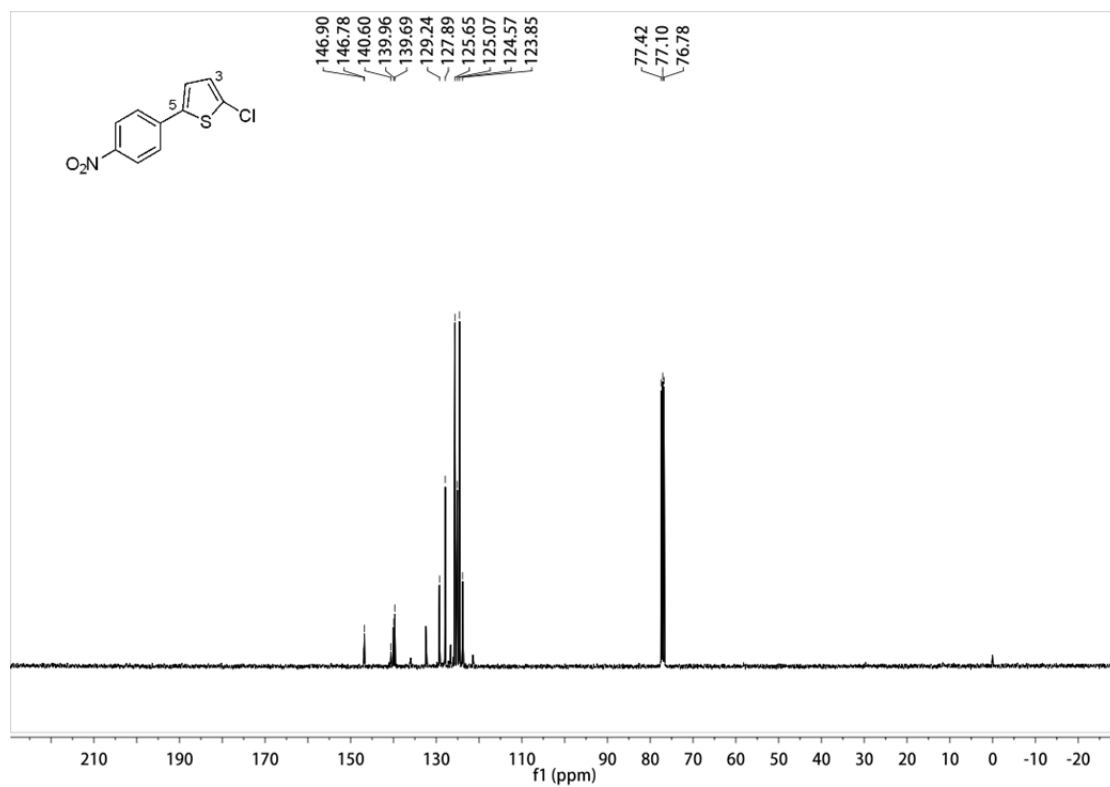
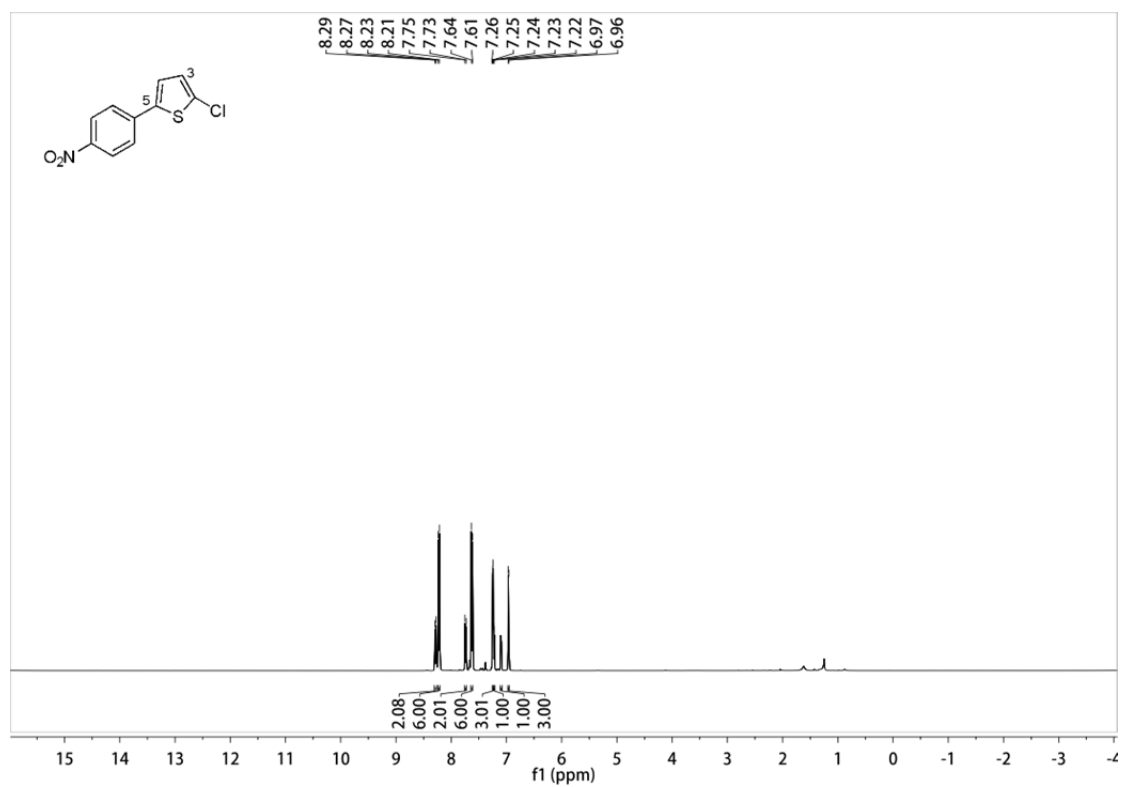
^1H NMR and ^{13}C NMR of compound **30**



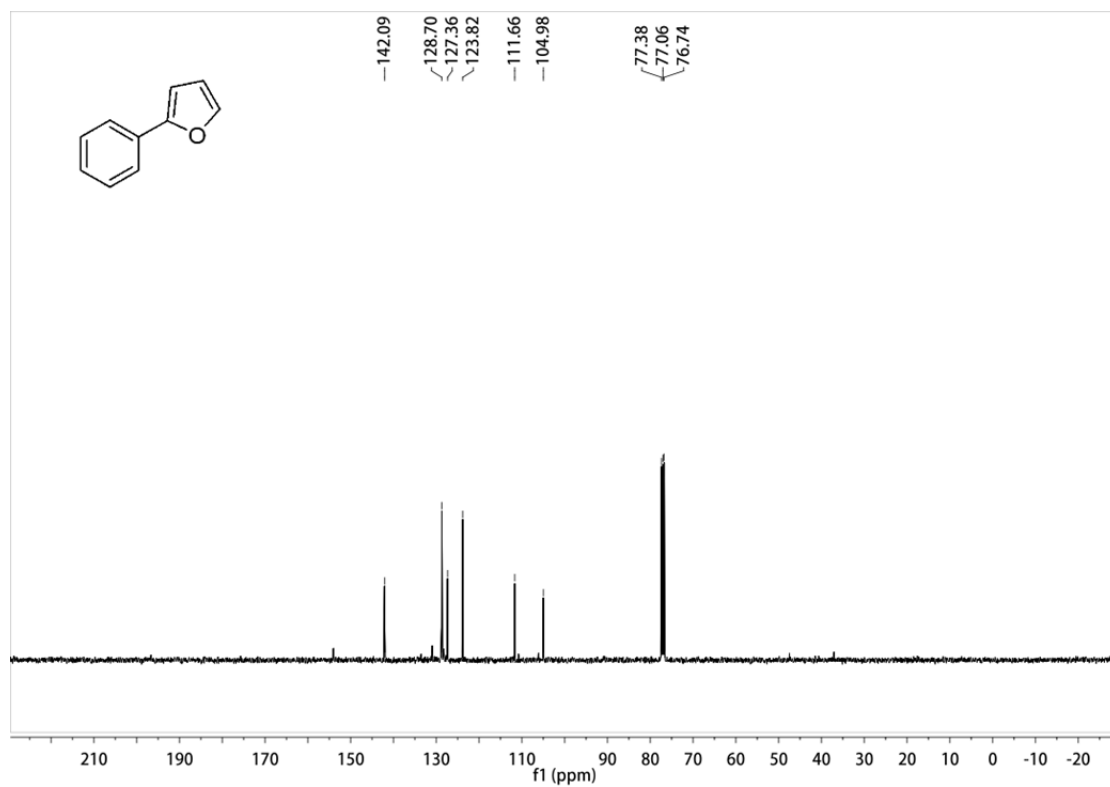
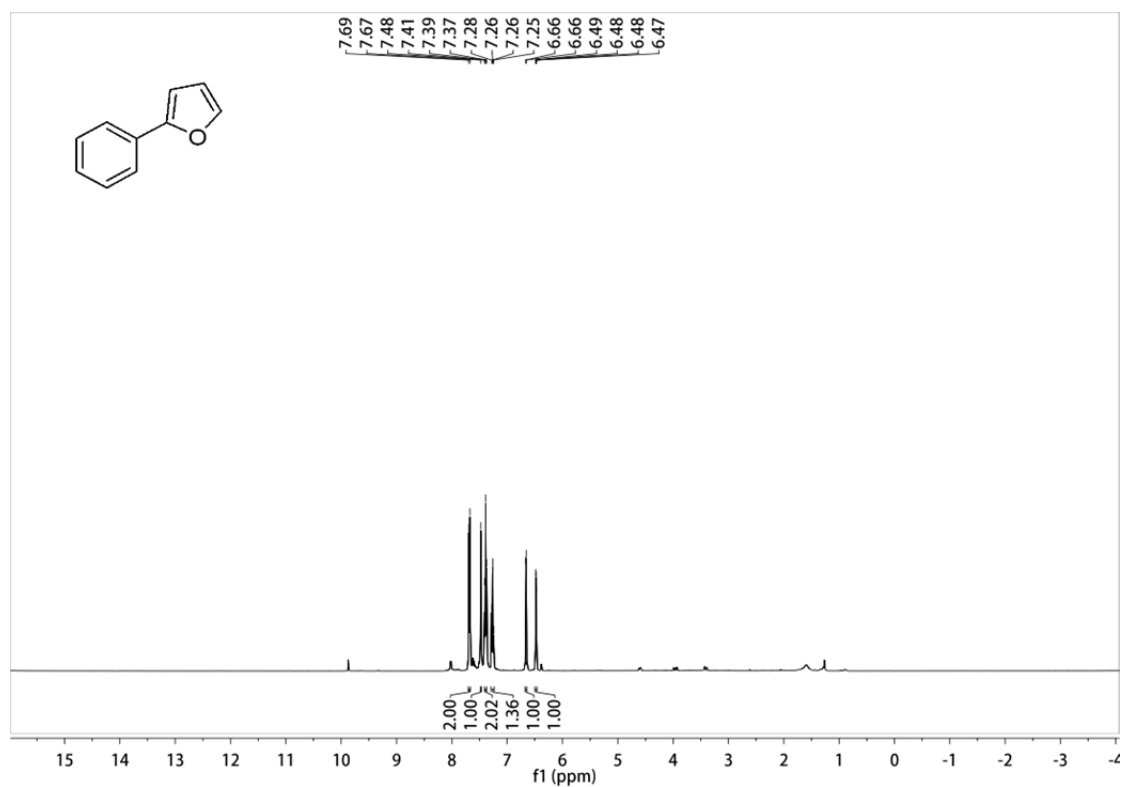
^1H NMR and ^{13}C NMR of compound **3p**



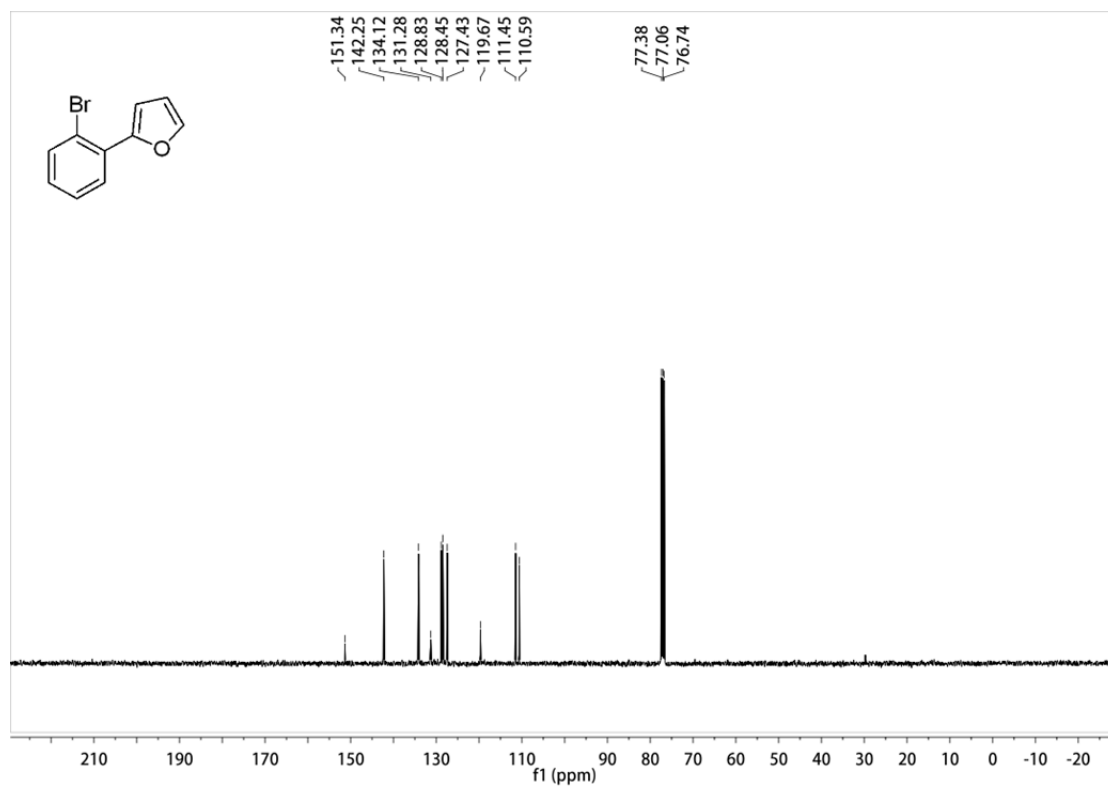
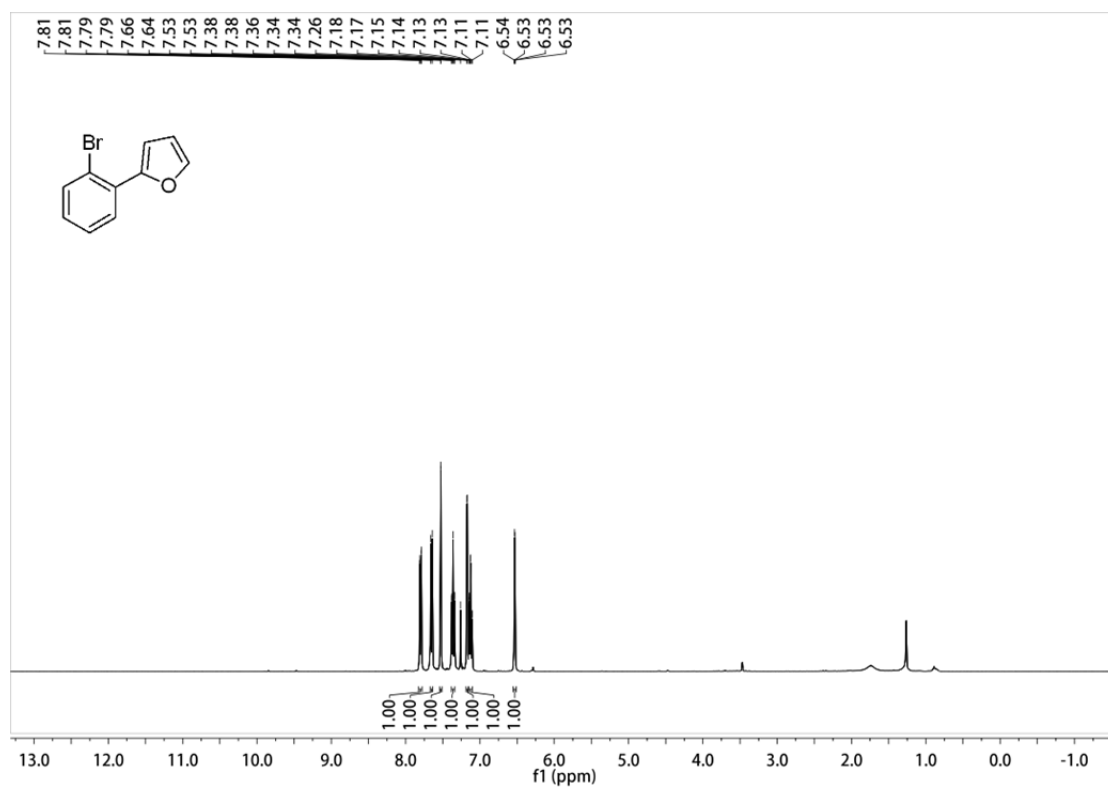
^1H NMR and ^{13}C NMR of compound **3q**



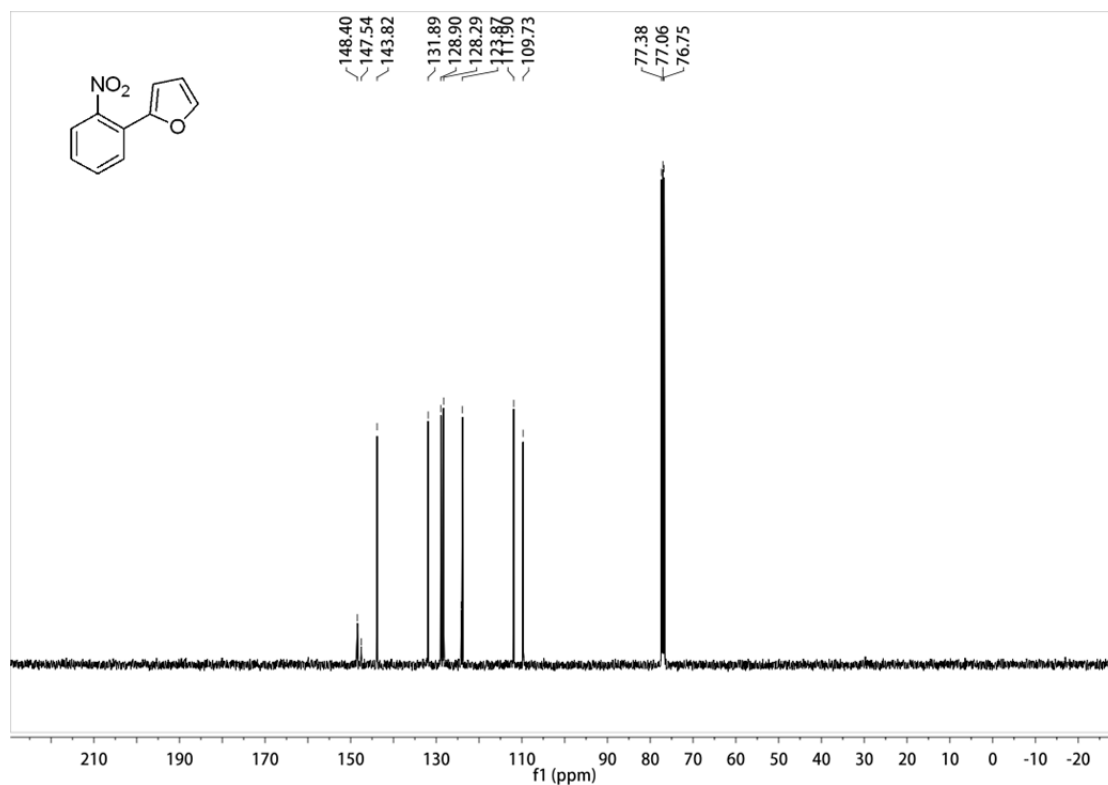
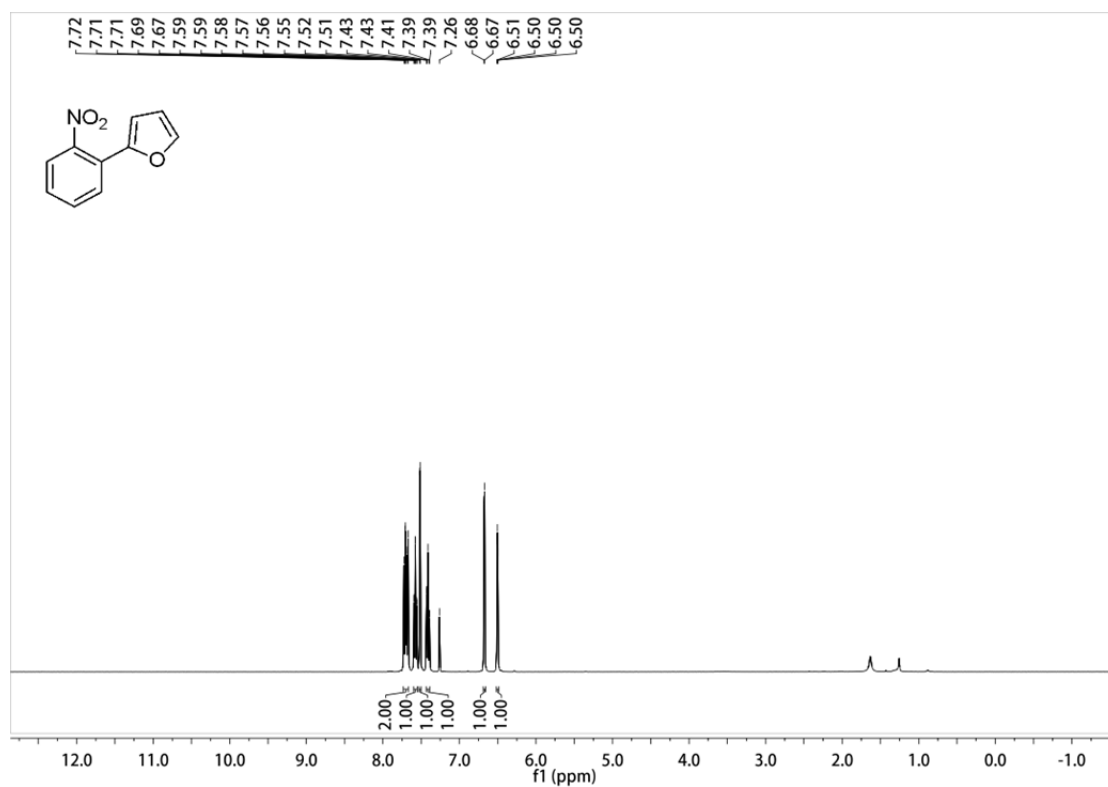
^1H NMR and ^{13}C NMR of compound **3r**



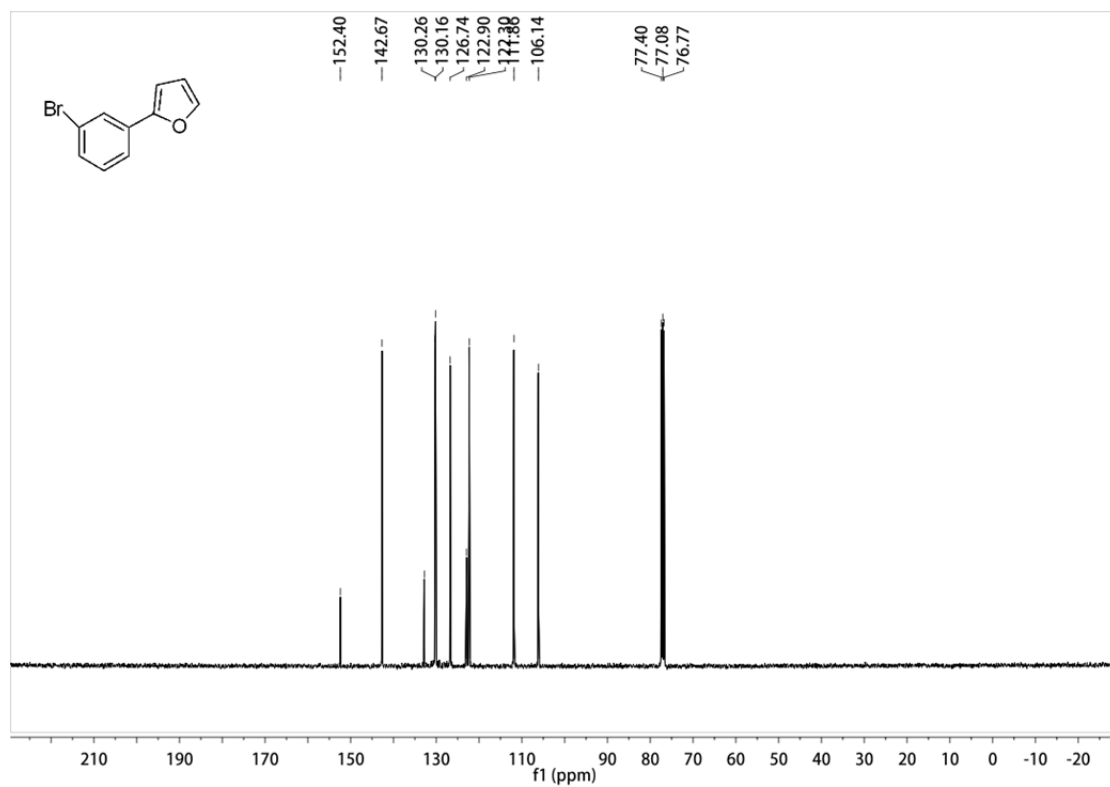
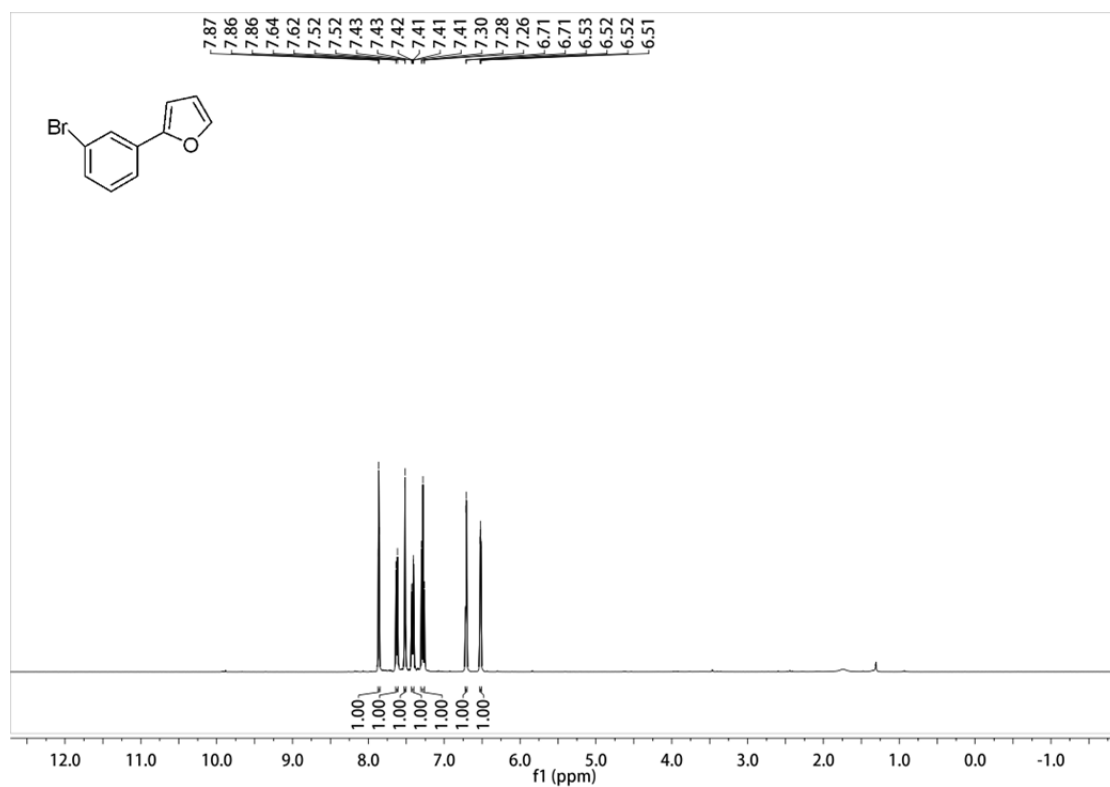
^1H NMR and ^{13}C NMR of compound **3s**



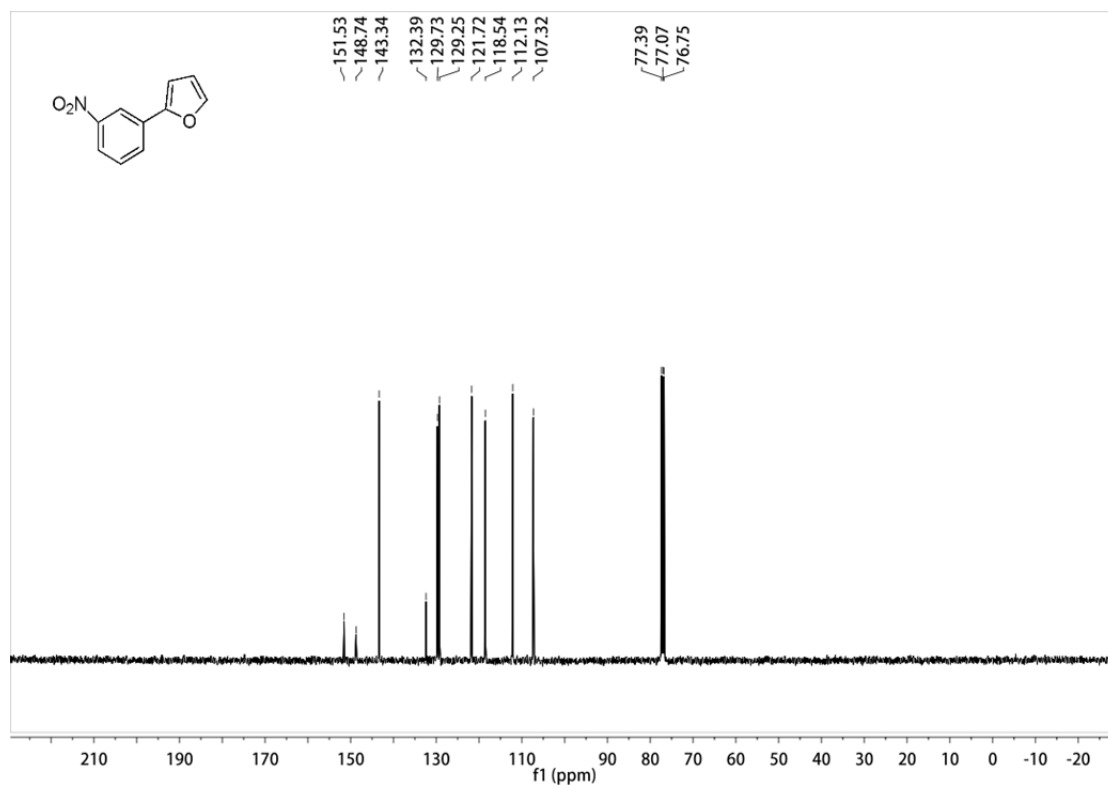
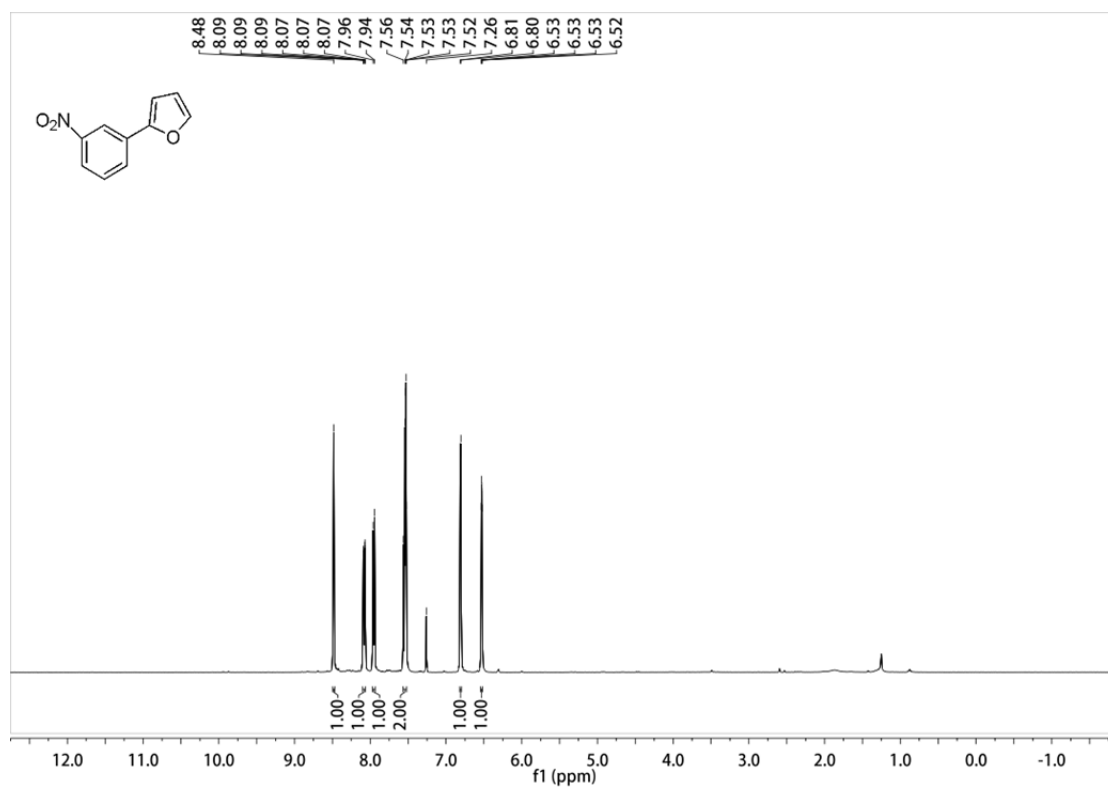
^1H NMR and ^{13}C NMR of compound **3t**



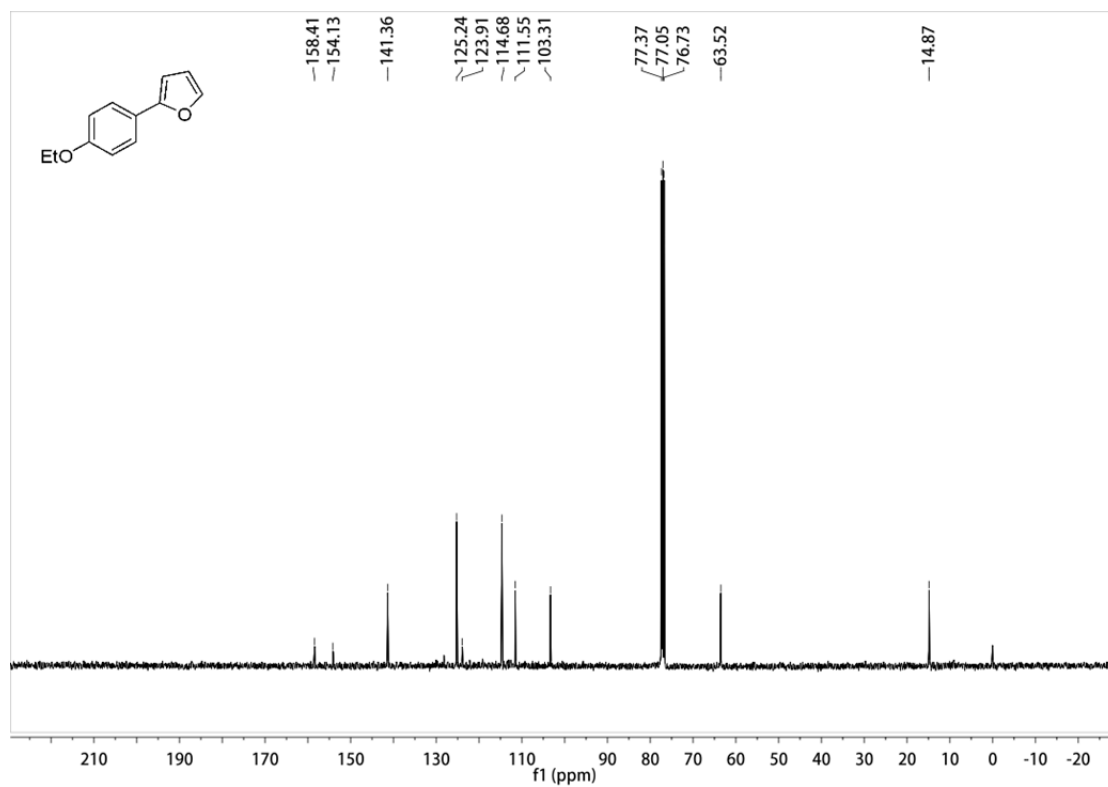
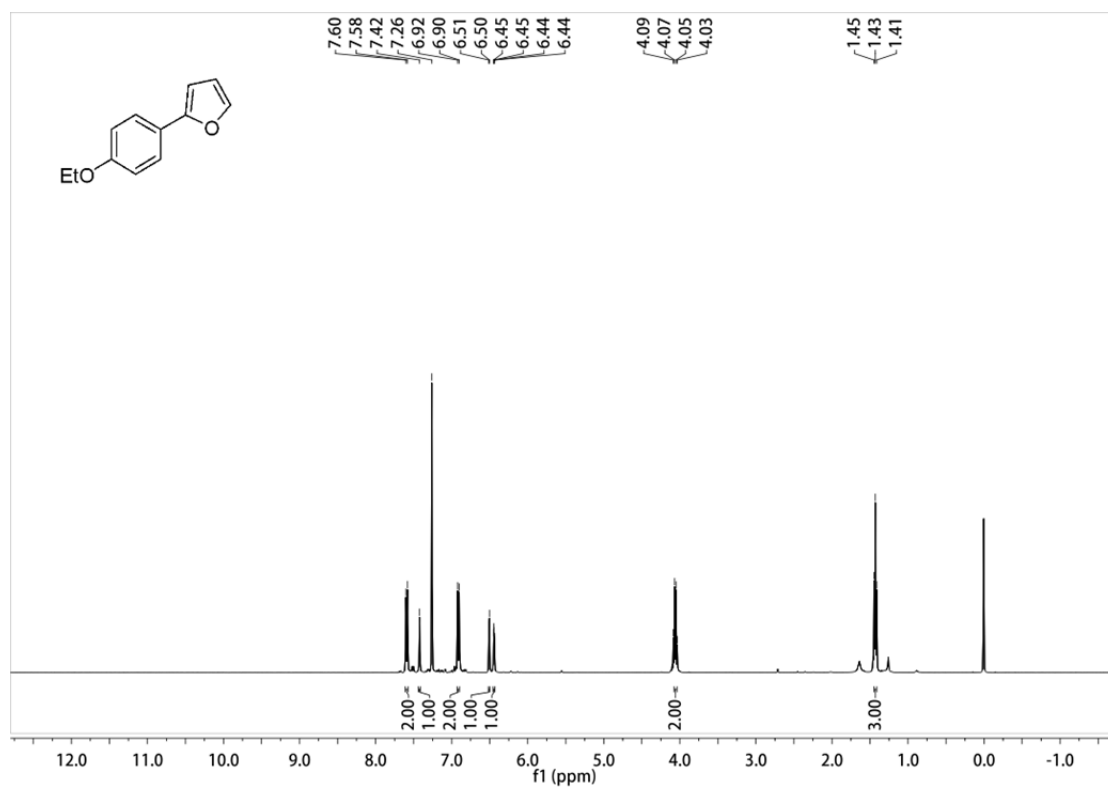
^1H NMR and ^{13}C NMR of compound **3u**



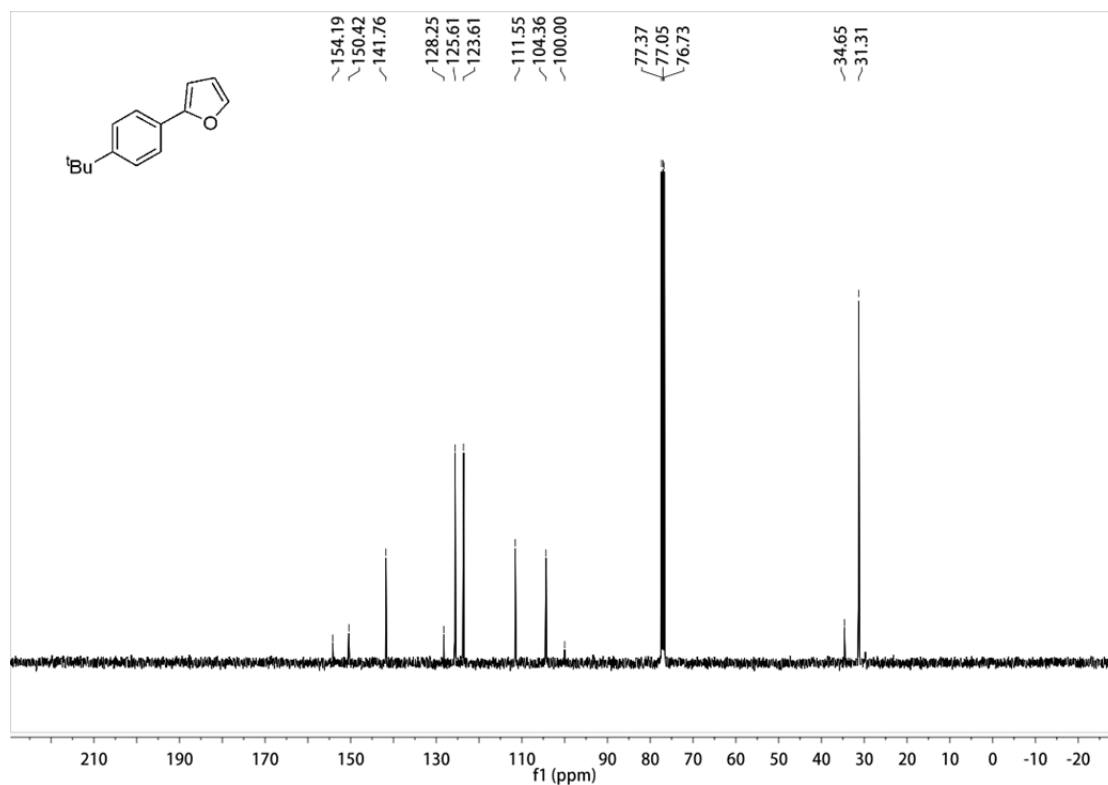
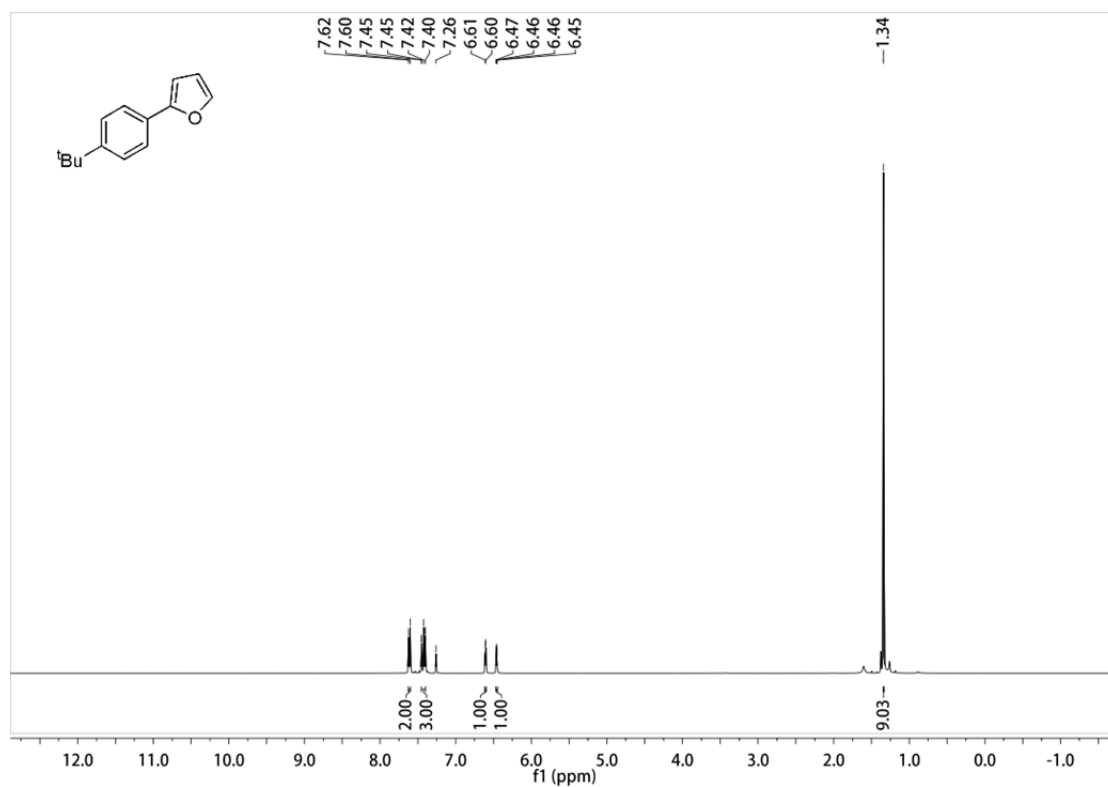
^1H NMR and ^{13}C NMR of compound **3v**



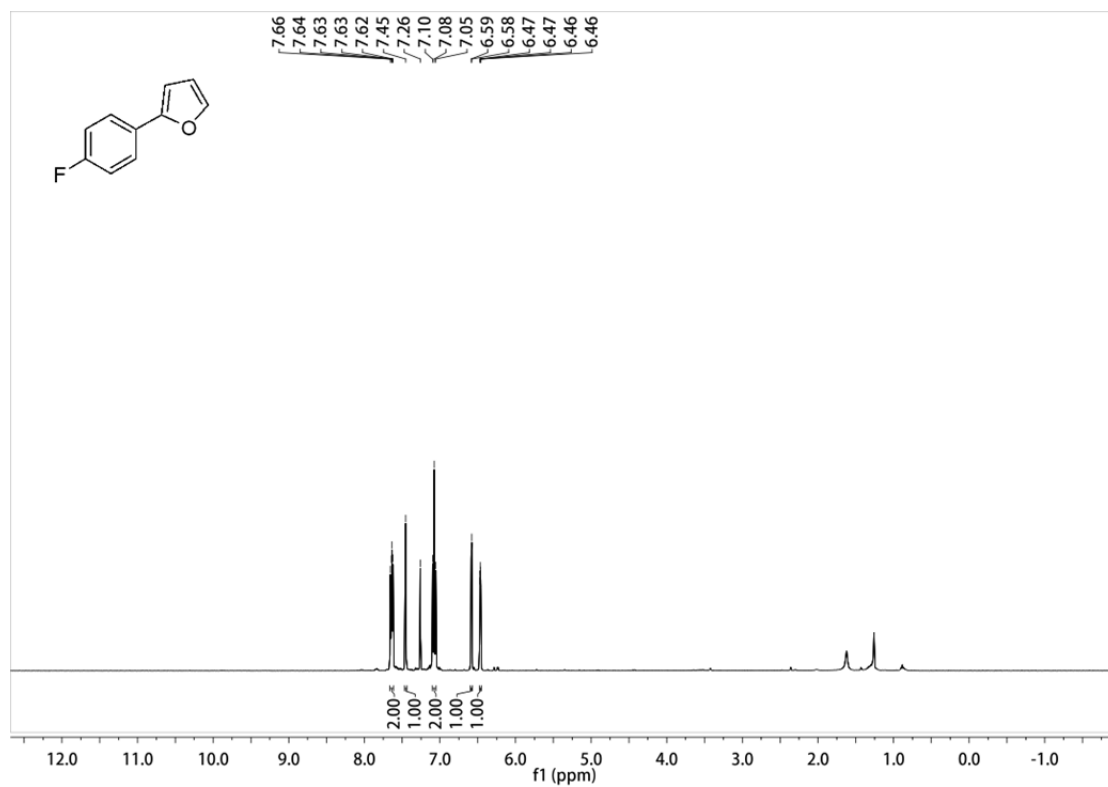
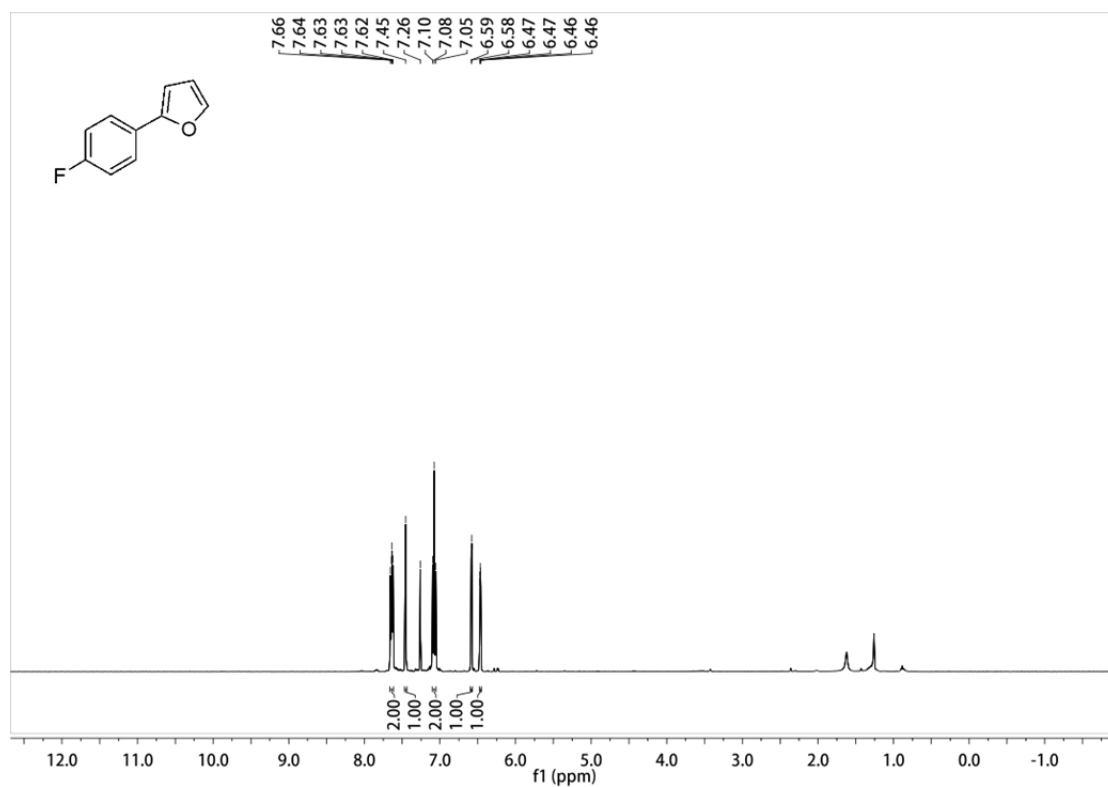
^1H NMR and ^{13}C NMR of compound **3w**



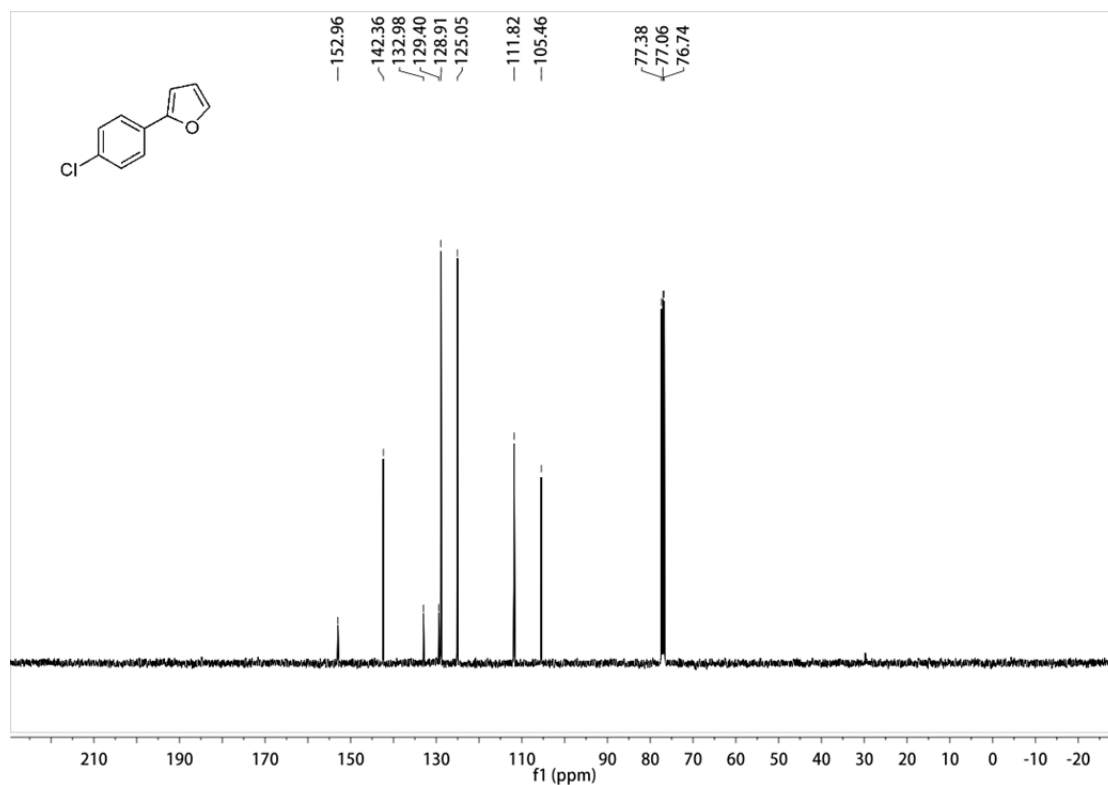
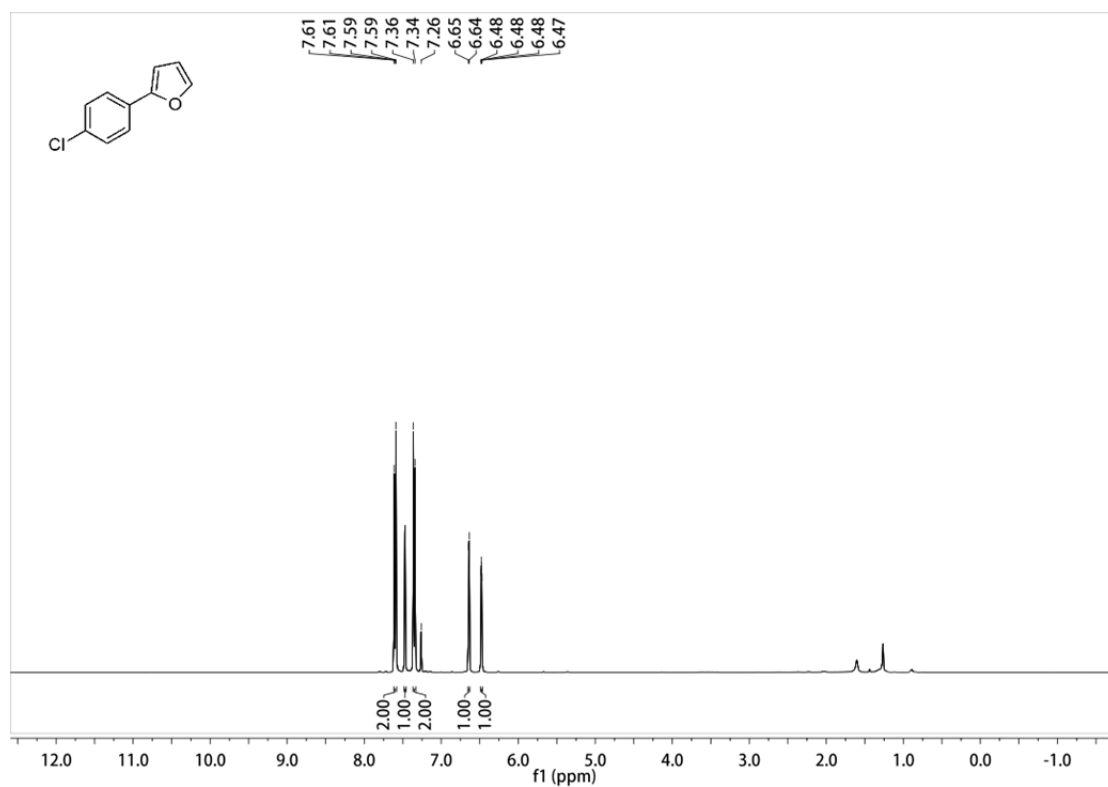
^1H NMR and ^{13}C NMR of compound **3x**



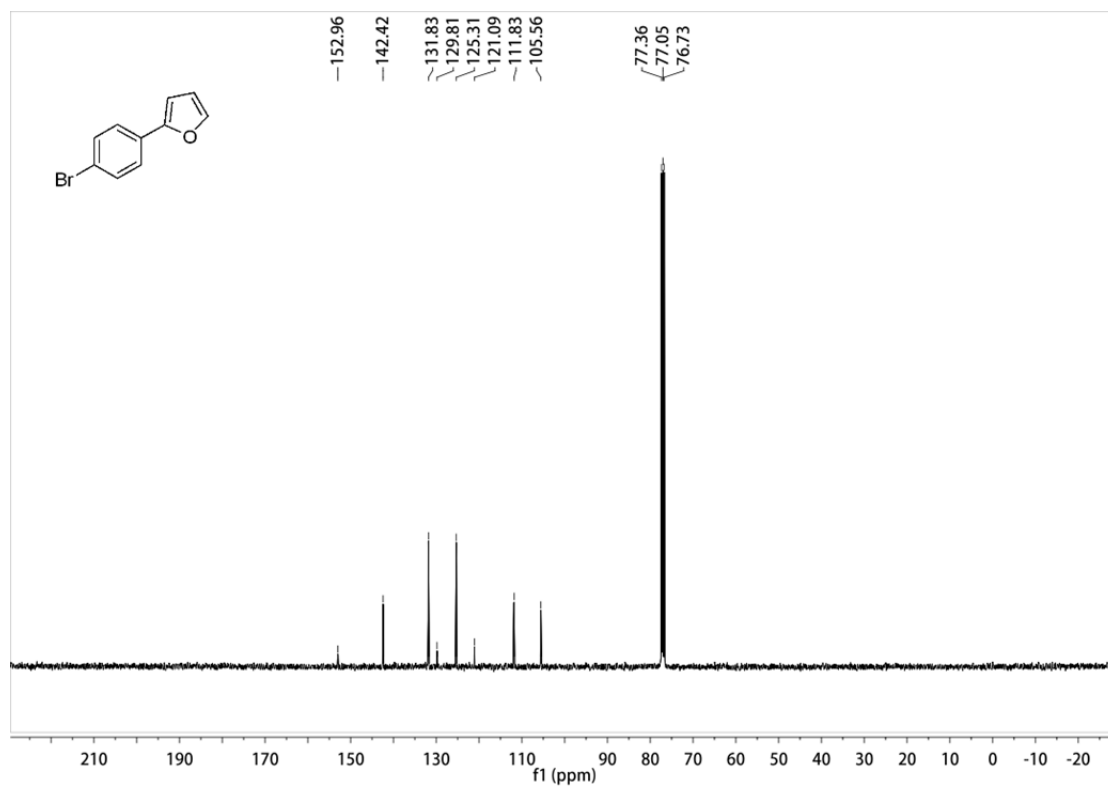
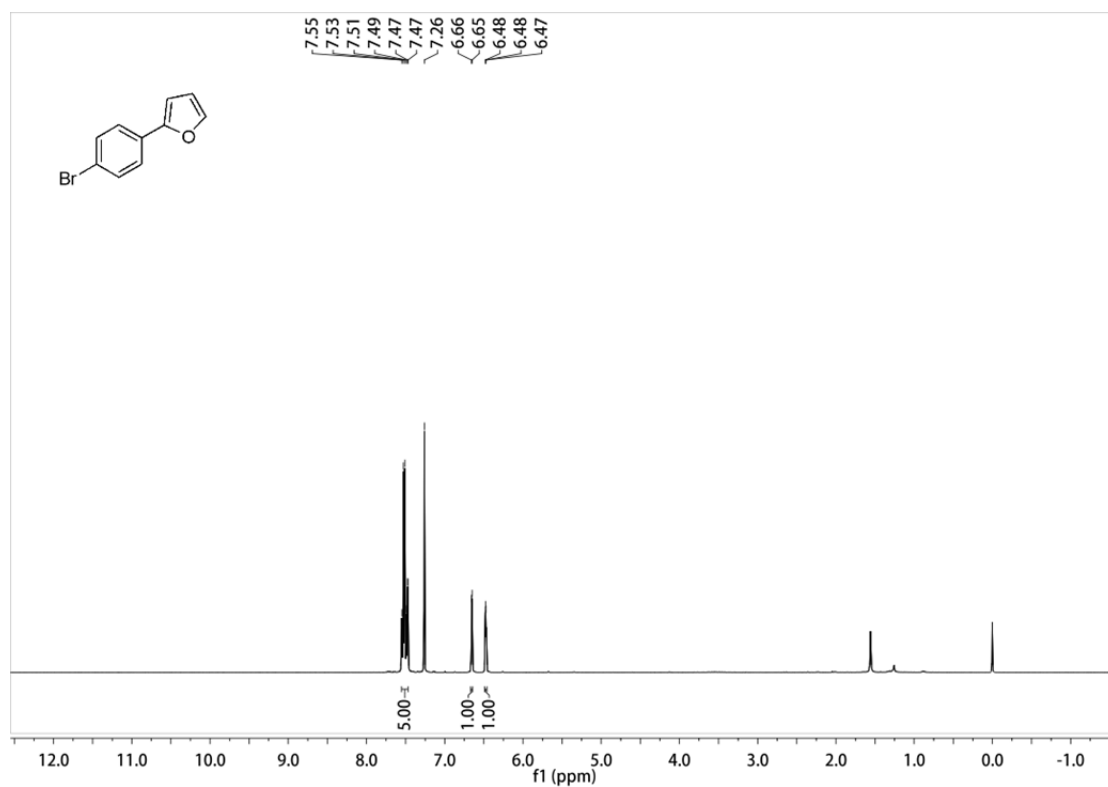
^1H NMR and ^{13}C NMR of compound **3y**



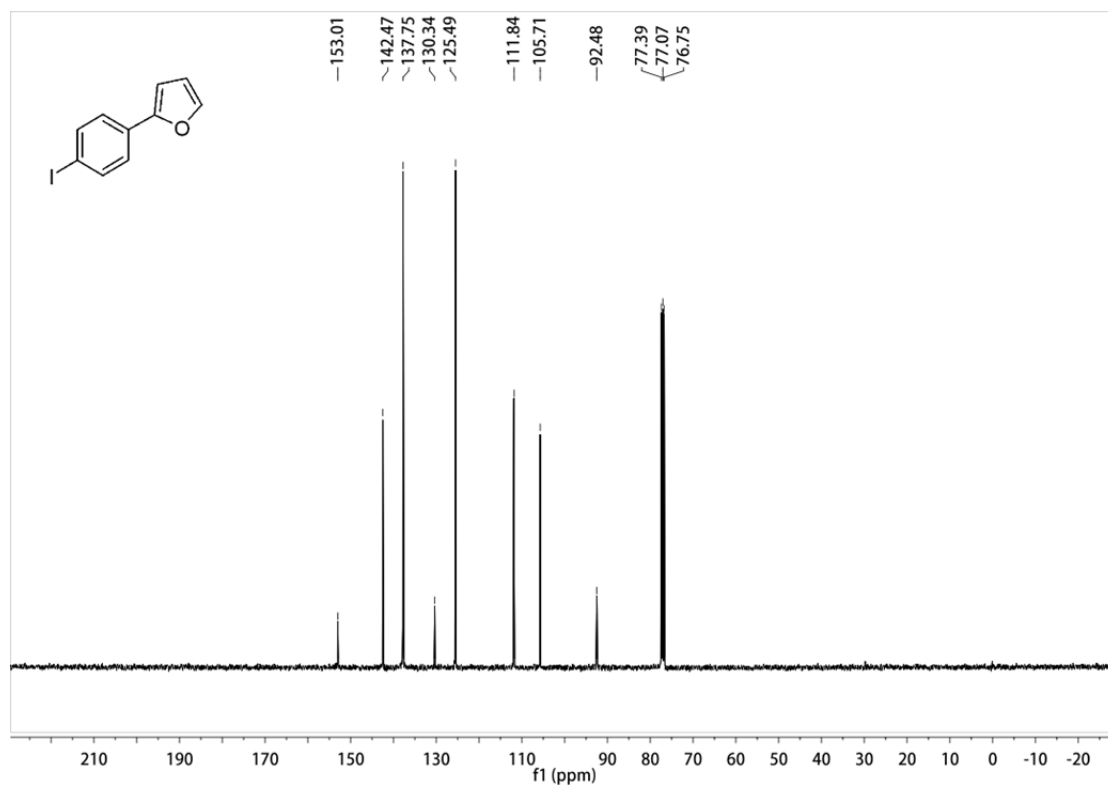
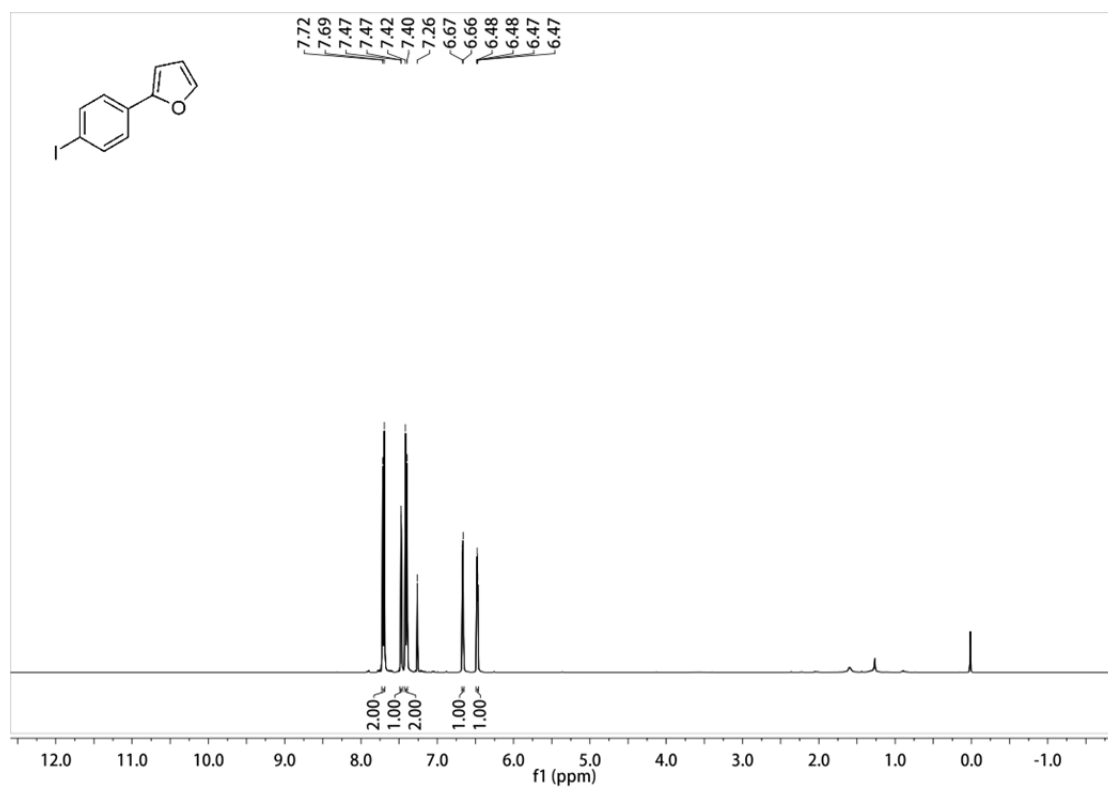
^1H NMR and ^{13}C NMR of compound **3z**



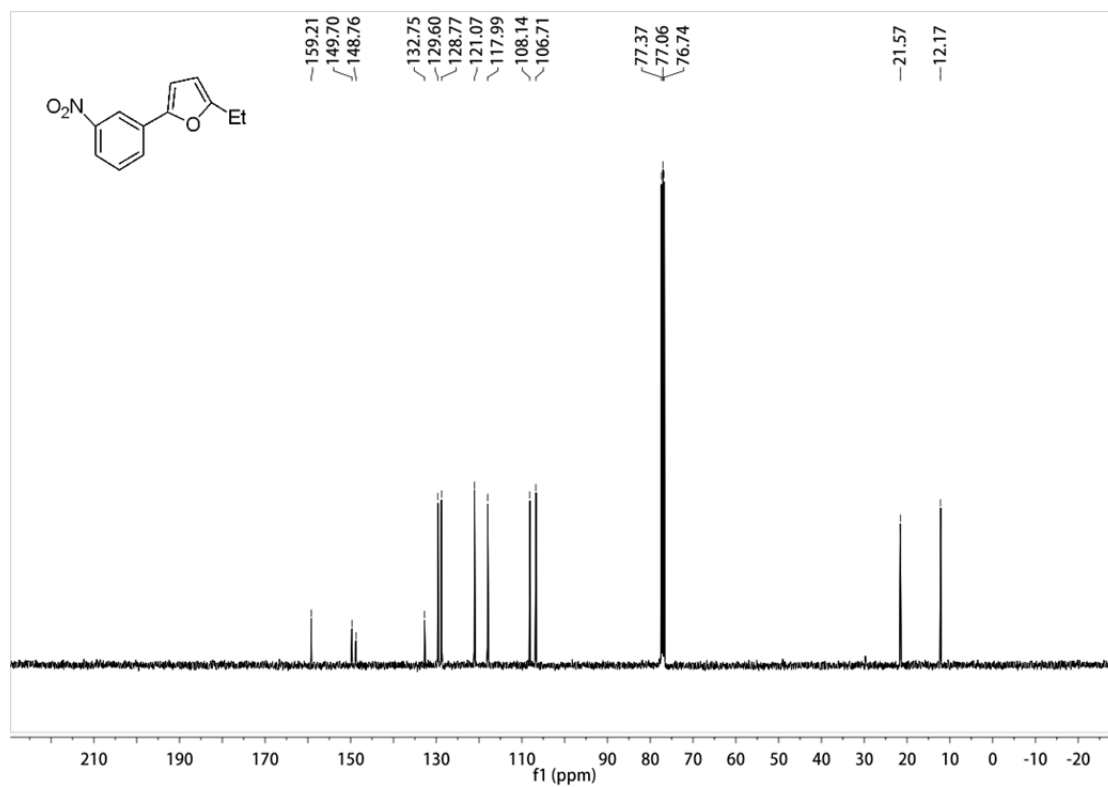
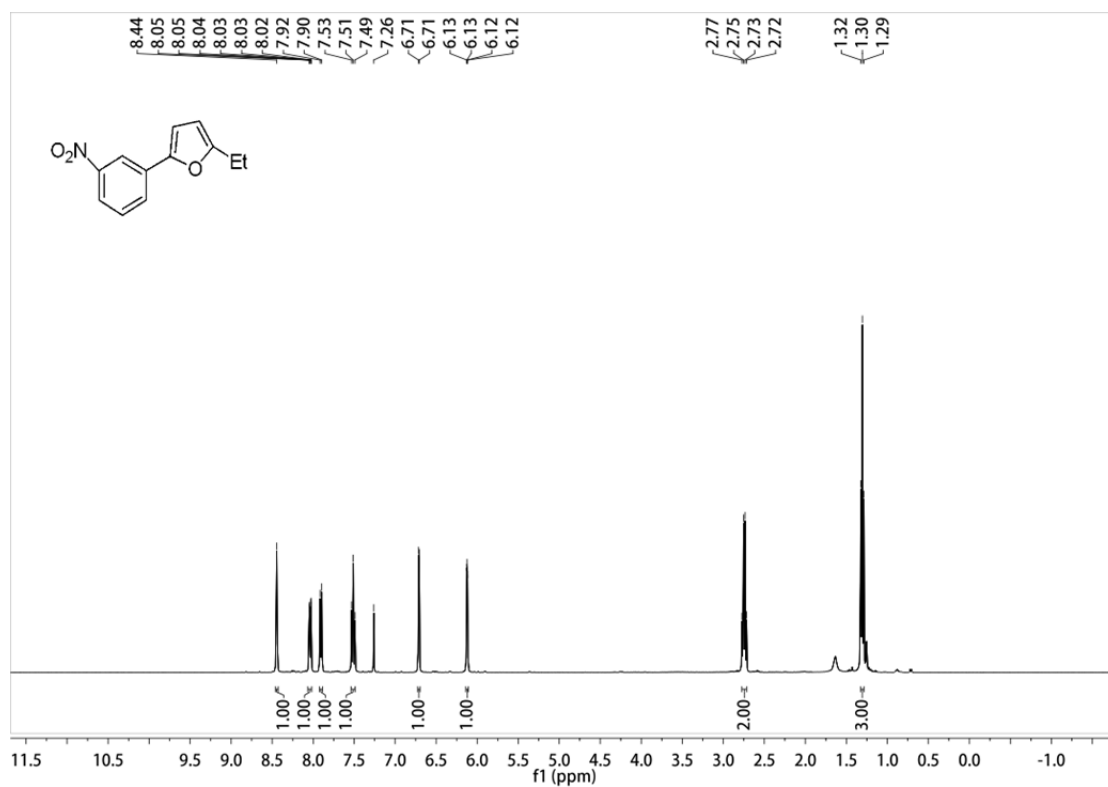
^1H NMR and ^{13}C NMR of compound **3aa**



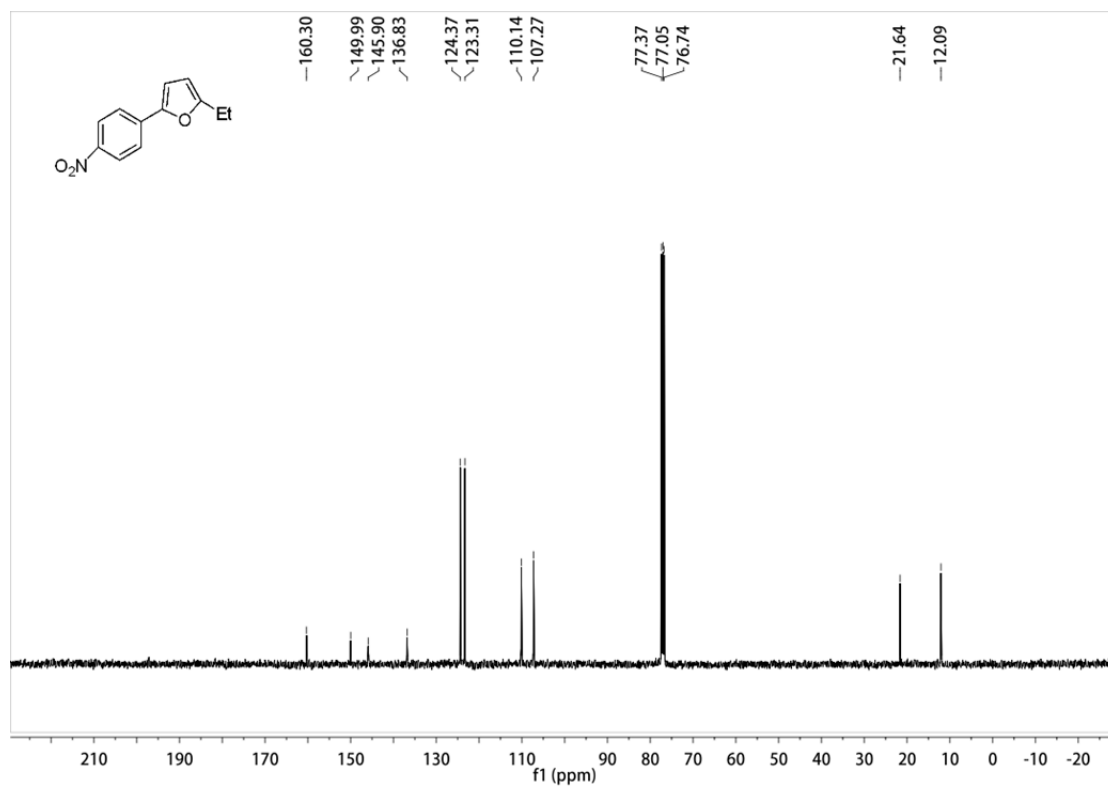
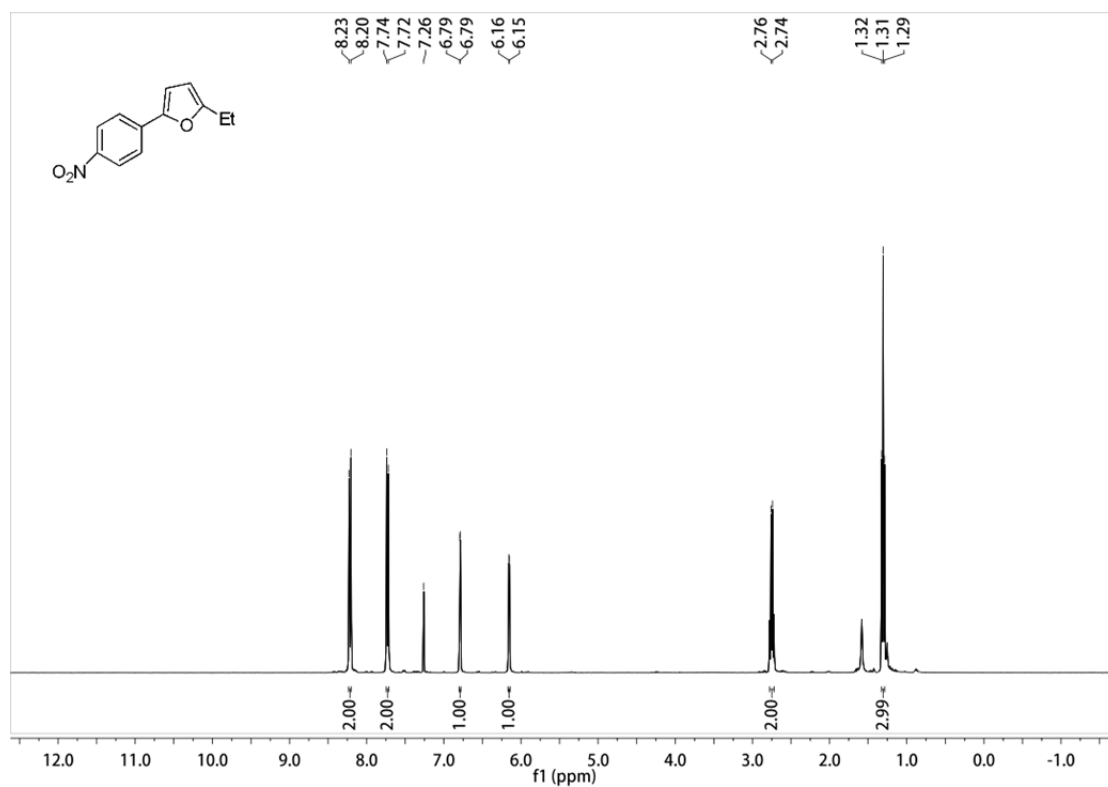
^1H NMR and ^{13}C NMR of compound **3ab**



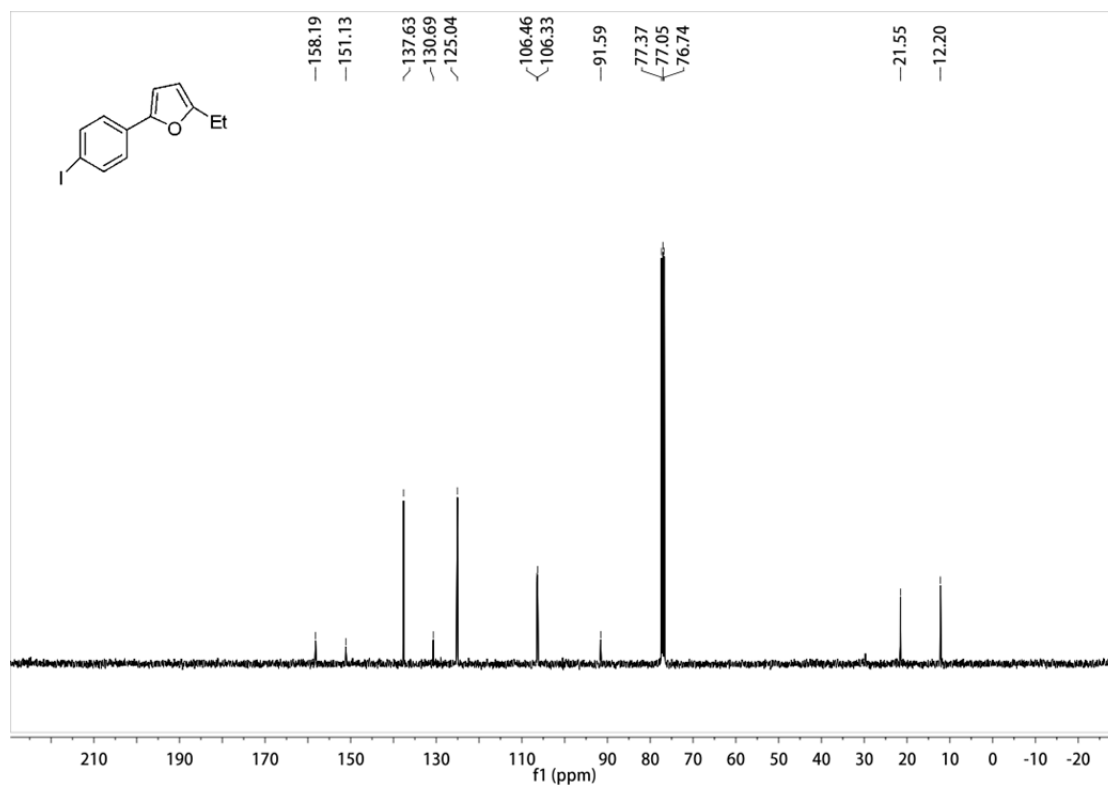
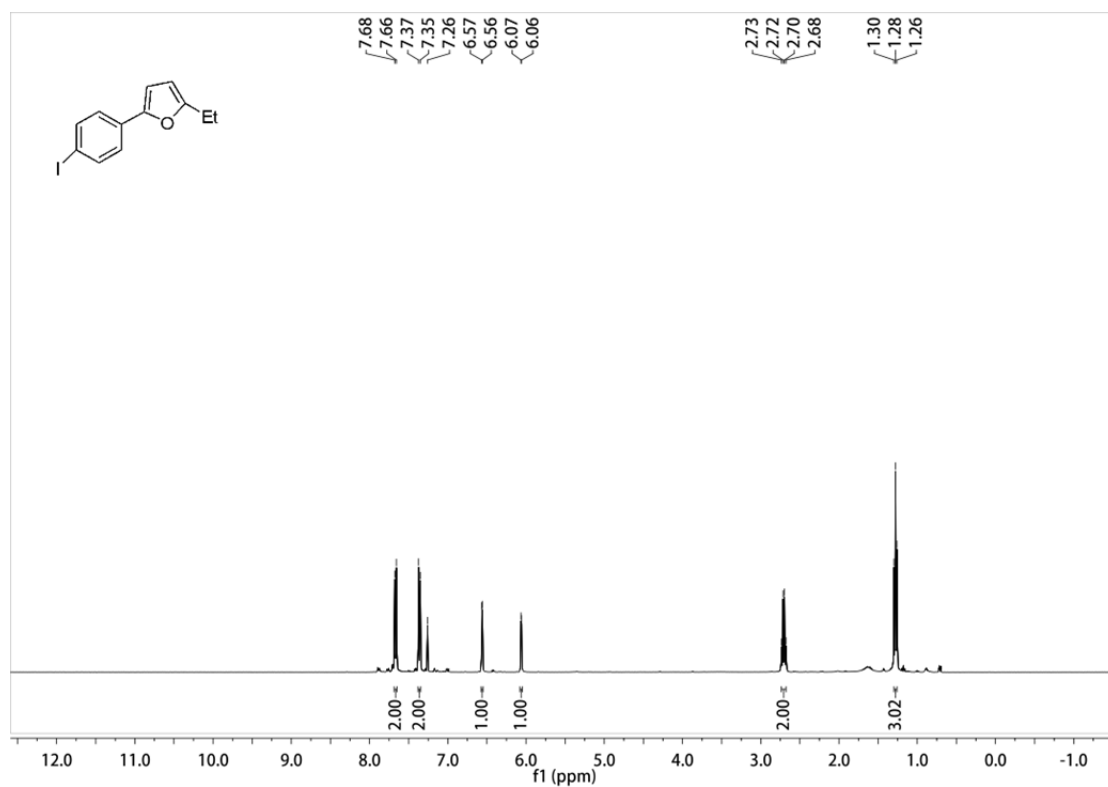
^1H NMR and ^{13}C NMR of compound **3ac**



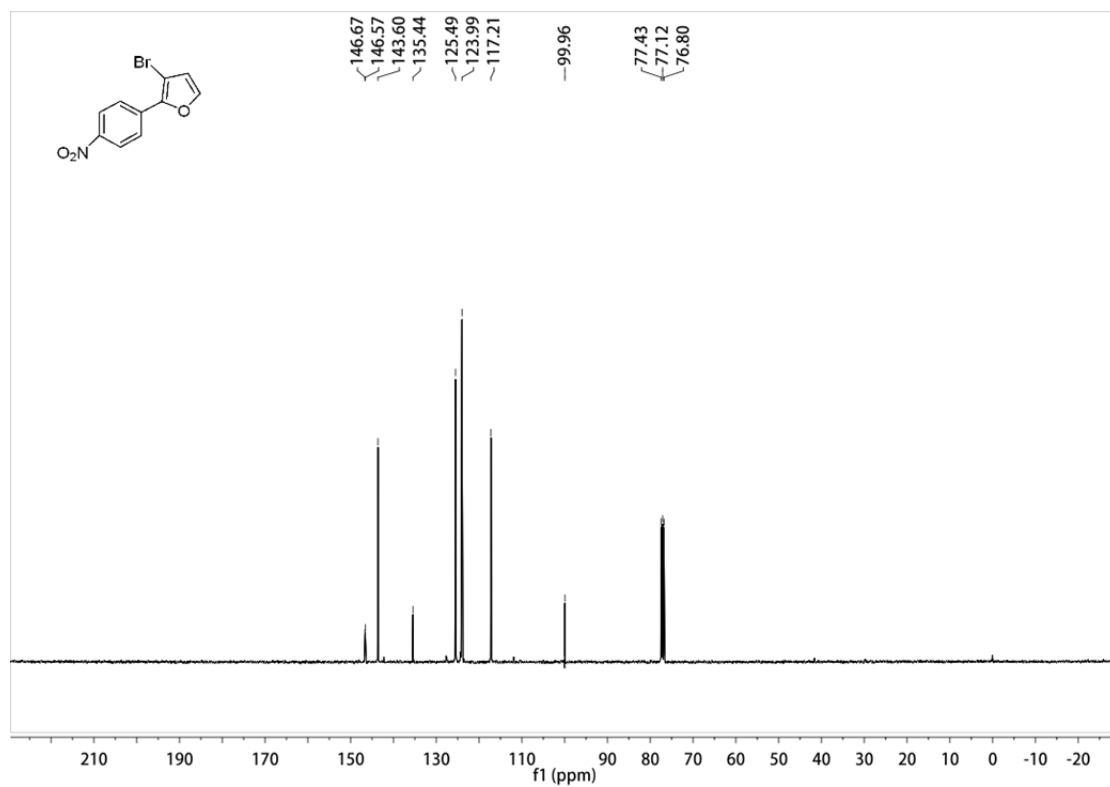
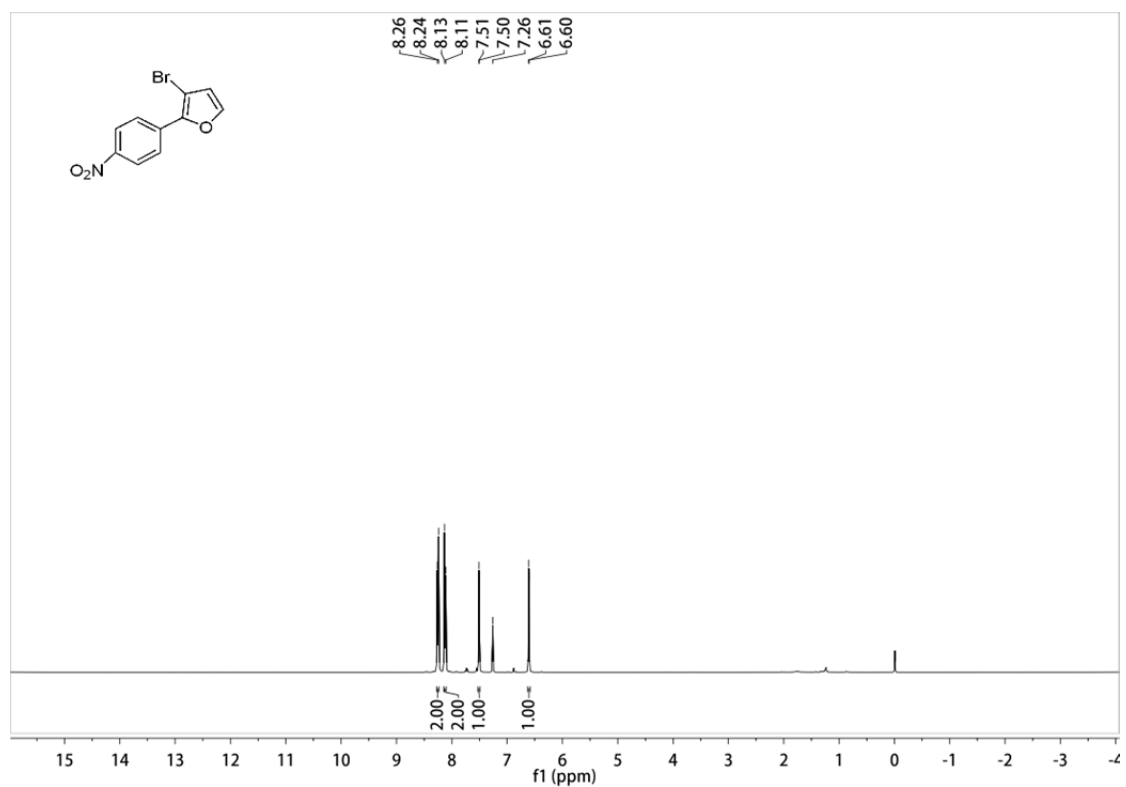
^1H NMR and ^{13}C NMR of compound **3ad**



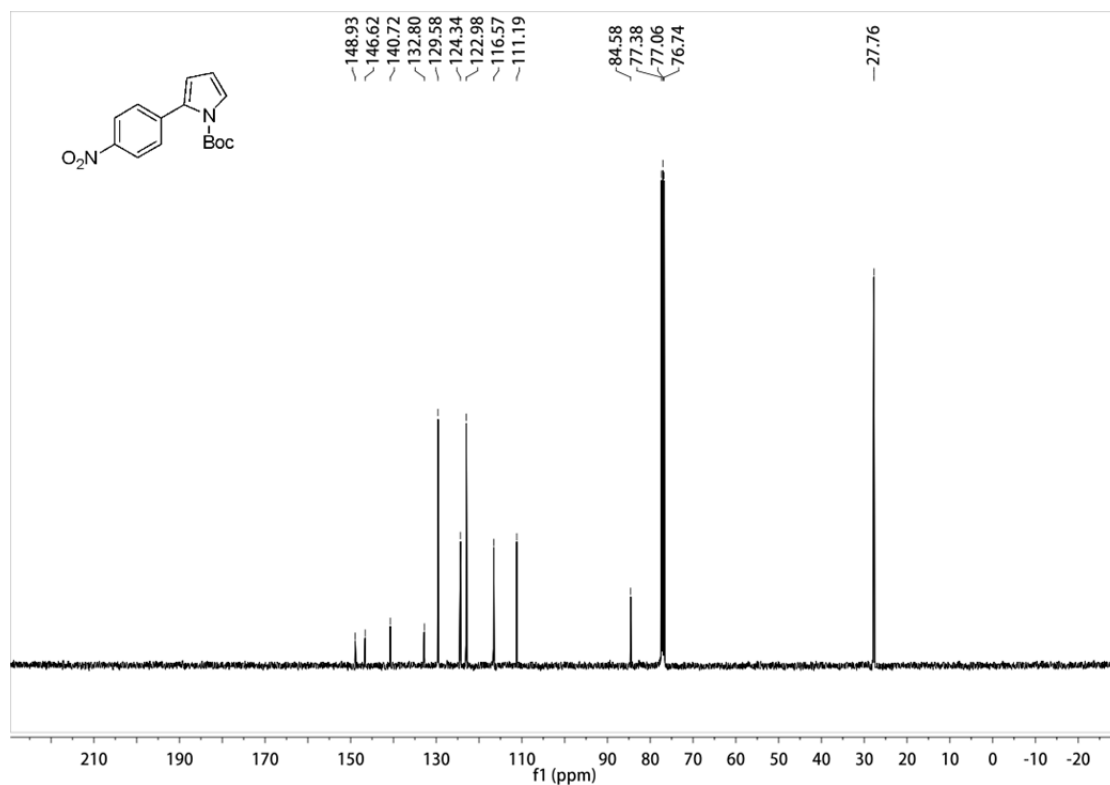
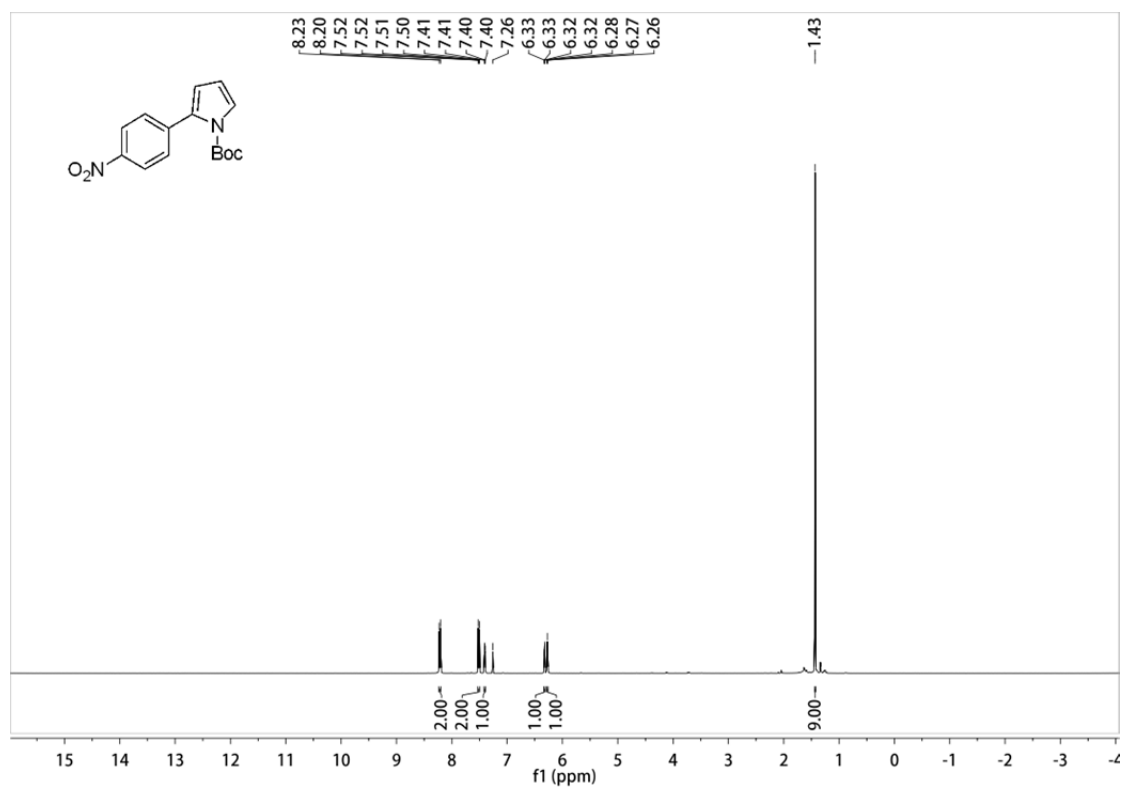
^1H NMR and ^{13}C NMR of compound **3ae**



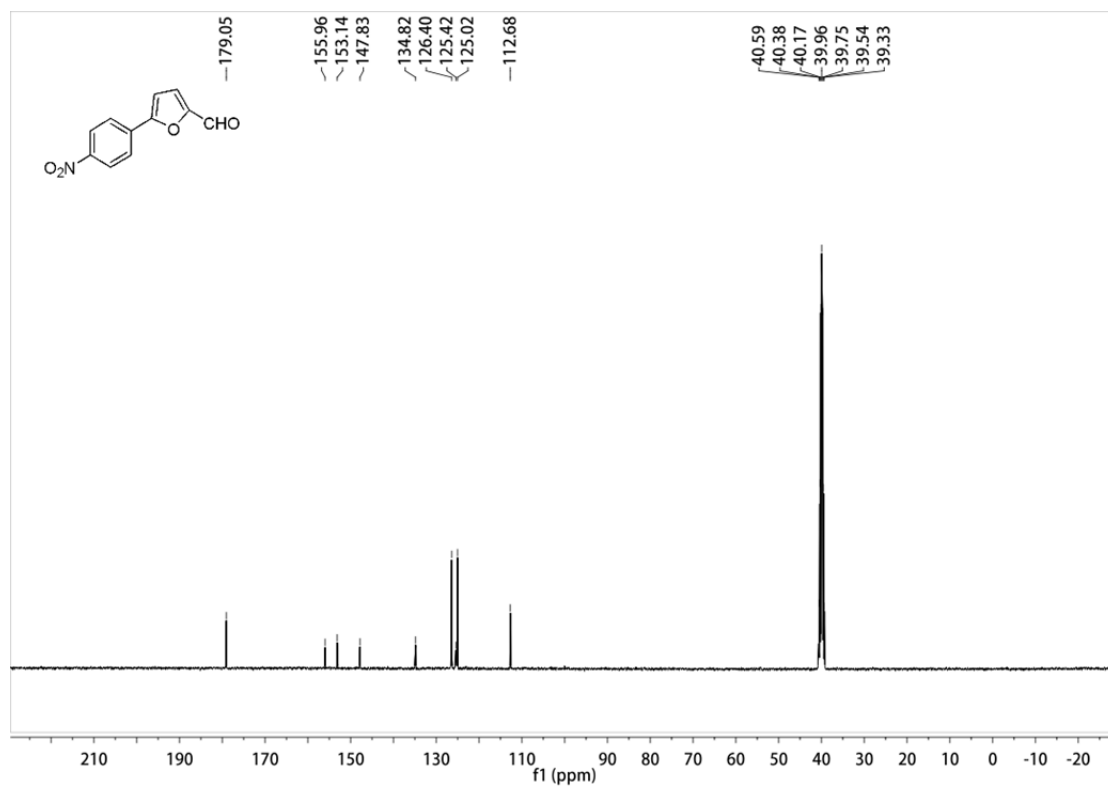
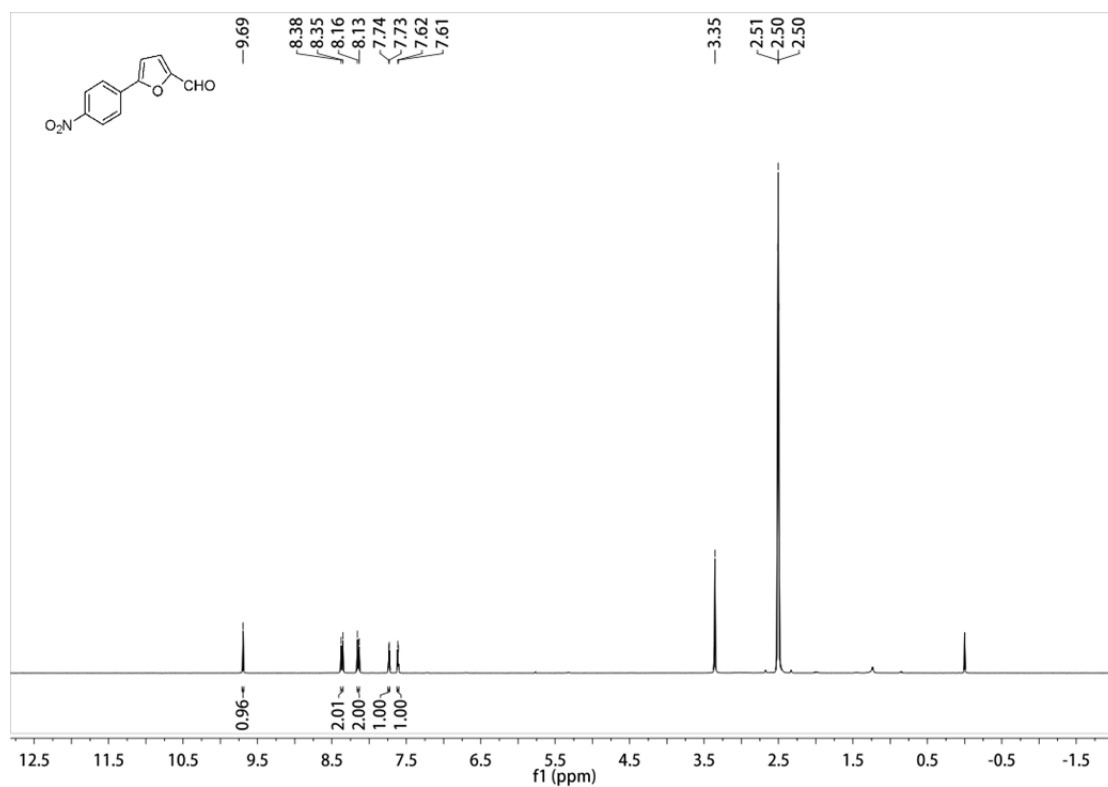
^1H NMR and ^{13}C NMR of compound **3af**



^1H NMR and ^{13}C NMR of compound **3ag**



^1H NMR and ^{13}C NMR of compound **3a**



^1H NMR and ^{13}C NMR of compound 4

