

Supporting Information

Palladium-catalyzed Regioselective Allylation of Five-membered Heteroarenes with Allyltributylstannane

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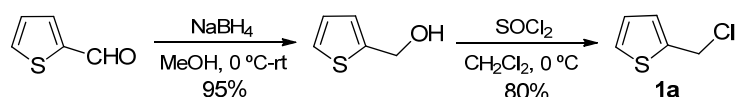
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1. General Information

All reactions were carried out under a nitrogen atmosphere unless otherwise noted. Solvents were purified by standard techniques without special instructions. ^1H and ^{13}C NMR spectra were recorded on either a Varian Inova-400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C) or a Bruker Avance II-400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C); CDCl_3 and TMS were used as a solvent and an internal standard, respectively. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants J are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on either a Q-TOF mass spectrometry or a GC-TOF mass spectrometry. TLC was carried out on SiO_2 (silica gel 60 F₂₅₄, Merck), and the spots were located with UV light, iodoplatinate reagent or 1% aqueous KMnO_4 . Flash chromatography was carried out on SiO_2 (silica gel 60, 200-300 mesh) or basic Al_2O_3 (Al_2O_3 90, 100-200 mesh). The starting materials **3a** and **3b** are commercially available.

2. Preparation and Characterization of Starting Materials

(1) Representative procedure for preparation of starting materials 1a-1d and 1l-1n:



To a solution of thiophene-2-carbaldehyde (1.12 g, 10 mmol) in MeOH (50 mL) at $0\text{ }^\circ\text{C}$, NaBH_4 (0.19 g, 5 mmol) was added slowly. After the resulting mixture was stirred overnight at room temperature, water (10 mL) was added slowly to quench the reaction. The product was extracted with ethyl ether (50 mL \times 2), and the combined organic layers were washed with brine ((50 mL \times 2), dried over Na_2SO_4 . The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 5:1) to afford thiophen-2-ylmethanol as a colorless oil (1.08 g, 95% yield).

To a solution of thiophen-2-ylmethanol (0.60 g, 5 mmol) in CH_2Cl_2 (20 mL) at $0\text{ }^\circ\text{C}$, thionyl chloride (SOCl_2 , 0.73 mL, 10 mmol) was slowly added. The resulting mixture was stirred overnight at room temperature, and then the solvent and excess of SOCl_2 were removed under reduced pressure. The residue obtained was dissolved in CH_2Cl_2

(20 mL), washed with saturated sodium bicarbonate solution, and dried over Na₂SO₄. The solvent was removed under reduced pressure to give 2-(chloromethyl)thiophene (**1a**)¹ as a brown oil (0.53 g, 80% yield), which was used without further purification in the allylation reaction. ¹H NMR (400 MHz, CDCl₃) δ 4.76 (s, 2H), 6.91 (dd, *J* = 4.0, 9.1 Hz, 1H), 7.04 (d, *J* = 3.2 Hz, 1H), 7.26 (d, *J* = 4.8 Hz, 1H).

3-Bromo-2-(chloromethyl)thiophene (1b):²

Brown oil (1.63 g, 77% yield). ¹H NMR (400 MHz, CDCl₃) δ 4.77 (s, 2H), 6.96 (d, *J* = 5.2 Hz, 1H), 7.32 (d, *J* = 5.6 Hz, 1H).

3-Chloro-2-(chloromethyl)thiophene (1c):

Brown oil (1.34 g, 80% yield). ¹H NMR (400 MHz, CDCl₃) δ 4.74 (s, 2H), 6.87 (d, *J* = 5.2 Hz, 1H), 7.26 (d, *J* = 5.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 37.7, 125.6, 125.9, 127.9, 132.5; IR (neat) 3112, 2959, 1527, 1428, 1355, 1264, 945, 855, 725, 620 cm⁻¹; HRMS (EI) calcd for C₅H₄Cl₂S: 165.9411 [M]⁺; found: 165.9418.

4-Bromo-2-(chloromethyl)thiophene (1d):³

Brown oil (1.62 g, 77% yield). ¹H NMR (400 MHz, CDCl₃) δ 4.73 (s, 2H), 7.00 (s, 1H), 7.20 (d, *J* = 1.2 Hz, 1H), 7.04 (d, *J* = 3.2 Hz, 1H), 7.26 (d, *J* = 4.8 Hz, 1H).

1-(5-(chloromethyl)thiophen-2-yl)ethanone (1l):

Colorless oil (0.59 g, 85% yield), mp 24–25 °C. ¹H NMR (400 MHz, CDCl₃) δ 2.55 (s, 3H), 4.76 (s, 2H), 7.10 (d, *J* = 4.0 Hz, 1H), 7.55 (d, *J* = 3.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 26.6, 39.9, 128.2, 132.2, 145.0, 148.6, 190.5; IR (KBr) 3094, 2961, 1661, 1457, 1275, 811 cm⁻¹; HRMS (EI) calcd for C₇H₇ClOS: 173.9906 [M]⁺; found: 173.9906.

methyl 5-(chloromethyl)thiophene-2-carboxylate (1m):

Yellow oil (0.91 g, 95% yield). ¹H NMR (400 MHz, CDCl₃) δ 3.78 (s, 3H), 4.66 (s, 2H), 6.96 (d, *J* = 3.2 Hz, 1H), 7.53 (d, *J* = 3.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 40.0, 52.4, 128.1, 133.4, 134.3, 147.3, 162.4; IR (neat) 2952, 1712, 1463, 1263, 1097, 749 cm⁻¹; HRMS (EI) calcd for C₇H₇ClO₂S: 189.9855 [M]⁺; found: 189.9864.

2-Bromo-5-(chloromethyl)thiophene (1n):

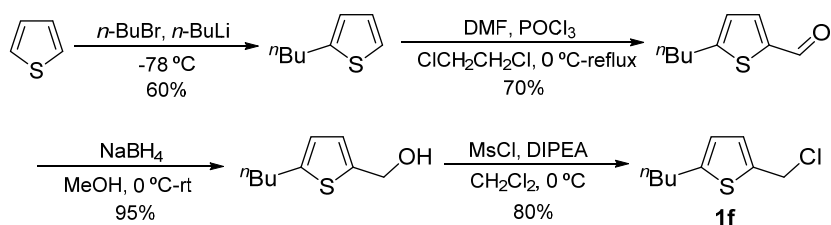
Brown oil (0.74 g, 70% yield). ¹H NMR (400 MHz, CDCl₃) δ 4.71 (s, 2H), 6.84 (d, *J* = 3.6 Hz, 1H), 6.90 (d, *J* = 4.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 40.2, 113.6, 128.0, 129.6, 141.6; IR (neat) 3098, 2955, 1433, 1260, 970, 797, 696, 486 cm⁻¹; HRMS (EI) calcd for C₅H₄BrClS: 209.8906 [M]⁺; found: 209.8906.

2-Chloro-5-(chloromethyl)thiophene (1n'):

Brown oil (0.63 g, 75% yield). ¹H NMR (400 MHz, CDCl₃) δ 4.69 (s, 2H), 6.76 (d, *J* = 3.6 Hz, 1H), 6.85 (d, *J* = 3.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 40.5, 126.0,

127.1, 131.4, 138.9; IR (neat) 3102, 2957, 1448, 1260, 1064, 998, 797, 698, 494 cm^{-1} ; HRMS (EI) calcd for $\text{C}_5\text{H}_4\text{Cl}_2\text{S}$: 165.9411 $[\text{M}]^+$; found: 165.9420.

(2) Representative procedure for preparation of starting materials 1e-1f and 5a-5h:



5-Butylthiophene-2-carbaldehyde was synthesized via butylation and formylation of thiophene according to the reported procedures^{4,5}. (5-Butylthiophen-2-yl)methanol was prepared through the reduction reaction of 5-butylthiophene-2-carbaldehyde (7 mmol) with NaBH_4 (colorless oil, 1.13 g, 95% yield).

(5-Butylthiophen-2-yl)methanol (0.17 g, 1 mmol) and *N,N*-diisopropylethylamine (DIPEA, 0.25 mL, 1.5 mmol) were dissolved in 4 mL of dry CH_2Cl_2 , and then, mesyl chloride (0.12 mL, 1.5 mmol) was added dropwise to the mixture at 0 °C. After the resulting mixture was stirred at 0 °C for 20 min, the mixture was allowed to warm slowly to room temperature over 1 h. The mixture obtained was diluted with CH_2Cl_2 (5 mL) and washed with cold water (10 mL), cold aqueous hydrochloric acid (10 wt%, 10 mL), and saturated sodium bicarbonate solution (20 mL) sequentially. The organic phase was dried over Na_2SO_4 and evaporated to give 2-butyl-5-(chloromethyl)thiophene (**1f**) as a colorless oil (0.15 g, 80% yield), which was used without further purification in the allylation reaction. ^1H NMR (400 MHz, CDCl_3) δ 0.92 (t, $J = 7.4$ Hz, 3H), 1.35–1.40 (m, 2H), 1.59–1.67 (m, 2H), 2.76 (t, $J = 7.6$ Hz, 2H), 4.71 (s, 2H), 6.58 (d, $J = 3.6$ Hz, 1H), 6.84 (d, $J = 3.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 22.3, 30.0, 33.7, 41.1, 123.8, 127.6, 137.4, 148.0; IR (neat) 2957, 2929, 2857, 1465, 1259, 801, 694 cm^{-1} ; HRMS (EI) calcd for $\text{C}_9\text{H}_{13}\text{ClS}$: 188.0427 $[\text{M}]^+$; found: 188.0434.

2-(Chloromethyl)-5-methylthiophene (1e)⁶:

Colorless oil (0.12 g, 80% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.46 (s, 3H), 4.74 (s, 2H), 6.59 (d, $J = 2.4$ Hz, 1H), 6.86 (d, $J = 3.2$ Hz, 1H).

2-(chloromethyl)-5-phenylthiophene (1g):

Yellow solid (0.17 g, 80% yield), mp 43–44 °C. ^1H NMR (400 MHz, CDCl_3) δ 4.59 (s, 2H), 6.83 (d, $J = 3.2$ Hz, 1H), 6.94 (d, $J = 3.2$ Hz, 1H), 7.12 (dd, $J = 7.2, 7.2$ Hz, 1H), 7.19 (dd, $J = 7.2, 7.6$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3)

δ 40.8, 122.8, 125.8, 127.9, 128.8, 129.0, 133.9, 139.3, 145.9; IR (KBr) 3062, 2963, 1461, 1259, 906, 810, 757, 688 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_9\text{ClS}$: 208.0113 $[\text{M}]^+$; found: 208.0122.

2-(chloromethyl)-5-(phenylethynyl)thiophene (1h):

Yellow solid (0.16 g, 70% yield), mp 21–22 °C. ^1H NMR (400 MHz, CDCl_3) δ 4.68 (s, 2H), 6.90 (d, $J = 3.6$ Hz, 1H), 7.07 (d, $J = 3.6$ Hz, 1H), 7.30 (dd, $J = 2.8, 3.2$ Hz, 3H), 7.46–7.49 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 40.3, 82.5, 94.1, 122.7, 124.9, 127.8, 128.6, 128.8, 131.6, 131.9, 141.7; IR (KBr) 3057, 2958, 2205, 1597, 1493, 1258, 1189, 806, 755, 689 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_9\text{ClS}$: 232.0113 $[\text{M}]^+$; found: 232.0117.

2-(chloromethyl)-5-styrylthiophene (1i):

Green solid (0.15 g, 65% yield), mp 47–48 °C. ^1H NMR (400 MHz, CDCl_3) δ 4.56 (s, 2H), 6.69 (d, $J = 3.6$ Hz, 1H), 6.72 (d, $J = 16.0$ Hz, 1H), 6.76 (d, $J = 3.6$ Hz, 1H), 6.97 (d, $J = 16.4$ Hz, 1H), 7.09 (dd, $J = 6.8, 7.6$ Hz, 1H), 7.17 (dd, $J = 7.6, 7.6$ Hz, 2H), 7.26 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 41.2, 121.8, 126.1, 126.7, 128.1, 128.7, 129.0, 129.3, 136.9, 139.0, 144.8; IR (KBr) 3081, 3056, 3020, 1445, 1258, 1191, 1042, 952, 805, 691 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{11}\text{ClS}$: 234.0270 $[\text{M}]^+$; found: 234.0281.

2-(5-(chloromethyl)thiophen-2-yl)-1,3-dioxolane (1j):

Yellow oil (0.14 g, 70% yield). ^1H NMR (400 MHz, CDCl_3) δ 3.99–4.02 (m, 2H), 4.10–4.13 (m, 2H), 4.75 (s, 2H), 6.05 (s, 1H), 6.96 (d, $J = 3.6$ Hz, 1H), 7.00 (d, $J = 3.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 40.6, 65.4, 100.2, 126.1, 127.4, 141.3, 143.5; IR (neat) 2959, 2889, 1387, 1212, 1080, 941, 811, 700 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_8\text{H}_{10}\text{ClO}_2\text{S}$: 205.0090 $[\text{M}+\text{H}]^+$; found: 205.0089.

2-(5-(Chloromethyl)thiophen-2-yl)-2-methyl-1,3-dioxolane (1k):

Yellow oil (0.14 g, 65% yield). ^1H NMR (400 MHz, CDCl_3) δ 1.75 (s, 3H), 3.93–4.05 (m, 4H), 4.73 (s, 2H), 6.87 (d, $J = 3.6$ Hz, 1H), 6.91 (d, $J = 3.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 27.5, 40.6, 65.0, 107.0, 123.9, 127.5, 139.6, 149.1; IR (neat) 2989, 2890, 1375, 1196, 1037, 871, 811 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_9\text{H}_{12}\text{ClO}_2\text{S}$: 219.0247 $[\text{M}+\text{H}]^+$; found: 219.0243.

2-(chloromethyl)-1-tosyl-1H-pyrrole (5a)⁷:

Pink solid (0.22 g, 83% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.40 (s, 3H), 4.83 (s, 2H), 6.24 (s, 1H), 6.36 (s, 1H), 7.28–7.30 (m, 3H), 7.77 (d, $J = 8.0$ Hz, 2H).

4-bromo-2-(chloromethyl)-1-tosyl-1H-pyrrole (5b):

Brown solid (0.26 g, 75% yield), mp 59–60 °C, ^1H NMR (400 MHz, CDCl_3) δ 2.43 (s,

3H), 4.77 (s, 2H), 6.36 (s, 1H), 7.32–7.34 (m, 3H), 7.80 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 36.7, 100.6, 119.06, 119.12, 123.1, 127.7, 130.3, 131.2, 135.3, 146.0; IR (KBr) 3145, 2924, 2854, 1596, 1373, 1175, 916, 666, 584, 541 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{11}\text{BrClNO}_2\text{S}$: 346.9382 $[\text{M}]^+$; found: 346.9385.

2-(Chloromethyl)-4-(thiophen-2-ylethynyl)-1-tosyl-1H-pyrrole (5c):

Yellow oil (0.28 g, 75% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.42 (s, 3H), 4.79 (s, 2H), 6.46 (s, 1H), 6.98 (dd, $J = 3.6, 8.4$ Hz, 1H), 7.22 (d, $J = 3.2$ Hz, 1H), 7.26 (d, $J = 5.2$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.53 (s, 1H), 7.81 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.8, 36.9, 83.7, 85.6, 108.1, 118.9, 123.1, 127.1, 127.2, 127.5, 127.6, 130.3, 130.8, 132.0, 135.3, 145.9; IR (neat) 3137, 2924, 2212, 1375, 1176, 1090, 701, 665, 584 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{ClNO}_2\text{S}_2$: 376.0233 $[\text{M}+\text{H}]^+$; found: 376.0227.

2-(Chloromethyl)-4-(phenylethynyl)-1-tosyl-1H-pyrrole (5d):

Yellow oil (0.30 g, 80% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.41 (s, 3H), 4.80 (s, 2H), 6.48 (s, 1H), 7.31–7.33 (m, 5H), 7.45–7.48 (m, 2H), 7.53–7.54 (m, 1H), 7.81 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 37.0, 81.9, 90.6, 108.4, 119.16, 119.21, 123.1, 127.0, 127.6, 128.5, 130.3, 130.7, 131.6, 135.4, 145.9; IR (neat) 3138, 2923, 2220, 1596, 1375, 1175, 1091, 667, 588 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{16}\text{ClNO}_2\text{S}$: 369.0590 $[\text{M}]^+$; found: 369.0595.

2-(Chloromethyl)-4-(p-tolyethynyl)-1-tosyl-1H-pyrrole (5e):

Yellow oil (0.31 g, 80% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.35 (s, 3H), 2.41 (s, 3H), 4.79 (s, 2H), 6.46 (s, 1H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.52 (s, 1H), 7.81 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.7, 21.8, 37.0, 81.2, 90.7, 108.6, 119.2, 120.0, 126.9, 127.6, 129.3, 130.2, 130.7, 131.5, 135.4, 138.6, 145.8, ; IR (neat) 3138, 2922, 2218, 1596, 1375, 1175, 1091, 815, 667, 587 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{18}\text{ClNO}_2\text{S}$: 383.0747 $[\text{M}]^+$; found: 383.0751.

2-(Chloromethyl)-4-(4-methylstyryl)-1-tosyl-1H-pyrrole (5f):

Yellow solid (0.27 g, 70% yield), mp 63–64 °C. ^1H NMR (400 MHz, CDCl_3) δ 2.35 (s, 3H), 2.42 (s, 3H), 4.71 (s, 2H), 6.16 (s, 1H), 6.23 (d, $J = 12.0$ Hz, 1H), 6.49 (d, $J = 12.0$ Hz, 1H), 7.09 (d, $J = 7.6$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.19 (s, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.75 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.5, 21.8, 37.4, 117.4, 120.8, 123.7, 127.5, 128.6, 129.1, 130.1, 130.2, 130.4, 134.7, 135.8, 137.2, 145.4; IR (KBr) 3017, 2922, 1370, 1173, 1092, 812, 667, 589 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{20}\text{ClNO}_2\text{S}$: 385.0903 $[\text{M}]^+$; found: 385.0909.

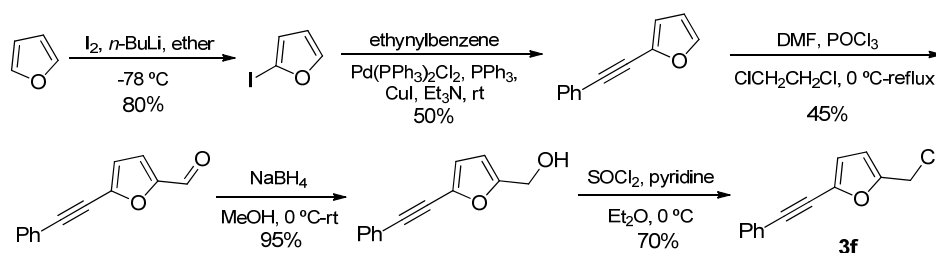
***tert*-butyl 2-(chloromethyl)-1*H*-pyrrole-1-carboxylate (5g):**

Brown oil (0.13 g, 60% yield). ¹H NMR (400 MHz, CDCl₃) δ 1.63 (s, 9H), 4.87 (s, 2H), 6.12 (dd, *J* = 3.2, 3.2 Hz, 2H), 6.31 (s, 1H), 7.31 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 28.0, 39.7, 84.7, 110.3, 116.0, 123.6, 130.2, 148.9; IR (neat) 2979, 2934, 1744, 1318, 1126, 848, 734 cm⁻¹; HRMS (EI) calcd for C₁₀H₁₄ClNO₂: 215.0713 [M]⁺; found: 215.0723.

***tert*-Butyl 2-(chloromethyl)-5-(phenylethynyl)-1*H*-pyrrole-1-carboxylate (5h):**

Brown oil (0.22 g, 70% yield). ¹H NMR (400 MHz, CDCl₃) δ 1.64 (s, 9H), 4.86 (s, 2H), 6.29 (d, *J* = 3.6 Hz, 1H), 6.51 (d, *J* = 3.6 Hz, 1H), 7.33–7.34 (m, 3H), 7.49–7.51 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 28.0, 39.8, 81.9, 85.4, 93.3, 114.9, 118.2, 119.0, 123.3, 128.45, 128.51, 131.5, 132.1, 148.5; IR (neat) 2981, 2933, 2210, 1749, 1311, 1117, 794, 691 cm⁻¹; HRMS (EI) calcd for C₁₈H₁₈ClNO₂: 315.1026 [M]⁺; found: 315.1031.

(3) Representative procedure for preparation of starting materials 3c-3h:



2-(Phenylethynyl)furan was synthesized via iodination of furan (2.04 g, 30 mmol) followed by Sonogashira reaction according to the reported procedures.⁸ (5-(Phenylethynyl)furan-2-yl)methanol was prepared via the formylation (45% yield) of 2-(phenylethynyl)furan followed by reduction reaction with NaBH₄ (95% yield).

To a solution of (5-(phenylethynyl)furan-2-yl)methanol (2 mmol, 0.40 g) and pyridine (2 mmol, 0.161 mL) in 2 mL of anhydrous ethyl ether, a solution of thionyl chloride (2 mmol, 0.145 mL) in 0.5 mL of ethyl ether was added dropwise with stirring at 0 °C. After the reaction mixture was kept at room temperature for 2 h, the solid was filtered off. The filtrate was washed with saturated aqueous NaHCO₃ and dried over Na₂SO₄. The solvent was removed under reduced pressure to give 2-(chloromethyl)-5-(phenylethynyl)furan (**3f**) as a yellow solid (0.30 g, 70% yield), mp 32–33 °C, which was used without further purification in the allylation reaction. ¹H NMR (400 MHz, CDCl₃) δ 4.60 (s, 2H), 6.42 (d, *J* = 3.6 Hz, 1H), 6.63 (d, *J* = 3.6 Hz, 1H), 7.37–7.39 (m, 3H), 7.55–7.57 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 37.3, 79.2, 94.0, 111.2, 116.4, 122.0, 128.5, 129.0, 131.5, 137.9, 151.0; IR (KBr) 3126,

3060, 2963, 2214, 1601, 1533, 1484, 1266, 1019, 972, 796, 756, 690 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_9\text{ClO}$: 216.0342 $[\text{M}]^+$; found: 216.0351.

(5-(Chloromethyl)furan-2-yl)methyl acetate (3c):

Colorless oil (0.30 g, 80% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.09 (s, 3H), 4.58 (s, 2H), 5.04 (s, 2H), 6.34 (d, $J = 3.2$ Hz, 1H), 6.36 (d, $J = 3.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.0, 37.5, 58.1, 110.8, 111.9, 150.6, 150.9, 170.7; IR (neat) 3131, 2962, 1743, 1376, 1235, 1021, 802 cm^{-1} ; HRMS (EI) calcd for $\text{C}_8\text{H}_9\text{ClO}_3$: 188.0240 $[\text{M}]^+$; found: 188.0248.

(5-(Chloromethyl)furan-2-yl)methyl butyrate (3d):

Colorless oil (0.33 g, 76% yield). ^1H NMR (400 MHz, CDCl_3) δ 0.94 (t, $J = 7.4$ Hz, 3H), 1.62–1.71 (m, 2H), 2.32 (t, $J = 7.4$ Hz, 2H), 4.57 (s, 2H), 5.05 (s, 2H), 6.34 (d, $J = 3.6$ Hz, 1H), 6.36 (d, $J = 3.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 18.5, 36.1, 37.5, 57.9, 110.8, 111.7, 150.76, 150.84, 173.3; IR (neat) 2966, 2877, 1739, 1170, 984, 800, 711 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{13}\text{ClO}_3$: 216.0553 $[\text{M}]^+$; found: 216.0555.

(5-(Chloromethyl)furan-2-yl)methyl benzoate (3e):

Yellow solid (0.35 g, 70% yield), mp 22–23 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 4.59 (s, 2H), 5.29 (s, 2H), 6.37 (d, $J = 3.2$ Hz, 1H), 6.45 (d, $J = 2.8$ Hz, 1H), 7.43 (dd, $J = 7.6$, 8.0 Hz, 2H), 7.56 (dd, $J = 7.2$, 7.6 Hz, 1H), 8.05 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 37.5, 58.6, 110.8, 112.0, 128.5, 129.9, 133.3, 150.6, 150.9, 166.3; IR (KBr) 3063, 2961, 1721, 1451, 1267, 1096, 1025, 800, 711 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{11}\text{ClO}_3$: 250.0397 $[\text{M}]^+$; found: 250.0406.

2-(Chloromethyl)-5-(p-tolyethynyl)furan (3g):

Yellow solid (0.32 g, 70% yield), mp 69–70 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 2.36 (s, 3H), 4.57 (s, 2H), 6.38 (d, $J = 3.2$ Hz, 1H), 6.56 (d, $J = 3.6$ Hz, 1H), 7.15 (d, $J = 8.0$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.7, 37.4, 78.6, 94.2, 111.2, 116.1, 119.0, 129.4, 131.6, 138.2, 139.4, 150.9; IR (KBr) 3125, 2918, 2211, 1534, 1265, 1020, 971, 818, 690 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{11}\text{ClO}$: 230.0498 $[\text{M}]^+$; found: 230.0505.

2-(Chloromethyl)-5-((4-methoxyphenyl)ethynyl)furan (3h):

Yellow solid (0.37 g, 74% yield), mp 49–50 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 3.82 (s, 3H), 4.57 (s, 2H), 6.39 (d, $J = 3.2$ Hz, 1H), 6.55 (d, $J = 3.2$ Hz, 1H), 6.87 (d, $J = 8.8$ Hz, 2H), 7.46 (d, $J = 9.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 37.4, 55.5, 78.0, 94.1, 111.2, 114.1, 114.3, 115.8, 133.3, 138.3, 150.8, 160.3; IR (KBr) 3124, 2961, 2834, 2210, 1608, 1257, 1020, 970, 804, 712 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{11}\text{ClO}_2$:

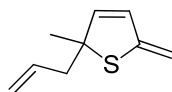
246.0448 [M]⁺; found: 246.0456.

3. Experimental Procedures and Characterization Data for All Compounds

Method A:

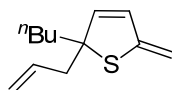
Representative Procedure for Obtaining Products 2e–2n, 4a–4h, and 6h: Allyltributylstannane (165.6 mg, 0.5 mmol) and **1e** (73.3 mg, 0.5 mmol) were added to a solution of Pd₂(dba)₃ (22.9 mg, 0.025 mmol) and PPh₃ (26.2 mg, 0.1 mmol) in acetone (3 mL) or CH₂Cl₂ (3 mL) at room temperature. The reaction mixture was stirred under N₂ atmosphere at room temperature. The reaction progress was monitored by TLC. After the starting material **1e** was consumed (10 h), the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography on basic alumina (eluent: petroleum ether) to afford 2-allyl-2-methyl-5-methylene-2,5-dihydrothiophene (**2e**) in 50% yield (38.1 mg) as a colorless oil.

2-Allyl-2-methyl-5-methylene-2,5-dihydrothiophene (**2e**)



Colorless oil (38.1 mg, 50% yield). ¹H NMR (400 MHz, CDCl₃) δ 1.53 (s, 3H), 2.48 (d, *J* = 7.2 Hz, 2H), 4.92 (s, 1H), 5.01 (s, 1H), 5.07–5.12 (m, 2H), 5.76–5.87 (m, 1H), 5.91 (d, *J* = 6.0 Hz, 1H), 6.13 (d, *J* = 6.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 28.8, 47.4, 65.8, 100.9, 118.4, 130.4, 134.2, 143.9, 151.2; IR (neat) 2921, 2854, 1686, 1639, 1448, 1373, 995, 917, 772 cm⁻¹; HRMS (EI) calcd for C₉H₁₂S: 152.0660 [M]⁺; found: 152.0662.

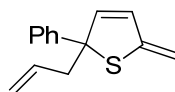
2-Allyl-2-butyl-5-methylene-2,5-dihydrothiophene (**2f**)



Colorless oil (49.6 mg, 51% yield). ¹H NMR (400 MHz, CDCl₃) δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.25–1.30 (m, 2H), 1.45–1.49 (m, 2H), 1.64–1.75 (m, 2H), 2.51 (dd, *J* = 6.8, 6.8 Hz, 2H), 4.93 (s, 1H), 5.00 (s, 1H), 5.07–5.11 (m, 2H), 5.76–5.82 (m, 1H), 5.85 (d, *J* = 7.6 Hz, 1H), 6.15 (d, *J* = 6.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 23.0, 27.4, 40.3, 45.8, 70.3, 100.6, 118.0, 131.1, 134.1, 142.5, 151.3; IR (neat) 2957, 2930,

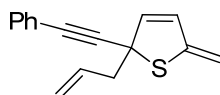
2859, 1584, 1436, 1378, 995, 916, 828 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{18}\text{S}$: 194.1129 $[\text{M}]^+$; found: 194.1134.

2-Allyl-5-methylene-2-phenyl-2,5-dihydrothiophene (2g)



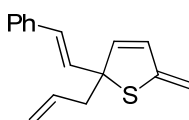
Colorless oil (83.6 mg, 78% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.96 (d, $J = 7.2$ Hz, 2H), 4.96 (s, 1H), 5.05–5.11 (m, 3H), 5.65–5.74 (m, 1H), 6.21 (d, $J = 6.0$ Hz, 1H), 6.30 (d, $J = 6.0$ Hz, 1H), 7.19–7.23 (m, 1H), 7.29–7.32 (m, 2H), 7.36–7.38 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 46.8, 71.1, 101.8, 118.6, 126.5, 127.2, 128.7, 131.6, 133.9, 141.4, 144.4, 150.8; IR (neat) 3059, 2924, 1584, 1446, 1210, 918, 834, 759, 696 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{14}\text{S}$: 214.0816 $[\text{M}]^+$; found: 214.0823.

2-Allyl-5-methylene-2-(phenylethynyl)-2,5-dihydrothiophene (2h)



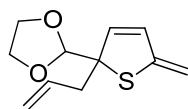
Colorless oil (95.3 mg, 80% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.70–2.83 (m, 2H), 4.98 (s, 1H), 5.11 (s, 1H), 5.19 (s, 1H), 5.23 (d, $J = 4.8$ Hz, 1H), 5.95–6.12 (m, 1H), 6.05 (d, $J = 6.4$ Hz, 1H), 6.24 (d, $J = 6.0$ Hz, 1H), 7.27–7.28 (m, 3H), 7.39–7.41 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 48.0, 60.8, 86.0, 88.8, 102.3, 119.2, 122.8, 128.2, 128.4, 131.5, 131.7, 133.1, 139.1, 149.7; IR (neat) 3078, 2925, 2853, 1585, 1489, 1208, 920, 840, 756, 691 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{14}\text{S}$: 238.0816 $[\text{M}]^+$; found: 238.0811.

2-Allyl-5-methylene-2-styryl-2,5-dihydrothiophene (2i)



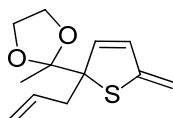
Colorless oil (90.1 mg, 75% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.73 (dd, $J = 1.2, 7.2$ Hz, 2H), 4.98 (s, 1H), 5.08 (s, 1H), 5.13 (s, 1H), 5.15–5.17 (m, 1H), 5.80–5.90 (m, 1H), 6.00 (d, $J = 6.0$ Hz, 1H), 6.26 (d, $J = 6.4$ Hz, 1H), 6.37 (d, $J = 16.0$ Hz, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 7.19–7.23 (m, 1H), 7.27–7.31 (m, 2H), 7.34–7.36 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 45.4, 69.5, 101.8, 118.7, 126.5, 127.7, 128.6, 128.9, 131.7, 132.6, 133.6, 136.8, 140.5, 150.4; IR (neat) 3079, 3026, 2924, 2853, 1583, 1448, 1207, 964, 919, 834, 792, 748, 693 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{16}\text{S}$: 240.0973 $[\text{M}]^+$; found: 240.0962.

2-(2-Allyl-5-methylene-2,5-dihydrothiophen-2-yl)-1,3-dioxolane (2j)



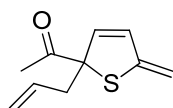
Colorless oil (78.9 mg, 75% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.60–2.62 (m, 2H), 3.90–3.93 (m, 2H), 4.02–4.04 (m, 2H), 4.97 (s, 1H), 5.01 (s, 1H), 5.05 (s, 1H), 5.07–5.14 (m, 2H), 5.78–5.88 (m, 1H), 5.93 (dd, $J = 1.2, 6.0$ Hz, 1H), 6.29 (d, $J = 6.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 38.6, 65.90, 65.92, 72.6, 102.0, 106.8, 118.1, 133.4, 133.9, 137.6, 150.5; IR (neat) 3076, 2978, 2886, 1613, 1585, 1162, 917, 836, 792 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{NaO}_2\text{S}$: 233.0612 $[\text{M}+\text{Na}]^+$; found: 233.0606.

2-(2-Allyl-5-methylene-2,5-dihydrothiophen-2-yl)-2-methyl-1,3-dioxolane (2k)



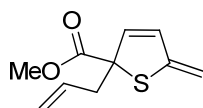
Colorless oil (79.6 mg, 71% yield). ^1H NMR (400 MHz, CDCl_3) δ 1.42 (s, 3H), 2.58–2.71 (m, 2H), 3.98–4.02 (m, 4H), 4.96 (s, 1H), 5.03–5.09 (m, 3H), 5.75–5.85 (m, 1H), 5.90 (d, $J = 6.0$ Hz, 1H), 6.25 (d, $J = 6.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.5, 38.8, 65.6, 65.8, 101.4, 112.5, 117.4, 133.5, 134.2, 138.9, 151.2; IR (neat) 3075, 2983, 1886, 1584, 1372, 1203, 1037, 949, 831, 566 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{16}\text{NaO}_2\text{S}$: 247.0769 $[\text{M}+\text{Na}]^+$; found: 247.0759.

1-(2-Allyl-5-methylene-2,5-dihydrothiophen-2-yl)ethanone (2l)



Colorless oil (57.7 mg, 64% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.24 (s, 3H), 2.74 (d, $J = 7.2$ Hz, 2H), 5.04 (s, 1H), 5.10 (s, 1H), 5.12–5.14 (m, 1H), 5.16 (s, 1H), 5.69–5.78 (m, 1H), 6.01 (dd, $J = 0.8, 6.0$ Hz, 1H), 6.41 (d, $J = 6.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 26.3, 40.7, 76.2, 103.2, 119.2, 133.0, 135.4, 137.6, 149.9, 203.7; IR (neat) 3077, 2979, 2916, 1709, 1354, 1191, 921, 787 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{12}\text{OS}$: 180.0609 $[\text{M}]^+$; found: 180.0617.

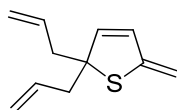
Methyl 2-allyl-5-methylene-2,5-dihydrothiophene-2-carboxylate (2m)



Colorless oil (69.7 mg, 71% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.71–2.85 (m, 2H), 3.75 (s, 3H), 4.99 (s, 1H), 5.11–5.16 (m, 3H), 5.68–5.79 (m, 1H), 6.13 (dd, $J = 0.8, 6.0$ Hz, 1H), 6.30 (d, $J = 6.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 44.0, 52.9, 70.3, 102.7, 119.5, 132.2, 133.1, 136.6, 149.2, 171.9 cm^{-1} ; IR (neat) 3079, 2952, 1732, 1435, 1211, 925, 844, 798 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}$: 196.0558 $[\text{M}]^+$; found:

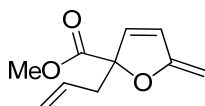
196.0559.

2,2-Diallyl-5-methylene-2,5-dihydrothiophene (2n)



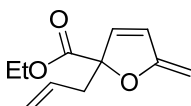
Colorless oil (66.0 mg, 74% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.52 (dd, $J = 7.2$, 7.2 Hz, 4H), 4.93 (s, 1H), 5.01 (s, 1H), 5.09 (d, $J = 6.8$ Hz, 2H), 5.13 (s, 2H), 5.76–5.87 (m, 2H), 5.89 (d, $J = 6.0$ Hz, 1H), 6.18 (d, $J = 6.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 45.3, 69.4, 101.2, 118.6, 131.6, 134.0, 142.1, 151.1; IR (neat) 3077, 2924, 2854, 1584, 1434, 995, 917, 831, 788 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{14}\text{S}$: 178.0816 $[\text{M}]^+$; found: 178.0810.

Methyl 2-allyl-5-methylene-2,5-dihydrofuran-2-carboxylate (4a)



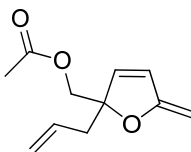
Colorless oil (42.3 mg, 47% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.56–2.74 (m, 2H), 3.73 (s, 3H), 4.03 (d, $J = 2.0$ Hz, 1H), 4.41 (d, $J = 1.2$ Hz, 1H), 5.09 (s, 1H), 5.12 (d, $J = 8.0$ Hz, 1H), 5.66–5.76 (m, 1H), 6.19 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 41.4, 52.6, 82.4, 94.1, 119.6, 127.2, 130.8, 134.4, 163.7, 170.4; IR (neat) 3082, 2955, 2924, 1736, 1436, 1228, 1029, 923, 799 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{12}\text{O}_3$: 180.0786 $[\text{M}]^+$; found: 180.0791.

Ethyl 2-allyl-5-methylene-2,5-dihydrofuran-2-carboxylate (4b)



Colorless oil (51.5 mg, 53% yield). ^1H NMR (400 MHz, CDCl_3) δ 1.29 (t, $J = 7.2$ Hz, 3H), 2.59–2.79 (m, 2H), 4.05 (d, $J = 2.0$ Hz, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 4.44 (s, 1H), 5.12 (s, 1H), 5.16 (d, $J = 9.2$ Hz, 1H), 5.70–5.80 (m, 1H), 6.22 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.3, 41.5, 61.8, 82.4, 94.1, 119.6, 127.2, 131.0, 134.6, 163.8, 170.0; IR (neat) 3081, 2982, 2936, 1752, 1732, 1227, 1031, 921, 793 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{14}\text{O}_3$: 194.0943 $[\text{M}]^+$; found: 194.0949.

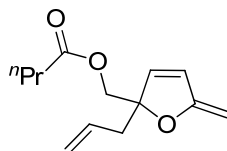
(2-Allyl-5-methylene-2,5-dihydrofuran-2-yl)methyl acetate (4c)



Colorless oil (55.4 mg, 57% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.06 (s, 3H), 2.49 (dd, $J = 5.2$, 6.0 Hz, 2H), 3.95 (s, 1H), 4.17 (dd, $J = 11.6$, 30.4 Hz, 2H), 4.30 (s, 1H),

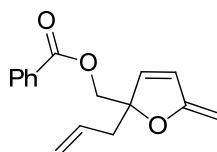
5.12 (d, $J = 12.8$ Hz, 2H), 5.67–5.78 (m, 1H), 6.08 (d, $J = 5.6$ Hz, 1H), 6.20 (d, $J = 5.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.0, 40.1, 66.7, 80.9, 92.9, 119.3, 127.7, 131.7, 135.6, 164.3, 170.9; IR (neat) 3079, 2980, 2937, 1745, 1381, 1231, 1044, 921, 790 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{14}\text{O}_3$: 194.0943 $[\text{M}]^+$; found: 194.0944.

(2-Allyl-5-methylene-2,5-dihydrofuran-2-yl)methyl butyrate (4d)



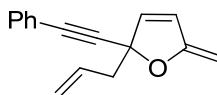
Colorless oil (50.0 mg, 45% yield). ^1H NMR (400 MHz, CDCl_3) δ 0.94 (t, $J = 7.4$ Hz, 3H), 1.59–1.68 (m, 2H), 2.30 (t, $J = 7.4$ Hz, 2H), 2.47–2.50 (m, 2H), 3.94 (s, 1H), 4.18 (dd, $J = 11.6, 38.8$ Hz, 2H), 4.28 (s, 1H), 5.10–5.14 (m, 2H), 5.68–5.78 (m, 1H), 6.08 (d, $J = 5.6$ Hz, 1H), 6.18 (d, $J = 6.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 18.4, 36.1, 40.0, 66.2, 80.7, 92.9, 119.1, 127.5, 131.6, 135.5, 164.2, 173.3; IR (neat) 3080, 2966, 2877, 1740, 1657, 1179, 981, 922, 789 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{18}\text{O}_3$: 222.1256 $[\text{M}]^+$; found: 222.1257.

(2-Allyl-5-methylene-2,5-dihydrofuran-2-yl)methyl benzoate (4e)



Colorless oil (32.0 mg, 25% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.58 (d, $J = 7.2$, 2H), 3.98 (s, 1H), 4.32 (s, 1H), 4.41 (dd, $J = 11.6, 60.0$ Hz, 2H), 5.13 (s, 1H), 5.17 (d, $J = 7.2$ Hz, 1H), 5.73–5.84 (m, 1H), 6.16 (d, $J = 5.6$ Hz, 1H), 6.22 (d, $J = 5.6$ Hz, 1H), 7.44 (dd, $J = 7.6, 7.6$ Hz, 2H), 7.56 (dd, $J = 7.2, 7.6$ Hz, 1H), 8.02 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 40.3, 67.1, 81.0, 93.0, 119.4, 127.8, 128.5, 129.9, 130.0, 131.7, 133.3, 135.6, 164.4, 166.3; IR (neat) 3076, 2980, 2949, 1723, 1272, 1112, 922, 712 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3$: 256.1099 $[\text{M}]^+$; found: 256.1105.

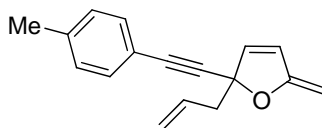
2-Allyl-5-methylene-2-(phenylethynyl)-2,5-dihydrofuran (4f)



Colorless oil (61.1 mg, 55% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.71 (dd, $J = 5.6, 6.4$ Hz, 2H), 4.04 (s, 1H), 4.37 (s, 1H), 5.18 (s, 1H), 5.20–5.22 (m, 1H), 5.86–5.97 (m, 1H), 6.19 (d, $J = 5.6$ Hz, 1H), 6.22–6.24 (m, 1H), 7.28–7.30 (m, 3H), 7.42–7.44 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 45.5, 81.8, 86.1, 87.2, 87.3, 119.5, 122.3, 125.9, 128.4, 128.8, 131.8, 131.9, 136.7, 163.5; IR (neat) 3080, 2981, 2911, 2229, 1657,

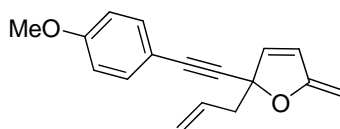
1490, 1294, 1009, 919, 793, 757, 691 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{14}\text{O}$: 222.1045 $[\text{M}]^+$; found: 222.1053.

2-Allyl-5-methylene-2-(p-tolyethynyl)-2,5-dihydrofuran (4g)



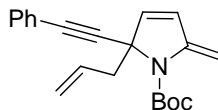
Colorless oil (59.1 mg, 50% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.33 (s, 3H), 2.71 (dd, $J = 5.6, 6.8$ Hz, 2H), 4.02 (s, 1H), 4.35 (s, 1H), 5.17 (s, 1H), 5.20 (d, $J = 4.4$ Hz, 1H), 5.86–5.96 (m, 1H), 6.18 (d, $J = 6.0$ Hz, 1H), 6.23 (d, $J = 5.2$ Hz, 1H), 7.09 (d, $J = 7.6$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.7, 45.5, 81.7, 85.5, 87.3, 87.5, 119.4, 125.9, 129.1, 131.9, 132.0, 136.9, 139.0, 163.5; IR (neat) 3081, 2922, 2229, 1774, 1510, 1293, 923, 817 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{16}\text{O}$: 236.1201 $[\text{M}]^+$; found: 236.1196.

2-Allyl-2-((4-methoxyphenyl)ethynyl)-5-methylene-2,5-dihydrofuran (4h)



Colorless oil (69.4 mg, 55% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.71 (dd, $J = 5.6, 6.8$ Hz, 2H), 3.79 (s, 3H), 4.02 (s, 1H), 4.35 (s, 1H), 5.17–5.21 (m, 2H), 5.86–5.96 (m, 1H), 6.18 (d, $J = 5.6$ Hz, 1H), 6.22–6.24 (m, 1H), 6.81 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 45.5, 55.4, 81.7, 84.8, 87.30, 87.34, 114.0, 114.4, 119.3, 125.8, 132.0, 133.5, 136.9, 160.0, 163.5; IR (neat) 3078, 3007, 2935, 2838, 2227, 1656, 1606, 1510, 1289, 1250, 1007, 832 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2$: 252.1150 $[\text{M}]^+$; found: 252.1153.

tert-Butyl 2-allyl-5-methylene-2-(phenylethynyl)-2,5-dihydro-1H-pyrrole-1-carboxylate (6h)



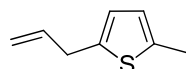
Colorless oil (72.3 mg, 45% yield). ^1H NMR (400 MHz, CDCl_3) δ 1.56 (s, 9H), 2.87–3.01 (m, 2H), 4.46 (s, 1H), 5.11 (s, 1H), 5.15 (d, $J = 4.8$ Hz, 1H), 5.36 (br, 1H), 5.66–5.76 (m, 1H), 5.95 (d, $J = 5.6$ Hz, 1H), 6.11 (d, $J = 5.6$ Hz, 1H), 7.30–7.33 (m, 3H), 7.39–7.40 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 28.6, 43.4, 68.2, 81.5, 84.6, 87.6, 92.0, 119.4, 123.0, 128.4, 128.7, 131.7, 131.8, 133.6, 147.4, 151.7; IR (neat) 3080, 2978, 2929, 2229, 1782, 1713, 1371, 1167, 919, 757, 691 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_2$: 321.1729 $[\text{M}]^+$; found: 321.1732.

Method B:

Representative Procedure for Obtaining Products 2a–2d and 6a–6g:

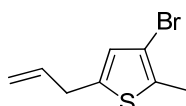
Allyltributylstannane (165.56 mg, 0.5 mmol) and **1a** (66.31 mg, 0.5 mmol) were added to a solution of Pd₂(dba)₃ (22.90 mg, 0.025 mmol) and PPh₃ (26.23 mg, 0.1 mmol) in acetone (3 mL) or CH₂Cl₂ (3 mL) at room temperature. The reaction mixture was stirred under N₂ atmosphere at room temperature. The reaction progress was monitored by TLC. After the starting material **1a** was consumed (10 h), 2-methylbenzoic acid (0.14 g, 1 mmol) was added into the mixture. The resulting mixture was stirred at room temperature for another 10 h, and then, the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography on basic alumina (eluent: petroleum ether) to afford 2-allyl-5-methylthiophene (**2a**) in 60% yield (41.5 mg) as a colorless oil.

2-Allyl-5-methylthiophene (**2a**)



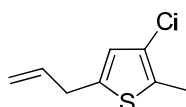
Colorless oil (41.5 mg, 60% yield). ¹H NMR (400 MHz, CDCl₃) δ 2.42 (s, 3H), 3.48 (d, *J* = 6.4 Hz, 2H), 5.06–5.15 (m, 2H), 5.91–6.01 (m, 1H), 6.56 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 15.4, 34.6, 116.1, 124.5, 124.9, 136.9, 138.2, 140.7; IR (neat) 3065, 2958, 2922, 2855, 1640, 1453, 991, 915, 795 cm⁻¹; HRMS (EI) calcd for C₈H₁₀S: 138.0503 [M]⁺; found: 138.0508.

5-Allyl-3-bromo-2-methylthiophene (**2b**)



Colorless oil (89.0 mg, 82% yield). ¹H NMR (400 MHz, CDCl₃) δ 2.33 (s, 3H), 3.45 (d, *J* = 6.4 Hz, 2H), 5.13 (dd, *J* = 11.2, 18.4 Hz, 2H), 5.87–5.97 (m, 1H), 6.60 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.7, 34.3, 108.2, 116.8, 127.18, 127.25, 132.3, 135.7, 140.0; IR (neat) 2955, 2923, 2852, 1640, 1458, 1069, 918, 797 cm⁻¹; HRMS (EI) calcd for C₈H₉BrS: 215.9608 [M]⁺; found: 215.9617.

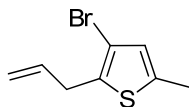
5-Allyl-3-chloro-2-methylthiophene (**2c**)



Colorless oil (64.8 mg, 75% yield). ¹H NMR (400 MHz, CDCl₃) δ 2.32 (s, 3H), 3.43 (d, *J* = 6.8 Hz, 2H), 5.09–5.17 (m, 2H), 5.86–5.96 (m, 1H), 6.56 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.1, 34.5, 117.0, 121.6, 125.1, 130.3, 135.9, 139.1; IR (neat) 3080, 2921, 2851, 1666, 1641, 1430, 1342, 991, 921, 822 cm⁻¹; HRMS (EI) calcd for

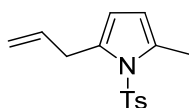
C₈H₉ClS: 172.0113 [M]⁺; found: 172.0117.

2-Allyl-3-bromo-5-methylthiophene (2d)



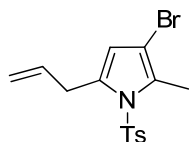
Colorless oil (63.0 mg, 58% yield). ¹H NMR (400 MHz, CDCl₃) δ 2.41 (s, 3H), 3.45 (d, *J* = 6.4 Hz, 2H), 5.09–5.15 (m, 2H), 5.86–5.94 (m, 1H), 6.58 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 15.5, 33.6, 107.8, 116.8, 127.8, 127.9, 134.7, 135.2, 138.1; IR (neat) 2923, 2854, 1638, 1544, 1174, 990, 917, 816 cm⁻¹; HRMS (EI) calcd for C₈H₉BrS: 215.9608 [M]⁺; found: 215.9616.

2-Allyl-5-methyl-1-tosyl-1H-pyrrole (6a)



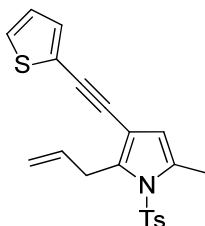
White solid (110.1 mg, 80% yield), mp 50–51 °C. ¹H NMR (400 MHz, CDCl₃) δ 2.37 (s, 3H), 2.40 (s, 3H), 3.56 (d, *J* = 6.4 Hz, 2H), 5.07–5.12 (m, 2H), 5.89–5.99 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 15.8, 21.7, 33.6, 111.6, 112.1, 116.9, 126.3, 130.1, 132.9, 135.3, 135.4, 137.7, 144.6; IR (KBr) 3080, 2964, 2928, 1598, 1364, 1170, 1119, 994, 919, 687, 546 cm⁻¹; HRMS (EI) calcd for C₁₅H₁₇NO₂S: 275.0980 [M]⁺; found: 275.0980.

2-Allyl-3-bromo-5-methyl-1-tosyl-1H-pyrrole (6b)



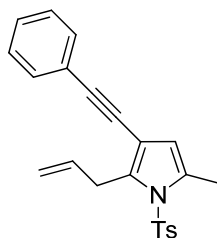
White solid (148.8 mg, 84% yield), mp 63–64 °C. ¹H NMR (400 MHz, CDCl₃) δ 2.34 (s, 3H), 2.40 (s, 3H), 3.66 (d, *J* = 6.0 Hz, 2H), 5.00–5.05 (m, 2H), 5.83–5.93 (m, 1H), 5.98 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 15.5, 21.7, 31.1, 102.9, 115.1, 116.2, 126.5, 130.2, 131.0, 132.5, 134.8, 136.9, 145.0; IR (KBr) 3079, 2979, 2930, 1597, 1369, 1249, 1175, 1107, 986, 917, 811, 670, 547 cm⁻¹; HRMS (EI) calcd for C₁₅H₁₆BrNO₂S: 353.0085 [M]⁺; found: 353.0095.

2-Allyl-5-methyl-3-(thiophen-2-ylethynyl)-1-tosyl-1H-pyrrole (6c)



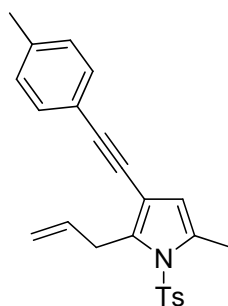
Colorless oil (150.7 mg, 79% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.33 (s, 3H), 2.39 (s, 3H), 3.79 (d, $J = 6.0$ Hz, 2H), 5.03 (d, $J = 9.6$ Hz, 1H), 5.13 (d, $J = 16.8$ Hz, 1H), 5.93–6.01 (m, 1H), 6.03 (s, 1H), 6.96 (dd, $J = 4.0, 4.8$ Hz, 1H), 7.18 (d, $J = 3.6$ Hz, 1H), 7.23 (d, $J = 5.2$ Hz, 1H), 7.27 (d, $J = 8.4$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 15.5, 21.7, 32.0, 85.7, 86.8, 107.9, 114.2, 116.4, 123.7, 126.4, 127.0, 127.2, 130.2, 131.5, 132.2, 135.5, 137.0, 138.5, 145.0; IR (neat) 3107, 3077, 2977, 2928, 2206, 1637, 1597, 1367, 1283, 1173, 1116, 992, 917, 811, 677, 593, 544 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_2\text{S}_2$: 381.0857 $[\text{M}]^+$; found: 381.0867.

2-Allyl-5-methyl-3-(phenylethynyl)-1-tosyl-1H-pyrrole (6d)



Colorless oil (140.8 mg, 75% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.34 (s, 3H), 2.39 (s, 3H), 3.82 (d, $J = 6.4$ Hz, 2H), 5.04 (dd, $J = 1.2, 10.0$ Hz, 1H), 5.14 (dd, $J = 1.2, 16.8$ Hz, 1H), 5.95–6.04 (m, 1H), 6.05 (s, 1H), 7.28–7.31 (m, 5H), 7.44–7.46 (m, 2H), 7.57 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 15.5, 21.7, 32.0, 83.1, 92.6, 108.3, 114.3, 114.4, 116.3, 123.7, 126.4, 128.1, 128.4, 130.1, 131.4, 132.1, 135.6, 137.1, 138.4, 145.0; IR (neat) 3078, 2977, 2929, 2854, 2212, 1598, 1489, 1367, 1295, 1175, 913, 811, 756, 592, 545 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_2\text{S}_2$: 375.1293 $[\text{M}]^+$; found: 375.1296.

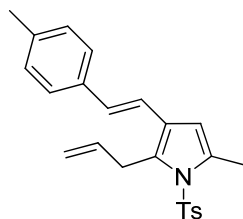
2-Allyl-5-methyl-3-(p-tolylethynyl)-1-tosyl-1H-pyrrole (6e)



Colorless oil (148.0 mg, 76% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.33 (s, 3H), 2.34 (s, 3H), 2.39 (s, 3H), 3.81 (d, $J = 6.0$ Hz, 2H), 5.03 (d, $J = 10.0$ Hz, 1H), 5.13 (d, $J = 17.2$ Hz, 1H), 5.95–6.01 (m, 1H), 6.04 (s, 1H), 7.12 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.56 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 15.5, 21.6, 21.7, 32.0, 82.3, 92.8, 108.4, 114.4, 116.2, 120.6, 126.4, 129.2, 130.1, 131.3, 132.1, 135.7, 137.1, 138.2, 144.9; IR (neat) 3077, 3028, 2977, 2926,

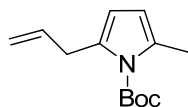
2211, 1597, 1506, 1367, 1295, 1174, 1130, 912, 815, 677, 591, 545 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_2\text{S}$: 389.1450 $[\text{M}]^+$; found: 389.1454.

2-Allyl-5-methyl-3-(4-methylstyryl)-1-tosyl-1H-pyrrole (6f)



Colorless oil (131.2 mg, 67% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.26 (s, 3H), 2.31 (s, 3H), 2.40 (s, 3H), 3.63 (d, $J = 5.6$ Hz, 2H), 4.95–5.00 (m, 2H), 5.73 (s, 1H), 5.85–5.93 (m, 1H), 6.24 (d, $J = 12.0$ Hz, 1H), 6.45 (d, $J = 12.0$ Hz, 1H), 7.01 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 15.8, 21.5, 21.8, 30.5, 113.3, 115.6, 120.8, 122.8, 126.4, 128.9, 129.0, 130.0, 130.1, 132.1, 132.2, 134.8, 136.0, 136.9, 137.7, 144.6; IR (neat) 3016, 2977, 2927, 1597, 1529, 1364, 1170, 1093, 914, 812, 670, 597, 544 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_2\text{S}$: 391.1606 $[\text{M}]^+$; found: 391.1611.

tert-Butyl 2-allyl-5-methyl-1H-pyrrole-1-carboxylate (6g)



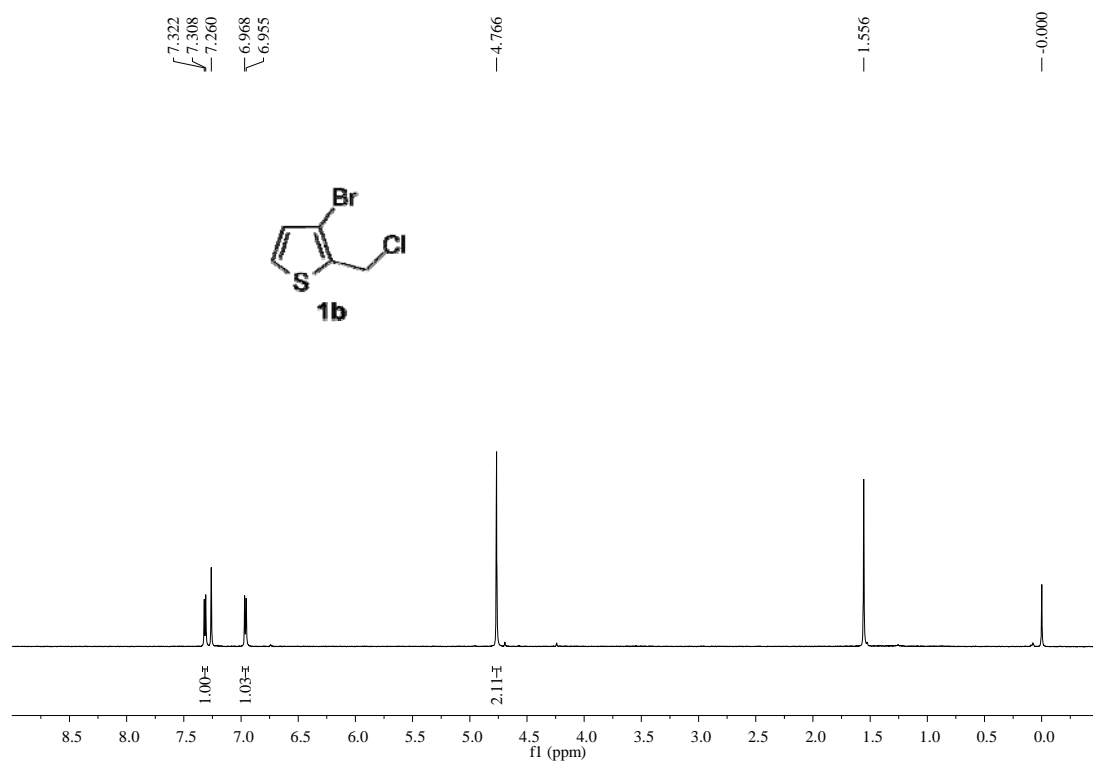
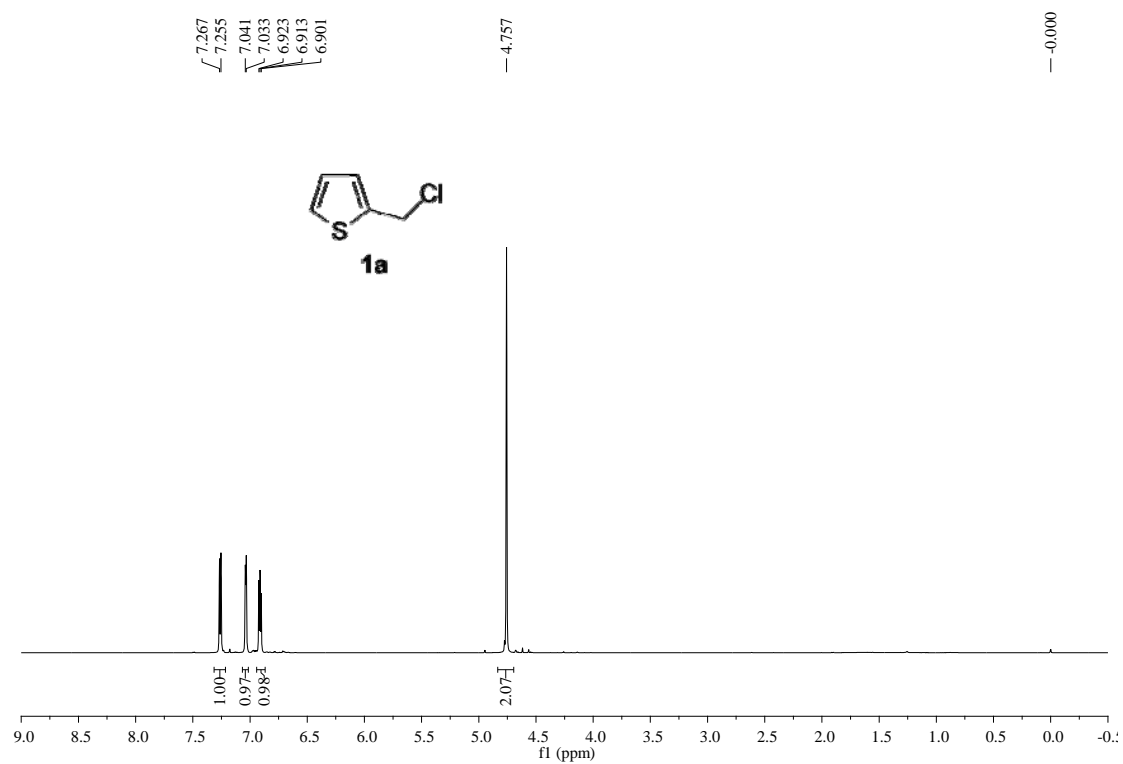
Colorless oil (78.6 mg, 71% yield). ^1H NMR (400 MHz, CDCl_3) δ 1.58 (s, 9H), 2.38 (s, 3H), 3.55 (d, $J = 6.0$ Hz, 2H), 5.01–5.06 (m, 2H), 5.82 (d, $J = 3.6$ Hz, 2H), 5.94–6.01 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 16.6, 28.2, 34.2, 83.6, 110.2, 110.3, 115.9, 131.8, 133.5, 136.4, 150.5; IR (neat) 3080, 2979, 2929, 1739, 1317, 1172, 1122, 852, 786 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_2$: 221.1416 $[\text{M}]^+$; found: 221.1426.

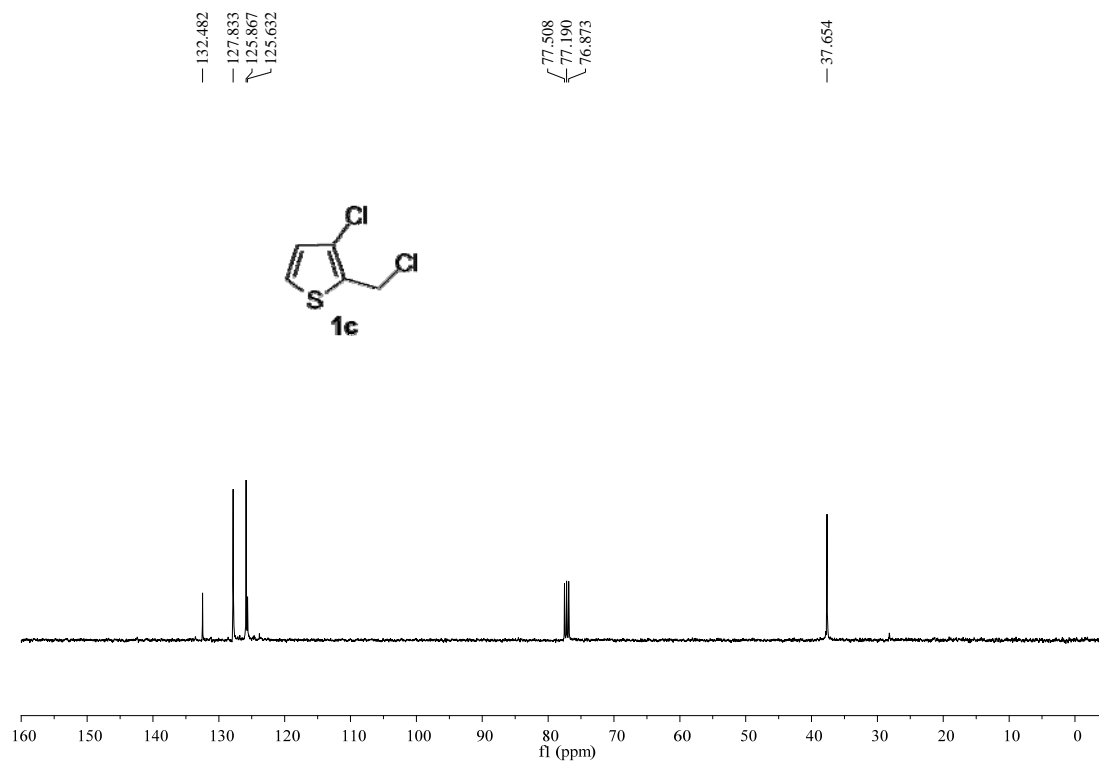
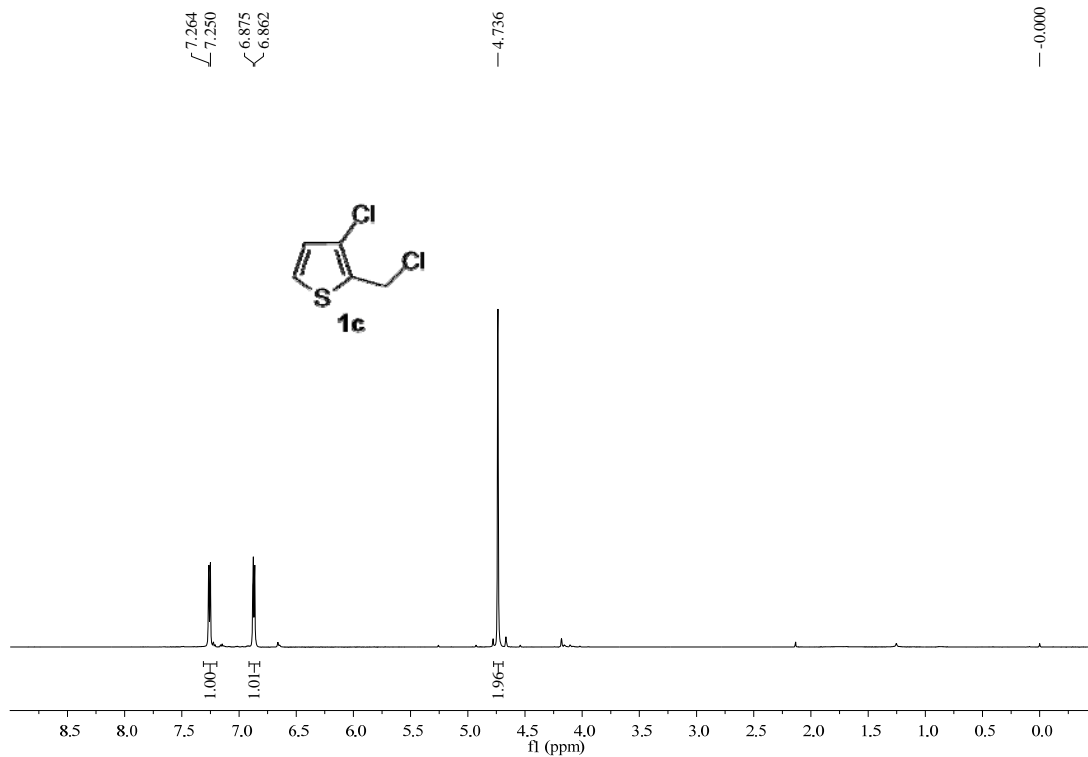
4. References

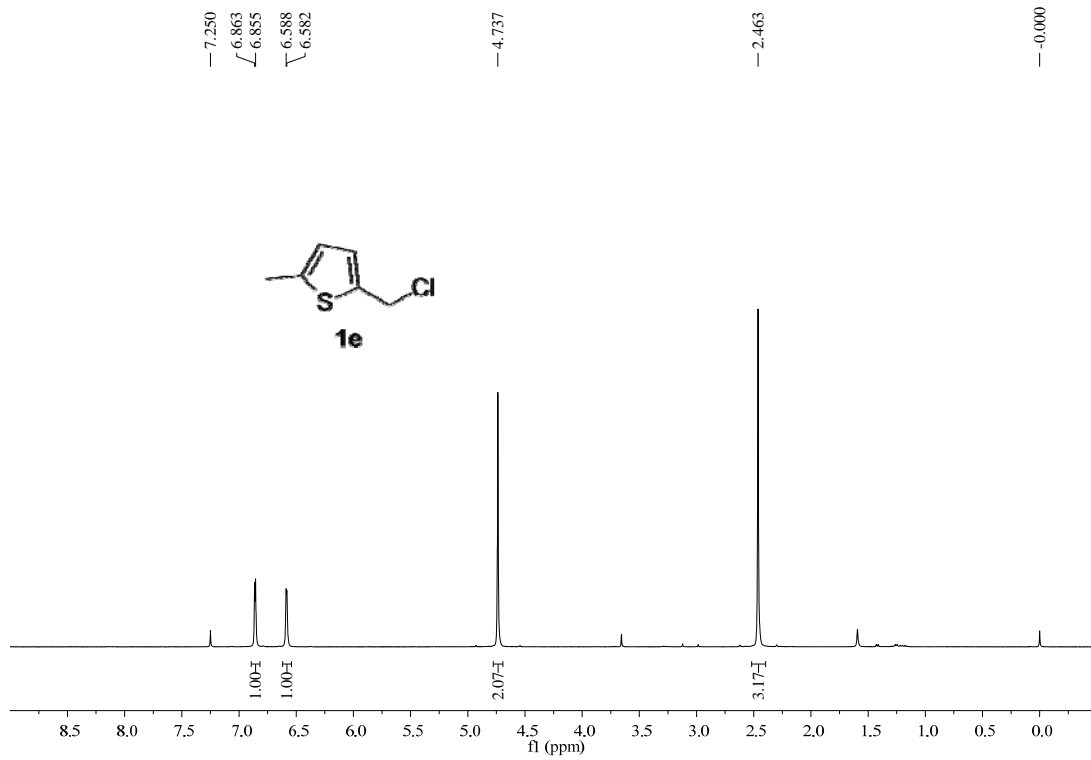
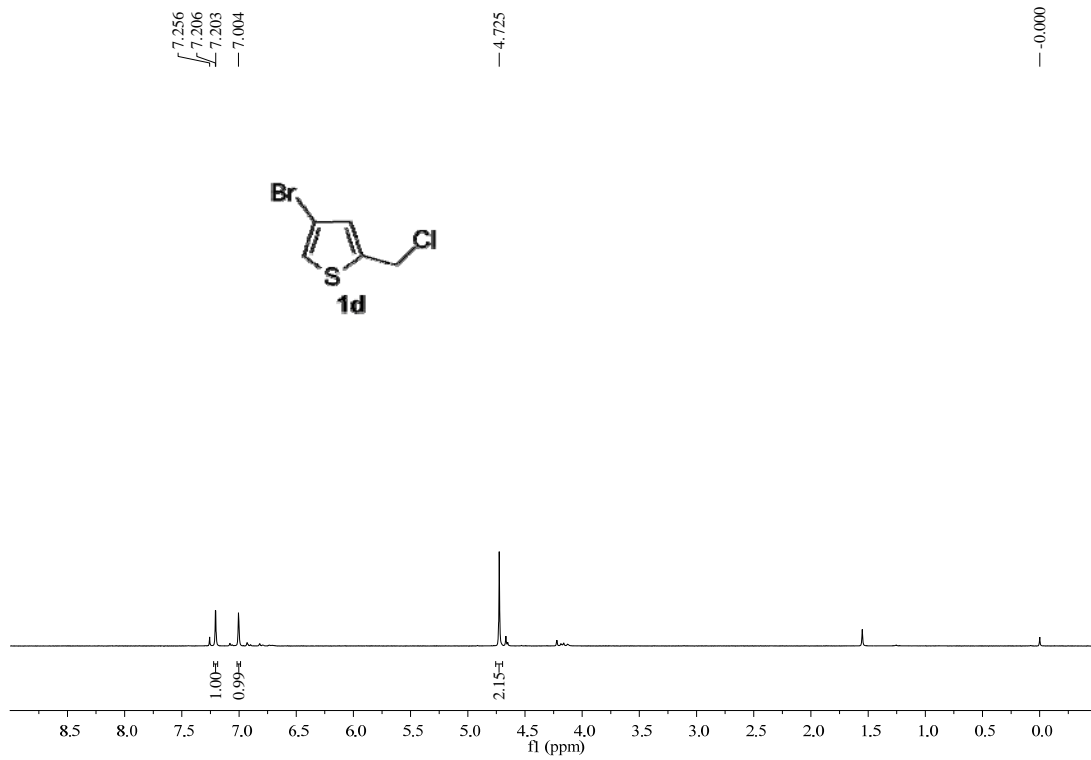
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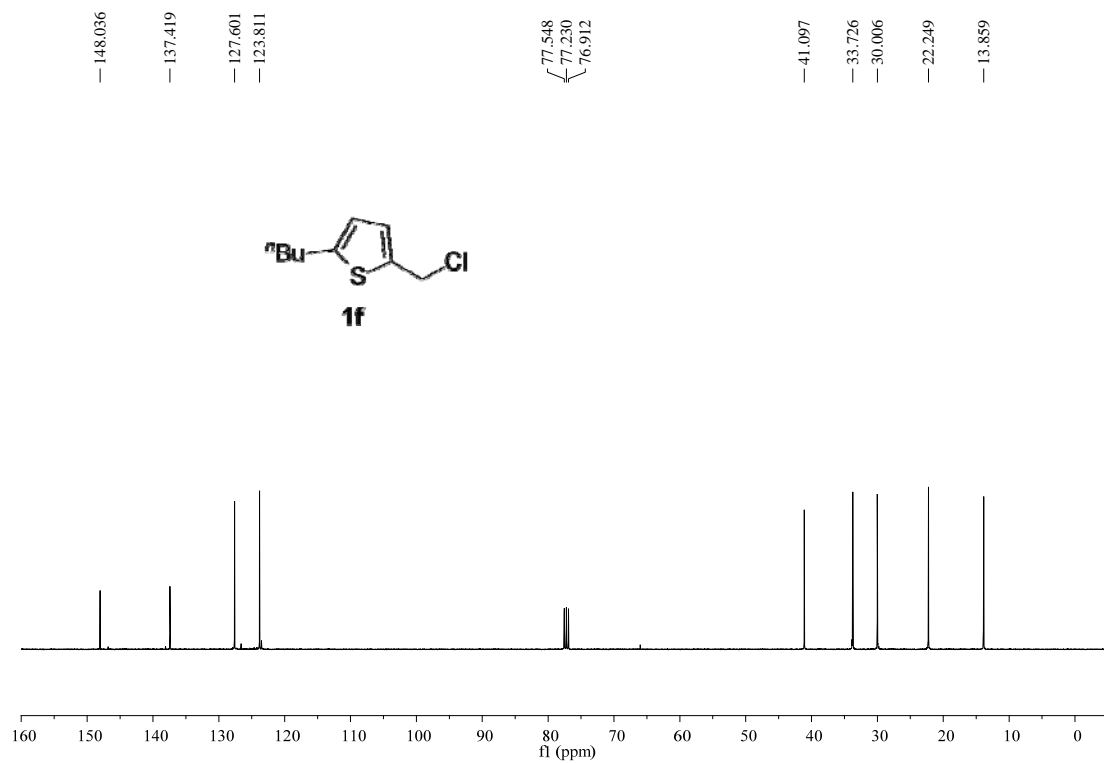
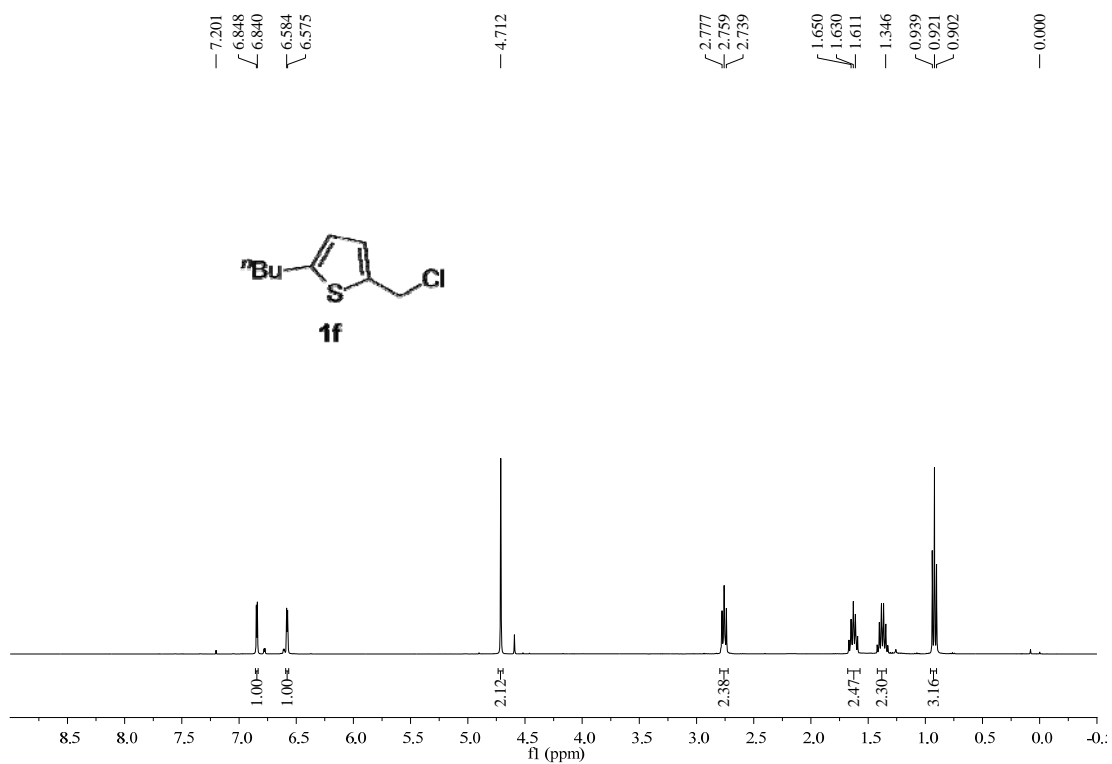
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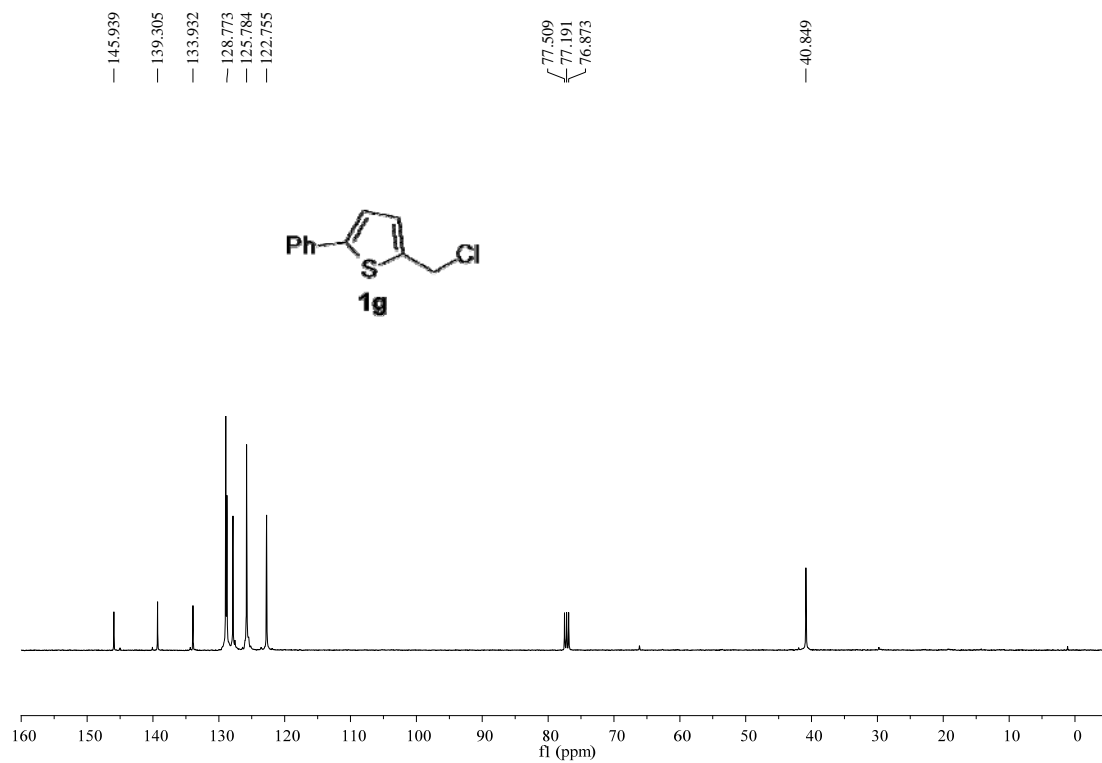
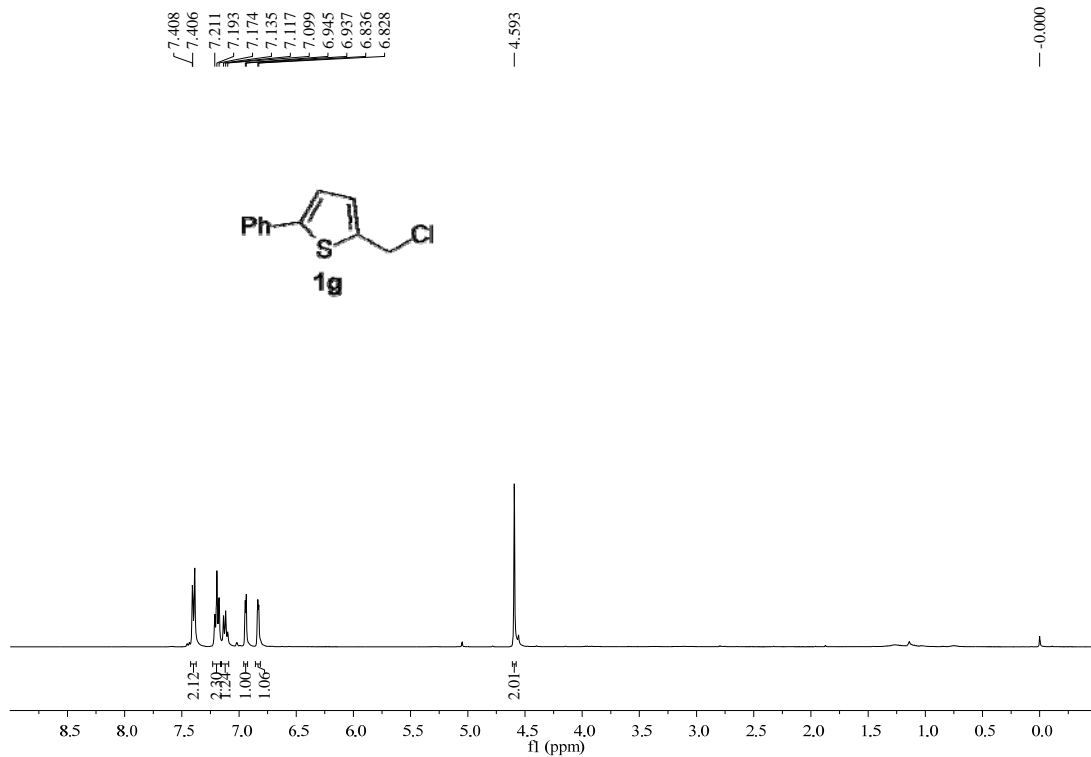
5. Copies of ^1H and ^{13}C NMR Spectra of Starting Materials and Products

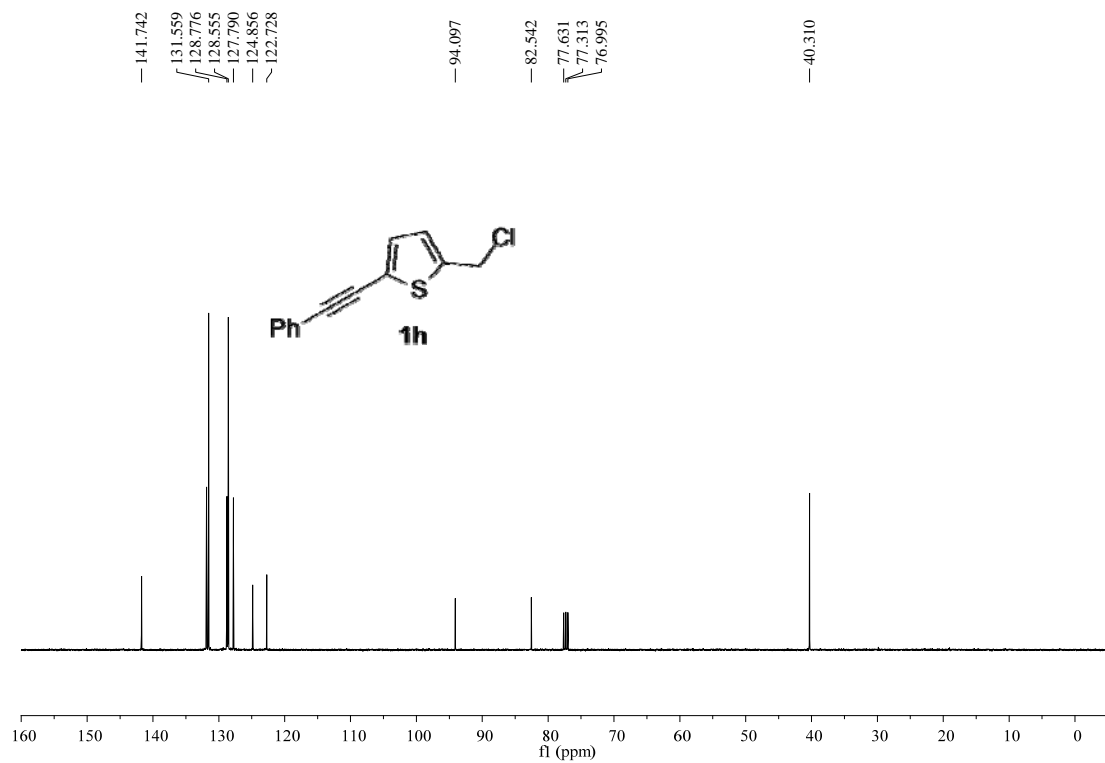
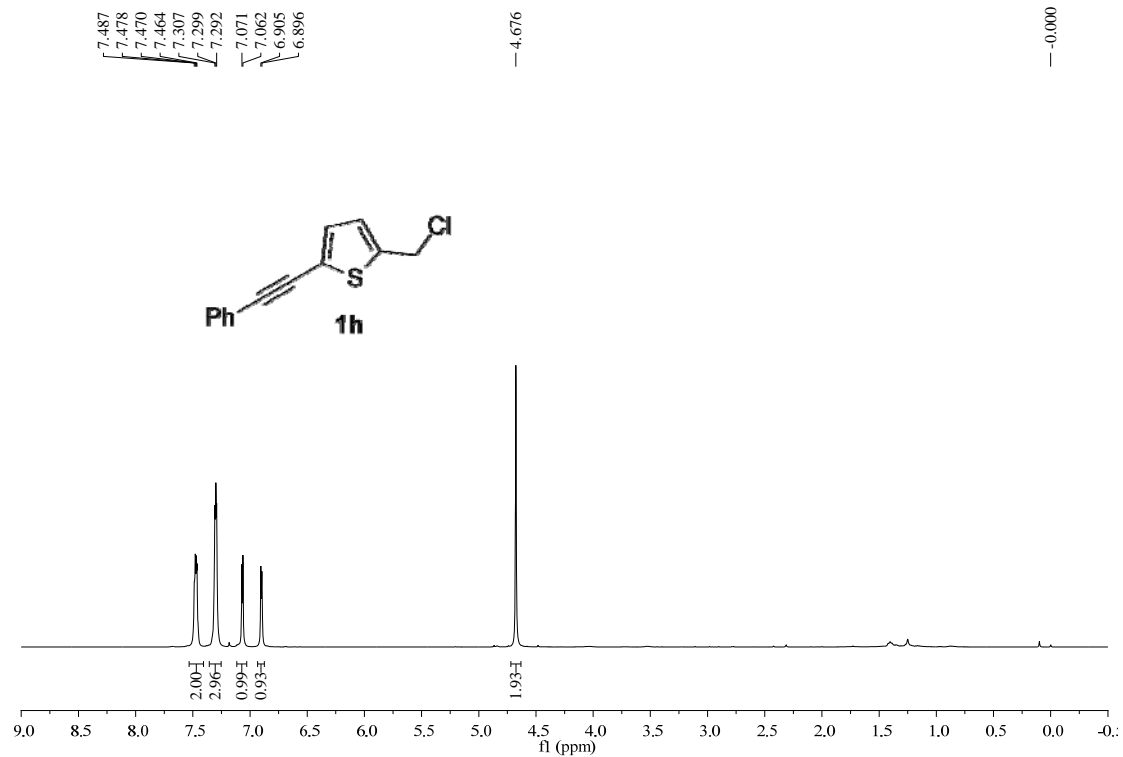


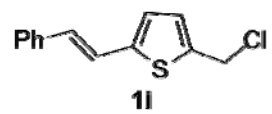
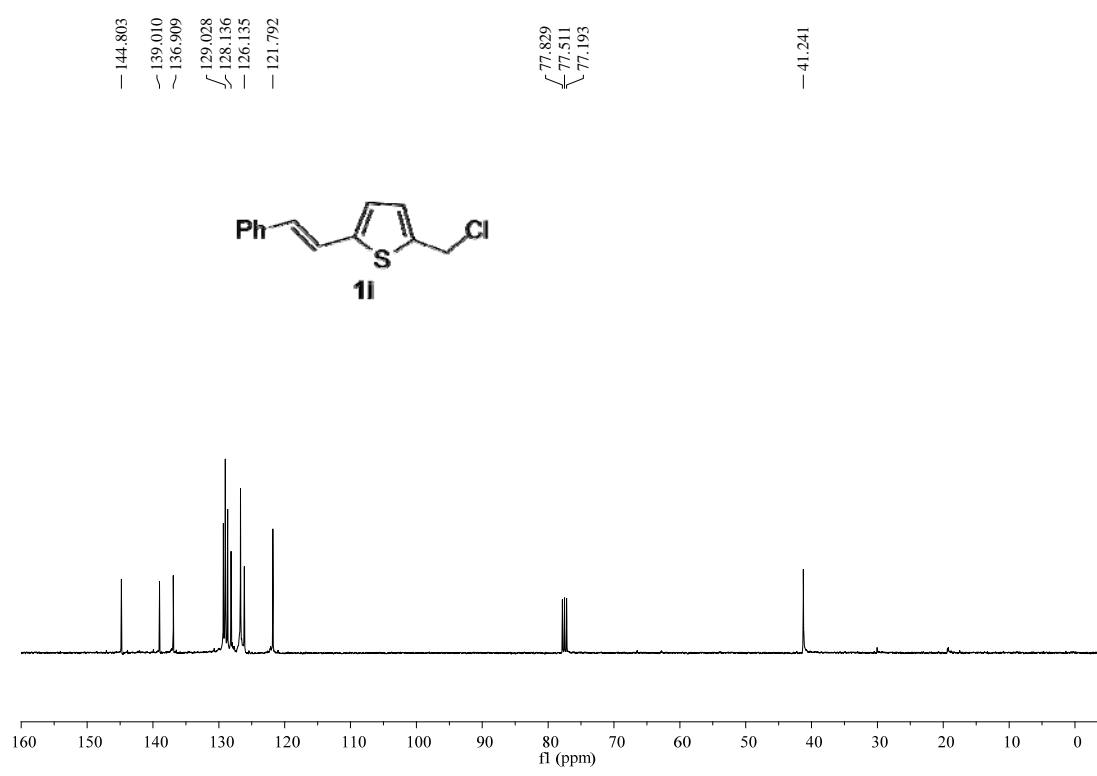
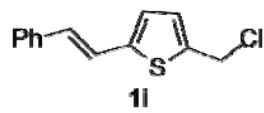
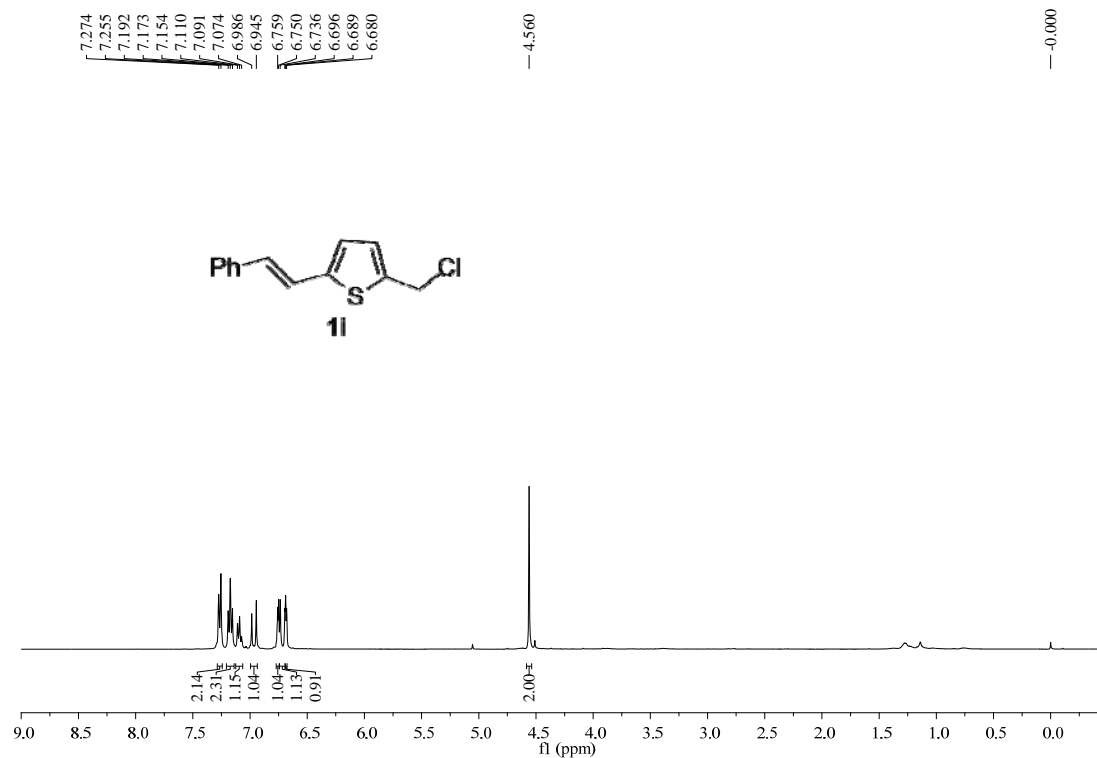


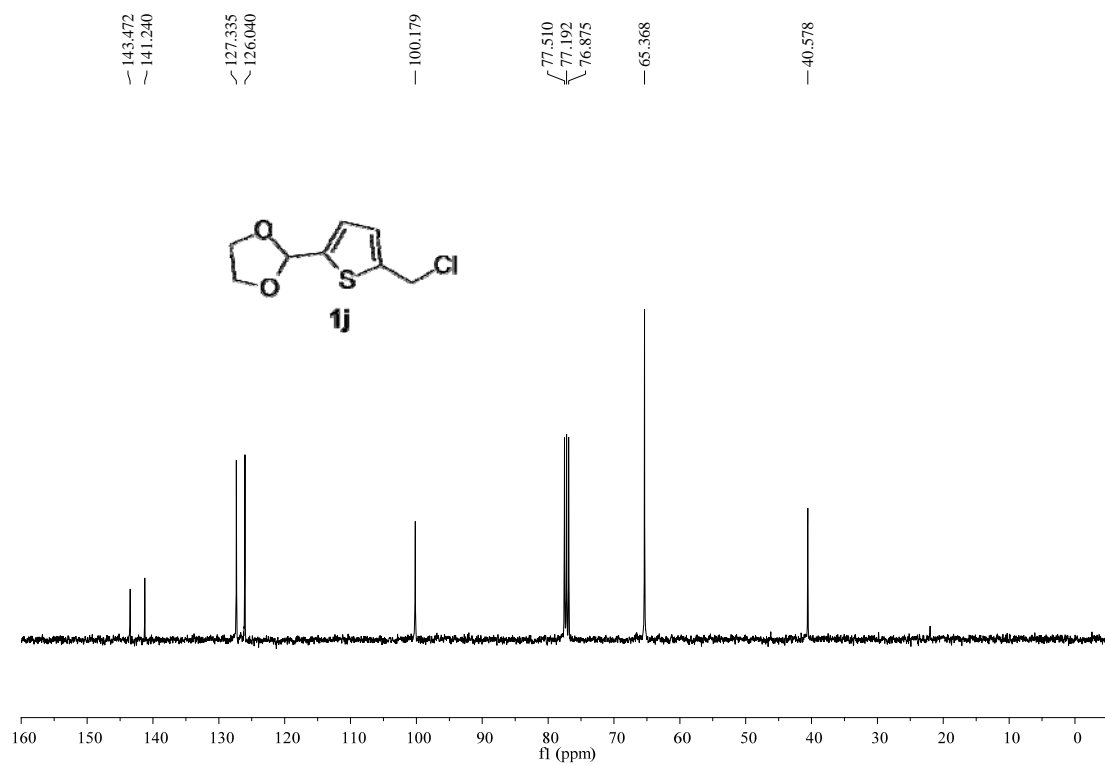
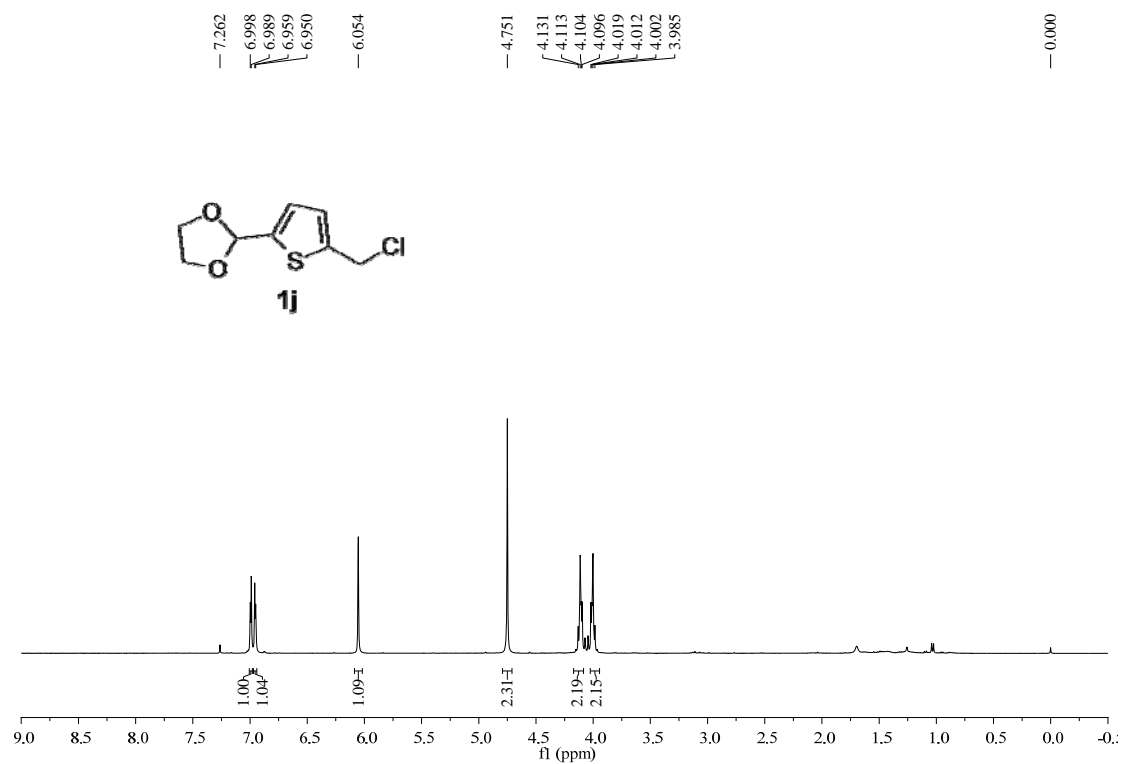


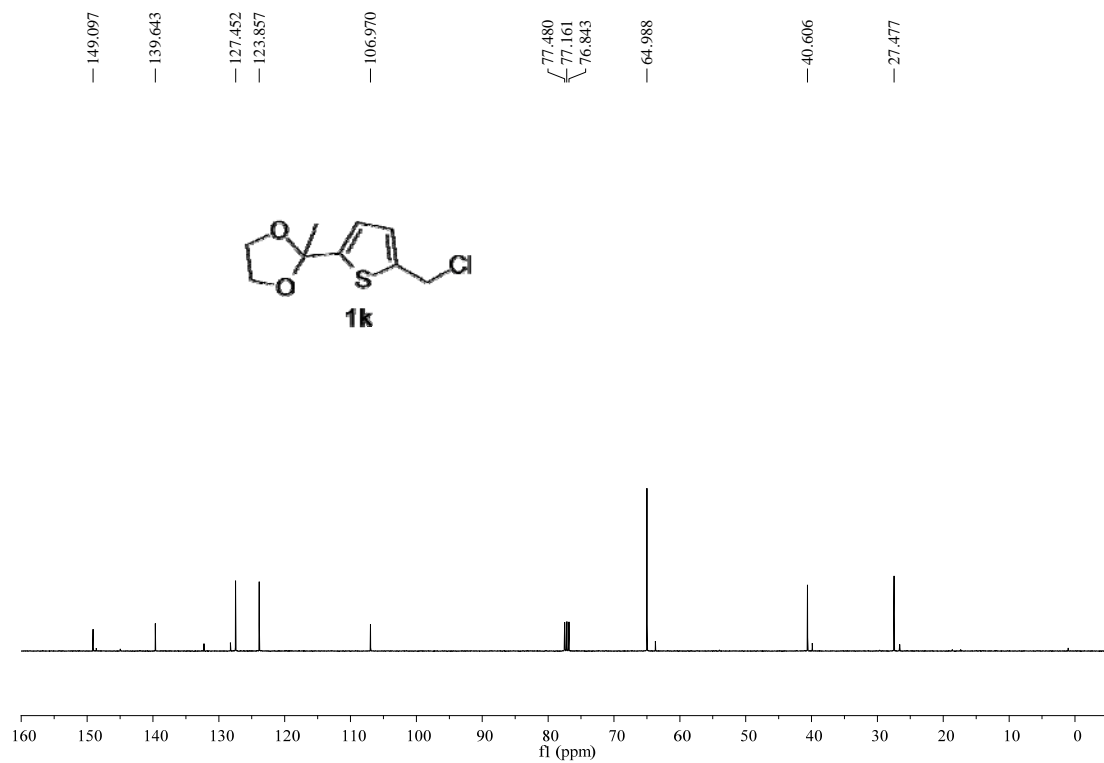
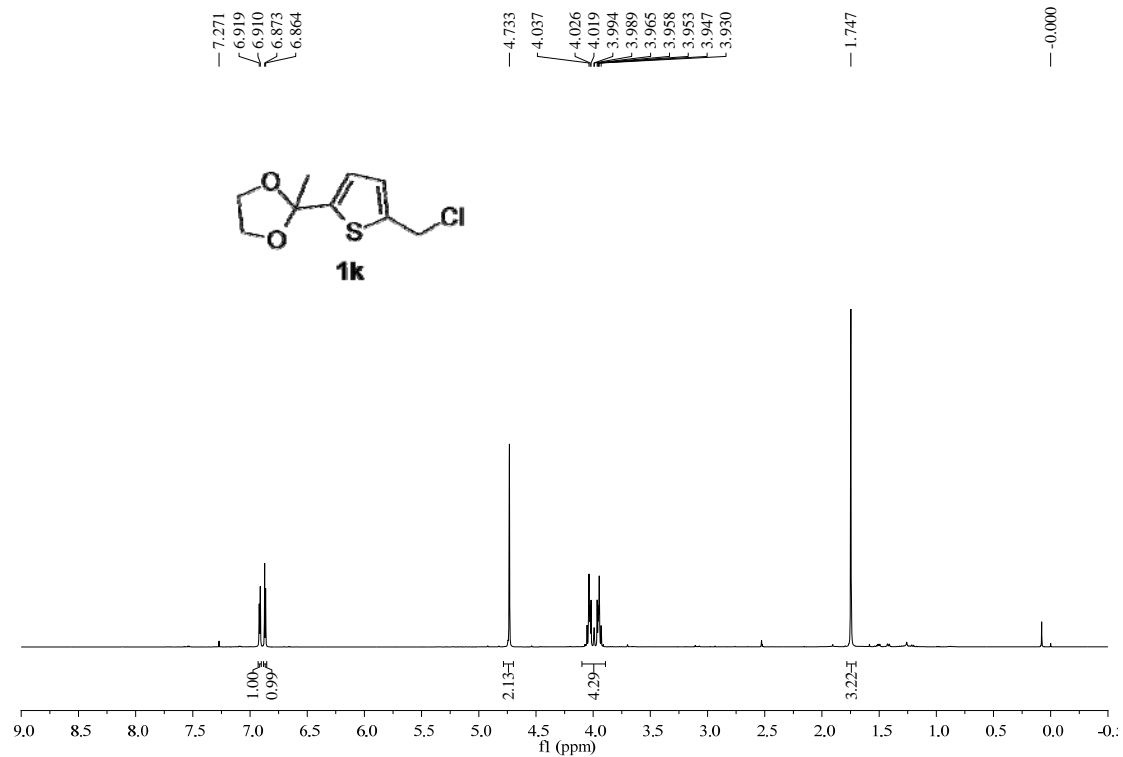


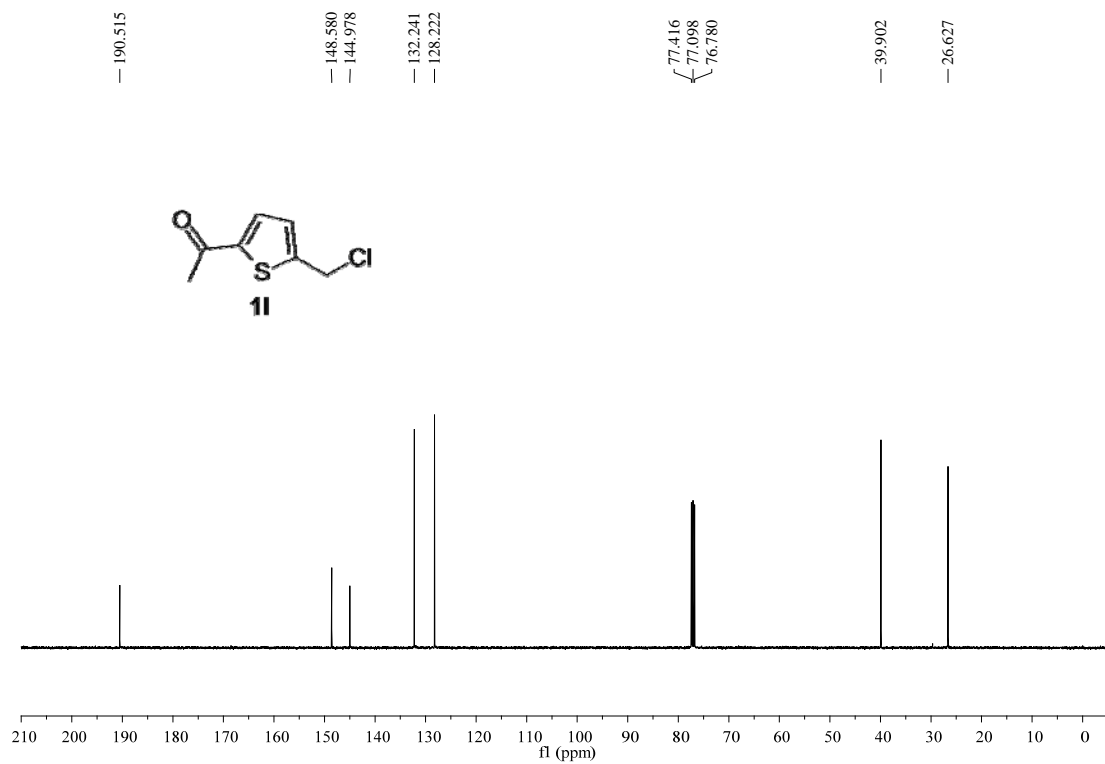
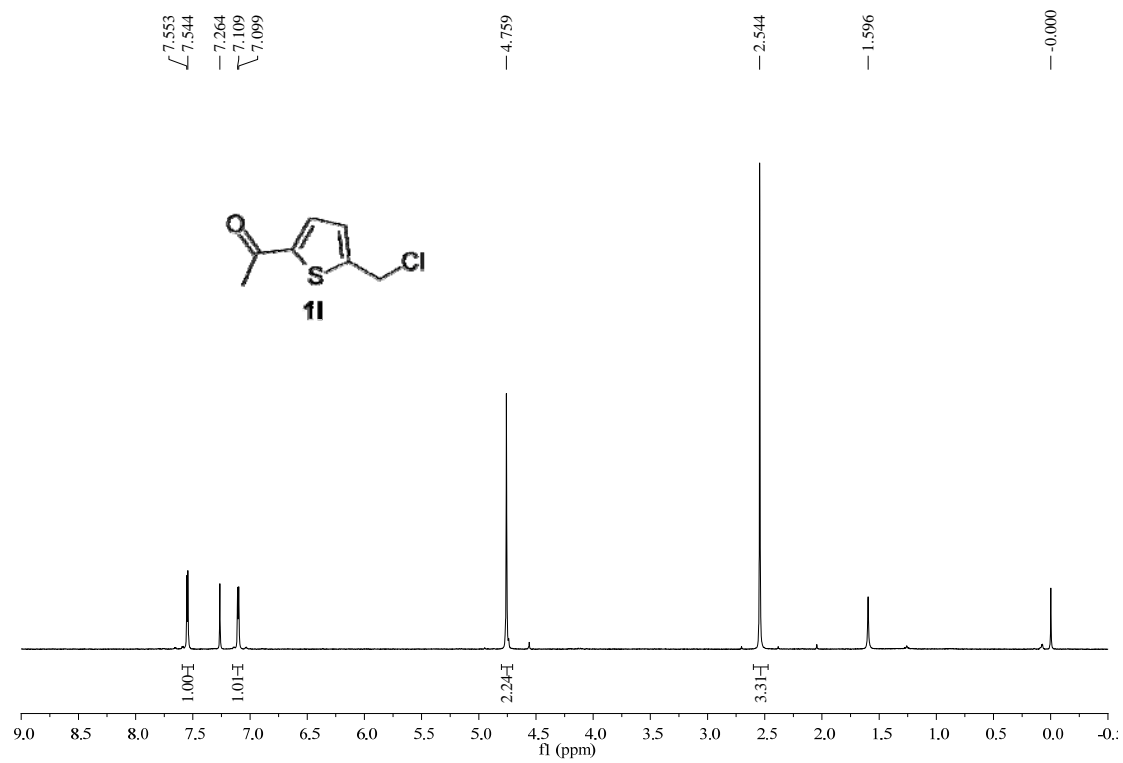


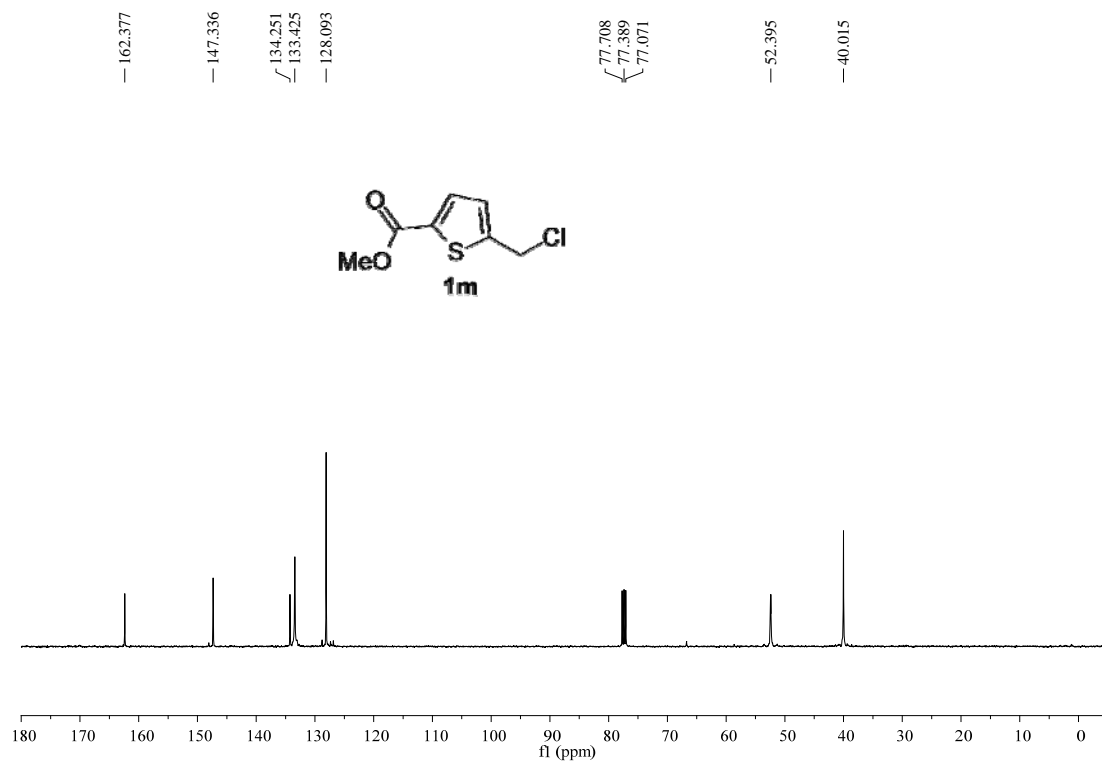
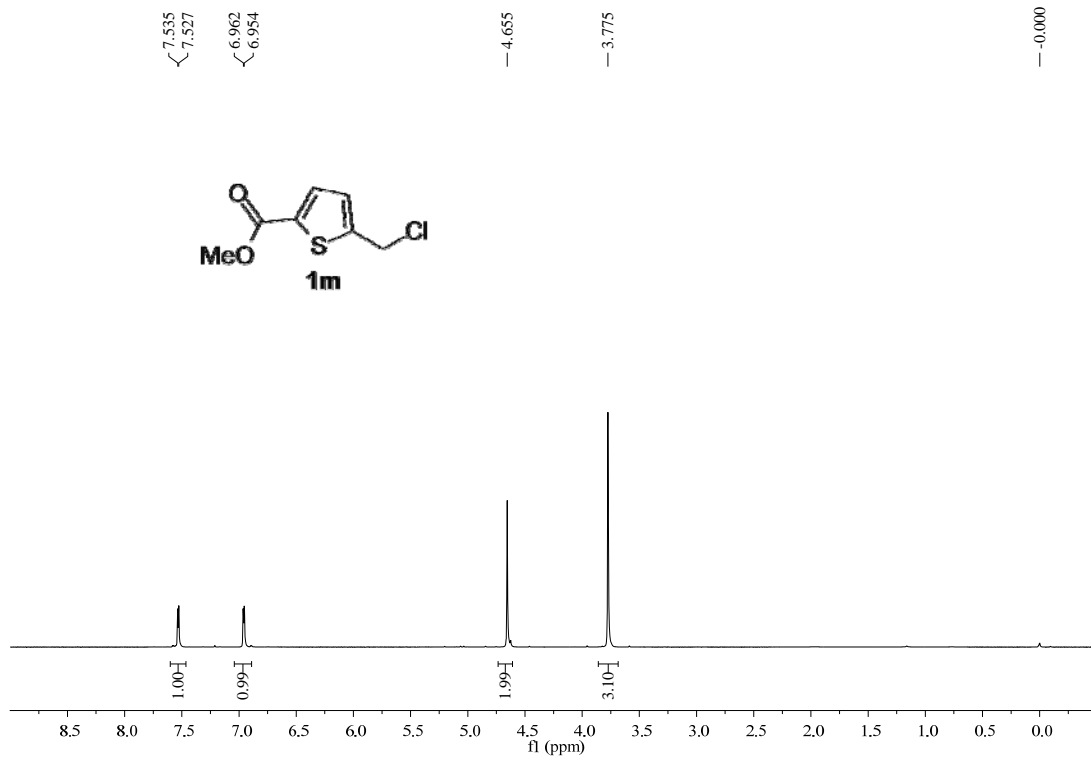


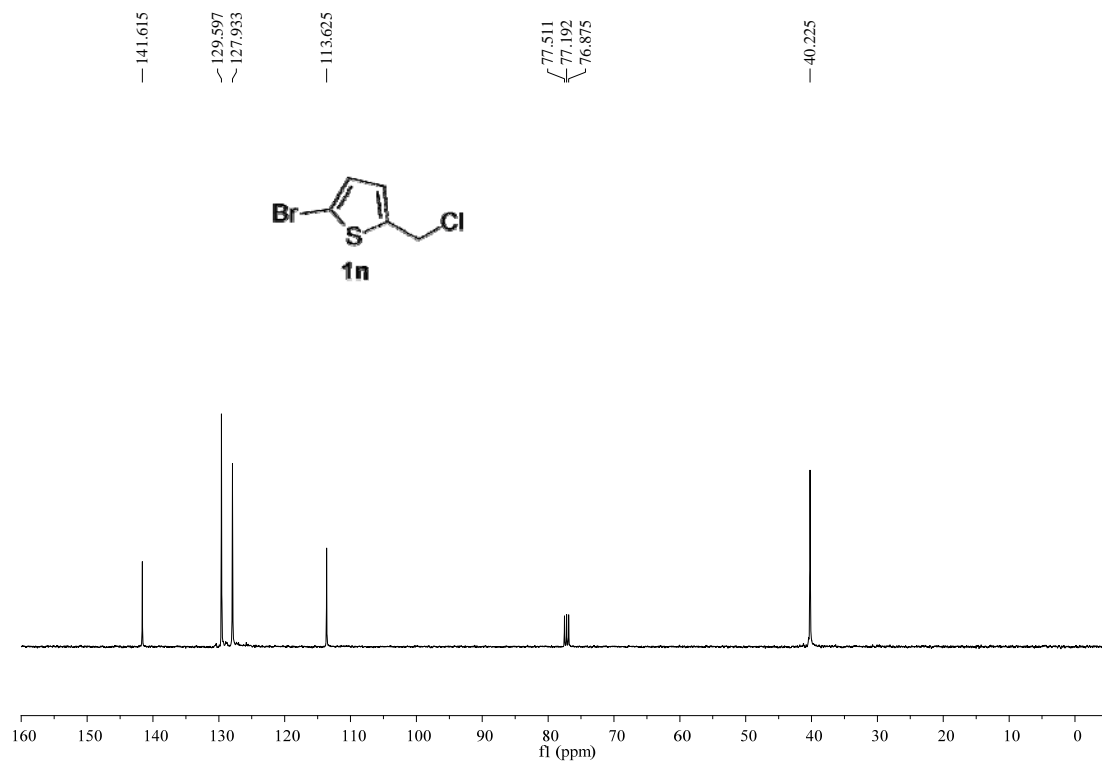
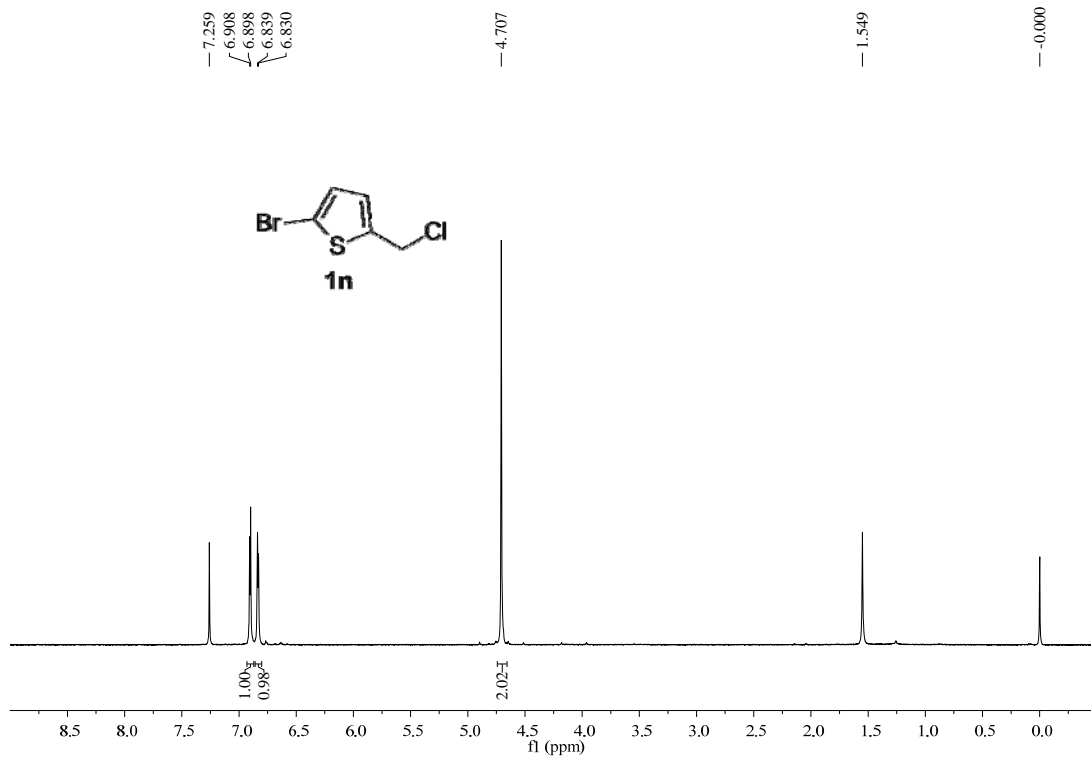


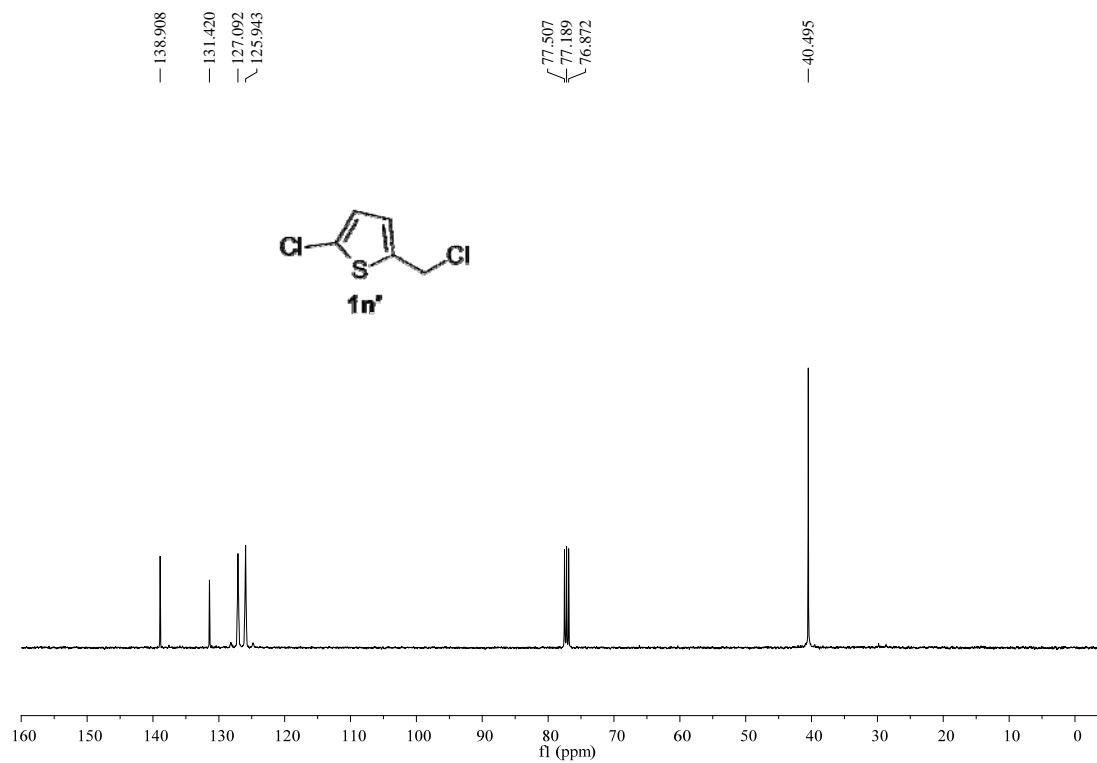
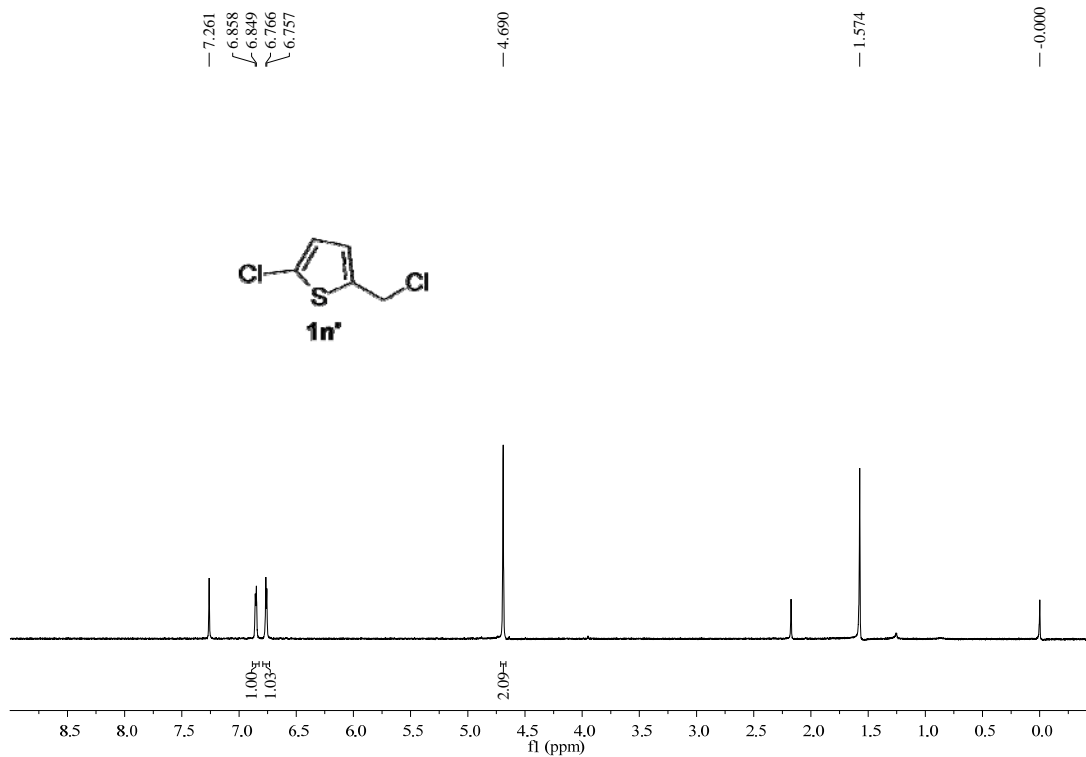


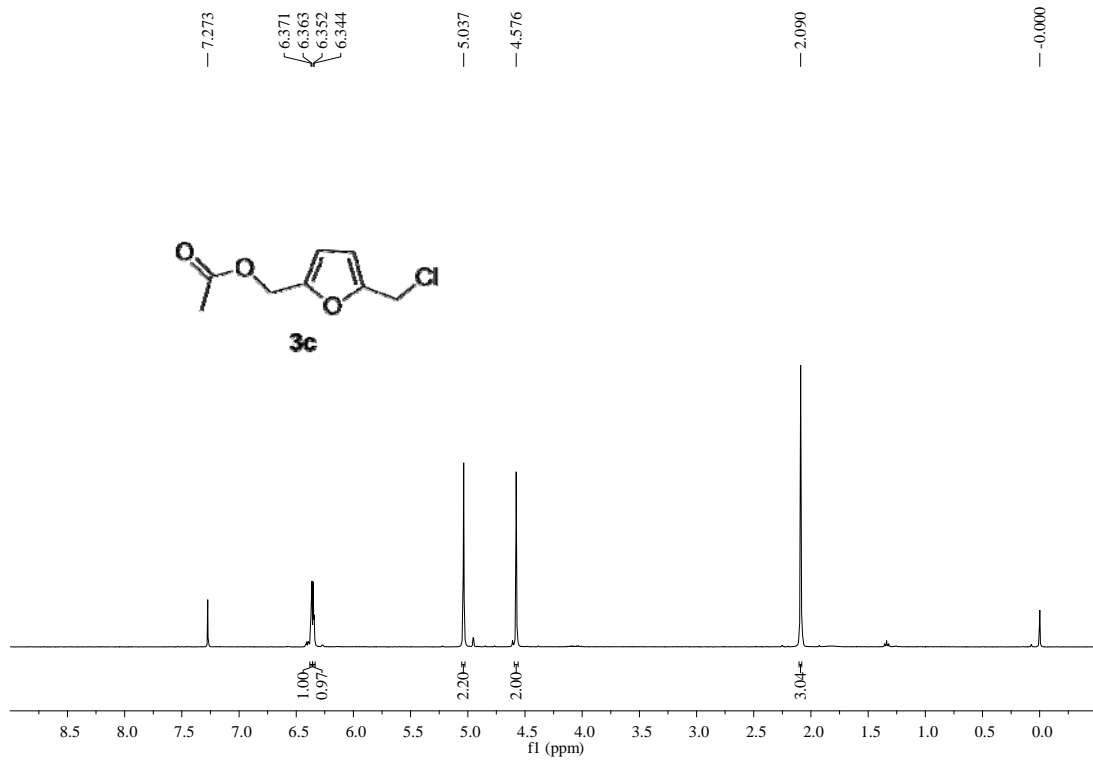


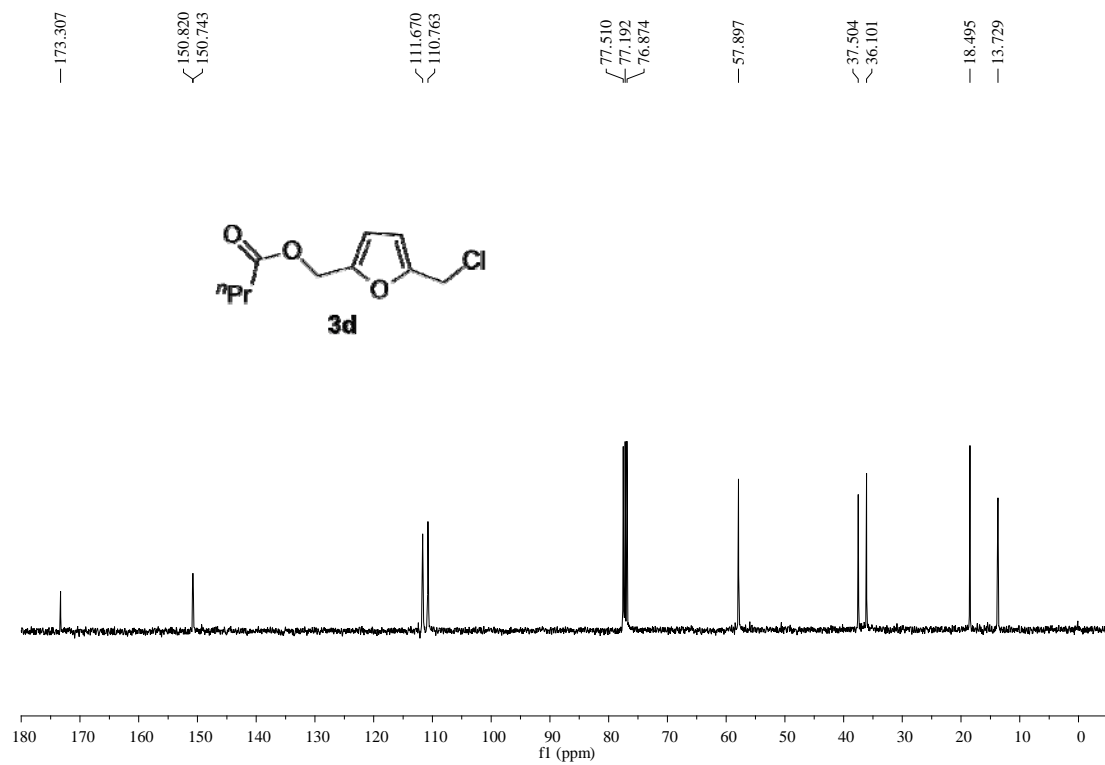
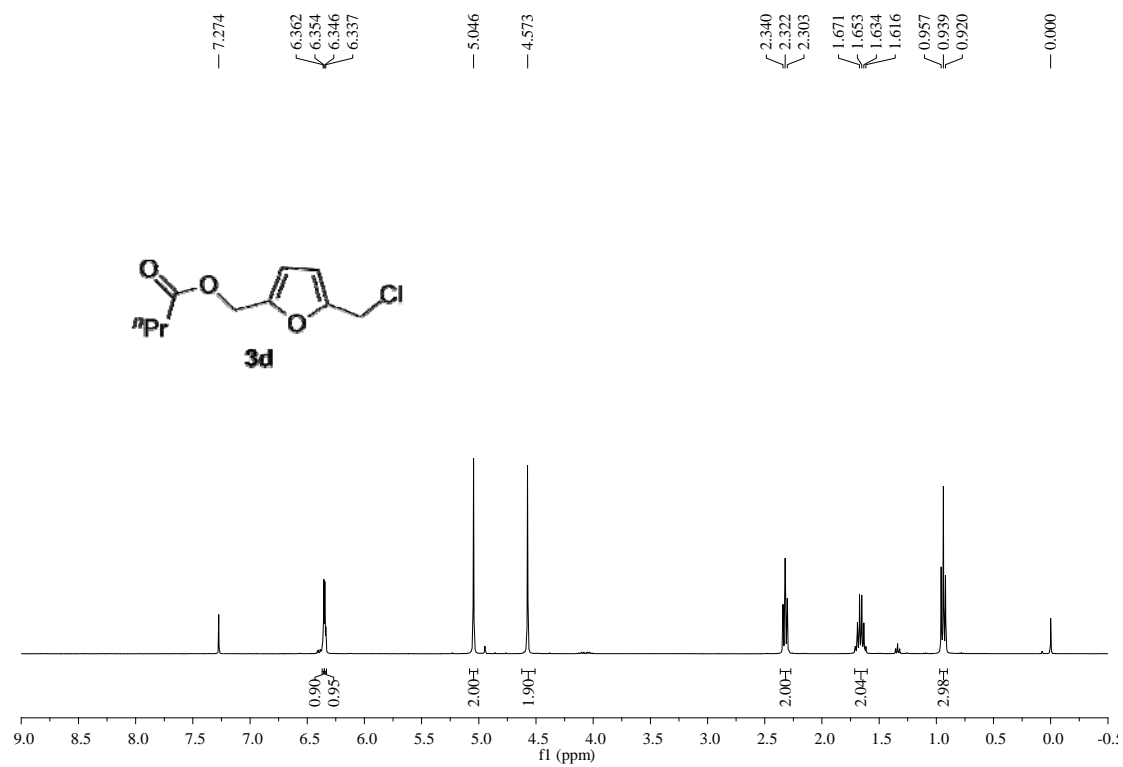


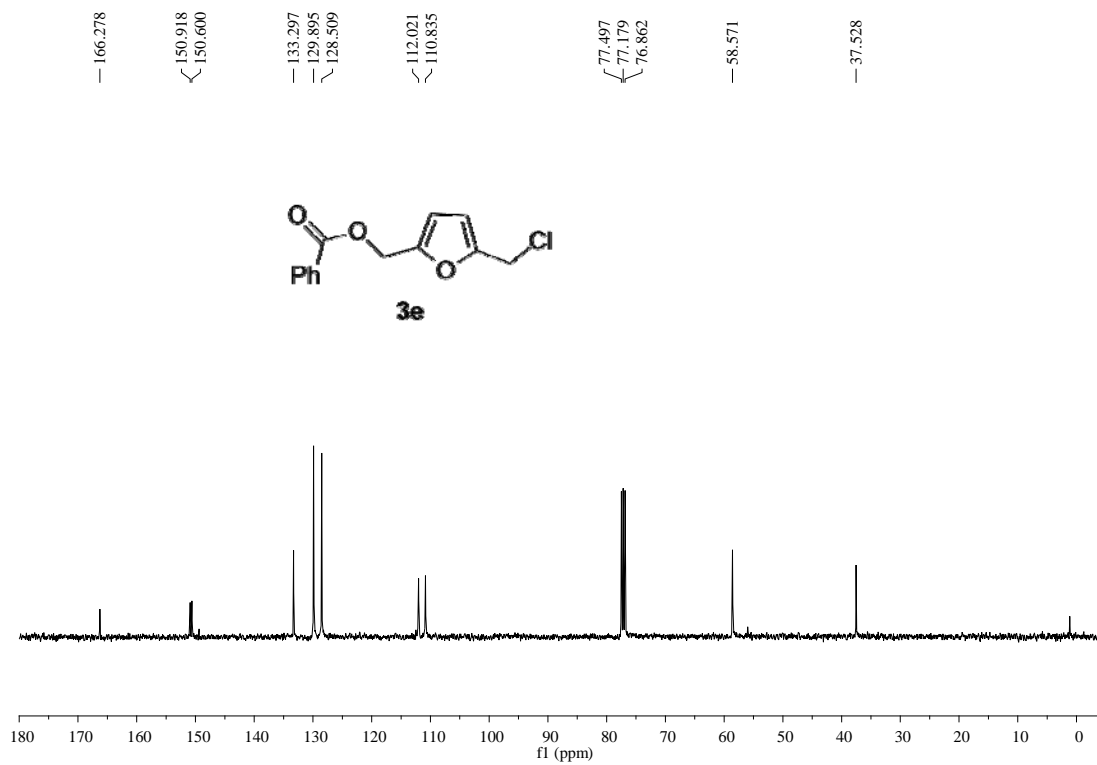
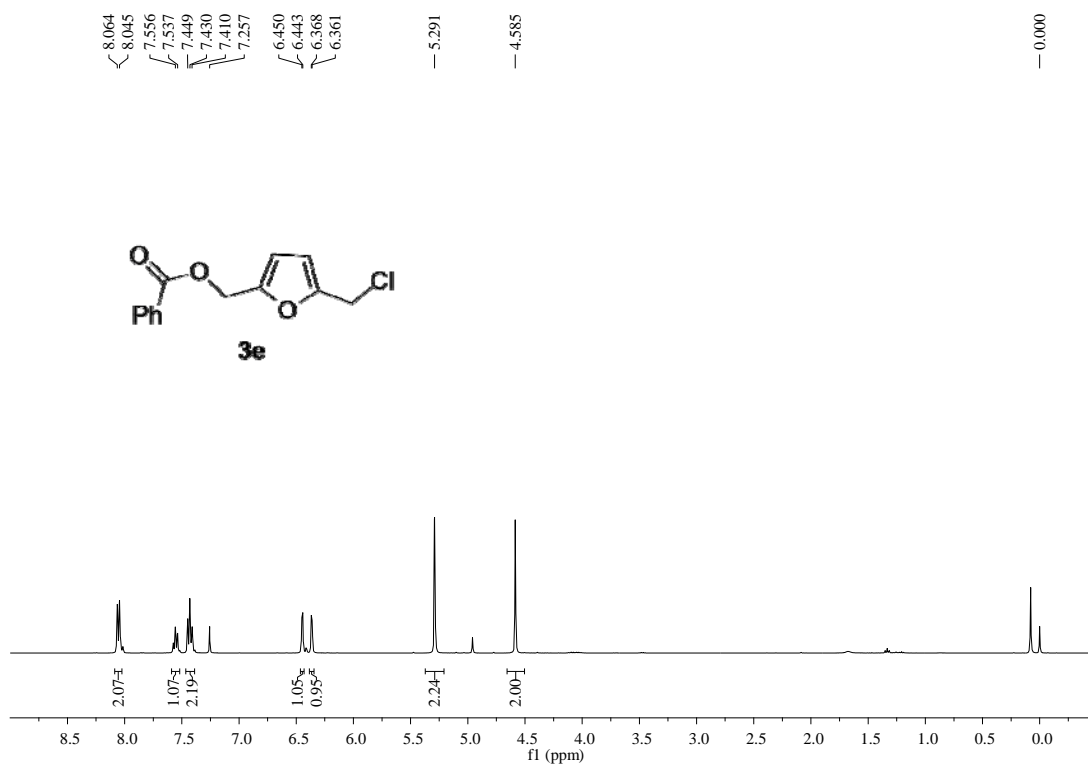


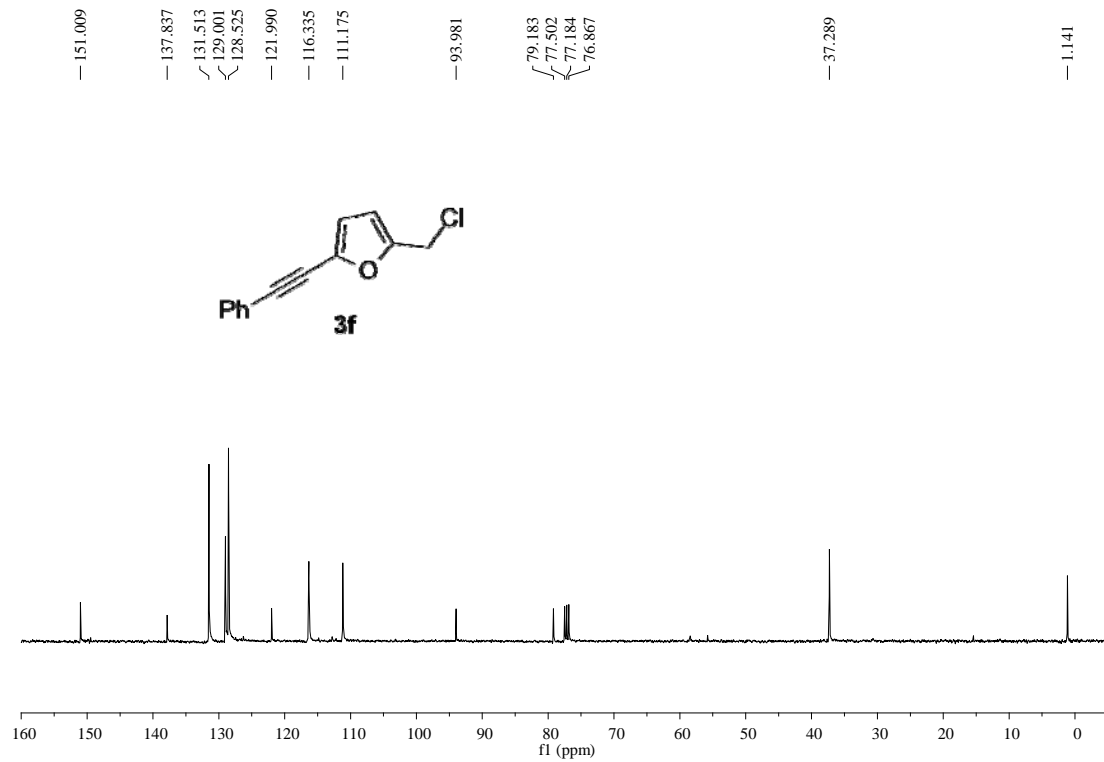
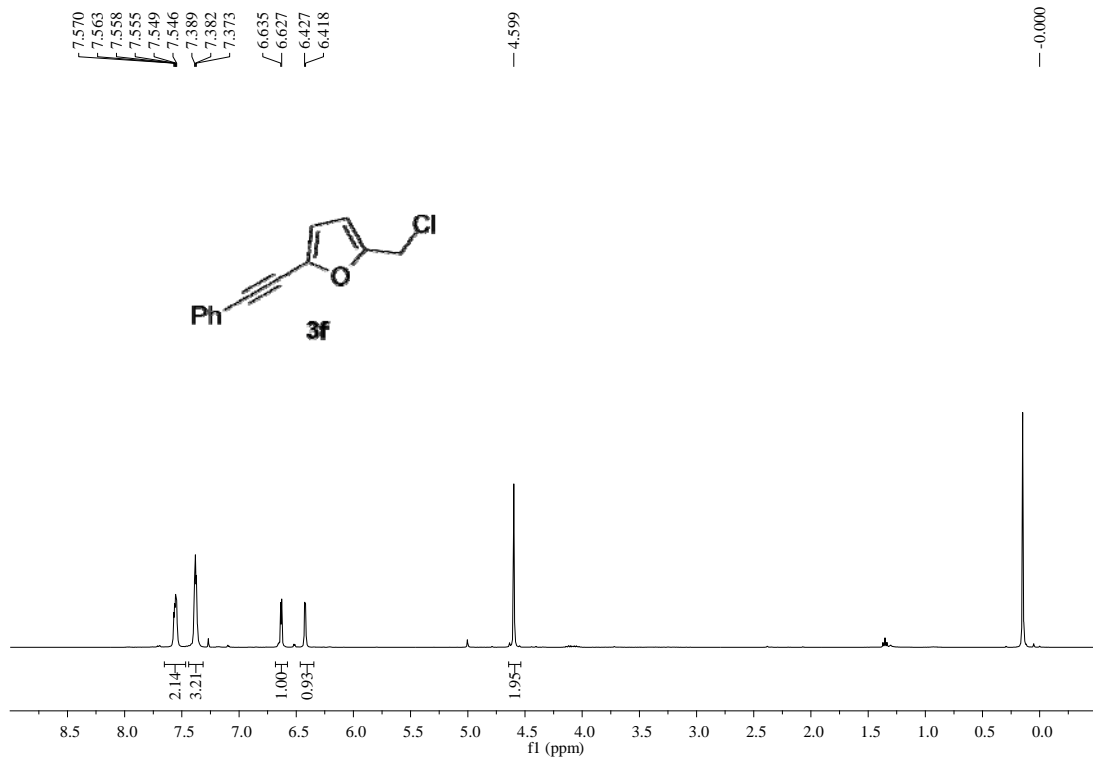


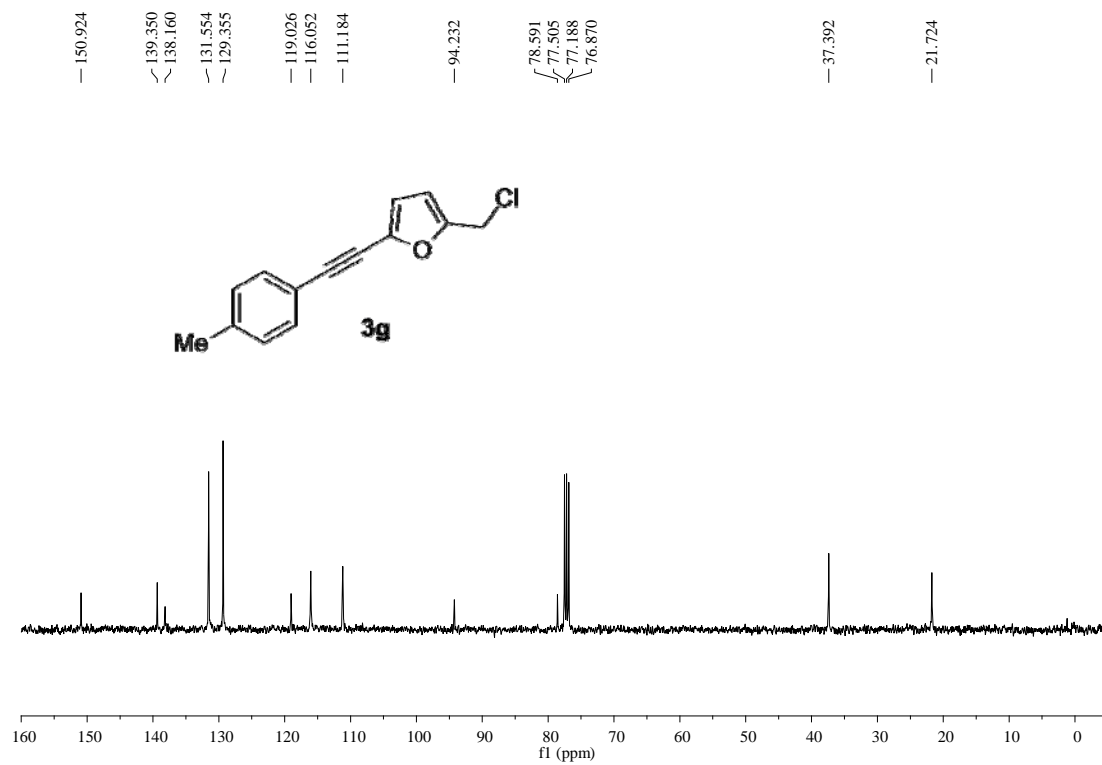
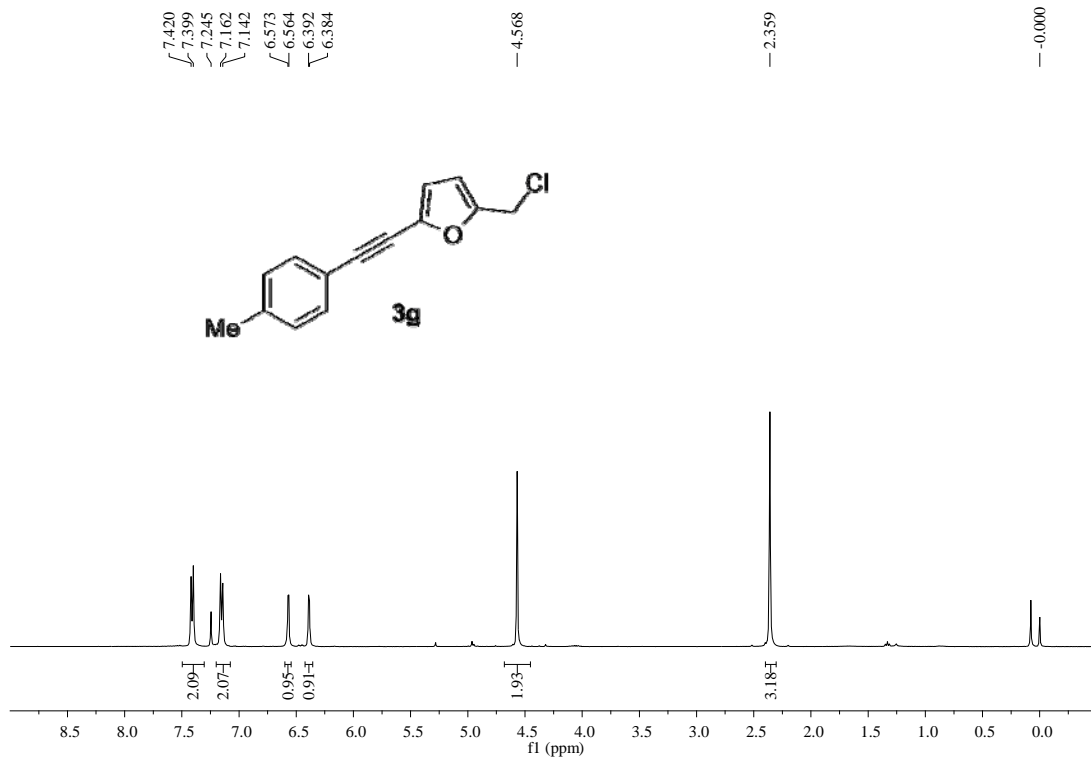


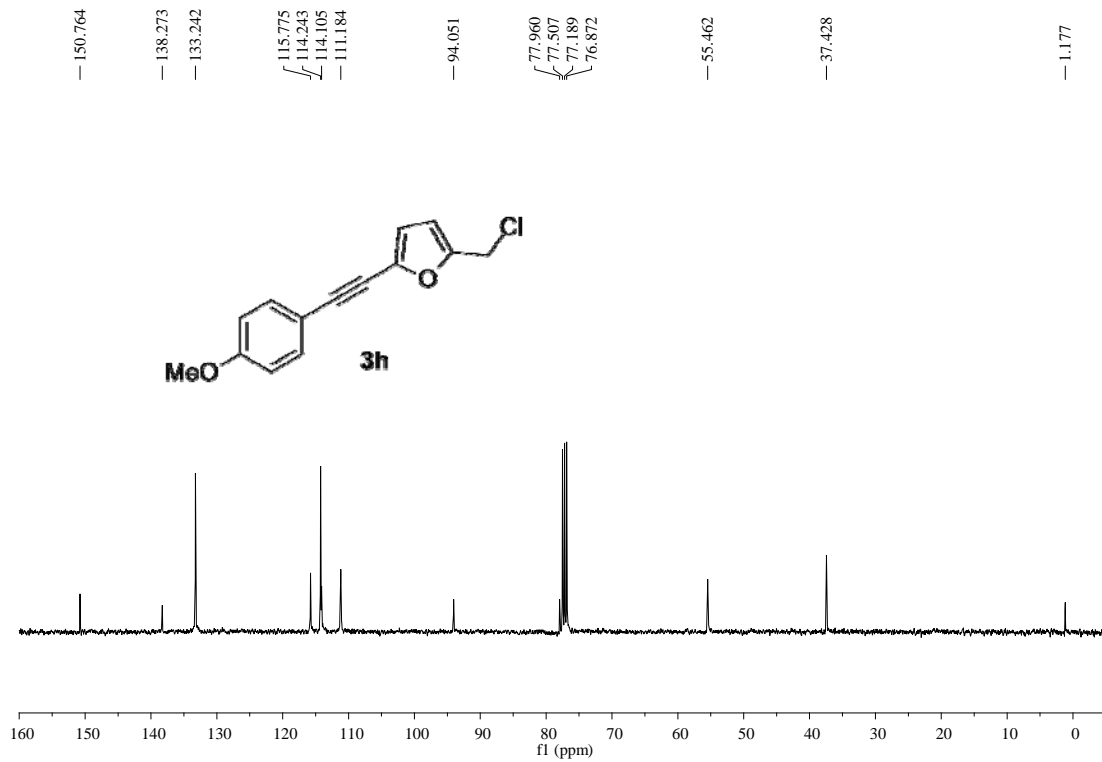
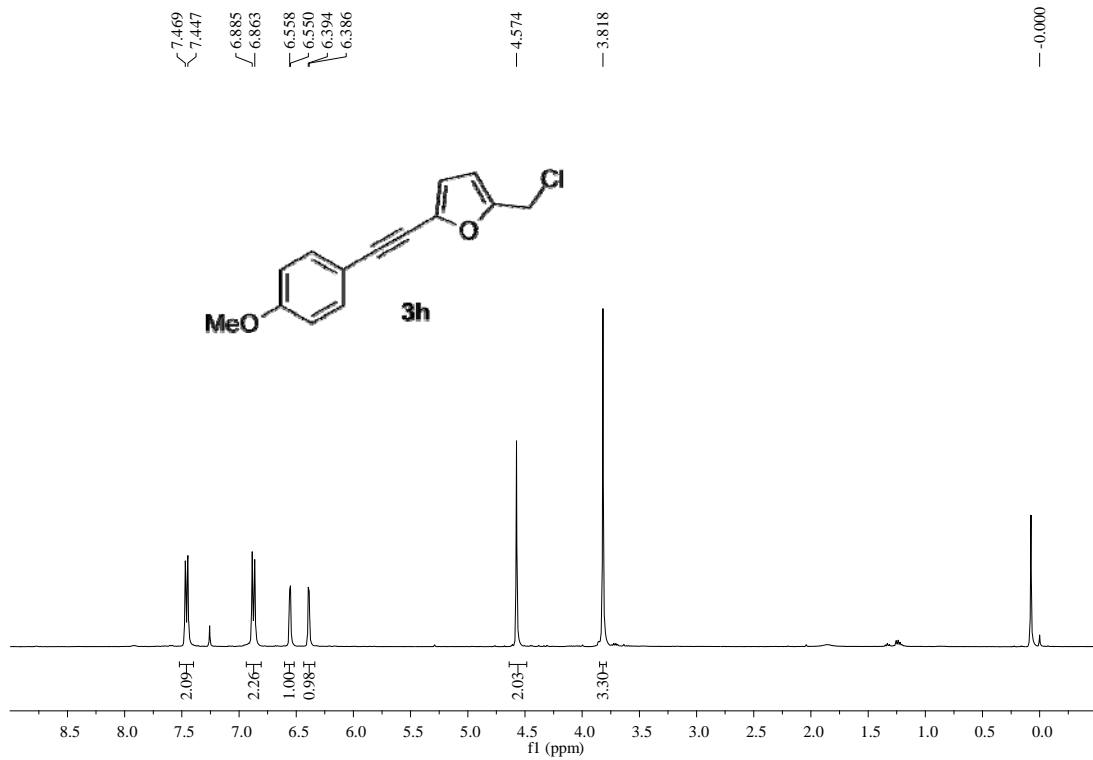


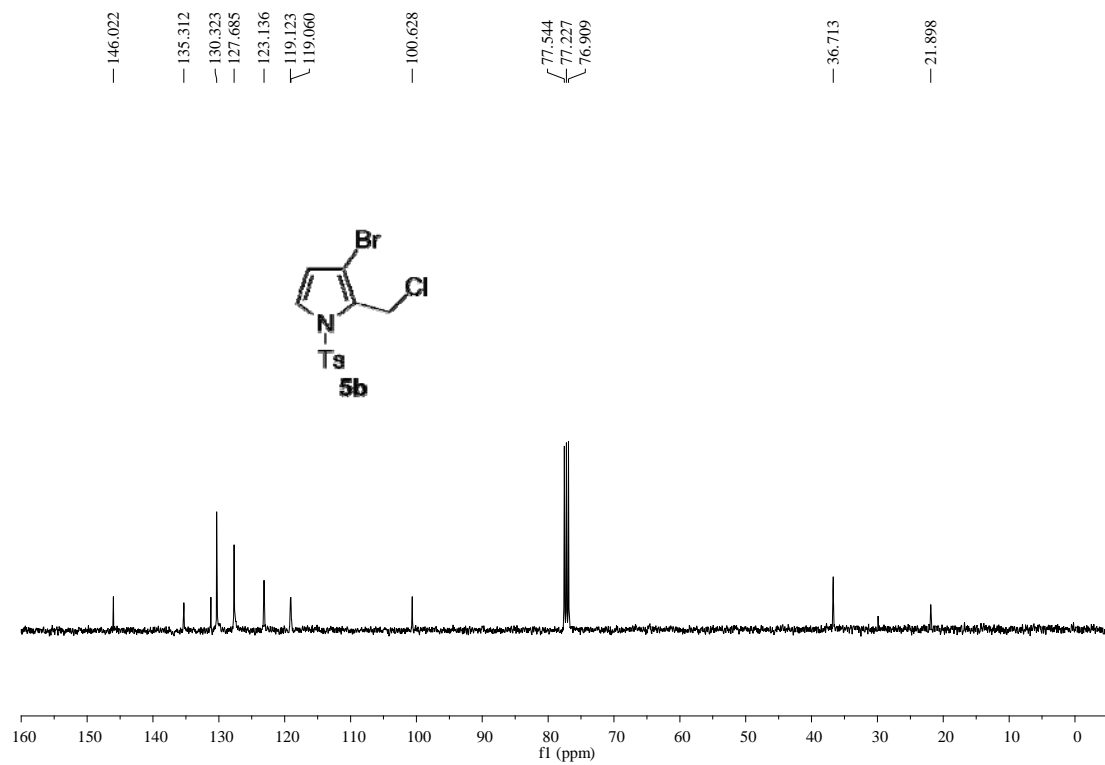
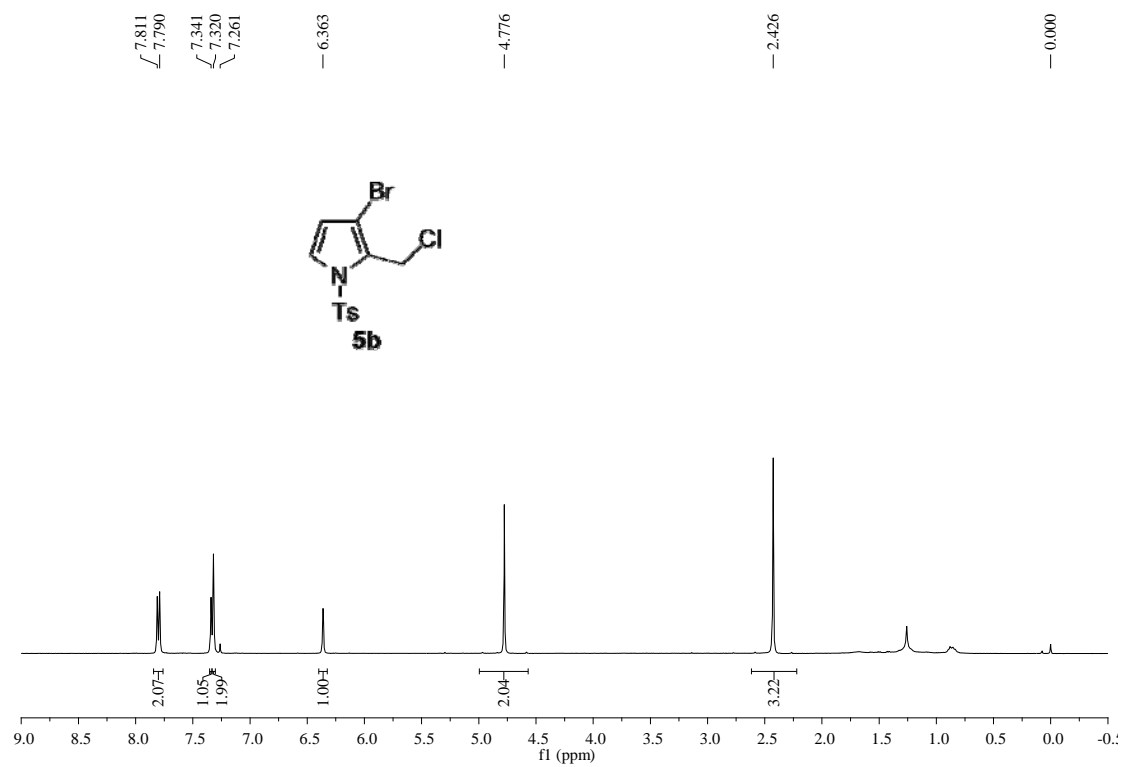


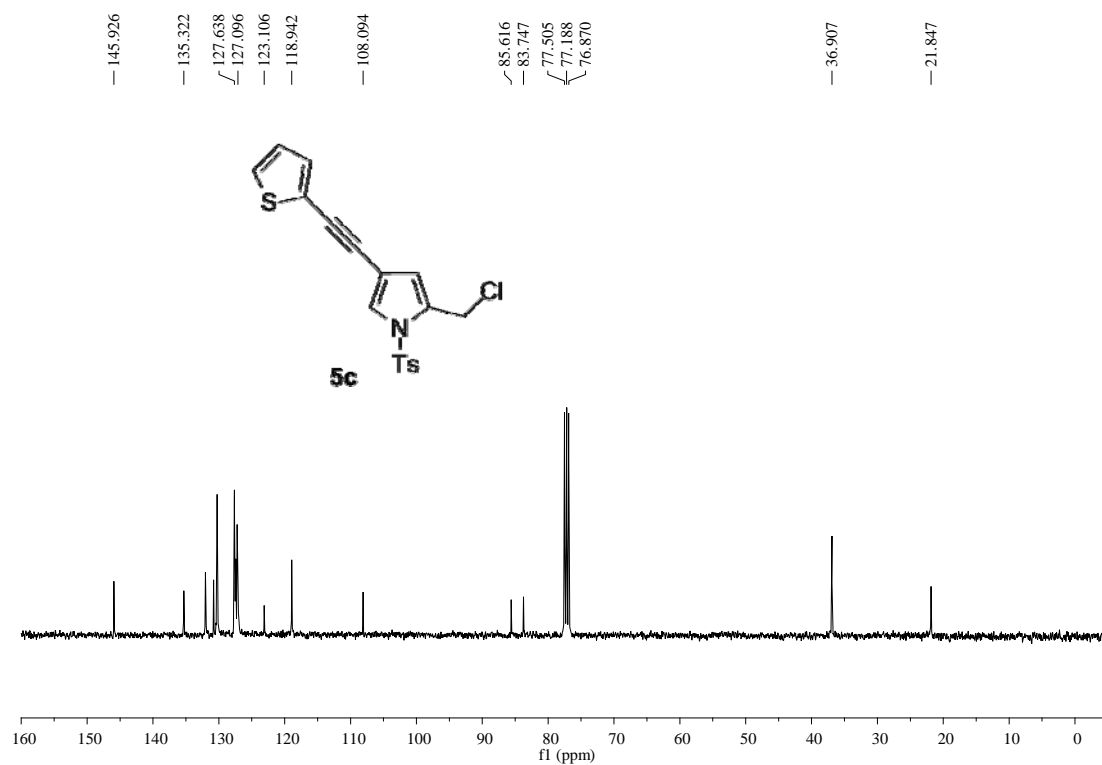
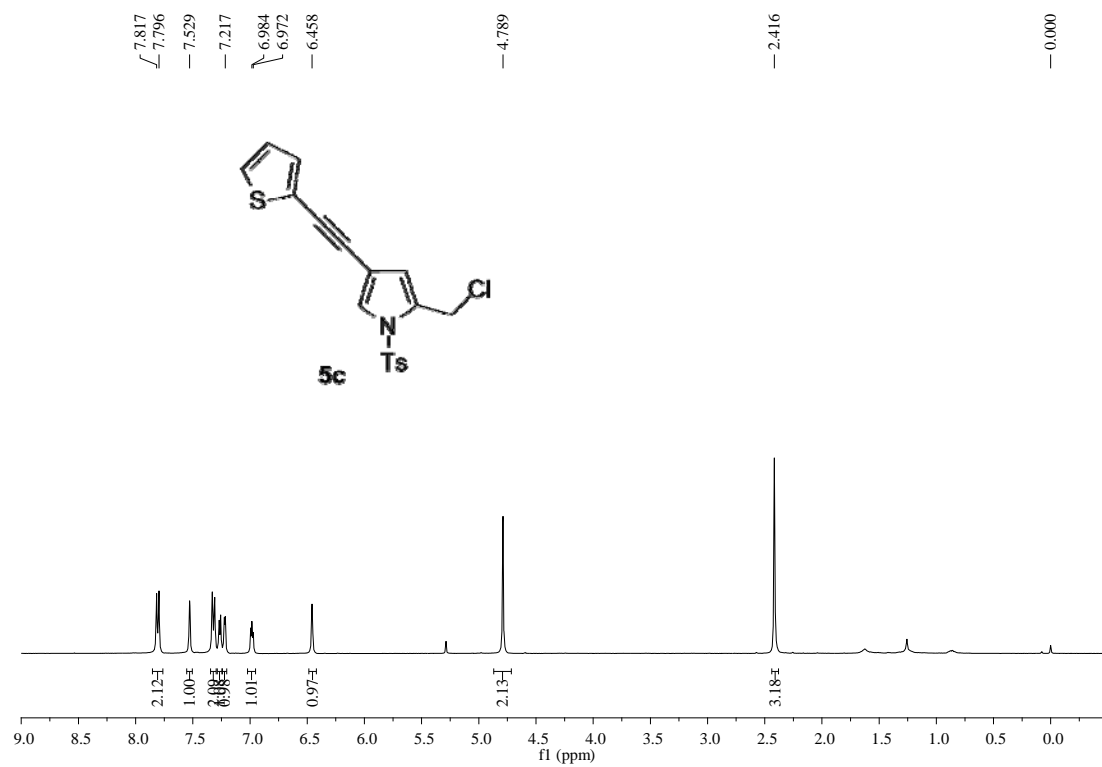


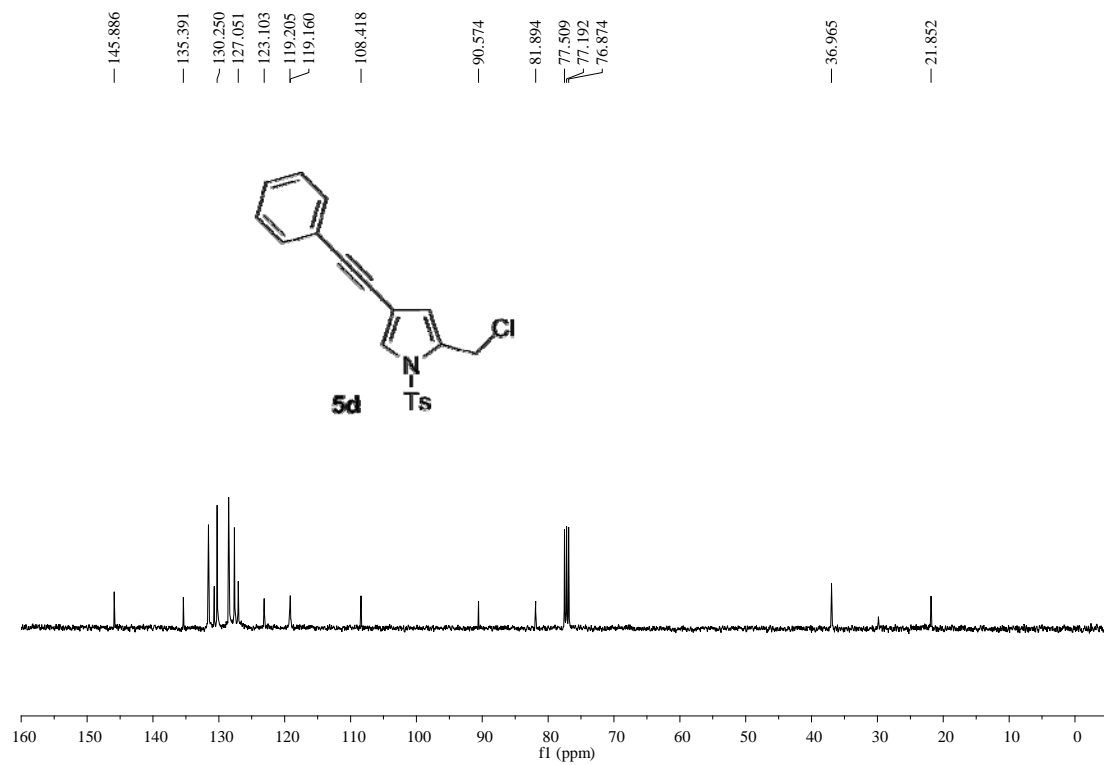
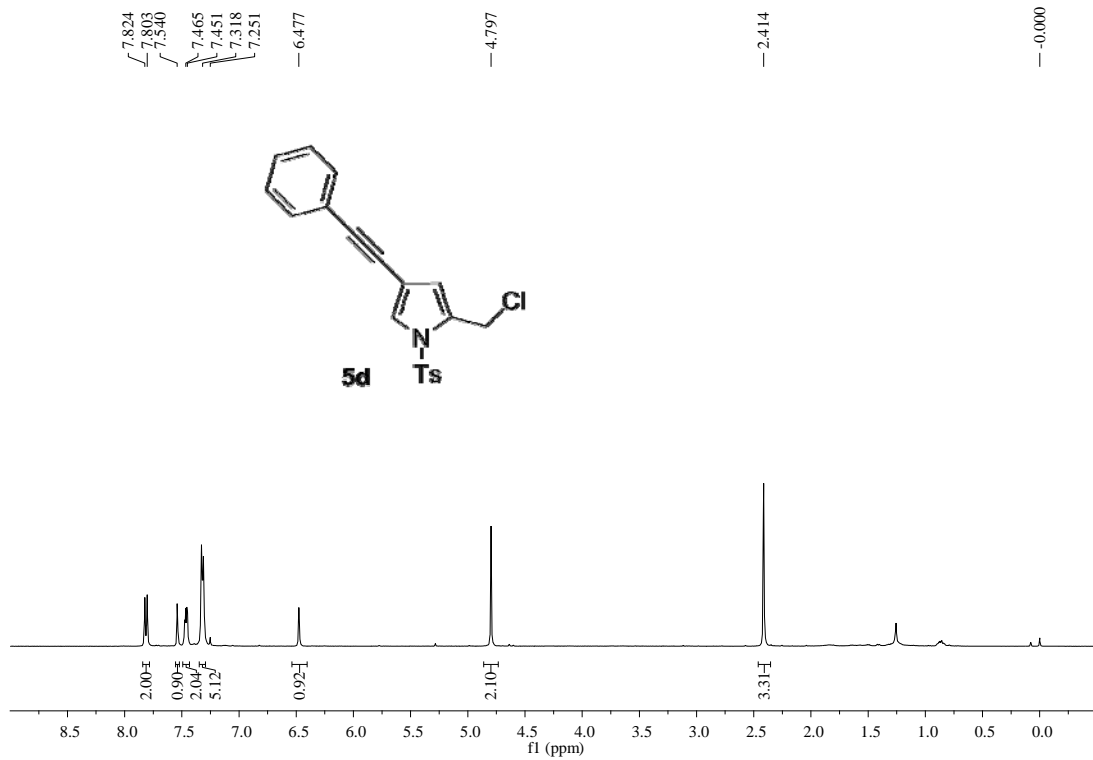


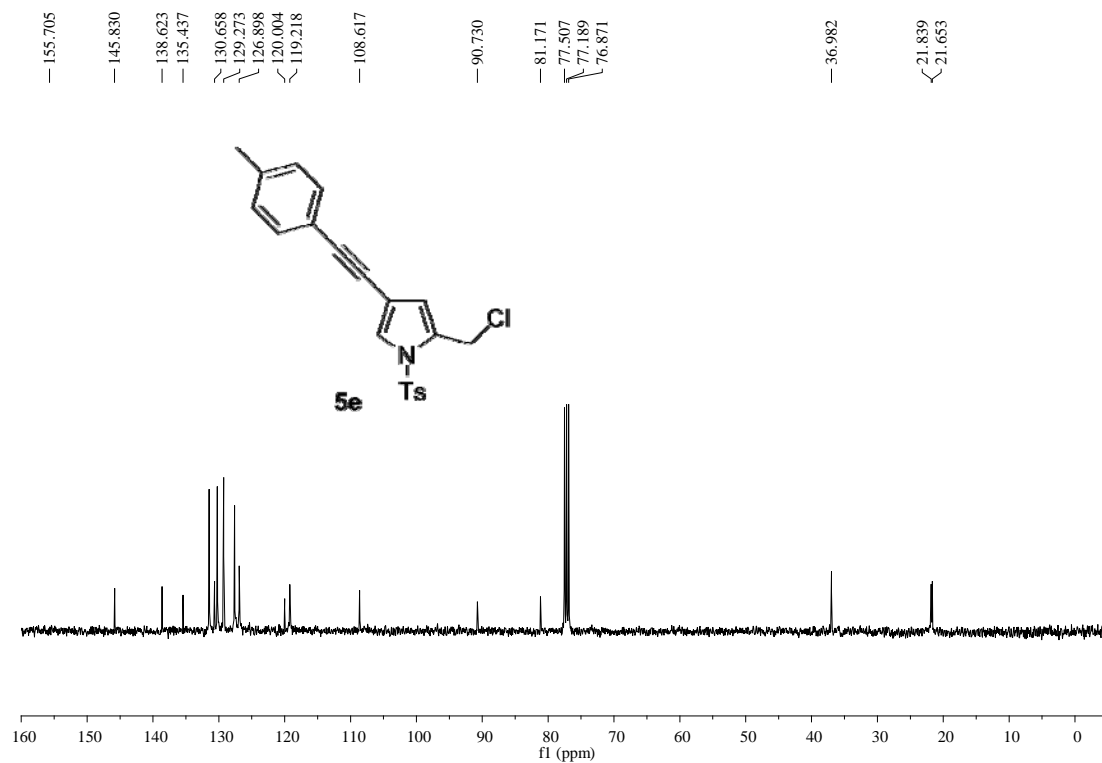
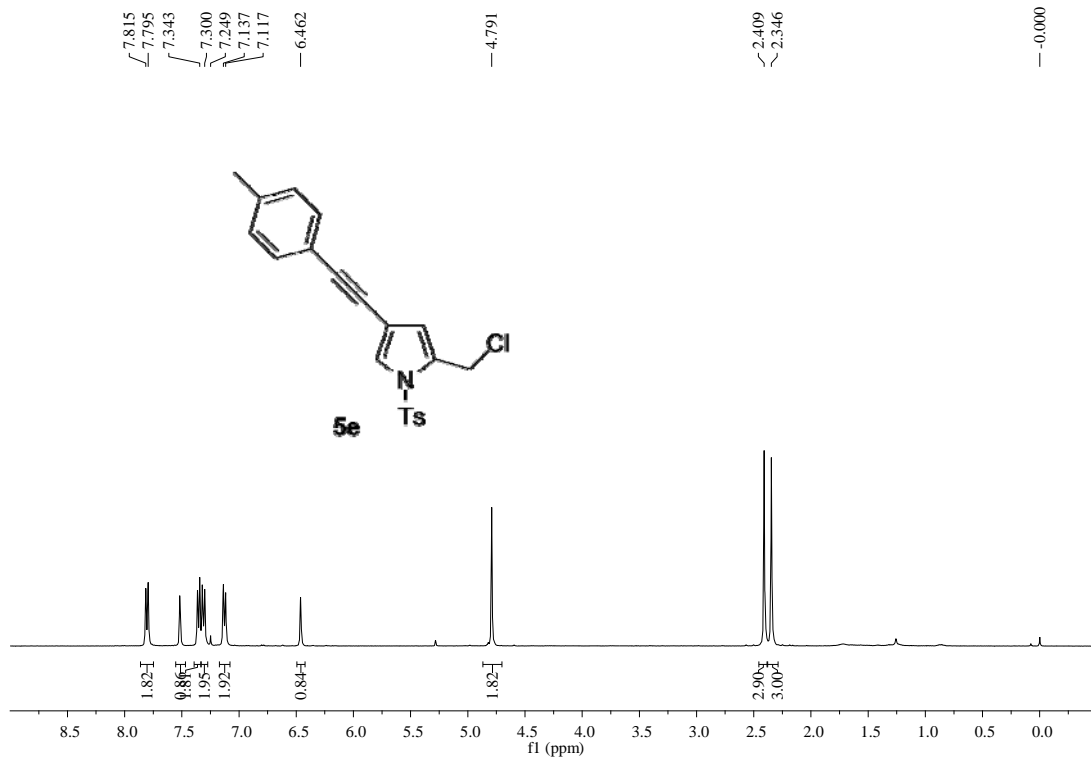


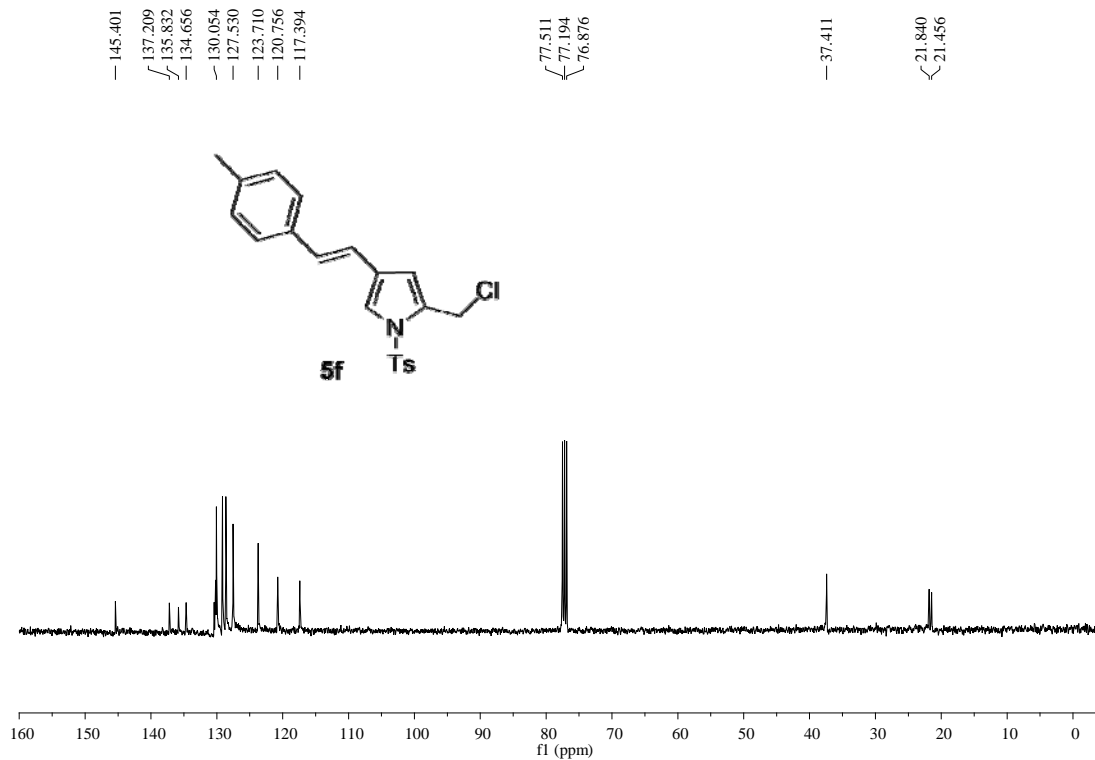
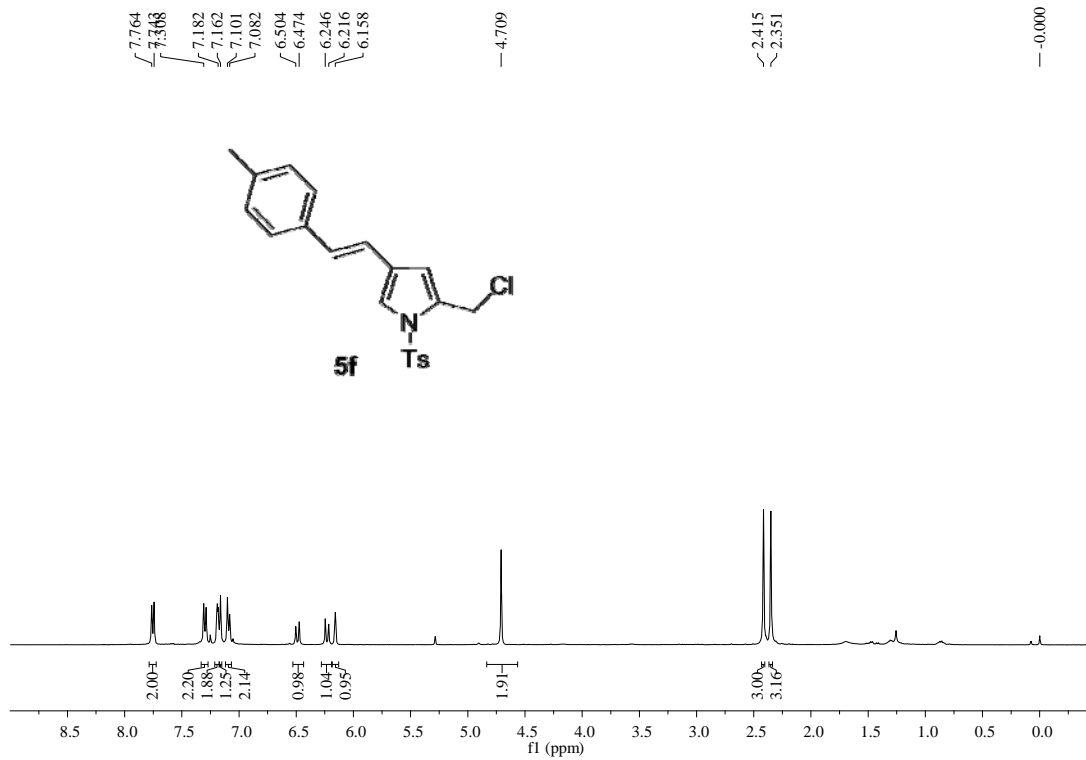


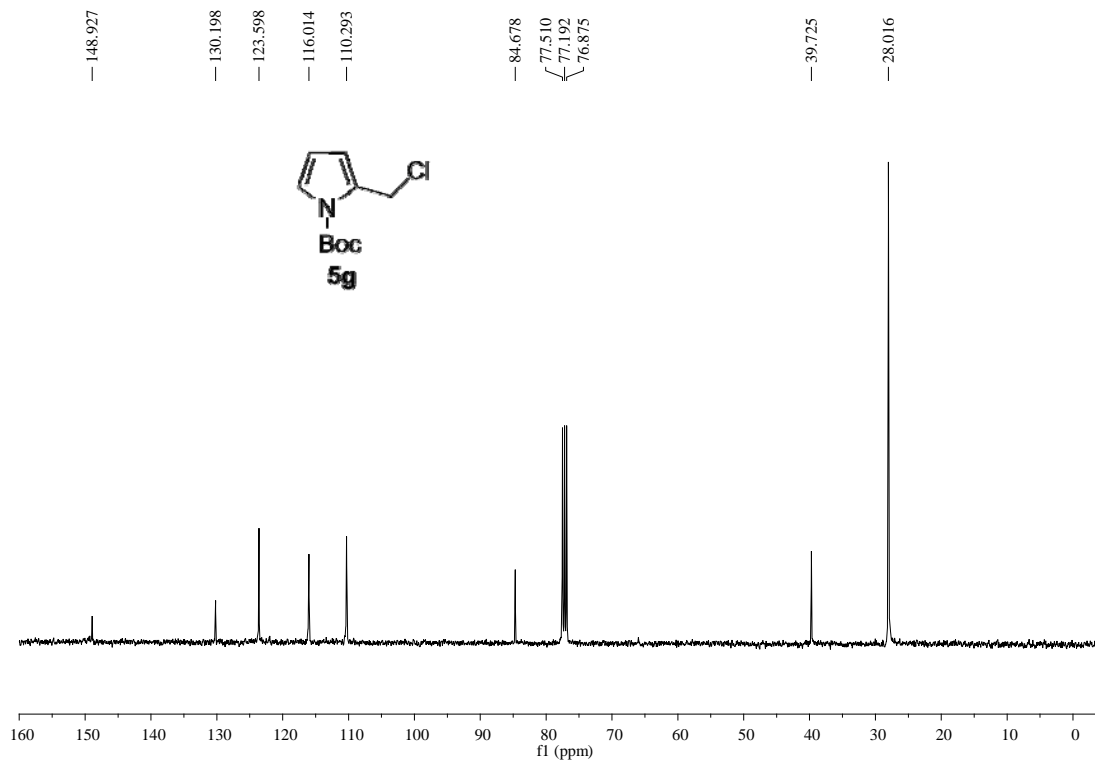
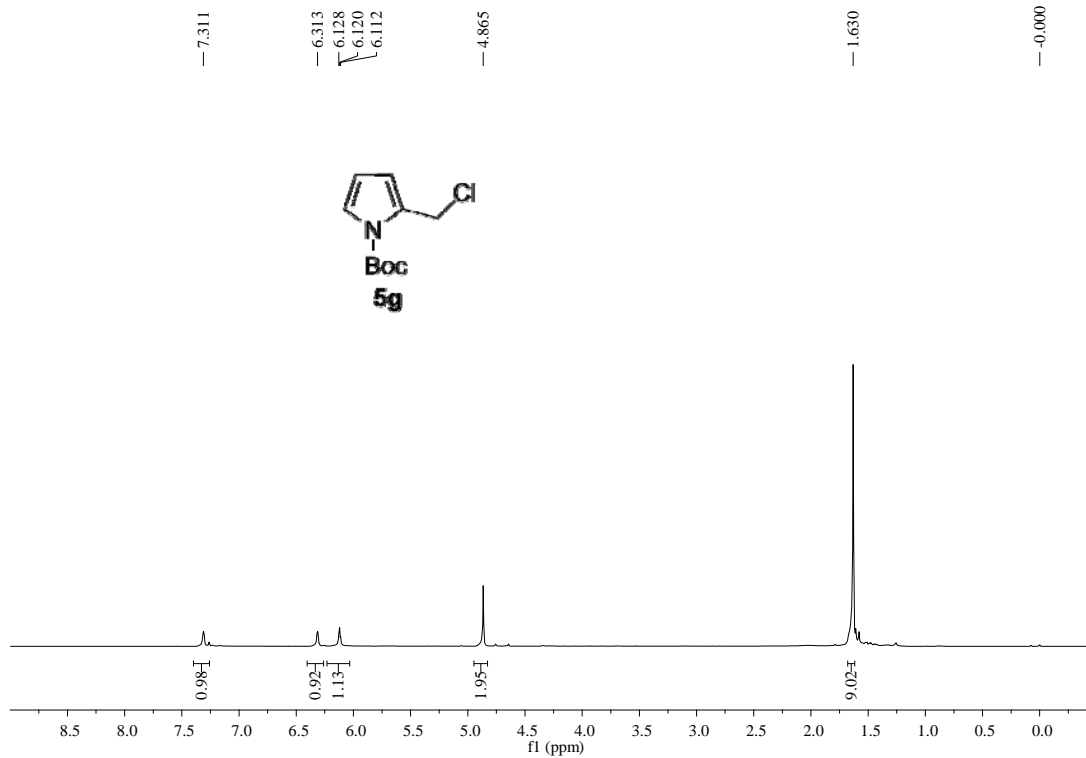


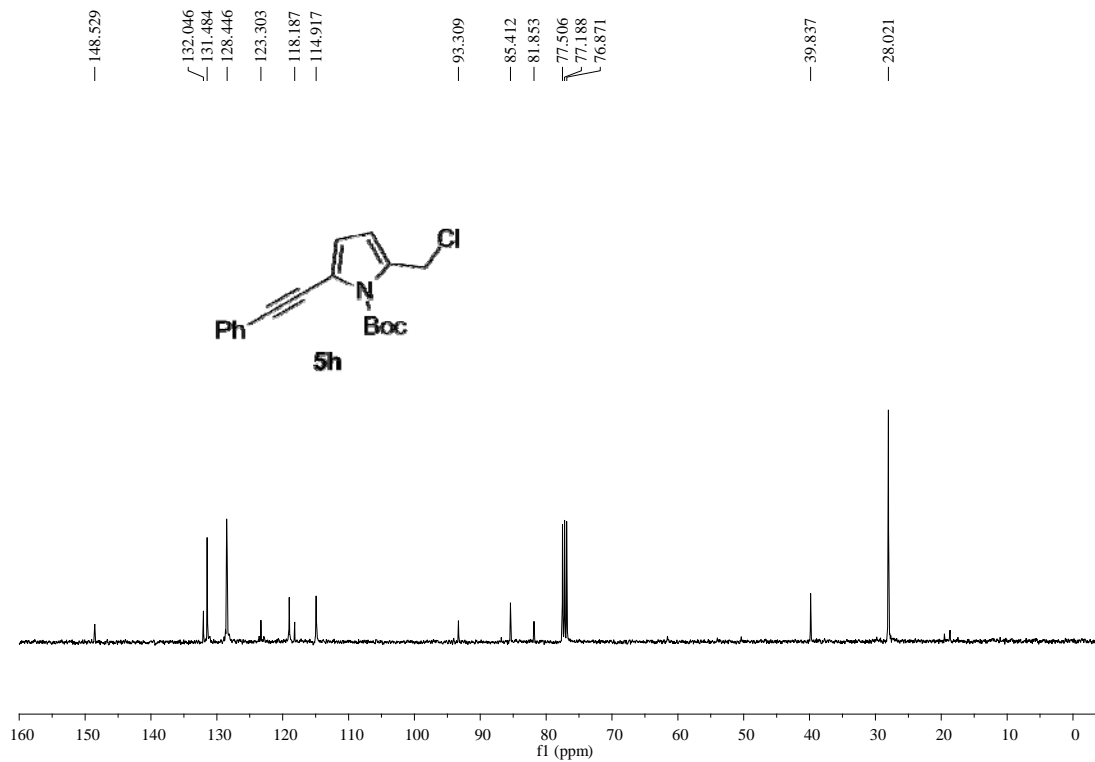
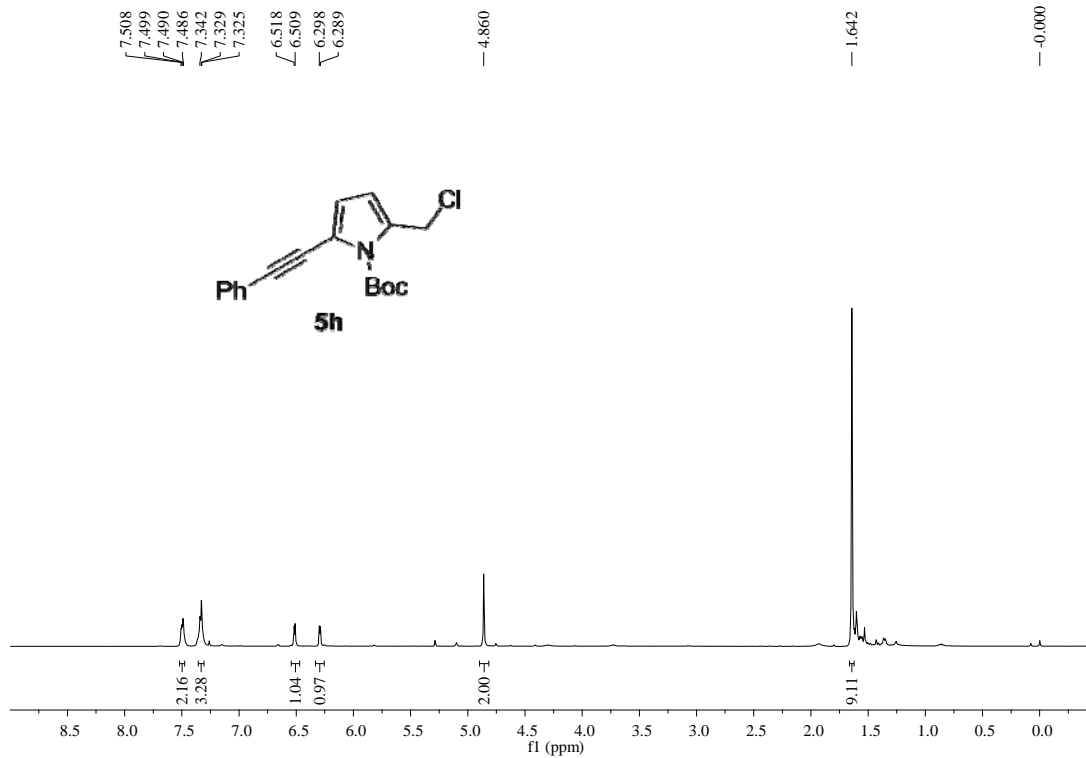


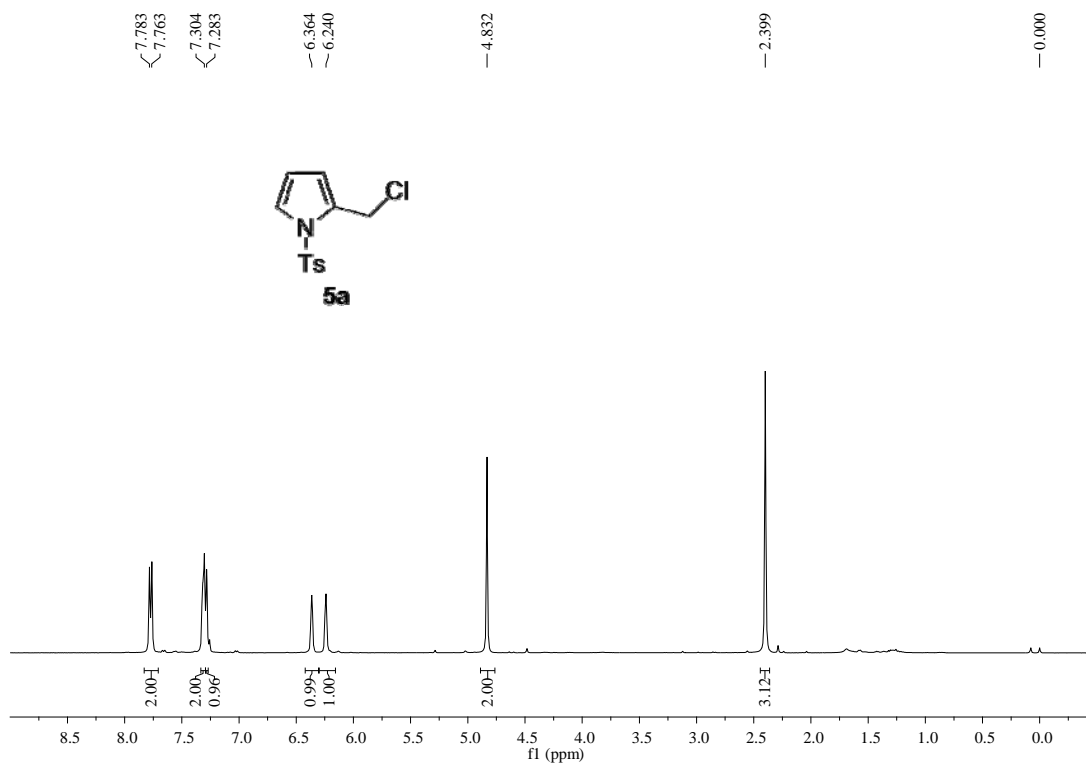


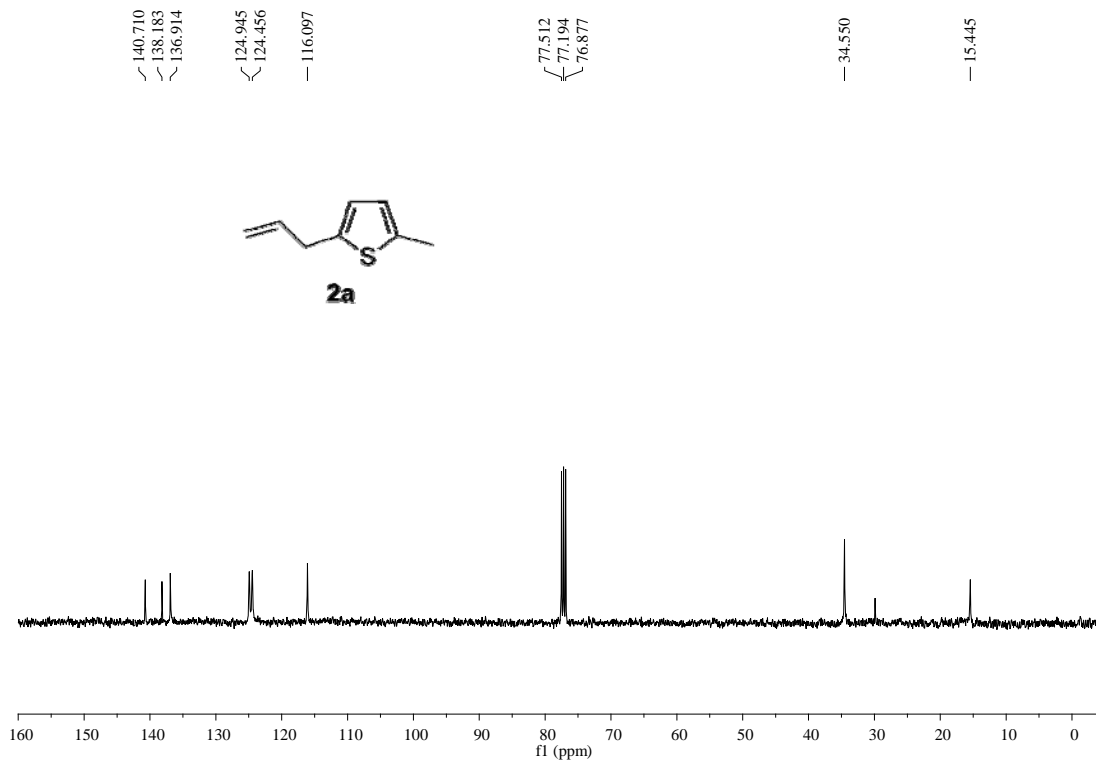
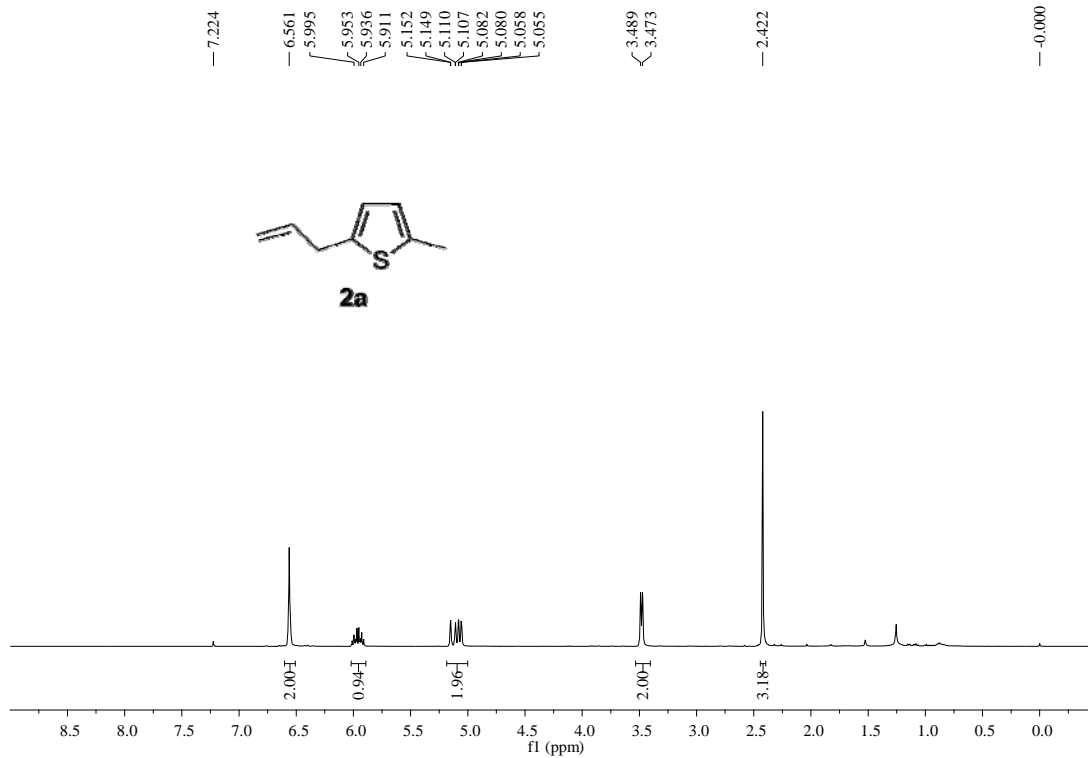


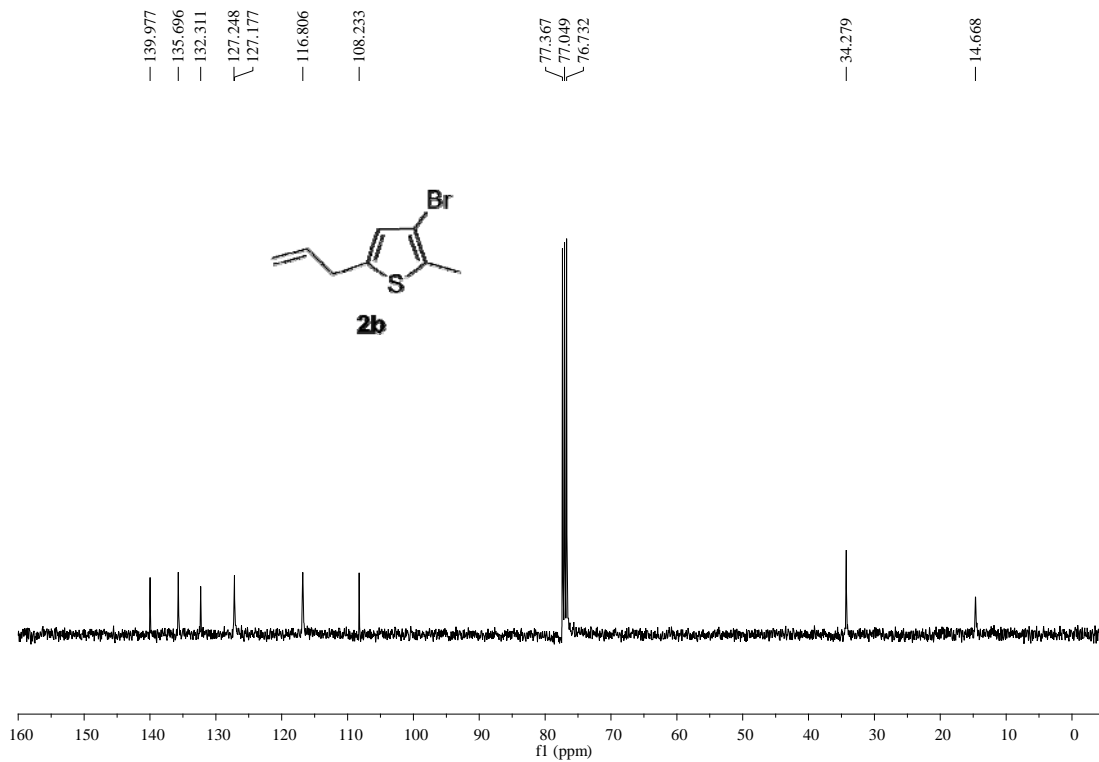
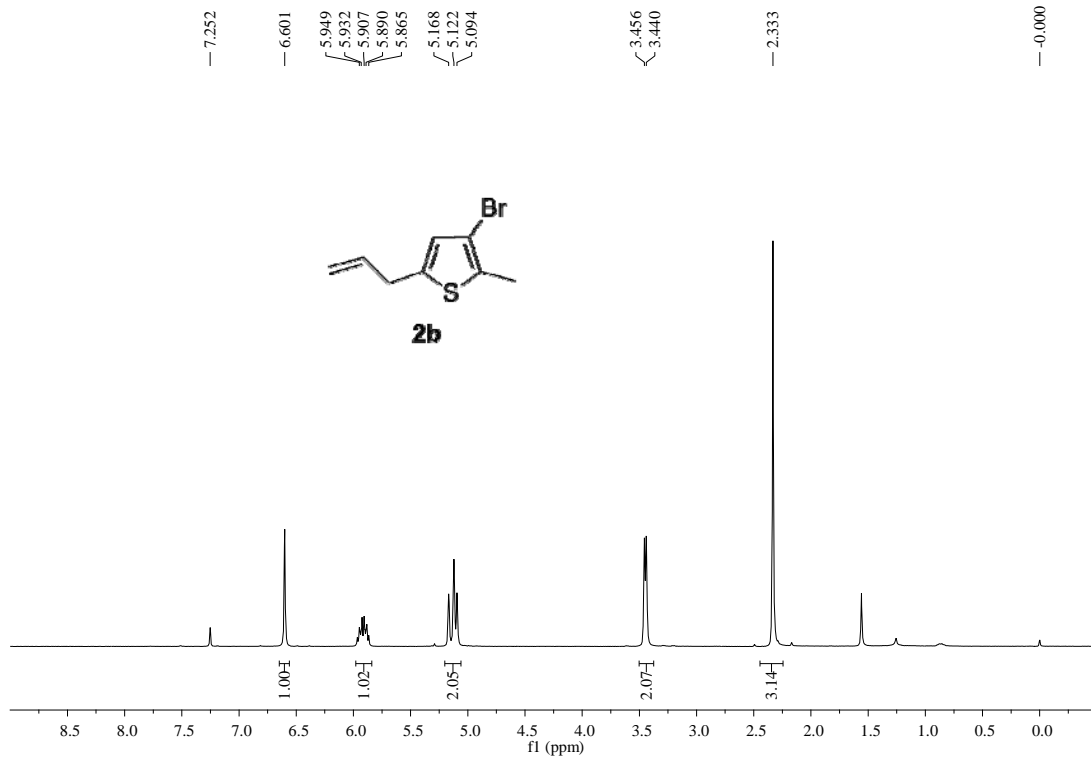


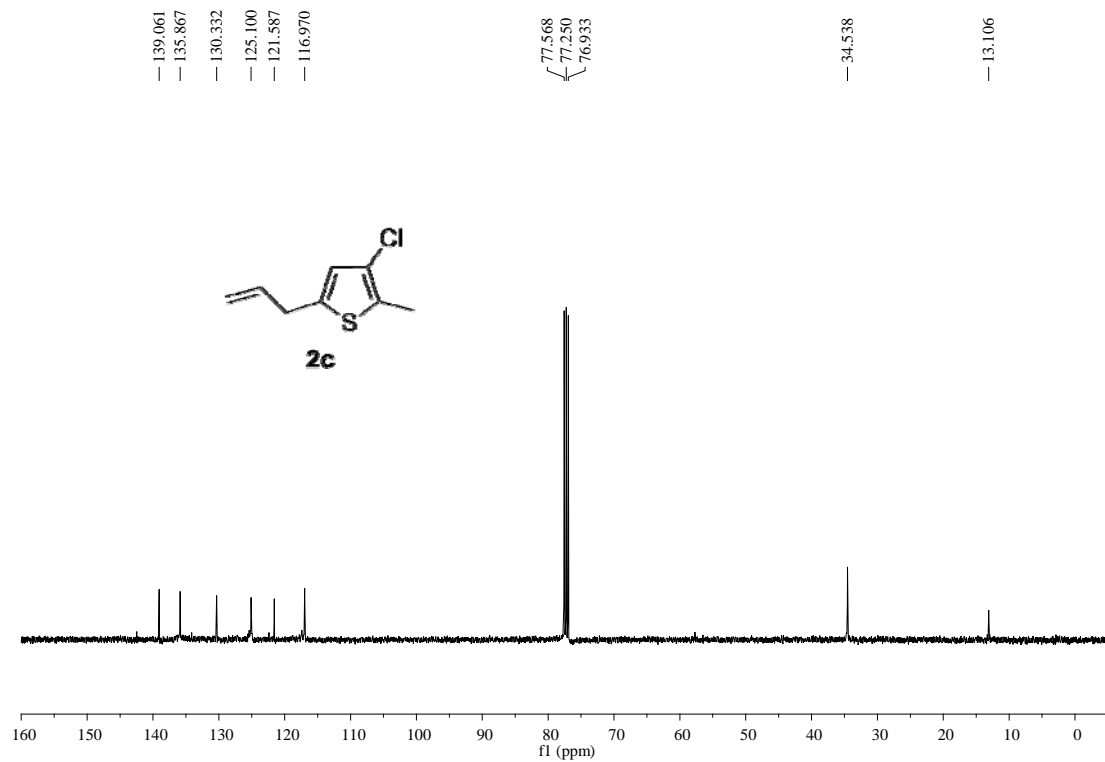
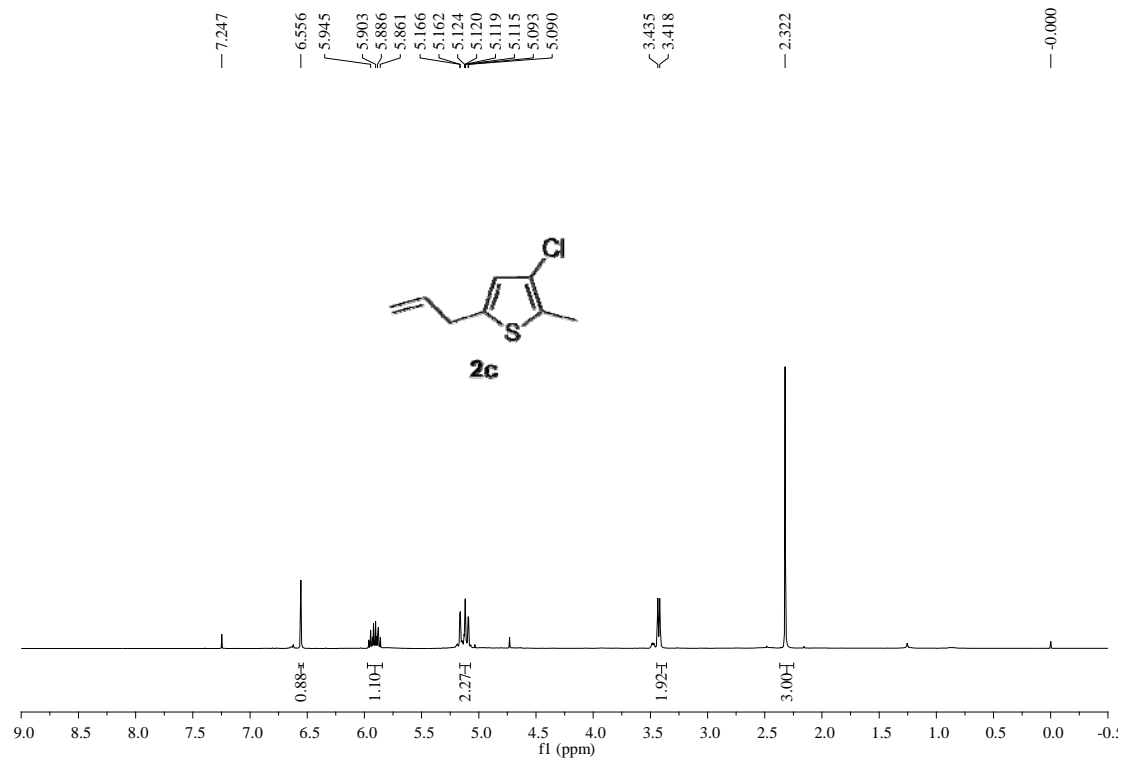


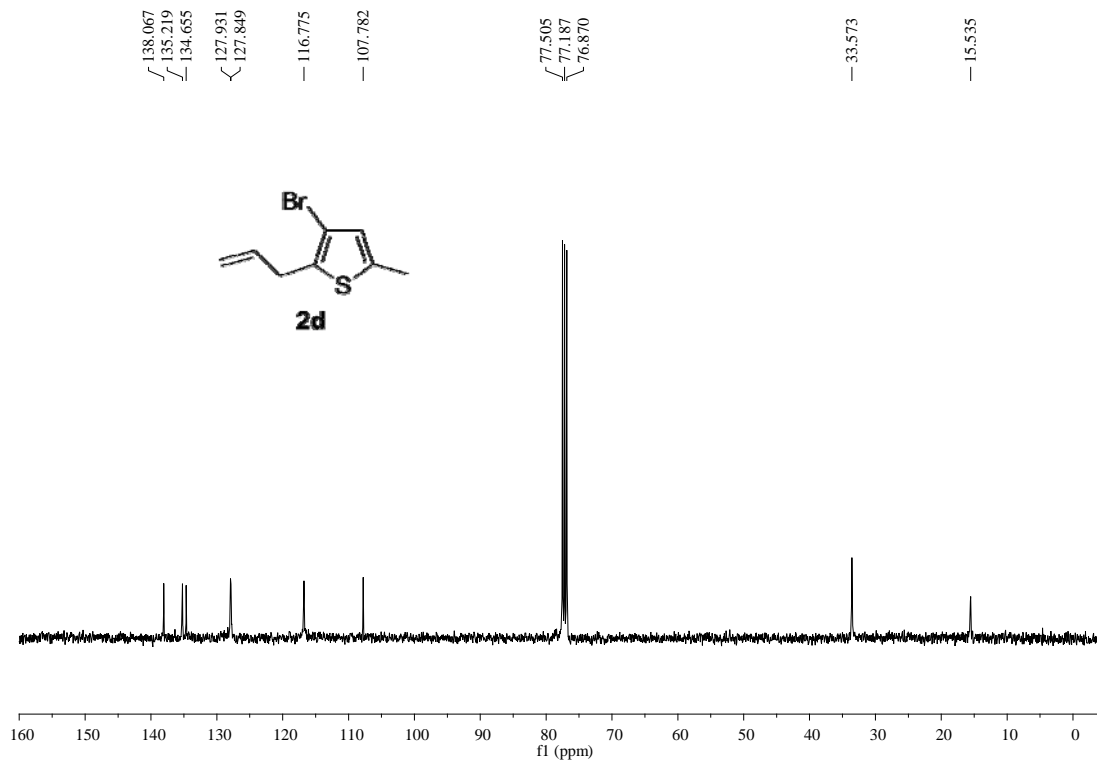
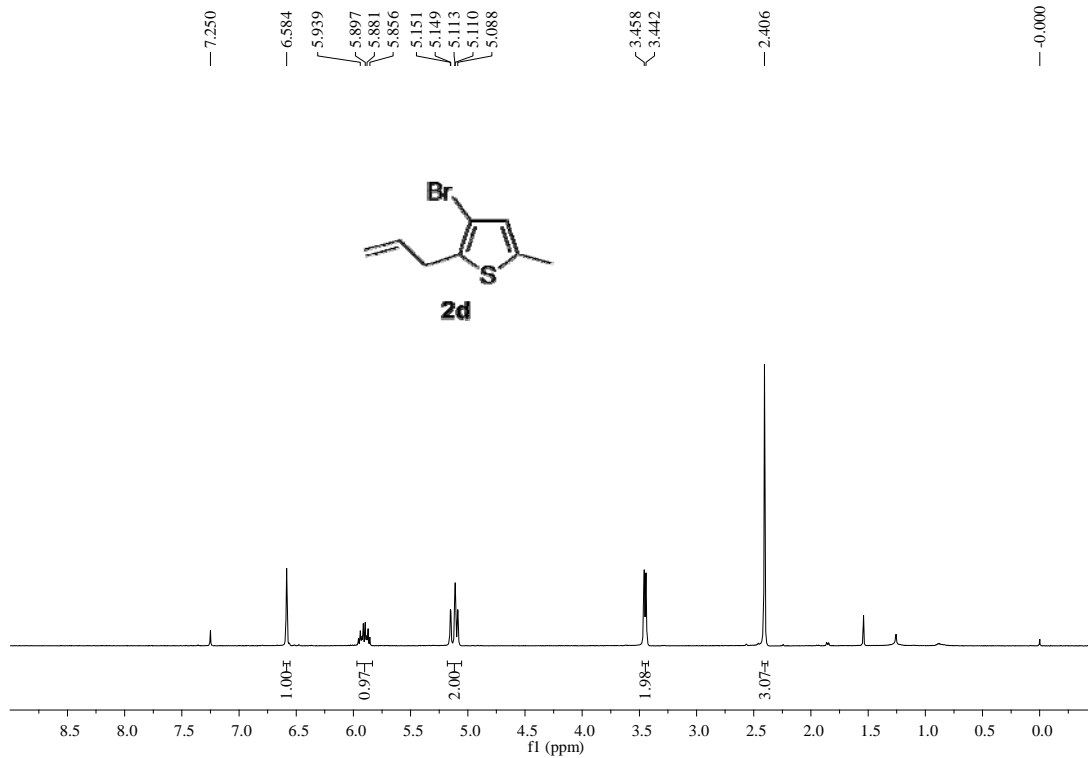


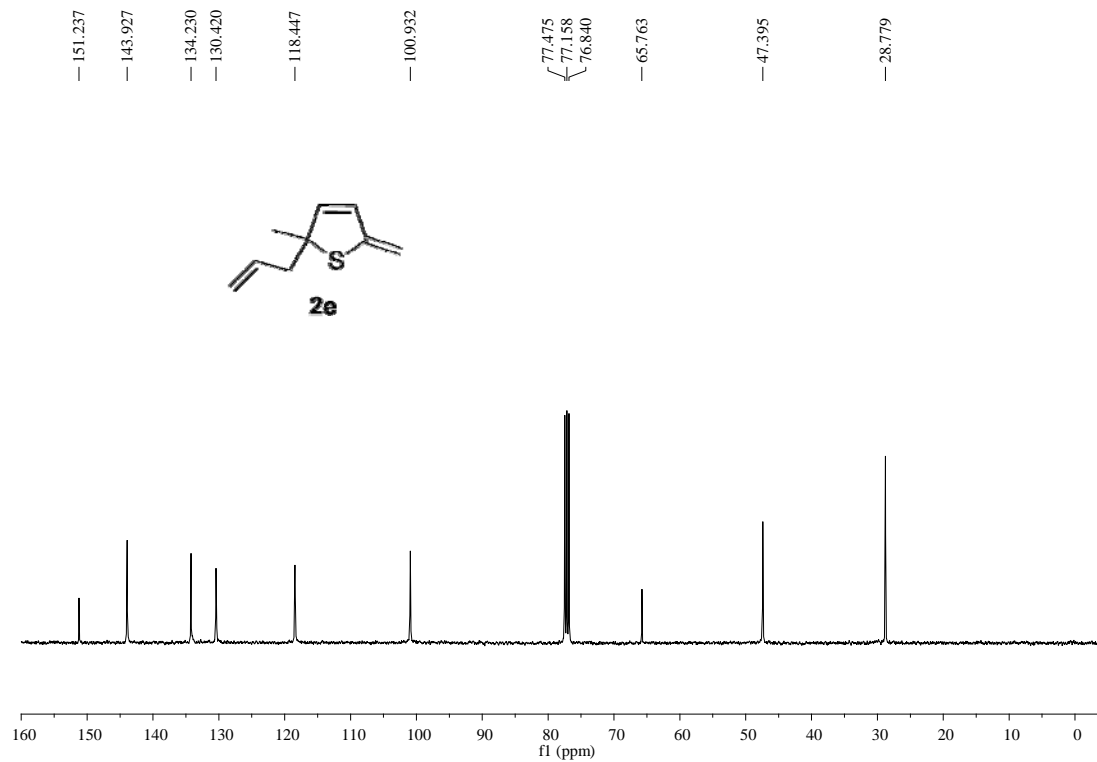
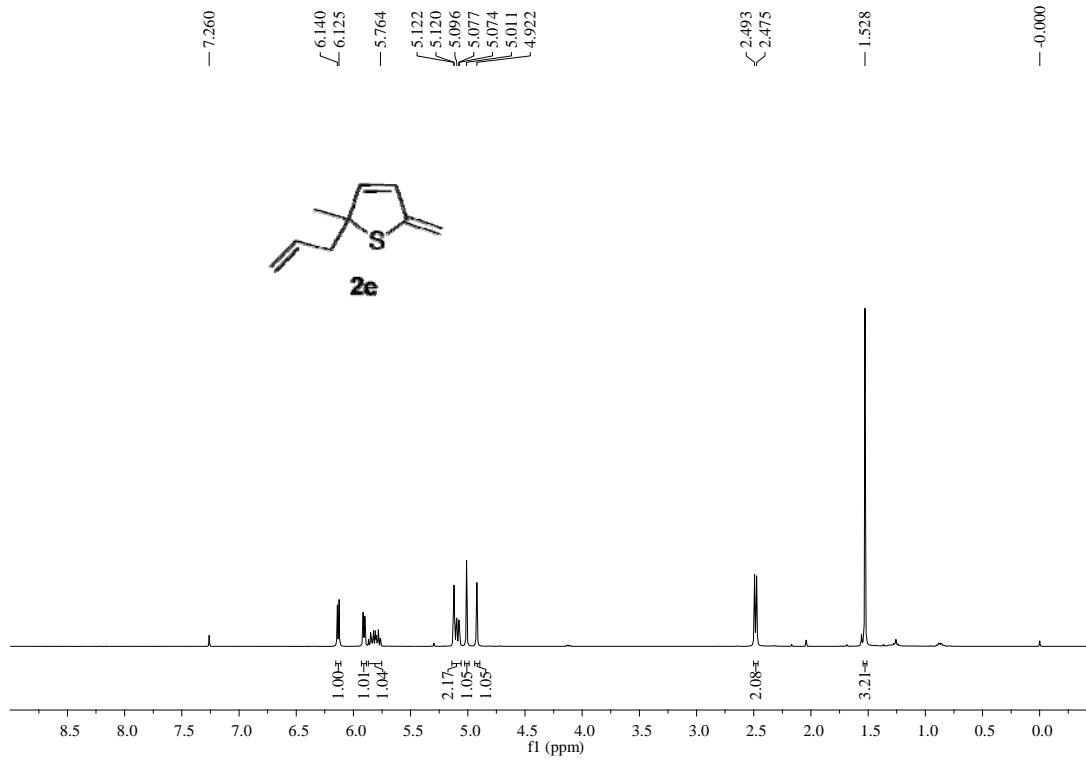


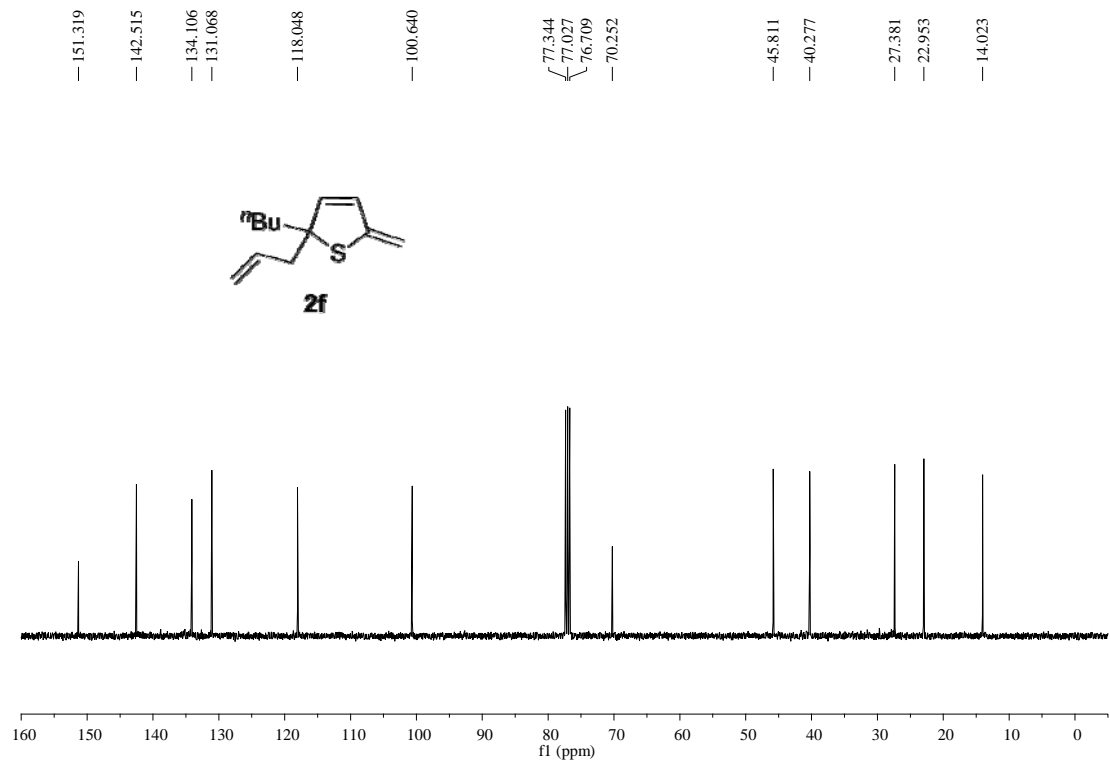
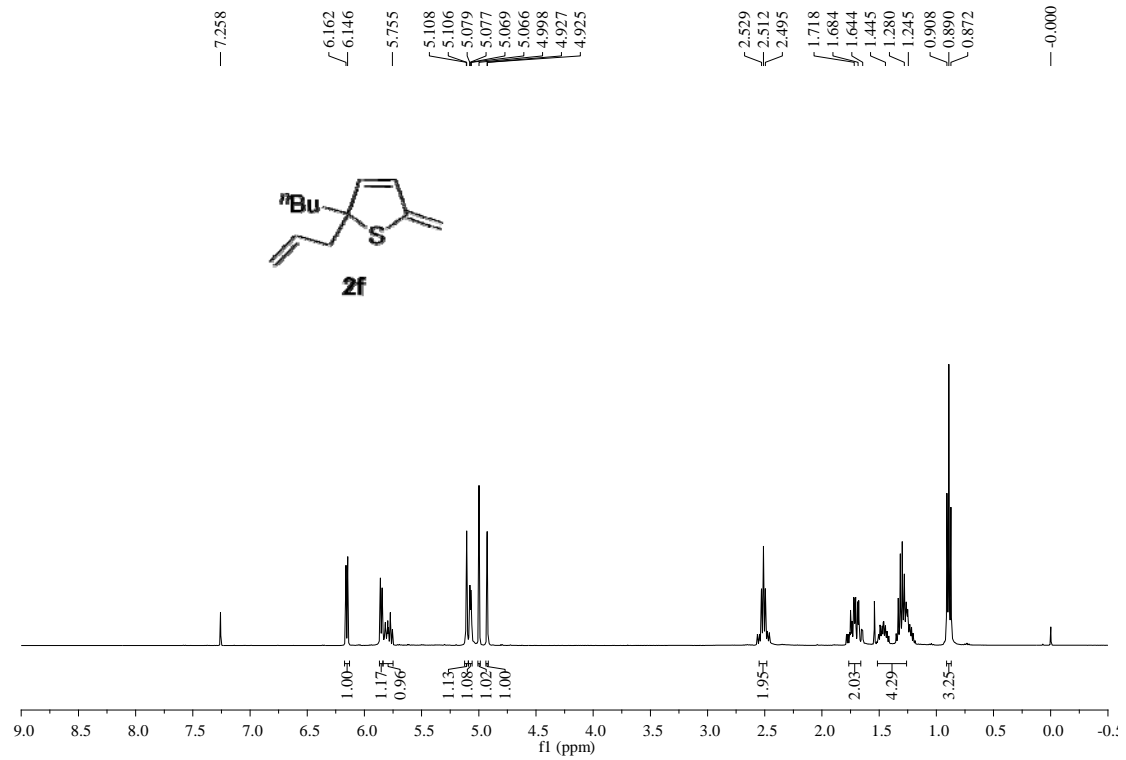


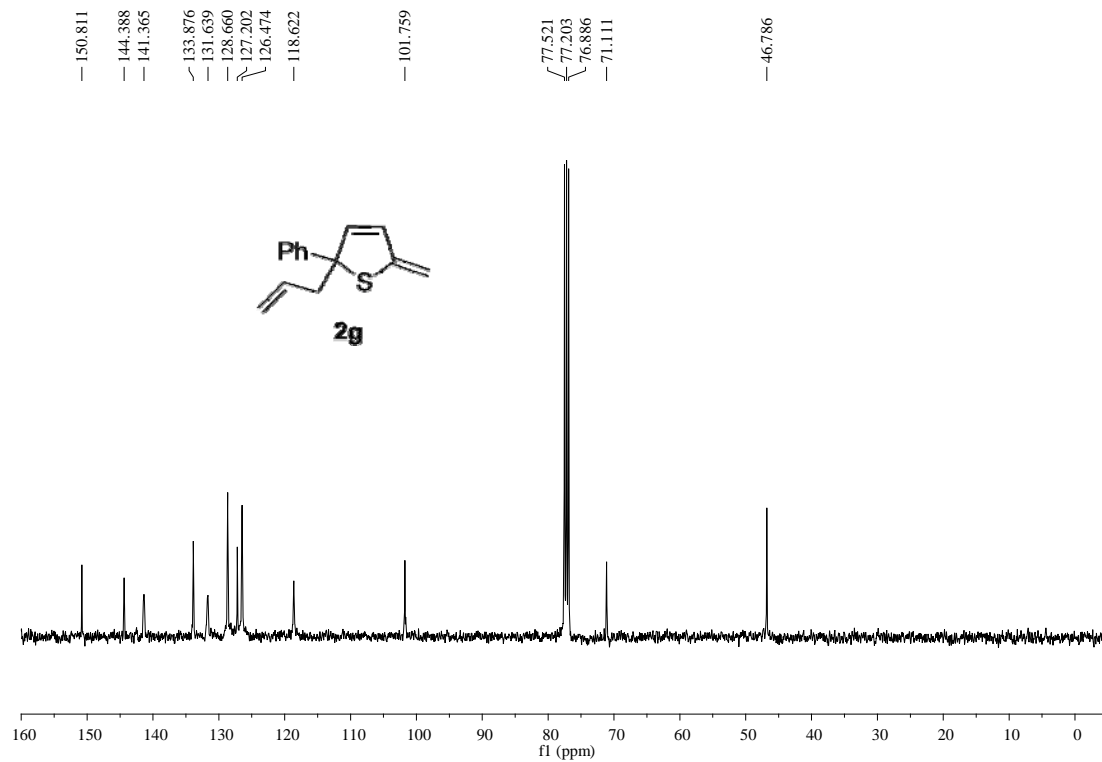
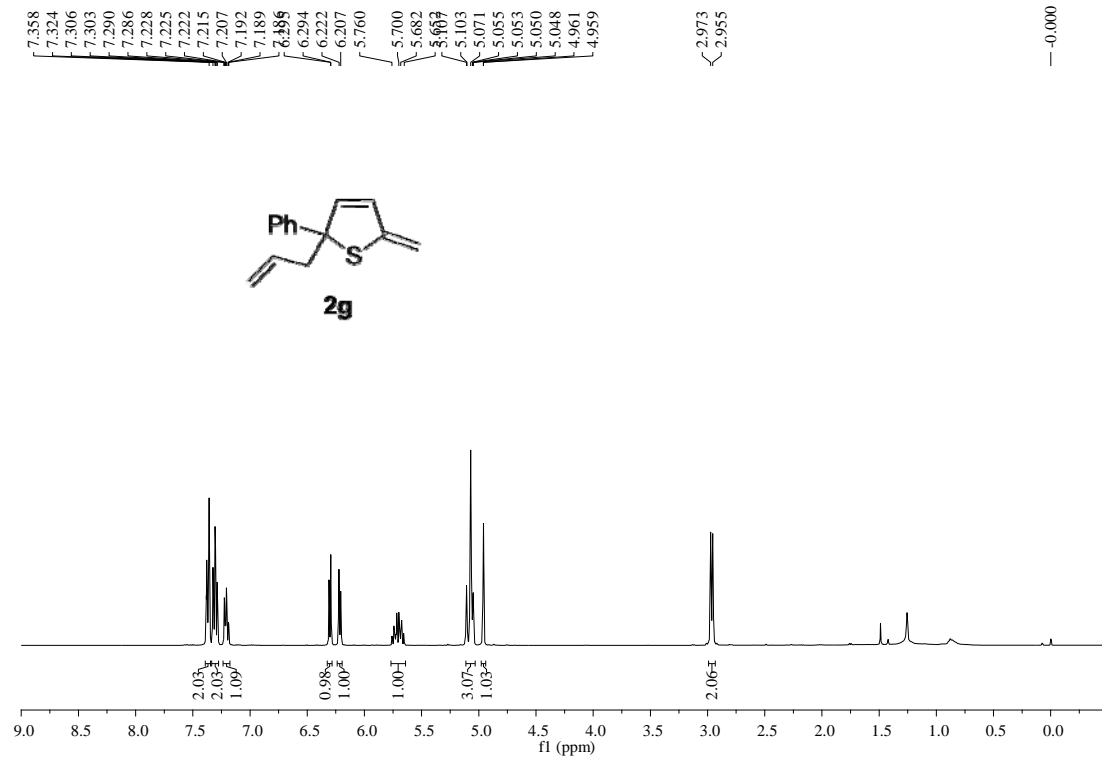


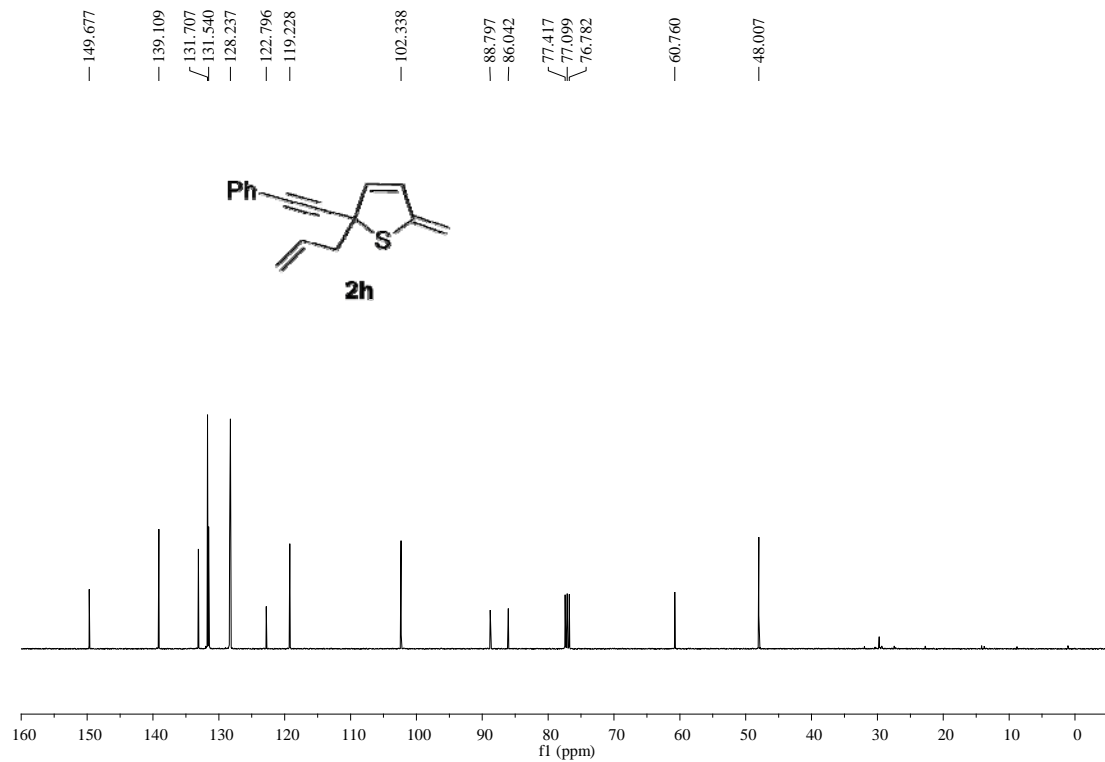
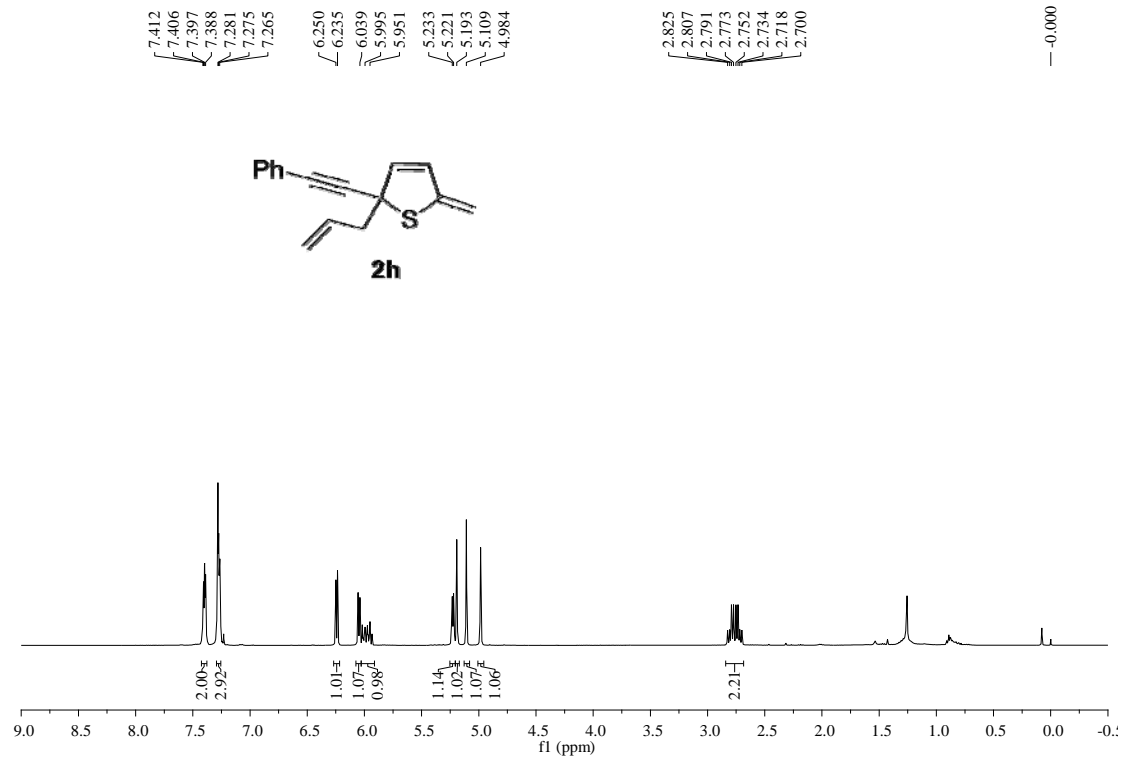


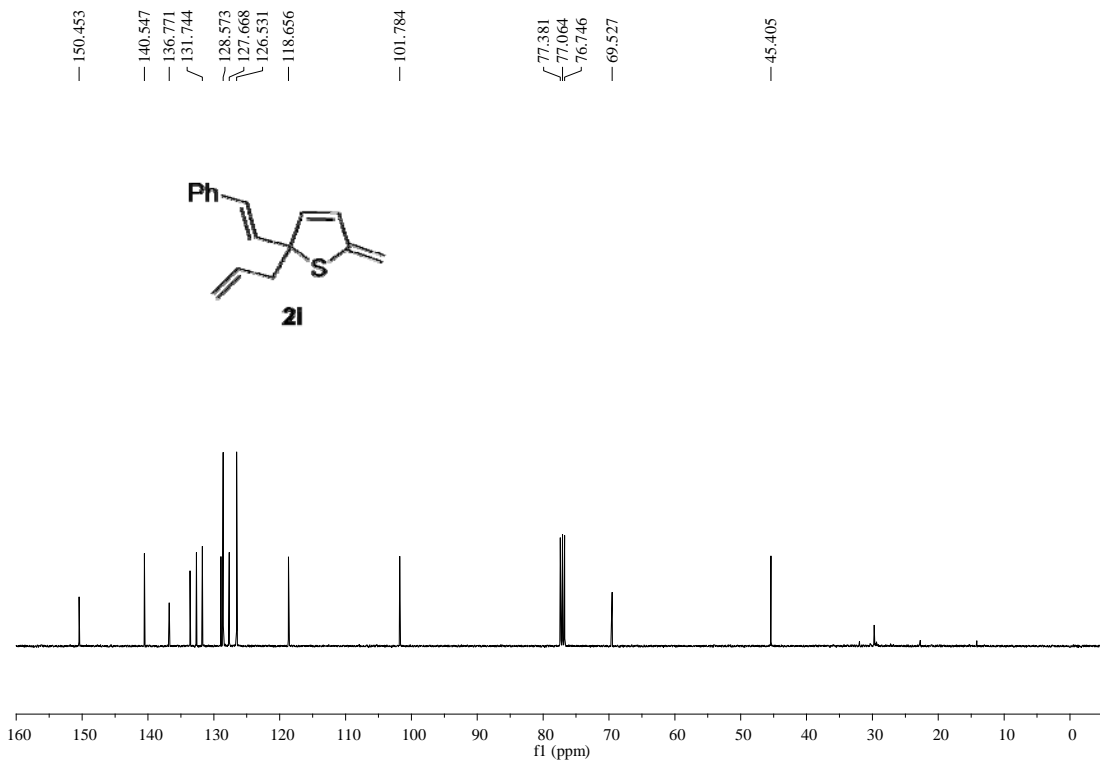
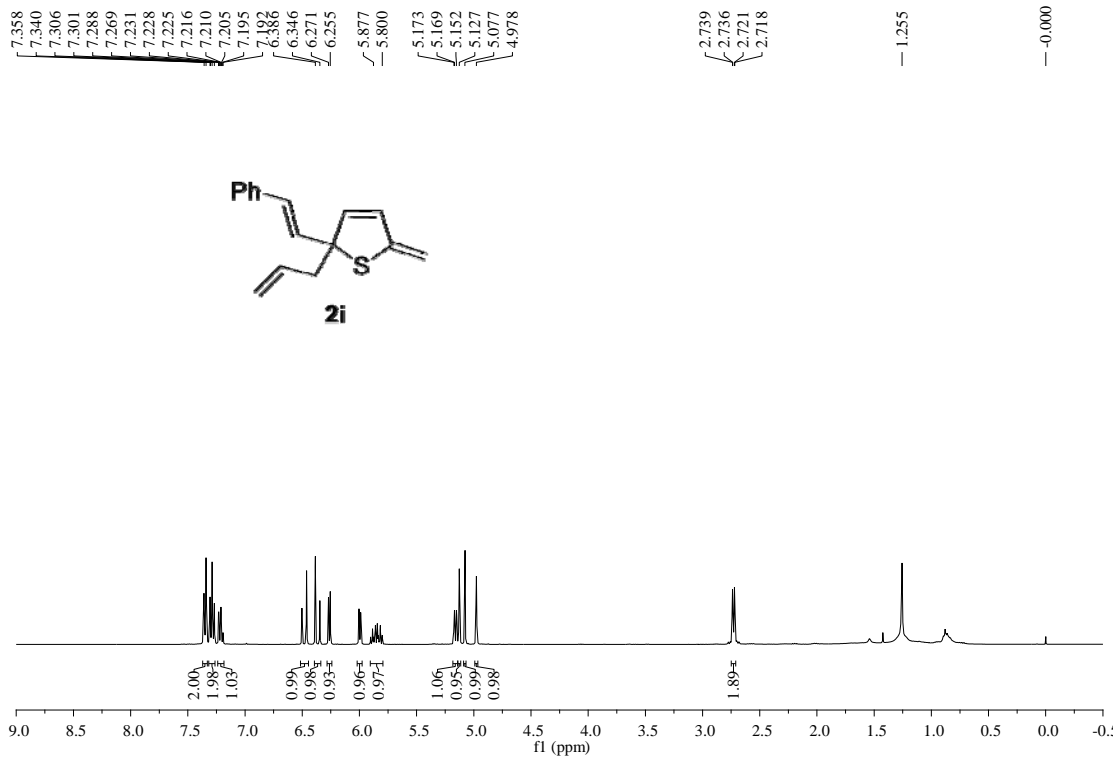


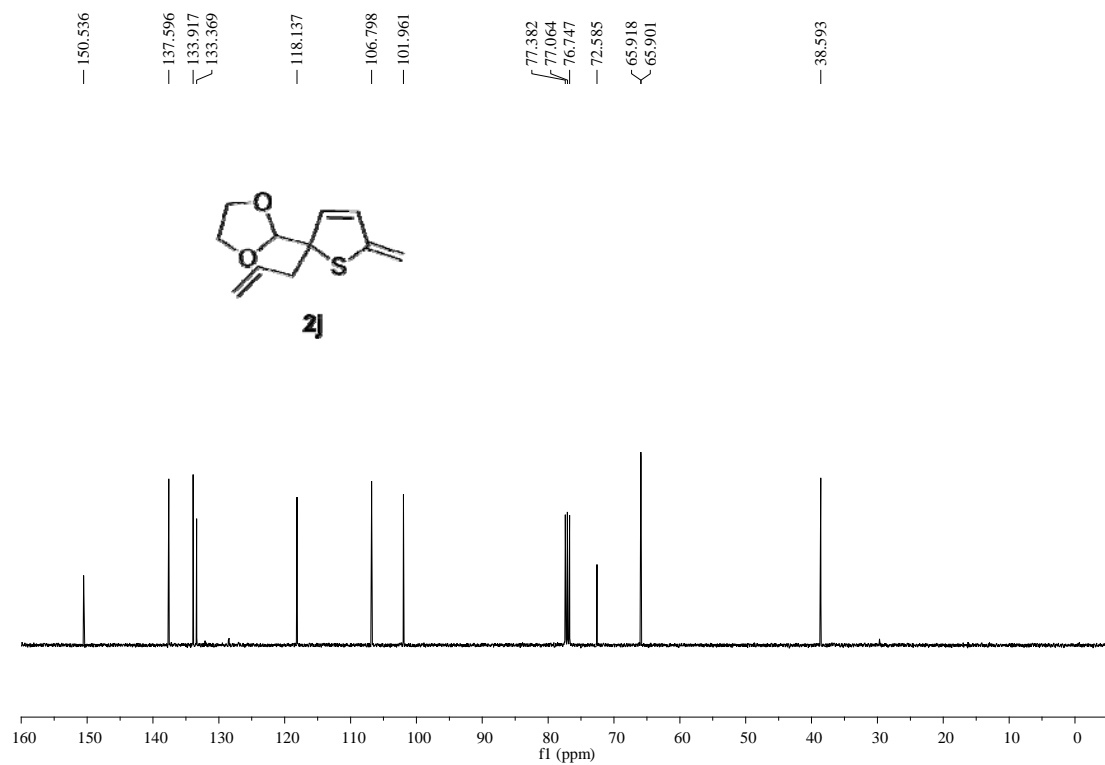
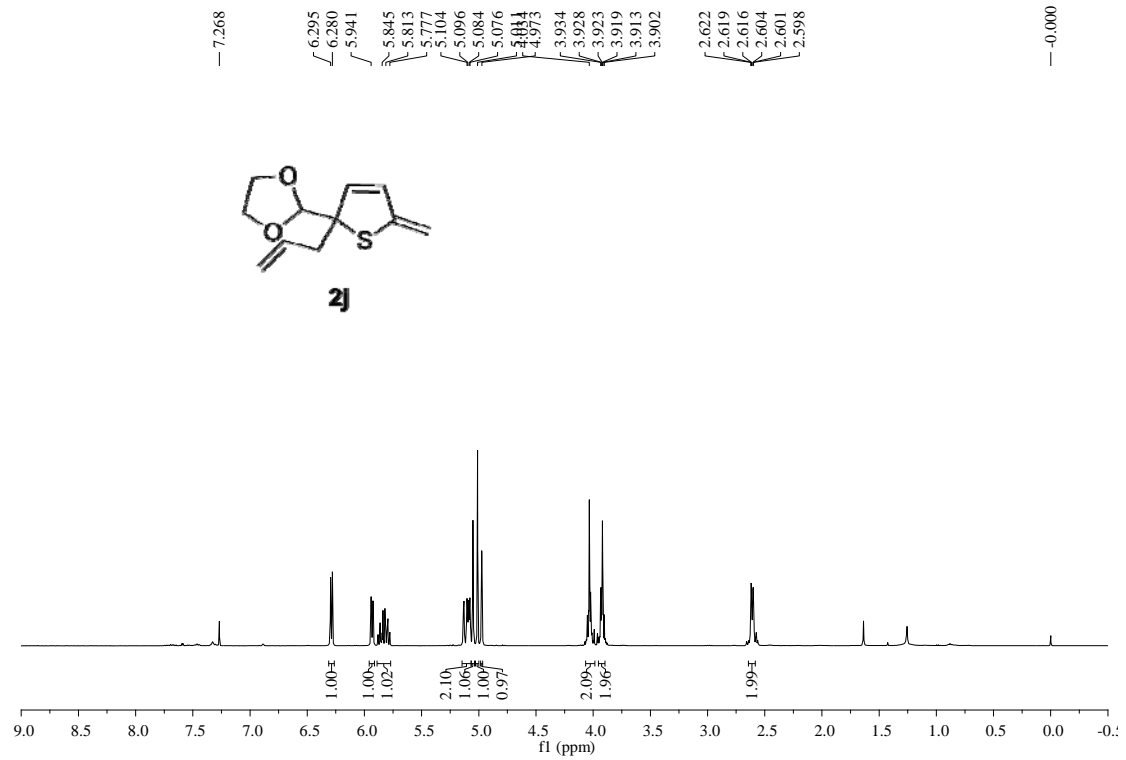


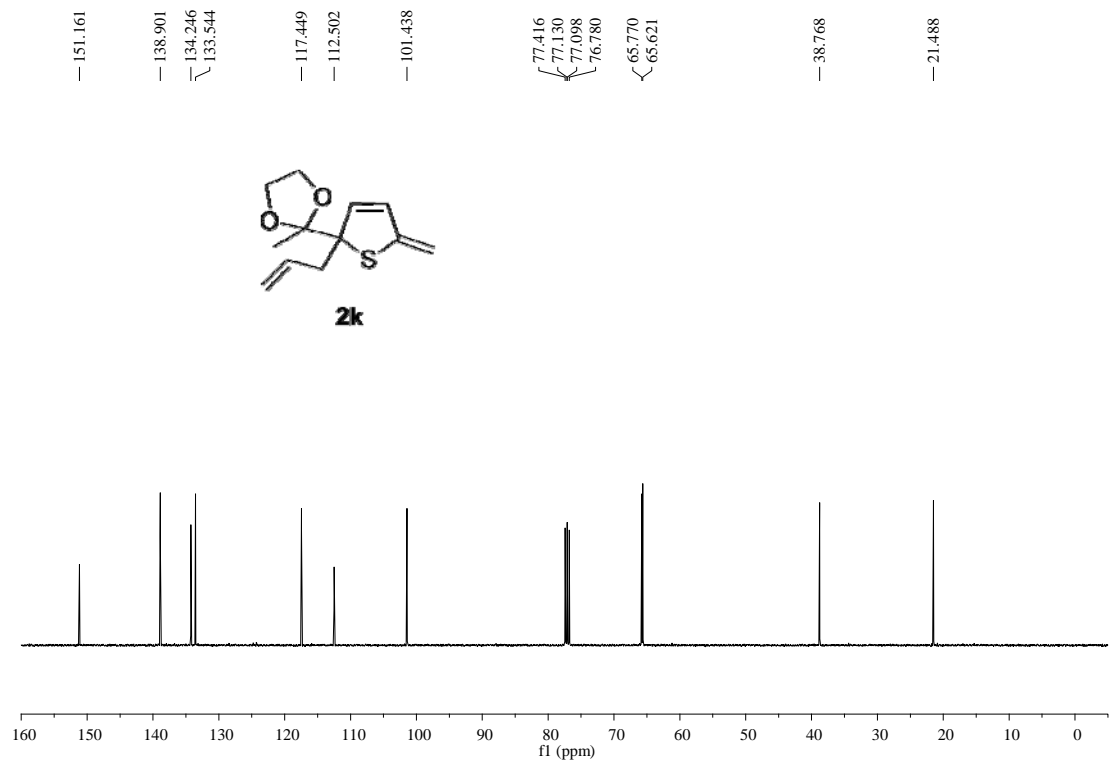
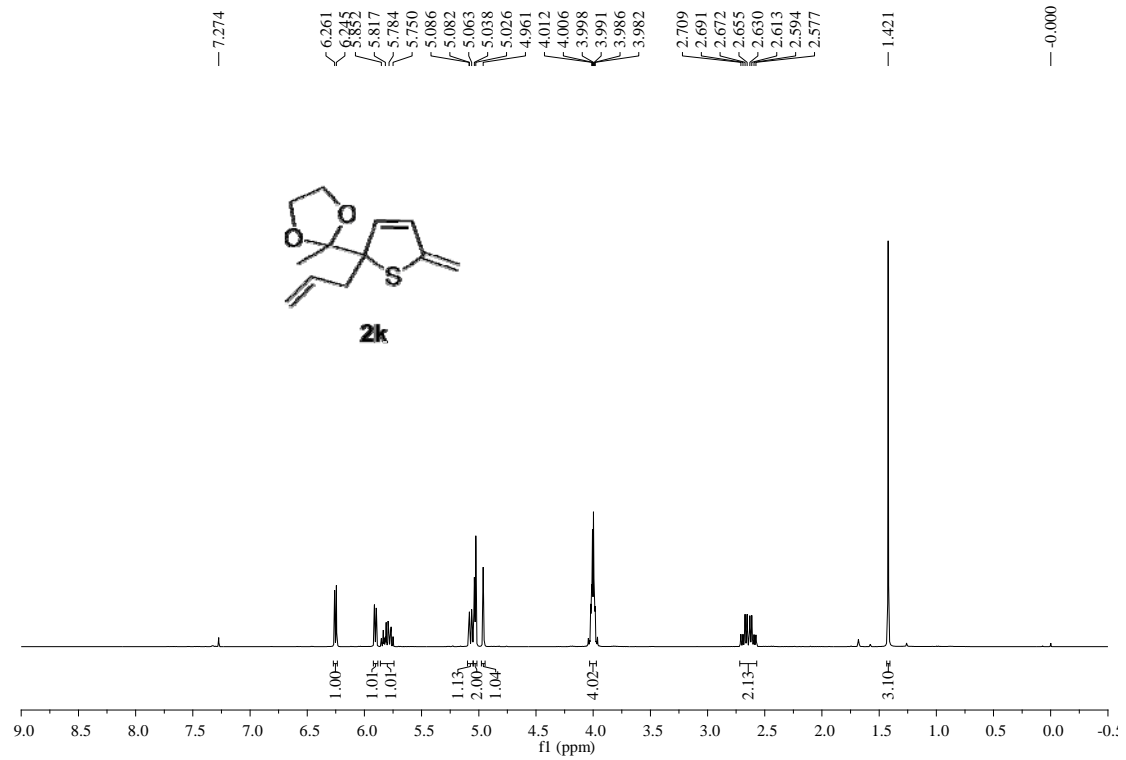


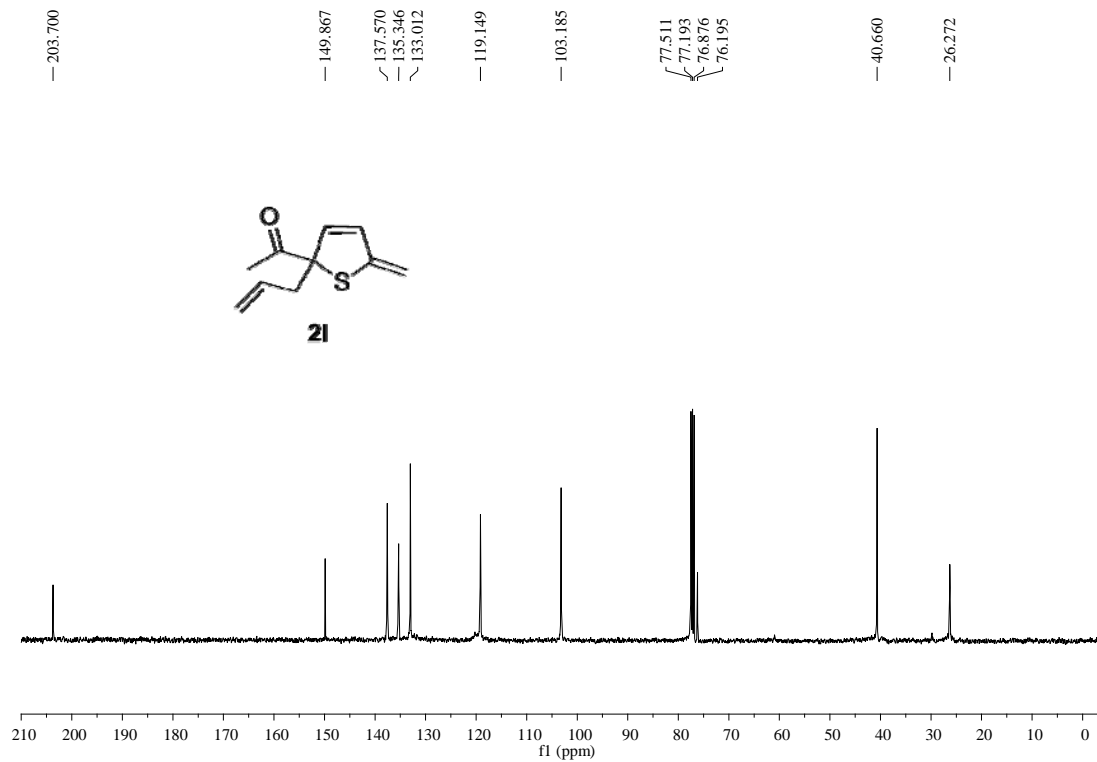
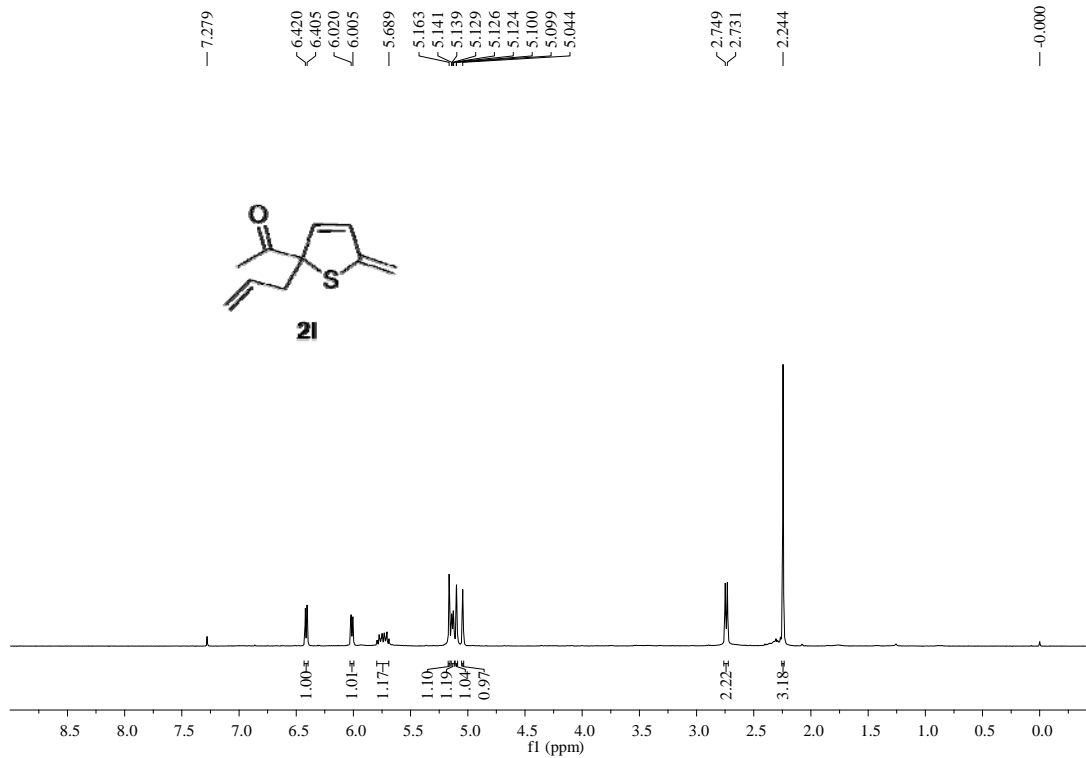


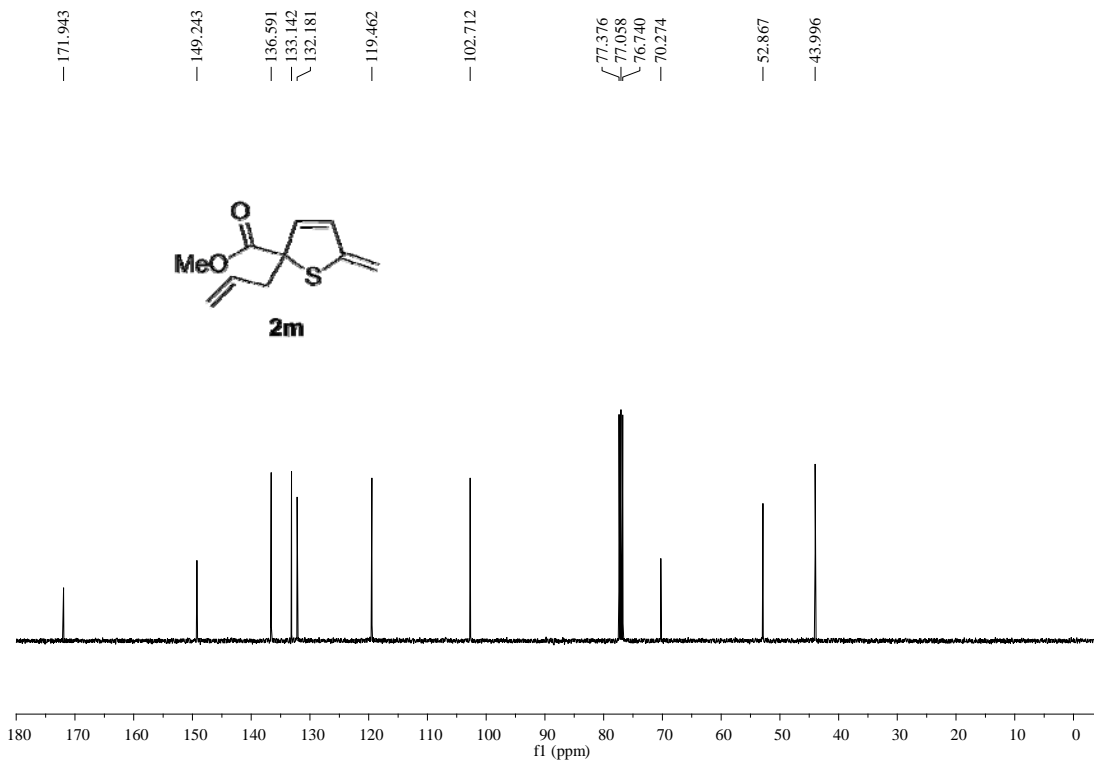
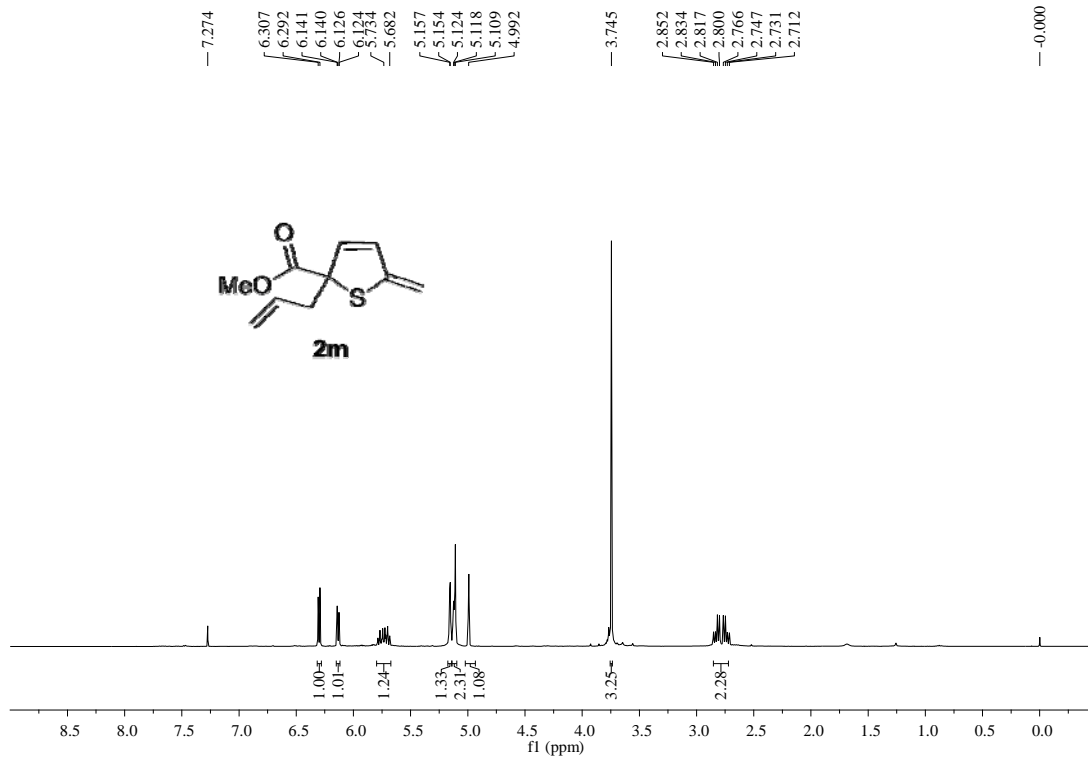


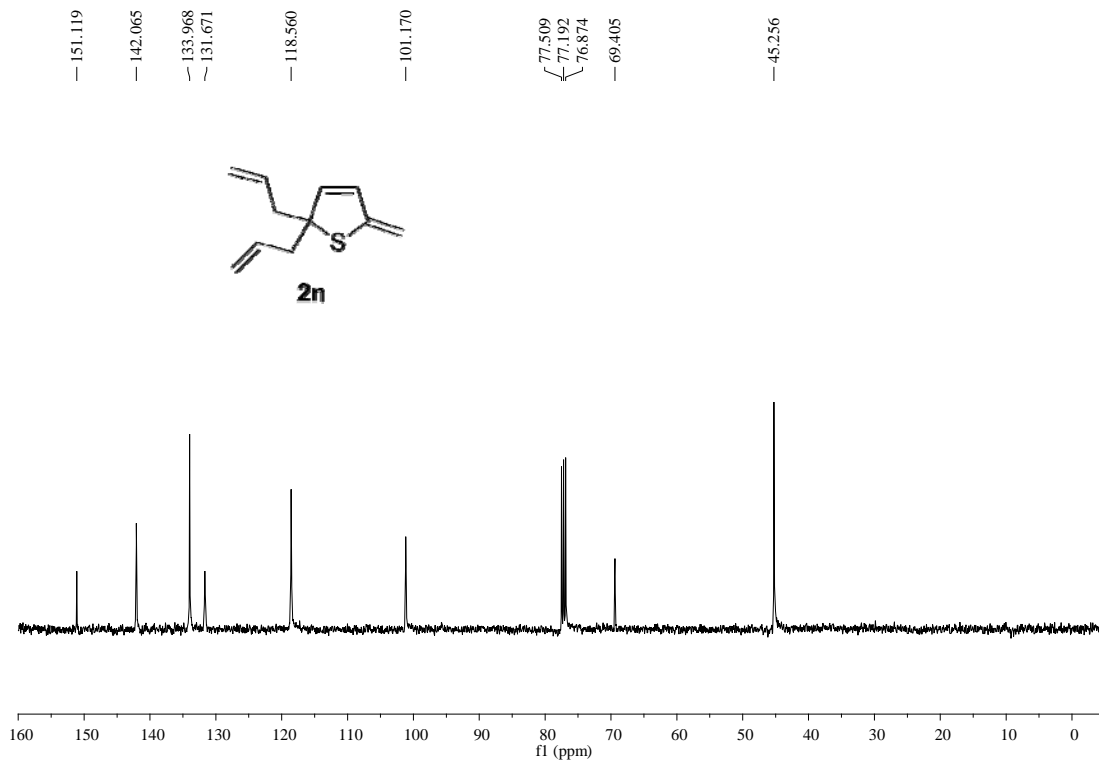
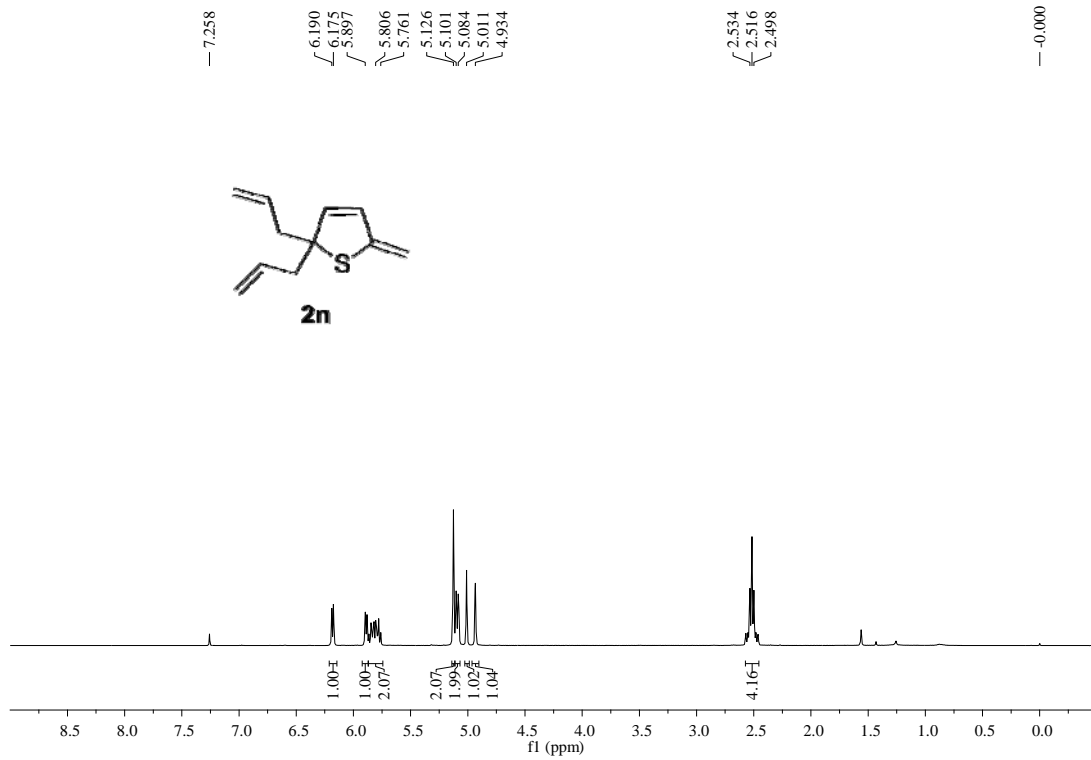


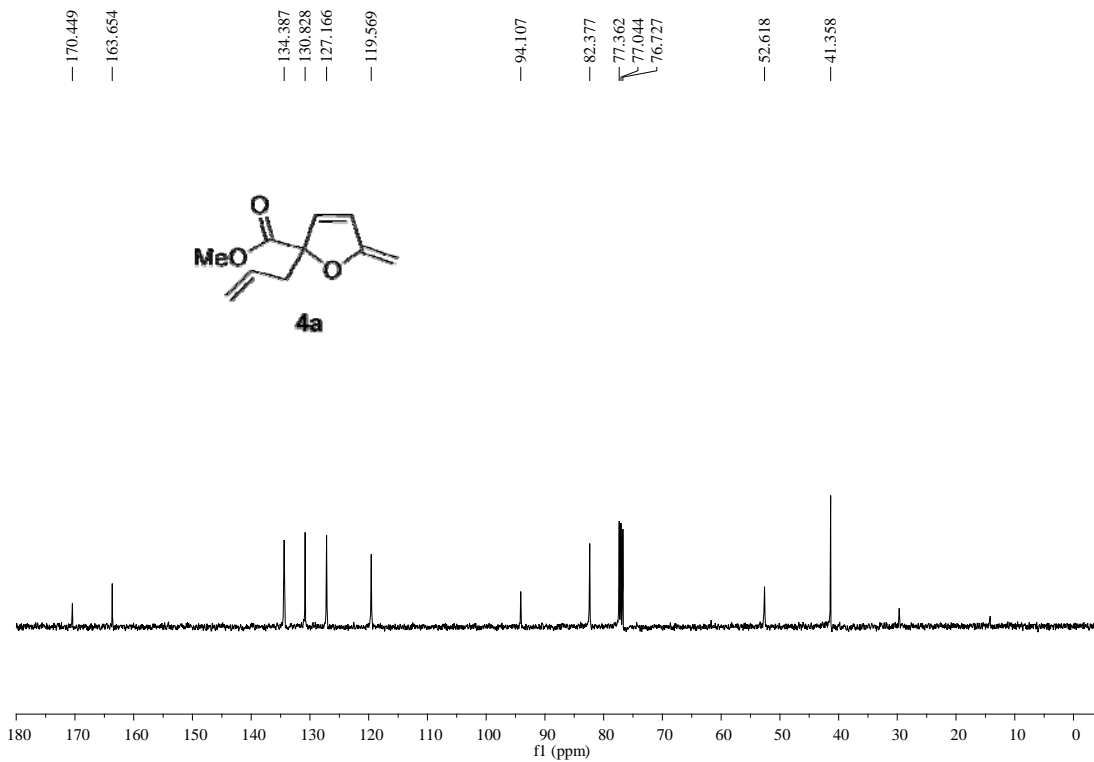
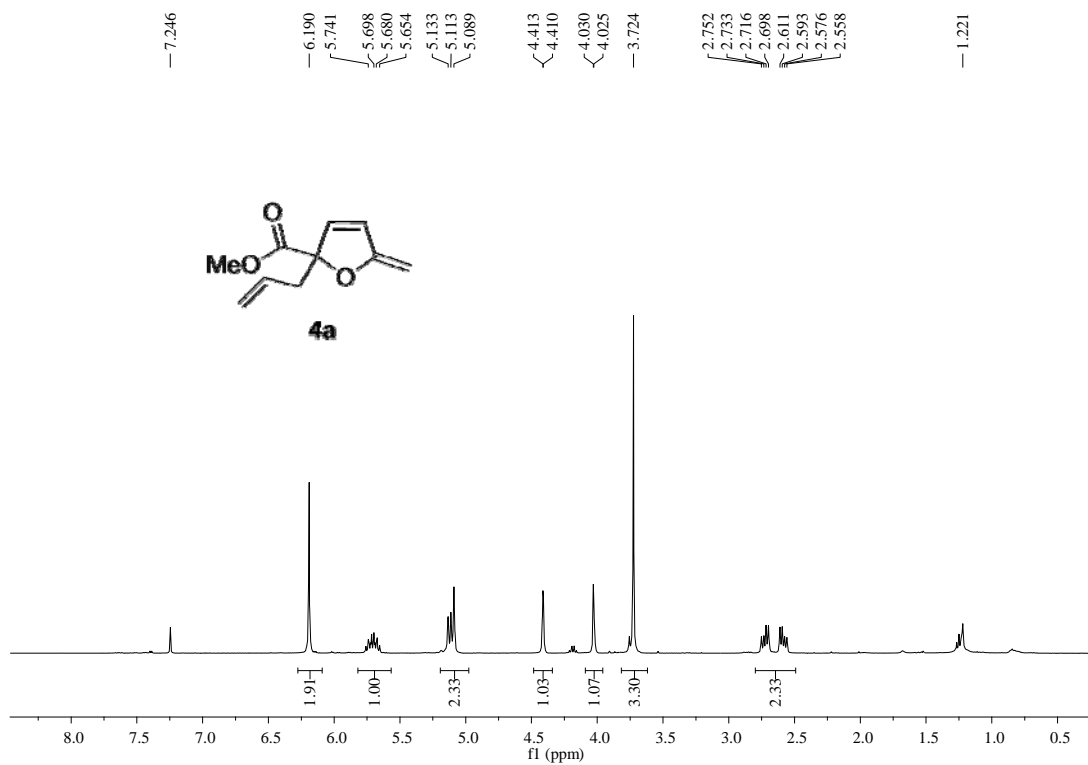


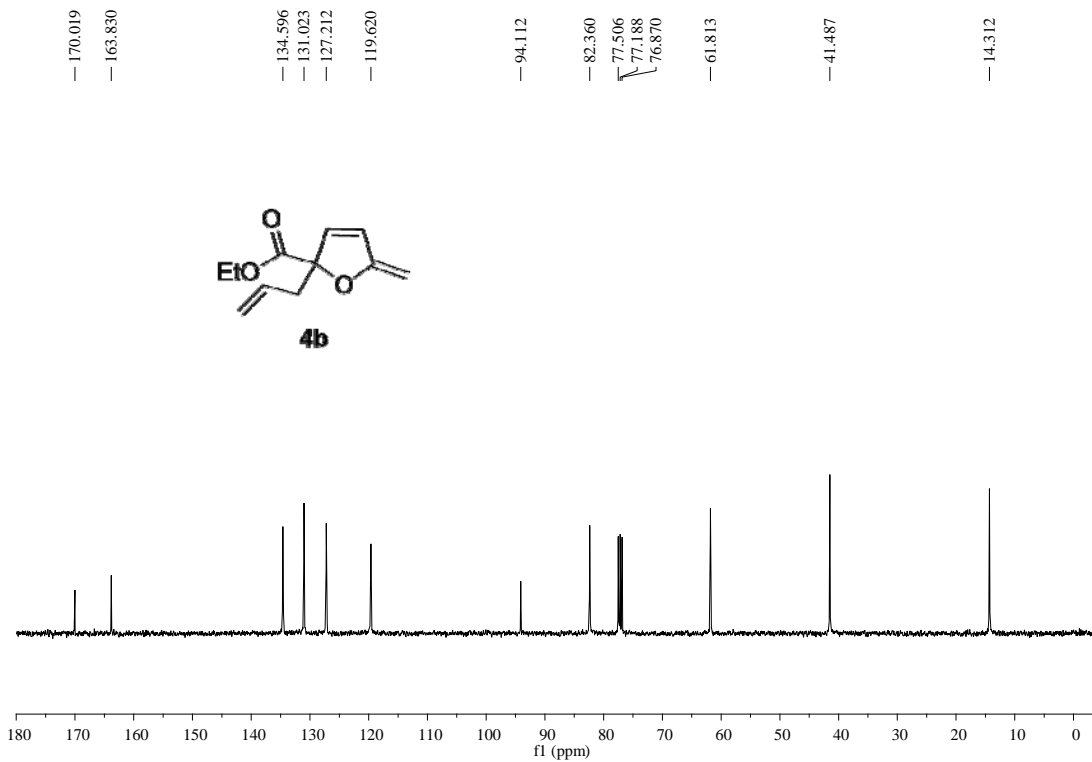
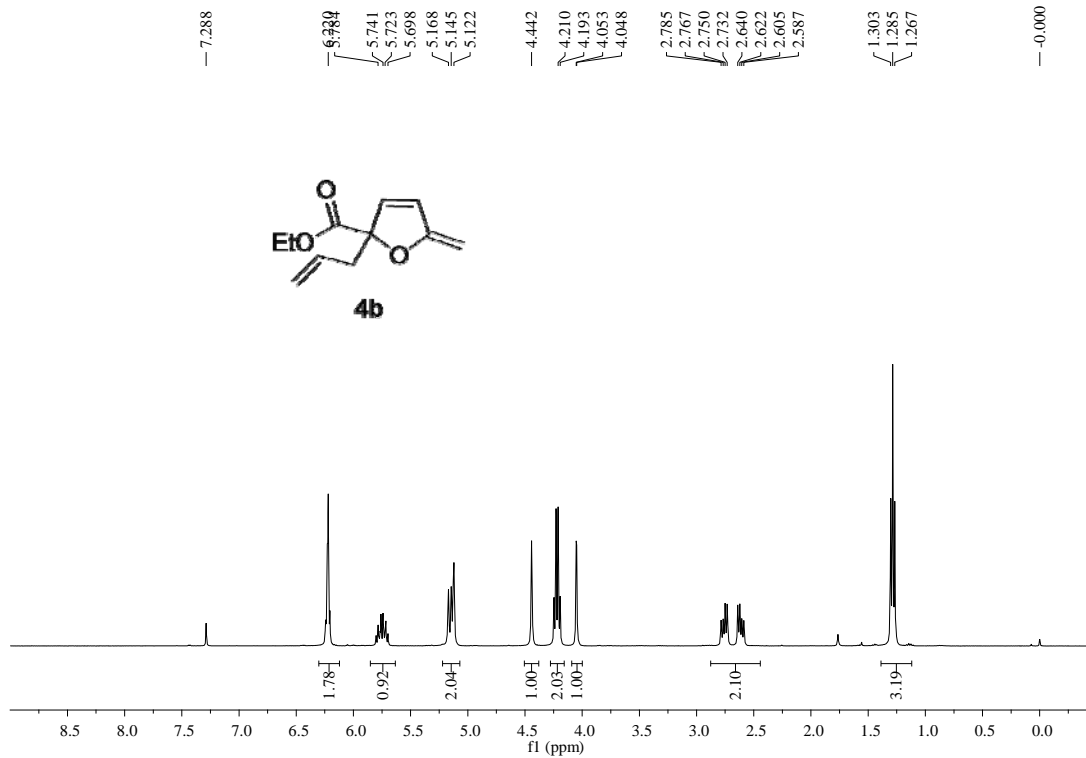


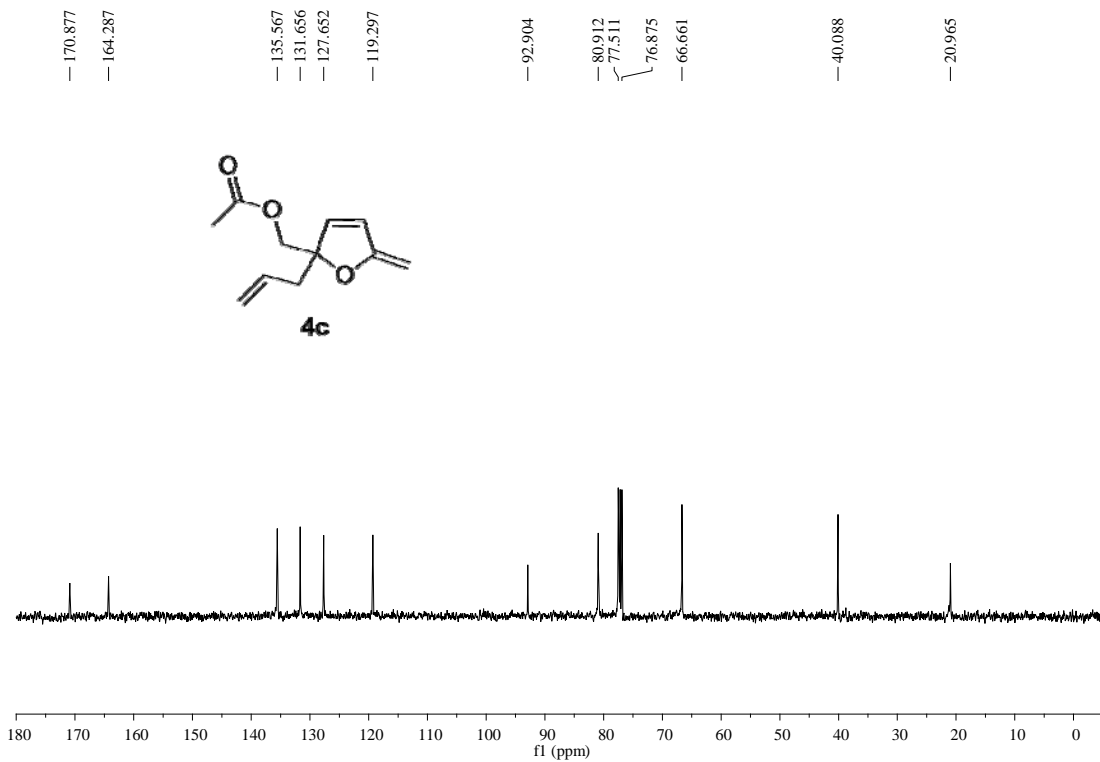
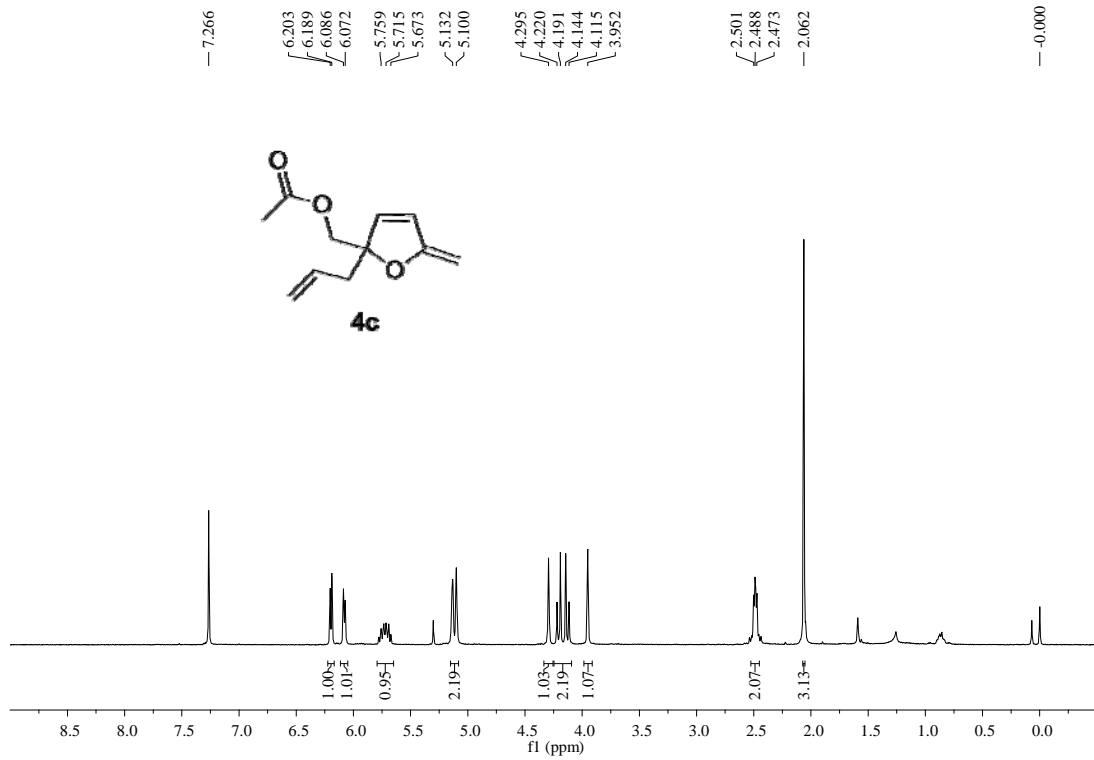


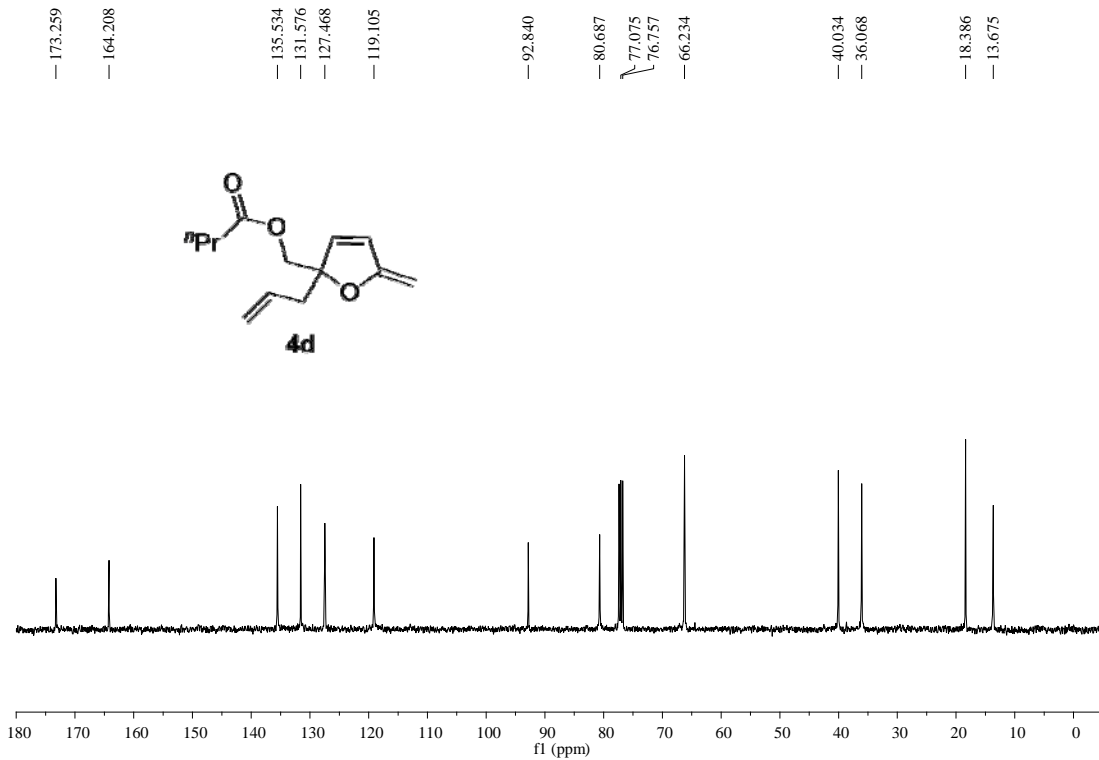
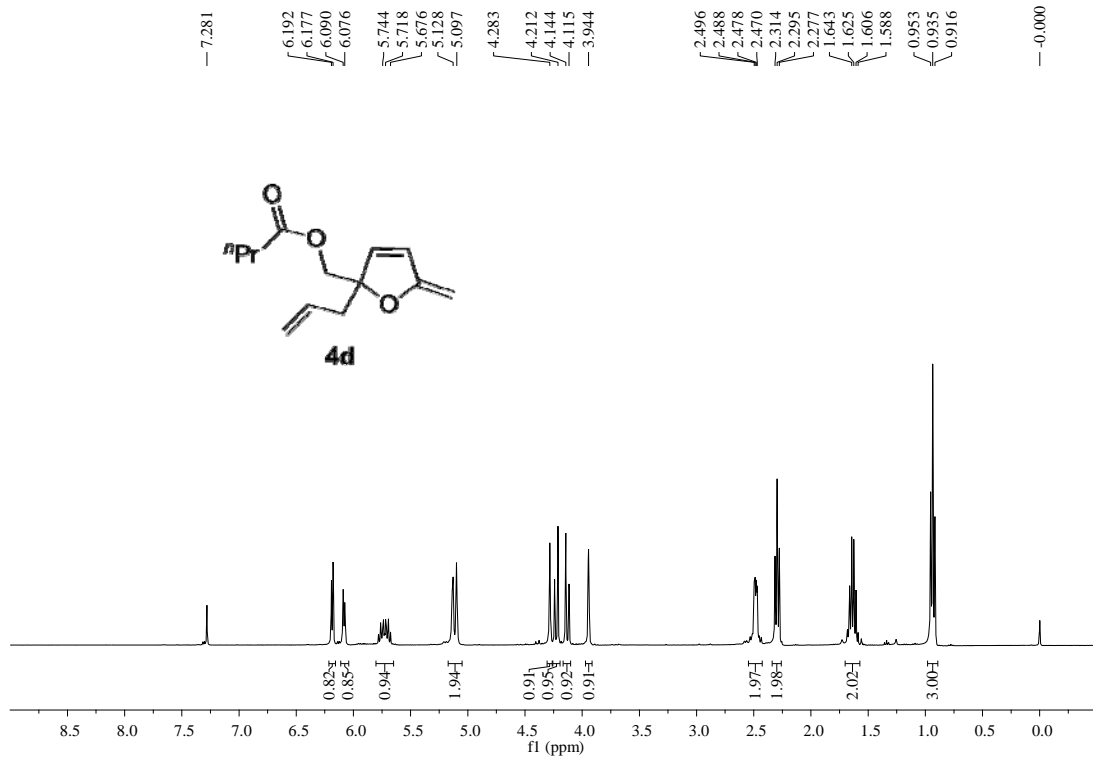




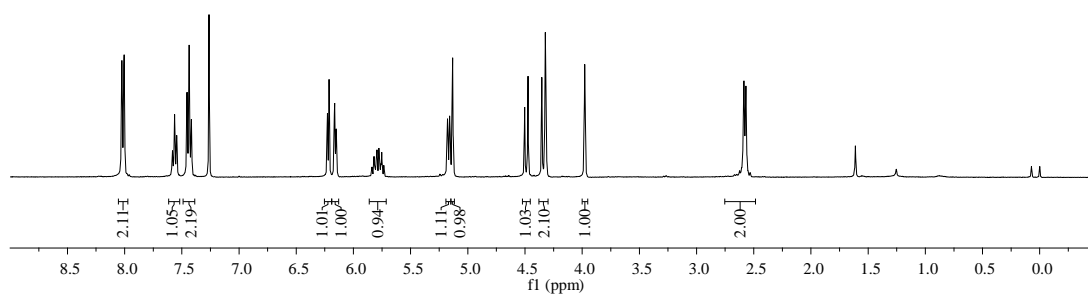
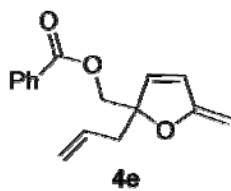








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