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Supporting Information

**Palladium-Catalyzed Heck Type Regioselective  $\beta$ -Vinylolation  
of Thiophenes Using a Bromo Substituent as Traceless  
Directing Group**

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## 1 General

Allylpalladium chloride dimer (98%) and 1,4-bis(diphenylphosphino)butane (dppb) (98%) were purchased from Aldrich. DMA (99+%) extra pure was purchased from ACROS. KO<sub>2</sub>Piv (95%) was purchased from Doug Discovery. These compounds were not purified before use. All reagents were weighed and handled in air. All reactions were carried out under an inert atmosphere with standard Schlenk techniques. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. High-resolution mass spectra were measured on a Bruker MaXis 4G spectrometer. Melting points were determined with a Kofler hot bench system. Chromatography purifications were performed using a CombiFlash NextGen 300 with Buchi FlashPure cartridges containing 40 μm irregular silica. The starting materials 2-(2-bromophenyl)thiophenes of scheme 2 were prepared using Suzuki coupling of 2-thienylboronic acid with 1,2-dihalobenzenes.<sup>[17b]</sup> The reagents **1**, **2** and **6** were prepared using our reported procedures.<sup>[17b,19]</sup>

## 2 Preparation of the PdCl(C<sub>3</sub>H<sub>5</sub>)(dppb) catalyst:<sup>[18]</sup>

An oven-dried 40 mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere, was charged with [Pd(C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). 10 mL of anhydrous dichloromethane were added, then, the solution was stirred at room temperature for twenty minutes. The solvent was removed in vacuum. The yellow powder was used without purification. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ = 19.3 (s).

## 3 Procedures and characterizations

**General procedure for the preparation of 2,5-diarylthiophenes 3-8:** As a typical experiment, the reaction of 2-(2-bromo-4-aryl)thiophene derivative (1 mmol), aryl bromide (1.3 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C during 16 h in DMA (4 mL) in the presence of PdCl(C<sub>3</sub>H<sub>5</sub>)(dppb) (12.2 mg, 0.02 mmol) under argon affords the coupling product after evaporation of the solvent and purification on silica gel.

### **2-(2-Bromo-4-methylphenyl)-5-(4-nitrophenyl)thiophene (3)**

From 2-(2-bromo-4-methylphenyl)thiophene (0.253 g, 1 mmol) and 4-bromonitrobenzene (0.263 g, 1.3 mmol), **3** was isolated in 79% (0.295 g) yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.23 (d,  $J = 8.6$  Hz, 2H), 7.74 (d,  $J = 8.6$  Hz, 2H), 7.53 (s, 1H), 7.45 (d,  $J = 3.7$  Hz, 1H), 7.40 (d,  $J = 7.9$  Hz, 1H), 7.31 (d,  $J = 3.7$  Hz, 1H), 7.17 (d,  $J = 7.9$  Hz, 1H), 2.38 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.8, 144.4, 141.7, 140.6, 140.2, 134.5, 131.6, 131.5, 129.2, 128.6, 125.9, 125.7, 124.6, 122.4, 20.9.

LRMS calcd for  $[\text{M}]^+$   $\text{C}_{17}\text{H}_{12}\text{BrNO}_2\text{S}$  375, found: 375.

### **2-(2-Bromo-5-fluorophenyl)-5-(4-nitrophenyl)thiophene (4)**

From 2-(2-bromo-5-fluorophenyl)thiophene (0.257 g, 1 mmol) and 4-bromonitrobenzene (0.263 g, 1.3 mmol), **4** was isolated in 80% (0.302 g) yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.26 (d,  $J = 8.6$  Hz, 2H), 7.76 (d,  $J = 8.6$  Hz, 2H), 7.66 (dd,  $J = 8.9, 5.4$  Hz, 1H), 7.47 (d,  $J = 3.7$  Hz, 1H), 7.36 (d,  $J = 7.9$  Hz, 1H), 7.28-7.24 (m, 1H), 7.00-6.94 (m, 1H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.8 (d,  $J = 248.3$  Hz), 147.0, 142.8 (d,  $J = 1.7$  Hz), 142.7, 140.2, 136.2 (d,  $J = 8.2$  Hz), 135.3 (d,  $J = 8.3$  Hz), 129.8, 126.1, 125.8, 124.6, 118.6 (d,  $J = 23.5$  Hz), 116.9 (d,  $J = 22.0$  Hz), 116.8 (d,  $J = 2.1$  Hz).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -114.2.

LRMS calcd for  $[\text{M}]^+$   $\text{C}_{16}\text{H}_9\text{BrFNO}_2\text{S}$  378, found: 378.

### **2-(2-Bromophenyl)-5-(4-nitrophenyl)thiophene (5)**

From 2-(2-bromophenyl)thiophene (0.239 g, 1 mmol) and 4-bromonitrobenzene (0.263 g, 1.3 mmol), **5** was isolated in 77% (0.277 g) yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.25 (d,  $J = 8.6$  Hz, 2H), 7.77 (d,  $J = 8.6$  Hz, 2H), 7.71 (d,  $J = 7.9$  Hz, 1H), 7.47 (d,  $J = 3.7$  Hz, 1H), 7.53 (dd,  $J = 7.8, 1.7$  Hz, 1H), 7.34 (d,  $J = 3.7$  Hz, 1H), 7.37 (td,  $J = 7.7, 1.3$  Hz, 1H), 7.23 (td,  $J = 7.7, 1.6$  Hz, 1H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.9, 144.2, 142.1, 140.5, 134.7, 134.1, 131.9, 129.8, 129.5, 127.8, 126.0, 125.8, 124.6, 122.8.

LRMS calcd for  $[\text{M}]^+$   $\text{C}_{16}\text{H}_{10}\text{BrNO}_2\text{S}$  361, found: 361.

### **2-(5-(2-Bromophenyl)thiophen-2-yl)benzonitrile (7)**

From 2-(2-bromophenyl)thiophene (0.239 g, 1 mmol) and 2-bromobenzonitrile (0.237 g, 1.3 mmol), **7** was isolated in 83% (0.282 g) yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.76 (d,  $J$  = 7.9 Hz, 1H), 7.72-7.63 (m, 3H), 7.60 (t,  $J$  = 8.1 Hz, 1H), 7.53 (dd,  $J$  = 7.8, 1.7 Hz, 1H), 7.42-7.32 (m, 3H), 7.21 (td,  $J$  = 7.7, 1.6 Hz, 1H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.8, 140.1, 137.3, 134.7, 134.6, 134.0, 133.1, 131.9, 129.6, 129.5, 129.0, 127.8, 127.7, 127.6, 122.7, 119.0, 109.9.

LRMS calcd for  $[\text{M}]^+$   $\text{C}_{17}\text{H}_{10}\text{BrNS}$  341, found: 341.

### **2-(2-Bromo-4-methylphenyl)-5-(2-nitrophenyl)thiophene (8)**

From 2-(2-bromo-4-methylphenyl)thiophene (0.253 g, 1 mmol) and 2-bromonitrobenzene (0.263 g, 1.3 mmol), **8** was isolated in 81% (0.303 g) yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.75 (d,  $J$  = 7.9 Hz, 1H), 7.63-7.54 (m, 2H), 7.52 (s, 1H), 7.45 (t,  $J$  = 8.1 Hz, 1H), 7.40 (d,  $J$  = 7.8 Hz, 1H), 7.25 (d,  $J$  = 3.7 Hz, 1H), 7.16 (d,  $J$  = 7.8 Hz, 1H), 7.08 (d,  $J$  = 3.7 Hz, 1H), 2.36 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.4, 143.8, 139.8, 137.5, 134.4, 132.2, 132.0, 131.7, 131.6, 128.7, 128.5, 128.3, 128.2, 127.1, 124.0, 122.3, 20.8.

LRMS calcd for  $[\text{M}]^+$   $\text{C}_{17}\text{H}_{12}\text{BrNO}_2\text{S}$  375, found: 375.

### **(E)-2-Methyl-5-(2-styrylphenyl)thiophene (9a)**

The reaction of 2-(2-bromophenyl)-5-methylthiophene **1** (0.253 g, 1 mmol), styrene (0.208 g, 2 mmol) and KO<sub>2</sub>Piv (0.420 g, 3 mmol) at 150 °C during 16 h in xylene (4 mL) in the presence of PdCl( $\text{C}_3\text{H}_5$ )(dppb) (12.2 mg, 0.02 mmol) under argon affords a mixture of **9a** and **9b** in 95:5 ratio and **9a** was isolated in 66% (0.182 g) yield as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.72 (d,  $J = 7.5, 1.6$  Hz, 1H), 7.52-7.25 (m, 9H), 7.06 (d,  $J = 16.2$  Hz, 1H), 6.92 (d,  $J = 3.5$  Hz, 1H), 6.79 (d,  $J = 3.5$  Hz, 1H), 2.57 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.6, 140.2, 137.8, 136.1, 134.0, 130.5, 130.1, 128.8, 128.2, 127.8, 127.8, 127.7, 127.6, 126.8, 126.7, 125.8, 15.5.

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{19}\text{H}_{17}\text{S}$  277.1046, found: 277.1048.

**General procedure for the preparation of products 9b and 10-24:** As a typical experiment, the reaction of the 2-(2-bromoaryl)thiophene derivative **1-8** (1 mmol), alkene (2 mmol) and KOAc (0.294 g, 3 mmol) at 150 °C during 16 h in DMA (4 mL) in the presence of  $\text{PdCl}(\text{C}_3\text{H}_5)(\text{dppb})$  (12.2 mg, 0.02 mmol) under argon affords the coupling product after evaporation of the solvent and purification on silica gel.

#### **(E)-5-Methyl-2-phenyl-3-styrylthiophene (9b)**

From 2-(2-bromophenyl)-5-methylthiophene **1** (0.253 g, 1 mmol) and styrene (0.208 g, 2 mmol), a mixture of **9a** and **9b** was obtained in 22:78 ratio and **9b** was isolated in 57% (0.157 g) yield as a yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.51-7.40 (m, 6H), 7.40-7.29 (m, 3H), 7.23 (t,  $J = 8.2$  Hz, 1H), 7.14 (d,  $J = 16.3$  Hz, 1H), 7.11 (s, 1H), 6.96 (d,  $J = 16.3$  Hz, 1H), 2.53 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.0, 138.7, 137.9, 135.1, 134.5, 129.7, 129.2, 128.8, 128.7, 127.6, 127.4, 126.4, 124.2, 122.6, 15.6.

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{19}\text{H}_{17}\text{S}$  277.1046, found: 277.1048.

#### **(E)-5-(4-Nitrophenyl)-3-styryl-2-(p-tolyl)thiophene (10)**

From 2-(2-bromo-4-methylphenyl)-5-(4-nitrophenyl)thiophene **3** (0.374 g, 1 mmol) and styrene (0.208 g, 2 mmol), **10** was isolated in 65% (0.258 g) yield as a yellow solid: mp 172-174 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.29 (d,  $J = 8.6$  Hz, 2H), 7.82 (d,  $J = 8.6$  Hz, 2H), 7.79 (s, 1H), 7.50-7.43 (m, 4H), 7.41-7.26 (m, 5H), 7.17 (d,  $J = 16.3$  Hz, 1H), 7.09 (d,  $J = 16.3$  Hz, 1H), 2.47 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ 146.9, 142.9, 140.5, 139.7, 138.7, 137.4, 136.5, 130.6, 130.3, 129.8, 129.6, 128.9, 127.9, 126.6, 126.0, 124.6, 124.5, 121.9, 21.5.

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{25}\text{H}_{20}\text{NO}_2\text{S}$  398.1209, found: 398.1210.

**(E)-3-(4-Methoxystyryl)-5-(4-nitrophenyl)-2-(p-tolyl)thiophene (11)**

From 2-(2-bromo-4-methylphenyl)-5-(4-nitrophenyl)thiophene **3** (0.374 g, 1 mmol) and 4-methoxystyrene (0.268 g, 2 mmol), **11** was isolated in 58% (0.248 g) yield as a yellow solid: mp 178-180 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ 8.25 (d,  $J = 8.6$  Hz, 2H), 7.77 (d,  $J = 8.6$  Hz, 2H), 7.74 (s, 1H), 7.43 (d,  $J = 8.1$  Hz, 2H), 7.38 (d,  $J = 8.1$  Hz, 2H), 7.29 (d,  $J = 8.1$  Hz, 2H), 7.04-6.99 (m, 2H), 6.88 (d,  $J = 8.1$  Hz, 2H), 3.83 (s, 3H), 2.44 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ 159.6, 146.8, 142.1, 140.6, 139.5, 138.5, 136.8, 130.8, 130.2, 129.8, 129.7, 129.5, 127.8, 125.9, 124.6, 124.5, 119.9, 114.4, 55.5, 21.4.

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{26}\text{H}_{22}\text{NO}_3\text{S}$  428.1315, found: 428.1311.

**(E)-3-(4-(tert-Butyl)styryl)-5-(4-nitrophenyl)-2-(p-tolyl)thiophene (12)**

From 2-(2-bromo-4-methylphenyl)-5-(4-nitrophenyl)thiophene **3** (0.374 g, 1 mmol) and 4-*tert*-butylstyrene (0.320 g, 2 mmol), **12** was isolated in 61% (0.276 g) yield as a yellow solid: mp 222-242 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ 8.27 (d,  $J = 8.6$  Hz, 2H), 7.79 (d,  $J = 8.6$  Hz, 2H), 7.76 (s, 1H), 7.42 (d,  $J = 8.1$  Hz, 2H), 7.41-7.35 (m, 4H), 7.28 (d,  $J = 8.1$  Hz, 2H), 7.11 (d,  $J = 16.3$  Hz, 1H), 7.05 (d,  $J = 16.3$  Hz, 1H), 2.44 (s, 3H), 1.33 (s, 9H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ 151.2, 146.9, 142.5, 140.6, 139.6, 138.6, 136.7, 134.6, 130.7, 130.1, 129.7, 129.5, 126.4, 125.9, 125.8, 124.6, 124.5, 121.2, 34.8, 31.4, 21.5.

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{29}\text{H}_{28}\text{NO}_2\text{S}$  454.1835, found: 454.1832.

**(E)-3-(4-Fluorostyryl)-5-(4-nitrophenyl)-2-(p-tolyl)thiophene (13)**

From 2-(2-bromo-4-methylphenyl)-5-(4-nitrophenyl)thiophene **3** (0.374 g, 1 mmol) and 4-fluorostyrene (0.244 g, 2 mmol), **13** was isolated in 63% (0.261 g) yield as a yellow solid: mp 172-174 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.27 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.75 (s, 1H), 7.45-7.37 (m, 4H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.07-7.00 (m, 4H), 2.44 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.6 (d, *J* = 247.9 Hz), 146.9, 142.9, 140.5, 139.7, 138.7, 136.3, 133.6 (d, *J* = 3.5 Hz), 130.6, 129.8, 129.5, 129.0, 128.1 (d, *J* = 7.8 Hz), 125.9, 124.6, 124.4, 121.7 (d, *J* = 22.4 Hz), 115.8 (d, *J* = 21.9 Hz), 21.5.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -113.9.

HRMS calcd for [M+H]<sup>+</sup> C<sub>25</sub>H<sub>19</sub>FNO<sub>2</sub>S 416.1115, found: 416.1117.

**(E)-3-(4-Chlorostyryl)-5-(4-nitrophenyl)-2-(p-tolyl)thiophene (14)**

From 2-(2-bromo-4-methylphenyl)-5-(4-nitrophenyl)thiophene **3** (0.374 g, 1 mmol) and 4-chlorostyrene (0.277 g, 2 mmol), **14** was isolated in 63% (0.272 g) yield as a yellow solid: mp 170-172 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.27 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.74 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 4H), 7.11 (d, *J* = 16.3 Hz, 1H), 7.01 (d, *J* = 16.3 Hz, 1H), 2.44 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 146.9, 143.3, 140.4, 139.8, 138.8, 136.2, 135.9, 133.5, 130.5, 129.8, 129.6, 129.1, 128.9, 127.7, 126.0, 124.6, 124.3, 122.5, 21.5.

HRMS calcd for [M+H]<sup>+</sup> C<sub>25</sub>H<sub>19</sub>ClNO<sub>2</sub>S 432.0819, found: 432.0819.

**(E)-3-(2,4-Dimethylstyryl)-5-(4-nitrophenyl)-2-(p-tolyl)thiophene (15)**

From 2-(2-bromo-4-methylphenyl)-5-(4-nitrophenyl)thiophene **3** (0.374 g, 1 mmol) and 2,4-dimethylstyrene (0.264 g, 2 mmol), **15** was isolated in 64% (0.272 g) yield as a yellow solid: mp 184-186 °C.



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.27 (d,  $J$  = 8.6 Hz, 2H), 7.80 (d,  $J$  = 8.6 Hz, 2H), 7.75 (s, 1H), 7.43 (d,  $J$  = 8.1 Hz, 2H), 7.36 (d,  $J$  = 8.1 Hz, 1H), 7.30-7.22 (m, 3H), 7.03-6.96 (m, 3H), 2.43 (s, 3H), 2.42 (s, 3H), 2.32 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.9, 142.5, 140.6, 139.6, 138.6, 137.7, 137.0, 135.7, 133.6, 131.4, 130.7, 129.7, 129.5, 128.0, 127.2, 126.0, 125.5, 124.7, 124.6, 122.4, 21.4, 21.3, 20.1.  
HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{27}\text{H}_{24}\text{NO}_2\text{S}$  426.1523, found: 426.1519.

#### **(E)-3-(2-(Naphthalen-2-yl)vinyl)-5-(4-nitrophenyl)-2-(p-tolyl)thiophene (16)**

From 2-(2-bromo-4-methylphenyl)-5-(4-nitrophenyl)thiophene **3** (0.374 g, 1 mmol) and 2-vinylnaphthalene (0.308 g, 2 mmol), **16** was isolated in 58% (0.259 g) yield as a yellow solid: mp 198-200 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.30 (d,  $J$  = 8.6 Hz, 2H), 7.88-7.78 (m, 7H), 7.65 (dd,  $J$  = 8.6, 1.7 Hz, 1H), 7.52-7.45 (m, 4H), 7.35 (d,  $J$  = 8.6 Hz, 2H), 7.29-7.27 (m, 2H), 2.48 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.9, 143.0, 140.5, 139.7, 138.7, 136.6, 134.9, 133.9, 133.2, 130.7, 130.4, 129.8, 129.6, 128.5, 128.1, 127.9, 126.7, 126.6, 126.2, 126.0, 124.6, 124.5, 123.5, 122.2, 21.5.

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{29}\text{H}_{22}\text{NO}_2\text{S}$  448.1366, found: 448.1369.

#### **(E)-5-(4-Nitrophenyl)-2-phenyl-3-styrylthiophene (17)**

From 2-(2-bromophenyl)-5-(4-nitrophenyl)thiophene **5** (0.360 g, 1 mmol) and styrene (0.208 g, 2 mmol), **17** was isolated in 62% (0.237 g) yield as a yellow solid: mp 148-150 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.27 (d,  $J$  = 8.6 Hz, 2H), 7.80 (d,  $J$  = 8.6 Hz, 2H), 7.78 (s, 1H), 7.57-7.41 (m, 7H), 7.39-7.32 (m, 2H), 7.26 (t,  $J$  = 8.2 Hz, 1H), 7.15 (d,  $J$  = 16.3 Hz, 1H), 7.08 (d,  $J$  = 16.3 Hz, 1H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.0, 142.6, 140.4, 140.0, 137.3, 136.8, 133.5, 130.6, 129.7, 129.1, 128.9, 128.6, 128.0, 126.6, 126.0, 124.6, 124.5, 121.8.

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{24}\text{H}_{18}\text{NO}_2\text{S}$  384.1053, found: 384.1051.

### **(E)-2-(5-Phenyl-4-styrylthiophen-2-yl)benzotrile (18)**

From 2-(5-(2-bromophenyl)thiophen-2-yl)benzotrile **7** (0.340 g, 1 mmol) and styrene (0.208 g, 2 mmol), **18** was isolated in 66% (0.240 g) yield as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.94 (s, 1H), 7.78 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.69 (d,  $J = 8.0, 1.3$  Hz, 1H), 7.63 (td,  $J = 7.6, 1.4$  Hz, 1H), 7.58-7.39 (m, 8H), 7.33 (t,  $J = 8.2$  Hz, 2H), 7.24 (t,  $J = 8.2$  Hz, 1H), 7.16 (d,  $J = 16.3$  Hz, 1H), 7.08 (d,  $J = 16.3$  Hz, 1H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.2, 138.1, 137.5, 137.4, 136.4, 134.6, 133.6, 133.2, 130.6, 129.8, 129.6, 129.0, 128.8, 128.4, 127.9, 127.8, 126.7, 126.5, 121.9, 119.0, 110.0.

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{25}\text{H}_{18}\text{NS}$  364.1155, found: 364.1157.

### **(E)-2-(3-Fluorophenyl)-5-(4-nitrophenyl)-3-styrylthiophene (19)**

From 2-(2-bromo-5-fluorophenyl)-5-(4-nitrophenyl)thiophene **4** (0.378 g, 1 mmol) and styrene (0.208 g, 2 mmol), **19** was isolated in 58% (0.232 g) yield as a yellow solid: mp 140-142 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.28 (d,  $J = 8.6$  Hz, 2H), 7.80 (d,  $J = 8.6$  Hz, 2H), 7.77 (s, 1H), 7.49-7.42 (m, 3H), 7.39-7.22 (m, 4H), 7.17-7.07 (m, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.9 (d,  $J = 247.6$  Hz), 147.0, 140.6 (d,  $J = 2.4$  Hz), 140.5, 140.2, 137.3, 137.1, 135.5 (d,  $J = 8.2$  Hz), 131.2, 130.6 (d,  $J = 8.5$  Hz), 128.9, 128.1, 126.6, 126.1, 125.4 (d,  $J = 3.0$  Hz), 124.7, 124.6, 121.3, 116.5 (d,  $J = 22.5$  Hz), 115.5 (d,  $J = 21.1$  Hz).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -111.9.

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{24}\text{H}_{17}\text{FNO}_2\text{S}$  402.0958, found: 402.0964.

### **(E)-2-(3-Fluorophenyl)-3-(4-methylstyryl)-5-(4-nitrophenyl)thiophene (20)**

From 2-(2-bromo-5-fluorophenyl)-5-(4-nitrophenyl)thiophene **4** (0.378 g, 1 mmol) and 4-methylstyrene (0.236 g, 2 mmol), **20** was isolated in 60% (0.249 g) yield as a yellow solid: mp 158-160 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.27 (d,  $J$  = 8.6 Hz, 2H), 7.79 (d,  $J$  = 8.6 Hz, 2H), 7.75 (s, 1H), 7.49-7.40 (m, 1H), 7.35 (d,  $J$  = 8.1 Hz, 2H), 7.34-7.29 (m, 1H), 7.28-7.22 (m, 1H), 7.17 (d,  $J$  = 8.1 Hz, 2H), 7.12 (td,  $J$  = 8.3, 2.6 Hz, 1H), 7.07 (s, 2H), 2.36 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  163.1 (d,  $J$  = 247.4 Hz), 147.1, 140.4, 140.2, 140.1 (d,  $J$  = 2.5 Hz), 138.2, 137.5, 135.6 (d,  $J$  = 8.3 Hz), 134.3, 131.2, 130.6 (d,  $J$  = 8.5 Hz), 129.6, 126.6, 126.1, 125.4 (d,  $J$  = 3.0 Hz), 124.6, 120.3, 116.5 (d,  $J$  = 22.5 Hz), 115.4 (d,  $J$  = 21.1 Hz), 21.4.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -112.0.

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{25}\text{H}_{19}\text{FNO}_2\text{S}$  416.1115, found: 416.1118.

### ***tert*-Butyl (*E*)-3-(5-(4-cyanophenyl)-2-(*p*-tolyl)thiophen-3-yl)acrylate (**21**)**

From 4-(5-(2-bromo-4-methylphenyl)thiophen-2-yl)benzotrile **2** (0.354 g, 1 mmol) and *tert*-butyl acrylate (0.256 g, 2 mmol), **21** was isolated in 52% (0.208 g) yield as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.72-7.65 (m, 4H), 7.62 (d,  $J$  = 15.8 Hz, 1H), 7.61 (s, 1H), 7.36 (d,  $J$  = 8.1 Hz, 2H), 7.27 (d,  $J$  = 8.1 Hz, 2H), 6.30 (d,  $J$  = 15.8 Hz, 1H), 2.42 (s, 3H), 1.51 (s, 9H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.6, 147.5, 140.6, 139.2, 138.1, 136.2, 133.9, 133.0, 129.8, 129.7, 129.6, 126.1, 123.8, 121.1, 118.8, 111.2, 80.7, 28.4, 21.4.

HRMS calcd for  $[\text{M}+\text{Na}]^+$   $\text{C}_{25}\text{H}_{23}\text{NO}_2\text{NaS}$  424.1342, found: 424.1344.

### ***tert*-Butyl (*E*)-3-(5-(4-nitrophenyl)-2-(*p*-tolyl)thiophen-3-yl)acrylate (**22**)**

From 2-(2-bromo-4-methylphenyl)-5-(4-nitrophenyl)thiophene **3** (0.374 g, 1 mmol) and *tert*-butyl acrylate (0.256 g, 2 mmol), **22** was isolated in 56% (0.236 g) yield as a yellow solid: mp 176-178 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.26 (d,  $J$  = 8.6 Hz, 2H), 7.74 (d,  $J$  = 8.6 Hz, 2H), 7.66 (s, 1H), 7.63 (d,  $J$  = 15.8 Hz, 1H), 7.37 (d,  $J$  = 8.1 Hz, 2H), 7.28 (d,  $J$  = 8.1 Hz, 2H), 6.32 (d,  $J$  = 15.8 Hz, 1H), 2.42 (s, 3H), 1.52 (s, 9H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.6, 148.1, 147.1, 140.1, 140.0, 139.4, 136.1, 134.1, 129.9, 129.7, 129.6, 126.0, 124.6, 124.3, 121.2, 80.7, 28.4, 21.4.

HRMS calcd for  $[M+H]^+$  C<sub>24</sub>H<sub>24</sub>NO<sub>4</sub>S 422.1421, found: 422.1426.

**(E)-1-(5-(2-Nitrophenyl)-2-(p-tolyl)thiophen-3-yl)oct-1-en-3-one (23)**

From 2-(2-bromo-4-methylphenyl)-5-(2-nitrophenyl)thiophene **8** (0.374 g, 1 mmol) and oct-1-en-3-one (0.252 g, 2 mmol), **23** was isolated in 55% (0.230 g) yield as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.81 (dd,  $J$  = 8.1, 1.2 Hz, 1H), 7.65-7.48 (m, 4H), 7.36 (d,  $J$  = 8.2 Hz, 2H), 7.31-7.25 (m, 3H), 6.57 (d,  $J$  = 15.8 Hz, 1H), 2.56 (t,  $J$  = 7.6 Hz, 2H), 2.42 (s, 3H), 1.64 (quint.,  $J$  = 7.6 Hz, 2H), 1.39-1.24 (m, 4H), 0.89 (t,  $J$  = 7.6 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  201.0, 149.4, 148.7, 139.2, 136.5, 135.0, 133.2, 132.4, 132.3, 129.8, 129.7, 129.6, 129.7, 127.9, 127.1, 125.9, 124.3, 41.1, 31.6, 24.3, 22.6, 21.4, 14.1.

HRMS calcd for  $[M+H]^+$  C<sub>25</sub>H<sub>26</sub>NO<sub>3</sub>S 420.1628, found: 420.1633.

**(E)-3-(4-(3-Oxoct-1-en-1-yl)-5-(p-tolyl)thiophen-2-yl)benzotrile (24)**

From 3-(5-(2-bromo-4-methylphenyl)thiophen-2-yl)benzotrile **6** (0.354 g, 1 mmol) and oct-1-en-3-one (0.252 g, 2 mmol), **24** was isolated in 57% (0.227 g) yield as a white solid: mp 142-144 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.89 (s, 1H), 7.83 (d,  $J$  = 8.0 Hz, 1H), 7.62-7.49 (m, 4H), 7.36 (d,  $J$  = 8.2 Hz, 2H), 7.29 (d,  $J$  = 8.2 Hz, 2H), 6.66 (d,  $J$  = 15.8 Hz, 1H), 2.59 (t,  $J$  = 7.6 Hz, 2H), 2.44 (s, 3H), 1.66 (quint.,  $J$  = 7.6 Hz, 2H), 1.39-1.24 (m, 4H), 0.90 (t,  $J$  = 7.6 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  200.9, 147.9, 140.4, 139.4, 135.1, 135.0, 133.9, 131.3, 130.1, 130.0, 129.9, 129.8, 129.7, 129.2, 127.2, 123.0, 118.5, 113.6, 41.2, 31.7, 24.4, 22.7, 21.5, 14.1.

HRMS calcd for  $[M+H]^+$  C<sub>26</sub>H<sub>26</sub>NOS 400.1730, found: 400.1734.

#### 4 References

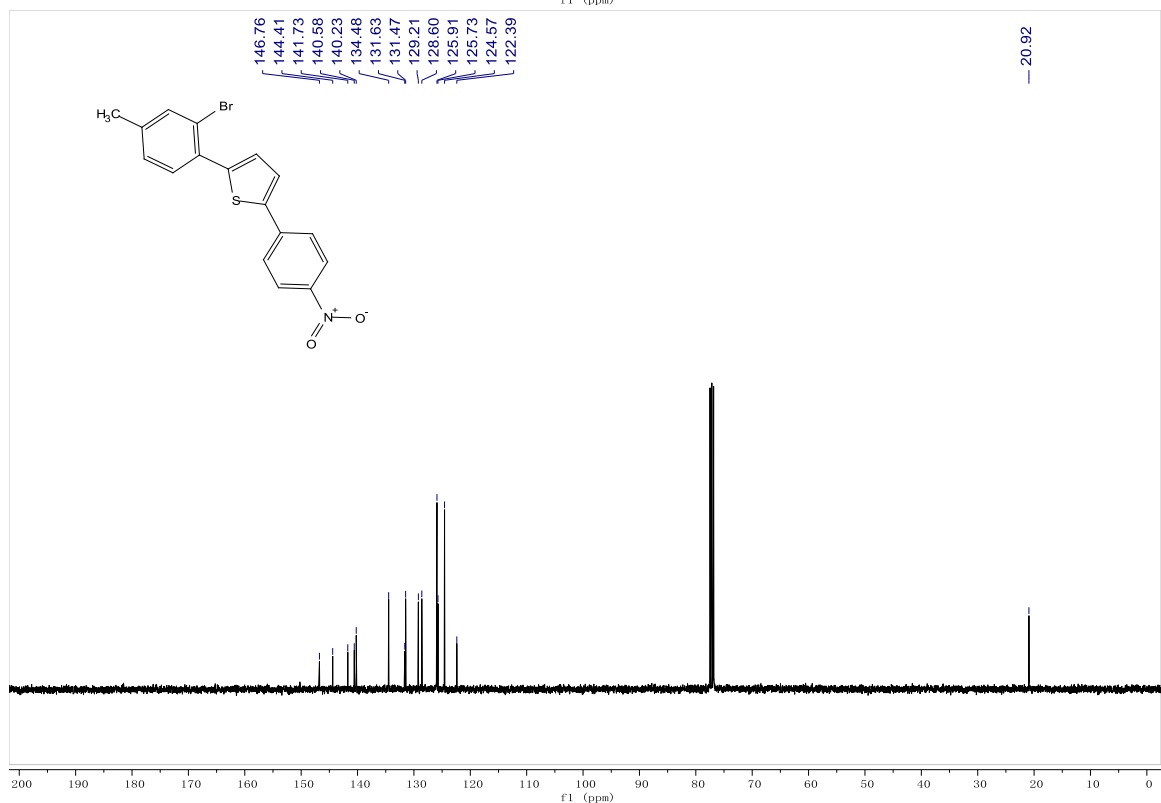
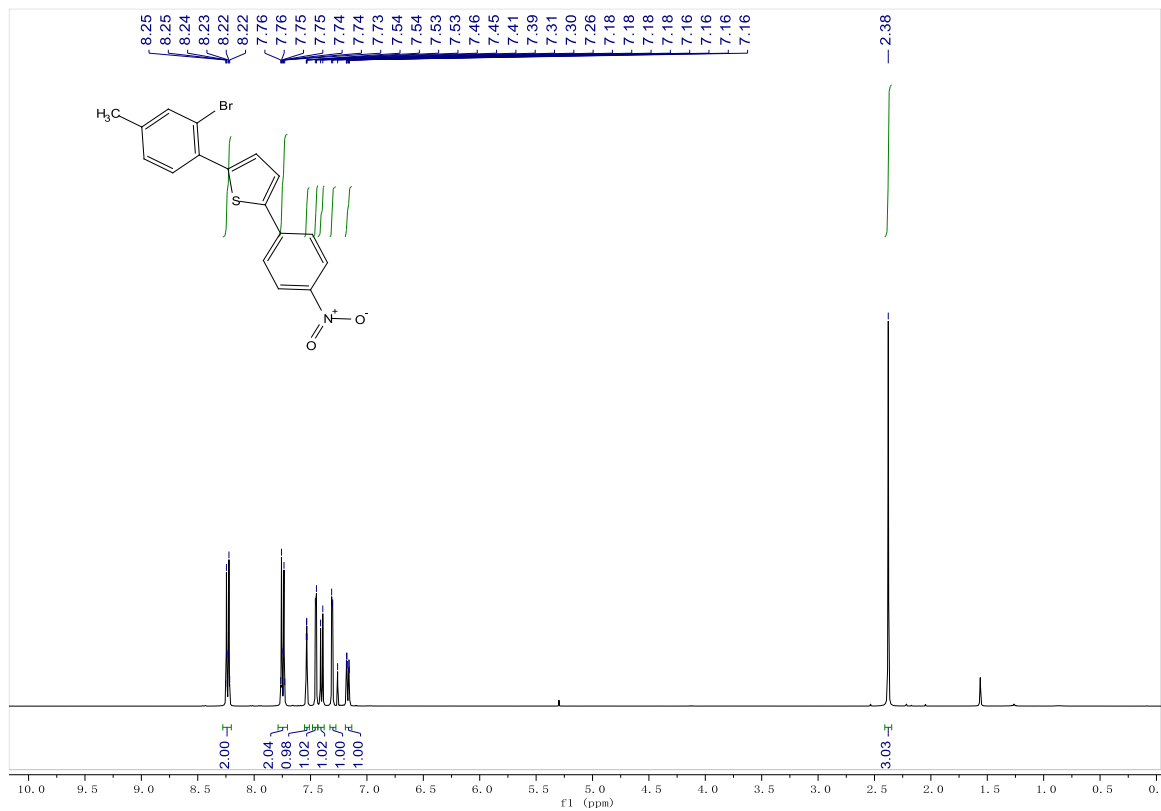
[17b] Liu, L.; Cordier, M.; Roisnel, T.; Doucet, H. Double C–H bond functionalization for C–C coupling at the  $\beta$ -position of thiophenes using palladium-catalyzed 1,4-migration associated with direct arylation. *Org. Chem. Front.* **2023**, *10*, 1441–1455.

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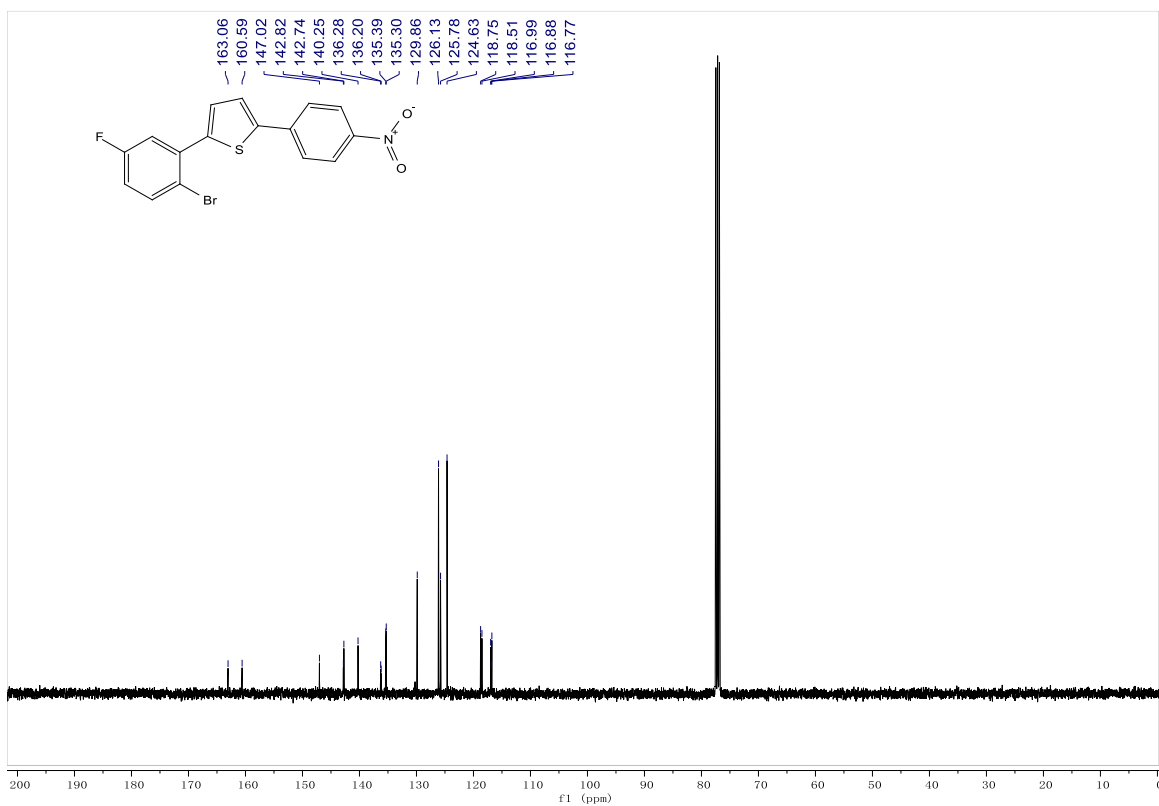
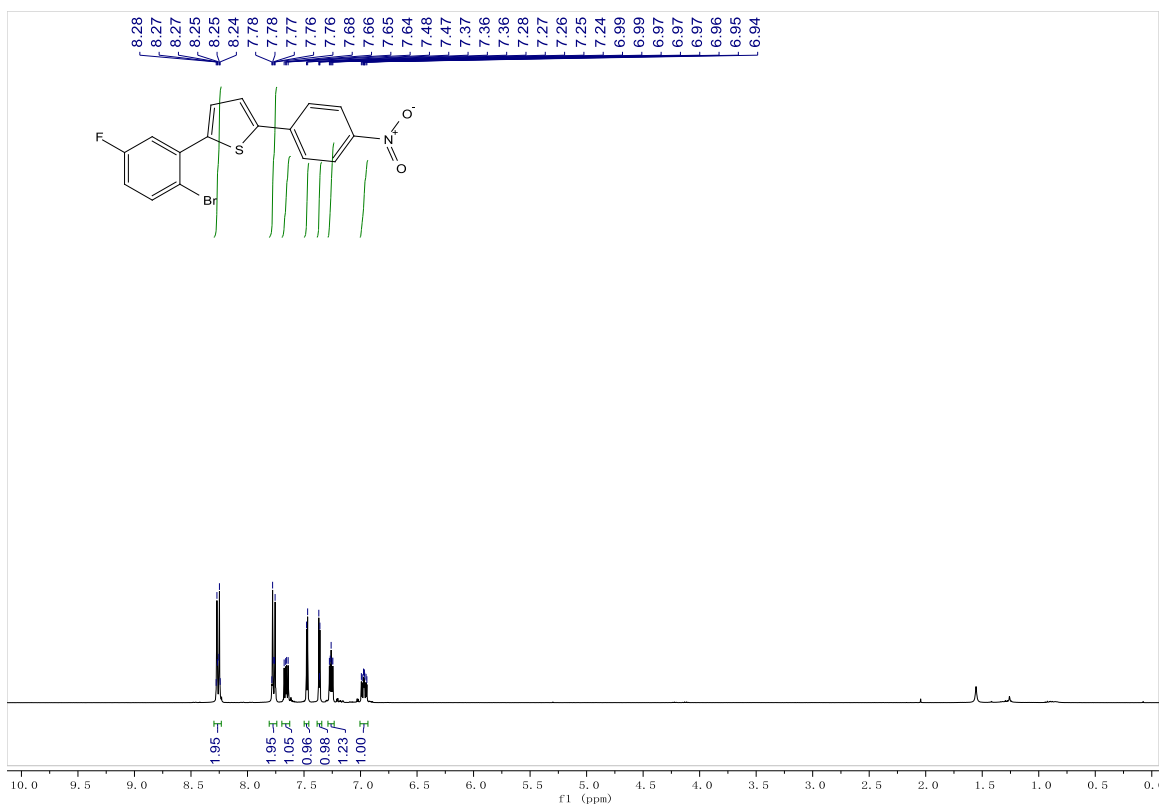
[19] K. Mitsudo, R. Matsuo, T. Yonezawa, H. Inoue, H. Mandai, S. Suga, *Angew. Chem. Int. Ed.* **2020**, *59*, 7803–7807.

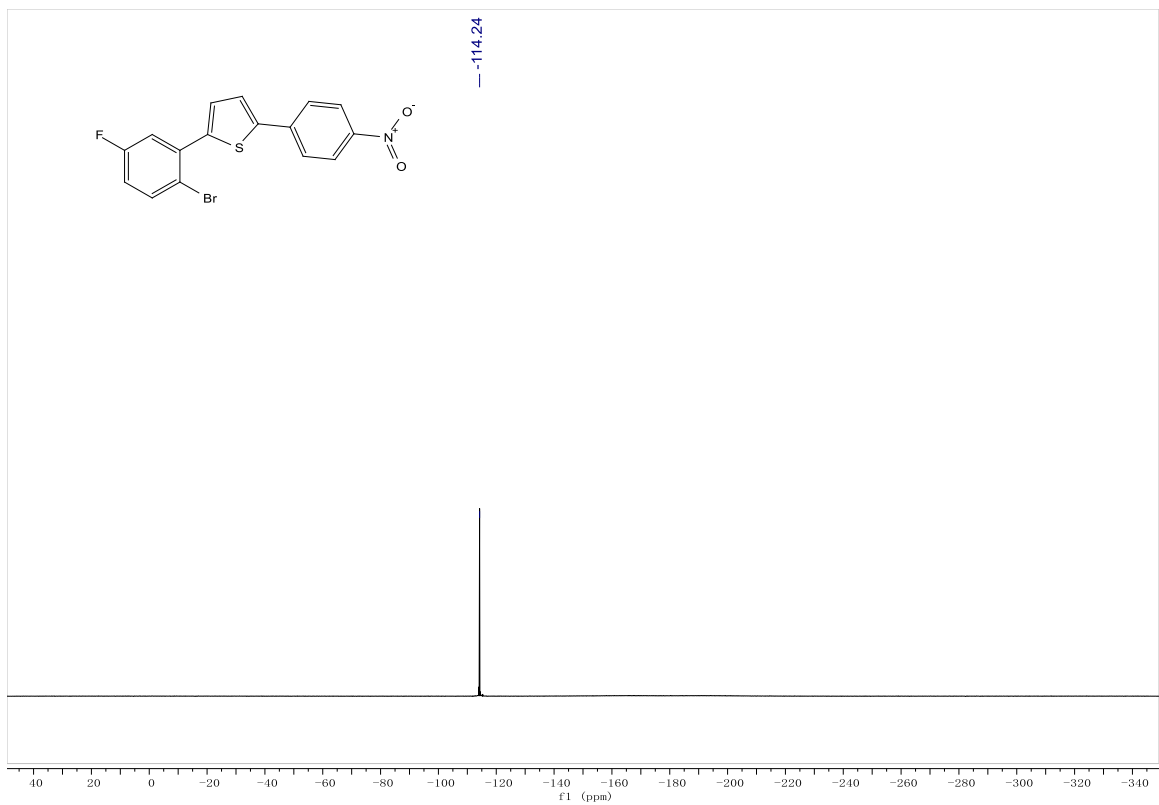
## 5 NMR Spectra

### 2-(2-Bromo-4-methylphenyl)-5-(4-nitrophenyl)thiophene (3)



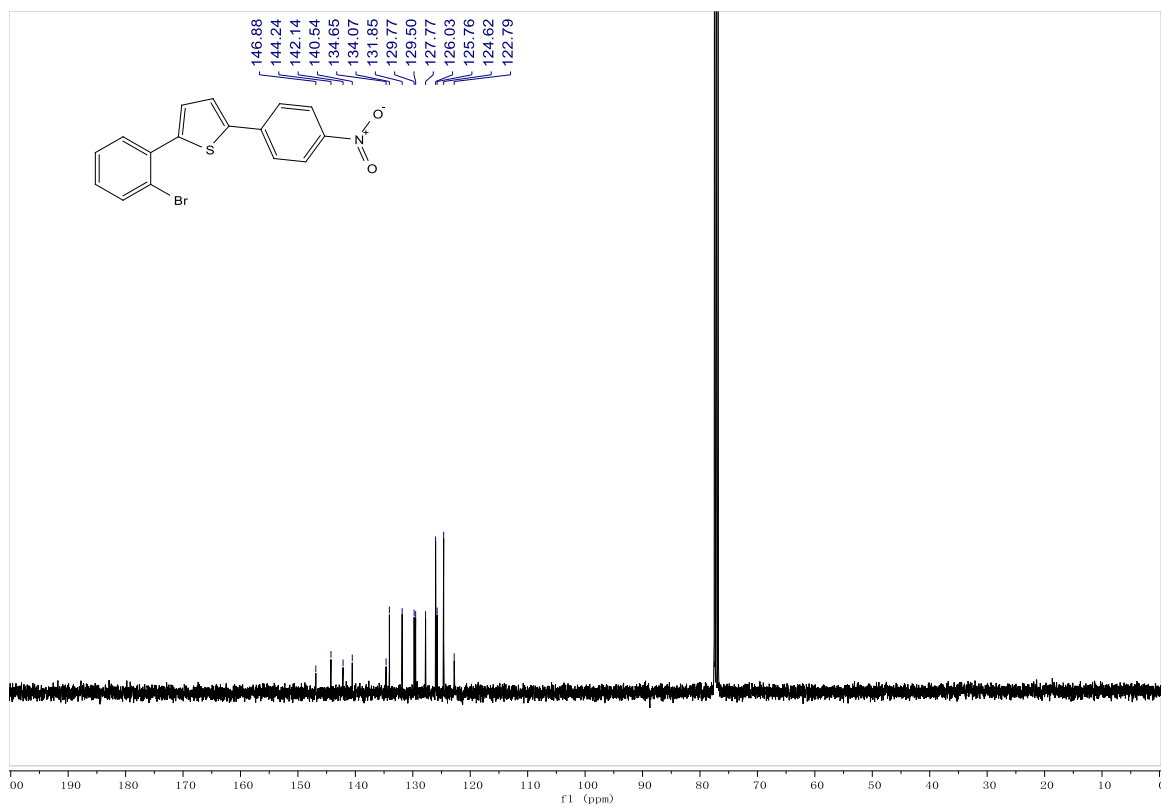
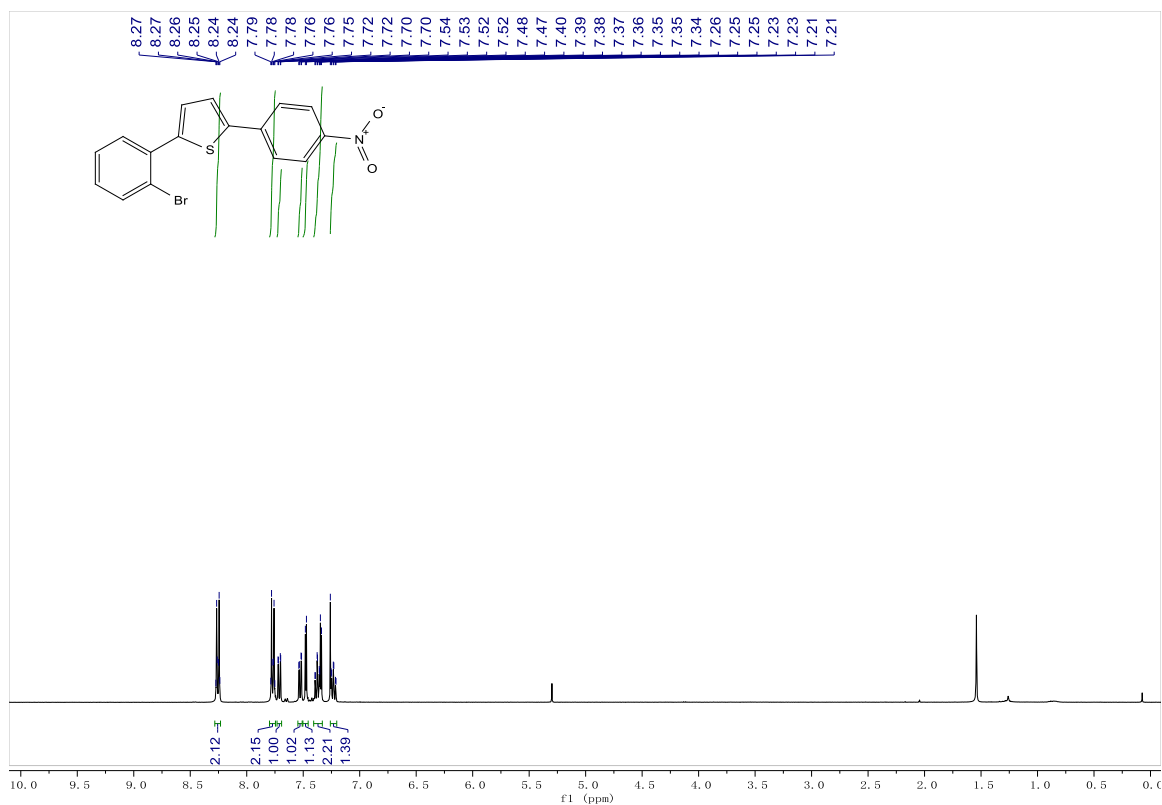
2-(2-Bromo-5-fluorophenyl)-5-(4-nitrophenyl)thiophene (4)



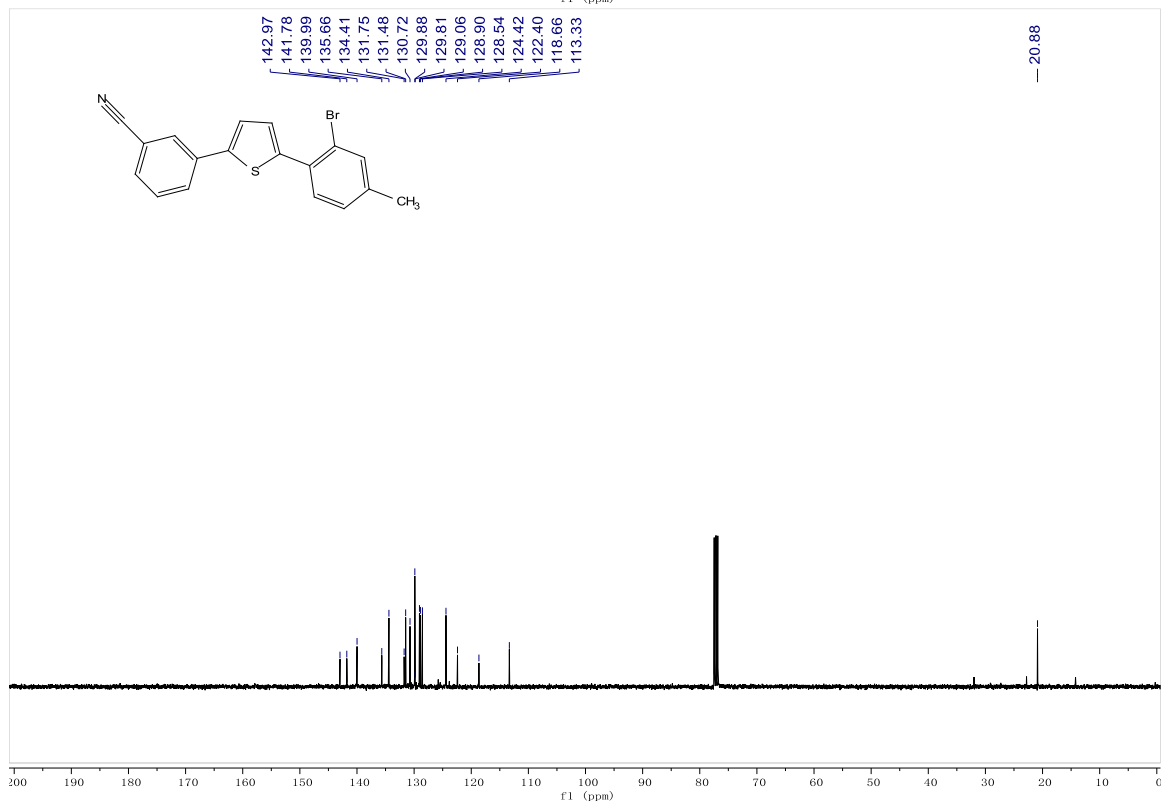
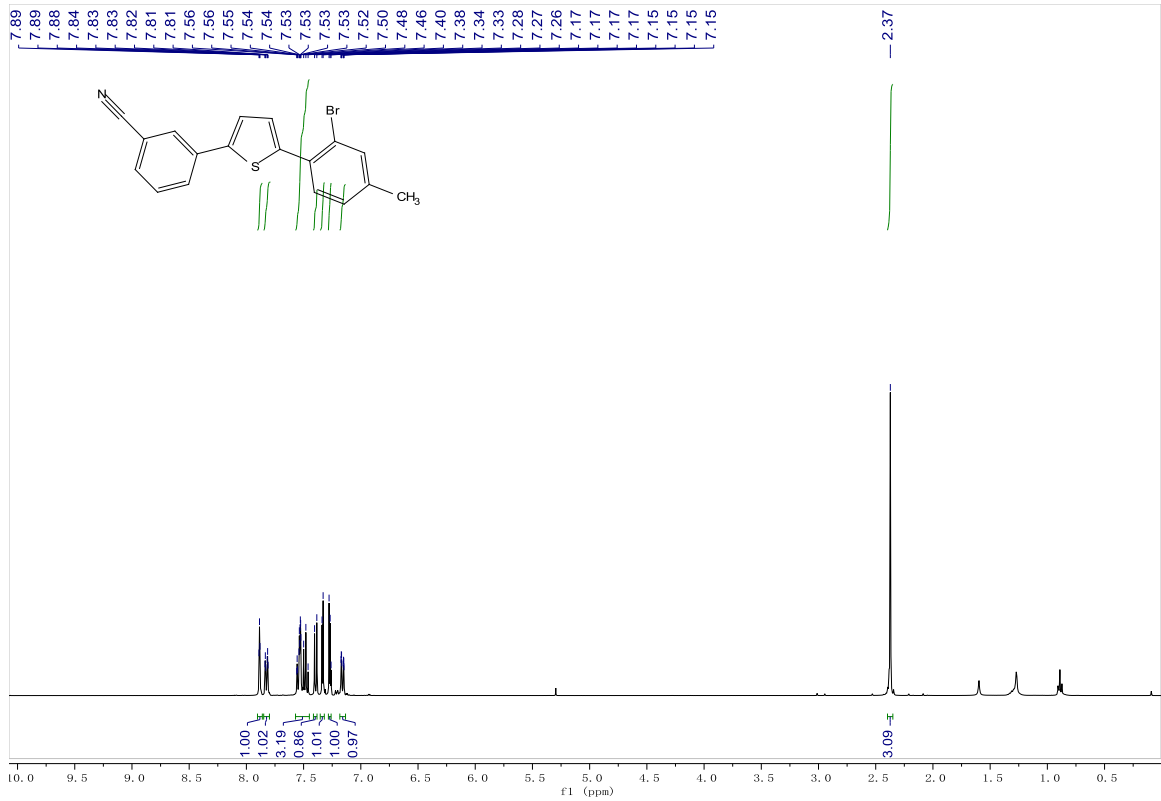




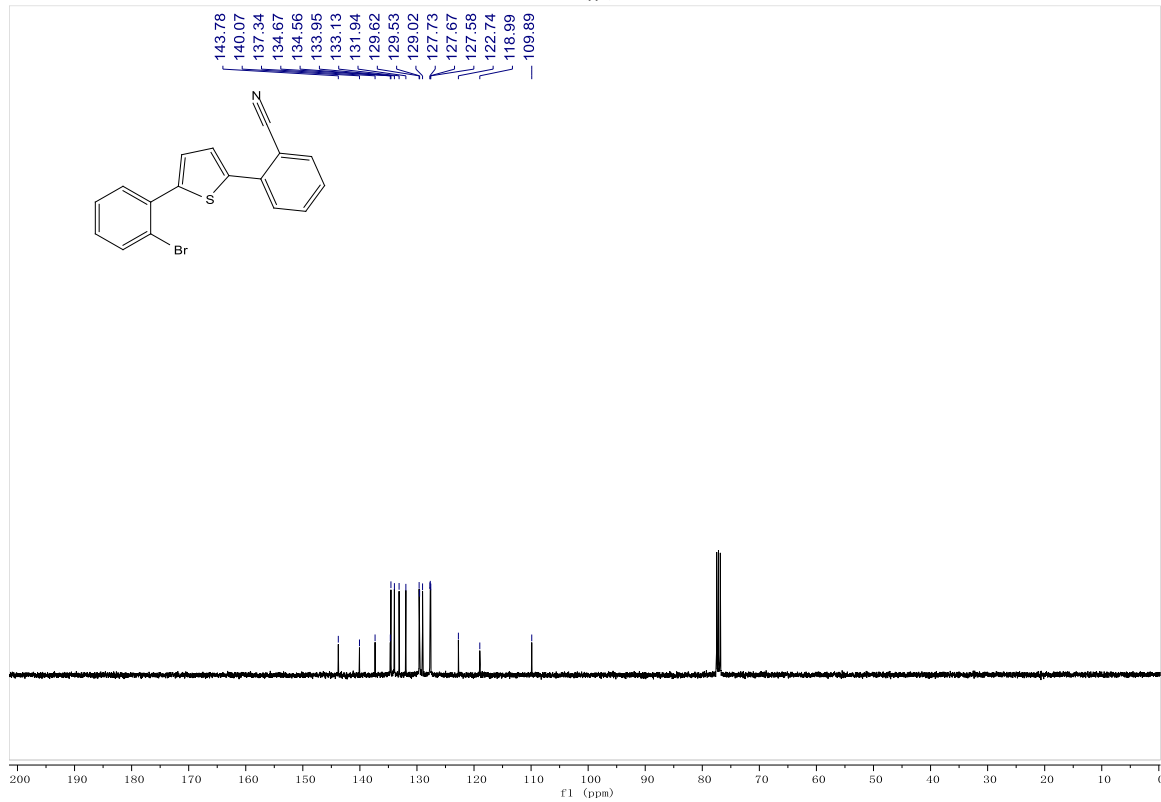
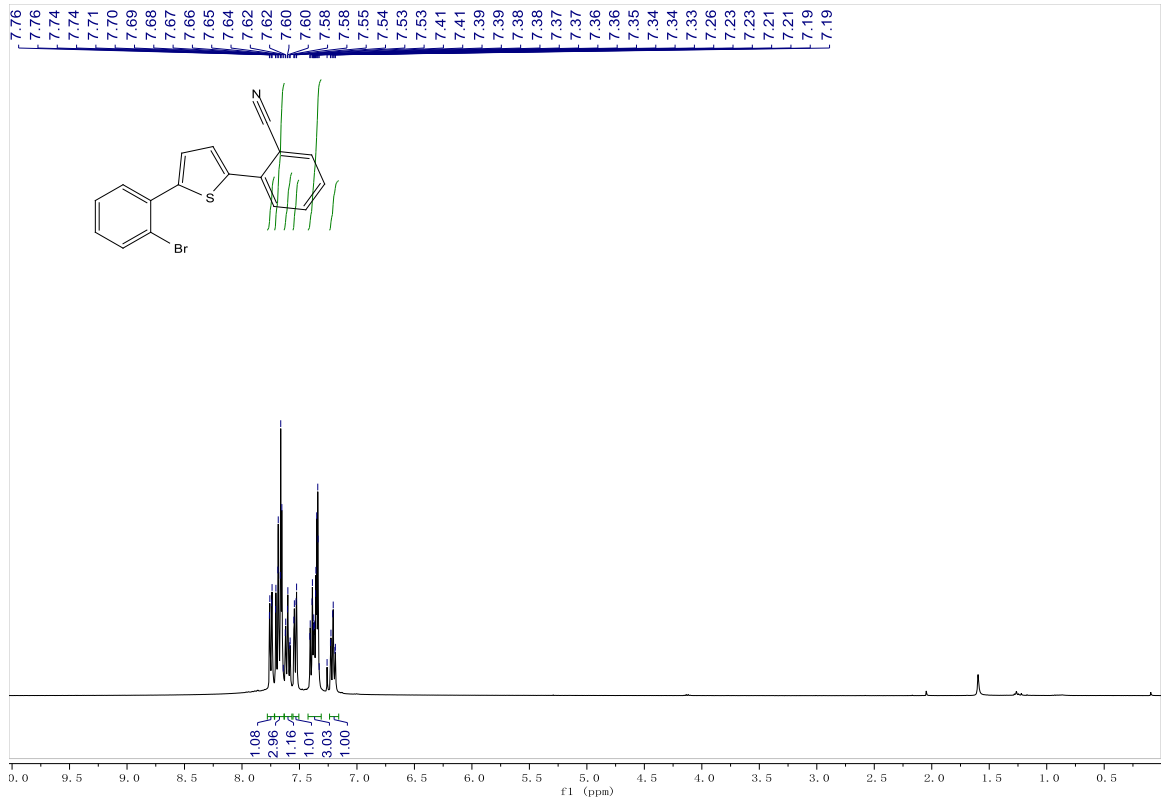
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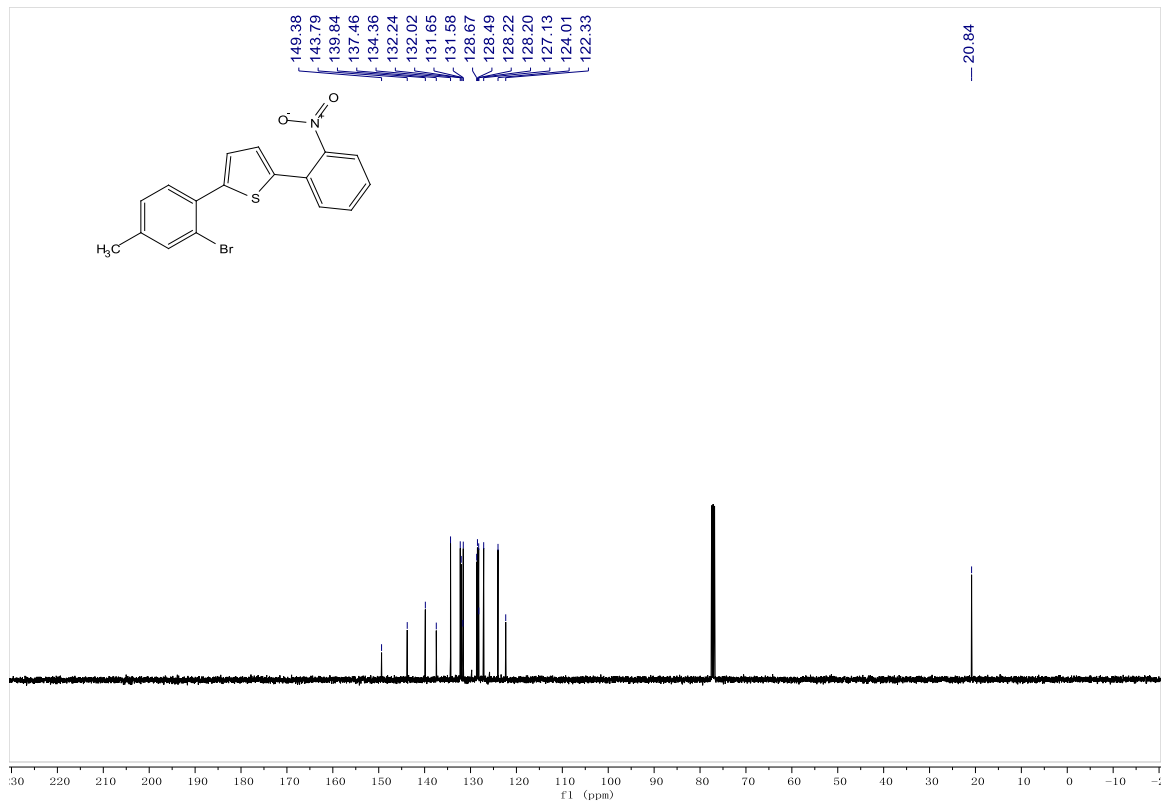
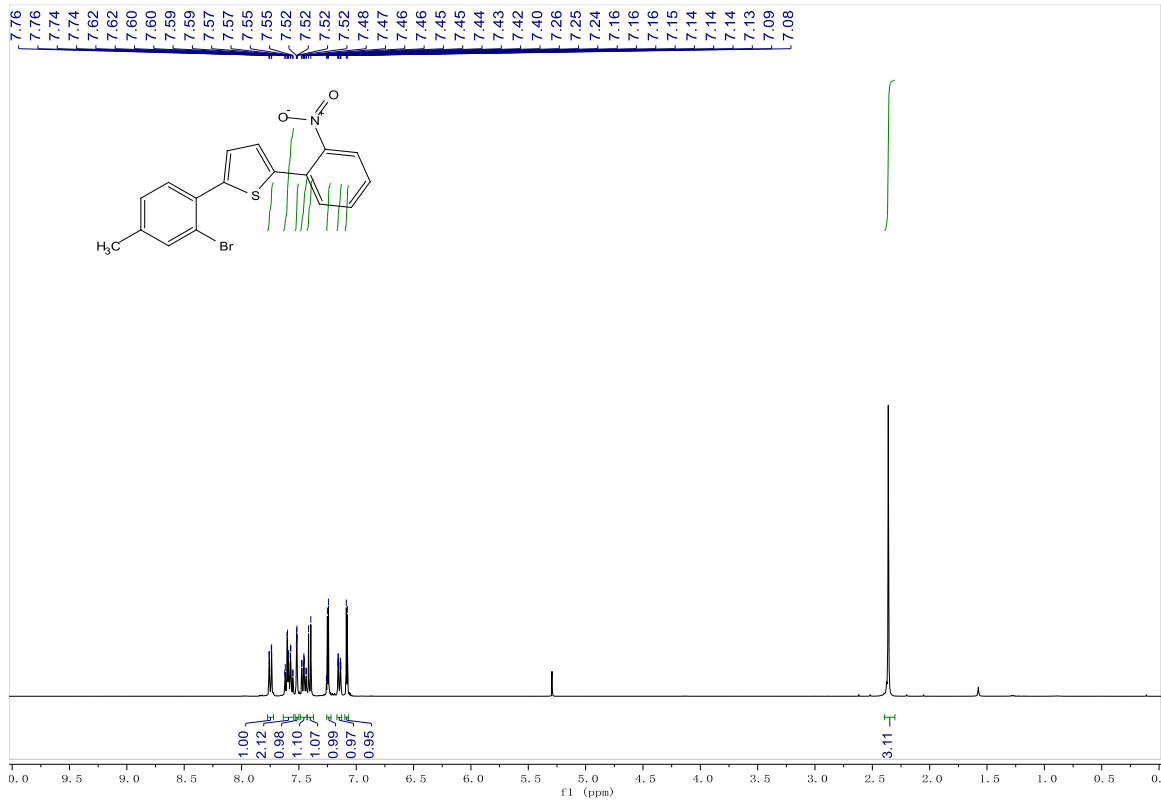
3-(5-(2-Bromo-4-methylphenyl)thiophen-2-yl)benzonitrile (6)



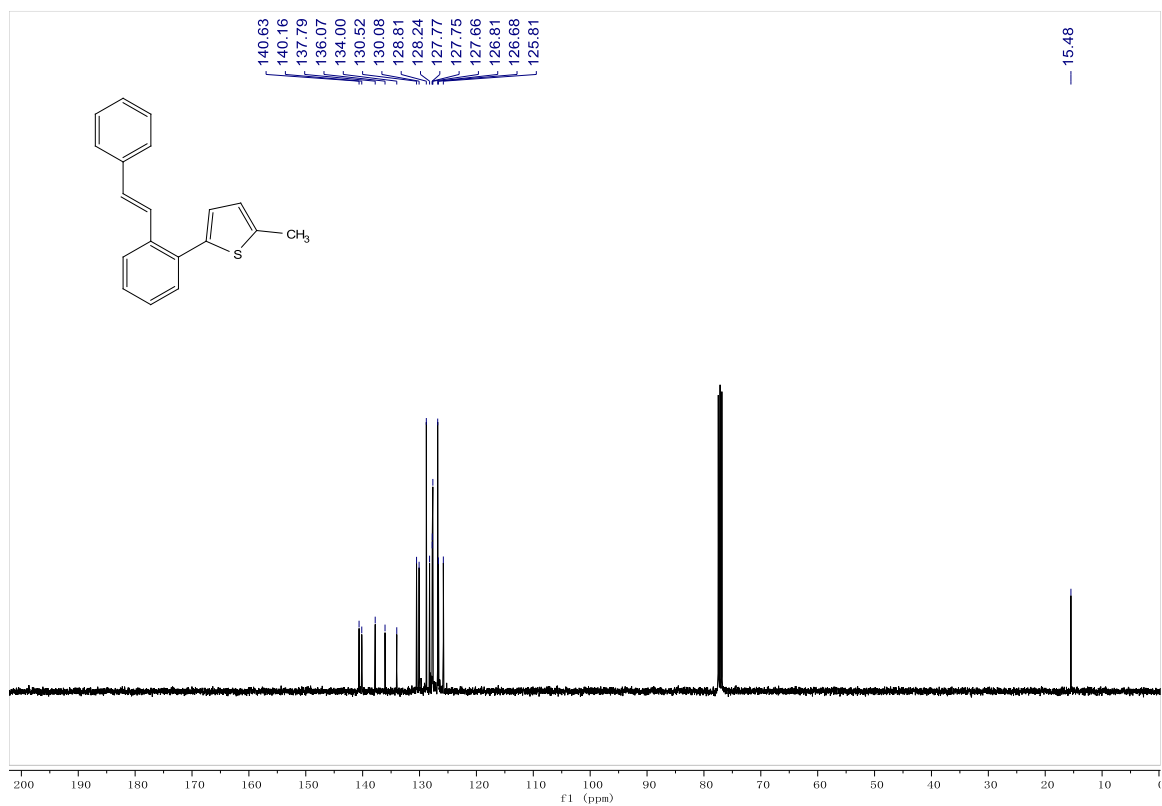
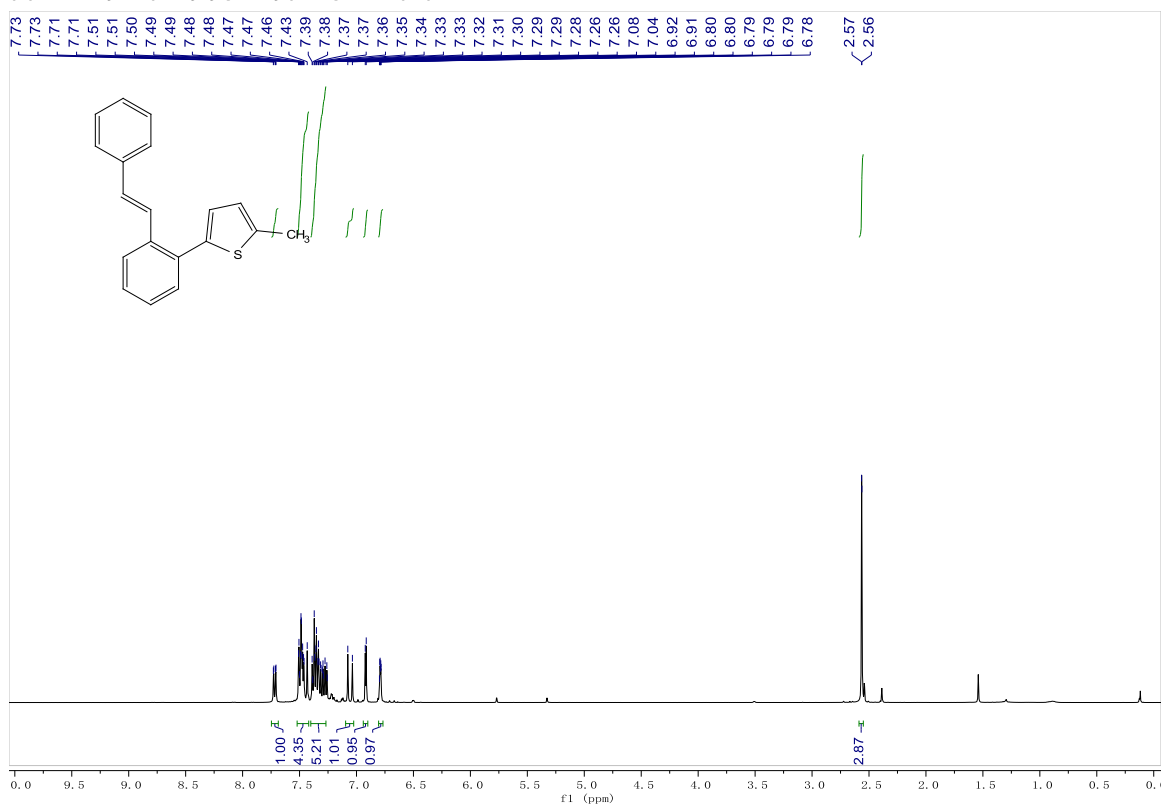
2-(5-(2-Bromophenyl)thiophen-2-yl)benzonitrile (7)



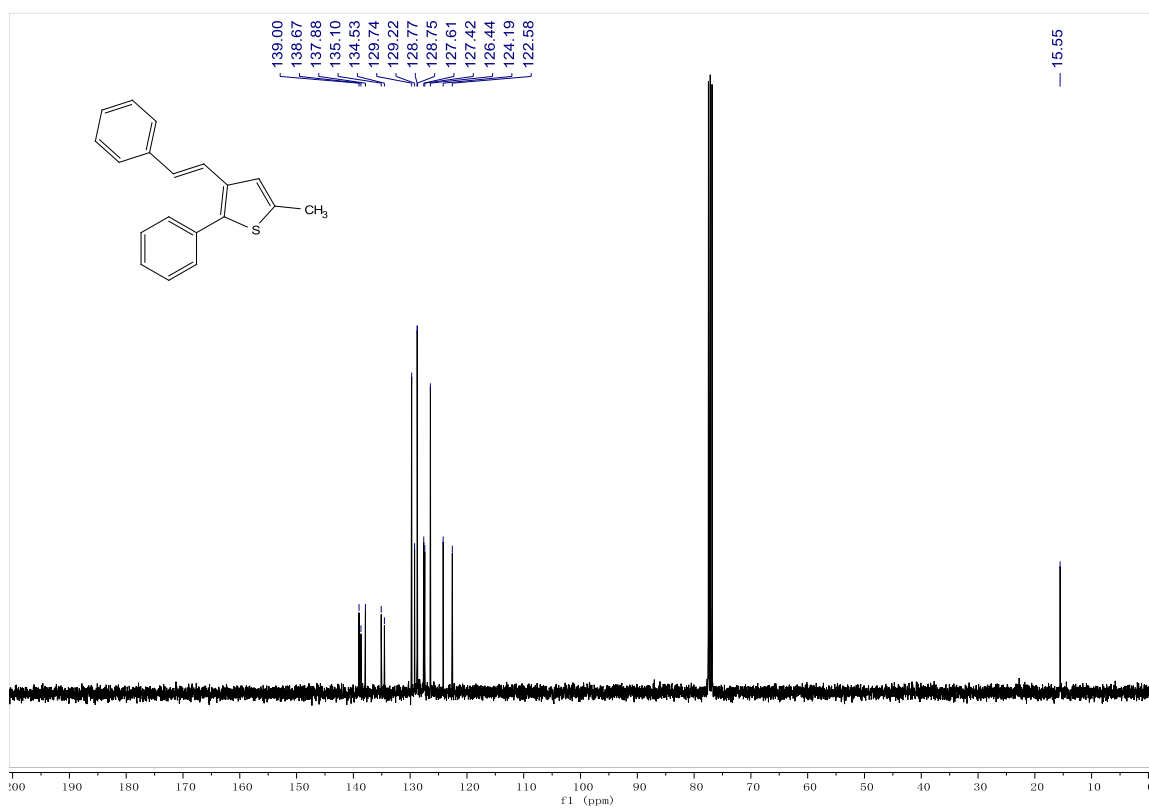
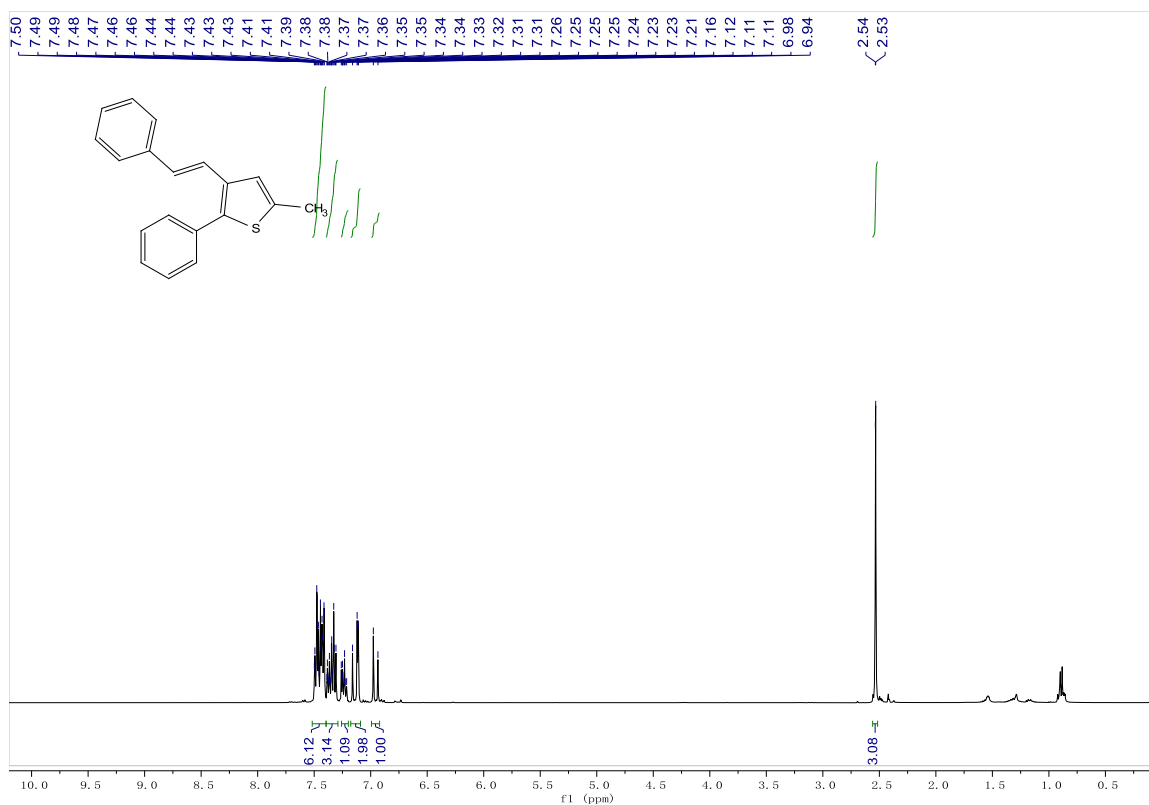
2-(2-Bromo-4-methylphenyl)-5-(2-nitrophenyl)thiophene (8)



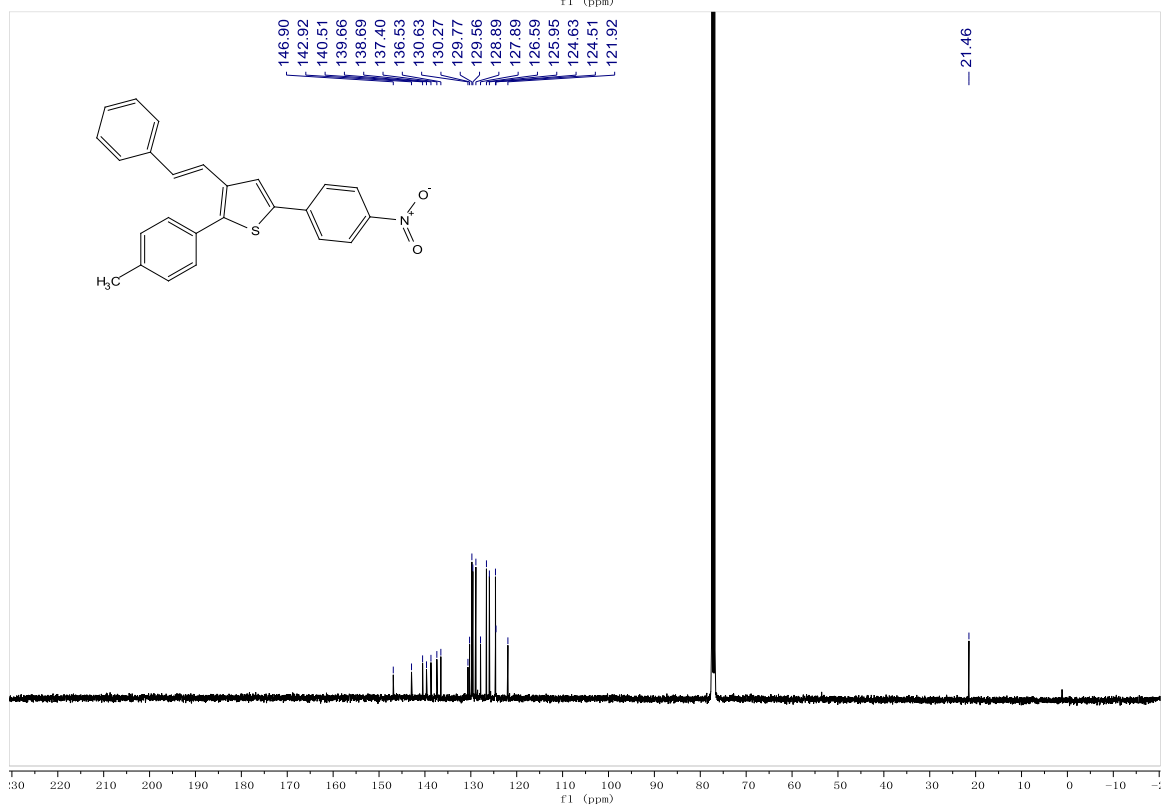
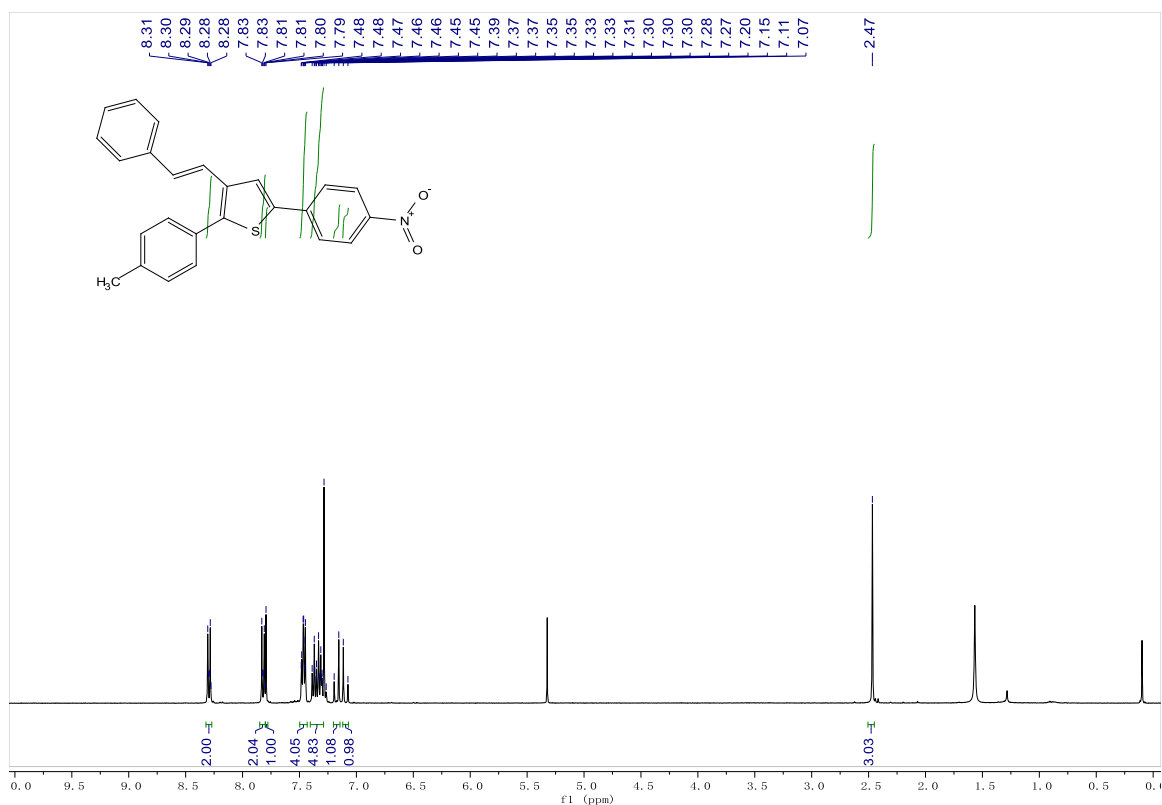
**(E)-2-Methyl-5-(2-styrylphenyl)thiophene (9a)**



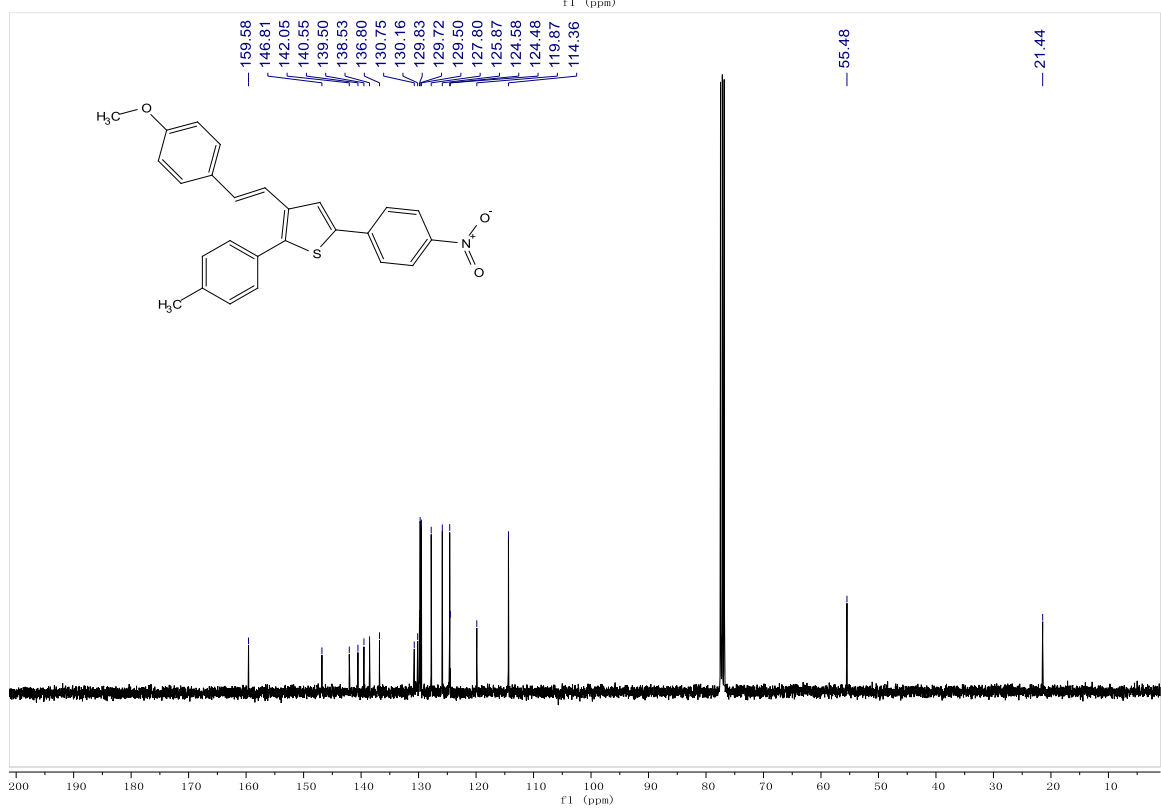
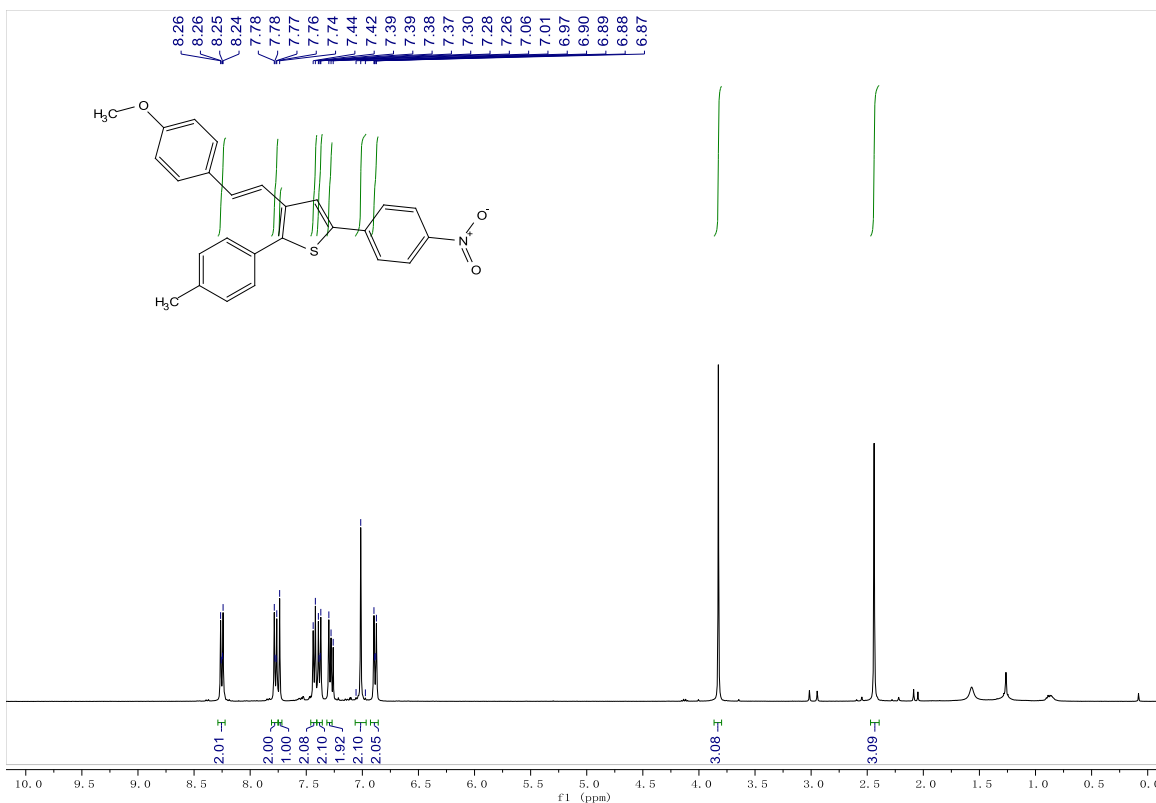
**(E)-5-Methyl-2-phenyl-3-styrylthiophene (9b)**



**(E)-5-(4-Nitrophenyl)-3-styryl-2-(p-tolyl)thiophene (10)**

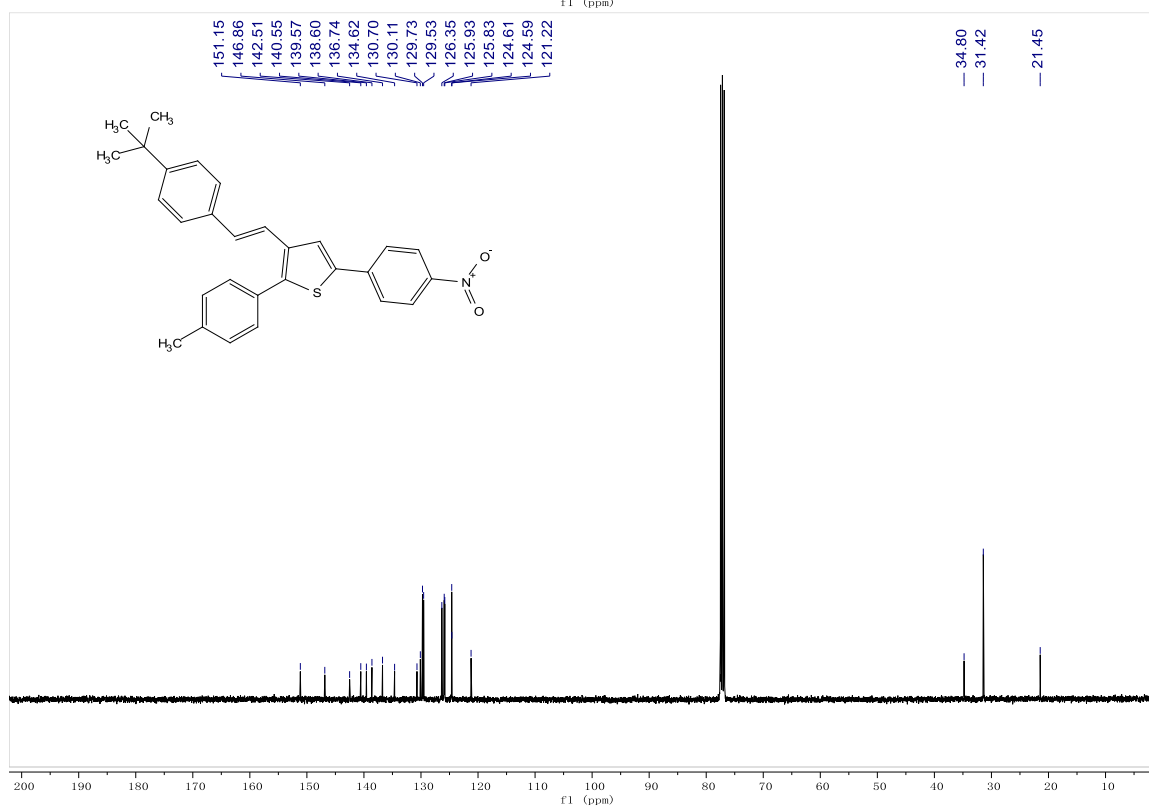
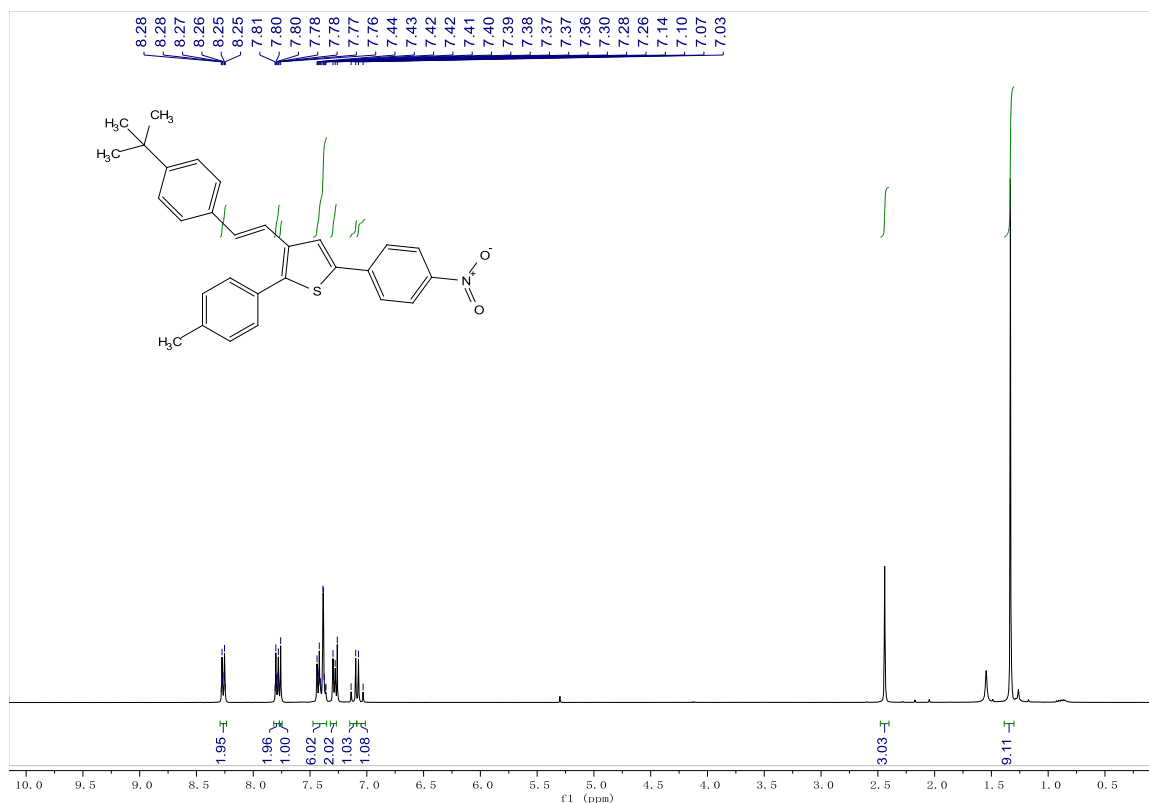


**(E)-3-(4-Methoxystyryl)-5-(4-nitrophenyl)-2-(p-tolyl)thiophene (11)**

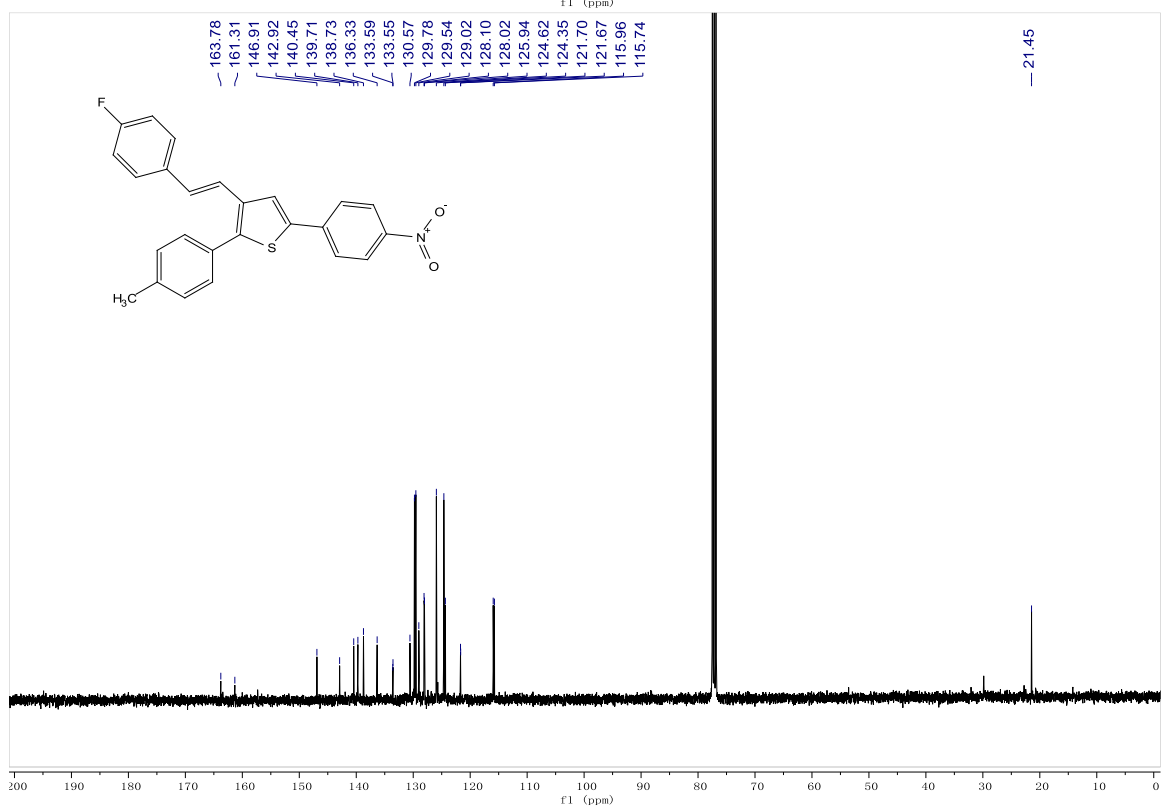
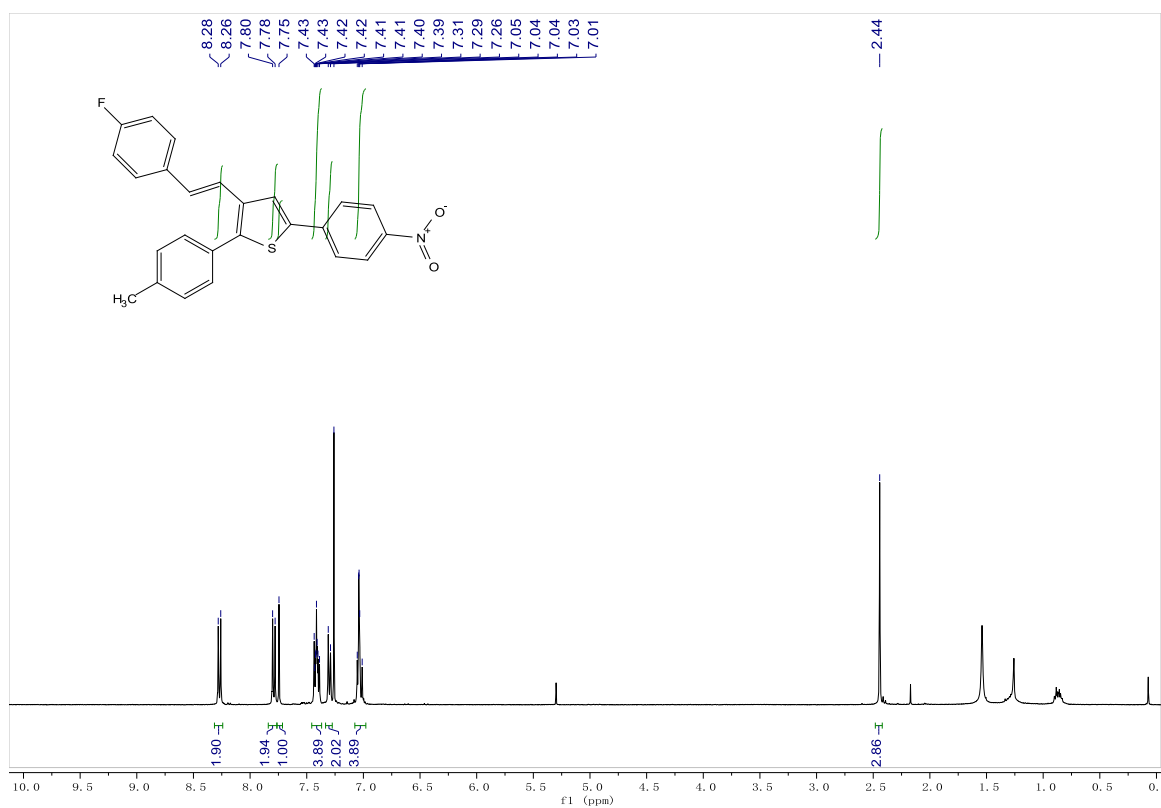


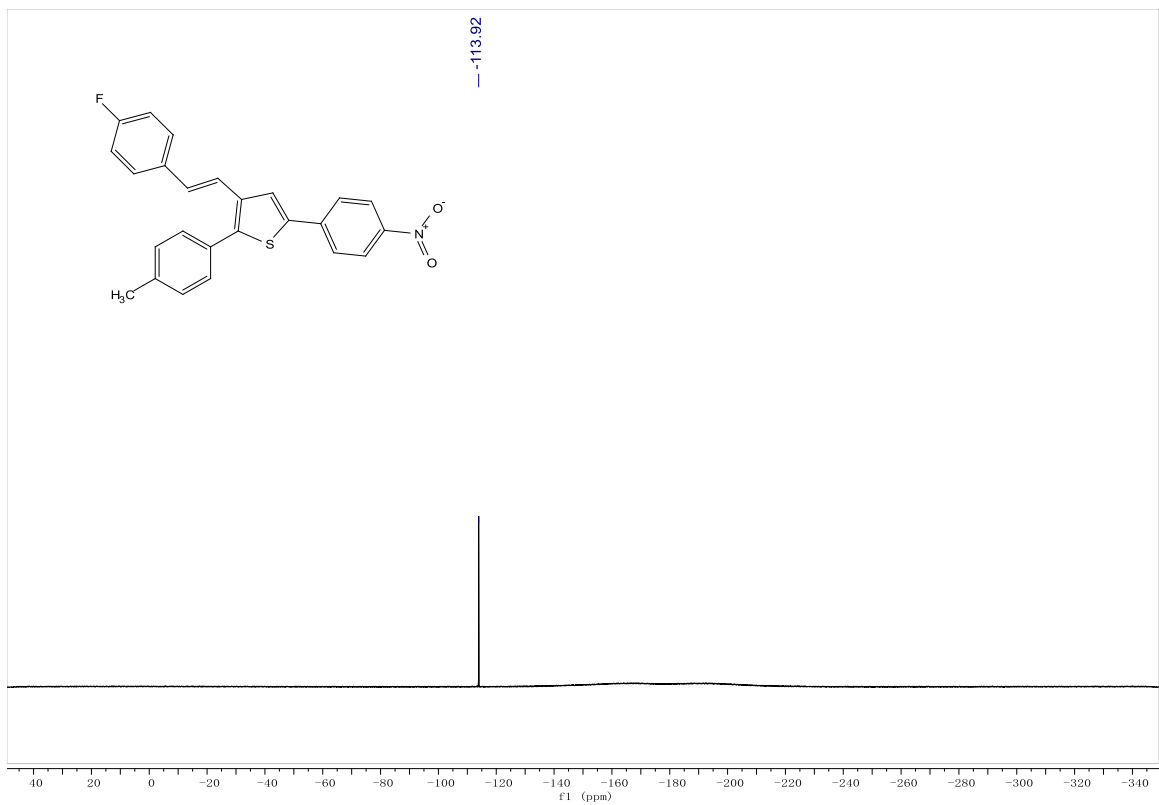


**(E)-3-(4-(*tert*-Butylstyryl)-5-(4-nitrophenyl)-2-(*p*-tolyl)thiophene (12)**

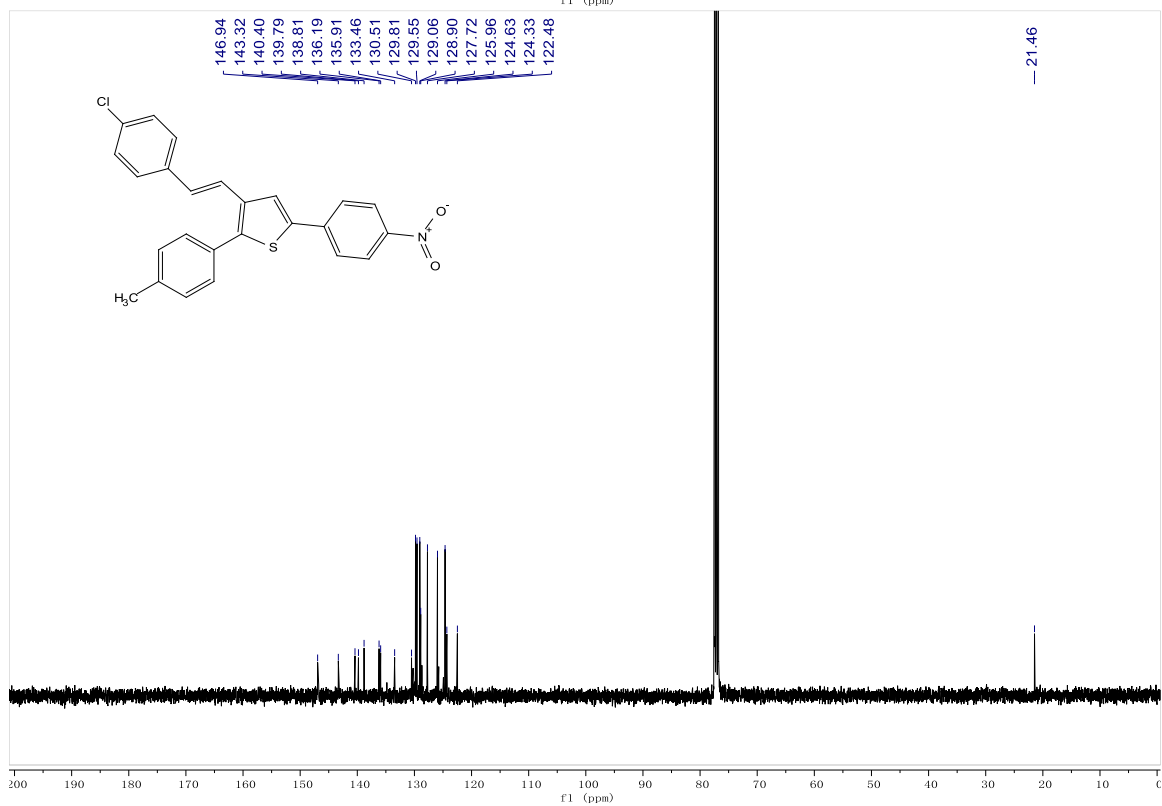
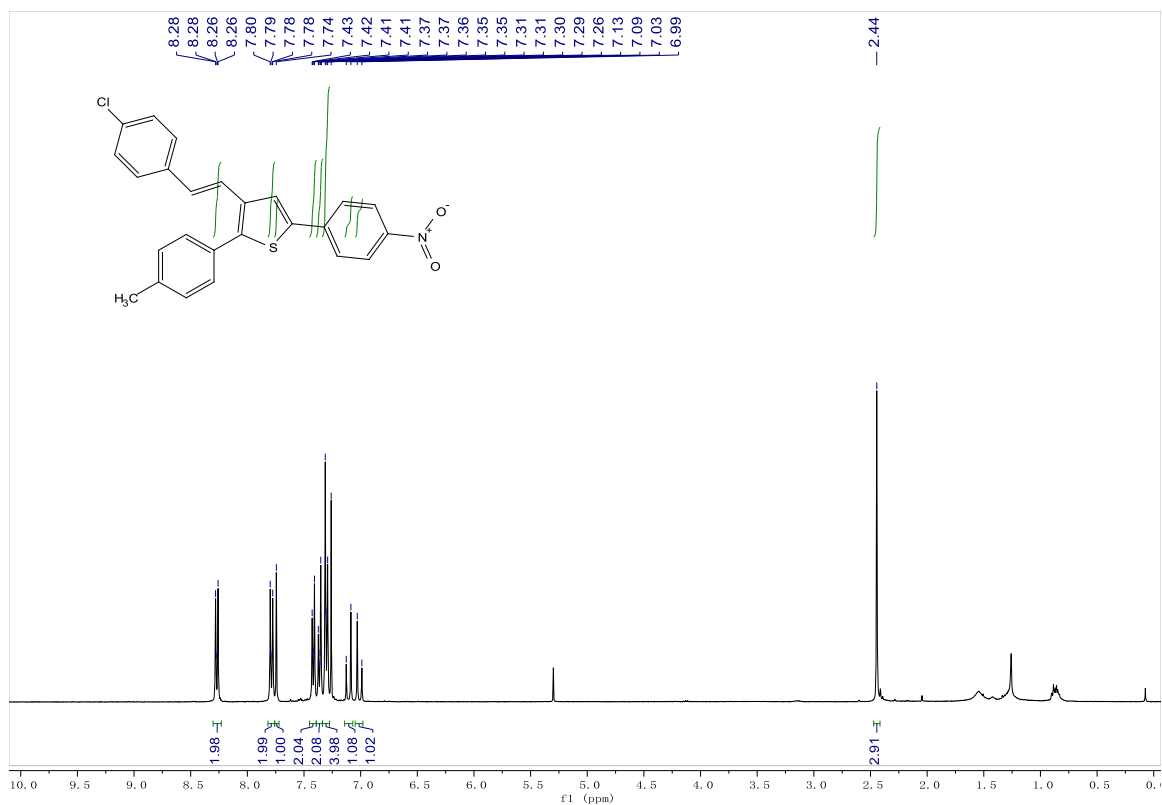


**(E)-3-(4-Fluorostyryl)-5-(4-nitrophenyl)-2-(p-tolyl)thiophene (13)**

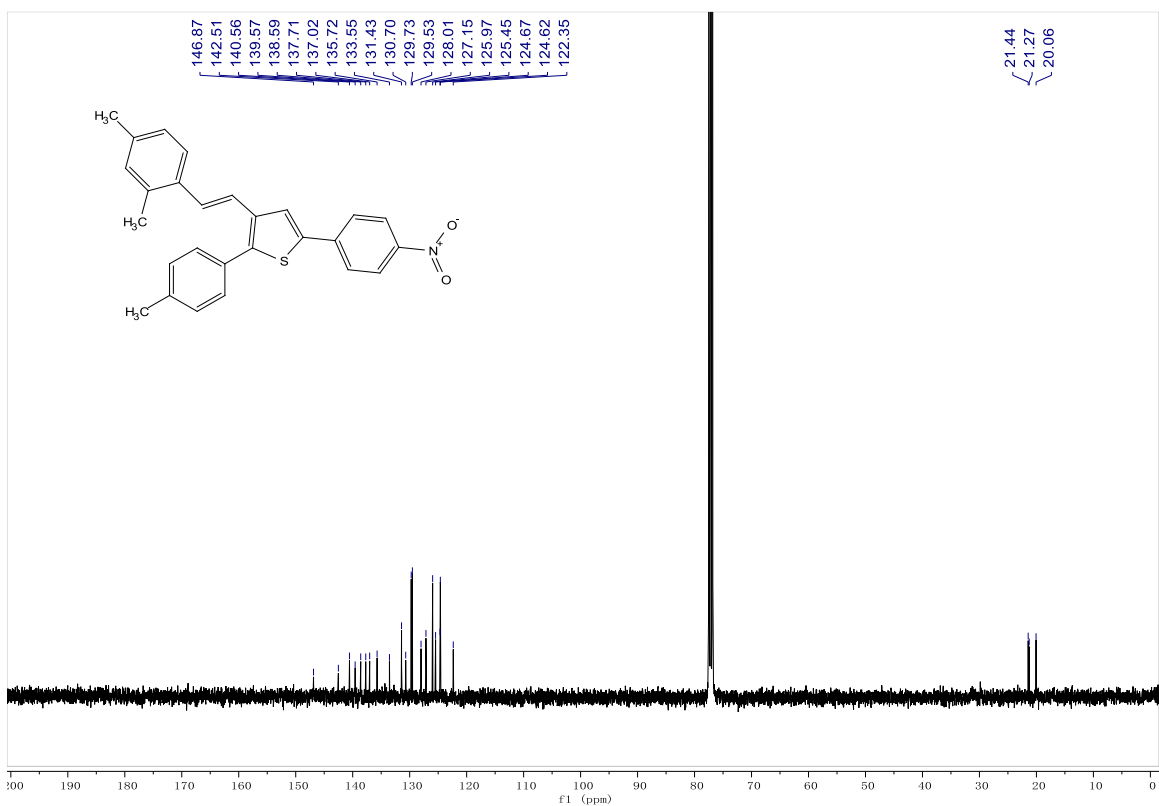
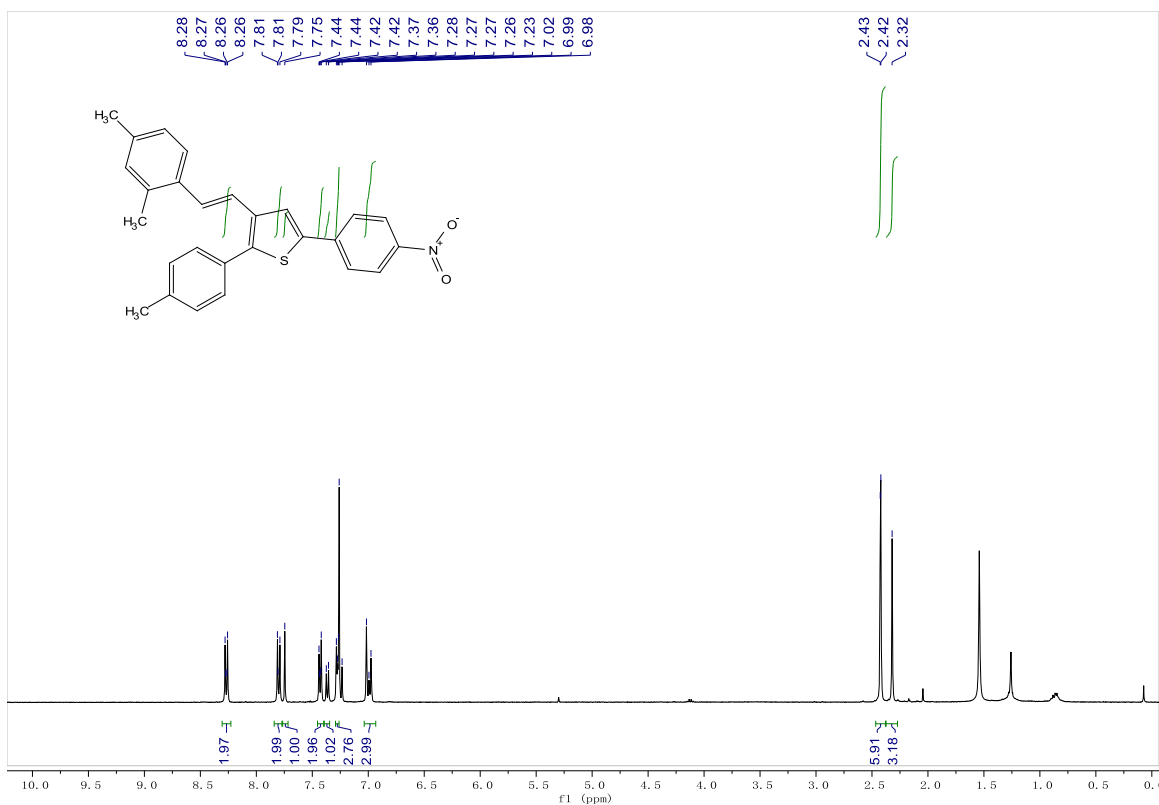




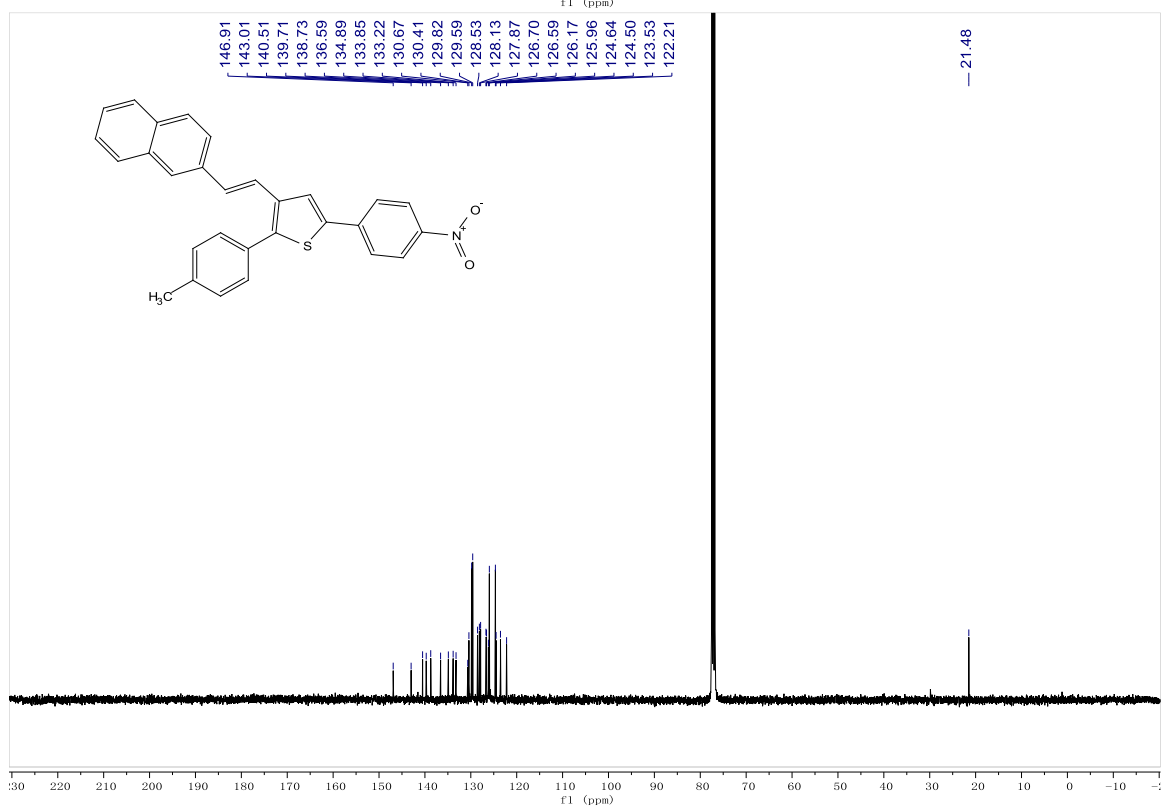
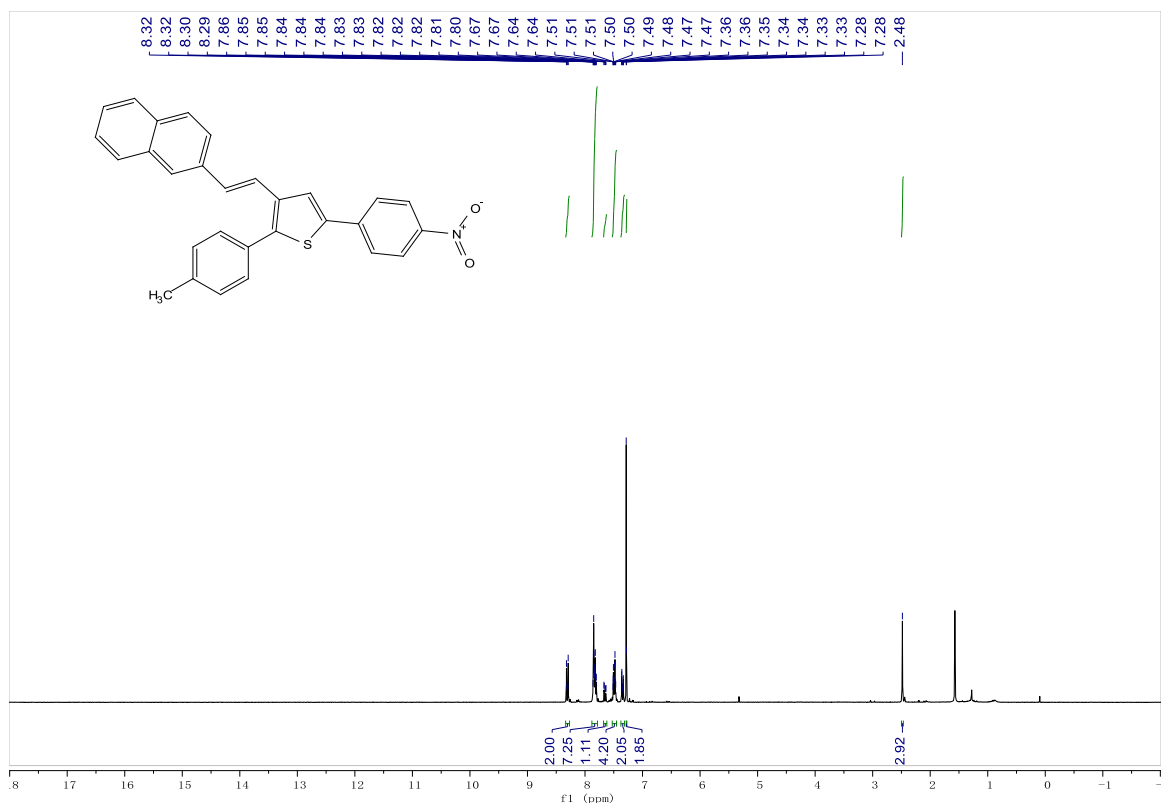
**(E)-3-(4-Chlorostyryl)-5-(4-nitrophenyl)-2-(p-tolyl)thiophene (14)**



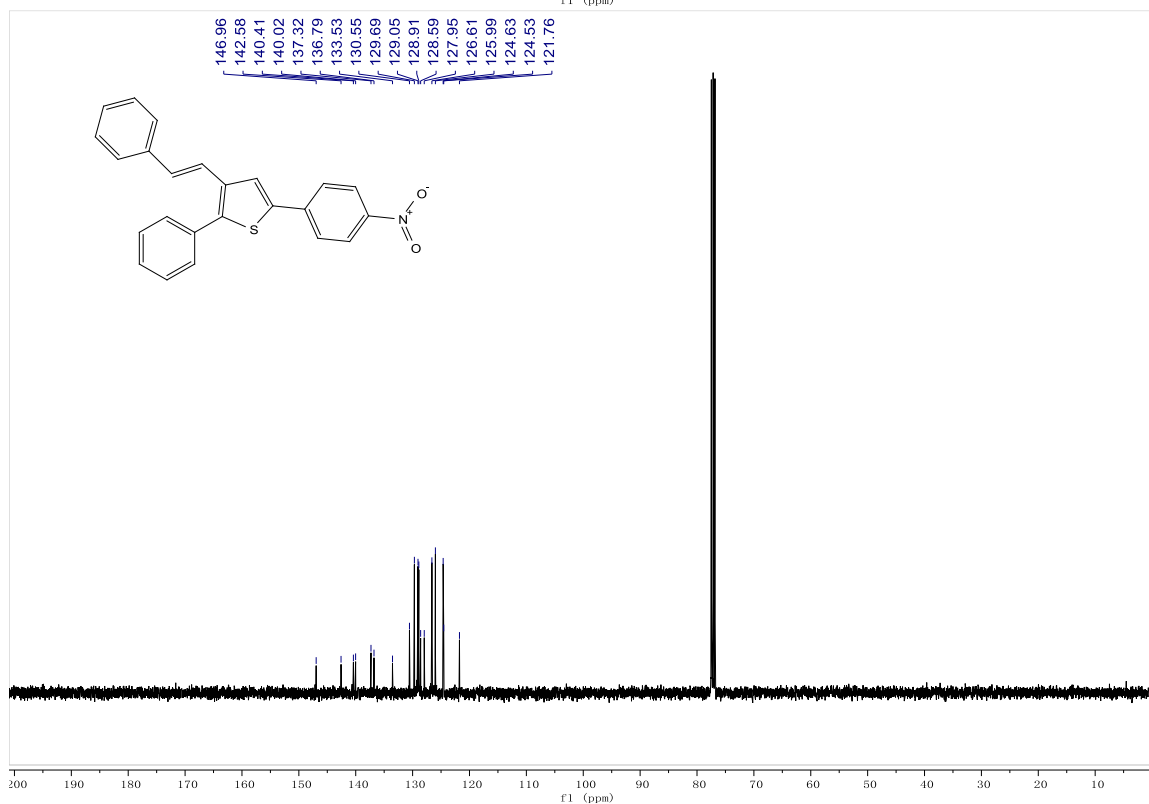
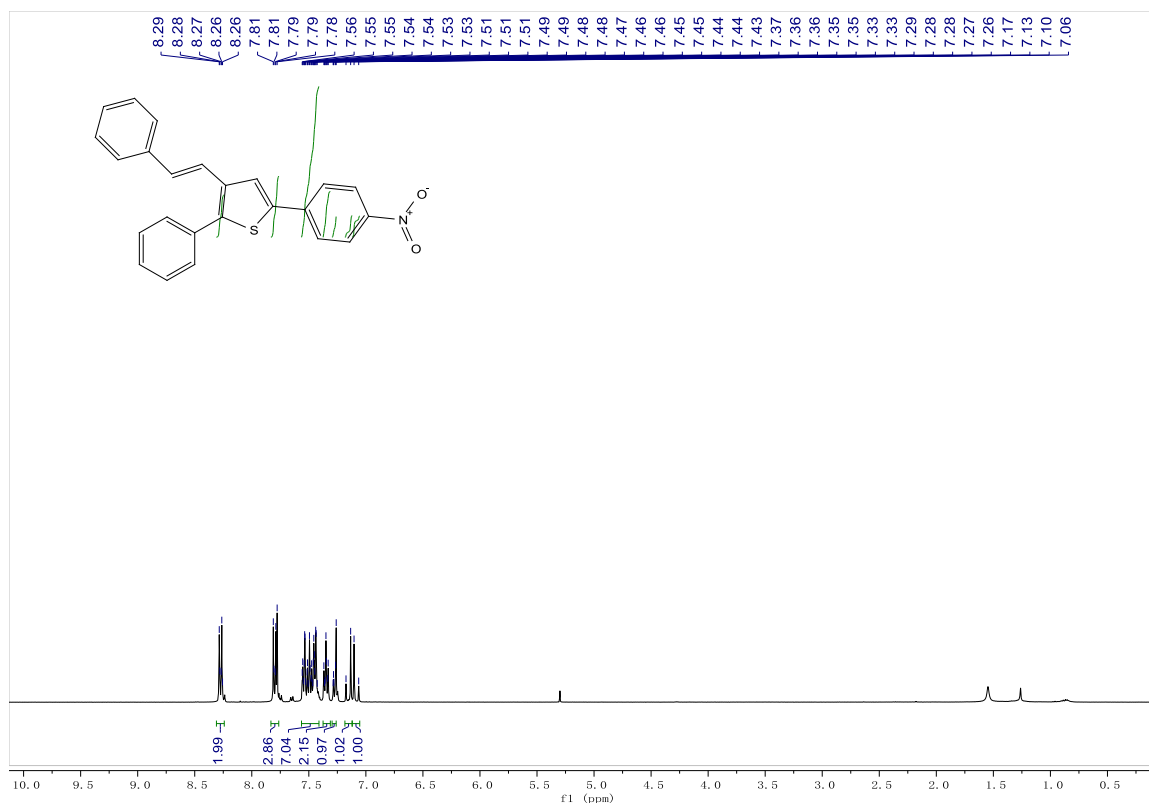
**(E)-3-(2,4-Dimethylstyryl)-5-(4-nitrophenyl)-2-(p-tolyl)thiophene (15)**



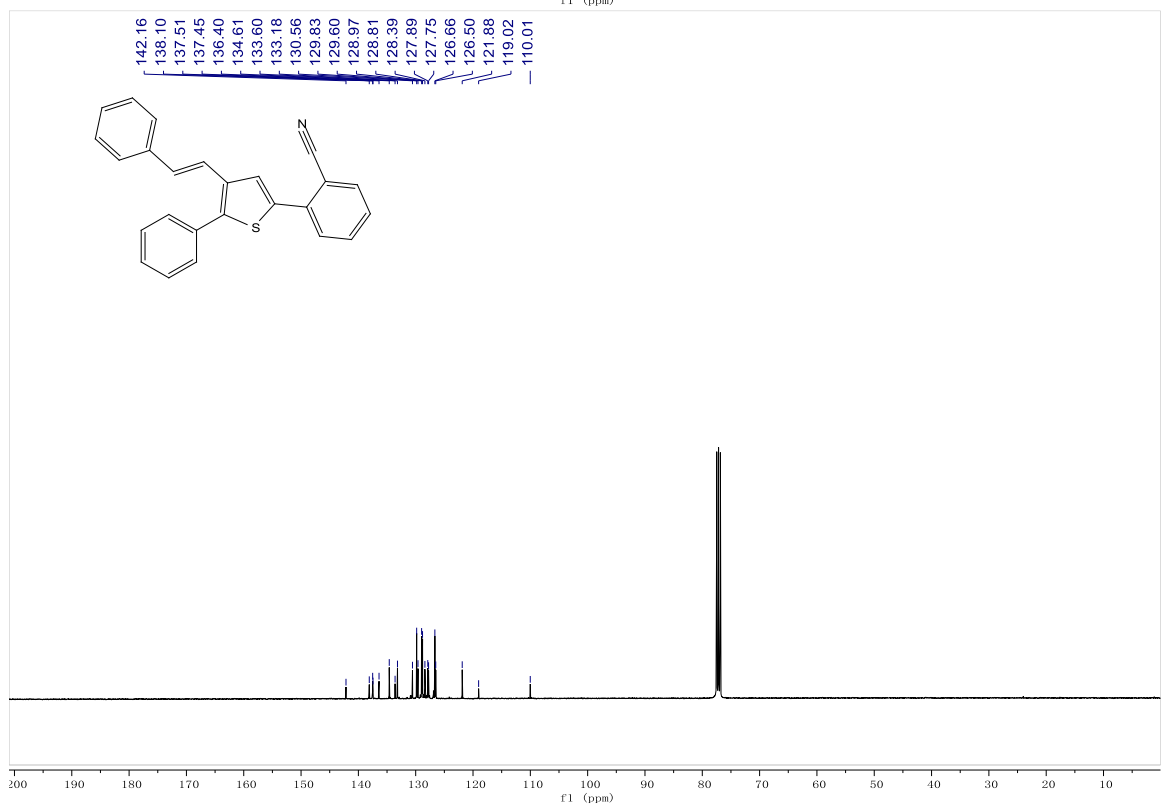
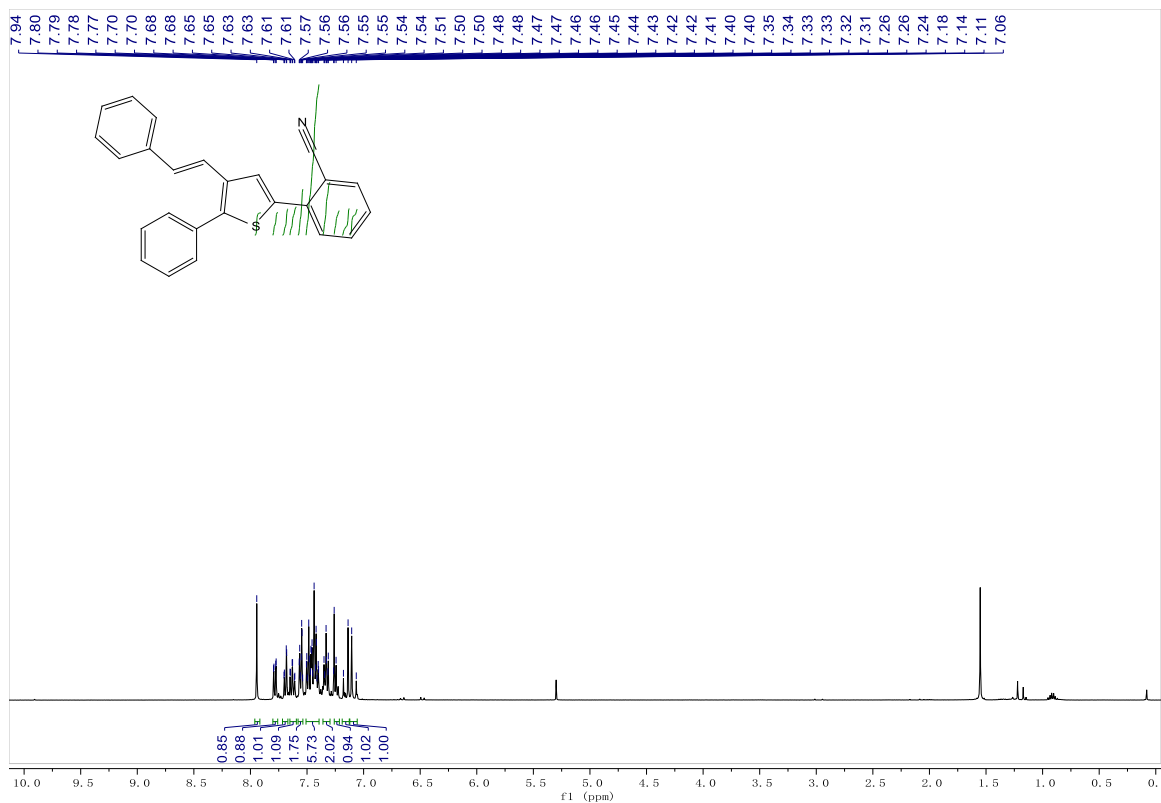
**(E)-3-(2-(Naphthalen-2-yl)vinyl)-5-(4-nitrophenyl)-2-(p-tolyl)thiophene (16)**



**(E)-5-(4-Nitrophenyl)-2-phenyl-3-styrylthiophene (17)**

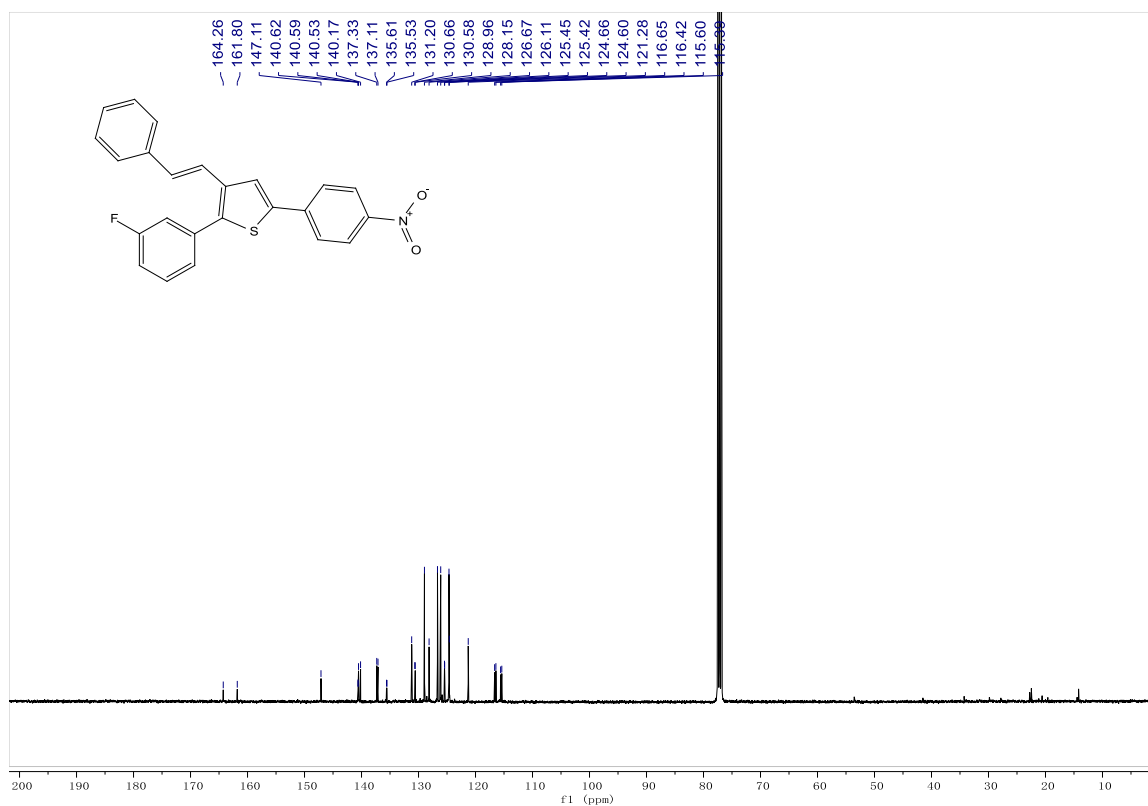
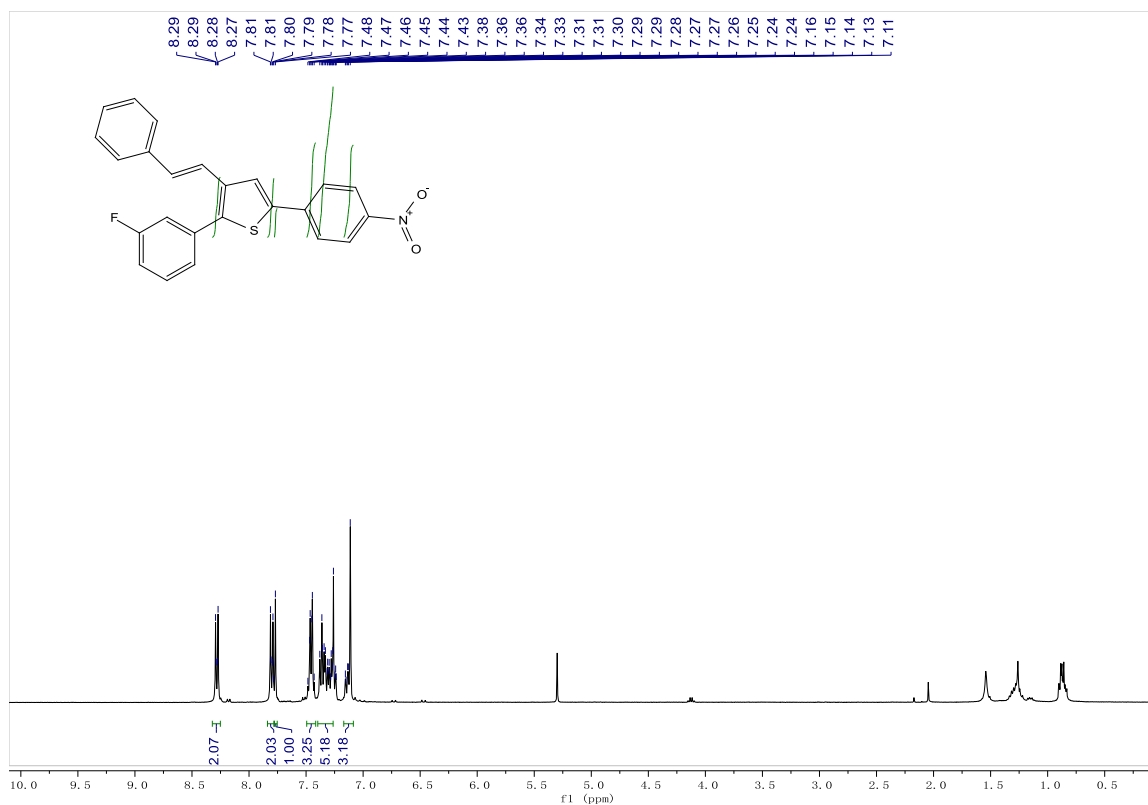


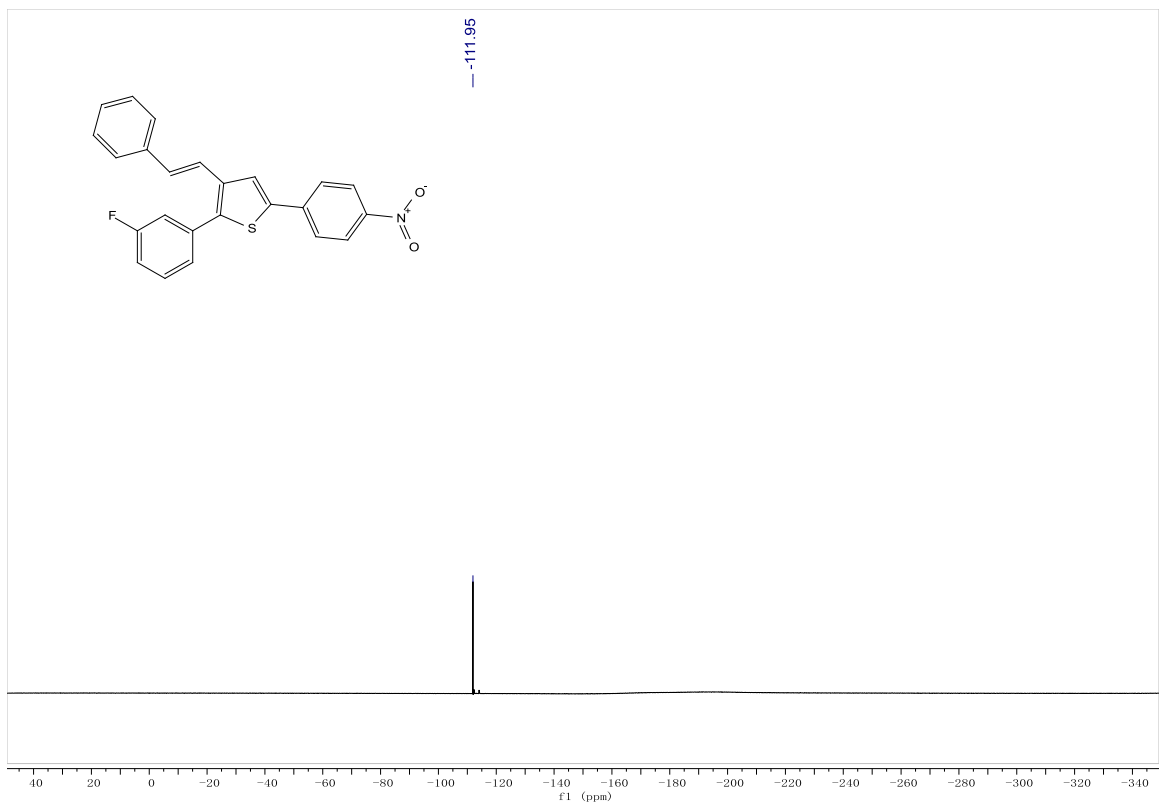
**(E)-2-(5-Phenyl-4-styrylthiophen-2-yl)benzonitrile (18)**



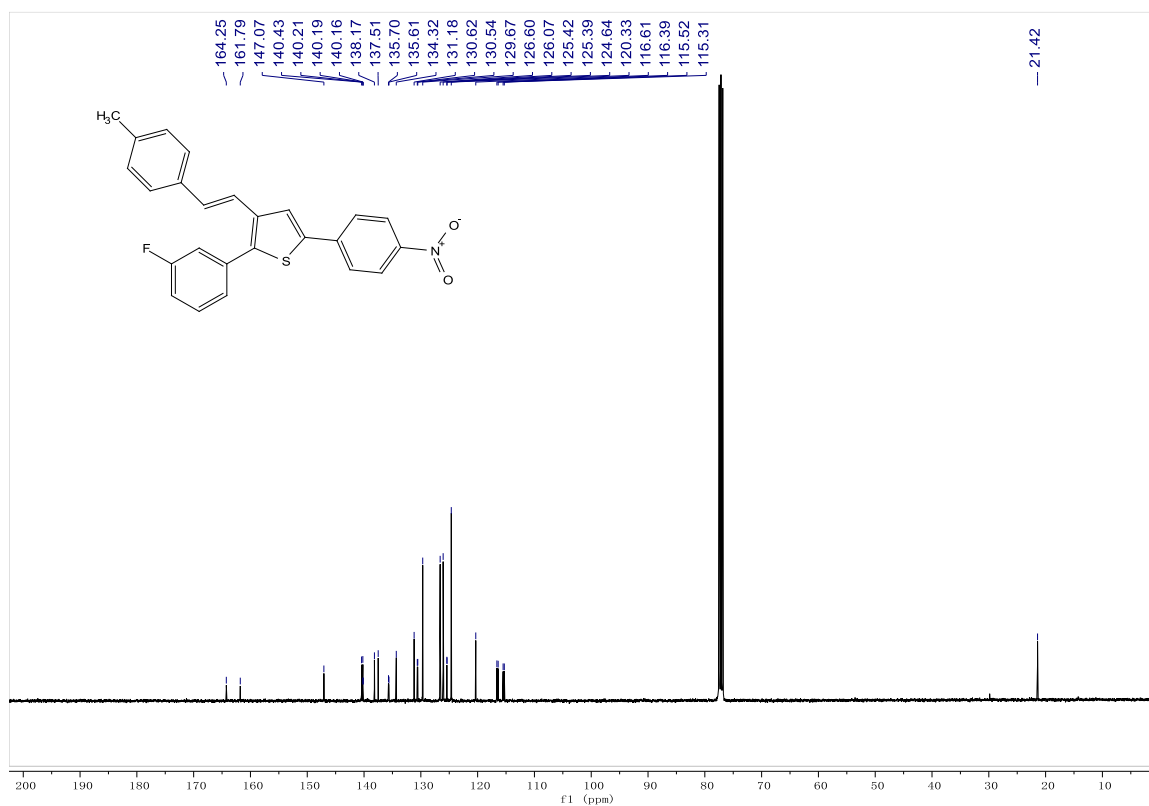
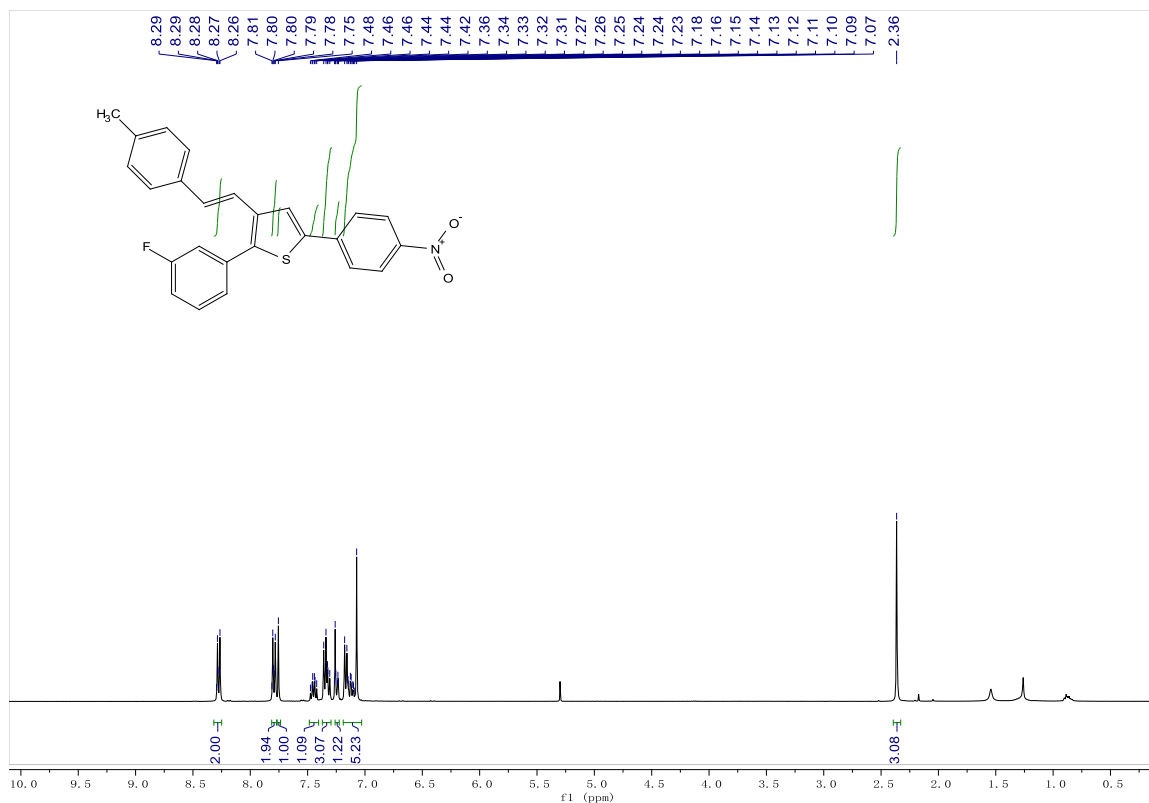


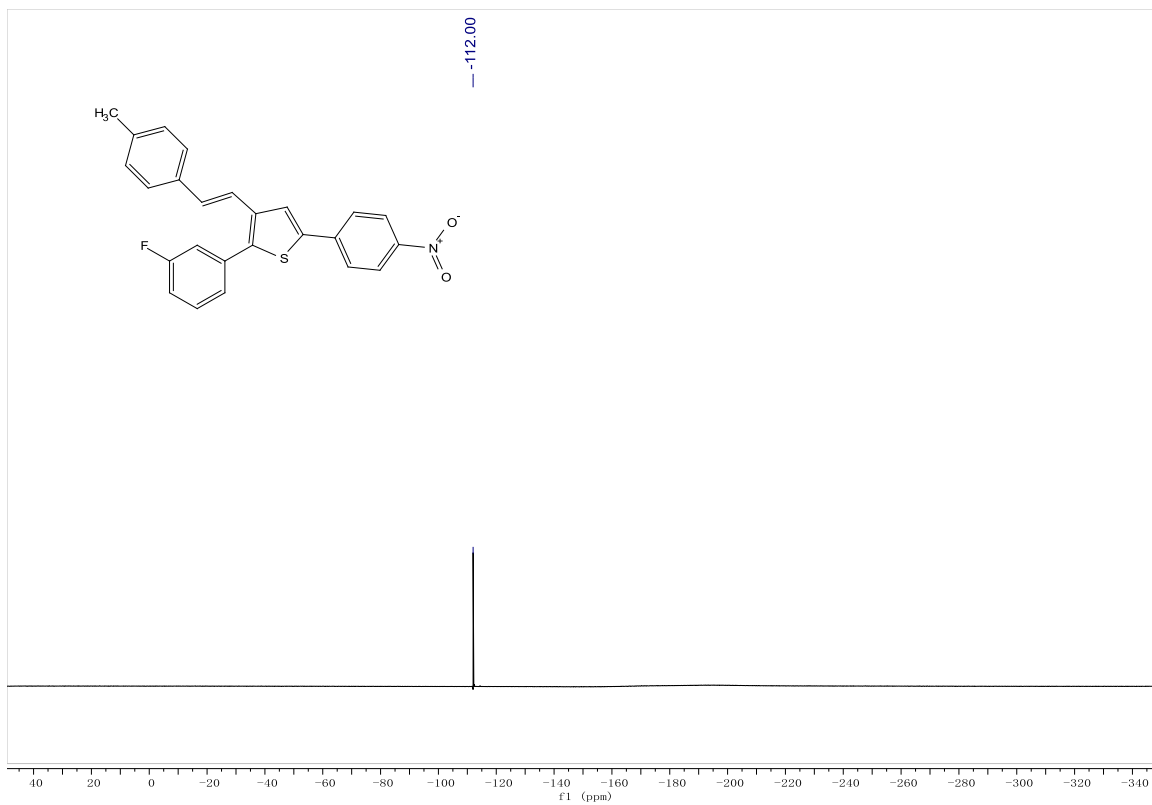
**(E)-2-(3-Fluorophenyl)-5-(4-nitrophenyl)-3-styrylthiophene (19)**



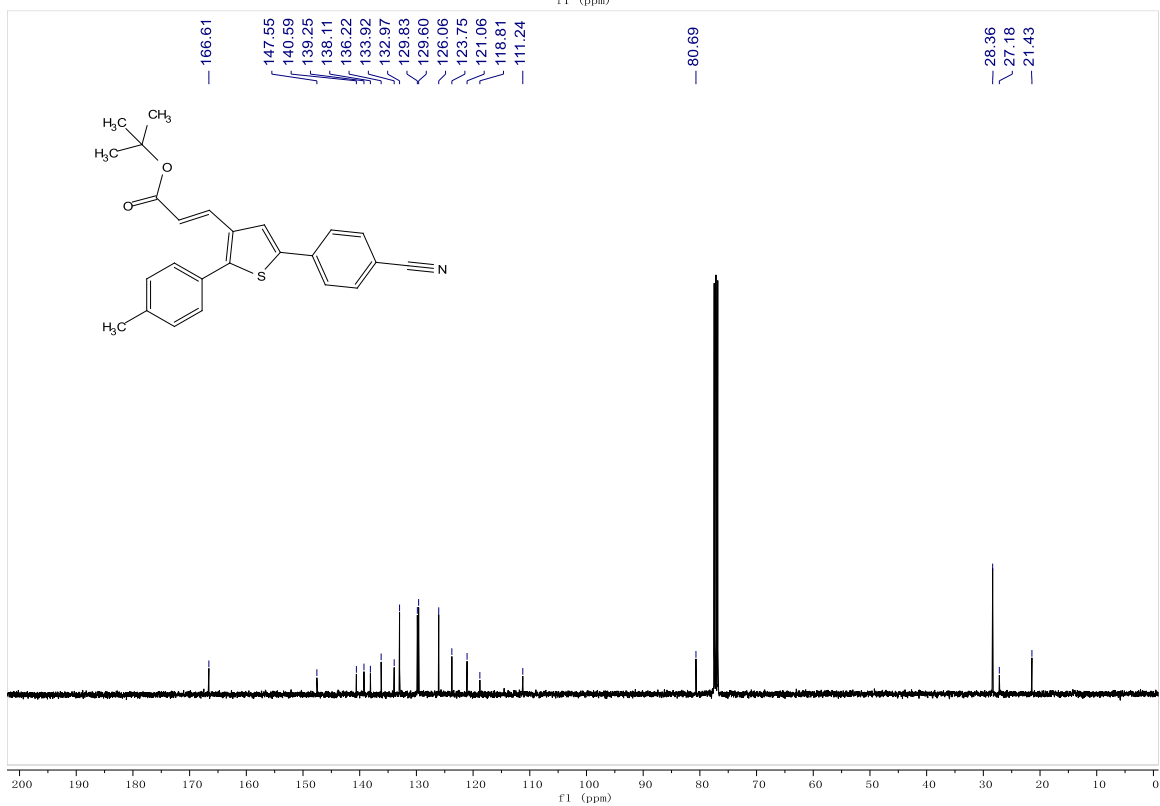
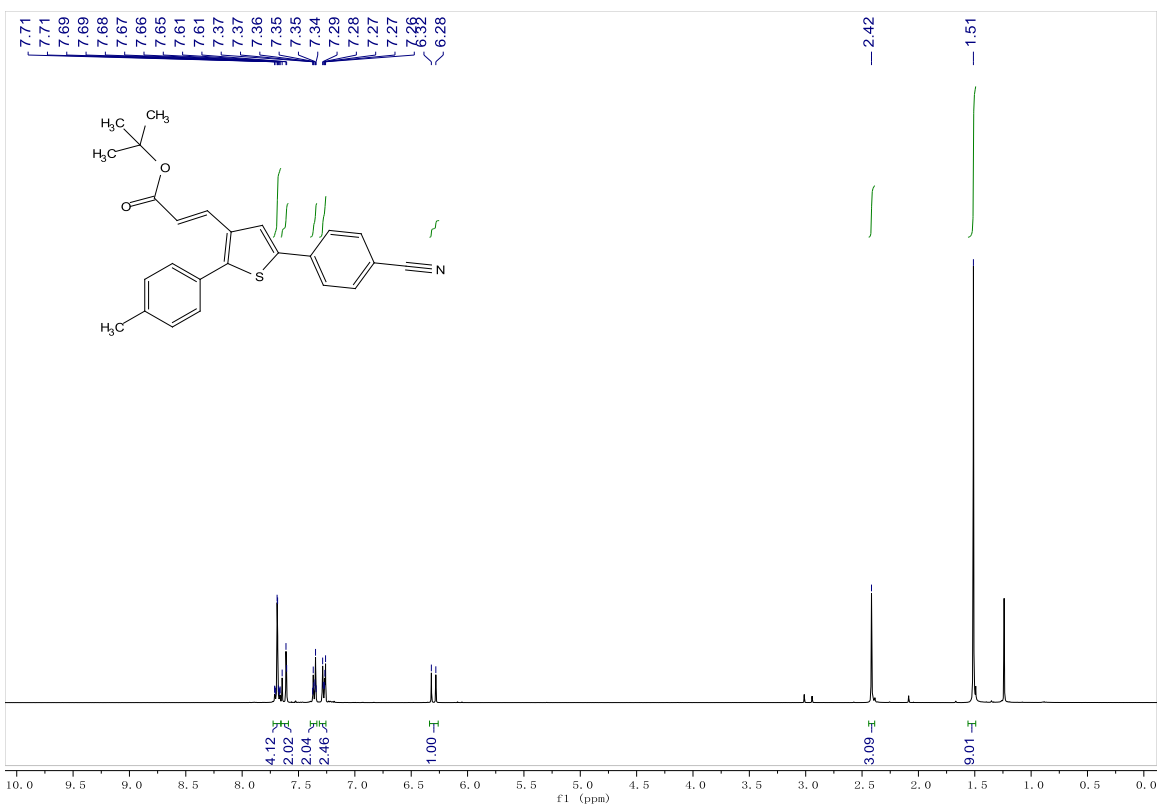


**(E)-2-(3-Fluorophenyl)-3-(4-methylstyryl)-5-(4-nitrophenyl)thiophene (20)**

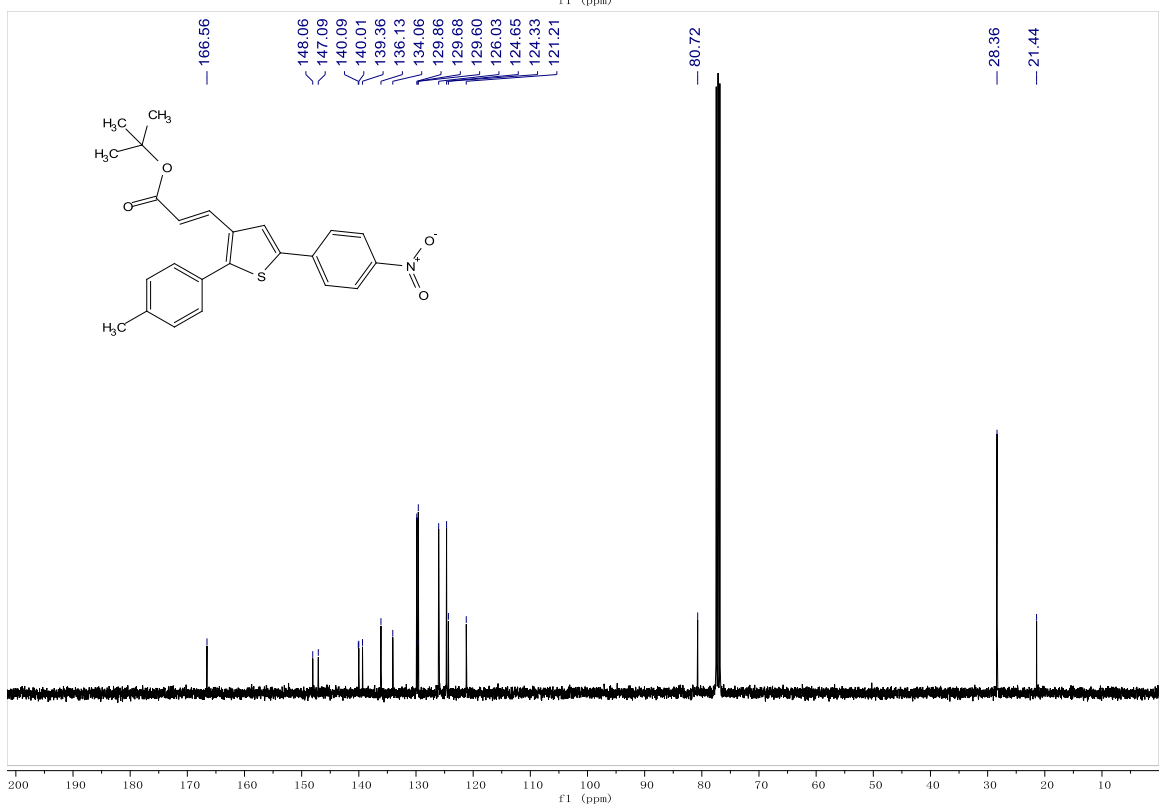
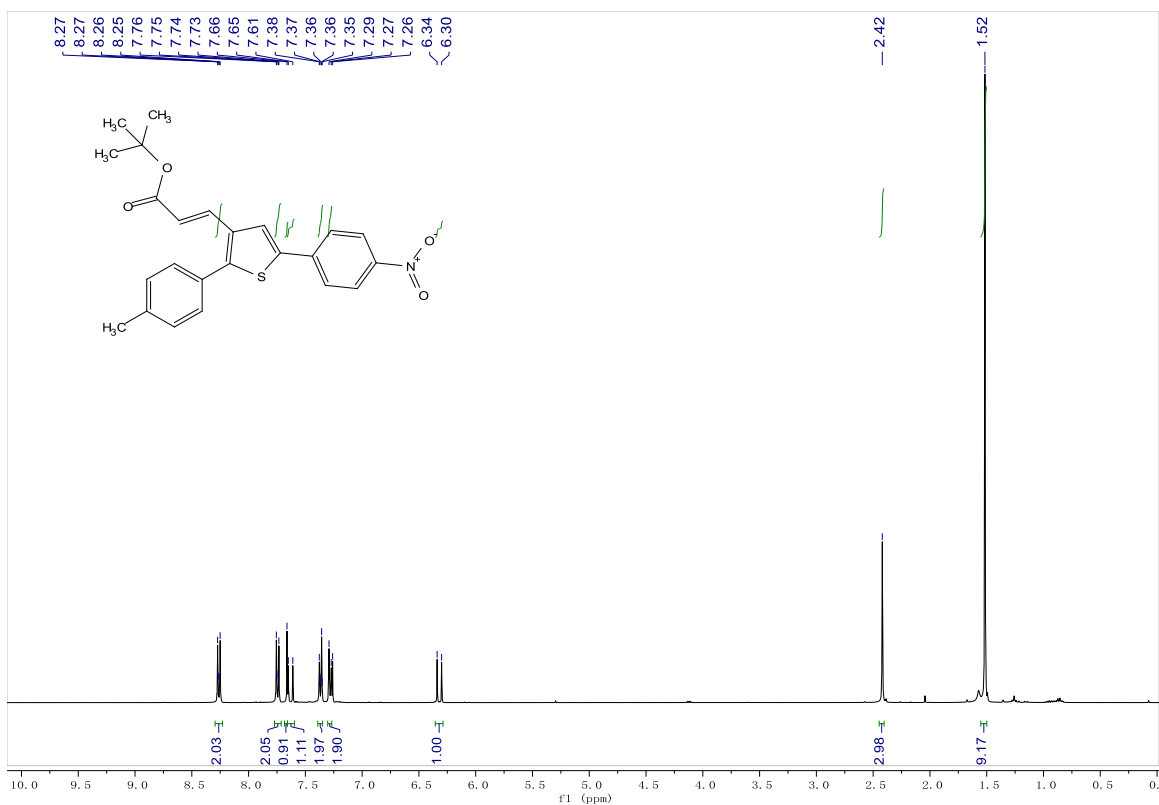




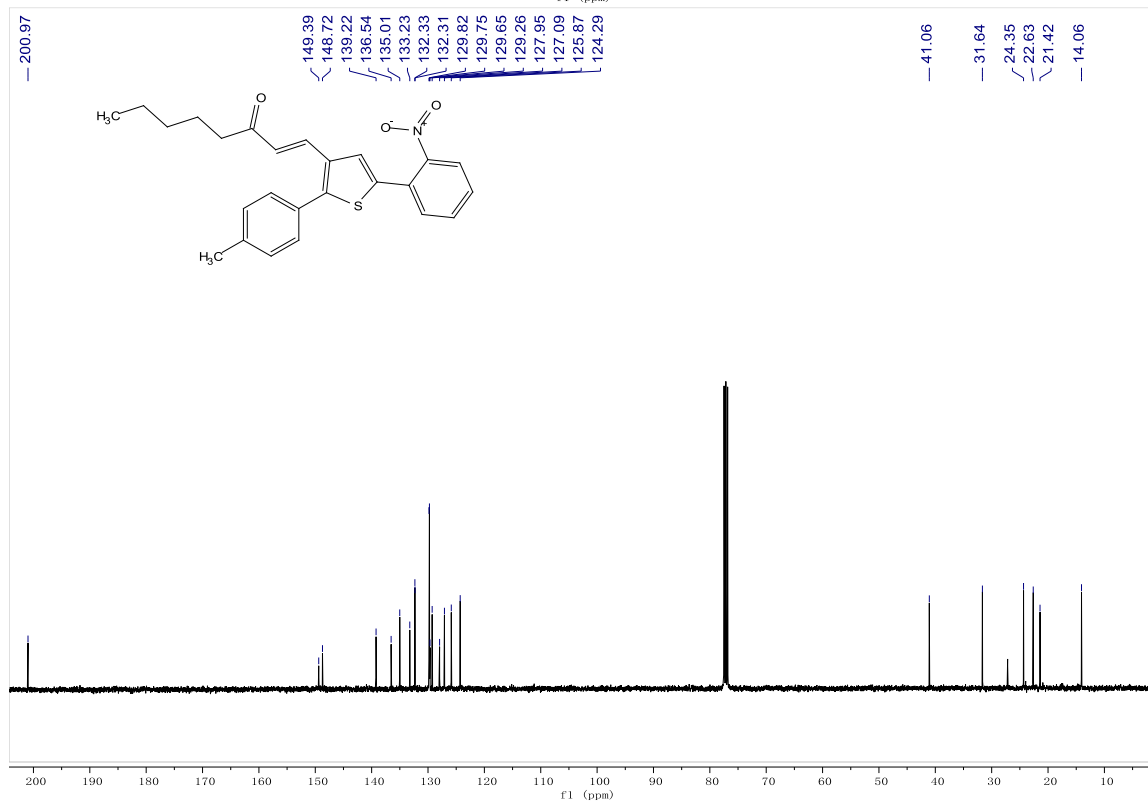
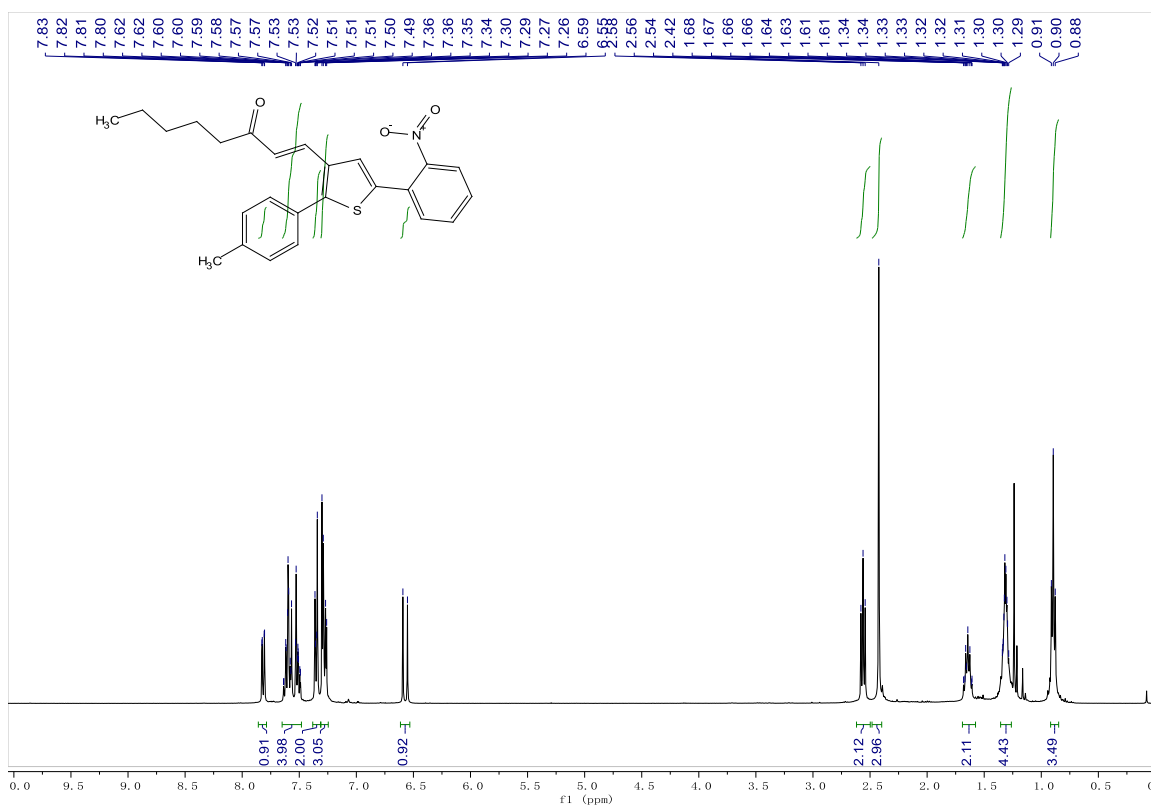
**tert-Butyl (E)-3-(5-(4-cyanophenyl)-2-(p-tolyl)thiophen-3-yl)acrylate (21)**



**tert-Butyl (E)-3-(5-(4-nitrophenyl)-2-(p-tolyl)thiophen-3-yl)acrylate (22)**



**(E)-1-(5-(2-Nitrophenyl)-2-(p-tolyl)thiophen-3-yl)oct-1-en-3-one (23)**



**(E)-3-(4-(3-Oxoct-1-en-1-yl)-5-(p-tolyl)thiophen-2-yl)benzonitrile (24)**

