

# Highly selective cross-coupling reactions of 1,1-dibromoethylenes with alkynylaluminums for the synthesis of aryl substituted conjugated enediynes and unsymmetric 1,3-diynes

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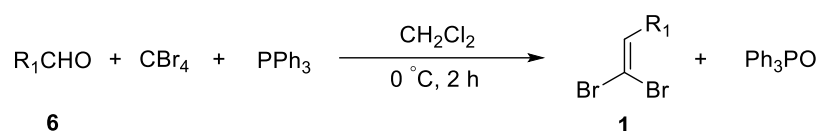
## Supporting Information

1. General.....	2
2. Typical procedure for the preparation of 1,1-dibromoethylenes <b>1</b> .....	2
3. Experimental procedure for the synthesis of alkynylaluminum reagents .....	2
4. Experimental procedure for the synthesis of conjugated enediynes <b>3</b> .....	3
5. Experimental procedure for the synthesis of unsymmetric 1,3-diynes <b>4</b> .....	3
6. Characterization of the products conjugated enediynes <b>3</b> .....	4
7. Characterization of the products unsymmetric 1,3-diynes <b>4</b> .....	12
8. Copy of <sup>1</sup> H, <sup>13</sup> C and <sup>19</sup> F NMR spectra for the conjugated enediynes <b>3</b> .....	16
9. Copy of <sup>1</sup> H, <sup>13</sup> C and <sup>19</sup> F NMR spectra for the unsymmetric 1,3-diynes <b>4</b> .....	49

## 1. General

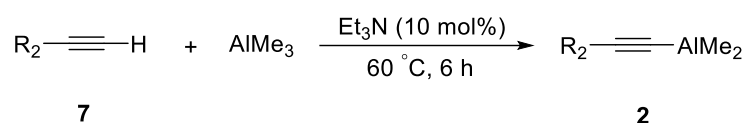
<sup>1</sup>H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl<sub>3</sub>: δ = 7.26). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, w = wide), coupling constants (Hz) and integration. <sup>13</sup>C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl<sub>3</sub>: δ = 77.0). ESI-HRMS spectra were recorded on a commercial apparatus and methanol or acetonitrile was used to dissolve the sample. Reagents obtained from commercial sources were used without further purification. CH<sub>2</sub>Cl<sub>2</sub> were distilled over CaH<sub>2</sub> before use. The THF and other solvents were distilled from sodium benzophenone ketyl before use.

## 2. Typical procedure for the preparation of 1,1-dibromoethylenes **1**



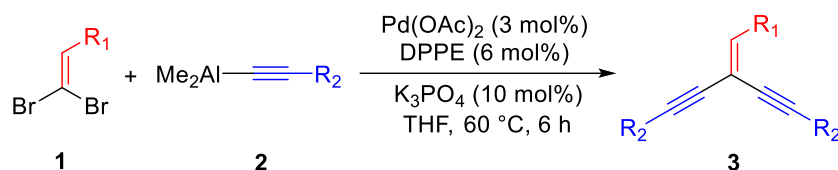
The 1,1-dibromoethylenes **1** were prepared according to the methods reported in the literature with a minor modification. Ph<sub>3</sub>P (5.25 g, 20.0 mmol) and CBr<sub>4</sub> (3.32 g, 10.0 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15.0 mL) and the reaction mixture was stirred at 0 °C for 10 min. And then the aldehydes **6** were added to the reaction mixtures. The reaction mixtures were stirred at 0 °C for additional 2 h. After that H<sub>2</sub>O (20.0 mL) was added and the organic layers were extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 15 mL). Then the organic layers were concentrated in *vacuo* and the crude products were purified directly by column chromatography on silica gel (petroleum ether/EtOAc = 10/1 to 50/1) to afford the corresponding 1,1-dibromoethylenes **1**.

## 3. Experimental procedure for the synthesis of alkynylaluminum reagents



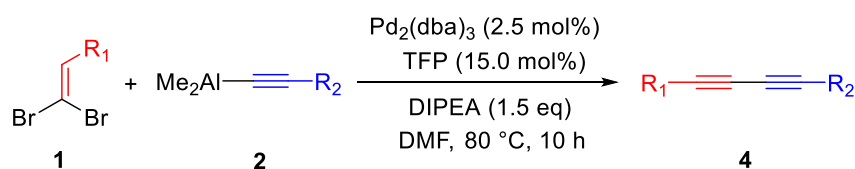
AlMe<sub>3</sub> (6.0 mmol), Et<sub>3</sub>N (0.6 mmol) were stirred in a dry Schlenk tube under Ar at rt for 10 min, and then terminal alkynes **7** (6.0 mmol) was added. After the reaction mixtures were stirred under Ar at 60 °C for 6 h, the crude alkynylaluminum reagents **2** were obtained. The crude alkynylaluminum reagents **2** were stored in the refrigerator and routinely used without further purification to the cross-coupling reactions.

#### 4. Experimental procedure for the synthesis of conjugated enediynes **3**



1,1-dibromoethylenes **1** (0.5 mmol),  $Pd(OAc)_2$  (3 mol%), DPPE (6 mol%),  $K_3PO_4$  (10 mol%) and THF (1.0 mL) were stirred in a dry reaction tube under Ar at rt for 5 min, and then alkynylaluminum reagents **2** (1.0 mmol) were added. After the reaction mixtures were stirred for 6 h at 60 °C, the saturated  $NH_4Cl$  solution (10 mL) was added and the organic layers were extracted with EtOAc (3 x 15 mL). Then the organic layers were concentrated in *vacuo* and the crude products were purified directly by column chromatography on silica gel to afford the desired products conjugated enediynes **3**.

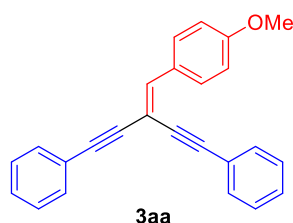
#### 5. Experimental procedure for the synthesis of unsymmetric 1,3-diynes **4**



1,1-dibromoethylenes **1** (0.5 mmol),  $Pd_2(dba)_3$  (2.5 mol%), TFP (15.0 mol%), DIPEA (1.5 eq) and DMF (3.0 mL) were stirred in a dry reaction tube under Ar at rt for 5 min, and then alkynylaluminum reagents **2** (0.8 mmol) were added. After the reaction mixtures were stirred for 10 h at 80 °C, the saturated  $NH_4Cl$  solution (10 mL) was added and the organic layers were extracted with EtOAc (3 x 15 mL). Then the organic layers were concentrated in *vacuo* and the crude products were purified directly by column chromatography on silica gel to afford the desired products unsymmetric 1,3-diynes **4**.

## 6. Characterization of the products conjugated enediynes **3**

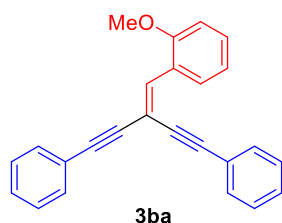
### (3-(4-methoxybenzylidene)penta-1,4-diyne-1,5-diyl)dibenzene **3aa**:



Prepared according to **general procedure**. 80% yield. Light yellow solid, m.p.: 72 – 75 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.93 (d, *J* = 8.8 Hz, 2H), 7.59 – 7.49 (m, 4H), 7.39 – 7.29 (m, 5H), 7.12 (s, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 160.34, 142.91, 131.62, 131.59, 130.74, 128.73, 128.60, 128.42, 128.29, 128.25, 123.13, 123.03, 113.87, 100.58, 94.23, 89.48, 87.73, 87.20, 55.34 ppm.

IR (KBr, thin film):  $\nu_{\max}$  = 3437, 2383, 2350, 1609, 1514, 1447, 1388, 1308, 1261, 1178, 890, 830, 758, 693, 535 cm<sup>-1</sup>. ES-HRMS Calcd for C<sub>25</sub>H<sub>18</sub>O[M + H]<sup>+</sup> m/z 335.1430, Found: m/z 335.1431.

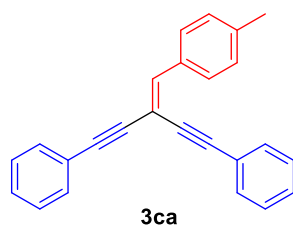
### (3-(4-methoxybenzylidene)penta-1,4-diyne-1,5-diyl)dibenzene **3ba**:



Prepared according to **general procedure**. 61% yield. Brown oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.39 (d, *J* = 7.6 Hz, 1H), 7.52 (s, 1H), 7.48 – 7.40 (m, 4H), 7.29 – 7.21 (m, 7H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 3.78 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 156.05, 136.59, 130.64, 130.58, 129.51, 127.63, 127.53, 127.32, 127.24, 123.66, 122.07, 121.96, 119.13, 109.47, 101.60, 92.90, 88.53, 86.92, 86.11, 54.51 ppm. IR

(KBr, thin film):  $\nu_{\max}$  = 3438, 2390, 2289, 1644, 1465, 1447, 1388, 1103, 754, 541 cm<sup>-1</sup>. ES-HRMS Calcd for C<sub>25</sub>H<sub>18</sub>O[M + H]<sup>+</sup> m/z 335.1430, Found: m/z 335.1432.

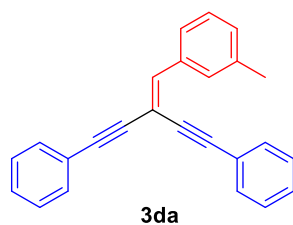
### (3-(4-methylbenzylidene)penta-1,4-diyne-1,5-diyl)dibenzene **3ca**:



Prepared according to **general procedure**. 83% yield. White solid, m.p.: 108 – 111 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.84 (d, *J* = 8.0 Hz, 2H), 7.58 – 7.48 (m, 4H), 7.38 – 7.28 (m, 6H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.14 (s, 1H), 2.35 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 143.39, 139.59, 133.11, 131.72, 131.67, 129.24, 129.14, 128.74, 128.49, 128.42, 128.38, 123.09, 123.02, 102.20, 94.56, 89.45, 88.13, 87.20, 21.58 ppm. IR (KBr,

thin film):  $\nu_{\max}$  = 3444, 2382, 1643, 1106, 750, 540 cm<sup>-1</sup>.

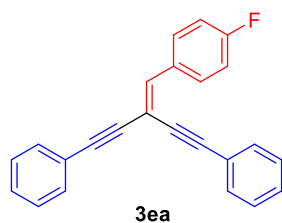
### (3-(3-methylbenzylidene)penta-1,4-diyne-1,5-diyl)dibenzene **3da**:



Prepared according to **general procedure**. 91% yield. Brown oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.72 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.38 (m, 4H), 7.29 – 7.16 (m, 7H), 7.07 – 7.02 (m, 2H), 2.28 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 142.33, 136.83, 134.60, 130.62, 130.54, 128.99, 128.60, 127.66, 127.38, 127.35, 127.26, 125.31, 121.90, 121.85, 101.93, 93.52, 88.22, 87.16, 86.06, 20.48 ppm. IR (KBr, thin film):  $\nu_{\max}$

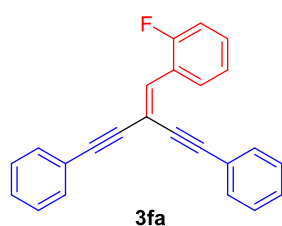
= 3463, 2378, 2350, 1662, 1498, 1388, 1105, 756, 693, 538 cm<sup>-1</sup>. ES-HRMS Calcd for C<sub>25</sub>H<sub>18</sub>[M + Na]<sup>+</sup> m/z 341.1301, Found: m/z 341.1353.

### (3-(4-fluorobenzylidene)penta-1,4-diyne-1,5-diyl)dibenzene 3ea:



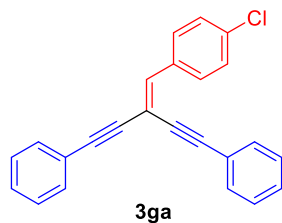
Prepared according to **general procedure**. 72% yield. Light yellow solid, m.p.: 89 – 92 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.91 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 5.6 Hz, 2H), 7.57 – 7.47 (m, 4H), 7.38 – 7.28 (m, 6H), 7.13 – 7.03 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 164.16, 161.67, 141.84, 132.07, 132.03, 131.74, 131.68, 131.01, 130.93, 128.92, 128.54, 128.40, 122.90, 122.72, 115.65, 115.43, 102.97, 102.94, 94.68, 89.06, 88.48, 86.73. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ = -110.36 ppm. IR (KBr, thin film): *V*<sub>max</sub> = 3472, 2378, 1643, 1507, 1387, 1107, 886, 830, 755, 690, 530 cm<sup>-1</sup>. ES-HRMS Calcd for C<sub>24</sub>H<sub>15</sub>F[M + H]<sup>+</sup> m/z 323.1231, Found: m/z 323.1247.

### (3-(2-fluorobenzylidene)penta-1,4-diyne-1,5-diyl)dibenzene 3fa:



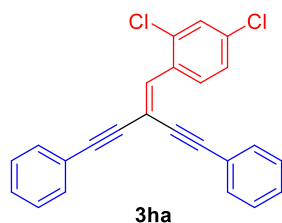
Prepared according to **general procedure**. 53% yield. Brown oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.46 (t, *J* = 7.6 Hz, 1H), 7.52 – 7.42 (m, 4H), 7.32 – 7.24 (m, 6H), 7.14 -6.96 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 161.42, 158.91, 134.07, 134.01, 131.77, 131.69, 130.72, 130.63, 128.91, 128.68, 128.66, 128.59, 128.46, 128.35, 123.84, 123.80, 122.76, 122.64, 115.49, 115.27, 104.87, 94.92, 88.95, 88.83, 86.59. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ = -108.80 ppm. IR (KBr, thin film): *V*<sub>max</sub> = 3444, 2938, 2381, 2350, 1662, 1498, 1388, 1109, 758, 696, 539 cm<sup>-1</sup>. ES-HRMS Calcd for C<sub>24</sub>H<sub>15</sub>F[M + Na]<sup>+</sup> m/z 345.1050, Found: m/z 345.0921.

### (3-(4-chlorobenzylidene)penta-1,4-diyne-1,5-diyl)dibenzene 3ga:



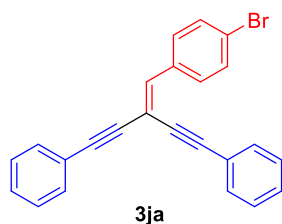
Prepared according to **general procedure**. 83% yield. Brown solid, m.p.: 85 – 87 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.87 (d, *J* = 8.8 Hz, 2H), 7.56 – 7.50 (m, 4H), 7.40 – 7.30 (m, 8H), 7.10 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 141.57, 134.76, 134.21, 131.72, 131.66, 130.20, 128.95, 128.65, 128.57, 128.51, 128.36, 122.79, 122.62, 103.93, 95.20, 88.94, 88.82, 86.62 ppm. IR (KBr, thin film): *V*<sub>max</sub> = 3447, 2939, 2381, 2350, 1662, 1497, 1448, 1387, 1098, 757, 694, 534 cm<sup>-1</sup>.

### (3-(2,4-dichlorobenzylidene)penta-1,4-diyne-1,5-diyl)dibenzene 3ha:



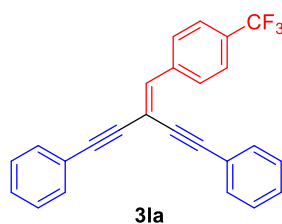
Prepared according to **general procedure**. 76% yield. Light yellow solid, m.p.: 99 – 105 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.39 (d, *J* = 8.4 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.50 – 7.44 (m, 2H), 7.43 – 7.38 (m, 2H), 7.36 – 7.30 (m, 6H), 7.25 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 137.39, 134.95, 134.67, 132.19, 131.84, 131.73, 130.13, 129.52, 129.09, 128.76, 128.53, 128.40, 126.77, 122.64, 122.40, 106.12, 95.10, 89.71, 88.67, 86.16 ppm. IR (KBr, thin film): *V*<sub>max</sub> = 3466, 2937, 2380, 2350, 2201, 1663, 1587, 1497, 1471, 1447, 1388, 1105, 872, 790, 754, 690, 538 cm<sup>-1</sup>. ES-HRMS Calcd for C<sub>24</sub>H<sub>14</sub>Cl<sub>2</sub>[M + H]<sup>+</sup> m/z 373.0545, Found: m/z 373.0877.

### (3-(4-fluorobenzylidene)penta-1,4-diyne-1,5-diyl)dibenzene 3ja:



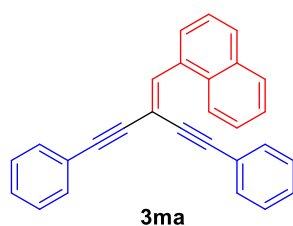
Prepared according to **general procedure**. 75% yield. Brown-yellow solid, m.p.: 89 – 95 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.79 (d, *J* = 8.5 Hz, 2H), 7.59 – 7.55 (m, 5H), 7.53 (s, 1H), 7.42 – 7.39 (m, 3H), 7.39 – 7.36 (m, 3H), 7.12 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 141.65, 134.62, 131.74, 131.67, 131.63, 130.44, 128.99, 128.61, 128.53, 128.39, 123.16, 122.80, 122.62, 104.09, 95.33, 89.00, 88.92, 86.67 ppm. IR (KBr, thin film):  $V_{\max}$  = 3463, 2381, 2349, 1662, 1490, 1447, 1388, 1104, 888, 758, 694, 538 cm<sup>-1</sup>.

### (3-(4-(trifluoromethyl)benzylidene)penta-1,4-diyne-1,5-diyl)dibenzene 3la:



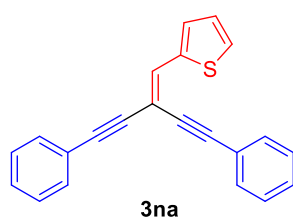
Prepared according to **general procedure**. 71% yield. Light yellow solid, m.p.: 122 – 125 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.02 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.56 – 7.50 (m, 4H), 7.39 – 7.33 (m, 6H), 7.16 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 140.97, 138.97, 138.96, 131.78, 131.72, 130.52, 130.20, 129.14, 129.05, 128.75, 128.55, 128.40, 125.38, 125.34, 125.30, 125.26, 122.60, 122.40, 105.95, 95.57, 89.49, 88.72, 86.39. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ = -162.67 ppm. IR (KBr, thin film):  $V_{\max}$  = 3448, 2377, 1643, 1498, 1388, 1330, 1126, 1075, 888, 755, 692, 537 cm<sup>-1</sup>. ES-HRMS Calcd for C<sub>25</sub>H<sub>15</sub>F<sub>3</sub>[M + H]<sup>+</sup> m/z 373.1199, Found: m/z 373.1584.

### 1-(4-phenyl-2-(phenylethynyl)but-1-en-3-yn-1-yl)naphthalene 3ma:



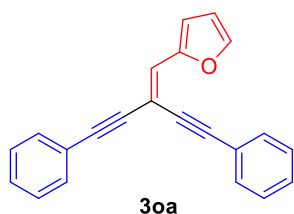
Prepared according to **general procedure**. 66% yield. Yellow solid, m.p.: 105 – 108 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.37 (d, *J* = 7.2 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.91 (s, 1H), 7.86 (t, *J* = 6.4 Hz, 2H), 7.62 – 7.47 (m, 5H), 7.44 – 7.47 (m, 5H), 7.32 – 7.27 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 140.57, 133.59, 132.20, 131.80, 131.72, 131.47, 129.58, 128.74, 128.65, 128.57, 128.40, 128.35, 127.07, 126.54, 126.01, 125.15, 123.74, 122.92, 122.84, 105.41, 93.39, 89.01, 88.80, 86.85 ppm. IR (KBr, thin film):  $V_{\max}$  = 3465, 2379, 2350, 1644, 1388, 1308, 1104, 748, 540 cm<sup>-1</sup>.

### 2-(4-phenyl-2-(phenylethynyl)but-1-en-3-yn-1-yl)thiophene 3na:



Prepared according to **general procedure**. 69% yield. Black solid, m.p.: 85 – 99 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.59 – 7.54 (m, 2H), 7.53 – 7.49 (m, 2H), 7.47 – 7.45 (m, 1H), 7.41 – 7.30 (m, 6H), 7.22 – 7.19 (m, 1H), 7.07 (s, 1H), 6.53 – 6.49 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 152.17, 143.22, 131.71, 131.69, 130.63, 128.81, 128.48, 128.46, 128.35, 122.92, 112.85, 112.83, 112.48, 100.17, 95.84, 89.38, 88.62, 87.02 ppm. IR (KBr, thin film):  $V_{\max}$  = 3464, 2937, 2381, 1644, 1498, 1104, 755, 694, 534 cm<sup>-1</sup>.

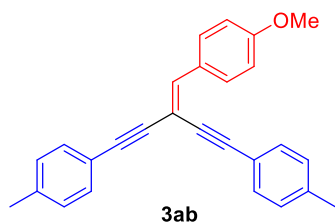
### 2-(4-phenyl-2-(phenylethynyl)but-1-en-3-yn-1-yl)furan 3oa:



Prepared according to **general procedure**. 51% yield. Yellow solid, m.p.: 108 – 115 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.69 – 7.65 (m, 2H), 7.57 – 7.53 (m, 2H), 7.43 (s, 1H), 7.43 – 7.38 (m, 4H), 7.37 – 7.33 (m, 4H), 7.09 (dd, *J*<sub>1</sub> = 5.2 Hz, *J*<sub>2</sub> = 3.6 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 140.00, 136.74, 131.65, 131.64, 131.09, 128.81, 128.54, 128.44, 128.39, 128.33, 126.75, 122.98, 122.94, 100.31, 97.59, 88.99, 88.67, 87.18 ppm.

IR (KBr, thin film):  $\nu_{\max}$  = 3438, 2936, 2865, 2379, 1644, 1497, 1386, 1104, 883, 755, 694, 532 cm<sup>-1</sup>. ES-HRMS Calcd for C<sub>22</sub>H<sub>14</sub>O[M + H]<sup>+</sup> m/z 295.1117, Found: m/z 295.1185.

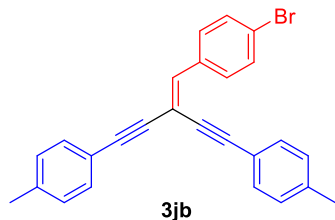
### 4,4'-(3-(4-methoxybenzylidene)penta-1,4-diyne-1,5-diyl)bis(methylbenzene) 3ab:



Prepared according to **general procedure**. 77% yield. Brown-yellow solid, m.p.: 58 – 65 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.84 (d, *J* = 8.8 Hz, 2H), 7.35 (dd, *J*<sub>1</sub> = 11.2 Hz, *J*<sub>2</sub> = 8.0 Hz, 4H), 7.07 (dd, *J* = 14.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 4H), 7.00 (s, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.74 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) = 160.20, 142.30, 138.82, 138.38, 131.53, 131.50, 130.66, 129.20,

129.08, 128.88, 120.08, 120.01, 113.84, 100.89, 94.45, 88.96, 87.87, 86.72, 55.34, 21.59, 21.55 ppm. IR (KBr, thin film):  $\nu_{\max}$  = 3435, 2381, 2350, 1644, 1514, 1387, 1262, 1115, 822, 747, 534 cm<sup>-1</sup>. ES-HRMS Calcd for C<sub>27</sub>H<sub>22</sub>O[M + H]<sup>+</sup> m/z 363.1743, Found: m/z 363.1743.

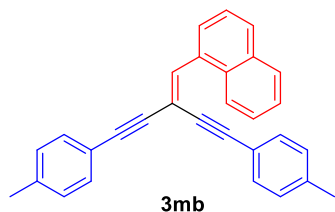
### 4,4'-(3-(4-bromobenzylidene)penta-1,4-diyne-1,5-diyl)bis(methylbenzene) 3jb:



Prepared according to **general procedure**. 88% yield. Yellow solid, m.p.: 85 – 95 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.73 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.35 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 1.6 Hz, 4H), 7.09 (dd, *J*<sub>1</sub> = 12.4 Hz, *J*<sub>2</sub> = 7.6 Hz, 4H), 6.98 (s, 1H), 2.31 (s, 3H), 2.29 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 140.93, 139.22, 138.74, 134.74, 131.60, 131.54, 130.33, 129.26, 129.12, 122.87, 119.70,

119.56, 104.34, 95.50, 90.70, 88.99, 88.43, 86.15, 21.60, 21.56 ppm. IR (KBr, thin film):  $\nu_{\max}$  = 3471, 2382, 2350, 1642, 1514, 1489, 1388, 1308, 1107, 818, 748, 534 cm<sup>-1</sup>. ES-HRMS Calcd for C<sub>26</sub>H<sub>19</sub>Br[M + H]<sup>+</sup> m/z 411.0743, Found: m/z 411.0747.

### 1-(4-(p-tolyl)-2-(p-tolyethynyl)but-1-en-3-yn-1-yl)naphthalene 3mb:

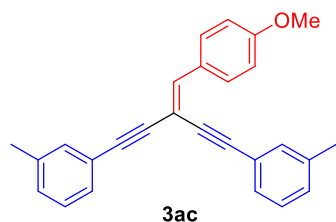


Prepared according to **general procedure**. 74% yield. Grey solid, m.p.: 105 – 108 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.30 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 7.0 Hz, 2H), 7.77 (d, *J* = 14.4 Hz, 1H), 7.46 – 7.36 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 2.25 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 139.82, 138.85, 138.71, 133.56,

132.39, 132.30, 131.68, 131.61, 131.46, 129.39, 129.16, 129.11, 128.70, 126.99, 126.46, 125.94, 125.15, 123.75, 119.84, 119.79, 105.65, 93.58, 88.92, 88.50, 86.36, 21.60, 21.58 ppm. IR (KBr, thin

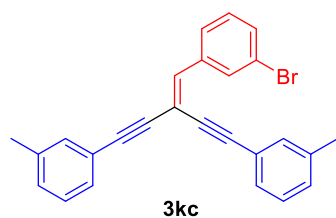
film):  $V_{\max} = 3472, 2382, 2350, 1643, 1514, 1389, 1107, 819, 534 \text{ cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{30}\text{H}_{22}[\text{M} + \text{H}]^+$   $m/z$  383.1794, Found:  $m/z$  383.1794.

### 3,3'-(3-(4-methoxybenzylidene)penta-1,4-diyne-1,5-diyl)bis(methylbenzene) 3ac:



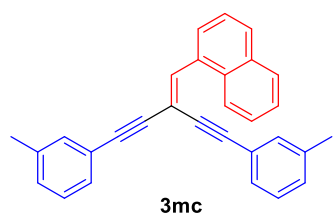
Prepared according to **general procedure**. 75% yield. Brown solid, m.p.:  $65 - 72 \text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.92$  (d,  $J = 8.8 \text{ Hz}$ , 2H), 7.39 – 7.30 (m, 4H), 7.28 – 7.18 (m, 2H), 7.14 (dd,  $J_1 = 15.2 \text{ Hz}$ ,  $J_2 = 7.6 \text{ Hz}$ , 2H), 7.09 (s, 1H), 6.91 (d,  $J = 8.8 \text{ Hz}$ , 2H), 3.83 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 160.28, 142.64, 138.11, 137.95, 132.21, 132.13, 130.71, 129.52, 129.16, 128.83, 128.71, 128.32, 128.19, 122.97, 122.88, 113.87, 100.77, 94.45, 89.25, 87.89, 86.93, 55.34, 21.28, 21.24 \text{ ppm}$ . IR (KBr, thin film):  $V_{\max} = 3466, 2938, 2379, 1611, 1515, 1387, 1260, 1105, 789, 694, 537 \text{ cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{27}\text{H}_{22}\text{O}[\text{M} + \text{H}]^+$   $m/z$  363.1743, Found:  $m/z$  363.1742.

### 3,3'-(3-(3-bromobenzylidene)penta-1,4-diyne-1,5-diyl)bis(methylbenzene) 3kc:



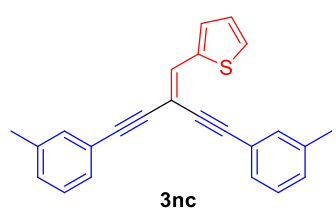
Prepared according to **general procedure**. 89% yield. Black oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.28$  (s, 1H), 7.56 (d,  $J = 7.6 \text{ Hz}$ , 1H), 7.36 – 7.23 (m, 4H), 7.17 – 7.04 (m, 6H), 6.96 (s, 1H), 2.27 (s, 3H), 2.26 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 140.77, 138.22, 138.06, 137.77, 132.44, 132.33, 131.77, 131.20, 129.94, 129.90, 129.57, 128.88, 128.85, 128.39, 128.28, 128.02, 122.53, 122.30, 105.05, 95.85, 89.28, 88.53, 86.31, 21.27 \text{ ppm}$ . IR (KBr, thin film):  $V_{\max} = 3461, 2936, 2380, 2350, 1663, 1488, 1387, 1103, 888, 787, 748, 691, 538 \text{ cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{26}\text{H}_{19}\text{Br}[\text{M} + \text{H}]^+$   $m/z$  411.0743, Found:  $m/z$  411.0746.

### 1-(4-(m-tolyl)-2-(m-tolyethynyl)but-1-en-3-yn-1-yl)naphthalene 3mc:



Prepared according to **general procedure**. 93% yield. Light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.29$  (d,  $J = 7.6 \text{ Hz}$ , 1H), 8.04 (d,  $J = 8.4 \text{ Hz}$ , 1H), 7.80 (s, 1H), 7.76 (t,  $J = 7.2 \text{ Hz}$ , 2H), 7.47 – 7.27 (m, 5H), 7.19 – 7.00 (m, 6H), 2.27 (s, 3H), 2.21 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 139.15, 136.97, 136.93, 132.50, 131.28, 131.17, 130.38, 128.47, 128.42, 128.39, 127.78, 127.74, 127.64, 127.21, 127.15, 125.96, 125.43, 124.90, 124.08, 122.65, 121.58, 121.67, 104.48, 92.54, 87.87, 87.69, 85.49, 20.21, 20.16 \text{ ppm}$ . IR (KBr, thin film):  $V_{\max} = 3447, 2381, 2350, 1642, 1388, 1107, 786, 693, 541 \text{ cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{30}\text{H}_{22}[\text{M} + \text{H}]^+$   $m/z$  383.1794, Found:  $m/z$  383.1794.

### 2-(4-(m-tolyl)-2-(m-tolyethynyl)but-1-en-3-yn-1-yl)thiophene 3nc:

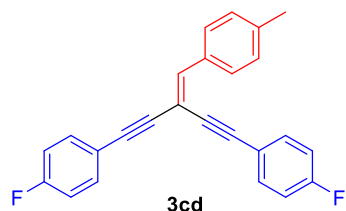


Prepared according to **general procedure**. 69% yield. Black oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.54 - 7.46$  (m, 2H), 7.45 – 7.41 (m, 2H), 7.40 – 7.33 (m, 3H), 7.32 – 7.14 (m, 4H), 7.10 (t,  $J = 4.0 \text{ Hz}$ , 1H), 2.41 (s, 3H), 2.38 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 140.09, 138.15, 138.02, 136.52, 132.23, 132.15, 131.00, 129.77, 129.34,$



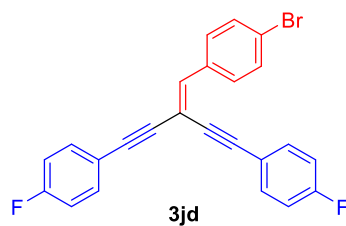
128.81, 128.74, 128.47, 128.36, 128.26, 126.75, 122.80, 122.77, 100.48, 97.85, 89.19, 88.46, 86.92, 21.33, 21.28 ppm. IR (KBr, thin film):  $V_{\max} = 3454, 2935, 2381, 1644, 1489, 1424, 1385, 1103, 883, 786, 695, 538 \text{ cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{24}\text{H}_{18}\text{S}[\text{M} + \text{H}]^+$   $m/z$  339.1202, Found:  $m/z$  339.1201.

#### 4,4'-(3-(4-methylbenzylidene)penta-1,4-diyne-1,5-diyl)bis(fluorobenzene) 3cd:



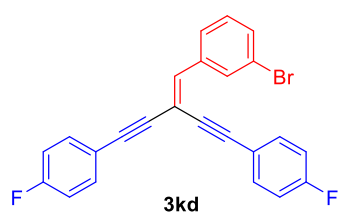
Prepared according to **general procedure**. 72% yield. Yellow solid, m.p.: 66 – 74 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.81$  (d,  $J = 8.4$  Hz, 2H), 7.53 – 7.47 (m, 4H), 7.19 (d,  $J = 8.8$  Hz, 2H), 7.12 (s, 1H), 7.09 – 6.98 (m, 4H), 2.37 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 164.01, 163.82, 161.53, 161.22, 143.45, 139.67, 133.61, 133.59, 133.53, 133.50, 132.98, 129.21, 129.05, 119.14, 119.11, 119.07, 119.03, 115.92, 115.70, 115.70, 115.54, 101.87, 93.41, 88.93, 88.91, 87.04, 86.75, 86.73, 21.51$ .  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta = -109.95, -110.56$  ppm. IR (KBr, thin film):  $V_{\max} = 3480, 2937, 2380, 2350, 1644, 1609, 1512, 1473, 1388, 1235, 1156, 1099, 890, 838, 530 \text{ cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{25}\text{H}_{16}\text{F}_2[\text{M} + \text{H}]^+$   $m/z$  355.1293, Found:  $m/z$  355.1292.

#### 4,4'-(3-(4-bromobenzylidene)penta-1,4-diyne-1,5-diyl)bis(fluorobenzene) 3jd:



Prepared according to **general procedure**. 89% yield. Yellow solid, m.p.: 108 – 110 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.78$  (d,  $J = 8.8$  Hz, 2H), 7.55 – 7.48 (m, 6H), 7.12 – 7.00 (m, 5H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 164.15, 163.92, 161.66, 161.43, 141.74, 134.46, 133.67, 133.65, 133.58, 133.56, 131.63, 130.35, 123.24, 118.82, 118.78, 118.64, 118.60, 116.02, 115.83, 115.80, 115.61, 103.71, 94.18, 88.48, 88.46, 87.83, 86.20, 86.18$ .  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta = -109.43, -110.16$  ppm. IR (KBr, thin film):  $V_{\max} = 3456, 2938, 2382, 1655, 1608, 1512, 1408, 1236, 1100, 1014, 888, 838, 531 \text{ cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{24}\text{H}_{13}\text{BrF}_2[\text{M} + \text{H}]^+$   $m/z$  419.0241, Found:  $m/z$  419.0241.

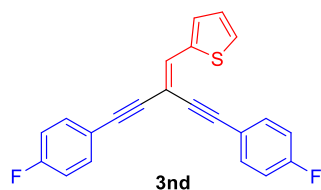
#### 4,4'-(3-(3-bromobenzylidene)penta-1,4-diyne-1,5-diyl)bis(fluorobenzene) 3kd:



Prepared according to **general procedure**. 84% yield. Brown solid, m.p.: 75 – 78 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.26$  (s, 1H), 7.55 (d,  $J = 7.6$  Hz, 1H), 7.50 (dd,  $J_1 = 8.4, J_2 = 5.6$  Hz, 2H), 7.44 (dd,  $J_1 = 8.4, J_2 = 5.6$  Hz, 2H), 7.37 (d,  $J = 8.0$  Hz, 1H), 7.17 (d,  $J = 8.0$  Hz, 1H), 7.04 – 6.93 (m, 5H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 164.21, 163.96, 161.71, 161.47, 141.11, 137.55, 133.82, 133.74, 133.72, 133.63, 131.91, 131.17, 129.93, 128.00, 122.53, 118.75, 118.71, 116.02, 115.85, 115.80, 115.63, 104.55, 94.51, 88.29, 88.28, 88.06, 86.15, 86.13$ .  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta = -109.36, -110.07$  ppm. IR (KBr, thin film):  $V_{\max} = 3470, 2382, 2350, 1662, 1608, 1512, 1474, 1388, 1235, 1100, 839, 784, 747, 682, 534 \text{ cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{24}\text{H}_{13}\text{BrF}_2[\text{M} + \text{H}]^+$   $m/z$  419.0241, Found:  $m/z$  419.0242.

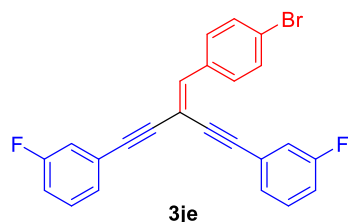
## 2-(4-(4-fluorophenyl)-2-((4-fluorophenyl)ethynyl)but-1-en-3-yn-1-yl)thiophene

### 3nd:



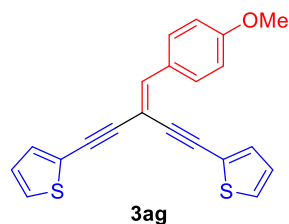
Prepared according to **general procedure**. 83% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.52$  (dd,  $J_1 = 8.8$  Hz,  $J_2 = 5.6$  Hz, 2H), 7.40 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 5.6$  Hz, 2H), 7.32 (d,  $J = 3.2$  Hz, 1H), 7.30 (s, 1H), 7.22 (d,  $J = 3.2$  Hz, 1H), 7.03 – 6.90 (m, 5H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 164.12, 163.82, 161.63, 161.33, 139.83, 136.89, 133.64, 133.58, 133.55, 133.50, 131.31, 128.63, 126.82, 119.04, 119.00, 118.97, 115.96, 115.79, 115.74, 115.57, 99.92, 96.58, 88.23, 88.21, 88.00, 86.80, 86.79$ .  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta = -109.74, -110.43$  ppm. IR (KBr, thin film):  $\nu_{\text{max}} = 3459, 2376, 1643, 1608, 1512, 1424, 1233, 1100, 838, 746, 708, 532$   $\text{cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{22}\text{H}_{12}\text{F}_2\text{S}[\text{M} + \text{H}]^+$   $m/z$  347.0701, Found:  $m/z$  347.0703.

## 3,3'-(3-(4-bromobenzylidene)penta-1,4-diyne-1,5-diyl)bis(fluorobenzene) 3je:



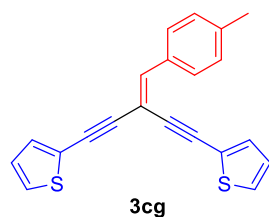
Prepared according to **general procedure**. 66% yield. Brown solid, m.p.: 82 – 87 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.78$  (d,  $J = 8.4$  Hz, 2H), 7.54 (d,  $J = 8.4$  Hz, 2H), 7.38 – 7.28 (m, 4H), 7.27 – 7.21 (m, 2H), 7.12 (s, 1H), 7.12 – 7.02 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 163.63, 163.57, 161.17, 161.12, 142.20, 137.33, 132.19, 131.30, 130.19, 130.10, 130.04, 129.97, 129.95, 128.06, 127.73, 127.70, 127.66, 127.63, 124.48, 124.39, 124.19, 124.10, 122.60, 118.64, 118.61, 118.41, 118.38, 116.58, 116.37, 116.18, 115.97, 104.13, 94.26, 94.23, 89.27, 87.97, 87.93, 87.00$ .  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta = -112.25, -112.65$  ppm. IR (KBr, thin film):  $\nu_{\text{max}} = 3474, 2378, 1616, 1586, 1489, 1437, 1407, 1269, 1192, 1148, 1081, 1012, 925, 875, 823, 786, 681, 540$   $\text{cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{24}\text{H}_{13}\text{BrF}_2[\text{M} + \text{H}]^+$   $m/z$  419.0241, Found:  $m/z$  419.0241.

## 2,2'-(3-(4-methoxybenzylidene)penta-1,4-diyne-1,5-diyl)dithiophene 3ag:



Prepared according to **general procedure**. 65% yield. Black solid, m.p.: 83 – 91 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.86$  (d,  $J = 8.4$  Hz, 2H), 7.35 – 7.21 (m, 4H), 7.07 (s, 1H), 7.00 (dt,  $J_1 = 14.4$  Hz,  $J_2 = 4.4$  Hz, 2H), 6.90 (d,  $J = 8.4$  Hz, 2H), 3.81 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 160.56, 143.09, 132.34, 132.15, 130.81, 128.56, 128.08, 127.46, 127.32, 127.15, 123.17, 122.93, 113.99, 99.96, 92.72, 90.69, 87.95, 81.37, 55.37$  ppm. IR (KBr, thin film):  $\nu_{\text{max}} = 3468, 2940, 2379, 1644, 1610, 1514, 1421, 1309, 1261, 1178, 1115, 833, 705, 536$   $\text{cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{21}\text{H}_{14}\text{OS}_2[\text{M} + \text{H}]^+$   $m/z$  347.0559, Found:  $m/z$  347.0562.

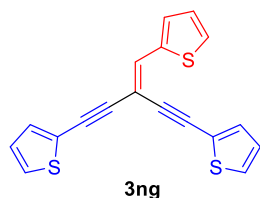
## 2,2'-(3-(4-methylbenzylidene)penta-1,4-diyne-1,5-diyl)dithiophene 3cg:



Prepared according to **general procedure**. 70% yield. Black solid, m.p.: 85 – 92 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.79$  (d,  $J = 8.4$  Hz, 2H), 7.33 – 7.24 (m, 4H), 7.19 (d,  $J = 8.0$  Hz, 2H), 7.10 (s, 1H), 7.03 – 6.96 (m, 2H), 2.36 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 143.39, 139.82, 132.90, 132.43, 132.28, 129.27, 129.10, 128.16, 127.58, 127.30, 127.16, 123.06,$

122.88, 101.59, 92.56, 90.59, 88.22, 81.67, 21.57 ppm. IR (KBr, thin film):  $\nu_{\max}$  = 3462, 2380, 2350, 1642, 1523, 1387, 1113, 705, 539  $\text{cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{21}\text{H}_{14}\text{S}_2[\text{M} + \text{H}]^+$   $m/z$  331.0610, Found:  $m/z$  331.0954.

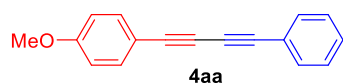
### 2,2'-(3-(2-thienyl)pentan-1,4-diyne-1,5-diy)dithiophene 3ng:



Prepared according to **general procedure**. 71% yield. Brown solid, m.p.: 119 – 123 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.46 – 7.36 (m, 4H), 7.36 – 7.27 (m, 2H), 7.30 (s, 1h), 7.08 (dd,  $J_1$  = 8.8 Hz,  $J_2$  = 4.0 Hz, 2H), 7.02 (t,  $J$  = 4.0 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 139.90, 136.81, 132.58, 132.29, 131.37, 128.85, 128.47, 127.64, 127.32, 127.17, 126.85, 122.97, 122.81, 99.64, 91.85, 91.53, 90.55, 82.60 ppm. IR (KBr, thin film):  $\nu_{\max}$  = 3480, 2380, 2350, 1662, 1523, 1387, 1100, 857, 748, 703, 541  $\text{cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{18}\text{H}_{10}\text{S}_3[\text{M} + \text{H}]^+$   $m/z$  323.0017, Found:  $m/z$  323.0017.

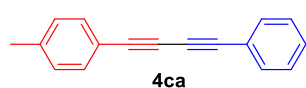
## 7. Characterization of the products unsymmetric 1,3-diynes 4

### 1-methoxy-4-(phenylbuta-1,3-diyn-1-yl)benzene 4aa:



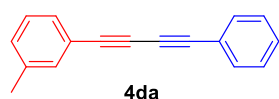
Prepared according to **general procedure**. 74% yield. White solid, m.p.: 37 – 40 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.52 (dd,  $J_1$  = 7.6 Hz,  $J_2$  = 2.0 Hz, 2H), 7.47 (d,  $J$  = 8.8 Hz, 2H), 7.37 – 7.30 (m, 3H), 6.86 (d,  $J$  = 8.8 Hz, 2H), 3.83 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 160.35, 134.11, 132.41, 129.00, 128.39, 121.99, 114.14, 109.99, 81.80, 81.00, 74.15, 72.72, 55.33 ppm. IR (KBr, thin film):  $\nu_{\text{max}}$  = 3487, 2381, 2350, 1643, 1105, 750, 536  $\text{cm}^{-1}$ .

### 1-methyl-4-(phenylbuta-1,3-diyn-1-yl)benzene 4ca:



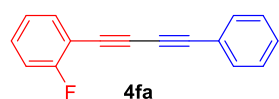
Prepared according to **general procedure**. 97% yield. White solid, m.p.: 117 – 118 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.54 – 7.50 (m, 3H), 7.41 (d,  $J$  = 8.0 Hz, 2H), 7.32 (dd,  $J_1$  = 8.0 Hz,  $J_2$  = 2.0, 2H), 7.13 (d,  $J$  = 8.0 Hz, 2H), 2.38 (s, 3H) ppm. IR (KBr, thin film):  $\nu_{\text{max}}$  = 3467, 2380, 2350, 1662, 1489, 1388, 1115, 752, 534  $\text{cm}^{-1}$ .

### 1-methyl-3-(phenylbuta-1,3-diyn-1-yl)benzene 4da:



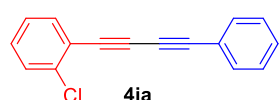
Prepared according to **general procedure**. 78% yield. Colorless liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.60 – 7.55 (m, 2H), 7.43 – 7.33 (m, 5H), 7.27 – 7.20 (m, 2H), 2.36 (s, 3H) ppm. IR (KBr, thin film):  $\nu_{\text{max}}$  = 3473, 2378, 1643, 1103, 787, 540  $\text{cm}^{-1}$ .

### 1-fluoro-2-(phenylbuta-1,3-diyn-1-yl)benzene 4fa:



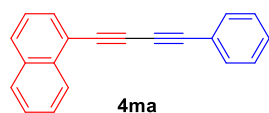
Prepared according to **general procedure**. 82% yield. Colorless liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.55 (dd,  $J_1$  = 8.0 Hz,  $J_2$  = 1.6 Hz, 2H), 7.55 (dd,  $J_1$  = 7.6 Hz,  $J_2$  = 2.0 Hz, 1H), 7.39 – 7.31 (m, 4H), 7.16 – 7.07 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 165.00, 162.48, 134.26, 132.54, 130.98, 130.90, 129.40, 128.47, 124.13, 124.09, 121.54, 115.77, 115.56, 110.72, 110.57, 82.66, 82.65, 78.72, 78.69, 74.79, 73.69, 73.68.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -108.66 ppm. IR (KBr, thin film):  $\nu_{\text{max}}$  = 3454, 2381, 1642, 1389, 1111, 835, 752, 534  $\text{cm}^{-1}$ .

### 1-chloro-2-(phenylbuta-1,3-diyn-1-yl)benzene 4ia:



Prepared according to **general procedure**. 78% yield. White solid, m.p.: 79 – 82 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.60 – 7.53 (m, 3H), 7.45 – 7.33 (m, 4H), 7.30 (dt,  $J_1$  = 9.2 Hz,  $J_2$  = 1.6 Hz, 1H), 7.27 – 7.21 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 136.89, 134.30, 132.57, 132.51, 130.14, 129.45, 128.50, 126.58, 121.97, 121.54, 83.13, 78.74, 78.01, 73.74 ppm. IR (KBr, thin film):  $\nu_{\text{max}}$  = 3469, 2380, 2350, 1643, 1105, 753, 535  $\text{cm}^{-1}$ .

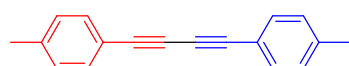
### 1-(phenylbuta-1,3-diyne-1-yl)naphthalene 4ma:



4ma

Prepared according to **general procedure**. 69% yield. White solid, m.p.: 75 – 88 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.41 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.63 – 7.60 (m, 3H), 7.56 (t, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 4.0 Hz, 1H), 7.42 – 7.36 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 133.92, 133.10, 132.54, 132.05, 129.76, 129.29, 128.51, 128.47, 127.24, 126.71, 126.11, 125.23, 121.84, 119.48, 82.66, 79.97, 78.61, 74.18 ppm. IR (KBr, thin film): *V*<sub>max</sub> = 3449, 2382, 1642, 1407, 1102, 755, 538 cm<sup>-1</sup>.

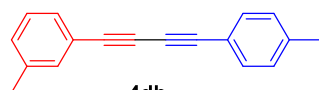
### 1,4-di-p-tolylbuta-1,3-diyne 4cb:



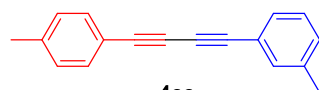
4cb

Prepared according to **general procedure**. 68% yield. White solid, m.p.: 181 – 183 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.42 (d, *J* = 8.0 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 4H), 2.37 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 139.49, 132.38, 129.21, 118.75, 81.54, 73.44, 21.63 ppm. IR (KBr, thin film): *V*<sub>max</sub> = 3469, 2379, 2350, 1643, 1389, 1113, 814, 747, 531 cm<sup>-1</sup>.

### 1-methyl-3-(p-tolylbuta-1,3-diyne-1-yl)benzene 4db or 4cc:



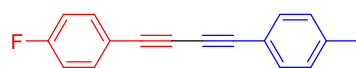
4db



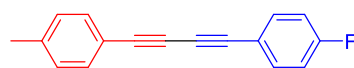
4cc

Prepared according to **general procedure**. **4db**: 99% yield, **4cc**: 74% yield. White solid, m.p.: 98 – 100 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.44 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 6.8 Hz, 2H), 7.27 – 7.20 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.36 (s, 3H) ppm. IR (KBr, thin film): *V*<sub>max</sub> = 3457, 2379, 1643, 1103, 815, 786, 746, 689, 533 cm<sup>-1</sup>.

### 1-fluoro-4-(p-tolylbuta-1,3-diyne-1-yl)benzene 4eb or 4cd:



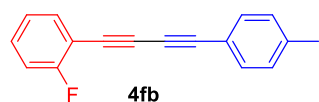
4eb



4cd

Prepared according to **general procedure**. **4eb**: 91% yield, **4cd**: 64% yield. White solid, m.p.: 157 – 160 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.53 – 7.49 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.06 – 7.01 (m, 3H), 2.37 (s, 3H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ = -108.86 ppm. IR (KBr, thin film): *V*<sub>max</sub> = 3458, 2378, 1643, 1104, 838, 749, 532 cm<sup>-1</sup>.

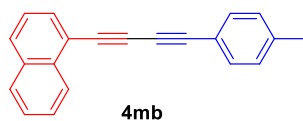
### 1-fluoro-2-(p-tolylbuta-1,3-diyne-1-yl)benzene 4fb:



4fb

Prepared according to **general procedure**. 81% yield. Yellow solid, m.p.: 110 – 111 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.56 – 7.48 (m, 1H), 7.46 – 7.40 (m, 2H), 7.39 – 7.30 (m, 1H), 7.19 – 7.06 (m, 4H), 2.37 (d, *J* = 1.6 Hz, 3H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ = -108.74 ppm. IR (KBr, thin film): *V*<sub>max</sub> = 3455, 2379, 2350, 1643, 1103, 834, 782, 747, 532 cm<sup>-1</sup>.

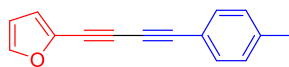
### 1-(p-tolylbuta-1,3-diyn-1-yl)naphthalene 4mb:



4mb

Prepared according to **general procedure**. 66% yield. Yellow solid, m.p.: 98 – 102 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.30 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.70 (dd, *J*<sub>1</sub> = 7.2 Hz, *J*<sub>2</sub> = 0.8 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.18 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.30 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 139.67, 133.89, 133.07, 132.43, 131.93, 129.60, 129.27, 128.40, 127.16, 126.65, 126.12, 125.20, 119.60, 118.68, 82.92, 79.56, 78.71, 73.50, 21.66 ppm. IR (KBr, thin film): *V*<sub>max</sub> = 3446, 2380, 1642, 1108, 538 cm<sup>-1</sup>. ES-HRMS Calcd for C<sub>21</sub>H<sub>14</sub>[M + H]<sup>+</sup> *m/z* 267.1168, Found: *m/z* 267.1169.

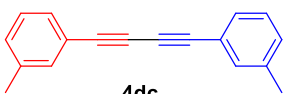
### 2-(p-tolylbuta-1,3-diyn-1-yl)furan 4ob:



4ob

Prepared according to **general procedure**. 59% yield. Yellow solid, m.p.: 70 – 73 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.35 (d, *J* = 8.0 Hz, 2H), 7.34 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 4.0 Hz, 1H), 6.37 – 6.33 (m, 1H), 2.30 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 144.52, 139.94, 136.58, 132.44, 129.25, 118.21, 117.90, 111.15, 84.54, 78.75, 72.74, 70.59, 21.67 ppm. IR (KBr, thin film): *V*<sub>max</sub> = 3473, 2381, 2350, 1662, 1112, 819, 743, 534 cm<sup>-1</sup>. ES-HRMS Calcd for C<sub>15</sub>H<sub>10</sub>O[M + Na]<sup>+</sup> *m/z* 229.0624, Found: *m/z* 229.0677.

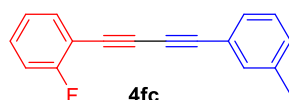
### 1,4-di-m-tolylbuta-1,3-diyne 4dc:



4dc

Prepared according to **general procedure**. 89% yield. Yellow solid, m.p.: 68 – 70 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.40 – 7.36 (w, 4H), 7.28 – 7.20 (m, 4H), 2.37 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 138.19, 133.00, 130.18, 129.64, 128.37, 121.65, 81.69, 73.74, 21.25 ppm. IR (KBr, thin film): *V*<sub>max</sub> = 3442, 2379, 2350, 1641, 1095, 911, 789, 690, 533 cm<sup>-1</sup>.

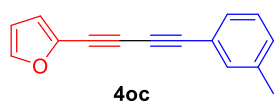
### 1-fluoro-2-(m-tolylbuta-1,3-diyn-1-yl)benzene 4fc:



4fc

Prepared according to **general procedure**. 77% yield. Yellow solid, m.p.: 58 – 62 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.51 (dt, *J*<sub>1</sub> = 7.6 Hz, *J*<sub>2</sub> = 1.6 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.14 – 7.08 (m, 2H), 2.35 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 164.98, 162.46, 138.21, 134.25, 133.01, 130.90, 130.82, 130.35, 129.66, 128.35, 124.10, 124.06, 121.32, 115.75, 115.54, 82.90, 78.79, 78.76, 74.56, 73.31, 73.30, 21.21. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ = -108.68 ppm. IR (KBr, thin film): *V*<sub>max</sub> = 3466, 2385, 1644, 1109, 755, 538 cm<sup>-1</sup>. ES-HRMS Calcd for C<sub>17</sub>H<sub>11</sub>F[M + K]<sup>+</sup> *m/z* 273.0476, Found: *m/z* 273.0940.

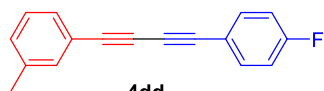
### 2-(m-tolylbuta-1,3-diyn-1-yl)furan 4oc:



4oc

Prepared according to **general procedure**. 61% yield. Black oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.35 (s, 1H), 7.27 (s, 1H), 7.26 (d,  $J$  = 7.6 Hz, 1H), 7.17 – 7.08 (m, 2H), 6.68 (d,  $J$  = 7.6 Hz, 1H), 6.36 – 6.32 (m, 1H), 2.27 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 144.57, 138.23, 136.50, 132.97, 130.44, 129.64, 128.367, 121.12, 118.00, 111.16, 84.49, 78.70, 72.97, 70.70, 21.21 ppm. IR (KBr, thin film):  $\nu_{\text{max}}$  = 3456, 2376, 1662, 1111, 749, 540  $\text{cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{15}\text{H}_{10}\text{O}[\text{M} + \text{Na}]^+$   $m/z$  229.0624, Found:  $m/z$  229.0676.

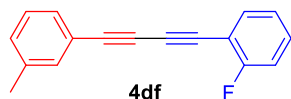
### 1-((4-fluorophenyl)buta-1,3-diyn-1-yl)-3-methylbenzene 4dd:



4dd

Prepared according to **general procedure**. 69% yield. Yellow solid, m.p.: 79 – 85 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.54 – 7.50 (m, 2H), 7.35 (d,  $J$  = 7.2 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.04 (t,  $J$  = 8.8 Hz, 2H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 164.29, 164.23, 161.79, 161.72, 138.20, 138.16, 134.57, 134.54, 134.49, 134.46, 132.98, 130.23, 130.11, 129.62, 129.61, 128.35, 128.32, 121.62, 121.45, 117.99, 117.95, 117.81, 117.78, 116.01, 115.97, 115.79, 115.75, 81.81, 81.60, 80.43, 80.24, 73.80, 73.79, 73.66, 73.40, 21.21.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -108.75 ppm. IR (KBr, thin film):  $\nu_{\text{max}}$  = 3490, 2381, 2350, 1643, 1104, 747, 537  $\text{cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{17}\text{H}_{11}\text{F}[\text{M} + \text{H}]^+$   $m/z$  235.0918, Found:  $m/z$  235.0939.

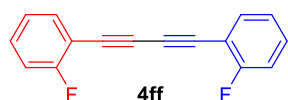
### 1-fluoro-2-(m-tolylbuta-1,3-diyn-1-yl)benzene 4df:



4df

Prepared according to **general procedure**. 70% yield. Yellow solid, m.p.: 59 – 62 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.50 (dt,  $J_1$  = 7.6 Hz,  $J_2$  = 1.6 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.24 (d,  $J$  = 8.4 Hz, 1H), 7.22 – 7.17 (m, 1H), 7.15 – 7.05 (m, 2H), 2.34 (s, 3H).

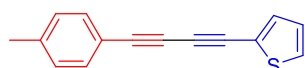
### 1,4-bis(2-fluorophenyl)buta-1,3-diyne 4ff:



4ff

Prepared according to **general procedure**. 63% yield. White solid, m.p.: 109 – 110 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.52 (dt,  $J_1$  = 7.2 Hz,  $J_2$  = 3.2 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.16 – 7.08 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 165.00, 162.47, 134.29, 131.17, 131.09, 124.15, 124.11, 115.79, 115.59, 110.50, 110.34, 78.38, 78.37, 78.35, 78.34, 75.86.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -108.48, -112.26 ppm. IR (KBr, thin film):  $\nu_{\text{max}}$  = 3467, 2379, 1643, 1106, 871, 787, 755, 678, 541  $\text{cm}^{-1}$ . ES-HRMS Calcd for  $\text{C}_{16}\text{H}_8\text{F}_2[\text{M} + \text{H}]^+$   $m/z$  239.0667, Found:  $m/z$  239.0697.

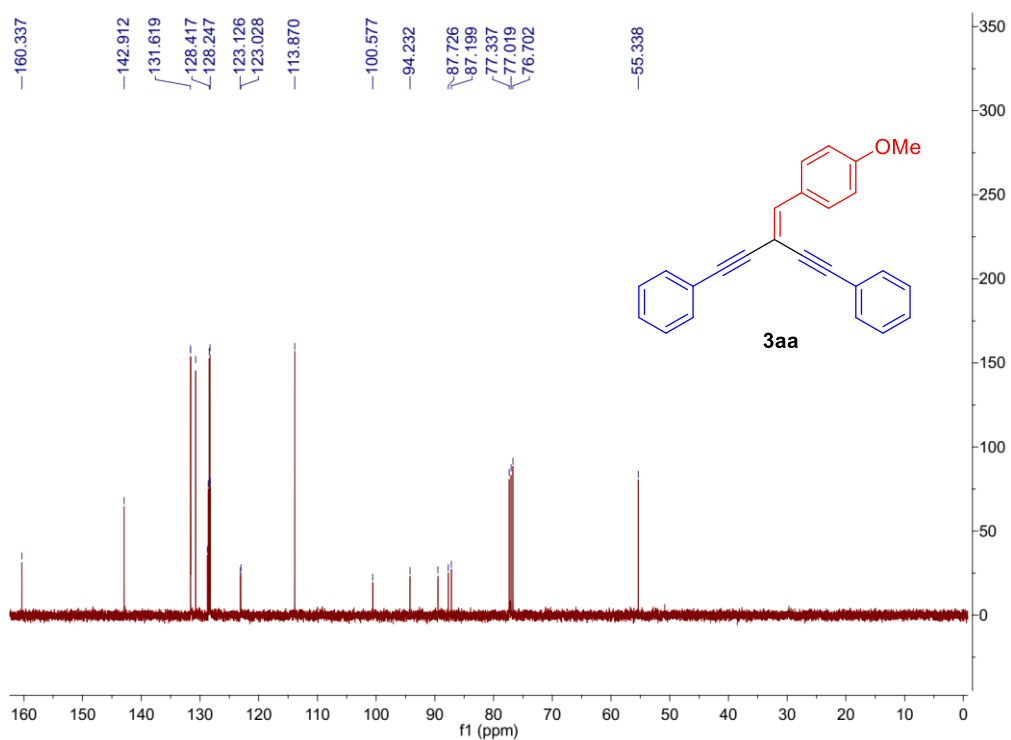
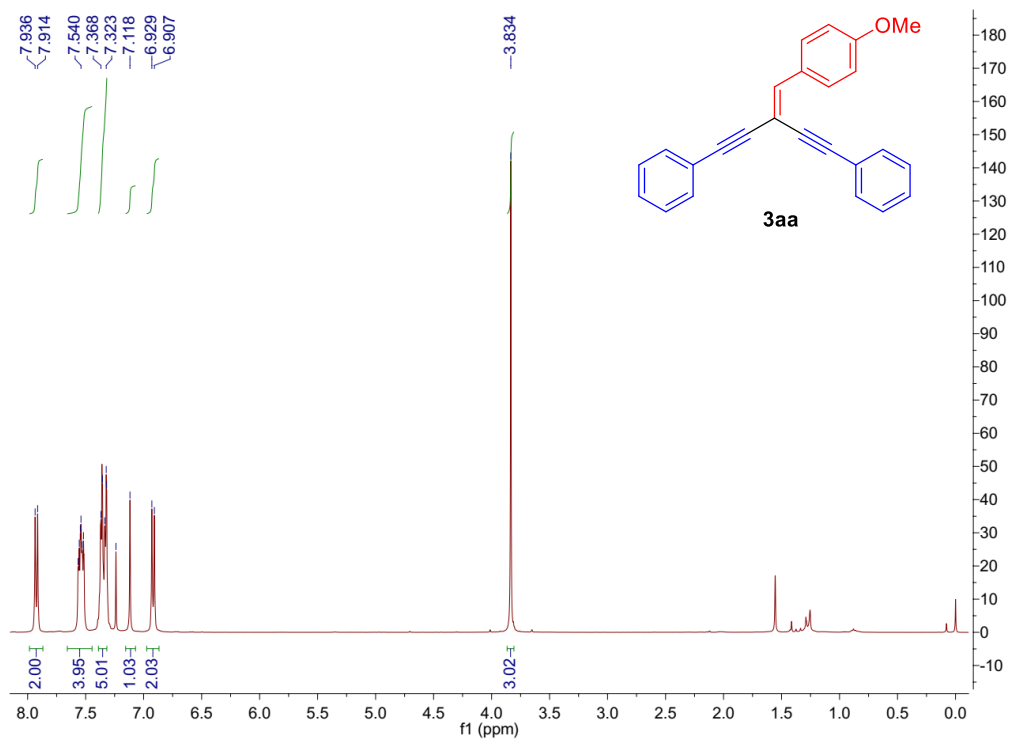
### 2-(p-tolylbuta-1,3-diyn-1-yl)thiophene 4cg:



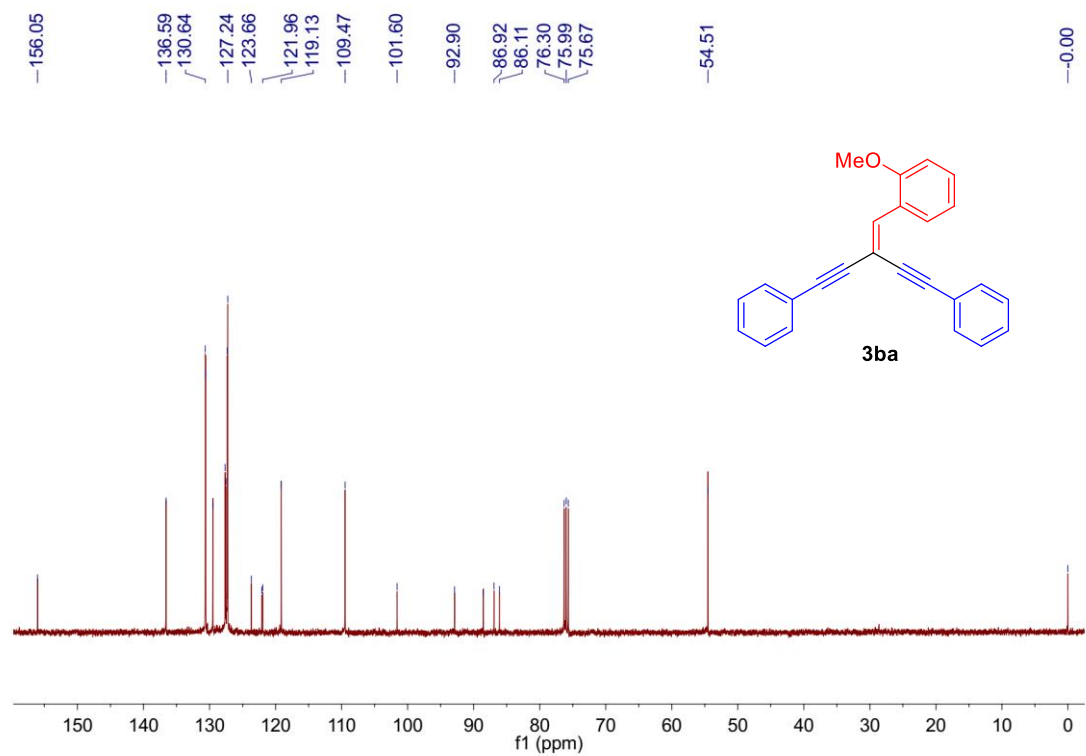
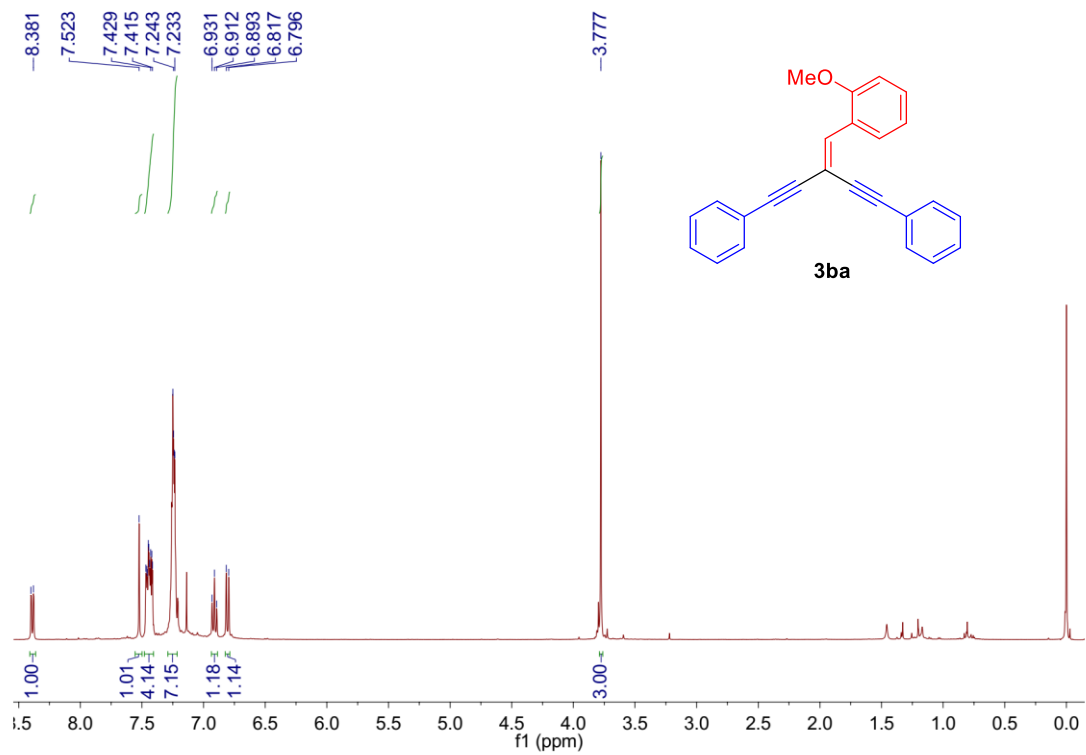
4cg

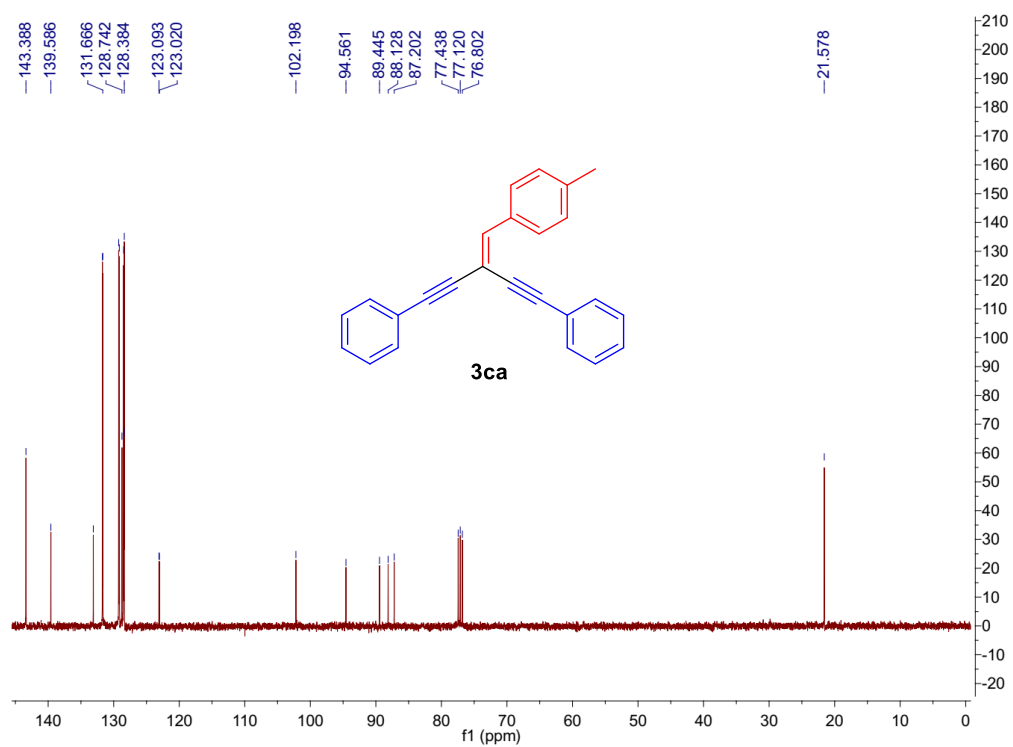
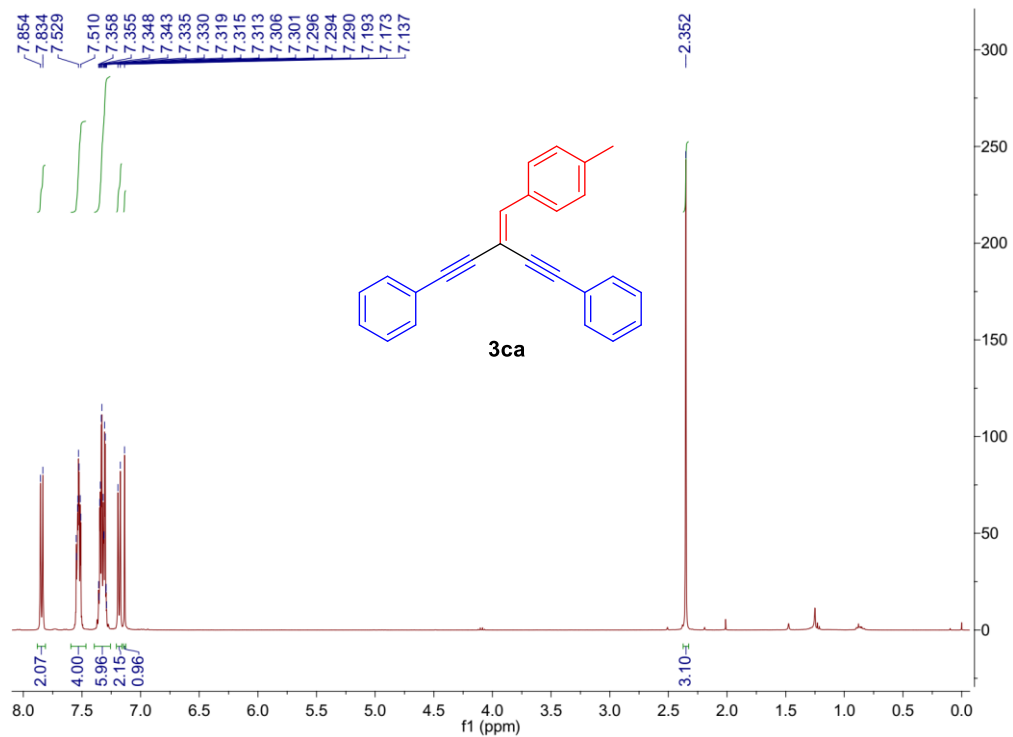
Prepared according to **general procedure**. 61% yield. Yellow solid, m.p.: 103 – 105 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.42 (d,  $J$  = 8.0 Hz, 2H), 7.33 (d,  $J$  = 3.2 Hz, 1H), 7.31 (d,  $J$  = 5.2 Hz, 1H), 7.15 (d,  $J$  = 8.0 Hz, 2H), 7.00 (dd,  $J_1$  = 5.2 Hz,  $J_2$  = 3.2 Hz, 1H), 2.37 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 139.75, 134.13, 132.38, 129.25, 128.55, 127.15, 122.17, 118.50, 83.95, 78.10, 74.21, 73.12, 21.66 ppm. IR (KBr, thin film):  $\nu_{\text{max}}$  = 3457, 2376, 1643, 1116, 857, 819, 750, 696, 533  $\text{cm}^{-1}$ .

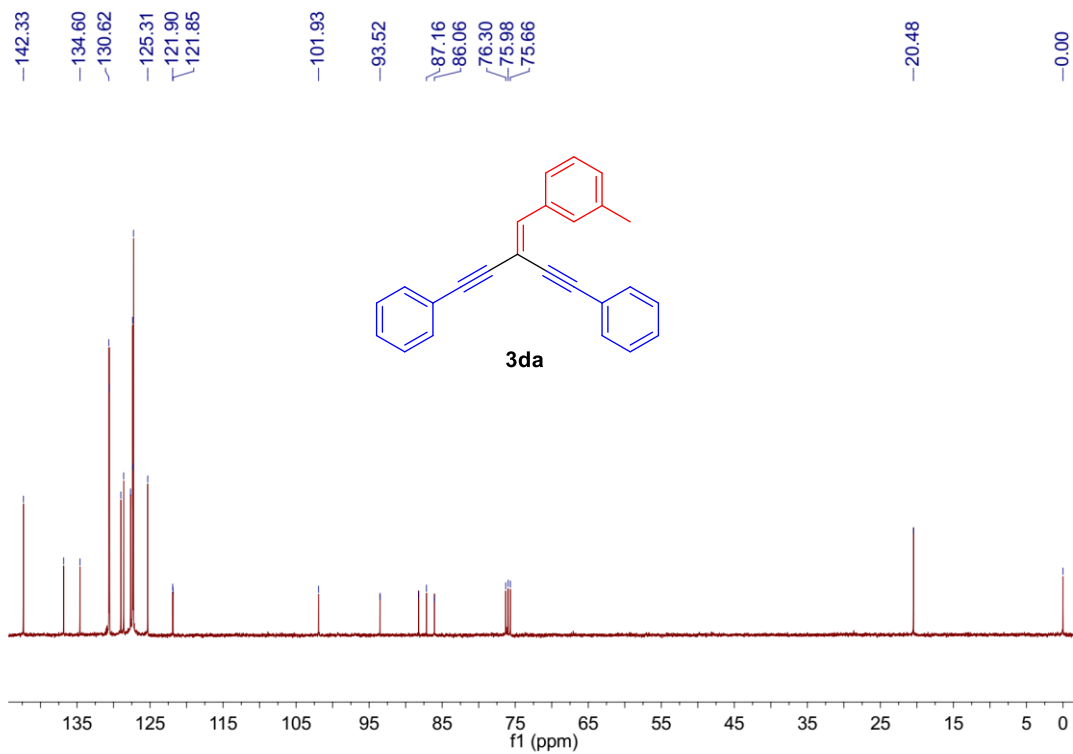
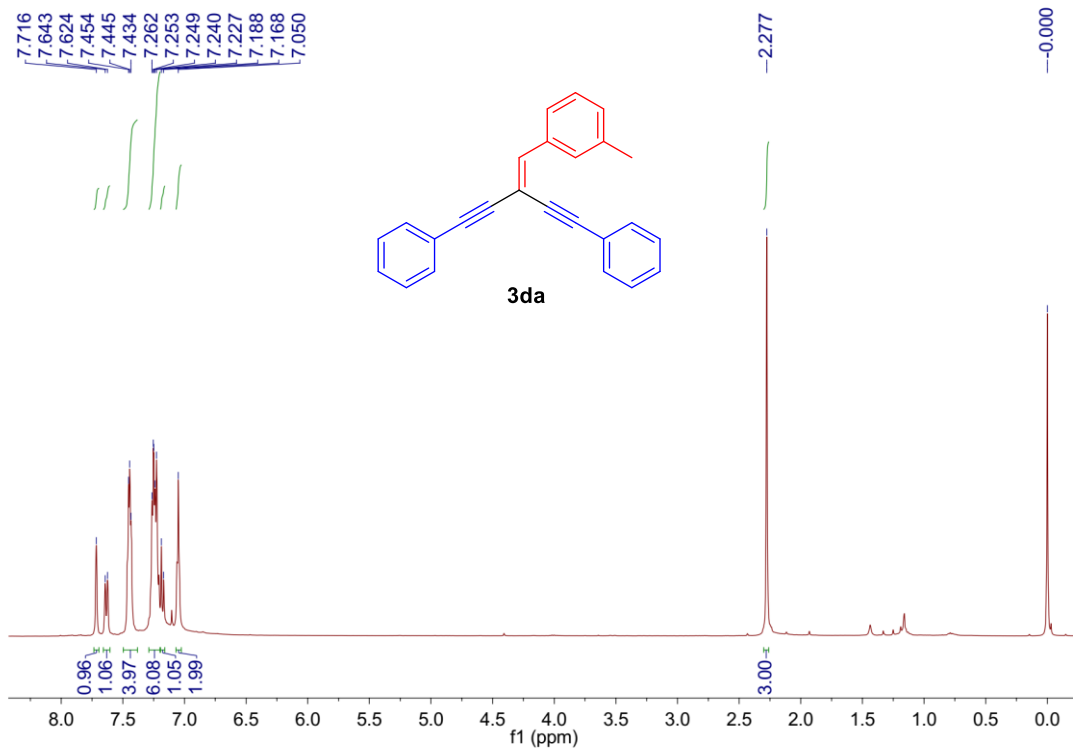
## 8. Copy of $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ NMR spectra for the conjugated enediynes **3**

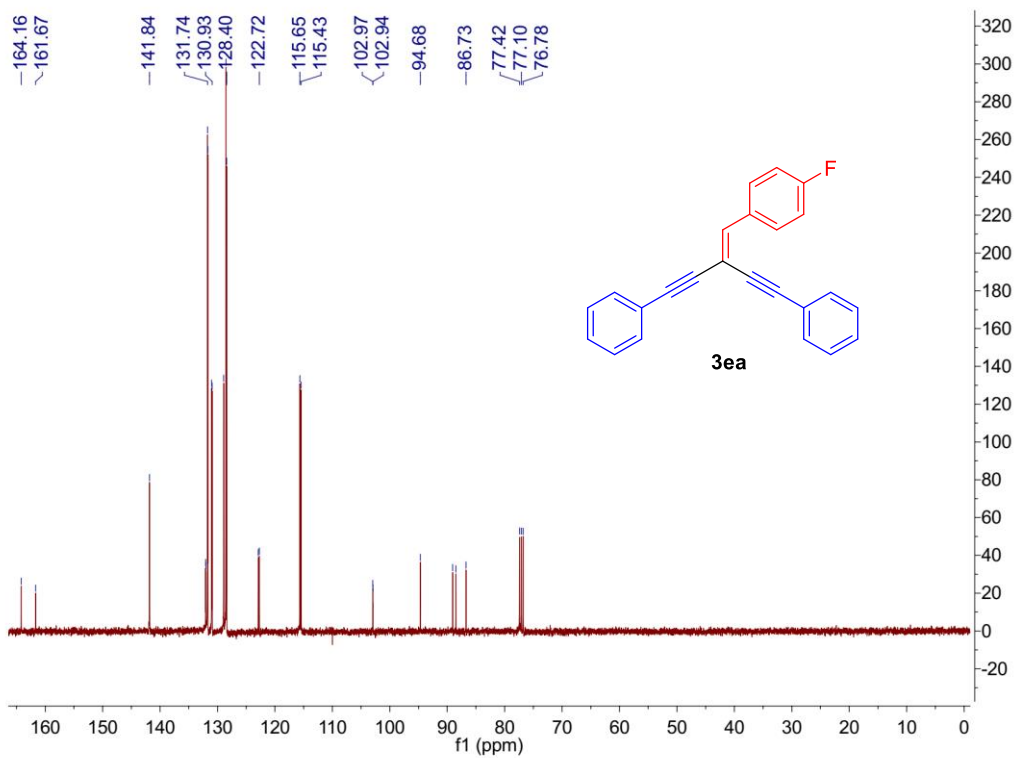
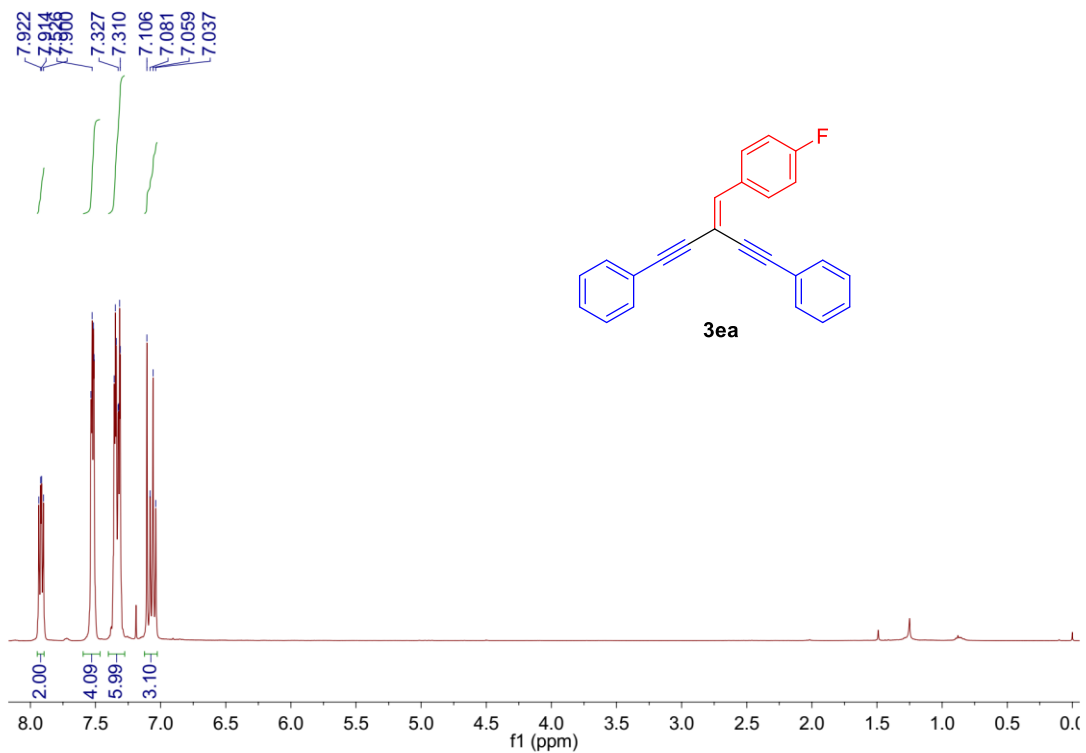


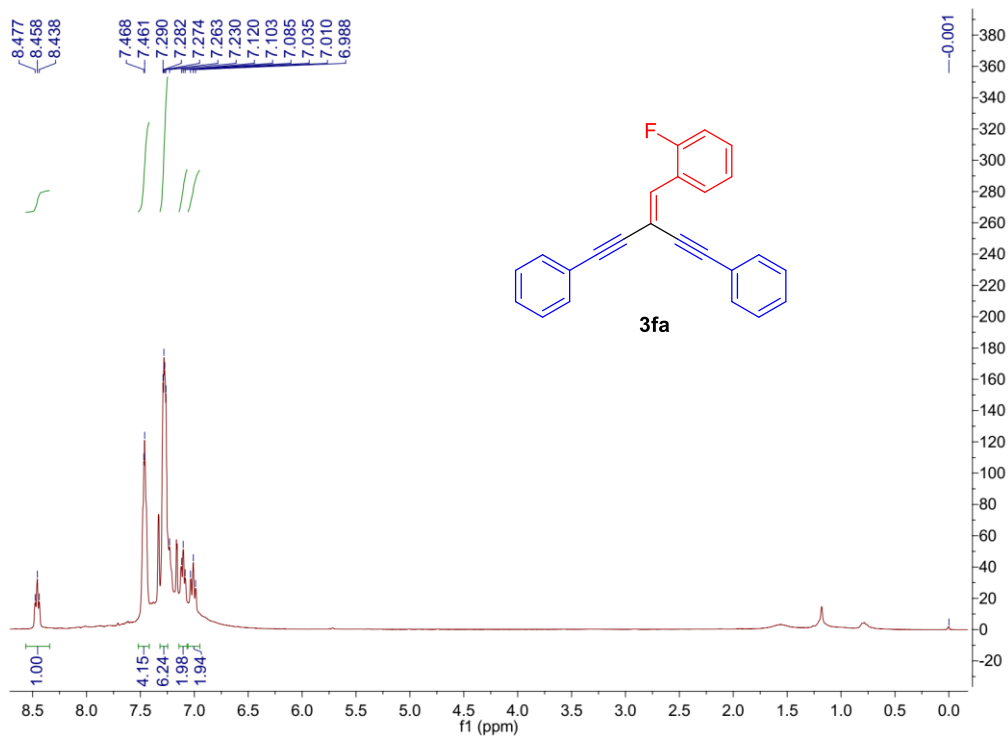
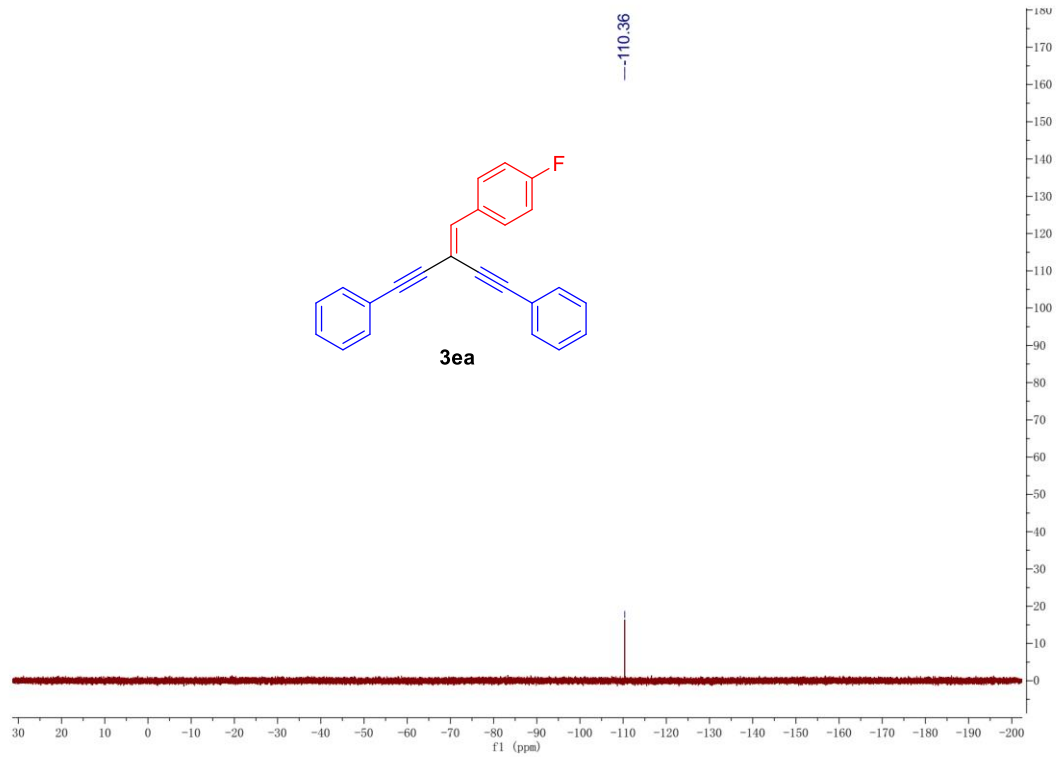


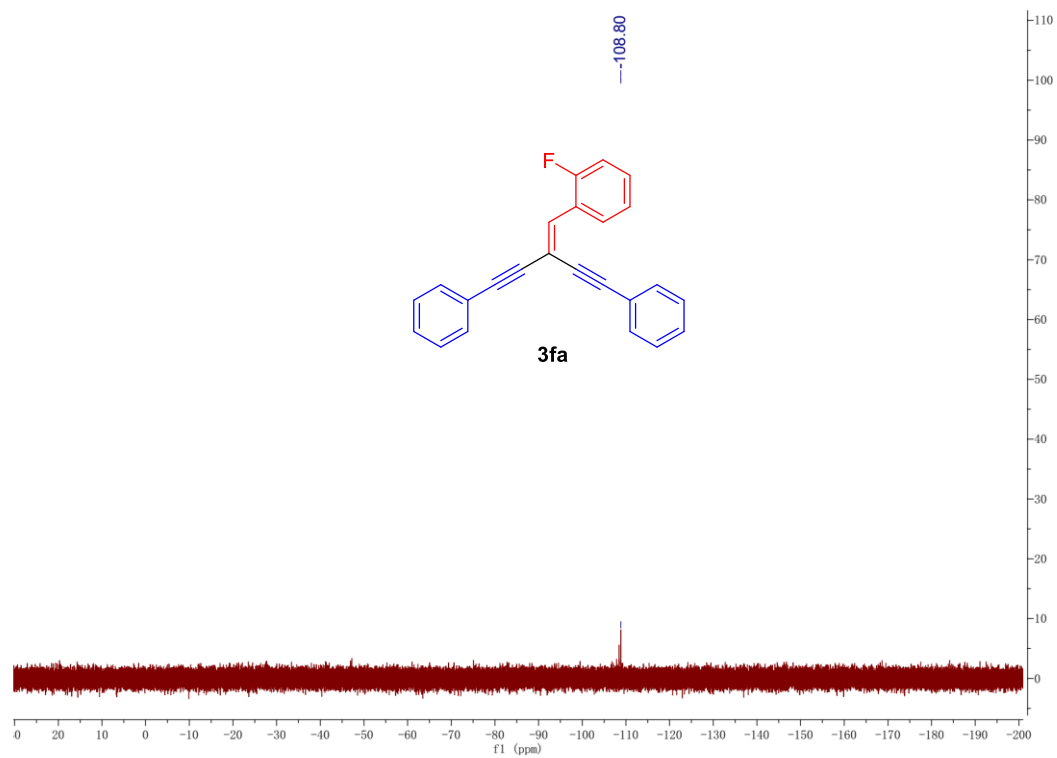
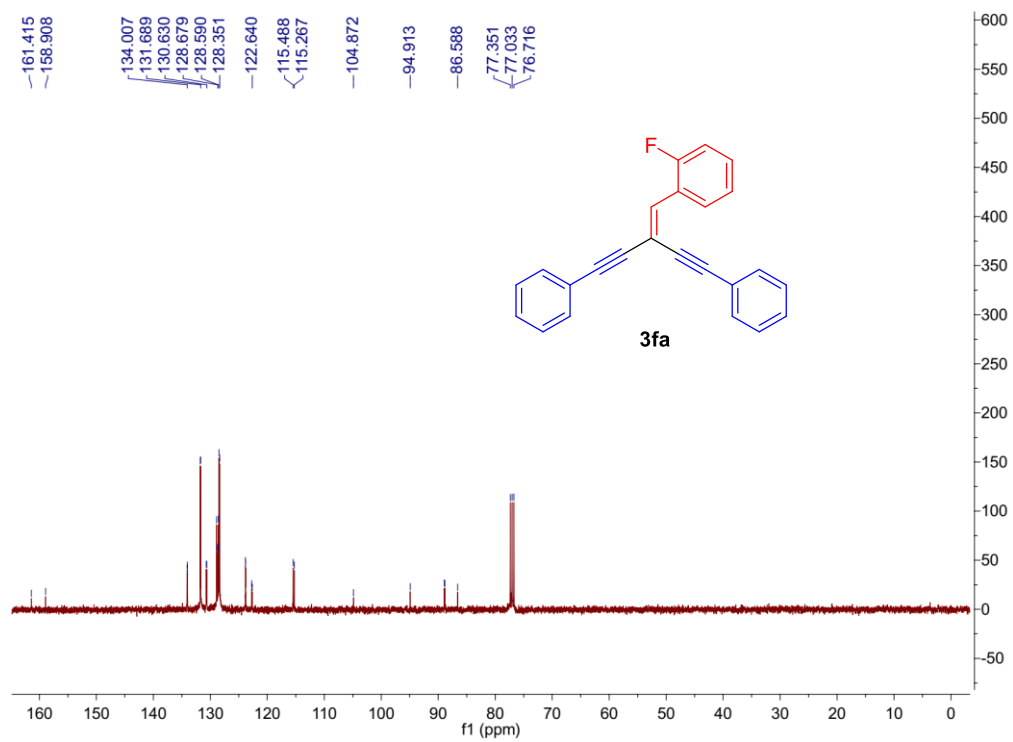


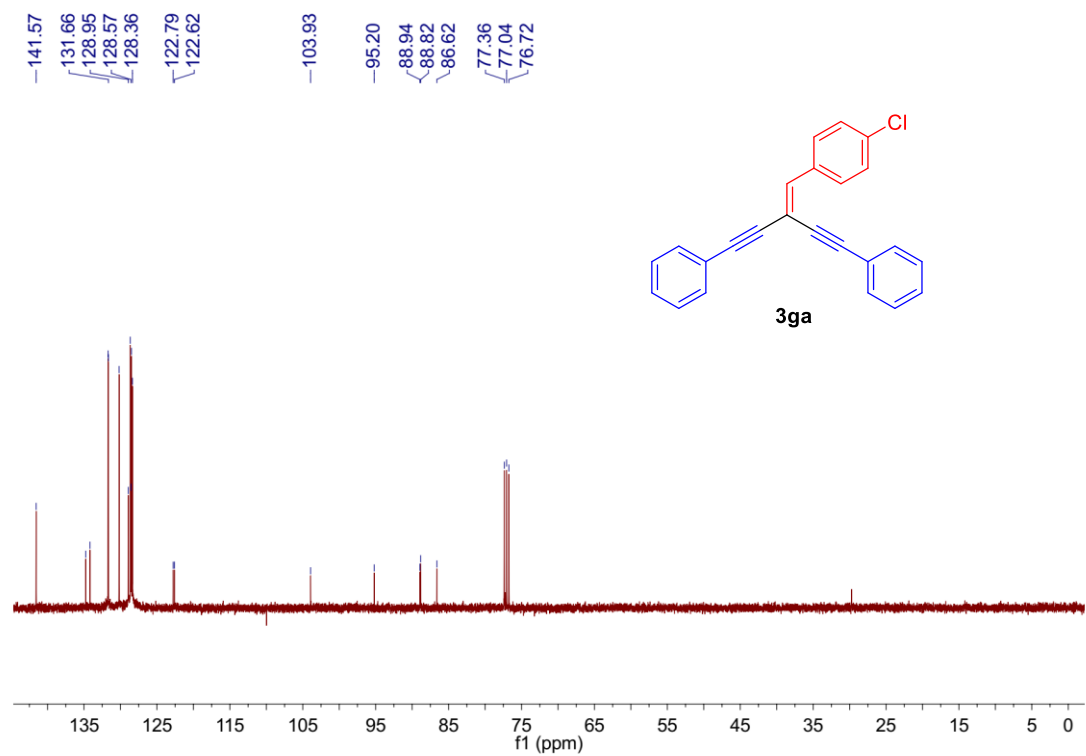
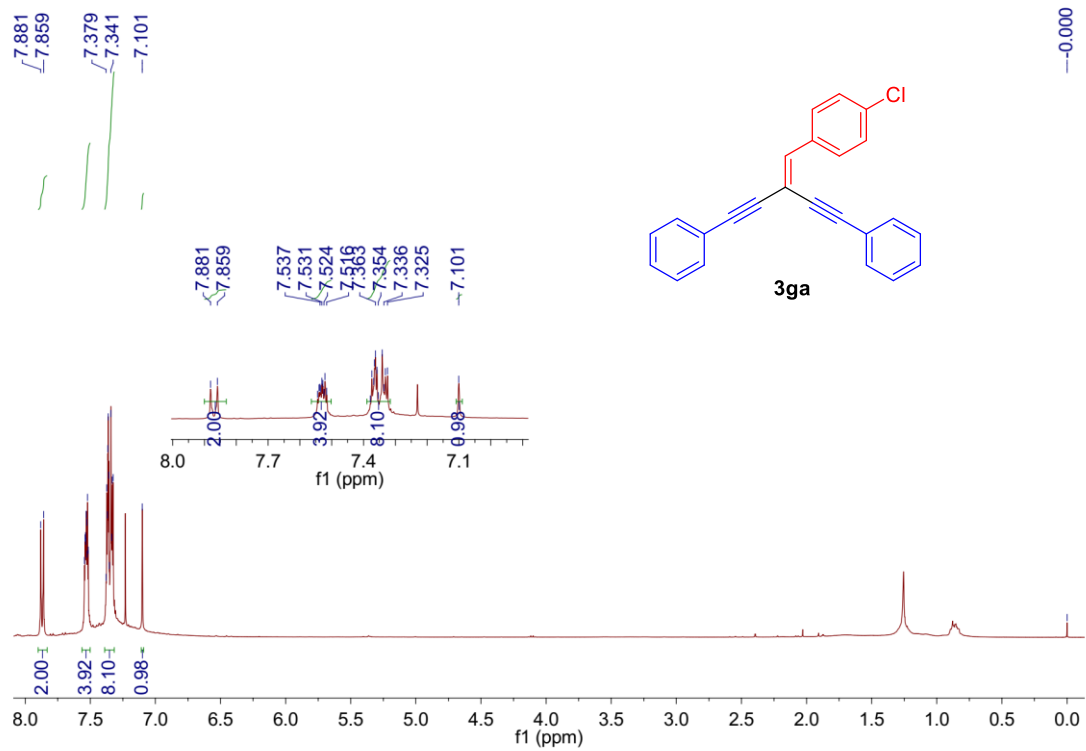


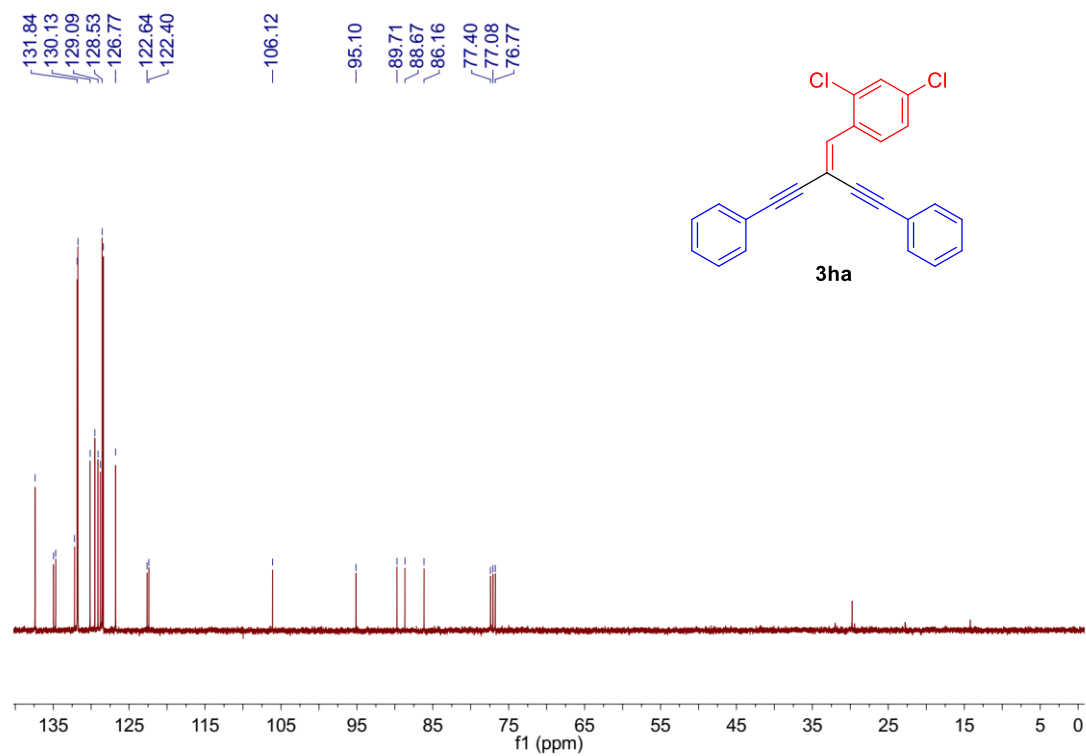
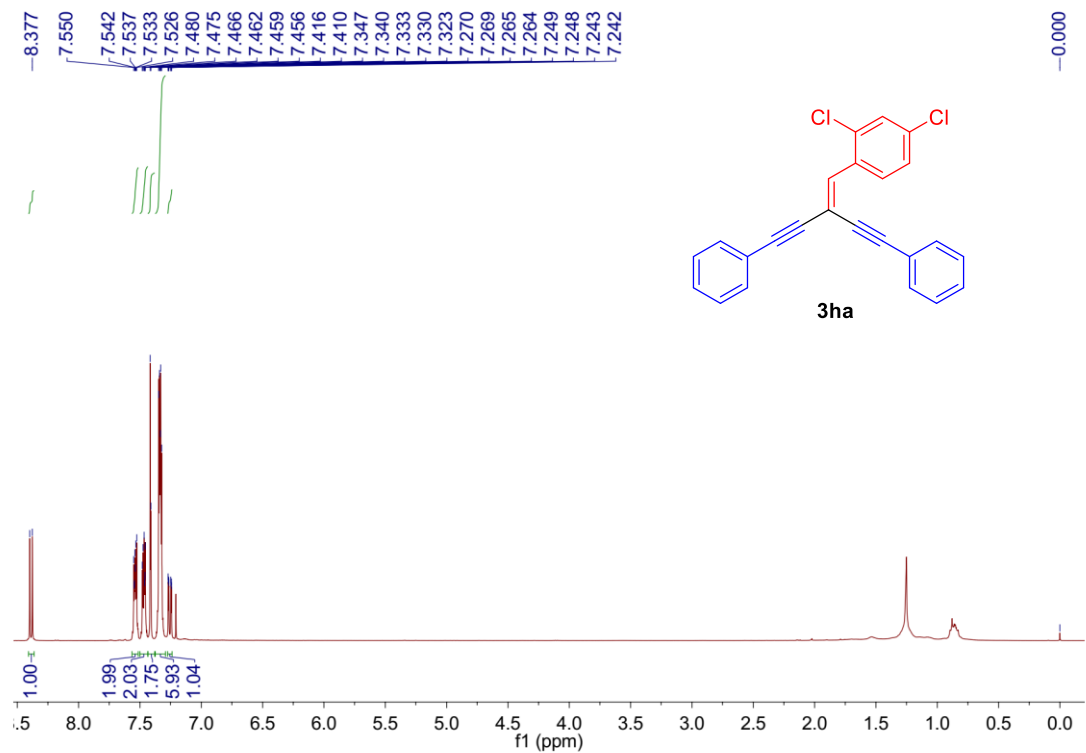




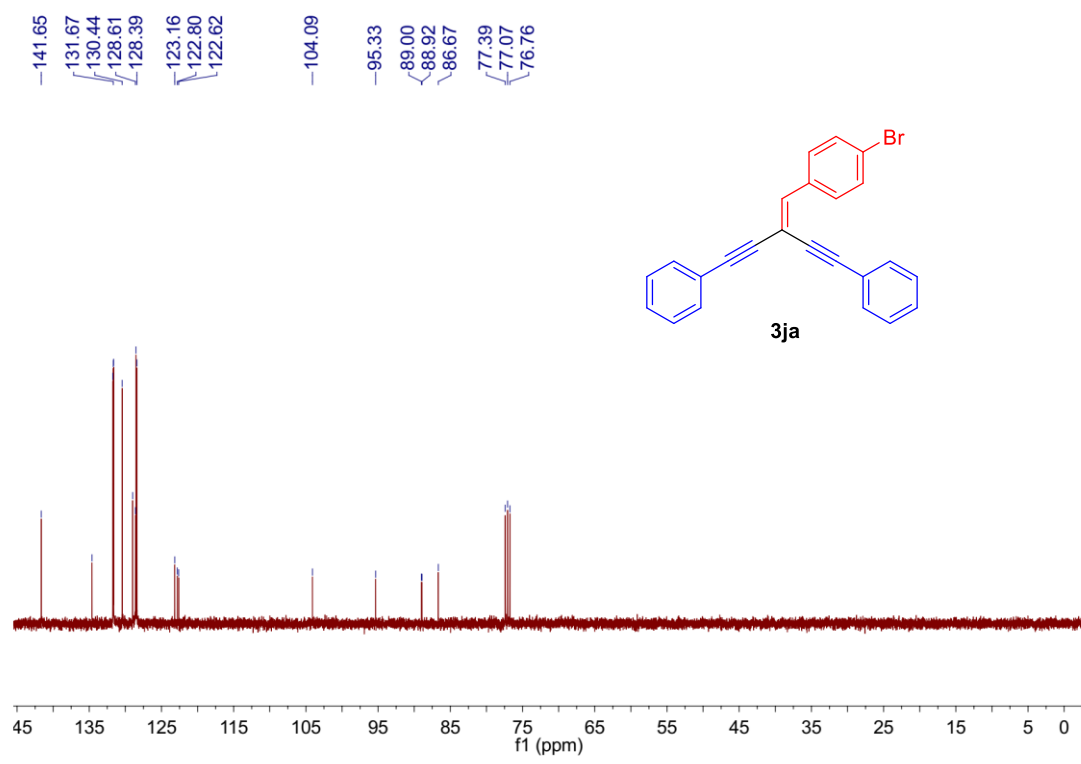
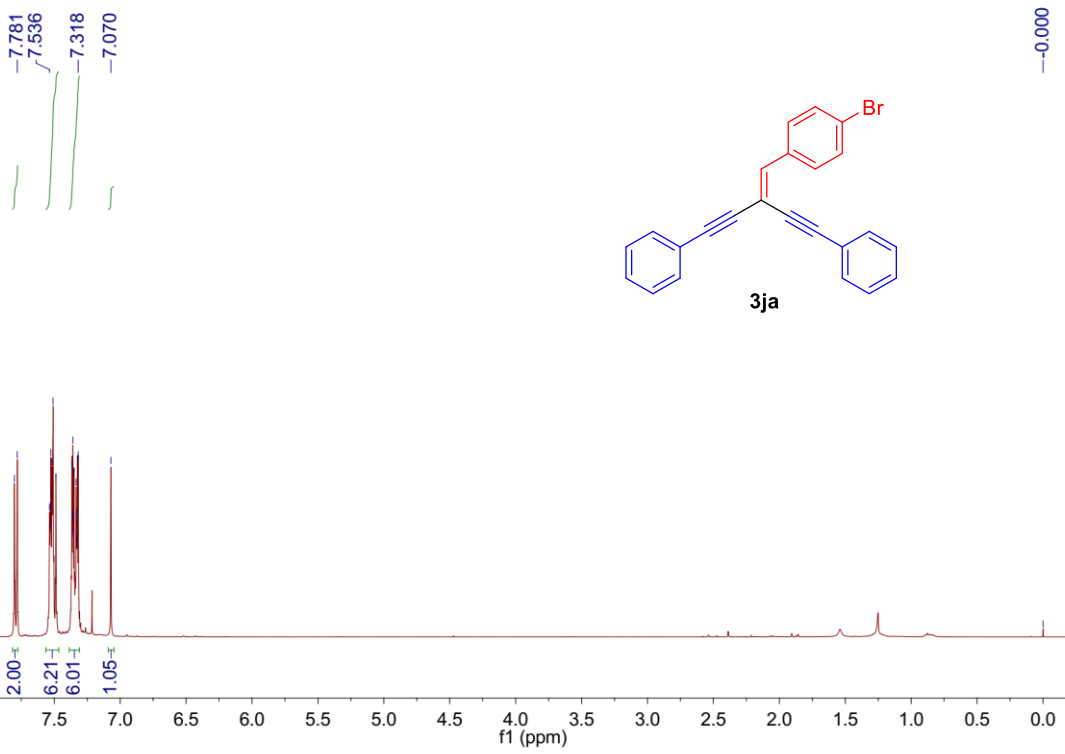


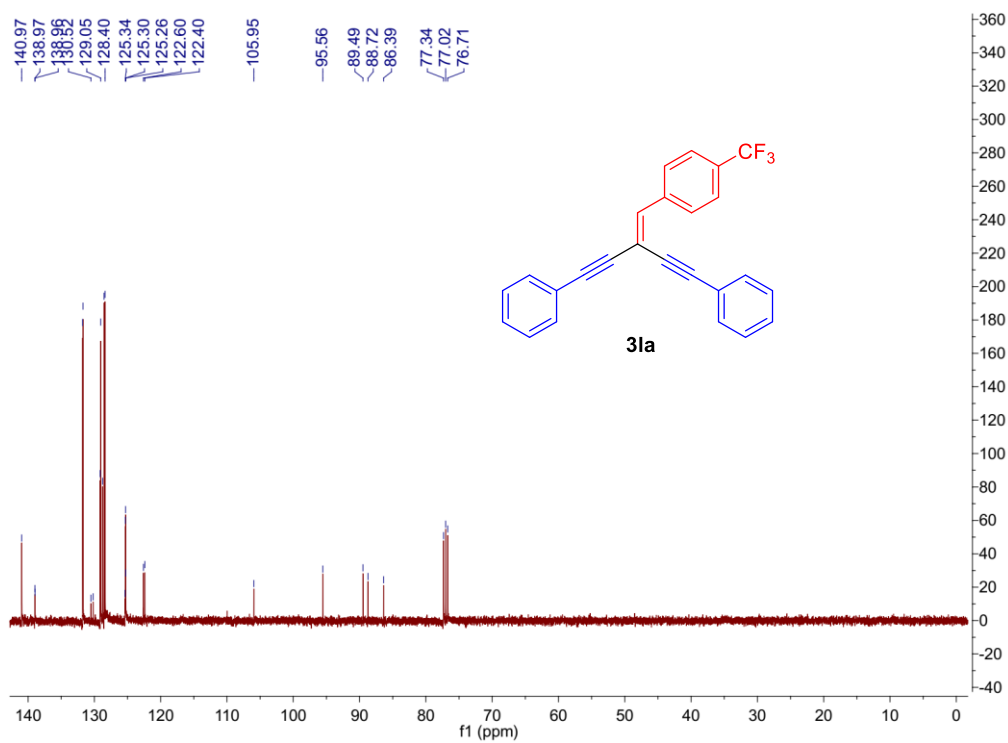
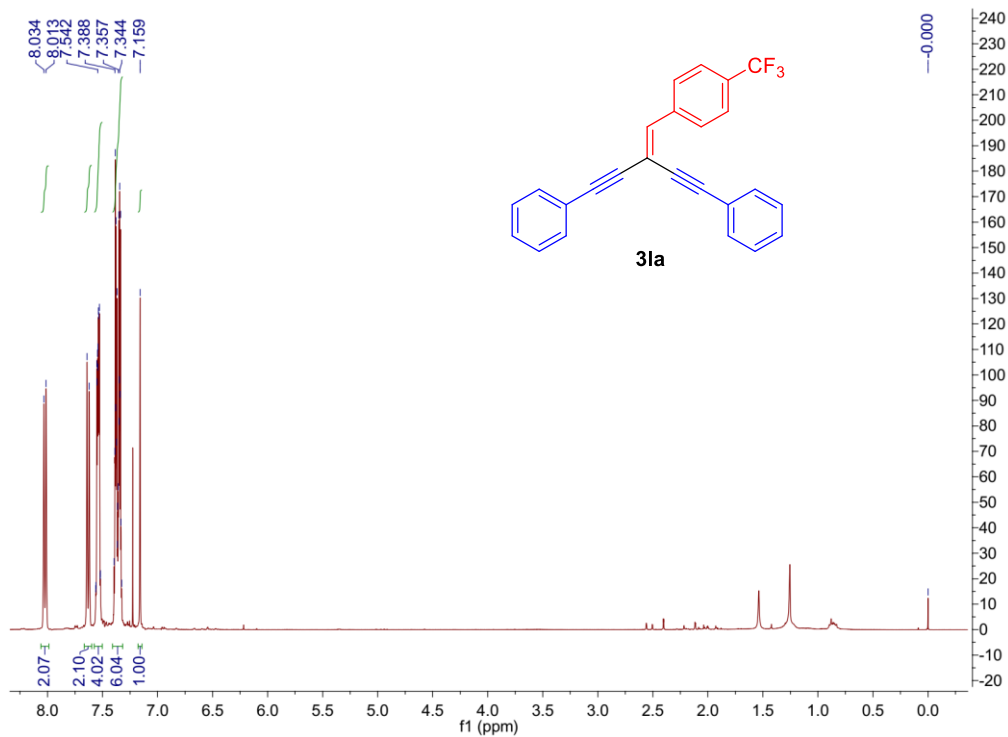


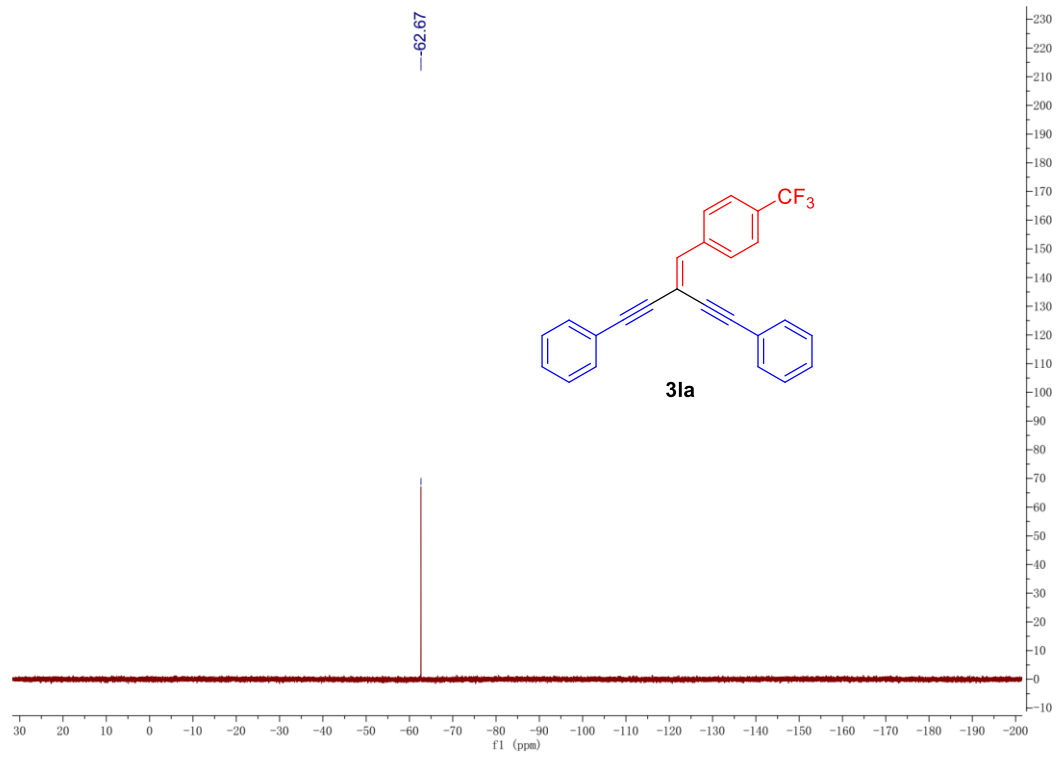


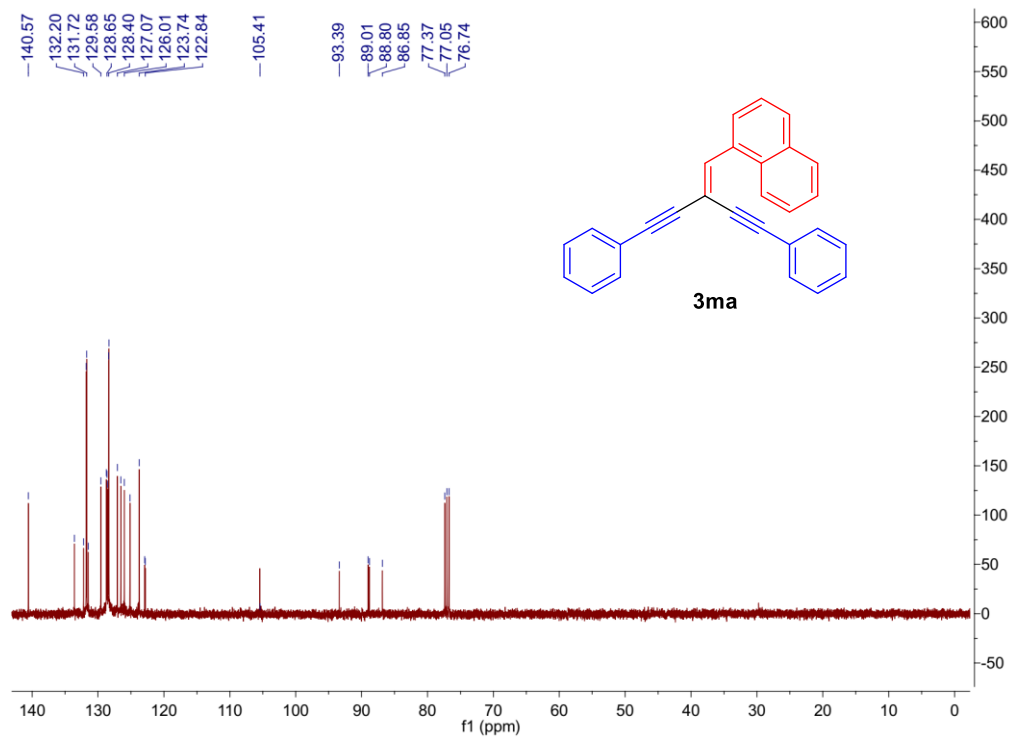
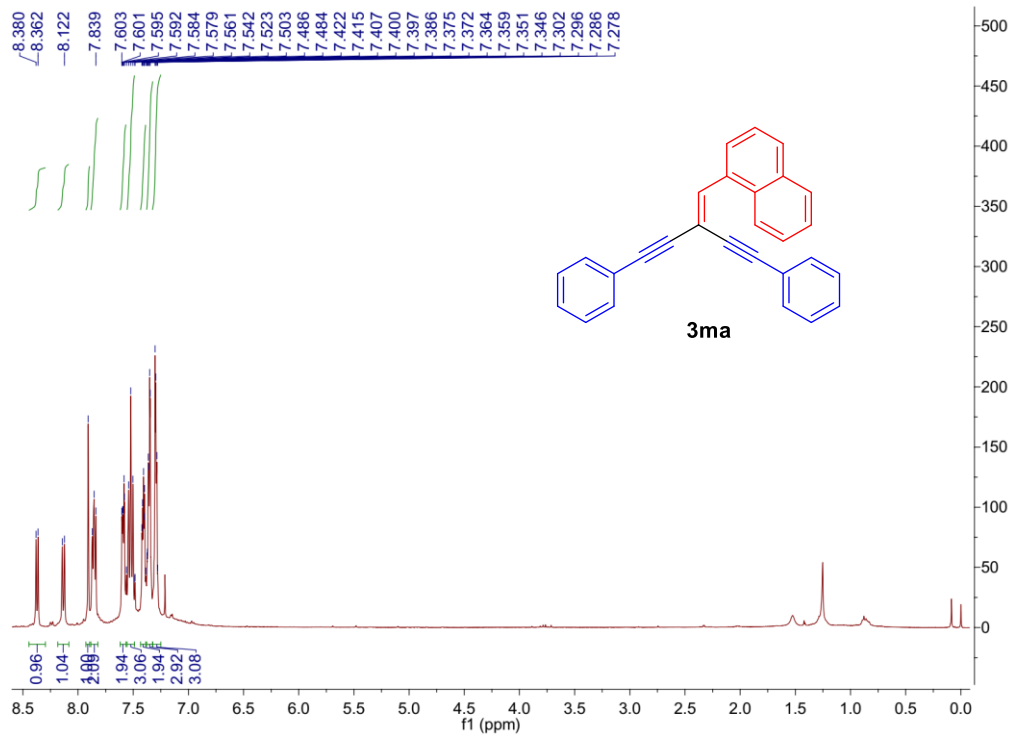


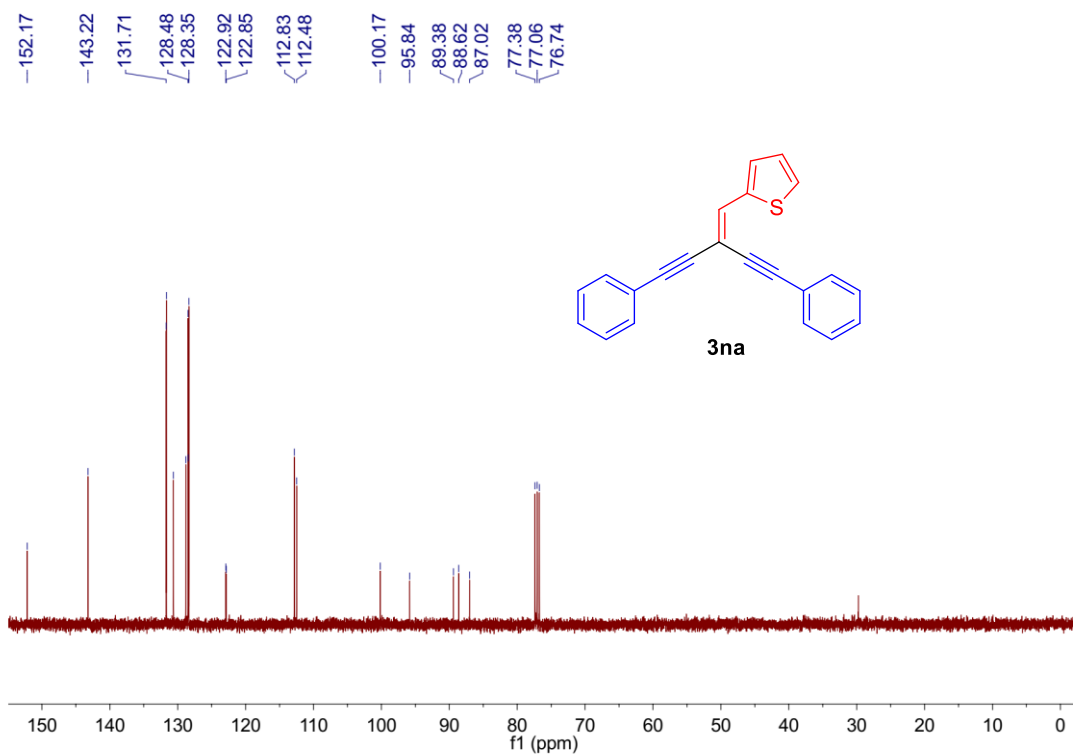
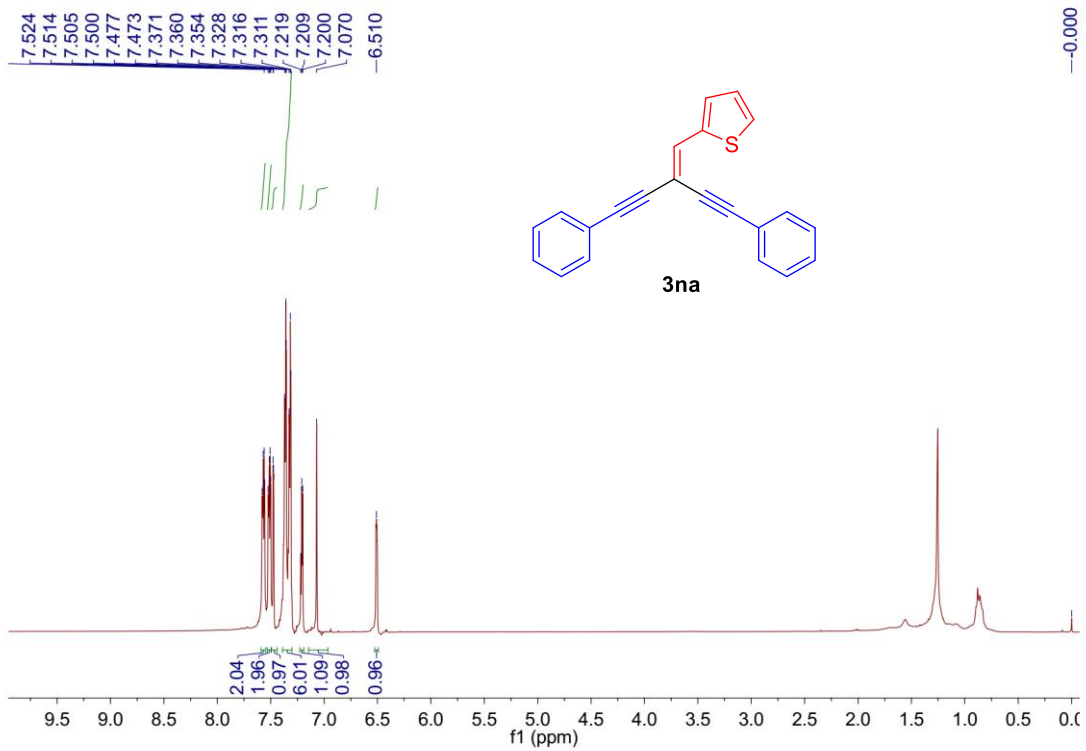




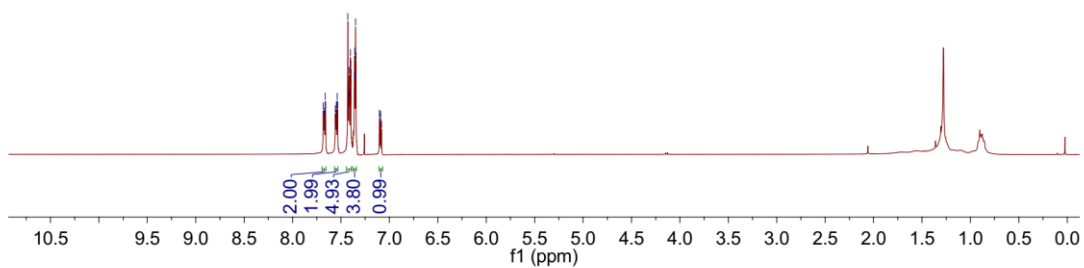
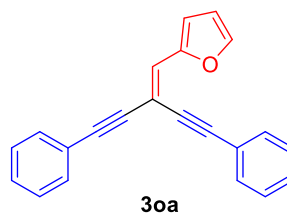




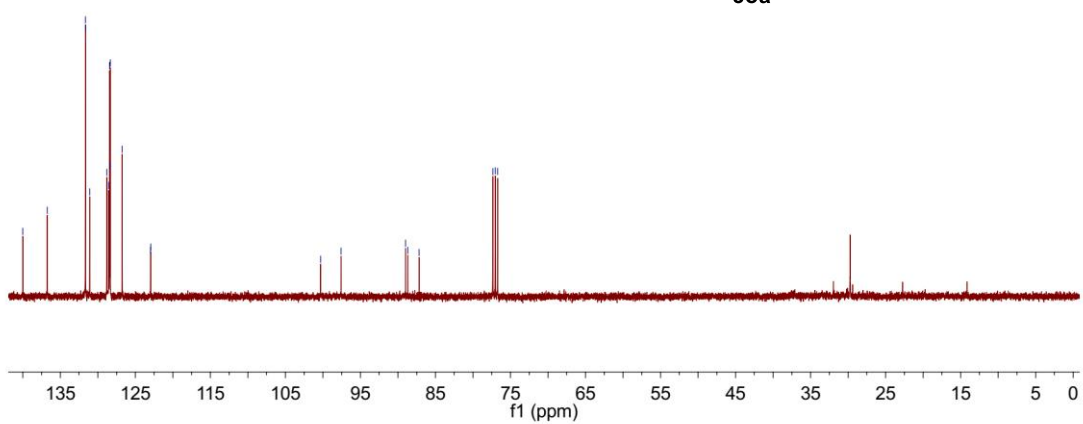
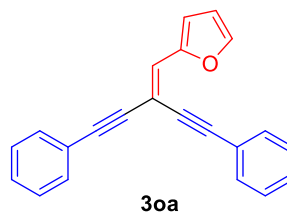


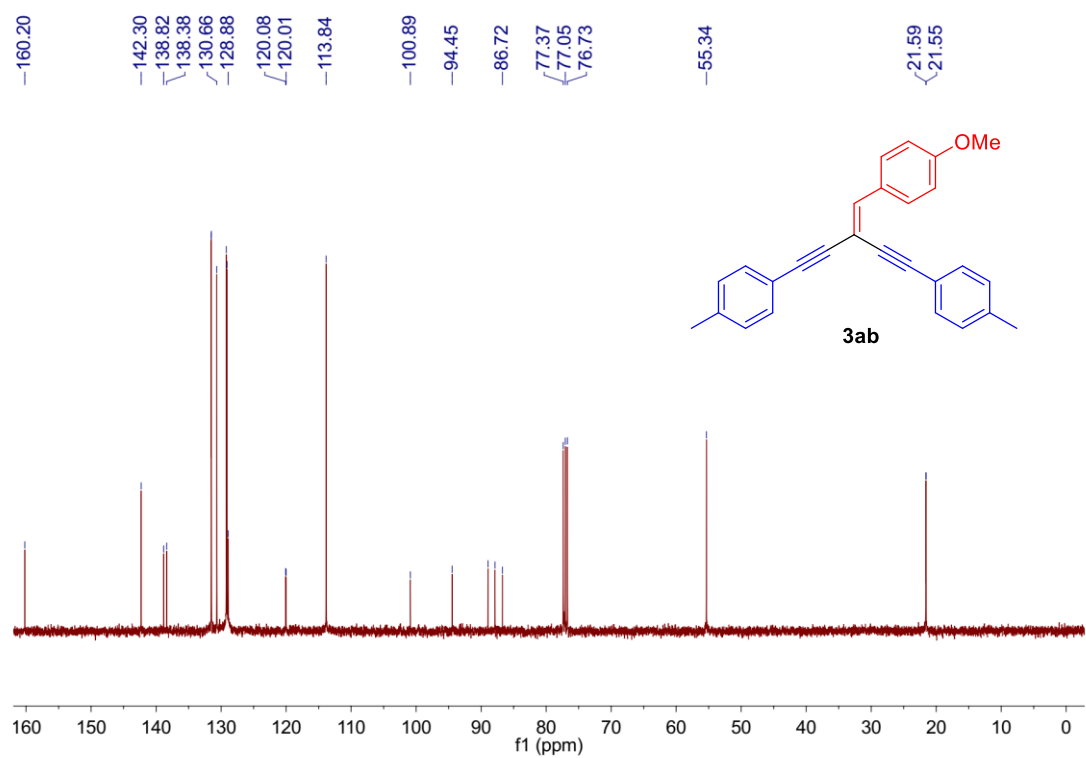
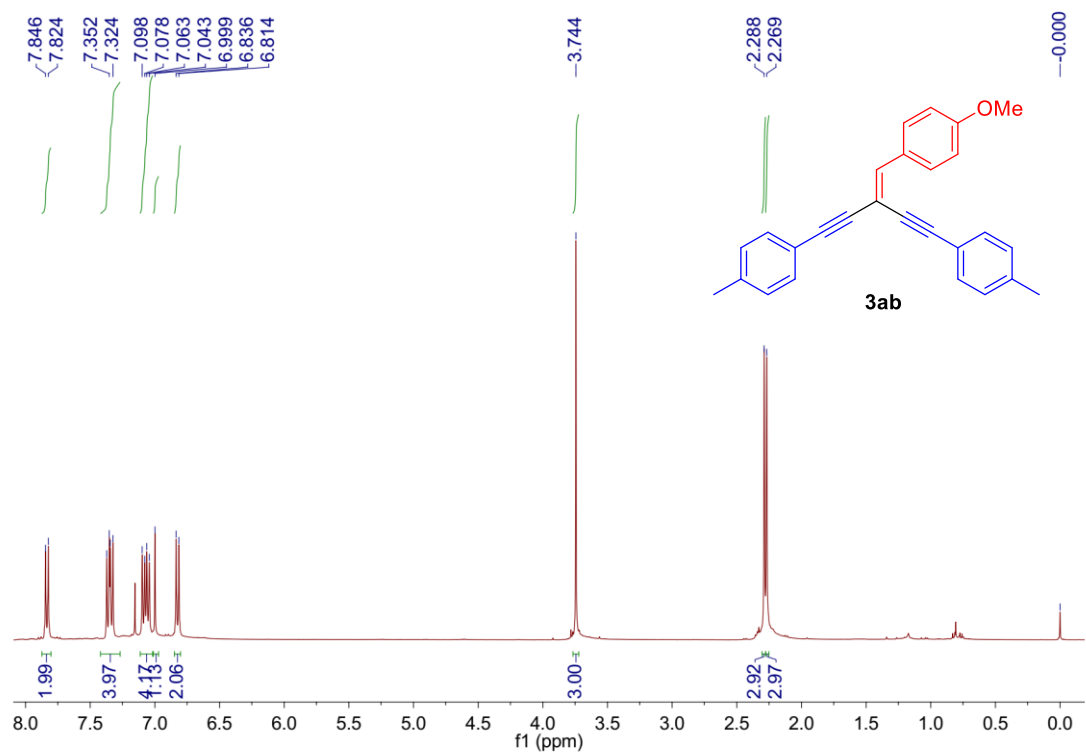


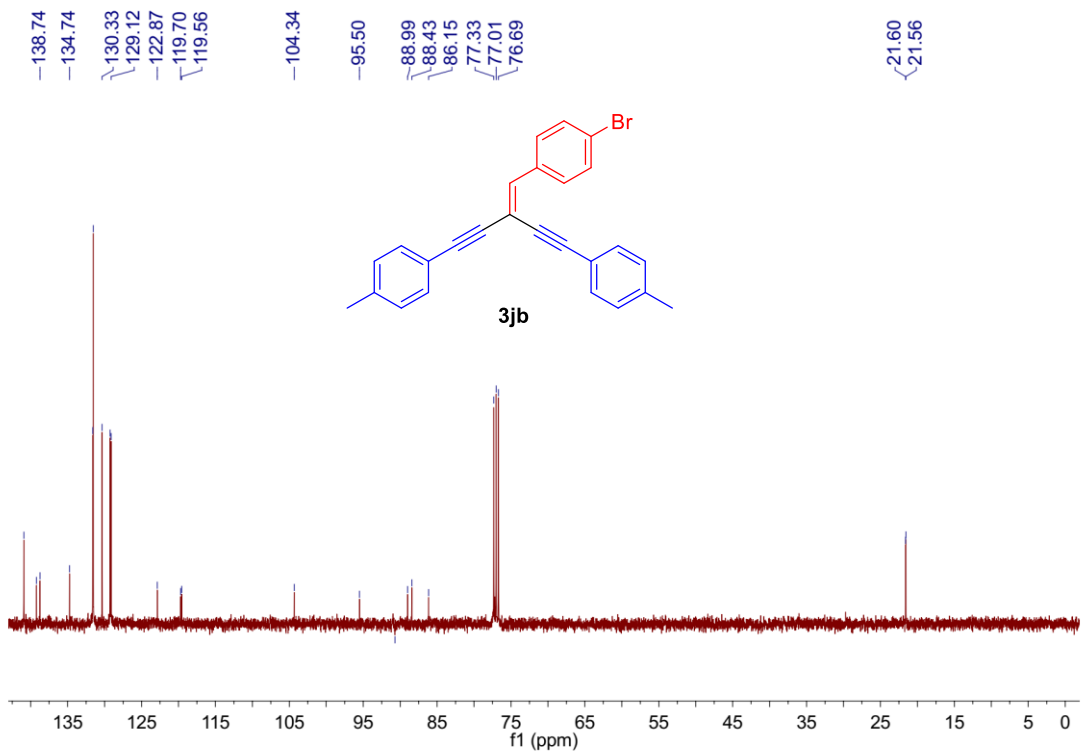
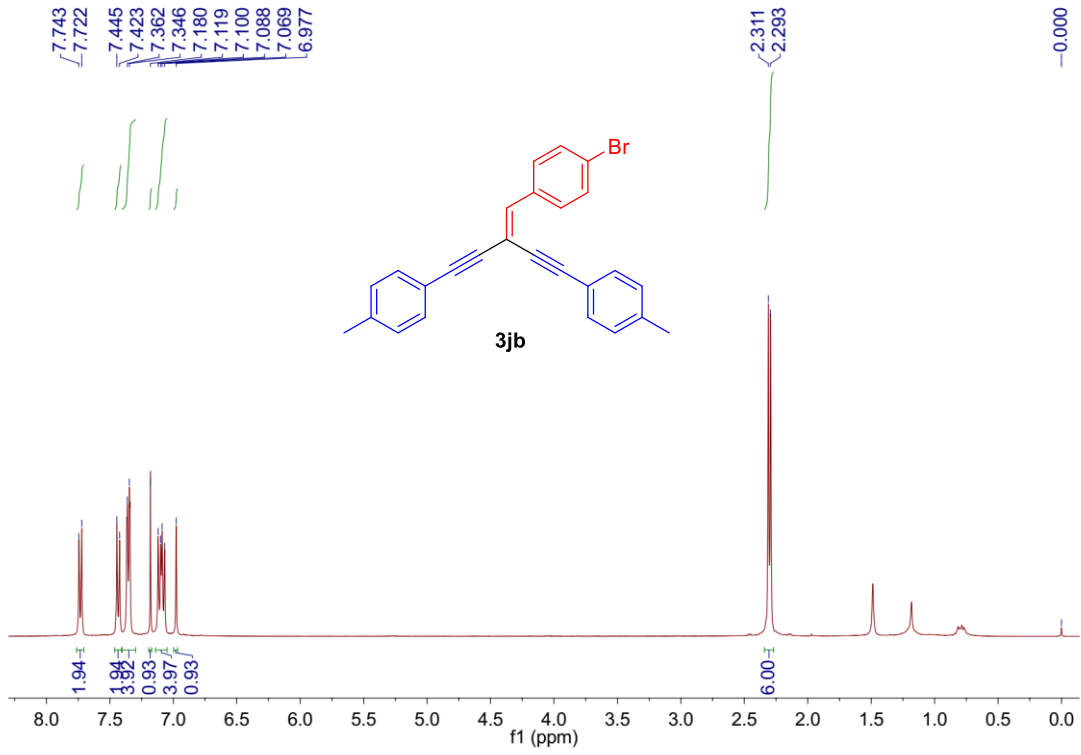
7.663  
7.659  
7.558  
7.550  
7.547  
7.539  
7.534  
7.430  
7.416  
7.411  
7.403  
7.398  
7.362  
7.358  
7.350  
7.345  
7.103  
7.094  
7.090  
7.081



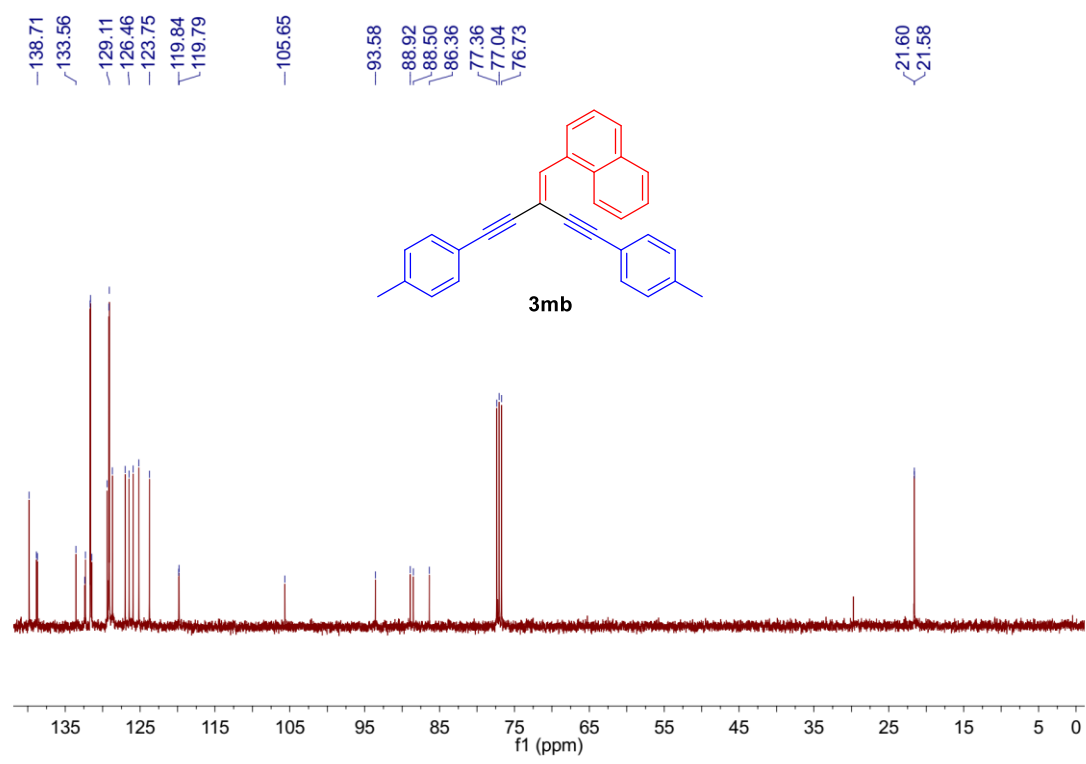
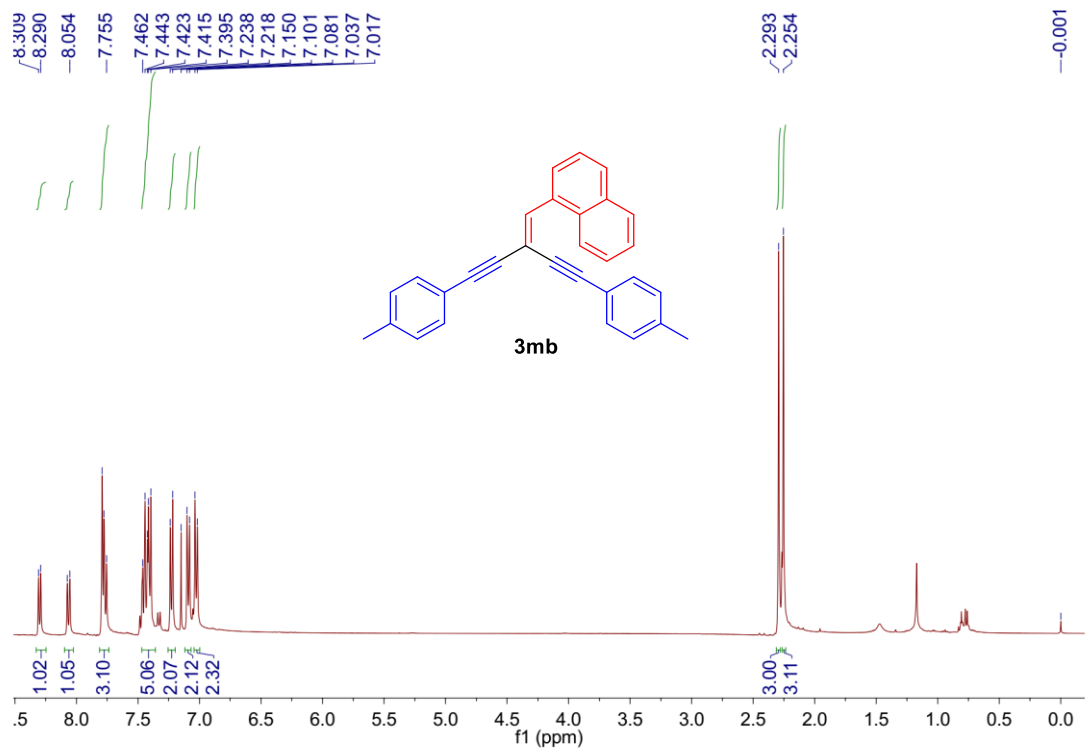
140.00  
136.74  
131.65  
126.75  
122.98  
122.94  
100.31  
97.59  
86.99  
86.67  
87.18  
77.35  
77.03  
76.72

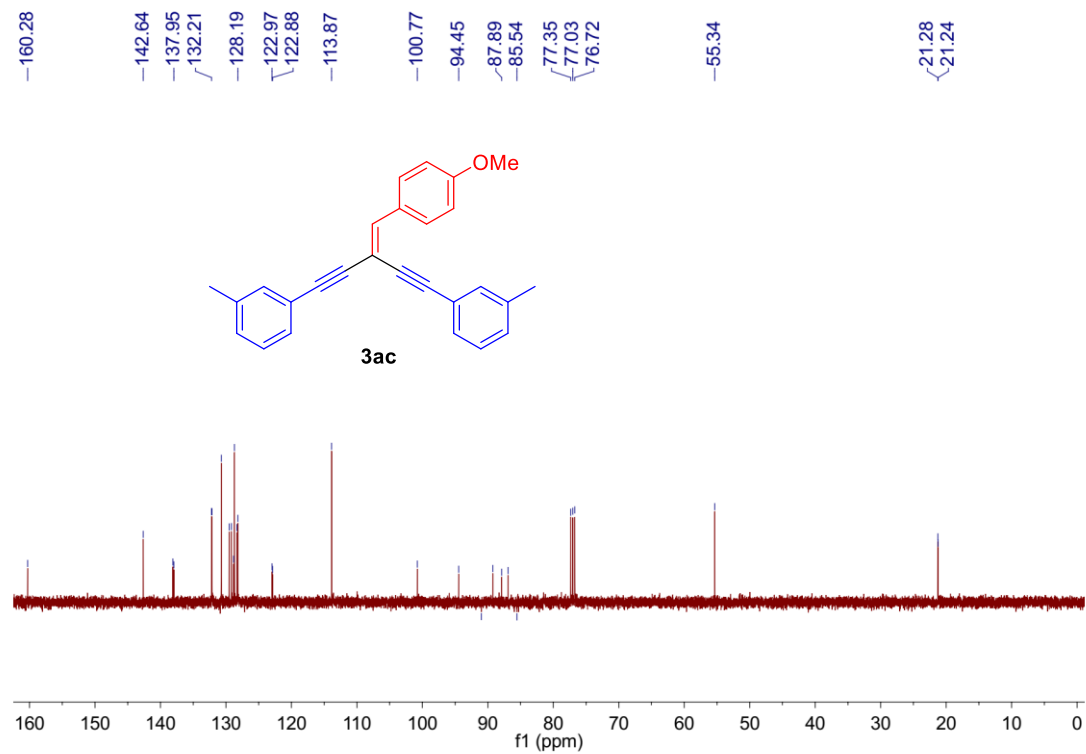
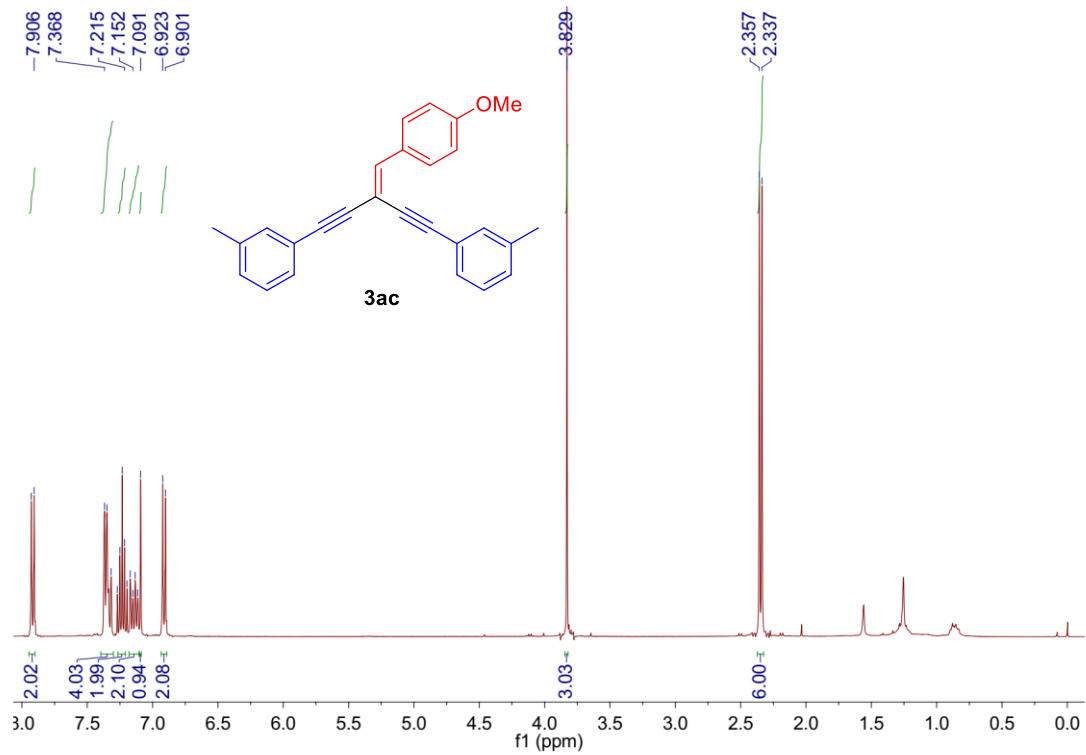


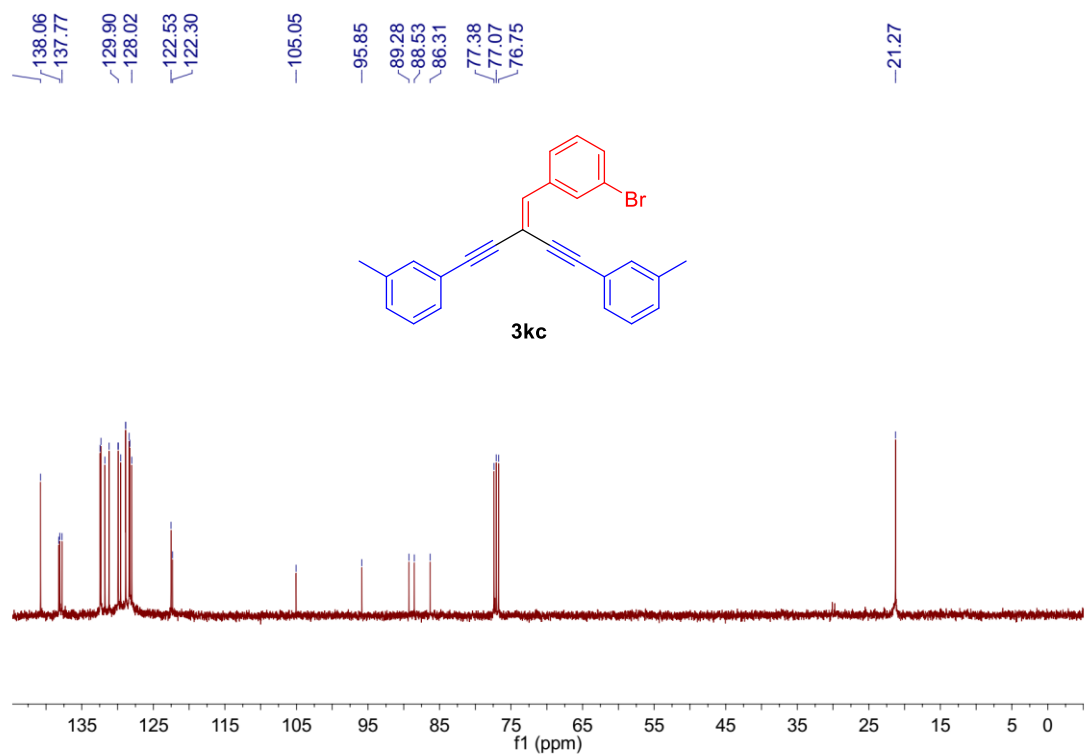
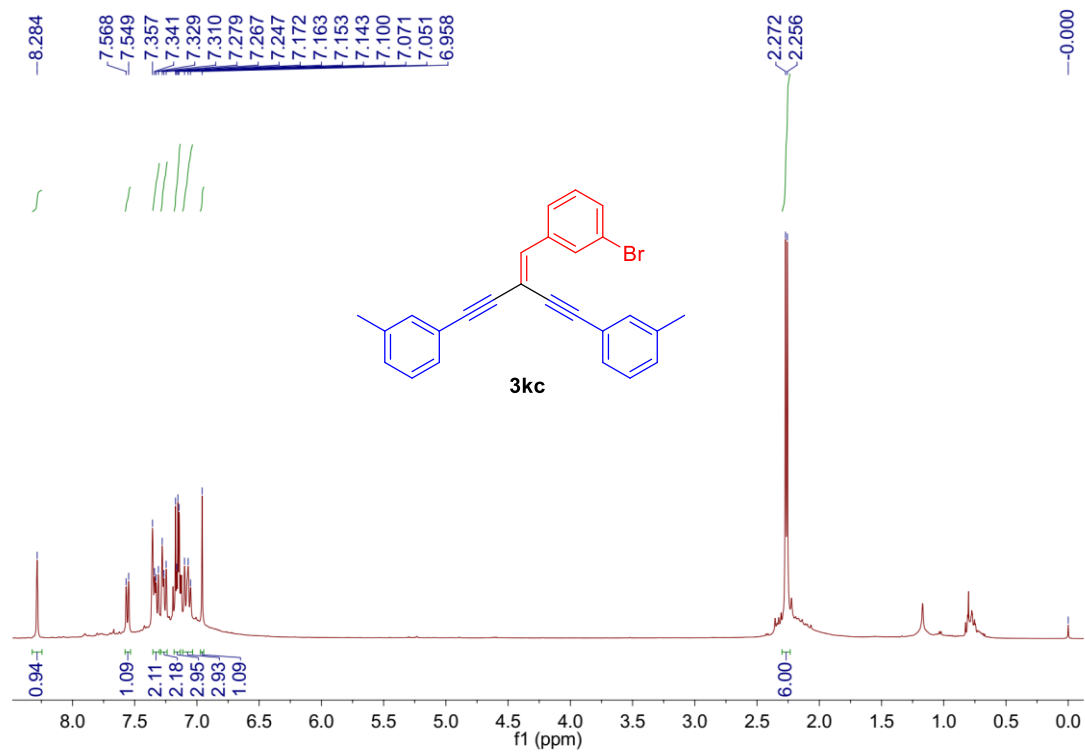


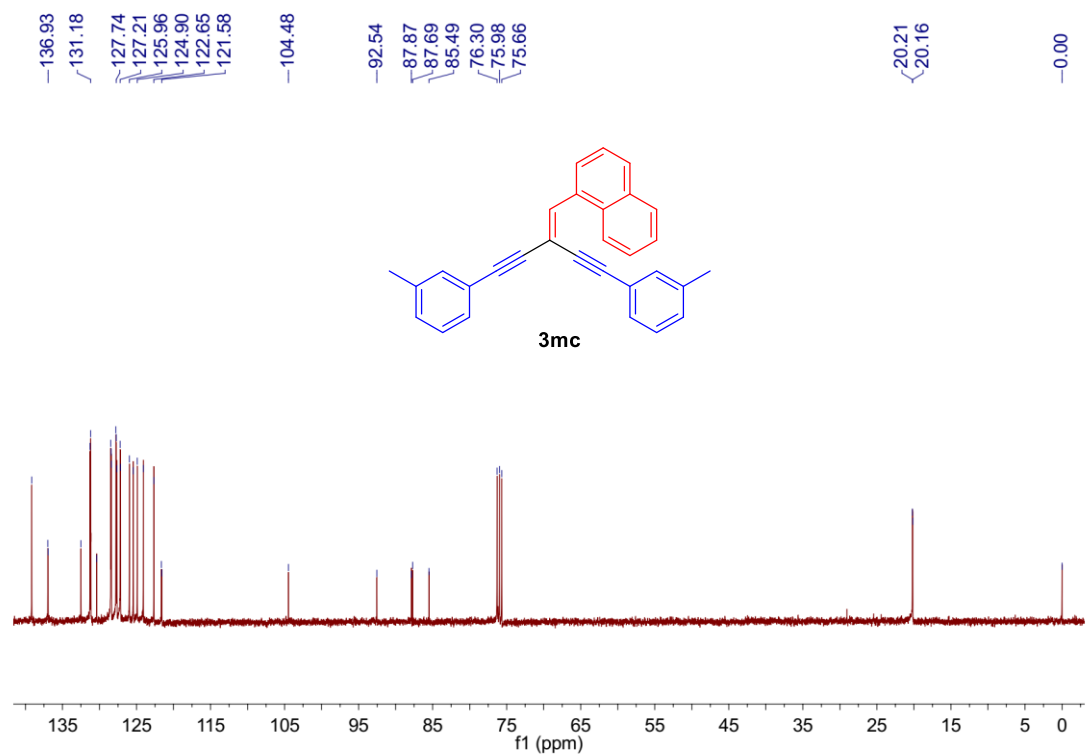
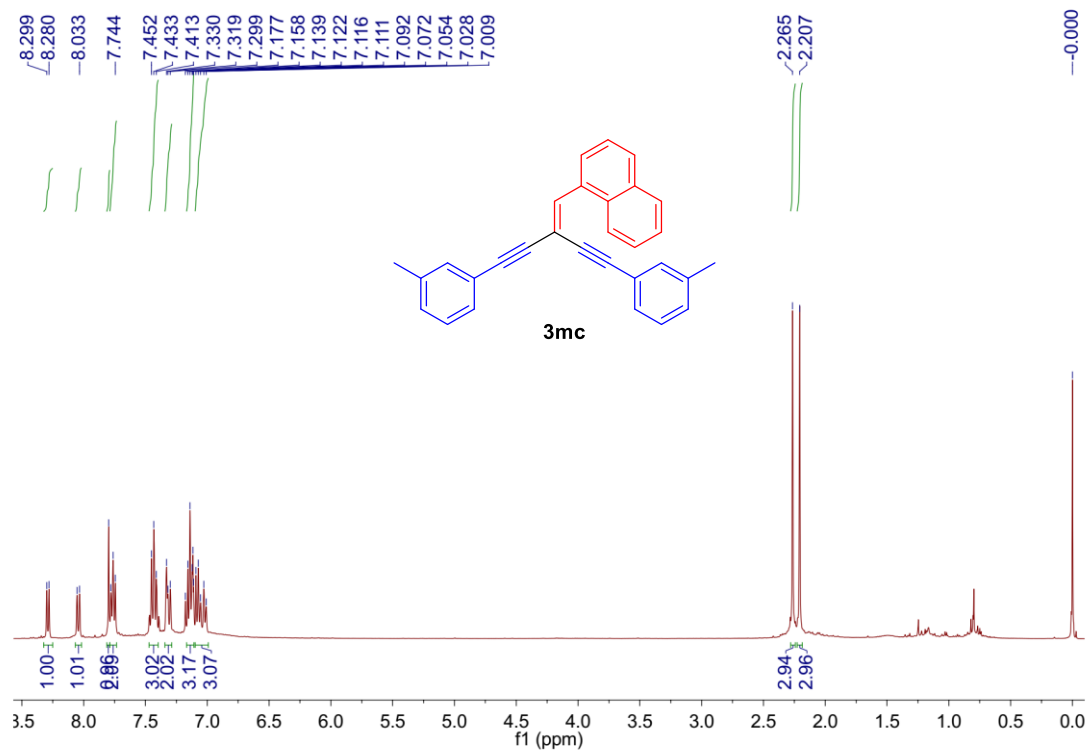


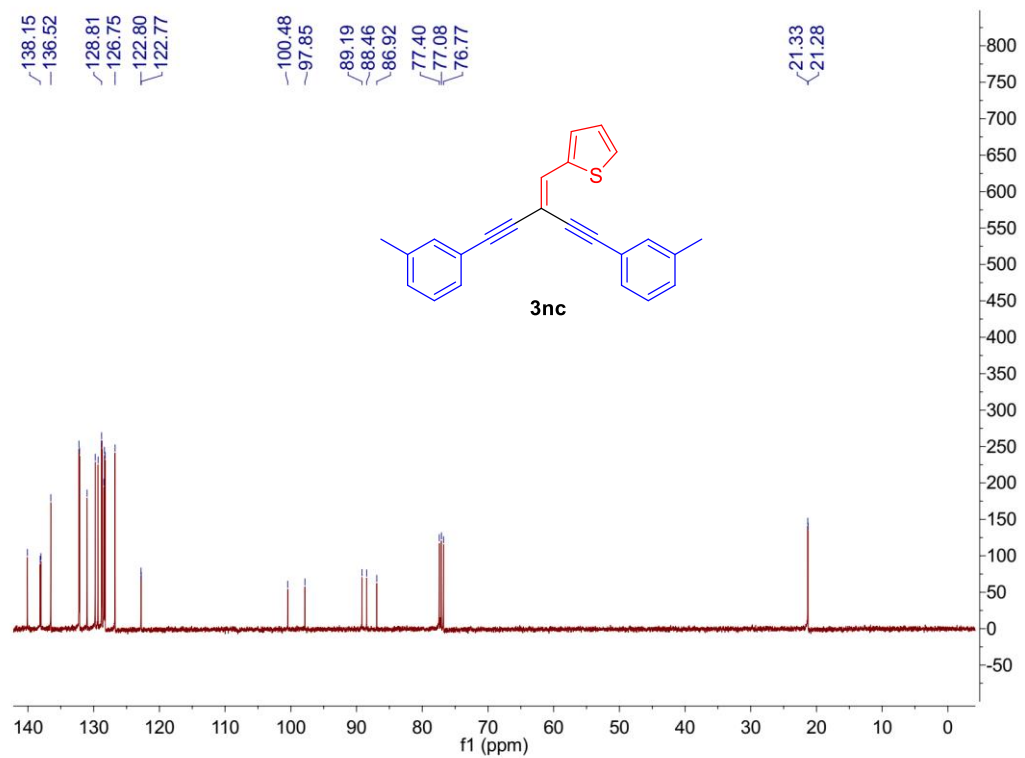
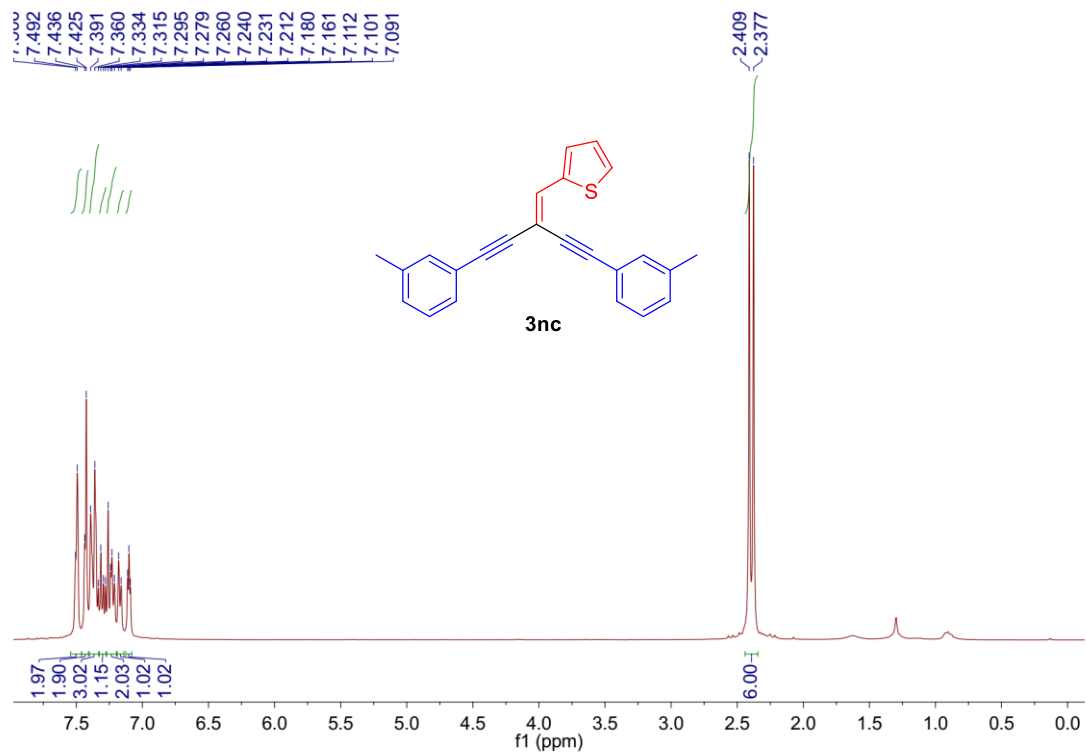


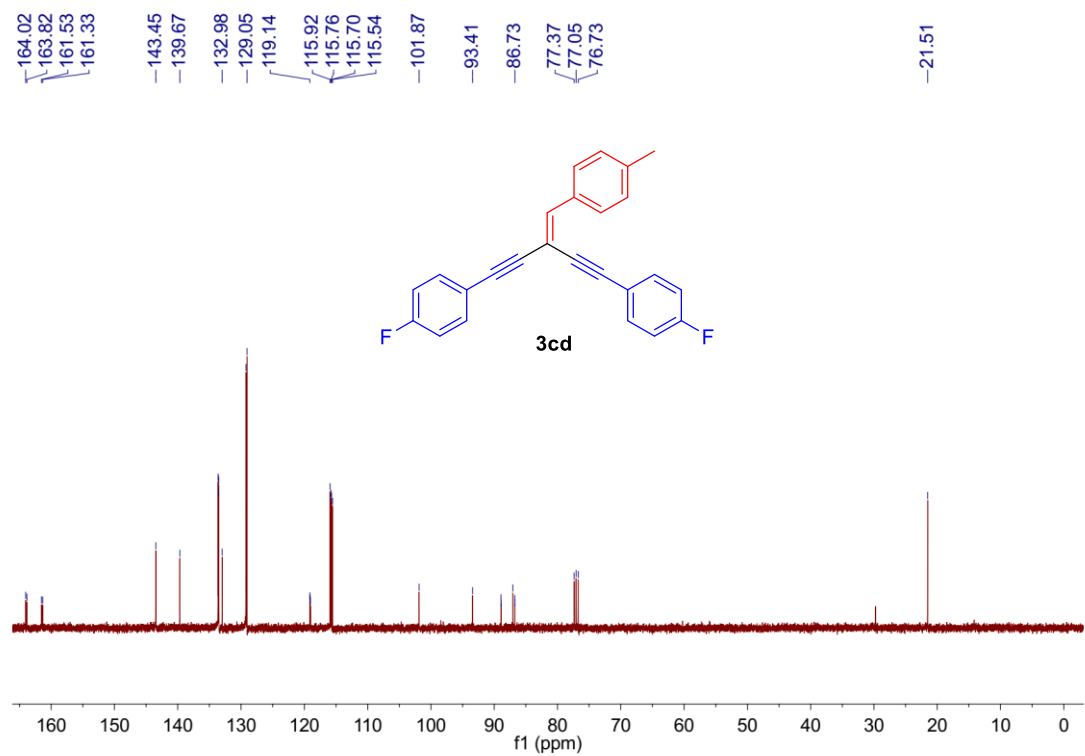
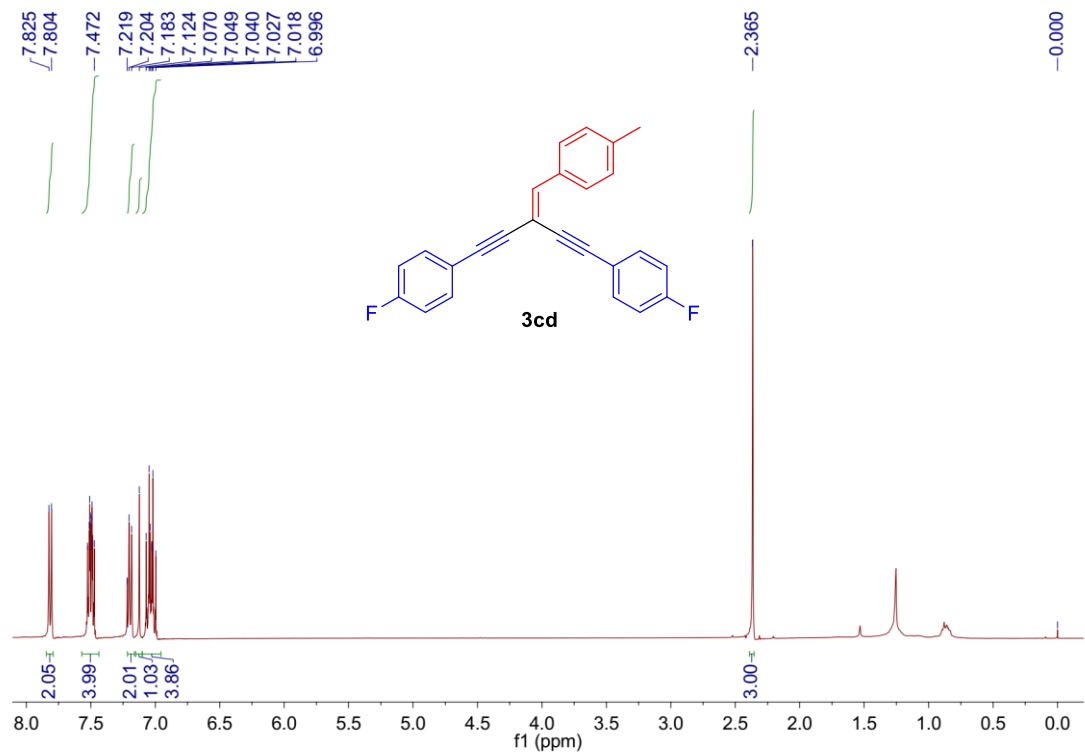


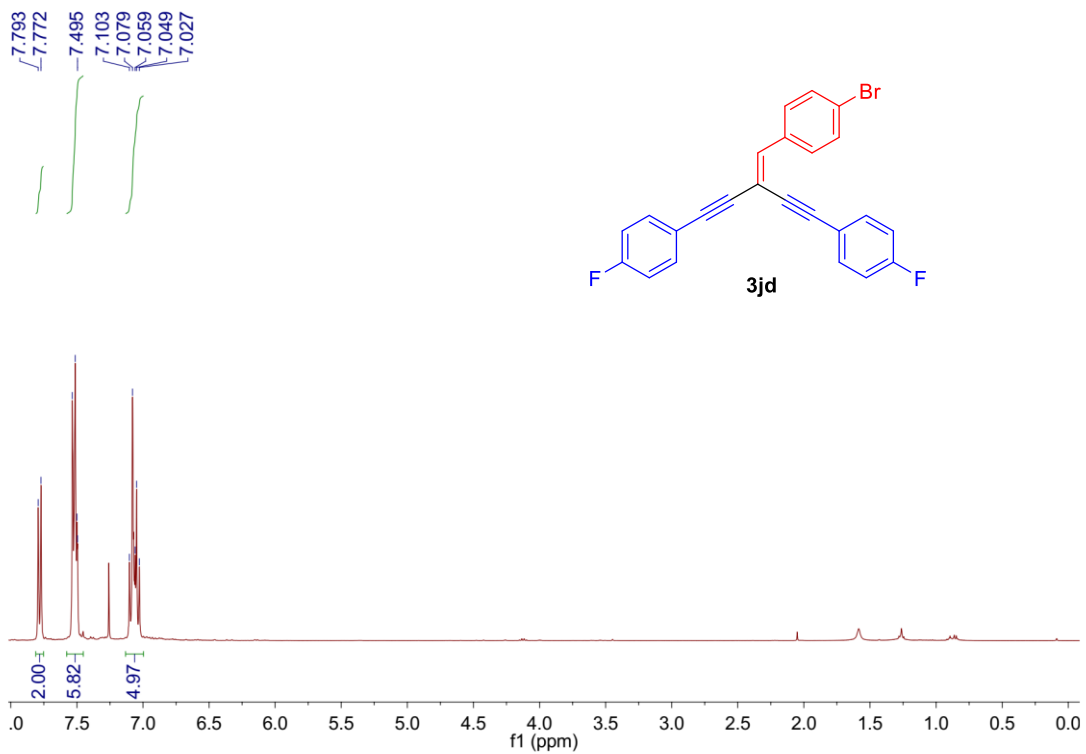
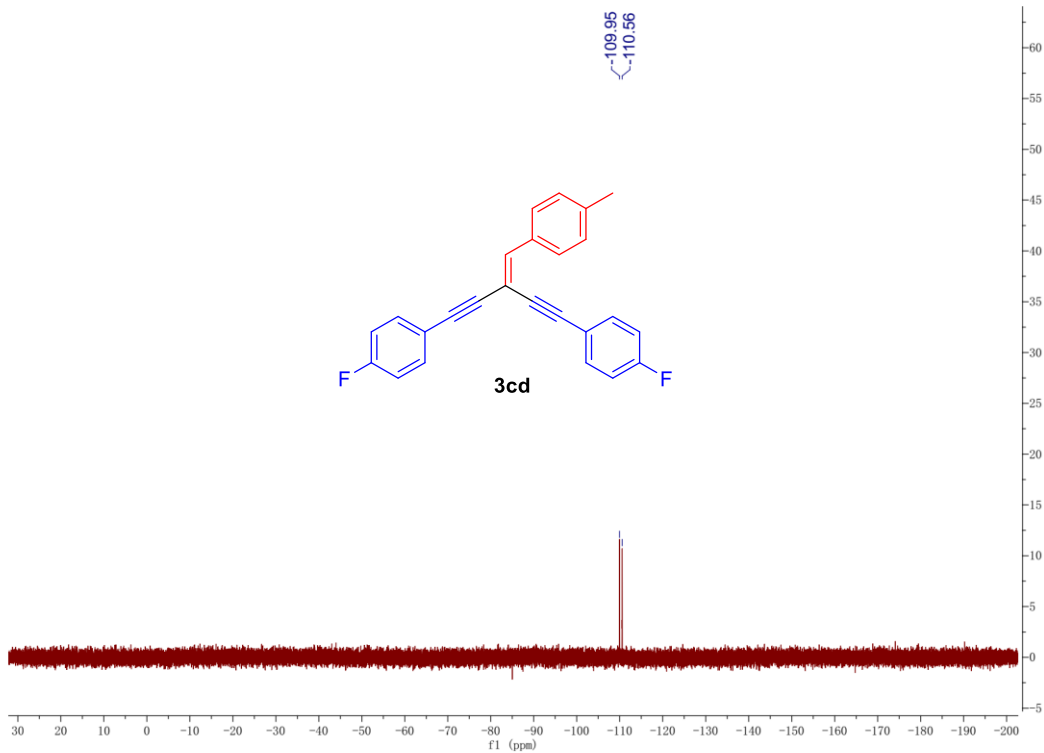


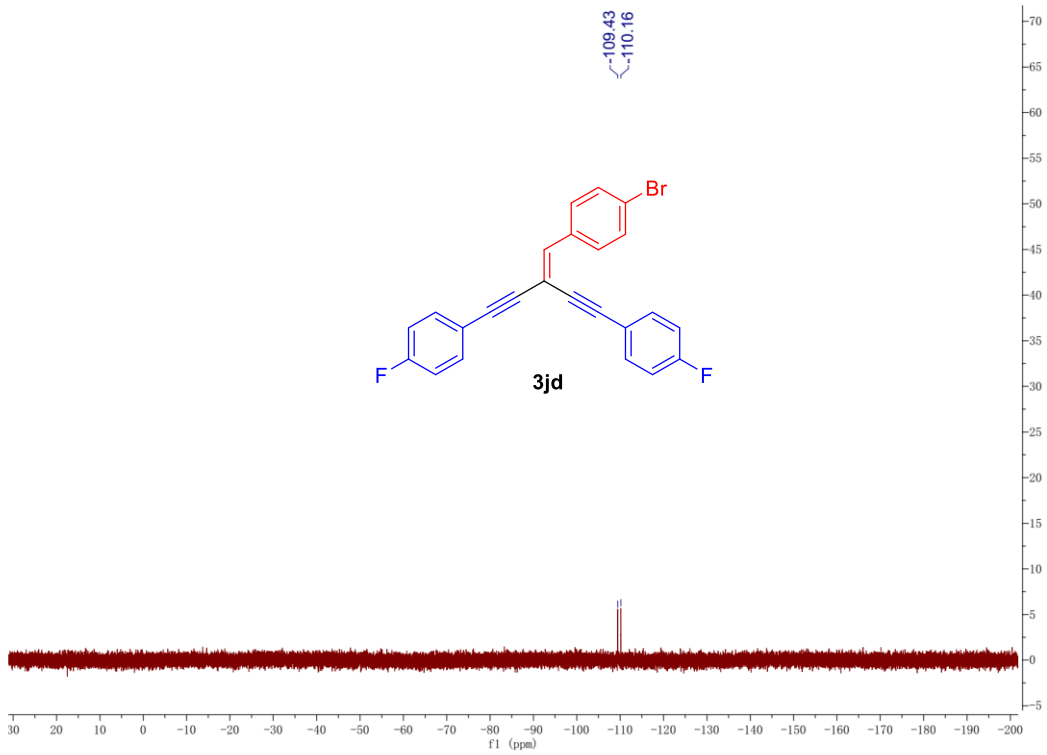
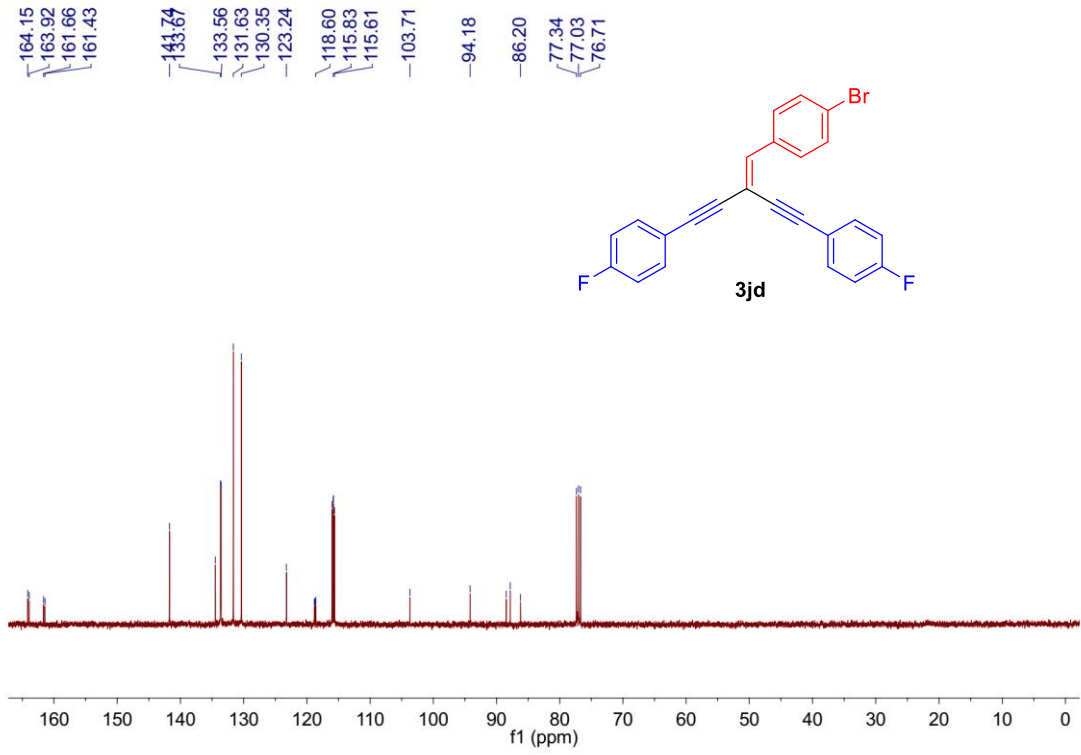




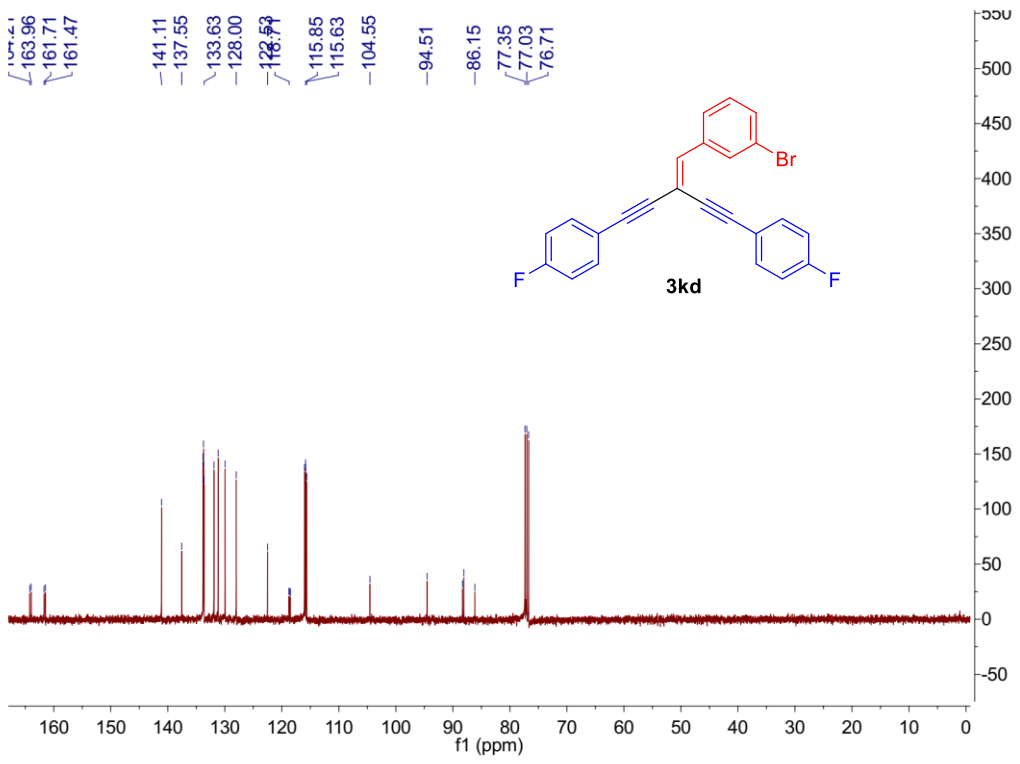
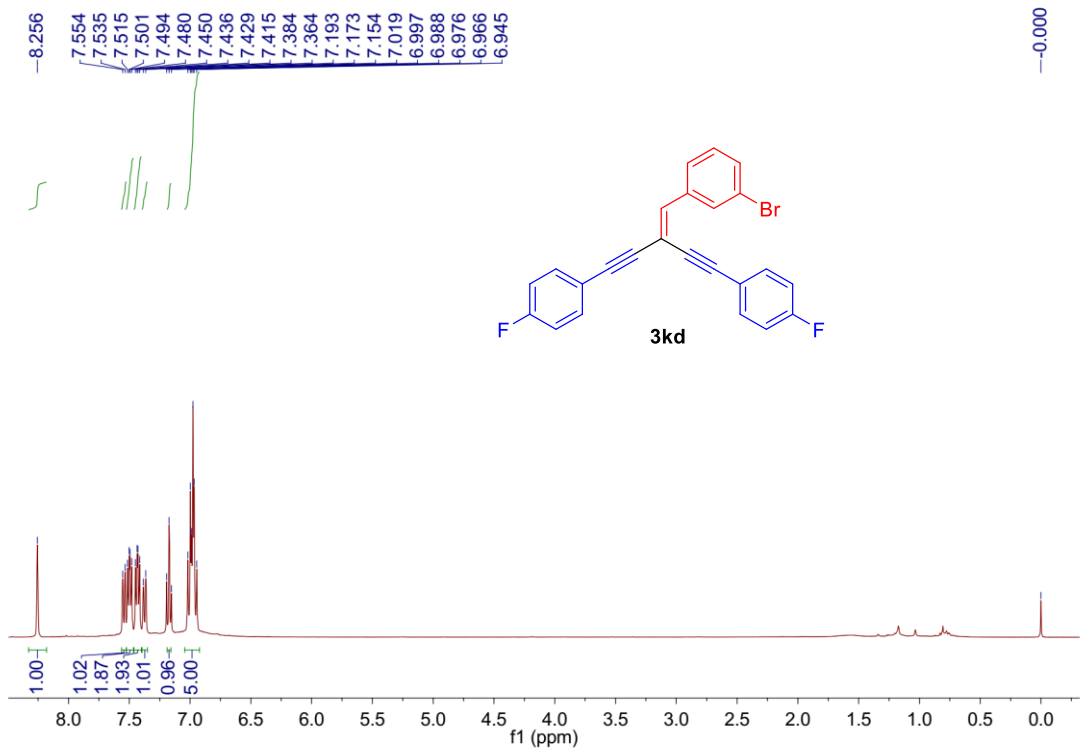


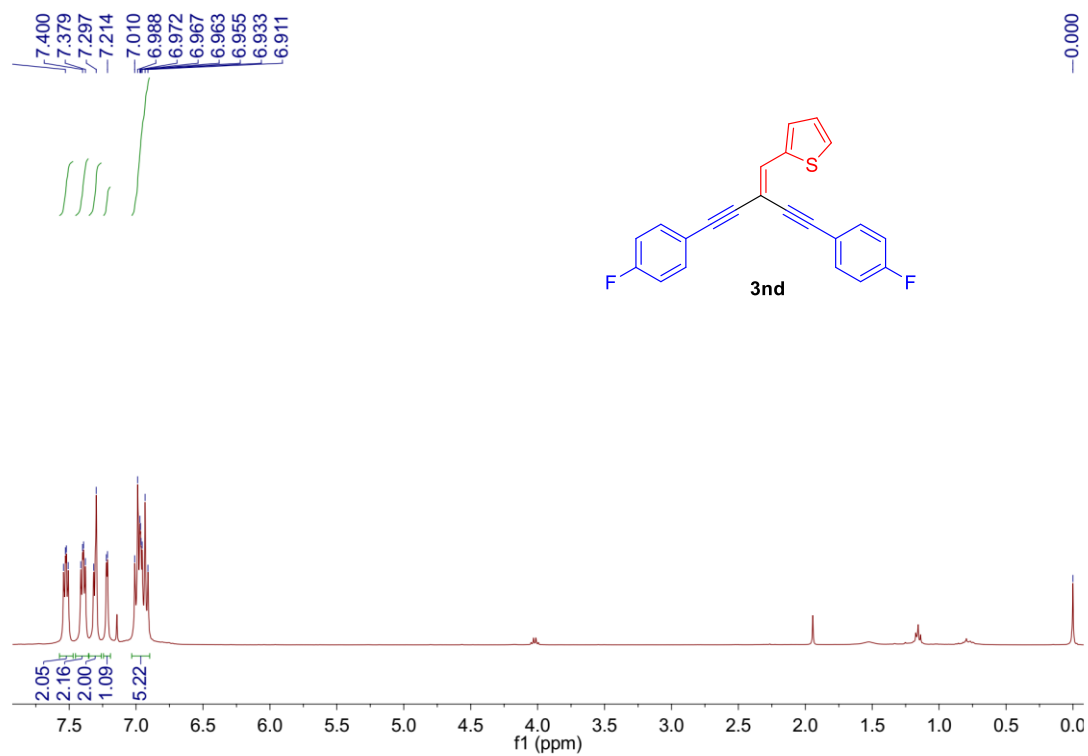
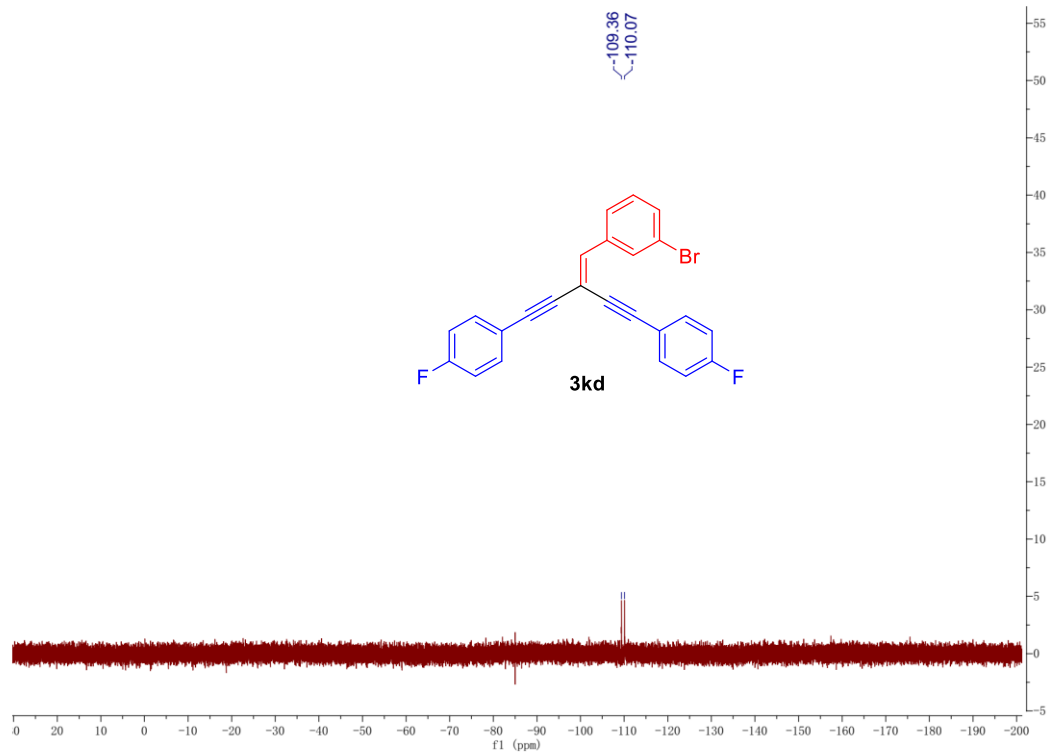


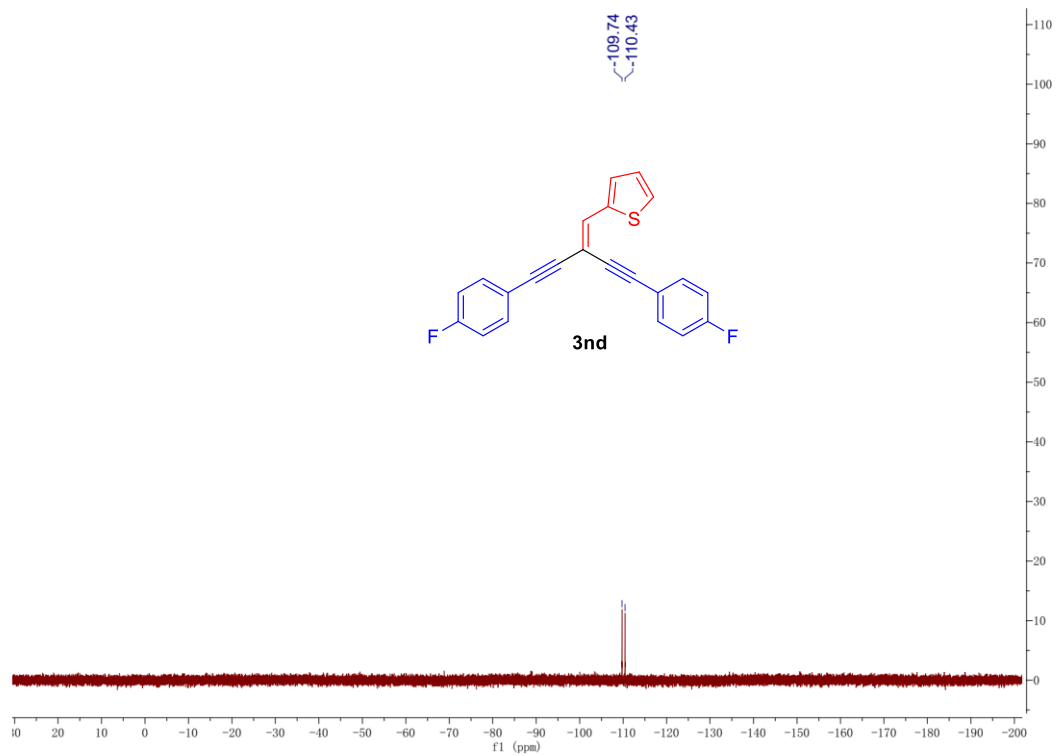
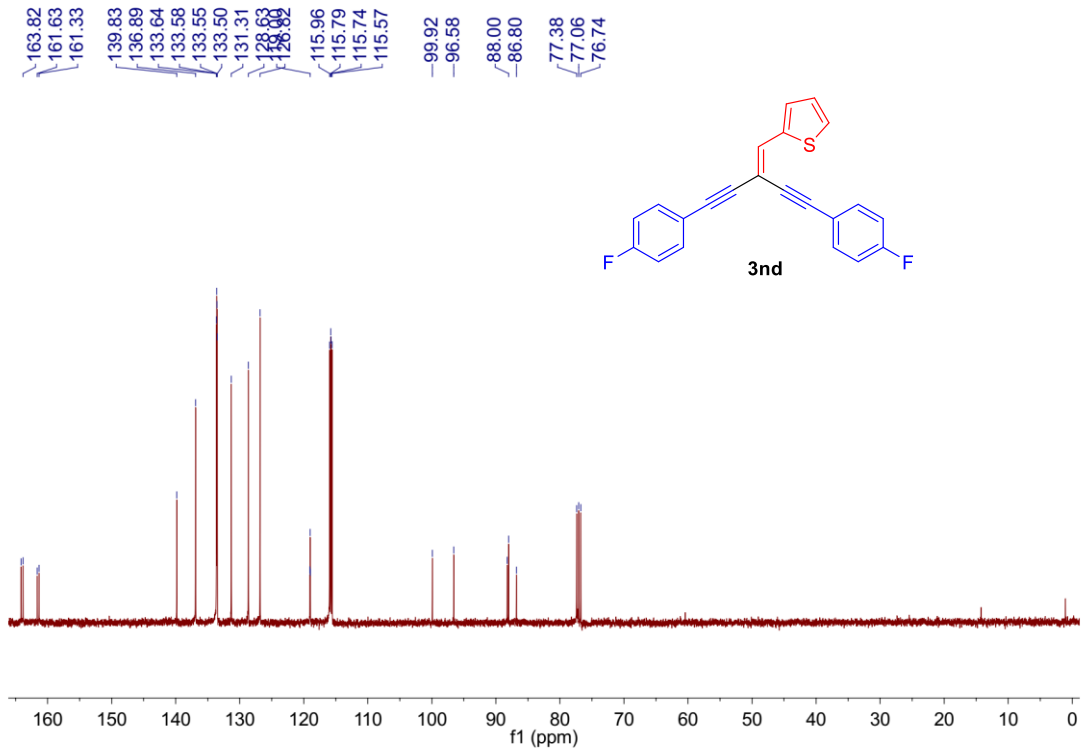


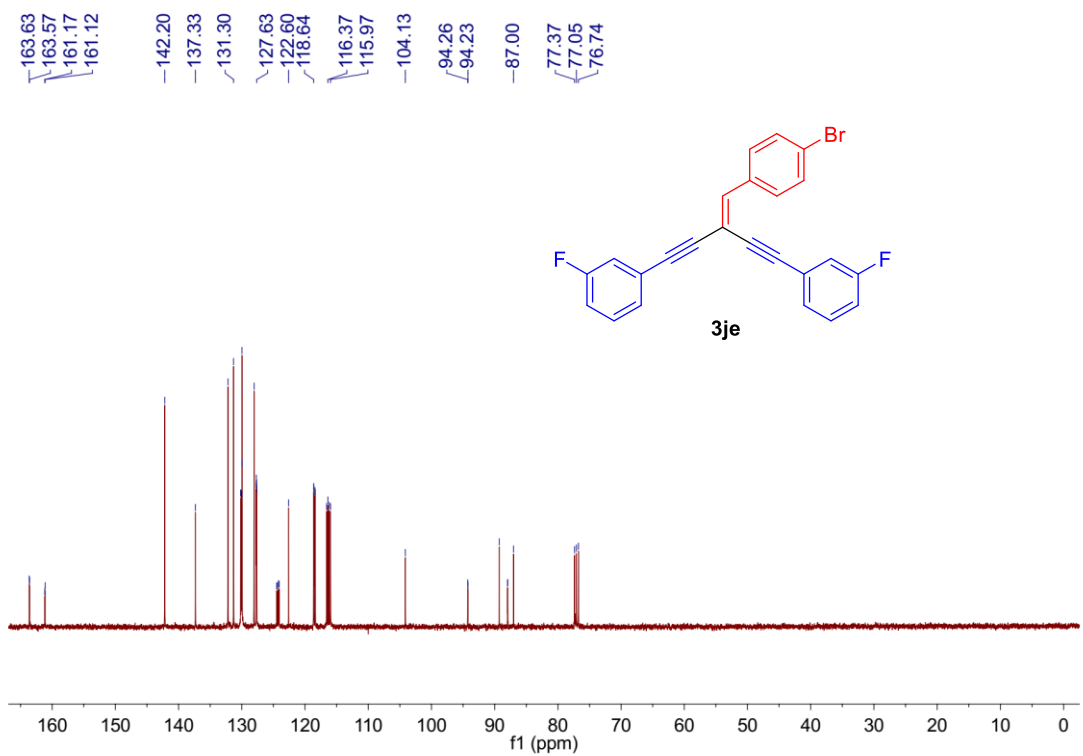
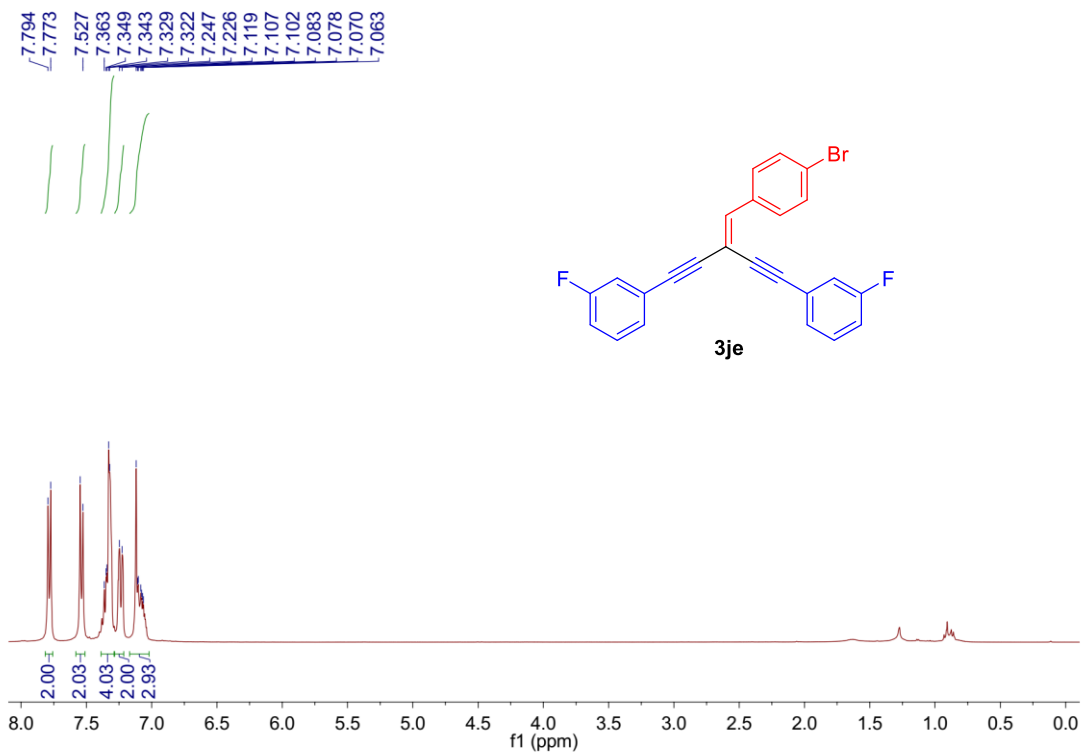


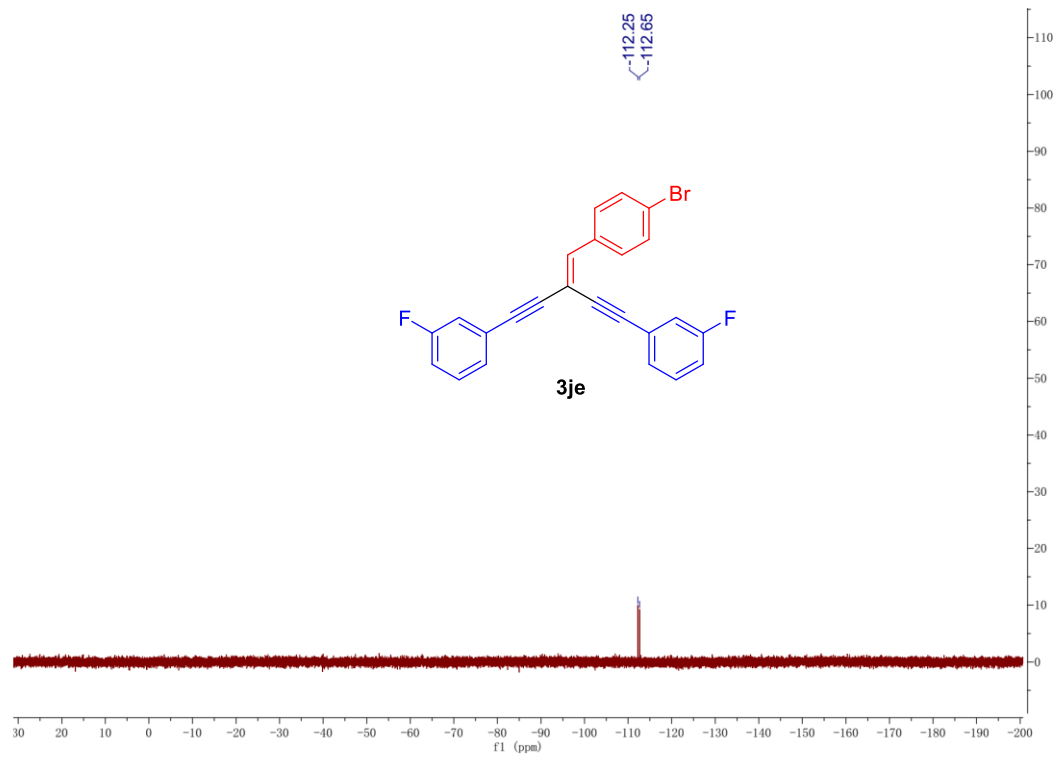


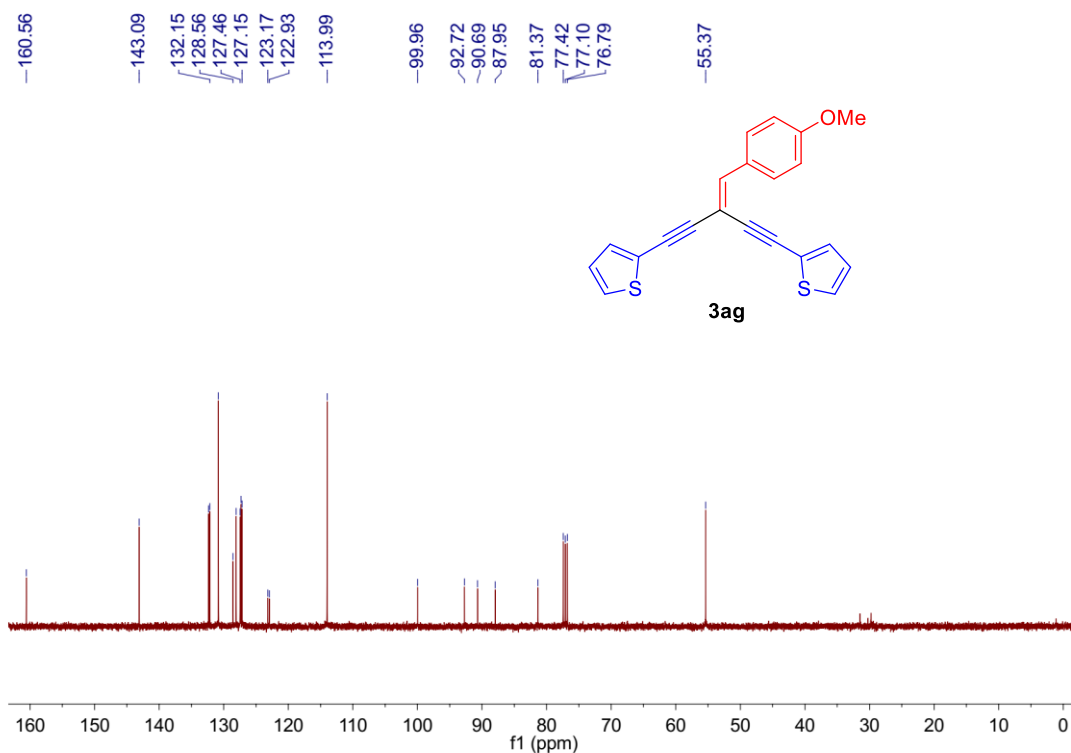
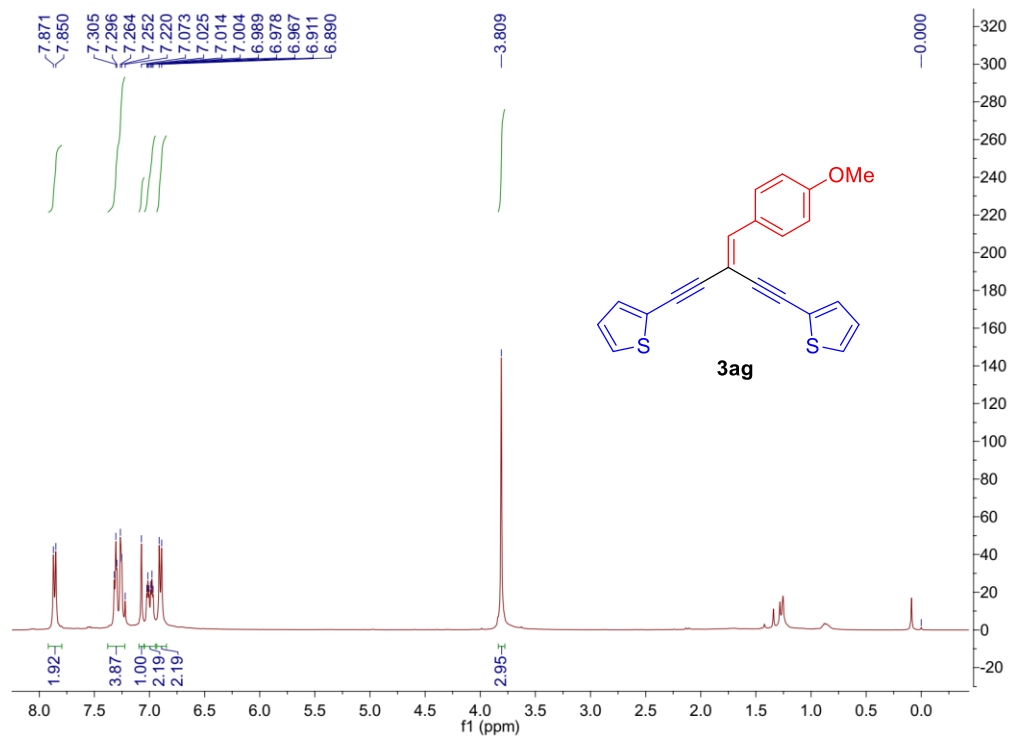


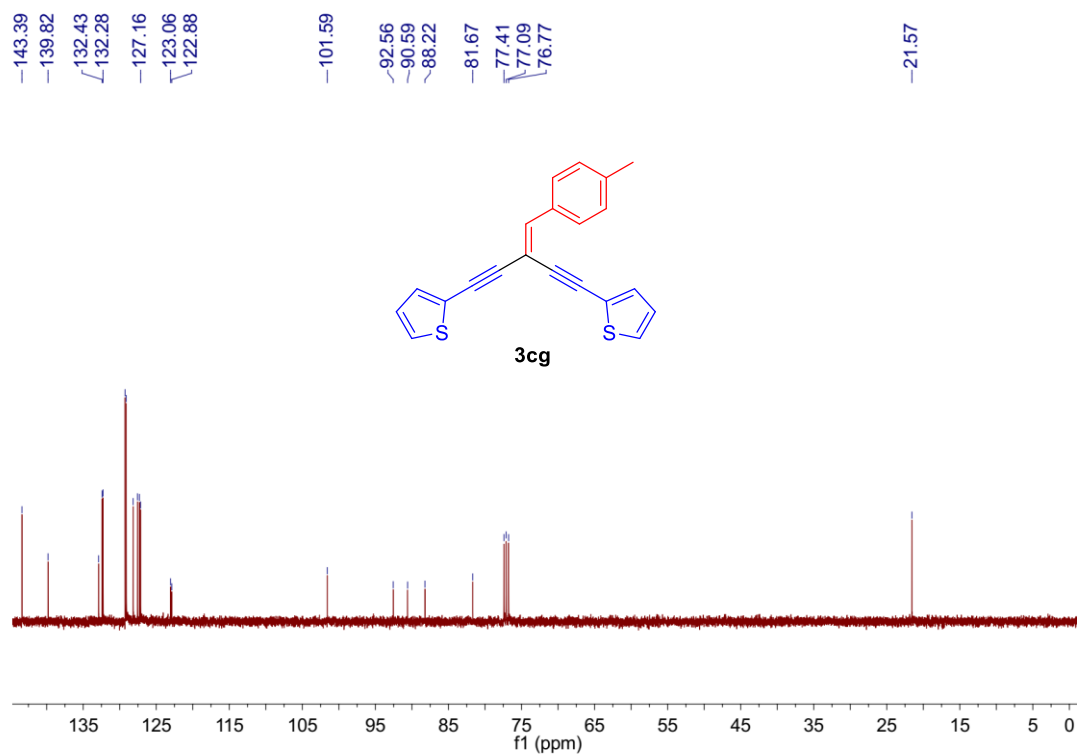
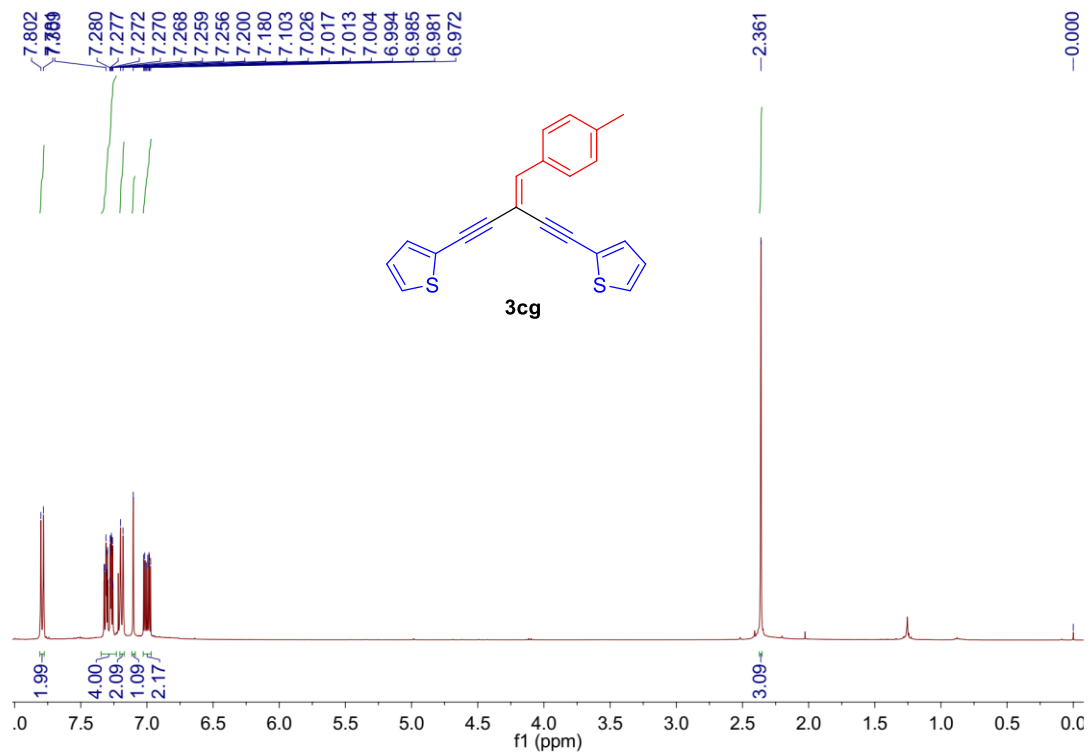


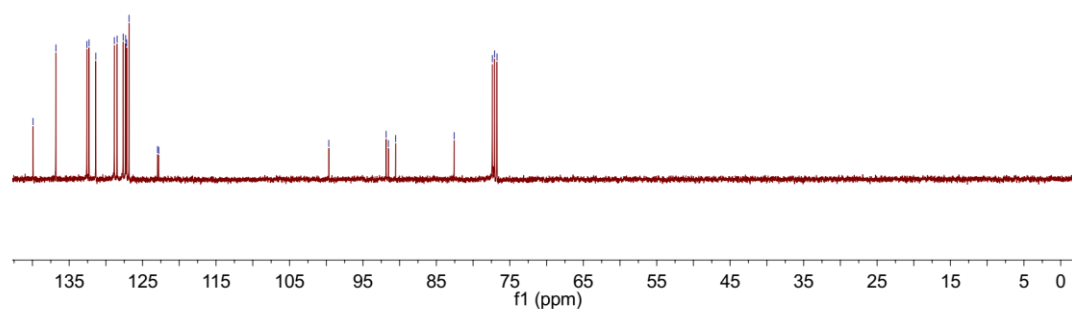
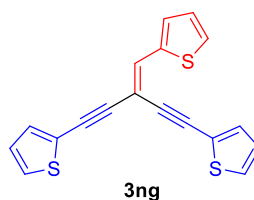
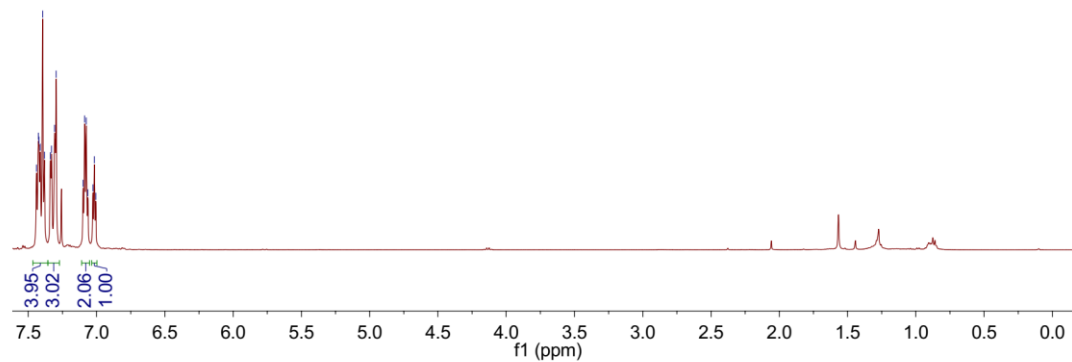
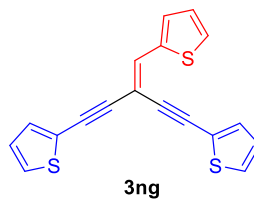
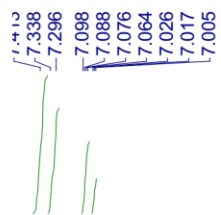














## 9. Copy of $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ NMR spectra for the unsymmetric 1,3-diyne 4

