

# **Light-Induced Intramolecular Iodine-Atom Transfer Radical Addition of Alkyne: An Approach from Aryl Iodide to Alkenyl Iodide**

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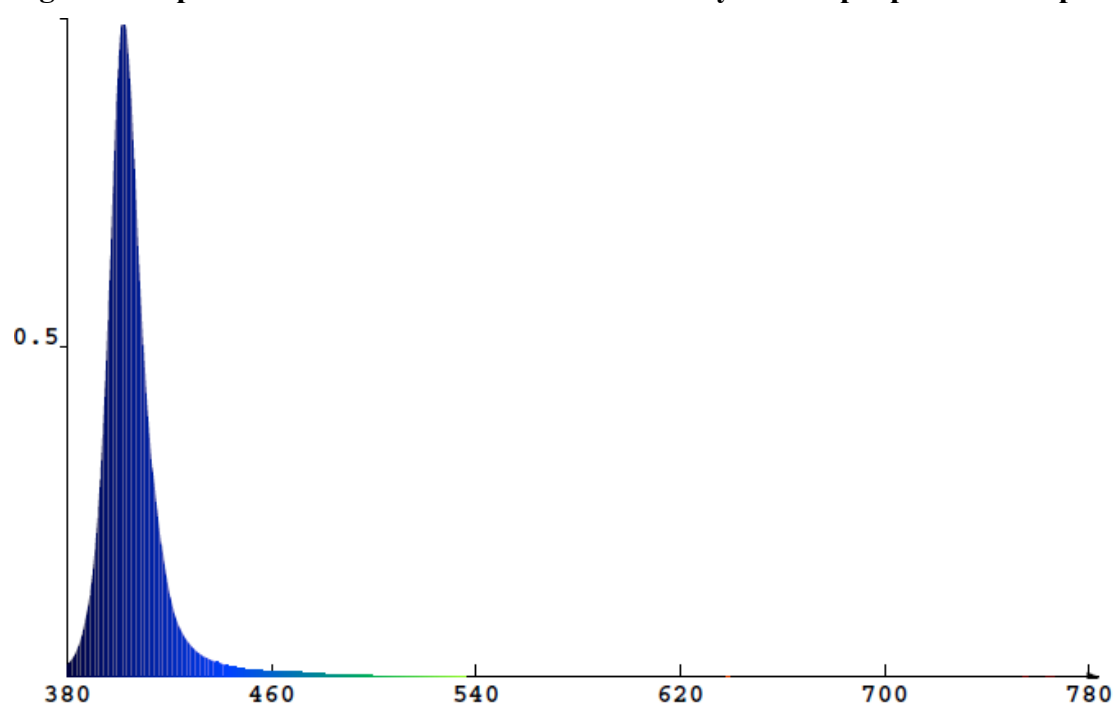
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<sup>b</sup> They contributed equally.

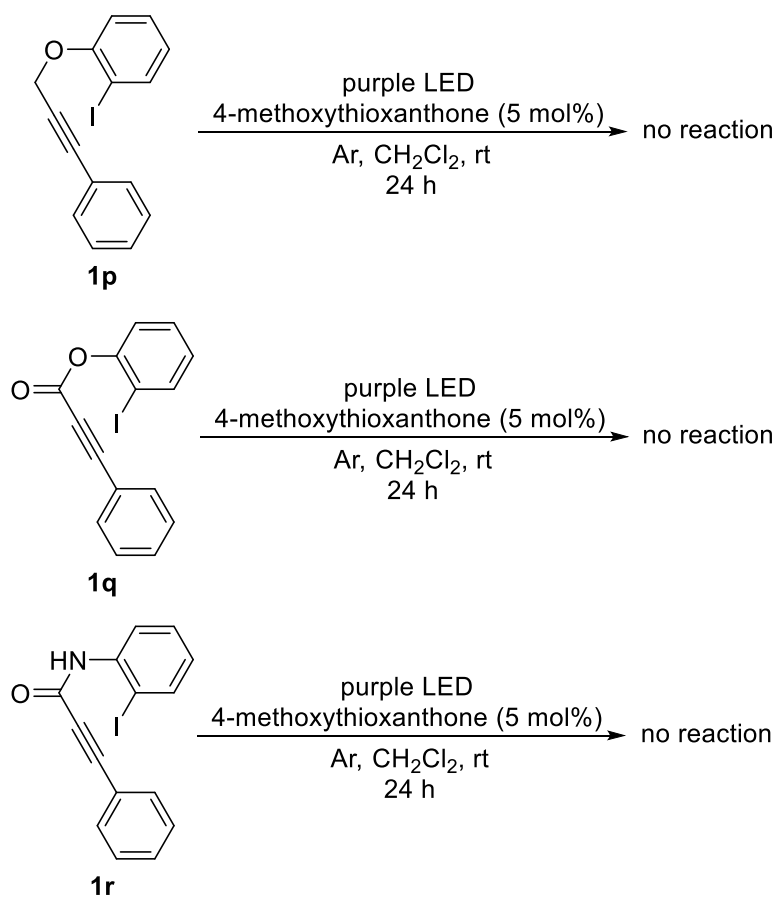
## **Supporting Information**

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**Figure S1. Spectral distribution of irradiance density for the purple LED strip**



**Scheme S1. Substrates without Ar<sup>I</sup> under Condition A**

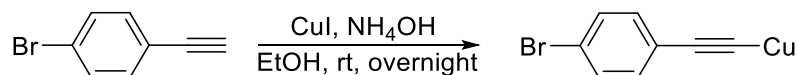


## Experimental Section

### General information

All the photo reactions were carried out using purple LED (2×1 m strip, Greethink 5050, 12 V/m) at a distance of 8-10 cm at rt unless stated otherwise. <sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz), and <sup>19</sup>F (376 MHz) NMR spectra of samples in CDCl<sub>3</sub> were recorded on an AVANCE III 400 spectrometer. IR spectra were recorded on an Avatar 360 FT-IR spectrometer. HRMS (EI) determinations were carried out on a Waters GCT CA176 spectrometer. HRMS (ESI) determinations were carried out on a Bruker Daltonics APEXIII ESI-FTICRMS spectrometer. Melting points were determined on a WRS-2 apparatus. Anhydrous DCM was distilled with CaH<sub>2</sub>. 2,2'-Diiodo-5,5'-dimethoxy-1,1'-biphenyl,<sup>1</sup> 2,2'-diiodo-1,1'-biphenyl,<sup>2</sup> **1a**,<sup>3</sup> **1b**,<sup>3</sup> **1c**,<sup>3</sup> **1e**,<sup>3</sup> **1h**,<sup>3</sup> **1i**,<sup>3</sup> **1j**,<sup>3</sup> **1k**,<sup>3</sup> **1m**,<sup>3</sup> **1p**,<sup>4</sup> **1q**<sup>5</sup> and **1r**<sup>6</sup> were synthesized according to literature procedures.

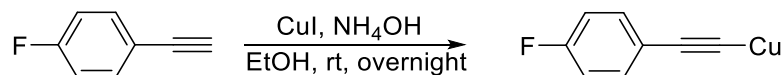
### Typical procedure I for the synthesis of ((4-bromophenyl)ethynyl)copper.



A solution of cuprous iodide (3.432 g, 18.0 mmol) in aqueous ammoniacal (60 mL) was poured into a solution of 4-bromophenylacetylene (3.258 g, 18.0 mmol) in ethanol (120 mL). The reaction mixture was allowed to stir at room temperature overnight. The bright chartreuse precipitate was filtered off and washed three times with water, ethanol, and ethyl acetate. The bright canary yellow solid was dried at 60 °C under reduced pressure with oil pump. The crude product was used without further purification.

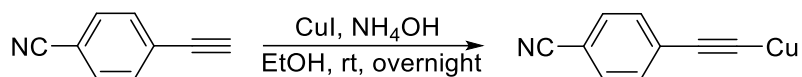
The following compounds were prepared according to Typical procedure I.

#### (1) ((4-Fluorophenyl)ethynyl)copper



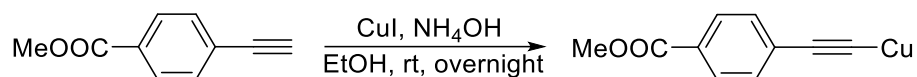
The reaction of 4-fluorophenylacetylene (2.446 g, 20.4 mmol), cuprous iodide (3.869 g, 20.3 mmol), aqueous ammoniacal (64 mL), and ethanol (120 mL) afforded ((4-fluorophenyl)ethynyl)copper.

#### (2) ((4-Cyanophenyl)ethynyl)copper



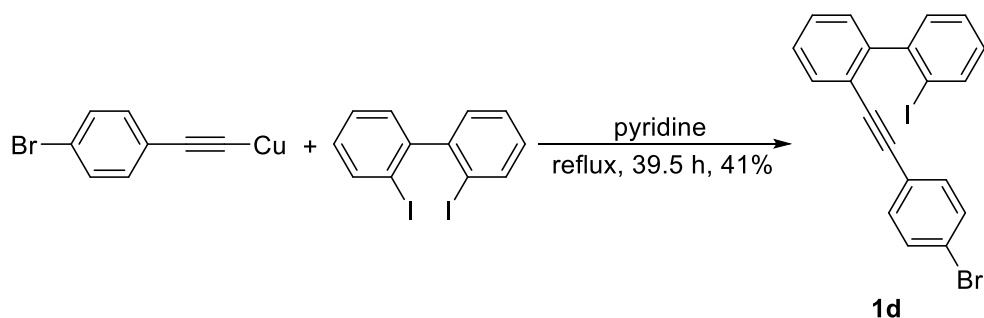
The reaction of 4-cyanophenylacetylene (2.545 g, 20.0 mmol), cuprous iodide (3.829 g, 20.1 mmol), aqueous ammoniacal (64 mL), and ethanol (150 mL) afforded ((4-cyanophenyl)ethynyl)copper.

### (3) ((4-Methoxycarbonylphenyl)ethynyl)copper



The reaction of 4-methoxycarbonylphenylacetylene (3.204 g, 20.0 mmol), cuprous iodide (3.819 g, 20.1 mmol), aqueous ammoniacal (64 mL), and ethanol (150 mL) afforded ((4-methoxycarbonylphenyl)ethynyl)copper.

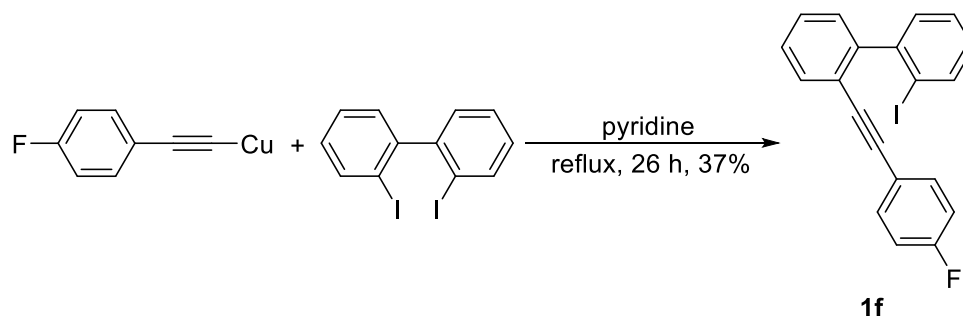
### Typical procedure II for the synthesis of 2-((4-bromophenyl)ethynyl)-2'-iodo-1,1'-biphenyl (**1d**) and its derivatives.



To a 250 mL of three necked flask was added 2,2'-diiodo-1,1'-biphenyl (2.031 g, 5.0 mmol), ((4-bromophenyl)ethynyl)copper (1.218 g, 5.2 mmol), and pyridine (50 mL). The mixture was refluxed for 39.5 h under argon atmosphere. The solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (eluent: petroleum ether) afforded **1d** as a solid (0.929 g, 41%); mp 71.5-72.3 °C (petroleum ether/ethyl acetate); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 (d, *J* = 8.0 Hz, 1 H), 7.62-7.59 (m, 1 H), 7.44-7.31 (m, 6 H), 7.29-7.23 (m, 1 H), 7.07 (t, *J* = 7.6 Hz, 1 H), 6.99 (d, *J* = 8.4 Hz, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 146.9, 145.7, 138.8, 137.3, 132.7, 131.6, 131.4, 130.3, 129.5, 129.0, 128.2, 127.8, 127.7, 122.3, 122.1, 99.4, 92.0, 89.5; IR (neat) 1625, 1577, 1555, 1494, 1479, 1458, 1436, 1424, 1412 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>20</sub>H<sub>12</sub>BrI: 457.9167, found: 457.9180.

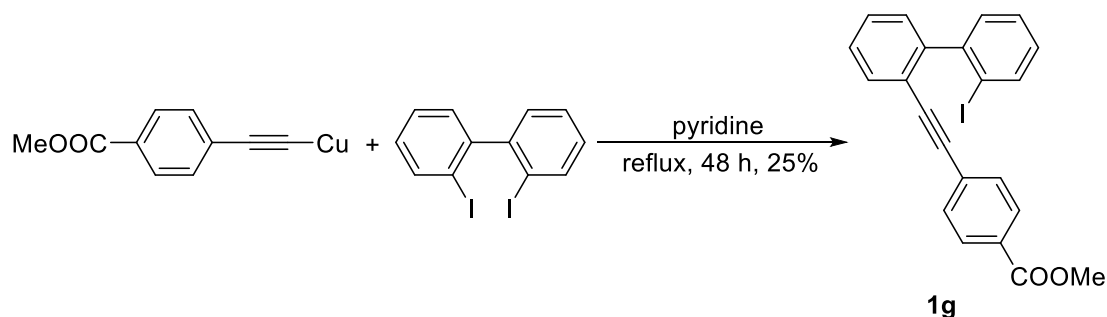
The following compounds were prepared according to Typical procedure II.

**(1) 9-((4-Fluorophenyl)ethynyl)-2'-iodo-1,1'-biphenyl (1f)**



The reaction of ((4-fluorophenyl)ethynyl)copper (1.838 g, 10.0 mmol) and 2,2'-diiodo-1,1'-biphenyl (4.060 g, 10.0 mmol) in pyridine (100 mL) afforded **1f** as a solid (1.479 g, 37%); mp 94.7-95.2 °C (petroleum ether/ethyl acetate);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J$  = 7.6 Hz, 1 H), 7.63-7.58 (m, 1 H), 7.45-7.38 (m, 3 H), 7.35 (dd,  $J$  = 7.6, 1.6 Hz, 1 H), 7.30-7.26 (m, 1 H), 7.15-7.06 (m, 3 H), 6.93 (t,  $J$  = 8.6 Hz, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6, 161.1, 146.8, 145.8, 138.8, 133.24, 133.15, 131.6, 130.3, 129.4, 129.0, 128.1, 127.8, 127.7, 122.6, 119.3, 115.6, 115.3, 99.5, 92.0, 88.1;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.0; IR (neat) 1598, 1583, 1510, 1461, 1436, 1424  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{12}\text{FI}$ : 397.9968, found: 397.9974.

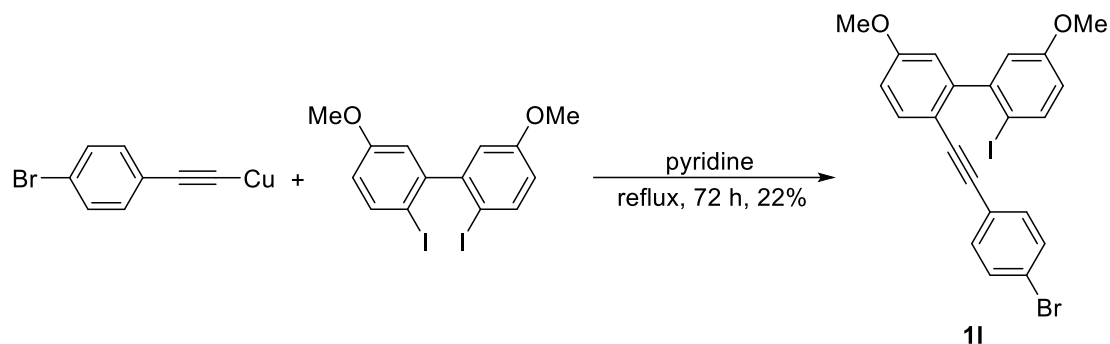
**(2) 2-((4-Methoxycarbonylphenyl)ethynyl)-2'-iodo-1,1'-biphenyl (1g)**



The reaction of ((4-methoxycarbonylphenyl)ethynyl)copper (1.235 g, 5.5 mmol) and 2,2'-diiodo-1,1'-biphenyl (2.031 g, 5.0 mmol) in pyridine (30 mL) afforded **1g** as a solid (0.539 g, 25%); mp 114.0-114.2 °C (petroleum ether/ethyl acetate);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (dd,  $J$  = 8.0, 1.2 Hz, 1 H), 7.90 (d,  $J$  = 8.4 Hz, 2 H), 7.65-7.62 (m, 1 H), 7.47-7.38 (m, 3 H), 7.37-7.33 (m, 1 H), 7.31-7.27 (m, 1 H), 7.19 (d,  $J$  = 8.8 Hz, 2 H), 7.13-7.07 (m, 1 H), 3.89 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 147.1, 145.6, 138.9, 131.8, 131.2, 130.3, 129.5, 129.3, 129.2, 129.1, 128.5, 127.92, 127.89, 127.7,

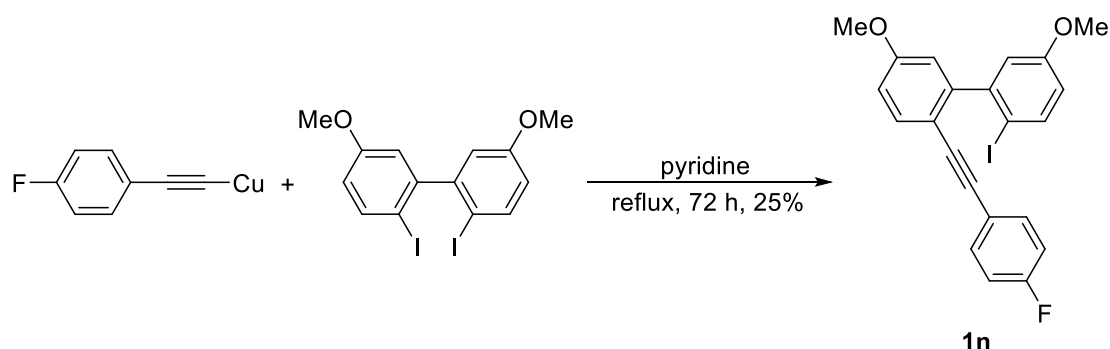
122.3, 99.4, 92.3, 91.4, 52.2; IR (neat) 1723, 1604, 1462, 1434  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{22}\text{H}_{16}\text{IO}_2$  ( $\text{M}+\text{H}^+$ ): 439.0189, found: 439.0185.

**(3) 2-((4-Bromophenyl)ethynyl)-2'-iodo-5,5'-dimethoxy-1,1'-biphenyl (**1l**)**



The reaction of ((4-bromophenyl)ethynyl)copper (0.842 g, 3.3 mmol) and 2,2'-diiodo-1,1'-biphenyl (1.399 g, 3.0 mmol) in pyridine (30 mL) afforded **1l** as a solid (0.334 g, 22%); mp 134.7-134.9 °C (petroleum ether/ethyl acetate);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J = 8.4$  Hz, 1 H), 7.53 (d,  $J = 8.4$  Hz, 1 H), 7.35 (d,  $J = 8.4$  Hz, 2 H), 7.01 (d,  $J = 8.4$  Hz, 2 H), 6.95-6.90 (m, 2 H), 6.81 (d,  $J = 2.4$  Hz, 1 H), 6.72-6.66 (m, 1 H), 3.85 (s, 3 H), 3.77 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 159.3, 148.1, 146.3, 139.3, 133.1, 132.5, 131.4, 122.5, 121.8, 115.9, 115.6, 115.0, 114.6, 113.8, 90.5, 89.6, 87.7, 55.41, 55.39; IR (neat) 1601, 1583, 1558, 1497, 1458  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{22}\text{H}_{16}\text{BrIO}_2$ : 517.9378, found: 517.9373.

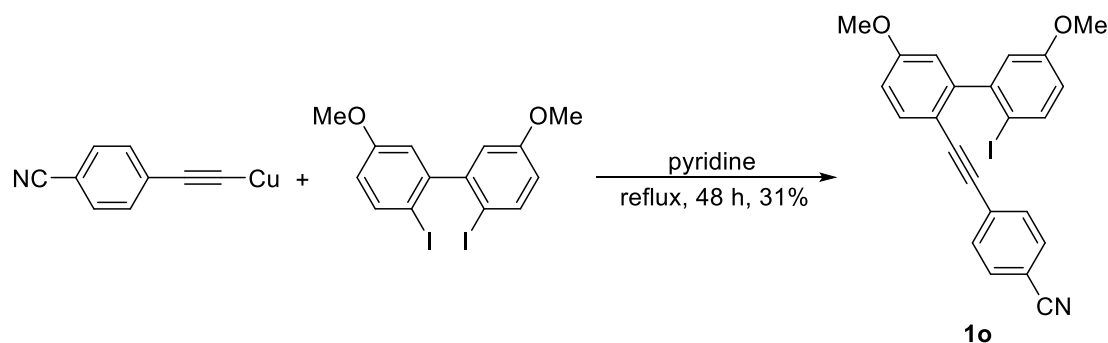
**(4) 2-((4-fluorophenyl)ethynyl)-2'-iodo-5,5'-dimethoxy-1,1'-biphenyl (**1n**)**



The reaction of ((4-fluorophenyl)ethynyl)copper (0.412 g, 2.2 mmol) and 2,2'-diiodo-1,1'-biphenyl (0.936 g, 2.0 mmol) in pyridine (20 mL) afforded **1n** as a solid (0.227 g, 25%); mp 117.2-117.8 °C (petroleum ether/ethyl acetate);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 8.4$  Hz, 1 H), 7.53 (d,  $J = 8.8$  Hz, 1 H), 7.17-7.10 (m, 2 H), 6.97-6.88 (m, 4 H), 6.81 (d,  $J = 2.4$  Hz, 1 H), 6.70 (dd,  $J = 8.8, 3.2$  Hz, 1 H), 3.86 (s, 3 H), 3.79 (s, 3

H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 160.9, 159.5, 159.2, 148.0, 146.5, 139.4, 133.0, 119.7, 115.9, 115.7, 115.5, 115.3, 115.0, 113.8, 90.5, 88.0, 87.8, 55.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.7; IR (neat) 1610, 1586, 1558, 1510, 1467, 1424  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{22}\text{H}_{16}\text{FIO}_2$ : 458.0179, found: 458.0174.

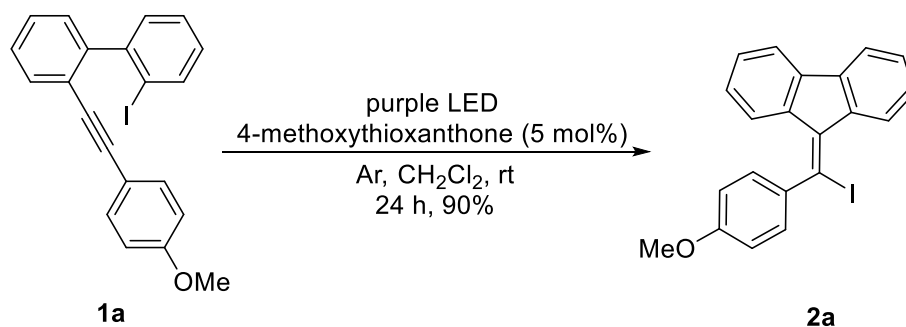
**(5) 2-((4-cyanophenyl)ethynyl)-2'-iodo-5,5'-dimethoxy-1,1'-biphenyl (1o)**



The reaction of ((4-cyanophenyl)ethynyl)copper (1.396 g, 3.0 mmol) and 2,2'-diiodo-1,1'-biphenyl (0.636 g, 3.3 mmol) in pyridine (25 mL) afforded **1o** as a solid (0.426 g, 31%); mp 119.7-120.1  $^{\circ}\text{C}$  (petroleum ether/ethyl acetate);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J$  = 8.4 Hz, 1 H), 7.55 (d,  $J$  = 8.8 Hz, 1 H), 7.50 (d,  $J$  = 8.4 Hz, 2 H), 7.20 (d,  $J$  = 8.0 Hz, 2 H), 6.98-6.86 (m, 2 H), 6.82 (d,  $J$  = 2.4 Hz, 1 H), 6.71 (dd,  $J$  = 8.8, 2.8 Hz, 1 H), 3.88 (s, 3 H), 3.80 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 159.4, 148.5, 146.1, 139.3, 133.3, 131.8, 131.4, 128.5, 118.6, 115.9, 115.6, 115.0, 113.9, 110.6, 93.2, 90.0, 87.5, 55.43, 55.39; IR (neat) 1598, 1558, 1507, 1461, 1439  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{23}\text{H}_{16}\text{INO}_2$ : 465.0226, found: 465.0232.

**Typical procedure III for the I-ATRA reactions.**

**Synthesis of 9-(iodo(4-methoxyphenyl)methylene)-9H-fluorene (2a)<sup>3</sup>**

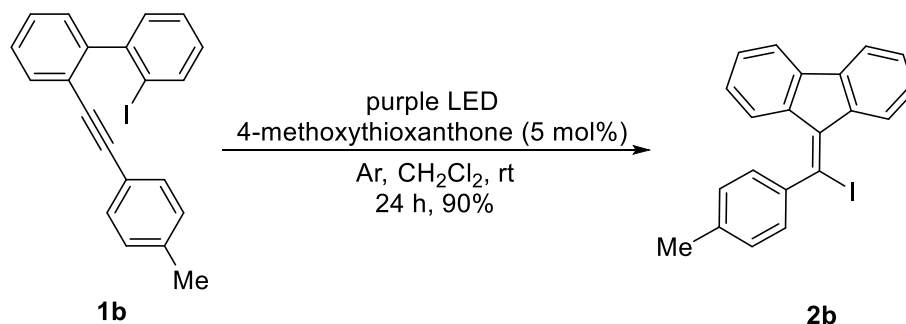


**1a** (41 mg, 0.1 mmol), 4-methoxythioxanthone (1.3 mg, 0.005 mmol), and anhydrous DCM (50 mL) were added subsequently into a 125 mL of dry Pyrex sealed tube. The

reaction mixture was degassed with three freeze-pump-thaw cycles (15 min per cycle). Then, the reaction mixture was irradiated by purple LED at rt under argon atmosphere. The reaction was completed after 24 h as monitored by TLC (eluent: petroleum ether: ethyl acetate = 100:1). The solvent was removed and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether) to afford **2a** as a solid (37 mg, 90%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.05 (d, *J* = 7.6 Hz, 1 H), 7.71 (d, *J* = 6.8 Hz, 1 H), 7.62 (d, *J* = 7.6 Hz, 1 H), 7.48-7.37 (m, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 7.22 (t, *J* = 7.6 Hz, 1 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 6.86 (t, *J* = 7.4 Hz, 1 H), 6.25 (d, *J* = 8.0 Hz, 1 H), 3.90 (s, 3 H).

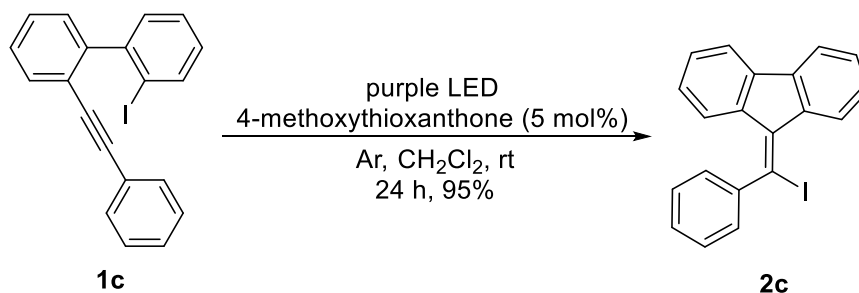
The following compounds were prepared according to Typical Procedure III.

**(1) 9-(Iodo(*p*-tolyl)methylene)-9*H*-fluorene (**2b**)<sup>3</sup>**



The reaction of **1b** (39 mg, 0.1 mmol), 4-methoxythioxanthone (1.2 mg, 0.005 mmol), and anhydrous DCM (50 mL) afforded **2b** as a solid (35 mg, 90%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.06 (d, *J* = 8.4 Hz, 1 H), 7.71 (d, *J* = 6.8 Hz, 1 H), 7.62 (d, *J* = 7.2 Hz, 1 H), 7.48-7.39 (m, 2 H), 7.28 (s, 4 H), 7.21 (t, *J* = 7.0 Hz, 1 H), 6.84 (t, *J* = 7.0 Hz, 1 H), 6.20 (d, *J* = 8.4 Hz, 1 H), 2.47 (s, 3 H).

**(2) 9-(Iodo(phenyl)methylene)-9*H*-fluorene (**2c**)<sup>3</sup>**

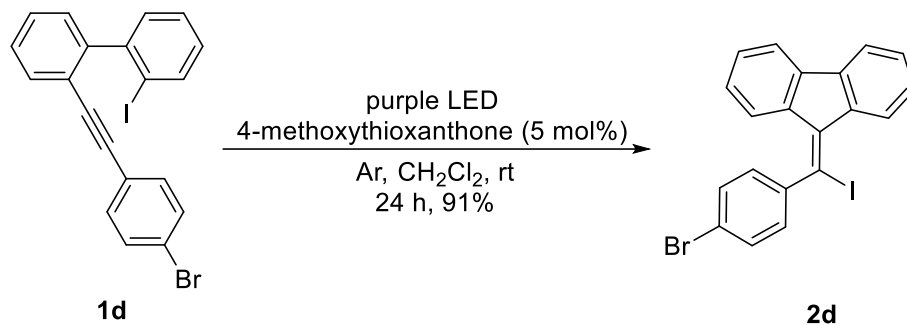


The reaction of **1c** (38 mg, 0.1 mmol), 4-methoxythioxanthone (1.3 mg, 0.005 mmol), and anhydrous DCM (50 mL) afforded **2c** as a solid (36 mg, 95%); <sup>1</sup>H NMR (400 MHz,



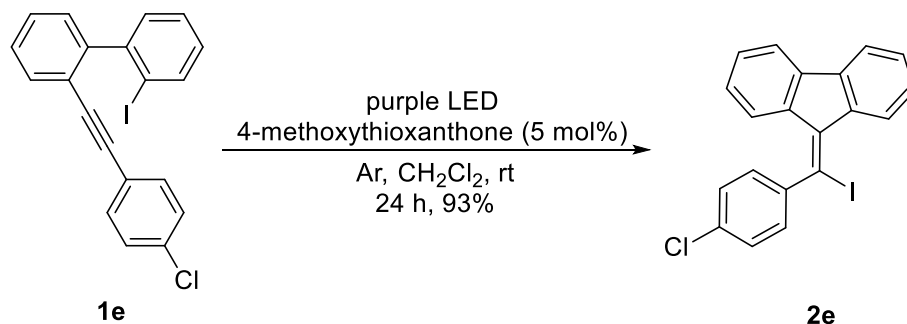
CDCl<sub>3</sub>)  $\delta$  9.06 (d,  $J$  = 7.6 Hz, 1 H), 7.71 (d,  $J$  = 7.4, 1 H), 7.62 (d,  $J$  = 7.6 Hz, 1 H), 7.50-7.35 (m, 7 H), 7.20 (t,  $J$  = 7.2 Hz, 1 H), 6.81 (t,  $J$  = 7.8 Hz, 1 H), 6.09 (d,  $J$  = 8.0 Hz, 1 H).

**(3) 9-((4-Bromophenyl)iodomethylene)-9H-fluorene (2d)**



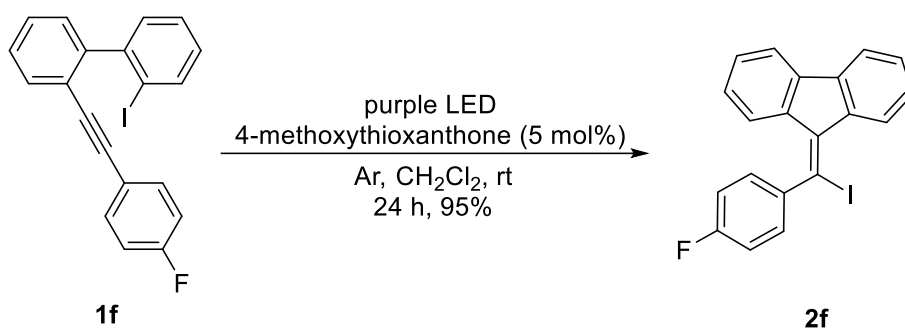
The reaction of **1d** (46 mg, 0.1 mmol), 4-methoxythioxanthone (1.2 mg, 0.005 mmol), and anhydrous DCM (50 mL) afforded **2d** as a solid (42 mg, 91%); mp 123.8-124.0 °C (petroleum ether/ethyl acetate); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.02 (d,  $J$  = 7.6 Hz, 1 H), 7.71 (d,  $J$  = 7.2 Hz, 1 H), 7.64-7.58 (m, 3 H), 7.50-7.37 (m, 2 H), 7.28-7.21 (m, 3 H), 6.88 (t,  $J$  = 7.8 Hz, 1 H), 6.21 (d,  $J$  = 8.0 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  146.3, 141.8, 139.5, 138.4, 138.3, 137.9, 132.4, 129.7, 129.5, 128.5, 127.0, 126.5, 125.2, 124.8, 122.8, 119.6, 119.4, 119.1; IR (neat) 1613, 1586, 1567, 1555, 1537, 1503, 1479, 1439 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>20</sub>H<sub>12</sub>BrI: 457.9167, found: 457.9171.

**(4) 9-((4-Chlorophenyl)iodomethylene)-9H-fluorene (2e)<sup>3</sup>**



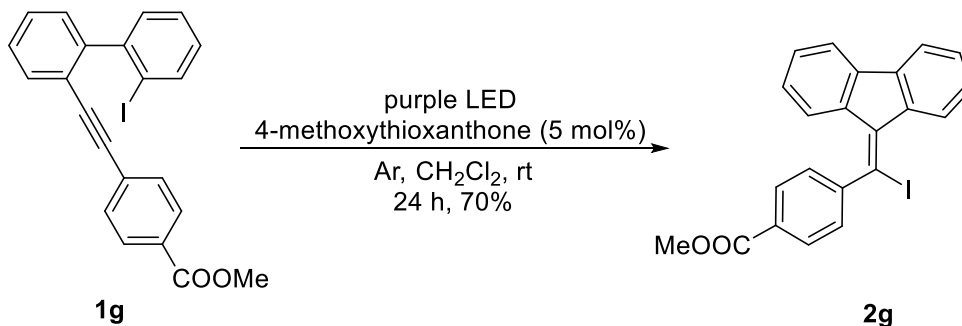
The reaction of **1e** (41 mg, 0.1 mmol), 4-methoxythioxanthone (1.3 mg, 0.005 mmol), and anhydrous DCM (50 mL) afforded **2e** as a solid (38 mg, 93%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.03 (d,  $J$  = 8.0 Hz, 1 H), 7.71 (d,  $J$  = 7.2 Hz, 1 H), 7.63 (d,  $J$  = 7.2 Hz, 1 H), 7.49-7.38 (m, 4 H), 7.33 (d,  $J$  = 8.4 Hz, 2 H), 7.25-7.20 (m, 1 H), 6.88 (t,  $J$  = 8.0 Hz, 1 H), 6.20 (d,  $J$  = 8.0 Hz, 1 H).

**(5) 9-((4-Fluorophenyl)iodomethylene)-9H-fluorene (2f)**



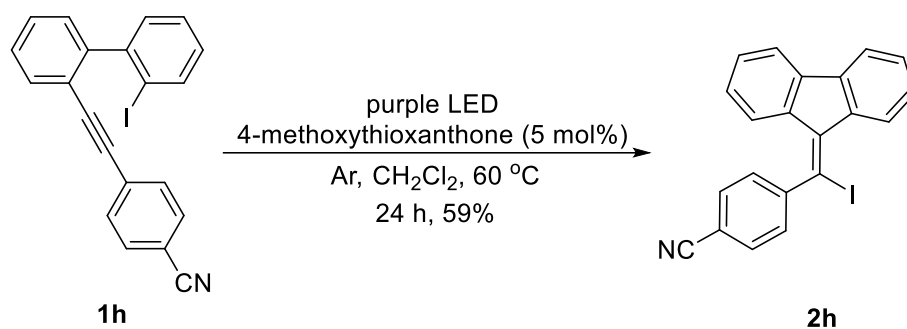
The reaction of **1f** (40 mg, 0.1 mmol), 4-methoxythioxanthone (1.3 mg, 0.005 mmol), and anhydrous DCM (50 mL) afforded **2f** as a solid (38 mg, 95%); mp 124.7-125.0 °C (petroleum ether/ethyl acetate);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.04 (d,  $J$  = 8.0 Hz, 1 H), 7.71 (d,  $J$  = 7.4 Hz, 1 H), 7.63 (d,  $J$  = 7.2 Hz, 1 H), 7.49-7.33 (m, 4 H), 7.26-7.13 (m, 3 H), 6.86 (t,  $J$  = 7.6 Hz, 1 H), 6.14 (d,  $J$  = 8.0 Hz, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.8, 161.4, 143.6, 141.7, 141.4, 139.5, 138.4, 138.0, 129.8, 129.7, 129.6, 128.4, 127.0, 126.5, 125.1, 124.8, 119.6, 119.0, 116.3, 116.1, 97.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.9; IR (neat) 1595, 1500, 1443  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{12}\text{FI}$ : 397.9968, found: 397.9964.

**(6) 9-((4-Methoxycarbonylphenyl)iodomethylene)-9H-fluorene (2g)**



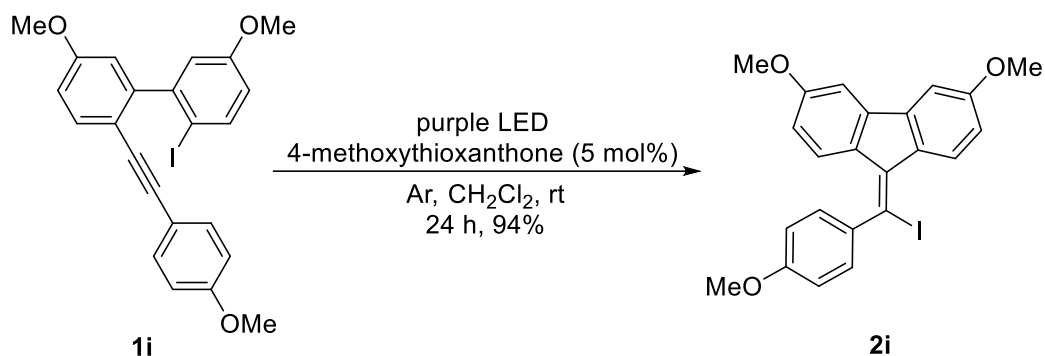
The reaction of **1g** (44 mg, 0.1 mmol), 4-methoxythioxanthone (1.2 mg, 0.005 mmol), and anhydrous DCM (50 mL) afforded **2g** as a solid (31 mg, 70%); mp 141.2-141.5 °C (petroleum ether/ethyl acetate);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.04 (d,  $J$  = 8.0 Hz, 1 H), 8.16 (d,  $J$  = 8.4 Hz, 2 H), 7.71 (d,  $J$  = 6.8 Hz, 1 H), 7.63 (d,  $J$  = 7.6 Hz, 1 H), 7.51-7.39 (m, 4 H), 7.22 (t,  $J$  = 7.6 Hz, 1 H), 6.81 (t,  $J$  = 7.8 Hz, 1 H), 6.10 (d,  $J$  = 8.0 Hz, 1 H), 3.98 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 151.6, 141.8, 141.2, 139.5, 138.3, 137.9, 130.5, 130.1, 129.8, 128.5, 127.8, 127.0, 126.5, 125.2, 124.8, 119.6, 119.1, 96.6, 52.3; IR (neat) 1722, 1607, 1445, 1433, 1405  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{22}\text{H}_{16}\text{IO}_2$  ( $\text{M}+\text{H}^+$ ): 439.0189, found: 439.0188.

**(7) 9-((4-Cyanophenyl)iodomethylene)-9H-fluorene (2h)<sup>3</sup>**



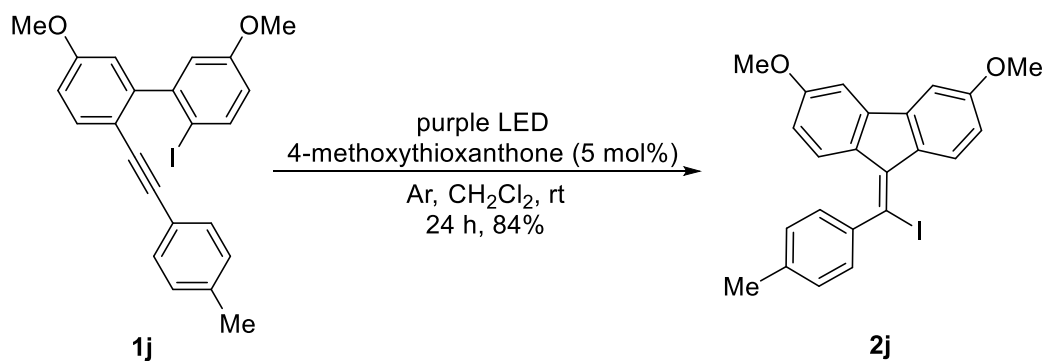
The reaction of **1h** (41 mg, 0.1 mmol), 4-methoxythioxanthone (1.2 mg, 0.005 mmol), and anhydrous DCM (50 mL) at 60 °C afforded **2h** as a solid (24 mg, 59%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.01 (d,  $J$  = 8.0 Hz, 1 H), 7.78 (d,  $J$  = 8.0 Hz, 2 H), 7.72 (d,  $J$  = 7.6 Hz, 1 H), 7.64 (d,  $J$  = 7.6 Hz, 1 H), 7.53-7.38 (m, 4 H), 7.28-7.21 (m, 1 H), 6.85 (t,  $J$  = 7.8 Hz, 1 H), 6.06 (d,  $J$  = 8.0 Hz, 1 H).

**(8) 9-(Iodo(4-methoxyphenyl)methylene)-3,6-dimethoxy-9H-fluorene (2i)<sup>3</sup>**



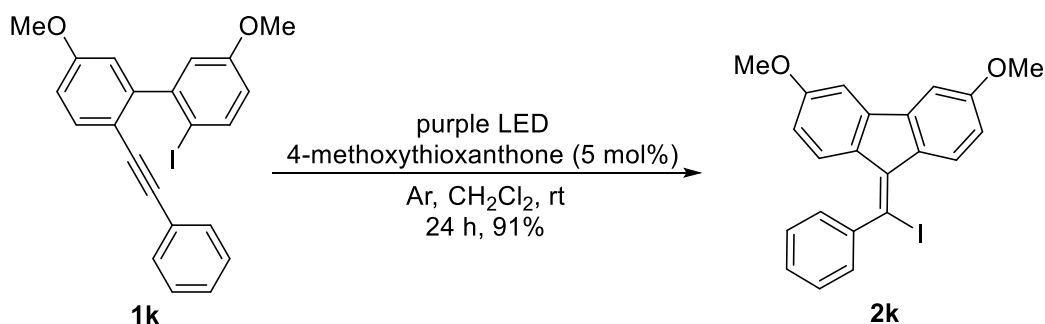
The reaction of **1i** (47 mg, 0.1 mmol), 4-methoxythioxanthone (1.2 mg, 0.005 mmol), and anhydrous DCM (50 mL) afforded **2i** as a solid (44 mg, 94%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.94 (d,  $J$  = 8.4 Hz, 1 H), 7.31 (d,  $J$  = 8.4 Hz, 2 H), 7.19 (d,  $J$  = 2.4 Hz, 1 H), 7.08 (d,  $J$  = 2.8 Hz, 1 H), 7.00-6.91 (m, 3 H), 6.41 (dd,  $J$  = 8.8, 2.4 Hz, 1 H), 6.13 (d,  $J$  = 8.4 Hz, 1 H), 3.93 (s, 3 H), 3.89 (s, 3 H), 3.81 (s, 3 H).

**(9) 9-(Iodo(*p*-tolyl)methylene)-3,6-dimethoxy-9H-fluorene (2j)<sup>3</sup>**



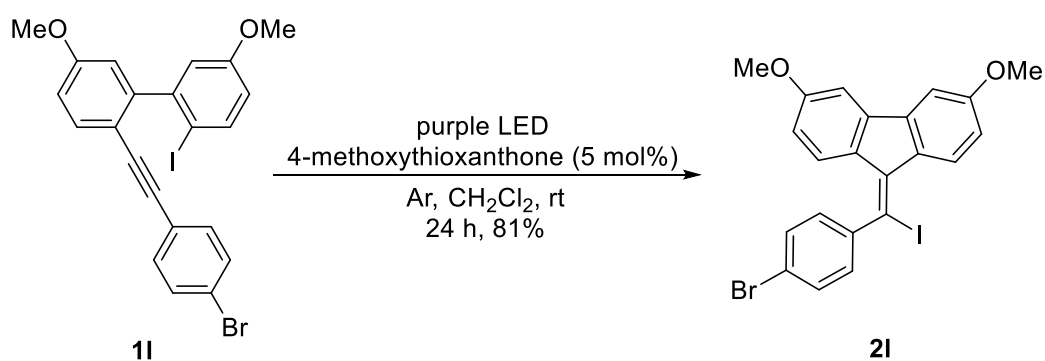
The reaction of **1j** (45 mg, 0.1 mmol), 4-methoxythioxanthone (1.2 mg, 0.005 mmol), and anhydrous DCM (50 mL) afforded **2j** as a solid (38 mg, 84%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.94 (d,  $J = 8.8$  Hz, 1 H), 7.29-7.23 (m, 4 H), 7.18 (d,  $J = 2.4$  Hz, 1 H), 7.08 (d,  $J = 2.4$  Hz, 1 H), 6.94 (dd,  $J = 8.8, 2.4$  Hz, 1 H), 6.39 (dd,  $J = 8.8, 2.8$  Hz, 1 H), 6.09 (d,  $J = 8.4$  Hz, 1 H), 3.92 (s, 3 H), 3.80 (s, 3 H), 2.45 (s, 3 H).

**(10) 9-(Iodo(phenyl)methylene)-3,6-dimethoxy-9H-fluorene (**2k**)<sup>3</sup>**



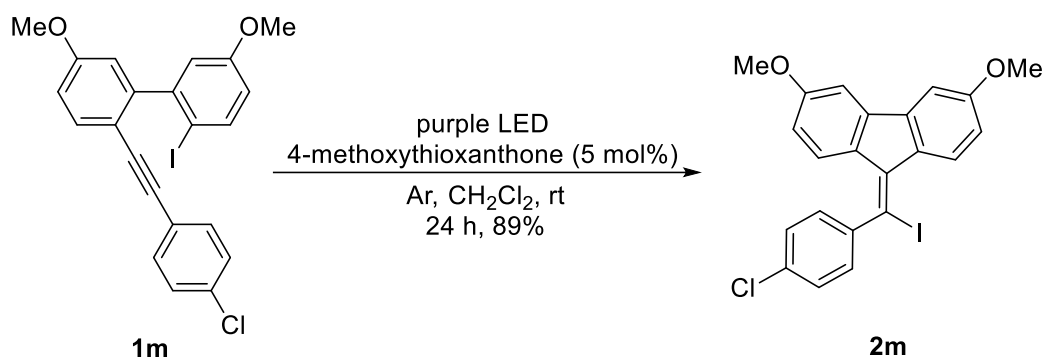
The reaction of **1k** (44 mg, 0.1 mmol), 4-methoxythioxanthone (1.2 mg, 0.005 mmol), and anhydrous DCM (50 mL) afforded **2k** as a solid (40 mg, 91%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.93 (d,  $J = 8.8$  Hz, 1 H), 7.49-7.40 (m, 2 H), 7.39-7.34 (m, 3 H), 7.17 (d,  $J = 2.4$  Hz, 1 H), 7.07 (d,  $J = 2.4$  Hz, 1 H), 6.93 (dd,  $J = 8.8, 2.4$  Hz, 1 H), 6.35 (dd,  $J = 8.8, 2.4$  Hz, 1 H), 5.97 (d,  $J = 8.4$  Hz, 1 H), 3.91 (s, 3 H), 3.78 (s, 3 H).

**(11) 9-((4-Bromophenyl)iodomethylene)-3,6-dimethoxy-9H-fluorene (**2l**)**



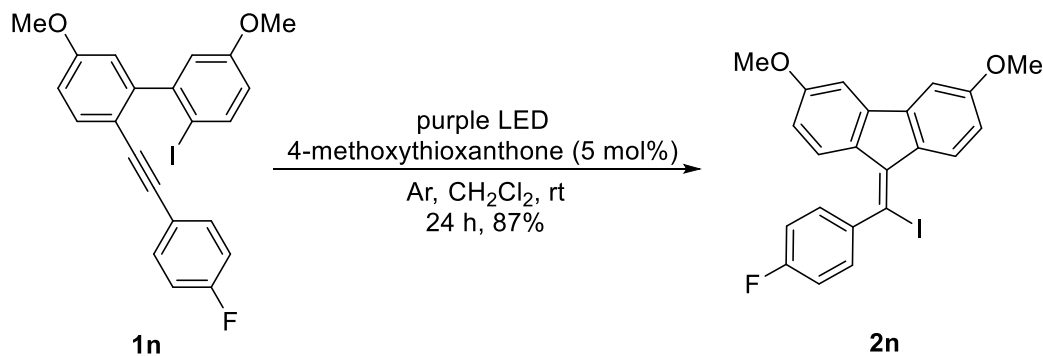
The reaction of **1l** (52 mg, 0.1 mmol), 4-methoxythioxanthone (1.2 mg, 0.005 mmol), and anhydrous DCM (50 mL) afforded **2l** as a solid (42 mg, 81%); mp 158.8-159.2 °C (petroleum ether/ethyl acetate); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.91 (d, *J* = 8.8 Hz, 1 H), 7.59 (d, *J* = 8.4 Hz, 2 H), 7.28-7.24 (m, 2 H), 7.18 (d, *J* = 2.8 Hz, 1 H), 7.09 (d, *J* = 2.4 Hz, 1 H), 6.94 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.42 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.11 (d, *J* = 8.8 Hz, 1 H), 3.93 (s, 3 H), 3.81 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.1, 160.1, 146.3, 143.3, 140.8, 140.2, 132.3, 132.2, 131.7, 129.9, 126.2, 126.0, 122.5, 112.7, 111.9, 105.0, 104.4, 91.4, 55.6, 55.5; IR (neat) 1607, 1574, 1494, 1455, 1427 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>22</sub>H<sub>16</sub>BrIO<sub>2</sub>: 517.9378, found: 517.9374.

**(12) 9-((4-Chlorophenyl)iodomethylene)-3,6-dimethoxy-9H-fluorene (2m)<sup>3</sup>**



The reaction of **1m** (47 mg, 0.1 mmol), 4-methoxythioxanthone (1.2 mg, 0.005 mmol), and anhydrous DCM (50 mL) afforded **2m** as a solid (42 mg, 89%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.91 (d, *J* = 8.8 Hz, 1 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 7.18 (d, *J* = 2.4 Hz, 1 H), 7.09 (d, *J* = 2.4 Hz, 1 H), 6.94 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.42 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.10 (d, *J* = 8.8 Hz, 1 H), 3.93 (s, 3 H), 3.81 (s, 3 H).

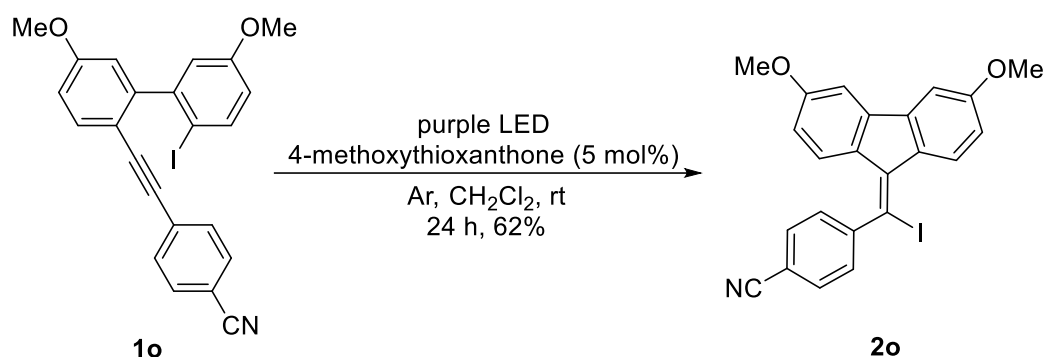
**(13) 9-((4-Fluorophenyl)iodomethylene)-3,6-dimethoxy-9H-fluorene (2n)**



The reaction of **1n** (46 mg, 0.1 mmol), 4-methoxythioxanthone (1.2 mg, 0.005 mmol),

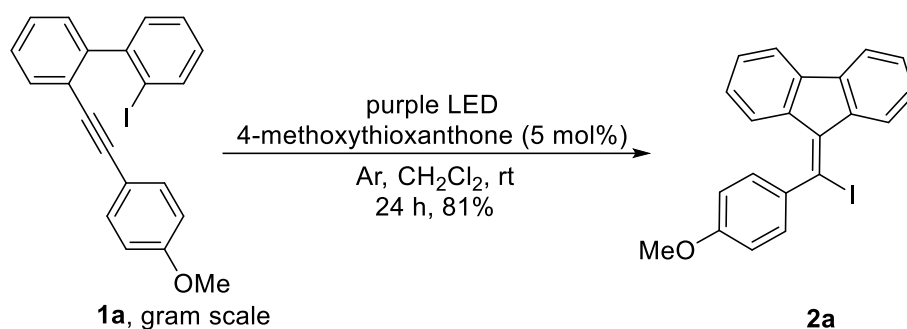
and anhydrous DCM (50 mL) afforded **2n** as a solid (40 mg, 87%); mp 130.3-130.9 °C (petroleum ether/ethyl acetate); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.92 (d, *J* = 8.8 Hz, 1 H), 7.39-7.31 (m, 2 H), 7.20-7.11 (m, 3 H), 7.08 (d, *J* = 2.4 Hz, 1 H), 6.94 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.40 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.04 (d, *J* = 8.8 Hz, 1 H), 3.93 (s, 3 H), 3.81 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.7, 161.0, 160.0, 143.6, 140.7, 131.7, 130.13, 130.05, 126.1, 126.0, 116.2, 116.0, 112.7, 111.9, 105.0, 104.2, 92.1, 55.6, 55.4; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -112.3; IR (neat) 1610, 1586, 1500, 1467, 1430 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>22</sub>H<sub>16</sub>FIO<sub>2</sub>: 458.0179, found: 458.0182.

**(14) 9-((4-Cyanophenyl)iodomethylene)-3,6-dimethoxy-9*H*-fluorene (2o)**



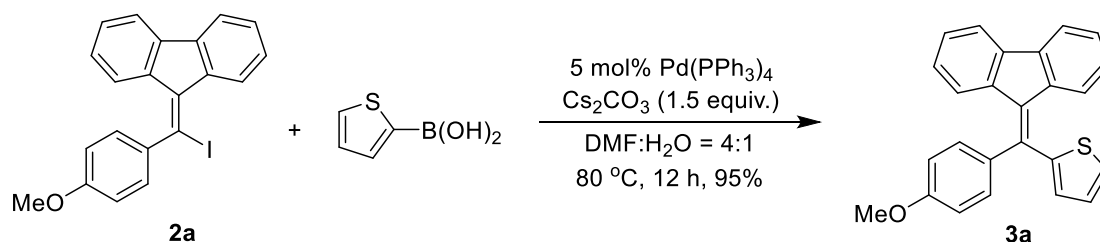
The reaction of **1o** (45 mg, 0.1 mmol), 4-methoxythioxanthone (1.2 mg, 0.005 mmol), and anhydrous DCM (50 mL) afforded **2o** as a solid (28 mg, 62%); decompose at 271.2 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.89 (d, *J* = 8.8 Hz, 1 H), 7.76 (d, *J* = 8.4 Hz, 2 H), 7.49 (d, *J* = 8.4 Hz, 2 H), 7.18 (d, *J* = 2.4 Hz, 1 H), 7.09 (d, *J* = 2.4 Hz, 1 H), 6.95 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.39 (dd, *J* = 8.8, 2.4 Hz, 1 H), 5.95 (d, *J* = 8.8 Hz, 1 H), 3.94 (s, 3 H), 3.81 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.3, 160.3, 151.6, 143.4, 141.1, 140.6, 132.9, 131.8, 131.5, 129.2, 126.01, 125.96, 118.4, 112.7, 112.1, 112.0, 105.2, 104.6, 89.0, 55.6, 55.5; IR (neat) 1607, 1577, 1491, 1463, 1430 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>23</sub>H<sub>16</sub>INO<sub>2</sub>: 465.0226, found: 465.0229.

**Gram scale synthesis of 9-(iodo(4-methoxyphenyl)methylene)-9*H*-fluorene (2a)**



**1a** (1.029 g, 2.5 mmol), 4-methoxythioxanthone (31 mg, 0.128 mmol), and anhydrous DCM (1.25 L) were added subsequently into a 2 L of dry Pyrex flask. The reaction mixture was bubbled with argon for 30 min. Then, the reaction mixture was irradiated by purple LED at rt under argon atmosphere. The reaction was completed after 24 h as monitored by TLC (eluent: petroleum ether: ethyl acetate = 50:1). The solvent was removed and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 50:1) to afford **2a** as a solid (837 mg, 81%).

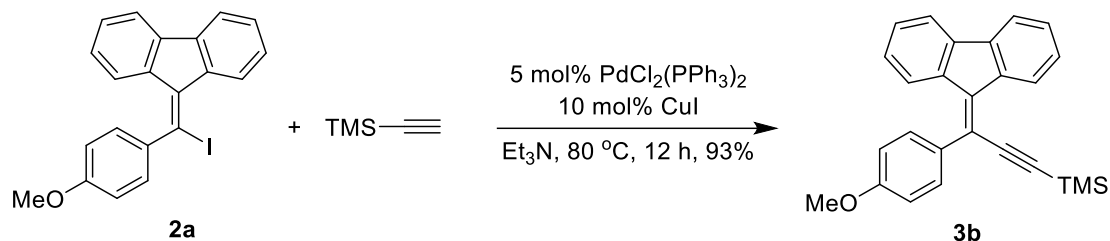
#### Synthesis of 2-((9*H*-fluoren-9-ylidene)(4-methoxyphenyl)methyl)thiophene (**3a**)



To a 25 mL of dry glass reaction tube was added **2a** (84 mg, 0.2 mmol), thiophen-2-ylboronic acid (32 mg, 0.24 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (13 mg, 0.01 mmol), Cs<sub>2</sub>CO<sub>3</sub> (104 mg, 0.32 mmol), DMF (1.6 mL), H<sub>2</sub>O (0.4 mL). The mixture was stirred at 80 °C under argon atmosphere. The reaction was completed after 12 h as monitored by TLC (eluent: petroleum ether: ethyl acetate = 50:1). The solvent was removed and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 50:1) to afford **3a** as a solid (71 mg, 95%); mp 200.5-200.6 °C (petroleum ether/ethyl acetate); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69 (dd, *J* = 7.2 Hz, 3.2 Hz, 2 H), 7.48 (d, *J* = 8.8 Hz, 1 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.28-7.19 (m, 2 H), 7.18 (d, *J* = 3.2 Hz, 1 H), 7.12-7.07 (m, 1 H), 7.04-6.99 (m, 2 H), 6.98-6.90 (m, 3 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 3.87 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.2, 145.3, 140.4, 140.3, 138.8, 137.2, 135.4, 135.0, 131.7, 129.2, 128.3, 127.64, 127.58, 127.4, 126.4, 126.3, 124.8, 124.6,

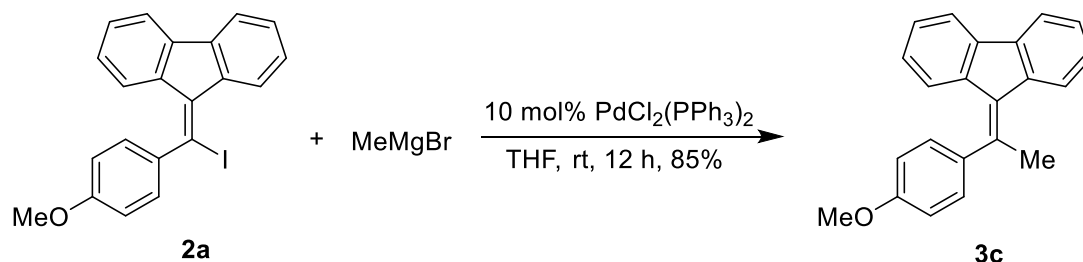
119.3, 119.2, 114.0, 55.3; IR (neat) 1604, 1573, 1504, 1445  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{25}\text{H}_{19}\text{OS}$  ( $\text{M}+\text{H}^+$ ): 367.1151, found: 367.1149.

### Synthesis of (3-(9H-fluoren-9-ylidene)-3-(4-methoxyphenyl)prop-1-yn-1-yl)trimethylsilane (**3b**)



To a 25 mL of dry glass reaction tube was added **2a** (82 mg, 0.2 mmol), ethynyltrimethylsilane (50  $\mu\text{L}$ , 0.35 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (9 mg, 0.013 mmol),  $\text{CuI}$  (4 mg, 0.021 mmol),  $\text{Et}_3\text{N}$  (2 mL). The mixture was stirred at 80  $^\circ\text{C}$  under argon atmosphere. The reaction was completed after 12 h as monitored by TLC (eluent: petroleum ether: ethyl acetate = 50:1). The solvent was removed and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 50:1) to afford **3b** as a solid (71 mg, 93%); mp 137.0-137.3  $^\circ\text{C}$  (petroleum ether/ethyl acetate);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.87 (d,  $J$  = 7.6 Hz, 1 H), 7.69 (d,  $J$  = 7.6 Hz, 1 H), 7.63 (d,  $J$  = 7.6 Hz, 1 H), 7.42-7.29 (m, 4 H), 7.21 (t,  $J$  = 7.6 Hz, 1 H), 6.99 (d,  $J$  = 8.0 Hz, 2 H), 6.89 (t,  $J$  = 7.8 Hz, 1 H), 6.59 (d,  $J$  = 8.0 Hz, 1 H), 3.89 (s, 3 H), 0.31 (s, 9 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 140.3, 140.2, 138.1, 137.6, 131.9, 130.4, 128.8, 128.4, 127.0, 126.6, 125.5, 125.1, 119.3, 119.2, 114.3, 108.2, 106.9, 55.3, -0.2; IR (neat) 1606, 1510, 1447  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{26}\text{H}_{25}\text{OSi}$  ( $\text{M}+\text{H}^+$ ): 381.1669, found: 381.1659.

### Synthesis of 9-(1-(4-methoxyphenyl)ethylidene)-9H-fluorene (**3c**)

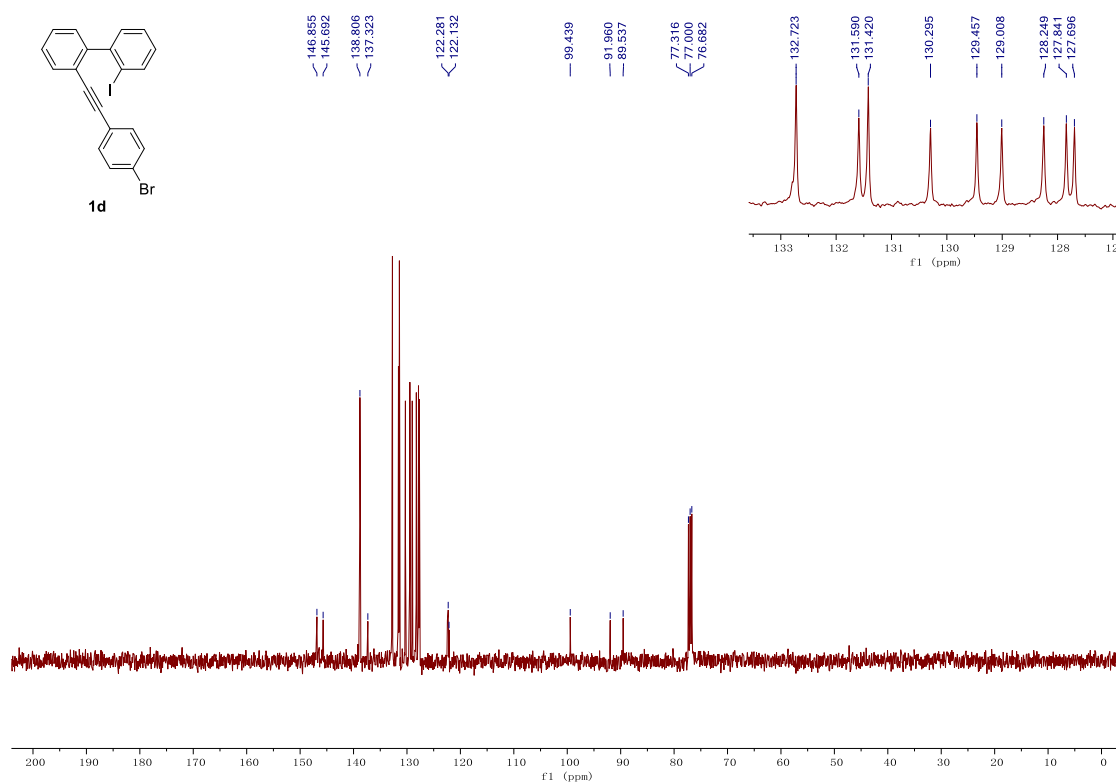
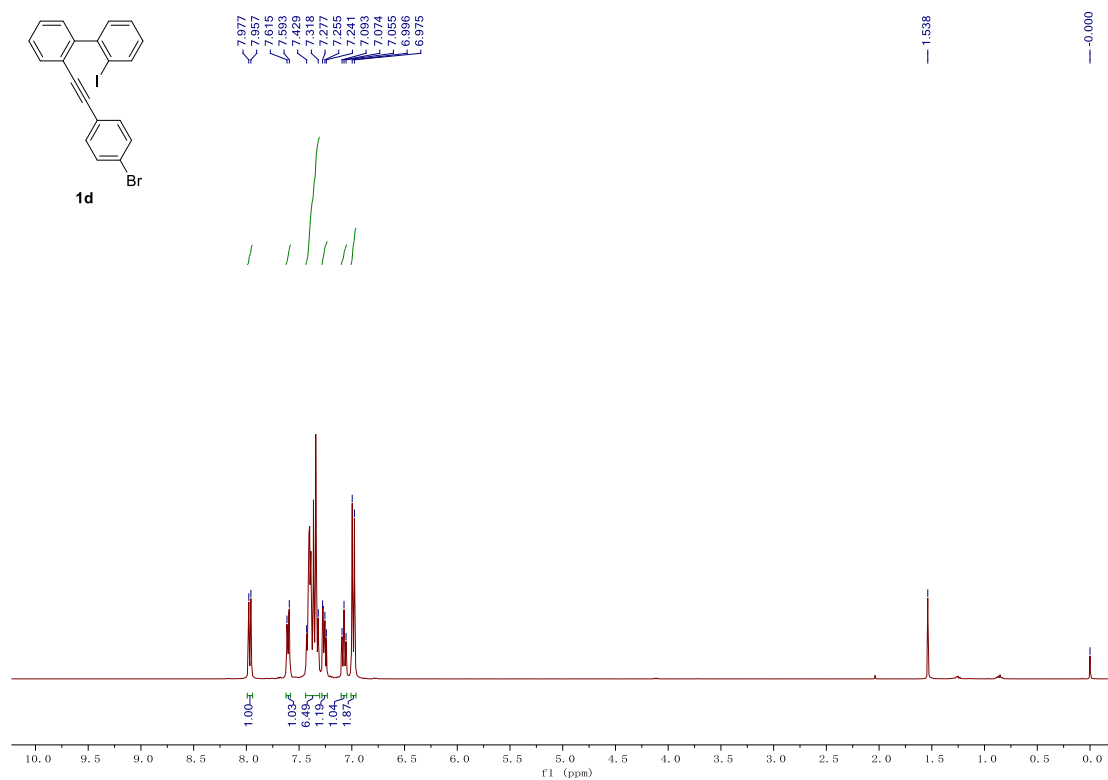


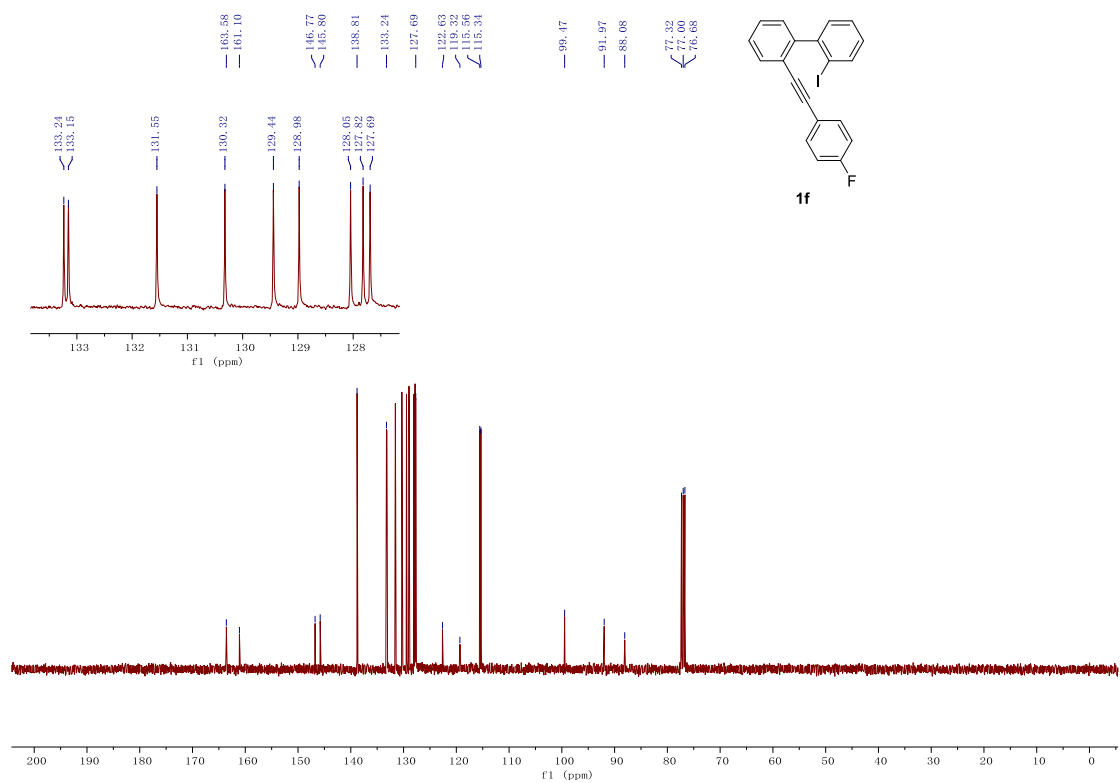
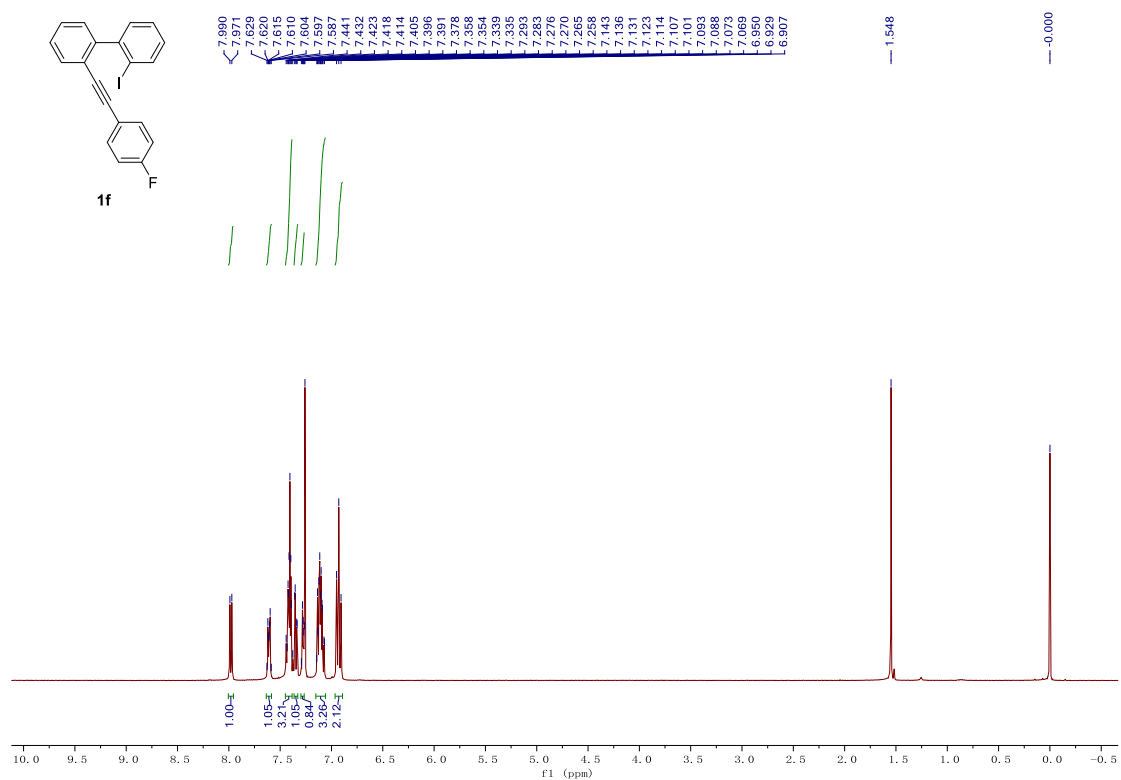
To a 25 mL of dry glass reaction tube was added **2a** (82 mg, 0.2 mmol),  $\text{MeMgBr}$  (1.0 M in THF, 0.4 mL, 0.4 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (9 mg, 0.013 mmol), THF (2 mL). The

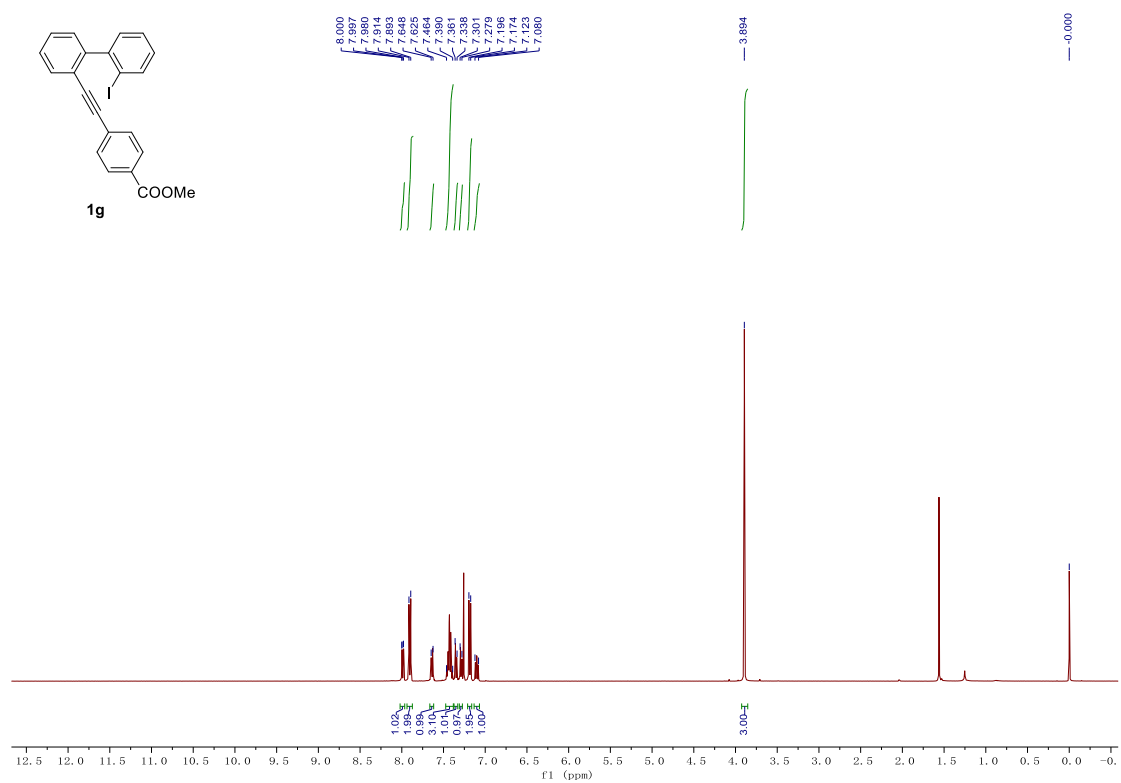
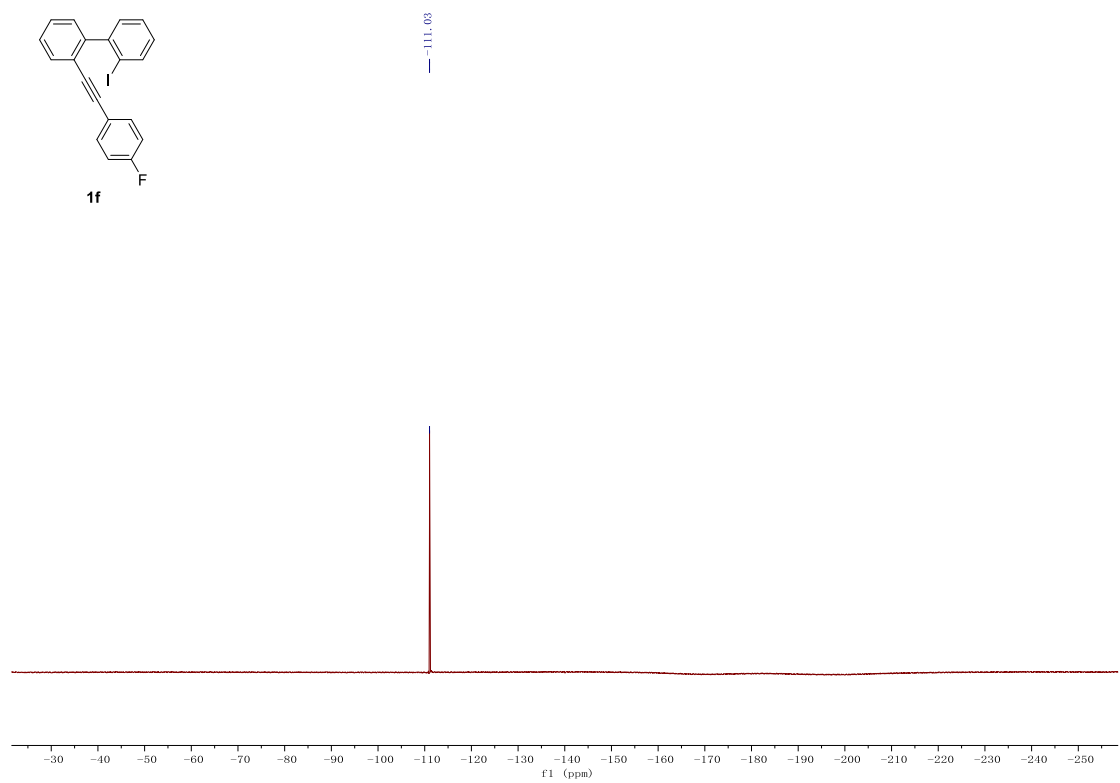


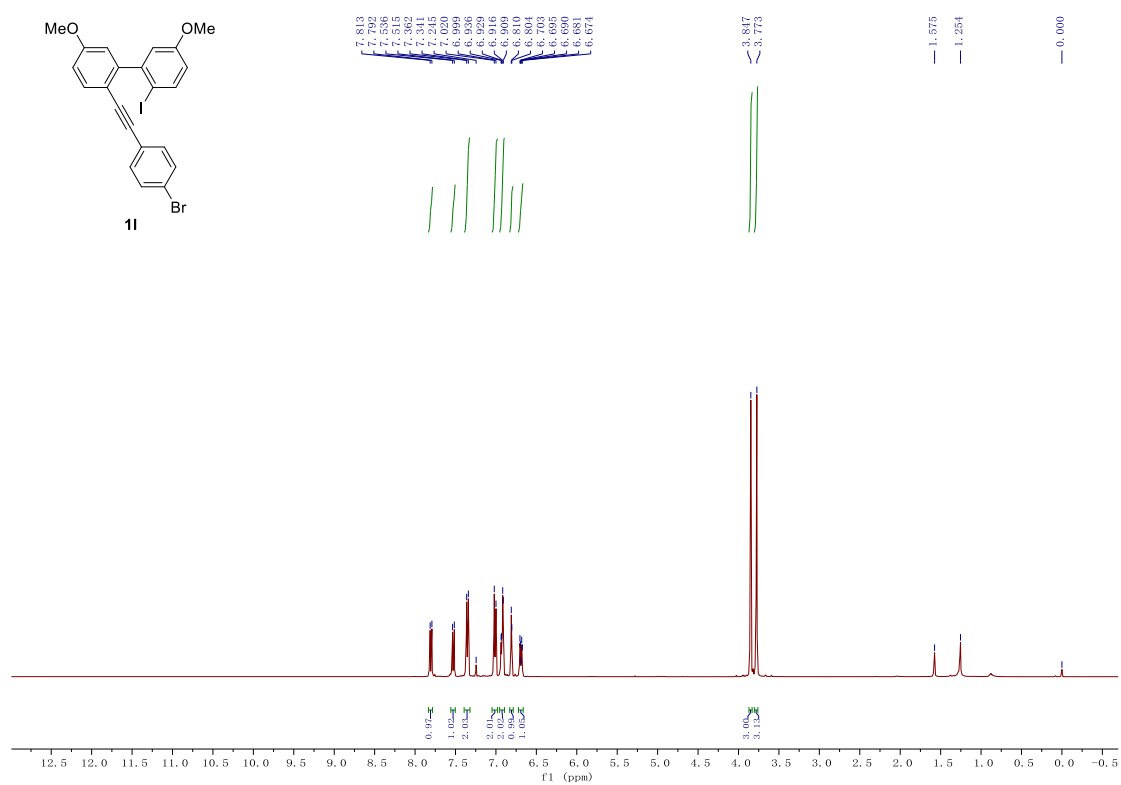
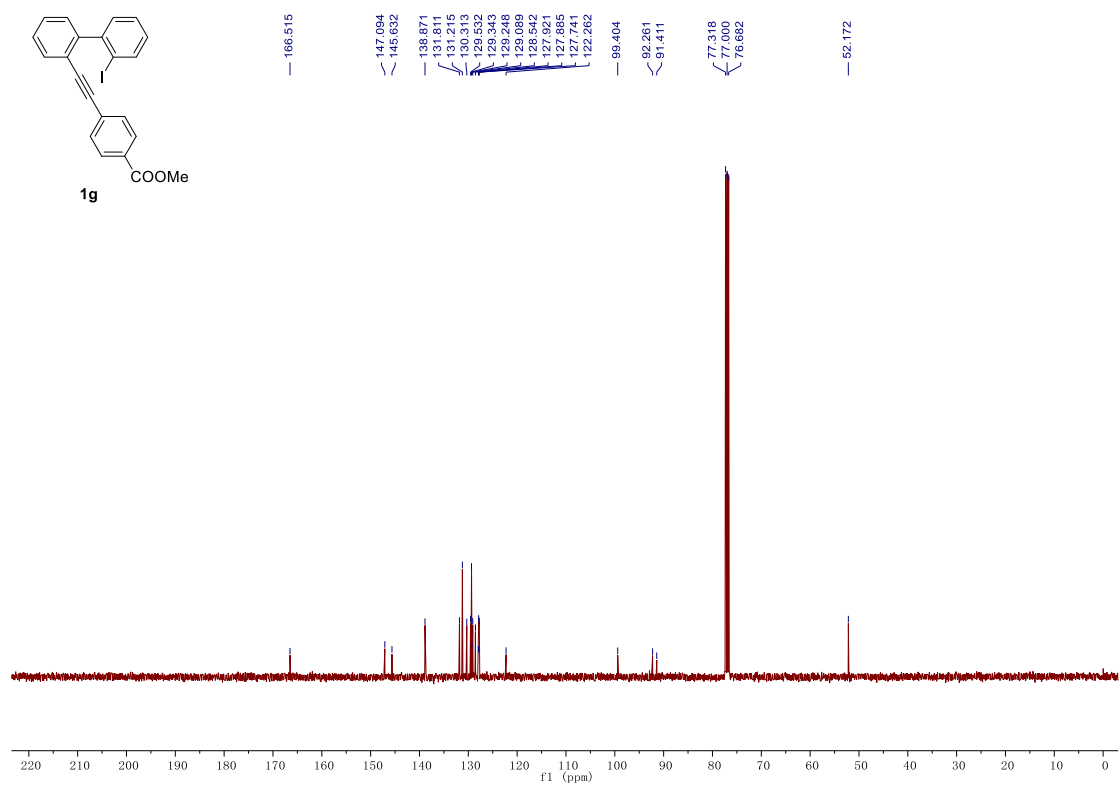
mixture was stirred at rt under argon atmosphere. The reaction was completed after 12 h as monitored by TLC (eluent: petroleum ether: ethyl acetate = 50:1). The solvent was removed and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 50:1) to afford **3c** as a solid (51 mg, 85%); mp 123.4-123.6 °C (petroleum ether/ethyl acetate); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 (d, *J* = 6.8 Hz, 1 H), 7.78 (d, *J* = 7.2 Hz, 1 H), 7.68 (d, *J* = 7.6 Hz, 1 H), 7.40-7.31 (m, 2 H), 7.29-7.21 (m, 2 H), 7.18 (t, *J* = 7.4 Hz, 1 H), 6.99 (d, *J* = 7.6 Hz, 2 H), 6.89 (t, *J* = 7.6 Hz, 1 H), 6.40 (d, *J* = 8.0 Hz, 1 H), 3.89 (s, 3 H), 2.74 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.2, 142.8, 140.4, 139.5, 139.0, 138.7, 137.7, 133.1, 129.2, 127.1, 126.8, 126.7, 126.4, 125.2, 124.5, 119.5, 119.0, 114.4, 55.3, 26.1; IR (neat) 1609, 1573, 1507, 1445 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>22</sub>H<sub>19</sub>O (M+H<sup>+</sup>): 299.1430, found: 299.1448

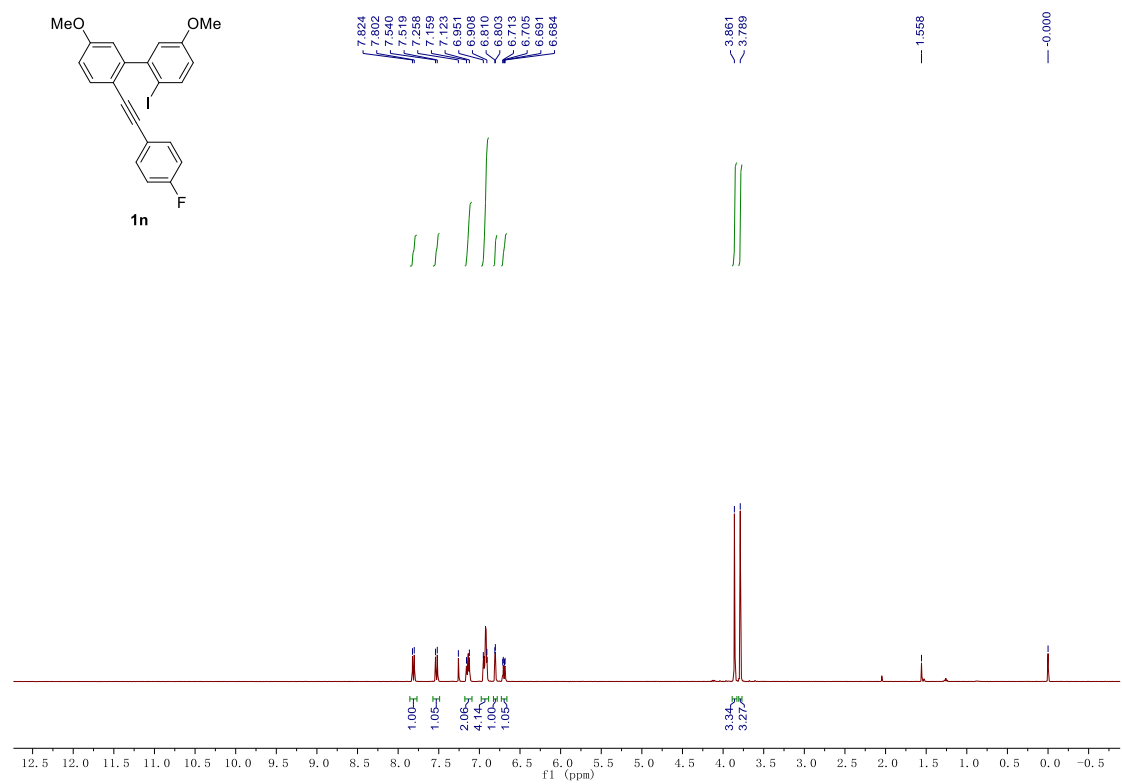
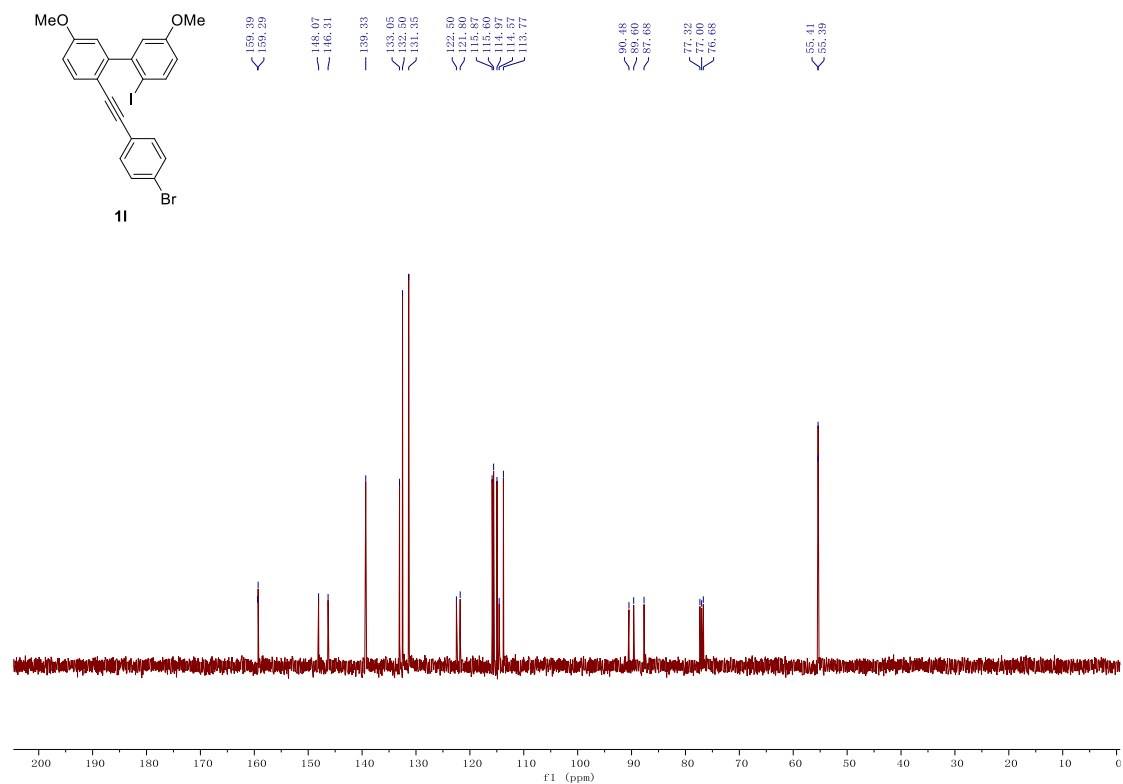
# NMR Spectra

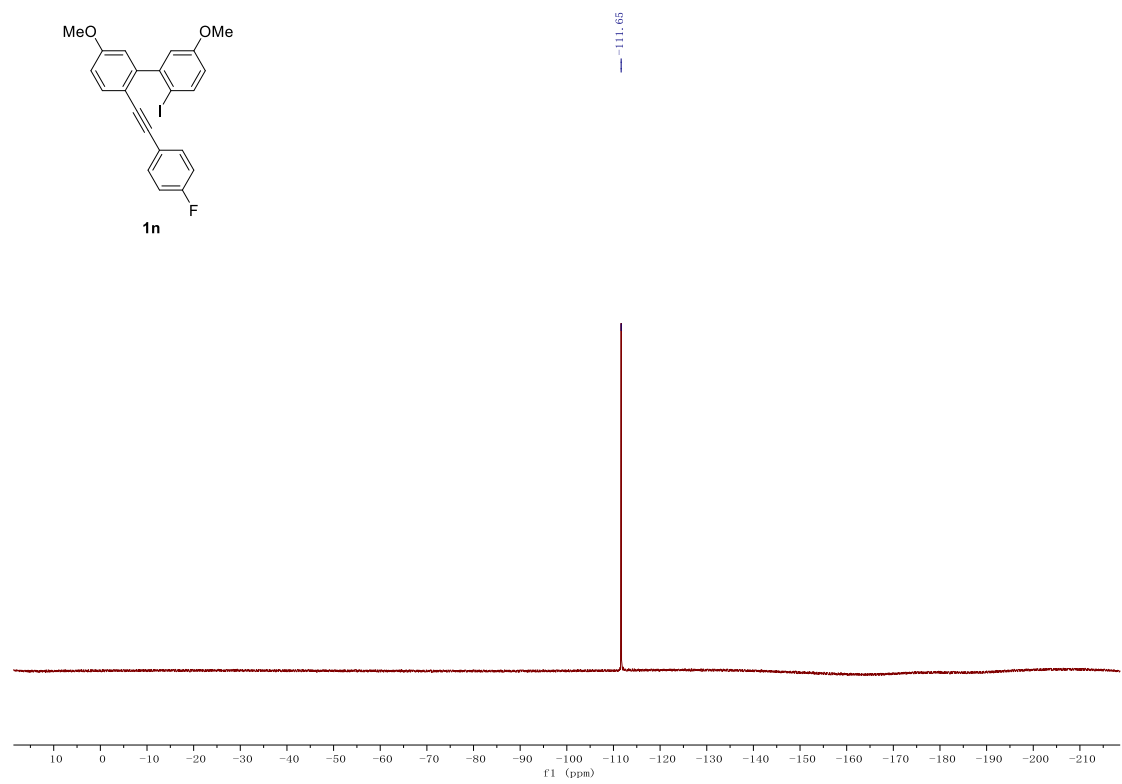
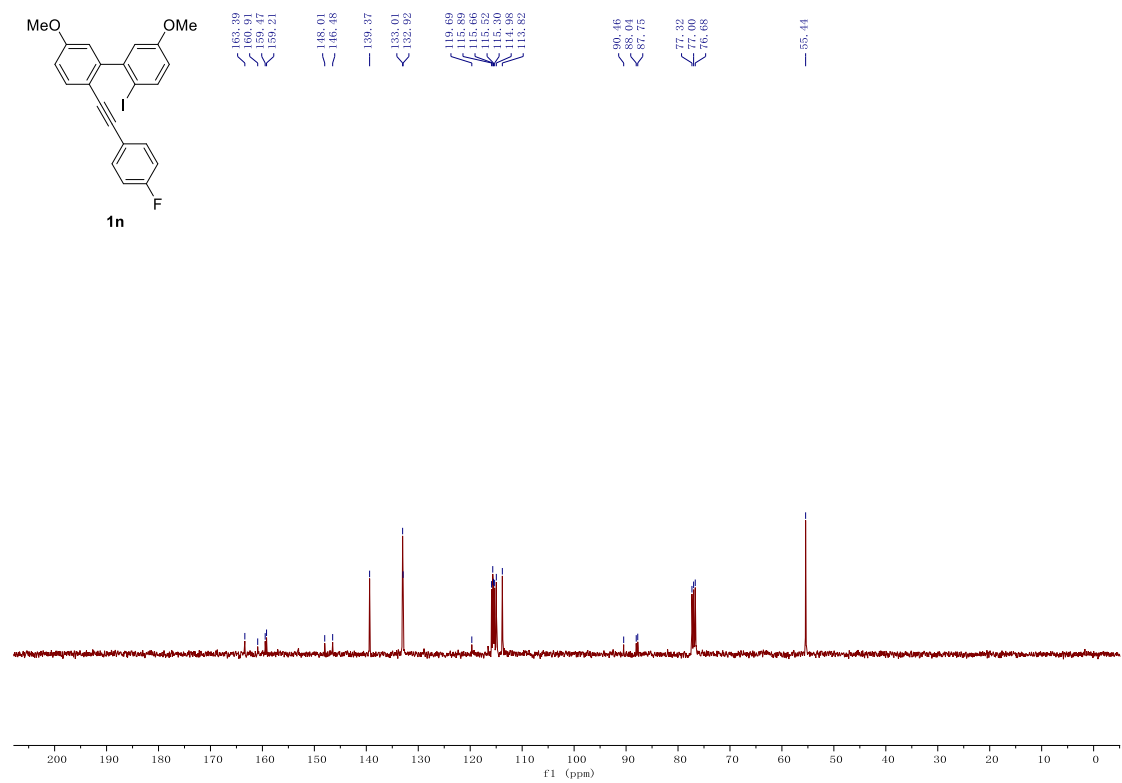


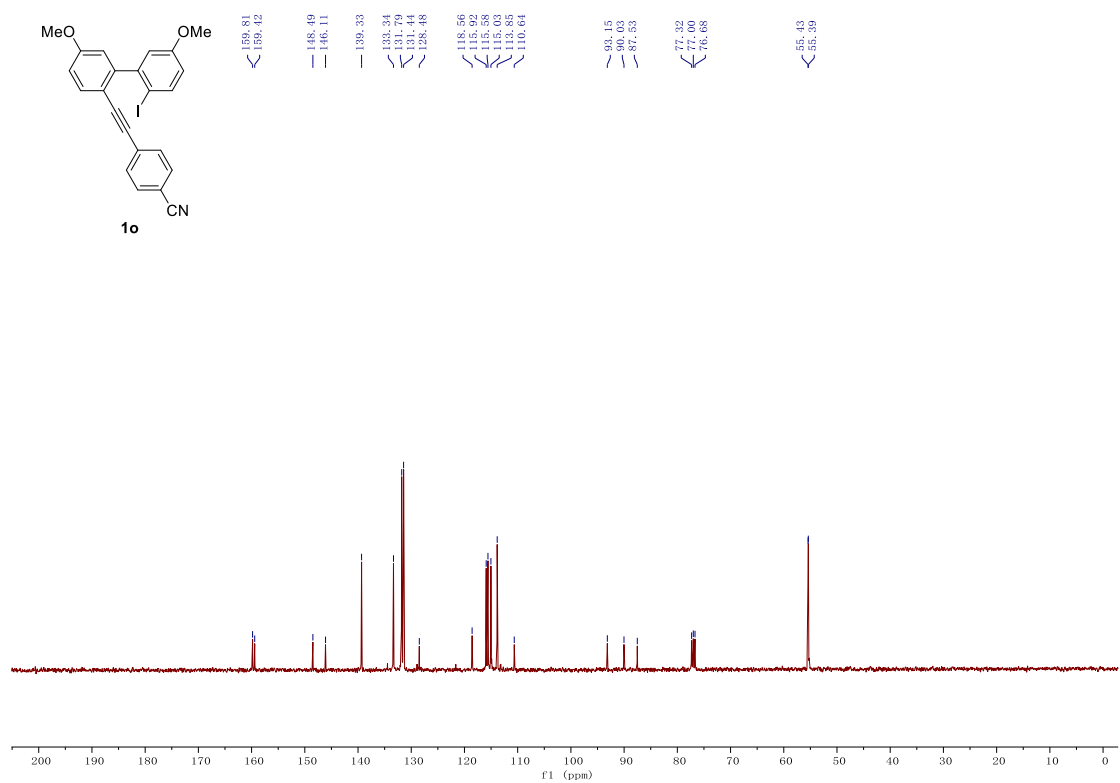
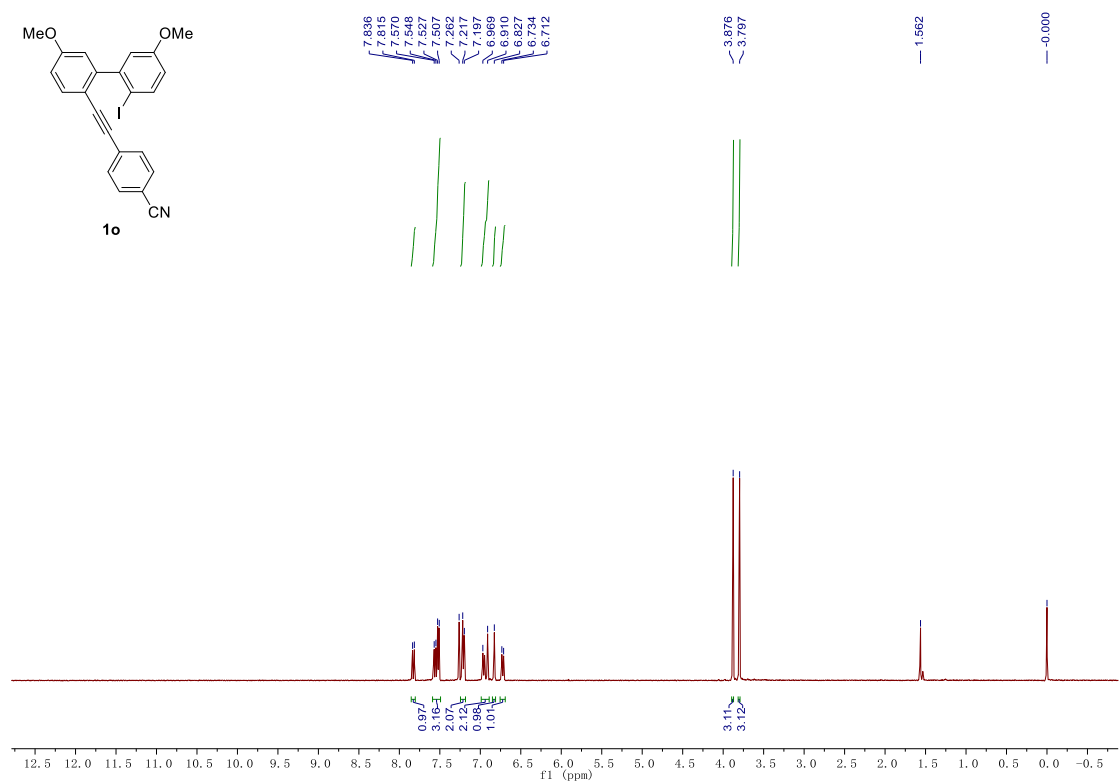




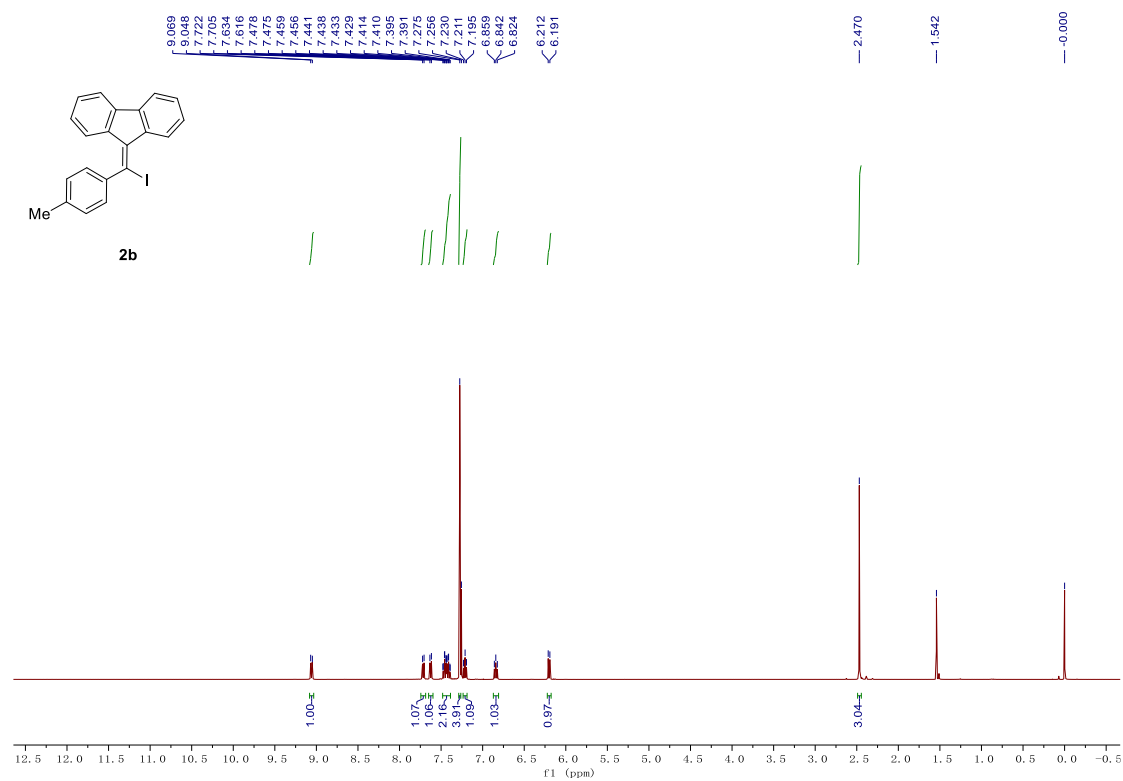
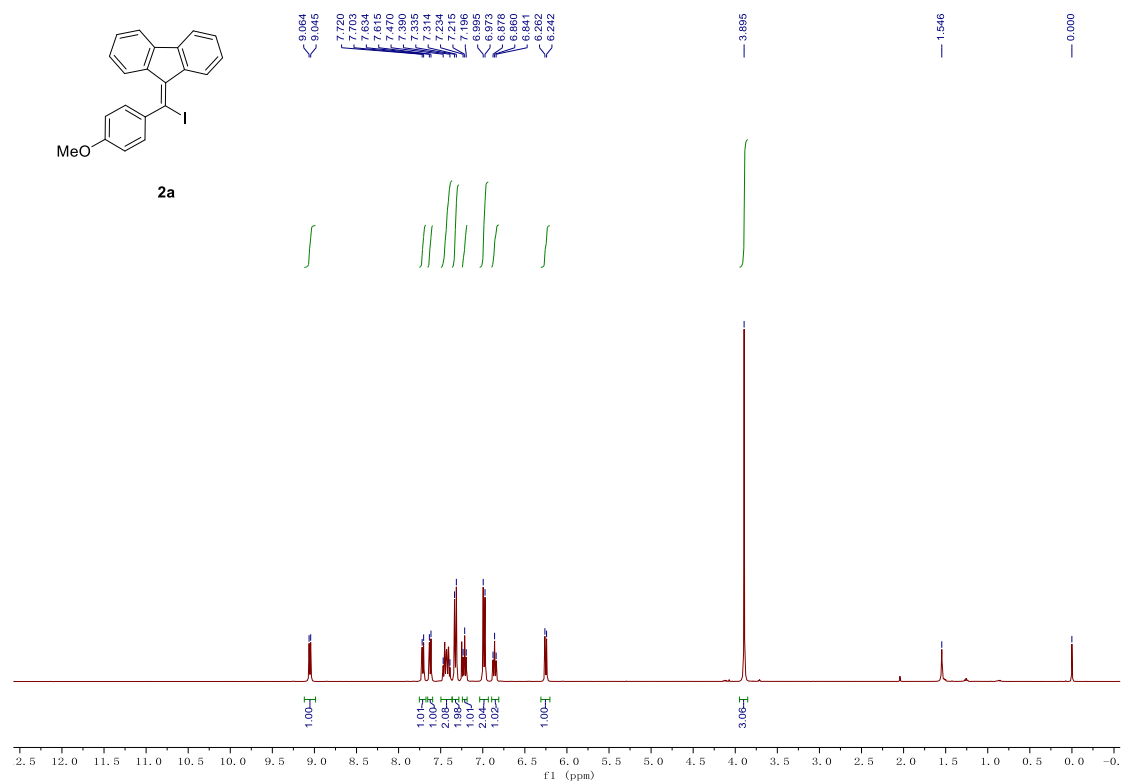


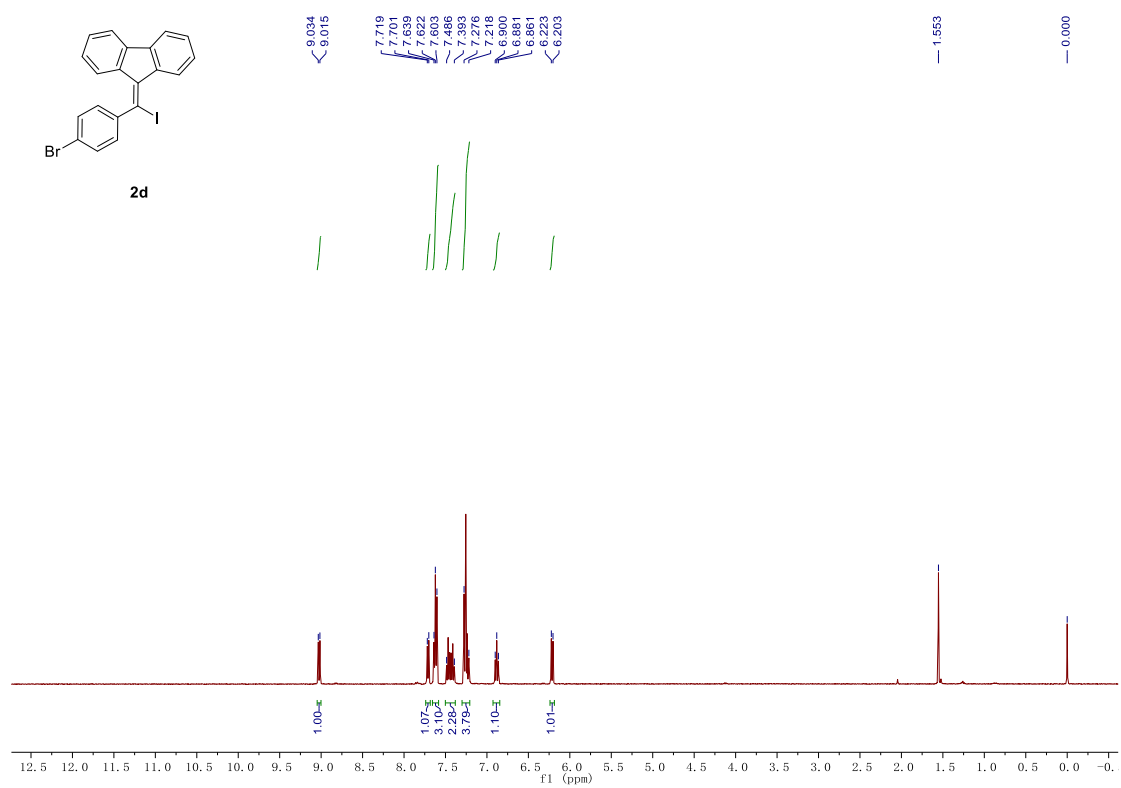
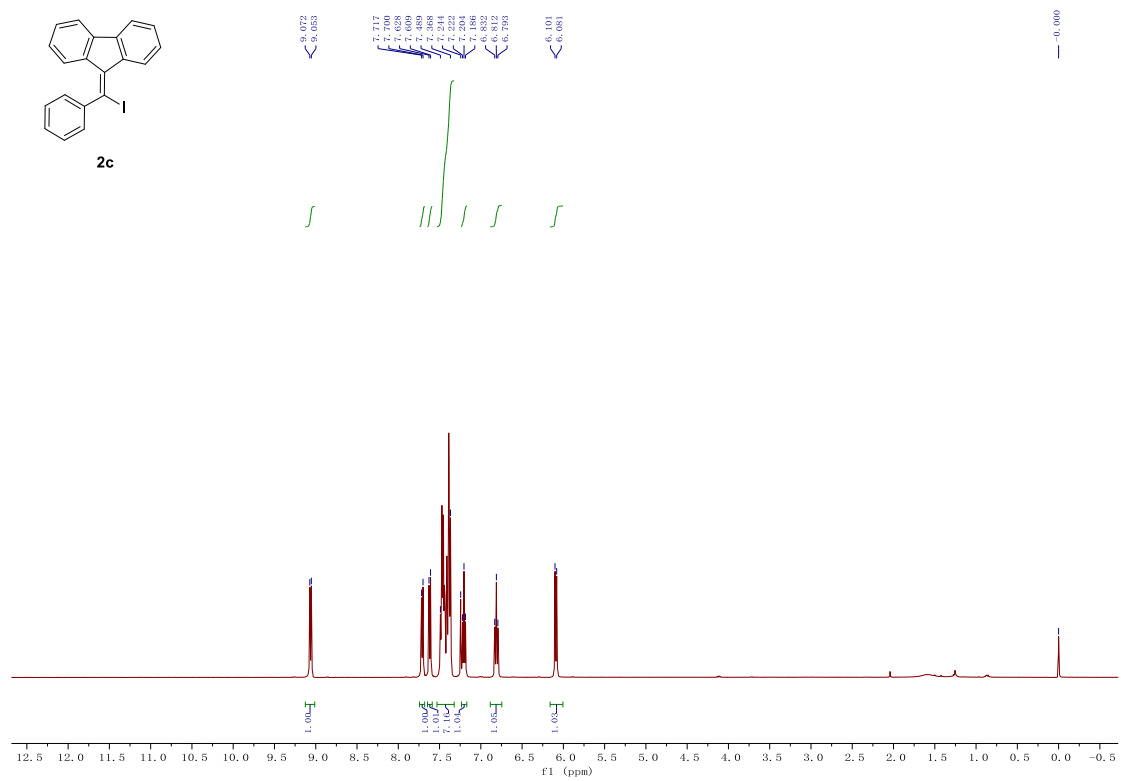


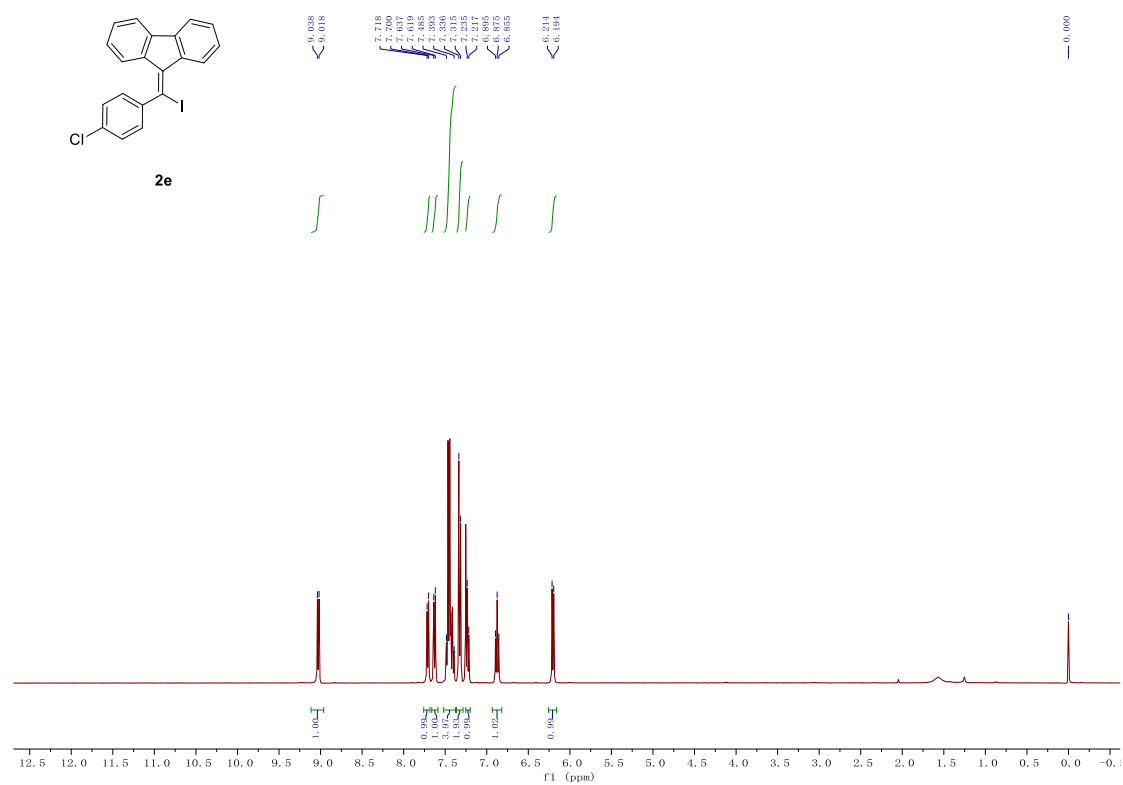
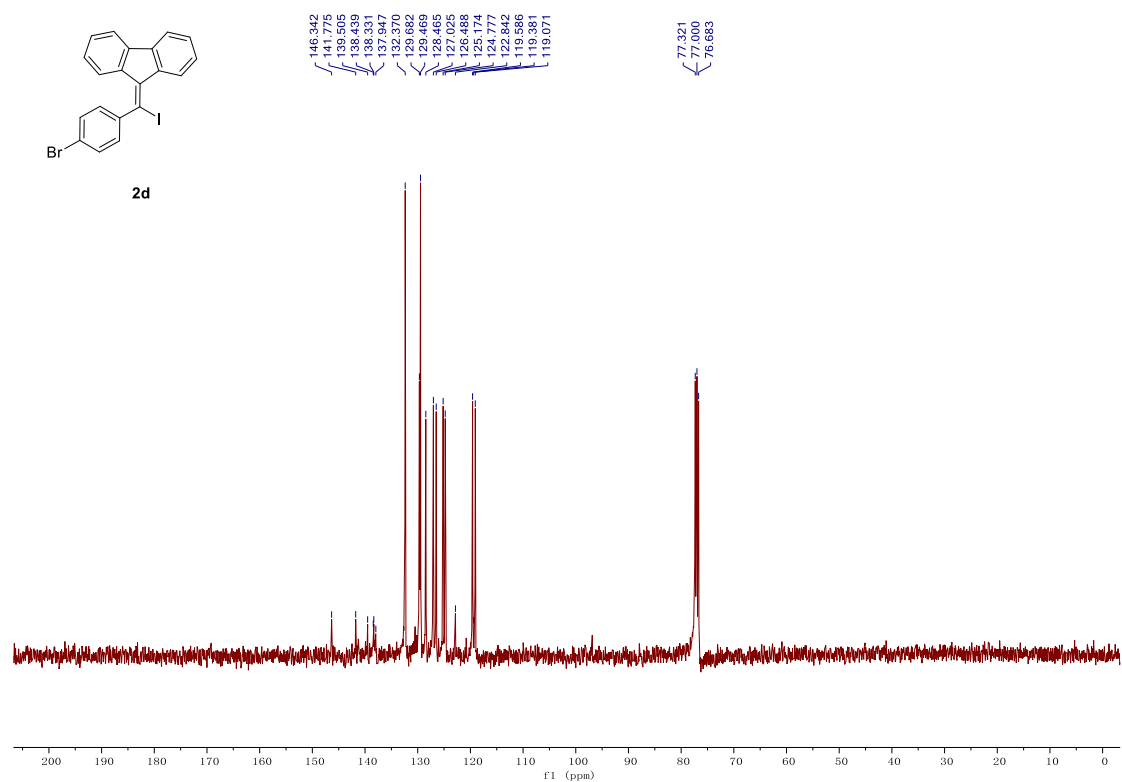


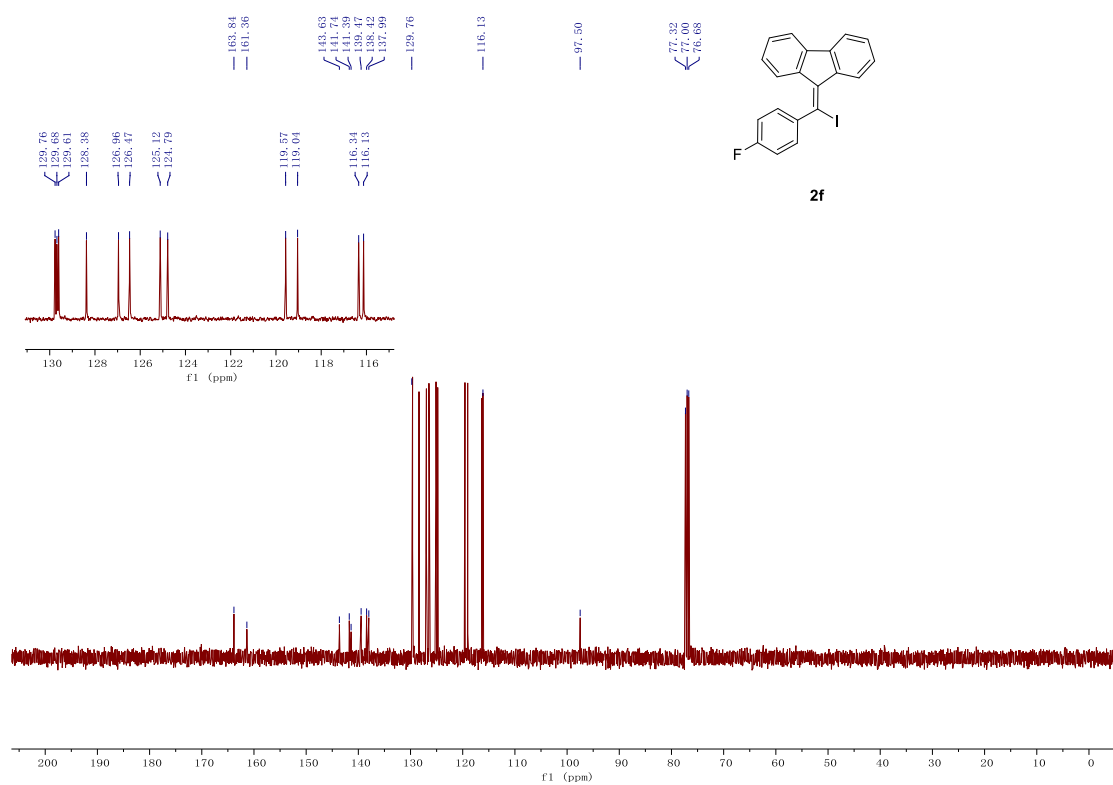
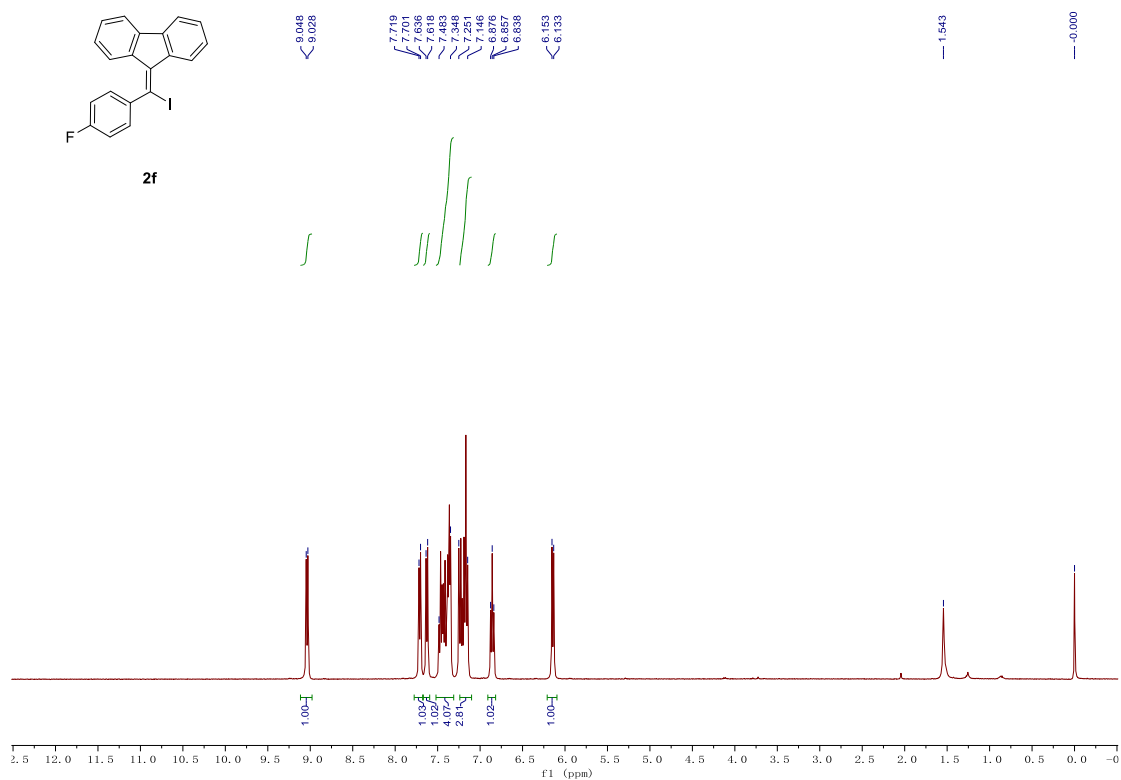


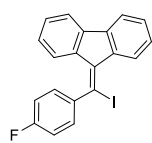




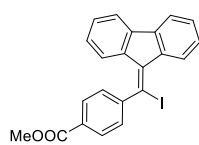
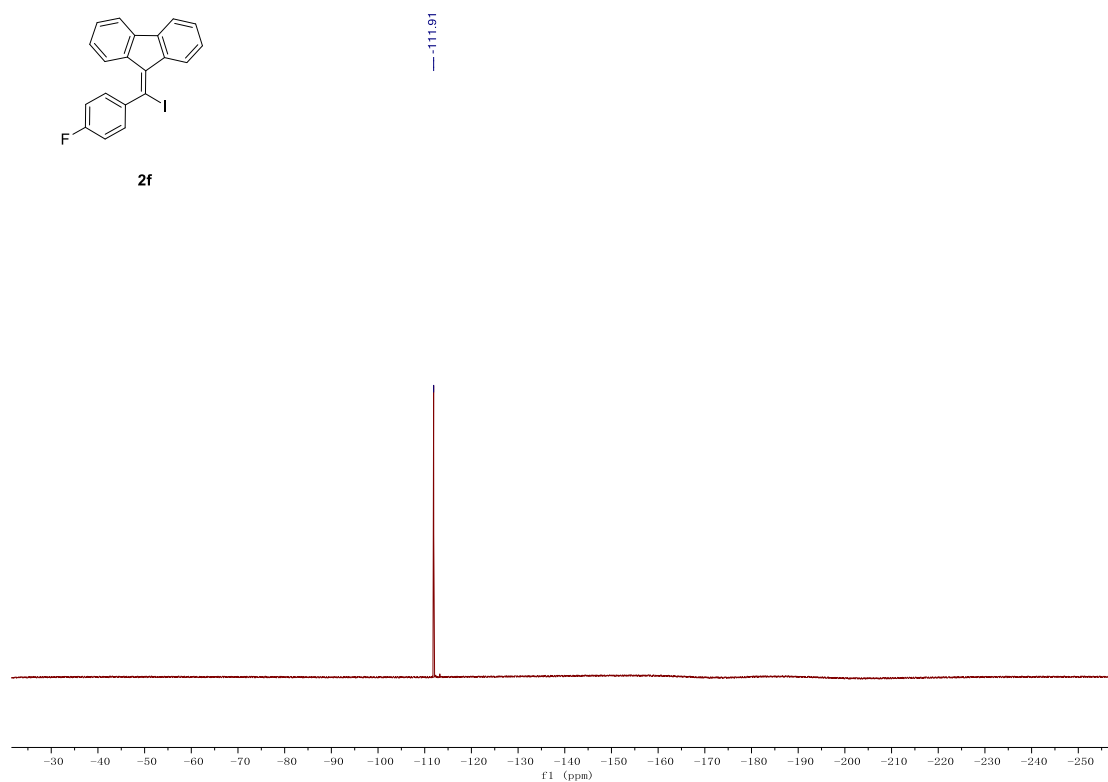




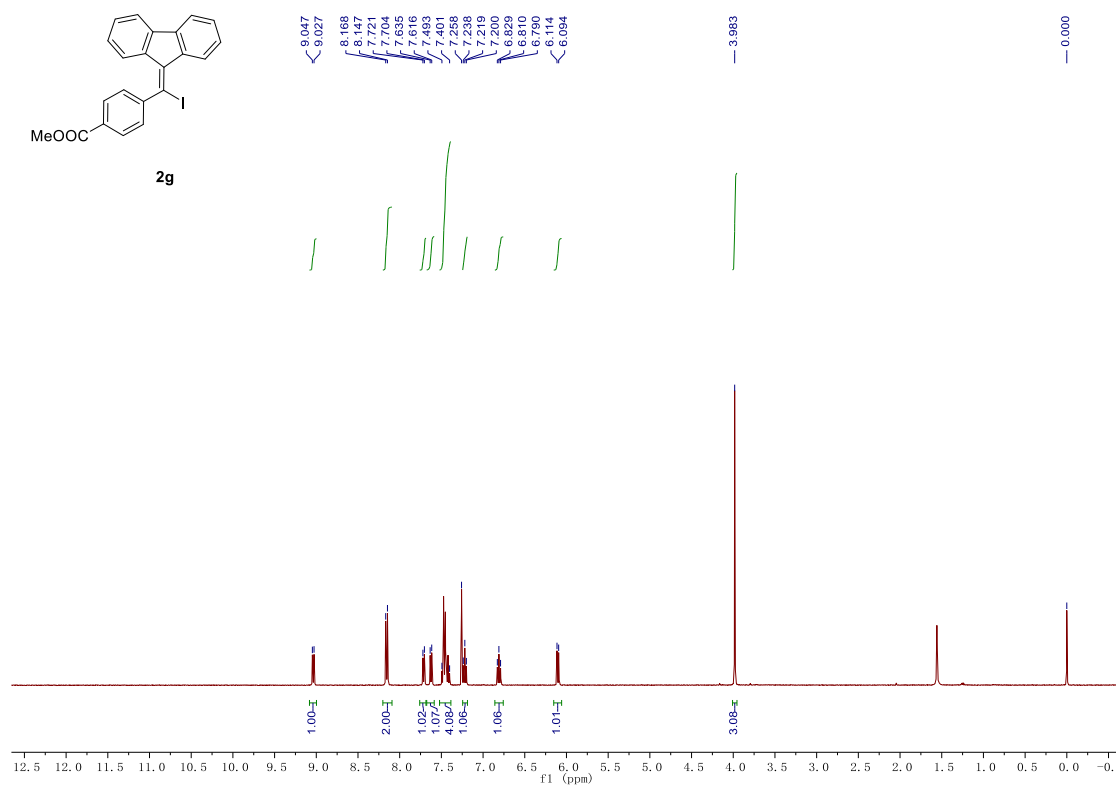


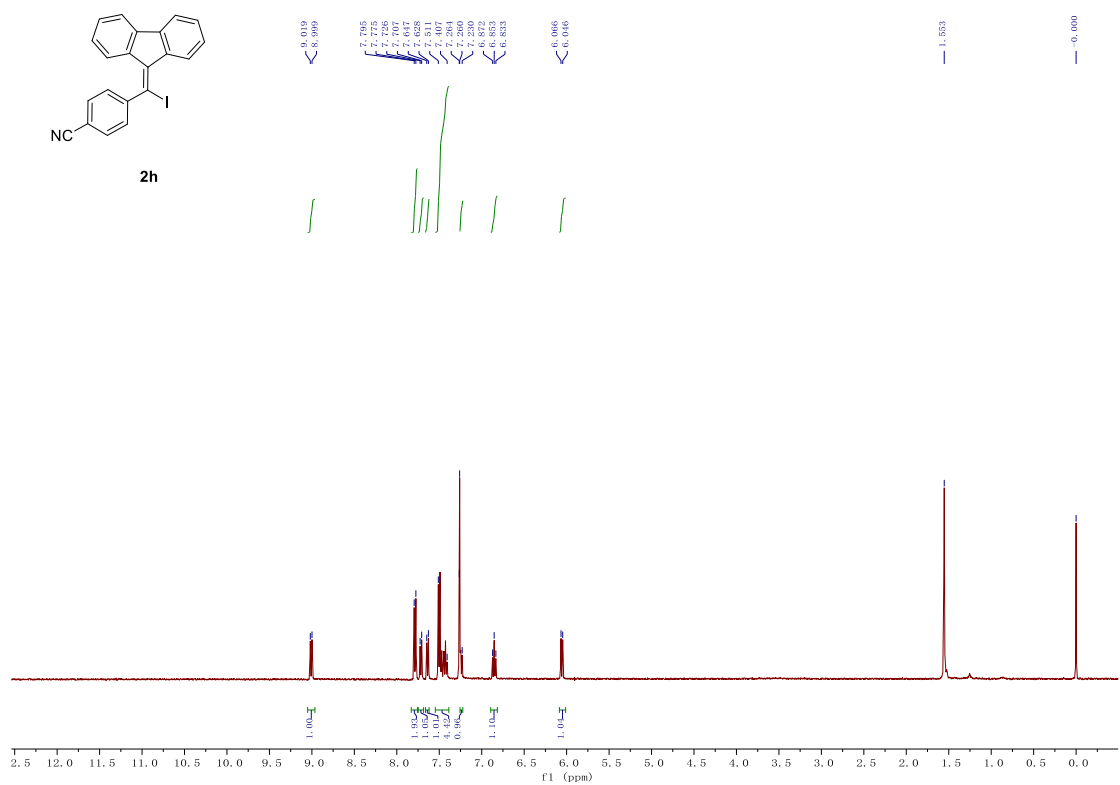
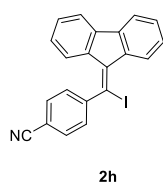
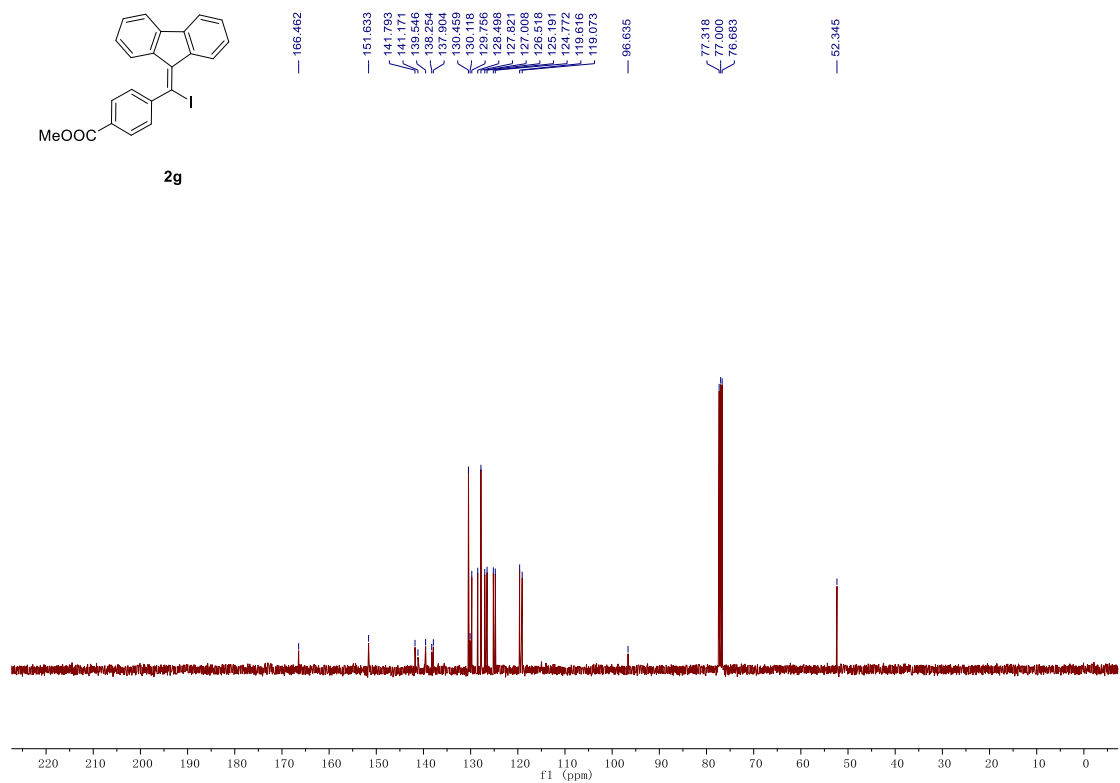
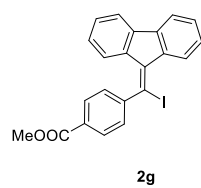


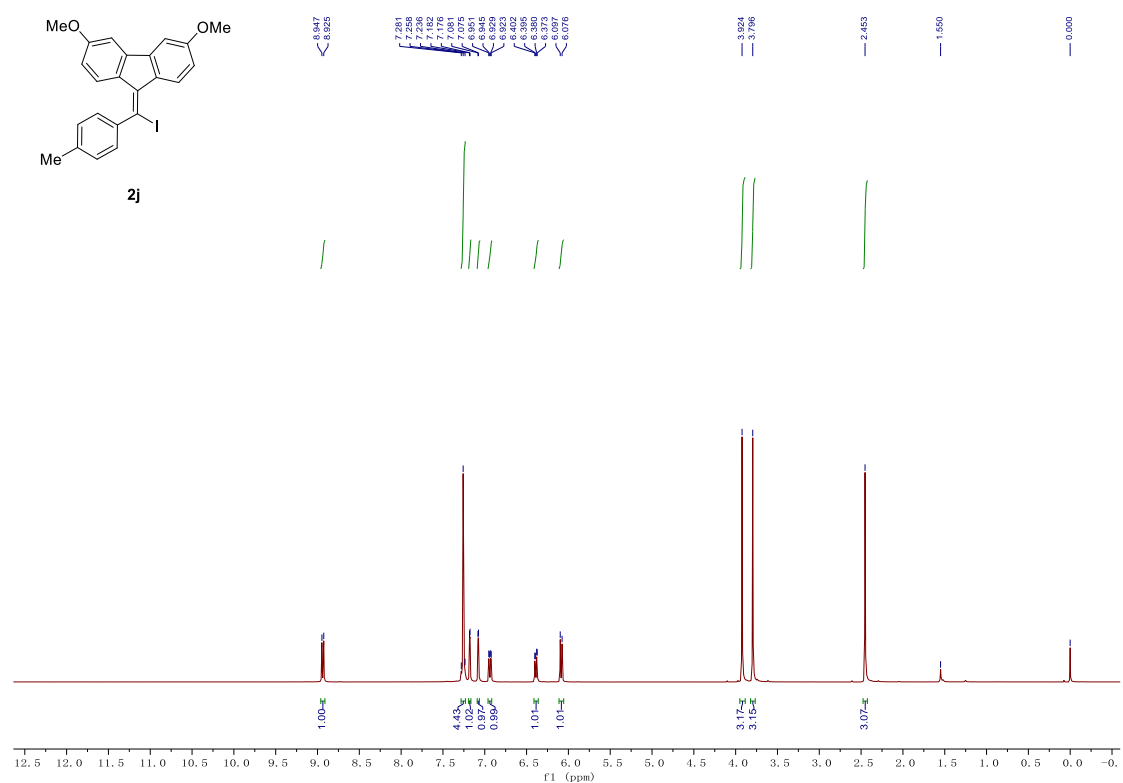
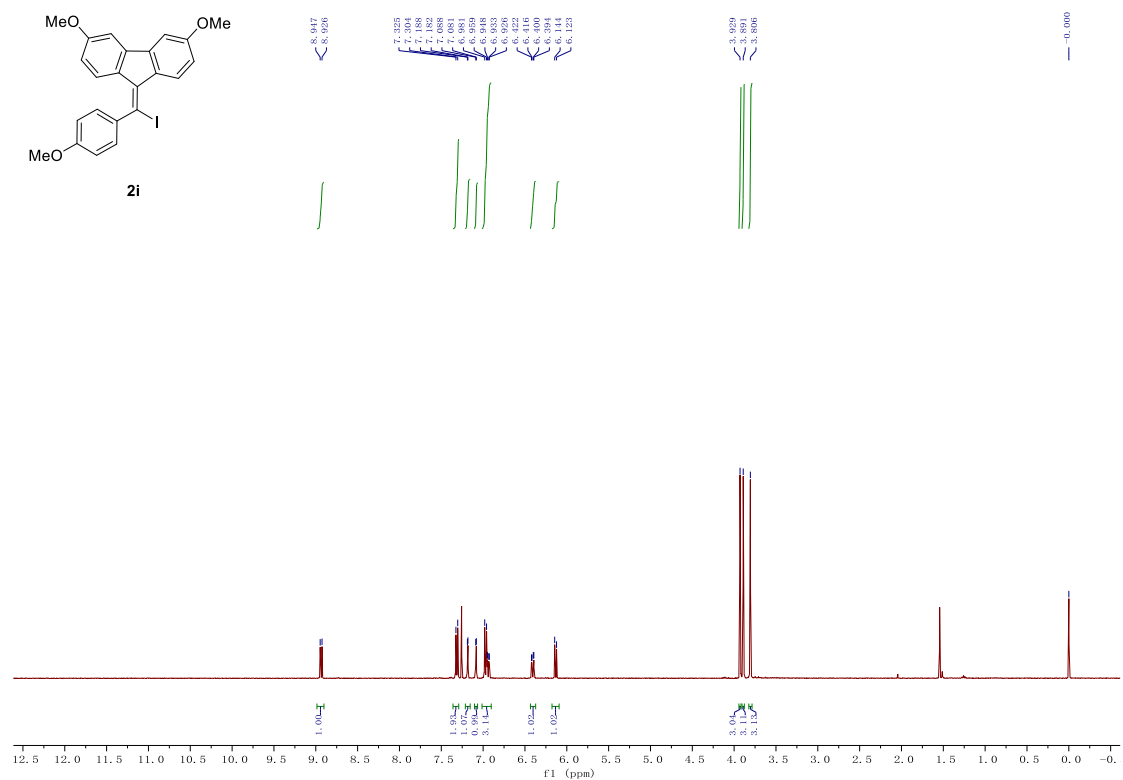
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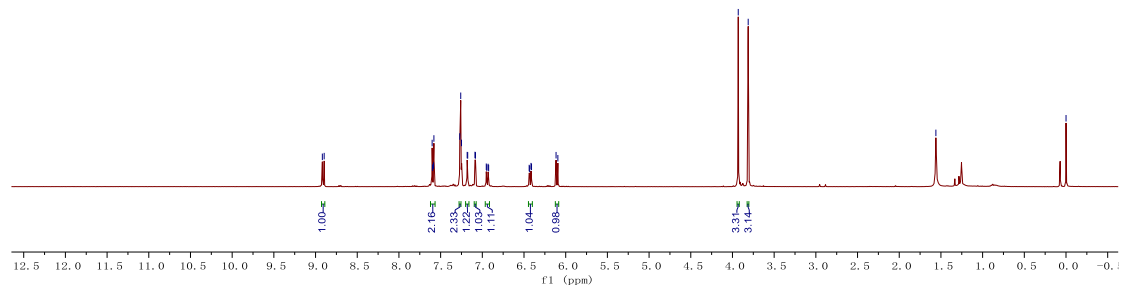
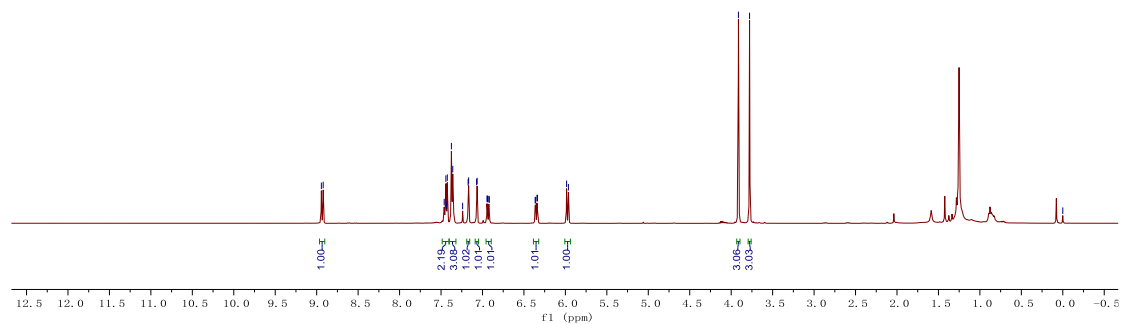


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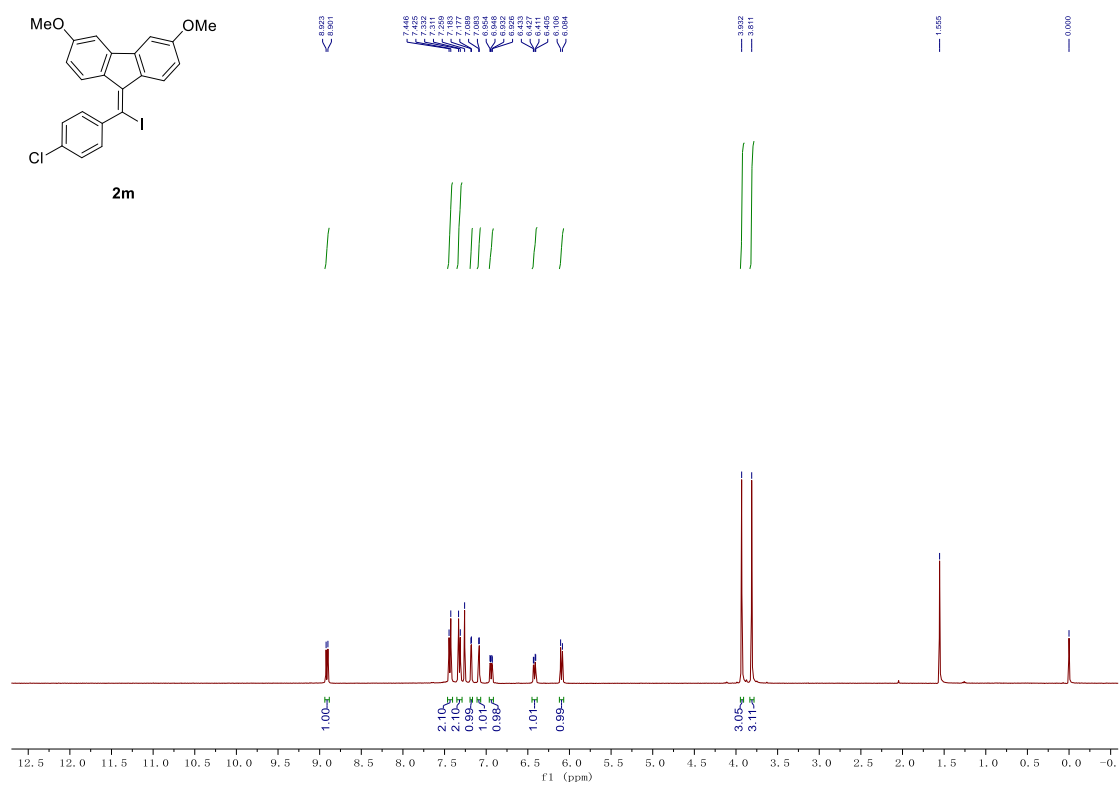
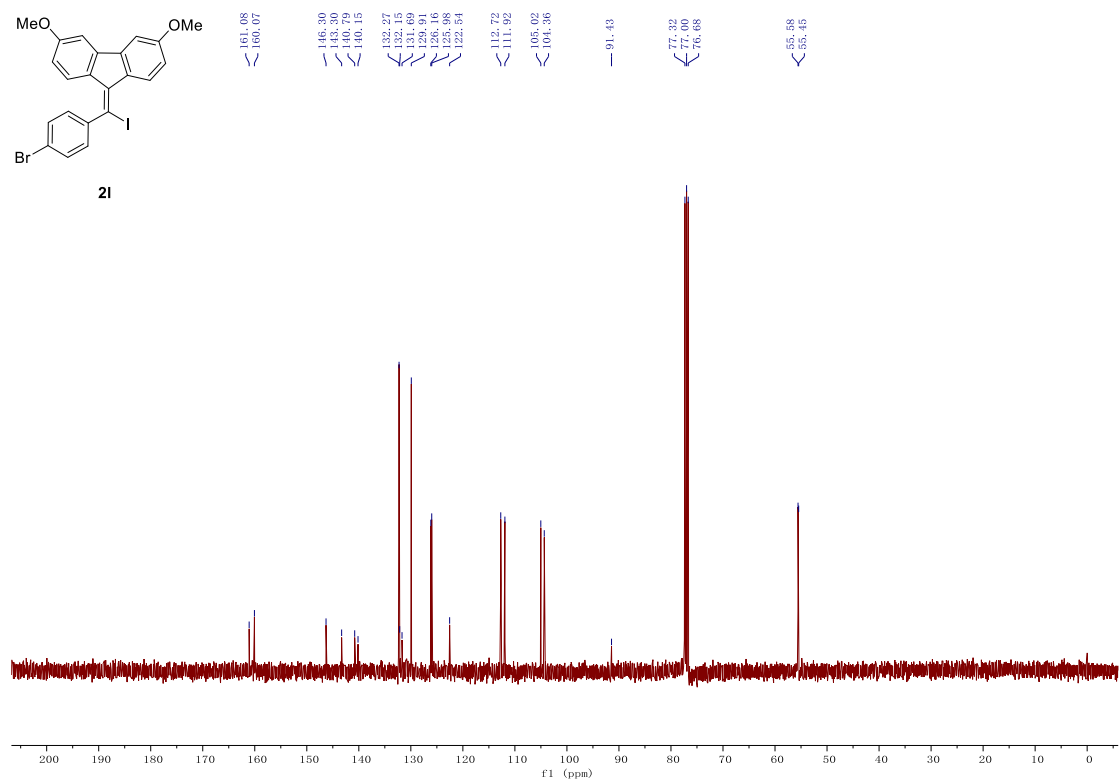


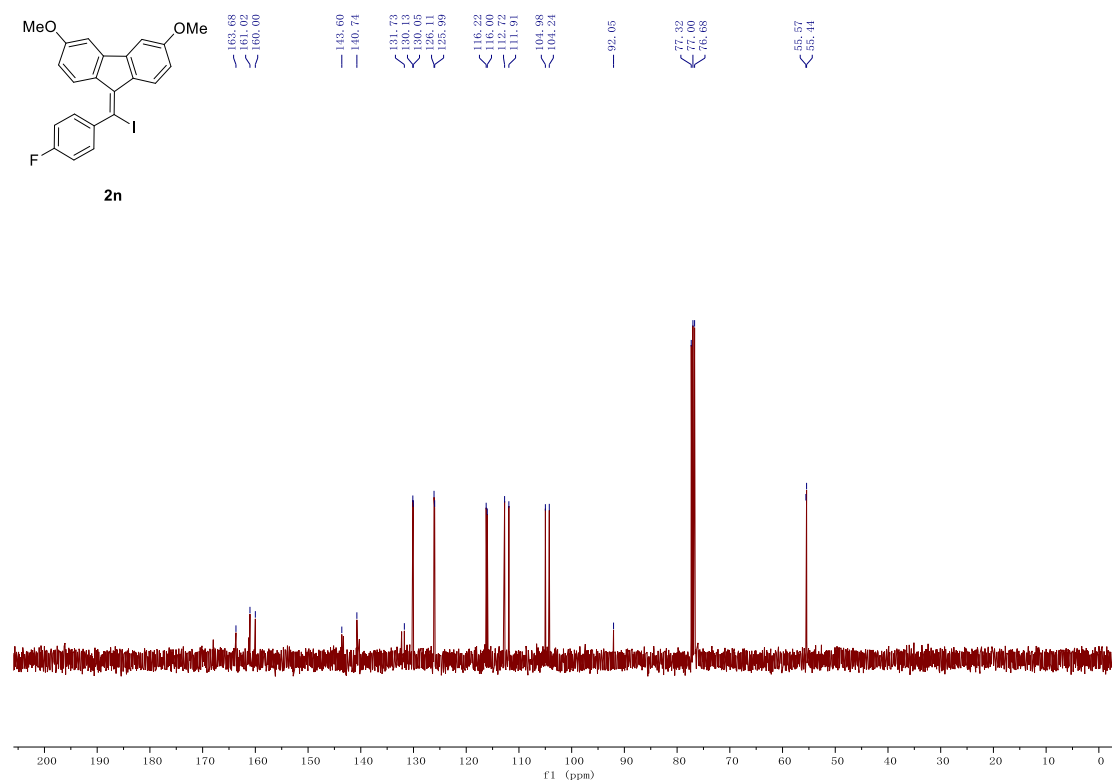
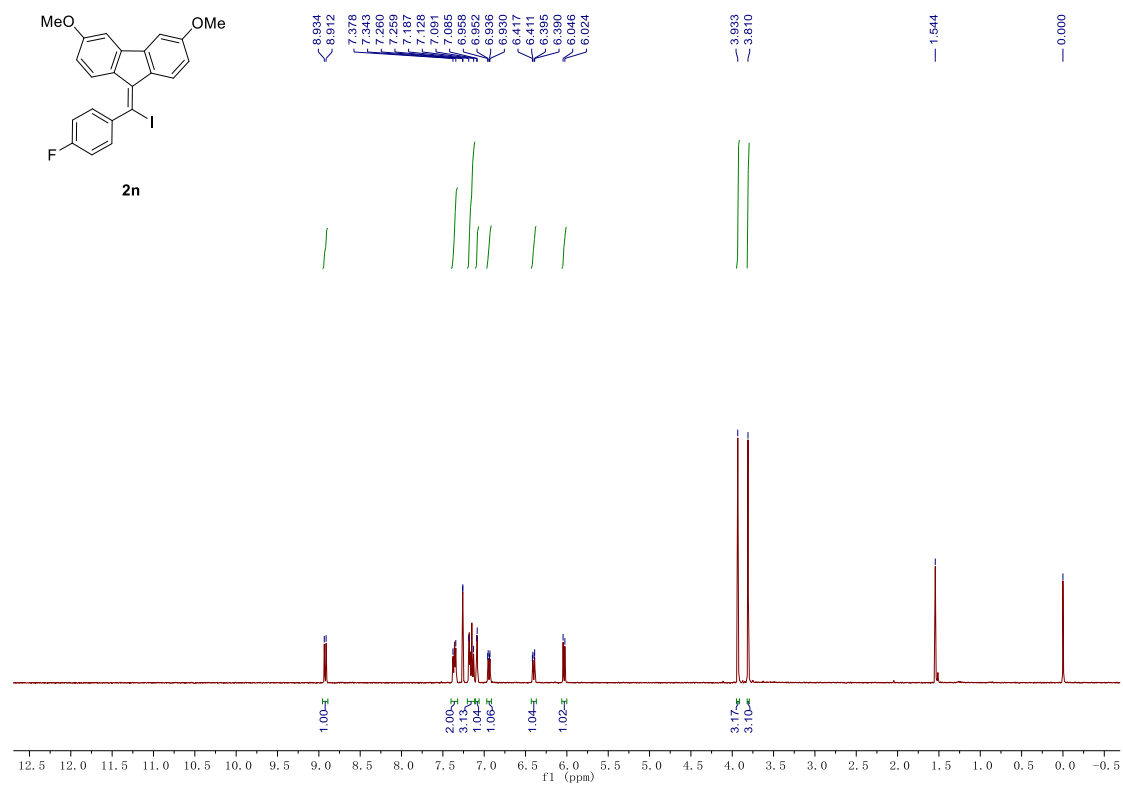


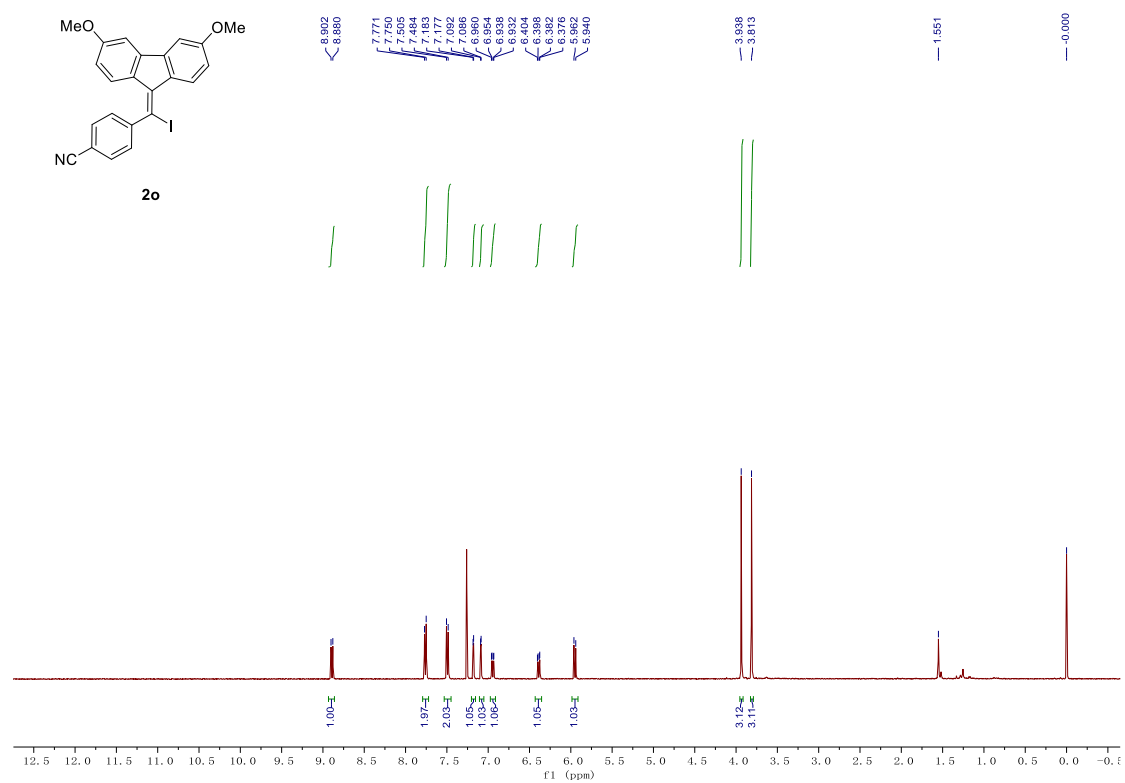
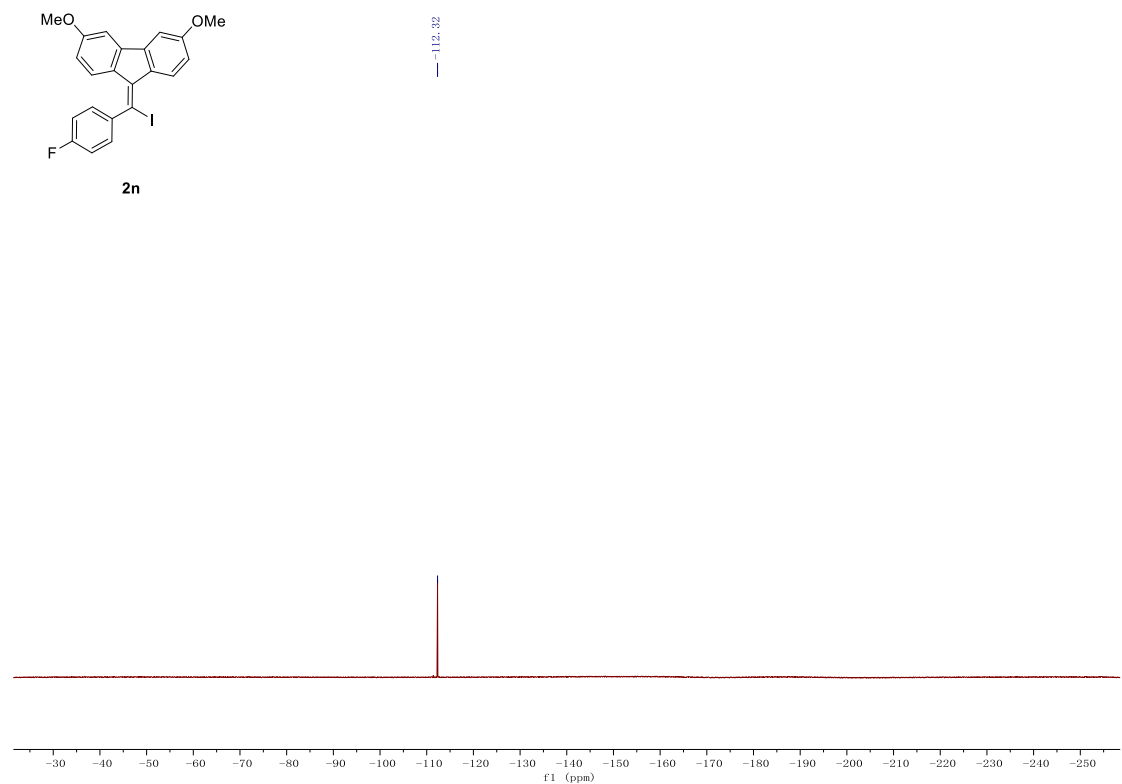


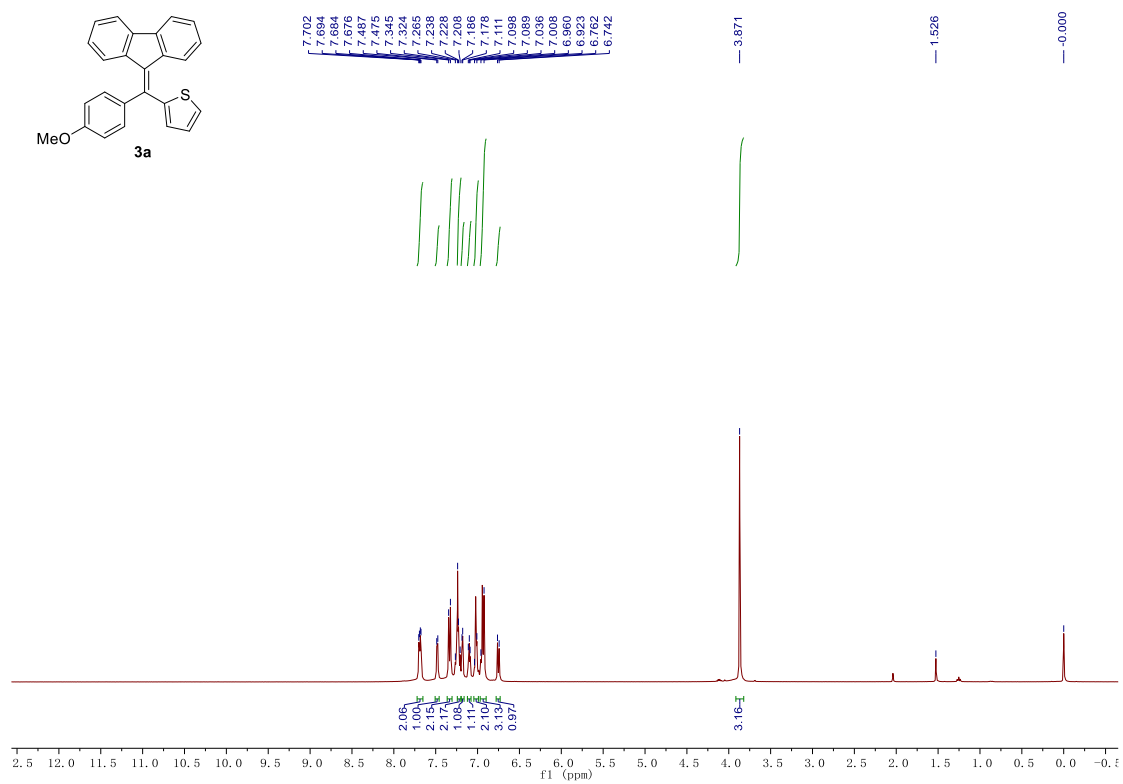
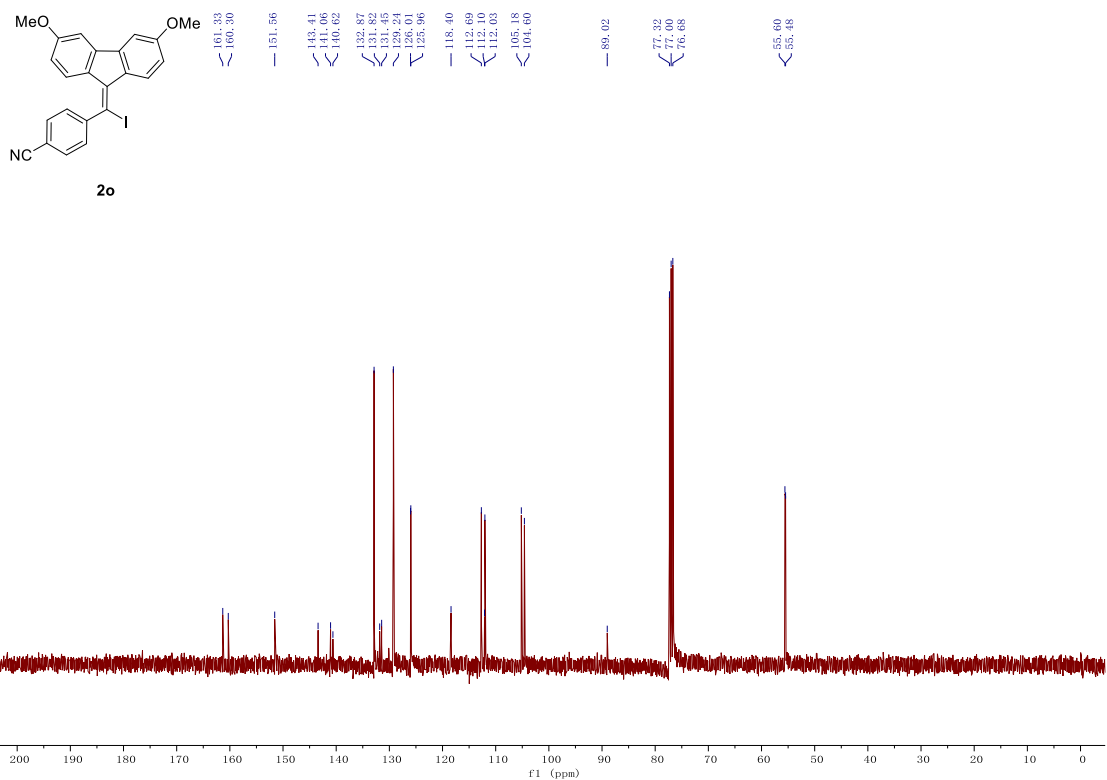


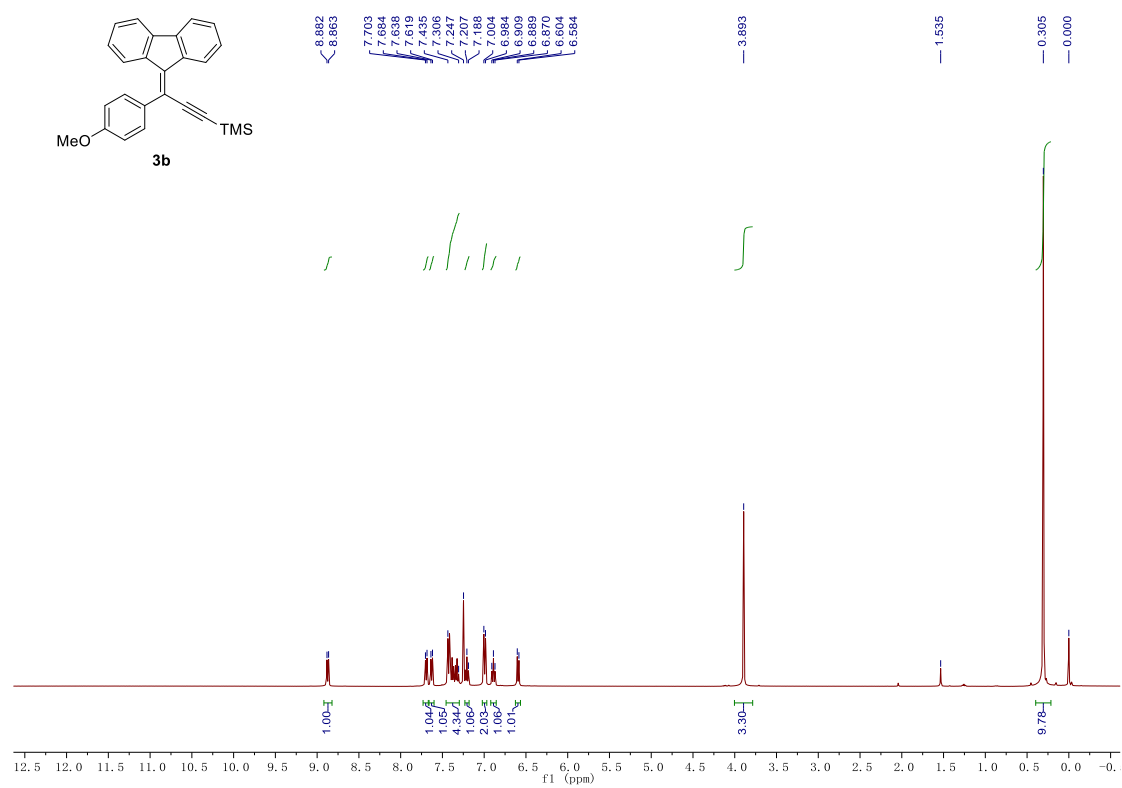
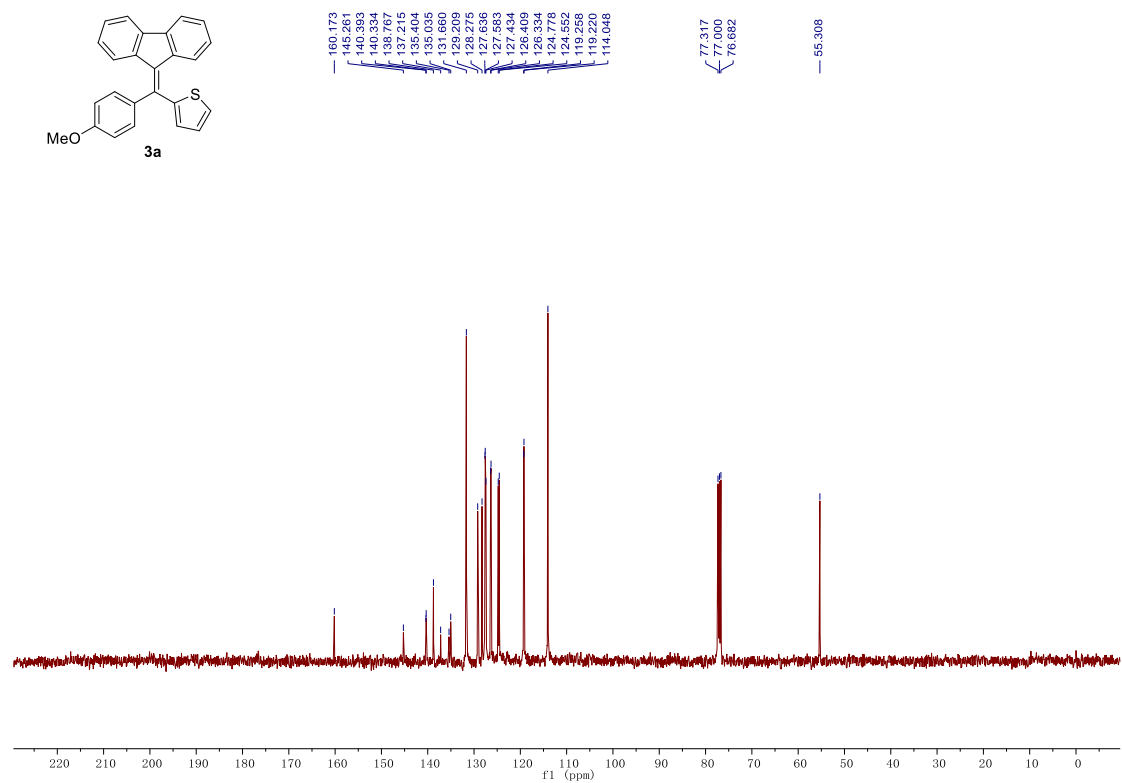


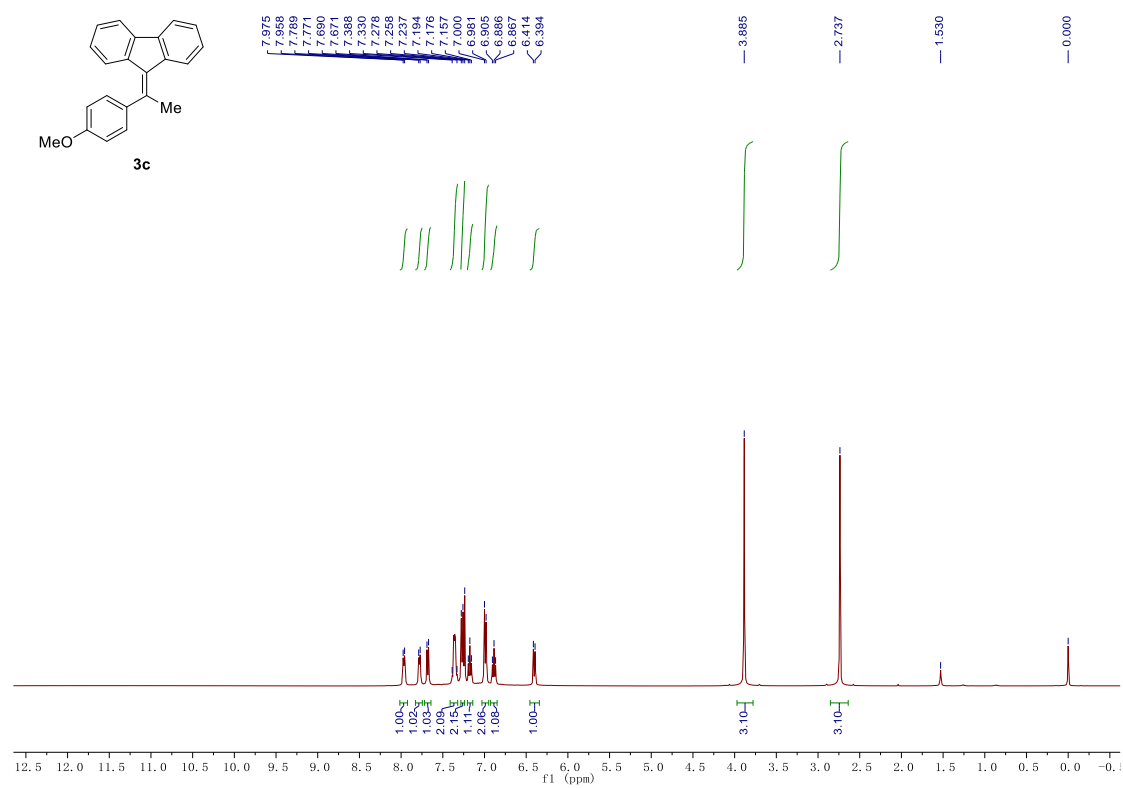
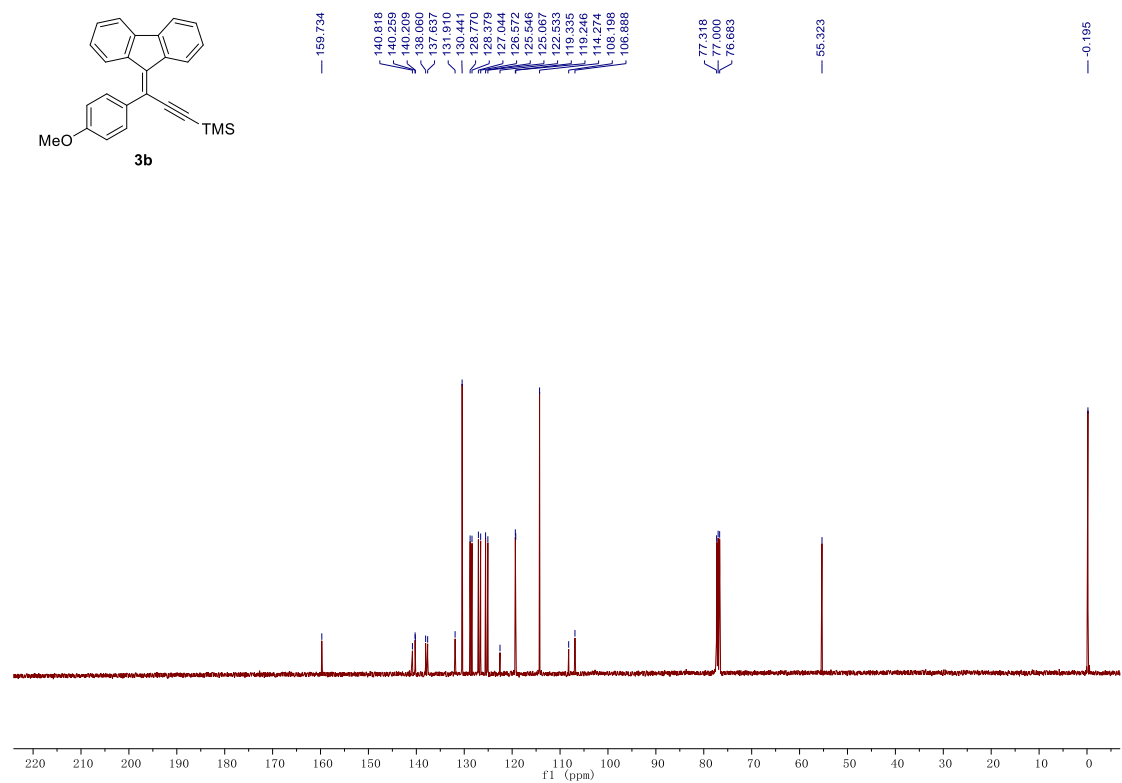


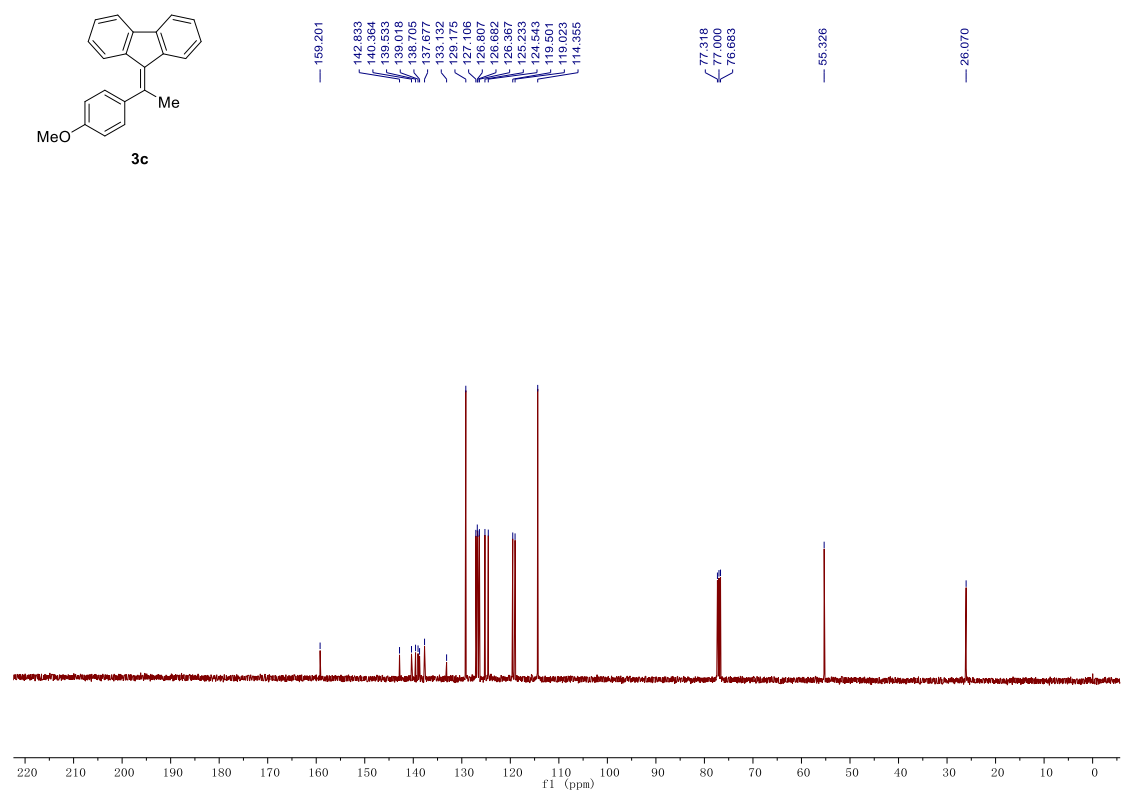












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