

## **Synthesis of 1*H*-Isoindoliums by Electrophile-Mediated Cascade Cyclization/Iodination of Propargylamine-based 1,6-Diynes**

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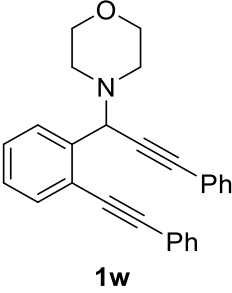
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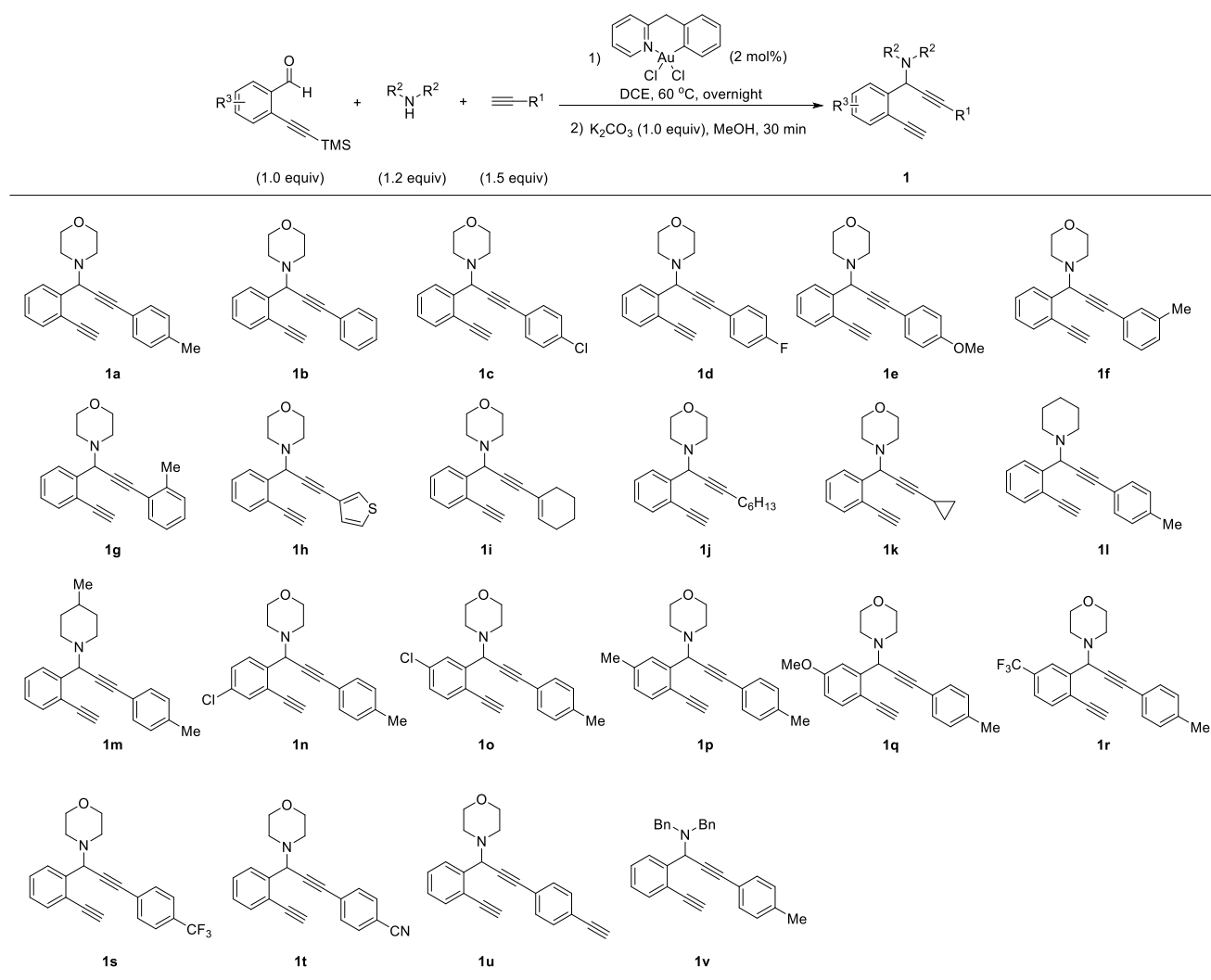
## **Supporting Information**

## Literature Reference

 <p style="text-align: center;"><b>1w</b></p>	<p style="text-align: center;">D. M. Lustosa, P. Cieslik, D. Hartmann, T. Bruckhoff, M. Rudolph, F. Romingera, A. S. K. Hashmi, <i>Org. Chem. Front.</i>, 2019, <b>6</b>, 1655.</p>
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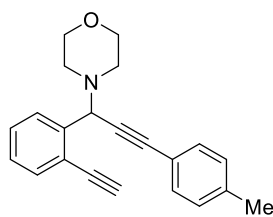
## General Methods

Chemicals purchased from commercial sources were used without further purification. Flash column chromatography was performed using silica gel 60 (230-400 mesh ASTM).  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra were recorded on Bruker DPX-400 and Ascend<sup>TM</sup>-600 spectrometers. Chemical shifts (ppm) were referenced to TMS and coupling constants are given in Hz. Data for  $^1\text{H}$  NMR were recorded as follows: chemical shift ( $\delta$ , ppm), multiplicity (s, singlet; brs, broad singlet; d, doublet; dd, double doublet; t, triplet; td, triple doublet; tt, triple triplet; q, quartet; qd, quadruple doublet, m, multiplet), coupling constant (Hz), integration. Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift ( $\delta$ , ppm). Data for  $^{19}\text{F}$  NMR are reported in terms of chemical shift ( $\delta$ , ppm). High resolution mass spectra (HRMS) were measured on Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS, Waters Synapt G2 Q-TOF MS and Thermo Scientific Q Executive.

**Table S1** Scope of gold-catalyzed three-component coupling of aldehydes, amines, alkynes.

### General procedure for three-component coupling of aldehydes, amines, and alkynes

Aldehyde (5 mmol, 1.0 equiv), amine (6 mmol, 1.2 equiv), alkyne (7.5 mmol, 1.5 equiv), Au(III) catalyst (0.1 mmol, 0.02 equiv) and DCE (10 mL) were added to a dried 50 mL round bottomed flask containing a magnetic stirring bar. The reaction mixture was stirred at 60 °C for overnight. The residues were purified by flash chromatography using EtOAc-Petroleum Ether as eluent to give the desired products. The product was then treated with K<sub>2</sub>CO<sub>3</sub> (5 mmol, 1 equiv) in MeOH (10 mL), the reaction mixture was stirred at rt. When the reaction was completed, as monitored by TLC, water was added. The solid product was separated by suction filtration if solid was precipitated. Or the liquid product was purified by extracting by EtOAc following by flash column chromatography using EtOAc-Petroleum Ether as eluent.



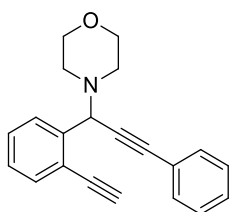
1a

White solid, 54% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.45 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 3H), 7.22 – 7.14 (m, 1H), 7.03 (d, *J* = 7.9 Hz, 2H), 5.09 (s, 1H), 3.67 – 3.54 (m, 4H), 3.24 (s, 1H), 2.68 – 2.48 (m, 4H), 2.26 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.54, 138.32, 133.14, 131.62, 128.99, 128.76, 128.49, 127.60, 122.46, 119.78, 87.93, 84.62, 81.85, 81.75, 67.04, 59.77, 50.01, 21.45.

**HRMS (ESI):** [M+H]<sup>+</sup> Calcd. for [C<sub>22</sub>H<sub>22</sub>NO]<sup>+</sup> 316.1696, found 316.1693.



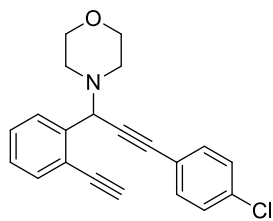
1b

White solid, 74% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 7.7 Hz, 1H), 7.54 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.37 (td, *J* = 7.6, 1.3 Hz, 1H), 7.34 – 7.25 (m, 4H), 5.18 (s, 1H), 3.75 – 3.66 (m, 4H), 3.33 (s, 1H), 2.73 – 2.62 (m, 4H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.47, 133.18, 131.75, 128.73, 128.49, 128.25, 128.22, 127.64, 122.91, 122.50, 87.86, 85.43, 81.88, 81.75, 67.04, 59.78, 50.05.

**HRMS (ESI):** [M+H]<sup>+</sup> Calcd. for [C<sub>21</sub>H<sub>20</sub>NO]<sup>+</sup> 302.1539, found 302.1545.



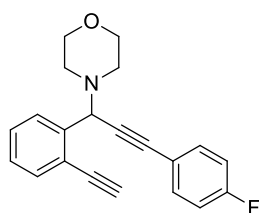
**1c**

White solid, 71% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.69 (d, *J* = 7.7 Hz, 1H), 7.54 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.44 – 7.34 (m, 3H), 7.31 – 7.25 (m, 3H), 5.17 (s, 1H), 3.73 – 3.65 (m, 4H), 3.34 (s, 1H), 2.72 – 2.60 (m, 4H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.20, 134.25, 133.22, 132.96, 128.64, 128.58, 128.53, 127.72, 122.49, 121.34, 86.69, 86.55, 81.98, 81.65, 66.99, 59.76, 50.06.

**HRMS (ESI):** [M+H]<sup>+</sup> Calcd. for [C<sub>21</sub>H<sub>19</sub>ClNO]<sup>+</sup> 336.1150, found 336.1161.



**1d**

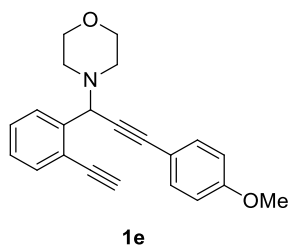
White solid, 28% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.49 – 7.42 (m, 2H), 7.40 – 7.33 (m, 1H), 7.31 – 7.24 (m, 1H), 7.00 (t, *J* = 8.7 Hz, 2H), 5.16 (s, 1H), 3.77 – 3.61 (m, 4H), 3.34 (s, 1H), 2.75 – 2.57 (m, 4H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 163.66, 161.18, 140.32, 133.64, 133.55, 133.18, 128.63, 128.50, 127.67, 122.48, 118.94, 118.91, 115.61, 115.39, 86.71, 85.16, 85.14, 81.96, 81.67, 66.98, 59.71, 50.04.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -110.90.

**HRMS (ESI):** [M+H]<sup>+</sup> Calcd. for [C<sub>21</sub>H<sub>19</sub>FNO]<sup>+</sup> 320.1445, found 320.1449.

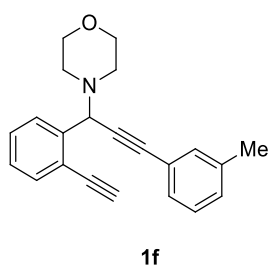


Grey solid, 50% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.17 (s, 1H), 3.81 (s, 3H), 3.76 – 3.64 (m, 4H), 3.33 (s, 1H), 2.76 – 2.56 (m, 4H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 159.44, 140.54, 133.07, 128.68, 128.42, 127.52, 122.37, 114.89, 113.78, 87.59, 83.82, 81.88, 81.69, 66.94, 59.69, 55.16, 49.95.

**HRMS (ESI):** [M+H]<sup>+</sup> Calcd. for [C<sub>22</sub>H<sub>22</sub>NO<sub>2</sub>]<sup>+</sup> 332.1645, found 332.1646.

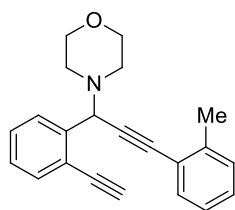


White solid, 64% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.46 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.1 Hz, 1H), 7.06 – 6.97 (m, 3H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.2 Hz, 1H), 4.91 (s, 1H), 3.55 – 3.33 (m, 4H), 3.06 (s, 1H), 2.55 – 2.26 (m, 4H), 2.07 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.50, 137.95, 133.17, 132.34, 129.12, 128.79, 128.75, 128.49, 128.16, 127.63, 122.67, 122.47, 88.05, 84.96, 81.86, 81.75, 67.04, 59.77, 50.01, 21.17.

**HRMS (ESI):** [M+H]<sup>+</sup> Calcd. for [C<sub>22</sub>H<sub>22</sub>NO]<sup>+</sup> 316.1696, found 316.1695.



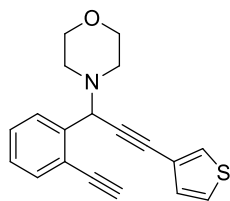
**1g**

White solid, 64% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.50 (s, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.05 – 6.91 (m, 3H), 6.90 – 6.81 (m, 1H), 4.98 (s, 1H), 3.60 – 3.28 (m, 4H), 3.08 (s, 1H), 2.58 – 2.31 (m, 4H), 2.20 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.61, 140.05, 133.19, 132.15, 129.39, 128.70, 128.43, 128.22, 127.61, 125.48, 122.71, 122.46, 89.15, 86.76, 81.88, 81.73, 67.01, 59.94, 49.98, 21.08.

**HRMS (ESI):** [M+H]<sup>+</sup> Calcd. for [C<sub>22</sub>H<sub>22</sub>NO]<sup>+</sup> 316.1696, found 316.1695.



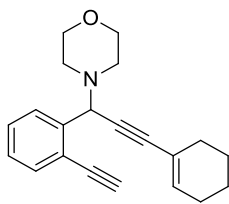
**1h**

White solid, 68% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.54 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.46 (dd, *J* = 2.9, 0.9 Hz, 1H), 7.37 (td, *J* = 7.6, 1.2 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.14 (dd, *J* = 5.0, 1.0 Hz, 1H), 5.16 (s, 1H), 3.81 – 3.60 (m, 4H), 3.33 (s, 1H), 2.77 – 2.55 (m, 4H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.40, 133.18, 130.01, 128.75, 128.69, 128.54, 127.67, 125.25, 122.47, 121.87, 85.06, 82.80, 81.91, 81.73, 67.03, 59.81, 50.07.

**HRMS (ESI):** [M+H]<sup>+</sup> Calcd. for [C<sub>19</sub>H<sub>18</sub>NOS]<sup>+</sup> 308.1104, found 308.1102.



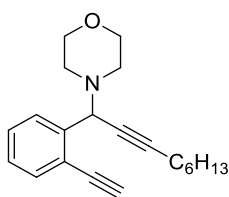
1i

Grey solid, 68% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.64 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.51 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.34 (td, *J* = 7.6, 1.6 Hz, 1H), 7.27 – 7.22 (m, 1H), 6.14 (m, 1H), 5.06 (s, 1H), 3.71 – 3.62 (m, 4H), 3.29 (s, 1H), 2.65 – 2.52 (m, 4H), 2.20 – 2.07 (m, 4H), 1.65 – 1.56 (m, 4H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.85, 134.79, 133.09, 128.72, 128.43, 127.48, 122.42, 120.37, 89.74, 82.37, 81.82, 81.71, 67.05, 59.68, 49.94, 29.49, 25.58, 22.28, 21.49.

**HRMS** (ESI): [M+H]<sup>+</sup> Calcd. for [C<sub>21</sub>H<sub>24</sub>NO]<sup>+</sup> 306.1852, found 306.1861.



1j

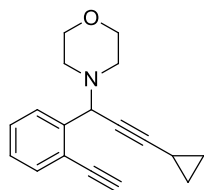
Red solid, 13% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.64 (d, *J* = 7.2 Hz, 1H), 7.51 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.34 (td, *J* = 7.6, 1.2 Hz, 1H), 7.23 (dd, *J* = 7.5, 1.2 Hz, 1H), 4.92 (t, *J* = 2.0 Hz, 1H), 3.73 – 3.61 (m, 4H), 3.29 (s, 1H), 2.65 – 2.45 (m, 4H), 2.27 (td, *J* = 7.0, 2.1 Hz, 2H), 1.54 (q, *J* = 7.3 Hz, 2H), 1.46 – 1.37 (m, 2H), 1.34 – 1.25 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 141.14, 133.05, 128.68, 128.41, 127.40, 122.39, 99.98, 88.21, 81.86, 81.65, 75.88, 67.06, 59.32, 49.96, 31.29, 28.89, 28.58, 22.55, 18.79, 14.02.

**HRMS** (ESI): [M+H]<sup>+</sup> Calcd. for [C<sub>21</sub>H<sub>28</sub>NO]<sup>+</sup> 310.2165, found 310.2172.





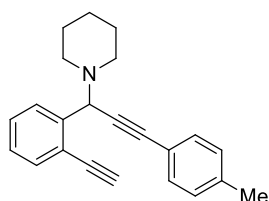
1k

White solid, 58% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.58 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.47 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.32 (td, *J* = 7.6, 1.5 Hz, 1H), 7.25 – 7.19 (m, 1H), 4.86 (d, *J* = 2.0 Hz, 1H), 3.69 – 3.59 (m, 4H), 3.26 (s, 1H), 2.60 – 2.45 (m, 4H), 1.32 – 1.25 (m, 1H), 0.80 – 0.71 (m, 2H), 0.71 – 0.63 (m, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 141.16, 133.19, 128.79, 128.58, 127.56, 122.52, 91.40, 81.96, 81.83, 71.23, 67.18, 59.40, 50.08, 8.58, 8.54, -0.30.

**HRMS** (ESI): [M+H]<sup>+</sup> Calcd. for [C<sub>18</sub>H<sub>20</sub>NO]<sup>+</sup> 266.1539, found 266.1544.



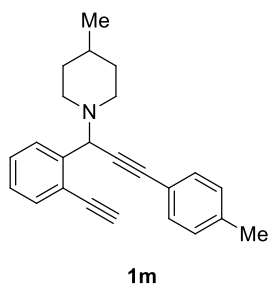
1l

Yellow solid, 63% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 7.7 Hz, 1H), 7.52 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.24 (td, *J* = 7.6, 1.2 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 5.16 (s, 1H), 3.31 (s, 1H), 2.71 – 2.50 (m, 4H), 2.34 (s, 3H), 1.56 (dq, *J* = 10.5, 5.4 Hz, 4H), 1.41 (dd, *J* = 11.4, 5.6 Hz, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 141.49, 138.04, 133.05, 131.63, 128.95, 128.79, 128.31, 127.25, 122.44, 120.22, 87.28, 85.80, 81.98, 81.63, 60.11, 50.86, 26.08, 24.47, 21.42.

**HRMS** (ESI): [M+H]<sup>+</sup> Calcd. for [C<sub>23</sub>H<sub>24</sub>N]<sup>+</sup> 314.1903, found 314.1918.

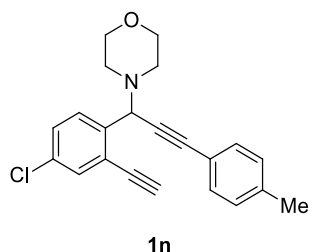


Yellow solid, 69% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.65 (d, *J* = 7.2 Hz, 1H), 7.45 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.18 (td, *J* = 7.6, 1.2 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 2H), 5.11 (s, 1H), 3.24 (s, 1H), 2.85 (t, *J* = 9.0 Hz, 2H), 2.35 – 2.25 (m, 4H), 2.16 (td, *J* = 11.6, 2.4 Hz, 1H), 1.58 – 1.45 (m, 2H), 1.33 – 1.05 (m, 3H), 0.81 (d, *J* = 6.2 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 141.54, 138.05, 133.04, 131.61, 128.94, 128.78, 128.35, 127.27, 122.39, 120.19, 87.27, 85.82, 81.95, 81.67, 59.78, 52.24, 48.30, 34.55, 34.21, 30.80, 21.84, 21.42.

**HRMS** (ESI): [M+H]<sup>+</sup> Calcd. for [C<sub>24</sub>H<sub>26</sub>N]<sup>+</sup> 328.2060, found 328.1956.

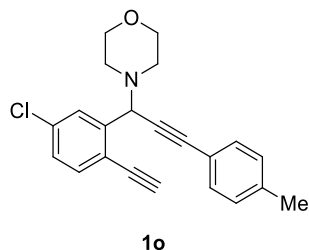


White solid, 69% yield for two steps

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.66 (d, *J* = 8.3 Hz, 1H), 7.52 (d, *J* = 2.3 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 5.10 (s, 1H), 3.77 – 3.62 (m, 4H), 3.37 (s, 1H), 2.73 – 2.54 (m, 4H), 2.36 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 139.30, 138.54, 133.35, 132.80, 131.66, 130.09, 129.07, 128.75, 124.09, 119.59, 88.35, 84.06, 82.97, 80.47, 67.03, 59.35, 50.02, 21.48.

**HRMS** (ESI): [M+H]<sup>+</sup> Calcd. for [C<sub>22</sub>H<sub>21</sub>ClNO]<sup>+</sup> 350.1306, found 350.1303.

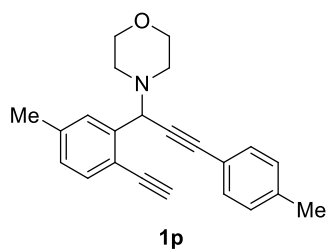


White solid, 35% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 2.1 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.25 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 5.11 (s, 1H), 3.76 – 3.62 (m, 4H), 3.36 (s, 1H), 2.73 – 2.56 (m, 4H), 2.35 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 142.64, 138.55, 134.65, 134.25, 131.68, 129.04, 128.90, 127.91, 120.95, 119.50, 88.55, 83.69, 82.75, 80.78, 66.97, 59.61, 50.04, 21.44.

**HRMS** (ESI): [M+H]<sup>+</sup> Calcd. for [C<sub>22</sub>H<sub>21</sub>ClNO]<sup>+</sup> 350.1306, found 350.1311.

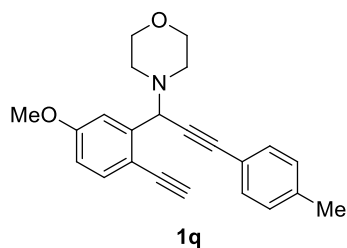


White solid, 74% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.51 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 1H), 5.13 (s, 1H), 3.76 – 3.64 (m, 4H), 3.28 (s, 1H), 2.77 – 2.67 (m, 2H), 2.67 – 2.58 (m, 2H), 2.37 (s, 3H), 2.34 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.31, 138.74, 138.25, 132.96, 131.62, 129.38, 128.97, 128.41, 119.88, 119.49, 87.70, 84.94, 81.93, 81.18, 67.01, 59.72, 50.12, 21.58, 21.40.

**HRMS** (ESI): [M+H]<sup>+</sup> Calcd. for [C<sub>23</sub>H<sub>24</sub>NO]<sup>+</sup> 330.1852, found 330.1855.

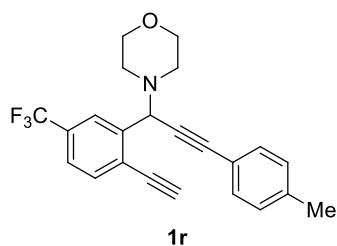


White solid, 70% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 2.6 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.80 (dd, *J* = 8.5, 2.7 Hz, 1H), 5.13 (s, 1H), 3.84 (s, 3H), 3.77 – 3.64 (m, 4H), 3.26 (s, 1H), 2.78 – 2.69 (m, 2H), 2.68 – 2.58 (m, 2H), 2.35 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 159.68, 142.39, 138.32, 134.42, 131.62, 128.98, 119.78, 114.73, 114.62, 112.98, 87.87, 84.68, 81.79, 80.44, 67.03, 59.85, 55.35, 50.15, 21.41.

**HRMS** (ESI): [M+H]<sup>+</sup> Calcd. for [C<sub>23</sub>H<sub>24</sub>NO<sub>2</sub>]<sup>+</sup> 346.1802, found 346.1801.



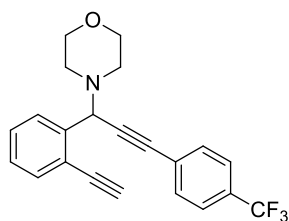
Yellow oil, 55% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.02 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.20 (s, 1H), 3.79 – 3.63 (m, 4H), 3.48 (s, 1H), 2.75 – 2.59 (m, 4H), 2.37 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 141.86, 138.64, 133.56, 131.66, 130.29 (q, *J* = 32.5 Hz), 129.07, 126.22 (q, *J* = 1.3 Hz), 125.43 (q, *J* = 11.4 Hz), 124.41 (q, *J* = 3.6 Hz), 123.75 (q, *J* = 270.8 Hz), 119.40, 88.94, 84.21, 83.33, 80.53, 66.93, 59.68, 50.01, 21.40.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.70.

**HRMS** (ESI): [M+H]<sup>+</sup> Calcd. for [C<sub>23</sub>H<sub>21</sub>F<sub>3</sub>NO]<sup>+</sup> 384.1570, found 384.1569.



**1s**

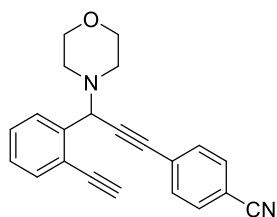
Yellow solid, 48% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.70 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.62 – 7.52 (m, 5H), 7.38 (td, *J* = 7.6, 1.5 Hz, 1H), 7.29 (td, *J* = 7.6, 1.4 Hz, 1H), 5.20 (s, 1H), 3.77 – 3.64 (m, 4H), 3.35 (s, 1H), 2.76 – 2.58 (m, 4H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 139.98, 133.28, 132.00, 130.01 (q, *J* = 32.6 Hz), 128.59, 128.55, 127.81, 126.67, 125.19 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 273.2 Hz), 122.55, 88.22, 86.52, 82.06, 81.59, 66.97, 59.79, 50.09.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.77.

**HRMS (ESI):** [M+H]<sup>+</sup> Calcd. for [C<sub>22</sub>H<sub>19</sub>F<sub>3</sub>NO]<sup>+</sup> 370.1413, found 370.1455.



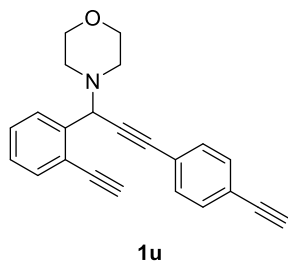
**1t**

Yellow solid, 40% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.69 – 7.63 (m, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 3H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.29 (td, *J* = 7.5, 1.2 Hz, 1H), 5.20 (s, 1H), 3.74 – 3.65 (m, 4H), 3.35 (s, 1H), 2.73 – 2.58 (m, 4H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 139.88, 133.50, 132.46, 132.16, 128.77, 128.70, 128.09, 127.91, 122.72, 118.54, 111.83, 90.58, 86.45, 82.34, 81.69, 67.12, 60.00, 50.29.

**HRMS (ESI):** [M+H]<sup>+</sup> Calcd. for [C<sub>22</sub>H<sub>19</sub>N<sub>2</sub>O]<sup>+</sup> 327.1492, found 327.1497.

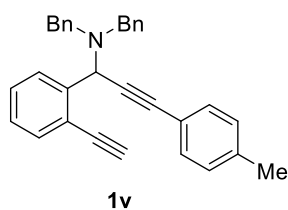


Pale yellow solid, 40% yield for two steps

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.70 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.55 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.43 (s, 4H), 7.38 (td, *J* = 7.6, 1.5 Hz, 1H), 7.31 – 7.26 (m, 1H), 5.19 (s, 1H), 3.70 (dt, *J* = 5.8, 3.8 Hz, 4H), 3.34 (s, 1H), 3.17 (s, 1H), 2.74 – 2.59 (m, 4H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 140.39, 133.43, 132.18, 131.84, 128.87, 128.75, 127.94, 123.55, 122.70, 122.12, 87.82, 87.49, 83.36, 82.18, 81.87, 79.05, 67.21, 60.02, 50.28.

**HRMS** (ESI): [M+H]<sup>+</sup> Calcd. for [C<sub>23</sub>H<sub>20</sub>NO]<sup>+</sup> 326.1539, found 326.1539.

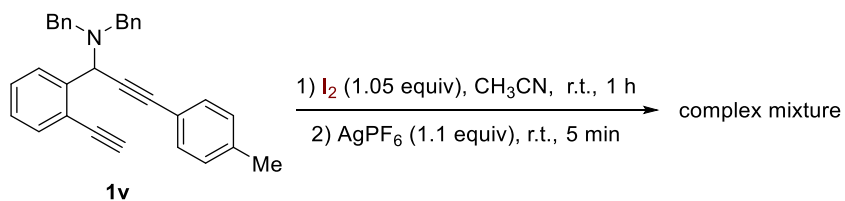


Yellow solid, 24% yield for two steps

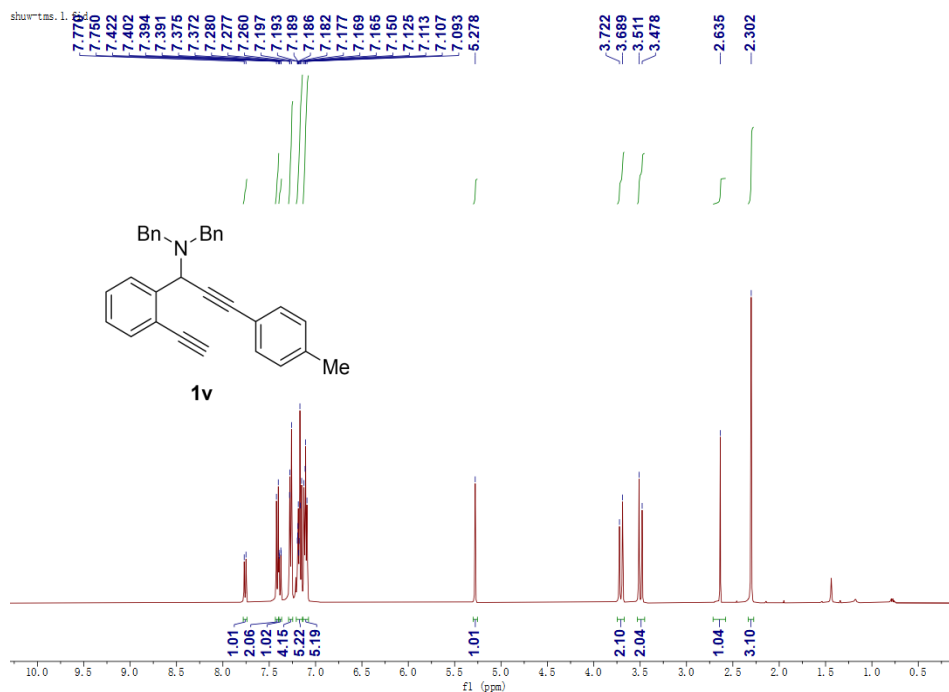
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.38 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.29 – 7.25 (m, 4H), 7.21 – 7.14 (m, 5H), 7.11 (dd, *J* = 7.6, 5.4 Hz, 5H), 5.28 (s, 1H), 3.71 (d, *J* = 13.3 Hz, 2H), 3.49 (d, *J* = 13.3 Hz, 2H), 2.64 (s, 1H), 2.30 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 141.18, 139.42, 138.51, 133.60, 131.94, 130.02, 129.81, 129.27, 128.20, 128.04, 127.66, 126.94, 122.68, 120.28, 88.87, 84.56, 82.17, 81.45, 55.73, 55.16, 21.66.

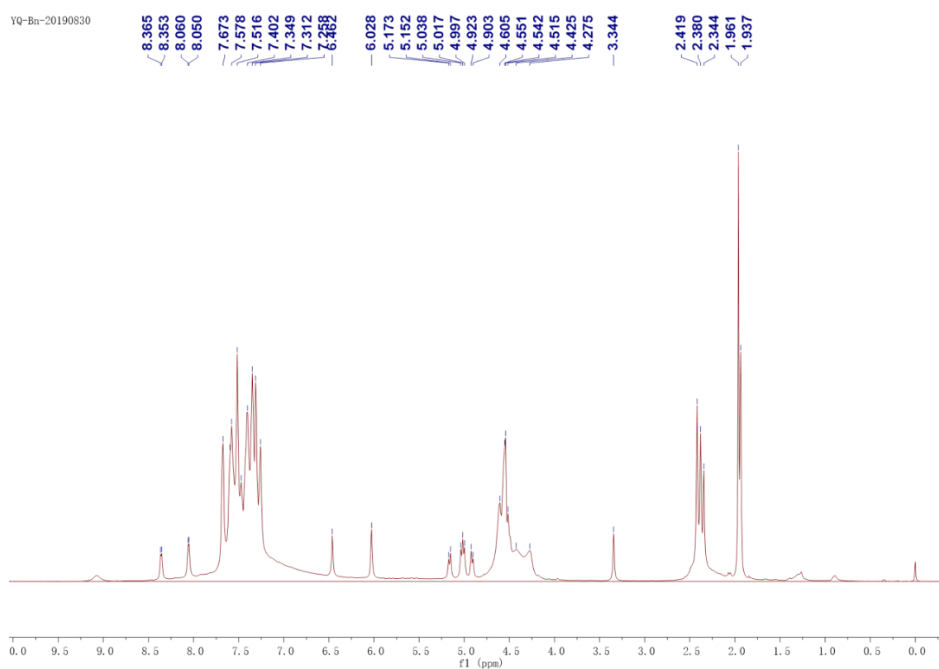
**HRMS** (ESI): [M+H]<sup>+</sup> Calcd. for [C<sub>32</sub>H<sub>28</sub>N]<sup>+</sup> 426.2216, found 426.2215.



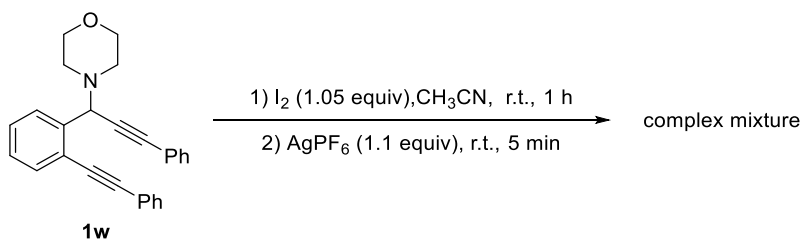
**Scheme S1** Reaction of **1v** with I<sub>2</sub> under the optimized reaction conditions



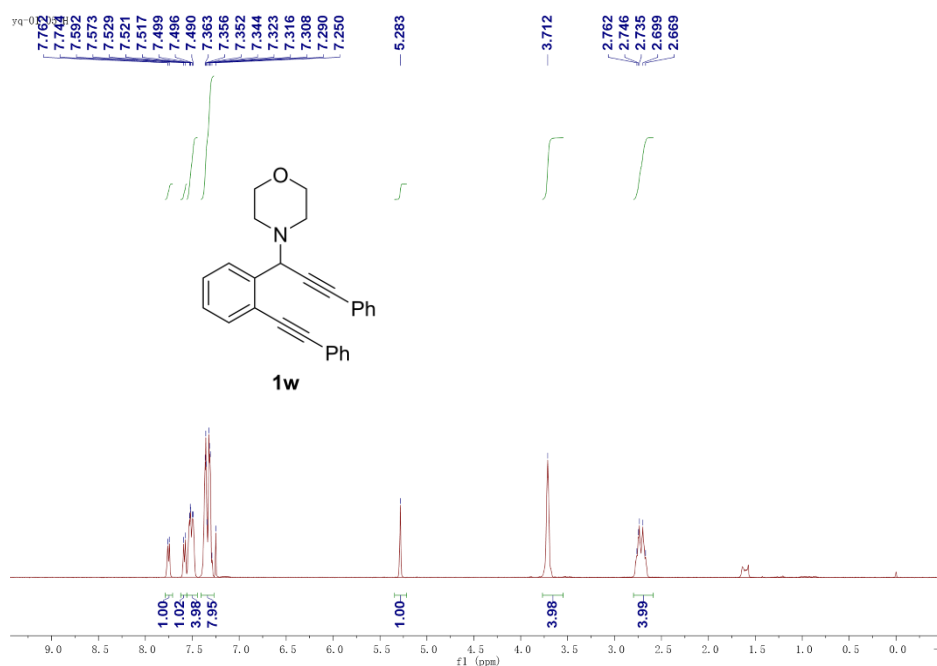
**Figure S1** <sup>1</sup>H NMR spectrum of **1v**



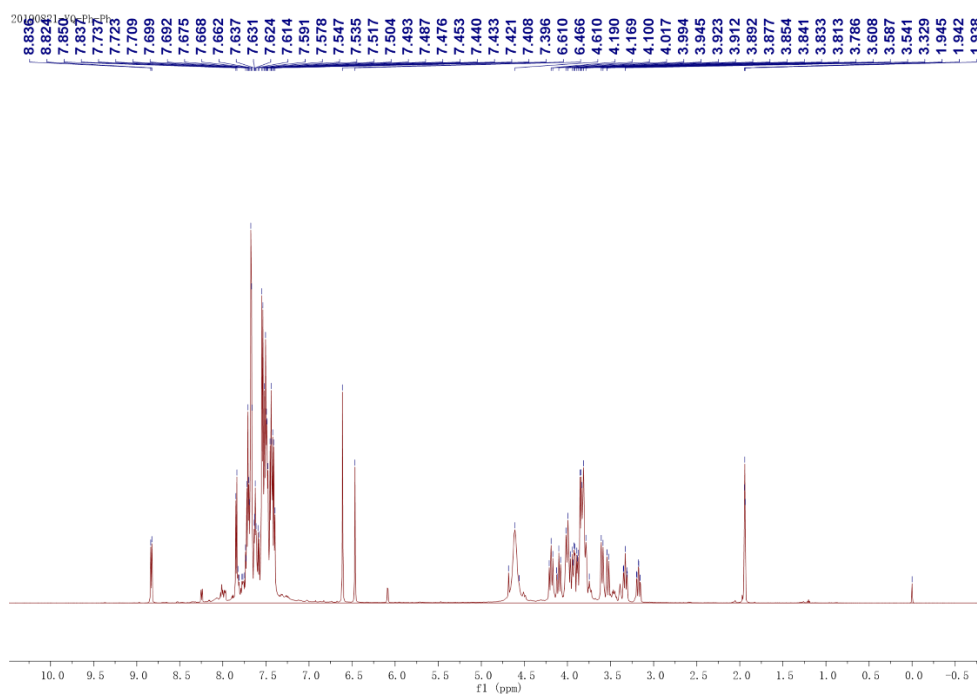
**Figure S2** <sup>1</sup>H NMR spectrum of crude reaction mixture of **1v** with I<sub>2</sub>



**Scheme S2** Reaction of **1w** with  $\text{I}_2$  under the optimized reaction conditions

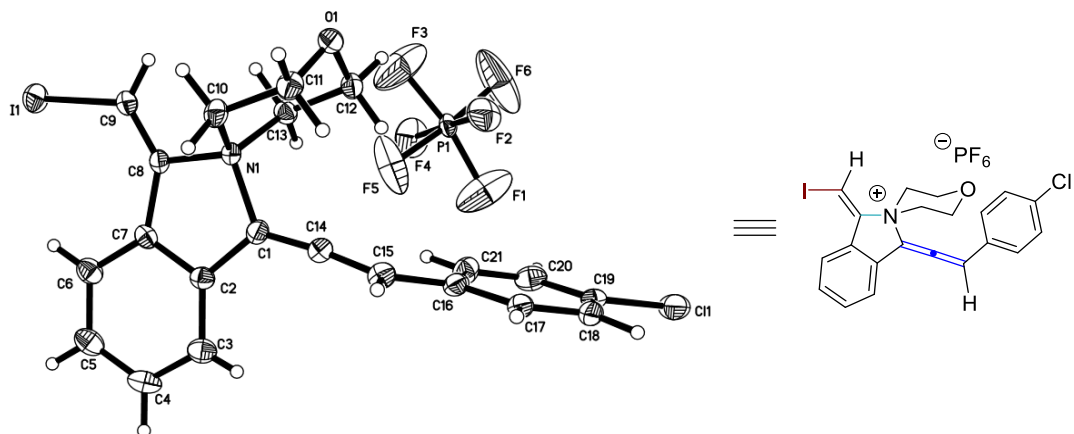


**Figure S3**  $^1\text{H}$  NMR spectrum of **1w**



**Figure S4**  $^1\text{H}$  NMR spectrum of the crude reaction mixture of **1w** with  $\text{I}_2$





**Figure S5** X-ray crystal structures of **3c**. Displacement ellipsoids are drawn at the 50% probability level. Solvent molecules are omitted for clarity

**Table S2** Crystal data and structure refinement for **3c**

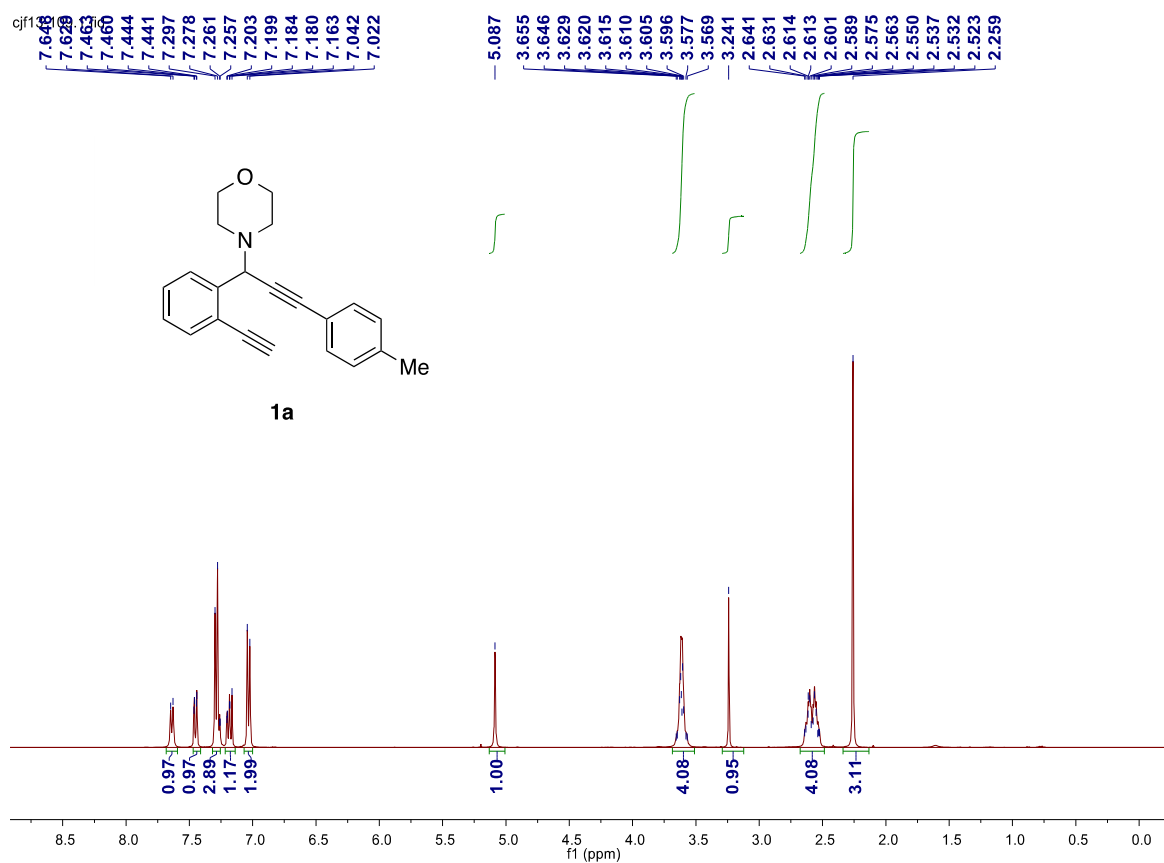
Identification code	cjf21	
Empirical formula	$C_{21}H_{18}NOCl \cdot PF_6$	
Formula weight	607.68	
Temperature	294(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	$a = 10.0081(9)$ Å	$\alpha = 90^\circ$ .
	$b = 12.9824(11)$ Å	$\beta = 93.944(3)^\circ$ .
	$c = 17.1316(16)$ Å	$\gamma = 90^\circ$ .
Volume	$2220.6(3)$ Å <sup>3</sup>	
Z	4	
Density (calculated)	1.818 Mg/m <sup>3</sup>	
Absorption coefficient	1.699 mm <sup>-1</sup>	
F(000)	1192	
Crystal size	0.16 x 0.12 x 0.08 mm <sup>3</sup>	
Theta range for data collection	2.29 to 27.53°.	
Index ranges	-12 ≤ h ≤ 13, -16 ≤ k ≤ 16, -22 ≤ l ≤ 22	
Reflections collected	64193	
Independent reflections	5096 [R(int) = 0.0399]	
Completeness to theta = 27.53°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6764	

Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	5096 / 15 / 312
Goodness-of-fit on $F^2$	1.000
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0622, wR2 = 0.1739
R indices (all data)	R1 = 0.0799, wR2 = 0.1851
Extinction coefficient	0.0006(3)
Largest diff. peak and hole	1.010 and -0.928 e. $\text{\AA}^{-3}$

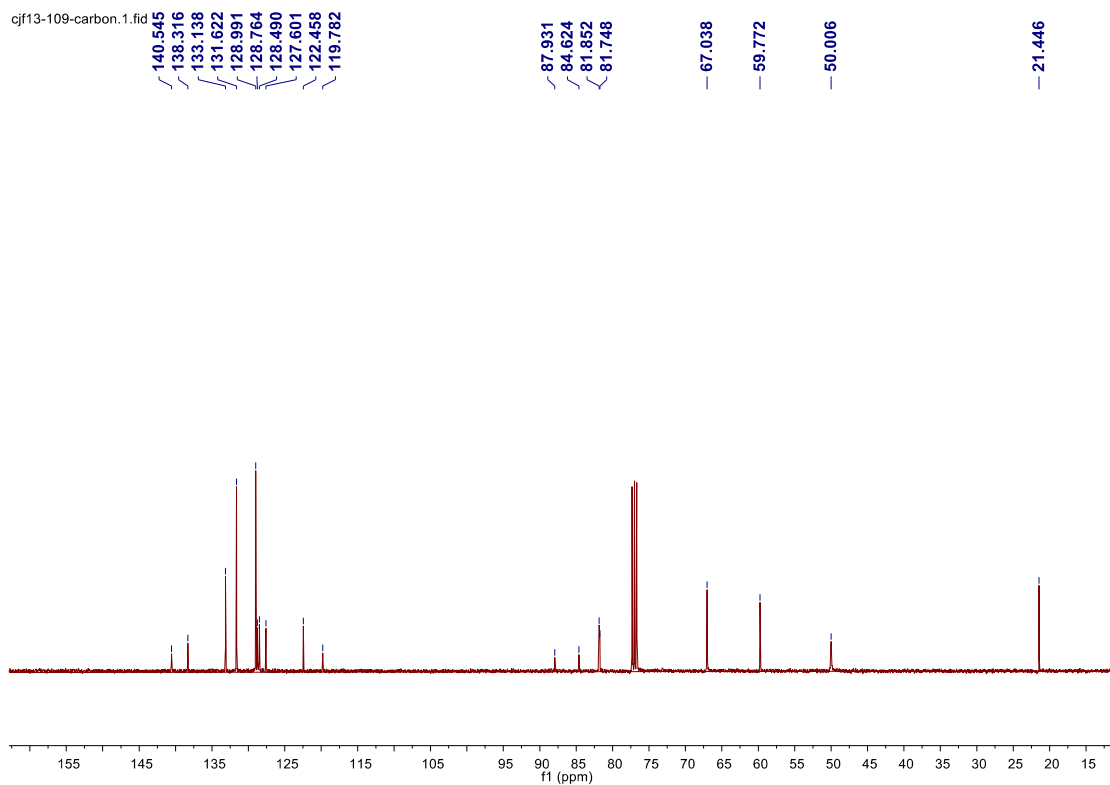
**Table S3** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for CJF21.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	$U(\text{eq})$
I(1)	13029(1)	5607(1)	666(1)	71(1)
Cl(1)	1962(1)	1244(1)	1784(1)	87(1)
O(1)	9809(3)	2825(2)	3008(2)	59(1)
N(1)	9576(3)	4521(2)	1932(2)	39(1)
C(1)	8185(4)	4997(3)	1841(2)	47(1)
C(2)	8247(4)	5855(3)	1303(2)	45(1)
C(3)	7248(5)	6514(4)	1060(3)	59(1)
C(4)	7534(6)	7304(4)	561(3)	67(1)
C(5)	8810(6)	7434(4)	317(3)	69(1)
C(6)	9808(5)	6767(4)	546(3)	58(1)
C(7)	9542(4)	5958(3)	1051(2)	45(1)
C(8)	10409(4)	5160(3)	1394(2)	43(1)
C(9)	11664(4)	4889(3)	1335(3)	51(1)
C(10)	10171(4)	4613(3)	2770(2)	50(1)
C(11)	9620(4)	3828(4)	3299(2)	55(1)
C(12)	9040(4)	2695(3)	2286(3)	54(1)
C(13)	9542(4)	3400(3)	1670(2)	48(1)
C(14)	7174(4)	4664(3)	2203(3)	53(1)
C(15)	6124(5)	4440(4)	2590(3)	59(1)
C(16)	5104(4)	3666(4)	2365(3)	51(1)
C(17)	4123(4)	3447(3)	2867(3)	52(1)
C(18)	3153(4)	2712(4)	2701(3)	54(1)
C(19)	3163(4)	2172(3)	2016(3)	56(1)
C(20)	4143(5)	2380(4)	1490(3)	66(1)
C(21)	5096(5)	3104(4)	1676(3)	61(1)
P(1)	7373(1)	1028(1)	354(1)	45(1)
F(1)	5884(5)	1252(7)	150(3)	197(3)
F(2)	7047(4)	977(3)	1255(2)	104(1)
F(3)	8893(5)	1051(9)	598(4)	231(4)
F(4)	7701(5)	1156(4)	-530(2)	122(2)
F(5)	7533(8)	2223(4)	485(3)	189(3)
F(6)	7370(10)	-138(4)	301(4)	271(4)

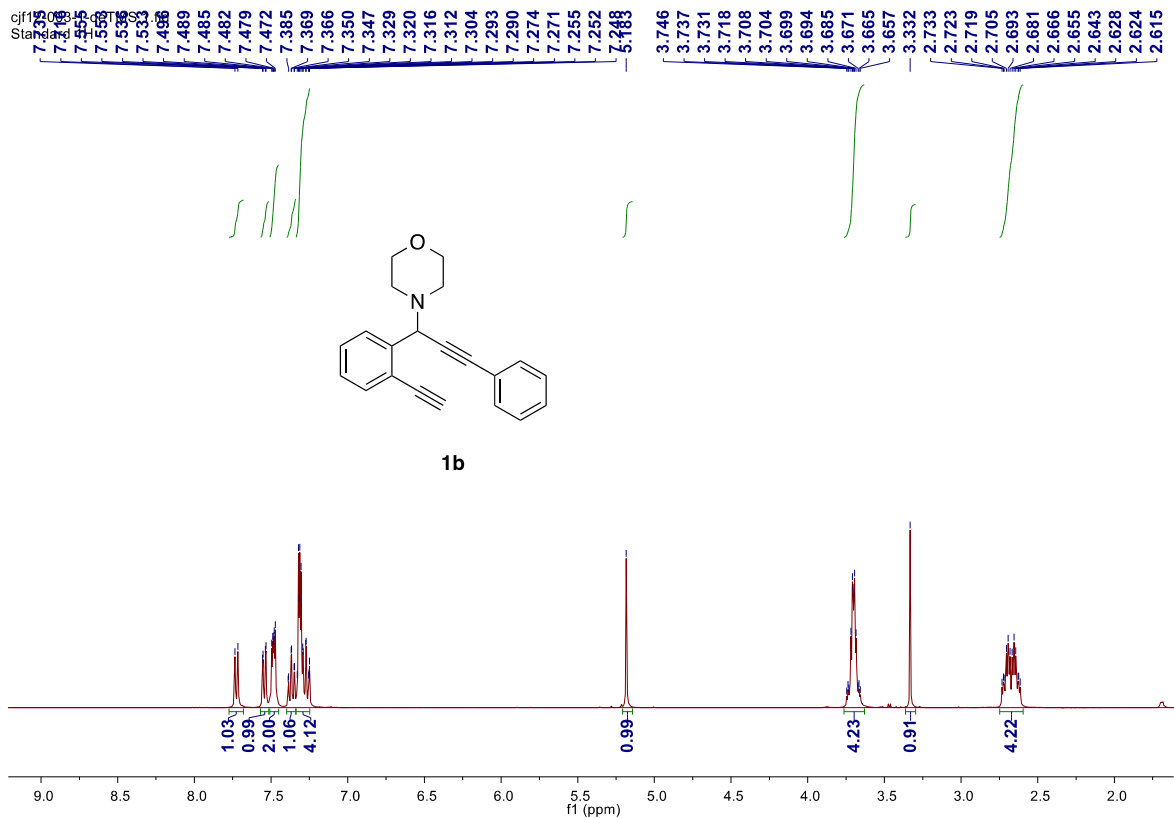
# <sup>1</sup>H NMR



# <sup>13</sup>C NMR

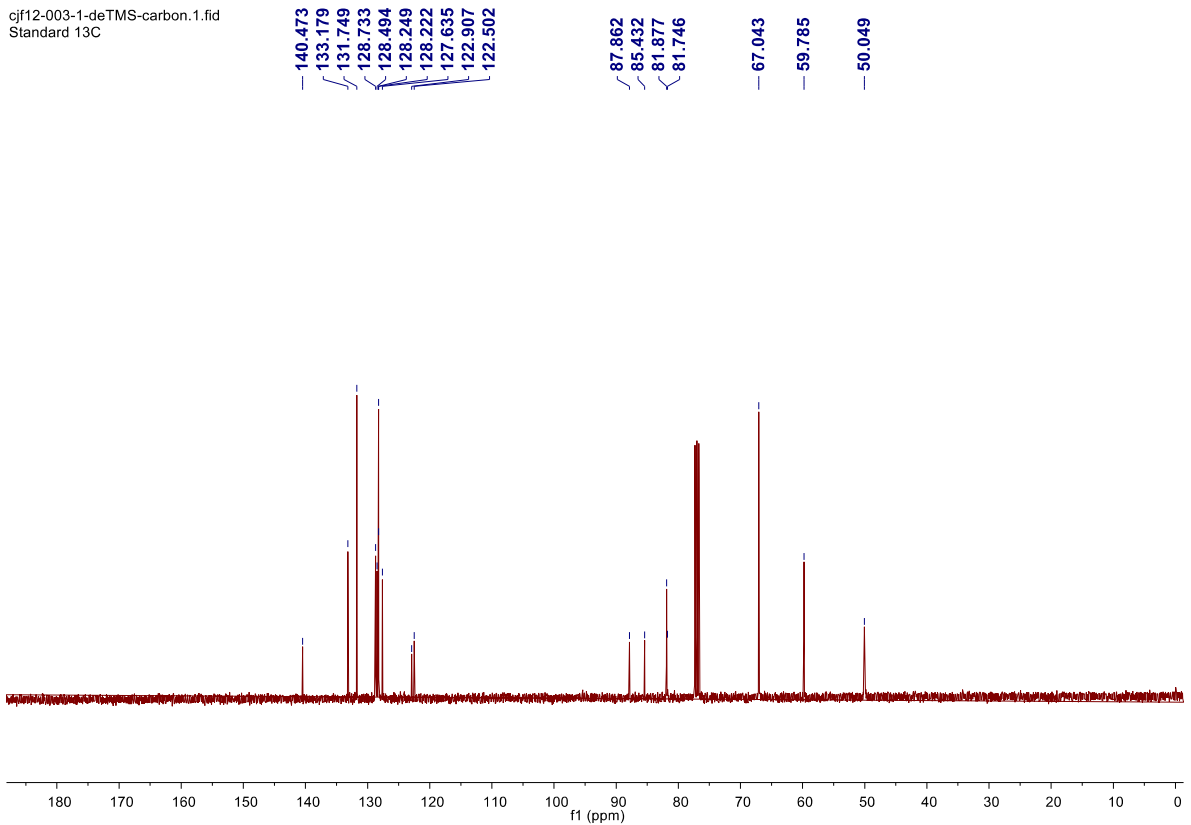


# $^1\text{H}$ NMR

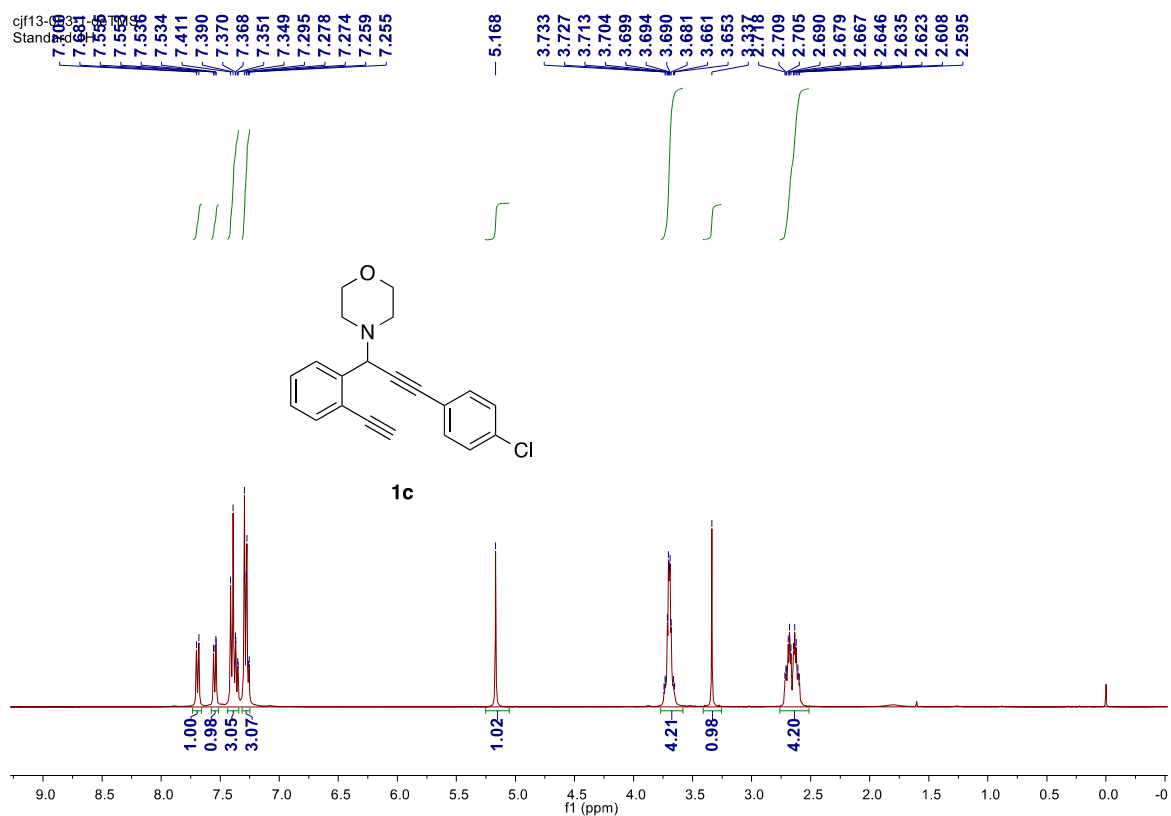


# $^{13}\text{C}$ NMR

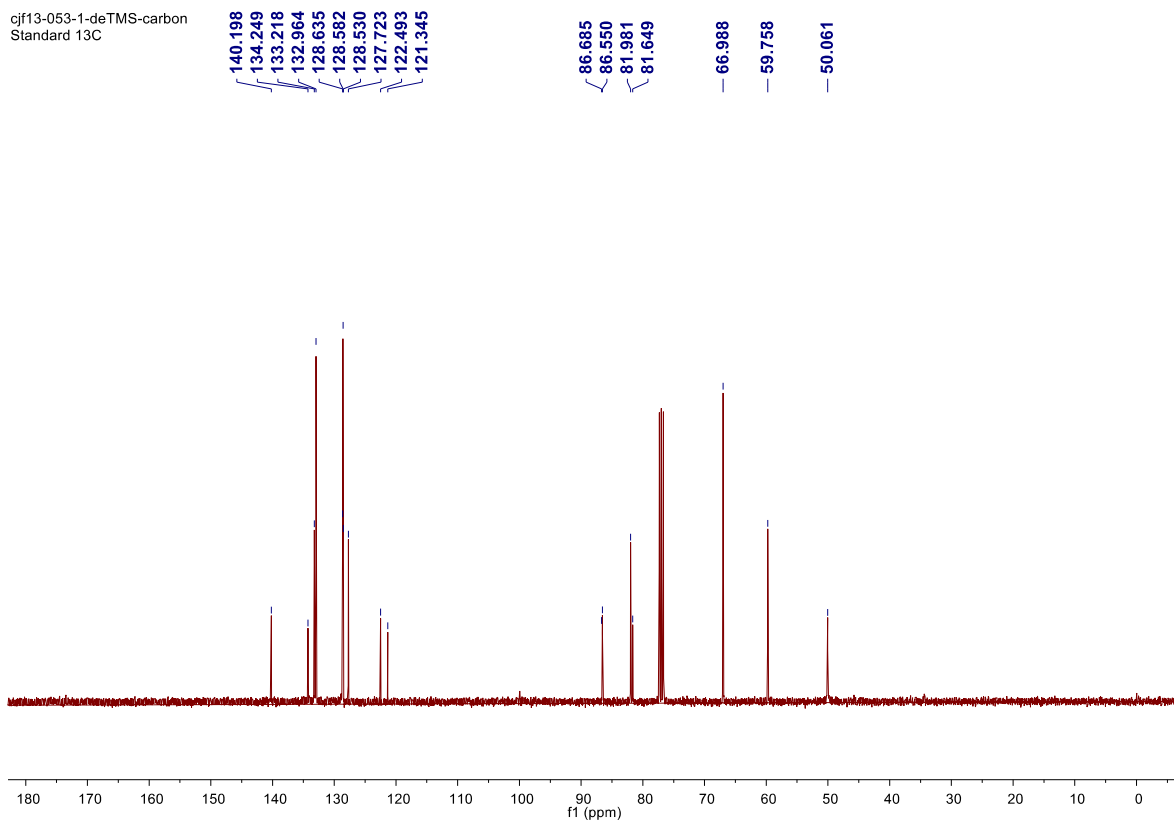
Standard 13C



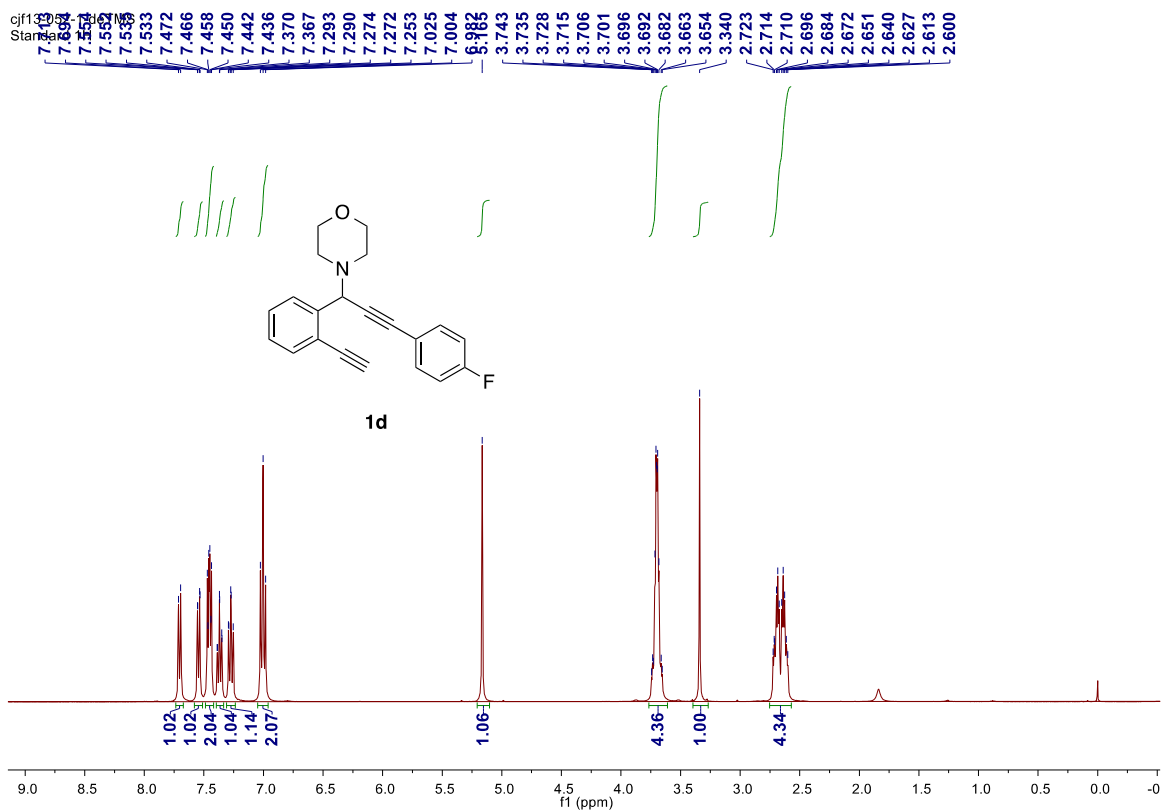
# <sup>1</sup>H NMR



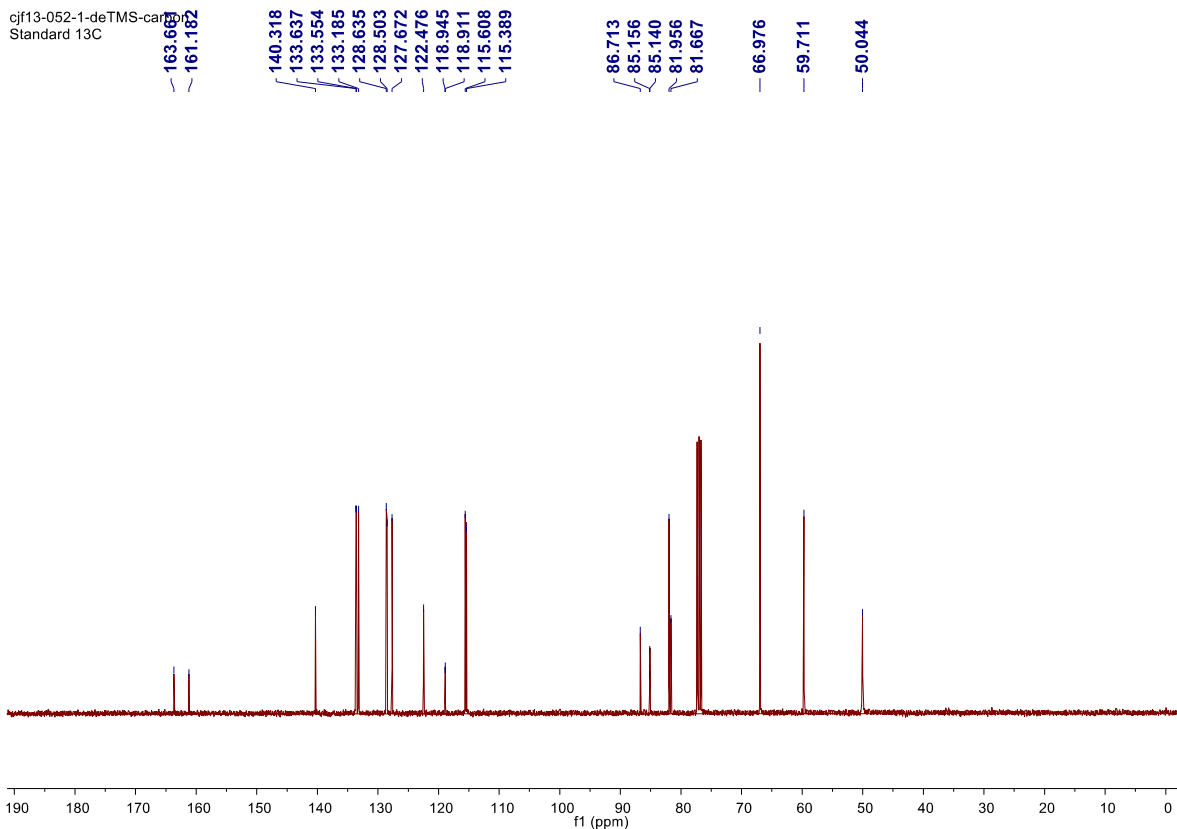
# <sup>13</sup>C NMR



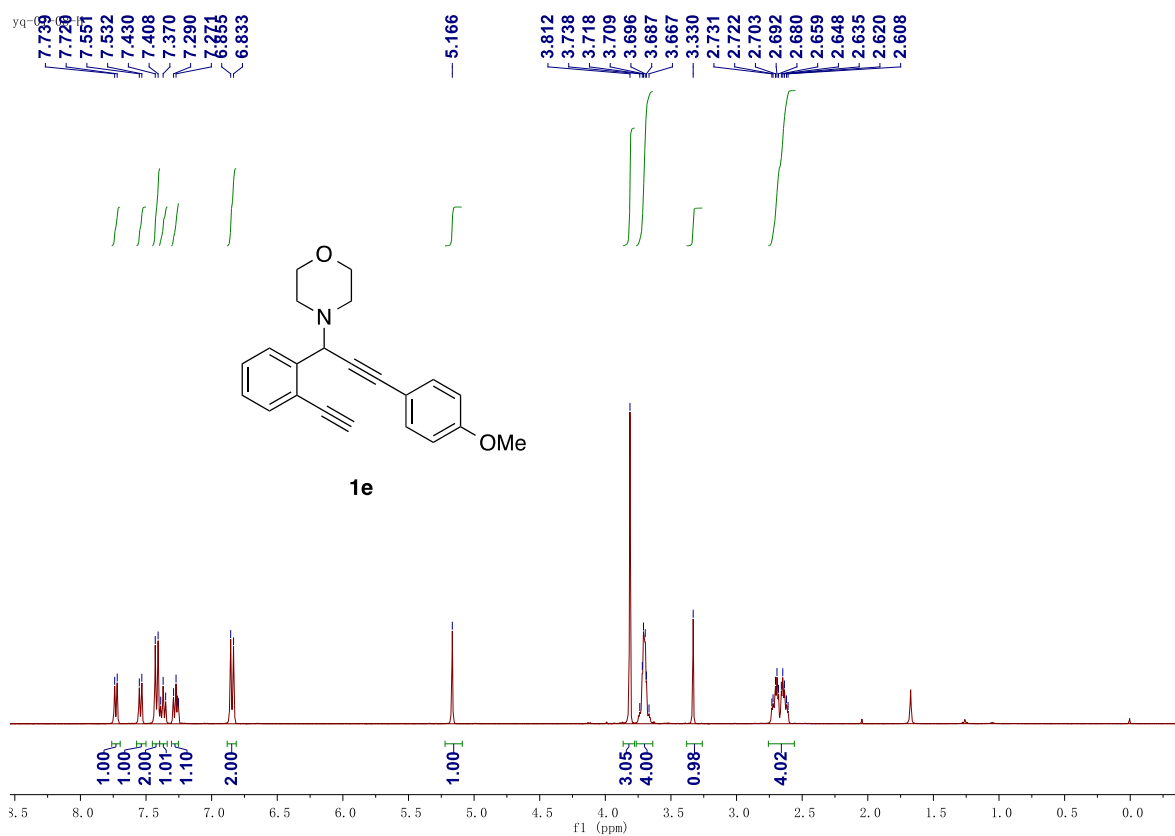
# <sup>1</sup>H NMR



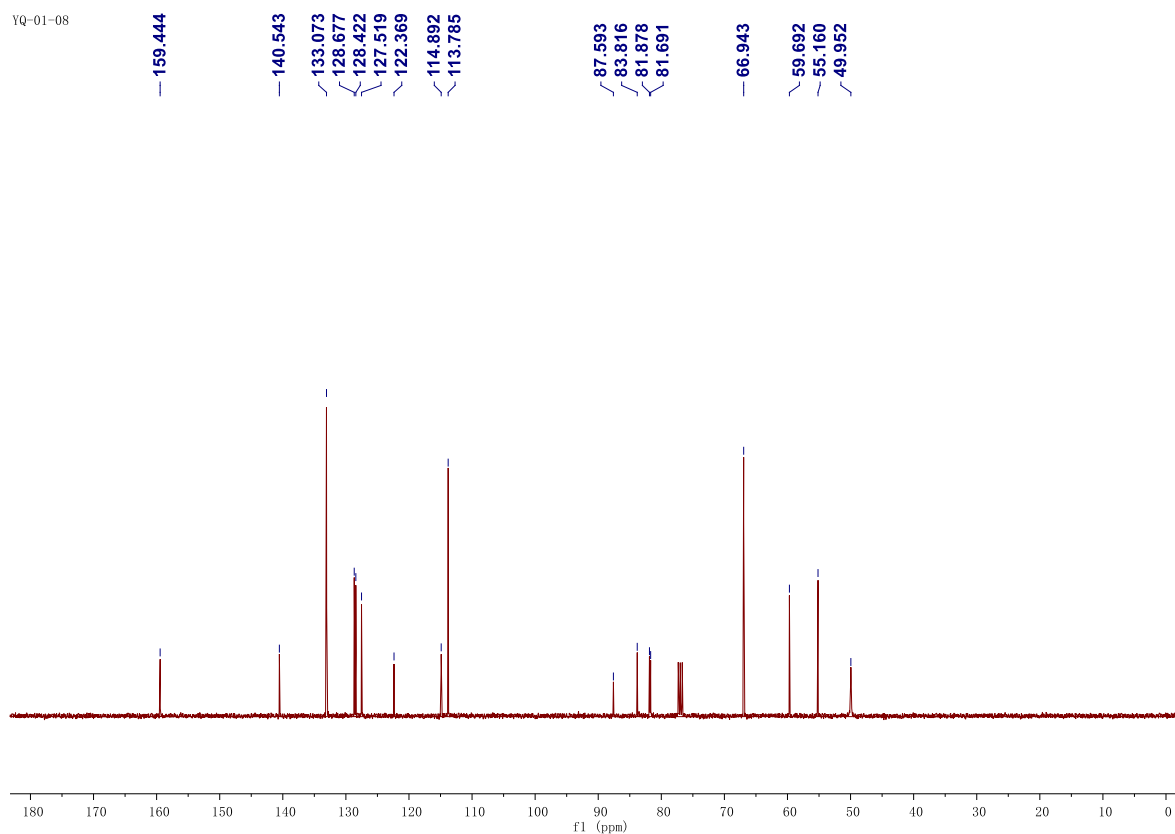
# <sup>13</sup>C NMR



# <sup>1</sup>H NMR

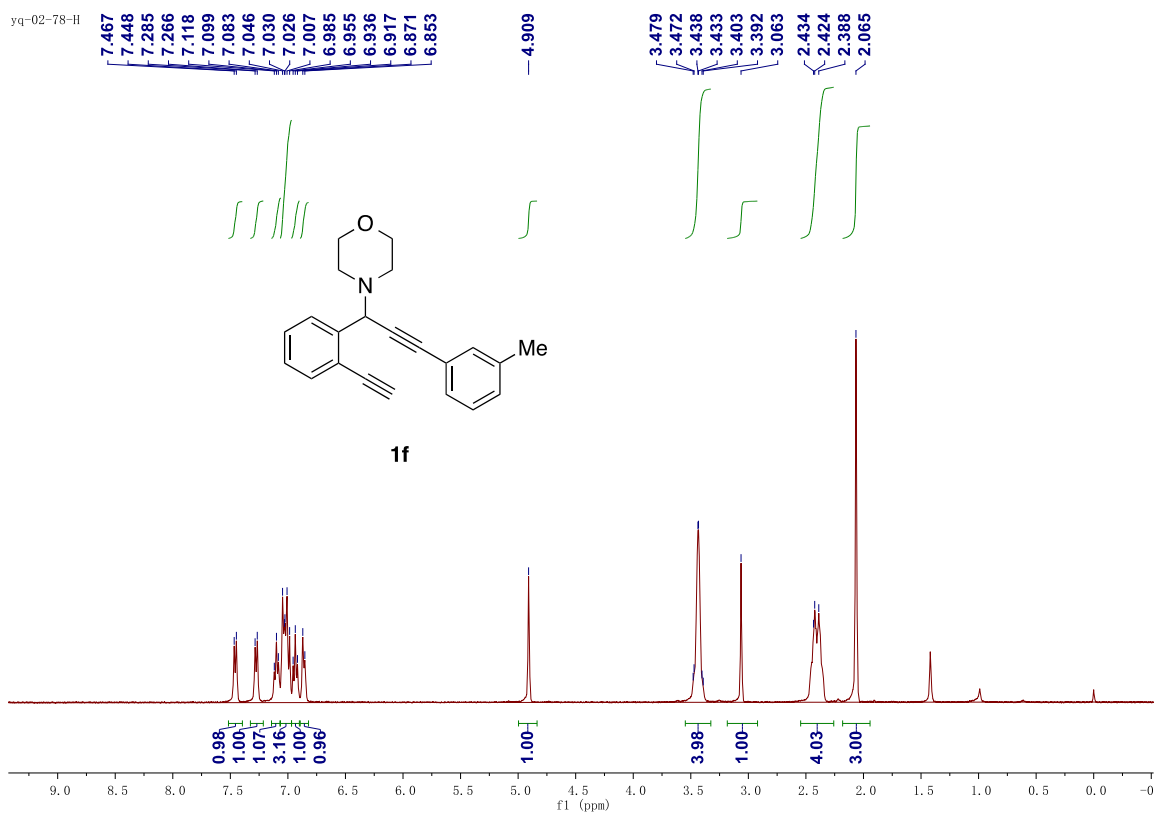


# <sup>13</sup>C NMR

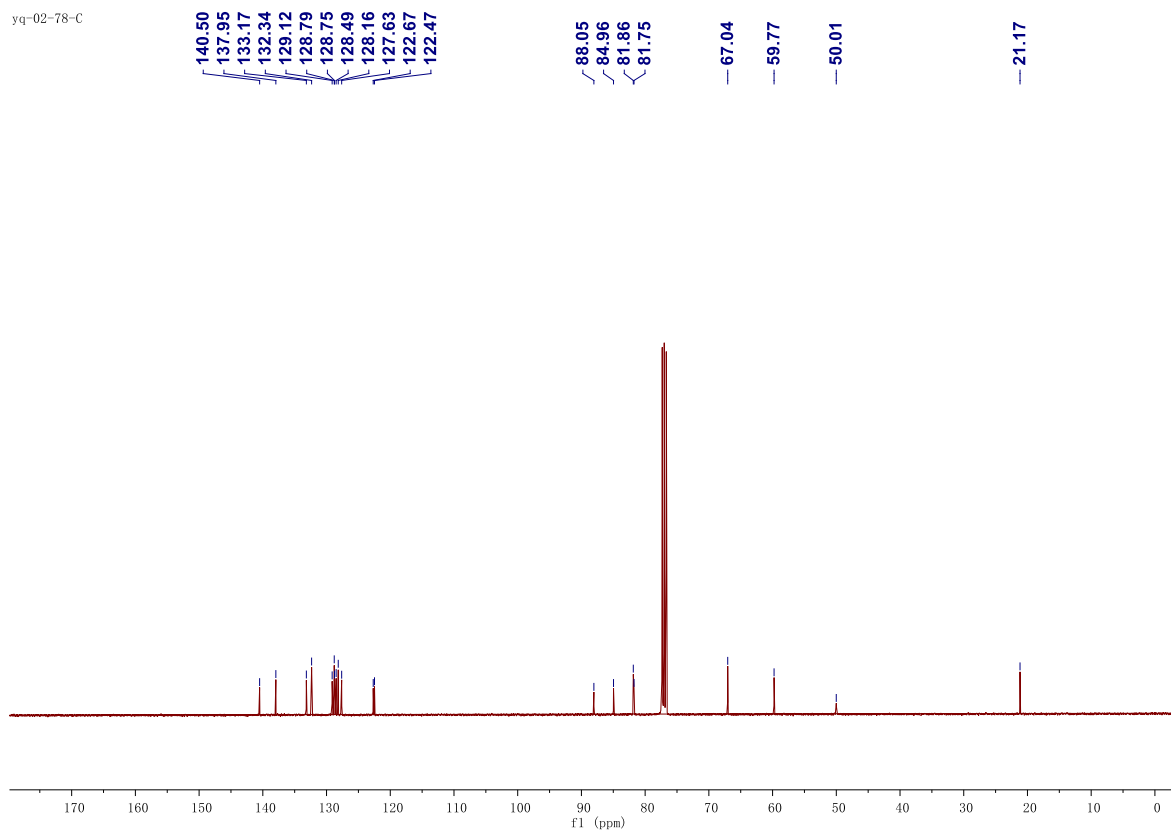




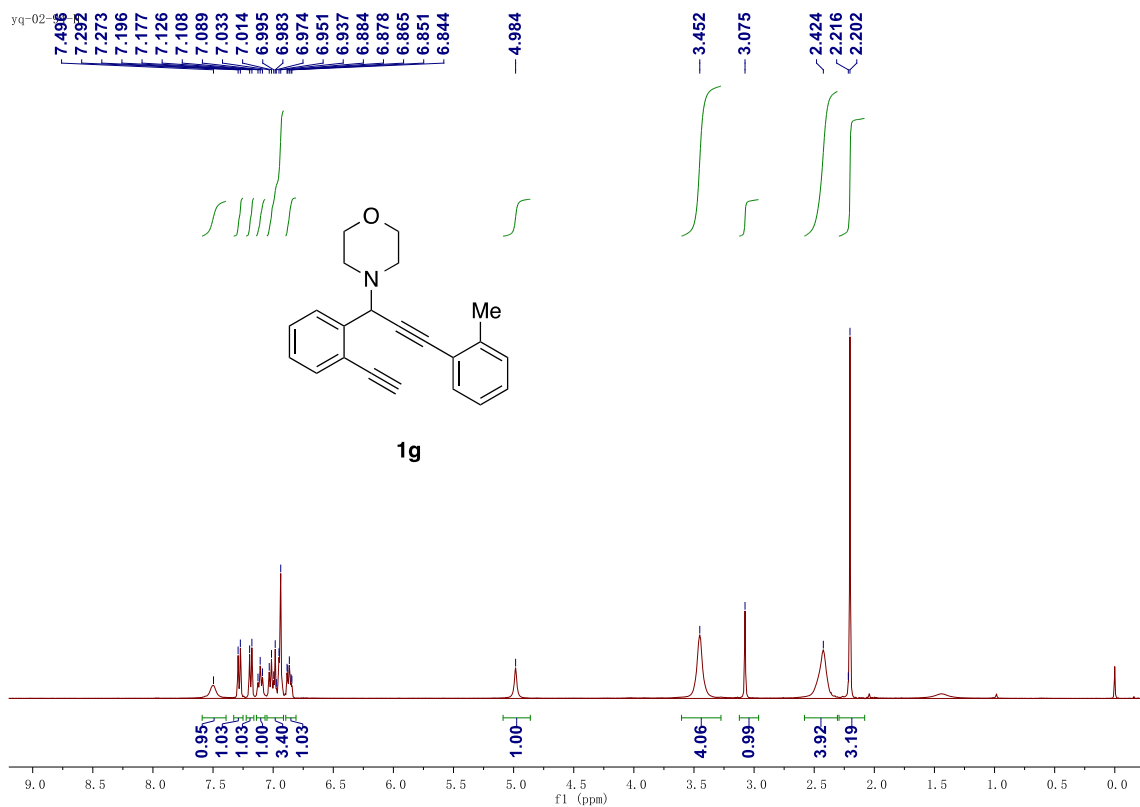
# <sup>1</sup>H NMR



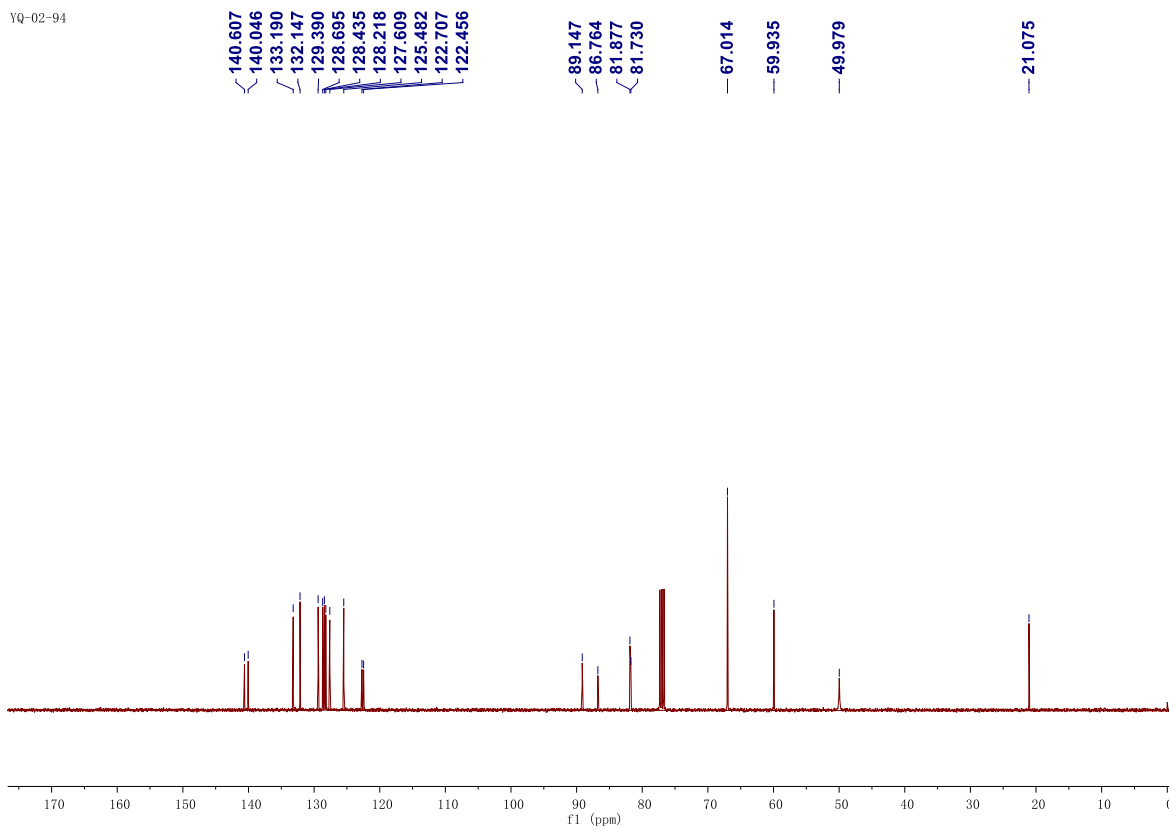
# <sup>13</sup>C NMR



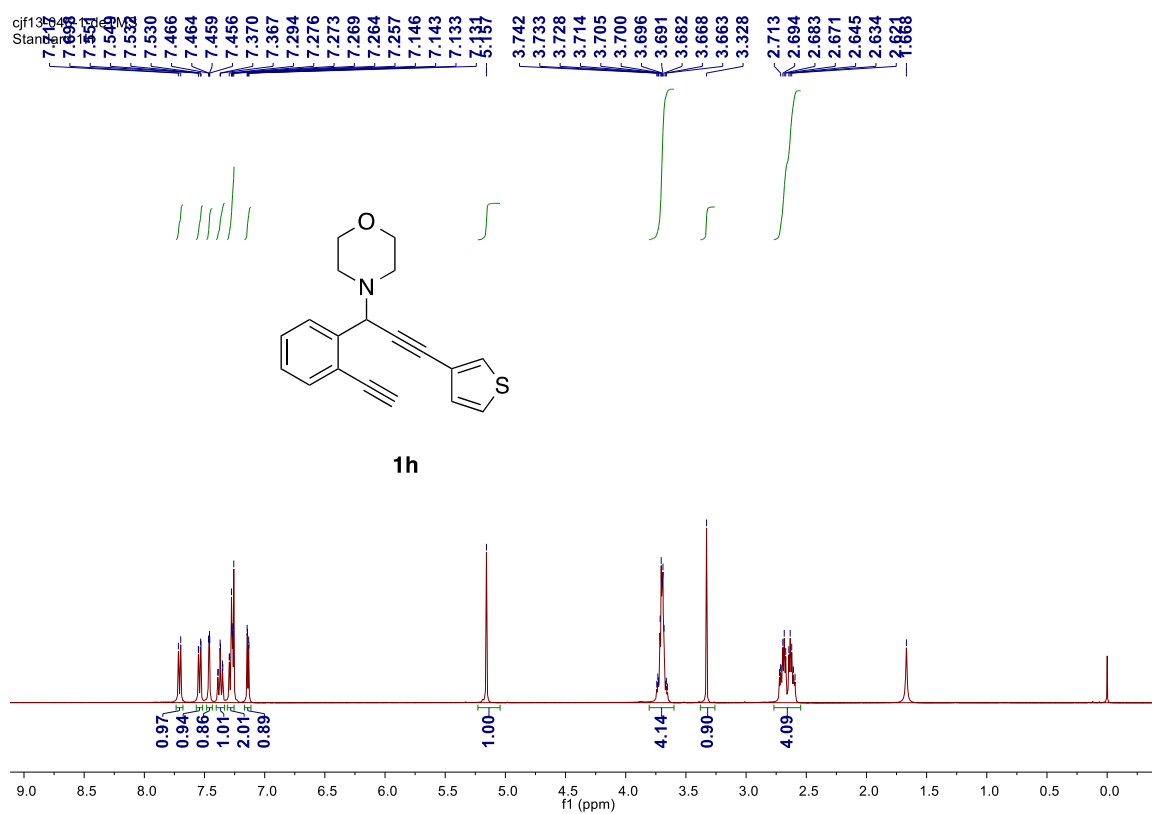
# <sup>1</sup>H NMR



# <sup>13</sup>C NMR

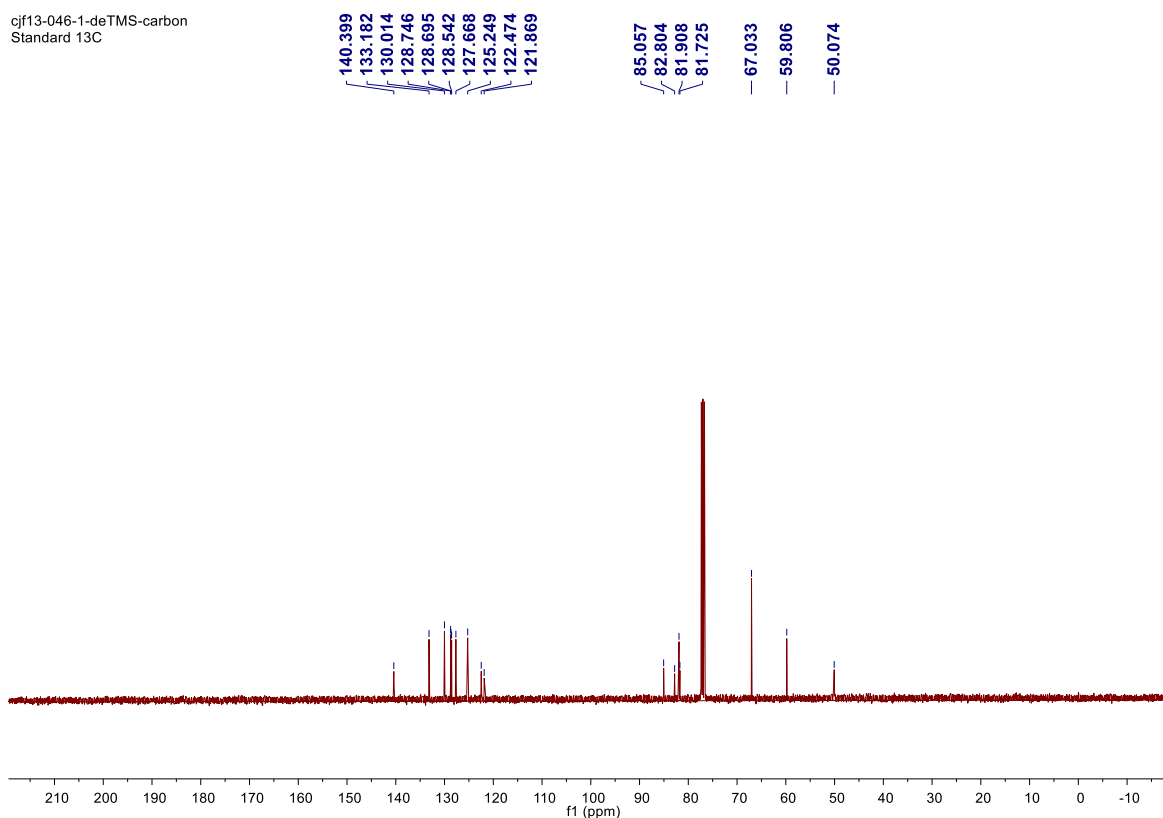


# <sup>1</sup>H NMR

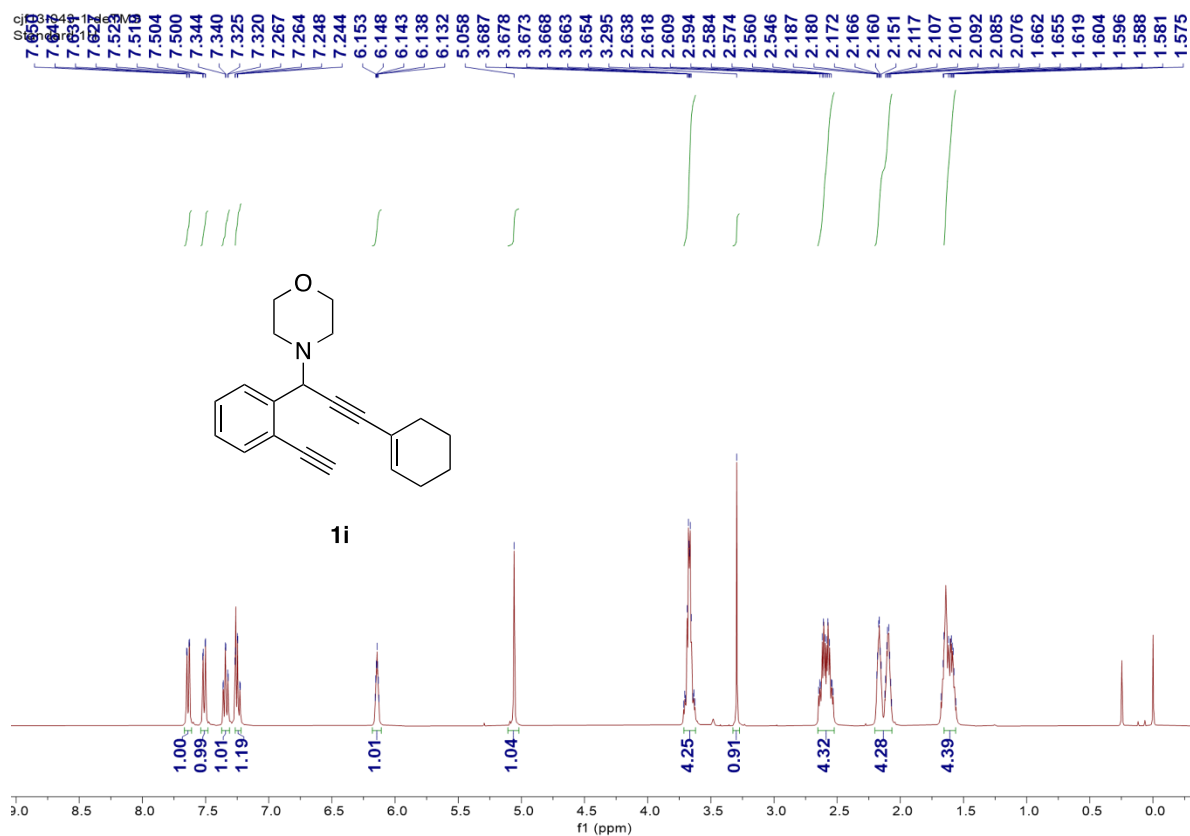


# <sup>13</sup>C NMR

Standard 13C



# <sup>1</sup>H NMR



# <sup>13</sup>C NMR

Standard 13C

140.843  
134.790  
133.094  
128.724  
128.431  
127.477  
122.416  
120.370

89.736

82.375  
81.815  
81.711

67.050

59.679

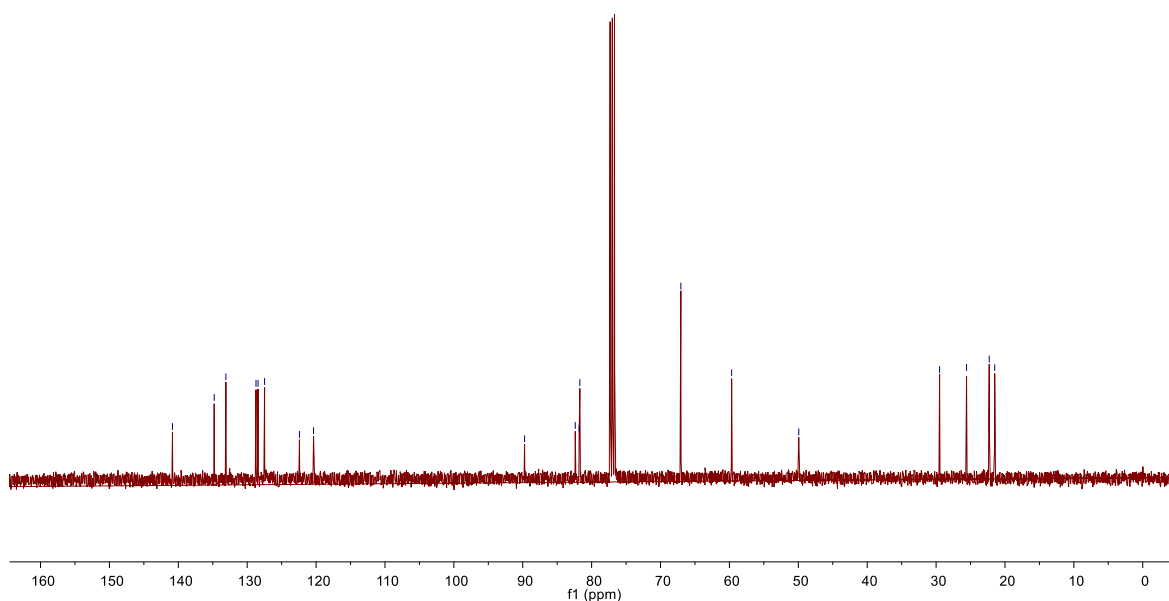
49.935

29.492

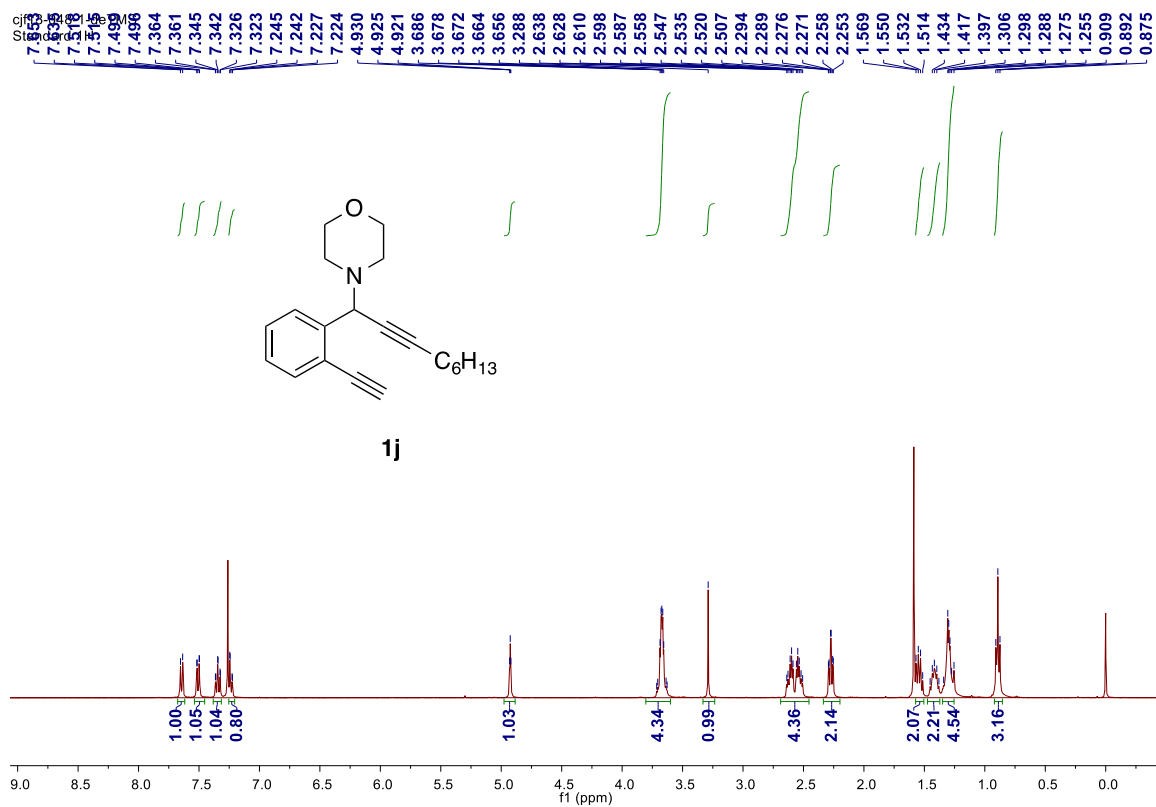
25.578

22.285

21.491

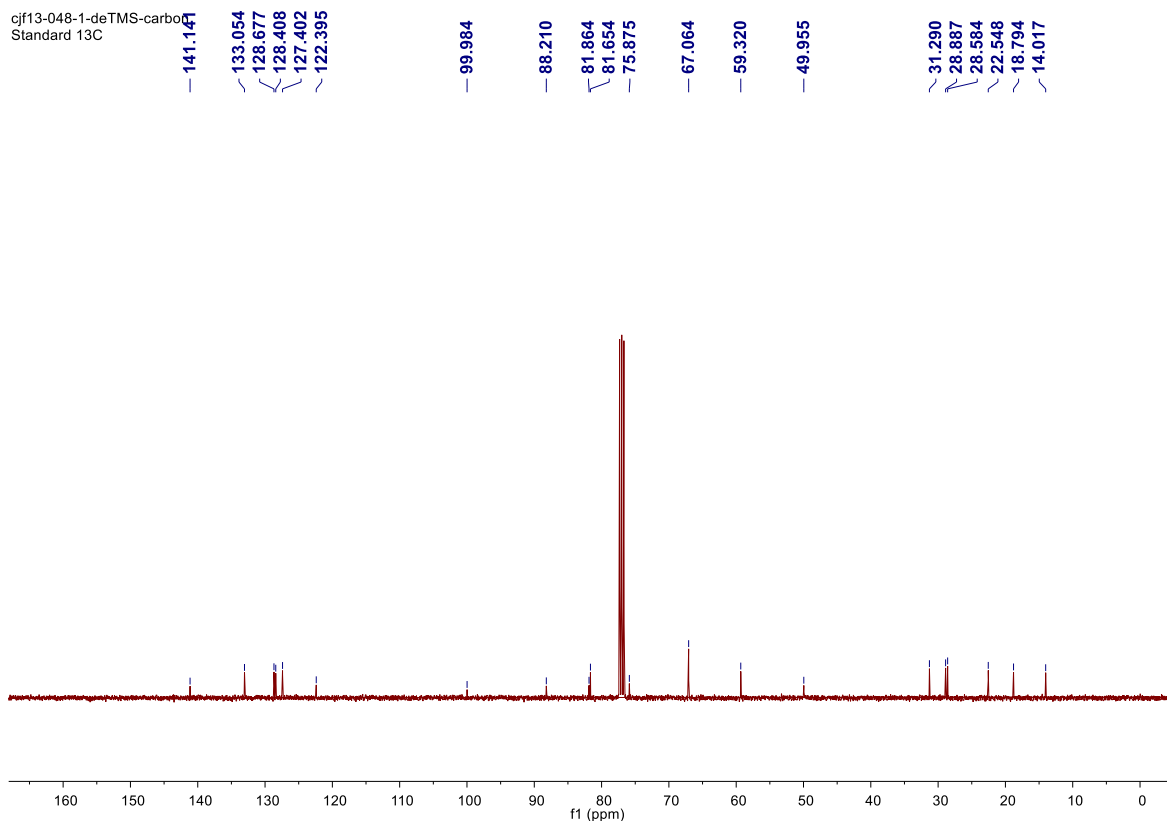


# <sup>1</sup>H NMR

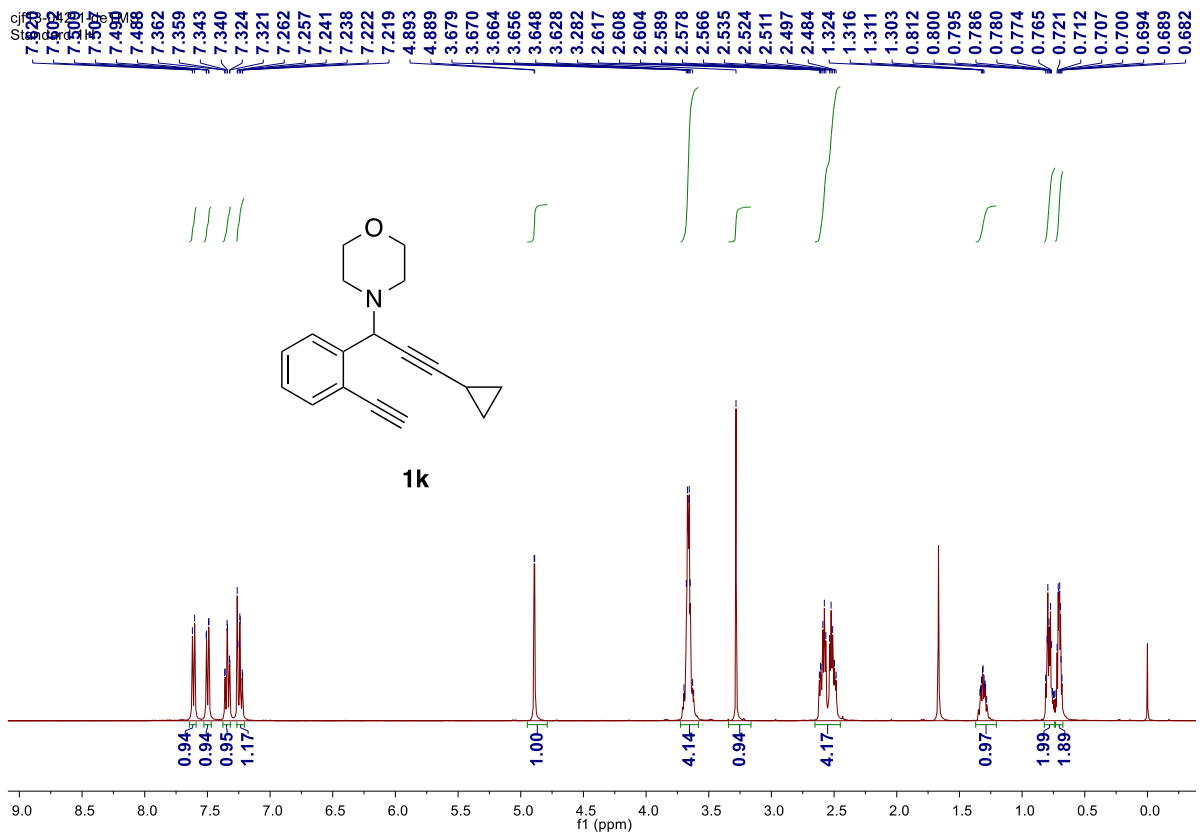


# <sup>13</sup>C NMR

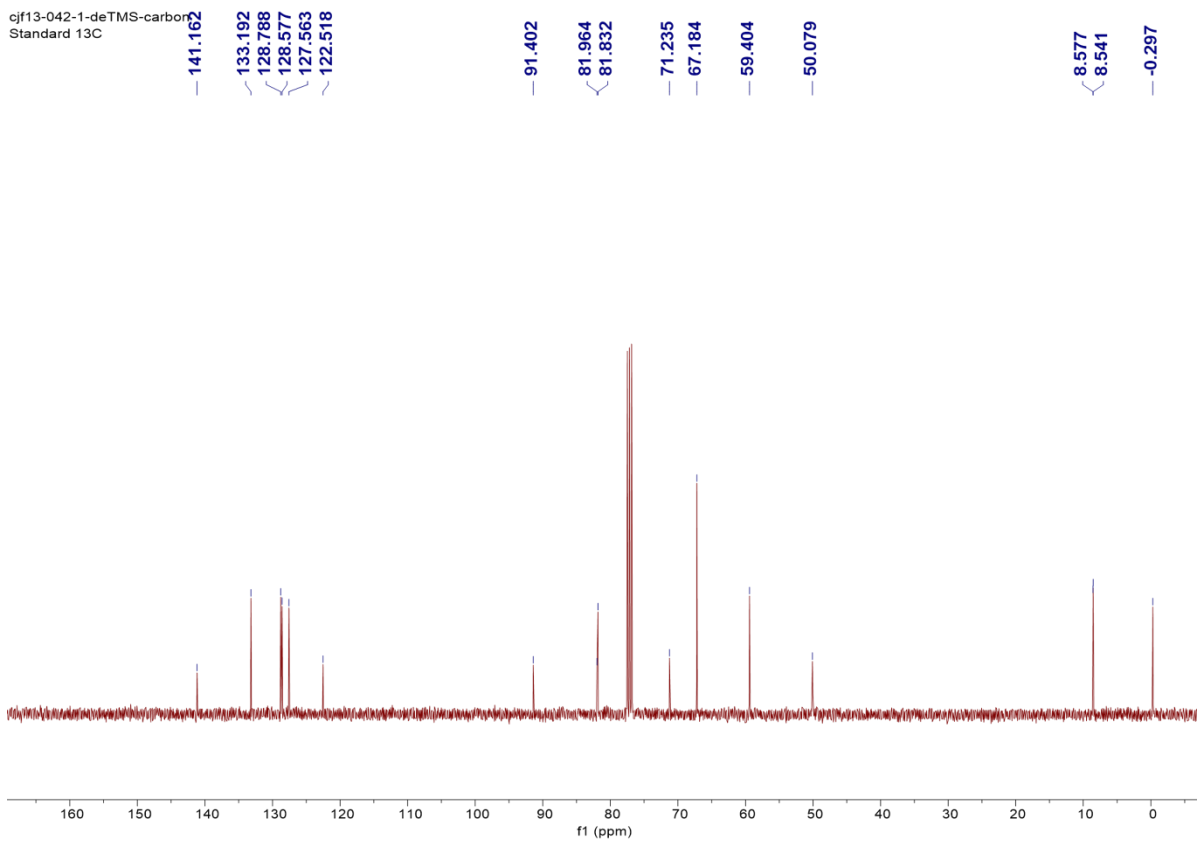
cjf13-048-1-deTMS-carbo  
Standard 13C



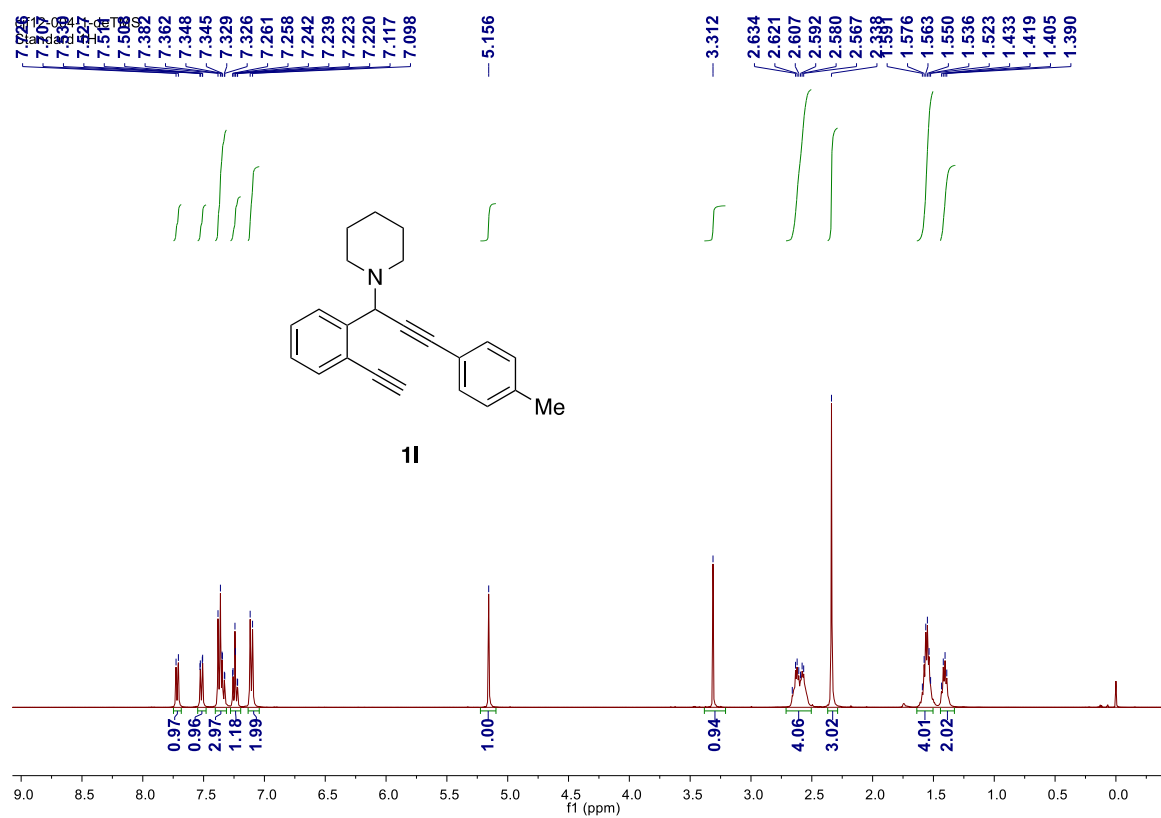
# <sup>1</sup>H NMR



# <sup>13</sup>C NMR

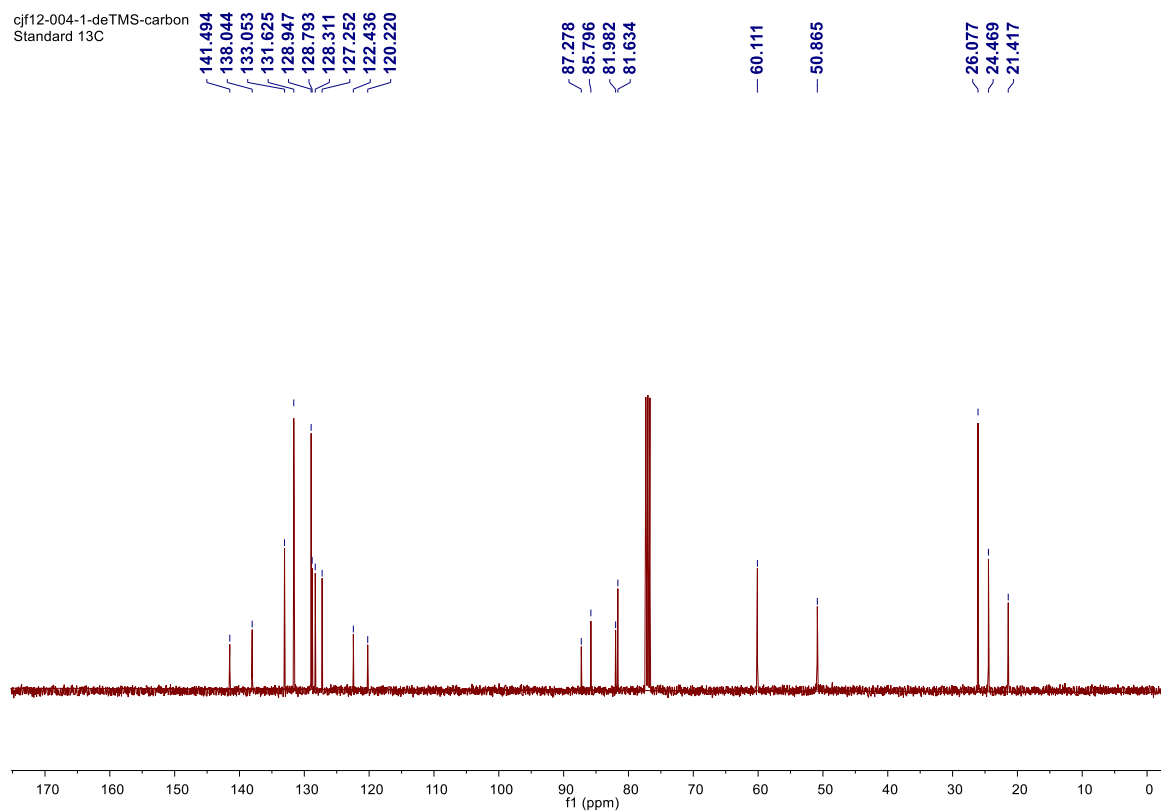


# <sup>1</sup>H NMR

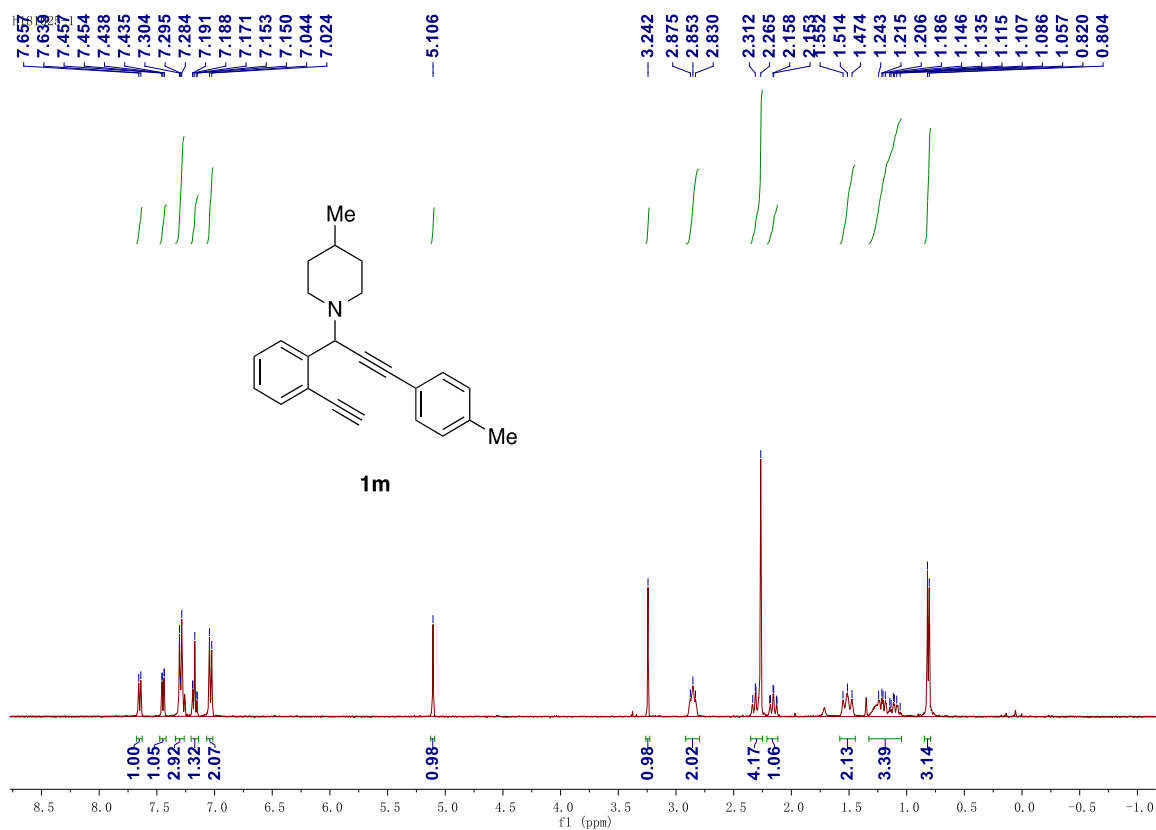


# <sup>13</sup>C NMR

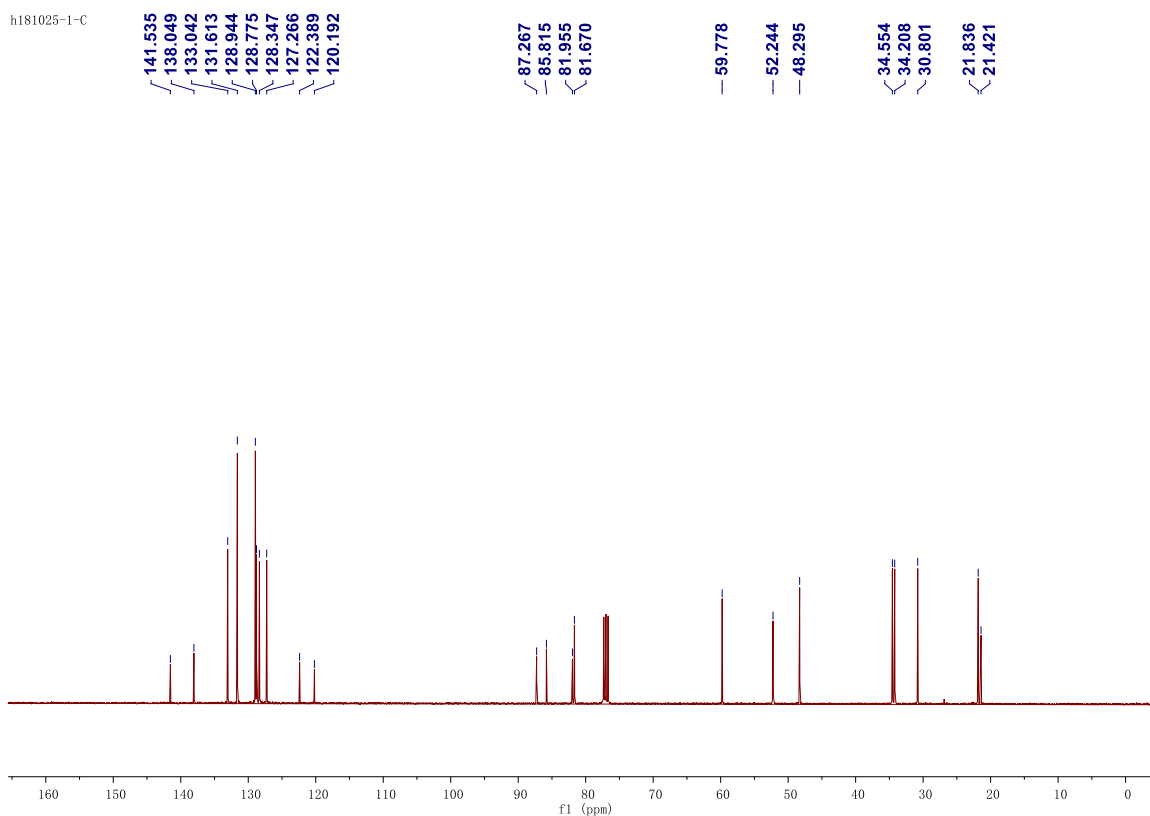
cyj12-004-1-deTMS-carbon  
Standard 13C



# <sup>1</sup>H NMR



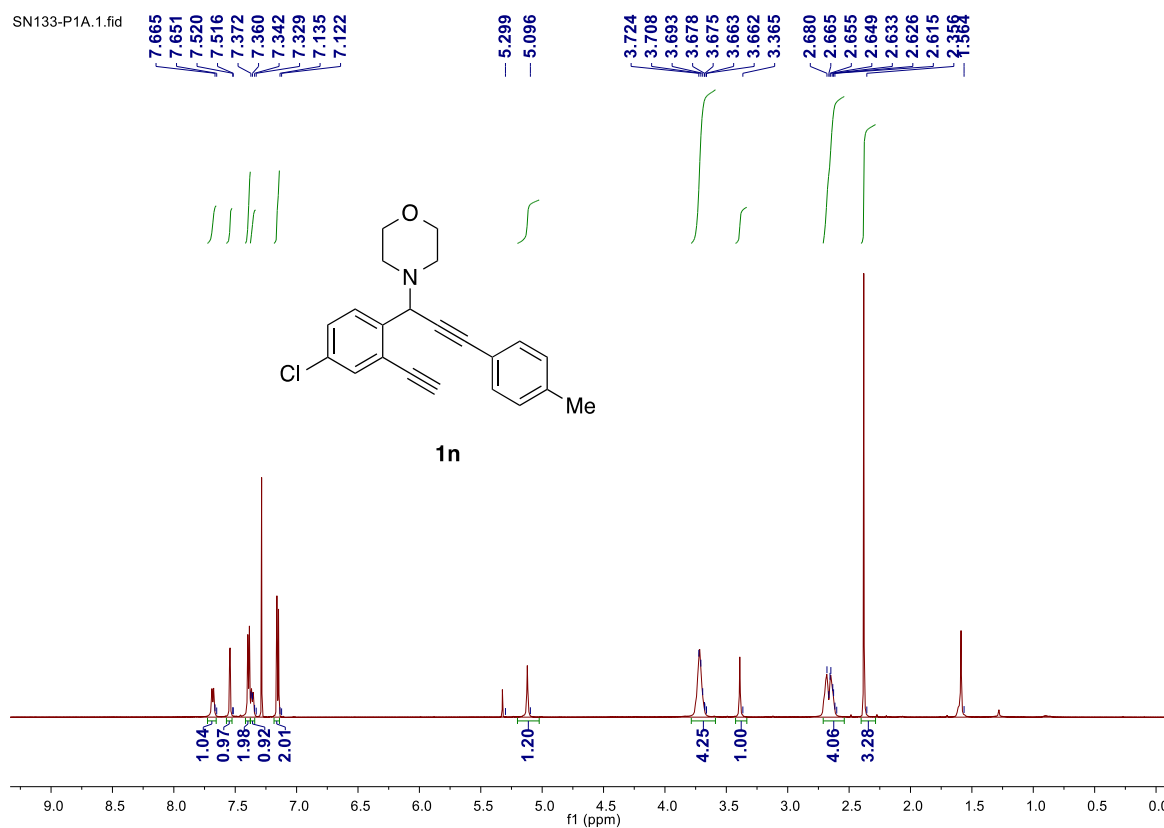
# <sup>13</sup>C NMR





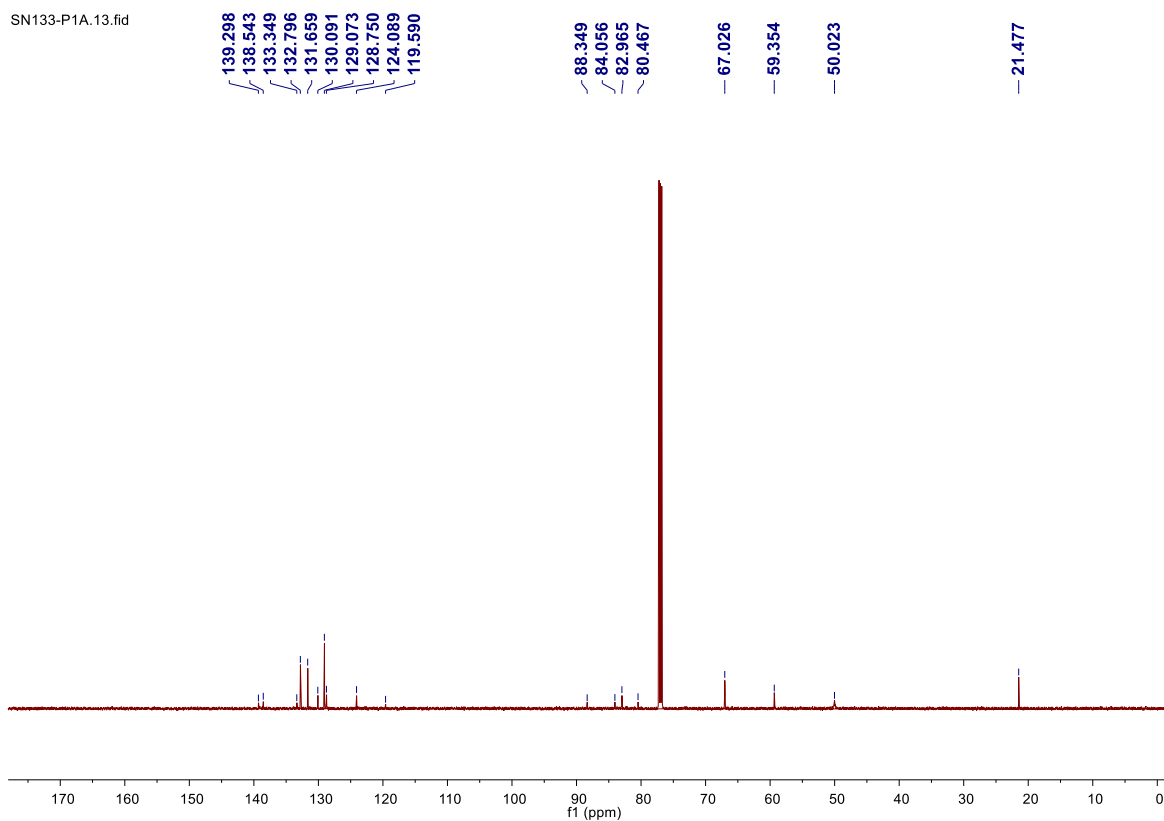
# <sup>1</sup>H NMR

SN133-P1A.1.fid



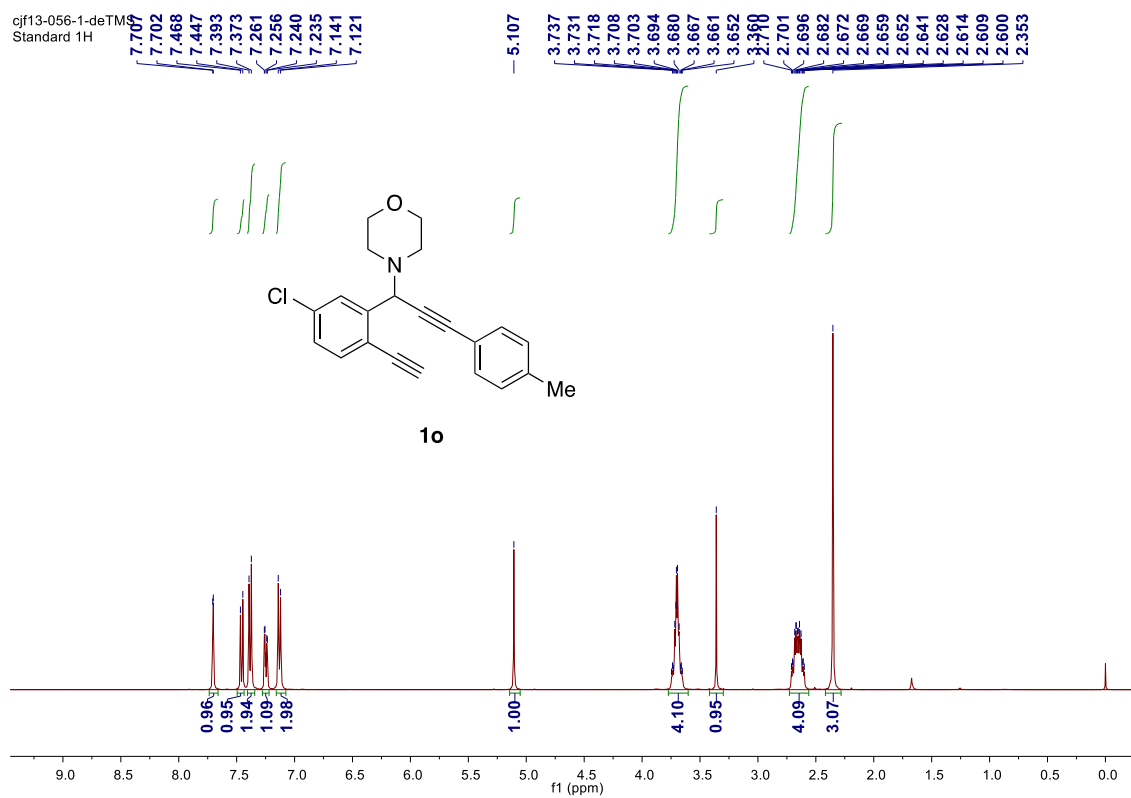
# <sup>13</sup>C NMR

SN133-P1A.13.fid



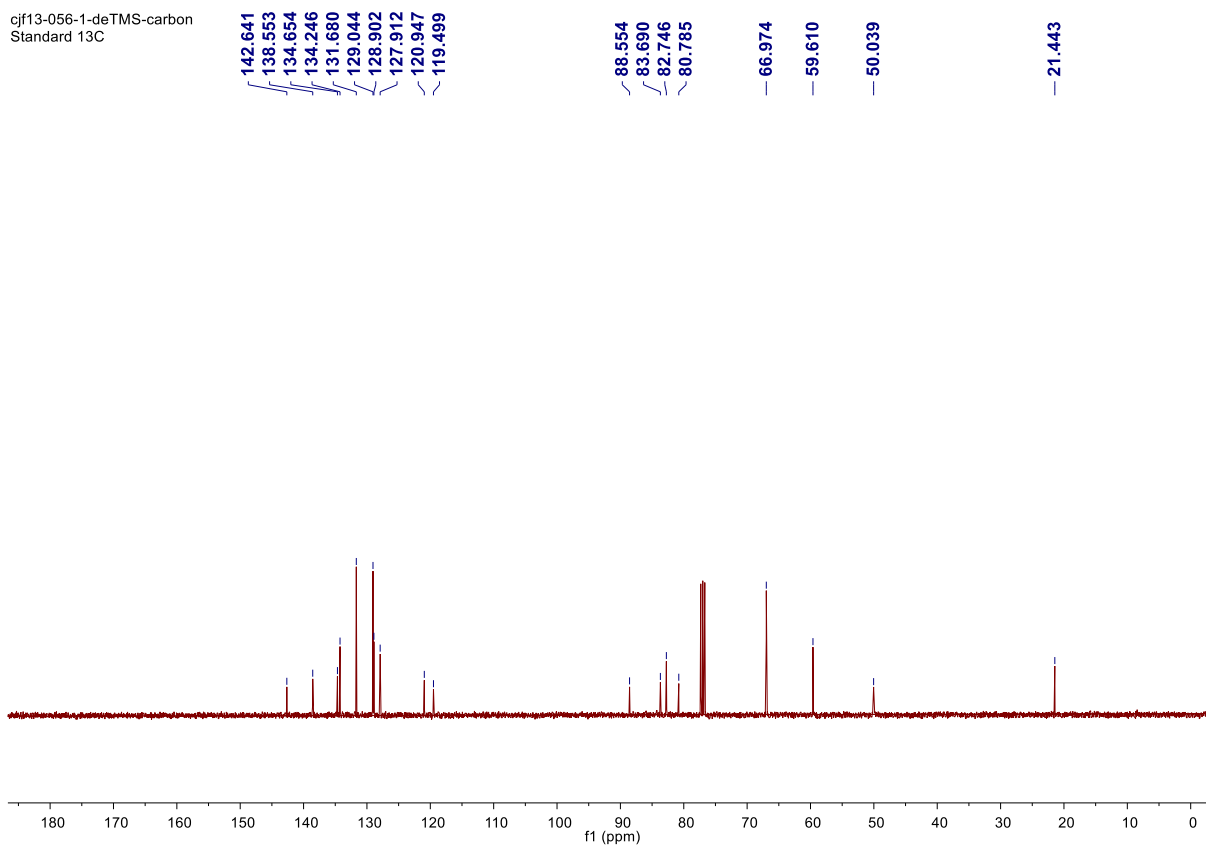
# <sup>1</sup>H NMR

cfj13-056-1-deTM  
Standard 1H

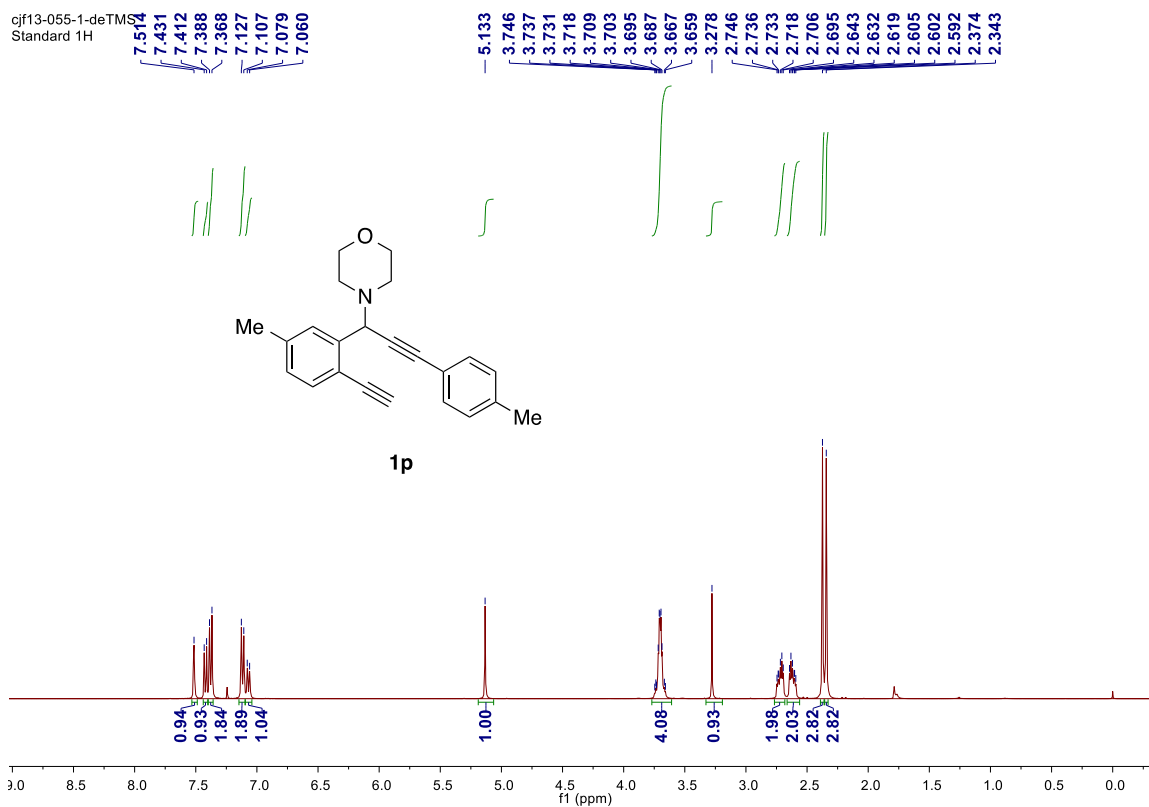


# <sup>13</sup>C NMR

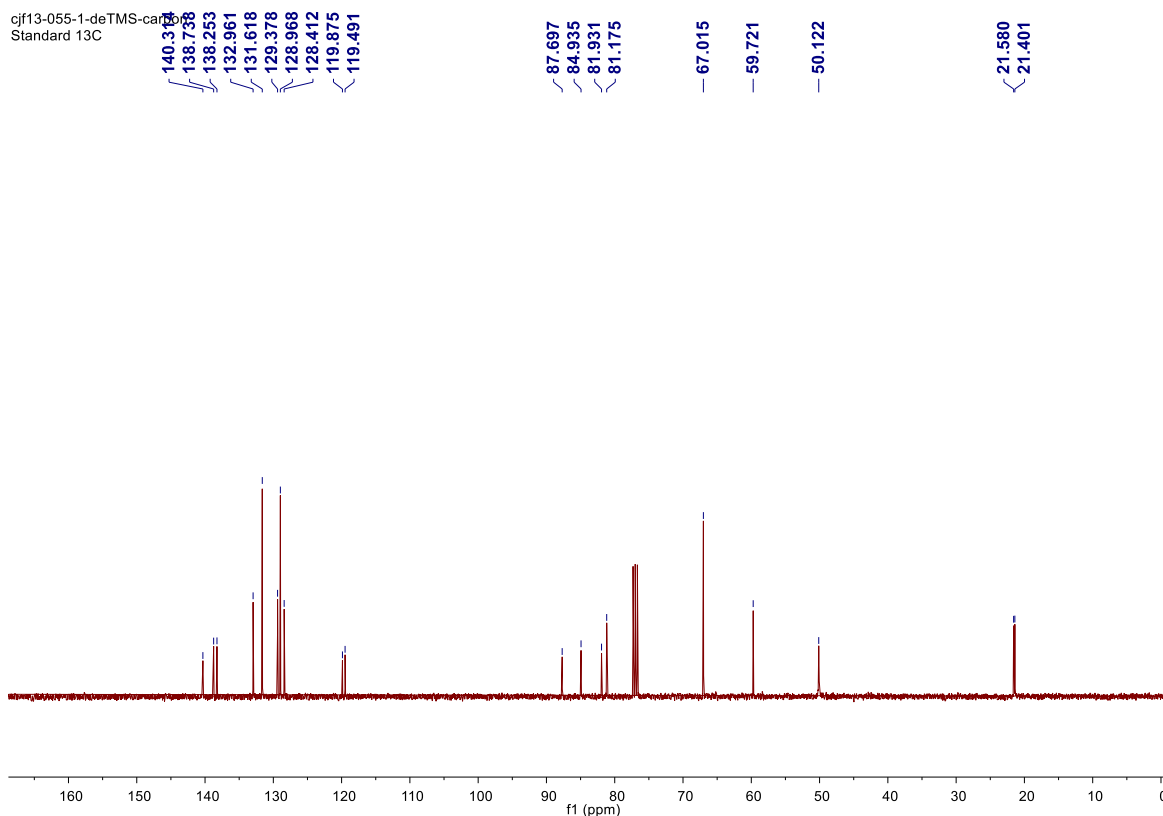
cfj13-056-1-deTMS-carbon  
Standard 13C



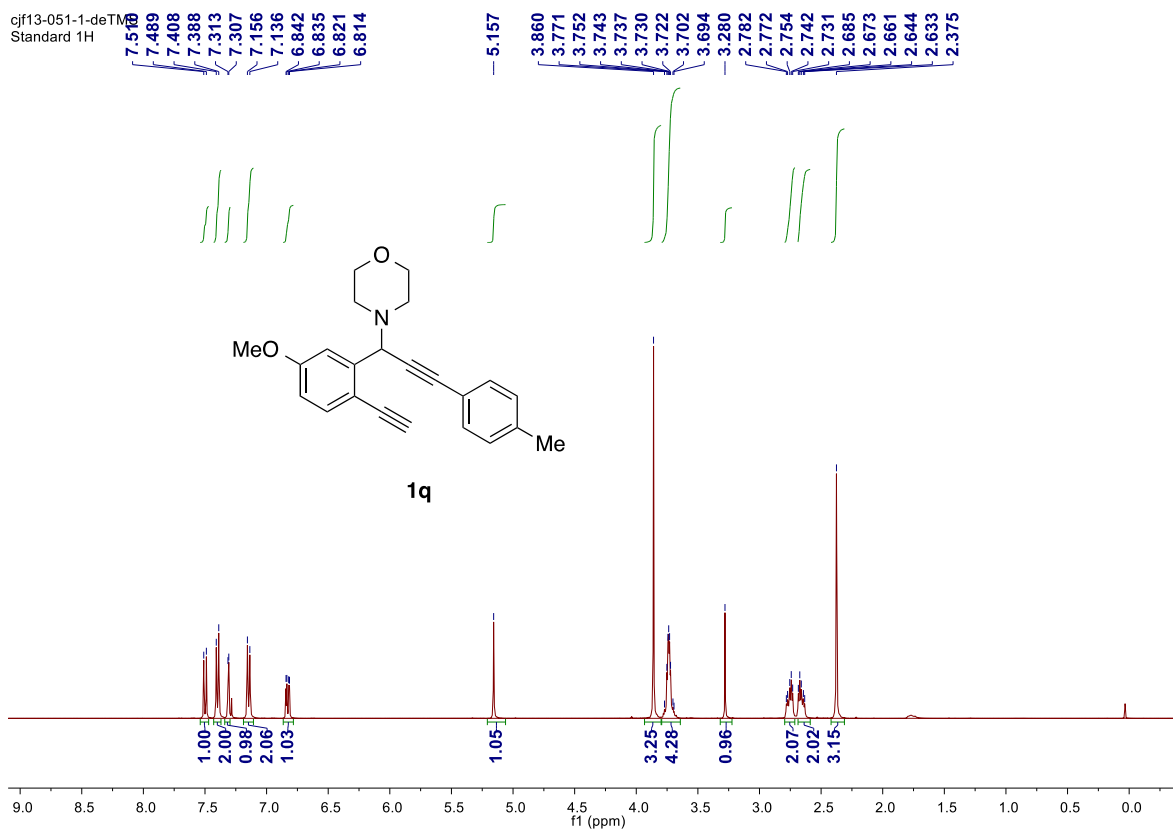
# <sup>1</sup>H NMR



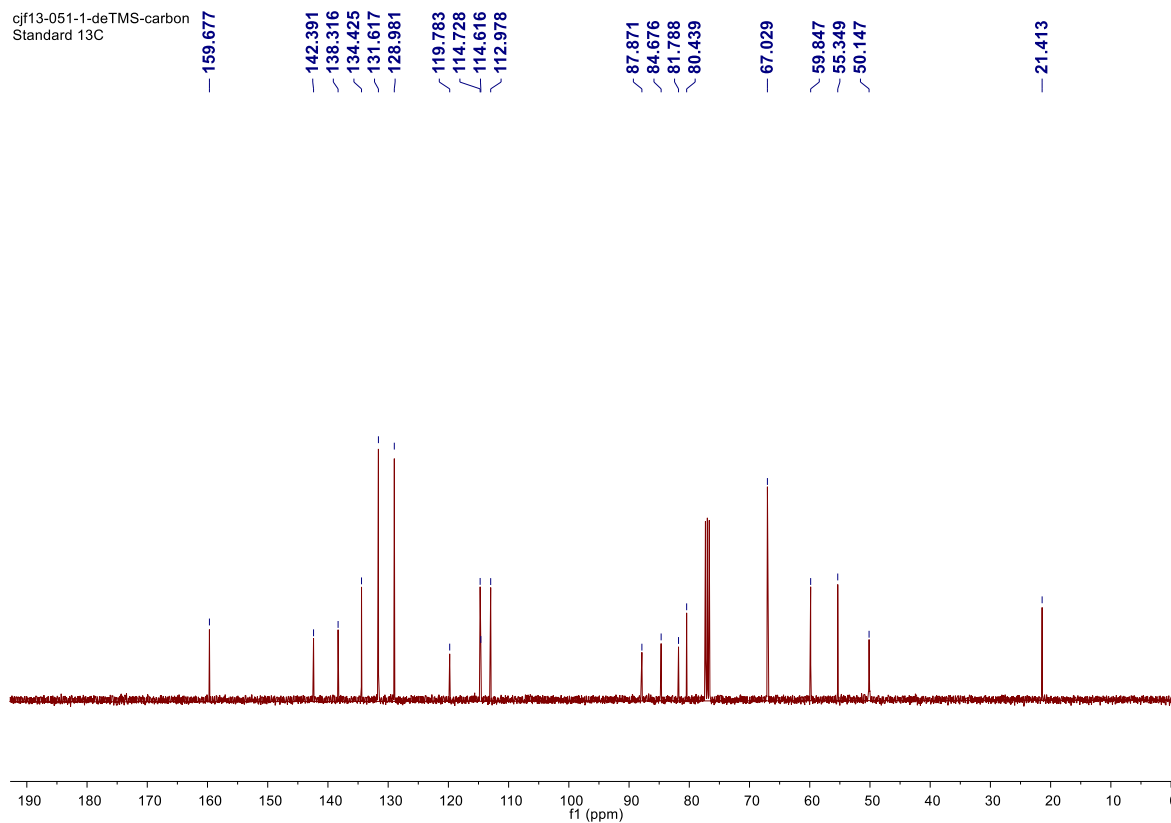
# <sup>13</sup>C NMR



# <sup>1</sup>H NMR

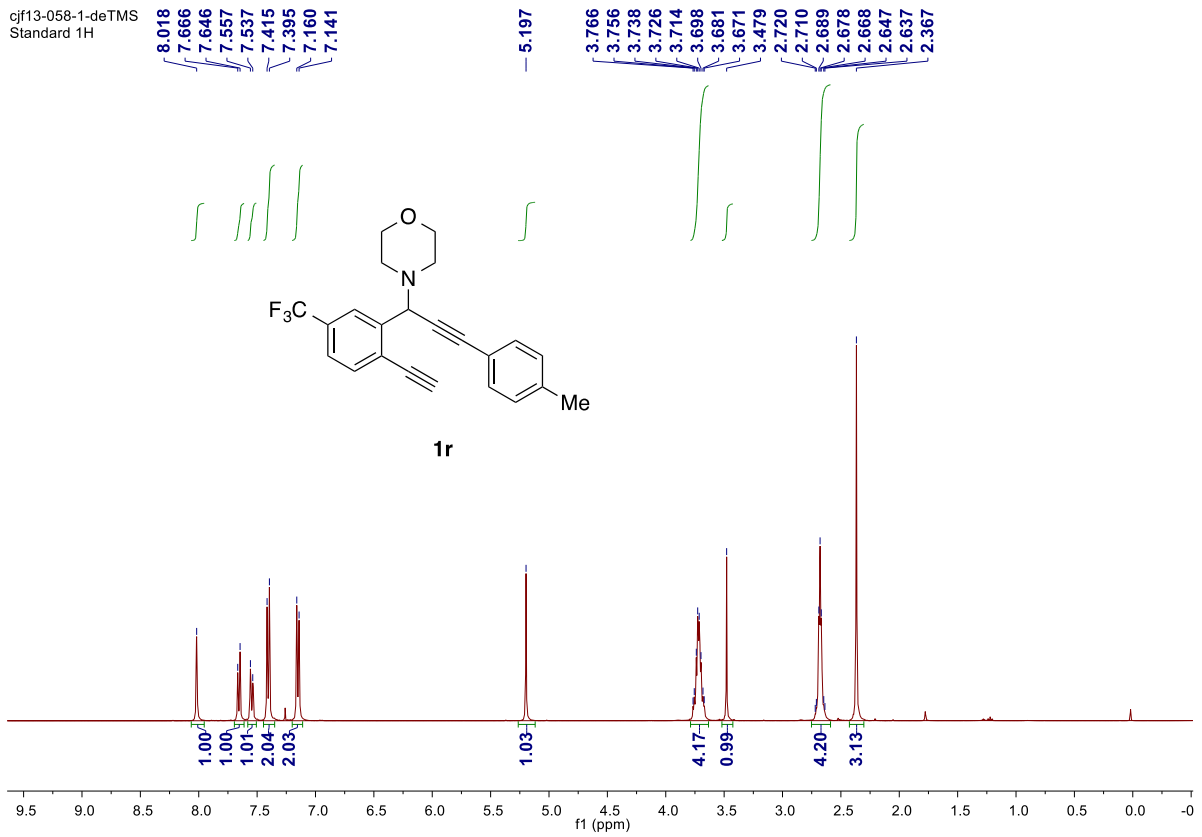


# <sup>13</sup>C NMR



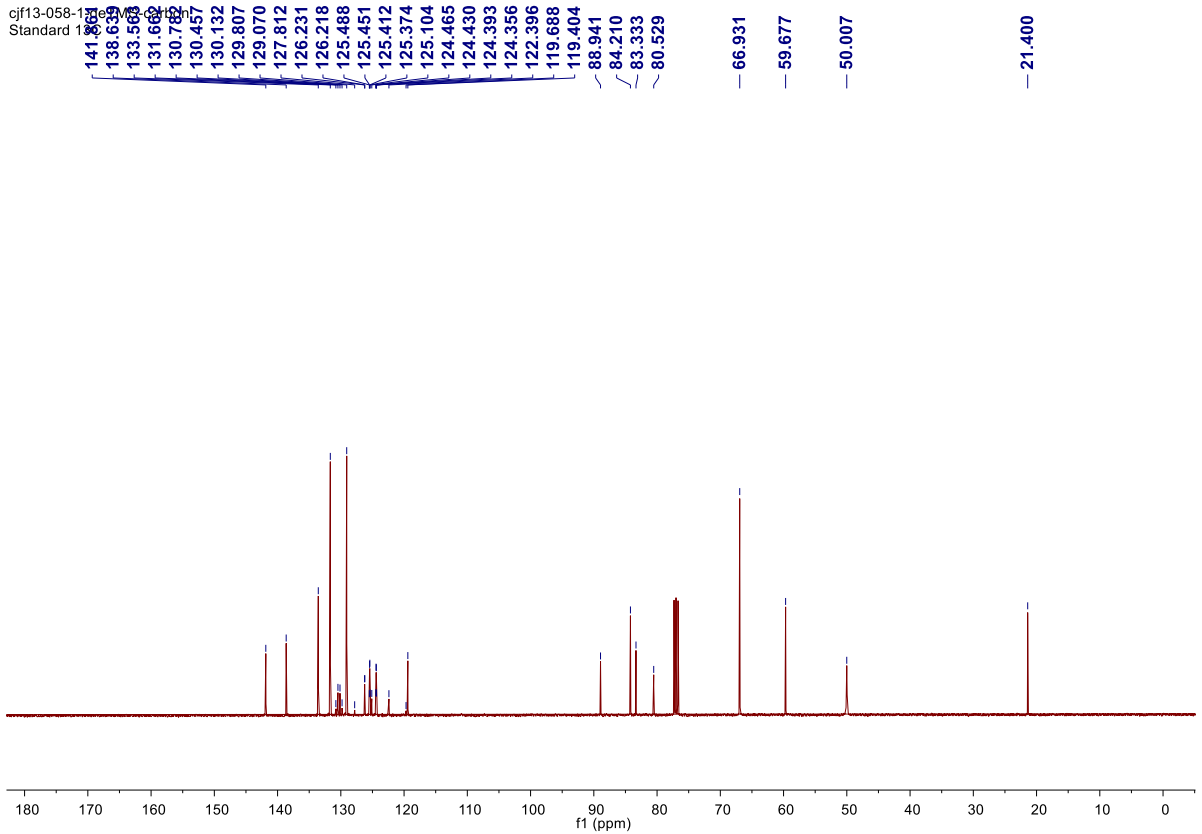
# <sup>1</sup>H NMR

cfj13-058-1-deTMS  
Standard 1H

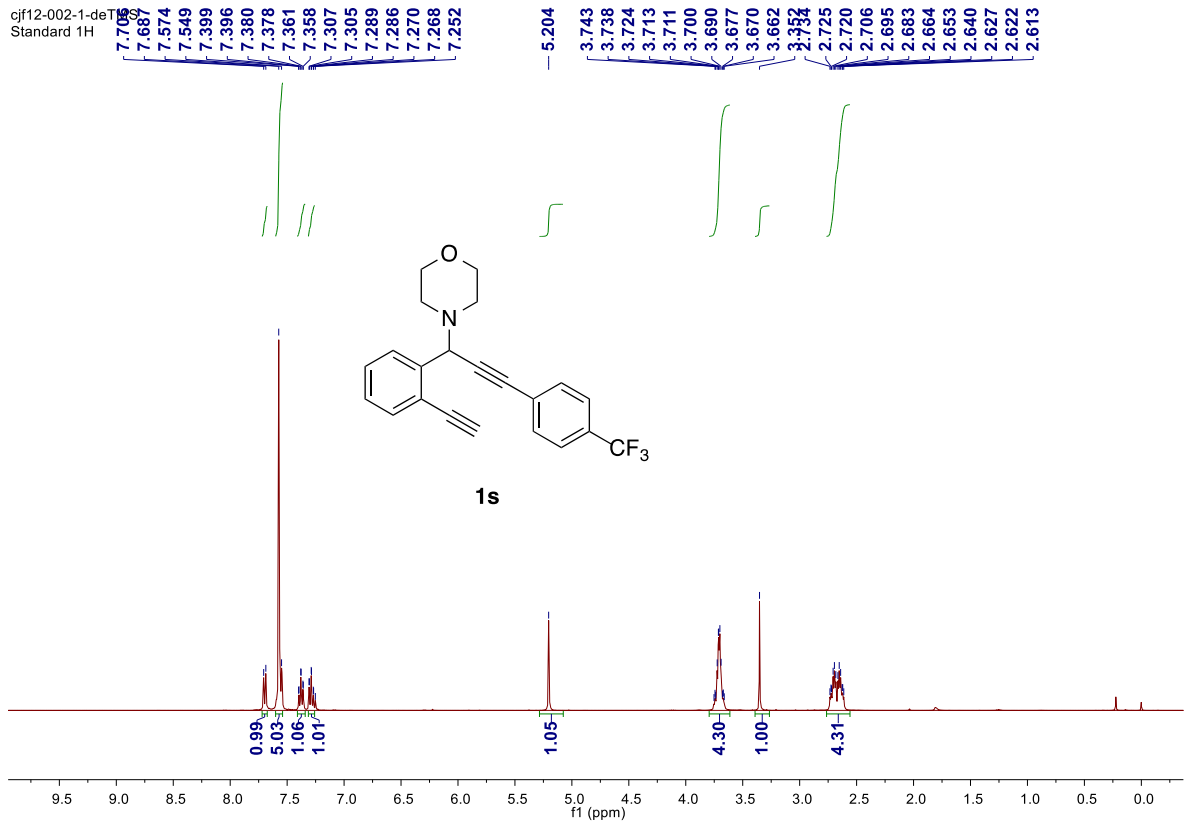


# <sup>13</sup>C NMR

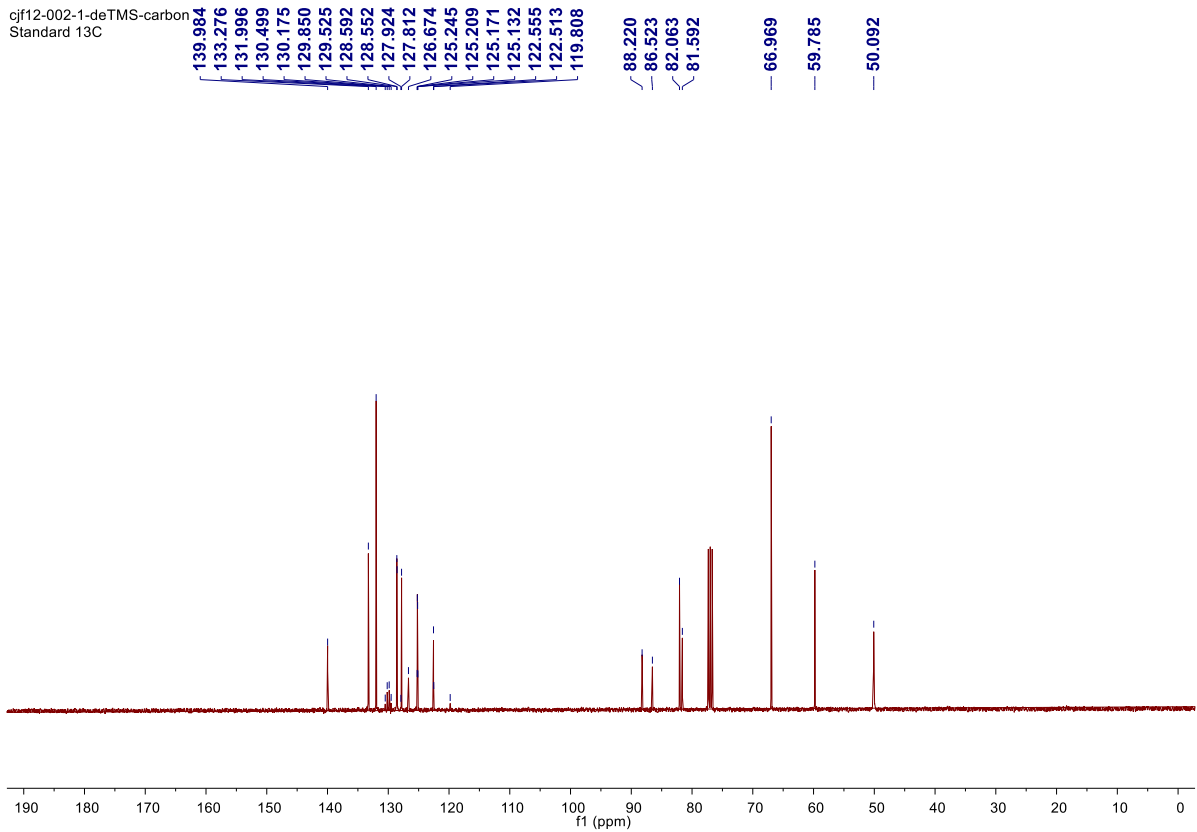
cfj13-058-1-deTMS  
Standard 13C



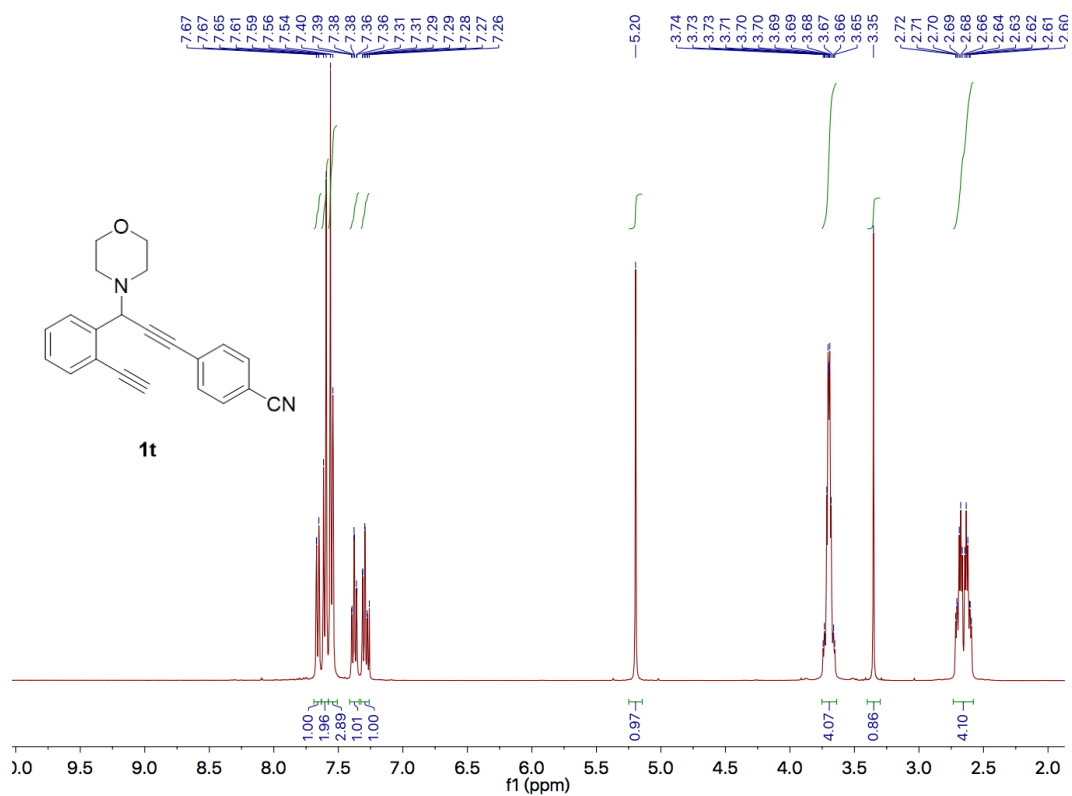
# <sup>1</sup>H NMR



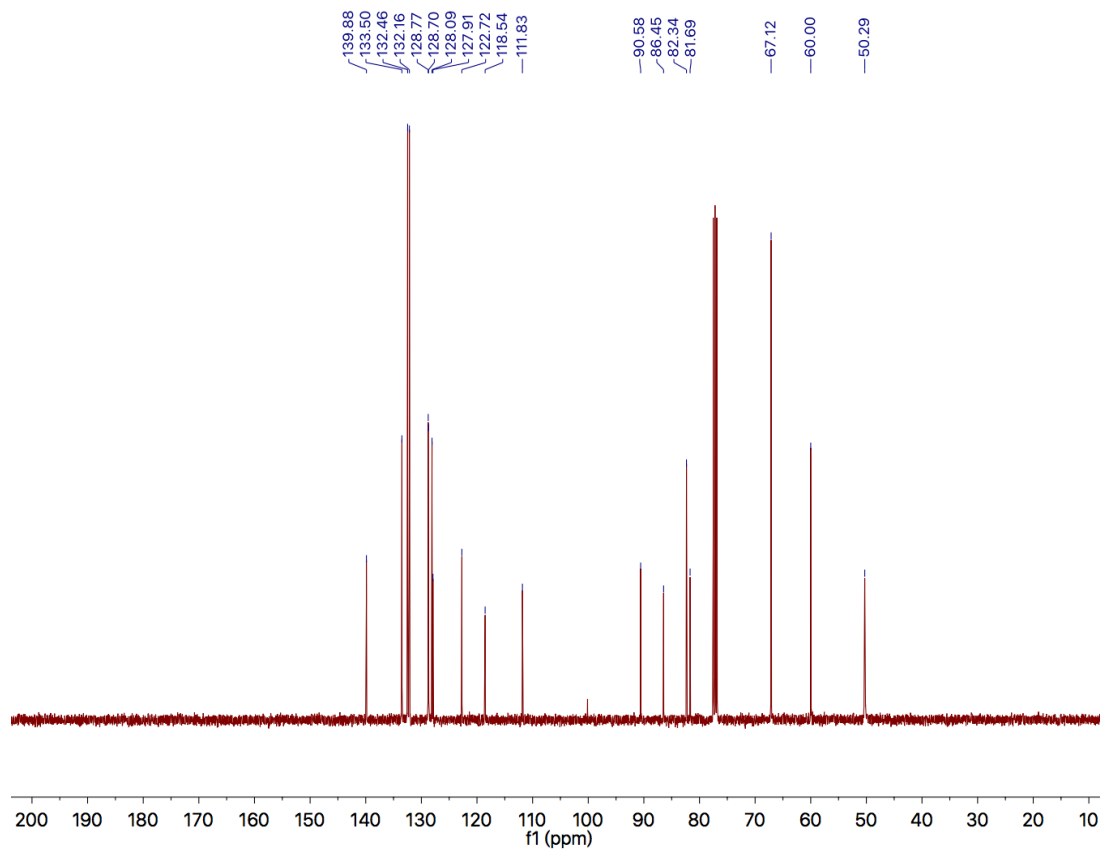
# <sup>13</sup>C NMR



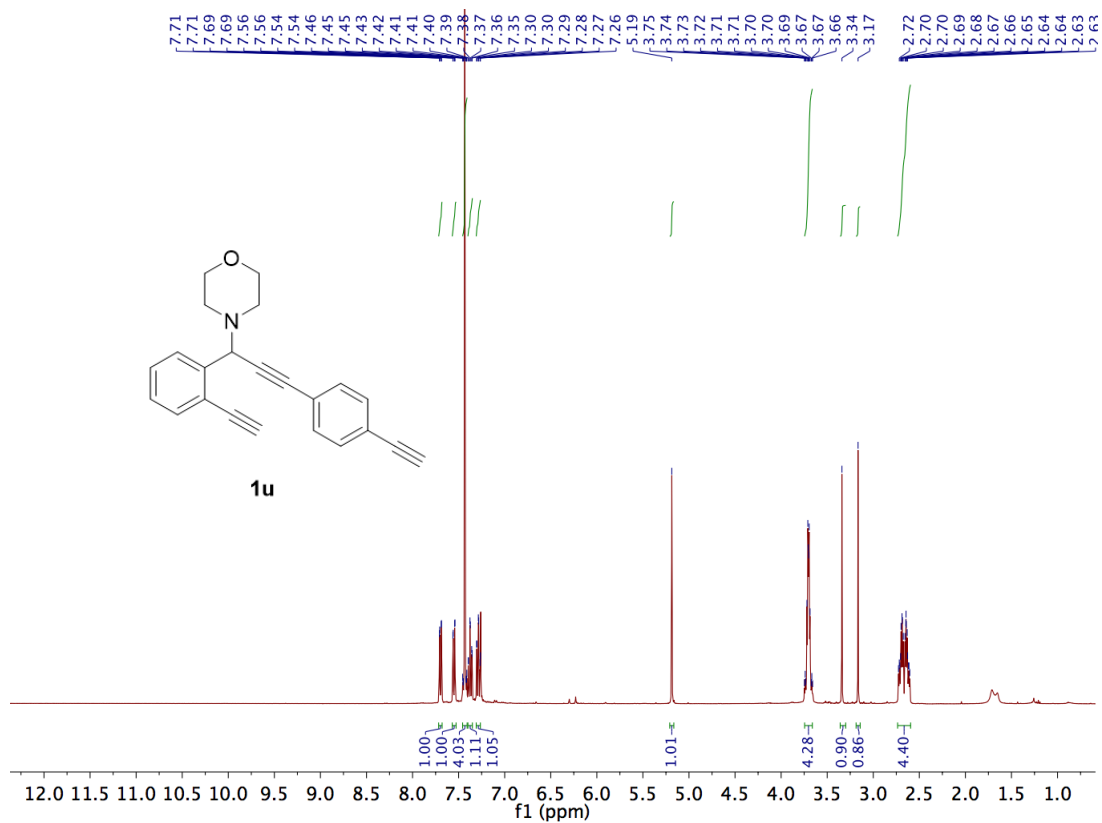
# <sup>1</sup>H NMR



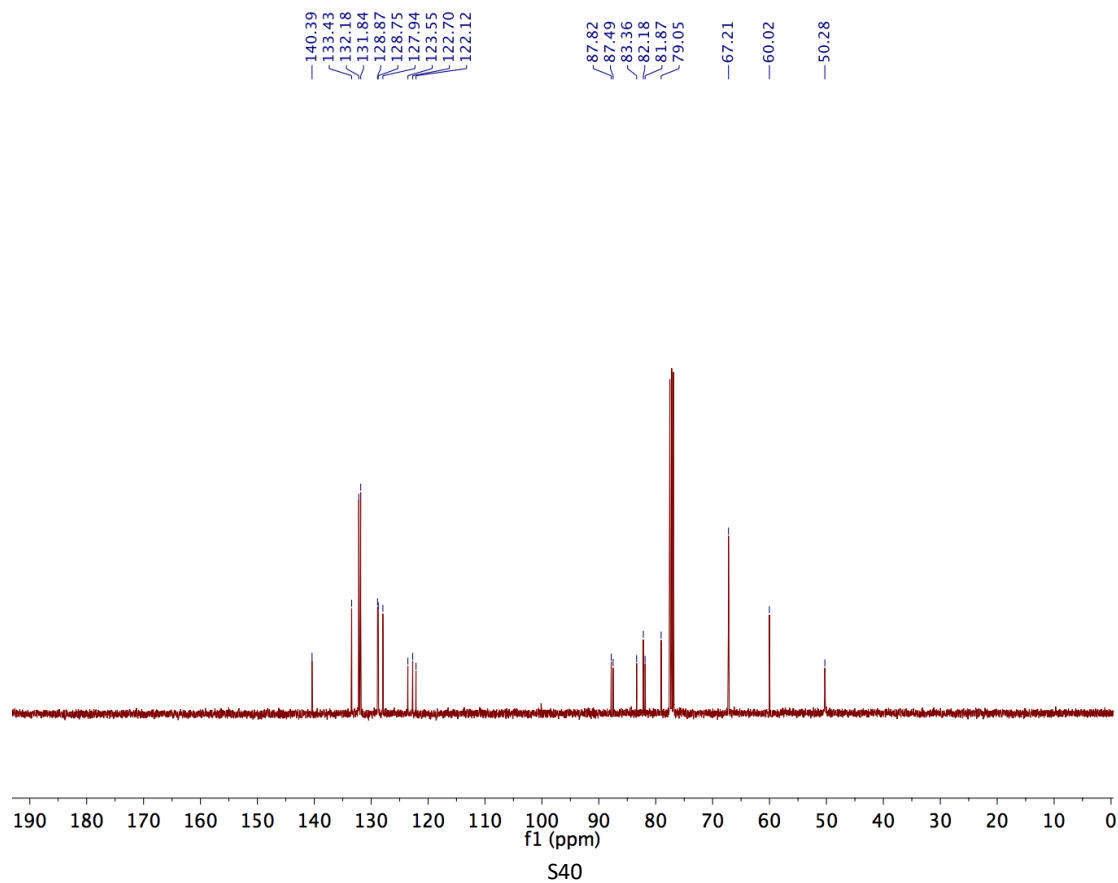
# <sup>13</sup>C NMR



# <sup>1</sup>H NMR

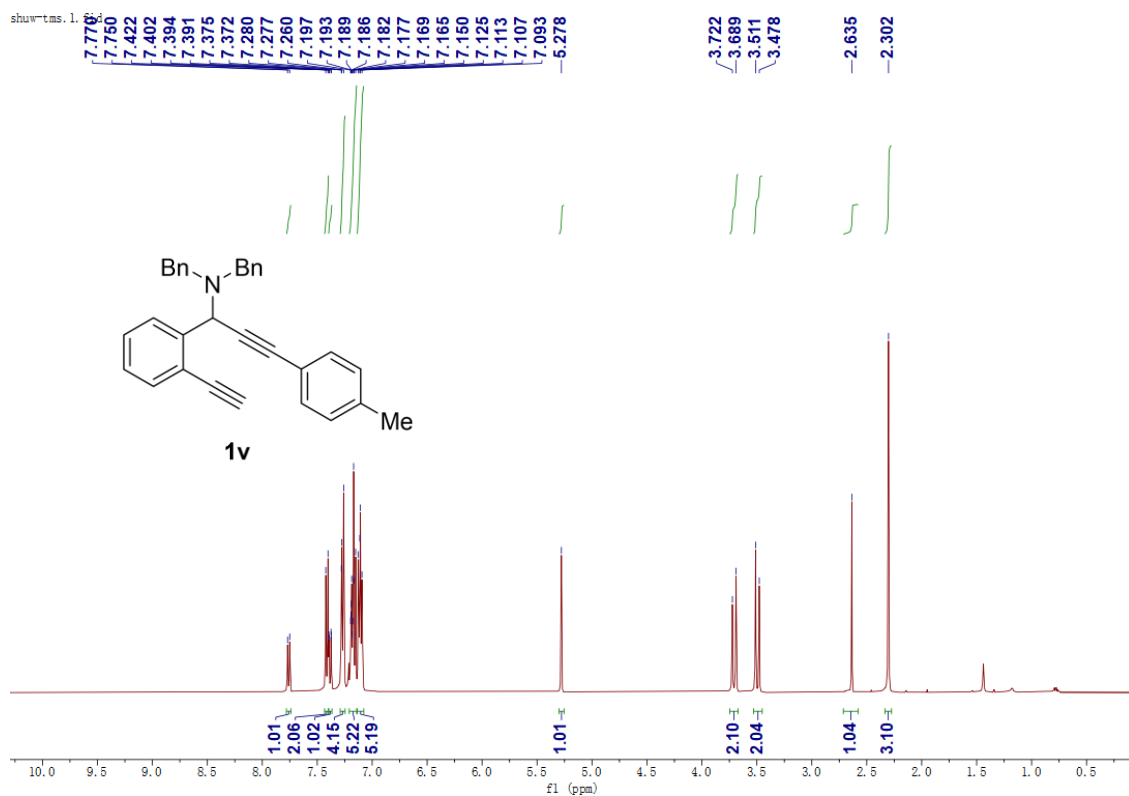


# <sup>13</sup>C NMR

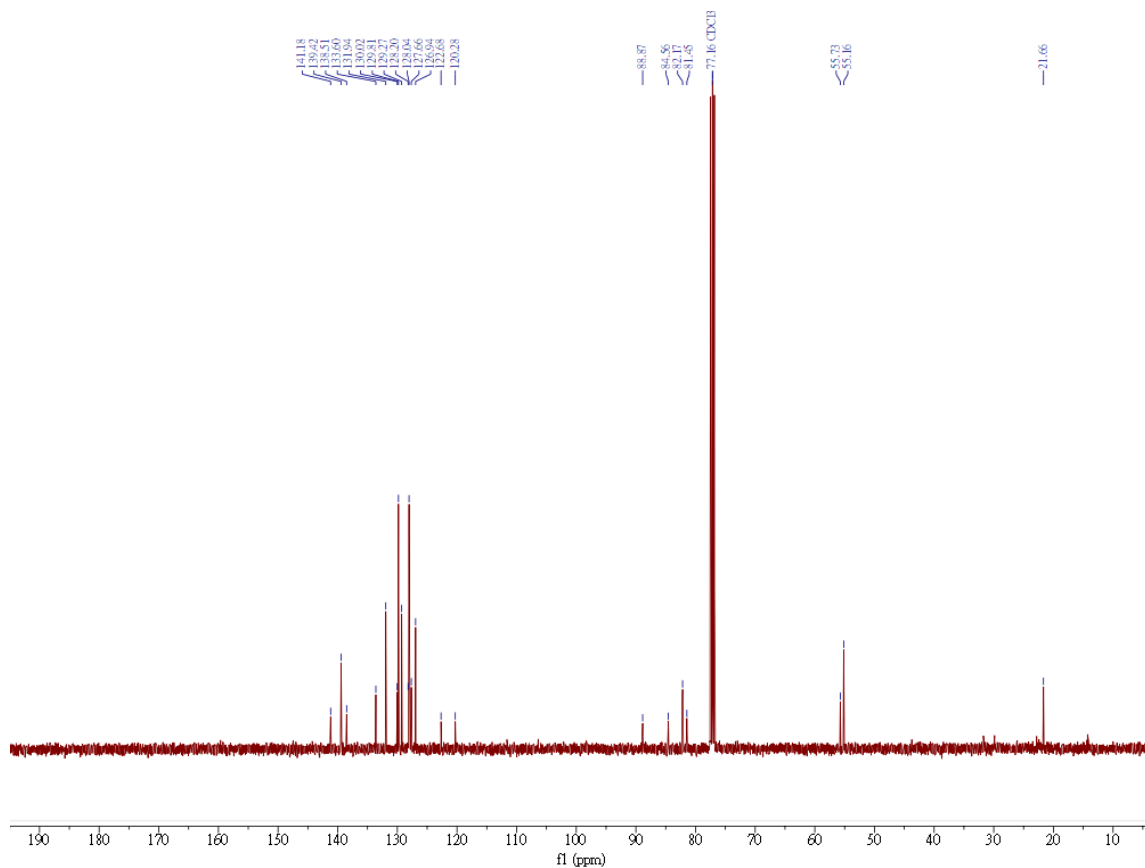




# <sup>1</sup>H NMR

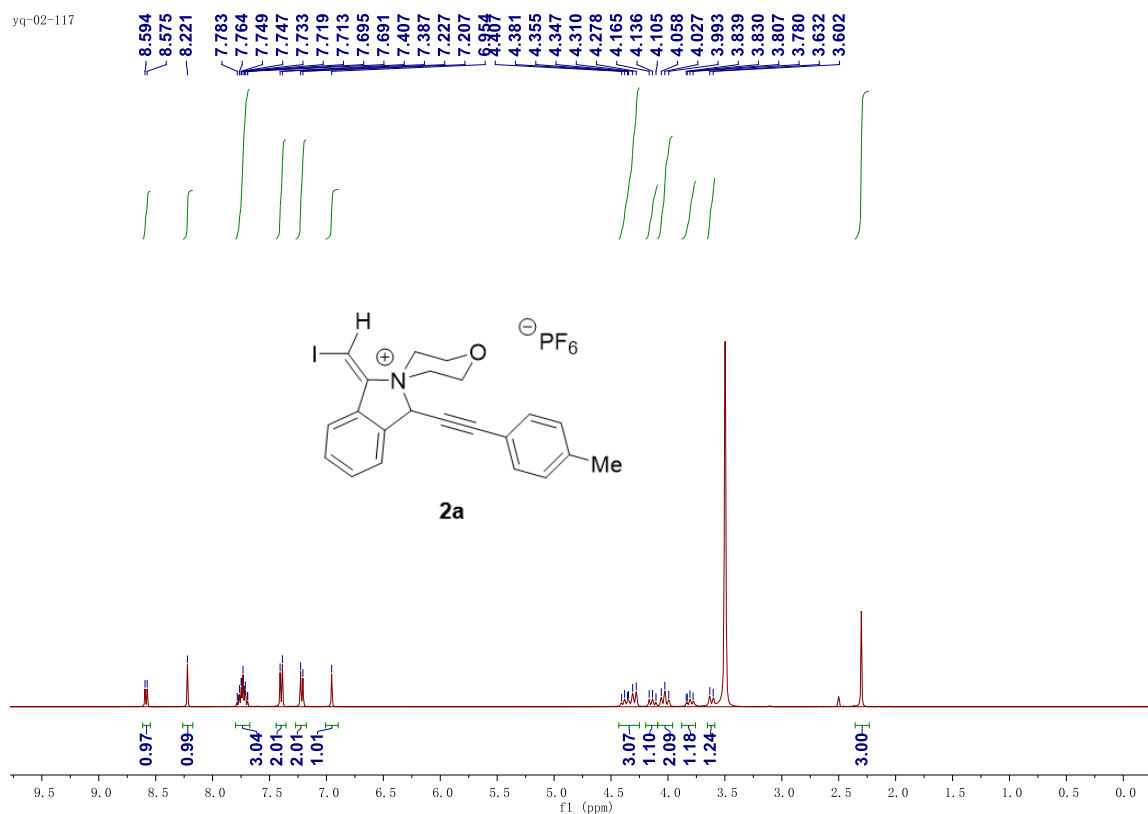


# <sup>13</sup>C NMR



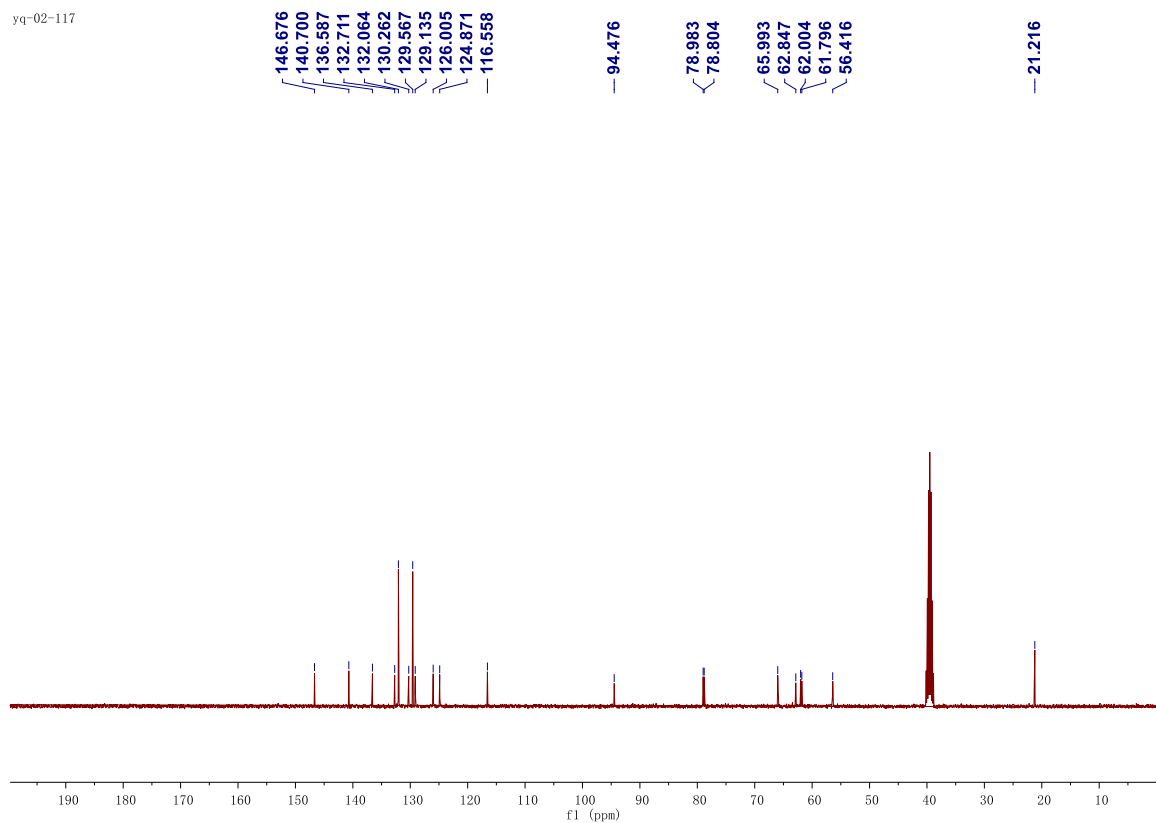
# <sup>1</sup>H NMR

yq-02-117



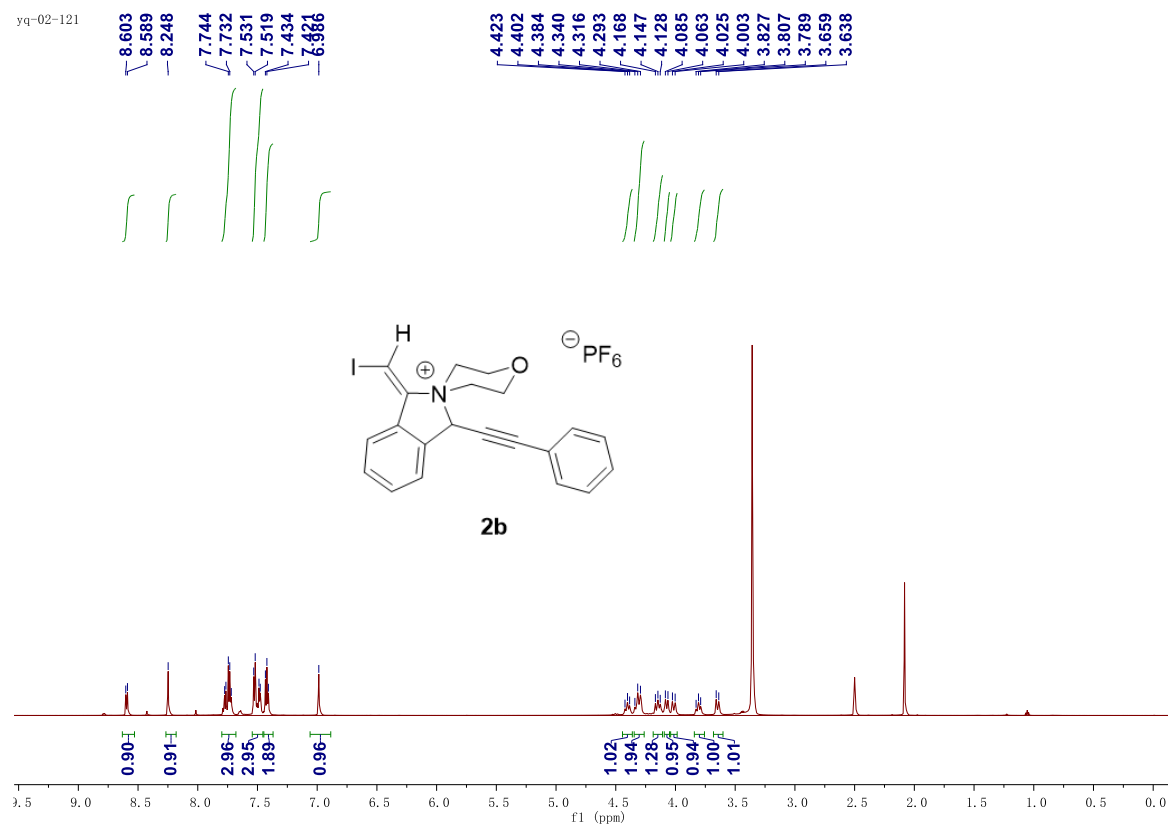
# <sup>13</sup>C NMR

yq-02-117



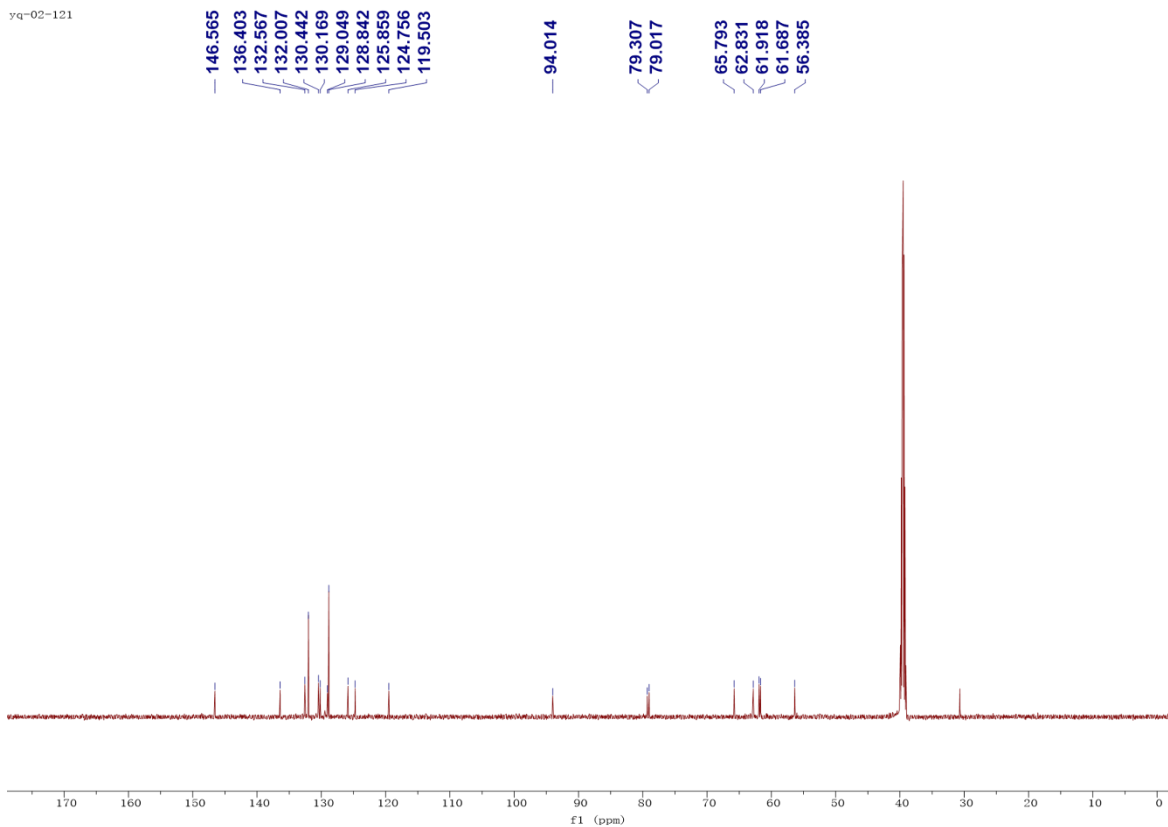
# <sup>1</sup>H NMR

yq-02-121



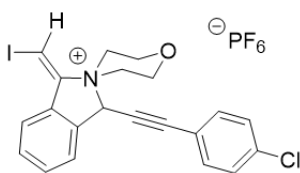
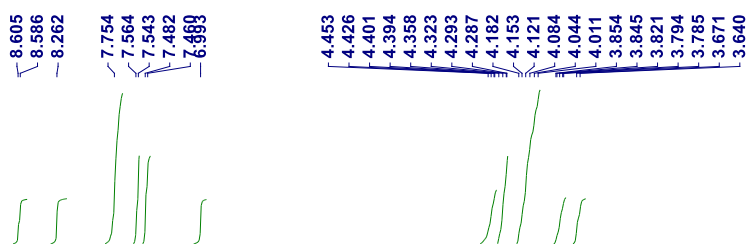
# <sup>13</sup>C NMR

yq-02-121

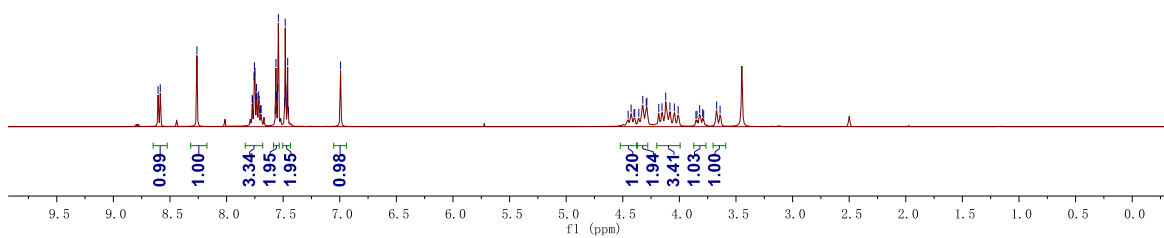


# <sup>1</sup>H NMR

YQ-01-48

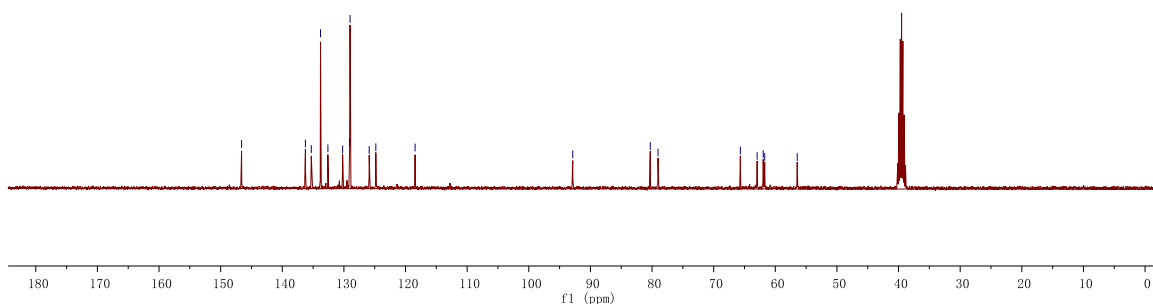


2c



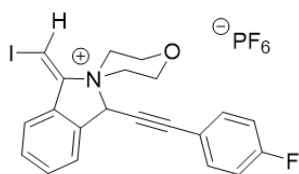
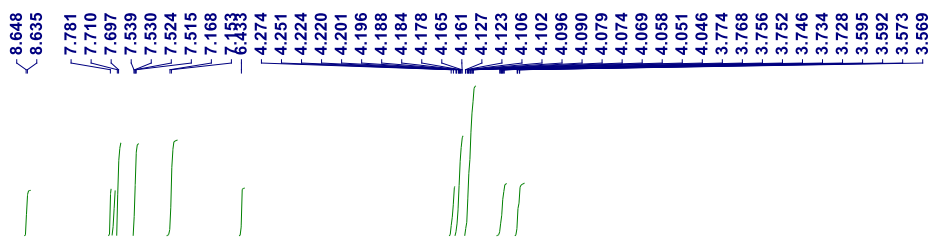
# <sup>13</sup>C NMR

YQ-01-48

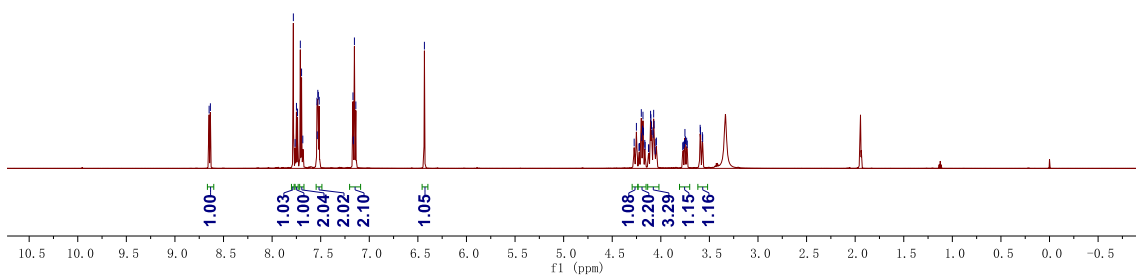


# <sup>1</sup>H NMR

YQ-F-20190707-1



2d



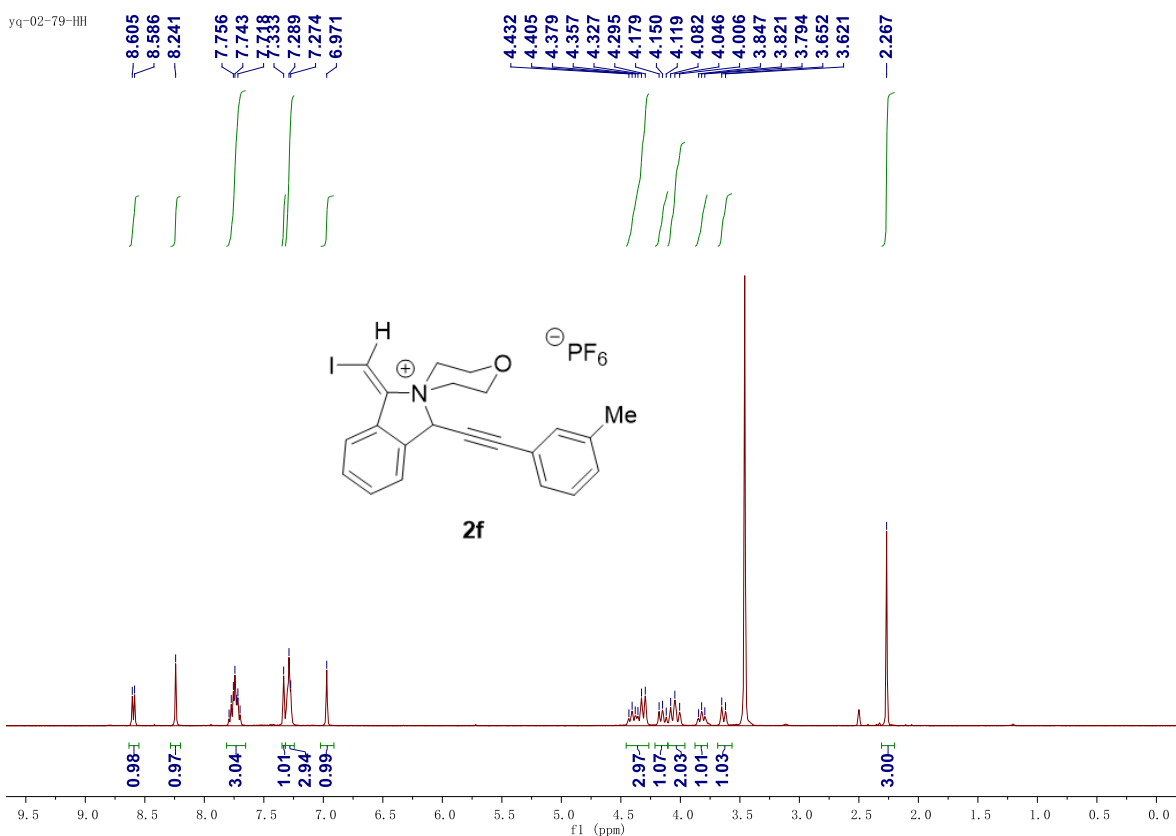
# <sup>13</sup>C NMR

YQ-F-20190707-C13



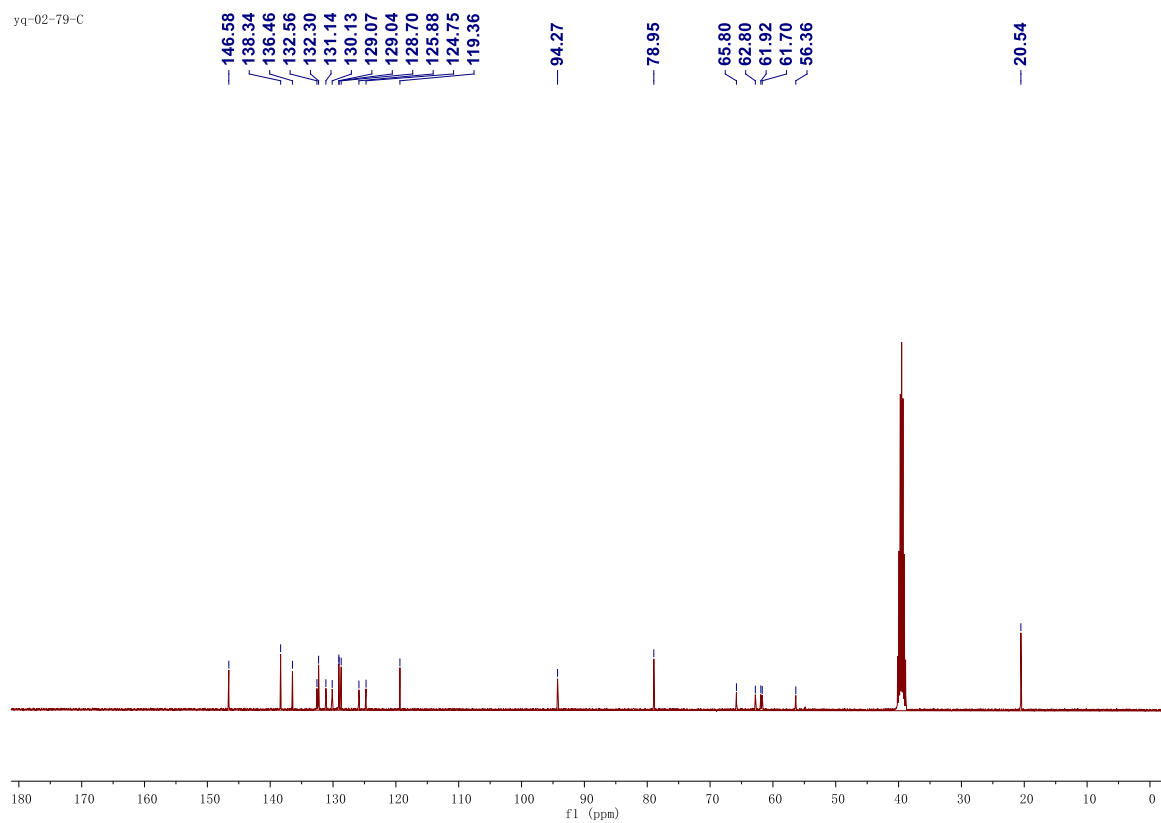
# <sup>1</sup>H NMR

yq-02-79-HH



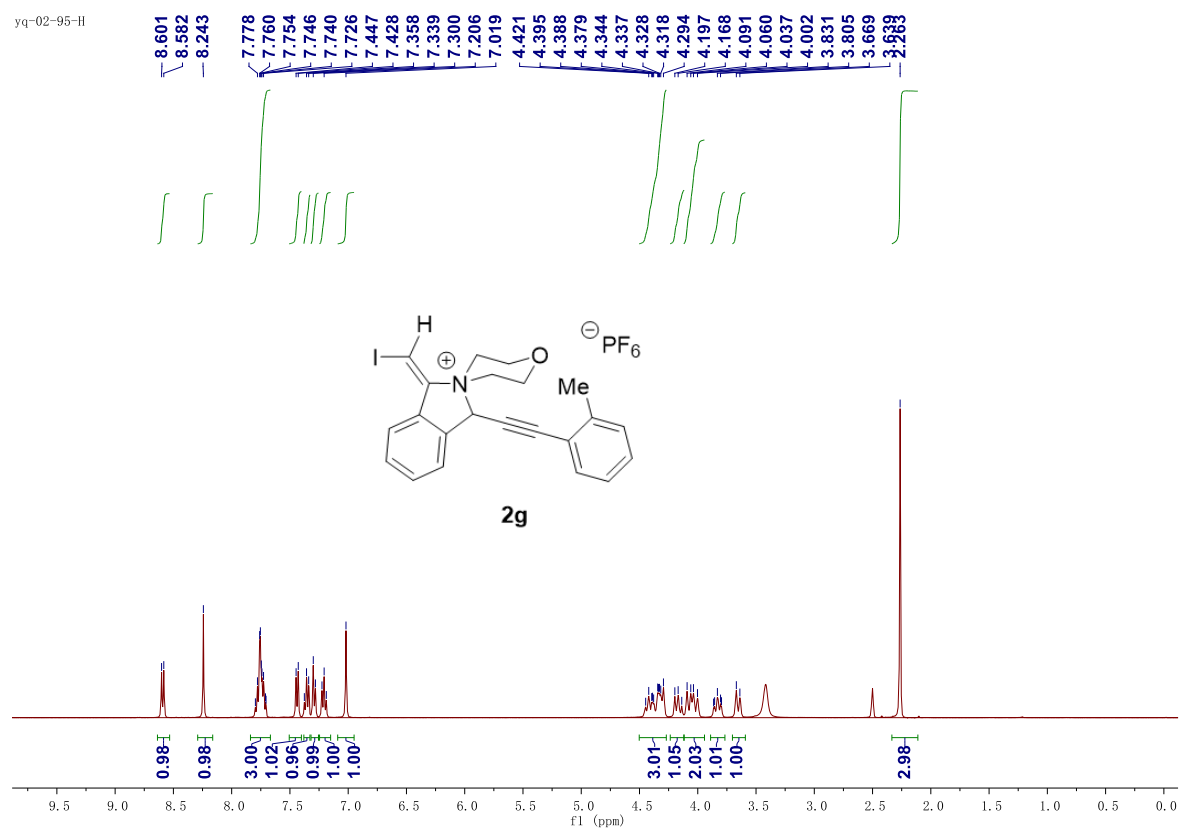
# <sup>13</sup>C NMR

yq-02-79-C



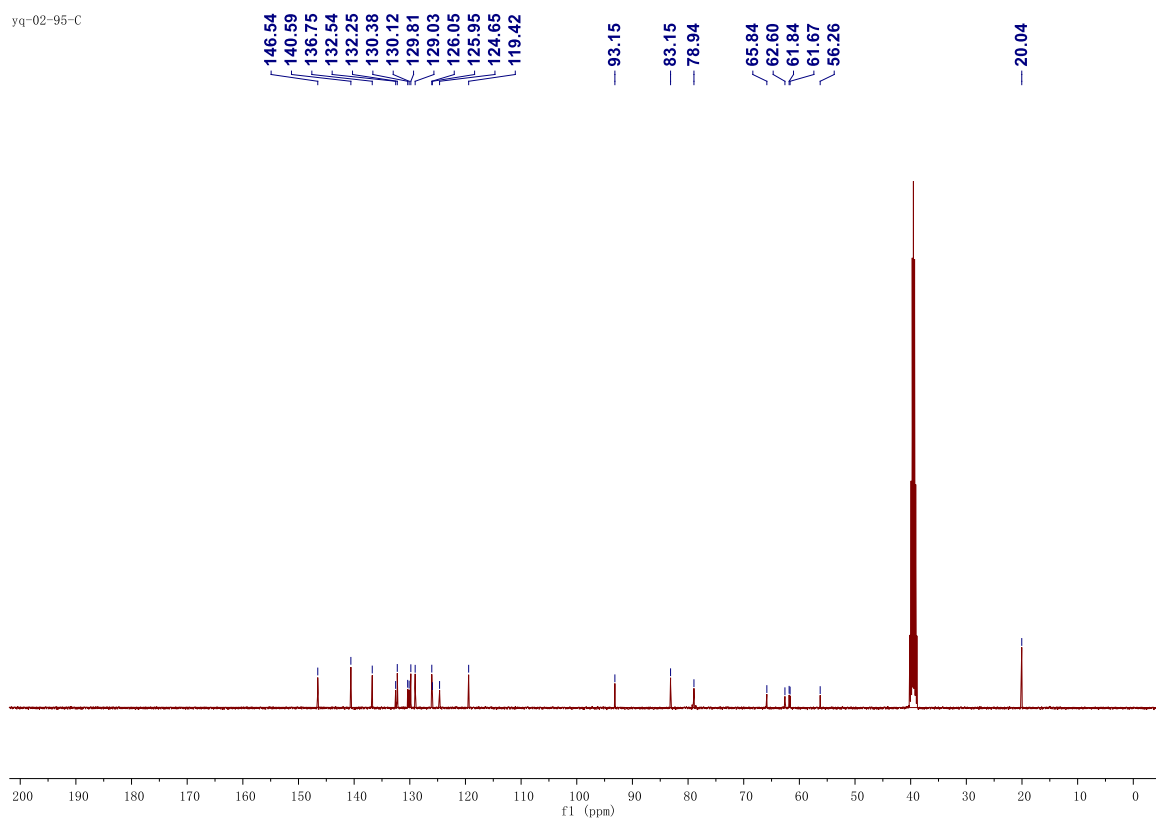
# <sup>1</sup>H NMR

yq-02-95-H

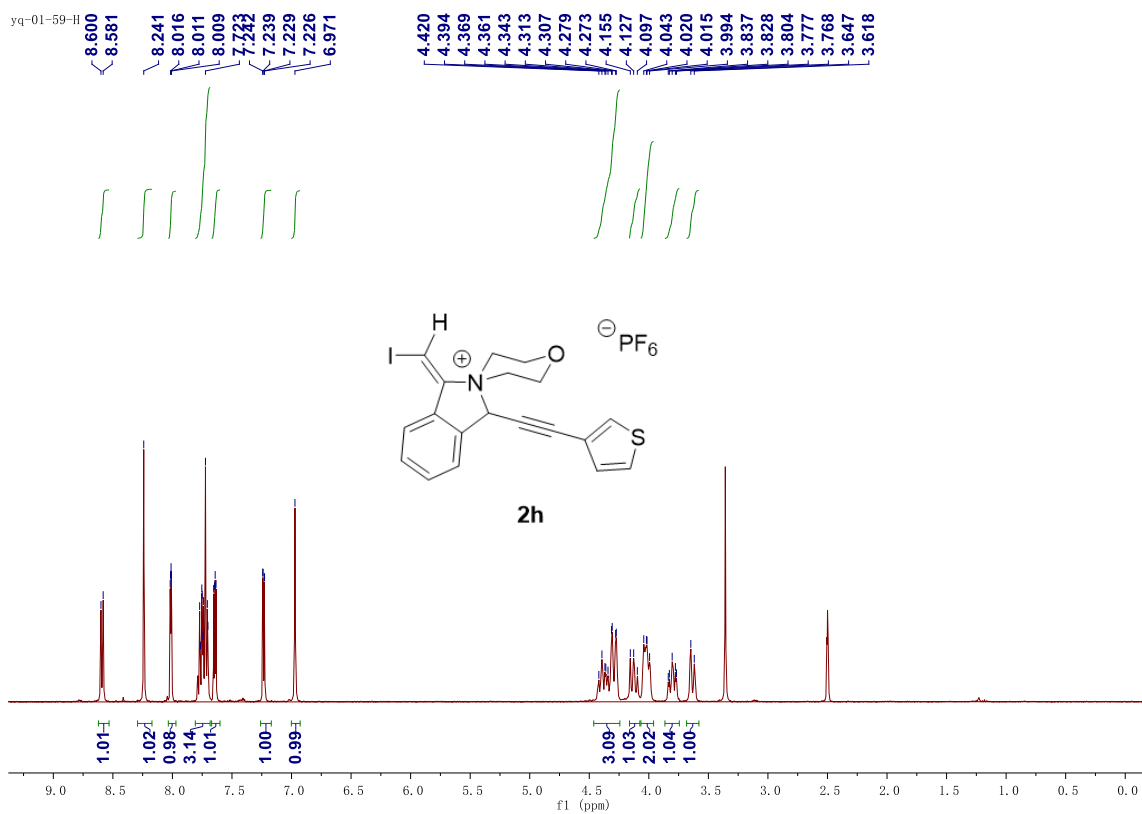


# <sup>13</sup>C NMR

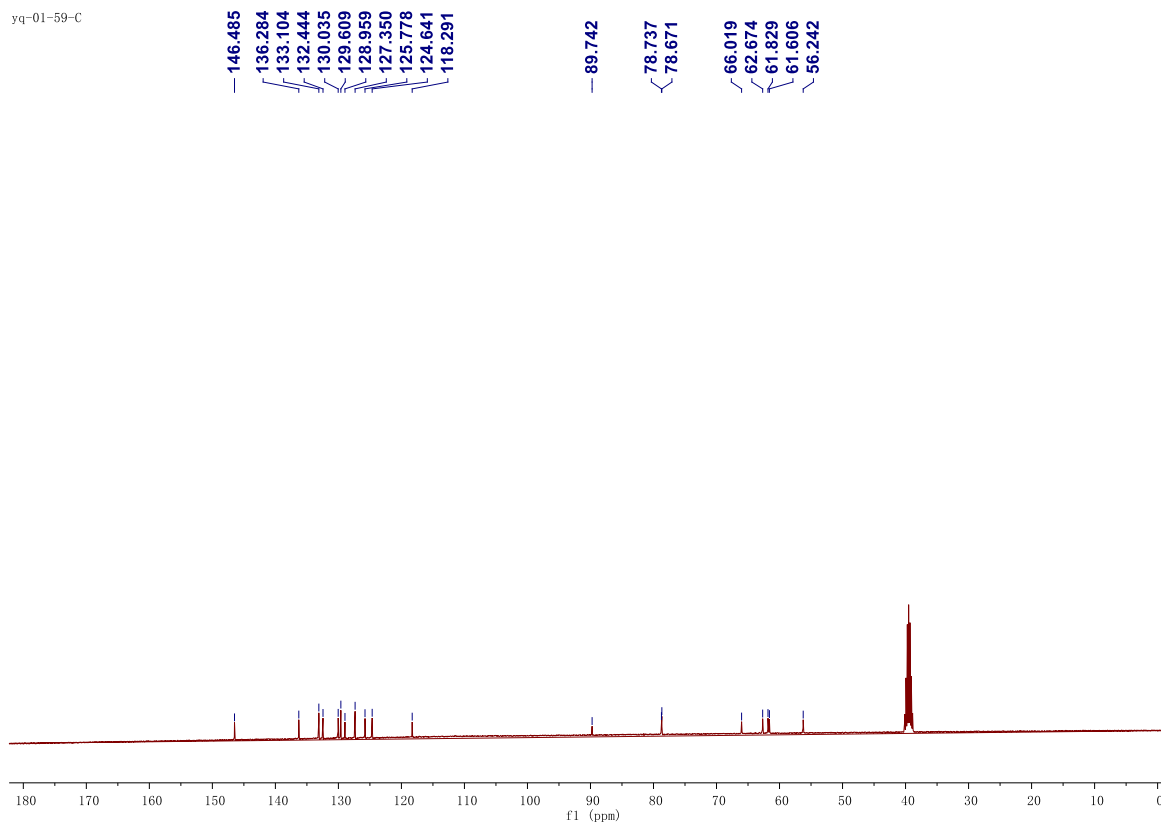
yq-02-95-C



# <sup>1</sup>H NMR



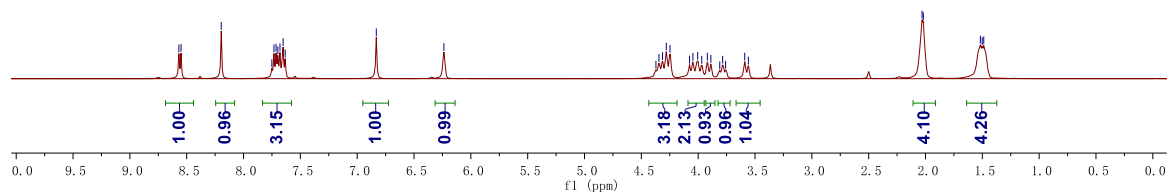
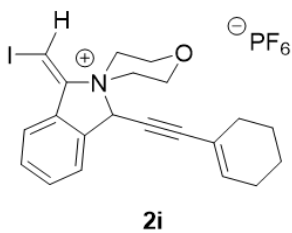
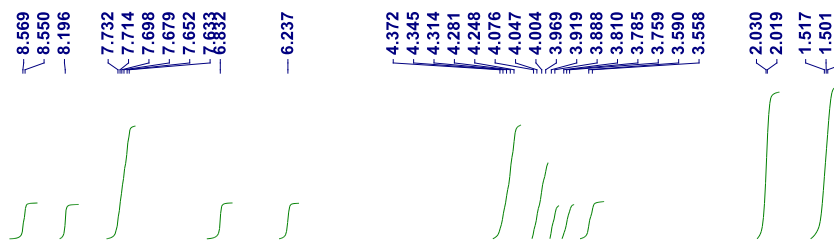
# <sup>13</sup>C NMR





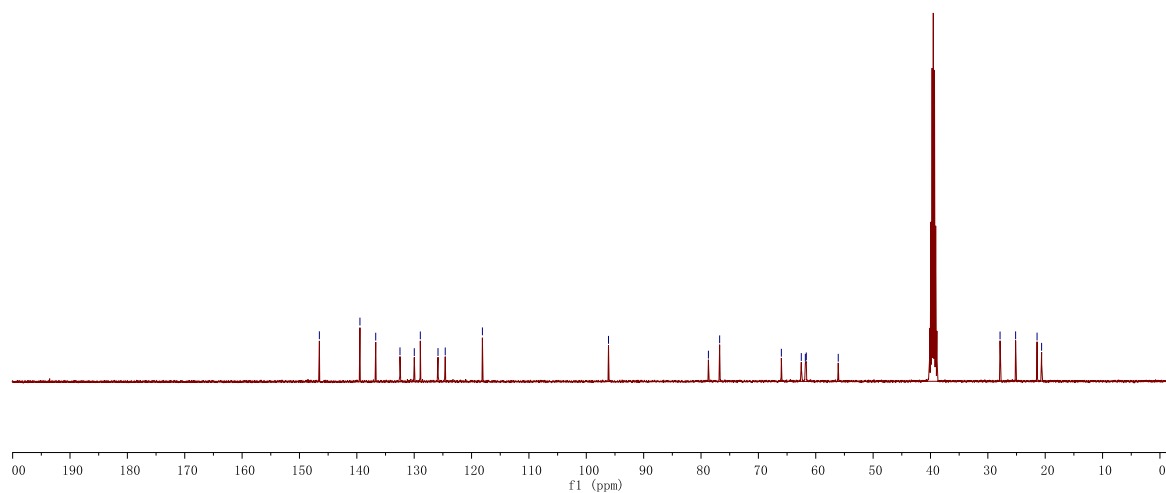
# <sup>1</sup>H NMR

yq-02-85-H

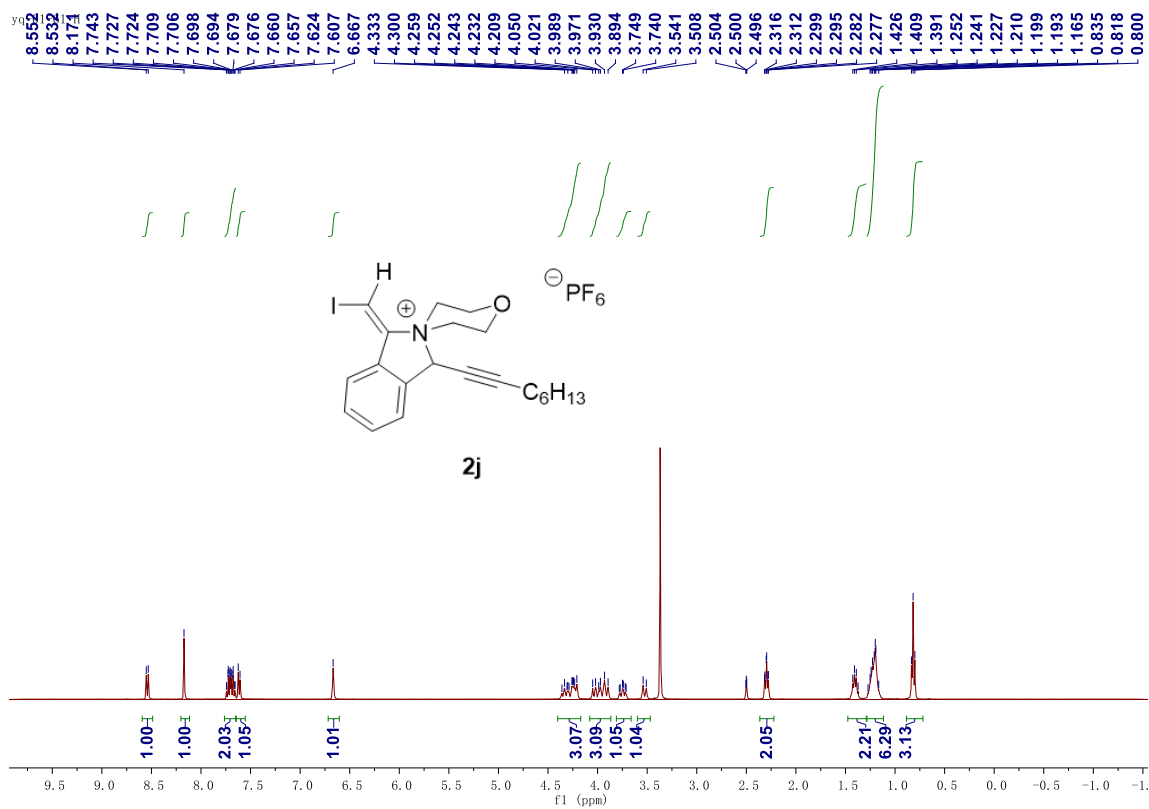


# <sup>13</sup>C NMR

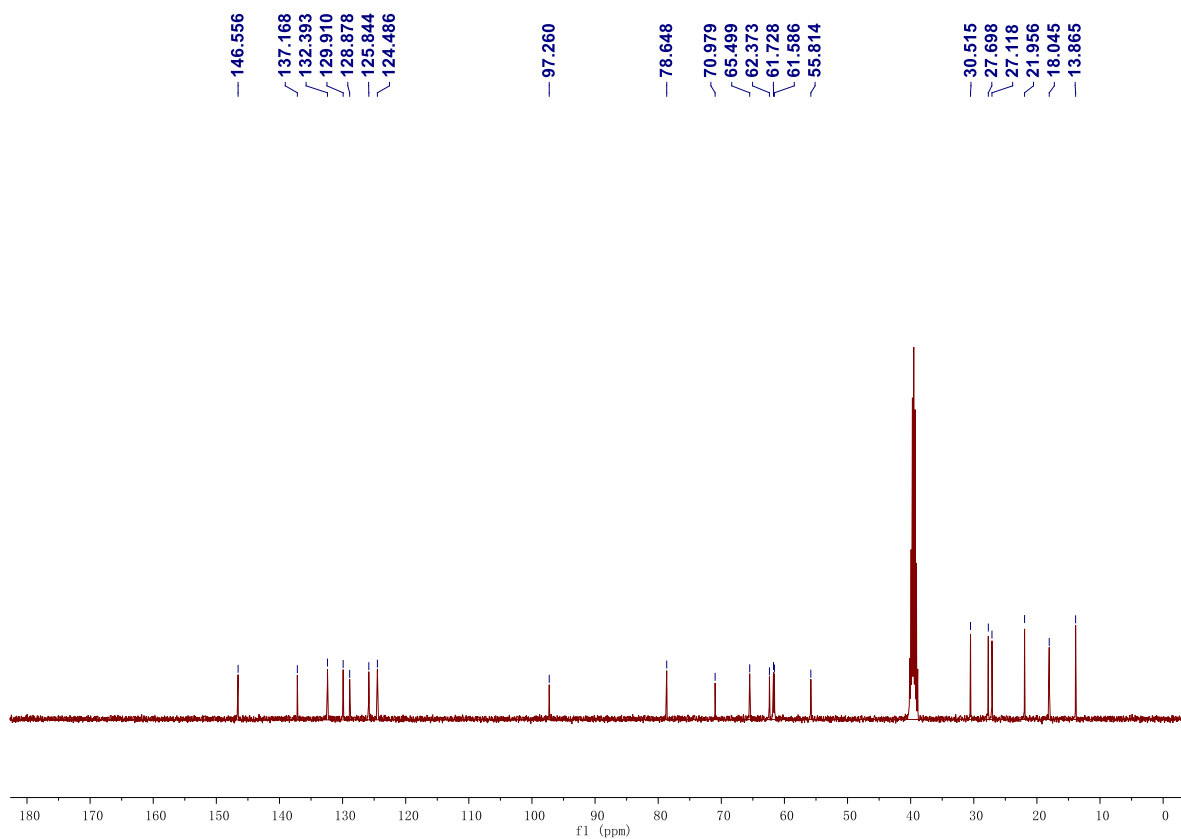
yq-02-85-C



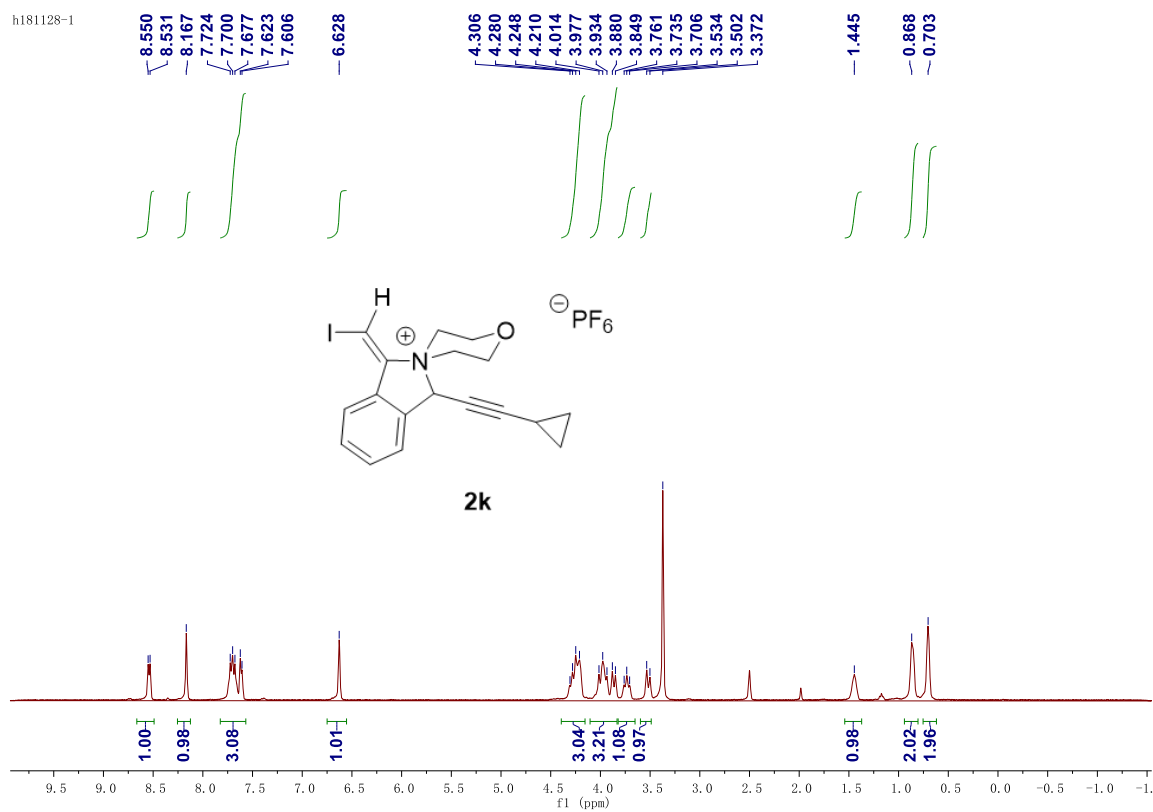
# <sup>1</sup>H NMR



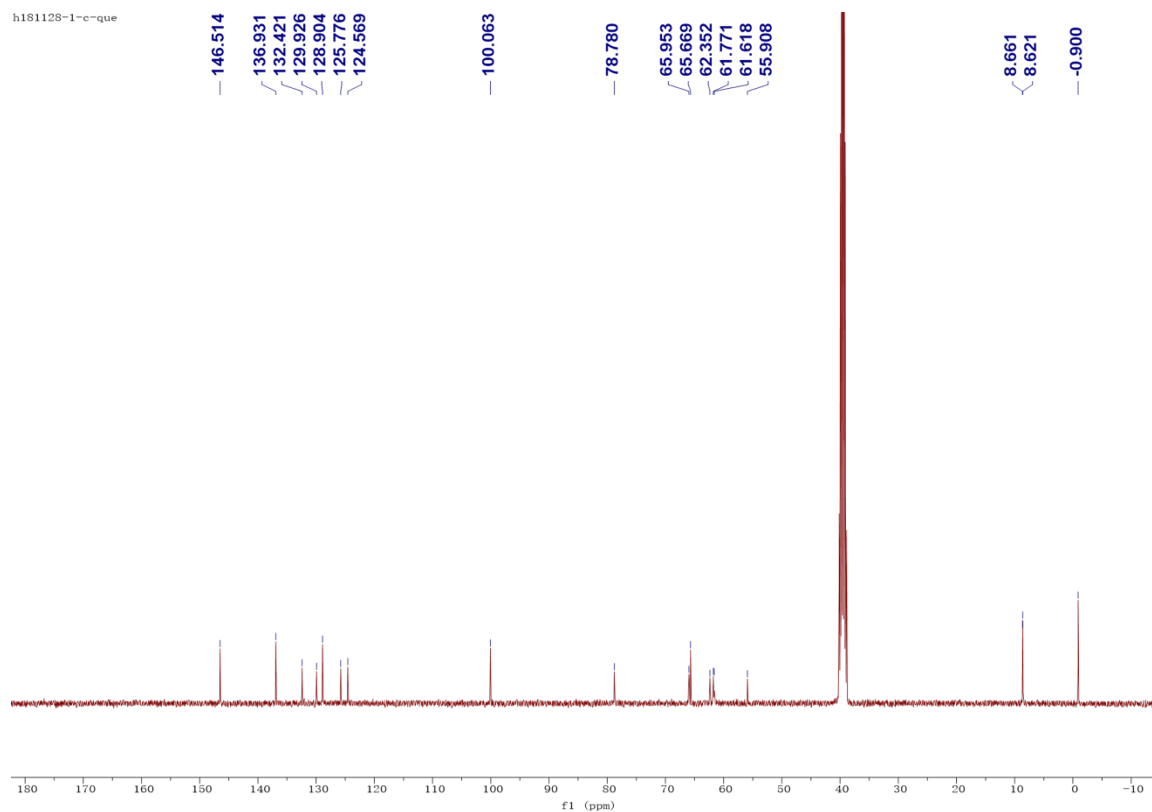
# <sup>13</sup>C NMR



# <sup>1</sup>H NMR

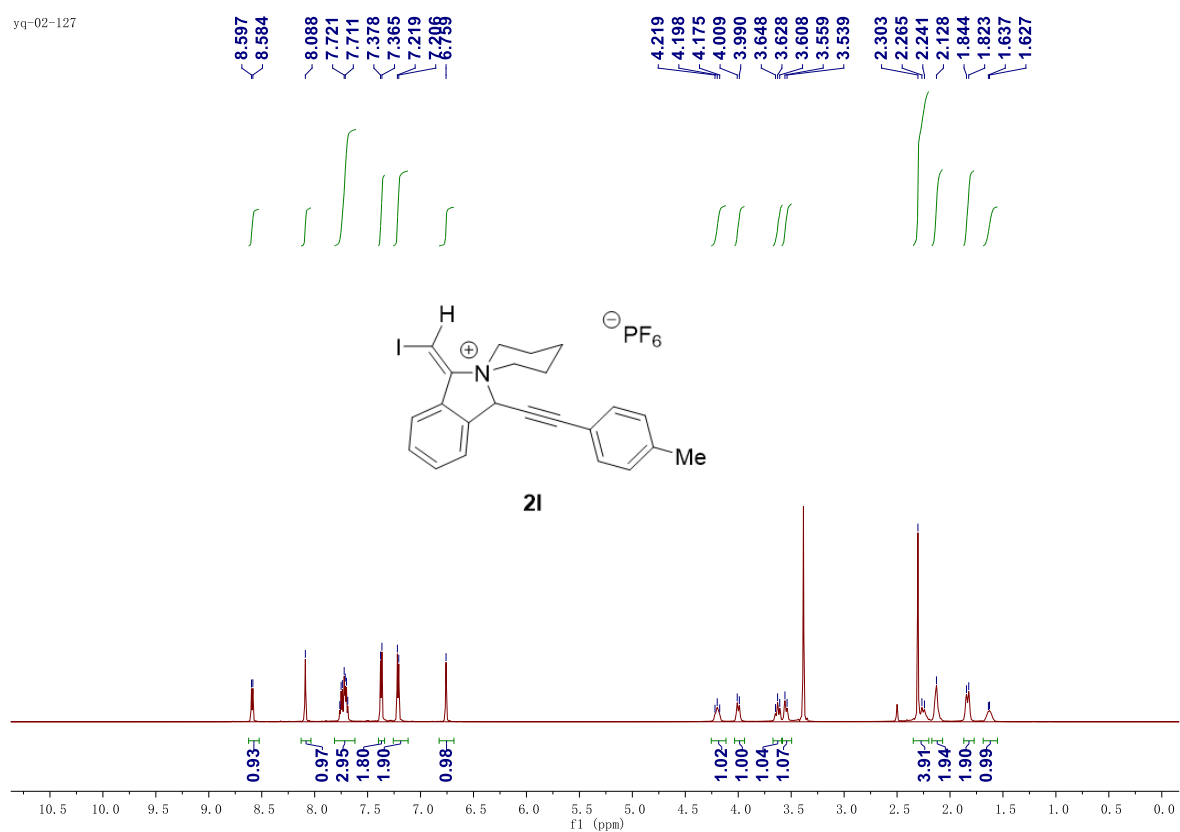


# <sup>13</sup>C NMR



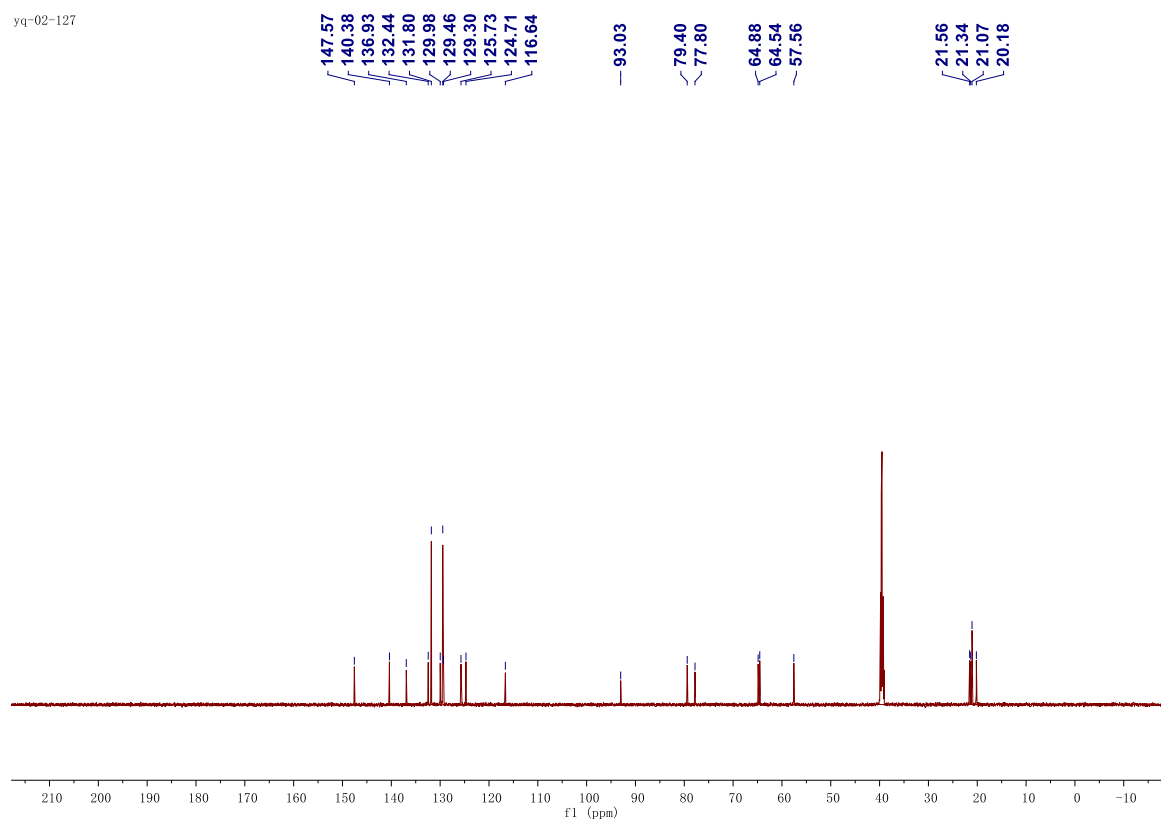
# <sup>1</sup>H NMR

yq-02-127



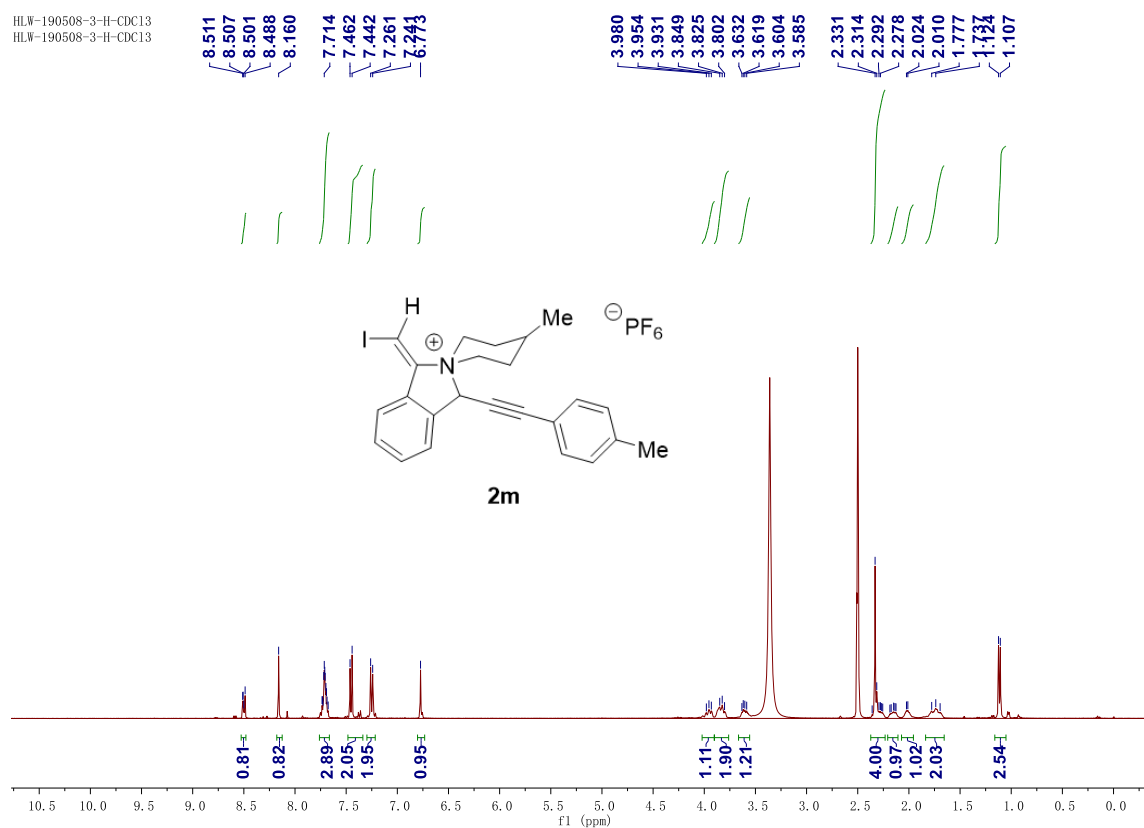
# <sup>13</sup>C NMR

yq-02-127



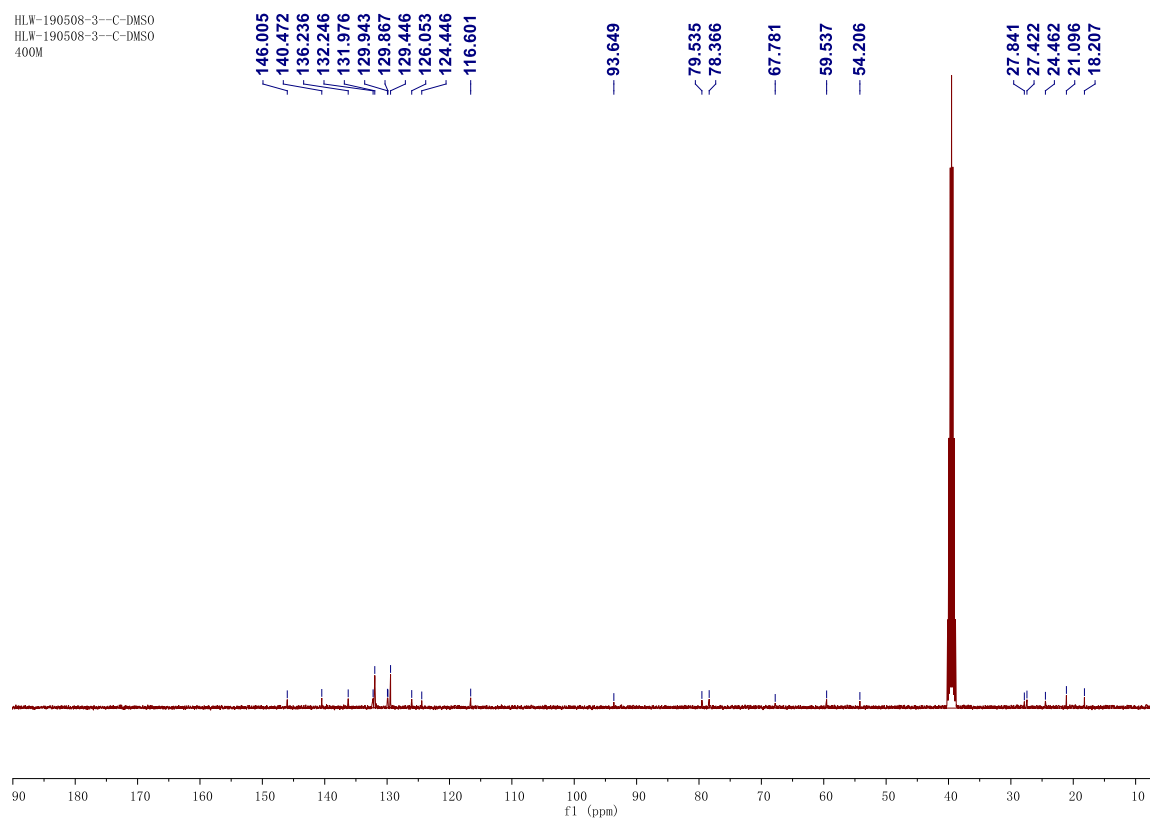
# <sup>1</sup>H NMR

HLW-190508-3-H-CDC13  
HLW-190508-3-H-CDC13



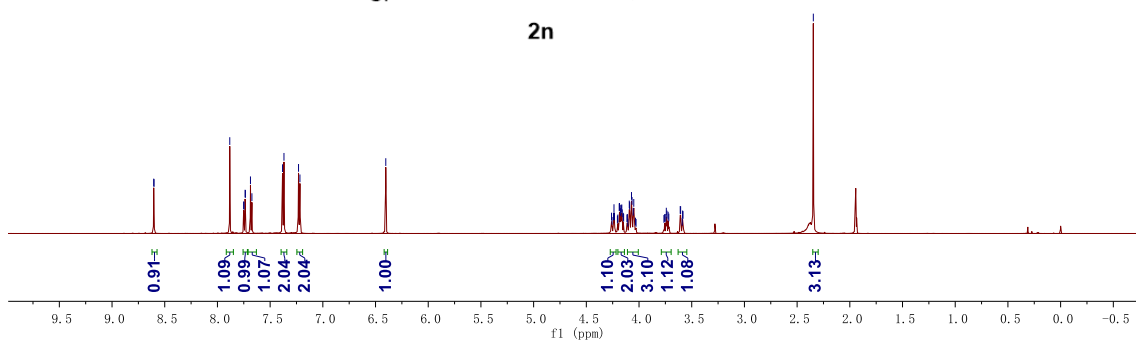
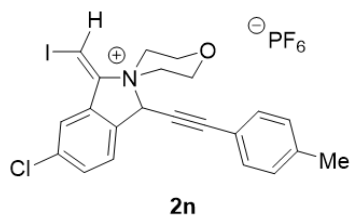
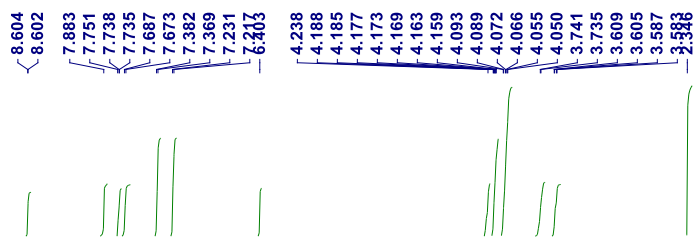
# <sup>13</sup>C NMR

HLW-190508-3--C-DMSO  
HLW-190508-3--C-DMSO  
400M



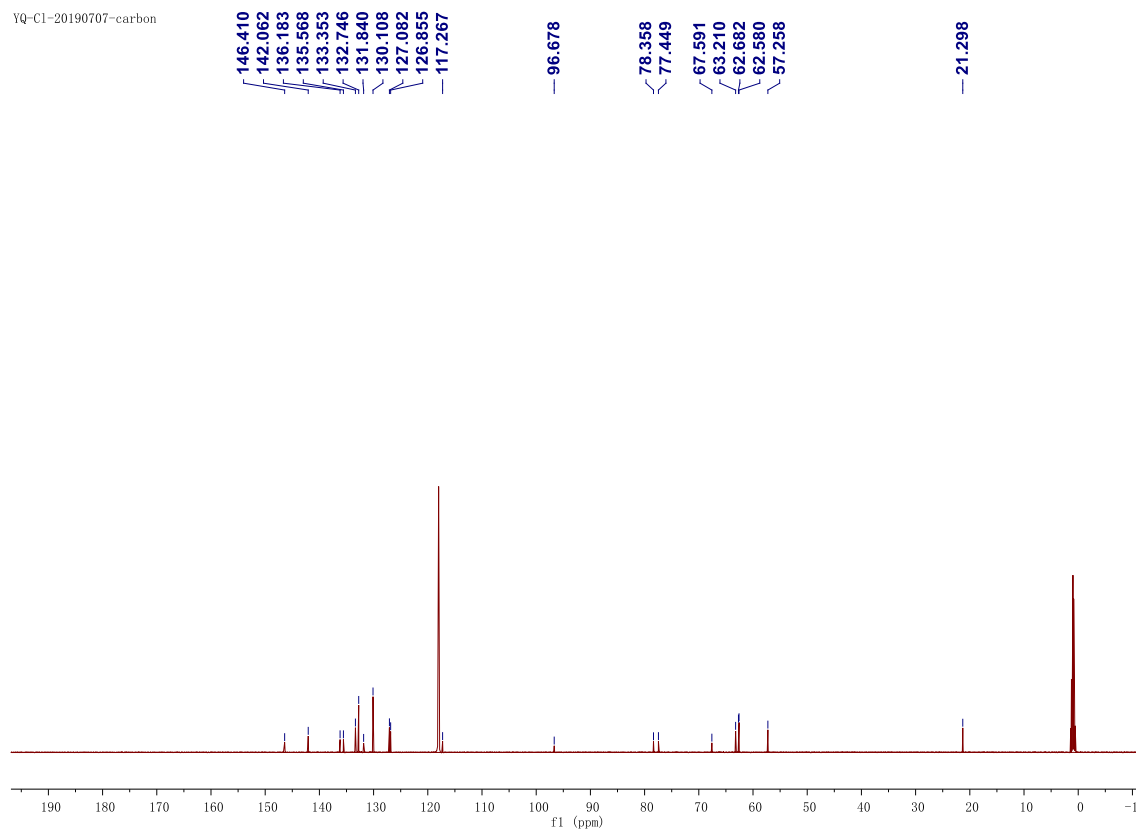
# <sup>1</sup>H NMR

YQ-C1-20190707



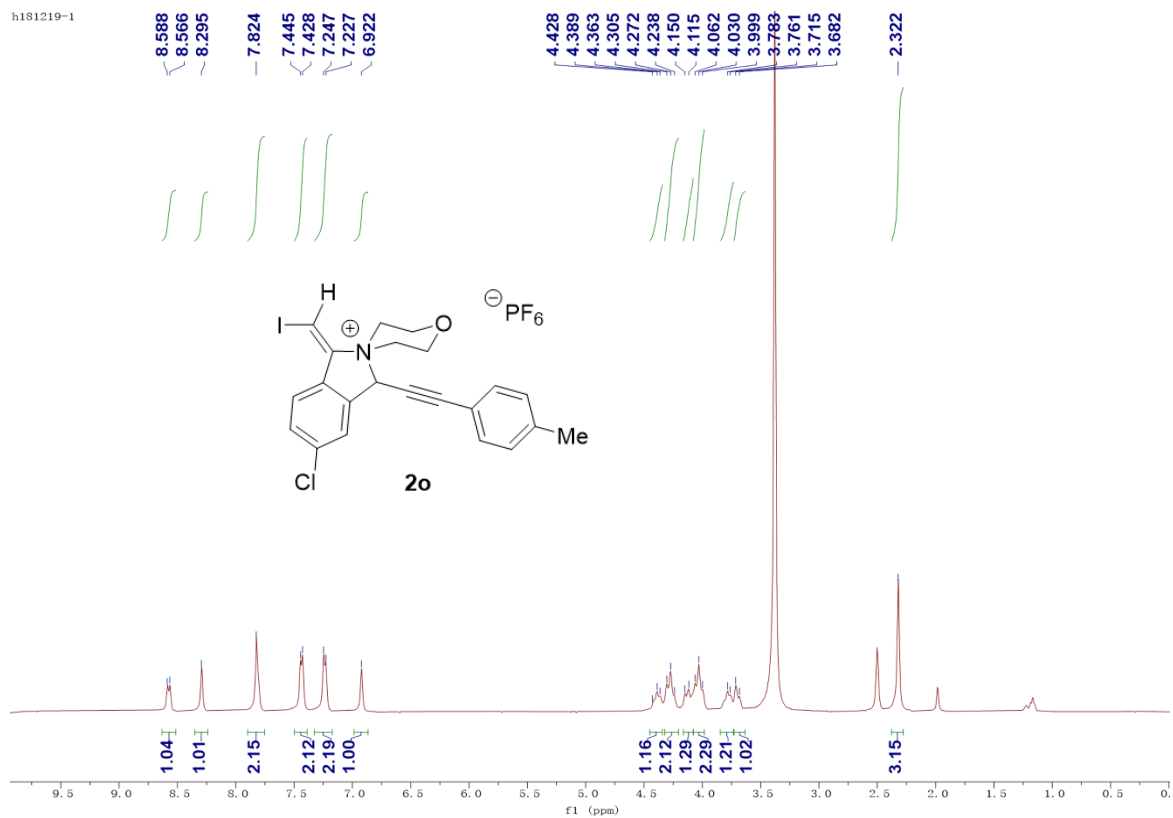
# <sup>13</sup>C NMR

YQ-C1-20190707-carbon



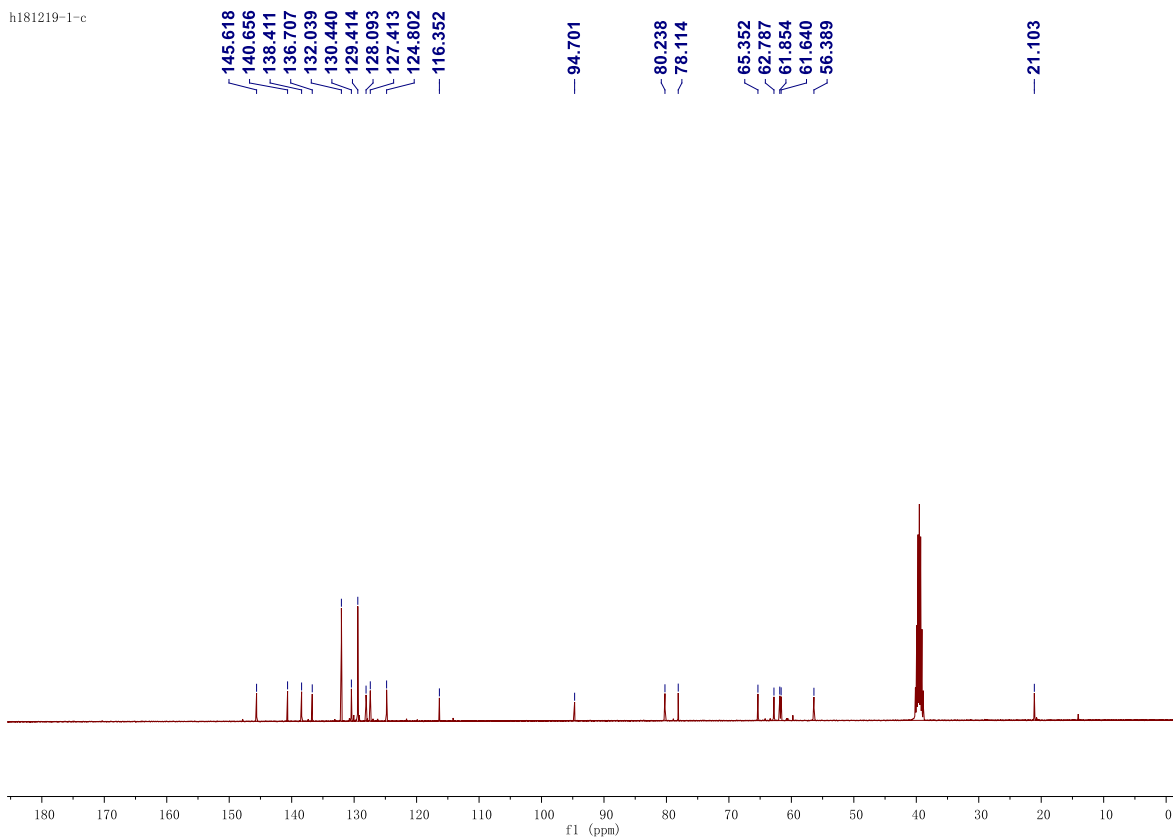
# <sup>1</sup>H NMR

h181219-1



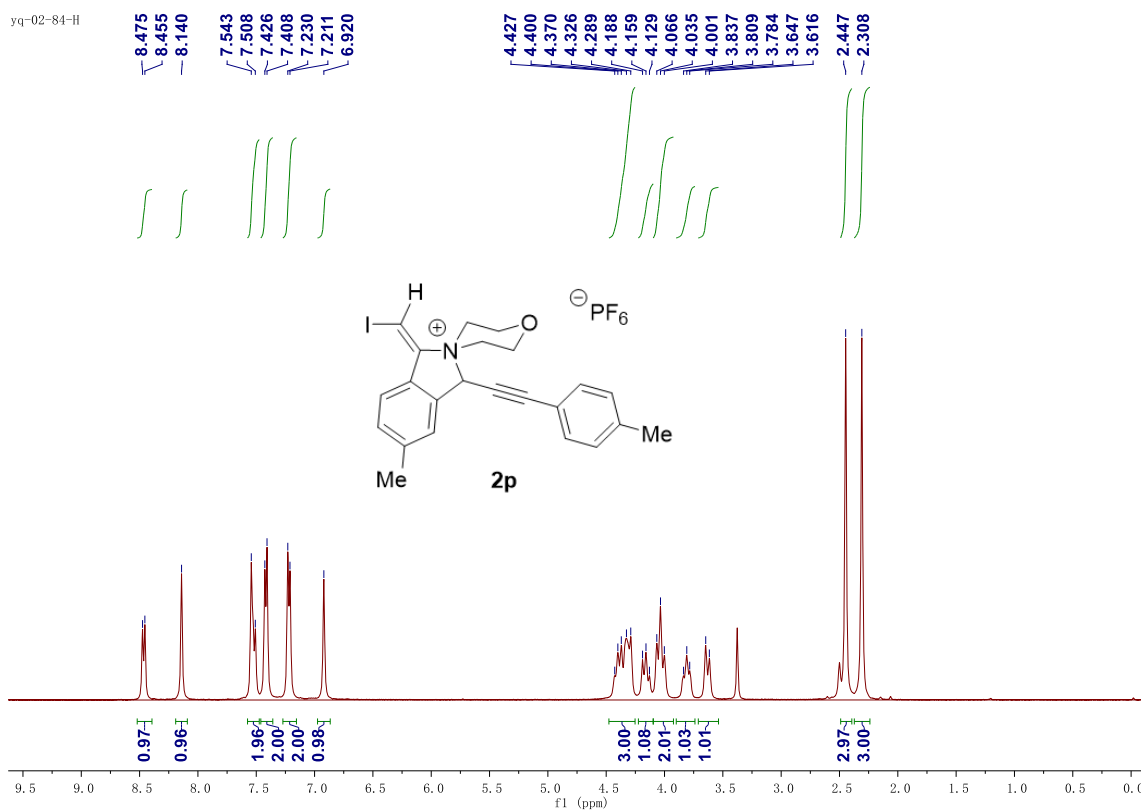
# <sup>13</sup>C NMR

h181219-1-c



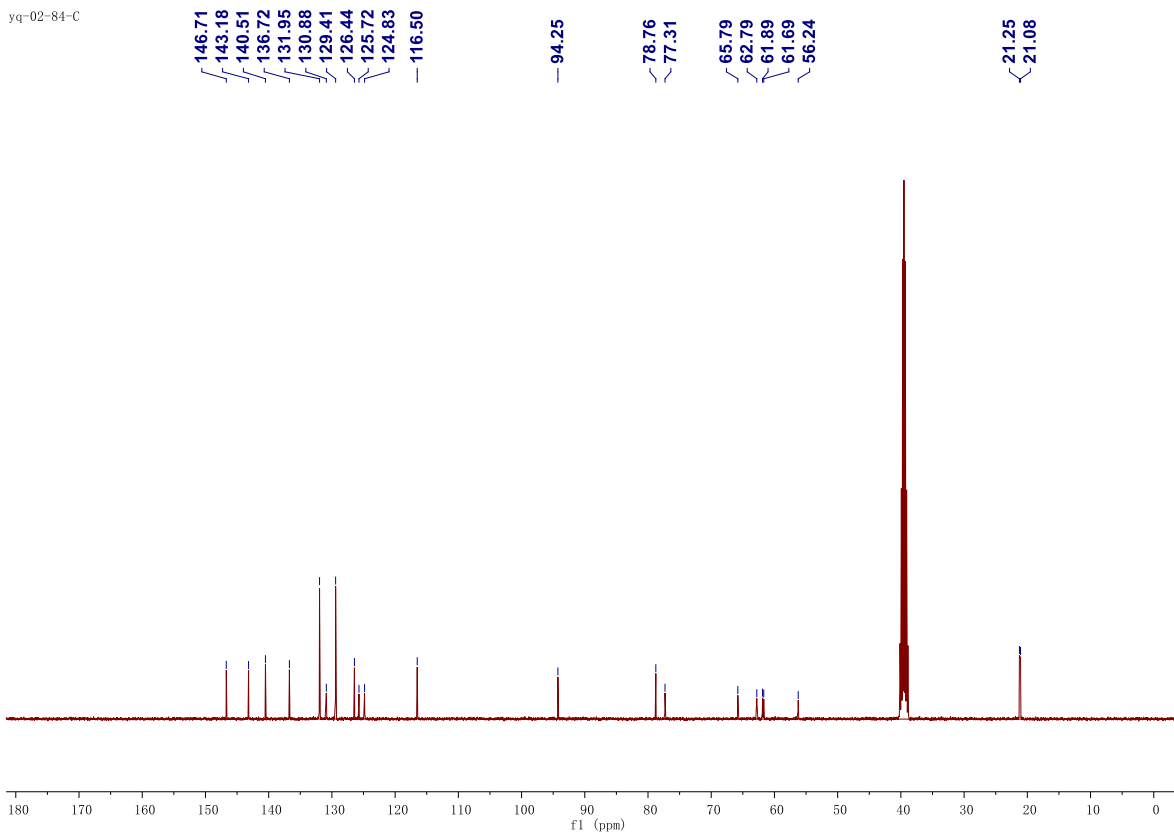
# <sup>1</sup>H NMR

yq-02-84-H



# <sup>13</sup>C NMR

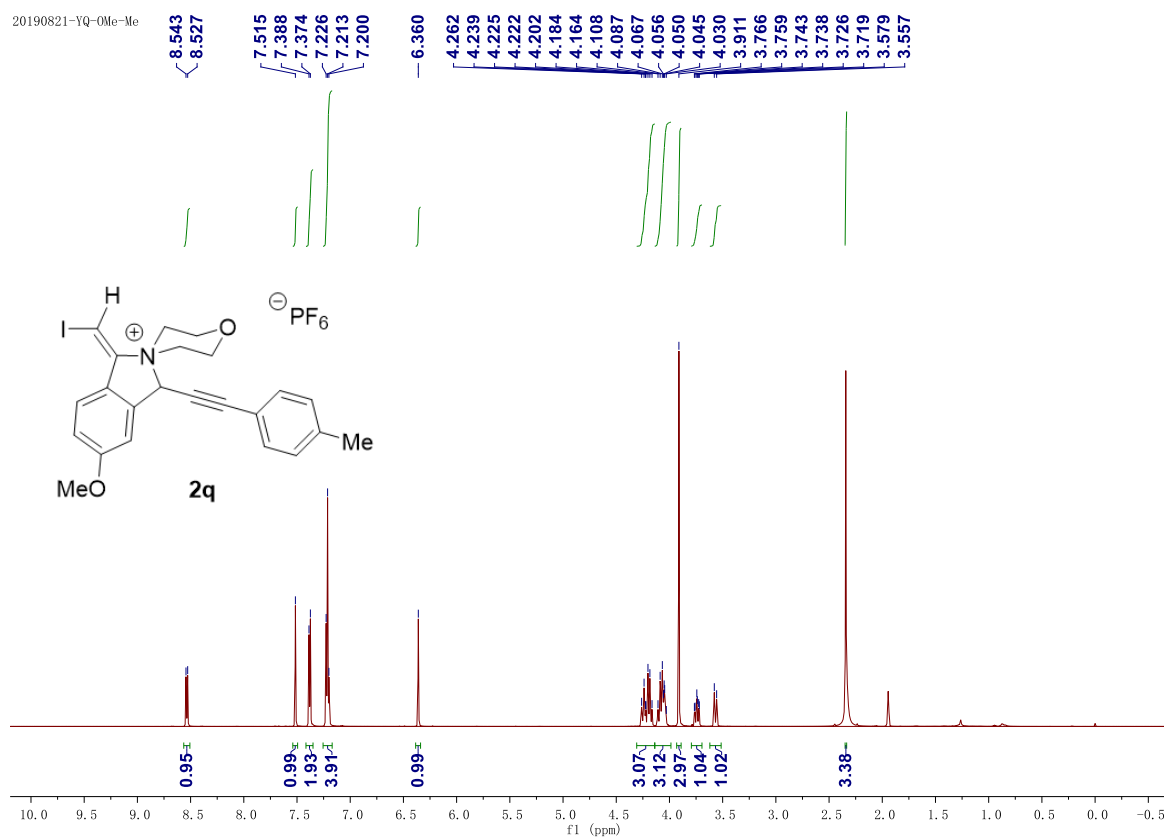
yq-02-84-C





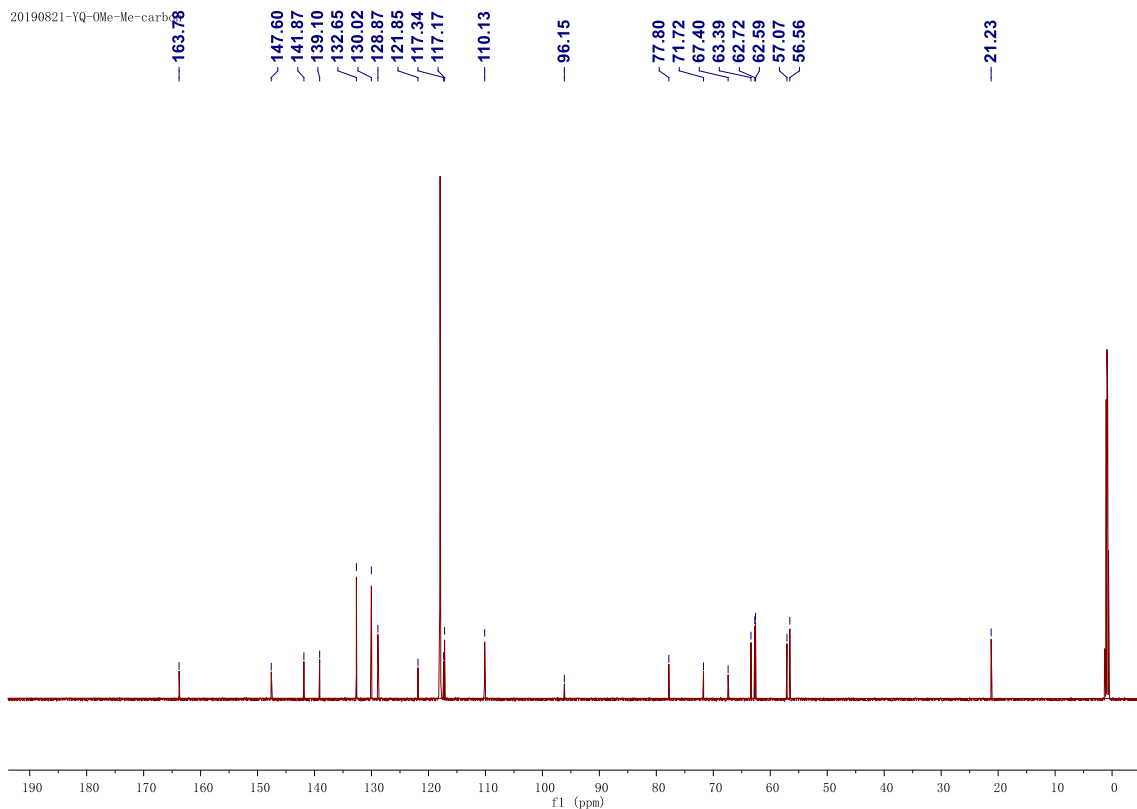
# <sup>1</sup>H NMR

20190821-YQ-OMe-Me

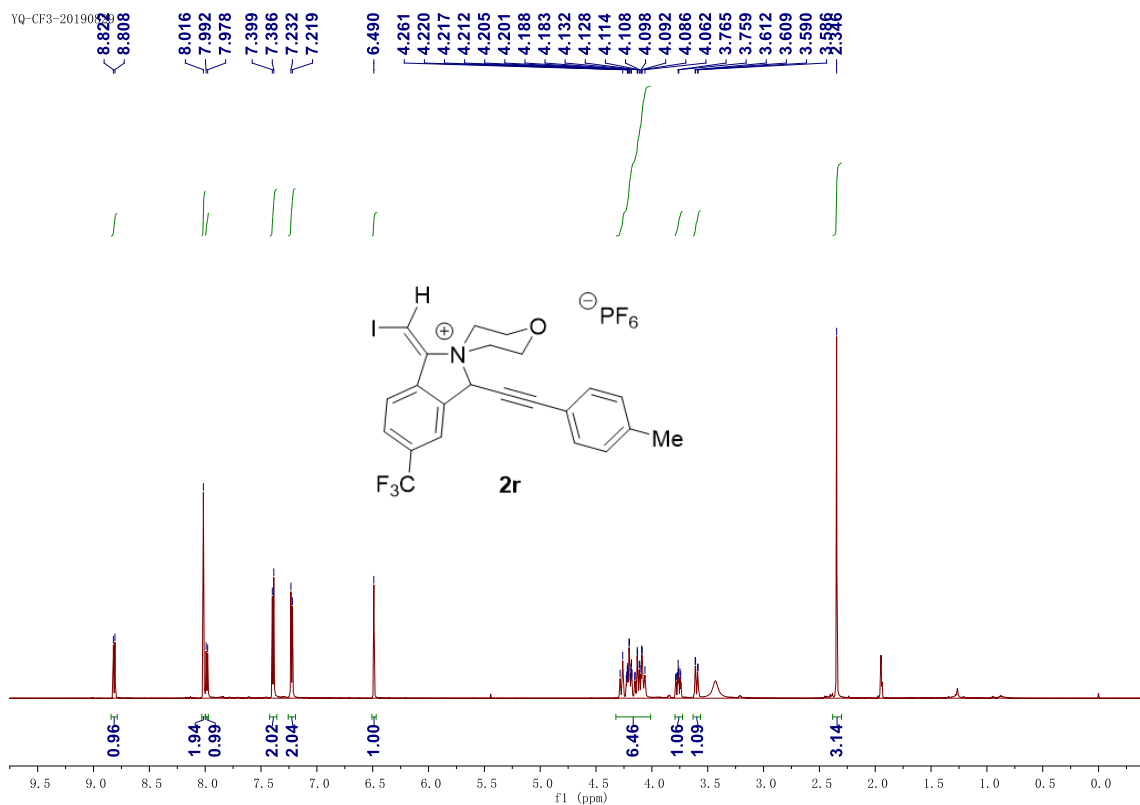


# <sup>13</sup>C NMR

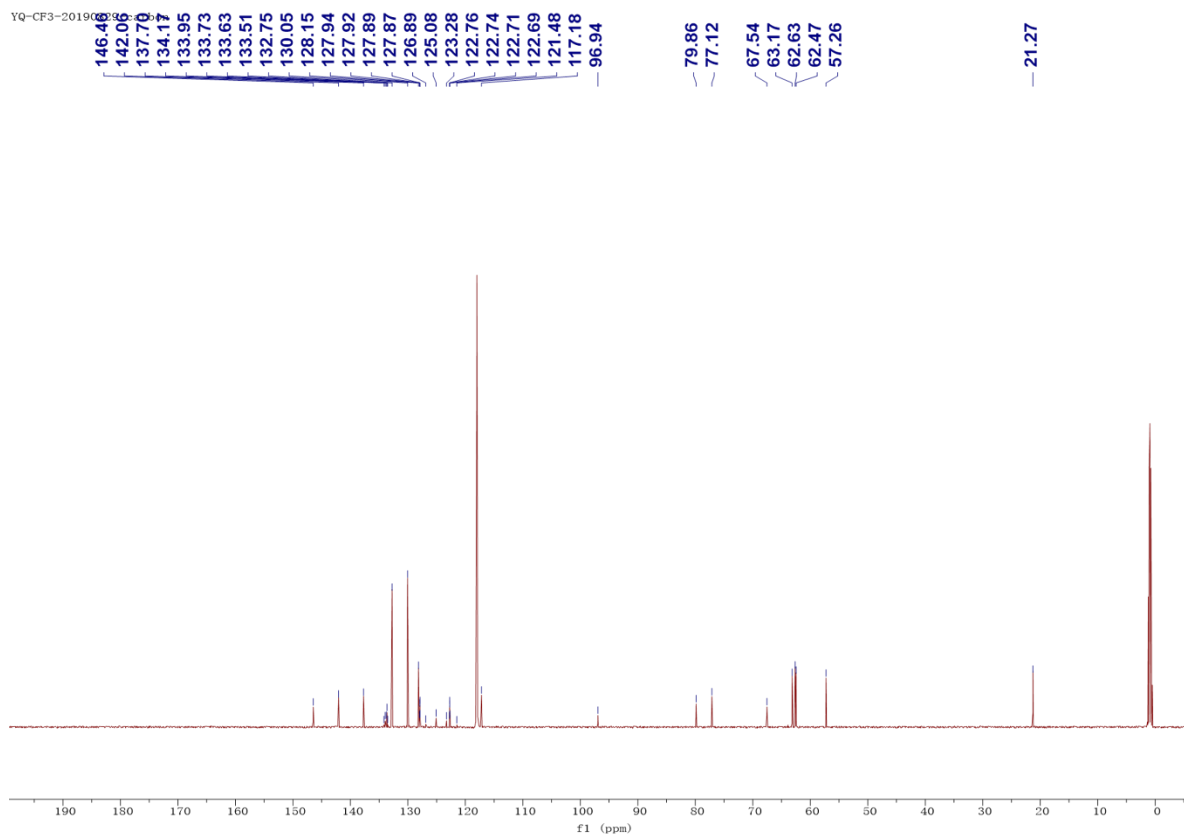
20190821-YQ-OMe-Me-carb



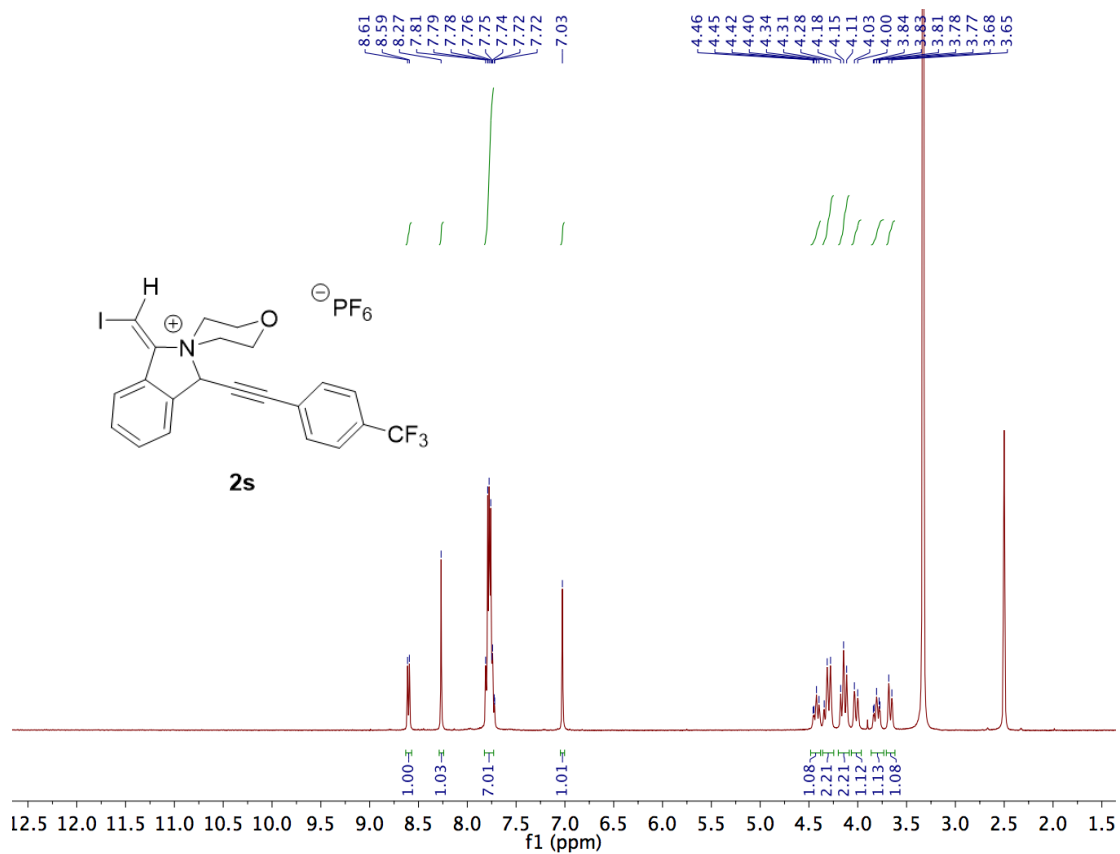
# <sup>1</sup>H NMR



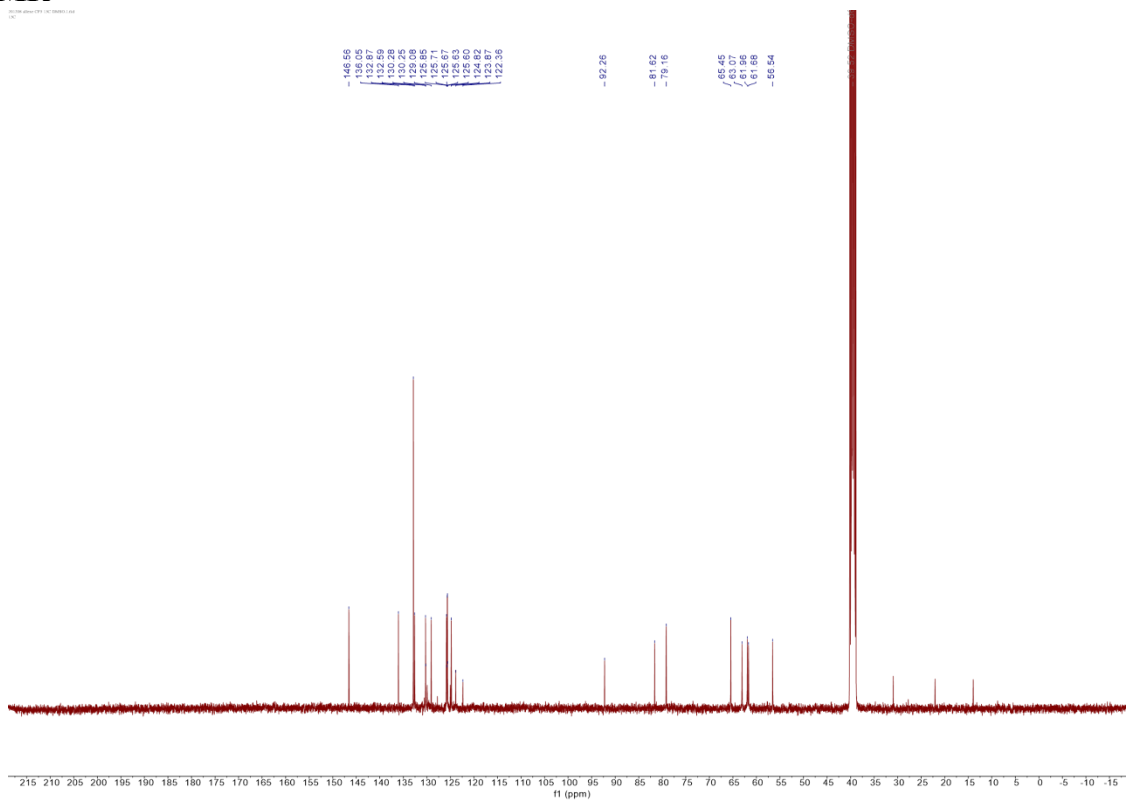
# <sup>13</sup>C NMR



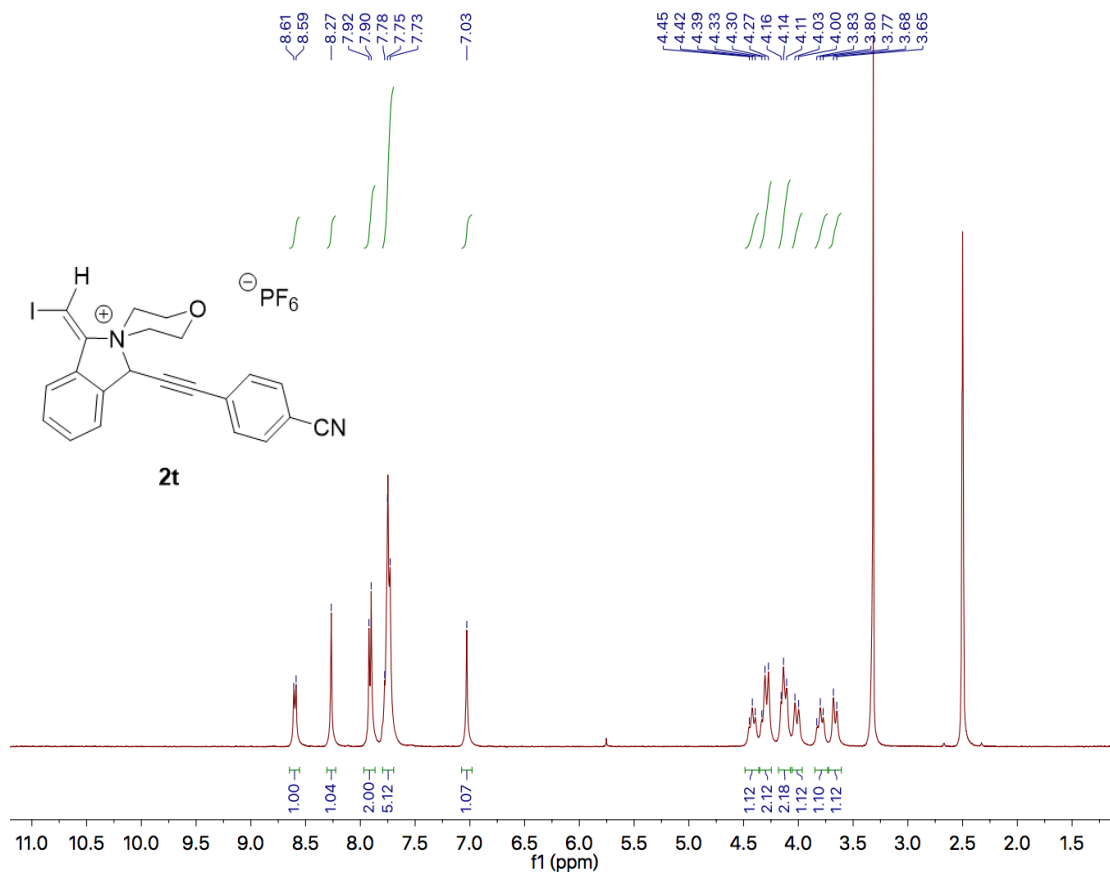
# <sup>1</sup>H NMR



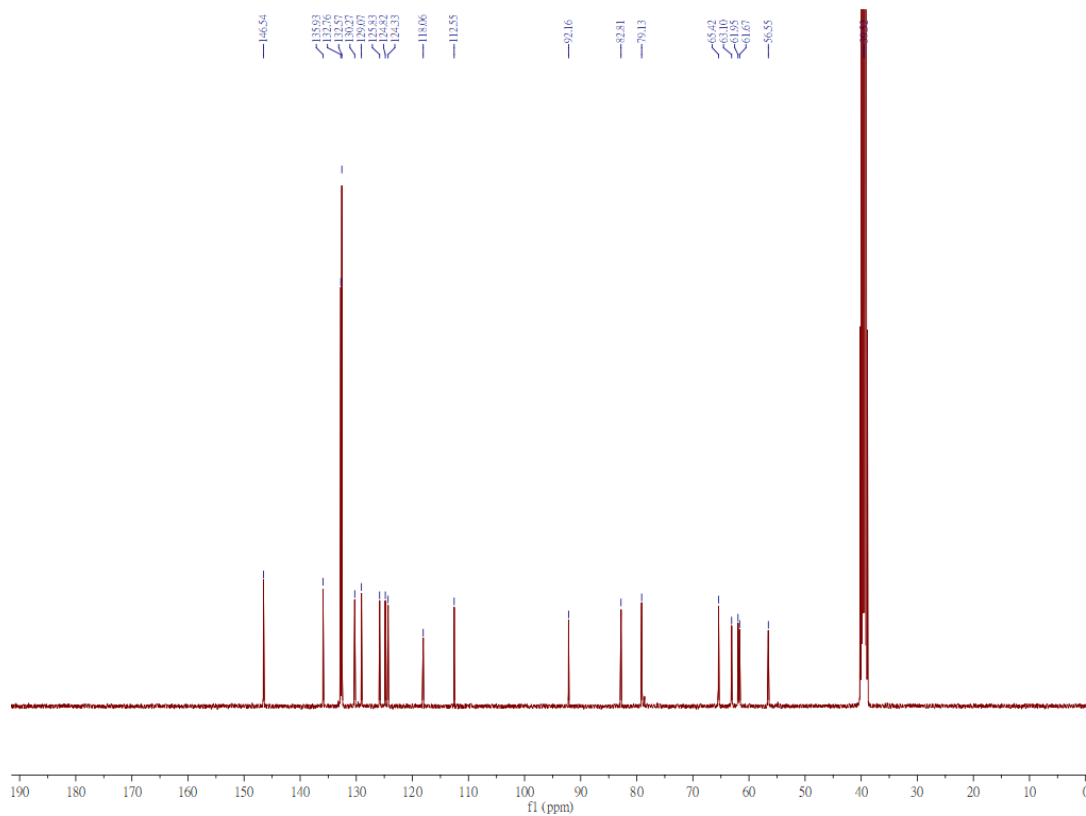
# <sup>13</sup>C NMR



# <sup>1</sup>H NMR

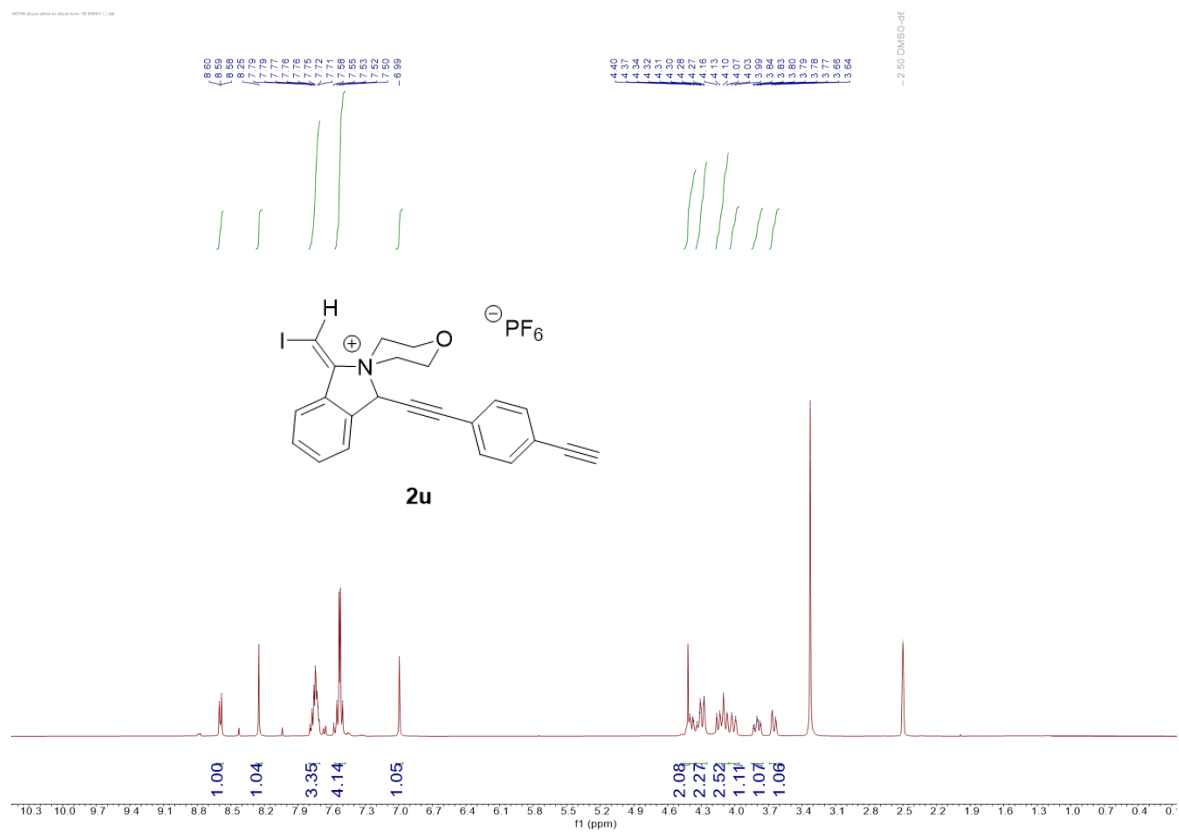


# <sup>13</sup>C NMR

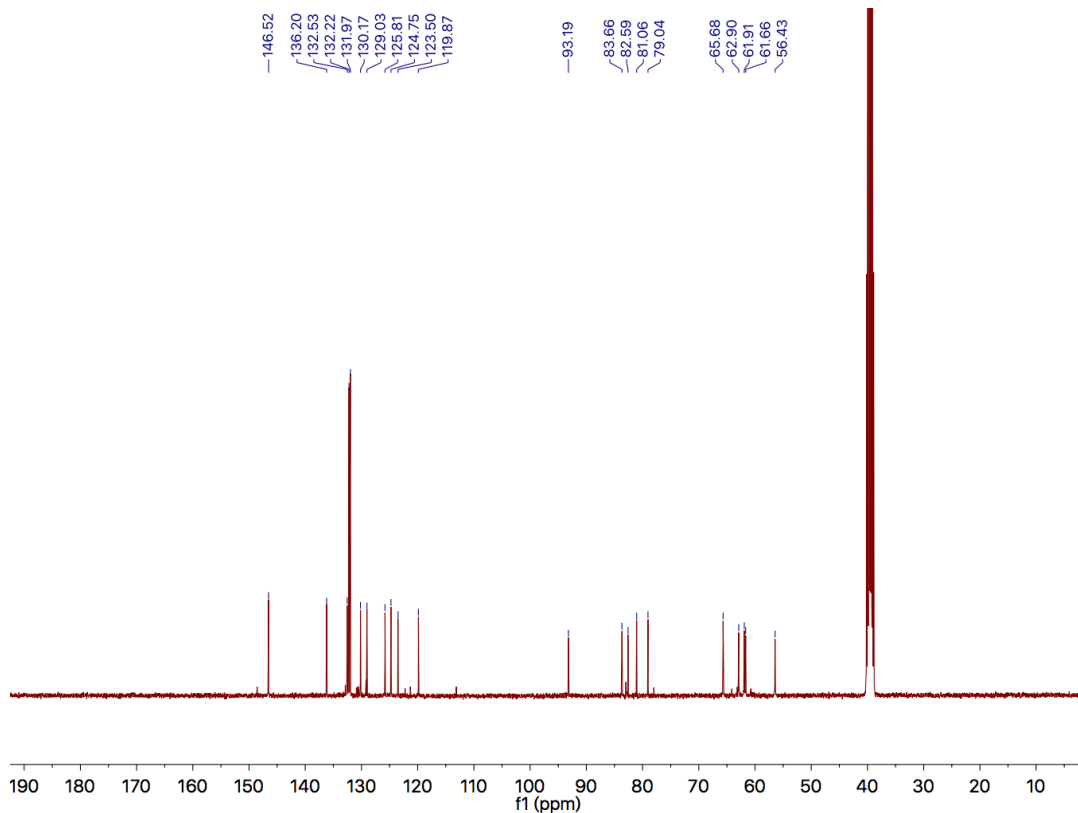


# <sup>1</sup>H NMR

0004 Acquisition 01-06-2016 09:59:11.04

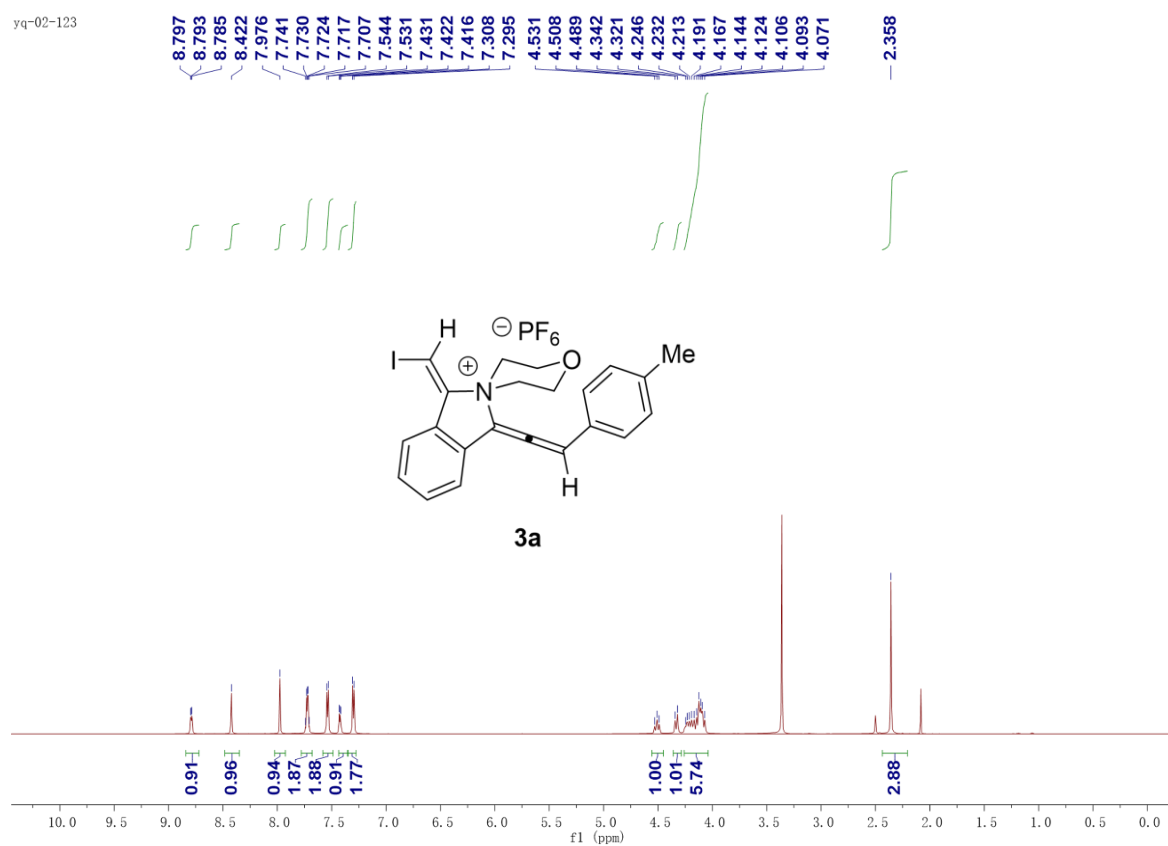


# <sup>13</sup>C NMR



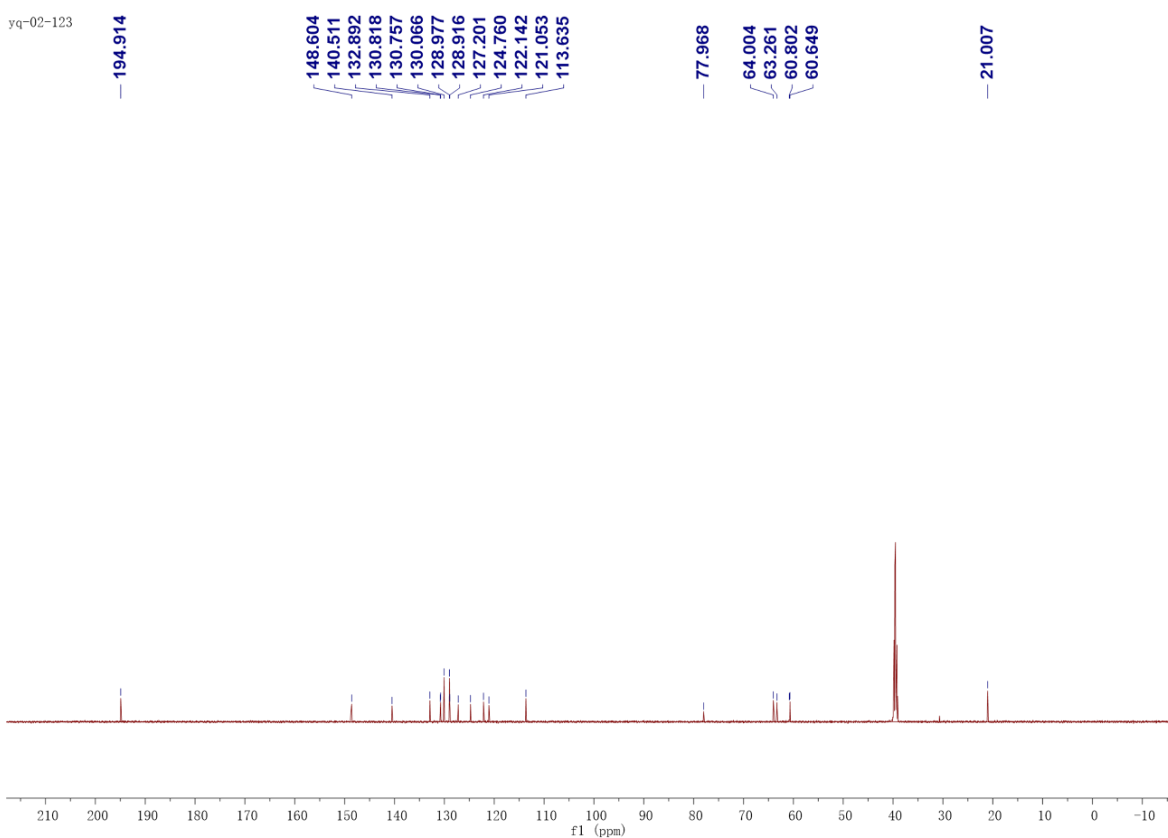
# <sup>1</sup>H NMR

yq-02-123



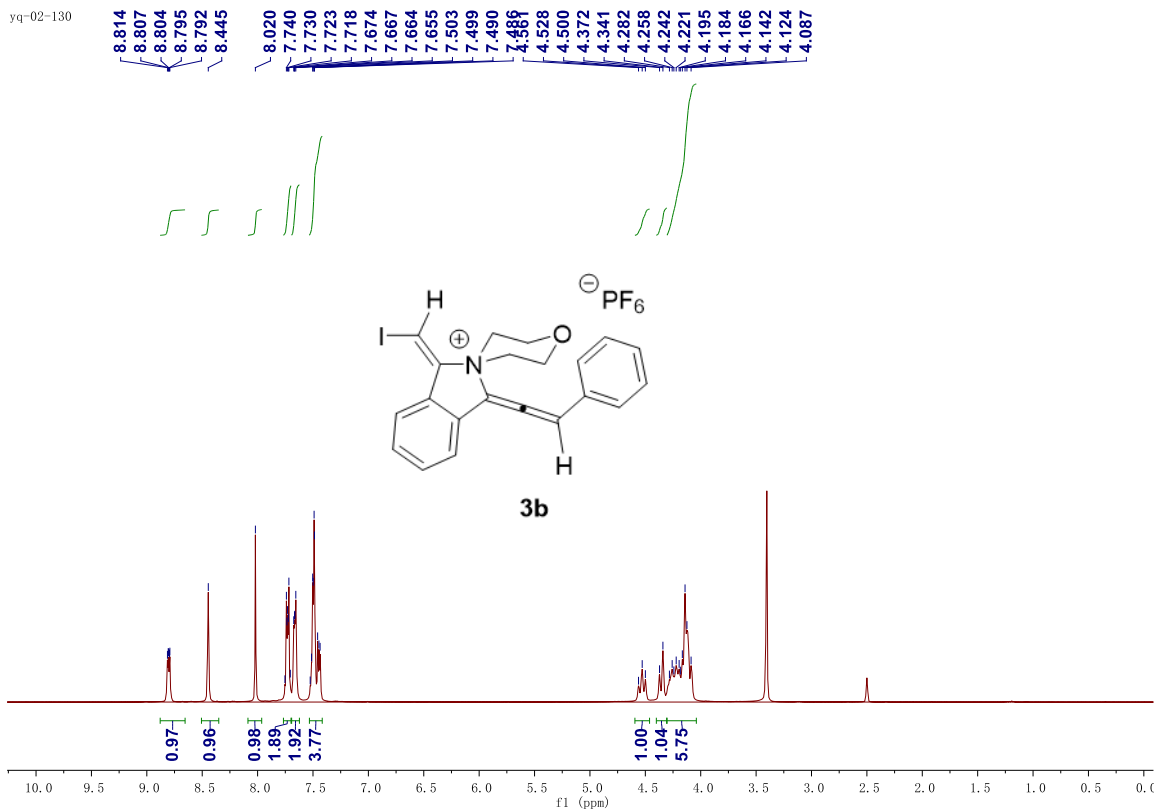
# <sup>13</sup>C NMR

yq-02-123



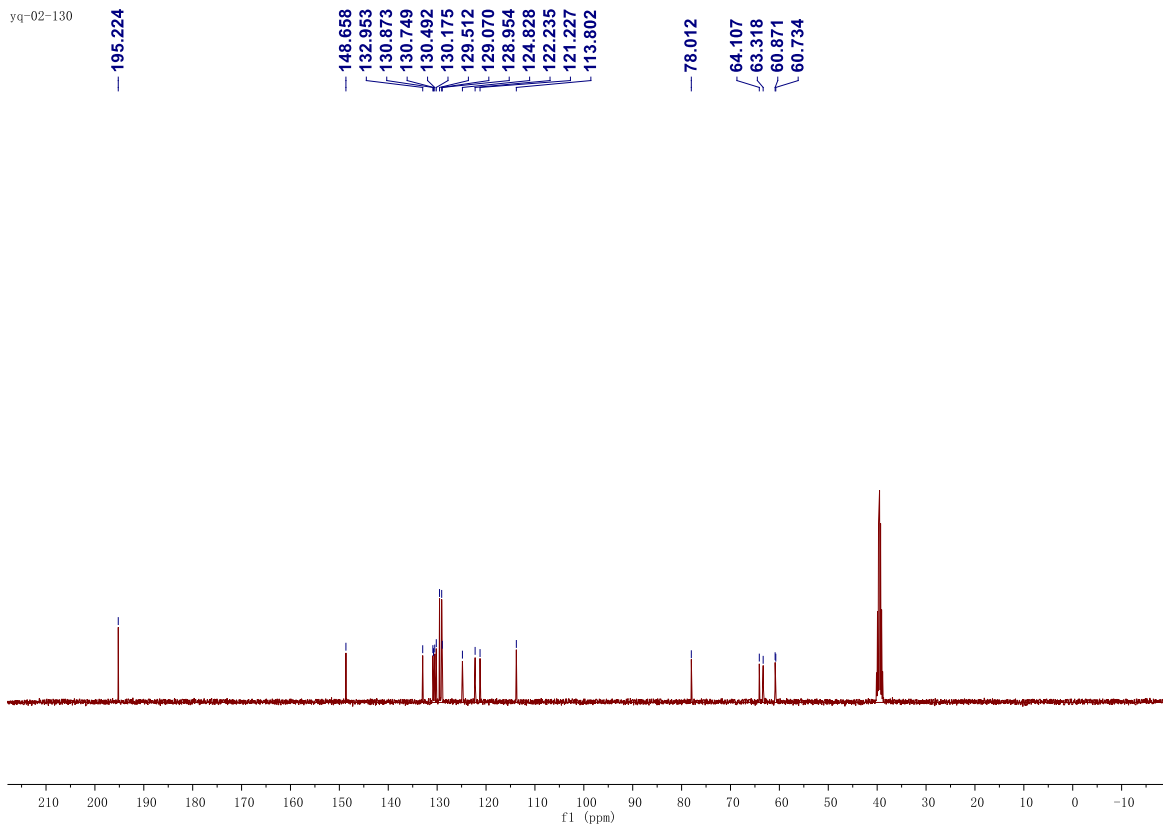
# <sup>1</sup>H NMR

yq-02-130



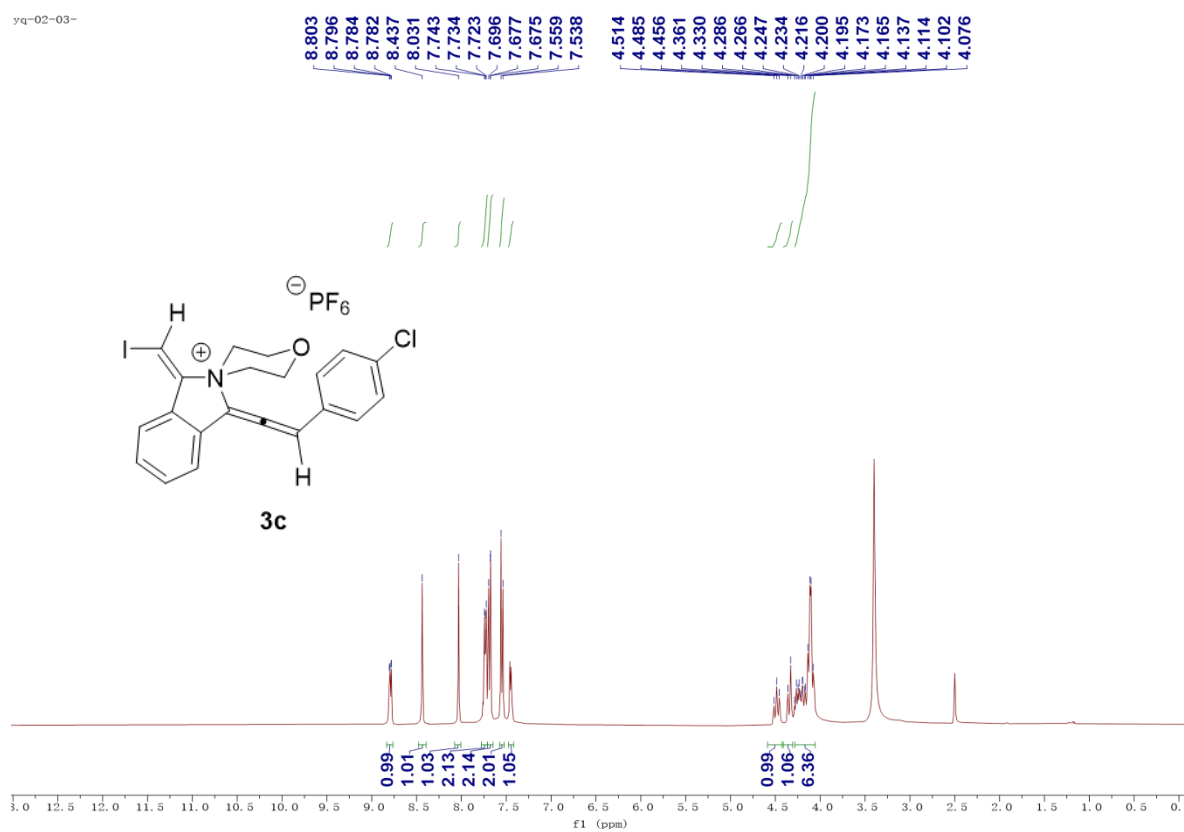
# <sup>13</sup>C NMR

yq-02-130



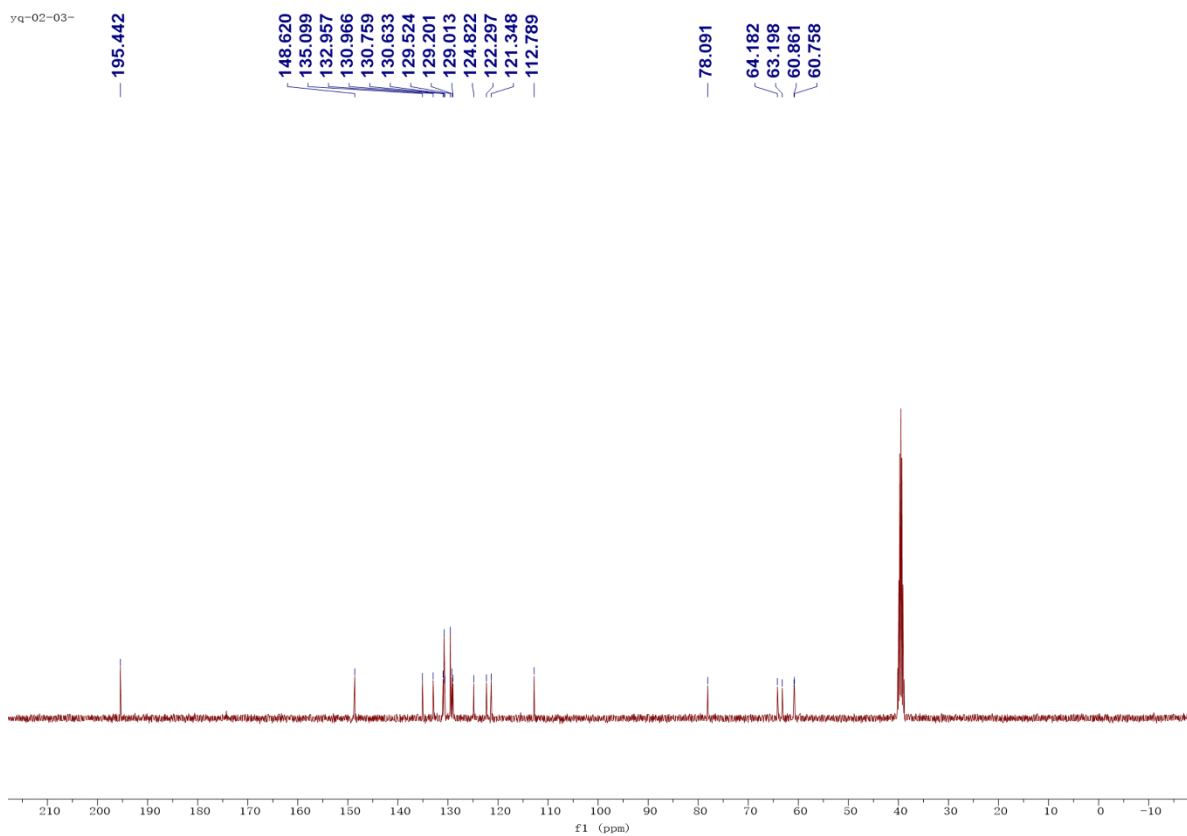
# <sup>1</sup>H NMR

yq-02-03-



# <sup>13</sup>C NMR

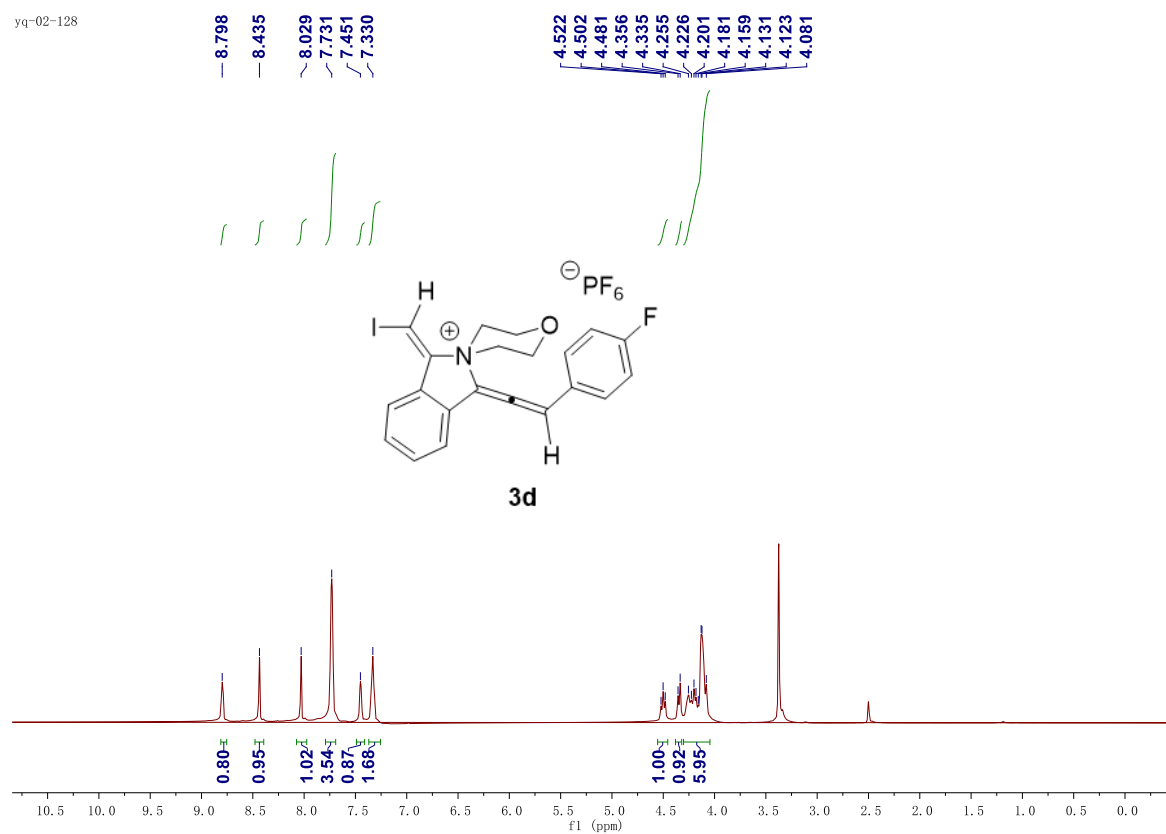
yq-02-03-





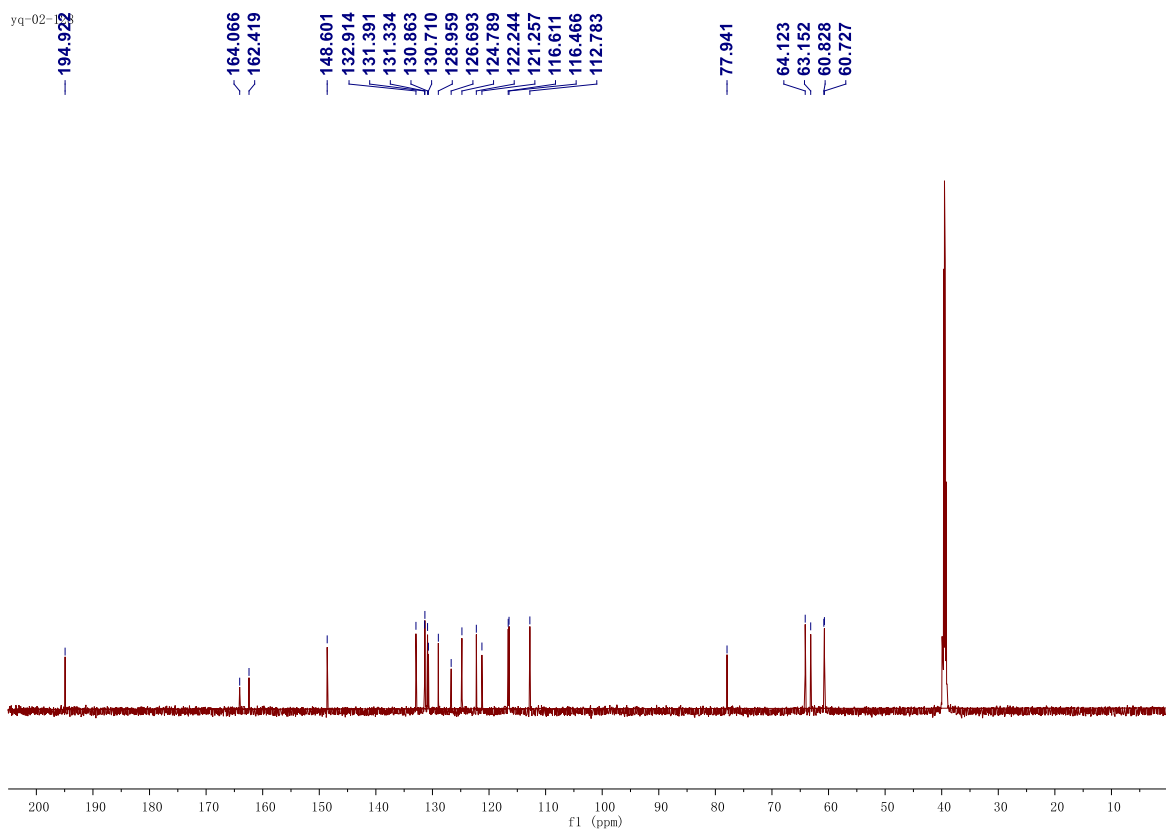
# <sup>1</sup>H NMR

yq-02-128

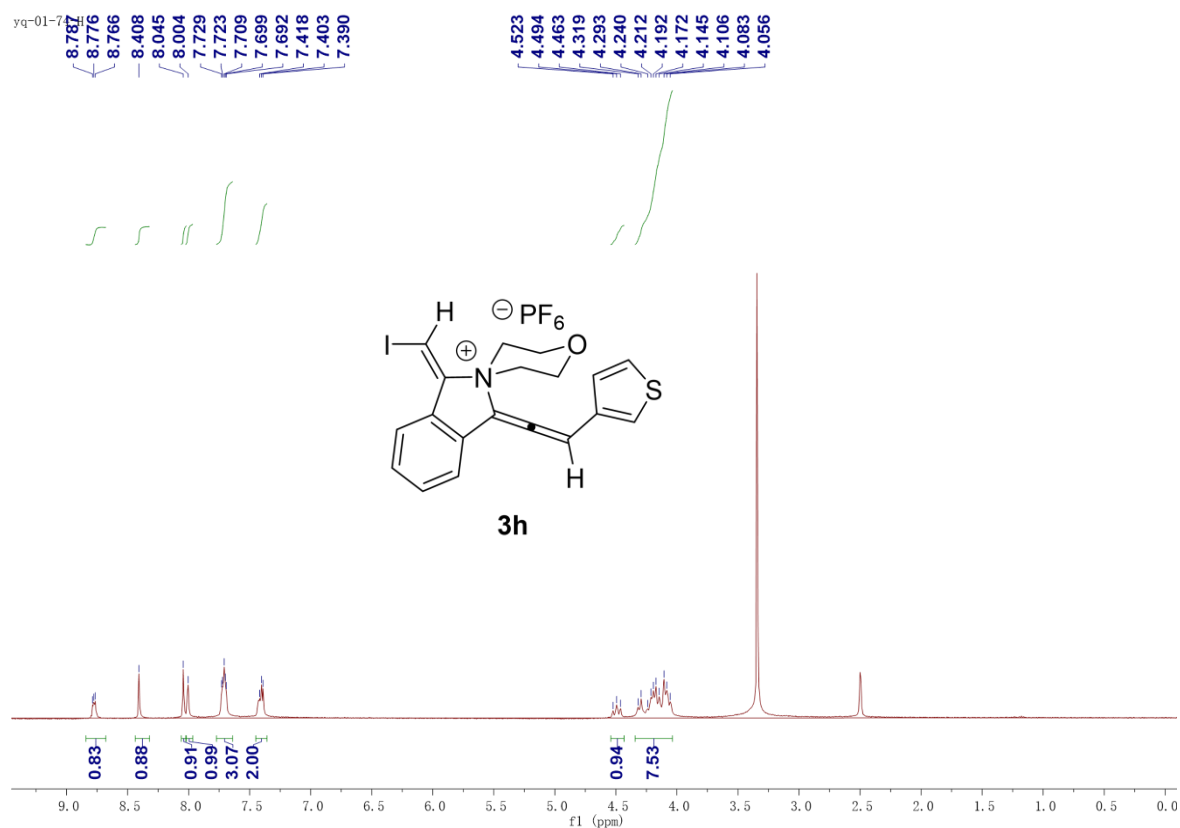


# <sup>13</sup>C NMR

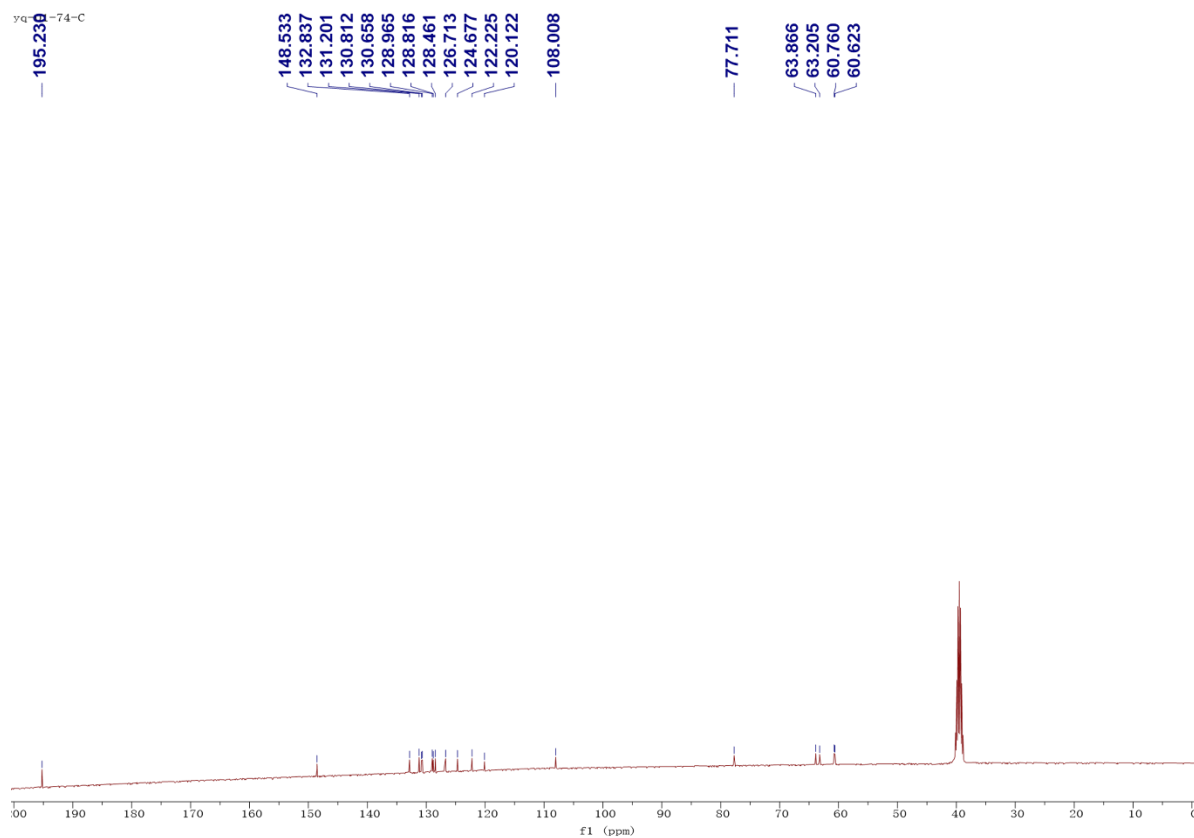
yq-02-128



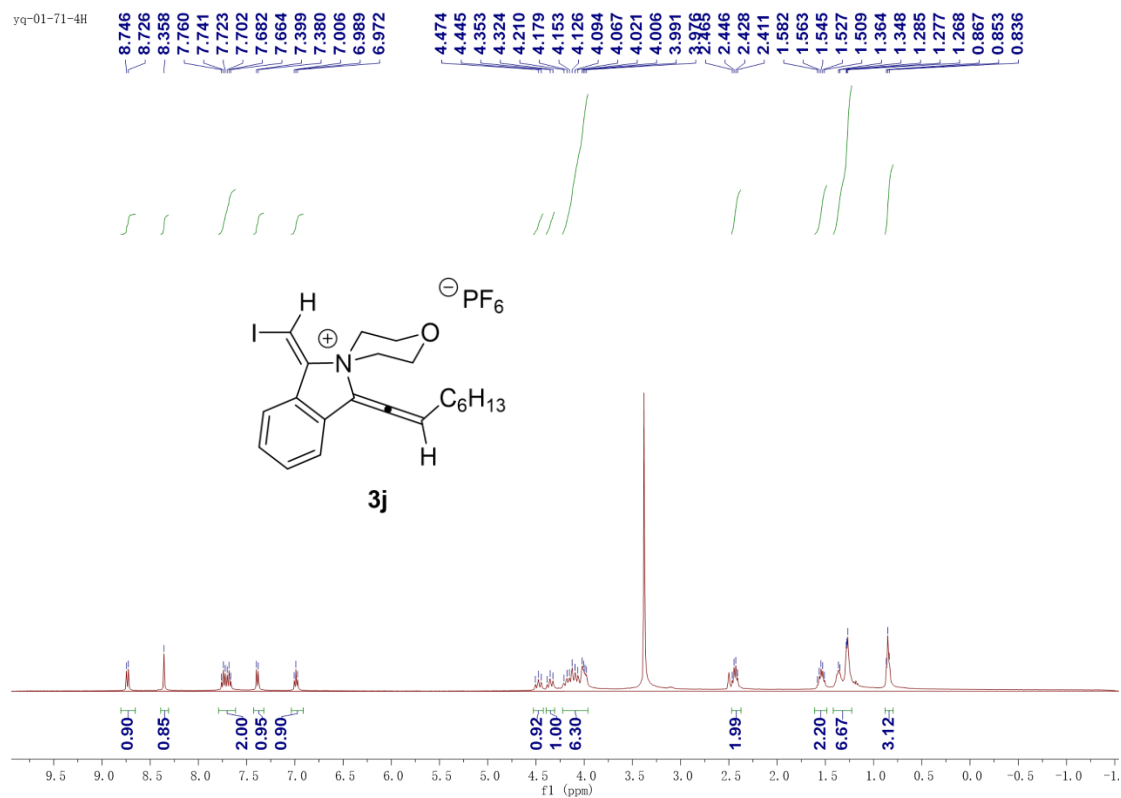
# <sup>1</sup>H NMR



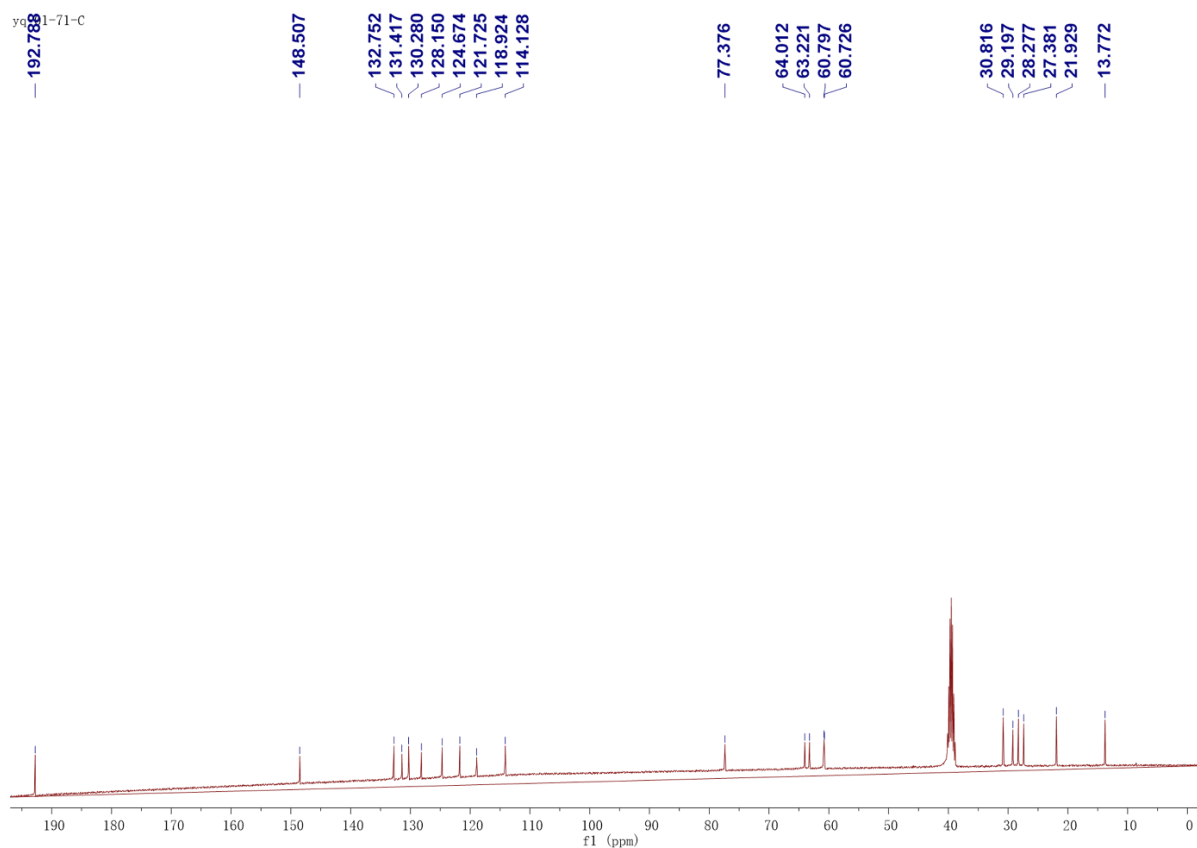
# <sup>13</sup>C NMR



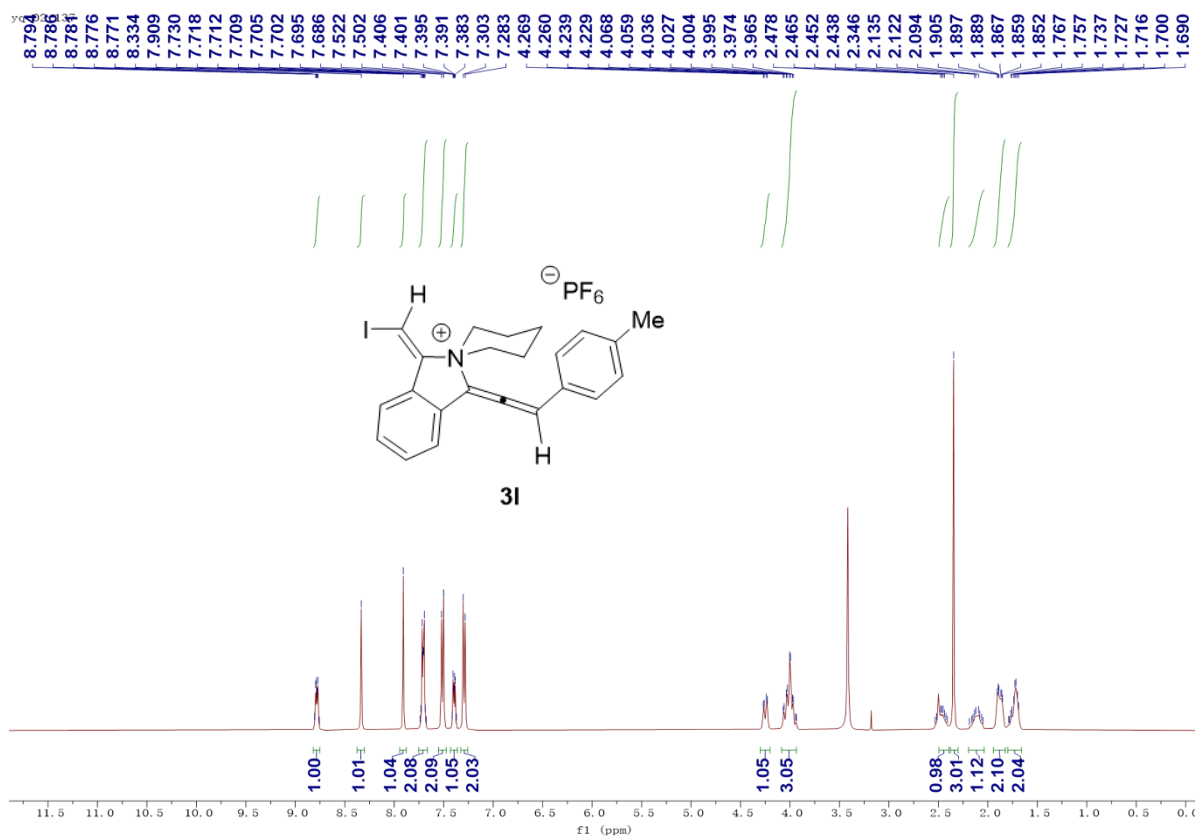
# <sup>1</sup>H NMR



# <sup>13</sup>C NMR

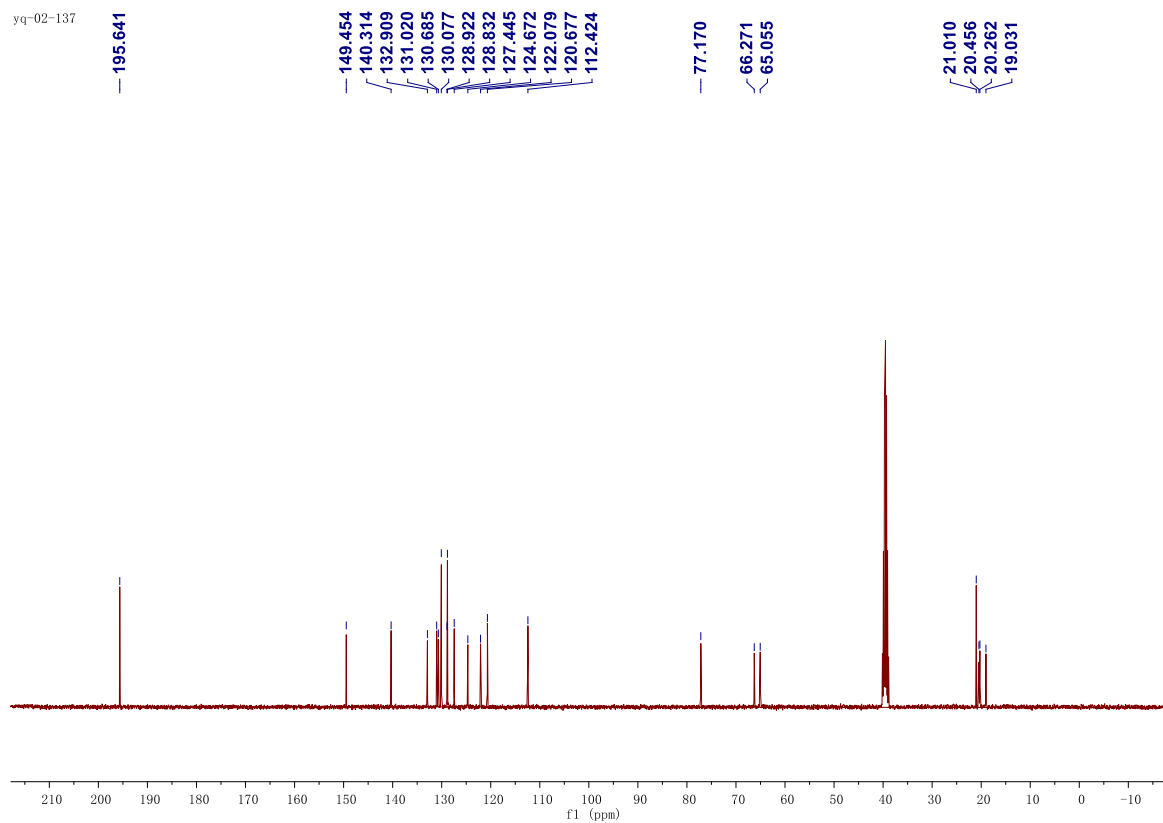


# <sup>1</sup>H NMR

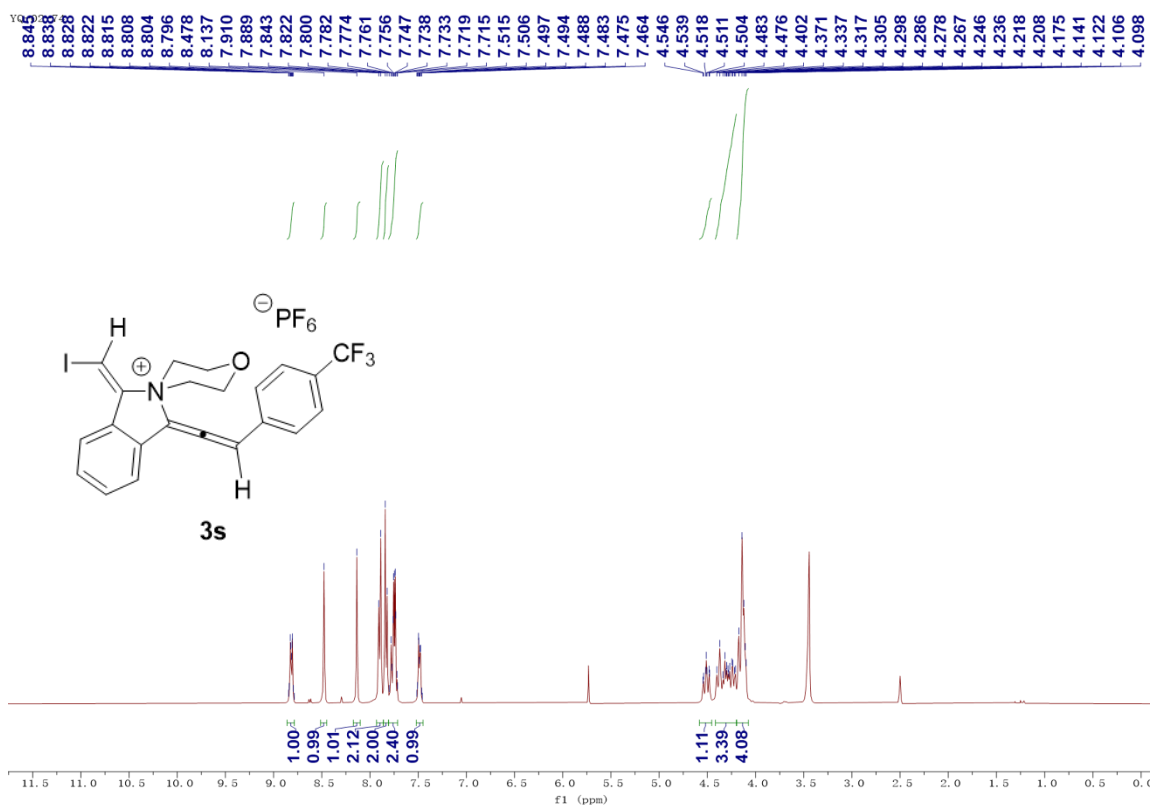


# <sup>13</sup>C NMR

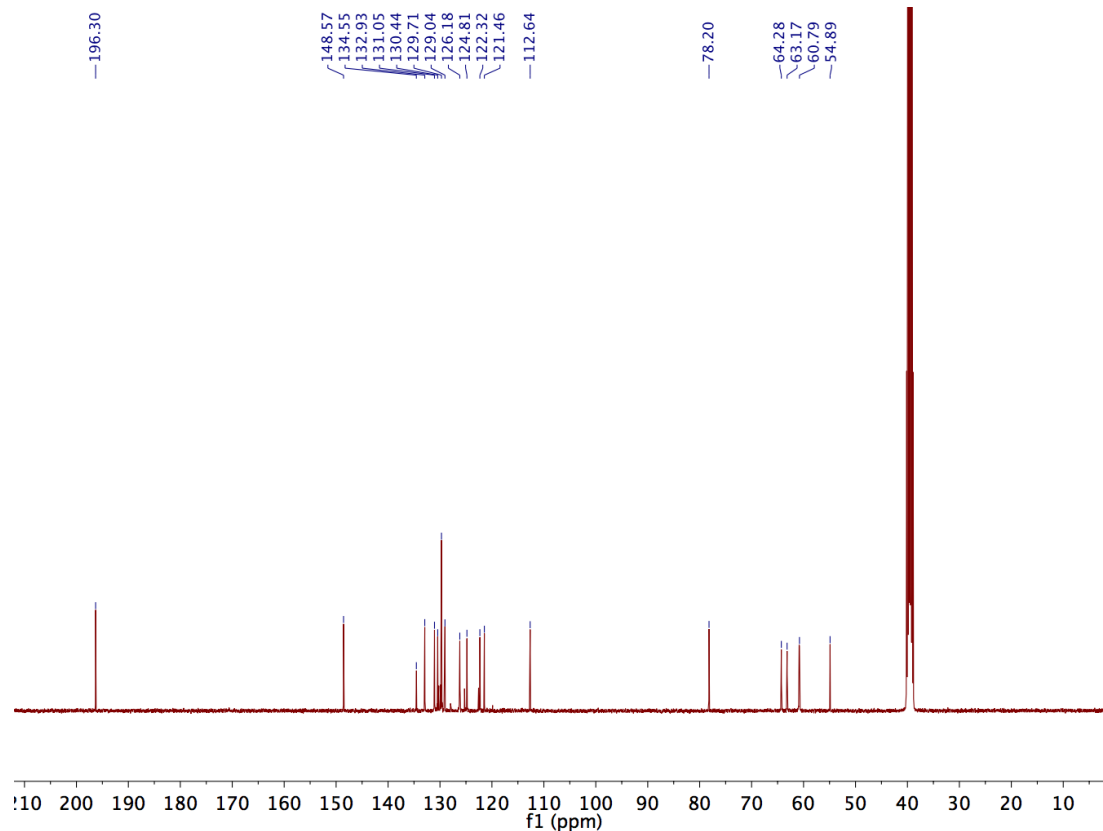
yq-02-137



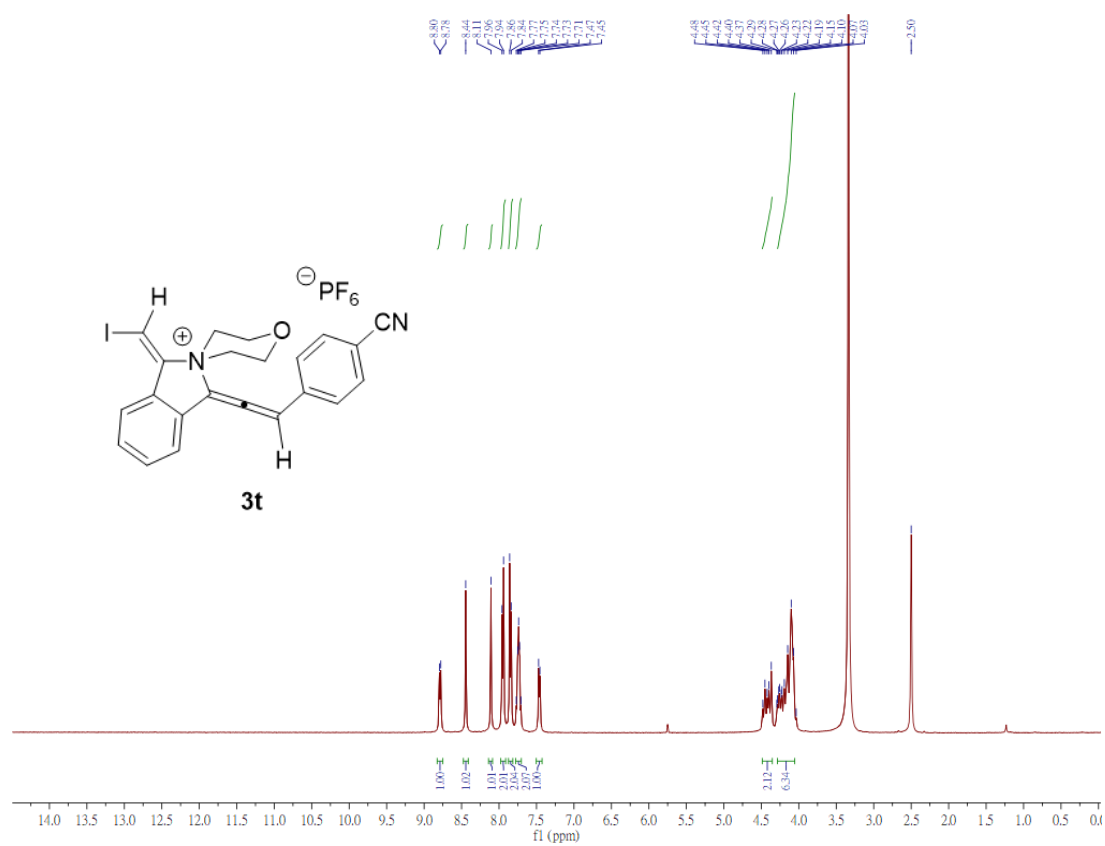
# <sup>1</sup>H NMR



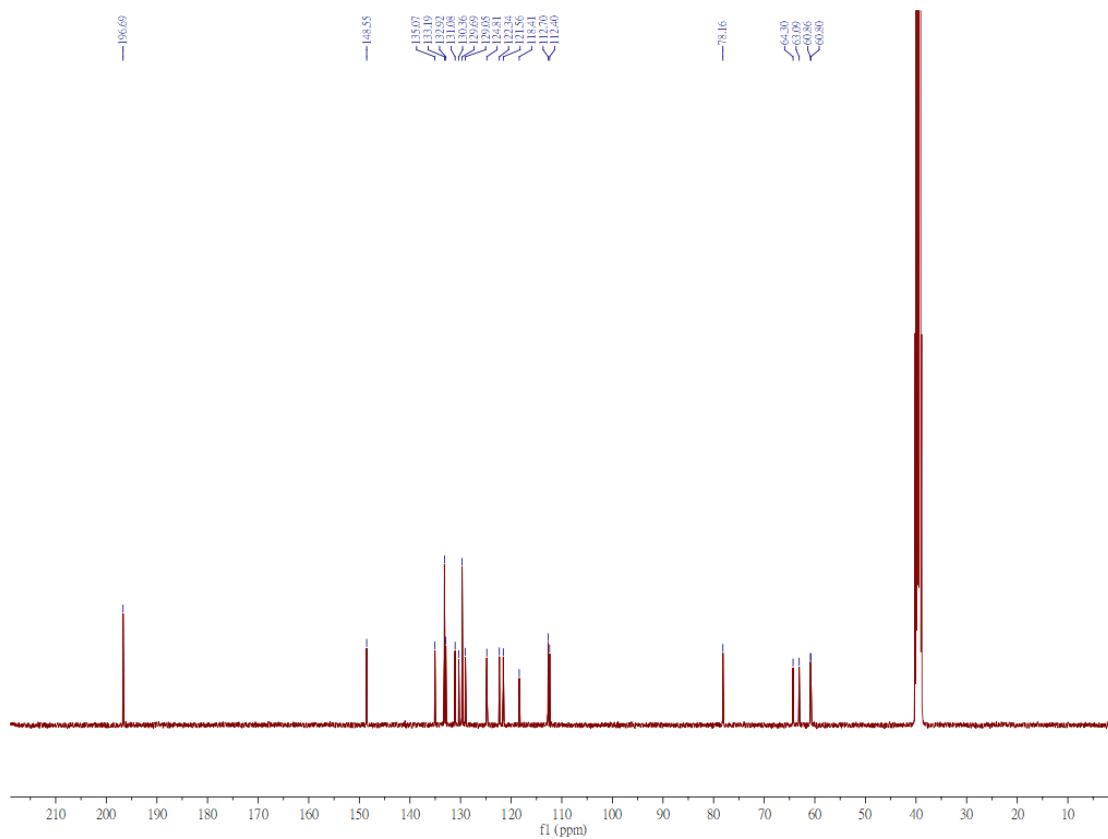
# <sup>13</sup>C NMR



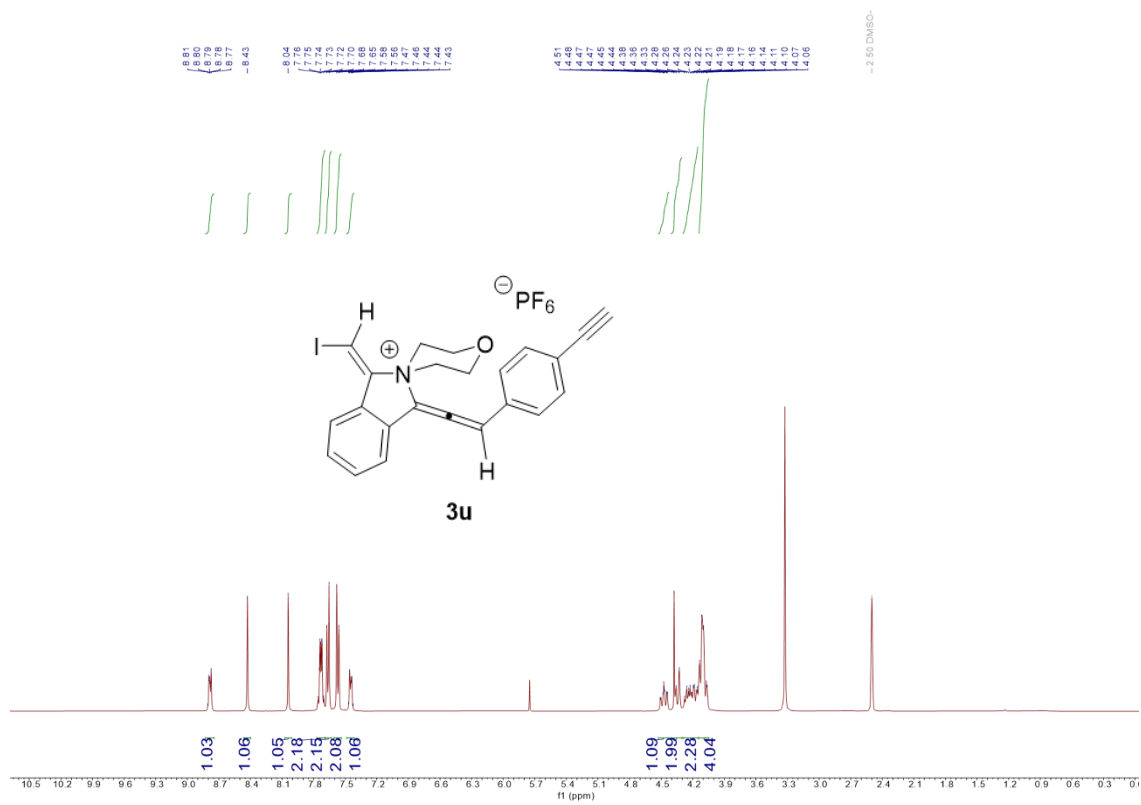
# <sup>1</sup>H NMR



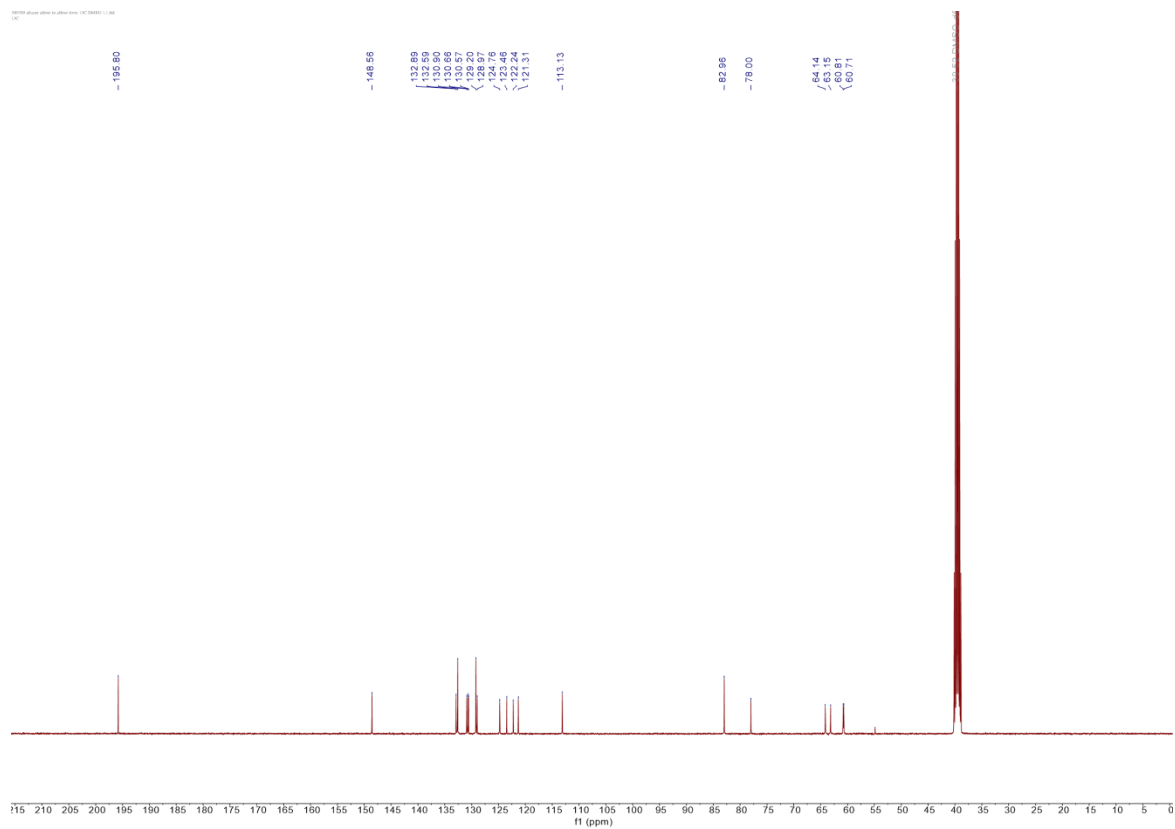
# <sup>13</sup>C NMR



# <sup>1</sup>H NMR



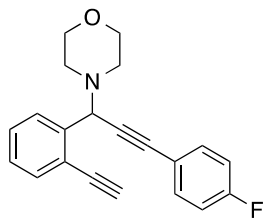
# <sup>13</sup>C NMR



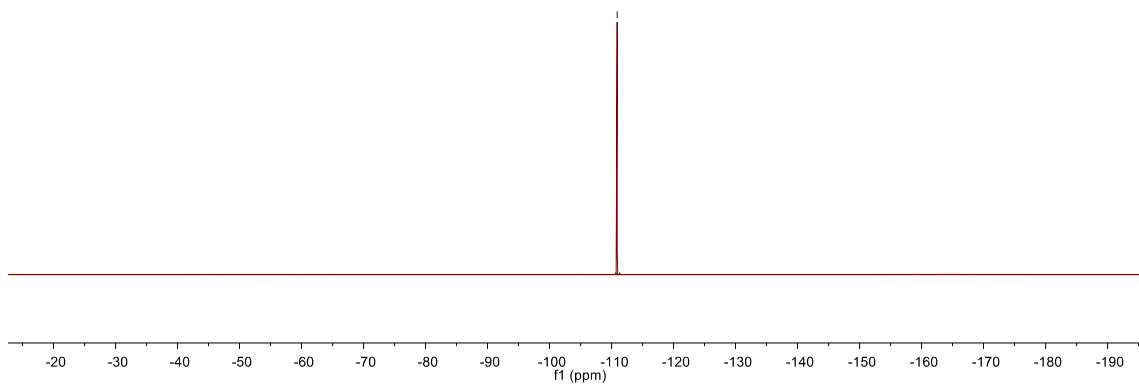
# <sup>19</sup>F NMR

cj13-052-1-deTMS-F  
Standard 19F 03 Nov 2016

-110.902



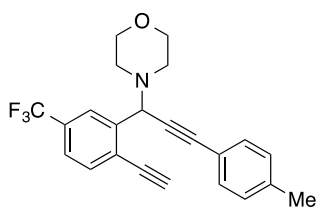
1d



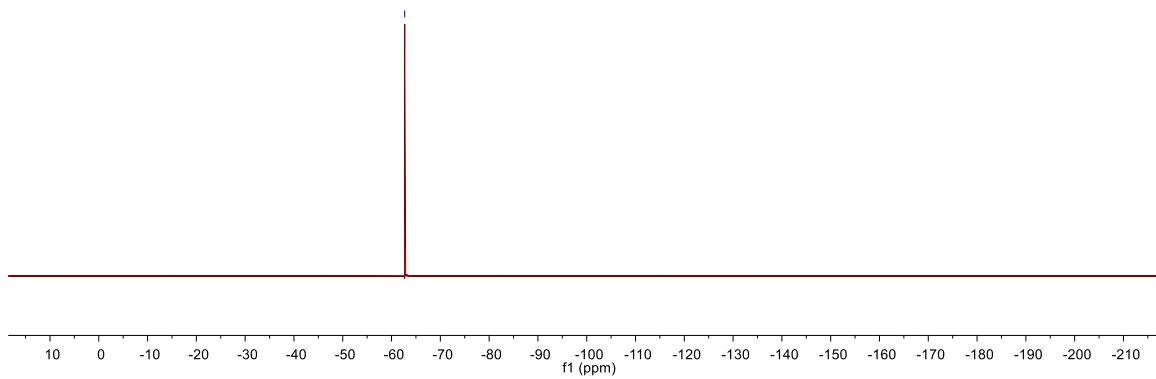
# <sup>19</sup>F NMR

cj13-058-1-deTMS-F  
Standard 19F 03 Nov 2016

-62.699



1r

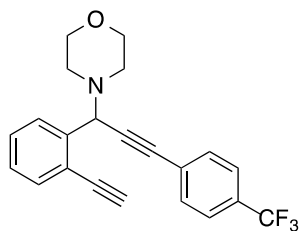




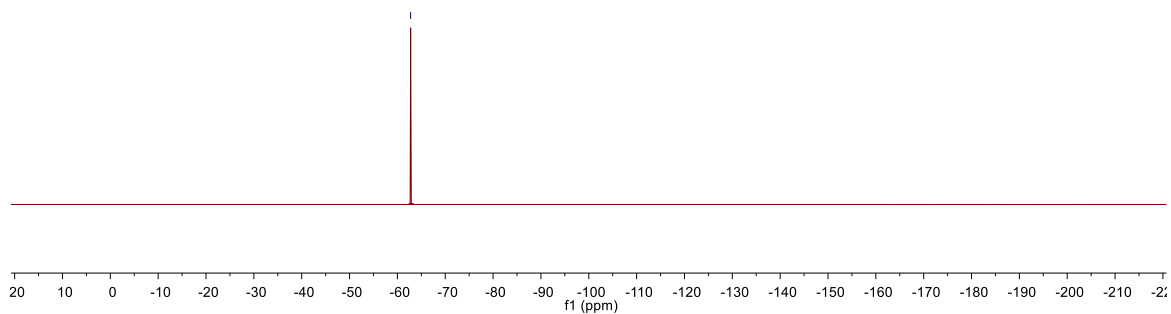
# <sup>19</sup>F NMR

cyj12-002-deTMS-F.1.fid

-62.768



1s

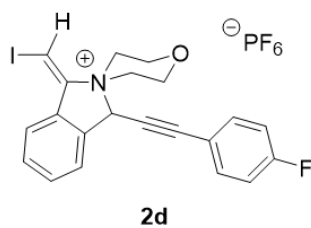


# <sup>19</sup>F NMR

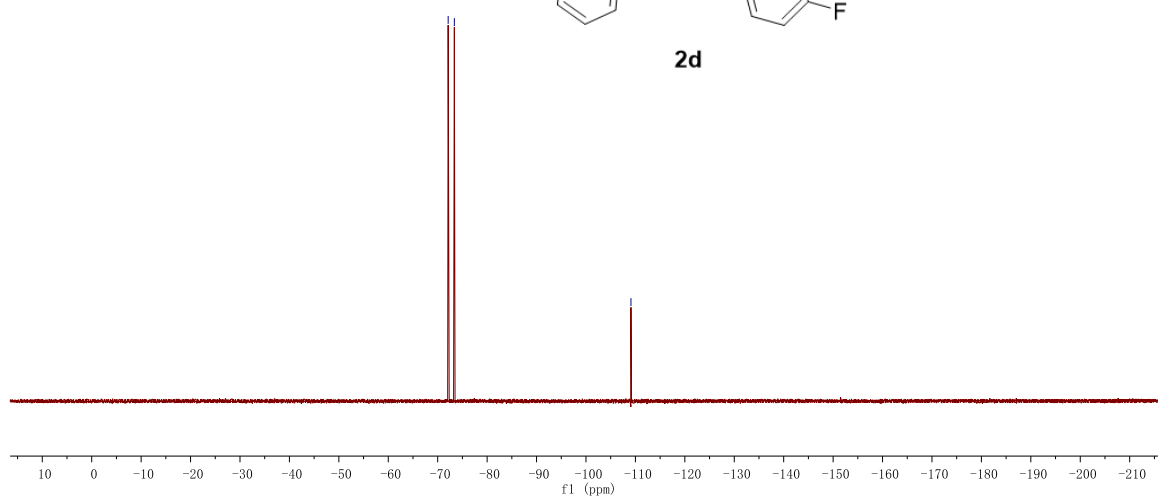
YQ-F-20190707-F19

-72.116  
-73.368

-109.100



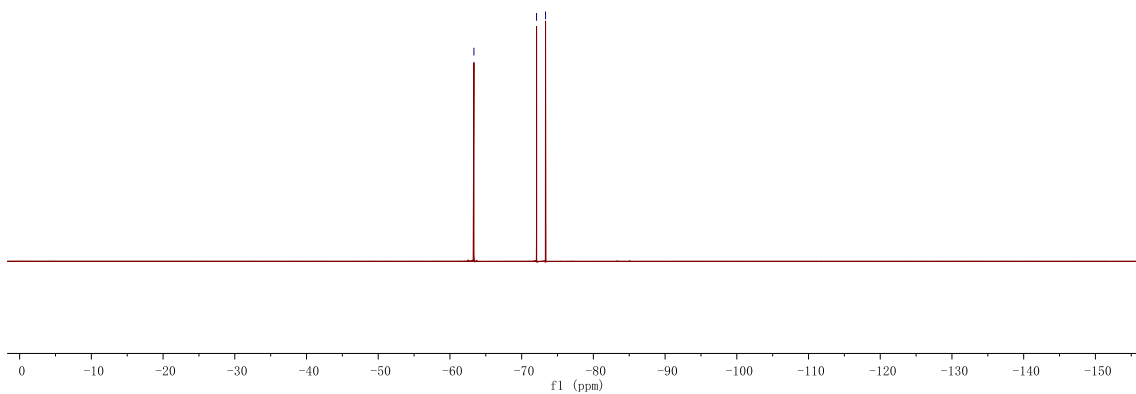
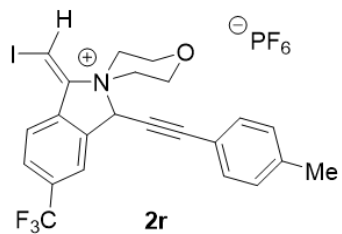
2d



# <sup>19</sup>F NMR

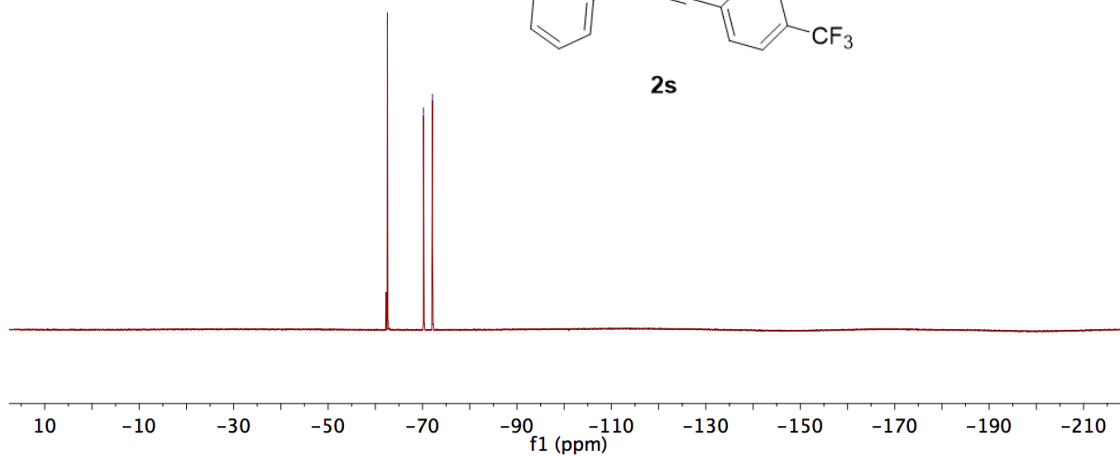
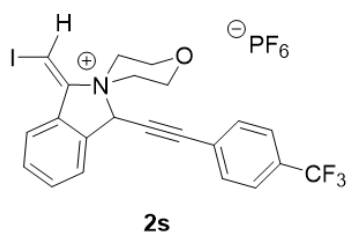
YQ-CF3-20190829-F

— -63.35  
~ -72.08  
~ -73.33



# <sup>19</sup>F NMR

— -62.55  
~ -70.21  
~ -72.10

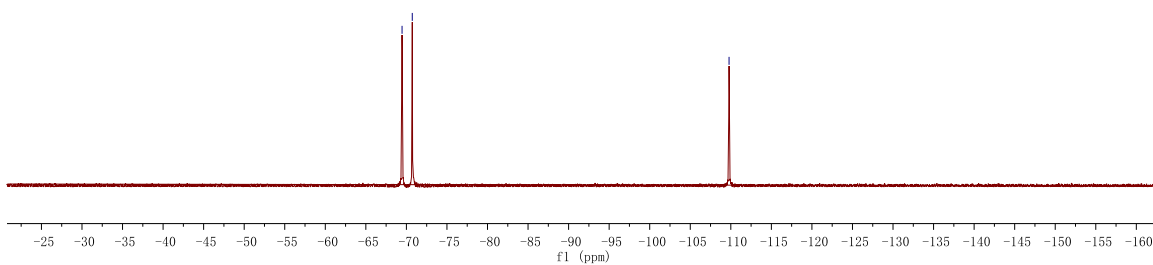
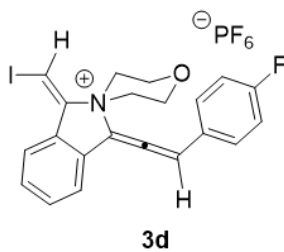


# <sup>19</sup>F NMR

yq-02-128

-69.46  
-70.72

-109.78



# <sup>19</sup>F NMR

-62.26  
-70.21  
-72.10

