

## ***Supporting Information***

### ***Manuscript Title:***

Synthesis of Semibullvalene Derivatives via  $\text{Co}_2(\text{CO})_8$ -Mediated Cyclodimerization of 1,4-Dilithio-1,3-butadienes

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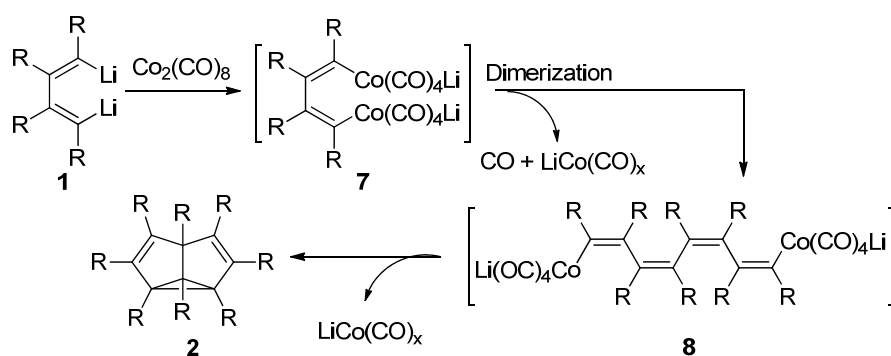
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### 1) A proposed reaction mechanism



**SScheme 1.** Proposed mechanism for  $\text{Co}_2(\text{CO})_8$ -mediated synthesis of semibullvalenes **2**

Addition of C-Li bond in **1** to  $\text{Co}_2(\text{CO})_8$  would form the butadienyl bis(lithium cobaltate) **7**, which would then undergo oxidative dimerization to afford **8**.<sup>1</sup> Intramolecular cyclization of **8** gives SBV **2** with elimination of lithium carbonylcobaltate aggregates.<sup>2</sup>

## 2) Experimental details and characterization data for all new compounds

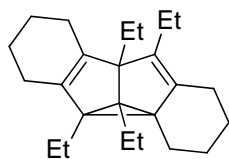
**General Methods:** All reactions were conducted under a slightly positive pressure of dry nitrogen using standard Schlenk line techniques or under a nitrogen atmosphere in a Mikrouna Super (1220/750) glovebox. The nitrogen in the glove box was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O<sub>2</sub>/H<sub>2</sub>O Combi-Analyzer to ensure both were always below 1 ppm. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. *n*-BuLi and *t*-BuLi were obtained from Acros. 1,4-Diiodo-1,3-butadienes **3** were prepared according to the literature method.<sup>3</sup>

Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes (Wilmad 528-JY). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker-500 spectrometer (FT, 500 MHz for <sup>1</sup>H; 125 MHz for <sup>13</sup>C) or a Bruker-400 spectrometer (FT, 400 MHz for <sup>1</sup>H; 100 MHz for <sup>13</sup>C) or a JEOL-AL300 spectrometer (FT, 300 MHz for <sup>1</sup>H; 75 MHz for <sup>13</sup>C) at room temperature, unless otherwise noted. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). Micro elemental analyses were performed on an Elemental Analyzer vario EL apparatus.

### Experimental details and characterization data for all new compounds:

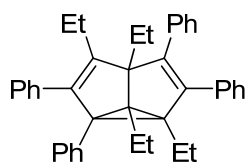
#### a) Co<sub>2</sub>(CO)<sub>8</sub>-mediated synthesis of semibullvalenes **2**

**General procedure for preparation of semibullvalenes **2** from 1,4-dilithio-1,3-dienes **1** and Co<sub>2</sub>(CO)<sub>8</sub>:** *t*-BuLi (4.0 mmol, 1.6 M in pentane) was added to a solution of diiodo compound **3** (1.0 mmol) in THF (5 mL) in a 20 ml Schlenk tube at -78 °C (dry ice/acetone bath). The reaction mixture was then stirred at room temperature for 1 h. After addition of Co<sub>2</sub>(CO)<sub>8</sub> (0.5 mmol, 171 mg) at -78 °C, the mixture was stirred at room temperature for 4 h. The reaction mixture was quenched by water, extracted with hexane (10 mL) for three times. The combined organic layer was washed with water and brine and dried over MgSO<sub>4</sub>. The solvent was evaporated in vacuum to give yellow oil, which was purified by column chromatography (neutral alumina, petroleum ether) to afford the corresponding semibullvalene **2**. The characterized data of compounds **2a-d**, **2f** have been published in our previous communication.<sup>4</sup>



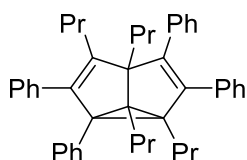
**2e**

**2e:** Colorless oil, isolated yield 40% (130 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.65 (t,  $J = 7.6\text{Hz}$ , 3H,  $\text{CH}_3$ ), 0.82 (t,  $J = 7.6\text{Hz}$ , 3H,  $\text{CH}_3$ ), 0.88 ( $J = 7.6\text{Hz}$ , 3H,  $\text{CH}_3$ ), 0.89 ( $J = 7.6\text{Hz}$ , 3H,  $\text{CH}_3$ ), 1.15-1.22 (m, 2H,  $\text{CH}_2$ ), 1.51-1.68 (m, 12H,  $\text{CH}_2$ ), 1.95-1.99 (m, 6H,  $\text{CH}_2$ ), 2.10-2.15 (m, 4H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  11.20, 14.22, 18.80, 19.45, 24.31, 24.74, 24.94, 25.65, 65.64, 96.99, 101.13, 128.40. HRMS:  $m/z$ : calcd for  $\text{C}_{24}\text{H}_{37}$   $[\text{M}+\text{H}]^+$ : 325.2895, found 325.2891.



**2g**

**2g:** Colorless solid, isolated yield 42% (218 mg);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.77 (t,  $J = 7.5\text{Hz}$ , 3H,  $\text{CH}_3$ ), 0.93 (t,  $J = 7.5\text{Hz}$ , 3H,  $\text{CH}_3$ ), 1.11 (t,  $J = 7.5\text{Hz}$ , 3H,  $\text{CH}_3$ ), 1.22 (t,  $J = 7.5\text{Hz}$ , 3H,  $\text{CH}_3$ ), 1.87-2.48 (m, 8H,  $\text{CH}_2$ ), 6.74-7.30 (m, 20H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  12.08, 14.31, 14.36, 14.45, 21.89, 22.14, 24.04, 25.55, 70.50, 105.32, 106.12, 126.16, 126.71, 127.49, 128.02, 128.07, 128.24, 129.42, 130.67, 131.31, 132.48, 136.61, 137.95, 139.41, 139.88, 141.28, 141.62, 142.40, 143.56. HRMS:  $m/z$ : calcd for  $\text{C}_{40}\text{H}_{40}$ : 520.3130, found 520.3143. Single crystals of **2g** suitable for X-ray analysis were grown in hexane at room temperature.



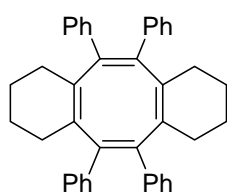
**2h**

**2h:** Yellow solid, isolated yield 41% (235 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.53 (t,  $J = 7.5\text{Hz}$ , 6H,  $\text{CH}_3$ ), 0.86-0.87 (m, 4H,  $\text{CH}_2$ ), 1.00 (t,  $J = 7.5\text{Hz}$ , 6H,  $\text{CH}_3$ ), 1.67-1.77 (m, 6H,  $\text{CH}_2$ ), 1.20-1.29 (m, 4H,  $\text{CH}_2$ ), 1.78-1.87 (m, 8H,  $\text{CH}_2$ ), 6.82-6.84 (m, 4H,  $\text{C}_6\text{H}_5$ ), 6.74-6.81 (m, 4H,  $\text{C}_6\text{H}_5$ ), 7.03-7.04 (m, 2H,  $\text{C}_6\text{H}_5$ ), 7.07-7.10 (m, 8H,  $\text{C}_6\text{H}_5$ ), 7.13-7.17 (m, 6H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.64, 15.50, 20.40, 22.88, 30.84, 32.26, 69.66, 104.18, 105.30, 125.42, 126.13, 127.38, 127.54, 129.05, 132.13, 135.93, 137.57, 130.26, 138.97. HRMS:  $m/z$ : calcd for  $\text{C}_{44}\text{H}_{49}$   $[\text{M}+\text{H}]^+$ : 577.3834, found 577.3830.

## b) $\text{Co}_2(\text{CO})_8$ -mediated synthesis of cyclooctatetraene **4**

Procedure for preparation of cyclooctatetraene **4** from 1,4-dilithio-1,3-diene **1i** and

**Co<sub>2</sub>(CO)<sub>8</sub>:** *t*-BuLi (4.0 mmol, 1.6 M in pentane) was added to a solution of 1,4-diiodo-1,4-diphenyl-2,3-tetramethylene-1,3-butadiene (1.0 mmol) in THF (5 mL) in a 20 ml Schlenk tube at -78 °C (dry ice/acetone bath). The reaction mixture was then stirred at room temperature for 1 h. After addition of Co<sub>2</sub>(CO)<sub>8</sub> (0.5 mmol, 171 mg) at -78 °C, the mixture was stirred at room temperature for 3 h. The reaction mixture was quenched by water, extracted with hexane (10 mL) for three times. The combined organic layer was washed with water and brine and dried over MgSO<sub>4</sub>. The solvent was evaporated in vacuum to give yellow oil, which was purified by column chromatography (silica gel, petroleum ether/diethyl ether = 100:1) to afford the corresponding cyclooctatetraene **4**.

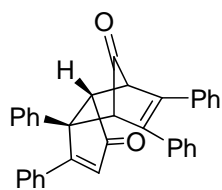


**4**

**4:** Colorless crystal, isolated yield 53% (273 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.58-1.69 (m, 8H, CH<sub>2</sub>), 2.11-2.30 (m, 8H, CH<sub>2</sub>), 7.05 (brs, 20H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 23.20, 29.47, 126.00, 127.47, 129.97, 135.92, 140.38, 141.30. HRMS: *m/z*: calcd for C<sub>18</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 517.2895, found 517.2892. Elemental Analysis Calcd (%) for C<sub>40</sub>H<sub>36</sub>: C, 92.98; H, 7.02; Found: C, 92.85; H, 7.13. Single crystals of **4** suitable for X-ray analysis were grown in hexane at room temperature.

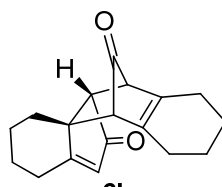
### c) Co<sub>2</sub>(CO)<sub>8</sub>-mediated synthesis of cyclopentadienone dimers **6**

**General procedure for preparation of cyclopentadienone dimer 6 from 1,4-dilithio-1,3-dienes 1j-k and Co<sub>2</sub>(CO)<sub>8</sub>:** *t*-BuLi (4.0 mmol, 1.6 M in pentane) was added to a solution of diiodo compound **3** (1.0 mmol) in THF (5 mL) in a 20 ml Schlenk tube at -78 °C (dry ice/acetone). The reaction mixture was then stirred at room temperature for 1 h. After addition of Co<sub>2</sub>(CO)<sub>8</sub> (0.5 mmol, 171 mg) at -78 °C, the mixture was stirred at room temperature for 4 h. The reaction mixture was quenched by water, extracted with hexane (10 mL) for three times. The combined organic layer was washed with water and brine and dried over MgSO<sub>4</sub>. The solvent was evaporated in vacuum to give yellow oil, which was purified by column chromatography (silica gel, petroleum ether/diethyl ether = 100:2) to afford the corresponding cyclopentadienone dimers **6**.



**6a**

**6a:** Colorless crystal, isolated yield 30% (139 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.14 (d,  $J = 4.8\text{Hz}$ , 1H, CH), 3.81 (d,  $J = 4.8\text{Hz}$ , 1H, CH), 4.43 (s, 1H, CH), 6.87-6.88 (m, 2H,  $\text{C}_6\text{H}_5$ ), 6.92-6.94 (m, 4H,  $\text{C}_6\text{H}_5$ ), 7.00 (s, H, CH), 7.25-7.27 (m, 3H,  $\text{C}_6\text{H}_5$ ), 7.34-7.38 (m, 2H,  $\text{C}_6\text{H}_5$ ), 7.48-7.50 (d,  $J = 7.6\text{ Hz}$ , 2H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  56.61, 58.28, 58.39, 59.60, 125.98, 127.44, 127.49, 127.98, 128.07, 128.21, 128.33, 128.78, 129.01, 129.55, 130.66, 132.14, 133.98, 134.06, 134.26, 136.77, 141.63, 173.85, 195.89, 205.80. HRMS:  $m/z$ : calcd for  $\text{C}_{34}\text{H}_{25}\text{O}_2$   $[\text{M}+\text{H}]^+$ : 465.1855, found 465.1851. Elemental Analysis Calcd (%) for  $\text{C}_{34}\text{H}_{24}\text{O}_2$ : C, 87.90; H, 5.21; Found: C, 87.69; H, 5.35. Single crystals of **6a** suitable for X-ray analysis were grown in hexane/EtOAc (10:1) at room temperature.



**6b**

**6b:** Colorless crystal, isolated yield 33% (88 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.26 (brs, 2H,  $\text{CH}_2$ ), 1.47-1.51 (m, 4H, CH), 1.59-1.68 (m, 4H,  $\text{CH}_2$ ), 2.04-2.40 (m, 6H,  $\text{CH}_2$ ), 2.39 (d,  $J = 4.58\text{ Hz}$ , 1H, CH), 2.94 (s, 2H, CH), 3.08 (d,  $J = 4.8\text{ Hz}$ , 1H, CH), 5.99 (s, 1H, CH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  22.57, 22.70, 22.87, 24.74, 25.07, 27.13, 30.01, 34.48, 51.74, 52.10, 53.45, 56.47, 132.18, 134.86, 135.67, 181.59, 198.99, 205.73. HRMS:  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{21}\text{O}_2$   $[\text{M}+\text{H}]^+$ : 269.1542, found 269.1540. Elemental Analysis Calcd (%) for  $\text{C}_{18}\text{H}_{20}\text{O}_2$ : C, 80.56; H, 7.51; Found: C, 80.50; H, 7.57. Single crystals of **6b** suitable for X-ray analysis were grown in hexane/diethyl ether (5:1) at room temperature.

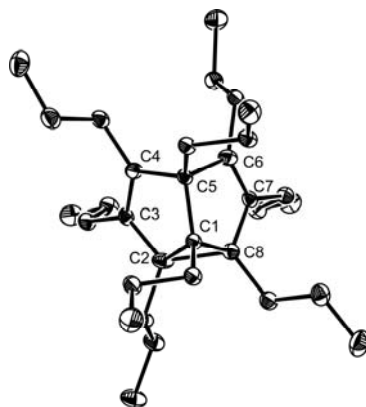
### 3) X-ray crystallographic studies

The single crystals of **2b\***, **2g**, **4**, **6a**, **6b** suitable for X-ray analysis were grown as shown in experimental section. Data collections for **2b\***, **2g** and **4** were performed at 20 °C, –130 °C, –150 °C on a Rigaku RAXIS RAPID IP diffractometer respectively, using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data collections for **6a**, **6b** were performed at –100 °C on a RIGAKU CCD SATURN 724 diffractometer, using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The determination of crystal class and unit cell parameters was carried out by the Rapid-AUTO (Rigaku 2000) program package for **2b\***, **2g**, **4** or CrystalClear (Rigaku Inc., 2007) for **6a**, **6b**. The raw frame data were processed using Crystal Structure (Rigaku/MSK 2000) for **2b\***, **2g**, **4** or CrystalClear (Rigaku Inc., 2007) for **6a**, **6b** to yield the reflection data file. The structures of **2b\***, **2g**, **4**, **6a**, **6b** were solved by use of SHELXTL program. Refinement was performed on F2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for compounds **2b\***, **2g**, **4**, **6a**, **6b** are summarized in **STable 1**. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-966204 (**2b\***), CCDC-966203 (**2g**), CCDC-971720 (**4**), CCDC-966206 (**6a**), CCDC-966207 (**6b**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

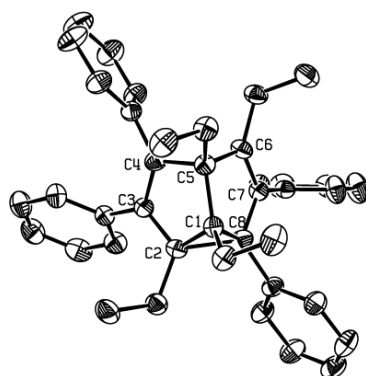
**Table S1.** Crystallographic data and structure refinement details for **2b\***, **2g**, **4**, **6a**, **6b**.

	<b>2b*</b>	<b>2g</b>	<b>4</b>	<b>6a</b>	<b>6b</b>
Formula	C <sub>32</sub> H <sub>56</sub>	C <sub>40</sub> H <sub>40</sub>	C <sub>40</sub> H <sub>36</sub>	C <sub>34</sub> H <sub>24</sub> O <sub>2</sub>	C <sub>18</sub> H <sub>20</sub> O <sub>2</sub>
<i>M<sub>w</sub></i>	440.77	520.72	516.69	464.53	268.34
crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic
space group	C2/c	P-1	P2(1)/n	P2(1)/c	P2(1)2(1)2(1)
<i>a</i> [Å]	35.265(7)	9.1290(18)	12.6639(4)	11.409(2)	9.1769(18)
<i>b</i> [Å]	19.026(4)	12.580(3)	16.9311(6)	8.8005(18)	10.289(2)
<i>c</i> [Å]	21.174(4)	15.035(3)	13.6040(4)	24.458(5)	14.620(3)
$\alpha$	90	81.14(3)	90	90	90
$\beta$ [°]	122.27(3)	73.69(3)	92.886(3)	102.84(3)	90
$\gamma$	90	70.31(3)	90	90	90
<i>V</i> [Å <sup>3</sup> ]	12012(4)	1556.9(5)	2913.20(16)	102.84(3)	1380.4(5)
<i>Z</i>	16	2	4	4	4
$\rho_{\text{calcd}}$ [gcm <sup>-3</sup> ]	0.975	1.111	1.178	1.289	1.291
$\mu$ [mm <sup>-1</sup> ]	0.054	0.062	0.066	0.079	0.082

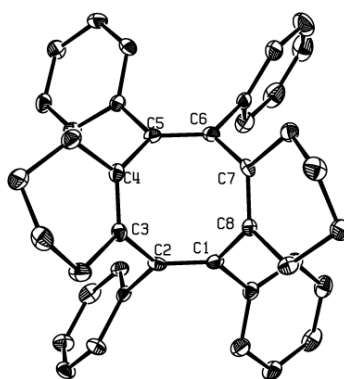
<i>F</i> (000)	3968	560	1104	976	576
$\theta$ range [°]	1.93-25.03	2.16-25.02	5.67-52.03	2.95-27.47	3.28-27.49
no of reflns collected	22640	9949	15003	15719	7672
no of indep reflns	10249	5270	5737	5384	1814
no of variables	578	362	361	325	200
<i>GOF</i>	0.987	1.010	1.020	1.217	1.168
<i>R</i> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0548	0.0552	0.0498	0.0744	0.0499
<i>R</i> <sub>w</sub>	0.1208	0.1309	0.0815	0.1370	0.1232



**Figure S1.** ORTEP drawing of **2b\*** with 30% probability thermal ellipsoids.

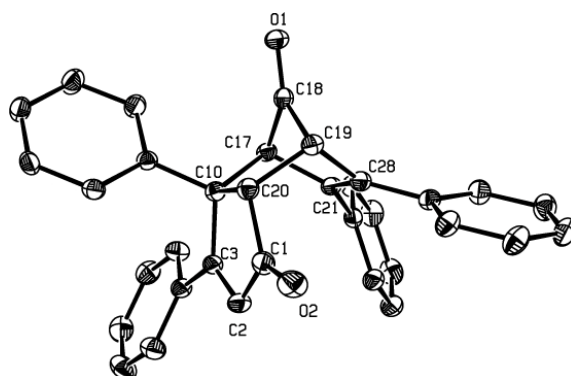


**Figure S2.** ORTEP drawing of **2g** with 30% probability thermal ellipsoids.

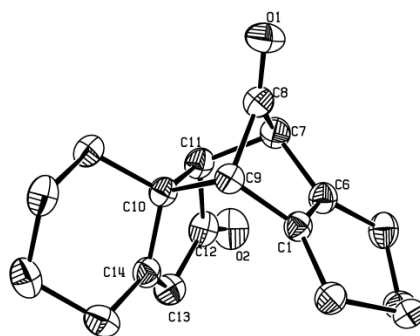




**Figure S3.** ORTEP drawing of **4** with 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.



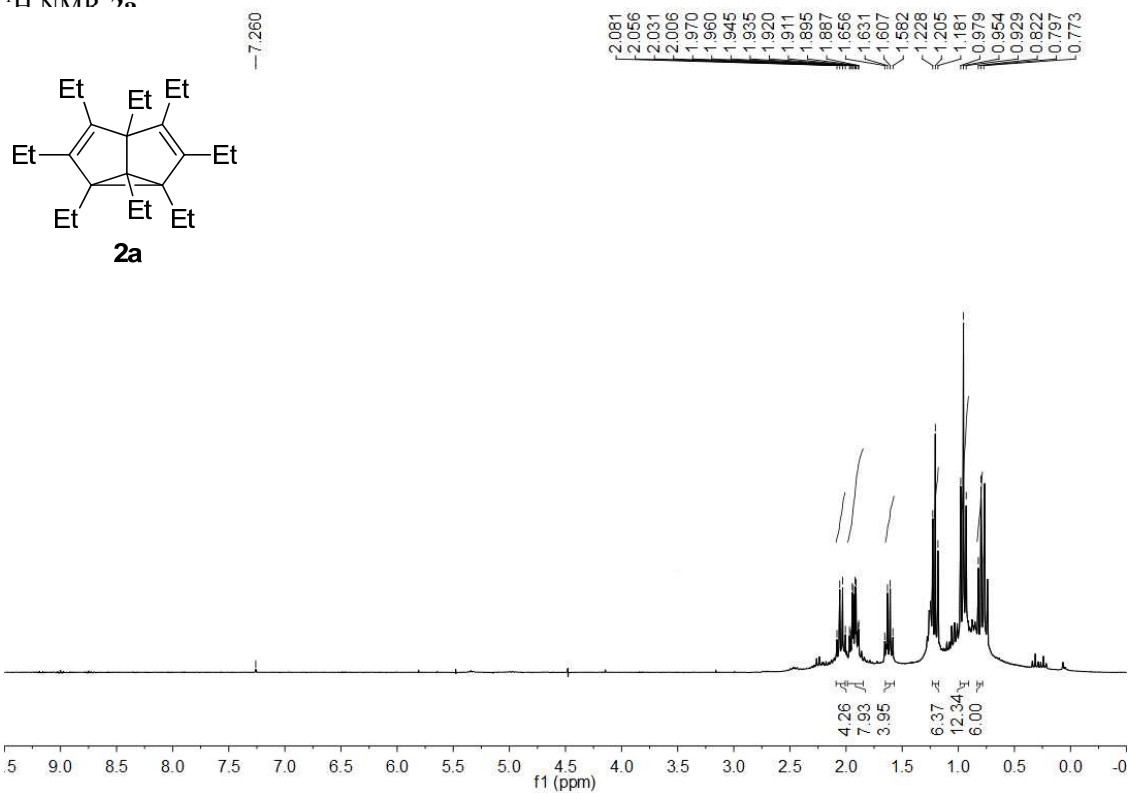
**Figure S4.** ORTEP drawing of **6a** with 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.



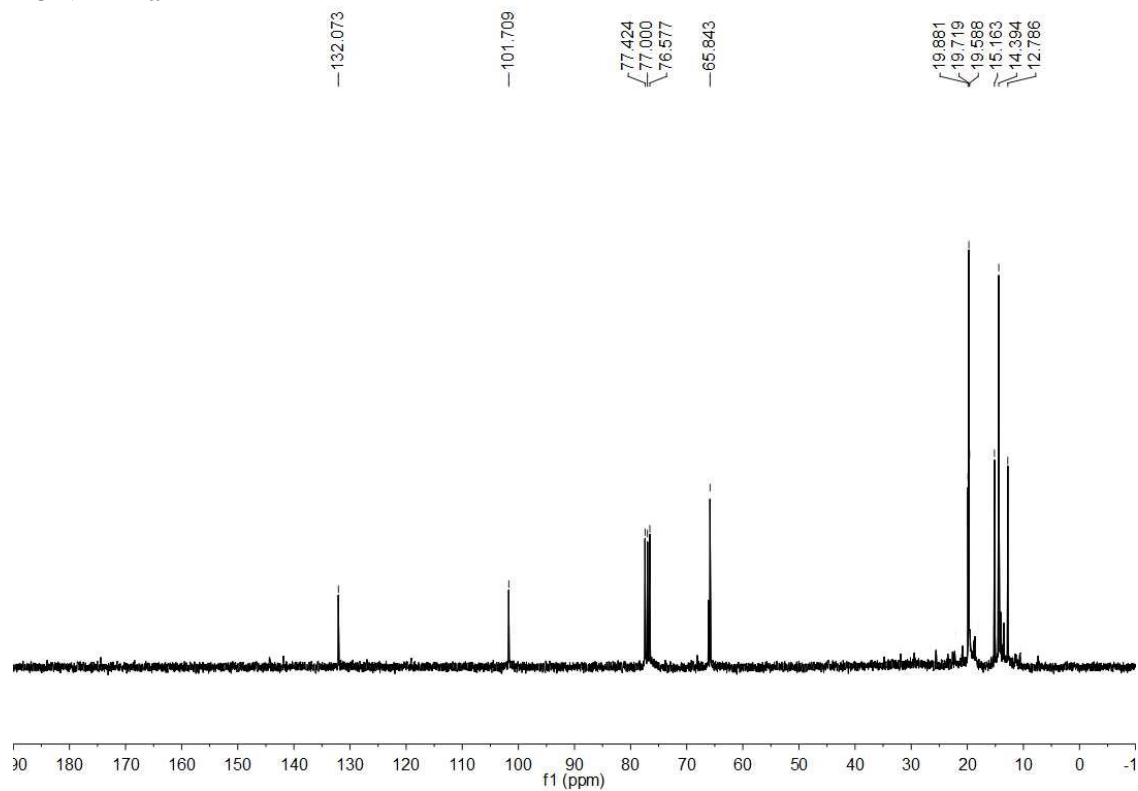
**Figure S5.** ORTEP drawing of **6b** with 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

#### 4) Scanned $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of all new compounds

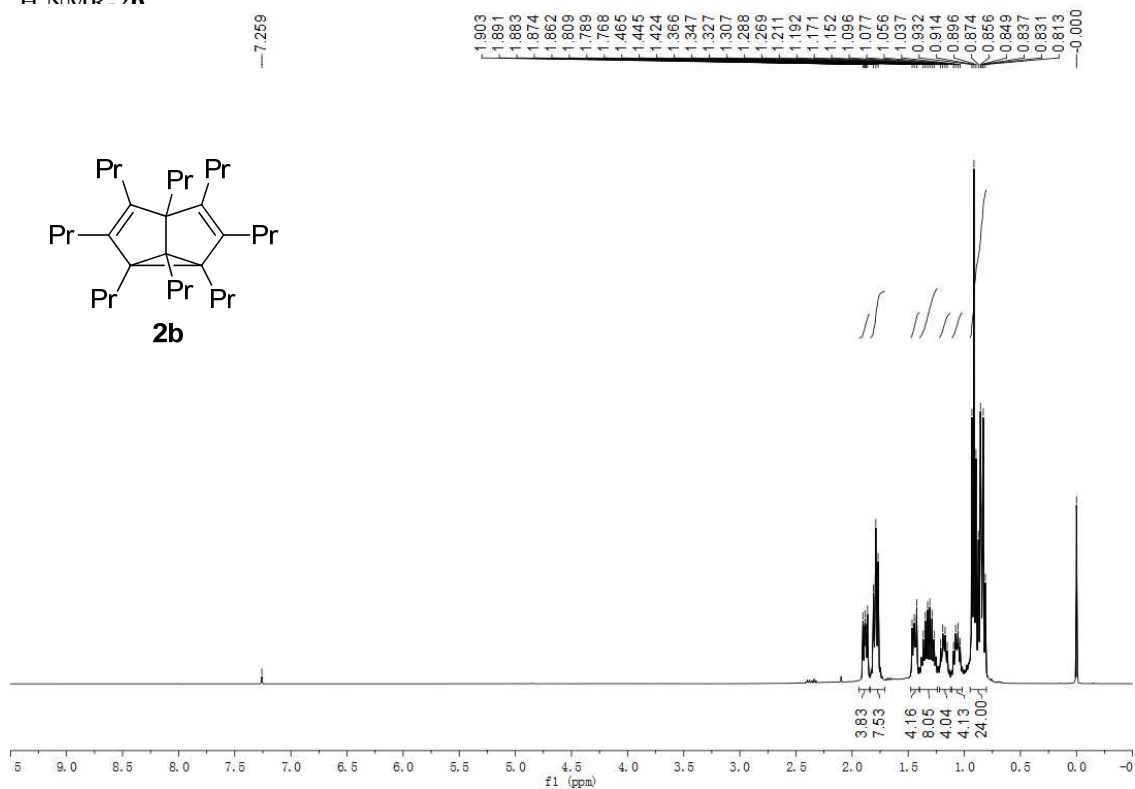
$^1\text{H}$  NMR - 2a



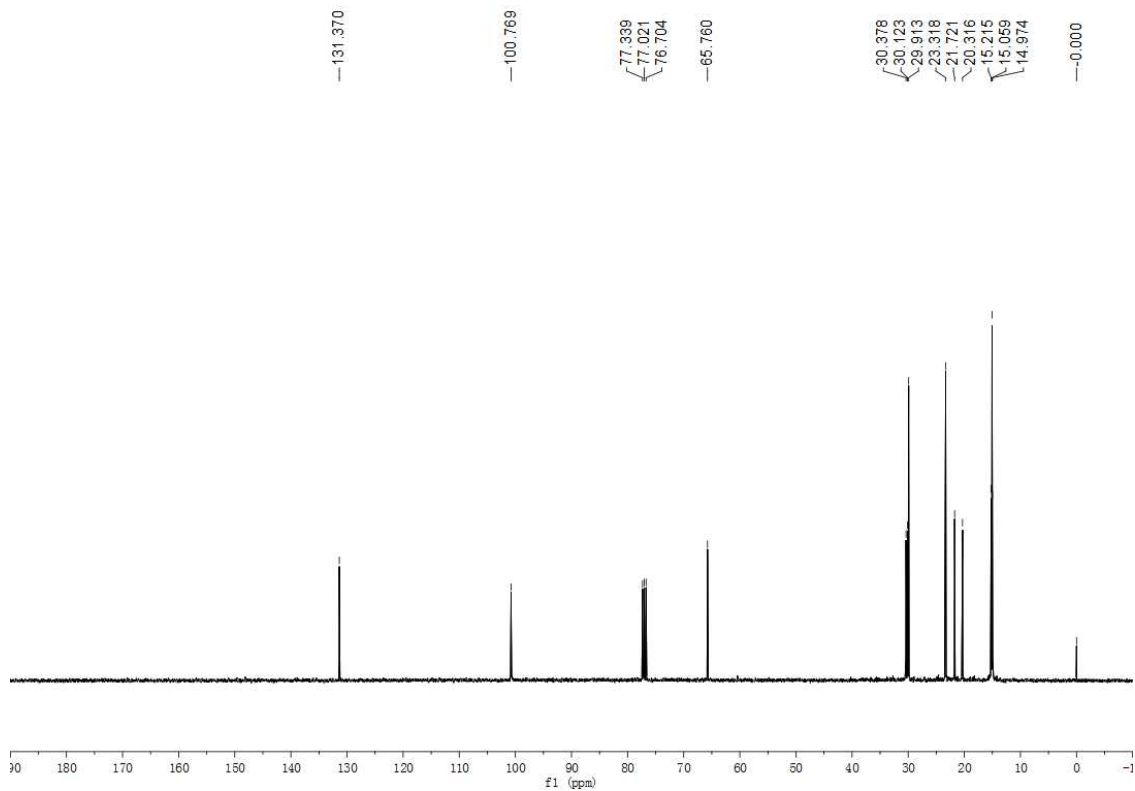
$^{13}\text{C}$  NMR - 2a



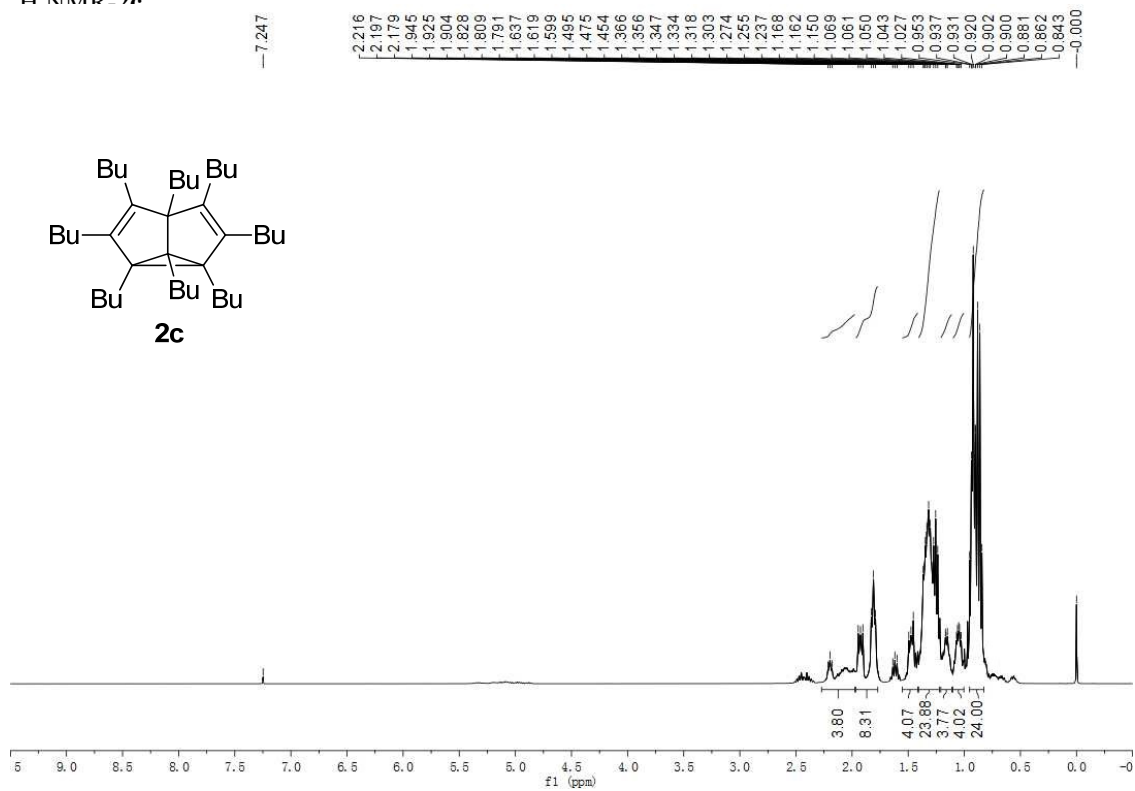
<sup>1</sup>H NMR-2b



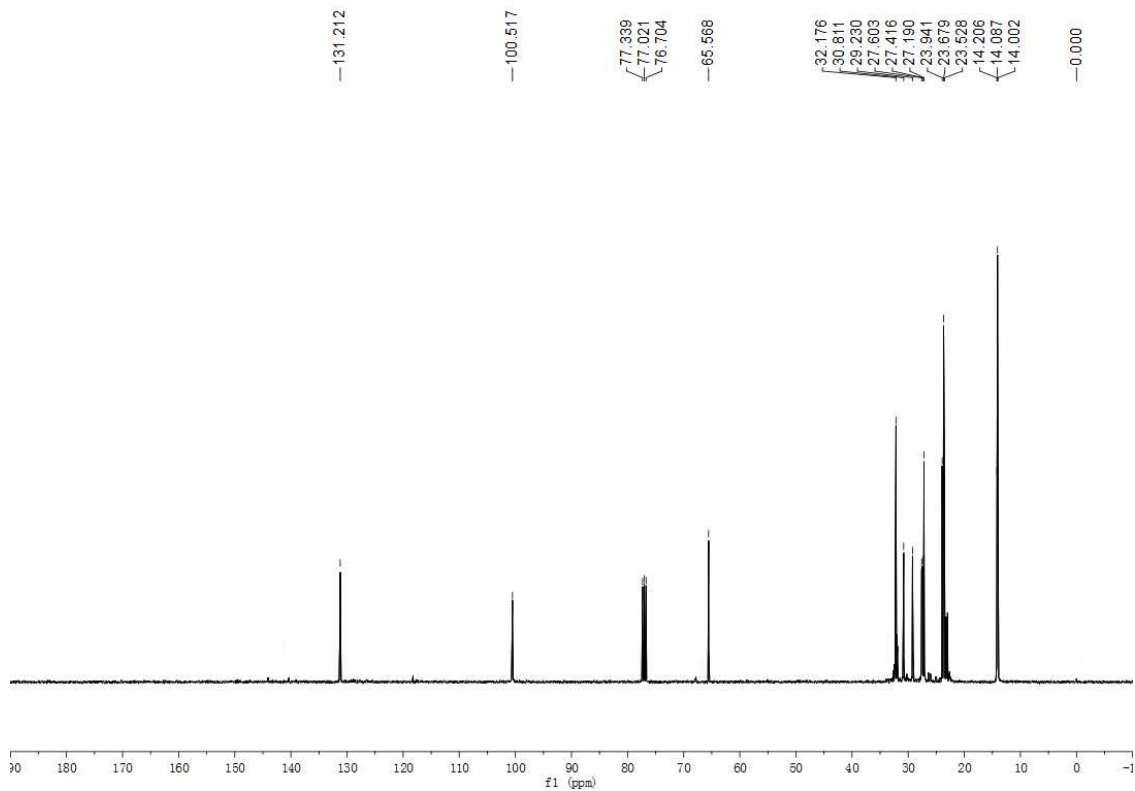
<sup>13</sup>C NMR-2b



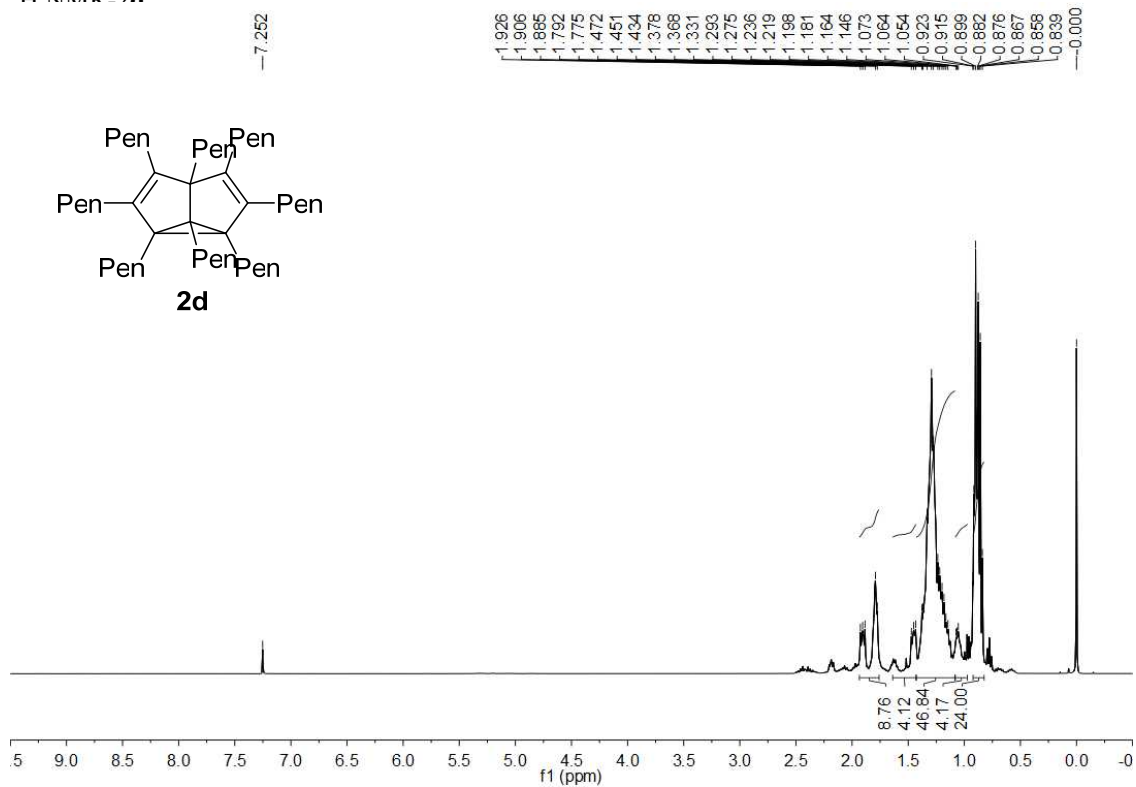
<sup>1</sup>H NMR-2c



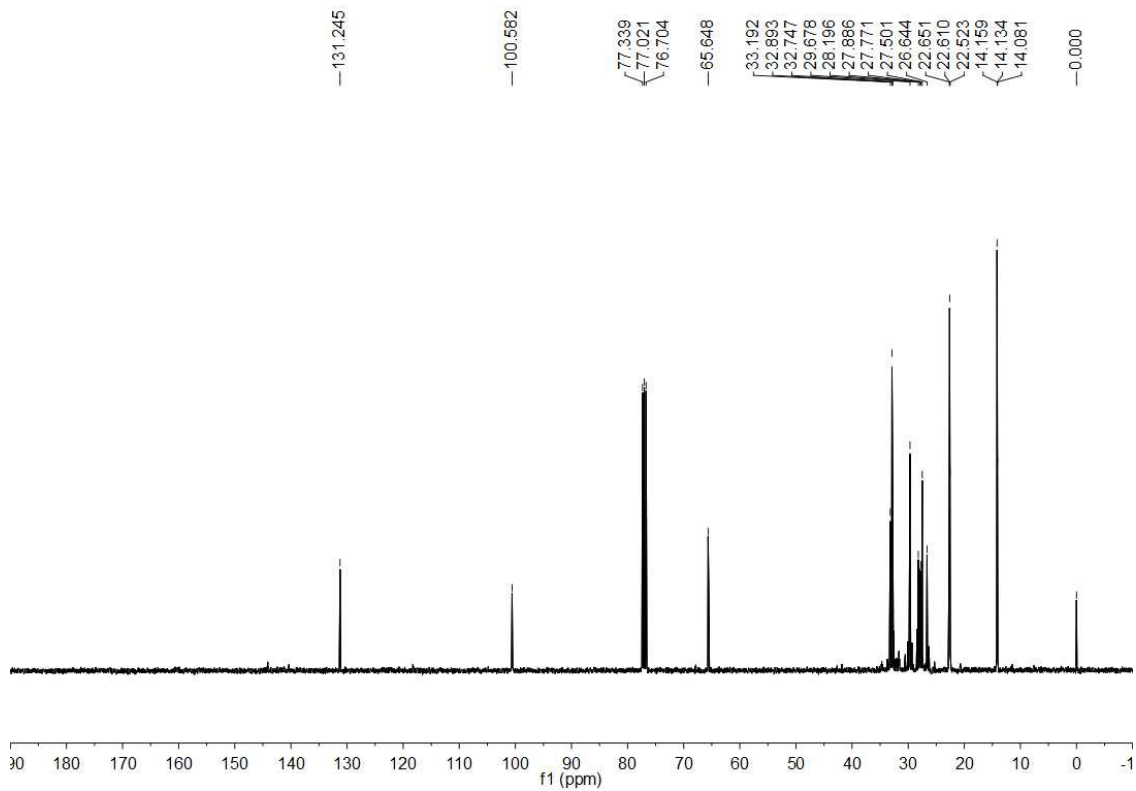
<sup>13</sup>C NMR-2c



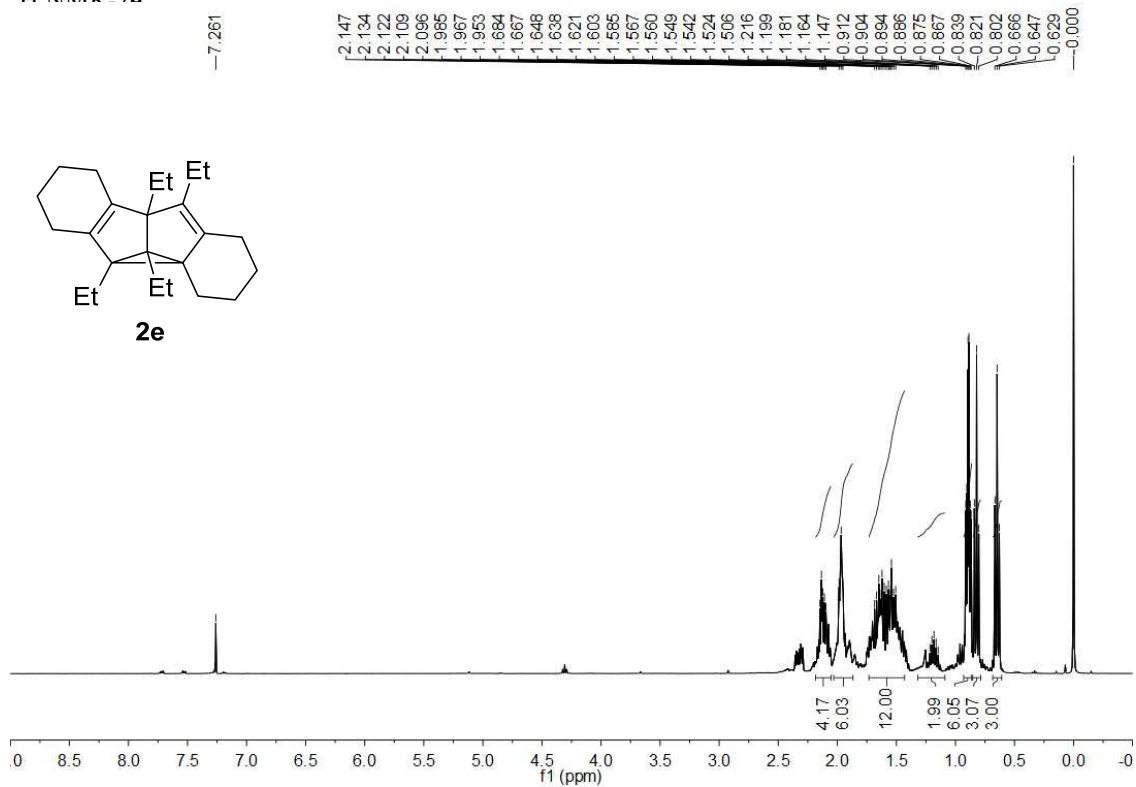
<sup>1</sup>H NMR-2d



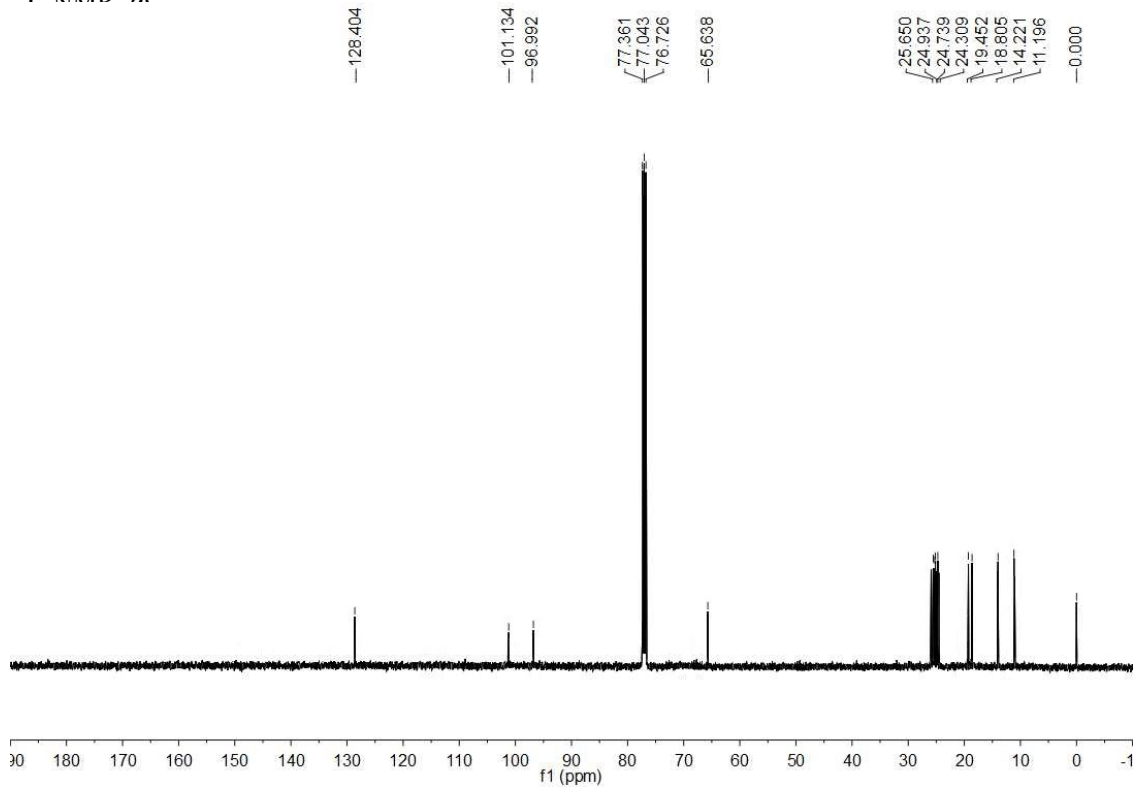
<sup>13</sup>C NMR-2d



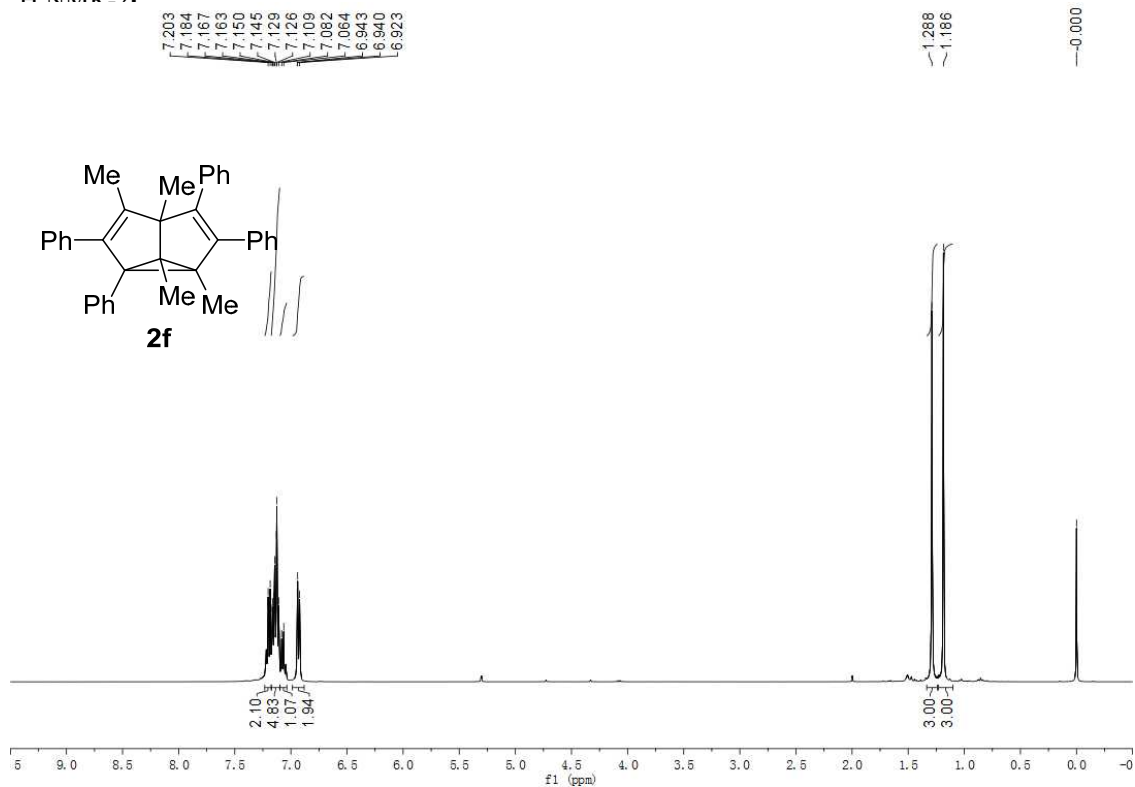
<sup>1</sup>H NMR 2e



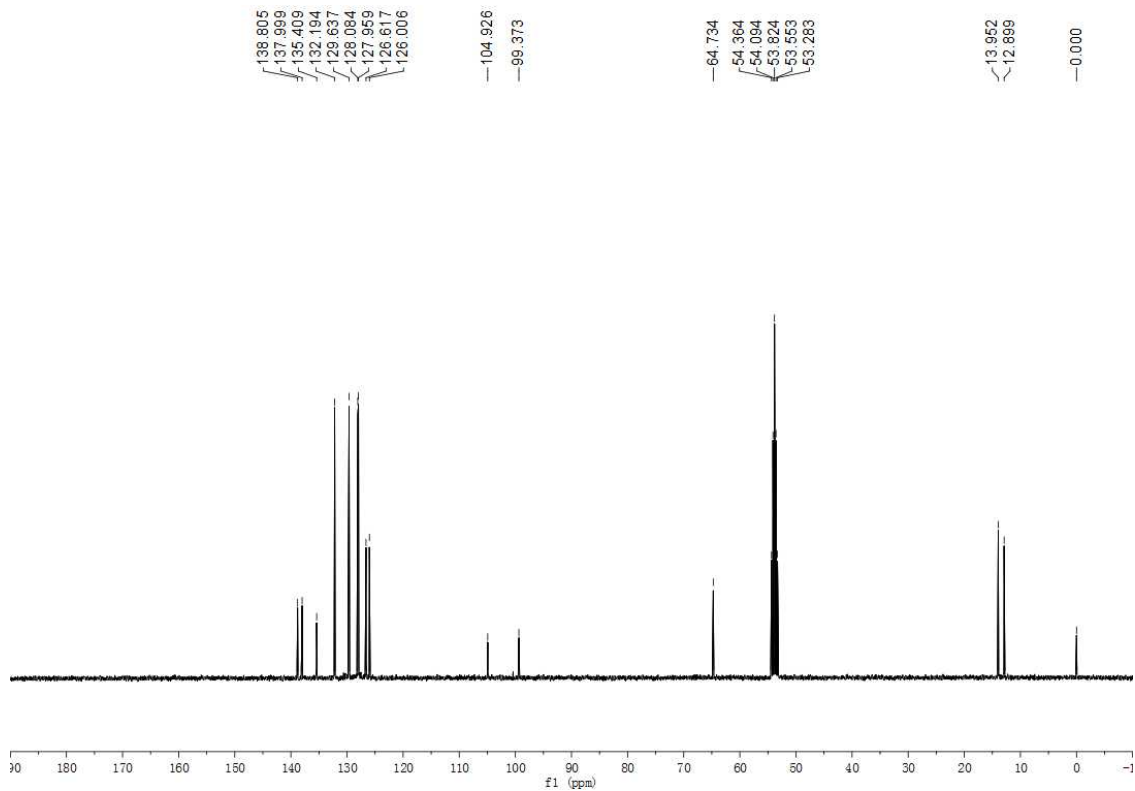
<sup>13</sup>C NMR 2e



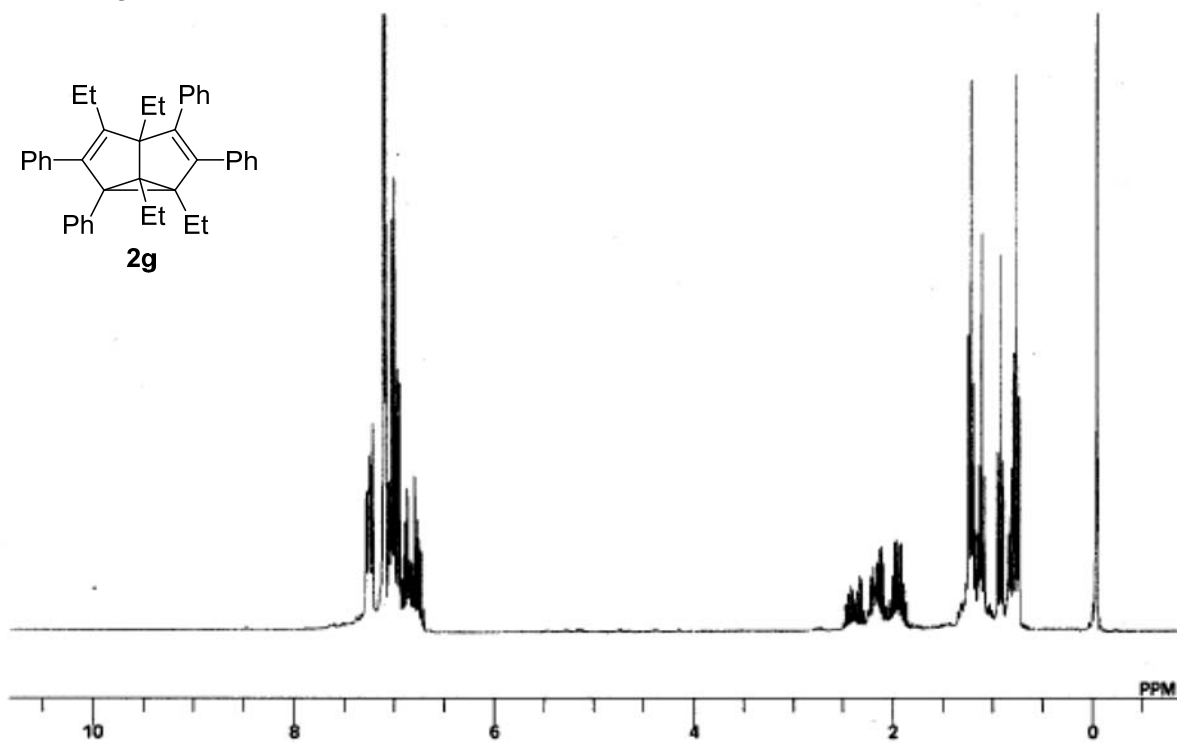
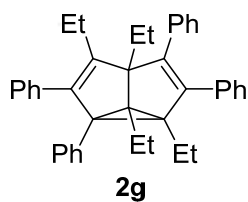
<sup>1</sup>H NMR-2f



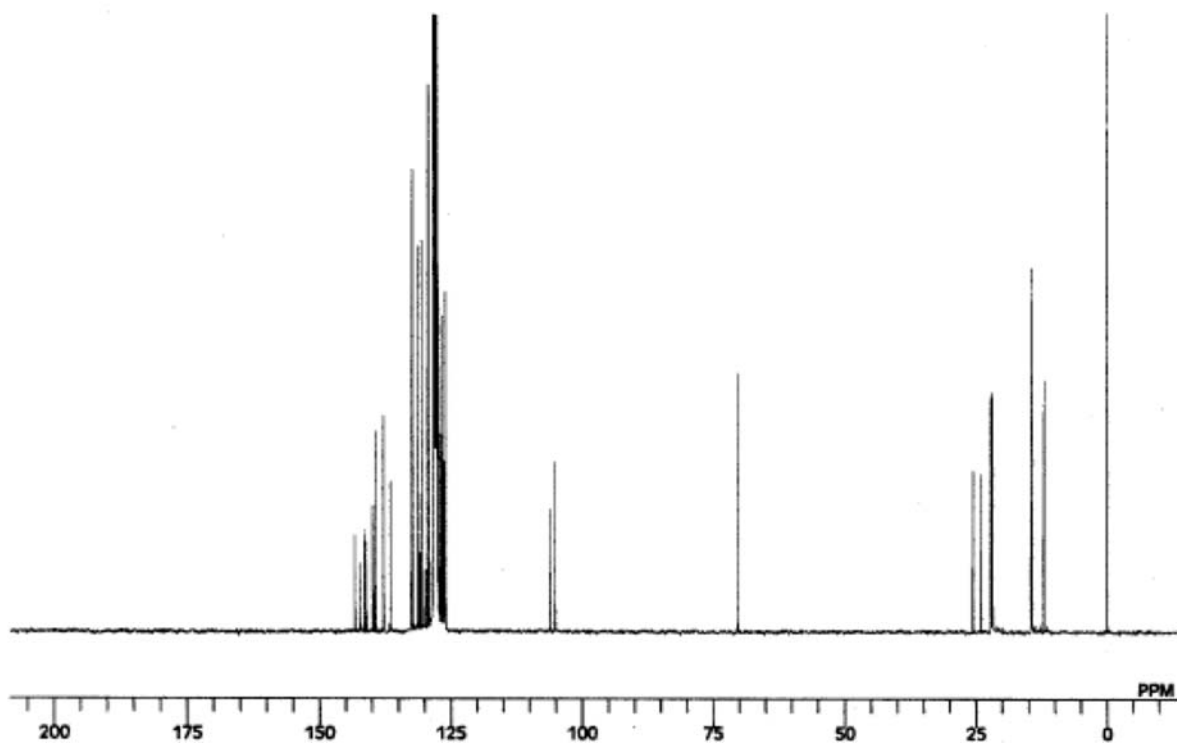
<sup>13</sup>C NMR-2f



$^1\text{H}$  NMR-2g

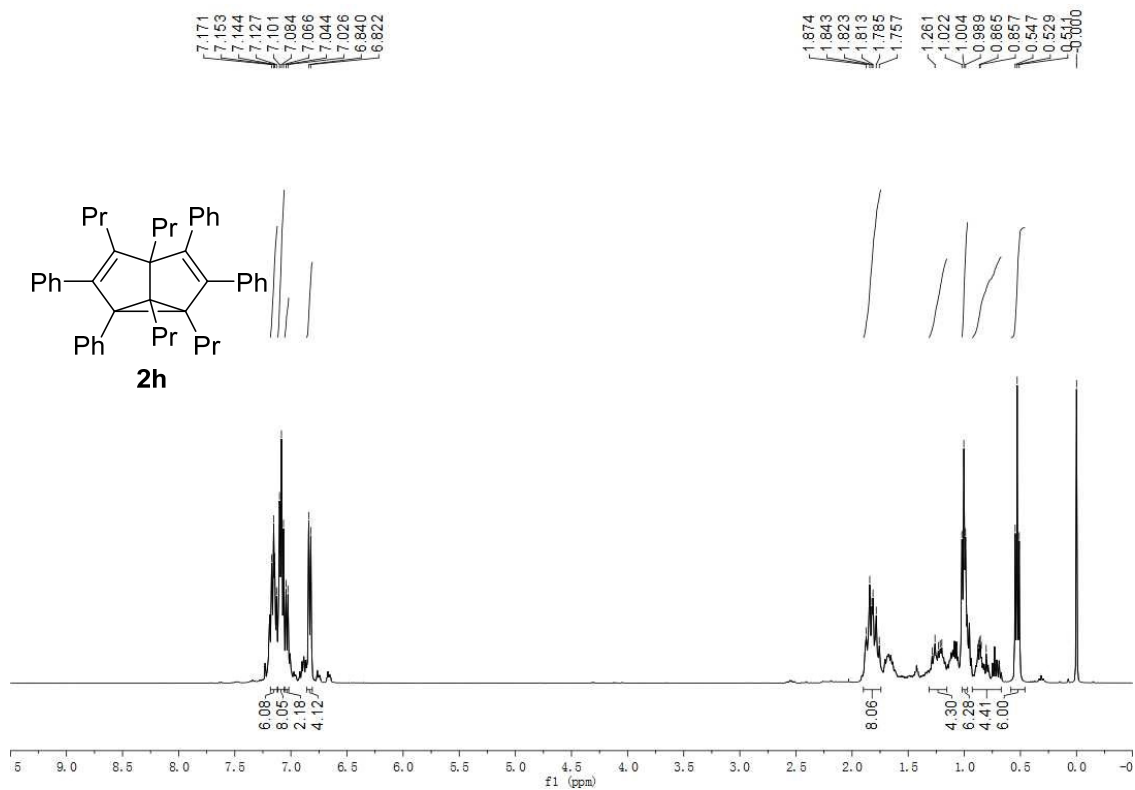


$^{13}\text{C}$  NMR- 2g

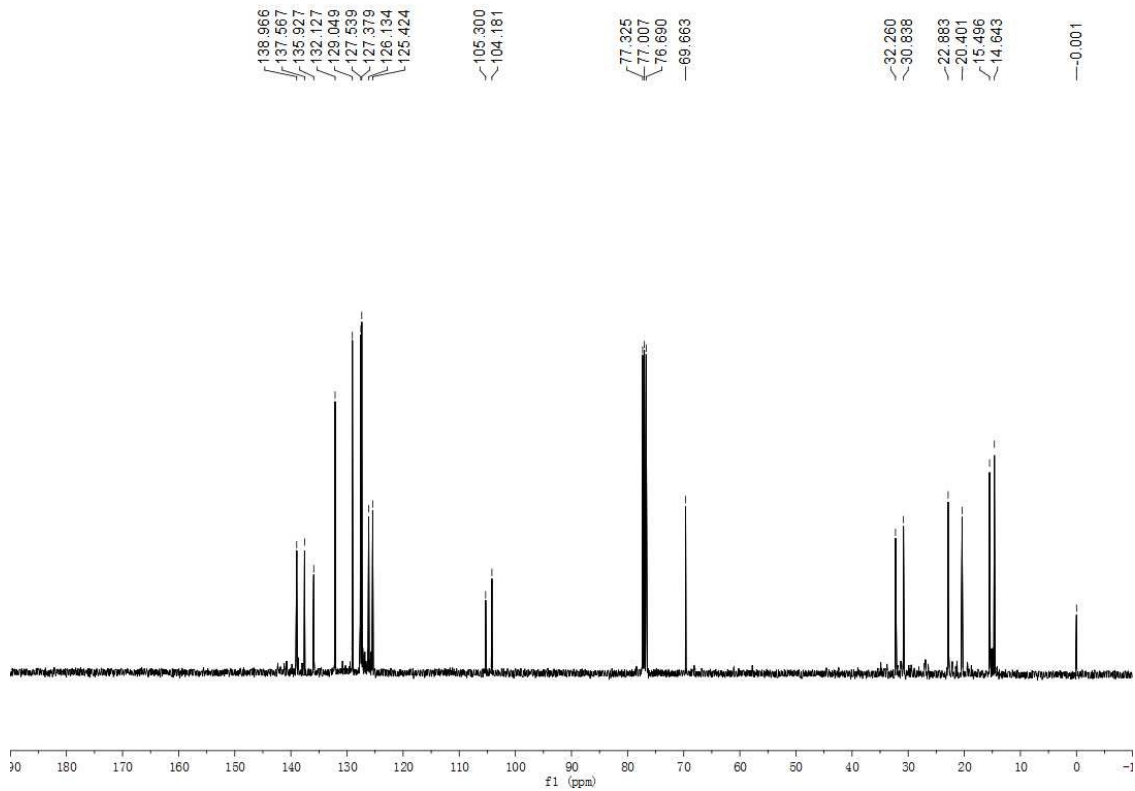




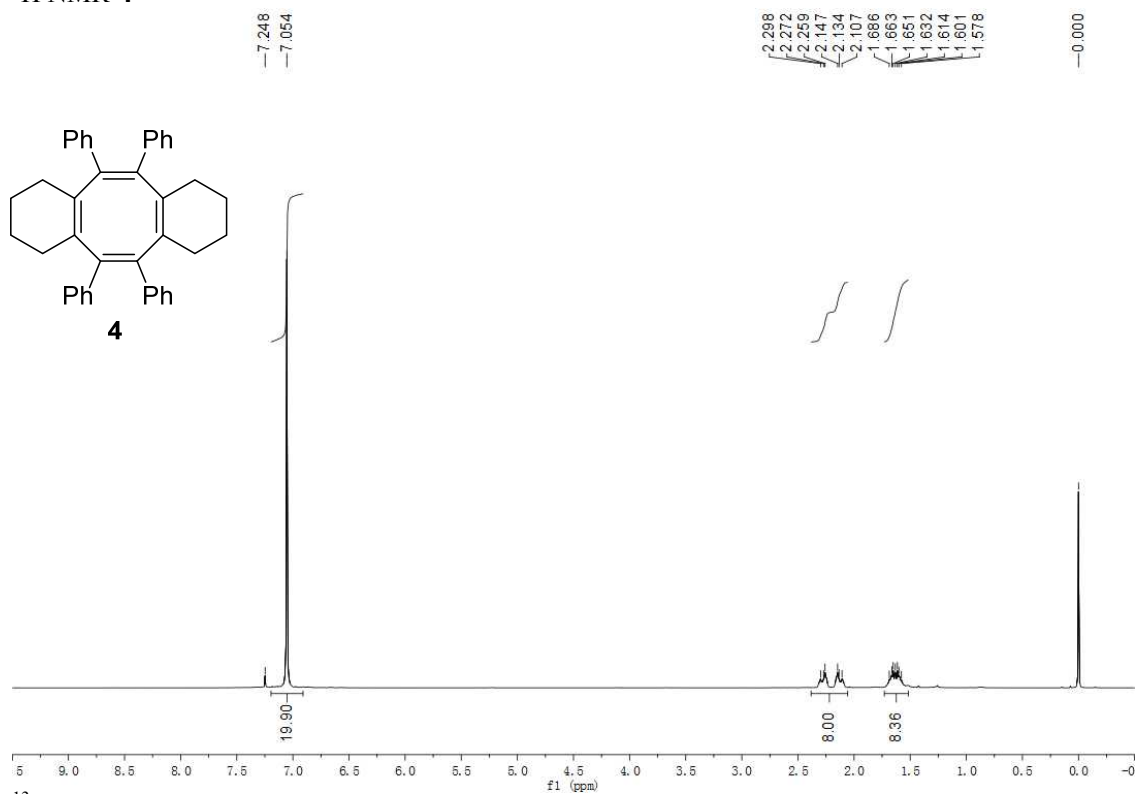
<sup>1</sup>H NMR-2h



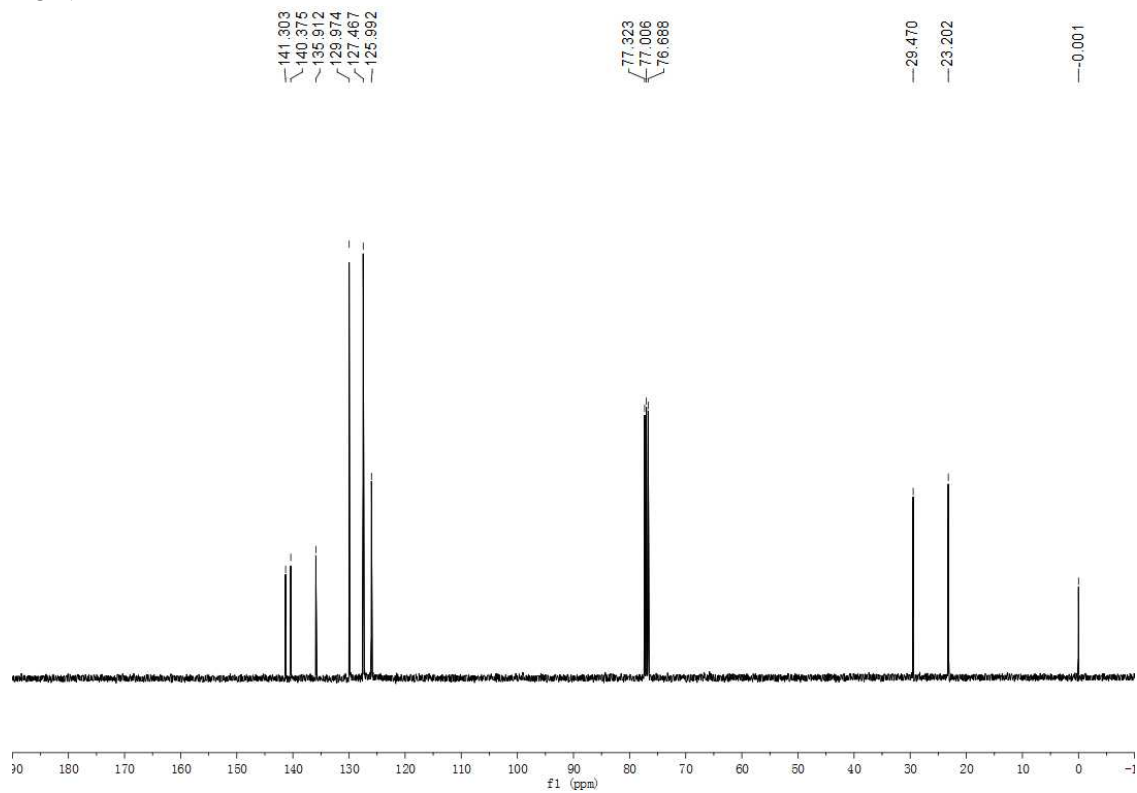
<sup>13</sup>C NMR- 2h

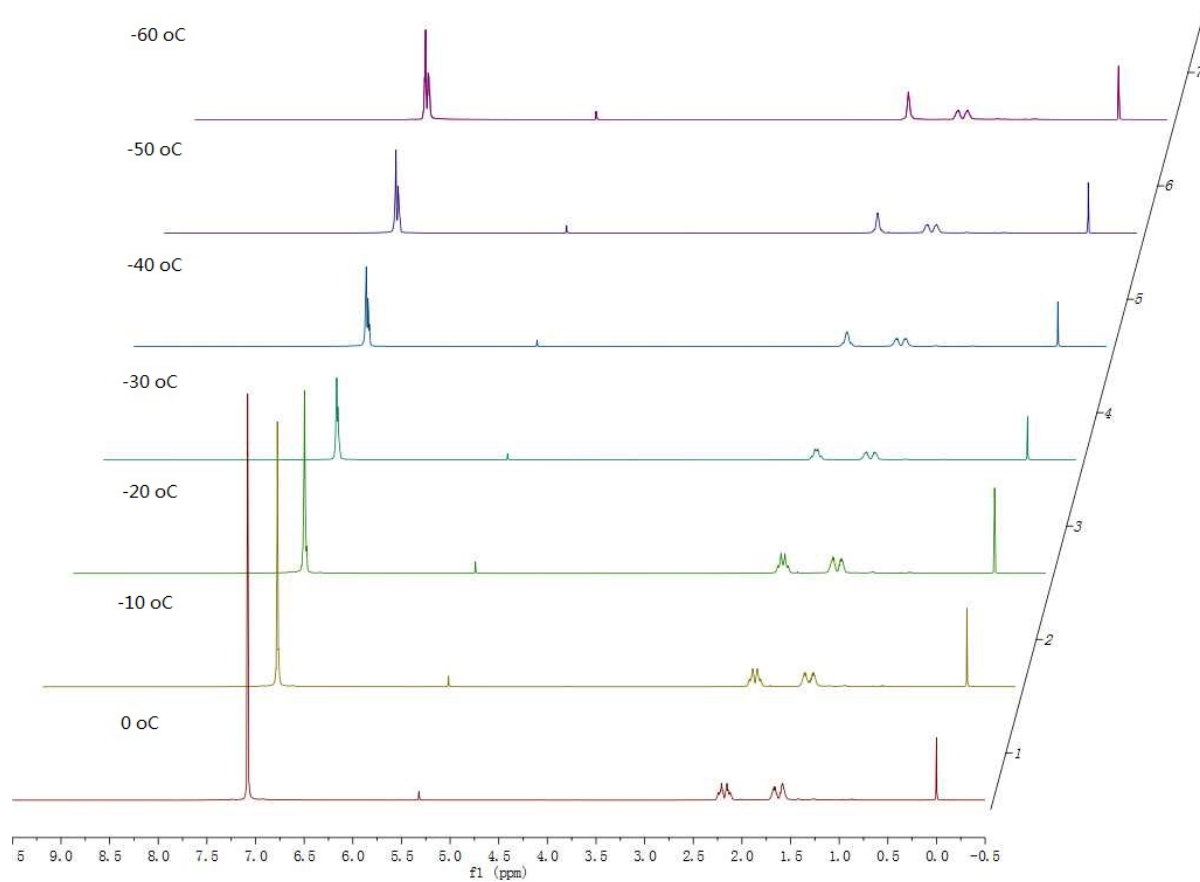


<sup>1</sup>H NMR-4



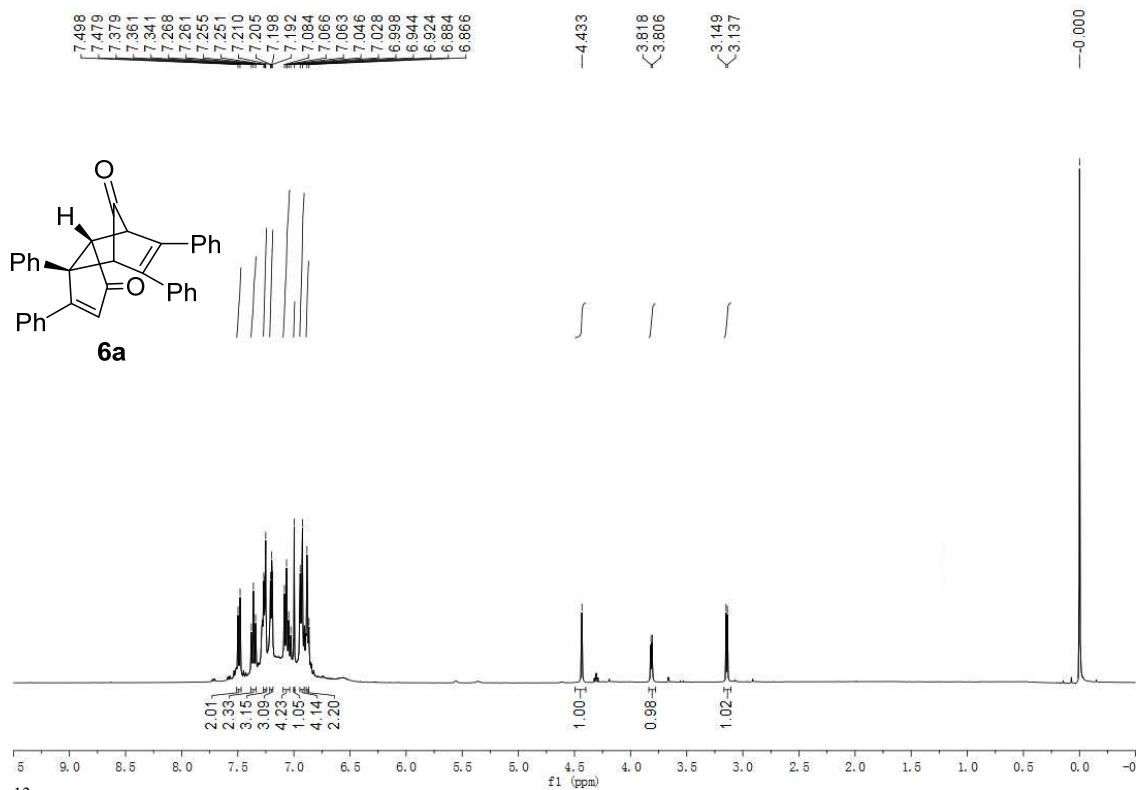
<sup>13</sup>C NMR-4



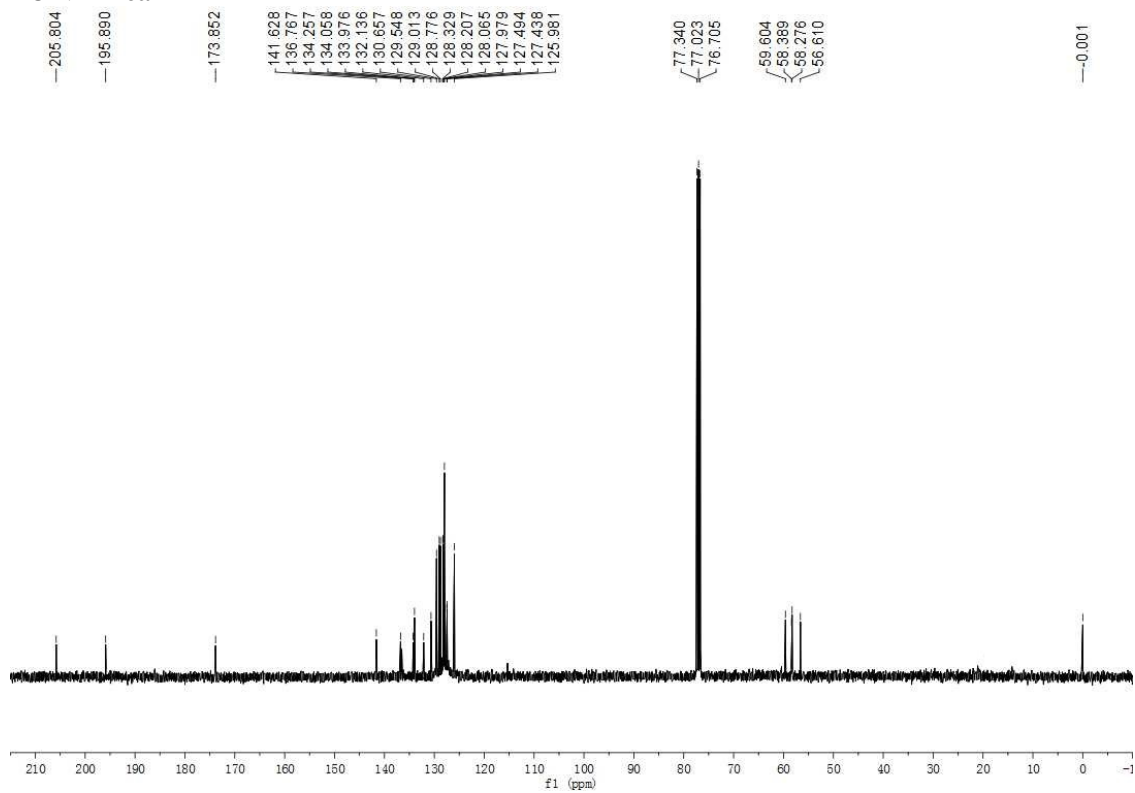


VT-NMR spectrum of compound **4** from 0 °C to -60 °C. (solvent: CD<sub>2</sub>Cl<sub>2</sub>)

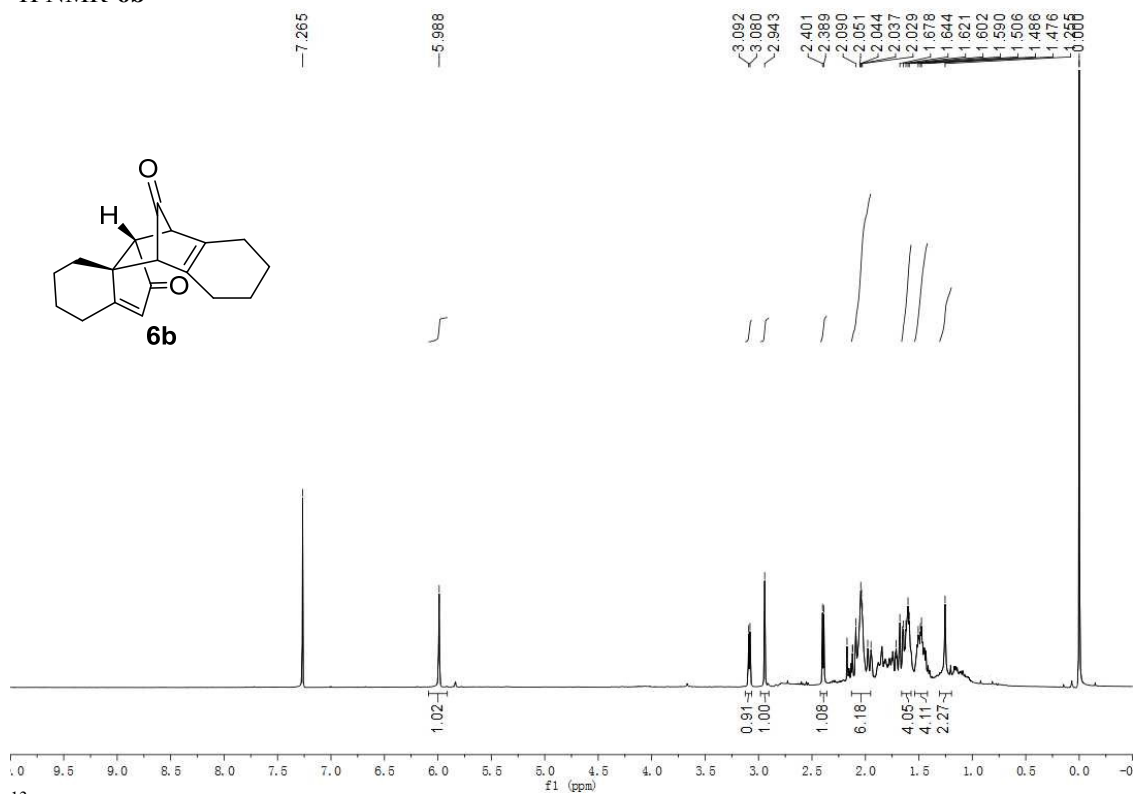
<sup>1</sup>H NMR-6a



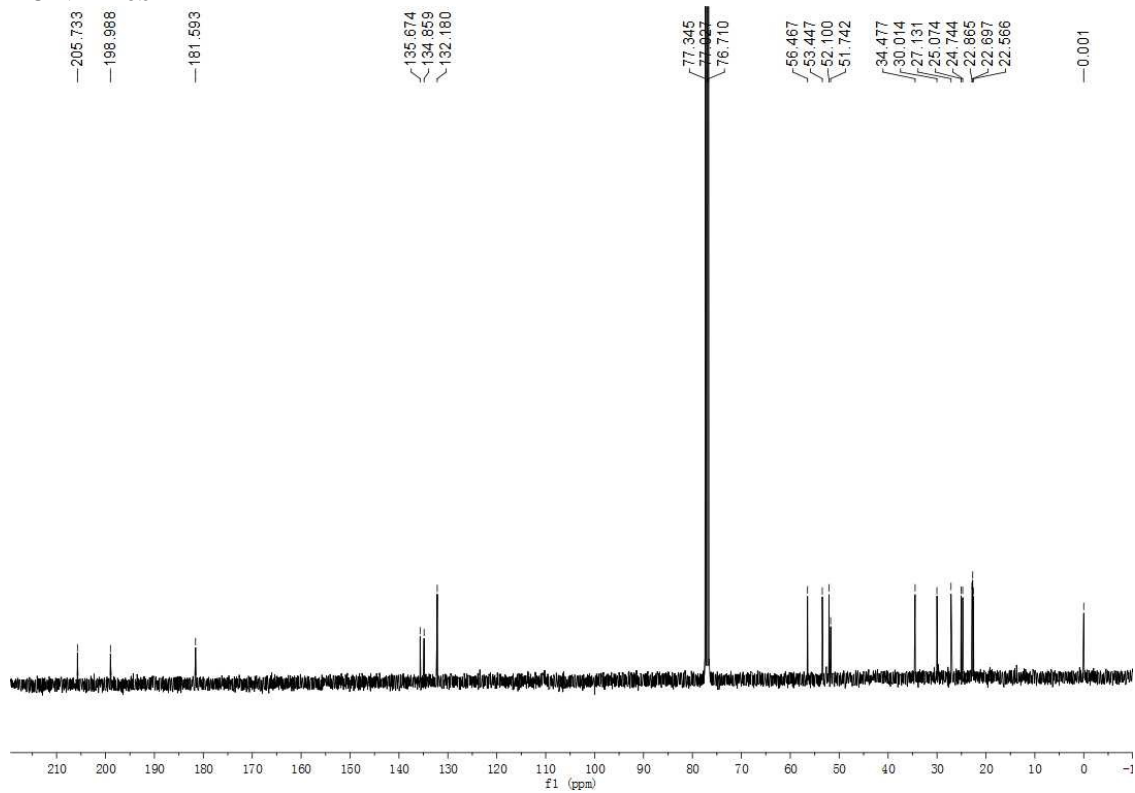
<sup>13</sup>C NMR-6a



<sup>1</sup>H NMR-6b



<sup>13</sup>C NMR-6b



## 5) References

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