

## Supporting information

### Direct Regioselective C-H Borylation of [5]Helicene

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#### Contents

<b>1. General</b>	<b>SI-2</b>
<b>2. Borylation of [5]helicene</b>	<b>SI-3</b>
<b>3. Table SI-1</b>	<b>SI-4</b>
<b>4. Table SI-2</b>	<b>SI-5</b>
<b>5. Cross-coupling reactions</b>	<b>SI-6</b>
<b>6. X-Ray</b>	<b>SI-9</b>
<b>7. References</b>	<b>SI-10</b>
<b>8. Copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra</b>	<b>SI-11</b>

## 1. General

Catalysts, reagents and solvents were obtained from commercial suppliers (Aldrich, TCI, Alfa Aesar, Strem Chemicals, Penta) and were used without further purification. Solvents for column chromatography were distilled prior to use. Argon was used as an inert gas. Silica gel 60 (0.035–0.070 mm) (Acros Organics) was used for column chromatography. TLC was performed on aluminum sheets with layer of Silica gel 60 F<sub>254</sub> purchased from MERCK. Spots on TLC plates were detected by using UV lamp ( $\lambda = 254$  nm) or basic permanganate solution. PTLC was performed on glass sheets with layer of Silica gel GF (Analtech).

NMR spectra were recorded on Varian VNMRS 300 ( $\nu(^1\text{H}) = 299.94$  MHz,  $\nu(^{13}\text{C}) = 75.43$  MHz), on Bruker Avance III (400 MHz) ( $\nu(^1\text{H}) = 400.13$  MHz,  $\nu(^{13}\text{C}) = 100.61$  MHz), or on Bruker Avance III (600 MHz) ( $\nu(^1\text{H}) = 600.17$  MHz,  $\nu(^{13}\text{C}) = 150.04$  MHz) in deuterated solvents and referenced to residual solvent peak ( $\text{CDCl}_3$   $^1\text{H}$ : 7.26 ppm,  $^{13}\text{C}$ : 77 ppm). Chemical shifts are given in  $\delta$ -scale, coupling constants  $J$  are given in Hz. Mass spectra were recorded on VG-Analytical ZAB-SEQ. All melting points are uncorrected and were determined on Kofler apparatus. HPLC separations were performed on a Gilson 321 H2 pumps with 25×250 mm preparative column (Labio, Czech Republic), filled with BIOSPHER PSI 120 C18 sorbent (7 $\mu\text{m}$  mesh).

$[\text{Ir}(\text{OH})\text{cod}]_2$  was prepared according to the reported procedure.<sup>[1]</sup>  $[\text{5}]$ Helicene **1** was prepared according to the reported procedure,<sup>[2]</sup> and recrystallized before use. Iridium complexes **C1** – **C7** were prepared according to reported procedure.<sup>[3]</sup>

## 2. Borylation of [5]helicene.

### First experiment and separation of products:

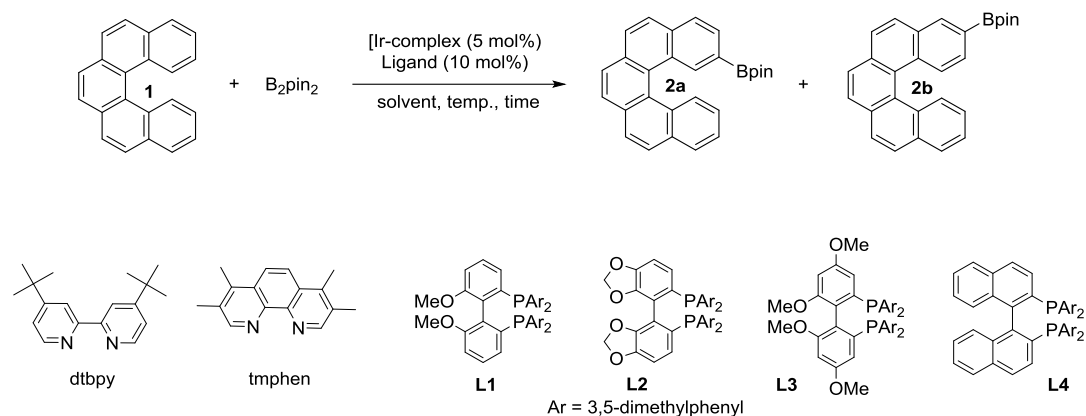
A flame dried 10 ml thick-wallet crimp reaction vial was charged with [Ir(OMe)cod]<sub>2</sub> (3.3 mg, 0.005 mmol), dtbpy (2.7 mg, 0.01 mmol), B<sub>2</sub>pin<sub>2</sub> (25 mg, 0.1 mmol), and [5]helicene (28 mg, 0.1 mmol). Then cyclohexane (0.8 mL) was added and argon was bubbled through the reaction mixture to remove O<sub>2</sub> and reduce the volume to 0.5 mL and the vessel was crimp-sealed with a septum cap under the flow of argon. Afterwards, the reaction mixture was stirred at 100 °C for 24 h. DCM (2 mL) was added and the solution was filtered through a short pad of silica gel (washed with DCM 5 mL). Volatiles were removed under reduced pressure and column chromatography of the residue (hexane/DCM from 100/0 to 0/100) afforded recovered [5]helicene (the first fraction, 22.1 mg, 79%), a mixture of **2a** and **2b** (the second fraction, 6.5 mg, 16%), and a trace of **2c** (the third fraction, ~1%). The second fraction was subsequently separated by preparative nonaqueous reversed-phase HPLC (NARP). Separation of the second fraction (MeCN) afforded 1.6 mg of **2a** (4%) and 4.8 mg of **2b** (12%).

### General procedures for the Table 1 and Table SI-1:

A flame dried 10 ml thick-wallet crimp reaction vial was charged with [Ir(OMe)cod]<sub>2</sub> (3.3 mg, 0.005 mmol) or [Ir(OH)cod]<sub>2</sub> (3.2 mg, 0.005 mmol), ligand (0.01 mmol), B<sub>2</sub>pin<sub>2</sub> (25 mg, 0.1 mmol), and [5]helicene (56 mg, 0.2 mmol). Then solvent (0.8 mL) was added and argon was bubbled through the reaction mixture to remove O<sub>2</sub> and reduce the volume to 0.5 mL and the vessel was crimp-sealed with a septum cap under the flow of argon. Afterwards, the reaction mixture was stirred and heated in an aluminum heating block at 120 °C for 24 hours. (Entry 7, microwave reactor was used). After cooling, volatiles were removed under reduced pressure, internal standard added (mesitylene) and the ratio of **2a:2b** was calculated by integration of aromatic region of <sup>1</sup>H NMR spectra of reaction mixture. Solitary singlet at δ = 9.03 ppm belongs to **2a** and solitary dd at δ = 7.64 ppm belongs to **2b**.

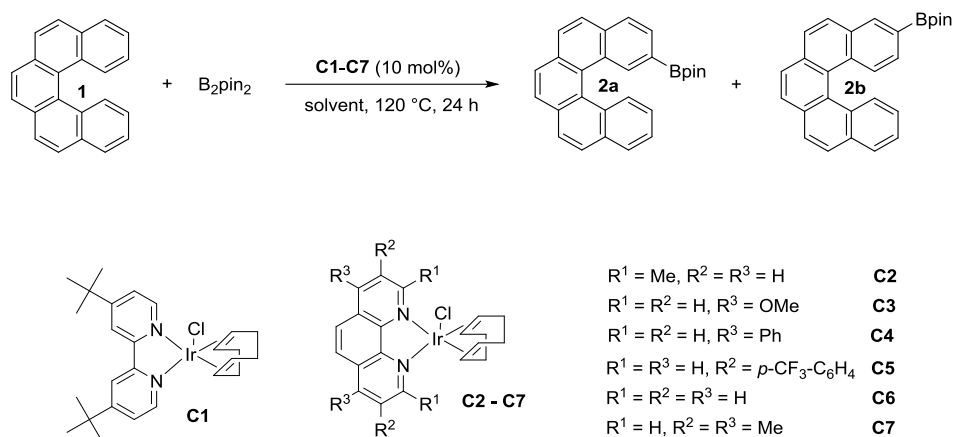
### General procedure for the Table 2 and Table SI-2:

A flame dried 10 ml thick-wallet crimp reaction vial was charged with catalyst **C** (0.01 mmol), B<sub>2</sub>pin<sub>2</sub> (25 mg, 0.1 mmol), and [5]helicene (56 mg, 0.2 mmol). Then solvent (0.8 mL) was added and argon was bubbled through the reaction mixture to remove O<sub>2</sub> and reduce the volume to 0.5 mL and the vessel was crimp-sealed with a septum cap under the flow of argon. Afterwards, the reaction mixture was stirred and heated in an aluminum heating block at 120 °C for 24 hours. After cooling, volatiles were removed under reduced pressure, internal standard added (mesitylene) and the ratio of **2a:2b** was calculated by integration of aromatic region of <sup>1</sup>H NMR spectra of reaction mixture. Solitary singlet at δ = 9.03 ppm belongs to **2a** and solitary dd at δ = 7.64 ppm belongs to **2b**.

**Table SI-1.** Ir-catalyzed borylation of **1** under various conditions.

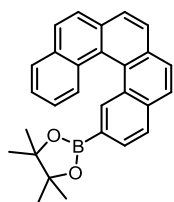
Entry	Ligand <sup>[a]</sup>	Solvent <sup>[b]</sup>	Temp. [°C]	Time [h]	Ratio <b>2a/2b</b>	Yield <b>2a + 2b</b> <sup>[c]</sup>
1	dtbpy	cyclohexane	23	16	n.d.	trace
2	dtbpy	cyclohexane	50	16	n.d.	~5
3	dtbpy	cyclohexane	80	16	n.d.	~10
4	dtbpy	cyclohexane	100	24	1/3	16
5	dtbpy	cyclohexane	120	24	1/3	26
6	dtbpy	1,4-dioxane	120	24	n.d.	0
7	dtbpy	Bu <sub>2</sub> O	120	24	1/3.6	20
8	dtbpy	EtOAc	120	24	1/3.2	19
9	dtbpy	2-Me-THF	120	24	n.d.	0
10	dtbpy	mesitylene	120	24	1/3.1	9
11	dtbpy	MTBE	120	24	1/3.5	21
12	dtbpy	MTBE	120 <sup>[d]</sup>	2	n.d.	--- <sup>[e]</sup>
13	dtbpy	octane	120	24	1/3.1	25
14	tmphen	cyclohexane	100	24	1/5	45
15	tmphen	cyclohexane	120	24	1/5	56
16	<b>L1</b>	cyclohexane	120	24	1/5	14
17	<b>L2</b>	cyclohexane	120	24	1/4.7	21
18	<b>L3</b>	cyclohexane	120	24	1/6	18
19	<b>L4</b>	cyclohexane	120	24	1/5.7	14

<sup>[a]</sup> dtbpy: 4,4'-di-tert-butyl-2,2'-dipyridyl combined with [Ir(OMe)cod]<sub>2</sub>; tmphen: 3,4,7,8-tetramethyl-1,10-phenanthroline combined with [Ir(OMe)cod]<sub>2</sub>; **L1**, **L2**, **L3** and **L4** combined with [Ir(OH)cod]<sub>2</sub>. <sup>[b]</sup> MTBE – Methyl *tert*-butyl ether. <sup>[c]</sup> Combined yield based on 1 eq. of **1**. <sup>[d]</sup> Microwave irradiation. <sup>[e]</sup> Complex mixture.

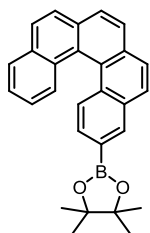
**Table SI-2.** Ir-catalyzed borylation of **1** under various conditions.

Entry	Catalyst <sup>[a]</sup>	Solvent <sup>[b]</sup>	Temp. [°C]	Time [h]	Ratio <b>2a/2b</b>	Yield <b>2a + 2b</b> <sup>[c]</sup>
1	<b>C1</b>	cyclohexane	120	24	1/5.4	60
2	<b>C2</b>	cyclohexane	120	24	1/3	66
3	<b>C3</b>	cyclohexane	120	24	1/4.3	51
4	<b>C4</b>	cyclohexane	120	24	1/3.3	49
5	<b>C5</b>	cyclohexane	120	24	1/2.3	42
6	<b>C6</b>	cyclohexane	120	24	1/6	52
7	<b>C7</b>	cyclohexane	120	24	1/8	89
8	<b>C7</b>	cyclohexane	100	24	1/8	54
9	<b>C7</b>	2-Me-THF	120	24	1/5	38
10	<b>C7</b>	mesitylene	120	24	n.d.	15
11	<b>C7</b>	Acetonitrile	120	24	n.d.	trace
12	<b>C7</b>	EtOAc	120	24	1/3.2	20
13	<b>C7</b>	1,4-dioxane	120	24	1/5	~7
14	<b>C7</b>	Bu <sub>2</sub> O	120	24	1/7	31
15	<b>C7</b>	CPME	120	24	1/8	21
16	tmphen/[Ir(Cl)cod] <sub>2</sub>	cyclohexane	120	24	1/6.4	70
17	tmphen/[Ir(cod) <sub>2</sub> ]BF <sub>4</sub>	cyclohexane	120	24	1/5	69
18	dtbpy/[Ir(Cl)cod] <sub>2</sub>	cyclohexane	120	24	1/4.7	80

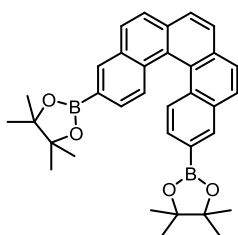
<sup>[a]</sup> dtbpy: 4,4'-di-tert-butyl-2,2'-dipyridyl; tmphen: 3,4,7,8-tetramethyl-1,10-phenanthroline. <sup>[b]</sup> CPME – Cyclopentyl methyl ether. <sup>[c]</sup> Combined yield based on 1 eq. of **1**.

**2-(Dibenzo[c,g]phenanthren-9-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a).**

A yellowish amorphous solid: m.p. 153.1 °C; <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 9.03 (s, 1H), 8.47 (d, *J* = 8.6 Hz, 1H), 7.96 – 7.92 (m, 3H), 7.91 (s, 2H), 7.89 – 7.86 (m, 4H), 7.49 (ddd, *J* = 7.9, 6.7, 0.9 Hz, 1H), 7.21 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 1.26 (d, *J* = 14.9 Hz, 12H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 136.96, 134.30, 132.64, 132.29, 132.14, 130.94, 130.88, 129.90, 128.69, 127.79, 127.65, 127.54, 127.37, 127.26, 127.21, 127.05 (2C), 126.88, 126.18, 126.04, 124.21, 83.65 (2C), 25.24 (2C), 24.14 (2C); EI-MS *m/z* (%) 404 (M<sup>+</sup>, 21), 320 (15), 303 (20), 276 (100), 138 (8); HRMS (EI<sup>+</sup>) calcd for C<sub>28</sub>H<sub>25</sub>O<sub>2</sub>B 404.1948, found 404.1951.

**2-(Dibenzo[c,g]phenanthren-8-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b).**

A colorless crystals: m.p. 201.8 °C (DCM/MeOH); <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 8.51 – 8.45 (m, 3H), 8.00 – 7.83 (m, 7H), 7.64 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.51 (ddd, *J* = 7.9, 6.8, 1.1 Hz, 1H), 7.28 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 1.42 (d, *J* = 6.3 Hz, 12H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 135.77, 132.89, 132.69, 132.56, 132.20, 131.80, 130.68, 129.33, 129.09, 128.06, 127.92, 127.77, 127.65, 127.51, 127.18 (2C), 126.79, 126.28, 126.26 (2C), 124.52, 83.96 (2C), 25.00 (2C), 24.90 (2C); EI-MS *m/z* (%) 404 (M<sup>+</sup>, 38), 302 (27), 276 (100), 138 (6); HRMS (EI<sup>+</sup>) calcd for C<sub>28</sub>H<sub>25</sub>O<sub>2</sub>B 404.1948, found 404.1945.

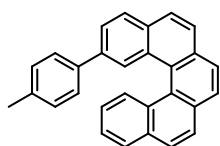
**8,13-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[c,g]phenanthrene (2c).**

A yellowish amorphous solid: m.p. 183.8 °C; <sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 8.48 – 8.42 (m, 2H), 8.42 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 8.6 Hz, 2H), 7.90 – 7.83 (m, 4H), 7.62 (dd, *J* = 8.5, 1.4 Hz, 2H), 1.42 (d, *J* = 3.4 Hz, 24H); <sup>13</sup>C NMR (75 MHz, cdcl<sub>3</sub>) δ 135.64 (2C), 132.83 (2C), 131.80 (2C), 129.48 (4C), 128.20 (2C), 127.96 (4C), 127.60 (2C), 126.17 (2C), 83.95 (4C), 24.96 (8C); +ESI-MS *m/z* (%) 553 (M + Na, 100), 531 (M + H, 30); HRMS (+ESI) calcd for C<sub>34</sub>H<sub>37</sub>O<sub>4</sub>B<sub>2</sub> 531.28725, found 531.28726.

### 5. Cross-coupling reactions of **2a** or **2b** with aryl iodides.

To a solution of **2a** or **2b** (20.2 mg, 0.05 mmol) in toluene/H<sub>2</sub>O (10/1, 1.5 mL) was added XPhos-Pd-G3 (2.2 mg, 5 mol%), K<sub>3</sub>PO<sub>4</sub> (21.3 mg, 200 mol%) and an aryl iodide (0.065 mmol) and the reaction mixture was stirred at 23 °C for 16h. All volatiles were evaporated, the residue redissolved in DCM and separated by preparative TLC (hexane/DCM 10:1) to give the corresponding product **3** or **4**.

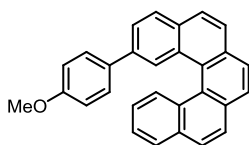
#### 9-(p-Tolyl)dibenzo[*c,g*]phenanthrene (**3a**). Yield 16.4 mg (89%); a yellowish amorphous



solid: m.p. 215.6 °C; <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 8.78 (s, 1H), 8.71 (d, *J* = 8.5 Hz, 1H), 7.97 – 8.02 (m, 2H), 7.93 (dd, *J* = 8.5, 3.3 Hz, 2H), 7.89 – 7.84 (m, 4H), 7.77 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.33 – 7.37 (m, 3H), 7.13 (d, *J* = 8.2 Hz, 2H), 2.33 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 138.13, 136.87 (2C), 132.72, 132.52, 132.27, 131.62,

131.01, 130.89, 129.36 (2C), 128.82, 128.32, 128.06, 127.46, 127.28 (2C), 127.15 (2C), 127.07 (2C), 126.97, 126.40, 126.23, 126.16, 125.48, 124.61, 21.02; EI-MS *m/z* (%) 368 (M<sup>+</sup>, 100), 350 (23), 337 (13), 276 (89), 263 (14); HRMS (EI<sup>+</sup>) calcd for C<sub>29</sub>H<sub>20</sub> 368.1565, found 368.1567.

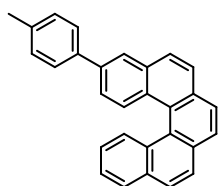
#### 9-(4-Methoxyphenyl)dibenzo[*c,g*]phenanthrene (**3b**). Yield 17.7 mg (92%); a yellowish



amorphous solid: m.p. 176.2 °C; <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 8.74 (d, *J* = 1.0 Hz, 1H), 8.71 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.98 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.89 – 7.84 (m, 4H), 7.74 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.57 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 7.38 (dm, *J* = 8.7 Hz, 2H), 7.35 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H),

6.85 (dm, *J* = 8.7 Hz, 2H), 3.80 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 159.05, 136.55, 133.61, 132.72, 132.54, 132.26, 131.40, 131.03, 130.87, 128.84, 128.33, 128.26 (2C), 128.09, 127.44, 127.29, 127.28, 127.16, 127.12, 127.06, 126.66, 126.44, 126.16, 126.10, 125.31, 124.56, 114.09, 55.29; EI-MS *m/z* (%) 384 (M<sup>+</sup>, 100), 351 (12), 337 (17), 276 (95); HRMS (EI<sup>+</sup>) calcd for C<sub>29</sub>H<sub>20</sub>O 384.1514, found 368.1512.

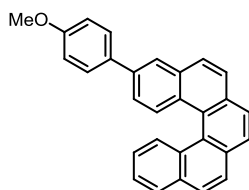
#### 8-(p-Tolyl)dibenzo[*c,g*]phenanthrene (**4a**). Yield 16.6 mg (90%); a colorless crystals: m.p.



198.8 °C (DCM/MeOH); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.60 (dt, *J* = 8.4, 1.0 Hz, 1H), 8.57 (dd, *J* = 8.8, 0.8 Hz, 1H), 8.16 (d, *J* = 2.0 Hz, 1H), 8.03 – 7.85 (m, 7H), 7.70 (dm, *J* = 8.2 Hz, 2H), 7.61 – 7.50 (m, 2H), 7.39 – 7.28 (m, 3H), 2.45 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.59, 137.68, 137.26, 132.99, 132.60, 132.32, 132.24, 130.79, 129.80, 129.61

(2C), 129.43, 129.02, 127.81, 127.69, 127.48, 127.23, 127.14, 127.03 (2C), 126.98, 126.96, 126.70, 126.35, 126.25, 125.17, 124.40, 123.49, 21.15; EI-MS *m/z* (%) 368 (M<sup>+</sup>, 100), 350 (24), 337 (20), 276 (41), 263 (30); HRMS (EI<sup>+</sup>) calcd for C<sub>29</sub>H<sub>20</sub> 368.1565, found 368.1563.

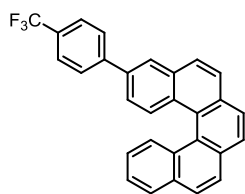
#### 8-(4-Methoxyphenyl)dibenzo[*c,g*]phenanthrene (**4b**). Yield 18.1 mg (94%); a yellowish



crystals: m.p. 216.8 °C (DCM/MeOH); <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 8.5 Hz, 1H), 8.54 (d, *J* = 8.8 Hz, 1H), 8.11 (d, *J* = 2.0 Hz, 1H), 8.00 – 7.85 (m, 7H), 7.73 (dm, *J* = 8.7 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.30 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.04 (dm, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 159.33, 138.27, 133.10, 133.04, 132.60, 132.33, 132.19, 130.80, 129.58, 129.45, 129.01, 128.24 (2C), 127.82, 127.66, 127.48, 127.25, 127.09,

126.98, 126.96, 126.72, 126.36, 126.25, 124.79, 124.40, 123.32, 114.35 (2C), 55.39; EI-MS  $m/z$  (%) 384 ( $M^+$ , 100), 351 (23), 337 (25), 276 (45), 263 (26); HRMS (EI+) calcd for  $C_{29}H_{20}O$  384.1514, found 368.1510.

**8-(4-(Trifluoromethyl)phenyl)dibenzo[c,g]phenanthrene (4c).** Yield 18.2 mg (86%); a



yellowish amorphous solid: m.p. 210.5 °C;  $^1H$  NMR (600 MHz, Chloroform-*d*)  $\delta$  8.59 (d,  $J = 8.8$  Hz, 1H), 8.55 (d,  $J = 8.5$  Hz, 1H), 8.16 (d,  $J = 2.0$  Hz, 1H), 8.00 – 7.84 (m, 9H), 7.75 (d,  $J = 8.1$  Hz, 2H), 7.55 (ddd,  $J = 8.0, 6.8, 1.2$  Hz, 1H), 7.51 (dd,  $J = 8.8, 2.0$  Hz, 1H), 7.31 (ddd,  $J = 8.4, 6.8, 1.4$  Hz, 1H);  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  144.11, 137.05, 132.86, 132.68, 132.52, 132.40, 130.69, 130.50, 129.75, 129.45 (q,  $J = 33$  Hz), 128.94, 127.92, 127.65, 127.59, 127.55, 127.44 (2C), 127.22, 127.11, 126.98, 126.80, 126.37, 126.34, 126.03, 125.79 (q,  $J = 3.8$  Hz), 124.49, 124.33 (q,  $J = 270$  Hz), 123.24; APCI-MS  $m/z$  (%) 423 ( $M + H$ , 100); HRMS (APCI) calcd for  $C_{29}H_{18}F_3$  423.13551, found 423.13562.



## 6. X-ray data.

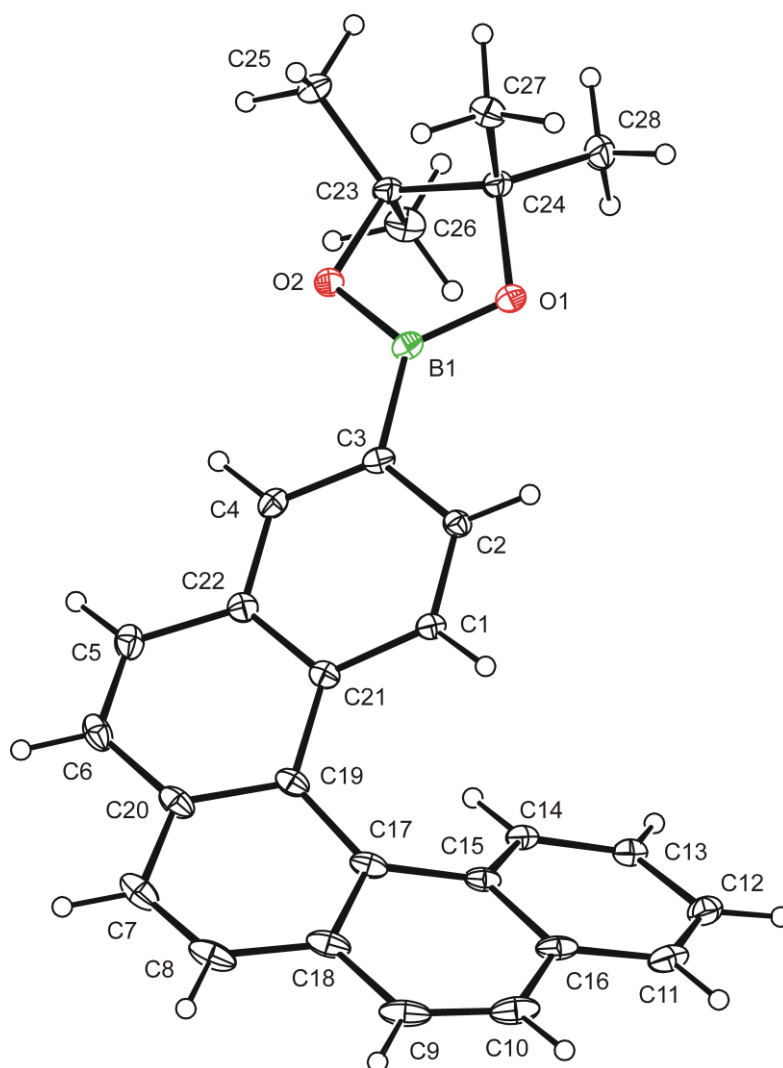
Crystallographic data for **2b** compound were collected on Bruker D8 VENTURE Kappa Duo PHOTON100 by  $I\mu S$  with Mo  $K\alpha$  0.71073 Å at a temperature of 120(2) K. The absorption corrections were carried on using multi-scan procedure.

The structures were solved by direct methods (XP)<sup>[4]</sup> and refined by full matrix least squares based on  $F^2$  (SHELXL2014).<sup>[5]</sup> The hydrogen atoms on carbons were fixed into idealised positions (riding model) and assigned temperature factors either  $H_{iso}(H) = 1.2 U_{eq}(\text{pivot atom})$  or  $H_{iso}(H) = 1.5 U_{eq}$  for methyl moiety. The crystal was refined as non-merohedral twin. Ration of twin parts : 0.53:0.47.

Single crystals of **2b** suitable for X-ray analysis were grown *via* methanol diffusion into a concentrated  $\text{CH}_2\text{Cl}_2$  solution of **2b**.

Crystal data for **2b**:  $\text{C}_{28}\text{H}_{25}\text{BO}_2$ ,  $M_r = 404.29$ ; Triclinic,  $P -1$  (No 2),  $a = 8.0397$  (5) Å,  $b = 9.6270$  (6) Å,  $c = 14.3024$  (8) Å,  $\alpha = 81.219$  (2)°,  $\beta = 79.289$  (2)°,  $\gamma = 86.038$  (2)°,  $V = 1074.00$  (11) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.250$  Mg m<sup>-3</sup>, colourless prism of dimensions 0.54 × 0.20 × 0.18 mm, multi-scans absorption correction ( $\mu = 0.08$  mm<sup>-1</sup>)  $T_{\min} = 0.94$ ,  $T_{\max} = 0.99$ ; a total of 25588 measured reflections ( $\theta_{\max} = 27.5^\circ$ ), from which 4946 were unique ( $R_{\text{int}} = 0.045$ ) and 4261 observed according to the  $I > 2\sigma(I)$  criterion. The refinement converged ( $\Delta/\sigma_{\max} = 0.001$ ) to  $R = 0.042$  for observed reflections and  $wR(F^2) = 0.105$ ,  $GOF = 1.06$  for 285 parameters and all 4946 reflections. The final difference map displayed no peaks of chemical significance ( $\Delta\rho_{\max} = 0.25$ ,  $\Delta\rho_{\min} -0.21$  e.Å<sup>-3</sup>).

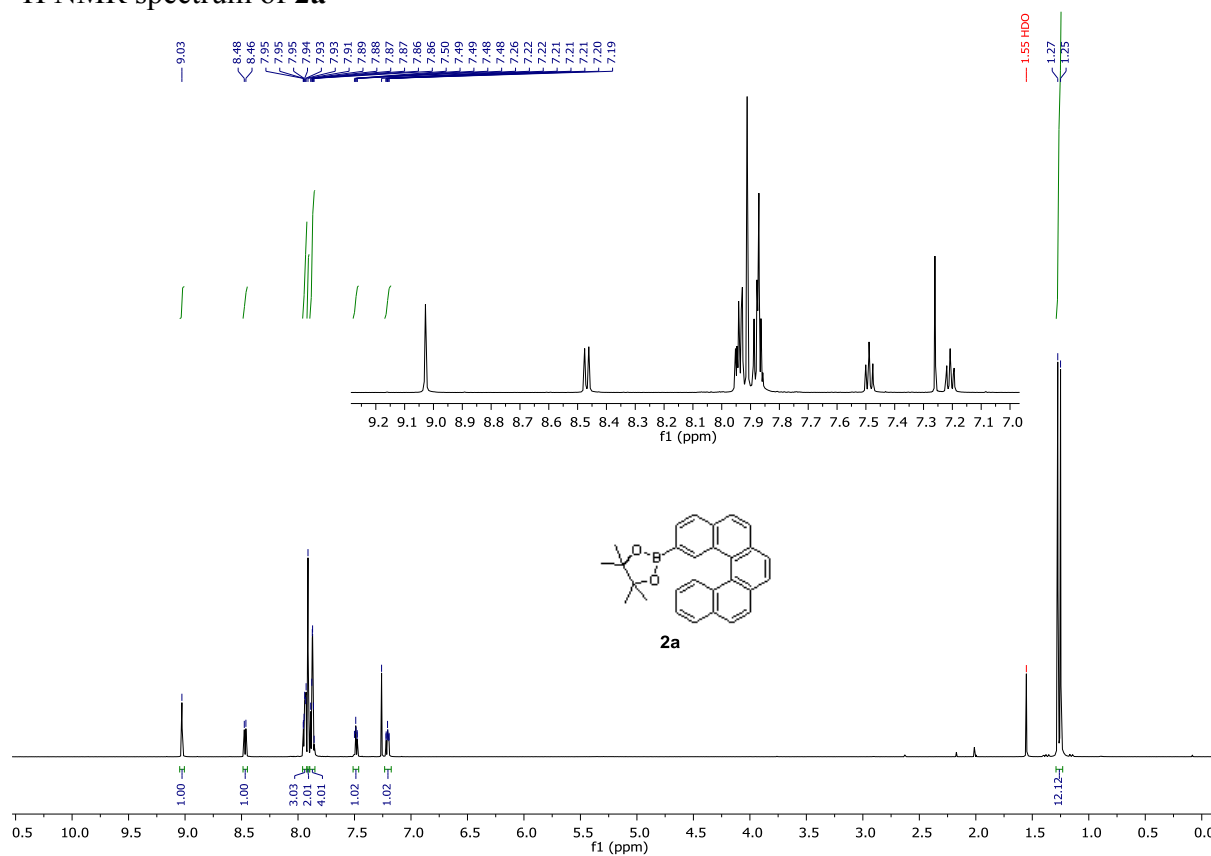
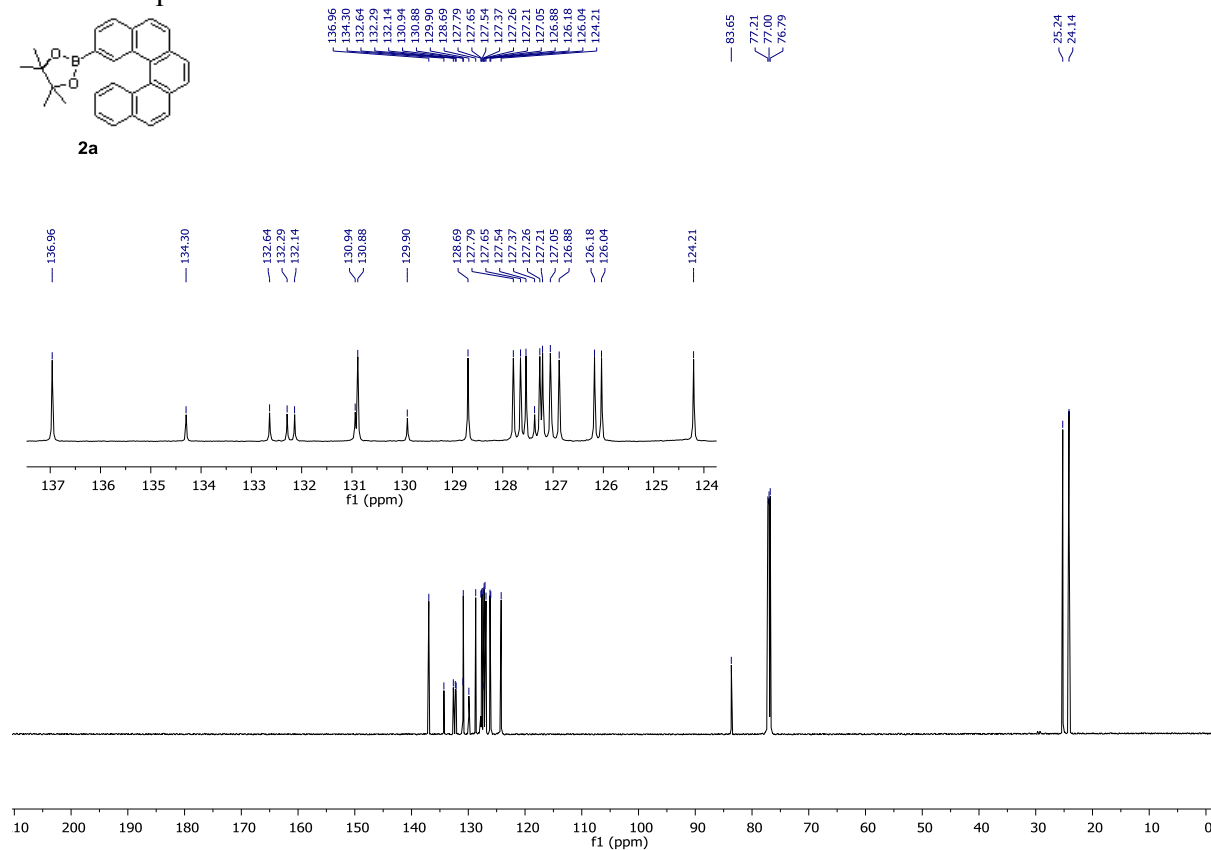
CCDC 1587494 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

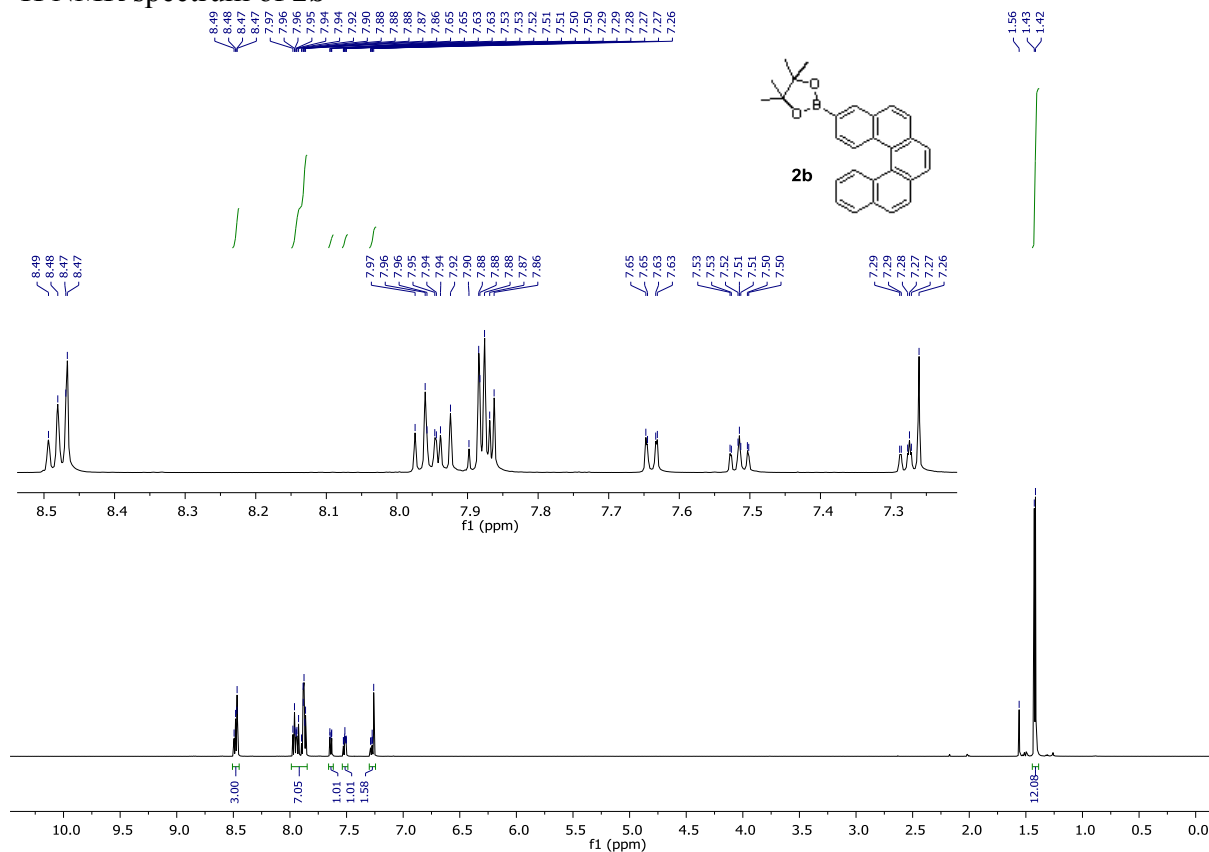
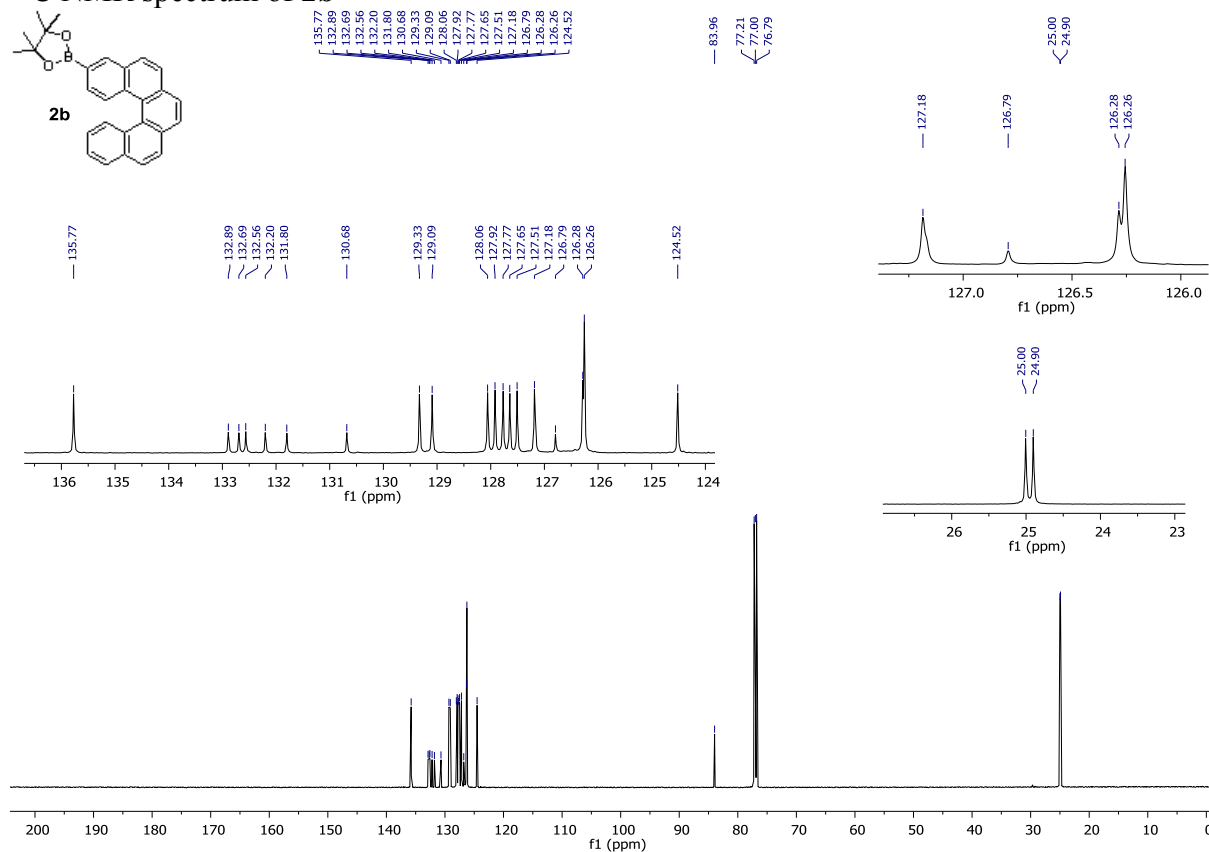


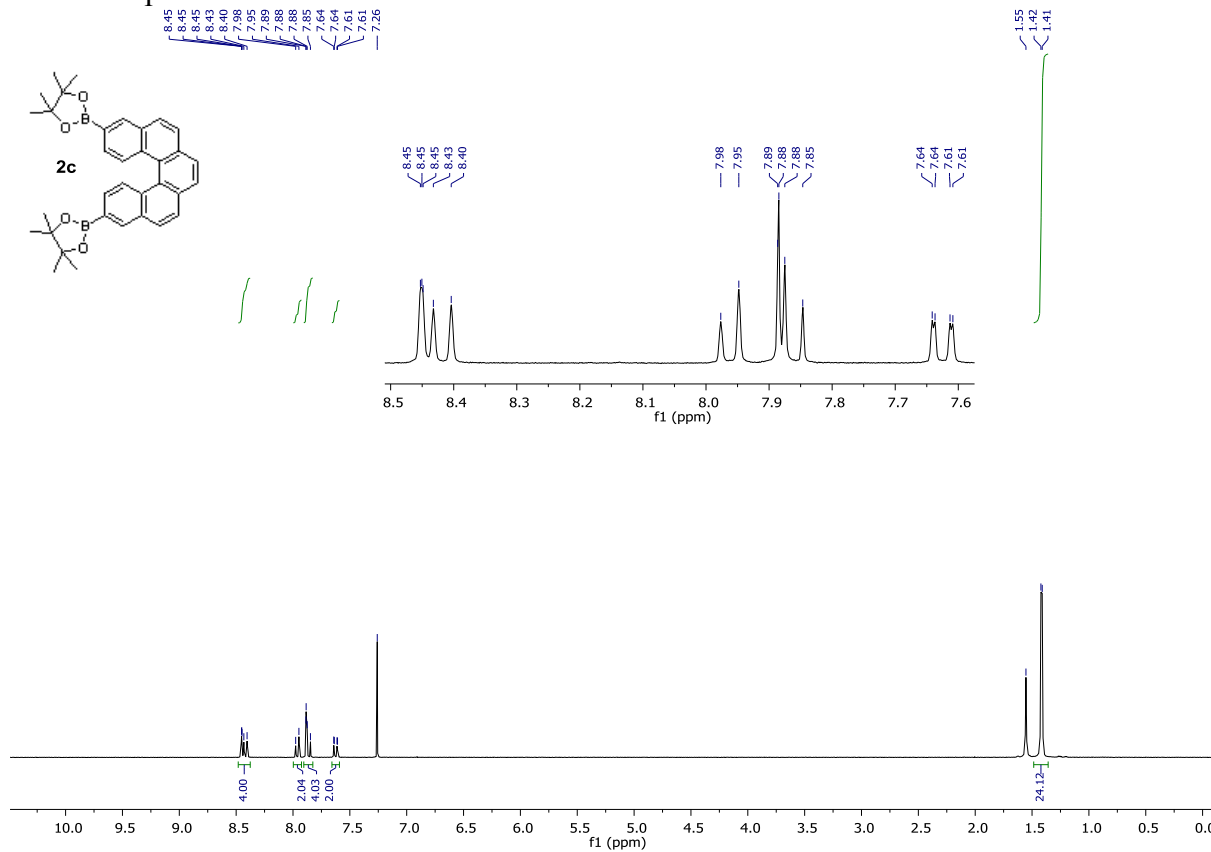
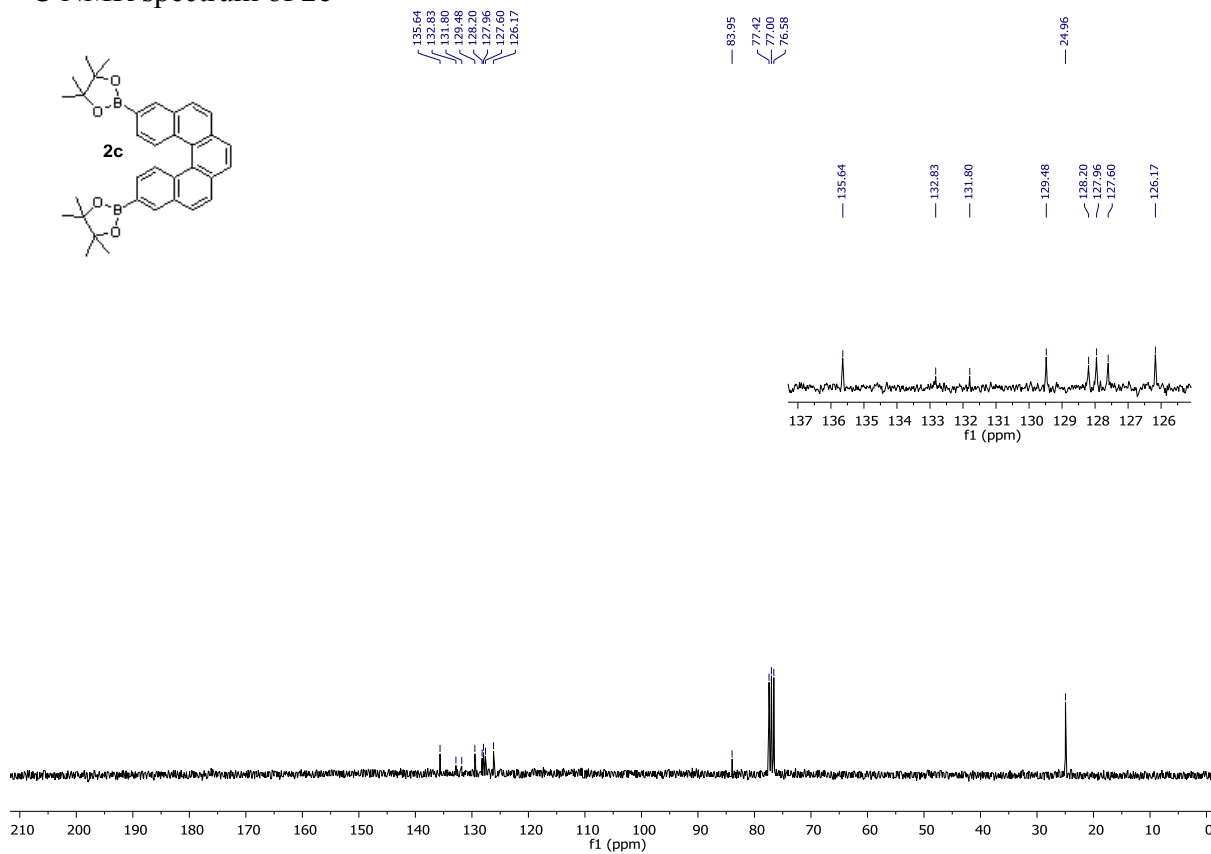
**Figure SI-1.** View of the molecule of **2b** with atom numbering scheme. The displacement ellipsoids are drawn with 30% probability level.

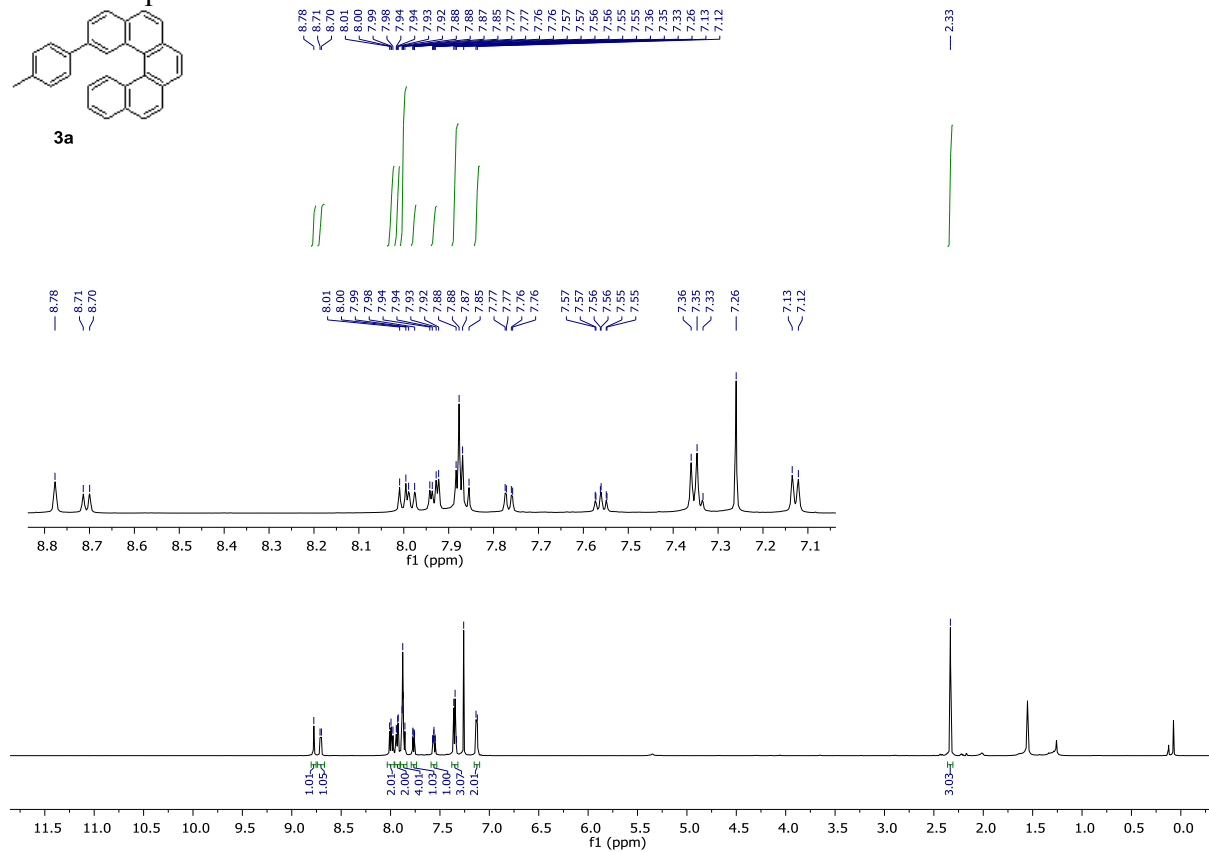
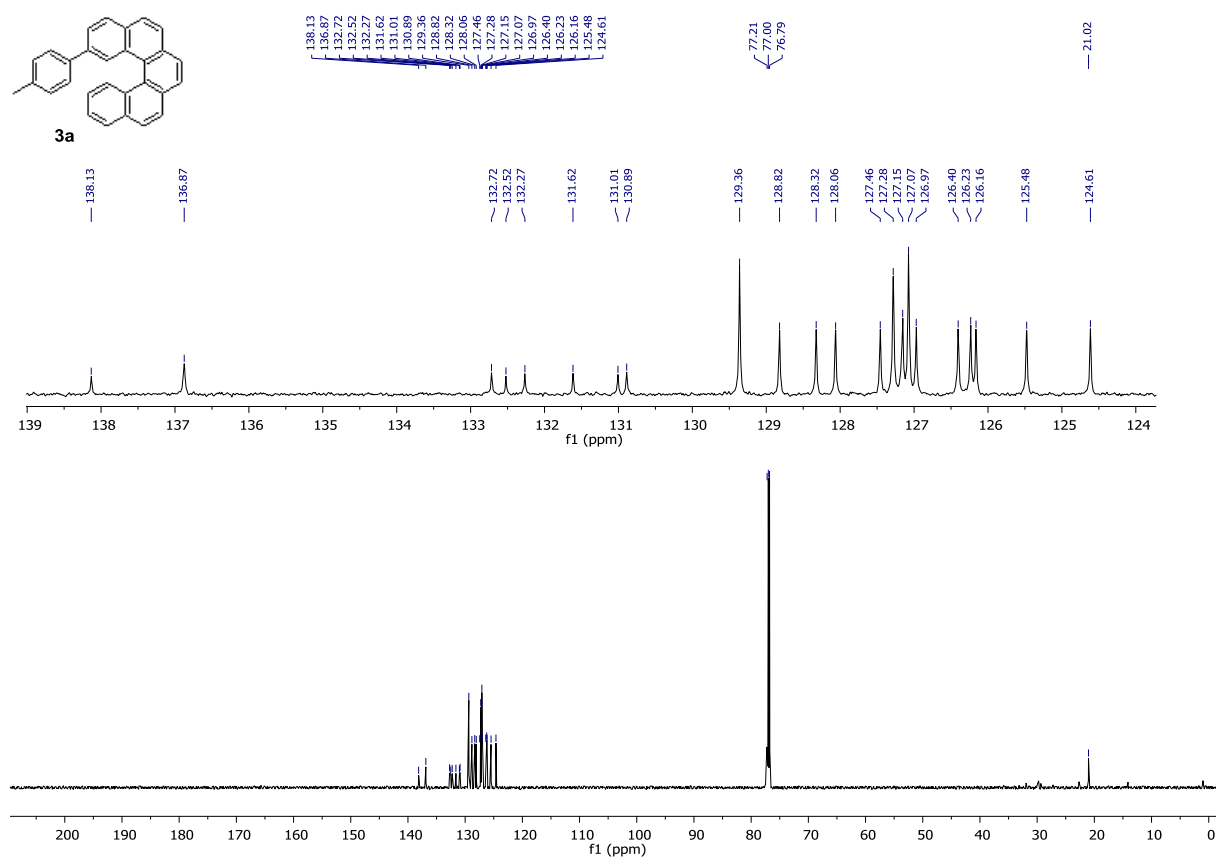
## 7. References.

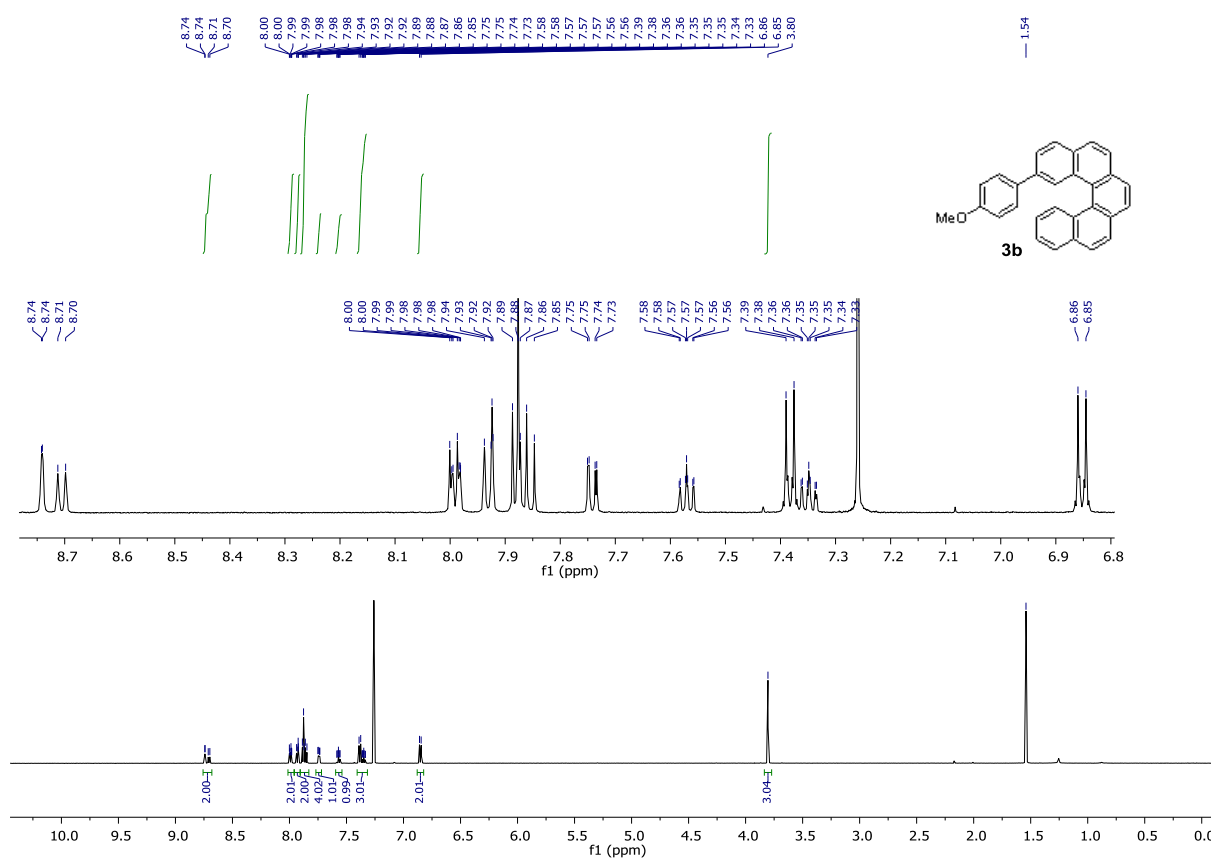
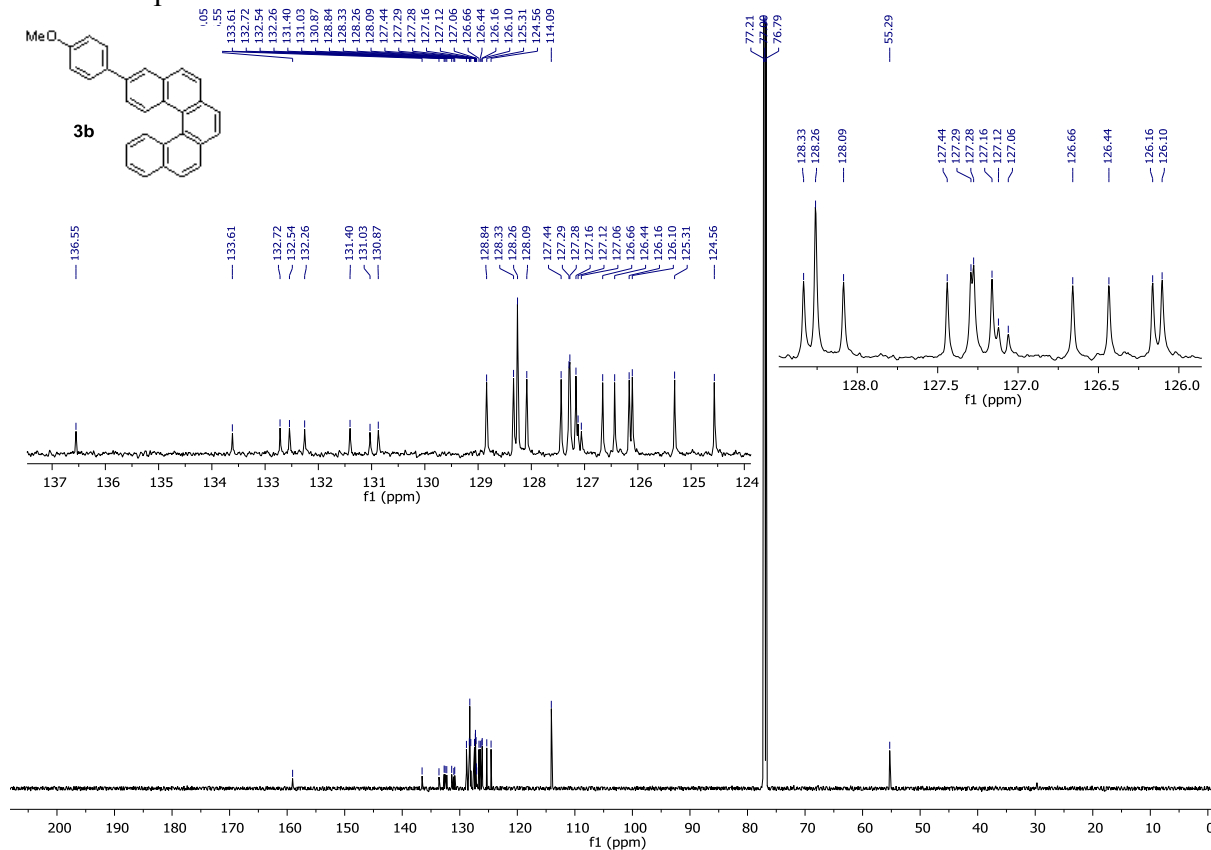
- [1] L. M. Green, D. W. Meek, *Organometallics* **1989**, *8*, 659–666.
- [2] M. Gingras, F. Dubois, *Tetrahedron Lett.* **1999**, *40*, 1309–1312.
- [3] C. C. C. J. Seechurn, V. Sivakumar, D. Satoskar, T. J. Colacot, *Organometallics* **2014**, *33*, 3514–3522.
- [4] G. M. Sheldrick, *Acta Crystallogr. Sect. Found. Adv.* **2015**, *71*, 3–8.
- [5] G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.

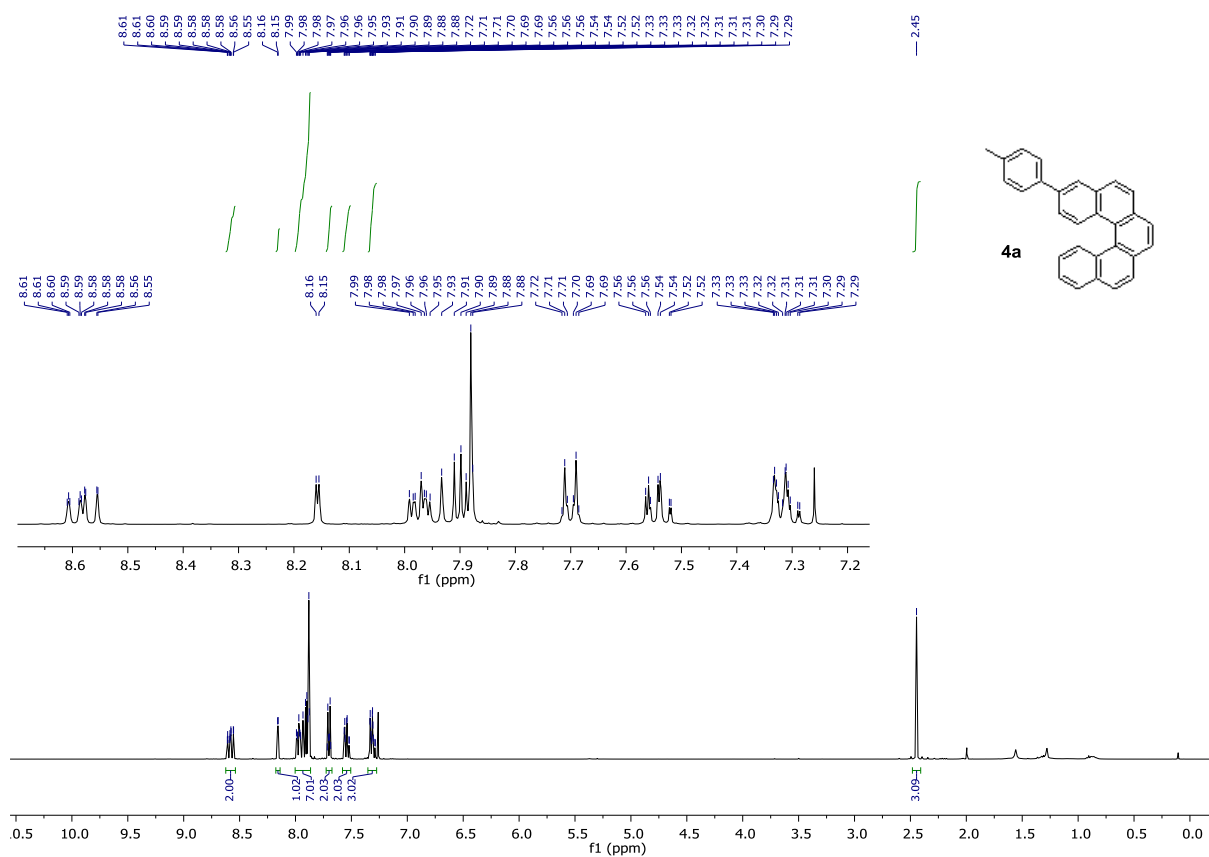
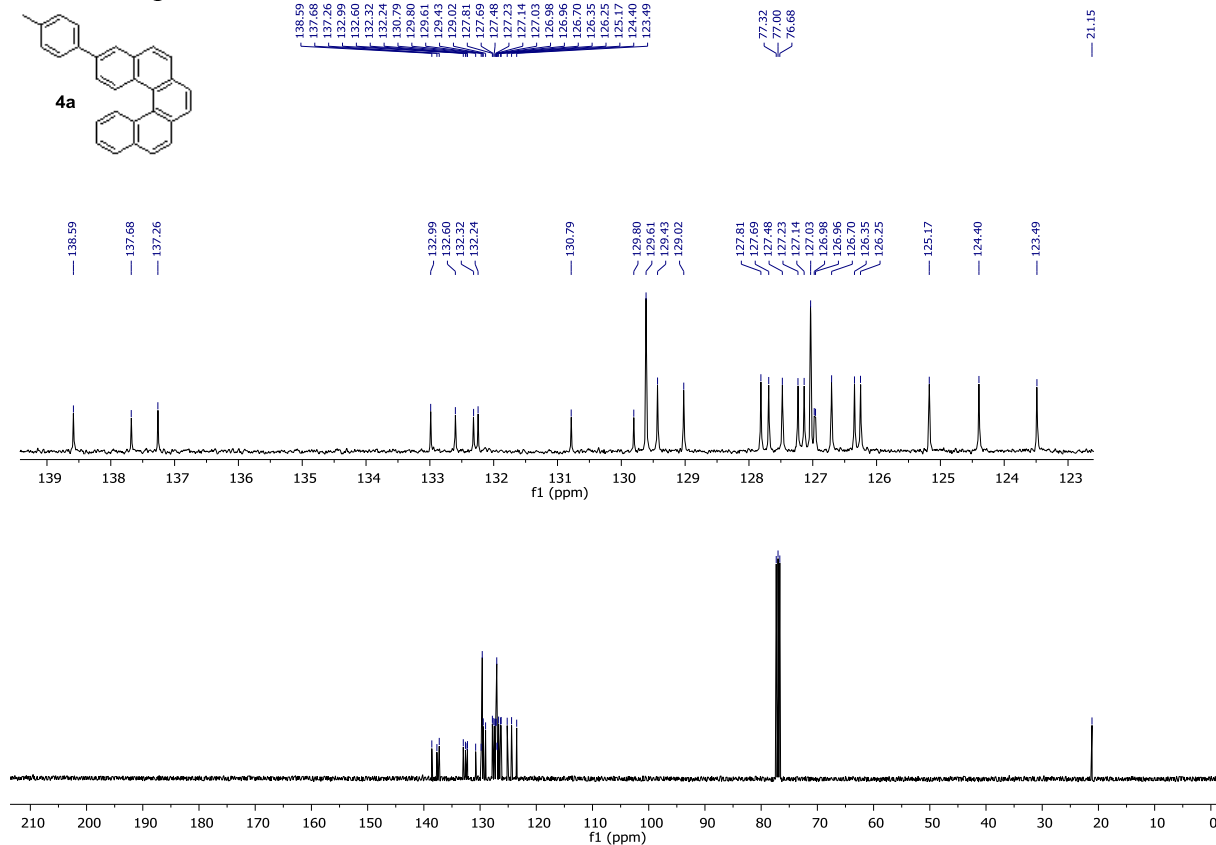
8.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. $^1\text{H}$  NMR spectrum of **2a** $^{13}\text{C}$  NMR spectrum of **2a**

<sup>1</sup>H NMR spectrum of **2b**<sup>13</sup>C NMR spectrum of **2b**

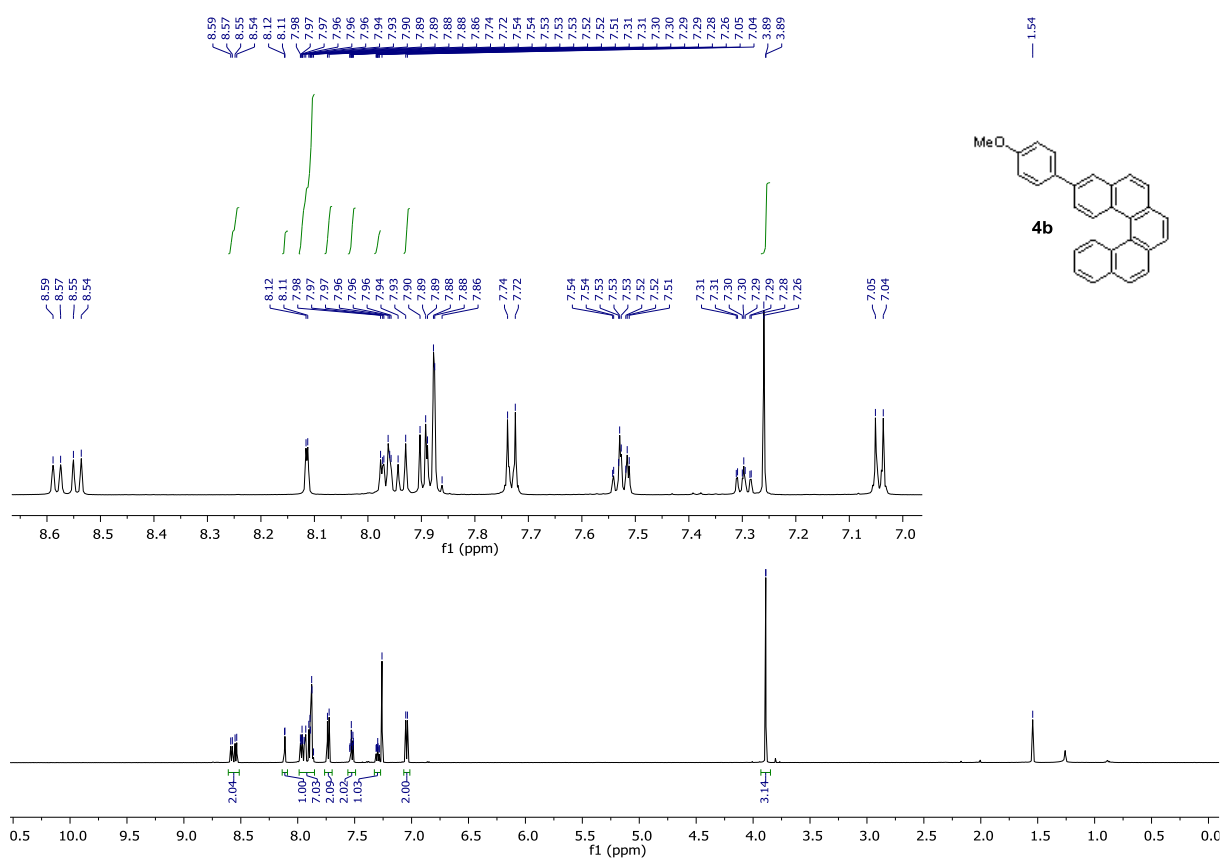
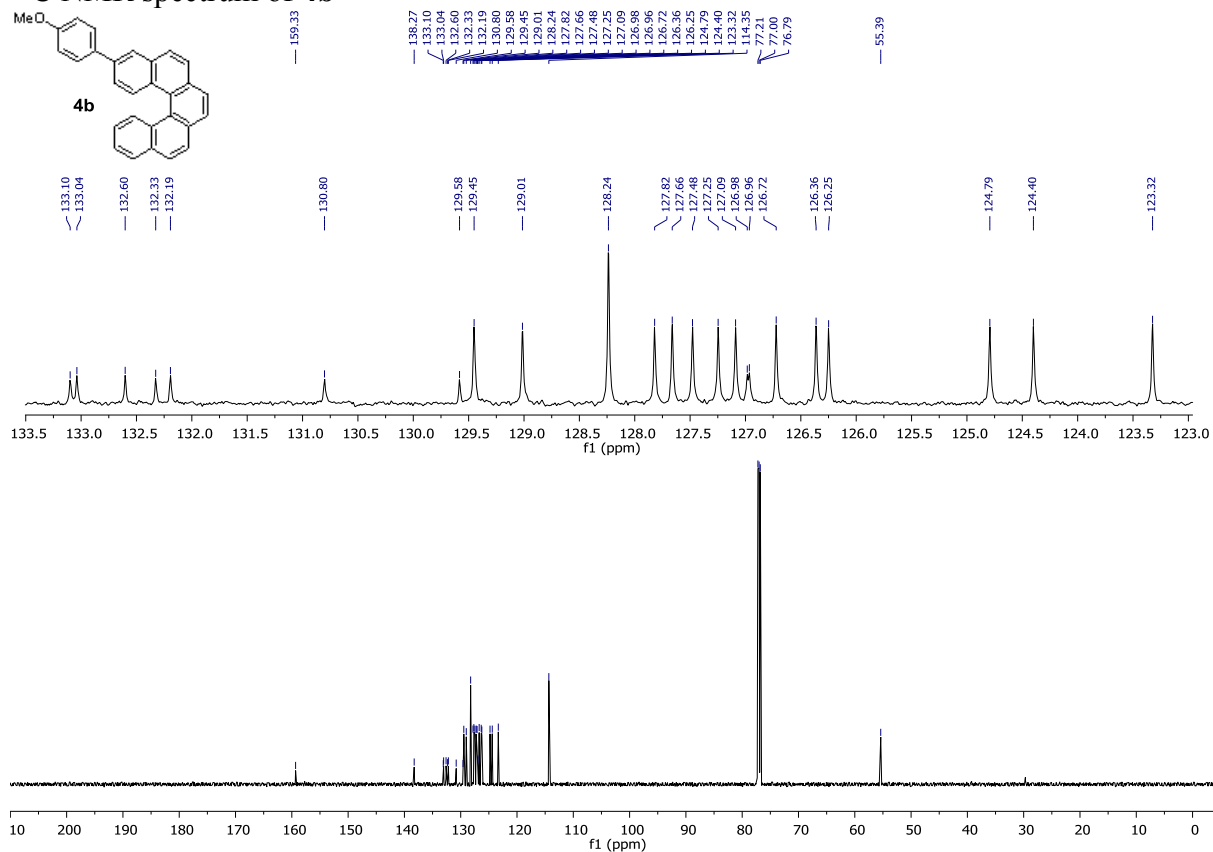
<sup>1</sup>H NMR spectrum of **2c**<sup>13</sup>C NMR spectrum of **2c**

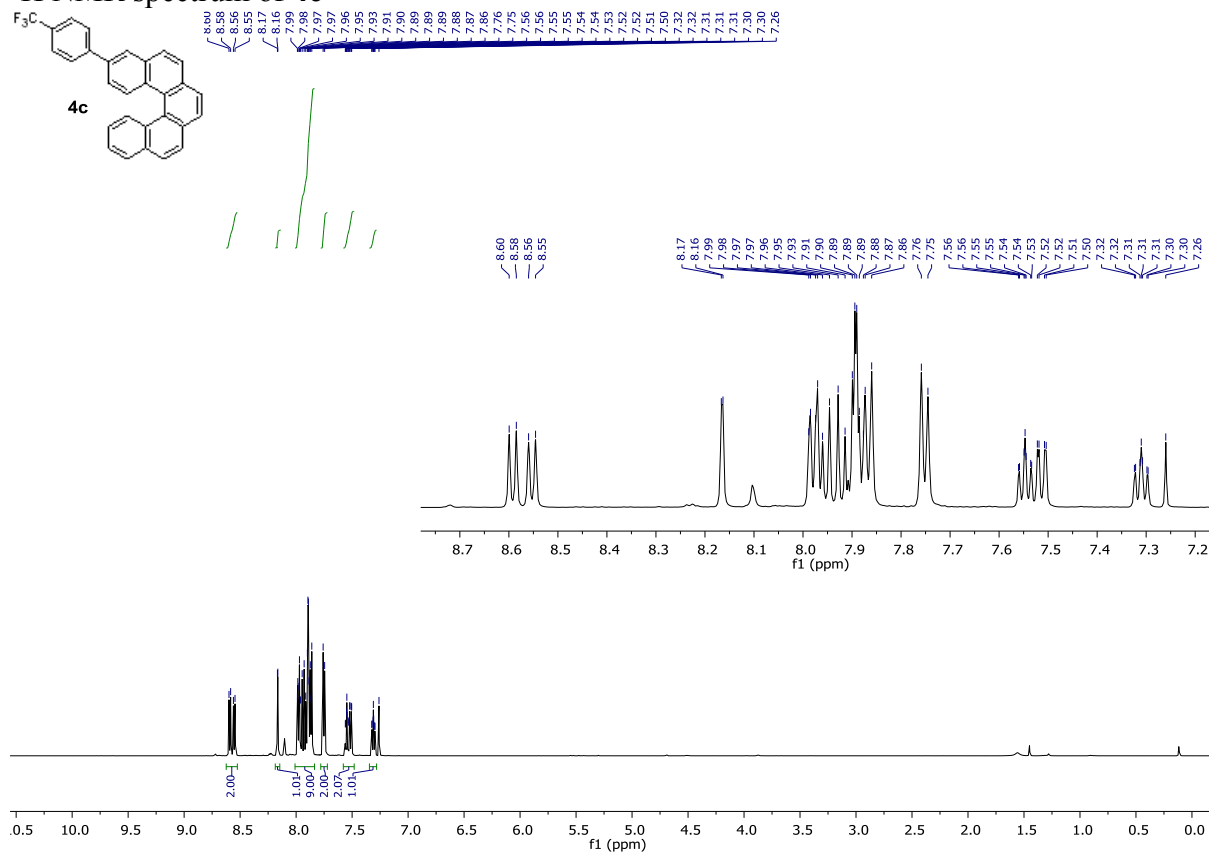
<sup>1</sup>H NMR spectrum of **3a**<sup>13</sup>C NMR spectrum of **3a**

$^1\text{H}$  NMR spectrum of **3b** $^{13}\text{C}$  NMR spectrum of **3b**

<sup>1</sup>H NMR spectrum of **4a**<sup>13</sup>C NMR spectrum of **4a**



<sup>1</sup>H NMR spectrum of **4b**<sup>13</sup>C NMR spectrum of **4b**

<sup>1</sup>H NMR spectrum of **4c**<sup>13</sup>C NMR spectrum of **4c**