

Supporting Information

Palladium-Catalyzed Sequential Vinyl C-H Activation/Dual Decarboxylation: Regioselective Synthesis of Phenanthrenes and Cyclohepta[1,2,3-de]naphthalenes

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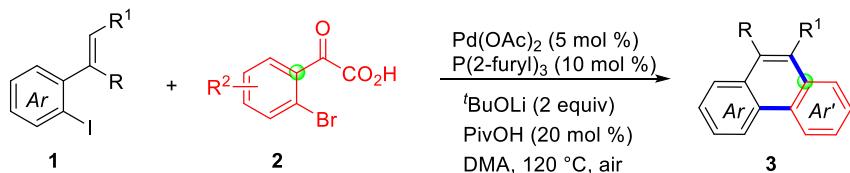
1. General considerations

All materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Solvents were purified and dried according to standard methods prior to use. For product purification by flash column chromatography, silica gel (200~300 mesh) and light petroleum ether (bp. 60~90) are used. ^1H NMR spectra were recorded on a Bruker advance III 400 MHz in CDCl_3 [^1H NMR: $\text{CD}(\text{H})\text{Cl}_3$ (7.26 ppm)] and ^{13}C NMR spectra were recorded on 101 MHz in CDCl_3 [^{13}C NMR: $\text{CD}(\text{H})\text{Cl}_3$ (77.00 ppm)]. Data for ^1H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR is reported in terms of chemical shift (δ , ppm). High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II.

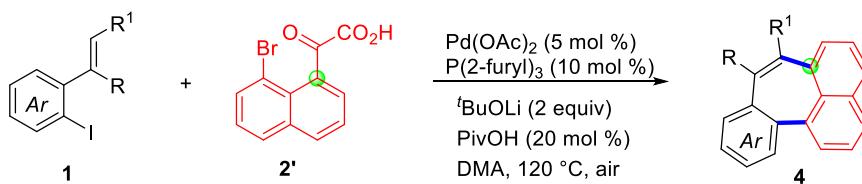
2. Preparation of substrates

Substrates **1** were synthesized according to literatures.¹⁻⁵ α -oxocarboxylic acids **2** were prepared from the corresponding methyl ketones via oxidation with SeO_2 through the known literatures.⁶⁻⁹

3. Experiment procedure



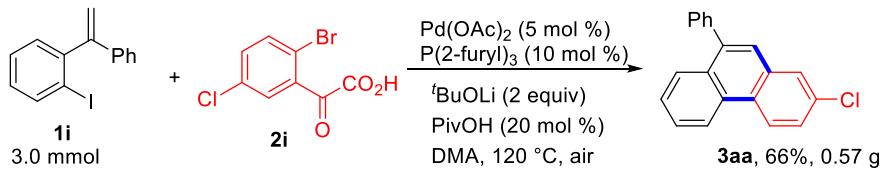
1 (0.2 mmol), **2** (0.3 mmol), $\text{Pd}(\text{OAc})_2$ (5 mol%), P(2-furyl)_3 (10 mol%), ${^t\text{BuOLi}}$ (0.6 mmol) and PivOH (20 mol %) were added to a sealed tube, DMA (2.0 mL) were added via syringe. The mixture was stirred at room temperature for 15 min firstly, and then was stirred in an oil bath at 120 °C about for 12 h until completion (monitored by TLC). After cooling at room temperature, the reaction mixture was filtered and the filtrate diluted in ethyl acetate and washed with water. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified through silica gel chromatography (petroleum ether/EtOAc) to afford the corresponding products **3**.



1 (0.2 mmol), 2-(8-bromonaphthalen-1-yl)-2-oxoacetic acid **2'** (0.3 mmol), $\text{Pd}(\text{OAc})_2$ (5 mol%), P(2-furyl)_3 (10 mol%), ${^t\text{BuOLi}}$ (0.6 mmol) and PivOH (20 mol %) were added to a sealed tube, DMA (2.0 mL) were added via syringe. The mixture was stirred at room temperature for 15 min firstly, and then was stirred in an oil bath at 120 °C about for 12 h until completion (monitored by TLC). After cooling at room temperature, the reaction

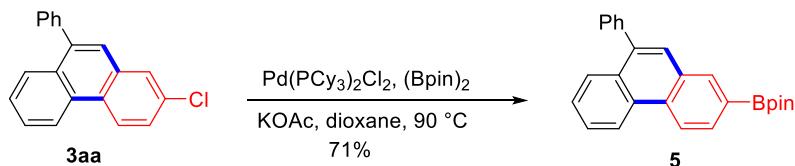
mixture was filtered and the filtrate diluted in ethyl acetate and washed with water. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified through silica gel chromatography (petroleum ether/EtOAc) to afford the corresponding products **4**.

4. Gram-scale reaction of **3aa**

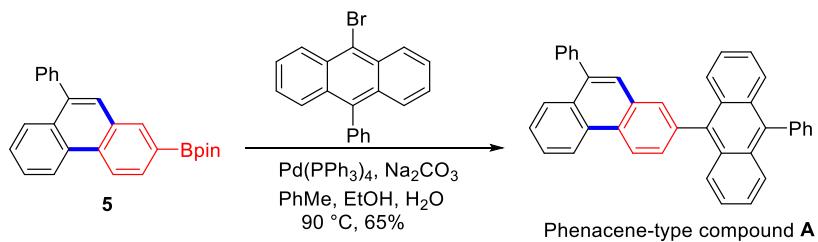


1i (3.0 mmol, 0.92 g), **2i** (4.5 mmol, 1.18 g), $\text{Pd}(\text{OAc})_2$ (5 mol%), $\text{P}(2\text{-furyl})_3$ (10 mol%), $t\text{-BuOLi}$ (9.0 mmol) and PivOH (20 mol %) were added to a sealed tube, DMA (30 mL) were added via syringe. The mixture was stirred at room temperature for 15 min firstly, and then was stirred in an oil bath at 120 °C about for 12 h until completion (monitored by TLC). After cooling at room temperature, the reaction mixture was filtered and the filtrate diluted in ethyl acetate and washed with water. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified through silica gel chromatography (petroleum ether/EtOAc = 50:1) to afford the corresponding products **3aa** in 66% yield.

5. Synthesis of Phenacene-type Compound A for OLEDs

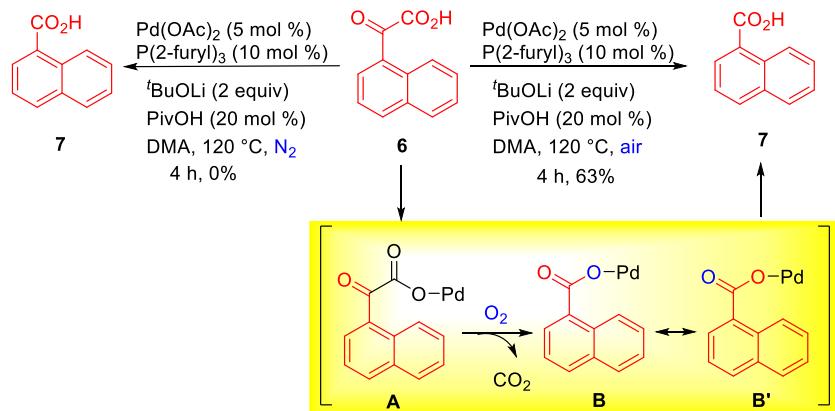


To a mixture of **3aa** (57.6 mg, 0.2 mmol), $(\text{Bpin})_2$ (60.6 mg, 0.24 mmol), $\text{Pd}(\text{PCy}_3)_2\text{Cl}_2$ (7.4 mg, 0.01 mmol) and KOAc (39 mg, 0.40 mmol) was added dioxane (2.0 mL) at room temperature under argon atmosphere. Then it was heated to 90 °C in an oil bath and stirred at this temperature for 5 h. After cooling to room temperature, water and CH_2Cl_2 were added to the mixture. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 . The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 . The solvent was removed under vacuo and the residue was purified by flash chromatography eluting with petroleum ether/ethyl acetate = 50:1 v/v to afford **5** (54 mg, 71% yield) as a white solid.

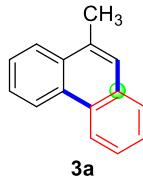


To a mixture of **5** (114 mg, 0.3 mmol), $\text{Pd}(\text{PPh}_3)_4$ (11.5 mg, 0.01 mmol), Na_2CO_3 (43 mg, 0.4 mmol) in a sealed tube was added 9-bromo-10-phenylanthracene (66.6 mg, 0.2 mmol) in 4.0 mL of toluene, 2.0 mL EtOH and 1.0 mL H_2O under argon atmosphere. The mixture was stirred at room temperature for 5 min and then reacted at 90 °C in an oil bath for further 14 h. After being cooled down to room temperature, the reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 v/v) to afford phenacene-type Compound **A** (66 mg, 65% yield) as a white solid.

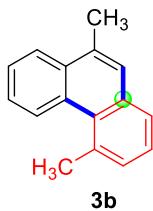
6. Control experiments



7. Spectra data

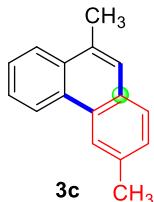


9-methylphenanthrene (3a): 27 mg; 70% yield; white solid; mp = 80-82 °C; Spectroscopic data matched reported literature data.¹⁰ **1H NMR** (400 MHz, CDCl_3) δ 8.68-8.62 (m, 1H), 8.59 (dd, J = 7.2, 2.3 Hz, 1H), 8.03-7.96 (m, 1H), 7.75 (dd, J = 7.3, 2.0 Hz, 1H), 7.64-7.57 (m, 2H), 7.53 (ddd, J = 6.4, 3.8, 1.9 Hz, 3H), 2.67 (d, J = 1.2 Hz, 3H). **13C NMR** (101 MHz, CDCl_3) δ 132.4, 132.0, 132.0, 130.3, 129.6, 127.8, 126.7, 126.5, 126.5, 126.2, 125.8, 124.6, 123.0, 122.4, 20.0.

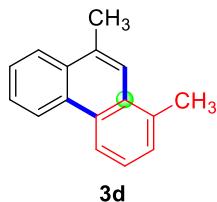


4,9-dimethylphenanthrene (3b): 26 mg; 63% yield; white solid; mp = 49-51 °C; **1H NMR** (400 MHz, CDCl_3) δ 8.94-8.86 (m, 1H), 8.11-8.03 (m, 1H), 7.73-7.59 (m, 3H), 7.54 (d, J =

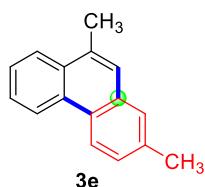
1.3 Hz, 1H), 7.46-7.39 (m, 2H), 3.11 (s, 3H), 2.69 (d, J = 1.1 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 135.1, 133.6, 133.3, 132.0, 131.8, 130.6, 129.5, 128.0, 127.7, 126.7, 125.9, 125.7, 125.1, 124.4, 27.3, 20.0. **HRMS** (ESI) m/z: [M+Na] $^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{Na}$ 229.0988; found: 229.0987.



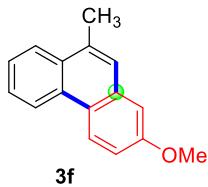
3,9-dimethylphenanthrene (3c): 30 mg; 72% yield; white solid; mp = 57-59 °C; **^1H NMR** (400 MHz, CDCl_3) δ 8.75-8.66 (m, 1H), 8.43 (s, 1H), 8.07-7.99 (m, 1H), 7.73-7.57 (m, 3H), 7.53 (s, 1H), 7.38 (dd, J = 8.1, 1.6 Hz, 1H), 2.70 (d, J = 1.1 Hz, 3H), 2.59 (s, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 135.4, 132.2, 131.4, 130.1, 129.9, 129.7, 128.3, 127.7, 126.5, 126.3, 126.0, 124.6, 122.9, 122.2, 22.1, 20.0. **HRMS** (ESI) m/z: [M+K] $^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{K}$ 245.0727; found: 245.0721.



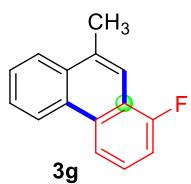
1,9-dimethylphenanthrene (3d): 22 mg; 54% yield; white solid; mp = 67-69 °C; **^1H NMR** (400 MHz, CDCl_3) δ 8.75-8.67 (m, 1H), 8.52 (d, J = 8.3 Hz, 1H), 8.08-8.01 (m, 1H), 7.76 (s, 1H), 7.62 (hept, J = 5.1 Hz, 2H), 7.46 (t, J = 7.7 Hz, 1H), 7.39 (d, J = 7.0 Hz, 1H), 2.73 (d, J = 12.7 Hz, 6H). **^{13}C NMR** (101 MHz, CDCl_3) δ 134.0, 132.2, 131.6, 130.7, 130.6, 129.6, 127.7, 126.3, 126.2, 125.3, 124.6, 123.3, 122.8, 120.7, 20.5, 19.9. **HRMS** (ESI) m/z: [M+Na] $^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{Na}$ 229.0988; found: 229.0987.



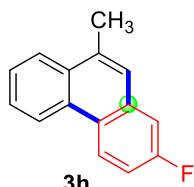
2,9-dimethylphenanthrene (3e): 27 mg; 66% yield; white solid; mp = 52-54 °C; Spectroscopic data matched reported literature data. **^{11}H NMR** (400 MHz, CDCl_3) δ 8.64 (dd, J = 7.6, 1.9 Hz, 1H), 8.49 (d, J = 8.4 Hz, 1H), 8.00 (dd, J = 7.4, 2.0 Hz, 1H), 7.64-7.51 (m, 3H), 7.46 (s, 1H), 7.38 (dd, J = 8.5, 1.8 Hz, 1H), 2.68 (s, 3H), 2.51 (s, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 136.2, 132.4, 132.1, 131.7, 130.4, 127.5, 127.5, 127.4, 126.5, 126.1, 126.0, 124.6, 122.8, 122.3, 21.5, 20.0.



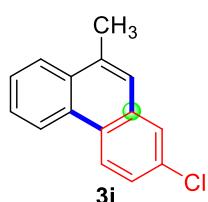
2-methoxy-9-methylphenanthrene (3f): 25 mg; 57% yield; white solid; mp = 96-98 °C; Spectroscopic data matched reported literature data.¹¹ **¹H NMR** (400 MHz, CDCl₃) δ 8.60-8.53 (m, 1H), 8.49 (d, J = 8.9 Hz, 1H), 8.02-7.94 (m, 1H), 7.62-7.51 (m, 2H), 7.46 (s, 1H), 7.21-7.10 (m, 2H), 3.89 (d, J = 1.5 Hz, 3H), 2.68 (d, J = 1.3 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 158.2, 133.3, 133.1, 131.0, 130.5, 126.3, 126.2, 125.4, 124.6, 124.0, 123.9, 122.4, 116.1, 107.9, 55.3, 20.0.



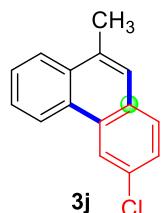
1-fluoro-9-methylphenanthrene (3g): 18 mg; 43% yield; white solid; mp = 61-63 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.69-8.62 (m, 1H), 8.38 (d, J = 8.3 Hz, 1H), 8.09-8.02 (m, 1H), 7.85 (s, 1H), 7.69-7.63 (m, 2H), 7.48 (td, J = 8.1, 5.7 Hz, 1H), 7.26-7.20 (m, 1H), 2.74 (d, J = 1.1 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 158.8 (d, J = 250.1 Hz), 133.2 (d, J = 1.9 Hz), 132.1, 131.6 (d, J = 4.4 Hz), 129.7, 127.0, 126.6, 125.6, (d, J = 8.6 Hz), 124.8, 123.4, 121.4 (d, J = 15.0 Hz), 118.2 (dd, J = 5.3, 3.7 Hz), 110.9 (d, J = 20.3 Hz), 20.3. **¹⁹F NMR** (376 MHz, CDCl₃) δ -123.20. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₁₅H₁₁NaF 233.0737; found: 233.0736.



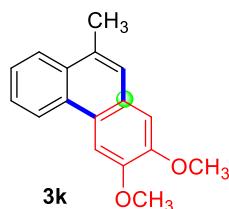
2-fluoro-9-methylphenanthrene (3h): 21 mg; 51% yield; white solid; mp = 86-88 °C; Spectroscopic data matched reported literature data.¹¹ **¹H NMR** (400 MHz, CDCl₃) δ 8.59 (ddd, J = 11.6, 8.0, 3.6 Hz, 2H), 8.03 (dd, J = 7.5, 1.9 Hz, 1H), 7.63 (pd, J = 7.1, 1.6 Hz, 2H), 7.48 (s, 1H), 7.41 (dd, J = 9.5, 2.8 Hz, 1H), 7.30 (td, J = 8.7, 2.7 Hz, 1H), 2.73-2.68 (m, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 161.4 (d, J = 246.7 Hz), 134.0, 133.4 (d, J = 8.8 Hz), 131.5 (d, J = 1.4 Hz), 130.1, 126.6, 126.3, 126.2, 126.0, 124.8, 124.8, 124.7, 122.8, 114.6 (d, J = 23.7 Hz), 111.8 (d, J = 20.4 Hz), 20.0. **¹⁹F NMR** (376 MHz, CDCl₃) δ -115.38.



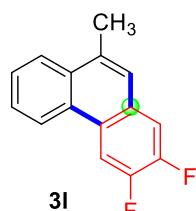
2-chloro-9-methylphenanthrene (3i): 28 mg; 62% yield; white solid; mp = 88-90 °C; Spectroscopic data matched reported literature data.¹¹ **¹H NMR** (400 MHz, CDCl₃) δ 8.66-8.59 (m, 1H), 8.53 (d, *J* = 8.8 Hz, 1H), 8.07-8.01 (m, 1H), 7.75 (d, *J* = 2.2 Hz, 1H), 7.65 (qd, *J* = 7.1, 3.4 Hz, 2H), 7.55-7.43 (m, 2H), 2.71 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 134.0, 133.0, 132.3, 131.9, 129.9, 128.0, 126.8, 126.7, 126.6, 126.2, 125.6, 124.8, 124.1, 122.9, 20.1.



3-chloro-9-methylphenanthrene (3j) : 24 mg; 53% yield; white solid; mp = 59-61 °C; Spectroscopic data matched reported literature data.¹¹ **¹H NMR** (400 MHz, CDCl₃) δ 8.65-8.59 (m, 2H), 8.08-8.03 (m, 1H), 7.76-7.65 (m, 3H), 7.56-7.47 (m, 2H), 2.72 (d, *J* = 1.1 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 132.9, 132.3, 131.7, 130.7, 130.2, 129.4, 129.2, 127.2, 127.1, 126.5, 126.0, 124.7, 123.0, 122.2, 20.0.

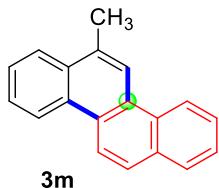


2,3-dimethoxy-9-methylphenanthrene (3k): 34 mg; 67% yield; white solid; mp = 123-125 °C; Spectroscopic data matched reported literature data.¹¹ **¹H NMR** (400 MHz, CDCl₃) δ 8.52 (d, *J* = 8.3 Hz, 1H), 8.00 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.93 (s, 1H), 7.64-7.53 (m, 2H), 7.44 (s, 1H), 7.11 (s, 1H), 4.07 (s, 3H), 3.99 (s, 3H), 2.68 (d, *J* = 1.2 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 149.2, 148.6, 131.2, 130.6, 129.8, 127.0, 125.8, 125.7, 125.4, 124.7, 123.9, 122.4, 107.6, 103.1, 55.9, 55.8, 19.8.

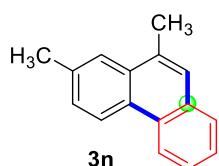


2,3-difluoro-9-methylphenanthrene (3l): 22 mg; 48% yield; white solid; mp = 73-75 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.52-8.45 (m, 1H), 8.34 (dd, *J* = 12.3, 7.9 Hz, 1H), 8.09-7.99 (m, 1H), 7.73-7.62 (m, 2H), 7.56-7.42 (m, 2H), 2.71 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 149.9 (d, *J* = 253.9 Hz), 149.6 (d, *J* = 250.3 Hz), 133.3, 133.2, 131.7, 131.7, 129.5, 129.5, 129.0, 128.9, 126.9, 126.6, 126.5, 125.3, 125.3, 125.3, 124.9, 123.0, 114.2(dd, *J* = 16.3, 1.4 Hz), 110.2 (dd, *J* = 17.8, 1.6 Hz), 20.0. **¹⁹F NMR** (376 MHz, CDCl₃) δ -138.36 (dd,

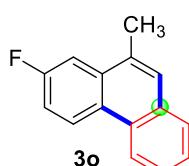
$J = 75.2, 21.4$ Hz, 2F). **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₁₅H₁₀F₂NNa 251.0643; found: 251.0631.



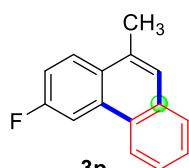
6-methylchrysene (3m): 38 mg; 79% yield; white solid; mp = 82-84 °C; Spectroscopic data matched reported literature data. ¹**H NMR** (400 MHz, CDCl₃) δ 9.16-9.09 (m, 1H), 9.05 (dt, $J = 7.4, 1.4$ Hz, 1H), 8.15 (dt, $J = 7.7, 1.6$ Hz, 1H), 7.98 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.85 (d, $J = 8.5$ Hz, 1H), 7.73 (dd, $J = 8.6, 1.1$ Hz, 1H), 7.70-7.61 (m, 4H), 7.61-7.54 (m, 1H), 2.78 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 133.2, 133.0, 133.0, 130.7, 130.4, 130.2, 128.5, 128.3, 127.8, 127.5, 127.1, 126.4, 126.3, 126.0, 125.8, 125.6, 125.4, 124.4, 19.7.



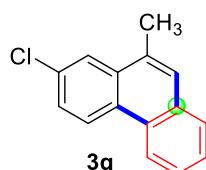
2,10-dimethylphenanthrene (3n): 30 mg; 73% yield; white solid; mp = 86-88 °C; ¹**H NMR** (400 MHz, CDCl₃) δ 8.59 (dd, $J = 8.6, 2.6$ Hz, 2H), 7.86-7.73 (m, 2H), 7.65-7.41 (m, 4H), 2.70 (d, $J = 1.1$ Hz, 3H), 2.58 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 136.2, 132.2, 132.2, 131.6, 129.7, 128.1, 127.9, 127.7, 126.7, 126.1, 125.7, 124.4, 122.9, 122.2, 21.8, 20.1. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₁₆H₁₄Na 229.0988; found: 229.0979.



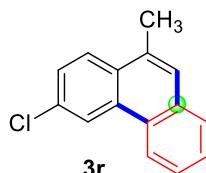
2-fluoro-10-methylphenanthrene (3o): 25 mg; 60% yield; white solid; mp = 84-86 °C; Spectroscopic data matched reported literature data. ¹²¹**H NMR** (400 MHz, CDCl₃) δ 8.61 (dd, $J = 9.1, 5.7$ Hz, 1H), 8.55-8.47 (m, 1H), 7.76 (dd, $J = 7.4, 1.8$ Hz, 1H), 7.65-7.49 (m, 4H), 7.40-7.31 (m, 1H), 2.62 (d, $J = 1.1$ Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 161.4 (d, $J = 246.5$ Hz), 160.2, 133.7 (d, $J = 7.8$ Hz), 131.7 (d, $J = 3.9$ Hz), 131.4 (d, $J = 1.3$ Hz), 129.3, 127.9 (d, $J = 10.1$ Hz), 126.9 (d, $J = 2.0$ Hz), 126.3 (d, $J = 21.1$ Hz), 125.2 (d, $J = 8.8$ Hz), 122.2, 114.9 (d, $J = 23.6$ Hz), 109.3 (d, $J = 21.1$ Hz), 19.9. ¹⁹**F NMR** (376 MHz, CDCl₃) δ -114.26.



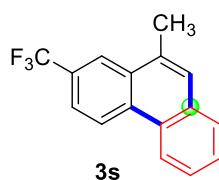
3-fluoro-10-methylphenanthrene (3p): 23 mg; 55% yield; white solid; mp = 83-85 °C; Spectroscopic data matched reported literature data. ¹²**H NMR** (400 MHz, CDCl₃) δ 8.46 (dd, *J* = 6.1, 3.4 Hz, 1H), 8.28 (dd, *J* = 11.2, 2.6 Hz, 1H), 7.98 (dd, *J* = 9.0, 5.9 Hz, 1H), 7.77 (dd, *J* = 6.0, 3.3 Hz, 1H), 7.56 (dt, *J* = 6.3, 3.5 Hz, 2H), 7.49 (s, 1H), 7.38-7.31 (m, 1H), 2.68 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 161.4 (d, *J* = 246.0 Hz), 132.4, 132.2, 132.1, 132.1, 129.1, 128.8, 127.9, 127.2, 126.8 (d, *J* = 8.9 Hz), 125.9, 125.9, 125.8, 122.6, 115.2 (d, *J* = 23.4 Hz), 108.10 (d, *J* = 22.0 Hz), 20.1. ¹⁹**F NMR** (376 MHz, CDCl₃) δ -114.51.



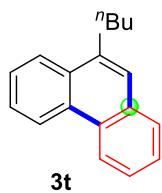
2-chloro-10-methylphenanthrene (3q): 29 mg; 64% yield; white solid; mp = 56-59 °C; Spectroscopic data matched reported literature data. ¹²**H NMR** (400 MHz, CDCl₃) δ 8.51 (dd, *J* = 14.6, 7.6 Hz, 2H), 7.94 (d, *J* = 2.2 Hz, 1H), 7.79-7.71 (m, 1H), 7.59-7.50 (m, 4H), 2.62 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 133.2, 132.4, 131.8, 131.5, 129.1, 128.6, 127.9, 127.8, 126.8, 126.5, 126.2, 124.5, 124.0, 122.3, 19.8.



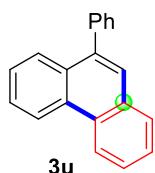
3-chloro-10-methylphenanthrene (3r): 30 mg; 67% yield; yellow oil; white solid; mp = 71-73 °C; ¹**H NMR** (400 MHz, CDCl₃) δ 8.59 (d, *J* = 2.1 Hz, 1H), 8.52-8.44 (m, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.79-7.71 (m, 1H), 7.59-7.44 (m, 4H), 2.64 (d, *J* = 1.2 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 132.3, 131.9, 131.6, 130.3, 128.6, 127.8, 127.1, 127.0, 126.8, 126.1, 126.0, 122.6, 122.5, 19.9. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₁₅H₁₁ClNa 249.0441; found: 249.0452.



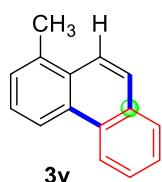
10-methyl-2-(trifluoromethyl)phenanthrene (3s): 24 mg; 47% yield; white solid; mp = 95-97 °C; ¹**H NMR** (400 MHz, CDCl₃) δ 8.70 (d, *J* = 8.7 Hz, 1H), 8.57 (dd, *J* = 6.2, 3.4 Hz, 1H), 8.25 (s, 1H), 7.79 (dt, *J* = 9.6, 2.6 Hz, 2H), 7.65-7.53 (m, 3H), 2.69 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 132.5 (d, *J* = 33.9 Hz), 132.4, 131.5, 128.8, 128.3, 127.9 (d, *J* = 2.0 Hz), 127.6, 126.3, 125.9 (t, *J* = 273.0 Hz), 123.8, 122.8, 122.0, 121.9, 19.8. ¹⁹**F NMR** (376 MHz, CDCl₃) δ -61.76. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₁₆H₁₁F₃Na 283.0705; found: 283.0713.



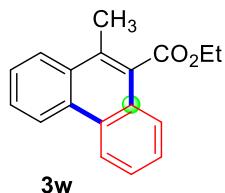
9-butylphenanthrene (3t): 35 mg, 75% yield, white solid; mp = 69-71 °C; Spectroscopic data matched reported literature data. ¹³**H NMR** (400 MHz, CDCl₃) δ 8.77-8.69 (m, 1H), 8.64 (d, *J* = 7.7 Hz, 1H), 8.16-8.07 (m, 1H), 7.86-7.78 (m, 1H), 7.73-7.49 (m, 5H), 3.11 (t, *J* = 7.8 Hz, 2H), 1.80 (t, *J* = 7.8 Hz, 2H), 1.54-1.47 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 136.9, 131.9, 131.3, 130.7, 129.6, 128.0, 126.5, 126.4, 126.0, 125.9, 125.8, 124.5, 123.2, 122.4, 33.2, 32.4, 22.9, 14.0.



9-phenylphenanthrene (3u): 39 mg; 77% yield; yellow solid; mp = 94-96 °C; Spectroscopic data matched reported literature data. ¹¹**H NMR** (400 MHz, CDCl₃) δ 8.77 (d, *J* = 8.3 Hz, 1H), 8.72 (d, *J* = 8.2 Hz, 1H), 7.90 (ddd, *J* = 10.6, 7.9, 1.5 Hz, 2H), 7.70-7.59 (m, 4H), 7.57-7.43 (m, 6H). ¹³**C NMR** (101 MHz, CDCl₃) δ 140.8, 138.7, 131.5, 131.1, 130.6, 130.0, 129.9, 128.6, 128.3, 127.5, 127.3, 126.9, 126.8, 126.6, 126.5, 126.4, 122.9, 122.5.

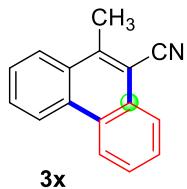


1-methylphenanthrene (3v): 14 mg; 36% yield; white solid; mp = 103-105 °C; Spectroscopic data matched reported literature data. ¹⁴**H NMR** (400 MHz, CDCl₃) δ 8.68 (d, *J* = 8.2 Hz, 1H), 8.56 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 9.2 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.76 (d, *J* = 9.1 Hz, 1H), 7.66-7.50 (m, 3H), 7.43 (d, *J* = 7.1 Hz, 1H), 2.74 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 134.8, 131.6, 130.8, 130.6, 130.3, 128.5, 127.7, 126.7, 126.5, 126.4, 126.1, 122.9, 122.8, 120.8, 19.9.

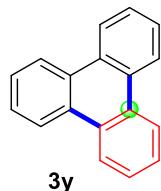


ethyl 10-methylphenanthrene-9-carboxylate (3w): 33 mg; 63% yield; white solid; mp = 74-76 °C; ¹**H NMR** (400 MHz, CDCl₃) δ 8.69 (ddd, *J* = 11.9, 7.7, 1.8 Hz, 2H), 8.16-8.08 (m, 1H), 7.78-7.51 (m, 5H), 4.58 (q, *J* = 7.1 Hz, 2H), 2.70 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 136.9, 131.9, 131.3, 130.7, 129.6, 128.0, 126.5, 126.4, 126.0, 125.9, 125.8, 124.5, 123.2, 122.4, 33.2, 32.4, 22.9, 14.0.

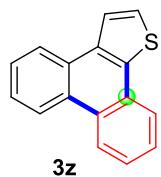
NMR (101 MHz, CDCl₃) δ 170.4, 130.9, 130.4, 130.4, 129.6, 129.4, 128.1, 127.2, 127.1, 127.0, 126.4, 125.2, 125.1, 122.9, 122.7, 61.5, 17.1, 14.4. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₁₈H₁₆NaO₂ 287.1043; found: 287.1043.



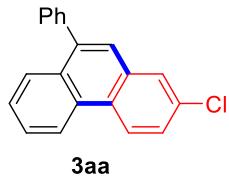
10-methylphenanthrene-9-carbonitrile (3x): 25 mg; 57% yield; white solid; mp = 166-168 °C; Spectroscopic data matched reported literature data.¹⁵ **¹H NMR** (400 MHz, CDCl₃) δ 8.61-8.50 (m, 2H), 8.21-8.11 (m, 1H), 8.01 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.76-7.59 (m, 4H), 2.90 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 142.0, 131.1, 129.8, 129.2, 128.9, 128.7, 127.9, 127.4, 127.3, 125.8, 125.6, 123.0, 122.6, 117.5, 109.1, 18.8.



triphenylene (3y): 37 mg; 81% yield; white solid; mp = 166-168 °C; Spectroscopic data matched reported literature data.¹⁶ **¹H NMR** (400 MHz, CDCl₃) δ 8.62 (dd, *J* = 6.2, 3.4 Hz, 6H), 7.62 (dd, *J* = 6.3, 3.3 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 129.7, 127.2, 123.3.

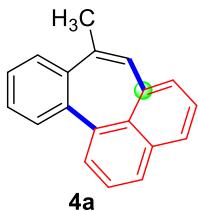


phenanthro[9,10-b]thiophene (3z): 30 mg; 64% yield; white solid; mp = 152-155 °C; Spectroscopic data matched reported literature data.¹⁶ **¹H NMR** (400 MHz, CDCl₃) δ 8.63 (ddd, *J* = 9.5, 4.3, 2.4 Hz, 2H), 8.29-8.23 (m, 1H), 8.14-8.06 (m, 1H), 7.90 (d, *J* = 5.3 Hz, 1H), 7.59 (ddd, *J* = 12.4, 6.3, 3.4 Hz, 4H), 7.50 (d, *J* = 5.3 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 136.6, 135.0, 129.0, 128.8, 128.6, 128.3, 127.2, 127.0, 126.3, 126.0, 124.9, 124.2, 124.2, 123.5, 123.4, 123.2.

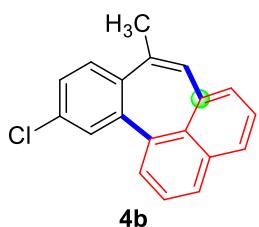


2-chloro-9-phenylphenanthrene (3aa): 570 mg; 66% yield (with 3.0 mmol **1i** as the substrate); white solid; mp = 72-73 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.59-8.52 (m, 2H), 7.86 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.59-7.52 (m, 2H), 7.49-7.38 (m,

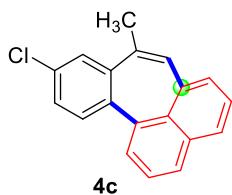
7H). **¹³C NMR** (101 MHz, CDCl₃) δ 140.4, 139.0, 132.4, 131.2, 130.9, 129.9, 129.7, 129.6, 128.3, 127.5, 127.2, 127.0, 126.9, 126.7, 126.6, 122.9, 122.2. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₂₀H₁₃NaCl 311.0598; found: 311.0568.



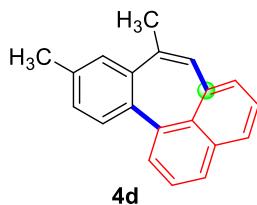
8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4a): 23 mg; 49% yield; white solid; mp = 61-63 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.64 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.54 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.49-7.41 (m, 3H), 7.37-7.27 (m, 3H), 7.17-7.09 (m, 2H), 6.59 (t, *J* = 1.2 Hz, 1H), 2.36 (d, *J* = 1.4 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 140.8, 139.1, 138.7, 138.1, 135.0, 134.8, 134.7, 134.6, 134.3, 129.7, 128.7, 128.4, 127.7, 127.5, 126.2, 126.2, 125.6, 24.6. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₁₉H₁₄Na 265.0988; found: 265.0982.



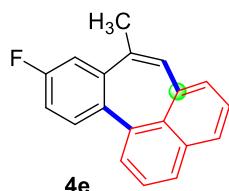
11-chloro-8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4b): 23 mg; 42% yield; white solid; mp = 72-75 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.66 (dd, *J* = 7.1, 2.3 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.47-7.42 (m, 2H), 7.38-7.29 (m, 2H), 7.24 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.14 (d, *J* = 7.1 Hz, 1H), 7.10 (d, *J* = 2.3 Hz, 1H), 6.56 (s, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 142.5, 137.8, 137.7, 137.3, 135.2, 135.0, 134.7, 134.3, 133.9, 133.7, 128.8, 128.7, 128.3, 127.5, 127.3, 126.4, 126.3, 125.7, 24.6. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₉H₁₄Cl 277.0779; found: 277.0777.



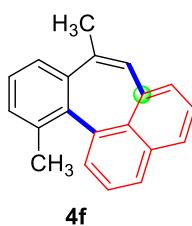
10-chloro-8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4c): 24 mg; 44% yield; white solid; mp = 93-95 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.63 (dd, *J* = 6.4, 2.9 Hz, 1H), 7.58-7.52 (m, 1H), 7.45-7.36 (m, 3H), 7.34-7.25 (m, 2H), 7.13 (d, *J* = 7.1 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.58 (s, 1H), 2.30 (d, *J* = 1.4 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 140.3, 139.2, 138.0, 137.8, 136.0, 135.9, 134.6, 134.3, 133.8, 133.3, 129.3, 128.9, 128.6, 128.0, 126.5, 126.3, 126.1, 125.7, 24.5. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₉H₁₄Cl 277.0779; found: 277.0769.



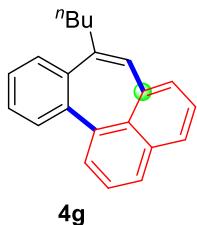
8,10-dimethylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4d): 25 mg; 50% yield; white solid; mp = 44-46 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.62 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.55-7.51 (m, 1H), 7.49-7.39 (m, 2H), 7.32-7.24 (m, 2H), 7.18-7.11 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.58 (s, 1H), 2.38-2.33 (m, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 139.1, 138.4, 138.0, 137.9, 137.2, 135.1, 134.8, 134.7, 134.7, 134.3, 130.5, 128.3, 128.2, 127.4, 127.0, 126.2, 126.2, 125.5, 24.7 21.0. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₂₀H₁₆Na 279.1144; found: 279.1139.



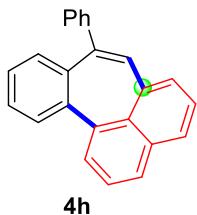
10-fluoro-8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4e): 20 mg; 38% yield; white solid; mp = 47-49 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.63 (dd, *J* = 6.9, 2.5 Hz, 1H), 7.56 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.46-7.39 (m, 2H), 7.31 (dd, *J* = 8.1, 7.1 Hz, 1H), 7.18 -7.10 (m, 2H), 7.08-7.00 (m, 2H), 6.60 (s, 1H), 2.32 (d, *J* = 1.4 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 162.5 (d, *J* = 247.5 Hz), 140.8 (d, *J* = 7.7 Hz), 138.2, 137.8, 136.8, 136.5 (d, *J* = 8.1 Hz), 135.8, 134.6, 134.3, 133.4 (d, *J* = 2.0 Hz), 128.8, 128.6, 127.7, 126.6, 126.3, 125.7, 116.2 (d, *J* = 20.9 Hz), 112.8 (d, *J* = 22.6 Hz), 24.5. **¹⁹F NMR** (376 MHz, CDCl₃) δ -116.07. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₁₉H₁₄NaF 287.0893; found: 287.0890.



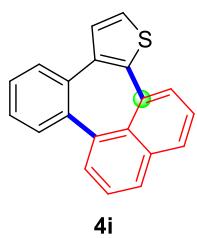
8,12-dimethylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4f): 13 mg; 26% yield; white solid; mp = 70-72 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.46-7.31 (m, 3H), 7.29-7.16 (m, 4H), 6.57 (s, 1H), 2.39 (d, *J* = 1.4 Hz, 3H), 1.95 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 139.7, 139.4, 139.1, 138.6, 134.9, 134.9, 134.7, 134.3, 133.7, 132.5, 132.4, 128.2, 127.2, 127.0, 125.5, 125.4, 124.7, 123.0, 24.5, 23.1. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₂₀H₁₆Na 279.1144; found: 279.1140.



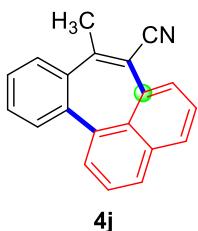
8-butylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4g): 30 mg; 53% yield; white solid; mp = 58-60 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.64 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.58-7.42 (m, 4H), 7.31 (ddt, *J* = 10.3, 7.6, 4.0 Hz, 3H), 7.16 (d, *J* = 7.1 Hz, 1H), 7.10 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.57 (s, 1H), 2.73 (t, *J* = 7.7 Hz, 2H), 1.61-1.55 (m, 2H), 1.39 (q, *J* = 7.5 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 141.5, 139.7, 139.2, 138.4, 137.7, 135.0, 135.0, 134.1, 134.1, 129.5, 128.6, 128.4, 127.6, 127.4, 126.2, 126.1, 125.6, 37.5, 31.4, 22.6, 14.0. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₂₂H₂₀Na 307.1457; found: 307.1452.



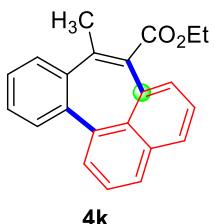
8-phenylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4h): 34 mg; 56% yield; white solid; mp = 70-72 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.63-7.51 (m, 3H), 7.48-7.40 (m, 3H), 7.39-7.33 (m, 2H), 7.32-7.23 (m, 3H), 7.22-7.17 (m, 1H), 7.13 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.07 (td, *J* = 7.5, 1.4 Hz, 1H), 6.96 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.66 (s, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 144.4, 141.8, 141.6, 139.0, 138.3, 138.3, 136.3, 134.6, 134.4, 134.4, 130.2, 129.9, 129.6, 128.9, 128.5, 128.4, 127.8, 127.1, 127.0, 126.9, 126.3, 125.6. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₂₄H₁₆Na 327.1144; found: 327.1145.



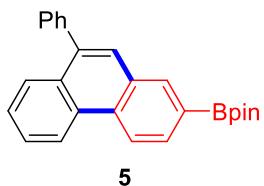
benzo[3,4]naphtho[1',8':5,6,7]cyclohepta[1,2-b]thiophene (4i): 22 mg; 38% yield; white solid; mp = 69-71 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.74-7.64 (m, 4H), 7.61-7.56 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.42-7.30 (m, 5H), 7.19-7.13 (m, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 142.8, 139.9, 137.9, 137.1, 136.1, 134.6, 134.3, 134.1, 131.2, 129.0, 129.0, 128.6, 128.4, 127.8, 127.6, 127.1, 126.2, 125.6, 124.8. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₂₀H₁₂NaS: 307.0552; found: 307.0560.



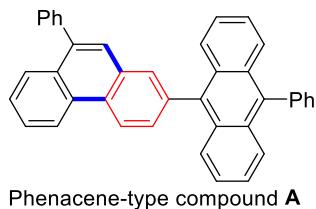
8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene-7-carbonitrile (4j): 18 mg; 33% yield; white solid; mp = 98-100 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.75-7.63 (m, 3H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.40 (q, *J* = 7.3 Hz, 2H), 7.36-7.29 (m, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 2.73 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 150.7, 141.6, 139.2, 137.1, 137.0, 134.5, 133.5, 131.2, 129.9, 128.9, 128.2, 128.0, 127.9, 127.9, 127.5, 126.6, 125.6, 119.5, 117.0, 24.9. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₂₀H₁₃NaN 290.0940; found: 290.0939.



ethyl 8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene-7-carboxylate (4k): 23 mg; 37% yield; white solid; mp = 93-95 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.66 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.60 (ddd, *J* = 7.3, 4.7, 1.3 Hz, 2H), 7.54-7.43 (m, 2H), 7.35-7.26 (m, 3H), 7.23 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.03-6.95 (m, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 170.1, 140.8, 139.8, 138.7, 137.7, 137.3, 134.2, 133.9, 133.6, 131.2, 129.5, 127.7, 127.4, 127.4, 127.2, 126.4, 126.3, 125.2, 61.1, 22.3, 14.0. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₂₂H₁₈NaO₂ 337.1199; found: 337.1201.



4,4,5,5-tetramethyl-2-(9-phenylphenanthren-2-yl)-1,3,2-dioxaborolane (5): 40 mg; 79% yield; white solid; mp = 134-136 °C; **¹H NMR** (400 MHz, CDCl₃) δ 9.23 (s, 1H), 8.92 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.95-7.81 (m, 2H), 7.69-7.61 (m, 2H), 7.56-7.38 (m, 6H), 1.41 (s, 12H). **¹³C NMR** (101 MHz, CDCl₃) δ 140.7, 139.9, 133.5, 132.1, 131.1, 130.9, 130.0, 130.0, 129.2, 128.3, 127.8, 127.4, 127.4, 126.8, 126.5, 126.4, 123.2, 83.9, 24.9. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₂₆H₂₅BNaO₂ 403.1840; found: 403.1842.



9-phenyl-2-(10-phenylanthracen-9-yl)phenanthrene (Phenacene-type compound A): 63 mg; 62% yield; white solid; mp = 130-132 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.86 (s, 1H), 8.72-8.65 (m, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.98 (dd, J = 8.0, 1.6 Hz, 1H), 7.86 (s, 1H), 7.79-7.72 (m, 5H), 7.65-7.59 (m, 4H), 7.59-7.47 (m, 8H), 7.38-7.26 (m, 4H). **¹³C NMR** (101 MHz, CDCl₃) δ 140.8, 139.2, 139.1, 137.4, 137.4, 137.2, 131.4, 131.3, 130.8, 130.6, 130.2, 130.2, 130.1, 130.0, 129.9, 128.7, 128.5, 128.4, 127.5, 127.5, 127.3, 127.0, 126.7, 126.6, 125.4, 125.2, 125.1, 123.1. **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₄₀H₂₆Na 529.1927; found: 529.1928.

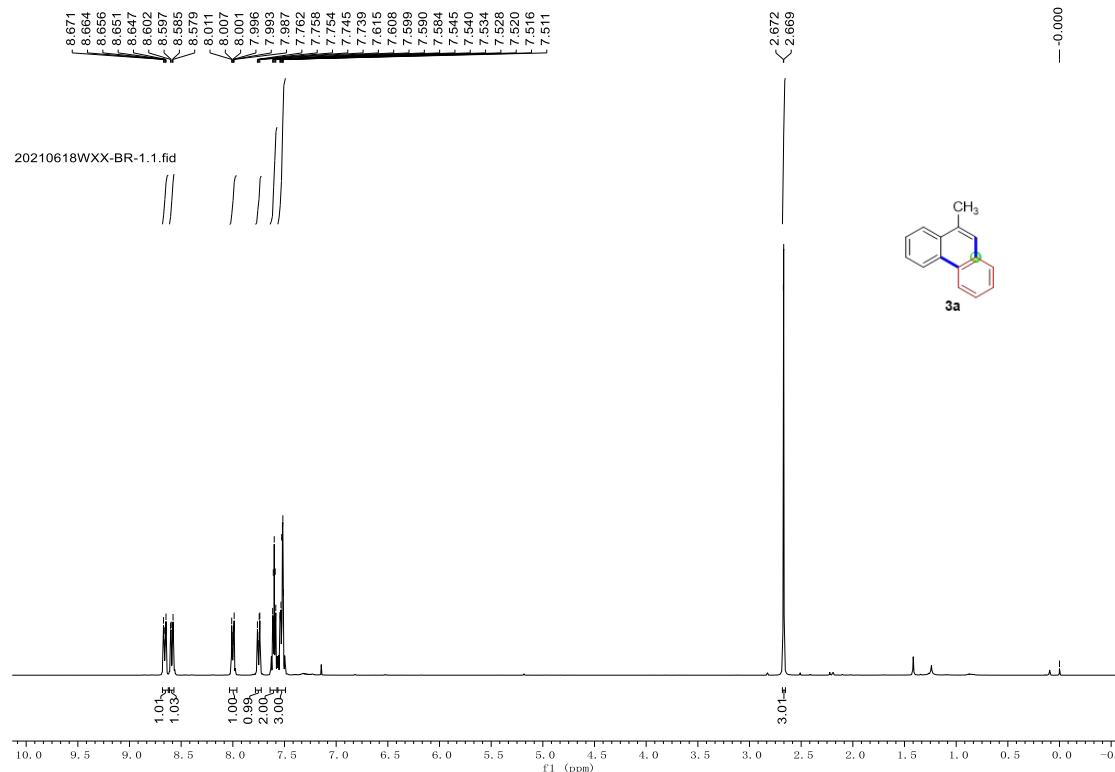
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9. NMR spectra

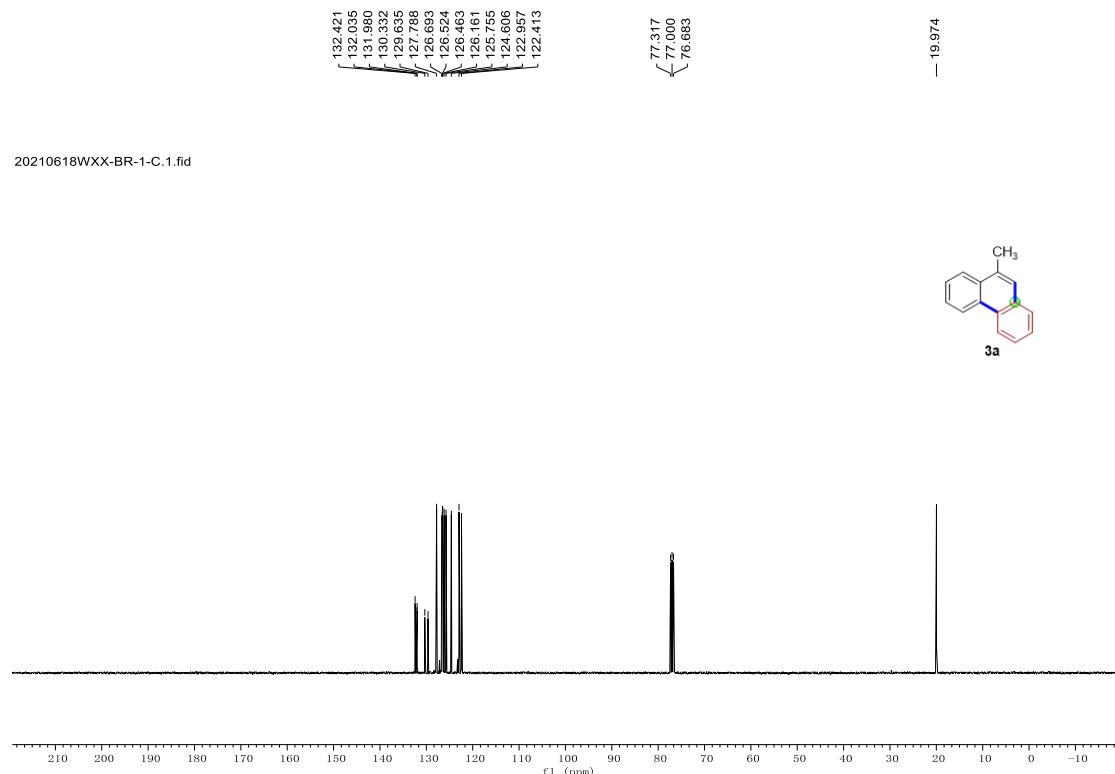
9-methylphenanthrene (3a):

(^1H NMR, CDCl_3 , 400 MHz)



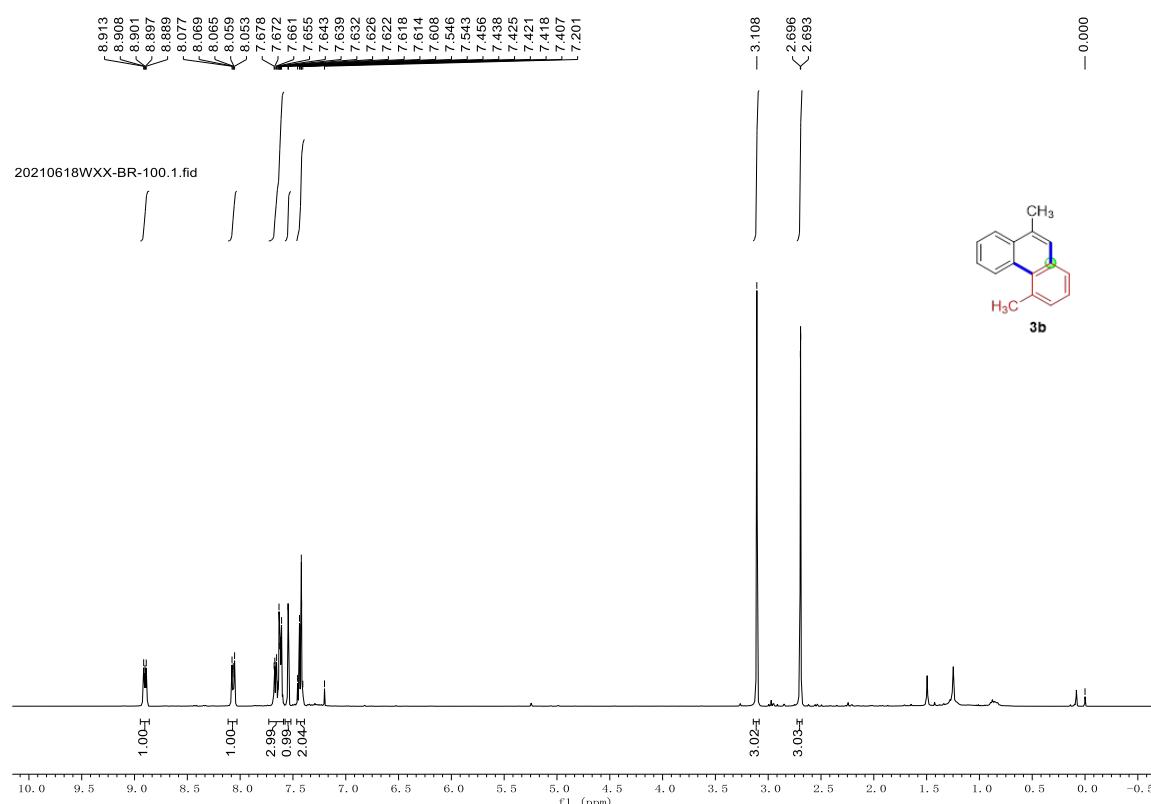
9-methylphenanthrene (3a):

(^{13}C NMR, CDCl_3 , 101 MHz)



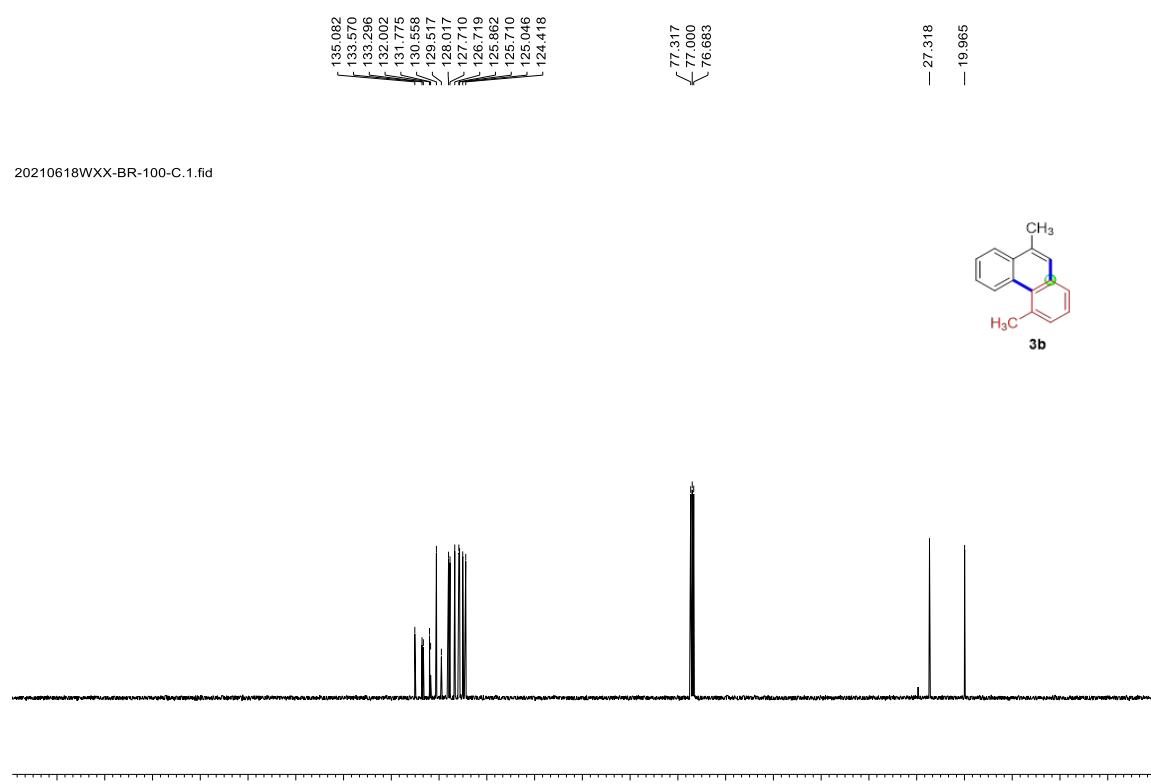
4,9-dimethylphenanthrene (3b):

(^1H NMR, CDCl_3 , 400 MHz)



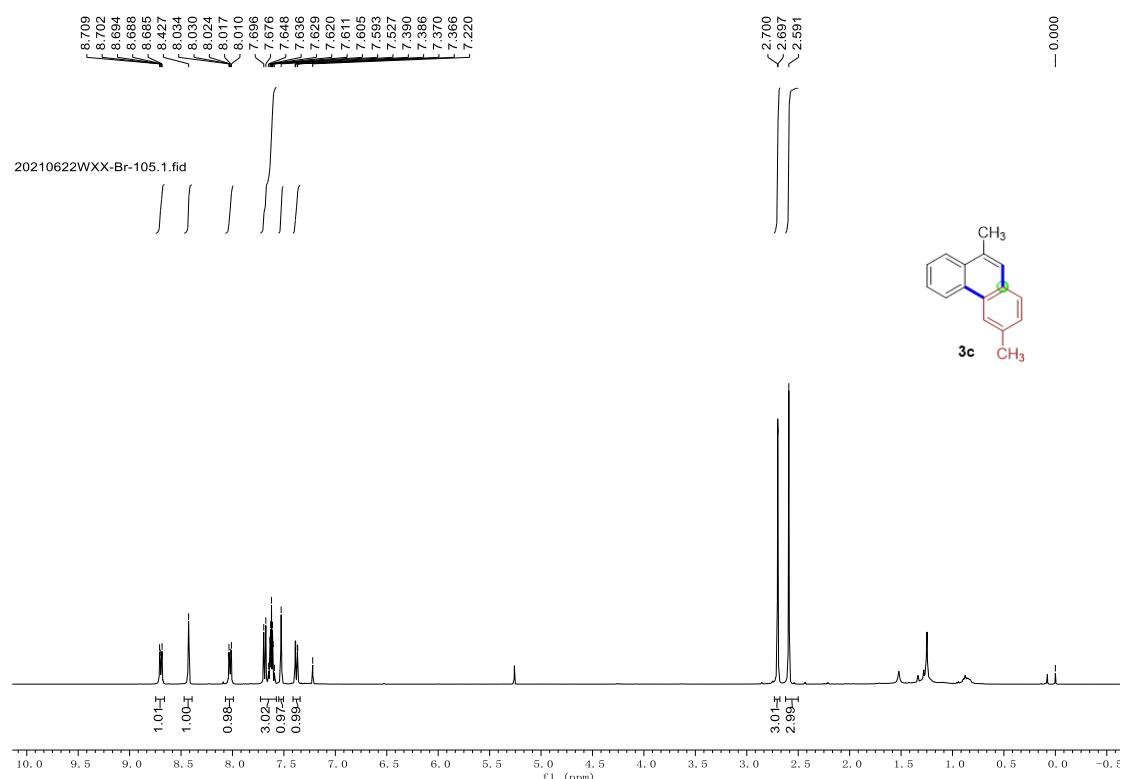
4,9-dimethylphenanthrene (3b):

(^{13}C NMR, CDCl_3 , 101 MHz)



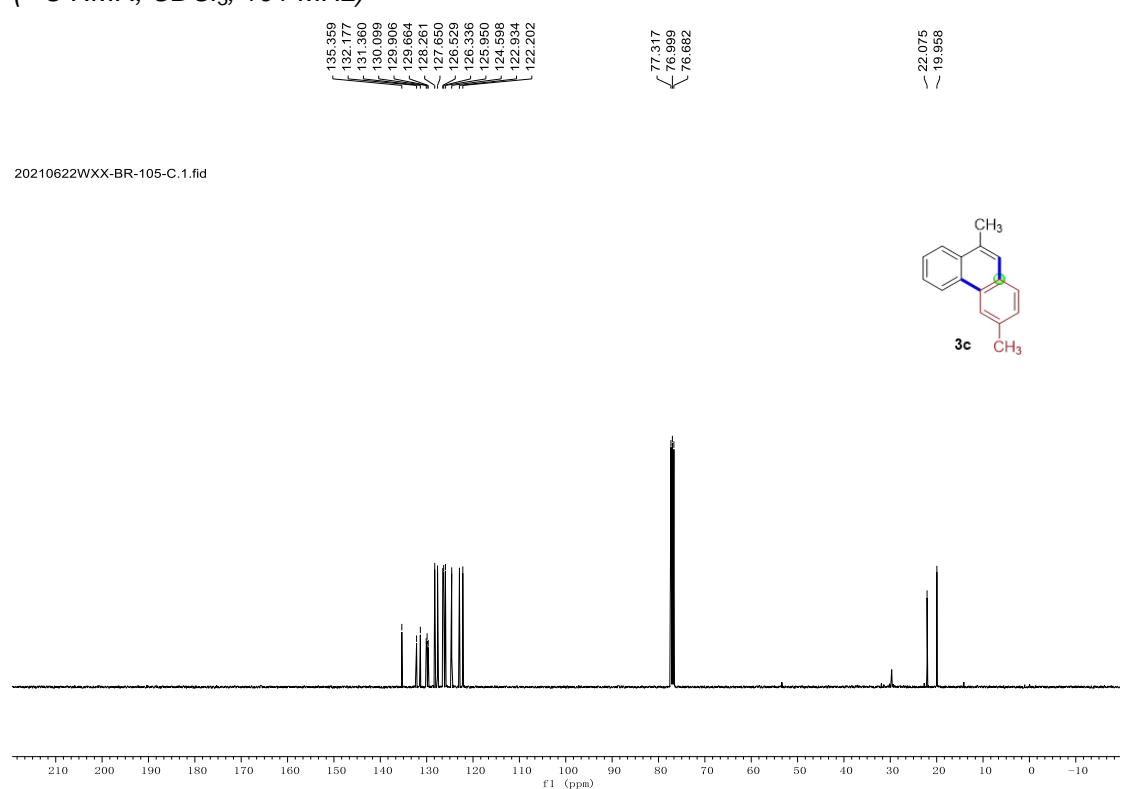
3,9-dimethylphenanthrene (3c):

(^1H NMR, CDCl_3 , 400 MHz)



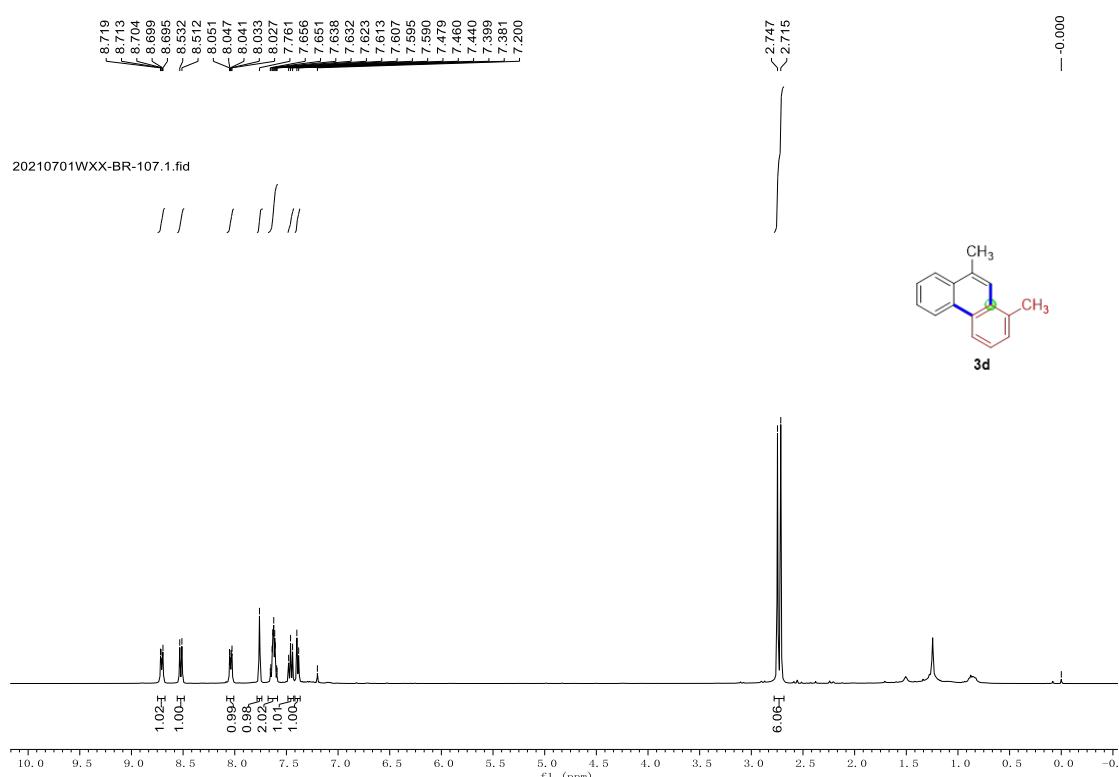
3,9-dimethylphenanthrene (3c):

(^{13}C NMR, CDCl_3 , 101 MHz)



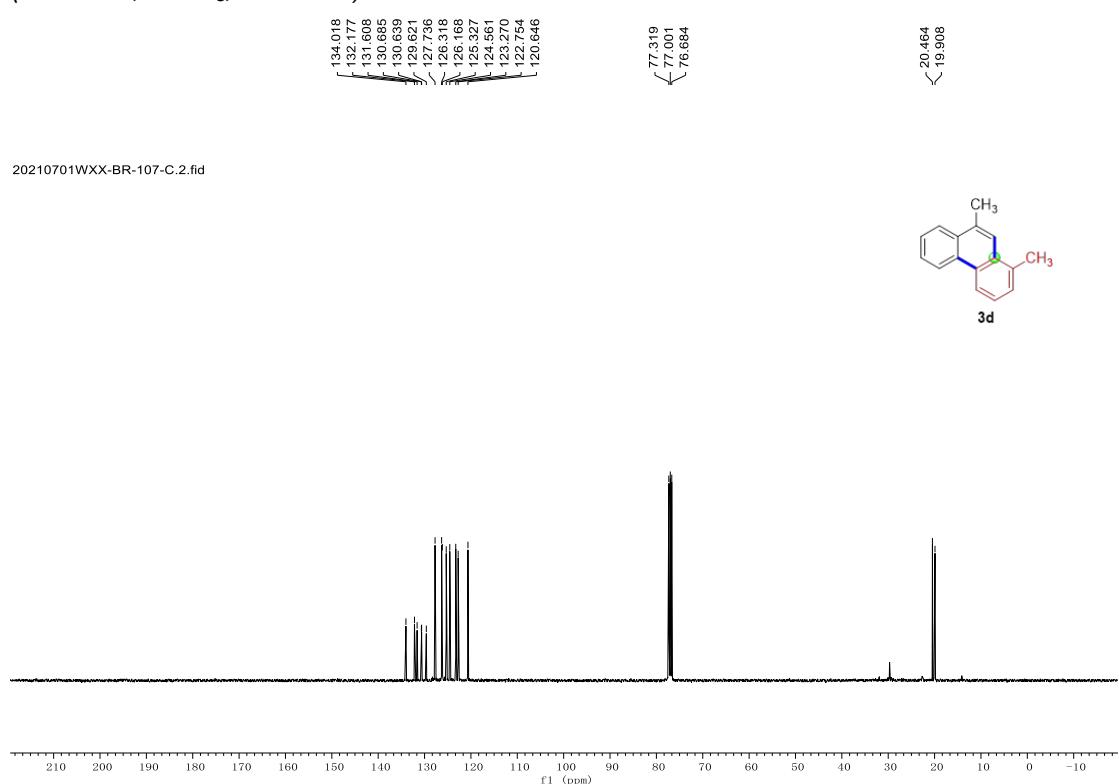
1,9-dimethylphenanthrene (3d):

(^1H NMR, CDCl_3 , 400 MHz)



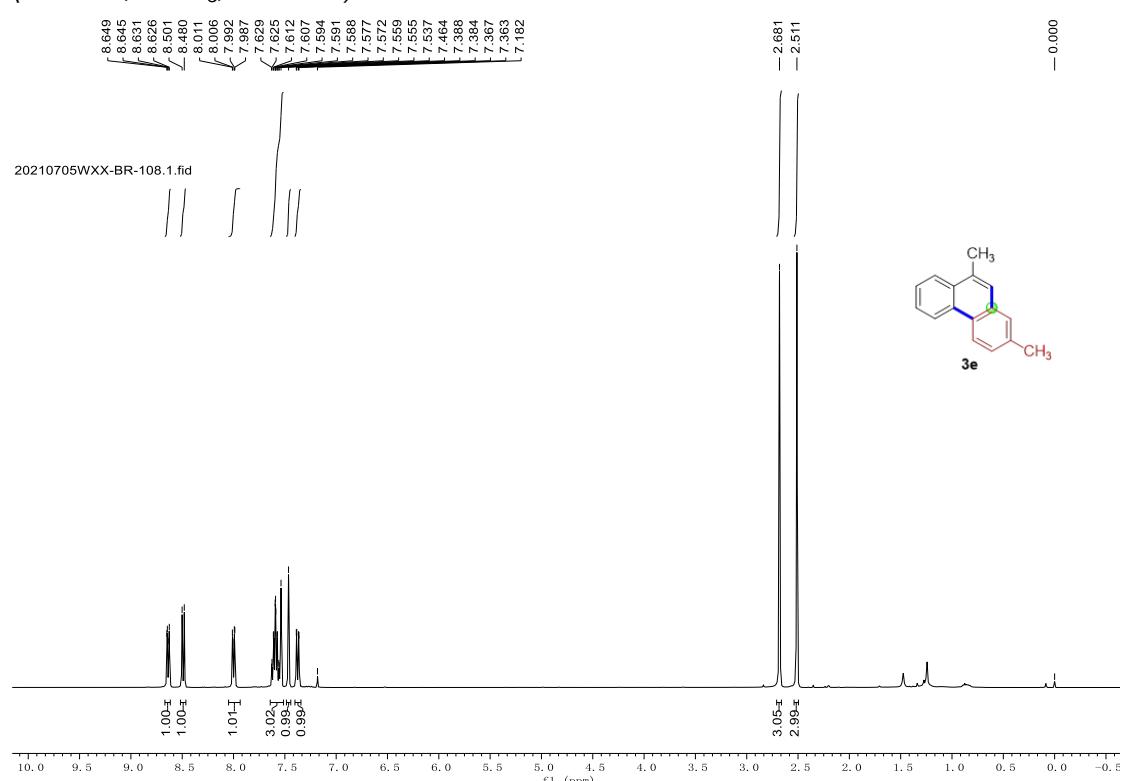
1,9-dimethylphenanthrene (3d):

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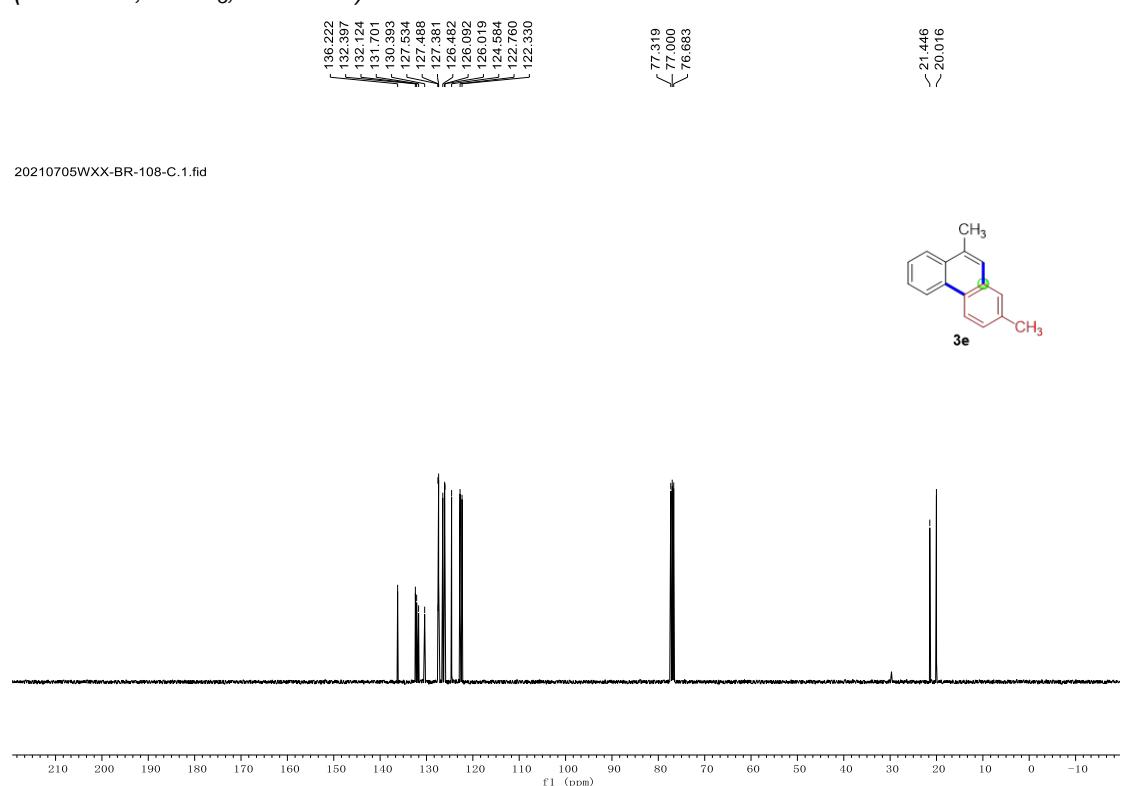
2,9-dimethylphenanthrene (3e):

(^1H NMR, CDCl_3 , 400 MHz)



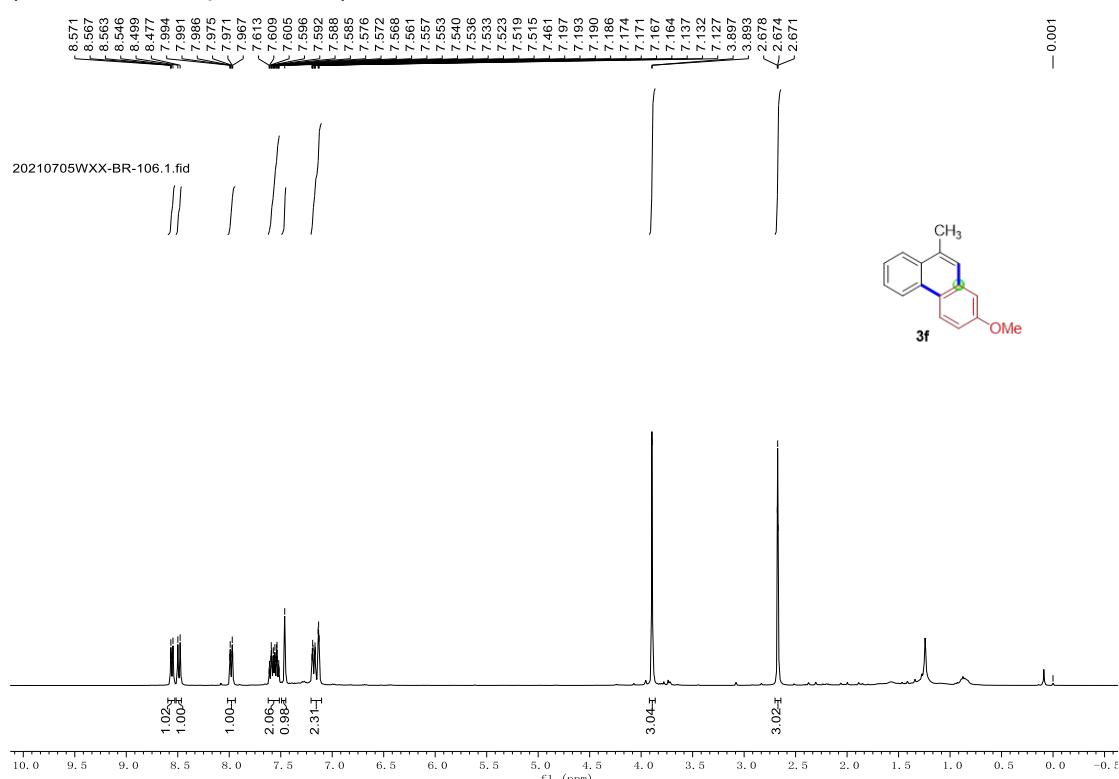
2,9-dimethylphenanthrene (3e):

(^{13}C NMR, CDCl_3 , 101 MHz)



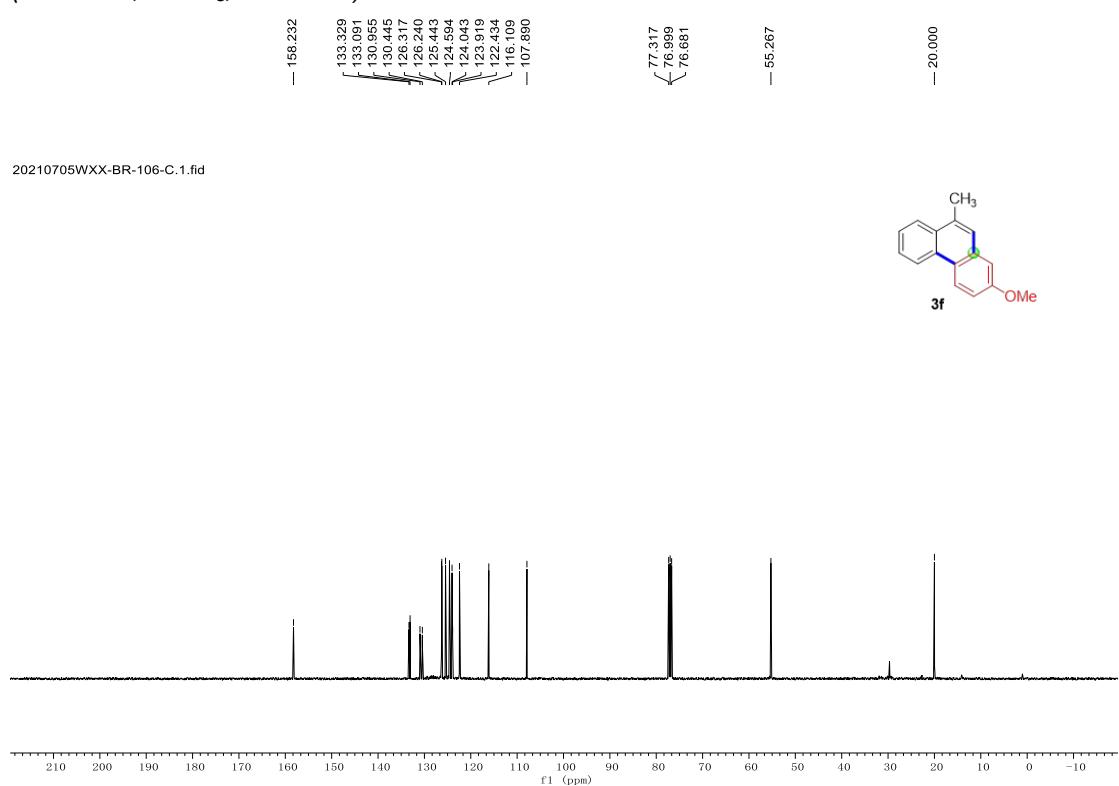
2-methoxy-9-methylphenanthrene (3f):

(^1H NMR, CDCl_3 , 400 MHz)



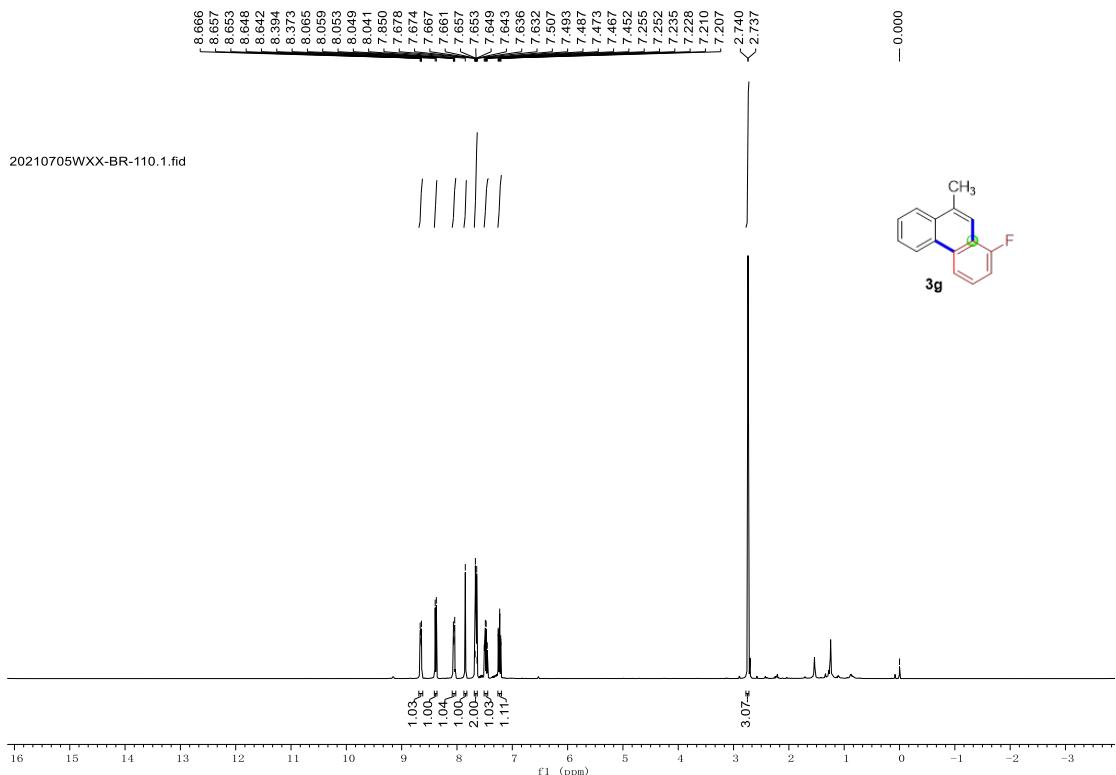
2-methoxy-9-methylphenanthrene (3f):

(^{13}C NMR, CDCl_3 , 101 MHz)



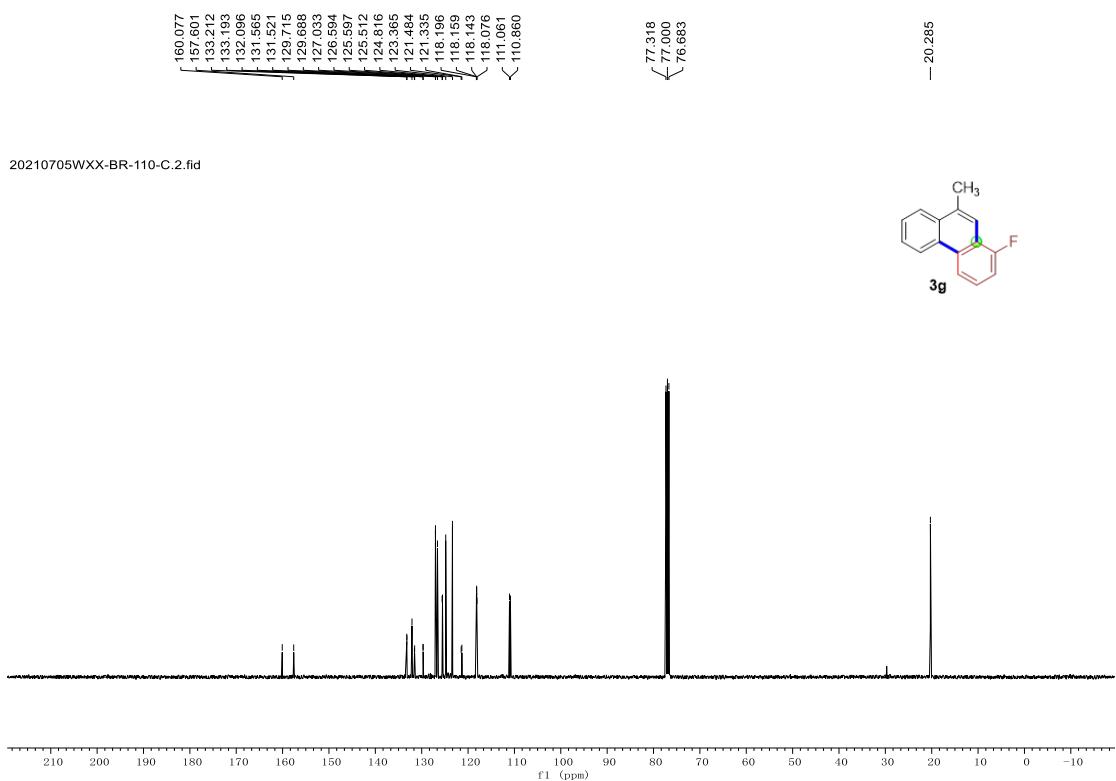
1-fluoro-9-methylphenanthrene (3g):

(^1H NMR, CDCl_3 , 400 MHz)



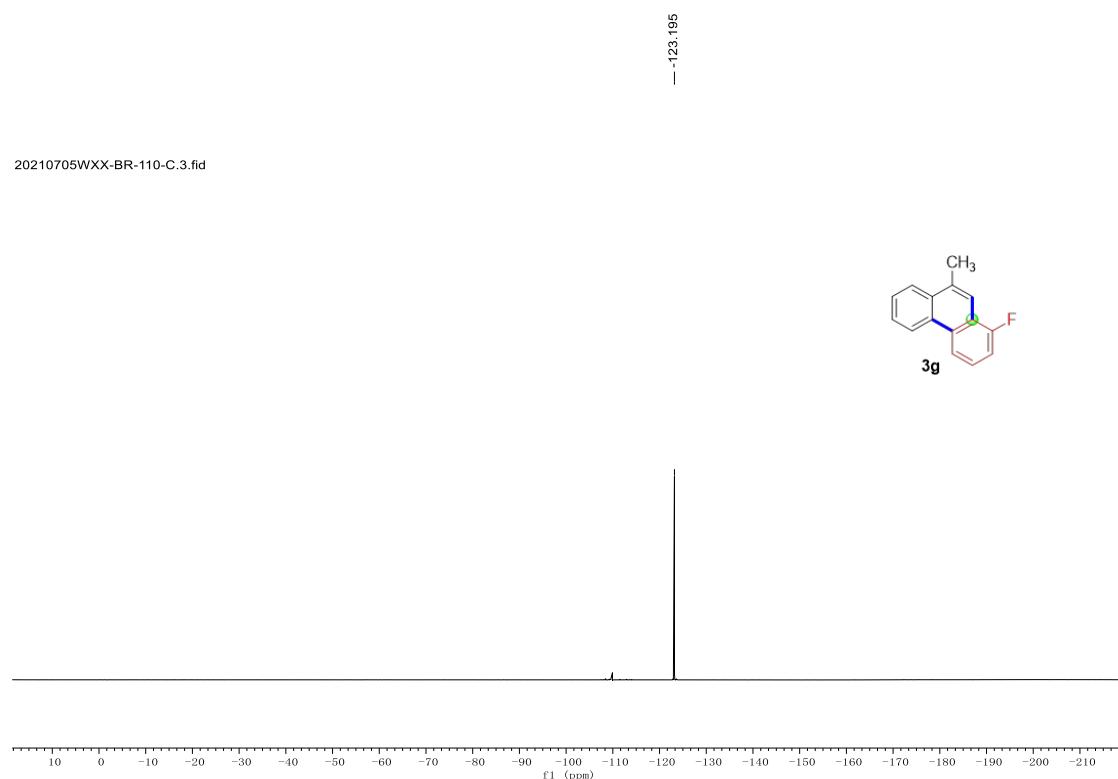
1-fluoro-9-methylphenanthrene (3g):

(^{13}C NMR, CDCl_3 , 101 MHz)



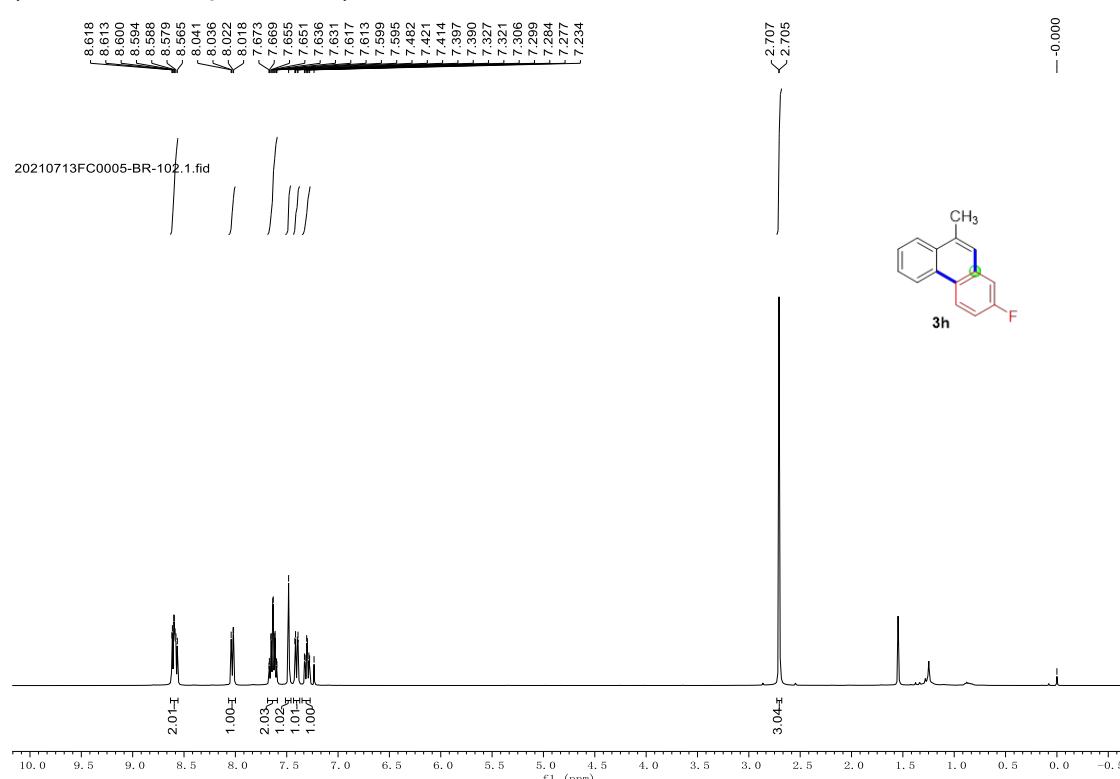
1-fluoro-9-methylphenanthrene (3g):

(^{19}F NMR, CDCl_3 , 376 MHz)



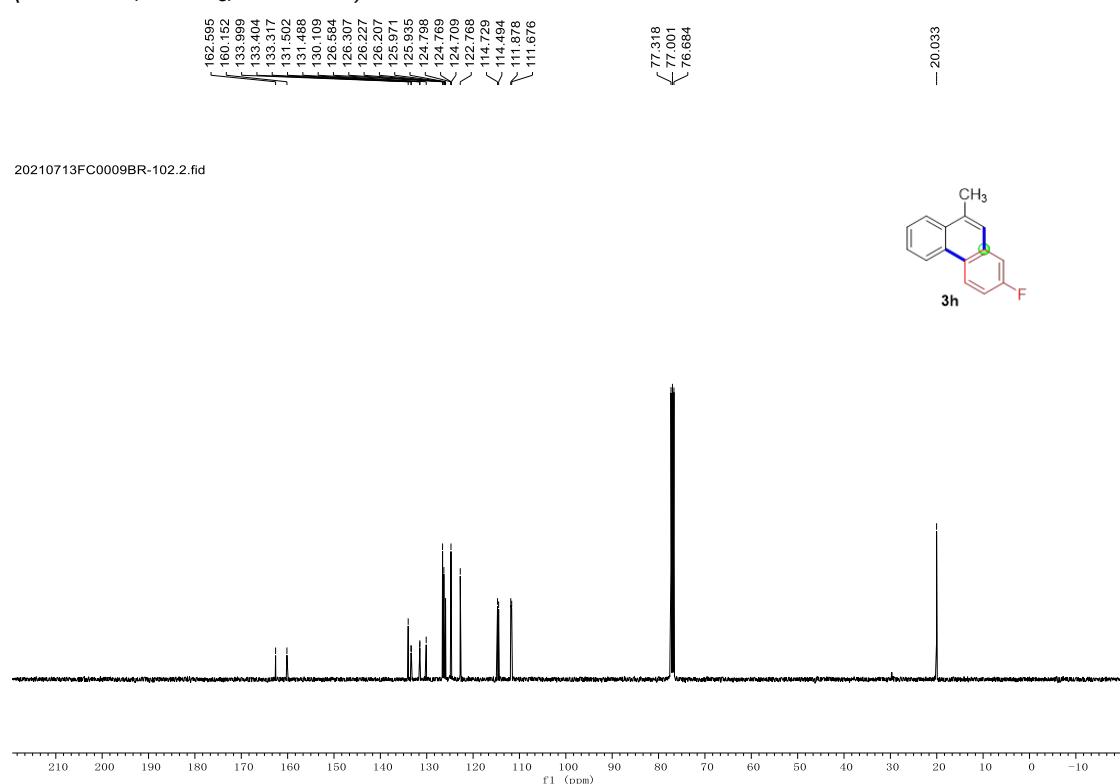
2-fluoro-9-methylphenanthrene (3h):

(^1H NMR, CDCl_3 , 400 MHz)



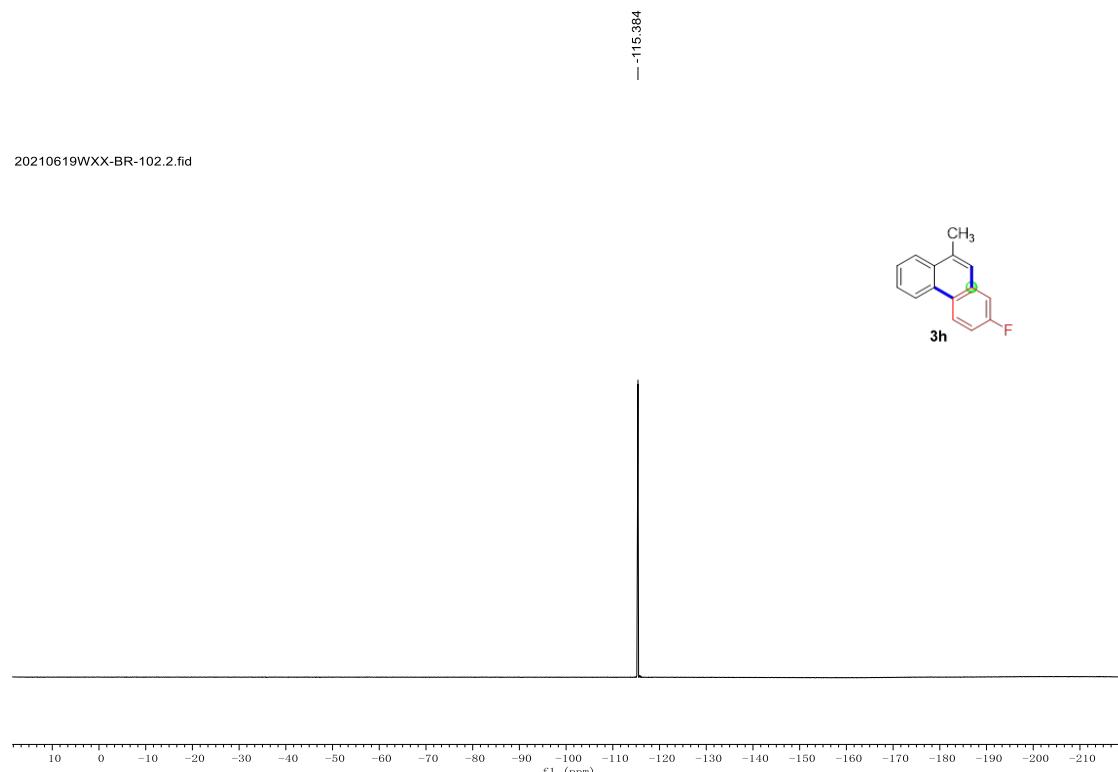
2-fluoro-9-methylphenanthrene (3h):

(^{13}C NMR, CDCl_3 , 101 MHz)



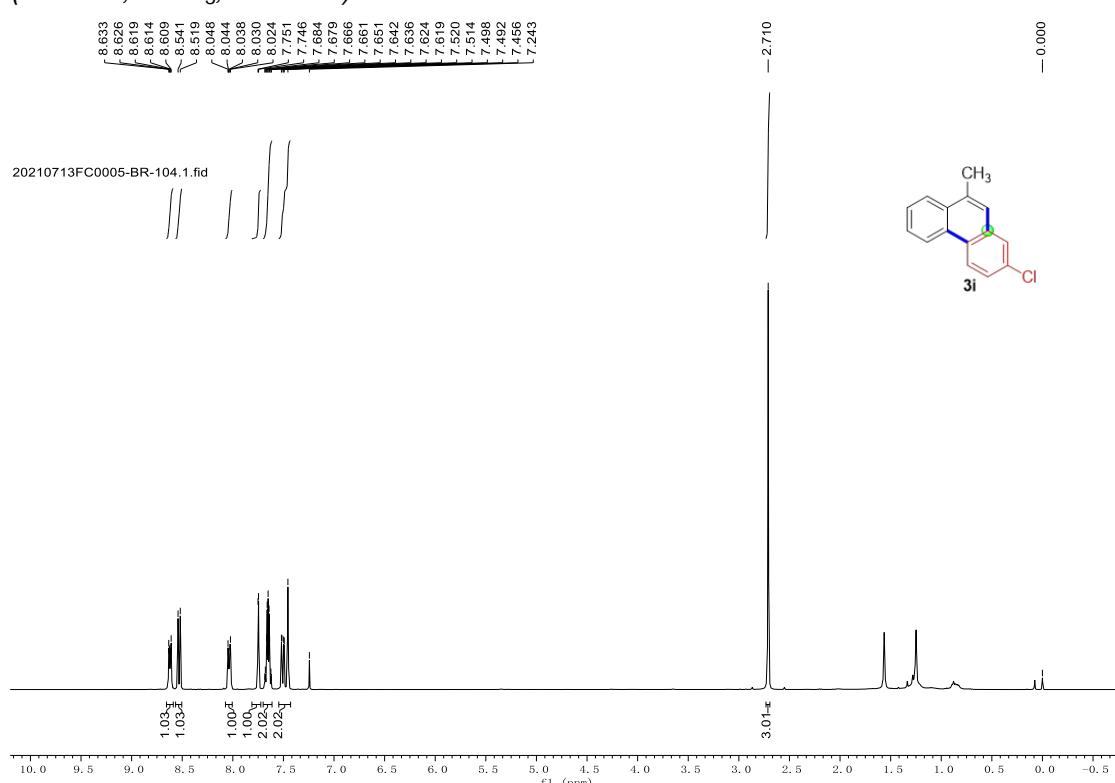
2-fluoro-9-methylphenanthrene (3h):

(^{19}F NMR, CDCl_3 , 376 MHz)



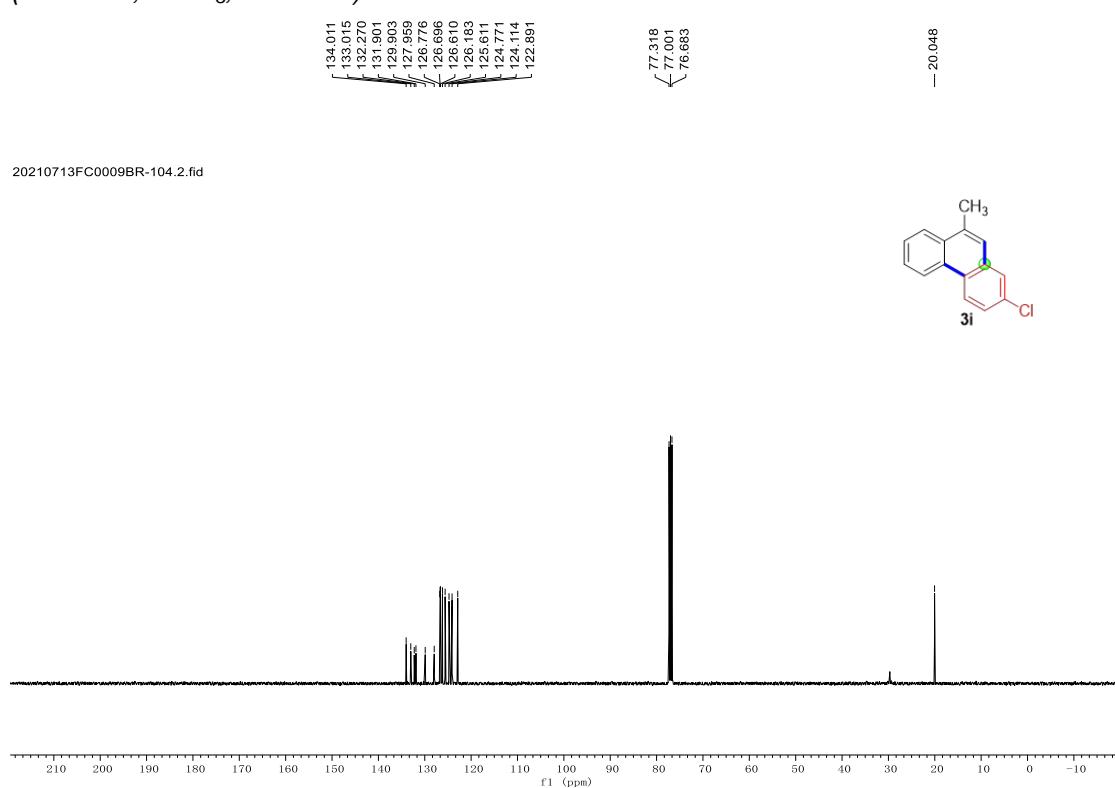
2-chloro-9-methylphenanthrene (3i):

(1H NMR, $CDCl_3$, 400 MHz)



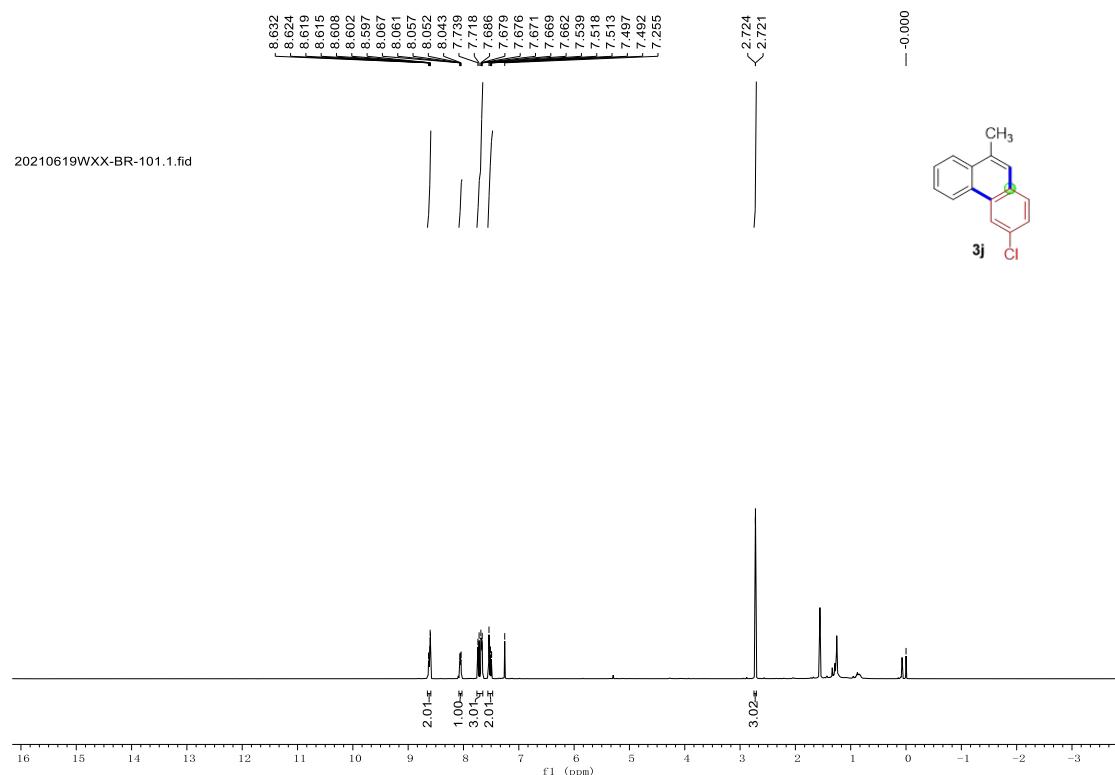
2-chloro-9-methylphenanthrene (3i):

(^{13}C NMR, CDCl_3 , 101 MHz)

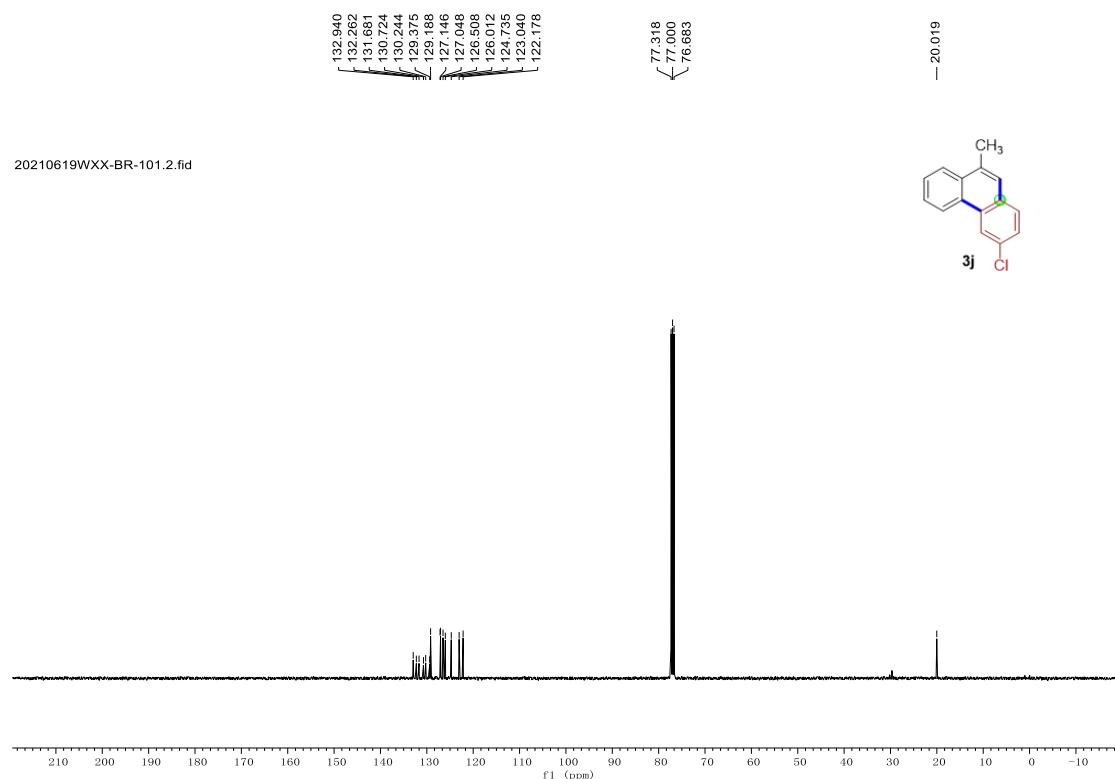


3-chloro-9-methylphenanthrene (3j) :

(^1H NMR, CDCl_3 , 400 MHz)

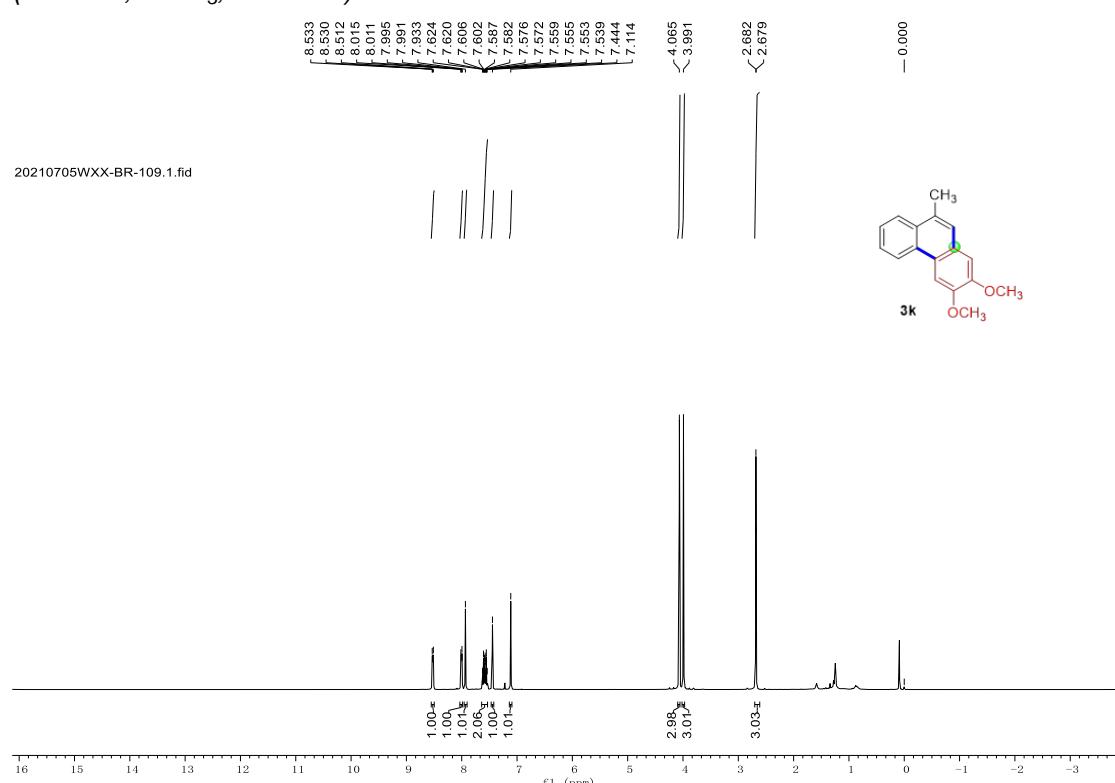


(^{13}C NMR, CDCl_3 , 101 MHz)



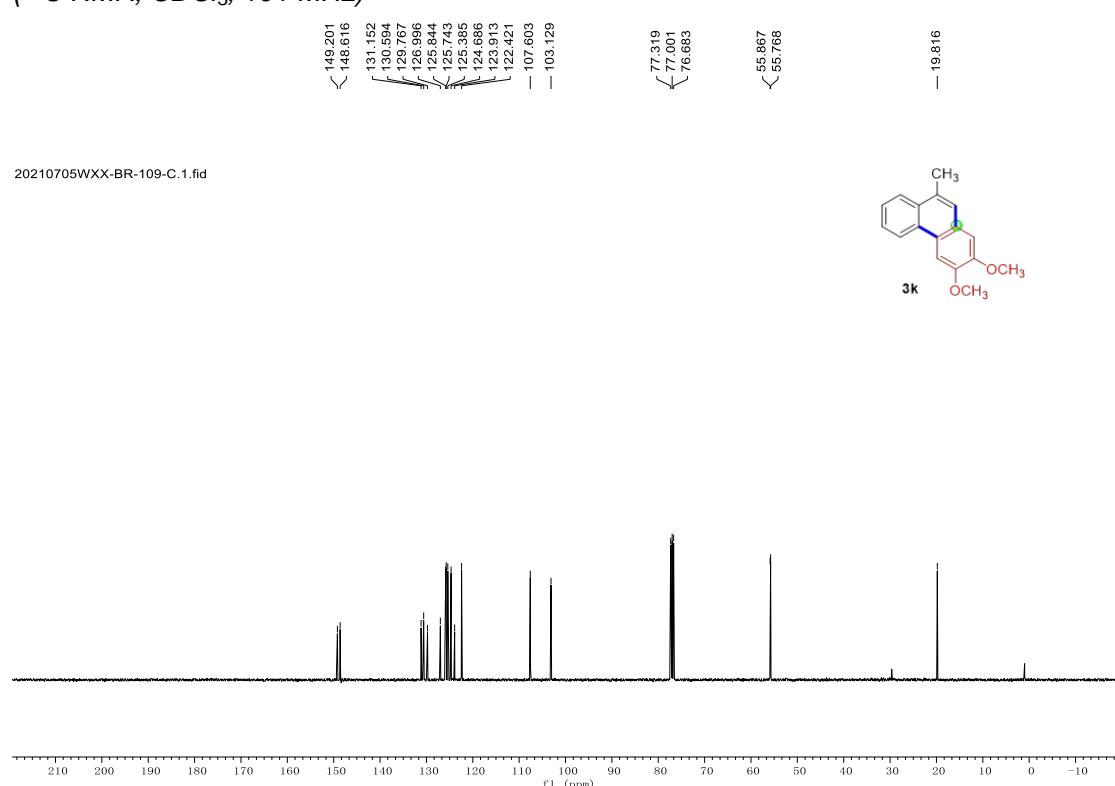
2,3-dimethoxy-9-methylphenanthrene (3k):

(^1H NMR, CDCl_3 , 400 MHz)



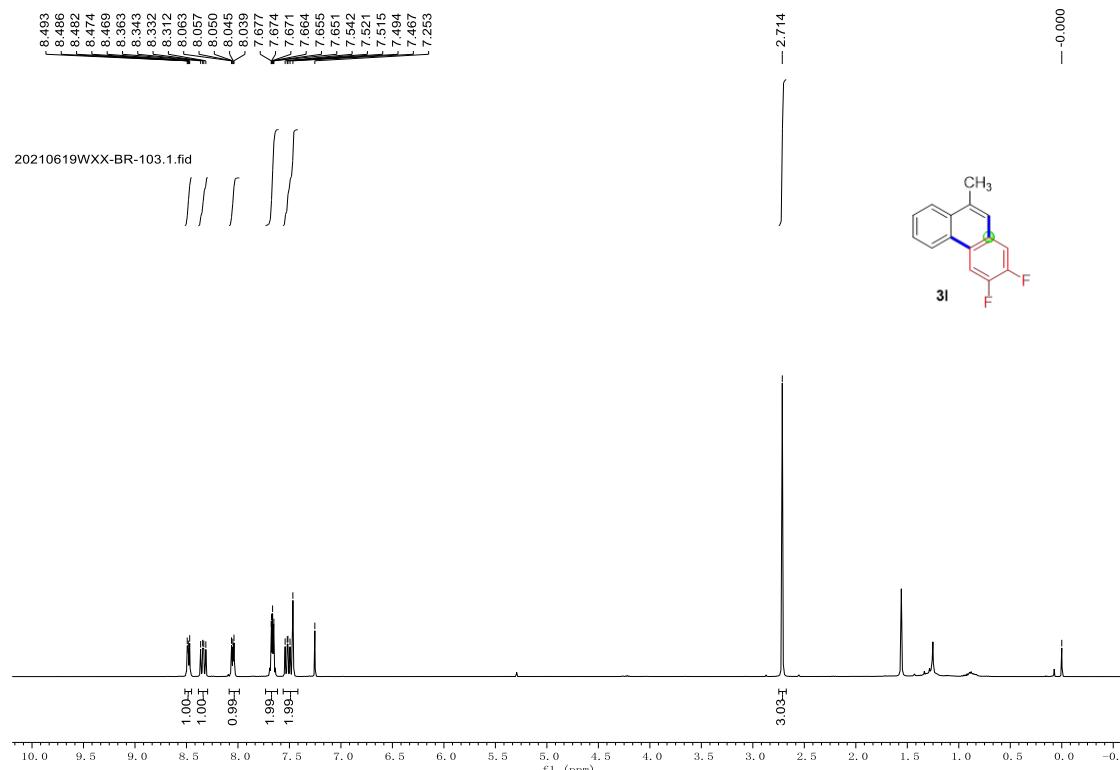
2,3-dimethoxy-9-methylphenanthrene (3k):

(^{13}C NMR, CDCl_3 , 101 MHz)



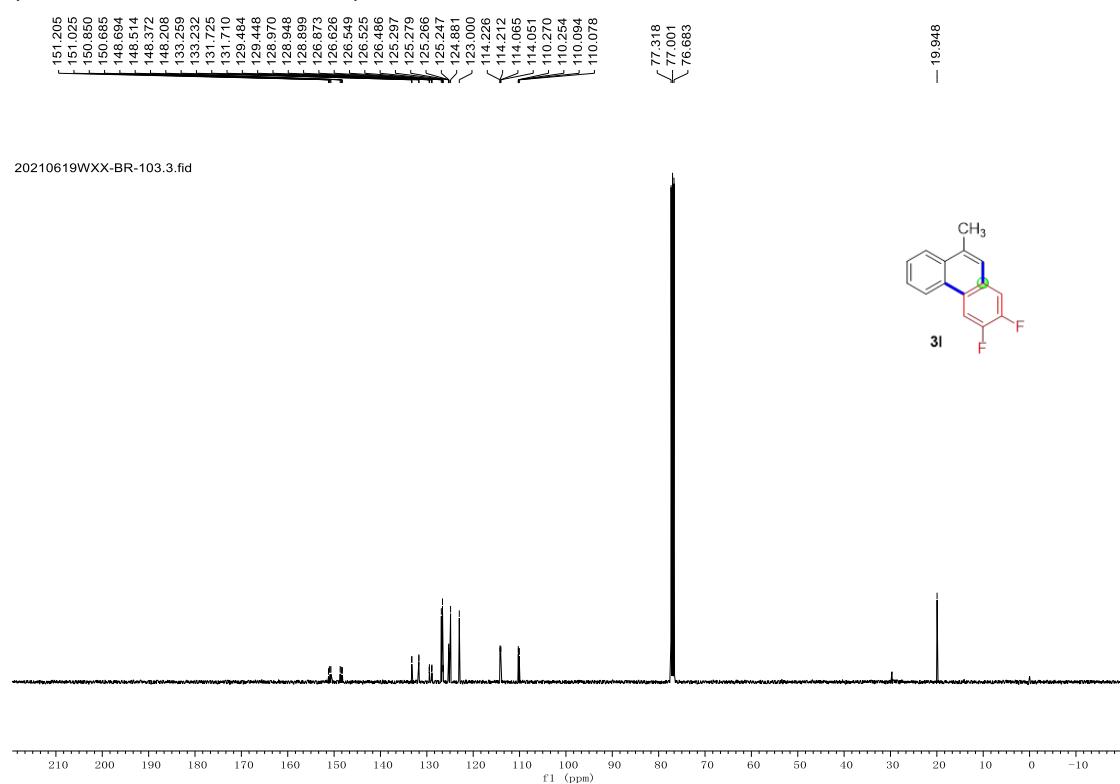
2,3-difluoro-9-methylphenanthrene (3l):

(^1H NMR, CDCl_3 , 400 MHz)



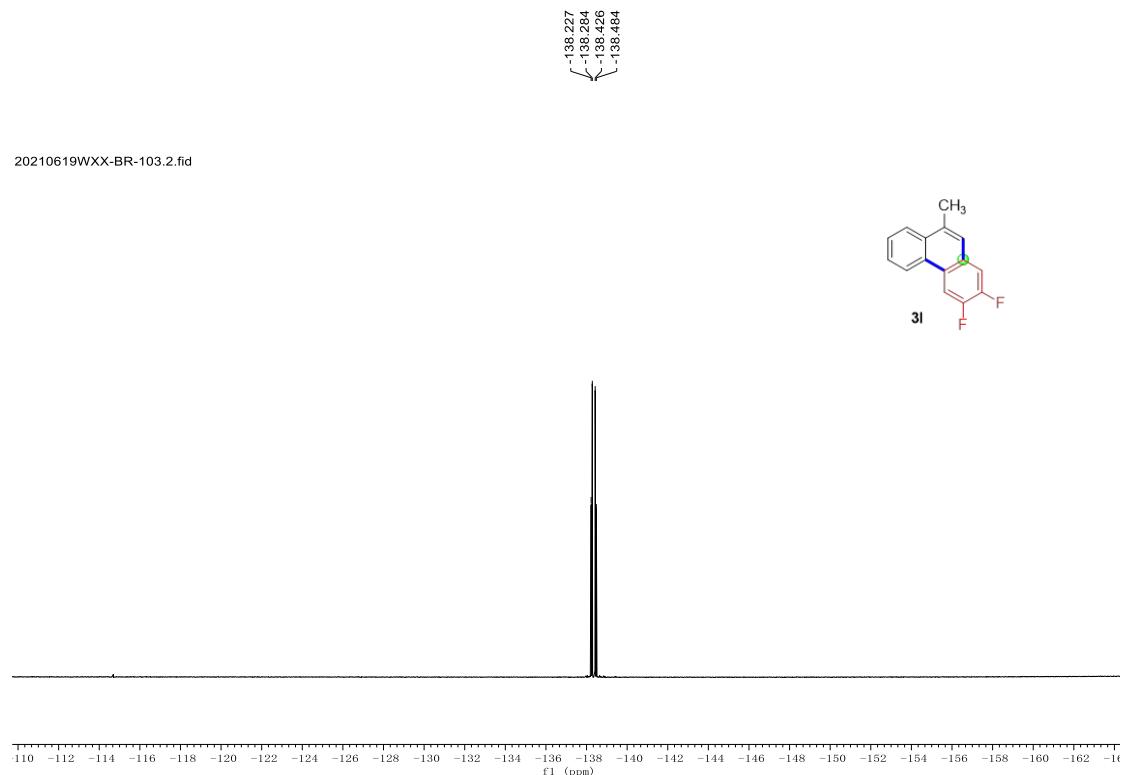
2,3-difluoro-9-methylphenanthrene (3l):

(^{13}C NMR, CDCl_3 , 101 MHz)



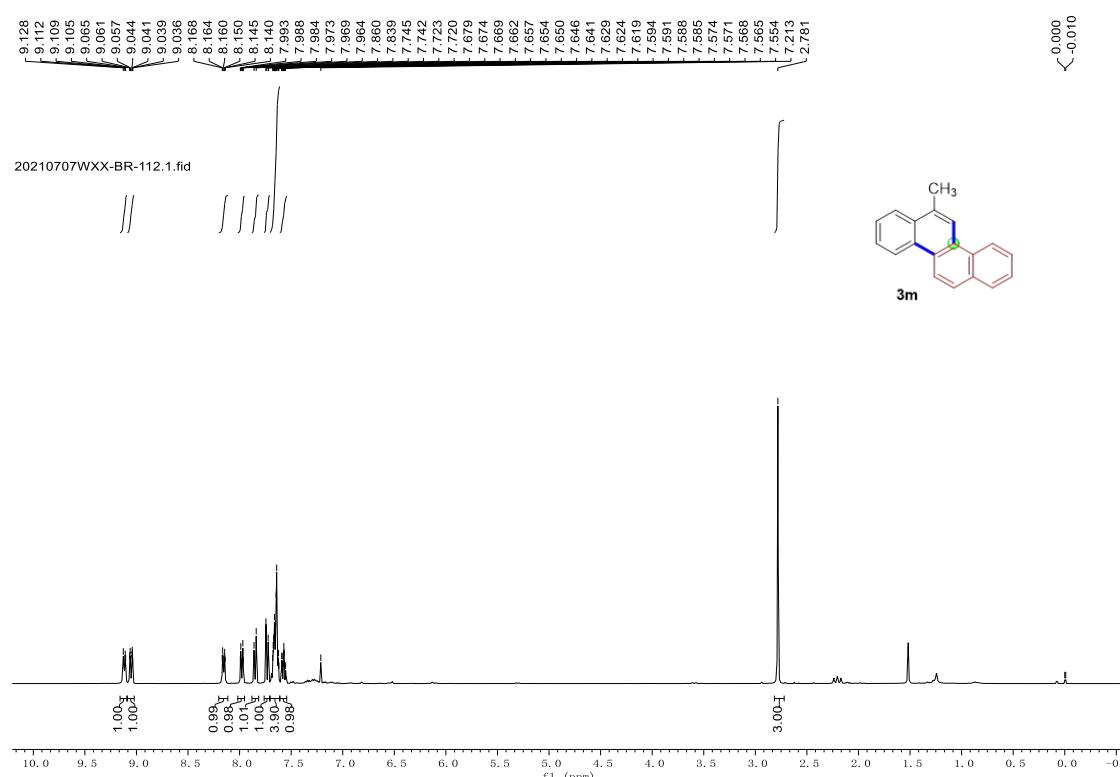
2,3-difluoro-9-methylphenanthrene (3l):

(^{19}F NMR, CDCl_3 , 376 MHz)



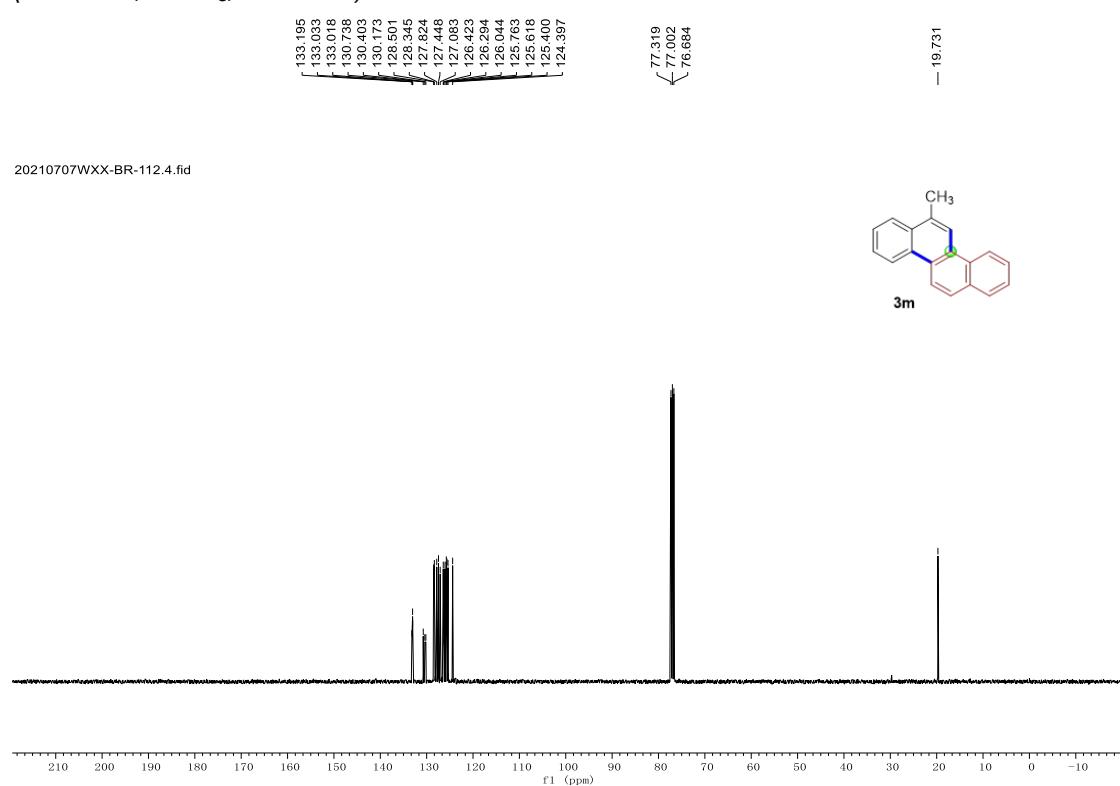
6-methylchrysene (3m):

(^1H NMR, CDCl_3 , 400 MHz)



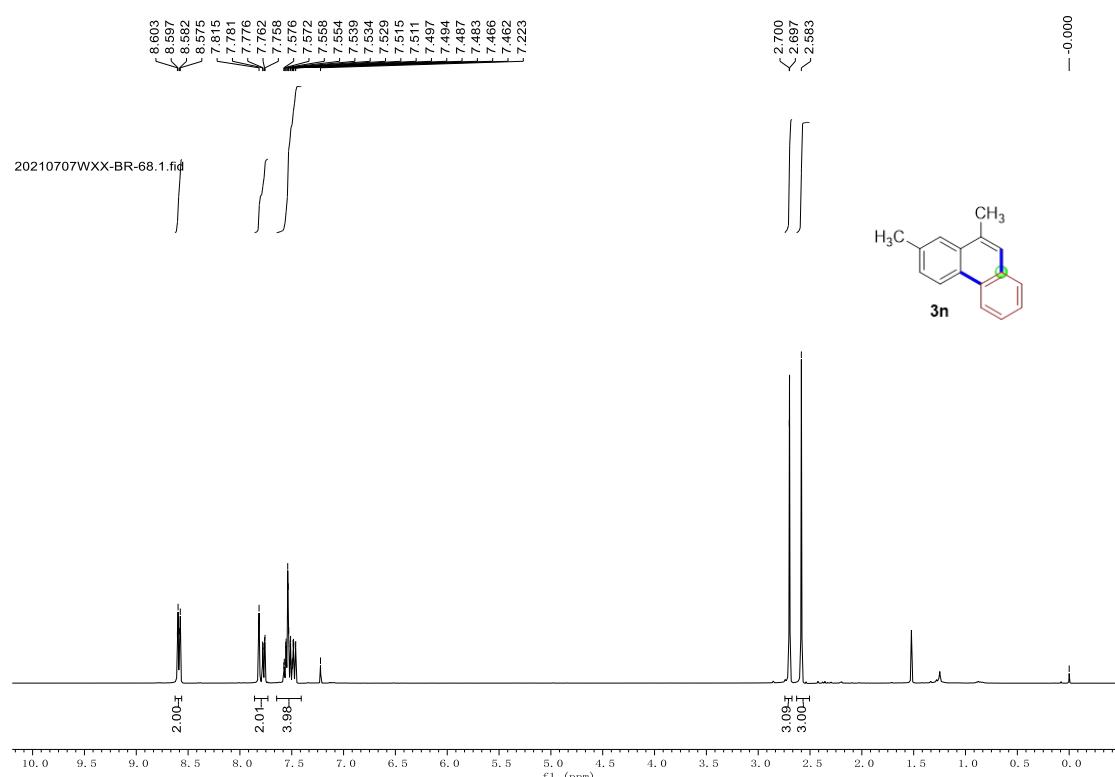
6-methylchrysene (3m):

(^{13}C NMR, CDCl_3 , 101 MHz)



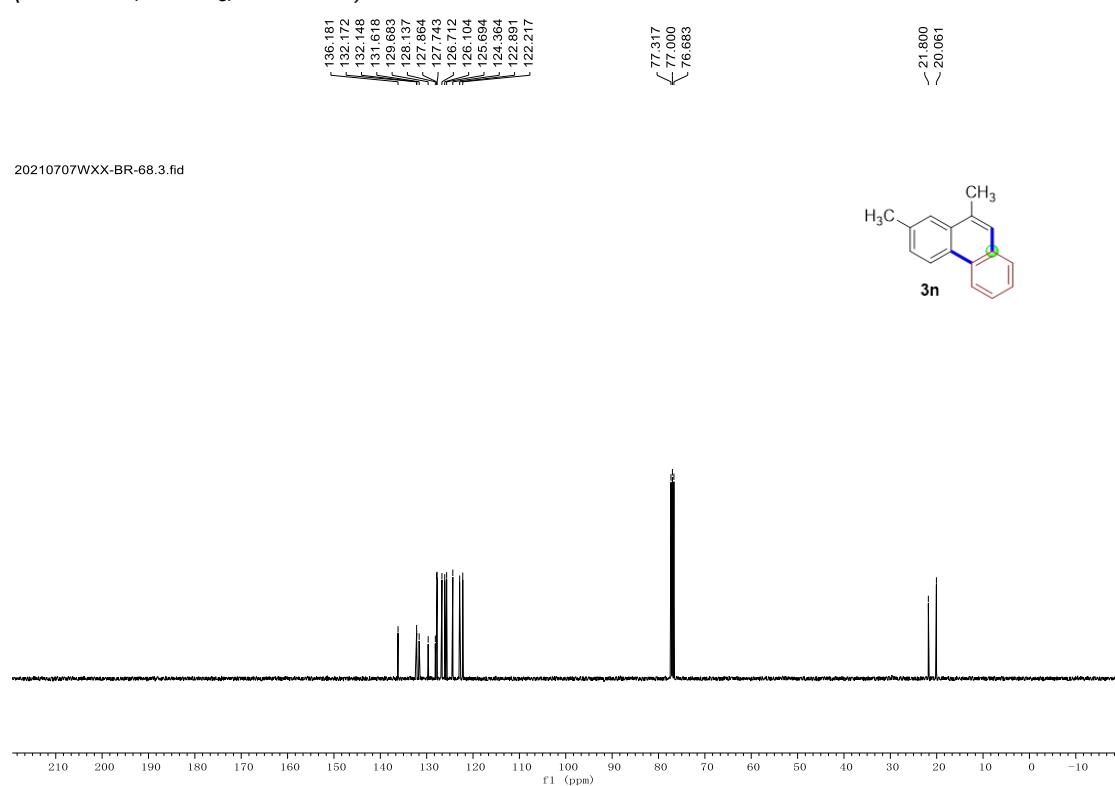
2,10-dimethylphenanthrene (3n):

(^1H NMR, CDCl_3 , 400 MHz)



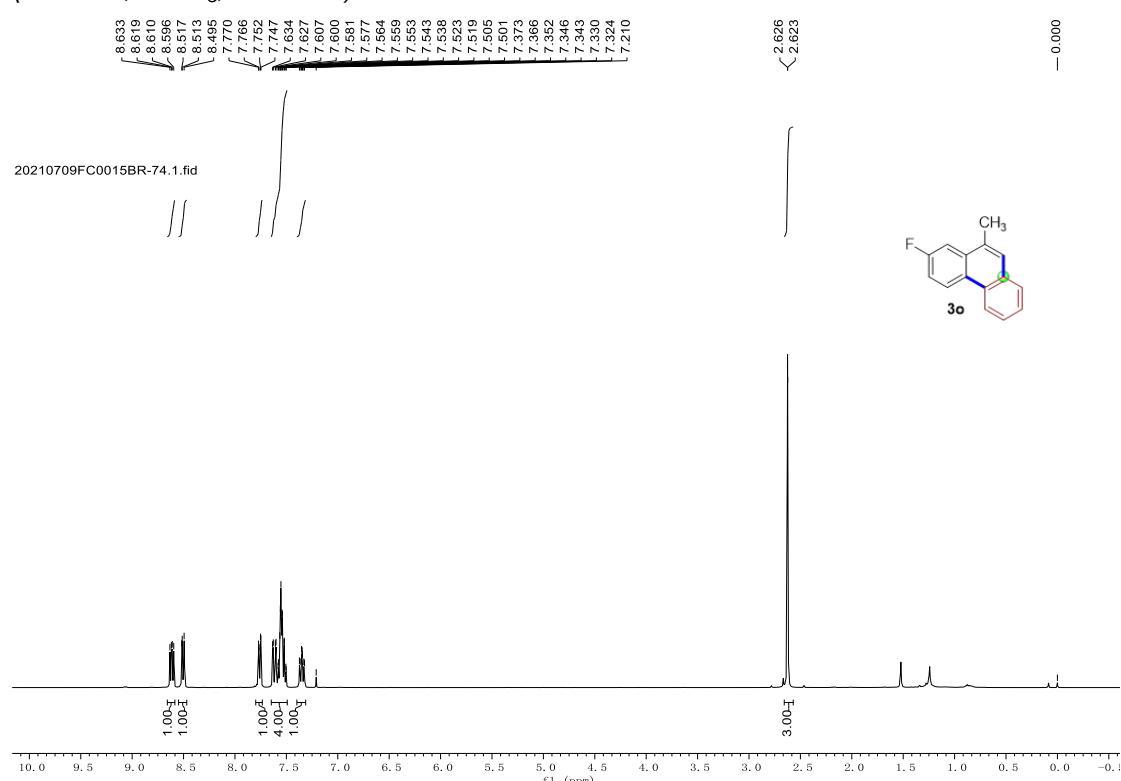
2,10-dimethylphenanthrene (3n):

(^{13}C NMR, CDCl_3 , 101 MHz)



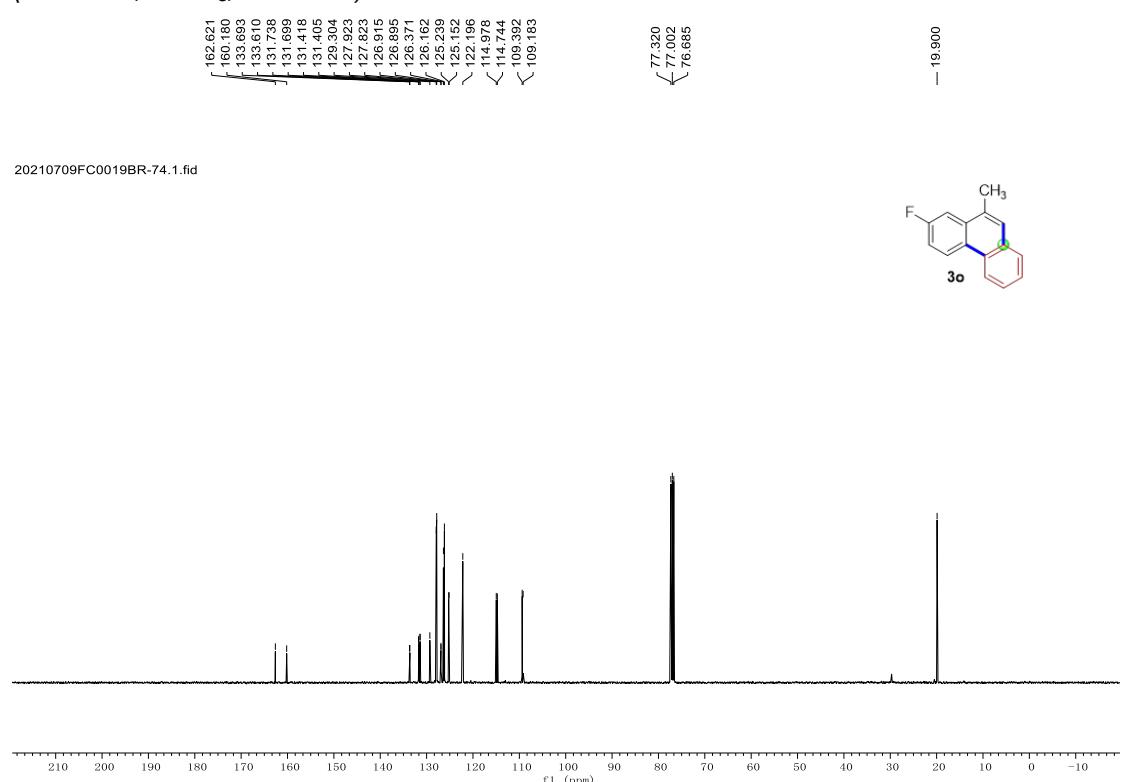
2-fluoro-10-methylphenanthrene (3o**):**

(^1H NMR, CDCl_3 , 400 MHz)



2-fluoro-10-methylphenanthrene (3o**):**

(^{13}C NMR, CDCl_3 , 101 MHz)

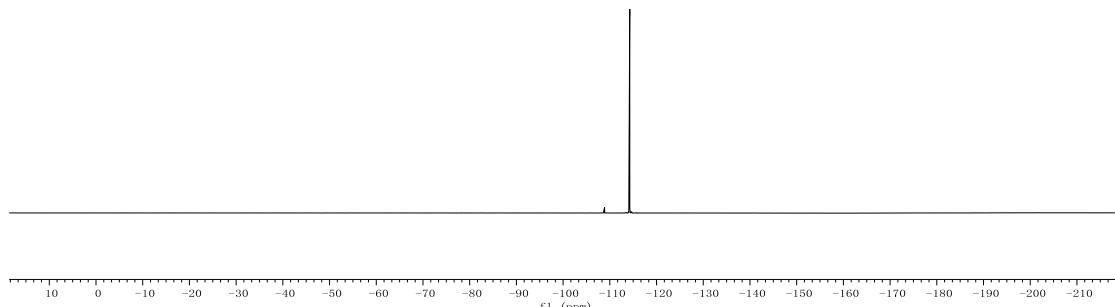
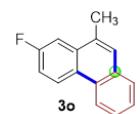


2-fluoro-10-methylphenanthrene (3o):

(^{19}F NMR, CDCl_3 , 376 MHz)

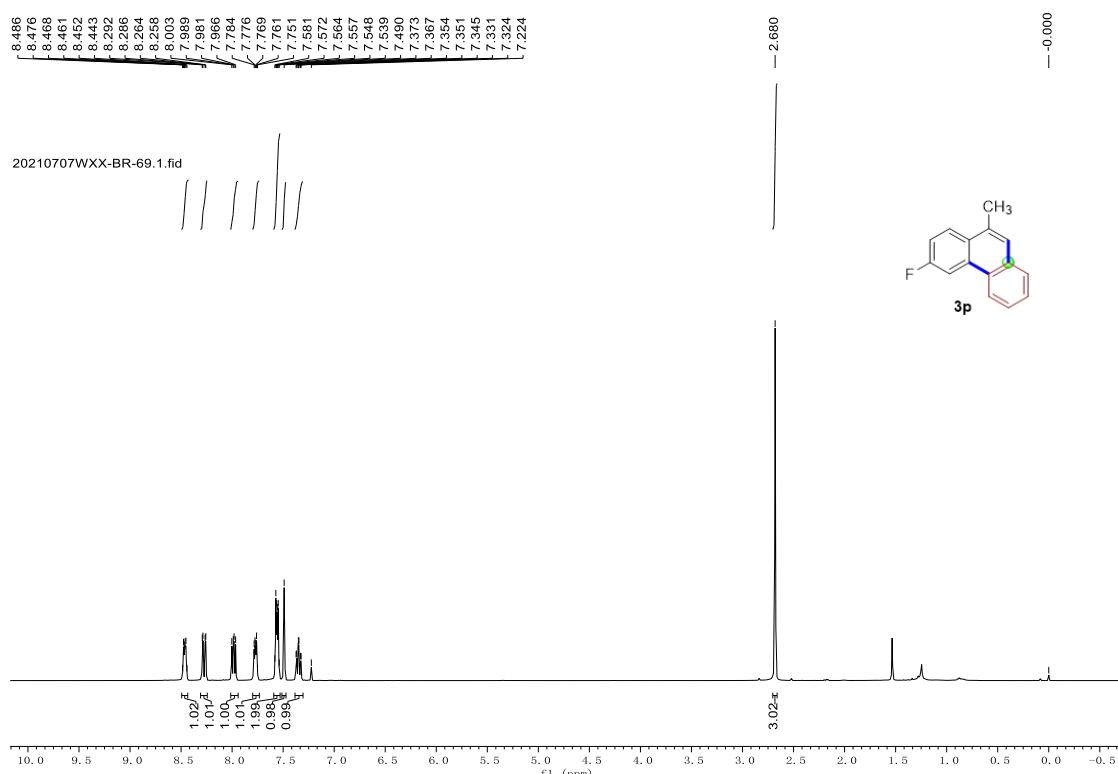
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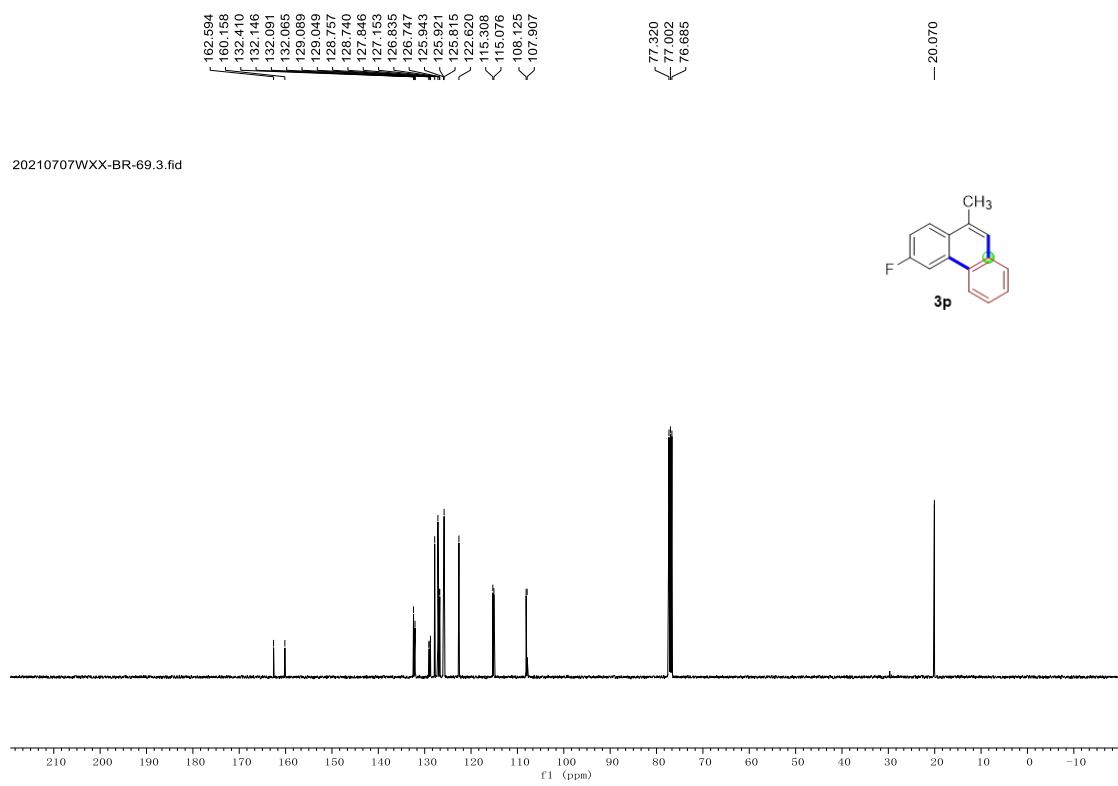
3-fluoro-10-methylphenanthrene (3p):

(1H NMR, $CDCl_3$, 400 MHz)



3-fluoro-10-methylphenanthrene (3p):

(^{13}C NMR, CDCl_3 , 101 MHz)

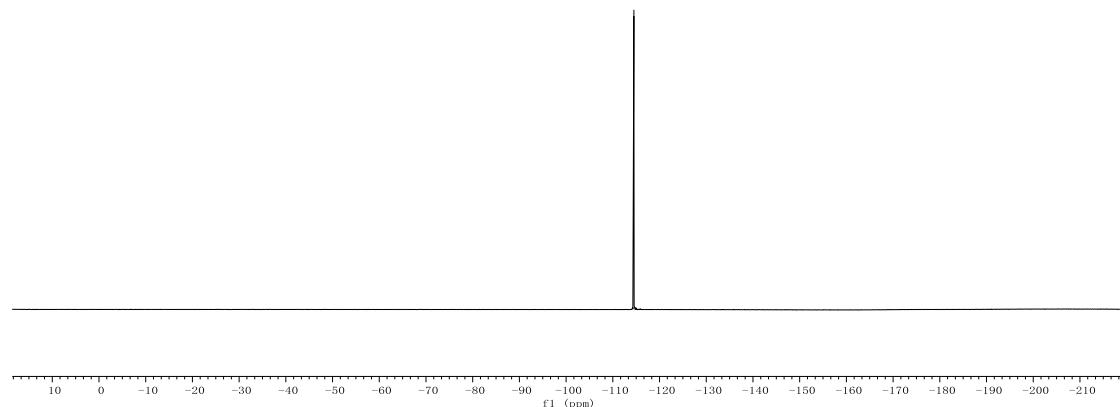
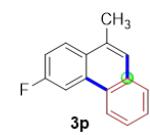


3-fluoro-10-methylphenanthrene (3p):

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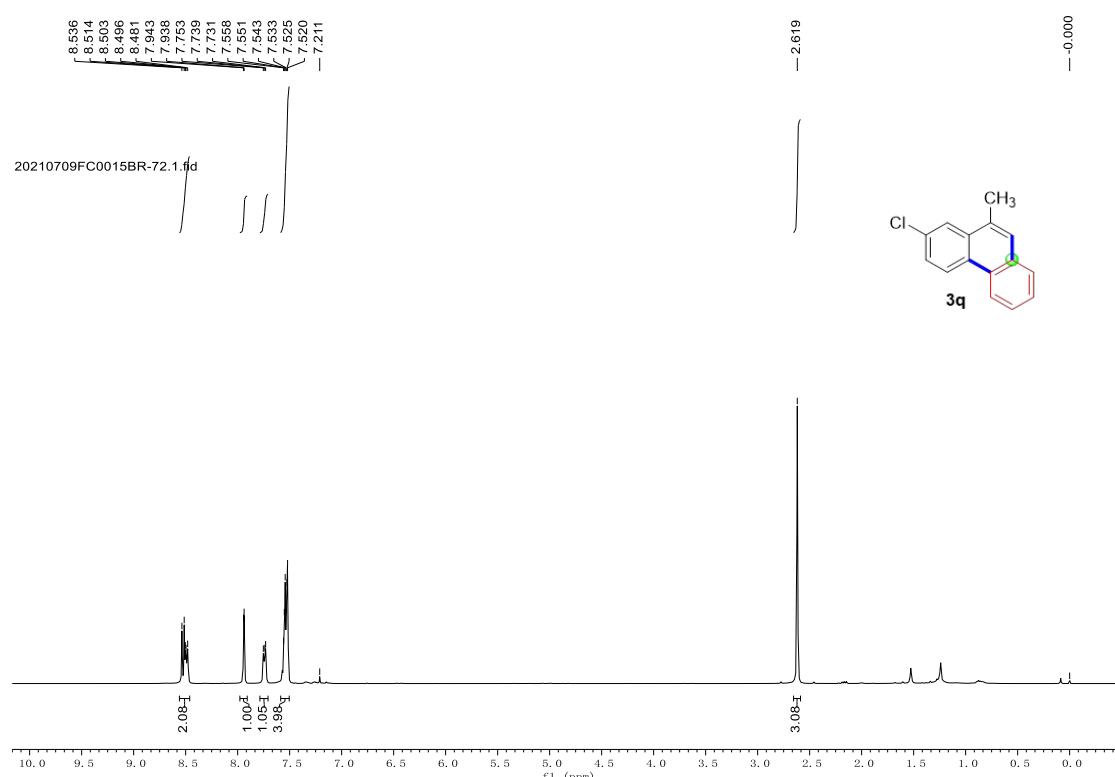
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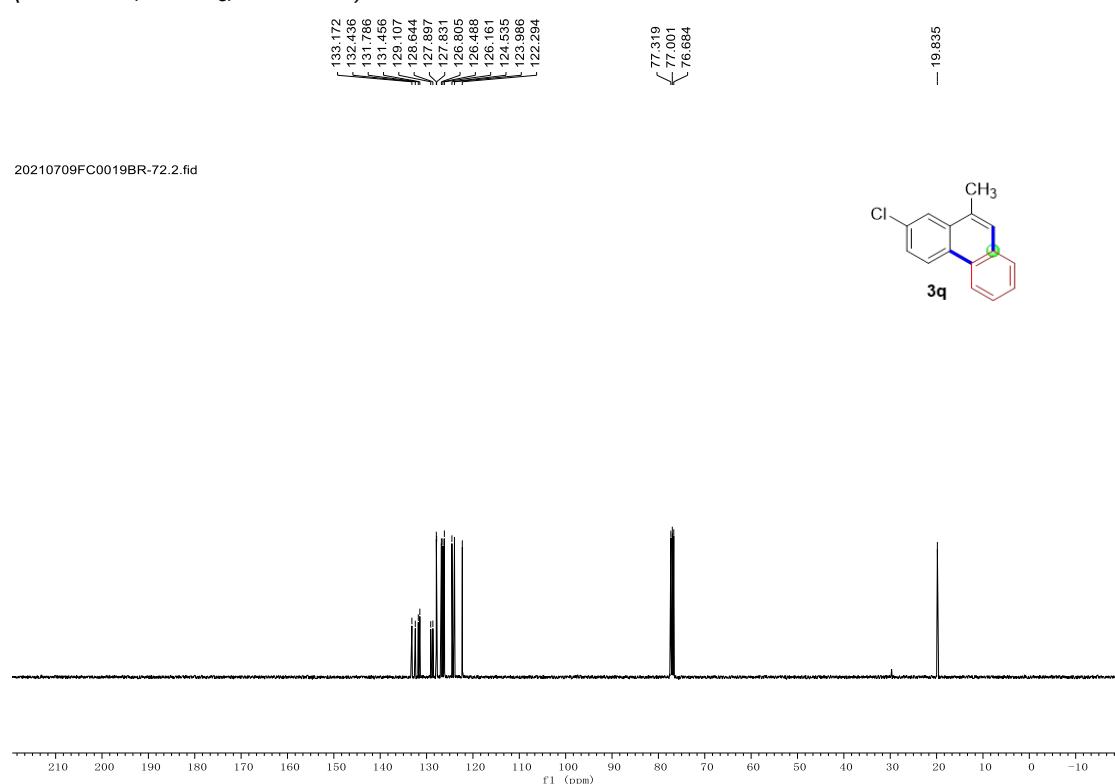
2-chloro-10-methylphenanthrene (3q):

(^1H NMR, CDCl_3 , 400 MHz)



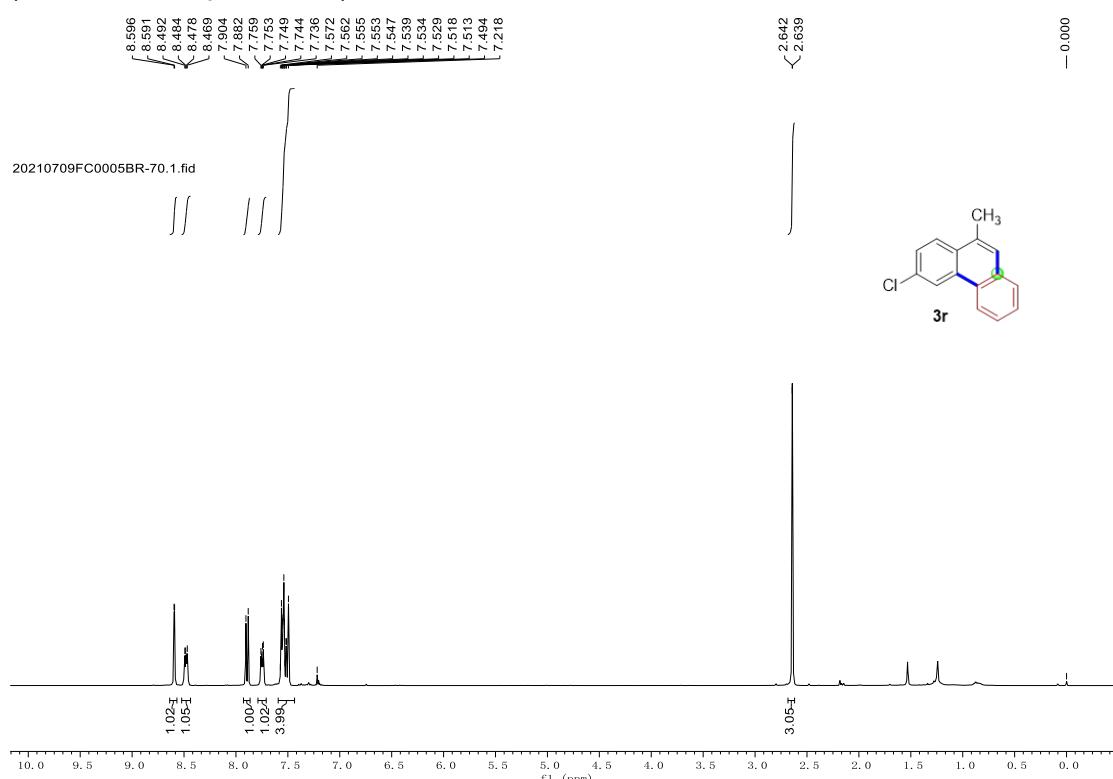
2-chloro-10-methylphenanthrene (3q):

(^{13}C NMR, CDCl_3 , 101 MHz)



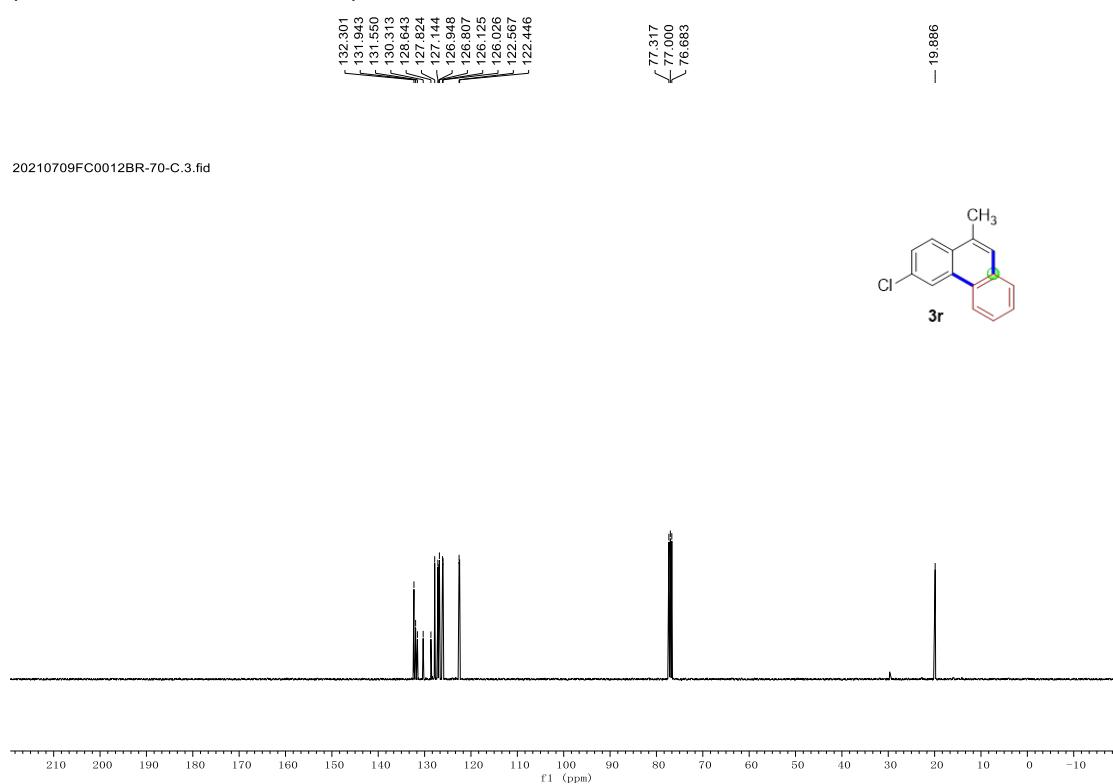
3-chloro-10-methylphenanthrene (3r):

(1H NMR, $CDCl_3$, 400 MHz)



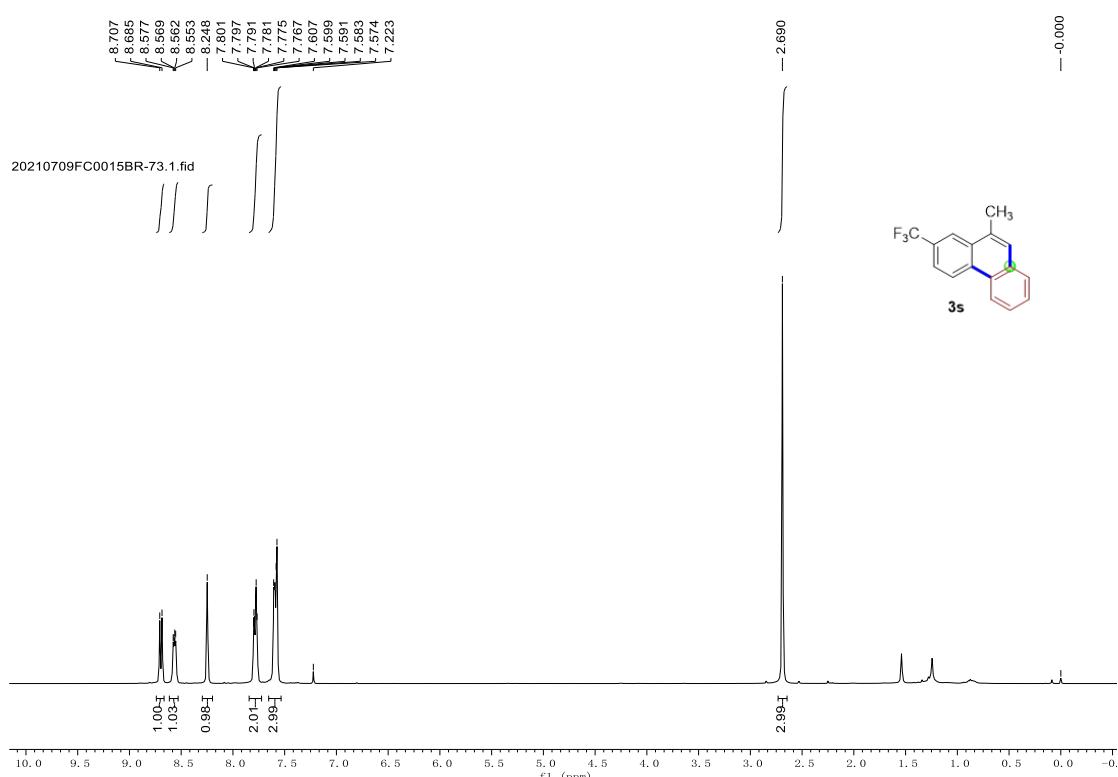
3-chloro-10-methylphenanthrene (3r):

(^{13}C NMR, CDCl_3 , 101 MHz)



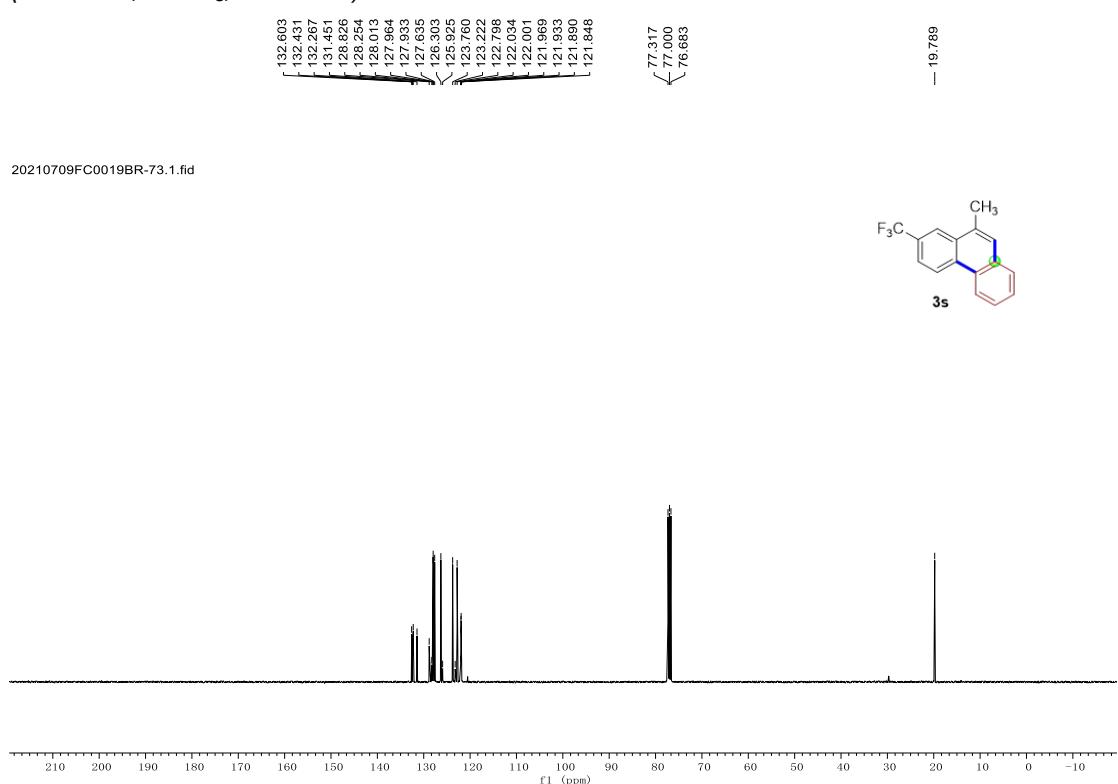
10-methyl-2-(trifluoromethyl)phenanthrene (3s):

(^1H NMR, CDCl_3 , 400 MHz)



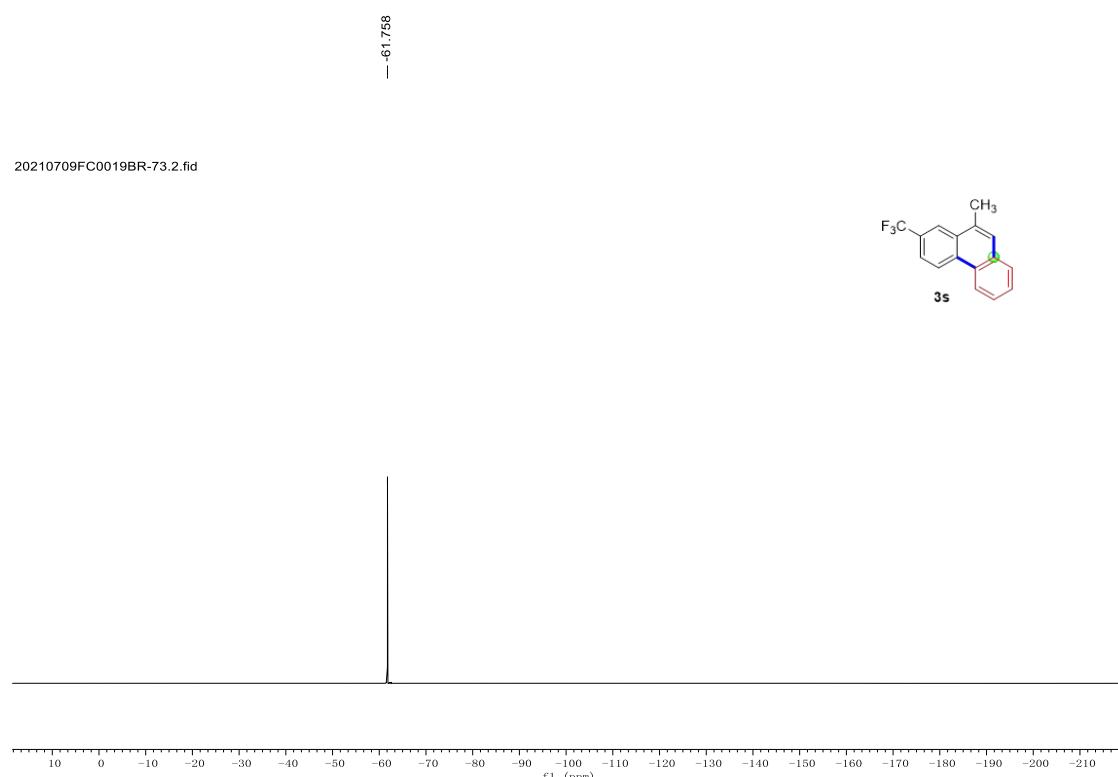
10-methyl-2-(trifluoromethyl)phenanthrene (3s):

(^{13}C NMR, CDCl_3 , 101 MHz)



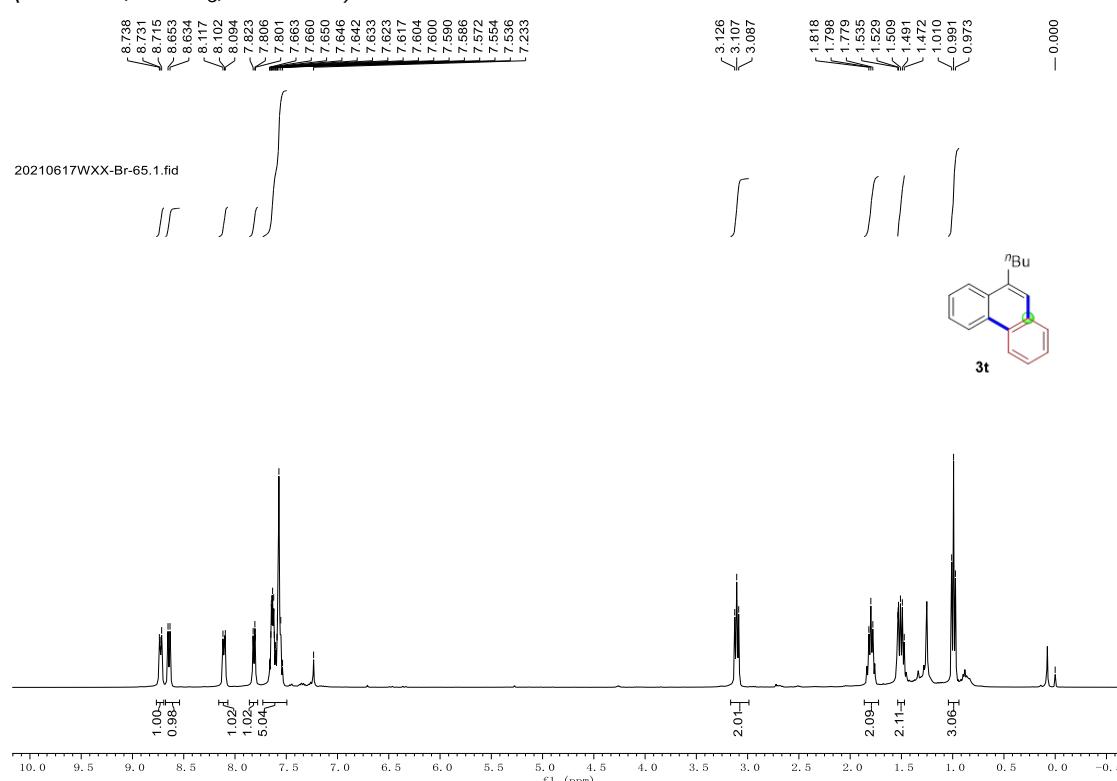
10-methyl-2-(trifluoromethyl)phenanthrene (3s):

(^{19}F NMR, CDCl_3 , 376 MHz)



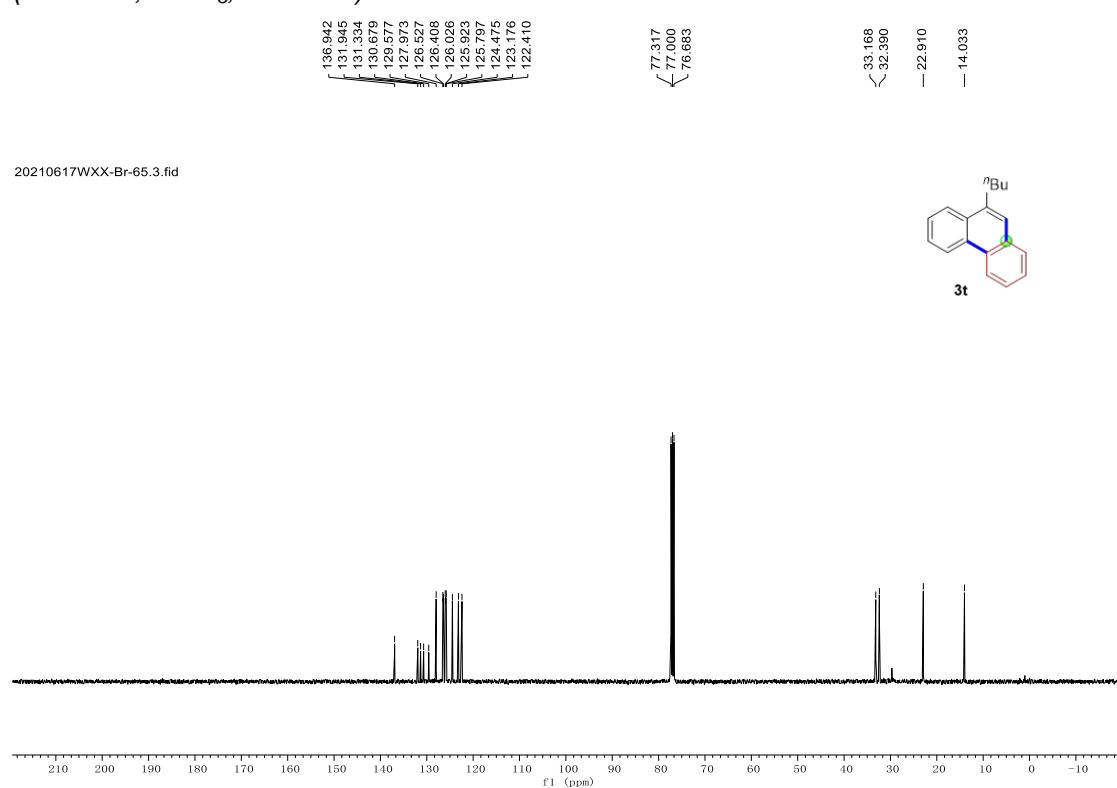
9-butylphenanthrene (3t):

(^1H NMR, CDCl_3 , 400 MHz)



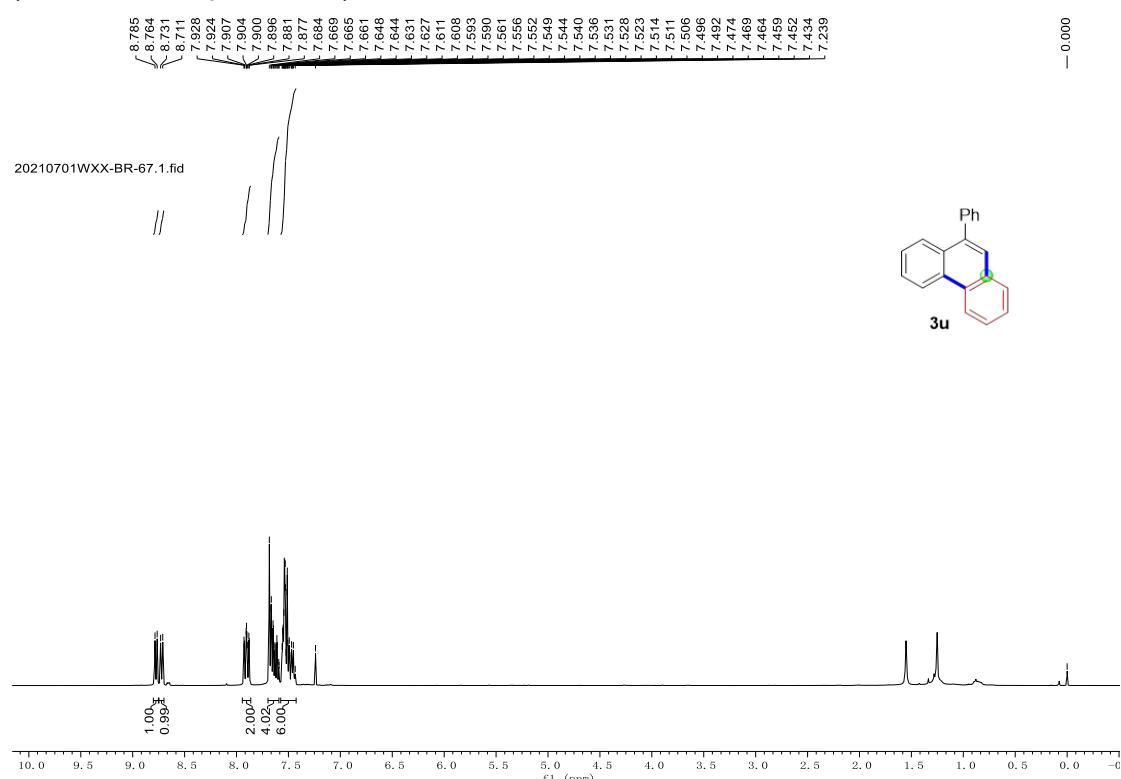
9-butylphenanthrene (3t):

(^{13}C NMR, CDCl_3 , 101 MHz)



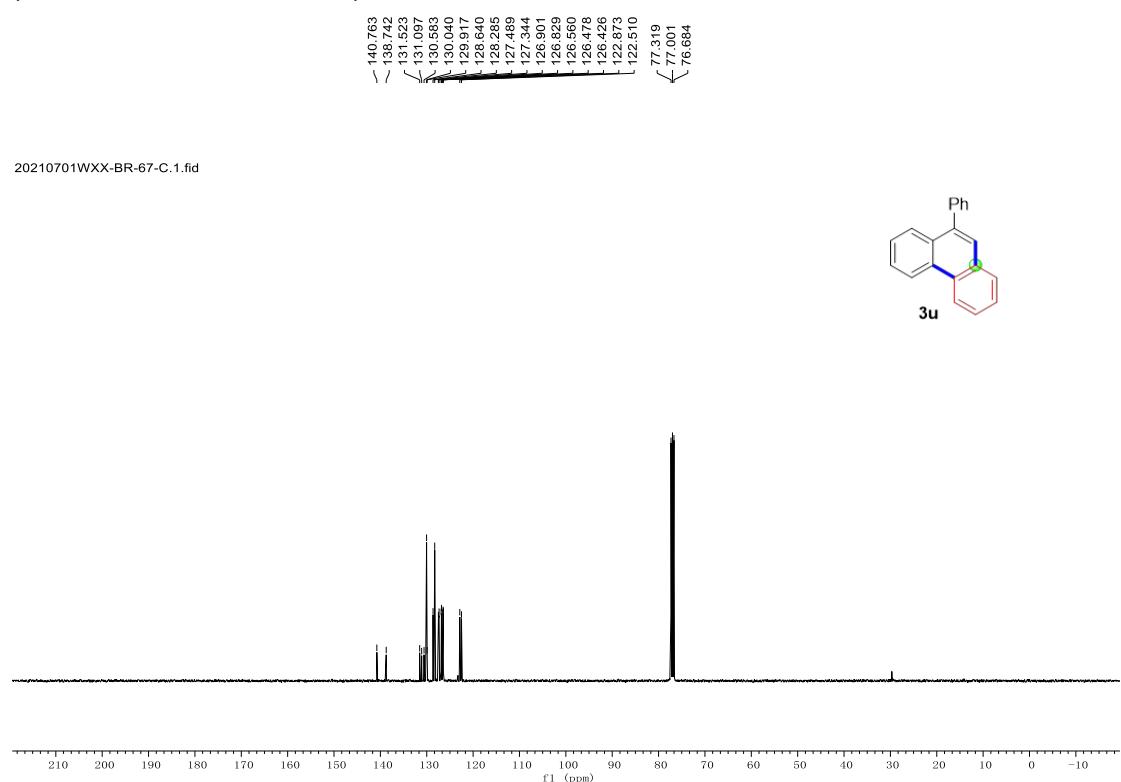
9-phenylphenanthrene (3u):

(^1H NMR, CDCl_3 , 400 MHz)



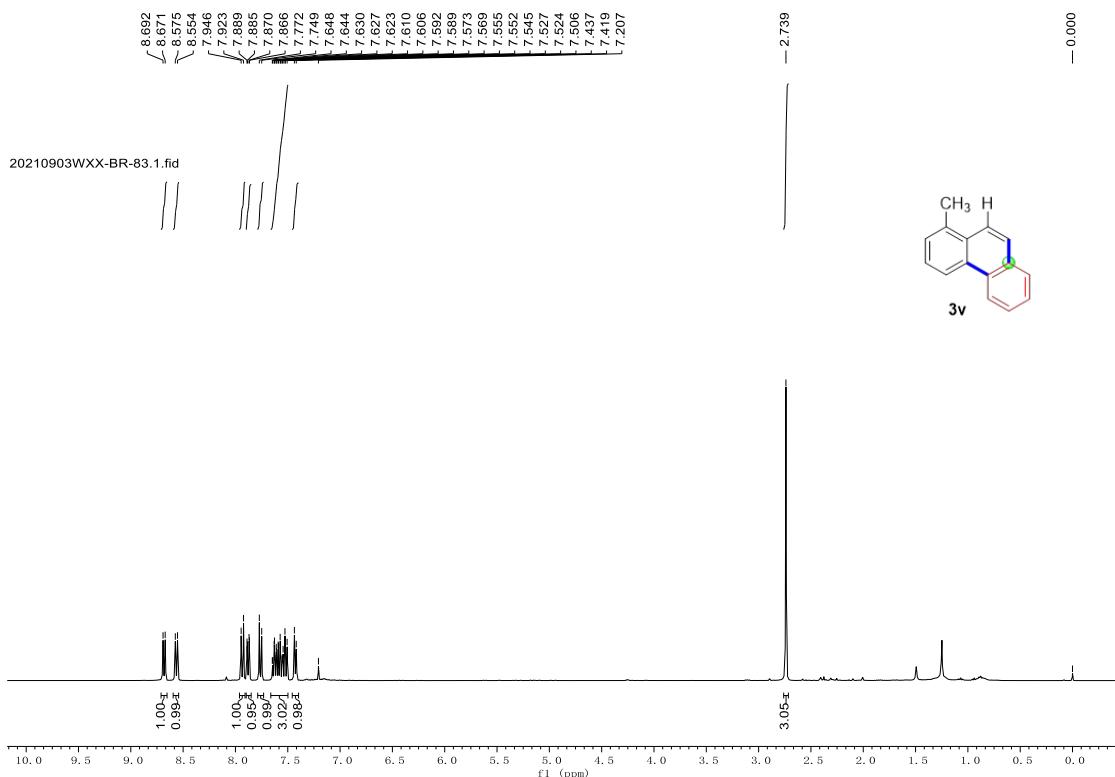
9-phenylphenanthrene (3u):

(^{13}C NMR, CDCl_3 , 101 MHz)



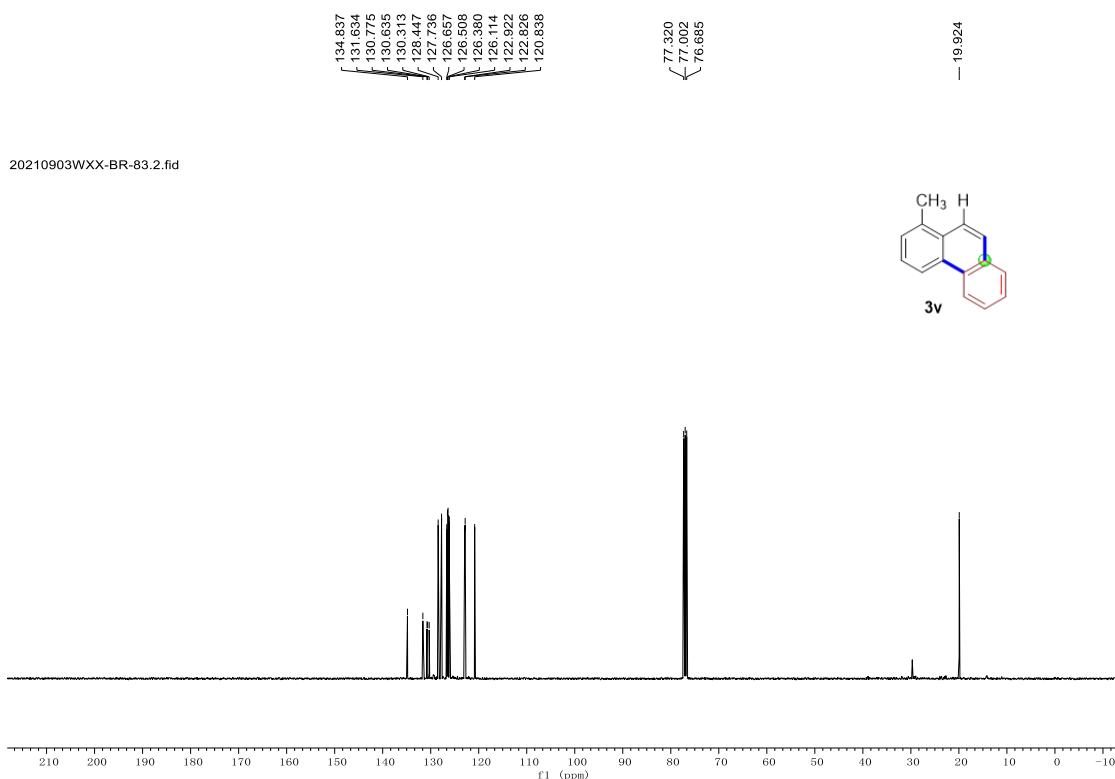
1-methylphenanthrene (3v):

(^1H NMR, CDCl_3 , 400 MHz)



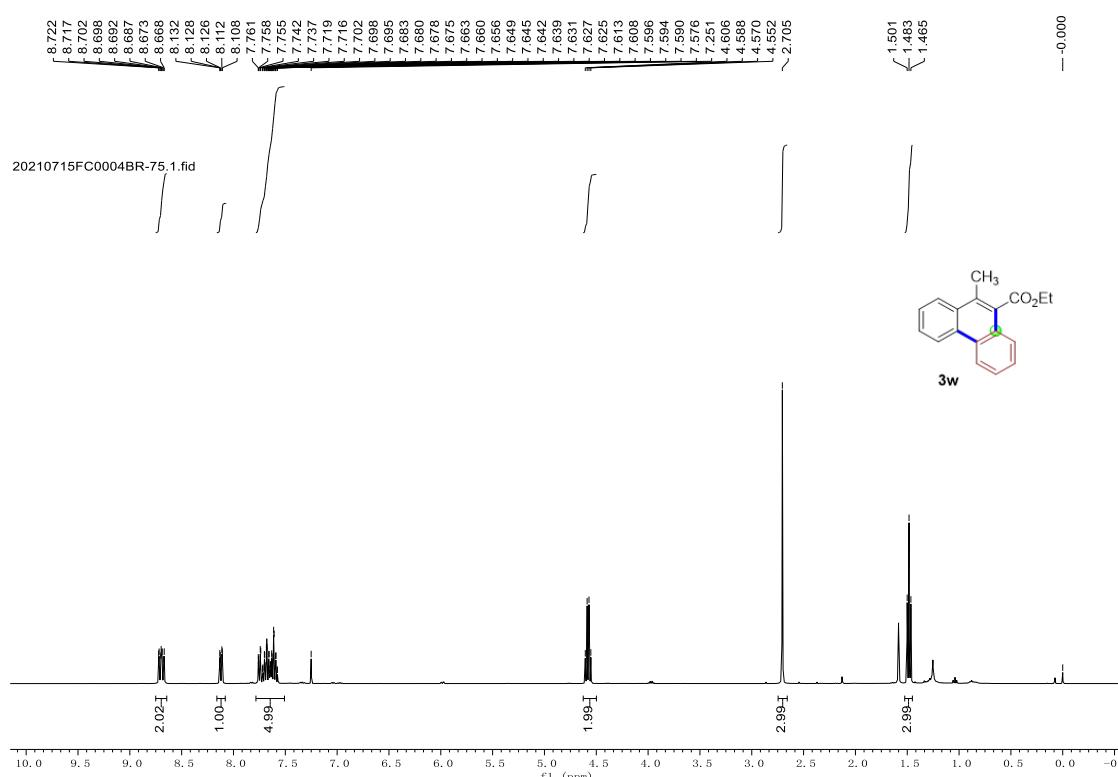
1-methylphenanthrene (3v):

(^{13}C NMR, CDCl_3 , 101 MHz)



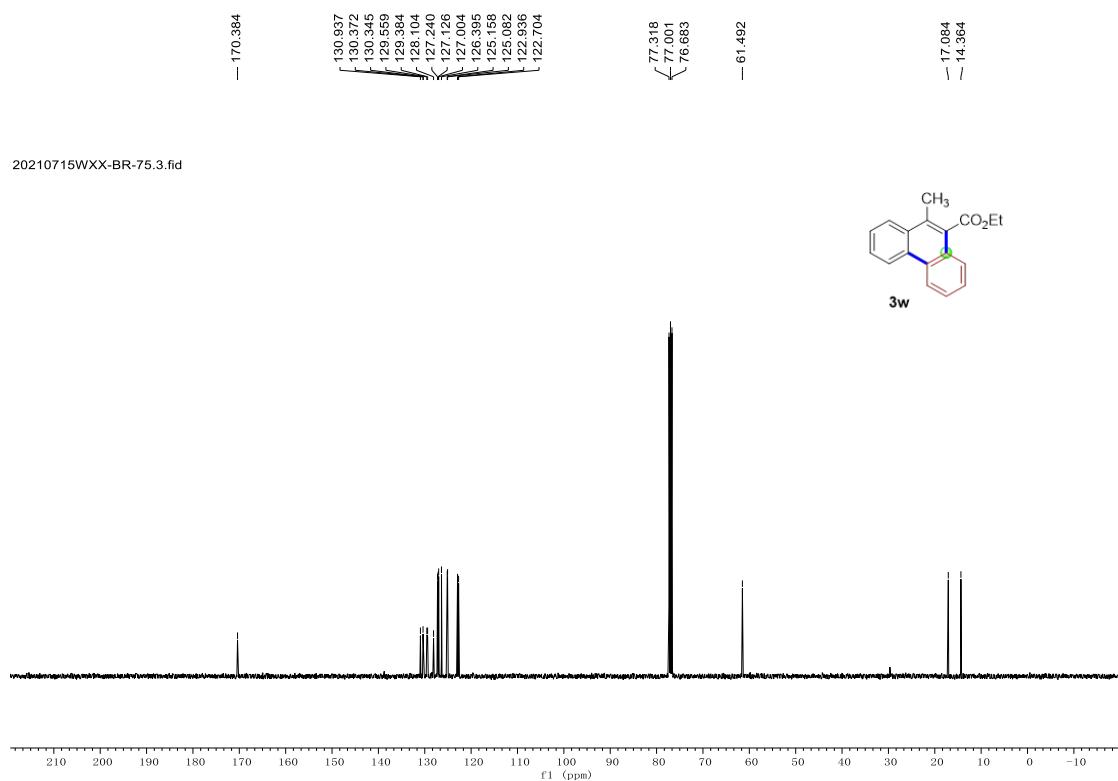
ethyl 10-methylphenanthrene-9-carboxylate (3w):

(^1H NMR, CDCl_3 , 400 MHz)



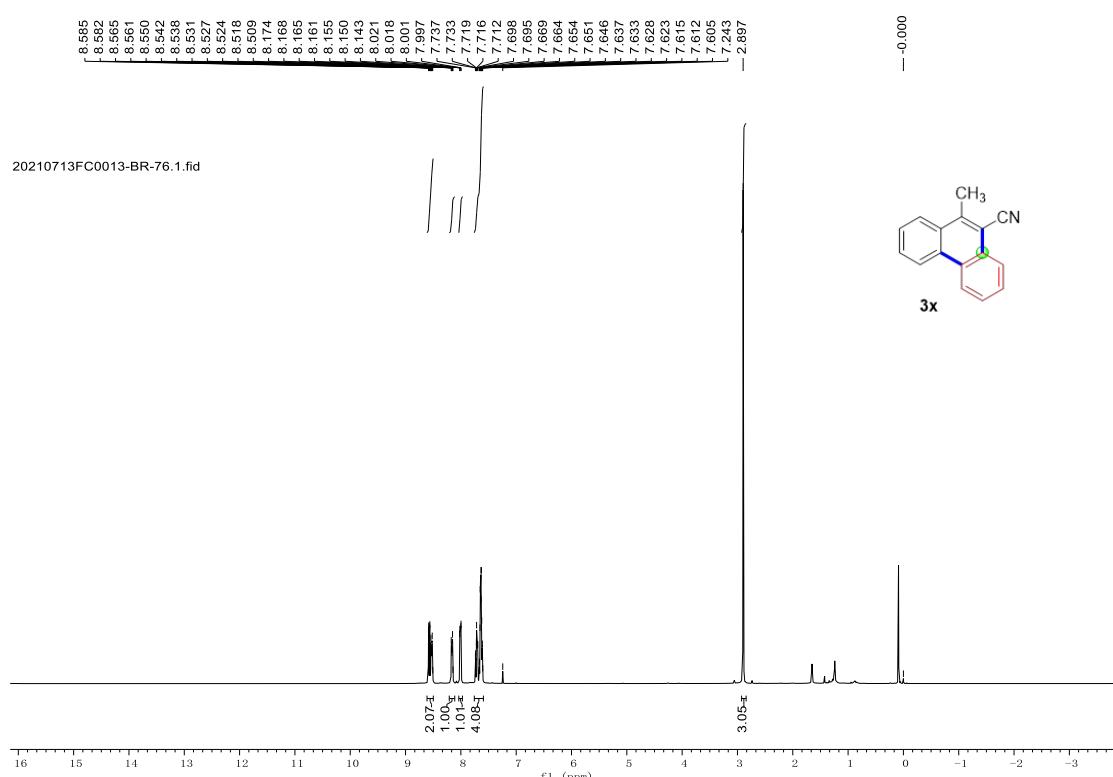
ethyl 10-methylphenanthrene-9-carboxylate (3w):

(^{13}C NMR, CDCl_3 , 101 MHz)



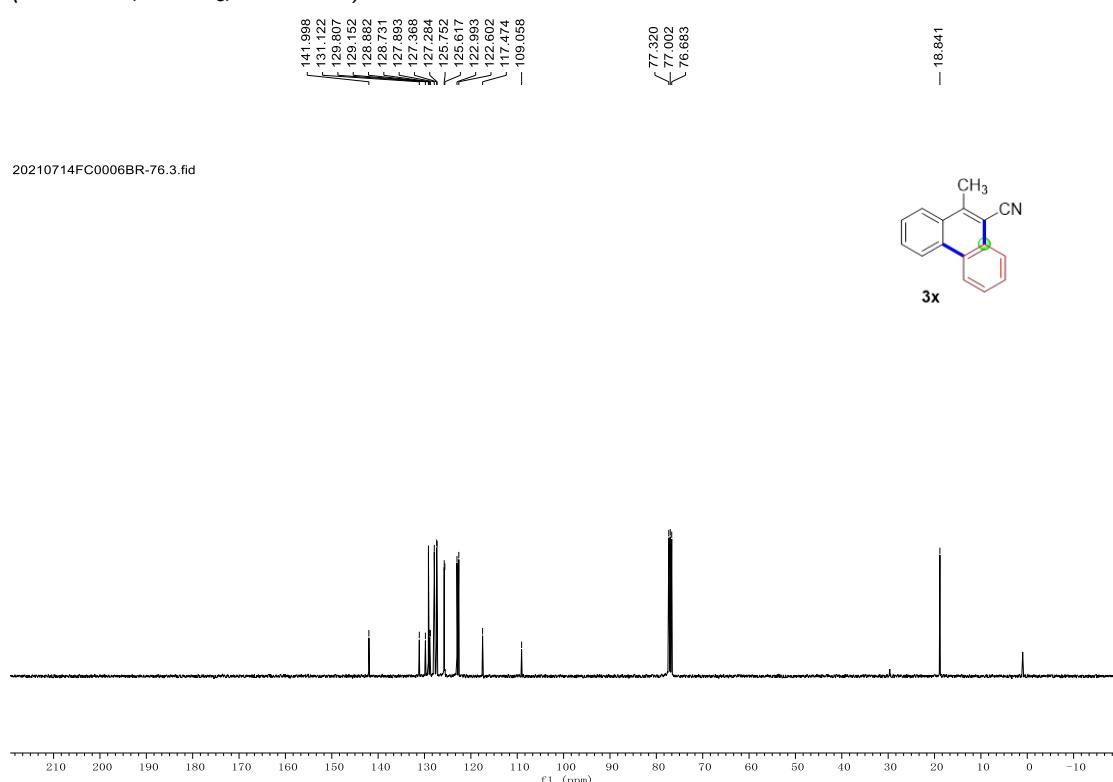
10-methylphenanthrene-9-carbonitrile (3x):

(^1H NMR, CDCl_3 , 400 MHz)

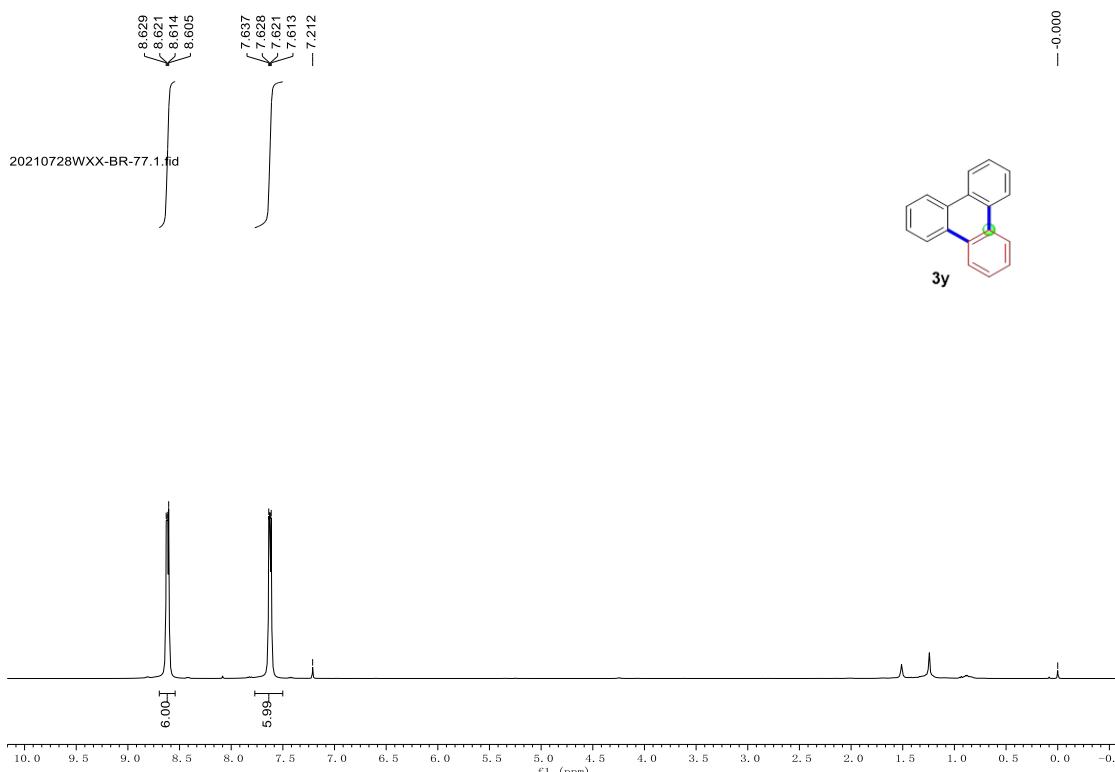


10-methylphenanthrene-9-carbonitrile (3x):

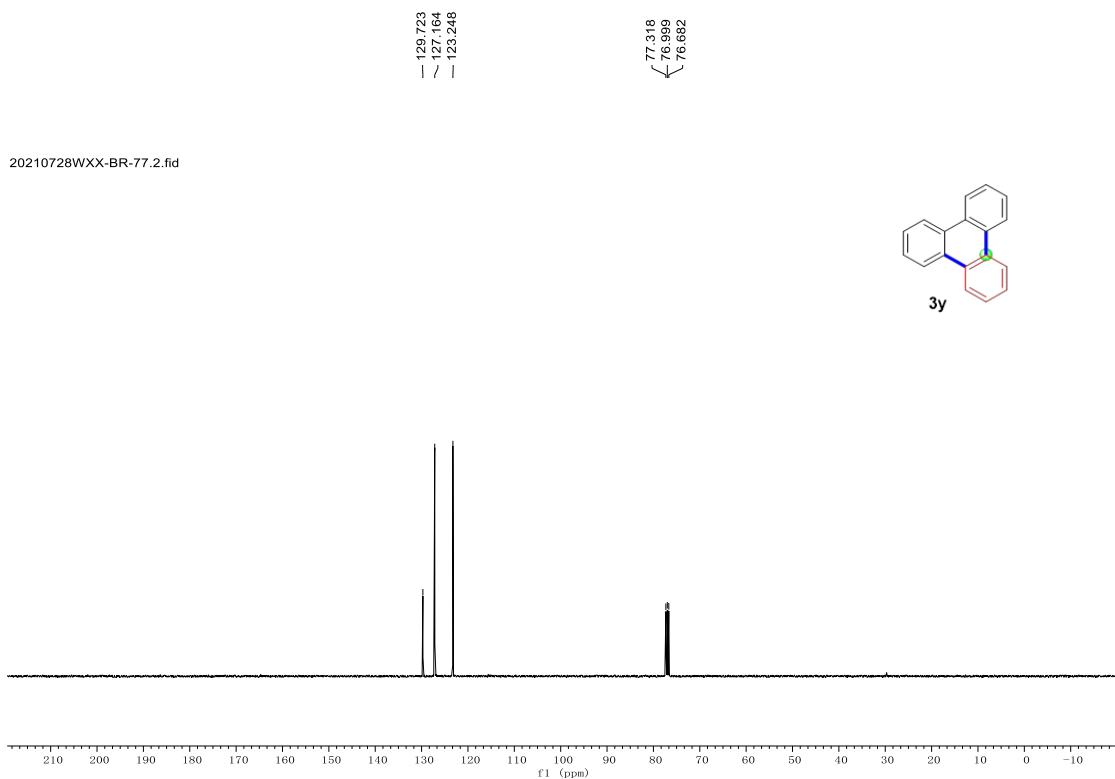
(^{13}C NMR, CDCl_3 , 101 MHz)



triphenylene (3y):
 $(^1\text{H NMR}, \text{CDCl}_3, 400 \text{ MHz})$

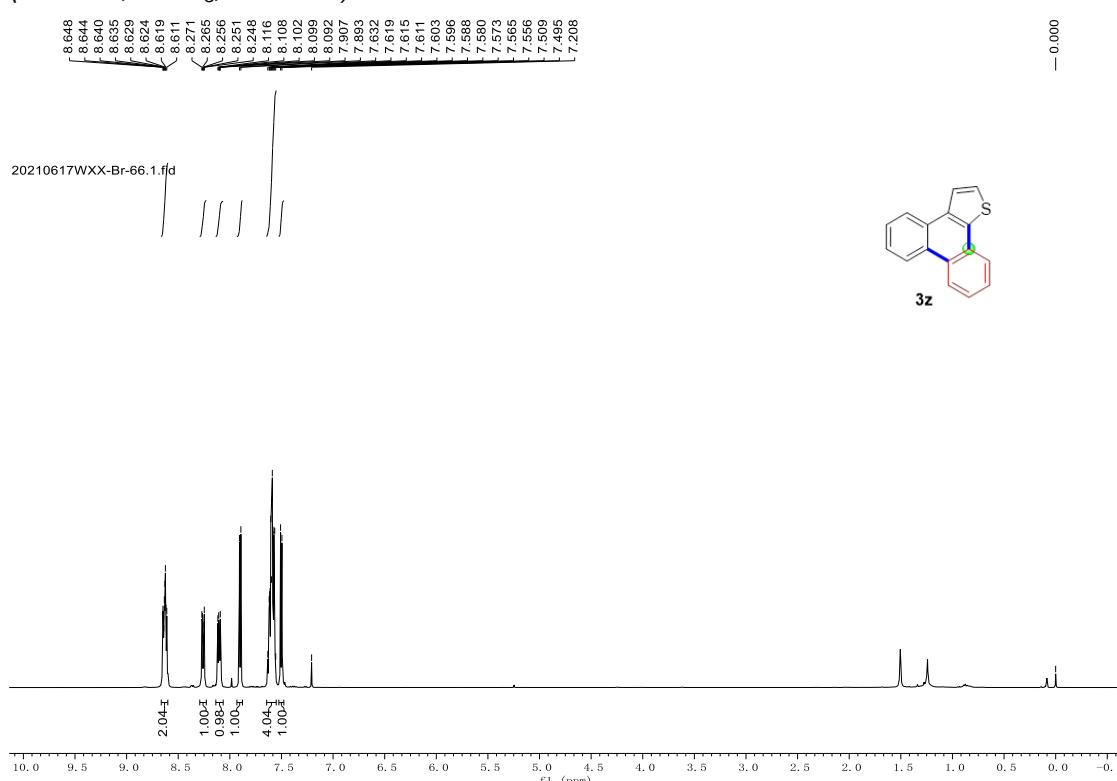


triphenylene (3y):
 $(^{13}\text{C NMR}, \text{CDCl}_3, 101 \text{ MHz})$



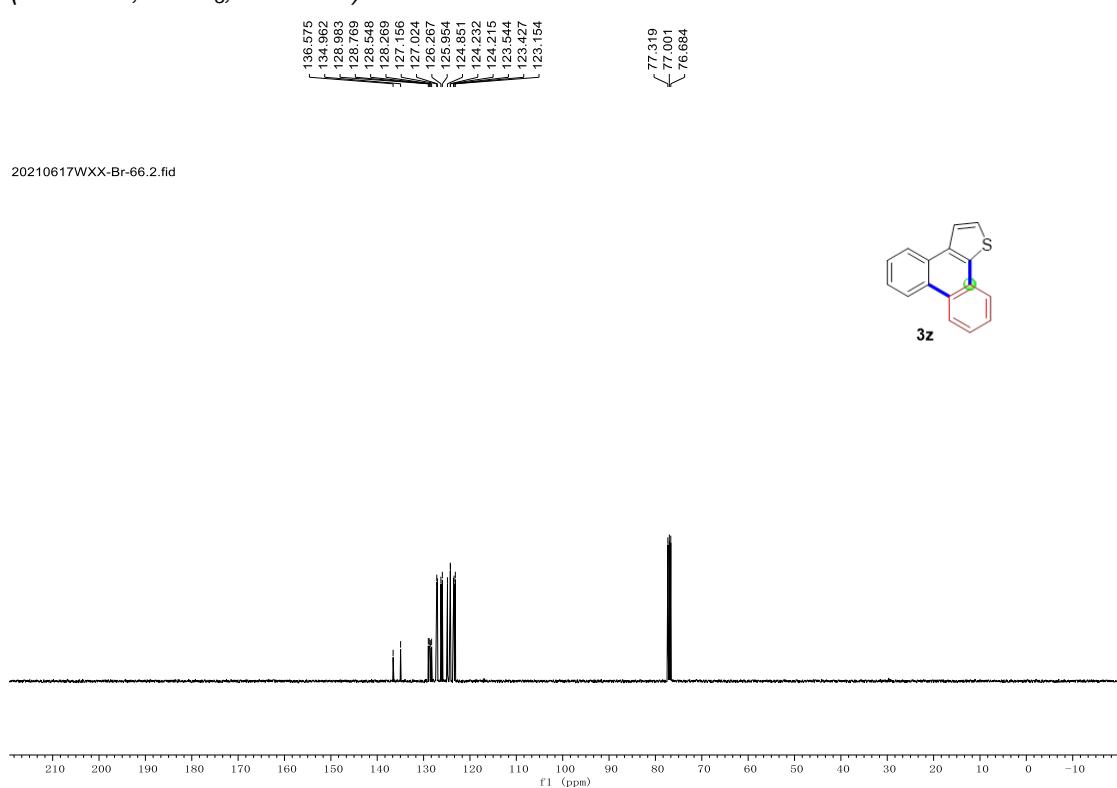
phenanthro[9,10-b]thiophene (3z):

(^1H NMR, CDCl_3 , 400 MHz)



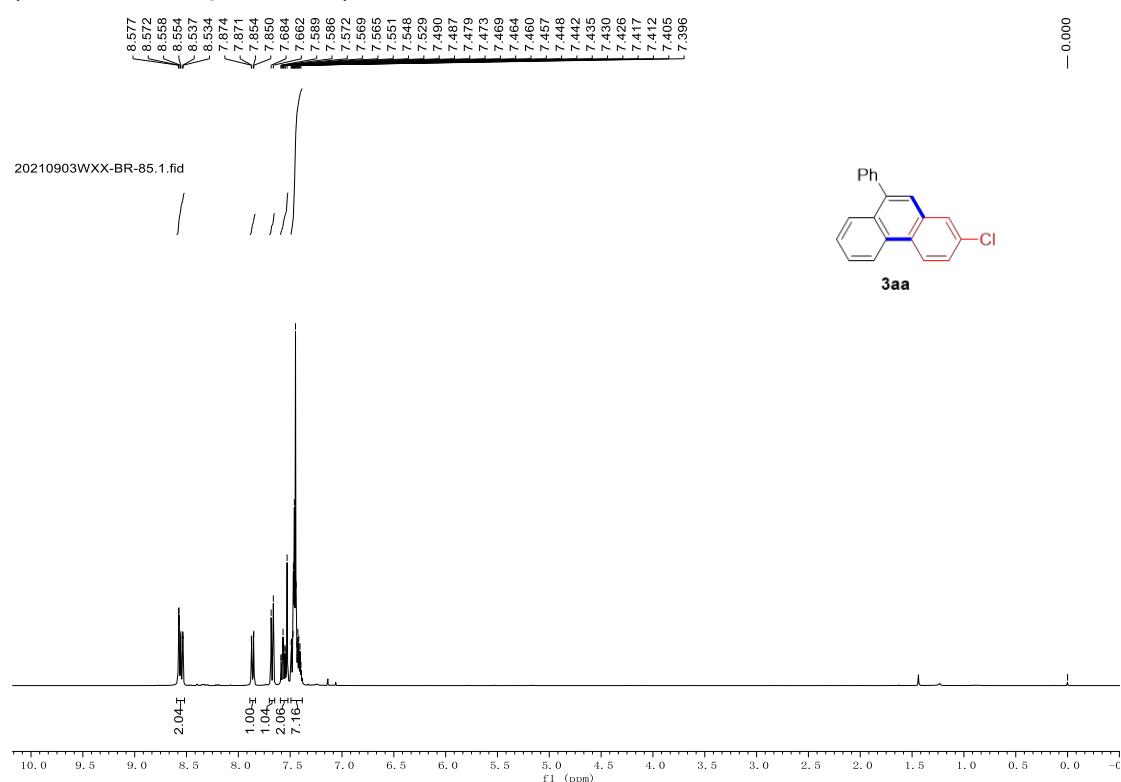
phenanthro[9,10-b]thiophene (3z):

(^{13}C NMR, CDCl_3 , 101 MHz)



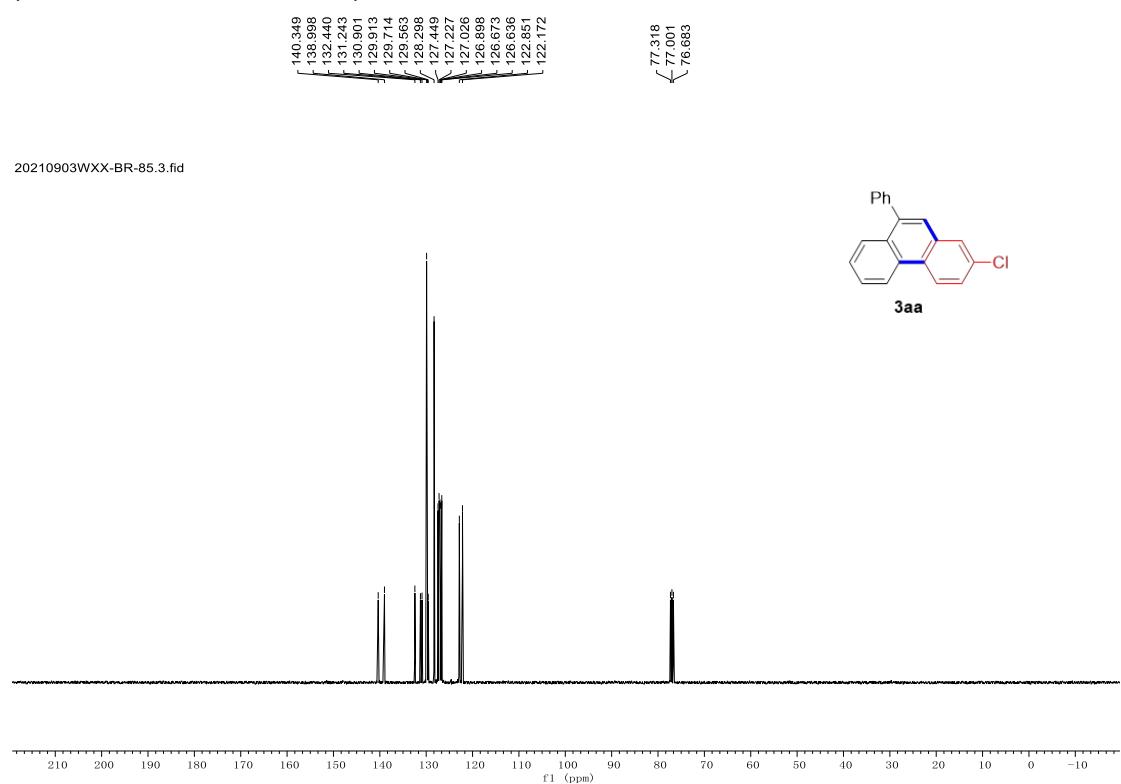
2-chloro-9-phenylphenanthrene (3aa):

(^1H NMR, CDCl_3 , 400 MHz)



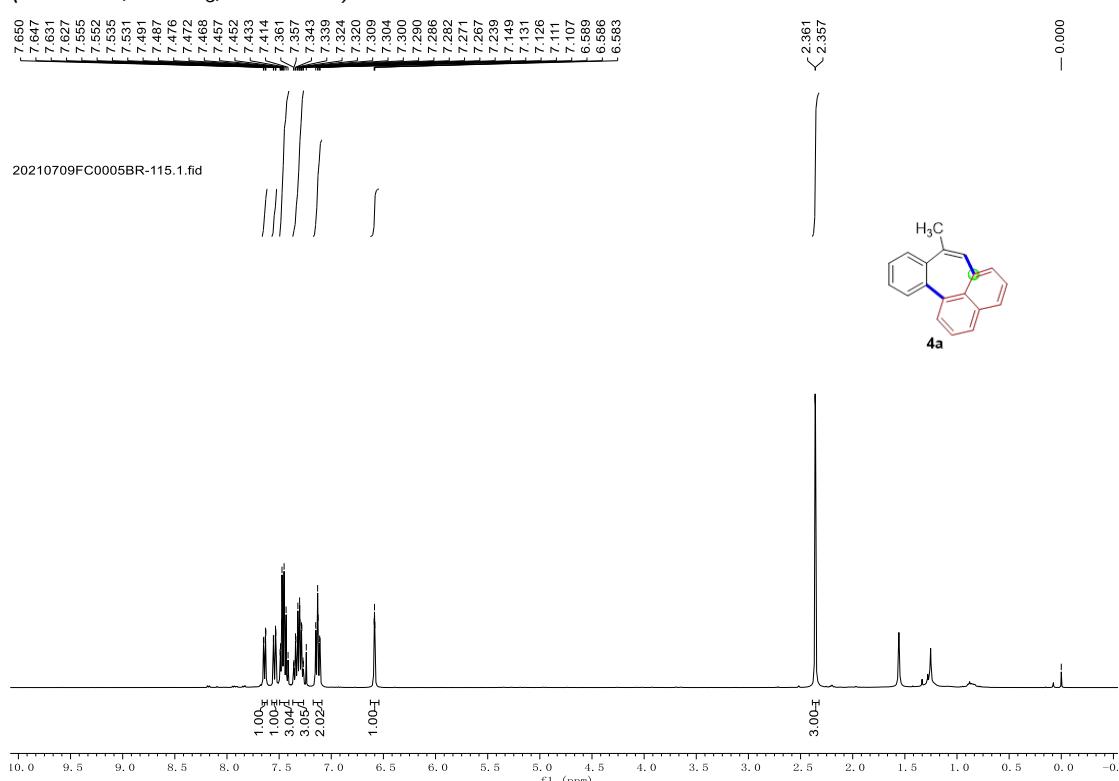
2-chloro-9-phenylphenanthrene (3aa):

(^{13}C NMR, CDCl_3 , 101 MHz)



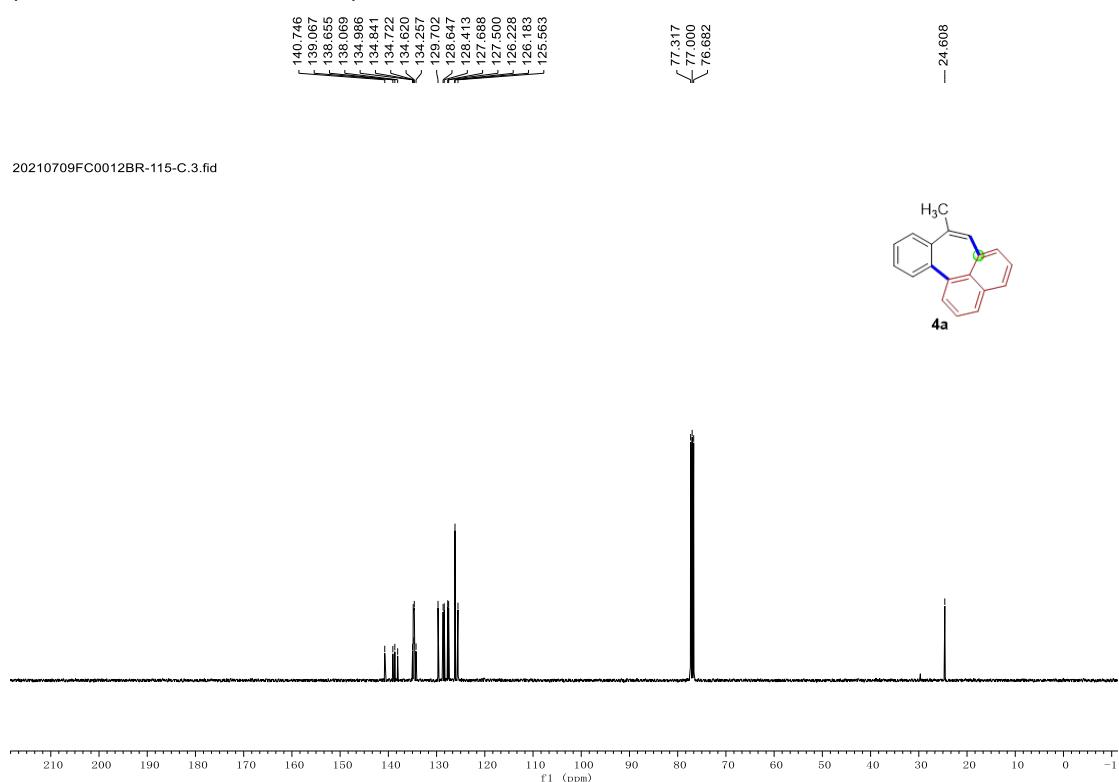
8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4a):

(^1H NMR, CDCl_3 , 400 MHz)



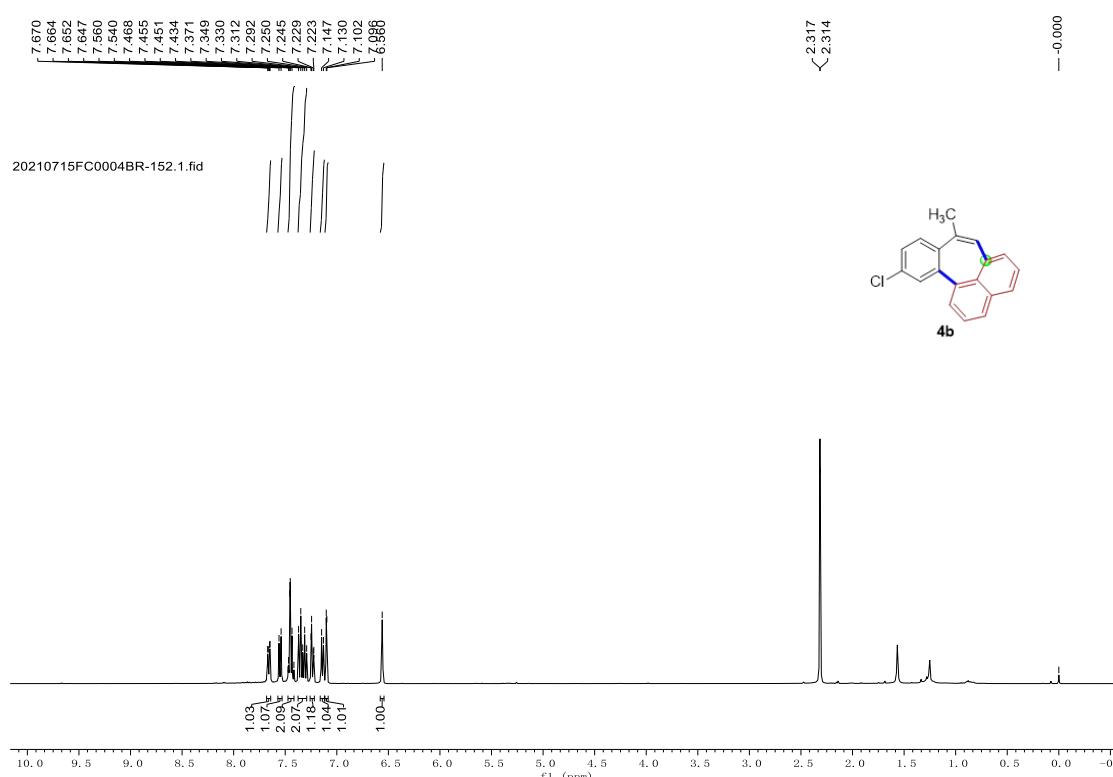
8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4a):

(^{13}C NMR, CDCl_3 , 101 MHz)



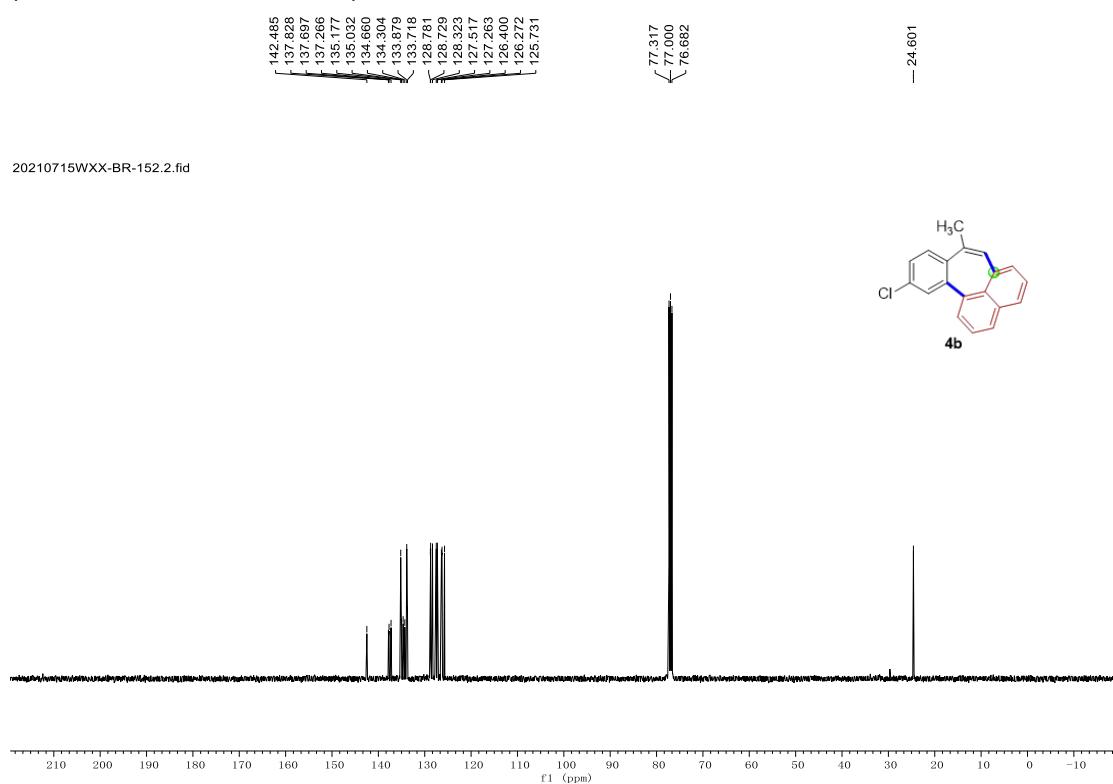
11-chloro-8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4b):

(^1H NMR, CDCl_3 , 400 MHz)



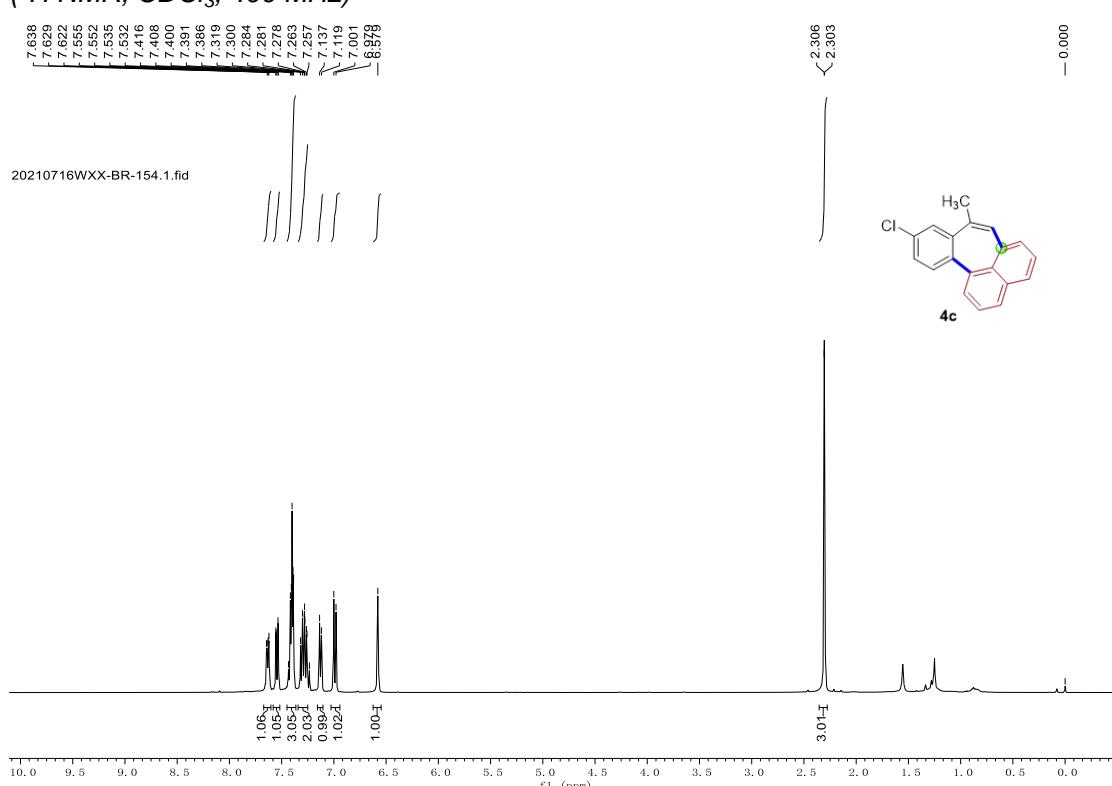
11-chloro-8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4b):

(^{13}C NMR, CDCl_3 , 101 MHz)



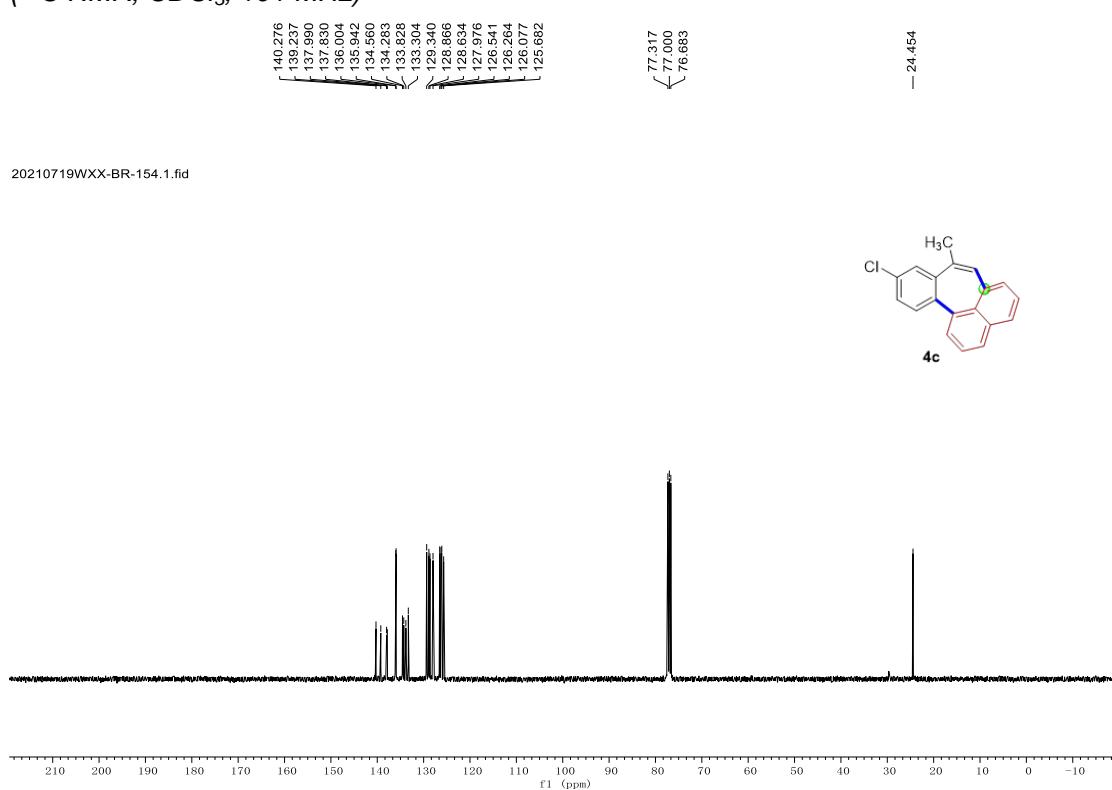
10-chloro-8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4c):

(^1H NMR, CDCl_3 , 400 MHz)



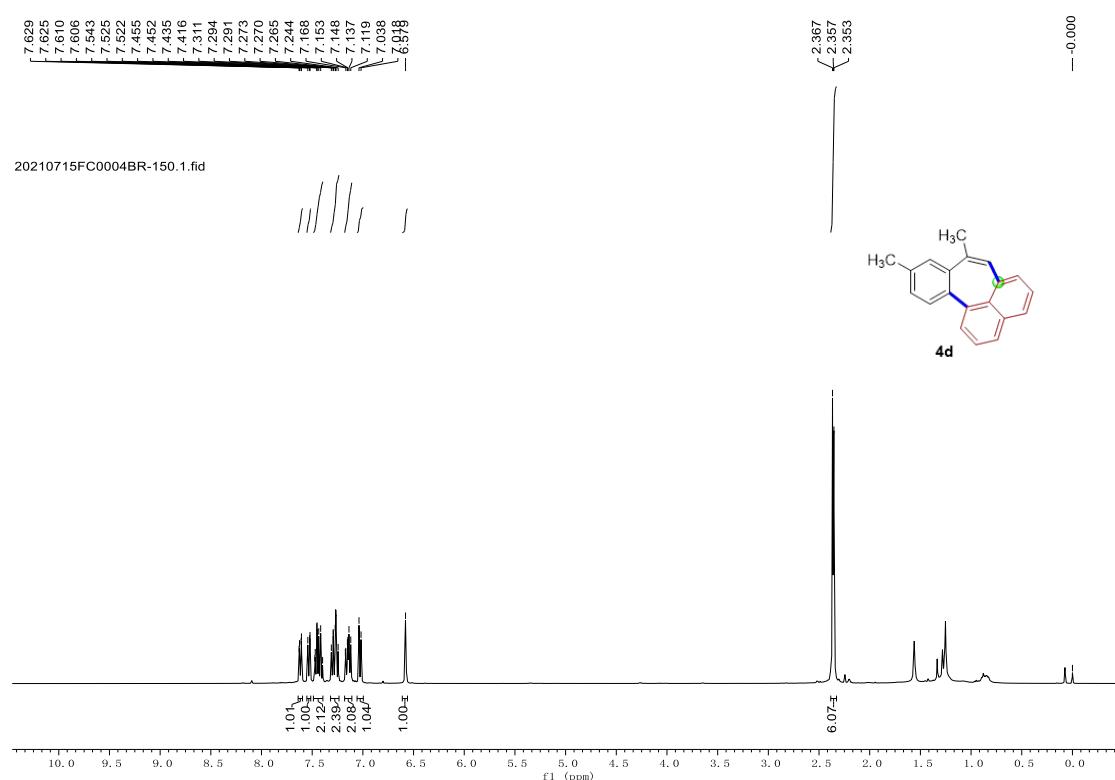
10-chloro-8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4c):

(^{13}C NMR, CDCl_3 , 101 MHz)



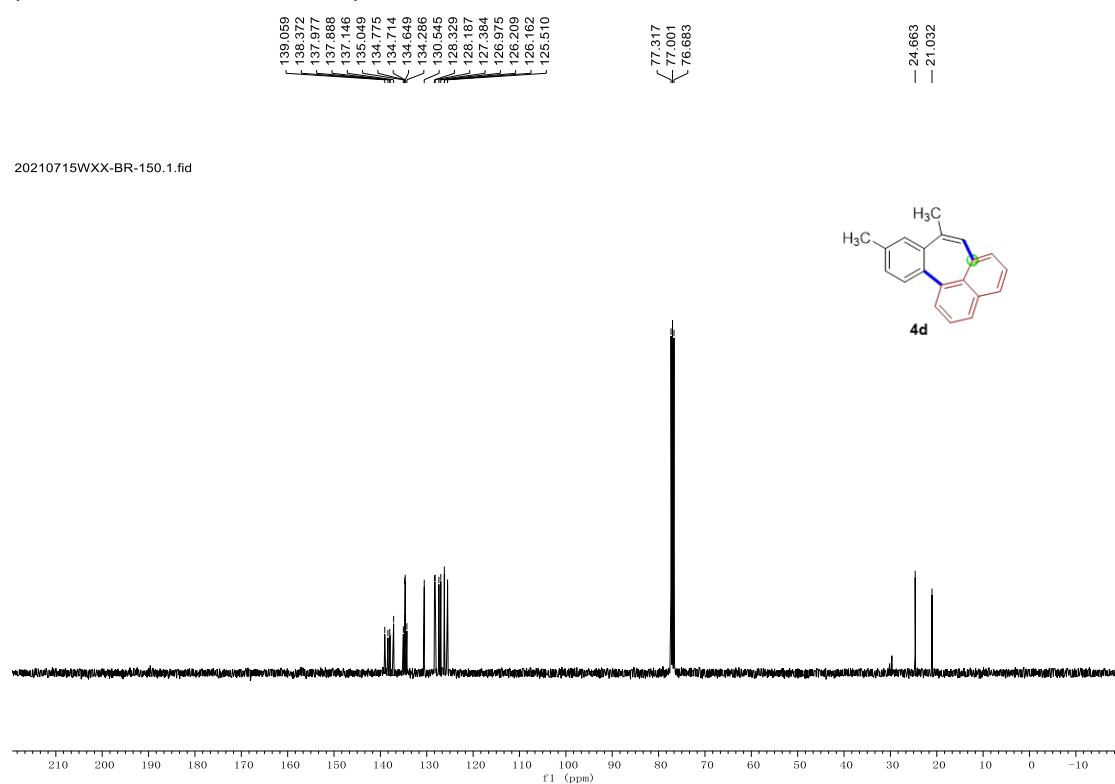
8,10-dimethylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4d):

(^1H NMR, CDCl_3 , 400 MHz)



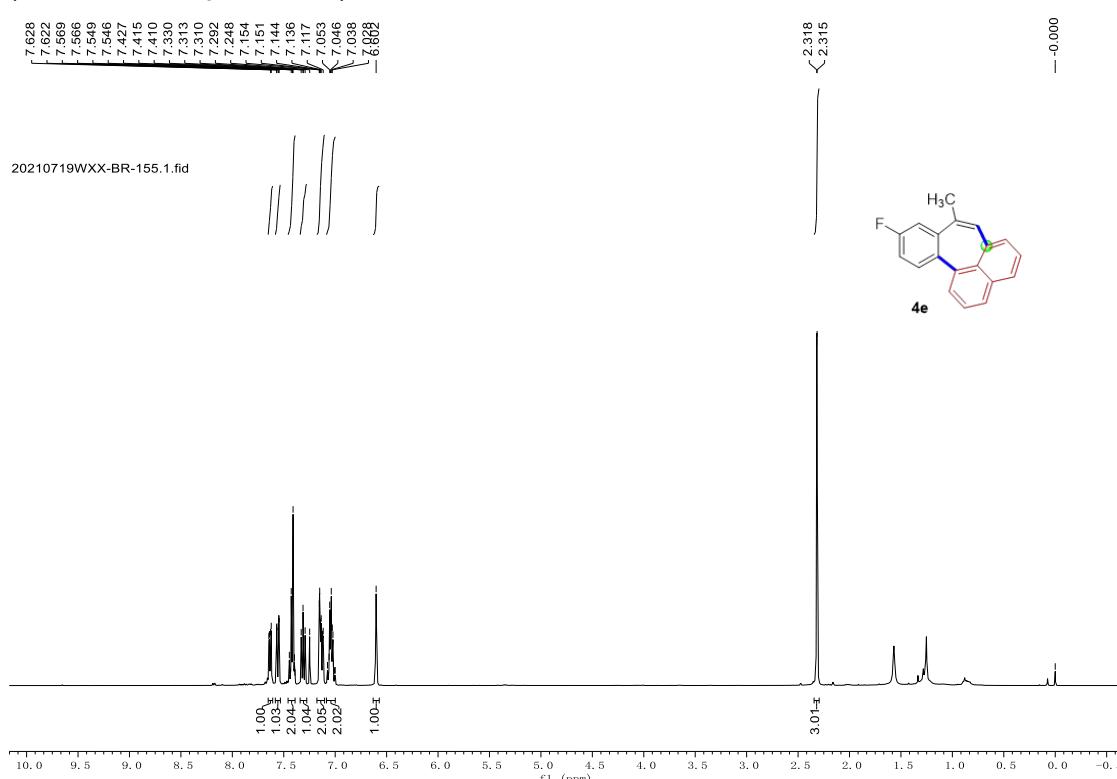
8,10-dimethylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4d):

(^{13}C NMR, CDCl_3 , 101 MHz)



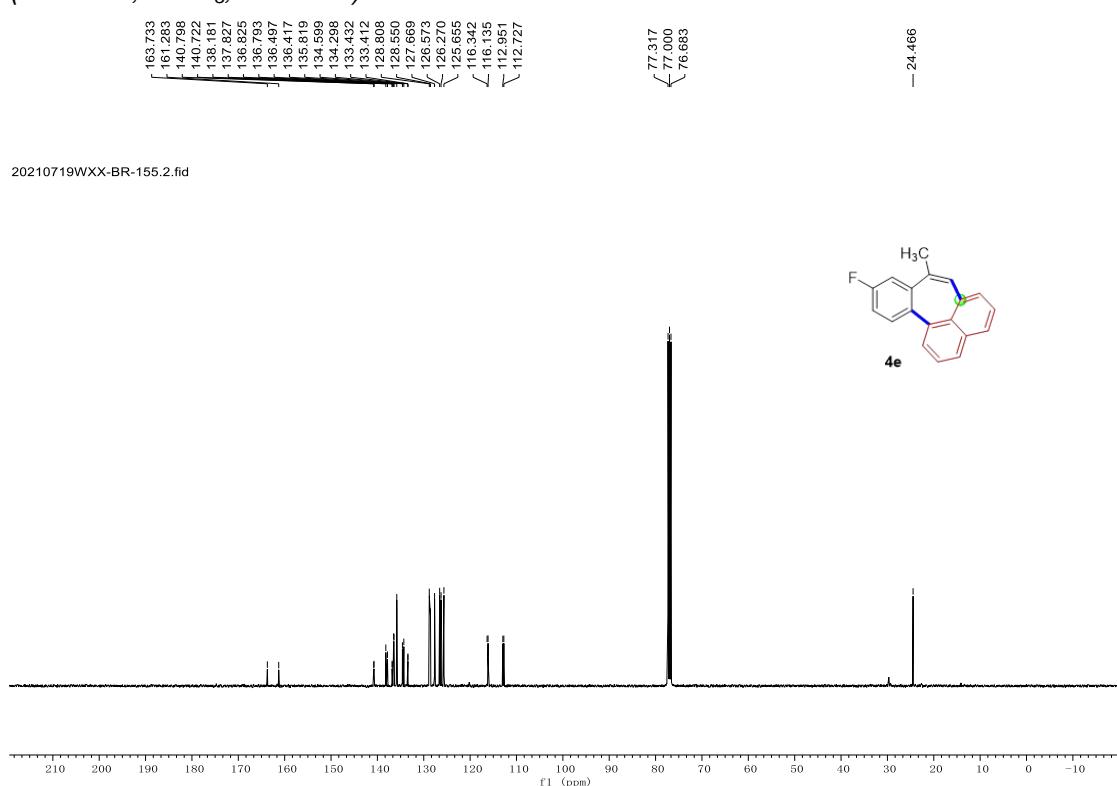
10-fluoro-8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4e):

(^1H NMR, CDCl_3 , 400 MHz)



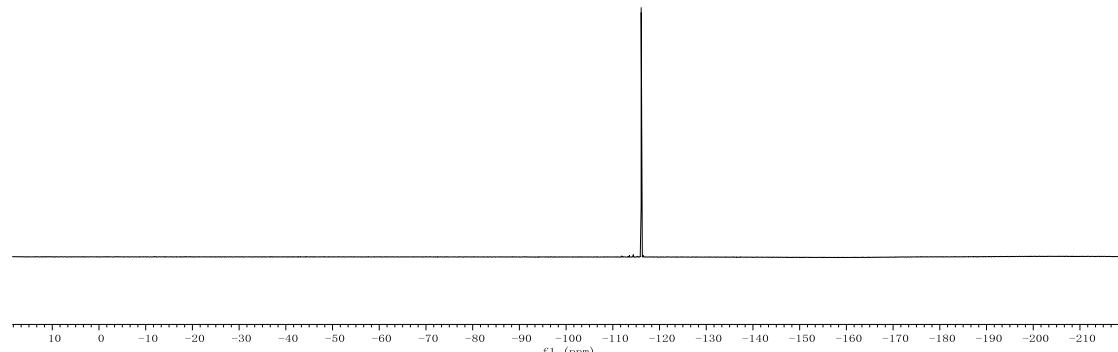
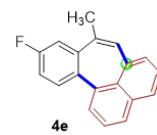
10-fluoro-8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4e):

(^{13}C NMR, CDCl_3 , 101 MHz)



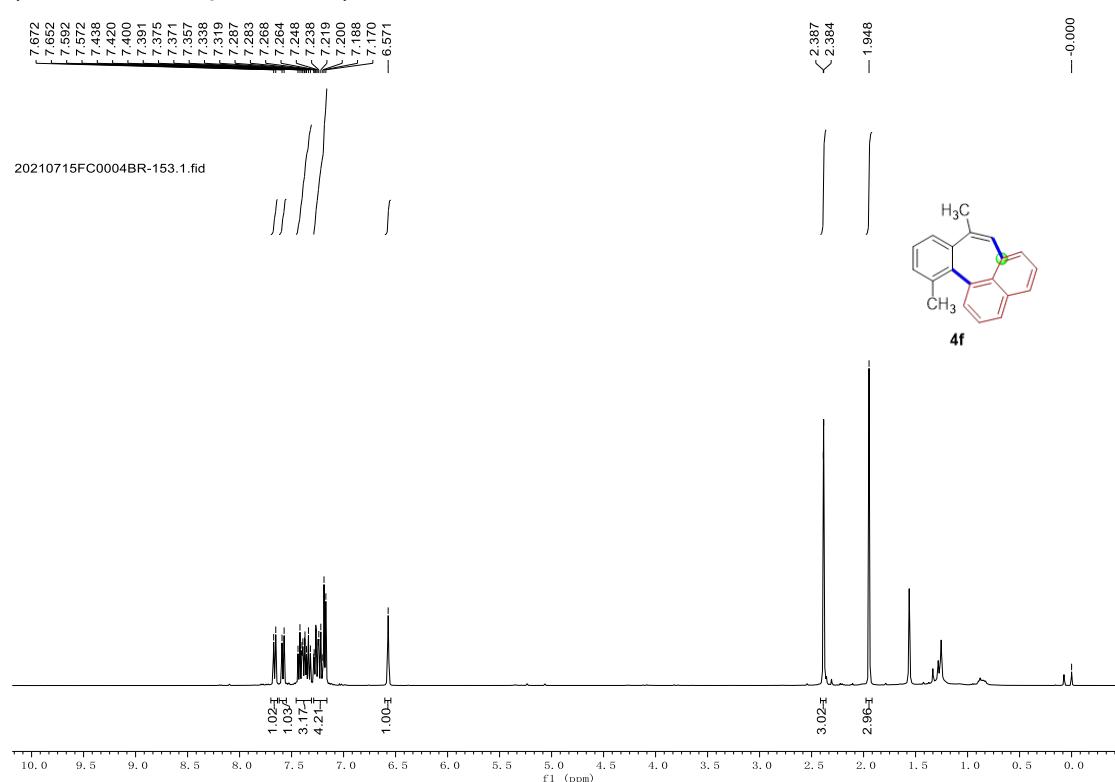
10-fluoro-8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4e):
(^{19}F NMR, CDCl_3 , 376 MHz)

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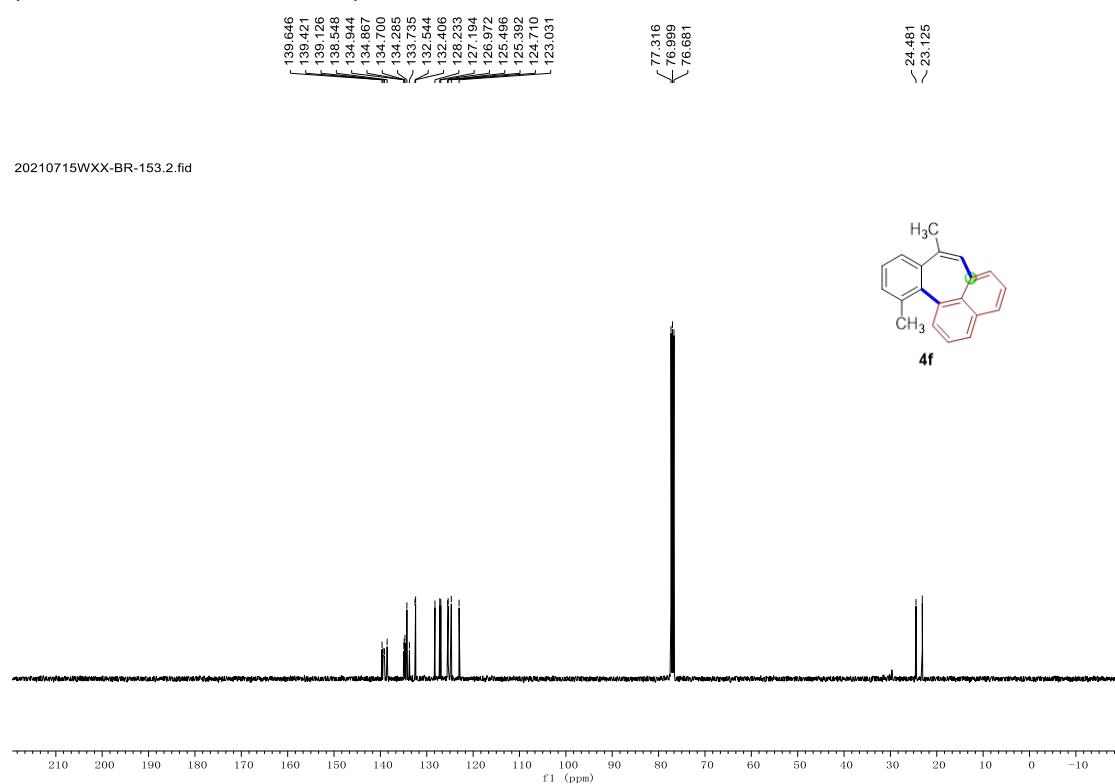
8,12-dimethylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4f):

(^1H NMR, CDCl_3 , 400 MHz)



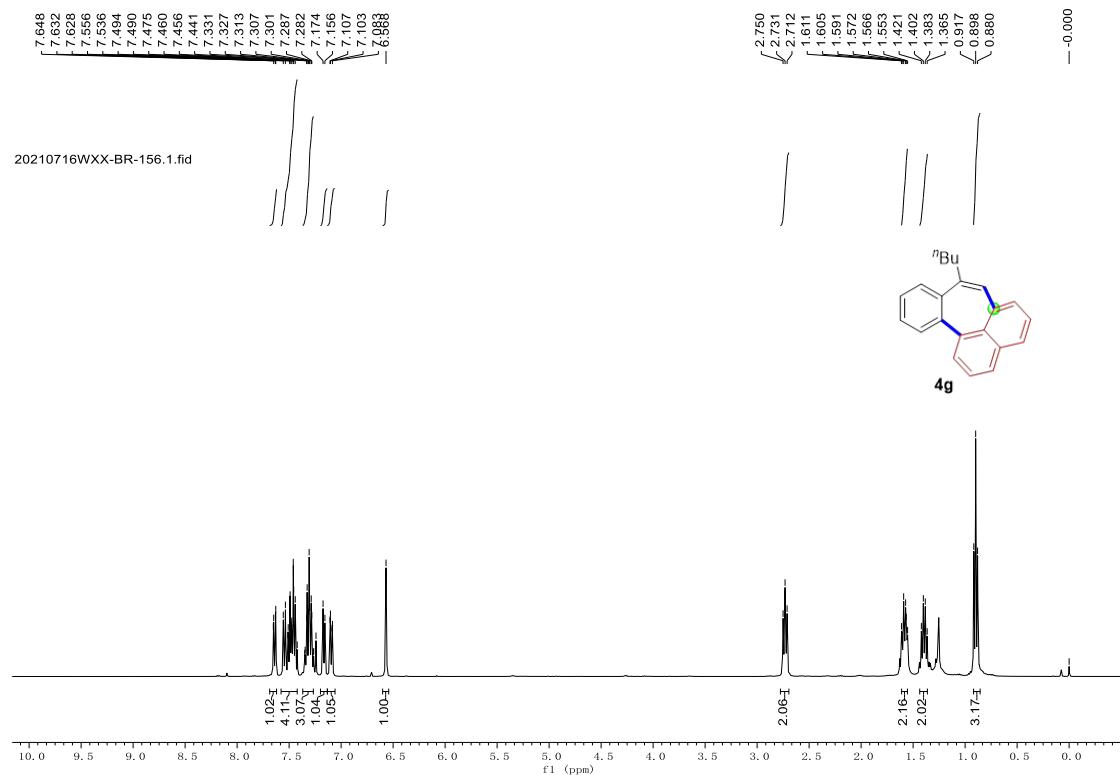
8,12-dimethylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4f):

(^{13}C NMR, CDCl_3 , 101 MHz)



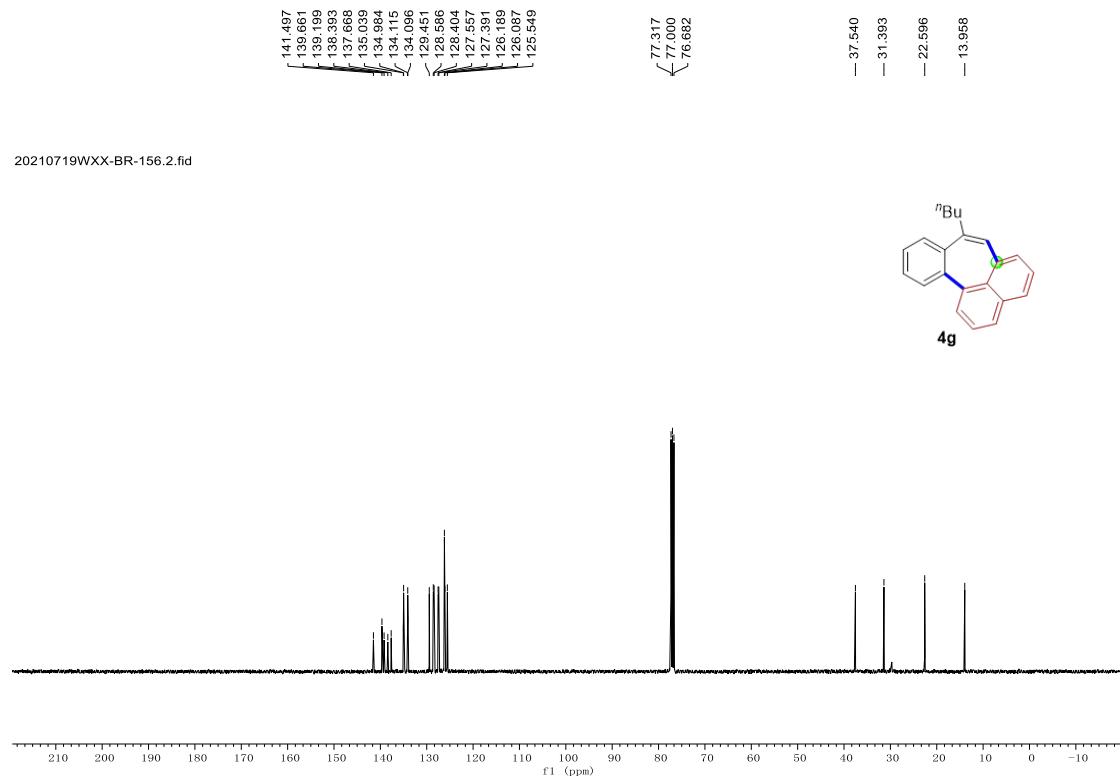
8-butylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4g):

(^1H NMR, CDCl_3 , 400 MHz)



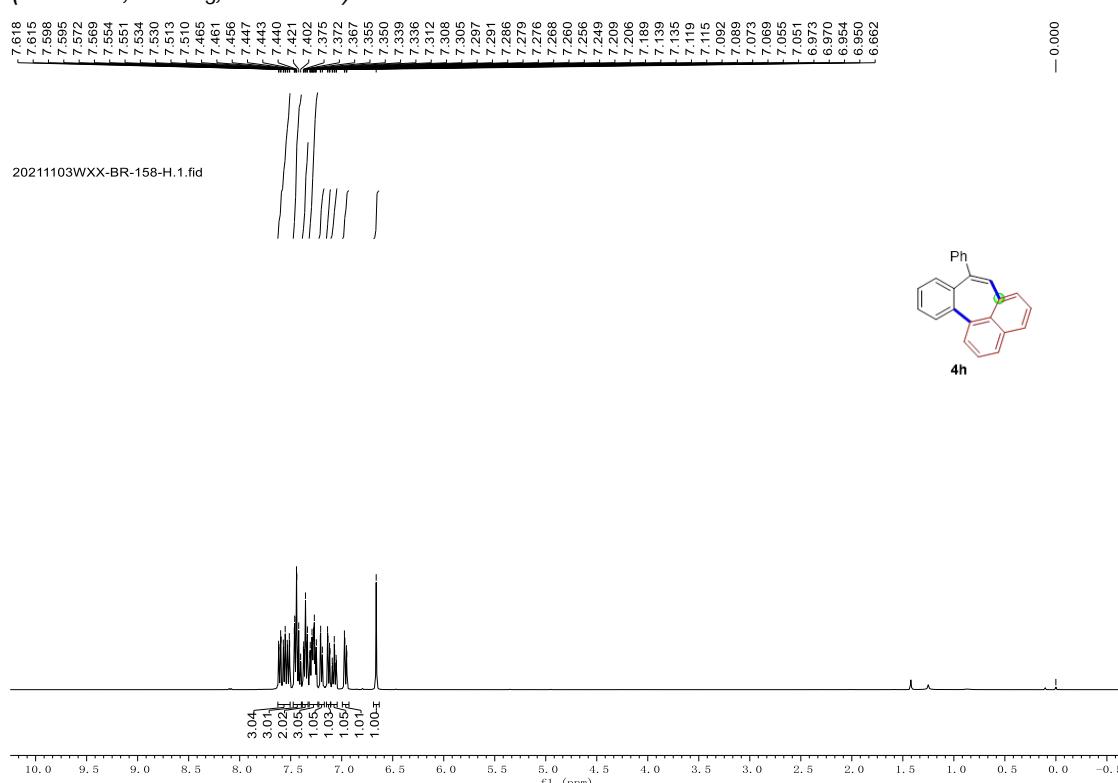
8-butylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4g):

(^{13}C NMR, CDCl_3 , 101 MHz)



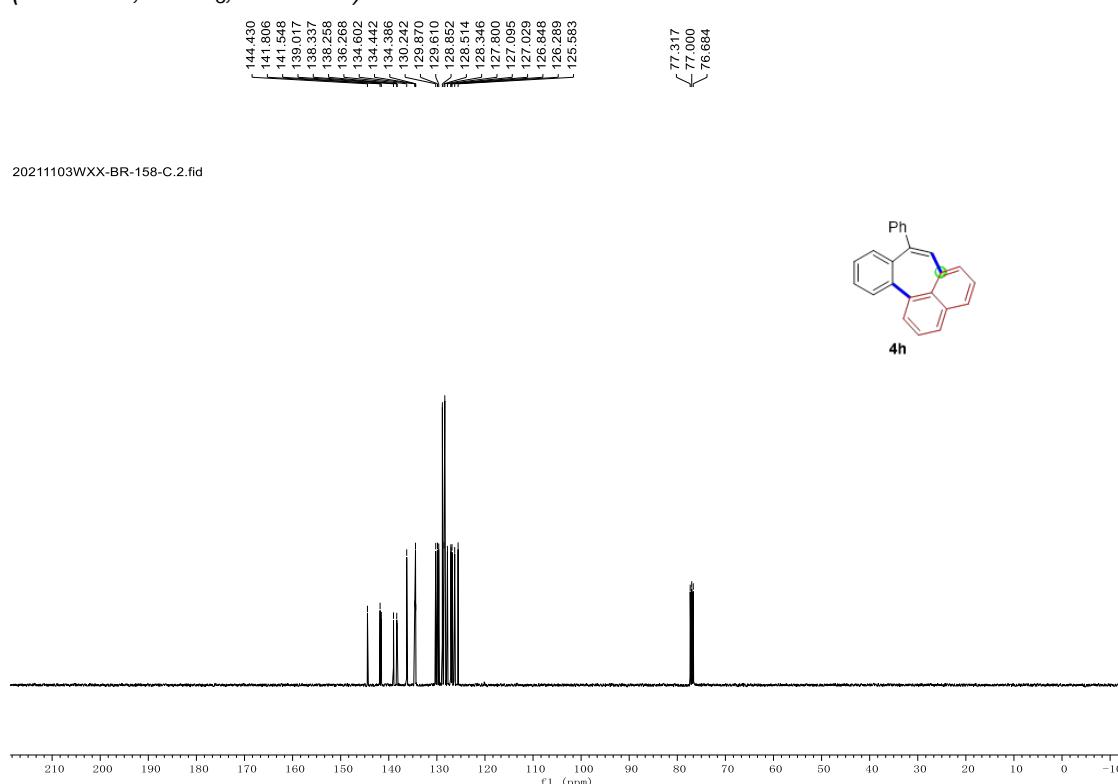
8-phenylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4h):

(^1H NMR, CDCl_3 , 400 MHz)



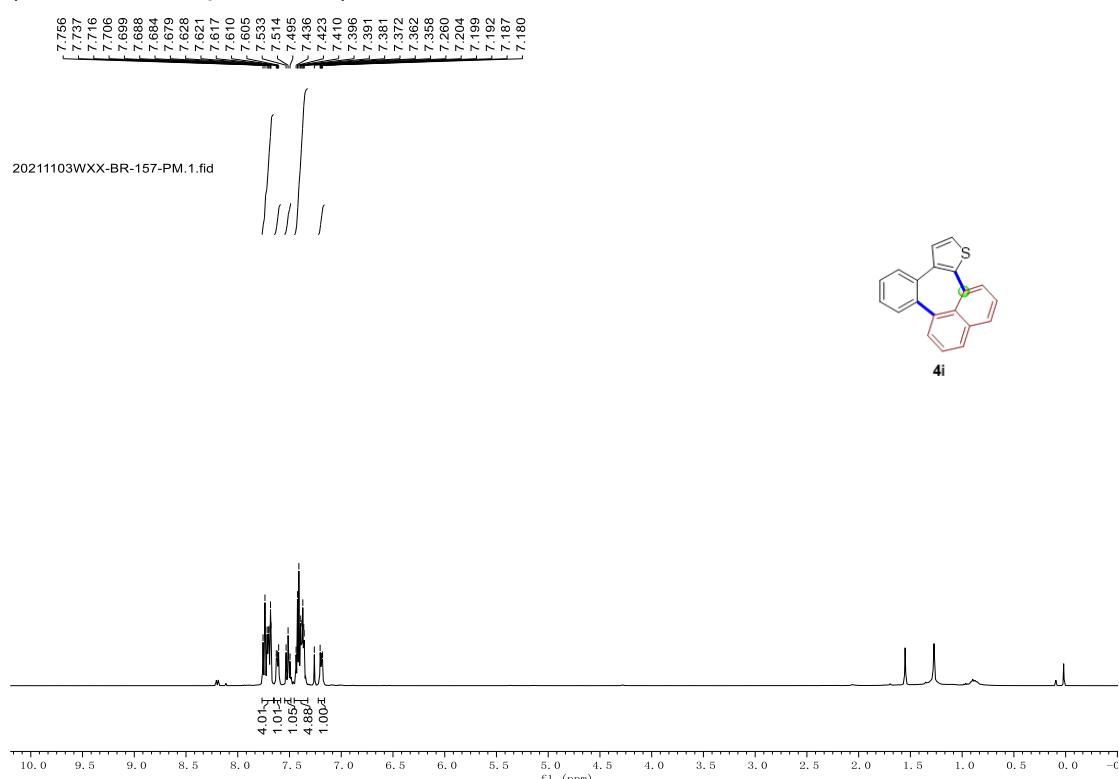
8-phenylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene (4h):

(^{13}C NMR, CDCl_3 , 101 MHz)



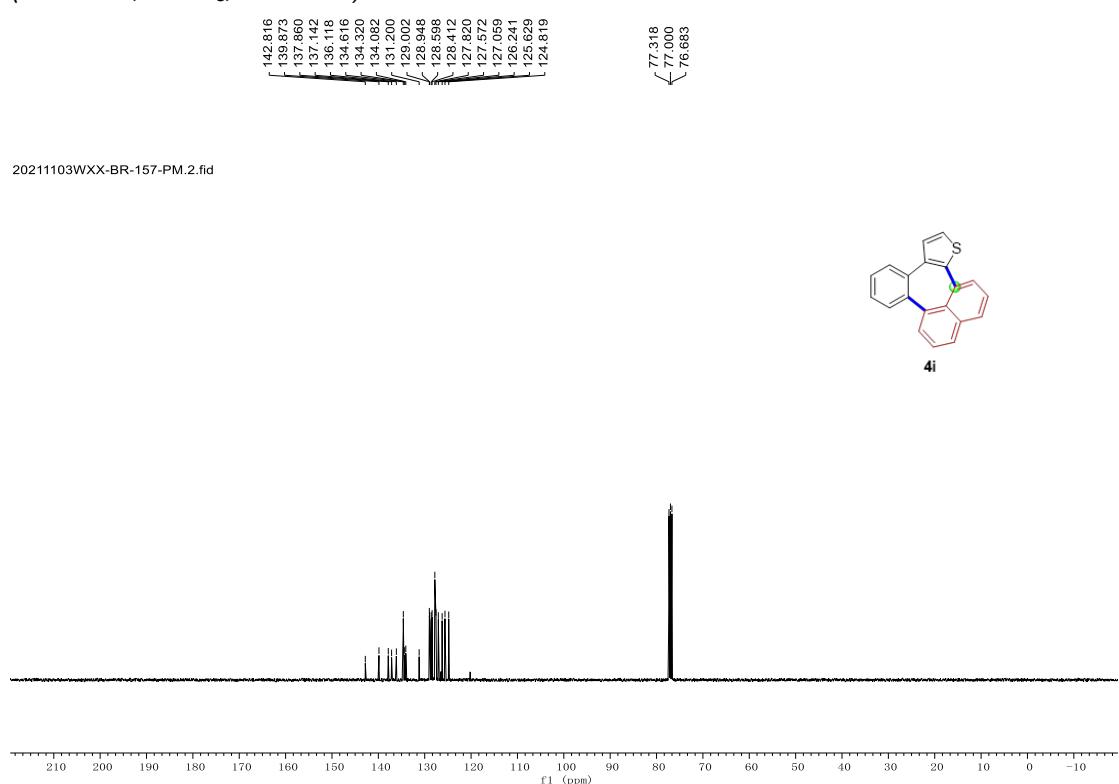
benzo[3,4]naphtho[1',8':5,6,7]cyclohepta[1,2-b]thiophene (4i):

(^1H NMR, CDCl_3 , 400 MHz)



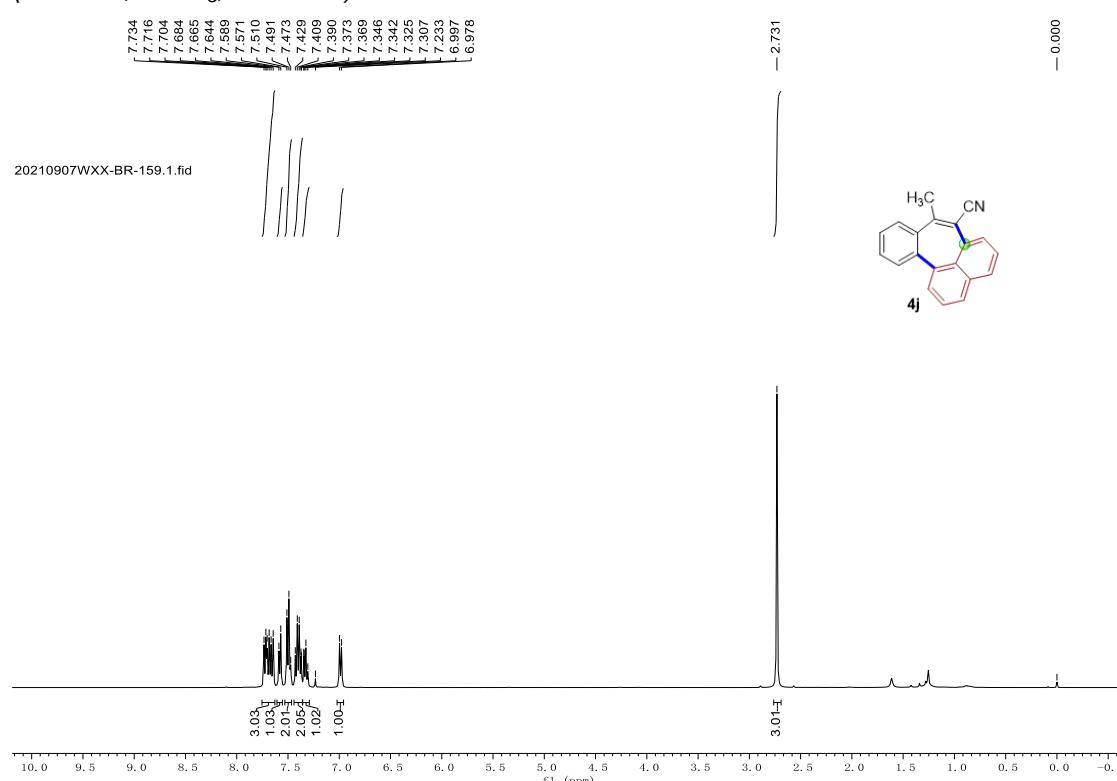
benzo[3,4]naphtho[1',8':5,6,7]cyclohepta[1,2-b]thiophene (4i):

(^{13}C NMR, CDCl_3 , 101 MHz)



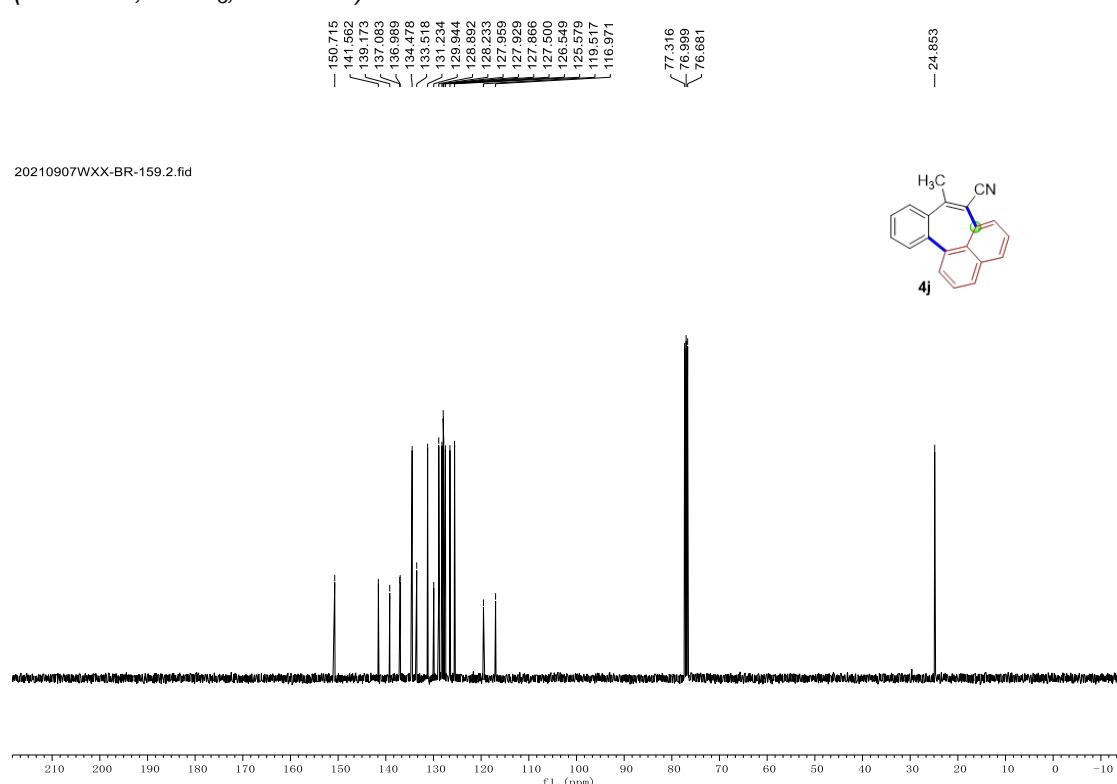
8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene-7-carbonitrile (4j):

(^1H NMR, CDCl_3 , 400 MHz)

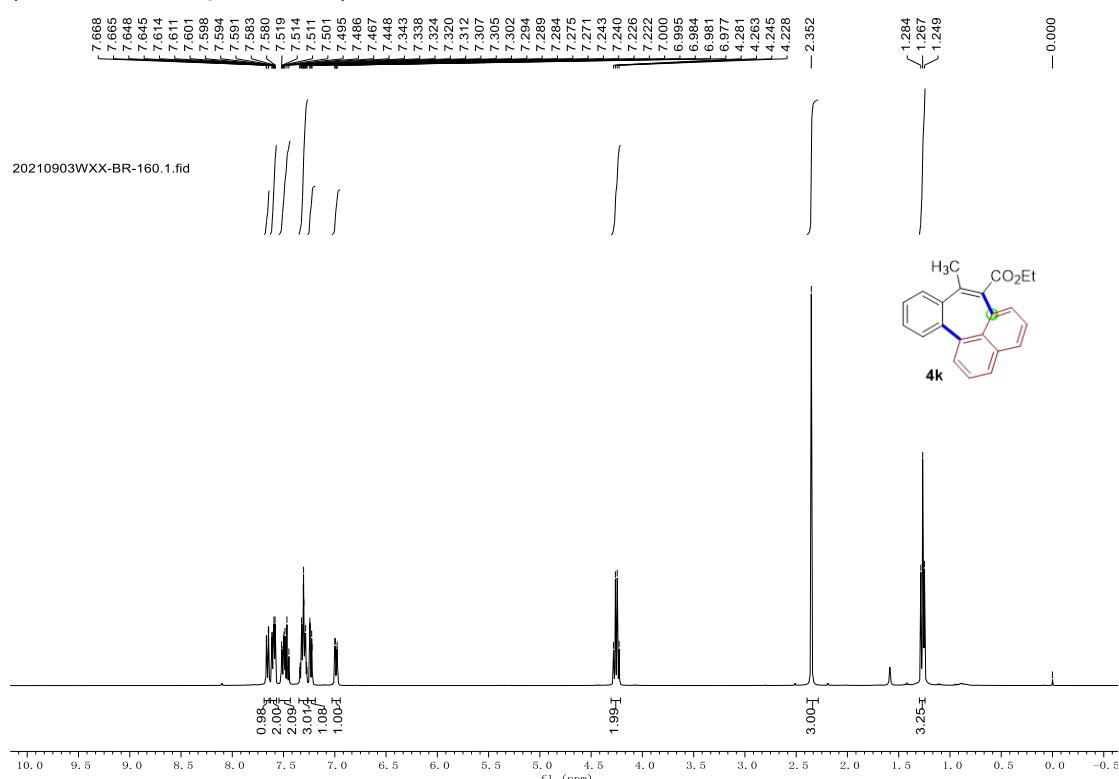


8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene-7-carbonitrile (4j):

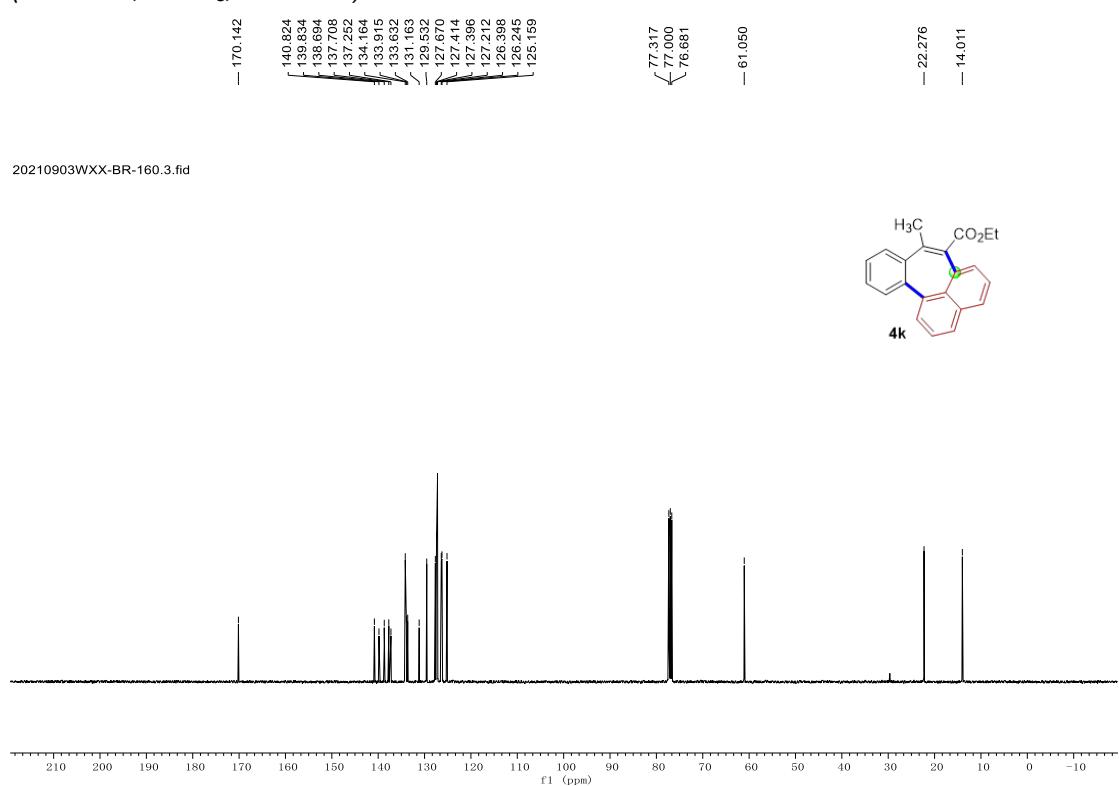
(^{13}C NMR, CDCl_3 , 101 MHz)



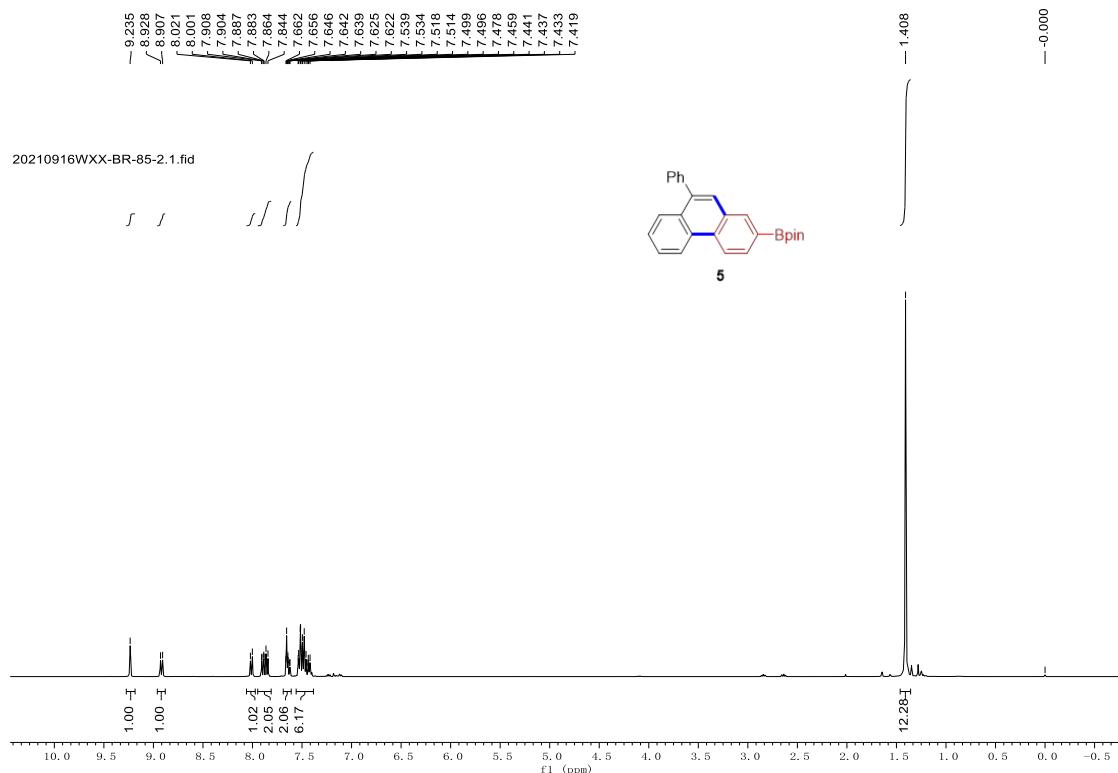
ethyl 8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene-7-carboxylate (4k):
 $(^1H$ NMR, $CDCl_3$, 400 MHz)



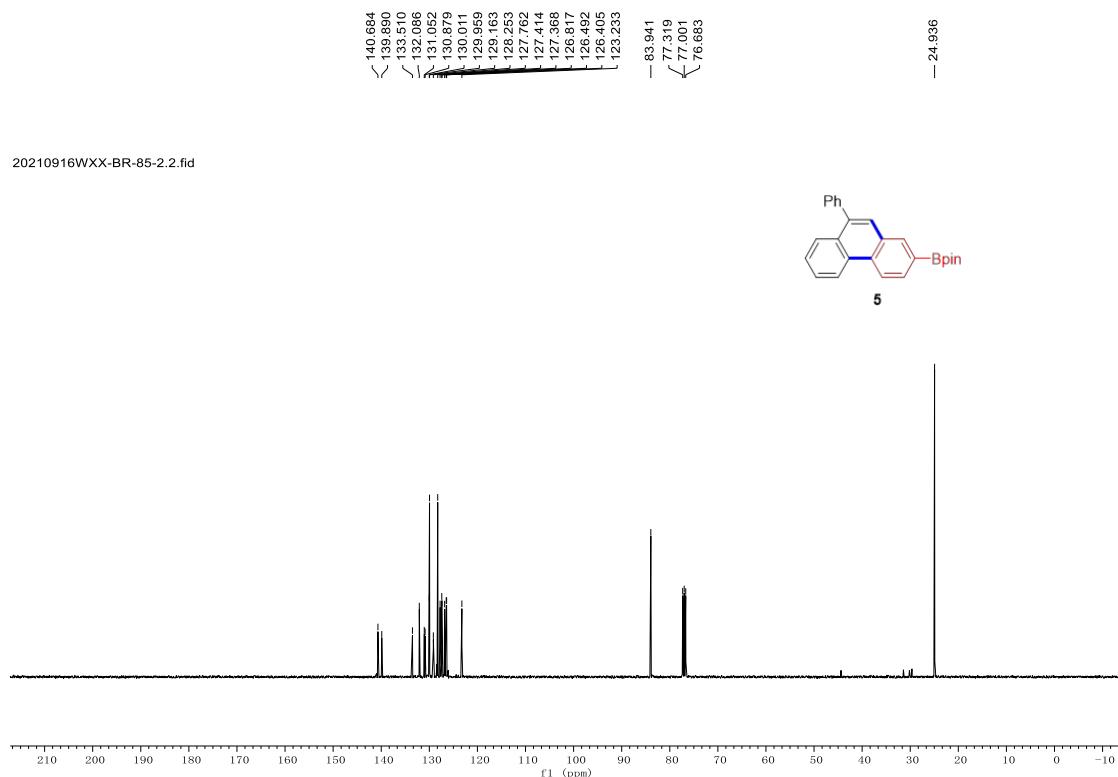
ethyl 8-methylbenzo[4,5]cyclohepta[1,2,3-de]naphthalene-7-carboxylate (4k):
 $(^{13}\text{C NMR, } \text{CDCl}_3, 101 \text{ MHz})$



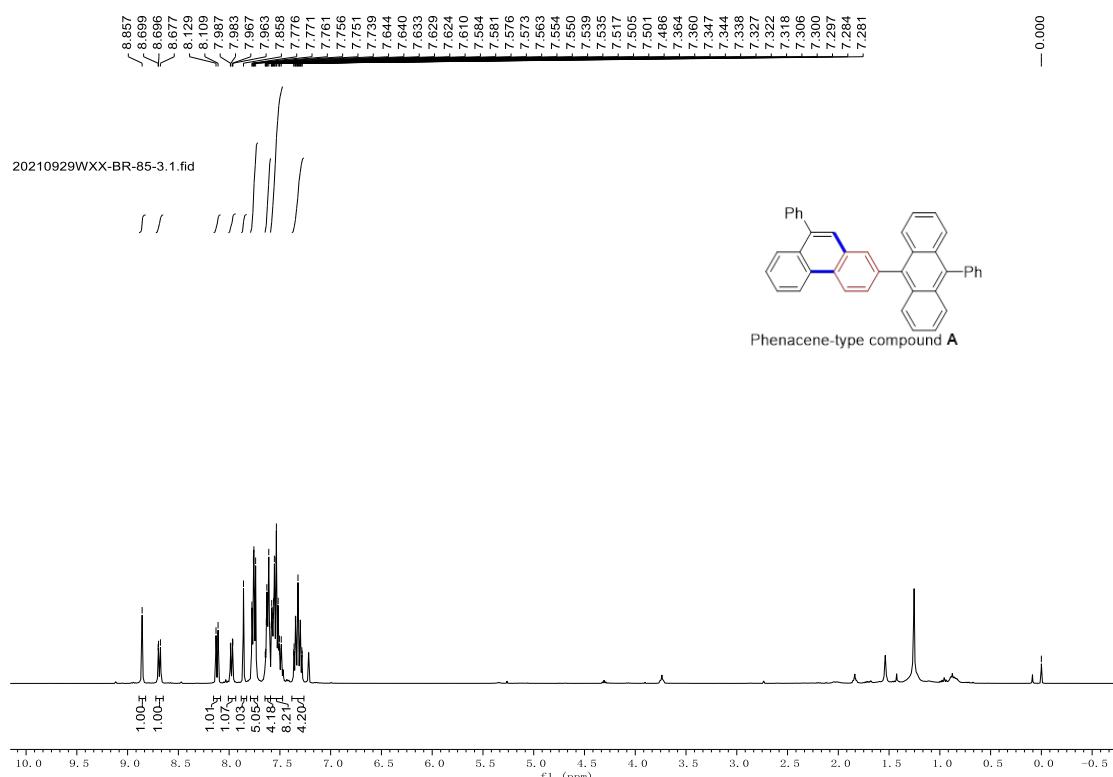
4,4,5,5-tetramethyl-2-(9-phenylphenanthren-2-yl)-1,3,2-dioxaborolane (5):
 $(^1H$ NMR, $CDCl_3$, 400 MHz)



4,4,5,5-tetramethyl-2-(9-phenylphenanthren-2-yl)-1,3,2-dioxaborolane (5):
 $(^{13}\text{C NMR, } \text{CDCl}_3, 101 \text{ MHz})$



9-phenyl-2-(10-phenylanthracen-9-yl)phenanthrene (Phenacene-type compound A):
 ^1H NMR, CDCl_3 , 400 MHz)



9-phenyl-2-(10-phenylanthracen-9-yl)phenanthrene (Phenacene-type compound A):
 ^{13}C NMR, CDCl_3 , 101 MHz)

