## Expedient Synthesis of 9,10-Phenanthrenes via LiOPiv-Promoted

## and Palladium-Catalysed Aryne Annulation by Vinyl Triflates

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#### **Materials and Methods**

**General.** All reactions dealing with air- and moisture-sensitive compounds were carried out in dry reaction vessels under a nitrogen atmosphere. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded on Agilent 600 MHz NMR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and CHCl<sub>3</sub> (77.0 ppm), respectively. ESI high-resolution mass spectra (HRMS) were recorded on a Waters SYNPAT G2. IR spectra were recorded in a PerkinElmer FT/IR-S100 spectrometer. Melting points were determined using a capillary melting point apparatus and are uncorrected.

**Materials.** Unless otherwise noted, materials were purchased from commercial suppliers and were used as received. Anhydrous MeCN was distilled over CaH<sub>2</sub> and stored under N<sub>2</sub>.

### Table S1. Effect of base on the reaction of 1a.

OTf +	OTf	5 mol% Pd <sub>2</sub> (dba) <sub>3</sub> 20 mol% P(o-tolyl) <sub>3</sub> 6.0 equiv CsF		Me ,	Me
Me Me	TMS	base MeCN (1.6 mL)			
0.1 mmol	0.3 mmol	60 °C, 12 h			
1a	2a		За		4
	Entry	Change of base	3a:4ª	Yield of 3a/% <sup>b</sup>	
	1	1.0 equiv LiOPiv	137:1	92	
	2	no base	7:1	85	
	3	1.0 equiv KOPiv	128:1	85	
	4	1.0 equiv CsOPiv	99:1	83	
	5	2.0 equiv CsOPiv	110:1	54	
	6	0.5 equiv CsOPiv	10:1	87	
	7	2.0 equiv LiOPiv	132:1	85	
	8	2.0 equiv NaOPiv	130:1	73	
	9	2.0 equiv KOPiv	127:1	70	
	10	2.0 equiv LiOAc	20:1	63	
	11	2.0 equiv NaOAc	14:1	43	
	12	2.0 equiv KOAc	28:1	44	
	13	2.0 equiv CsOAc	9:1	37	
	14	2.0 equiv Li <sub>2</sub> CO <sub>3</sub>	6:1	80	
	15	2.0 equiv Cs <sub>2</sub> CO <sub>3</sub>	8:1	62	

<sup>a</sup>Determined by <sup>1</sup>H NMR analysis of the crude reaction mixture.

<sup>b</sup>Yields of 3a determined by <sup>1</sup>H NMR analysis against a known amount of 1,1,2,2-tetrachloroethane as an internal standard that was added to the reaction mixture following workup and immediately prior to preparation of the NMR sample.

#### Table S2. Effect of base on the reaction of 1s.



<sup>a</sup>Determined by <sup>1</sup>H NMR analysis of the crude reaction mixture. Yields of 3s determined by <sup>1</sup>H NMR analysis against a known amount of 1,1,2,2-tetrachloroethane as an internal standard that was added to the reaction mixture following workup and immediately prior to preparation of the NMR sample.

Table S3. Control Experiments of 1am

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We tried the following conditions and did not find the target product. In the following conditions, we found the by-product triphenylene, which was produced from benzyne precursor 2a, phenyl pivalate and tert-butoxybenzene.

Entry	Base	T/ °C
1	No base	60
2	LiOPiv	60
3	LiOPiv	90
4	LiOPiv	120
5	$Cs_2CO_3$	60
6	LiO <sup>t</sup> Bu	60
7	NaO <sup>t</sup> Bu	60
8	KO <sup>t</sup> Bu	60
9	LiN(TMS) <sub>2</sub>	60
10	$Cs_2CO_3$	90
11	LiO <sup>t</sup> Bu	90
12	NaO <sup>t</sup> Bu	90
13	KO <sup>t</sup> Bu	90
14	LiN(TMS) <sub>2</sub>	90

## Table S4. Control Experiments of 1an and 1ao



We used these two substrates (1an, 1ao) to instead of 1a, but we did not find the 3a product at all.

## Table S5. The Failed Cyclic Vinyl Triflates Used in the Transformation

Under Standard Conditions or enhance the reaction tempratures



#### **Preparation of Substrates**

#### Synthesis of enol triflates

**General procedure A<sup>1</sup>**: To solution of Cyclohexanone derivative (5 mmol) in anhydrous THF (25 mL) was added LiHMDS (6 mL, 6 mmol, 1.0 M in THF, 1.2 equiv) at -78 °C. After 1 h at -78 °C under an argon atmosphere, a solution of PhNTf<sub>2</sub> (2.5 g, 7 mmol, 1.4 equiv) in anhydrous THF (5 mL) was slowly added to the mixture solution at -78 °C. The mixture solution was allowed to warm to rt over a period of 4 h and stirred for additional 12 h. After the completion of the reaction, the resulting solution was treated with saturated aqueous NH<sub>4</sub>Cl (10 ml) and extracted with ethyl acetate (3 x 20 mL). The combined organic solution was washed with saturated aqueous Na<sub>2</sub>CO<sub>3</sub> (20 mL), dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue oil was purified by flash column chromatography on silica gel to afford the product as a pale yellow oil.

Following the general procedure A to produce 1c, 1o, 1p, 1q, 1r.

General procedure  $B^2$ : To a solution of Cyclohexanone derivative (5 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added 2-chloropyiride (0.52 mL, 5.5 mmol, 1.1 equiv) at 0 °C. After 10 min at 0 °C, trifluoromethanesulfonic anhydride (1.0 mL, 6 mmol, 1.2 equiv) was added dropwise. The resulting solution was warmed to rt and stirred for 2 h under an argon atmosphere. After the completion of the reaction, the solution was concentrated and the resulting cherry-color oil was purified by flash column chromatography on silica gel to afford the product as a pale yellow oil. Following the general procedure B to produce 1a, 1b, 1d, 1e, 1f, 1g, 1h, 1i, 1j, 1ai, 1aj, 1al.

**General procedure C<sup>3</sup>**: To solution of Cyclohexanone derivative (5 mmol) in anhydrous THF (25 mL) was added LDA (3 mL, 6 mmol, 2.0 M in THF, 1.2 equiv) at -78 °C. After 1 h at -78 °C under an argon atmosphere, a solution of PhNTf<sub>2</sub> (1.79 g, 5 mmol, 1.0 equiv) in anhydrous THF (5 mL) was slowly added to the mixture solution at -78 °C. The mixture solution was allowed to warm to rt over a period of 4 h and stirred for additional 12 h. After the completion of the reaction, the resulting solution was treated with saturated aqueous NH<sub>4</sub>Cl (10 ml) and extracted with ethyl acetate (3 x 20 mL). The combined organic solution was washed with saturated aqueous Na<sub>2</sub>CO<sub>3</sub> (20 mL), dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue oil was purified by flash column chromatography on silica gel to afford the product as a pale yellow oil.

Following the general procedure C to produce 1k, 1l, 1m, 1n.

#### **General procedure D**<sup>4</sup>:

#### Preparation of saturated aqueous LiOH solution.

55.14g of LiOH was dissolved in 460mL of deionized H2O to obtain a saturated solution (approximately 5M).

#### General Procedure for the Synthesis of (Z)-Enol Triflates

The starting acetoacetate derivative (4 mmol) was added to a round-bottom flask and dissolved in either hexanes or toluene (20 mL, 0.2M). The solution was cooled with an ice bath to  $5-10^{\circ}$ C (internal temperature) followed by addition of a saturated aqueous solution of LiOH (6 mL, ~30)

mmol) in one portion. The resulting biphasic mixture was *vigorously stirred* at 5-10°C for ~5 minutes followed by the addition of triflic anhydride (10 mmol) dropwise at a rate to maintain the internal temperature between 5-15 °C. Upon completion of the reaction (as judged by TLC, typically <10 min), the biphasic solution was diluted with H2O (5mL) and the layers were separated. The aqueous layer was extracted with EtOAc (1 x 10mL). The combined organic layers were washed with H2O (1 x 5mL), brine (1 x 5mL), and dried over MgSO4. The organic layer was filtered and concentrated under reduced pressure to yield the corresponding crude (Z)-enol triflate.

Following the general procedure D to produce 1s, 1t, 1u, 1v, 1w, 1x, 1y, 1z, 1aa, 1ab, 1ac, 1ad, 1ae, 1af, 1ag, 1ah.

Below are summaried characterization data for newly synthesized starting materials. <sup>1</sup>H and <sup>13</sup>C NMR spectra data for the known ones showed good agreement with the literature data.



1h

**4-(tert-pentyl)cyclohex-1-en-1-yl trifluoromethanesulfonate (1h)**: Following the general procedure B; Colorless oil; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  5.77 – 5.72 (m, 1H), 2.42 – 2.34 (m, 1H), 2.34 – 2.28 (m, 1H), 2.19 – 2.10 (m, 1H), 1.99 – 1.94 (m, 1H), 1.91 – 1.88 (m, 1H), 1.45 – 1.33 (m, 2H), 1.32 – 1.25 (m, 2H), 0.83 – 0.80 (m, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  149.15, 118.51, 118.50 (q, <sup>1</sup>*J*<sub>C-F</sub> = 320.2 Hz), 40.34, 34.36, 32.43, 28.57, 24.86, 23.81, 23.77, 23.65, 8.06.



1n

**4-(1,4-dioxaspiro[4.5]decan-8-yl)cyclohexan-1-yl trifluoromethanesulfonate** (**1n**): Following the general procedure C; Colorless oil; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  5.73 (m, 1H), 3.93 (m, 4H), 2.43 – 2.34 (m, 1H), 2.34 – 2.27 (m, 1H), 2.25 – 2.18 (m, 1H), 1.98 – 1.89 (m, 2H), 1.79 – 1.75 (m, 2H), 1.74 – 1.66 (m, 2H), 1.54 – 1.48(m, 2H), 1.47 – 1.40 (m, 2H), 1.37 – 1.28 (m, 2H), 1.26 – 1.20 (m, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  149.10, 118.48 (q, <sup>1</sup>*J*<sub>C-F</sub> = 320.2 Hz), 118.00, 108.74, 64.21, 40.30, 37.13, 34.64, 27.86, 27.48, 27.22, 26.98, 26.19; HRMS (ESI): Calcd for C<sub>15</sub>H<sub>21</sub>F<sub>3</sub>O<sub>5</sub>S [M + Na]<sup>+</sup> 393.0954, found 393.0955.



1t

**ethyl** (**Z**)-**3-(p-tolyl)-3-(((trifluoromethyl)sulfonyl)oxy)acrylate** (**1t**): Following the general procedure D; White solid; Mp = 57-58 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.47 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 6.21 (s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.35 (td, *J* = 7.2, 1.1

Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  162.94, 155.25, 142.47, 129.72, 128.91, 126.38, 118.24 (q, <sup>1</sup>*J*<sub>C-F</sub> = 320.2 Hz), 110.65, 61.33, 21.46, 14.05; **HRMS** (ESI): Calcd for C<sub>13</sub>H<sub>13</sub>F<sub>3</sub>O<sub>5</sub>S [M + Na]<sup>+</sup> 361.0328, found 361.0335.



ethyl (Z)-3-(4-(trifluoromethyl)phenyl)-3-(((trifluoromethyl)sulfonyl)oxy)acrylate (1u): Following the general procedure D; White solid; Mp = 56-57 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 – 7.67 (m, 4H), 6.32 (s, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  162.29, 153.18, 135.23, 133.39 (q, *J* = 33.2 Hz), 126.83, 126.10 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.6 Hz), 123.34 (q, <sup>2</sup>*J*<sub>C-F</sub> = 273.3 Hz), 118.19 (q, <sup>1</sup>*J*<sub>C-F</sub> = 320.2 Hz), 113.66, 61.75, 13.99; HRMS (ESI): Calcd for C<sub>13</sub>H<sub>10</sub>F<sub>6</sub>O<sub>5</sub>S [M + Na]<sup>+</sup> 415.0045, found 415.0045.



1w

ethyl (Z)-3-(4-nitrophenyl)-3-(((trifluoromethyl)sulfonyl)oxy)acrylate (1w): Following the general procedure D; Yellow solid; Mp = 77-78 °C <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.35 – 8.30 (m, 2H), 7.80 – 7.74 (m, 2H), 6.38 (s, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  162.03, 152.23, 149.42, 137.64, 127.47, 124.30, 118.17 (q, <sup>1</sup>*J*<sub>C-F</sub> = 320.2 Hz), 114.85, 61.92, 13.97; HRMS (ESI): Calcd for C<sub>12</sub>H<sub>10</sub>F<sub>3</sub>NO<sub>7</sub>S [M + H]<sup>+</sup> 370.0203, found 370.0205.



1x

ethyl (Z)-3-(naphthalen-2-yl)-3-(((trifluoromethyl)sulfonyl)oxy)acrylate (1x): Following the general procedure D; White solid; Mp = 51-52 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.11 (d, *J* = 1.9 Hz, 1H), 7.93 – 7.85 (m, 3H), 7.64 – 7.55 (m, 3H), 6.40 (s, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  162.87, 155.06, 134.50, 132.57, 129.10, 128.90, 128.88, 128.28, 127.82, 127.34, 127.25, 122.42, 118.29 (q, <sup>1</sup>*J*<sub>C-F</sub> = 321.6 Hz), 111.77, 61.46, 14.07; HRMS (ESI): Calcd for C<sub>16</sub>H<sub>13</sub>F<sub>3</sub>O<sub>5</sub>S [M + Na]<sup>+</sup> 397.0328, found 397.0330.





ethyl (Z)-3-cyclopropyl-3-(((trifluoromethyl)sulfonyl)oxy)acrylate (1ad): Following the general

procedure D; Colorless oil; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  5.60 (s, 1H), 4.22 (q, J = 7.2 Hz, 2H), 1.62 (tq, J = 9.8, 4.9, 4.4 Hz, 1H), 1.29 (td, J = 7.2, 1.5 Hz, 3H), 1.06 – 1.00 (m, 2H), 0.88 – 0.82 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  162.67, 160.60, 118.43 (q, <sup>1</sup>J<sub>C-F</sub> = 320.2 Hz), 108.82, 61.18, 14.76, 13.99, 8.35; HRMS (ESI): Calcd for C<sub>9</sub>H<sub>11</sub>F<sub>3</sub>O<sub>5</sub>S [M + H]<sup>+</sup> 289.0352, found 289.1050.



1ae

ethyl (Z)-3-cyclobutyl-3-(((trifluoromethyl)sulfonyl)oxy)acrylate (1ae): Following the general procedure D; Colorless oil; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  5.74 (s, 1H), 4.25 (q, *J* = 7.4 Hz, 2H), 3.26 (p, *J* = 8.6 Hz, 1H), 2.28 (qd, *J* = 8.3, 7.5, 3.9 Hz, 2H), 2.14 – 2.05 (m, 2H), 2.05 – 1.97 (m, 1H), 1.91 – 1.82 (m, 1H), 1.30 (td, *J* = 7.2, 1.5 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  162.70, 161.76, 118.32 (q, <sup>1</sup>*J*<sub>C-F</sub> =320.2 Hz), 110.01, 61.20, 38.05, 27.03, 17.68, 14.00; HRMS (ESI): Calcd for C<sub>10</sub>H<sub>13</sub>F<sub>3</sub>O<sub>5</sub>S [M + Na]<sup>+</sup> 325.0328, found 325.0332.



1af

ethyl (Z)-3-cyclohexyl-3-(((trifluoromethyl)sulfonyl)oxy)acrylate (1af): Following the general procedure D; Colorless oil; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  5.69 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.29 – 2.20 (m, 1H), 2.06 – 1.96 (m, 2H), 1.83 (dt, *J* = 13.1, 3.5 Hz, 2H), 1.76 – 1.69 (m, 1H), 1.35 – 1.23 (m, 5H), 1.18 (dt, *J* = 11.7, 3.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  162.90, 162.79, 118.34 (q, <sup>1</sup>*J*<sub>C-F</sub> =320.2 Hz), 109.96, 61.20, 42.64, 30.30, 25.61, 25.57, 13.99; HRMS (ESI): Calcd for C<sub>12</sub>H<sub>17</sub>F<sub>3</sub>O<sub>5</sub>S [M + H]<sup>+</sup> 331.0822, found 330.9962.



1ag

ethyl (Z)-3-(tetrahydrofuran-2-yl)-3-(((trifluoromethyl)sulfonyl)oxy)acrylate (1ag): Following the general procedure D; Colorless oil; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  6.12 (s, 1H), 4.51 (dd, J = 7.8, 5.5 Hz, 1H), 4.29 – 4.20 (m, 2H), 4.00 – 3.94 (m, 1H), 3.91 – 3.84 (m, 1H), 2.25 – 2.17 (m, 1H), 2.04 – 1.90 (m, 3H), 1.30 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  162.61, 158.05, 118.35 (q, <sup>1</sup> $J_{C-F}$  = 320.2 Hz), 110.42, 76.38, 69.19, 61.29, 30.22, 25.03, 13.97; HRMS (ESI): Calcd for C<sub>10</sub>H<sub>13</sub>F<sub>3</sub>O<sub>6</sub>S [M + Na]<sup>+</sup> 341.0277, found 341.0280.



(Z)-3-oxo-1,3-diphenylprop-1-en-1-yl trifluoromethanesulfonate (1ai): Following the general procedure B; Yellow solid; Mp = 80-81 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.01 (dd, J = 8.2, 1.4 Hz, 2H), 7.71 – 7.67 (m, 2H), 7.64 – 7.60 (m, 1H), 7.57 – 7.48 (m, 5H), 7.18 (s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  187.26, 153.89, 137.32, 133.72, 132.21, 131.82, 129.12, 128.80, 128.56, 126.64, 118.21 (q, <sup>1</sup> $J_{C-F}$  = 320.2 Hz), 114.90; HRMS (ESI): Calcd for C<sub>16</sub>H<sub>11</sub>F<sub>3</sub>O<sub>4</sub>S [M + H]<sup>+</sup> 357.0403, found 356.9525.



1aj

(Z)-2-cyano-1-phenylvinyl trifluoromethanesulfonate (1aj): Following the general procedure B; Colorless oil; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.63 – 7.57 (m, 3H), 7.51 (dd, J = 8.8, 7.1 Hz, 2H), 5.76 (s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  161.56, 133.11, 130.35, 129.45, 126.36, 118.23 (q, <sup>1</sup> $J_{C-F}$  = 320.2 Hz), 112.46, 90.40; HRMS (ESI): Calcd for C<sub>10</sub>H<sub>6</sub>F<sub>3</sub>NO<sub>3</sub>S [M + Na]<sup>+</sup> 299.9913, found 299.9918.

#### Synthesis of phenanthrene

#### A General Procedure for Pd-catalyzed aryne annulation by enol triflates

A 10 mL of Schlenk tube equipped with a stirrer bar was charged with  $Pd_2(dba)_3$  (5 mol %), tri-*o*-tolylphosphane (20 mol %), CsF (1.2 mmol, 6.0 equiv), and LiOPiv (0.2 mmol, 1.0 equiv) in the glove box. Then, the Schlenk tube removed from glove box and quickly evacuated and refilled with Ar for three times, followed by the addition of MeCN (3.2 mL), enol triflates (0.20 mmol, 1.0 equiv), and silylaryl triflate (0.60 mmol, 3.0 equiv). The Schlenk tube was sealed with a Teflon screwcap under Ar flow and the reaction mixture was stirred at 60 °C for 12 h. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with ethyl acetate (20 mL). Subsequently, the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.



2,2-dimethyl-1,2,3,4-tetrahydrotriphenylene (3a): Following the general procedure; White solid

(87% yield, eluent = petroleum ether); Mp = 126-127 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.73 (dt, J = 6.2, 1.9 Hz, 2H), 8.15 – 8.07 (m, 2H), 7.69 – 7.58 (m, 4H), 3.20 (ddt, J = 6.9, 5.1, 1.9 Hz, 2H), 2.96 (s, 2H), 1.80 (t, J = 6.6 Hz, 2H), 1.14 (s, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  132.06, 131.71, 129.46, 129.40, 129.24, 128.88, 126.56, 126.51, 125.51, 125.49, 123.53, 123.31, 122.77, 122.73, 40.64, 35.36, 29.09, 28.43, 24.49; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 3077, 2949, 2916, 2860, 2829, 1433; **HRMS** (ESI): Calcd for C<sub>20</sub>H<sub>20</sub> [M + H]<sup>+</sup> 261.1638, found 261.1645.



**2-methyl-1,2,3,4-tetrahydrotriphenylene (3b)**: Following the general procedure; White solid (81% yield, eluent = petroleum ether); Mp = 111-112 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.76 – 8.67 (m, 2H), 8.14 – 8.03 (m, 2H), 7.62 (qd, J = 6.7, 3.5 Hz, 4H), 3.32 (dd, J = 16.7, 4.8 Hz, 2H), 3.16 – 3.07 (m, 1H), 2.69 (ddt, J = 16.7, 10.2, 2.0 Hz, 1H), 2.16 – 2.10 (m, 1H), 2.06 – 1.97 (m, 1H), 1.61 – 1.55 (m, 1H), 1.24 (d, J = 6.6 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  131.81, 131.78, 129.99, 129.88, 129.31, 129.23, 126.54, 126.51, 125.48, 123.44, 123.34, 122.71, 35.47, 31.01, 28.88, 26.95, 22.13; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 3073, 2947, 2919, 2863, 2829, 1433; **HRMS** (ESI): Calcd for C<sub>19</sub>H<sub>18</sub> [M + H]<sup>+</sup> 247.1481, found 247.1488.



**1,2,3,4-tetrahydrotriphenylene (3c)**: Following the general procedure; White solid (77% yield, eluent = petroleum ether); Mp = 118-119 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.74 – 8.68 (m, 2H), 8.11 – 8.05 (m, 2H), 7.66 – 7.58 (m, 4H), 3.18 (h, *J* = 3.9, 3.1 Hz, 4H), 2.01 (hept, *J* = 4.7 Hz, 4H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  131.92, 130.26, 129.22, 126.53, 125.49, 123.29, 122.70, 26.87, 22.92; IR (neat):  $\upsilon$  (cm<sup>-1</sup>) 3074, 2934, 2870, 2848, 1435; HRMS (ESI): Calcd for C<sub>18</sub>H<sub>16</sub> [M + H]<sup>+</sup> 233.1325, found 233.1335.



**2-ethyl-1,2,3,4-tetrahydrotriphenylene (3d)**: Following the general procedure; White solid (63% yield, eluent = petroleum ether); Mp = 78-79 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.74 – 8.67 (m, 2H), 8.13 – 8.05 (m, 2H), 7.67 – 7.57 (m, 4H), 3.33 (td, *J* = 16.6, 4.6 Hz, 2H), 3.13 – 3.05 (m, 1H),

2.71 (ddt, J = 16.7, 10.3, 2.1 Hz, 1H), 2.20 (ddt, J = 13.0, 5.2, 2.4 Hz, 1H), 1.79 (tdd, J = 11.4, 5.5, 3.0 Hz, 1H), 1.64 – 1.56 (m, 2H), 1.54 – 1.49 (m, 1H), 1.11 (t, J = 7.5 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  131.90, 131.78, 130.17, 129.96, 129.31, 129.22, 126.53, 126.51, 125.47, 123.44, 123.31, 122.72, 122.70, 35.59, 33.38, 29.32, 28.60, 26.94, 11.61; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 3072, 2956, 2925, 2869, 1434; **HRMS** (ESI): Calcd for C<sub>20</sub>H<sub>20</sub> [M + H]<sup>+</sup> 261.1638, found 261.1646.



**2-propyl-1,2,3,4-tetrahydrotriphenylene (3e)**: Following the general procedure; White solid (60% yield, eluent = petroleum ether); Mp = 96-98 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.74 – 8.67 (m, 2H), 8.13 – 8.03 (m, 2H), 7.65 – 7.58 (m, 4H), 3.32 (td, *J* = 16.8, 4.6 Hz, 2H), 3.14 – 3.06 (m, 1H), 2.76 – 2.68 (m, 1H), 2.18 (ddq, *J* = 13.1, 5.5, 2.6 Hz, 1H), 1.94 – 1.85 (m, 1H), 1.56 – 1.49 (m, 4H), 1.02 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): <sup>13</sup>C NMR (151 MHz, Chloroform-*d*)  $\delta$  131.90, 131.78, 130.16, 129.97, 129.32, 129.23, 126.53, 126.51, 125.50, 125.47, 123.46, 123.33, 122.73, 122.69, 38.97, 33.69, 33.54, 29.04, 26.91, 20.18, 14.45; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 3074, 2959, 2922, 2870, 2835, 1434; **HRMS** (ESI): Calcd for C<sub>21</sub>H<sub>22</sub> [M + H]<sup>+</sup> 275.1794, found 275.1803.



**2-pentyl-1,2,3,4-tetrahydrotriphenylene (3f)**: Following the general procedure; White solid (67% yield, eluent = petroleum ether); Mp = 96-97 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.74 – 8.67 (m, 2H), 8.12 – 8.04 (m, 2H), 7.62 (dt, *J* = 6.6, 3.2 Hz, 4H), 3.32 (td, *J* = 15.4, 14.1, 4.6 Hz, 2H), 3.09 (ddd, *J* = 17.0, 9.8, 5.6 Hz, 1H), 2.75 – 2.67 (m, 1H), 2.18 (ddt, *J* = 10.6, 5.6, 2.7 Hz, 1H), 1.87 (dh, *J* = 14.6, 3.4 Hz, 1H), 1.53 (qd, *J* = 8.6, 8.0, 5.6 Hz, 5H), 1.39 (dtd, *J* = 13.6, 9.4, 8.7, 5.2 Hz, 4H), 0.96 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  131.90, 131.78, 130.16, 129.99, 129.31, 129.22, 126.53, 126.50, 125.47, 123.44, 123.32, 122.72, 122.70, 36.68, 33.84, 33.74, 32.25, 29.04, 26.92, 26.79, 22.77, 14.17; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 3074, 2952, 2921, 2869, 2845, 1434; **HRMS** (ESI): Calcd for C<sub>23</sub>H<sub>26</sub> [M + H]<sup>+</sup> 303.2107, found 303.2115.



2-(tert-butyl)-1,2,3,4-tetrahydrotriphenylene (3g): Following the general procedure; White solid

(66% yield, eluent = petroleum ether); Mp = 121-122 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.75 – 8.66 (m, 2H), 8.15 – 8.03 (m, 2H), 7.67 – 7.57 (m, 4H), 3.38 (dd, *J* = 16.8, 4.8 Hz, 1H), 3.32 – 3.25 (m, 1H), 3.10 – 3.00 (m, 1H), 2.84 (tt, *J* = 12.4, 2.1 Hz, 1H), 2.25 (ddt, *J* = 12.8, 5.6, 2.2 Hz, 1H), 1.62 (tdd, *J* = 12.0, 5.0, 2.2 Hz, 1H), 1.47 (qd, *J* = 12.5, 4.9 Hz, 1H), 1.09 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): <sup>13</sup>C NMR (151 MHz, Chloroform-*d*)  $\delta$  132.10, 131.71, 130.44, 130.27, 129.33, 129.18, 126.53, 126.50, 125.47, 123.46, 123.22, 122.76, 122.69, 44.38, 32.57, 28.52, 28.30, 27.37, 24.23.; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 3077, 2949, 2866, 2839, 1492, 1433; **HRMS** (ESI): Calcd for C<sub>22</sub>H<sub>24</sub> [M + H]<sup>+</sup> 289.1951, found 289.1959.



**2-(tert-pentyl)-1,2,3,4-tetrahydrotriphenylene (3h)**: Following the general procedure; White solid (61% yield, eluent = petroleum ether); Mp = 74-76 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.74 – 8.68 (m, 2H), 8.09 (ddd, J = 36.3, 7.0, 1.9 Hz, 2H), 7.63 (dqd, J = 10.6, 6.9, 3.1 Hz, 4H), 3.37 (dd, J = 16.8, 4.8 Hz, 1H), 3.28 – 3.21 (m, 1H), 3.10 – 3.01 (m, 1H), 2.92 – 2.84 (m, 1H), 2.21 (ddt, J = 12.6, 5.7, 2.2 Hz, 1H), 1.73 (tdd, J = 12.1, 4.9, 2.2 Hz, 1H), 1.55 – 1.43 (m, 3H), 1.04 (s, 6H), 0.93 (t, J = 7.5 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  132.13, 131.73, 130.57, 130.32, 129.33, 129.18, 126.54, 126.51, 125.47, 123.45, 123.24, 122.77, 122.70, 41.76, 34.88, 32.62, 28.35, 28.12, 24.10, 23.96, 23.86, 8.28; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 3077, 2959, 2875, 2859, 1463, 1433; **HRMS** (ESI): Calcd for C<sub>23</sub>H<sub>26</sub> [M + H]<sup>+</sup> 303.2107, found 303.2113.



3i

**2-phenyl-1,2,3,4-tetrahydrotriphenylene (3i)**: Following the general procedure; White solid (57% yield, eluent = petroleum ether); Mp = 181-182 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.73 (dt, *J* = 7.8, 2.5 Hz, 2H), 8.13 – 8.01 (m, 2H), 7.69 – 7.57 (m, 3H), 7.41 (d, *J* = 3.3 Hz, 3H), 7.31 (ddt, *J* = 8.6, 6.1, 3.1 Hz, 1H), 3.59 – 3.52 (m, 1H), 3.41 (ddd, *J* = 17.1, 5.7, 2.6 Hz, 1H), 3.31 – 3.11 (m, 3H), 2.39 (ddq, *J* = 12.7, 5.5, 2.4 Hz, 1H), 2.12 (qd, *J* = 11.7, 5.4 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  146.75, 131.64, 131.60, 129.89, 129.78, 129.39, 129.35, 128.59, 127.05, 126.67, 126.65, 126.36, 125.70, 125.68, 123.52, 123.32, 122.78, 40.46, 35.44, 29.60, 27.41; IR (neat): v (cm<sup>-1</sup>) 3072, 3031, 2925, 2879, 2835, 1494, 1433; HRMS (ESI): Calcd for C<sub>24</sub>H<sub>20</sub> [M + H]<sup>+</sup> 309.1638, found 309.1290.



ethyl 1,2,3,4-tetrahydrotriphenylene-2-carboxylate (3j): Following the general procedure; White solid (80% yield, eluent = petroleum ether/EtOAc (50:1)); Mp = 127-129 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.73 – 8.68 (m, 2H), 8.06 (ddd, J = 27.0, 6.7, 3.9 Hz, 2H), 7.63 (dt, J = 6.1, 3.3 Hz, 4H), 4.26 (qt, J = 6.8, 3.5 Hz, 2H), 3.51 (dd, J = 16.7, 5.3 Hz, 1H), 3.40 – 3.29 (m, 2H), 3.20 – 3.12 (m, 1H), 2.88 (tdd, J = 10.9, 5.2, 2.8 Hz, 1H), 2.50 – 2.43 (m, 1H), 2.01 (qd, J = 11.9, 5.4 Hz, 1H), 1.35 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  175.67, 131.44, 131.37, 129.37, 129.35, 129.26, 128.37, 126.70, 125.78, 123.40, 123.35, 123.31, 123.27, 122.78, 122.76, 60.62, 39.90, 29.17, 26.35, 25.51, 14.33; IR (neat):  $\upsilon$  (cm<sup>-1</sup>) 3077, 2979, 2956, 2843, 1723, 1436, 1183; HRMS (ESI): Calcd for C<sub>21</sub>H<sub>20</sub>O<sub>2</sub> [M + Na]<sup>+</sup> 327.1356, found 327.1365.



**3,4-dihydro-1H-dibenzo[f,h]isochromene (3k)**: Following the general procedure; White solid (91% yield, eluent = petroleum ether/EtOAc (30:1)); Mp = 131-133 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.74 – 8.69 (m, 2H), 8.04 – 7.97 (m, 1H), 7.73 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.68 – 7.58 (m, 4H), 5.25 (t, *J* = 1.8 Hz, 2H), 4.18 (t, *J* = 5.6 Hz, 2H), 3.21 (ddd, *J* = 7.7, 4.7, 1.8 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  130.98, 129.42, 129.09, 128.70, 127.93, 127.29, 126.84, 126.13, 126.06, 123.07, 123.04, 122.88, 121.72, 66.46, 64.82, 25.72; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 3070, 2949, 2886, 2824, 1495, 1427, 1121; **HRMS** (ESI): Calcd for C<sub>17</sub>H<sub>14</sub>O [M + Na]<sup>+</sup> 257.0937, found 257.0947.



**3,4-dihydro-1H-spiro[triphenylene-2,2'-[1,3]dioxolane]** (**31**): Following the general procedure; White solid (85% yield, eluent = petroleum ether/EtOAc (10:1)); Mp = 136-138 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.70 (dt, *J* = 6.2, 3.4 Hz, 2H), 8.08 (dd, *J* = 6.1, 3.4 Hz, 1H), 8.00 – 7.94 (m, 1H), 7.62 (dt, *J* = 6.2, 3.4 Hz, 4H), 4.19 – 4.05 (m, 4H), 3.47 – 3.35 (m, 4H), 2.17 (t, *J* = 6.6 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  131.44, 131.25, 129.63, 129.45, 128.95, 127.88, 126.67, 126.65, 125.83, 125.78, 123.69, 123.13, 122.81, 122.75, 108.45, 64.66, 37.06, 31.15, 25.91; **IR** (neat): v (cm<sup>-1</sup>) 3070, 2953, 2885, 1598, 1494, 1369, 1118; **HRMS** (ESI): Calcd for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub> [M + H]<sup>+</sup>



**5',5'-dimethyl-3,4-dihydro-1H-spiro[triphenylene-2,2'-[1,3]dioxane]** (**3m**): Following the general procedure; White solid (86% yield, eluent = petroleum ether/EtOAc (20:1)); Mp = 208-209 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.69 (dq, *J* = 7.2, 3.5 Hz, 2H), 8.09 – 7.99 (m, 2H), 7.62 (qd, *J* = 7.0, 6.5, 4.2 Hz, 4H), 3.75 (d, *J* = 11.4 Hz, 2H), 3.60 (d, *J* = 11.4 Hz, 2H), 3.49 (s, 2H), 3.28 (t, *J* = 6.7 Hz, 2H), 2.39 (t, *J* = 6.6 Hz, 2H), 1.15 (s, 3H), 0.97 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  131.50, 131.24, 129.63, 129.44, 129.00, 127.14, 126.67, 126.60, 125.74, 125.72, 123.60, 123.15, 122.79, 122.75, 97.55, 70.52, 36.97, 30.32, 26.64, 24.90, 22.91, 22.51; IR (neat): v (cm<sup>-1</sup>) 3070, 2949, 2858, 1598, 1497, 1366, 1116; HRMS (ESI): Calcd for C<sub>23</sub>H<sub>24</sub>O<sub>2</sub> [M + H]<sup>+</sup> 333.1849, found 333.1858.



3n

**8**-(**1**,**2**,**3**,**4**-tetrahydrotriphenylen-2-yl)-1,**4**-dioxaspiro[**4**.**5**]decane (3n): Following the general procedure; White solid (56% yield, eluent = petroleum ether/EtOAc (10:1)); Mp = 155-157 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.69 (dt, *J* = 7.3, 2.5 Hz, 2H), 8.12 – 8.03 (m, 2H), 7.64 – 7.58 (m, 4H), 3.99 (s, 4H), 3.31 (ddd, *J* = 30.5, 16.7, 4.6 Hz, 2H), 3.10 – 3.02 (m, 1H), 2.90 – 2.82 (m, 1H), 2.21 (ddd, *J* = 13.0, 6.1, 2.8 Hz, 1H), 1.99 – 1.91 (m, 2H), 1.87 (dt, *J* = 12.8, 2.7 Hz, 2H), 1.75 (d, *J* = 13.2 Hz, 1H), 1.63 (tt, *J* = 13.1, 3.6 Hz, 2H), 1.57 – 1.42 (m, 4H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  131.91, 131.68, 130.16, 129.98, 129.31, 129.21, 126.55, 126.52, 125.52, 125.50, 123.43, 123.29, 122.74, 122.70, 109.12, 64.29, 41.34, 38.63, 34.89, 30.93, 27.43, 27.31, 27.26, 26.36; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 3070, 2950, 2862, 1573, 1495, 1360, 1120; **HRMS** (ESI): Calcd for C<sub>26</sub>H<sub>28</sub>O<sub>2</sub> [M + H + MeOH]<sup>+</sup> 405.2424, found 405.092.



**ethyl 10-phenylphenanthrene-9-carboxylate** (**3s**): Following the general procedure; White solid (95% yield, eluent = petroleum ether/EtOAc (100:1~50:1)); Mp = 126-128 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.79 – 8.74 (m, 2H), 7.94 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.75 – 7.61 (m, 4H), 7.57 – 7.40 (m,

6H), 4.12 (q, J = 7.1 Hz, 2H), 0.97 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  169.20, 138.07, 136.44, 130.80, 130.64, 130.60, 130.31, 129.88, 128.05, 127.90, 127.77, 127.42, 127.39, 127.05, 126.83, 125.86, 122.78, 122.62, 61.12, 13.70; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 3067, 2987, 2900, 1715, 1490, 1440, 1390, 1225, 1153; **HRMS** (ESI): Calcd for C<sub>23</sub>H<sub>18</sub>O<sub>2</sub> [M + Na]<sup>+</sup> 349.1199, found 349.1210.



ethyl 10-(p-tolyl)phenanthrene-9-carboxylate (3t): Following the general procedure; White solid (93% yield, eluent = petroleum ether/EtOAc (100:1)); Mp = 155-156 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.76 (dd, J = 8.3, 3.4 Hz, 2H), 7.92 (dd, J = 8.1, 1.4 Hz, 1H), 7.73 – 7.62 (m, 4H), 7.51 (ddd, J = 8.2, 6.8, 1.1 Hz, 1H), 7.35 – 7.27 (m, 4H), 4.15 (q, J = 7.1 Hz, 2H), 2.47 (s, 3H), 1.02 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  169.32, 137.44, 136.49, 134.99, 130.99, 130.68, 130.59, 130.16, 129.82, 128.73, 127.94, 127.83, 127.35, 127.34, 126.95, 126.77, 125.80, 122.77, 122.60, 61.09, 21.32, 13.75; IR (neat):  $\upsilon$  (cm<sup>-1</sup>) 3070, 2975, 2899, 1719, 1492, 1447, 1376, 1221, 1154; HRMS (ESI): Calcd for C<sub>24</sub>H<sub>20</sub>O<sub>2</sub> [M + H]<sup>+</sup> 341.1536, found 341.1545.



ethyl 10-(4-(trifluoromethyl)phenyl)phenanthrene-9-carboxylate (3u): Following the general procedure; White solid (86% yield, eluent = petroleum ether/EtOAc (100:1)); Mp = 190-192 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.78 (d, J = 8.3 Hz, 2H), 7.95 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 7.9 Hz, 2H), 7.76 – 7.70 (m, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.59 (d, J = 7.9 Hz, 2H), 7.56 – 7.51 (m, 2H), 4.14 (q, J = 7.1 Hz, 2H), 0.98 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 168.79, 142.07, 134.87, 130.84, 130.81, 130.63, 130.17, 130.14 (q, <sup>1</sup> $_{JC-F} = 32.5$  Hz), 130.06, 130.03, 127.72, 127.60, 127.56, 127.46, 127.10, 125.97, 125.05 (q, <sup>2</sup> $_{JC-F} = 3.4$  Hz), 123.28, 122.85, 122.82, 61.30, 13.61; IR (neat): ν (cm<sup>-1</sup>) 3074, 2984, 2902, 1719, 1495, 1407, 1321, 1221, 1158, 1117, 1104, 1066, 1020; HRMS (ESI): Calcd for C<sub>24</sub>H<sub>17</sub>F<sub>3</sub>O<sub>2</sub> [M + H]<sup>+</sup> 395.1253, found 395.0314.



ethyl 10-(benzo[d][1,3]dioxol-5-yl)phenanthrene-9-carboxylate (3v): Following the general

procedure; White solid (45% yield, eluent = petroleum ether/EtOAc (100:1~50:1)); Mp = 163-164 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.75 (dd, J = 8.4, 2.8 Hz, 2H), 7.91 (dd, J = 8.0, 1.2 Hz, 1H), 7.75 – 7.62 (m, 4H), 7.54 (t, J = 7.6 Hz, 1H), 6.99 – 6.86 (m, 3H), 6.06 (dd, J = 12.3, 1.4 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 1.12 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  169.22, 147.33, 147.24, 135.83, 131.55, 130.98, 130.91, 130.59, 129.86, 127.78, 127.75, 127.42, 127.39, 127.07, 126.86, 125.82, 123.82, 122.78, 122.63, 111.03, 108.10, 101.13, 61.15, 13.97; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 3072, 2990, 2899, 1716, 1487, 1450, 1233, 1218, 1175, 1038; **HRMS** (ESI): Calcd for C<sub>24</sub>H<sub>18</sub>O<sub>4</sub> [M + Na]<sup>+</sup> 393.1097, found 393.1105.



ethyl 10-(4-nitrophenyl)phenanthrene-9-carboxylate (3w): Following the general procedure; Pale yellow solid (70% yield, eluent = petroleum ether/EtOAc (100:1~50:1)); Mp = 210-212 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.78 (ddd, J = 8.4, 3.8, 1.0 Hz, 2H), 8.41 – 8.34 (m, 2H), 7.94 (dd, J = 8.2, 1.3 Hz, 1H), 7.75 (dddd, J = 14.0, 8.3, 6.9, 1.3 Hz, 2H), 7.69 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.54 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.46 (dd, J = 8.2, 1.2 Hz, 1H), 4.15 (q, J= 7.2 Hz, 2H), 1.03 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  168.57, 147.59, 145.33, 133.98, 131.48, 130.85, 130.64, 130.16, 129.75, 127.91, 127.73, 127.41, 127.26, 127.16, 126.04, 123.32, 122.96, 122.91, 61.45, 13.84; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 3070, 2915, 1719, 1586, 1372, 1159, 1115, 1076; **HRMS** (ESI): Calcd for C<sub>23</sub>H<sub>17</sub>NO<sub>4</sub> [M + Na + MeOH]<sup>+</sup> 426.1312, found 426.0461.



**3**x

ethyl 10-(naphthalen-2-yl)phenanthrene-9-carboxylate (3x): Following the general procedure; White solid (77% yield, eluent = petroleum ether/EtOAc (100:1)); Mp = 175-177 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.80 (dd, J = 8.4, 5.0 Hz, 2H), 8.04 – 7.93 (m, 4H), 7.92 – 7.87 (m, 1H), 7.77 – 7.64 (m, 4H), 7.57 (dddd, J = 13.8, 11.2, 6.0, 1.6 Hz, 3H), 7.50 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 4.05 (p, J = 7.1 Hz, 2H), 0.83 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  169.20, 136.34, 135.70, 133.15, 132.79, 131.01, 130.91, 130.64, 129.98, 129.17, 128.48, 128.12, 128.02, 127.84, 127.77, 127.51, 127.47, 127.15, 126.92, 126.37, 126.33, 125.92, 122.86, 122.70, 61.12, 13.65; IR (neat):  $\upsilon$  (cm<sup>-1</sup>) 3060, 3001, 2953, 2893, 1724, 1494, 1446, 1212, 1195, 1155, 1100; HRMS (ESI): Calcd for C<sub>27</sub>H<sub>20</sub>O<sub>2</sub> [M + H]<sup>+</sup> 377.1536, found 377.1520.



ethyl 10-methylphenanthrene-9-carboxylate (3y): Following the general procedure; White solid (59% yield, eluent = petroleum ether/EtOAc (100:1)); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.71 (dd, J = 18.2, 8.1 Hz, 2H), 8.13 (dd, J = 8.1, 1.4 Hz, 1H), 7.76 (dd, J = 8.1, 1.4 Hz, 1H), 7.73 – 7.65 (m, 2H), 7.65 – 7.58 (m, 2H), 4.59 (q, J = 7.2 Hz, 2H), 2.72 (s, 3H), 1.49 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  170.36, 130.96, 130.39, 130.37, 129.56, 129.40, 128.12, 127.24, 127.12, 127.00, 126.39, 125.17, 125.09, 122.94, 122.70, 61.48, 17.08, 14.38; HRMS (ESI): Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>2</sub> [M + Na]<sup>+</sup> 287.1043, found 287.1054.



ethyl 10-ethylphenanthrene-9-carboxylate (3aa): Following the general procedure; Colorless oil (75% yield, eluent = petroleum ether/EtOAc (100:1)); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.76 – 8.72 (m, 1H), 8.71 – 8.67 (m, 1H), 8.16 (dd, J = 8.1, 1.4 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.73 – 7.57 (m, 4H), 4.59 (q, J = 7.2 Hz, 2H), 3.12 (q, J = 7.6 Hz, 2H), 1.49 (t, J = 7.2 Hz, 3H), 1.41 (t, J = 7.6 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  170.32, 135.39, 130.89, 129.84, 129.74, 129.42, 128.12, 127.12, 127.09, 126.99, 126.43, 125.25, 125.11, 123.21, 122.69, 61.43, 24.43, 15.22, 14.37; IR (neat):  $\upsilon$  (cm<sup>-1</sup>) 3070, 2995, 1719, 1490, 1462, 1227, 1118; HRMS (ESI): Calcd for C<sub>19</sub>H<sub>18</sub>O<sub>2</sub> [M + Na]<sup>+</sup> 301.1199, found 301.1205.



**ethyl 10-isopropylphenanthrene-9-carboxylate (3ab)**: Following the general procedure; Colorless oil (79% yield, eluent = petroleum ether/EtOAc (100:1)); <sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.76 (dd, J = 8.4, 1.3 Hz, 1H), 8.68 (dd, J = 8.2, 1.3 Hz, 1H), 8.39 (d, J = 8.3 Hz, 1H), 7.76 – 7.56 (m, 5H), 4.57 (q, J = 7.2 Hz, 2H), 3.54 (m, 1H), 1.76 – 1.59 (m, 6H), 1.48 (t, J = 7.1 Hz, 3H); <sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>):  $\delta$  170.89, 138.40, 131.40, 129.44, 128.15, 127.15, 126.75, 126.54, 126.21, 125.30, 123.46, 122.59, 61.39, 22.21, 14.29; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 3069, 2990, 1719, 1475, 1450, 1219, 1169, 1027; **HRMS** (ESI): Calcd for C<sub>20</sub>H<sub>20</sub>O<sub>2</sub> [M + H]<sup>+</sup> 293.1535, found 293.0731.



ethyl 10-phenethylphenanthrene-9-carboxylate (3ac): Following the general procedure, but using silylaryl triflate (0.80 mmol, 4.0 equiv) CsF (1.2 mmol, 8.0 equiv); White solid (74% yield, eluent = petroleum ether/EtOAc (100:1)); Mp = 151-153 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.79 – 8.76 (m, 1H), 8.72 (dd, J = 8.2, 1.3 Hz, 1H), 8.28 – 8.23 (m, 1H), 7.79 (dd, J = 7.8, 1.5 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.65 (dddd, J = 21.6, 8.1, 6.9, 1.4 Hz, 2H), 7.41 – 7.35 (m, 4H), 7.30 – 7.26 (m, 1H), 4.61 (q, J = 7.1 Hz, 2H), 3.42 – 3.37 (m, 2H), 3.13 – 3.08 (m, 2H), 1.50 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 170.24, 141.85, 133.13, 130.93, 130.47, 129.82, 129.58, 128.62, 128.19, 128.13, 127.24, 127.22, 127.20, 126.64, 126.21, 125.37, 124.93, 123.32, 122.75, 61.60, 36.94, 33.44, 14.44; IR (neat): v (cm<sup>-1</sup>) 2989, 2902, 1706, 1494, 1450, 1382, 1208, 1064; HRMS (ESI): Calcd for C<sub>25</sub>H<sub>22</sub>O<sub>2</sub> [M + Na]<sup>+</sup> 377.1512, found 377.1521.



ethyl 10-cyclopropylphenanthrene-9-carboxylate (3ad): Following the general procedure; White solid (78% yield, eluent = petroleum ether/EtOAc (100:1)); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.74 – 8.65 (m, 3H), 7.89 (dd, J = 8.0, 1.3 Hz, 1H), 7.73 – 7.58 (m, 4H), 4.59 (q, J = 7.2 Hz, 2H), 2.35 (tt, J = 8.5, 5.8 Hz, 1H), 1.49 (t, J = 7.2 Hz, 3H), 1.20 – 1.15 (m, 2H), 0.83 (td, J = 6.0, 4.3 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  170.02, 134.55, 131.85, 131.66, 130.55, 129.67, 128.06, 127.21, 127.11, 126.70, 126.68, 126.42, 125.11, 122.80, 122.65, 61.37, 14.31, 13.26, 7.27; IR (neat):  $\upsilon$  (cm<sup>-1</sup>) 3065, 2975, 1716, 1497, 1376, 1211, 1113; HRMS (ESI): Calcd for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub> [M + Na]<sup>+</sup> 313.1199, found 313.1211.



**ethyl 10-cyclobutylphenanthrene-9-carboxylate (3ae)**: Following the general procedure; White solid (80% yield, eluent = petroleum ether/EtOAc (100:1)); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.71 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.67 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.16 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.82 (dt, *J* = 8.2, 1.2 Hz, 1H), 7.71 – 7.57 (m, 4H), 4.52 (q, *J* = 7.2 Hz, 2H), 4.32 (tt, *J* = 10.5, 7.7 Hz, 1H), 2.59 (qq, *J* = 7.2, 2.3 Hz, 2H), 2.45 (qd, *J* = 11.0, 8.6 Hz, 2H), 2.10 (qt, *J* = 10.4, 8.1 Hz, 1H), 1.92 – 1.84 (m, 1H), 1.47 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 170.77, 137.15, 130.74, 130.21,

129.30, 128.39, 128.21, 127.11, 126.96, 126.49, 126.45, 126.00, 124.90, 123.04, 122.54, 61.41, 39.40, 30.48, 19.05, 14.16; **IR** (neat): v (cm<sup>-1</sup>) 3066, 2992, 1716, 1489, 1369, 1118; **HRMS** (ESI): Calcd for C<sub>21</sub>H<sub>20</sub>O<sub>2</sub> [M + Na]<sup>+</sup> 327.1356, found 327.1362.



ethyl 10-cyclohexylphenanthrene-9-carboxylate (3af): Following the general procedure; White solid (83% yield, eluent = petroleum ether/EtOAc (100:1)); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.75 (dd, J = 8.1, 1.5 Hz, 1H), 8.67 (d, J = 8.1 Hz, 1H), 8.57 (d, J = 8.3 Hz, 1H), 7.76 – 7.56 (m, 5H), 4.58 (q, J = 7.2 Hz, 2H), 3.61 (s, 1H), 3.16 – 2.91 (m, 1H), 2.40 (d, J = 13.4 Hz, 1H), 2.00 (q, J = 18.7, 11.8 Hz, 4H), 1.86 (d, J = 9.5 Hz, 2H), 1.50 (t, J = 7.2 Hz, 3H), 1.48 – 1.40 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 170.86, 137.54, 131.47, 130.75, 129.91, 129.47, 128.05, 127.50, 127.13, 126.65, 126.52, 125.85, 125.46, 123.39, 122.57, 61.33, 46.49, 31.49, 27.55, 26.17, 14.48; **IR** (neat):  $\nu$  (cm<sup>-1</sup>) 3065, 2987, 1716, 1492, 1367, 1116; **HRMS** (ESI): Calcd for C<sub>23</sub>H<sub>24</sub>O<sub>2</sub> [M + H]<sup>+</sup> 333.1849, found 333.1754.



ethyl 10-(tetrahydrofuran-2-yl)phenanthrene-9-carboxylate (3ag): Following the general procedure; White solid (64% yield, eluent = petroleum ether/EtOAc (50:1~10:1)); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.73 (dd, J = 8.4, 1.2 Hz, 1H), 8.69 – 8.66 (m, 1H), 8.01 (dd, J = 8.4, 1.2 Hz, 1H), 7.79 (dd, J = 7.9, 1.5 Hz, 1H), 7.70 – 7.59 (m, 4H), 5.77 (t, J = 7.3 Hz, 1H), 4.53 (qt, J = 9.7, 4.8 Hz, 2H), 4.15 – 4.09 (m, 1H), 3.98 (dt, J = 8.2, 6.8 Hz, 1H), 2.64 (dtt, J = 14.1, 7.0, 3.4 Hz, 1H), 2.18 – 2.11 (m, 1H), 2.06 (ddq, J = 14.8, 9.3, 7.2 Hz, 2H), 1.47 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  170.57, 133.99, 130.60, 129.72, 128.78, 128.52, 127.64, 127.25, 126.98, 126.86, 126.77, 125.35, 124.76, 123.16, 122.58, 78.39, 69.13, 60.86, 34.46, 26.14, 14.35; IR (neat):  $\upsilon$  (cm<sup>-1</sup>) 3066, 2990, 1719, 1496, 1390, 1121; HRMS (ESI): Calcd for C<sub>21</sub>H<sub>20</sub>O<sub>3</sub> [M + Na]<sup>+</sup> 343.1305, found 343.1320.



2,2-dimethyl-1-(10-methylphenanthren-9-yl)propan-1-one (3ah): Following the general

procedure; White solid (86% yield, eluent = petroleum ether/EtOAc (100:1)); <sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.73 – 8.67 (m, 2H), 8.13 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.71 – 7.57 (m, 5H), 2.74 (s, 3H), 1.74 (s, 9H); **HRMS** (ESI): Calcd for [M + Na]<sup>+</sup> 315.1356, found 315.1366.



**phenyl(10-phenylphenanthren-9-yl)methanone (3ai)**: Following the general procedure; White solid (96% yield, eluent = petroleum ether/EtOAc (100:1)); Mp = 158-160 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.83 (d, J = 8.4 Hz, 2H), 7.77 – 7.67 (m, 3H), 7.64 (d, J = 7.9 Hz, 3H), 7.54 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.5 Hz, 3H), 7.25 (d, J = 8.0 Hz, 3H), 7.19 – 7.00 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 199.37, 138.09, 137.12, 135.74, 135.68, 133.17, 131.61, 131.00, 130.60, 130.26, 129.86, 129.47, 128.91, 128.23, 127.60, 127.53, 127.32, 127.30, 127.04, 126.94, 126.47, 122.87, 122.67; IR (neat): υ (cm<sup>-1</sup>) 2988, 2903, 1662, 1448, 1225, 1077; HRMS (ESI): Calcd for C<sub>27</sub>H<sub>18</sub>O [M + Na]<sup>+</sup> 381.1250, found 381.1251.



3aj

**10-phenylphenanthrene-9-carbonitrile (3aj)**: Following the general procedure; White solid (97% yield, eluent = petroleum ether/EtOAc (100:1)); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.76 (td, *J* = 7.3, 1.3 Hz, 2H), 8.43 – 8.38 (m, 1H), 7.83 – 7.76 (m, 3H), 7.71 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.63 – 7.55 (m, 4H), 7.54 – 7.48 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  147.39, 137.02, 131.75, 130.16, 129.91, 129.61, 129.44, 128.93, 128.82, 128.72, 128.66, 128.32, 128.07, 127.41, 126.46, 122.90, 122.88, 117.27, 109.59; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 2988, 2901, 2224, 1487, 1442, 1373, 1074; **HRMS** (ESI): Calcd for C<sub>21</sub>H<sub>13</sub>N [M + H]<sup>+</sup> 280.1121, found 280.0330.



**6,7,10,11-tetramethoxy-1,2,3,4-tetrahydrotriphenylene (3ao)**:Following the general procedure; White solid (60% yield, eluent = petroleum ether/EtOAc (5:1)); Mp = 239-241 °C; <sup>1</sup>H NMR (600

MHz, CDCl<sub>3</sub>):  $\delta$  7.83 (s, 2H), 7.36 (s, 2H), 4.12 (s, 6H), 4.05 (s, 6H), 3.10 (p, *J* = 3.1 Hz, 4H), 2.00 (p, *J* = 3.3 Hz, 4H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  148.50, 148.19, 127.93, 126.25, 123.25, 103.97, 103.23, 56.02, 55.80, 27.05, 23.04; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 3072, 2993, 2889, 2820, 1489, 1425, 1125; **HRMS** (ESI): Calcd for C<sub>22</sub>H<sub>24</sub>O<sub>4</sub> [M + H]<sup>+</sup> 353.1747, found 353.1736.



ethyl 2,3,6,7-tetramethoxy-10-phenylphenanthrene-9-carboxylate (3ap): Following the general procedure; White solid (70% yield, eluent = petroleum ether/EtOAc (5:1)); Mp = 180-181 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.83 (d, *J* = 7.3 Hz, 2H), 7.49 – 7.45 (m, 2H), 7.45 – 7.40 (m, 3H), 7.31 (s, 1H), 6.96 (s, 1H), 4.13 (s, 3H), 4.12 (s, 3H), 4.06 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 3.73 (s, 3H), 0.93 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  169.74, 149.82, 149.46, 149.30, 148.68, 138.91, 134.51, 130.21, 128.09, 127.77, 127.62, 125.20, 125.03, 124.23, 122.36, 107.79, 105.75, 102.85, 102.59, 61.00, 56.05, 56.02, 55.86, 55.57, 13.66; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 2990, 2973, 2902, 1718, 1618, 1511, 1470, 1423, 1265, 1208, 1117, 1051; **HRMS** (ESI): Calcd for C<sub>27</sub>H<sub>26</sub>O<sub>6</sub> [M + H]<sup>+</sup> 447.1802, found 447.1811.



ethyl 6-phenylphenanthro[2,3-d:6,7-d']bis([1,3]dioxole)-5-carboxylate (3aq): Following the general procedure; White solid (79% yield, eluent = petroleum ether/EtOAc (5:1)); Mp = 191-193 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.83 (d, J = 4.0 Hz, 2H), 7.48 – 7.40 (m, 3H), 7.40 – 7.35 (m, 2H), 7.24 (s, 1H), 6.91 (s, 1H), 6.10 (s, 2H), 6.05 (s, 2H), 4.05 (q, J = 7.1 Hz, 2H), 0.93 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  169.53, 148.50, 148.20, 147.77, 147.27, 138.62, 134.56, 130.27, 128.75, 128.10, 127.66, 127.11, 126.55, 126.17, 123.50, 104.97, 103.09, 101.49, 101.45, 100.52, 100.35, 61.10, 13.65; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 2990, 2901, 1713, 1454, 1232, 1191, 1074, 1040; **HRMS** (ESI): Calcd for C<sub>25</sub>H<sub>18</sub>O<sub>6</sub> [M + H]<sup>+</sup> 415.1176, found 415.1188.



ethyl 7-phenylpentaphene-6-carboxylate (3ar): Following the general procedure; Pale yellow oil (27% yield, eluent = petroleum ether/EtOAc (100:1)); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  9.33 (d, *J* = 4.5 Hz, 2H), 8.32 (s, 1H), 8.17 (dd, *J* = 8.2, 5.3 Hz, 2H), 8.07 – 7.99 (m, 2H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.48 (m, 9H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.00 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  169.16, 138.08, 136.89, 132.41, 132.30, 132.17, 132.03, 130.94, 130.29, 129.80, 128.88, 128.36, 128.28, 128.26, 128.20, 128.13, 128.08, 127.97, 127.68, 126.67, 126.51, 126.45, 126.27, 126.11, 124.88, 122.14, 121.96, 61.20, 13.73; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 2990, 2897, 1709, 1437, 1225, 1159, 1062; **HRMS** (ESI): Calcd for C<sub>31</sub>H<sub>22</sub>O<sub>2</sub> [M + H]<sup>+</sup> 427.1693, found 427.1700.



3as+3at

6,10-dimethyl-1,2,3,4-tetrahydrotriphenylene 7,10-dimethyl-1,2,3,4-tetrahydrotriphenylene (3as+3at):Following the general procedure; Colorless oil (73% yield, eluent = petroleum ether); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.58 (dd, J = 8.4, 1.9 Hz, 1H), 8.55 (dd, J = 8.4, 1.4 Hz, 1H), 8.49 (s, 1H), 8.45 (s, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.84 (s, 2H), 7.43 (ddt, J = 9.7, 7.8, 3.1 Hz, 4H), 3.14 (dh, J = 9.2, 2.6 Hz, 8H), 2.62 (dd, J = 5.8, 2.4 Hz, 6H), 2.59 (d, J = 2.4 Hz, 6H), 2.03 – 1.97 (m, 8H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  135.95, 135.62, 134.87, 134.72, 132.16, 131.63, 130.16, 129.99, 129.96, 129.46, 129.32, 129.13, 129.05, 128.93, 128.03, 127.73, 127.08, 127.05, 126.91, 126.81, 123.19, 123.09, 123.07, 122.62, 122.51, 122.45, 122.34, 26.92, 26.88, 26.81, 26.77, 23.01, 22.98, 21.93, 21.91, 21.87, 21.86; HRMS (ESI): Calcd for C<sub>20</sub>H<sub>20</sub> [M + H]<sup>+</sup> 261.1638, found 261.1645.

#### **Gram-scale Reaction for Preparation of 3a**



A 250 mL of Schlenk bottle equipped with a stirrer bar was charged with  $Pd_2(dba)_3$  (368 mg, 5 mol %), tri-*o*-tolylphosphane (480 mg, 20 mol %), CsF (7.3g, 48.0 mmol, 6.0 equiv), and LiOPiv (864 mg, 8.0 mmol, 1.0 equiv) in the glove box. Then, the Schlenk bottle was removed from glove box and quickly evacuated and refilled with Ar for three times, followed by the addition of MeCN (50 mL), enol triflates **1a** (2.06g, 8.0 mmol, 1.0 equiv), and silylaryl triflate **2a** (5.52 mL, 24.0 mmol, 3.0 equiv). The Schlenk bottle was sealed with a Teflon screwcap under Ar flow and the reaction mixture was stirred at 60 °C for 12 h. Upon cooling to room temperature, the reaction mixture was diluted with 20 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with ethyl acetate (50 mL). Subsequently, the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **3a** (1.623g, yiled= 78%).

#### Gram-scale Reaction for Preparation of 3s



3s, 1.427 g, 87%

A 250 mL of Schlenk bottle equipped with a stirrer bar was charged with  $Pd_2(dba)_3$  (230 mg, 5 mol %), tri-*o*-tolylphosphane (300 mg, 20 mol %), CsF (4.56g, 30.0 mmol, 6.0 equiv), and LiOPiv (540 mg, 5.0 mmol, 1.0 equiv) in the glove box. Then, the Schlenk bottle was removed from glove box and quickly evacuated and refilled with Ar for three times, followed by the addition of MeCN (30 mL), enol triflates **1s** (1.62g, 5.0 mmol, 1.0 equiv), and silylaryl triflate **2a** (3.45 mL, 15.0 mmol, 3.0 equiv). The Schlenk bottle was sealed with a Teflon screwcap under Ar flow and the reaction mixture was stirred at 60 °C for 12 h. Upon cooling to room temperature, the reaction mixture was diluted with 20 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with ethyl acetate (50 mL). Subsequently, the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **3s** (1.427g, yiled= 87%).

#### **Friedel-Crafts cyclisation**



**Step 1.** The **ethyl 10-phenylphenanthrene-9-carboxylate (3s)** (326.4 mg, 1.0 mmol) was added to a mixture of concentrated aqueous HBr (5mL) and glacial AcOH (20 mL) and then refluxed for 10 h. Upon cooling to room temperature, the reaction mixture was diluted with 20 mL of ethyl acetate, washed with water (50 mL), dried (MgSO<sub>4</sub>) and concentrated. The residue was purified by chromatography to afford the desired product **10-phenylphenanthrene-9-carboxylic acid** (233 mg, 78%) as a white solid.



**10-phenylphenanthrene-9-carboxylic acid (5)**: White solid (78% yield, eluent = DCM/MeOH (20:1)); <sup>1</sup>H NMR (600 MHz, d-DMSO): δ 13.27 (s, 1H), 8.94 (t, J = 7.6 Hz, 2H), 7.87 (d, J = 7.9 Hz, 1H), 7.75 (dt, J = 23.0, 7.6 Hz, 3H), 7.57 (t, J = 7.6 Hz, 1H), 7.48 (ddd, J = 32.1, 16.1, 7.9 Hz, 4H), 7.38 (d, J = 7.3 Hz, 2H); <sup>13</sup>C NMR (150 MHz, d-DMSO): δ 170.18, 137.84, 134.56, 132.41, 130.71, 130.56, 130.11, 129.72, 128.65, 128.34, 128.19, 128.01, 127.90, 127.78, 127.50, 127.34, 126.18, 123.74, 123.63.

**Step 2.** A 10 wt% solution of PPA acid in methanesulfonic acid (15 mL) was heated to 90 °C and then **10-phenylphenanthrene-9-carboxylic acid** was added over the course of 10 min. Once the addition was completed the suspension was heated at 120 °C for 4 hours until a dark solution was observed, which was then cooled to room temperature and poured into ice water. After that, NaOH (cold sat. aqueous solution) were sequentially added to the mixture. The aqueous layer was extracted with ethyl acetate (3×20 mL), the combined organic layers were dried over MgSO4, filtrated and concentrated in vacuo. The crude material was purified by flash column chromatography on silica gel to afford the desired product **13H-indeno[1,2-I]phenanthren-13-one** (203 mg, 93%) as an orange solid.



**13H-indeno[1,2-l]phenanthren-13-one (6)**: Orange solid (78% yield, eluent = petroleum ether/EtOAc (15:1)); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  9.19 – 9.14 (m, 1H), 8.61 (d, *J* = 8.3 Hz, 1H), 8.51 (d, *J* = 8.2 Hz, 2H), 7.92 (d, *J* = 7.4 Hz, 1H), 7.74 – 7.68 (m, 1H), 7.67 – 7.56 (m, 4H), 7.44 (td, *J* = 7.6, 1.2 Hz, 1H), 7.28 (t, *J* = 7.3 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  195.77, 144.52, 143.73, 134.53, 134.21, 133.86, 130.90, 129.10, 128.76, 128.29, 127.52, 127.48, 127.28, 127.11, 125.93, 125.60, 125.21, 123.77, 123.39, 123.25, 122.56; **IR** (neat):  $\upsilon$  (cm<sup>-1</sup>) 2988, 2899, 1699, 1602, 1504, 1195, 1064.

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## <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>FNMR Spectra

## <sup>1</sup>H NMR Spectrum of 1h

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## <sup>1</sup>H NMR Spectrum of 1n





## <sup>13</sup>C NMR Spectrum of 1n

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## <sup>13</sup>C NMR Spectrum of 1t











S32



## <sup>13</sup>C NMR Spectrum of 1x





## <sup>1</sup>H NMR Spectrum of 1ad

PROTON\_01

# 



## <sup>13</sup>C NMR Spectrum of 1ad



## <sup>1</sup>H NMR Spectrum of 1ae



## <sup>1</sup>H NMR Spectrum of 1af

PROTON\_01



<sup>13</sup>C NMR Spectrum of 1af


## <sup>1</sup>H NMR Spectrum of 1ag



# <sup>1</sup>H NMR Spectrum of 1ai



#### <sup>13</sup>C NMR Spectrum of 1ai





#### <sup>1</sup>H NMR Spectrum of 1aj







# <sup>13</sup>C NMR Spectrum of 1aj



#### <sup>1</sup>H NMR Spectrum of 3a



<sup>13</sup>C NMR Spectrum of 3a



## <sup>1</sup>H NMR Spectrum of 3b





#### <sup>13</sup>C NMR Spectrum of 3b



## <sup>1</sup>H NMR Spectrum of 3c

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<sup>13</sup>C NMR Spectrum of 3c



#### <sup>1</sup>H NMR Spectrum of 3d





<sup>13</sup>C NMR Spectrum of 3d



## <sup>1</sup>H NMR Spectrum of 3e





#### <sup>13</sup>C NMR Spectrum of 3e

CARBON\_01





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#### <sup>1</sup>H NMR Spectrum of 3f





#### <sup>13</sup>C NMR Spectrum of 3f

CARBON\_01

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### <sup>1</sup>H NMR Spectrum of 3g



#### <sup>13</sup>C NMR Spectrum of 3g



#### <sup>1</sup>H NMR Spectrum of 3h



# <sup>13</sup>C NMR Spectrum of 3h



#### <sup>1</sup>H NMR Spectrum of 3i









#### <sup>1</sup>H NMR Spectrum of 3j











#### <sup>1</sup>H NMR Spectrum of 3k

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S50

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#### <sup>1</sup>H NMR Spectrum of 31

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#### <sup>1</sup>H NMR Spectrum of 3n



#### <sup>13</sup>C NMR Spectrum of 3n



#### <sup>1</sup>H NMR Spectrum of 3s





### <sup>1</sup>H NMR Spectrum of 3t



















# <sup>19</sup>F NMR Spectrum of 3u

HJT-6-3-3\_CDCL3\_F19 STANDARD FLUORINE PARAMETERS

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---62.53

<sup>1</sup>H NMR Spectrum of 3v

PROTON\_01







CARBON\_01



-13.97





#### <sup>1</sup>H NMR Spectrum of 3w







CARBON\_01



## <sup>1</sup>H NMR Spectrum of 3x











#### <sup>1</sup>H NMR Spectrum of 3y















## <sup>1</sup>H NMR Spectrum of 3aa









#### <sup>1</sup>H NMR Spectrum of 3ab











#### <sup>1</sup>H NMR Spectrum of 3ac







#### <sup>1</sup>H NMR Spectrum of 3ad







 

110 100 fl (ppm)

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140 130

-1

#### <sup>1</sup>H NMR Spectrum of 3ae

PROAL 









110 100 f1 (ppm)

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#### <sup>1</sup>H NMR Spectrum of 3af



## <sup>1</sup>H NMR Spectrum of 3ag











#### <sup>1</sup>H NMR Spectrum of 3ah



#### <sup>1</sup>H NMR Spectrum of 3ai

PROTON\_01







#### <sup>1</sup>H NMR Spectrum of 3aj





#### <sup>13</sup>C NMR Spectrum of 3aj




## <sup>1</sup>H NMR Spectrum of 3ap







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## <sup>1</sup>H NMR Spectrum of 3ar

8.8.10 (100) (10)









<sup>1</sup>H NMR Spectrum of 3as+3at







## <sup>1</sup>H NMR Spectrum of 5



<sup>13</sup>C NMR Spectrum of 5



## <sup>1</sup>H NMR Spectrum of 6



<sup>13</sup>C NMR Spectrum of 6

