Supporting Information:

# Putting corannulene in its place. Reactivity studies comparing corannulene with other aromatic hydrocarbons

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#### Friedel-Crafts acylation using aluminium(III) trichloride and acetyl chloride

To a stirred suspension of aluminium(III) trichloride (51.2 mg, 384  $\mu$ mol) and the respective aromatic starting material (128  $\mu$ mol) in dichloromethane (5 mL) at either -78°C or 0°C<sup>1</sup> was added acetyl chloride (22.8  $\mu$ L, 320  $\mu$ mol) using a micro-syringe under dynamic nitrogen. After coming to room temperature, the darkened reaction mixture was stirred for a further hour before being cooled back to 0°C. After careful quenching with water (30 mL) and further dilution with dichloromethane (30 mL), the lower organic layer was separated, was further washed with 2 M hydrochloric acid (2 x 30 mL) before being dried over magnesium sulfate. Filtration was followed by removal of the solvent under reduced pressure to yield the desired acylated species<sup>2</sup> in quantitative yield as yellow solids. No attempt was made to separate regioisomers.

## Acetophenone 1-Ac

15.3 mg, quantitative. <sup>1</sup>H NMR (300 MHz, Chloroform-*d*)  $\delta$  7.97 (dd, J = 8.4, 1.4 Hz, 2H, Ar<u>H</u>), 7.69 – 7.55 (m, 1H, Ar<u>H</u>), 7.53 – 7.42 (m, 2H, Ar<u>H</u>), 2.62 (s, **1-Ac** 3H, ArCOC<u>H\_3</u>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  199.54 (Ar<u>C</u>OCH<sub>3</sub>), 138.53 (Ar<u>C</u>), 134.51 (Ar<u>C</u>), 129.98 (Ar<u>C</u>), 129.71 (Ar<u>C</u>), 28.02 (ArCO<u>C</u>H<sub>3</sub>).



*1-Acetylnaphthalene* **2-Ac-a** and *2-acetylnaphthalene* **2-Ac-b** (*ca.* 1:2) 21.8 mg, quantitative. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.74 (d, *J* = 8.5 Hz, 1H, Ar<u>H</u>), 8.47 (s, 0.4H), 8.15 – 7.79 (m, 4.7H, Ar<u>H</u>), 7.55 (m, 4H, Ar<u>H</u>), 2.75 (s, 3H, ArCOC<u>H</u><sub>3</sub>, Ar<u>H</u>), 2.73 (s, 1.5H, ArCOC<u>H</u><sub>3</sub>). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 203.38 (1-ArCOCH<sub>3</sub>), 199.63 (2-Ar<u>C</u>), 137.01 (Ar<u>C</u>), 136.84 (Ar<u>C</u>), 135.88 (Ar<u>C</u>), 135.39 (Ar<u>C</u>), 134.50

<sup>&</sup>lt;sup>1</sup> It was later found the temperature did not affect the purity of the resulting products.

<sup>&</sup>lt;sup>2</sup> Melting points were not taken, although <sup>13</sup>C NMR data was used to further confirm identity.

(Ar<u>C</u>), 133.92 (Ar<u>C</u>), 131.67 (Ar<u>C</u>), 131.54 (Ar<u>C</u>), 130.99 (Ar<u>C</u>), 130.15 (Ar<u>C</u>), 129.93 (Ar<u>C</u>), 129.85 (Ar<u>C</u>), 129.51 (Ar<u>C</u>), 129.22 (Ar<u>C</u>), 128.22 (Ar<u>C</u>), 127.88 (Ar<u>C</u>), 127.41 (Ar<u>C</u>), 125.77 (Ar<u>C</u>), 125.31 (Ar<u>C</u>), 31.45 (1-ArCO<u>C</u>H<sub>3</sub>), 28.17 (2-ArCO<u>C</u>H<sub>3</sub>).

#### 1-Acetylpyrene 6-Ac

31.3, quantitative. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  9.06 (d, J = 9.5 Hz, 1H, Ar<u>H</u>), 8.37 (d, J = 8.0 Hz, 1H, Ar<u>H</u>), 8.28 – 8.18 (m, 3H, Ar<u>H</u>), 8.18 – 8.12 (m, 2H, Ar<u>H</u>), 8.10 – 7.99 (m, 2H, Ar<u>H</u>), 2.90 (s, 3H, ArCOC<u>H\_3</u>). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  203.63 (ArCOCH<sub>3</sub>), 135.42 (Ar<u>C</u>), 133.28 (Ar<u>C</u>), 132.46 (Ar<u>C</u>), 131.89 (Ar<u>C</u>), 131.18 (Ar<u>C</u>), 131.07 (Ar<u>C</u>), 130.89 (Ar<u>C</u>), 128.58 (Ar<u>C</u>), 128.49 (Ar<u>C</u>), 127.82 (Ar<u>C</u>), 127.77 (Ar<u>C</u>), 127.53 (Ar<u>C</u>), 126.39 (Ar<u>C</u>), 125.67 (Ar<u>C</u>), 125.40 (Ar<u>C</u>), 31.94 (ArCO<u>C</u>H<sub>3</sub>).

## 2-Acetyltriphenylene 7-Ac

34.6 mg, quantitative. <sup>1</sup>H NMR (300 MHz, Chloroform-*d*)  $\delta$  9.29 (d, J =1.8 Hz, 1H, 1-Ar<u>H</u>), 8.91 – 8.54 (m, 5H, Ar<u>H</u>), 8.21 (dd, J = 8.6, 1.8 Hz, 1H, 3-Ar<u>H</u>), 7.87 – 7.61 (m, 4H, Ar<u>H</u>), 2.83 (s, 2H, ArCOC<u>H</u><sub>3</sub>). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  199.38 (Ar<u>C</u>OCH<sub>3</sub>), 136.61 (Ar<u>C</u>), 134.72 (Ar<u>C</u>), 132.13 (Ar<u>C</u>), 131.35 (Ar<u>C</u>), 130.94 (Ar<u>C</u>), 130.92 (Ar<u>C</u>), 130.31 (Ar<u>C</u>), 129.80 (Ar<u>C</u>), 129.22 (Ar<u>C</u>), 128.87 (Ar<u>C</u>), 127.62 (Ar<u>C</u>), 125.44 (Ar<u>C</u>), 125.43 (2 x Ar<u>C</u>), 125.03 (Ar<u>C</u>), 124.84 (Ar<u>C</u>), 124.83 (Ar<u>C</u>), 124.78 (Ar<u>C</u>), 28.26 (ArCO<u>C</u>H<sub>3</sub>).

#### 3,9-Diacetylfluoranthene 5-Ac

36.6, quantitative. <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  8.85 (d, J = 8.5 Hz, 0. 1H, ArH), 8.44 - 8.39 (m, 1H, ArH), 8.17 (d, J = 7.3 Hz, 1H, ArH), 7.99 (dd, J = 7.9, 1.3 Hz, 1H, ArH), 7.92 (t, J = 6.8 Hz, 2H, ArH), 7.86 (d, J = 7.9 Hz, 1H, ArH), 7.71 (dd, J = 8.4, 7.0 Hz, 1H, ArH), 2.80 (s, 3H, ArCOCH<sub>3</sub>), 2.71 =0 (s, 3H, ArCOCH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, Chloroform-d)  $\delta$  201.77 5-Ac (ArCOCH<sub>3</sub>), 199.07 (ArCOCH<sub>3</sub>), 146.02 (ArC), 142.12 (ArC), 139.59 (ArC),

137.75 (ArC), 136.96 (ArC), 135.30 (ArC), 135.03 (ArC), 133.60 (ArC), 131.65 (ArC), 130.98 (ArC), 129.82 (ArC), 129.17 (ArC), 123.37 (ArC), 123.22 (ArC), 122.60 (ArC), 120.67 (ArC), 30.51 (ArCOCH<sub>3</sub>), 28.29 (ArCOCH<sub>3</sub>).

#### 1-Acetylcorannulene 8-Ac



37.4 mg, quantitative. M.p. 107.3-110.1°C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.57 (d, *J* = 9.0 Hz, 1H, ArH), 8.42 (s, 1H, ArH), 8.06 -7.57 (m, 7H, ArH), 2.82 (s, 3H, ArCOCH3). <sup>13</sup>C NMR (101 MHz, 8-Ac Chloroform-d) & 201.09 (ArCOCH<sub>3</sub>), 138.85 (ArC), 137.83 (ArC), 137.61 (ArC), 137.13 (ArC), 136.53 (ArC), 136.26 (ArC), 133.67 (ArC), 133.39 (ArC), 132.15 (ArC), 132.14 (ArC), 130.08 (ArC), 129.83 (ArC), 129.75 (ArC), 129.64 (ArC), 129.51 (ArC), 128.96 (ArC), 128.83 (ArC), 128.51 (ArC), 128.46 (ArC), 128.40 (ArC), 29.94 (ArCOCH<sub>3</sub>). IR (solid press, cm<sup>-1</sup>) 827 (sh, s), 880 (sh, m), 1077 (sh, br), 1244 (sh, m), 1325 (sh, w), 1430 (sh, w), 1658 (sh, s), 2848 (sh, w), 3339 (br, w). Found HR-MS (ESI) m/z: 293.0960 ([M+H<sup>+</sup>], 100), 294.0093 ([M+H<sup>+</sup>], 24); C<sub>22</sub>H<sub>12</sub>OH<sup>+</sup> requires m/z: 293.0961 ([M+H<sup>+</sup>], 100), 294.0994 ([M+H<sup>+</sup>], 25). (Found: C, 84.16; H, 4.62%. (C<sub>22</sub>H<sub>12</sub>O)<sub>5</sub>(H<sub>2</sub>O)<sub>6</sub> requires C, 84.17; H, 4.62%).

#### Acylation of polycyclic aromatic compounds - competition reactions

The competition reactions were carried out under reaction conditions the same as described previously for the formation of the acylated derivatives at 0°C with the exception that equimolar amounts of two aromatic species were present and the amount of acetyl chloride was reduced to half an equivalent based on the total amount of aromatic species present (8.0  $\mu$ L, 112  $\mu$ mol) and added as a solution in dichloromethane (0.1 mL of a solution of 0.31 mL acetyl chloride in 10 mL dichloromethane). The extents of conversion were determined through comparison of the integrations of the signals due to the starting material (spectra were taken for commercial samples) and the product (spectra obtained above) in each case. This data was then analysed using Equation 1. This allowed determination of the relative rates of reaction. Each process was carried out in triplicate and the results are tabulated below (Table S1).

 $\frac{\ln(x_1)}{\ln(x_2)} = \frac{k_1}{k_2}$ 

Where:  $x_1$  is the extent of conversion of compound 1,  $x_2$  is the extent of conversion of compound 2,  $k_1$  is the rate constant for the acylation of compound 1, and  $k_2$  is the rate constant for the acylation of compound 2.

**Equation 1.** A measure of the ratio of the respective reaction rates as calculated from their extents of conversion as per Yau et. al.<sup>125</sup>

Compound 1	Compound 2 Extents of conversion / %		onversion / %
		Compound 1	Compound 2
	naphthalene 2	0	47
benzene 1		0	45
		0	44
		0	49
naphthalene 2	pyrene 6	0	42
Î		0	38
	corannulene 8	0	44
naphthalene 2		0	47
		0	39
pyrene 6	triphenylene 7	44	0
		41	0
		40	0
		45	0
pyrene 6	corannulene 8	48	0
	$\begin{array}{c cccc} 0 & 44 \\ 0 & 49 \\ 0 & 42 \\ 0 & 38 \\ 0 & 42 \\ 0 & 38 \\ 0 & 42 \\ 0 & 39 \\ 0 & 44 \\ 0 & 47 \\ 0 & 39 \\ 44 & 0 \\ 1 & 0 \\ 1 & 0 \\ 45 & 0 \\ 1 & 0 \\ 45 & 0 \\ 48 & 0 \\ 48 & 0 \\ 48 & 0 \\ 48 & 0 \\ 1 & 43 \\ 1 & 37 \\ 1 &$	0	
		4	43
triphenylene 7	corannulene 8	4	37
		2	30

**Table S1** - The extents of conversions noted, alongside the ratio of the rate constants as determined using Equation 1, for the competition reactions between aromatic systems.

# Attempted bromination of corannulene 8 using N-bromosuccinimide

To a stirred solution of corannulene **8** (100 mg, 400  $\mu$ mol) in *N*,*N*-dimethylformamide (3 mL) was added *N*-bromosuccinimide in *N*,*N*-dimethylformamide (3 mL) dropwise over 10 minutes at 0°C. After stirring for 24 hours at room temperature, the reaction mixture was added to water (25 mL) and extracted into ether (25 mL). The organic layer was then washed with aqueous hydrochloric acid (3M, 3 x 50 mL), dried over magnesium sulfate and the solvent removed under reduced pressure. <sup>1</sup>H NMR spectroscopy indicated a large amount of starting material still present as indicated by the signal at  $\delta$  *ca*. 7.8 alongside a complex mixture of products. The ratio of the integration of the starting material signal to the other aromatic signals was approximately 1.6:1, which correlates to approximately 57% of unreacted material if a 1:1 mixture of dibrominated and mono-brominated materials are considered the likely products.

#### Preparation of ketones 15 and 16

#### Corannulenyl(phenyl)methanone 15



anhydrous dichloromethane (25 mL) under dynamic nitrogen and the reaction mixture was stirred for 5 minutes before corannulene 8 (0.200 g, 0.799 mmol) was added. After a further 5 minutes of stirring, the suspension was cooled over an ice bath before benzoyl chloride (0.110 mL, 0.956 mmol) was added in one portion via a syringe. The solution turned dark red after a few minutes and was stirred for a further 2 hours at room temperature. After returning to 0°C, the reaction mixture was quenched with water (25 mL) followed by concentrated hydrochloric acid (3 mL) and the now bright yellow lower organic layer collected. The aqueous layer was extracted with additional dichloromethane (25 mL) and the combined organic layers dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The yellow solid residue was purified using flash column chromatography (gradient elution from 9:1 to 1:1 hexane:dichloromethane) to yield the desired product as a white solid 15 (0.163 g, 58%). M.p. 203.5-205.8°C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.20 (s, 1H, ArH), 8.06 (d, J = 8.9 Hz, 1H, ArH), 8.02 - 7.97 (m, 2H, ArH), 7.88 - 7.76 (m, 7H, ArH), 7.70 - 7.62 (m, 1H, Ar<u>H</u>), 7.54 (t, J = 7.7 Hz, 2H, Ar<u>H</u>). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  198.36 (ArCOAr), 140.31 (ArC), 138.53 (ArC), 137.96 (ArC), 137.80 (ArC), 137.09 (ArC), 136.90 (ArC), 136.63 (ArC), 134.37 (ArC), 133.71 (ArC), 133.32 (ArC), 132.39 (ArC), 132.36 (ArC), 131.92 (ArC), 130.45 (ArC), 130.18 (ArC), 129.92 (2 x ArC), 129.56 (ArC), 129.40 (ArC), 129.15 (ArC), 128.98 (ArC), 128.65 (ArC), 128.63 (ArC), 128.57 (ArC). IR (solid press, cm<sup>-1</sup>) 724 (sh, s), 829 (sh, s), 1003 (sh, m), 1161 (sh, w), 1253 (sh, m), 1433 (sh, w), 1645 (*sh*, *m*). Found HR-MS (ESI) *m/z*: 377.0930 ([M+H<sup>+</sup>], 100), 378.0965 ([M+H<sup>+</sup>], 16);

Aluminium(III) chloride (0.320 g, 2.40 mmol) was added to

8

 $C_{27}H_{14}OH^+$  requires *m/z*: 377.0937 ([M+H<sup>+</sup>], 100), 378.0970 ([M+H<sup>+</sup>], 28). (Found: C, 89.06; H, 3.91%.); ( $C_{27}H_{14}O$ )<sub>2</sub>(H<sub>2</sub>O) requires C, 89.24; H, 4.16%.)

# 2-Triphenylenyl(phenyl)methanone 16

This compound was made in an analogous manner to corannulenyl(phenyl)methanone *16.* Starting material (0.400 g, 1.75 mmol). Aluminium trichloride (0.467 mg, 3.5 mmol). Benzoyl chloride (369 mg, 2.63 mmol). 161 mg, 32%. M.p. 163.5 - 165.5°C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  9.16 (s, 1H, Ar<u>H</u>), 8.80 - 8.63 (m, 5H, Ar<u>H</u>), 8.13-8.09 (m, 1H, Ar<u>H</u>), 7.98 - 7.94 (m, 2H, Ar<u>H</u>), 7.79 - 7.66 (m, 5H, Ar<u>H</u>), 7.61 - 7.56 (m, 2H, Ar<u>H</u>). IR (solid press, cm<sup>-1</sup>) 723 (*sh*, *s*), 953 (*sh*, *m*), 1270 (*sh*, *s*), 1401 (*sh*, *w*), 1646 (*sh*, *m*). Found HR-MS (ESI) *m/z*: 333.1271 ([M+H<sup>+</sup>], 100), 334.1302 ([M+H<sup>+</sup>], 24); C<sub>25</sub>H<sub>17</sub>OH<sup>+</sup> requires *m/z*: 333.1274 ([M+H<sup>+</sup>], 100), 334.1307 ([M+H<sup>+</sup>], 27). (Found: C, 86.96; H, 4.63%. (C<sub>25</sub>H<sub>17</sub>O)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> requires C, 87.18; H, 5.07%).

#### Preparation of the alcohols 10-OH to 14-OH

#### General reduction of the ketone precursors using lithium aluminium hydride

To an ice-cooled solution of the appropriate ketone precursor (0.277 mmol) in anhydrous tetrahydrofuran (10 mL) under dynamic nitrogen was added lithium aluminium hydride (15.8 mg, 0.416 mmol) in one portion at 0°C. After the addition was complete, the reaction mixture was stirred at 0°C for one hour before being very carefully quenched with water until no further bubbling was noted (*ca.* 1 mL). The resulting white suspension was filtered and the residue was washed with ether (30 mL). The filtrate was dried over magnesium sulfate, filtered and concentrated under reduced pressure to yield the products **127-130** as white solids.

## Benzyhydrol 10-OH

49.8 mg, 95%. M.p. 64.3 - 66.6°C (Lit.<sup>1</sup> 68°C). <sup>1</sup>H NMR (300 MHz, Chloroform-*d*)  $\delta$  7.76 - 7.58 (m, 5H, Ar<u>H</u>), 7.49 - 7.30 (m, 5H, Ar<u>H</u>), 5.60 (s, 1H, C<u>H</u>OH). <sup>1</sup>H NMR (500 MHz, Methanol- *d*<sub>4</sub>)  $\delta$  7.35 (d, *J* = 7.5 Hz, 4H, Ar<u>H</u>), 7.29 (t, *J* = 7.5 Hz, 4H, Ar<u>H</u>), 7.21 (t, *J* = 7.5 Hz, 2H, Ar<u>H</u>), 5.76 (s, 1H, C<u>H</u>OH).

#### 2-Triphenylenyl(phenyl)methanone 13-OH



84.7 mg, 91%. M.p. 197.3 - 200.0°C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.76 (s, 1H, Ar<u>H</u>), 8.72 - 8.62 (m, 5H, Ar<u>H</u>), 7.71 - 7.64 (m, 5H, Ar<u>H</u>), 7.51 (d, J = 7.4 Hz, 2H, Ar<u>H</u>), 7.40 (t, J = 7.7 Hz, 2H, Ar<u>H</u>), 7.33 (t, J = 7.5 Hz, 2H, Ar<u>H</u>), 6.15 (s, 1H,

ArCHOHPh). IR (solid press, cm<sup>-1</sup>) 715 (sh, s), 753 (sh, s), 806 (sh, w), 1034 (sh, m), 1404 (sh, m), 1490 (sh, w), 3380 (br, w). Found HR-MS (ESI) *m/z*: 357.1252 ([M+Na<sup>+</sup>], 100),

358.1284 ([M+Na<sup>+</sup>], 27); C<sub>25</sub>H<sub>16</sub>ONa<sup>+</sup> requires *m/z*: 357.1250 ([M+Na<sup>+</sup>], 100), 358.1283 ([M+Na<sup>+</sup>], 28). (Found: C, 88.25; H, 5.47%. (C<sub>25</sub>H<sub>16</sub>O)<sub>4</sub>H<sub>2</sub>O requires C, 88.60; H, 5.50%).

1-Corannulenyl-1-phenylmethanol 14-OH



0.123 g, 95%. M.p. 107.0-110.1°C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.94 (s, 1H, Ar<u>H</u>), 7.90 (d, J = 8.9 Hz, 1H, Ar<u>H</u>), 7.83 – 7.67 (m, 7H, Ar<u>H</u>), 7.58 (d, J = 7.5 Hz, 2H, Ar<u>H</u>), 7.38 (t, J= 7.5 Hz, 2H, Ar<u>H</u>), 7.32 (d, J = 7.3 Hz, 1H, Ar<u>H</u>), 6.51 (s, 1H,

ArCHOHAr). <sup>13</sup>C NMR (101 MHz, Chloroform-d) & 144.90

(ArC), 143.34 (ArC), 137.50 (ArC), 137.01 (ArC), 136.97 (ArC), 136.95 (ArC), 132.31 (ArC), 132.24 (ArC), 131.91 (ArC), 131.79 (ArC), 130.21 (ArC), 130.07 (ArC), 129.87 (ArC), 129.21 (ArC), 128.67 (ArC), 128.64 (ArC), 128.60 (ArC), 128.52 (ArC), 128.49 (ArC), 128.44 (ArC), 128.39 (ArC), 128.33 (ArC), 126.96 (ArC), 126.02 (ArC), 76.24 (ArCHOHAr). IR (solid press, cm<sup>-1</sup>) 696 (*sh*, *s*), 796 (*sh*, *s*), 883 (*sh*, *w*), 1015 (*sh*, *s*), 1077 (*sh*, *m*), 1258 (*sh*, *m*). Found HR-MS (ESI) m/z: 379.1095 ([M+Na<sup>+</sup>], 100), 380.1128 ([M+Na<sup>+</sup>], 29); C<sub>27</sub>H<sub>16</sub>ONa<sup>+</sup> requires m/z: 379.1093 ([M+Na<sup>+</sup>], 100), 380.1127 ([M+Na<sup>+</sup>], 29). (Found: C, 83.59; H, 5.07%. (C<sub>14</sub>H<sub>16</sub>O)<sub>4</sub>(H<sub>2</sub>O)<sub>7</sub> requires C, 83.43; H, 5.02%).

#### 2-Naphthyl(phenylmethanol) 11-OH



To a solution of 2-naphthaldehyde (2.10 g, 13.5 mmol) in anhydrous ether (50 mL) was added an ethereal solution of phenyllithium (1.9 M in di<sup>n</sup>butylether, 10.6 mL, 20.2 mmol) dropwise at 0°C over two

minutes whilst under dynamic nitrogen. The reaction mixture was then heated to reflux for 3 hours. After cooling to room temperature, the dark solution was quenched with water (50 mL) and the organic phase separated. The aqueous phase was further extracted with ether (2

x 50 mL) and the combined organic layers dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. Boiling hexane (200 mL) was added to the dark residue and the mixture was vigorously stirred until no further dissolution was noted, at which point the hexane was carefully decanted from any insoluble material. Upon cooling to -20°C, the product **11-OH** solidified as a white solid that was collected using vacuum filtration (1.67 g, 53%). M.p. 85.0 - 87.2°C (Lit.<sup>2</sup> 87-88 °C). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.93 (s, 1H, Ar<u>H</u>), 7.90 - 7.78 (m, 3H, Ar<u>H</u>), 7.56 - 7.42 (m, 5H, Ar<u>H</u>), 7.37 (t, *J* = 7.5 Hz, 2H, Ar<u>H</u>), 7.34 - 7.29 (m, 1H, Ar<u>H</u>), 6.04 (s, 1H, C<u>H</u>OH).

#### 9-Phenanthryl(phenylmethanol) 12-OH



<sup>n</sup>Butyl lithium (1.6 M in hexanes, 2.67 mL, 4.28 mmol) was added dropwise over 3 minutes to a solution of 9-bromophenanthrene (1.00 g, 3.89 mmol) in anhydrous tetrahydrofuran (25 mL) at -78°C under dynamic nitrogen. After the reaction mixture had been stirred for 1

hour at -78°C, benzaldehyde (0.5 mL, 4.9 mmol) was added over 2 minutes to the solution. The reaction was allowed to warm to room temperature, was quenched with water (25 mL) and the mixture was extracted with dichloromethane (3 x 20 mL). The organic fractions were combined, dried over magnesium sulfate and the solvent removed under reduced pressure. The product **12-OH** was isolated using flash column chromatography (hexane followed by hexane:ethyl acetate, 4:1) as a white solid (0.723 g, 72%). M.p. 130-134°C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  8.76 (d, *J* = 8.3 Hz, 1H, Ar<u>H</u>), 8.70 (d, *J* = 8.2 Hz, 1H, Ar<u>H</u>), 8.06 (d, *J* = 8.1 Hz, 1H, Ar<u>H</u>), 8.00 (s, 1H, ArC10-<u>H</u>), 7.97 – 7.90 (m, 1H, Ar<u>H</u>), 7.73 – 7.61 (m, 3H, Ar<u>H</u>), 7.54 (m, 1H, Ar<u>H</u>), 7.49 (d, *J* = 7.2 Hz, 2H, Ar<u>H</u>), 7.41 – 7.30 (m, 3H, Ar<u>H</u>), 6.58 (s, 1H, C<u>H</u>OH). <sup>1</sup>H NMR (500 MHz, Methanol-*d*<sub>4</sub>)  $\delta$  8.79 (d, *J* = 8.2 Hz, 1H, Ar<u>H</u>), 8.74 (d, *J* = 8.2 Hz, 1H, Ar<u>H</u>), 8.08 (d, *J* = 7.9 Hz, 1H, Ar<u>H</u>), 7.97 (s, 1H, ArC10-<u>H</u>), 7.93 – 7.89 (m, 1H,

Ar<u>H</u>), 7.66 (ddd, J = 8.3, 7.1, 1.5 Hz, 1H, Ar<u>H</u>), 7.63 – 7.57 (m, 2H, Ar<u>H</u>), 7.49 (ddd, J = 8.2, 7.0, 1.1 Hz, 1H, Ar<u>H</u>), 7.44 (d, J = 7.2 Hz, 2H, Ar<u>H</u>), 7.32 (t, J = 7.5 Hz, 2H, Ar<u>H</u>), 7.28 – 7.23 (m, 1H, Ar<u>H</u>), 6.50 (s, 1H, C<u>H</u>OH). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  144.21 (Ar<u>C</u>), 138.20 (Ar<u>C</u>), 132.76 (Ar<u>C</u>), 132.30 (Ar<u>C</u>), 131.75 (Ar<u>C</u>), 131.13 (Ar<u>C</u>), 130.47 (Ar<u>C</u>), 130.09 (Ar<u>C</u>), 129.32 (Ar<u>C</u>), 128.77 (Ar<u>C</u>), 128.31 (Ar<u>C</u>), 128.25 (Ar<u>C</u>), 128.05 (Ar<u>C</u>), 127.75 (Ar<u>C</u>), 126.96 (Ar<u>C</u>), 126.36 (Ar<u>C</u>), 124.63 (Ar<u>C</u>), 123.93 (Ar<u>C</u>), 75.46 (Ar<u>C</u>HOHAr). IR (solid press, cm<sup>-1</sup>) 695 (*sh*, *s*), 742 (*sh*, *s*), 807 (*sh*, *w*), 983 (*sh*, *w*), 1060 (*sh*, *m*), 1290 (*sh*, *w*), 1423 (*sh*, *w*), 1684 (*br*, *w*). Found HR-MS (ESI) *m/z*: 307.1089 ([M+Na<sup>+</sup>], 100), 308.1122 ([M+Na<sup>+</sup>], 21); C<sub>21</sub>H<sub>16</sub>ONa<sup>+</sup> requires *m/z*: 307.1093 ([M+Na<sup>+</sup>], 100), 308.1127 ([M+Na<sup>+</sup>], 22). (Found: C, 87.13; H, 5.79%.; (C<sub>21</sub>H<sub>16</sub>O)<sub>4</sub>(H<sub>2</sub>O) requires C, 87.32; H, 5.76%).

#### General method for the formation of the methyl ethers 10-OCH<sub>3</sub> to 14-OCH<sub>3</sub>

The appropriate alcohol (271  $\mu$ mol) was added to methanol (5 mL) followed by concentrated sulfuric acid (0.5 mL). The reaction mixture was then stirred at the temperature specified for t hours as noted below. The reaction mixture was added to water (10 mL) and extracted thrice with ether (3 x 15 mL). The combined organic layers were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure to yield the products as clear oils (unless otherwise noted), which required no further purification (unless otherwise noted). It is worth noting that the triphenylenyl system **13-OH** degraded into a complex mixture of unknown materials as determined by <sup>1</sup>H NMR spectroscopy.

# 1,1-Diphenylmethyl methyl ether 10-OCH<sub>3</sub>

Reflux, 16 hours. 52.1 g, 97%. <sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.56
7.21 (m, 10H, Ar<u>H</u>), 5.32 (s, 1H, ArC<u>H</u>OCH<sub>3</sub>Ar), 3.46 (s, 3H, OC<u>H<sub>3</sub></u>).
<sup>1</sup>H NMR (600 MHz, Methanol-*d*<sub>4</sub>) δ 7.45 – 7.28 (m, 8H, Ar<u>H</u>), 7.27 – 7.19
(m, 2H, Ar<u>H</u>), 5.29 (s, 1H ArC<u>H</u>OCH<sub>3</sub>Ar), 3.35 (s, 3H, OC<u>H<sub>3</sub></u>). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 142.08 (Ar<u>C</u>), 128.40 (Ar<u>C</u>), 127.46 (Ar<u>C</u>), 126.92 (Ar<u>C</u>), 85.44 (Ar<u>C</u>HOCH<sub>3</sub>Ar), 57.03 (ArCHO<u>C</u>H<sub>3</sub>Ar).

## 2-(Methoxy(phenyl)methyl)naphthalene 11-OCH<sub>3</sub>

Room temperature, 16 hours. 64.8 mg, 96%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.92 – 7.80 (m, 4H, Ar<u>H</u>), 7.54 – 7.42 (m, 5H), 7.37 **11-OCH<sub>3</sub>** (m, 2H, Ar<u>H</u>), 7.33 – 7.27 (m, 1H, Ar<u>H</u>), 5.45 (s, 1H, ArC<u>H</u>OCH<sub>3</sub>Ar), 3.48 (s, 3H, ArCHOC<u>H</u><sub>3</sub>Ar). <sup>1</sup>H NMR (500 MHz, Methanol-*d*<sub>4</sub>)  $\delta$  7.88 – 7.74 (m, 4H, Ar<u>H</u>), 7.52 – 7.38 (m, 5H, Ar<u>H</u>), 7.32 (t, *J* = 7.6 Hz, 2H, Ar<u>H</u>), 7.24 (t, *J* = 7.3 Hz, 1H, Ar<u>H</u>), 5.45 (s, 1H, ArC<u>H</u>OCH<sub>3</sub>Ar), 3.48 (s, 3H, ArCHOC<u>H</u><sub>3</sub>Ar). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  143.49 (ArC), 140.98 (ArC), 134.76 (ArC), 134.44 (ArC), 129.98 (ArC), 129.87 (ArC), 129.56 (ArC), 129.23 (ArC), 129.08 (ArC), 128.56 (ArC), 127.66 (ArC), 127.44 (ArC), 127.27 (ArC), 126.51 (ArC), 86.99 (ArCHOCH<sub>3</sub>Ar), 58.59 (ArCHOCH<sub>3</sub>Ar). IR (solid press, cm<sup>-1</sup>) 728 (*sh*, *s*), 813 (*sh*, *s*), 1089 (*sh*, *s*), 1189 (*sh*, *m*), 1449 (*sh*, *m*), 1506 (*sh*, *m*), 1598 (*sh*, *w*), 2927 (*br*, *m*). Found HR-MS (ESI) *m/z*: 271.1090 ([M+Na<sup>+</sup>], 100), 272.1124 ([M+Na<sup>+</sup>], 16); C<sub>18</sub>H<sub>16</sub>ONa<sup>+</sup> requires *m/z*: 271.1093 ([M+Na<sup>+</sup>], 100), 272.1127 ([M+Na<sup>+</sup>], 20).

#### 9-(Methoxy(phenyl)methyl)phenanthrene 12 -OCH3

Heated to reflux, 16 hours. Isolated as a white solid. 0.780 g, 97%. M.p.  $\cap$ 102.4-105.1°C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.78 (d, J = 7.8Hz, 1H, ArH), 8.73 (d, J = 8.2 Hz, 1H, ArH), 8.19 – 8.12 (m, 1H, ArH), 12-0CH<sub>3</sub> 8.01 - 7.93 (m, 2H, ArH), 7.75 - 7.61 (m, 3H, ArH), 7.57 (m, 1H, ArH), 7.51 (d, J = 7.1 Hz, 2H, ArH), 7.41 – 7.29 (m, 3H, ArH), 5.98 (s, 1H, ArCHOCH<sub>3</sub>Ar), 3.58 (s, 3H, ArCHOCH<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, Methanol- $d_4$ )  $\delta$  8.79 (d, J = 8.3 Hz, 1H, Ar<u>H</u>), 8.75 (d, J = 8.2 Hz, 1H, ArH), 8.14 – 8.09 (m, 1H, ArH), 7.92 (dd, J = 7.8, 1.3 Hz, 1H, ArH), 7.88 (s, 1H, ArH), 7.68 (m, 1H, ArH), 7.64 – 7.59 (m, 2H, ArH), 7.50 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H, ArH), 7.44 (d, J = 7.1 Hz, 2H, ArH), 7.35 - 7.29 (m, 2H, ArH), 7.28 - 7.22 (m, 1H, ArH), 5.98 (s, 1H, ArCHOCH<sub>3</sub>Ar), 3.51 (s, 3H, ArCHOCH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, Chloroform-d)  $\delta$  142.46 (ArC), 136.17 (ArC), 132.78 (ArC), 132.43 (ArC), 131.85 (ArC), 131.52 (ArC), 130.40 (ArC), 129.86 (ArC), 129.13 (ArC), 128.95 (ArC), 128.29 (ArC), 128.21 (ArC), 127.99 (2 x ArC), 127.73 (ArC), 126.58 (ArC), 124.58 (ArC), 123.96 (ArC), 85.32 (ArCHO CH<sub>3</sub>Ar), 58.89 (ArCHOCH<sub>3</sub>Ar). IR (solid press, cm<sup>-1</sup>) 701(*sh*, *s*), 719 (*sh*, *s*), 973 (*sh*, *w*), 1028 (*sh*, w), 1091 (sh, m), 1446 (sh, m), 1492 (sh, m), 2838 (sh, m), 3359 (br, w). Found HR-MS (ESI) m/z: 321.1244 ([M+Na<sup>+</sup>], 100), 322.1275 ([M+Na<sup>+</sup>], 22); C<sub>22</sub>H<sub>18</sub>ONa<sup>+</sup> requires m/z:

321.1250 ([M+Na<sup>+</sup>], 100), 322.1283 ([M+Na<sup>+</sup>], 26). (Found: C, 87.24; H, 5.85%.; (C<sub>22</sub>H<sub>18</sub>O)<sub>5</sub>(H<sub>2</sub>O) requires C, 87.50; H, 6.14%).

# 1-Corannulenyl-1-phenylmethyl methyl ether 14-OCH3



Room temperature, 16 hours. 51.8 mg, 93%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.98 (d, J = 8.9 Hz, 1H, Ar<u>H</u>), 7.91 – 7.69 (m, 8H, Ar<u>H</u>), 7.53 (m, 2H, Ar<u>H</u>), 7.40 – 7.27 (m, 3H, Ar<u>H</u>), 5.91 (s, 1H, ArC<u>H</u>OCH<sub>3</sub>Ar), 3.47 (s, 3H, ArCHOC<u>H</u><sub>3</sub>Ar). <sup>1</sup>H NMR (400

MHz, Methanol- $d_4$ )  $\delta$  8.03 (d, J = 8.9 Hz, 1H, ArH), 7.94 – 7.73 (m, 8H, ArH), 7.57 – 7.50 (m, 2H, ArH), 7.38 – 7.32 (m, 2H, ArH), 7.30 – 7.23 (m, 1H, ArH), 5.98 (s, 1H, ArCHOCH<sub>3</sub>Ar), 3.43 (s, 3H, ArCHOCH<sub>3</sub>Ar). <sup>13</sup>C NMR (101 MHz, Chloroform-d)  $\delta$  143.22 (ArC), 141.57 (ArC), 137.52 (ArC), 137.00 (ArC), 136.98 (ArC), 136.96 (ArC), 136.92 (ArC), 132.25 (ArC), 132.19 (ArC), 131.78 (ArC), 130.51 (ArC), 129.90 (ArC), 129.04 (ArC), 128.68 (2 x ArC), 128.60 (ArC), 128.57 (ArC), 128.50 (2 x ArC), 128.46 (ArC), 128.37 (ArC), 128.35 (ArC), 127.22 (ArC), 126.72 (ArC),.78(ArCHOCH<sub>3</sub>Ar), 58.76 (ArCHOCH<sub>3</sub>Ar). Found HR-MS (ESI) m/z: 393.1245 ([M+Na<sup>+</sup>], 100), 394.1283 ([M+Na<sup>+</sup>], 30).

#### Measurement of the rate of methanolysis of 10-OH to 14-OH

A fresh solution of concentrated sulfuric acid (35.4 mg, 361  $\mu$ mol) in deuterated methanol (0.6 mL) was generated. Of this, a portion (0.5 mL) was added to an NMR tube that already contained the desired amount (28.0  $\mu$ mol) of the respective alcohols. The reaction was held at the desired temperature of 23.8°C either in a NMR spectrometer. The extent of reaction at a given time was determined through comparing the integration due to signals due to the starting material (at the chemical shifts noted below) relative to the integration of the product signals (at the chemical shifts noted below). This allowed calculation of observed first order rate constants, which are tabulated below (Table S2). As their protiated derivatives were not formed as per the previous case of **13-OCH<sub>3</sub>** their product signals are also noted here.

Compound	Amount of alcohol / mg	Observed rate constant (k <sub>obs</sub> ) / s <sup>-1</sup>	Average k <sub>obs</sub> / s <sup>-1</sup>
	5.0	6.45 x 10 <sup>-5</sup>	
benzhydrol 10-OH	4.8	6.71 x 10 <sup>-5</sup>	6.55(14) x 10 <sup>-5</sup>
·	4.8	6.50 x 10 <sup>-5</sup>	
2-napthyl(phenyl)methanol 11-OH	6.1	2.21 x 10 <sup>-4</sup>	
	6.3	2.14 x 10 <sup>-4</sup>	2.10(14) x 10 <sup>-5</sup>
	6.4	1.95 x 10 <sup>-4</sup>	
	7.5	1.86 x 10 <sup>-4</sup>	
9-phenanthryl(phenyl)methanol 12-OH	7.5	2.15 x 10 <sup>-4</sup>	1.93(19) x 10 <sup>-4</sup>
	8.5	1.77 x 10 <sup>-4</sup>	× /
	8.8	4.15 x 10 <sup>-4</sup>	
2-tripnenylenyl(pnenyl)methanol	5.8	3.44 x 10 <sup>-4</sup>	3.38(79) x 10 <sup>-4</sup>
13-0H	9.8	2.56 x 10 <sup>-4</sup>	, í
	10.6	3.57 x 10 <sup>-4</sup>	
corannulenyl(phenyl)methanol <sup>a</sup> 14-OH	11.5	4.11 x 10 <sup>-4</sup>	3.86(27) x 10 <sup>-4</sup>
	11.3	3.89 x 10 <sup>-4</sup>	

<sup>a</sup> Due to speed of the reaction at this temperature, the sample was first dissolved in 400  $\mu$ L of hot deuterated methanol before the addition of the acid catalyst in a further 100  $\mu$ L of deuterated methanol at room temperature. A dummy sample was locked in the NMR spectrometer before the sample was added and shimmed at 60°C. The sample was routinely already at 60% extent of conversion, but this had no bearing on our ability to monitor the reaction as it proceeded to completion.

**Table S2** - The amounts of starting material used, the resulting observed first-orderrate constants and the observed first order rate constants for the methanolysisreactions of the alcohols noted and the uncertainties the averages reported as half therange of the data.

# 2-Triphenylenyl-phenylmethyl methyl ether 14-OCH<sub>3</sub>



# 1-Acetylcorannulene 8-Ac



# 2-Triphenylenyl(phenyl)methanone 16





# Corannulenyl(phenyl)methanone 15



## 9-Phenanthryl(phenyl)methanol 12-OH



# 2-Triphenylenyl(phenyl)methanol 13-OH



# Corannulenyl(phenyl)methanol 14-OH







#### 2-(Methoxy(phenyl)methyl)naphthalene 12-OCH<sub>3</sub>





# 1-Corannulenyl-1-phenylmethyl methyl ether 14-OCH<sub>3</sub>

# **Computational data**



Starting material	Energy / E <sub>h</sub>	Intermediate	Energy / E <sub>h</sub>	<b>Relative energy</b> / kcal mol <sup>-1</sup>
1	-230.666	1-Int	-382.689	134
2	-383.290	2-Inta	-535.330	119
2	-383.290	2-Intb	-535.336	123
6	-611.660	6-Int	-763.734	102
7	-688.542	7-Int	-840.591	117
8	-763.049	8-Int	-915.099	117

**Table S3** – The energies of the starting materials 1, 2 and 6-8 along with the energiesof the corresponding intermediates 1-Int, 2-Inta,b and 6-8-Int. Relative energies foreach system are thus given, taking into account the energy of acetyl chloride $(-611.801 E_h)$  and chloride  $(-459.565 E_h)$ .



Figure S1 – Reaction coordinate for the process outlined in Scheme 1 (left) showing the energies of each of the starting materials 1, 2 and 6-8 with acetyl chloride (normalised to the same energy) relative to the corresponding intermediates. Note that energy differences are labelled and are not to scale.

Intermediate	НОМО	LUMO
1-Int		
2-Inta		
2-Intb		
6-Int		
7-Int		
8-Int		

Table S4 – Frontier molecular orbitals for the intermediates in the reaction of each of<br/>the species 1, 2 and 6-8 with acetyl chloride (Scheme 1, left).





**Table S5** – Mulliken charges for the starting materials and intermediates in thereaction of each of the species 1, 2 and 6-8 with acetyl chloride (Scheme 1, left).



Starting material	Energy / E <sub>h</sub>	Intermediate	Energy / E <sub>h</sub>	<b>Relative energy / kcal mol<sup>-1</sup></b>
<b>S1</b>	-269.693	<b>S1</b> <sup>+</sup>	-268.840	535
<b>S2</b>	-422.319	S2+	-421.471	532
<b>S3</b>	-574.944	<b>S3</b> <sup>+</sup>	-574.103	527
<b>S4</b>	-727.570	S4+	-726.729	527
<b>S5</b>	-802.078	<b>S5</b> <sup>+</sup>	-801.240	526

Table S6 – The energies of the starting materials S1-S5 along with the energies of the corresponding intermediates  $S1^+$ - $S5^+$ ; relative energies for each system are also given.



Figure S2 – Energy profile showing the energies of each of the neutral species S1-S5 (normalised to the same energy) relative to the corresponding cations S1<sup>+</sup>-S5<sup>+</sup>. Note that energy differences are labelled and are not to scale.

Cation	НОМО	LUMO
S1+		
S2+		
<b>S3</b> +		
S4+		
S5 <sup>+</sup>		

Table S7 – Frontier molecular orbitals for the cations  $S1^+$ - $S5^+$ .





Table S8 – Mulliken charges for the neutral species S1-S5 and cations S1<sup>+</sup>-S5<sup>+</sup>.

- 1. Marvel, C. S.; Hansen, N. A., Org. Synth. 1928, 8, 24.
- 2. Kuriyama, M.; Shimazawa, R.; Enomoto, T.; Shirai, R., J. Org. Chem. 2008, 73, 6939.