Generation of benzyne from benzoic acid using C-H activation

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Supporting Information

General Methods

1H and 13C NMR spectra were recorded on an Ava 400 MHz instrument and are calibrated to residual solvent peaks (CDCl3 7.26 ppm and 77.0 ppm). The data is reported as chemical shift (ppm) followed by peak signal shape with relevant coupling constants quoted to the nearest 0.1 Hertz. Electrospray high resolution mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea, using a Finigan MAT 900 XTL double focusing mass spectrometer. EI HRMS was carried out by the University of Edinburgh using a Kratos MS50 instrument. The data is recorded as the ionization method followed by the calculated and measured masses. T.L.C. was performed on Merck 60F254 aluminium backed silica plates and visualized by uv light (both 254 nm and 365 nm). Final compounds were purified by wet flash chromatography using Merck Kieselgel 60 (particle size 35-70) silica under a positive pressure. All chemicals were purchased from a chemical supplier and used as received unless otherwise stated.

General procedure for triphenylene synthesis

Benzoic acid (111 mg, 0.9 mmol, 1 equiv), palladium (II) acetate (25 mg, 0.11 mmol, 12.5 mol %), 1,10 phenanthroline (21.3 mg, 0.11 mmol, 12.5 mol %) and sulfolane (25 mL) were placed in an oven dried RB flask. The mixture was heated to around 40 °C to allow sulfolane to become less viscous and the reaction was sonicated until all solids were dissolved. Copper (II) acetate (123 mg, 0.68 mmol, 0.75 equiv), potassium phosphate dibasic (314 mg, 1.8 mmol, 2 equiv), tetrabutylammonium bromide (298 mg, 0.9 mmol, 1 equiv) and 4Å MS (0.4 g) were then added to the mixture. The mixture was then heated to 150 °C for 16 hr, open to air, before allowing to cool. The reaction was then filtered through silica and the silica was washed with ethyl acetate (~150 mL). The resulting solution was then washed 4 times with water, once with 1M NaOH solution and once with brine. The organics were then dried over MgSO4, filtered and evaporated to dryness. The resulting residue was then purified using column chromatography (SiO2, DCM:hexane 0:100 – 5:95) to yield triphenylene as a white solid (32 mg, 47 % yield).
2, 6, 11-Trimethyltriphenylene 6b. The general procedure was followed using a 1 mmol scale, yielding 6b (39.4 mg, 34%) as a white solid. $^1$H NMR $\delta$: 8.50 (3H, m), 8.43 (2H, s), 7.39 (3H, m), 7.44 (3H, m), 2.62 (6H, s), 2.61 (3H, s); $^{13}$C NMR $\delta$: 136.5 (Q), 136.2 (Q), 136.2 (Q), 129.8 (Q), 129.5 (Q), 129.3 (Q), 128.4 (CH), 128.4 (CH), 128.1 (CH), 127.7 (Q), 127.5 (Q), 127.2 (Q), 123.2 (CH), 122.9 (CH), mpt 142 °C; HRMS (EI) calc for C$_{21}$H$_{18}$ 270.1403, found 270.1395.

2, 6, 11-Tri-(tert-butyl)triphenylene 6c. The general procedure was followed yielding 6c (39.4 mg, 33%) as a white solid. $^1$H NMR $\delta$: 8.65 (4H, m), 8.55 (2H, m), 7.71 (3H, m), 1.53 (18H, s), 1.51 (9H, s). $^{13}$C NMR $\delta$: 149.4 (Q), 149.3 (Q), 149.2 (Q), 129.6 (Q), 129.2 (Q), 129.0 (Q), 127.8 (Q), 127.6 (Q), 127.2 (Q), 124.9 (CH), 124.9 (CH), 124.7 (2CH), 123.0 (CH), mpt 142 °C; HRMS (EI) calc for C$_{36}$H$_{42}$F$_{18}$ 582.2865, found 582.2865.

2, 6, 11-Trifluorotriphenylene 6d. The general procedure was followed yielding 6d (30 mg, 35%) as a white solid. $^1$H NMR 800 MHz $\delta$: 8.47 (2H, dt, J=5.9, 8.6), 8.42 (1H, dd, J=2.3, 8.9), 8.04 (2H, m), 7.38 (2H, m), 7.35 (1H, ddd, J=2.3, 7.8, 9.0) $^{13}$C NMR, 200 MHz $\delta$: 165.1 (Q, d, J=248), 164.8 (Q, d, J=246), 164.6 (Q, d, J=247), 131.4 (Q, dd, J=3.0, 8.0), 130.7 (Q, d, J=8.0), 125.9 (Q, m), 125.9 (CH, d, J=8.8), 125.4 (CH, dd, J=8.7, 16.2), 116.3 (CH, d, J=22.4), 116.2 (CH, d, J=22.2), 115.5 (CH, dd, J=3.1, 22.9), 109.1 (CH, dd, J=2.8, 22.8), 109.0 (CH, dd, J=2.6, 22.5), 109.0 (CH, d, J=7.8), 108.7 (CH, d, J=6.8); $^{19}$F NMR, 250 MHz $\delta$: -112.69, -113.88, -113.93. mpt 230 °C; HRMS (EI) calc for C$_{18}$H$_9$F$_3$ 282.0651, found 282.0650.

2, 6, 11-Trimethoxytriphenylene 6e. The general procedure was followed yielding 6e (16.5 mg, 17%) as a yellow solid. $^1$H NMR, $\delta$: 8.43 (3H, m), 7.92 (3H, m), 7.25 (2H, td, J=2.7, 9.0), 7.19 (1H, dd, J=2.7, 9.0), 4.02 (3H, s), 4.01 (3H, s), 4.00 (3H, s); $^{13}$C NMR $\delta$: 158.7 (Q), 158.2 (Q), 158.0 (Q), 131.3 (Q), 130.2 (Q), 129.7 (Q), 125.0 (CH), 124.4 (CH), 124.3 (Q), 124.3 (CH), 123.8 (Q), 122.9 (Q), 115.6 (CH), 115.4 (CH), 114.8 (CH), 106.1 (2CH), 105.2 (CH), 55.5 (2CH$_3$), 55.4 (CH$_3$). Spectroscopic data were in agreement with that previously published.$^1$

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2, 6, 11-Trifluoromethyltriphenylene 6f. The general procedure was followed, using the higher temperature of 160 °C, to yield 6f (24.9 mg, 19%) as a yellow solid. $^1$H NMR ((CD$_3$)$_2$CO), 500 MHz $\delta_{H}$; 9.33 (2H, s), 9.24-9.20 (2H, m), 9.1 (2H, dd, 2.9, 8.7), 8.14-8.09 (3H, m). $^{13}$C NMR, 125 MHz $\delta_{C}$; 134.0 (Q), 133.9 (Q), 133.6 (Q), 132.0 (Q, q, J= 32.3), 131.9 (Q, q, J= 32.3), 131.8 (Q), 131.5 (Q, q, J= 33.3), 131.5 (Q), 131.4 (Q), 127.6 (CH), 127.6 (CH), 127.3 (CH), 126.7 (CH, q, J=3.4), 126.4 (CH, q, J=3.5), 126.4 (CF$_3$, q, J=271.9), 126.3 (CF$_3$, q, J=271.9), 126.3 (CF$_3$, q, J=271.8), 123.5 (3CH, m). $^{19}$F NMR, 400 MHz $\delta_{F}$; 114.9 (CF$_3$), 114.9 (CF$_3$), 114.8 (CF$_3$). mpt 280°C. HRMS (EI) calc for C$_{21}$H$_9$F$_9$, 432.0555 found 432.0560.

1, 5, 12-Trimethyltriphenylene 8a. The general procedure was followed yielding 8a (19 mg, 23%) of product as a yellow solid. $^1$H NMR, $\delta_{H}$; 8.46 (5H, m), 7.44 (4H, m), 3.04 (3H, s), 2.62 (3H, s), 2.60 (3H, s); $^{13}$C NMR $\delta_{C}$; 136.6 (Q), 136.0 (Q), 135.0 (Q), 131.1 (CH), 131.0 (Q), 130.9 (Q), 130.0 (Q), 129.8 (Q), 128.6 (Q), 128.5 (CH), 128.4 (CH), 128.1 (Q), 126.8 (CH), 125.8 (CH), 123.6 (CH), 123.2 (CH), 123.0 (CH), 120.8 (CH), 26.7 (CH$_3$), 21.8 (CH$_3$), 21.7 (CH$_3$); mpt 100 °C. HRMS (EI) calc for C$_{21}$H$_{18}$ 270.1403, found 270.1398.

6H-Dibenzo[b,d]pyran-6-one, 7. Benzoic acid (111 mg, 0.9 mmol, 1 equiv), palladium (II) acetate (25 mg, 0.11 mmol, 12.5 mol %), tert-butyl XPhos (96 mg, 0.11 mmol, 12.5 mol %) and sulfolane (25 mL) were placed in an oven dried RB flask. The mixture was heated to around 40 °C to allow sulfolane to become less viscous and the reaction was sonicated until all solids were dissolved. Copper (II) acetate (328 mg, 1.8 mmol, 2 equiv), potassium phosphate dibasic (314 mg, 1.8 mmol, 2 equiv), tetrabutylammonium bromide (298 mg, 0.9 mmol, 1 equiv) and 4Å MS (0.4 g) were then added to the mixture. The mixture was then heated to 150 °C for 16 hr, open to air, before allowing to cool. The reaction was then filtered through silica and the silica was washed with ethyl acetate (~150 mL). The resulting solution was then washed 4 times with water, once with 1M NaOH solution and once with brine. The organics were then dried over MgSO$_4$, filtered and evaporated to dryness. The resulting residue was then purified using column chromatography (EtOAc/hexane 0-6%) to yield 6H-dibenzo[b,d]pyran-6-one (22 mg, 25 % yield) as a white solid.
**9,10-Diphenylphenanthrene.** Benzoic acid (111 mg, 0.9 mmol, 1 equiv), palladium(II) acetate (25 mg, 0.11 mmol, 12.5%), 1,10 phenanthroline (21.3 mg, 0.11 mmol, 12.5%) and sulfolane (25 mL) were placed in an oven dried RB flask. The mixture was heated to around 40 °C to allow sulfolane to become less viscous and the reaction was sonicated until all solids were dissolved. Copper (II) acetate (123 mg, 0.68 mmol, 0.75 equiv), potassium phosphate dibasic (314 mg, 1.8 mmol, 2 equiv), tetrabutylammonium bromide (298 mg, 0.9 mmol, 1 equiv), diphenylacetylene (20 mg, 0.11 mmol, 0.125 equiv) and 4Å MS (0.4 g) were then added to the mixture. The mixture was then heated to 130 °C for 16 hr, open to air, before allowing to cool. The reaction was then filtered through silica and the silica was washed with ethyl acetate (~150 mL). The resulting solution was then washed 4 times with water, once with 1M NaOH solution and once with brine. The organics were then dried over MgSO₄, filtered and evaporated to dryness. The resulting residue was then purified using column chromatography (DCM:hexane 0:100 - 5:95) to yield 9,10-diphenylphenanthrene (35.5 mg, 48% yield) and triphenylene (38.1 mg, 25% yield, based on benzoic acid) as white solids. ¹H NMR 400 MHz δH: 8.88 (2H, d, J= 8.3), 7.73 (2H, d, J= 1.4, 6.9, 8.3), 7.70 (2H, d, J= 1.1, 8.3), 7.47 (2H, d, J= 1.1, 6.9, 8.2), 7.35-7.20 (10H, m). ¹³C NMR, 100 MHz δC: 139.5 (Q), 137.2 (Q), 131.9 (Q), 131.0 (2CH), 127.8 (CH), 127.6 (2CH), 126.6 (CH), 126.5 (CH), 126.4 (CH), 122.5 (CH). Spectroscopic data was in agreement with that previously published.²

**1,2,3,4-Tetraphenylnaphthalene.** Benzoic acid (111 mg, 0.9 mmol, 1 equiv), palladium(II) acetate (25 mg, 0.11 mmol, 12.5%), 1,10 phenanthroline (21.3 mg, 0.11 mmol, 12.5%) and sulfolane (25 mL) were placed in an oven dried RB flask. The mixture was heated to around 40°C to allow sulfolane to become less viscous and the reaction was sonicated until all solids were dissolved. Copper (II) acetate (123 mg, 0.68 mmol, 0.75 equiv), potassium phosphate dibasic (314 mg, 1.8 mmol, 2 equiv), tetrabutylammonium bromide (298 mg, 0.9 mmol, 1 eq), diphenylacetylene (962 mg, 5.4 mmol, 6 equiv) and 4Å MS (0.4 g) were then added to the mixture. The mixture was then heated to 120 °C for 16 hr open to air before allowing to cool. The reaction was then filtered through silica and the silica was washed with ethyl acetate (~150 mL). The resulting solution was then washed 4 times with water, once with 1M NaOH solution and once with brine. The organics were then dried over MgSO₄, filtered and evaporated to dryness. The resulting residue was then purified using column chromatography (DCM:hexane 0:100 – 5:95) to yield 1,2,3,4-tetraphenylnaphthalene (268 mg, 69% yield) as a white solid. ¹H NMR 400 MHz δH: 7.82 (2H, d, J= 3.3, 5.5), 7.56 (2H, d, J= 3.3, 6.5), 7.45-7.33 (10H, m), 7.06-6.96 (10H, m). ¹³C NMR, 100 MHz δC: 140.5 (2Q), 139.6 (2Q), 138.9 (2Q), 138.4 (2Q), 132.0

(2Q), 131.3 (8CH), 127.5 (4CH), 127.0 (2CH), 126.5 (4CH), 126.4 (2CH), 125.8 (2CH), 125.3 (2CH). Spectroscopic data was in agreement with that previously published.\(^3\)

Compound 6c
Compound 6d
Compound 8a
Compound 6f
Compound 9
Compound 10

Supplementary Material (ESI) for Chemical Communications
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