Supporting Information for:

Radiaannulenes: Synthesis, electrochemistry, and solid-state structure

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**Compound 3a.** A mixture of compound 5\(^1\) (107 mg, 0.288 mmol) and K\(_2\)CO\(_3\) (8 mg, 0.06 mmol) in THF (1 mL) and MeOH (1 mL) was stirred for 1 h. Et\(_2\)O and H\(_2\)O were added, the organic phase separated, washed with saturated NH\(_4\)Cl (2 x 20 mL), dried (MgSO\(_4\)), and reduced to 2 mL. This ethereal solution of 6 was deoxygenated* and added to a deoxygenated mixture of 1,2-diiodobenzene (95 mg, 0.288 mmol), CuI (15 mg, 0.08 mmol), Pd(PPh\(_3\))\(_4\) (23 mg, 0.02 mmol), iPr\(_2\)NH (3 mL) in dry THF (5 mL). The resulting mixture was refluxed under a N\(_2\) atmosphere for 18 h. After the reaction was cooled, solvent removal and purification by column chromatography (silica gel, hexanes/CH\(_2\)Cl\(_2\) 7:1 to 3:1) and then re-crystallization from CH\(_2\)Cl\(_2\) by the addition of hexanes gave 3a (27 mg, 31%) as a pale yellow solid. Mp >300 °C (decomp.); R\(_f\) = 0.43 (hexanes/CH\(_2\)Cl\(_2\) 1:1); UV-vis (THF) \(\lambda_{\text{max}}\) 413 nm; IR (CH\(_2\)Cl\(_2\), cast) 3078, 3050, 3022, 2924, 2852, 2194 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 7.59–7.57 (m, 8H), 7.45–7.43 (m, 12H), 7.23–7.21 (m, 4H), 7.08–7.06 (m, 4H); \(^{13}\)C NMR (125 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 157.6, 140.7, 132.2, 131.1, 129.3, 128.5, 128.1, 125.4, 102.2, 92.9, 90.7. EI HRMS calcd. for C\(_{48}\)H\(_{28}\) (M\(^+\)) 604.2186, found 604.2185. MALDI TOF HRMS calcd. for C\(_{48}\)H\(_{28}\) (M\(^+\)) 604.2186, found 604.2185.

**Compound 3b.** Compound 11 (64 mg, 0.15 mmol) was dissolved in ether (8 mL) and the solution deoxygenated.* The deoxygenated ethereal solution of 11 was added to a deoxygenated mixture of 9\(^2\) (50 mg, 0.15 mmol), CuI (9 mg, 0.05 mmol), Pd(PPh\(_3\))\(_4\) (9 mg, 0.008 mmol), iPr\(_2\)NH (3 mL) in dry THF (5 mL). The resulting mixture was refluxed under a N\(_2\) atmosphere for 20 h. The reaction crude was cooled washed with saturated NH\(_4\)Cl (2 X 20 mL), H\(_2\)O (40 mL) and extracted with CH\(_2\)Cl\(_2\). After removing the solvent, a solution of hexanes/CH\(_2\)Cl\(_2\) (50 mL, 1:1) was added resulting in dispersed red solid. The solid was filtered on a fritted funnel (a 10–20 microns), the solid washed with hexanes (~500 mL) on the frit, and then allowed to air dry. This 3b (81 mg, 90%) as a highly insoluble red solid. Mp >300 °C (decomp.); R\(_f\) = 0.4 (hexanes/CH\(_2\)Cl\(_2\) 1:1); UV-vis (THF) \(\lambda_{\text{max}}\) 345, 446, 472 nm; IR (CH\(_2\)Cl\(_2\), cast) 3055, 2960, 2925, 2856 cm\(^{-1}\); \(^1\)H NMR

* Solutions were deoxygenated by bubbling N\(_2\) through the solution for ca. 30 min.
(500 MHz, C$_2$D$_2$Cl$_4$) $\delta$ 8.85–8.33 (m, 4H), 7.80–7.79 (m, 4H), 7.75–7.74 (m, 4H), 7.56–7.54 (m, 4H), 7.47–7.45 (m, 8H); $^{13}$C NMR (125 MHz, C$_2$D$_2$Cl$_4$, 65 °C) $\delta$ 146.1, 140.3, 137.4, 131.8, 129.8, 128.9, 127.4, 125.54, 125.47, 119.7, 101.1, 96.0, 93.1. MALDI TOF HRMS calcd. for C$_{48}$H$_{24}$ (M$^+$) 600.1873, found 600.1870.

**Compound 11.** A mixture of compound 7$^3$ (150 mg, 0.423 mmol) and K$_2$CO$_3$ (13 mg, 0.09 mmol) in a mixture of THF (2 mL) and MeOH (2 mL) was stirred for 1 h. Et$_2$O and H$_2$O were added, the organic phase separated, washed with saturated NH$_4$Cl (2 x 20 mL), dried (MgSO$_4$), and reduced to 2 mL. This ethereal solution of 8 was deoxygenated* and added to a deoxygenated* mixture of 9 (71 mg, 0.21 mmol), Cul (12 mg, 0.06 mmol), Pd(PPh$_3$)$_4$ (24 mg, 0.02 mmol), tPr$_2$NH (3 mL) in dry THF (5 mL). The resulting mixture was refluxed under a N$_2$ atmosphere for 20 h. Solvent removal and purification by column chromatography (silica gel, hexanes/CH$_2$Cl$_2$ 5:1) afforded 10$^\dagger$ as an orange liquid. To a solution of 10 in THF (2 mL) was added TBAF (0.2 mL, 0.2 mmol, 1M in THF) and the mixture stirred at rt for 30 min. Et$_2$O and H$_2$O were added, the organic phase separated, washed with saturated NH$_4$Cl (2 x 20 mL), and dried (MgSO$_4$). Solvent removal and column chromatography (silica gel, hexanes/CH$_2$Cl$_2$ 4:1) gave 11 (68 mg, 75%) as a yellow solid. Mp >300 °C (decomp.); $R_f$ = 0.6 (hexanes/CH$_2$Cl$_2$ 1:1); UV-vis (THF) $\lambda_{max}$ (e) nm 396 (26700), 414 (26200); IR (CH$_2$Cl$_2$, cast) 3289, 3059, 2926, 2181, 2108 cm$^{-1}$; $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 8.33 (d, J = 7.6 Hz, 2H), 7.03–7.00 (m, 4H), 6.96–6.94 (m, 2H), 6.79–6.70 (m, 6H), 6.64 (td, J = 7.6, 1.2 Hz, 2H), 2.78 (s, 2H); $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$) $\delta$ 145.8, 140.7, 137.6, 133.4, 132.9, 130.3, 129.34, 129.25, 127.8, 126.4, 126.0, 124.8, 120.0, 100.9, 97.1, 92.6, 82.5, 82.1. MALDI TOF HRMS calcd. for C$_{34}$H$_{18}$ (M$^+$) 426.1403, found 426.1403.

$^\dagger$ For unknown reasons, compound 10 appears to be unstable to chromatographic separation on either silica gel or alumina oxide supports. It was thus taken on directly to the desilylation step without additional purification.

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Figure S1. UV-Vis spectra of 3a and 3b in THF.
Figure S2. Edge on view of 3a from X-ray crystallographic analysis.

Figure S3. Edge on view of 3b from X-ray crystallographic analysis.
Figure S4. Top right) Cyclic voltammograms of radiaannulenes 3a and 3b. Top left) Cathodic section of the CV of radiaannulenes 3a and 3b. Bottom) Cyclic voltammograms of enediynes 5 and 12.
Figure S5. OSWV of radiaannulenes 3a and 3b.
Figure S6. $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$) for radiaannulene 3a.
Figure S7. $^{13}$C NMR spectrum (125 MHz, CD$_2$Cl$_2$) for radiaannulene 3a.
Figure S8. $^1$H NMR spectrum (500 MHz, C$_2$D$_2$Cl$_4$) for radiaannulene 3b.
Figure S9. $^{13}$C NMR spectrum (125 MHz, C$_2$D$_2$Cl$_4$) for radiaannulene 3b.
Figure S10. $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$) for 11.
Figure S11. $^{13}$C NMR spectrum (125 MHz, CD$_2$Cl$_2$) for 11.
References: