

Supplementary Information for

**Exploring the Chemical Dynamics of Phenanthrene (C₁₄H₁₀) Formation via
the Bimolecular Gas-Phase Reaction of the Phenylethynyl Radical (C₆H₅CC)
with Benzene (C₆H₆)**

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Precursor Synthesis and Characterization

The synthesis of (2-bromoethynyl)benzene was performed analogously to a reported procedure¹ with an increase in the concentration of the starting materials due to the large scale of precursor needed. Regarding the purification, batches performed with less than 10 g of phenylacetylene could be purified by either column chromatography or distillation for both precursors whereas larger batches (20–50 g) decomposed before affording the desired product and, thus, had to be purified by column chromatography. A solution of phenylacetylene (8.0 mL, 7.44 g, 72 mmol) in MeOH (50 mL) was cooled down to 0 °C and KOH (10.0 g, 180 mmol) was added. After 20 min of stirring at 0 °C, N-bromosuccinimide (15.3 g, 86 mmol) was added to the mixture in portions and stirred at 0 °C for 15 min. The cold bath was replaced by a rt water bath and the mixture was stirred for 30 min. Then, Et₂O (200 mL) was added and the mixture was extracted with brine (3 x 100 mL), dried over MgSO₄, filtered and evaporated to afford a brown oil/liquid. This liquid was purified by column chromatography (SiO₂; hexane) to afford the product as a light-yellow oil (9.63 g, 73%). ¹H NMR (200 MHz, CDCl₃) δ: 7.44 (dd, 2H), 7.31 (m, 3H) ppm. ¹³C NMR (50 MHz, CDCl₃) δ: 132.10, 128.78, 128.44, 122.78, 80.19 and 49.93 ppm. MS: m/z 180.0 [M⁺] 101.1 [M⁺–Br]. The characteristic C≡C stretching vibration was found at 2202 cm⁻¹ whereas for the starting material it is observed at 2110 cm⁻¹. The provided characterization is in accordance with the literature.² ¹H and ¹³C NMR data were recorded with a Bruker DPX-200 NMR spectrometer referenced towards CDCl₃ (7.26 ppm for ¹H NMR and 77.16 ppm for ¹³C NMR). The GC-MS data were recorded with an Agilent 7820A GC spectrometer. IR data were recorded with a Bruker Equinox 55 FT-IR spectrometer.

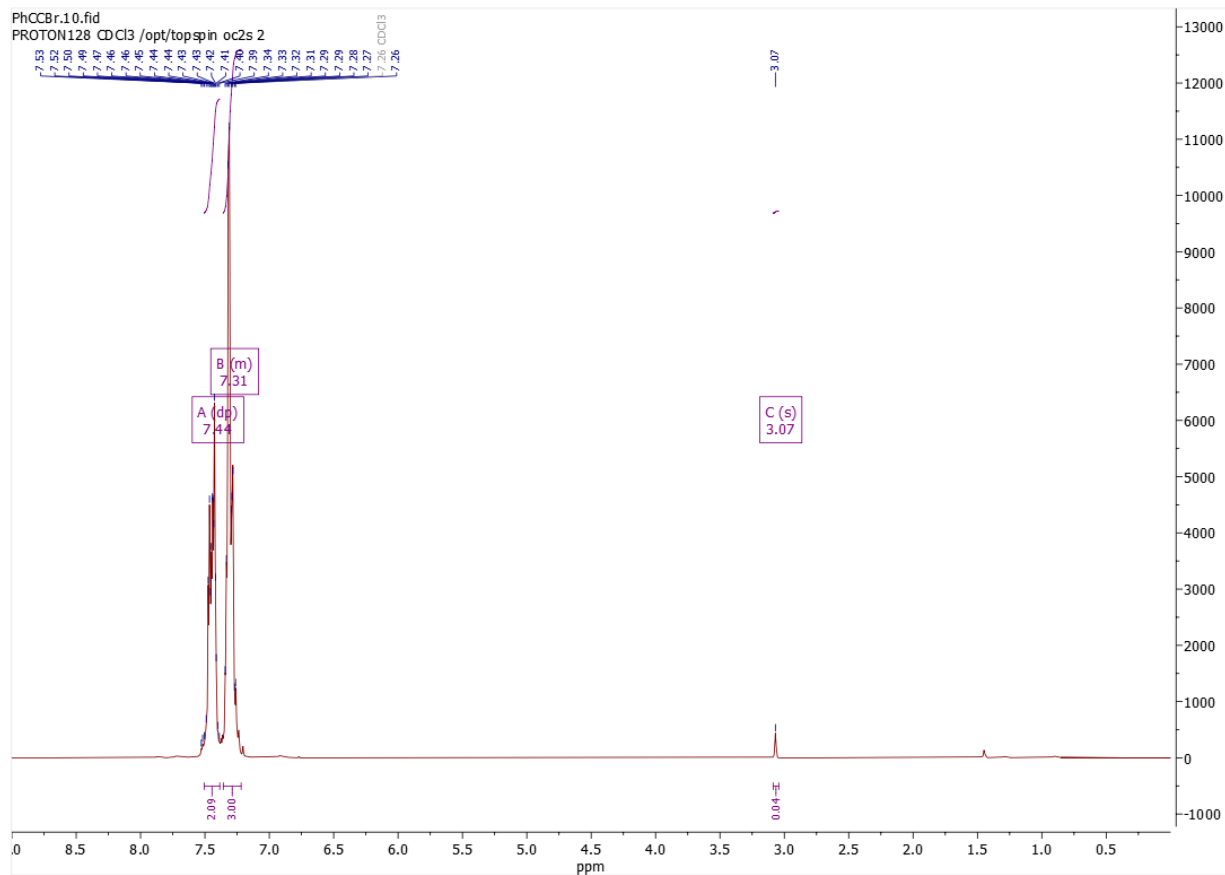


Fig. S1 ¹H NMR spectrum of (2-bromoethynyl)benzene. A small impurity of phenylacetylene is still observed at 3.07 ppm and was later removed by distillation.

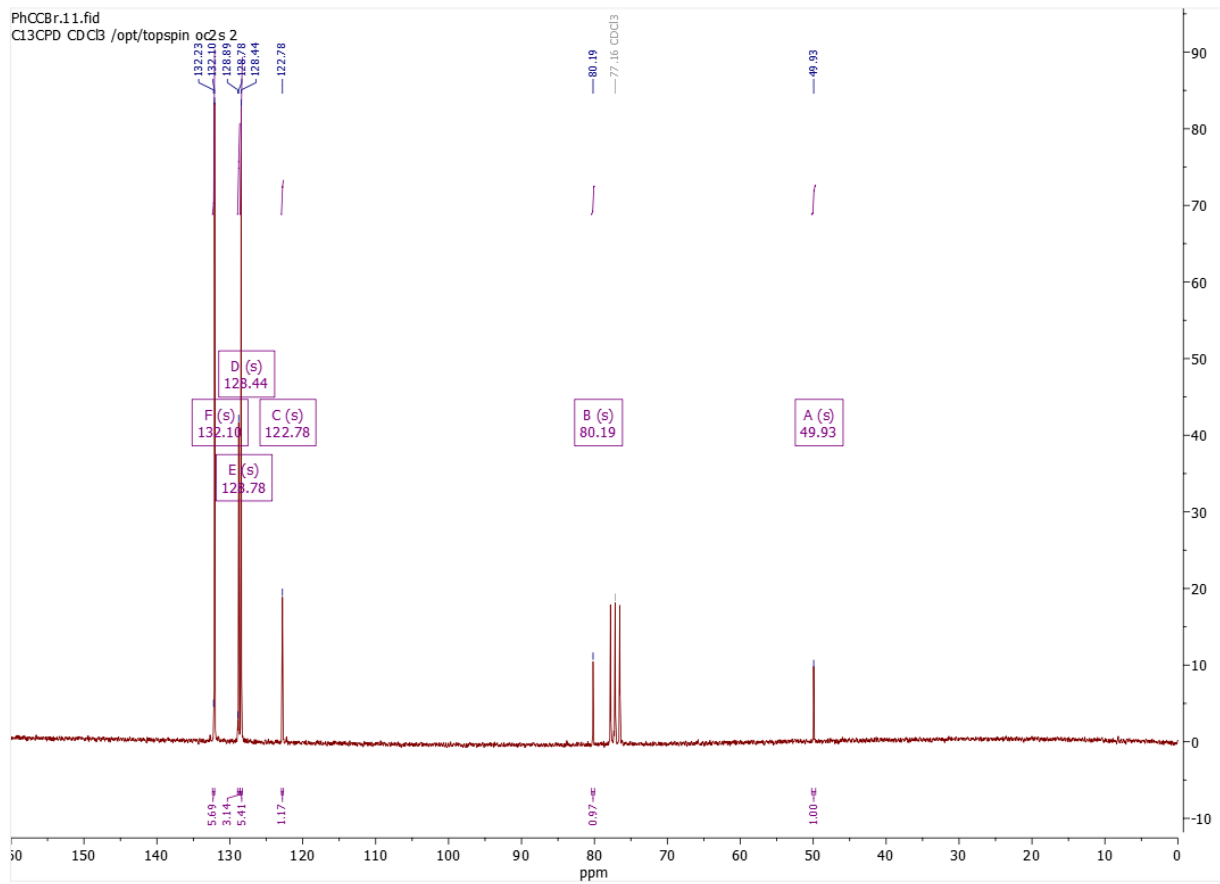


Fig. S2 ^{13}C NMR spectrum of (2-bromoethynyl)benzene.

Supplementary References

- 1 M. V. Russo, C. Lo Sterzo, P. Franceschini, G. Biagini and A. Furlani, *J. Organomet. Chem.*, 2001, **619**, 49-61.
- 2 M. X.-W. Jiang, M. Rawat and W. D. Wulff, *J. Am. Chem. Soc.*, 2004, **126**, 5970-5971.