

## Supplementary Material

Photoswitchable enediynes: use of cyclopropanone as photocleavable masking group for the enediyne triple bond

by Andrei Poloukhine and Vladimir V. Popik

**General Procedures.** Photolyses were performed by irradiation of methanol solutions of 2,3-benzobicyclo[8.1.0]undec-1(10)-ene-4yn-11-one (**1**) in a 1 cm quartz cell or NMR tube using a RMR-600 Rayonet™ photochemical reactor equipped with carousel and a set of six lamps with  $\lambda_{\text{max}}$  of emission at 300 nm. High-resolution mass spectral analysis was performed by the Mass Spectrometry Laboratory, University of Illinois at Urbana-Champaign, IL.

**Materials.** Moisture- and oxygen-sensitive reactions were carried out in flame-dried glassware under an argon atmosphere. Tetrahydrofuran and diethyl ether were distilled from sodium, and dichloromethane was distilled from phosphorus pentoxide under argon immediately before use. Hexanes used in column chromatography were distilled from sodium; ethyl acetate and acetone were distilled from anhydrous calcium chloride. All other reagents were used as purchased. Purification of products by column chromatography was performed using 40-63  $\mu\text{m}$  silica gel.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded using TMS or a residual solvent peak as an internal standard.

**1,2-Bis[2-(trimethylsilyl)ethynyl]benzene (3).** A thoroughly degassed solution of diiodobenzene (6.6 g, 20 mmol), trimethylsilylacetylene (4.3 g, 44.00 mmol), triethylamine (16 mL),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (0.7 g), triphenylphosphine (0.26 g), CuI (0.38 g) in 120 mL of THF was heated in a sealed vessel for 14 hours at 40°C. Solid impurities were removed by filtration, solvent removed in vacuum, the residue re-dissolved in ethyl acetate – hexanes (1:25) and passed through a layer of silica gel to give 4.97 g of crude **3** as slightly orange

oil.  $R_f=0.63$  (ethyl acetate – hexanes 1:20);  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52-7.45 (m, 2 H), 7.29-7.24 (m, 2 H), 0.30 (s, 18 H); MS calc for  $\text{C}_{16}\text{H}_{22}\text{Si}_2$  ( $\text{M}^+$ ) 270, found 270. Lit.<sup>1</sup>

**1,2-Diethynylbenzene (4).** A solution of **3** (4.97 g) in methanol (140 mL) and potassium carbonate powder (6.16 g, 44.00 mmol) were stirred at room temperature for 45 min. The reaction was quenched by the addition of an aqueous solution of  $\text{NH}_4\text{Cl}$ , most of the solvent removed in vacuum, the residue was re-dissolved in ethyl acetate, washed with water, brine, dried over anhydrous  $\text{MgSO}_4$ , concentrated, and purified by the chromatography on silica gel (ethyl acetate – hexanes 1:40) to give 2.12 g of **4** (16.8 mmol, 84% over two steps) as a slightly yellow oil that darkens when stored at room temperature.  $R_f=0.42$  (ethyl acetate – hexanes 1:20);  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56-7.51 (m, 2 H), 7.36-7.32 (m, 2 H), 3.36 (s, 2 H). Lit.<sup>1</sup>

**3,4-Benzocyclodeca-1,5-diyne (2).** *n*-BuLi (2.5M solution in hexanes, 14.1 mL, 35.4 mmol) was added to a solution of 1,2-diethynylbenzene (**14**) (2.12 g, 16.8 mmol) in THF (400 mL) at  $-78^\circ\text{C}$  under argon. An hour later, 1,4-diiobutane (5.30 g, 17.0 mmol) was added dropwise at  $-78^\circ\text{C}$ , and stirring continued for ca. 72 hours at room temperature. The reaction was quenched by the addition of a phosphate buffer, concentrated, and then diluted with ether and water. The organic layer was separated, washed with water, brine, dried over anhydrous magnesium sulfate, and solvents were removed in vacuum. The residue was purified by the chromatography on silica gel ( $\text{CH}_2\text{Cl}_2$  – hexanes 1:5) to give 1.213 g of **2c** (6.74 mmol, 40%) as white crystalline solid.  $R_f=0.44$ ; (ethyl acetate – hexanes 1:20);  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.27 (m, 2 H), 7.22-7.16 (m, 2 H), 2.44

---

<sup>1</sup> Zhou, Q.; Carroll, P.J.; Swager, T.M. *J. Org. Chem.* **1994**, *59*, 1294.

(m, 4 H), 1.97-1.91 (m, 4 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  129.8, 128.7, 127.2, 100.0, 82.3, 28.7, 21.5. Lit.<sup>2</sup>

**2,3-Benzobicyclo[8.1.0]undec-1(10)-en-4-yn-11-one (1).** A solution of *n*-BuLi (2.5 M solution in hexanes, 2.53 mL, 6.3 mmol) was added dropwise over 30 min to a solution of **2c** (0.52g, 2.89 mmol) and chloroform (0.86 g, 7.2 mmol) in THF (50 mL) at  $-78^\circ\text{C}$ . After 10 min the reaction was quenched by the addition of concentrated hydrochloric acid, allowed to warm up to room temperature, and stirred for another 30 min. The reaction mixture was concentrated, diluted with ether, washed with saturated solution of sodium bicarbonate, water, brine, dried over anhydrous magnesium sulfate, and solvents removed in vacuum. The residue was purified by the chromatography on silica gel ( $\text{CH}_2\text{Cl}_2$  – hexanes 1:5  $\rightarrow$   $\text{CH}_2\text{Cl}_2$   $\rightarrow$  ethyl acetate) to give 0.084 g (0.40 mmol, 67% calculated on recovered enediyne) of **1** as an orange oil. 0.41g, (2.28 mmol) of **2** were also recovered.  $R_f=0.4$  (ethyl acetate);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (td,  $J=7.2, 1.2$  Hz 1 H), 7.50-7.40 (m, 3 H), 2.97 (t,  $J=6.45$  Hz, 2 H), 2.44 (t,  $J=6$  Hz, 2 H), 2.1-2.0 (m, 2 H), 1.75 (p,  $J=6$  Hz, 2 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 157.1, 155.4, 131.9, 131.5, 129.7, 128.1, 127.8, 123.7, 99.3, 82.0, 26.06, 26.01, 25.7, 18.2; IR ( $\text{CCl}_4$ ) 3128 (w), 2983 (m), 2859 (w), 2228 (w), 1841 (s), 1633 (s), 1446 (w); MS calc for  $\text{C}_{15}\text{H}_{12}\text{O}$  ( $\text{M}^+$ ) 208, found 208; HRMS calc for  $\text{C}_{15}\text{H}_{12}\text{O}$  ( $\text{M}^+$ ) 208.0888, found 208.0887.

#### Spectra of cyclopropenone **1**

$^1\text{H}$ .....	S4
$^{13}\text{C}$ .....	S5
IR.....	S6

<sup>2</sup> Semmelhack, M.F.; Neu, T.; Foubelo, F. *J.Org.Chem.*, **1994**, *59*, 5038 -47.





