SUPPORTING INFORMATION

The Synthesis of Benzo[c]selenophene and Derivatives Via New Routes

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Experimental Section:

1,3-Diethoxycarbonylbenzo[c]selenophene (10). To a stirred suspension of 2,2-dibromo-1,3-dihydrobenzo[c]selenophene (0.40 g, 1.16 mmol) in dry THF (20 mL) under N₂ was added 2 mL of 1.23 M LHMDs solution (THF) at 0 °C. The mixture was stirred at 0 °C for 30 min. It was then cooled to -78 °C followed by addition of 1.2 mL of 2.5M BuLi in hexane. The reaction mixture was maintained at the same temperature for another 30 min and ethyl chloroformate (0.25 g, 2.30 mmol) was added and the mixture was stirred for 3h. It was poured over crushed ice. The crude product was extracted into CH₂Cl₂ (3x15 mL). The organic phase was dried and concentrated. The oily residue was subject to column chromatography (SiO₂), using hexane:methylene chloride 1:1. Evaporation of the eluant and crystallization of the residue from acetonitrile gave **10** as yellow microcrystals. Yield: 0.22 g (58%), mp 135-136 °C. ¹H NMR (CDCl₃) δ 8.47 (dd, *J* = 7.1 3.1 Hz, 2H), 7.30 (dd, *J* = 7.1 3.1 Hz, 2H), 4.45 (q, *J* = 7.2 Hz, 4H), 1.34 (t, *J* = 7.1 Hz, 6H). ¹³C NMR δ 166.8, 151.1, 138.0, 127.1, 123.15, 61.7, 14.61. MS *m/e* (relative intensity): 326 (M⁺, 100), 322 (13.4), 281 (51), 270 (24), 253 (76), 226 (28), 208 (11). HRMS calcd for C₁₄H₁₄O₄⁸⁰Se: 326.005731, found 326.003500.

Benzo[c]selenophene-1,3-dicarboxaldehyde (11): To a solution of Benzo[c]selenophene-1,3-dinitrile (**6**)¹ (0.20 g, 0.87 mmol) in 30 ml of dry ether under nitrogen was added dropwise, 1.22 mL of a 1.5 M solution of DIBAL-H in toluene and the solution was heated at reflux for 24 h. After that time, the mixture was cooled, followed by careful addition of methanol (5 mL) and water (5 mL) successively. Then, over a period of 30 min, a small amount of HCl (1M) was added until all the precipitate was dissolved and two layers could be observed. The two layers were separated, the aqueous layer was washed with ether and the combined ether layer was washed successively with water, saturated NaHCO₃ solution and water. The organic phase was dried over sodium sulfate and the solvent was distilled to give crude **11**. An analytical sample of **11** was obtained after recrystallization from acetonitrile. Yield: 0.11 g (53%), mp 219-220 °C. ¹H NMR δ : 10.43 (s, 2H), 8.43 dd, *J* = 7.3, 3.3 Hz, 2H), 7.53 (dd, *J* = 7.2, 3.3 Hz, 2H). ¹³C NMR δ : 182.1, 140.9, 139.27, 126.6, 121.5. MS *m/e* (relative intensity): 238 (M⁺, 100), 209 (45), 167 (35), 149 (24). Anal. Calcd. For C₁₀H₆O₂Se: C, 50.65; H, 2.55. Found: C, 50.18, H, 2.51.

¹ Amaresh, R. R.; Lakshmikantham M. V.; Baldwin, J. W.; Cava, M. P.; Metzger R. M.; Rogers, R. D. *J. Org. Chem.* **2002**, *67*, 2453

1,3-Dihydro-5-nitrobenzo[c]selenophene (13): To a colorless solution of sodium selenide prepared from selenium (2 g, 25.33 mmol) and sodium borohydride (2 g, 52.90 mmol) in 20 ml water (pH = 9) at room temperature, was added dropwise, a solution of the 1,2-bis(bromomethyl)-5-nitrobenzene² (7.8 g, 25.33 mmol) in THF (150 mL). The reaction mixture was stirred for 5h. The mixture was poured into water (200 mL). Extraction with methylene chloride (3x30) and subsequent recrystallization of the residue from ethanol gave **13** (3.16 g, 55%) as pale yellow microcrystals. mp 132-133 °C. ¹H NMR (CDCl₃) δ : 8.1 (d, J = 1.8 Hz, 1H), 8.0 (dd, J = 10.8, 3 Hz, 1H), 7.35 (d J = 10.8 Hz, 1H), 4.35 (s, 4H). ¹³C NMR (CDCl₃): 149.5, 147.2, 143.9, 126.6, 122.1, 121.8, 29.2, 28.9. MS m/e (relative intensity): 229 (M⁺, 100), 221 (12), 182 (61). HRMS Calcd for C₈H₇NO₂Se: 228.9642. Found 228.9577.

1,3-Dihydro-2,2-dibromo-5-nitrobenzo[c]selenophene (14): A solution of bromine (8.8 mL, 1 mmol/mL) in chloroform was added dropwise with stirring to a solution of **13** (2.0 g, 8.77 mmol) in chloroform (25 mL). The resulting precipitate was collected by filtration to give **14** (3.4 g, 94%). mp 298 °C turns gray, 233 °C (dec). ¹H NMR (DMSO-d₆) δ : 8.38 (s 1H), 8.22(d, J = 7.1 Hz, 1H), 7.72 (d, J = 7.1 Hz, 1H), 5.30 (s, 4H). ¹³C NMR (DMSO-d₆) δ : 142.9, 145.2, 143.3, 130.6, 124.5, 122.0, 45.90. MS m/e 226.94 (M⁺ -2HBr, 100).

5-Nitrobenzo[c]selenophene 15:

Method A: To a suspension of **14** (0.50 g, 1.23 mmol) in 15 mL dry THF at 0 °C was added slowly LHMDS 12 M in THF (1 mL). The mixture was stirred at the same temperature for 30 min. The THF was then evaporated and the resulting oil was subject to column chromatography (SiO₂) using hexane:CH₂Cl₂ 1:1. Two fractions were obtained. The first fraction contained the dihydro derivative **13**. The second fraction contained the expected product **15**. A pure sample of **15** was obtained by recrystallization from nitromethane. Compound **15** was obtained as small yellow microcrystals. Yield 0.16g (55%). mp 112 °C (dec). ¹H NMR (CDCl₃) δ = 8.94 (d J = 2.8, 1H), 8.59 (d, J = 2.8, 1H), 8.55 (s, 1H), 7.72 (dd J = 7.2, 3.6 Hz, 1H), 7.56 (d, J = 7.2 Hz, 1H). ¹³C NMR (CDCl₃) δ = 147.9, 145.9, 134.3, 128.5, 126.9, 126, 123, 115.8. HREMS Calcd for C₈H₅NO₂⁸⁰Se: 226.9485. Found: 226.9507. Anal. Calcd for C₈H₅NO₂Se: C, 42.50; H, 2.23; N, 6.20. Found: C, 42.33; H, 2.21; N, 6.18.

Method B: To a solution of 1,3-Dihydro-5-nitrobenzo[c]selenophene **13** (0.20 g, 0.88 mmol) in CH₂Cl₂ (10 mL) was added (0.3 g, 0.93 mmol) of iodobenzenediacetate. The mixture was stirred for 2h at room temperature. The solution was concentrated by partial evaporation of the solvent. The product **15** (0.12 g, 60% yield, mp 112 °C, dec.) was separated from unreacted **13** by column chromatography (SiO₂) using CH₂Cl₂:Hexane 1:1. Increasing the reaction time or the use of 2 equivalents of did not lead to any changes in the yield of this reaction.

² Huang, Z.; Lakshmikantham M. V.; Cava, M. P. *J. Org. Chem.* **2000**, 65, 5413