

Palladium-Catalyzed Annulation of Arynes by 2-Halobenzaldehydes: Synthesis of Fluoren-9-ones

Xiaoxia Zhang and Richard C. Larock*

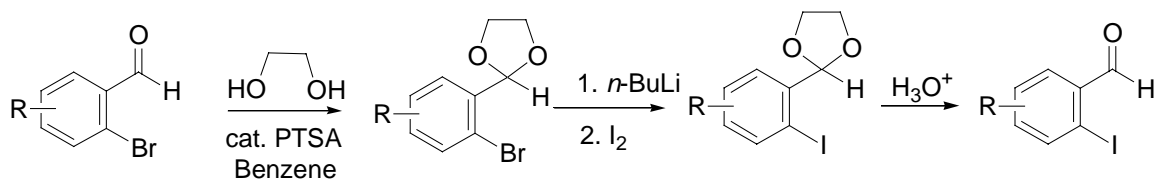
Department of Chemistry, Iowa State University, Ames, Iowa 50011

Supporting Information

General. The ^1H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz or 400 and 100 MHz respectively. All melting points are uncorrected. High resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV. All reagents were used directly as obtained commercially unless otherwise noted.

Synthesis of Starting Materials. Compounds **1**, **2**, **4** and **11** were purchased from Sigma-Aldrich Co. Compounds **5**,¹ **14**,² **17**³ and **19**⁴ were prepared according to literature procedures.

Compounds **7**, **9** and **12** were prepared from the respective commercially available 2-bromobenzaldehydes by the previously reported three-step procedure shown below.⁵ Compound **7** was obtained as a light yellow solid in a 75% overall yield.



The spectral properties were identical with those previously reported.⁵ Compound **9** was obtained as a white solid in an 80% overall yield. The spectral properties were identical with those previously reported.⁶

1-Iodo-2-naphthalenecarboxaldehyde (12). Compound **12** was obtained as a light yellow solid in a 60% overall yield: mp 106-107 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.57-7.60 (m, 2H), 7.70-7.73 (m, 2H), 7.78-7.81 (d, *J* = 8.7 Hz, 1H), 8.31-8.35 (m, 1H); ¹³C NMR (CDCl₃, 300 MHz) δ 124.96, 128.71, 128.83, 129.50, 129.94, 133.45, 134.03, 134.61, 137.10, 197.72; IR (CHCl₃) 1680 cm⁻¹; HRMS *m/z* 281.9545 (calcd for C₁₁H₇IO, 281.9542).

General Procedure for the Palladium-Catalyzed Synthesis of Fluoren-9-ones.

The 2-iodobenzaldehyde (0.30 mmol), the 2-(trimethylsilyl)aryl triflate (1.50 mmol), CsF (1.50 mmol), Pd(dba)₂ (0.015 mmol), P(*o*-tolyl)₃ (0.015 mmol), 2 mL of toluene, and 2 mL of MeCN were placed in a 4 dram vial and the vial was sealed. The reaction mixture was stirred first at room temperature for 1 min and then heated to 110 °C for 12 h. The mixture was allowed to cool to room temperature (CAUTION: OPENING THE VIAL AT HIGH TEMPERATURE CAN BE DANGEROUS!), diluted with diethyl ether, washed with brine, dried over anhydrous MgSO₄, and concentrated under reduced pressure. The product was isolated by flash chromatography on silica gel.

Compounds **3**,⁷ **13**,⁸ **18**,⁹ **20**,⁹ and **21**⁹ were obtained after flash chromatography, and their spectral properties are identical with these previously reported.

1-Fluoro-9H-fluoren-9-one (6). The indicated compound was obtained as a yellow solid in an 82% yield. The reaction mixture was chromatographed using 10:1 hexane/EtOAc: mp 117-119 °C; ¹H NMR (CDCl₃, 300 MHz) δ 6.89-6.95 (t, *J* = 8.4 Hz, 1H), 7.29-7.35 (m, 2H), 7.43-7.53 (m, 3H), 7.65-7.67 (d, *J* = 7.5 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 116.61, 116.65, 117.59, 117.87, 120.12, 120.29, 120.88, 124.69, 129.90, 134.19, 134.86, 137.23, 137.34, 143.59, 143.63, 146.56, 146.61, 157.79, 161.29,

190.36 (extra peaks due to F splitting); IR (CHCl₃) 2923, 1716, 1600, 1471 cm⁻¹; HRMS *m/z* 198.0485 (calcd for C₁₃H₇FO, 198.0481).

9H-Fluoreno[2,3-*d*][1,3]dioxol-9-one (8). The reaction mixture was chromatographed using 10:1 hexane/EtOAc and the indicated compound was obtained as a yellow solid in a 56% yield: mp 145-147 °C; ¹H NMR (CDCl₃, 400 MHz) δ 6.05 (s, 2H), 6.95 (s, 1H), 7.09 (s, 1H), 7.18-7.22 (m, 1H), 7.31-7.33 (d, *J* = 7.6 Hz, 1H), 7.39-7.43 (m, 1H), 7.53-7.55 (d, *J* = 7.6 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 101.76, 102.27, 105.18, 119.31, 123.81, 128.39, 128.71, 134.38, 134.76, 141.74, 143.67, 148.50, 153.37, 192.45; IR (CHCl₃) 1709, 1593, 1477, 1458 cm⁻¹; HRMS *m/z* 224.0476 (calcd for C₁₄H₈O₃, 224.0473).

10H-Fluoreno[1,2-*d*][1,3]dioxol-10-one (10). The reaction mixture was chromatographed using 20:1 hexane/EtOAc and the indicated compound was obtained as a yellow solid in a 72% yield (from the aryl iodide) or 50 % (from the aryl bromide): mp 161-163 °C; ¹H NMR (CDCl₃, 400 MHz) δ 6.12 (s, 2H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 7.24-7.26 (m, 1H), 7.45-7.46 (m, 2H), 7.65 (d, *J* = 7.6 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 103.05, 111.96, 113.60, 115.44, 119.94, 124.41, 128.21, 134.24, 134.62, 136.89, 144.60, 145.00, 150.44, 190.92; IR (CHCl₃) 1710, 1468, 1250 cm⁻¹; HRMS *m/z* 224.0478 (calcd for C₁₄H₈O₃, 224.0473).

2,3-Dimethyl-9H-fluoren-9-one (15). The reaction mixture was chromatographed using 20:1 hexane/EtOAc and the indicated compound was obtained as a yellow solid in a 71% yield: mp 88-89 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.22-7.25 (m, 2H), 7.41-7.43 (m, 3H), 7.59 (d, *J* = 7.6 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 19.95, 20.77, 119.84, 121.82, 124.11, 125.59, 128.55, 132.34, 134.41, 134.64, 137.62, 142.55,

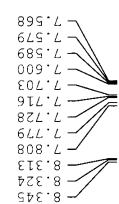
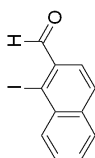
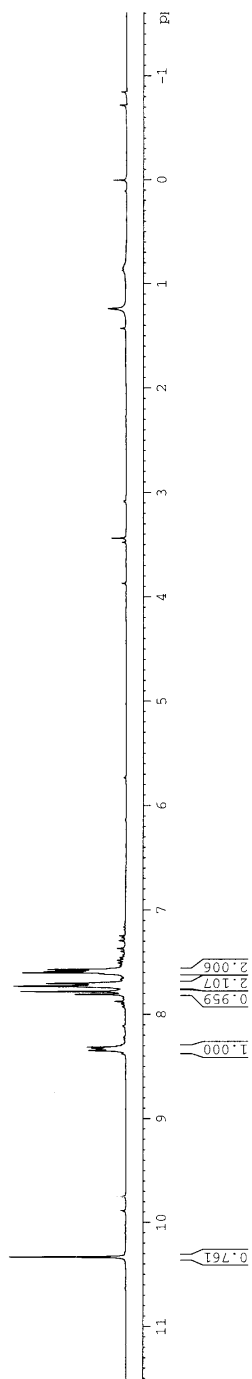
144.19, 144.65, 194.12 IR (CHCl₃) 2922, 1707, 1601, 1452 cm⁻¹; HRMS *m/z* 208.0891 (calcd for C₁₅H₁₂O, 208.0888).

1-Fluoro-6,7-dimethyl-9H-fluoren-9-one (16). The reaction mixture was chromatographed using 20:1 hexane/EtOAc and the indicated compound was obtained as a yellow solid in a 73% yield: mp 165-167 °C; ¹H NMR (CDCl₃, 400 MHz) δ 2.24 (s, 3H), 2.29 (s, 3H), 6.82-6.87 (t, *J* = 8.8 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.21 (s, 1H), 7.36-7.39 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 19.99, 20.73, 115.92, 115.95, 116.88, 117.09, 120.20, 120.32, 122.07, 125.60, 132.10, 136.70, 136.78, 138.39, 141.48, 141.51, 144.24, 146.62, 146.66, 157.91, 160.52, 190.35 (extra peaks are due to F-splitting); IR (CHCl₃) 2920, 1713, 1618, 1454 cm⁻¹; HRMS *m/z* 226.0798 (calcd for C₁₅H₁₁FO, 226.0794).

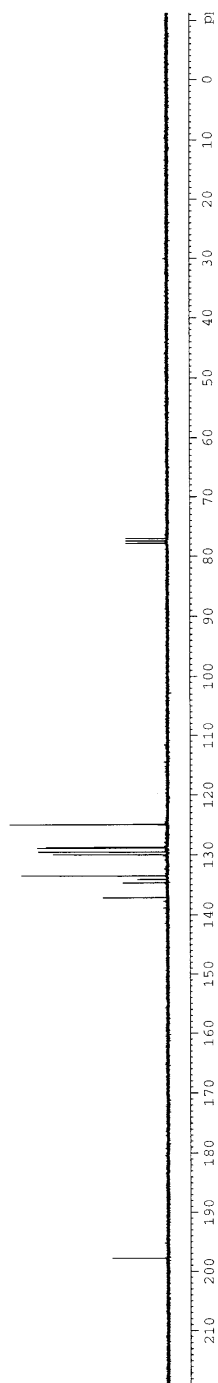
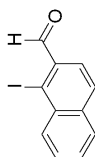
References

- (1) Bridges, A. J.; Lee, A.; Maduakor, E. C.; Schwartz, C. E. *Tetrahedron Lett.* **1992**, 33, 7499.
- (2) Yoshida, H.; Sugiura, S.; Kunai, A. *Org. Lett.* **2002**, 4, 2767.
- (3) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, 121, 5827.
- (4) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, 123, 7280.
- (5) Bogucki, D. E.; Charlton, J. L. *J. Org. Chem.* **1995**, 60, 588.
- (6) Mattson, R. J.; Sloan, C. P.; Lockhart, C. C.; Catt, J. D.; Gao, Q.; Huang, S. *J. Org. Chem.* **1999**, 64, 8004.
- (7) This compound was identified by comparing the ¹H and ¹³C NMR spectra and melting point with an authentic sample obtained from Aldrich Chemical Co., Inc.

- (8) Campo M. A.; Larock, R. C. *Org. Lett.* **2000**, 2, 3675.
- (9) Campo M. A.; Larock, R. C. *J. Org. Chem.* **2002**, 67, 5616.



10.332



Year	Average number of children per woman
1960	2.10
1965	2.05
1970	2.00
1975	1.95
1980	1.90
1985	1.85
1990	1.80
1995	1.75
2000	1.70
2005	1.65
2010	1.60

197.718

