Supporting Information

Cyclization of Aryllithiums Tethered to Methylenecycloalkanes: Stereoselective Synthesis of 4a-Substituted *cis*-Hexahydrofluorenes

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2-(*o*-Bromobenzyl)cyclohexanone. Following the procedure described above, 2.50 g (25.5 mmol) of cyclohexanone gave 4.22 g (62 %) of the previously reported¹⁶ title ketone as a colorless oil: ¹H NMR (CDCl₃) δ 1.45 – 1.48 (m, 1 H), 1.63 – 1.70 (m, 2 H), 1.87 – 1.90 (m, 1 H), 2.05 – 2.11 (m, 2 H), 2.36 – 2.46 (m, 2 H), 2.57 (dd, *J* = 13.8 Hz, *J* = 8.0 Hz, 1 H), 2.73 – 2.76 (m, 1 H), 3.36 (dd, *J* = 13.8, *J* = 5.2 Hz, 1 H), 7.07 (td, *J* = 8.0 Hz, *J* = 2.0 Hz, 1 H), 7.22 – 7.30 (m, 2 H), 7.54 (m, 1 H).

2-(*o*-Bromobenzyl)cycloheptanone. Following the procedure described above, 2.50 g (22.3 mmol) of cycloheptanone gave 3.75 g (60 %) of the previously reported² title ketone as a colorless oil: ¹H NMR (CDCl₃) δ 1.32 – 1.41 (m, 3 H), 1.62 – 1.85 (m, 5 H), 2.46 – 2.49 (m, 2 H), 2.66 (dd, *J* = 13.7 Hz, *J* = 7.8 Hz, 1 H), 3.00 (m, 1 H), 3.16 (dd, *J* = 13.7 Hz, *J* = 6.2 Hz, 1 H), 7.03 (td, *J* = 8.0 Hz, *J* = 3.2 Hz, 1 H), 7.19 – 7.20 (m, 2 H), 7.50 (d, *J* = 8.0 Hz, 1 H).

2-(*o*-Bromobenzyl)-1-methylenecyclohexane (2). Following the procedure described for the preparation of **1**, 5.10 g (19.0 mmol) of 2-(*o*-bromobenzyl)cyclohexanone afforded 3.70 g (73 %) of the known¹⁷ title compound as a colorless oil: ¹H NMR (CDCl₃) δ 1.27 – 1.69 (m, 6 H), 2.09 – 2.13 (m, 1 H), 2.33 – 2.46 (m, 2 H), 2.70 (dd, *J* = 13.5 Hz, *J* = 9.0 Hz, 1 H), 3.06 (dd, *J* = 13.5 Hz, *J* = 5.5 Hz, 1 H), 4.60 (apparent s, 1 H), 4.70 (apparent s, 1 H), 7.03 – 7.07 (td, *J* = 7.8 Hz, *J* = 1.8 Hz, 1 H), 7.15 – 7.25 (2 H, m), 7.53 (d, *J* = 7.9 Hz, 1 H), ¹³C NMR (CDCl₃) δ 24.67, 28.63, 32.74, 35.34, 38.87, 42.88, 105.97, 125.00, 127.00, 127.40, 131.34, 132.81, 140.54, 152.21.

2-(*o*-Bromobenzyl)-1-methylenecycloheptane (3). Following the procedure described for the preparation of **1**, 3.75 g (13.3 mmol) of 2-(*o*-bromobenzyl)cycloheptanone afforded 2.73 g (74 %) of the known² title compound as a colorless oil: ¹H NMR (CDCl₃) δ 1.23 – 1.34 (m, 4 H), 1.72 – 1.89 (m, 4 H), 2.10 – 2.16 (m, 1 H), 2.28 – 2.30 (m, 1 H), 2.66 – 2.81 (m, 3 H), 4.51 (apparent s, 1 H), 4.76 (apparent s, 1 H), 7.04 – 7.20 (m, 3 H), 7.52 (dd, *J* = 7.3 Hz, *J* = 0.6 Hz, 1 H); ¹³C NMR (CDCl₃) δ 26.44, 30.68, 31.54, 33.29, 33.53, 42.97, 46.32, 112.52, 125.01, 126.80, 127.41, 131.76, 132.66, 140.41, 153.62.

2-Benzyl-1-methylenecyclohexane (5). Following the procedure described for the preparation of **4**, 382 mg (1.44 mmol) of 2-(*o*-bromobenzyl)-1-methylenecyclohexane (**2**) was converted to 260 mg (98 %) of the known² title hydrocarbon: ¹H NMR (CDCl₃) δ 1.22 – 1.28 (m, 1 H), 1.42 – 1.60 (m, 2 H), 1.73 – 1.79 (m, 3 H), 2.1 – 2.18 (m, 1 H), 2.38 – 2.45 (m, 2 H), 2.59 (dd, *J* = 13.4 Hz, *J* = 9.4 Hz, 1 H), 3.05 – 3.1 (dd, *J* = 13.4 Hz, *J* = 5.4 Hz, 1 H), 4.70 (apparent s, 1 H), 4.78 (apparent s, 1 H), 7.23 – 7.34 (m, 5 H).

2-Benzyl-1-methylenecycloheptane (6). Following the procedure described for the preparation of **4**, 279 mg (1.0 mmol) of 2-(*o*-bromobenzyl)-1-methylenecycloheptane (**3**) was converted to 195 mg (98 %) of the known² title hydrocarbon: ¹H NMR (CDCl₃) δ 1.34 – 1.54 (m, 5 H), 1.83 – 2.02 (m, 4 H), 2.24 – 2.27 (m, 1 H), 2.39 – 2.42 (m, 1 H), 2.73 – 2.82 (m, 2 H), 4.79 (apparent s, 1 H), 4.95 (apparent s, 1 H), 7.31 – 7.46 (m, 5 H).

References and Notes (continued)

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