

Supplementary Material
for
Preparation of Benzocycloheptene Derivatives from
Zirconacyclopentadienes

Tamotsu Takahashi,* Wen-Hua Sun, Zheng Duan and Baojian Shen

*Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University, and CREST, Science and Technology Corporation (JST),
Sapporo 060-0811, Japan*

Typical procedure for benzocycloheptene: To a solution of zirconacyclopentadiene (1.0 mmol) in 5 ml THF, CuCl (2.0 mmol, 198 mg) and DMPU (2.5 mmol, 0.30 mL) and 1.0 eq 2-iodobenzyl halide were added. The reaction mixture was stirred at 50 °C for one hour. After cooled to room temperature, the reaction mixture was quenched with 3N HCl and extracted with ether. Combined organic extracts were washed with aqueous NaHCO₃, water, and dried (MgSO₄). Concentrated under reduced pressure, the residual compounds were chromatographed on silica gel with hexane as eluting agent to afford the product.

5,6,7,8-Tetraethyl-9H-benzocycloheptene (3a): GC yield 89%, isolated 70% colorless liquid. ¹H NMR (CDCl₃, Me₄Si) δ 0.70 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H), 1.05 (t, *J* = 7.5 Hz, 3H), 1.06 (t, *J* = 7.5 Hz, 3H), 2.02 - 2.16 (m, 3H), 2.17 - 2.24 (m, 1H), 2.30 - 2.36 (m, 1H), 2.54 - 2.60 (m, 1H), 2.61 - 2.69 (m, 1H), 2.70 - 2.78 (m, 1H), 2.82 (dd, *J* = 38.9 Hz and *J* = 11.9 Hz, 2H), 7.07 - 7.10 (m, 1H), 7.11 - 7.15 (m, 2H), 7.38 - 7.40 (m, 1H); ¹³C NMR (CDCl₃, Me₄Si) δ 13.72, 14.21, 15.10, 15.44, 21.95, 23.53, 25.93, 26.84, 38.78, 124.93, 125.10, 126.21, 126.26, 131.64, 138.23, 138.30, 138.73, 141.01, 142.81. HRMS Calcd. for C₁₉H₂₆: 254.2033; Found: 254.2037.

5,6,7,8-Tetrapropyl-9H-benzocycloheptene (3b): GC yield 92%, isolated 78% colorless liquid. ^1H NMR (CDCl_3 , Me_4Si) δ 0.52 (t, $J = 7.4$ Hz, 3H), 0.84 - 0.90 (m, 6H), 0.95 (t, $J = 7.4$ Hz, 3H), 1.10 - 1.19 (m, 1H), 1.28 - 1.42 (m, 4H), 1.47 - 1.58 (m, 3H), 2.01 - 2.12 (m, 3H), 2.13 - 2.20 (m, 1H), 2.27 - 2.38 (m, 1H), 2.46 - 2.53 (m, 1H), 2.60 - 2.70 (m, 2H), 2.81 (dd, $J = 38.5$ Hz and $J = 10.7$ Hz, 2H), 7.04 - 7.07 (m, 1H), 7.10 - 7.14 (m, 2H), 7.35 - 7.38 (m, 1H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.49, 13.98, 14.39, 14.53, 21.90, 22.50, 23.51, 23.86, 30.75, 32.86, 34.68, 36.02, 39.15, 124.86, 125.01, 126.12, 126.29, 131.24, 137.07, 137.09, 139.07, 139.98, 142.53. HRMS Calcd. for $\text{C}_{23}\text{H}_{34}$: 310.2659; Found: 310.2652.

5,6,7,8-Tetrabutyl-9H-benzocycloheptene (3c): GC yield 93%, isolated 74% colorless liquid. ^1H NMR (CDCl_3 , Me_4Si) δ 0.70 (t, $J = 7.1$ Hz, 3H), 0.84 - 0.95 (m, 13H), 1.02 - 1.09 (m, 1H), 1.21 - 1.50 (m, 11H), 1.98 - 2.34 (m, 5H), 2.49 - 2.72 (m, 3H), 2.80 (dd, $J = 28.2$ and $J = 11.8$ Hz, 2H), 7.04 - 7.07 (m, 1H), 7.10 - 7.13 (m, 2H), 7.36 - 7.38 (m, 1H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.92, 13.95, 14.07, 14.11, 22.29, 22.67, 23.10, 23.17, 28.56, 30.42, 31.02, 31.55, 32.41, 32.61, 33.01, 33.71, 39.14, 124.85, 124.99, 126.09, 126.24, 131.15, 136.98, 137.04, 139.13, 139.95, 142.49. HRMS Calcd. for $\text{C}_{27}\text{H}_{42}$: 366.3284; Found: 366.3286.

6,7,8,9,11-Pentahydro-5,10-diethyl-dibenzo[a,d]cycloheptene (3d): GC yield 88%, isolated 71% colorless liquid. ^1H NMR (CDCl_3 , Me_4Si) δ 1.01 - 1.05 (m, 6H), 1.55 - 1.63 (m, 2H), 1.70 - 1.75 (m, 2H), 1.80 - 1.84 (m, 1H), 2.06 - 2.12 (m, 1H), 2.19 - 2.26 (m, 2H), 2.47 - 2.51 (m, 1H), 2.63 - 2.67 (m, 1H), 2.72 - 2.79 (m, 2H), 2.86 - 2.93 (m, 2H), 7.08 - 7.10 (m, 1H), 7.13 - 7.17 (m, 2H), 7.43 - 7.46 (m, 1H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.49, 15.16, 25.89, 26.34, 26.37, 26.82, 28.40, 30.24, 39.05, 125.00, 125.21, 126.26, 126.40, 129.03, 135.99, 136.44, 137.96, 139.00, 141.61. HRMS Calcd. for $\text{C}_{19}\text{H}_{24}$: 252.1877; Found: 252.1885.

9,10-Dibutyl-11H-dibenzo[a,c]cycloheptene (3e): GC yield 50%, isolated 41% colorless liquid. ^1H NMR (CDCl_3 , Me_4Si) δ 0.89 (t, $J = 7.1$ Hz, 6H), 1.26 - 1.45 (m, 8H), 2.67 - 2.89 (m, 4H), 3.51 - 3.58 (m, 2H), 7.07 - 7.36 (m, 8H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.98, 23.07, 32.61, 34.19, 41.03, 125.58, 125.77, 126.72, 126.89, 137.64,

138.11, 142.08. HRMS Calcd. for C₂₃H₂₈: 304.2191; Found: 304.2191.

6,7,9,10,12-Pentahydro-5,11-Diethyl-8-benzyl-azepin[4.5.b]-benzo-[e]-cycloheptene (3f): GC yield 54%, isolated 29% colorless liquid. ¹H NMR (CDCl₃, Me₄Si) δ 0.97 (t, *J* = 7.4 Hz, 3H), 1.06 (t, *J* = 7.5 Hz, 3H), 2.10 - 3.00 (m, 14H), 3.54 (d, *J* = 13.3 Hz, 1H), 3.68 (d, *J* = 13.3 Hz, 1H), 7.10 - 7.45 (m, 9H); ¹³C NMR (CDCl₃, Me₄Si) δ 13.30, 14.48, 26.00, 26.21, 29.96, 32.17, 39.04, 55.62, 56.80, 62.87, 125.03, 125.37, 126.23, 126.61, 126.85, 128.19 (2C), 128.98 (2C), 131.62, 137.51, 137.58, 138.16, 139.35, 140.29, 141.82. HRMS Calcd. for C₂₆H₃₁: 357.2456; Found: 357.2463.

1,2,3,4-tetramethyl-5,6,7,8-Tetraethyl-9H-benzocycloheptene (3g): Isolated 22% colorless liquid. ¹H NMR (CDCl₃, Me₄Si) δ 0.67 (t, *J* = 7.5 Hz, 3H), 0.85 (t, *J* = 7.5 Hz, 3H), 1.01 (t, *J* = 7.5 Hz, 3H), 1.09 (t, *J* = 7.5 Hz, 3H), 1.90 - 2.03 (m, 2H), 2.10 - 2.36 (m, 15H) [including four siglets as 2.15 (s, 3H), 2.17 (s, 3H), 2.22 (s, 3H), 2.36 (s, 3H)], 2.48 - 2.56 (m, 2H), 2.75 (d, *J* = 12.4 Hz, 1H), 2.79 - 2.88 (m, 1H), 3.23 (d, *J* = 12.4 Hz, 1H); ¹³C NMR (CDCl₃, Me₄Si) δ 13.73 (2CH₃), 14.72, 15.63, 16.31, 16.55, 16.89, 19.63, 20.71, 22.43, 25.44, 28.50, 33.77, 126.74, 130.56, 131.92, 132.00, 132.41, 137.55, 140.25, 140.70, 140.98, 142.31. HRMS Calcd. for C₂₃H₃₄: 310.2659; Found: 310.2667.

Typical procedure for benzocycloheptenone: To a solution of zirconacyclopentadiene (1.0 mmol) in 5 ml THF, CuCl (2.0 mmol, 198 mg) and DMPU (2.5 mmol, 0.30 mL) and 1.0 eq 2-iodobenzoyl halide were added. The reaction mixture was stirred at 50 °C for one hour. After cooled to room temperature, the reaction mixture was quenched with 3N HCl and extracted with ether. Combined organic extracts were washed with aqueous NaHCO₃, water, and dried (MgSO₄). Concentrated under reduced pressure, the residual compounds were chromatographed on silica gel with hexane as eluting agent to afford the product.

2,3,4,5-Tetraethyl-benzocycloheptenone (6a): GC yield 62%, isolated 49% colorless liquid. ¹H NMR (CDCl₃, Me₄Si) δ 0.92 (t, *J* = 7.4 Hz, 3H), 0.97 - 1.04 (m, 9H), 2.39 (q, *J* = 7.6 Hz, 2H), 2.45 - 2.51 (m, 4H), 2.67 (q, *J* = 7.6 Hz, 2H), 7.30 -

7.39 (m, 2H), 7.42 - 7.46 (m, 1H), 7.57 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.61, 14.33, 14.69, 14.86, 23.67, 24.07, 24.26, 27.09, 124.72, 126.48, 127.28, 129.70, 136.86, 137.02, 138.23, 142.26, 143.15, 144.41, 201.71. HRMS Calcd. for $\text{C}_{19}\text{H}_{24}\text{O}$: 268.1826; Found: 268.1819.

2,3,4,5-Tetrapropyl-benzocycloheptenone (6b): GC yield 46%, isolated 38% colorless liquid. ^1H NMR (CDCl_3 , Me_4Si) δ 0.72 (t, $J = 7.3$ Hz, 3H), 0.82 - 0.91 (m, 9H), 1.22 - 1.46 (m, 8H), 2.32 (t, $J = 7.6$ Hz, 2H), 2.41 (t, $J = 7.3$ Hz, 4H), 2.59 (t, $J = 8.0$ Hz, 2H), 7.30 - 7.35 (m, 2H), 7.40 - 7.44 (m, 1H), 7.52 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.87, 14.11, 14.17, 14.21, 22.15, 22.95, 23.26, 23.54, 32.51, 33.05, 33.16, 36.24, 124.69, 126.47, 127.08, 129.57, 135.57, 137.23, 137.37, 141.59, 142.15, 144.22, 201.96. HRMS Calcd. for $\text{C}_{23}\text{H}_{32}\text{O}$: 324.2452; Found: 324.2458.

















