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Equatorial Preference in the C-H Activation of Cycloalkanes

GaCl₃-Catalyzed Aromatic Alkylation Reaction

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JUN 30 2003

Journal of Organic Chemistry

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Supporting Information

Reaction of 1-Methylnaphthalene 6 and Bicyclo[4.4.0]decane 1. (Decahydronaphthalenyl)-1-methylnaphthalenes: GC analysis indicated the presence of 6 major isomers in a 3:2:2:1:1:1 ratio. Anal. Calcd. for C₂₁H₂₆: C, 90.59; H, 9.41%. Found: C, 90.51; H, 9.52%. ¹H-NMR (400 MHz, CDCl₃) δ 0.70-0.84 (m), 0.94-1.38 (m), 1.42-1.78 (m), 1.80-1.89 (m), 1.92-2.01 (m), 2.26-2.43 (m), 2.61-2.82 (m), 2.66 (s), 2.67 (s), 2.678 (s), 2.683 (s), 7.15 (s), 7.20-7.46 (m), 7.48 (s), 7.50-7.58 (m), 7.61-7.72 (m), 7.74-7.80 (m), 7.89-7.95 (m). ¹³C-NMR (100 MHz, CDCl₃) δ 19.4, 19.55, 19.58, 19.62, 26.8, 26.9, 31.4, 31.5, 34.0, 34.1, 34.3, 34.37, 34.40, 34.5, 35.86, 35.89, 36.0, 41.7, 41.8, 41.9, 43.05, 43.08, 43.40, 43.42, 43.52, 43.54, 44.0, 44.5, 44.6, 44.7, 45.1, 47.9, 48.0, 48.1, 51.2, 51.3, 51.7, 120.8, 122.8, 123.7, 123.77, 123.84, 124.49, 124.55, 124.6, 124.7, 125.0, 125.29, 125.33, 125.36, 125.44, 125.55, 125.60, 125.8, 125.9, 125.94,

125.95, 126.0, 126.4, 126.9, 127.3, 128.0, 128.1, 128.3, 131.1, 131.18, 131.23, 132.05, 132.08, 132.55, 132.60, 133.5, 133.58, 133.60, 133.67, 133.75, 133.77, 133.81, 143.4, 143.7, 144.1, 144.61, 144.62, 144.9, 145.0. IR (neat) 3049, 2917, 2849, 1628, 1601, 1507, 1446, 871, 825, 745 cm^{-1} . MS (EI, 70 eV) m/z (%) 278 (100, M^+), 168 (36), 156 (37). HRMS (EI, 70 eV) Calcd. for $\text{C}_{21}\text{H}_{26}$: 278.2033. Found: 278.2027 (M^+).

Bis(decahydronaphthalenyl)-1-methylnaphthalenes: ^1H -NMR (400 MHz, CDCl_3) δ 0.70-0.83 (m), 0.94-0.38 (m), 1.40-1.88 (m), 1.90-1.99 (m), 2.23-2.39 (m), 2.64 (s), 2.66 (s), 2.66-2.79 (m), 7.07 (s), 7.11 (s), 7.13 (s), 7.17 (s), 7.22-7.39 (m), 7.43 (br s), 7.48-7.53 (m), 7.55-7.58 (m), 7.63 (s), 7.70 (d, $J = 8.4$ Hz), 7.84 (d, $J = 8.8$ Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 19.5, 19.60, 19.64, 19.7, 26.8, 26.9, 31.5, 34.0, 34.2, 34.4, 34.57, 34.62, 35.88, 35.90, 41.75, 41.79, 42.0, 43.1, 43.46, 43.54, 43.6, 43.85, 43.94, 44.0, 44.5, 44.6, 45.1, 48.0, 48.1, 51.2, 51.3, 51.6, 120.6, 120.7, 122.4, 122.5, 123.6, 123.7, 124.6, 124.7, 124.9, 125.0, 125.36, 125.39, 126.0, 126.1, 126.8, 127.8, 127.9, 129.8, 129.9, 131.26, 131.28, 132.25, 132.33, 133.25, 133.34, 133.5, 133.6, 133.9, 134.0, 142.5, 142.8, 143.4, 143.7, 143.8, 144.0, 144.1, 144.55, 144.59, 144.61. IR (neat) 2917, 2849, 1630, 1607, 1508, 1446, 1371, 907, 875, 816, 758, 734 cm^{-1} . MS (EI, 70 eV) m/z (%) 414 (100, M^+), 137 (10), 95 (15), 81 (21). HRMS (EI, 70 eV) Calcd. for $\text{C}_{31}\text{H}_{42}$: 414.3284. Found: 414.3288 (M^+).

3-(5,6,7,8-Tetrahydro-2-naphthyl)-1-methylnaphthalene by the Partial Dehydrogenation of Decahydronaphthylated 1-Methylnaphthalene with DDQ. Under an argon atmosphere, DDQ (161 mg, 0.7 mmol) was added to a mixture of decahydronaphthylated 1-methylnaphthalenes (197 mg, 0.7 mmol, 6 isomers in a 3:2:2:1:1:1 ratio by GC) in dry toluene (7.1 mL), and the mixture was heated at reflux for 1 h. After cooled to room temperature, saturated aqueous NaHCO_3 was added, and the insoluble materials were removed by passing through celite. The organic layer was separated, washed with water, and dried over MgSO_4 . Solvents were removed *in vacuo*, and the residue was purified by flash column chromatography (silica gel, hexane) and GPC. The starting materials (136 mg, 69%) were recovered, and a

mixture of 3 isomers of (5,6,7,8-tetrahydro-2-naphthyl)-1-methylnaphthalenes (7 : 2.5 : 1 ratio by ^1H -NMR) was obtained (13 mg, 7%). A pure sample of 3-(5,6,7,8-tetrahydro-2-naphthyl)-1-methylnaphthalene **15** was obtained by GPC (CHCl_3) (8 mg, 4%). ^1H -NMR (400MHz, CDCl_3) δ 1.85 (4H, quint, $J = 3.2$ Hz), 2.75 (3H, s), 2.83 (2H, br s), 2.87 (2H, br s), 7.17 (1H, d, $J = 7.6$ Hz), 7.43 (1H, s), 7.45 (1H, d, $J = 8.0$ Hz), 7.48-7.51 (2H, m), 7.58 (1H, s), 7.87 (1H, s), 7.87-7.89 (1H, m), 7.98-8.00 (1H, m). ^{13}C -NMR (100MHz, CDCl_3) δ 19.7, 23.4, 29.3, 29.7, 123.7, 123.8, 124.4, 125.4, 125.8, 126.2, 127.8, 128.6, 129.5, 131.5, 133.8, 134.5, 136.3, 137.4, 138.1, 138.2. MS (EI, 70eV) m/z (%) 272 (100, M^+), 257 (7), 244 (17), 229 (11), 215 (8). HRMS (EI, 70eV) Calcd. for $\text{C}_{21}\text{H}_{20}$: 272.1564. Found: 272.1569 (M^+).

NOE

Reaction of 1,2-Dimethylnaphthalene **8** and Bicyclo[4.4.0]decane **1**.

(Decahydronaphthalenyl)-1,2-dimethylnaphthalenes: GC analysis indicated the presence of 4 major isomers in a 3:3:1:1 ratio. Anal. Calcd. for $\text{C}_{22}\text{H}_{28}$: C, 90.35; H, 9.65%. Found: C, 89.29; H, 10.10%. ^1H -NMR (400 MHz, CDCl_3) δ 0.70-0.84 (m), 0.96-1.38 (m), 1.42-1.79 (m), 1.79-1.88 (m), 1.92-2.00 (m), 2.27-2.44 (m), 2.45 (s), 2.46 (s), 2.56 (s), 2.58 (s), 2.59-2.80 (m), 7.21 (d, $J = 8.4$ Hz), 7.24 (d, $J = 8.4$ Hz), 7.29 (dd, $J = 6.8, 1.7$ Hz), 7.31 (dd, $J = 6.8, 1.8$ Hz), 7.36 (dd, $J = 8.8, 1.8$ Hz), 7.50-7.58 (m), 7.70 (d, $J = 8.4$ Hz), 7.72 (br s), 7.79 (d, $J = 1.2$ Hz), 7.94 (d, $J = 8.4$ Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 14.59, 14.64, 20.7, 20.9, 26.8, 26.9, 31.4, 31.5, 34.0, 34.1, 34.2, 34.4, 34.55, 34.57, 34.64, 35.8, 36.0, 41.6, 41.7, 42.0, 43.1, 43.40, 43.44, 43.5, 43.6, 43.9, 44.3, 45.2, 48.05, 48.10, 51.0, 51.8, 120.5, 123.4, 124.1, 124.4, 124.9, 123.0, 125.1, 125.16, 125.23, 125.3, 125.8, 126.4, 126.9, 127.9, 128.0, 128.1, 128.2, 128.8, 129.8, 130.0,

130.3, 130.5, 130.65, 130.69, 130.76, 130.80, 131.3, 131.4, 131.89, 131.92, 132.3, 132.4, 132.5, 132.75, 132.80, 142.2, 143.4, 143.6, 144.8. IR (neat) 3044, 2917, 2849, 1627, 1603, 1505, 1446, 1381, 885, 835, 816, 800 cm^{-1} . MS (EI, 70 eV) m/z (%) 292 (100, M^+), 195 (11), 182 (30), 170 (25), 156 (16). HRMS (EI, 70 eV) Calcd. for $\text{C}_{22}\text{H}_{28}$: 292.2190. Found: 292.2185 (M^+).

Bis(decahydronaphthalenyl)-1,2-dimethylnaphthalenes: ^1H -NMR (400 MHz, CDCl_3) δ 0.68-0.83 (m), 0.94-1.39 (m), 1.42-2.05 (m), 2.24-2.40 (m), 2.41 (s), 2.45 (s), 2.46 (s), 2.47 (s), 2.54 (s), 2.55 (s), 2.58 (s), 2.60 (s), 2.66-2.80 (m), 2.94 (br t, $J = 12.8$ Hz), 3.28-3.42 (m), 7.12 (s), 7.16 (s), 7.20 (br s), 7.27-7.38 (m), 7.46-7.64 (m), 7.67 (br s), 7.75 (br s), 7.82 (d, $J = 7.2$ Hz), 7.85 (br s), 7.90 (br d, $J = 8.4$ Hz), 7.97 (d, $J = 8.6$ Hz), 8.00 (d, $J = 9.0$ Hz), 8.04 (d, $J = 8.8$ Hz).

^{13}C -NMR (100 MHz, CDCl_3) δ 14.66, 14.69, 15.2, 15.4, 15.7, 15.8, 19.5, 20.9, 21.0, 21.2, 21.3, 26.8, 26.9, 30.9, 31.0, 31.1, 31.4, 34.0, 34.2, 34.4, 34.5, 34.55, 34.58, 34.7, 35.9, 36.0, 36.4, 38.8, 38.9, 39.1, 39.4, 41.4, 41.50, 41.54, 41.6, 41.7, 42.0, 42.1, 43.0, 43.36, 43.40, 43.46, 43.54, 43.6, 43.7, 43.8, 43.9, 43.9, 44.3, 44.5, 44.6, 44.98, 45.02, 45.3, 45.5, 48.06, 48.13, 48.5, 48.7, 51.4, 51.6, 52.1, 118.4, 120.3, 120.45, 120.51, 120.6, 121.1, 121.3, 121.6, 121.7, 121.8, 121.9, 122.5, 123.2, 123.3, 123.4, 123.6, 124.0, 124.2, 124.3, 124.4, 124.6, 124.7, 124.8, 125.0, 125.1, 125.2, 125.3, 125.4, 126.00, 126.04, 126.1, 127.6, 127.7, 127.9, 128.2, 128.3, 128.49, 128.52, 128.6, 130.0, 131.0, 131.3, 131.5, 131.7, 132.2, 132.4, 133.2, 140.1, 140.2, 140.4, 140.5, 142.9, 143.1, 143.4, 143.8, 144.1, 144.4, 144.6. IR (neat) 2916, 2845, 1604, 1509, 1446, 1382, 1347, 1215, 907, 817, 759, 734 cm^{-1} . MS (EI, 70 eV) m/z (%) 428 (100, M^+), 305 (7), 135 (11), 95 (18), 81 (23). HRMS (EI, 70 eV) Calcd. for $\text{C}_{32}\text{H}_{44}$: 428.3441. Found: 428.3437 (M^+).

Partial Dehydrogenation of Decahydronaphthylated 1,2-Dimethylnaphthalene with DDQ.

6-(5,6,7,8-Tetrahydro-2-naphthyl)-1,2-dimethylnaphthalene (7%) and 7-(5,6,7,8-tetrahydro-2-naphthyl)-1,2-dimethylnaphthalene (4%) were obtained, with recovery of the starting materials (70%). Pure samples were obtained by repeated GPC (CHCl_3).

6-(5,6,7,8-Tetrahydro-2-naphthyl)-1,2-dimethylnaphthalene: ^1H -NMR (400MHz, CDCl_3) δ 1.85 (4H, quint, $J = 3.2$ Hz), 2.49 (3H, s), 2.62 (3H, s), 2.83 (2H, br s), 2.87 (2H, br s), 7.17 (1H, d, $J = 7.6$ Hz), 7.30 (1H, d, J

= 8.4 Hz), 7.43 (1H, s), 7.46 (1H, d, $J = 8.0$ Hz), 7.65 (1H, d, $J = 8.8$ Hz), 7.74 (1H, dd, $J = 8.8$, 2.0 Hz), 7.96 (1H, d, $J = 2.0$ Hz), 8.07 (1H, d, $J = 8.8$ Hz). ^{13}C -NMR (100MHz, CDCl_3) δ 14.7, 20.9, 23.4, 29.3, 29.7, 124.1, 124.3, 125.2, 125.7, 125.8, 127.8, 129.2, 129.5, 130.9, 131.7, 132.4, 132.9, 136.2, 137.0, 137.4, 138.1. MS (EI, 70eV) m/z (%) 286 (100, M^+), 271 (11), 258 (12), 243 (10), 228 (5). HRMS (EI, 70eV) Calcd. for $\text{C}_{22}\text{H}_{22}$: 286.1720. Found: 286.1724 (M^+).

7-(5,6,7,8-Tetrahydro-2-naphthyl)-1,2-dimethylnaphthalene: ^1H -NMR (400MHz, CDCl_3) δ 1.86 (4H, quint, $J = 3.2\text{Hz}$), 2.50 (3H, s), 2.65 (3H, s), 2.84 (2H, br s), 2.89 (2H, br s), 7.19 (1H, d, $J = 8.0\text{Hz}$), 7.28 (1H, d, $J = 8.4\text{Hz}$), 7.43 (1H, s), 7.46 (1H, d, $J = 7.6\text{Hz}$), 7.63 (1H, d, $J = 8.8\text{Hz}$), 7.65 (1H, dd, $J = 8.4$, 1.6Hz), 7.84 (1H, d, $J = 8.4\text{Hz}$), 8.18 (1H, s). ^{13}C -NMR (100MHz, CDCl_3) δ 14.7, 20.9, 23.4, 29.3, 29.7, 124.1, 124.3, 125.2, 125.7, 125.8, 127.8, 129.2, 129.5, 130.9, 131.7, 132.4, 132.9, 136.2, 137.0, 137.4, 138.1. MS (EI, 70eV) m/z (%) 286 (100, M^+), 271 (7), 243 (7), 228 (3). HRMS (EI, 70eV) Calcd. for $\text{C}_{22}\text{H}_{22}$: 286.1720. Found: 286.1721 (M^+).

NOE

Reaction of 2-Chloronaphthalene 11 and *cis*-Bicyclo[4.4.0]decane 1.

(Decahydronaphthalenyl)-2-chloronaphthalenes: GC analysis indicated the presence of 4 isomers in a 11:7:2:1 ratio. Anal. Calcd. for $\text{C}_{20}\text{H}_{23}$: C, 80.50; H, 7.77%. Found: C, 80.65; H, 7.46%. ^1H -NMR (400 MHz, CDCl_3) δ 0.72-0.82 (m), 0.99-1.33 (m), 1.43-1.57 (m), 1.60-1.78 (m), 1.83 (br d, $J = 13.2$ Hz), 1.95 (br d, $J = 13.2$ Hz), 2.33 (br t, $J = 11.6$ Hz), 2.72 (br t, $J = 11.6$ Hz), 7.29-7.43 (m), 7.47 (br s), 7.52 (br s), 7.58 (br s), 7.65-7.76 (m), 7.83 (s). ^{13}C -NMR

(100 MHz, CDCl₃) δ 26.6, 26.7, 26.77, 26.80, 31.4, 33.9, 34.1, 34.27, 34.32, 34.5, 35.8, 41.6, 43.1, 43.4, 43.5, 44.57, 44.61, 48.0, 51.25, 51.30, 123.6, 124.3, 125.6, 125.68, 125.74, 125.8, 126.05, 126.09, 126.14, 126.37, 126.44, 126.5, 126.7, 126.8, 127.2, 127.3, 127.46, 127.50, 128.0, 128.9, 128.96, 129.00, 130.1, 130.2, 130.4, 130.5, 131.3, 131.7, 131.8, 132.1, 132.5, 132.6, 134.1, 134.2, 144.3, 145.1, 145.5, 146.3. IR (neat) 3054, 2917, 2849, 1630, 1593, 1502, 1446, 1360, 1075, 931, 876, 836, 810, 745 cm⁻¹. MS (EI, 70 eV) m/z (%) 298 (100, M^+), 264 (68), 188 (45), 176 (41), 165 (22), 154 (28), 142 (46), 128 (9). HRMS (EI, 70 eV) Calcd. for C₂₀H₂₃Cl: 298.1487. Found: 298.1473 (M^+).

Reaction of Phenanthrene 12 and Bicyclo[4.4.0]decane 1.

(Decahydronaphthalenyl)phenanthrenes: GC analysis indicated the presence of 4 major isomers in a 3:1:1:1 ratio. Anal. Calcd. for C₂₄H₂₆: C, 91.67; H, 8.33%. Found: C, 91.78; H, 8.13%.

¹H-NMR (400 MHz, CDCl₃) δ 0.74-0.90 (m), 0.95-1.44 (m), 1.45-1.82 (m), 1.82-1.94 (m), 1.96-2.06 (m), 2.34-2.50 (m), 2.79 (tt, J = 12.1, 3.5 Hz), 2.85 (tt, J = 12.1, 3.3 Hz), 7.42 (dd, J = 8.0, 1.7 Hz), 7.47 (dd, J = 6.4, 1.6 Hz), 7.50-7.66 (m), 7.67 (s), 7.69 (s), 7.70 (s), 7.81 (d, J = 8.0 Hz), 7.86 (dt, J = 8.0, 1.2 Hz), 8.43 (br s), 8.50 (br s), 8.59 (d, J = 8.8 Hz), 8.64 (d, J = 8.0 Hz), 8.71 (d, J = 8.0 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 26.7, 26.8, 31.39, 31.44, 33.9, 34.1, 34.3, 34.4, 34.45, 34.50, 34.7, 36.0, 36.1, 41.8, 42.0, 43.0, 43.35, 43.40, 43.44, 43.5, 44.4, 45.1, 48.1, 51.1, 51.8, 120.0, 122.29, 122.32, 122.4, 122.5, 125.6, 125.8, 125.86, 125.88, 126.0, 126.09, 126.11, 126.16, 126.24, 126.57, 126.60, 126.7, 126.8, 128.28, 128.30, 128.4, 130.1, 130.15, 130.21, 130.3, 131.6, 132.0, 144.7, 145.8. IR (neat) 3051, 2917, 2848, 1619, 1603, 1446, 836, 809, 744, 716 cm⁻¹. MS (EI, 70 eV) m/z (%) 314 (100, M^+), 217 (13), 204 (36), 191 (22), 186 (31). HRMS (EI, 70 eV) Calcd. for C₂₄H₂₆: 314.2033. Found: 314.2034 (M^+).

Bis(decahydronaphthalenyl)phenanthrenes: ¹H-NMR (400 MHz, CDCl₃) δ 0.72-0.90 (m), 0.94-1.44 (m), 1.46-1.83 (m), 1.84-1.96 (m), 1.96-2.05 (m), 2.33-2.54 (m), 2.72-2.92 (m), 7.44 (td, J = 8.1, 1.5 Hz), 7.46-7.52 (m), 7.58-7.62 (m), 7.63 (s), 7.65 (s), 7.78 (dd, J = 8.0, 3.2 Hz), 8.38 (br s), 8.40 (br s), 8.44 (s), 8.47 (s), 8.54 (d, J = 8.4 Hz), 8.60 (d, J = 8.6 Hz). ¹³C-NMR (100 MHz,

CDCl₃) δ 26.77, 26.83, 31.4, 34.0, 34.1, 34.37, 34.40, 34.49, 34.53, 34.60, 34.64, 34.7, 36.0, 36.1, 41.8, 41.9, 42.05, 42.13, 43.1, 43.4, 43.5, 43.58, 43.62, 44.4, 45.2, 45.3, 48.2, 51.1, 51.8, 51.9, 119.8, 119.9, 120.1, 122.2, 122.3, 122.4, 125.5, 125.55, 125.61, 125.7, 125.8, 125.86, 125.91, 126.0, 126.4, 126.5, 126.6, 126.7, 128.2, 128.3, 128.4, 128.5, 129.98, 130.02, 130.1, 130.2, 130.4, 131.7, 132.2, 145.3, 145.6, 145.7. IR (neat) 3013, 2916, 2848, 1622, 1446, 1215, 836, 815, 759, 735 cm⁻¹. MS (EI, 70 eV) *m/z* (%) 450 (100, **M**⁺), 322 (18), 185 (10), 137 (9). HRMS (EI, 70 eV) Calcd. for C₃₄H₄₂: 450.3284. Found: 450.3279 (**M**⁺).

Partial Dehydrogenation of Decahydronaphthylated Phenanthrene with DDQ. 2-(5,6,7,8-Tetrahydro-2-naphthyl)phenanthrene (2%) and 3-(5,6,7,8-tetrahydro-2-naphthyl)-

phenanthrene (4%) were obtained as determined by ¹H-NMR with the recovery of the starting materials (79%). Pure samples were obtained by repeated GPC. 2-(5,6,7,8-Tetrahydro-2-

naphthyl)phenanthrene: ¹H-NMR (400MHz, CDCl₃) δ 1.86 (4H, quint, *J* = 3.2 Hz), 2.85 (2H, br s), 2.89 (2H, br s), 7.20 (1H, d, *J* = 8.4 Hz), 7.48 (1H, s), 7.50 (1H, d, *J* = 7.6 Hz), 7.57-7.61 (1H, m), 7.64-7.68 (1H, m), 7.75 (1H, d, *J* = 9.6 Hz), 7.79 (1H, d, *J* = 8.8 Hz), 7.88-7.91 (2H, m), 8.07 (1H, d, *J* = 2.0 Hz), 8.69 (1H, d, *J* = 8.0 Hz), 8.72 (1H, d, *J* = 8.4 Hz). ¹³C-NMR (100MHz, CDCl₃) δ 23.4, 29.3, 29.7, 31.7, 122.5, 123.0, 124.4, 126.1, 126.3, 126.5, 127.0, 127.1, 127.9, 128.5, 129.6, 131.9, 132.3, 136.5, 137.5, 137.9. MS (EI, 70eV) *m/z* (%) 308 (100, **M**⁺), 280 (22), 265 (11). HRMS (EI, 70eV) Calcd. for C₂₄H₂₀: 308.1564. Found: 308.1574 (**M**⁺).

3-(5,6,7,8-Tetrahydro-2-naphthyl)phenanthrene: ¹H-NMR (400MHz, CDCl₃) δ 1.87 (4H, quint, *J* = 3.2 Hz), 2.86 (2H, br s), 2.91 (2H, br s), 7.22 (1H, d, *J* = 8.0 Hz), 7.49 (1H, s), 7.51 (1H, d, *J* = 7.6 Hz), 7.58-7.62 (1H, m), 7.64-7.68 (1H, m), 7.72 (1H, d, *J* = 8.8 Hz), 7.76 (1H, d, *J* = 8.8 Hz), 7.82 (1H, dd, *J* = 8.4, 1.6 Hz), 7.90 (1H, dd, *J* = 8.0, 1.2 Hz), 7.93 (1H, d, *J* = 8.4 Hz), 8.77 (1H, d, *J* = 8.0 Hz), 8.85 (1H, s). ¹³C-NMR (100MHz, CDCl₃) δ 15.4, 23.4, 29.3, 29.8, 120.7, 122.6, 124.6, 125.9, 126.4, 126.5, 126.6, 128.1, 128.5, 128.8, 129.6, 130.3, 130.4, 130.8, 132.2, 136.5, 137.5, 138.6, 139.4. MS (EI, 70eV) *m/z* (%) 308 (100, **M**⁺), 280 (21), 265 (9). HRMS (EI, 70eV) Calcd. for C₂₄H₂₀: 308.1564. Found: 308.1573 (**M**⁺).

NOE

Reaction of *m*-Xylene 16 and Bicyclo[4.4.0]decane 1. Under an argon atmosphere, a 1.0 M solution of GaCl₃ in bicyclo[4.4.0]decane **1** (*cis* : *trans* = 1 : 1) (1.0 mL) was added to a solution of *m*-xylene **16** (1.2 mL, 10 mmol) and **1** (*cis* : *trans* = 1 : 1) (1.5 mL). The mixture was heated to 70 °C, and stirred for 12 h at the temperature under irradiation using a high-pressure mercury lamp (400 W). After quenching the reaction by the addition of water, the organic layer was separated, washed with saturated aqueous NH₄Cl and water, and dried over MgSO₄. Solvents were removed *in vacuo*, and the residue was purified by flash column chromatography (silica gel, hexane) and GPC giving monoalkylated products (63 mg, 26% based on GaCl₃) as a 1 : 3 mixture of 2-(3,5-dimethylphenyl)decahydronaphthalene **17** and 3-(3,5-dimethylphenyl)decahydronaphthalene. Anal. Calcd. for C₁₈H₂₆: C, 89.18; H, 10.82%. Found: C, 89.23; H, 10.79%. ¹H-NMR (400 MHz, CDCl₃) δ 0.93-1.32 (m), 1.40-1.51 (m), 1.58-1.88 (m), 2.29 (s), 2.50 (tt, *J* = 12.0, 3.6 Hz), 6.75 (s), 6.82 (s). ¹³C-NMR (100 MHz, CDCl₃) δ 21.49, 21.52, 26.8, 26.9, 31.4, 34.0, 34.1, 34.4, 34.5, 34.6, 36.0, 41.4, 43.1, 43.5, 43.6, 44.5, 124.5, 127.27, 127.31, 137.3, 137.5, 146.2, 147.6. IR (neat) 3014, 2917, 2849, 1604, 1446, 1375, 1122, 1036, 971, 927, 845, 705 cm⁻¹. MS (EI, 70eV) *m/z* (%) 242 (71, M⁺), 146 (17), 132 (100), 120 (44), 105 (14). HRMS (EI, 70eV) Calcd. for C₁₈H₂₆: 242.2033. Found: 242.2035 (M⁺).

Reaction of Naphthalene 2 and Methylcyclohexane 18. 2-(Methylcyclohexyl)naphthalenes: GC analysis indicated the presence of three major isomers in a 5:4:1 ratio. Anal. Calcd. for C₁₇H₂₀: C, 91.01; H, 8.99%. Found: C, 90.83; H, 9.08%. ¹H-NMR (400 MHz, CDCl₃) δ 0.67

(d, $J = 6.4$ Hz), 0.95 (d, $J = 6.4$ Hz), 0.98-1.28 (m), 1.30-1.64 (m), 1.64-1.99 (m), 2.23 (td, $J = 10.8, 2.0$ Hz), 2.60 (tt, $J = 12.0, 3.6$ Hz), 2.69 (br t, $J = 11.6$ Hz), 7.32 (dd, $J = 8.4, 1.6$ Hz), 7.34-7.45 (m), 7.58 (br s), 7.62 (br s), 7.73-7.80 (m). ^{13}C -NMR (100 MHz, CDCl_3) δ 21.0, 22.9, 23.1, 26.80, 26.83, 27.1, 33.0, 33.3, 34.0, 34.4, 35.7, 35.9, 37.7, 43.1, 44.3, 44.6, 52.7, 124.37, 124.41, 124.8, 124.9, 125.55, 125.58, 125.7, 126.0, 127.36, 127.39, 127.43, 127.56, 127.58, 127.62, 132.1, 133.5, 133.6, 144.2, 145.05, 145.09. IR (neat) 3054, 2920, 2851, 1633, 1601, 1508, 1446, 1374, 852, 814, 744 cm^{-1} . MS (EI, 70 eV) m/z (%) 224 (100, M^+), 181 (18), 167 (45), 154 (29), 142 (50), 128 (18). HRMS (EI, 70 eV) Calcd. for $\text{C}_{17}\text{H}_{20}$: 224.1564. Found: 224.1566 (M^+). Bis(methylcyclohexyl)naphthalenes: GC analysis indicated the presence of 5 major isomers in a 3:2:1:1:1 ratio. Anal. Calcd. for $\text{C}_{24}\text{H}_{32}$: C, 89.94; H, 10.06%. Found: C, 89.74; H, 10.15%. ^1H -NMR (400 MHz, CDCl_3) δ 0.67 (d, $J = 6.4$ Hz), 0.95 (d, $J = 6.8$ Hz), 0.96-1.28 (m), 1.36-1.98 (m), 2.21 (br t, $J = 11.2$ Hz), 2.59 (br t, $J = 12.4$ Hz), 2.68 (br t, $J = 11.2$ Hz), 7.28 (dd, $J = 8.4, 1.7$ Hz), 7.31 (br d, $J = 8.4$ Hz), 7.56 (br s), 7.69 (d, $J = 8.3$ Hz), 7.70 (d, $J = 8.2$ Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 21.0, 22.9, 23.0, 26.9, 27.5, 32.6, 33.3, 34.09, 34.11, 34.5, 35.1, 35.8, 35.9, 43.2, 44.35, 44.43, 44.56, 44.62, 124.07, 124.09, 124.10, 124.12, 125.26, 125.29, 125.4, 125.97, 125.99, 127.23, 127.24, 127.3, 130.6, 130.7, 132.2, 133.74, 133.75, 133.77, 144.2, 144.3, 144.4, 145.07, 145.10. IR (neat) 3050, 2919, 2850, 1634, 1605, 1510, 1455, 1374, 837, 813 cm^{-1} . MS (EI, 70 eV) m/z (%) 320 (43, M^+), 237 (12), 228 (15), 167 (17), 141 (12), 97 (47). HRMS (EI, 70 eV) Calcd. for $\text{C}_{24}\text{H}_{32}$: 320.2500. Found: 320.2502 (M^+).

2-(Methylphenyl)naphthalenes by Dehydrogenation. Under an argon atmosphere, DDQ (454 mg, 2 mmol) was added to a solution of 2-(methylcyclohexyl)naphthalenes (45 mg, 0.20 mmol, 3 major isomers in 1:5:4 ratio by GC) in dry toluene (2 mL), and the mixture was heated at reflux for 30 min. After cooled to room temperature, saturated aqueous NaHCO_3 was added, and the insoluble materials were removed by filtration through celite. The organic layer was separated, washed with water, and dried over MgSO_4 . Solvents were removed *in vacuo*, and the residue was purified by flash column chromatography (silica gel, hexane) giving a mixture of 2-

(methylphenyl)naphthalenes (28 mg, 65%). The isomer ratio (*o* : *m* : *p* = 1 : 3 : 1) was determined by ^1H -NMR comparing with the authentic samples.

Reaction of Naphthalene 2 and Propylcyclohexane 22. 2-(Propylcyclohexyl)naphthalenes:

GC analysis indicated the presence of 4 major isomers in a 10:4:2:1 ratio. Anal. Calcd. for $\text{C}_{19}\text{H}_{24}$: C, 90.41; H, 9.59%. Found: C, 90.33; H, 9.41%. ^1H -NMR (400 MHz, CDCl_3) δ 0.68 (t, $J = 6.8$ Hz), 0.89 (t, $J = 7.2$ Hz), 0.92 (t, $J = 6.8$ Hz), 1.04-1.15 (m), 1.16-1.29 (m), 1.35 (q, $J = 7.2$ Hz), 1.43-1.49 (m), 1.50-1.69 (m), 1.80-1.99 (m), 2.59-2.72 (m), 7.32 (dd, $J = 8.4, 1.6$ Hz), 7.36-7.45 (m), 7.57 (br s), 7.59 (br s), 7.62 (br s), 7.65 (br s), 7.75-7.80 (m). ^{13}C -NMR (100 MHz, CDCl_3) δ 14.4, 14.5, 19.6, 20.1, 20.2, 21.0, 21.6, 23.0, 26.4, 26.8, 27.1, 30.3, 32.2, 33.1, 33.4, 33.7, 33.8, 33.96, 34.40, 34.5, 35.2, 36.3, 36.7, 36.9, 37.2, 37.9, 39.8, 40.0, 41.3, 41.9, 44.6, 44.8, 124.4, 124.9, 125.6, 126.1, 127.40, 127.42, 127.55, 127.58, 132.0, 133.5, 145.2, 145.3. IR (neat) 3054, 2922, 2850, 1632, 1601, 1508, 1446, 1377, 1270, 1125, 1018, 947, 887, 851, 815, 744 cm^{-1} . MS (EI, 70 eV) m/z (%) 252 (100, M^+), 209 (11), 167 (43), 154 (45), 141 (57), 128 (24). HRMS (EI, 70 eV) Calcd. for $\text{C}_{19}\text{H}_{24}$: 252.1877. Found: 252.1879 (M^+).

Bis(propylcyclohexyl)naphthalenes: ^1H -NMR (400 MHz, CDCl_3) δ 0.66-0.69 (m), 0.87-0.95 (m), 1.04-1.63 (m), 1.80-1.97 (m), 2.20 (t, $J = 7.6$ Hz), 2.31 (t, $J = 11.2$ Hz), 2.57-2.69 (m), 7.25-7.33 (m), 7.46 (br s), 7.51 (br s), 7.53 (br s), 7.56 (br s), 7.62 (br s), 7.68-7.71 (m). ^{13}C -NMR (100 MHz, CDCl_3) δ 14.3, 14.4, 14.55, 14.58, 19.59, 20.1, 20.2, 21.0, 21.6, 22.8, 23.2, 26.3, 26.4, 26.8, 27.1, 29.8, 30.3, 32.2, 33.1, 33.7, 34.4, 34.48, 34.51, 36.4, 36.7, 37.2, 37.9, 39.8, 40.0, 41.3, 41.9, 44.57, 44.63, 44.7, 44.8, 46.3, 51.2, 51.3, 124.08, 124.7, 125.3, 126.0, 127.2, 127.25, 127.30, 127.38, 127.40, 128.5, 129.6, 129.9, 130.6, 130.7, 132.2, 133.7, 143.6, 144.3, 144.4, 144.5, 144.9, 145.1, 145.2, 145.3. IR (neat) 2954, 2922, 2850, 1633, 1605, 1446, 1377, 1262, 1133, 882, 837, 813, 739, 678 cm^{-1} . MS (EI, 70 eV) m/z (%) 376 (100, M^+), 279 (17), 265 (13), 167 (20), 149 (23), 125 (15). HRMS (EI, 70 eV) Calcd. for $\text{C}_{28}\text{H}_{40}$: 376.3128. Found: 376.3125 (M^+).

Reaction of Naphthalene 2 and Isopropylcyclohexane 23. 2-

(Isopropylcyclohexyl)naphthalenes: GC analysis indicated the presence of 3 major isomers in a 9:3:1 ratio. Anal. Calcd. for $C_{19}H_{24}$: C, 90.41; H, 9.59%. Found: C, 90.47; H, 9.91%. ^1H -NMR (400 MHz, $CDCl_3$) δ 0.70 (d, J = 6.4 Hz), 0.78 (d, J = 7.2 Hz), 0.89-0.93 (m), 0.94-0.97 (m), 1.01-1.10 (m), 1.19-1.35 (m), 1.43-1.52 (m), 1.79 (d, J = 11.2 Hz), 1.87-1.96 (m), 2.02 (d, J = 12.0 Hz), 2.52-2.62 (m), 2.68 (t, J = 11.2 Hz), 7.36-7.45 (m), 7.59 (br s), 7.63 (br s), 7.76-7.80 (m). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 19.9, 19.96, 20.03, 27.0, 29.5, 30.2, 33.0, 33.2, 34.4, 34.56, 38.0, 43.9, 44.6, 44.8, 44.9, 124.4, 124.9, 125.6, 126.1, 127.41, 127.43, 127.55, 127.60, 132.0, 133.5, 145.2, 145.4. IR (neat) 3054, 2925, 2852, 1633, 1601, 1507, 1446, 1384, 1366, 1271, 1125, 1018, 944, 887, 851, 815, 745 cm^{-1} . MS (EI, 70 eV) m/z (%) 252 (100, M^+), 209 (12), 167 (38), 154 (45), 141 (61), 128 (23). HRMS (EI, 70 eV) Calcd. for $C_{19}H_{24}$: 252.1877. Found: 252.1861 (M^+). Bis(isopropylcyclohexyl)naphthalenes: ^1H -NMR (400 MHz, $CDCl_3$) δ 0.68-0.70 (m), 0.76-0.78 (m), 0.88-0.92 (m), 1.00-1.11 (m), 1.18-1.33 (m), 1.36-1.51 (m), 1.76-2.01 (m), 2.55-2.65 (m), 7.28-7.34 (m), 7.57 (br s), 7.70-7.71 (m). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 19.89, 19.96, 20.03, 27.0, 29.5, 29.8, 30.2, 33.0, 33.2, 34.4, 34.6, 38.0, 43.4, 44.5, 44.7, 44.8, 44.9, 124.1, 124.4, 125.28, 125.31, 125.5, 126.0, 127.2, 127.3, 127.4, 130.6, 132.2, 133.8, 144.4, 144.6, 145.1, 145.4. IR (neat) 3049, 2924, 2852, 1635, 1605, 1511, 1447, 1384, 1367, 906, 838, 814, 734, 679 cm^{-1} . MS (EI, 70 eV) m/z (%) 376 (100, M^+), 278 (5), 265 (10), 252 (5), 167 (10), 141 (9), 125 (12). HRMS (EI, 70 eV) Calcd. for $C_{28}H_{40}$: 376.3128. Found: 376.3118 (M^+).

Reaction of Naphthalene 2 and Methylcyclopentane 26. 2-(Methylcyclopentyl)naphthalenes: GC analysis indicated the presence of 2 major isomers in a 1:1 ratio. Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63%. Found: C, 91.64; H, 8.82%. ^1H -NMR (400 MHz, $CDCl_3$) δ 0.95 (d, J = 6.4 Hz), 1.08 (d, J = 6.4 Hz), 1.10 (d, J = 6.4 Hz), 1.24-1.46 (m), 1.68-2.34 (m), 2.58 (q, J = 8.8 Hz), 3.17-3.26 (m), 3.32 (sext, J = 8.4 Hz), 7.34-7.46 (m), 7.61-7.65 (m), 7.74-7.80 (m). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 18.8, 21.1, 21.7, 24.1, 33.7, 33.9, 34.2, 34.9, 35.0, 35.3, 35.4, 39.8, 42.5, 43.0, 44.2, 44.7, 46.4, 54.7, 124.6, 124.8, 125.6, 125.9, 126.0, 126.1, 127.3, 127.36, 127.38,

127.42, 127.64, 127.67, 127.72, 131.86, 131.91, 132.1, 133.45, 133.49, 142.7, 143.8, 144.3. IR (neat) 3053, 2951, 2866, 1633, 1601, 1507, 1450, 1373, 852, 816, 744 cm^{-1} . MS (EI, 70 eV) m/z (%) 210 (100, M^+), 195 (10), 181 (14), 167 (49), 154 (49), 142 (40), 128 (24). HRMS (EI, 70 eV) Calcd. for $\text{C}_{16}\text{H}_{18}$: 210.1408. Found: 210.1418 (M^+).

Bis(methylcyclopentyl)naphthalene: GC analysis indicated the presence of 6 major isomers in a 3:2:2:2:1:1 ratio. Anal. Calcd. for $\text{C}_{24}\text{H}_{32}$: C, 90.35; H, 9.65%. Found: C, 89.92; H, 10.00%. ^1H -NMR (400 MHz, CDCl_3) δ 0.56-0.62 (m), 0.90-0.98 (m), 1.08 (d, $J = 6.4$ Hz), 1.10 (d, $J = 6.4$ Hz), 1.22-1.56 (m), 1.65-1.86 (m), 1.87-2.34 (m), 2.50-2.62 (m), 3.21 (br quint, $J = 9.6$ Hz), 3.31 (quint, $J = 8.4$ Hz), 7.27-7.38 (m), 7.57 (s), 7.58 (s), 7.66-7.75 (m). ^{13}C -NMR (100 MHz, CDCl_3) δ 16.5, 18.73, 18.76, 18.79, 21.1, 21.75, 21.77, 23.5, 24.0, 24.1, 29.07, 29.09, 29.5, 33.6, 33.77, 33.80, 33.90, 33.93, 34.21, 34.23, 34.9, 35.0, 35.32, 35.34, 35.43, 35.45, 35.47, 38.3, 39.8, 42.5, 43.00, 43.01, 44.2, 44.61, 44.63, 44.7, 46.37, 46.38, 46.44, 54.7, 54.8, 122.96, 123.02, 123.1, 124.22, 124.23, 124.25, 124.26, 124.27, 124.30, 124.4, 125.1, 125.18, 125.20, 125.29, 125.33, 125.4, 125.6, 125.9, 125.95, 125.99, 126.05, 126.08, 127.2, 127.27, 127.30, 127.33, 127.36, 127.39, 127.55, 127.59, 127.63, 130.35, 130.40, 130.46, 130.58, 130.64, 130.8, 131.90, 131.93, 131.96, 132.02, 132.13, 132.15, 132.2, 133.55, 133.61, 141.82, 141.84, 142.7, 142.93, 142.95, 143.50, 143.52, 143.78, 143.80, 144.4. IR (neat) 3049, 2950, 2866, 1634, 1605, 1512, 1450, 1373, 881, 838, 815 cm^{-1} . MS (EI, 70 eV) m/z (%) 292 (100, M^+), 167 (18), 83 (40), 55 (28). HRMS (EI, 70 eV) Calcd. for $\text{C}_{22}\text{H}_{28}$: 292.2190. Found: 292.2183 (M^+).

Reaction of Naphthalene 2 and Methylcycloheptane 27. 2-(Methylcycloheptyl)naphthalenes: GC analysis indicated the presence of 6 major isomers in a 3:3:3:1:1:1 ratio. ^1H -NMR (400 MHz, CDCl_3) δ 0.55 (t, $J = 7.6$ Hz), 0.65 (t, $J = 7.6$ Hz), 0.72 (t, $J = 7.6$ Hz), 0.89-0.98 (m), 1.08-1.29 (m), 1.31 (d, $J = 6.8$ Hz), 1.46-1.61 (m), 1.67-1.86 (m), 1.91-2.01 (m), 2.36 (t, $J = 11.2$ Hz), 2.57-2.71 (m), 2.78-2.92 (m), 7.29-7.44 (m), 7.55 (br s), 7.57 (br s), 7.59 (br s), 7.62 (br s), 7.64 (br s), 7.74-7.79 (m). ^{13}C -NMR (100 MHz, CDCl_3) δ 10.9, 11.6, 11.7, 12.50, 12.54, 14.3, 19.0, 20.5, 21.56, 22.59, 22.8, 23.8, 24.2, 24.3, 24.5, 24.66, 24.72, 25.2, 25.7, 25.8, 26.6, 26.66, 26.68,

26.8, 26.85, 26.90, 27.1, 27.6, 28.4, 28.5, 28.9, 29.5, 29.8, 29.90, 29.94, 30.1, 30.3, 30.8, 31.5, 31.7, 31.8, 32.0, 32.7, 33.3, 33.5, 33.6, 34.0, 34.36, 34.43, 34.5, 34.7, 35.1, 35.4, 35.7, 35.9, 36.0, 36.1, 36.2, 36.5, 36.8, 36.9, 37.05, 37.11, 37.8, 38.2, 38.3, 39.2, 40.0, 40.6, 40.9, 41.9, 42.7, 43.7, 43.8, 44.2, 44.3, 44.6, 44.8, 45.9, 46.1, 46.7, 46.9, 47.6, 50.8, 124.1, 124.15, 124.20, 124.4, 124.5, 124.6, 124.80, 124.82, 124.9, 125.4, 125.59, 125.62, 125.8, 125.9, 126.1, 126.16, 126.21, 126.3, 127.3, 127.38, 127.41, 127.43, 127.53, 127.55, 127.58, 127.64, 127.68, 127.71, 131.78, 131.85, 131.92, 131.95, 132.00, 133.3, 133.5, 144.3, 144.5, 145.0, 145.2, 145.3, 147.1, 147.3. IR (neat) 3054, 2923, 2851, 1633, 1601, 1507, 1447, 1377, 1269, 1125, 1018, 889, 852, 815, 744 cm^{-1} . MS (EI, 70 eV) m/z (%) 238 (100, M^+), 224 (35), 209 (13), 181 (16), 167 (62), 155 (68), 141 (58), 128 (22). HRMS (EI, 70 eV) Calcd. for $\text{C}_{19}\text{H}_{24}$: 238.1720. Found: 238.1728 (M^+).

Reaction of Naphthalene 2 and Cyclohexane 28. 2-Cyclohexylnaphthalene **29**:²⁷ ^1H -NMR (400 MHz, CDCl_3) δ 1.23-1.36 (1H, m), 1.38-1.59 (4H, m), 1.74-1.82 (1H, m), 1.88 (2H, br d, $J = 12.4$ Hz), 1.96 (2H, br d, $J = 12.4$ Hz), 2.66 (1H, tt, $J = 10.4, 3.2$ Hz), 7.34-7.45 (3H, m), 7.62 (1H, br s), 7.74-7.80 (3H, m). ^{13}C -NMR (100 MHz, CDCl_3) δ 26.3, 27.0, 34.5, 44.7, 124.4, 124.8, 125.5, 126.0, 127.37, 127.44, 127.6, 132.0, 133.6, 145.2. IR (neat) 3053, 2925, 2849, 1632, 1602, 1507, 1447, 851, 816, 745 cm^{-1} . MS (EI, 70 eV) m/z (%) 210 (100, M^+), 167 (57), 154 (20), 142 (36), 128 (37). HRMS (EI, 70 eV) Calcd. for $\text{C}_{16}\text{H}_{18}$: 210.1408. Found: 210.1415 (M^+).

Reaction of Naphthalene 2 and Isobutane. 2-(*t*-Butyl)naphthalene:²⁸ Anal. Calcd. for $\text{C}_{14}\text{H}_{16}$: C, 91.24; H, 8.76%. Found: C, 91.41; H, 8.80%. ^1H -NMR (400 MHz, C_6D_6) δ 1.30 (9H, s), 7.25-7.32 (2H, m), 7.43 (1H, dd, $J = 8.8, 2.0$ Hz), 7.66 (1H, d, $J = 8.8$ Hz), 7.65-7.70 (2H, m), 7.73 (1H, d, $J = 2.0$ Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 31.4, 34.9, 122.7, 124.6, 125.1, 125.6, 127.2, 127.4, 127.8, 131.5, 133.2, 148.3. IR (neat) 3057, 2963, 2869, 1599, 1505, 1478, 1462, 1363, 1277, 1135, 889, 854, 817, 745 cm^{-1} . MS (EI, 70 eV) m/z (%) 184 (38, M^+), 169 (100), 152 (9), 141 (32), 129 (14). HRMS (EI, 70 eV) Calcd. for $\text{C}_{14}\text{H}_{16}$: 184.1251. Found: 184.1243 (M^+). 2,6- and 2,7-Bis(*t*-butyl)naphthalene:²⁹ GC analysis indicated the

presence of 2 isomers in a 1:1 ratio. Anal. Calcd. for $C_{18}H_{24}$: C, 89.93; H, 10.07%. Found: C, 89.60; H, 10.09%. ^1H -NMR (400 MHz, $CDCl_3$) δ 1.40 (s), 1.41 (s), 7.49-7.54 (m), 7.71 (d, $J = 1.6$ Hz), 7.73 (d, $J = 8.4$ Hz), 7.74 (d, $J = 8.4$ Hz). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 31.4, 34.8, 34.9, 122.2, 122.8, 124.0, 124.6, 126.8, 127.4, 129.7, 131.4, 133.1, 147.7, 148.3. IR (KBr) 3056, 2959, 1631, 1603, 1509, 1463, 1362, 1282, 1210, 1149, 904, 887, 847, 820, 689 cm^{-1} . MS (EI, 70 eV) m/z (%) 240 (42, M^+), 225 (100), 152 (5), 141 (6), 128 (4), 57 (39). HRMS (EI, 70 eV) Calcd. for $C_{18}H_{24}$: 240.1877. Found: 240.1879 (M^+).

Reaction of Naphthalene 2 and 2,3-Dimethylbutane. 2,3-Dimethyl-2-(2-naphthyl)butane **30**: GC analysis indicated the presence of 2 isomers in a 6:1 ratio. Anal. Calcd. for $C_{16}H_{20}$: C, 90.50; H, 9.50%. Found: C, 90.51; H, 9.58%. ^1H -NMR (400 MHz, $CDCl_3$) δ 0.79 (d, $J = 6.8$ Hz), 0.92 (s), 1.35 (d, $J = 7.6$ Hz), 2.05 (quint, $J = 6.8$ Hz), 2.73 (q, $J = 7.2$ Hz), 7.33 (dd, $J = 8.4, 2.0$ Hz), 7.38-7.45 (m), 7.51 (dd, $J = 8.4, 2.0$ Hz), 7.58 (s), 7.70 (d, 2.0 Hz), 7.72 (d, $J = 8.8$ Hz), 7.75 (s), 7.77-7.80 (m). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 16.1, 18.1, 24.8, 28.0, 34.1, 37.9, 40.7, 50.1, 124.0, 124.9, 125.0, 125.0, 125.49, 125.52, 126.5, 127.1, 127.1, 127.3, 127.5, 127.8, 127.9, 131.5, 131.9, 133.0, 133.1, 142.8, 147.7. IR (neat) 3057, 2967, 2871, 1600, 1506, 1459, 1377, 1363, 855, 819, 748 cm^{-1} . MS (EI, 70 eV) m/z (%) 212 (29, M^+), 155 (100), 141 (16), 128 (8). HRMS (EI, 70 eV) Calcd. for $C_{16}H_{20}$: 212.1564. Found: 212.1559 (M^+).

Reaction of Naphthalene 2 and Methane. Nitrogen was charged in a 30 mL autoclave, to which a mixture of $GaCl_3$ (176 mg, 1 mmol) and **2** (640 mg, 5.0 mmol) in benzene (5 mL) was added. The apparatus was cooled in a liquid nitrogen bath, and methane was charged for 1 min. The amount of methane must be carefully controlled to avoid application of too high pressure. The mixture was warmed to room temperature, and stirred at 180 °C for 3 h (ca. 190 atm). After cooled to room temperature, methane was released, and the reaction was quenched by addition of water. The organic layer was separated, washed with saturated aqueous NH_4Cl and water, and dried over $MgSO_4$. Solvents were removed *in vacuo*, and the residue was flash column chromatographed (silica gel, hexane) to remove polar substances. 2-Methylnaphthalene was

detected in 0.1% yield based on GaCl₃ by GC employing nitrobenzene as internal standard.

Reaction of Naphthalene 2 and 1,2-Dimethylcyclohexane 31. 2-(3,4-Dimethylcyclohexyl)naphthalenes and 2-(2,3-dimethylcyclohexyl)naphthalenes: GC analysis indicated the presence of 4 major isomers in a 5:2:2:1 ratio. Anal. Calcd. for C₁₈H₂₂: C, 90.70; H, 9.30%. Found: C, 90.68; H, 9.10%. ¹H-NMR (400 MHz, CDCl₃) δ 0.70 (d, *J* = 6.4 Hz), 0.88 (d, *J* = 6.8 Hz), 0.93 (d, *J* = 7.2 Hz), 0.968 (d, *J* = 6.0 Hz), 0.974 (d, *J* = 6.4 Hz), 1.16-1.65 (m), 1.70-1.98 (m), 2.32 (td, *J* = 11.2, 3.2 Hz), 2.54-2.61 (m), 2.72 (tt, *J* = 12.0, 3.4 Hz), 2.87 (tt, *J* = 12.4, 3.2 Hz), 7.31-7.45 (m), 7.58 (br s), 7.63 (br s), 7.65 (br s), 7.75-7.80 (m). ¹³C-NMR (100 MHz, CDCl₃) δ 14.3, 17.7, 20.2, 20.4, 20.8, 22.9, 24.4, 24.80, 26.83, 29.9, 30.2, 31.4, 33.3, 33.6, 34.2, 34.5, 36.0, 36.2, 36.3, 38.9, 39.0, 39.3, 39.5, 39.8, 40.2, 43.4, 43.9, 44.68, 44.72, 47.5, 52.4, 124.3, 124.4, 124.5, 124.8, 124.9, 125.5, 125.6, 125.8, 126.0, 126.08, 126.12, 127.3, 127.39, 127.42, 127.6, 127.7, 132.0, 133.5, 145.0, 145.09, 145.15. IR (neat) 3053, 2922, 2868, 1633, 1600, 1507, 1452, 1370, 850, 815, 744 cm⁻¹. MS (EI, 70 eV) *m/z* (%) 238 (100, M⁺), 195 (6), 181 (15), 167 (30), 154 (43), 141 (32). HRMS (EI, 70 eV) Calcd. for C₁₈H₂₂: 238.1720. Found: 238.1728 (M⁺). Bis(3,4-dimethylcyclohexyl)naphthalenes: GC analysis indicated the presence of 7 major isomers in a 2:2:2:1:1:1:1 ratio. Anal. Calcd for C₂₆H₃₆: C, 89.59; H, 10.41%. Found: C, 89.39; H, 10.28%. ¹H-NMR (400 MHz, CDCl₃) δ 0.69 (d, *J* = 6.4 Hz), 0.96 (d, *J* = 6.2 Hz), 0.97 (d, *J* = 6.4 Hz), 1.01-1.45 (m), 1.45-1.98 (m), 2.29 (br t, *J* = 12.7 Hz), 2.48-2.60 (m), 2.69 (br t, *J* = 12.1 Hz), 2.78-2.88 (m), 7.25-7.37 (m), 7.53 (br s), 7.57 (s), 7.59 (s), 7.67-7.74 (m). ¹³C-NMR (100 MHz, CDCl₃) δ 17.2, 17.8, 20.2, 20.4, 20.87, 22.92, 24.41, 24.43, 24.8, 26.86, 29.93, 30.3, 31.4, 32.5, 33.0, 33.3, 33.7, 34.15, 34.21, 34.23, 34.6, 36.1, 36.2, 36.3, 38.9, 39.1, 39.3, 39.5, 39.8, 40.1, 40.2, 43.5, 43.9, 44.66, 44.69, 44.8, 47.7, 47.6, 52.4, 52.5, 124.05, 124.07, 124.13, 124.16, 124.18, 125.23, 125.26, 125.5, 125.9, 125.95, 126.01, 127.25, 127.28, 127.4, 130.67, 130.72, 132.2, 133.8, 143.6, 144.06, 144.12, 144.15, 144.21, 144.27, 144.4, 144.9, 144.97, 145.03. IR (neat) 3050, 2921, 2867, 1635, 1605, 1510, 1453, 1370, 837, 814, 758 cm⁻¹. MS (EI, 70 eV) *m/z* (%) 348 (100, M⁺), 111 (30), 69 (32). HRMS (EI, 70 eV)

Calcd. for $C_{26}H_{36}$: 348.2815. Found: 348.2821 (M^+). Reaction of **2** and *cis*-**31** gave the monoalkylated products (4 isomers in a 4:1:1:1 ratio by GC) in 560% and dialkylated products in 117% yield. *Trans*-**31** gave the monoalkylated products (4 isomers in a 3:1:1:1 ratio by GC) in 37%. The compositions of the monoalkylated products were essentially the same in both reactions.

2-(2,3-Dimethylphenyl)naphthalene and 2-(3,4-Dimethylphenyl)naphthalene. A mixture of 2-(dimethylcyclohexyl)naphthalenes (4 isomers in 5:2:2:1) was dehydrogenated with DDQ giving a mixture of 2,3-isomer and 3,4-isomer in a 1:3.6 ratio (48% total yield). The structures were confirmed by comparison with the authentic samples.

Reaction of Naphthalene 2 and 1,3-Dimethylcyclohexane 34. 2-(3,5-Dimethylcyclohexyl)naphthalenes and 2-(2,4-Dimethylcyclohexyl)naphthalenes: GC analysis indicated the presence of 6 major isomers in a 10:5:2:2:1:1 ratio. Anal. Calcd. for $C_{18}H_{22}$: C, 90.70; H, 9.30%. Found: C, 90.69; H, 9.21%. ^1H -NMR (400 MHz, $CDCl_3$) δ 0.68 (d, $J = 6.8$ Hz), 0.958 (d, $J = 6.8$ Hz), 0.963 (d, $J = 6.4$ Hz), 1.09-1.19 (m), 1.30-1.68 (m), 1.73-1.93 (m), 2.19 (td, $J = 12.0, 3.6$ Hz), 2.26-2.58 (m), 2.75 (tt, $J = 12.0, 3.6$ Hz), 7.32 (dd, $J = 8.4, 1.6$ Hz), 7.35-7.46 (m), 7.58 (br s), 7.62 (br s), 7.74-7.80 (m). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 20.9, 22.8, 22.9, 24.8, 28.0, 28.5, 28.67, 29.69, 30.2, 31.3, 32.2, 32.9, 33.0, 33.3, 35.2, 35.4, 35.6, 35.68, 35.74, 37.2, 37.4, 37.5, 37.6, 37.9, 42.7, 43.9, 44.3, 44.7, 52.3, 124.4, 124.8, 124.9, 125.57, 125.61, 126.1, 127.3, 127.39, 127.42, 127.57, 127.61, 131.96, 132.04, 132.1, 133.5, 144.1, 145.0, 145.2. IR (neat) 3054, 2948, 2913, 2867, 1633, 1600, 1507, 1455, 1374, 850, 815, 744 cm^{-1} . MS (EI, 70 eV) m/z (%) 238 (100, M^+), 181 (29), 167 (27), 154 (35), 142 (36). HRMS (EI, 70 eV) Calcd. for $C_{18}H_{22}$: 238.1720. Found: 238.1720 (M^+). Bis(3,5-dimethylcyclohexyl)naphthalenes: GC analysis indicated the presence of 4 major isomers in a 1:1:1:1 ratio. Anal. Calcd. for $C_{26}H_{36}$: C, 89.59; H, 10.41%. Found: C, 89.44; H, 10.47%. ^1H -NMR (400 MHz, $CDCl_3$) δ 0.65-0.73 (m), 0.92 (d, $J = 6.1$ Hz), 0.96 (d, $J = 6.6$ Hz), 1.00-1.44 (m), 1.56-1.94 (m), 2.16 (br t, $J = 11.0$ Hz), 2.26 (br t, $J = 9.6$ Hz), 2.72 (br t, $J = 12.1$ Hz), 7.21-

7.34 (m), 7.53 (br s), 7.57 (br s), 7.66-7.74 (m). ^{13}C -NMR (100 MHz, CDCl_3) δ 22.7, 22.8, 22.9, 23.1, 27.0, 28.7, 32.96, 32.99, 33.3, 35.5, 35.69, 35.73, 35.8, 36.1, 37.46, 37.50, 39.52, 39.7, 40.6, 42.7, 42.8, 42.9, 43.4, 44.0, 44.25, 44.30, 44.4, 44.8, 52.25, 52.34, 52.4, 52.5, 124.0, 124.05, 124.08, 124.2, 125.2, 125.26, 125.33, 125.4, 125.5, 125.9, 125.96, 126.01, 127.2, 127.27, 127.30, 130.6, 130.7, 130.8, 132.17, 132.20, 132.3, 133.75, 133.79, 143.16, 143.24, 143.95, 144.00, 144.07, 144.12, 144.85, 144.88. IR (neat) 3050, 2912, 2850, 1635, 1605, 1511, 1455, 1374, 902, 835, 813 cm^{-1} . MS (EI, 70 eV) m/z (%) 348 (100, M^+), 111 (41), 69 (43). HRMS (EI, 70 eV) Calcd. for $\text{C}_{26}\text{H}_{36}$: 348.2815. Found: 348.2824 (M^+). Reaction of **2** and *trans*-**34** gave monoalkylated products (6 isomers in a 14:6:3:2:1:1 ratio by GC) in 264% and the dialkylated products in 15% yield. *Cis*-**34** gave the monoalkylated products (6 isomers in a 13:11:5:2:2:1 ratio by GC) in 84%. The compositions of the monoalkylated products were essentially the same in both reactions.

2-(2,4-Dimethylphenyl)naphthalene and 2-(3,5-Dimethylphenyl)naphthalene: A mixture of 2-(dimethylcyclohexyl)naphthalenes (6 isomers in 10:5:2:1:1:1) was dehydrogenated with DDQ giving a mixture of three isomers in total 31% yield, which contained 3,5-isomer, 2,4-isomer, and an unidentified product in a ratio of 6:1:1. The structures of the former two compounds were confirmed by comparison with the authentic samples.

Reaction of Naphthalene 2 and 1,4-Dimethylcyclohexane 37. 2-(2,5-Dimethylcyclohexyl)naphthalenes **38**: GC analysis indicated the presence of 2 major isomers in a 12 : 1 ratio. Anal. Calcd. for $\text{C}_{18}\text{H}_{22}$: C, 90.70; H, 9.30%. Found: C, 90.74; H, 9.08%. ^1H -NMR (400 MHz, CDCl_3) δ 0.69 (3H, d, $J = 6.4$ Hz), 0.93 (3H, d, $J = 6.4$ Hz), 1.09-1.33 (4H, m), 1.49-1.94 (4H, m), 2.29 (1H, td, $J = 11.2, 3.2$ Hz), 7.32 (1H, dd, $J = 8.4, 1.6$ Hz), 7.38-7.45 (2H, m), 7.58 (1H, br s), 7.75-7.80 (3H, m). ^{13}C -NMR (100 MHz, CDCl_3) δ 20.65, 22.70, 33.3, 35.5, 35.8, 37.2, 44.38, 52.42, 124.8, 125.6, 125.7, 126.0, 127.35, 127.42, 127.6, 132.1, 133.5, 144.1. IR (neat) 3053, 2948, 2912, 1633, 1601, 1507, 1455, 1374, 854, 814, 744 cm^{-1} . MS (EI, 70 eV) m/z (%) 238 (100, M^+), 181 (74), 167 (26), 154 (39), 142 (72). HRMS (EI, 70 eV)

Calcd. for $C_{18}H_{22}$: 238.1720. Found: 238.1727 (M^+). Bis(2,5-dimethylcyclohexyl)naphthalenes: GC analysis indicated the presence of 4 major isomers in a 4:3:1:1 ratio. Anal. Calcd. for $C_{26}H_{36}$: C, 89.59; H, 10.41%. Found: C, 89.77; H, 10.31%. ^1H -NMR (400 MHz, $CDCl_3$) δ 0.68 (d, $J = 5.9$ Hz), 0.69 (d, $J = 6.2$ Hz), 0.92 (d, $J = 6.6$ Hz), 0.96 (d, $J = 6.4$ Hz), 1.00-1.36 (m), 1.40-1.95 (m), 2.16 (br t, $J = 8.1$ Hz), 2.27 (br t, $J = 11.6$ Hz), 2.73 (br t, $J = 11.6$ Hz), 7.22-7.35 (m), 7.51 (s), 7.53 (br s), 7.70 (dd, $J = 8.3, 7.1$ Hz). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 20.70, 20.73, 20.96, 20.99, 22.7, 22.8, 22.9, 32.96, 33.00, 33.3, 33.65, 34.68, 35.5, 35.7, 35.8, 37.27, 37.31, 37.5, 42.8, 44.0, 44.28, 44.33, 44.46, 44.50, 44.8, 52.3, 52.35, 52.40, 52.5, 124.0, 124.1, 125.16, 125.19, 125.4, 125.38, 125.41, 125.44, 125.9, 126.0, 127.27, 127.33, 130.8, 130.9, 132.2, 132.3, 133.8, 143.2, 143.3, 143.96, 144.02, 144.1, 144.8. IR (neat) 3049, 2911, 2850, 1634, 1605, 1503, 1455, 1375, 883, 841, 813 cm^{-1} . MS (EI, 70 eV) m/z (%) 348 (100, M^+), 111 (43), 69 (40). HRMS (EI, 70 eV) Calcd. for $C_{26}H_{36}$: 348.2815. Found: 348.2816 (M^+). Reaction of **2** and *cis*-**37** gave the monoalkylated product **38** (2 isomers in a 5:1 ratio by GC) in 219% and the dialkylated products in 8% yield. *Trans*-**37** gave **38** (2 isomers in a 6:1 ratio by GC) in 143% and dialkylated product in 5% yield.

Reaction of Naphthalene 2 and 4-(*t*-Butyl)-1-methylcyclohexane 39. 1-(*t*-Butyl)-3-(2-naphthyl)-4-methylcyclohexane **40**: The starting material 4-(*t*-butyl)-1-methylcyclohexane used was a 1 : 1 mixture of *cis*- and *trans*-isomers, and **40** was obtained as a single isomer by GC. Anal. Calcd. for $C_{21}H_{28}$: C, 89.93; H, 10.07%. Found: C, 89.71; H, 10.00%. ^1H -NMR (400 MHz, $CDCl_3$) δ 0.69 (3H, d, $J = 6.4$ Hz), 0.86 (9H, s), 1.14-1.40 (4H, m), 1.60-1.71 (1H, m), 1.85-1.94 (3H, m), 2.26 (1H, td, $J = 11.2, 3.6$ Hz), 7.34 (1H, dd, $J = 8.8, 1.6$ Hz), 7.38-7.45 (2H, m), 7.59 (1H, s), 7.77-7.81 (3H, m). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 20.7, 27.6, 27.7, 32.6, 36.2, 36.9, 37.5, 48.6, 52.9, 124.8, 125.6, 125.7, 126.1, 127.4, 127.5, 127.8, 132.1, 133.5, 144.4. IR (neat) 3053, 3018, 2950, 2867, 1632, 1600, 1507, 1455, 1391, 1364, 1271, 1243, 1226, 1124, 1018, 958, 945, 908, 889, 852, 816, 744 cm^{-1} . MS (EI, 70 eV) m/z (%) 280 (98, M^+), 265 (3), 223 (18), 181 (17), 167 (29), 155 (36), 141 (100), 128 (14). HRMS (EI, 70

eV) Calcd. for $C_{21}H_{28}$: 280.2190. Found: 280.2183 (M^+).

2-(2,3-Dimethylphenyl)naphthalene. Under an argon atmosphere, to a solution of 2-bromonaphthalene (311 mg, 1.5 mmol) and tetrakis(triphenylphosphine)palladium (0) (17 mg, 15 μ mol) in tetrahydrofuran (5 mL) was added dropwise a 1.0 M solution of 2,3-dimethylphenylmagnesium bromide (2 mmol) in ether (2 mL) at 70-80 °C.³⁰ After the mixture was heated at reflux for 2.5 h, the reaction was quenched by addition of water. The organic layer was separated, washed with 10 % aqueous HCl and saturated aqueous $NaHCO_3$, and then dried over $MgSO_4$. Solvents were removed *in vacuo*, and the residue was purified by flash column chromatography (silica gel, hexane) giving the title compound (230 mg, 66%). Mp 77-79 °C (Ethanol). ^1H -NMR (400MHz, CD_2Cl_2) δ 2.20 (3H, s), 2.37(3H, s), 7.15-7.21 (3H, m), 7.45 (1H, dd, J = 8.4, 2.0Hz), 7.48-7.53 (2H, m), 7.75 (1H, s), 7.86-7.91 (3H, m). ^{13}C -NMR (100MHz, CD_2Cl_2) δ 16.6, 20.2, 124.8, 125.3, 125.6, 126.8, 127.1, 127.27, 127.32, 127.4, 127.6, 128.4, 131.8, 132.9, 133.7, 136.8, 139.7, 141.6. IR (KBr) 3051, 2937, 1598, 1499, 1477, 1456, 1268, 1130, 1075, 1016, 987, 947, 893, 861, 827, 784, 742, 724 cm^{-1} . MS (EI, 70eV) m/z (%) 232 (100, M^+), 217 (45), 202 (15). HRMS (EI, 70eV) Calcd. for $C_{18}H_{16}$: 232.1251. Found: 232.1254 (M^+).

2-(2,4-Dimethylphenyl)naphthalene. ^1H -NMR (400MHz, $CDCl_3$) δ 2.28 (3H, s), 2.39 (3H, s), 7.10 (1H, d, J = 7.2Hz), 7.13 (1H, s), 7.22 (1H, d, J = 8.0Hz), 7.45-7.50 (3H, m), 7.75 (1H, s), 7.84-7.88 (3H, m). ^{13}C -NMR (100MHz, $CDCl_3$) δ 20.6, 21.2, 125.6, 126.0, 126.4, 127.3, 127.5, 127.7, 127.77, 127.82, 129.8, 131.0, 132.1, 133.2, 135.2, 136.8, 138.9, 139.4. IR (neat) 3053, 2920, 1600, 1498, 1449, 1269, 1231, 1192, 1130, 1028, 947, 896, 859, 814, 748 cm^{-1} . MS (EI, 70eV) m/z (%) 232 (100, M^+), 217 (49), 202 (20). HRMS (EI, 70eV) Calcd. for $C_{18}H_{16}$: 232.1251. Found: 232.1255 (M^+).

2-(3,5-Dimethylphenyl)naphthalene. Mp 63-65 °C (Ethanol). ^1H -NMR (400MHz, $CDCl_3$) δ 2.41 (6H, s), 7.02 (1H, s), 7.33 (2H, s), 7.43-7.50 (2H, m), 7.72 (1H, dd, J = 8.8, 2.0Hz), 7.83-7.89 (3H, m), 8.01 (1H, s). ^{13}C -NMR (100MHz, $CDCl_3$) δ 21.6, 125.2, 125.57, 125.61, 125.63,

126.0, 127.5, 128.0, 128.1, 128.9, 132.5, 133.7, 138.2, 138.7, 141.0. IR (KBr) 3054, 2909, 1600, 1504, 1458, 1270, 1129, 1038, 1017, 951, 889, 846, 818, 747 cm^{-1} . MS (EI, 70eV) m/z (%) 232 (100, M^+), 215 (20), 202 (11). HRMS (EI, 70eV) Calcd. for $\text{C}_{18}\text{H}_{16}$: 232.1251. Found: 232.1253 (M^+).

2-(3,4-Dimethylphenyl)naphthalene. Mp 62-64 °C (Ethanol). ^1H -NMR (400MHz, C_6D_6) δ 2.09 (3H, s), 2.11 (3H, s), 7.10 (1H, d, $J = 8.0\text{Hz}$), 7.25-7.32 (2H, m), 7.43 (1H, dd, $J = 8.0, 1.6\text{Hz}$), 7.45 (1H, s), 7.66-7.72 (4H, m), 8.00 (1H, s). ^{13}C -NMR (100MHz, CDCl_3) δ 19.6, 20.1, 124.6, 125.2, 125.5, 125.6, 126.0, 127.5, 128.0, 128.1, 128.5, 130.0, 132.3, 133.6, 135.7, 136.8, 138.4, 138.5. IR (KBr) 3051, 2971, 1596, 1496, 1446, 1271, 1130, 1018, 989, 949, 901, 888, 859, 816, 787, 742, 715 cm^{-1} . MS (EI, 70eV) m/z (%) 232 (100, M^+), 217 (30), 202 (11). HRMS (EI, 70eV) Calcd. for $\text{C}_{18}\text{H}_{16}$: 232.1251. Found: 232.1263 (M^+).

2-(2-Methylphenyl)naphthalene.³¹ ^1H -NMR (400 MHz, CDCl_3) δ 2.31 (3H, s), 7.25-7.34 (4H, m), 7.45-7.52 (3H, m), 7.77 (1H, br s), 7.83-7.89 (3H, m). ^{13}C -NMR (100 MHz, CDCl_3) δ 20.6, 125.7, 126.0, 127.2, 127.3, 127.49, 127.54, 127.6, 127.8, 129.8, 130.2, 132.1, 133.1, 135.3, 139.3, 141.6 (Two carbons overlapped). IR (KBr) 3054, 3017, 2953, 1597, 1491, 1455, 1380, 1272, 944, 898, 858, 822, 772, 758, 725 cm^{-1} . MS (EI, 70 eV) m/z (%) 218 (100, M^+), 202 (27). HRMS (EI, 70 eV) Calcd. for $\text{C}_{17}\text{H}_{14}$: 218.1095. Found: 218.1082 (M^+).

2-(3-Methylphenyl)naphthalene.³² ^1H -NMR (400 MHz, CDCl_3) δ 2.45 (3H, s), 7.19 (1H, br d, $J = 7.2\text{ Hz}$), 7.37 (1H, t, $J = 7.2\text{ Hz}$), 7.44-7.54 (4H, m), 7.73 (1H, dd, $J = 8.4, 1.6\text{ Hz}$), 7.83-7.92 (3H, m), 8.02 (1H, d, $J = 1.6\text{ Hz}$). ^{13}C -NMR (100 MHz, CDCl_3) δ 21.6, 124.4, 125.5, 125.55, 125.64, 126.0, 127.4, 127.9, 128.0, 128.1, 128.6, 132.4, 133.5, 138.1, 138.4, 140.8 (Two carbons overlapped). IR (neat) 3054, 2919, 1604, 1490, 889, 856, 820, 785, 745, 701 cm^{-1} . MS (EI, 70 eV) m/z (%) 218 (100, M^+), 202 (24). HRMS (EI, 70 eV) Calcd. for $\text{C}_{17}\text{H}_{14}$: 218.1095. Found: 218.1102 (M^+).

2-(4-Methylphenyl)naphthalene.³³ Mp 91-93 °C (Ethanol). ^1H -NMR (400 MHz, CDCl_3) δ 2.42 (3H, s), 7.28 (2H, d, $J = 8.0\text{ Hz}$), 7.43-7.51 (2H, m), 7.62 (2H, d, $J = 8.0\text{ Hz}$), 7.73 (1H, dd, J

= 8.4, 2.0 Hz), 7.82-7.90 (3H, m), 8.01 (1H, s). ^{13}C -NMR (100 MHz, CDCl_3) δ 21.2, 125.2, 125.4, 125.6, 126.0, 127.0, 127.5, 128.0, 128.2, 129.4, 132.3, 133.5, 136.9, 138.0, 138.2. IR (KBr) 3053, 1598, 1501, 1343, 1129, 1113, 893, 856, 811, 747 cm^{-1} . MS (EI, 70 eV) m/z (%) 218 (100, M^+), 202 (19). HRMS (EI, 70 eV) Calcd. for $\text{C}_{17}\text{H}_{14}$: 218.1095. Found: 218.1092 (M^+).

1,2-Binaphthyl.³⁴ ^1H -NMR (400MHz, CDCl_3) δ 7.40-7.44 (1H, m), 7.48-7.58 (5H, m), 7.64 (1H, dd, J = 8.4, 0.4 Hz), 7.88-7.96 (7H, m). ^{13}C -NMR (100MHz, CDCl_3) δ 125.3, 125.7, 125.9, 125.96, 125.97, 126.2, 127.1, 127.5, 127.6, 127.9, 128.2, 128.3, 128.6, 131.6, 132.4, 133.3, 133.7, 138.2, 140.0. IR (KBr) 3038, 2924, 1588, 1503, 1394, 1270, 1197, 1131, 1014, 966, 952, 893, 859, 832, 801, 776, 745 cm^{-1} . MS (EI, 70eV) m/z (%) 254 (100, M^+), 126 (28). HRMS (EI, 70eV) Calcd. for $\text{C}_{20}\text{H}_{14}$: 254.1095. Found: 254.1092 (M^+).

2,2-Binaphthyl.³⁴ Mp 186-188 °C (Ethanol). ^1H -NMR (400MHz, CDCl_3) δ 7.48-7.55 (4H, m), 7.88-7.90 (4H, m), 7.93-7.95 (4H, m), 8.17 (2H, s). ^{13}C -NMR (100MHz, CDCl_3) δ 125.6, 125.9, 126.0, 126.2, 127.5, 128.1, 128.4, 132.5, 133.6, 138.3. IR (KBr) 3052, 1593, 1497, 1390, 1277, 1200, 1130, 1010, 964, 951, 882, 853, 812, 747, 738 cm^{-1} . MS (EI, 70eV) m/z (%) 254 (100, M^+), 126 (14). HRMS (EI, 70eV) Calcd. for $\text{C}_{20}\text{H}_{14}$: 254.1095. Found: 254.1091 (M^+).

Reaction of Naphthalene 2 and Adamantane 41. Under an argon atmosphere, a 1.0 M solution of GaCl_3 in cyclohexane (0.20 mL) was added to a solution of **2** (513 mg, 4.0 mmol) and **41** (545 mg, 4 mmol) in cyclohexane (1.8 mL). The mixture was heated to 70 °C, and stirred for 12 h at the temperature. After quenching the reaction by the addition of water, the organic layer was separated, washed with saturated aqueous NH_4Cl and water, and dried over MgSO_4 . Solvents were removed *in vacuo*, and the residue was heated with 5% Pd/C (210 mg) in refluxing 1-methylnaphthalene **6** (0.4 mL) for 4 h. The mixture was diluted with ether, and filtered by passing through celite. The solvents were removed *in vacuo*, and the residue was purified by flash column chromatography (silica gel, hexane) and GPC giving a monoalkylated product **42**

(140 mg, 267% based on GaCl₃) and a dialkylated product **43** (9 mg, 11% based on GaCl₃). 2-(1-Adamantyl)naphthalene **42**:³⁵ Mp 136-138 °C (Ethanol). Anal. Calcd for C₁₇H₂₀: C, 91.55; H, 8.45%. Found: C, 90.80; H, 8.50%. ¹H-NMR (400MHz, CDCl₃) δ 1.81 (6H, br s), 2.01 (6H, d, *J* = 2.8 Hz), 2.13 (3H, br s), 7.38-7.45 (2H, m), 7.56 (1H, dd, *J* = 8.8, 2.0 Hz), 7.71 (1H, s), 7.77-7.81 (3H, m). ¹³C-NMR (100MHz, CDCl₃) δ 29.1, 36.5, 37.0, 43.2, 122.7, 124.0, 125.0, 125.5, 127.2, 127.3, 127.8, 131.6, 133.4, 148.6. IR (KBr) 3053, 2908, 2844, 1633, 1593, 1504, 1447, 1342, 1127, 1034, 855, 804, 742 cm⁻¹. MS (EI, 70eV) *m/e*(%) 262 (100, M⁺), 205 (64), 168 (17), 141 (16). HRMS (EI, 70eV) Calcd. for C₂₀H₂₂: 262.1720. Found: 262.1710 (M⁺).

2,7-Bis(1-adamantyl)naphthalene **43**:³⁵ Mp >300 °C (Ethanol). ¹H-NMR (400MHz, CDCl₃) δ 1.81 (12H, br t, *J* = 14.4 Hz), 2.01 (12H, d, *J* = 2.8 Hz), 2.14 (6H, br s), 7.51 (2H, dd, *J* = 8.4, 2.0 Hz), 7.70 (2H, d, *J* = 0.4 Hz), 7.74 (2H, d, *J* = 8.4 Hz). ¹³C-NMR (100MHz, CDCl₃) δ 29.1, 36.4, 37.0, 43.3, 122.8, 123.3, 126.8, 129.9, 133.4. IR (KBr) 3056, 2900, 2845, 1631, 1603, 1513, 1447, 1341, 1315, 1254, 1102, 1034, 977, 902, 839, 812, 734 cm⁻¹. MS (EI, 70eV) *m/e*(%) 396 (100, M⁺), 344 (21), 302 (5), 275 (6), 205 (6), 135 (65), 107 (9), 93 (23), 79 (23), 67 (13), 55 (12), 41 (14). HRMS (EI, 70eV) Calcd. for C₃₀H₃₆: 396.2815. Found: 396.2820 (M⁺).

NOE

Reaction of Naphthalene 2 and 1-Methyladamantane 44. 2-(4-Methyl-1-adamantyl)naphthalene **45**: Mp 92-94°C (Ethanol). Anal. Calcd. for C₂₁H₂₄: C, 91.24, H, 8.76%. Found: C, 91.17, H, 8.76%. ¹H-NMR (400MHz, CDCl₃) δ 0.90 (3H, s), 1.52 (4H, br s), 1.70 (4H, br s), 1.89 (2H, br d, *J* = 12.4 Hz), 1.96 (2H, br d, *J* = 11.6 Hz), 2.18 (br s), 7.38-7.45 (2H, m), 7.56 (1H, dd, *J* = 8.8, 2.0 Hz), 7.71 (1H, s), 7.77-7.81 (3H, m). ¹³C-NMR (100MHz, CDCl₃) δ 29.6, 30.9, 31.3, 36.2, 37.4, 42.5, 43.9, 50.2, 122.7, 124.1, 125.0, 125.5,

127.2, 127.3, 127.8, 131.6, 133.4, 148.2. IR (KBr) 3054, 2904, 2842, 1631, 1595, 1504, 1454, 1362, 1341, 1319, 856, 809, 769, 742 cm^{-1} . MS (EI, 70eV) $m/e(\%)$ 276 (100, M^+), 219 (44), 205 (18), 168 (12), 141 (13). HRMS (EI, 70eV) Calcd. for $\text{C}_{21}\text{H}_{24}$: 276.1877. Found 276.1870 (M^+).

Reaction of Naphthalene 2 and 1,3-Dimethyladamantane 46. 2-(3,5-Dimethyl-1-adamantyl)naphthalene **47**: Anal. Calcd for $\text{C}_{22}\text{H}_{26}$: C, 90.97, H, 9.03%. Found: C, 90.62, H, 9.02%. ^1H -NMR (400MHz, CDCl_3) δ 0.91 (6H, s), 1.24-1.29 (2H, m), 1.40-1.48 (4H, m), 1.63 (4H, q, $J = 12.8$ Hz), 1.84 (2H, br s), 2.22 (1H, quint, $J = 3.2$ Hz), 7.38-7.45 (2H, m), 7.56 (1H, dd, $J = 8.4, 2.0$ Hz), 7.71 (1H, d, $J = 2.0$ Hz), 7.77-7.81 (3H, m). ^{13}C -NMR (100MHz, CDCl_3) δ 30.1, 30.9, 31.7, 38.3, 41.8, 43.1, 49.5, 51.0, 122.8, 124.1, 125.0, 125.5, 127.2, 127.3, 127.8, 131.7, 133.4, 147.9. IR (neat) 3056, 2898, 2840, 1633, 1598, 1505, 1453, 1373, 1357, 1340, 852, 815, 742 cm^{-1} . MS (EI, 70eV) $m/e(\%)$ 290 (100, M^+), 233 (22), 219 (33), 141 (15). HRMS (EI, 70eV) Calcd. for $\text{C}_{22}\text{H}_{26}$: 290.2033. Found 290.2027 (M^+).

Reaction of Naphthalene 2 and 1,3,5-Trimethyladamantane 48. 2-(3,5,7-Trimethyl-1-adamantyl)naphthalene **49**: ^1H -NMR (400MHz, CDCl_3) δ 0.93 (9H, s), 1.15-1.22 (6H, m), 1.57 (6H, s), 7.39-7.47 (2H, m), 7.57 (1H, dd, $J = 8.4, 2.0$ Hz), 7.72 (1H, s), 7.78-7.82 (3H, m). ^{13}C -NMR (100MHz, CDCl_3) δ 30.5, 32.4, 39.2, 48.9, 50.4, 122.8, 124.2, 125.0, 125.6, 127.2, 127.3, 127.8, 131.7, 133.4, 147.6. IR (neat) 3057, 2943, 2890, 2861, 2836, 1633, 1599, 1505, 1454, 1352, 853, 820, 801, 743 cm^{-1} . MS (EI, 70eV) $m/e(\%)$ 304 (100, M^+), 289 (6), 233 (28), 141 (14), 121 (26). HRMS (EI, 70eV) Calcd. for $\text{C}_{23}\text{H}_{28}$: 304.2190. Found: 304.2197 (M^+).

Reaction of 2-Chloronaphthalene 11 and Adamantane 41. Under an argon atmosphere, a 1.0 M solution of GaCl_3 in cyclohexane (0.04 mL) was added to a solution of **11** (130 mg, 0.8 mmol) and **41** (109 mg, 0.8 mmol) in cyclohexane (0.36 mL). The mixture was heated to 70 $^\circ\text{C}$, and stirred for 12 h at the temperature. After quenching the reaction by addition of water, the organic layer was separated, washed with saturated aqueous NH_4Cl and water, and dried over MgSO_4 . Solvents were removed *in vacuo*, and the residue was passed through short silica gel

column (hexane). The concentrated crude products were heated at reflux with DDQ (1816 mg, 8.0 mmol) in dry toluene (8.0 mL) for 4 h. After cooled to room temperature, saturated aqueous NaHCO_3 was added, and the insoluble materials were removed by filtration through celite. The organic layer was separated, washed with water, and dried over MgSO_4 . Solvents were removed *in vacuo*, and the residue was purified by flash column chromatography (silica gel, hexane) and GPC giving monoalkylated products (22 mg, 181% based on GaCl_3) as a 1 : 1 mixture of 6-(1-adamantyl)-2-chloronaphthalene **50** and 7-(1-adamantyl)-2-chloronaphthalene **51**. The structures of **50** and **51** at the aromatic moiety were determined by the presence of 4 broad singlets/doublets (*meta* coupling), 4 doublets of doublet (*ortho* and *meta* coupling), and 4 doublets (*ortho* coupling) by ^1H -NMR. ^1H -NMR (600MHz, C_6D_6) δ 1.81 (12H, br q, $J = 12.4$ Hz), 2.00 (12H, br s), 2.15 (6H, br s), 7.35 (1H, dd, $J = 8.7, 2.1$ Hz), 7.38 (1H, dd, $J = 8.7, 2.1$ Hz), 7.57 (1H, dd, $J = 8.7, 1.9$ Hz), 7.60 (1H, dd, $J = 8.7, 1.9$ Hz), 7.62 (1H, br s), 7.69 (1H, br s), 7.71 (1H, d, $J = 8.3$ Hz), 7.72 (1H, d, $J = 8.5$ Hz), 7.74 (1H, d, $J = 8.7$ Hz), 7.767 (1H, d, $J = 8.8$ Hz), 7.774 (1H, br s), 7.79 (1H, d, $J = 1.7$ Hz). ^{13}C -NMR (150MHz, C_6D_6) δ 29.0, 36.5, 36.8, 43.1, 122.1, 122.8, 124.5, 125.3, 126.1, 126.1, 126.6, 126.7, 127.4, 128.9, 129.6, 130.0, 130.8, 131.4, 131.8, 132.4, 134.2, 149.2, 150.0. IR (KBr) 2901, 2848, 1629, 1591, 1497, 1453, 1074, 901, 872, 838, 815, 798 cm^{-1} . MS (EI, 70 eV) m/z (%) 296 (100, M^+), 239 (48), 204 (37), 188 (13), 175 (27), 165 (20), 152 (15), 141 (11), 127 (6). HRMS (EI, 70 eV) Calcd for $\text{C}_{20}\text{H}_{21}\text{Cl}$: 296.1428. Found: 296.1319 (M^+).

1-(1-Methylcyclohexyl)naphthalene.³⁶ Under an argon atmosphere, to a solution of naphthalene (128 mg, 1.0 mmol) in dichloromethane (8 mL) was added a 1.0 M solution of GaCl_3 in methylcyclohexane (2.0 mL) at -78°C . To this mixture, 1-methylcyclohexene (110 mg, 1.0 mmol) in dichloromethane (2 mL) was added. After being stirred at -78°C for 2 h, THF (3 mL) and water were added, and the mixture was warmed to room temperature. The organic layer was separated, and dried over MgSO_4 . Solvents were removed *in vacuo*, and the residue was purified by GPC to give 1-(1-methylcyclohexyl)naphthalene (23 mg, 10%). ^1H -NMR (400

MHz, CDCl₃) δ 1.26 (3H, s), 1.40-1.55 (4H, m), 1.55-1.72 (4H, m), 2.08-2.20 (2H, m), 7.36-7.46 (2H, m), 7.55 (1H, dd, J = 8.8, 2.0 Hz), 7.75-7.82 (3H, m). ¹³C-NMR (100 MHz, acetone-*d*₆) δ 23.4, 27.1, 30.8, 38.5, 124.7, 125.5, 125.8, 126.2, 127.8, 128.3, 128.5, 132.4, 134.4, 147.7. IR (neat) 3057, 2929, 2856, 1599, 1505, 1454, 852, 815, 744 cm⁻¹. MS (EI, 70 eV) m/z (%) 224 (100, **M**⁺), 209 (46), 181 (73), 168 (28), 155 (27), 141 (71). HRMS (EI, 70 eV) Calcd. for C₁₇H₂₀: 224.1564. Found: 224.1567 (**M**⁺).

Reaction of 1-(1-Methylcyclohexyl)naphthalene with GaCl₃. Under an argon atmosphere, a 1.0 M solution of GaCl₃ (0.086 mmol) in methylcyclohexane (0.086 mL) was added to a solution of 1-(1-methylcyclohexyl)naphthalene (49 mg, 0.22 mmol) in cyclohexane (2.1 mL) at room temperature. After being stirred for 40 h at 70 °C, the reaction was quenched by addition of water. The organic layer was separated, dried over MgSO₄, and concentrated. Naphthalene **2** (50% based on GaCl₃) and 2-methylcyclohexylnaphthalenes **19**, **20**, and **21** (3 isomers in a 1 : 3 : 2 ratio by GC, 50% based on GaCl₃) were detected by ¹H-NMR using dibromomethane (7.0 μ L, 0.1 mmol) as internal standard. GC analysis indicated that the former products were identical with those obtained by the reaction of methylcyclohexane **18** and naphthalene **2** in the presence of GaCl₃.

(1*R**,3*R**,6*R**)-2-(Decahydronaphthalen-3-yl)naphthalene and (1*R**,3*S**,6*R**)-2-(Decahydro-naphthalen-3-yl)naphthalene. Under an argon atmosphere, to a solution of *trans*-2-decalone¹³ (133 mg, 0.88 mmol) in Et₂O (1 mL) was added dropwise a 1.0 M solution of 2-naphthylmagnesium bromide in Et₂O (1 mL, 1 mmol). After heated at reflux for 1 h, the mixture was cooled to 0 °C in an ice bath, and saturated aqueous NH₄Cl was added. The organic layer was separated, washed with 10 % aqueous HCl and water, and then dried over MgSO₄. Solvents were removed *in vacuo*, and the residue was purified by flash column chromatography (silica gel, hexane : ethyl acetate = 10 : 1) giving (1*R**,6*R**)-3-(2-naphthyl)decahydronaphthalen-3-ol (66 mg, 27%). Under an argon atmosphere, to a solution of

the alcohol (35 mg, 0.12 mmol) and triethylsilane (0.04 mL, 0.25 mmol) in dichloromethane (1 mL) was added dropwise boron trifluoride diethyl etherate (0.03 mL, 0.25 mmol). The mixture was stirred for 0.5 h at 25 °C, and the reaction was quenched by addition of saturated aqueous NaHCO₃. The organic layer was separated, and dried over MgSO₄. Solvents were removed *in vacuo*, and the residue was purified by flash column chromatography (silica gel, hexane : ethyl acetate = 5 : 1) giving the title compound as a 1 : 1 mixture of diastereomers regarding the 3-carbon (17 mg, 51%). ¹H-NMR (400MHz, CDCl₃) δ 0.81-0.94 (1H, m), 0.96-1.35 (13H, m), 1.46-1.78 (13H, m), 1.83-1.99 (3H, m), 2.19 (1H, dd, *J* = 14.0, 2.8 Hz), 2.38 (1H, dt, *J* = 14.0, 2.8 Hz), 2.74 (benzylic proton of **3**, 1H, tt, *J* = 12.4, 3.6 Hz), 3.29 (1H, br s), 7.36-7.50 (6H, m), 7.63 (**3**, 1H, s), 7.75-7.82 (7H, m). ¹³C-NMR (100MHz, CDCl₃) δ 26.7, 26.76, 26.77 (**3**), 26.8 (**3**), 29.5, 29.9, 33.93, 33.95 (**3**), 34.1 (**3**), 34.3, 34.36 (**3**), 34.40 (**3**), 37.2, 37.9, 38.2, 41.8 (**3**), 43.1 (**3**), 43.5 (**3**), 44.0, 44.7 (**3**), 124.4 (**3**), 124.9 (**3**), 125.0, 125.5, 125.58 (**3**), 125.60, 126.1 (**3**), 126.8, 127.3, 127.4, 127.39 (**3**), 127.42 (**3**), 127.55 (**3**), 127.59 (**3**), 131.4, 132.0, 133.3, 133.52 (**3**), 142.55, 145.1 (**3**). IR (neat) 3054, 2918, 2849, 1633, 1599, 1507, 1447, 852, 816, 749 cm⁻¹. MS (EI, 70eV) *m/z* (%) 264 (100, **M**⁺), 167 (18), 154 (90), 142 (30), 128 (21). HRMS (EI, 70eV) Calcd. for C₂₀H₂₄: 264.1879. Found: 264.1881 (**M**⁺).

(1*R**,3*R**,6*S**)-2-(Decahydronaphthalen-3-yl)naphthalene and **(1*S**,3*R**,6*R**)-2-(Decahydro-**

naphthalen-3-yl)naphthalene: ¹H-NMR (400MHz, CDCl₃) δ 1.25-1.32 (m), 1.35-1.45 (m), 1.51-1.59 (m), 1.66-1.83 (m), 1.86-2.01 (m), 2.71 (benzylic proton, 1H, br s), 2.86 (benzylic proton, 1H, br s), 7.35-7.44 (6H, m), 7.62 (1H, br s), 7.64 (1H, br s), 7.74-7.79 (6H, m). ¹³C-NMR (100MHz, CDCl₃) δ 21.1, 21.2, 26.0, 26.3, 26.7, 27.2, 27.3, 28.6, 32.3, 32.5, 32.8, 33.9, 34.7, 35.6, 35.9, 36.6, 36.9, 38.5, 40.6, 45.2, 124.3, 124.5, 124.85, 124.87, 125.60, 125.62, 126.1, 126.2, 127.39, 127.41, 127.43, 127.5, 127.6, 131.9, 133.5, 145.2, 145.3. IR (KBr) 3052, 2924, 2856, 1631, 1599, 1505, 1599, 1440, 862, 815, 745 cm⁻¹. MS (EI, 70eV) *m/z* (%) 264 (100, **M**⁺), 167 (21), 154 (75), 142 (28), 128 (24). HRMS (EI, 70eV) Calcd. for C₂₀H₂₄: 264.1877.

Found: 264.1880 (M^+).

(1*R**,3*R**,6*R**)-5-(Decahydronaphthalen-3-yl)-1,3-dimethylbenzene 17 and (1*R**,3*S**,6*R**)-5-(Decahydronaphthalen-3-yl)-1,3-dimethylbenzene: ^1H -NMR (400 MHz, CDCl_3) δ 0.88-1.11 (6H, m), 1.14-1.29 (5H, m), 1.40-1.81 (18H, m), 1.85 (1H, d, $J = 12.8$ Hz), 2.04 (1H, d, $J = 13.6$ Hz), 2.22 (1H, d, $J = 14.0$ Hz), 2.29 (6H, s), 2.31 (6H, s), 2.50 (benzylic proton of **17**, 1H, t, $J = 11.4$ Hz), 3.06 (benzylic proton, 1H, br s), 6.81 (**17**, 4H, s), 6.96 (2H, s). ^{13}C -NMR (100 MHz, CDCl_3) δ 21.5 (**17**), 21.7, 26.7, 26.75 (**17**), 26.81, 26.84 (**17**), 29.6, 29.9, 34.0 (**17**), 34.1 (**17**), 34.3, 34.4 (**17**), 34.5 (**17**), 36.9, 37.7, 38.3, 41.9, 43.1 (**17**), 43.5 (**17**), 44.0, 44.5 (**17**), 124.5 (**17**), 125.4, 126.6, 127.3 (**17**), 137.2, 137.5 (**17**), 145.1, 147.6 (**17**). IR (neat) 3013, 2918, 2850, 1604, 1447, 847, 706 cm^{-1} . MS (EI, 70 eV) m/z (%) 242 (48, M^+), 146 (9), 132 (100), 120 (18). HRMS (EI, 70 eV) Calcd. for $\text{C}_{18}\text{H}_{26}$: 242.2033. Found: 242.2033 (M^+).

Reaction of *cis*-Bicyclo[4.4.0]decane 1 with GaCl_3 . Under an argon atmosphere, a 1.0 M solution of GaCl_3 in *cis*-**1** (0.25 mL, 0.25 mmol) was added to *cis*-**1** (1.25 mL), and the mixture was heated at 70 °C for 70 h. The solution was directly analyzed by GC, which was shown to be a 1.3 : 1.0 mixture of the *cis*-**1** and *trans*-**1** after 40 h, and a 1.0 :14.2 mixture after 70 h.

Deuteration Experiment of 1-Methylnaphthalene 6. Under an argon atmosphere, a 1.0 M solution of GaCl_3 in cyclohexane (1.0 mL, 1 mmol) was added to a solution of **6** (0.14 mL, 1 mmol) in cyclohexane (9.0 mL), and the mixture was stirred at room temperature for 1 h. Then, the mixture was added to a 2.0 M solution of sodium deuterioxide in deuterium oxide (2 mL). After being stirred for 10 min, the organic layer was separated, washed with sat. aqueous NH_4Cl and water, and dried over MgSO_4 . Solvents were removed *in vacuo*, and the residue was purified by flash chromatography (silica gel, hexane) giving deuterated 1-methylnaphthalene **6-d** (110 mg, 77%). Deuteration ratio was determined by ^1H - and ^2H -NMR employing 1,3,5-trimethylbenzene and dimethylsulfoxide- d_6 as internal standard, respectively.

References

- (27) Moreau, P.; Finiels, A.; Geneste, P.; Moreau, F.; Solofo, J. *J. Org. Chem.* **1992**, *57*, 5040-5041. (28) Fieser, L. F.; Price, C. C. *J. Am. Chem. Soc.*, **1936**, *58*, 1838-1843.
- (29) (a) Koch, K-H.; Müllen, K. *Chem. Ber.*, **1991**, *124*, 2091-2100. (b) Weitz, I. S.; Rabinovitz, M. *J. Chem. Soc. Perkin. Trans. 1*, **1993**, 117-120.
- (30) Sekiya, A.; Ishikawa, N. *J. Organomet. Chem.*, **1977**, *125*, 281-290.
- (31) Friedel, R. A.; Orchin, M.; Reggel, L. *J. Am. Chem. Soc.* **1948**, *70*, 199-204.
- (32) Simonitsch, E.; Eisenhuth, W.; Stamm, O. A.; Schmid, H. *Helv. Chim. Acta.* **1964**, *47*, 1459-1475.
- (33) Phillips, D. D.; Chatterjee, D. N. *J. Am. Chem. Soc.* **1958**, *80*, 1360-1366.
- (34) Ibuki, E.; Ozawa, S.; Fujioka, Y.; Mizutani, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 845-851.
- (35) (a) Rarog, B. G.; Topchii, V. A.; Yurchenko, A. G. *J. Org. Chem. USSR, Engl. Transl.* **1981**, *17*, 470-472. (b) Zhukov, A. G.; Topchii, V. A.; Sungurova, V. P.; Bass, S. I.; Yurchenko, A. G. *J. Org. Chem. USSR, Engl. Transl.* **1990**, *26*, 296-299.
- (36) Khromov, S. I.; Balenkova, E. S. *Chem. Abstr.* **1956**, 11305.

^1H -NMR and ^{13}C -NMR spectra

¹H-NMR (400 MHz, CDCl₃) of **15**

¹³C-NMR (100 MHz, CDCl₃) of **15**

^{13}C -NMR (100 MHz, CDCl_3)

^{13}C -NMR (100 MHz, CDCl_3)

^{13}C -NMR (100 MHz, CDCl_3)