

products were determined by capillary GLC. An analytical sample was obtained by bulb-to-bulb distillation or recrystallization.

4-[3-(phenylethynyl)bicyclo[2.2.1]hept-2-yl]butan-2-one: >98% isomeric purity; a pale yellow oil; bp 150 °C (2 mmHg); $R_f = 0.35$ (hexane/AcOEt = 10:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 1.13 (dt, $J = 10.4, 1.8$ Hz, 1 H), 1.19–1.22 (m, 2 H), 1.50–1.56 (m, 3 H), 1.60–1.67 (m, 1 H), 1.71–1.79 (dt, $J = 10.4, 1.8$ Hz, 1 H), 1.88–1.95 (m, 1 H), 2.00 (s, 1 H), 2.11 (s, 3 H), 2.41 (s, 1 H), 2.41–2.49 (m, 1 H), 2.61–2.64 (m, 1 H), 2.66 (d, $J = 9.1$ Hz, 1 H), 7.23–7.28 (m, 5 H); $^{13}\text{C NMR}$ (125.7 MHz, CDCl_3) δ 27.15, 28.16, 29.91, 30.02, 34.24, 39.26, 41.62, 43.32, 44.79, 45.39, 82.67, 91.48, 124.07, 127.42, 128.18, 131.40, 209.32; IR (neat) 2955, 1716, 768 cm^{-1} ; GC/MS (EI, 70 eV) m/z (rel intensity) 266 (M^+ , 70), 115 (100). Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}$: C, 85.67; H, 8.32. Found: C, 85.57; H, 8.45.

(3R*,1'S*,2'S*,3'S*,4'R*)-3-[3'-[(Trimethylsilyl)ethynyl]bicyclo[2.2.1]hept-2'-yl]cyclopentanone (9a): 98% de; a colorless crystal (hexane); mp 53.5–54.5 °C; $R_f = 0.31$ (hexane/AcOEt = 10:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 0.10 (s, 9 H), 1.11–1.17 (c, 3 H), 1.42 (t, $J = 9.2$ Hz, 1 H), 1.48–1.60 (c, 3 H), 1.66–1.70 (m, 1 H), 1.73 (ddd, $J = 18.0, 9.4, 1.5$ Hz, 1 H), 2.08–2.17 (m, 1 H), 2.20–2.30 (c, 4 H), 2.36 (br s, 1 H), 2.48 (dd, $J = 8.6, 1.2$ Hz, 1 H), 2.76 (ddt, $J = 18.0, 6.7, 1.2$ Hz, 1 H); $^{13}\text{C NMR}$ (125.7 MHz, CDCl_3) δ 0.02, 27.28, 28.95, 30.48, 34.39, 38.41, 39.11, 39.59, 44.95, 46.02, 52.94, 86.14, 109.21, 219.86; IR (neat) 2959, 2164, 1742, 1249, 843, 760, 637 cm^{-1} ; GC/MS (EI, 70 eV) m/z (rel intensity) 274 (M^+ , 3), 259 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{OSi}$: C, 74.39; H, 9.55. Found: C, 74.20; H, 9.58.

(3R*,1'S*,2'S*,3'S*,4'R*)- and (3S*,1'S*,2'S*,3'S*,4'R*)-3-(3'-Methyl[2.2.1]hept-2'-yl)cyclopentanone (9b and 10b): 1:1 mixture; a colorless oil; bp 125 °C (1 mmHg); $R_f = 0.28$ (hexane/AcOEt = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 0.89 (d, $J = 7.3$ Hz, 1.5 H), 0.96 (d, $J = 7.3$ Hz, 1.5 H), 0.90–1.28 (c, 3 H), 1.33–1.63 (c, 8 H), 1.70–2.51 (c, 6 H); $^{13}\text{C NMR}$ (100.4 MHz, CDCl_3) δ 16.38, 16.62, 29.03, 29.11, 29.66, 30.49, 30.67, 31.17, 32.77, 32.95, 37.00, 37.29, 38.33, 38.55, 39.34, 40.35, 40.40, 40.50, 45.01, 45.05, 45.17, 47.00, 52.26, 53.73, 219.74, 220.29; IR (neat) 2955, 2872, 1741, 1462, 1165, 733 cm^{-1} ; GC/MS (EI, 70 eV) m/z (rel intensity) 192 (M^+ , 59), 109 (100). Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{O}$: C, 81.20; H, 10.48. Found: C, 81.17; H, 10.51.

(3R*,1'S*,4'R*,5'R*,6'R*)-3-[6'-[(Trimethylsilyl)ethynyl]bicyclo[2.2.1]hepten-5'-yl]cyclopentanone (9c): 84% de; a colorless oil; bp 80 °C (1.5 mmHg); $R_f = 0.37$ (hexane/AcOEt = 9:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 0.12 (s, 9 H), 1.37–1.45 (m, 2 H), 1.56–1.67 (m, 1 H), 1.72–1.83 (c, 2 H), 2.08–2.23 (m, 1 H), 2.24–2.38 (c, 4 H), 2.82 (br s, 1 H), 2.89 (dd, $J = 18.6, 7.5$ Hz, 1 H), 2.95 (br s, 1 H), 6.06 (dd, $J = 8.5, 3.1$ Hz, 1 H), 6.16 (dd, $J = 8.5, 3.1$ Hz, 1 H); $^{13}\text{C NMR}$ (125.7 MHz, CDCl_3) δ 0.04, 28.94, 34.58, 38.44, 39.62, 44.02, 46.29, 49.52, 50.45, 85.16, 109.67, 135.75, 138.62, 219.76; IR (neat) 2959, 2164, 1744, 1460, 1250, 1161, 845, 760, 710 cm^{-1} ; GC/MS of major (EI, 70 eV) m/z (rel intensity) 272 (M^+ , 6), 207 ($\text{M}^+ - \text{C}_5\text{H}_5$, 29), 191 (52), 73 (40), 66 (100); GC/MS of minor (EI, 70 eV) m/z (rel intensity) 272 (M^+ , 13), 257 ($\text{M}^+ - \text{Me}$, 59), 73 (100); HRMS for $\text{C}_{12}\text{H}_{19}\text{OSi}$ ($\text{M}^+ - \text{C}_5\text{H}_5$) calcd 207.1205, found 207.1215.

(3R*,1'S*,2'S*,3'S*,4'R*)-3-[3'-[(Trimethylsilyl)ethynyl]bicyclo[2.2.1]hept-2'-yl]cyclohexanone (9d): 96% de; a pale yellow oil; bp 120 °C (1 mmHg); $R_f = 0.40$ (hexane/AcOEt = 8:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 0.12 (s, 9 H), 1.08–1.19 (c, 3 H), 1.30 (t, $J = 7.7$ Hz, 1 H), 1.42–1.55 (c, 3 H), 1.61–1.71 (c, 2 H), 1.96–2.12 (c, 4 H), 2.21–2.38 (c, 4 H), 2.52 (dd, $J = 8.4$ Hz, 1 H), 2.69 (m, 1 H); $^{13}\text{C NMR}$ (125.4 MHz, CDCl_3) δ 0.05, 24.82, 27.79, 29.39, 31.06, 34.69, 37.57, 39.57, 39.93, 41.45, 44.70, 48.26, 50.93, 86.60, 108.57, 211.70; IR (neat) 2955, 2874, 2162, 1713, 1250, 843, 760 cm^{-1} ; GC/MS (EI, 70 eV) m/z (rel intensity) 288 (M^+ , 3), 273 (100). Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{OSi}$: C, 74.94; H, 9.78. Found: C, 74.56; H, 9.57.

(4R*,1'S*,2'S*,3'S*,4'R*)-3,3-Dimethyl-4-[3'-[(trimethylsilyl)ethynyl]bicyclo[2.2.1]hept-2'-yl]cyclopentanone (9e): >98% de; a colorless oil; bp 130 °C (1 mmHg); $R_f = 0.36$ (hexane/AcOEt = 10:1); $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 0.09 (s, 9 H), 0.97 (s, 3 H), 1.11–1.18 (c, 3 H), 1.33 (s, 3 H), 1.43–1.54 (c, 3 H), 1.63–1.87 (c, 2 H), 2.03–2.23 (c, 3 H), 2.36–2.49 (c, 3 H), (dd, $J = 19.0, 8.0$ Hz, 1 H); $^{13}\text{C NMR}$ (67.8 MHz, CDCl_3) δ 0.02, 21.96, 27.55, 30.42, 30.78, 34.31, 38.65, 39.01, 40.31, 44.85, 45.48, 47.35, 50.62, 57.23, 86.13, 109.52, 218.18; IR (neat) 2961, 2874, 2164, 1741, 1250, 841 cm^{-1} ; GC/MS (EI, 70 eV) m/z (rel intensity) 302 (M^+ , 4), 287 (100); HRMS for $\text{C}_{18}\text{H}_{27}\text{OSi}$ ($\text{M}^+ - \text{Me}$) calcd 287.1831, found 287.1825.

Preparation of Dioxolane 12. Ketone **9a** ($[\alpha]_D^{25}$ -8.8° (c 0.56, CHCl_3), 68 mg, 0.25 mmol), (*2R,3R*)-2,3-butanediol (120 mg, 1.332 mmol), and *p*-toluenesulfonic acid (8 mg, 0.04 mmol) were placed in a 30-mL round-bottom flask and dissolved in 20 mL of dry toluene. The flask was fit with a Dean–Stark trap, and the mixture was refluxed for 24 h. The solution was concentrated, and the product was purified by silica gel chromatography (hexane/AcOEt = 10:1) to give dioxolane **12** (60 mg) in 70% yield. This procedure was repeated with racemic ketone **9a**, which provided racemic dioxolane **12**. The optically active ketone **9a** obtained from the nickel-catalyzed coupling reaction in the presence of (*S*)-**11** was determined to be 6% ee by capillary GLC analysis of both diastereomers of dioxolane **12**. Spectral data for **12**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 0.14 (s, 9 H), 1.04–2.11 (c, 20 H), 2.25–2.50 (m, 3 H), 3.45–3.58 (m, 2 H); IR (neat) 2961, 2872, 2166, 1249, 1097, 842, 760 cm^{-1} ; GC/MS (EI, 70 eV) m/z (rel intensity) 346 (M^+ , 38), 127 (100); HRMS for $\text{C}_{21}\text{H}_{34}\text{O}_2\text{-Si}$ (M^+) calcd, 346.2328, found, 346.2335.

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Supporting Information Available: Copies of $^{13}\text{C NMR}$ spectra for **9c** and **9e** and X-ray crystallographic details for **9a** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Additions and Corrections

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A. Sofia E. Karlström, Magnus Rönn, Atli Thorarensen, and Jan-E. Bäckvall*. A Versatile Route to 2-Substituted Cyclic 1,3-dienes via a Copper(I)-Catalyzed Cross-Coupling Reaction of Dienyl Triflates with Grignard Reagents.

Page 2522. The number of pages of Supporting Information should be changed from 14 to 28.

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