SUPPORTING INFORMATION

An Efficient [4+2+1] Entry to Seven-Membered Rings

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Unless otherwise noted, reagents were commercially available and were used without purification. Tetrahydrofuran (THF) was treated under nitrogen using a solvent purification system (Innovative Technology, Inc., Model # SPS-400-3). Ni(COD)₂ (Strem Chemicals, Inc., used as received) was stored and weighed in an inert atmosphere glovebox. All reactions were conducted in flame-dried glassware under a nitrogen or argon atmosphere. ¹H and ¹³C spectra were obtained in CDCl₃ at rt, unless otherwise noted, on a Varian Mercury 400 or Varian Unity 500 MHz instrument. Chemical shifts of ¹H NMR spectra were recorded in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.27 ppm). Chemical shifts of ¹³C NMR spectra were recorded in ppm from the central peak of CDCl₃ (77.0 ppm) on the δ scale. High resolution mass spectra (HRMS) were obtained on a Kratos MS 80 mass spectrometer by the Central Instrumentation Facility, Department of Chemistry, Wayne State University, Detroit, Michigan.

Starting materials **1a**,¹ **1c** and **1f**,² **1d**,³ **1e**,⁴ and **1g**⁵ were prepared using literature procedures with minor modifications. **1b** and **1h** were prepared and fully characterized as described in the supporting information.

^1H NMR (500 MHz, CDCl_3) δ 6.24 (dt, $J = 16.5, 10.0$ Hz, 1H), 6.13 (dd, $J = 15.0, 10.0$ Hz, 1H), 5.45 (dt, $J = 15.5, 7.5$ Hz, 1H), 5.11 (d, $J = 16.5$ Hz, 1H), 5.00 (d, $J = 10.5$ Hz, 1H), 3.71 (s, 6H), 2.80 (d, $J = 8.0$ Hz, 2H), 2.76 (d, $J = 2.5$ Hz, 2H), 2.01 (t, $J = 2.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.3, 136.7, 135.9, 127.2, 117.1, 78.9, 71.8, 57.3, 53.0, 35.6, 23.0.

4-Methyl-*N*-penta-2,4-dienyl-*N*-prop-2-ynyl-benzenesulfonamide (1b). To a 28 mL THF suspension of NaH (96 mg, 2.4 mmol, 60%) and tetrabutylammonium iodide (75 mg, 0.2 mmol) was added a 2 mL THF solution of 4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (420 mg, 2 mmol) at 0 °C. The resulting mixture was allowed to warm to rt and stirred at rt for 1 h, then a 2 mL THF solution of 5-chloro-penta-1,3-diene (248 mg, 2.4 mmol) was added dropwise. The final solution was stirred at rt overnight. The reaction mixture was quenched with saturated NH_4Cl . Standard extraction and column chromatography provided 480 mg (87%) of product **1b** as a light oil. ^1H NMR (500 MHz, CDCl_3) δ 7.72 (d, $J = 8.5$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 6.30 (dt, $J = 16.5, 10.0$ Hz, 1H), 6.21 (dd, $J = 15.0, 10.5$ Hz, 1H), 5.56 (dt, $J = 14.5, 7.0$ Hz, 1H), 5.20 (d, $J = 16.0$ Hz, 1H), 5.11 (d, $J = 10.5$ Hz, 1H), 4.07 (d, $J = 2.5$ Hz, 2H), 3.85 (d, $J = 6.5$ Hz, 2H), 2.42 (s, 3H), 2.01 (t, $J = 2.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.8, 136.2, 136.0, 135.8, 129.7, 128.0, 127.1, 118.7, 76.7, 74.0, 48.2, 36.0, 21.8. IR (film) 3291,

2922, 2121, 1599 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2\text{S}$ 275.0980, found 275.0980 (M^+).

^1H NMR (500 MHz, CDCl_3) δ 6.35 (m, 1H), 6.29 (m, 1H), 5.76 (dt, $J = 14.5, 6.5$ Hz, 1H), 5.23 (m, 1H), 5.12 (m, 1H), 4.15 (d, $J = 2.5$ Hz, 2H), 4.11 (d, $J = 7.0$ Hz, 2H), 2.44 (t, $J = 2.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 136.4, 134.4, 129.2, 118.3, 79.9, 74.7, 69.9, 57.2.

^1H NMR (500 MHz, CDCl_3) δ 6.26 (dt, $J = 17.5, 10.5$ Hz, 1H), 6.12 (dd, $J = 15.5, 10.5$ Hz, 1H), 5.48 (dt, $J = 15.0, 7.5$ Hz, 1H), 5.13 (d, $J = 16.5$ Hz, 1H), 5.01 (d, $J = 10.0$ Hz, 1H), 3.72 (s, 6H), 2.80 (d, $J = 7.5$ Hz, 2H), 2.72 (q, $J = 2.5$ Hz, 2H), 1.75 (t, $J = 2.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.7, 136.8, 135.6, 127.7, 116.8, 79.2, 73.4, 57.7, 52.9, 35.7, 23.4, 3.7.

^1H NMR (500 MHz, CDCl_3) δ 6.34 (m, 1H), 6.27 (m, 1H), 5.76 (dt, $J = 15.5, 6.2$ Hz, 1H), 5.21 (m, 1H), 5.10 (m, 1H), 4.09 (q, $J = 2.5$ Hz, 2H), 4.07 (dd, $J = 6.5, 1.5$ Hz, 2H), 1.85 (t, $J = 2.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 136.5, 134.0, 129.6, 118.0, 82.8, 75.3, 69.8, 57.9, 3.8.

^1H NMR (300 MHz, CDCl_3) δ 6.20 (dd, $J = 15.0, 10.5$ Hz, 1H), 6.03 (ddq, $J = 15.0, 10.5, 1.5$ Hz, 1H), 5.71 (dq, $J = 15.0, 6.9$ Hz, 1H), 5.57 (dt, $J = 15.3, 6.6$ Hz, 1H), 4.10 (d, $J = 2.4$ Hz, 2H), 4.05 (d, $J = 6.6$ Hz, 2H), 2.40 (t, $J = 2.4$ Hz, 1H), 1.73 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 134.4, 130.9, 130.7, 125.8, 80.0, 74.6, 70.2, 56.9, 18.3.

^1H NMR (400 MHz, CDCl_3) δ 6.20 (dd, $J = 15.5, 10.5$ Hz, 1H), 6.03 (dd, $J = 15.6, 10.5$ Hz, 1H), 5.69 (dq, $J = 15.2, 6.5$ Hz, 1H), 5.59 (dt, $J = 15.2, 6.4$ Hz, 1H), 4.06 (q, $J = 2.4$ Hz, 2H), 4.03 (d, $J = 6.4$ Hz, 2H), 1.84 (t, $J = 2.0$ Hz, 3H), 1.74 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 134.1, 131.0, 130.5, 126.2, 82.6, 75.4, 70.1, 57.6, 18.4, 3.9.

(1-But-2-ynyloxy-4-methyl-penta-2,4-dienyl)-benzene (1h). The procedure (Wipf, P. et al, *Org. Lett.* **2003**, 5, 2449) was followed to prepare the alcohol **A** (4-methyl-1-phenyl-penta-2,4-dien-1-ol). The procedure of making **1b** was followed using NaH (96 mg, 2.4 mmol), tetrabutylammonium iodide (75 mg, 0.2 mmol), alcohol **A** (350 mg, 2 mmol), 1-bromo-2-butyne (210 μL , 2.4 mmol) to afford 360 mg (80%) of product **1h** as a light oil. ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.25 (m, 5H), 6.37 (d, $J = 15.5$ Hz, 1H), 5.76 (dd, $J = 15.0, 7.0$ Hz, 1H), 5.06 (d, $J = 7.5$ Hz, 1H), 5.00 (s, 2H), 4.12 (dq, $J = 15.0, 2.5$ Hz,

1H), 4.06 (dq, $J = 15.0, 2.5$ Hz, 1H), 1.87 (t, $J = 2.5$ Hz, 3H), 1.84 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 141.6, 140.9, 135.2, 129.9, 128.7, 128.0, 127.3, 117.6, 82.6, 81.1, 75.4, 56.2, 18.8, 3.9; IR (film) 2919, 2855, 2222, 1609, 1452 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{15}\text{H}_{15}\text{O}$ 211.1123, found 211.1124 ($\text{M}-\text{CH}_3$) $^+$.

General procedure for the $\text{Ni}(\text{COD})_2$ catalyzed [4+2+1] cycloadditions:

To a premixed THF solution of dienyne (1 equiv, 0.1 M) and TMSCHN_2 (2 equiv) was added a THF solution of $\text{Ni}(\text{COD})_2$ (10 mol%) at 60 $^\circ\text{C}$. The resulting brown solution was stirred at 60 $^\circ\text{C}$ for 10 – 30 minutes and allowed to cool to rt. The solvent was removed by rotary evaporation and the residue was absorbed onto silica gel. Flash column chromatography provided the bicyclic products. All compounds were fully characterized by spectroscopic methods.

7-Trimethylsilylanyl-3,3a,6,7-tetrahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester (2a). General procedure was followed using 50 mg (0.2 mmol) of dienyne, 0.2 mL (0.4 mmol, 2.0 M in Et_2O) of TMSCHN_2 , 6 mg (0.02 mmol) of $\text{Ni}(\text{COD})_2$ to afford 49 mg (76%, 13 : 1 as judged by GC analysis on the crude reaction mixture) of product **2a**. ^1H NMR (500 MHz, CDCl_3) δ 5.70 (dtd, $J = 10.5, 6.5, 2.0$ Hz, 1H), 5.55 (dt, $J = 10.0, 2.0$ Hz, 1H), 5.50 (m, 1H), 3.75 (m, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 2.98 (d, $J = 16.0$ Hz, 1H), 2.91 (dq, $J = 16.0, 2.5$ Hz, 1H), 2.70 (m, 1H), 2.60 (ddd, $J = 12.5, 8.5, 1.0$ Hz, 1H), 2.05 (dd, $J = 12.5, 11.0$ Hz, 1H), 2.01 (m, 1H), 1.74 (m, 1H), -0.01 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 172.5, 172.2, 138.7, 134.0, 130.6, 123.7, 58.6, 53.0, 52.9, 42.1, 41.6, 39.7, 27.7, 27.3, -1.9; IR (film) 2952, 2844, 1736, 1434, 1249 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{17}\text{H}_{26}\text{O}_4\text{Si}$ 322.1600, found 322.1599 (M^+).

2-(Toluene-4-sulfonyl)-7-trimethylsilyl-1,2,3,3a,6,7-hexahydro-cyclohepta[c]-

pyrrole (2b). General procedure was followed using 138 mg (0.5 mmol) of dienyne, 0.5 mL (1.0 mmol, 2.0 M in Et₂O) of TMSCHN₂, 15 mg (0.05 mmol) of Ni(COD)₂ to afford 124 mg (68%, > 95 : 5 as judged by GC analysis on the crude reaction mixture) of product **2b**. ¹H NMR (500 MHz, CDCl₃) δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 5.75 (dtd, *J* = 11.0, 6.5, 2.5 Hz, 1H), 5.50 (d, *J* = 5.0 Hz, 1H), 5.39 (d, *J* = 10.5 Hz, 1H), 3.97 (d, *J* = 13.0 Hz, 1H), 3.73 (m, 2H), 3.62 (d, *J* = 13.0 Hz, 1H), 2.75 (m, 1H), 2.66 (m, 1H), 2.43 (s, 3H), 2.03 (dt, *J* = 15.0, 7.0 Hz, 1H), 1.71 (m, 1H), -0.06 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 143.8, 134.7, 132.9, 131.9, 129.9, 129.8, 128.1, 124.4, 54.6, 53.9, 40.5, 28.0, 27.4, 21.8, -1.8; IR (film) 2952, 2844, 1598, 1456, 1348, 1248, 1164 cm⁻¹; HRMS (EI) *m/e* calcd for C₁₉H₂₆NO₂SiS 360.1454, found 360.1459 (M-H)⁺.

Trimethyl-(3,5,6,8a-tetrahydro-1*H*-cyclohepta[c]furan-5-yl)-silane (2c). General procedure was followed using 62 mg (0.5 mmol) of dienyne, 0.5 mL (1.0 mmol, 2.0 M in Et₂O) of TMSCHN₂, 15 mg (0.05 mmol) of Ni(COD)₂ to afford 75 mg (65%, 10 : 1 as

judged by NMR analysis on the purified sample) of inseparable isomers of product **2c**. ^1H NMR (500 MHz, CDCl_3) δ 5.82 (dtd, $J = 10.5, 6.5, 3.0$ Hz, 1H), 5.52 (dt, $J = 10.5, 2.5$ Hz, 1H), 5.51 (m, 1H), 4.39 (dq, $J = 12.5, 2.0$ Hz, 1H), 4.25 (dq, $J = 12.2, 2.0$ Hz, 1H), 4.20 (t, $J = 8.0$ Hz, 1H), 3.83 (m, 1H), 3.47 (dd, $J = 10.0, 8.0$ Hz, 1H), 2.81 (m, 1H), 2.12 (dt, $J = 14.5, 6.8$ Hz, 1H), 1.78 (m, 1H), 0.02 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 138.7, 131.8, 129.9, 120.7, 74.7, 73.1, 41.4, 27.7, 27.6, -1.8; IR (film) 2952, 2843, 1652, 1449, 1248 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{12}\text{H}_{20}\text{OSi}$ 208.1283, found 208.1288 (M^+).

8-Methyl-7-trimethylsilyl-3,3a,6,7-tetrahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester (2d). General procedure was followed using 125 mg (0.5 mmol) of dienyne, 0.5 mL (1.0 mmol, 2.0 M in Et_2O) of TMSCHN_2 , 15 mg (0.05 mmol) of $\text{Ni}(\text{COD})_2$ to afford 131 mg (78%, $> 95 : 5$ as judged by NMR analysis on the purified sample) of product **2d**. ^1H NMR (500 MHz, CDCl_3) δ 5.77 (dtd, $J = 9.5, 6.5, 2.5$ Hz, 1H), 5.58 (dt, $J = 10.0, 2.2$ Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.65 (m, 1H), 3.01 (d, $J = 17.0$ Hz, 1H), 2.84 (dd, $J = 16.5, 1.5$ Hz, 1H), 2.73 (m, 1H), 2.57 (ddd, $J = 13.0, 8.0, 1.5$ Hz, 1H), 2.05 (dt, $J = 15.0, 6.5$ Hz, 1H), 1.98 (t, $J = 12.5$ Hz, 1H), 1.76 (m, 1H), 1.60 (s, 3H), 0.02 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 172.6, 172.5, 134.1, 131.0, 130.9, 130.2, 58.1, 52.9, 52.8, 41.8, 40.5, 40.1, 34.1, 28.4, 22.9, 0.04; IR (film) 2952, 2845, 1735, 1434, 1249 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{18}\text{H}_{28}\text{O}_4\text{Si}$ 336.1757, found 336.1754 (M^+).

Trimethyl-(4-methyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-yl)-silane (2e).

General procedure was followed using 136 mg (1.0 mmol) of diyne, 1.0 mL (2.0 mmol, 2.0 M in Et₂O) of TMSCHN₂, 28 mg (0.1 mmol) of Ni(COD)₂ to afford 135 mg (62%, 16 : 1 as judged by NMR analysis on the purified sample) of inseparable isomers of product **2e**. ¹H NMR (400 MHz, CDCl₃) δ 5.89 (dtd, *J* = 10.0, 6.8, 2.8 Hz, 1H), 5.56 (dt, *J* = 10.4, 2.4 Hz, 1H), 4.44 (d, *J* = 12.8 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 4.17 (t, *J* = 7.8 Hz, 1H), 3.75 (m, 1H), 3.43 (dd, *J* = 10.8, 7.8 Hz, 1H), 2.84 (m, 1H), 2.14 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.75 (m, 1H), 1.54 (s, 3H), 0.05 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 132.0, 130.3, 130.1, 128.7, 74.8, 72.2, 41.7, 33.7, 28.7, 22.4, 0.1; IR (film) 2951, 2839, 1653, 1247 cm⁻¹; HRMS (EI) *m/e* calcd for C₁₃H₂₂OSi 222.1440, found 222.1443 (M⁺).

Trimethyl-(6-methyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-yl)-silane (2f).

General procedure was followed using 70 mg (0.5 mmol) of diyne, 0.5 mL (1.0 mmol, 2.0 M in Et₂O) of TMSCHN₂, 15 mg (0.05 mmol) of Ni(COD)₂ to afford 50 mg (45%, 4 : 1 as judged by GC analysis on the crude reaction mixture) of inseparable isomers of

product **2f** (note: Two conformers of the major isomer of **2f** interconvert slowly on the NMR time scale. Signals for the major isomer begin to sharpen at 55 °C in C₆D₆). ¹H NMR (500 MHz, C₆D₆, VT = 55 °C) δ 5.45 (ddd, *J* = 10.0, 6.0, 2.8 Hz, 1H), 5.36 (m, 1H), 5.20 (d, *J* = 10.0 Hz, 1H), 4.35 (d, *J* = 12.5 Hz, 1H), 4.17 (dd, *J* = 12.5, 2.0 Hz, 1H), 4.03 (t, *J* = 8.5 Hz, 1H), 3.61 (m, 1H), 3.34 (dd, *J* = 10.5, 7.5 Hz, 1H), 2.98 (br s, 1H), 1.71 (br s, 1H), 0.95 (d, *J* = 7.0 Hz, 3H), -0.01 (s, 9H); ¹³C NMR (125 MHz, C₆D₆, 55 °C, complete listing for both isomers) δ 138.8, 136.1, 126.7, 120.1, 74.8, 74.3, 73.0, 72.6, 44.6, 41.9, 35.8, 34.7, 34.1, 29.9, 24.2, 20.6, -0.3, -1.4; ¹H NMR (500 MHz, CDCl₃, 25 °C) δ 5.60 (ddd, *J* = 10.0, 6.0, 3.0 Hz, 1H), 5.52 (m, 1H), 5.39 (m, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.25 (dd, *J* = 12.0, 2.0 Hz, 1H), 4.20 (t, *J* = 8.2 Hz, 1H), 3.78 (m, 1H), 3.44 (dd, *J* = 10.5, 8.0 Hz, 1H), 3.14 (br m, 1H), 1.83 (br m, 1H), 1.07 (d, *J* = 8.0 Hz, 3H), 0.04 (s, 9H); ¹³C NMR (125 MHz, CDCl₃, 25 °C, complete listing for both isomers) δ 139.4, 138.6, 136.8, 126.4, 125.4, 121.1, 119.9, 75.0, 74.6, 73.2, 73.0, 44.0, 41.7, 36.0, 34.8, 33.8, 29.9, 24.3, 21.1, 0.1, -1.0; IR (film) 2953, 2844, 1653, 1457, 1248 cm⁻¹; HRMS (EI) *m/e* calcd for C₁₂H₁₉OSi 207.1205, found 207. 1201 (M-CH₃)⁺.

(4,6-Dimethyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-yl)-trimethyl-silane (2g).

General procedure was followed using 150 mg (1.0 mmol) of dienyne, 1.0 mL (2.0

mmol, 2.0 M in Et₂O) of TMSCHN₂, 28 mg (0.1 mmol) of Ni(COD)₂ to afford 115 mg (49%, > 95 : 5 as judged by NMR analysis on the purified sample) of product **2g** (note: Two conformers of **2g** interconvert very slowly on the NMR time scale, and sharp signals in the ¹H NMR for both conformers are noted at 25 °C in CDCl₃. The signals broaden and approach coalescence at 75 °C in C₆D₆). Major conformer: ¹H NMR (500 MHz, CDCl₃, 25 °C) δ 5.74 (ddd, *J* = 9.5, 7.0, 3.0 Hz, 1H), 5.45 (d, *J* = 9.5 Hz, 1H), 4.43 (d, *J* = 12.0 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 4.16 (t, *J* = 8.0 Hz, 1H), 3.72 (m, 1H), 3.42 (dd, *J* = 12.5, 7.5 Hz, 1H), 3.27 (m, 1H), 1.56 (m, 1H), 1.53 (s, 3H), 1.12 (d, *J* = 7.5 Hz, 3H), 0.06 (s, 9H); ¹³C NMR (125 MHz, CDCl₃, 25 °C) δ 139.4, 129.8, 128.1, 125.9, 74.2, 72.2, 42.8, 42.6, 36.1, 23.4, 21.6, 2.0; Minor conformer: ¹H NMR (500 MHz, CDCl₃) δ 5.54 (m, 1H), 5.19 (d, *J* = 10.5 Hz, 1H), 4.36 (d, *J* = 12.5 Hz, 1H), 4.28 (m, 1H), 4.21 (t, *J* = 8.2 Hz, 1H), 3.70 (m, 1H), 3.45 (d, *J* = 8.5 Hz, 1H), 2.51 (m, 1H), 2.46 (m, 1H), 1.70 (s, 3H), 1.00 (d, *J* = 7.5 Hz, 3H), 0.10 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 141.4, 138.8, 127.1, 125.6, 75.9, 70.7, 41.9, 38.1, 33.2, 21.9, 18.6, 0.0; IR (film) 2955, 2836, 1652, 1457, 1248 cm⁻¹; HRMS (EI) *m/e* calcd for C₁₄H₂₄OSi 236.1596, found 236.1592 (M⁺).

(4,7-Dimethyl-1-phenyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-yl)-trimethylsilane (2h). General procedure was followed using 140 mg (0.6 mmol) of dienyne, 0.6

mL (1.2 mmol, 2.0 M in Et₂O) of TMSCHN₂, 18 mg (0.06 mmol) of Ni(COD)₂ to afford 138 mg (74%, > 95 : 5 as judged by NMR analysis on the purified sample) of product **2h**.
¹H NMR (500 MHz, CDCl₃) δ 7.44 - 7.28 (m, 5H), 5.24 (d, *J* = 1.5 Hz, 1H), 4.65 (d, *J* = 12.5 Hz, 1H), 4.44 (dd, *J* = 12.5, 1.5 Hz, 1H), 4.43 (d, *J* = 10.0 Hz, 1H), 3.50 (d, *J* = 9.0 Hz, 1H), 2.70 (d, *J* = 15.0 Hz, 1H), 2.03 (dd, *J* = 15.0, 7.0 Hz, 1H), 1.80 (m, 1H), 1.72 (s, 3H), 1.62 (s, 3H), 0.10 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 140.6, 139.3, 133.6, 128.6, 128.3, 128.2, 127.2, 122.8, 88.0, 71.6, 49.8, 33.8, 33.6, 26.3, 21.6, -0.2; IR (film) 2950, 2846, 1683, 1454, 1248 cm⁻¹; HRMS (EI) *m/e* calcd for C₁₉H₂₅OSi 297.1675, found 297.1679 (M-CH₃)⁺.

3,3a,6,7-Tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester (3). To a 3 mL THF solution of **2a** (46 mg, 0.14 mmol) was added TBAF (0.3 mL, 1.0 M in THF) at rt. The resulting brown solution was warmed to 60 °C and stirred for 30 minutes. The solvent was removed by rotary evaporation and the residue was absorbed onto silica gel.

Flash column chromatography on silica gel (Hexane : Ethyl ether = 10 : 1) afforded **3** (29 mg, 82%) as a light oil. ^1H NMR (500 MHz, CDCl_3) δ 5.68 (m, 1H), 5.63 (m, 1H), 5.49 (d, J = 10.5 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.67 (m, 1H), 3.00 – 2.89 (m, 2H), 2.65 (ddd, J = 13.0, 8.0, 1.5 Hz, 1H), 2.38 – 2.28 (m, 2H), 2.09 – 2.02 (m, 2H), 2.01 (dd, J = 12.8, 10.8 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 172.3, 172.1, 142.6, 132.2, 130.4, 122.5, 58.8, 53.0, 52.9, 41.7, 41.5, 39.8, 26.4, 25.9; IR (film) 2955, 2843, 1734, 1653, 1435, 1250 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$ 250.1205, found 250.1205 (M^+).

3,3a,6,8a-Tetrahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester (4). To a 3 mL CH_2Cl_2 solution of **2a** (26 mg, 0.08 mmol) was added $\text{BF}_3 \cdot 2\text{HOAc}$ complex (35 μL , 0.24 mmol) at 0 $^\circ\text{C}$. The resulting orange solution was allowed to warm to rt and stirred for 20 minutes. The reaction mixture was diluted with 5 mL ethyl ether and quenched with saturated NaHCO_3 . Extraction with ethyl ether (3 $\times$ 10 mL) and chromatographic purification on silica gel (Hexane : Ethyl ether = 10 : 1) afforded **4** (16 mg, 80%) as a light oil (d.r. = 3 : 1, *cis* : *trans*). ^1H NMR (500 MHz, CDCl_3) δ 5.71 – 5.65 (m, 2H_{maj} + 2H_{min}), 5.57 – 5.53 (dt, J = 11.0, 4.5 Hz, 2H_{min}), 5.47 (d, J = 10.5 Hz, 2H_{maj}), 3.72 (s, 6H_{maj} + 6H_{min}), 2.99 – 2.88 (m, 3H_{maj} + 2H_{min}), 2.70 (dd, J = 13.0, 7.0 Hz, 2H_{min}), 2.61 – 2.53 (m, 1H_{maj} + 2H_{min}), 2.37 (dd, J = 13.5, 7.0 Hz, 2H_{maj}), 2.31 (dd, J = 13.0, 6.5 Hz, 2H_{maj}), 1.93 (t, J = 12.2 Hz, 2H_{min}); ^{13}C NMR (125 MHz, CDCl_3) δ 173.7, 173.3, 173.1, 132.0, 131.7, 129.5, 127.3, 58.0, 53.1, 53.0, 52.9, 44.2, 42.7, 41.4, 40.8, 29.9, 27.9; IR

(film) 2953, 1733, 1652, 1435, 1249 cm^{-1} ; HRMS (EI) m/e calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$ 250.1205, found 250.1202 (M^+).

References:

- [1] Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, 113, 5066.
- [2] Gilbertson, S. R.; DeBoef, B. *J. Am. Chem. Soc.* **2002**, 124, 8784.
- [3] Wender, P. A.; Deschamps, N. M.; Gamber, G. G. *Angew. Chem. Int. Ed.* **2003**, 42, 1853.
- [4] Ezoe, A.; Kimura, M.; Inoue, T.; Mori, M.; Tamaru, Y. *Angew. Chem. Int. Ed.* **2002**, 41, 2784.
- [5] Wang, B.; Cao, P.; Zhang, X. *Tetrahedron Lett.* **2000**, 41, 8041.

Pulse Sequence: s2pul

Pulse Sequence: s2pul

Pulse Sequence: s2pul

Pulse Sequence: s2pul

Pulse Sequence: s2pu1

Pulse Sequence: s2pul

3

Pulse Sequence: szpul