Gold(I)-Catalyzed Ring Expansion of Cyclopropanols and Cyclobutanols

Jordan P. Markham, Steven T. Staben, and F. Dean Toste

Department of Chemistry, University of California, Berkeley, California 94720

Experimental

General Information: Unless otherwise noted all commercial materials were used without further purification. Small-scale reactions (< 3mL) were carried out in Fisher Scientific disposable scintillation vials. Dichloromethane was obtained from EMD and used without further purification. Alkynyl cyclopropanols were prepared according to literature procedures.¹ Flash column chromatography was carried out on Merck 60 silica gel (32-63 μm). ^1H and ^{13}C NMR spectra were recorded with Bruker AV-300, AVQ and AVB-400 and DRX-500 spectrometers and referenced to CDCl_3 or C_6D_6 . Mass spectral and CHN data were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of Berkeley.

Representative procedure for ring expansion

1-(3,3-dimethylbutynyl)cyclopropanol (1.00 mmol) was added to a stirring suspension of gold triphenylphosphine chloride (0.005 mmol) and silver hexafluoroantimonate (0.005 mmol) in dichloromethane (1 ml) and stirred for 6 hours at room temperature. After removal of the solvent under reduced pressure, silica gel flash chromatography eluting with 10% ethyl acetate in hexanes afforded cyclobutanone product as a white crystalline solid (157 mg, 99%).

(2) (*E*)-2-Benzylidene-cyclobutanone (2): 12 hours with 0.5% catalyst. Yield: 157 mg white crystalline solid, 95% (silica gel chromatography, eluent 10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.54-7.51 (m, 2H), 7.44-7.39 (m, 3H), 7.04 (t, J = 2.8 Hz, 1H) 3.18-3.14 (m, 2H), 3.02-2.99 (m, 2H); ^{13}C (125 MHz, CDCl_3) δ 199.7, 146.1, 134.5, 130.0, 128.9, 128.5, 126.4, 45.7, 23.5; IR: 2960, 1736, 1645 cm^{-1} ; HRMS (EI) calc'd for $\text{C}_{11}\text{H}_{10}\text{O}$: 158.0733, found: 158.0732; Anal. calc'd for $\text{C}_{11}\text{H}_{10}\text{O}$: C, 83.51; H, 6.37. Found: C, 83.50; H, 6.17.

(5) (E)-2-Heptylidene-cyclobutanone (5): 12 hours with 1% catalyst. Yield: 94 mg colorless oil, 81% (silica gel chromatography, eluent 5% ether in hexanes); ^1H NMR (500 MHz, C_6D_6) δ 6.15–6.05 (m, 1H), 2.47 (dd, $J = 10.8, 10.8$ Hz, 2H), 2.09–2.01 (m, 2H), 1.70 (dd, $J = 14.4, 7.2$ Hz, 2H), 1.25–1.03 (m, 8H), 0.86 (t, $J = 7.2$ Hz, 3H; ^{13}C NMR (100 MHz, C_6D_6) δ 197.0, 148.9, 129.5, 43.6, 31.9, 29.2, 28.8, 28.4, 22.9, 20.2, 14.3; HRMS (EI) calc'd for $\text{C}_{11}\text{H}_{18}\text{O}$: 166.1357, found: 166.1358.

(7) (E)-2-(2,2-Dimethylpropylidene)-cyclobutanone (7): 6 hours with 0.5% catalyst. Yield: 136 mg colorless oil, 98% (silica gel chromatography, eluent 5% ether in hexanes); ^1H NMR (400 MHz, CDCl_3) δ 6.17 (t, $J = 2.8$ Hz, 1H) 2.94–2.89 (m, 2H), 2.77–2.70 (m, 2H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.8, 144.1, 140.0, 45.0, 33.7, 29.1, 29.1, 22.1; IR: 2960, 2862, 1758, 1660 cm^{-1} ; HRMS (EI) calc'd for $\text{C}_9\text{H}_{14}\text{O}$: 138.1045, found: 138.1040; Anal. calc'd for $\text{C}_9\text{H}_{14}\text{O}$: C, 78.21; H, 10.21. Found: C, 78.14; H, 10.38.

(9) (E)-2-(4-Chlorobenzylidene)cyclobutanone (9): 12 hours with 0.5% catalyst. Yield: 45 mg white crystalline solid, 93% (silica gel chromatography, eluent 20% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.00 (app. t, $J = 2.6$ Hz, 1H), 3.17–3.13 (m, 2H), 2.98–2.93 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.2, 146.6, 135.9, 133.0, 131.1, 129.2, 125.0, 45.8, 23.4; IR: 2975, 1733, 1648 cm^{-1} ; Anal. calc'd for $\text{C}_{11}\text{H}_9\text{OCl}$: C, 58.58; H, 4.71. Found: C, 68.72; H, 4.94. HRMS (EI) calc'd for $\text{C}_{11}\text{H}_9\text{OCl}$: 192.0342, found: 192.0343.

(11) (E)-2-(4-(Trifluoromethyl)benzylidene)cyclobutanone (11): 12 hours with 0.5% catalyst. Yield: 108 mg white crystalline solid, 96% (silica gel chromatography, eluent 20% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 8.4$ Hz, 2H), 7.58 (d, $J = 8.4$ Hz, 2H), 7.01 (bs, 1H) 3.20–3.16 (m, 2H), 3.03–

3.01 (m, 2H); ^{13}C (100 MHz, CDCl_3) δ 199.1, 148.7, 138.0, 131.3, 130.0, 125.8, 124.5, 123.5, 46.1, 23.7; IR: 2934, 1730, 1650 cm^{-1} ; HRMS (EI) calc'd for $\text{C}_{12}\text{H}_9\text{OF}_4$: 226.0606, found: 226.0604. Anal. calc'd for $\text{C}_{12}\text{H}_9\text{F}_3\text{O}$: C, 63.72; H, 4.01. Found: C, 63.44; H, 4.03.

4-((*E*-(4-(Cyano)benzylidene)cyclobutanone (13): 12 hours with 0.5% catalyst. Yield: 91 mg pale yellow solid, 98% (silica gel chromatography, eluent 20% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.00 (t, J = 2.8 Hz, 1H) 3.29-3.19 (m, 2H), 3.05-3.00 (m, 2H); IR: 2960, 2224, 1746, 1642 cm^{-1} ; ^{13}C (125 MHz, CDCl_3) δ 198.8, 149.6, 138.9, 132.5, 130.1, 124.0, 118.3, 112.9, 46.2, 23.8. HRMS (EI) calc'd for $\text{C}_{12}\text{H}_9\text{NO}$: 183.0684, found: 183.0680.

(*E*)-2-(4-Methoxybenzylidene)cyclobutanone (15): 12 hours with 0.5% catalyst. Yield: 88 mg white crystalline solid, 94% (silica gel chromatography, eluent 5% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, J = 8.8 Hz, 2H), 6.99 (t, J = 2.8 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 3.13-3.09 (m, 2H), 2.95-2.90 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.5, 161.1, 143.5, 131.8, 127.2, 126.3, 114.4, 55.3, 45.5, 23.2; IR: 2974, 1733, 1648 cm^{-1} ; HRMS (EI) calc'd for $\text{C}_{12}\text{H}_{12}\text{O}_2$: 188.0837, found: 188.0834. Anal. calc'd for $\text{C}_{12}\text{H}_{12}\text{O}_2$: C, 76.57; H, 6.43. Found: C, 76.69; H, 6.40.

(*E*)-2-(Iodomethylene)cyclobutanone (21) : Reaction with 1% catalyst loading for 8 hrs at 40°C gave 146 mg (88%) of an off-white solid (silica-gel chromatography 10:1 hexanes: Et_2O). ^1H NMR (CDCl_3) δ 7.44 (t, J = 3.0, 1H), 2.89 (t, J = 8.0, 2H), 2.50 (td, J = 8.0, 3.0, 2H). ^{13}C NMR (CDCl_3) δ 192.41, 160.71, 85.33, 40.58, 26.14. IR: 3053, 2930, 1750, 1622 cm^{-1} . This compound decomposed rapidly at room temperature. Anal. Calcd.: C, 28.87; H, 2.42, found: C, 25.47; H, 2.02.

(E)-2-Benzylidene-3,3-dimethylcyclobutanone (23): 12 hours with

1% catalyst. Yield: 61 mg, 61% pale yellow oil (silica gel chromatography, eluent 2% acetone in hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.50-7.47 (m, 2H), 7.43-7.35 (m, 3H), 7.03 (s, 1H), 2.92 (s, 2H), 1.59 (s, 6H); ^{13}C (100 MHz, CDCl_3) δ 200.2, 153.2, 133.4, 130.9, 129.7, 128.8, 127.2, 60.2, 38.0, 26.2; IR: 2959, 1742, 1632 cm^{-1} ; HRMS (EI) calc'd for $\text{C}_8\text{H}_{14}\text{OSi}$: 154.0809, found: 154.0814; Anal. calc'd for $\text{C}_8\text{H}_{14}\text{OSi}$: C, 62.281; H, 9.15. Found: C, 62.41; H, 9.21.

(E)-1-Benzylidenespiro[3.5]nona-2-one (25): Reaction with 5%

catalyst loading for 48 hr at room temperature gave 63 mg (74%) of a light yellow oil (4:1 mixture with a cyclopentenone isomer, silica gel chromatography 15:1 hexanes:EtOAc). ^1H NMR (CDCl_3): δ 7.55 (m, 2H), 7.45-7.35 (m, 3H), 7.05 (s, 1H), 2.85 (s, 2H), 2.08 (m, 2H), 1.85-1.30 (m, 8H). ^{13}C NMR (CDCl_3) δ 200.57, 153.01, 134.61, 130.99, 129.61, 128.71, 127.72, 56.05, 44.15, 34.06, 25.51, 23.43; IR: 2927, 2853, 1742, 1632 cm^{-1}

2-Methylene-3-neopentylcyclopentanone (27): 10 hours with 1%

catalyst. Yield: 16 mg, 76% colorless oil (silica gel chromatography, eluent 5% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3) δ 6.03 (d, J = 3.2 Hz, 1H), 5.23 (d, J = 2.8 Hz, 1H), 2.76-2.66 (m, 1H), 2.46-2.21 (m, 3H), 1.69 (dd, J = 14.4, 3.2 Hz, 1H), 1.56-1.45 (m, 1H), 1.33 (dd, J = 14.0, 8.4 Hz, 1H), 0.99 (s, 9H); ^{13}C (100 MHz, CDCl_3) δ 207.3, 150.3, 116.3, 48.9, 38.3, 37.5, 31.0, 30.1, 29.7; HRMS (EI) calc'd for $\text{C}_{11}\text{H}_{18}\text{O}$: 166.1358, found: 166.1336.

(3aR,7aR)-Hexahydro-1-methylene-1H-inden-2(3H)-one (29):

Reaction with 2% catalyst loading for 24 hr at room temperature gave 66 mg (66%) of a colorless oil (silica gel chromatography 8:1 hexanes:Et₂O). **29** had characterization data consistent with that of the literature²: ¹H NMR (CDCl₃) δ 6.07 (d, *J* = 3.0, 1H), 5.20 (d, *J* = 2.3, 1H), 2.84 (m, 1H), 2.37-2.23 (m, 2H), 2.11 (dd, *J* = 17.1, 2.1, 1H), 1.91 (br m, 1H), 1.70 (m, 1H), 1.61-1.50 (m, 2H), 1.40 (m, 1H), 1.34-1.22 (m, 2H), 1.00 (m, 1H). ¹³C NMR (CDCl₃) δ 207.57, 146.97, 116.17, 44.36, 14.07, 33.55, 28.74, 26.02, 23.98, 20.63. IR: 2931, 2857, 1705, 1643 cm⁻¹

1-Methylenespiro[4.6]undeca-2-one (31):

Reaction with 2% catalyst loading for 20 hr at 40°C gave 77 mg (72%) of a colorless oil (silica gel chromatography 15:1 hexanes:Et₂O). ¹H NMR (CDCl₃) δ 5.92 (br s, 1H), 5.24 (br s, 1H), 2.32 (t, *J* = 7.8, 2H), 1.80 (t, *J* = 7.8, 2H), 1.65-1.47 (m, 12H). ¹³C NMR (CDCl₃) δ 208.32, 156.14, 115.20, 46.44, 40.03, 35.34, 32.63, 29.71, 23.31. IR: 2922, 2853, 1723, 1630 cm⁻¹ HRMS (EI) calc. for [C₁₂H₁₈O]⁺ 178.1358, found 178.1360. Anal. Calcd.: C, 80.85; H, 10.18, found: C, 80.83; H, 10.36.

8,8-Dimethyl-1-methylenespiro[4.5]deca-2-one (33):

Reaction with 2% catalyst loading for 16 hr at 40°C gave 132 mg (82%) as a light yellow oil (silica gel chromatography 10:1 hexanes:Et₂O). ¹H NMR (CDCl₃) δ 6.02 (br s, 1H), 5.27 (br s, 1H), 2.34 (t, *J* = 7.9, 2H), 1.86 (t, *J* = 7.9, 2H), 1.64 (m, 2H), 1.46-1.30 (m, 6H), 0.99 (s, 3H), 0.98 (s, 3H). ¹³C NMR (CDCl₃) δ 208.29, 154.95, 115.98, 43.29, 35.35, 35.28, 33.09, 32.15, 29.55, 29.21, 24.76. IR: 2954, 2926, 2861, 1725, 1634 cm⁻¹ Calcd.: C, 81.20; H, 10.48, found: C, 81.01; H, 10.58.

2-Methylene-3-isopropylcyclopentanone (35a): Reaction with 1% catalyst loading for 10 min at room temperature gave 96mg (80%) of a light yellow oil (silica gel chromatography, 12:1 pentane:Et₂O). ¹H NMR (CDCl₃) δ 5.75 (d, *J* = 2.7, 1H), 5.12 (d, *J* = 2.2, 1H), 3.07 (dd, *J* = 17.3, 8.9, 1H), 2.77 (m, 1H), 2.67 (dd, *J* = 17.3, 6.0, 1H), 1.82 (m, 1H), 1.06 (d, *J* = 6.6, 3H), 0.98 (d, *J* = 6.6, 3H). ¹³C NMR (CDCl₃) δ 199.60, 157.65, 112.49, 48.61, 42.67, 32.11, 20.44, 20.13. IR: 2962, 2874, 1740, 1651 cm⁻¹ HRMS (EI) calc. for [C₈H₁₂O]⁺ 124.0888, found 124.0886.

(E)-2-Benzylidene-3-isopropylcyclobutanone (35b): Reaction with 1% catalyst loading for 10 min at room temperature (determined by crude ¹H NMR analysis to be a 4.6:1 **(35b:36b)** mixture of regioisomers) gave 28 mg (82%) of a colorless oil (isolated as a 4:1 **(35b:36b)** mixture of regioisomers, silica gel chromatography 10:1 hexanes:Et₂O). ¹H NMR (CDCl₃) δ 7.52 (m, 2H), 7.44-7.37 (m, 3H), 7.09 (d, *J* = 2.6, 1H), 3.48 (m, 1H), 3.08 (dd, *J* = 17.5, 9.0, 1H), 2.87 (dd, *J* = 17.5, 5.1, 1H), 2.41 (m, 1H), 0.99 (d, *J* = 6.8, 3H), 0.81 (d, *J* = 6.8, 3H). ¹³C NMR (CDCl₃) δ 200.21, 148.17, 134.61, 130.24, 129.82, 128.85, 127.45, 46.03, 42.05, 28.05, 21.37, 16.05. IR: 2959, 2871, 1744, 1638 cm⁻¹ HRMS (EI) calc. for [C₁₄H₁₆O]⁺ 200.1201, found 200.1202.

(E)-2-Benzylidene-4-isopropylcyclobutanone (36c): Reaction with 1% catalyst loading for 70 min at room temperature gave 51 mg (91%) of a colorless solid (silica gel chromatography 10:1 hexanes:Et₂O). ¹H NMR (CDCl₃) δ 7.54 (m, 2H), 7.42-7.36 (m, 3H), 7.04 (t, *J* = 2.5, 1H), 3.16-3.05 (m, 2H), 2.71 (ddd, *J* = 15.5, 5.5, 2.5, 1H), 2.00 (m, 1H), 1.09 (d, *J* = 7.0, 3H), 0.98 (d, *J* = 7.0, 3H). ¹³C NMR (CDCl₃) δ 202.86, 144.04, 134.78, 130.03, 129.86, 128.86, 126.40, 65.67, 29.64, 28.45, 20.40,

20.24. IR: 2956, 2870, 1740, 1646 cm^{-1} HRMS (EI) calc. for $[\text{C}_{14}\text{H}_{16}\text{O}]^+$ 200.1201, found 200.1204.

Methylene-4-benzylcyclobutanone (35d) and Methylene-3-benzylcyclobutanone (36d): Reaction with 1% catalyst loading for 5 min at room temperature (determined by crude ^1H NMR analysis to be a 1.7:1 (**35d**:**36d**) mixture of regioisomers) gave 44 mg (88%) of a colorless oil (1.8:1 mixture of **35d**:**36d**, silica gel chromatography 10:1 hexanes:Et₂O). ^1H NMR (CDCl_3) major isomer **35d**: δ 7.35-7.28 (m, 2H), 7.26-7.18 (m, 3H), 5.72 (d, $J = 2.6$, 1H), 4.87 (d, $J = 1.9$, 1H), 3.32 (m, 1H), 3.13 (dd, $J = 17.7$, 9.0, 1H), 2.96 (m, 1H), 2.80 (m, 1H), 2.73 (dd, $J = 17.7$, 6.0, 1H) the following peaks could be observed for the minor isomer **36d**: δ 5.78 (t, $J = 2.9$, 1H), 5.10 (t, $J = 2.3$, 1H), 3.53-3.46 (m, 1H), 2.46-2.41 (m, 1H). ^{13}C NMR (CDCl_3) major isomer **35d**: δ 199.14, 158.12, 139.43, 128.75, 128.69, 126.45, 112.59, 50.71, 40.21, 36.26 the following peaks could be observed for the minor isomer **36d**: δ 202.25, 152.72, 138.81, 126.36, 113.59, 57.91, 35.48, 28.9. HRMS (EI) calc. for $[\text{C}_{12}\text{H}_{12}\text{O}]^+$ 172.0888, found 172.0888.

(E)-2-Benzylidene-cis-3,4-dimethylcyclobutanone (38a): 2 hours with 1% catalyst. Yield: 861 mg colorless oil, 99% (silica gel chromatography, eluent 2% ethyl acetate in hexanes); Structure confirmed by NOESY. ^1H NMR (500 MHz, CDCl_3) δ 7.54-7.46 (m, 2H), 7.44-7.33 (m, 3H), 7.00 (d, $J = 2.5$ Hz, 1H), 3.60-3.49 (m, 1H), 3.49-3.42 (m, 1H), 1.28 (d, $J = 7.5$ Hz, 3H), 1.16 (d, $J = 7.5$ Hz, 3H); ^{13}C (125 MHz, CDCl_3) δ 204.3, 149.8, 134.0, 130.2, 129.7, 128.8, 126.6, 55.6, 34.0, 12.0, 8.6; IR: 2962, 2853, 1745, 1643 cm^{-1} ; HRMS (EI) calc'd for $\text{C}_{13}\text{H}_{14}\text{O}$: 186.1045, found: 186.1045; Anal. calc'd for $\text{C}_{13}\text{H}_{14}\text{O}$: C, 83.83; H, 7.58. Found: C, 83.82; H, 7.70.

(*E*)-2-Benzylidene-*trans*-3,4-dimethylcyclobutanone (38a): 12 hours with 1% catalyst. Yield: 70 mg colorless oil, 94% (silica gel chromatography, eluent 2% ethyl acetate in hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.51-7.45 (m, 2H), 7.42-7.34 (m, 3H), 7.07 (d, J = 2.5 Hz, 1H), 3.06-2.98 (m, 1H), 2.90-2.82 (m, 1H), 1.41 (d, J = 7 Hz, 3H), 1.27 (d, J = 7 Hz, 3H); ^{13}C (125 MHz, CDCl_3) δ 203.8, 148.8, 133.8, 130.3, 129.7, 128.7, 127.7, 61.0, 39.5, 17.2, 14.2; IR: 2961, 2868, 1739, 1640 cm^{-1} ; HRMS (EI) calc'd for $\text{C}_{13}\text{H}_{14}\text{O}$: 186.1045, found: 186.1045; Anal. calc'd for $\text{C}_{13}\text{H}_{14}\text{O}$: C, 83.83; H, 7.58. Found: C, 84.10; H, 7.71.

($\pm$)-(2*S*,3*S*,4*R*)-2-Benzyl-3,4-dimethyl-5-methylenecyclopentanone

(40): 12 hours with 1% catalyst. Yield: 74 mg colorless oil, 69% (silica gel chromatography, eluent 2% ethyl acetate in hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.32-7.21 (m, 5H), 6.12 (d, J = 3.5 Hz, 1H), 5.23 (d, J = 2.5 Hz, 1H), 3.31 (dd, J = 10.0, 4.5 Hz, 1H), 2.82-2.69 (m, 2H), 2.54 (dd, 14.5, 10.0 Hz, 1H), 2.38-2.28 (m, 1H), 1.15 (d, 7.0 Hz, 3H), 0.70 (d, 7.5 Hz, 3H); ^{13}C (125 MHz, CDCl_3) δ 206.1, 148.6, 140.3, 128.5, 128.4, 126.0, 116.5, 56.2, 38.8, 35.0, 30.4, 13.5, 9.2; HRMS (EI) calc'd for $\text{C}_{15}\text{H}_{18}\text{O}$: 214.1358, found: 214.1357.

($\pm$)-(3*S*,4*R*,5*R*)-3-Benzyl-4,5-dimethyl-2-methylenecyclopentanone

(41): Yield: 20 mg colorless oil, 19% (silica gel chromatography, eluent 2% ethyl acetate in hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.35-7.19 (m, 5H), 6.12 (d, J = 3.0 Hz, 1H), 5.26 (d, J = 3.0 Hz, 1H), 3.20-3.10 (m, 2H), 2.68 (dd, J = 16.0, 11.5 Hz, 1H), 2.47-2.38 (m, 1H), 2.35-2.27 (m, 1H), 1.06 (d, J = 7.0 Hz, 3H), 0.68 (d, J = 7.5 Hz, 3H); ^{13}C (125 MHz, CDCl_3) δ 207.6, 147.2, 139.6, 128.5, 128.5, 126.2, 116.6, 48.8, 45.2, 34.8, 34.3, 9.4, 9.2; HRMS (EI) calc'd for $\text{C}_{15}\text{H}_{18}\text{O}$: 214.1358, found: 214.1359.

((Z)-44) (Z)-2-((Trimethylsilyl)methylene)cyclobutanone: Yield: 91 mg, 83% colorless oil (silica gel chromatography, eluent 1% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3) δ 5.91 (t, $J = 2.4$ Hz, 1H), 2.87 (dd, $J = 8.4, 8.4$ Hz, 2H), 2.60 (td, $J = 8.6, 2.1$ Hz, 2H), 0.16 (s, 9H); ^{13}C (100 MHz, CDCl_3) δ 200.3, 162.0, 138.0, 42.8, 24.3, -1.1; HRMS (EI) calc'd for $\text{C}_8\text{H}_{14}\text{OSi}$: 154.0809, found: 154.0814; Anal. calc'd for $\text{C}_8\text{H}_{14}\text{OSi}$: C, 62.281; H, 9.15. Found: C, 62.41; H, 9.21.

((E)-44) (E)-2-((Trimethylsilyl)methylene)cyclobutanone: Yield: 12 mg, 13% colorless oil (silica gel chromatography, eluent 1% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3) δ 6.37 (t, $J = 3.0$ Hz, 1H), 2.99 (dd, $J = 8.4, 8.4$ Hz, 2H), 2.71 (td, $J = 8.6, 2.1$ Hz, 2H), 0.17 (s, 9H); ^{13}C (100 MHz, CDCl_3) δ 199.6, 161.4, 130.4, 44.7, 24.0, -1.2; HRMS (EI) calc'd for $\text{C}_8\text{H}_{14}\text{OSi}$: 154.0809, found: 154.0814; Anal. calc'd for $\text{C}_8\text{H}_{14}\text{OSi}$: C, 62.281; H, 9.15. Found: C, 62.41; H, 9.21.

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