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A Readily Available and User-Friendly Chiral Catalyst for Efficient Enantioselective Olefin Metathesis

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General. Infrared (IR) spectra were recorded on Perkin Elmer 781 and 1608 spectrophotometers, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded on Varian GN-400 (400 MHz), Mercury 300 (300 MHz), Inova 500 (500MHz), and Inova 501 (500 MHz) spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 or C_6H_6: δ 7.16). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), integration, coupling constants (Hz), and assignment. ^{13}C NMR spectra were recorded on Varian GN-400 (100 MHz) and Inova 501 (125.836 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: δ 77.7 ppm). ^{13}C spectra were referenced vs C_6D_6 at 128.4 ppm. ^{31}P NMR chemical shifts are reported in ppm using a standard of PPh_3 in C_6D_6 (-4.8 ppm). Enantiomer ratios were determined by chiral GLC (Supelco alphadex 120 column (30m x 0.25mm) or Betadex 120 column (30m x 0.25mm)) or chiral HPLC analysis (Chiral Technologies chiralcel OD and chiralpak AD (0.46cm θ x 25cm)) in comparison with authentic racemic materials. Microanalyses were performed by Robertson Microlit Laboratories (Madison, New Jersey). High resolution mass spectrometry was performed by the University of Illinois Mass Spectrometry Laboratories.

All reactions were conducted in oven (135 °C) and flame-dried glassware under an inert atmosphere of dry Ar or N_2. Et_2O, toluene, and pentane were sparged with N_2, then passed through activated alumina. THF, methylene chloride, and benzene were distilled from sodium benzophenone. Benzyl potassium was prepared by the literature method.[1] All reagents were used as received from Aldrich Chemical Company, Lancaster Synthesis, Kankyo Kagaku Center Co. Ltd., or Strem Chemicals, Inc. Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mühlheim an der Ruhr, Germany. $Mo(NAr)(CHCMe_2Ph)(OTf)_2$•DME,[2] Mo(N-2,6-(*i*-

[1]) L. Lochmann, J. Trekoval *J. Organomet. Chem.* **1987**, *326*, 1-7.

[2]) R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. DiMare, M. O'Regan *J. Am. Chem. Soc.* **1990**, *112*, 3875-3886.

$Pr)_2C_6H_3)(CHCMe_2Ph)((S)$-(-)-*t*-$Bu_2Me_4$(biphen)),[3] and (*R*) – (+)-Mo(N-2,6-*i*-$Pr_2C_6H_3)(CHMe_2Ph)$(-3,3'-Bis(2,4,6-triisopropylphenyl)-2,2'-dihydroxy-1,1'-dinaphthyl)(THF)[4] were synthesized based on previously reported procedures.

(*R*)-5,5',6,6',7,7',8,8'-Octahydro-1,1'-bi-2-naphthol ((*R*)-5). Bi-2-naphthol (20 g, 69.8 mmol) and PtO_2•xH_2O (2.5 g, 11.3 mmol) were weighed out into a 1 L glass vessel designed for reactions under pressure and glacial acetic acid (250 mL) was added. The apparatus was then flushed with H_2 and pressurized to 100 psi. The reaction mixture was stirred for 72 h. The acid solution was diluted with water (200 mL). Dichloromethane (125 mL) was added to give a biphasic solution, which was then filtered in order to remove the catalyst. The layers were then separated, and the CH_2Cl_2 layer was washed with water (100 mL) and a saturated solution of $NaHCO_3$ (2 x 100 mL). The dichloromethane layer was dried over $MgSO_4$ and filtered. The solvent was removed from the filtrate in vacuo to leave 20.3 g of a cream-colored powder (69.1 mmol, >98 %): ^{1}H NMR (C_6D_6): δ 6.93 (d, 2, aryl CH), 4.50 (s, 2, O*H*), 2.55 (t, 4, cyclohexyl), 2.33 (dt, 2, cyclohexyl), 2,16 (dt, 2, cyclohexyl), 1.48 (m, 4, cyclohexyl), 1.44 (m, 4, cyclohexyl).

(-)-Menthol phosphate derived from (*R*)-5. PCl_2((-)menthol) (218 mg, 0.85 mmol) was dissolved in dry CH_2Cl_2 (10 mL). Triethylamine (171 mg, 1.70 mmol) was added to the stirring solution by a syringe. A sample of (*R*)-**5** (250 mg, 0.62 mmol) was dissolved in CH_2Cl_2 (1 mL) and added to the solution through a syringe. The resulting yellow solution was allowed to stir for 14 h. Volatile components were removed in vacuo to give the desired (-)-menthol phosphate: ^{31}P NMR (C_6D_6) δ 144.9. Deuterated solvent was removed from the above sample in vacuo, and CH_2Cl_2 (5 mL) was added. At this time, H_2O_2 (16% w / v, 4 mL) was added and the biphasic mixture was stirred for 6 h at 22 °C. The resulting mixture was washed with H_2O (2 x 10 mL), and the organic layer was dried over anhydrous $MgSO_4$. The solution was filtered and the solvent was removed to give a white solid, which was taken up in hot HOAc (5 mL) to produce white crystals. The resulting crystals were isolated by filtration and dried in vacuo to afford the desired (-)-menthol phosphonate (34 mg, 6.9×10^{-5} mmol): ^{1}H NMR (C_6D_6) δ 7.18 (s, 1, aryl CH), 7.13 (s, 1, aryl), 4.52 (m, 1, OC*H*), 2.83 (d, 1H), 2.66-2.61 (m, 2H), 2.55-2.40 (m, 4H), 2.11 (m, 2H), 1.73 (s, 9, C(CH_3)$_3$), 1.59 (m, 1H), 1.58 (s, 9, C(CH_3)$_3$), 1.49 (m, 6H), 1.40-1.13 (m, 7H), 0.80 (m, 1H), 0.76 (d, 3, CH(CH_3)), 0.67 (d, 3, CH(CH_3)$_2$), 0.65 (d, 3, CH(CH_3)$_2$), 0.60 (m, 1H); ^{31}P NMR (C_6D_6) δ -4.9. Repeating the synthesis with *rac*-**5** produced both diastereomers of each compound: ^{31}P NMR (C_6D_6) δ 144.4 and 139.2 for phosphate; δ -4.9 and -3.3 for phosphonate.

(*R*)-5,5',6,6',7,7',8,8'-Octahydro-3,3'-di-*tert*-butyl-1,1'-bi-2-naphthol (protonated 6). 5,5',6,6',7,7',8,8'-Octahydro-1,1'-bi-2-naphthol (10.0 g, 34.0 mmol) was added to a 125 mL pressure vessel. Sulfuric acid (10 mL) and glacial acetic acid (90 mL) were mixed and added to the vessel. The vessel was flushed with isobutylene and pressurized to 1 atm atmospheric pressure. The reaction vessel was heated to 70 °C and stirred for 14 h. The pressure was released and water (50 mL) was added. The biphasic mixture was washed with diethyl ether (2 x 25 mL). The ether layers were collected, washed with a saturated solution of $NaHCO_3$ (2 x 25 mL), and dried over $MgSO_4$. The ether solvent

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[3]) J. B. Alexander, D. S. La, D. R. Cefalo, A. H. Hoveyda, R. R. Schrock *J. Am. Chem. Soc.* **1998**, *120*, 4041-4042.

[4]) S. Zhu, D. R. Cefalo, D. S. La, J. Y. Jamieson, W. M. Davis, A. H. Hoveyda, R. R. Schrock *J. Am. Chem. Soc.* **1999**, *121*, 8251-8259.

was removed in vacuo to yield a tan liquid. Vacuum distillation at 85 °C (0.03 mm Hg) partially removed oligoisobutylene and produced 7.81 g of the unpurified product as a brown solid (65%). Racemic material may be further purified by washing with cold methanol. Enantiomerically pure material must be purified by silica gel chromatography. Unpurified product residue (2.0 g, 4.9 mmol) was loaded onto silica gel and eluted with pentane. The volatiles were removed in vacuo to yield 790 mg of a white solid (1.94 mmol, 40%): ^{1}H NMR (C_6D_6) δ 7.14 (s, 2, aryl CH), 4.85 (br s, 2, O*H*), 2.62 (t, 4, cyclohexyl), 2.21 (m, 4, cyclohexyl), 1.53 (m, 8, cyclohexyl), 1.51 (s, 18, C(C*H*$_3$)$_3$); ^{13}C NMR (C_6D_6) δ 151.04, 134.91, 134.54, 129.79, 129.31, 120.22, 35.20, 30.23, 27.62, 23.94, 23.92.

Bis(potassium) salt (*R*)-6. Hydrogenated binaphthol (*R*)-**5** (7.0 g, 23.8 mmol) was first alkylated in the manner described above. The unpurified protonated (*R*)-**6**, obtained as a brown solid, was dissolved in THF (20 mL) and KH (1.91 g, 47.6 mmol) was added slowly in portions. The resulting mixture was allowed to stir for 1 h at 22 °C, then diluted with Et_2O (10 mL) and THF (5 mL) and filtered through Celite. Removal of the volatiles in vacuo produced a brown solid, which was washed with pentane (4 x 10 mL) and dried in vacuo to yield 9.8 g of (*R*)-**6** as cream-colored powder (20.3 mmol, 85%). This material can be used directly in the synthesis of (*R*)-**3** described below.

Chiral Mo catalyst (*R*)-3. **Method 1.** Protonated (*R*)-**6** (411 mg, 1.01 mmol) was dissolved in THF (15 mL). Solid benzyl potassium (276 mg, 2.12 mmol) was added, and the resulting orange solution was stirred for 1 h. Mo-triflate **7** (800 mg, 1.01 mmol) was dissolved in THF (5 mL) and added to the stirring solution. The dark red solution was stirred at 22 °C for 2 h. The solvent was then removed in vacuo to give a brown solid. The product was taken up in pentane and filtered. The pentane was removed in vacuo to yield a dark orange powder. The unpurified product (**3**•MeCN) was precipitated from MeCN as an orange solid (330 mg, 41 %) and the MeCN was removed in vacuo.

Method 2. Diolate (*R*)-**6** (500 mg, 1.04 mmol) was dissolved in cold (-30 °C) THF (10 mL) and added to a stirring solution of **7** (820 mg, 1.04 mmol) in cold THF (25 mL). The solution was allowed to warm to 22 °C and stirred for 0.5 h. The solvent was removed in vacuo to give a brown solid. The product was taken up in pentane (20 mL) and filtered. The pentane was removed in vacuo to yield **3**•MeCN as a dark orange powder, which was precipitated from acetonitrile as an orange solid (1.67 g, 55%); solvent free (*R*)-**3** was obtained by subjection of the former complex to vacuum. ^{1}H NMR (C_6D_6) δ 10.97 (s, 1, MoC*H*), 7.46 (d, 2, neophyl *ortho*-H), 7.39 (s, 1, Bitet aromatic), 7.20 (t, 2, neophyl *meta*-H), 7.12 (s, 1, Bitet aromatic), 7.04 (t, 1, neophyl *para*-H), 6.93 (s, 3, imido aromatic), 3.67(sept, 2, C*H*(CH$_3$)$_2$), 2.69 (t, 2, cyclohexyl), 2.60 (qt, 3, cyclohexyl), 2.503(dt, 1, cyclohexyl), 2.30 (dt, 1, cyclohexyl), 2.00 (m, 2, cyclohexyl), 1.87 (s, 3, C(C*H*$_3$)$_2$Ph), 1.622 (s, 9, t-Bu), 1.55 (s, 9, t-Bu), 1.53(m, 8, cyclohexyl), 1.15 (d, 6, CH(C*H*$_3$)$_2$), 1.11 (s, 3, C(C*H*$_3$)$_2$Ph), 0.93 (d, 6, CH(C*H*$_3$)$_2$); ^{13}C NMR (C_6D_6) δ 275.96, 155.09, 154.39, 153.82, 151.47, 146.61, 140.18, 138.32, 136.55, 135.78, 132.17, 131.68, 131.64, 130.54, 128.80, 128.65, 128.61, 127.85, 127.81, 126.29, 123.69, 53.54, 36.00, 35.68, 30.69, 30.54, 29.17, 28.13, 27.84, 23.93, 23.77, 23.63, 33.37, 32.99, 30.83, 30.36, 24.74, 24.64. Anal. Calcd for $C_{50}H_{65}MoNO_2$: C 74.32, H 8.11, N 1.73. Found: C 74.22, H 8.04, N 1.70

Allyl-(1-cyclohexyl-allyloxy)-dimethylsilane (11): IR: 3075 (w), 2924 (s), 2855 (m), 1640 (w), 1262 (m), 1162 (m), 1073 (m), 1029 (m), 897 (m), 847 (m), 658 (m) cm^{-1}. ^{1}H NMR (400 MHz,

$CDCl_3$): δ 5.84-5.73 (m, 2H, CHC*H*=CH_2, $SiCH_2CH$=CH_2), 5.12-5.05 (m, 2H, CHC=CH_2), 4.90-4.83 (m, 2H, $SiCH_2CH$=CH_2), 3.74 (dd, *J*=6.8, 6.8 Hz, 1H, C*H*O), 1.84-1.81 (m, 1H, Cy-*H*) 1.71-1.69 (m, 2H, Cy-*H*), 1.65-1.57 (m, 5H, Cy-*H*, SiCH_2CH), 1.35-1.02 (m, 4H, Cy-*H*), 0.96-0.86 (m, 2H, Cy-*H*), 0.09 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 135.4, 115.8, 114.4, 79.8, 45.0, 30.0, 29.7, 27.6, 27.2, 27.2, 26.1, -0.7, -0.9. HRMS (EI+) calcd for $C_{14}H_{26}OSi$: 238.1753. Found: 238.1749. Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.42; H, 10.75.

(*R*)-6-Cyclohexyl-2,2-dimethyl-1-oxa-2-sila-cyclohex-4-ene (12): IR: 3018 (w), 2936 (s), 2848 (s), 1646 (w), 1457 (m), 1394 (w), 1256 (s), 1168 (s), 1111 (s), 904 (s), 841 (s), 834 (s), 797 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90–5.85 (m, 1H, OCHCH=C*H*) 5.57-5.54 (m, 1H, OCHC*H*=CH), 4.18 (dd, *J*=2.0, 0.8 Hz, 1H, SiOC*H*), 1.72 (d, *J*=9.6 Hz, 2H, SiCH_2), 1.67-1.62 (m, 2H, Cy-*H*), 1.43-1.37(m, 2H, Cy-*H*), 1.27-0.96 (m, 7H, Cy-*H*), 0.16 (s, 3H, SiCH_3), 0.13 (s, 3H, SiCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.9, 125.0, 77.3, 45.8, 29.3, 28.5, 27.3, 27.1, 27.0, 13.2, 1.0, 0.0. HRMS (EI+) calcd for $C_{12}H_{22}OSi$: 210.1440. Found: 210.1440.

1-(Allyldimethylsiloxy)-1-cyclohexyl-2-methyl-2-propene (13): IR: 3072 (m), 2923 (s), 2858 (s), 1631 (m), 1446 (m), 1257 (s), 1162 (m), 1062 (s), 898 (s), 863 (s), 833(s), 748 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.83-5.72 (m, 1H, **H**C=CH_2), 4.89-4.78 (m, 4H, CH_2=CCH$_3$, CH_2-=CH), 3.65 (d, *J*=7.6 Hz, 1H, C*H*OSi), 1.95-1.92 (m, 1H, Cy-*H*) 1.75-1.67 (m, 2H, Cy-*H*), 1.64 (s, 3H, CH_3C), 1.60 (d, *J*=8.0 Hz, 2H, SiCH_2CH), 1.44-1.25 (m, 2H, Cy-*H*), 1.25-1.06 (m, 4H, Cy-*H*) 0.89-0.76 (m, 2H, Cy-*H*),), 0.08 (s, 3H, SiCH_3), 0.07 (s, 3H, SiCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 135.2, 114.0, 112.9, 83.0, 41.5, 30.2, 29.9, 27.3, 26.9, 26.8, 25.6, 17.6, -1.3, -1.4. HRMS (EI+) calcd for $C_{15}H_{28}OSi$: 252.1909. Found: 252.1908. Anal. Calcd for $C_{15}H_{28}OSi$: C, 71.36; H, 11.18. Found: C, 71.54; H, 11.22.

(*R*)-1-Oxa-6-cyclohexyl-2-sila-2,2,5-trimethyl-cyclohex-4-ene (14): IR: 2930 (s), 2861 (m), 1464 (w), 1256 (m), 1111 (m), 847 (s), 803 (s), 494 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.64 (d, *J*=8.4 Hz, 1H, $SiCH_2CH$), 4.04 (s, 1H, SiOC*H*), 1.77-1.72 (m, 2H, Cy-*H*), 1.63-1.34 (m, 9H, CH_3C=CH, Cy-*H*), 1.28-1.02 (m, 5H, SiCH_2CH, Cy-*H*), 0.17 (s, 3H, SiCH_3), 0.07 (s, 3H, SiCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 120.6, 81.7, 43.5, 31.0, 27.5, 27.2, 27.2, 26.7, 23.3, 13.2, 0.9, 0.2. Anal. Calcd for $C_{13}H_{24}OSi$: C, 69.58; H, 10.78. Found: C, 69.64; H, 10.62.

3-Allyl-(2,5-dimethyl-1-hexenyl) ether (17). IR: 3081 (w), 2955 (s), 2924 (s), 2867 (s), 1652 (m), 1463 (m), 1367 (m), 1136 (m), 1092 (s), 922 (m), 910 (s), 570 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90 (dddd, J=17.2, 15.6, 11.6, 6.0 Hz, 1H, *H*C=CH_2), 5.24 (ddd, J=17.2, 3.6, 2.0 Hz, 1H, HC=C*H*H), 5.14 (ddd, J=10.4, 3.2, 1.6 Hz, 1H, HC=CH*H*), 4.90 (dd, J=3.6, 2.0 Hz, 1H, C=C*H*H), 4.88 (d, J=0.8 Hz, 1H, C=CH*H*), 3.94 (ddt, J=14.4, 5.2, 1.6 Hz, 1H, OC*H*), 3.77-3.70 (m, 2H, OCH_2), 1.71-1.63 (m, 1H, C*H*(CH_3)$_2$), 1.65 (t, J=0.8 Hz, 3H, CCH_3), 1.54 (ddd, J=9.6, 8.0, 6.8 Hz, 1H, OCHC*H*H), 1.29 (ddd, J=13.2, 6.8, 5.6 Hz, 1H, OCHCH*H*), 0.89 (dd, J=6.8, 1.2 Hz, 6H, CH(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 136.9, 117.3, 113.8, 82.2, 69.6, 43.6, 25.2, 23.6, 23.3, 17.2. HRMS Calcd for $C_{11}H_{20}O$: 168.1514. Found: 168.1513. Anal. Calcd for $C_{11}H_{20}O$: C, 77.09; H, 11.50. Found: C, 78.77; H, 11.80.

2-*iso*-Butyl-3-methyl-2,5-dihydrofuran (18). IR: 2962 (s), 2936 (s), 2861 (m), 1256 (m), 1080 (s), 1029 (s), 897 (w), 797 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.43 (t, J=1.6 Hz, 1H, C=C*H*), 4.65-4.49 (m, 3H, H_2COCH), 1.85 (tqq, J=2.8, 2.8, 2.8 Hz, 1H, $CH(CH_3)_2$), 1.68 (d, J=1.2 Hz, 3H, CCH_3), 1.35 (dd, J= 6.8, 6.8 Hz, 2H, $OCHCH_2$), 0.94 (d, J=6.8 Hz, 6H, $CH(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 120.6, 86.6, 74.7, 44.1, 25.6, 24.7, 22.5, 13.1. Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.89; H, 11.20.

3-Allyl-(2,4-dimethyl-1,4-pentadienyl) ether (19). IR: 3074 (s), 2974 (s), 2941 (s), 2919 (s), 2855 (s), 1810 (w), 1647 (s), 1449 (s), 1427 (s), 1372 (s), 1330 (w), 1269 (w), 1236 (w), 1136 (s), 1086 (s (br)), 1015 (s), 997 (s), 903 (s (br)), 834 (w) cm^{-1}; ^1H NMR (300 MHz, C_6D_6): δ 5.85 (ddt, J = 17.3, 10.6, 5.4 Hz, 1H, $CH_2=CH$), 5.30 (dq, J = 17.2, 2.0 Hz, 1H, *H*HC=CH), 5.15 (m, 2H, $CH_3C=CHH$), 5.05 (dq, J = 10.3, 2.0 Hz, 1H, H*H*C=CH), 4.94 (m, 2H, $CH_3C=CHH$), 3.99 (s, 1H, OC*H*C), 3.82 (dt, J = 5.2, 2.0 Hz, 2H, OCH_2), 1.61 (s, 6H,$CH_3C=CH_2$). ^{13}C (125 MHz, C_6D_6): δ 143.24, 135.26, 116.38, 112.88, 85.92, 69.01, 18.13. HRMS Calcd for $C_{10}H_{16}O$: 152.1201; Found: 152.1201.

2-*iso*-Propenyl-3-methyl-2,5-dihydrofuran (20). IR: 3074 (s), 2973 (s), 2946 (s), 2917 (s), 2845 (s), 2673 (w), 1802 (w), 1669 (w), 1648 (s), 1478 (w), 1447 (s (br)), 1381 (s), 1370 (s), 1346 (s), 1250 (s), 1184 (s), 1070 (s (br)), 1015 (s), 940 (s), 921 (s), 900 (s), 830 (s), 774 (w), 759 (w) cm^{-1}; ^1H NMR (300 MHz, C_6D_6): δ 5.17 (septet, J = 1.7 Hz, 1H, $C=CHCH_2$), 5.02 (t (br), J = 4.2 Hz, 1H, $C=CHCH_2$), 4.89 (t (br), J = 1.7 Hz, 1H, $CH_3C=CHH$), 4.82 (quintet, J = 1.7 Hz, 1H, $CH_3C=CHH$), 4.50 (d, J = 1.8 Hz, 2H, $OCH_2CH=C$), 1.64 (t (br), J = 1.3 Hz, $CH_3C=CH_2$), 1.38 (m, 1H, $CH_3C=CHCH_2$). ^{13}C NMR (125 MHz, C_6D_6): δ 146.2, 137.2, 122.4, 113.4, 93.5, 76.1, 16.4, 12.4. HRMS Calcd for $C_8H_{12}O$: 124.0888; Found: 124.0888.

3-(Allyldimethylsiloxy)-2,4-dimethyl-1,4-pentadiene (21): IR: 3069 (w), 2974 (m), 2917 (m), 2357 (m), 2332, (m), 1634 (m), 1457 (w), 1262 (s), 1099 (s), 897 (s), 834 (m), 570 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.85-5.72 (m, 1H, *H*C=CH_2), 5.01 (t, *J*=0.8 Hz, 2H, $(CHH=C)_2$), 4.90-4.83 (m, 4H, $(CHH=C)_2$, $CH_2=CH$), 4.41 (s (br), 1H, C*H*O), 1.61 (d, *J*=8.0 Hz, 2H, $SiCH_2CH$), 1.58 (s, 6H, $(CH_3C)_2$), 0.10 (s, 6H, $Si(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 135.0, 114.1, 112.1, 80.6, 25.5, 18.3, -1.5. HRMS (EI+) calcd for $C_{12}H_{22}OSi$: 210.1440. Found: 210.1442. Anal. Calcd for $C_{12}H_{22}OSi$: C, 68.51; H, 10.54. Found: C, 68.60; H, 10.60.

(*R*)-1-Oxa-6-(2-propenyl)-2-sila-2,2,5-trimethyl-cyclohex-4-ene (22): IR: 2974 (m), 2924 (m), 2836 (w), 1464 (w), 1275 (s), 1099 (s), 1055 (s), 922 (m), 847 (m), 797 (m), 545 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.72-5.70 (m, 1H, *H*C=CCH_3), 4.92 (dd, *J*=1.2, 1.2 Hz, 1H, *H*HC=CCH_3), 4.85 (t, *J*=1.2 Hz, 1H, H*H*C=CCH_3), 4.62 (s (br), 1H, OC*H*), 1.66 (t, *J*=0.8 Hz, 3H, HC=CCH_3), 1.55 (dd, *J*=1.2, 1.2 Hz, 3H, $CH_2=CCH_3$), 1.35-1.14 (m, 2H, $SiCH_2CH$), 0.19 (s, 3H, $SiCH_3$), 0.12 (s, 3H, $SiCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 136.0, 121.1, 113.8, 82.1, 22.4, 17.2, 13.0, 0.8, 0.0. HRMS (EI+) calcd for $C_{10}H_{18}OSi$: 182.1127. Found: 182.1129. Anal. Calcd for $C_{10}H_{18}OSi$: C, 65.87; H, 9.95. Found: C, 65.80; H, 10.00.