Supporting Information

A facile, catalytic and environmentally benign method for selective of deprotection of *tert*-butyldimethylsilyl ether mediated by phosphomolybdic acid supported on silica gel

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Table of Content

General experimental methods	S2
General experimental procedures	S2 – S3
Spectral data for all compounds	S3 – S21
XRD powder pattern	S22

General Experimental Methods: Melting points were determined in a capillary using melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on 400 MHz NMR spectrometer and ^{13}C NMR spectra were recorded on 100 MHz NMR spectrometer respectively, using TMS as an internal standard. Chemical shifts have been expressed in (ppm) downfield from TMS. IR spectra were recorded on an IR 470 instrument. Mass spectra were recorded on Q-tof mass spectrometer. Optical rotations were measured by a polarimeter. XRD measurements were carried out on a diffractometer and PW 1730 X-ray generator using monochromatized Cu K α radiation. All the reactions are monitored by thin layer chromatography (TLC) carried out on 0.25 mm silica gel plates (60 F₂₅₄ grade) with UV light, iodine, alkali KMnO₄, ceric ammonium molybdate as detecting agents. Silica gel (100-200 mesh) is used for column chromatography.

General experimental procedures

(a) Preparation of PMA/SiO₂ (10 % by wt) catalyst:

To a solution of H₃PMo₁₂O₄₀.24H₂O (100 mg, 0.1 equiv. by wt) in MeOH (5 mL), silica gel (900 mg, 0.9 equiv. by wt, 100 – 200 mesh) was added slowly and stirred at room temperature for 6h. Evaporation of MeOH under reduced pressure gave a dry yellowish powder, which contained 10 % (by weight) of PMA.

(b) General experimental procedure for the preparation of TBDMS ether:

To a solution of alcohol (1 mmol) and imidazole (2.5 mmol) in DMF (3 mL), *tert*-butyldimethylsilyl chloride (1.2 mmol) was added portion wise and the resultant mixture was stirred at room temperature. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with EtOAc. The organic layer was washed with water, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to give crude compound. Purification of the crude compound by column chromatography over silica gel (100 – 200 mesh) afforded pure TBDMS ether in good yield.

(c) General experimental procedure for the deprotection of TBDMS ether:

A mixture of TBDMS ether (1 mmol) and PMA/SiO₂ (113 mg, 0.005 mmol based on PMA) in THF (3 mL) was stirred at room temperature. After completion of the reaction, as indicated by TLC, the reaction mixture was filtered. The filtrate was concentrated under reduced pressure and the crude compound was purified by column chromatography over silica gel (100-200 mesh) to afford the pure alcohol.

Spectral data for all compounds

1a **tert-Butyl-hex-2-enyloxy-dimethyl-silane:** IR (neat) 2976, 2880, 1465, 1376, 1248, 1104, 1056, 960, 838 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 5.54 – 5.48 (m, 2H), 4.05 (d, J = 5.1 Hz, 2H), 1.93 (q, J = 7.1 Hz, 2H), 1.32 (sextet, J = 7.4 Hz, 2H), 0.84 – 0.81 (m, 3H), 0.84 (s, 9H), -0.02 (s, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 131.2, 129.2, 64.0, 34.2, 25.9, 22.3, 18.3, 13.6, -5.1; MS (EI) m/z (relative intensity, %) 214 (M^+ , 5), 157 (15), 127 (100), 101 (30).

2a **tert-Butyl-dimethyl-[5-(tetrahydro-pyran-2-yloxy)-pentyloxy]-silane:** IR (neat) 2944, 2848, 1459, 1385, 1353, 1254, 1120, 1091, 1024, 832, 774 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 4.53 (m, 1H), 3.82 – 3.33 (m, 4H), 3.56 (t, J = 6.5 Hz, 2H), 1.79 – 1.34 (m, 12H), 0.84 (s, 9H), 0.00 (s, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 98.7, 67.5, 63.1, 62.2, 32.6, 30.7, 29.5, 25.9, 25.4, 22.5, 19.5, 18.3, -5.3; MS (EI) m/z (relative intensity, %) 245 ($\text{M}^+ - \text{C}_4\text{H}_9$, 2), 187 (12), 159 (25), 85 (100).

2b **5-(tetrahydro-pyran-2-yloxy)-pentan-1-ol:** IR (neat) 3424, 2944, 2864, 1446, 1347, 1276, 1132, 1120, 1024, 803 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 4.48 (m, 1H), 3.76 – 3.30 (m, 6H), 3.50 (t, J = 6.3 Hz, 1H), 3.02 (bs, 1H), 1.73 – 1.34 (m, 13H); ^{13}C NMR [100 MHz, CDCl_3] δ 98.7, 67.4, 62.2, 32.4, 30.6, 29.3, 25.5, 22.5, 19.5; MS (ESI) $\text{C}_{10}\text{H}_{20}\text{O}_3\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 211.1463.

cis and trans 2-(tert-Butyl-dimethyl-silanyloxymethyl)-3-propyl-1-(toluene-4-sulfonyl)-aziridine (1 : 0.2): IR (neat) 2928, 2864, 1596, 1465, 1324, 1254, 1138, 1091 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 7.86 – 7.29 (m, 4H), 3.82 – 3.78 (m, 2H), 2.90 – 2.89 (m, 1H), 2.73 – 2.72 (m, 1H), 2.42 (s, 3H), 1.46 – 1.44 (m, 2H), 1.42 – 1.41 (m, 2H), 0.96 – 0.91 (m, 3H), 0.92 (s, 9H), 0.84 (2d, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 143.5, 137.6, 129.2, 127.2, 61.7, 49.1, 47.4, 30.9, 25.7, 21.3, 20.6, 18.0, 13.4; MS (EI) m/z (relative intensity, %) 324 ($\text{M}^+ - \text{C}_4\text{H}_9$, 5), 131 (10), 91 (60), 75 (100).

[3-Propyl-1-(toluene-4-sulfonyl)-aziridin-2-yl]-methanol:¹ IR (neat) 3488, 2960, 2880, 1600, 1452, 1318, 1152, 1091, 809 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 7.87 (d, $J = 7.9$ Hz, 2H), 7.35 (d, $J = 7.6$ Hz, 2H), 4.13 – 3.92 (m, 2H), 2.98 – 2.96 (m, 2H), 2.76 (bs, 1H), 2.47 (s, 3H), 1.68 – 1.55 (m, 2H), 1.33 (q, $J = 7.2$ Hz, 2H), 0.89 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR [100 MHz, CDCl_3] δ 144.2, 137.2, 129.6, 127.3, 60.9, 51.6, 46.3, 32.1, 21.5, 20.3, 13.5; MS (ESI) $\text{C}_{13}\text{H}_{19}\text{NO}_3\text{SNa}$ ($\text{M} + \text{Na}$)⁺ 292.3632.

1-(tert-Butyl-diphenyl-silanyloxy)-5-(tert-butyl-dimethyl-silanyloxy)-pentane: IR (neat) 2960, 2864, 1484, 1382, 1248, 1129, 1088, 998, 921, 832, cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 7.63 – 7.61 (m, 4H), 7.36 – 7.30 (m, 6H), 5.42 ($J = 6.3$ Hz, 2H), 3.54 (t, $J = 6.3$ Hz, 2H), 1.55 – 1.51 (m, 2H), 1.51 – 1.44 (m, 2H), 1.37 – 1.36 (m, 2H), 1.00 (s, 9H), 0.79 (s, 9H), 0.00 (s, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 135.5, 134.1, 129.5, 127.6, 63.9, 63.2, 32.6, 32.4, 26.8, 26.0, 22.2, 19.2, 18.4, -5.2; MS (ESI) $\text{C}_{27}\text{H}_{44}\text{Si}_2\text{O}_2$ (M^+) 457.2662.

¹ Jeong, J. U.; Tao, B.; Sagasser, I.; Henniges, H.; K. B. Sharpless, K. B. *J. Am. Chem. Soc.* **1998**, *120*, 6844.

5-(*tert*-Butyl-diphenyl-silanyloxy)-pentanol-1-ol: IR (neat) 3488, 2960, 2864, 1484, 1382, 1248, 1129, 1088, 998, 921, 832, 771, cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 7.67 – 7.65 (m, 4H), 7.42 – 7.35 (m, 6H), 3.66 (t, J = 6.2 Hz, 2H), 3.58 (t, J = 6.5 Hz, 2H), 1.75 (bs, 1H), 1.60 – 1.49 (m, 4H), 1.44 – 1.38 (m, 2H), 1.05 (s, 9H); ^{13}C NMR [100 MHz, CDCl_3] δ 135.6, 134.4, 129.5, 127.6, 63.8, 62.8, 32.4, 32.2, 26.9, 22.0, 19.5; MS (ESI) $\text{C}_{21}\text{H}_{30}\text{SiO}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 365.2879.

Acetic acid 4-(*tert*-butyl-dimethyl-silanyloxy)-but-2-enyl ester: IR (neat) 2944, 2864, 1744, 1462, 1372, 1235, 1091, 1030, 832, 771 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 5.64 – 5.50 (m, 2H), 4.56 (d, J = 6.8 Hz, 2H), 4.20 (d, J = 5.8 Hz, 2H), 1.98 (s, 3H), 0.82 (s, 9H), 0.00 (s, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 170.7, 134.0, 124.0, 60.3, 59.4, 25.8, 20.8, 18.2, -5.2; MS (EI) m/z (relative intensity, %) 187 ($\text{M}^+ - \text{C}_4\text{H}_9$, 2), 127 (15), 117 (100), 75 (60).

Acetic acid 4-hydroxy-but-2-enyl ester: IR (neat) 3408, 2912, 1737, 1376, 1248, 1027, 851 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 5.86 – 5.58 (m, 2H), 4.66 (d, J = 6.8 Hz, 2H), 4.24 (d, J = 5.3 Hz, 2H), 2.96 (bs, 1H), 2.06 (s, 3H); ^{13}C NMR [100 MHz, CDCl_3] δ 171.1, 133.2, 125.1, 60.0, 58.0, 20.7; MS (ESI) $\text{C}_6\text{H}_{10}\text{O}_3\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 153.0416.

(2-Allyloxy-2-phenyl-ethoxy)-*tert*-butyl-dimethyl-silane: IR (neat) 2960, 2864, 1484, 1452, 1382, 1248, 1193, 1129, 1088, 998, 921, 832, 771, 694 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 7.36 – 7.26 (m, 5H), 5.97 – 5.89 (m, 1H), 5.32 – 5.27 (m, 1H), 5.18 – 5.16 (m, 1H), 4.49 (dd, J = 6.8 Hz, 4.8 Hz, 1H), 4.07 – 4.03 (m, 1H), 3.94 – 3.84 (m, 2H), 3.70 – 3.67 (m, 1H), 0.89 (s, 9H), 0.24 (2d, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 139.8, 135.0, 128.1, 127.6, 127.0, 116.4, 82.3, 69.9, 68.1, 25.8, 18.3, -5.3; HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{28}\text{O}_2\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$ 315.1756, found 315.1769.

2-Allyloxy-2-phenyl-ethanol: IR (neat) 3488, 2912, 1724, 1491, 1443, 1404, 1065, 928, cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 7.31 (m, 5H), 5.91- 5.89 (m, 1H), 5.25 – 5.23 (m, 1H), 5.17 – 5.14 (m, 1H), 4.48 (dd, J = 8.4, 3.6 Hz, 1H), 4.01 (dd, J = 12.6, 5.0 Hz, 1H), 3.85 (dd, J = 12.4 and 6.0 Hz, 1H), 3.73 – 3.59 (m, 2H), 2.57 (bs, 1H); ^{13}C NMR [100 MHz, CDCl_3] δ 138.5, 134.5, 128.5, 128.1, 126.9, 227.2, 82.2, 69.8, 67.3; MS (EI) m/z (relative intensity, %) 178 (M^+ , 1.4), 147 (100), 121 (8.6), 105 (60).

(2-Azido-cyclohexyloxy)-tert-butyl-dimethyl-silane: IR (neat) 2960, 2864, 2112, 1465, 1376, 1360, 1299, 1251, 1097, 1014, 918, 873, 832, 777, 665 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 3.34 – 3.30 (m, 1H), 3.28 – 3.08 (m, 1H), 1.86 – 1.14 (m, 8H), 0.82 (s, 9H), 0.04 (2d, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 75.0, 67.5, 34.7, 30.6, 26.1, 24.3, 23.9, 18.3, -5.3; HRMS (ESI) calcd. for $\text{C}_{12}\text{H}_{25}\text{OSiNa}$ ($\text{M}+\text{Na}$) $^+$ 278.1665, found 278.1674.

trans-1-Azido-cyclohexanol:² IR (neat) 3376, 2960, 2112, 1449, 1398, 1257, 1068, 988, 844, 665 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 3.38 (ddd, J = 9.7 Hz, 9.3 Hz, 3.9 Hz, 1H), 3.18 (ddd, J = 10.3 Hz, 10.3 Hz, 4.4 Hz, 1H), 2.29 (bs, 1H), 2.07 – 1.75 (m, 4H), 1.35 (m, 4H); ^{13}C NMR [100 MHz, CDCl_3] δ 73.5, 67.1, 33.0, 29.7, 24.1, 23.8; MS (EI) m/z (relative intensity, %) 141 (M^+ , 2), 99 (0.2), 81 (7), 57 (100).

² Sabitha, G.; Satheesh Babu, R.; Raj Kumar, M.; Yadav, J. S. *Org. Lett.* **2002**, *4*, 343.

(2-Azido-1-chloromethyl-ethoxy)-tert-butyl-dimethyl-silane: IR (neat) 2960, 2848, 2112, 1465, 1436, 1360, 1276, 1254, 1113, 956, 834, 774 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 3.83 – 3.81 (m, 1H), 3.41 – 3.28 (m, 3H), 3.17 (dd, $J = 5.08$ Hz, 12.6 Hz, 1H), 0.77 (s, 9H), 0.00 (s, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 72.1, 54.1, 45.0, 25.6, 17.7, -5.07; HRMS (ESI) calcd. for $\text{C}_9\text{H}_{20}\text{ClN}_3\text{OSiNa}$ ($\text{M}+\text{Na}$) $^+$ 272.0962, found 272.0973.

1-Azido-3-chloro-propan-2-ol:³ IR (neat) 3424, 2944, 2096, 1440, 1276, 1100, 931, 745 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 4.01 (sextet, $J = 16.0$ Hz, 10.4 Hz, 5.2 Hz, 1H), 3.67 – 3.59 (m, 2H), 3.47 (d, $J = 5.2$ Hz, 2H), 2.54 (d, $J = 5.2$ Hz, 1H); ^{13}C NMR [100 MHz, CDCl_3] δ 70.3, 53.5, 46.3; MS (EI) m/z (relative intensity, %) 135 (M^+ , 5.6), 122 (0.7), 108 (0.5), 99 (0.8), 86 (7.6), 79 (100).

tert- Butyl-hept-2-ynyloxy-dimethyl-silane:⁴ IR (neat) 2932, 2883, 1398, 1135, 1010 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 4.16 (t, $J = 1.9$ Hz, 2H), 2.24 (t, $J = 6.8$ Hz, 2H), 1.53 – 1.33 (m, 4H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.84 (s, 9H), 0.02 (s, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 87.4, 78.2, 53.3, 29.8, 20.7, 18.3, 13.8, 12.7, 10.6, -5.4; MS (EI) m/z (relative intensity, %) 169 ($\text{M}^+ - \text{C}_4\text{H}_9$, 5), 154 (12), 79 (55), 70 (80), 55 (100).

2-Heptyn-1-ol:⁵ IR (neat) 3458, 2928, 2880, 1405, 1139, 1011 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 4.24 (t, $J = 2.0$ Hz, 2H), 2.21 (t, $J = 6.9$ Hz, 2H), 2.00 (bs, 1H), 1.51 – 1.37 (m, 4H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR [100 MHz, CDCl_3] δ 86.4, 78.2, 51.2, 30.6, 21.8, 18.3, 13.5; MS (EI) m/z (relative intensity, %) 112 (M^+ , 5), 83 (60), 79 (55), 70 (80), 55 (100).

³ Sabitha, G.; Satheesh Babu, R.; Shashi Kumar reddy, M.; Yadav, J. S. *Synthesis* **2002**, 2254.

⁴ Batten, R. J.; Dixon, A. J.; Taylor, R. J. K.; Newton, R. F. *Synthesis* **1980**, 3, 234.

⁵ Ogle, C. A.; Wilson, T. E.; Stowe, J. A. *Synthesis* **1990**, 495.

***tert*-Butyl-dimethyl-(3,7,11-trimethyl-dodeca-2,6,10-trienyl)-**

silane: IR (neat) 2928, 2864, 1462, 1433, 1376, 1251, 1107, 1062, 835, 771 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 5.24 (t, $J = 6.7$ Hz, 1H), 5.04 – 5.03 (m, 2H), 4.12 (d, $J = 6.4$ Hz, 2H), 2.02 – 1.90 (m, 8H), 1.60 (s, 3H), 1.55 (s, 3H), 1.52 (s, 6H), 0.83 (s, 9H), 0.00 (s, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 137.1, 135.4, 131.4, 124.8, 124.7, 124.3, 60.6, 40.0, 39.8, 27.0, 26.6, 26.3, 25.9, 18.7, 17.9, 16.6, 16.2, –4.7; MS (EI) m/z (relative intensity, %) 279 ($\text{M}^+ - \text{C}_4\text{H}_9$, 25), 203 (10), 134 (12), 75 (100).

2-(*tert*-Butyl-dimethyl-silanyloxy)-1,1,2-triphenyl-ethanol: $[\alpha]_D^{30} + 68.2$ (c 0.5, CHCl_3); IR (neat) 3584, 3074, 2944, 2880, 1488, 1452, 1360, 1257, 1171, 937, 840 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 7.80 (d, $J = 7.8$ Hz, 2H), 7.46 – 7.09 (m, 13H), 5.56 (s, 1H), 3.58 (bs, 1H, OH), 0.77 (s, 9H), 0.00 (s, 3H), –0.25 (s, 3H); ^{13}C NMR [100 MHz, CDCl_3] δ 145.8, 143.0, 139.5, 128.7, 127.8, 127.3, 127.0, 126.9, 126.8, 126.4, 126.4, 81.0, 80.0, 25.6, 17.9, –4.2, –5.2; HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{32}\text{O}_2\text{SiNa}$ ($\text{M} + \text{Na}$) $^+$ 427.2069, found 427.2049.

***tert*-Butyl-(2-isopropyl-5-methyl-cyclohexyloxy)-dimethyl-silane:**

IR (neat) 2960, 2944, 2864, 1462, 1369, 1254, 1107, 1081, 1065, 1004, 931, 870, 835, 768 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 3.28 (ddd, $J = 10.2$ Hz, 10.2 Hz, 4.3 Hz, 1H), 2.17 – 2.16 (m, 1H), 1.98 – 1.95 (m, 1H), 1.59 – 1.51 (m, 2H), 1.70 (m, 1H), 1.08 – 1.07 (m, 2H), 1.08 – 0.75 (m, 6H), 0.83 (s, 9H), 0.67 (d, $J = 6.9$ Hz, 3H), 0.01 (2d, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 72.3, 50.2, 45.4, 34.5, 31.6, 25.9, 24.9, 22.7, 22.5, 21.3, 18.0, 15.7, –4.5, –5.0; MS (EI) m/z (relative intensity, %) 270 (M^+ , 0.2), 213 (50), 137 (45), 75 (100).

3-(*tert*-Butyl-dimethyl-silanyloxy)-4,4-dimethyl-dihydro-furan-2-one:⁶ Solid; mp 96 – 97 °C; $[\alpha]_D^{27}$ -32.9 (*c* 1.3, CHCl₃); IR (KBr) 2976, 2880, 1795, 1603, 1456, 1363, 1251, 1212, 1142, 1008, 867, 780 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 3.86 (s, 1H), 3.85 (d, *J* = 7.9 Hz, 1H), 3.75 (d, *J* = 8.8 Hz, 1H), 1.01 (s, 3H), 0.92 (s, 3H), 0.80 (s, 9H), 0.06 (s, 3H), 0.00 (s, 3H); ¹³C NMR [100 MHz, CDCl₃] δ 175.8, 76.7, 75.7, 40.9, 25.6, 23.0, 19.1, 18.2, -4.4, -5.3; MS (EI) *m/z* (relative intensity, %) 245 (*M*⁺+1, 5), 230 (15), 187 (20), 75 (100).

1-(*tert*-Butyl-dimethyl-silanyloxy)-2-(*tert*-butyl-silanyloxymethyl)-benzene:⁷ Solid; mp 125 – 127 °C; IR (KBr) 2960, 2848, 1603, 1548, 1484, 1452, 1372, 1244, 1113, 1078, 924, 838, 780 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 7.36 – 6.62 (m, 4H), 4.66 (s, 2H), 0.90 (s, 9H), 0.85 (s, 9H), 0.11 (s, 6H), 0.00 (s, 6H); ¹³C NMR [100 MHz, CDCl₃] δ 151.9, 132.2, 127.2, 127.0, 121.1, 117.8, 60.5, 26.0, 25.7, 18.4, 18.2, -5.3, -4.1; MS (ESI) C₁₉H₃₈O₂SiNa (*M*+Na)⁺ 375.1776.

[1-(*tert*-Butyl-dimethyl-silanyloxy)-phenyl]-methanol: IR (neat) 3376, 2960, 2832, 1600, 1580, 1484, 1446, 1251, 1110, 1040, 915, 825, 780, 752 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 7.20 – 6.71 (m, 4H), 4.58 (s, 2H), 2.03 (bs, 1H), 0.92 (s, 9H), 0.16 (s, 6H); ¹³C NMR [100 MHz, CDCl₃] δ 153.5, 131.4, 128.8, 128.6, 121.3, 118.4, 62.0, 25.7, 18.1, -4.1; MS (ESI) C₁₃H₂₂SiO₂Na (*M*+Na)⁺ 261.0954.

(4-Bromo-phenoxy)-*tert*-butyl-dimethyl-silane: IR (neat) 2960, 2848, 1580, 1484, 1388, 1360, 1260, 1161, 1091, 1068, 1001, 905, 835, 796, 777, 723, 868 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 7.13 (d, *J* = 8.7 Hz, 2H), 6.52 (d, *J* = 8.7 Hz, 2H), 0.79 (s, 9H), 0.00 (s, 6H); ¹³C NMR [100 MHz, CDCl₃] δ 154.8, 132.0, 122.2, 113.9, 25.6, 18.5, -4.18; MS (EI) *m/z* (relative intensity, %) 288 (*M*⁺+2, 0.1), 287 (*M*⁺+1, 0.2), 286 (*M*⁺, 0.1), 231 (100), 150 (35), 135 (40).

⁶ Miyaoka, H.; Sagawa, S.; Nagaoka, H.; Yamada, Y. *Tetrahedron: Asymmetry* **1995**, 6, 587.

⁷ Mawhinney, T. P.; Madson, M. A. *J. Org. Chem.* **1982**, 47, 3336.

[1-(*tert*-Butyl-dimethyl-silanyloxymethyl)-2-methyl-propyl]-

carbamic acid benzyl ester: $[\alpha]_D^{26}$ -18.7 (*c* 1, MeOH); IR (neat) 3452, 2958, 2862, 1710, 1492, 1250, 1368, 1250, 830 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 7.33 – 7.22 (m, 5H), 5.07 (s, 2H), 4.88 (d, J = 10.2 Hz, 1H), 3.68 (dd, J = 10.2 Hz, 3.6 Hz, 1H), 3.56 (dd, J = 9.7 Hz, 4.3 Hz, 1H), 3.42 – 3.38 (m, 1H), 1.64 (septet, J = 7.1 Hz, 1H), 0.90 (d, J = 6.8 Hz, 3H), 0.89 (d, J = 6.8 Hz, 3H), 0.84 (s, 9H), 0.00 (s, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 156.3, 136.7, 128.4, 128.3, 128.0, 66.5, 63.0, 57.7, 29.0, 25.8, 19.5, 18.6, 18.2, -5.5; HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{33}\text{NO}_3\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$ 374.2128, found 374.2136.

(1-Hydroxymethyl-2-methyl-propyl)-carbamic acid benzyl ester:⁸

Solid; mp 114 – 116 °C; $[\alpha]_D^{25}$ -15.9 (*c* 1, MeOH); IR (KBr) 3360, 2977, 2880, 1689, 1520, 1452, 1228, 1052, 736 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 7.37 – 7.29 (m, 5H), 5.23 (bs, 1H), 5.09 (AB quartet, J = 12.1 Hz, 2H), 3.68 – 3.50 (m, 3H), 3.12 (bs, 1H), 1.83 (octet, J = 6.7 Hz, 1H), 0.93 (2d, J = 6.7 Hz, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 157.2, 136.4, 128.5, 128.1, 128.0, 66.8, 63.3, 58.5, 29.2, 19.5, 18.5; MS (ESI) $\text{C}_{13}\text{H}_{19}\text{NO}_3\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 260.2852.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-1-phenyl-ethyl]-carbamic acid

***tert*-butyl ester:** $[\alpha]_D^{26}$ +21.1 (*c* 1, MeOH); IR (neat) 3428, 2960, 2864, 1708, 1496, 1360, 1251, 1164, 1107, 834, 777 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 7.36 – 7.27 (m, 5H), 5.45 (bs, 1H), 4.80 (s, 1H), 3.90 – 3.80 (m, 2H), 1.51 (s, 9H), 0.92 (s, 9H), 0.02 (2d, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 155.3, 140.6, 128.1, 127.1, 126.7, 79.1, 65.5, 56.1, 28.3, 25.7, 18.1, -5.6, -5.7; HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{33}\text{NO}_3\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$ 374.2127, found 374.2148.

⁸ Kashima, C.; Harada, K.; Fujioka, Y.; Maruyama, T.; Omote, Y. *J. Chem. Soc., Perkin Trans I* **1988**, 535.

(2-Hydroxy-1-phenyl-ethyl)-carbamic acid *tert*-butyl ester:⁹ Solid; mp 136 – 137 °C; $[\alpha]_D^{27} +38.7$ (*c* 1, CHCl₃); IR (KBr) 3376, 3280, 3072, 1667, 1545, 1366, 1289, 1174, 1052, 864, 838, 700 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 7.37 – 7.26 (m, 5H), 5.45 (bs, 1H), 4.76 (s, 1H), 3.79 (s, 2H), 3.06 (bs, 1H), 1.44 (s, 9H); ¹³C NMR [100 MHz, CDCl₃] δ 156.2, 139.6, 128.6, 127.5, 126.5, 79.9, 66.5, 56.7, 28.3; MS (ESI) C₁₃H₁₉NO₃Na (M+Na)⁺ 260.0621.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-1-phenyl-ethyl]-carbamic acid *9H*-fluoren-9-ylmethyl ester: Solid; mp 178 – 180 °C; $[\alpha]_D^{26} +18.7$ (*c* 0.5, CHCl₃); IR (KBr) 2944, 2848, 1715, 1500, 1449, 1328, 1251, 1110, 834 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 7.77 – 7.27 (m, 12H), 5.60 (bs, 1H), 4.81 (bs, 1H), 4.46– 4.39 (m, 3H), 3.96 – 3.79 (m, 2H), 0.94 (s, 9H), 0.12 (2d, 6H); ¹³C NMR [100 MHz, CDCl₃] δ 156.0, 143.9, 141.3, 140.2, 128.4, 127.6, 127.4, 127.0, 126.7, 125.1, 125.0, 119.9, 66.8, 56.5, 56.3, 47.2, 25.8, 18.2, -5.5; HRMS (ESI) calcd. for C₂₉H₃₅NO₃SiNa (M+Na)⁺ 496.2284, found 497.2276.

(2-hydroxyl-1-phenyl-ethyl)-carbamic acid *9H*-fluoren-9-ylmethyl ester: $[\alpha]_D^{27} +17.9$ (*c* 1, CHCl₃); IR (KBr) 3328, 1688, 1536, 1449, 1360, 1283, 1248, 1145, 1014, 752, 736, 697 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 7.75 – 7.71 (m, 12H), 5.56 (bs, 1H), 4.81 (bs, 1H), 4.43 – 4.41 (m, 2H), 4.19 – 4.12 (m, 1H), 3.82 (bs, 2H), 2.27 (bs, 1H); ¹³C NMR [100 MHz, CDCl₃] δ 156.4, 143.8, 141.3, 139.0, 128.8, 127.8, 127.6, 127.0, 126.5, 125.0, 119.0, 66.7, 57.0, 47.2; MS (ESI) C₂₃H₂₁NO₃Na (M+Na)⁺ 382.6067.

⁹ Cox, G. G.; Harwood, L. M. *Tetrahedron: Asymmetry* **1994**, 5, 1669.

[1-(*tert*-Butyl-dimethyl-silanyloxymethyl)-2-phenyl-ethyl]-carbamic acid *tert*-butyl ester:¹⁰ $[\alpha]_D^{26}$ -22.3 (*c* 1.1, CHCl₃); IR (neat) 3429, 2963, 2861, 1709, 1496, 1360, 1251, 1164, 1107, 834, 777 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 7.24 – 7.14 (m, 5H), 4.71 (bs, 1H), 3.79 (s, 1H), 3.47 – 3.44 (m, 2H), 2.78 (d, *J* = 7.0 Hz, 2H), 1.37 (s, 9H), 0.87 (s, 9H), 0.00 (s, 6H); ¹³C NMR [100 MHz, CDCl₃] δ 155.4, 138.4, 129.5, 129.2, 126.3, 79.2, 62.9, 53.1, 38.2, 29.8, 25.7, 18.0, -5.6; HRMS (ESI) calcd. for C₂₀H₃₅NO₃SiNa (M+Na)⁺ 388.2284, found 388.2268.

(1-Hydroxymethyl-2-phenyl-ethyl)-carbamic acid *tert*-butyl ester:¹¹ Solid; mp 94 – 95 °C; $[\alpha]_D^{26}$ -19.5 (*c* 1, CHCl₃); IR (KBr) 3376, 3280, 3072, 1667, 1545, 1366, 1289, 1174, 1052, 864, 838, 700 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 7.31 – 7.20 (m, 5H), 4.83 (bs, 1H), 3.86 (s, 1H), 3.64 (dd, *J* = 11.0 Hz, 3.5 Hz, 1H), 3.53 (dd, *J* = 10.7 Hz, 5.7 Hz, 1H), 2.83 (d, *J* = 6.9 Hz, 2H), 1.41 (s, 9H); ¹³C NMR [100 MHz, CDCl₃] δ 156.1, 137.8, 129.3, 128.5, 126.5, 79.7, 64.2, 53.7, 37.4, 28.3; MS (ESI) C₁₄H₂₁NO₃Na (M+Na)⁺ 274.2352.

[1-(*tert*-Butyl-dimethyl-silanyloxymethyl)-2-phenyl-ethyl]-carbamic acid benzyl ester: $[\alpha]_D^{30}$ -9.5 (*c* 3, CHCl₃); IR (neat) 3440, 3344, 2960, 2880, 1721, 1497, 1241, 1100, 831 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 7.29 – 7.15 (m, 10H), 5.03 (s, 2H), 3.89 (bs, 1H), 3.49 (s, 2H), 2.82 (d, *J* = 7.0 Hz, 2H), 0.88 (s, 9H), 0.01 (s, 6H); ¹³C NMR [100 MHz, CDCl₃] δ 155.8, 138.1, 136.7, 129.4, 128.5, 128.4, 128.0, 126.4, 66.5, 62.9, 53.6, 38.1, 25.7, 18.0, -5.4; HRMS (ESI) calcd. for C₂₃H₃₃NO₃SiH (M+H)⁺ 400.2308, found 400.2323.

¹⁰ Medina, E.; Moyano, A.; Pericàs, M. A.; Riera, A. *J. Org. Chem.* **1998**, 63, 8574.

¹¹ Konda, Y.; Takahashi, Y.; Arima, S.; Sato, N.; Takeda, K.; Dobashi, K.; Baba, M.; Harigaya, Y. *Tetrahedron* **2001**, 57, 2001.

(1-Hydroxymethyl-2-phenyl-ethyl)-carbamic acid benzyl ester:¹²

Solid; mp 91 – 92 °C; $[\alpha]^{30}_{\text{D}} -41.5$ (*c* 1, MeOH); IR (KBr) 3360, 3040, 2960, 2928, 2880, 1689, 1536, 1449, 1312, 1254, 1052, 1014 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 7.30 – 7.11 (m, 10H), 5.04 (bs, 1H), 4.97 (s, 2H), 3.87 (m, 1H), 3.58 – 3.49 (m, 2H), 2.78 (d, $J = 6.9$ Hz, 2H), 2.27 (bs, 1H); ^{13}C NMR [100 MHz, CDCl_3] δ 156.4, 137.5, 136.3, 129.2, 128.6, 128.5, 128.1, 128.0, 126.6, 66.8, 63.9, 54.1, 37.3; MS (ESI) $\text{C}_{17}\text{H}_{19}\text{NO}_3\text{Na}$ ($\text{M}+\text{Na}$)⁺ 307.9293.

[1-(*tert*-Butyl-dimethyl-silanyloxymethyl)-3-methyl-butyl]-

carbamic acid benzyl ester : $[\alpha]^{30}_{\text{D}} -15.5$ (*c* 2, CHCl_3); IR (neat) 3440, 3328, 2944, 2880, 1715, 1510, 1465, 1254, 1100, 834 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 7.31 – 7.26 (m, 5H), 5.05 (s, 2H), 4.83 (d, $J = 8.6$ Hz, 1H), 3.72 (m, 1H), 3.57 – 3.52 (m, 2H), 1.60 (heptet, $J = 5.7$ Hz, 1H), 1.32 (t, $J = 6.7$ Hz, 2H), 0.90 – 0.85 (m, 6H), 0.80 (s, 9H), 0.04 (s, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 156.0, 136.7, 128.4, 128.3, 128.1, 66.5, 65.0, 50.6, 40.8, 24.7, 23.0, 22.6, 22.3, 18.4, -5.4; HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{35}\text{NO}_3\text{SiNa}$ ($\text{M}+\text{Na}$)⁺ 388.2284, found 388.2273.

(1-Hydroxymethyl-3-methyl-butyl)-carbamic acid benzyl ester:¹³

$[\alpha]^{27}_{\text{D}} -25.5$ (*c* 1, MeOH); IR (neat) 3524, 2928, 1715, 1510, 1463, 1255, 1109 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 7.31 – 7.18 (s, 5H), 5.01 (s, 2H), 4.88 (bs, 1H), 3.71 – 3.70 (m, 1H), 3.59 – 3.56 (m, 1H), 3.42 (dd, $J = 10.2$ Hz, 5.2 Hz, 1H), 2.60 (bs, 1H), 1.57 (heptet, $J = 6.7$ Hz, 1H), 1.27 – 1.22 (m, 2H), 0.84 (d, $J = 6.3$ Hz, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 156.8, 136.3, 128.5, 128.1, 128.0, 66.8, 65.9, 51.4, 40.4, 24.7, 23.0, 22.1; MS (ESI) $\text{C}_{14}\text{H}_{21}\text{NO}_3\text{Na}$ ($\text{M}+\text{Na}$)⁺ 274.3184.

¹² Maeda, H.; Maki, T.; Ohmori, H. *Tetrahedron Lett.* **1992**, 33, 1347.

¹³ Maeda, H.; Maki, T.; Ohmori, H. *Tetrahedron Lett.* **1992**, 33, 1347.

tert-Butyl-(6-methoxy-2,2-dimethyl-tetrahydro-furo[3,4-d][1,3]dioxol-4-ylmethoxy)-dimethyl-silane: $[\alpha]_D^{23}$ -58.4 (*c* 1.6, CHCl₃); IR (neat) 2928, 2864, 1465, 1365, 1257, 1209, 1109, 1011, 835 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 4.86 (s, 1H), 4.55 (d, *J* = 5.9 Hz, 1H), 4.49 (d, *J* = 5.9 Hz, 1H), 4.20 (dd, *J* = 5.7 Hz, 3.2 Hz, 1H), 3.56 (dd, *J* = 10.2 Hz, 5.7 Hz, 1H), 3.46 (t, *J* = 9.4 Hz, 1H), 3.23 (s, 3H), 1.41 (s, 3H), 1.25 (s, 3H), 0.83 (s, 9H), 0.00 (s, 6H); ¹³C NMR [100 MHz, CDCl₃] δ 112.1, 109.3, 87.0, 85.1, 81.9, 63.7, 54.6, 25.8, 25.6, 25.0, 18.2, -5.4; HRMS (ESI) calcd. for C₁₅H₃₀O₅SiNa (M+Na)⁺ 341.1760, found 341.1781.

(6-methoxy-2,2-dimethyl-tetrahydro-furo[3,4-d][1,3]dioxol-4-yl)-methanol:¹⁴ $[\alpha]_D^{23}$ -76.9 (*c* 1.5, CHCl₃); IR (neat) 3440, 2928, 1454, 1379, 1270, 1200, 1155, 1081, 867 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 4.93 (s, 1H), 4.78 (d, *J* = 5.8 Hz, 1H), 4.55 (d, *J* = 5.8 Hz, 1H), 4.36 (t, *J* = 9.3 Hz, 1H), 3.70 – 3.50 (m, 2H), 3.39 (s, 3H), 3.26 (bs, 1H), 1.45 (s, 3H), 1.28 (s, 3H); ¹³C NMR [100 MHz, CDCl₃] δ 111.9, 109.7, 88.0, 85.5, 81.3, 63.7, 55.1, 26.1, 24.5; MS (ESI) C₉H₁₆O₅Na (M+Na)⁺ 227.3544.

¹⁴ Barrett, A. G. M.; Lebold, S. A. *J. Org. Chem.* **1990**, 55, 3853.

tert-Butyl-dimethyl-(2,2,7,7-tetramethyl-tetrahydro

bis[1,3]dioxolo[5,4-b:4',5'-d]pyran-5-ylmethoxy)-silane:¹⁵ $[\alpha]^{29}_{\text{D}} -52.1$ (*c* 1.6, CHCl_3); IR (neat) 2928, 2864, 1465, 1365, 1257, 1209, 1109, 1011, 835 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 5.51 (d, $J = 5.0$ Hz, 1H, H-1), 4.57 (dd, $J = 7.8$ Hz and 2.2 Hz, 1H, H-6'), 4.30 – 4.27 (m, 2H, H-4, H-6), 3.82 – 3.73 (m, 3H, H-5, H-3, H-2), 1.57 (s, 3H), 1.53 (s, 3H), 1.33 (s, 6H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 108.9 ($\text{C}(\text{CH}_3)_2\text{O}_2$), 108.3 (C1), 96.3 ($\text{C}(\text{CH}_3)_2\text{O}_2$), 70.9 (C2), 70.6 (C4), 70.5 (C3), 68.3 (C5), 61.9 (C6), 26.0 ($\text{C}(\text{CH}_3)_2\text{O}_2$), 25.9 ($\text{C}(\text{CH}_3)_2\text{O}_2$), 25.8 ($-\text{C}(\text{CH}_3)_3$), 24.9 ($\text{C}(\text{CH}_3)_2\text{O}_2$), 24.3 ($\text{C}(\text{CH}_3)_2\text{O}_2$), 18.3 ($-\text{C}(\text{CH}_3)_3$), -5.4 ($-\text{Si}(\text{CH}_3)_2$); MS (ESI) $\text{C}_{18}\text{H}_{34}\text{SiO}_6$ (M)⁺ 375.1830.

(2,2,7,7-Tetramethyl-tetrahydro-bis[1,3]dioxolo[4,5-b:4',5'-

d]pyran-5-yl)-methanol:¹⁶ $[\alpha]^{29}_{\text{D}} -57.1$ (*c* 1.2, CHCl_3); IR (neat) 3442, 2932, 1452, 1375, 1210, 1155, 1089 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 5.57 (d, $J = 5.1$ Hz, 1H, H-1), 4.61 (dd, $J = 7.9$ Hz and 2.3 Hz, 1H, H-6'), 4.33 (dd, $J = 4.9$ Hz and 2.3 Hz, 1H, H-6), 4.27 (d, $J = 7.7$ Hz, 1H, H-3), 3.88 – 3.84 (m, 2H, H-2, H-5), 3.75 (t, $J = 7.5$ Hz, 1H, H-4), 1.53 (s, 3H), 1.46 (s, 3H), 1.32 (s, 6H); ^{13}C NMR [100MHz, CDCl_3] δ 109.4 ($\text{C}(\text{CH}_3)_2\text{O}_2$), 108.6 (C1), 96.2 ($\text{C}(\text{CH}_3)_2\text{O}_2$), 71.6 (C2), 70.7 (C4), 70.5 (C3), 68.1 (C5), 62.3 (C6), 26.0, 25.9, 24.9, 24.2 ($\text{C}(\text{CH}_3)_2\text{O}_2$); MS (ESI) $\text{C}_{12}\text{H}_{20}\text{O}_6\text{Na}$ (M+Na)⁺ 283.0751.

¹⁵ Khan, A. T.; Mondal, E. *Synlett* **2003**, 694

¹⁶ Khan, A. T.; Mondal, E. *Synlett* **2003**, 694.

3-(*tert*-Butyldimethylsilane)-1,2:4,5-Di-Oisopropylidene- β -D-

fructopyranoside: Solid; mp 112 – 113 °C; $[\alpha]^{33}_{\text{D}}$ -83.7 (*c* 1, CHCl₃); IR (KBr) 3447, 1375, 1210, 1155, 1089 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 4.09 (dd, *J* = 5.6 Hz and 2.5 Hz, 1H), 4.04 (dd, *J* = 13.5 Hz and 2.6 Hz, 1H), 4.01 – 3.99 (m, 2H), 3.89 (d, *J* = 13.2 Hz, 1H), 3.82 (d, *J* = 8.3 Hz, 1H), 3.56 (d, *J* = 7.2 Hz, 1H), 1.43 (s, 3H), 1.39 (s, 3H), 1.32 (s, 3H), 1.26 (s, 3H), 0.82 (s, 9H), 0.07 (s, 3H), 0.00 (s, 3H); ¹³C NMR [100MHz, CDCl₃] δ 111.9, 108.7, 105.1, 77.9, 73.7, 71.8, 71.5, 60.3, 28.2 (C(CH₃)₂O₂), 26.7, 26.3, 25.9, 25.6 (-C(CH₃)₃), 18.1 (-C(CH₃)₃), -3.57 (-Si(CH₃)), -5.26 (-Si(CH₃)); HRMS (ESI) calcd. for C₁₈H₃₄SiO₆Na (M+Na)⁺ 397.2022, found 397.2005.

1,2:4,5-Di-Oisopropylidene- β -D-fructopyranose:¹⁷ Solid; mp 119 – 120 °C; $[\alpha]^{30}_{\text{D}}$ -146.1 (*c* 1, CHCl₃); IR (KBr) 3543, 1356, 1201, 1079 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 4.21 (dd, *J* = 5.8 Hz and 2.2 Hz, 1H), 4.19 – 4.11 (m, 2H), 4.10 (d, *J* = 2.4 Hz, 1H), 4.03 – 3.97 (m, 2H), 3.68 – 3.66 (m, 1H), 2.06 (d, *J* = 7.7 Hz, 1H), 1.53 (s, 3H), 1.51 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H); ¹³C NMR [100MHz, CDCl₃] δ 111.8, 109.4, 104.5, 76.7, 73.3, 72.3, 70.4, 60.7, 27.9 (C(CH₃)₂O₂), 26.4, 26.2, 25.9; MS (ESI) C₁₂H₂₀O₆Na (M+Na)⁺ 283.0751.

¹⁷ Tu, Y.; Frohn, M.; Wang, Z.-X.; Shi, Y. *Organic Syntheses*, 80, 1.

2-(*tert*-Butyl-dimethyl-silanyloxymethyl)-6-methoxy-tetrahydro-pyran-3,4,5-triol:¹⁸ Solid; mp 155 – 156 °C; $[\alpha]_D^{29} +56.8$ (*c* 0.75, MeOH); IR (KBr) 3436, 2994, 2894, 1470, 1252, 1140, 1044, 1016, 970, 836, 774 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 5.11 (bs, 1H, H-1), 4.63 (s, 1H, H-4), 4.44 (bs, 1H, H-5), 4.28 (bs, 1H, H-2), 3.78 (s, 1H, H-3), 3.71 – 3.65 (m, 1H, H-6), 3.46 – 3.41 (m, 1H), 3.31 (s, 4H), 3.16 (bs, 2H), 0.81 (s, 9H), 0.00 (s, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 99.3 (C1), 74.2 (C3), 71.9 (C5), 71.5 (C2), 71.0 (C4), 63.4 (C6), 54.9 (OCH_3), 25.9 ($-\text{C}(\text{CH}_3)_3$), 18.3 ($-\text{C}(\text{CH}_3)_3$), -5.3 ($-\text{Si}(\text{CH}_3)_2$); MS (ESI) $\text{C}_{13}\text{H}_{28}\text{SiO}_6\text{Na}$ ($\text{M}+\text{Na}$)⁺ 331.1537.

Acetic acid 3,5-diacetoxy-2-(*tert*-butyl-dimethyl-silanyloxymethyl)-6-methoxy-tetrahydro-pyran-4-yl ester:¹⁹ $[\alpha]_D^{29} +74.8$ (*c* 1.6, MeOH); IR (neat) 2960, 2880, 1747, 1462, 1436, 1363, 1257, 1049, 931, 835, 777 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 5.46 (t, $J = 9.7$ Hz, 1H, H-1), 5.00 (t, $J = 9.7$ Hz, 1H, H-3), 4.93 (d, $J = 3.4$ Hz, 1H, H-2), 4.86 (dd, $J = 10.1$ Hz, 3.4 Hz, 1H, H-4), 3.83 – 3.80 (m, 1H, H-5), 3.68 (d, $J = 3.6$ Hz, 2H, H-6), 3.40 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 170.2 (COCH_3), 170.1 (COCH_3), 169.5 (COCH_3), 96.4 (C1), 70.9 (C2), 70.4 (C4), 69.8 (C6), 69.0 (C3), 62.1 (C5), 55.0 (OCH_3), 25.8 (COCH_3), 20.8, 20.7, 20.6 ($-\text{C}(\text{CH}_3)_3$), 18.2 ($-\text{C}(\text{CH}_3)_3$), -5.4 ($-\text{Si}(\text{CH}_3)_2$); MS (ESI) $\text{C}_{19}\text{H}_{34}\text{O}_9\text{SiNa}$ ($\text{M}+\text{Na}$)⁺ 457.1533.

¹⁸ Rockwell, G. D.; Grindley, T. B. *J. Am. Chem. Soc.* **1998**, *120*, 10953.

¹⁹ Franke, F.; Guthrie, R. D. *Aust. J. Chem.* **1977**, *30*, 639.

Aceticacid3, 5-diacetoxy-2-hydroxymethyl-6-methoxy-tetrahydro-pyran-4-yl ester:²⁰ Solid; mp 110 – 111 °C; $[\alpha]_D^{29} +115.8$ (c 1.1, MeOH); IR (KBr) 3520, 2960, 1747, 1372, 1232, 1036 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 5.46 (t, $J = 9.8$ Hz, 1H, H-1), 4.95 (t, $J = 9.8$ Hz, 1H, H-3), 4.90 (d, $J = 3.7$ Hz, 1H, H-2), 4.80 (dd, $J = 10.2$ Hz and 3.6 Hz, 1H, H-4), 3.73 – 3.70 (m, 1H, H-6), 3.68 - 3.64 (m, 1H, H-5), 3.53 (dd, $J = 12.6$ Hz and 4.0 Hz, 1H, H-6), 3.34 (s, 3H), 2.36 (bs, 1H), 2.01 (s, 3H), 1.99 (s, 3H), 1.95 (s, 3H); ^{13}C NMR [100 MHz, CDCl_3] δ 170.6 (COCH_3), 170.2 (COCH_3), 170.0 (COCH_3), 96.7 (C1), 70.9 (C2), 69.7 (C4), 69.2 (C3), 68.8 (C5), 60.9 (C6), 55.4 (OCH_3), 20.8, 20.7, 20.6 (COCH_3); MS (ESI) $\text{C}_{13}\text{H}_{20}\text{O}_9\text{Na}$ ($\text{M}+\text{Na}$)⁺ 343.2959.

Methanesulfonicacid 6-(*tert*-butyl-dimethyl-silanyloxymethyl)-4,5-bis-methanesulfonyloxy-2-methoxy-tetrahydro-pyran-3-yl ester: $[\alpha]_D^{33} +51.9$ (c 1, CHCl_3); IR (neat) 3520, 2960, 1416, 1372, 1232, 1036 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 5.02 (t, $J = 9.7$ Hz, 1H), 4.96 (d, $J = 3.6$ Hz, 1H), 4.71 (dd, $J = 10.2$ Hz and 3.6 Hz, 1H), 3.82 – 3.72 (m, 3H), 3.36 (s, 3H), 3.11 (s, 3H), 3.09 (s, 3H), 3.07 (s, 3H), 0.84 (s, 9H), 0.02 (2d, 6H); ^{13}C NMR [100 MHz, CDCl_3] δ 97.1 (C1), 76.0 (C6), 74.8 (C5), 73.9 (C2), 69.6 (C4), 61.3 (C3), 55.8 (OCH_3), 39.4 ($-\text{SO}_2\text{CH}_3$), 38.8 ($-\text{SO}_2\text{CH}_3$), 38.7 ($-\text{SO}_2\text{CH}_3$), 25.7 ($-\text{C}(\text{CH}_3)_3$), 14.1 ($-\text{C}(\text{CH}_3)_3$), -5.2 ($-\text{SiCH}_3$), -5.4 ($-\text{SiCH}_3$); HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{34}\text{O}_{12}\text{S}_3\text{SiNa}$ ($\text{M}+\text{Na}$)⁺ 565.0879, found 565.0869.

²⁰ Franke, F.; Guthrie, R. D. *Aust. J. Chem.* **1977**, *30*, 639.

Methanesulfonicacid-2-hydroxymethyl-4,5-bis-ethanesulfonyloxy-6-methoxy-tetrahydro-pyran-3-ylester:²¹ $[\alpha]^{33}_{\text{D}}$ +50.3 (*c* 1, CHCl₃); IR (KBr) 3520, 2960, 1416, 1372, 1232, 1036 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 5.14 – 5.09 (m, 2H), 4.88 (t, *J* = 9.5 Hz, 1H), 4.69 (dd, *J* = 9.8 Hz and 3.6 Hz, 1H), 3.91 – 3.83 (m, 3H), 3.47 (s, 3H), 3.23 (s, 3H), 3.20 (s, 3H), 3.17 (s, 3H), 2.78 (bs, 1H); ¹³C NMR [100 MHz, CDCl₃] δ 97.1 (C1), 75.9 (C6), 74.8 (C5), 73.3 (C2), 69.5 (C4), 60.0 (C3), 55.9 (OCH₃), 39.3 (-SO₂CH₃), 38.9 (-SO₂CH₃), 38.7 (-SO₂CH₃); MS (ESI) C₁₀H₂₀O₁₂S₃Na (M+Na)⁺ 451.1432.

Benzoicacid3,5-dibenzoxy-2-(tert-butyl-dimethyl-silanyloxymethyl)-6-methoxy-tetrahydro-pyran-4-yl ester: $[\alpha]^{33}_{\text{D}}$ -84.5 (*c* 1, CHCl₃); IR (neat) 2928, 2864, 1728, 1600, 1452, 1452, 1263, 1097, 1068, 1024, 972, 839, 771, 709 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 7.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.50 – 7.13 (m, 9H), 5.86 (t, *J* = 9.7 Hz, 1H, H-1), 5.74 (dd, *J* = 10.3 Hz and 3.4 Hz, 1H, H-3), 5.56 (t, *J* = 3.8 Hz, 1H, H-2), 4.88 (s, 1H, H-4), 4.10 – 4.00 (m, 1H, H-5), 3.78 – 3.77 (m, 2H, H-6), 3.40 (s, 3H), 0.80 (s, 9H), 0.00 (s, 6H); ¹³C NMR [100 MHz, CDCl₃] δ 165.5 (COPh), 165.5 (COPh), 165.3 (COPh), 133.3, 133.1, 132.9, 129.9, 129.7, 129.6, 129.4, 129.2, 128.4, 128.3, 128.1, 98.5 (C1), 71.4 (C2), 70.6 (C6), 70.4 (C3), 66.9 (C5), 62.2 (C4), 55.2 (OCH₃), 25.8 (-C(CH₃)₃), 18.2 (-C(CH₃)₃), -3.6 (-SiCH₃), -5.4 (-SiCH₃); HRMS (ESI) calcd. for C₃₄H₄₀O₉SiNa (M+Na)⁺ 643.2339, found 643.2354.

²¹ Sinclair, H. B. *J. Org. Chem.* **1981**, *46*, 2450.

Benzoic acid 3,5-dibenzyloxy-2-hydroxymethyl-6-methoxy-

tetrahydro-pyran-4-yl ester:²² $[\alpha]_D^{29}$ -83.3 (*c* 1, CHCl₃); IR (neat) 3520, 2944, 1724, 1603, 1452, 1267, 1027 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 8.01 (d, *J* = 7.3 Hz, 2H), 7.89 (d, *J* = 7.3 Hz, 2H), 7.74 (d, *J* = 7.4 Hz, 2H), 7.52 – 7.28 (m, 7H), 7.17 (t, *J* = 7.8 Hz, 2H), 5.88 (t, *J* = 8.3 Hz, 1H-1), 5.75 (t, *J* = 10.1 Hz, 1H, H-3), 5.58 (dd, *J* = 3.0 Hz, 1.6 Hz, 1H, H-2), 4.92 (s, 1H, H-4), 3.97 – 3.95 (m, 1H, H-5), 3.75 – 3.70 (m, 2H, H-6), 3.42 (s, 3H), 2.74 (bs, 1H); ¹³C NMR [100 MHz, CDCl₃] δ 166.6 (COPh), 165.6 (COPh), 165.5 (COPh), 133.8, 133.7, 133.6, 133.3, 129.9, 129.7, 129.1, 128.9, 128.7, 128.6, 128.5, 128.3, 98.6 (C1), 70.7 (C2), 70.4 (C3), 69.4 (C4), 67.1 (C5), 61.2 (C6), 55.5 (OCH₃); MS (ESI) C₂₈H₂₆O₉Na (M+Na)⁺ 528.8799.

3,4-Bis-benzyloxy-5-(tert-butyl-dimethyl-silanyloxy)-6-(tert-

diphenyl-silanyloxymethyl)-2-methoxy-tetrahydro-pyran: $[\alpha]_D^{33}$ + 28.4 (*c* 1, CHCl₃); IR (neat) 2978, 2880, 1462, 1424, 1366, 1254, 1065, 905, 838, 729 cm⁻¹; ¹H NMR [400 MHz, CDCl₃] δ 7.85 – 7.82 (m, 5H), 7.56 – 7.40 (m, 15H), 5.19 (d, *J* = 11.3 Hz, 1H, PhCH₂), 4.87 (d, *J* = 12.0 Hz, 1H, PhCH₂), 4.84 (d, *J* = 12.2 Hz, 1H, PhCH₂), 4.74 (d, *J* = 11.7 Hz, 1H, PhCH₂), 4.73 (d, *J* = 3.6 Hz, 1H, H-1), 4.05 – 4.03 (m, 1H, H-6'), 3.89 – 3.85 (m, 2H, H-3 and H-4), 3.83 – 3.81 (m, 1H, H-5), 3.67 – 3.63 (m, 2H, H-2 and H-6), 3.55 (s, 3H, OCH₃), 1.21 (s, 9H), 0.92 (s, 9H), 0.11 (s, 3H), 0.00 (s, 3H); ¹³C NMR [100 MHz, CDCl₃] δ 139.2, 138.1, 135.8, 135.7, 128.4, 128.1, 127.8, 127.7, 127.5, 127.5, 127.3, 127.0, 97.3 (C1), 81.8 (PhCH₂), 80.6 (PhCH₂), 75.1 (C2), 73.1 (C5), 72.7 (C3), 71.1 (C4), 63.6 (C6), 54.7 (OCH₃), 26.8 (-C(CH₃)₃), 25.9 (-C(CH₃)₃), 19.2 (-C(CH₃)₃), 17.9 (-C(CH₃)₃), -3.7 (-SiCH₃), -4.7 (-SiCH₃); HRMS (ESI) calcd. for C₄₃H₅₈O₆Si₂Na (M+Na)⁺ 749.3670, found 749.3662.

²² Gan, L. X.; Whistler, R. L.; Whistler, C. *Carbohydr. Res.* **1990**, 206, 65.

4,5-Bis-benzyloxy-2-(*tert*-butyl-diphenyl-silanyloxymethyl)-6-

methoxy-tetrahydro-pyran-3-ol:²³ $[\alpha]^{30}_{\text{D}} + 13.1$ (*c* 1.6, CHCl_3); IR (neat) 3472, 2944, 2880, 1462, 1424, 1376, 1252, 1113, 1046, 816, 750 cm^{-1} ; ^1H NMR [400 MHz, CDCl_3] δ 7.69 – 7.65 (m, 5H), 7.41 – 7.29 (m, 15H), 4.77 and 4.60 (AB quartet, $J = 12.0$ Hz, 2H, PhCH_2), 4.82 and 4.75 (AB quartet, $J = 11.6$ Hz, 2H, PhCH_2), 4.62 (d, $J = 3.4$ Hz, 1H, H-1), 3.86 – 3.77 (m, 3H, H-3, H-4 and H-6), 3.62 – 3.57 (m, 2H, H-2 and H-5), 3.50 (dd, $J = 9.6$ Hz and 3.6 Hz, 1H, H-6), 3.35 (s, 3H, OCH_3), 2.01 (bs, 1H, OH), 1.06 (s, 9H); ^{13}C NMR [100 MHz, CDCl_3] δ 138.8, 138.1, 135.6, 133.2, 129.7, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 127.6, 97.9 (C1), 81.6 (PhCH_2), 79.7 (PhCH_2), 75.5 (C2), 73.1 (C5), 71.3 (C3), 70.9 (C4), 64.1 (C6), 55.0 (OCH_3), 26.8 ($-\text{C}(\text{CH}_3)_3$), 19.2 ($-\text{C}(\text{CH}_3)_3$); HRMS (ESI) calcd. for $\text{C}_{37}\text{H}_{44}\text{O}_6\text{SiNa}$ ($\text{M}+\text{Na}$)⁺ 635.8246, found 635.1932.

²³ Ito, Y.; Ogawa, T. *Tetrahedron Lett.* **1988**, 29, 1061.

IV. Powder X-ray diffraction (XRD) pattern of PMA/SiO₂²⁴

XRD patterns were obtained in order to make sure that phosphomolybdic acid was effectively supported on silica gel before and after the deprotection of TBDMS ether. Two very weak diffraction peaks around $2\theta = 12.5^\circ$ and 24.5° , are characteristic diffraction peaks of 10% by wt of PMA on SiO₂.³⁸ This pattern indicates that the dispersion state of the PMA on silica gel is unaltered even after the reaction.

XRD powder pattern of (a) PMA/SiO₂ before the reaction (b) PMA/SiO₂ after the reaction and (c) bulk PMA.

²⁴ Kuang, W.; Rives, A.; Fourbier, M.; Hubaut, R. *Appl. Catal. A: General* **2003**, 250, 221.