Supplementary Information

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Experimental procedures

Preparation of SmI_2 in THF

Fresh SmI_2 in THF (0.11 M) was readily prepared from Sm-powder (1.7 g, 11.3 mmol), I_2 (2.8 g, 11 mmol) and THF (100 mL). The reagents were mixed and after 2 hours in an ultrasonic bath SmI_2 (0.11 M) was generated. No further purification was needed.

General allylation procedure

The alcohol (or carbohydrate) (15 mmol, 1 equiv.) was dissolved in THF (50 mL, dried over Na), deprotonated with NaH (18 mmol, 1.2 equiv.) and then allyl bromide (30 mmol, 2 equiv.) was added. The mixture was left standing over night. The reaction mixture was quenched with water, extracted with n-hexane (3×50 mL), dried over $MgSO_4$, filtrated, and finally the solvents were evaporated. The product was purified by flash chromatography on silica with EtOAc:n-hexane or EtOAc:toluene.

Characterization of substrates and alcohol products (commercially available compounds have been left out):

Table 1:

entry 1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (m, 4H), 1.66 (br s, 2H), 1.99 (d, 2H), 3.26 (m, 2H), 4.15 (d, 4H), 5.15 (d, 2H), 5.29 (d, 2H), 5.93 (m, 2H). MS (EI): *m/z* 197 (M+1), 139, 127, 121, 109, 92, 81.

entry 2: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60 (s, 3H), 1.67 (d, 6H), 2.08 (m, 4H), 4.00 (m, 4H), 5.10 (t, 1H), 5.20 (d, 1H), 5.30 (d, 1H), 5.38 (t, 1H), 5.95 (m, 1H). MS (EI): *m/z* 194 (M+), 179, 153, 137, 123, 110, 95, 81, 67.

entry 3: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (d, 3H), 1.18 (m, 1H), 1.37 (m, 2H), 1.6-1.7 (m, 8H), 2.00 (m, 2H), 3.47 (m, 2H), 3.99 (d, 2H), 5.10 (t, 1H), 5.18 (d, 1H), 5.28 (d, 1H), 5.93 (m, 1H). MS (EI): *m/z* 197 (M+1), 149, 138, 123, 109, 95, 81.

entry 4: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, 3H), 1.30 (m, 10H), 1.59 (m, 2H), 3.43 (t, 2H), 3.98 (d, 2H), 5.18 (d, 1H), 5.28 (d, 1H), 5.94 (m, 1H). MS (EI): *m/z* 171 (M+1), 141, 110, 97, 82, 71, 40.

entry 5: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 (t, 2H), 3.67 (t, 2H), 4.01 (d, 2H), 5.20 (d, 1H), 5.28 (d, 1H), 5.92 (m, 1H), 7.27 (m, 5H). MS (EI): *m/z* 162 (M+), 145, 105, 91, 77, 65.

entry 6: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (s, 3H), 3.55-3.70 (m, 8H), 4.04 (d, 2H), 5.19 (d, 1H), 5.28 (d, 1H), 5.92 (m, 1H). MS (EI): *m/z* 161 (M+), 129, 103, 99, 70.

entry 7: Garegg, P. J.; Hultberg, H. *Carbohydr. Res.* **1981**, *93*, C10-C11.

entry 8: substrate: Garegg, P. J.; Hultberg, H. *Carbohydr. Res.* **1981**, *93*, C10-C11. product: Schneider, J.; Lee, Y. C.; Flowers, H. M. *Carbohydr. Res*. **1974**, *36*, 245-252.

entry 9: substrate: ^{13}C NMR (400 MHz, $CDCl_3$) δ 15.1, 25.4 (SCH_2CH_3), 55.4, 69.3, 71.6, 71.9, 72.0, 72.4, 75.2, 75.8, 80.4, 81.9 (C1-C6, CH_2 benzyl, allyl), 116.9 (allyl), 127.7-134.9 (aromatic, allyl). product: Verduyn, R.; Belien, J. J. A; Freef-Tromp, C. M.; Van der Marel, G. A.; Van Boom, J. H. *Tetrahedron Lett.* **1991**, *32*, 6637.

entry 10: substrate: ^{13}C NMR (400 MHz, $CDCl_3$) δ 15.2, 25.5 (SCH_2CH_3), 69.4, 72.1, 72.2, 72.5, 75.3, 76.5, 80.5, 82.0 (C1-C6, CH_2 benzyl), 116.9 (allyl), 127.8-138.8 (aromatic, allyl). product: ^{13}C NMR (400 MHz, $CDCl_3$) δ15.0, 25.5 (SCH_2CH_3), 62.4, 72.3, 72.5, 72.5, 75.1, 75.3, 76.7, 80.5, 82.3 (C1-C6, CH_2 benzyl), 127.8-138.5 (aromatic, allyl).

entry 11: Thiem, J.; Duckstein, V.; Pranst, A.; Matzke, M. *Liebigs. Ann. Chem.* **1987**, 289-295.

entry 12: substrate: ^{13}C NMR (400 MHz, $CDCl_3$) δ 67.8, 69.4, 71.2, 71.8, 72.1, 72.4, 74.0, 74.9, 75.0, 79.6, 97.3 (C1-C6, allyl), 116.6, 116.6, 116.8, 117.3, 117.4, 133.9, 135.0, 135.1, 135.2,

135.2 (allyl). product: ^{13}C NMR (400 MHz, $CDCl_3$) δ 20.4-20.6 (CH_3 acetyl), 62.3, 66.0, 68.4, 68.9, 69.4, 96.4 (C1-C6), 118.1 (allyl), 125.1-132.8 (aromatic, allyl), 169.4-170.2 (C=O acetyl).

Scheme 1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.58 (d, 2H), 5.30 (d, 1H), 5.42 (d, 2H), 6.08 (m, 1H), 6.95 (m, 3H), 7.28 (m, 2H). *m/z* 134 (M+), 119, 102, 87.

Scheme 2: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (m, 5H), 1.55 (m, 1H), 1.76 (m, 2H), 1.93 (m, 2H), 3.29 (m, 1H), 4.01 (d, 2H), 5.15 (d, 1H), 5.28 (d, 1H), 5.94 (m, 1H). *m/z* 140 (M+), 113, 95, 83, 67.

Table 2:

entry 1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (d, 3H), 4.55 (d, 2H), 5.65 (m, 1H), 5.80 (m, 1H), 6.85 (m, 3H), 7.22 (m, 2H). MS (EI): *m/z* 148 (M+), 117, 94.

entry 2: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 4.42 (s, 2H), 4.99 (s, 1H), 5.10 (s, 1H), 6.94 (m, 3H), 7.26 (m, 2H). MS (EI): *m/z* 148 (M+), 133, 102.

entry 3: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (d, 3H), 4.40 (d, 2H), 5.65 (m, 1H), 5.80 (m, 1H), 6.85 (m, 3H), 7.22 (m, 2H). MS (EI): *m/z* 148 (M+), 114, 93.

entry 4: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (d, 2H), 5.11 (d, 1H), 5.30 (d, 1H), 5.99 (m, 1H), 6.65 (m, 3H), 7.23 (m, 2H). MS (EI): *m/z* 134 (M+1), 117, 103, 88.

entry 5: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (d, 2H), 5.09 (d, 1H), 5.15 (d, 1H), 5.89 (m, 1H), 7.21 (t, 1H), 7.27-7.26 (m, 4H). MS (EI): *m/z* 151 (M+1), 134, 114, 67.

entry 6: ^{1}H NMR (400 MHz, $CDCl_3$) cis/trans mixture δ 1.71 (d, 3H), 4.90 (m, 0.6H), 5.40 (m, 0.4H), 6.42 (m, 1H), 7.03 (m, 2H), 7.32 (m, 2H). MS (EI): *m/z* 134 (M+), 119, 102, 65.

entry 7: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (d, 3H), 3.85 (m, 2H), 4.50 (q, 1H), 5.18 (d, 1H), 5.26 (d, 1H), 5.93 (m, 1H), 7.35 (m, 5H). MS (EI): *m/z* 161, 147, 131, 106, 77.

Scheme 3: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, 6H), 1.30 (br m, 21H), 1.59 (m, 3H), 3.25 (q, 1H), 3.50 (q, 1H), 3.59 (q, 1H), 5.15 (s, 1H), 5.19 (d, 1H), 5.67 (m, 1H). *m/z* 268 (M+), 197, 112.

Table 3:

entry 1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 3H), 1.33 (br m, 6H), 1.47 (m, 1H), 1.61 (m, 1H), 3.68 (q, 1H), 3.86 (dd, 1H)), 4.05 (dd, 1H), 5.15 (d, 1H), 5.19 (d, 1H), 5.27 (d, 2H) , 5.68 (m, 1H), 5.91 (m, 1H). MS (EI): *m/z* 167 (M-1), 151, 139, 125, 111, 95, 81, 69.

entry 2: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (d, 2H), 4.58 (d, 2H), 4.62 (s, 2H), 5.21 (d, 1H), 5.29 (d, 1H), 5.34 (d, 1H), 5.43 (d, 1H), 6.02 (m, 2H), 6.87 (d, 1H) 6.98 (t, 1H), 7.25 (t, 1H), 7.43 (d, 1H). MS (EI): *m/z* 204 (M+), 175, 160, 148, 131, 115, 104.

entry 3: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (d, 2H), 4.48 (s, 2H), 5.16 (d, 1H), 5.26 (d, 1H), 5.91 (m, 1H), 7.25 (m, 5H). MS (EI): *m/z* 147 (M-1), 131, 105, 91, 65.

entry 4: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (d, 2H), 4.67 (s, 2H), 5.24 (d, 1H), 5.35 (d, 1H), 5.99 (m, 1H), 7.20 (t, 1H), 7.47 (d, 1H), 7.71 (t, 1H), 8.56 (d, 1H). MS (EI): *m/z* 150 (M+1), 120, 93, 65.

Standard SmI_2/H_20/Amine mediated deprotection of allyl ethers into alcohols

Micro-scale

In a standard micro-scale procedure, SmI_2 in THF (0.5 mmol, 5 equiv.) was added to a dry Schlenk tube, containing a magnetic stirrer bar and fitted with a septum, inside a glove box under nitrogen atmosphere. The amine (2.0 mmol, 20 equiv. isopropylamine) and the allyl substrate (0.1 mmol, 1 equiv.) were added under stirring. To this mixture the proton donor, i.e. H_2O (1.5 mmol, 15 equiv.), was added slowly at 20.0 °C. The reaction was finished in a few minutes. To the quenched solution was added diethyl ether and HCl (0.1 mL, 0.12 M), and finally saturated $Na_2S_2O_3$ (5 dr.) to remove excess iodine. The water phase was extracted additionally 2 times with diethyl ether. The combined organic phase was dried over Na_2SO_4, filtered, and evaporated. The products were examined on GC, GC-MS and ^{1}H- and ^{13}C-NMR. All products were also compared with authentic samples.

Kinetic investigation

In a standard initial rate measurement, SmI_2 in THF (0.1 M) was added to a dry Schlenk tube, fitted with a septum and containing a magnetic stirrer bar, inside a glove box with nitrogen atmosphere. The amine and the proton donor, i.e. H_2O were added at 20.0 °C. Finally the allyl substrate was added using a gastight syringe. Small portions of the mixture (100 μL) were removed via a syringe and quenched with I_2 in n-hexane (0.1 M, 0.1 mL) every ten seconds. Diethyl ether (1 mL) and HCl (0.12 M, 0.1 mL) were added to the quenched solutions to dissolve the inorganic salts and finally $Na_2S_2O_3$ to remove excess iodine. The organic layer was transferred to a vial and the yield of the reaction was analyzed with GC. All products were compared with authentic samples on GC. The reaction orders in SmI_2, H_2O and amine, were determined separately by varying one of the additives while the other were kept constant (pseudo first-order rate conditions). Further details are available in reference 11c.

Large scale

SmI_2 in THF (2.23 mmol, 5 equiv., 0.1 M) was added to a dry round-bottomed flask, containing a magnetic stirrer bar and fitted with a septum, inside a glove box under nitrogen atmosphere. Triethyl amine (0.77 mL, 8.9 mmol, 20 equiv.) and allylcitronellol (Table 1, entry 3) (88 mg, 0.446 mmol, 1 equiv.) were added under stirring. H_2O (6.7 mmol, 15 equiv.) was then added slowly at room temperature. The reaction was finished in less than five minutes. The reaction mixture was diluted with diethyl ether (100 ml) and washed with HCl (2*50 ml, 0.1 M), saturated $Na_2S_2O_3$ (2*50 ml) and finally brine (50 ml). The organic phase was dried over $MgSO_4$, filtered and evaporated yielding the product as oil (60 mg, 87% yield).

Gas Chromatography

The products were separated on a achiral stationary phase GC column: Equity Low Bleed column (∅ = 0.25 mm, length = 30 m) using nitrogen as carrier gas at a flow rate of 2 ml/min. The injector temperature was 225 °C. The column temperature program started at 70 °C for 4 minutes, followed by heating to 250 °C (10 °C/min) for 10 min. The detector temperature was 250 °C (FID).

The products were also separated on GC/MS using a CP-Sil 8 CB Low Bleed column (∅ = 0.25 mm, length = 30 m), using helium as carrier gas at a flow rate of 1 ml/min. The standard method included an injector temperature of 225 °C, and a column temperature at initially 70 °C for 4 min, followed by heating to 250 °C (10 °C/min) for 10 min. The detector temperature was 250 °C (FID).