Alkenes from Terminal Epoxides using Lithium 2,2,6,6-Tetramethylpiperidide and Organolithiums or Grignard ReagentsDavid M. Hodgson,^{*†} Matthew J. Fleming[†] and Steven J. Stanway[‡][†]*Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Mansfield Road, Oxford OX1 3TA, U.K.*[‡]*GlaxoSmithKline, New Frontiers Science Park, Third Avenue, Harlow, Essex, CM19 5AW, U.K.*

General Directions All reactions required anhydrous conditions and were conducted in flame-dried glassware under an atmosphere of argon. Syringes and needles for the transfer of reagents were oven-dried and allowed to cool in a desiccator over self-indicating silica gel. All solvents were distilled under an atmosphere of argon; ethers from sodium benzophenone ketyl and hydrocarbons from CaH₂. 2,2,6,6-Tetramethylpiperidine (TMP) and 1,2-epoxydodecane were distilled from CaH₂ prior to use. Petrol refers to the fraction of light petroleum boiling at 30–40 °C. Reactions were monitored by thin layer chromatography using commercially available aluminium backed plates pre-coated with silica containing a fluorescent indicator (0.2 mm, Merck 60 F₂₅₄) which were developed using phosphomolybdic acid solution. Column chromatography was performed on silica gel (Kieselgel 60, 40–63 µm) or octadecyl-functionalized (C₁₈) silica gel. Infra-red spectra were obtained with liquid films of the compounds on NaCl discs on a Perkin-Elmer Paragon 1750 FTIR spectrophotometer. Peak intensities are specified as strong (s), medium (m), weak (w) or broad (br). Only selected absorbencies (ν_{max}) are reported. ¹H and ¹³C NMR spectra were recorded in CDCl₃ at 25 °C, with Bruker DPX400, AV400 or AMX500 spectrometers. Chemical shifts are reported relative to CHCl₃ for ¹H NMR (7.27 ppm) and CDCl₃ for ¹³C NMR (77.0 ppm). Coupling constants (J) are given in Hz, multiplicities are given as broad singlet (br), multiplet (m), singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint.) and septet (sept.). GCMS analyses were performed on a Micromass GCT spectrometer with BPX5 column - HP 6890 (dimethylsilicon capillary column, 30 m, 0.25 mm i.d.) equipped with a mass selective detector operating at 60 eV (CI). Flow rate (He) = 1 mL/min. Mass spectra were obtained using a Micromass GCT spectrometer or by the EPSRC National Mass Spectrometry Service Centre at the University of Swansea using a 900 XLT high resolution double focusing mass spectrometer with tandem Ion Trap. Solutions of commercially available and prepared organolithiums and

Grignard reagents were titrated prior to use using *s*-BuOH and 1,10-phenanthroline.¹

Procedures and Spectroscopic Data

General procedure A: for alkene formation using preformed or commercially available organolithiums, described for:

(*E*)-1-Phenyl-1-dodecene² **6a**

To a solution of 2,2,6,6-tetramethylpiperidine (232 mg, 1.64 mmol) in hexane (12 mL) at 0 °C (ice bath) was added *n*-BuLi (1.6 M in hexanes; 1.03 mL, 1.64 mmol) dropwise. The reaction mixture was stirred at this temperature for 15 min and then a solution of PhLi (2.0 M in Bu₂O; 0.53 mL, 1.07 mmol) was added dropwise. The reaction was stirred for a further 5 min and then 1,2-epoxydodecane (151 mg, 0.82 mmol) was added. The ice bath was removed and the reaction mixture was left stirring for 2 h. After quenching with saturated brine solution (10 mL), the layers were separated. The aqueous layer was extracted with Et₂O (2 x 10 mL), the combined organic layers were dried (MgSO₄) and solvent removed *in vacuo*. The residue was purified by column chromatography (SiO₂, petrol) to give (*E*)-alkene **6a** (200 mg, 93%, *E*:*Z* = 98:2, by GCMS analysis, *t_R* (*Z*)-**6a** = 13.02 min, *t_R* (*E*)-**6a** = 14.22 min initial temp. = 80 °C, max. temp. = 280 °C, rate = 10 °C/min) as a colourless oil; *R_f* 0.48 (SiO₂, petrol). IR (neat)/cm⁻¹ 3025m, 2956s, 2925s, 2853s, 1625w, 1599w, 1494w, 1466m, 927s; ¹H NMR (400 MHz) δ 7.38-7.29 (m, 4H), 7.21 (tt, *J* = 7.3, 1.5, 1H), 6.41 (d, *J* = 15.9, 1H), 6.26 (dt, *J* = 15.9, 6.8, 1H), 2.22 (dt, *J* = 6.8, 6.8, 2H), 1.53-1.45 (m, 2H), 1.40-1.25 (m, 14H), 0.92 (t, *J* = 6.7, 3H); ¹³C NMR (100 MHz) δ 138.0, 131.3, 129.7, 128.5, 126.7, 125.9, 33.1, 32.0, 29.7, 29.6, 29.4, 29.3, 22.7, 14.1; MS *m/z* (CI) 245 (M+H⁺, 18), 244 (57), 117 (47), 104 (100), 91 (14); HRMS calcd for C₁₈H₂₉ (M+H⁺) 245.2269; found 245.2267.

¹ Schlosser, M. *Organometallics in Synthesis*, 2nd ed. Wiley, New York, **2002**, p. 671.

² Terao, J.; Watabe, H.; Miyamoto, M.; Kambe, N. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2209-2214.

(E)-1,3-Tetradecadiene³ **6c**

Following general procedure A, the addition of 1,2-epoxydodecane (100 mg, 0.54 mmol) to a solution of LTMP (1.08 mmol) in hexane (8 mL) and vinylolithium⁴ (1.5 M in Et₂O; 0.54 mL, 0.81 mmol) gave after workup and column chromatography (SiO₂, petrol) (*E*)-diene **6c** (77 mg, 73%, *E:Z* = 98:2 by GCMS analysis, *t_R* (*Z*)-**6** = 6.83 min, *t_R* (*E*)-**6c** = 7.05 min, initial temp. = 80 °C, max. temp. = 280 °C, rate = 20 °C/min) as a colourless oil; *R_f* 0.58 (SiO₂, petrol). IR (neat, cm⁻¹) 3008m, 2925s, 2855s, 1794w, 1654m, 1603m, 1466s, 1378w, 1001s, 949m, 895s; ¹H NMR (400 MHz) δ 6.33 (ddd, *J* = 16.9, 10.2, 10.2, 1H), 6.06 (dd, *J* = 15.1, 10.2, 1H), 5.72 (dt, *J* = 15.1, 7.1, 1H), 5.10 (d, *J* = 16.9, 1H), 4.96 (d, *J* = 10.2, 1H), 2.08 (dt, *J* = 7.1, 7.1, 2H), 1.40-1.22 (m, 16H), 0.90 (t, *J* = 6.7, 3H); ¹³C NMR (100 MHz) δ 137.4, 135.6, 130.8, 114.5, 32.6, 31.9, 29.6, 29.6, 29.5, 29.3, 22.7, 14.1; MS *m/z* (CI) 212 (M+NH₄⁺, 60), 193 (9), 195 (100), 123 (8), 109 (13), 95 (28), 68 (9); HRMS calcd for C₁₄H₃₀N (M+NH₄⁺) 212.2378, found 212.2379.

(2E,4E)-2,4-Pentadecadiene **6e**

Following general procedure A, the addition of 1,2-epoxydodecane (100 mg, 0.54 mmol) to a solution of LTMP (1.08 mmol) in hexane (8 mL) and (*E*)-propenyllithium⁵ (2.0 M in Et₂O; 0.35 mL, 0.70 mmol) gave after workup and column chromatography (SiO₂, petrol) (*E,E*)-diene **6e** (92 mg, 82%, *EE:ZE* = 98:2 by GCMS analysis, *t_R* (*Z,E*)-**6e** = 10.82 min, *t_R* (*E,E*)-**6e** = 10.98 min, initial temp. = 100 °C, max. temp. = 280 °C, rate = 8 °C/min) as a colourless oil; *R_f* 0.64 (SiO₂, petrol). IR (neat)/cm⁻¹ 3016m, 2957s, 2925s, 2854s, 1466m, 1378w, 986s; ¹H NMR (400 MHz) δ 6.07-5.95 (m, 2H), 5.62-5.52 (m, 2H), 2.05 (dt, *J* = 7.1, 7.1, 2H), 1.74 (d, *J* = 6.6, 3H), 1.40-1.22 (m, 16H), 0.89 (t, *J* = 6.8, 3H); ¹³C NMR (100 MHz) δ 132.3, 131.7, 130.2, 126.6, 32.6, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 22.7, 18.0, 14.1; MS *m/z* (CI) 226 (M+NH₄⁺, 33), 208 (100), 207 (17), 95 (22), 81 (48); HRMS calcd for C₁₅H₃₂N (M+NH₄⁺) 226.2535, found 226.2535.

³ Suzuki, K.; Hasegawa, T.; Imai, T.; Maeta, H.; Ohba, S. *Tetrahedron* **1995**, 51, 4483-4494.

⁴ Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1961**, 83, 3583-3586.

⁵ Seyferth, D.; Vaughan, L. G. *J. Am. Chem. Soc.* **1964**, 86, 883-890.

(1*E*,3*E*)-1-Phenyl-1,3-tetradecadiene **6g**

Following general procedure A, the addition of 1,2-epoxydodecane (230 mg, 1.25 mmol) to a solution of LTMP (2.50 mmol) in hexane (19 mL) and (*E*)-2-phenylethenyllithium⁶ (1.1 M in Et₂O; 1.48 mL, 1.63 mmol) gave after workup and reverse phase column chromatography (C₁₈ silica, MeCN)⁷ (*E,E*)-diene **6g** (243 mg, 72%, *EE:ZE* = 98:2, by GCMS analysis, *t_R* (*Z,E*)-**6g** = 11.55 min, *t_R* (*E,E*)-**6g** = 11.83 min, initial temp. = 80 °C, max. temp. = 280 °C, rate = 20 °C/min) as a colourless oil; *R_f* 0.26 (C₁₈ silica, MeCN). IR (neat)/cm⁻¹ 3022m, 2955s, 2925s, 2853s, 1644w, 1597w, 1495w, 1466w, 1448w, 986s; ¹H NMR (400 MHz) δ 7.40-7.37 (m, 2H), 7.33-7.28 (m, 2H), 7.20 (tt, *J* = 7.3, 1.3, 1H), 6.76 (dd, *J* = 15.7, 10.4, 1H), 6.44 (d, *J* = 15.7, 1H), 6.20 (dd, *J* = 14.9, 10.4, 1H), 5.83 (dt, *J* = 14.9, 6.8, 1H), 2.14 (dt, *J* = 6.8, 6.8, 1H), 1.47-1.22 (m, 16H), 0.88 (t, *J* = 6.8, 3H); ¹³C NMR (100 MHz) δ 137.7, 136.1, 130.4, 129.9, 129.5, 128.5, 127.0, 126.1, 32.9, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1; MS *m/z* (CI) 271 (*M*+H⁺ 100), 270 (64), 143 (25), 128 (14); HRMS calcd for C₂₀H₃₁ (*M*+H⁺) 271.2426; found 271.2429.

(2*Z*,4*E*)-2,4-Pentadecadiene **6h**

Following general procedure A, the addition of 1,2-epoxydodecane (100 mg, 0.54 mmol) to a solution of LTMP (1.08 mmol) in hexane (8 mL) and (*Z*)-propenyllithium⁵ (1.4 M in Et₂O; 0.50 mL, 0.70 mmol) gave after workup and column chromatography (SiO₂, petrol) (*Z,E*)-diene-**6h** (79 mg, 70%, *ZE:EE* = 90:10 by GCMS analysis, *t_R* (*Z,E*)-**6h** = 10.82 min, *t_R* (*E,E*)-**6h** = 10.98 min, initial temp. = 100 °C, max. temp. = 280 °C, rate = 8 °C/min) as a colourless oil; *R_f* 0.64 (SiO₂, petrol). IR (neat)/cm⁻¹ 3015m, 2960s, 2920s, 2844s, 1466m, 1349w, 970s; ¹H NMR (400 MHz) δ 6.33 (ddq, *J* = 10.9, 10.1, 1.5, 1H), 6.02-5.95 (m, 1H), 5.67 (dt, *J* = 14.9, 7.3, 1H), 5.38 (dq, *J* = 10.9, 7.1, 1H), 2.15-2.07 (m, 2H), 1.75 (dd, *J* = 7.1, 1.5, 3H), 1.44-1.20 (m, 16H), 0.89 (t, *J* = 6.8, 3H); ¹³C NMR (100 MHz) δ 134.7, 129.5, 125.3, 123.8, 32.9, 31.9, 29.6, 29.5, 29.4, 29.4, 29.3, 22.7, 14.1, 13.3; MS *m/z* (CI) 226

⁶ Prepared by the addition of (*E*)-β-bromostyrene to Li metal in Et₂O at 0 °C.

⁷ Forina, V. *J. Org. Chem.* **1991**, *56*, 4985-4987.

($M+NH_4^+$, 52), 208 (100), 207 (11), 166 (87), 95 (10), 81 (22); HRMS calcd for $C_{15}H_{32}N$ ($M+NH_4^+$) 226.2535; found 226.2541.

(*E*)-1-Trimethylsilyl-2-tridecene⁸ **7a**

Following general procedure A, the addition of 1,2-epoxydodecane (100 mg, 0.54 mmol) to a solution of LTMP (0.81 mmol) in Et_2O (8 mL) and (trimethylsilylmethyl)lithium (1.0 M in pentane; 0.81 mL, 0.81 mmol) gave after workup and column chromatography (SiO_2 , 100% petrol) (*E*)-allylsilane **7a** (89 mg, 65%, *E*:*Z* = 97:3, by GCMS analysis, t_R (*E*)-**7a** = 8.22 min, t_R (*Z*)-**7a** = 8.30 min, initial temp. = 80 °C, max. temp. = 280 °C, rate = 20 °C/min) as a colourless oil; R_f 0.63 (SiO_2 , petrol). IR (neat)/ cm^{-1} 3007m, 2928s, 2854s, 1659w, 1466s, 1416m, 1378w, 1248s, 1155s, 934s, 857s; 1H NMR (400 MHz) δ 5.42-5.33 (m, 1H), 5.29-5.23 (m, 1H), 2.29 (dt, J = 6.8, 6.8, 2H), 1.41 (dd, J = 7.6, 1.0, 2H), 1.33-1.27 (m, 16H), 0.90 (t, J = 6.8, 3H), 0.00 (s, 9H); ^{13}C NMR (100 MHz) δ 129.1, 125.9, 32.8, 31.9, 30.0, 29.7, 29.6, 29.5, 29.4, 29.1, 22.7, 22.6, 14.1, -2.0; MS m/z (CI) 255 ($M+H^+$, 25), 90 (100), 73(10); HRMS calcd for $C_{16}H_{36}Si$ ($M+H^+$) 255.2508; found 255.2501.

(*E*)-(4-Methylpent-2-enyl)-trimethylsilane⁹ **7b**

Following general procedure A, the addition of 3-methyl-1,2-epoxybutane (123 mg, 1.43 mmol) to a solution of LTMP (2.15 mmol) in THF (21 mL) and (trimethylsilylmethyl)lithium (1.0 M in pentane; 2.15 mL, 2.15 mmol) gave after workup and column chromatography (SiO_2 , petrol) (*E*)-allylsilane **7b** (159 mg, 71%, *E*:*Z* = 98:2, by GCMS analysis, t_R (*E*)-**7b** = 3.15 min, t_R (*Z*)-**7b** = 3.23 min initial temp. = 60 °C, max. temp. = 240 °C, rate = 20 °C/min) as a colourless oil; R_f 0.66 (SiO_2 , petrol). IR (neat)/ cm^{-1} 2957s, 2926s, 2871m, 1466w, 1248s, 859s, 840s; 1H NMR (400 MHz) δ 5.39-5.30 (m, 1H), 5.23 (dd, J = 15.2, 6.8, 1H), 2.24 (d, sept, J = 6.8, 6.8, 1H), 1.39 (d, J = 7.6, 1H), 0.97 (d, J = 6.8, 6H), 0.00 (s, 9H); ^{13}C NMR (100

⁸ Masao, A.; Yamaguchi, H.; Fujita, E.; Nagao, Y.; Ochiai, M. *Chem. Pharm. Bull.* **1989**, 37, 3221-3324.

⁹ Shimizu, N.; Imazu, S.; Shibata, F.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1991**, 64, 1122-1128.

MHz) δ 136.4, 122.8, 31.3, 23.0, 22.4, -2.1; MS m/z (CI) 157 ($M+H^+$, 12), 91 (12), 90 (100); HRMS calcd for $C_9H_{22}Si$ ($M+H^+$) 157.1413; found 157.1416.

(*E*)-(4,4-Dimethyl-pent-2-enyl)-trimethylsilane⁹ **7c**

Following general procedure A, the addition of dimethyl 1,2-epoxybutane (123 mg, 1.23 mmol) to a solution of LTMP (1.85 mmol) in THF (18 mL) and (trimethylsilylmethyl)lithium (1.0 M in pentane; 1.85 mL, 1.85 mmol) gave after workup and column chromatography (SiO_2 , petrol) (*E*)-allylsilane **7c** (132 mg, 63%, *E*-only by GCMS analysis, t_R (*E*)-**7c** = 4.33 min, initial temp. = 50 °C, max. temp. = 240 °C, rate = 20 °C/min) as a colourless oil; R_f 0.63 (SiO_2 , petrol). IR (neat)/ cm^{-1} 2925s, 2854s, 2361w, 1464w, 1378m, 1248w, 1156m, 969m, 851m; 1H NMR (400 MHz) δ 5.30–5.25 (m, 2H), 1.39 (dd, J = 4.8, 2.0, 2H), 0.99 (s, 9H), -0.01 (s, 9H); ^{13}C NMR (100 MHz) δ 140.2, 120.4, 32.9, 30.0, 22.4, -2.1; MS m/z (CI) 171 ($M+H^+$, 27), 155 (9), 148 (10), 91 (12), 90 (100), 73 (23); HRMS calcd for $C_{10}H_{23}Si$ ($M+H^+$) 171.1569; found 171.1561.

General Procedure B: for alkene formation using *in-situ* formation of organolithium, described for:

(*E*)-1-Dodec-1-enyl-4-methoxy-benzene **6b**

To a solution of 4-bromoanisole (131 mg, 0.70 mmol) in THF (1.5 mL) at -78 °C was added *t*-BuLi (1.5 M in pentane; 0.94 mL, 1.40 mmol) dropwise. The reaction mixture was stirred at this temperature for 1 h and then warmed to 0 °C (ice bath). After 5 min a solution of LTMP (prepared by the addition of *n*-BuLi (1.6 M in hexanes; 0.68 mL, 1.08 mmol) to 2,2,6,6-tetramethylpiperidine (153 mg, 1.08 mmol) in hexane (8 mL) at 0 °C) was added dropwise. The reaction was left for a further 5 min at 0 °C and then 1,2-epoxydodecane (100 mg, 0.54 mmol) was added. The ice bath was removed and the reaction mixture was stirred for a further 2 h. After quenching with saturated brine solution (10 mL), the layers were separated. The aqueous layer was extracted with Et_2O (2 x 10 mL), the combined organic layers

were dried (MgSO_4) and solvent evaporated *in vacuo*. The residue was purified by column chromatography (SiO_2 , 2% Et_2O in petrol) to give (*E*)-alkene **6b** (104 mg, 70%, *E*:*Z* = 98:2 by GCMS analysis, t_R (*Z*)-**6b** = 16.18 min, t_R (*E*)-**6b** = 16.78 min, initial temp. = 100 °C, max. temp. = 280 °C, rate = 10 °C/min) as a white solid; R_f 0.48 (SiO_2 , 10% Et_2O in petrol), mp = 36-39 °C. IR (CHCl_3)/ cm^{-1} 2954m, 2920s, 2850m, 1608w, 1513w, 1465w, 1251w, 1176w, 1023w, 962w; ^1H NMR (400 MHz) δ 7.31 (d, J = 8.8, 2H), 6.87 (d, J = 8.8, 2H), 6.35 (d, J = 15.7, 1H), 6.12 (dt, J = 15.7, 7.1, 1H), 3.82 (s, 3H), 2.21 (dt, J = 7.1, 7.1, 2H), 1.52-1.44 (m, 2H), 1.41-1.25 (m, 14H), 0.92 (t, J = 6.9, 3H); ^{13}C NMR (100 MHz) δ 158.6, 130.8, 129.1, 129.0, 127.0, 113.9, 55.3, 33.1, 32.0, 29.7, 29.6, 29.6, 29.4, 29.3, 22.7, 14.1; MS m/z (CI) 275 ($\text{M}+\text{H}^+$, 100), 274 (69), 147 (63), 134 (18), 121 (25); HRMS calcd for $\text{C}_{19}\text{H}_{31}\text{O}$ ($\text{M}+\text{H}^+$) 275.2375; found 275.2373.

(*E*)-2,3-Dimethyl-2,4-pentadecadiene **6d**

Following general procedure B, 2-bromo-3-methyl-2-butene (105 mg, 0.70 mmol), *t*-BuLi (1.5 M in pentane; 0.94 mL, 1.40 mmol) in THF (1.5 mL) then a solution of LTMP (1.08 mmol) in hexane (8 mL) and then 1,2-epoxydodecane (100 mg, 0.54 mmol) gave after workup and column chromatography (SiO_2 , petrol) (*E*)-diene **6d** (109 mg, 85%, *E*-only by GCMS analysis, t_R (*E*)-**6d** = 7.10 min, initial temp. = 80 °C, max. temp. = 280 °C, rate = 20 °C/min) as a colourless oil; R_f 0.56 (SiO_2 , petrol). IR (neat)/ cm^{-1} 2923s, 2854s, 1465m, 1375m, 1170w, 959s; ^1H NMR (400 MHz) δ 6.05 (d, J = 15.4, 1H), 5.59 (dt, J = 15.4, 7.1, 1H), 2.12 (dt, J = 7.0, 7.0, 2H), 1.82 (s, 3H), 1.78 (s, 3H), 1.76 (s, 3H), 1.33-1.24 (m, 16H), 0.89 (t, J = 6.8, 3H); ^{13}C NMR (100 MHz) δ 129.1, 128.5, 128.4, 126.1, 33.4, 31.9, 30.0, 29.6, 29.6, 29.4, 29.3, 22.7, 21.6, 20.2, 14.4, 14.1; MS m/z (CI) 237 ($\text{M}+\text{H}^+$, 100), 109 (21); HRMS calcd for $\text{C}_{17}\text{H}_{33}$ ($\text{M}+\text{H}^+$), 237.2582; found 237.2585.

(7*E*,9*E*)-7,9-Icosadiene **6f**

Following general procedure B, (*E*)-1-iodo-1-octene¹⁰ (134 mg, 0.56 mmol), *t*-BuLi (1.5 M in pentane; 0.74 mL, 1.12 mmol) in Et₂O (1.0 mL) then a solution of LTMP (0.87 mmol) in hexane (7 mL) and then 1,2-epoxydodecane (80 mg, 0.43 mmol) gave after workup and column chromatography (SiO₂, petrol) (*E,E*)-diene **6f** (101 mg, 84%, *EE:ZE* = 99:1, by GCMS analysis, *t_R* (*Z,E*)-**6f** = 16.68 min, *t_R* (*E,E*)-**6f** = 17.07 min, initial temp. = 80 °C, max. temp. = 280 °C, rate = 10 °C/min) as a colourless oil; *R_f* 0.59 (SiO₂, petrol). IR (neat)/cm⁻¹ 3014w, 2957s, 2925s, 2854s, 1460m, 1378w, 986s; ¹H NMR (400 MHz) δ 6.03-5.98 (m, 2H), 5.61-5.53 (m, 2H), 2.05 (dt, *J* = 7.1, 7.1, 4H), 1.42-1.21 (m, 24H), 0.89 (t, *J* = 6.8, 6H); ¹³C NMR (100 MHz) δ 132.4, 130.3, 32.6, 31.9, 31.7, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 22.7, 22.6, 14.1, 14.1; MS *m/z* (CI) 296 (M+NH₄⁺, 30), 279 (63), 278 (100), 277 (56), 276 (20), 275 (17), 138 (13), 95 (16), 81 (15); HRMS calcd for C₂₀H₄₂N (M+NH₄⁺) 296.3317; found 296.3310.

(7*Z*,9*E*)-7,9-Icosadiene¹¹ **6i**

Following general procedure B, (*Z*)-1-iodo-1-octene¹² (134 mg, 0.56 mmol), *t*-BuLi (1.5 M in pentane; 0.74 mL, 1.12 mmol) in Et₂O (1.0 mL) then a solution of LTMP (0.87 mmol) in hexane (7 mL) and then 1,2-epoxydodecane (80 mg, 0.43 mmol) gave after workup and column chromatography (SiO₂, petrol) (*Z,E*)-diene **6i** (96 mg, 80%, *ZE:EE:other isomer* = 91:5:4 by GCMS analysis, *t_R* (*Z,E*)-**6i** = 16.68 min, *t_R* other isomer = 16.90, *t_R* (*E,E*)-**6i** = 17.07 min, initial temp. = 80 °C, max. temp. = 280 °C, rate = 10 °C/min) as a colourless oil; *R_f* 0.59 (SiO₂, petrol). IR (neat)/cm⁻¹ 3019m, 2926s, 2854s, 1466s, 1378s, 982m, 946m; ¹H NMR (400 MHz) δ 6.35-6.26 (m, 1H), 6.03-5.92 (m, 1H), 5.67 (dt, *J* = 15.2, 7.3, 1H), 5.31 (dt, *J* = 10.6, 7.6, 1H), 2.20-2.02 (m, 4H), 1.43-1.21 (m, 24H), 0.89 (t, *J* = 6.8, 3H); ¹³C NMR (100 MHz) δ 134.7, 130.1, 128.6, 125.6, 32.9, 31.9, 31.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 27.7, 22.7, 22.6, 14.1, 14.1; MS *m/z* (CI) 296 (M+NH₄⁺, 31), 279 (75), 278 (100),

¹⁰ Schwartz, J.; Hart, D. W.; Blackburn, T. F. *J. Am. Chem. Soc.* **1975**, 97, 679-680.

¹¹ Bestmann, H. J.; Vostrowsky, O.; Paulus, H.; Billmann, W.; Stransky, W. *Tetrahedron Lett.* **1977**, 18, 121-124.

¹² Brown, H. C.; Blue, C. D.; Nelson, D. J.; Bhat, N. G. *J. Org. Chem.* **1989**, 54, 6064-6067.

277 (31), 276 (13), 166 (10), 138 (14), 96 (14), 81 (19); HRMS calcd for $C_{20}H_{42}N$ ($M+NH_4^+$) 296.3317; found 296.3325.

(5*E*,7*E*)-5-Methyl-5,7-octadecadiene **6j**

Following general procedure B, (*E*)-1-iodo-2-methyl-1-hexene¹³ (198 mg, 0.88 mmol), *t*-BuLi (1.5 M in pentane; 1.18 mL, 1.77 mmol) in Et₂O (2 mL) then a solution of LTMP (1.36 mmol) in hexane (10 mL) and then 1,2-epoxydodecane (125 mg, 0.68 mmol) gave after workup and column chromatography (SiO₂, 100% petrol) (*E,E*)-diene **6j** (153 mg, 85% *EE:ZE* = 91:9 by GCMS analysis, *t_R* (*Z,E*)-**6j** = 9.78 min, *t_R* (*E,E*)-**6j** = 10.00 min, initial temp. = 80 °C, max. temp. = 280 °C, rate = 20 °C/min) as a colourless oil; *R_f* 0.69 (SiO₂, petrol). IR (neat)/cm⁻¹ 3020m, 2924s, 2854s, 1642w, 1466s, 1378m, 963s; ¹H NMR (400 MHz) δ 6.25 (dd, *J* = 14.9, 10.9, 1H), 5.81 (d, *J* = 10.9, 1H), 5.59 (dt, *J* = 14.9, 7.1, 1H), 2.09 (dt, *J* = 7.1, 7.1, 2H), 2.04 (t, *J* = 7.6, 2H), 1.74 (s, 3H), 1.44-1.26 (m, 20H), 0.93-0.88 (m, 6H); ¹³C NMR (100 MHz) δ 136.7, 132.4, 126.6, 124.5, 39.5, 33.0, 31.9, 30.1, 29.6, 29.6, 29.4, 29.3, 29.3, 22.7, 22.4, 16.4, 14.1, 14.0; MS *m/z* (CI) 265 ($M+H^+$, 100), 264 (29), 263 (10), 137 (10); HRMS calcd for $C_{19}H_{37}$ ($M+H^+$) 265.2895; found 265.2889.

General Procedure C: for allylsilane formation using *in-situ* formation of α-silyllithium, described for:

(*E*)-(1-Pentyltridec-2-en-1-yl)trimethylsilane **7d**

To a solution of vinyltrimethylsilane (109 mg, 1.09 mmol) in THF (1 mL) at -78 °C was added *n*-BuLi (1.5 M in hexanes; 0.54 mL, 0.81 mmol) dropwise. The reaction mixture was stirred at this temperature for 2 h and then at -30 °C for 2 h. The reaction mixture was warmed to 0 °C (ice bath) and a solution of LTMP (prepared from the addition of *n*-BuLi (1.5 M in hexanes; 0.54 mL, 0.81 mmol) to 2,2,6,6-tetramethylpiperidine (114 mg, 0.81 mmol) in hexane (7 mL) at 0 °C) was added dropwise. After 5 min 1,2-epoxydodecane (100 mg, 0.54 mmol) was added and the reaction mixture was left stirring for 2 h. After quenching with

¹³ Negishi, E.; Van Horn, D. E.; Yoshida, T. *J. Am. Chem. Soc.* **1985**, 107, 6639-6647.

saturated brine solution (10 mL), the layers were separated. The aqueous layer was extracted with Et₂O (2 x 10 mL), the combined organic layers were dried (MgSO₄) and solvent evaporated *in vacuo*. The residue was purified by reverse phase column chromatography (C₁₈ silica, 15% Et₂O in MeCN)⁷ to give (*E*)-allylsilane **7d** (130 mg, 74%, *E*-only by GCMS analysis, (*E*)-**7d** = 10.18 min, initial temp. = 80 °C, max. temp. = 280 °C, rate = 20 °C/min) as a colourless oil; R_f 0.13 (C₁₈ silica, 15% Et₂O in MeCN). IR (neat)/cm⁻¹ 2924s, 2854s, 1467m, 1378w, 1258m, 969m, 861m; ¹H NMR (400 MHz) δ 5.24-5.12 (m, 2H), 1.99 (dt, *J* = 6.5, 6.5, 2H), 1.42-1.16 (m, 25 H), 0.91-0.86 (m, 6H), -0.01 (s, 9H); ¹³C NMR (100 MHz) δ 131.5, 128.2, 32.9, 32.9, 31.9, 31.8, 30.1, 29.7, 29.6, 29.5, 29.4, 29.1, 29.0, 28.9, 22.7, 22.6, 14.2, 14.1, -3.1; MS *m/z* (CI) 325 (M+H⁺, 34), 251 (13), (8), 250 (48), 90 (100), 73 (25); HRMS calcd for C₂₁H₄₅Si (M+H⁺) 325.3291; found 325.3287.

(*E*)-(1-pentylundeca-2,10-dien-1-yl)trimethylsilane **7e**

Following general procedure C, the addition of 1,2-epoxy-9-decene (83 mg, 0.54 mmol) instead of 1,2-epoxydodecane gave after workup and reverse phase column chromatography (C₁₈ silica, MeCN)⁷ (*E*)-allylsilane **7e** (120 mg, 75%, *E*-only by GCMS analysis, (*E*)-**7e** = 11.57 min, initial temp. = 80 °C, max. temp. = 280 °C, rate = 15 °C/min) as a colourless oil; R_f 0.13 (C₁₈ silica, MeCN). IR (neat)/cm⁻¹ 3078s, 2926s, 2854s, 1642w, 1464w, 1247s, 836s; ¹H NMR (400 MHz) δ 5.87-5.77 (m, 1H), 5.24-5.12 (m, 2H), 5.03-4.92 (m, 2H), 2.05 (dt, *J* = 6.8, 6.8, 2H), 1.99 (dt, *J* = 6.5, 6.5, 2H), 1.44-1.14 (m, 17H), 0.89 (t, *J* = 6.9, 3H), -0.05 (s, 9H); ¹³C NMR (100 MHz) δ 139.3, 131.5, 128.1, 114.1, 33.8, 32.9, 32.8, 31.8, 30.0, 29.0, 28.9, 28.9, 28.8, 22.7, 14.1, -3.2; MS *m/z* (CI) 295 (M+H⁺, 40), 220 (29), 90 (100); HRMS calcd for C₁₉H₃₉Si (M+H⁺) 295.2821; found 295.2822.

(E)-(1-pentyl-5-phenylpent-2-en-1-yl)trimethylsilane 7f

Following general procedure C, the addition of 1,2-epoxy-4-phenylbutane¹⁴ (80 mg, 0.54 mmol) instead of 1,2-epoxydodecane gave after workup and column chromatography (SiO₂, petrol) (*E*)-allylsilane **7f** (122 mg, 78%, *E*:*Z* = 98:2 by GCMS analysis, *t_R* (*Z*)-**7f** = 12.33 min, *t_R* (*E*)-**7f** = 12.43 min, initial temp. = 80 °C, max. temp. = 280 °C, rate = 15 °C/min) as a colourless oil; *R_f* 0.48 (SiO₂, petrol). IR (neat)/cm⁻¹ 3064w, 3027m, 2925s, 2853s, 1605w, 1496m, 1454m, 1247s; ¹H NMR (400 MHz) δ 7.37-7.28 (m, 2H), 7.24-7.18 (m, 3H), 5.31-5.20 (m, 2H), 2.70 (t, *J* = 7.3, 2H), 2.40 (dt, *J* = 7.3, 7.3, 2H), 1.47-1.13 (m, 9H), 0.92 (t, *J* = 7.1, 3H), -0.04 (s, 9H); ¹³C NMR (100 MHz) δ 142.2, 132.4, 128.5, 128.2, 127.0, 125.6, 36.6, 34.7, 33.0, 31.8, 29.0, 28.8, 22.6, 14.2, -3.2; MS *m/z* (CI) 289 (*M*+H⁺, 100) 215 (19), 214 (91), 197 (29), 123 (23), 90 (40); HRMS calcd for C₁₉H₃₃Si (*M*+H⁺) 289.2352; found 289.2344.

(E)-1-(*tert*-Butyldimethylsilyloxy)-6-(trimethylsilyl)undec-4-ene 7g

Following general procedure C, the addition of 1-*tert*-butyldimethylsilyloxy-4,5-epoxypentane¹⁵ (117 mg, 0.54 mmol) instead of 1,2-epoxydodecane gave after workup and column chromatography (SiO₂, petrol) (*E*)-allylsilane **7g** (138 mg, 71%, *E*-only by GCMS analysis, (*E*)-**7g** = 10.17 min, initial temp. = 80 °C, max. temp. = 280 °C, rate = 15 °C/min) as a colourless oil; *R_f* 0.20 (SiO₂, petrol). IR (neat)/cm⁻¹ 2929m, 2857m, 1471w, 1388w, 1248m, 1105m, 969w, 836m; ¹H NMR (400 MHz) δ 5.25-5.14 (m, 2H), 3.62 (t, *J* = 6.8, 2H), 2.05 (dt, *J* = 6.8, 6.8, 2H), 1.58 (dd, *J* = 6.8, 6.8, 2H), 1.47-1.12 (m, 9H), 0.91 (s, 9H), 0.88 (t, *J* = 6.8, 3H), 0.06 (s, 6H), -0.05 (s, 9H); ¹³C NMR (100 MHz) δ 131.9, 127.5, 62.8, 33.2, 33.0, 31.8, 29.1, 29.0, 28.8, 26.0, 22.6, 18.4, 14.2, -3.1, -5.3; MS *m/z* (CI) 357 (*M*+H⁺, 31), 299 (32), 269 (21), 242 (16), 228 (19), 225 (77), 164 (43), 147 (100), 90 (46), 73 (55); HRMS calcd for C₂₁H₄₅Si (*M*+H⁺) 357.3009; found 357.3011.

¹⁴ Elings, J. A.; Downing, R. S.; Sheldon, R. A. *Eur. J. Org. Chem.* **1999**, 837-846.

¹⁵ Yang, L.; Weber, A. E.; Greenlee, W. J.; Patchett, A. A. *Tetrahedron Lett.* **1993**, 34, 7035-7038.

General procedure A was used for alkene formation using deuterated epoxides *cis* and *trans* **8**¹⁶ (Table 3), *E:Z* ratio was determined by GCMS analysis and the deuterium content at the vinylic position (¹H NMR analysis) determined by mass spectrometry.

General Procedure D: for alkene formation using alkyl Grignard reagents and LTMP, described for:

(*E*)-5-Hexadecene **6k**

To a solution of 2,2,6,6-tetramethylpiperidine (153 mg, 1.08 mmol) in Et₂O (8 mL) at 0 °C (ice bath) was added *n*-BuLi (1.6 M in hexanes; 0.68 mL, 1.08 mmol) dropwise. The reaction mixture was stirred at this temperature for 15 min and then a solution of BuMgCl (2.0 M in Et₂O; 0.38 mL, 0.76 mmol) was added dropwise. The reaction was stirred for a further 5 min and then 1,2-epoxydodecane (100 mg, 0.54 mmol) was added. The ice bath was removed and the reaction mixture was left stirring for 3 h. After quenching with saturated brine solution (10 mL), the layers were separated. The aqueous layer was extracted with Et₂O (2 x 10 mL) and the combined organic layers were dried (MgSO₄) and solvent removed *in vacuo*. The residue was purified by column chromatography (SiO₂, petrol) to give (*E*)-alkene **6k** (84 mg, 69%, *E:Z* = 96:4, by ¹H NMR analysis of vinylic region) as a colourless oil; R_f 0.70 (SiO₂, petrol). IR (neat)/cm⁻¹ 2924s, 2854s 1466m, 1378w, 966m; ¹H NMR (500 MHz) δ 5.43-5.83 (m, 2H), 2.03-1.93 (m, 4H), 1.39-1.22 (m, 20H), 0.93-0.87 (m, 6H); ¹³C NMR (125 MHz) δ 130.3, 130.2, 32.6, 32.2, 31.9, 31.8, 29.6, 29.5, 29.3, 29.1, 22.6, 22.1, 14.0, 13.9; MS *m/z* (EI) 224 (M⁺, 21), 111 (39), 98 (29), 97 (88), 84 (47), 84 (47), 83 (100), 71 (32), 70 (59), 69 (92), 67 (41), 57 (30), 55 (65); HRMS calcd for C₁₆H₃₂ (M⁺) 224.2504; found 224.2514.

(*E*)-2-Tridecene **6l**

Following general procedure D, the addition of 1,2-epoxydodecane (100 mg, 0.54 mmol) to a solution of LTMP (0.81 mmol) in hexane (8 mL) and MeMgCl (2.2 M in

¹⁶ (a) Yanagisawa, A.; Yasue, K.; Yamamoto, H. *J. Chem. Soc., Chem. Commun.* **1994**, 2103-2104; (b) Patrick, D. W.; Truesdale, L. K.; Biller, S. A.; Sharpless, K. B. *J. Org. Chem.* **1978**, 43, 2628-2638.

THF; 0.45 mL, 0.98 mmol) gave after workup and column chromatography (SiO₂, petrol) (*E*)-alkene **6i** (70 mg, 71%, *E*:*Z* = 98:2 by GCMS analysis, *t_R* (*E*)-**6i** = 9.10 min, *t_R* (*Z*)-**6i** = 9.25 min, initial temp. = 80 °C, max. temp. = 280 °C, rate = 10 °C/min) as a colourless oil; *R_f* 0.66 (SiO₂, petrol). IR (neat, cm⁻¹) 2925s, 2855s, 1465m, 1378w, 964m; ¹H NMR (400 MHz) δ 5.44-5.40 (m, 2H), 1.99-1.94 (m, 2H), 1.66-1.64 (m, 3H), 1.35-1.24 (m, 16H), 0.89 (t, *J* = 6.8, 3H); ¹³C NMR (100 MHz) δ 131.7, 124.5, 32.6, 31.9, 29.6, 29.5, 29.4, 29.2, 22.7, 17.9, 14.1; MS *m/z* (EI) 182 (*M*⁺, 41), 111 (32), 98 (34), 97 (87), 84 (61), 83 (94), 71 (37), 70 (83), 69 (100), 67 (38), 55 (71); HRMS calcd for C₁₃H₂₆ (*M*⁺) 182.2035, found 182.2035.

General Procedure E: for alkene formation using vinyl Grignard reagents and LTMP, described for:

(7*Z*,9*E*)-7,9-Icosadiene¹⁰ **6i**

To a solution of (*Z*)-1-iodo-1-octene¹¹ (181 mg, 0.76 mmol) in THF (2 mL) at -78 °C was added *t*-BuLi (1.5 M in pentane; 1.01 mL, 1.52 mmol) dropwise. The reaction mixture was stirred at this temperature for 1 h and then warmed to 0 °C (ice bath). Anhydrous MgCl₂ (72 mg, 0.76 mmol) was added in one portion and the reaction mixture left stirring at 0 °C for 1 h. A solution of LTMP (prepared by the addition of *n*-BuLi (1.6 M in hexanes; 0.68 mL, 1.08 mmol) to 2,2,6,6-tetramethylpiperidine (153 mg, 1.08 mmol) in Et₂O (8 mL) at 0 °C) was added dropwise. The reaction was left for a further 5 min at 0 °C and then 1,2-epoxydodecane (100 mg, 0.54 mmol) was added. The ice bath was removed and the reaction mixture was stirred for a further 3 h. After quenching with saturated brine solution (10 mL), the layers were separated. The aqueous layer was extracted with Et₂O (3 x 10 mL), the combined organic layers were dried (MgSO₄) and solvent evaporated *in vacuo*. The residue was purified by column chromatography (SiO₂, petrol) to give (*Z,E*)-diene **6i** (96 mg, 67%, *ZE:EE*:other isomer = 91:5:4 by GCMS analysis) as a colourless oil.

See above for data.

(5*E*,7*E*)-5-Methyl-5,7-octadecadiene **6j**

Following general procedure E (*E*)-1-iodo-2-methyl-1-hexene¹² (170 mg, 0.76 mmol), *t*-BuLi (1.5 M in pentane; 1.01 mL, 1.52 mmol) in THF (2 mL) then anhydrous MgCl₂ (72 mg, 0.76 mmol), a solution of LTMP (1.08 mmol) in Et₂O (8 mL) and then 1,2-epoxydodecane (100 mg, 0.54 mmol) gave after workup and column chromatography (SiO₂, petrol) (*E,E*)-diene **6j** (101 mg, 70% *EE:ZE* = 94:6 by GCMS analysis) as a colourless oil.

See above for data.

Table 4 The addition of excess organolithium to 1,2-epoxydodecane **5** without LTMP present^a

$\text{C}_{10}\text{H}_{21}\text{epoxide} + \text{R-Li (3 equiv)} \xrightarrow{0\text{ }^{\circ}\text{C to rt, 14 h}} \text{C}_{10}\text{H}_{21}\text{CH(OH)CH}_2\text{R}$ <p style="text-align: center;">9</p>					
Entry	RLi	Product		Yield (%) ^b	<i>E:Z</i> ^c
1	PhLi		9a	69	-
2			9b	72	-
3			9c	99	97:3
4			9d	90	1:99
5 ^d			9e	75	-
6			9f	70	-

^a Hexane as solvent unless otherwise indicated. ^b isolated yield. ^c Determined by GCMS. ^d Reaction in Et₂O.

General Procedure F: for alcohol formation using organolithiums, described for:

1-Phenyl-dodecan-2-ol **9a**

To a solution of 1,2-epoxydodecane (100 mg, 0.54 mmol) in hexane (8 mL) at 0 °C was added PhLi (2.0 M in Bu₂O; 0.82 mL, 1.63 mmol) dropwise. The ice bath was removed and the reaction was left stirring for a 14 h. After quenching with saturated brine solution (5 mL), the layers were separated. The aqueous layer was extracted with Et₂O (2 x 10 mL), the combined organic layers were dried (MgSO₄) and solvent evaporated *in vacuo*. The residue was purified by column chromatography (SiO₂, 15% Et₂O in petrol) to give *alcohol 9a* (98 mg, 69%) as a white solid; R_f 0.16 (10% Et₂O in petrol), mp = 40-41 °C. IR (CHCl₃)/cm⁻¹ 3367br, 3027m, 2919s, 1496w, 1466s, 1350w; ¹H NMR (400 MHz) δ 7.35-7.31 (m, 2H), 7.27-7.22 (m, 3H), 3.85-3.79 (m, 1H), 2.84 (dd, *J* = 13.4, 4.3, 1H), 2.65 (dd, *J* = 13.4, 8.6, 1H), 1.52-1.46 (m, 3H), 1.35-1.24 (m, 16H), 0.90 (t, *J* = 6.9, 3H); ¹³C NMR (100 MHz) δ 138.7, 129.4, 128.5, 126.4, 72.7, 44.1, 36.9, 31.9, 29.7, 29.6, 29.3, 25.8, 22.7, 14.1; MS *m/z* (CI) 280 (M+NH₄⁺, 100), 262 (6), 244 (36), 169 (12), 117 (27), 104 (64), 92 (76), 91 (40); HRMS calcd for C₁₈H₃₄NO (M+NH₄⁺) 280.2640; found 280.2632.

Tetradec-1-en-4-ol¹⁷ **9b**

Following general procedure F, 1,2-epoxydodecane (100 mg, 0.54 mmol), vinylolithium⁴ (1.5 M in Et₂O; 1.09 mL, 1.63 mmol) in hexane (8 mL) gave after workup and column chromatography (SiO₂, 15% Et₂O in petrol) *alcohol 9b* (83 mg, 72%) as a white solid; R_f 0.20 (15% Et₂O in petrol), mp = 45-46 °C. IR (CHCl₃)/cm⁻¹ 3341br, 2925s, 2854s, 1641w, 1466w, 994w, 912w; ¹H NMR (400 MHz) δ 5.89-5.78 (m, 1H), 5.17-5.14 (m, 1H), 5.13-5.11 (m, 1H), 3.68-3.61 (m, 1H), 2.34-2.27 (m, 1H), 2.18-2.10 (m, 1H), 1.63 (br, 1H), 1.48-1.22 (m, 18H), 0.88 (t, *J* = 7.1, 3H); ¹³C NMR (100 MHz) δ 134.9, 118.0, 70.7, 41.9, 36.8, 31.9, 29.7, 29.6, 29.3, 25.7, 22.7, 14.1; MS *m/z* (CI) 230 (M+NH₄, 100), 211 (34), 169 (25), 97 (9); HRMS calcd for C₁₄H₃₂NO (M+NH₄⁺) 230.2484; found 230.2478.

¹⁷ Chang, Y. H.; Uang, B. J.; Wu, C.M.; Yu, T.H. *Synthesis* **1990**, 1033-1034.

(E)-Pentadec-2-en-5-ol 9c

Following general procedure F, 1,2-epoxydodecane (100 mg, 0.543 mmol), (*E*)-propenyllithium⁵ (2.0 M in Et₂O; 0.81 mL, 1.63 mmol) in hexane (8 mL) gave after workup and column chromatography (SiO₂, 15% Et₂O in petrol) *alcohol 9c* (122 mg, 99%, *E*:*Z* = 97:3 by GCMS analysis, *t_R* (*E*)-**9c** = 12.77 min, *t_R* (*Z*)-**9c** = 12.95 min, initial temp. = 100 °C, max. temp. = 280 °C, rate = 8 °C/min) as a colourless oil; *R_f* 0.16 (10% Et₂O in petrol). IR (neat)/cm⁻¹ 3351br, 2925m, 2855m, 1466w, 967w; ¹H NMR (400 MHz) δ 5.60–5.52 (m, 1H), 5.48–5.40 (m, 1H), 3.61–3.54 (m, 1H), 2.27–2.19 (m, 1H), 2.09–2.01 (m, 1H), 1.70 (dd, *J* = 6.3, 1.1, 3H), 1.60 (br, 1H), 1.47–1.23 (m, 18H), 0.88 (t, *J* = 6.8, 3H); ¹³C NMR (100 MHz) δ 128.9, 127.2, 70.9, 40.7, 36.8, 31.9, 29.7, 29.6, 29.3, 25.7, 22.7, 18.1, 14.1; MS *m/z* (CI) 244 (*M*+NH₄⁺, 100), 242 (63), 227 (35), 226 (37), 225 (63), 207 (20), 169 (41); HRMS calcd for C₁₅H₃₄NO (*M*+NH₄⁺) 244.2640; found 244.2644.

(Z)-Pentadec-2-en-5-ol 9d

Following general procedure F, 1,2-epoxydodecane (100 mg, 0.54 mmol), (*Z*)-propenyllithium⁵ (1.4 M in Et₂O; 1.16 mL, 1.63 mmol) in hexane (8 mL) gave after column chromatography (SiO₂, 15% Et₂O in petrol) *alcohol 9d* (111 mg, 90%, *Z*:*E* = 99:1 by GCMS analysis, *t_R* (*E*)-**9d** = 12.77 min, *t_R* (*Z*)-**9d** = 12.95 min, initial temp. = 100 °C, max. temp. = 280 °C, rate = 8 °C/min) as a colourless oil; *R_f* 0.16 (10% Et₂O in petrol). IR (neat)/cm⁻¹ 3349br, 3017m, 2923s, 2854s, 1657w, 1467s, 1077m, 1027m; ¹H NMR (400 MHz) δ 5.71–5.61 (m, 1H), 5.49–5.40 (m, 1H), 3.64 (quint., *J* = 6.1, 1H), 2.23 (t, *J* = 6.1, 2H), 1.65 (d, *J* = 6.8, 3H), 1.57 (br, 1H), 1.52–1.20 (m, 18H), 0.89 (t, *J* = 6.8, 3H); ¹³C NMR (100 MHz) δ 127.3, 126.2, 71.5, 36.9, 35.0, 31.9, 29.7, 29.6, 29.3, 25.8, 22.7, 14.1, 13.0; MS *m/z* (CI) 244 (*M*+NH₄⁺, 100), 242 (81), 227 (30), 226 (40), 225 (69), 208 (25), 169 (19); HRMS calcd for C₁₅H₃₄NO (*M*+NH₄⁺) 244.2640; found 244.2639.

1-Trimethylsilanyl-tridecan-3-ol **9e**

Following general procedure F, 1,2-epoxydodecane (100 mg, 0.54 mmol) and (trimethylsilylmethyl)lithium (1.0 M in pentane, 1.63 mL, 1.63 mmol) in hexane (8 mL) gave after column chromatography (SiO₂, 10% Et₂O in petrol) *alcohol 9e* (111 mg, 75%) as a colourless oil; R_f 0.20 (10% Et₂O in petrol). IR (neat)/cm⁻¹ 3346br, 2925s, 2854s, 1466m, 1378m, 1248s, 1179m, 1127m, 1076m, 1007m; ¹H NMR (400 MHz) δ 3.50-3.44 (m, 1H), 1.74 (br, 1H), 1.48-1.20 (m, 20H), 0.86 (t, *J* = 6.8, 3H), 0.59 (ddd, *J* = 13.9, 13.9, 4.6, 1H) 0.40 (ddd, *J* = 13.9, 12.9, 5.1, 1H), -0.02 (s, 9H); ¹³C NMR (100 MHz) δ 74.1, 36.7, 31.9, 31.5, 29.8, 29.6, 29.3, 25.7, 22.7, 14.1, 12.0, -1.8; MS *m/z* (CI) 290 (M+NH₄⁺, 100), 288 (18), 272 (25), 92 (26), 91 (34), 90 (83); HRMS calcd for C₁₆H₄₀NOSi (M+NH₄⁺) 290.2874; found 290.2877.

6-Trimethylsilanyl-octadecan-8-ol **9f**

Following general procedure F, 1,2-epoxydodecane (100 mg, 0.54 mmol) and 1-(trimethylsilyl)hexyllithium (1.1 M in THF, 1.79 mL, 1.63 mmol) in hexane (8 mL) gave after column chromatography (SiO₂, 10% Et₂O in petrol) *alcohol 9f* (130 mg, 70% 50:50 diastereoisomers by GC analysis, t_R = 11.23 min, t_R = 11.28 min, initial temp. = 80 °C, max. temp. = 280 °C, rate = 20 °C/min) as a colourless wax; R_f 0.24 (10% Et₂O in petrol). IR (neat)/cm⁻¹ 3360br, 2925s, 2855s, 1730w, 1467m, 1378w, 1248s, 834m; ¹H NMR (400 MHz) δ 3.70-3.60 (m, 1H), 1.60 (br, 1H), 1.58-1.20 (m, 27H), 0.88 (t, *J* = 6.6, 6H), 0.81-0.75 (m, 1H), 0.69-0.62 (m, 1H), -0.01 (s, 9H); ¹³C NMR (100 MHz) δ 71.5, 70.0, 38.2, 37.7, 37.3, 32.5, 32.3, 31.9, 29.8, 29.7, 29.7, 29.6, 29.3, 29.0, 28.8, 25.8, 25.6, 22.7, 22.6, 22.6, 22.2, 21.9, 14.1, -2.2, -2.3; MS *m/z* (CI) 360 (M+H⁺, 52), 325 (5), 90 (100); HRMS: *m/z* calcd for C₂₁H₅₀SiNO (M+NH₄⁺) 360.3656; found 360.3651.

^1H and ^{13}C NMR for **6a**

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^1H and ^{13}C NMR for **6b**

^1H and ^{13}C NMR for **6c**

^1H and ^{13}C NMR for **6d**

^1H and ^{13}C NMR for **6f**

^1H and ^{13}C NMR for **6g**

^1H and ^{13}C NMR for **6h**

^1H and ^{13}C NMR for **6i**

^1H and ^{13}C NMR for **6j**

^1H and ^{13}C NMR for **7a**

^1H and ^{13}C NMR for **7b**

^1H and ^{13}C NMR for **7c**

^1H and ^{13}C NMR for **7d**

^1H and ^{13}C NMR for **7e**

^1H and ^{13}C NMR for **7f**

^1H and ^{13}C NMR for **7g**

^1H and ^{13}C NMR for **6k**

^1H and ^{13}C NMR for **9a**

^1H and ^{13}C NMR for **9b**

^1H and ^{13}C NMR for **9c**

^1H and ^{13}C NMR for **9d**

^1H and ^{13}C NMR for **9e**

^1H and ^{13}C NMR for **9f**