Supporting information for

The Reactivity of Epoxides with Lithium 2,2,6,6-Tetramethylpiperidide
in Combination with Organolithiums or Grignard Reagents

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(I) Initial investigations

We first evaluated a variety of organolithiums to ascertain which were (in)capable of deprotonating terminal epoxides. Mioskowski and co-workers demonstrated that reductive alkylation in THF was highly efficient ($\geq 91\%$ yield) for terminal epoxides with alkyllithiums:¹ secondary and tertiary alkyllithiums giving exclusively $E$-isomers, while primary alkyllithiums gave $E:Z$ mixtures. However, the addition of excess of an aryllithium (PhLi) to a terminal epoxide gave only 20% yield of the corresponding $E$-alkene.¹a We repeated this latter reaction and found that the major product was alcohol $16b$ formed in 69% yield in THF. A similar result was obtained when the reaction was carried in hexane, where alcohol $16b$ was obtained in 65%

yield along with alkene 14b in 10% yield (Table 13, entry 1). Evidently, nucleophilic ring-opening of the epoxide by PhLi out-competed deprotonation of the epoxide by PhLi. A variety of other organolithiums were also screened with 1,2-epoxydodecane 13 to investigate whether alkene 14 or alcohol 16 was the predominant product. Use of 2-furanyl- and 2-thienyllithium gave only the corresponding secondary alcohols 16d and 16e in 98% and 91% yield, respectively (entries 2 and 3). Vinyllithium gave 72% yield of homoallylic alcohol 16f and trace amounts of diene 14f (entry 4; 81% of 16f obtained in THF). (E)-Propenyllithium gave 99% yield of (E)-homoallylic alcohol 16h, while (Z)-propenyllithium gave 90% yield of (Z)-16h. LiCH₂SiMe₃ gave predominantly secondary alcohol 16l in 41% yield (entry 7; 84% yield of 16l obtained in THF), along with allylsilane 14l (14% yield, mixture of stereoisomers) and some recovered epoxide (22%). The more substituted α-silyllithium, 1-(trimethylsilyl)hexyllithium, also predominantly gave the corresponding secondary alcohol 16m in 70% yield, along with E-allylsilane 14m in 17% yield (entry 8). 1-Hexynyllithium was unreactive giving ≥90% recovered epoxide (entry 9).
Table 13. Reactions of organolithiums with epoxide 13

![Chemical reaction image]

<table>
<thead>
<tr>
<th>Entry</th>
<th>RLi</th>
<th>Alcohol 16</th>
<th>Yield, %&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Alkene 14&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Yield, %&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Recovered 13, %</th>
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<tr>
<td>7</td>
<td>LiCH&lt;sub&gt;2&lt;/sub&gt;SiMe&lt;sub&gt;3&lt;/sub&gt;</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>41</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>14&lt;sup&gt;c&lt;/sup&gt;</td>
<td>15</td>
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<tr>
<td>8</td>
<td><img src="image" alt="Chemical structure" /></td>
<td><img src="image" alt="Chemical structure" /></td>
<td>70&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>17</td>
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<tr>
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<td>–</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>–</td>
<td>&gt;90</td>
</tr>
</tbody>
</table>

<sup>a</sup>Isolated yield. <sup>b</sup>E:Z>98:2 (determined by GCMS) unless stated otherwise. <sup>c</sup>E:Z = 73:27. <sup>d</sup>dr = 50:50.

As the alkynyllithium was unreactive with 1,2-epoxydodecane in hexane (Table 13, entry 9), this organolithium was considered as an ideal starting point to try to develop a modified reductive alkylation procedure, as any competing nucleophilic ring-opening of the epoxide would be absent. Initial experiments aimed to synthesize enyne 14a by adding a base to a solution of 1,2-epoxydodecane 13 and 1-hexynyllithium (Scheme 7). It was envisaged that the base could deprotonate the epoxide to generate α-lithiated epoxide 53, which would then be
trapped out by the excess alkynyllithium and then undergo the usual process of reductive alkylation (cf 54 to 14a) to give enyne 14a.

**Scheme 7.** Possible enyne 14a formation from epoxide 13 and 1-hexynyllithium and a base

As s-BuLi is known to deprotonate terminal epoxides efficiently in a regio- and stereoselective manner, it was chosen as the base to generate the α-lithiated epoxide in the presence of the alkynyllithium. The general procedure was to add 1 equiv of s-BuLi (1.6 M in hexanes) dropwise over 1 h to a solution of the epoxide (0.2 M) and excess alkynyllithium (4 equiv) in THF. The temperature at which s-BuLi was added was varied from −90 to 0 °C (Table 14, entries 1–5). After addition of s-BuLi, the reaction was left at that temperature for 1 h and then allowed to warm to room temperature overnight. The results of these reactions were essentially identical, in that 35–42% of undesired E-alkene 14p was produced, via the reductive alkylation of the epoxide by s-BuLi and 50–65% of the epoxide was recovered. None of the desired enyne 14a was observed.

**Table 14.** Attempted enyne 14a formation using s-BuLi as the base

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp, °C</th>
<th>14p yield, %</th>
<th>13 recovered, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>−90</td>
<td>35</td>
<td>65</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>−78</td>
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<td>3</td>
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<td>THF</td>
<td>0</td>
<td>41</td>
<td>52</td>
</tr>
<tr>
<td>6b</td>
<td>THF</td>
<td>−50</td>
<td>38</td>
<td>50</td>
</tr>
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<td>7b</td>
<td>Et2O</td>
<td>−50</td>
<td>40</td>
<td>58</td>
</tr>
<tr>
<td>8b</td>
<td>hexane</td>
<td>−50</td>
<td>42</td>
<td>51</td>
</tr>
</tbody>
</table>

*a 1.6 M s-BuLi unless otherwise indicated. *b 0.2 M s-BuLi used.
As 1-hexynyllithium proved to be unsuccessful it was next investigated whether more nucleophilic 2-thienyllithium\(^2\) (cf; Table 13) could undergo this chemistry while using s-BuLi as the base. Following a similar procedure as before, a solution of s-BuLi (0.2 M in hexane) was added dropwise (over 1 h) to a mixture of 1,2-epoxydodecane and 2-thienyllithium (3 equiv) in various solvents and at different temperatures with the aim of producing arylated alkene 14e. However, only unwanted \(E\)-alkene 14p (27–41% yield) and secondary alcohol 16e (36–55% yield) were isolated (Table 15, entries 1–4). These reactions possibly failed because deprotonation of the epoxide and insertion of the resulting carbenoid into the organolithium could be essentially intramolecular events (due to the aggregate state of s-BuLi).\(^3\) An additional experiment was performed wherein 1,2-epoxydodecane (13) was added to a mixture of s-BuLi (1 equiv) and 2-thienyllithium (2.5 equiv) in hexane at \(-50 \, ^\circ C\). The two organolithiums were stirred together for 12 h prior to addition of the epoxide to maximize possible formation of mixed aggregates. This reaction generated for the first time the desired arylated alkene 14e, albeit in only 7% yield (Table 15, entry 5). The secondary alcohol 16e and alkene 14p were isolated as the main products. Attempts to improve the yield of alkene 14e by varying temperature, solvent and number of equivalents of organolithium used all failed.

Table 15. Attempted modified reductive alkylation with 2-thienyllithium\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp °C</th>
<th>14e yield, %(^b)</th>
<th>16e yield, %(^b)</th>
<th>14p yield, %(^b,c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>(-78)</td>
<td>–</td>
<td>38</td>
<td>41</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>(-50)</td>
<td>–</td>
<td>51</td>
<td>33</td>
</tr>
<tr>
<td>3</td>
<td>Et(_2)O</td>
<td>(-50)</td>
<td>–</td>
<td>36</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>hexane</td>
<td>0</td>
<td>–</td>
<td>55</td>
<td>27</td>
</tr>
<tr>
<td>5(^d)</td>
<td>THF</td>
<td>(-50)</td>
<td>7</td>
<td>21</td>
<td>48</td>
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</table>

\(^a\) Reactions left at specified temperature for 1 h then allowed to warm to rt and left for 3 h.  
\(^b\) Isolated yields.  
\(^c\) \(E\)-isomer only.  
\(^d\) Organolithiums left for 14 h prior to addition of epoxide.

The above studies indicated that it was possible to generate a modified reductive alkylation procedure by deprotonation of an epoxide with one type of organolithium and then ring-open the resulting lithiated epoxide with another type of organolithium, however the yield

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\(^2\) 62% of alcohol 16e is formed within 2 h when 2-thienyllithium is added to epoxide 13 compared with 23% of alcohol 16b when PhLi is added to epoxide 13 under same reaction conditions (3 equiv organolithium, hexane, 0 °C, 0.2 M)

of the corresponding alkene (Table 15, entry 5) was very low. So it was next investigated whether changing the base (to LTMP) would influence the reaction.

(II) General directions

All reactions required anhydrous conditions and were conducted in flame-dried glassware under an atmosphere of argon. 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. Solutions of commercially available and prepared organolithiums and Grignard reagents were titrated prior to use using s-BuOH and 1,10-phenanthroline. 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 as liquid films of the compounds on NaCl discs. 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. Data are expressed as chemical shifts in parts per million (ppm) relative to residual chloroform (¹H δ 7.27) or CDCl₃ (¹³C δ 77.0) as the internal standard on the δ scale. The multiplicity of each signal is designated by the following abbreviations; s, singlet; d, doublet; t, triplet; br, broad. Coupling constants J are given in Hz. GCMS analyses were preformed on a spectrometer with a BPX5 column - HP 6890 (dimethylsilicon capillary column, 30 m, 0.25 mm i.d.) equipped with a mass selective detector operating at 60 eV (Cl). Flow rate (He) = 1 mL/min.

(III) General procedures

**General Procedure A:** Optimized conditions for alkene formation via LTMP-modified reductive alkylation using preformed or commercially available organolithiums, or Grignard reagents.

To a solution of 2,2,6,6-tetramethylpiperidine (1.5–2 equiv) in the stated solvent at 0 °C was added \( n\)-BuLi (1.5–2 equiv) dropwise. The reaction mixture was stirred at this temperature for 10 min and then a solution of the appropriate organometallic reagent (1.3–1.5 equiv) was added dropwise. The reaction was left for a further 5 min and then the epoxide (1 equiv) was added. After 2 h the reaction was quenched with sat. brine solution (10 mL) and the layers were separated. The aqueous layer was extracted with Et\(_2\)O (2 x 10 mL), the combined organic layers were dried (MgSO\(_4\)) and solvent removed *in vacuo*. The residue was purified by column chromatography (petrol/Et\(_2\)O) to give the alkene.

**General Procedure B:** Optimized conditions for alkene formation via LTMP-modified reductive alkylation using organolithiums generated *in situ* via halogen-lithium exchange.

To a solution of the organohalide (1.3 equiv) in the stated solvent at −78 °C was added \( t\)-BuLi (2.6 equiv) dropwise. The reaction mixture was stirred at this temperature for 30 min and then warmed to 0 °C. After 5 min a solution of LTMP [prepared by the addition of \( n\)-BuLi (2 equiv) to 2,2,6,6-tetramethylpiperidine (2 equiv) in the stated solvent at 0 °C] was added dropwise. The reaction was left for a further 5 min at 0 °C and then the appropriate epoxide (1 equiv) was added. After 2 h the reaction was quenched with sat. brine solution (10 mL) and the layers were separated. The aqueous layer was extracted with Et\(_2\)O (2 x 10 mL), the combined organic layers were dried (MgSO\(_4\)) and solvent evaporated *in vacuo*. The residue was purified by column chromatography (Et\(_2\)O/petrol) to give the alkene.

**General Procedure C:** Optimized conditions for allylsilane formation via LTMP modified reductive alkylation using 1-(trimethylsilyl)hexyllithium generated *in situ*.

To a solution of vinyltrimethylsilane (84 mg, 84 mmol, 1.55 equiv) in THF (1 mL) at −78 °C was added \( n\)-BuLi (1.6 M in hexanes; 0.44 mL, 0.70 mmol, 1.3 equiv) 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 and a solution of LTMP [prepared from the addition of \( n\)-BuLi (1.6 M in hexanes; 0.44 mL, 0.70 mmol, 1.3 equiv) to 2,2,6,6-tetramethylpiperidine (99 mg, 0.70 mmol, 1.3 equiv) in hexane (7 mL) at 0 °C] was added dropwise. After 5 min the epoxide (0.54 mmol, 1 equiv) was added and the reaction mixture was left stirring for 2 h at 0 °C. After quenching
with sat. 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 (petrol/Et₂O/MeCN/CH₂Cl₂) to give the corresponding allylsilane.

**General Procedure D:** Secondary/tertiary alcohol formation generated by addition of an epoxide to excess organolithium.

The appropriate epoxide (1 equiv) was added dropwise to the organolithium (3 equiv) in the stated solvent at 0 °C. The ice bath was removed and the reaction was left stirring for 14 h. After quenching with sat. brine solution (10 mL), the layers were separated. The aqueous layer was extracted with Et₂O (2 x 20 mL), the combined organic layers were dried (MgSO₄) and solvent evaporated *in vacuo*. The residue was purified by column chromatography (Et₂O/petrol) to give the secondary/tertiary alcohol.

**(IV) Experimental data**

*(E)- and (Z)-7-Octadecen-5-yne 14a (Table 1, entry 14 conditions)*

To a solution of 2,2,6,6-tetramethylpiperidine (153 mg, 1.08 mmol) and 1-hexyne (133 mg, 1.62 mmol) in hexane (8 mL) at 0 °C was added *n*-BuLi (1.6 M in hexanes; 1.69 mL, 2.70 mmol) dropwise. The reaction mixture was left at this temperature for 15 min and then 1,2-epoxydodecane 13 (100 mg, 0.54 mmol) was added. After 2 h the reaction was quenched with sat. brine solution (10 mL) and the layers were separated. The aqueous layer was extracted with Et₂O (2 x 20 mL) and the combined organic layers were dried (MgSO₄) and solvent evaporated *in vacuo*. The residue was purified by column chromatography (Et₂O/petrol) to give the secondary/tertiary alcohol.
(E)-1-Phenyl-1-dodecene \(^5\) \(14b\)

Following general procedure A, the addition of 1,2-epoxydodecane \(13\) (100 mg, 0.54 mmol) to a solution of LTMP [prepared by the addition of \(n\)-BuLi (1.6 M in hexanes; 0.68 mL, 1.08 mmol) to TMP (153 mg, 1.08 mmol) in hexane (8 mL)] and PhLi (2.0 M in \(n\)-Bu\(_2\)O; 0.35 mL, 0.70 mmol) gave after workup and column chromatography (100% petrol) alkene \(14b\) (123 mg, 93%, \(E:Z = 98:2\), by GCMS analysis, \(t_R\) Z-\(14b\) 13.02 min, \(t_R\) E-\(14b\) 14.22 min, initial temp. 80 °C, max. temp. 280 °C, rate 10 °C/min) as a colorless oil; \(R_f\) 0.48 (100% petrol); IR (neat)/cm\(^{-1}\) 3025m, 2956s, 2925s, 2853s, 1625w, 1599w, 1494w, 1466m, 927s; \(^1\)H NMR (400 MHz) \(\delta\) 7.38−7.29 (m, 4H), 7.21 (tt, \(J = 7.5, 1.5, 1H\)), 6.41 (d, \(J = 16, 1H\)), 6.26 (dt, \(J = 16, 7, 1H\)), 2.22 (dt, \(J = 7, 7, 2H\)), 1.53−1.45 (m, 2H), 1.40−1.25 (m, 14H), 0.92 (t, \(J = 6.5, 3H\)); \(^{13}\)C NMR (100 MHz) \(\delta\) 138.0, 131.3, 129.7, 128.5, 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 C\(_{18}\)H\(_{29}\)(M+H\(^+\)) 245.2269, found 245.2267.

\(^{(E)}\)-(1-Dodec-1-enyl)-4-methoxybenzene \(^6\) \(14c\)

Following general procedure B, the addition of 1,2-epoxydodecane \(13\) (100 mg, 0.54 mmol) to a solution of LTMP [prepared by the addition of \(n\)-BuLi (1.6 M in hexanes; 0.68 mL, 1.08 mmol) to TMP (153 mg, 1.08 mmol) in hexane (8 mL)] and (4-methoxyphenyl)lithium [prepared by the addition of \(t\)-BuLi (1.5 M in pentane; 0.94 mL, 1.40 mmol) to 4-bromoanisole (131 mg, 0.70 mmol) in THF (1 mL)] gave after column chromatography (2% Et\(_2\)O in petrol) alkene \(14c\) (104 mg, 70%, \(E:Z = 98:2\) by GCMS analysis, \(t_R\) Z-\(14c\) 14.35 min, \(t_R\) E-\(14c\) 16.78 min, initial temp. 100 °C, max. temp. 30 °C, rate 10 °C/min) as a white solid; \(R_f\) 0.48 (10% Et\(_2\)O in petrol); mp 36−39 °C; IR (CHCl\(_3\))/cm\(^{-1}\) 2954m, 2920s, 2850m, 1608w, 1513w, 1465w, 1251w, 1176w, 1023w, 962w; \(^1\)H NMR (400 MHz) \(\delta\) 7.31 (d, \(J = 9, 2H\)), 6.87 (d, \(J = 9, 2H\)), 6.35 (d, \(J = 16, 1H\)), 6.12 (dt, \(J = 16, 7, 1H\)), 3.82 (s, 3H), 2.21 (q, \(J = 7, 2H\)), 1.52−1.44 (m, 2H), 1.41−1.25 (m, 14H), 0.92 (t, \(J = 7, 3H\)); \(^{13}\)C NMR (400 MHz) \(\delta\) 158.6, 130.8, 129.1, 129.0, 127.0, 113.9, 55.2.

Following general procedure A, the addition of 1,2-epoxydodecane 13 (308 mg, 1.67 mmol) to a solution of LTMP [prepared by the addition of n-BuLi (1.6 M in hexanes; 2.09 mL, 3.34 mmol) to TMP (472 mg, 3.34 mmol) in hexane (24 mL)] and 2-furanyllithium [prepared by the addition of t-BuLi (1.5 M in pentane; 1.45 mL, 2.17 mmol) to furan (148 mg, 2.17 mmol) at 0 °C in Et₂O (2 mL)] gave after workup and column chromatography (100% petrol) alkene 14d (125 mg, 32%, E:Z = 98:2 by GCMS analysis, tᵣ Z-14d 8.88 min, tᵣ E-14d 9.27 min, initial temp. 80 °C, max. temp. 280 °C, rate 20 °C/min) as a colorless oil; Rᵣ 0.40 (100% petrol); IR (neat)/cm⁻¹ 2923s, 2854s, 1465m, 1378w, 1254w, 1152m, 1075m, 1012m, 959m, 926w, 884w, 727s; ¹H NMR (400 MHz) δ 7.31 (d, J = 2, 1H), 6.35 (dd, J = 3.5, 2, 1H), 6.22–6.19 (m, 2H), 6.13 (d, J = 3.5, 1H), 2.20–2.17 (m, 2H), 1.49–1.42 (m, 2H), 1.37–1.22 (m, 14H), 0.89 (t, J = 7, 3H); ¹³C NMR (100 MHz) δ 153.4, 141.1, 130.3, 118.4, 111.0, 105.8, 32.8, 31.9, 29.6, 29.5, 29.3, 29.2, 29.2, 22.7, 14.1; MS m/z (CI) 235 (M+H⁺, 100), 234 (28), 107 (24), 94 (28); HRMS calcd for C₁₆H₂₇O (M+H⁺) 235.2062, found 235.2052.

(E)-2-(Dodec-1-enyl)thiophene 14e

Following general procedure A, the addition of 1,2-epoxydodecane 13 (100 mg, 0.54 mmol) to a solution of LTMP [prepared by the addition of n-BuLi (1.6 M in hexanes; 0.68 mL, 1.08 mmol) to TMP (153 mg, 1.08 mmol) in hexane (8 mL)] and 2-thienyllithium (1.0 M in THF; 0.70 ml, 0.70 mmol) gave after workup and column chromatography (100% petrol) alkene 14e (53 mg, 39%, E:Z = 99:1, by GCMS analysis, tᵣ Z-14e 7.41 min, tᵣ E-14e 8.02 min, initial temp. 80 °C, max. temp. 280 °C, rate 20 °C/min) as a colorless oil; Rᵣ 0.53 (100% petrol); IR (neat)/cm⁻¹ 2923s, 2854s, 1465m, 1437m, 1378w, 1284w, 1239w, 1204w, 1041w, 953s; ¹H NMR (400 MHz) δ 7.08 (d, J = 5, 1H), 6.94 (dd, J = 5, 3.5, 1H), 6.87 (d, J = 3.5, 1H), 6.50 (d, J = 15.5, 1H), 6.08 (dt, J = 15.5, 7, 1H), 2.18 (dt, J = 7, 1.5, 2H), 1.49–1.42 (m, 2H), 1.35–1.21 (m, 14H), 0.89 (t, J = 7, 3H); ¹³C NMR (100 MHz) δ 143.2, 131.3, 127.2, 124.0, 122.9, 122.9, 32.8, 31.9, 29.6, 29.5, 29.5, 29.3, 29.2, 29.2, 22.7, 14.1; MS m/z (CI) 251 (M+H⁺, 100), 234 (28), 107 (24), 94 (28); HRMS calcd for C₁₆H₂₇S (M+H⁺) 251.1862, found 251.1852.
Following general procedure A, the addition of 1,2-epoxydodecane 13 (100 mg, 0.54 mmol) to a solution of LTMP [prepared by the addition of n-BuLi (1.6 M in hexanes; 0.68 mL, 1.08 mmol) to TMP (153 mg, 1.08 mmol) in hexane (8 mL)] and vinyllithium 8 (1.5 M in Et₂O; 0.47 mL, 0.70 mmol) gave after workup and column chromatography (100% petrol) diene 14f (77 mg, 73%, E:Z = 98:2 by GCMS analysis, tᵣ Z-14f 6.83 min, tᵣ E-14f 7.05 min, initial temp. 80 °C, max. temp. 280 °C, rate 20 °C/min) as a colorless oil; Rᶠ 0.58 (100% 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 = 17, 10, 10, 1H), 6.06 (dd, J = 15, 10, 1H), 5.10 (d, J = 17, 1H), 4.96 (d, J = 10, 1H), 2.08 (dt, J = 7, 7, 2H), 1.78 (s, 3H), 1.76 (s, 3H), 1.33–1.24 (m, 16H), 0.90 (t, J = 7, 3H); ¹³C NMR (100 MHz) δ 137.4, 135.6, 130.8 126.1, 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) 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.

Following general procedure B, the addition of 1,2-epoxydodecane 13 (100 mg, 0.54 mmol) to a solution of LTMP [prepared by the addition of n-BuLi (1.6 M in hexanes; 0.68 mL, 1.08 mmol) to TMP (153 mg, 1.08 mmol) in hexane (8 mL)] and (3-methylbut-2-en-2-yl)lithium [prepared by the addition of t-BuLi (1.5 M in pentane; 0.94 mL, 1.40 mmol) to 2-bromo-3-methyl-2-butene (105 mg, 0.70 mmol) in THF (1.5 mL)] gave after workup and column chromatography (100% petrol) diene 14g (109 mg, 85%, E-only by GCMS analysis, tᵣ E-14g 7.10 min, initial temp. 80 °C, max. temp. 280 °C, rate 20 °C/min) as a colorless oil; Rᶠ 0.56 (100% petrol); IR (neat)/cm⁻¹ 2923s, 2854s, 1465m, 1375m, 1170w, 959s; ¹H NMR (400 MHz) δ 6.05 (d, J = 15.5, 1H), 5.59 (dt, J = 15.5, 7, 1H), 2.12 (dt, J = 7, 7, 2H), 1.82 (s, 3H), 1.78 (s, 3H), 1.76 (s, 3H), 1.33–1.24 (m, 16H), 0.89 (t, J = 7, 3H); ¹³C 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 (M⁺H⁺, 100), 109 (21); HRMS calcd for C₁₇H₃₃(M⁺H⁺), 237.2582, found 237.2585.

(2E,4E)-2,4-Pentadecadiene\textsuperscript{6} 14h

Following general procedure A, the addition of 1,2-epoxydodecane 13 (100 mg, 0.54 mmol) to a solution of LTMP [prepared by the addition of \textit{n}-BuLi (1.6 M in hexanes; 0.68 mL, 1.08 mmol) to TMP (153 mg, 1.08 mmol) in hexane (8 mL)] and \((E)-\text{propenyllithium}\)\textsuperscript{9} (2.0 M in Et\textsubscript{2}O; 0.35 mL, 0.70 mmol) gave after workup and column chromatography (100%, petrol) diene 14h (92 mg, 82%, \(E,E:Z,E = 98:2\) by GCMS analysis, \(t_{R} Z,E-14h 10.82 \text{ min}, t_{R} E,E-14h 10.98 \text{ min}, \) initial temp. 100 °C, max. temp. 280 °C, rate 8 °C/min) as a colorless oil; \(R_{f} 0.64 \) (100% petrol); IR (neat)/cm\textsuperscript{−1} 3016m, 2957s, 2925s, 2854s, 1466m, 1378w, 986s; \(^1\)H NMR (400 MHz) \(\delta 6.07 - 5.95 \) (m, 2H), 5.62 - 5.52 (m, 2H), 2.05 (dt, \(J = 7, 7, 2\)H), 1.74 (d, \(J = 6.5, 3\)H), 1.40 - 1.22 (m, 16H), 0.89 (t, \(J = 7, 3\)H); \(^{13}\)C NMR (100 MHz) \(\delta 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 \textit{m/z} (CI) 226 (M+\textit{NH}_4\textsuperscript{+}, 33), 208 (100), 207 (17), 95 (22), 81 (48); HRMS calcd for C\textsubscript{15}H\textsubscript{32}N (M+\textit{NH}_4\textsuperscript{+}) 226.2535, found 226.2535.

(7E,9E)-7,9-Icosadiene\textsuperscript{6} 14i

Following general procedure B, the addition of 1,2-epoxydodecane 13 (80 mg, 0.43 mmol) to a solution of LTMP [prepared by the addition of \textit{n}-BuLi (1.6 M in hexanes; 0.54 mL, 0.87 mmol) to TMP (123 mg, 0.87 mmol) in hexane (7 mL)] and \((E)-1\text{-octenyllithium}\) [prepared by the addition of \textit{t}-BuLi (1.5 M in pentane; 0.74 mL, 1.12 mmol) to \((E)-1\text{-iodo-1-octene}\)\textsuperscript{10} (133 mg, 0.56 mmol) in Et\textsubscript{2}O (1.0 mL)] gave after workup and column chromatography (100% petrol) diene 14i (101 mg, 84%, \(E,E:Z,E = 99:1\), by GCMS analysis, \(t_{R} Z,E-14i 16.68 \text{ min}, t_{R} E,E-14i 17.07 \text{ min}, \) initial temp. 80 °C, max. temp. 280 °C, rate 10 °C/min) as a colorless oil; \(R_{f} 0.59 \) (100% petrol); IR (neat)/cm\textsuperscript{−1} 3014w, 2957s, 2925s, 2854s, 1466m, 1378w, 986s; \(^1\)H NMR (400 MHz) \(\delta 6.03 - 5.98 \) (m, 2H), 5.57 (dt, \(J = 14.5, 7, 2\)H), 2.05 (dt, \(J = 7, 7, 4\)H), 1.42 - 1.21 (m, 24H), 0.89 (t, \(J = 7, 6\)H); \(^{13}\)C NMR (100 MHz) \(\delta 132.4, 130.3, 32.6, 31.9, 29.6, 29.5, 29.4, 29.3, 22.7, 22.6, 14.1, 14.1; MS \textit{m/z} (CI) 296 (M+\textit{NH}_4\textsuperscript{+}, 30), 279 (63), 278 (100), 277 (56), 276 (20), 275 (17), 138 (13), 95 (16), 81 (15); HRMS calcd for C\textsubscript{20}H\textsubscript{42}N (M+\textit{NH}_4\textsuperscript{+}) 296.3317, found 296.3310.

(1E,3E)-1-Phenyl-1,3-tetradecadiene\textsuperscript{6} 14j

Following general procedure A, the addition of 1,2-epoxydodecane (230 mg, 1.25 mmol) to a solution of LTMP [prepared by the addition of \textit{n}-BuLi (1.6 M in hexanes; 1.56 mL, 2.50 mmol)


to TMP (353 mg, 2.50 mmol) in hexane (19 mL) and (E)-2-phenylethyllithium\(^{11}\) (1.1 M in Et\(_2\)O; 1.48 mL, 1.63 mmol) gave after workup and reverse phase column chromatography (C\(_{18}\) silica, MeCN)\(^{12}\) diene \(14j\) (243 mg, 72%, \(E,E:E,Z = 98:2\), by GCMS analysis, \(t_r E,E-14j = 11.55\) min, \(t_r E,Z-6g = 11.83\) min, initial temp. 80 °C, max. temp. 280 °C, rate 20 °C/min) as a colourless oil; \(R_f 0.26\) (C\(_{18}\) silica, MeCN). IR (neat)/cm\(^{-1}\) 3022\(m\), 2955\(s\), 2925\(s\), 2853\(s\), 1644\(w\), 1597\(w\), 1495\(w\), 1466\(w\), 1448\(w\), 986\(s\); \(^1\)H NMR (400 MHz) \(\delta 7.40-7.37\) (m, 2H), \(7.33-7.28\) (m, 2H), \(7.20\) (tt, \(J = 7.5, 1.5\), 1H), \(6.76\) (dd, \(J = 15.5, 10.5\), 1H), \(6.44\) (d, \(J = 15.5\), 1H), \(6.20\) (dd, \(J = 15, 10.5\), 1H), \(5.83\) (dt, \(J = 15, 7\), 1H), \(2.14\) (dt, \(J = 7, 7\), 2H), \(1.47-1.22\) (m, 16H), \(0.88\) (t, \(J = 7\), 3H); \(^{13}\)C NMR (100 MHz) \(\delta 137.7, 136.1, 130.4, 129.9, 129.5, 128.5, 127.0, 126.1, 32.9, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1\); MS m/z (CI) 271 (M+H\(^+\) 100), 270 (64), 143 (25), 128 (14); HRMS calc'd for C\(_{20}\)H\(_{31}\) (M+H\(^+\)) 271.2429, found 271.2429.

\(\text{(2Z,4E)-2,4-Pentadecadiene}^{6} 14h\)

Following general procedure A, the addition of 1,2-epoxydodecane \(13\) (100 mg, 0.54 mmol) to a solution of LTMP \([\text{prepared by the addition of } n-\text{BuLi (1.6 M in hexanes; 0.68 mL, 1.08 mmol)}\) to TMP (153 mg, 1.08 mmol) in hexane (8 mL)] and (Z)-propenyllithium\(^{9}\) (1.4 M in Et\(_2\)O; 0.50 mL, 0.70 mmol) gave after workup and column chromatography (100% petrol) diene-\(14h\) (79 mg, 70%, \(Z,E:E,E = 90:10\) by GCMS analysis, \(t_r Z,E-14h = 10.82\) min, \(t_r E,E-14h = 10.98\) min, initial temp. 100 °C, max. temp. 280 °C, rate 8 °C/min) as a colorless oil; \(R_f 0.64\) (100% petrol); IR (neat)/cm\(^{-1}\) 3015\(m\), 2960\(s\), 2920\(s\), 2844\(s\), 1466m, 1349w, 970s; \(^1\)H NMR (400 MHz) \(\delta 6.33\) (ddq, \(J = 11, 10, 1.5\), 1H), \(6.02-5.95\) (m, 1H), \(5.67\) (dt, \(J = 15, 7.5\), 1H), \(5.38\) (dq, \(J = 11, 7\), 1H), \(2.15-2.07\) (m, 2H), \(1.75\) (dd, \(J = 7, 1.5\), 3H), \(1.44-1.20\) (m, 16H), \(0.89\) (t, \(J = 7\), 3H); \(^{13}\)C NMR (100 MHz) \(\delta 134.7, 129.5, 125.3, 123.8, 32.9, 31.9, 29.6, 29.5, 29.4, 29.3, 22.7, 14.1, 13.3\); MS m/z (CI) 226 (M+NH\(_4^+\) 52), 208 (100), 207 (11), 166 (87), 95 (10), 81 (22); HRMS calc'd for C\(_{13}\)H\(_{32}\)N (M+NH\(_4^+\)) 226.2535, found 226.2541.

\(\text{(7Z,9E)-7,9-Icosadiene}^{13} 14i\)

Following general procedure B, the addition of 1,2-epoxydodecane \(13\) (80 mg, 0.43 mmol) to a solution of LTMP \([\text{prepared by the addition of } n-\text{BuLi (1.6 M in hexanes; 0.54 mL, 0.87 mmol)}\] to TMP (353 mg, 2.50 mmol) in hexane (19 mL)] and (E)-2-phenylethyllithium\(^{11}\) (1.1 M in Et\(_2\)O; 1.48 mL, 1.63 mmol) gave after workup and reverse phase column chromatography (C\(_{18}\) silica, MeCN)\(^{12}\) diene \(14j\) (243 mg, 72%, \(E,E:E,Z = 98:2\), by GCMS analysis, \(t_r E,E-14j = 11.55\) min, \(t_r E,Z-6g = 11.83\) min, initial temp. 80 °C, max. temp. 280 °C, rate 20 °C/min) as a colourless oil; \(R_f 0.26\) (C\(_{18}\) silica, MeCN). IR (neat)/cm\(^{-1}\) 3022\(m\), 2955\(s\), 2925\(s\), 2853\(s\), 1644\(w\), 1597\(w\), 1495\(w\), 1466\(w\), 1448\(w\), 986\(s\); \(^1\)H NMR (400 MHz) \(\delta 7.40-7.37\) (m, 2H), \(7.33-7.28\) (m, 2H), \(7.20\) (tt, \(J = 7.5, 1.5\), 1H), \(6.76\) (dd, \(J = 15.5, 10.5\), 1H), \(6.44\) (d, \(J = 15.5\), 1H), \(6.20\) (dd, \(J = 15, 10.5\), 1H), \(5.83\) (dt, \(J = 15, 7\), 1H), \(2.14\) (dt, \(J = 7, 7\), 2H), \(1.47-1.22\) (m, 16H), \(0.88\) (t, \(J = 7\), 3H); \(^{13}\)C NMR (100 MHz) \(\delta 137.7, 136.1, 130.4, 129.9, 129.5, 128.5, 127.0, 126.1, 32.9, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1\); MS m/z (CI) 271 (M+H\(^+\) 100), 270 (64), 143 (25), 128 (14); HRMS calc'd for C\(_{20}\)H\(_{31}\) (M+H\(^+\)) 271.2429, found 271.2429.

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\(11\) Prepared by the addition of (E)-\(\beta\)-bromostyrene to Li metal in Et\(_2\)O at 0 °C.

\(12\) Farina, V. \(J. \text{Org. Chem.}\) 1991, 56, 4985–4987.

to TMP (123 mg, 0.87 mmol) in hexane (7 mL) and (Z)-1-octenyllithium [prepared by the addition of t-BuLi (1.5 M in pentane; 0.74 mL, 1.12 mmol) to (Z)-1-iodo-1-octene\textsuperscript{(14)} (133 mg, 0.56 mmol) in Et\textsubscript{2}O (1.0 mL)] gave after workup and column chromatography (100% petrol) \textit{diene} \textbf{14i} (96 mg, 80%, Z:E:E:other isomer = 91:5:4 by GCMS analysis, \(t_R\) Z,E-\textbf{14i} 16.68 min, \(t_R\) other isomer 16.90, \(t_R\) E,E-\textbf{14i} 17.07 min, initial temp. 80 °C, max. temp. 280 °C, rate 10 °C/min) as a colorless oil; \(R_f\) 0.59 (100% petrol); IR (neat)/cm\textsuperscript{−1} 3019m, 2926s, 2854s, 1466s, 1378s, 982m, 946m; \(^1\)H NMR (400 MHz) \(\delta\) 6.31 (dd, \(J = 15, 11, 1\)H), 5.97 (dd, \(J = 11, 10.5, 1\)H), 5.67 (dt, \(J = 15, 7.5, 1\)H), 5.31 (dt, \(J = 10.5, 7.5, 1\)H), 2.20−2.02 (m, 4H), 1.43−1.21 (m, 24H), 0.89 (t, \(J = 7, 3\)H); \(^{13}\)C NMR (100 MHz) \(\delta\) 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+NH\textsubscript{4}\textsuperscript{+}, 31), 279 (75), 278 (100), 277 (31), 276 (13), 166 (10), 138 (14), 96 (14), 81 (19); HRMS calcd for C\textsubscript{20}H\textsubscript{42}N (M+NH\textsubscript{4}\textsuperscript{+}) 296.3317, found 296.3325.

\((5E,7E)-5\)-Methyl-5,7-octadecadiene\textsuperscript{(6)} \textbf{14k}

Following general procedure B, the addition of 1,2-epoxydodecane \textbf{13} (125 mg, 0.68 mmol) to a solution of LTMP [prepared by the addition of n-BuLi (1.6 M in hexanes; 0.85 mL, 1.36 mmol) to TMP (192 mg, 1.36 mmol) in hexane (10 mL)] and (E)-(2-methyl-1-hexenyl)lithium [prepared by the addition of t-BuLi (1.5 M in pentane; 1.18 mL, 1.77 mmol) to (E)-1-iodo-2-methyl-1-hexene\textsuperscript{(15)} (198 mg, 0.88 mmol) in Et\textsubscript{2}O (2 mL)] gave after workup and column chromatography (100% petrol) \textit{diene} \textbf{14k} (153 mg, 85% E,E:Z,E = 91:9 by GCMS analysis, \(t_R\) Z,E-\textbf{14k} 9.78 min, \(t_R\) E,E-\textbf{14k} 10.00 min, initial temp. 80 °C, max. temp. 280 °C, rate 20 °C/min) as a colorless oil; \(R_f\) 0.69 (100% petrol); IR (neat)/cm\textsuperscript{−1} 3020m, 2924s, 2854s, 1642w, 1466s, 1378m, 963s; \(^1\)H NMR (400 MHz) \(\delta\) 6.25 (dd, \(J = 15, 11, 1\)H), 5.81 (d, \(J = 11, 1\)H), 5.59 (dt, \(J = 15, 7, 1\)H), 2.09 (dt, \(J = 7, 7, 2\)H), 2.04 (t, \(J = 7.5, 2\)H), 1.74 (s, 3H), 1.44−1.26 (m, 20H), 0.93−0.88 (m, 6H); \(^{13}\)C NMR (100 MHz) \(\delta\) 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\textsuperscript{+}, 100), 264 (29), 263 (10), 137 (10); HRMS calcd for C\textsubscript{19}H\textsubscript{37} (M+H\textsuperscript{+}) 265.2895, found 265.2889.

\((E)-1\)-Trimethylsilyl-2-tridecene\textsuperscript{(16)} \textbf{14l} (from Table 4, entry 4 conditions)

Following general procedure A, the addition of 1,2-epoxydodecane \textbf{13} (100 mg, 0.54 mmol) to a solution of LTMP [prepared by the addition of n-BuLi (1.6 M in hexanes; 0.68 mL, 1.08 mmol)

to TMP (153 mg, 1.08 mmol) in Et₂O (8 mL) and (trimethylsilylmethyl)lithium (1.0 M in pentane; 0.70 mL, 0.70 mmol) gave after workup and column chromatography (100% petrol) allylsilane 14l (89 mg, 65%, E:Z = 97:3, by GCMS analysis, tₑ E-14l 8.22 min, tₑ Z-14l 8.30 min, initial temp. 80 °C, max. temp. 280 °C, rate 20 °C/min) as a colorless oil; Rᵋ 0.63 (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 = 7, 7, 2H), 1.41 (dd, J = 7.5, 1, 2H), 1.33–1.27 (m, 16H), 0.90 (t, J = 7, 3H), 0.00 (s, 9H); ¹³C 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 C₁₆H₃₅Si (M+H⁺) 255.2508, found 255.2501.

When Z-isomer 14l was formed in appreciable amounts along with the E-isomer (Table 4, entries 1–3) it was identified from the allylic protons and allylic/vinylic/−SiMe₃ carbons: ¹H NMR (400 MHz) δ 1.48 (d, J = 8, 2H); ¹³C NMR (100 MHz) δ 127.8, 125.2, 27.4, −1.8.

(E)-(1-Pentyl-1-tridecen-1-yl)trimethylsilane⁶ 14m

Following general procedure C, using 1,2-epoxydodecane 13 (100 mg, 0.54 mmol) gave after workup and reverse phase column chromatography¹² (C₁₈ silica, 15% Et₂O in MeCN) allylsilane 14m (130 mg, 74%, E-only by GCMS analysis, E-14m 10.18 min, initial temp. 80 °C, max. temp. 280 °C, rate 20 °C/min) as a colorless oil; Rᵋ 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)-5-Hexadecene⁶ 14n (Table 10, entry 3 conditions)

Following general procedure A (except reaction left for 3 h), the addition of 1,2-epoxydodecane 13 (100 mg, 0.54 mmol) to a solution of LTMP [prepared by the addition of n-BuLi (1.6 M in hexanes; 0.68 mL, 1.08 mmol) to TMP (153 mg, 1.08 mmol) in Et₂O (8 mL)] and n-BuMgCl (2.0 M in Et₂O; 0.38 mL, 0.76 mmol) gave after workup and column chromatography (100% petrol) alkene 14n (84 mg, 69%, E:Z = 96:4, by ¹H NMR analysis of vinylic protons in the δ 6.00−5.00 region) as a colorless oil; Rᵋ 0.70 (100% 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); $^{13}$C 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), 83 (100), 71 (32), 70 (59), 69 (92), 67 (41), 57 (30), 55 (65); HRMS calcd for C_{16}H_{32} (M+) 224.2504, found 224.2514.

When Z-isomer 14n was formed in appreciable amounts along with the E-isomer (Table 9, entries 1–5) it was identified from the vinylic protons and carbons: $^1$H NMR (500 MHz) δ 5.36 (dt, J = 7.5, 6, 2H); $^{13}$C NMR (125 MHz) δ 129.9, 129.8.

$(E)$-2-Tridecene $^{6}$ 14o (Table 11, entry 4 conditions)

Following general procedure A (except reaction left for 3 h), the addition of 1,2-epoxydodecane 13 (100 mg, 0.54 mmol) to a solution of LTMP [prepared by the addition of n-BuLi (1.6 M in hexanes; 0.51 mL, 0.81 mmol) to TMP (114 mg, 0.81 mmol) in hexane (8 mL)] and MeMgCl (2.2 M in THF; 0.45 mL, 0.98 mmol) gave after workup and column chromatography (100% petrol) alkene 14o (70 mg, 71%, E:Z = 98:2 by GCMS analysis, t$_r$ E-14o 9.10 min, t$_r$ Z-14o 9.25 min, initial temp. 80 °C, max. temp. 280 °C, rate 10 °C/min) as a colorless oil; R$_f$ 0.66 (100% petrol); IR (neat)/cm$^{-1}$ 2925s, 2855s, 1465m, 1378w, 964m; $^1$H 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 = 7, 3H); $^{13}$C 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 C$_{13}$H$_{26}$ (M$^+$) 182.2035, found 182.2035.

When Z-isomer 14o was formed in appreciable amounts along with the E-isomer (Table 8, entries 1, 3–6) it was identified from the allylic protons and vinylic carbons: $^1$H NMR (400 MHz) δ 1.61 (dd, J = 6, 1, 3H); $^{13}$C NMR (100 MHz) δ 130.9, 123.5.

When E-alkene 14p was observed it was identified as follows:

$(E)$-3-Methyl-4-pentadecene 14p

Colorless oil; R$_f$ 0.75 (100% petrol); IR (neat)/cm$^{-1}$ 2959s, 2924s, 2854s, 1458s, 1378m, 1158w; $^1$H NMR (400 MHz) δ 5.36 (dt, J = 15.5, 6.5, 1H), 5.25 (dd, J = 15.5, 7.5, 1H), 2.07-1.90 (m, 3H), 1.40–1.20 (m, 18H), 0.96 (d, J = 7, 3H), 0.89 (t, J = 7, 3H), 0.85 (t, J = 7.5, 3); $^{13}$C NMR (100 MHz) δ 136.1, 128.7, 38.4, 32.6, 31.9, 29.9, 29.7, 29.6, 29.5, 29.3, 29.1, 22.7, 20.5, 14.1, 11.8; MS m/z (CI) 242 (M+NH$_4^+$, 5), 224 (48), 195 (30), 125 (24), 111 (35), 97 (49), 83 (100); HRMS calcd for C$_{16}$H$_{36}$N (M+NH$_4^+$) 242.2848, found 242.2850.
When aldehyde 15 was observed it was identified as follows:

Dodecanal<sup>17</sup> 15

![Structure of Dodecanal](image)

Colourless oil; R<sub>f</sub> 0.36 (5% Et<sub>2</sub>O in petrol); <sup>1</sup>H NMR (400 MHz) δ 9.72 (t, J = 2, 1H), 2.38 (td, J = 7, 2, 2H), 1.70–1.48 (m, 2H), 1.40–1.08 (m, 16H), 0.84 (t, J = 6.5, 3H); <sup>13</sup>C NMR (100 MHz) δ 203.0, 44.3, 31.9, 29.6, 29.4, 29.3, 29.2, 22.7, 22.1, 14.1.

1-Phenyldodecan-2-ol<sup>6</sup> 16b

![Structure of 1-Phenyldodecan-2-ol](image)

Following general procedure D, the addition of 1,2-epoxydodecane 13 (100 mg, 0.54 mmol) to PhLi (2.0 M in n-Bu<sub>2</sub>O; 0.82 mL, 1.63 mmol) in hexane (8 mL) gave after workup and column chromatography (15% Et<sub>2</sub>O in petrol) alcohol 16b (98 mg, 69%) as a white solid; R<sub>f</sub> 0.16 (10% Et<sub>2</sub>O in petrol); mp 40–41 °C; IR (CHCl<sub>3</sub>) cm<sup>−1</sup> 3367br, 3027m, 2919s, 1496w, 1466s, 1350w; <sup>1</sup>H 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 = 13.5, 4.5, 1H), 2.65 (dd, J = 13.5, 8.5, 1H), 1.52–1.46 (m, 3H), 1.35–1.24 (m, 16H), 0.90 (t, J = 7, 3H); <sup>13</sup>C 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+NH<sub>4</sub><sup>+</sup>, 100), 262 (6), 244 (36), 169 (12), 117 (27), 104 (64), 92 (76), 91 (40); HRMS calcd for C<sub>18</sub>H<sub>34</sub>NO (M+NH<sub>4</sub><sup>+</sup>) 280.2640, found 280.2632.

1-(4-Methoxy-phenyl)dodecanol-2-ol 16c

![Structure of 1-(4-Methoxy-phenyl)dodecanol-2-ol](image)

Following general procedure D, the addition of 1,2-epoxydodecane 13 (100 mg, 0.54 mmol) to (4-methoxyphenyl)lithium [prepared by the addition of t-BuLi (1.5 M in hexanes; 2.17 mL, 3.26 mmol) to 4-bromoanisole (305 mg, 1.63 mmol) at −78 °C in THF (2.5 mL)] in hexane (7 mL) gave after column chromatography (10% Et<sub>2</sub>O in petrol) alcohol 16c (132 mg, 83%) as a white solid; R<sub>f</sub> 0.11 (10% Et<sub>2</sub>O in petrol); mp 55–56 °C; IR (KBr) cm<sup>−1</sup> 3418br, 2924s, 1460s, 1378s, 1032w; <sup>1</sup>H NMR (400 MHz) δ 7.14 (d, J = 8.5, 2H), 6.87 (d, J = 8.5, 2H), 3.81 (s, 3H), 3.80–3.74 (m, 1H), 2.79 (dd, J = 13.5, 4.5, 1H), 2.58 (dd, J = 13.5, 8.5, 1H), 1.58–1.22 (m, 19H), 0.89 (t, J = 7, 3H); <sup>13</sup>C NMR (400 MHz) δ 158.2, 130.3, 114.0, 99.6, 72.8, 55.2, 43.1, 36.7, 31.9, 29.7, 29.6, 29.3, 25.8, 22.7, 14.1; MS m/z (CI) 310 (M+NH<sub>4</sub><sup>+</sup>, 100), 275 (11), 122 (38), 121 (12); HRMS calcd for C<sub>19</sub>H<sub>36</sub>NO<sub>2</sub> (M+NH<sub>4</sub><sup>+</sup>) 310.2741, found 310.2742.

(17) Spectra matched commercially available (Aldrich, product no. D222003) material.
1-(Furan-2-yl)dodecan-2-ol 16d

Following general procedure D, the addition of 1,2-epoxydodecane 13 (100 mg, 0.54 mmol) to 2-furanyllithium [prepared by the addition of t-BuLi (1.5 M in pentane; 1.08 mL, 1.62 mmol) to furan (110 mg, 1.62 mmol) at 0 °C in Et₂O (2 mL)] in hexane (8 mL) gave after workup and column chromatography (10% Et₂O in petrol) alcohol 16d (134 mg, 98%) as a white solid; R₇ 0.10 (15% Et₂O in petrol); mp 46–47 °C; IR (CHCl₃)/cm⁻¹ 3357m, 2930s, 2855s, 1597w, 1507w, 1466w, 1147w, 1081w, 1099w; ¹H NMR (400 MHz) δ 7.35 (dd, J = 2, 1, 1H), 6.32 (dd, J = 3, 2, 1H), 6.12 (dd, J = 3, 1, 1H), 3.91–3.88 (m, 1H), 2.83 (dd, J = 15, 4, 1H), 2.72 (dd, J = 15, 8, 1H), 1.76 (d, J = 4, 1H), 1.52–1.46 (m, 2H), 1.35–1.24 (m, 16H). 0.89 (t, J = 7, 3H); ¹³C NMR (100 MHz) δ 152.9, 141.6, 110.3, 107.0, 70.5, 36.7, 36.1, 31.9, 29.6, 29.3, 25.6, 22.7, 14.1; MS m/z (CI) 270 (M+NH₄⁺, 6), 268 (24), 253 (58), 235 (33), 233 (22), 170 (13), 98 (13), 82 (14); HRMS calcd for C₁₆H₂₉O₂ (M+H⁺) 253.2168, found 253.2176.

1-(Thiophen-2-yl)dodecan-2-ol 16e

Following general procedure D, the addition of 1,2-epoxydodecane 13 (100 mg, 0.54 mmol) to 2-thienyllithium (1.0 M in THF; 1.62 mL, 1.62 mmol) in hexane (8 mL) gave after workup and column chromatography (15% Et₂O in petrol) alcohol 16e (131 mg, 91%) as a white solid; R₇ 0.15 (10% Et₂O in petrol); mp 46–47 °C; IR (CDCl₃)/cm⁻¹ 13368s, 2923s, 2853s, 1640w, 1534w, 1466s, 1439s, 1078m, 1045m, 1021m; ¹H NMR (400 MHz) δ 7.18 (d, J = 5.5, 1H), 6.97 (dd, J = 5.5, 3.5, 1H), 6.88 (d, J = 3.5, 1H), 3.85–3.79 (m, 1H), 3.04 (dd, J = 15, 4, 1H), 2.89 (dd, J = 15, 8, 1H), 1.69 (s, 1H), 1.57–1.44 (m, 2H), 1.35–1.22 (m, 16H), 0.89 (t, J = 7, 3H); ¹³C NMR (100 MHz) δ 140.6, 127.0, 126.0, 124.1, 72.4, 37.9, 36.5, 31.9, 29.6, 29.3, 25.7, 22.7, 14.1; MS m/z (CI) 286 (M+NH₄⁺, 100), 269 (11), 98 (11); HRMS calcd for C₁₆H₃₂NOS (M+NH₄⁺) 286.2199, found 286.2201.

1-Tetradecen-4-ol 16f

Following general procedure D, the addition of 1,2-epoxydodecane 13 (100 mg, 0.54 mmol) to vinyllithium (1.0 M in THF; 1.62 mL, 1.62 mmol) in hexane (8 mL) gave after workup and column chromatography (15% Et₂O in petrol) alcohol 16f (83 mg, 72%) as a white solid; R₇ 0.01 (15% Et₂O in petrol); mp 46–47 °C; IR (CHCl₃)/cm⁻¹ 3357m, 2930s, 2855s, 1597w, 1507w, 1466w, 1147w, 1081w, 1099w; ¹H NMR (400 MHz) δ 7.35 (dd, J = 2, 1, 1H), 6.32 (dd, J = 3, 2, 1H), 6.12 (dd, J = 3, 1, 1H), 3.91–3.88 (m, 1H), 2.83 (dd, J = 15, 4, 1H), 2.72 (dd, J = 15, 8, 1H), 1.76 (d, J = 4, 1H), 1.52–1.46 (m, 2H), 1.35–1.24 (m, 16H). 0.89 (t, J = 7, 3H); ¹³C NMR (100 MHz) δ 152.9, 141.6, 110.3, 107.0, 70.5, 36.7, 36.1, 31.9, 29.6, 29.3, 25.6, 22.7, 14.1; MS m/z (CI) 270 (M+NH₄⁺, 100), 268 (24), 253 (58), 235 (33), 233 (22), 170 (13), 98 (13), 82 (14); HRMS calcd for C₁₆H₂₉O₂ (M+H⁺) 253.2168, found 253.2176.

0.20 (15% Et₂O in petrol); mp 45–46 °C; IR (CHCl₃)/cm⁻¹ 3341 br, 2925 s, 2854 s, 1641 w, 1466 w, 994 w, 912 w; 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, 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.

(E)-2-Pentadecen-5-ol 16h

Following general procedure D, the addition of 1,2-epoxydodecane (100 mg, 0.54 mmol) to (E)-propenyllithium (2.0 M in Et₂O; 0.81 mL, 1.63 mmol) in hexane (8 mL) gave after workup and column chromatography (15% Et₂O in petrol) alcohol 16h (122 mg, 99%, E:Z = 97:3 by GCMS analysis, tᵣE-16h 12.77 min, tᵣZ-16h 12.95 min, initial temp. 100 °C, max. temp. 280 °C, rate 8 °C/min) as a colourless oil; Rᵣ 0.16 (10% Et₂O in petrol); IR (neat)/cm⁻¹ 3351 br, 2925 m, 2855 m, 1657 w, 1466 w, 967 w; ¹H NMR (400 MHz) δ 5.56 (dq, J = 15, 6, 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 (81), 227 (35), 226 (37), 225 (63), 207 (20), 169 (41); HRMS calcd for C₁₅H₃₄NO (M+NH₄⁺) 244.2640, found 244.2644.

(Z)-2-Pentadecen-5-ol 16h

Following general procedure D, the addition of 1,2-epoxydodecane (100 mg, 0.54 mmol) to (Z)-propenyllithium (1.4 M in Et₂O; 1.16 mL, 1.63 mmol) in hexane (8 mL) gave after column chromatography (15% Et₂O in petrol) alcohol 16h (111 mg, 90%, Z:E = 99:1 by GCMS analysis, tᵣE-16h 12.77 min, tᵣZ-16h 12.95 min, initial temp. 100 °C, max. temp. 280 °C, rate 8 °C/min) as a colourless oil; Rᵣ 0.16 (10% Et₂O in petrol); IR (neat)/cm⁻¹ 3349 br, 3017 m, 2923 m, 2854 s, 1657 w, 1467 s, 1077 m, 1027 m; ¹H NMR (400 MHz) δ 5.66 (dq, J = 11, 7, 1H), 5.49–5.40 (m, 1H), 3.64 (quint, J = 6, 1H), 2.23 (t, J = 6, 2H), 1.65 (d, J = 7, 3H), 1.57 (br, 1H), 1.52–1.20 (m, 18H), 0.89 (t, J = 7, 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.
Following general procedure D, the addition of 1,2-epoxydodecane 13 (100 mg, 0.54 mmol) to (trimethylsilylmethyl)lithium (1.0 M in pentane, 1.63 mL, 1.63 mmol) in THF (8 mL) gave after column chromatography (10% Et₂O in petrol) alcohol 16l (123 mg, 84%) as a colorless oil; R<sub>f</sub> 0.20 (10% Et₂O in petrol); IR (neat)/cm<sup>−1</sup> 3346br, 2925s, 2854s, 1466m, 1378m, 1248s, 1179m, 1127m, 1076m, 1007m; <sup>1</sup>H NMR (400 MHz) δ 3.50−3.44 (m, 1H), 1.74 (br, 1H), 1.48−1.20 (m, 20H), 0.86 (t, <i>J</i> = 7, 3H), 0.59 (ddd, <i>J</i> = 14, 14, 4.5, 1H) 0.40 (ddd, <i>J</i> = 14, 13, 5, 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 <i>m/z</i> (Cl) 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.

When alcohol 16n was observed it was identified as follows:

Hexadecan-6-ol<sup>19</sup> 16n

White solid; mp 41−42 °C; R<sub>f</sub> 0.13 (10% Et₂O in petrol); IR (CHCl₃)/cm<sup>−1</sup> 3340br, 2920w, 2859w, 1467w; <sup>1</sup>H NMR (400 MHz) δ 3.63−3.56 (m, 1H), 1.51−1.19 (m, 27H), 0.93−0.83 (m,

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When alcohol 160 was observed it was identified as follows:

Tridecan-3-ol\(^{20}\) 160

\[
\text{OH}
\]

Colorless oil; \(R_f\) 0.15 (10\% Et\(_2\)O in petrol); IR (neat)/cm\(^{-1}\) 3347br, 2925s, 2855s, 1464w, 967w;

\(^1\)H NMR (400 MHz) \(\delta\) 3.56−3.50 (m, 1H), 1.58−1.20 (m, 21H), 0.95 (t, \(J = 7.5\), 3H), 0.89 (t, \(J = 7\), 3H); \(^{13}\)C NMR (100 MHz) \(\delta\) 73.3, 36.9, 31.9, 30.1, 29.7, 29.6, 25.7, 22.6, 18.3, 14.1, 9.9; MS \(m/z\) (Cl) 218 (M+H\(^+\), 34), 216 (100), 152 (30), 90 (38), 60 (88); HRMS calcd for C\(_{13}\)H\(_{32}\)NO (M+H\(^+\)) 218.2478, found 218.2479.

\((3E,5Z)-3,5\text{-}\text{tert-Butyldodecadienyl(oxydimethyl)silane 19}\)

Following general procedure B, the addition of \textit{tert}-butyldimethyl(2-oxiranylethoxy)silane\(^{21}\) 17 (241 mg, 1.19 mmol) to a solution of LTMP [prepared by the addition of \textit{n}-BuLi (1.6 M in hexanes; 1.49 mL, 2.38 mmol) to TMP (336 mg, 2.38 mmol) in hexane (11 mL)] and (\(Z\))-1-octenyllithium [prepared by the addition of \textit{t}-BuLi (1.5 M in pentane; 2.06 mL, 3.09 mmol) to (\(Z\))-1-iodo-1-octene\(^{14}\) (368 mg, 1.55 mmol) in Et\(_2\)O (2 mL)] gave after workup and column chromatography (100\% petrol→3\% Et\(_2\)O in petrol) \textit{diene 19} (247 mg, 70\%, \(E,Z,E,E\):other isomer = 92:5:3 by GCMS analysis; \(t_R\) other isomer 14.73 min, \(t_R\ E,Z-19\) 15.58 min, \(t_R\ E,E-19\) 15.93 min, initial temp. 100 \(^\circ\)C, max. temp. 280 \(^\circ\)C, rate 8 \(^\circ\)C/min) as a colorless oil; \(R_f\) 0.18 (100\% petrol); IR (neat)/cm\(^{-1}\) 2928s, 2857s, 1471w, 1256m, 1103s, 836s; \(^1\)H NMR (400 MHz) \(\delta\) 6.37 (ddd, \(J = 15\), 11, 1.5, 1H), 5.95 (dd, \(J = 11\), 11, 1H), 5.65 (dt, \(J = 15\), 7, 1H), 5.34 (dt, \(J = 11\), 7, 1H), 3.66 (t, \(J = 7\), 2H), 2.33 (t, \(J = 7\), 2H), 2.16 (t, \(J = 7\), 2H), 1.42−1.25 (m, 8H), 0.91−0.88 (m, 12H), 0.06 (s, 6H); \(^{13}\)C NMR (100 MHz) \(\delta\) 130.8, 130.3, 128.4, 127.6, 63.0, 36.5, 31.8, 29.7, 29.0, 27.7, 25.9, 22.6, 18.3, 14.1, −5.2; MS \(m/z\) (CI) 297 (M+H\(^+\), 16), 256 (15), 239 (56), 165 (100) 74 (18); HRMS calcd for C\(_{18}\)H\(_{37}\)OSi (M+H\(^+\)) 297.2614, found 297.2613.

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(3E,5Z)-3,5-dodecadienyl acetate\textsuperscript{22} 20

Diene \textit{19} (200 mg, 0.67 mmol) was added to a solution of TBAF (1.0 M in THF; 0.67 mL, 0.67 mmol) and stirred for 1 h. After the addition of Et\textsubscript{2}O (3 mL) and sat. brine solution (3 mL), the layers were separated. The aqueous layer was extracted with Et\textsubscript{2}O (2 x 3 mL), the combined organic layers were dried (MgSO\textsubscript{4}) and solvent evaporated \textit{in vacuo} to give the crude \textit{alcohol}. To this was added Ac\textsubscript{2}O (0.11 mL, 1.1 mmol), pyridine (0.16 mL, 2.01 mmol) and DMAP (15 mg, 0.12 mmol) and the reaction was left stirring for 3 h at rt. After addition of 1 M HCl solution (4 mL), the layers were separated. The aqueous layer was extracted with Et\textsubscript{2}O (5 mL), the combined organic layers were dried (MgSO\textsubscript{4}) and solvent evaporated \textit{in vacuo}. The residue was purified by column chromatography (3% Et\textsubscript{2}O in petrol) to give \textit{diene 20} (120 mg, 80%, \textit{E,Z:E:other isomer} = 92:5:3 by GCMS analysis; \textit{t\textsubscript{R}} \textit{other isomer} 20 10.02 min, \textit{t\textsubscript{R}} \textit{E,Z-20} 10.48 min, \textit{t\textsubscript{R}} \textit{E,E-20} 10.68 min, initial temp. 100 °C, max. temp. 280 °C, rate 8 °C/min) as a colorless oil; \textit{R\textsubscript{f}} 0.15 (3% Et\textsubscript{2}O in petrol). Further purification on AgNO\textsubscript{3} impregnated silica\textsuperscript{23} (3% Et\textsubscript{2}O in petrol) gave \textit{diene 20} (96 mg, 64%, \textit{E,Z:E = 99:1} by GCMS analysis); IR (neat)/cm\textsuperscript{-1} 2927s, 2856m, 1744s, 1458m, 1364m, 1237s, 1035m; \textit{1H NMR} (400 MHz) \delta 6.39 (ddd, \textit{J} = 15, 11, 1.5, 1H), 5.95 (dd, \textit{J} = 11, 11, 1H), 5.60 (dt, \textit{J} = 15, 7, 1H), 5.37 (dt, \textit{J} = 11, 7, 1H), 4.12 (t, \textit{J} = 7, 2H), 2.43 (q, \textit{J} = 7, 2H), 2.16 (q, \textit{J} = 7, 2H), 2.06 (s, 3H) 1.42–1.22 (m, 8H), 0.89 (t, \textit{J} = 7, 3H); \textit{13C NMR} (100 MHz) \delta 171.1, 131.6, 128.6, 128.2, 128.0, 63.8, 32.1, 31.7, 29.6, 28.9, 27.7, 22.6, 21.0, 14.1; MS \textit{m/z} (Cl) 242 (M+NH\textsubscript{4}\textsuperscript{+}, 100), 165 (92), 164 (85), 93 (29), 80 (94); HRMS calcd for C\textsubscript{14}H\textsubscript{28}NO\textsubscript{2} (M+NH\textsubscript{4}\textsuperscript{+}) 242.2120, found 242.2122.

\textit{(E)-(4-Methyl-2-pentenyl)trimethylsilane}\textsuperscript{24} 21 (from Table 4, entry 6 conditions)

Following general procedure A, the addition of isopropyloxirane (123 mg, 1.43 mmol) to a solution of LTMP [prepared by the addition of \textit{n}-BuLi (1.6 M in hexanes; 1.79 mL, 2.86 mmol) to TMP (404 mg, 2.86 mmol) in THF (21 mL)] and (trimethylsilylmethyl)lithium (1.0 M in pentane; 1.86 mL, 1.86 mmol) gave after workup and column chromatography (100% petrol) \textit{allylsilane 21} (159 mg, 71%, \textit{E:Z = 98:2}, by GCMS analysis, \textit{t\textsubscript{R}} \textit{E-21} 3.15 min, \textit{t\textsubscript{R}} \textit{Z-21} 3.23 min, initial temp. 60 °C, max. temp. 240 °C, rate 20 °C/min) as a colorless oil; \textit{R\textsubscript{f}} 0.66 (100% petrol); IR (neat)/cm\textsuperscript{-1} 2957s, 2926s, 2871m, 1466w, 1248s, 859s, 840s; \textit{1H NMR} (400 MHz) \delta

5.39–5.30 (m, 1H), 5.23 (dd, J = 15, 7, 1H), 2.24 (d, sept, J = 7, 7, 1H), 1.39 (d, J = 7.5, 2H), 0.97 (d, J = 7, 6H), 0.00 (s, 9H); 13C NMR (100 MHz) δ 136.4, 122.8, 31.3, 23.0, 22.4, −2.1; MS m/z (Cl) 157 (M+H+, 12), 91 (12), 90 (100); HRMS calcd for C9H22Si (M+H+) 157.1413, found 157.1416.

When Z-isomer 21 was formed in appreciable amounts along with the E-isomer (Table 4, entry 5) it was identified from the vinylic/allylic protons and allylic carbons: 1H NMR (400 MHz) δ 5.10 (dd, J = 10, 9.5, 1H), 2.53 (d, sept, J = 7, 7, 1H), 1.48 (d, J = 8, 2H); 13C NMR (100 MHz) δ 18.4.

**[(E)-(4,4-Dimethyl-2-pentenyl)trimethylsilane]24 22 (from Table 4, entry 9 conditions)**

Following general procedure A, the addition of isobutyloxirane (123 mg, 1.23 mmol) to a solution of LTMP [prepared by the addition of n-BuLi (1.6 M in hexanes; 1.16 mL, 1.85 mmol) to TMP (261 mg, 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 (100% petrol) allylsilane 22 (132 mg, 63%, E-only by GCMS analysis, tR E-22 4.33 min, initial temp. 50 °C, max. temp. 240 °C, rate 20 °C/min) as a colorless oil; Rf 0.63 (100% petrol); IR (neat)/cm⁻¹ 2925s, 2854s, 2361w, 1464w, 1378m, 1248w, 1156m, 969m, 851m; 1H NMR (400 MHz) δ 5.10 (dd, J = 10, 9.5, 1H), 2.53 (d, sept, J = 7, 7, 1H), 1.48 (d, J = 8, 2H); 13C NMR (100 MHz) δ 140.2, 120.4, 32.9, 30.0, 22.4, −2.1; MS m/z (Cl) 171 (M+H+, 27), 155 (9), 148 (10), 91 (12), 90 (100), 73 (23); HRMS calcd for C10H23Si (M+H+) 171.1569, found 171.1561.

When Z-isomer 22 was formed in appreciable amounts along with the E-isomer (Table 4, entry 8) it was identified as follows: 1H NMR (400 MHz) δ 5.25–5.15 (m, 2H), 1.61 (dd, J = 5, 2 Hz, 2H), 1.11 (s, 9H), 0.05 (s, 9H); 13C NMR (100 MHz) δ 140.2, 120.4, 32.9, 30.0, 22.4, −2.1; MS m/z (Cl) 171 (M+H+, 27), 155 (9), 148 (10), 91 (12), 90 (100), 73 (23); HRMS calcd for C10H23Si (M+H+) 171.1569, found 171.1561.

When alcohol 23 was observed it was identified as follows:

**4-Methyl-(1-trimethylsilanyl)pentan-3-ol 23**

Colorless oil; Rf 0.13 (10% Et₂O in petrol); IR (neat)/cm⁻¹ 3368br, 2958s, 2875s, 1470m, 1248s, 864s, 836s; 1H NMR (400 MHz) δ 3.27 (dt, J = 8, 5, 1H), 1.75–1.65 (m, 1H), 1.54–1.30 (m, 3H), 0.93 (d, J = 7, 3H), 0.91 (d, J = 7, 3H), 0.65 (ddt, J = 13, 4.5, 1.5, 1H), 0.41 (ddt, J = 12.5, 5, 1.5, 1H), 0.00 (s, 9H); 13C NMR (100 MHz) δ 79.0, 32.7, 28.2, 19.1, 17.0, 12.2, −1.8; MS m/z
(CI) 192.2 (M+NH\textsubscript{4}\textsuperscript{+}, 13), 157.1 (30), 90.1 (100), 91.1 (28); HRMS calcd for C\textsubscript{9}H\textsubscript{26}NOSi (M+NH\textsubscript{4}\textsuperscript{+}) 192.1778, found 192.1778.

When alcohol 24 was observed it was identified as follows:

4,4-Dimethyl-(1-trimethylsilanyl)pentan-3-ol\textsuperscript{25} 24

\[
\begin{align*}
\text{SiMe}_3 &\text{OH} \\
&
\end{align*}
\]

Colorless oil; \(R_f\) 0.26 (15\% Et\textsubscript{2}O in petrol); IR (neat)/cm\textsuperscript{-1} 3368br, 2958s, 2875s, 1470m, 1250s; \(^1\)H NMR (400 MHz) \(\delta\) 3.09 (dd, \(J = 10.5, 2, 1\)H), 1.55 (ddddd, \(J = 14, 13, 10, 4, 1\)H), 1.46 (br, 1H), 1.19 (ddddd, \(J = 14, 12, 4.8, 1.8, 1\)H), 0.89 (s, 9H), 0.80 (ddddd, \(J = 14, 13, 4.5, 1\)H), 0.36 (ddddd, \(J = 14, 12, 5, 1\)H), 0.00 (s, 9H); \(^13\)C NMR (100 MHz) \(\delta\) 82.6, 35.0, 25.8, 25.4, 13.6, 1.7; MS \(m/z\) (CI) 206 (M+NH\textsubscript{4}\textsuperscript{+}, 50); 90 (100); HRMS calcd for C\textsubscript{10}H\textsubscript{28}NOSi (M+NH\textsubscript{4}\textsuperscript{+}) 206.1940, found 206.1941.

When aldehyde 25 was observed it was identified as follows:

3-Methylbutanal\textsuperscript{26} 25

\[
\begin{align*}
\text{O} &
\end{align*}
\]

Colorless oil; \(R_f\) 0.40 (5\% Et\textsubscript{2}O in petrol); \(^1\)H NMR (400 MHz) \(\delta\) 9.70 (t, \(J = 1.5, 1\)H), 2.28 (dd, \(J = 7, 1.5, 2\)H), 2.21 (d, sept, \(J = 7, 6.5, 1\)H), 0.97 (d, \(J = 6.5, 6\)H); \(^13\)C NMR (100 MHz) \(\delta\) 205.3, 52.7, 24.8, 22.5, 22.1.

When aldehyde 26 was observed it was identified as follows:

3,3-Dimethylbutanal\textsuperscript{27} 26

\[
\begin{align*}
\text{O} &
\end{align*}
\]

Colorless oil; \(R_f\) 0.50 (10\% Et\textsubscript{2}O in petrol); IR (neat)/cm\textsuperscript{-1} 2960s, 2905s, 1723w, 1455w; \(^1\)H NMR (400 MHz) \(\delta\) 9.90 (t, \(J = 1.5, 1\)H), 2.22 (d, \(J = 1.5, 2\)H), 1.06 (s, 9H); \(^13\)C NMR (100 MHz) \(\delta\) 205.3, 56.2, 31.4, 30.0; MS \(m/z\) (CI) 118 (M+NH\textsubscript{4}\textsuperscript{+}, 100), HRMS calcd for C\textsubscript{6}H\textsubscript{16}NO (M+NH\textsubscript{4}\textsuperscript{+}) 118.1232, found 118.1233.

\footnotesize{(26) Spectra matched commercially available (Aldrich, product no. 59820) material.}
When allylic alcohol 27 was observed it was identified as follows:

1-Tridecen-3-ol$^{28}$ 27

![1-Tridecen-3-ol](image)

Colorless oil; $R_f$ 0.13 (10% Et$_2$O in petrol); IR (neat)/cm$^{-1}$ 3355s, 1645m, 1465w, 990s; $^1$H NMR (400 MHz) $\delta$ 5.92–5.83 (m, 1H), 5.16 (dq, $J = 17$, 1.5, 1H), 5.11 (dq, $J = 10.5$, 1.5, 1H), 4.10 (q, $J = 6$, 1H), 1.60 (br, 1H), 1.55–1.21 (m, 18 H), 0.88 (t, $J = 6.5$, 3H); $^{13}$C NMR (100 MHz) $\delta$ 141.3, 114.5, 73.3, 37.0, 29.6, 29.5, 29.3, 25.3, 22.7, 14.1; MS $m/z$ (CI) 216 (M+NH$_4^+$, 61), 198 (100), 180 (84), 81 (42); HRMS calcd for C$_{13}$H$_{30}$NO (M+NH$_4^+$) 216.2327, found 216.2323.

When allylic alcohol 28 was observed it was identified as follows:

4-Methyl-1-penten-3-ol$^{29}$ 28

![4-Methyl-1-penten-3-ol](image)

Colorless oil; $R_f$ 0.23 (10% Et$_2$O in petrol); IR (neat)/cm$^{-1}$ 3361br, 3052s, 1717w; $^1$H NMR (400 MHz) $\delta$ 5.91 (ddd, $J = 6.5$, 10.5, 17, 1H), 5.30 (ddd, $J = 17$, 1.5, 1, 1H), 5.13 (ddd, $J = 10.5$, 1.5, 1, 1H), 4.05 (ddd, $J = 7$, 6.5, 1, 1, 1H), 2.6 (br, 1H), 1.76 (d, sept, $J = 7$, 6.5, 1H), 1.24 (d, $J = 6.5$, 3H), 0.96 (d, $J = 6.5$, 3H); $^{13}$C NMR (100 MHz) $\delta$ 139.3, 115.5, 78.1, 33.4, 17.7, 15.1; MS $m/z$ (CI) 118 (M+NH$_4^+$, 100), HRMS calcd for C$_6$H$_{16}$NO (M+NH$_4^+$) 118.1232, found 118.1234.

When allylic alcohol 29 was observed it was identified as follows:

4,4-Dimethyl-1-penten-3-ol$^{30}$ 29

![4,4-Dimethyl-1-penten-3-ol](image)

Colorless oil; $R_f$ 0.30 (10% Et$_2$O in petrol); IR (neat)/cm$^{-1}$ 3404br, 2956s, 1365s, 1073m; $^1$H NMR (400 MHz) $\delta$ 5.91 (ddd, $J = 16.5$, 9.5, 6.5, 1H), 5.18 (ddd, $J = 16.5$, 1.5, 1, 1H), 5.12 (ddd, $J = 9.5$, 1.5, 1, 1H), 3.70 (ddd, $J = 6.5$, 1, 1, 1H), 2.20 (br, 1H), 0.91 (s, 9H); $^{13}$C NMR (100 MHz) $\delta$ 139.3, 115.5, 78.1, 25.4, 13.6; MS $m/z$ (CI) 132 (M+NH$_4^+$, 100), HRMS calcd for C$_7$H$_{18}$NO (M+NH$_4^+$) 132.1388, found 132.1395.

(E)-(1-Pentyl-2,10-undecadien-1-yl)trimethylsilane\textsuperscript{6} 30

\[
\text{SiMe}_3
\]

Following general procedure C, using 1,2-epoxy-9-decene (83 mg, 0.54 mmol) gave after workup and reverse phase column chromatography\textsuperscript{12} (C\textsubscript{18} silica, MeCN) allylsilane 30 (120 mg, 75%, E-only by GCMS analysis, \(E\)-30 11.57 min, initial temp. 80 °C, max. temp. 280 °C, rate 15 °C/min) as a colorless oil; \(R_f \) 0.13 (C\textsubscript{18} silica, MeCN); IR (neat)/cm\textsuperscript{−1} 3078s, 2926s, 2854s, 1642w, 1464w, 1247s, 836s; \(^1\)H NMR (400 MHz) \(\delta \) 5.87–5.77 (m, 1H), 5.24–5.12 (m, 2H), 5.03–4.92 (m, 2H), 2.05 (dt, \(J = 7, 7, 2H\)), 1.99 (dt, \(J = 6.5, 6.5, 2H\)), 1.44–1.14 (m, 17H), 0.89 (t, \(J = 7, 3H\)), −0.05 (s, 9H); \(^{13}\)C NMR (100 MHz) \(\delta \) 139.3, 131.5, 128.1, 114.1, 33.8, 32.9, 32.8, 31.8, 30.0, 29.0, 28.9, 28.8, 28.7, 14.1, −3.2; MS \(m/z\) (CI) 295 (M+H\textsuperscript{+}, 40), 220 (29), 90 (100); HRMS calcd for C\textsubscript{19}H\textsubscript{39}Si (M+H\textsuperscript{+}) 295.2821, found 295.2822.

\[
\text{Ph}
\]

(E)-(1-pentyl-5-phenyl-2-penten-1-yl)trimethylsilane\textsuperscript{6} 31

Following general procedure C, using 1,2-epoxy-4-phenylbutane\textsuperscript{31} (80 mg, 0.54 mmol) gave after workup and column chromatography (100% petrol) allylsilane 31 (109 mg, 70%, \(E:Z = 98:2\) by GCMS analysis, \(t_R Z\)-31 12.33 min, \(t_R E\)-31 12.43 min, initial temp. 80 °C, max. temp. 280 °C, rate 15 °C/min) as a colorless oil; \(R_f \) 0.48 (100% petrol); IR (neat)/cm\textsuperscript{−1} 3064w, 3027m, 2925w, 1642w, 1464w, 1247s, 836s; \(^1\)H NMR (400 MHz) \(\delta \) 7.37–7.28 (m, 2H), 7.24–7.18 (m, 3H), 5.31–5.20 (m, 2H), 2.70 (t, \(J = 7.5, 2H\)), 2.40 (dt, \(J = 7.5, 7.5, 2H\)), 1.47–1.13 (m, 9H), 0.92 (t, \(J = 7, 3H\)), −0.04 (s, 9H); \(^{13}\)C NMR (100 MHz) \(\delta \) 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\textsuperscript{+}, 100) 215 (19), 214 (91), 197 (29), 123 (23), 90 (40); HRMS calcd for C\textsubscript{19}H\textsubscript{33}Si (M+H\textsuperscript{+}) 289.2352, found 289.2344.

(E)-1-(t-Butyldimethylsilyloxy)-6-(trimethylsilyl)-4-undecene\textsuperscript{6} 32

Following general procedure C, using 1-t-Butyldimethylsilyoxy-4,5-epoxypentane\textsuperscript{32} (117 mg, 0.54 mmol) gave after workup and column chromatography (100% petrol) allylsilane 32 (126 mg, 65%, \(E\)-only by GCMS analysis, \(E\)-32 10.17 min, initial temp. 80 °C, max. temp. 280 °C, rate 15 °C/min) as a colorless oil; \(R_f \) 0.20 (100% petrol); IR (neat)/cm\textsuperscript{−1} 2929m, 2857m, 1471w, 1388w, 1248m, 1105m, 969w, 836m; \(^1\)H NMR (400 MHz) \(\delta \) 5.25–5.14 (m, 2H), 3.62 (t, \(J = 7,$
2H), 2.05 (dt, \( J = 7, 7, 2H \)), 1.58 (dd, \( J = 7, 7, 2H \)), 1.47−1.12 (m, 9H), 0.91 (s, 9H), 0.88 (t, \( J = 7, 3H \)), 0.06 (s, 6H), −0.05 (s, 9H); 13C NMR (100 MHz) \( \delta \) 131.9, 127.5, 62.8, 33.2, 33.0, 31.8, 29.1, 29.0, 28.8, 26.0, 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 \( \text{C}_{21}\text{H}_{45}\text{Si} \) (M+H⁺) 357.3009, found 357.3011.

\((E)-(3\text{-Cyclohexyl-1-pentyl-allyl})\text{trimethylsilane 33}\)

\[\text{\includegraphics[width=1\textwidth]{structure33}}\]

Following general procedure C, using 2-cyclohexyloxirane (69 mg, 0.54 mmol) gave after workup and reverse phase column chromatography\(^{(33)}\) (C\(_{18}\) silica, 10% CH\(_2\)Cl\(_2\) in MeCN) \textbf{allylsilane 33} (115 mg, 80%, \( E \)-only by GCMS analysis, \( E \)-33 12.63 min, initial temp. 80 °C, max. temp. 280 °C, rate 10 °C/min) as colorless oil; \( R_f \) 0.22 (C\(_{18}\) silica, 10% CH\(_2\)Cl\(_2\) in MeCN); IR (neat)/cm\(^{-1}\) 2920s, 2852s, 1449s, 1247s, 968s, 836; \(^1\)H NMR (400 MHz) \( \delta \) 5.20−5.09 (m, 2H), 1.95−1.88 (m, 1H), 1.72−1.62 (m, 6H), 1.42−1.01 (m, 13H), 0.88 (t, \( J = 7, 3H \)), −0.05 (s, 9H); 13C NMR (100 MHz) \( \delta \) 134.4, 128.8, 41.1, 33.8, 33.7, 32.8, 31.7, 28.9, 28.8, 26.3, 26.2, 22.6, 14.1, −3.2; MS \( m/z \) (CI) 267 (M+H⁺, 45), 193 (23), 192 (100), 90 (61), 73 (69); HRMS calcd for \( \text{C}_{17}\text{H}_{35}\text{Si} \) (M+H⁺) 267.2508, found 267.2507.

\((E)-1-(3\text{-Cyclohexyl-1-pentyl-allyl})\text{dimethylphenylsilane 34}\)

\[\text{\includegraphics[width=1\textwidth]{structure34}}\]

Following general procedure C, using 2-cyclohexyloxirane\(^{(33)}\) (69 mg, 0.54 mmol) and dimethylphenylvinylsilane (136 mg, 0.84 mmol) instead of vinyltrimethylsilane gave after workup and reverse phase column chromatography\(^{(33)}\) (C\(_{18}\) silica, 100% MeCN) \textbf{allylsilane 34} (128 mg, 72%, \( E \)-only by GCMS analysis, \( E \)-34 14.45 min, initial temp. 80 °C, max. temp. 280 °C, rate 15 °C/min) as colorless oil; \( R_f \) 0.39 (C\(_{18}\) silica, 100% MeCN); IR (neat)/cm\(^{-1}\) 3070m, 2923s, 2852s, 1449m, 1428m, 1247m, 1113m, 969m; \(^1\)H NMR (400 MHz) \( \delta \) 7.51−7.48 (m, 2H), 7.36−7.35 (m, 3H), 5.19−5.08 (m, 2H), 1.95−1.87 (m, 1H), 1.72−1.60 (m, 6H), 1.41−1.03 (m, 13H), 0.85 (t, \( J = 7, 3H \)), 0.26 (s, 3H), 0.24 (3H); 13C NMR (100 MHz) \( \delta \) 138.4, 135.1, 134.1, 128.7, 128.2, 127.5, 41.1, 33.7, 33.6, 32.3, 31.6, 28.8, 28.8, 26.3, 26.1, 22.6, 14.1, −4.3, −5.1;

MS m/z (Cl) 329 (M+H\(^+\), 6), 193 (10), 192 (38), 152 (100), 135 (68); HRMS calcd for C\(_{22}\)H\(_{37}\)Si (M+H\(^+\)) 329.2665, found 329.2667.

\((E)\)-Dimethyl(1-pentyl-2-pentenyl)phenylsilane \(35\)

Following general procedure C, using 1,2-epoxybutane (39 mg, 0.54 mmol) and dimethylphenylvinylsilane (136 mg, 0.84 mmol) instead of vinyltrimethylsilane gave after workup, and reverse phase column chromatography\(^{12}\) (C\(_{18}\) silica, 100% MeCN) allylsilane \(35\) (107 mg, 72%, \(E:Z = 95:5\), by GCMS analysis, \(t_r E-35\) 11.28 min, \(t_r Z-35\) 11.43 min initial temp. 80 °C, max. temp. 280 °C, rate 15 °C/min) as a colorless oil; \(R_f\) 0.35 (C\(_{18}\) silica, 100% MeCN); IR (neat)/cm\(^{-1}\) 3055, 2958, 2924, 2852, 1460, 1428, 1248, 1113, 969; \(\nu\)H NMR (400 MHz) \(\delta\) 7.53–7.48 (m, 2H), 7.36–7.30 (m, 3H), 5.29–5.22 (m, 1H), 5.18–5.11 (m, 1H), 2.00 (quint, \(J = 7.5\), 2H), 1.65–1.58 (m, 1H), 1.44–1.06 (m, 8H), 0.95 (t, \(J = 7\), 3H), 0.85 (t, \(J = 7\), 3H), 0.26 (s, 3H), 0.25 (s, 3H); \(\nu\)C NMR (100 MHz) \(\delta\) 138.4, 134.1, 130.5, 129.9, 128.7, 127.5, 32.3, 31.6, 31.5, 28.9, 25.9, 22.6, 14.5, 14.1, −4.3, −5.1; MS m/z (Cl) 275 (M+H\(^+\), 6), 153 (15), 152 (100), 135 (59); HRMS calcd for C\(_{18}\)H\(_{31}\)Si (M+H\(^+\)) 275.2195, found 275.2188.

\((E)\)-Trimethyl(1-pentyl-2-pentenyl)silane\(^{34}\) \(36\)

Following general procedure C, using 1,2-epoxybutane (39 mg, 0.54 mmol) gave after workup, and reverse phase column chromatography\(^{12}\) (C\(_{18}\) silica, 15% Et\(_2\)O in MeCN) allylsilane \(36\) (88 mg, 77%, \(E:Z = 94:6\), by GCMS analysis, \(t_r E-36\) 6.93 min, \(t_r Z-36\) 7.17 min, initial temp. 80 °C, max. temp. 280 °C, rate 10 °C/min) as a colorless oil; \(R_f\) 0.34 (C\(_{18}\) silica, 15% Et\(_2\)O in MeCN); IR (neat)/cm\(^{-1}\) 2959s, 2925s, 2873s, 1461m, 1259m, 1247s, 968m, 836s; \(\nu\)H NMR (400 MHz) \(\delta\) 5.31–5.13 (m, 2H), 2.01 (quint, \(J = 7\), 2H), 1.45–1.21 (m, 9H), 0.97 (t, \(J = 7\), 3H), 0.89 (t, \(J = 7\), 3H), −0.05 (s, 9H); \(\nu\)C NMR (100 MHz) \(\delta\) 130.5, 129.8, 32.9, 31.8, 29.0, 28.9, 26.0, 22.6, 14.6, 14.1, −3.2; MS m/z (Cl) 213 (M+H\(^+\), 59), 138 (61), 90 (100); HRMS calcd for C\(_{13}\)H\(_{29}\)Si (M+H\(^+\)) 213.2039, found 213.2043.

**Cis-1-Deuterio-1,2-epoxydecane**

To a solution of 1-decyne (5.0 g, 36.2 mmol) in hexane (100 mL) at 0 °C was added n-BuLi (1.6 M in hexanes; 27.1 mL, 43.4 mmol) dropwise. The reaction mixture was stirred at this temperature for 5 min and then D₂O (25 mL) added and the reaction was stirred for a further 10 min at this temperature. The organic layer was separated, dried (MgSO₄) and solvent removed *in vacuo* to yield the crude deuterated alkyne (5.0 g). To a solution of deuterated alkyne (5.0 g) in pentane (20 mL) at rt was added DIBAL-H (1 M in hexanes; 43.4 mL, 43.4 mmol) dropwise. The reaction mixture was heated to 50 °C and stirred at this temperature for 3 h. After cooling to rt the reaction mixture was diluted with pentane (60 mL) then H₂O (10 mL) was added dropwise to the vigorously stirred solution which was then left for 12 h. The reaction mixture was filtered and solvent removed *in vacuo* to yield the crude Z-deuterated alkene (4.1 g). To a solution of the Z-deuterated alkene (4.1 g) in CH₂Cl₂ (100 mL) at 0 °C was added a solution of mCPBA (5.17 g, 30 mmol in 100 mL CH₂Cl₂) dropwise. The reaction was left at rt for 14 h then quenched with sat. aq. NaSO₃ solution (50 mL). The layers were separated and the organic layer was washed with sat. aq. NaHCO₃ solution (4 x 50 mL), then dried (MgSO₄) and solvent evaporated *in vacuo*. The residue was purified by column chromatography (5% Et₂O in petrol) to give Z-epoxide (3.45 g, 61%, 97% D incorporation determined by mass spectrometry) as a colorless oil; *Rf* 0.29 (10% Et₂O in petrol); IR (neat)/cm⁻¹ 2927s, 2857s, 2228w, 1467m, 1428m, 836m; ¹H NMR (400 MHz) δ 2.93–2.89 (m, 1H), 2.74 (d, *J* = 4, 1H), 1.55–1.25 (m, 14H), 0.89 (t, *J* = 7, 3H); ¹³C NMR (100 MHz) δ 52.3, 46.7, 32.4, 31.8, 29.5, 29.4, 29.2, 25.9, 22.6, 14.0; MS *m/z* (Cl) 175 (100, M+H⁺), 158(37), 157 (27); HRMS calcd for C₁₀H₂₀DO (M+H⁺), 158.1655, found 158.1658.

**Trans-1-Deuterio-1,2-epoxydecane**

To a solution of 1-decyne (5.0 g, 36.2 mmol) in pentane (10 mL) at rt was added DIBAL-H (1 M in hexanes; 43.4 mL, 43.4 mmol) dropwise. The reaction mixture was warmed to 50 °C and stirred at this temperature for 3 h. After cooling to rt the reaction mixture was diluted with pentane (50 mL) then D₂O (10 mL) was added dropwise to the vigorously stirred solution which was left stirring for 12 h. The reaction mixture was filtered and solvent removed *in vacuo* to yield the crude *trans*-deuterated alkene (4.2 g). To a solution of the *trans*-deuterated alkene (4.2

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g) in CH$_2$Cl$_2$ (100 mL) at 0 °C was added a solution of mCPBA (5.30 g, 30.7 mmol in 100 mL CH$_2$Cl$_2$) dropwise. The reaction was left at rt for 14 h then quenched with sat. aq. NaSO$_3$ solution (50 mL). The layers were separated and the organic layer was washed with sat. aq. NaHCO$_3$ solution (4 x 50 mL), then dried (MgSO$_4$) and solvent evaporated in vacuo. The residue was purified by column chromatography (5% Et$_2$O in petrol) to give the $E$-epoxide 37 (3.67 g, 65%, 96% D incorporation determined by mass spectrometry) as a colourless oil; $R_f$ 0.20 (5% Et$_2$O in petrol); IR (neat)/cm$^{-1}$ 2927s, 2856s, 2242w, 1466m, 1431m, 901m; $^1$H NMR (400 MHz) $\delta$ 2.90 (td, $J = 3$, 5.5, 1H), 2.45 (d, $J = 3$, 1H), 1.55−1.25 (m, 14), 0.89 (t, $J = 7$ Hz, 3H); $^{13}$C NMR (100 MHz) $\delta$ 52.6, 46.8, 32.4, 31.8, 29.5, 29.4, 29.2, 25.9, 22.6, 14.0; MS $m/z$ (CI) 175 (100, M+H$^+$), 158 (18), 157 (11); HRMS calcd for C$_{10}$H$_{20}$DO (M+H$^+$) 158.1655, found 158.1653.

General procedure A was used for alkene 38 formation using cis/trans-deuterated epoxides 37. The $E$/Z ratio was determined by GCMS analysis. The deuterium incorporation of each isomer was determined by analysis of the molecular ion peak in the mass spectrum and then verified by analysis of the $^1$H NMR spectrum.

Benzyldienecyclododecane$^{36}$ 42 and (Z)-cyclododecenylmethanol$^{37}$

Following general procedure A, the addition of 1-oxa-spiro[2.11]tetradecane $^{33}$ 41 (100 mg, 0.51 mmol) to a solution of LTMP [prepared by the addition of $n$-BuLi (1.6 M in hexanes; 0.48 mL, 0.77 mmol) to TMP (109 mg, 0.77 mmol) in hexane (7 mL)] and PhLi (2.0 M in $n$-Bu$_2$O; 0.38 mL, 0.77 mmol) gave after workup and column chromatography (100% petrol→10% Et$_2$O in petrol) alkene 42 (55 mg, 42%) as a colorless oil; $R_f$ 0.58 (100% petrol); IR (neat)/cm$^{-1}$ 3452br, 3027w, 2936s, 2862s, 1600w, 1494s, 1470m, 1347w; $^1$H NMR (400 MHz) $\delta$ 7.35−7.31 (m, 2H), 7.26−7.18 (m, 3H), 6.34 (s, 1H), 2.28 (t, $J = 7$, 2H), 2.23 (t, $J = 7$, 2H), 1.69−1.53 (m, 4H), 1.47−1.34 (m, 14H); $^{13}$C NMR (100 MHz) $\delta$ 142.7, 138.9, 128.6, 128.0, 125.8, 125.5, 32.6, 27.9, 25.2, 24.9, 24.4, 24.2, 24.1, 23.9, 23.0, 22.4; MS $m/z$ (CI) 257 (M+H$^+$, 25), 256 (100), 148 (28); HRMS calcd for C$_{19}$H$_{29}$ (M+H$^+$) 257.2269, found 257.2258.

Also isolated was (Z)-cyclododecenylmethanol$^{37}$ (47 mg, 47%) as a colorless oil; $R_f$ 0.10 (10% Et$_2$O in petrol); IR (neat)/cm$^{-1}$ 3320br, 2925s, 1461s, 1247m, 1013s; $^1$H NMR (400 MHz) $\delta$ 5.51 (t, $J = 8$, 1H), 4.18 (s, 2H), 2.23−2.19 (m, 2H), 2.17−2.12 (m, 2H), 1.52−1.45 (m, 4H), 1.42−1.35 (m, 14H).

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1.38−1.22 (m, 13H); $^{13}$C NMR (100 MHz) $\delta$ 136.9, 131.8, 59.2, 33.5, 27.4, 26.8, 26.6, 25.6, 24.4, 24.4, 24.4, 23.5; MS $m/z$ (CI) 197 (M+H$^+$, 3), 196 (25), 179 (100); HRMS calcld for C$_{13}$H$_{25}$O (M+H$^+$) 197.1905, found 197.1900. The geometry of the double bond was determined by a NOSEY experiment.

(2-Cyclododecylideneethyl)trimethylsilane 43

Following general procedure A, the addition of 1-oxa-spiro[2.11]tetradecane 33 (236 mg, 1.02 mmol) to a solution of LTMP [prepared by the addition of n-BuLi (1.6 M in hexanes; 0.96 mL, 1.53 mmol) to TMP (216 mg, 1.53 mmol) in hexane (8 mL)] and (trimethylsilyl)methyllithium (1.0 M in pentane; 1.53 mL, 1.53 mmol) gave after workup and column chromatography (100% petrol) alkene 43 (109 mg, 40%) as a colorless oil; $R_f$ 0.63 (100% Et$_2$O in petrol); IR (neat)/cm$^{-1}$ 3006m, 2930s, 2854s, 1658w, 1466s, 1416m, 1380w, 1241s, 1152s; $^1$H NMR (400 MHz) $\delta$ 5.23 (t, $J = 8$, 1H), 2.02 (q, $J = 7$, 4H), 1.57−1.26 (m, 20H), $-0.01$ (s, 9H); $^{13}$C NMR (100 MHz) $\delta$ 135.6, 120.3, 32.1, 27.6, 24.7, 24.6, 24.5, 24.4, 24.3, 24.0, 23.9, 23.9, 23.1, 22.3, 18.3, $-1.7$; MS $m/z$ (CI) 267 (M+H$^+$, 100), 266 (52), 192 (27), 90 (100); HRMS calcld for C$_{17}$H$_{35}$Si (M+H$^+$) 267.2508, found 267.2496.

(E)- and (Z)-1,2-Diphenyl-1-propene 38

Following general procedure A, the addition of 2-methyl-2-phenyloxirane 33 (100 mg, 0.75 mmol) to a solution of LTMP [prepared by the addition of n-BuLi (1.6 M in hexanes; 0.71 mL, 1.13 mmol) to TMP (159 mg, 1.13 mmol) in hexane (8 mL)] and PhLi (2.0 M in n-Bu$_2$O; 0.57 mL, 1.13 mmol) gave after workup and column chromatography (100% petrol) alkene 45 (60 mg, 41%, $E:Z = 84:16$ by GCMS analysis, $t_R$ Z-$45$ 8.07 min, $t_R$ E-$45$ 9.02 min, initial temp. 80 °C, max. temp. 280 °C, rate 20 °C/min) as a white solid; $R_f$ 0.25 (100% petrol); mp 80−81°C; IR (KBr)/cm$^{-1}$ 3453s, 1625w, 1443m, 1079m; $^1$H NMR (400 MHz) $\delta$ 6.72 (d, $J = 1.5$, 0.8H), 2.17 (d, $J = 1.5$, 2.4H) (E-isomer), 6.35 (d, $J = 1.5$, 0.2H), 2.10 (d, $J = 1.5$, 0.6H) (Z-isomer), 7.42−7.09 (m, 10H) (E- and Z-isomers); $^{13}$C NMR (100 MHz) $\delta$ 144.5, 144.0, 138.9, 138.4, 128.0, 137.5, 129.7, 129.2, 129.0, 128.9, 128.7, 128.5, 128.4, 128.2, 127.9, 127.7, 127.2, 127.0, 126.5, 126.0, 18.0, 17.5 (E- and Z-isomers); MS $m/z$ (CI) 195 (M+H$^+$, 88), 194 (100), 179 (40), 178 (28), 115 (15); HRMS calcld for C$_{15}$H$_{15}$ (M+H$^+$) 195.1174, found 195.1175.

(E)- and (Z)-1,2-Diphenyl-1-butene\textsuperscript{39} 47

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\begin{align*}
\text{Et} & \quad \text{Ph} \\
\text{Ph} & \quad \text{SiMe}_3
\end{align*}
\]

Following general procedure A, the addition of 2-ethyl-2-phenyloxirane\textsuperscript{33} 46 (100 mg, 0.68 mmol) to a solution of LTMP [prepared by the addition of n-BuLi (1.6 M in hexanes; 0.64 mL, 1.02 mmol) to TMP (144 mg, 1.02 mmol) in hexane (8 mL)] and PhLi (2.0 M in nBu2O; 0.51 mL, 1.02 mmol) gave after workup and column chromatography (100% petrol) alkene 47 (88 mg, 62%, E:Z = 82:18 by GCMS analysis, t\textsubscript{R} Z-47 7.04 min, t\textsubscript{R} E-47 7.62 min, initial temp. 80 °C, max. temp. 280 °C, rate 20 °C/min) as a colorless oil; R\textsubscript{f} 0.28 (100% petrol); IR (neat)/cm\textsuperscript{−1} 3023m, 2966m, 2874m, 1599m, 1495m, 1445m, 1376m; \textsuperscript{1}H NMR (400 MHz) \delta 6.74 (s, 0.8H), 2.79 (q, J = 7.5, 1.6H) (E-isomer), 6.47 (s, 0.2H), 2.55 (q, J = 7.5, 0.4H) (Z-isomer), 7.66–7.07 (m, 10H), 1.11 (t, J = 7.5, 3H) (E- and Z-isomers); \textsuperscript{13}C NMR (100 MHz) \delta 145.0, 144.5, 142.7, 141.5, 138.3, 137.6, 129.0, 128.8, 128.6, 128.5, 128.4, 128.3, 127.8, 127.6, 127.2, 126.8, 126.7, 126.6, 126.1, 125.1, 33.6, 23.3, 13.5, 12.9 (E- and Z-isomers); MS m/z (CI) 226 (M+NH\textsubscript{4}\textsuperscript{+}, 33), 209 (39), 208 (100), 193 (17), 178 (11); HRMS calcd for C\textsubscript{16}H\textsubscript{20}N (M+NH\textsubscript{4}\textsuperscript{+}) 226.1596, found 226.1601.


(E)- and (Z)-Trimethyl(3-phenyl-2-pentenyl)silane 49

Following general procedure A, the addition of 2-ethyl-2-phenyloxirane 33 (100 mg, 0.68 mmol) to a solution of LTMP [prepared by the addition of n-BuLi (1.6 M in hexanes; 0.64 mL, 1.02 mmol) to TMP (144 mg, 1.02 mmol) in hexane (8 mL)] and (trimethylsilyl)methyl lithium (1.0 M in pentane; 1.02 mL, 1.02 mmol) gave after workup and column chromatography (100% petrol) alkene 49 (65 mg, 44% E:Z = 53:47 by GCMS analysis, t<sub>R</sub> Z-49 4.12 min, t<sub>R</sub> E-49 5.03 min, initial temp. 80 °C, max. temp. 280 °C, rate 20 °C) as a colorless oil; R<sub>f</sub> 0.53 (100% petrol); IR (neat)/cm<sup>−1</sup> 3023w, 2958s, 1676w, 1599w, 1493w, 1248s, 1150m; ¹H NMR (400 MHz) δ 5.72 (t, J = 9, 0.5H), 2.51 (q, J = 8, 1H), 1.68 (d, J = 8.5, 1H), 0.99 (t, J = 7.5, 1.5H), 0.09 (s, 4.5H) (E-isomer), 5.48 (t, J = 9, 0.5H), 2.35 (q, J = 7.5, 1H), 1.39 (d, J = 8.5, 1H), 0.98 (t, J = 7.5, 1.5H), −0.03 (s, 4.5H) (Z-isomer), 7.39–7.13 (m, 5H) (E- and Z-isomers); ¹³C NMR (100 MHz) δ 143.5, 141.9, 140.9, 139.1, 128.8, 128.1, 127.9, 126.2, 126.0, 126.0, 124.4, 121.4, 32.5, 22.3, 19.8, 19.0, 13.5, 13.3, −1.6, −1.7; MS m/z (CI) 219 (M+H<sup>+</sup>, 100), 218 (61), 148 (12), 90 (80), 73 (20); HRMS calcd for C<sub>14</sub>H<sub>23</sub>Si (M+H<sup>+</sup>) 219.1569, found 219.1573. The geometry of the double bond was determined by a NOSEY experiment.

When allylic alcohol 52 was observed it was identified as follows:

2-Dodecen-1-ol<sup>41</sup> 52

Colorless oil; E:Z = 87:13 (by ¹H NMR analysis of allylic protons in the δ 4.50–4.00 region); R<sub>f</sub> 0.10 (10% Et<sub>2</sub>O in petrol); IR (neat)/cm<sup>−1</sup> 3338m, 2924s, 2843s, 1670w; ¹H NMR (400 MHz) δ 4.09 (d, J = 5.5, 1.6H) (E-isomer), 4.19 (d, J = 6, 0.4H) (Z-isomer), 5.74–5.54 (m, 2 H), 2.04 (dt, J = 7.5, 7.5, 2H), 1.44–1.22 (m, 15H), 0.89 (t, J = 7, 3H) (E- and Z-isomer); ¹³C NMR (100 MHz) δ 133.6, 133.3, 128.8, 128.3, 63.8, 58.6, 32.2, 31.9, 29.6, 29.5, 29.3, 29.2, 29.1, 22.7, 14.1 (E- and Z-isomers); MS m/z (Cl) 202 (M+NH<sub>4</sub><sup>+</sup>), 220 (44), 184 (100), 167 (34), 166 (100), 96 (33), 95 (45), 81 (60); HRMS calcd for C<sub>12</sub>H<sub>28</sub>NO (M+NH<sub>4</sub><sup>+</sup>) 202.2171, found 202.2163.

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(III) $^1$H and $^{13}$C NMR spectra of all products
(E,E)-14h
SiMe₃

14m
$\text{(E)-16h}$
S60

![Chemical structure of 16i with chemical shifts and spectra](image-url)
SiMe$_2$Ph

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