Supporting Information

Reductive Radical Annulation Strategy toward Bicyclo[3.2.1]octanes:

Synthesis of ent-Kaurane and Beyerane Diterpenoids

Junming Zhuo,†‡ Chunlin Zhu,†‡ Jinbao Wu,‡ Zijian Li,† Chao Li*,†‡,§

†Graduate School of Peking Union Medical College and Chinese Academy of Medical Sciences, Beijing, 100730, China
‡National Institute of Biological Sciences, Beijing, 102206, China
§Tsinghua Institute of Multidisciplinary Biomedical Research, Tsinghua University, Beijing, 100084, China

*Correspondence to: lichao@nibs.ac.cn

Table of Contents

Preparation of Homoallylic Tertiary Alcohols .......................................................... S4
Scheme S1. Synthesis of homoallylic tertiary alcohol 1 ............................................... S4
Scheme S2. Synthesis of homoallylic tertiary alcohols rac-S8 and (−)-S8 ....................... S4
Scheme S3. Synthesis of homoallylic tertiary alcohol S16 ........................................ S5
Scheme S4. Synthesis of homoallylic tertiary alcohol S22 ........................................ S5
Scheme S5. Synthesis of homoallylic tertiary alcohol 17 ........................................... S5

Optimization of the reductive [3+2] radical annulation ............................................. S6
General procedure for the reaction optimization ...................................................... S6
Table S1. Optimization of the reaction concentration ............................................... S6
Table S2. Optimization of the reaction temperature ................................................. S6
Table S3. Screening of ligands ................................................................................. S7
Table S4. Screening of nickel catalysts ...................................................................... S7
Table S5. Optimization of Lewis acids ...................................................................... S8
Table S6. Optimization of aminoxyl radicals ............................................................. S8
Table S7. Screening of hydrogen donors ................................................................... S9
Table S8. Screening of additives ............................................................................. S9
Table S9. Optimization using the oxalate 7 ............................................................... S10

Proposed Mechanism ............................................................................................. S11
Scheme S6. Proposed mechanisms .......................................................................... S11
Mechanistic Investigation

1. Experiments on the reduction of TEMPO
   A. Reduction of TEMPO in MeOH-d4 ....................................................... S13
   B. Reduction of TEMPO in DMF-d7 ......................................................... S14
2. Tracing the H source(s) of C12 .............................................................. S17
   Scheme S9. Deuterium-labeling studies .................................................. S17
3. Evidences for the TEMPO-mediated S1H2 reaction .................................. S18
   Scheme S10. Performing the annulation in the presence of D2O ................... S18
   Scheme S11. Performing the annulation with Zn(TEMPO)2 instead of TEMPO ...... S19
4. Evidences for the TEMPO-mediated hydrogen atom transfer (HAT) pathway .... S19
   Scheme S12. Performing the annulation in the presence of TEMPOD .............. S20
   Scheme S13. Performing the annulation in the presence of TEMPOH .......... S20
5. Preparation of TEMPOH and TEMPOD .................................................... S20
   Scheme S14. Preparation of TEMPOH ..................................................... S20
   Scheme S15. Preparation of TEMPOD ..................................................... S20
6. Preparation of PBI-d1 ........................................................................... S22
   Scheme S16. Preparation of PBI-d1 ........................................................ S22
7. Preparation of Zn(TEMPO)2 .................................................................. S23
   Scheme S17. Preparation of EtZn(TEMPO) .............................................. S23
   Scheme S18. Preparation of Zn(TEMPO)D ................................................ S24

Scheme S19. Other attempts using some known conditions for dehydroxylative
Giese-type reactions ................................................................. S25

Acyclic substrates for the [3+2] radical annulation ........................................ S26
   Table S10. Attempts of acyclic substrates ................................................. S26

Experimental Procedure and Spectroscopic Data .......................................... S27
   General procedure for the preparation of tertiary alkyl oxalates (General Procedure A) . S43
   General procedure for the reductive radical [3+2] annulation (General Procedure B) .... S48

Scheme 20. Collective syntheses of ent-kaurane- and beyerene-type diterpenoids
                                                                                   S58

Single Crystal X-ray Diffraction Data ........................................................... S88

References ............................................................................................ S119

NMR spectra ........................................................................................... S122
General Information

NMR spectra were recorded on Varian 400 MHz or Bruker DRX-600 MHz instruments at ambient temperature with CDCl₃ as the solvent unless otherwise stated. Chemical shifts are reported in parts per million relative to CDCl₃ (¹H, δ 7.26 for CDCl₃; ¹³C, δ 77.16 for CDCl₃ unless otherwise stated). Data for ¹H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and bra = broad), coupling constants (Hz), and integration. High resolution mass spectra (HRMS) were recorded at NIBS Metabolomics Center using an Agilent Tech. 6540 UHD Accurate-Mass Q-TOF LC/MS, or at Peking University Analysis Center using a Bruker Solarix XR FTMS. Optical rotations were recorded on an AUTOPOL III digital polarimeter at 589 nm and are recorded as [α]₂₀ (concentration in grams/100 mL solvent). Chiral HPLC analysis was performed on an Agilent 1220 series. Analytical thin layer chromatography was performed using 0.25 mm silica gel 60-F plates. Column chromatography was performed using 300-400 mesh silica gel. Yields refer to chromatographically and spectroscopically pure materials, unless otherwise stated. All reactions were carried out under an inert argon atmosphere with dry solvents under anhydrous conditions unless otherwise stated. All glassware was dried in a drying oven before using. Dry CH₃CN (acetonitrile), CH₂Cl₂ (dichloromethane), Et₂O (diethyl ether), THF (tetrahydrofuran), and toluene (PhMe) were obtained by passing the previously degassed solvents through activated alumina columns. The Peking University X-ray Diffraction Laboratory collected and analyzed all X-ray diffraction data.
Preparation of Homoallylic Tertiary Alcohols.

Scheme S1. Synthesis of homoallylic tertiary alcohol 1.

Scheme S2. Synthesis of homoallylic tertiary alcohols rac-S8 and (-)-S8.

A. Synthesis of rac-S8

B. Synthesis of (-)-S8
Scheme S3. Synthesis of homoallylic tertiary alcohol S16.

Scheme S4. Synthesis of homoallylic tertiary alcohol S22.

Scheme S5. Synthesis of homoallylic tertiary alcohol 17.
Optimization of the reductive [3+2] radical annulation.

General procedure for the reaction optimization.

We initially used rac-S26 and 8 as coupling partners for the reaction optimization.

General procedure: A 10 mL oven-dried reaction culture tube charged with rac-S26 (10 mg, 0.03 mmol, 1.0 equiv), Zn (600 mesh), the ligand, and TEMPO was moved into a glovebox. MgCl₂, TMSCl, benzyl acrylate, and DMA were added to the reaction tube. The tube was then capped with a rubber septum before being moved out of the glovebox. The reaction mixture was stirred vigorously for 16 hours. The resulting mixture was directly loaded onto a preparative TLC, which was then eluted with petroleum ether/EtOAc (20:1). The band containing the product was collected.

Table S1. Optimization of the reaction concentration.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Concentration (M)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>0.075</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>35</td>
</tr>
<tr>
<td>5</td>
<td>0.03</td>
<td>27</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yields were determined by <sup>1</sup>H NMR with CH₂Br₂ as the internal standard.

Table S2. Optimization of the reaction temperature.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>r.t.</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>36</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>33</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>32</td>
</tr>
<tr>
<td>6</td>
<td>55</td>
<td>32</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>30</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yields were determined by <sup>1</sup>H NMR with CH₂Br₂ as the internal standard.
### Table S3. Screening of ligands.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PBI (1.0 equiv)</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>PBI (3.0 equiv)</td>
<td>&lt;5</td>
</tr>
<tr>
<td>3</td>
<td><strong>PBI (5.0 equiv)</strong></td>
<td><strong>36</strong></td>
</tr>
<tr>
<td>4</td>
<td>PBI (6.0 equiv)</td>
<td>35</td>
</tr>
<tr>
<td>5</td>
<td>L2 (5.0 equiv)</td>
<td>34</td>
</tr>
<tr>
<td>6</td>
<td>L3 (5.0 equiv)</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>L4 (5.0 equiv)</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yields were determined by <sup>1</sup>H NMR with CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

### Table S4. Screening of nickel catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ni (0.1 equiv)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>37</td>
</tr>
<tr>
<td>2</td>
<td>NiCl&lt;sub&gt;2&lt;/sub&gt;(py)&lt;sub&gt;4&lt;/sub&gt;</td>
<td>36</td>
</tr>
<tr>
<td>3</td>
<td>Ni(COD)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>Ni(OTf)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>33</td>
</tr>
<tr>
<td>5</td>
<td>NiCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>NiI&lt;sub&gt;2&lt;/sub&gt;</td>
<td>27</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yields were determined by <sup>1</sup>H NMR with CH<sub>2</sub>Br<sub>2</sub> as the internal standard.
Table S5. Optimization of Lewis acids.

<table>
<thead>
<tr>
<th>Entry</th>
<th>MgCl₂ (x equiv)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>37</td>
</tr>
<tr>
<td>4</td>
<td>3.0</td>
<td>33</td>
</tr>
<tr>
<td>5</td>
<td>ZnCl₂ (2.5 equiv) instead of MgCl₂</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>MgBr₂ (2.5 equiv) instead of MgCl₂</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yields were determined by <sup>1</sup>H NMR with CH₃Br₂ as the internal standard.

Table S6. Optimization of aminoxyl radicals.

<table>
<thead>
<tr>
<th>Entry</th>
<th>TEMPO (x equiv)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>16</td>
</tr>
<tr>
<td>2</td>
<td>3.0</td>
<td>27</td>
</tr>
<tr>
<td>3</td>
<td>4.0</td>
<td>36</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>33</td>
</tr>
<tr>
<td>5</td>
<td>A₁ instead of TEMPO</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>A₂ instead of TEMPO</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>A₃ instead of TEMPO</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yields were determined by <sup>1</sup>H NMR with CH₃Br₂ as the internal standard.
**Table S7. Screening of hydrogen donors.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Hydrogen donor</th>
<th>Yield (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Et$_3$SiH (1.0 equiv)</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Ph$_2$SiH$_2$ (1.0 equiv)</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>$^a$Bu$_3$SnH (1.0 equiv)</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Hantzsch ester (1.0 equiv)</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>Hantzsch ester (3.0 equiv)</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>H1 (3.0 equiv)</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>H2 (3.0 equiv)</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>H3 (3.0 equiv)</td>
<td>8</td>
</tr>
<tr>
<td>9</td>
<td>H4 (3.0 equiv)</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>H5 (3.0 equiv)</td>
<td>&lt;5</td>
</tr>
<tr>
<td>11</td>
<td>H6 (3.0 equiv)</td>
<td>10</td>
</tr>
</tbody>
</table>

$^a$Yields were determined by $^1$H NMR with CH$_2$Br$_2$ as the internal standard.

**Table S8. Screening of additives.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>Yield (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CsF (1.0 equiv)</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>HMPA (1.0 equiv)</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>TMSOTf (1.0 equiv)</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>TMSCl (1.0 equiv)</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>TMSCl (2.0 equiv)</td>
<td><strong>50 (48)$^b$</strong></td>
</tr>
</tbody>
</table>

$^a$Yields were determined by $^1$H NMR with CH$_2$Br$_2$ as the internal standard. $^b$Isolated yield.
To obtain a general set of conditions for this reductive [3+2] radical annulation, we conducted further optimization by using the oxalate 7.

Table S9. Optimization using the oxalate 7.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Deviation from above</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>57 (54)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>without MgCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>without PBI</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>without Zn</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>without TEMPO</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>Without TMSCl</td>
<td>44</td>
</tr>
<tr>
<td>7</td>
<td>r.t.</td>
<td>40</td>
</tr>
<tr>
<td>8</td>
<td>60 °C</td>
<td>48</td>
</tr>
<tr>
<td>9</td>
<td>DMA (0.1 M)</td>
<td>49</td>
</tr>
<tr>
<td>10</td>
<td>PBI (3.0 equiv)</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>PBI (4.0 equiv)</td>
<td>54</td>
</tr>
<tr>
<td>12</td>
<td>L&lt;sub&gt;2&lt;/sub&gt; instead of PBI</td>
<td>55</td>
</tr>
<tr>
<td>13</td>
<td>L&lt;sub&gt;3&lt;/sub&gt; instead of PBI</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>L&lt;sub&gt;4&lt;/sub&gt; instead of PBI</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>L&lt;sub&gt;5&lt;/sub&gt; instead of PBI</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>TEMPO (1.0 equiv)</td>
<td>26</td>
</tr>
<tr>
<td>17</td>
<td>TEMPO (3.0 equiv)</td>
<td>54</td>
</tr>
<tr>
<td>18</td>
<td>A&lt;sub&gt;1&lt;/sub&gt; instead of TEMPO</td>
<td>40</td>
</tr>
<tr>
<td>19</td>
<td>A&lt;sub&gt;2&lt;/sub&gt; instead of TEMPO</td>
<td>30</td>
</tr>
<tr>
<td>20</td>
<td>A&lt;sub&gt;3&lt;/sub&gt; instead of TEMPO</td>
<td>17</td>
</tr>
<tr>
<td>21</td>
<td>NiCl&lt;sub&gt;2&lt;/sub&gt; (0.1 equiv)</td>
<td>53</td>
</tr>
<tr>
<td>22</td>
<td>NiBr&lt;sub&gt;2&lt;/sub&gt; (0.1 equiv)</td>
<td>54</td>
</tr>
<tr>
<td>23</td>
<td>NiCl&lt;sub&gt;2&lt;/sub&gt;(py)&lt;sub&gt;4&lt;/sub&gt; (0.1 equiv)</td>
<td>55</td>
</tr>
<tr>
<td>24</td>
<td>ZnCl&lt;sub&gt;2&lt;/sub&gt; instead of MgCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>Mn instead of Zn</td>
<td>53</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yields were determined by <sup>1</sup>H NMR with CH<sub>2</sub>Br<sub>2</sub> as the internal standard. <sup>b</sup>Isolated yield.
**Proposed Mechanism**

Scheme S6. Proposed mechanisms: (A) $S_{N}2$ (bimolecular homolytic substitution) pathway; (B) Hydrogen atom transfer (HAT) pathway.

**Discussion:** The possibility that forming the TEMPO-alkyl adduct first, followed by a C–O bond cleavage could be ruled out based on the following five lines of evidences:

i) We demonstrated that the TEMPO could be fully and rapidly reduced in our reaction conditions (30 min, quantitative NMR yield, see Schemes S7 and S8).

ii) We did not detect any TEMPO–alkyl adduct in our reaction (by using LC/MS and chromatographic isolation), even though we stopped the reaction before the full conversion of the starting material—the alkyl oxalate.

iii) As shown below, we noticed that all substrates that could undergo TEMPO–C bond cleavage were phenyl/vinyl-substituted or ketone-substituted alkoxyamines (eq. A and B). So far, to the best of our knowledge, there is no report on the homolysis of TEMPO–C bond in the dialkyl-substituted alkoxyamines (eq. C).
iv) Prof. Armido Studer also observed the above tendency in 2001, and they briefly explained the reason based on the BDE(C–O) of alkoxyamines derived from TEMPO, which was first reported by Mulder and co-workers in 1999. In Mulder’s report, it was clearly shown that the BDE of TEMPO–C bonds in the dialkyl-substituted alkoxyamines were significantly higher (ca. 10 kcal/mol) than the BDE of TEMPO–C bonds in phenyl/vinyl-substituted or ketone-substituted alkoxyamines. Note that the BDE of TEMPO–C bonds in ketone-substituted alkoxyamines could be calculated from the BDE of α-C–H bonds in ketone through Mulder’s Equation. Moreover, based on the above tendency, the corresponding synthetic strategy has been successfully used in the syntheses of several structurally complex natural products.

v) To directly demonstrate that the C–O bond of dialkyl-substituted alkoxyamines derived from TEMPO cannot be cleaved in our reaction condition, we performed the following experiment under our reaction conditions. As expected, no TEMPO–C bond cleavage product or N–C bond cleavage product was detected, and we could recover most of the starting material. The starting material was prepared according to a known procedure.

Overall, we can fully rule out the possibility that radical II (in scheme S6) is trapped by TEMPO, and the subsequent adduct is then reduced by Zn to give desired product 15.
Mechanistic Investigation

1. Experiments on the reduction of TEMPO.

A. Reduction of TEMPO in MeOH-d₄

1H NMR studies revealed that TEMPO could be completely reduced by Zn in 0.5 h in the presence of PBI and MgCl₂ in MeOH-d₄ (Scheme S7, entry 1). Control experiments demonstrated that the presence of MgCl₂ was required for this reduction (entries 3 and 4), while the presence of PBI was not necessary (entry 2).

Procedure for this reduction: In a glove box, to a 10 mL reaction culture tube charged with TEMPO (12.5 mg, 0.08 mmol, 1.0 equiv), Zn (6.6 mg, 0.1 mmol, 1.25 equiv), PBI (19.5 mg, 0.1 mmol, 1.25 equiv), MgCl₂ (4.8 mg, 0.05 mmol, 0.625 equiv), and PhOMe (8.7 μL, 0.08 mmol, 1.0 equiv) was added MeOH-d₄ (0.4 mL). After 0.5 hour stirring at 40 °C. The reaction mixture (0.1 mL) was filtered through glass wool and rinsed with MeOH-d₄ (0.3 mL) into a NMR tube. The NMR tube was then sealed and move out of the glove box for NMR experiment.

Scheme S7. Reduction of TEMPO in MeOH-d₄.

<table>
<thead>
<tr>
<th>Entry</th>
<th>deviation from above</th>
<th>Yield (%)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>w/o PBI</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>w/o MgCl₂</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>w/o PBI and MgCl₂</td>
<td>0</td>
</tr>
</tbody>
</table>

ᵃYields were determined by ¹H NMR with PhOMe as the internal standard.

The NMR spectra of the above experiments were illustrated in Figure S1.
Figure S1. $^1$H NMR spectra of reduction of TEMPO in MeOH-$d_4$. PhOMe (1 equiv) was used as internal standard for the calculation of the yield.

B. Reduction of TEMPO in DMF-$d_7$

$^1$H NMR studies revealed that TEMPO could also be completely reduced by Zn in 0.5 h in the presence of PBI and MgCl$_2$ in DMF-$d_7$ (Scheme S8, entry 1). Control experiments demonstrated that the presence of PBI was required for this reduction (entries 2–4) in aprotic solvent DMF-$d_7$, which was different from the reduction in MeOH-$d_4$. The NMR spectra of these experiments are shown in the following Figure S2.

Note that the Zn(TEMPO)$_2$ was likely produced in this reaction, since the $^1$H NMR spectrum of the TEMPO derivative generated in this reaction is matched well with Zn(TEMPO)$_2$ (Figure S3).

The procedure for this reduction is identical with the reduction in MeOH-$d_4$ (as mentioned above), except the solvent is changed to DMF-$d_7$. 

---

**Figure S2.** NMR spectra of reduction of TEMPO in DMF-$d_7$. The spectra are shown for different entries, with PhOMe (1 equiv) used as internal standard for the calculation of the yield. The Zn(TEMPO)$_2$ was likely produced in this reaction, as indicated by the matching of the $^1$H NMR spectrum of the TEMPO derivative generated in this reaction with Zn(TEMPO)$_2$ (Figure S3).
Scheme S8. Reduction of TEMPO in DMF-\textit{d}_7.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Deviation from above</th>
<th>Yield (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>w/o MgCl$_2$, 1 hour</td>
<td>36</td>
</tr>
<tr>
<td>3</td>
<td>w/o MgCl$_2$, 0.5 hour</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>w/o PBI</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>w/o MgCl$_2$ and PBI</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$Yields were determined by $^1$H NMR with PhOMe as the internal standard.

Figure S2. $^1$H NMR spectra of the reductions of TEMPO in DMF-\textit{d}_7. PhOMe (1 equiv) was used as internal standard for the calculation of the yields.
Figure S3. A. The $^1$H NMR spectrum of TEMPOH with MgCl$_2$ (0.65 equiv); B. Reaction mixture of entry 1, Scheme S8; C. The $^1$H NMR spectrum of Zn(TEMPO)$_2$ in DMF–$d_7$. 
2. Tracing the H source(s) of C12.

Scheme S9. Deuterium-labeling studies.

<table>
<thead>
<tr>
<th>entry</th>
<th>deviation from above</th>
<th>yield(^a)</th>
<th>C12 D/H ratio(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMA-d(_2) instead of DMA</td>
<td>48%</td>
<td>1:99</td>
</tr>
<tr>
<td>2</td>
<td>PBI-d(_1) instead of PBI</td>
<td>29%</td>
<td>30:70</td>
</tr>
<tr>
<td>3</td>
<td>PBI-d(_1), without TMSCl</td>
<td>25%</td>
<td>30:70</td>
</tr>
</tbody>
</table>

\(^a\)Yields were determined by \(^1\)H NMR with CH\(_2\)Br\(_2\) as the internal standard. \(^b\)The ratios of deuterium were determined by HRMS.

The above experiments (Scheme S9) demonstrated that the deuterium at C12 was obtained from PBI-d\(_1\) (entry 2) instead of the solvent DMA (entry 1) and TMSCl (entry 3). Since the ratios of deuterium were determined by HRMS, we also performed the following control experiment to exclude the possibility that the deuterium was incorporated at C16—the \(\alpha\) position of the ester—in our reaction conditions.

Figure S4. Mass spectrometry for entry 2 in inset table in Scheme S9
3. Evidences for the TEMPO-mediated $\text{S}_{2}\text{H}_{2}$ reaction.

**Scheme S10.** Performing the annulation in the presence of D$_2$O.

<table>
<thead>
<tr>
<th>entry</th>
<th>deviation from above</th>
<th>yield</th>
<th>C$<em>{12}$ D$</em>{2}$H ratio$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>D$_2$O (5.0 equiv)</td>
<td>22%</td>
<td>13/87</td>
</tr>
<tr>
<td>2</td>
<td>D$_2$O (10.0 equiv)</td>
<td>20%</td>
<td>20/80</td>
</tr>
<tr>
<td>3</td>
<td>D$_2$O (20.0 equiv)</td>
<td>9%</td>
<td>31/69</td>
</tr>
<tr>
<td>4</td>
<td>PBI-d$_5$ (5.0 equiv), D$_2$O (20.0 equiv)</td>
<td>5%</td>
<td>80/40</td>
</tr>
<tr>
<td>5</td>
<td>PBI-d$_5$ (5.0 equiv), without D$_2$O</td>
<td>29%</td>
<td>30/70</td>
</tr>
</tbody>
</table>

$^a$Yields were determined by $^1$H NMR with CH$_2$Br$_2$ as the internal standard. $^b$The ratios of deuterium were determined by HRMS.

We also performed the following control experiment to exclude the possibility that the deuterium was incorporated at C16 in our reaction conditions.

**Figure S5.** Mass spectrometry for entry 4 in the inset table in Scheme S10.
Scheme S11. Performing the annulation with Zn(TEMPO)$_2$ instead of TEMPO.

<table>
<thead>
<tr>
<th>entry</th>
<th>deviation from above</th>
<th>yield$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>44%</td>
</tr>
<tr>
<td>2</td>
<td>Zn (3.0 equiv) instead of Zn (5.0 equiv)</td>
<td>42%</td>
</tr>
</tbody>
</table>

$^a$Yields were determined by $^1$H NMR with CH$_2$Br$_2$ as the internal standard.

4. Evidences for the TEMPO-mediated hydrogen atom transfer (HAT) pathway.

Scheme S12. Performing the annulation in the presence of TEMPOD.

<table>
<thead>
<tr>
<th>entry</th>
<th>deviation from above</th>
<th>yield$^a$</th>
<th>D$_2$OH ratio$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>48%</td>
<td>0/100</td>
</tr>
<tr>
<td>2</td>
<td>TEMPOD instead of TEMPO</td>
<td>44%</td>
<td>6.6/93.4</td>
</tr>
<tr>
<td>3</td>
<td>PBI-d$_3$ (5.0 equiv), TEMPOD (4.0 equiv), without TMSCI</td>
<td>20%</td>
<td>45/55</td>
</tr>
<tr>
<td>4</td>
<td>PBI-d$_3$ (5.0 equiv), without TMSCI</td>
<td>25%</td>
<td>30/70</td>
</tr>
</tbody>
</table>

$^a$Yields were determined by $^1$H NMR with CH$_2$Br$_2$ as the internal standard. $^b$The ratios of deuterium were determined by HRMS.

Scheme S13. Performing the annulation in the presence of TEMPOH.

Discussion: i) When TEMPOH was used directly in this reaction, we could also obtain the desired product in 43% yield (Scheme S13, entry 1); ii) When 3 equiv of Zn was used along with TEMPO (4 equiv), the yield of the desired product 9 dropped to 27% (Scheme S13, entry 2). iii) When TEMPOH (4 equiv) was used directly along with 3 equiv of Zn, the yield of this reaction could be rescued to 46% (Scheme S13, entry 3).
5. Preparation of TEMPOH and TEMPOD.

Scheme S14. Preparation of TEMPOH.

\[
\begin{array}{c}
\text{TEMPO} \xrightarrow{\text{sodium ascorbate}} \text{TEMPOH}
\end{array}
\]

TEMPOH was prepared from TEMPO according to the literature procedure with slight modifications.\textsuperscript{11}

To a 50 mL round bottom-flask charged with TEMPO (1.02 g, 6.5 mmol) and (+)-sodium L-ascorbate (2.10 g, 10.6 mmol) under an atmosphere of argon was added deoxygenated water (18 mL). The reaction mixture was stirred for 2 h at room temperature. Then the resulting mixture was extracted with deoxygenated ethyl ether (20 mL ×3). The combined organic layers were washed with deoxygenated water (20 mL), brine (20 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, filtrated, and concentrated under reduced pressure to give TEMPOH as a white solid.

\textsuperscript{1}H NMR of TEMPOH (CD\textsubscript{3}CN): δ 1.061 (s, CH\textsubscript{3}, 12 H), 1.450 (s, CH\textsubscript{2}, 6 H), 5.330 (s, OH, 1 H) (Figure S6).

Scheme S15. Preparation of TEMPOD.

\[
\begin{array}{c}
\text{TEMPO} \xrightarrow{\text{CD\textsubscript{3}OD, r.t.}} \text{TEMPOD}
\end{array}
\]

To a 10 mL reaction culture tube charged with freshly prepared TEMPOH (50 mg) was added CD\textsubscript{3}OD (0.4 mL). After 1 h stirring at room temperature, the reaction mixture was concentrated under reduced pressure. The above process was repeated for three times to give the TEMPOD as a white solid.

\textsuperscript{1}H NMR of TEMPOD (CD\textsubscript{3}CN): δ 1.060 (s, CH\textsubscript{3}, 12 H), 1.449 (s, CH\textsubscript{2}, 6 H) (Figure S7).

Note that TEMPOH and TEMPOD was very unstable. They were used in freshly prepared form.
Figure S6. $^1$H NMR spectrum of TEMPOH in MeCN-$d_3$

Figure S7. $^1$H NMR spectrum of TEMPOD in MeCN-$d_3$
6. Preparation of PBI-\textit{d}_{1}

\textit{Procedure for the preparation of PBI-\textit{d}_{1}}: To a 10 mL reaction culture tube charged with PBI (100 mg) was added CD$_3$OD/CDC$_3$ (v/v = 1:1, 1 mL). After 1 hour stirring at room temperature, the reaction mixture was concentrated under reduced pressure. The above process was repeated for three times to get the PBI-\textit{d}_{1} as a light yellow solid.

\textbf{Scheme S16. Preparation of PBI-\textit{d}_{1}}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{SchemeS16.png}
\caption{\textbf{Figure S8.} $^1$H NMR spectrum of PBI in MeCN-\textit{d}_{3}}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{FigureS8.png}
\caption{\textbf{Figure S9.} $^1$H NMR spectrum of PBI-\textit{d} in MeCN-\textit{d}_{3}}
\end{figure}
7. Preparation of Zn(TEMPO)$_2$.

Zn(TEMPO)$_2$ was prepared according to the literature procedure with slight modifications.$^{12}$

Scheme S17. Preparation of EtZn(TEMPO).

In a glovebox, to the solution of TEMPO (312 mg, 2.0 mmol, 2.0 equiv) in toluene (2 mL) was added Et$_2$Zn (2.0 M in toluene, 0.5 mL, 1.0 mmol, 1.0 equiv) dropwise. During the addition, the color of the reaction mixture turned yellow. After stirring for 10 minutes at room temperature, the volatiles were removed in vacuo. The deeply yellow residue was dissolved in $n$-hexane (2 mL), the resulting mixture was crystallize at $–30\, ^\circ C$ overnight. The solvent was removed through a syringe, and the light yellow crystal was washed with $n$-hexane at $–40\, ^\circ C$ to afford EtZn(TEMPO) (99 mg, 20%) as a light yellow solid. $^1$H NMR (400 MHz, C$_6$D$_6$): 1.63 (t, $J = 8.1$ Hz, 3 H), 1.47 – 1.41 (m, 4 H), 1.32 – 1.24 (m, 2 H), 1.20 (s, 12 H), 0.84 (q, $J = 8.1$ Hz, 4 H) ppm. Note that this $^1$H NMR data matches that in the literatures.$^{12,13}$

Figure S10. $^1$H NMR spectrum of EtZn(TEMPO) in C$_6$D$_6$
Scheme S18. Preparation of Zn(TEMPO)$_2$.

In a glovebox, to a solution of EtZn(TEMPO) (270 mg, 1.08 mmol, 1.0 equiv) in toluene (1 mL) was added a solution of TEMPO (169 mg, 1.08 mmol, 1.0 equiv) in toluene (1 mL) dropwise. The reaction mixture was stirred vigorously at 40 °C for 4 hours. Then the volatiles were removed under vacuo. The residue was suspended in n-hexane (2 mL), and the resulting suspension was deposited at −30 °C overnight. The solvent was removed through a syringe, and the remaining solid was washed with n-hexane at −40 °C to afford Zn(TEMPO)$_2$ (100 mg, 25%) as a white solid (Figure S12). $^1$H NMR (400 MHz, C$_6$D$_6$): 1.62 (brs, 4 H), 1.55 – 1.24 (m, 32 H) ppm. Note that this $^1$H NMR data matches that in the literatures.$^{14}$

Figure S11. $^1$H NMR spectrum of Zn(TEMPO)$_2$ in C$_6$D$_6$

Figure S12. Freshly prepared Zn(TEMPO)$_2$. 
Scheme S19. Other attempts using some known conditions for dehydroxylative Giese-type reactions.

A. Shu’s conditions\textsuperscript{15}

\[
\begin{align*}
\text{TBSCO} & \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{OH} \\
1 & \quad \text{(1.0 equiv)} \\
\end{align*}
\]

\[
\begin{align*}
\text{Cp}^+\text{TiCl}_2 (0.1 \text{ equiv}) \\
\text{TSCl} (3.0 \text{ equiv}), 5\AA \text{ MS} \\
\text{THF}, 60 \degree \text{C}, 12 \text{ h} \\
\end{align*}
\]

\[
\begin{align*}
\text{Zn} (3.0 \text{ equiv}) \\
\text{TESCl} (3.0 \text{ equiv}) \\
\text{THF}, 60 \degree \text{C}, 12 \text{ h} \\
\end{align*}
\]

\[
\begin{align*}
\text{TBSO} & \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{CO}_2\text{Bn} \\
\text{Scheme S29} (90\%) \\
\end{align*}
\]

B. Overman and Macmillan’s conditions\textsuperscript{16}

\[
\begin{align*}
\text{TBSCO} & \quad \text{Me} \quad \text{Me} \quad \text{OCO}_2\text{Ce} \\
\text{S28} & \quad \text{(1.1 equiv)} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ir}^{\text{II}}(\text{ppy})_2(\text{dbtbpy})\text{PF}_6 \quad (2.01 \text{ equiv}) \\
\text{DMF/DMSO} (3:1, 1 \text{ mL}) \\
\text{H}_2\text{O} (10 \text{ equiv}) \\
\text{40} \degree \text{C}, 34 \text{ w Blue LEDs} \\
\end{align*}
\]

\[
\begin{align*}
\text{TBSCO} & \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{CO}_2\text{Bn} \\
\text{90\%} \\
\end{align*}
\]

C. Gong’s conditions\textsuperscript{17}

\[
\begin{align*}
\text{TBSCO} & \quad \text{Me} \quad \text{Me} \quad \text{OCO}_2\text{Me} \\
7 & \quad \text{(1.2 equiv)} \\
\end{align*}
\]

\[
\begin{align*}
\text{NiCl}_2(\text{ppy})_2 (0.1 \text{ equiv}) \\
\text{DMA} (0.1 \text{ M}) \\
\text{60} \degree \text{C}, 12 \text{ h} \\
\end{align*}
\]

\[
\begin{align*}
\text{TBSCO} & \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{CO}_2\text{Bn} \\
\text{90\%} \\
\end{align*}
\]

\[
\begin{align*}
\text{Note that we also planned to try the conditions developed by the group of Overman using tert-alkyl N-phthalimidoyl oxalate as starting material.}\textsuperscript{18} \text{ However, we failed to prepare the tert-alkyl N-phthalimidoyl oxalate S29.}
\end{align*}
\]
Acyclic substrates for the [3+2] radical annulation

Table S10. Attempts of acyclic substrates

<table>
<thead>
<tr>
<th>homoallylic alcohols</th>
<th>alkyl oxalates</th>
<th>[3+2] radical annulation products</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="S35" alt="Image" /></td>
<td><img src="S36" alt="Image" /></td>
<td><img src="S37" alt="Image" />, 47%, dr = 4.0:1</td>
</tr>
<tr>
<td><img src="S38" alt="Image" /></td>
<td><img src="S39" alt="Image" /></td>
<td><img src="S40" alt="Image" />, 39%, dr = 2.1:1</td>
</tr>
<tr>
<td><img src="S41" alt="Image" /></td>
<td><img src="S42" alt="Image" /></td>
<td><img src="S43" alt="Image" />, 48%, dr = 3.7:1</td>
</tr>
</tbody>
</table>

The homoallylic alcohols S35, S38, S41 were prepared according to the reported procedures. 19
Experimental Procedure and Spectroscopic Data

Compound S1 was prepared from 2 according to the literature procedure with slight modifications. 20

To a 200 mL round-bottom flask charged with K2CO3 (4.15 g, 30 mmol, 3.0 equiv), K3[Fe(CN)6] (9.88 g, 30 mmol, 3.0 equiv), MeSO2NH2 (951 mg, 10 mmol, 1.0 equiv), ent-Corey-Noe-Lin ligand (L1) (120 mg, 0.1 mmol, 0.01 equiv), and K2OsO4·2H2O (18.4 mg, 0.05 mmol, 0.5% equiv) was added H2O/t-BuOH (1:1, 100 mL) at room temperature. The resulting suspension was cooled to 0 °C and stirred vigorously for 20 minutes before the addition of farnesyl acetate (2) 21 (2.64 g, 10 mmol, 1.0 equiv). The reaction mixture was stirred vigorously at 4 °C. After 19 h stirring, saturated aq. Na2SO3 (50 mL) was added, and the resulting mixture was stirred for 1 hour at room temperature. The resulting mixture was extracted with EtOAc (100 mL), the organic layer was washed with aq. KOH (1 M, 100 mL) and brine (100 mL) sequentially whereby the aqueous layers were back-extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over anhydrous Na2SO4, filtered, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 5:2) gave the diol S1 (1.82 g, 6.1 mmol, 61%) as a colorless oil. Rf = 0.4 (petroleum ether/EtOAc = 1:1);

1H NMR (400 MHz, CDCl3): δ 5.37 – 5.30 (m, 1 H), 5.20 – 5.13 (m, 1 H), 4.59 (d, J = 7.1 Hz, 2 H), 3.35 (dd, J = 10.5, 1.9 Hz, 1 H), 2.28 – 2.19 (m, 1 H), 2.18 – 2.03 (m, 5 H), 2.05 (s, 3 H), 1.70 (d, J = 0.7 Hz, 3 H), 1.62 (d, J = 0.7 Hz, 3 H), 1.64 – 1.54 (m, 1 H), 1.47 – 1.35 (m, 1 H), 1.20 (s, 3 H), 1.16 (s, 3 H) ppm;

13C NMR (101 MHz, CDCl3): δ 171.3, 142.0, 135.3, 124.2, 118.4, 78.0, 73.0, 61.5, 39.4, 36.7, 29.8, 26.5, 26.1, 23.3, 21.1, 16.4, 16.0 ppm;

HRMS (ESI): Calcd for C17H31O4·[M+H]+: 299.2219, found: 299.2213;

[a]D21 = −17.2° (c = 3.0, MeOH).

To a 500 mL round-bottom flask charged with diol S1 (10.1 g, 33.89 mmol, 1.0 equiv) was added CH2Cl2 (170 mL) and pyridine (7.92 mL, 98.3 mmol, 2.9 equiv). The resulting solution was cooled to 0 °C, and Tf2O (6.84 mL, 40.67 mmol, 1.2 equiv) was added dropwise. After 1 h stirring at 0 °C, sat. aq. NH4Cl (60 mL) and water (60 mL) was added to the reaction mixture. The resulting mixture was extracted with CH2Cl2 (3 × 100 mL). The combined organic layers were washed with brine (100 mL), dried over Na2SO4, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded epoxide 3 (8.45 g, 89%, 91% ee) as a colorless oil.

S27
$R_f = 0.56$ (petroleum ether/EtOAc = 5:1);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.36 – 5.29 (m, 1 H), 5.18 – 5.10 (m, 1 H), 4.57 (d, $J = 7$ Hz, 2 H), 2.69 (t, $J = 6.3$ Hz, 1 H), 2.22 – 1.99 (m, 6 H), 2.04 (s, 3 H), 1.71 – 1.68 (m, 3 H), 1.67 – 1.53 (m, 2 H), 1.61 (d, $J = 1.2$ Hz, 3 H), 1.29 (s, 3 H), 1.25 (s, 3 H) ppm;

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 171.2, 142.2, 134.7, 124.4, 118.5, 64.3, 61.5, 58.4, 39.6, 36.4, 27.6, 26.3, 25.0, 21.2, 18.9, 16.6, 16.1 ppm;

HRMS (ESI): Calcd for C$_{17}$H$_{29}$O$_3$ [M+H]$^+$: 281.2117, found: 281.2108;

$[\alpha]_{D}^{25} = +2.87^\circ$ (c = 3.0, CHCl$_3$).

*Note: Rac-3 was prepared according to the literature reported procedure.*

Method for the determination of the ee value of 3:
Column: Chiralpak® IF;
Dimensions: 4.6 mm × 250 mm;
Eluent: n-hexane : isopropanol = 99 : 1;
Flow rate: 1 mL/min.
Acq. Instrument : LC 1220  
Location : 41  
Injection Date : 15/04/2021 00:02:20  
Inj : 1  
Inj Volume : 3.000 µl  
Different Inj Volume from Sample Entry! Actual Inj Volume : 2.000 µl  
(modified after loading)  
Sample Info : eje-1557racemic-29250414-3, If, 210 nm. 90% hexane, 1% isopro, 1m/ min  
Additional Info : Peak(s) manually integrated

Area Percent Report

Sorted By : Signal  
Multiplier : 2.0000  
Dilution : 1.0000  
*See Multiplier & Dilution Factor with ISTDs  
Signal 1: ValDIA, Wavelength=210 nm

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.086</td>
<td>MM</td>
<td>0.134</td>
<td>3695</td>
<td>32837</td>
<td>70.707</td>
<td>59.0428</td>
</tr>
<tr>
<td>2</td>
<td>7.595</td>
<td>MM</td>
<td>0.146</td>
<td>3798</td>
<td>87456</td>
<td>49.879</td>
<td>40.9562</td>
</tr>
</tbody>
</table>

Peak RetTime Type Width Area Height Area %

Totals : 76843609293

*** End of Report ***
Acq. Instrument: LC 1220
Location: 43
Injection Date: 14/04/2021 21:24:16
Inj: 1
Inj Volume: 3.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume: 2.000 µl
Last changed: 15/04/2021 08:59:21 by SYSTEM
(modified after loading)
Sample Info: zm-2157-asymmetric-20210414-1, if, 210 nm, 99% hexane, 1% iprc, 1ml/min

Additional Info: Peak(s) manually integrated

---

Area Percent Report
---

Sorted By: Signal
Multiplier: 2.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD A, Wavelength=210 nm

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[nAµft]</td>
<td>[nAµf]</td>
</tr>
<tr>
<td>---------------</td>
<td>--------</td>
<td>--------</td>
<td>---------</td>
<td>--------</td>
</tr>
<tr>
<td>1</td>
<td>7.083</td>
<td>0.1182</td>
<td>299.11087</td>
<td>29.49290</td>
</tr>
<tr>
<td>2</td>
<td>7.576</td>
<td>0.1531</td>
<td>4717.98447</td>
<td>533.55078</td>
</tr>
</tbody>
</table>

Peak RetTime Type Width Area Height Area
# [min] [min] [nAµft] [nAµf] %
---------------|--------|---------|---------|--------|
Totals: 4026.19534 543.05368

---

*** End of Report ***
Compound 4 was prepared from 3 according to the literature procedures with slight modifications.\textsuperscript{22,23}

A mixture of Mn dust (13.1 g, 239 mmol, 8.0 equiv) and Cp\textsubscript{2}TiCl\textsubscript{2} (1.5 g, 6 mmol, 0.2 equiv) was suspended in THF (240 mL), the resulting suspension was stirred at room temperature. When the color of the reaction mixture changed from reddish to grey-greenish, a solution of epoxide 3 (8.37 g, 29.8 mmol, 1.0 equiv) and 2,4,6-collidine (27.6 mL, 209 mmol, 7.0 equiv) in THF (24 mL) was added followed by the addition of TMSCl (15.2 mL, 119.6 mmol, 4.0 equiv). The resulting suspension was stirred vigorously for 12 h at room temperature. The reaction mixture was directly filtered through a pad of Celite and rinsed with EtOAc (40 mL). The filtrate was cooled to 0 °C and acidified by 1 M HCl to pH = 2. The resulting mixture was extracted with EtOAc (3 × 100 mL), the combined organic layers were washed with sat. aq. CuSO\textsubscript{4} (100 mL), brine (100 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, and concentrated under reduced pressure.

The above brownish oily residue was dissolved in THF (200 mL), a solution of TBAF (1.0 M, 120 mL, 120 mmol, 4 equiv) was added. After 2 h stirring at room temperature, the reaction was quenched by H\textsubscript{2}O (100 mL). The resulting mixture was extracted with EtOAc (3 × 100 mL), and the combined organic layers were washed with brine (100 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 5:1) gave compound S2 as a brown oil (5.18 g), which contained some unknown impurities. This mixture was used in next step without further purification.

The above compound S2 (5.18 g, 18.5 mmol, 1.0 equiv) was dissolved in anhydrous DMF (265 mL). To the stirred solution was added TBSCI (12.06 g, 80 mmol, 4.3 equiv) and imidazole (5.45 g, 80 mmol, 4.3 equiv) sequentially. The reaction mixture was stirred at room temperature overnight before being quenched with water (100 mL). The resulting mixture was extracted with Et\textsubscript{2}O (3 × 100 mL). The combined organic layers were washed with brine (100 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, and concentrated under reduced pressure. Purification by column chromatography (silica gel; petroleum ether/EtOAc = 20:1) gave the product 4 (6.5 g) as colorless oil, which contained some unknown impurities. This mixture was used in next step without further purification.

A solution of the alkene 4 (6.5 g, 16.5 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (165 mL) was bubbled with a flow of ozone at −78 °C. When the color of the solution turned to blue, the reaction mixture bubbled with a flow of argon until the blue color disappeared. Zn powder (43 g, 660 mmol, 40.0 equiv) and AcOH (29 mL, 495 mmol, 30.0 equiv) were simultaneously added slowly at −78 °C. The resulting suspension was allowed to warm to room temperature and stirred vigorously for additional 2 hours. The resulting mixture
was filtered through a pad of Celite and rinsed with CH₂Cl₂ (50 mL). The filtrate was concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded the ketone S₃ (3.3 g, 28% over 4 steps) as a white solid.

Rₛ = 0.36 (petroleum ether/EtOAc = 10:1);

¹H NMR (400 MHz, CDCl₃): δ 4.39 (dd, J = 11.0, 8.1 Hz, 1 H), 4.17 (dd, J = 11.0, 3.2 Hz, 1 H), 3.34 – 3.27 (m, 1 H), 2.46 (dd, J = 13.5, 4.8, 2.1 Hz, 1 H), 2.42 – 2.28 (m, 2 H), 2.11 – 2.03 (m, 1 H), 2.0 (s, 3 H), 1.80 – 1.68 (m, 2 H), 1.64 – 1.57 (m, 2 H), 1.56 – 1.44 (m, 2 H), 1.0 (s, 3 H), 0.89 (s, 9 H), 0.79 (s, 3 H), 0.77 (s, 3 H), 0.06 (s, 6 H) ppm;

¹³C NMR (101 MHz, CDCl₃): δ 209.6, 171.3, 78.9, 62.2, 59.0, 53.3, 42.0, 41.7, 40.0, 36.9, 28.9, 27.8, 26.0, 23.6, 21.2, 18.2, 16.0, 15.6, – 3.7, – 4.8 ppm;

HRMS (ESI): Calcd for C₂₂H₄₀O₄SiNa [M+Na]⁺: 419.2594, found: 419.2582;

[α]₂₅D = +19° (c = 0.1, CHCl₃);

Melting point: 61–63 °C.

To a solution of ketone S₃ (3.05 g, 7.7 mmol, 1.0 equiv) in Et₂O (77 mL) was slowly added a solution of allylmagnesium bromide (1.0 M in ether, 31 mL, 4.0 equiv) at 0 °C, the reaction mixture was allowed to warm to room temperature. After 2 hours stirring, the reaction was quenched with sat. aq. NH₄Cl (30 mL). The resulting mixture was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 10:1) afforded the diol S₄ (2.41 g, 79%) as a white solid.

Rₛ = 0.44 (petroleum ether/EtOAc = 5:1);

¹H NMR (400 MHz, CDCl₃): δ 5.90 – 5.78 (m, 1 H), 5.15 – 5.13 (m, 1 H), 5.12 – 5.08 (m, 1 H), 4.09 (dd, J = 11.8, 1.9 Hz, 1 H), 4.03 (dd, J = 11.8, 3.8 Hz, 1 H), 3.16 (dd, J = 11.5, 4.5 Hz, 1 H), 2.48 – 2.35 (m, 2 H), 1.88 (dt, J = 12.9, 3.6 Hz, 1 H), 1.75 – 1.62 (m, 3 H), 1.58 – 1.43 (m, 3 H), 1.24 (s, 3 H), 1.03 – 0.94 (m, 1 H), 0.93 – 0.91 (m, 1 H), 0.90 (s, 3 H), 0.89 (s, 9 H), 0.79 (s, 3 H), 0.75 – 0.70 (m, 1 H), 0.04 (s, 3 H), 0.03 (s, 3 H) ppm;

¹³C NMR (101 MHz, CDCl₃): δ 134.4, 118.6, 79.4, 75.7, 59.8, 56.1, 54.9, 47.5, 39.6, 39.5, 38.5, 38.2, 26.0, 27.7, 26.1, 18.3, 18.1, 17.3, 16.1, – 3.6, – 4.8 ppm;

HRMS (ESI): Calcd for C₂₃H₄₄O₄SiNa [M+Na]⁺: 419.2957, found: 419.2925;

[α]₂₅D = –18° (c = 0.1, CHCl₃);

Melting point: 164 – 165.1 °C.
To a 100 mL flame-dried round-bottom flask charged with diol S4 (3.72 g, 9.4 mmol, 1.0 equiv), TsCl (4.47 g, 23.5 mmol, 2.5 equiv), and DMAP (115 mg, 0.94 mmol, 0.1 equiv) was added anhydrous pyridine (19 mL) at room temperature. After 12 hours stirring, the reaction mixture was concentrated directly under reduced pressure. Purification by column chromatography (silica gel; petroleum ether/EtOAc = 20:1) gave 5 (5.13 g, 99%) as a white solid. 

\[ \text{Rf} = 0.52 \text{ (petroleum ether/EtOAc = 5:1);} \]

\[ ^1H\text{ NMR (400 MHz, CDCl}_3\text{): } \delta 7.83 - 7.77 \text{ (m, 2 H), 7.38 - 7.32 (m, 2 H), 5.81 - 5.67 (m, 1 H), 5.11 (dd, } J = 10.1, 2.2 \text{ Hz, 1 H), 4.98 - 4.90 (m, 1 H), 4.25 (dd, } J = 10.6, 4.5 \text{ Hz, 1 H), 4.13 (dd, } J = 10.6, 2.0 \text{ Hz, 1 H), 3.14 (dd, } J = 11.2, 4.7 \text{ Hz, 1 H), 2.45 (s, 3 H), 2.15 - 2.0 (m, 2 H), 1.67 - 1.40 (m, 7 H), 1.33 - 1.21 (m, 2 H), 1.08 - 0.97 (m, 1 H), 0.95 - 0.81 (m, 14 H), 0.79 - 0.66 (m, 1 H), 0.73 (s, 3 H), 0.03 (s, 3 H), 0.02 (s, 3 H) \text{ ppm;} \]

\[ ^{13}\text{C NMR (101 MHz, CDCl}_3\text{): } \delta 144.8, 133.3, 132.9, 129.9, 128.1, 119.6, 79.1, 73.2, 68.2, 56.0, 54.3, 46.7, 39.4, 39.0, 37.9, 37.4, 28.7, 27.3, 26.0, 21.7, 18.1, 17.7, 16.1, 16.0, -3.7, -4.9 \text{ ppm;} \]

\[ \text{HRMS (ESI): Caled for C}_{30}\text{H}_{50}\text{O}_5\text{S}_{3}\text{SiNa} [\text{M+Na}]^+ : 573.3046, \text{ found: 573.3038; } [\alpha]^D_{	ext{o} = 22^\circ} (c = 0.1, \text{ CHCl}_3); \]

\[ \text{Melting point: 66.3 - 68.2 °C.} \]

A 10 mL culture tube charged with CuCl\textsubscript{2} (20.2 mg, 0.15 mmol) and LiCl (12.7 mg, 0.3 mmol) was heated under vacuum with a heat gun to remove water. Then the reaction tube was backfilled with argon and allowed to cool to room temperature. THF (1.5 mL) was added, and resulting mixture was stirred until the solids were dissolved.

To a 250 mL round-bottom flask charged with alkene 5 (2.2 g, 4.0 mmol, 1.0 equiv) was added toluene (80 mL). The resulting solution was cooled to 0 °C, and a solution of fresh prepared Li\textsubscript{2}CuCl\textsubscript{4} (1.2 mL, 0.03 equiv) was added dropwise. After 30 minutes vigorous stirring at 0 °C, a solution of vinylmagnesium bromide (1.0 M in THF, 16 mL, 16 mmol, 4.0 equiv) was added dropwise. The reaction mixture was stirred at 0 °C for 12 hours before being quenched with sat. NH\textsubscript{4}Cl (40 mL) and water (40 mL). The resulting mixture was extracted with EtOAc (3 × 80 mL). The combined organic layers were washed with brine (100 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded 6 (1.1 g, 68%) as a light yellow solid.

\[ \text{Rf} = 0.46 \text{ (petroleum ether/EtOAc = 10:1);} \]

\[ ^1H\text{ NMR (400 MHz, CDCl}_3\text{): } \delta 5.89 - 5.75 \text{ (m, 2 H), 5.15 - 4.87 (m, 4 H), 3.17 (dd, } J = 11.4, 4.6 \text{ Hz, 1 H), 2.35 - 2.23 (m, 2 H), 2.16 - 2.06 (m, 2 H), 1.77 - 1.65 (m, 2 H), 1.64 - 1.39 (m, 5 H), 1.26 (brs, 1 H), 1.05 - 0.95 (m, 2 H), 0.98 (s, 3 H), 0.9 (s, 3 H), 0.88 (s, 9 H), 0.82 - 0.71 (m, 1 H), 0.76 (s, 3 H), 0.03 (s, 3 H), 0.03 (s, 3 H) \text{ ppm;} \]

\[ ^{13}\text{C NMR (101 MHz, CDCl}_3\text{): } \delta 141.7, 134.2, 119.0, 114.1, 79.5, 74.6, 57.1, 55.0, 46.9, 39.6, 39.4, 39.0, 38.0, 29.4, 28.8, 27.5, 26.1, 18.3, 18.1, 16.1, 15.4, -3.6, -4.8 \text{ ppm;} \]
HRMS (ESI): Calcd for C\textsubscript{25}H\textsubscript{46}O\textsubscript{2}NH\textsubscript{4}Si [M+NH\textsubscript{4}]\textsuperscript{+}: 424.3611, found: 424.3760; 
[\alpha]_D^{25} = -18^\circ \, (c = 0.1, \text{CHCl}_3);

**Melting point:** 53.1 – 55 °C.

To a solution of diene 6 (2.2 g, 5.4 mmol, 1.0 equiv) in CH\textsubscript{2}Cl\textsubscript{2} (320 mL) was added a solution of Grubbs catalyst 2\textsuperscript{nd} generation (230 mg, 0.27 mmol, 0.05 equiv) in CH\textsubscript{2}Cl\textsubscript{2} (10 mL). The reaction mixture was stirred at room temperature overnight. The reaction mixture was concentrated directly under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded the tertiary alcohol 1 (1.96 g, 96%) as a white solid.

R\textsubscript{f} = 0.42 (petroleum ether/EtOAc = 20:1);

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 5.82 – 5.73 (m, 1 H), 5.58 – 5.50 (m, 1 H), 3.18 (dd, J = 11.2, 4.6 Hz, 1 H), 2.12 – 1.98 (m, 3 H), 1.94 (dt, J = 13.7, 3.1 Hz, 1 H), 1.70 – 1.57 (m, 3 H), 1.56 – 1.43 (m, 3 H), 1.37 (td, J = 13.5, 4.7 Hz, 1 H), 1.26 (dd, J = 10.6, 6.9 Hz, 1 H), 1.03 (s, 3 H), 1.01 – 0.94 (m, 1 H), 0.92 (s, 3 H), 0.89 (s, 9 H), 0.87 – 0.82 (m, 1 H), 0.80 (s, 3 H), 0.04 (s, 3 H), 0.03 (s, 3 H) ppm;

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 127.2, 123.4, 79.5, 69.6, 55.4, 51.5, 43.1, 41.3, 39.5, 37.8, 36.6, 29.0, 27.6, 26.0, 21.7, 18.4, 18.2, 16.4, 14.9, –3.7, –4.8 ppm;

HRMS (ESI): Calcd for C\textsubscript{23}H\textsubscript{42}O\textsubscript{2}SiK [M+K]\textsuperscript{+}: 417.2591, found: 417.2549;

[\alpha]_D^{25} = -10^\circ \, (c = 0.1, \text{CHCl}_3);

**Melting point:** 108.2 – 109.5 °C.

A solution of allylmagnesium bromide (1.0 M in ethyl ether, 43 mL, 1.5 equiv) was added to a solution of S6\textsuperscript{1} (6.78 g, 28.9 mmol, 1.0 equiv) in anhydrous Et\textsubscript{2}O (60 mL) over 5 minutes at 0 °C. After 2 hours stirring at 0 °C, sat. aq. NH\textsubscript{4}Cl (30 mL) was added to the reaction mixture. The resulting mixture was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded alcohol S7 (5.6 g, 70%) as a colorless oil.

R\textsubscript{f} = 0.37 (petroleum ether/EtOAc = 20:1);

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 5.89 – 5.76 (m, 1 H), 5.14 – 5.09 (m, 1 H), 5.09 – 5.03 (m, 1 H), 5.03 – 4.97 (m, 1 H), 4.93 – 4.88 (m, 1 H), 2.33 – 2.24 (m, 2 H), 2.17 – 2.08 (m, 2 H), 1.77 – 1.66 (m, 2 H), 1.65 – 1.55 (m, 1 H), 1.55 – 1.45 (m, 3 H), 1.44 – 1.32 (m, 3 H), 1.19 – 1.08 (m, 1 H), 1.06 (dd, J = 5.0, 3.1 Hz, 1 H), 0.98 (s, 3 H), 0.93 – 0.76 (m, 2 H), 0.86 (s, 3 H), 0.83 (s, 3 H) ppm;

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 141.9, 134.3, 118.9, 114.0, 74.9, 57.2, 56.0, 47.0, 42.1, 39.8, 39.4, 39.3, 33.6, 33.4, 29.4, 21.9, 18.4, 18.1, 15.3 ppm;

To a solution of tertiary alcohol S7 (1.3 g, 4.7 mmol, 1.0 equiv) in CH_2Cl_2 (260 mL) was added a solution of Grubbs catalyst 2nd generation (200 mg, 0.236 mmol, 0.05 equiv) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature overnight before being concentrated directly under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded the tertiary alcohol S8 (1.05 g, 90%) as a colorless oil. 

R_f = 0.35 (petroleum ether/EtOAc = 20:1);

^1H NMR (400 MHz, CDCl_3): δ 5.85 - 5.70 (m, 1 H), 5.60 - 5.46 (m, 1 H), 2.15 - 1.85 (m, 5 H), 1.70 - 1.46 (m, 5 H), 1.45 - 1.34 (m, 3 H), 1.33 - 1.24 (m, 1 H), 1.21 - 1.08 (m, 1 H), 1.03 (s, 3 H), 0.95 - 0.78 (m, 1 H), 0.88 (s, 3 H), 0.87 (s, 3 H) ppm;

^13C NMR (101 MHz, CDCl_3): δ 127.4, 123.5, 70.0, 56.3, 51.7, 43.3, 42.1, 41.2, 39.6, 37.0, 33.3, 22.1, 21.7, 18.6, 18.5, 14.9 ppm;

HRMS (ESI): Calcd for C_{17}H_{29}O [M+H]^+: 249.2219, found: 249.2128.

To a 25 mL flame-dried round-bottom flask charged with tertiary alcohol 1 (114 mg, 0.3 mmol, 1.0 equiv) and CSA (139 mg, 0.6 mmol, 2.0 equiv) was added anhydrous MeOH (15 mL). The reaction mixture was stirred at room temperature overnight before being quenched with sat. aq. NaHCO_3 (10 mL). The resulting mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 10:1) afforded diol S9 (71.3 mg, 90%) as a white solid.

R_f = 0.35 (petroleum ether/EtOAc = 10:3);

^1H NMR (400 MHz, CDCl_3): δ 5.83 - 5.72 (m, 1 H), 5.59 - 5.49 (m, 1 H), 3.27 - 3.17 (m, 1 H), 2.13 - 1.91 (m, 4 H), 1.72 - 1.51 (m, 5 H), 1.48 (s, 2 H), 1.43 - 1.33 (m, 1 H), 1.32 - 1.23 (m, 1 H), 1.04 (s, 3 H), 1.01 (s, 3 H), 0.92 - 0.80 (m, 1 H), 0.85 (s, 3 H) ppm;

^13C NMR (101 MHz, CDCl_3): δ 127.2, 123.5, 79.1, 69.7, 55.4, 51.5, 43.1, 41.1, 39.0, 37.8, 36.8, 28.6, 27.2, 21.7, 18.3, 15.9, 14.9 ppm;

HRMS (ESI): Calcd for C_{17}H_{20}O_2 [M+H]^+: 265.2168, found: 262.2166; 

[α]_D^{23} = -25° (c = 0.2, CHCl_3);

Melting point: 110 – 112.5 °C.
To a 10 mL reaction culture tube charged with alcohol S9 (10.6 mg, 0.04 mmol, 1.0 equiv), TCDI (19.3 mg, 0.108 mmol, 2.7 equiv), and DMAP (5.4 mg, 0.044 mmol, 1.1 equiv) was added toluene (1 mL). The reaction mixture was stirred at 78 °C overnight before being quenched with H2O (1 mL). The resulting mixture was extracted with EtOAc (3 × 1 mL). The combined organic layers were washed with brine (3 mL), dried over Na2SO4, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 5:1) afforded the ester S10 (14.2 mg, 95%) as a white solid. 

\[ R_f = 0.50 \text{ (petroleum ether/EtOAc = 5:2);} \]

\(^1\)H NMR (400 MHz, CDCl3): \( \delta 8.33 \text{ (s, 1 H), 7.65 – 7.55 (m, 1 H), 7.06 – 7.00 (m, 1 H), 5.84 – 5.74 (m, 1 H), 5.61 – 5.50 (m, 1 H), 5.23 (dd, } J = 11.7, 4.6 \text{ Hz, 1 H), 2.15 – 1.93 (m, 5 H), 1.83 – 1.66 (m, 3 H), 1.63 – 1.53 (m, 2 H), 1.47 – 1.29 (m, 2 H), 1.28 – 1.02 (m, 2 H), 1.12 (s, 3 H), 1.08 (s, 3 H), 0.99 (s, 3 H) ppm; \]

\(^13\)C NMR (101 MHz, CDCl3): \( \delta 184.1, 136.8, 130.8, 127.0, 123.4, 117.9, 91.6, 69.5, 55.4, 51.2, 43.0, 40.9, 38.7, 37.2, 36.7, 28.6, 22.3, 21.8, 18.0, 17.9, 14.9 \text{ ppm;} \)


\([\alpha]_{D}^{24} = -32^\circ (c = 0.2, \text{ CHCl}_3);\]

Melting point: 239.8 – 241.2 °C.

To a sealed tube charged with thiocarbamate S10 (109 mg, 0.29 mmol, 1.0 equiv), nBu3SnH (0.24 mL, 0.874 mmol, 3.0 equiv), and AIBN (10 mg, 0.058 mmol) was added toluene (45 mL). The reaction mixture was stirred at 150 °C for 10 minutes. The temperature was then cooled to 125 °C, and the reaction mixture was stirred for additional 20 minutes before being cooled to room temperature. The resulting mixture was concentrated directly under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 50:1) afforded the alcohol S8 (64.8 mg, 90%) as a colorless oil. 

\[ R_f = 0.35 \text{ (petroleum ether/EtOAc = 20:1);} \]

\(^1\)H NMR (400 MHz, CDCl3): \( \delta 5.85 – 5.70 \text{ (m, 1 H), 5.60 – 5.46 (m, 1 H), 2.15 – 1.85 (m, 5 H), 1.70 – 1.46 (m, 5 H), 1.45 – 1.34 (m, 3 H), 1.33 – 1.24 (m, 1 H), 1.21 – 1.08 (m, 1 H), 1.03 (s, 3 H), 0.95 – 0.78 (m, 1 H), 0.88 (s, 3 H), 0.87 (s, 3 H) ppm; \]

\(^13\)C NMR (101 MHz, CDCl3): \( \delta 127.4, 123.5, 70.0, 56.3, 51.7, 43.3, 42.1, 41.2, 39.6, 37.0, 33.9, 33.3, 22.1, 21.7, 18.6, 18.5, 14.9 \text{ ppm;} \)


\([\alpha]_{D}^{22} = -6^\circ (c = 0.15, \text{ CHCl}_3).\]
TBSCI (19.4 g, 129 mmol, 4.3 equiv) and imidazole (8.78 g, 129 mmol, 4.3 equiv) were added sequentially to a solution of andrographolide S11 (10.5 g, 30 mmol, 1.0 equiv) in anhydrous DMF (430 mL). After 12 hours stirring at room temperature, water (200 mL) was added to the reaction mixture. The resulting mixture was extracted with Et₂O (3 × 150 mL). The combined organic layers were washed with brine (150 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 50:1) afforded S12 (19.7 g, 95%) as a white solid.

\[ R_f = 0.47 \pm \text{(petroleum ether/EtOAc = 4:1)} \]

\( ^1H \) NMR (400 MHz, CDCl₃): \( \delta \) 6.86 (td, \( J = 6.3, 1.7 \) Hz, 1 H), 5.09 – 5.01 (m, 1 H), 4.87 – 4.81 (m, 1 H), 4.55 – 4.49 (m, 1 H), 4.46 – 4.37 (m, 1 H), 4.13 – 4.05 (m, 1 H), 3.94 – 3.86 (m, 1 H), 3.64 – 3.56 (m, 1 H), 3.29 (dd, \( J = 11.6, 4.4 \) Hz, 1 H), 2.62 – 2.50 (m, 1 H), 2.46 – 2.32 (m, 2 H), 1.92 – 1.48 (m, 7 H), 1.27 – 1.16 (m, 1 H), 1.14 – 1.08 (m, 1 H), 1.00 (s, 3 H), 0.91 (s, 9 H), 0.89 (s, 9 H), 0.86 (s, 9 H), 0.81 (s, 3 H), 0.17 (s, 3 H), 0.12 (s, 3 H), 0.05 (s, 3 H), 0.03 (s, 3 H), 0.01 (s, 6 H) ppm;

\( ^13C \) NMR (101 MHz, CDCl₃): \( \delta \) 170.1, 148.9, 147.7, 127.3, 108.7, 79.4, 74.1, 67.1, 64.4, 56.6, 55.5, 43.9, 39.2, 38.8, 38.0, 28.4, 26.2, 26.1, 26.0, 25.7, 25.0, 23.7, 18.3, 18.2, 18.0, 14.6, –3.7, –4.1, –4.6, –4.9, –5.5, –5.6 ppm;

HRMS (ESI): Calcd for C₃₈H₃₅O₅Si₃ [M+H]⁺: 693.4766, found: 693.4755;  
\( [\alpha]_{D}^{25} = -68^\circ \) (c = 0.2, CHCl₃);

Melting point: 158.8 – 160.2 °C.

A solution of S12 (20.7 g, 30 mmol, 1.0 equiv) in CH₂Cl₂ (300 mL, 0.1 M) was slowly bubbled with a flow of ozone at –78 °C until the color of the solution turned to blue. The reaction mixture was then bubbled with a flow of argon until the blue color disappeared. Zn powder (15.7 g, 240 mmol, 8.0 equiv) and AcOH (10.6 mL, 180 mmol, 6.0 equiv) were simultaneously added slowly at –78 °C. The suspension was allowed to warm to room temperature and stirred vigorously for additional 2 hours. The resulting mixture was filtered through a pad of Celite and rinsed with CH₂Cl₂ (20 mL). The filtrate was concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded the ketone S13 (13.1 g, 88%) as white solid.

\[ R_f = 0.45 \pm \text{(petroleum ether/EtOAc = 10:1)} \]

\( ^1H \) NMR (400 MHz, CDCl₃): \( \delta \) 9.85 – 9.78 (m, 1 H), 3.98 – 3.88 (m, 1 H), 3.68 – 3.59 (m, 1 H), 3.42 – 3.32 (m, 1 H), 3.05 – 2.92 (m, 1 H), 2.80 (dd, \( J = 9.3, 2.9 \) Hz, 1 H), 2.43 (dt, \( J = 13.2, 3.3 \) Hz, 1 H), 2.32 – 2.10 (m, 4 H), 1.73 – 1.50 (m, 6 H), 1.45 – 1.23 (m, 2 H), 1.09 (s, 3 H), 0.89 (s, 9 H), 0.85 (s, 9 H), 0.06 (s, 3 H), 0.04 (s, 3 H), 0.01 (s, 3 H), 0.01 (s, 3 H) ppm;

\( ^13C \) NMR (101 MHz, CDCl₃): \( \delta \) 210.6, 201.3, 79.1, 64.4, 58.0, 54.1, 43.9, 42.4, 41.2, 37.7, 37.4, 27.9, 26.0, 25.9, 25.2, 23.9, 18.3, 18.1, 15.1, –3.8, –4.9, –5.5, –5.7 ppm.

HRMS (ESI): Calcd for C₂₇H₃₃O₅Si₂ [M+H]⁺: 497.3482, found: 497.3478;
$[\alpha]_{D}^{25.3} = -14.5^\circ \ (c = 0.2, \text{CHCl}_3);
\textbf{Melting point:} 111.0 - 112.6 ^\circ \text{C}.

To a 250 mL of round-bottom flask charged with $t$-BuOK (1 g, 9.3 mmol, 1.5 equiv) and (Ph$_3$)PCH$_2$Br (3.54 g, 9.9 mmol, 1.6 equiv) was added THF (47 mL) at 0 °C. After 30 minutes stirring at 0 °C, a solution of S13 (3.08 g, 6.2 mmol, 1.0 equiv) in THF (34 mL) was added over a period of 5 minutes. The resulting mixture was stirred for additional 10 minutes before being quenched with 40 mL ice water. The resulting mixture was extracted with petroleum ether (3 × 50 mL). The combined organic layers were washed with brine (100 mL), dried over Na$_2$SO$_4$, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded S14 (2.48 g, 81 %) as a colorless solid.

$R_f = 0.54$ (petroleum ether/EtOAc = 20:1);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.82 – 5.70 (m, 1 H), 5.01 – 4.85 (m, 2 H), 3.97 – 3.89 (m, 1 H), 2.56 – 2.46 (m, 1 H), 2.42 – 2.34 (m, 1 H), 1.98 – 1.88 (m, 1H), 1.80 (dt, $J = 13.1, 3.6$ Hz, 1H), 1.73 – 1.47 (m, 3 H), 1.36 (td, $J = 13.5, 4.1$ Hz, 1H), 1.07 (s, 3 H), 0.89 (s, 9 H), 0.86 (s, 9 H), 0.84 (s, 3 H), 0.06 (s, 3 H), 0.04 (s, 3 H), -0.02 (s, 6 H) ppm;

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 211.6, 138.6, 115.1, 79.3, 64.4, 64.3, 54.6, 44.0, 43.5, 42.6, 37.6, 28.1, 26.6, 26.0, 25.9, 25.9, 23.8, 18.3, 18.1, 14.7, – 3.8, – 4.9, – 5.5, – 5.7 ppm.

HRMS (ESI): Calcd for C$_{28}$H$_{55}$O$_3$Si$_2$ [M+H]$^+$: 495.3690, found: 495.3684;

$[\alpha]_{D}^{25.3} = -3^\circ \ (c = 0.2, \text{CHCl}_3);
\textbf{Melting point:} 89.1 – 92.1 ^\circ \text{C}.$

To a solution of ketone S14 (4.18 g, 8.46 mmol, 1.0 equiv) in Et$_2$O (45 mL) was added a solution of allylmagnesium bromide (1.0 M in ether, 13 mL, 12.7 mmol, 1.5 equiv) dropwise at 0 °C. After 2 hour stirring at 0 °C, the reaction mixture was quenched with sat. aq. NH$_4$Cl (30 mL). The resulting mixture was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over Na$_2$SO$_4$, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 10:1) gave the tertiary alcohol product S15 (4.22 g, 93%) as a white solid.

$R_f = 0.55$ (petroleum ether/EtOAc = 20:1);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.90 – 5.73 (m, 2 H), 5.13 – 4.86 (m, 4 H), 3.96 – 3.87 (m, 1 H), 3.62 – 3.54 (m, 1 H), 3.24 (dd, $J = 11.8, 4.5$ Hz, 1H), 2.40 – 2.23, (m, 2 H), 2.16 - 2.02 (m, 2 H), 1.95 – 1.83 (m, 1 H), 1.77 (dt, $J = 13.1, 3.4$ Hz, 1H), 1.71 – 1.58 (m, 3 H), 1.56 – 1.40 (m, 3 H), 1.36 – 1.25 (m, 1 H), 1.07 (s, 3 H), 1.00 (s, 3 H), 0.88
(s, 18 H), 0.83 – 0.71 (m, 1 H), 0.03 (s, 3 H), 0.02 (s, 3 H), 0.00 (s, 3 H), – 0.01 (s, 3 H) ppm.

13C NMR (101 MHz, CDCl3): δ 141.8, 134.4, 118.7, 114.1, 79.6, 74.6, 64.8, 57.4, 55.7, 46.6, 43.7, 40.2, 39.1, 38.4, 29.7, 27.5, 26.1, 26.0, 23.6, 20.1, 18.4, 18.2, 15.1, – 3.7, – 4.9, – 5.4, – 5.6 ppm;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;

HRMS (ESI): Calcd for C31H61O3Si2 [M+H]+: 537.4159, found: 537.4154;


[α]24° = – 24.5° (c = 0.2, CHCl3);

Melting point: 137.6 – 140.3 °C.

To a 25 mL flame-dried round-bottom flask charged with Na (345 mg, 15 mmol, 3.0 equiv) was added anhydrous ethanol (10 mL) at 0 °C. The reaction mixture was stirred until the Na disappeared.

The above solution of EtONa was added to the solution of S20 (1.32 g, 5 mmol, 1.0 equiv) in anhydrous ethanol (13 mL) at 0 °C, the resulting suspension was stirred at the same temperature for 4 hours. The reaction was quenched with 1 N aq. HCl to pH = 3 at 0 °C. The resulting mixture was extracted with CH2Cl2 (3 × 20 mL). The combined organic layers were washed with brine (40 mL), dried over Na2SO4, and concentrated under reduced pressure. Purification by column chromatography (silica
gel, petroleum ether/EtOAc = 10:1) afforded tertiary alcohol S21 (1.19 g, 90 %) as a white solid.

Rf = 0.40 (petroleum ether/EtOAc = 4:1);

1H NMR (400 MHz, CDCl3): δ 2.47 – 2.35 (m, 2 H), 2.32 – 2.21 (m, 2 H), 2.02 – 1.86 (m, 2 H), 1.78 – 1.52 (m, 6 H), 1.47 – 1.38 (m, 3 H), 1.24 – 1.12 (m, 1 H), 0.99 (s, 3 H), 0.98 – 0.91 (m, 2 H), 0.89 (s, 3 H), 0.86 (s, 3 H) ppm;

13C NMR (101 MHz, CDCl3): δ 210.8, 75.7, 57.5, 56.3, 55.4, 42.3, 42.1, 41.6, 40.0, 37.6, 33.8, 33.4, 21.9, 21.6, 18.5, 18.1, 15.5 ppm;


[α]D = +27° (c = 0.2, CHCl3).

To a 50 mL round-bottom flask charged with methyltriphenylphosphonium bromide (1.14 g, 3.2 mmol, 1.6 equiv) and t-BuOK (340 mg, 3 mmol, 1.5 equiv) was added THF (10 mL) at 0 °C. The resulting yellow-green suspension was stirred vigorously at 0 °C for 30 minutes before the addition of the solution of ketone S21 (528 mg, 2 mmol, 1.0 equiv) in THF (10 mL). After 1 hour stirring at 0 °C, ice water (10 mL) was added to the reaction mixture. The resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (30 mL), dried over Na2SO4, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 10:1) afforded S22 (509 mg, 97 %) as a white solid.

Rf = 0.5 (petroleum ether/EtOAc = 20:1);

1H NMR (400 MHz, CDCl3): δ 4.85 – 4.63 (m, 2 H), 2.43 – 2.28 (m, 1 H), 2.05 (s, 2 H), 1.94 (td, J = 13.1, 4.9 Hz, 1 H), 1.82 – 1.46 (m, 7 H), 1.45 – 1.23 (m, 4 H), 1.19 – 1.09 (m, 1 H), 1.07 (dd, J = 12.7, 3.3 Hz, 1 H), 0.95 (s, 3 H), 0.93 – 0.78 (m, 1 H), 0.87 (s, 3 H), 0.85 (s, 3 H) ppm;

13C NMR (101 MHz, CDCl3): δ 146.5, 110.9, 72.3, 56.5, 56.2, 51.2, 42.3, 41.4, 39.8, 37.5, 35.3, 33.9, 33.5, 22.9, 21.9, 18.6, 18.6, 15.5 ppm;

HRMS (ESI): Calcd for C18H31O [M+H]+: 263.2375, found: 263.2365;

[α]D = –28° (c = 0.2, CHCl3);

Melting point: 61.0 – 62.3 °C.

To a solution of CuBr-SMe2 (150 mg, 0.73 mmol, 0.04 equiv) in THF (18 mL) was added a solution of MeMgBr (3.0 M in THF, 9 mL, 1.7 equiv) at 0 °C. The resulting mixture was stirred at the same temperature for 30 minutes before the addition of α, β-unsaturated ketone S23 (1.8 mL, 15.8 mmol, 1.0 equiv). The reaction mixture was
stirred at 0 °C for additional 35 minutes. DMPU (12 mL) and allyl bromide (7 mL) was then added dropwise sequentially, and the resulting solution was stirred at 0 °C for 40 minutes before being warmed to room temperature. After 4.5 hours stirring, the reaction was quenched with sat. aq. NH₄Cl (20 mL). The resulting mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (100 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded S24 (1.21 g, 46 %) as a colorless oil.

**Rf = 0.52 (petroleum ether/EtOAc = 10:1);**

**¹H NMR (400 MHz, CDCl₃):** \( \delta 5.82 – 5.70 \) (m, 1 H), 5.03 – 4.96 (m, 1 H), 4.95 – 4.90 (m, 1 H), 2.50 – 2.40 (m, 1 H), 2.37 – 2.20 (m, 3 H), 2.10 – 2.02 (m, 1 H), 1.95 – 1.75 (m, 2 H), 1.70 – 1.55 (m, 2 H), 1.07 (s, 3 H), 0.79 (s, 3 H) ppm;

**¹³C NMR (101 MHz, CDCl₃):** \( \delta 212.6, 138.0, 115.3, 61.1, 41.4, 39.8, 39.3, 29.6, 28.7, 23.2, 22.2 \) ppm;

**HRMS (ESI):** Calcd for C₁₁H₁₉O \([\text{M+H}]^+\): 167.1436, found: 167.1430.

To a 100 mL flame-dried round-bottom flask charged with ketone S24 (800 mg, 4.8 mmol, 1.0 equiv) was added Et₂O (25 mL). The resulting solution was cooled to 0 °C, and a solution of allylmagnesium bromide (1.0 M in ether, 7.2 mL, 7.2 mmol, 1.5 equiv) was added dropwise. After 4 hours stirring at room temperature, sat. aq. NH₄Cl (30 mL) was added to the reaction mixture. The resulting mixture was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 10:1) afforded S25 (960 mg, 96 %) as a colorless oil.

**Rf = 0.52 (petroleum ether/EtOAc = 10:1);**

**¹H NMR (400 MHz, CDCl₃):** \( \delta 5.87 – 5.69 \) (m, 2 H), 5.08 – 5.03 (m, 1 H), 5.03 – 4.93 (m, 2 H), 4.88 – 4.83 (m, 1 H), 2.32 – 2.20 (m, 2 H), 2.13 – 2.05 (m, 2 H), 1.72 – 1.59 (m, 1 H), 1.57 – 1.49 (m, 1 H), 1.39 – 1.26 (m, 3 H), 1.21 (brs, 1 H), 1.12 (dd, \( J = 13.4, 3.2 \) Hz, 1 H), 1.07 (dd, \( J = 5.3, 3.4 \) Hz, 1 H), 0.93 (s, 3 H), 0.84 (s, 3 H) ppm;

**¹³C NMR (101 MHz, CDCl₃):** \( \delta 141.9, 134.2, 119.0, 114.2, 74.7, 52.2, 47.0, 42.1, 38.1, 35.1, 32.4, 30.1, 21.9, 18.1 \) ppm;

**HRMS (ESI):** Calcd for C₁₄H₂₅O \([\text{M+H}]^+\): 209.1906, found: 209.1900.

A solution of Grubbs catalyst 2nd generation (162 mg, 0.2 mmol, 0.05 equiv) in CH₂Cl₂ (5 mL) was added to a solution of dialkene S25 (960 mg, 4.6 mmol, 1.0 equiv)
in CH$_2$Cl$_2$ (60 mL). The reaction mixture was stirred at room temperature overnight before being concentrated directly under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded 17 (530 mg, 64%) as a brown oil

R$_f$ = 0.49 (petroleum ether/EtOAc = 10:1);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.83 – 5.75 (m, 1 H), 5.58 – 5.51 (m, 1 H), 2.19 – 2.02 (m, 3 H), 2.00 – 1.91 (m, 1 H), 1.84 – 1.76 (m, 2 H), 1.51 – 1.35 (m, 3 H), 1.34 – 1.18 (m, 2 H), 1.01 (s, 3 H), 0.86 (s, 3 H) ppm;

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 127.5, 123.6, 69.8, 46.9, 42.9, 42.6, 39.8, 32.7, 31.8, 22.7, 21.7, 18.2 ppm;


To a solution of S44 (1.5 g, 5.95 mmol, 1.0 equiv), zinc powder (583 mg, 8.9 mmol, 1.5 equiv), and ammonium acetate (688 mg, 8.9 mmol, 1.5 equiv) in THF (24 mL) was added allyl bromide (0.77 mL, 8.9 mmol, 1.5 equiv) dropwise at 0 °C. After 10 min stirring at the same temperature, the reaction mixture was quenched by addition of 20 mL of sat. aq. NaHCO$_3$ and allowed to warm to room temperature over 20 min. The resulting mixture was extracted with EtOAc (3 times). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and concentrated under reduced pressure to afford S38 (1.76 g, quant. yield) which was used further without purification.

R$_f$ = 0.20 (petroleum ether/EtOAc = 4:1);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.66 – 7.61 (m, 2 H), 7.34 – 7.28 (m, 2 H), 5.86 – 5.73 (m, 1 H), 5.22 – 5.09 (m, 2 H), 3.60 – 3.52 (m, 2 H), 2.64 (td, $J$ = 11.9, 2.9 Hz, 2H), 2.43 (s, 3 H), 2.19 (d, $J$ = 7.6 Hz, 2 H), 1.78 – 1.67 (m, 2 H), 1.62 – 1.53 (m, 2 H), 1.29 (brs, 1 H) ppm;

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 143.6, 133.4, 132.2, 129.8, 127.8, 120.4, 68.17, 47.38, 42.3, 36.3, 21.7 ppm;

HRMS (ESI): Calcd for C$_{15}$H$_{23}$NO$_3$S [M+H]$^+$: 296.1315, found: 296.1308.
General procedure for the preparation of tertiary alkyl oxalates (General Procedure A)

The homoallylic tertiary alkyl oxalates were prepared according to a literature procedure from the corresponding tertiary alcohols.16

To a 10 mL flame-dried culture tube charged with tertiary alcohol (1.0 equiv) was added THF (0.2 M). The resulting solution was cooled to −78 °C, then a solution of "BuLi (2.5 M in hexane, 1.1 equiv) was added dropwise. After 15 min stirring at the same temperature, methyl chlorooxoacetate (1.7 equiv) was added dropwise. After 1 hour stirring at −78 °C, the reaction mixture was warmed to room temperature and quenched with sat. aq. NH₄Cl. The resulting mixture was extracted with EtOAc (3 times). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. Purification by column chromatography (silica gel) afforded the oxalates.

On 1.0 mmol scale, General Procedure A was followed with tertiary alcohol 1. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded 7 as a white solid (363 mg, 78%).

R_f = 0.51 (petroleum ether/EtOAc = 10:1);

1H NMR (400 MHz, CDCl₃): δ 5.77 – 5.69 (m, 1 H), 5.45 – 5.37 (m, 1 H), 3.84 (s, 3 H), 3.32 – 3.23 (m, 1 H), 3.18 (dd, J = 11.3, 4.5 Hz, 1 H), 3.07 – 2.98 (m, 1 H), 2.35 – 2.20 (m, 1 H), 2.06 – 1.94 (m, 2 H), 1.70 – 1.25 (m, 8 H), 1.03 (s, 3 H), 1.07 – 0.93 (m, 1 H), 0.92 (s, 3 H), 0.89 (s, 9 H), 0.78 (s, 3 H), 0.04 (s, 3 H) ppm;

13C NMR (101 MHz, CDCl₃): δ 158.7, 156.1, 127.1, 121.3, 86.1, 79.2, 55.1, 53.3, 53.0, 39.4, 37.7, 36.6, 35.4, 35.2, 28.8, 27.5, 25.9, 21.8, 18.1, 17.9, 16.3, 14.7, –3.8, –5.0 ppm.

HRMS (ESI): Calcd for C₂₆H₄₈O₅SiN [M+NH₄]⁺: 482.3302, found: 482.3315;

[α]_D²⁷° = −5.1° (c = 0.118, CHCl₃);

Melting point: 110 – 111 °C.

On 0.27 mmol scale, General Procedure A was followed with tertiary alcohol S8. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded S26 as a colorless oil (66 mg, 73%).

R_f = 0.43 (petroleum ether/EtOAc = 20:1);

1H NMR (400 MHz, CDCl₃): δ 5.80 – 5.67 (m, 1 H), 5.47 – 5.34 (m, 1 H), 3.84 (s, 3 H), 3.27 (dd, J = 19.1, 4.9 Hz, 1 H), 3.08 – 2.95 (m, 1 H), 2.34 – 2.16 (m, 1 H), 2.13 – 1.93 (m, 2 H), 1.73 – 1.49 (m, 3 H), 1.46 – 1.23 (m, 5 H), 1.20 – 1.07 (m, 1 H), 1.04 (s, 3 H), 0.97 – 0.75 (m, 2 H), 0.87 (s, 3 H), 0.85 (s, 3 H) ppm;
\[^{13}\text{C NMR (101 MHz, CDCl}_3\): \(\delta\) 158.9, 156.3, 127.4, 121.4, 86.7, 56.1, 53.4, 53.2, 41.9, 39.6, 37.1, 35.5, 33.8, 33.3, 2.1, 21.8, 18.5, 18.1, 14.8 ppm;\
\[\text{HRMS (ESI): Calcd for } C_{20}H_{31}O_4 [M+H]^+ : 335.2222, \text{ found: 335.2306; } [\alpha]_D^{23} = +13.5^\circ (c = 0.2, \text{ CHCl}_3).\]

On 0.9 mmol scale, **General Procedure A** was followed with tertiary alcohol S16. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded S29 as a white solid (337 mg, 63 %). 

\[^{1}\text{H NMR (400 MHz, CDCl}_3\): \(\delta\) 5.77 – 5.69 (m, 1 H), 5.46 – 5.38 (m, 1 H), 3.98 (d, \(J = 10.6\) Hz, 1 H), 3.82 (s, 3 H), 3.56 (d, \(J = 10.6\) Hz, 1 H), 3.31 – 3.20 (m, 2 H), 2.98 (dt, \(J = 14.9, 3.0\) Hz, 1 H), 2.35 – 2.20 (m, 1 H), 2.10 – 1.93 (m, 2 H), 1.87 – 1.55 (m, 5 H), 1.54 – 1.44 (m, 1 H), 1.28 (dd, \(J = 11.6, 5.7\) Hz, 1 H), 1.14 (s, 3 H), 1.24 – 1.07 (m, 1 H), 1.02 (s, 3 H), 1.06 – 0.95 (m, 1 H), 0.87 (s, 9 H), 0.84 (s, 9 H), 0.03 (s, 3 H), 0.02 (s, 3 H), -0.02 (s, 3 H) ppm;\
\[^{13}\text{C NMR (101 MHz, CDCl}_3\): \(\delta\) 158.8, 156.3, 127.1, 121.5, 86.3, 79.6, 65.5, 56.1, 53.2, 53.2, 43.7, 38.5, 37.0, 36.6, 35.2, 27.7, 26.0, 26.0, 23.9, 22.0, 20.2, 18.3, 18.2, 14.5, – 3.7, – 4.9, – 5.6, – 5.7 ppm;\
\[\text{HRMS (ESI): Calcd for } C_{32}H_{59}O_6Si_2 [M+H]^+ : 595.3850, \text{ found: 595.3850; } [\alpha]_D^{23} = -1^\circ (c = 0.2, \text{ CHCl}_3);\
\text{Melting point: 117.1 – 117.8 }^\circ\text{C.}\]

On 2.0 mmol scale, **General Procedure A** was followed with tertiary alcohol S22. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded S30 as a colorless oil (613 mg, 88 %). 

\[^{1}\text{H NMR (400 MHz, CDCl}_3\): \(\delta\) 4.74 – 4.53 (m, 2 H), 3.85 (s, 3 H), 3.39 (dd, \(J = 14.2, 2.1\) Hz, 1 H), 2.91 – 2.77 (m, 1 H), 2.42 – 2.31 (m, 1 H), 2.05 – 1.94 (m, 1 H), 1.92 (dd, \(J = 14.0, 1.4\) Hz, 1 H), 1.76 – 1.48 (m, 5 H), 1.46 – 1.32 (m, 4 H), 1.21 – 1.11 (m, 2 H), 0.88 (s, 3 H), 0.96 – 0.89 (m, 2 H), 0.87 (s, 3 H), 0.83 (s, 3 H) ppm;\
\[^{13}\text{C NMR (101 MHz, CDCl}_3\): \(\delta\) 158.9, 155.9, 144.3, 110.2, 89.4, 57.6, 56.2, 53.3, 43.7, 42.0, 39.7, 37.5, 35.1, 34.6, 33.7, 33.3, 22.2, 21.9, 18.6, 18.1, 15.2 ppm;\
\[\text{HRMS (ESI): Calcd for } C_{21}H_{32}O_4K [M+K]^+ : 387.1934, \text{ found: 387.1801; } [\alpha]_D^{23} = -34^\circ (c = 1, \text{ MeOH).}\]
On 0.4 mmol scale, **General Procedure A** was followed with tertiary alcohol 17. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded S31 as a colorless oil (63.8 mg, 60 %). 

**Rf** = 0.4 (petroleum ether/EtOAc = 20:1);

**1H NMR (400 MHz, CDCl3):** δ 5.78 – 5.67 (m, 1 H), 5.48 – 5.35 (m, 1 H), 3.83 (s, 3 H), 3.22 (dd, J = 18.9, 4.8 Hz, 1 H), 2.88 (ddd, J = 14.6, 5.1, 2.7 Hz, 1 H), 2.30 – 2.17 (m, 1 H), 2.14 – 1.95 (m, 2 H), 1.60 – 1.36 (m, 4 H), 1.34 – 1.20 (m, 2 H), 1.01 (s, 3 H), 0.90 (s, 3 H) ppm;

**13C NMR (101 MHz, CDCl3):** δ 158.9, 156.4, 127.4, 121.6, 86.6, 53.3, 48.5, 42.1, 35.0, 34.2, 32.1, 22.7, 21.6, 17.9 ppm;


On 1.0 mmol scale, **General Procedure A** was followed with 1-methylcyclohex-3-en-1-ol.24,25 Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded S32 as a colorless oil (119 mg, 60 %). 

**Rf** = 0.4 (petroleum ether/EtOAc = 20:3);

**1H NMR (400 MHz, CDCl3):** δ 5.72 – 5.65 (m, 1 H), 5.58 – 5.51 (m, 1 H), 3.86 (s, 3 H), 2.68 – 2.58 (m, 1 H), 2.39 – 2.30 (m, 1 H), 2.29 – 2.21 (m, 1 H), 2.20 – 2.04 (m, 2 H), 1.88 – 1.79 (m, 1 H), 1.61 (s, 3 H) ppm;

**13C NMR (101 MHz, CDCl3):** δ 159.0, 156.9, 126.2, 123.4, 85.1, 53.4, 36.6, 32.3, 23.8, 23.1 ppm;

**HRMS (ESI):** Calcd for C10H14O4Na [M+Na]+: 221.0790, found: 221.0839.

To a solution of tertiary alcohol S35 (315 mg, 2.5 mmol, 1.0 equiv) in CH2Cl2 (25 mL) was added Et3N (0.42 mL, 3.0 mmol, 1.2 equiv) and DMAP (31 mg, 0.25 mmol, 0.1 equiv) at 0 °C. Methyl oxalyl chloride (0.28 mL, 3.0 mmol, 1.2 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature. After 1 hour stirring at room temperature, the reaction mixture was quenched with water (10 mL). The resulting mixture was extracted with CH2Cl2 (3 × 20 mL). The combined organic layers were washed with brine (30 mL), dried over Na2SO4, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded S36 as a colorless oil (376 mg, 71 %).
$R_f = 0.53$ (petroleum ether/EtOAc = 10:1);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.82 – 5.68 (m, 1 H), 5.13 – 5.03 (m, 2 H), 3.84 (s, 3 H), 2.76 (dt, $J = 7.3, 1.2$ Hz, 2 H), 2.24 – 2.10 (m, 2 H), 1.87 – 1.54 (m, 6 H) ppm;

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 158.9, 156.9, 132.8, 118.7, 96.2, 53.3, 41.0, 37.0, 23.8 ppm;

HRMS (ESI): Calcd for C$_{11}$H$_{16}$K$_2$O$_4$ [M+K]$^+$: 251.0680, found: 221.0679.

To a solution of tertiary alcohol S$_38$ (1 g, 3.4 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (34 mL) was added Et$_3$N (0.57 mL, 4.1 mmol, 1.2 equiv) and DMAP (42 mg, 0.34 mmol, 0.1 equiv) at 0 °C. Methyl oxalyl chloride (0.38 mL, 4.1 mmol, 1.2 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature. After 1 hour stirring at room temperature, the reaction mixture was quenched with water (20 mL). The resulting mixture was extracted with CH$_2$Cl$_2$ (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over Na$_2$SO$_4$, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 10:1) afforded S$_39$ as a white solid (940 mg, 72.8%).

$R_f = 0.25$ (petroleum ether/EtOAc = 4:1);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.66 – 7.61 (m, 2 H), 7.35 – 7.29 (m, 2 H), 5.71 – 5.59 (m, 1 H), 5.16 – 5.04 (m, 2 H), 3.75 (s, 3 H), 3.61 (dt, $J = 12.1, 3.0$ Hz, 2 H), 2.68 (d, $J = 7.4$ Hz, 2 H), 2.57 (td, $J = 12.2, 2.6$ Hz, 2 H), 2.43 (S, 3 H), 2.36 (dd, $J = 14.7, 2.4$ Hz, 2 H), 1.84 – 1.71 (m, 2 H) ppm;

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 158.2, 156.2, 143.6, 133.3, 130.5, 129.7, 127.7, 120.2, 84.3, 53.3, 41.8, 41.3, 33.1, 21.6 ppm;

HRMS (ESI): Calcd for C$_{18}$H$_{24}$N$_2$O$_6$S [M+H]$^+$: 382.1319, found: 382.1323.

To a solution of tertiary alcohol S$_41$ (995 mg, 5.4 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (54 mL) was added Et$_3$N (0.9 mL, 6.5 mmol, 1.2 equiv) and DMAP (66 mg, 0.54 mmol, 0.1 equiv) at 0 °C. Methyl oxalyl chloride (0.6 mL, 6.5 mmol, 1.2 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature. After 1 hour stirring at room temperature, the reaction mixture was quenched with water (40 mL). The resulting mixture was extracted with CH$_2$Cl$_2$ (3 × 40 mL). The combined organic layers were washed with brine (100 mL), dried over Na$_2$SO$_4$, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded S$_42$ as a colorless oil (864 mg, 59.2%).

$R_f = 0.63$ (petroleum ether/EtOAc = 10:1);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.80 – 5.67 (m, 1 H), 5.15 – 5.07 (m, 2 H), 3.86 (s, 3 H), 2.68 – 2.63 (m, 2 H), 1.91 – 1.83 (m, 4 H), 1.37 – 1.20 (m, 8 H), 0.90 (t, $J = 7.0$ Hz, 6 H) ppm;
$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 159.0, 156.5, 132.3, 118.9, 91.6, 53.2, 39.6, 34.8, 25.3, 22.9, 14.0 ppm;

General procedure for the reductive radical [3+2] annulation (General Procedure B)

A 10 mL oven-dried reaction culture tube charged with the oxalate (1.0 equiv), Zn (600 mesh, 5.0 equiv), PBI (5.0 equiv), and TEMPO (4.0 equiv) was moved into a glovebox. TMSCl (2.0 equiv), anhydrous MgCl₂ (2.5 equiv), benzyl acrylate (1.0 equiv), and DMA (0.05 M) were added. The tube was capped with a rubber septum before being moved out of the glovebox. The resulting mixture was stirred vigorously at 40 °C for 16 hours. The reaction mixture was directly loaded onto a preparative TLC (silica gel) for purification.

On 0.03 mmol scale, General Procedure B was followed with oxalate 7 and benzyl acrylate. Purification by preparative TLC (petroleum ether/EtOAc = 20:1) afforded 9 as colorless oil (8.5 mg, 54%, C16 dr = 2 : 1), along with byproduct 10 (2.7 mg, 13%) as a white solid.

For characterization, two isomers of 9 was separated by analytical TLC (petroleum ether/EtOAc = 100:1).

**Major isomer**

R_f = 0.6 (petroleum ether/EtOAc = 20:1);

**¹H NMR (400 MHz, CDCl₃):** δ 7.43 – 7.27 (m, 5 H), 5.09 (s, 2 H), 3.15 (dd, J = 11.4, 4.7 Hz, 1 H), 2.66 (dd, J = 9.0, 5.9 Hz, 1 H), 2.48 (bars, 1 H), 1.87 (d, J = 11.7 Hz, 1H), 1.81 – 1.68 (m, 2 H), 1.67 – 1.42 (m, 10 H), 1.40 – 1.15 (m, 3 H), 1.05 – 0.93 (m, 1 H), 0.98 (s, 3 H), 0.92 – 0.80 (m, 3 H), 0.88 (s, 9 H), 0.73 (s, 3 H), 0.78 – 0.66 (m, 1 H), 0.03 (s, 3 H), 0.03 (s, 3 H) ppm;

**¹³C NMR (101 MHz, CDCl₃):** δ 177.4, 136.5, 128.7, 128.2, 79.6, 66.3, 56.1, 55.3, 45.7, 45.0, 44.9, 41.4, 41.2, 39.5, 39.0, 38.8, 38.2, 31.4, 28.9, 27.9, 26.1, 20.9, 18.6, 18.3, 17.7, 16.2, – 3.6, – 4.8 ppm;

**HRMS (ESI):** Calcd for C₃₃H₅₂O₃SiNa [M+Na]+: 547.3583, found: 547.3565;

[α]_D^25 = – 55° (c = 0.1, CDCl₃);

**Melting point:** 81.2 – 82.6 °C.

**Minor isomer:**

R_f = 0.6 (petroleum ether/EtOAc = 20:1);

**¹H NMR (400 MHz, CDCl₃):** δ 7.43 – 7.28 (m, 5 H), 5.19 – 5.07 (m, 2 H), 3.15 (dd, J = 11.4, 4.8 Hz, 1 H), 2.97 – 2.88 (m, 1 H), 2.59 – 2.52 (m, 1 H), 2.05 – 2.00 (m, 1 H), 1.95 (ddd, J = 13.7, 6.1, 2.0 Hz, 1 H), 1.84 – 1.69 (m, 1 H), 1.67 – 1.53 (m, 5 H), 1.52 – 1.41 (m, 5 H), 1.40 – 1.23 (m, 2 H), 1.14 – 0.95 (m, 2 H), 0.97 (s, 3H), 0.88 (s, 12 H), 0.78 – 0.69 (m, 1 H), 0.72 (s, 3 H), 0.03 (s, 3 H), 0.03 (s, 3 H) ppm;

**¹³C NMR (101 MHz, CDCl₃):** δ 174.8, 136.5, 128.6, 128.4, 128.2, 79.6, 66.2, 57.1, 55.3, 45.7, 44.4, 42.0, 41.8, 40.7, 40.1, 39.5, 39.0, 38.7, 28.9, 27.9, 27.7, 26.1, 20.5, 18.3, 18.1, 17.8, 16.1, – 3.6, – 4.8 ppm;
HRMS (ESI): Caled for C_{33}H_{52}O_{3}SiNa [M+Na]^+: 547.3583, found: 547.3565; 
|α|_D^{25} = − 47° (c = 0.1, CDCl3); 
Melting point: 113.0 – 114.2 °C.

R_f = 0.6 (petroleum ether/EtOAc = 10:1);

^1^H NMR (400 MHz, CDCl3): δ 7.40 – 7.27 (m, 10 H), 5.15 – 5.03 (m, 4 H), 3.14 (dd, J = 11.3, 4.7 Hz, 1 H), 2.62 (dd, J = 9.2, 5.9 Hz, 1 H), 2.45 – 2.24 (m, 3 H), 1.83 – 1.67 (m, 3 H), 1.66 – 1.42 (m, 10 H), 1.39 – 1.20 (m, 3 H), 1.05 – 0.77 (m, 5H), 0.89 (s, 12 H), 0.76 – 0.64 (m, 1 H), 0.72 (s, 3 H), 0.04 (s, 3 H), 0.03 (s, 3 H) ppm;

^1^C NMR (101 MHz, CDCl3): δ 177.1, 173.7, 136.4, 136.2, 128.7, 128.7, 128.7, 128.4, 128.3, 128.2, 128.0, 79.6, 66.3, 66.3, 56.0, 55.2, 45.0, 44.8, 44.8, 40.7, 40.6, 39.5, 39.2, 39.1, 38.8, 38.7, 32.0, 29.9, 29.0, 27.9, 26.1, 20.7, 18.3, 17.6, 16.2, −3.4, −4.8 ppm;

HRMS (ESI): Caled for C_{43}H_{63}O_{5}Si [M+H]^+: 687.4415, found: 687.4434; 
|α|_D^{25} = − 37.6° (c = 0.125, CDCl3);
Melting point: 83.3 – 84.7 °C.

On 0.03 mmol scale, General Procedure B was followed with oxalate 7 and acrylonitrile. Purification by preparative TLC (petroleum ether/EtOAc = 10:1) afforded 13 as white solid (6.0 mg, 48%, C16 dr = 1.2 : 1).

For characterization, two isomers of 13 was separated by reverse-phase preparative HPLC (99% CH3CN/H2O).

Major isomer
R_f = 0.43 (petroleum ether/EtOAc = 20:1);

^1^H NMR (400 MHz, CDCl3): δ 3.14 (dd, J = 11.4, 4.8 Hz, 1 H), 2.63 (dd, J = 8.8, 5.1 Hz, 2 H), 2.05 (d, J = 12.0 Hz, 1 H), 1.85 (dd, J = 13.7, 9.5, 2.2 Hz, 1 H), 1.75 (dt, J = 13.0, 3.5 Hz, 1 H), 1.70 – 1.57 (m, 4 H), 1.54 – 1.45 (m, 3 H), 1.43 – 1.23 (m, 4 H), 1.05 – 0.91 (m, 1 H), 0.98 (s, 3 H), 0.88 (s, 12 H), 0.87 – 0.76 (m, 2 H), 0.73 (s, 3 H), 0.76 – 0.67 (m, 1 H), 0.03 (s, 3 H), 0.02 (s, 3 H) ppm;

^1^C NMR (101 MHz, CDCl3): δ 125.0, 79.5, 55.9, 55.2, 46.5, 45.3, 42.8, 40.8, 39.5, 39.0, 38.7, 38.4, 30.5, 30.2, 28.9, 27.8, 26.1, 20.8, 18.3, 18.2, 17.7, 16.1, −3.6, −4.8 ppm.

HRMS (ESI): Caled for C_{26}H_{45}NOSiK [M+K]^+: 454.2908, found: 454.2918;
|α|_D^{25} = − 58° (c = 0.05, CDCl3);
Melting point: 165.2 – 168.1 °C.

Minor isomer
R_f = 0.43 (petroleum ether/EtOAc = 20:1);
On 0.03 mmol scale, **General Procedure B** was followed with oxalate 7 and ethyl acrylate. Purification by preparative TLC (petroleum ether/EtOAc =20:1) afforded 14 as white solid (5.7 mg, 41%, C16 H16 O5 Si = 1.5 : 1).

For characterization, two isomers of 14 was separated by reverse-phase preparative HPLC (99% CH3CN/H2O).

**Major isomer**

Rf = 0.48 (petroleum ether/EtOAc = 20:1);

**1H NMR (400 MHz, CDCl3):** δ 3.16 (dd, J = 11.3, 4.8 Hz, 1 H), 2.88 – 2.78 (m, 1 H), 2.49 (brs, 1 H), 2.08 (dd, J = 12.0, 1.3 Hz, 1 H), 1.88 – 1.75 (m, 3 H), 1.72 – 1.44 (m, 8 H), 1.39 – 1.24 (m, 2 H), 1.05 – 0.92 (m, 2 H), 1.00 (s, 3 H), 0.88 (s, 12 H), 0.91 – 0.82 (m, 1 H), 0.79 – 0.66 (m, 1 H), 0.73 (s, 3 H), 0.03 (s, 3 H), 0.03 (s, 3 H) ppm;

**13C NMR (101 MHz, CDCl3):** δ 122.3, 79.5, 56.5, 55.2, 45.1, 44.6, 41.0, 39.5, 39.4, 39.3, 39.0, 38.7, 29.0, 28.9, 27.8, 26.1, 20.6, 18.3, 18.1, 17.7, 16.1, – 3.6, – 4.8 ppm;

**HRMS (ESI):** Calcd for C28H45NOSi [M+K]⁺: 454.2908, found: 454.2918; [α]D28 = −62° (c = 0.1, CDCl3);

**Melting point:** 177.7 – 179.8 °C.

**Minor isomer**

Rf = 0.48 (petroleum ether/EtOAc = 20:1);

**1H NMR (400 MHz, CDCl3):** δ 4.10 (q, J = 7.1, 6.4 Hz, 2 H), 3.15 (dd, J = 11.4, 4.7 Hz, 1 H), 2.58 (dd, J = 9.1, 5.9 Hz, 1 H), 2.45 (brs, 1 H), 1.86 (d, J = 11.7 Hz, 1 H), 1.77 (dt, J = 13.2, 3.5 Hz, 1 H), 1.69 (dd, J = 13.4, 5.9 Hz, 1 H), 1.65 – 1.57 (m, 4 H), 1.55 – 1.41 (m, 6 H), 1.40 – 1.29 (m, 1 H), 1.24 (t, J = 7.1 Hz, 3 H), 1.22 – 1.16 (m, 1 H), 0.99 (s, 3 H), 1.05 – 0.80 (m, 2 H), 0.88 (s, 12 H), 0.79 – 0.66 (m, 1 H), 0.73 (s, 3 H), 0.03 (s, 3 H), 0.02 (s, 3 H) ppm;

**13C NMR (101 MHz, CDCl3):** δ 177.7, 79.7, 60.4, 56.1, 55.3, 45.7, 45.0, 44.9, 41.4, 41.2, 39.5, 39.0, 38.8, 38.2, 31.5, 28.9, 27.9, 26.1, 20.9, 18.7, 18.3, 17.7, 16.2, 14.4, – 3.6, – 4.8 ppm;

**HRMS (ESI):** Calcd for C28H45O3Si [M+H]⁺: 463.3608, found: 463.3597; [α]D28 = −43.6° (c = 0.14, CDCl3);

**Melting point:** 98.3 – 101.1 °C.

---

**S50**
\([\alpha]^{25.8}_D = -19.2^\circ (c = 0.0625, \text{CDCl}_3)\);

**Melting point:** 127.8 – 130.1 °C.

On 0.163 mmol scale, **General Procedure B** was followed with oxalate S27 and benzyl acrylate. Purification by preparative TLC (petroleum ether/EtOAc = 20:1) afforded 15 as colorless oil (31 mg, 48 %, C16 dr = 1.9 : 1).

For characterization, two isomers of 15 was separated by analytical TLC (petroleum ether/EtOAc = 100:1).

**Major isomer**

\(R_f = 0.57\) (petroleum ether/EtOAc = 20:1); 

\(^1\text{H NMR (400 MHz, CDCl}_3\): \(\delta 7.40 – 7.27\) (m, 5 H), 5.10 (s, 2 H), 2.66 (dd, \(J = 8.8, 6.2\) Hz, 1 H), 2.48 (brs, 1 H), 1.89 (d, \(J = 11.6\) Hz, 1 H), 1.79 (d, \(J = 12.7\) Hz, 1 H), 1.74 – 1.25 (m, 13 H), 1.21 (dd, \(J = 11.5, 4.8\) Hz, 1 H), 1.12 (td, \(J = 13.4, 4.4\) Hz, 1 H), 1.06 – 0.92 (m, 1 H), 0.99 (s, 3 H), 0.91 – 0.62 (m, 2 H), 0.88 (s, 3 H), 0.80 (s, 3 H) ppm;  

\(^{13}\text{C NMR (101 MHz, CDCl}_3\): \(\delta 177.5, 136.5, 128.7, 128.2, 66.2, 56.3, 56.2, 45.7, 45.3, 45.1, 42.2, 41.5, 41.1, 40.6, 39.4, 38.3, 33.8, 33.4, 31.5, 21.8, 20.9, 18.8, 18.5, 17.6\) ppm;  

**HRMS (ESI):** Calcd for C\(_{27}\)H\(_{39}\)O\(_2\) [M+H\(^+\)]': 395.2950, found: 395.2774;  

\([\alpha]^{24.5}_D = -53^\circ (c = 0.175, \text{CDCl}_3)\);

**Melting point:** 50 – 52.9 °C.

**Minor isomer**

\(R_f = 0.48\) (petroleum ether/EtOAc = 20:1);  

\(^1\text{H NMR (400 MHz, CDCl}_3\): \(\delta 7.42 – 7.28\) (m, 5 H), 5.16 – 5.10 (m, 2 H), 2.96 – 2.88 (m, 1 H), 2.55 (brs, 1 H), 2.04 (d, \(J = 10.8\) Hz, 1 H), 1.96 (ddd, \(J = 13.7, 6.1, 2.1\) Hz, 1 H), 1.79 – 1.72 (m, 1 H), 1.65 – 1.0 (m, 14 H), 0.98 (s, 3 H), 0.93 – 0.88 (m, 1 H), 0.84 (s, 3 H), 0.82 – 0.68 (m, 2 H), 0.79 (s, 3 H) ppm;  

\(^{13}\text{C NMR (101 MHz, CDCl}_3\): \(\delta 174.9, 136.5, 128.6, 128.3, 128.2, 66.2, 57.2, 56.3, 45.7, 44.6, 42.2, 42.2, 41.8, 40.9, 40.4, 40.1, 39.4, 33.8, 33.4, 27.7, 21.7, 20.6, 18.8, 18.0, 17.8\) ppm;  

**HRMS (ESI):** Calcd for C\(_{27}\)H\(_{39}\)O\(_2\) [M+H\(^+\)]': 395.2950, found: 395.2774;  

\([\alpha]^{24.5}_D = -40^\circ (c = 0.075, \text{CDCl}_3)\);

**Melting point:** 67.2 – 69.1 °C.

On 0.1 mmol scale, **General Procedure B** was followed with oxalate S29 and benzyl acrylate. Purification by preparative TLC (petroleum ether/EtOAc = 20:1) afforded 16 as white solid (21.6 mg, 33 %, C16 dr = 2:1).
Two isomers of 16 could not be separated, and the NMR spectra of the mixture were provided.

Rf = 0.50 (petroleum ether/EtOAc = 20:1);

1H NMR (400 MHz, CDCl3): δ 7.43 – 7.27 (m, 8 H), 5.13 (s, 1 H), 5.08 (s, 2 H), 3.90 (d, J = 10.5 Hz, 2 H), 3.53 (d, J = 10.5 Hz, 2 H), 3.21 (dd, J = 11.7, 4.4 Hz, 2 H), 2.96 – 2.87 (m, 1 H), 2.65 (dd, J = 8.9, 5.8 Hz, 2H), 2.54 (brs, 1 H), 2.48 (brs, 1 H) ppm.

13C NMR (101 MHz, CDCl3): δ 177.4, 174.9, 136.5, 128.7, 128.4, 128.2, 79.8, 66.2, 66.2, 65.3, 57.4, 56.4, 55.9, 45.8, 45.2, 44.8 44.4, 43.7, 42.9, 42.2, 41.9, 41.3, 40.2, 40.0, 39.3, 39.2, 39.1, 37.7, 37.5, 31.4, 27.9, 27.9, 27.6, 26.1, 26.0, 23.9, 23.8, 23.2, 22.9, 18.8, 18.4, 18.2, 17.1, 17.0, –3.7, –4.9, –5.5, –5.6 ppm.


On 0.03 mmol scale, General Procedure B was followed with oxalate S30 and benzyl acrylate. Purification by preparative TLC (petroleum ether/EtOAc = 20:1) afforded 24 and S48 as white solid (5.0 mg, 41 %, 24 : S48 = 2.3 : 1).

For characterization, two isomers were separated by reverse-phase preparative HPLC (99% CH3CN/H2O).

Rf = 0.53 (petroleum ether/EtOAc = 20:1);

1H NMR (400 MHz, CDCl3): δ 7.41 – 7.27 (m, 5 H), 5.12 – 5.02 (m, 2 H), 2.53 (dd, J = 8.6, 6.0 Hz, 1 H), 2.26 (ddd, J = 13.5, 8.9, 2.2 Hz, 1 H), 1.71 – 1.45 (m, 11 H), 1.40 – 1.33 (m, 2 H), 1.32 – 1.18 (m, 3 H), 1.17 – 1.07 (m, 1 H), 1.0 – 0.92 (m, 1 H), 0.90 (s, 3 H), 0.88 (s, 3 H), 0.85 (s, 3 H), 0.83 – 0.74 (m, 1 H), 0.80 (s, 3 H) ppm;

13C NMR (101 MHz, CDCl3): δ 177.1, 136.3, 128.6, 128.6, 128.3, 66.2, 56.6, 56.2, 55.4, 52.2, 44.3, 43.8, 42.1, 41.2, 40.7, 39.8, 38.0, 37.8, 33.8, 33.3, 23.4, 22.1, 20.3, 20.1, 18.6, 15.6 ppm;


[a]25D = –37.6° (c = 0.085, CDCl3);

Melting point: 109 – 111 ºC.
\(^{13}\)C NMR (101 MHz, CDCl\(_3\))\: δ 177.4, 136.3, 128.7, 128.6, 128.3, 66.2, 56.4, 55.4, 53.6, 49.7, 46.2, 45.8, 44.9, 42.2, 41.3, 40.6, 40.3, 39.3, 33.8, 33.4, 24.1, 21.8, 21.0, 19.5, 18.8, 17.6 ppm;

HRMS (ESI): Calculated for C\(_{28}\)H\(_{40}\)O\(_2\)Na \([\text{M}+\text{Na}]^+\): 431.2926, found: 431.2967;

\([\alpha]\)\(^D\) 49.7° (c = 0.225, CDCl\(_3\));

Melting point: 99.2 – 101.5 °C.

On 0.1 mmol scale, General Procedure B was followed with oxalate S31 and benzyl acrylate. Purification by preparative TLC (petroleum ether/EtOAc = 20:1) afforded 18 as colorless oil (13 mg, 40%, C12 dr = 1.6:1).

Two isomers of 18 could not be separated, and the NMR spectra of the mixture were provided.

R\(_f\) = 0.47 (petroleum ether/EtOAc = 20:1);

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.42 – 7.28 (m, 10 H), 5.17 – 5.07 (m, 4 H), 2.94 (dt, J = 12.3, 6.2 Hz, 1 H), 2.69 (dd, J = 8.8, 6.2 Hz, 2 H), 2.58 – 2.51 (m, 1 H), 2.50 – 2.45 (m, 1 H), 2.04 – 1.93 (m, 2 H), 1.85 (d, J = 11.7 Hz, 1 H), 1.75 – 1.60 (m, 6 H), 1.56 – 1.32 (m, 19 H), 1.27 – 1.19 (m, 3 H), 1.18 – 1.0 (m, 7 H), 0.99 – 0.90 (m, 7 H), 0.89 – 0.85 (m, 7 H), 0.84 – 0.79 (m, 1 H) ppm;

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ 177.4, 174.8, 136.5, 128.7, 128.6, 128.2, 128.2, 66.3, 66.2, 51.8, 50.8, 45.8, 45.7, 45.1, 44.7, 44.3, 42.4, 42.3, 41.8, 41.2, 40.5, 40.2, 39.7, 39.8, 37.7, 35.0, 34.9, 33.9, 30.8, 27.2, 23.9, 23.8, 21.4, 21.0, 19.6, 19.1 ppm;

HRMS (ESI): Calculated for C\(_{22}\)H\(_{31}\)O\(_2\) [M+H]\(^+\): 327.2324, found: 327.2328.

To a 10 mL reaction culture tube charged with benzyl ester 18 (6.0 mg) was added 10% KOH in MeOH (1 mL). The reaction mixture was stirred vigorously at 60 °C. After 20 hours stirring, the reaction mixture was cooled to 0 °C and acidified with 1 N HCl (pH = 3). The resulting mixture was extracted with EtOAc (3 ×2 mL). The combined organic layers were washed with brine (5 mL), dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. Purification by column chromatography (silica gel; petroleum ether/EtOAc = 10:1) afforded acid 19 (3.0 mg, 70%, C2 dr = 11:1) as a white solid.

Major isomer of 19

R\(_f\) = 0.51 (petroleum ether/EtOAc = 5:1);

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 2.75 – 2.63 (m, 1 H), 2.54 – 2.50 (m, 1 H), 1.86 (d, J = 11.5 Hz, 1 H), 1.75 – 1.57 (m, 3 H), 1.55 – 1.45 (m, 3 H), 1.44 – 1.34 (m, 3 H), 1.27 – 1.06 (m, 3 H), 0.97 (s, 3 H), 0.88 (s, 3 H), 0.94 – 0.78 (m, 2 H) ppm;
\textbf{\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3})}: \(\delta\) 182.9, 50.8, 45.5, 45.1, 44.5, 42.4, 41.3, 39.8, 37.7, 35.0, 33.9, 30.8, 23.8, 21.4, 19.6 ppm;

\textbf{HRMS (ESI)}: Calcd for C\textsubscript{15}H\textsubscript{24}O\textsubscript{2}Na [M+Na]\textsuperscript{+}: 259.1674, found: 259.1699;

\textbf{Melting point}: 153.1 – 154.6 °C.

On 0.1 mmol scale, General Procedure B was followed with oxalate S32 and benzyl acrylate. Purification by preparative TLC (petroleum ether/EtOAc = 20:1) afforded 21 as colorless oil (9.3 mg, 36 %, C1 dr = 1.7 : 1).

Two isomers of 21 could not be separated, and the NMR spectra of the mixture were provided.

\(R_f = 0.48\) (petroleum ether/EtOAc = 20:1);

\textbf{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})}: \(\delta\) 7.41 – 7.28 (m, 10 H), 5.14 (s, 1 H), 5.10 (s, 2 H), 3.06 (dt, \(J = 12.1, 6.2\) Hz, 1 H), 2.69 (dd, \(J = 8.1, 6.4\) Hz, 2 H), 2.54 – 2.48 (m, 1 H), 2.47 – 2.42 (m, 1 H), 2.04 (ddd, \(J = 13.5, 6.1, 2.1\) Hz, 1 H), 1.78 – 1.68 (m, 3 H), 1.67 – 1.47 (m, 9 H), 1.46 – 1.21 (m, 11 H), 1.15 (d, \(J = 11.2\) Hz, 2 H), 1.03 (s, 4 H), 1.01 (s, 2 H), 0.86 – 0.78 (m, 1 H) ppm;

\textbf{\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3})}: \(\delta\) 177.1, 174.5, 136.5, 128.7, 128.6, 128.3, 128.2, 128.2, 66.2, 66.1, 47.8, 47.5, 47.4, 44.8, 41.3, 40.8, 40.2, 40.1, 39.9, 39.8, 39.2, 36.9, 31.7, 28.3, 27.9, 27.3, 20.2, 19.9 ppm;

\textbf{HRMS (ESI)}: Calcd for C\textsubscript{17}H\textsubscript{22}O\textsubscript{2}Na [M+Na]\textsuperscript{+}: 281.1518, found: 281.1465.

To a 10 mL reaction culture tube charged with benzyl ester 21 (51.6 mg, 0.2 mmol) was added 10 % KOH in MeOH (1 mL). The resulting mixture was stirred vigorously at 60 °C. After 20 hours stirring, the reaction mixture was cooled to 0 °C and acidified with 1 N HCl (to pH = 3). The resulting mixture was extracted with EtOAc (3 × 2 mL). The combined organic layers were washed with brine (5 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, and concentrated under reduced pressure. Purification by column chromatography (silica gel; petroleum ether/EtOAc = 10:1) afforded acid S33 (30.2 mg, 90%, C1 dr = 12:1) as a colorless oil.

\textbf{Major isomer of S33}

\(R_f = 0.51\) (petroleum ether/EtOAc = 4:1);

\textbf{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})}: \(\delta\) 2.67 (dd, \(J = 8.2, 6.5\) Hz, 1 H), 2.49 (brs, 1 H), 1.80-1.68 (m, 2 H), 1.66 – 1.53 (m, 3 H), 1.52 – 1.44 (m, 1 H), 1.43 – 1.36 (m, 1 H), 1.35 – 1.24 (m, 2 H), 1.16 (d, \(J = 11.2\) Hz, 1 H), 1.03 (s, 3 H) ppm;

\textbf{\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3})}: \(\delta\) 183.7, 47.4, 44.8, 41.4, 40.9, 39.9, 39.2, 31.7, 27.2, 20.2 ppm;

\textbf{HRMS (ESI)}: Calcd for C\textsubscript{10}H\textsubscript{17}O\textsubscript{2} [M+H]\textsuperscript{+}: 169.1229, found: 169.1228.
A solution of LAH (1.0 M in THF, 0.29 mL, 0.29 mmol, 2.5 equiv) was added dropwise to a solution of acid S33 (20 mg, 0.119 mmol, 1.0 equiv) in THF (1 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature. After 2 hours stirring, the reaction was quenched by adding Na₂SO₄.10H₂O slowly until no gas produced. The suspension was filtered through a short pad of Celite and rinsed with CH₂Cl₂ (2 mL). The filtrate was concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded S34 (14.1 mg, 77 %) as a colorless oil. 

\[ RF = 0.4 \text{ (petroleum ether/EtOAc = 4:1);} \]

\[^1\text{H NMR (400 MHz, CDCl}_3\text{):} \delta 3.40, 2.03, 1.92, 1.68, 1.58, 1.49, 1.42, 1.29, 1.28, 1.11 \text{ ppm;} \]

\[^13\text{C NMR (101 MHz, CDCl}_3\text{):} \delta 67.6, 45.7, 44.1, 40.6, 40.4, 39.5, 38.5, 32.0, 27.8, 20.5 \text{ ppm;} \]

HRMS (ESI): Calcd for C\(_{10}\)H\(_{18}\)O\(_2\)Na [M+Na\(^+\)]: 177.1255, found: 177.1272.

To a 10 mL reaction culture tube charged with alcohol S34 (6 mg, 0.039 mmol, 1.0 equiv), 3,5-dinitrobenzoyl chloride (13.4 mg, 0.058 mmol, 1.5 equiv), and DMAP (0.5 mg, 0.0039 mmol, 0.1 equiv) was added CH₂Cl₂ (0.5 mL). Et₃N (11 \(\mu\)L, 0.078 mmol, 2.0 equiv) was then added. The reaction mixture was stirred at room temperature for 2 hours before being directly loaded onto a preparative TLC. Purification by this preparative TLC (silica gel, petroleum ether/EtOAc = 10:1) afforded ester 22 (12 mg, 88%) as light yellow solid. 

\[ RF = 0.5 \text{ (petroleum ether/EtOAc = 10:1);} \]

\[^1\text{H NMR (400 MHz, CDCl}_3\text{):} \delta 9.24, 9.17, 4.31, 2.32, 2.11, 1.78, 1.70, 1.11, 1.03 \text{ ppm;} \]

\[^13\text{C NMR (101 MHz, CDCl}_3\text{):} \delta 162.8, 134.3, 129.5, 122.5, 71.0, 44.1, 41.7, 40.9, 40.4, 39.3, 38.9, 31.8, 27.7, 20.3 \text{ ppm;} \]


Melting point: 56.3 – 58.9 °C
On 0.1 mmol scale, General Procedure B was followed with oxalate S35 and benzyl acrylate. Purification by preparative TLC (petroleum ether/EtOAc = 20:1) afforded S37 as colorless oil (12.8 mg, 47%, dr = 4.0:1).

Two isomers of S37 could not be separated, and the NMR spectra of the mixture were provided.

\[ R_f = 0.51 \text{ (petroleum ether/EtOAc = 20:1);} \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\]: \delta 7.43 - 7.28 (m, 14 H), 5.13 (s, 1 H), 5.12 - 5.10 (m, 4 H), 3.01 - 2.93 (m, 3 H), 2.50 - 2.37 (m, 3 H), 2.35 - 2.20 (m, 1 H), 1.99 (dd, \( J = 13.1, 9.1 \) Hz, 3 H), 1.85 (dd, \( J = 8.9, 3.3 \) Hz, 1 H), 1.80 (dd, \( J = 12.6, 7.5 \) Hz, 1 H), 1.74 - 1.67 (m, 5 H), 1.66 - 1.54 (m, 16 H), 1.51 - 1.31 (m, 8 H), 1.21 (dd, \( J = 12.5, 10.1 \) Hz, 1 H), 1.06 (d, \( J = 6.5 \) Hz, 2 H), 0.91 (dd, \( J = 7.0, 2.3 \) Hz, 7 H) ppm; \]

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3\]: \delta 176.2, 175.3, 136.3, 128.6, 128.5, 128.3, 128.2, 128.1, 66.1, 66.1, 51.9, 50.0, 49.9, 48.1, 47.6, 47.3, 43.3, 41.1, 40.6, 40.3, 40.0, 39.8, 38.8, 36.3, 24.6, 24.4, 24.3, 20.0, 17.1 ppm; \]

HRMS (ESI): Calcd for C\textsubscript{18}H\textsubscript{2}SO\textsubscript{2} [M+H]+: 273.1849, found: 273.1843.

On 0.1 mmol scale, General Procedure B was followed with oxalate S39 and benzyl acrylate. Purification by preparative TLC (petroleum ether/EtOAc = 5:1) afforded S40 as colorless oil (17.2 mg, 39%, dr = 2.1:1).

Two isomers of S40 could not be separated, and the NMR spectra of the mixture were provided.

\[ R_f = 0.46 \text{ (petroleum ether/EtOAc = 5:1);} \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\]: \delta 7.65 - 7.60 (m, 5 H), 7.39 - 7.28 (m, 17 H), 5.09 (s, 2 H), 5.06 (d, \( J = 3.1 \) Hz, 3 H), 3.08 - 2.95 (m, 6 H), 2.94 - 2.80 (m, 8 H), 2.43 (s, 8 H), 2.41 - 2.32 (m, 3 H), 2.28 - 2.15 (m, 2 H), 1.80 - 1.45 (m, 17 H), 1.27 - 1.15 (m, 3 H), 1.00 (d, \( J = 6.5 \) Hz, 3 H), 0.86 (d, \( J = 7.0 \) Hz, 6 H) ppm; \]

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3\]: \delta 176.2, 175.3, 136.3, 128.7, 128.6, 128.4, 128.3, 128.2, 127.8, 126.4, 66.4, 66.3, 51.0, 47.3, 47.2, 45.5, 44.5, 44.0, 43.8, 43.6, 41.2, 39.8, 39.7, 39.2, 38.3, 38.2, 38.0, 37.3, 36.8, 35.8, 21.7, 19.4, 16.9 ppm; \]

HRMS (ESI): Calcd for C\textsubscript{25}H\textsubscript{32}NO\textsubscript{4}S [M+H]+: 442.2047, found: 442.2049.
On 0.1 mmol scale, **General Procedure B** was followed with oxalate S42 and benzyl acrylate. Purification by preparative TLC (petroleum ether/EtOAc = 20:1) afforded S43 as colorless oil (16 mg, 48%, dr = 3.7:1).

Two isomers of S43 could not be separated, and the NMR spectra of the mixture were provided.

R_f = 0.52 (petroleum ether/EtOAc = 20:1);

^{1}H NMR (400 MHz, CDCl₃): δ 7.44 – 7.28 (m, 6 H), 5.13 (s, 0.54 H), 5.11 (d, J = 1.1 Hz, 2 H), 2.97 (dt, J = 16.9, 8.4 Hz, 1 H), 2.51 – 2.33 (m, 2 H), 2.31 – 2.18 (m, 0.6 H), 1.86 – 1.62 (m, 5 H), 1.43 – 1.35 (m, 2 H), 1.34 – 1.10 (m, 16 H), 1.02 (d, J = 6.4 Hz, 1 H), 0.93 – 0.86 (m, 11 H) ppm;

^{13}C NMR (101 MHz, CDCl₃): δ 176.0, 175.4, 136.5, 136.3, 128.6, 128.5, 128.2, 128.1, 66.1, 66.1, 51.7, 47.3, 47.2, 46.3, 44.5, 44.0, 42.5, 40.2, 40.0, 39.9, 39.6, 38.5, 37.6, 35.7, 27.5, 26.9, 26.7, 23.7, 19.3, 17.3, 14.3 ppm;

**HRMS (ESI):** Calcd for C$_{22}$H$_{35}$O$_{2}$ [M+H]$^{+}$: 331.2632, found: 331.2630.
Scheme 20. Collective syntheses of ent-kaurane- and beyerene-type diterpenoids

A. Synthesis of C3 oxygenated ent-kauranoids from 9

1. LAH, 0 °C
2. ArSeCN, BuP, then H2O2, 70% over 2 steps
3. LiBF4, 70%

4. Ac2O, Et3N
5. NMO, 93%

B. Synthesis of ent-kauranoids from 15

1. LAH, 0 °C
2. ArSeCN, BuP, then H2O2, 80% over 2 steps
3. Co(acac)3, PhSH, O2, 69%

C. Synthesis of C3, C19 dioxygenated ent-kauranoids from 16

1. LAH, 90%
2. ArSeCN, BuP, then H2O2, 99%

D. Synthesis of beyeranes from 24

1. Pd/C, H2
2. Ph(OAc)3, Cu(OAc)2, 51%
3. m-CPBA, 74%

X-ray of 27
X-ray of 26

X-ray of 32
X-ray of 35

X-ray of 37
X-ray of 38
A solution of LAH (1.0 M in THF, 0.32 mL, 0.32 mmol, 1.2 equiv) was added dropwise to a solution of benzyl ester 9 (138 mg, 0.264 mmol, 1.0 equiv) in THF (3 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 2 hours before being quenched by adding Na2SO4·10H2O slowly until no gas produced. The suspension was filtered through a short pad of Celite® and rinsed with CH2Cl2 (5 mL). The filtrate was concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded the alcohol (100 mg, 90%, C16 dr = 2 : 1) as a white solid.

nBu3P (108 μL, 0.43 mmol, 1.8 equiv) was added slowly to a solution of the above alcohol (100 mg, 0.238 mmol, 1.0 equiv) and 2-nitrophenyl selenocyanate (82 mg, 0.36 mmol, 1.5 equiv) in toluene (6 mL). The resulting solution was heated at 78 °C. After 1.5 h stirring, the reaction mixture was cooled to 0 °C and diluted with THF (12 mL). H2O2 (30% in water, 123 μL, 1.2 mmol, 5 equiv) was added. After 12 hours stirring at room temperature, the reaction mixture was quenched with water (10 mL). The resulting mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (50 mL), dried over Na2SO4, and concentrated under reduced pressure. Purification by column chromatography (silica gel containing 5% AgNO3; petroleum ether/EtOAc = 100:1) afforded alkene S45 (83 mg, 87%) as a white solid.

Rf = 0.32 (silica gel merged with 5% AgNO3, petroleum ether/EtOAc = 100:1);
1H NMR (400 MHz, CDCl3): δ 4.82–4.67 (m, 2 H), 3.16 (dd, J = 11.4, 4.7 Hz, 1 H), 2.63 (brs, 1 H), 2.07–2.01 (m, 2 H), 1.97 (d, J = 11.0 Hz, 1 H), 1.79 (dt, J = 13.1, 3.6 Hz, 1 H), 1.71–1.20 (m, 12 H), 1.09 (dd, J = 11.3, 5.1 Hz, 1 H), 1.01 (s, 3 H), 0.95–0.80 (m, 3 H), 0.88 (s, 9 H), 0.79–0.65 (m, 1 H), 0.74 (s, 3 H), 0.03 (s, 3 H), 0.02 (s, 3 H) ppm;
13C NMR (101 MHz, CDCl3): δ 156.2, 103.1, 79.7, 56.1, 55.4, 49.2, 44.2, 44.1, 41.5, 39.9, 39.6, 39.1, 38.9, 33.4, 28.9, 27.9, 26.1, 20.4, 18.4, 18.3, 17.8, 16.2, –3.6, –4.8 ppm;
HRMS (ESI): Caled for C26H46OSiK [M+K]+: 441.2956, found: 441.2972;
[a]D26 = --53° (c = 0.1, CHCl3);
Melting point: 136.2 – 138.1 °C.

To a 25 mL round-bottom flask charged with alkene S45 (56 mg, 0.14 mmol, 1.0 equiv) and LiBF4 (282 mg, 3.0 mmol, 20 equiv) was added CH2Cl2 (4 mL) and MeCN (2 mL). After 72 hours stirring at room temperature, the reaction was quenched by adding water (5 mL). The resulting mixture was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (10 mL), dried over Na2SO4, and concentrated under reduced pressure. Purification by column chromatography (silica
gel, petroleum ether/EtOAc = 20:1) afforded ent-3β-hydroxykaur-16-ene 25 (28.2 mg, 70%) as a white solid. 

$R_f = 0.40$ (petroleum ether/EtOAc = 10:1);

$^1$H NMR (400 MHz, CDCl$3$): $\delta$ 4.80 (brs, 1 H), 4.74 (s, 1 H), 3.20 (dd, $J = 10.9, 5.4$ Hz, 1 H), 2.64 (brs, 1 H), 2.10 – 2.01 (m, 2 H), 1.97 (d, $J = 11.3$ Hz, 1 H), 1.85 (dt, $J = 13.2, 3.6$ Hz, 1 H), 1.70 – 1.44 (m, 9 H), 1.43 – 1.21 (m, 2 H), 1.11 (dd, $J = 11.4, 5.0$ Hz, 1 H), 1.02 (s, 3 H), 0.98 (s, 3 H), 0.94 – 0.85 (m, 1 H), 0.83 – 0.70 (m, 1 H), 0.78 (s, 3 H) ppm;

$^{13}$C NMR (101 MHz, CDCl$3$): $\delta$ 155.8, 103.0, 79.1, 55.9, 55.2, 49.0, 44.0, 43.9, 41.2, 39.7, 39.0, 38.8, 38.7, 33.2, 28.4, 27.4, 20.0, 18.3, 17.6, 15.5 ppm;

HRMS (ESI): Calcd for C$_{20}$H$_{33}$O $[M+H]^+$: 289.2532, found: 289.2575; $[\alpha]^{26.5}_D = -67^\circ$ ($c = 0.11$, MeOH);

Melting point: 168.1 – 170.5 ℃.

![Diagram 1](image1)

$\text{Ac}_2\text{O} (9 \mu$L, 0.096 mmol, 1.2 equiv) and Et$_3$N (16.7 µL, 0.12 mmol, 1.5 equiv) were added sequentially to a solution of ent-3β-acetoxykaur-16-ene 25 (23 mg, 0.08 mmol, 1.0 equiv) and catalytic amount of DMAP (2 mg) in CH$_2$Cl$_2$ (1 mL) at 0 ℃. The reaction mixture was stirred at 0 ℃ for 2 hours before being quenched with ice water (2 mL). The resulting mixture was extracted with CH$_2$Cl$_2$ ($3 \times 2$ mL). The combined organic layers were washed with brine (5 mL), dried over Na$_2$SO$_4$, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 50:1) afforded ent-3β-acetoxykaur-16-ene 26 (24.8 mg, 94%) as a white solid.

$R_f = 0.54$ (petroleum ether/EtOAc = 20:1);

$^1$H NMR (400 MHz, CDCl$3$): $\delta$ 4.80 (m, 1 H), 4.74 (m, 1 H), 4.47 (dd, $J = 11.0, 5.6$ Hz, 1 H), 2.64 (brs, 1 H), 2.13 – 2.0 (m, 2 H), 2.05 (s, 3 H), 1.97 (d, $J = 11.3$ Hz, 1 H), 1.85 (dt, $J = 13.4, 3.6$ Hz, 1 H), 1.70 – 1.45 (m, 10 H), 1.43 – 1.34 (m, 1 H), 1.11 (dd, $J = 11.4, 5.1$ Hz, 1 H), 1.05 (s, 3 H), 1.01 – 0.92 (m, 2 H), 0.86 (s, 3 H), 0.85 (s, 3 H) ppm;

$^{13}$C NMR (101 MHz, CDCl$3$): $\delta$ 171.0, 155.7, 103.1, 81.0, 55.7, 55.3, 49.0, 44.0, 43.9, 41.0, 39.7, 38.9, 38.3, 37.7, 33.2, 28.3, 23.7, 21.3, 19.9, 18.3, 17.6, 16.6 ppm;

HRMS (ESI): Calcd for C$_{22}$H$_{38}$O$_2$N $[M+NH_4]^+$: 348.2903, found: 348.2884; $[\alpha]^{26.5}_D = -60.4^\circ$ ($c = 0.23$, CHCl$_3$);

Melting point: 151.2 – 153.6 ℃.

![Diagram 2](image2)
To a 10 mL reaction culture tube charged with ent-3β-acetoxykaur-16-ene 26 (4.0 mg, 0.012 mmol, 1.0 equiv) and NMO (10 mg, 0.04 mmol, 3.3 equiv) was added 1BuOH (0.56 mL) and THF (0.16 mL). Then a solution of K₂O₃S₄Et₂O (2 mg) in H₂O (80 μL) was added. The reaction mixture was stirred at room temperature overnight before being quenched with sat. aq. Na₂SO₄ (1 mL). The resulting mixture was stirred at room temperature for 15 minutes and extracted with EtOAc (3 × 1 mL). The combined organic layers were washed with brine (5 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 10:3) afforded ent-3β-acetoxykaur-16b,17-diol 27 (4.06 mg, 93%) as a white solid.

\[ R_f = 0.40 \text{ (petroleum ether/EtOAc = 1:1)}; \]

\[ ^1H \text{ NMR (400 MHz, CD}_{3}OD): \delta 4.44 \text{ (dd, } J = 11.4, 5.1 \text{ Hz, 1 H}), 3.70 \text{ (d, } J = 11.3 \text{ Hz, 1 H}), 3.59 \text{ (d, } J = 11.4 \text{ Hz, 1 H}), 2.03 \text{ (s, 3 H), 1.93 \text{ (d, } J = 11.2 \text{ Hz, 1 H}), 1.87 \text{ (dt, } J = 13.3, 3.6 \text{ Hz, 1 H}), 1.82 – 1.21 \text{ (m, 15 H), 1.09 \text{ (s, 3 H), 1.06 – 1.01 \text{ (m, 1 H), 1.00 – 0.91 \text{ (m, 2 H), 0.91 – 0.89 \text{ (m, 1 H), 0.88 \text{ (s, 3 H), 0.86 \text{ (s, 3 H)}} ppm};} \]

\[ ^13C \text{ NMR (101 MHz, CD}_{3}OD): \delta 171.4, 81.4, 81.1, 65.4, 56.5, 55.1, 52.3, 44.9, 44.1, 41.6, 38.7, 38.0, 37.4, 36.7, 27.3, 25.8, 23.2, 19.7, 19.6, 18.0, 16.7, 15.6 \text{ ppm}; \]

HRMS (ESI): Calcd for C₂₆H₄₆O₄Na [M+Na]⁺: 457.3114, found: 457.3111; \[ [\alpha]_D^{24.7} = 52° (c = 0.11, CHCl₃); \]

Melting point: 165.2 – 167.5 °C.

To a 10 mL reaction culture tube charged with benzyl ester 9 (50 mg, 0.095 mmol) was added 10 % KOH in MeOH (1 mL). The reaction mixture was stirred vigorously at 60 °C. After 20 hours stirring, the reaction mixture was cooled to 0 °C and acidified with 1 N HCl (to pH = 3). The resulting mixture was extracted with EtOAc (3 × 2 mL). The combined organic layers were washed with brine (5 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 10:1 with 5% acetic acid) afforded acid S46 (39.2 mg, 95%, C16 dr = 13 : 1) as a white solid.

\[ R_f = 0.63 \text{ (petroleum ether/EtOAc = 4:1)}; \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3): \delta 3.15 \text{ (dd, } J = 11.4, 4.7 \text{ Hz, 1 H), 2.64 \text{ (dd, } J = 9.1, 6.0 \text{ Hz, 1 H), 2.53 \text{ (brs, 1 H), 1.88 \text{ (d, } J = 11.8 \text{ Hz, 1 H), 1.78 \text{ (dt, } J = 13.2, 3.5 \text{ Hz, 1 H), 1.72 \text{ (dd, } J = 13.5, 6.0 \text{ Hz, 1H), 1.67 – 1.43 \text{ (m, 9 H), 1.40 – 1.23 \text{ (m, 3 H), 1.20 \text{ (dd, } J = 11.7, 5.0 \text{ Hz, 1H), 1.15 – 0.95 \text{ (m, 1 H), 0.99 \text{ (s, 3 H), 0.88 \text{ (s, 9 H), 0.94 – 0.80 \text{ (m, 3 H), 0.79 – 0.65 \text{ (m, 1 H), 0.73 \text{ (s, 3 H), 0.03 \text{ (s, 3 H), 0.03 \text{ (s, 3 H)}} ppm};} \]

\[ ^13C \text{ NMR (101 MHz, CDCl}_3): \delta 182.3, 79.6, 56.1, 55.3, 45.3, 45.1, 44.8, 41.5, 41.2, 39.5, 39.0, 38.8, 38.2, 31.4, 29.0, 27.9, 26.1, 20.9, 18.6, 18.3, 17.7, 16.2, – 3.6, – 4.8 \text{ ppm}; \]

HRMS (ESI): Calcd for C₂₆H₄₆O₃Si [M+Na]⁺: 457.3114, found: 457.3111; \[ [\alpha]_D^{24.7} = 45° (c = 0.1, CHCl₃); \]

Melting point: 224.2 – 226.5 °C.
BF₃·Et₂O (23 μL, 0.185 mmol, 5.0 equiv) was added to a solution of acid S₄⁶ (16 mg, 0.037 mmol, 1.0 equiv) in CHCl₃ (1.5 mL) at 0 °C. The resulting reaction mixture was stirred at room temperature for 2 hours before being quenched with H₂O (1 mL). The resulting mixture was extracted with EtOAc (3 × 2 mL). The combined organic layers were washed with brine (5 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc/AcOH = 5:1:0.3) afforded acid S₄⁷ (10.7 mg, 90%) as a white solid. Rf = 0.4 (petroleum ether/EtOAc = 10:3);

¹H NMR (400 MHz, CDCl₃): δ 3.20 (dd, J = 11.2, 5.2 Hz, 1 H), 2.65 (dd, J = 8.9, 6.0 Hz, 1 H), 2.54 (brs, 1 H), 1.92 – 1.79 (m, 2 H), 1.77 – 1.45 (m, 11 H), 1.42 – 1.17 (m, 3 H), 1.10 – 0.86 (m, 2 H), 1.0 (s, 3 H), 0.97 (s, 3 H), 0.77 (s, 3 H) ppm;

¹³C NMR (101 MHz, CDCl₃): δ 182.8, 79.2, 56.0, 55.2, 45.4, 45.1, 44.7, 41.5, 41.0, 39.1, 39.0, 38.8, 38.2, 31.4, 28.5, 27.5, 20.6, 18.6, 17.6, 15.6 ppm;

HRMS (ESI): Calcd for C₂₀H₃₂O₃Nᵃ⁺ [M⁺Na⁺]: 343.2249, found: 343.2242;

[α]_D²³ = −43.2° (c = 0.125, CHCl₃).

To a 10 mL reaction culture tube charged with acid S₄⁷ (6 mg, 0.019 mmol) was added Ac₂O (0.1 mL) and pyridine (0.1 mL). After 12 hours stirring at room temperature, the reaction mixture was concentrated directly under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 10:1) afforded frittilebic acid 2₈ (6.1 mg, 90%) as a white solid. Rf = 0.4 (petroleum ether/EtOAc = 4:1);

¹H NMR (400 MHz, CDCl₃): δ 4.46 (dd, J = 10.8, 5.8 Hz, 1 H), 2.65 (dd, J = 9.0, 6.0 Hz, 1 H), 2.54 (brs, 1 H), 2.05 (s, 3 H), 1.90 – 1.80 (m, 1 H), 1.76 – 1.45 (m, 11 H), 1.43 – 1.34 (m, 1 H), 1.25 (brs, 1 H), 1.21 (dd, J = 11.7, 5.1 Hz, 1 H), 1.02 (S, 3 H), 1.05 – 0.92 (m, 2 H), 0.85 (s, 3 H), 0.84 (s, 3 H) ppm;

¹³C NMR (101 MHz, CDCl₃): δ 181.7, 171.0, 80.9, 55.7, 55.2, 45.1, 44.9, 44.4, 41.3, 40.7, 38.9, 38.3, 38.0, 37.7, 31.2, 28.3, 23.6, 21.3, 20.4, 18.5, 17.5, 16.6 ppm;

HRMS (ESI): Calcd for C₂₂H₃₂O₄N+ [M+NH₄⁺]: 380.2801, found: 380.2776;

[α]_D²³ = −32° (c = 0.0125, CHCl₃).

Melting point: 231 – 233 °C.
To a 10 mL reaction culture tube charged with fritillebic acid 28 (3 mg, 0.0083 mmol, 1.0 equiv), *ent*-3β-acetoxykaur-16b,17-diol 27 (3 mg, 0.0083 mmol, 1.0 equiv), and DMAP (0.1 mg, 0.00083 mmol, 0.1 equiv) was added CH₂Cl₂ (0.4 mL) followed by EDCI (1.74 mg, 0.009 mmol, 1.5 equiv) at 0 °C. After 5 hours stirring at room temperature, the reaction mixture was quenched by adding ice water (1 mL). The resulting mixture was extracted with EtOAc (3 × 2 mL). The combined organic layers were washed with brine (5 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 10:1) afforded fritillebin B 29 (4.4 mg, 74%) as a white solid.

Rf = 0.45 (petroleum ether/EtOAc = 4:1);

¹H NMR (400 MHz, CDCl₃): δ 4.46 (dd, J = 10.1, 4.9 Hz, 2 H), 4.20 (dd, J = 20.9, 11.2 Hz, 2 H), 2.98 (d, J = 29.0 Hz, 1 H), 2.69 – 2.61 (m, 1 H), 2.46 (brs, 1 H), 2.04 (s, 6 H), 1.97 – 1.75 (m, 5 H), 1.74 – 1.43 (m, 21 H), 1.42 – 1.15 (m, 8 H), 1.03 (s, 3 H), 1.01 (s, 3 H), 1.08 – 0.92 (m, 2 H), 0.85 (s, 3 H), 0.84 (s, 6 H) ppm;

¹³C NMR (101 MHz, CDCl₃): δ 177.5, 171.0, 171.0, 80.9, 80.8, 80.2, 80.1, 75.9, 85.2, 55.7, 55.5, 55.0, 52.7, 46.1, 45.6, 44.9, 44.6, 44.6, 41.6, 41.3, 40.8, 38.9, 38.9, 38.3, 38.2, 38.1, 37.7, 37.7, 37.0, 31.2, 28.3, 28.2, 26.2, 23.6, 23.5, 21.3, 21.3, 20.4, 20.0, 18.5, 18.3, 17.8, 17.5, 16.6, 16.5 ppm;


[α]D²⁵ = −52° (c = 0.108, CHCl₃);

Melting point: 245.1 – 246.5 °C.

To a 10 mL reaction culture tube charged with benzyl ester 15 (50 mg, 0.127 mmol) was added 10 % KOH in MeOH (1 mL). The resulting mixture was stirred vigorously at 60 °C. After 20 hours stirring, the reaction mixture was cooled to 0 °C and acidified with 1 N HCl (to pH = 3). The resulting mixture was extracted with EtOAc (3 × 2 mL). The combined organic layers were washed with brine (5 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 10:1) afforded 16α-H-ent-kauran-17-oic acid 32 (36.7 mg, 95%, C₁₆ dr = 13:1) as a white solid.

Rf = 0.50 (petroleum ether/EtOAc = 4:1);

¹H NMR (400 MHz, CDCl₃): δ 2.64 (dd, J = 8.5, 6.5 Hz, 1 H), 2.52 (brs, 1 H), 1.90 (d, J = 11.6 Hz, 1 H), 1.79 (d, J = 12.4 Hz, 1 H), 1.73 – 1.45 (m, 9 H), 1.43 – 1.24 (m, 4
H), 1.19 (dd, J = 11.8, 4.7 Hz, 1 H), 1.16 – 1.07 (m, 1 H), 1.05 – 0.95 (m, 1 H), 0.99 (s, 3 H), 0.93 – 0.67 (m, 2 H), 0.85 (s, 3 H), 0.80 (s, 3 H) ppm;

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 182.7, 56.2, 56.0, 45.2, 45.1, 44.7, 42.0, 41.4, 40.9, 40.4, 39.3, 38.1, 33.7, 33.2, 31.3, 21.6, 20.7, 18.6, 18.4, 17.5 ppm;

HRMS (ESI): Caled for C$_{20}$H$_{33}$O$_2$ [M+H]$^+$: 305.2481, found: 305.2468;

$\alpha_25^D = -55^\circ$ (c = 0.075, CHCl$_3$);

Melting point: 221.7 – 222.9 °C.

A solution of LAH (1.0 M in THF, 110 μL, 0.11 mmol, 2.5 equiv) was added dropwise to a solution 15 (17.5 mg, 0.044 mmol, 1.0 equiv) in THF (0.5 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 2 hours before being quenched by adding Na$_2$SO$_4$·10H$_2$O slowly until no gas produced. The suspension filtered through a thin pad of celite and rinsed with small amount of CH$_2$Cl$_2$. The combined organic layers were concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded the alcohol (12 mg, 93 %, C16 dr = 1.9:1) as a white solid.

$n$Bu$_3$P (18 μL, 0.072 mmol, 1.8 equiv) was added dropwise to a solution of the above alcohol (12 mg, 0.04 mmol, 1.0 equiv) and 2-nitrophenyl selenocyanate (13.6 mg, 0.06 mmol, 1.5 equiv) in toluene (1 mL). The resulting dark solution was heated at 78 °C. After 1.5 h stirring, the reaction mixture was cooled to 0 °C and diluted with THF (2 mL). H$_2$O$_2$ (30% in water, 20.4 μL, 0.2 mmol, 5.0 equiv) was added, and the reaction mixture was stirred at room temperature for 12 hours before being quenched with water (3 mL). The resulting mixture was extracted with EtOAc (3 × 2 mL). The combined organic layers were washed with brine (5 mL), dried over Na$_2$SO$_4$, and concentrated under reduced pressure. Purification by column chromatography (silica gel containing 5% AgNO$_3$, petroleum ether/EtOAc = 20:1) afforded ent-kauran-16-ene 30 (9.5 mg, 87%) as a white solid.

R$_f$ = 0.32 (silica gel containing 5% AgNO$_3$, petroleum ether/EtOAc = 100:1);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.83 – 4.68 (m, 2 H), 2.63 (brs, 1 H), 2.12 – 1.94 (m, 3 H), 1.85 – 1.74 (m, 1 H), 1.70 – 1.45 (m, 6 H), 1.43 – 1.22 (m, 4 H), 1.19 – 0.98 (m, 3 H), 1.02 (s, 3 H), 0.95 – 0.68 (m, 3 H), 0.85 (s, 3 H), 0.81 (s, 3 H) ppm;

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 156.4, 103.0, 56.4, 56.2, 49.4, 44.4, 44.2, 42.2, 41.4, 40.6, 40.0, 39.5, 33.8, 33.5, 33.4, 21.8, 20.4, 18.8, 18.3, 17.8 ppm;

HRMS (ESI): Caled for C$_{20}$H$_{33}$ [M+H]$^+$: 273.2582, found: 273.2617;

$\alpha_2^D = -63^\circ$ (c = 0.095, CHCl$_3$);

Melting point: 41 – 42 °C.
To a solution of \textit{ent}-kauran-16-ene 30 (5.4 mg, 0.02 mmol, 1.0 equiv) in \(i\)-PrOH (1.25 mL) was added Co(acac)\(2\) (1 mg, 0.004 mmol, 0.2 equiv) and Ph\(SiH_3\) (5 \(\mu\)L, 0.04 mmol, 2.0 equiv) sequentially. The reaction mixture was stirred at room temperature under an atmosphere of oxygen for 19 hours before being quenched with sat. aq. Na\(\text{SO}_2\text{O}_3\) (1 mL). The resulting mixture was extracted with Et\(\text{OAc}\) (3 × 2 mL). The combined organic layers were washed with brine (5 mL), dried over Na\(\text{SO}_4\), and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/Et\(\text{OAc}\) = 20:1) afforded \textit{ent}-kauran-16b-ol 31 (4 mg, 69%) as a white solid.

\(R_f = 0.40\) (petroleum ether/Et\(\text{OAc}\) = 20:1);

\(^{1}H\) NMR (400 MHz, CDCl\(3\)): \(\delta\) 1.93 (d, \(J = 11.7\) Hz, 1 H), 1.85 – 1.81 (m, 1 H), 1.80 – 1.74 (m, 1 H), 1.65 – 1.44 (m, 11 H), 1.43 – 1.14 (m, 4 H), 1.36 (s, 3 H), 1.11 (td, \(J = 13.8, 4.4\) Hz, 1 H), 1.02 (s, 3 H), 1.00 – 0.95 (m, 1 H), 0.90 – 0.67 (m, 2 H), 0.84 (s, 3 H), 0.80 (s, 3 H) ppm;

\(^{13}C\) NMR (101 MHz, CDCl\(3\)): \(\delta\) 79.5, 58.2, 57.0, 56.4, 49.2, 45.5, 42.2, 40.5, 39.5, 37.9, 33.7, 33.4, 27.1, 24.6, 21.7, 20.6, 18.1, 18.1, 17.9 ppm;

HRMS (ESI): Calcd for C\(_{20}\)H\(_{35}\)O \([M+H]^+\): 291.2688, found: 291.2731; \([\alpha]\)\(_b\)\(^{24}\) = –46° (c = 0.05, CHCl\(3\));

\textit{Melting point}: 216 – 218 °C.

A solution of LAH (1.0 M in THF, 75 \(\mu\)L, 0.075 mmol, 2.5 equiv) was added dropwise to a solution of 16 (19.8 mg, 0.03 mmol, 1.0 equiv) in THF (0.4 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 2 hours before being quenched by adding Na\(\text{SO}_4\)10H\(\text{O}\) slowly until no gas produced. The suspension was filtered through a thin pad of celite and rinsed with small amount of CH\(\text{Cl}_2\). The filtrate was concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/Et\(\text{OAc}\) = 20:1) afforded the alcohol 33 (14.9 mg, 90%, C16 dr = 2 : 1) as a white solid.

\textit{16\(\alpha\)-H-33}

\(R_f = 0.42\) (petroleum ether/Et\(\text{OAc}\) = 10:1);

\(^{1}H\) NMR (400 MHz, CDCl\(3\)): \(\delta\) 3.90 (d, \(J = 10.6\) Hz, 1 H), 3.53 (d, \(J = 10.1\) Hz, 1 H), 3.44 – 3.33 (m, 2 H), 3.21 (dd, \(J = 11.8, 4.6\) Hz, 1 H), 2.05 (brs, 1 H), 1.97 – 1.87 (m, 1 H), 1.86 – 1.78 (m, 2 H), 1.69 – 1.62 (m, 2 H), 1.61 – 1.56 (m, 2 H), 1.55 – 1.47 (m, 4 H), 1.45 – 1.36 (m, 2 H), 1.35 – 1.20 (m, 2 H), 1.09 (s, 3 H), 0.98 (s, 3 H), 0.96 – 0.80 (m, 3 H), 0.88 (s, 9 H), 0.87 (s, 9 H), 0.74 – 0.66 (m, 1 H), 0.02 (s, 3 H), 0.01 (s, 3 H), 0.00 (s, 3 H), -0.01 (s, 3 H) ppm;

\(^{13}C\) NMR (101 MHz, CDCl\(3\)): \(\delta\) 79.9, 67.8, 65.3, 56.7, 56.0, 45.2, 44.8, 43.7, 42.9, 39.4, 39.2, 38.5, 36.9, 31.7, 29.9, 28.0, 26.1, 26.0, 23.9, 23.2, 19.1, 18.4, 18.2, 17.1, – 3.7, – 4.9, – 5.4, – 5.6 ppm;

HRMS (ESI): Calcd for C\(_{32}\)H\(_{63}\)O\(_2\)Si\(_2\) \([M+H]^+\): 551.4316, found: 551.4313; \([\alpha]\)\(_b\)\(^{24}\) = –52.4° (c = 0.25, CHCl\(3\));
Melting point: 142.3 – 144.6 °C.

16β-H-33

Rf = 0.42 (petroleum ether/EtOAc = 10:1);

H NMR (400 MHz, CDCls): δ 3.90 (d, J = 10.5 Hz, 1 H), 3.76 – 3.65 (m, 2 H), 3.53 (d, J = 10.5 Hz, 1 H), 3.22 (dd, J = 11.7, 4.7 Hz, 1 H), 2.22 – 2.09 (m, 2 H), 1.99 (d, J = 11.3 Hz, 1 H), 1.80 (dt, J = 13.1, 3.5 Hz, 1 H), 1.73 – 1.60 (m, 3 H), 1.59 – 1.42 (m, 5 H), 1.35 – 1.28 (m, 1 H), 1.27 – 1.13 (m, 2 H), 1.10 (s, 3 H), 1.06 – 0.95 (m, 1 H), 0.98 (s, 3 H), 0.95 – 0.81 (m, 3 H), 0.89 (s, 9 H), 0.87 (s, 9 H), 0.72 (dd, J = 8.5, 5.4 Hz, 1 H), 0.02 (s, 3 H), 0.01 (s, 3 H), -0.01 (s, 3 H) ppm;

C NMR (101 MHz, CDCls): δ 79.8, 65.2, 64.5, 57.8, 55.9, 44.3, 43.7, 43.4, 40.0, 39.4, 39.2, 37.2, 29.9, 27.9, 26.2, 26.1, 26.0, 23.8, 23.0, 19.4, 18.4, 18.2, 17.2, –3.6, –4.9, –5.4, –5.6 ppm;

HRMS (ESI): Calcd for C32H63O3Si2 [M+H]+: 551.4316, found: 551.4313;

[α]D = –37.3° (c = 0.295, CHCl3).

To a solution of 16α-H-33 (9.5 mg, 0.018 mmol, 1.0 equiv) in CHCl3 (0.5 mL) was added BF3 Et2O (11.2 μL, 0.09 mmol, 5.0 equiv) slowly at 0 °C. The resulting reaction mixture was stirred at room temperature for 2 hours before being quenched with H2O (1 mL). The resulting mixture was extracted with EtOAc (3 × 2 mL). The combined organic layers were washed with brine (5 mL), dried over Na2SO4, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 1:1) afforded the 16α-H-ent-kaurane-3β,17,19-triol 34 (4.6 mg, 80%) as a white solid.

Rf = 0.30 (petroleum ether/EtOAc = 2:3);

H NMR (400 MHz, CD6D5N): δ 4.49 (d, J = 11.0 Hz, 1 H), 3.72 – 3.53 (m, 4 H), 2.37 (brs, 1 H), 2.21 – 2.12 (m, 1 H), 2.10 – 1.97 (m, 1 H), 1.96 – 1.87 (m, 1 H), 1.81 – 1.72 (m, 2 H), 1.68 – 1.47 (m, 4 H), 1.50 (s, 3 H), 1.45 – 1.39 (m, 2 H), 1.38 – 1.17 (m, 3 H), 1.15 – 1.03 (m, 2 H), 0.96 (s, 3 H), 0.94 – 0.79 (m, 3 H) ppm;

C NMR (101 MHz, CD6D5N): δ 80.3, 67.0, 64.5, 57.8, 56.5, 56.0, 45.7, 44.8, 44.2, 43.9, 38.9, 38.9, 37.3, 31.9, 28.6, 23.9, 21.3, 19.1, 18.3 ppm;

HRMS (ESI): Calcd for C20H34O3Na [M+Na]+: 345.2406, found: 345.2423;

[α]D = –22° (c = 0.095, CHCl3);

Melting point: 246.2 – 247.6 °C.
Bu₃P (37 μL, 0.147 mmol, 1.8 equiv) was slowly added to a solution of alcohol 33 (45 mg, 0.082 mmol, 1.0 equiv) and 2-nitrophenyl selenocyanate (28 mg, 0.123 mmol, 1.5 equiv) in toluene (2 mL). The resulting dark solution was heated at 78 °C. After 1.5 h stirring, the reaction mixture was cooled to 0 °C and diluted with THF (4 mL). H₂O₂ (30% in water, 43 μL, 0.41 mmol, 5.0 equiv) was added. After 12 hours stirring at room temperature, the reaction mixture was quenched with water (5 mL). The resulting mixture was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (20 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petrol ether) to give the alkene 35 (43 mg, 99%) as a white solid.

Rf = 0.30 (silica gel merged with 5% AgNO₃, petroleum ether/EtOAc = 100:1);

¹H NMR (400 MHz, CDCl₃): δ 4.81 – 4.67 (m, 2 H), 3.95 – 3.88 (m, 1 H), 3.54 (d, J = 10.3 Hz, 1 H), 3.22 (dd, J = 11.8, 4.7 Hz, 1 H), 2.63 (brs, 1 H), 2.05 -2.01 (m, 1 H), 1.96 (d, J = 10.9 Hz, 1 H), 1.83 (dt, J = 13.2, 3.6 Hz, 1 H), 1.75 – 1.59 (m, 4 H), 1.51 – 1.42 (m, 3 H), 1.37 – 1.19 (m, 6 H), 1.17 – 1.03 (m, 4 H), 0.99 (s, 3 H), 0.88 (s, 9 H), 0.87 (s, 9 H), 0.76 – 0.69 (m, 1 H), 0.03 (s, 3 H), 0.03 (s, 3 H), 0.01 (s, 3 H), 0.00 (s, 3 H) ppm;

¹³C NMR (101 MHz, CDCl₃): δ 156.5, 102.9, 79.9, 65.3, 56.4, 56.0, 49.1, 44.3, 44.1, 43.8, 42.5, 39.4, 39.2, 33.4, 29.9, 27.9, 26.1, 26.0, 23.9, 22.6, 18.6, 18.4, 18.2, 17.1, – 37, – 4.9, – 5.4, – 5.6 ppm;

HRMS (ESI): Calcd for C₃₂H₃₆O₃Si₂ [M+H]⁺: 533.4210, found: 533.4206;

[a]D²⁴ = −33.7° (c = 0.0475, CHCl₃);

Melting point: 111.9 – 114.3 °C.

To a solution of alkene 35 (10.6 mg, 0.02 mmol, 1.0 equiv) in CH₂Cl₂ (0.6 mL) and MeCN (0.3 mL) was slowly added LiBF₄ (37.5 mg, 0.4 mmol, 20 equiv). The reaction mixture was stirred at room temperature overnight before being quenched with H₂O (1 mL). The resulting mixture was extracted with EtOAc (3 × 2 mL). The combined organic layers were washed with brine (5 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc = 1:1) afforded the ent-3β,19-dihydroxy-kaur-16-ene 36 (5.4 mg, 89%) as a white solid.

Rf = 0.45 (petroleum ether/EtOAc = 5:2);

¹H NMR (400 MHz, CDCl₃): δ 4.82 – 4.77 (m, 1 H), 4.76 – 4.71 (m, 1 H), 4.20 (d, J = 11.2 Hz, 1 H), 3.42 (ddd, J = 11.8, 4.8, 1.3 Hz, 1 H), 3.31 (dd, J = 11.2, 1.3 Hz, 1 H), 2.64 (brs, 1 H), 2.04 (m, 2 H), 1.94 – 1.78 (m, 3 H), 1.75 – 1.56 (m, 4 H), 1.54 – 1.42 (m, 3 H), 1.34 – 1.23 (m, 2 H), 1.22 (s, 3 H), 1.13 – 1.06 (m, 1 H), 1.05 – 1.00 (m, 1 H), 0.98 (s, 3 H), 0.95 – 0.83 (m, 2 H) ppm;

¹³C NMR (101 MHz, CDCl₃): δ 155.7, 103.3, 81.1, 64.5, 56.0, 55.9, 49.0, 44.1, 44.0, 43.1, 41.5, 39.7, 38.9, 38.6, 33.2, 27.9, 22.8, 20.2, 18.5, 18.3 ppm;

HRMS (ESI): Calcd for C₂₀H₃₃O₂ [M+H]⁺: 305.2481, found: 305.2470;
\[ \alpha \text{D}^{25.5} = -62^\circ \ (c = 0.1, \text{CHCl}_3); \]

**Melting point:** 152.0 – 154.9 °C.

To a solution of compound 24 (21 mg, 0.051 mmol, 1.0 equiv) in ethry acetate (1 mL) was added Pd/C (3 mg, palladium on carbon, witted with 55% H\textsubscript{2}O). The mixture was stirred at room temperature under hydrogen atmosphere for 5 hours. The mixture was filtrated through celite pad and concentrated under reduced pressure to give the acid (16 mg), which was used in next step without purification.

To a solution of above acid (16 mg, 0.05 mmol, 1.0 equiv) in benzene (0.25 mL) was added Cu(OAc)\textsubscript{2} (5.3 mg, 0.029 mmol, 0.58 equiv) at room temperature. After 5 minutes stirring, the tube was wrapped in aluminum foil. Pb(OAc)\textsubscript{4} (14 mg, 0.032 mmol) was added. After 30 min stirring, another portion of Pb(OAc)\textsubscript{4} (7 mg, 0.016 mmol) was added followed by benzene (0.2 mL). After 30 min, a further portion of Pb(OAc)\textsubscript{4} (10 mg, 0.022 mmol) was added followed by benzene (0.1 mL) and dry DMF (0.04 mL). The resulting mixture was heated to 78 °C and stirred overnight. The aluminum foil was removed, and reaction was stirred for additional 1 h. The resulting green solution was cooled to room temperature, filtered through a pad of silica gel and rinsed with small amount of EtOAc. The filtrate was concentrated under reduced pressure. Purification by column chromatography (silica gel merged with 5% AgNO\textsubscript{3}, petroleum ether/EtOAc = 100:1) afforded the hibaene 37 (6.9 mg, 51%) as white solid.

\[ R_f = 0.40 \ (\text{silica gel merged with 5% AgNO}_3, \text{petroleum ether/EtOAc} = 100:1); \]

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 5.69 (d, \( J = 5.7 \text{ Hz}, \ 1 \text{ H} \)), 5.44 (d, \( J = 5.7 \text{ Hz}, \ 1 \text{ H} \)), 1.65 – 1.42 (m, 6 H), 1.41 – 1.32 (m, 4 H), 1.31 – 1.20 (m, 3 H), 1.18 – 1.07 (m, 1 H), 1.04 – 0.93 (m, 2 H), 0.99 (s, 3 H), 0.90 – 0.77 (m, 2 H), 0.86 (s, 3 H), 0.82 (s, 3 H), 0.74 (s, 3 H) ppm;

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): \( \delta \) 136.1, 135.3, 61.1, 55.9, 52.8, 49.0, 43.5, 42.0, 39.1, 37.2, 37.2, 33.6, 33.1, 33.1, 24.9, 21.9, 20.1, 20.0, 18.5, 15.0 ppm;

HRMS (ESI): Caled for C\textsubscript{20}H\textsubscript{33} [M+H]+: 273.2582, found: 273.2615;

\[ \alpha \text{D}^{23.1} = -15^\circ \ (c = 0.1, \text{CHCl}_3); \]

**Melting point:** 28 – 30 °C.

\( m \)-CPBA (6.6 mg, 0.036, 3.0 equiv) was added to a solution of hibaene 37 (3.5 mg, 0.012 mmol, 1.0 equiv) in CH\textsubscript{2}Cl\textsubscript{2} (0.7 mL) at 0 °C. After 4 hours stirring at room temperature, the reaction was quenched with sat. NaHCO\textsubscript{3} (0.5 mL). The resulting mixture was extracted with EtOAc (3 × 1 mL). The combined organic layers were washed with brine (3 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, and concentrated under reduced pressure.
Purification by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded hibaene epoxide 38 (2.6 mg, 74%) as a white solid. 

\( R_f = 0.52 \) (petroleum ether/EtOAc = 20:1); 

\( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 3.45 – 3.39 (m, 1 H), 3.05 – 2.98 (m, 1 H), 1.92 – 1.82 (m, 1 H), 1.65 – 1.45 (m, 7 H), 1.43 – 1.32 (m, 3 H), 1.30 – 1.08 (m, 4 H), 1.01 (s, 3 H), 0.92 (s, 3 H), 0.89 – 0.76 (m, 2 H), 0.87 (s, 3 H), 0.84 (s, 3 H), 0.52 (d, \( J = 10.8 \) Hz, 1 H) ppm; 

\( ^{13}C \) NMR (101 MHz, CDCl\(_3\)): \( \delta \) 60.4, 56.6, 56.3, 56.2, 47.0, 44.4, 42.1, 39.5, 39.2, 37.6, 35.5, 33.7, 33.3, 33.3, 22.0, 21.7, 20.0, 19.4, 18.7, 15.9 ppm; 

HRMS (ESI): Calcd for C\(_{20}\)H\(_{33}\)O [M+H]\(^+\): 289.2532, found: 289.2572; 

\( [\alpha]_{D}^{25} = -9.2^\circ \) (\( c = 0.065 \), CHCl\(_3\)); 

**Melting point**: 72.1 – 73.9 °C.
**ent-3β-acetoxykaur-16-ene 25: ¹H spectra comparison:**

![Chemical Structure](attachment:image.png)

<table>
<thead>
<tr>
<th>C</th>
<th>Natural 25&lt;sup&gt;26&lt;/sup&gt; ¹H NMR (300 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;)</th>
<th>Synthetic 25 ¹H NMR (400 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δ [ppm, mult, J (Hz)]</td>
<td>δ [ppm, mult, J (Hz)]</td>
</tr>
<tr>
<td>1</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>3.12 (dd, J = 10.8, 5.5 Hz, 1 H)</td>
<td>3.20 (dd, J = 10.9, 5.4 Hz, 1 H)</td>
</tr>
<tr>
<td>4</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>11</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>12</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>13</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>14</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>15</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>16</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>17</td>
<td>4.73 (s, 1 H), 4.80 (d if t, J = 1.5 Hz, 1 H)</td>
<td>4.74 (s, 1 H), 4.80 (b r s, 1 H)</td>
</tr>
<tr>
<td>18</td>
<td>0.98 (s, 3 H)</td>
<td>0.98 (s, 3 H)</td>
</tr>
<tr>
<td>19</td>
<td>1.02 (s, 3 H)</td>
<td>1.02 (s, 3 H)</td>
</tr>
<tr>
<td>20</td>
<td>0.78 (s, 3 H)</td>
<td>0.78 (s, 3 H)</td>
</tr>
</tbody>
</table>

*Note: The original isolation paper only provided partial ¹H NMR data which was shown as above.*<sup>26</sup>

Natural ent-3β-acetoxykaur-16-ene 25: [α]<sub>D</sub> = −69.2° (c = 0.32, MeOH);

Synthetic ent-3β-acetoxykaur-16-ene 25: [α]<sub>D</sub><sup>26</sup> = −67° (c = 0.11, MeOH).

Natural ent-3β-acetoxykaur-16-ene 25: Melting point: 177 – 178 °C;

Synthetic ent-3β-acetoxykaur-16-ene 25: Melting point: 168.1 – 170.5 °C.
**ent-3β-acetoxykaur-16-ene 25: $^{13}$C spectra comparison:**

![ent-3β-acetoxykaur-16-ene](image)

<table>
<thead>
<tr>
<th></th>
<th>Natural 25$^{26}$</th>
<th></th>
<th>Synthetic 25</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ (ppm)</td>
<td>$^1$H NMR (101 MHz, CDCl$_3$) $\delta$ (ppm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ (ppm)</td>
<td>$^1$H NMR (101 MHz, CDCl$_3$) $\delta$ (ppm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>39.74</td>
<td>39.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>24.41</td>
<td>27.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>79.07</td>
<td>79.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>38.83</td>
<td>38.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>55.18</td>
<td>55.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>20.02</td>
<td>19.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>41.19</td>
<td>41.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>44.00</td>
<td>43.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>55.89</td>
<td>55.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>39.03</td>
<td>39.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>18.27</td>
<td>18.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>33.24</td>
<td>33.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>43.95</td>
<td>43.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>38.69</td>
<td>38.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>49.01</td>
<td>48.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>155.84</td>
<td>155.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>103.01</td>
<td>102.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>28.38</td>
<td>28.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>15.48</td>
<td>15.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>17.59</td>
<td>17.58</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**ent-3β-acetoxykaur-16-ene 26: **\(^1\)H spectra comparison:

<table>
<thead>
<tr>
<th>C</th>
<th>Natural 26(^{27}) (\delta [\text{ppm}, \text{mult}, J (\text{Hz})])</th>
<th>Synthetic 26 (\delta [\text{ppm}, \text{mult}, J (\text{Hz})])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.98 (ddd, (J = 13.4, 12.8, 4.7 \text{ Hz}, 1 \text{ H}))&lt;br&gt;1.85 (ddd, (J = 13.4, 3.8, 3.5 \text{ Hz}, 1 \text{ H}))</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>1.65 (m, 1 H), 1.67 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>4.47&lt;br&gt;(dd, (J = 11.1, 5.5 \text{ Hz}, 1 \text{ H}))</td>
<td>4.47&lt;br&gt;(dd, (J = 11.0, 5.6 \text{ Hz}, 1 \text{ H}))</td>
</tr>
<tr>
<td>4</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>0.85 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>1.36 (m, 1 H), 1.53 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>1.51 (m, 1 H), 1.53 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>1.06 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>11</td>
<td>1.54 (m, 1 H), 1.64 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>12</td>
<td>1.11 (dddd, (J = 11.4, 5.0, 1.8, 1.6 \text{ Hz}, 1 \text{ H}))&lt;br&gt;1.97 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>13</td>
<td>2.64 (m, 1 H)</td>
<td>2.64 (brs, 1 H)</td>
</tr>
<tr>
<td>14</td>
<td>1.48 (m, 1 H), 1.64 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>15</td>
<td>2.06 (m, 1 H), 2.07 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>16</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>17</td>
<td>4.74 (m, 1 H), 4.79 (m, 1 H)</td>
<td>4.74 (m, 1 H), 4.80 (m, 1 H)</td>
</tr>
<tr>
<td>18</td>
<td>0.86 (s, 3 H)</td>
<td>0.86 (s, 3 H)</td>
</tr>
<tr>
<td>19</td>
<td>0.85 (s, 3 H)</td>
<td>0.85 (s, 3 H)</td>
</tr>
<tr>
<td>20</td>
<td>1.05 (s, 3 H)</td>
<td>1.05 (s, 3 H)</td>
</tr>
<tr>
<td>OAc</td>
<td>2.04 (s, 3 H)</td>
<td>2.05 (s, 3 H)</td>
</tr>
</tbody>
</table>

Natural ent-3β-acetoxykaur-16-ene 26: \(\{\alpha\}_D^{20} = -28.56^\circ (c = 0.5, \text{CHCl}_3)\);
Synthetic ent-3β-acetoxykaur-16-ene 26: \(\{\alpha\}_D^{26.5} = -60.4^\circ (c = 0.23, \text{CHCl}_3)\).
Natural ent-3β-acetoxykaur-16-ene 26: Melting point: 160.3 – 162.5 \(^\circ\)C; Synthetic ent-3β-acetoxykaur-16-ene 26: Melting point: 151.2 – 153.6 \(^\circ\)C.
**ent-3β-acetoxykaur-16-ene 26: $^{13}$C spectra comparison:**

![ent-3β-acetoxykaur-16-ene](image)

<table>
<thead>
<tr>
<th></th>
<th>Natural 26 $^{27}$</th>
<th>Synthetic 26</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>$^{13}$C NMR (101 MHz, CDCl$_3$)</td>
<td>$^1$H NMR (101 MHz, CDCl$_3$)</td>
</tr>
<tr>
<td></td>
<td>$\delta$ (ppm)</td>
<td>$\delta$ (ppm)</td>
</tr>
<tr>
<td>1</td>
<td>39.75</td>
<td>39.70</td>
</tr>
<tr>
<td>2</td>
<td>23.65</td>
<td>23.65</td>
</tr>
<tr>
<td>3</td>
<td>80.98</td>
<td>80.98</td>
</tr>
<tr>
<td>4</td>
<td>37.78</td>
<td>37.74</td>
</tr>
<tr>
<td>5</td>
<td>55.27</td>
<td>55.26</td>
</tr>
<tr>
<td>6</td>
<td>19.86</td>
<td>19.86</td>
</tr>
<tr>
<td>7</td>
<td>41.05</td>
<td>41.04</td>
</tr>
<tr>
<td>8</td>
<td>44.02</td>
<td>43.98</td>
</tr>
<tr>
<td>9</td>
<td>55.74</td>
<td>55.73</td>
</tr>
<tr>
<td>10</td>
<td>38.94</td>
<td>38.92</td>
</tr>
<tr>
<td>11</td>
<td>18.29</td>
<td>18.27</td>
</tr>
<tr>
<td>12</td>
<td>33.21</td>
<td>33.20</td>
</tr>
<tr>
<td>13</td>
<td>43.86</td>
<td>43.89</td>
</tr>
<tr>
<td>14</td>
<td>38.36</td>
<td>38.33</td>
</tr>
<tr>
<td>15</td>
<td>48.98</td>
<td>48.95</td>
</tr>
<tr>
<td>16</td>
<td>155.70</td>
<td>155.70</td>
</tr>
<tr>
<td>17</td>
<td>103.10</td>
<td>103.06</td>
</tr>
<tr>
<td>18</td>
<td>28.36</td>
<td>28.34</td>
</tr>
<tr>
<td>19</td>
<td>16.64</td>
<td>16.62</td>
</tr>
<tr>
<td>20</td>
<td>17.65</td>
<td>17.63</td>
</tr>
<tr>
<td>OAc</td>
<td>171.00</td>
<td>170.97</td>
</tr>
<tr>
<td></td>
<td>21.30</td>
<td>21.31</td>
</tr>
</tbody>
</table>
**ent-3β-acetoxykaur-16β,17-diol 27: **$^1$H spectra comparison:

<table>
<thead>
<tr>
<th>C</th>
<th>Natural 27$^{28}$ $^1$H NMR (500 MHz, CD$_3$OD)</th>
<th>Synthetic 27 $^1$H NMR (400 MHz, CD$_3$OD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta$ [ppm, mult, $J$ (Hz)]</td>
<td>$\delta$ [ppm, mult, $J$ (Hz)]</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4.43 (dd, $J = 11.6$, 4.9 Hz, 1 H)</td>
<td>4.44 (dd, $J = 11.4$, 5.1 Hz, 1 H)</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.03 (d, $J = 4.3$ Hz, 1 H)</td>
<td>1.03 (brs, 1 H)</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.96 (d, $J = 4.0$ Hz, 1 H)</td>
<td>1.0 – 0.92 (m, 1 H)</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>0.90 (m, 1 H)</td>
<td>0.90 (m, 1 H)</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>3.64 (m, 2 H)</td>
<td>3.65 (m, 2 H)</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td>0.86 (s, 3 H)</td>
</tr>
<tr>
<td>19</td>
<td>0.86(d, $J = 6.9$ Hz, 6 H)</td>
<td>0.88 (s, 3 H)</td>
</tr>
<tr>
<td>20</td>
<td>1.09 (s, 3 H)</td>
<td>1.09 (s, 3 H)</td>
</tr>
<tr>
<td>OAc</td>
<td>2.02 (s, 3 H)</td>
<td>2.03 (s, 3 H)</td>
</tr>
</tbody>
</table>

*Note: The original isolation paper didn’t provide the optical rotation and melting point.*$^{28}$
**ent-3β-acetoxypurpur-16β,17-diol 27: $^{13}$C spectra comparison:**

![Diagram of ent-3β-acetoxypurpur-16β,17-diol 27](image)

<table>
<thead>
<tr>
<th>C</th>
<th>Natural 27$^{28}$ $^{13}$C NMR (125 MHz, CD$_3$OD) $\delta$ (ppm)</th>
<th>Synthetic 26 $^1$H NMR (101 MHz, CD$_3$OD) $\delta$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>38.0</td>
<td>38.0</td>
</tr>
<tr>
<td>2</td>
<td>23.2</td>
<td>23.2</td>
</tr>
<tr>
<td>3</td>
<td>81.1</td>
<td>81.1</td>
</tr>
<tr>
<td>4</td>
<td>37.4</td>
<td>37.4</td>
</tr>
<tr>
<td>5</td>
<td>55.1</td>
<td>55.1</td>
</tr>
<tr>
<td>6</td>
<td>19.6</td>
<td>19.6</td>
</tr>
<tr>
<td>7</td>
<td>41.6</td>
<td>41.6</td>
</tr>
<tr>
<td>8</td>
<td>44.1</td>
<td>44.1</td>
</tr>
<tr>
<td>9</td>
<td>56.5</td>
<td>56.5</td>
</tr>
<tr>
<td>10</td>
<td>38.7</td>
<td>38.7</td>
</tr>
<tr>
<td>11</td>
<td>18.0</td>
<td>18.0</td>
</tr>
<tr>
<td>12</td>
<td>25.8</td>
<td>25.8</td>
</tr>
<tr>
<td>13</td>
<td>44.9</td>
<td>44.9</td>
</tr>
<tr>
<td>14</td>
<td>36.7</td>
<td>36.7</td>
</tr>
<tr>
<td>15</td>
<td>52.4</td>
<td>52.3</td>
</tr>
<tr>
<td>16</td>
<td>81.4</td>
<td>81.4</td>
</tr>
<tr>
<td>17</td>
<td>65.4</td>
<td>65.4</td>
</tr>
<tr>
<td>18</td>
<td>27.3</td>
<td>27.3</td>
</tr>
<tr>
<td>19</td>
<td>15.6</td>
<td>15.6</td>
</tr>
<tr>
<td>20</td>
<td>17.0</td>
<td>17.0</td>
</tr>
<tr>
<td>OAc</td>
<td>171.4</td>
<td>171.4</td>
</tr>
<tr>
<td></td>
<td>19.7</td>
<td>19.7</td>
</tr>
</tbody>
</table>
fritillebric acid 28: $^1$H spectra comparison:

<table>
<thead>
<tr>
<th></th>
<th>Natural 28&lt;sup&gt;29&lt;/sup&gt;</th>
<th>Synthetic 28</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^1$H NMR (600 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>$^1$H NMR (400 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;)</td>
</tr>
<tr>
<td></td>
<td>$\delta$ [ppm, mult, $J$ (Hz)]</td>
<td>$\delta$ [ppm, mult, $J$ (Hz)]</td>
</tr>
<tr>
<td>1</td>
<td>1.82 (dt, $J = 13.4$, 7.0 Hz, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>0.96 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>1.62 (m, 1 H), 1.67 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>4.47 (dd, $J = 11.8$, 5.5 Hz, 1 H)</td>
<td>4.46</td>
</tr>
<tr>
<td></td>
<td>(dd, $J = 10.8$, 5.8 Hz, 1 H)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>0.83 (d, $J = 2.1$ Hz, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>1.37 (dddd, $J = 12.1$, 12.1, 4.2, 4.2 Hz, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1.57 (m, 1 H)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1.55 (m, 1 H), 1.53 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>0.98 (d, $J = 4.6$ Hz, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>11</td>
<td>1.59 (m, 2 H)</td>
<td>–</td>
</tr>
<tr>
<td>12</td>
<td>1.52 (d, $J = 3.7$ Hz, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1.50 (d, $J = 3.3$ Hz, 1 H)</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>2.54 (brs, 1 H)</td>
<td>2.54 (brs, 1 H)</td>
</tr>
<tr>
<td>14</td>
<td>1.88 (d, $J = 11.7$ Hz),</td>
<td>1.88 (d, $J = 12.8$ Hz, 1 H)</td>
</tr>
<tr>
<td></td>
<td>1.21 (dd, $J = 11.6$, 4.9 Hz)</td>
<td>1.21 (dd, $J = 11.7$, 5.1 Hz, 1 H)</td>
</tr>
<tr>
<td>15</td>
<td>1.72 (dd, $J = 13.5$, 5.9 Hz)</td>
<td>1.73 (dd, $J = 13.6$, 6.0 Hz, 1 H)</td>
</tr>
<tr>
<td></td>
<td>1.64 (m, 1 H)</td>
<td>1.64 (m, 1 H)</td>
</tr>
<tr>
<td>16</td>
<td>2.64 (dd, $J = 8.9$, 6.1 Hz)</td>
<td>2.65 (dd, $J = 9.0$, 6.0 Hz)</td>
</tr>
<tr>
<td>17</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>18</td>
<td>11.53 (brs, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>19</td>
<td>0.852 (s, 3 H)</td>
<td>0.845 (s, 3 H)</td>
</tr>
<tr>
<td>20</td>
<td>0.856 (s, 3 H)</td>
<td>0.853 (s, 3 H)</td>
</tr>
<tr>
<td>21</td>
<td>1.05 (s, 3 H)</td>
<td>1.02 (s, 3 H)</td>
</tr>
<tr>
<td>OAc</td>
<td>2.05 (s, 3 H)</td>
<td>2.05 (s, 3 H)</td>
</tr>
</tbody>
</table>

Natural fritillebric acid 28: $[\alpha]_b^{20^\circ} = -60.6^\circ$ ($c = 1.0$, CHCl<sub>3</sub>);
Synthetic fritillebric acid 28: $[\alpha]_b^{23.8^\circ} = -32^\circ$ ($c = 0.0125$, CHCl<sub>3</sub>).
Natural fritillebric acid 28: Melting point: 235 –237 ºC;
Synthetic fritillebric acid 28: Melting point: 231 – 233 ºC.
fritillebric acid 28: $^{13}$C spectra comparison:

![fritillebric acid diagram](image)

<table>
<thead>
<tr>
<th></th>
<th>Natural 28$^{29}$ $^{13}$C NMR (75 MHz, CDCl$_3$)</th>
<th>Synthetic 28 $^{1}$H NMR (101 MHz, CDCl$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δ (ppm)</td>
<td>δ (ppm)</td>
</tr>
<tr>
<td>1</td>
<td>38.4</td>
<td>38.3</td>
</tr>
<tr>
<td>2</td>
<td>23.7</td>
<td>23.6</td>
</tr>
<tr>
<td>3</td>
<td>81.0</td>
<td>81.0</td>
</tr>
<tr>
<td>4</td>
<td>37.8</td>
<td>37.7</td>
</tr>
<tr>
<td>5</td>
<td>55.2</td>
<td>55.2</td>
</tr>
<tr>
<td>6</td>
<td>20.4</td>
<td>20.4</td>
</tr>
<tr>
<td>7</td>
<td>40.8</td>
<td>40.7</td>
</tr>
<tr>
<td>8</td>
<td>44.9</td>
<td>44.9</td>
</tr>
<tr>
<td>9</td>
<td>55.7</td>
<td>55.7</td>
</tr>
<tr>
<td>10</td>
<td>38.9</td>
<td>38.9</td>
</tr>
<tr>
<td>11</td>
<td>18.5</td>
<td>18.5</td>
</tr>
<tr>
<td>12</td>
<td>31.2</td>
<td>31.2</td>
</tr>
<tr>
<td>13</td>
<td>41.4</td>
<td>41.3</td>
</tr>
<tr>
<td>14</td>
<td>38.0</td>
<td>38.0</td>
</tr>
<tr>
<td>15</td>
<td>44.5</td>
<td>44.4</td>
</tr>
<tr>
<td>16</td>
<td>45.4</td>
<td>45.1</td>
</tr>
<tr>
<td>17</td>
<td>183.3</td>
<td>181.7</td>
</tr>
<tr>
<td>18</td>
<td>28.4</td>
<td>28.3</td>
</tr>
<tr>
<td>19</td>
<td>16.6</td>
<td>16.6</td>
</tr>
<tr>
<td>20</td>
<td>17.5</td>
<td>17.5</td>
</tr>
<tr>
<td>OAc</td>
<td>171.0</td>
<td>171.0</td>
</tr>
<tr>
<td></td>
<td>21.3</td>
<td>21.3</td>
</tr>
</tbody>
</table>
fritillebin B 29: $^1$H spectra comparison:

![Chemical structure of fritillebin B 29](image)

<table>
<thead>
<tr>
<th></th>
<th>Natural 29$^{29}$</th>
<th>Synthetic 29</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H</strong></td>
<td>$^1$H NMR (600 MHz, CDCl$_3$)</td>
<td>$^1$H NMR (400 MHz, CDCl$_3$)</td>
</tr>
<tr>
<td></td>
<td>$\delta$ [ppm, mult, $J$ (Hz)]</td>
<td>$\delta$ [ppm, mult, $J$ (Hz)]</td>
</tr>
<tr>
<td>Me</td>
<td>0.84 (s, 3 H)</td>
<td>0.84 (s, 3 H)</td>
</tr>
<tr>
<td></td>
<td>0.84 (s, 3 H)</td>
<td>0.84 (s, 3 H)</td>
</tr>
<tr>
<td></td>
<td>0.85 (s, 3 H)</td>
<td>0.84 (s, 3 H)</td>
</tr>
<tr>
<td></td>
<td>0.85 (s, 3 H)</td>
<td>0.85 (s, 3 H)</td>
</tr>
<tr>
<td></td>
<td>1.02 (s, 3 H)</td>
<td>1.02 (s, 3 H)</td>
</tr>
<tr>
<td></td>
<td>1.04 (s, 3 H)</td>
<td>1.03 (s, 3 H)</td>
</tr>
<tr>
<td>3-H</td>
<td>4.47 (dd, $J= 10.8, 5.6$ Hz, 1 H)</td>
<td>4.46 (dd, $J= 10.1, 4.9$ Hz, 1 H)</td>
</tr>
<tr>
<td>3'-H</td>
<td>4.47 (dd, $J= 10.8, 5.6$ Hz, 1 H)</td>
<td>4.46 (dd, $J= 10.1, 4.9$ Hz, 1 H)</td>
</tr>
<tr>
<td>OAc</td>
<td>2.04 (s, 3 H)</td>
<td>2.05 (s, 3 H)</td>
</tr>
<tr>
<td></td>
<td>2.04 (s, 3 H)</td>
<td>2.05 (s, 3 H)</td>
</tr>
<tr>
<td>17'-2H</td>
<td>4.23, 4.18 (AB, $J= 11.3$ Hz, 2 H)</td>
<td>4.22, 4.18 (AB, $J= 11.2$ Hz, 2 H)</td>
</tr>
</tbody>
</table>

*Note: The original isolation paper only provided partial $^1$H NMR data which was shown as above.$^{29}*

Natural fritillebin B 29: $[\alpha]_D^{28} = -56.9^\circ$ ($c = 0.4$, CHCl$_3$);
Synthetic fritillebin B 29: $[\alpha]_D^{25} = -52^\circ$ ($c = 0.108$, CHCl$_3$).
Natural fritillebin B 29: Melting point: 243 –245 °C;
Synthetic f fritillebin B 29: Melting point: 245.1 – 246.5 °C
Fritillebin B 29: $^{13}$C spectra comparison:

![Fritillebin B 29](image)

<table>
<thead>
<tr>
<th>Natural 29$^{29}$</th>
<th>Synthetic 29</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}$C NMR (75 MHz, CDCl$_3$)</td>
<td>$^1$H NMR (101 MHz, CDCl$_3$)</td>
</tr>
<tr>
<td>(\delta) (ppm)</td>
<td>(\delta) (ppm)</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>1</td>
<td>38.4</td>
</tr>
<tr>
<td>2</td>
<td>23.6</td>
</tr>
<tr>
<td>3</td>
<td>80.9</td>
</tr>
<tr>
<td>4</td>
<td>37.8</td>
</tr>
<tr>
<td>5</td>
<td>55.1</td>
</tr>
<tr>
<td>6</td>
<td>20.4</td>
</tr>
<tr>
<td>7</td>
<td>40.9</td>
</tr>
<tr>
<td>8</td>
<td>44.9</td>
</tr>
<tr>
<td>9</td>
<td>55.8</td>
</tr>
<tr>
<td>10</td>
<td>38.9</td>
</tr>
<tr>
<td>11</td>
<td>18.5</td>
</tr>
<tr>
<td>12</td>
<td>31.3</td>
</tr>
<tr>
<td>13</td>
<td>41.4</td>
</tr>
<tr>
<td>14</td>
<td>38.1</td>
</tr>
<tr>
<td>15</td>
<td>44.7</td>
</tr>
<tr>
<td>16</td>
<td>45.6</td>
</tr>
<tr>
<td>17</td>
<td>177.4</td>
</tr>
<tr>
<td>18</td>
<td>28.3</td>
</tr>
<tr>
<td>19</td>
<td>16.6</td>
</tr>
<tr>
<td>20</td>
<td>17.5</td>
</tr>
<tr>
<td>OAc</td>
<td>170.9</td>
</tr>
<tr>
<td></td>
<td>21.3</td>
</tr>
</tbody>
</table>
**ent-kauran-16-ene 30: $^1$H spectra comparison:**

<table>
<thead>
<tr>
<th>C</th>
<th>Natural 30&lt;sup&gt;30&lt;/sup&gt; $^1$H NMR (400 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;) δ [ppm, mult, J (Hz)]</th>
<th>Synthetic 30 $^1$H NMR (400 MHz, CDCl&lt;sub&gt;3&lt;/sub&gt;) δ [ppm, mult, J (Hz)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.82 (d, $J = 12.8$, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>0.73 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>1.59 (m, 1 H), 1.40 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>1.36 (m, 1 H), 1.12 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>0.78 (dd, $J = 13.0$, 2.0 Hz, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>1.54 (m, 1 H), 1.31 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>1.50 (m, 2 H)</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>1.06 (dd, $J = 13.0$, 7.0 Hz, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>11</td>
<td>1.59 (m, 2 H)</td>
<td>–</td>
</tr>
<tr>
<td>12</td>
<td>1.62 (m, 1 H), 1.47 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>13</td>
<td>2.63 (brs, 1 H)</td>
<td>2.63 (brs, 1 H)</td>
</tr>
<tr>
<td>14</td>
<td>1.98 (dd, $J = 10.0$, 1.6 Hz, 1 H)</td>
<td>1.10 (m, 1 H)</td>
</tr>
<tr>
<td></td>
<td>1.0 (m, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>15</td>
<td>2.0 (d, $J = 10$ Hz, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>2.05 (d, $J = 10$ Hz, 1 H)</td>
<td>–</td>
</tr>
<tr>
<td>16</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>17</td>
<td>4.79 (brs, 1 H), 4.73 (brs, 1 H)</td>
<td>4.79 (m, 1 H), 4.73 (m, 1 H)</td>
</tr>
<tr>
<td>18</td>
<td>0.80 (s, 3 H)</td>
<td>0.81 (s, 3 H)</td>
</tr>
<tr>
<td>19</td>
<td>0.85 (s, 3 H)</td>
<td>0.85 (s, 3 H)</td>
</tr>
<tr>
<td>20</td>
<td>1.02 (s, 3 H)</td>
<td>1.02 (s, 3 H)</td>
</tr>
</tbody>
</table>

*Note: The original isolation paper didn’t provided the optical rotation and melting point.*<sup>30</sup>
**ent-kauran-16-ene 30: $^{13}$C spectra comparison:**

![ent-kauran-16-ene 30](image)

<table>
<thead>
<tr>
<th>C</th>
<th>Natural 30$^{30}$ $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm)</th>
<th>Synthetic 30 $^{1}$H NMR (101 MHz, CDCl$_3$) $\delta$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40.7</td>
<td>40.6</td>
</tr>
<tr>
<td>2</td>
<td>18.9</td>
<td>18.8</td>
</tr>
<tr>
<td>3</td>
<td>42.3</td>
<td>42.2</td>
</tr>
<tr>
<td>4</td>
<td>33.5</td>
<td>33.4</td>
</tr>
<tr>
<td>5</td>
<td>56.5</td>
<td>56.4</td>
</tr>
<tr>
<td>6</td>
<td>20.5</td>
<td>20.4</td>
</tr>
<tr>
<td>7</td>
<td>41.5</td>
<td>41.4</td>
</tr>
<tr>
<td>8</td>
<td>44.5</td>
<td>44.4</td>
</tr>
<tr>
<td>9</td>
<td>56.3</td>
<td>56.2</td>
</tr>
<tr>
<td>10</td>
<td>39.6</td>
<td>39.5</td>
</tr>
<tr>
<td>11</td>
<td>18.4</td>
<td>18.3</td>
</tr>
<tr>
<td>12</td>
<td>33.5</td>
<td>33.5</td>
</tr>
<tr>
<td>13</td>
<td>44.3</td>
<td>44.2</td>
</tr>
<tr>
<td>14</td>
<td>40.1</td>
<td>40.0</td>
</tr>
<tr>
<td>15</td>
<td>49.4</td>
<td>49.4</td>
</tr>
<tr>
<td>16</td>
<td>156.4</td>
<td>156.4</td>
</tr>
<tr>
<td>17</td>
<td>103.0</td>
<td>103.0</td>
</tr>
<tr>
<td>18</td>
<td>21.9</td>
<td>21.8</td>
</tr>
<tr>
<td>19</td>
<td>33.9</td>
<td>33.8</td>
</tr>
<tr>
<td>20</td>
<td>17.8</td>
<td>17.8</td>
</tr>
</tbody>
</table>
*ent*-kauran-16β-ol 31: ¹H spectra comparison:

<table>
<thead>
<tr>
<th>Natural 31</th>
<th>Synthetic 31</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹H NMR (400 MHz, CDCl₃)</td>
<td>¹H NMR (400 MHz, CDCl₃)</td>
</tr>
<tr>
<td>δ [ppm, mult, J (Hz)]</td>
<td>δ [ppm, mult, J (Hz)]</td>
</tr>
<tr>
<td>0.80 (s, 3 H)</td>
<td>0.80 (s, 3 H)</td>
</tr>
<tr>
<td>0.84 (s, 3 H)</td>
<td>0.84 (s, 3 H)</td>
</tr>
<tr>
<td>1.02 (s, 3 H)</td>
<td>1.02 (s, 3 H)</td>
</tr>
<tr>
<td>1.36 (s, 3 H)</td>
<td>1.36 (s, 3 H)</td>
</tr>
</tbody>
</table>

**Note:** The original isolation paper only provided partial ¹H NMR data which was shown as above.³¹

Natural *ent*-kauran-16β-ol 31: [α]₂⁰ = −37.7° (c = 1.22, CHCl₃);
Synthetic *ent*-kauran-16β-ol 31: [α]₂⁰ = −46° (c = 0.05, CHCl₃).
Natural *ent*-kauran-16β-ol 31: Melting point: 218–220 °C;
Synthetic *ent*-kauran-16β-ol 31: Melting point: 216–218 °C
**ent-kauran-16β-ol 31: $^{13}$C spectra comparison:**

<table>
<thead>
<tr>
<th></th>
<th>Natural 31$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm)</th>
<th>Synthetic 31 $^1$H NMR (101 MHz, CDCl$_3$) $\delta$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42.1</td>
<td>42.1</td>
</tr>
<tr>
<td>2</td>
<td>18.6</td>
<td>18.6</td>
</tr>
<tr>
<td>3</td>
<td>42.1</td>
<td>42.1</td>
</tr>
<tr>
<td>4</td>
<td>33.3</td>
<td>33.2</td>
</tr>
<tr>
<td>5</td>
<td>56.3</td>
<td>56.2</td>
</tr>
<tr>
<td>6</td>
<td>20.5</td>
<td>20.4</td>
</tr>
<tr>
<td>7</td>
<td>40.4</td>
<td>40.3</td>
</tr>
<tr>
<td>8</td>
<td>45.4</td>
<td>45.4</td>
</tr>
<tr>
<td>9</td>
<td>56.9</td>
<td>56.9</td>
</tr>
<tr>
<td>10</td>
<td>39.4</td>
<td>39.3</td>
</tr>
<tr>
<td>11</td>
<td>17.8</td>
<td>17.8</td>
</tr>
<tr>
<td>12</td>
<td>27.0</td>
<td>26.9</td>
</tr>
<tr>
<td>13</td>
<td>49.1</td>
<td>49.0</td>
</tr>
<tr>
<td>14</td>
<td>37.7</td>
<td>37.7</td>
</tr>
<tr>
<td>15</td>
<td>58.1</td>
<td>58.0</td>
</tr>
<tr>
<td>16</td>
<td>79.3</td>
<td>79.4</td>
</tr>
<tr>
<td>17</td>
<td>24.5</td>
<td>24.5</td>
</tr>
<tr>
<td>18</td>
<td>33.6</td>
<td>33.6</td>
</tr>
<tr>
<td>19</td>
<td>21.6</td>
<td>21.5</td>
</tr>
<tr>
<td>20</td>
<td>18.0</td>
<td>18.0</td>
</tr>
</tbody>
</table>
ent-3β,19-dihydroxy-kaur-16-ene 36: ¹H spectra comparison:

<table>
<thead>
<tr>
<th>C</th>
<th>Natural 36⁰²</th>
<th>Synthetic 36</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>¹H NMR (600 MHz, CDCl₃)</td>
<td>¹H NMR (400 MHz, CDCl₃)</td>
</tr>
<tr>
<td></td>
<td>δ [ppm, mult, J (Hz)]</td>
<td>δ [ppm, mult, J (Hz)]</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.42 (ddd, J = 11.8, 4.4, 1.3 Hz, 1 H)</td>
<td>3.42 (ddd, J = 11.8, 4.8, 1.3 Hz, 1 H)</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>2.64 (t, J = 5 Hz, 1 H)</td>
<td>2.64 (brs, 1 H)</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>2.05 (t, J = 2.5 Hz, 2 H)</td>
<td>2.04 (m, 2 H)</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>4.73 (ddt, J = 2.5, 1.8, 1.3 Hz, 1 H)</td>
<td>4.73 (brs, 1 H)</td>
</tr>
<tr>
<td></td>
<td>4.79 (m, 1 H)</td>
<td>4.79 (m, 1 H)</td>
</tr>
<tr>
<td>18</td>
<td>1.22 (s, 3 H)</td>
<td>1.22 (s, 3 H)</td>
</tr>
<tr>
<td>19</td>
<td>4.20 (d, J = 11.2 Hz)</td>
<td>4.20 (d, J = 11.2 Hz)</td>
</tr>
<tr>
<td></td>
<td>3.31 (dd, J = 11.2, 1.3 Hz, 1 H)</td>
<td>3.31 (dd, J = 11.2, 1.3 Hz, 1 H)</td>
</tr>
<tr>
<td>20</td>
<td>0.98 (s, 3 H)</td>
<td>0.98 (s, 3 H)</td>
</tr>
</tbody>
</table>

Note: The original isolation paper only provided partial ¹H NMR data which was shown as Above²²

Natural ent-3β,19-dihydroxy-kaur-16-ene 36: [α]²⁰ = −26.4° (c = 1.5, CHCl₃);²⁷
Synthetic ent-3β,19-dihydroxy-kaur-16-ene 36: [α]²⁰⁵⁵ = −62° (c = 0.1, CHCl₃).
Natural ent-3β,19-dihydroxy-kaur-16-ene 36: Melting point: 180.9 – 182.2 °C;²⁷
Synthetic ent-3β,19-dihydroxy-kaur-16-ene 36: Melting point: 152.0 – 154.9 °C
ent-3β,19-dihydroxy-kaur-16-ene 36: $^{13}$C spectra comparison:

![ent-3β,19-dihydroxy-kaur-16-ene 36](image)

<table>
<thead>
<tr>
<th>C</th>
<th>Natural 36$^{13}$</th>
<th>Synthetic 36$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{13}$C NMR (150 MHz, CDCl$_3$)</td>
<td>$^1$H NMR (101 MHz, CDCl$_3$)</td>
</tr>
<tr>
<td></td>
<td>$\delta$ (ppm)</td>
<td>$\delta$ (ppm)</td>
</tr>
<tr>
<td>1</td>
<td>38.6</td>
<td>38.6</td>
</tr>
<tr>
<td>2</td>
<td>27.9</td>
<td>27.9</td>
</tr>
<tr>
<td>3</td>
<td>81.1</td>
<td>81.1</td>
</tr>
<tr>
<td>4</td>
<td>43.1</td>
<td>43.1</td>
</tr>
<tr>
<td>5</td>
<td>55.9</td>
<td>55.9</td>
</tr>
<tr>
<td>6</td>
<td>20.2</td>
<td>20.2</td>
</tr>
<tr>
<td>7</td>
<td>41.5</td>
<td>41.5</td>
</tr>
<tr>
<td>8</td>
<td>44.1</td>
<td>44.1</td>
</tr>
<tr>
<td>9</td>
<td>56.0</td>
<td>56.0</td>
</tr>
<tr>
<td>10</td>
<td>38.9</td>
<td>38.9</td>
</tr>
<tr>
<td>11</td>
<td>18.5</td>
<td>18.5</td>
</tr>
<tr>
<td>12</td>
<td>39.7</td>
<td>39.7</td>
</tr>
<tr>
<td>13</td>
<td>44.0</td>
<td>44.0</td>
</tr>
<tr>
<td>14</td>
<td>33.2</td>
<td>33.2</td>
</tr>
<tr>
<td>15</td>
<td>49.0</td>
<td>49.0</td>
</tr>
<tr>
<td>16</td>
<td>155.7</td>
<td>155.7</td>
</tr>
<tr>
<td>17</td>
<td>103.3</td>
<td>103.3</td>
</tr>
<tr>
<td>18</td>
<td>22.8</td>
<td>22.8</td>
</tr>
<tr>
<td>19</td>
<td>64.5</td>
<td>64.5</td>
</tr>
<tr>
<td>20</td>
<td>18.3</td>
<td>18.3</td>
</tr>
</tbody>
</table>
hibaene 37: $^1$H spectra comparison:

<table>
<thead>
<tr>
<th>Natural $^\text{37}$ $^\text{33}$</th>
<th>Synthetic $^\text{37}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H NMR (500 MHz, CDCl$_3$)</td>
<td>$^1$H NMR (400 MHz, CDCl$_3$)</td>
</tr>
<tr>
<td>$\delta$ [ppm, mult, $J$ (Hz)]</td>
<td>$\delta$ [ppm, mult, $J$ (Hz)]</td>
</tr>
<tr>
<td>5.70 (d, $J = 5.0$ Hz, 1 H)</td>
<td>5.69 (d, $J = 5.7$ Hz, 1 H)</td>
</tr>
<tr>
<td>5.45 (d, $J = 5.0$ Hz, 1 H)</td>
<td>5.44 (d, $J = 5.7$ Hz, 1 H)</td>
</tr>
<tr>
<td>1.64 – 1.43 (m, 6 H)</td>
<td>1.64 – 1.43 (m, 6 H)</td>
</tr>
<tr>
<td>1.38 – 1.22 (m, 7 H)</td>
<td>1.38 – 1.22 (m, 7 H)</td>
</tr>
<tr>
<td>1.16 – 1.10 (dt, $J = 13.0$, 5.0 Hz, 1 H)</td>
<td>1.16 – 1.10 (m, 1 H)</td>
</tr>
<tr>
<td>0.99 (m, 5 H)</td>
<td>0.99 (s, 3 H), 1.04 – 0.93 (m, 2 H)</td>
</tr>
<tr>
<td>0.86 – 0.80 (m, 8 H)</td>
<td>0.86 (s, 3 H), 0.82 (s, 3 H), 0.89 – 0.77 (m, 2 H)</td>
</tr>
<tr>
<td>0.74 (s, 3 H)</td>
<td>0.74 (s, 3 H)</td>
</tr>
</tbody>
</table>

Note: The original isolation paper only provided partial $^1$H NMR data which was shown as above. $^\text{33}$

Natural hibaene 37: $[\alpha]_{D}^{23} = -49.9^\circ$ (c = 1.0, CHCl$_3$); $^\text{34}$
Synthetic hibaene 37: $[\alpha]_{D}^{23} = -15^\circ$ (c = 0.1, CHCl$_3$).
Natural hibaene 37: Melting point: 29.5 – 30.5 °C; $^\text{26}$
Synthetic hibaene 37: Melting point: 28 – 30 °C.
hibaene 37: $^{13}$C spectra comparison:

<table>
<thead>
<tr>
<th></th>
<th>Natural 37$^{35}$</th>
<th>Synthetic 37</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{13}$C NMR (25.2 MHz, CDCl$_3$)</td>
<td>$^1$H NMR (101 MHz, CDCl$_3$)</td>
</tr>
<tr>
<td></td>
<td>δ (ppm)</td>
<td>δ (ppm)</td>
</tr>
<tr>
<td>1</td>
<td>39.1</td>
<td>39.1</td>
</tr>
<tr>
<td>2</td>
<td>18.6</td>
<td>18.5</td>
</tr>
<tr>
<td>3</td>
<td>42.0</td>
<td>42.0</td>
</tr>
<tr>
<td>4</td>
<td>33.1</td>
<td>33.1</td>
</tr>
<tr>
<td>5</td>
<td>55.9</td>
<td>55.9</td>
</tr>
<tr>
<td>6</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>7</td>
<td>37.2</td>
<td>37.2</td>
</tr>
<tr>
<td>8</td>
<td>48.9</td>
<td>49.0</td>
</tr>
<tr>
<td>9</td>
<td>52.7</td>
<td>52.8</td>
</tr>
<tr>
<td>10</td>
<td>37.2</td>
<td>37.2</td>
</tr>
<tr>
<td>11</td>
<td>20.1</td>
<td>20.1</td>
</tr>
<tr>
<td>12</td>
<td>33.1</td>
<td>33.1</td>
</tr>
<tr>
<td>13</td>
<td>43.5</td>
<td>43.5</td>
</tr>
<tr>
<td>14</td>
<td>61.1</td>
<td>61.1</td>
</tr>
<tr>
<td>15</td>
<td>135.1</td>
<td>135.3</td>
</tr>
<tr>
<td>16</td>
<td>136.0</td>
<td>136.1</td>
</tr>
<tr>
<td>17</td>
<td>24.9</td>
<td>24.9</td>
</tr>
<tr>
<td>18</td>
<td>33.6</td>
<td>33.6</td>
</tr>
<tr>
<td>19</td>
<td>21.9</td>
<td>21.9</td>
</tr>
<tr>
<td>20</td>
<td>15.0</td>
<td>15.0</td>
</tr>
</tbody>
</table>
Single Crystal X-ray Diffraction Data

X-ray crystallographic data for 1

<table>
<thead>
<tr>
<th>Crystal data and structure refinement for 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
</tr>
<tr>
<td>Empirical formula</td>
</tr>
<tr>
<td>Formula weight</td>
</tr>
<tr>
<td>Temperature/K</td>
</tr>
<tr>
<td>Crystal system</td>
</tr>
<tr>
<td>Space group</td>
</tr>
<tr>
<td>a/Å</td>
</tr>
<tr>
<td>b/Å</td>
</tr>
<tr>
<td>c/Å</td>
</tr>
<tr>
<td>α/°</td>
</tr>
<tr>
<td>β/°</td>
</tr>
<tr>
<td>γ/°</td>
</tr>
<tr>
<td>Volume/Å^3</td>
</tr>
<tr>
<td>Z</td>
</tr>
<tr>
<td>ρ_{calc}/g/cm^3</td>
</tr>
<tr>
<td>μ/mm^-1</td>
</tr>
<tr>
<td>F(000)</td>
</tr>
<tr>
<td>Crystal size/mm^3</td>
</tr>
<tr>
<td>Radiation</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
</tr>
<tr>
<td>Index ranges</td>
</tr>
<tr>
<td>Reflections collected</td>
</tr>
<tr>
<td>Independent reflections</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
</tr>
<tr>
<td>Goodness-of-fit on F^2</td>
</tr>
<tr>
<td>Final R indexes [I&gt;2σ(I)]</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å^-3</td>
</tr>
</tbody>
</table>
### Table S12. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1. U(eq) is defined as 1/3 of of the trace of the orthogonalised U_ij tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si17</td>
<td>5819.5(8)</td>
<td>5845.2(6)</td>
<td>733.1(2)</td>
<td>25.39(15)</td>
</tr>
<tr>
<td>Si43</td>
<td>9077.9(8)</td>
<td>5551.6(6)</td>
<td>8130.5(2)</td>
<td>28.09(16)</td>
</tr>
<tr>
<td>O41</td>
<td>6191(2)</td>
<td>5219.3(15)</td>
<td>4906.4(6)</td>
<td>25.7(3)</td>
</tr>
<tr>
<td>O15</td>
<td>7465(2)</td>
<td>4762.6(16)</td>
<td>3949.5(6)</td>
<td>27.2(3)</td>
</tr>
<tr>
<td>O42</td>
<td>7734(2)</td>
<td>5635.5(18)</td>
<td>7602.2(6)</td>
<td>31.4(4)</td>
</tr>
<tr>
<td>O16</td>
<td>5366(2)</td>
<td>5704.2(18)</td>
<td>1308.1(6)</td>
<td>30.3(4)</td>
</tr>
<tr>
<td>C40</td>
<td>9501(3)</td>
<td>4084(2)</td>
<td>5308.7(8)</td>
<td>22.9(4)</td>
</tr>
<tr>
<td>C38</td>
<td>7796(3)</td>
<td>2775(2)</td>
<td>4691.4(8)</td>
<td>25.4(5)</td>
</tr>
<tr>
<td>C31</td>
<td>6094(3)</td>
<td>5458(2)</td>
<td>6783.9(8)</td>
<td>25.6(5)</td>
</tr>
<tr>
<td>C36</td>
<td>7822(3)</td>
<td>4080(2)</td>
<td>5585.8(8)</td>
<td>20.6(4)</td>
</tr>
<tr>
<td>C39</td>
<td>9355(3)</td>
<td>3220(2)</td>
<td>4890.8(8)</td>
<td>24.4(5)</td>
</tr>
<tr>
<td>C2</td>
<td>6664(4)</td>
<td>6599(2)</td>
<td>3603.8(9)</td>
<td>32.8(5)</td>
</tr>
<tr>
<td>C51</td>
<td>8381(3)</td>
<td>6176(2)</td>
<td>5861.2(9)</td>
<td>27.7(5)</td>
</tr>
<tr>
<td>C7</td>
<td>7835(3)</td>
<td>4893(3)</td>
<td>1861.7(9)</td>
<td>31.4(5)</td>
</tr>
<tr>
<td>C37</td>
<td>6022(3)</td>
<td>3102(2)</td>
<td>4859.8(8)</td>
<td>25.7(5)</td>
</tr>
<tr>
<td>C30</td>
<td>6157(3)</td>
<td>4855(2)</td>
<td>6267.4(8)</td>
<td>22.0(4)</td>
</tr>
<tr>
<td>C10</td>
<td>9184(3)</td>
<td>5445(2)</td>
<td>3281.9(8)</td>
<td>25.5(5)</td>
</tr>
<tr>
<td>C32</td>
<td>7730(3)</td>
<td>5039(2)</td>
<td>7141.9(8)</td>
<td>25.4(5)</td>
</tr>
<tr>
<td>C33</td>
<td>9505(3)</td>
<td>5196(2)</td>
<td>6925.2(8)</td>
<td>27.3(5)</td>
</tr>
<tr>
<td>C4</td>
<td>6477(3)</td>
<td>6057(2)</td>
<td>2698.4(8)</td>
<td>25.6(5)</td>
</tr>
<tr>
<td>C5</td>
<td>5274(3)</td>
<td>6018(2)</td>
<td>2185.0(8)</td>
<td>29.7(5)</td>
</tr>
<tr>
<td>C25</td>
<td>7083(3)</td>
<td>3878(2)</td>
<td>2876.8(9)</td>
<td>30.6(5)</td>
</tr>
<tr>
<td>C3</td>
<td>5414(3)</td>
<td>6210(3)</td>
<td>3145.9(9)</td>
<td>33.0(6)</td>
</tr>
<tr>
<td>C28</td>
<td>4421(3)</td>
<td>4256(2)</td>
<td>5455.8(8)</td>
<td>26.0(5)</td>
</tr>
<tr>
<td>C6</td>
<td>6494(3)</td>
<td>5872(3)</td>
<td>1768.6(8)</td>
<td>27.5(5)</td>
</tr>
<tr>
<td>C9</td>
<td>7904(3)</td>
<td>5076(2)</td>
<td>2807.4(8)</td>
<td>23.5(4)</td>
</tr>
<tr>
<td>C27</td>
<td>6128(3)</td>
<td>4176(2)</td>
<td>5198.8(8)</td>
<td>21.7(4)</td>
</tr>
<tr>
<td>C34</td>
<td>9463(3)</td>
<td>4540(2)</td>
<td>6433.1(8)</td>
<td>24.9(5)</td>
</tr>
<tr>
<td>C29</td>
<td>4570(3)</td>
<td>5151(2)</td>
<td>5872.1(8)</td>
<td>26.2(5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>C1</td>
<td>8230(3)</td>
<td>5772(2)</td>
<td>3740.2(8)</td>
<td>25.8(5)</td>
</tr>
<tr>
<td>C26</td>
<td>3833(3)</td>
<td>5060(3)</td>
<td>2145.5(9)</td>
<td>42.2(7)</td>
</tr>
<tr>
<td>C35</td>
<td>7953(3)</td>
<td>4946(2)</td>
<td>6032.7(8)</td>
<td>21.5(4)</td>
</tr>
<tr>
<td>C52</td>
<td>4395(3)</td>
<td>5036(3)</td>
<td>7001.2(9)</td>
<td>34.7(6)</td>
</tr>
<tr>
<td>C8</td>
<td>9004(3)</td>
<td>5032(3)</td>
<td>2362.3(9)</td>
<td>30.1(5)</td>
</tr>
<tr>
<td>C13</td>
<td>11848(3)</td>
<td>4919(3)</td>
<td>3912.5(10)</td>
<td>38.6(6)</td>
</tr>
<tr>
<td>C50</td>
<td>6020(4)</td>
<td>6786(3)</td>
<td>6765.4(10)</td>
<td>34.9(6)</td>
</tr>
<tr>
<td>C14</td>
<td>10712(3)</td>
<td>4577(3)</td>
<td>3435.3(9)</td>
<td>32.7(5)</td>
</tr>
<tr>
<td>C49</td>
<td>10036(4)</td>
<td>4064(3)</td>
<td>8234.8(11)</td>
<td>42.3(6)</td>
</tr>
<tr>
<td>C12</td>
<td>11340(3)</td>
<td>5697(3)</td>
<td>4228.4(9)</td>
<td>37.0(6)</td>
</tr>
<tr>
<td>C11</td>
<td>9583(4)</td>
<td>6327(2)</td>
<td>4141.0(9)</td>
<td>32.7(5)</td>
</tr>
<tr>
<td>C44</td>
<td>7568(3)</td>
<td>5944(3)</td>
<td>8616.6(9)</td>
<td>39.1(6)</td>
</tr>
<tr>
<td>C47</td>
<td>6687(5)</td>
<td>7117(4)</td>
<td>8487.8(13)</td>
<td>57.6(9)</td>
</tr>
<tr>
<td>C48</td>
<td>10960(4)</td>
<td>6607(3)</td>
<td>8130.1(12)</td>
<td>43.7(7)</td>
</tr>
<tr>
<td>C24</td>
<td>4308(5)</td>
<td>7183(3)</td>
<td>2100.4(11)</td>
<td>53.0(9)</td>
</tr>
<tr>
<td>C18</td>
<td>3580(17)</td>
<td>6129(11)</td>
<td>360(4)</td>
<td>33(2)</td>
</tr>
<tr>
<td>C21</td>
<td>3810(30)</td>
<td>6168(17)</td>
<td>-192(8)</td>
<td>47(4)</td>
</tr>
<tr>
<td>C45</td>
<td>6084(4)</td>
<td>5021(4)</td>
<td>8620.7(11)</td>
<td>54.3(9)</td>
</tr>
<tr>
<td>C46</td>
<td>8645(4)</td>
<td>6020(4)</td>
<td>9137.5(10)</td>
<td>53.8(9)</td>
</tr>
<tr>
<td>C22</td>
<td>7390(20)</td>
<td>4720(14)</td>
<td>539(3)</td>
<td>39(3)</td>
</tr>
<tr>
<td>C23</td>
<td>6840(30)</td>
<td>7293(14)</td>
<td>664(4)</td>
<td>51(3)</td>
</tr>
<tr>
<td>C19</td>
<td>2252(11)</td>
<td>5167(11)</td>
<td>445(2)</td>
<td>46(2)</td>
</tr>
<tr>
<td>C20</td>
<td>2812(10)</td>
<td>7294(9)</td>
<td>499(2)</td>
<td>40(2)</td>
</tr>
<tr>
<td>C18A</td>
<td>3508(16)</td>
<td>5678(10)</td>
<td>346(4)</td>
<td>28(2)</td>
</tr>
<tr>
<td>C20A</td>
<td>2231(10)</td>
<td>6619(9)</td>
<td>484(2)</td>
<td>42(2)</td>
</tr>
<tr>
<td>C21A</td>
<td>3750(30)</td>
<td>5756(15)</td>
<td>-224(8)</td>
<td>41(3)</td>
</tr>
<tr>
<td>C19A</td>
<td>2741(10)</td>
<td>4481(9)</td>
<td>455(2)</td>
<td>38(2)</td>
</tr>
<tr>
<td>C23A</td>
<td>7520(20)</td>
<td>7043(14)</td>
<td>673(5)</td>
<td>35(3)</td>
</tr>
<tr>
<td>C22A</td>
<td>6760(30)</td>
<td>4430(14)</td>
<td>545(5)</td>
<td>39(3)</td>
</tr>
</tbody>
</table>
Table S13. Crystal data and structure refinement for 10

Identification code: 2119290
Empirical formula: C₄₃H₆₂O₅Si
Formula weight: 687.01
Temperature/K: 100.01(10)
Crystal system: monoclinic
Space group: P2₁

\[\begin{array}{ll}
a/\text{Å} & 11.77380(11) \\
b/\text{Å} & 7.56179(5) \\
c/\text{Å} & 22.10780(17) \\
\alpha/° & 90 \\
\beta/° & 97.3032(8) \\
\gamma/° & 90 \\
Volume/Å³ & 1952.31(3) \\
Z & 2 \\
\rho_{calc}/\text{g/cm}³ & 1.169 \\
\mu/\text{mm}⁻¹ & 0.86 \\
F(000) & 748 \\
Crystal size/mm³ & 0.22 \times 0.09 \times 0.04 \\
Radiation & CuKα (λ = 1.54184) \\
\theta range for data collection/° & 7.57 to 148.968 \\
Index ranges & -14 \leq h \leq 12, -9 \leq k \leq 9, -27 \leq l \leq 27 \\
Reflections collected & 70439 \\
Independent reflections & 7901 [R_{int} = 0.0490, R_{sigma} = 0.0238] \\
Data/restraints/parameters & 7901/1/450 \\
Goodness-of-fit on F² & 1.03 \\
Final R indexes [I>=2σ (I)] & R₁ = 0.0321, wR₂ = 0.0740 \\
Final R indexes [all data] & R₁ = 0.0341, wR₂ = 0.0750 \\
Largest diff. peak/hole / e Å⁻³ & 0.19/-0.20
\end{array}\]
Flack parameter \(-0.003(7)\)

Table S14. Fractional Atomic Coordinates \((\times10^4)\) and Equivalent Isotropic Displacement Parameters \((\text{Å}^2\times10^3)\) for 10. \(U_{eq}\) is defined as 1/3 of the trace of the orthogonalised \(U_{ij}\) tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(U_{eq})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si0A</td>
<td>2047.8(4)</td>
<td>3645.8(6)</td>
<td>6712.1(2)</td>
<td>19.35(11)</td>
</tr>
<tr>
<td>O0AA</td>
<td>1788.3(11)</td>
<td>3005.5(17)</td>
<td>5996.9(6)</td>
<td>22.4(3)</td>
</tr>
<tr>
<td>O1AA</td>
<td>4496.3(13)</td>
<td>3145.3(19)</td>
<td>1330.2(6)</td>
<td>28.1(3)</td>
</tr>
<tr>
<td>O2AA</td>
<td>1858.0(16)</td>
<td>7959(2)</td>
<td>622.9(6)</td>
<td>37.7(4)</td>
</tr>
<tr>
<td>O3AA</td>
<td>5524.7(18)</td>
<td>1224(3)</td>
<td>1944.9(7)</td>
<td>50.9(5)</td>
</tr>
<tr>
<td>O4AA</td>
<td>2536(2)</td>
<td>9736(2)</td>
<td>1393.9(8)</td>
<td>58.3(6)</td>
</tr>
<tr>
<td>C0AA</td>
<td>3128.2(16)</td>
<td>2002(2)</td>
<td>4574.9(8)</td>
<td>19.4(4)</td>
</tr>
<tr>
<td>C1AA</td>
<td>4220.8(17)</td>
<td>770(3)</td>
<td>3768.1(9)</td>
<td>24.4(4)</td>
</tr>
<tr>
<td>C2AA</td>
<td>2818.3(18)</td>
<td>6864(2)</td>
<td>2239.3(8)</td>
<td>22.7(4)</td>
</tr>
<tr>
<td>C3AA</td>
<td>3206.5(15)</td>
<td>3521(3)</td>
<td>2371.4(8)</td>
<td>20.6(4)</td>
</tr>
<tr>
<td>C4AA</td>
<td>3938.7(16)</td>
<td>2363(2)</td>
<td>3350.9(8)</td>
<td>20.4(4)</td>
</tr>
<tr>
<td>C5AA</td>
<td>2678.0(14)</td>
<td>3602(2)</td>
<td>4171.7(8)</td>
<td>18.4(3)</td>
</tr>
<tr>
<td>C6AA</td>
<td>3053.7(17)</td>
<td>1961(2)</td>
<td>2795.3(8)</td>
<td>21.1(4)</td>
</tr>
<tr>
<td>C7AA</td>
<td>1988.3(18)</td>
<td>4880(3)</td>
<td>5134.5(9)</td>
<td>24.7(4)</td>
</tr>
<tr>
<td>C8AA</td>
<td>2456.9(16)</td>
<td>3304(2)</td>
<td>5511.7(8)</td>
<td>20.5(4)</td>
</tr>
<tr>
<td>C9AA</td>
<td>3325.9(17)</td>
<td>5582(2)</td>
<td>3286.5(8)</td>
<td>21.1(4)</td>
</tr>
<tr>
<td>C0BA</td>
<td>2732.2(16)</td>
<td>5211(2)</td>
<td>2635.8(8)</td>
<td>20.3(4)</td>
</tr>
<tr>
<td>C1BA</td>
<td>3305.9(18)</td>
<td>378(2)</td>
<td>4180.2(9)</td>
<td>23.8(4)</td>
</tr>
<tr>
<td>C2BA</td>
<td>2494.2(16)</td>
<td>1586(2)</td>
<td>5138.5(8)</td>
<td>20.4(4)</td>
</tr>
<tr>
<td>C3BA</td>
<td>4152(2)</td>
<td>2760(3)</td>
<td>236.1(9)</td>
<td>29.1(4)</td>
</tr>
<tr>
<td>C4BA</td>
<td>2659.2(17)</td>
<td>5223(2)</td>
<td>4598.3(9)</td>
<td>22.7(4)</td>
</tr>
<tr>
<td>C5BA</td>
<td>4528.7(16)</td>
<td>3598(3)</td>
<td>2392.0(8)</td>
<td>23.1(4)</td>
</tr>
<tr>
<td>C6BA</td>
<td>1291.1(18)</td>
<td>797(3)</td>
<td>4981.1(9)</td>
<td>27.8(4)</td>
</tr>
<tr>
<td>C7BA</td>
<td>869.5(17)</td>
<td>2534(3)</td>
<td>7074.3(9)</td>
<td>23.5(4)</td>
</tr>
<tr>
<td>C8BA</td>
<td>3578.1(16)</td>
<td>3972(2)</td>
<td>3719.4(8)</td>
<td>18.5(4)</td>
</tr>
<tr>
<td>C9BA</td>
<td>970.6(18)</td>
<td>528(3)</td>
<td>6993.7(9)</td>
<td>26.7(4)</td>
</tr>
<tr>
<td>C0CA</td>
<td>-297.0(18)</td>
<td>3157(3)</td>
<td>6759.4(11)</td>
<td>33.0(5)</td>
</tr>
<tr>
<td>C1CA</td>
<td>1461.9(16)</td>
<td>3349(3)</td>
<td>3833.9(9)</td>
<td>24.1(4)</td>
</tr>
<tr>
<td>C2CA</td>
<td>4916.5(19)</td>
<td>2506(3)</td>
<td>1884.6(9)</td>
<td>28.9(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>C3CA</td>
<td>2251(2)</td>
<td>8297(3)</td>
<td>1209.2(9)</td>
<td>33.1(5)</td>
</tr>
<tr>
<td>C4CA</td>
<td>3127.9(19)</td>
<td>3685(3)</td>
<td>194.5(10)</td>
<td>32.4(4)</td>
</tr>
<tr>
<td>C5CA</td>
<td>4988.4(16)</td>
<td>2874(3)</td>
<td>3028.2(8)</td>
<td>24.6(4)</td>
</tr>
<tr>
<td>C6CA</td>
<td>4627(2)</td>
<td>2387(3)</td>
<td>-297.1(10)</td>
<td>32.6(5)</td>
</tr>
<tr>
<td>C7CA</td>
<td>3081(2)</td>
<td>3890(3)</td>
<td>-893.4(10)</td>
<td>42.4(6)</td>
</tr>
<tr>
<td>C8CA</td>
<td>2271(2)</td>
<td>6636(3)</td>
<td>1582.4(9)</td>
<td>29.9(5)</td>
</tr>
<tr>
<td>C9CA</td>
<td>1339(3)</td>
<td>8885(3)</td>
<td>-410.7(10)</td>
<td>41.8(6)</td>
</tr>
<tr>
<td>C0DA</td>
<td>2593(2)</td>
<td>4264(3)</td>
<td>-368.8(11)</td>
<td>38.0(5)</td>
</tr>
<tr>
<td>C1DA</td>
<td>3486.8(17)</td>
<td>2864(3)</td>
<td>7065.6(9)</td>
<td>28.1(4)</td>
</tr>
<tr>
<td>C2DA</td>
<td>3207.5(19)</td>
<td>242(3)</td>
<td>5549.9(9)</td>
<td>28.0(4)</td>
</tr>
<tr>
<td>C3DA</td>
<td>4082(2)</td>
<td>2939(3)</td>
<td>-858.6(10)</td>
<td>40.0(6)</td>
</tr>
<tr>
<td>C4DA</td>
<td>1966.2(19)</td>
<td>6098(3)</td>
<td>6776.5(11)</td>
<td>30.7(5)</td>
</tr>
<tr>
<td>C5DA</td>
<td>4746(2)</td>
<td>2050(3)</td>
<td>826.5(9)</td>
<td>34.2(5)</td>
</tr>
<tr>
<td>C6DA</td>
<td>971(2)</td>
<td>2934(3)</td>
<td>7759.5(10)</td>
<td>38.7(5)</td>
</tr>
<tr>
<td>C7DA</td>
<td>229(3)</td>
<td>8318(4)</td>
<td>-554.8(12)</td>
<td>47.9(6)</td>
</tr>
<tr>
<td>C8DA</td>
<td>2058(3)</td>
<td>8903(4)</td>
<td>-866.8(13)</td>
<td>51.7(7)</td>
</tr>
<tr>
<td>C9DA</td>
<td>547(3)</td>
<td>7780(4)</td>
<td>-1581.9(11)</td>
<td>56.7(8)</td>
</tr>
<tr>
<td>C0EA</td>
<td>-164(3)</td>
<td>7755(4)</td>
<td>-1139.4(13)</td>
<td>55.0(7)</td>
</tr>
<tr>
<td>C1EA</td>
<td>1651(3)</td>
<td>8354(4)</td>
<td>-1447.5(13)</td>
<td>59.0(8)</td>
</tr>
<tr>
<td>C2EA</td>
<td>1786(4)</td>
<td>9471(3)</td>
<td>218.5(12)</td>
<td>71.7(12)</td>
</tr>
</tbody>
</table>
X-ray crystallographic data for 15

![X-ray crystal structure diagram](image)

**Table S15. Crystal data and structure refinement for 15**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>2119298</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{27}H_{38}O_{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>394.57</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100.01(11)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_1/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>14.63930(10)</td>
</tr>
<tr>
<td>b/Å</td>
<td>6.21040(10)</td>
</tr>
<tr>
<td>c/Å</td>
<td>24.2652(2)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>101.3290(10)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>2163.11(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρ_{calc}/g/cm³</td>
<td>1.212</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.566</td>
</tr>
<tr>
<td>F(000)</td>
<td>864</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.28 × 0.12 × 0.05</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα (λ = 1.54184)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>7.432 to 155.448</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-18 ≤ h ≤ 18, -6 ≤ k ≤ 7, -28 ≤ l ≤ 30</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>46952</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>4469 [R_{int} = 0.0348, R_{sigma} = 0.0152]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>4469/0/265</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.055</td>
</tr>
<tr>
<td>Final R indexes [I&gt;2σ(I)]</td>
<td>R_1 = 0.0390, wR_2 = 0.0977</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R_1 = 0.0410, wR_2 = 0.0993</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.25/-0.21</td>
</tr>
</tbody>
</table>
Table S16. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\AA^2 \times 10^3$) for 15. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$ tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O18</td>
<td>2688.8(5)</td>
<td>4431.5(13)</td>
<td>2918.8(3)</td>
<td>22.14(18)</td>
</tr>
<tr>
<td>O20</td>
<td>3452.1(6)</td>
<td>7178.0(14)</td>
<td>3411.3(3)</td>
<td>29.3(2)</td>
</tr>
<tr>
<td>C13</td>
<td>5423.2(7)</td>
<td>2953.8(17)</td>
<td>4005.5(4)</td>
<td>16.0(2)</td>
</tr>
<tr>
<td>C5</td>
<td>7190.9(7)</td>
<td>1706.9(17)</td>
<td>4202.0(4)</td>
<td>16.4(2)</td>
</tr>
<tr>
<td>C4</td>
<td>6212.1(7)</td>
<td>1699.0(17)</td>
<td>3798.3(4)</td>
<td>15.8(2)</td>
</tr>
<tr>
<td>C10</td>
<td>7036.9(7)</td>
<td>973.9(17)</td>
<td>4792.5(4)</td>
<td>17.0(2)</td>
</tr>
<tr>
<td>C9</td>
<td>7927.3(7)</td>
<td>462.8(18)</td>
<td>5243.3(4)</td>
<td>19.4(2)</td>
</tr>
<tr>
<td>C16</td>
<td>5488.1(7)</td>
<td>5400.4(17)</td>
<td>3919.3(4)</td>
<td>17.7(2)</td>
</tr>
<tr>
<td>C6</td>
<td>7809.5(7)</td>
<td>-4.9(19)</td>
<td>3992.5(4)</td>
<td>20.4(2)</td>
</tr>
<tr>
<td>C1</td>
<td>5214.2(7)</td>
<td>5606.9(17)</td>
<td>3278.7(4)</td>
<td>17.9(2)</td>
</tr>
<tr>
<td>C14</td>
<td>4473.9(7)</td>
<td>2452.2(17)</td>
<td>3612.6(4)</td>
<td>18.3(2)</td>
</tr>
<tr>
<td>C11</td>
<td>6334.3(7)</td>
<td>2442.7(18)</td>
<td>5003.7(4)</td>
<td>19.6(2)</td>
</tr>
<tr>
<td>C15</td>
<td>4330.7(7)</td>
<td>4202.7(17)</td>
<td>3140.3(4)</td>
<td>17.7(2)</td>
</tr>
<tr>
<td>C2</td>
<td>5999.5(7)</td>
<td>4678.6(18)</td>
<td>3016.2(4)</td>
<td>19.6(2)</td>
</tr>
<tr>
<td>C12</td>
<td>5388.2(7)</td>
<td>2301.0(18)</td>
<td>4608.0(4)</td>
<td>19.0(2)</td>
</tr>
<tr>
<td>C27</td>
<td>7680.4(7)</td>
<td>3895.4(18)</td>
<td>4208.3(4)</td>
<td>20.5(2)</td>
</tr>
<tr>
<td>C3</td>
<td>6210.6(7)</td>
<td>2310.3(18)</td>
<td>3176.9(4)</td>
<td>18.4(2)</td>
</tr>
<tr>
<td>C17</td>
<td>3467.2(7)</td>
<td>5480.4(18)</td>
<td>3172.6(4)</td>
<td>19.5(2)</td>
</tr>
<tr>
<td>C21</td>
<td>1389.4(7)</td>
<td>6865(2)</td>
<td>2534.5(4)</td>
<td>22.4(2)</td>
</tr>
<tr>
<td>C8</td>
<td>8548.2(7)</td>
<td>-1093.9(19)</td>
<td>4986.2(5)</td>
<td>22.1(2)</td>
</tr>
<tr>
<td>C7</td>
<td>8721.1(7)</td>
<td>-428(2)</td>
<td>4409.6(5)</td>
<td>23.6(2)</td>
</tr>
<tr>
<td>C28</td>
<td>8487.8(8)</td>
<td>2453.7(19)</td>
<td>5487.9(5)</td>
<td>24.6(2)</td>
</tr>
<tr>
<td>C26</td>
<td>1758.0(8)</td>
<td>8941(2)</td>
<td>2505.1(5)</td>
<td>25.0(2)</td>
</tr>
<tr>
<td>C29</td>
<td>7630.4(8)</td>
<td>-738(2)</td>
<td>5735.6(5)</td>
<td>24.7(2)</td>
</tr>
<tr>
<td>C19</td>
<td>1805.0(7)</td>
<td>5348(2)</td>
<td>3000.1(5)</td>
<td>26.6(3)</td>
</tr>
<tr>
<td>C22</td>
<td>636.3(8)</td>
<td>6196(2)</td>
<td>2125.2(5)</td>
<td>27.5(3)</td>
</tr>
<tr>
<td>C25</td>
<td>1349.9(8)</td>
<td>10312(2)</td>
<td>2069.9(5)</td>
<td>31.3(3)</td>
</tr>
<tr>
<td>C23</td>
<td>249.7(8)</td>
<td>7577(2)</td>
<td>1691.6(5)</td>
<td>33.7(3)</td>
</tr>
<tr>
<td>C24</td>
<td>603.5(9)</td>
<td>9626(2)</td>
<td>1662.7(5)</td>
<td>35.2(3)</td>
</tr>
</tbody>
</table>
X-ray crystallographic data for 19

Table S17. Crystal data and structure refinement for 19

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>2119300</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{15}H_{24}O_{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>236.34</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100.01(10)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>a/Å</td>
<td>7.3323(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>8.5275(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>11.3531(6)</td>
</tr>
<tr>
<td>α/°</td>
<td>101.157(3)</td>
</tr>
<tr>
<td>β/°</td>
<td>103.254(4)</td>
</tr>
<tr>
<td>γ/°</td>
<td>101.069(2)</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>656.81(4)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>ρ_{calc}/g/cm³</td>
<td>1.195</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.601</td>
</tr>
<tr>
<td>F(000)</td>
<td>260</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.24 × 0.16 × 0.02</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα (λ = 1.54184)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>10.914 to 136.486</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-8 ≤ h ≤ 8, -10 ≤ k ≤ 10, -7 ≤ l ≤ 13</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>2371</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2371 [R_{int} = ?, R_{sigma} = 0.0233]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>2371/0/158</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.116</td>
</tr>
<tr>
<td>Final R indexes [I≥2σ (I)]</td>
<td>R_{I} = 0.0683, wR_{2} = 0.1796</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R_{I} = 0.0735, wR_{2} = 0.1825</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.27/-0.20</td>
</tr>
</tbody>
</table>
Table S18. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\AA^2 \times 10^3$) for 19. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$ tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O15</td>
<td>2421(3)</td>
<td>9689(3)</td>
<td>5390(2)</td>
<td>43.9(6)</td>
</tr>
<tr>
<td>O14</td>
<td>-174(3)</td>
<td>8569(3)</td>
<td>3769(2)</td>
<td>43.9(6)</td>
</tr>
<tr>
<td>C13</td>
<td>1522(4)</td>
<td>8696(3)</td>
<td>4294(3)</td>
<td>30.8(6)</td>
</tr>
<tr>
<td>C1</td>
<td>1941(4)</td>
<td>4642(3)</td>
<td>2985(3)</td>
<td>29.6(6)</td>
</tr>
<tr>
<td>C12</td>
<td>720(4)</td>
<td>5410(3)</td>
<td>2076(3)</td>
<td>28.5(6)</td>
</tr>
<tr>
<td>C8</td>
<td>3402(4)</td>
<td>2716(3)</td>
<td>1530(3)</td>
<td>30.7(6)</td>
</tr>
<tr>
<td>C4</td>
<td>2047(4)</td>
<td>7123(3)</td>
<td>2305(3)</td>
<td>30.9(6)</td>
</tr>
<tr>
<td>C7</td>
<td>3741(4)</td>
<td>4300(3)</td>
<td>2582(3)</td>
<td>29.6(6)</td>
</tr>
<tr>
<td>C3</td>
<td>2753(4)</td>
<td>7713(4)</td>
<td>3743(3)</td>
<td>33.2(7)</td>
</tr>
<tr>
<td>C6</td>
<td>4938(4)</td>
<td>5897(4)</td>
<td>2388(3)</td>
<td>37.7(7)</td>
</tr>
<tr>
<td>C9</td>
<td>2099(5)</td>
<td>1267(4)</td>
<td>1789(3)</td>
<td>37.8(7)</td>
</tr>
<tr>
<td>C5</td>
<td>3749(5)</td>
<td>6960(4)</td>
<td>1770(3)</td>
<td>39.9(8)</td>
</tr>
<tr>
<td>C2</td>
<td>2596(5)</td>
<td>6063(4)</td>
<td>4178(3)</td>
<td>37.1(7)</td>
</tr>
<tr>
<td>C16</td>
<td>2541(5)</td>
<td>2885(4)</td>
<td>203(3)</td>
<td>36.9(7)</td>
</tr>
<tr>
<td>C10</td>
<td>258(5)</td>
<td>1617(4)</td>
<td>2057(3)</td>
<td>42.0(8)</td>
</tr>
<tr>
<td>C11</td>
<td>774(5)</td>
<td>3077(4)</td>
<td>3190(3)</td>
<td>39.0(7)</td>
</tr>
<tr>
<td>C17</td>
<td>5353(5)</td>
<td>2293(4)</td>
<td>1554(3)</td>
<td>43.7(8)</td>
</tr>
</tbody>
</table>
X-ray crystallographic data for 22

Table S19. Crystal data and structure refinement for 22

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>2119301</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{17}H_{20}N_{2}O_{6}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>348.35</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100.02(10)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_1/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>18.9063(5)</td>
</tr>
<tr>
<td>b/Å</td>
<td>8.9222(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>10.4159(2)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>100.453(2)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>1727.85(7)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>(\rho_{\text{calc}}) g/cm³</td>
<td>1.339</td>
</tr>
<tr>
<td>(\mu) mm(^{-1})</td>
<td>0.859</td>
</tr>
<tr>
<td>F(000)</td>
<td>736</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.17 \times 0.09 \times 0.01</td>
</tr>
<tr>
<td>Radiation</td>
<td>Cu Kα ((\lambda = 1.54184))</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>9.514 to 134.148</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-22 ≤ h ≤ 22, -10 ≤ k ≤ 10, -10 ≤ l ≤ 12</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>22798</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3083 [R_{\text{int}} = 0.0370, R_{\text{sigma}} = 0.0236]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>3083/4/256</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.057</td>
</tr>
<tr>
<td>Final R indexes [I(\geq2\sigma) (I)]</td>
<td>R₁ = 0.0491, wR₂ = 0.1331</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0552, wR₂ = 0.1386</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.32/-0.23</td>
</tr>
</tbody>
</table>

Table S20. Fractional Atomic Coordinates (\(\times10^4\)) and Equivalent Isotropic Displacement Parameters (Å\(^2\)\(\times10^3\)) for 22. \(U_{\text{eq}}\) is defined as 1/3 of the trace of the orthogonalised \(U_{\text{ij}}\) tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O001</td>
<td>5875.6(7)</td>
<td>3028.7(14)</td>
<td>5825.3(11)</td>
<td>38.5(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>O002</td>
<td>3732.5(7)</td>
<td>4095.2(14)</td>
<td>2565.3(12)</td>
<td>40.0(3)</td>
</tr>
<tr>
<td>O003</td>
<td>3775.4(7)</td>
<td>5787.9(13)</td>
<td>1090.0(12)</td>
<td>40.5(3)</td>
</tr>
<tr>
<td>O004</td>
<td>6944.4(7)</td>
<td>3643.3(15)</td>
<td>5312.5(12)</td>
<td>43.1(3)</td>
</tr>
<tr>
<td>O005</td>
<td>6085.0(8)</td>
<td>7173.5(14)</td>
<td>113.1(12)</td>
<td>44.1(4)</td>
</tr>
<tr>
<td>O006</td>
<td>7059.6(8)</td>
<td>6288.5(17)</td>
<td>1296.4(14)</td>
<td>50.4(4)</td>
</tr>
<tr>
<td>N007</td>
<td>4062.8(8)</td>
<td>4954.0(15)</td>
<td>1972.1(14)</td>
<td>35.0(4)</td>
</tr>
<tr>
<td>N008</td>
<td>6409.6(9)</td>
<td>6444.0(17)</td>
<td>1039.7(15)</td>
<td>39.9(4)</td>
</tr>
<tr>
<td>C009</td>
<td>4846.2(10)</td>
<td>4988.1(18)</td>
<td>2335.8(16)</td>
<td>33.5(4)</td>
</tr>
<tr>
<td>C00A</td>
<td>5907.5(10)</td>
<td>4333.5(17)</td>
<td>3839.6(16)</td>
<td>33.7(4)</td>
</tr>
<tr>
<td>C00B</td>
<td>5167.6(10)</td>
<td>4307.5(17)</td>
<td>3489.5(16)</td>
<td>33.5(4)</td>
</tr>
<tr>
<td>C00C</td>
<td>5237.3(10)</td>
<td>5708.5(18)</td>
<td>1520.2(16)</td>
<td>35.0(4)</td>
</tr>
<tr>
<td>C00D</td>
<td>5974.0(11)</td>
<td>5697.3(18)</td>
<td>1900.1(17)</td>
<td>35.4(4)</td>
</tr>
<tr>
<td>C00E</td>
<td>6322.9(11)</td>
<td>5034.4(19)</td>
<td>3037.1(17)</td>
<td>36.0(4)</td>
</tr>
<tr>
<td>C00F</td>
<td>6235.1(10)</td>
<td>3593.9(19)</td>
<td>5104.2(17)</td>
<td>36.1(4)</td>
</tr>
<tr>
<td>C00G</td>
<td>7317.6(12)</td>
<td>2987(2)</td>
<td>6535(2)</td>
<td>48.6(5)</td>
</tr>
<tr>
<td>C1</td>
<td>8064.4(15)</td>
<td>3563(3)</td>
<td>6806(3)</td>
<td>50.2(7)</td>
</tr>
<tr>
<td>C2</td>
<td>8447(2)</td>
<td>3023(4)</td>
<td>8195(4)</td>
<td>60.5(9)</td>
</tr>
<tr>
<td>C3</td>
<td>8095.0(18)</td>
<td>5306(4)</td>
<td>6921(3)</td>
<td>55.8(8)</td>
</tr>
<tr>
<td>C4</td>
<td>8327(2)</td>
<td>4335(5)</td>
<td>9112(4)</td>
<td>69.9(9)</td>
</tr>
<tr>
<td>C5</td>
<td>9326(5)</td>
<td>5642(13)</td>
<td>8339(8)</td>
<td>88(2)</td>
</tr>
<tr>
<td>C6</td>
<td>9248(2)</td>
<td>2820(6)</td>
<td>8242(5)</td>
<td>91.0(13)</td>
</tr>
<tr>
<td>C7</td>
<td>8503.5(19)</td>
<td>5665(4)</td>
<td>8281(4)</td>
<td>66.6(9)</td>
</tr>
<tr>
<td>C8</td>
<td>8294(3)</td>
<td>7156(5)</td>
<td>8821(5)</td>
<td>94.1(13)</td>
</tr>
<tr>
<td>C9</td>
<td>9570(2)</td>
<td>4224(5)</td>
<td>7744(6)</td>
<td>99.3(14)</td>
</tr>
<tr>
<td>C1A</td>
<td>7791(6)</td>
<td>4213(12)</td>
<td>7221(10)</td>
<td>50.2(7)</td>
</tr>
<tr>
<td>C3A</td>
<td>8315(6)</td>
<td>4947(14)</td>
<td>6402(12)</td>
<td>55.8(8)</td>
</tr>
<tr>
<td>C7A</td>
<td>9089(7)</td>
<td>4830(12)</td>
<td>7217(11)</td>
<td>66.6(9)</td>
</tr>
<tr>
<td>C8A</td>
<td>9634(9)</td>
<td>4664(19)</td>
<td>6424(16)</td>
<td>94.1(13)</td>
</tr>
<tr>
<td>C4A</td>
<td>8972(8)</td>
<td>3410(14)</td>
<td>7979(12)</td>
<td>69.9(9)</td>
</tr>
<tr>
<td>C2A</td>
<td>8302(8)</td>
<td>3616(18)</td>
<td>8504(16)</td>
<td>60.5(9)</td>
</tr>
<tr>
<td>C5A</td>
<td>9246(19)</td>
<td>5970(60)</td>
<td>8100(30)</td>
<td>88(2)</td>
</tr>
<tr>
<td>C9A</td>
<td>8672(8)</td>
<td>6251(19)</td>
<td>8960(20)</td>
<td>99.3(14)</td>
</tr>
<tr>
<td>C6A</td>
<td>8450(9)</td>
<td>4835(17)</td>
<td>9588(17)</td>
<td>91.0(13)</td>
</tr>
</tbody>
</table>
### X-ray crystallographic data for 23

![Image](217x668 to 377x747)

**Table S21. Crystal data and structure refinement for 23.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>2119302</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{18}H_{30}O</td>
</tr>
<tr>
<td>Formula weight</td>
<td>262.42</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>99.99(10)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_1</td>
</tr>
<tr>
<td>a/Å</td>
<td>11.38680(10)</td>
</tr>
<tr>
<td>b/Å</td>
<td>7.36790(10)</td>
</tr>
<tr>
<td>c/Å</td>
<td>18.6455(3)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>92.5060(10)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>1562.80(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>(\rho_{\text{calc}})/g/cm³</td>
<td>1.115</td>
</tr>
<tr>
<td>(\mu)/mm⁻¹</td>
<td>0.497</td>
</tr>
<tr>
<td>F(000)</td>
<td>584</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.06 × 0.05 × 0.05</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα (λ = 1.54184)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>7.772 to 147.006</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-14 ≤ h ≤ 14, -9 ≤ k ≤ 9, -23 ≤ l ≤ 23</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>23691</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>6205 [R_{int} = 0.0337, R_{sigma} = 0.0334]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>6205/1/351</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.026</td>
</tr>
<tr>
<td>Final R indexes [I&gt;2σ (I)]</td>
<td>R_1 = 0.0314, wR_2 = 0.0779</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R_1 = 0.0341, wR_2 = 0.0790</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.22/-0.18</td>
</tr>
<tr>
<td>Atom</td>
<td>x</td>
</tr>
<tr>
<td>------</td>
<td>-------</td>
</tr>
<tr>
<td>O15</td>
<td>4531.2(10)</td>
</tr>
<tr>
<td>O34</td>
<td>4592.3(10)</td>
</tr>
<tr>
<td>C9</td>
<td>2231.3(14)</td>
</tr>
<tr>
<td>C33</td>
<td>3312.9(15)</td>
</tr>
<tr>
<td>C32</td>
<td>2883.4(15)</td>
</tr>
<tr>
<td>C30</td>
<td>1065.9(16)</td>
</tr>
<tr>
<td>C38</td>
<td>2874.1(15)</td>
</tr>
<tr>
<td>C25</td>
<td>2504.4(14)</td>
</tr>
<tr>
<td>C17</td>
<td>3272.4(15)</td>
</tr>
<tr>
<td>C1</td>
<td>3393.5(14)</td>
</tr>
<tr>
<td>C5</td>
<td>928.3(14)</td>
</tr>
<tr>
<td>C6</td>
<td>53.1(15)</td>
</tr>
<tr>
<td>C2</td>
<td>2823.8(15)</td>
</tr>
<tr>
<td>C26</td>
<td>2018.4(14)</td>
</tr>
<tr>
<td>C4</td>
<td>1633.1(14)</td>
</tr>
<tr>
<td>C23</td>
<td>3095.6(16)</td>
</tr>
<tr>
<td>C11</td>
<td>3203.3(16)</td>
</tr>
<tr>
<td>C13</td>
<td>4145.5(16)</td>
</tr>
<tr>
<td>C22</td>
<td>4078.7(16)</td>
</tr>
<tr>
<td>C3</td>
<td>2480.0(14)</td>
</tr>
<tr>
<td>C28</td>
<td>167.3(16)</td>
</tr>
<tr>
<td>C24</td>
<td>2766.4(15)</td>
</tr>
<tr>
<td>C8</td>
<td>1288.3(15)</td>
</tr>
<tr>
<td>C27</td>
<td>828.9(15)</td>
</tr>
<tr>
<td>C7</td>
<td>621.5(16)</td>
</tr>
<tr>
<td>C20</td>
<td>3567.3(14)</td>
</tr>
<tr>
<td>C10</td>
<td>2633.9(14)</td>
</tr>
<tr>
<td>C21</td>
<td>3858.3(15)</td>
</tr>
<tr>
<td>C31</td>
<td>1771.4(15)</td>
</tr>
</tbody>
</table>

Table S22. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 23. U_eq is defined as 1/3 of of the trace of the orthogonalised U_ij tensor.
X-ray crystallographic data for 24

Table S23. Crystal data and structure refinement for 24

<table>
<thead>
<tr>
<th>Identification code</th>
<th>2119303</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{56}H_{80}O_{4}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>817.2</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100.01(10)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P1</td>
</tr>
<tr>
<td>a/Å</td>
<td>6.19730(10)</td>
</tr>
<tr>
<td>b/Å</td>
<td>12.66010(10)</td>
</tr>
<tr>
<td>c/Å</td>
<td>15.25140(10)</td>
</tr>
<tr>
<td>α/°</td>
<td>104.6070(10)</td>
</tr>
<tr>
<td>β/°</td>
<td>91.0550(10)</td>
</tr>
<tr>
<td>γ/°</td>
<td>91.505(2)</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>1157.14(2)</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
</tr>
<tr>
<td>ρ_{calc}/g/cm³</td>
<td>1.173</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.545</td>
</tr>
<tr>
<td>F(000)</td>
<td>448</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.36 × 0.07 × 0.05</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα (λ = 1.54184)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>7.22 to 136.472</td>
</tr>
</tbody>
</table>
Index ranges
-7 ≤ h ≤ 7, -13 ≤ k ≤ 15, -18 ≤ l ≤ 18

Reflections collected
72218

Independent reflections
8224 [R(int) = 0.0852, R(sigma) = 0.0334]

Data/restraints/parameters
8224/3/549

Goodness-of-fit on F²
1.045

Final R indexes [I>2σ (I)]
R₁ = 0.0854, wR₂ = 0.2464

Final R indexes [all data]
R₁ = 0.0864, wR₂ = 0.2474

Largest diff. peak/hole / e Å⁻³
0.94/-0.35

Flack parameter
0.00(11)

Table S24. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 24. U(eq) is defined as 1/3 of the trace of the orthogonalised Uᵢⱼ tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O18</td>
<td>5820(7)</td>
<td>5631(3)</td>
<td>3144(3)</td>
<td>25.7(9)</td>
</tr>
<tr>
<td>O48</td>
<td>538(7)</td>
<td>4306(3)</td>
<td>6823(3)</td>
<td>27.3(9)</td>
</tr>
<tr>
<td>O20</td>
<td>6663(8)</td>
<td>7375(4)</td>
<td>3160(3)</td>
<td>32.2(10)</td>
</tr>
<tr>
<td>O50</td>
<td>1354(8)</td>
<td>2578(4)</td>
<td>6824(3)</td>
<td>32.8(10)</td>
</tr>
<tr>
<td>C2</td>
<td>6139(8)</td>
<td>7908(5)</td>
<td>5126(4)</td>
<td>20.3(11)</td>
</tr>
<tr>
<td>C47</td>
<td>1127(9)</td>
<td>3298(5)</td>
<td>6415(4)</td>
<td>24.2(12)</td>
</tr>
<tr>
<td>C17</td>
<td>6446(9)</td>
<td>6659(5)</td>
<td>3548(4)</td>
<td>24.3(12)</td>
</tr>
<tr>
<td>C40</td>
<td>2482(9)</td>
<td>-51(5)</td>
<td>2550(4)</td>
<td>21.0(12)</td>
</tr>
<tr>
<td>C35</td>
<td>1991(9)</td>
<td>1169(5)</td>
<td>2617(4)</td>
<td>20.0(11)</td>
</tr>
<tr>
<td>C36</td>
<td>2851(10)</td>
<td>1455(5)</td>
<td>1755(4)</td>
<td>26.6(13)</td>
</tr>
<tr>
<td>C3</td>
<td>6875(9)</td>
<td>6798(5)</td>
<td>4551(4)</td>
<td>21.9(11)</td>
</tr>
<tr>
<td>C21</td>
<td>7125(9)</td>
<td>4883(5)</td>
<td>1621(4)</td>
<td>23.3(12)</td>
</tr>
<tr>
<td>C38</td>
<td>2573(10)</td>
<td>-514(5)</td>
<td>850(4)</td>
<td>27.9(13)</td>
</tr>
<tr>
<td>C34</td>
<td>3336(9)</td>
<td>1889(5)</td>
<td>3457(4)</td>
<td>21.6(11)</td>
</tr>
<tr>
<td>C1</td>
<td>8087(8)</td>
<td>8524(5)</td>
<td>5679(4)</td>
<td>20.1(11)</td>
</tr>
<tr>
<td>C16</td>
<td>9879(9)</td>
<td>8052(5)</td>
<td>5040(4)</td>
<td>21.8(12)</td>
</tr>
<tr>
<td>C13</td>
<td>7304(9)</td>
<td>10057(5)</td>
<td>7473(4)</td>
<td>21.2(11)</td>
</tr>
<tr>
<td>C7</td>
<td>8447(8)</td>
<td>8209(5)</td>
<td>6591(4)</td>
<td>18.6(11)</td>
</tr>
<tr>
<td>C51</td>
<td>1968(9)</td>
<td>5044(5)</td>
<td>8359(4)</td>
<td>23.7(12)</td>
</tr>
<tr>
<td>C43</td>
<td>3052(8)</td>
<td>1554(5)</td>
<td>4358(4)</td>
<td>19.6(11)</td>
</tr>
<tr>
<td>C8</td>
<td>7019(8)</td>
<td>8802(5)</td>
<td>7395(4)</td>
<td>19.5(11)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>---------</td>
</tr>
<tr>
<td>C9</td>
<td>7931(9)</td>
<td>8577(5)</td>
<td>8274(4)</td>
<td>23.6(12)</td>
</tr>
<tr>
<td>C45</td>
<td>1550(9)</td>
<td>3166(5)</td>
<td>5432(4)</td>
<td>23.1(12)</td>
</tr>
<tr>
<td>C58</td>
<td>-436(9)</td>
<td>1394(5)</td>
<td>2669(4)</td>
<td>23.4(12)</td>
</tr>
<tr>
<td>C59</td>
<td>2808(11)</td>
<td>-1992(5)</td>
<td>1633(4)</td>
<td>30.4(13)</td>
</tr>
<tr>
<td>C12</td>
<td>6478(10)</td>
<td>10856(5)</td>
<td>8336(4)</td>
<td>23.4(12)</td>
</tr>
<tr>
<td>C44</td>
<td>988(9)</td>
<td>2005(5)</td>
<td>4851(4)</td>
<td>23.1(12)</td>
</tr>
<tr>
<td>C39</td>
<td>1757(10)</td>
<td>-906(5)</td>
<td>1667(4)</td>
<td>26.6(13)</td>
</tr>
<tr>
<td>C49</td>
<td>34(10)</td>
<td>4538(5)</td>
<td>7785(4)</td>
<td>28.1(13)</td>
</tr>
<tr>
<td>C14</td>
<td>6611(9)</td>
<td>10324(5)</td>
<td>6587(4)</td>
<td>21.4(13)</td>
</tr>
<tr>
<td>C11</td>
<td>7384(10)</td>
<td>10508(5)</td>
<td>9171(4)</td>
<td>25.7(12)</td>
</tr>
<tr>
<td>C4</td>
<td>9391(9)</td>
<td>6836(5)</td>
<td>4765(4)</td>
<td>23.6(12)</td>
</tr>
<tr>
<td>C19</td>
<td>5253(11)</td>
<td>5391(5)</td>
<td>2177(4)</td>
<td>29.4(13)</td>
</tr>
<tr>
<td>C54</td>
<td>5551(11)</td>
<td>6002(6)</td>
<td>9425(4)</td>
<td>33.4(14)</td>
</tr>
<tr>
<td>C37</td>
<td>2001(11)</td>
<td>663(5)</td>
<td>873(4)</td>
<td>28.6(13)</td>
</tr>
<tr>
<td>C22</td>
<td>7438(11)</td>
<td>3758(5)</td>
<td>1400(4)</td>
<td>30.6(14)</td>
</tr>
<tr>
<td>C56</td>
<td>3462(11)</td>
<td>4399(5)</td>
<td>8659(4)</td>
<td>27.6(13)</td>
</tr>
<tr>
<td>C33</td>
<td>3037(10)</td>
<td>3121(5)</td>
<td>3613(4)</td>
<td>25.4(12)</td>
</tr>
<tr>
<td>C52</td>
<td>2287(11)</td>
<td>6167(5)</td>
<td>8601(4)</td>
<td>30.2(13)</td>
</tr>
<tr>
<td>C41</td>
<td>1870(10)</td>
<td>-362(5)</td>
<td>3425(4)</td>
<td>25.3(12)</td>
</tr>
<tr>
<td>C27</td>
<td>10732(11)</td>
<td>6202(6)</td>
<td>3996(4)</td>
<td>31.2(14)</td>
</tr>
<tr>
<td>C15</td>
<td>8065(9)</td>
<td>9763(5)</td>
<td>5826(4)</td>
<td>21.0(11)</td>
</tr>
<tr>
<td>C32</td>
<td>4294(11)</td>
<td>3800(5)</td>
<td>4449(4)</td>
<td>28.4(13)</td>
</tr>
<tr>
<td>C5</td>
<td>9764(10)</td>
<td>6400(5)</td>
<td>5618(4)</td>
<td>25.0(12)</td>
</tr>
<tr>
<td>C57</td>
<td>5223(10)</td>
<td>4099(6)</td>
<td>6102(4)</td>
<td>31.3(14)</td>
</tr>
<tr>
<td>C26</td>
<td>8654(11)</td>
<td>5524(5)</td>
<td>1323(4)</td>
<td>26.6(12)</td>
</tr>
<tr>
<td>C25</td>
<td>10376(10)</td>
<td>5050(6)</td>
<td>799(4)</td>
<td>30.4(13)</td>
</tr>
<tr>
<td>C6</td>
<td>8397(11)</td>
<td>6953(5)</td>
<td>6415(4)</td>
<td>27.1(13)</td>
</tr>
<tr>
<td>C55</td>
<td>5225(11)</td>
<td>4874(6)</td>
<td>9191(4)</td>
<td>32.3(14)</td>
</tr>
<tr>
<td>C10</td>
<td>6989(10)</td>
<td>9302(5)</td>
<td>9135(4)</td>
<td>26.3(13)</td>
</tr>
<tr>
<td>C31</td>
<td>4033(9)</td>
<td>3355(5)</td>
<td>5287(4)</td>
<td>24.9(12)</td>
</tr>
<tr>
<td>C29</td>
<td>4658(9)</td>
<td>8398(5)</td>
<td>7266(4)</td>
<td>24.7(12)</td>
</tr>
<tr>
<td>C53</td>
<td>4080(12)</td>
<td>6646(5)</td>
<td>9125(5)</td>
<td>33.7(15)</td>
</tr>
<tr>
<td>C46</td>
<td>4810(9)</td>
<td>2183(5)</td>
<td>5049(4)</td>
<td>24.1(12)</td>
</tr>
<tr>
<td>C28</td>
<td>3982(10)</td>
<td>10932(5)</td>
<td>8371(4)</td>
<td>29.6(13)</td>
</tr>
<tr>
<td>C23</td>
<td>9074(11)</td>
<td>3278(5)</td>
<td>888(4)</td>
<td>31.7(14)</td>
</tr>
</tbody>
</table>
X-ray crystallographic data for 26

Table S25. Crystal data and structure refinement for 26

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>2119304</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{22}H_{34}O_{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>330.49</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100.01(10)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_{1}2_{1}2_{1}</td>
</tr>
<tr>
<td>a/Å</td>
<td>6.3478(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>12.9401(4)</td>
</tr>
<tr>
<td>c/Å</td>
<td>23.2315(7)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>90</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>1908.26(10)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρ calc/g/cm³</td>
<td>1.15</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.547</td>
</tr>
<tr>
<td>F(000)</td>
<td>728</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.19 × 0.07 × 0.04</td>
</tr>
<tr>
<td>Radiation</td>
<td>Cu Kα (λ = 1.54184)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>7.61 to 149.94</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-7 ≤ h ≤ 7, -14 ≤ k ≤ 16, -28 ≤ l ≤ 28</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>16261</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3754 [R_{int} = 0.0540, R_{sigma} = 0.0370]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>3754/0/221</td>
</tr>
</tbody>
</table>
Goodness-of-fit on $F^2$  
1.076

Final R indexes [I>=2σ (I)]
$R_1 = 0.0492, wR_2 = 0.1267$

Final R indexes [all data]
$R_1 = 0.0529, wR_2 = 0.1295$

Largest diff. peak/hole / e Å$^{-3}$
0.34/-0.23

Flack parameter
-0.01(15)

Table S26. Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for 26 $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{ij}$ tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U(eq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O11</td>
<td>4788(3)</td>
<td>3601.1(15)</td>
<td>5783.8(7)</td>
<td>28.8(4)</td>
</tr>
<tr>
<td>O13</td>
<td>7838(3)</td>
<td>2729.5(16)</td>
<td>5851.4(8)</td>
<td>35.2(5)</td>
</tr>
<tr>
<td>C12</td>
<td>6573(5)</td>
<td>3199(2)</td>
<td>5568.6(11)</td>
<td>26.3(6)</td>
</tr>
<tr>
<td>C7</td>
<td>2079(4)</td>
<td>3520(2)</td>
<td>8144.0(11)</td>
<td>26.3(6)</td>
</tr>
<tr>
<td>C1</td>
<td>4489(4)</td>
<td>3556(2)</td>
<td>6406.7(10)</td>
<td>25.2(5)</td>
</tr>
<tr>
<td>C8</td>
<td>1852(4)</td>
<td>3533.9(19)</td>
<td>7470.9(10)</td>
<td>22.5(5)</td>
</tr>
<tr>
<td>C9</td>
<td>2957(4)</td>
<td>2568.0(19)</td>
<td>7224.3(11)</td>
<td>25.1(5)</td>
</tr>
<tr>
<td>C24</td>
<td>461(4)</td>
<td>3500(2)</td>
<td>7277.3(11)</td>
<td>25.0(5)</td>
</tr>
<tr>
<td>C22</td>
<td>1516(5)</td>
<td>4823(2)</td>
<td>6232.6(12)</td>
<td>30.3(6)</td>
</tr>
<tr>
<td>C3</td>
<td>3089(4)</td>
<td>4501.0(19)</td>
<td>7250.2(11)</td>
<td>25.5(5)</td>
</tr>
<tr>
<td>C6</td>
<td>1545(5)</td>
<td>4543(2)</td>
<td>8468.1(12)</td>
<td>28.9(6)</td>
</tr>
<tr>
<td>C2</td>
<td>3491(5)</td>
<td>4586(2)</td>
<td>6590.6(12)</td>
<td>27.2(6)</td>
</tr>
<tr>
<td>C10</td>
<td>3231(5)</td>
<td>2609.0(19)</td>
<td>6568.4(10)</td>
<td>25.9(6)</td>
</tr>
<tr>
<td>C20</td>
<td>-844(5)</td>
<td>4691(2)</td>
<td>8552.9(13)</td>
<td>32.9(6)</td>
</tr>
<tr>
<td>C18</td>
<td>976(5)</td>
<td>2595(2)</td>
<td>8444.0(12)</td>
<td>31.7(6)</td>
</tr>
<tr>
<td>C4</td>
<td>2231(5)</td>
<td>5492(2)</td>
<td>7527.0(13)</td>
<td>32.2(6)</td>
</tr>
<tr>
<td>C5</td>
<td>2601(5)</td>
<td>5464(2)</td>
<td>8173.4(13)</td>
<td>36.9(7)</td>
</tr>
<tr>
<td>C14</td>
<td>6778(5)</td>
<td>3439(2)</td>
<td>4938.3(12)</td>
<td>36.8(7)</td>
</tr>
<tr>
<td>C23</td>
<td>5132(5)</td>
<td>5439(2)</td>
<td>6483.8(13)</td>
<td>33.2(6)</td>
</tr>
<tr>
<td>C16</td>
<td>459(7)</td>
<td>3908(3)</td>
<td>9414.5(13)</td>
<td>45.7(8)</td>
</tr>
<tr>
<td>C19</td>
<td>-1261(6)</td>
<td>2803(3)</td>
<td>8686.2(14)</td>
<td>40.9(8)</td>
</tr>
<tr>
<td>C15</td>
<td>2241(5)</td>
<td>4442(3)</td>
<td>9104.1(13)</td>
<td>40.2(8)</td>
</tr>
<tr>
<td>C21</td>
<td>-1372(5)</td>
<td>3842(2)</td>
<td>8990.8(13)</td>
<td>40.3(8)</td>
</tr>
<tr>
<td>C17</td>
<td>446(8)</td>
<td>3558(3)</td>
<td>9953.3(14)</td>
<td>59.2(10)</td>
</tr>
</tbody>
</table>
X-ray crystallographic data for 27

![Crystal structure](image)

### Table S27. Crystal data and structure refinement for 27

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>2119305</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{22}H_{37}O_{4.5}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>373.51</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2</td>
</tr>
<tr>
<td>a/Å</td>
<td>13.1317(3)</td>
</tr>
<tr>
<td>b/Å</td>
<td>6.2704(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>24.7142(6)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>97.393(2)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>2018.08(9)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρ calc/g/cm³</td>
<td>1.229</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.668</td>
</tr>
<tr>
<td>F(000)</td>
<td>820</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.36 × 0.08 × 0.03</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα (λ = 1.54184)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>7.214 to 151.286</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-16 ≤ h ≤ 13, -7 ≤ k ≤ 7, -30 ≤ l ≤ 31</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>17742</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3989 [R_{int} = 0.0884, R_{sigma} = 0.0475]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>3989/1/249</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.07</td>
</tr>
<tr>
<td>Final R indexes [I&gt;=2σ (I)]</td>
<td>R₁ = 0.0478, wR₂ = 0.1276</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0500, wR₂ = 0.1290</td>
</tr>
</tbody>
</table>

S107
Largest diff. peak/hole / e Å\(^{-3}\) 0.29/0.24

Flack parameter 0.0(2)

Table S28. Fractional Atomic Coordinates (×10\(^4\)) and Equivalent Isotropic Displacement Parameters (Å\(^2\)×10\(^3\)) for 27. \(U_{eq}\) is defined as 1/3 of the trace of the orthogonalised \(U_{ij}\) tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(U(eq))</th>
</tr>
</thead>
<tbody>
<tr>
<td>O20</td>
<td>6586.3(16)</td>
<td>6542(3)</td>
<td>790.0(8)</td>
<td>25.7(4)</td>
</tr>
<tr>
<td>O22</td>
<td>7384.4(17)</td>
<td>9704(4)</td>
<td>901.4(9)</td>
<td>32.7(5)</td>
</tr>
<tr>
<td>O19</td>
<td>4882.2(16)</td>
<td>1239(4)</td>
<td>4359.2(9)</td>
<td>28.5(5)</td>
</tr>
<tr>
<td>O18</td>
<td>6279.7(16)</td>
<td>3786(4)</td>
<td>5054.2(9)</td>
<td>28.8(5)</td>
</tr>
<tr>
<td>O27</td>
<td>5000</td>
<td>7425(5)</td>
<td>5000</td>
<td>34.4(7)</td>
</tr>
<tr>
<td>C4</td>
<td>5615.7(19)</td>
<td>4888(4)</td>
<td>2095.1(11)</td>
<td>19.9(5)</td>
</tr>
<tr>
<td>C21</td>
<td>6973(2)</td>
<td>8337(5)</td>
<td>608.4(11)</td>
<td>24.0(6)</td>
</tr>
<tr>
<td>C9</td>
<td>6571.4(19)</td>
<td>3644(4)</td>
<td>2382.4(11)</td>
<td>18.1(5)</td>
</tr>
<tr>
<td>C10</td>
<td>6540.1(19)</td>
<td>3882(4)</td>
<td>3012.5(10)</td>
<td>18.3(5)</td>
</tr>
<tr>
<td>C8</td>
<td>7539.4(19)</td>
<td>4783(5)</td>
<td>2231.5(10)</td>
<td>19.7(5)</td>
</tr>
<tr>
<td>C1</td>
<td>5507(2)</td>
<td>3283(4)</td>
<td>3219.4(11)</td>
<td>21.0(6)</td>
</tr>
<tr>
<td>C6</td>
<td>6592(2)</td>
<td>6306(5)</td>
<td>1377.5(10)</td>
<td>21.1(5)</td>
</tr>
<tr>
<td>C16</td>
<td>7445(2)</td>
<td>2828(5)</td>
<td>3387.2(11)</td>
<td>23.8(6)</td>
</tr>
<tr>
<td>C7</td>
<td>7529.5(19)</td>
<td>5049(4)</td>
<td>1614.5(11)</td>
<td>21.1(5)</td>
</tr>
<tr>
<td>C14</td>
<td>5827(2)</td>
<td>1961(5)</td>
<td>4177.3(12)</td>
<td>25.1(6)</td>
</tr>
<tr>
<td>C26</td>
<td>5310(2)</td>
<td>3317(5)</td>
<td>1112.2(12)</td>
<td>26.3(6)</td>
</tr>
<tr>
<td>C24</td>
<td>6631(2)</td>
<td>1306(5)</td>
<td>2202.5(11)</td>
<td>22.2(6)</td>
</tr>
<tr>
<td>C5</td>
<td>5564(2)</td>
<td>5302(5)</td>
<td>1471.3(11)</td>
<td>21.9(6)</td>
</tr>
<tr>
<td>C3</td>
<td>4617(2)</td>
<td>3999(5)</td>
<td>2263.8(12)</td>
<td>24.6(6)</td>
</tr>
<tr>
<td>C17</td>
<td>6630(2)</td>
<td>2332(5)</td>
<td>4675.2(12)</td>
<td>28.4(6)</td>
</tr>
<tr>
<td>C15</td>
<td>5548(2)</td>
<td>3958(5)</td>
<td>3829.7(12)</td>
<td>23.6(6)</td>
</tr>
<tr>
<td>C2</td>
<td>4605(2)</td>
<td>4350(5)</td>
<td>2869.9(12)</td>
<td>24.8(6)</td>
</tr>
<tr>
<td>C11</td>
<td>5379(2)</td>
<td>839(5)</td>
<td>3263.2(12)</td>
<td>25.5(6)</td>
</tr>
<tr>
<td>C12</td>
<td>6138(2)</td>
<td>329(5)</td>
<td>3764.1(12)</td>
<td>27.7(6)</td>
</tr>
</tbody>
</table>
X-ray crystallographic data for 32

Table S29. Crystal data and structure refinement for 32

<table>
<thead>
<tr>
<th>Identification code</th>
<th>2119307</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{20}H_{32}O_{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>304.45</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100.01(10)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_{1}2_{1}2_{1}</td>
</tr>
<tr>
<td>a/Å</td>
<td>6.5032(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>21.7632(5)</td>
</tr>
<tr>
<td>c/Å</td>
<td>24.2096(6)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>90</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>3426.40(16)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>ρ_{calc}/g/cm³</td>
<td>1.18</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.567</td>
</tr>
<tr>
<td>F(000)</td>
<td>1344</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.1 × 0.03 × 0.02</td>
</tr>
<tr>
<td>Radiation</td>
<td>Cu Kα (λ = 1.54184)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>7.302 to 155.974</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-8 ≤ h ≤ 8, -27 ≤ k ≤ 26, -30 ≤ l ≤ 30</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>33389</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>7011 [R_{int} = 0.0945, R_{sigma} = 0.0560]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>7011/0/405</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.055</td>
</tr>
</tbody>
</table>
Final R indexes [I>=2σ (I)]  \( R_1 = 0.0655, \ wR_2 = 0.1699 \)

Final R indexes [all data]  \( R_1 = 0.0787, \ wR_2 = 0.1774 \)

Largest diff. peak/hole / c Å⁻³  0.39/−0.25

Flack parameter  0.0(2)

Table S30. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 32. \( U_{eq} \) is defined as 1/3 of of the trace of the orthogonalised \( U_{ij} \) tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( U(\text{eq}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O15</td>
<td>3620(5)</td>
<td>7378.8(12)</td>
<td>4607.1(13)</td>
<td>41.0(7)</td>
</tr>
<tr>
<td>O14</td>
<td>1389(5)</td>
<td>7809.2(13)</td>
<td>4034.9(13)</td>
<td>45.0(8)</td>
</tr>
<tr>
<td>O37</td>
<td>4204(5)</td>
<td>6567.0(13)</td>
<td>3770.8(12)</td>
<td>40.4(7)</td>
</tr>
<tr>
<td>O36</td>
<td>1741(8)</td>
<td>6968.9(18)</td>
<td>3254.9(19)</td>
<td>71.2(13)</td>
</tr>
<tr>
<td>C8</td>
<td>2493(5)</td>
<td>10498.5(15)</td>
<td>5085.7(14)</td>
<td>23.9(7)</td>
</tr>
<tr>
<td>C12</td>
<td>3609(6)</td>
<td>9214.6(16)</td>
<td>4380.4(16)</td>
<td>28.3(8)</td>
</tr>
<tr>
<td>C13</td>
<td>2352(6)</td>
<td>7822.4(16)</td>
<td>4464.8(16)</td>
<td>30.8(8)</td>
</tr>
<tr>
<td>C9</td>
<td>971(5)</td>
<td>10787.7(15)</td>
<td>4661.7(15)</td>
<td>24.8(7)</td>
</tr>
<tr>
<td>C7</td>
<td>1837(6)</td>
<td>9807.2(15)</td>
<td>5158.5(14)</td>
<td>24.3(7)</td>
</tr>
<tr>
<td>C4</td>
<td>4304(5)</td>
<td>8732.6(16)</td>
<td>4799.9(16)</td>
<td>28.0(8)</td>
</tr>
<tr>
<td>C10</td>
<td>1023(6)</td>
<td>10441.3(16)</td>
<td>4116.6(15)</td>
<td>28.2(8)</td>
</tr>
<tr>
<td>C1</td>
<td>1545(5)</td>
<td>9432.7(15)</td>
<td>4620.6(15)</td>
<td>24.3(7)</td>
</tr>
<tr>
<td>C16</td>
<td>2140(7)</td>
<td>10831.9(16)</td>
<td>5644.4(15)</td>
<td>31.3(8)</td>
</tr>
<tr>
<td>C2</td>
<td>545(5)</td>
<td>8802.9(15)</td>
<td>4767.1(16)</td>
<td>27.9(8)</td>
</tr>
<tr>
<td>C21</td>
<td>4779(6)</td>
<td>10569.6(16)</td>
<td>4937.5(16)</td>
<td>28.5(8)</td>
</tr>
<tr>
<td>C11</td>
<td>255(6)</td>
<td>9784.3(16)</td>
<td>4202.7(16)</td>
<td>29.6(8)</td>
</tr>
<tr>
<td>C6</td>
<td>3125(6)</td>
<td>9434.2(16)</td>
<td>5581.5(15)</td>
<td>28.3(8)</td>
</tr>
<tr>
<td>C19</td>
<td>1024(6)</td>
<td>11503.2(16)</td>
<td>4602.0(17)</td>
<td>31.7(8)</td>
</tr>
<tr>
<td>C5</td>
<td>4890(6)</td>
<td>9052.0(17)</td>
<td>5339.1(17)</td>
<td>32.4(8)</td>
</tr>
<tr>
<td>C3</td>
<td>2307(6)</td>
<td>8345.7(15)</td>
<td>4871.1(16)</td>
<td>28.2(7)</td>
</tr>
<tr>
<td>C42</td>
<td>6011(7)</td>
<td>3972.5(19)</td>
<td>2394.4(18)</td>
<td>37.9(9)</td>
</tr>
<tr>
<td>C35</td>
<td>3183(8)</td>
<td>6567.6(18)</td>
<td>3352.6(18)</td>
<td>40.3(10)</td>
</tr>
<tr>
<td>C30</td>
<td>3689(7)</td>
<td>4030.3(19)</td>
<td>2340.8(16)</td>
<td>33.1(8)</td>
</tr>
<tr>
<td>C22</td>
<td>-869(6)</td>
<td>11705.7(18)</td>
<td>4263(2)</td>
<td>39.2(10)</td>
</tr>
<tr>
<td>C23</td>
<td>2868(7)</td>
<td>4958.2(19)</td>
<td>3001.0(15)</td>
<td>34.6(9)</td>
</tr>
<tr>
<td>C38</td>
<td>3056(7)</td>
<td>3804.0(19)</td>
<td>1757.8(16)</td>
<td>38.9(9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>C31</td>
<td>2425(7)</td>
<td>3628.7(19)</td>
<td>2753.6(16)</td>
<td>36.3(9)</td>
</tr>
<tr>
<td>C41</td>
<td>2608(8)</td>
<td>2912.5(19)</td>
<td>2685.9(17)</td>
<td>40.6(10)</td>
</tr>
<tr>
<td>C29</td>
<td>2923(7)</td>
<td>4705.2(18)</td>
<td>2408.9(15)</td>
<td>33.8(8)</td>
</tr>
<tr>
<td>C34</td>
<td>4959(7)</td>
<td>5184.4(19)</td>
<td>3206.2(17)</td>
<td>37.8(9)</td>
</tr>
<tr>
<td>C18</td>
<td>804(7)</td>
<td>11784.3(17)</td>
<td>5181.2(18)</td>
<td>38.5(9)</td>
</tr>
<tr>
<td>C20</td>
<td>2922(6)</td>
<td>11751.6(17)</td>
<td>4304.8(18)</td>
<td>35.1(9)</td>
</tr>
<tr>
<td>C25</td>
<td>3280(8)</td>
<td>6098(2)</td>
<td>2893.8(18)</td>
<td>43.8(11)</td>
</tr>
<tr>
<td>C39</td>
<td>3431(8)</td>
<td>3118(2)</td>
<td>1664.9(18)</td>
<td>43.4(10)</td>
</tr>
<tr>
<td>C17</td>
<td>2316(7)</td>
<td>11532.7(18)</td>
<td>5598.3(18)</td>
<td>39.6(9)</td>
</tr>
<tr>
<td>C26</td>
<td>5348(8)</td>
<td>5754(2)</td>
<td>2857.9(19)</td>
<td>41.9(10)</td>
</tr>
<tr>
<td>C32</td>
<td>2684(8)</td>
<td>3863(2)</td>
<td>3343.6(17)</td>
<td>42.6(10)</td>
</tr>
<tr>
<td>C33</td>
<td>1828(8)</td>
<td>4503(2)</td>
<td>3393.7(17)</td>
<td>43.7(10)</td>
</tr>
<tr>
<td>C28</td>
<td>3951(8)</td>
<td>5185(2)</td>
<td>2020.3(17)</td>
<td>43.9(10)</td>
</tr>
<tr>
<td>C27</td>
<td>5727(8)</td>
<td>5548(2)</td>
<td>2260.7(19)</td>
<td>46.4(11)</td>
</tr>
<tr>
<td>C40</td>
<td>2204(8)</td>
<td>2756(2)</td>
<td>2074.2(18)</td>
<td>45.2(10)</td>
</tr>
<tr>
<td>C24</td>
<td>1649(7)</td>
<td>5578(2)</td>
<td>3007(2)</td>
<td>45.2(11)</td>
</tr>
<tr>
<td>C44</td>
<td>847(9)</td>
<td>2618(2)</td>
<td>3020(2)</td>
<td>55.2(13)</td>
</tr>
<tr>
<td>C43</td>
<td>4657(9)</td>
<td>2643(2)</td>
<td>2879(2)</td>
<td>53.5(13)</td>
</tr>
</tbody>
</table>
X-ray crystallographic data for 35

Table S31. Crystal data and structure refinement for 35

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>2119308</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C(<em>{32})H(</em>{60})O(_2)Si(_2)</td>
</tr>
<tr>
<td>Formula weight</td>
<td>532.98</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100.01(10)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(_1)2(_1)2(_1)</td>
</tr>
<tr>
<td>a/Å</td>
<td>7.53230(10)</td>
</tr>
<tr>
<td>b/Å</td>
<td>15.4908(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>28.2979(3)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>90</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å(^3)</td>
<td>3301.84(7)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>(\rho_{\text{calc}})/g/cm(^3)</td>
<td>1.072</td>
</tr>
<tr>
<td>(\mu)/mm(^{-1})</td>
<td>1.147</td>
</tr>
<tr>
<td>F(000)</td>
<td>1184</td>
</tr>
<tr>
<td>Crystal size/mm(^3)</td>
<td>0.07 \times 0.05 \times 0.02</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuK(_\alpha) ((\lambda) = 1.54184)</td>
</tr>
<tr>
<td>2(\Theta) range for data collection/°</td>
<td>6.504 to 153.732</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-6 ≤ h ≤ 9, -18 ≤ k ≤ 19, -35 ≤ l ≤ 25</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>19649</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>6636 [R(<em>{int}) = 0.0260, R(</em>{sigma}) = 0.0266]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>6636/12/370</td>
</tr>
<tr>
<td>Goodness-of-fit on F(^2)</td>
<td>1.035</td>
</tr>
<tr>
<td>Final R indexes [I(&gt;)2(\sigma) (I)]</td>
<td>R(_1) = 0.0323, wR(_2) = 0.0838</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R(_1) = 0.0342, wR(_2) = 0.0847</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å(^{-3})</td>
<td>0.28/-0.21</td>
</tr>
<tr>
<td>Flack parameter</td>
<td>-0.002(8)</td>
</tr>
</tbody>
</table>
Table S32. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\AA^2 \times 10^3$) for 35. $U_{eq}$ is defined as $1/3$ of of the trace of the orthogonalised $U_{ij}$ tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si20</td>
<td>1646.4(7)</td>
<td>6982.3(3)</td>
<td>5846.8(2)</td>
<td>25.33(13)</td>
</tr>
<tr>
<td>Si28</td>
<td>5599.3(16)</td>
<td>4032.3(8)</td>
<td>7156.7(4)</td>
<td>24.2(2)</td>
</tr>
<tr>
<td>O27</td>
<td>4734(2)</td>
<td>4407.1(10)</td>
<td>6674.4(5)</td>
<td>29.0(3)</td>
</tr>
<tr>
<td>O19</td>
<td>2203.6(19)</td>
<td>5974.1(10)</td>
<td>5745.6(5)</td>
<td>31.0(3)</td>
</tr>
<tr>
<td>C9</td>
<td>5417(2)</td>
<td>4227.7(12)</td>
<td>5157.4(7)</td>
<td>21.5(4)</td>
</tr>
<tr>
<td>C6</td>
<td>4754(3)</td>
<td>4051.8(13)</td>
<td>6206.2(7)</td>
<td>24.6(4)</td>
</tr>
<tr>
<td>C8</td>
<td>6667(3)</td>
<td>3740.1(13)</td>
<td>5497.0(7)</td>
<td>23.5(4)</td>
</tr>
<tr>
<td>C4</td>
<td>3523(2)</td>
<td>4212.1(12)</td>
<td>5383.4(7)</td>
<td>22.4(4)</td>
</tr>
<tr>
<td>C36</td>
<td>6181(3)</td>
<td>5137.6(13)</td>
<td>5079.4(8)</td>
<td>28.8(4)</td>
</tr>
<tr>
<td>C5</td>
<td>3348(3)</td>
<td>4531.7(12)</td>
<td>5906.0(7)</td>
<td>24.6(4)</td>
</tr>
<tr>
<td>C10</td>
<td>5310(2)</td>
<td>3692.2(12)</td>
<td>4685.9(7)</td>
<td>22.6(4)</td>
</tr>
<tr>
<td>C3</td>
<td>2140(3)</td>
<td>4583.2(14)</td>
<td>5040.1(8)</td>
<td>28.7(4)</td>
</tr>
<tr>
<td>C15</td>
<td>3679(3)</td>
<td>3249.3(15)</td>
<td>3941.5(8)</td>
<td>31.5(5)</td>
</tr>
<tr>
<td>C1</td>
<td>3798(2)</td>
<td>3939.1(13)</td>
<td>4338.3(7)</td>
<td>25.1(4)</td>
</tr>
<tr>
<td>C16</td>
<td>7084(3)</td>
<td>3597.6(15)</td>
<td>4412.1(8)</td>
<td>29.6(4)</td>
</tr>
<tr>
<td>C7</td>
<td>6619(2)</td>
<td>4085.1(13)</td>
<td>6002.7(7)</td>
<td>24.4(4)</td>
</tr>
<tr>
<td>C2</td>
<td>2031(2)</td>
<td>4014.4(15)</td>
<td>4601.5(8)</td>
<td>29.2(4)</td>
</tr>
<tr>
<td>C21</td>
<td>32(3)</td>
<td>7080.5(14)</td>
<td>6355.3(8)</td>
<td>33.7(5)</td>
</tr>
<tr>
<td>C14</td>
<td>4971(3)</td>
<td>3527.3(18)</td>
<td>3562.2(8)</td>
<td>40.0(6)</td>
</tr>
<tr>
<td>C18</td>
<td>3570(3)</td>
<td>5511.6(13)</td>
<td>5983.4(8)</td>
<td>30.4(5)</td>
</tr>
<tr>
<td>C11</td>
<td>4278(3)</td>
<td>4743.6(15)</td>
<td>4047.4(8)</td>
<td>34.3(5)</td>
</tr>
<tr>
<td>C29</td>
<td>4430(3)</td>
<td>4621.8(16)</td>
<td>7648.4(8)</td>
<td>36.2(5)</td>
</tr>
<tr>
<td>C35</td>
<td>1517(3)</td>
<td>4269.6(15)</td>
<td>6098.8(8)</td>
<td>31.4(4)</td>
</tr>
<tr>
<td>C25</td>
<td>3668(3)</td>
<td>7645.7(16)</td>
<td>5962.8(9)</td>
<td>39.0(5)</td>
</tr>
<tr>
<td>C12</td>
<td>5723(3)</td>
<td>4398.4(18)</td>
<td>3717.3(8)</td>
<td>39.7(6)</td>
</tr>
<tr>
<td>C13</td>
<td>7411(3)</td>
<td>4238.4(18)</td>
<td>4006.5(8)</td>
<td>38.1(5)</td>
</tr>
<tr>
<td>C26</td>
<td>562(4)</td>
<td>7314.5(19)</td>
<td>5284.0(10)</td>
<td>50.5(7)</td>
</tr>
<tr>
<td>C32</td>
<td>4890(40)</td>
<td>4390(20)</td>
<td>8163(5)</td>
<td>38(2)</td>
</tr>
<tr>
<td>C17</td>
<td>5355(4)</td>
<td>3107(2)</td>
<td>3164.8(10)</td>
<td>60.9(8)</td>
</tr>
<tr>
<td>C24</td>
<td>-1595(4)</td>
<td>6519(2)</td>
<td>6263.4(14)</td>
<td>61.2(9)</td>
</tr>
<tr>
<td>C22</td>
<td>-587(5)</td>
<td>8019.1(19)</td>
<td>6398.0(15)</td>
<td>69.6(10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>C33</td>
<td>8019(4)</td>
<td>4291(3)</td>
<td>7201.8(12)</td>
<td>49.0(8)</td>
</tr>
<tr>
<td>C30</td>
<td>2375(4)</td>
<td>4465(3)</td>
<td>7584.7(11)</td>
<td>43.2(9)</td>
</tr>
<tr>
<td>C34</td>
<td>5272(5)</td>
<td>2845.8(18)</td>
<td>7172.5(13)</td>
<td>47.6(8)</td>
</tr>
<tr>
<td>C23</td>
<td>896(5)</td>
<td>6797(3)</td>
<td>6815.7(11)</td>
<td>73.1(11)</td>
</tr>
<tr>
<td>C31</td>
<td>4781(7)</td>
<td>5575(2)</td>
<td>7633.4(13)</td>
<td>51.9(11)</td>
</tr>
<tr>
<td>Si</td>
<td>5011(9)</td>
<td>3845(4)</td>
<td>7221(2)</td>
<td>27.2(12)</td>
</tr>
<tr>
<td>C33A</td>
<td>7288(15)</td>
<td>3377(12)</td>
<td>7235(6)</td>
<td>49.0(8)</td>
</tr>
<tr>
<td>C34A</td>
<td>3370(20)</td>
<td>2952(8)</td>
<td>7293(6)</td>
<td>47.6(8)</td>
</tr>
<tr>
<td>C31A</td>
<td>5760(30)</td>
<td>5423(10)</td>
<td>7577(7)</td>
<td>51.9(11)</td>
</tr>
<tr>
<td>C30A</td>
<td>2625(17)</td>
<td>4999(14)</td>
<td>7662(6)</td>
<td>43.2(9)</td>
</tr>
<tr>
<td>C32A</td>
<td>5030(20)</td>
<td>4194(14)</td>
<td>8119(4)</td>
<td>38(2)</td>
</tr>
</tbody>
</table>
X-ray crystallographic data for 38

Table S33. Crystal data and structure refinement for 38

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>2119309</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{20}H_{32}O</td>
</tr>
<tr>
<td>Formula weight</td>
<td>288.45</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>99.98(10)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_{1}2_{1}2_{1}</td>
</tr>
<tr>
<td>a/Å</td>
<td>6.22520(10)</td>
</tr>
<tr>
<td>b/Å</td>
<td>11.2924(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>23.4400(3)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>90</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>1647.77(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρ_{calc} / g/cm³</td>
<td>1.163</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.515</td>
</tr>
<tr>
<td>F(000)</td>
<td>640</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.12 × 0.1 × 0.01</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα (λ = 1.54184)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>7.544 to 153.692</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-7 ≤ h ≤ 4, -13 ≤ k ≤ 13, -27 ≤ l ≤ 29</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>9028</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3318 [R_{int} = 0.0279, R_{sigma} = 0.0290]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>3318/0/194</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.041</td>
</tr>
<tr>
<td>Final R indexes [I≥2σ (I)]</td>
<td>R₁ = 0.0335, wR₂ = 0.0881</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0348, wR₂ = 0.0889</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.19/-0.18</td>
</tr>
</tbody>
</table>
Table S34. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\AA^2 \times 10^3$) for 38. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{ij}$ tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U(\text{eq})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>2467(2)</td>
<td>5163.6(11)</td>
<td>4656.0(5)</td>
<td>20.3(3)</td>
</tr>
<tr>
<td>C15</td>
<td>5880(3)</td>
<td>4336.0(15)</td>
<td>4250.5(7)</td>
<td>13.9(3)</td>
</tr>
<tr>
<td>C19</td>
<td>4451(3)</td>
<td>2871.5(15)</td>
<td>3114.8(7)</td>
<td>16.7(3)</td>
</tr>
<tr>
<td>C12</td>
<td>7604(3)</td>
<td>2109.3(14)</td>
<td>3735.0(7)</td>
<td>14.3(3)</td>
</tr>
<tr>
<td>C7</td>
<td>6767(3)</td>
<td>3095.9(14)</td>
<td>3324.7(6)</td>
<td>13.7(3)</td>
</tr>
<tr>
<td>C5</td>
<td>6319(3)</td>
<td>5390.6(15)</td>
<td>3293.5(7)</td>
<td>16.8(3)</td>
</tr>
<tr>
<td>C10</td>
<td>9367(3)</td>
<td>1009.5(16)</td>
<td>2922.0(7)</td>
<td>18.6(4)</td>
</tr>
<tr>
<td>C13</td>
<td>6276(3)</td>
<td>2081.2(15)</td>
<td>4289.5(7)</td>
<td>16.3(3)</td>
</tr>
<tr>
<td>C6</td>
<td>6977(3)</td>
<td>4299.9(14)</td>
<td>3651.5(7)</td>
<td>13.5(3)</td>
</tr>
<tr>
<td>C11</td>
<td>8010(3)</td>
<td>862.2(15)</td>
<td>3467.7(7)</td>
<td>16.8(3)</td>
</tr>
<tr>
<td>C14</td>
<td>6488(3)</td>
<td>3253.1(14)</td>
<td>4608.5(7)</td>
<td>16.7(3)</td>
</tr>
<tr>
<td>C2</td>
<td>3114(3)</td>
<td>5833.9(16)</td>
<td>4157.1(7)</td>
<td>18.3(4)</td>
</tr>
<tr>
<td>C17</td>
<td>6573(3)</td>
<td>5502.6(14)</td>
<td>4538.9(7)</td>
<td>16.1(3)</td>
</tr>
<tr>
<td>C20</td>
<td>5950(3)</td>
<td>158.0(16)</td>
<td>3337.7(8)</td>
<td>20.3(4)</td>
</tr>
<tr>
<td>C3</td>
<td>5270(3)</td>
<td>6452.8(15)</td>
<td>4221.0(7)</td>
<td>16.9(3)</td>
</tr>
<tr>
<td>C9</td>
<td>8537(3)</td>
<td>1940.0(16)</td>
<td>2506.8(7)</td>
<td>19.1(4)</td>
</tr>
<tr>
<td>C16</td>
<td>3468(3)</td>
<td>4549.3(15)</td>
<td>4179.6(7)</td>
<td>16.7(3)</td>
</tr>
<tr>
<td>C4</td>
<td>6276(3)</td>
<td>6570.5(15)</td>
<td>3623.6(7)</td>
<td>18.0(3)</td>
</tr>
<tr>
<td>C8</td>
<td>8247(3)</td>
<td>3144.7(15)</td>
<td>2796.1(7)</td>
<td>16.7(3)</td>
</tr>
<tr>
<td>C21</td>
<td>9358(3)</td>
<td>116.0(16)</td>
<td>3884.4(8)</td>
<td>22.1(4)</td>
</tr>
<tr>
<td>C18</td>
<td>5124(3)</td>
<td>7645.7(16)</td>
<td>4522.9(8)</td>
<td>23.2(4)</td>
</tr>
</tbody>
</table>
X-ray crystallographic data for S48

Table S35. Crystal data and structure refinement for S48

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>2128501</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{28}H_{40}O_{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>408.6</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100.01(10)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_12_12_1</td>
</tr>
<tr>
<td>a/Å</td>
<td>6.19870(10)</td>
</tr>
<tr>
<td>b/Å</td>
<td>17.4983(4)</td>
</tr>
<tr>
<td>c/Å</td>
<td>21.2930(5)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>90</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å^3</td>
<td>2309.58(8)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>(\rho_{\text{calc}}) g/cm^3</td>
<td>1.175</td>
</tr>
<tr>
<td>(\mu) mm(^{-1})</td>
<td>0.546</td>
</tr>
<tr>
<td>F(000)</td>
<td>896</td>
</tr>
<tr>
<td>Crystal size/mm(^3)</td>
<td>0.59 \times 0.03 \times 0.02</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuK(\alpha) (\lambda = 1.54184)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>6.538 to 149.916</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-7 ≤ h ≤ 7, -21 ≤ k ≤ 15, -23 ≤ l ≤ 26</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>13409</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>4575 [R(<em>{\text{int}}) = 0.0487, R</em>{\text{sigma}} = 0.0494]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>4575/0/276</td>
</tr>
<tr>
<td>Goodness-of-fit on F^2</td>
<td>1.025</td>
</tr>
<tr>
<td>Final R indexes [I&gt;=2σ (I)]</td>
<td>R_1 = 0.0356, wR_2 = 0.0925</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R_1 = 0.0402, wR_2 = 0.0941</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å(^{-3})</td>
<td>0.26/-0.14</td>
</tr>
<tr>
<td>Flack parameter</td>
<td>0.04(13)</td>
</tr>
</tbody>
</table>
Table S36. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\AA^2 \times 10^3$) for S48. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$ tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U(eq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O18</td>
<td>3753(2)</td>
<td>2325.8(7)</td>
<td>4024.1(6)</td>
<td>23.4(3)</td>
</tr>
<tr>
<td>O20</td>
<td>4257(3)</td>
<td>3044.2(8)</td>
<td>4885.6(7)</td>
<td>28.4(3)</td>
</tr>
<tr>
<td>C17</td>
<td>4043(3)</td>
<td>2994.2(10)</td>
<td>4325.8(9)</td>
<td>21.0(4)</td>
</tr>
<tr>
<td>C4</td>
<td>5105(3)</td>
<td>5404.4(10)</td>
<td>3430.1(8)</td>
<td>16.4(4)</td>
</tr>
<tr>
<td>C5</td>
<td>6677(3)</td>
<td>6089.5(10)</td>
<td>3305.9(8)</td>
<td>16.7(4)</td>
</tr>
<tr>
<td>C13</td>
<td>5355(3)</td>
<td>4988.0(10)</td>
<td>4068.8(8)</td>
<td>16.4(4)</td>
</tr>
<tr>
<td>C10</td>
<td>6489(3)</td>
<td>6635.4(9)</td>
<td>3883.9(9)</td>
<td>17.8(4)</td>
</tr>
<tr>
<td>C3</td>
<td>4952(3)</td>
<td>4807.6(10)</td>
<td>2891.5(9)</td>
<td>20.5(4)</td>
</tr>
<tr>
<td>C2</td>
<td>6425(3)</td>
<td>4106.7(10)</td>
<td>2963.1(9)</td>
<td>20.8(4)</td>
</tr>
<tr>
<td>C6</td>
<td>5861(3)</td>
<td>6526.4(10)</td>
<td>2720.3(9)</td>
<td>21.6(4)</td>
</tr>
<tr>
<td>C11</td>
<td>7021(3)</td>
<td>6214.4(10)</td>
<td>4495.5(9)</td>
<td>21.4(4)</td>
</tr>
<tr>
<td>C27</td>
<td>7970(3)</td>
<td>3081.6(11)</td>
<td>3644.7(10)</td>
<td>24.3(4)</td>
</tr>
<tr>
<td>C9</td>
<td>7559(3)</td>
<td>7440.2(10)</td>
<td>3816.7(10)</td>
<td>21.7(4)</td>
</tr>
<tr>
<td>C8</td>
<td>6711(3)</td>
<td>7800.5(10)</td>
<td>3205.4(10)</td>
<td>24.4(4)</td>
</tr>
<tr>
<td>C7</td>
<td>6961(3)</td>
<td>7299.1(11)</td>
<td>2626.4(10)</td>
<td>24.8(4)</td>
</tr>
<tr>
<td>C28</td>
<td>9006(3)</td>
<td>5829.9(10)</td>
<td>3173.6(9)</td>
<td>21.3(4)</td>
</tr>
<tr>
<td>C16</td>
<td>7256(3)</td>
<td>4427.0(10)</td>
<td>4070.8(9)</td>
<td>17.6(4)</td>
</tr>
<tr>
<td>C12</td>
<td>5406(3)</td>
<td>5568.2(10)</td>
<td>4605.2(9)</td>
<td>21.1(4)</td>
</tr>
<tr>
<td>C14</td>
<td>3465(3)</td>
<td>4422.4(10)</td>
<td>4164.1(10)</td>
<td>21.1(4)</td>
</tr>
<tr>
<td>C21</td>
<td>2865(3)</td>
<td>992.1(10)</td>
<td>4073.4(9)</td>
<td>22.5(4)</td>
</tr>
<tr>
<td>C15</td>
<td>4135(3)</td>
<td>3650.2(10)</td>
<td>3864.2(9)</td>
<td>19.3(4)</td>
</tr>
<tr>
<td>C1</td>
<td>6507(3)</td>
<td>3785.1(10)</td>
<td>3632.3(9)</td>
<td>18.1(4)</td>
</tr>
<tr>
<td>C29</td>
<td>6817(4)</td>
<td>7951.9(11)</td>
<td>4360.2(10)</td>
<td>29.5(5)</td>
</tr>
<tr>
<td>C22</td>
<td>817(3)</td>
<td>1067.5(11)</td>
<td>3817.2(10)</td>
<td>26.4(4)</td>
</tr>
<tr>
<td>C19</td>
<td>3905(4)</td>
<td>1647.0(11)</td>
<td>4414.7(10)</td>
<td>27.6(4)</td>
</tr>
<tr>
<td>C26</td>
<td>3909(4)</td>
<td>288.0(11)</td>
<td>4036.6(10)</td>
<td>29.5(5)</td>
</tr>
<tr>
<td>C30</td>
<td>10039(3)</td>
<td>7432.9(11)</td>
<td>3822.2(11)</td>
<td>28.3(4)</td>
</tr>
<tr>
<td>C25</td>
<td>2894(5)</td>
<td>-326.6(12)</td>
<td>3749.3(11)</td>
<td>37.5(6)</td>
</tr>
<tr>
<td>C23</td>
<td>-174(4)</td>
<td>456.0(13)</td>
<td>3524.3(11)</td>
<td>34.4(5)</td>
</tr>
<tr>
<td>C24</td>
<td>867(5)</td>
<td>-246.8(13)</td>
<td>3493.7(11)</td>
<td>37.8(6)</td>
</tr>
</tbody>
</table>


NMR spectra

\[ ^1H \text{ NMR (400 MHz, } \text{CDCl}_3 \text{)} \]
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

S125
$^{13}$C NMR (101 MHz, CDCl₃)
S4

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}C$ NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CCl$_4$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}C$ NMR (100 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
TBSO
Me
Me
S14

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl₃)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$\text{H NMR (400 MHz, CDCl}_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
^1H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
\[^{13}C\text{ NMR (101 MHz, CDCl}_3\text{)}\]
\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{)}\]
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

S36
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)
\[ ^{1}H \text{NMR (101 MHz, CDCl}\_3) \]
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

S191
1H NMR (400 MHz, CDCl$_3$)

13, major isomer
$^{13}$C NMR (121 MHz, CDCl$_3$)

13. major isomer

S193
13, minor isomer

$^1$H NMR (101 MHz, CDCl$_3$)
1H NMR (400 MHz, CD3CN)
$^{13}$C NMR (101 MHz, CDCl$_3$)

14, major isomer

-177.65
$^1$H NMR (400 MHz, CDCl$_3$)
14. minor isomer

$^{13}$C NMR (101 MHz, CDCl$_3$)
1H NMR (400 MHz, CDCl3)

15, major isomer
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
15. 1H NMR (400 MHz, CDCl3)

13C NMR (101 MHz, CDCl3)
$^1$H NMR (400 MHz, CDCl$_3$)
$1^H$ NMR (500 MHz, CDCl$_3$)

$\delta$ = 1:6:1
18. dr = 1.6:1
$^{13}$C NMR (101 MHz, CDCl$_3$)
$\text{Me} \cdot \text{H} \cdot \text{Me}$

$\text{Me} \cdot \text{H} \cdot \text{Me}$

$1^\text{H NMR} (400 \text{ MHz, CDCl}_3)$

$19, \text{ dr } = 1:1$
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{21} \text{, dr} = 1:7$
S33, dr = 12:1

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)

S34, dr = 12:1

S215
$22$, $dr = 12:1$

$^1$H NMR (400 MHz, CDCl$_3$)
S217
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

24, major isomer
$^1$H NMR (400 MHz, CDCl$_3$)
S37, dr = 4.0:1

$^1\text{H}$ NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
S40, dr = 2:1:1

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$S_{40}$, $dr = 2:1:1$
S43, dr = 3.7:1

$^1$H NMR (400 MHz, CDCl₃)
\( ^{13}C \) NMR (101 MHz, CDCl\textsubscript{3})

S43, dr = 3:7:1
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
25 endo-3β-hydroxykaur-16-ene

$\text{$^{13}$C NMR (101 MHz, CDCl}_3$}
$^{13}$C NMR (101 MHz, CDCl$_3$)
S234
ent-3α-acetoxyster-16β,17-diol

$^{13}$C NMR (101 MHz, CD$_3$OD)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDC$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
28

Trihalic acid

$^1H$ NMR (400 MHz, CDCl$_3$)
9H-Norbiobic acid

$^{13}$C NMR (101 MHz, CDCl$_3$)

AcO

Me

Me

CO$_2$H

28
fritilarin B (28)

$^1$H NMR (400 MHz, CDCl$_3$)

S242
18α-H-enkaiuren-17-αc acid

$^1$H NMR (400 MHz, CDCl$_3$)
32
18α-H-ent-kauran-17-ol acid
$^{13}$C NMR (101 MHz, CDCl$_3$)
ent-kauran-15-ene

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)

33, major isomer
$^1$H NMR (400 MHz, CDCl$_3$)
TBSO
Me
Me
OH

33, minor isomer

$^1^3$C NMR (101 MHz, CDCl$_3$)
18a-H and kaurane-3(21)/17,19-triol

$^1$H NMR (400 MHz, CD$_3$OD)
16α-H-ent-kaurene-3β,17,19-triol

13C NMR (101 MHz, C4D3N)
$^{13}$C NMR (101 MHz, CDCl$_3$)
enantiomer 3,5,19-trihydroxy-kaurene

$^1$H NMR (400 MHz, CDCl$_3$)
37
hibane

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
38 hbaena epoxide

$^1$H NMR (400 MHz, CDCl$_3$)