Supporting Information

Formation of Allylated Quaternary Carbon Centers via C–O/C–O Bond Fragmentation of Oxalates and Allyl Carbonates

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I. Experimental Section

Part 1. General Information

1. Chemicals and Reagents.

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk or glove box techniques. DMA (N, N-dimethylacetamide, 99.5%, extra dry, Acros) was purchased and used directly. Deuterated solvents were used as received (CDCl$_3$ from Maclin Co., China). Fe(acac)$_3$ (Sigma-Aldrich), FePc (TCI), FeCl$_3$ (Alfa Aesar), FeBr$_3$ (Alfa Aesar), Fe$_2$(SO$_4$)$_3$ (Adamas), Ni(COD)$_2$ (Strem), Fe$_2$(OTf)$_3$ (Alfa Aesar), Ni(acac)$_2$ (Maclin Co., China), Co(acac)$_2$ (Alfa Aesar), CuI (Alfa Aesar) were used as received. Zinc powder (Aladdin) was activated with hydrochloric acid before use. Anhydrous MgCl$_2$ (Alfa Aesar) and anhydrous LiCl (TCI) were purchased and used directly. DMAP (4-(dimethylamine) pyridine (>99%, Adamas), Dtbbipy (98%, Alfa Aesar) were purchased and used directly. Procedures for the ligand synthesis have been reported.$^{[1]}$ Tertiary alcohols and allylic carbonates were prepared according to literature procedures$^{[2,3]}$ or purchased and used directly. Methyl magnesium bromide (3M in THF, Adamas) was purchased and used directly.

2. Physical Method.

Column chromatography was performed using silica gel 200-300 mesh (purchased from Qingdao-Haiyang Co., China) as the solid support. All NMR spectra were recorded on a Bruker Avance 600 MHz spectrometer, a Bruker Avance 500 MHz spectrometer, or a JEOL 400 MHz at STP, unless otherwise indicated. $^1$H NMR and $^{13}$C NMR chemical shifts are reported in $\delta$ units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in $^1$H NMR and $^{13}$C NMR spectra were set at 7.26 ppm and 77.0 ppm, respectively. High-resolution mass spectra (HRMS) were obtained using a Bruker APEXIII 7.0 or IonSpec 4.7 TESLA FTMS instruments. Melting points were recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China). In situ IR spectra were recorded on a Thermo Scientific Nicolet iS10 Fourier transform infrared (FT-IR) spectrometer. GC chromatograms were recorded on a GCMS-QP2010 SE (SHIMADZU) using an Agilent column CP7502 and Rxi-5 ms (Restek).
Part 2. Details of Optimization and Control Experiments

Method A: To a flame-dried Schlenk tube equipped with a stir bar was loaded zinc power (29.4 mg, 0.45 mmol, 300 mol %), followed by addition of MgCl$_2$ (42.9 mg, 0.45 mmol, 300 mol %), ligand (0.03 mmol, 20 mol %) and Fe (acac)$_3$ (0.015 mmol, 10 mol %). The tube was evacuated and refilled nitrogen (N$_2$) three times. A solvent (1.0 mL) was added via a syringe, followed by addition of tertiary alkyl oxalate (0.15 mmol, 100 mol %), and allylic carbonate (0.3 mmol, 200 mol %). After the reaction mixture was stirred for 12 h under a N$_2$ atmosphere at 45 °C, the reaction mixture was loaded onto a silica column. Flash column chromatography provided the product as an oil or a solid.

1. Reaction of methyl (2-arylallyl) carbonate with different oxalates.

Table S1. Screening of the catalyst for the coupling of tert-butyl methyl oxalate with methyl 2-(4-fluorophenyl) allyl carbonate.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>yield$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni (TMHD)$_2$</td>
<td>21%</td>
</tr>
<tr>
<td>2</td>
<td>Ni (COD)$_2$</td>
<td>13%</td>
</tr>
<tr>
<td>3</td>
<td>NiBr$_2$ glyme</td>
<td>14%</td>
</tr>
<tr>
<td>4</td>
<td>NiBr$_2$ diglyme</td>
<td>13%</td>
</tr>
<tr>
<td>5</td>
<td>Ni (acac)$_2$</td>
<td>11%</td>
</tr>
<tr>
<td>6</td>
<td>Ni$_2$</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>NiBr$_2$</td>
<td>6%</td>
</tr>
<tr>
<td>8</td>
<td>NiCl$_2$</td>
<td>11%</td>
</tr>
<tr>
<td>9</td>
<td>NiCl$_2$ (Py)$_4$</td>
<td>15%</td>
</tr>
<tr>
<td>10</td>
<td>Ni (ClO$_4$)$_2$6H$_2$O</td>
<td>11%</td>
</tr>
<tr>
<td>11</td>
<td>NiCl$_2$ DME</td>
<td>16%</td>
</tr>
</tbody>
</table>

$^a$NMR yield using 2,5-dimethyl-furan as internal reference.

Scheme S1. Use of methyl and tert-butyl oxalates (NMR yield using 2,5-dimethylyfuran as internal reference).
Table S2. Screening of the iron salts for the coupling of di-tert-butyl oxalate with methyl 2-(4-fluorophenyl) allyl carbonate.

<table>
<thead>
<tr>
<th>entry</th>
<th>iron salt</th>
<th>yield a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe (acac)₃</td>
<td>57%</td>
</tr>
<tr>
<td>2</td>
<td>FeCl₃</td>
<td>56%</td>
</tr>
<tr>
<td>3</td>
<td>FeBr₃</td>
<td>36%</td>
</tr>
<tr>
<td>4</td>
<td>FeF₃</td>
<td>52%</td>
</tr>
<tr>
<td>5</td>
<td>FeBr₂</td>
<td>36%</td>
</tr>
<tr>
<td>6</td>
<td>Dppf</td>
<td>56%</td>
</tr>
<tr>
<td>7</td>
<td>FeCp₂</td>
<td>55%</td>
</tr>
<tr>
<td>8</td>
<td>FeSO₄·7H₂O</td>
<td>45%</td>
</tr>
<tr>
<td>9</td>
<td>Fe₂(SO₄)₃</td>
<td>48%</td>
</tr>
</tbody>
</table>

a NMR yield using 2,5-dimethyl-furan as internal reference.

Table S3. Screening of the loading of LiCl

<table>
<thead>
<tr>
<th>Entry.</th>
<th>X%</th>
<th>yield a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>68%</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>55%</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>57%</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>58%</td>
</tr>
</tbody>
</table>

a NMR yield using 2,5-dimethyl-furan as internal reference.
Table S4. Screening of solvent for the coupling of di-tert-butyl oxalate with methyl (2-phenyl allyl) carbonate.

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>yield a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 a</td>
<td>DMA</td>
<td>69%</td>
</tr>
<tr>
<td>2 b</td>
<td>THF</td>
<td>ND</td>
</tr>
<tr>
<td>3 a</td>
<td>DMF</td>
<td>30%</td>
</tr>
<tr>
<td>4 b</td>
<td>NMP</td>
<td>ND</td>
</tr>
<tr>
<td>5 b</td>
<td>1,4-Dioxane</td>
<td>ND</td>
</tr>
<tr>
<td>6 b</td>
<td>DMSO</td>
<td>ND</td>
</tr>
<tr>
<td>7 b</td>
<td>DME</td>
<td>ND</td>
</tr>
<tr>
<td>8 b</td>
<td>MeCN</td>
<td>ND</td>
</tr>
</tbody>
</table>

aNMR yield using 2,5-dimethyl-furan as internal reference. bDetected by TLC.

Table S5. Screening of reductant for the coupling of di-tert-butyl oxalate with methyl (2-phenyl allyl) carbonate.

<table>
<thead>
<tr>
<th>entry</th>
<th>reductant</th>
<th>yield a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zn</td>
<td>61%</td>
</tr>
<tr>
<td>2</td>
<td>Mn</td>
<td>31%</td>
</tr>
<tr>
<td>3</td>
<td>(BPin)2</td>
<td>ND</td>
</tr>
<tr>
<td>4</td>
<td>TDAE</td>
<td>trace</td>
</tr>
</tbody>
</table>

aNMR yield using 2,5-dimethyl-furan as internal reference.
Table S6. Screening of ligands for the coupling of di-tert-butyl oxalate with methyl (2-phenyl allyl) carbonate.

![Chemical structures and reaction conditions](image)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Yield</th>
<th>Recovered Oxalate</th>
<th>Recovered Carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1a</td>
<td>84%</td>
<td>7%</td>
<td>106%</td>
</tr>
<tr>
<td>L1b</td>
<td>61%</td>
<td>6%</td>
<td>88%</td>
</tr>
<tr>
<td>L1c</td>
<td>74%</td>
<td>5%</td>
<td>94%</td>
</tr>
<tr>
<td>L1d</td>
<td>74%</td>
<td>trace</td>
<td>84%</td>
</tr>
<tr>
<td>L1e</td>
<td>64%</td>
<td>33%</td>
<td>98%</td>
</tr>
<tr>
<td>L2</td>
<td>58%</td>
<td>33%</td>
<td>132%</td>
</tr>
<tr>
<td>L3</td>
<td>53%</td>
<td>not detected</td>
<td>112%</td>
</tr>
<tr>
<td>L4</td>
<td>60%</td>
<td>15%</td>
<td>70%</td>
</tr>
<tr>
<td>L5</td>
<td>60%</td>
<td>24%</td>
<td>74%</td>
</tr>
<tr>
<td>L6</td>
<td>47%</td>
<td>10%</td>
<td>118%</td>
</tr>
<tr>
<td>L7</td>
<td>69%</td>
<td>10%</td>
<td>118%</td>
</tr>
<tr>
<td>L8</td>
<td>44%</td>
<td>23%</td>
<td>120%</td>
</tr>
</tbody>
</table>

2. Optimization for unsubstituted allyl electrophiles.

Table S7. Screening of the allylic substrates.

![Chemical structures and reaction conditions](image)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Yield</th>
<th>Recovered Oxalate</th>
<th>Recovered Carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCOOMe</td>
<td>25%</td>
<td>5%</td>
<td>ND</td>
</tr>
<tr>
<td>OTs</td>
<td>6%</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>OTMS</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>TMS</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>OAc</td>
<td>27%</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>OCOOPh</td>
<td>19%</td>
<td>25%</td>
<td>13%</td>
</tr>
<tr>
<td>OBoc</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>OPh</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>OCOOBn</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>
Table S8. Screening of metal salts.

<table>
<thead>
<tr>
<th>entry</th>
<th>metal salt</th>
<th>yield</th>
<th>entry</th>
<th>metal salt</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FeCl₃·6H₂O</td>
<td>8%</td>
<td>15</td>
<td>Fe (OAc)₂</td>
<td>Trace</td>
</tr>
<tr>
<td>2</td>
<td>FeBr₂</td>
<td>8%</td>
<td>16</td>
<td>FeBr₃</td>
<td>Trace</td>
</tr>
<tr>
<td>3</td>
<td>FeF₃</td>
<td>Trace</td>
<td>17</td>
<td>Fe (ClO₄)₂·6H₂O</td>
<td>Trace</td>
</tr>
<tr>
<td>4</td>
<td>FeS</td>
<td>ND</td>
<td>18</td>
<td>Ni (COD)₂</td>
<td>Trace</td>
</tr>
<tr>
<td>5</td>
<td>Fe₂(SO₄)₃</td>
<td>Trace</td>
<td>19</td>
<td>NiBr₂·glyme</td>
<td>ND</td>
</tr>
<tr>
<td>6</td>
<td>Fe₂(C₂O₄)₃·6H₂O</td>
<td>33%</td>
<td>20</td>
<td>NiBr₂·diglyme</td>
<td>ND</td>
</tr>
<tr>
<td>7</td>
<td>Fe (dibm)₃</td>
<td>11%</td>
<td>21</td>
<td>NiI₂</td>
<td>ND</td>
</tr>
<tr>
<td>8</td>
<td>Fe (dmp)₃</td>
<td>Trace</td>
<td>22</td>
<td>Ni (CF₃SO₃)₂</td>
<td>12%</td>
</tr>
<tr>
<td>9</td>
<td>Fe (acac)₂</td>
<td>Trace</td>
<td>23</td>
<td>Ni (acac)₂</td>
<td>Trace</td>
</tr>
<tr>
<td>10</td>
<td>Fe (acac)₃</td>
<td>11%</td>
<td>24</td>
<td>NiBr₂</td>
<td>ND</td>
</tr>
<tr>
<td>11</td>
<td>FeCl₁</td>
<td>Trace</td>
<td>25</td>
<td>Ni (TMHD)₂</td>
<td>trace</td>
</tr>
<tr>
<td>12</td>
<td>FeCp₂</td>
<td>Trace</td>
<td>26</td>
<td>Co (acac)₂</td>
<td>12%</td>
</tr>
<tr>
<td>13</td>
<td>Fe (OTf)₃</td>
<td>Trace</td>
<td>27</td>
<td>CoPc</td>
<td>Trace</td>
</tr>
<tr>
<td>14</td>
<td>FePc</td>
<td>33%</td>
<td>28</td>
<td>without Fe salt</td>
<td>no reaction</td>
</tr>
</tbody>
</table>

*Detected by NMR using 2,5-dimethylfuran as internal reference.

Scheme S2. Screening of the concentrations of reaction (NMR yield using 2,5-dimethylfuran as internal reference).

Scheme S3. Mass balance for 1b for the coupling with allyl acetate.
3. Examination of 1- and 3-phenyl substituted allylic carbonates

The reaction of 1a with 1-phenyl and 3-phenyl allyl carbonates indicated that all the starting 1a was consumed. However, substantial amounts of allylic carbonates were recovered, indicating the low reactivities of the 1-phenyl and 3-phenyl allyl carbonates as compared to the 2-phenyl analog (2a).

![Scheme S4](image)

**Scheme S4.** Reaction of 1a with 1-phenyl and 3-phenyl allyl carbonates.

4. Product distribution

![Scheme S5](image)

**Scheme S5.** The product distribution of the reaction of 1b with 2a using method A.

![Scheme S6](image)

**Scheme S6.** The product distribution of the scale-up reaction 1b with 2a using method A.

![Scheme S7](image)

**Scheme S7.** The product distribution of the three-component reaction of di-tert-butyl oxalate 1a, methyl acrylate and 2a using method B.
Scheme S8. The product distribution of the three-component reaction of oxalate 1b, methyl acrylate and 2b using method B.


1. Monitoring the reaction progress.

Table S9. Tracking the reaction progress.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time/h</th>
<th>Recovered A</th>
<th>Recovered 2a</th>
<th>12a</th>
<th>A-OH</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5h</td>
<td>29%</td>
<td>132%</td>
<td>30%</td>
<td>41%</td>
<td>0%</td>
</tr>
<tr>
<td>2</td>
<td>1h</td>
<td>19%</td>
<td>120%</td>
<td>53%</td>
<td>29%</td>
<td>Trace</td>
</tr>
<tr>
<td>3</td>
<td>2h</td>
<td>5%</td>
<td>108%</td>
<td>72%</td>
<td>22%</td>
<td>Trace</td>
</tr>
<tr>
<td>4</td>
<td>3h</td>
<td>Trace</td>
<td>91%</td>
<td>78%</td>
<td>16%</td>
<td>Trace</td>
</tr>
<tr>
<td>5</td>
<td>4h</td>
<td>Trace</td>
<td>80%</td>
<td>78%</td>
<td>11%</td>
<td>7%</td>
</tr>
<tr>
<td>6</td>
<td>5h</td>
<td>Trace</td>
<td>80%</td>
<td>79%</td>
<td>9%</td>
<td>7%</td>
</tr>
<tr>
<td>7</td>
<td>8h</td>
<td>Trace</td>
<td>55%</td>
<td>82%</td>
<td>4%</td>
<td>8%</td>
</tr>
</tbody>
</table>

*a* Detected by NMR using 2,5-dimethyl-furan as internal reference.
Figure S1. Monitoring the reaction progress

2. Control experiments

Scheme S9. Control experiment in the absence of oxalate 1a.

Scheme S10. Control experiment in the absence of Fe salts.
Scheme S11. Control experiments using previously reported Ni-catalyzed reaction conditions.\textsuperscript{2a}

Scheme S12. Nickel catalyzed allylation of 3-bromo-3-methylbutyl benzoate with (Z)-methyl (2-phenylallyl-3-d) carbonate (2a-d).\textsuperscript{2a}

3. $^1$H NMR spectroscopic analysis

Figure S2. $^1$H NMR spectra of Fe(acac)$_3$, 2a, and an equimolar mixture of Fe(acac)$_3$ and 2a in DMSO-$d_6$. The $^1$H NMR spectra was recorded after stirring overnight. No obvious changes of the chemical shifts were detected.
Figure S3. $^1$H NMR spectra of allyl carbonate 2a (0.15 M) without (above) and with (bottom) MgCl$_2$ (1.5 equiv) in DMSO-$d_6$ (bottom). The spectra were recorded about 10 minutes after the sample was prepared.

Figure S4. The $^1$H NMR spectra for ethyl acetate (top) and its mixture with MgCl$_2$ (saturated, bottom) in DMSO-$d_6$. 
4. Roles of Fe

In this time, we are still far from fully understanding the role of iron complex in the radical addition process. However, there are key points that we would like to highlight.

First, without an iron salt, the radical addition/allyl C-O bond fragmentation product 3a was obtained in ~40% yield, indicating that the reaction was governed by Zn and MgCl₂. Thus, iron complex only acts to promote the reaction.

Second, we speculate Fe³⁺ or Fe²⁺ may serve as a Lewis acid to coordinate with allyl carbonate similar to Mg²⁺ (Figure S3). However, no appreciable interaction of Fe³⁺ nor Fe²⁺ with allylic carbonate was detected for a mixture of these two species in DMSO-d₆ (Figure S2). In addition, such an interaction was not seen for a pre-formed bipy-FeCl₃ (see below) with allyl carbonate from ¹H NMR studies, although a control experiment showed that bipy-FeCl₃ gave 3a in 65% yield. Thus, coordination of Fe³⁺ or Fe²⁺ with allyl carbonate so as to promote allyl C-O bond cleavage or activation of alkenes within the allyl groups is not clear.

Third, since Hu has reported Fe⁺ is likely to mediate the addiction of unactivated tertiary alkyl radical with alkynes by formation of vinyl-Fe after addition of tertiary alkyl radical to alkyne. The formation of tertiary benzyl-Feᴵᴵ intermediate may operate in our work, which may facilitate the allyl C-O bond scission by elimination of a Fe-O product.
**Part 4. Preparation of Allylic Carbonates.**

*General procedure for the preparation of allylic carbonates.* Methyl chloroformate (200 mol%) was added to a solution of allylic alcohol (100 mol %) and pyridine (300 mol %) in DCM (0.4 M) at 0°C. The reaction mixture was warmed to room temperature, and stirred overnight, at which point it was washed with brine and extracted with DCM. The combined organic layer was washed with HCl (1N), dried over MgSO₄. Silica gel was added, and the solvent was removed under reduced pressure. The residue was loaded to a silica column. Flash chromatography provided the desired allylic carbonate.

**Methyl (2-(thiophen-2-yl) allyl) carbonate**

The title compound was prepared according the general procedure using 2-(thiophen-2-yl) prop-2-en-1-ol [⁴] (1.40 g, 10.0 mmol). After purification by a flash column chromatography (SiO₂: 3% ethyl acetate in petroleum ether), the title compound was isolated in 92% yield (1.82 g, 9.2 mmol) as a colorless liquid.

¹H NMR (600 MHz, Chloroform-d): δ 7.21 (d, J = 5.4 Hz, 1H), 7.08 (d, J = 3.6 Hz, 1H), 6.99 (dd, J = 7.2, 3.6 Hz, 1H), 5.60 (s, 1H), 5.30 (s, 1H), 4.99 (s, 2H), 3.81 (s, 3H).

¹³C NMR (150 MHz, Chloroform-d): δ 155.5, 141.42, 135.78, 127.51, 124.86, 124.13, 114.28, 68.84, 54.92.

HRMS (ESI) exact mass calculated for [M+Na⁺] (C₉H₁₀NaO₃S⁺): m/z 221.0243; found: 221.0249.

**2-(Benzo[d] [1,3] dioxol-5-yl) allyl methyl carbonate**

The title compound was prepared according the general procedure using 2-(benzo[d] [1,3] dioxol-5-yl) prop-2-en-1-ol [⁵] (1.78 g, 10.0 mmol). After purification by a flash column chromatography (SiO₂: 3% ethyl acetate in petroleum ether), the title compound was isolated in 91% yield (2.15 g, 9.1 mmol) as a colorless liquid.

¹H NMR (600 MHz, Chloroform-d): δ 6.93 (d, J = 1.8 Hz, 1H), 6.91 (dd, J = 7.8, 1.8 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 5.96 (s, 2H), 5.46 (s, 1H), 5.32 (s, 1H), 4.97 (s, 2H), 3.79 (s, 3H).

¹³C NMR (150 MHz, Chloroform-d): δ 155.56, 147.87, 147.55, 141.49, 131.96, 119.64, 114.83,
108.19, 106.57, 101.13, 69.22, 54.84.

HRMS (ESI) exact mass calculated for [M+H+] (C12H13O5+): m/z 237.0757; found: 237.0764.

Methyl (2-methylenebut-3-en-1-yl) carbonate

The title compound was prepared according the general procedure using 2-methylenebut-3-en-1-ol [6] (0.84 g, 10.0 mmol). After purification by a flash column chromatography (SiO2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 96% yield (1.36 g, 9.6 mmol) as a colorless liquid.

1H NMR (600 MHz, Chloroform-d): δ 6.34 (dd, J = 18.0, 10.8 Hz, 1H), 5.28 (s, 1H), 5.24 (d, J = 18.0 Hz, 1H), 5.21 (s, 1H), 5.12 (d, J = 10.8 Hz, 1H), 4.79 (s, 2H), 3.76 (s, 3H).

13C NMR (150 MHz, Chloroform-d): δ 155.47, 139.98, 135.67, 118.18, 114.63, 66.76, 54.68.

HRMS (ESI) exact mass calculated for [M+Na+] (C7H10NaO3+): m/z 165.0522; found: 165.0517.

Methyl (2-(naphthalen-2-yl) allyl) carbonate

The title compound was prepared according the general procedure using 2-(naphthalen-2-yl) prop-2-en-1-ol [6] (1.84 g, 10.0 mmol). After purification by a flash column chromatography (SiO2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 91% yield (2.20 g, 9.1 mmol) as a colorless liquid.

1H NMR (600 MHz, Chloroform-d): δ 7.87 - 7.82 (m, 4H), 7.61 (d, J = 8.4 Hz, 1H), 7.51 - 7.47 (m, 2H), 5.74 (s, 1H), 5.53 (s, 1H), 5.18 (s, 2H), 3.81 (s, 3H).

13C NMR (150 MHz, Chloroform-d): δ 155.62, 141.82, 134.92, 133.24, 133.02, 128.25, 128.13, 127.51, 126.27, 126.17, 124.86, 124.03, 116.14, 69.07, 54.83.


Methyl (2-(pyren-1-yl) allyl) carbonate

The title compound was prepared according the general procedure using 2-(pyren-1-yl) prop-2-en-1-ol (2.58 g, 10.0 mmol). After purification by a flash column chromatography (SiO2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 86% yield (2.72 g, 8.6 mmol) as a colorless liquid.
**Methyl (2-(3,4,5-trifluorophenyl) allyl) carbonate**

The title compound was prepared according the general procedure using 2-((tert-butoxy carbonyl) oxy) methyl) acrylate. The product was isolated in 88% yield (2.17 g, 8.8 mmol) as a colorless liquid. 

**Methyl 2-((tert-butoxy carbonyl) oxy) methyl) acrylate**

The title compound was prepared according the general procedure using methyl 2-((tert-butoxy carbonyl) oxy) methyl) acrylate. The product was isolated in 60% yield (1.30g, 6.0 mmol) as a colorless liquid.
Methyl (1-phenylallyl) carbonate [8]

The title compound was prepared according the general procedure using 1-phenylprop-2-en-1-ol (1.34 g, 10.0 mmol). After purification by a flash column chromatography (SiO2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 91% yield (1.75 g, 9.1 mmol) as a light-yellow liquid.

\(^1\)H NMR (600 MHz, Chloroform-d): \(\delta 7.37 - 7.33 (m, 4H), 7.31 - 7.28 (m, 1H), 6.08 (d, J = 6.0\) Hz, 1H), 6.05 - 6.00 (m, 1H), 5.34 (d, \(J = 17.4\) Hz, 1H), 5.26 (d, \(J = 10.2\) Hz, 1H), 3.75 (s, 3H).

\(^13\)C NMR (150 MHz, Chloroform-d): \(\delta 154.91, 138.20, 135.69, 128.49, 128.30, 126.95, 117.32, 80.05, 54.65.

HRMS (ESI) exact mass calculated for \([M+Na]^+\) (C\(_{11}\)H\(_{12}\)NaO\(_3\))^+: m/z 215.0679; found: 215.0678.

(Z)-methyl (2-phenylallyl-3-d) carbonate

The title compound was prepared according the general procedure using (Z)-2-phenylprop-2-en-3-d-1-ol-d [9] (1.36 g, 10.0 mmol). After purification by a flash column chromatography (SiO2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 91% yield (1.76 g, 9.1 mmol) as a colorless liquid.

\(^1\)H NMR (600 MHz, Chloroform-d): \(\delta 7.44 (d, J = 7.2\) Hz, 2H), 7.36 (t, \(J = 7.2\) Hz, 2H), 7.31 (t, \(J = 7.2\) Hz, 1H), 5.56 (s, 1H), 5.42 (d, \(J = 0.6\) Hz, 0.13H), 5.05 (s, 2H), 3.80 (s, 3H).

\(^13\)C NMR (150 MHz, Chloroform-d): \(\delta 155.56, 141.90, 137.70, 128.48, 128.09, 125.95, 116.64, 115.48, 115.32, 115.16, 69.00, 54.80.

\(^2\)D NMR (61 MHz, CHCl\(_3\)) \(\delta 5.47.

HRMS (ESI) exact mass calculated for \([M+Na]^+\) (C\(_{11}\)H\(_{12}\)DNaO\(_3\))^+: m/z 216.0741; found: 216.0746.

Part 5. Preparation of Tertiary Alkyl Oxalates.

General procedure for the preparation of tertiary alkyl oxalates. The tertiary alkyl oxalates were prepared according to a literature procedure from the corresponding tertiary alcohols. [10] To a solution of alcohol (10.0 mmol, 100 mol%) in CH\(_2\)Cl\(_2\) (50 mL) was added pyridine (20.0 mmol, 200 mol%), DMAP (1.0 mmol, 10 mol%) at 0 °C. Following this, tert-butyl 2-chloro-2-oxoacetate
(12.0 mmol, 120 mol%) was added dropwise. The reaction mixture was allowed to warm to r.t. and stirred overnight. The reaction mixture was diluted with Et₂O, washed with water, saturated NaHCO₃, and brine. The organic phase was collected, dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by column chromatograph to afford the product as a solid or oil.

**tert-Butyl tert-pentyl oxalate**

The title compound was prepared according the general procedure using 2-methylbutan-2-ol (0.88 g, 10.0 mmol). After purification by a flash column chromatography (SiO₂: 1% ethyl acetate in petroleum ether), the title compound was isolated in 95% yield (2.05 g, 9.5 mmol) as a colorless liquid.

**¹H NMR (600 MHz, Chloroform-d):** δ 1.85 (q, J = 15.0 Hz, 2H), 1.54 (s, 9H), 1.51 (s, 6H), 0.93 (t, J = 15.0 Hz, 3H).

**¹³C NMR (150 MHz, Chloroform-d):** δ 157.80, 157.76, 86.78, 84.16, 33.31, 27.74, 25.13, 8.14.

**HRMS (ESI) exact mass calculated for [M+Na⁺] (C₁₁H₂₀NaO₄⁺):** m/z 239.1254; found: 239.1259.

**tert-Butyl (2-methyl-1-phenylpropan-2-yl) oxalate**

The title compound was prepared according the general procedure using 2-methyl-1-phenylpropan-2-ol (1.50 g, 10.0 mmol). After purification by a flash column chromatography (SiO₂: 2% ethyl acetate in petroleum ether), the title compound was isolated in 88% yield (2.45 g, 8.8 mmol) as a colorless liquid.

**¹H NMR (400 MHz, Chloroform-d):** δ 7.33 - 7.19 (m, 5H), 3.09 (d, J = 10.3 Hz, 2H), 1.56 (s, 6H), 1.53 (s, 6H).

**¹³C NMR (100 MHz, Chloroform-d):** δ 157.65, 157.47, 136.44, 130.68, 127.97, 126.65, 85.85, 84.22, 46.96, 27.72, 25.23.

**HRMS (ESI) exact mass calculated for [M+Na⁺] (C₁₆H₂₂NaO₄⁺):** m/z 301.1410; found: 301.1419.

**tert-Butyl (2-methyl-4-phenylbutan-2-yl) oxalate**
The title compound was prepared according the general procedure using 2-methyl-4-phenylbutan-2-ol (1.64 g, 10.0 mmol). After purification by a flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (2.63 g, 9.0 mmol) as a colorless liquid.

$^1$H NMR (400 MHz, Chloroform-d): $\delta$ 7.31 - 7.25 (m, 2H), 7.20 (dd, $J = 7.2$, 3.9 Hz, 3H), 2.76 - 2.65 (m, 2H), 2.20 - 2.09 (m, 2H), 1.60 (s, 6H), 1.56 (s, 6H).

$^{13}$C NMR (100 MHz, Chloroform-d): $\delta$ 157.67, 157.59, 141.63, 128.39, 128.30, 125.88, 85.89, 84.25, 42.62, 30.15, 27.71, 25.61.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{17}$H$_{24}$NaO$_4^+$): m/z 315.1567; found: 315.1573.

tert-Butyl (2-methyl-4-oxopentan-2-yl) oxalate

The title compound was prepared according the general procedure using 4-hydroxy-4-methylpentan-2-one (1.16 g, 10.0 mmol). After purification by a flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (2.20 g, 9.0 mmol) as a colorless liquid.

$^1$H NMR (400 MHz, Chloroform-d): $\delta$ 2.99 (s, 2H), 2.19 (s, 3H), 1.60 (s, 6H), 1.52 (s, 9H).

$^{13}$C NMR (100 MHz, Chloroform-d): $\delta$ 205.50, 157.44, 157.16, 84.58, 84.15, 52.57, 31.84, 27.67, 25.67.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{12}$H$_{20}$NaO$_5^+$): m/z 267.1203; found: 267.1211.

tert-Butyl (1-methoxy-2-methylpropan-2-yl) oxalate

The title compound was prepared according the general procedure using 1-methoxy-2-methylpropan-2-ol (1.04 g, 10.0 mmol). After purification by a flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (2.09 g, 9.0 mmol) as a colorless liquid.

$^1$H NMR (400 MHz, Chloroform-d): $\delta$ 3.52 (s, 2H), 3.38 (s, 3H), 1.51 (s, 15H).

$^{13}$C NMR (100 MHz, Chloroform-d): $\delta$ 157.48, 157.26, 84.88, 84.25, 77.62, 59.44, 27.63, 22.80.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{11}$H$_{20}$NaO$_5^+$): m/z 255.1203; found: 255.1213.
**tert-Butyl (2-methyltridecan-2-yl) oxalate**

The title compound was prepared according the general procedure using 2-methyltridecan -2-ol (2.14 g, 10.0 mmol). After purification by a flash column chromatography (SiO₂: 1% ethyl acetate in petroleum ether), the title compound was isolated in 93% yield (3.19 g, 9.3 mmol) as a colorless liquid.

\[ ^1H \text{NMR (600 MHz, Chloroform-}d) : \delta 1.80 - 1.77 (m, 2H), 1.53 (s, 9H), 1.50 (s, 6H), 1.34 - 1.31 (m, 2H), 1.27 (d, J = 3.6 Hz, 6H), 1.25 (s, 10H), 0.87 (t, J = 7.2 Hz, 3H). \]

\[ ^{13}C \text{NMR (150 MHz, Chloroform-}d) : \delta 157.77, 157.72, 86.60, 84.06, 40.57, 31.87, 29.77, 29.61, 29.58, 29.55, 29.49, 29.30, 27.71, 25.59, 23.74, 22.64, 14.07. \]

HRMS (ESI) exact mass calculated for [M+Na⁺] (C₂₀H₃₈NaO₄⁺): m/z 365.2662; found: 365.2675.

**tert-Butyl (2-methylnonadecan-2-yl) oxalate**

The title compound was prepared according the general procedure using 2-methylnonadecan-2-ol (2.99 g, 10.0 mmol). After purification by a flash column chromatography (SiO₂: 1% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (3.84 g, 9.0 mmol) as a white solid.

\[ ^1H \text{NMR (600 MHz, Chloroform-}d) : \delta 1.79 - 1.77 (m, 2H), 1.53 (s, 9H), 1.50 (s, 6H), 1.25 (s, 30H), 0.87 - 0.86 (m, 3H). \]

\[ ^{13}C \text{NMR (150 MHz, Chloroform-}d) : \delta 157.77, 157.73, 86.59, 84.04, 40.58, 31.90, 29.79, 29.67, 29.63, 29.56, 29.50, 29.33, 27.71, 25.59, 23.75, 22.66, 14.08. \]

HRMS (ESI) exact mass calculated for [M+Na⁺] (C₂₆H₅₀NaO₄⁺): m/z 449.3601; found: 449.3618.

M.P.: 40.8 - 41.5 °C.

**(Z)- tert-Butyl (2-methylnonadec-10-en-2-yl) oxalate**

The title compound was prepared according the general procedure using (Z)-2-methylnonadec-10-en-2-ol (2.97 g, 10.0 mmol). After purification by a flash column chromatography (SiO₂: 1% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (3.82 g, 9.0 mmol) as a colorless liquid.
$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 5.33 (t, $J = 6.0$ Hz, 2H), 2.00 (q, $J = 6.6$ Hz, 4H), 1.80 - 1.77 (m, 2H), 1.53 (s, 9H), 1.50 (s, 6H), 1.33 - 1.26 (m, 22H), 0.87 (t, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 157.75, 157.71, 129.90, 129.74, 86.55, 84.04, 40.57, 31.86, 29.75, 29.73, 29.70, 29.48, 29.39, 29.28, 29.20, 27.70, 27.17, 27.15, 25.58, 23.74, 22.64, 14.06.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{26}$H$_{48}$NaO$_4$)$^+$: m/z 447.3445; found: 447.3457.

4-(Benzoyloxy)-2-methylbutan-2-yl tert-butyl oxalate

The title compound was prepared according the general procedure using 3-hydroxy-3-methylbutyl benzoate (2.08 g, 10.0 mmol). After purification by a flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether), the title compound was isolated in 97% yield (3.26 g, 9.7 mmol) as a colorless liquid.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 8.02 (d, $J = 7.6$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 2H), 4.46 (t, $J = 6.8$ Hz, 2H), 2.34 (t, $J = 6.8$ Hz, 2H), 1.63 (s, 6H), 1.51 (s, 9H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 166.43, 157.59, 157.32, 132.94, 130.07, 129.52, 128.36, 84.60, 84.40, 60.83, 39.11, 27.67, 26.01.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{18}$H$_{24}$NaO$_6$)$^+$: m/z 359.1465; found: 359.1474.

tert-Butyl (2-methyl-4-((4-(trifluoromethyl) benzoyl) oxy) butan-2-yl) oxalate

The title compound was prepared according the general procedure using 3-hydroxy-3-methylbutyl 4-(trifluoromethyl) benzoate (2.76 g, 10.0 mmol). After purification by a flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether), the title compound was isolated in 92% yield (3.72 g, 9.2 mmol) as a colorless liquid.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 8.13 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 7.8$ Hz, 2H), 4.50 (t, $J = 6.7$ Hz, 2H), 2.35 (t, $J = 6.7$ Hz, 2H), 1.63 (s, 6H), 1.49 (s, 9H).

$^{19}$F NMR (376 MHz, Chloroform-d): $\delta$ -63.04.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{19}$H$_{23}$FNaO$_6$)$^+$: m/z 427.1339; found: 427.1345.
**tert-Butyl (2-methyl-4-((4-methylbenzoyl) oxy) butan-2-yl) oxalate**

The title compound was prepared according the general procedure using 3-hydroxy-3-methylbutyl 4-methylbenzoate (2.22 g, 10.0 mmol). After purification by a flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether), the title compound was isolated in 95% yield (3.33 g, 9.5 mmol) as a colorless liquid.

$^1$H NMR (400 MHz, Chloroform-$d$): δ 7.90 (d, $J$ = 8.2 Hz, 2H), 7.23 (d, $J$ = 8.5 Hz, 2H), 4.44 (t, $J$ = 6.7 Hz, 2H), 2.40 (s, 3H), 2.33 (t, $J$ = 6.7 Hz, 2H), 1.63 (s, 6H), 1.51 (s, 9H).

$^{13}$C NMR (100 MHz, Chloroform-$d$): δ 166.51, 157.57, 157.30, 143.62, 129.54, 129.07, 127.30, 84.67, 84.40, 60.63, 39.08, 27.64, 25.98, 21.60.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{19}$H$_{26}$NaO$_6$): m/z 373.1622; found: 373.1631.

**tert-Butyl (2-methyl-4-((thiophene-2-carbonyl) oxy) butan-2-yl) oxalate**

The title compound was prepared according the general procedure using 3-hydroxy-3-methylbutyl thiophene-2-carboxylate (2.14 g, 10.0 mmol).

After purification by a flash column chromatography (SiO$_2$: 4% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (3.08 g, 9.0 mmol) as a colorless liquid.

$^1$H NMR (600 MHz, Chloroform-$d$): δ 7.78 (s, 1H), 7.54 (s, 1H), 7.08 (s, 1H), 4.43 (t, $J$ = 6.0 Hz, 2H), 2.30 (t, $J$ = 6.0 Hz, 2H), 1.62 (s, 6H), 1.51 (s, 9H).

$^{13}$C NMR (150 MHz, Chloroform-$d$): δ 161.20, 157.55, 157.31, 133.44, 132.41, 127.75, 84.56, 84.40, 60.95, 39.10, 27.67, 25.99.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{16}$H$_{22}$NaO$_6$S): m/z 365.1029; found: 365.1035.

**tert-Butyl (4-((furan-2-carbonyl) oxy)-2-methylbutan-2-yl) oxalate**

The title compound was prepared according the general procedure using 3-hydroxy-3-methylbutyl furan-2-carboxylate (1.98 g, 10.0 mmol).

After purification by a flash column chromatography (SiO$_2$: 4% ethyl acetate in petroleum ether), the title compound was isolated in 95% yield (3.38 g, 9.5 mmol) as a colorless liquid.

$^1$H NMR (600 MHz, Chloroform-$d$): δ 7.81 (s, 1H), 7.52 (s, 1H), 7.09 (s, 1H), 4.43 (t, $J$ = 6.0 Hz, 2H), 2.23 (t, $J$ = 6.0 Hz, 2H), 1.62 (s, 6H), 1.51 (s, 9H).

$^{13}$C NMR (150 MHz, Chloroform-$d$): δ 163.00, 158.65, 158.11, 133.42, 132.41, 127.75, 84.58, 84.40, 60.95, 39.10, 27.67, 25.99.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{18}$H$_{22}$NaO$_6$): m/z 387.1035; found: 387.1043.
acetate in petroleum ether), the title compound was isolated in 90% yield (2.94 g, 9.0 mmol) as a colorless liquid.

\(^1\)H NMR (600 MHz, Chloroform-\(d\)): \(\delta\) 7.56 (s, 1H), 7.15 (s, 1H), 6.49 (s, 1H), 4.43 (t, \(J = 6.0\) Hz, 2H), 2.29 (t, \(J = 6.0\) Hz, 2H), 1.60 (s, 6H), 1.51 (s, 9H).

\(^1\)C NMR (150 MHz, Chloroform-\(d\)): \(\delta\) 158.49, 157.54, 157.29, 146.36, 144.53, 117.94, 111.79, 84.45, 60.72, 39.06, 27.67, 25.95.

HRMS (ESI) exact mass calculated for [M+Na\(^+\)] (C\(_{16}\)H\(_{22}\)NaO\(_7\)+): m/z 349.1258; found: 349.1265.

(R)-\(\text{tert-Butyl (2-(4-methylcyclohex-3-en-1-yl) propan-2-yl) oxalate}\)

The title compound was prepared according the general procedure using (R)-2-(4-methylcyclohex-3-en-1-yl) propan-2-ol (1.54 g, 10.0 mmol).

After purification by a flash column chromatography (SiO\(_2\): 1% ethyl acetate in petroleum ether), the title compound was isolated in 91% yield (2.57 g, 9.1 mmol) as a colorless liquid.

\(^1\)H NMR (600 MHz, Chloroform-\(d\)): \(\delta\) 5.36 (s, 1H), 2.10 - 1.94 (m, 4H), 1.88 - 1.82 (m, 2H), 1.64 (s, 3H), 1.53 (s, 9H), 1.50 (d, \(J = 11.8\) Hz, 6H), 1.36 - 1.29 (m, 1H).

\(^1\)C NMR (150 MHz, Chloroform-\(d\)): \(\delta\) 157.79, 157.73, 133.93, 120.03, 88.99, 84.08, 42.69, 30.73, 27.74, 26.27, 23.75, 23.25, 22.96, 22.75.

HRMS (ESI) exact mass calculated for [M+Na\(^+\)] (C\(_{16}\)H\(_{26}\)NaO\(_4\)+): m/z 305.1723; found: 305.1727.

\(\text{tert-Butyl ((5R)-5-((3R,10S,13R)-3-methoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-methylhexan-2-yl) oxalate}\)

The title compound was prepared according the general procedure using (5R)-5-((3R,10S,13R)-3-methoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-methylhexan-2-ol (4.04 g, 10.0 mmol). After purification by a flash column chromatography (SiO\(_2\): 5% ethyl acetate in petroleum ether), the title compound was isolated in 82% yield (4.37 g, 8.2 mmol) as a white
solid.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 3.34 (s, 3H), 3.17 - 3.12 (m, 1H), 1.93 (d, $J = 12.6$ Hz, 1H), 1.84 - 1.78 (m, 4H), 1.75 - 1.65 (m, 3H), 1.59 - 1.54 (m, 2H), 1.52 (s, 9H), 1.49 (d, $J = 7.8$ Hz, 6H), 1.41 - 1.32 (m, 8H), 1.25 - 1.20 (m, 4H), 1.12 - 1.08 (m, 4H), 1.02 (d, $J = 7.2$ Hz, 2H), 0.89 (d, $J = 8.4$ Hz, 6H), 0.62 (s, 3H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 157.81, 157.75, 86.81, 84.02, 80.37, 56.42, 55.69, 55.50, 42.63, 42.01, 40.29, 40.09, 36.79, 35.81, 35.68, 35.27, 34.85, 32.74, 29.47, 28.14, 27.72, 27.29, 26.74, 26.37, 25.67, 25.53, 24.16, 23.38, 20.75, 18.66, 11.98.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{33}H_{56}NaO_5^+$): m/z 555.4020; found: 555.4009.

M.P.: 91.2 - 91.6 °C.

**tert-Butyl** ((5R)-2-methyl-5-((3R,7R,10S,12S,13R)-3,7,12-trimethoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl) hexan-2-yl) oxalate

The title compound was prepared according the general procedure using (5R)-2-methyl 5-((3R,7R,10S,12S,13R)-3,7,12-trimethoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl) hexan-2-ol (4.65 g, 10.0 mmol).

After purification by a flash column chromatography (SiO$_2$: 5% ethyl acetate in petroleum ether), the title compound was isolated in 69% yield (4.09 g, 6.9 mmol) as a white foam solid.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 3.35 (s, 1H), 3.32 (s, 3H), 3.25 (s, 3H), 3.20 (s, 3H), 3.13 (d, $J = 2.4$ Hz, 1H), 3.01 - 2.96 (m, 1H), 2.19 (q, $J = 12.0$ Hz, 1H), 2.11 - 2.03 (m, 2H), 1.94 (q, $J = 9.6$ Hz, 1H), 1.84 - 1.79 (m, 4H), 1.78 - 1.71 (m, 3H), 1.67 (d, $J = 13.2$ Hz, 1H), 1.63 - 1.57 (m, 2H), 1.53 (s, 9H), 1.49 (d, $J = 10.8$ Hz, 6H), 1.46 - 1.25 (m, 5H), 1.20 - 1.14 (m, 3H), 1.04 - 0.99 (m, 1H), 0.91 (d, $J = 6.6$ Hz, 3H), 0.89 (s, 3H), 0.64 (s, 3H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 157.86, 157.79, 86.91, 84.02, 81.96, 80.73, 55.82, 55.66, 55.37, 46.11, 46.02, 42.64, 41.96, 39.63, 36.74, 35.43, 35.26, 34.90, 34.43, 29.47, 27.98, 27.75, 27.35, 26.71, 25.76, 25.52, 23.12, 22.84, 21.93, 17.80, 12.43.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{35}H_{60}NaO_7^+$): m/z 615.4231; found: 615.4216.
1-(1-(tert-Butoxy carbonyl)-1H-indol-3-yl)-2-methylpropan-2-yl tert-butyl oxalate

The title compound was prepared according the general procedure using tert-butyl 3-(2-hydroxy-2-methylpropyl)-1H-indole-1-carboxylate (2.89 g, 10.0 mmol). After purification by a flash column chromatography (SiO₂: 5% ethyl acetate in petroleum ether), the title compound was isolated in 88% yield (3.67 g, 8.8 mmol) as a colorless semi-solid.

\[ ^1H \text{NMR (600 MHz, Chloroform-d): } \delta 8.13 \text{ (bs, 1H), 7.59 (d, } J = 7.8 \text{ Hz, 1H), 7.54 (s, 1H), 7.30 (t, } J = 7.6 \text{ Hz, 1H), 7.24 (t, } J = 7.6 \text{ Hz, 1H), 3.19 (s, 2H), 1.68 (s, 9H), 1.61 (s, 6H), 1.55 (s, 9H). \]

\[ ^{13}C \text{NMR (150 MHz, Chloroform-d): } \delta 157.84, 157.55, 149.66, 131.30, 125.15, 124.11, 122.39, 119.43, 115.34, 115.06, 85.98, 84.25, 83.48, 36.00, 28.15, 27.68, 25.49. \]

HRMS (ESI) exact mass calculated for [M+Na⁺] (C_{23}H_{31}NNaO_6⁺): m/z 440.2044; found: 440.2042.

tert-Butyl (3-methyloctan-3-yl) oxalate

The title compound was prepared according the general procedure using 3-methyloctan-3-ol (1.44 g, 10.0 mmol). After purification by a flash column chromatography (SiO₂: 1% ethyl acetate in petroleum ether), the title compound was isolated in 96% yield (2.59 g, 9.6 mmol) as a colorless liquid.

\[ ^1H \text{NMR (600 MHz, Chloroform-d): } \delta 1.90 - 1.72 \text{ (m, 4H), 1.51 (s, 9H), 1.49 (d, } J = 3.6 \text{ Hz, 9H), 1.43 (d, } J = 3.6 \text{ Hz, 3H), 1.26 - 1.24 \text{ (m, 6H), 0.85 - 0.84 \text{ (m, 6H).} \]

\[ ^{13}C \text{NMR (150 MHz, Chloroform-d): } \delta 157.75, 157.63, 89.22, 83.87, 37.37, 31.90, 30.56, 27.62, 23.03, 22.85, 22.39, 13.84, 7.79. \]

HRMS (ESI) exact mass calculated for [M+Na⁺] (C_{15}H_{28}NaO_4⁺): m/z 295.1880; found: 295.1884.

tert-Butyl (3,7-dimethyloctan-3-yl) oxalate

The title compound was prepared according the general procedure using 3,7-dimethyloctan-3-ol (1.58 g, 10.0 mmol). After purification by a flash column chromatography (SiO₂: 1% ethyl acetate in petroleum ether), the title compound was isolated in 94% yield (2.69 g, 9.4 mmol) as a colorless liquid.

\[ ^1H \text{NMR (400 MHz, Chloroform-d): } \delta 2.00 - 1.67 \text{ (m, 4H), 1.51 (m, 10H), 1.45 (s, 3H), 1.35 -} \]


1.22 (m, 2H), 1.19 - 1.10 (m, 2H), 0.90 - 0.81 (m, 9H).

$^{13}$C NMR (100 MHz, Chloroform-d): δ 157.60, 89.91, 84.10, 32.76, 27.72, 26.05, 26.00, 23.83, 22.27, 21.85, 19.27.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{16}$H$_{30}$NaO$_4$): m/z 309.2036; found: 309.2046.

tert-Butyl (3-ethylpentan-3-yl) oxalate

The title compound was prepared according the general procedure using 3-ethylpentan-3-ol (1.16 g, 10.0 mmol). After purification by a flash column chromatography (SiO$_2$: 1% ethyl acetate in petroleum ether), the title compound was isolated in 95% yield (2.32 g, 9.5 mmol) as a colorless liquid.

$^1$H NMR (600 MHz, Chloroform-d): δ 1.88 (q, $J = 7.5$ Hz, 6H), 1.51 (s, 9H), 0.84 (t, $J = 7.5$ Hz, 9H).

$^{13}$C NMR (150 MHz, Chloroform-d): δ 157.90, 157.65, 92.47, 83.97, 27.72, 26.66, 7.51.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{13}$H$_{24}$NaO$_4$): m/z 267.1567; found: 267.1574.

tert-Butyl (1-methylcyclopentyl) oxalate

The title compound was prepared according the general procedure using 1-methylcyclopentan-1-ol (1.00 g, 10.0 mmol). After purification by a flash column chromatography (SiO$_2$: 1% ethyl acetate in petroleum ether), the title compound was isolated in 93% yield (2.12 g, 9.3 mmol) as a colorless liquid.

$^1$H NMR (400 MHz, Chloroform-d): δ 2.24 - 2.12 (m, 2H), 1.78 - 1.70 (m, 4H), 1.67 - 1.61 (m, 2H), 1.60 (s, 3H), 1.53 (s, 9H).

$^{13}$C NMR (100 MHz, Chloroform-d): δ 158.00, 157.65, 92.47, 83.97, 27.72, 26.66, 7.51.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{12}$H$_{20}$NaO$_4$): m/z 251.1254; found: 251.1256.

tert-Butyl (1-methylcyclohexyl) oxalate

The title compound was prepared according the general procedure using 1-methylcyclohexan-1-ol (1.14 g, 10.0 mmol). After purification by a flash column chromatography (SiO$_2$: 1% ethyl acetate in petroleum ether), the title compound was
isolated in 90% yield (2.18 g, 9.0 mmol) as a colorless liquid.

\(^1\)H NMR (400 MHz, Chloroform-d): \(\delta 2.20 (dt, J = 15.3, 3.5\) Hz, 2H), 1.62 - 1.56 (m, 2H), 1.54 (s, 13H), 1.51 (m, 3H), 1.47 (m, 1H), 1.29 (m, 1H).

\(^13\)C NMR (100 MHz, Chloroform-d): \(\delta 157.80, 157.67, 85.88, 84.11, 36.27, 27.74, 25.17, 21.92.\)

HRMS (ESI) exact mass calculated for [M+Na\(^{+}\)] (C\(_{13}\)H\(_{22}\)NaO\(_4\)\(^{+}\)): m/z 265.1410; found: 265.1415.

**tert-Butyl (4-methyltetrahydro-2H-thiopyran-4-yl) oxalate**

The title compound was prepared according the general procedure using 4-methyltetrahydro-2H-thiopyran-4-ol (1.32 g, 10.0 mmol). After purification by a flash column chromatography (SiO\(_2\): 5% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (2.34 g, 9.0 mmol) as a white solid.

\(^1\)H NMR (600 MHz, Chloroform-d): \(\delta 2.89 (t, J = 12.0\) Hz, 2H), 2.58 (d, \(J = 14.4\) Hz, 2H), 2.44 (d, \(J = 14.4\) Hz, 2H), 1.78 - 1.73 (m, 2H), 1.56(s, 3H), 1.55 (s, 9H).

\(^13\)C NMR (150 MHz, Chloroform-d): \(\delta 157.37, 157.29, 84.54, 83.52, 37.15, 27.75, 25.96, 23.88.\)

HRMS (ESI) exact mass calculated for [M+Na\(^{+}\)] (C\(_{12}\)H\(_{20}\)NaO\(_5\)\(^{+}\)): m/z 283.0975; found: 283.0986.

M.P.: 72.3 - 73.4 °C.

**tert-Butyl (4-methyltetrahydro-2H-pyran-4-yl) oxalate**

The title compound was prepared according the general procedure using 4-methyltetrahydro-2H-pyran-4-ol (1.16 g, 10.0 mmol). After purification by a flash column chromatography (SiO\(_2\): 5% ethyl acetate in petroleum ether), the title compound was isolated in 87% yield (2.13 g, 8.7 mmol) as a colorless liquid.

\(^1\)H NMR (600 MHz, Chloroform-d): \(\delta 3.74 - 3.67 (m, 4H), 2.19 - 2.18 (m, 2H), 1.77 - 1.75 (m, 2H), 1.62(s, 3H), 1.56 (s, 9H).

\(^13\)C NMR (150 MHz, Chloroform-d): \(\delta 157.58, 157.36, 84.51, 84.44, 82.38, 63.55, 36.43, 27.71, 24.82.

HRMS (ESI) exact mass calculated for [M+Na\(^{+}\)] (C\(_{12}\)H\(_{20}\)NaO\(_5\)\(^{+}\)): m/z 267.1203; found: 267.1211.

**1-((Benzoyloxy)methyl) cyclohexyl tert-butyl oxalate**

The title compound was prepared according the general procedure using (1-hydroxycyclohexyl) methyl benzoate (2.34 g, 10.0 mmol). After purification
by a flash column chromatography (SiO$_2$: 3% ethyl acetate in petroleum ether), the title compound was isolated in 73% yield (2.65 g, 7.3 mmol) as a colorless liquid.

$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 8.04 (d, $J = 8.2$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.4$ Hz, 2H), 4.70 (s, 2H), 2.42 - 2.29 (m, 2H), 1.62 - 1.58 (m, 6H), 1.55 (d, $J = 1.2$ Hz, 2H), 1.54 (s, 9H).

$^{13}$C NMR (150 MHz, Chloroform-$d$): $\delta$ 165.99, 157.61, 133.08, 129.68, 128.35, 85.26, 84.39, 66.32, 31.73, 27.72, 25.15, 21.19.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{20}$H$_{26}$NaO$_6$): m/z 385.1622; found: 385.1631.

*tert-Butyl (1-methylcyclopentyl) oxalate*

The title compound was prepared according the general procedure using 1-methylcycloheptan-1-ol (1.28 g, 10.0 mmol). After purification by a flash column chromatography (SiO$_2$: 1% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (2.31 g, 9.0 mmol) as a colorless liquid.

$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 2.21 (dd, $J = 14.8, 8.5$ Hz, 2H), 1.83 - 1.78 (m, 2H), 1.62 - 1.60 (m, 5H), 1.57 (s, 3H), 1.54 (s, 9H), 1.51 - 1.49 (m, 1H), 1.45 - 1.42 (m, 2H).

$^{13}$C NMR (150 MHz, Chloroform-$d$): $\delta$ 157.93, 157.86, 90.30, 84.08, 39.89, 39.86, 29.28, 29.20, 27.75, 26.56, 22.54.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{14}$H$_{24}$NaO$_4$): m/z 279.1567; found: 279.1575.

*tert-Butyl (1-methylcyclooctadecyl) oxalate*

The title compound was prepared according the general procedure using 1-methylcyclododecan-1-ol (1.98 g, 10.0 mmol). After purification by a flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether), the title compound was isolated in 97% yield (3.17 g, 9.7 mmol) as a colorless liquid.

$^1$H NMR (400 MHz, Chloroform-$d$): $\delta$ 2.07 - 1.95 (m, 2H), 1.66 (ddt, $J = 13.7, 11.7, 4.5$ Hz, 2H), 1.53 (d, $J = 2.1$ Hz, 12H), 1.34 (s, 18H).

$^{13}$C NMR (100 MHz, Chloroform-$d$): $\delta$ 157.60, 89.91, 84.10, 32.76, 27.72, 26.05, 26.00, 23.83, 22.27, 21.85, 19.27.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{19}$H$_{34}$NaO$_4$): m/z 349.2349; found: 349.2355.
**tert-Butyl (1-methylocyclopentadecyl) oxalate**

The title compound was prepared according the general procedure using 1-methylocyclopentadecan-1-ol (2.40 g, 10.0 mmol). After purification by a flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether), the title compound was isolated in 78% yield (2.87 g, 7.8 mmol) as a colorless liquid.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 1.98 - 1.93 (m, 2H), 1.74 - 1.69 (m, 2H), 1.55 (s, 3H), 1.54 (s, 9H), 1.37 - 1.34 (m, 12H), 1.31 (m, 12H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 157.86, 157.68, 89.68, 84.10, 36.59, 27.77, 27.47, 26.94, 26.68, 26.65, 26.29, 24.23, 23.46, 21.77.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{22}$H$_{40}$NaO$_4$): m/z 391.2819; found: 391.2823.

**tert-Butyl ((1r,3r,5r,7r)-2-methyladamantan-2-yl) oxalate**

The title compound was prepared according the general procedure using (1r,3r,5r,7r)-2-methyladamantan-2-ol (1.66 g, 10.0 mmol).

After purification by a flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether), the title compound was isolated in 88% yield (2.59 g, 8.8 mmol) as a colorless liquid.

$^1$H NMR (400 MHz, Chloroform-d): $\delta$ 2.34 (s, 2H), 2.06 (d, $J = 12.7$ Hz, 2H), 1.91 - 1.70 (m, 8H), 1.67 (s, 3H), 1.58 (d, $J = 12.2$ Hz, 2H), 1.53 (s, 9H).

$^{13}$C NMR (100 MHz, Chloroform-d): $\delta$ 157.36, 90.96, 84.04, 37.96, 35.96, 34.46, 32.83, 27.73, 27.17, 26.49, 21.93.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{17}$H$_{26}$NaO$_4$): m/z 317.1723; found: 317.1725.

**tert-Butyl ((3R,3aR,7R)-3,6,8,8-tetramethyloctahydro-1H-3a,7-methanoazulen-6-yl) oxalate**

The title compound was prepared according the general procedure using (3R,3aR,7R)-3,6,8,8-tetramethyloctahydro-1H-3a,7-methanoazulen-6-ol (2.22 g, 10.0 mmol).

After purification by a flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether), the title compound was isolated in 93% yield (3.26 g, 9.3 mmol) as a white solid.

$^1$H NMR (400 MHz, Chloroform-d): $\delta$ 2.38 (d, $J = 5.2$ Hz, 1H), 2.17 (dd, $J = 13.6$, 5.7 Hz, 1H),
2.04 (ddd, \( J = 14.2, 12.5, 6.8, 1.1 \) Hz, 1H), 1.93 - 1.77 (m, 2H), 1.67 (ddt, \( J = 9.0, 6.7, 3.5 \) Hz, 2H), 1.60 (s, 3H), 1.52 (s, 9H), 1.49 - 1.22 (m, 7H), 1.18 (s, 3H), 0.98 (s, 3H), 0.90 - 0.85 (m, 1H), 0.83 (d, \( J = 7.1 \) Hz, 3H).

\( ^{13} \)C NMR (100 MHz, Chloroform-d): \( \delta 157.61, 90.33, 83.98, 56.98, 56.65, 53.86, 43.47, 41.21, 41.00, 36.90, 32.73, 31.25, 28.37, 27.72, 26.97, 25.30, 25.24, 15.47. \)

HRMS (ESI) exact mass calculated for [M+Na\(^+\)] (C\(_{21}\)H\(_{34}\)NaO\(_4\)+): m/z 373.2349; found: 373.2361.

M.P.: 47.2 - 48.3 °C.

8-Benzyl 1-methyl 3a-(2-(tert-butoxy)-2-oxoacetoxy)-2,3,3a,8a-tetrahydropyrrolo[2,3-b] indole-1,8-dicarboxylate

The title compound was prepared according the general procedure using 8-benzyl 1-methyl 3a-hydroxy-2,3,3a,8a-tetrahydropyrrolo[2,3-b] indole-1,8-dicarboxylate \([12]\) (3.68 g, 10.0 mmol). After purification by a flash column chromatography (SiO\(_2\): 10% ethyl acetate in petroleum ether), the title compound was isolated in 79% yield (3.92 g, 7.9 mmol) as a white solid.

\( ^{1} \)H NMR (600 MHz, Chloroform-d): \( \delta 7.79 \) (bs, 1H), 7.53 (d, \( J = 7.8 \) Hz, 1H), 7.44 (d, \( J = 7.8 \) Hz, 2H), 7.38 (t, \( J = 7.2 \) Hz, 3H), 7.35 - 7.32 (m, 1H), 7.01 (t, \( J = 7.2 \) Hz, 1H), 6.53 (s, 1H), 5.30 (s, 2H), 4.03 (t, \( J = 8.0 \) Hz, 1H), 3.52 (bs, 3H), 2.91 (td, \( J = 12.0, 5.4 \) Hz, 1H), 2.75 (dd, \( J = 12.0, 5.4 \) Hz, 1H), 2.53 (dt, \( J = 12.0, 8.4 \) Hz, 1H), 1.52 (s, 9H).

\( ^{13} \)C NMR (150 MHz, Chloroform-d): \( \delta 156.90, 156.08, 153.08, 144.07, 135.88, 131.42, 128.52, 128.38, 128.24, 127.02, 125.14, 124.03, 116.52, 85.38, 79.78, 67.87, 52.69, 45.08, 27.64. \)

HRMS (ESI) exact mass calculated for [M+H\(^+\)] (C\(_{26}\)H\(_{29}\)N\(_2\)O\(_8\)+): m/z 497.1918; found: 497.1923.

M.P.: 74.3 - 75.1 °C

1,8-Di-tert-butyl 2-methyl 3a-(2-(tert-butoxy)-2-oxoacetoxy)-2,3,3a,8a-tetrahydropyrr[2,3-b] indole-1,2,8-tricarboxylate

The title compound was prepared according the general procedure using 1,8-di-tert-butyl 2-methyl 3a-hydroxy-2,3,3a,8a-tetrahydro pyrrolo[2,3-b] indole-1,2,8-tricarboxylate \([13]\) (4.34 g, 10.0 mmol). After purification by a flash column chromatography (SiO\(_2\): 10% ethyl acetate in petroleum ether), the title compound was isolated in 80% yield (4.50 g, 8.0 mmol) as a white solid.
\[ 1^H\text{NMR} \ (600\text{ MHz, Chloroform-}d): \delta 7.61 \ (d, J = 6.6\text{ Hz, 1H}), 7.38 \ (t, J = 7.2\text{ Hz, 1H}), 7.10 \ (t, J = 7.2\text{ Hz, 1H}), 6.40 \ (s, 1H), 3.97 \ (dd, J = 9.0, 7.2\text{ Hz, 1H}), 3.74 \ (s, 3H), 3.34 \ (bs, 1H), 2.58 \ (t, J = 11.4\text{ Hz, 1H}), 1.58 \ (s, 9H), 1.49 \ (s, 9H), 1.41 \ (bs, 9H). \]

\[ 1^C\text{NMR} \ (150\text{ MHz, Chloroform-}d): \delta 171.84, 156.59, 155.94, 152.21, 144.44, 131.45, 126.09, 123.89, 89.41, 85.19, 82.07, 79.94, 58.90, 52.33, 36.64, 28.23, 27.61. \]

HRMS (ESI) exact mass calculated for [M+H\(^{+}\)] (C\(_{28}\)H\(_{39}\)N\(_2\)O\(_{10}\)+): m/z 563.2599; found: 563.2597.

**M.P.:** 125.3 - 126.2 °C.

![Chemical structure](image)

**tert-Butyl (2-methyl-1-((3-methylbut-2-en-1-yl) oxy) propan-2-yl) oxalate**

The title compound was prepared according the general procedure using 2-methyl-1-((3-methylbut-2-en-1-yl) oxy) propan-2-ol (1.58 g, 10.0 mmol). After purification by a flash column chromatography (SiO\(_2\): 1% ethyl acetate in petroleum ether), the title compound was isolated in 94% yield (2.69 g, 9.4 mmol) as a colorless liquid.

\[ 1^H\text{NMR} \ (400\text{ MHz, Chloroform-}d): \delta 5.33 \ (t, J = 6.8\text{ Hz, 1H}), 4.03 \ (d, J = 6.9\text{ Hz, 2H}), 3.57 \ (s, 2H), 1.74 \ (s, 3H), 1.66 \ (s, 3H), 1.53 \ (s, 15H). \]

\[ 1^C\text{NMR} \ (100\text{ MHz, Chloroform-}d): \delta 157.59, 157.39, 137.24, 120.96, 85.26, 84.29, 74.91, 67.98, 27.70, 25.78, 22.95, 18.04. \]

HRMS (ESI) exact mass calculated for [M+Na\(^{+}\)] (C\(_{15}\)H\(_{26}\)NaO\(_5\)+): m/z 309.1672; found: 309.1672.

![Chemical structure](image)

**1-(Allyloxy)-2-methylpropan-2-yl tert-butyl oxalate**

The title compound was prepared according the general procedure using 1-(allyloxy)-2-methylpropan-2-ol (1.30 g, 10.0 mmol). After purification by a flash column chromatography (SiO\(_2\): 1% ethyl acetate in petroleum ether), the title compound was isolated in 89% yield (2.30 g, 8.9 mmol) as a colorless liquid.

\[ 1^H\text{NMR} \ (400\text{ MHz, Chloroform-}d): \delta 2.00 - 1.67 \ (m, 4H), 1.51 \ (m, 10H), 1.45 \ (s, 3H), 1.35 - 1.22 \ (m, 2H), 1.19 - 1.10 \ (m, 2H), 0.90 - 0.81 \ (m, 9H). \]

\[ 1^C\text{NMR} \ (100\text{ MHz, Chloroform-}d): \delta 157.60, 89.91, 84.10, 32.76, 27.72, 26.05, 26.00, 23.83, 22.27, 21.85, 19.27. \]

HRMS (ESI) exact mass calculated for [M+Na\(^{+}\)] (C\(_{13}\)H\(_{22}\)NaO\(_5\)+): m/z 281.1359; found: 281.1367.
The title compound was prepared according the general procedure using (E)-1-(but-2-en-1-yloxy)-2-methylpropan-2-ol (1.44 g, 10.0 mmol). After purification by a flash column chromatography (SiO$_2$: 1% ethyl acetate in petroleum ether), the title compound was isolated in 78% yield (2.12 g, 7.8 mmol) as a colorless liquid.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 5.72 - 5.67 (m, 1H), 5.57 - 5.52 (m, 1H), 3.96 (d, $J = 6.2$ Hz, 2H), 3.56 (s, 2H), 1.70 (d, $J = 6.5$ Hz, 3H), 1.52 (d, $J = 1.6$ Hz, 15H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 157.57, 157.39, 129.44, 127.45, 85.16, 84.24, 74.80, 72.24, 27.70, 22.95, 17.71.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{14}$H$_{32}$NaO$_5$$^+$): m/z 295.1516; found: 295.1524.

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**Part 6. Allylation of Tertiary Alkyl Oxalates with Allylic Electrophiles.**

*Method A*: To a flame-dried Schlenk tube equipped with a stir bar was loaded zinc power (29.4 mg, 0.45 mmol, 300 mol %), followed by addition of MgCl$_2$ (42.9 mg, 0.45 mmol, 300 mol %), dtbbipy L$_{1a}$ (7.9 mg, 0.03 mmol, 20 mol %) and Fe (acac)$_3$ (5.3 mg, 0.015 mmol, 10 mol%). The tube was evacuated and refilled nitrogen (N$_2$) three time. DMA (1.0 mL) was added via a syringe, followed by addition of tertiary alkyl oxalate (0.15 mmol, 100 mol %), and allylic carbonate (0.3 mmol, 200 mol %). After the reaction mixture was allowed to stir for 12 hours under a N$_2$ atmosphere at 45°C. The reaction was loaded onto a silica column. Flash column chromatography provided the product as an oil or a solid.

*(4,4-Dimethylpent-1-en-2-yl) benzene (3a).*

According to method A, flash column chromatography (SiO$_2$: 1% ethyl acetate in petroleum ether) provided this compound in 84% yield (21.9 mg, 0.126 mmol) as colorless oil.
\(^1\)H NMR (500 MHz, Chloroform-d): \(\delta \) 7.42 (d, \(J = 7.0\) Hz, 2H), 7.34 (t, \(J = 7.0\) Hz, 2H), 7.27 (t, \(J = 7.0\) Hz, 1H), 5.29 (d, \(J = 2.0\) Hz, 1H), 5.06 (d, \(J = 2.0\) Hz, 1H), 2.51 (s, 2H), 0.85 (s, 9H).

\(^1\)C NMR (125 MHz, Chloroform-d): \(\delta\) 147.58, 143.70, 128.08, 126.91, 126.53, 116.27, 48.91, 31.72, 30.06.

HRMS (ESI) exact mass calculated for \([\text{M+Na}^+\] (C\(_{13}\)H\(_{18}\)Na\(^+\)): m/z 197.1301; found: 197.1309.

(4,4-Dimethylhex-1-en-2-yl) benzene (4)

According to method A, flash column chromatography (SiO\(_2\): 1% ethyl acetate in petroleum ether) provided this compound in 71% yield (20.1 mg, 0.107 mmol) as colorless oil.

\(^1\)H NMR (600 MHz, Chloroform-d): \(\delta\) 7.37 (d, \(J = 6.9\) Hz, 2H), 7.29 (t, \(J = 7.6\) Hz, 2H), 7.23 (t, \(J = 7.3\) Hz, 1H), 5.23 (d, \(J = 2.1\) Hz, 1H), 5.02 (dd, \(J = 2.0, 1.0\) Hz, 1H), 2.46 (s, 2H), 1.18 (q, \(J = 7.5\) Hz, 2H), 0.78 (t, \(J = 7.5\) Hz, 3H), 0.72 (s, 6H).

\(^1\)C NMR (150 MHz, Chloroform-d): \(\delta\) 147.54, 143.99, 128.04, 126.86, 126.55, 116.45, 46.70, 34.86, 34.25, 26.91, 8.45.

HRMS (ESI) exact mass calculated for \([\text{M+Na}^+\] (C\(_{14}\)H\(_{20}\)Na\(^+\)): m/z 211.1457; found: 211.1455.

(2,2-dimethylpent-4-ene-1,4-diyl) dibenzene (5a)

According to method A, flash column chromatography (SiO\(_2\): 1% ethyl acetate in petroleum ether) provided this compound in 85% yield (31.9 mg, 0.128 mmol) as colorless oil.

\(^1\)H NMR (600 MHz, Chloroform-d): \(\delta\) 7.44 (d, \(J = 7.2\) Hz, 2H), 7.36 (t, \(J = 7.5\) Hz, 2H), 7.34 - 7.29 (m, 3H), 7.26 (t, \(J = 7.3\) Hz, 1H), 7.16 (d, \(J = 6.8\) Hz, 2H), 5.36 (d, \(J = 2.0\) Hz, 1H), 5.13 - 5.10 (m, 1H), 2.63 (s, 2H), 2.56 (s, 2H), 0.80 (s, 6H).

\(^1\)C NMR (150 MHz, Chloroform-d): \(\delta\) 147.10, 143.75, 139.16, 130.67, 128.15, 127.57, 126.98, 126.50, 125.75, 116.92, 49.63, 48.01, 35.43, 26.84.

HRMS (ESI) exact mass calculated for \([\text{M+Na}^+\] (C\(_{19}\)H\(_{22}\)Na\(^+\)): m/z 273.1614; found: 273.1619.

(3,3-Dimethylhex-5-ene-1,5-diyl) dibenzene (6)

According to method A, flash column chromatography (SiO\(_2\): 1% ethyl acetate
in petroleum ether) provided this compound in 56% yield (22.2 mg, 0.084 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 7.43 (d, $J = 7.0$ Hz, 2H), 7.35 (t, $J = 7.5$ Hz, 2H), 7.31 - 7.25 (m, 3H), 7.18 (t, $J = 7.4$ Hz, 1H), 7.05 (d, $J = 7.0$ Hz, 2H), 5.29 (d, $J = 2.0$ Hz, 1H), 5.14 - 5.08 (m, 1H), 2.59 (s, 2H), 2.58 - 2.53 (m, 2H), 1.52 - 1.47 (m, 2H), 0.88 (s, 6H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 147.32, 143.93, 143.32, 128.25, 128.21, 128.17, 126.98, 126.63, 125.45, 116.86, 46.67, 44.62, 34.40, 30.74, 27.74.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{20}$H$_{24}$Na$^+$): m/z 287.1770; found: 287.1777.

4,4-Dimethyl-6-phenylhept-6-en-2-one (7)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 80% yield (26.0 mg, 0.12 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 7.34 (d, $J = 6.9$ Hz, 2H), 7.29 (t, $J = 7.5$ Hz, 2H), 7.23 (t, $J = 7.2$ Hz, 1H), 5.24 (d, $J = 2.1$ Hz, 1H), 5.05 - 5.00 (m, 1H), 2.66 (s, 2H), 2.20 (s, 2H), 1.87 (s, 3H), 0.91 (s, 6H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 208.67, 147.09, 143.41, 128.25, 127.12, 126.64, 117.23, 53.36, 46.14, 34.14, 31.83, 28.22.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{15}$H$_{20}$NaO$^+$): m/z 239.1406; found: 239.1411.

(5-Methoxy-4,4-dimethylpent-1-en-2-yl) benzene (8)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 56% yield (17.2 mg, 0.084 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 7.39 (d, $J = 6.9$ Hz, 2H), 7.29 (t, $J = 7.5$ Hz, 2H), 7.23 (t, $J = 7.3$ Hz, 1H), 5.26 (d, $J = 2.1$ Hz, 1H), 5.06 - 5.02 (m, 1H), 3.10 (s, 3H), 2.87 (s, 2H), 2.54 (d, $J = 0.9$ Hz, 2H), 0.79 (s, 6H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 146.97, 143.43, 128.01, 126.95, 126.53, 116.64, 80.99, 58.69, 43.65, 35.56, 25.28.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{14}$H$_{20}$NaO$^+$): m/z 227.1406; found: 227.1411.
(4,4-Dimethylpentadec-1-en-2-yl) benzene (9)

According to method A, flash column chromatography (SiO₂: 1% ethyl acetate in petroleum ether) provided this compound in 67% yield (31.6 mg, 0.1005 mmol) as colorless oil.

¹H NMR (600 MHz, Chloroform-d): δ 7.37 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 5.23 (d, J = 2.1 Hz, 1H), 5.02 (d, J = 2.1 Hz, 1H), 2.47 (s, 2H), 1.28 (d, J = 5.5 Hz, 14H), 1.14 - 1.08 (m, 4H), 0.90 (t, J = 7.0 Hz, 5H), 0.74 (s, 6H).

¹³C NMR (150 MHz, Chloroform-d): δ 128.03, 126.84, 126.57, 116.44, 46.87, 46.13, 42.61, 34.19, 32.41, 31.94, 31.93, 30.48, 29.75, 29.70, 29.66, 29.63, 29.61, 29.56, 29.38, 29.36, 27.64, 25.14, 24.10, 22.71, 14.12.

HRMS (ESI) exact mass calculated for [M+Na⁺] (C₂₃H₄₈Na⁺): m/z 337.2866; found: 337.2871.

(4,4-Dimethylenicos-1-en-2-yl) benzene (10)

According to method A, flash column chromatography (SiO₂: 1% ethyl acetate in petroleum ether) provided this compound in 56% yield (33.5 mg, 0.084 mmol) as colorless oil.

¹H NMR (600 MHz, Chloroform-d): δ 7.37 (d, J = 7.1 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 5.23 (d, J = 2.1 Hz, 1H), 5.02 (d, J = 2.0 Hz, 1H), 2.47 (s, 2H), 1.28 (s, 30H), 0.90 (t, J = 6.9 Hz, 5H), 0.74 (s, 6H).

¹³C NMR (150 MHz, Chloroform-d): δ 147.61, 128.03, 126.85, 126.57, 116.44, 46.87, 46.13, 42.62, 34.19, 32.41, 31.94, 30.48, 29.73, 29.70, 29.68, 29.38, 27.64, 25.14, 24.11, 22.71, 14.12.

HRMS (ESI) exact mass calculated for [M+Na⁺] (C₂₉H₅₀Na⁺): m/z 421.3805; found: 421.3808.

(Z)-(4,4-Dimethylenicosa-1,12-dien-2-yl) benzene (11)

According to method A, flash column chromatography (SiO₂: 1% ethyl acetate in petroleum ether) provided this compound in 61% yield (36.3 mg, 0.0915 mmol) as colorless oil.
$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 7.37 (d, $J = 6.8$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.23 (t, $J = 7.3$ Hz, 1H), 5.38 - 5.36 (m, 2H), 5.23 (d, $J = 2.1$ Hz, 1H), 5.02 (d, $J = 2.0$ Hz, 1H), 2.47 (s, 2H), 2.03 (t, $J = 6.7$ Hz, 4H), 1.33 - 1.29 (m, 18H), 1.11 (dt, $J = 11.5$, 3.7 Hz, 4H), 0.90 (t, $J = 6.9$ Hz, 5H), 0.74 (s, 6H).

$^{13}$C NMR (150 MHz, Chloroform-$d$): $\delta$ 129.89, 128.03, 126.85, 126.57, 116.44, 46.87, 46.12, 42.60, 34.18, 32.40, 31.92, 30.44, 29.78, 29.57, 29.54, 29.44, 29.34, 29.23, 27.64, 27.23, 27.21, 24.09, 22.69, 14.11.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{29}$H$_{48}$Na$^+$): m/z 419.3648; found: 419.3654.

3,3-Dimethyl-5-phenylhex-5-en-1-yl benzoate (12a)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 78% yield (36.1 mg, 0.117 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 8.08 (d, $J = 7.1$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.49 - 7.39 (m, 4H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.27 (t, $J = 7.3$ Hz, 1H), 5.33 (d, $J = 2.0$ Hz, 1H), 5.12 (d, $J = 1.9$ Hz, 1H), 4.39 (t, $J = 7.3$ Hz, 2H), 2.61 (s, 2H), 1.73 (t, $J = 7.3$ Hz, 2H), 0.91 (s, 6H).

$^{13}$C NMR (150 MHz, Chloroform-$d$): $\delta$ 166.43, 146.66, 143.42, 132.63, 130.34, 129.37, 128.16, 128.08, 126.97, 126.38, 117.01, 62.13, 47.34, 40.19, 33.55, 27.59.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{21}$H$_{24}$NaO$_2$$^+$): m/z 331.1669; found: 331.1677.

3,3-Dimethyl-5-phenylhex-5-en-1-yl 4-(trifluoromethyl) benzoate (13)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 71% yield (40.1 mg, 0.107 mmol) as colorless oil.

$^1$H NMR (400 MHz, Chloroform-$d$): $\delta$ 8.11 (d, $J = 8.0$ Hz, 2H), 7.74 - 7.67 (m, 2H), 7.38 (dd, $J = 8.3$, 1.4 Hz, 2H), 7.30 (t, $J = 7.3$ Hz, 2H), 7.23 (t, $J = 7.2$ Hz, 1H), 5.29 (d, $J = 1.9$ Hz, 1H), 5.10 - 5.05 (m, 1H), 4.36 (t, $J = 7.3$ Hz, 2H), 2.57 (d, $J = 0.8$ Hz, 2H), 1.68 (t, $J = 7.3$ Hz, 2H), 0.87 (s, 6H).

$^{13}$C NMR (100 MHz, Chloroform-$d$): $\delta$ 165.40, 146.71, 143.51, 133.62, 129.89, 128.22, 127.12, 126.50, 125.35 (q, $J = 3.6$ Hz), 117.24, 62.89, 47.48, 40.11, 33.68, 27.69.

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$^{19}$F NMR (376 MHz, Chloroform-d): $\delta$ -62.95.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{22}$H$_{23}$FNaO$_2$)$^+$: m/z 399.1542; found: 399.1548.

3,3-Dimethyl-5-phenylhex-5-en-1-yl 4-methylbenzoate (14)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 70% yield (33.9 mg, 0.105 mmol) as colorless oil.

$^1$H NMR (400 MHz, Chloroform-d): $\delta$ 7.91 (d, $J$ = 8.3 Hz, 2H), 7.38 (d, $J$ = 7.1 Hz, 2H), 7.30 - 7.32 (m, 3H), 5.28 (d, $J$ = 1.9 Hz, 1H), 5.09 - 5.06 (m, 1H), 4.33 (t, $J$ = 7.3 Hz, 2H), 2.57 (s, 2H), 2.41 (s, 4H), 1.68 (t, $J$ = 3.7 Hz, 2H), 0.86 (s, 6H).

$^{13}$C NMR (100 MHz, Chloroform-d): $\delta$ 166.71, 146.80, 143.56, 143.39, 129.51, 129.00, 128.18, 127.69, 127.05, 126.49, 117.12, 62.08, 47.46, 40.31, 33.67, 27.67, 21.61.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{22}$H$_{26}$NaO$_2$)$^+$: m/z 345.1825; found: 345.1827.

3,3-Dimethyl-5-phenylhex-5-en-1-yl thiophene-2-carboxylate (15)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 62% yield (29.2 mg, 0.093 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 7.77 (dd, $J$ = 3.7, 1.3 Hz, 1H), 7.54 (dd, $J$ = 5.0, 1.3 Hz, 1H), 7.37 (d, $J$ = 6.9 Hz, 2H), 7.30 (t, $J$ = 7.7 Hz, 2H), 7.23 (t, $J$ = 7.3 Hz, 1H), 7.09 (dd, $J$ = 5.0, 3.7 Hz, 1H), 5.28 (d, $J$ = 1.9 Hz, 1H), 5.10 - 5.05 (m, 1H), 4.31 (t, $J$ = 7.2 Hz, 2H), 2.56 (s, 2H), 1.65 (t, $J$ = 7.2 Hz, 2H), 0.85 (s, 6H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 162.26, 146.79, 143.57, 134.09, 133.20, 132.15, 128.19, 127.66, 127.07, 126.51, 117.15, 62.48, 47.48, 40.29, 33.69, 27.66.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{19}$H$_{22}$NaO$_2$S)$^+$: m/z 337.1233; found: 337.1237.

3,3-Dimethyl-5-phenylhex-5-en-1-yl furan-2-carboxylate (16)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 71% yield (31.8
mg, 0.1065 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 7.57 (s, 1H), 7.37 (d, $J = 7.0$ Hz, 2H), 7.29 (t, $J = 7.6$ Hz, 2H), 7.25 - 7.20 (m, 1H), 7.13 (d, $J = 3.5$ Hz, 1H), 6.53 - 6.45 (m, 1H), 5.27 (d, $J = 1.9$ Hz, 1H), 5.07 (d, $J = 1.9$ Hz, 1H), 4.32 (t, $J = 7.4$ Hz, 2H), 2.55 (s, 2H), 1.65 (t, $J = 7.4$ Hz, 2H), 0.83 (s, 6H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 158.77, 146.75, 146.17, 144.89, 143.55, 128.20, 127.07, 126.50, 117.64, 117.18, 111.74, 62.31, 47.46, 40.23, 33.66, 27.64.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{19}$H$_{22}$NaO$_3$$^+$): m/z 321.1461; found: 321.1463.

(R)-(4-Methyl-4-(4-methylcyclohex-3-en-1-yl) pent-1-en-2-yl) benzene (17)

According to method A, flash column chromatography (SiO$_2$: 1% ethyl acetate in petroleum ether) provided this compound in 79% yield (30.1 mg, 0.119 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 7.38 (d, $J = 7.2$ Hz, 2H), 7.30 (t, $J = 7.2$ Hz, 2H), 7.24 (t, $J = 7.2$ Hz, 1H), 5.37 (d, $J = 3.6$ Hz, 1H), 5.25 (d, $J = 1.8$ Hz, 1H), 5.06 - 5.02 (m, 1H), 2.60 - 2.47 (m, 2H), 2.00 - 1.93 (m, 1H), 1.92 - 1.85 (m, 1H), 1.81 - 1.79 (m, 2H), 1.64 (s, 3H), 1.35 - 1.27 (m, 2H), 1.22 - 1.15 (m, 1H), 0.71 (d, $J = 4.8$ Hz, 6H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 147.54, 144.14, 133.94, 128.07, 126.85, 126.55, 121.23, 116.79, 44.61, 42.62, 36.19, 31.33, 26.59, 25.24, 24.37, 24.16, 23.32.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{19}$H$_{26}$Na$^+$): m/z 277.1927; found: 277.1936.

(3R,10S,13R)-17-((R)-5,5-Dimethyl-7-phenyloct-7-en-2-yl)-3-methoxy-10,13-dimethyl hexadecahydro-1H-cyclopenta[a]phenanthrene (18)

According to method A, flash column chromatography (SiO$_2$: 4% ethyl acetate in petroleum ether) provided this compound in 55% yield (41.6 mg, 0.0825 mmol) as foam solid.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 7.35 (d, $J = 7.2$ Hz, 2H), 2.28 (t, $J = 7.2$ Hz, 2H), 7.22 (t, $J = 7.2$ Hz, 1H), 5.22 (s, 1H), 5.02 (s, 1H), 3.35 (s, 3H), 3.18 - 3.14 (m, 1H), 2.45 (dd, $J = 28.2$, 13.2 Hz, 2H), 1.93 (d, $J = 11.4$ Hz, 1H), 1.88 - 1.82 (m, 2H), 1.80 - 1.75 (m, 2H), 1.71 (s, 2H), 1.55 (d,
$J = 5.4$ Hz, 2H), 1.42 - 1.31 (m, 6H), 1.29 - 1.18 (m, 4H), 1.13 - 1.08 (m, 3H), 1.06 - 1.01 (m, 3H), 0.92 (s, 6H), 0.80 (d, $J = 6.6$ Hz, 3H), 0.71 (d, $J = 2.4$ Hz, 5H), 0.65 (s, 1H), 0.61 (s, 3H).

$^{13}$C NMR (150 MHz, Chloroform-d): δ 147.55, 144.00, 128.00, 126.78, 126.52, 116.41, 80.38, 56.41, 55.97, 55.46, 46.99, 42.58, 42.02, 40.30, 40.12, 38.73, 36.16, 35.81, 35.27, 34.84, 34.06, 32.73, 29.70, 28.16, 27.53, 27.50, 27.31, 26.74, 26.38, 24.18, 23.39, 20.76, 18.59, 11.97.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{36}$H$_{56}$NaO$_3^+$): m/z 527.4223; found: 527.4240.

(3R,7R,10S,12S,13R)-17-((R)-5,5-Dimethyl-7-phenyloct-7-en-2-yl)-3,7,12-trimethoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene (19)

According to method A, flash column chromatography (SiO$_2$: 5% ethyl acetate in petroleum ether) provided this compound in 47% yield (39.8 mg, 0.0705 mmol) as foam solid.

$^{1}$H NMR (600 MHz, Chloroform-d): δ 7.35 (s, 2H), 7.28 (s, 2H), 7.22 (s, 1H), 5.21 (s, 1H), 5.01 (s, 1H), 3.37 (s, 1H), 3.33 (s, 3H), 3.25 (s, 3H), 3.21 (s, 3H), 3.14 (s, 1H), 2.99 (s, 1H), 2.44 (dd, $J = 27.6$, 12.6 Hz, 2H), 2.20 (dd, $J = 23.4$, 11.4 Hz, 1H), 2.09 - 2.04 (m, 3H), 1.84 - 1.67 (m, 9H), 1.59 (d, $J = 10.8$ Hz, 2H), 1.51 - 1.45 (m, 3H), 1.34 - 1.14 (m, 10H), 0.98 (m, 4H), 0.89 (s, 6H), 0.80 (s, 3H), 0.71 (s, 5H), 0.62 (s, 3H).

$^{13}$C NMR (150 MHz, Chloroform-d): δ 147.58, 143.99, 127.98, 126.76, 126.52, 116.37, 81.99, 80.69, 76.95, 55.77, 55.64, 55.31, 46.88, 46.32, 45.94, 42.36, 41.92, 39.59, 38.67, 35.94, 35.22, 34.85, 34.38, 34.07.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{38}$H$_{60}$NaO$_3^+$): m/z 587.4435; found: 587.4440.

Tert-butyl 3-(2,2-dimethyl-4-phenylpent-4-en-1-yl)-1H-indole-1-carboxylate (20)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 70% yield (40.9 mg, 0.105 mmol) as colorless oil.

$^{1}$H NMR (600 MHz, Chloroform-d): δ 8.14 (s, 1H), 7.50 (d, $J = 7.8$ Hz, 1H), 7.42 (d, $J = 7.8$ Hz, 2H), 7.34 - 7.30 (m, 3H), 7.27 - 7.22 (m, 3H), 5.32 (d, $J = 1.8$ Hz, 1H), 5.09 (d, $J = 1.8$ Hz, 1H), 2.65 (s, 2H), 2.59 (s, 2H), 1.70 (s, 9H), 0.82 (s, 6H).
\(^{13}\text{C NMR (150 MHz, Chloroform-d)}\): \(\delta 147.16, 143.70, 128.17, 127.01, 126.52, 124.34, 123.85, 122.17, 119.73, 117.98, 116.97, 114.98, 47.98, 37.97, 35.64, 28.22, 27.30\).

HRMS (ESI) exact mass calculated for [M+H\(^+\)] (C\(_{26}\)H\(_{32}\)NO\(_2\)+): m/z 390.2428; found: 390.2437.

(4-Ethyl-4-methylnon-1-en-2-yl) benzene (21)

According to method A, flash column chromatography (SiO\(_2\): 1% ethyl acetate in petroleum ether) provided this compound in 78% yield (28.6 mg, 0.117 mmol) as colorless oil.

\(^1\text{H NMR (600 MHz, Chloroform-d)}\): \(\delta 7.36 (d, J = 6.9\ \text{Hz}, 2\text{H}), 7.29 (t, J = 7.5\ \text{Hz}, 2\text{H}), 7.23 (t, J = 7.3\ \text{Hz}, 1\text{H}), 5.20 (d, J = 2.1\ \text{Hz}, 1\text{H}), 5.03 - 5.01 (m, 1\text{H}), 2.45 (s, 2\text{H}), 1.22 (p, J = 7.5\ \text{Hz}, 2\text{H}), 1.19 - 1.10 (m, 4\text{H}), 1.09 - 1.03 (m, 4\text{H}), 0.85 (t, J = 7.4\ \text{Hz}, 3\text{H}), 0.73 (t, J = 7.5\ \text{Hz}, 3\text{H}), 0.65 (s, 3\text{H}).

\(^{13}\text{C NMR (150 MHz, Chloroform-d)}\): \(\delta 147.67, 144.31, 127.99, 126.79, 126.60, 116.62, 44.38, 38.61, 36.63, 32.67, 31.60, 24.99, 23.23, 22.69, 14.11, 8.04\).

HRMS (ESI) exact mass calculated for [M+Na\(^+\)] (C\(_{18}\)H\(_{28}\)Na\(^+\)): m/z 267.2083; found: 267.2091.

(4,4-Diethylhex-1-en-2-yl) benzene (22)

According to method A, flash column chromatography (SiO\(_2\): 1% ethyl acetate in petroleum ether) provided this compound in 67% yield (30.0 mg, 0.1005 mmol) as colorless oil.

\(^1\text{H NMR (600 MHz, Chloroform-d)}\): \(\delta 7.36 (d, J = 6.2\ \text{Hz}, 2\text{H}), 7.29 (t, J = 7.2\ \text{Hz}, 2\text{H}), 7.23 (t, J = 7.2\ \text{Hz}, 1\text{H}), 5.20 (d, J = 1.8\ \text{Hz}, 1\text{H}), 5.02 (m, 1\text{H}), 2.45 (s, 2\text{H}), 1.49 - 1.42 (m, 1\text{H}), 1.22 - 1.16 (m, 2\text{H}), 1.15 - 1.09 (m, 2\text{H}), 1.07 - 1.03 (m, 2\text{H}), 0.98 - 0.92 (m, 2\text{H}), 0.83 (dd, J = 6.6, 1.2\ \text{Hz}, 6\text{H}), 0.74 (t, J = 7.2\ \text{Hz}, 3\text{H}), 0.66 (s, 3\text{H}).

\(^{13}\text{C NMR (150 MHz, Chloroform-d)}\): \(\delta 147.67, 144.32, 128.01, 126.79, 126.59, 116.64, 44.38, 39.78, 38.84, 36.68, 31.67, 27.97, 25.00, 22.69, 22.64, 21.29, 8.06\).

HRMS (ESI) exact mass calculated for [M+Na\(^+\)] (C\(_{19}\)H\(_{30}\)Na\(^+\)): m/z 281.2240; found: 281.2249.

(4,4-Diethylhex-1-en-2-yl) benzene (23)
According to method A, flash column chromatography (SiO$_2$: 1% ethyl acetate in petroleum ether) provided this compound in 61% yield (19.8 mg, 0.092 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 7.34 (d, $J = 6.9$ Hz, 2H), 7.28 (t, $J = 7.4$ Hz, 2H), 7.23 (t, $J = 7.2$ Hz, 1H), 5.17 (d, $J = 2.1$ Hz, 1H), 5.08 - 5.03 (m, 1H), 2.40 (d, $J = 0.9$ Hz, 2H), 1.12 (q, $J = 7.5$ Hz, 6H), 0.66 (t, $J = 7.5$ Hz, 9H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 147.88, 144.65, 127.91, 126.73, 126.66, 116.80, 40.07, 39.32, 27.58, 7.54.

HRMS (ESI) exact mass calculated for [M+H$^+$] (C$_{16}$H$_{25}$+): m/z 217.1951; found: 217.1949.

(3-(1-Methylcyclopentyl) prop-1-en-2-yl) benzene (24)

According to method A, flash column chromatography (SiO$_2$: 1% ethyl acetate in petroleum ether) provided this compound in 76% yield (22.8 mg, 0.114 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 7.38 (d, $J = 7.2$ Hz, 2H), 7.30 (t, $J = 7.2$ Hz, 2H), 7.25 (t, $J = 7.2$ Hz, 1H), 5.21 (d, $J = 1.8$ Hz, 1H), 5.05 (m, 1H), 2.58 (s, 2H), 1.57 - 1.55 (m, 4H), 1.38 - 1.32 (m, 2H), 1.19 - 1.15 (m, 2H), 0.82 (s, 3H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 148.12, 143.76, 128.03, 126.92, 126.63, 115.92, 46.97, 43.05, 39.46, 26.08, 23.84.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{15}$H$_{20}$Na$^+$): m/z 223.1457; found: 223.1459.

(3-(1-Methylcyclohexyl) prop-1-en-2-yl) benzene (25)

According to method A, flash column chromatography (SiO$_2$: 1% ethyl acetate in petroleum ether) provided this compound in 79% yield (25.4 mg, 0.119 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 7.38 (d, $J = 7.2$ Hz, 2H), 7.30 (t, $J = 7.2$ Hz, 2H), 7.24 (t, $J = 7.2$ Hz, 1H), 5.23 (d, $J = 1.8$ Hz, 1H), 5.04 - 5.01 (m, 1H), 2.50 (s, 2H), 1.41 (qd, $J = 8.7$, 6.8, 4.2 Hz, 3H), 1.35 (qt, $J = 10.3$, 4.8 Hz, 2H), 1.26 - 1.12 (m, 5H), 0.74 (s, 3H).
\[^{13}\text{C NMR (150 MHz, Chloroform-}d\text{): } \delta 147.19, 144.18, 128.03, 126.84, 126.55, 116.55, 38.22, 34.16, 26.37, 22.12.\]

\[^{1}\text{H NMR (600 MHz, Chloroform-}d\text{): } \delta 7.36 (d, J = 7.3 \text{ Hz, 2H}), 7.30 (t, J = 7.5 \text{ Hz, 2H}), 7.24 (t, J = 7.2 \text{ Hz, 1H}), 5.26 (d, J = 2.0 \text{ Hz, 1H}), 5.04 (m, 1H), 2.62 - 2.58 (m, 2H), 2.51 (s, 2H), 2.49 - 2.45 (m, 2H), 1.59 - 1.55 (m, 2H), 1.52 - 1.48 (m, 2H), 0.77 (s, 3H).\]

\[^{13}\text{C NMR (125 MHz, Chloroform-}d\text{): } \delta 146.25, 143.65, 128.17, 127.09, 126.44, 117.33, 47.53, 38.60, 33.17, 24.41, 23.86.\]

\[^{1}\text{H NMR (500 MHz, Chloroform-}d\text{): } \delta 7.37 (d, J = 6.9 \text{ Hz, 2H}), 7.30 (d, J = 14.8 \text{ Hz, 2H}), 7.27 - 7.23 (m, 1H), 5.27 (d, J = 2.0 \text{ Hz, 1H}), 5.07 - 5.03 (m, 1H), 3.65 (dt, J = 11.8, 4.6 \text{ Hz, 2H}), 3.53 (ddd, J = 12.0, 9.5, 3.0 \text{ Hz, 2H}), 2.56 (s, 2H), 1.46 (ddd, J = 13.8, 9.5, 4.3 \text{ Hz, 2H}), 1.21 - 1.14 (m, 2H), 0.86 (s, 3H).\]

\[^{13}\text{C NMR (125 MHz, Chloroform-}d\text{): } \delta 146.25, 143.65, 128.17, 127.09, 117.14, 63.91, 37.95, 31.90.\]

\[^{1}\text{H NMR (500 MHz, Chloroform-}d\text{): } \delta 7.37 (d, J = 6.9 \text{ Hz, 2H}), 7.30 (d, J = 14.8 \text{ Hz, 2H}), 7.27 - 7.23 (m, 1H), 5.27 (d, J = 2.0 \text{ Hz, 1H}), 5.07 - 5.03 (m, 1H), 3.65 (dt, J = 11.8, 4.6 \text{ Hz, 2H}), 3.53 (ddd, J = 12.0, 9.5, 3.0 \text{ Hz, 2H}), 2.56 (s, 2H), 1.46 (ddd, J = 13.8, 9.5, 4.3 \text{ Hz, 2H}), 1.21 - 1.14 (m, 2H), 0.86 (s, 3H).\]

HRMS (ESI) exact mass calculated for [M+Na\(^+\)] (C\(_{16}\)H\(_{22}\)Na\(^+\)): m/z 237.1614; found: 237.1621.

**4-Methyl-4-(2-phenylallyl) tetrahydro-2H-thiopyran (26)**

According to *method A*, flash column chromatography (SiO\(_2\): 3% ethyl acetate in petroleum ether) provided this compound in 70% yield (24.4 mg, 0.105 mmol) as colorless oil.

**4-Methyl-4-(2-phenylallyl) tetrahydro-2H-pyran (27)**

According to *method A*, flash column chromatography (SiO\(_2\): 3% ethyl acetate in petroleum ether) provided this compound in 61% yield (19.8 mg, 0.0915 mmol) as colorless oil.

Tert-butyl 4-methyl-4-(2-phenylallyl) piperidine-1-carboxylate (28)

According to *method A*, flash column chromatography (SiO\(_2\): 4% ethyl acetate in petroleum ether) provided this compound in 78% yield (36.9 mg, 0.117 mmol)
as colorless oil.

$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 7.35 (d, $J$ = 6.9 Hz, 2H), 7.30 (t, $J$ = 7.5 Hz, 2H), 7.24 (t, $J$ = 7.2 Hz, 1H), 5.25 (d, $J$ = 1.9 Hz, 1H), 5.05 - 5.02 (m, 1H), 3.53 (s, 2H), 3.07 (ddd, $J$ = 13.5, 9.8, 3.6 Hz, 2H), 2.57 - 2.47 (m, 2H), 1.43 (s, 9H), 1.35 - 1.29 (m, 2H), 1.17 (d, $J$ = 13.2 Hz, 2H), 0.80 (s, 3H).

$^{13}$C NMR (150 MHz, Chloroform-$d$): $\delta$ 146.27, 143.59, 128.18, 127.09, 126.44, 117.18, 79.09, 47.24, 32.67, 28.41, 23.55.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{20}$H$_{29}$NNaO$_2$)$^+$: m/z 338.2091; found: 338.2096.

(1-(2-Phenylallyl) cyclohexyl) methyl benzoate (29)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 63% yield (31.6 mg, 0.0945 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 8.02 (d, $J$ = 7.2 Hz, 2H), 7.58 (t, $J$ = 7.2 Hz, 1H), 7.46 (t, $J$ = 7.8 Hz, 2H), 7.37 - 7.35 (m, 2H), 7.20 - 7.17 (m, 3H), 5.26 (d, $J$ = 1.8 Hz, 1H), 5.09 (d, $J$ = 1.8 Hz, 1H), 3.99 (s, 2H), 2.75 (s, 2H), 1.48 - 1.35 (m, 10H).

$^{13}$C NMR (150 MHz, Chloroform-$d$): $\delta$ 166.23, 146.18, 143.31, 132.72, 130.54, 129.45, 128.29, 128.09, 127.11, 126.42, 117.41, 37.38, 33.27, 26.05, 21.48.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{23}$H$_{26}$NaO$_2$)$^+$: m/z 357.1825; found: 357.1841.

1-Methyl-1-(2-phenylallyl) cycloheptane (30)

According to method A, flash column chromatography (SiO$_2$: 1% ethyl acetate in petroleum ether) provided this compound in 92% yield (31.5 mg, 0.138 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 7.38 (d, $J$ = 7.2 Hz, 2H), 7.360 (t, $J$ = 7.2 Hz, 2H), 7.24 (t, $J$ = 7.2 Hz, 1H), 5.25 (d, $J$ = 2.4 Hz, 1H), 5.03 (m, 1H), 2.48 (s, 2H), 1.48 - 1.45 (m, 5H), 1.42 - 1.38 (m, 5H), 1.35 - 1.32 (m, 4H), 1.25 - 1.20 (m, 2H), 0.70 (s, 3H).

$^{13}$C NMR (150 MHz, Chloroform-$d$): $\delta$ 147.45, 144.07, 128.04, 126.83, 126.53, 116.74, 47.75, 40.58, 37.32, 30.92, 28.19, 22.85.
HRMS (ESI) exact mass calculated for [M+Na\(^+\)] (C\(_{17}\)H\(_{24}\)Na\(^+\)): m/z 251.1770; found: 251.1777.

1-Methyl-1-(2-phenylallyl) cyclododecane (31)

According to method A, flash column chromatography (SiO\(_2\): 1% ethyl acetate in petroleum ether) provided this compound in 52% yield (23.3 mg, 0.078 mmol) as colorless oil.

\(^1\)H NMR (600 MHz, Chloroform-\(d\)): \(\delta\) 7.36 (d, \(J = 7.2\) Hz, 2H), 7.29 (t, \(J = 7.2\) Hz, 2H), 7.23 (t, \(J = 7.2\) Hz, 1H), 5.22 (d, \(J = 1.8\) Hz, 1H), 5.04 (m, 1H), 2.44 (s, 2H), 1.37 - 1.16 (m, 22H), 0.59 (s, 3H).

\(^{13}\)C NMR (150 MHz, Chloroform-\(d\)): \(\delta\) 147.51, 144.37, 127.98, 126.80, 126.57, 116.62, 45.92, 36.94, 34.86, 26.99, 26.21, 26.10, 22.89, 22.43, 19.27.

HRMS (ESI) exact mass calculated for [M+Na\(^+\)] (C\(_{22}\)H\(_{34}\)Na\(^+\)): m/z 321.2553; found: 321.2556.

1-Methyl-1-(2-phenylallyl) cyclopentadecanone (32)

According to method A, flash column chromatography (SiO\(_2\): 1% ethyl acetate in petroleum ether) provided this compound in 61% yield (31.2 mg, 0.0915 mmol) as colorless oil.

\(^1\)H NMR (600 MHz, Chloroform-\(d\)): \(\delta\) 7.38 (d, \(J = 7.2\) Hz, 2H), 7.30 (t, \(J = 7.2\) Hz, 2H), 7.24 (t, \(J = 7.2\) Hz, 1H), 5.23 (d, \(J = 1.8\) Hz, 1H), 5.03 (m, 1H), 2.46 (s, 2H), 1.37 - 1.29 (m, 18H), 1.23 - 1.18 (m, 4H), 1.17 - 1.13 (m, 6H), 0.67 (s, 3H).

\(^{13}\)C NMR (150 MHz, Chloroform-\(d\)): \(\delta\) 147.49, 144.26, 127.97, 126.79, 126.58, 116.59, 46.05, 38.29, 36.68, 27.95, 26.96, 26.85, 26.68, 26.24, 25.93, 21.64.

HRMS (ESI) exact mass calculated for [M+Na\(^+\)] (C\(_{25}\)H\(_{40}\)Na\(^+\)): m/z 363.3022; found: 363.3028.

(10R,13S,17R)-10,13,17-Trimethyl-17-(2-phenylallyl)-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one (33)

According to method A, flash column chromatography (SiO\(_2\): 5% ethyl acetate in petroleum ether) provided this compound in 37% yield (22.3 mg, 0.0555 mmol) as colorless oil.
The stereochemistry was assigned based on the weak correlation of Me$^a$ and Me$^b$, Me$^c$ and H18, Ph and Me$^e$, and no correlation was detected between H18 and Me$^b$ in the NOSEY spectra.

$^1$H NMR (600 MHz, Chloroform-\textit{d}): $\delta$ 7.35 (d, $J = 7.8$ Hz, 2H), 7.30 (t, $J = 7.8$ Hz, 2H), 7.23 (t, $J = 7.2$ Hz, 1H), 5.74 (s, 1H), 5.01 (d, $J = 1.8$ Hz, 1H), 2.57 (d, $J = 13.2$ Hz, 2H, H18), 2.46 - 2.39 (m, 2H), 2.35 (d, $J = 13.2$ Hz, 2H, H18$^*$), 2.30 - 2.26 (m, 1H), 2.06 - 2.03 (m, 1H), 1.82 - 1.83 (m, 1H), 1.75 - 1.69 (m, 2H), 1.65 - 1.58 (m, 4H), 1.53 - 1.47 (m, 2H), 1.45 (d, $J = 3.0$ Hz, 2H), 1.20 (s, 3H), 1.12 - 1.07 (m, 3H), 0.77 (s, 3H), 0.75 (s, 3H, Me$^b$).

$^{13}$C NMR (150 MHz, Chloroform-\textit{d}): $\delta$ 199.59, 171.57, 128.20, 126.93, 126.27, 123.78, 117.47, 53.98, 50.13, 46.65, 45.71, 40.99, 38.71, 35.77, 33.99, 32.99, 32.42, 31.64, 30.88, 24.58, 21.69, 20.76, 17.40, 15.96.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{29}$H$_{38}$NaO$^+$): m/z 425.2815; found: 425.2816.

(1R,3S,5r,7r)-2-Methyl-2-(2-phenylallyl) adamantane (34)

According to method A, flash column chromatography (SiO$_2$: 1% ethyl acetate in petroleum ether) provided this compound in 63% yield (25.2 mg, 0.0945 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-\textit{d}): $\delta$ 7.37 (d, $J = 7.0$ Hz, 2H), 7.29 (t, $J = 7.5$ Hz, 2H), 7.24 (t, $J = 7.3$ Hz, 1H), 5.19 (d, $J = 2.1$ Hz, 1H), 5.08 - 5.04 (m, 1H), 2.77 (s, 2H), 2.17 (d, $J = 12.7$ Hz, 2H), 2.03 (d, $J = 12.8$ Hz, 2H), 1.82 (d, $J = 42.7$ Hz, 2H), 1.66 (s, 2H), 1.49 (d, $J = 12.6$ Hz, 4H), 1.36 (s, 2H), 0.89 (s, 3H).

$^{13}$C NMR (150 MHz, Chloroform-\textit{d}): $\delta$ 148.30, 144.70, 127.94, 126.74, 126.65, 116.62, 43.73, 39.79, 38.95, 36.02, 33.39, 33.10, 28.04, 27.85, 24.05.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{20}$H$_{26}$Na$^+$): m/z 289.1927; found: 289.1932.

(3R,3aR,6R,7S)-3,6,8,8-Tetramethyl-6-(2-phenylallyl) octahydro-1H-3a,7-methanoazulene (35)

According to method A, flash column chromatography (SiO$_2$: 1% ethyl acetate in petroleum ether) provided this compound in 65% yield (31.4 mg, 0.0975 mmol) as colorless oil.
The stereochemistry is assigned based on the correlation between Me\textsuperscript{d} with Me\textsuperscript{e}, H12 with H11 and H12 with H6 in the NOESY spectra.

\textsuperscript{1}H NMR (600 MHz, Chloroform-d): \(\delta\) 7.35 (d, \(J = 7.2\) Hz, 2H), 7.30 (t, \(J = 7.2\) Hz, 1H), 7.23 (t, \(J = 7.2\) Hz, 2H), 5.19 (d, \(J = 1.8\) Hz, 1H), 5.04 (d, \(J = 2.4\) Hz, 1H), 2.63 (q, \(J = 13.2\) Hz, 2H), H12), 1.89 - 1.84 (m, 1H), 1.73 - 1.68 (m, 2H, H6, H11), 1.65 (q, \(J = 6.6\) Hz, 1H, H10), 1.53 - 1.47 (m, 2H), 1.46 - 1.43 (m, 2H), 1.41 - 1.40 (m, 1H), 1.39 - 1.37 (m, 2H), 1.28 - 1.27 (m, 1H), 1.26 - 1.25 (m, 1H), 1.16 (s, 3H, Me\textsuperscript{e}), 0.96 (s, 3H), 0.87 (s, 3H, Me\textsuperscript{d}), 0.85 (d, \(J = 7.2\) Hz, 3H, Me\textsuperscript{a}).

\textsuperscript{13}C NMR (150 MHz, Chloroform-d): \(\delta\) 148.21, 144.63, 127.98, 126.73, 126.72, 116.99, 58.86, 57.29, 53.56, 46.07, 44.58, 41.82, 40.38, 39.10, 36.77, 32.75, 30.55, 29.85, 29.51, 27.59, 25.29, 15.54.

HRMS (ESI) exact mass calculated for [M+Na\textsuperscript{+}] (C\textsubscript{24}H\textsubscript{34}Na\textsuperscript{+}): m/z 345.2553; found: 345.2555.

8-Benzyl 1-methyl (3aS)-3a-(2-phenylallyl)-2,3,3a,8a-tetrahydropyrrolo[2,3-b] indole-1,8-dicarboxylate (36)

According to method A, flash column chromatography (SiO\textsubscript{2}: 3% ethyl acetate in petroleum ether) provided this compound in 43% yield (30.2 mg, 0.0645 mmol) as a white foam solid.

\textsuperscript{1}H NMR (600 MHz, Chloroform-d): \(\delta\) 7.62 (bs, 1H), 7.43 (s, 2H), 7.39 (t, \(J = 7.2\) Hz, 2H), 7.34 (t, \(J = 7.2\) Hz, 1H), 7.17 - 7.13 (m, 6H), 7.01 (d, \(J = 7.2\) Hz, 1H), 6.92 (t, \(J = 7.2\) Hz, 1H), 6.02 (s, 1H), 5.24 (s, 2H), 5.15 (s, 1H), 4.93 (s, 1H), 3.70 (s, 1H), 3.47 (s, 3H), 3.02 (d, \(J = 13.8\) Hz, 1H), 2.87 (d, \(J = 13.8\) Hz, 1H), 2.83 - 2.78 (m, 1H), 1.96 - 1.93 (m, 2H).

\textsuperscript{13}C NMR (150 MHz, Chloroform-d): \(\delta\) 154.98, 153.12, 152.89, 144.63, 141.95, 141.43, 136.16, 134.04, 128.38, 128.31, 128.24, 128.11, 128.05, 127.42, 127.28, 126.15, 126.10, 123.27, 117.88, 116.42, 67.35, 52.20, 45.80, 43.18, 43.05.

HRMS (ESI) exact mass calculated for [M+H\textsuperscript{+}] (C\textsubscript{29}H\textsubscript{29}N\textsubscript{2}O\textsubscript{4}+): m/z 469.2122; found: 469.2131.

1,8-Di-tert-butyl 2-methyl (3aS)-3a-(2-(2-methoxyphenyl) allyl)-2,3,3a,8a-tetrahydropyrrolo[2,3-b] indole-1,2,8-tricarboxylate (37)
According to method A, flash column chromatography (SiO$_2$: 5% ethyl acetate in petroleum ether) provided this compound in 52% yield (44.0 mg, 0.078 mmol) as foam solid.

$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 7.48 (bs, 1H), 7.15 (t, $J$ = 7.2 Hz, 1H), 7.10 (t, $J$ = 7.2 Hz, 1H), 6.90 (dd, $J$ = 18.6, 7.2 Hz, 2H), 6.82 (t, $J$ = 7.2 Hz, 1H), 6.78 (t, $J$ = 7.2 Hz, 1H), 6.74 (d, $J$ = 7.8 Hz, 1H), 6.02 (s, 1H), 5.09 (s, 1H), 5.07 (s, 1H), 3.79 - 3.75 (m, 4H), 3.67 (s, 3H), 3.14 (d, $J$ = 13.8 Hz, 1H), 2.73 (d, $J$ = 13.8 Hz, 1H), 2.27 (q, $J$ = 6.0 Hz, 1H), 2.01 (t, $J$ = 11.4 Hz, 1H), 1.59 (s, 9H), 1.36 (bs, 9H).

$^{13}$C NMR (150 MHz, Chloroform-$d$): $\delta$ 172.93, 155.96, 152.32, 144.07, 141.93, 134.83, 131.34, 129.87, 128.52, 128.18, 123.01, 120.60, 119.97, 110.45, 81.15, 80.52, 65.26, 59.39, 55.17, 51.92, 42.91, 41.94, 28.30, 28.17.

HRMS (ESI) exact mass calculated for [M+H$^+$] (C$_{32}$H$_{41}$N$_2$O$_7$)$^+$: m/z 565.2908; found: 565.2929.

5-(2-Methoxyphenyl)-3,3-dimethylhex-5-en-1-yl benzoate (12b)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 57% yield (28.9 mg, 0.0855 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 8.01 (d, $J$ = 7.2 Hz, 2H), 7.55 (t, $J$ = 7.2 Hz, 1H), 7.43 (t, $J$ = 7.8 Hz, 2H), 7.22 - 7.19 (m, 2H), 6.91 (t, $J$ = 1.8 Hz, 1H), 6.83 (d, $J$ = 8.4 Hz, 1H), 5.15 (d, $J$ = 2.4 Hz, 1H), 5.13 (d, $J$ = 2.4 Hz, 1H), 4.29 (t, $J$ = 7.2 Hz, 2H), 3.83 (s, 3H), 2.62 (s, 2H), 1.63 (t, $J$ = 7.2 Hz, 2H), 0.87 (s, 6H).

$^{13}$C NMR (150 MHz, Chloroform-$d$): $\delta$ 166.60, 156.32, 146.39, 133.18, 132.68, 130.51, 130.18, 129.46, 128.23, 120.56, 118.79, 110.61, 62.34, 55.26, 47.94, 40.01, 33.53, 27.73.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{22}$H$_{34}$NaO$_3$)$^+$: m/z 361.1774; found: 361.1786.

5-(3-Methoxyphenyl)-3,3-dimethylhex-5-en-1-yl benzoate (12c)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 66% yield (33.5 mg, 0.099 mmol) as colorless oil.
$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 8.02 (d, $J = 6.6$ Hz, 2H), 7.95 (t, $J = 7.2$ Hz, 1H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.22 (t, $J = 7.3$ Hz, 1H), 6.99 - 6.97 (m, 1H), 6.93 (t, $J = 1.8$ Hz, 1H), 6.80 - 6.78 (m, 1H), 5.30 (d, $J = 1.8$ Hz, 1H), 5.07 (d, $J = 1.8$ Hz, 1H), 4.35 (t, $J = 7.2$ Hz, 2H), 3.80 (s, 3H), 2.55 (s, 2H), 1.69 (t, $J = 7.2$ Hz, 2H), 0.88 (s, 6H).

$^{13}$C NMR (150 MHz, Chloroform-$d$): $\delta$ 166.58, 159.41, 146.64, 145.09, 132.72, 130.43, 129.45, 129.11, 128.25, 119.08, 117.17, 112.51, 116.2, 62.25, 55.11, 47.51, 40.22, 33.66, 27.62.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{22}H_{26}NaO_3$)$^+$: m/z 361.1774; found: 361.1790.

5-(4-Methoxyphenyl)-3,3-dimethylhex-5-en-1-yl benzoate (12d)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 63% yield (32.0 mg, 0.0945 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 8.01 (d, $J = 6.8$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.31 (d, $J = 8.7$ Hz, 2H), 6.83 (d, $J = 8.7$ Hz, 2H), 5.22 (d, $J = 1.9$ Hz, 1H), 5.01 - 4.96 (m, 1H), 4.34 (t, $J = 7.3$ Hz, 2H), 3.77 (s, 3H), 2.53 (s, 2H), 1.67 (t, $J = 7.3$ Hz, 2H), 0.86 (s, 6H).

$^{13}$C NMR (150 MHz, Chloroform-$d$): $\delta$ 166.66, 158.82, 146.13, 136.01, 132.77, 130.47, 129.49, 128.29, 127.56, 115.78, 113.53, 62.33, 55.17, 47.47, 40.29, 33.66, 27.75.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{22}H_{26}NaO_3$)$^+$: m/z 361.1774; found: 361.1789.

5-(Benzo[d][1,3] dioxol-5-yl)-3,3-dimethylhex-5-en-1-yl benzoate (12e)

According to method A, flash column chromatography (SiO$_2$: 1% ethyl acetate in petroleum ether) provided this compound in 67% yield (35.4 mg, 0.1005 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 8.02 (d, $J = 7.1$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.8$ Hz, 2H), 6.88 - 6.84 (m, 2H), 6.74 (d, $J = 8.0$ Hz, 1H), 5.91 (s, 2H), 5.20 (d, $J = 1.9$ Hz, 1H), 4.99 (d, $J = 1.8$ Hz, 1H), 4.34 (t, $J = 7.3$ Hz, 2H), 2.49 (s, 2H), 1.68 (t, $J = 7.3$ Hz, 2H), 0.88 (s, 6H).

$^{13}$C NMR (150 MHz, Chloroform-$d$): $\delta$ 166.62, 147.50, 146.71, 146.25, 137.86, 132.76, 130.44, 129.48, 128.29, 119.88, 116.26, 107.94, 107.14, 100.94, 62.28, 47.70, 40.25, 33.68, 27.68.
HRMS (ESI) exact mass calculated for [M+Na⁺] (C_{22}H_{24}NaO_{4}⁺): m/z 375.1567; found: 375.1574.

5-(3-Fluorophenyl)-3,3-dimethylhex-5-en-1-yl benzoate (12f)

According to method A, flash column chromatography (SiO₂: 1% ethyl acetate in petroleum ether) provided this compound in 71% yield (34.7 mg, 0.1065 mmol) as colorless oil.

^1^H NMR (600 MHz, Chloroform-d): δ 8.01 (d, J = 6.6 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.26 - 7.22 (m, 1H), 7.15 - 7.14 (m, 1H), 7.07 (dt, J = 10.2, 1.8 Hz, 1H), 6.93 - 6.90 (m, 1H), 5.30 (d, J = 1.8 Hz, 1H), 5.09 (d, J = 1.2 Hz, 1H), 4.34 (t, J = 7.2 Hz, 2H), 2.52 (s, 2H), 1.67 (t, J = 7.2 Hz, 2H), 0.85 (s, 6H).

^1^C NMR (150 MHz, Chloroform-d): δ 166.59, 145.89, 145.65, 132.78, 130.39, 129.67, 129.61, 129.47, 128.28, 122.15, 122.13, 118.03, 113.93, 113.79, 113.49, 113.35, 62.16, 47.42, 40.30, 33.70, 27.57.

^1^9^F NMR (564 MHz, Chloroform-d): δ -113.50.

HRMS (ESI) exact mass calculated for [M+Na⁺] (C_{21}H_{23}FNaO_{2}⁺): m/z 349.1574; found: 349.1588.

5-(4-Fluorophenyl)-3,3-dimethylhex-5-en-1-yl benzoate (12g)

According to method A, flash column chromatography (SiO₂: 1% ethyl acetate in petroleum ether) provided this compound in 63% yield (30.8 mg, 0.0945 mmol) as colorless oil.

^1^H NMR (600 MHz, Chloroform-d): δ 8.01 (d, J = 6.6 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.2 Hz, 2H), 7.34 (dd, J = 8.4, 5.4 Hz, 2H), 6.99 (t, J = 8.4 Hz, 2H), 5.24 (d, J = 1.8 Hz, 1H), 5.06 (m, 1H), 4.34 (t, J = 7.2 Hz, 2H), 2.53 (s, 2H), 1.67 (t, J = 7.2 Hz, 2H), 0.86 (s, 6H).

^1^C NMR (150 MHz, Chloroform-d): δ 166.62, 145.74, 132.80, 130.40, 129.47, 128.30, 128.03, 127.98, 117.16, 115.09, 114.95, 62.20, 47.66, 40.32, 33.69, 27.67.

^1^9^F NMR (564 MHz, Chloroform-d): δ -115.71.

HRMS (ESI) exact mass calculated for [M+Na⁺] (C_{21}H_{23}FNaO_{2}⁺): m/z 349.1574; found: 349.1580.

3,3-Dimethyl-5-(3,4,5-trifluorophenyl) hex-5-en-1-yl benzoate (12h)
According to method A, flash column chromatography (SiO2: 1% ethyl acetate in petroleum ether) provided this compound in 65% yield (35.3 mg, 0.0975 mmol) as colorless oil.

1H NMR (400 MHz, Chloroform-d): δ 8.02 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.04 - 6.94 (m, 2H), 5.29 (d, J = 1.3 Hz, 1H), 5.13 (s, 1H), 4.36 (t, J = 7.2 Hz, 2H), 2.47 (s, 2H), 1.68 (t, J = 7.2 Hz, 2H), 0.86 (s, 6H).

13C NMR (100 MHz, Chloroform-d): δ 166.59, 152.18, 144.01, 139.70, 132.87, 130.27, 129.46, 128.33, 118.99, 110.56, 110.50, 110.40, 62.00, 47.21, 40.29, 33.75, 27.46.


3,3-Dimethyl-5-(naphthalen-2-yl) hex-5-en-1-yl benzoate (12i)

According to method A, flash column chromatography (SiO2: 1% ethyl acetate in petroleum ether) provided this compound in 81% yield (43.6 mg, 0.1215 mmol) as colorless oil.

1H NMR (600 MHz, Chloroform-d): δ 7.96 (d, J = 8.2 Hz, 2H), 7.85 - 7.75 (m, 4H), 7.54 (t, J = 7.3 Hz, 2H), 7.49 - 7.38 (m, 4H), 5.42 (d, J = 1.8 Hz, 1H), 5.18 (d, J = 1.8 Hz, 1H), 4.36 (t, J = 7.3 Hz, 2H), 2.68 (s, 2H), 1.71 (t, J = 7.3 Hz, 2H), 0.89 (s, 6H).

13C NMR (150 MHz, Chloroform-d): δ 146.71, 140.97, 133.34, 132.74, 132.64, 130.41, 129.47, 128.27, 128.04, 127.80, 127.52, 126.07, 125.66, 125.21, 125.00, 117.78, 62.28, 47.48, 40.33, 33.79, 27.75.

HRMS (ESI) exact mass calculated for [M+Na+] (C25H26NaO22+): m/z 381.1825; found: 381.1830.

3,3-Dimethyl-5-(pyren-1-yl) hex-5-en-1-yl benzoate (12j)

According to method A, flash column chromatography (SiO2: 1% ethyl acetate in petroleum ether) provided this compound in 48% yield (31.1 mg, 0.072 mmol) as colorless oil.

1H NMR (600 MHz, Chloroform-d): δ 8.49 (d, J = 9.2 Hz, 1H), 8.16 (d, J = 7.7 Hz, 2H), 8.12 (d, J = 7.9 Hz, 1H), 8.07 (d, J = 9.2 Hz, 1H), 8.03 - 7.98 (m, 3H), 7.94 (d, J = 7.9 Hz, 1H), 7.83 (d, J =
7.2 Hz, 2H), 7.50 (t, \( J = 7.4 \) Hz, 1H), 7.33 (t, \( J = 7.8 \) Hz, 2H), 5.63 (d, \( J = 2.1 \) Hz, 1H), 5.41 (d, \( J = 2.1 \) Hz, 1H), 4.24 (t, \( J = 7.3 \) Hz, 2H), 2.86 (s, 2H), 1.69 (t, \( J = 7.3 \) Hz, 2H), 0.90 (s, 6H).

**\(^{13}\)C NMR (150 MHz, Chloroform-d):** \( \delta \) 166.50, 145.87, 139.81, 132.64, 130.92, 130.16, 129.36, 128.17, 127.36, 127.25, 127.11, 125.92, 125.85, 125.37, 125.19, 124.99, 124.73, 124.42, 121.36, 62.13, 51.15, 40.10, 34.19, 27.81.

**HRMS (ESI) exact mass calculated for [M+Na\(^+\)] (C\(_{31}\)H\(_{28}\)NaO\(_2\)\(^+\)):** m/z 455.1982; found: 455.1982.

3,3-Dimethyl-5-(thiophen-2-yl) hex-5-en-1-yl benzoate (12k)

According to method A, flash column chromatography (SiO\(_2\): 2% ethyl acetate in petroleum ether) provided this compound in 43% yield (20.3 mg, 0.0645 mmol) as colorless oil.

**\(^1\)H NMR (600 MHz, Chloroform-d):** \( \delta \) 8.03 (d, \( J = 7.8 \) Hz, 2H), 7.55 (t, \( J = 7.8 \) Hz, 1H), 7.44 (t, \( J = 7.8 \) Hz, 2H), 7.14 (d, \( J = 4.8 \) Hz, 1H), 7.03 (d, \( J = 3.0 \) Hz, 1H), 6.95 (t, \( J = 3.0 \) Hz, 1H), 5.51 (s, 1H), 4.97 (s, 1H), 4.41 (t, \( J = 7.2 \) Hz, 2H), 2.52 (s, 2H), 1.78 (t, \( J = 7.2 \) Hz, 2H), 0.97 (s, 6H).

**\(^{13}\)C NMR (150 MHz, Chloroform-d):** \( \delta \) 166.64, 147.05, 139.04, 132.79, 130.41, 129.49, 128.30, 127.22, 124.06, 123.71, 115.43, 62.27, 47.74, 40.46, 33.71, 27.41.

**HRMS (ESI) exact mass calculated for [M+Na\(^+\)] (C\(_{19}\)H\(_{22}\)NaO\(_2\)\(^+\)):** m/z 337.1233; found: 337.1238.

3,3-Dimethyl-5-methylenehept-6-en-1-yl benzoate (12l)

According to method A, flash column chromatography (SiO\(_2\): 2% ethyl acetate in petroleum ether) provided this compound in 38% yield (14.7 mg, 0.057 mmol) as colorless oil. Further purification of the product was performed using a preparation TLC.

**\(^1\)H NMR (600 MHz, Chloroform-d) \( \delta \) 8.04 (d, \( J = 7.4 \) Hz, 2H), 7.55 (t, \( J = 7.4 \) Hz, 1H), 7.44 (t, \( J = 7.4 \) Hz, 2H), 6.40 (dd, \( J = 18.0, 10.8 \) Hz, 1H), 5.26 (d, \( J = 18.0 \) Hz, 1H), 5.21 (s, 1H), 5.05 (d, \( J = 10.8 \) Hz, 1H), 4.96 (s, 1H), 4.42 (t, \( J = 7.3 \) Hz, 2H), 2.24 (s, 2H), 1.77 (t, \( J = 7.3 \) Hz, 2H), 0.98 (s, 6H).

**\(^{13}\)C NMR (150 MHz, Chloroform-d) \( \delta \) 166.69, 143.45, 140.43, 132.79, 130.47, 129.51, 128.31, 119.03, 113.69, 62.40, 43.04, 40.58, 33.32, 27.47.

**HRMS (ESI) exact mass calculated for [M+Na\(^+\)] (C\(_{17}\)H\(_{22}\)NaO\(_2\)\(^+\)):** m/z 281.1512; found: 281.1519.
3,3,5-Trimethylhex-5-en-1-yl benzoate (12m)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 43% yield (15.9 mg, 0.0645 mmol) as colorless oil. Further purification of the product was performed using a preparation TLC.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.04 (dd, $J = 8.3$, 1.5 Hz, 2H), 7.59 - 7.52 (m, 1H), 7.44 (t, $J = 7.7$ Hz, 2H), 4.91 - 4.86 (m, 1H), 4.68 (dd, $J = 1.7$, 0.8 Hz, 1H), 4.40 (t, $J = 7.4$ Hz, 2H), 2.04 (d, $J = 0.7$ Hz, 2H), 1.80 (dd, $J = 1.5$, 0.8 Hz, 3H), 1.76 (t, $J = 7.4$ Hz, 2H), 1.01 (s, 6H).

$^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 166.71, 143.09, 132.80, 130.44, 129.51, 128.31, 114.63, 62.42, 50.13, 40.37, 33.24, 27.66, 25.44.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{16}H_{22}NaO_2^+$): m/z 269.1512; found: 269.1515.

5-(Methoxycarbonyl)-3,3-dimethylhex-5-en-1-yl benzoate (12n)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 57% yield (24.8 mg, 0.0855 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 8.02 (d, $J = 7.2$ Hz, 2H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.43 (t, $J = 7.8$ Hz, 2H), 6.24 (d, $J = 1.2$ Hz, 1H), 5.52 (d, $J = 1.2$ Hz, 1H), 4.41 (t, $J = 7.2$ Hz, 2H), 3.74 (s, 3H), 2.39 (s, 2H), 1.71 (t, $J = 7.2$ Hz, 2H), 0.95 (s, 6H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 168.51, 166.62, 137.90, 132.80, 130.40, 129.49, 128.31, 127.99, 62.16, 51.89, 43.10, 39.92, 33.37, 27.71, 26.59.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{17}H_{22}NaO_4^+$): m/z 313.1410; found: 313.1416.

3,3-Dimethylhex-5-en-1-yl benzoate (12o)

To a flame-dried Schlenk tube equipped with a stir bar was loaded zinc power (29.4 mg, 0.45 mmol, 300 mol %), followed by addition of MgCl$_2$ (42.9 mg, 0.45 mmol, 300 mol %), tBu-terpyridine L4 (6.0 mg, 0.015 mmol, 10 mol %) and FePc (8.5 mg, 0.015 mmol, 10 mol%). The tube was evacuated and refilled nitrogen (N$_2$) three time. DMA (0.5 mL) was added via a syringe, followed by addition of tertiary alkyl oxalate (0.15 mmol, 100 mol %),
and allyl acetate (0.6 mmol, 400 mol %). After the reaction mixture was allowed to stir for 12 hours under a N₂ atmosphere at 25 °C. The reaction mixture was loaded onto a silica column. Flash column chromatography (SiO₂: 1% ethyl acetate in petroleum ether) provided this compound in 49% yield (17.1 mg, 0.0735 mmol) as colorless oil. Further purification of the product was performed using a preparation TLC.

¹H NMR (600 MHz, Chloroform-d) δ 8.04 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 5.85 (ddt, J = 17.4, 10.3, 7.5 Hz, 1H), 5.07 - 5.03 (m, 2H), 4.39 (t, J = 7.2 Hz, 2H), 2.05 (d, J = 7.8 Hz, 2H), 1.72 (t, J = 7.2 Hz, 2H), 0.98 (s, 6H).

¹³C NMR (150 MHz, Chloroform-d) δ 166.68, 135.00, 132.78, 130.46, 129.50, 128.30, 117.35, 62.28, 46.87, 39.66, 32.58, 27.14.

HRMS (APCI) exact mass calculated for [M+H⁺] (C₁₅H₂₁O₂⁺): m/z 233.1356; found: 233.1597.

(4,4-dimethylpent-1-en-1-yl) benzene (3b)

According to method A, using methyl (1-phenylallyl) carbonate, flash column chromatography (SiO₂: petroleum ether) provided this compound in 35% yield (9.0 mg, 0.0525 mmol) as colorless oil.

¹H NMR (600 MHz, Chloroform-d) δ 7.36 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.2 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 6.37 (d, J = 15.7 Hz, 1H), 6.29 - 6.24 (m, 1H), 2.09 (dd, J = 7.6, 0.6 Hz, 2H), 0.95 (s, 9H).

¹³C NMR (150 MHz, Chloroform-d) δ 137.94, 131.80, 128.45, 128.23, 126.78, 125.97, 47.57, 31.41, 29.39.

HRMS (ESI) exact mass calculated for [M+Na⁺] (C₁₃H₁₈Na⁺): m/z 197.1301; found: 197.1298.

(4-cyclopropyl-2,2-dimethylpent-4-en-1-yl) benzene (5b)

According to method A, flash column chromatography (SiO₂: 1% ethyl acetate in petroleum ether) provided this compound in 26% yield (8.36 mg, 0.039 mmol) as colorless oil.
$^1$H NMR (600 MHz, Chloroform-d): $\delta$ 7.26 (t, $J = 7.0$ Hz, 2H), 7.20 (t, $J = 7.2$ Hz, 1H), 7.14 (d, $J = 7.2$ Hz, 2H), 4.61 (s, 1H), 4.57 (s, 1H), 2.58 (s, 2H), 2.15 (s, 2H), 1.23 - 1.20 (m, 1H), 0.92 (s, 6H), 0.71 - 0.68 (m, 2H), 0.48 - 0.45 (m, 2H).

$^{13}$C NMR (150 MHz, Chloroform-d): $\delta$ 149.30, 139.37, 130.73, 127.58, 125.74, 108.31, 50.98, 49.59, 34.97, 26.80, 17.49, 8.78.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{16}$H$_{22}$Na$^+$): m/z 237.1614; found: 237.1619.

Part 7. Three Component Reaction

Method B: To a flame-dried Schlenk tube equipped with a stir bar was loaded zinc power (58.8 mg, 0.90 mmol, 300 mol %), followed by addition of MgCl$_2$ (85.8 mg, 0.90 mmol, 300 mol %), DtbBipy L.1a (7.9 mg, 0.03 mmol, 10 mol %) and Fe (acac)$_3$ (5.3 mg, 0.015 mmol, 5 mol%). The tube was evacuated and refilled nitrogen (N$_2$) three time. DMA (1.0 mL) was added via syringe, followed by addition of tertiary alkyl oxalate (0.30 mmol, 100 mol %), allylic carbonate (0.6 mmol, 200 mol %) and methyl acrylate (0.6 mmol, 200%). After the reaction mixture was allowed to stir for 12 hours under a N$_2$ atmosphere at 45°C. The reaction mixture was loaded onto a silica column. Flash column chromatography provided the product as an oil or a solid.

Methyl (S)-2-neopentyl-4-phenylpent-4-enoate (38a)

According to method B, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 49% yield (38.3 mg, 0.147 mmol) as colorless oil.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.40 - 7.31 (m, 4H), 7.31 - 7.26 (m, 1H), 5.29 (d, $J = 1.6$ Hz, 1H), 5.07 (d, $J = 1.5$ Hz, 1H), 3.58 (s, 3H), 2.88 - 2.76 (m, 1H), 2.60 - 2.49 (m, 2H), 1.79 (dd, $J = 13.9$, 9.4 Hz, 1H), 1.31 (d, $J = 15.9$ Hz, 1H), 0.77 (s, 9H).
\textbf{13C NMR (100 MHz, Chloroform-d)}: \( \delta 177.30, 145.86, 140.34, 128.32, 127.55, 126.27, 114.85, 51.34, 45.33, 40.71, 40.53, 30.52, 29.20. \)

\textbf{HRMS (ESI)} exact mass calculated for [M+H\(^{+}\)] (C\(_{17}\)H\(_{25}\)O\(_{2}\)\(^{+}\)): m/z 261.1849; found: 261.1851.

\textbf{Ethyl (S)-2-neopentyl-4-phenylpent-4-enoate (38b)}

According to \textit{method B}, flash column chromatography (SiO\(_2\): 2\% ethyl acetate in petroleum ether) provided this compound in 42\% yield (34.6 mg, 0.126 mmol) as colorless oil.

\textbf{1H NMR (400 MHz, Chloroform-d)} \( \delta 7.41 - 7.26 \text{ (m, 5H)}, 5.29 (d, J = 1.5 \text{ Hz, 1H}), 5.08 (d, J = 1.3 \text{ Hz, 1H}), 4.04 (q, J = 7.1 \text{ Hz, 2H}), 2.88 - 2.77 \text{ (m, 1H)}, 2.60 - 2.46 \text{ (m, 2H)}, 1.80 (dd, J = 14.1, 9.9 \text{ Hz, 1H}), 1.21 (t, J = 7.1 \text{ Hz, 4H}), 0.77 (s, 9H). \)

\textbf{13C NMR (100 MHz, Chloroform-d)}: \( \delta 176.86, 145.85, 140.40, 128.30, 127.52, 126.29, 114.83, 60.09, 45.34, 40.73, 40.58, 30.59, 29.26, 14.13. \)

\textbf{HRMS (ESI)} exact mass calculated for [M+Na\(^{+}\)] (C\(_{18}\)H\(_{32}\)NaO\(_{3}\)\(^{+}\)): m/z 297.1825; found: 297.1828.

\textbf{Tert-butyl (S)-4-(4-methoxyphenyl)-2-neopentylpent-4-enoate (38c)}

According to \textit{method B}, flash column chromatography (SiO\(_2\): 2\% ethyl acetate in petroleum ether) provided this compound in 46\% yield (45.9 mg, 0.138 mmol) as colorless oil.

\textbf{1H NMR (600 MHz, Chloroform-d)} \( \delta 7.33 \text{ (d, J = 8.7 \text{ Hz, 2H})}, 6.87 \text{ (d, J = 8.7 \text{ Hz, 2H})}, 5.22 \text{ (d, J = 1.5 \text{ Hz, 1H})}, 5.00 \text{ (d, J = 1.6 \text{ Hz, 1H})}, 3.82 \text{ (s, 3H)}, 2.76 \text{ (dd, J = 14.0, 7.6 \text{ Hz, 1H})}, 2.46 \text{ (dd, J = 14.1, 7.2 \text{ Hz, 1H})}, 2.38 \text{ (q, J = 9.1, 8.4 \text{ Hz, 1H})}, 1.77 \text{ (dd, J = 14.1, 9.9 \text{ Hz, 1H})}, 1.41 \text{ (s, 9H)}, 1.22 \text{ (dd, J = 14.1, 1.9 \text{ Hz, 1H})}, 0.78 \text{ (s, 9H)}. \)

\textbf{13C NMR (150 MHz, Chloroform-d)}: \( \delta 176.17, 159.07, 145.10, 132.96, 127.38, 113.63, 113.22, 79.89, 55.23, 45.24, 41.24, 40.92, 30.61, 29.39, 28.00. \)

\textbf{HRMS (ESI)} exact mass calculated for [M+Na\(^{+}\)] (C\(_{21}\)H\(_{32}\)NaO\(_{3}\)\(^{+}\)): m/z 355.2244; found: 355.2250.

\textbf{Phenyl (S)-4-(4-methoxyphenyl)-2-neopentylpent-4-enoate (38d)}
According to *method B*, flash column chromatography (SiO\(_2\): 2% ethyl acetate in petroleum ether) provided this compound in 45% yield (46.5 mg, 0.132 mmol) as colorless oil.

\(^1\)H NMR (600 MHz, Chloroform-\(d\)): \(\delta\) 7.38 (d, \(J = 8.8\) Hz, 2H), 7.35 (d, \(J = 8.0\) Hz, 2H), 7.21 (t, \(J = 7.4\) Hz, 1H), 7.01 (d, \(J = 8.7\) Hz, 2H), 6.89 (d, \(J = 8.7\) Hz, 2H), 5.32 (d, \(J = 1.5\) Hz, 1H), 5.11 (d, \(J = 1.5\) Hz, 1H), 3.82 (s, 3H), 2.96 (dd, \(J = 13.8, 8.1\) Hz, 1H), 2.81 - 2.74 (m, 1H), 2.68 (dd, \(J = 13.8, 6.8\) Hz, 1H), 1.96 (dd, \(J = 14.2, 10.1\) Hz, 1H), 1.42 (dd, \(J = 14.2, 2.0\) Hz, 1H), 0.89 (s, 9H).

\(^{13}\)C NMR (150 MHz, Chloroform-\(d\)): \(\delta\) 175.30, 159.25, 150.82, 144.89, 132.60, 129.31, 127.39, 127.19, 125.63, 121.46, 113.82, 113.71, 55.25, 45.64, 40.94, 40.77, 30.76, 29.40.

HRMS (ESI) exact mass calculated for [M+H\(^+\)] (C\(_{23}\)H\(_{28}\)O\(_3\)+): m/z 353.2111; found: 353.2111.

(S)-4-(4-methoxyphenyl)-2-neopentylpent-4-enenitrile (38e)

According to *method B*, flash column chromatography (SiO\(_2\): 3% ethyl acetate in petroleum ether) provided this compound in 48% yield (37.1 mg, 0.144 mmol) as colorless oil.

\(^1\)H NMR (600 MHz, Chloroform-\(d\)): \(\delta\) 7.29 (d, \(J = 9.0\) Hz, 2H), 6.88 (d, \(J = 9.0\) Hz, 2H), 5.33 (d, \(J = 0.6\) Hz, 1H), 5.13 (d, \(J = 0.6\) Hz, 1H), 3.82 (s, 3H), 2.88 (dd, \(J = 14.4, 7.8\) Hz, 1H), 2.65 (dd, \(J = 14.4, 7.8\) Hz, 1H), 2.55 - 2.50 (m, 1H), 1.66 (dd, \(J = 14.4, 10.8\) Hz, 1H), 1.42 (dd, \(J = 14.4, 2.4\) Hz, 1H), 0.88 (s, 9H).

\(^{13}\)C NMR (150 MHz, Chloroform-\(d\)): \(\delta\) 159.47,143.27, 131.62, 127.36, 123.26, 115.03, 113.98, 55.27, 45.42, 40.31, 30.62, 29.22, 25.64.

HRMS (ESI) exact mass calculated for [M+H\(^+\)] (C\(_{17}\)H\(_{24}\)NO\(_3\)+): m/z 258.1852; found: 258.1859.

(S)-2-(2,2-Dimethyl-3-phenylpropyl)-N, N-diethyl-4-(4-methoxyphenyl) pent-4-enamide (38f)

According to *method B*, flash column chromatography (SiO\(_2\): 5% ethyl acetate in petroleum ether) provided this compound in 43% yield (42.7 mg, 0.129 mmol) as colorless oil.
1H NMR (600 MHz, Chloroform-d): δ 7.31 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.20 (d, J = 1.2 Hz, 1H), 5.02 (s, 1H), 3.82 (s, 3H), 3.37 - 3.32 (m, 1H), 3.31 - 3.25 (m, 1H), 3.21 - 3.11 (m, 2H), 2.71 (dd, J = 13.8, 5.4 Hz, 1H), 2.68 - 2.63 (m, 1H), 2.52 (dd, J = 13.8, 8.4 Hz, 1H), 1.96 (dd, J = 13.8, 9.0 Hz, 1H), 1.32 (dd, J = 13.8, 2.4 Hz, 1H), 1.05 (q, J = 7.2 Hz, 6H), 0.77 (s, 9H).

13C NMR (150 MHz, Chloroform-d): δ 175.41, 159.11, 145.56, 133.46, 127.44, 113.74, 113.63, 55.27, 44.91, 41.61, 40.82, 40.10, 35.74, 30.60, 29.73, 14.40, 12.54.

HRMS (ESI) exact mass calculated for [M+H+] (C21H34NO2+): m/z 332.2584; found: 332.2580.

Methyl 2-fluoro-4-(4-methoxyphenyl)-2-neopentylpent-4-enoate (38g)

According to method B, flash column chromatography (SiO2: 2% ethyl acetate in petroleum ether) provided this compound in 50% yield (46.3 mg, 0.15 mmol) as colorless oil.

1H NMR (600 MHz, Chloroform-d): δ 7.28 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 5.30 (d, J = 1.5 Hz, 1H), 5.11 (s, 1H), 3.80 (s, 3H), 3.43 (s, 3H), 3.03 (dd, J = 31.2, 14.9 Hz, 1H), 2.93 (t, J = 14.1 Hz, 1H), 2.03 (dd, J = 39.1, 14.9 Hz, 1H), 1.84 (dd, J = 14.9, 6.2 Hz, 1H), 0.92 (s, 9H).

13C NMR (150 MHz, Chloroform-d): δ 172.03, 171.86, 159.06, 141.68, 133.74, 127.72, 116.94, 113.44, 55.24, 51.76, 50.11, 49.97, 45.58, 45.43, 30.95, 30.26, 30.25.

19F NMR (565 MHz, Chloroform-d): δ -165.23.

HRMS (ESI) exact mass calculated for [M+H+] (C18H26F3O3+): m/z 309.1860; found: 309.1861.

Methyl (S)-4-(4-methoxyphenyl)-2-((1-methylcyclopentyl) methyl) pent-4-enoate (38h)

According to method B, flash column chromatography (SiO2: 2% ethyl acetate in petroleum ether) provided this compound in 27% yield (22.1 mg, 0.081 mmol) as colorless oil.

1H NMR (600 MHz, Chloroform-d): δ 7.40 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 7.2 Hz, 1H), 5.50 (s, 1H), 5.42 - 5.36 (m, 1H), 5.13 (d, J = 1.5 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 3.37 (s, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.05 (s, 9H).

13C NMR (150 MHz, Chloroform-d): δ 170.17, 145.22, 144.63, 140.80, 128.61, 128.08, 127.35, 126.25, 114.71, 60.37, 42.14, 33.30, 29.76, 14.07.
HRMS (ESI) exact mass calculated for [M+Na⁺] (C₁₈H₂₄NaO₂⁺): m/z 295.1669; found: 295.1674.

(S)-5-(Methoxycarbonyl)-7-(4-methoxyphenyl)-3,3-dimethyloct-7-en-1-yl benzoate (39)

According to method B, flash column chromatography (SiO₂: 3% ethyl acetate in petroleum ether) provided this compound in 41% yield (52.2 mg, 0.123 mmol) as colorless oil.

\(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 8.01 (d, \(J = 7.5\) Hz, 2H), 7.55 (t, \(J = 7.5\) Hz, 2H), 7.31 (d, \(J = 8.2\) Hz, 2H), 6.85 (d, \(J = 8.2\) Hz, 2H), 5.26 - 5.20 (m, 1H), 5.02 - 4.95 (m, 1H), 4.32 - 4.23 (m, 2H), 3.76 (s, 3H), 3.60 (s, 3H), 2.83 (dd, \(J = 12.8, 6.1\) Hz, 1H), 2.63 - 2.46 (m, 2H), 1.89 (dd, \(J = 14.1, 9.6\) Hz, 1H), 1.58 (t, \(J = 7.3\) Hz, 2H), 1.41 (d, \(J = 14.1\) Hz, 1H), 0.85 (s, 3H), 0.81 (s, 3H).

\(^{13}\)C NMR (100 MHz, Chloroform-d): \(\delta\) 177.10, 166.55, 159.14, 144.81, 132.80, 132.35, 130.36, 129.47, 128.29, 127.32, 113.71, 62.05, 55.14, 51.48, 43.41, 40.52, 40.14, 39.90, 32.42, 26.99, 26.72.

HRMS (ESI) exact mass calculated for [M+Na⁺] (C₂₆H₃₂NaO₅⁺): m/z 447.2142; found: 447.2145.

Phenyl (S)-4-(4-methoxyphenyl)-2-neopentylpent-4-enoate (40)

According to method B, flash column chromatography (SiO₂: 2% ethyl acetate in petroleum ether) provided this compound in 43% yield (47.3 mg, 0.129 mmol) as colorless oil.

\(^1\)H NMR (600 MHz, Chloroform-d): \(\delta\) 7.29 (d, \(J = 8.6\) Hz, 2H), 7.26 - 7.22 (m, 2H), 7.19 (t, \(J = 7.2\) Hz, 1H), 7.05 (d, \(J = 7.3\) Hz, 2H), 6.86 (d, \(J = 8.6\) Hz, 2H), 5.20 (d, \(J = 1.5\) Hz, 1H), 4.98 (s, 1H), 3.81 (s, 3H), 3.58 (s, 3H), 2.78 (dd, \(J = 13.7, 8.0\) Hz, 1H), 2.62 (q, \(J = 8.5, 8.0\) Hz, 1H), 2.53 (dd, \(J = 13.7, 7.0\) Hz, 1H), 2.40 (s, 2H), 1.84 (dd, \(J = 14.1, 10.3\) Hz, 1H), 1.37 (d, \(J = 14.1\) Hz, 1H), 0.72 (d, \(J = 16.6\) Hz, 6H).

\(^{13}\)C NMR (150 MHz, Chloroform-d): \(\delta\) 177.23, 159.16, 145.11, 138.79, 130.61, 127.61, 127.36, 125.83, 113.70, 113.48, 55.24, 51.37, 48.65, 44.15, 40.80, 40.53, 34.32, 26.41, 25.90.

HRMS (ESI) exact mass calculated for [M+H⁺] (C₂₄H₃₀O₃⁺): m/z 367.2268; found: 367.2267.

Methyl (S)-4-(4-methoxyphenyl)-2-((1-methylcyclopentyl) methyl) pent-4-enoate (41)
According to method B, flash column chromatography (SiO₂: 2% ethyl acetate in petroleum ether) provided this compound in 56% yield (53.1 mg, 0.168 mmol) as colorless oil.

^1^H NMR (600 MHz, Chloroform-d): δ 7.31 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 5.21 (d, J = 1.5 Hz, 1H), 4.99 (d, J = 1.5 Hz, 1H), 3.82 (s, 3H), 3.58 (s, 3H), 2.79 (dd, J = 12.7, 6.6 Hz, 1H), 2.59 - 2.50 (m, 2H), 1.84 (dd, J = 13.9, 9.7 Hz, 1H), 1.59 - 1.52 (m, 4H), 1.46 (dd, J = 14.0, 2.2 Hz, 1H), 1.27 - 1.19 (m, 4H), 0.78 (s, 3H).

^1^C NMR (150 MHz, Chloroform-d): δ 177.34, 159.13, 145.21, 132.83, 127.32, 113.68, 113.23, 55.24, 51.33, 43.90, 42.10, 41.56, 40.49, 39.66, 39.06, 25.02, 24.12, 23.78.


Phenyl (S)-4-(4-methoxyphenyl)-2-neopentylenpent-4-enoate (42)

According to method B, flash column chromatography (SiO₂: 2% ethyl acetate in petroleum ether) provided this compound in 52% yield (53.7 mg, 0.156 mmol) as colorless oil.

^1^H NMR (600 MHz, Chloroform-d): δ 7.31 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 5.22 (d, J = 1.5 Hz, 1H), 4.99 (s, 1H), 3.82 (s, 3H), 3.59 (s, 3H), 2.80 (q, J = 6.0 Hz, 1H), 2.56 - 2.47 (m, 2H), 1.78 (dd, J = 14.3, 9.7 Hz, 1H), 1.45 (d, J = 4.5 Hz, 4H), 1.35 - 1.29 (m, 6H), 1.21 - 1.18 (m, 3H), 0.68 (s, 3H).

^1^C NMR (150 MHz, Chloroform-d): δ 177.53, 159.14, 145.15, 132.72, 127.35, 113.68, 113.39, 55.24, 51.36, 44.17, 40.79, 40.69, 40.16, 40.00, 36.00, 30.75, 30.64, 26.91, 22.82, 22.68.

HRMS (ESI) exact mass calculated for [M+H]^+ (C₂₂H₃₃O₃^+): m/z 345.2424; found: 345.2425.
Part 8. Cyclization/Allylation Reactions

3,3-Dimethyl-4-(2-methyl-4-phenylpent-4-en-2-yl) tetrahydrofuran (43)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 61% yield (23.6 mg, 0.0915 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 7.38 (d, $J = 7.3$ Hz, 2H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.29 - 7.25 (m, 1H), 5.29 (d, $J = 1.9$ Hz, 1H), 5.07 (d, $J = 1.9$ Hz, 1H), 4.00 (t, $J = 8.6$ Hz, 1H), 3.94 - 3.88 (m, 1H), 3.43 (s, 2H), 2.65 - 2.49 (m, 2H), 1.91 (t, $J = 9.5$ Hz, 1H), 1.17 (s, 3H), 1.11 (s, 3H), 0.88 (s, 3H), 0.84 (s, 3H).

$^{13}$C NMR (150 MHz, Chloroform-$d$): $\delta$ 146.80, 143.88, 128.20, 127.04, 126.47, 117.53, 83.36, 69.92, 56.93, 47.63, 41.71, 36.99, 26.89, 26.45, 26.04, 22.99.

HRMS (ESI) exact mass calculated for [M+Na$^+$] (C$_{18}$H$_{26}$NaO$^+$): m/z 281.1876; found: 281.1883.

3,3-Dimethyl-4-(3-phenylbut-3-en-1-yl) tetrahydrofuran (44)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 39% yield (13.5 mg, 0.0585 mmol) as colorless oil.

$^1$H NMR (400 MHz, Chloroform-$d$): $\delta$ 7.41 - 7.26 (m, 5H), 5.28 (d, $J = 1.4$ Hz, 1H), 5.07 (d, $J = 1.4$ Hz, 1H), 4.11 (t, $J = 8.1$ Hz, 1H), 3.57 - 3.43 (m, 3H), 2.55 - 2.37 (m, 2H), 1.91 - 1.79 (m, 1H), 1.59 (dtt, $J = 10.2$, 6.7, 3.6 Hz, 2H), 0.96 (s, 3H), 0.87 (s, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$): $\delta$ 148.30, 140.97, 128.32, 127.42, 126.06, 112.55, 81.41, 73.14, 48.38, 40.63, 34.61, 26.21, 24.39, 20.57.

HRMS (ESI) exact mass calculated for [M+H$^+$] (C$_{16}$H$_{23}$O$^+$): m/z 231.1743; found: 231.1747.

3,3-Dimethyl-4-((R)-4-phenylpent-4-en-2-yl) tetrahydrofuran (45)

According to method A, flash column chromatography (SiO$_2$: 2% ethyl acetate in petroleum ether) provided this compound in 41% yield (15.0 mg, 0.0615 mmol) as colorless oil.

$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 7.43 - 7.37 (m, 4H), 7.34 - 7.31 (m, 1H), 5.33 (s, 1H), 5.09
(S)-3,3-Dimethyl-5-phenylhex-5-en-1-yl-4-d benzoate (12a-d)

According to method A, flash column chromatography (SiO₂: 2% ethyl acetate in petroleum ether) provided this compound in 72% yield (33.4 mg, 0.108 mmol) as colorless oil.

¹H NMR (600 MHz, Chloroform-d): δ 8.02 (d, J = 7.0 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.38 (d, J = 7.3 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 5.29 (d, J = 1.9 Hz, 1H), 5.08 (d, J = 1.1 Hz, 1H), 4.34 (t, J = 7.3 Hz, 2H), 2.56 (d, J = 10.9 Hz, 1H), 1.68 (t, J = 7.3 Hz, 2H), 0.87 (s, 6H).

¹³C NMR (150 MHz, Chloroform-d): δ 166.63, 146.76, 143.56, 132.76, 130.45, 129.48, 128.28, 128.19, 127.07, 126.50, 117.10, 62.29, 47.23, 47.11, 46.98, 40.30, 33.60, 27.69, 27.67, 27.65.

²D NMR (61 MHz, CHCl₃) δ 2.58.

HRMS (ESI) exact mass calculated for [M+Na⁺] (C₂₁H₂₃DNaO₂⁺): m/z 332.1731; found: 332.1737.
II. Spectral Data for New Compounds

\[
\text{O} \quad \text{OCO} \text{Me}
\]

- \( \delta \approx 1.2 \) ppm
- \( \delta \approx 1.8 \) ppm
- \( \delta \approx 2.0 \) ppm
- \( \delta \approx 5.6 \) ppm

- \( \delta \approx 6.6 \) ppm
- \( \delta \approx 6.9 \) ppm
- \( \delta \approx 7.1 \) ppm

- \( \delta \approx 128.4 \) ppm
- \( \delta \approx 128.4 \) ppm
- \( \delta \approx 141.4 \) ppm

- \( \delta \approx 141.4 \) ppm
- \( \delta \approx 151.4 \) ppm
- \( \delta \approx 155.5 \) ppm
S63

\[
\text{\text{OCOOMe}}
\]
20

\[
\text{Boc}
\]

\[
\text{Ph}
\]
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DEPT-135
HMOC
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<td></td>
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3b
III. References


(8) Nagasawa, S.; Sasano, Y.; Iwabuchi, Y. Synthesis of 1,3-Cycloalkadienes from Cycloalkenes:


