Chapter 3 – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

Acknowledgment: Results presented in this chapter was carried out together with J.T. Bauer, who performed the reactions in Table 1 (Entries 1-11) and Table 4. All other reactions presented in this chapter were the work of the author.
3.1 Introduction

Since the 1850’s when Alexander Williamson first developed the synthesis of ethers\(^1\) the process has become vital in both research and industry alike. Although the Williamson ether synthesis reaction is the most widely used in the formation of ethers, the harsh basic conditions and often high temperatures can lead to undesirable side reactions. Further complications can arise upon the use of more sterically encumbered reagents which will either prove to be unreactive, or when attempting to form tertiary ethers, the elimination pathway is more highly favoured.\(^2\), \(^3\)

![Figure 1 Tertiary Alkyl Allylic Ether](image1)

Thus, alkyl-tertiary allylic ethers (3.1, Figure 1) are difficult to make via conventional methods. Although tertiary allylic alcohols are easy to access (via vinyl Grignard addition to ketones, for example), attempted etherification of the corresponding sterically hindered alkoxides (with an alkyl halide) tends to lead to the elimination rather than the substitution pathway.

![Figure 2 Vinylglycidol](image2)

A possible route to access tert-allylic ethers was devised by Trost et. al. as they were attempting to enantioselectively synthesise vinylglycidols (3.2, Figure 2) by adding an alcohol to a vinyl-epoxide, unfortunately, they found that the palladium catalysed reaction does not proceed.\(^4\) However, upon the addition of tri-alkyl boranes, the reactivity of the alcohols increased and upon optimisation of the co-catalyst the reaction became regio-, chemo-, and enantioselective (Scheme 1).\(^4\)
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

Scheme 1 Tertiary Allylic Ether Formation via Alcohol Additions to Epoxides

Forming tertiary allylic ethers from epoxides (Scheme 1), although very effective in terms of yield and selectivities, is limited by the scope of the epoxides and appears only effective in the production of vinylglycidols.

Scheme 2 Secondary Allylic Ether Formation

While exploring rhodium catalysed allylic etherification with secondary alcohols to form secondary allylic ethers (Scheme 2), Evans showed that using a tertiary alcohol and increased catalyst loading, successfully produced a tertiary allylic ether (Scheme 3).

Scheme 3 Tertiary Allylic Ether Formation
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The reaction produces reasonable yield and selectivity but unfortunately there appears to be no real scope with this reaction to make a range of various tertiary allylic ethers. In recent years the synthetic routes to primary, secondary and even tertiary ethers have been improved,\textsuperscript{6,7} however, good, general and easily achievable reactions had not been published for the formation of tertiary alkyl allylic ethers when the work described in this chapter was initiated.
3.2 Results and Discussion

After the initial investigations into gold(I) activation of cyclopropenes yielded the rearrangement products (Chapter 2) we were eager to examine our hypothesis that gold(I) could be an effective catalyst in the activation of cyclopropenes towards an external nucleophile, such as alcohol.

We had already observed that when the ester moiety was present, the cyclopropene would rearrange upon activation by gold(I) (Scheme 10, Chapter 2). We decided to replace the ester group with an alkyl (R and R' in 3D), removing the possibility of intramolecular rearrangement, and thus giving the external alcohol a chance to react. The cyclopropene was made by forming the dibromocyclopropane 3B from the alkene 3A, which was then partially reduced to produce 3C and HBr was eliminated to give the cyclopropenes 3D used in this chapter (Scheme 4).

![Scheme 4 Cyclopropene Formation](image)

We began the study by looking at a range of alcohols to investigate if gold(I) would catalyse the reaction of cyclopropenes in the presence of nucleophiles. During our initial studies, we found that gold(I) could indeed catalyse the intermolecular addition of alcohols to 3,3-disubstituted cyclopropene 3.13 in a highly regioselective manner to produce alkyl tert-allylic ethers, 3E, in good yields (Table 1). Primary alcohols add with good yields and excellent regioselectivities (Entries 1-7). Pleasingly isopropanol also added with good yields and selectivities (Entry 9, 70% yield, 97:3) however, tertiary alcohols do not react under these conditions (<5% conversion, Entry 10). The steric bulk of the tertiary alcohol is very likely to blame for the diminished activity. Water can successfully act as a nucleophile to produce the corresponding tertiary alcohol, albeit in low conversion and yield due to solubility issues (34%, Entry 11). An attempt to replace the alcohol nucleophile with a phenol, however, was not successful (Entry 12), presumably due to the reduced
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

nucleophilicity of phenol. Throughout the initial alcohol screen the air stable gold(I) catalyst, PPh₃AuNTf₂,⁹ was utilised as it was easier to handle and, in most cases, outperformed PPh₃AuOTf (formed in situ with PPh₃AuCl and AgOTf, Entries 2-3, 8-9). Due to the enhanced activity observed and the ease of use of PPh₃AuNTf₂ it became the catalyst of choice for the rest of the study.

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<table>
<thead>
<tr>
<th>Entryᵃ</th>
<th>ROH</th>
<th>Method</th>
<th>Yield of 3E</th>
<th>Product</th>
<th>Ratio 3E:3Fᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1ᵉ</td>
<td>MeOH</td>
<td>B</td>
<td>86%</td>
<td>3.14</td>
<td>&gt;99:1</td>
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<tr>
<td>2ᵉ</td>
<td>EtOH</td>
<td>A</td>
<td>64%</td>
<td>3.15</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>3ᵉ</td>
<td>EtOH</td>
<td>B</td>
<td>83%</td>
<td>3.15</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>4ᵉ</td>
<td>Allyl alcohol</td>
<td>B</td>
<td>88%</td>
<td>3.16</td>
<td>&gt;99:1</td>
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<tr>
<td>5ᵉ</td>
<td>Benzyl alcohol</td>
<td>A</td>
<td>78%</td>
<td>3.17</td>
<td>&gt;99:1</td>
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<tr>
<td>6ᵉ</td>
<td>HOCH₂CH₂CH=CH₂</td>
<td>B</td>
<td>88%</td>
<td>3.18</td>
<td>&gt;99:1</td>
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<td>7ᵉ</td>
<td>HOCH₂CH₂Ph</td>
<td>B</td>
<td>77%</td>
<td>3.19</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>8ᵉ</td>
<td>i-PrOH</td>
<td>A</td>
<td>N/A</td>
<td>3.20</td>
<td>2.5:1</td>
</tr>
<tr>
<td>9ᵉ</td>
<td>i-PrOH</td>
<td>B</td>
<td>70%</td>
<td>3.20</td>
<td>97:3</td>
</tr>
<tr>
<td>10ᵉ</td>
<td>t-BuOH</td>
<td>B</td>
<td>traces</td>
<td>3.21</td>
<td>N/A</td>
</tr>
<tr>
<td>11ᵈ,ᵉ</td>
<td>H₂O</td>
<td>B</td>
<td>34%</td>
<td>3.22</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>12</td>
<td>4-methoxyphenol</td>
<td>B</td>
<td>-</td>
<td>-</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 1 Initial Alcohol and Gold(I)Catalyst Screen

ᵃ All reactions were carried out at 20 °C in CH₂Cl₂ for 1-2 h unless otherwise stated. ᵇ Determined by ¹H-NMR analysis of the crude mixture. ᶜ Reaction was allowed to stir for 4 days, after which ~50% conversion was observed. ᵈ 15 eq. of t-BuOH was added as a co-solvent and the reaction was allowed to stir for 24 h. ᵉ Reactions carried out by J. T. Bauer.

The reactions with primary alcohol nucleophiles such as EtOH (Entry 3, Table 1) are facile and often complete within 10 min with 5 mol% catalyst. Repeating the experiment in Entry 3 and reducing the gold(I) catalyst loading (1 mol%) is not detrimental to the reaction, producing complete conversion to the tert-allylic ether (>99% regioselectivity) within 1.5 h.
After observing how efficient a range of nucleophile alcohols can attack cyclopropene 3.13, we wanted to expand the scope of the cyclopropenes and investigate what effect that would have on the reaction (Table 2).

Changing a substituent from alkyl (e.g. Entries 1-2) to benzyl has no detrimental effect on the regioselectivity or yield (Entries 3-4). Even more sterically encumbered 3,3 cyclopropenes with substituents such as isopropyl and benzyl allow the nucleophile alcohol to attack producing excellent regioselectivity and good yield (>99:1, 73%, Entry 5). Remarkably, a cyclopropene with the more sterically hindered tert-butyl substituent still provides good regioselectivity (87:1) with a primary alcohol nucleophile at room temperature (Entry 6). Upon cooling the reaction mixture down to 0 °C, excellent regioselectivity (>99:1) is observed with a moderate 64% yield. When combining a sterically hindered cyclopropene with a hindered secondary alcohol, the regioselectivity and yield begins to drop (92:8, 45%, Entry 7).

Aryl substituents are also tolerated (Entries 8 and 9) which was encouraging since there is literature precedence for intramolecular rearrangements of aryl substituted cyclopropenes to form indenes in the presence of gold(I). It is pleasing that intermolecular alcohol additions are observed although the results with respects to regioselectivity are rather surprising. Reaction with nBuOH under standard conditions produces a non-regioselective 1:1 mixture of primary and tertiary ethers. Reducing the temperature to 10 °C and increasing the alcohol to 15 equivalents successfully yields the tertiary ether regioselectively (65%, Entry 8). Surprisingly, changing the alcohol nucleophile to phenethyl alcohol completely switches the regioselectivity to the primary ether 3.35 (Entry 9, 3.35 formed regio- and stereoselectively, 65%)! These results suggest that with aryl substituted cyclopropene 3.27, nBuOH might be more effective in inhibiting the isomerisation of the tert-allylic ether product 3.34 to the primary allylic ether (vide infra). One possible explanation is that the O-bound Au(I) complex with phenethyl alcohol is in equilibrium with the Au(I)-arene complex, which might still be catalytically active for isomerisation of the tertiary allylic ether to primary. Examples of stable Au(I)-arene complexes are known although it should be noted that phenethyl alcohol is not a problematic reagent for 3,3-dialkyl-substituted cyclopropene 3.13 (Entry 7,
Table 1), suggesting that the presence of aryl substituents facilitates allylic isomerisation.

We were keen to increase the complexity of our tertiary allylic ethers and introducing a diol would help us achieve this. We postulated that the unprotected diol (Entry 10) would react chemoselectively at the primary alcohol since tertiary alcohols do not react under these conditions. Indeed, the reaction proceeds smoothly, chemo- and regioselectively to produce the tertiary allylic ether in 58% yield (Entry 10). Neopentyl glycol, however, behaves differently and forms a 1:1 mixture of primary and tertiary ether products under standard conditions (room temperature, Entry 11). Due to the proximity of a pendant alcohol, we postulate that it promotes the gold(I)-catalysed isomerisation of the tertiary to primary ether (vide infra). Cooling the reaction mixture increases the regioselectivity (>99:1) but the yield remains modest (44%) due to oligomeric by-products being formed.

When optically pure (R)-PhMeCHCH₂OH is employed as the nucleophile, the reaction is still regioselective, but not diastereoselective (Entry 12). Even employment of a secondary chiral alcohol (R)-PhMeCHOH with a more sterically encumbered cyclopropene results in no diastereoselectivity (d.r. ~1:1), although the regioselectivity is still good (96:4, Entry 13).
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

![Chemical Reaction Diagram](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cyclopropene</th>
<th>ROH</th>
<th>Product</th>
<th>Yield</th>
<th>Regioselectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="Cyclopropene" /></td>
<td><img src="image" alt="ROH" /></td>
<td><img src="image" alt="Product" /></td>
<td>83%</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Cyclopropene" /></td>
<td><img src="image" alt="ROH" /></td>
<td><img src="image" alt="Product" /></td>
<td>87%</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="Cyclopropene" /></td>
<td><img src="image" alt="ROH" /></td>
<td><img src="image" alt="Product" /></td>
<td>80%</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="Cyclopropene" /></td>
<td><img src="image" alt="ROH" /></td>
<td><img src="image" alt="Product" /></td>
<td>86%</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>5</td>
<td><img src="image" alt="Cyclopropene" /></td>
<td><img src="image" alt="ROH" /></td>
<td><img src="image" alt="Product" /></td>
<td>73%</td>
<td>&gt;99:1</td>
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<td>6</td>
<td><img src="image" alt="Cyclopropene" /></td>
<td><img src="image" alt="ROH" /></td>
<td><img src="image" alt="Product" /></td>
<td>64%</td>
<td>&gt;99:1 (0 °C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>87:1 (20 °C)</td>
</tr>
<tr>
<td>7</td>
<td><img src="image" alt="Cyclopropene" /></td>
<td><img src="image" alt="ROH" /></td>
<td><img src="image" alt="Product" /></td>
<td>45%</td>
<td>92:8</td>
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<tr>
<td>8</td>
<td><img src="image" alt="Cyclopropene" /></td>
<td><img src="image" alt="ROH" /></td>
<td><img src="image" alt="Product" /></td>
<td>65%</td>
<td>&gt;99:1</td>
</tr>
</tbody>
</table>
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

9

(3.27)  

(3.35)  

65%  >1:99

10

(3.13)  

(3.36)  

58%  >99:1

11

(3.13)  

(3.37)  

16%  1:1 (20 °C)  

45%  >99:1 (10 °C)

12

(3.13)  

(3.38)  

65%  \(\text{dr} \sim 1:1\)

13

(3.24)  

(3.39)  

46%  96:4  \(\text{dr} \sim 1:1\)

\(^a\) All reactions carried out with \(\text{PPh}_3\text{AuNTf}_2\) (5 mol\%) and 6 equiv. ROH at 20 °C in \(\text{CH}_2\text{Cl}_2\) for 1-2 h unless otherwise stated. \(^b\) Isolated yield, unless otherwise stated. \(^c\) Determined by \(^1\)H-NMR analysis of the crude mixture. Regioselectivity of the tertiary:primary allylic ether product. \(^d\) Reaction was carried out at 0 °C for 16 h. \(^e\) 15 Equiv. ROH, 10 °C, 4 h. \(^f\) Reaction carried out with 2 equiv. diol for 16 h.

Table 2 Expanding The Cyclopropene Scope of Gold(I) Catalysed Additions of Alcohols

A catalyst screen shows gold(I) catalysts to be unique in their selectivity for the tertiary allylic ether product 3.25 (Table 3). The gold(I) catalyst \(\text{PPh}_3\text{AuOTf}\), formed \textit{in situ} from \(\text{PPh}_3\text{AuCl}\) and AgOTf results in excellent selectivity for 3.25 and moderately good isolated yield (64% 3.25, Entry 1). Changing the silver co-catalyst from AgOTf to AgSbF\(_6\) does not affect the selectivity, but the isolated yield is slightly lower (55% 3.25, Entry 2). Switching from \(\text{PPh}_3\) to an \(N\)-heterocyclic carbene (NHC) ligand on Au(I) [(IPr)AuCl/AgOTf] also provides 3.25 exclusively (69%, Entry 3). The gold (I) catalysts so far are activated \textit{in situ} via the co-catalyst, a hygroscopic silver salt, resulting in the possibility of there being slight traces of TfOH, HSbF\(_6\) or [LAu-OH\(_2\)]\(^+\) present during the reaction. When the air stable \(\text{PPh}_3\text{AuNTf}_2\), which does not require any hygroscopic co-catalyst, is used the
reaction produces an even better yield of the product 3.25 (83%, Entry 4).

In an effort to ascertain whether the reaction is truly gold-catalysed, we carried out some control reactions. Employing 5 mol% of TfOH as catalyst results in no reaction, suggesting that traces of acid are not catalytically active (Entry 5). Silver salts have been known to activate π-systems, however the reaction with Ag(OTf) as the catalyst is also greatly inferior to gold(I), resulting in incomplete consumption of the cyclopropene, along with a complex mixture of products (Entry 6). Rhodium (II) catalysts are believed to ring-open related cyclopropenes to form the corresponding rhodium carbene intermediates, so we wanted to see if Rh(OAc)$_2$ could catalyse this reaction. Although employment of Rh(OAc)$_2$ as a catalyst seems to cause ring-opening, the reactivity differs from that of Au (I) and produces a mixture of the aldehyde 3.41, along with traces of both 3.25 and 3.40 (Entry 7). Interestingly, the use of Au(III) instead of Au(I) catalyst also completely changes the outcome of the reaction, with the aldehyde 3.41 being the major product (Entry 8). This difference in reactivity illustrates the contrast in gold(I) and gold(III) as catalysts.
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

![Catalyst Screen](image)

<table>
<thead>
<tr>
<th>Entry&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Catalyst</th>
<th>Time</th>
<th>Result and Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PPh₃AuCl/AgOTf</td>
<td>1.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.25&lt;sup&gt;b&lt;/sup&gt; only, 64% yield</td>
</tr>
<tr>
<td>2</td>
<td>PPh₃AuCl/AgSbF₆</td>
<td>1.5</td>
<td>3.25&lt;sup&gt;b&lt;/sup&gt; only, 55% yield</td>
</tr>
<tr>
<td>3</td>
<td>(IPr)AuCl/AgOTf</td>
<td>1.5</td>
<td>3.25&lt;sup&gt;b&lt;/sup&gt; only, 69% yield</td>
</tr>
<tr>
<td>4</td>
<td>PPh₃AuNTf₂</td>
<td>1.5</td>
<td>3.25&lt;sup&gt;b&lt;/sup&gt; only, 83% yield</td>
</tr>
<tr>
<td>5</td>
<td>HOTf</td>
<td>24</td>
<td>No reaction&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>AgOTf</td>
<td>24</td>
<td>7:4 ratio of 3.13:3.25 along with traces of 3.40, 3.41 and other unidentified by-products&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>7</td>
<td>Rh(OAc)₂</td>
<td>24</td>
<td>Major product: 3.41 (with traces of 3.25 and 3.40 with other unidentified by-products)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>8</td>
<td>AuCl₃</td>
<td>24</td>
<td>Complex mixture of products: 3.41 (with traces of 3.25 and 3.40 with other unidentified by-products)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> No change in yield or selectivity is observed if the reaction is allowed to stir for 24 h. <sup>b</sup> Isolated yield; 3.40 and 3.41 were not detected by <sup>1</sup>H-NMR analysis of the crude mixture. <sup>c</sup> By <sup>1</sup>H-NMR analysis of the crude mixture. (IPr = NHC ligand bis-2,6-diisopropylphenyl imidazolyldiene)

**Table 3 Catalyst Screen**

Our proposed mechanism for the regioselective gold(I) catalysed ring-opening addition of cyclopropene 3.13 with alcohols is shown in Scheme 5. The strained cyclopropene double bond is activated by gold(I) resulting in ring-opening to produce the proposed intermediate I, which can be represented as mesomeric structures II, III or IV. Alcohol is then able to attack at the C-3 position followed by protodemetalation producing the tert-allylic ether 3.25.
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

In order to probe the validity of our proposed mechanism, the reaction was carried out using CD$_3$OD as the nucleophilic alcohol (Scheme 6). Deuterium becomes incorporated at the C-1 position (90%), lending support to our proposed mechanism.

Throughout the study it became apparent that an excess of alcohol is necessary to ensure good regioselectivity (Table 4). When the amount of alcohol nucleophile is reduced from excess to 1 equivalent, the regioselectivity of 3.25:3.40 drops from >99:1 to 2:1. However, when the reaction is carried out with 1 equiv. of EtOH and 5 equiv. of t-BuOH, as an additive, we observe excellent regioselectivity again (>99% 3.25, 64% yield). This means the alcohol nucleophile need not be in excess, as long as a non-reactive alcohol such as t-BuOH is present in excess to help maintain the high regioselectivities. Should an expensive alcohol nucleophile need to be employed we are able to introduce a cheap, non-reacting alcohol additive to lower the costs of the reaction. Temperature also seems to have an effect on regioselectivities, carrying out the reaction at ~25 °C rather than 20 °C resulted in a 96:4 ratio of 3.25:3.40 (c.f. >99:1 at 20 °C). When the ambient temperature is >20 °C, the reaction should thus be cooled to 15-20 °C to maintain good regioselectivities.
Next, we wanted to explain the need for excess alcohol to ensure good regioselectivity. In order to do this the tert-allylic ether product 3.25 was isolated and then resubjected to the reaction conditions in the absence and presence of excess methanol (Scheme 7). Under gold(I)-catalysis conditions and with no alcohol present the tertiary ether 3.25 isomerises to the primary ether 3.40. When the reaction is repeated with the addition of excess alcohol, no reaction occurs, meaning the alcohol seems to stop this isomerisation. The isomerisation 3.25→3.40 is not reversible, both in the absence and presence of excess MeOH, even under prolonged reaction times. The isomerisation appears to be catalyst dependent as subjection of 3.25 to NHC-gold catalyst (IPr)AuCl/AgOTf (5 mol%) in CH₂Cl₂ at room temperature results in no reaction. In contrast, PPh₃AuCl/AgOTf (5 mol%) results in a mixture of 3.25, 3.40 and other unidentified by-products after 1 hour at room temperature. The inability of (IPr)AuOTf to isomerise tert-allylic ethers could be due to either the steric bulk of the IPr ligand, or the less electrophilic gold(I) centre caused by the more σ-donating NHC catalyst.

Table 4 The Effect of Excess Alcohol

<table>
<thead>
<tr>
<th>Entry</th>
<th>Equivalents of EtOH</th>
<th>Ratio 3.25:3.40</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2:1</td>
</tr>
<tr>
<td>4</td>
<td>1 + 5 equiv. tBuOH</td>
<td>&gt;99:1</td>
</tr>
</tbody>
</table>

*aReactions carried out by J. T. Bauer

Scheme 7 Effect of Alcohol on the Isomerisation
From these results we propose that the gold(I) catalysed addition of alcohols to 3,3-disubstituted cyclopropenes \(3D\) occurs regioselectively to produce the kinetic tert-allylic ether product \(3G\). In the absence of excess alcohol, this kinetic product can be isomerised by gold(I) to the more stable primary allylic ether \(3H\) (Scheme 8). A related conclusion was proposed \(via\) DFT studies for gold(I)-catalysed hydroalkoxylation of allenes to form primary allylic ethers. In the presence of excess alcohol, we postulate that the gold(I) catalyst \(\text{PPh}_3\text{AuNTf}_2\) is deactivated, through the possible formation of \([\text{LAu-O(H)R}]^+\) complex, leaving the catalyst unable to isomerise \(3G\rightarrow3H\), thus excellent regioselectivity for the tertiary ether \(3G\) is observed.

\[ \text{Scheme 8 Alcohol Stops Isomerisation from Tertiary to Primary Allylic Ether} \]

As the NHC catalyst (IPr)AuOTf does not isomerise tertiary ether \(3.25\) to primary ether \(3.40\) even in the absence of excess alcohol \(\text{vide supra}\), in principle we should not need to use excess alcohol in order to achieve good selectivities with this catalyst system. The alcohol addition to cyclopropene \(3.13\) was repeated using (IPr)AuCl/AgOTf (5 mol%) with only 1 equiv. of alcohol and indeed, only the tertiary ether \(3.25\) is observed (Scheme 9). The isolated yield, however, is not as high as with \(\text{PPh}_3\text{AuNTf}_2\) as catalyst under our standard conditions (51\% vs. 83\%).

\[ \text{Scheme 9 NHC Ligand Effect – No Isomerisation} \]

After a successful study into the gold(I) catalysed regioselective additions of alcohols to cyclopropenes we were keen to look into the possibility of carrying out the reaction enantioselectively.
Although enantioselective gold(I) catalysis is in its infancy with relatively few publications in the literature, enantioccontrol can be achieved in gold(I) catalysis by either the ligand\textsuperscript{19-22} or the counterion\textsuperscript{23} being optically active. As a first step, we hypothesized that it may be possible to achieve some enantioselectivity by employing chiral ligands on the gold(I) catalyst and keeping the counterion the same. We opted to employ the (R)-DTBM-segPhos(AuCl)\textsubscript{2} catalyst (Figure 3) as it is commercially available, and to give the reaction the best opportunity to deliver enantioselectivity, we decided to use the more sterically encumbered cyclopropenes at 0 °C. Finally to examine the results of the reaction we would have to use chiral HPLC in an attempt to separate the enantiomers.

![Figure 3 (R)-DTBM-segPhos(AuCl)\textsubscript{2}]

Although due to time constraints we were not able to complete the entire study, we were able to produce some preliminary results (Table 5). The initial reaction was carried out with cyclopropene 3.26 and phenethyl alcohol (Entries 1 and 2). Unfortunately we struggled to gain any separation in the HPLC (columns tried – Daicel Chiralcel OD-H, Chiralpak AD and Chiralpak AS) as the final products were very non-polar. Encouragingly the reaction compares well using the chiral gold(I) catalyst as to the non-chiral gold(I) catalyst (64% / 62 % yields with excellent regioselectivity). Repeating the reaction using a diol introduces polarity to the product which will allow greater separation \textit{via} chiral HPLC. Once more the reactions performed well (Entries 3 and 4) but this time we observed 3 – 4 peaks in the chromatogram, even though the \textsuperscript{1}H NMR
showed little signs of impurity. We believed this was due to the chromophore being weak (only a double bond) causing the UV detection parameters to be stretched. We could not definitively confirm which peaks were the enantiomer peaks, however, the diol improved separation. Finally, with an aromatic group in the cyclopropene and tertiary alcohol placed in the product we hoped to gain both good detection and separation during HPLC analysis (Entries 5 and 6), thankfully we were able to gain both. With the racemic reaction (Entry 5) two equally sized peaks were observed in the chromatogram (chiralcel OD-H column) whereas when the chiral gold(I) catalyst was employed (Entry 6) we were able to see a difference in the peak areas which enabled us to calculate that we had achieved 22% ee. This encouraging preliminary result has shown that it is possible to have some degree of enantiocontrol by employing a chiral gold(I) catalyst and we believe that future optimisation of this reaction can deliver much greater levels of enantiopurity in the products.
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\[
3I + \text{ROH} \xrightarrow{\text{A: } \text{PPh}_3\text{AuNTf}_2} \xrightarrow{\text{B: } (R)-\text{DTBM-segPhos(AuCl)}_2 / 2 \text{AgOTf}} 3J
\]

DCM, 0 °C, 48 h
### Table 5 Enantioselective Gold(I) Catalysed Addition of Alcohol to Cyclopropanes

We have been able to demonstrate and explain a highly regioselective gold(I)-catalysed addition of alcohols to 3,3-disubstituted cyclopropenes to produce alkyl tert-allylic ethers in good yields. The reaction is facile (as quick as <10 min), mild...
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(20 °C), efficient (as low as 1 mol% catalyst) with an inert atmosphere and distilled solvents not being required. The reaction is tolerant of sterically hindered substituents on the cyclopropene as well as primary and secondary alcohols as nucleophiles. Future work in this area could concentrate on the optimisation of the gold(I) enantioselective reaction *via* chiral ligand and counterion screening.
3.3 Experimental

General Experimental

$^1$H NMR spectra were recorded on Bruker AC200, AV 300, DPX 400 and AV 400 spectrometers at 200, 300 and 400 MHz respectively and referenced to residual solvent. $^{13}$C NMR spectrum were recorded using the same spectrometers at 50, 75 and 100 MHz respectively. Chemical shifts (δ in ppm) were referenced to tetramethylsilane (TMS) or to residual solvent peaks (CDCl$_3$ at δH 7.26). J values are given in Hz and s, d, dd, t, q and m abbreviations correspond to singlet, doublet, doublet of doublet, triplet, quartet and multiplet. Mass spectra were obtained at the EPSRC National Mass Spectrometry Service Centre in Swansea. Infrared spectra were obtained on Perkin-Elmer Spectrum 100 FT-IR Universal ATR Sampling Accessory, deposited neat or as a chloroform solution to a diamond/ZnSe plate.

Flash column chromatography was carried out using Matrix silica gel 60 from Fisher Chemicals and TLC was performed using Merck silica gel 60 F254 precoated sheets and visualised by UV (254 nm) or stained by the use of aqueous acidic KMnO$_4$ or aqueous acidic ammonium molybdate as appropriate. Reactions that were kept at 0 °C overnight used a jacketed reaction vessel attached to a Julabo FP40 Bohdan mini block temperature controlled recirculator with a Julabo temperature regulator. Tetrahydrofuran was dried by distillation from sodium – benzophenone under nitrogen, dimethylsulfoxide, acetonitrile and toluene were dried over calcium hydride. Petrol ether refers to petroleum ether (40 – 60 %). Dichloromethane (DCM) was purchased from Fisher and used without further purification. All indole substrates were purchased from Aldrich and used without further purification. The gold(I)-catalysed reactions were carried out without the need for dry solvents or inert atmosphere, unless stated otherwise. All other reactions were carried out under an atmosphere of N$_2$ unless otherwise stated.
Cyclopropenes \(3.13, 3.23, 24\; 3.24, 3.25, 3.26\) and \(3.27\) were synthesised following a general procedure by Gevorgyan (Scheme 10).

Scheme 10 General Procedure for Cyclopropene Synthesis

Representative general procedure for cyclopropene synthesis is shown below for 3.13.

3.45, 1,1-Dibromo-2-methyl-2-nonylcyclopropane

Bromoform (30.9 g, 122 mmol) and dichloromethane (5 mL) were added dropwise to a stirring mixture of aqueous sodium hydroxide (30 mL, 11.2 g, 280.0 mmol), cetrimide (2.52 g), 2-methylundec-1-ene (10.3 g, 61.2 mmol) and dichloromethane (10 mL). The mixture was allowed to stir at 25 °C. After 48 h, the reaction mixture was diluted with water (75 mL). Dichloromethane (30 ml) was added and the layers partitioned. The aqueous layer was washed twice with dichloromethane (30 ml). The combined organic layers were washed with brine (50 mL), dried over magnesium sulphate and concentrated under reduced pressure. The resulting material was purified by flash column chromatography (hexanes) and the remaining bromoform was evaporated under high vacuum (10 h, 30 °C) to yield 1,1-dibromo-2-methyl-2-nonylcyclopropane 3.45 (16.8 g, 49.5 mmol, 81%) as a colourless oil.

\(v_{\text{max}}/\text{cm}^{-1} \) 689 s (Br-C); \(\delta_H\) (200 MHz, CDCl\(_3\)) 1.67 – 1.18 (21H, m, alkyl-H), 0.88 (3H, t, \(J = 6.6, \text{H-1}\)); \(\delta_C\) (50 MHz, CDCl\(_3\)) 39.9 (C), 38.8 (CH\(_2\)), 34.8 (CH\(_2\)), 31.8 (CH\(_2\)), 29.7 (C), 29.6 (CH\(_2\)), 29.5 (CH\(_2\)), 29.3 (CH\(_2\)), 26.4 (CH\(_2\)), 22.7 (CH\(_2\)), 22.5 (CH\(_3\)), 14.1 (CH\(_3\)); \(M^+\) (EI) = 338.0245 required \(M = 338.0245\).
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

3.46, 2-Bromo-1-methyl-1-nonylcyclopropane

A solution of ethylmagnesium bromide (1.38 M in Et₂O, 38.6 mL, 53.3 mmol) was added over 1 hour to a stirring solution of 1,1-dibromo-2-methyl-2-nonylcyclopropane 3.45 (14.1 g, 41.5 mmol), Ti(OiPr)₄ (0.235 g, 0.827 mmol) and tetrahydrofuran (100 mL). The solution was allowed to stir for an additional hour at 20 °C. The reaction was quenched by slow addition of water (20 mL), then 20% aqueous sulphuric acid (50 mL) was added and the mixture stirred for 30 minutes. Diethyl ether (50 mL) was added and the layers were partitioned. The aqueous layer was washed further three times with diethyl ether (50 mL). The combined organic layers were washed twice with saturated sodium bicarbonate (50 mL), washed with brine (50 mL), dried over magnesium sulphate and concentrated under reduced pressure. The crude material was purified by flash column chromatography (eluent: petrol ether) to yield a mixture of the two diastereomers of 2-bromo-1-methyl-1-nonylcyclopropane 3.46 (8.25 g, 31.6 mmol, 77%) as a colourless oil.

δH (200 MHz, CDCl₃) 2.82 (1H x 2, m, CHBr), 1.55 – 0.82 (22H x 2, m, alkyl-H), 0.62 (2H x 2, m, CHBrCH₂); δC (50 MHz, CDCl₃) 38.9 (CH₂), 36.4 (CH₂), 31.9 (CH₂), 30.7 (CH₂), 30.1 (CH), 29.8 (CH), 29.7 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 26.5 (CH₂), 26.3 (CH₂), 22.8 (CH₂), 22.7 (CH₂), 22.5 (CH₂), 22.1 (CH₃), 21.3 (C), 21.0 (C), 20.2 (CH₃), 14.1 (CH₃); M⁺(EI) = 260.1121 required M = 260.1140.
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

3.13, 3-Methyl-3-nonylcycloprop-1-ene

Potassium tert-butoxide (12.21 g, 109.0 mmol) and dimethyl sulfoxide (168 mL) were heated to 50 °C and allowed to stir for 30 minutes at this temperature. The solution was cooled to room temperature and 2-bromo-1-methyl-1-nonylcyclopropane 3.46 (14.36 g, 55.0 mmol) was added dropwise over 3 hours. The reaction mixture was allowed to stir for 22 h at 25 °C, then quenched by addition of water (200 mL). Pentane (200 mL) was added and the layers partitioned. The aqueous layer was washed three times with pentane (200 mL). The combined organic layers were washed twice with brine (300 mL), dried over magnesium sulphate and concentrated under reduced pressure. The resulting material was purified by flash column chromatography (pentane) to yield 3-methyl-3-nonylcycloprop-1-ene 3.13 (9.20 g, 51.1 mmol, 93%) as a colourless oil.

$\nu_{\text{max}}/\text{cm}^{-1} 1628 \text{ v w (C=C)}$; $\delta_{\text{H}} (200 \text{ MHz, CDCl}_3) 7.34 (2\text{H, s, C=CH})$, 1.54 – 1.03 (19H, m, alkyl-H), 0.88 (3H, t, $J = 6.4$, CH$_2$CH$_3$); $\delta_{\text{C}} (50 \text{ MHz, CDCl}_3) 122.1$ (CH), 40.2 (CH$_2$), 31.9 (CH$_2$), 29.8 (CH$_2$), 29.6 (CH$_2$), 29.6 (C), 29.4 (CH$_2$), 27.3 (CH$_3$), 27.1 (CH$_2$), 22.7 (CH$_2$), 14.1 (CH$_3$); $M^+$(EI) = 180.1897 required $M = 180.1878$. 

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Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

3.23, Spiro[2.5]oct-1-ene<sup>24</sup>

\[
\begin{align*}
\text{Br} & \quad \text{KO}^+\text{Bu} \quad \text{DMSO, } 20^\circ\text{C}, 48 \text{ h} \quad \text{3.23, 9\%} \\
\end{align*}
\]

\(\nu_{\text{max}}/\text{cm}^{-1}\) 2920 s (C-H), 1678 w (C=C); \(\delta_H\) (200 MHz, CDCl<sub>3</sub>) 7.52 (2H, s, C=CH<sub>2</sub>), 1.45 (6H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 0.90 (4H, t, \(J = 6.2\), C-CH<sub>2</sub>); \(\delta_C\) (50 MHz, CDCl<sub>3</sub>) 123.9 (CH), 39.9 (C), 26.8 (CH<sub>2</sub>), 26.5 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>).

3.24, ((1-Methylcycloallyl)methyl)benzene

\[
\begin{align*}
\text{Br} & \quad \text{KO}^+\text{Bu} \quad \text{DMSO, } 20^\circ\text{C}, 48 \text{ h} \quad \text{3.24, 60\%} \\
\end{align*}
\]

\(\nu_{\text{max}}/\text{cm}^{-1}\) 1629 w (C=C), 1604 w, 1495 m, 1452 m, (Ar C=C); \(\delta_H\) (200 MHz, CDCl<sub>3</sub>) 7.28 (2H, s, C=CH), 7.25-7.00 (5H, m, ArH), 2.70 (2H, s, CH<sub>2</sub>Ph), 1.12 (3H, s, CH<sub>3</sub>); \(\delta_C\) (50 MHz, CDCl<sub>3</sub>) 141.1 (C), 129.2 (CH), 128.0 (CH), 125.5 (CH), 122.0 (CH), 47.7 (CH<sub>2</sub>), 26.8 (CH<sub>3</sub>), 21.6 (C); M<sup>+</sup>(El) = 143.0853 required \(M = 143.0855\).

3.25, ((1-Isopropylcycloallyl)methyl)benzene

\[
\begin{align*}
\text{Br} & \quad \text{KO}^+\text{Bu} \quad \text{DMSO, } 20^\circ\text{C}, 48 \text{ h} \quad \text{3.25} \\
\end{align*}
\]

\(\nu_{\text{max}}/\text{cm}^{-1}\) 2956 m (C-H), 1630 w (C=C), 1604, 1495, 1453 (Ar C=C); \(\delta_H\) (200 MHz, CDCl<sub>3</sub>) 7.36-7.00 (7H, m, Ar-H + C=CH<sub>2</sub>), 2.84 (2H, s, CH<sub>2</sub>), 1.90 (1H, sept, \(J = 6.6\), CH<sub>3</sub>), 0.72 (6H, d, \(J = 6.6\), (CH<sub>3</sub>)<sub>2</sub>); \(\delta_C\) (50 MHz, CDCl<sub>3</sub>) 141.1 (C), 129.6 (CH), 128.1 (CH), 116.8 (CH), 43.8 (CH<sub>2</sub>), 32.4 (CH), 31.9 (C), 20.2 (CH<sub>3</sub>).
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3.26, 3-tert-Butyl-3-methylcycloprop-1-ene

\[
\begin{align*}
\text{Br} & \quad \xrightarrow{\text{KO}^\text{Bu}_\text{DMSO}, 20 \, ^\circ\text{C}, 48 \, \text{h}} \quad \text{3.26 55\%}
\end{align*}
\]

\(\nu_{\text{max/ cm}^{-1}}\) 2956, 2868 (C-H), 1629 md (C=C); \(\delta_H\) (200 MHz, CDCl\(_3\)) 7.32 (2H, s, C=CH\(_2\)), 1.10 (3H, s, CH\(_3\)), 0.79 (9H, s, CH\(_3\)); \(\delta_C\) (50 MHz, CDCl\(_3\)) 120.6 (CH), 31.2(C), 28.7 (CH\(_3\)), 28.1 (C), 23.0 (CH\(_3\)). LR-Cl m/z = 111.0 [M+H]\(^+\)

3.27, (1-Methylcycloallyl)benzene

\[
\begin{align*}
\text{Br} & \quad \xrightarrow{\text{KO}^\text{Bu}_\text{DMSO}, 20 \, ^\circ\text{C}, 48 \, \text{h}} \quad \text{3.27 100\%}
\end{align*}
\]

\(\nu_{\text{max/ cm}^{-1}}\) 2969 md (C-H), 1638 md (C=C), 1578, 1492, 1444 (Ar C=C); \(\delta_H\) (200 MHz, CDCl\(_3\)) 7..33-7.00 (7H, m, Ar-H, C=CH\(_2\)), 1.58 (3H, s, CH\(_3\)); \(\delta_C\) (50 MHz, CDCl\(_3\)) 149.7 (C), 128.1 (CH), 125.9 (CH), 124.8 (CH), 115.2 (CH), 25.2 (CH\(_3\)), 21.6 (C).

General Procedure: Gold(I) catalysed addition of alcohols to cyclopropene 3.13

Method A: Ph\(_3\)PAuCl (5 mol%) and AgOTf (5 mol%) were added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (1 eq.) and ROH (6 eq.) in dichloromethane (0.55 M). The reaction mixture was allowed to stir for 1-2 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography to yield the corresponding tert-allylic ether product.

Method B: Ph\(_3\)PAuNTf\(_2\) (as the 2:1 toluene adduct) (5 mol%) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (1 eq.) and ROH (6 eq.) in dichloromethane (0.55 M). The reaction mixture was allowed to stir for 1-2 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography to yield the corresponding tert-allylic ether product.
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3.14, 3-Methoxy-3-methyldodec-1-ene

Ph₃PAuNTf₂ (as the 2:1 toluene adduct) (9.1 mg, 1.15 x 10⁻⁵ mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (48.2 mg, 0.267 mmol) and methanol (48.5 mg, 1.51 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (95% petrol ether, 5% diethyl ether) to yield 3-methoxy-3-methyldodec-1-ene 3.14 (49.0 mg, 0.231 mmol, 86%) as a colourless oil.

υₜₐₓ/cm⁻¹ 1639 vw (C=C), 1079 s (C-O); δ_H (200 MHz, CDCl₃) 5.74 (1H, dd, J = 17.4, 10.8, H-1), 5.15 (1H, dd, J = 10.8, 1.7, H-2), 5.10 (1H, dd, J = 17.4, 1.7, H-3), 3.14 (3H, s, OCH₃), 1.33 - 0.81 (22H, m, alkyl-H); δ_C (50 MHz, CDCl₃) 143.0 (CH), 114.5 (CH₂), 77.4 (C), 50.0 (CH₃), 39.7 (CH₂), 31.9 (CH₂), 30.2 (CH₂), 29.6 (CH₂), 29.3 (CH₂), 23.6 (CH₂), 22.7 (CH₂), 21.2 (CH₃), 14.1 (CH₃); M⁺(EI) = 212.2153 required M⁺ = 212.2140.
**3.15, 3-Ethoxy-3-methylundec-1-ene**

![Diagram of 3.15](image)

Ph₃PAuNTf₂ (as the 2:1 toluene adduct) (11.7 mg, 1.49 x 10⁻⁵ mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (53.6 mg, 0.297 mmol) and ethanol (85.9 mg, 1.86 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 3-ethoxy-3-methylundec-1-ene 3.15 (55.7 mg, 0.246 mmol, 83%) as a colourless oil.

ν_max/cm⁻¹ 1660 vw (C=C), 1070 s (C-O); δ_H (200 MHz, CDCl₃) 5.76 (1H, dd, J = 17.0, 11.2, H-1), 5.12 (1H, dd, J = 11.2, 1.2, H-2), 5.08 (1H, dd, J = 17.0, 1.2, H-3), 3.22 (2H, q, J = 7.1, H-4), 1.62 – 1.19 (19H, m, alkyl-H), 1.14 (3H, t, J = 7.1, H-5), 0.87 (3H, t, J = 6.4, H-6); δ_C (50 MHz, CDCl₃) 143.7 (CH), 113.9 (CH₂), 77.2 (C), 57.3 (CH₂), 39.9 (CH₂), 31.9 (CH₂), 29.6 (CH₂), 29.3 (CH₂), 27.6 (CH₂), 23.6 (CH₂), 22.6 (CH₂), 22.1 (CH₃), 16.0 (CH₃), 14.1 (CH₃); M⁺(EI) = 226.2291 required M = 226.2292.
3.16, 3-(Allyloxy)-3-methyldec-1-ene

Ph₃PAuNTf₂ (as the 2:1 toluene adduct) (11.0 mg, 1.40 x 10⁻⁵ mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (50.0 mg, 0.277 mmol) and 2-propen-1-ol (97 mg, 1.66 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 3-(allyloxy)-3-methyldec-1-ene 3.16 (58.1 mg, 0.244 mmol, 88%) as a colourless oil.

ν_max/cm⁻¹ 1712 vw (C=C), 1646 w (C=C), 1060 s (C-O); δ_H (200 MHz, CDCl₃) 6.00 - 5.70 (2H, m, CH=CH₂ x 2), 5.32 – 5.07 (4H, m, CH=CH₂ x 2), 3.82 (2H, dt, J = 5.4, 1.7, OCH₂), 1.50 – 1.16 (19H, m, alkyl-H), 0.87 (3H, t, J = 6.2, CH₃CH₂); δ_C (50 MHz, CDCl₃) 143.2 (CH), 136.0 (CH), 115.5 (CH₂), 114.4 (CH₂), 77.6 (C), 63.5 (CH₂), 40.1 (CH₂), 31.8 (CH₂), 30.1 (CH₂), 29.6 (CH₂), 29.3 (CH₂), 23.6 (CH₂), 22.7 (CH₂), 21.9 (CH₃), 14.1 (CH₃); [M+NH₄]⁺(ESI) = 256.2636 required M = 256.2635.
3.17, 1-((3-Methyldodec-1-en-3-ylo)xy)methyl)benzene

Ph₃PAuCl (7.2 mg, 14.6 μmol) and AgOTf (3.5 mg, 13.6 μmol) were added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (50.9 mg, 0.282 mmol) and phenylmethanol (180 mg, 1.66 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 2 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 1-((3-methyldodec-1-en-3-yloxy)methyl)benzene 3.17 (63.5 mg, 0.220 mmol, 78%) as a colourless oil.

ν₁ max/cm⁻¹: 1639 vw (C=C), 1607 vw, 1497 w, 1454 m, (Ar C=C), 1060 s (C-O); δ₁H (400 MHz, CDCl₃) 7.38 – 7.24 (5H, m, aryl-H), 5.89 (1H, dd, J = 18.2, 10.3, H-1), 5.22 (1H, dd, J = 10.3, 1.2, H-2), 5.21 (1H, dd, J = 18.2, 1.2, H-3), 4.40 (2H, s, H-4), 1.67 – 1.25 (19H, m, alkyl-H), 0.91 (3H, t, J = 6.9, H-5) ; δ₁C (100 MHz, CDCl₃) 143.4 (CH), 139.9 (C), 128.2 (CH), 127.2 (CH), 127.0 (CH), 114.6 (CH₂), 77.9 (C), 64.4 (CH₂), 40.2 (CH₂), 31.9 (CH₂), 30.2 (CH₂), 29.6 (CH₂), 29.3 (CH₂), 23.7 (CH₂), 22.7 (CH₂), 22.1 (CH₃), 14.1 (CH₃); M⁺(El) = 288.2449 required M = 288.2453.
3.18, 3-(But-3-enyloxy)-3-methyldodec-1-ene

Ph$_3$PAuNTf$_2$ (as the 2:1 toluene adduct) (11.2 mg, $1.42 \times 10^{-5}$ mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (58.4 mg, 0.268 mmol) and 3-buten-1-ol (119 mg, 1.65 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 3-(but-3-enyloxy)-3-methyldodec-1-ene 3.18 (59.6 mg, 0.236 mmol, 88%) as a colourless oil.

$\nu_{max}$/cm$^{-1}$ 1722 vw (C=C), 1641 w (C=C), 1083 s (C-O); $\delta_H$ (200 MHz, CDCl$_3$) 5.92 - 5.69 (2H, m, CH=CH$_2$), 5.15 – 4.96 (4H, m, CH=CH$_2$ x 2), 3.03 (2H, dt, $J = 1.2, 7.1$, OCH$_2$), 2.27 (2H, m, CH$_2$CH=CH$_2$), 1.50 – 1.18 (19H, m, alkyl-H), 0.87 (3H, t, $J = 5.8$, CH$_2$CH$_3$); $\delta_C$ (50 MHz, CDCl$_3$) 143.5 (CH), 135.7 (CH), 115.9 (CH$_2$), 114.1 (CH$_2$), 77.2 (C), 61.5 (CH$_2$), 39.9 (CH$_2$), 35.0 (CH$_2$), 31.8 (CH$_2$), 30.1 (CH$_2$), 29.6 (CH$_2$), 29.3 (CH$_2$), 23.6 (CH$_2$), 22.7 (CH$_2$), 21.9 (CH$_3$), 14.1 (CH$_3$); [M+NH$_4$]$^+$ (ESI) = 270.2793 required $M = 270.2791$. 

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Ph$_3$PAuNTf$_2$ (as the 2:1 toluene adduct) (11.4 mg, 1.45 x 10$^{-5}$ mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (50.0 mg, 0.277 mmol) and 2-phenylethanol (203 mg, 1.66 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 1-(2-(3-methyldodec-1-en-3-yl)oxy)ethyl)benzene 3.19 (64.5 mg, 0.213 mmol, 77%) as a colourless oil.

$\nu_{\text{max}}$/cm$^{-1}$ 1642 vw (C=C), 1605 vw, 1496 w, 1456 m, (Ar C=C), 1077 s (C-O); $\delta_H$ (200 MHz, CDCl$_3$) 7.25 – 7.07 (5H, m, aryl-H), 5.63 (1H, dd, $J = 17.4$, 10.8, H-1), 5.02 (1H, dd, $J = 10.8$, 1.2, H-2), 4.98 (1H, dd, $J = 17.4$, 1.2, H-3), 3.35 (2H, t, $J = 7.5$, H-4), 2.75 (2H, t, $J = 7.5$, H-5), 1.51 – 1.08 (19H, m, alkyl-H), 0.81 (3H, t, $J = 6.5$, H6) ; $\delta_C$ (50 MHz, CDCl$_3$) 143.4 (CH), 139.4 (C), 129.0 (CH), 128.1 (CH), 126.0 (CH), 114.2 (CH$_2$), 77.4 (C), 63.4 (CH$_2$), 40.0 (CH$_2$), 37.2 (CH$_2$), 31.9 (CH$_2$), 30.1 (CH$_2$), 29.6 (CH$_2$), 29.3 (CH$_2$), 23.6 (CH$_2$), 22.7 (CH$_2$), 21.9 (CH$_3$), 14.1 (CH$_3$); $M^+$(EI) = 302.2604 required $M = 302.2603$.
Ph₃PAuNTf₂ (as the 2:1 toluene adduct) (11.4 mg, 1.45 x 10⁻⁵ mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (51.0 mg, 0.283 mmol) and propan-2-ol (107 mg, 1.78 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. ¹H-NMR analysis of the crude product showed 97:3 ratio of 3.20 and 3.49. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 3-isopropoxy-3-methyldodec-1-ene 3.20 (47.7 mg, 0.198 mmol, 70%) as a colourless oil (97:3 ratio of 3°/1° ether).

ν max/cm⁻¹ 1639 vw (C=C), 1102 s (C-O); δH (200 MHz, CDCl₃) 5.82 (1H, dd, J = 17.4, 11.2, H-1), 5.12 (1H, dd, J = 11.2, 1.2, H-2), 5.07 (1H, dd, J = 17.4, 1.2, H-3), 3.66 (1H, septet, J = 6.2, CHMe₂), 1.62 – 1.19 (19H, m, alkyl-H), 1.09 (3H, d, J = 6.2, CH₃), 1.07 (3H, d, J = 6.2, CH₃), 0.87 (3H, t, J = 6.0, CH₂CH₃); δC (50 MHz, CDCl₃) 144.2 (CH), 114.0 (CH₂), 77.9 (C), 64.2 (CH), 41.2 (CH₂), 31.9 (CH₂), 30.2 (CH₂), 29.6 (CH₂), 29.3 (CH₂), 25.0 (CH₂), 24.9 (CH₃), 23.9 (CH₂), 22.7 (CH₂), 22.0 (CH₃), 14.1 (CH₃); M⁺(EI) = 240.2448 required M = 240.2447.
3.22, 3-Methyldodec-1-en-3-ol

Ph$_3$PAuNTf$_2$ (as the 2:1 toluene adduct) (5.8 mg, 7.37 $\times$ 10$^{-6}$ mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (25.2 mg, 0.140 mmol), water (16.1 mg, 0.893 mmol), tert-butanol§ (154 mg, 2.07 mmol) and dichloromethane (0.2 mL). The reaction mixture was allowed to stir for 24 h at 20 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (50% petrol ether, 50% diethyl ether) to yield 3-methyldodec-1-en-3-ol 3.22 (9.4 mg, 0.0474 mmol, 34%) as a colourless oil.

$\nu_{\text{max}}$/cm$^{-1}$ 3391 br (OH), 1641 vw (C=C); $\delta_H$ (200 MHz, CDCl$_3$) 5.91 (1H, dd, $J$ = 17.4, 10.8, H-1), 5.19 (1H, dd, $J$ = 17.4, 1.2, H-2), 5.04 (1H, dd, $J$ = 10.8, 1.2, H-3), 1.59 – 1.16 (19H, m, alkyl-H), 0.87 (3H, t, $J$ = 6.2, CH$_3$CH$_3$); $\delta_C$ (50 MHz, CDCl$_3$) 145.2 (CH), 111.4 (CH$_2$), 73.3 (C), 42.3 (CH$_2$), 31.8 (CH$_2$), 30.0 (CH$_2$), 29.6 (CH$_2$), 29.3 (CH$_2$), 27.6 (CH$_3$), 23.9 (CH$_2$), 22.6 (CH$_2$), 14.1 (CH$_3$); $M^+$(EI) = 198.1970 required $M$ = 198.1984.

§ t-BuOH was added as a co-solvent to homogenize the layers. In the absence of t-BuOH co-solvent, a lower yield of 17% was observed. This lower yield is probably due to the biphasic nature (H$_2$O/CH$_2$Cl$_2$) of the resulting reaction mixture.
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

3.28, (4-(1-Vinylcyclohexyloxy)butyl)benzene

Ph₃PAuNTf₂ (as the 2:1 toluene adduct) (7.7 mg, 9.74 x 10⁻⁶ mol) was added to a solution of spiro[2.5]oct-1-ene 3.23²³ (20.0 mg, 0.185 mmol), 4-phenylbutan-1-ol (0.17 mL, 1.11 mmol) and dichloromethane (0.4 mL). The reaction mixture was allowed to stir for 2 h at ambient temperature (17 °C). Then, the solvent was evaporated and the residue was purified by flash column chromatography (98% n-pentane, 2% diethyl ether) to yield (4-(1-vinylcyclohexyloxy)butyl)benzene 3.28 (41.5 mg, 0.161 mmol, 87%) as a colourless oil.

ν_max/cm⁻¹ 1638 vw (C=C), 1604 vw, 1495 w, 1451 m, (Ar C=C), 1073 s (C-O); δ_H (400 MHz, CDCl₃) 7.21-7.07 (5H, m, ArH), 5.64 (1H, dd, J = 17.7, 11.0, CH=CH₂), 5.04 (2H, m, CH=CH₂), 3.16 (2H, t, J = 6.5, OCH₂), 2.56 (2H, t, J = 7.6, PhCH₂), 1.69 – 1.11 (14H, m, CH₂); δ_C (100 MHz, CDCl₃) 143.8 (CH), 142.7 (C), 128.4 (CH), 128.2 (CH), 125.6 (CH), 114.2 (CH₂), 75.2 (C), 61.0 (CH₂), 35.9 (CH₂), 34.3 (CH₂), 30.1 (CH₂), 28.3 (CH₂), 25.8 (CH₂), 21.9 (CH₂); [M+ NH₄]⁺ (ESI) = 276.2326 required [M+ NH₄]⁺ = 276.2322.
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

3.29, 2-Ethoxy-2-methylbut-3-enyl)benzene

\[
\text{Ph}_3\text{P} \text{AuNTf}_2 \text{ (as the 2:1 toluene adduct) } (11.0 \text{ mg}, 1.4 \times 10^{-5} \text{ mol}) \text{ was added to a solution of } ((1\text{-methylcycloallyl})\text{methyl})\text{benzene } 3.24 \text{ (39.0 mg, 0.270 mmol) and ethanol (77 mg, 1.66 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. The crude product was filtered through a plug of silica (eluent: diethyl ether) and a crude } ^1\text{H-NMR spectra was obtained. The solvent was evaporated and the residue was purified by flash column chromatography (98% pentane, 2% diethyl ether) to yield 2-ethoxy-2-methylbut-3-enyl)benzene } 3.29 \text{ (40.9 mg, 0.215 mmol, 80%) as a colourless oil.}
\]

\[\begin{align*}
\text{H}_2\text{C} \text{Ph} \\
\text{3.24} \\
\text{CH}_2\text{Cl}_2, 20^\circ\text{C, 1.5 h} \\
\text{H}_2\text{C} \text{Ph} \\
\text{3.29}
\end{align*}\]

\[\begin{align*}
\text{H}_2\text{C} \text{Ph} + \text{HO} & \rightarrow \text{H}_2\text{C} \text{Ph} \text{OEt} \\
\text{3.24} & \rightarrow 3.29 \\
\text{Ph}_3\text{P} \text{AuNTf}_2
\end{align*}\]

\[\text{v}_{\text{max/cm}^{-1}} \quad 1646 \text{ vw (C=C)}, \quad 1602 \text{ vw,} \quad 1495 \text{ w,} \quad 1454 \text{ w,} \quad (\text{Ar C=C}), \quad 1063 \text{ s (C-O)}; \quad \delta_{\text{H}} (200 \text{ MHz, CDCl}_3) \quad 7.22-7.02 \text{ (5H, m, ArH),} \quad 5.71 \text{ (1H, dd, J = 17.4, 10.8, CH=CH}_2), \quad 5.07 \text{ (1H, dd, J = 10.8, 1.2, CH=CH}_2)\text{cis}), \quad 4.96 \text{ (1H, dd, J = 17.4, 1.2, CH=CH}_2\text{trans}), \quad 3.31 \text{ (2H, q, J = 6.6, OCH}_2), \quad 2.80 \text{ (1H, d, J = 13.3, CHHPh),} \quad 2.71 \text{ (1H, d, J = 13.3, CHHPh),} \quad 1.11 \text{ (3H, s, CH}_3), \quad 1.10 \text{ (3H, t, J = 6.6, OCH}_2\text{CH}_3); \quad \delta_{\text{C}} (50 \text{ MHz, CDCl}_3) \quad 142.9 \text{ (CH),} \quad 137.6 \text{ (C),} \quad 130.8 \text{ (CH),} \quad 127.6 \text{ (CH),} \quad 126.0 \text{ (CH),} \quad 114.7 \text{ (CH}_2), \quad 57.6 \text{ (CH}_2), \quad 47.2 \text{ (CH}_2), \quad 21.1 \text{ (CH}_3), \quad 15.9 \text{ (CH}_3). \quad [\text{M-H}]^+ = 189.1274 \text{ required } [\text{M-H}]^+ = 189.1274.\]
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

3.30, (4-(2-Methyl-1-phenylbut-3-en-2-yloxy)butyl)benzene

Ph₃PAuNTf₂ (as the 2:1 toluene adduct) (13.4 mg, 1.7 x 10⁻⁵ mol) was added to a solution of ((1-methylcycloallyl)methyl)benzene 3.24 (46.8 mg, 0.325 mmol) and 4-phenyl-1-butanol (0.3 mL, 1.95 mmol) in dichloromethane (0.7 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. The crude product was filtered through a plug of silica (eluent: diethyl ether) and a crude ¹H-NMR spectra was obtained. The solvent was evaporated and the residue was purified by flash column chromatography (98% pentane, 2% diethyl ether) to yield (4-(2-methyl-1-phenylbut-3-en-2-yloxy)butyl)benzene 3.30 (82.4 mg, 0.284 mmol, 86%) as a colourless oil.

ν_max/cm⁻¹ 1630 vw (C=C), 1603 w, 1495 m, 1453 m, (Ar C=C), 1077 s (C=O); δ_H (CDCl₃, 200 MHz) δ 7.34 - 7.14 (10H, m, Ar-H), 5.78 (1H, dd, J = 17.6, 10.9, HC=CH₂), 5.15 (1H, dd, J = 10.9, 1.3, HC=CH₂), 5.05 (1H, dd, J = 17.6, 1.3, HC=CH₂), 3.34 (2H, t, J = 6.3, O-CH₂), 2.82 (2H, dd, J = 15.5, 2.2 Ar-CH₂-C), 2.63 (2H, t, J = 7.2, Ar-CH₂-CH₂), 1.64 (4H, m, CH₂), 1.19, (3H, s, CH₃); δ_C (CDCl₃, 50 MHz) δ 143.2 (CH), 142.9 (C), 137.9 (C), 131.1 (CH), 128.6 (CH), 128.4 (CH), 127.8 (CH), 126.3 (CH), 125.8 (CH)115.0 (CH₂), 77.6 (C), 62.2 (CH₂), 47.8 (CH₂), 36.0 (CH₂), 30.3 (CH₂), 28.4 (CH₂), 21.1 (CH₃); [M + NH₄]^⁺ = 312.2326 required [M + NH₄]^⁺ = 312.2322.
Ph3PAuNTf2 (as the 2:1 toluene adduct) (7.2 mg, 9.16 x 10^-6 mol) was added to a solution of ((1-isopropylcycloallyl)methyl)benzene 3.25 (30.0 mg, 0.174 mmol), 4-phenylbutan-1-ol (0.16 mL, 1.02 mmol) and dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 2 h at 17 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (99% n-pentane, 1% diethyl ether) to yield (4-(3-benzyl-4-methylpent-1-en-3-yloxy)butyl)benzene 3.31 (40.8 mg, 0.127 mmol, 73%) as a colourless oil.

υ_{max}/cm^{-1} 1639 vw (C=C), 1603 w, 1496 m, 1453 m, (Ar C=C), 1080 s (C-O); δ_H (200 MHz, CDCl_3) 7.36-7.11 (10H, m, Ar-H), 5.77 (1H, dd, J = 17.7, 11.3, HC=CH_2), 5.27 (1H, dd, J = 11.3, 1.6, H-2), 5.13 (1H, dd, J = 17.7, 1.6, H-3), 3.42 (2H, m, O-CH_2), 3.03 (1H, d, J = 14.8, H-4), 2.84 (1H, d, J = 14.8, H-4’), 2.63 (2H, t, J = 7.1, Ph-CH_2), 1.95-1.50 (5H, m, 2xCH_2 + HC(CH_3)_2), 0.88 (3H, d, J = 6.8, HC-(CH_3)_2), 0.82 (3H, d, J = 6.8, HC-(CH_3)_2); δ_C (100 MHz, CDCl_3) 142.7 (C), 139.0 (CH), 137.9 (C), 130.5 (CH), 128.4 (CH), 128.2 (CH), 127.8 (CH), 125.9 (CH), 125.6 (CH), 116.5 (CH_2), 81.8 (C), 61.4 (CH_2), 36.6 (CH_2), 35.8 (CH_2), 32.7 (CH), 29.9 (CH_2), 28.2 (CH_2), 17.6 (CH_3), 16.8 (CH_3); [M+ NH_4]^+ (ESI) = 340.2639 required [M+ NH_4]^+ = 340.2635.
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

**3.32, (4-(3,4,4-Trimethylpent-1-en-3-yloxy)butyl)benzene**

![Diagram of the reaction](image)

Ph₃PAuNTf₂ (as the 2:1 toluene adduct) (11.6 mg, 1.47 x 10⁻⁵ mol) was added to a solution of 3-tert-butyl-3-methylcyclopropene 3.32²⁴ (30.8 mg, 0.280 mmol), phenethyl alcohol (0.20 mL, 1.680 mmol) and dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 2 h at 0 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (98% n-pentane, 2% diethyl ether) to yield (4-(3,4,4-trimethylpent-1-en-3-yloxy)butyl)benzene 3.26 (41.5 mg, 0.179 mmol, 64%) as a colourless oil.

ν<sub>max</sub> cm⁻¹: 1642 vw (C=C), 1605 vw, 1496 w, 1454 m (Ar C=C), 1064 s (C-O); δ<sub>H</sub> (200 MHz, CDCl₃) 7.14-7.30 (5H, m, ArH), 5.72 (1H, dd, J = 17.7, 11.1, H-1), 5.14 (1H, dd, J = 17.7, 1.7, H-2), 4.95 (1H, dd, J = 11.1, 1.7, H-3), 3.44 (2H, m, OCH₂), 2.79 (2H, t, J = 6.9, CH₂Ph), 1.13 (3H, s, CH₃), 0.87 (9H, s, C(CH₃)₃); δ<sub>C</sub> (100 MHz, CDCl₃) 141.4 (CH), 140.1 (C), 129.0 (CH), 128.0 (CH), 125.8 (CH), 115.7 (CH₂), 81.2 (C), 63.4 (CH₂), 37.8 (C), 37.3 (CH₂), 25.5 (CH₃), 15.8 (CH₃); \([\text{M+ NH₄}]^+\) (ESI) = 250.2165 required \([\text{M+ NH₄}]^+\) = 250.2168.
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

3.33, (2-Isopropoxy-2-isopropylbut-3-enyl)benzene

Ph$_3$PAuNTf$_2$ (as the 2:1 toluene adduct) (6.2 mg, 7.93 x 10$^{-6}$ mol) was added to a solution of ((1-isopropylcycloallyl)methyl)benzene 3.25 (26 mg, 0.151 mmol), propan-2-ol (69 µL, 0.906 mmol) and dichloromethane (0.3 mL). The reaction mixture was allowed to stir for 48 h at 20 °C. Then, the solvent was evaporated and the residue was purified twice by flash column chromatography (99% n-pentane, 1% diethyl ether) to yield (2-isopropoxy-2-isopropylbut-3-enyl)benzene 3.33 (15.6 mg, 0.0672 mmol, 45%) as a pale green oil.

$\nu$/cm$^{-1}$ 1637 vw (C=C), 1602 w, 1495 m, 1454 m, (Ar C=C), 1076 s (C-O); $\delta_H$ (400 MHz, CDCl$_3$) 7.47-7.11 (5H, m, Ar-H), 5.93 (1H, dd, $J = 17.9, 11.4$, HC=CH$_2$), 5.35 (1H, dd, $J = 11.4, 1.3$, HC=CHH), 5.26 (1H, dd, $J = 17.9, 1.3$, HC=CHH), 3.93 (1H, septet, $J = 6.2$, O-CH(CH$_3$)$_2$), 3.05 (1H, d, $J = 14.9$, H-4), 2.94 (1H, d, $J = 14.9$, H-4’), 1.89 (1H, septet, $J = 6.8$, CH(CH$_3$)$_2$), 1.21 (3H, d, $J = 6.2$, CH(CH$_3$)$_2$), 1.18 (3H, d, $J = 6.2$, CH(CH$_3$)$_2$), 0.96 (3H, d, $J = 6.8$, CH(CH$_3$)$_2$), 0.76 (3H, d, $J = 6.8$, CH(CH$_3$)$_2$); $\delta_C$ (100 MHz, CDCl$_3$) 139.5 (CH), 130.8 (C), 128.4 (CH), 127.7 (CH), 125.9 (CH), 116.3 (CH$_2$), 82.8 (C), 77.2 (CH), 38.2 (CH$_2$), 32.8 (CH), 25.2 (CH$_3$), 21.9 (CH$_3$), 17.3 (CH$_3$), 17.2 (CH$_3$); [M+H]$^+$ = 233.1902 required [M+H]$^+$ = 233.1900.
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

((2-Butoxybut-3-en-2-yl)benzene 15

\[
\begin{align*}
\text{Ph} & \quad \text{3.27} \\
\text{HO} & \quad \Rightarrow \\
\text{Ph} & \quad \text{O-} \\
& \quad \text{3.34}
\end{align*}
\]

Ph\(_3\)PAuNTf\(_2\) (as the 2:1 toluene adduct) (6.4 mg, 8.09 x 10\(^{-6}\) mol) was added to a solution of (1-methylcycloallyl)benzene 3.27 (20.0 mg, 0.154 mmol), butan-1-ol (0.21 mL, 2.310 mmol) and dichloromethane (0.3 mL). The reaction mixture was allowed to stir for 5 h at 10 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (99.2% n-pentane, 0.8% diethyl ether) to yield ((2-Butoxybut-3-en-2-yl)benzene 3.34 (20.4 mg, 0.100 mmol, 65%) as a colourless oil.

\[\delta_H (400 \text{ MHz, CDCl}_3) 7.45 \text{ (2H, m, Ar-H)}, 7.35-7.25 \text{ (3H, m, Ar-H)}, 6.04 \text{ (1H, dd, } J = 17.5, 10.7, \text{ HC=CH}_2), 5.27 \text{ (1H, dd, } J = 17.5, 1.4, \text{ HC=CHH}), 5.23 \text{ (1H, dd, } J = 10.7, 1.4, \text{ HC=CHH}), 3.32 \text{ (2H, m, O-CH}_2), 1.62 \text{ (3H, s, O-C-CH}_3), 1.40 \text{ (2H, m, CH}_2), 0.93 \text{ (5H, m, CH}_3\text{CH}_3); \delta_C (100 \text{ MHz, CDCl}_3) 145.3 (\text{C}), 143.4 (\text{CH}), 128.0 (\text{CH}), 126.8 (\text{CH}), 126.2 (\text{CH}), 114.0 (\text{CH}_2), 78.7 (\text{C}), 62.4 (\text{CH}_2), 32.6 (\text{CH}_2), 24.3 (\text{CH}_3), 19.5 (\text{CH}_2), 14.0 (\text{CH}_3); [[M+H]]^+(\text{EI}) = 205.1587 \text{ required } [M+H]^+ = 205.1587.\]
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

3.35, \((E)-(4\text{-Phenethoxybut}-2\text{-en}-2\text{-yl})\text{benzene}

\[
\begin{array}{c}
\text{Ph} \\
\text{3.27} \\
\end{array}
\quad +
\begin{array}{c}
\text{HO} \\
\text{Ph} \\
\end{array}
\quad \xrightarrow{\text{Ph}_3\text{PAuNTf}_2, \text{CH}_2\text{Cl}_2, 10 \, ^\circ\text{C, 4 h}}
\begin{array}{c}
\text{Ph} \\
\text{3.35} \\
\end{array}
\]

\(\text{Ph}_3\text{PAuNTf}_2\) (as the 2:1 toluene adduct) (6.4 mg, \(8.09 \times 10^{-6}\) mol) was added to a solution of (1-methylcycloallyl)benzene 3.27 (20.0 mg, 0.154 mmol), 2-phenylethanol (0.28 mL, 2.310 mmol) and dichloromethane (0.3 mL). The reaction mixture was allowed to stir for 4 h at 10 \(^\circ\text{C}\). Then, the solvent was evaporated and the residue was purified by flash column chromatography (98\% n-pentane, 2\% diethyl ether) to yield \((E)-(4\text{-phenethoxybut}-2\text{-en}-2\text{-yl})\text{benzene 3.35}\) (25.3 mg, 0.100 mmol, 65\%) as a colourless oil.

\(\nu_{\text{max}}/\text{cm}^{-1}\) 1648 vv (C=C), 1602 w, 1495 m, 1453 m, (Ar C=C), 1097 s (C-O); \(\delta_H\) (400 MHz, CDCl\(_3\)) 7.45 – 7.17 (10H, m, Ar-\(\text{H}\)), 5.95 (1H, tq, \(J = 6.5, 1.4, \text{C=CH}\)), 4.25 (2H, d, \(J = 6.6, \text{HC-CH}_2\text{-O}\)), 3.74 (2H, t, \(J = 7.3, \text{O-CH}_2\text{CH}_2\)), 2.97 (2H, t, \(J = 7.3, \text{O-CH}_2\text{CH}_2\)), 2.09 (3H, d, \(J = 1.4, \text{CH}_3\)); \(\delta_C\) (100 MHz, CDCl\(_3\)) 143.0 (C), 139.0 (C), 138.1 (C), 128.9 (CH), 128.4 (CH), 128.2 (CH), 127.2 (CH), 126.2 (CH), 125.8 (CH), 124.5 (CH), 71.4 (CH\(_2\)), 68.0 (CH\(_2\)), 36.5 (CH\(_2\)), 16.2 (CH\(_3\)); \([M+NH_4]^{+}\) = 270.1853 required \(M = 270.1852\).

\(E\) Stereochemistry confirmed by 400 MHz NOESY:
3.36, 2-Methyl-4-(3-methyldodec-1-en-3-yloxy)butan-2-ol

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{8 CH}_3 \\
3.13 & \\
\text{HO} & \quad \text{OH} \\
\text{Ph}_3\text{PAuNTf}_2 & \quad \text{CH}_2\text{Cl}_2, 17 ^\circ\text{C}, 16 \text{ h} \\
3.36 & \\
\end{align*}
\]

Ph\textsubscript{3}PAuNTf\textsubscript{2} (as the 2:1 toluene adduct) (5.8 mg, 7.8 x 10\textsuperscript{-6} mol) was added to a solution of 3-methyl-3-nonylcyclopent-1-ene 3.13 (50.4 mg, 0.28 mmol), 3-methyl-1,3-butadiol (90 \mu L, 0.84 mmol), and dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 16 h at 17 \degree C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (6:1 n-pentane / diethyl ether) to yield 2-methyl-4-(3-methyldodec-1-en-3-yloxy)butan-2-ol 3.36 (45.6 mg, 0.16 mmol, 58%) as a colourless oil.

\[\nu_{\max}/\text{cm}^{-1} 3452 \text{ br (OH)}, 1632 \text{ vv (C=C)}, 1076 \text{ s (C-O)}; \delta_H (200 \text{ MHz, CDCl}_3) 5.75 (1H, dd, \textit{J} = 17.5, 11.0, \text{H-1}), 5.16 (1H, dd, \textit{J} = 11.0, 1.3, \text{H-3}), 5.08 (1H, dd, \textit{J} = 17.5, 1.3, \text{H-2}), 3.92 (1H, s, OH), 3.52 (2H, m, \text{H}_2\text{C-O}), 1.68 (2H, t, \textit{J} = 5.8, \text{H}_2\text{C-(CH}_2\text{-C)} 1.59 - 1.10 (25H, m, alkyl-H), 0.84 (3H, t, \textit{J} = 6.1, \text{CH}_2\text{CH}_3); \delta_C (100 \text{ MHz, CDCl}_3) 142.6 \text{ (CH)}, 114.8 \text{ (CH}_2\text{)}, 77.9 \text{ (C)}, 70.6 \text{ (C)}, 59.6 \text{ (CH}_2\text{)}, 41.5 \text{ (CH}_2\text{)}, 40.2 \text{ (CH}_2\text{)}, 31.9 \text{ (CH}_2\text{)}, 30.1 \text{ (CH}_2\text{)}, 29.6 \text{ (CH}_2\text{)}, 29.5 \text{ (CH}_2\text{)}, 29.3 \text{ (CH}_3\text{)}, 29.2 \text{ (CH}_3\text{)}, 23.6 \text{ (CH}_2\text{)}, 22.7 \text{ (CH}_2\text{)}, 21.4 \text{ (CH}_3\text{)}, 14.1 \text{ (CH}_3\text{)}; [\text{M+Na}^+] (\text{ESI}) = 307.2604 \text{ required [M+Na}^+] = 307.2608.\]

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**3.37, 2,2-Dimethyl-3-(3-methyldodec-1-en-3-yl)propan-1-ol**

![Chemical Structure](image)

Ph$_3$PAuNTf$_2$ (as the 2:1 toluene adduct) (5.8 mg, 7.35 × 10$^{-6}$ mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (25.2 mg, 0.14 mmol), neopentyl glycol (87.4 mg, 0.84 mmol), and dichloromethane (0.3 mL). The reaction mixture was allowed to stir for 5 h at 10 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (7:1 n-pentane / diethyl ether) to yield 2,2-Dimethyl-3-(3-methyldodec-1-en-3-yl)propan-1-ol 3.37 (17.8 mg, 0.063 mmol, 45%) as a colourless oil.

$\nu_{\text{max/cm}^{-1}}$ 3383 br (OH), 1639 vw (C=O), 1070 s (C-O); $\delta_H$ (400 MHz, CDCl$_3$) 5.74 (1H, dd, $J = 17.6$, 10.9, H-1), 5.16 (1H, dd, $J = 11.0$, 1.3, H-3), 5.10 (1H, dd, $J = 17.6$, 1.3, H-2), 3.44 (2H, d, $J = 5.2$, OCH$_2$), 3.20 – 3.12 (3H, m, OCH$_2$ and OH), 1.56 – 1.47 (2H, m, CH$_2$), 1.37 – 1.23 (14H, m, alkyl-H), 1.22 (3H, s, CH$_3$), 0.91 (3H, s, CH$_3$), 0.90 (3H, s, CH$_3$), 0.88 (3H, t, $J = 6.9$ Hz, CH$_2$CH$_3$); $\delta_C$ (101 MHz, CDCl$_3$) 142.9 (CH), 114.7 (CH$_2$), 77.5 (C), 72.9 (CH$_2$), 72.2 (CH$_2$), 40.1 (CH$_2$), 35.6 (C), 31.9 (CH$_2$), 30.3 (CH$_2$), 30.1 (CH$_2$), 29.6 (CH$_2$), 29.3 (CH$_2$), 23.6 (CH$_2$), 22.7 (CH$_2$), 22.1 (CH$_3$), 22.0 (CH$_3$), 21.6 (CH$_3$), 14.1 (CH$_3$); [M+Na]$^+$ (ESI) = 307.2611 required [M+Na]$^+$ = 307.2608.
Ph₃PAuNTf₂ (as the 2:1 toluene adduct) (5.8 mg, 7.37 x 10⁻⁶ mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (25.2 mg, 0.140 mmol) and \((R)-2\)-phenyl-1-propanol (0.12 mL, 0.84 mmol) in dichloromethane (0.3 mL). The reaction mixture was allowed to stir for 2 h at 18 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (98% n-pentane, 2% diethyl ether) to yield a 1:1 inseparable mixture of the diastereomers 3.38 (28.7 mg, 0.0908 mmol, 65%) as a colourless oil.

$$\text{v}_{\text{max/cm}^{-1}} 1635 \text{vw (C=C), 1604 vw, 1495 w, 1453 m, (Ar C=C), 1080 s (C-O); } \delta_H (400 \text{ MHz, CDCl}_3) 7.09-7.23 (5H x 2, m, Ar-H), 5.64 (1H, dd, J = 17.6, 10.8, H-1), 5.58 (1H, dd, J = 17.6, 10.8, H-1'), 5.04-4.93 (2H x 2, m, H-2, H-3), 3.34-3.27 (1H x 2, m, CHHO), 3.22-3.15 (1H x 2, m, CHHO), 2.88-2.79 (1H x 2, m, CHPh), 1.35-1.45 (2H x 2, m, CH₂), 1.23-1.14 (17H x 2, m, CH₂, CH₃), 1.10 (3H x 2, J = 11.2, CH₃CHPh), 0.81 (3H, t, J = 6.4, CH₂CH₃); \delta_C (100 \text{ MHz, CDCl}_3) 145.0 (C), 144.95 (C), 143.69 (CH), 143.66 (CH), 128.14 (CH), 128.12 (CH), 127.49 (CH), 127.47 (CH), 126.1 (CH x 2), 114.1 (CH₂), 114.0 (CH₂), 77.2 (C), 77.1 (C), 69.2 (CH₂ x 2), 40.6 (CH x 2), 40 2 (CH₂), 40.0 (CH₂), 31.9 (CH₂ x 2), 30.1 (CH₂ x 2), 29.62 (CH₂), 29.59 (CH₂), 29.3 (CH₂ x 2), 23.54 (CH₂), 23.52 (CH₂), 22.7 (CH₂ x 2), 22.0 (CH₃), 21.9 (CH₃), 18.28 (CH₃), 18.25 (CH₃), 14.11 (CH₃ x 2); [M+ NH₄]⁺ (ESI) = 334.3106 required [M+ NH₄]⁺ = 334.3104.
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

3.39, (R)-(1-(2-Methyl-1-phenylbut-3-en-2-yloxy)ethyl)benzene

Ph₃PAuNTf₂ (as the 2:1 toluene adduct) (6.2 mg, 7.88 x 10⁻⁶ mol) was added to a solution of ((1-methylcycloallyl)methyl)benzene 3.24 (21.6 mg, 0.150 mmol) and (R)-sec-phenethyl alcohol (0.11 mL, 0.90 mmol) in dichloromethane (0.3 mL). The reaction mixture was allowed to stir for 2 h at 17 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (98% n-pentane, 2% diethyl ether) to yield a 1:1 inseparable mixture of the diastereomers 3.39 (18.2 mg, 0.0684 mmol, 46%, dr 1:1) as a yellow oil.

ν_max/cm⁻¹ 1668 vw (C=C), 1605 vw, 1493 w, 1452 m, (Ar C=C), 1091 s (C-O); δ_H (400 MHz, CDCl₃) 7.40 – 7.16 (5H x 2, m, Ar-H), 5.90 (1H, dd, J = 17.9, 10.9, H-1), 5.58 (1H, dd, J = 17.9, 10.6, H-1’), 5.23 (1H, dd, J = 10.9, 1.5, H-3), 5.10 (1H, dd, J = 17.9, 1.3, H-2), 5.00 (1H, dd, J = 17.9, 1.5, H-2’), 4.99 (1H, dd, J = 10.6, 1.5, H-3’), 4.60 (1H, m, HCO), 2.90 (2H x 2, m, CH₂Ph), 1.39 (3H, d, J = 6.5, H₃C-CH), 1.37 (3H, d, J = 6.5, H₃C-CH), 1.32 (3H, s, CH₃), 0.96 (3H, s, CH₃); δ_C (100 MHz, CDCl₃) 147.6 (C), 147.0 (C), 143.2 (CH), 143.1 (CH), 137.7 (2 x C), 131.1 (CH), 131.1 (CH), 128.0 (CH), 128.0 (CH), 127.5 (CH), 127.5 (CH), 126.4 (CH), 126.1 (CH), 125.8 (2 x CH), 125.5 (2 x CH), 115.1 (CH₂), 114.6, (CH₂), 79.2 (C), 77.2 (C), 71.0 (CH), 70.7 (CH), 49.1 (CH₂), 48.7 (CH₂), 26.6 (CH₃), 26.5 (CH₃), 21.8 (CH₃), 21.7 (CH₃); [M+ NH₄]⁺ (ESI) = 284.2012 required [M+ NH₄]⁺ = 284.2009.
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

**Reaction with CD$_3$OD**

![Chemical structure](image)

Ph$_3$PAuNTf$_2$ (as the 2:1 toluene adduct) (4.4 mg, 5.6 x 10$^{-6}$ mol) was added to a solution of 3-methyl-3-thenylcyclopentene 3.13 (100 mg, 0.555 mmol) and d$_4$-methanol (0.14 mL, 3.33 mmol) in dichloromethane (1 mL) with 3 Å molecular sieves. The reaction mixture was allowed to stir for 1.5 h at 20 °C. The solvent was evaporated and the product purified by column chromatography (diethyl ether) to yield 3.42 (47 mg, 0.22 mmol, 40%) as a mixture of the E and Z isomers (ratio 1:1, 90% D incorporation) as a colourless oil.

$\nu_{\text{max}}$/cm$^{-1}$ 2198 w (C-D), 2063 m (C-D), 1639 vw (C=C), 1117 s (C-O); $\delta_H$ (400 MHz, CDCl$_3$) 5.77 – 5.70 (1H, m, H-1), 5.15 (1H, d, $J$ = 10.9, H-2$_{\text{cis}}$), 5.09 (1H, d, $J$ = 17.7, H-2$_{\text{trans}}$), 1.55 – 1.20 (19H, m, alkyl-H), 0.87 (3H, t, $J$ = 6.7, H-3); $\delta_C$ (50 MHz, CDCl$_3$) 142.9 (CH=CHD), 114.2 (t, $J$ = 24.0, CH=CHD), 77.3 (COCD$_3$), 49.1 (septet, $J$ = 21.4, CD$_3$), 39.7 (CH$_2$), 31.9 (CH$_2$), 30.2 (CH$_2$), 29.6 (CH$_2$), 29.3 (CH$_2$), 23.6 (CH$_2$), 22.7 (CH$_2$), 21.3 (CH$_3$), 14.1 (CH$_3$); $M^+$ (EI) = 216.2.
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

Control Reactions

Catalyst: Trifluoromethanesulfonic acid
Trifluoromethanesulfonic acid (21 μL of a 0.666 M solution in dichloromethane, 14.0 μmol) were added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (48.9 mg, 0.271 mmol) and ethanol (77.2 mg, 1.68 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir at 20 °C. After 1.5 h the reaction was monitored by TLC (eluent: 90% petrol ether, 10% diethyl ether) and there was no sign of any product formed. After a further 22.5 h at 20 °C the solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether). Analysis of the crude mixture by 1H-NMR (200 MHz, CDCl3) showed that no reaction took place (>95% of starting material).

Catalyst: AgOTf
AgOTf (3.7 mg, 14.4 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (48.3 mg, 0.268 mmol) and ethanol (70.1 mg, 1.72 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir at 20 °C. After 1.5 h the reaction was monitored by TLC (eluent: 90% petrol ether, 10% diethyl ether) and only traces of product were detected. After a further 22.5 h at room temperature the solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether) to give 48.4 mg of a mixture of unreacted 3.13:3.25 (7:4 ratio) along with traces of 3.40, 3.41 and other unidentified by-products. The products were identified and ratios determined by 1H-NMR (200 MHz, CDCl3).
Catalyst: Rh(OAc)$_2$

[Rh(OAc)$_2$]$_2$ (3.1 mg, 7.01 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (47.3 mg, 0.262 mmol) and ethanol (76.3 mg, 1.66 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir at 20 °C. After 1.5 h the reaction was monitored by TLC (eluent: 90% petrol ether, 10% diethyl ether) and only traces of products were detected. After a further 22.5 h at 20 °C the solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether) to give 18.4 mg of a mixture of 3.41 along with traces of 3.40 and 3.25. The products were identified by $^1$H-NMR (200 MHz, CDCl$_3$) analysis of the crude mixture.

Catalyst: AuCl$_3$

AuCl$_3$ (1.7 mg, 5.60 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene 3.13 (21.7 mg, 0.120 mmol) and ethanol (34.7 mg, 0.753 mmol) in dichloromethane (0.2 mL). The reaction mixture was allowed to stir at 20 °C. After 1.5 h the reaction was monitored by TLC (eluent: 90% petrol ether, 10% diethyl ether) and only traces of product were detected. After a further 22.5 h at 20 °C the solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether) to give 25.3 mg of a mixture mainly 3.41 along with traces of 3.25, 3.40 and other unidentified by-products. The products were identified by $^1$H-NMR (200 MHz, CDCl$_3$) analysis of the crude mixture. Purification by column chromatography (9:1 hexane:ether) produced a mixture of 3.41 as a colourless oil (12 mg, 61 μmol, 50%).
Development of Gold-Catalysed Reactions – Gold(I)-Catalysed Nucleophilic Addition of Alcohols to Cyclopropenes

Stereoselective reactions

**Reaction A; \(PPh_3AuNTf_2\)**

\[
\begin{align*}
\text{Ph}_3\text{PAuNTf}_2 \quad \text{DCM, 0 °C, 48 h} & \quad \text{Ph}\_3\text{Me} + \text{OH} \quad \text{OH} \quad \text{3.27} \\
& \quad \text{Ph}\_3\text{Me} \quad \text{OH} \quad \text{3.44} \\
\end{align*}
\]

\(\text{Ph}_3\text{PAuNTf}_2\) (as the 2:1 toluene adduct) (3.9 mg, 5.00 x 10^{-6} mol) was added to a solution of (1-methylcycloallyl)benzene \(\text{3.27}\) (13.0 mg, 0.10 mmol) and 3-methyl-1,3-butadiol (64.0 \(\mu\)L, 0.60 mmol) in dichloromethane (0.6 mL) at 0 °C. The reaction mixture was allowed to stir for 48 h at 0 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (8:1 to 1:1, hexane:diethyl ether) to yield \(\text{3.44}\) (4.4 mg, 0.019 mmol, 19%, 1:2 3\(\alpha\)/1\(\beta\)).

\[\delta_H (400 \text{ MHz, CDCl}_3) \quad 7.42 \quad (2\text{H, m, Ar-H}), \quad 7.37-7.24 \quad (3\text{H, m, Ar-H}), \quad 6.03 \quad (1\text{H, dd, } J = 17.6, 10.9, \text{HC}=\text{CH}_2), \quad 5.29 \quad (1\text{H, dd, } J = 17.6, 1.5, \text{HC}=\text{CHH}), \quad 5.26 \quad (1\text{H, dd, } J = 10.9, 1.5, \text{HC}=\text{CHH}), \quad 3.57 \quad (2\text{H, app. m, O-CH}_3), \quad 1.78 \quad (2\text{H, app m, O(\text{CH}_2)}\text{-CH}_2), \quad 1.64 \quad (3\text{H, s, O-C-CH}_3), \quad 1.25 \quad (3\text{H, s, CH}_3), \quad 1.23 \quad (3\text{H, s, CH}_3); \quad \delta_C \quad (100 \text{ MHz, CDCl}_3) \quad 144.2 \quad (\text{C}), \quad 142.4 \quad (\text{CH}), \quad 128.2 \quad (\text{CH}), \quad 127.2 \quad (\text{CH}), \quad 126.1 \quad (\text{CH}), \quad 114.7 \quad (\text{CH}_2), \quad 79.7 \quad (\text{C}), \quad 70.6 \quad (\text{C}), \quad 60.2 \quad (\text{CH}_2), \quad 41.8 \quad (\text{CH}_2), \quad 29.4 \quad (\text{CH}_3), \quad 29.3 \quad (\text{CH}_3), \quad 24.0 \quad (\text{CH}_3); \quad [\text{M+ Na}^+] = 257.1516
\]

HPLC: Daicel Chiracel OD-H, 99% hexane, 1% IPA, 1.25 ml/min: \(R_T\) 4.85 minutes and 5.36 minutes.
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**Reaction B: (R)-DTBM-segPhos(AuCl)₂ / 2(AgOTf)**

(R)-DTBM-segPhos(AuCl)₂ (8.2 mg, 5.00 x 10⁻⁶ mol) and AgOTf (2.6 mg, 10.00 x 10⁻⁶ mol) was added to a solution of (1-methylcycloallyl)benzene 3.27 (13.4 mg, 0.10 mmol) and 3-methyl-1,3-butadiol (64.0 μL, 0.60 mmol) in dichloromethane (0.6 mL) at 0 °C. The reaction mixture was allowed to stir for 48 h at 0 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (2:1 hexane:diethyl ether) to yield 3.44 (6.1 mg, 0.026 mmol, 26%, 1.3:1 3°/1°).

Data as on page 91;

HPLC: Daicel Chiralcel OD-H, 99% hexane, 1% IPA, 1.25 ml/min: Rₜ 4.85 minutes and 5.36 minutes; e.e. = 22%
3.4 References