Supporting Information

New Gold-Catalysed Azidation of Allenes

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Electronic Supplementary Material (ESI) for Chemical Communications

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General experimental details:

All reagents were purchased from commercial sources and used without further purification, unless noted otherwise. Solvents were dried using nitrogen atmosphere and used fresh every day for reaction. Deuterated solvents were acquired from Apollo Scientific Limited and stored over molecular sieves. Glassware, standard Schlenk tubes, and Schlenk tubes from Carouse 12 Plus Reaction Station from Radleys were flame-dried and flushed with nitrogen. Thin layer chromatography was performed on Aluminium oxide TLC-Cards with Fluorescent indicator 254 nm over aluminium oxide matrix from Sigma-Aldrich, and on Silica TLC-plates (60 F 254 Merk), and components were visualize by illumination with UV light (λ = 254 nm), or by staining with potassium permanganate solution. Purification of allenes was performed by flash column chromatography using silica gel from Macherey-Nagel GmbH & Co. KG (particle size of 40 to 63 µm) as stationary phase. Purification of products was performed by flash column chromatography using Aluminum oxide activated, basic, Brockmann I of pore size 58 Å, pH 9.5 ± 0.5 in H2O. Accurate weights were obtained with a Denver Instrument SI-234. Reactions under microwave irradiation were carried out in a Biotage Initiator+ Microwave system. 1H and 13C NMR spectra were recorded at room temperature in CDCl3 on a Bruker Avance III 500 MHz NMR spectrometer, fitted with a 5mm broadband observed, BBFO plus Z-gradient SmartProbeTM probe or using a Bruker Avance III nanobay 400 MHz NMR spectrometer, fitted with a 5mm broadband observe BBFO plus Z-gradient probe. Calibration was made using the deuterated solvent (δH = 7.26 ppm and δC = 77.36 ppm).1 Chemical shifts (δ) are given in parts per million (ppm) and coupling constants values (J) are given in Hertz (Hz). Abbreviations for multiplicities are as follows: (s) singlet, (d) doublet, (dd) doublet doublet, (t) triplet, (q) quartet, (m) multiplet. 13C NMR was recorded using broad-band proton decoupling. Low resolution mass spectra were recorded using electrospray (ESI) technique in the positive and negative ion mode with a Shimadzu LCMS spectrometer. Phenomenex pre-column filter (Security Guard, ODS C18, 4 x 3 mm i.d.) was used to prevent rapid deterioration of the pre-column. Elution was carried out using a mobile phase comprising methanol, at a flow rate of 0.2 mL min-1. All solvents were HPLC grade. High resolution mass spectra were obtained.

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from the EPSRC Mass Spectrometry Service at the University of Swansea by FTMS technique. Melting points were measured with a BÜCHI Melting Point B-545. Infrared spectra were acquired using a Perkin Elmer System 400 FT-IR spectrophotometer. Solid samples were run as thin films of their solution in DCM. Liquid samples were run neat.

Synthesis of starting materials:

Allenes 1a, 1h, are commercially available (Sigma-Aldrich) and were used without further purification. Allenes 1b, 1c, 1d, 1e, 1f, 1g, and 1n were prepared from the corresponding alkynes by Crabbé reaction\textsuperscript{2} using the microwave version.\textsuperscript{3} Allene 1i was performed by a modified Crabbé reaction.\textsuperscript{4} Allenes 1j, 1k, 1l, and 1m, were synthesised by a modified Crabbé homologation under microwave conditions.\textsuperscript{5} Allenes 1o and 1p were synthesised by a modified cadmium iodide allenylation of terminal alkynes with aldehydes.\textsuperscript{6}

Crabbé reaction under microwave conditions: propargyl-derivative (1.0 Eq.), HCHO (2.5 Eq.), CuBr (0.3 Eq.), iPr$_2$NH (2 Eq.), in dioxane heated under microwave at 150 °C for 10 min. Straight purification by column chromatography (silica) gave the corresponding allene derivatives in yields: (1b) 49%, (1c) 45%, (1d) 43%, (1e) 53%, (1f) 89%, (1g) 88%, (1n) 35%.

Synthesis of 1i: 1-Decyne (1.0 Eq.), benzaldehyde (1.8 Eq.), Morpholine (1.4 Eq.), ZnI$_2$ (0.8 Eq.), in Toluene, reflux at 130°C during 7.2 h. The solution was filtered through Celite washing with Et$_2$O and purification by silica column chromatography using hexane as eluent, gave the corresponding allene 1i in 50% yield.

Crabbé homologation for 1,3-disubstituted allenes under microwave conditions: Microwave vial (2-5 ml), 1-Alkyne (1.0 Eq.), aldehyde (1.5 Eq.), Cy$_2$NH (1.51 Eq.), CuI (0.1 Eq.) in Toluene at 200°C, following conversion reaction by TLC. Straight purification by silica column chromatography gave the corresponding 1,3-disubstituted allenes in (1j) 28%, (1k) 63%, (1l) 39%, (1m) 77% yield.

Cadmium iodide allenylation of terminal alkynes with aldehydes: CdI$_2$ (0.8 Eq.) was added in a previously dried-vacuum schlenk flask under inert atmosphere in a glove

\textsuperscript{5} S. Kitagaki, M. Komizu and C. Mukai, \textit{Synlett} 2011, \textbf{8}, 1129-1132.
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box. Then the corresponding alkyne (1 Eq.), aldehyde (1.8 Eq.), and pyrrolidine (1.4 Eq.) were dissolved in dry Toluene (0.24 M) at 130 °C during 4 h. Straight purification by silica column chromatography gave the corresponding 1,3-disubstituted allenes in (1o) 30%, (1p) 29% yield.

All these allenes were prepared according to described procedures and their NMR spectra were fully accordance with the described products.

Table 1S. Optimisation of conditions: different azides, acids and solvents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Azide (Eq.)</th>
<th>Acid (Eq.)</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>time (h)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaN3 (1.5)</td>
<td>H2O (2)</td>
<td>THF</td>
<td>30</td>
<td>20</td>
<td>n.r.</td>
</tr>
<tr>
<td>2</td>
<td>NaN3 (1.5)</td>
<td>HCl (2)</td>
<td>THF</td>
<td>30</td>
<td>21</td>
<td>n.r.</td>
</tr>
<tr>
<td>3</td>
<td>NaN3 (3)</td>
<td>H2SO4 (3)</td>
<td>DCM</td>
<td>30</td>
<td>48</td>
<td>11, 2a 9, 4a</td>
</tr>
<tr>
<td>4</td>
<td>NaN3 (3)</td>
<td>AcOH (3)</td>
<td>THF</td>
<td>30</td>
<td>48</td>
<td>n.r.</td>
</tr>
<tr>
<td>5</td>
<td>NaN3 (3)</td>
<td>HCl (3)</td>
<td>DCM</td>
<td>30</td>
<td>21</td>
<td>n.r.</td>
</tr>
<tr>
<td>6</td>
<td>TMSN3 (1.5)</td>
<td>AcOH (1.5)</td>
<td>DCM</td>
<td>30</td>
<td>19</td>
<td>7, 2a</td>
</tr>
<tr>
<td>7</td>
<td>TMSN3 (3)</td>
<td>H2O (3)</td>
<td>THF</td>
<td>30</td>
<td>20</td>
<td>n.r.</td>
</tr>
<tr>
<td>8</td>
<td>TMSN3 (3)</td>
<td>H2O (3)</td>
<td>DCM</td>
<td>30</td>
<td>22</td>
<td>20, 2a:2a':3a':4a, 5.9:1.3:5.3</td>
</tr>
<tr>
<td>9</td>
<td>TMSN3 (3)</td>
<td>H2SO4 (3)</td>
<td>DCM</td>
<td>30</td>
<td>18</td>
<td>50, 2a (Decomposition of 1a and 2a at 48 h)</td>
</tr>
<tr>
<td>10</td>
<td>TMSN3 (3)</td>
<td>H2SO4 (3)</td>
<td>DCM</td>
<td>30</td>
<td>18</td>
<td>38, 2a:2a':4, 1.7:1:1.2</td>
</tr>
<tr>
<td>11</td>
<td>TMSN3 (3)</td>
<td>C2F3COOH (3)</td>
<td>DCM</td>
<td>30</td>
<td>18</td>
<td>100, 2a:2a':3a:4a, 5:1:4:4</td>
</tr>
<tr>
<td>12</td>
<td>TMSN3 (3)</td>
<td>C2F3SO3H (3)</td>
<td>DCM</td>
<td>30</td>
<td>18</td>
<td>Decomposition</td>
</tr>
</tbody>
</table>

[a] Similar results were obtained with the phosphite-gold complex. [b] Reaction carried out with (PhO)3PAuCl as catalysts.
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Table 2S. Optimisation of catalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>Gold complex[a]</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>Ratio 2a:2a’:3a:4a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NHC-1</td>
<td>48</td>
<td>20</td>
<td>1:0:1.3:0</td>
</tr>
<tr>
<td>2</td>
<td>NHC-2</td>
<td>48</td>
<td>20</td>
<td>1:0:1.3:0</td>
</tr>
<tr>
<td>3</td>
<td>NHC-3</td>
<td>48</td>
<td>10</td>
<td>1:0:0:0</td>
</tr>
<tr>
<td>4</td>
<td>Cat-Au SbF₆[¹b]</td>
<td>48</td>
<td>65</td>
<td>1.3:0:10:1</td>
</tr>
<tr>
<td>5</td>
<td>(PhO)₃PAuCl</td>
<td>22</td>
<td>100</td>
<td>8.5:1:1:4.5</td>
</tr>
</tbody>
</table>

[a] See Figure 1 for the structure of the gold complexes. [b] Reaction without silver salt added.

Figure 1. Gold(I) complexes screened in the hydroazidation of allenes.

Gold complexes NHC-1, NHC-2, and NHC-3 were synthesised in Prof. Hashmi’s laboratories following their reported procedures.⁷

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### Table 3S. Final optimisation: concentration, temperature, purification.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive (Eq.)</th>
<th>Concentration (M)</th>
<th>T (ºC)</th>
<th>Isolated Yield (Ratio 2a:2a')</th>
<th>Isolated Yield (Ratio 3a)</th>
<th>(Ratio 3a')</th>
<th>Method of Purification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1[a]</td>
<td>~</td>
<td>0.11</td>
<td>30</td>
<td>~</td>
<td>(6.6:1)</td>
<td>(0.9) ~</td>
<td>Silica</td>
</tr>
<tr>
<td>2[b]</td>
<td>~</td>
<td>0.27</td>
<td>30</td>
<td>37% (3.2:1)</td>
<td>13% (2.1)</td>
<td>(0.25) ~</td>
<td>Silica</td>
</tr>
<tr>
<td>3</td>
<td>H₂O (3)</td>
<td>0.41</td>
<td>30</td>
<td>41% (3.4:1)</td>
<td>15% (2.2)</td>
<td>(0.24) (0.17)</td>
<td>Silica</td>
</tr>
<tr>
<td>4</td>
<td>H₂O (5)</td>
<td>0.41</td>
<td>30</td>
<td>46% (3.7:1)</td>
<td>14% (2.0)</td>
<td>(0.33) (0.32)</td>
<td>Silica</td>
</tr>
<tr>
<td>5[b]</td>
<td>H₂O (5)</td>
<td>0.41</td>
<td>40</td>
<td>46% (3.8:1)</td>
<td>8% (2.0)</td>
<td>(0.22) (0.25)</td>
<td>Basic Alumina</td>
</tr>
<tr>
<td>6</td>
<td>CH₃COOH (5)</td>
<td>0.41</td>
<td>r.t.</td>
<td>40% (4.0:1)</td>
<td>12% (2.4)</td>
<td>(0.38) (0.22)</td>
<td>Basic Alumina</td>
</tr>
<tr>
<td>7</td>
<td>NH₄OH (5)</td>
<td>0.41</td>
<td>r.t.</td>
<td>43% (4.1:1)</td>
<td>12% (4.4)</td>
<td>(0.25) (0.15)</td>
<td>Basic Alumina</td>
</tr>
<tr>
<td>8</td>
<td>MeOH (5)</td>
<td>0.41</td>
<td>r.t.</td>
<td>43% (4.1:1)</td>
<td>9% (0.38)</td>
<td>(0.05) (0.01)</td>
<td>Basic Alumina</td>
</tr>
<tr>
<td>9</td>
<td>H₂O (5)</td>
<td>0.41</td>
<td>0</td>
<td>61% (0.75:1)</td>
<td>9% (0.38)</td>
<td>(0.05) (0.01)</td>
<td>Basic Alumina</td>
</tr>
<tr>
<td>10</td>
<td>H₂O (5)</td>
<td>0.41</td>
<td>r.t.</td>
<td>59% (3.7:1)</td>
<td>15% (2.1)</td>
<td>(0.17) (0.22)</td>
<td>Basic Alumina</td>
</tr>
</tbody>
</table>

[a] After 22h, conversion ≈ 25%. [b] Carried out under microwave heating during 4 hours.

Reaction in the absence of acid, gave low conversion (≈ 30%) to the allyl azides 2a:2a', as a 7.3:1 mixture. Reaction without the gold complex and/or the silver salt, reaction in the presence of gold complex and TfOH (no silver), and reaction in the absence of gold and silver but in the presence of 5 mol% TfOH gave no conversion.

We have evidence of formation of vinyl triflates and ketones in the reaction of allenes and stoichiometric amounts of TfOH. See for example:

---

[a] After 22h, conversion ≈ 25%. [b] Carried out under microwave heating during 4 hours.

---

Cyclohexylallene (100 mg, 0.818 mmol) was dissolved in dry chloroform (2 mL) and added to a schlenk. TfOH (71 µl, 0.80 mmol) was added slowly. The reaction mixture was stirred for 3 hours at room temperature. Work up with DCM and Water was carried out. A short filtration was carried out with hexane: diethyl ether (20:1). The solvent was evaporated and the mixture was tentatively characterised without further purification by $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR and 2D NMR experiments HSQC and NOESY. All the attempts to purify the mixture by silica column chromatography gave decomposition so we couldn’t obtain a pure sample for HRMS.

$^1$H NMR (500 MHz, CDCl$_3$, ppm) δ = 5.38 (d, J = 9.94 Hz, 1H, H3, major), 5.07 (d, J = 9.94 Hz, 1H, H3, minor), 2.39 (m, 1H, minor), 2.07 (m, 1H, major), 2.04 (s, 3H, H1, major), 2.03 (s, 3H, H1, minor), 1.75 - 1.60 (m, 6H), 1.30 - 1.00 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 207 (Cq, C2), 145.53 (CF$_3$, major), 143.47 (CF$_3$, minor), 127.59 (CH, C3, major), 127.45 (CH, C3, minor), 36.58 (CH, C4, major), 35.51 (CH, C4, minor), 32.75 (CH$_2$, x 2, major), 32.54 (CH$_2$, x 2, minor), 25.91 (CH$_2$), 25.81 (CH$_2$ x 2), 25.67 (CH$_2$ x 2), 25.59 (CH$_2$), 19.95 (CH$_3$, C1, minor), 16.33 (CH$_3$, C1, major). $^{19}$F NMR (470 MHz, CDCl$_3$, ppm) δ = -73.91 (OTf, major), -74.98 (OTf, minor).
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Synthesis of chloro (triphenylphosphite) gold(I): ⁹,¹⁰

The synthesis was undertaken according to the procedure described by Toste and co-workers. Under nitrogen atmosphere, AuCl₃ (125 mg, 0.41 mmol, 1.0 Eq.) was dissolved in 2.5 ml of absolute methanol. The solution was stirred for a few minutes at 0 °C and under exclusion of light. Me₂S, (76 µl, 1.03 mmol, 2.5 Eq.) was added dropwise. The decolouration of the solution and formation of a white precipitation could be observed immediately. The reaction was stirred for 1 hour and then the stirring was stopped and the solid left to settle. The yellow solution was extracted with a syringe and the solid was washed with MeOH (2.0 ml), Et₂O (2.0 ml), and with petroleum ether (2.0 ml). The solvent was removed by syringe in all cases and after the last washed, the vial was dried by vacuum for a few minutes. Dry chloroform (2.5 ml) was added to the solid and stirred in the dark at 0°C for a few minutes. Then, a solution of (PhO)₃P (119 µl, 0.45 mmol, 1.1 Eq) in hexane (3.7 ml) was added dropwise whereby the white solid dissolved. The solution was stirred for 1h at room temperature. After complete reaction the solvent was removed in vacuum, triturated with hexane and filtered by vacuum. 154 mg, 0.28 mmol of a beige powder was obtained (69%).

Chloro (triphenylphospite) gold(I)

¹H NMR (500 MHz, CDCl₃, 25 °C, TMS) δ = 7.37 – 7.32 (m, 2H; H₆), 7.25 – 7.20 (m, 1H; H₅), 7.17 – 7.13 (m, 2H; H₇). ³¹P NMR (202 MHz, CDCl₃, 25 °C) δ = 109.96.

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General procedure for gold-catalysed hydroazidation of allenes under best reaction conditions:

(PhO)₃PAuCl, (0.05 Eq.) and silver triflate (0.05 Eq) were added into a previously dried-vacuum schlenk flask under N₂. The solids were dissolved in dry dichloromethane (0.41 M) and stirred for a few minutes at 0 °C. Then, the corresponding allene (1 Eq.) was added dropwise neat or dissolved in DCM at 0 °C and under stirring. TMSN₃ (3 Eq.), distilled water (5 Eq.), and trifluoroacetic acid (3 Eq.) were then added dropwise at 0 °C. The mixture was then warmed up and stirred at room temperature until complete conversion, followed by TLC. The crude was filtered through Celite, and washed with dichloromethane. The solvent was removed under vacuum, and the product was purified by column chromatography over basic alumina using Hexane / Et₂O or EtOAc as eluent. Yields were lowered in some cases due to purification issues.

All the products obtained were air stable and in solution, but we recommend to keep them in the fridge or freezer and in the dark.

Characterisation of products:
Products obtained from the gold-catalysed hydroazidation of different allenes using the procedure described before.

Allyl azide 2a

\[
\begin{align*}
&\text{From allene 1a (119 µl, 0.82 mmol), (PhO)₃PAuCl (22 mg, 0.04 mmol), silver triflate (10} \\
&\text{mg, 0.04 mmol), TMSN₃ (323 µl, 2.45 mmol), distilled water (74 µl, 4.09 mmol),} \\
&\text{trifluoroacetic acid (196 µl, 2.45 mmol) and 2.0 ml dry DCM. Obtained after column} \\
&\text{chromatography, Hex/EtOAc, 90:1 then 2:1: 2a:2a* (3.7:1), 80 mg, 0.48 mmol, 59\% (pale} \\
&\text{yellow oil), and 4a, 19 mg, 0.12 mmol, 15\% (yellow oil).} \\
&\text{H NMR (500 MHz, CDCl₃, 25 °C, TMS) δ = 5.73 - 5.68 (m, 1H; H-3), 5.44 (dt, J = 15.4,} \\
&6.7, 1.3 Hz, 1H; H-2), 3.69 (d, J = 6.7 Hz, 2H; H-1), 2.05 - 1.97 (m, 1H; H-4), 1.77 - 1.63} \\
&\text{(m, 5H; H-5 to H-9), 1.32 - 0.94 (m, 5H; H-5 to H-9). ¹³C NMR (126 MHz, CDCl₃, 25 °C)}
\end{align*}
\]
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\[ \delta = 143.40 \text{ (CH; C-3), 120.45 (CH; C-2), 53.29 (CH}_2; \text{C-1), 40.79 (CH; C-4), 33.14 (2x CH}_2; \text{C-5 and C-9), 26.41 (CH}_2; \text{C-7), 26.25 (CH}_2; \text{C-6 and C-8).} \]

Allyl azide 2a*

\[
\begin{array}{c}
\text{N}_3 \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{H} \\
\end{array}
\]

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C, TMS) \( \delta = 5.76 \) (m, 1H; H-2), 5.31 - 5.21 (m, 2H; H-1), 3.60 (t, \( J = 7.7 \text{ Hz, 1H; H-3)\), 1.69 - 1.78 (m, 5H; H-5 to H-9), 1.38 (m, 1H; H-4), 0.83-1.30 (m, 5H; H-5 to H-9). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C) \( \delta = 134.80 \) (CH; C-2), 119.24 (CH$_2$; C-1), 71.34 (CH; C-3), 42.01 (CH; C-4), 29.74 (CH$_2$), 29.61 (CH$_2$), 26.65 (CH$_2$). The other carbon signals of the cyclohexyl ring overlapped with signals from compound 2a.


Amide 4a**

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{H} \\
\end{array}
\]

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C, TMS) \( \delta = 5.50 \) (s, broad, 1H; NH-3), 3.08 (t, \( J = 6.4 \text{ Hz, 2H; H-4)\), 1.98 (s, 3H, H-1), 1.78 - 1.62 (m, 5H; H-6 to H-10), 1.50 - 1.38 (m, 1H; H-5), 1.29 - 1.09 (m, 3H; H-5 to H-10), 0.99 - 0.83 (m, 2H; H-5 to H-10). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C) \( \delta = 170.38 \) (C$_q$; C-2), 46.21 (CH$_2$; C-4), 38.22 (CH; C-5), 31.16 (CH$_2$; C-6 to C-10), 26.72 (CH$_2$; C-6 to C-10), 26.13(CH$_2$; C-6 to C-10), 23.75 (CH$_3$; C-1). IR (Film, cm$^{-1}$): \( \nu = 3592, 3583, 3289, 3090, 2922, 2851, 1653, 1560, 1448, 1301, 991. \) HRMS

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Allyl azide 2b

From allene 1b (100 mg, 0.80 mmol), (PhO)₃PAuCl (22 mg, 0.04 mmol), silver triflate (10 mg, 0.04 mmol), TMSN₃ (318 µl, 2.42 mmol), distilled water (73 µl, 4.02 mmol), trifluoroacetic acid (193 µl, 2.42 mmol) and 2.0 ml dry DCM. Obtained after column chromatography, Hex/Et₂O, 60:1 then 2:1: 2b:2b* (1.9:1), 65 mg, 0.38 mmol, 48% (pale yellow oil) and 4b, 9 mg, 0.06 mmol, 16% (pale yellow liquid).

¹H NMR (500 MHz, CDCl₃, 25 °C, TMS) δ = 5.79 - 5.72 (m, 1H; H-3), 5.51 (dtt, J = 15.0, 6.7, 1.4 Hz, 1H; H-2), 3.70 (d, J = 6.7 Hz, 2H; H-1), 2.12 - 2.05 (m, 2H; H-4), 1.43 - 1.35 (m, 2H; H-5), 1.35 - 1.23 (m, 6H; H-6 to H-8), 0.88 (t, J = 6.6 Hz, 3H; H-9). ¹³C NMR (126 MHz, CDCl₃, 25 °C) δ = 137.65 (CH; C-3), 123.02 (CH; C-2), 53.25 (CH₂; C-1), 32.58 (CH₂; C-4), 32.01 (CH₂; C-5), 29.37 (CH₂), 29.09 (CH₂), 22.93 (CH₂), 14.41 (CH₃; C-9).

Allyl azide 2b*

¹H NMR (500 MHz, CDCl₃, 25 °C, TMS) δ = 5.74 - 5.69 (m, 1H; H-2), 5.28 - 5.24 (m, 2H; H-1), 3.83 - 3.77 (m, 1H; H-3), 1.59 - 1.46 (m, 2H; H-4), 1.44 - 1.38 (m, 2H; H-5), 1.35 - 1.23 (m, 6H; H-6 to H-8), 0.91 - 0.85 (m, 3H; H-9). ¹³C NMR (126 MHz, CDCl₃, 25 °C) δ = 136.31 (CH; C-2), 118.23 (CH₂; C-1), 65.46 (CH; C-3), 34.61 (CH₂; C-4), 29.27 (CH₂; C-5), 29.17 (CH₂), 26.09 (CH₂), 22.90(CH₂), 14.38 (CH₃; C-9).

2b and 2b*: IR (Film, cm⁻¹) ν = 2958, 2929, 2857, 2097, 1643, 1237, 969. HRMS (FTMS + APCI) Calc. for C₉H₁₈N₁ [M-N₂+H]^+: 140.1434. Found: 140.1430.
Supporting Information

Ketone 4b\textsuperscript{12,13}

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\begin{array}{ccccccc}
8 & 6 & 4 & 0 & 2 & 1 \\
9 & 7 & 5 & 3 & 2 & 1
\end{array}
\]

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, 25 °C, TMS) δ = 2.40 (t, J = 7.5 Hz, 2H; H-3), 2.12 (s, 3H; H-1), 1.52 - 1.58 (m, 2H; H-4), 1.20 - 1.35 (m, 8H; H-5 to H-8), 0.87 (t, J = 7.0 Hz; 3H, H-9).

\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}, 25 °C) δ = 209.75 (C\textsubscript{6}; C-2), 44.18 (CH\textsubscript{2}; C-3), 32.02 (CH\textsubscript{2}), 30.19 (CH\textsubscript{2}), 29.49 (CH\textsubscript{2}), 29.41 (CH\textsubscript{2}), 24.23 (CH\textsubscript{2}), 22.95 (CH\textsubscript{2}), 14.41 (CH\textsubscript{3}; C-9).

Allyl azide 2c

From allene 1c (50 mg, 0.33 mmol), (PhO)\textsubscript{3}PAuCl (9 mg, 0.02 mmol), silver triflate (4 mg, 0.02 mmol), TMSN\textsubscript{3} (131 µl, 0.98 mmol), trifluoroacetic acid (75 µl, 0.98 mmol) and 4.0 ml dry DCM. Obtained after column chromatography, Hexane then Hex/Et\textsubscript{2}O, 5:1: 2c:2c* (1.8:1), 30 mg, 0.15 mmol, 47% (colourless oil).

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, 25 °C, TMS) δ = 5.79 - 5.72 (m, 1H; H-3), 5.52 (m, 1H; H-2), 3.69 (d, J = 6.7 Hz, 2H; H-1), 2.08 (m, 2H; H-4), 1.61 - 1.46 (m, 2H; H-5), 1.40 - 1.27 (m, 10H; H-6 to H-8), 0.88 (t, J = 6.8 Hz, 3H; H-9). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}, 25 °C) δ = 137.66 (CH; C-3), 123.00 (CH; C-2), 53.26 (CH\textsubscript{2}; C-1), 32.59 (CH\textsubscript{2}; C-4), 32.22 (CH\textsubscript{2}), 29.77 (CH\textsubscript{2}), 29.60 (CH\textsubscript{2}), 29.44 (CH\textsubscript{2}), 29.41 (CH\textsubscript{2}), 23.00 (CH\textsubscript{2}), 14.41 (CH\textsubscript{3}; C-9).

Allyl azide 2c*

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, 25 °C, TMS) δ = 5.74 (m, 1H; H-2), 5.26 (m, 2H; H-1), 3.80 (m, 1H; H-3), 1.59 - 1.23 (m, 12H; H-6 to H-8), 0.88 (t, J = 6.8 Hz, 3H; H-9). Protons on the cyclohexyl ring overlapped with protons of 2c. \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}, 25 °C) δ = 136.30 (CH; C-2), 118.24 (CH\textsubscript{2}; C-1), 65.47 (CH; C-3), 34.62 (CH\textsubscript{2}), 32.19 (CH\textsubscript{2}), 30.06 (CH\textsubscript{2}), 29.79 (CH\textsubscript{2}), 29.62 (CH\textsubscript{2}), 29.56 (CH\textsubscript{2}), 26.15 (CH\textsubscript{2}), 14.45 (CH\textsubscript{3}; C-9).

\textsuperscript{12} V. V. Negrebetskii, Russ. J. Gen. Chem., 1993, 63, 1436-1440.

Supporting Information


Allyl azide 2d¹⁴,¹⁵,¹⁶,¹⁷,¹⁸

From allene 1d (100 mg, 0.86 mmol), (PhO)₃PAuCl (23 mg, 0.04 mmol), silver triflate (11 mg, 0.04 mmol), TMSN₃ (340 µl, 2.58 mmol), distilled water (78 µl, 4.30 mmol), trifluoroacetic acid (207 µl, 2.58 mmol) and 2.1 ml dry DCM. Obtained after column chromatography, Hex/Et₂O, 20:1: 2d, 85 mg, 0.53 mmol, 62% (yellow oil).

¹H NMR (500 MHz, CDCl₃, 25 °C, TMS) δ = 7.44 - 7.39 (m, 2H; H-5 and H-9), 7.37 - 7.32 (m, 2H; H-6 and H-8), 7.31 - 7.27 (m, 1H; H-7), 6.66 (d, J = 15.8 Hz, 1H; H-3), 6.25 (dt, J = 15.8, 6.7 Hz, 1H; H-2), 3.95 (dd, J = 6.7, 0.7 Hz, 2H; H-1). ¹³C NMR (126 MHz, CDCl₃, 25 °C) δ = 136.34 (C₈; C-4), 134.89 (CH; C-3), 129.00 (CHA; C-5 and C-9), 128.52 (CHA; C-7), 126.98 (CHA; C-6 and C-8), 122.73 (CH; C-2), 53.35 (CH₂; C-1). IR (Film, cm⁻¹) υ = 3029, 2927, 2099, 1702, 1654, 1598, 1492, 1235, 967, 747, 693. MS-EI: C₉H₉N₃ m/z (%) 159 [M⁺] (3), 118 (31), 117 (100), 115 (32), 105 (20), 91 (28), 77 (20).

Allyl azide 2e¹⁹

From allene 1e (100 mg, 0.54 mmol), (PhO)₃PAuCl (15 mg, 0.03 mmol), silver triflate (7 mg, 0.03 mmol), TMSN₃ (214 µl, 1.63 mmol), distilled water, (49 µl, 2.72 mmol), trifluoroacetic acid (130 µl, 1.63 mmol) and 1.3 ml dry DCM. Obtained after column

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Supporting Information

chromatography, Hex/EtOAc, 30:1 then 2:1: 2e:2e’ (3.8:1), 53 mg, 0.23 mmol, 43% (yellow oil), and 4e’, 19 mg, 0.09 mmol, 17% (yellow oil).

\(^{1}\)H NMR (500 MHz, CDCl\(_3\), 25 °C, TMS) \(\delta = 5.78 - 5.68\) (m, 1H; H-3 or H-2), 5.68 - 5.59 (m, 1H; H-3 or H-2), 3.74 (s, 6H; H-8 and H-9), 3.69 (d, \(J = 6.3\) Hz, 2H; H-1), 3.47 (t, \(J = 7.5\) Hz, 1H; H-5), 2.68 (m, 2H; H-4). \(^{13}\)C NMR (126 MHz, CDCl\(_3\), 25 °C) \(\delta = 169.40\) (C\(_q\); C-6 and C-7), 131.80 (CH; C-3), 126.74 (CH; C-2), 52.98 (CH; C-1), 52.70 (CH; C-5), 51.74 (CH\(_2\); C-4), 31.75 (CH\(_3\); C-8 or C-9), 30.05 (CH\(_3\); C-8 or C-9).

Allyl azide 2e’

\(^{1}\)H NMR (500 MHz, CDCl\(_3\), 25 °C, TMS) \(\delta = 5.63 - 5.60\) (m, 1H; H-2), 5.35 - 5.31 (m, 2H; H-1), 3.75 (s, 6H; H-8 and H-9), 3.55 (dd, \(J = 8.2, 6.5\) Hz, 1H; H-3), 3.46 - 3.42 (m, 1H; H-5), 2.19 - 2.03 (m, 2H; H-4). \(^{13}\)C NMR signals could not be extracted from the spectra of the mixture 2e+2e’ due to the low concentration of 2e’.

2e and 2e’: IR (Film, cm\(^{-1}\)) \(\nu = 2924, 2853, 2099, 1736, 1437, 1260, 973, 801, 749\). MS (ESI\(^{+}\) in MeOH): \(m/z = 225.05\) C\(_9\)H\(_{14}\)KO\(_4\) [M-N\(_3\)+K\(^+\)+H\(^+\)]. HRMS (FTMS + p NSI) (DCM / MeOH + NH\(_4\)OAc): Calc. for C\(_9\)H\(_{17}\)N\(_4\)O\(_4\) [M+NH\(_4\)\(^+\)]: 245.1244 Found: 245.1247.

Ketone 4e’\(^{20}\)

\(^{1}\)H NMR (500 MHz, CDCl\(_3\), 25 °C, TMS) \(\delta = 3.73\) (s, 6H; H-8 and H-9), 3.43 (t, \(J = 7.2\) Hz, 1H; H-5), 2.53 (t, \(J = 7.2\) Hz, 2H; H-3), 2.16 (m, 2H; H-4), 2.13 (s, 3H; H-1). \(^{13}\)C NMR (126 MHz, CDCl\(_3\), 25 °C) \(\delta = 207.43\) (C\(_q\); C-2), 169.85 (C\(_q\); C-6 and C-7), 52.89 (CH\(_3\); C-8 and C-9), 50.64 (CH; C-5), 40.72 (CH\(_2\); C-3), 30.26 (CH\(_3\); C-1), 22.83 (CH\(_2\); C-

Supporting Information

4). IR (Film, cm\(^{-1}\)) \(\nu = 2941, 2854, 1732, 1642, 1436, 1275, 1156, 750\). HRMS (FTMS + p APCI). Calc. for C\(_9\)H\(_{18}\)NO\(_5\) [M+NH\(_4\)]\(^+\): 220.1179 Found: 220.1176.

Allyl azide 2f

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\begin{array}{c}
\text{N}_3 \\
\text{O} \\
\text{O} \\
\text{N} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\end{array}
\]

From allene 1f (100 mg, 0.50 mmol), (PhO)\(_3\)PAuCl (14 mg, 0.02 mmol), silver triflate (6 mg, 0.02 mmol), TMSN\(_3\) (198 \(\mu\)l, 1.51 mmol), distilled water (45 \(\mu\)l, 2.51 mmol), trifluoroacetic acid (172 \(\mu\)l, 1.51 mmol) and 1.2 ml dry DCM. Obtained after column chromatography, Hex/EtOAc, 10:1 then 2:1: 2f, 55 mg, 0.23 mmol, 48% (yellow oil), 2f*, 9 mg, 0.04 mmol, 7% (yellow oil) and 4f*, 35 mg, 0.16 mmol, 32%, (white solid).

\(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C, TMS) \(\delta = 7.89 - 7.84\) (m, 2H; H\(_{Ar}\)), 7.75 - 7.71 (m, 2H; H\(_{Ar}\)), 5.88 - 5.81 (dt, \(J = 15.4, 5.6, 1.1\) Hz, 1H; H-3), 5.81 - 5.85 (dt, \(J = 15.4, 5.6, 1.1\) Hz, 1H; H-2), 4.33 (dd, \(J = 5.6, 1.1\) Hz, 2H; H-4), 3.77 (d, \(J = 5.6\) Hz, 2H; H-1), \(^{13}\)C NMR (126 MHz, CDCl\(_3\), 25 °C) \(\delta = 168.14\) (C\(_{4}\); C-5 and C-6), 134.42 (CH\(_{Ar}\)), 132.41 (C\(_{5}\); C-7 and C-8), 128.63 (CH; C-3), 127.55 (CH; C-2), 123.74 (CH\(_{Ar}\)), 52.27 (CH\(_2\); C-1), 39.10 (CH\(_3\); C-4).

Allyl azide 2f*

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\begin{array}{c}
\text{N}_3 \\
\text{O} \\
\text{O} \\
\text{N} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
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\text{C} \\
\text{C} \\
\end{array}
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C, TMS) \(\delta = 7.89 - 7.85\) (m, 2H; H\(_{Ar}\)), 7.77 - 7.69 (m, 2H; H\(_{Ar}\)), 5.86 - 5.77 (m, 1H; H-2), 5.42 - 5.38 (m, 1H; H-1), 5.38 - 5.36 (m, 1H; H-1), 4.37 - 4.30 (m, 1H; H-3), 3.83 (dd, \(J = 13.9, 8.3\) Hz, 1H; H-4), 3.72 (dd, \(J = 13.9, 6.3\) Hz, 1H; H-4). \(^{13}\)C NMR (126 MHz, CDCl\(_3\), 25 °C) \(\delta = 168.36\) (C\(_{4}\); C-5 and C-6), 134.54 (2x CH\(_{Ar}\)), 132.90 (CH; C-2) 132.20 (2x C\(_{4}\); C-7 and C-8), 123.86 (2x CH\(_{Ar}\)), 121.41 (CH\(_2\); C-1), 62.73 (CH; C-3), 41.07 (CH\(_2\); C-4). IR (Film, cm\(^{-1}\)) \(\nu = 2923, 2852, 2098, 1771, 1717, 1614, 1466, 1426, 1391, 717\). HRMS (FTMS + p NSI), ((DCM)/MeOH + NH\(_4\)OAc): Calc. for C\(_{12}\)H\(_{14}\)N\(_3\)O\(_2\) [M+NH\(_4\)]\(^+\): 260.1142 Found: 260.1143.
Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

2f and 2f': IR (Film, cm$^{-1}$) $\nu = 2922, 2851, 2097, 1771, 1710, 1466, 1426, 1391, 1187, 949, 711$. HRMS (FTMS + p NSI) (DCM / MeOH + NH$_4$OAc): Calc. for C$_{12}$H$_{14}$N$_5$O$_2$ [M+NH$_4$]$^+$: 260.1142 Found: 260.1145.

Ketone 4f$^{21,22}$

1H NMR (500 MHz, CDCl$_3$, 25 °C, TMS) $\delta = 7.85 - 7.81$ (m, 2H; H-11 and H-12), 7.73 – 7.69 (m, 2H; H-9 and H-10), 3.98 – 3.93 (m, 2H; H-4), 2.87 (t, $J = 7.4$ Hz; 1H, H-3), 2.18 (s, 3H; H-1). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C) $\delta = 206.13$ (C$_{q}$; C-2), 168.44 (C$_{q}$; C-5 and C-6), 134.35 (CH$_{Ar}$), 132.40 (C$_{q}$; C-7 and C-8), 123.63 (CH$_{Ar}$), 41.95 (CH$_2$; C-3), 33.32 (CH$_2$; C-4), 30.27 (CH$_3$; C-1). IR (Film, cm$^{-1}$): $\nu = 3465, 2957, 2926, 2856, 1709, 1634, 1467, 1435, 1260, 1029, 797, 718$. HRMS (FTMS + p APCI), ((DCM)/MeOH + NH$_4$OAc): Calc. for C$_{12}$H$_{12}$NO$_3$ [M+ H]$^+$: 218.0812 Found: 218.0810. M. p. = 111 ºC.

Allyl azide 2g

From allene 1g (100 mg, 0.39 mmol), (PhO)$_3$PAuCl (11 mg, 0.02 mmol), silver triflate (5 mg, 0.02 mmol), TMSN$_3$ (154 µl, 1.17 mmol), distilled water (35 µl, 1.96 mmol), trifluoroacetic acid (94 µl, 1.17 mmol) and 957 µl dry DCM. Obtained after column chromatography, Hex/EtOAc, 10:1: 2g, 32 mg, 0.15 mmol, 38%, (yellow oil).

1H NMR (500 MHz, CDCl$_3$, 25 °C, TMS) $\delta = 5.78$ (m, 1H; H-3 or H-2), 5.74 (m, 1H; H-3 or H-2), 4.13 (m, 2H; H-4 or H-1), 4.08 (m, 2H; H-4 or H-1), 1.47 (s, 9H; t-Bu H-7, H-8 and H-9). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C) $\delta = 154.66$ (C$_{q}$; C-5), 126.22 (CH; C-3 or C-2), 126.11 (CH; C-2 or C-3), 79.61 (CH; C-6), 53.44 (CH$_2$; C-1 or C-4), 53.18 (CH$_2$; C-1 or C-4), 28.87 (3 x CH$_3$; C-7, C-8 and C-9). IR (Film, cm$^{-1}$) $\nu = 3332$ (broad), 2976, 2925, 2853, 2100, 1706, 1685, 1609, 1410, 1368, 1257, 1170, 1140, 887, 765. HRMS of this compound could not be obtained due to rapid decomposition of this product.


Supporting Information

Allyl azide 2h23,24

From allene 1h (20 mg, 0.29 mmol), (PhO)3PAuCl (8 mg, 0.01 mmol), silver triflate (4 mg, 0.01 mmol), TMSN3 (116 µl, 0.88 mmol), distilled water (26 µl, 1.47 mmol), trifluoroacetic acid (70 µl, 0.88 mmol) and 718 µl dry DCM. Obtained: 100% conversion 2h:2h’ (3.7:1). This product could not be isolated due to volatility issues.

1H NMR (500 MHz, CDCl3, 25 °C) δ = 5.35 - 5.29 (m, 1H; H-2), 3.76 (d, J = 7.5 Hz, 2H; H-1), 1.79 (s, 3H; H-4 or H-5), 1.71 (s, 3H; H-4 or H-5). 13C NMR (126 MHz, CDCl3, 25 °C) δ = 130.91 (Cq; C-3), 117.42 (CH2; C-2), 48.48 (CH2; C-1), 25.90 (CH3; C-4 or C-5), 18.25 (CH3; C-4 or C-5).

Allyl azide 2h’

1H NMR (500 MHz, CDCl3, 25 °C, TMS) δ = 5.85 (dd, J = 17.3, 10.6 Hz, 1H; H-2), 5.22 (dd, J = 17.3, 0.5 Hz, 1H; H-1), 5.16 (dd, J = 10.6, 0.5 Hz, 1H; H-1), 1.33 (s, 6H; H-4 and H-5). 13C NMR (126 MHz, CDCl3, 25 °C) δ = 141.33 (CH2; C-2), 114.26 (CH2; C-1), 62.57 (Cq; C-3), 26.25 (2x CH3; C-4 and C-5).

2h and 2h’: IR (Film, cm⁻¹) ν = 2962, 2905, 2109, 1679, 1587, 1484, 1261, 1092, 1025, 940, 799, 687.

Allyl azide 2i

From allene 1i (100 mg, 0.44 mmol), (PhO)3PAuCl (12 mg, 0.02 mmol), silver triflate (6 mg, 0.02 mmol), TMSN3 (173 µl, 1.31 mmol), distilled water (39 µl, 2.19 mmol),

Supporting Information

trifluoroacetic acid (105 μl, 1.31 mmol) and 1.1 ml dry DCM. Obtained after column chromatography, using as eluent hexane: 2i, 91 mg, 0.33 mmol, 76%, (yellow oil).

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C, TMS) $\delta$ = 7.43 - 7.40 (m, 2H; H-17 and H-13), 7.37 - 7.32 (m, 2H; H-16 and H-14), 7.30 - 7.26 (m, 1H; H-15), 6.61 (d, $J$ = 15.8 Hz, 1H; H-11), 6.12 (dd, $J$ = 15.8, 8.1 Hz, 1H; H-10), 4.00 (q, $J$ = 7.2 Hz, 1H; H-9), 1.70 - 1.56 (m, 2H; H-8), 1.45 - 1.36 (m, 2H; H-7), 1.36 - 1.23 (m, 10H; H-6, H-5, H-4, H-3 and H-2), 0.91 - 0.87 (m, 3H; H-1). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C) $\delta$ = 136.44 (C$_4$; C-12), 133.44 (CH; C-11), 128.98 (CH$_2$; C-14 and C-16), 128.41 (CH$_2$; C-15), 127.67 (CH; C-10), 126.98 (CH$_2$; C-13 and C-17), 65.27 (CH; C-9), 35.14 (CH$_2$; C-8), 32.18 (CH$_2$; C-7), 29.79 (CH$_2$), 29.64 (CH$_2$), 29.56 (CH$_2$), 26.25 (CH$_2$), 22.99 (CH$_2$), 14.43 (CH$_3$; C-1). IR (Film, cm$^{-1}$) $\nu$ = 3061, 3028, 2957, 2927, 2856, 2097, 1800, 1599, 1494, 1466, 1450, 1260, 1095, 966, 803, 749, 692. HRMS (FTMS + p APCI) (DCM + NH$_4$OAc): Calc. for C$_{17}$H$_{26}$N$_1$ [M$-$N$_2$ + H]$^+$: 244.2060 Found: 244.2056, Calc. for C$_{17}$H$_{25}$ [M$-$N$_3$]$^+$: 229.1951 Found: 229.1948

**Allyl azide 2j**

From allene 1j (100 mg, 0.58 mmol), (PhO)$_3$PAuCl (16 mg, 0.03 mmol), silver triflate (7 mg, 0.03 mmol), TMSN$_3$ (229 μl, 1.74 mmol), distilled water (52 μl, 2.90 mmol), trifluoroacetic acid (139 μl, 1.74 mmol) and 1.4 ml dry DCM. Obtained after column chromatography, using as eluent hexane: 2j:2j$^*$ (1.3:1), 84 mg, 0.39 mmol, 67%, (yellow oil).

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C, TMS) $\delta$ = 7.35 - 7.25 (m, 2H; H$_{Ar}$), 7.25 - 7.22 (m, 1H; H$_{Ar}$), 7.21 - 7.17 (m, 2H; H$_{Ar}$), 5.90 - 5.84 (m, 1H; H-6), 5.49 - 5.44 (m, 1H; H-5), 3.84 (dd, $J$ = 14.7, 7.3 Hz, 1H; H-4), 3.49 - 3.38 (m, 2H; H-7), 1.59 - 1.44 (m, 2H; H-3), 1.44 - 1.33 (m, 2H; H-2), 0.88 (t, $J$ = 7.3 Hz, 3H; H-1). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C) $\delta$ = 139.91 (C$_6$; C-8), 133.92 (CH; C-6), 129.66 (CH; C-5), 128.91 (2x CH$_{Ar}$), 128.86 (2x CH$_{Ar}$), 126.98 (CH$_{Ar}$; C-11), 64.66 (CH; C-4), 38.93 (CH$_2$; C-7), 37.05 (CH$_2$; C-3), 22.58 (CH$_2$; C-2), 14.07 (CH$_3$; C-1).
Supporting Information

Allyl azide 2j'

![Structure of 2j']

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C, TMS) $\delta = 7.35 - 7.28$ (m, 2H; H$_{Ar}$), 7.25 - 7.22 (m, 1H; H$_{Ar}$-11), 7.21 - 7.17 (m 4H; H$_{Ar}$), 5.70 - 5.63 (m, 1H; H-4), 5.43 - 5.39 (m, 1H; H-5), 4.05 (dd, $J = 14.8, 7.3$ Hz, 1H; H-6), 2.80 (d, $J = 7.3$ Hz, 2H; H-7), 2.08 - 2.00 (m, 2H; H-3), 1.44 - 1.33 (m, 2H; H-2), 0.92 (t, $J = 7.3$ Hz, 3H; H-1). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C) $\delta = 137.88$ (C$_{q}$; C-8), 136.10 (CH; C-4), 129.80 (2x CH$_{Ar}$), 128.69 (2x CH$_{Ar}$), 127.46 (CH; C-5), 126.60 (CH$_{Ar}$; C-11), 66.12 (CH; C-6), 41.67 (CH$_2$; C-7), 34.55 (CH$_2$; C-3) 19.50 (CH$_2$; C-2), 13.84 (CH$_3$; C-1).

2j and 2j': IR (Film, cm$^{-1}$) $\nu =$3029, 2960, 2931, 2873, 2097, 1603, 1454, 1237, 970, 747, 698. HRMS (FTMS + p APCI): Calc. for C$_{13}$H$_{21}$N$_4$ [M+NH$_4$]$^+$: 233.1761 Found: 233.1760.

Allyl azide 2k

![Structure of 2k]

From allene 1k (86 mg, 0.50 mmol), (PhO)$_2$PAuCl (14 mg, 0.02 mmol), silver triflate (6 mg, 0.02 mmol), TMSN$_3$ (197 µl, 1.50 mmol), distilled water (45 µl, 2.50 mmol), trifluoroacetic acid (120 µl, 1.50 mmol) and 1.2 ml dry DCM. Obtained after column chromatography, using as eluent hexane: 2k:2k' (1.67:1), 59 mg, 0.27 mmol, 55%, (yellow oil).

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C, TMS) $\delta = 7.34 - 7.29$ (m, 2H; H$_{Ar}$), 7.25 - 7.17 (m, 3H; H$_{Ar}$), 5.88 (ddt, $J = 15.2, 6.9, 0.6$ Hz, 1H; H-6), 5.48 (ddt, $J = 15.2, 8.5, 1.5$ Hz, 1H; H-5), 3.63 (dd, $J = 8.5, 6.9$ Hz, 1H; H-4), 3.48 - 3.44 (m, 2H; H-7), 1.79 - 1.67 (m, 1H; H-3), 0.95 (d, $J = 6.9$ Hz, 3H; H-1 or H-2), 0.91 (d, $J = 6.9$ Hz, 3H; H-1 or H-2). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C) $\delta = 139.95$ (C$_{q}$; C-8), 134.99 (CH; C-6), 128.90 (2x CH$_{Ar}$), 128.85 (2x CH$_{Ar}$), 127.98 (CH; C-5), 126.59 (CH$_{Ar}$; C-11), 71.32 (CH; C-4), 39.03 (CH$_2$; C-7), 32.85 (CH; C-3), 19.23 (CH$_3$; C-1 or C-2), 19.22 (CH$_3$; C-1 or C-2).
Supporting Information

**Allyl azide 2k**

![Diagram of allyl azide 2k](image)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C, TMS) $\delta$ = 7.36 - 7.28 (m, 2H; H$_{Ar}$), 7.25 - 7.18 (m, 3H; H$_{Ar}$), 5.64 (ddd, $J$ = 15.4, 6.8, 0.6 Hz, 1H; H-4), 5.37 (dd, $J$ = 15.4, 8.1, 1.3 Hz, 1H; H-5), 4.06 - 4.00 (m, 1H; H-6), 2.83 - 2.79 (m, 2H; H-7), 2.32 (ddq, $J$ = 13.4, 6.8, 1.3 Hz, 1H; H-3), 1.00 (d, $J$ = 6.8 Hz, 3H; H-1 or H-2), 0.99 (d, $J$ = 6.8 Hz, 3H; H-1 or H-2). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C) $\delta$ = 143.23 (CH; C-4), 137.88 (C$_q$; C-8), 129.83 (2x CH$_{Ar}$), 128.66 (2x CH$_{Ar}$), 126.97 (CH$_{Ar}$; C-11), 124.30 (CH; C-5), 65.99 (CH; C-6), 41.71 (CH$_2$; C-7), 31.22 (CH; C-3), 22.73 (CH$_3$; C-1 or C-2), 22.60 (CH$_3$; C-1 or C-2).

**2k and 2k':** IR (Film, cm$^{-1}$) $\nu$ = 3064, 3030, 2929, 2962, 2095, 1454, 1260, 1094, 1029, 803, 699, 666. HRMS (FTMS + p APCI): Calc. for C$_{13}$H$_{21}$N$_4$ [M+NH$_4$]$^+$: 233.1761 Found: 233.1760.

**Allyl azide 2l**

![Diagram of allyl azide 2l](image)

From allene 1l (100 mg, 0.54 mmol), (PhO)$_3$PAuCl (15 mg, 0.03 mmol), silver triflate (7 mg, 0.03 mmol), TMSN$_3$ (212 µl, 1.61 mmol), distilled water (48 µl, 2.69 mmol), trifluoroacetic acid (129 µl, 1.61 mmol) and 1.3 ml dry DCM. Obtained after column chromatography, using as eluent hexane: **2l; 2l'** (1.13:1), 85 mg, 0.37 mmol, 70%, (yellow oil).

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C, TMS) $\delta$ = 7.33 - 7.27 (m, 2H; H$_{Ar}$), 7.23 - 7.16 (m, 3H; H$_{Ar}$), 5.74 - 5.67 (m, 1H; H-4), 5.44 - 5.38 (m, 1H; H-5), 3.82 - 3.78 (m, 1H; H-6), 2.70 - 2.65 (m, 2H; H-8), 2.11 - 2.05 (m, 2H; H-3), 1.91 - 1.75 (m, 2H; H-7), 1.47 - 1.41 (m, 2H; H-2), 0.93 (t, $J$ = 7.4 Hz; 3H, H-1). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C) $\delta$ = 141.53 (C$_q$; C-9), 136.15 (CH; C-4), 128.80 (4x CH$_{Ar}$), 127.84 (CH; C-5), 126.36 (CH$_{Ar}$; C-12), 64.34 (CH; C-6), 36.61 (CH$_2$; C-7), 34.60 (CH$_2$; C-3), 32.43 (CH$_2$; C-8), 22.65 (CH$_2$; C-2), 13.89 (CH$_3$; C-1).
Supporting Information

Allyl azide 21′

From allene 1m (100 mg, 0.54 mmol), (PhO)₃PAuCl (15 mg, 0.03 mmol), silver triflate (7 mg, 0.03 mmol), TMSN₃ (212 µl, 1.61 mmol), distilled water (48 µl, 2.69 mmol), trifluoroacetic acid (129 µl, 1.61 mmol) and 1.3 ml dry DCM. Obtained after column chromatography, using as eluent hexane: 2m:21′ (1:1), 98 mg, 0.43 mmol, 80%, (yellow oil).

1H NMR (500 MHz, CDCl₃, 25 °C, TMS) δ = 7.33 - 7.27 (m, 2H; H Ar), 7.23 - 7.16 (m, 3H; H Ar), 5.76 - 5.71 (m, 1H; H-6), 5.43 - 5.37 (m, 1H; H-5), 3.55 (dd, J = 8.5, 6.8 Hz, 1H; H-4), 2.80 - 2.71 (m, 2H; H-8), 2.49 - 2.40 (m, 2H; H-7), 1.67 (dq, J = 13.5, 6.8 Hz, 1H; H-2), 0.90 (d, J = 6.8 Hz, 3H; H-1 or H-3), 0.84 (d, J = 6.8 Hz 3H; H-1 or H-3). 13C NMR (126 MHz, CDCl₃, 25 °C) δ = 141.53 (C q; C-9), 135.55 (CH; C-6), 128.80 (2x CH Ar), 128.69 (2x CH Ar), 127.13 (CH; C-5), 126.36 (CH Ar; C-12), 71.48 (CH; C-4), 36.10 (CH₂;
Supporting Information

C-8), 34.34 (CH$_2$; C-7), 32.77 (CH; C-2), 19.18 (CH$_3$; C-1 or C-3), 19.13 (CH$_3$; C-1 or C-3).

Allyl azide 2m$^+$

![Diagram](attachment:diagram.png)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C, TMS) $\delta$ = 7.33 - 7.27 (m, 2H; H$_{Ar}$), 7.23 - 7.16 (m, 3H; H$_{Ar}$), 5.71 - 5.67 (m, 1H; H-4), 5.38 - 5.32 (m, 1H; H-5), 3.80 - 3.73 (m, 1H; H-6), 2.71 - 2.64 (m, 2H; H-8), 2.39 - 2.32 (m, 1H; H-3), 1.91 - 1.75 (m, 2H; H-7), 1.04 (dd, $J$ = 6.8, 2.0 Hz, 6H; H-1 and H-2). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C) $\delta$ = 143.43 (CH; C-4), 141.73 (C$_q$; C-9), 128.80 (CH$_{Ar}$), 126.26 (CH$_{Ar}$; C-12) 124.61 (CH; C-5), 64.21 (CH; C-6), 36.61 (CH$_2$; C-7), 32.43 (CH$_2$; C-8), 31.28 (CH; C-3), 22.83 (CH$_3$; C-1 or C-2), 22.71 (CH$_3$; C-1 or C-2).

2m and 2m$^+$: IR (Film, cm$^{-1}$) $\nu$ = 3064, 3028, 2961, 2927, 2870, 2095, 1603, 1496, 1454, 1367, 1241, 971, 747, 699. HRMS (FTMS$^+$ p APCI) Calc. for C$_{14}$H$_{23}$N$_4$ [M+NH$_4^+$]: 247.1917. Found: 247.1917.

Allyl azide 2n$^{25}$

From allene 1n (100 mg, 0.54 mmol), (PhO)$_3$PAuCl (15 mg, 0.03 mmol), silver triflate (7 mg, 0.03 mmol), TMSN$_3$ (214 µl, 1.63 mmol), distilled water (49 µl, 2.72 mmol), trifluoroacetic acid (186 µl, 1.63 mmol) and 1.3 ml dry DCM. The reaction was then warm up at 30 °C during 60 h. Obtained after column chromatography, Hex/Et$_2$O, 80:1, 91.1 mg, 0.40 mmol, 74% (pale yellow oil).

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C, TMS) $\delta$ = 7.59 (d, $J$ = 8.2 Hz, 2H; H-7 and H-8), 7.50 (d, $J$ = 8.2 Hz, 2H; H-5 and H-6), 6.69 (d, $J$ = 15.8 Hz, 1H; H-3), 6.33 (dt, $J$ = 15.8, 6.4 Hz, 1H; H-2), 3.99 (dd, $J$ = 6.4, 0.8 Hz, 2H; H-1). $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C) $\delta$ =

Supporting Information

139.82 (C₄; C-4), 133.13 (CH; C-3), 130.33 (q, J = 32.4 Hz, C₄; C-9), 127.14 (CH₆; C-5 and C-6), 126.00 (q, J = 3.8 Hz, CH₆-7 and CH₆-8), 125.63 (CH; C-2), 124.42 (q, J = 271.9 Hz, C-F), 53.07 (CH₂; C-1). ¹⁹F NMR (471 MHz, CDCl₃) δ = -62.59. IR (Film, cm⁻¹): ν = 3042, 2927, 2855, 2644, 2510, 2102, 1616, 1415, 1326, 1124, 1016, 853.

Allyl azide 2o

From allene 1o (99.8 mg, 0.44 mmol), (PhO)₃PAuCl (12 mg, 0.02 mmol), silver triflate (6 mg, 0.02 mmol), TMSN₃ (174 µl, 1.32 mmol), distilled water (40 µl, 2.21 mmol), trifluoroacetic acid (106 µl, 1.32 mmol) and 1.1 ml dry DCM. The reaction was then warm up at 30 °C during 60 h. Obtained after column chromatography, Pentane/Et₂O, 80:1, 79 mg, 0.30 mmol, 67% (yellow oil).

¹H NMR (500 MHz, CDCl₃, 25 °C, TMS) δ = 7.59 (d, J = 8.2 Hz, 2H; H-10 and H-11), 7.50 (d, J = 8.2 Hz, 2H; H-8 and H-9), 6.64 (d, J = 15.8 Hz, 1H; H-6), 6.20 (dd, J = 15.8, 7.8 Hz, 1H; H-5), 4.07 – 4.01 (m, 1H; H-4), 1.71 – 1.55 (m, 2H; H-3), 1.51 – 1.37 (m, 2H; H-2), 0.96 (t, J = 7.3 Hz, 3H; H-1). ¹³C NMR (126 MHz, CDCl₃, 25 °C) δ = 139.90 (C₄, C-7), 131.85 (CH; C-6), 130.43 (CH; C-5), 130.24 (q, J = 32.5 Hz; C₄; C-12), 127.14 (CH₆; C-8 and C-9), 125.97 (q, J = 3.8 Hz; CH₆; C-11 and C-10), 124.44 (q, J = 271.9 Hz; CF; C-13), 64.61 (CH; C-4), 37.05 (CH₂; C-3), 19.47 (CH₂; C-2), 14.08 (CH₃; C-1). ¹⁹F NMR (471 MHz, CDCl₃) δ = -62.58. IR (Film, cm⁻¹): ν = 2963, 2936, 2876, 2647, 2483, 2327, 2100, 1617, 1325, 1166, 1067, 1030, 967. HRMS (APCI (ASAP)) with added NH₄OAc: Calc. for C₁₃H₁₅F₅N [M–N₂+H⁺]: 242.1151. Found: 242.1148. Calc. for C₁₃H₁₄F₃ [M–N₃]⁺: 227.1042. Found: 227.1040. Calc. for C₁₃H₁₄F₃N [M⁺]: 269.1140. Found: 269.1143.

Allyl azide 2p
Supporting Information

From allene 1p (106.7 mg, 0.46 mmol), (PhO)₃PAuCl (12 mg, 0.02 mmol), silver triflate (6 mg, 0.02 mmol), TMSN₃ (180 µl, 1.37 mmol), distilled water (41 µl, 2.28 mmol), trifluoroacetic acid (109 µl, 1.37 mmol) and 1.1 ml dry DCM. Obtained after column chromatography, Hex/Et₂O, 80:1, 91.1 mg, 0.33 mmol, 72% (yellow oil).

¹H NMR (500 MHz, CDCl₃, 25 °C, TMS) δ = 7.34 – 7.32 (m, 2H; H-13 and H-14), 7.31 – 7.29 (m, 2H; H-11 and H-12), 6.55 (d, J = 15.8 Hz, 1H; H-9), 6.08 (dd, J = 15.8, 8.0 Hz, 1H; H-8), 4.01 – 3.95 (m, 1H; H-7), 1.70 – 1.53 (m, 2H; H-6), 1.44 – 1.21 (m, 8H; H-5 to H-2), 0.89 (t, J = 7.0 Hz, 3H; H-1).

¹³C NMR (126 MHz, CDCl₃, 25 °C) δ = 134.93 (C₉), 134.10 (C₉), 132.11 (CH; C-9), 129.17 (2x CH₃), 128.41 (CH; C-8), 128.18 (2x CH₃), 65.09 (CH; C-7), 35.08 (CH₂; C-6), 32.02 (CH₂; C-5), 29.30 (CH₂; C-4), 26.20 (CH₂; C-3), 22.91 (CH₂; C-2), 14.39 (CH₃; C-1). IR (Film, cm⁻¹): ν = 2956, 2929, 2857, 2730, 2583, 2470, 2097, 1491, 1238, 1091, 967. HRMS (APCI (ASAP)) with added NH₄OAc: Calc. for C₁₅H₂₁ClN [M–N₂+H]⁺: 250.1357. Found: 250.1354. Calc. for C₁₅H₂₁ClN [M–N₂]: 252.1328. Found: 252.1323. Calc. for C₁₅H₂₀ClN [M–N₃]⁺: 235.1248. Found: 235.1247. Calc. for C₁₅H₂₀ClN [M–N₃]⁺: 237.1219. Found: 237.1215. C₁₅H₂₀ClN [M]⁺: 277.1346. Found: 277.1346.
Supporting Information

Proposed mechanism for formation of amide 4a

Amide 4a was obtained as by-product in the reaction with cyclohexylallene 1a. We propose that this amide comes from a gold-catalysed Schmidt reaction of the corresponding ketone with the *in situ* formed hydrazoic acid. The ketone can be formed by protonation of the allene by the strong acid and attack of water into the central carbon of the allenic system, which is supported by the isolation of methyl ketones 4b', 4e' and 4f' in the reaction with allenes 1b, 1e and 1f (entries 2, 5, and 6, Table 1 in the main manuscript).  

Gold-catalysed Schmidt reaction of ethyl methyl ketone.

To further test this hypothesis we carried out the reaction of commercially available ethyl methyl ketone, under our reaction conditions, and we observed 53% conversion to the corresponding amide in 28 h.

(PhO)₃PAuCl (0.05 Eq., 16 mg, 0.03 mmol) and silver triflate (0.05 Eq., 8 mg, 0.03 mmol) were added into a previously dried-vacuum schlenk flask under N₂. The solids were dissolved in dry dichloromethane (1.4 ml, 0.41 M) and stirred for a few minutes at 0°C. Then ethyl methyl ketone (1 Eq., 62 µl, 0.58 mmol) was added dropwise at 0°C and under stirring. TMSN₃ (3 Eq., 229 µl, 1.74 mmol), distilled water, (5 Eq., 52 µl, 2.90 mmol), and trifluoroacetic acid, (3 Eq., 139 µl, 1.74 mmol) were added dropwise at 0°C. The mixture was then warmed up and stirred at room temperature during 28h. The reaction was stopped at 28h with 53% conversion of N-ethylacetamide. The crude was filtered through Celite.
Supporting Information

and washed with dichloromethane. The solvent was removed by vacuum, and the crude was analysed without purification by NMR.

\[ N\text{-ethyacetamide}^{28,29} \]

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{H} \\
\text{1} \\
\text{2} \\
\text{3} \\
\text{4} \\
\text{5} \\
\text{6} \\
\text{7}
\end{array}
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C, TMS) \( \delta = 6.87 \) (broad s, 1H; NH-2), 3.41 - 3.32 (m, 2H; H-3), 2.17 (s, 3H; H-1), 1.19 (t, \( J = 7.2 \) Hz, 3H; H-4).

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Supporting Information

Deuteration experiment:

We also carried out deuterium-labelling experiments to support the protonation of the allene in the terminal position by the acid. Thus, reaction with $d$-TFA and D$_2$O gave the allyl azides $d$-$2a$ and $d$-$2a'$ with high deuterium incorporation in the expected positions, also confirming the involvement of vinyl-gold intermediates, and the amide $4a$ was obtained as a mixture of compounds with different deuterium incorporation in the methyl group, as well as deuteration in the amide nitrogen, observed before purification.

Experimental procedure for the deuteration experiment:

(PhO)$_3$PAuCl (0.05 Eq., 22 mg, 0.04 mmol) and silver triflate (0.05 Eq., 10.5 mg, 0.04 mmol) were added into a previously washed with D$_2$O and dried-vacuum schlenk flask under N$_2$. The solids were dissolved in dry dichloromethane (2.0 ml, 0.41 M) and stirred for a few minutes at 0ºC. Then, allene $1a$ (1 Eq., 119 µl, 0.82 mmol) was added dropwise to schlenk flask. TMSN$_3$ (3 Eq., 323 µl, 2.45 mmol), D$_2$O (5 Eq., 74 µl, 4.09 mmol) and $d$-TFA (3 Eq., 189 µl, 2.45 mmol) were added dropwise at 0ºC and under stirring. The mixture was then warmed up and stirred at room temperature during 22h. The crude was filtered through celite and the solvent was removed by vacuum. The mixture was analysed by $^1$H and $^2$H NMR without purification in CDCl$_3$.

We observed deuterium incorporation in the following positions:

- $2a$: the signal at 5.44 ppm showed 80% of deuterium incorporation.
- $2a'$: the signal at 5.76 ppm showed 80% of deuterium incorporation.
- $4a$: we observed deuterium incorporation at the amide proton 5.50 ppm, before purification and a mixture of $d_0$, $d_1$, $d_2$, $d_3$ in the signal at 1.98 ppm (methyl group).
Supporting Information

$^1$H NMR in CDCl$_3$:

$^2$H NMR in CHCl$_3$:
Supporting Information

General procedure for gold-catalysed iodoazidation of allenes:

Gold(I)-complex (5 mol%), silver triflate (5 mol%) and NIS (1.05 Eq.) were added into a previously dried-vacuum schlenk flask under N2. The corresponding allene (1 Eq.) in dry dichloromethane (0.1 M) and TMSN3 (3 Eq.) were added and stirred for a few minutes at 0°C. The mixture was then warmed up at 30 °C and stirred at that temperature until complete conversion, followed by TLC. The crude was filtered through Celite, and washed with dichloromethane. The solvent was removed by vacuum, and the product was purified by column chromatography over silica gel using Hexane/Et2O as eluent.

![Scheme](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Allene</th>
<th>[Au]</th>
<th>Conversion (%)</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
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<td>1</td>
<td>R = Cy, 1a</td>
<td>(PhO)3PAuCl</td>
<td>71</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>R = Cy, 1a</td>
<td>NHC-1</td>
<td>84</td>
<td>73, 5a</td>
</tr>
<tr>
<td>3</td>
<td>R = Cy, 1a</td>
<td>NHC-2</td>
<td>78</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>R = Cy, 1a</td>
<td>NHC-3</td>
<td>83</td>
<td>65, 5a</td>
</tr>
<tr>
<td>5</td>
<td>R = Cy, 1a</td>
<td>Cat-Au SbF6</td>
<td>46</td>
<td>--</td>
</tr>
<tr>
<td>6</td>
<td>R = Cy, 1a</td>
<td>Ph3PAuCl</td>
<td>100 (E/Z = 1:1)</td>
<td>60, Z-5a</td>
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<tr>
<td>7</td>
<td>R = n-octyl, 1c</td>
<td>NHC-1</td>
<td>100</td>
<td>40, 5c</td>
</tr>
</tbody>
</table>

[a] See Figure 1 in SI for structure of gold-complexes.

Vinyl-iodide 5a

![Structure](image)

Rf in hexane/ethyl acetate (20:1): 0.73. 1H NMR (400 MHz, CDCl3, 25° C, TMS) δ = 5.68 (d, J = 8.6 Hz, 1H; H-3), 4.05 (s, 2H; H-1), 2.22-2.32 (m, 1H; H-4), 1.63-1.77 (m, 5H; H-5 to H-9), 1.11-1.40 (m, 5H; H-5 to H-9). 13C NMR (101 MHz, CDCl3, 25° C) δ = 145.09 (CH; C-3), 96.48 (Cq; C-2), 62.51 (CH2; C-1), 45.05 (CH; C-4), 31.50 (2x CH2; C-5 and C-9), 25.78 (CH2; C-7), 25.46 (2x CH2; C-6 and C-8). IR (Film, cm⁻¹): ν = 2926, 2815, 2096, 1635, 1448, 1318, 1260, 1060, 1029, 893, 838, 802, 689, 559. MS (ESI⁺ in MeOH): m/z (%) = 264.0 [M-N₂⁺H]⁺. HRMS (FTMS + APCI) (DCM + NH₄OAc) Calcd. for C₉H₁₃N₄ [M+NH₄]⁺, 309.0569. Found, 309.0571.
**Supporting Information**

Vinyl-iodide 5c

\[
\text{R}_f \text{ in hexane/ethyl acetate (20:1): 0.68. } ^1H \text{ NMR (500 MHz, CDCl}_3, 25^\circ \text{C, TMS)} \delta = 5.87 \text{ (t, J = 6.6, 0.9 Hz, 1H), 4.08 (s, 2H), 2.18 (m, 2H), 1.30-1.27 (m, 12H), 0.88 (t, J = 6.9 Hz, 3H). } ^{13}C \text{ NMR (126 MHz, CDCl}_3, 25^\circ \text{C) } \delta = 139.21 \text{ (CH), 98.17 (C}\_2\text{), 61.54 (CH}_2\text{), 34.91 (CH}_2\text{), 30.81 (CH}_2\text{), 28.35 (CH}_2\text{), 28.16 (CH}_2\text{), 28.08 (CH}_2\text{), 27.00 (CH}_2\text{), 21.63 (CH}_2\text{), 13.07 (CH). IR (Film, cm}^{-1}\text{): } \nu = 3419, 2955, 2925, 2855, 2099, 1639, 1465, 1269, 1237, 1132, 889, 829, 722. MS (ESI\textsuperscript{+} in MeOH): m/z = 321.0 [M]\textsuperscript{+}, 322.0 [M+H]\textsuperscript{+}. HRMS (FTMS (DCM+NH}_4\text{OAc)): Calcd. for C\textsubscript{11}H\textsubscript{20}IN\textsubscript{3} [M+], 321.0696. Found, 321.0693. Calculated for C\textsubscript{11}H\textsubscript{21}IN [M-N\textsubscript{2}+H]\textsuperscript{+}, 294.0713. Found, 294.0714.
\]

**Orthogonal functionalization of allenes by using the gold-catalysed azidation methodology**

**Click reaction of vinyl iodide 5a**

Copper (II) sulfate pentahydrate (15 mol%, 9 mg, 0.04 mmol), sodium ascorbate (0.8 Eq., 38 mg, 0.19 mmol) and tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA) (15 mol%, 19 mg, 0.04 mmol) were added into a (2.0-5.0 ml) microwave vial. To the solids (Z)-(3-azido-2-iodoprop-1-en-1-yl)cyclohexane 5a (1.0 Eq., 70 mg, 0.24 mmol) dissolved in DMF (3 ml) and phenylacetylene (1.0 Eq., 30 µl, 0.24 mmol) were added. The suspension was heated in the microwave at 70 °C for 1h. The reaction mixture was quenched with water and extracted with dichloromethane (x 3). The combined organic phases were dried over anhydrous sodium sulfate and filtrated. After removing the solvent in vacuum the product was separated and purified by column chromatography over silica gel with hexane/ethyl acetate (5:1 then 3:1) as eluent. After evaporating the solvent 6a was obtained as a pale yellow solid (54 mg, 57%).
Supporting Information

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS) $\delta$ = 7.77 (d, $J$ = 7.5 Hz, 2H; H-13 and H-17), 7.72 (s, 1H; H-10), 7.35 (t, $J$ = 7.5 Hz, 2H; H-14 and H-16), 7.26 (t, $J$ = 7.5 Hz, 1H; H-15), 5.70 (d, $J$ = 8.5 Hz, 1H; H-3), 5.17 (s, 2H; H-1), 2.20 (m, 1H; H-4), 1.65 (m, 4H; H-5 and H-9), 1.15 (m, 6H; H6, H-7 and H-8). $^{13}$C NMR (126 MHz, CDCl$_3$, 25°C) $\delta$ = 147.92 (C$_9$; C-11), 146.46 (CH; C-3), 130.46 (C$_4$; C-12), 128.77 (2x CH$_{Ar}$; C-14 and C-16), 128.16 (CH$_{Ar}$; C-15), 125.73 (2x CH$_{Ar}$; C-13 and C-17), 119.54 (CH; C-10), 95.32 (C$_4$; C-2), 61.70 (CH$_2$; C-1), 45.10 (CH; C-4), 31.13 (2x CH$_2$; C-5 and C-9), 25.66 (CH$_2$; C-7), 25.35 (2x CH$_2$; C-6 and C-8). IR (Film, cm$^{-1}$): $\bar{\nu}$ = 509, 694, 762, 973, 1044, 1075, 1225, 1345, 1500, 1638, 2850, 2923, 3423. HRMS (FTMS (DCM / MeOH + NH$_4$OAc)): Calc. for C$_{17}$H$_{20}$N$_3$ [M+H]$^+$, 394.0775. Found, 394.0775.

Phenylboronic acid (2.0 Eq., 22 mg, 0.18 mmol), PdCl$_2$ (5 mol%, 0.8 mg, 0.005 mmol), PPh$_3$ (10 mol%, 2.4 mg, 0.009 mmol) and CsF (2.0 Eq., 27 mg, 0.18 mmol) were added into a flushed schlenk flask under N$_2$. To the solids (Z)-1-(3-cyclohexyl-2-idoallyl)-4-phenyl-1H-1,2,3-triazole 6a (1.0 Eq., 36 mg, 0.09 mmol) dissolved in a mixture of toluene:EtOH:H$_2$O (1.3 ml : 1.3 ml : 0.4 ml) was added. The mixture was degassed by bubbling N$_2$ into the solution for 5 min and then stirred at 80 °C for 18h. The reaction mixture was quenched with water and extracted with dichloromethane (x 3). The combined organic phases were dried over anhydrous sodium sulfate and filtrated. After removing the solvent in vacuum the product was separated and purified by column chromatography over silica gel and hexane/ethyl acetate (5:1) as eluent. After evaporating the solvent 7a was obtained as of a white-yellow solid (26 mg, 85%).

Rf in hexane/ethyl acetate (3:1): 0.51. $^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS): $\delta$ = 7.68 (dd, $J$ = 7.4, 1.2 Hz, 2H; H-13 and H-17), 7.47 (s, 1H; H-10), 7.31 (t, $J$ = 7.4 Hz, 2H; H-14 and H-16), 7.27-7.20 (m, 2H; H-20 and H-22), 7.20-7.13 (m, 2H; H-15 and H-21), 7.00 (dd, $J$ = 6.8, 1.5 Hz, 2H; H-19 and H-23), 5.54 (d, $J$ = 10.1 Hz; 1H, H-3), 5.11 (s, 2H; H-1), 2.01 (m, 1H; H-4), 1.58 (m, 5H; H-5 to H-9), 1.06 (m, 5H; H-5 to H-9). $^{13}$C NMR (126
**Supporting Information**

MHz, CDCl3, 25 °C) δ = 147.74 (C_q, C-11), 139.78 (CH; C-3), 137.55(C_q, C-18), 133.16 (C_q, C-2), 130.86 (C_q; C-12), 128.87 (2x CH_Ar), 128.67 (2x CH_Ar), 128.41 (2x CH_Ar), 128.13 (2x CH_Ar); C-3), 138.75 (CH; C-18), 133.16 (C_q, C-2), 128.86 (2x CH_Ar), 128.67 (2x CH_Ar), 128.41 (2x CH_Ar), 128.13 (CH; C-10), 57.89 (CH; C-1), 37.68 (CH; C-4), 33.05 (2x CH; C-6 and C-8), 25.91 (CH; C-7), 25.53 (2x CH; C-5 and C-9).

IR (Film, cm⁻¹): ν = 764, 973, 1646, 1675, 1225, 1338, 1444, 2850, 2924.


M. p.: 129 °C.

**Attempts to trap the vinyl-gold intermediate via oxidative cross-coupling:**

We have unsuccessfully attempted the reaction to engage the vinyl-gold intermediate in a cross-coupling reaction as reported by Zhang *et al.*[^30] However, the substrates and reaction conditions reported by Zhang are quite different from our catalytic system and more detailed tuning of the reaction might be needed to get a successful outcome. Further efforts into this and other couplings are being made in our lab, as we believe that this transformation will indeed enhance the synthetic utility of this reaction.

![Chemical Structure](image)

- The oxidative cross-coupling was attempted using **Zhang’s conditions**: Ph₃PAuCl, (0.05 Eq., 10 mg, 0.02 mmol), selectfluor (2 Eq., 290 mg, 0.82 mmol), PhB(OH)₂ (4 Eq., 200 mg, 1.64 mmol) were added into a previously dried-vacuum schlenk flask under N₂. The solids were dissolved in dry acetonitrile / H₂O (20:1) (0.05 M) and stirred for a few minutes at 0 °C. Then, allene 1α (1 Eq., 60 μl, 0.41 mmol) was added drop wise neat at 0 °C and under stirring. TMSN₃ (3 Eq., 161 μl, 1.23 mmol), was then added drop wise at 0 °C. The mixture was then warmed up at 80 °C . The reaction was followed by TLC, and after 6 h the crude was filtered through Celite and a pad MgSO₄, and washed with dichloromethane. The solvent was removed under vacuum, and the crude was

Supporting Information

analysed by NMR. No signals corresponding of the expected product were observed. The allene signals disappeared possibly by decomposition at 80 °C.

- A second experiment was carried out under the conditions of our azidation reaction: (PhO)$_3$PAuCl, (0.05 Eq., 11 mg, 0.02 mmol), silver triflate (0.05 Eq., 5 mg, 0.02 mmol), selectfluor (2 Eq., 290 mg, 0.82 mmol), PhB(OH)$_2$ (4 Eq., 200 mg, 1.64 mmol) were added into a previously dried-vacuum schlenk flask under N$_2$. The solids were dissolved in dry DCM (0.41 M) and stirred for a few minutes at 0 °C. Then, allene 1a (1 Eq., 60 µl, 0.41 mmol) was added drop wise neat at 0 °C and under stirring. TMSN$_3$ (3 Eq., 161 µl, 1.23 mmol), was then added drop wise at 0 °C. The mixture was then warmed up and stirred at room temperature. The reaction was followed by TLC, and after 6 h the crude was filtered through Celite, and washed with dichloromethane. The solvent was removed under vacuum and the crude was analysed by NMR. Signals of the unreacted allene and phenyl boronic acid were observed.
Supporting Information

Allenes that did not work in the reaction

Allenes bearing oxygen and groups sensitive to acidic conditions gave decomposition products (equation a).

Interestingly, ethyl 2,3-butanodionate and ethyl 2,3-pentanodionate gave very slow reaction and only traces of the corresponding allyl azides were observed after 5 days of reaction (equation b).

Tri- and tetra-substituted allenes gave traces of the azidation products, but side reactions are observed. More investigations are being carried out in our lab with these allenes (equation c).
Supporting Information

Synthesis of gold-azide complex

(PhO)₃PAuCl (15 mg, 0.027 mmol, 1 Eq.), and AgOTf (7 mg, 0.027 mmol, 1 Eq.) were dissolved in DCM (2 ml) under N₂. An excess of TMSN₃ (29 µl, 0.216 mmol, 8 Eq.) was added and the mixture stirred at room temperature for 1h. The mixture was filtered through celite, the solvent was evaporated and the solid washed with hexane to remove excess of azide to give (PhO)₃PAuN₃ as a gummy oil. This complex has to be kept in the fridge and in the dark and decomposes very quickly. No HRMS could be obtained due to fast decomposition. All the attempts to crystallise the complex have failed so far.

¹H NMR (500 MHz, CDCl₃, 25 ºC, TMS): δ = 7.43 (app t, J = 7.4 Hz, 2H), 7.31 (tq, J = 7.4, 1.2 Hz, 1H), 7.23 (app dd, J = 7.4, 1.2 Hz, 2H). ³¹P NMR (202 MHz, CDCl₃, 25º C): δ = 105.80 ppm. IR (Film, cm⁻¹): ν = 2059.66 (υas N₃⁻).

Stoichiometric NMR Experiments

Three parallel experiments were designed using stoichiometric amounts of all the components and the order of addition of the different components of the reaction were varied as follows:

A) (PhO)₃PAuCl + AgOTf + TMSN₃ + Allene 1a + TFA + H₂O
B) (PhO)₃PAuCl + AgOTf + Allene 1a + TMSN₃ + TFA
C) (PhO)₃PAuCl + AgOTf + TFA + TMSN₃ + Allene 1a

¹H, ³¹P NMR and ¹⁹F NMR spectra were recorded at room temperature after each addition and after several time intervals in between additions.

The following amounts were used in CDCl₃ (0.7 ml):
(PhO)₃PAuCl (5 mg, 0.009 mmol)
AgOTf (2 mg, 0.009 mmol)
TMSN₃ (1 µl, 0.009 mmol)
Allene 1a (1 mg, 0.009 mmol)
TFA (1 µl, 0.009 mmol)
H₂O (1 µl, 0.05 mmol, 6 Eq.)

³¹R₃PAuN₃ complexes have been reported with similar IR bands, for Ph₃PAuN₃ (2050 cm⁻¹), see: W. Beck et al., Z. Anorg. Allg. Chem., 2001, 627, 1669-1674; for Cy₃PAuN₃ (2049 cm⁻¹), see: D. V. Partyka, PNAS, 2008, 105, 14293-14297.
Supporting Information

$^{31}$P NMR profile of Experiment A:

$^{31}$P NMR profile of Experiment B:
Supporting Information

$^{31}$P NMR profile of Experiment C:
Supporting Information

$^1$H NMR profile of Experiment A:

The signals used to measure integrals are:

Allene 1a: 5.07 ppm (q, $J = 6.5$ Hz, 1H)
E-Allyl azide 2a: 3.69 ppm (d, $J = 6.70$ Hz, 2H)
Allyl azide 2a$: 3.60 ppm (t, $J = 7.73$ Hz, 1H)
Amide 4a: 3.10 ppm (t, $J = 6.44$ Hz, 2H)
Ketone: 3.38 ppm (m, 2H)
TFA-adduct 3a: 4.77 (d, $J = 6.76$ Hz, 2H)

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Addition Time (min) Allene 1a E-Allyl Azide 2a Amide 4a Ketone TFA-adduct 3a
AgOTf
TMSN$_3$

Conversion (%)

Addition Time (min) Allene 1a E-Allyl Azide 2a Amide 4a Ketone TFA-adduct 3a
AgOTf
TMSN$_3$

Allene 0 100 0 0 0 0 0
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280 39.96 16.90 18.67 10.46 9.34 4.67
H$_2$O

400 33.25 18.74 16.96 14.67 9.58 6.79
1260 12.78 29.47 15.97 18.53 12.86 10.38
Supporting Information

![Graph showing conversion (%) over time (min) for various compounds.]

- Allene 1a
- E-Allyl Azide 2a
- Vinyl-allyl azide 2a'
- Amide 4a
- Ketone
- TFA-adduct 3a
## Supporting Information

### \(^1\)H NMR profile of Experiment B:

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Supporting Information

![Graph](image)

- Allene 1a
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- Vinyl-allyl azide 2a'
- Amide 4a
- Ketone
- TFA-adduct 3a

Electronic Supplementary Material (ESI) for Chemical Communications
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Supporting Information

$^1$H NMR profile of Experiment C:

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<td>2.03</td>
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<td>1405</td>
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<td>1.68</td>
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<td>0.67</td>
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Conversion (%)

<table>
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<tr>
<th>Addition</th>
<th>Time (min)</th>
<th>Allene 1a</th>
<th>E-Allyl Azide 2a</th>
<th>Allyl azide 2a$'$</th>
<th>Amide 4a</th>
<th>Ketone</th>
<th>TFA-adduct 3a</th>
</tr>
</thead>
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<tr>
<td>AgOTf</td>
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<td></td>
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<tr>
<td>TFA</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>TMSN$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0</td>
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<td>16.46</td>
<td>27.65</td>
<td>4.12</td>
<td>11.03</td>
</tr>
</tbody>
</table>
Supporting Information

Catalytic NMR experiment:

\[
\begin{align*}
(\text{PhO})_3\text{PAuCl/AgOTf (5 mol\%)}
\end{align*}
\]

\[
\text{TMSN}_3 (3 \text{ equiv.}), \text{CF}_3\text{CO}_2\text{H} (3 \text{ equiv.}),
\text{H}_2\text{O} (5 \text{ equiv.})
\]

\[
\text{CDCl}_3 (0.41 \text{mM}), \text{rt}
\]

\[
\begin{align*}
\text{2a, } X = \text{N}_3 \\
\text{3a, } X = \text{OCOCF}_3 \\
\text{3a', } X = \text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{1a} & \rightarrow \text{2a} + \text{3a} + \text{3a'} + \text{4a}
\end{align*}
\]

(PhO)_3PAuCl, (0.05 Eq., 22 mg, 0.04 mmol) and (1 Eq., 119 µl, 0.82 mmol) of allene 1a in CDCl_3 (2.0 ml, 0.41 mM) were added into a previously dried-vacuum schlenk flask under N_2 and stirred for a few minutes at 0°C. TMSN_3, (3 Eq., 323 µl, 2.45 mmol), distilled water, (5 Eq., 74 µl, 4.09 mmol), and trifluoroacetic acid, (3 Eq., 196 µl, 114.02 mmol) were added drop wise at 0°C. The mixture was then warmed up and stirred at room temperature during 22h. Samples (0.1 mL) were extracted directly from the schlenk according to the time with a syringe and diluted with CDCl_3 for the NMR experiment.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Allene 1a</th>
<th>Allyl Azide 2a</th>
<th>Allyl Azide 2a'</th>
<th>3a (TFA)</th>
<th>3a' (OH)</th>
<th>Amide 4a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>1</td>
<td>0.785</td>
<td>0.65</td>
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<td>0.24</td>
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<td>1.46</td>
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<td>1.75</td>
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Conversion (%)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Allene 1a</th>
<th>Allyl Azide 2a</th>
<th>Allyl Azide 2a'</th>
<th>3a (TFA)</th>
<th>3a' (OH)</th>
<th>Amide 4a</th>
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<tr>
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<td>24.98</td>
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<tr>
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<tr>
<td>9</td>
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<td>12.51</td>
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<td>1.62</td>
<td>23.11</td>
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</tbody>
</table>
Supporting Information

![Conversion vs Time Graph]

- Allene (1a)
- Allyl azide (2a)
- Allyl azide (2a')
- TFA-adduct (3a)
- Allyl alcohol (3a')
- Amide (4a)
Supporting Information

Catalytic IR experiment:

(PhO)$_3$PAuCl, (0.14 Eq., 31 mg, 0.06 mmol) and silver triflate (0.14 Eq., 15 mg, 0.06 mmol) were added into a previously dried-vacuum schlenk flask under N$_2$. The solids were dissolved in CDCl$_3$ dry over molecular sieves (3A) (0.41 M) and stirred for a few minutes at 0 ºC. Then, allene 1a (1 Eq., 60 µl, 0.41 mmol) was added drop wise neat at 0 ºC and under stirring. TMSN$_3$ (3 Eq., 161 µl, 1.23 mmol), distilled water (5 Eq., 37 µl, 2.05 mmol), and trifluoroacetic acid (3 Eq., 98 µl, 1.23 mmol) were then added drop wise at 0 ºC. The mixture was then warmed up and stirred at room temperature. Drops of the reaction mixture were transferred directly form the schlenk to the IR disc according to the time, and the IR experiments were run neat in the following minutes.

Copies of the IR spectra at some of the times analysed are shown below: The peak of the azide in the final product (2097 cm$^{-1}$) is observed from the beginning of the reaction, overlapping with the possible peak of the Au-N$_3$ at 2060 cm$^{-1}$. No clear conclusion about the formation of Au-N$_3$ complexes can be extracted from this experiment.

30 min
Supporting Information

1h 45 min

![Graph showing spectral data at 1 hour 45 minutes](image1)

6 h

![Graph showing spectral data at 6 hours](image2)

9h 30 min

![Graph showing spectral data at 9 hours 30 minutes](image3)
Supporting Information

After 9.5 h, the mixture was filtered through celite, and analysed directly by $^1$H and $^{31}$P NMR. The spectra are shown below and are consistent with the previous experiments.

$^1$H NMR (Crude of reaction, 9h 30 min)

$^{31}$P NMR (Crude of reaction, 9h 30 min)
SI – NMR Spectra

New Gold-Catalysed Azidation of Allenes

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Earlham Road, Norwich, NR4 7TJ, UK.
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NMR Spectra
SI – NMR Spectra

Chloro (triphenylphosphite) gold (I)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{31}$P NMR (202 MHz, CDCl$_3$, 25 °C)
SI – NMR Spectra

Allyl azides 2a and 2a’ (3.7:1):

\[ \text{Allyl azides 2a and 2a’ (3.7:1)} \]

\[ \text{1H NMR (500 MHz, CDCl}_3\text{, 25 °C)} \]

\[ \text{13C NMR (126 MHz, CDCl}_3\text{, 25 °C)} \]
SI – NMR Spectra

Amide 4a:

\[
\text{\begin{center}
\includegraphics[width=0.5\textwidth]{amide4a.png}
\end{center}}\]

\(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C)

\(^{13}\)C NMR (126 MHz, CDCl\(_3\), 25 °C)
SI – NMR Spectra

Allyl azides 2b and 2b’ (1.9:1):

\[ \text{N}_3 \text{CH} = \text{CHCH}_2 \text{N}_3 \]

\(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C)

\(^{13}\)C NMR (126 MHz, CDCl\(_3\), 25 °C)
SI – NMR Spectra

2D gCOSY (CDCl₃):

2D HSQC (CDCl₃):
SI – NMR Spectra

Ketone 4b':

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C)
SI – NMR Spectra

Allyl azides 2e and 2e' (1.8:1)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C)
SI – NMR Spectra

2D gCOSY (CDCl₃):

2D HSQC (CDCl₃):
SI – NMR Spectra

Allyl azide 2d

\[ \text{N}_3 \]

\(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C)

\[^{13}\text{C} \) NMR (126 MHz, CDCl\(_3\), 25 °C)
SI – NMR Spectra

Allyl azides 2e and 2e' (3.8:1):

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{N}_3 \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{N}_3 \\
\text{O} & \quad \text{O}
\end{align*}
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C)

\(^{13}\)C NMR (126 MHz, CDCl\(_3\), 25 °C)
SI – NMR Spectra

Ketone 4e':

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

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C)
SI – NMR Spectra

Allyl azide 2f:

1H NMR (500 MHz, CDCl₃, 25 °C)

13C NMR (126 MHz, CDCl₃, 25 °C)
SI – NMR Spectra

Allyl azide 2f*:

\[
\text{\begin{center}
\begin{tikzpicture}
\end{tikzpicture}
\end{center}
}\]

\( ^1\text{H} \text{NMR} (500 \text{ MHz, CDCl}_3, 25 \degree \text{C}) \)

\( ^{13}\text{C} \text{NMR} (126 \text{ MHz, CDCl}_3, 25 \degree \text{C}) \)
SI – NMR Spectra

2D gCOSY (CDCl₃):
SI – NMR Spectra

Ketone 4f:

\[
\begin{align*}
\end{align*}
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C)

\(^{13}\)C NMR (126 MHz, CDCl\(_3\), 25 °C)
SI – NMR Spectra

2D HSQC (CDCl₃):
SI – NMR Spectra

 Allyl azide 2g:

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{H} & \quad \text{N}_3
\end{align*}
\]

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C)
SI – NMR Spectra

Allyl azides 2h and 2h’ (3.7:1):

\[ \text{N}_3 \quad + \quad \text{N}_3 \]

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C)
**SI – NMR Spectra**

2D gCOSY (CDCl₃):

![2D gCOSY Graph](image1)

2D HSQC (CDCl₃):

![2D HSQC Graph](image2)
SI – NMR Spectra

Allyl azide 2i:

\[ \text{H}_3\text{C} - \text{CH} \equiv \text{CH} - \text{CH}_2 - \text{N}_3 \]

\(^1\text{H}\) NMR (500 MHz, CDCl\(_3\), 25 °C)

\(^{13}\text{C}\) NMR (126 MHz, CDCl\(_3\), 25 °C)
SI – NMR Spectra

2D gCOSY (CDCl₃):

2D HSQC (CDCl₃)
SI – NMR Spectra

Allyl azide 2j and 2j′:

\[
\begin{align*}
\text{N}_3
\end{align*}
\]

\[\text{N}_3\]

\(1^1\text{H NMR (500 MHz, CDCl}_3, 25^\circ\text{C)}\)

\(1^3\text{C NMR (126 MHz, CDCl}_3, 25^\circ\text{C)}\)
SI – NMR Spectra

2D HSQC (CDCl$_3$):
SI – NMR Spectra

Allyl azides 2k and 2k' (:)

**1H NMR (500 MHz, CDCl₃, 25 °C)**

![1H NMR Spectrum](image)

**13C NMR (126 MHz, CDCl₃, 25 °C)**

![13C NMR Spectrum](image)
SI – NMR Spectra

2D gCOSY (CDCl₃):

2D HSQC (CDCl₃):
SI – NMR Spectra

Allyl azides 2l and 2l' (1:1.13):

\[
\begin{align*}
\text{N}_3 & \quad + \\ 
\text{N}_3
\end{align*}
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C)

\(^13\)C NMR (126 MHz, CDCl\(_3\), 25 °C)
SI – NMR Spectra

2D gCOSY (CDCl₃):

2D HSQC (CDCl₃):
SI – NMR Spectra

Allyl azide 2m and 2m’ (1:1):

\[
\begin{align*}
\text{\(N_3\)} & \quad \text{\(N_3\)} \\
\text{\(\text{Ph} - \text{CH} = \text{CH} - \text{CH}_2\text{CH}_2\text{CH}_3\)} & \quad + \quad \text{\(\text{Ph} - \text{CH} = \text{CH} - \text{CH}_2\text{CH}_2\text{CH}_3\)}
\end{align*}
\]

\(^1H\) NMR (500 MHz, CDCl\(_3\), 25 °C)

\(^13C\) NMR (126 MHz, CDCl\(_3\), 25 °C)
SI – NMR Spectra

2D gCOSY (CDCl₃):

2D HSQC (CDCl₃):
SI – NMR Spectra

Allyl azide 2n:

\[
\text{F}_3\text{C} \quad \text{N}_3
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C)

\(^{13}\)C NMR (126 MHz, CDCl\(_3\), 25 °C)
SI – NMR Spectra

$^{19}$F NMR (471 MHz, CDCl$_3$, 25 °C)

2D gCOSY (CDCl$_3$):
SI – NMR Spectra

Allyl azide 2O:

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{N}_3 \\
\end{align*}
\]

\( ^1\text{H} \text{NMR (500 MHz, CDCl}_3, 25 \, ^\circ\text{C} ) \)

\( ^{13}\text{C} \text{NMR (126 MHz, CDCl}_3, 25 \, ^\circ\text{C} ) \)
$^{19}$F NMR (471 MHz, CDCl$_3$, 25 °C)
SI – NMR Spectra

Allyl azide 2P:

\[
\begin{array}{c}
\text{Cl} \\
\text{N}_3 \\
\end{array}
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C)

\(^{13}\)C NMR (126 MHz, CDCl\(_3\), 25 °C)
SI – NMR Spectra

2D gCOSY (CDCl₃):

2D HSQC (CDCl₃):
**SI – NMR Spectra**

Vinyl-iodide 5c:

\[ \text{\(1^1H\) NMR (500 MHz, CDCl\(_3\), 25 °C)} \]

\[ 8.0 \quad 7.5 \quad 7.0 \quad 6.5 \quad 6.0 \quad 5.5 \quad 5.0 \quad 4.5 \quad 4.0 \quad 3.5 \quad 3.0 \quad 2.5 \quad 2.0 \quad 1.5 \quad 1.0 \quad 0.5 \quad \text{ppm} \]

\[ \text{\(13^1C\) NMR (126 MHz, CDCl\(_3\), 25 °C)} \]

\[ 140 \quad 130 \quad 120 \quad 110 \quad 100 \quad 90 \quad 80 \quad 70 \quad 60 \quad 50 \quad 40 \quad 30 \quad 20 \quad 10 \quad \text{ppm} \]
SI – NMR Spectra

Vinyl-iodide 5a:

$\text{C} = \text{N}_3$

$^1\text{H NMR (500 MHz, CDCl}_3, 25 \, ^\circ\text{C}}$

$^{13}\text{C NMR (126 MHz, CDCl}_3, 25 \, ^\circ\text{C}}$
SI – NMR Spectra

Triazole-vinyl-iodide 6a:

\begin{center}
\includegraphics[width=0.8\textwidth]{SI_NMR_Spectra_6a.png}
\end{center}

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C)
SI – NMR Spectra

Triazole 7a:

\[
\text{Ph} - \text{N} - \text{N} - \text{N} - \text{Ph}
\]

\(^1\text{H} \text{ NMR (500 MHz, CDCl}_3, 25 ^\circ\text{C})\)

\(^{13}\text{C} \text{ NMR (126 MHz, CDCl}_3, 25 ^\circ\text{C})\)
SI – NMR Spectra

Vinyl triflate 8a:

\[
\text{OTf} \quad \text{Me}
\]

\text{E/Z, 2:1}

\(^1^H\) NMR (500 MHz, CDCl\textsubscript{3}, 25 °C)

\[^{13}C\) NMR (126 MHz, CDCl\textsubscript{3}, 25 °C)
SI – NMR Spectra

$^{19}$F NMR (470 MHz, CDCl$_3$, 25 °C)
SI – NMR Spectra

(Triphenylphosphite) gold(I) - azide

\[ \text{Ph}\text{Ph}\text{Ph} \text{P} - \text{Au}-\text{N}_3 \]

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{31}$P NMR (202 MHz, CDCl$_3$, 25 °C)
SI – NMR Spectra

IR (Film, cm\(^{-1}\))