Electronic Supplementary Information for:

**Copper-catalyzed direct transformation of simple alkynes to alkenyl nitriles via aerobic oxidative N-incorporation**

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General Remarks

All commercially available compounds were purchased from Sigma-Aldrich, Alfa-Aesar, Acros, Beijing Ouhe and Beijing Chemical Works, Ltd. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Analysis of crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. Products were purified by flash chromatography on silica gel. $^1$H-NMR spectra were recorded on Bruker AVANCE III-400 spectrometers. Chemical shifts (in ppm) were referenced TMS in CDCl$_3$ (0 ppm). $^{13}$C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl$_3$ ($\delta$ = 77.00 ppm). Mass spectra were recorded using a PE SCLEX QSTAR spectrometer. High resolution mass spectra were obtained with a Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer. Infrared spectra were recorded on a Nicolet Avatar 330 Fourier transform spectrometer (FT-IR) and are reported in wave numbers (cm$^{-1}$).
### Screening of Different Reaction Parameters

#### Table S1  Screening of pyridine derivates

<table>
<thead>
<tr>
<th>Reaction conditions: 1a (0.20 mmol), TMSN₃ (0.40 mmol), CuBr (0.04 mmol), pyridine derivates (0.40 mmol), and NaOAc (0.20 mmol) in PhCl (1.0 mL) was stirred at 90 °C for 48 h. Yield and Z/E ratio were determined by ¹H NMR measurement of the crude mixture.</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No ligand</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>No reaction</strong></td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>2a: 78% Z/E = 1.9:1</td>
<td>2a: &lt; 10%</td>
<td>2a: 66% Z/E = 1.5:1</td>
<td>2a: 50% Z/E = 1.5:1</td>
<td></td>
</tr>
<tr>
<td>2a: 64% Z/E = 1.5:1</td>
<td>2a: 51% Z/E = 1.5:1</td>
<td>No reaction</td>
<td>2a: &lt; 5%</td>
<td>No reaction</td>
</tr>
<tr>
<td>No reaction</td>
<td>No reaction</td>
<td>No reaction</td>
<td>No reaction</td>
<td>No reaction</td>
</tr>
<tr>
<td>No reaction</td>
<td>No reaction</td>
<td>No reaction</td>
<td>No reaction</td>
<td>No reaction</td>
</tr>
<tr>
<td>2a: &lt; 5%</td>
<td>2a: &lt; 5%</td>
<td>No reaction</td>
<td>No reaction</td>
<td>No reaction</td>
</tr>
</tbody>
</table>

*aReaction conditions: 1a (0.20 mmol), TMSN₃ (0.40 mmol), CuBr (0.04 mmol), pyridine derivates (0.40 mmol), and NaOAc (0.20 mmol) in PhCl (1.0 mL) was stirred at 90 °C for 48 h. Yield and Z/E ratio were determined by ¹H NMR measurement of the crude mixture.
Table S2  Screening of ligands-1<sup>a</sup>

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Yield</th>
<th>Z/E</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPrHCl</td>
<td>&lt;5%</td>
<td></td>
<td>Not detected&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>P(O)Ph&lt;sub&gt;3&lt;/sub&gt;</td>
<td>29%&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1.22:1</td>
<td>2a: 29%&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: 1a (0.20 mmol), TMSN<sub>3</sub> (0.40 mmol), CuBr (0.04 mmol), Ligand (40 mmol%), Pyridine (0.32 mmol), and NaOAc (0.20 mmol) in PhCl (1.0 mL) was stirred at 90 °C for 48 h. Yield and Z/E ratio were determined by <sup>1</sup>H NMR measurement of the crude mixture. <sup>b</sup>Pyridine (0.40 mmol) was employed. <sup>c</sup>Ligand (0.40 mmol) was employed without Pyridine. <sup>d</sup>Ligand (0.10 mmol) was employed without Pyridine. <sup>e</sup>Ligand (20 mmol%), Pyridine (0.40 mmol) was employed without NaOAc.
Table S3  Screening of ligands-2
e
![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Yield</th>
<th>Z/E Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>34%</td>
<td>1.6:1</td>
</tr>
<tr>
<td>2a</td>
<td>64%</td>
<td>1.7:1</td>
</tr>
<tr>
<td>2a</td>
<td>44%</td>
<td>1.75:1</td>
</tr>
<tr>
<td>2a</td>
<td>62%</td>
<td>1.67:1</td>
</tr>
<tr>
<td>2a</td>
<td>35%</td>
<td>1.67:1</td>
</tr>
<tr>
<td>2a</td>
<td>50%</td>
<td>1.44:1</td>
</tr>
<tr>
<td>2a</td>
<td>53%</td>
<td>1.47:1</td>
</tr>
<tr>
<td>2a</td>
<td>22%</td>
<td>1.20:1</td>
</tr>
<tr>
<td>2a</td>
<td>47%</td>
<td>1.39:1</td>
</tr>
<tr>
<td>2a</td>
<td>44%</td>
<td>1.44:1</td>
</tr>
<tr>
<td>2a</td>
<td>35%</td>
<td>1.67:1</td>
</tr>
</tbody>
</table>

*Reaction conditions: 1a (0.20 mmol), TMSN₃ (0.40 mmol), CuBr (0.04 mmol), Ligand (20 mmol%), Pyridine (0.32 mmol), and NaOAc (0.20 mmol) in PhCl (1.0 mL) was stirred at 90 °C for 48 h. Yield and Z/E ratio were determined by ¹H NMR measurement of the crude mixture. †without NaOAc.
Table S4  Screening of metal

<table>
<thead>
<tr>
<th>Entry</th>
<th>Metal (mol%)</th>
<th>Yield of 2a</th>
<th>E/Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh2(OAc)4 (2 mol%)</td>
<td>41%</td>
<td>1.47:1</td>
</tr>
<tr>
<td>2</td>
<td>Rh2(OI)4 (2 mol%)</td>
<td>34%</td>
<td>1.38:1</td>
</tr>
<tr>
<td>3</td>
<td>Rh(PPh3)Cl (5 mol%)</td>
<td>37%</td>
<td>~2:1</td>
</tr>
<tr>
<td>4</td>
<td>Cp*RhCl3 (2.5 mol%)</td>
<td>25%</td>
<td>1.5:1</td>
</tr>
<tr>
<td>5</td>
<td>Pd(OAc)2 (5 mol%)</td>
<td>&lt;20%</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Fe(OAc)3 (10 mol%)</td>
<td>43%</td>
<td>1.44:1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Entry</th>
<th>Metal (mol%)</th>
<th>Yield of 2a</th>
<th>E/Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh2(OAc)4 (2 mol%)</td>
<td>41%</td>
<td>1.47:1</td>
</tr>
<tr>
<td>2</td>
<td>Rh2(OI)4 (2 mol%)</td>
<td>34%</td>
<td>1.38:1</td>
</tr>
<tr>
<td>3</td>
<td>Rh(PPh3)Cl (5 mol%)</td>
<td>37%</td>
<td>~2:1</td>
</tr>
<tr>
<td>4</td>
<td>Cp*RhCl3 (2.5 mol%)</td>
<td>25%</td>
<td>1.5:1</td>
</tr>
<tr>
<td>5</td>
<td>Pd(OAc)2 (5 mol%)</td>
<td>&lt;20%</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Fe(OAc)3 (10 mol%)</td>
<td>43%</td>
<td>1.44:1</td>
</tr>
</tbody>
</table>

*Reaction conditions: 1a (0.20 mmol), TMSN3 (0.40 mmol), CuBr (0.04 mmol), pyridine (0.40 mmol), and Metal (2-10 mol%) in PhCl (2.0 mL) was stirred at 90 °C for 48 h. Determined by 1H NMR measurement of the crude mixture.

Table S5  Screening of the additives

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additives (equiv)</th>
<th>Yield of 2a (%)</th>
<th>Z/E</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>48</td>
<td>64:36</td>
</tr>
<tr>
<td>2</td>
<td>NaOAc (1.0)</td>
<td>78</td>
<td>65:35</td>
</tr>
<tr>
<td>3</td>
<td>LiOAc (1.0)</td>
<td>50</td>
<td>64:36</td>
</tr>
<tr>
<td>4</td>
<td>NaOMe (1.0)</td>
<td>47</td>
<td>67:33</td>
</tr>
<tr>
<td>5d</td>
<td>mCPBA (0.15)</td>
<td>50</td>
<td>63:37</td>
</tr>
<tr>
<td>6d</td>
<td>FeCl2 (0.1)</td>
<td>43</td>
<td>64:36</td>
</tr>
<tr>
<td>7d</td>
<td>Yb(OTf)2 + H2O (0.1)</td>
<td>50</td>
<td>63:37</td>
</tr>
<tr>
<td>8d</td>
<td>CsOPiv (0.1)</td>
<td>41</td>
<td>63:37</td>
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<tr>
<td>9d</td>
<td>NHPI (0.1)</td>
<td>46</td>
<td>62:38</td>
</tr>
<tr>
<td>10d</td>
<td>NH4F (1.0)</td>
<td>43</td>
<td>63:37</td>
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<tr>
<td>11a</td>
<td>PhCOONa (1.0)</td>
<td>48</td>
<td>58:42</td>
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<tr>
<td>12a</td>
<td>Na2CO3 (1.0)</td>
<td>38</td>
<td>61:39</td>
</tr>
<tr>
<td>13a</td>
<td>NaOPiv (1.0)</td>
<td>24</td>
<td>63:37</td>
</tr>
<tr>
<td>14a</td>
<td>NaOTf (1.0)</td>
<td>32</td>
<td>57:43</td>
</tr>
<tr>
<td>15a</td>
<td>NaOTFA (1.0)</td>
<td>40</td>
<td>63:37</td>
</tr>
<tr>
<td>16a</td>
<td>NaOPO (1.0)</td>
<td>35</td>
<td>61:39</td>
</tr>
<tr>
<td>17a</td>
<td>KPF4 (1.0)</td>
<td>44</td>
<td>60:40</td>
</tr>
<tr>
<td>18a</td>
<td>dppp (0.2)</td>
<td>&lt;5</td>
<td>\</td>
</tr>
<tr>
<td>19a</td>
<td>P(OME)3 (1.0)</td>
<td>12</td>
<td>\</td>
</tr>
</tbody>
</table>

*Reaction conditions: 1a (0.40 mmol), TMSN3 (0.80 mmol), CuBr (0.08 mmol), pyridine (0.80 mmol), and Additives in PhCl (2.0 mL) was stirred at 90 °C for 48 h. Determined by 1H NMR measurement of the crude mixture. PhCl : 1,4-dioxane (10 : 1) was used instead of PhCl. 0.2 mmol scale, NMR yield.
Table S6  Screening of the additives with addition of NaOAc

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additives (equiv)</th>
<th>Yield of 2a (%)</th>
<th>Z/E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>NH₄I (1.0) or NaI (1.0)</td>
<td>0</td>
<td>/</td>
</tr>
<tr>
<td>2&lt;sup&gt;d&lt;/sup&gt;</td>
<td>KBr (1.0)</td>
<td>66</td>
<td>62:38</td>
</tr>
<tr>
<td>3&lt;sup&gt;d&lt;/sup&gt;</td>
<td>NaBr (1.0)</td>
<td>69</td>
<td>61:39</td>
</tr>
<tr>
<td>4</td>
<td>NaBO₂·H₂O (0.1)</td>
<td>71</td>
<td>65:35</td>
</tr>
<tr>
<td>5</td>
<td>dpdp (0.1)</td>
<td>66</td>
<td>63:37</td>
</tr>
<tr>
<td>6</td>
<td>FeCl₂ (0.1)</td>
<td>65</td>
<td>63:35</td>
</tr>
<tr>
<td>7</td>
<td>NaClO₄ (1)</td>
<td>50</td>
<td>66:34</td>
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<tr>
<td>8</td>
<td>NH₄F (2)</td>
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<tr>
<td>9</td>
<td>DMF (10)</td>
<td>82</td>
<td>65:35</td>
</tr>
<tr>
<td>10</td>
<td>MS-4A (200 mg)</td>
<td>63</td>
<td>66:34</td>
</tr>
<tr>
<td>11</td>
<td>Sc(OTf)₃ (0.1)</td>
<td>66</td>
<td>65:35</td>
</tr>
<tr>
<td>12</td>
<td>Mg(OTf)₂ (0.1)</td>
<td>70</td>
<td>67:33</td>
</tr>
<tr>
<td>13</td>
<td>InCl₃ (0.1)</td>
<td>60</td>
<td>64:36</td>
</tr>
<tr>
<td>14</td>
<td>NH₄Br (0.5)</td>
<td>66</td>
<td>63:37</td>
</tr>
<tr>
<td>15</td>
<td>H₂O (10)</td>
<td>44</td>
<td>69:31</td>
</tr>
<tr>
<td>16</td>
<td>TBA (0.1)</td>
<td>37</td>
<td>67:33</td>
</tr>
<tr>
<td>17</td>
<td>NaHSO₃ (0.1)</td>
<td>73</td>
<td>64:36</td>
</tr>
<tr>
<td>18</td>
<td>PhCOOH (0.1)</td>
<td>76</td>
<td>64:36</td>
</tr>
<tr>
<td>19</td>
<td>KHF₂ (0.1)</td>
<td>77</td>
<td>65:35</td>
</tr>
<tr>
<td>20</td>
<td>NH₄SCN (0.1)</td>
<td>23</td>
<td>60:40</td>
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</tbody>
</table>

<sup>a</sup>Reaction conditions: 1a (0.40 mmol), TMSN₃ (0.80 mmol), CuBr (0.08 mmol), pyridine (0.80 mmol), NaOAc (0.4 mmol) and Additives in PhCl (2.0 mL) was stirred at 90 °C for 48 h. <sup>b</sup>Isolated yield. <sup>c</sup>Determined by ¹H NMR measurement of the crude mixture. <sup>d</sup>0.2 mmol scale, NMR yield.
Table S7  Screening of the catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Cat.] (xx mol%)</th>
<th>Yield of 2a (%)</th>
<th>Z/E&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>CuBr (20 mol%)</td>
<td>78</td>
<td>65:35</td>
</tr>
<tr>
<td>3</td>
<td>CuOTf (20 mol%)</td>
<td>70</td>
<td>64:36</td>
</tr>
<tr>
<td>4</td>
<td>Cu₂O (20 mol%)</td>
<td>51</td>
<td>65:35</td>
</tr>
<tr>
<td>5</td>
<td>Cu(OAc)&lt;sub&gt;2&lt;/sub&gt; (20 mol%)</td>
<td>49</td>
<td>69:31</td>
</tr>
<tr>
<td>6</td>
<td>CuBr₂ (20 mol%)</td>
<td>62</td>
<td>67:33</td>
</tr>
<tr>
<td>7</td>
<td>Cu(ClO₄)₆·6H₂O (20 mol%)</td>
<td>42</td>
<td>71:29</td>
</tr>
<tr>
<td>8</td>
<td>CuBr (10 mol%)</td>
<td>41</td>
<td>63:37</td>
</tr>
<tr>
<td>9</td>
<td>CuOAc</td>
<td>60</td>
<td>67:33</td>
</tr>
<tr>
<td>10&lt;sup&gt;f&lt;/sup&gt;</td>
<td>FeCl₂ (10 mol%)</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>11&lt;sup&gt;f&lt;/sup&gt;</td>
<td>FeCl₃ (10 mol%)</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>12&lt;sup&gt;f&lt;/sup&gt;</td>
<td>CoCl₂</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>13&lt;sup&gt;f&lt;/sup&gt;</td>
<td>Co(acac)₃</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>14&lt;sup&gt;f&lt;/sup&gt;</td>
<td>Mn(OAc)&lt;sub&gt;2&lt;/sub&gt;·2H₂O (10 mol%)</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>15&lt;sup&gt;f&lt;/sup&gt;</td>
<td>MnO₂</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>16&lt;sup&gt;f&lt;/sup&gt;</td>
<td>AgNO₃</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: 1a (0.40 mmol), TMSN₃ (0.80 mmol), catalyst, pyridine (0.80 mmol), and NaOAc (0.40 mmol) in PhCl (2.0 mL) was stirred at 90 °C for 48 h. <sup>b</sup>Isolated yield. <sup>c</sup>Determined by <sup>1</sup>H NMR measurement of the crude mixture. <sup>f</sup>without NaOAc.

Table S8  Screening of the reaction temperatures

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp. (°C)</th>
<th>Yield of 2a (%)</th>
<th>Z/E&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70</td>
<td>67</td>
<td>63:37</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>78</td>
<td>65:35</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>31</td>
<td>69:31</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: 1a (0.40 mmol), TMSN₃ (0.80 mmol), CuBr (0.08 mmol), pyridine (0.80 mmol), and NaOAc (0.40 mmol) in PhCl (2.0 mL) was stirred at Temp. °C for 48 h. <sup>b</sup>Isolated yield. <sup>c</sup>Determined by <sup>1</sup>H NMR measurement of the crude mixture.
### Table S9  Screening of the solvents

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield of 2a (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Z/E&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhCl</td>
<td>45</td>
<td>/</td>
</tr>
<tr>
<td>2</td>
<td>PhCH₃</td>
<td>30</td>
<td>/</td>
</tr>
<tr>
<td>3</td>
<td>1,1,2-trichloroethane</td>
<td>43</td>
<td>/</td>
</tr>
<tr>
<td>4</td>
<td>1,2-dichlorobenzene</td>
<td>39</td>
<td>/</td>
</tr>
<tr>
<td>5</td>
<td>DMF</td>
<td>40</td>
<td>/</td>
</tr>
<tr>
<td>6</td>
<td>PhOMe</td>
<td>40</td>
<td>/</td>
</tr>
<tr>
<td>7</td>
<td>DMAc</td>
<td>37</td>
<td>/</td>
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<tr>
<td>8</td>
<td>DMSO</td>
<td>15</td>
<td>/</td>
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<tr>
<td>9</td>
<td>cumene</td>
<td>25</td>
<td>/</td>
</tr>
<tr>
<td>10&lt;sup&gt;f&lt;/sup&gt;</td>
<td>THF</td>
<td>0</td>
<td>/</td>
</tr>
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<td>11&lt;sup&gt;g&lt;/sup&gt;</td>
<td>PhCH₃</td>
<td>68</td>
<td>1.73:1</td>
</tr>
<tr>
<td>12&lt;sup&gt;g&lt;/sup&gt;</td>
<td>1,1,2,2-tetrachloroethane</td>
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<td>PhOMe</td>
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<tr>
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<td>MeCN</td>
<td>&lt;10</td>
<td>/</td>
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<td>15&lt;sup&gt;h&lt;/sup&gt;</td>
<td>dioxane</td>
<td>0</td>
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<td>16&lt;sup&gt;h&lt;/sup&gt;</td>
<td>AcOPr</td>
<td>68</td>
<td>1.71:1</td>
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<tr>
<td>17&lt;sup&gt;h&lt;/sup&gt;</td>
<td>PhCl</td>
<td>78</td>
<td>1.86:1</td>
</tr>
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<sup>a</sup>Reaction conditions: 1a (0.40 mmol), TMSN<sub>3</sub> (0.80 mmol), CuBr (0.08 mmol), pyridine (0.80 mmol), and NaOAc (0.40 mmol) in solvent (2.0 mL) was stirred at 90 °C for 24 h. <sup>b</sup>Isolated yield. <sup>c</sup>Not Determined. <sup>f</sup>Under reflux conditions. <sup>g</sup>0.2 mmol scale, NMR yield.
Table S10  Evaluation of isomerization reaction-1

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat. (20 mol%)</th>
<th>Recovery of 2a (%)</th>
<th>Z/E Selectivity</th>
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<tr>
<td>1</td>
<td>PPh3</td>
<td>&gt; 95</td>
<td>NO improvement</td>
</tr>
<tr>
<td>2</td>
<td>PMe3 (THF)</td>
<td>&gt; 95</td>
<td>form 2.1:1 to 1:1.06</td>
</tr>
<tr>
<td>3</td>
<td>PMe3 (THF)</td>
<td>&gt; 95</td>
<td>NO improvement</td>
</tr>
<tr>
<td>4</td>
<td>PPh3</td>
<td>&gt; 95</td>
<td>from 2.1:1 to 1:1.14</td>
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<tr>
<td>5</td>
<td>DABCO</td>
<td>&gt; 85</td>
<td>NO improvement</td>
</tr>
<tr>
<td>6</td>
<td>DBU</td>
<td>&gt; 70</td>
<td>NO improvement</td>
</tr>
<tr>
<td>7</td>
<td>PPh3</td>
<td>&gt; 95</td>
<td>NO improvement</td>
</tr>
<tr>
<td>8</td>
<td>HMPA</td>
<td>&gt; 99</td>
<td>NO improvement</td>
</tr>
<tr>
<td>9</td>
<td>R-(+)-Binap</td>
<td>&gt; 80</td>
<td>NO improvement</td>
</tr>
<tr>
<td>10</td>
<td>lPr</td>
<td>&gt; 50</td>
<td>NO improvement</td>
</tr>
<tr>
<td>11</td>
<td>CIrRh(PCy3)3</td>
<td>&gt; 95</td>
<td>NO improvement</td>
</tr>
<tr>
<td>12</td>
<td>CIrRh(PCy3)3</td>
<td>&gt; 95</td>
<td>NO improvement</td>
</tr>
<tr>
<td>13</td>
<td>Pd(TFA)2/iPrOH</td>
<td>&gt; 95</td>
<td>NO improvement</td>
</tr>
</tbody>
</table>

*aReaction conditions: 2a (0.20 mmol), catalyst (0.04 mmol) in DCM (1.0 mL) was stirred at rt for 12 h. Recovery and Z/E ratio was determined by NMR measurement.

Table S11  Evaluation of isomerization reaction-2

![Chemical structure](image)

<table>
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<tr>
<th>Entry</th>
<th>PnBu3 (x mol%)</th>
<th>Temp</th>
<th>Solvent</th>
<th>Additive</th>
<th>Recovery of 2a (%)</th>
<th>Z/E Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 mol%</td>
<td>rt</td>
<td>DCM</td>
<td>/</td>
<td>&gt; 95</td>
<td>from 2.1:1 to 1:1.14</td>
</tr>
<tr>
<td>2</td>
<td>20 mol%</td>
<td>80 °C</td>
<td>PhCH3</td>
<td>/</td>
<td>&gt; 95</td>
<td>from 1.23:1 to 1:1.19</td>
</tr>
<tr>
<td>3</td>
<td>20 mol%</td>
<td>100 °C</td>
<td>PhCH3</td>
<td>/</td>
<td>&gt; 95</td>
<td>from 1.23:1 to 1:1.22</td>
</tr>
<tr>
<td>4</td>
<td>20 mol%</td>
<td>140 °C</td>
<td>MeCN</td>
<td>/</td>
<td>&gt; 95</td>
<td>from 1.23:1 to 1:1.20</td>
</tr>
<tr>
<td>5</td>
<td>50 mol%</td>
<td>80 °C</td>
<td>MeCN</td>
<td>/</td>
<td>&gt; 95</td>
<td>from 1.09:1 to 1:1.14</td>
</tr>
<tr>
<td>6</td>
<td>100 mol%</td>
<td>80 °C</td>
<td>MeCN</td>
<td>/</td>
<td>&gt; 95</td>
<td>from 1.09:1 to 1:1.07</td>
</tr>
<tr>
<td>7</td>
<td>20 mol%</td>
<td>rt</td>
<td>DCM</td>
<td>HOAc</td>
<td>&gt; 95</td>
<td>NO improvement</td>
</tr>
<tr>
<td>8</td>
<td>20 mol%</td>
<td>rt</td>
<td>DCM</td>
<td>NaOAc</td>
<td>&gt; 99</td>
<td>from 1.37:1 to 1:1.14</td>
</tr>
<tr>
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<td>20 mol%</td>
<td>rt</td>
<td>DCM</td>
<td>BF3 Et2O</td>
<td>&gt; 95</td>
<td>NO improvement</td>
</tr>
<tr>
<td>10</td>
<td>20 mol%</td>
<td>rt</td>
<td>EA</td>
<td>/</td>
<td>&gt; 95</td>
<td>from 2.10:1 to 1:48:1</td>
</tr>
<tr>
<td>11</td>
<td>20 mol%</td>
<td>rt</td>
<td>MeCN</td>
<td>/</td>
<td>&gt; 95</td>
<td>from 2.10:1 to 1:1</td>
</tr>
<tr>
<td>12</td>
<td>20 mol%</td>
<td>rt</td>
<td>MeOH</td>
<td>/</td>
<td>&gt; 95</td>
<td>from 2.10:1 to 1:1</td>
</tr>
<tr>
<td>13</td>
<td>20 mol%</td>
<td>rt</td>
<td>hexane</td>
<td>/</td>
<td>&gt; 95</td>
<td>from 2.10:1 to 1:43:1</td>
</tr>
<tr>
<td>14</td>
<td>20 mol%</td>
<td>rt</td>
<td>PhCl</td>
<td>/</td>
<td>&gt; 95</td>
<td>from 2.10:1 to 1:64:1</td>
</tr>
<tr>
<td>15</td>
<td>20 mol%</td>
<td>rt</td>
<td>DMF</td>
<td>/</td>
<td>&gt; 95</td>
<td>from 2.10:1 to 1:105:1</td>
</tr>
</tbody>
</table>

*aReaction conditions: 2a (0.20 mmol), PnBu3 (0.04 mmol) in solvent (1.0 mL) was stirred under Ar for 12 h. Recovery and Z/E ratio was determined by NMR measurement.
Experimental Procedure and Characterization Data for Products

01) **5-Phenylpent-2-enenitrile (2a):**

**Typical procedure:** Mix pent-4-yn-1-ylbenzene 1a (57.7 mg, 0.40 mmol), TMSN₃ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O₂ (balloon). The reaction mixture was stirred at 90 °C for 48 hours. After cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to afford 49.3 mg (78%) of 2a. 2a: obtained as a 65:35 mixture of Z/E isomers. Colorless liquid.

**¹H NMR (CDCl₃, 400 MHz):** δ = 7.35-7.25 (m, 2H), 7.24-7.12 (m, 3H), 6.70 (dt, J₁ = 16.4 Hz, J₂ = 7.0 Hz, 1H, E-isomer), 6.46 (dt, J₁ = 10.8 Hz, J₂ = 5.4 Hz, 1H, Z-isomer), 5.33-5.26 (m, 1H), 2.83-2.70 (m, 2H, Z-isomer), 2.57-2.49 (m, 2H, E-isomer);

**¹³C NMR (CDCl₃, 100 MHz):** δ = 154.6, 153.7, 139.8, 139.7, 128.6, 128.5, 128.3, 128.2, 126.40, 126.35, 117.3, 115.7, 100.4, 100.1, 34.8, 34.2, 33.8, 33.2 ppm; **MS (70 eV) m/z (%):** found 157.1 (M⁺)

02) **4-Phenylbut-2-enenitrile (2b):**

The reaction of but-3-yn-1-ylbenzene 1b (52.1 mg, 0.40 mmol), TMSN₃ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O₂ at 90 °C for 48 hours, afforded 25.0 mg (44%) of 2b. 2b: obtained as a 67:33 mixture of Z/E isomers. Colorless liquid.

**Z-isomer:** **¹H NMR (CDCl₃, 400 MHz):** δ = 7.36-7.30 (m, 2H), 7.29-7.23 (m, 1H), 7.23-7.18 (m, 2H), 6.61 (dt, J₁ = 10.8 Hz, J₂ = 5.4 Hz, 1H), 5.41 (dt, J₁ = 10.8 Hz, J₂ = 1.4 Hz, 1H), 3.75 (d, J = 7.6 Hz, 2H); **¹³C NMR (CDCl₃, 100 MHz):** δ = 152.8,
136.8, 128.9, 128.5, 127.0, 115.9, 99.9, 38.0 ppm;

\(^1\)H NMR for the minor \(E\)-isomer: 7.37-7.30 (m, 2H), 7.29-7.22 (m, 1H), 7.16-7.12 (m, 2H), 6.87 (dt, \(J_1 = 16.0\) Hz, \(J_2 = 6.6\) Hz, 1H), 5.27 (dt, \(J_1 = 16.4\) Hz, \(J_2 = 1.8\) Hz, 1H), 3.53 (dd, \(J_1 = 6.4\) Hz, \(J_2 = 1.6\) Hz, 1H).

**MS (70 eV) m/z (%):** found 143.1 (M\(^+\)).

03)

Undec-2-enenitrile (2c):\(^3\)
The reaction of undec-1-yne 1c (60.9 mg, 0.40 mmol), TMSN\(_3\) (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under \(\text{O}_2\) at 90 °C for 48 hours, afforded 50.0 mg (76%) of 2c. 2c: obtained as a 61:39 mixture of \(Z/E\) isomers. Colorless liquid.

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 6.72\) (dt, \(J_1 = 16.4\) Hz, \(J_2 = 7.0\) Hz, 1H, \(E\)-isomer), 6.49 (dt, \(J_1 = 10.8\) Hz, \(J_2 = 5.6\) Hz, 1H, \(Z\)-isomer), 5.37-5.27 (m, 1H), 2.42 (td, \(J_1 = 7.5\) Hz, \(J_2 = 7.5\) Hz, 2H, \(Z\)-isomer), 2.26-2.15 (m, 2H, \(E\)-isomer), 1.53-1.40 (m, 2H), 1.35-1.21 (m, 10H), 0.88 (t, \(J = 6.6\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 156.2, 155.3, 117.6, 116.0, 99.5, 99.3, 33.3, 31.8, 31.7, 29.2, 29.08, 29.06, 29.0, 28.9, 28.2, 27.5, 22.6, 14.0\) ppm;

**MS (70 eV) m/z (%):** found 150.1 ([M-CH\(_3\)]\(^+\)).

04)

Dec-2-enenitrile (2d):\(^4\)
The reaction of dec-1-yne 1d (55.3 mg, 0.40 mmol), TMSN\(_3\) (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under \(\text{O}_2\) at 90 °C for 48 hours, afforded 37.7 mg (62%) of 2d. 2d: obtained as a 66:34 mixture of \(Z/E\) isomers. Colorless liquid.

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 6.72\) (dt, \(J_1 = 16.4\) Hz, \(J_2 = 7.0\) Hz, 1H, \(E\)-isomer),
S12

6.48 (dt, $J_1 = 10.8$ Hz, $J_2 = 5.4$ Hz, 1H, Z-isomer), 5.35-5.28 (m, 1H), 2.46-2.39 (m, 2H, Z-isomer), 2.26-2.19 (m, 2H, E-isomer), 1.52-1.40 (m, 2H), 1.35-1.23 (m, 8H), 0.89 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 156.2, 155.3, 117.6, 116.1, 99.6, 99.4, 33.3, 31.9, 31.7, 31.6, 29.0, 28.92, 28.88, 28.2, 27.6, 22.6, 14.0$ ppm; MS (70 eV) m/z (%): found 136.1 ([M-CH$_3$]$^+$).

05)

3-Cyclohexylacrylonitrile (2e):$^5$
The reaction of prop-2-yn-1-ylcyclohexane 1e (48.9 mg, 0.40 mmol), TMSN$_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O$_2$ at 90 °C for 48 hours, afforded 34.3 mg (63%) of 2e. 2e: obtained as a 60:40 mixture of Z/E isomers. Colorless liquid.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 6.67$ (dd, $J_1 = 16.4$ Hz, $J_2 = 6.4$ Hz, 1H, E-isomer), 6.32 (dd, $J_1 = 10.8$ Hz, $J_2 = 10.4$ Hz, 1H, Z-isomer), 5.27 (dd, $J_1 = 16.4$ Hz, $J_2 = 1.6$ Hz, 1H, E-isomer), 5.21 (dd, $J_1 = 10.8$ Hz, $J_2 = 0.4$ Hz, 1H, Z-isomer), 2.68-2.55 (m, 1H, Z-isomer), 2.20-2.09 (m, 1H, E-isomer), 1.80-1.65 (m, 5H), 1.42-1.08 (m, 5H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 160.8, 160.1, 117.9, 116.1, 97.5, 97.1, 41.4, 41.0, 31.7, 31.1, 25.6, 25.5, 25.4, 25.1$ ppm; MS (70 eV) m/z (%): found 135.1 (M$^+$)

06)

2-Cyclohexylideneacetonitrile (2f):$^6$
The reaction of ethynylcyclohexane 1f (43.3 mg, 0.40 mmol), TMSN$_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O$_2$ at 90 °C for 48 hours, afforded 29.8 mg (61%) of 2f. Colorless liquid.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 5.04$ (s, 1H), 2.49 (t, $J = 6.0$ Hz, 2H), 2.25 (t, $J =$
5.6 Hz, 2H), 1.71-1.58 (m, 6H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 168.7, 117.0, 91.9, 35.9, 33.1, 27.9, 27.5, 25.6\) ppm;

**MS (70 eV) m/z (%):** found 121.1 (M\(^+\))

6-((tert-Butyldimethylsilyloxy)hex-2-enenitrile (2g):
The reaction of tert-butyl(hex-5-yn-1-yloxy)dimethylsilane 1g (85.0 mg, 0.40 mmol), TMSN\(_3\) (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O\(_2\) at 90 °C for 48 hours, afforded 61.0 mg (68%) of 2g. 2g: obtained as a 69:31 mixture of Z/E isomers. Colorless liquid.

**\(^1\)H NMR (CDCl\(_3\), 400 MHz):** \(\delta = 6.74\) (dt, \(J_1 = 16.4\) Hz, \(J_2 = 7.0\) Hz, 1H, E-isomer), 6.52 (dt, \(J_1 = 10.8\) Hz, \(J_2 = 5.6\) Hz, 1H, Z-isomer), 5.33 (dt, \(J_1 = 16.4\) Hz, \(J_2 = 1.6\) Hz, 1H, E-isomer), 5.31 (dt, \(J_1 = 10.8\) Hz, \(J_2 = 1.4\) Hz, 1H, Z-isomer), 3.66-3.58 (m, 2H), 2.49 (tdd, \(J_1 = 7.6\) Hz, \(J_2 = 7.6\) Hz, \(J_3 = 1.2\) Hz, 2H, Z-isomer), 2.30 (tdd, \(J_1 = 7.2\) Hz, \(J_2 = 7.2\) Hz, \(J_3 = 1.2\) Hz, 2H, E-isomer), 1.72-1.61 (m, 2H), 0.879 (s, 9H, Z-isomer), 0.875 (s, 9H, E-isomer), 0.04 (s, 6H, Z-isomer), 0.03 (m, 6H, E-isomer); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 155.8, 155.0, 117.4, 115.9, 99.8, 99.4, 62.0, 61.7, 31.3, 30.6, 29.9, 28.6, 25.83, 25.80, 18.2, -5.5\) ppm;

**HRMS m/z (ESI) cacld for C\(_{12}\)H\(_{23}\)NNaOSi (M + Na\(^+\) 248.1441, found 248.1440.

**IR (neat):** v\(_{\text{max}}\) = 2953, 2933, 2859, 2222, 1628, 1105, 839.

6-(Nonyloxy)hex-2-enenitrile (2h):
The reaction of 1-(hex-5-yn-1-yloxy)nonane 1h (89.8 mg, 0.40 mmol), TMSN\(_3\) (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc
(32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O₂ at 90 °C for 48 hours, afforded 55.9 mg (59%) of 2h. 2h: obtained as a 69:31 mixture of Z/E isomers. Colorless liquid.

**1H NMR (CDCl₃, 400 MHz):** δ = 6.74 (dt, J₁ = 16.4 Hz, J₂ = 7.0 Hz, 1H, E-isomer), 6.53 (dt, J₁ = 10.8 Hz, J₂ = 5.6 Hz, 1H, Z-isomer), 5.35 (dt, J₁ = 16.4 Hz, J₂ = 1.8 Hz, 1H, E-isomer), 5.32 (dt, J₁ = 10.8 Hz, J₂ = 1.4 Hz, 1H, Z-isomer), 3.46-3.56 (m, 4H), 2.49 (tdd, J₁ = 7.4 Hz, J₂ = 7.4 Hz, J₃ = 1.2 Hz, 2H, Z-isomer), 2.30 (tdd, J₁ = 7.2 Hz, J₂ = 7.2 Hz, J₃ = 1.2 Hz, 2H, E-isomer), 1.80-1.70 (m, 2H), 1.60-1.50 (m, 2H), 1.38-1.21 (m, 12H), 0.88 (t, J = 6.8 Hz, 3H); **13C NMR (CDCl₃, 100 MHz):** δ = 155.5, 154.8, 117.4, 115.9, 99.9, 99.6, 71.13, 71.08, 69.6, 69.2, 31.8, 30.2, 29.6, 29.5, 29.4, 29.2, 28.9, 28.3, 27.8, 26.1, 22.6, 14.0 ppm;

**HRMS m/z (ESI) calcd for C₁₅H₂₇NNaO (M + Na)⁺ 260.1985, found 260.1982.**

**IR (neat):** νmax = 2927, 2856, 2222, 1632, 1465, 1117, 739.

Methyl 10-cyanodec-9-enoate (2i):

The reaction of (pent-4-yn-1-yloxy)benzene 1i (64.1 mg, 0.40 mmol), TMSN₃ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O₂ at 90 °C for 48 hours, afforded 41.6 mg (60%) of 2i. 2i: obtained as a 68:32 mixture of Z/E isomers. Colorless liquid.

**1H NMR (CDCl₃, 400 MHz):** δ = 7.33-7.25 (m, 2H), 7.00-6.91 (m, 1H), 6.91-6.85 (m, 2H), 6.79 (dt, J₁ = 16.4 Hz, J₂ = 6.8 Hz, 1H, E-isomer), 6.66 (dt, J₁ = 11.2 Hz, J₂ = 5.6 Hz, 1H, Z-isomer), 5.47 (dt, J₁ = 16.4 Hz, J₂ = 1.6 Hz, 1H, E-isomer), 5.43 (dt, J₁ = 11.2 Hz, J₂ = 1.4 Hz, 1H, Z-isomer), 4.10-4.02 (m, 2H), 2.93-2.85 (m, 2H, Z-isomer), 2.67 (tdd, J₁ = 6.4 Hz, J₂ = 6.4 Hz, J₃ = 1.6 Hz, 2H, E-isomer); **13C NMR (CDCl₃, 100 MHz):** δ = 158.5, 158.3, 151.9, 151.1, 129.62, 129.59, 121.3, 121.2, 117.2, 115.8, 114.6, 102.0, 101.6, 65.6, 65.2, 33.1, 31.8 ppm;

**HRMS m/z (EI) calcd for C₁₂H₁₃NNaO₂ (M + Na)⁺ 226.0839, found 226.0835.**

**IR (neat):** νmax = 3070, 2925, 2879, 2222, 1634, 1600, 1496, 1244, 1042, 755.
5-(4-Methoxyphenoxy)pent-2-enenitrile (2j):

The reaction of 1-methoxy-4-(pent-4-yn-1-yloxy)benzene 1j (76.1 mg, 0.40 mmol), TMSN₃ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O₂ at 90 °C for 48 hours, afforded 41.0 mg (50%) of 2j. 2j: obtained as a 69:31 mixture of Z/E isomers. Colorless liquid.

Z-isomer: ¹H NMR (CDCl₃, 400 MHz): δ = 6.85-6.82 (m, 4H), 6.67 (dt, J₁ = 10.8 Hz, J₂ = 5.6 Hz, 1H), 5.45 (dt, J₁ = 11.2 Hz, J₂ = 1.4 Hz, 1H), 4.04 (t, J = 6.0 Hz, 2H), 3.77 (s, 3H), 2.91-2.84 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 154.1, 152.5, 151.2, 115.7, 115.5, 114.7, 101.5, 66.3, 55.7, 31.9 ppm;

¹H NMR for the minor E-isomer: 6.85-6.76 (m, 5H), 5.48 (dt, J₁ = 16.4 Hz, J₂ = 1.6 Hz, 1H), 4.05-3.89 (m, 2H), 3.77 (s, 3H), 2.70-2.62 (m, 2H).

HRMS m/z (ESI) calcd for C₁₂H₁₃NNaO₂ (M + Na)+ 226.0839, found 226.0835.

IR (neat): νmax = 3070, 2953, 2220, 1624, 1509, 1232, 1042, 828.

6-(4-(Trifluoromethyl)phenoxy)hex-2-enenitrile (2k):

The reaction of 1-(hex-5-yn-1-yloxy)-4-(trifluoromethyl)benzene 1k (91.3 mg, 0.40 mmol), TMSN₃ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O₂ at 90 °C for 48 hours, afforded 63.8 mg (66%) of 2k. 2k: obtained as a 63:37 mixture of Z/E isomers. Colorless liquid.

Z-isomer: ¹H NMR (CDCl₃, 400 MHz): δ = 7.55 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 6.66 (dt, J₁ = 10.8 Hz, J₂ = 5.6 Hz, 1H), 5.49 (dt, J₁ = 10.8 Hz, J₂ = 1.2 Hz, 1H), 4.14 (t, J = 6.0 Hz, 2H), 2.93 (td, J₁ = 6.0 Hz, J₂ = 6.0 Hz, J₃ = 1.2 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 160.8, 150.4, 126.9 (q, J = 3.7 Hz), 124.3 (q, J = 269.5 Hz, 2H).
Hz), 123.3 (q, \( J = 32.4 \) Hz), 115.6, 114.4, 102.1, 65.8, 31.5 ppm;

\(^1\)H NMR for the minor \( E \)-isomer: 7.58-7.54 (m, 2H), 6.98-6.92 (m, 2H), 6.81 (dt, \( J_1 = 16.4 \) Hz, \( J_2 = 6.8 \) Hz, 1H). 5.54-5.46 (m, 1H), 4.17-4.07 (m, 2H), 2.77-2.70 (m, 2H).

**HRMS m/z (ESI)**: calcd for C\(_{12}\)H\(_{10}\)F\(_3\)NNaO (M + Na\(^+\)) 264.0607, found 264.0601.

**IR (neat):** \( \nu_{\max} = \) 3075, 2938, 2225, 1617, 1331, 1258, 1113, 839.

12)

**5-(2-Chlorophenoxy)pent-2-enenitrile (2l):**

The reaction of 1-chloro-2-(pent-4-yn-1-yl)oxy)benzene \( 1l \) (77.9 mg, 0.40 mmol), TMSN\(_3\) (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O\(_2\) at 90 °C for 48 hours, afforded 58.6 mg (71%) of \( 2l \). \( 2l \): obtained as a 36:34 mixture of \( Z/E \) isomers. Colorless liquid.

**Z-isomer: \(^1\)H NMR (CDCl\(_3\), 400 MHz):** \( \delta = 7.39-7.35 \) (m, 1H), 7.21 (td, \( J_1 = 8.0 \) Hz, \( J_2 = 1.6 \) Hz, 1H), 6.96-6.88 (m, 2H), 6.76 (dt, \( J_1 = 11.2 \) Hz, \( J_2 = 5.4 \) Hz, 1H), 5.48 (d, \( J = 11.2 \) Hz, 1H), 4.15 (t, \( J = 5.8 \) Hz, 2H), 2.99-2.92 (tdd, \( J_1 = 6.4 \) Hz, \( J_2 = 6.4 \) Hz, \( J_3 = 1.2 \) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \( \delta = 153.8, 150.7, 130.3, 127.7, 123.1, 121.9, 115.6, 113.6, 101.7, 66.8, 31.6 \) ppm;

\(^1\)H NMR for the minor \( E \)-isomer: 7.37 (dd, \( J_1 = 8.0 \) Hz, \( J_1 = 1.2 \) Hz, 1H), 7.22 (td, \( J_1 = 8.0 \) Hz, \( J_2 = 1.6 \) Hz, 1H), 6.96-6.86 (m, 2H), 6.86 (dt, \( J_1 = 11.2 \) Hz, \( J_2 = 7.0 \) Hz, 1H), 5.55 (d, \( J = 16.4 \) Hz, 1H), 4.13 (t, \( J = 6.0 \) Hz, 2H), 2.75 (tdd, \( J_1 = 7.6 \) Hz, \( J_2 = 7.6 \) Hz, \( J_3 = 1.6 \) Hz, 2H).

**HRMS m/z (ESI)**: calcd for C\(_{11}\)H\(_{10}\)ClNNaO (M + Na\(^+\)) 230.0343, found 230.0339.

**IR (neat):** \( \nu_{\max} = \) 3066, 2934, 2225, 1636, 1250, 1063, 751.

13)

**5-(Naphthalen-2-yl)oxy)pent-2-enenitrile (2m):**
The reaction of 1-(pent-4-yn-1-yloxy)naphthalene 1m (84.1 mg, 0.40 mmol), TMSN₃ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O₂ at 90 °C for 48 hours, afforded 54.0 mg (60%) of 2m. 2m: obtained as a 64:36 mixture of Z/E isomers. Colorless liquid. **Z-isomer:** ¹H NMR (CDCl₃, 400 MHz): δ = 8.27-8.21 (m, 1H), 7.82-7.76 (m, 1H), 7.53-7.42 (m, 3H), 7.36 (t, J = 8.0 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H), 6.74 (dt, J₁ = 10.8 Hz, J₂ = 5.4 Hz, 1H), 5.49 (dt, J₁ = 10.8 Hz, J₂ = 1.2 Hz, 1H), 4.25 (t, J = 6.0 Hz, 2H), 3.04 (ddd, J₁ = 6.4 Hz, J₂ = 6.4 Hz, J₃ = 1.2 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 154.1, 151.1, 134.4, 127.5, 126.5, 125.7, 125.40, 125.35, 121.8, 120.7, 115.8, 104.6, 101.8, 65.7, 31.9 ppm; ¹H NMR for the minor E-isomer: 8.20-8.15 (m, 1H), 7.82-7.76 (m, 1H), 7.52-7.41 (m, 3H), 7.35 (t, J = 7.8 Hz, 1H), 6.87 (dt, J₁ = 16.4 Hz, J₂ = 6.8 Hz, 1H), 6.78-6.72 (m, 1H), 5.56-5.44 (m, 1H), 4.25-4.17 (m, 2H), 2.79 (ddd, J₁ = 7.2 Hz, J₂ = 7.2 Hz, J₃ = 1.6 Hz, 2H); HRMS m/z (ESI) calcd for C₁₅H₁₃NNaO (M + Na⁺) 246.0889, found 246.0885.

IR (neat): νmax = 3056, 2931, 2880, 2220, 1626, 1508, 1270, 1101, 773.

5-(Naphthalen-2-yloxy)pent-2-enenitrile (2n):
The reaction of 2-(pent-4-yn-1-yloxy)naphthalene 1n (84.1 mg, 0.40 mmol), TMSN₃ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O₂ at 90 °C for 48 hours, afforded 51.3 mg (57%) of 2n. 2n: obtained as a 64:36 mixture of Z/E isomers. Colorless liquid. **Z-isomer:** ¹H NMR (CDCl₃, 400 MHz): δ = 7.80-7.70 (m, 3H), 7.48-7.41 (m, 1H), 7.38-7.31 (m, 1H), 7.17-7.11 (m, 2H), 6.71 (dt, J₁ = 10.8 Hz, J₂ = 5.4 Hz, 1H), 5.47 (dt, J₁ = 10.8 Hz, J₂ = 1.4 Hz, 1H), 4.20 (t, J = 6.2 Hz, 2H), 2.99-2.93 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 156.4, 151.0, 134.4, 129.5, 129.1, 127.7, 126.7, 126.5, 123.8, 118.7, 115.7, 106.7, 101.7, 65.6, 31.7 ppm;
**1H NMR for the minor E-isomer:** 7.80-7.70 (m, 3H), 7.48-7.41 (m, 1H), 7.38-7.31 (m, 1H), 7.17-7.08 (m, 2H), 6.82 (dt, $J_1 = 16.4$ Hz, $J_2 = 6.8$ Hz, 1H), 5.52 (dt, $J_1 = 16.4$ Hz, $J_2 = 1.6$ Hz, 1H), 4.20-4.12 (m, 2H), 2.75-2.68 (m, 2H).

**HRMS $m/z$ (ESI)** calculated for C$_{15}$H$_{13}$NNaO (M + Na)$^+$ 246.0889, found 246.0884.

**IR (neat):** $\nu_{\text{max}}$ = 3059, 2945, 2220, 1628, 1508, 1250, 1144, 837, 753.

**Methyl 10-cyanodec-9-enoate (2o):**

The reaction of methyl undec-10-ynoate 1o (78.5 mg, 0.40 mmol), TMSN$_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O$_2$ at 90 °C for 48 hours, afforded 58.0 mg (69%) of 2o. 2o: obtained as a 69:31 mixture of Z/E isomers. Colorless liquid.

**1H NMR (CDCl$_3$, 400 MHz):** $\delta$ = 6.72 (dt, $J_1 = 16.4$ Hz, $J_2 = 7.0$ Hz, 1H, E-isomer), 6.49 (dt, $J_1 = 11.2$ Hz, $J_2 = 5.4$ Hz, 1H, Z-isomer), 5.37-5.29 (m, 1H), 3.67 (s, 3H), 2.42 (td, $J_1 = 7.4$ Hz, $J_2 = 7.4$ Hz, 2H, Z-isomer), 2.31 (t, $J = 7.4$ Hz, 2H), 2.26-2.18 (m, 2H, E-isomer), 1.66-1.58 (m, 2H), 1.52-1.42 (m, 2H), 1.37-1.28 (m, 6H);

**13C NMR (CDCl$_3$, 100 MHz):** $\delta$ = 174.1, 174.0, 155.9, 155.0, 117.4, 115.9, 99.6, 99.4, 51.3, 33.9, 33.8, 33.1, 31.7, 28.79, 18.78, 28.75, 28.63, 28.60, 28.0, 27.4, 24.69, 24.67, 24.67 ppm;

**HRMS $m/z$ (ESI)** calculated for C$_{12}$H$_{19}$NNaO$_2$ (M + Na)$^+$ 232.1308, found 232.1305.

**IR (neat):** $\nu_{\text{max}}$ = 2933, 2858, 2221, 1738, 1631, 1249, 1173, 743.

**3-Methylbut-3-en-1-yl 10-cyanodec-9-enoate (2p):**

Mix 3-methylbut-3-en-1-yl undec-10-ynoate 1p (100.2 mg, 0.40 mmol), TMSN$_3$ (69.2 mg, 0.60 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O$_2$. After stirring at 90 °C for 24 hours, another portion of TMSN$_3$ (69.2 mg, 0.60 mmol) was added. Then the mixture was
stirred for another 24 hours. After cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel to afford 41.7 mg (40%) of 2p. 2p: obtained as a 64:36 mixture of Z/E isomers. Colorless liquid.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 6.72$ (dt, $J_1 = 16.4$ Hz, $J_2 = 6.8$ Hz, 1H, E-isomer), 6.48 (dt, $J_1 = 11.2$ Hz, $J_2 = 5.4$ Hz, 1H, Z-isomer), 5.38-5.29 (m, 1H), 4.80 (s, 1H), 4.73 (s, 1H), 4.19 (t, $J = 6.8$ Hz, 2H), 2.46-2.39 (m, 2H, Z-isomer), 2.34 (t, $J = 6.8$ Hz, 2H), 2.29 (t, $J = 7.4$ Hz, 2H), 2.25-2.18 (m, 2H, E-isomer), 1.76 (s, 3H), 1.65-1.58 (m, 2H), 1.52-1.42 (m, 2H), 1.38-1.28 (m, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 173.73$, 173.68, 156.0, 155.1, 141.7, 117.5, 116.0, 112.2, 99.7, 99.5, 62.4, 36.7, 34.21, 34.18, 33.2, 31.8, 28.87, 28.86, 28.8, 28.7, 28.1, 27.5, 24.81, 24.79, 22.4 ppm; HRMS m/z (ESI) calecd for C$_{16}$H$_{25}$NNaO$_2$ (M + Na)$^+$ 286.1778, found 286.1778.

IR (neat): $\nu_{\text{max}} = 3077, 2933, 2858, 2221, 1735, 1651, 1632, 1457, 1176, 836.$

5-Cyanopent-4-en-1-yl thiophene-2-carboxylate (2q):
The reaction of hex-5-yn-1-yl thiophene-2-carboxylate 1q (83.3 mg, 0.40 mmol), TMSN$_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O$_2$ (ballon) at 90 $^\circ$C for 60 hours, afforded 65.0 mg (73%) of 2q. 2q: obtained as a 34:66 mixture of Z/E isomers. Colorless liquid.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.76-7.71$ (m, 1H), 7.52-7.47 (m, 1H), 7.06-7.01 (m, 1H), 6.68 (dt, $J_1 = 16.4$ Hz, $J_2 = 6.8$ Hz, 1H, E-isomer), 6.46 (dt, $J_1 = 10.8$ Hz, $J_2 = 5.4$ Hz, 1H, Z-isomer), 5.36-5.28 (m, 1H), 4.29-4.22 (m, 2H), 2.56-2.48 (m, 2H, Z-isomer), 2.36-2.28 (m, 2H, E-isomer), 192-1.80 (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 162.0$, 161.9, 154.3, 153.4, 133.5, 133.4, 133.3, 132.53, 133.47, 127.8, 127.7, 117.1, 115.6, 100.6, 100.5, 63.72, 63.67, 29.9, 28.4, 27.3, 26.8 ppm; HRMS m/z (ESI) calecd for C$_{11}$H$_{11}$NNaO$_2$S (M + Na)$^+$ 244.0403, found 244.0398.
IR (neat): $\nu_{\text{max}} = 3104, 2958, 2222, 1709, 1633, 1262, 1098, 751$.

18) 5-(1,3-Dioxoisindolin-2-yl)pent-2-enenitrile (2r):
The reaction of 2-(pent-4-yn-1-yl)isoindoline-1,3-dione 1r (87.9 mg, 0.40 mmol), TMSN$_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O$_2$ (ballon) at 90 °C for 72 hours, afforded 58.9 mg (65%) of 2r. 2r: obtained as a 69:31 mixture of Z/E isomers. Colorless liquid.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.89-7.84$ (m, 2H), 7.78-7.72 (m, 2H), 6.70 (dt, $J_1$ = 16.4 Hz, $J_2$ = 7.2 Hz, 1H, E-isomer), 6.53 (dt, $J_1$ = 11.2 Hz, $J_2$ = 5.6 Hz, 1H, Z-isomer), 5.46-5.36 (m, 1H), 3.92-3.81 (m, 2H, Z-isomer), 2.88-2.80 (m, 2H, E-isomer);

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 168.0, 167.9, 151.1, 150.4, 134.14, 134.08, 131.72, 131.65, 123.32, 123.30, 116.7, 115.2, 102.3, 102.0, 35.8, 35.7, 32.2, 31.1$ ppm;

HRMS m/z (ESI) calcd for C$_{13}$H$_{10}$N$_2$NaO$_2$ (M + Na)$^+$ 249.0635, found 249.0630.

IR (neat): $\nu_{\text{max}} = 3064, 2939, 2220, 1773, 1708, 1619, 1397, 722$.

19) N-(5-Cyanopent-4-en-1-yl)-4-methylbenzenesulfonamide (2s):
The reaction of N-(hex-5-yn-1-yl)-4-methylbenzenesulfonamide 1s (100.5 mg, 0.40 mmol), TMSN$_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O$_2$ (ballon) at 90 °C for 48 hours, afforded 64.5 mg (61%) of 2s. 2s: obtained as a 70:30 mixture of Z/E isomers. Colorless liquid.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.77-7.73$ (m, 2H), 7.34-7.30 (m, 2H), 6.60 (dt, $J_1$ = 16.0 Hz, $J_2$ = 7.0 Hz, 1H, E-isomer), 6.44 (dt, $J_1$ = 10.8 Hz, $J_2$ = 5.4 Hz, 1H,
Z-isomer), 5.36-5.26 (m, 1H), 5.12-4.96 (m, 2H), 2.46-2.39 (s, 2H, Z-isomer), 2.44 (s, 3H), 2.30-2.22 (m, 2H, E-isomer), 1.72-1.58 (m, 2H); **13C NMR (CDCl₃, 100 MHz):** δ = 154.2, 153.5, 143.7, 143.6, 136.7, 129.8, 127.0, 117.2, 115.7, 100.7, 100.5, 42.3, 42.0, 29.9, 28.8, 28.2, 27.6, 21.5 ppm;

**HRMS m/z (ESI):** calcd for C₁₃H₁₆N₂NaO₂S (M + Na)⁺, 287.0825, found 287.0818.

**IR (neat):** νmax = 3280, 3068, 2929, 2872, 2222, 1624, 1326, 1159.

**8-Phenyloct-2-en-7-ynenitrile (2t):**

The reaction of octa-1,7-diyn-1-ylbenzene 1t (72.9 mg, 0.40 mmol), TMSN₃ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O₂ at 90 °C for 72 hours, afforded 35.6 mg (46%) of 2t. 2t: obtained as a 66:34 mixture of Z/E isomers. Colorless liquid.

**1H NMR (CDCl₃, 400 MHz):** δ = 7.44-7.35 (m, 2H), 7.31-7.26 (m, 3H), 6.75 (dt, J₁ = 16.0 Hz, J₂ = 7.0 Hz, 1H, E-isomer), 6.53 (dt, J₁ = 11.2 Hz, J₂ = 5.6 Hz, 1H, Z-isomer), 5.39 (dt, J₁ = 16.0 Hz, J₂ = 1.6 Hz, 1H, E-isomer), 5.36 (dt, J₁ = 11.2 Hz, J₂ = 1.2 Hz, 1H, Z-isomer), 2.62 (tdd, J₁ = 7.6 Hz, J₂ = 7.6 Hz, J₃ = 1.2 Hz, 2H, Z-isomer), 2.50-2.43 (m, 2H), 2.45-2.38 (m, 2H, E-isomer), 1.84-1.71 (m, 2H); **13C NMR (CDCl₃, 100 MHz):** δ = 154.8, 153.9, 131.52, 131.49, 128.23, 128.19, 127.8, 127.7, 123.6, 123.5, 117.3, 115.8, 100.5, 100.3, 88.6, 88.4, 81.7, 81.6, 32.2, 30.9, 27.3, 26.5, 18.9, 18.7 ppm;

**HRMS m/z (ESI):** calcd for C₁₄H₁₃KN (M + K)⁺, 234.0680, found 234.0679.

**IR (neat):** νmax = 3057, 2931, 2863, 2237, 2222, 1626, 1490, 758, 693.

**21) (1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 10-cyanodec-9-enoate (4a):**
The reaction of \((1R,2S,5R)-2\text{-isopropyl-5-methylcyclohexyl}\) undec-10-ynoate 3a (128.2 mg, 0.40 mmol), TMSN\(_3\) (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O\(_2\) at 90 °C for 48 hours, afforded 65.3 mg (49%) of 4a. 4a: obtained as a 65:35 mixture of Z/E isomers. Colorless liquid.

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 6.71\) (dt, \(J_1 = 16.0\) Hz, \(J_2 = 7.0\) Hz, 1H, \(E\)-isomer), 6.48 (dt, \(J_1 = 11.2\) Hz, \(J_2 = 5.4\) Hz, 1H, \(Z\)-isomer), 5.35-5.28 (m, 1H), 4.68 (td, \(J_1 = 11.0\) Hz, \(J_2 = 4.4\) Hz, 1H, \(Z\)-isomer), 2.46-2.38 (m, 2H, \(Z\)-isomer), 2.28 (t, \(J = 7.4\) Hz, 2H), 2.25-2.18 (m, 2H, \(E\)-isomer), 2.01-1.94 (m, 1H), 1.91-1.82 (m, 1H), 1.72-1.57 (m, 4H), 1.52-1.28 (m, 10H), 1.12-0.83 (m, 3H), 0.90 (d, \(J = 6.4\) Hz, 3H), 0.89 (d, \(J = 7.2\) Hz, 3H), 0.76 (d, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 173.31, 173.27, 156.0, 155.1, 117.5, 116.0, 99.7, 99.5, 73.91, 73.89, 47.0, 40.9, 34.9, 34.63, 34.59, 34.2, 33.2, 31.8, 31.3, 28.89, 28.88, 28.86, 28.8, 28.7, 28.1, 27.5, 26.2, 25.0, 24.9, 23.4, 22.0, 20.7, 16.3 ppm;

HRMS m/z (ESI) calcd for C\(_{21}\)H\(_{35}\)NNaO\(_2\) (M + Na\(^+\)), 356.2560, found 356.2557.

IR (neat): \(\nu_{\text{max}} = 2930, 2861, 2222, 1729, 1629, 1459, 1181\).

22)

\(\text{2-(2-Methyl-5-nitro-1H-imidazol-1-yl)ethyl 10-cyanodec-9-enoate (4b):}\)

The reaction of 2-(2-methyl-5-nitro-1H-imidazol-1-yl)ethyl undec-10-ynoate 3b (134.2 mg, 0.40 mmol), TMSN\(_3\) (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O\(_2\) at 90 °C for 48 hours, afforded 84.1 mg (60%) of 4b. 4b: obtained as a 68:32 mixture of Z/E isomers. Colorless liquid.

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 7.95\) (s, 1H), 6.72 (dt, \(J_1 = 16.4\) Hz, \(J_2 = 7.0\) Hz, 1H, \(E\)-isomer), 6.48 (dt, \(J_1 = 11.2\) Hz, \(J_2 = 5.4\) Hz, 1H, \(Z\)-isomer), 5.36-5.29 (m, 1H), 4.60 (t, \(J = 5.2\) Hz, 2H), 4.41 (t, \(J = 5.2\) Hz, 2H), 2.52 (s, 3H), 2.46-2.38 (m, 2H, \(Z\)-isomer), 2.29-2.24 (m, 2H), 2.24-2.18 (m, 2H, \(E\)-isomer), 1.60-1.51 (m, 2H), 1.50-1.40 (m, 2H), 1.36-1.23 (m, 6H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 172.93, 172.89, 155.9,\)
155.0, 150.8, 150.7, 138.5, 133.03, 133.01, 117.5, 115.0, 99.7, 99.5, 62.2, 45.0, 44.9, 33.7, 33.2, 31.7, 28.8, 28.73, 28.71, 28.6, 28.0, 27.4, 24.5, 14.3 ppm; 

HRMS m/z (ESI) calced for C_{17}H_{25}N_{4}O_{4} (M + H)^+ 349.1870, found 349.1868.

IR (neat): \nu_{\text{max}} = 2932, 2858, 2220, 1740, 1630, 1468, 1190.

23)

(3S,5S,6R,6aS)-5-((S)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 10-cyanodec-9-enoate (4c):

The reaction of (3S,5S,6R,6aS)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl undec-10-ynoate 3c (169.8 mg, 0.40 mmol), TMSN$_3$ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O$_2$ at 90°C for 48 hours, afforded 116.9 mg (67%) of 4c. 4c: obtained as a 67:33 mixture of Z/E isomers. Colorless liquid.

$^{1}$H NMR (CDCl$_3$, 400 MHz): $\delta = 6.71$ (dt, $J_1 = 16.4$ Hz, $J_2 = 7.0$ Hz, 1H, E-isomer), 6.48 (dt, $J_1 = 10.8$ Hz, $J_2 = 5.4$ Hz, 1H, Z-isomer), 5.89-5.86 (m, 1H), 5.36-5.30 (m, 1H), 5.27 (d, $J_1 = 1.6$ Hz, 1H), 4.49-4.46 (m, 1H), 4.21-4.19 (m, 2H), 4.11-3.98 (m, 2H), 2.46-2.38 (m, 2H, Z-isomer), 2.35 (td, $J_1 = 7.8$ Hz, $J_2 = 2.0$ Hz, 2H), 2.25-2.18 (m, 2H, E-isomer), 1.67-1.59 (m, 2H), 1.52 (s, 3H), 1.50-1.41 (m, 2H), 1.41 (s, 3H), 1.36-1.28 (m, 12H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 172.19$, 172.16, 155.9, 155.0, 117.5, 116.0, 112.22, 112.20, 109.2, 105.0, 99.7, 99.6, 83.3, 79.8, 75.80, 75.78, 72.4, 67.2, 34.1, 33.2, 31.7, 28.84, 28.80, 28.76, 28.7, 28.0, 27.5, 26.74, 26.66, 26.1, 25.2, 24.7 ppm;

HRMS m/z (ESI) calced for C$_{23}$H$_{35}$NNaO$_7$ (M + Na)$^+$, 460.2306, found 460.2295.

IR (neat): \nu_{\text{max}} = 2988, 2935, 2859, 2221, 1745, 1631, 1377, 1077, 847.
(1S,2R,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 10-cyano-dec-9-enoate (4d):
The reaction of (1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl undec-10-ynoate 3d (127.4 mg, 0.40 mmol), TMSN₃ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O₂ at 90 °C for 48 hours, afforded 97.3 mg (73%) of 4d. 4d: obtained as a 65:35 mixture of Z/E isomers. Colorless liquid.

^1H NMR (CDCl₃, 400 MHz): \( \delta = 6.71 \) (dt, \( J₁ = 16.4 \) Hz, \( J₂ = 7.0 \) Hz, 1H, E-isomer), 6.48 (dt, \( J₁ = 10.8 \) Hz, \( J₂ = 5.4 \) Hz, 1H, Z-isomer), 5.36-5.28 (m, 1H), 4.92-4.85 (m, 1H), 4.44-4.38 (m, 2H, Z-isomer), 2.38-2.28 (m, 3H), 1.98-1.90 (m, 1H), 1.80-1.70 (m, 1H), 1.69-1.60 (m, 3H), 1.52-1.41 (m, 2H), 1.38-1.18 (m, 8H), 0.95 (dd, \( J₁ = 13.6 \) Hz, \( J₂ = 3.6 \) Hz, 1H), 0.91 (s, 3H), 0.87 (s, 3H), 0.83 (s, 3H); ^13C NMR (CDCl₃, 100 MHz): \( \delta = 174.1, 174.0, 156.0, 155.1, 117.5, 116.0, 99.7, 99.5, 79.60, 79.57, 48.7, 47.7, 44.8, 36.8, 34.60, 34.57, 33.2, 31.8, 28.90, 28.88, 28.80, 28.7, 28.1, 28.0, 27.5, 27.1, 25.0, 19.7, 18.8, 13.5 ppm;

HRMS m/z (ESI) calcd for C₂₁H₃₃NNaO₂ (M + Na)^+ 354.2404, found 354.2403.

IR (neat): \( \nu_{\text{max}} = 2933, 2860, 2221, 1731, 1631, 1455, 1186. \)

5-(2-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-yn-2-yl)ethoxy)pent-2-enenitrile (4e):
The reaction of (1R,5S)-6,6-dimethyl-2-(2-(pent-4-yn-1-yl)oxy)ethyl)bicyclo[3.1.1]hept-2-ene 3e (92.9 mg, 0.40 mmol), TMSN₃ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O₂ at 90 °C for 48 hours, afforded 50.2 mg (52%) of 4e. 4e: obtained as a 63:37 mixture of
Z/E isomers. Colorless liquid.

**Z-isomer:** \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 6.59\) (dt, \(J_1 = 10.8\) Hz, \(J_2 = 5.6\) Hz, 1H), 5.38 (dt, \(J_1 = 10.8\) Hz, \(J_2 = 1.4\) Hz, 1H), 5.28-5.23 (m, 1H), 3.54 (t, \(J = 6.2\) Hz, 2H), 3.47-3.40 (m, 2H), 2.72-2.64 (m, 2H), 2.35 (dt, \(J_1 = 8.4\) Hz, \(J_2 = 4.2\) Hz, 1H), 2.29-2.13 (m, 4H), 2.10-2.05 (m, 1H), 2.03 (td, \(J_1 = 5.6\) Hz, \(J_2 = 1.6\) Hz, 1H), 1.27 (s, 3H), 1.14 (d, \(J = 8.4\) Hz, 1H), 0.82 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 152.2, 144.9, 118.0, 115.9, 100.8, 69.4, 68.3, 45.8, 40.7, 38.0, 37.0, 32.3, 31.6, 31.3, 26.3, 21.1\) ppm:

\(^1\)H NMR for the minor \(E\)-isomer: 6.75 (dt, \(J_1 = 16.4\) Hz, \(J_2 = 6.8\) Hz, 1H), 5.46-5.38 (m, 1H), 5.28-5.23 (m, 1H), 3.56-3.48 (m, 2H), 3.47-3.38 (m, 2H), 2.50-2.48 (m, 2H), 2.40-2.32 (m, 1H), 2.29-2.13 (m, 4H), 2.10-2.00 (m, 2H), 1.27 (s, 3H), 1.14 (d, \(J = 8.4\) Hz, 1H), 0.82 (s, 3H).

**HRMS m/z (ESI)** calcld for C\(_{16}\)H\(_{24}\)NO (M + H\(^+\)) \(246.1852\), found 246.1845.

**IR (neat):** \(\nu_{\max} = 2918, 2873, 2223, 1726, 1632, 1367, 1114\).

---

5-(((3\(R\),8\(S\),9\(S\),10\(R\),13\(R\),14\(S\),17\(R\))-10,13-Dimethyl-17-((\(R\))-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1\(H\)-cyclopenta[\(a\)]phenanthren-3-yl)oxy)pent-2-enenitrile (4f):

The reaction of (3\(R\),8\(S\),9\(S\),10\(R\),13\(R\),14\(S\),17\(R\))-10,13-dimethyl-17-((\(R\))-6-methylheptan-2-yl)-3-(pent-4-yn-1-yloxy)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1\(H\)-cyclopenta[\(a\)]phenanthrene 3f (90.6 mg, 0.20 mmol), TMSN\(_3\) (46.1 mg, 0.40 mmol), CuBr (5.8 mg, 0.04 mmol), Py (31.6 mg, 0.40 mmol) and NaOAc (16.4 mg, 0.20 mmol) in PhCl (1.0 mL) under O\(_2\) at 90 °C for 48 hours, afforded 46.7 mg (50%) of 4f. 4f: obtained as a 68:32 mixture of Z/E isomers. White solid.
1H NMR (CDCl3, 400 MHz): δ = 6.75 (dt, J1 = 16.4 Hz, J2 = 6.8 Hz, 1H, E-isomer), 6.48 (dt, J1 = 11.2 Hz, J2 = 5.4 Hz, 1H, Z-isomer), 5.46-5.36 (m, 1H), 5.36-5.32 (m, 1H), 3.61-3.54 (m, 2H), 3.20-3.08 (m, 1H), 2.70-2.63 (m, 2H, Z-isomer), 2.50-2.43 (m, 2H, E-isomer), 2.36-2.29 (m, 1H), 2.22-2.13 (m, 1H), 2.04-1.92 (m, 2H), 1.91-1.77 (m, 3H), 1.61-1.04 (m, 20H), 1.04-0.96 (m, 1H), 0.99 (s, 3H), 0.91 (d, J = 6.8 Hz, 3H), 0.860 (d, J = 6.4 Hz, 3H), 0.855 (d, J1 = 6.8 Hz, 3H), 0.67 (s, 3H); 13C NMR (CDCl3, 100 MHz): δ = 153.0, 152.3, 140.7, 140.6, 121.8, 121.7, 117.4, 115.8, 101.2, 100.7, 79.4, 79.2, 65.7, 65.3, 56.7, 56.1, 50.2, 42.3, 39.7, 39.5, 39.02, 38.99, 37.2, 36.8, 36.2, 35.7, 34.0, 32.7, 31.91, 31.86, 28.35, 28.31, 28.2, 28.0, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8 ppm;

HRMS m/z (ESI) calcd for C32H51NNaO (M + Na)+ 488.3863, found 488.3858.

IR (neat): νmax = 2936, 2868, 2222, 1733, 1672, 1632, 1466, 1380, 1107.
Mechanistic Studies

(1) Control experiment with allene

\[
\text{Ph} = \text{H} \quad \xrightarrow{\text{standard conditions}} \quad \text{2a, 0\%} \quad (1)
\]

Allene 5 was prepared according to Ma’s report.\(^7\) Mix 5 (57.7 mg, 0.40 mmol), TMSN\(_3\) (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O\(_2\) (balloon). The reaction mixture was stirred at 90 °C for 48 hours. After cooling down to room temperature, the residue was analyzed by TLC and GC-MS. NO 2a was detected.

(2) Control experiment with propargylic azide

\[
\text{Ph} = \text{H} \quad \text{N}_3 \quad \xrightarrow{\text{standard conditions \ with or without TMSN}_3} \quad \text{2a, 0\%} \quad (2)
\]

Propargylic azide 6 was prepared according to literature report.\(^8\) Mix 6 (74.1 mg, 0.40 mmol), TMSN\(_3\) (0.80 mmol or 0 mmol, for two independent reactions), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O\(_2\) (balloon). The reaction mixture was stirred at 90 °C for 48 hours. After cooling down to room temperature, the residue was analyzed by TLC and GC-MS. NO 2a was detected.

(3) Control experiment with allyl azide

\[
\text{H}_2\text{C}=\text{C} = \text{H} \quad \text{N}_3 \quad \xrightarrow{\text{standard conditions \ with or without TMSN}_3} \quad \text{NR} \quad (3)
\]

Allyl azide 7 was prepared according to literature report.\(^9\) Mix 7 (61.3 mg, 0.40 mmol), TMSN\(_3\) (0.80 mmol or 0 mmol, for two independent reactions), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O\(_2\) (balloon). The reaction mixture was stirred at 90 °C for 48 hours. After cooling down to room temperature, the residue was analyzed by TLC and GC-MS. NO 2a was detected. And 7 remained.
(4) Preparation of copper(I)-acetylide

\[
\begin{align*}
&\text{Copper(I)-acetylide } 8 \\
\text{was prepared according to the reported procedure.}^{10} \\
&\text{Add undec-1-yne (0.46 g, 3 mmol) to a solution of copper iodide (1.15 g, 6.0 mmol) in a mix-} \\
&\text{ture of ammonium hydroxide (28% NH}_3\text{ solution, 28 mL) and ethanol (9 mL) by dropwise under Ar atmosphere. The deep blue reac-} \\
&\text{tion mixture was stirred overnight at room temperature and the yellow precipitate was collected by filtration and successively washed with ammonium hydroxide (10% NH}_3\text{ solution, 3 x 15 mL), water (3 x 15 mL), ethanol (3 x 15 mL), and diethyl ether (3 x 15 mL). The bright yellow solid was then dried under high vacuum overnight to afford the desired Copper(I)-acetylide 8 (0.56 g, 86%).}
\end{align*}
\]

(5) Control experiment with copper(I)-acetylide

\[
\begin{align*}
&\text{Mix } 8 \text{ (85.9 mg, 0.40 mmol), TMSN}_3 \text{ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O}_2 \text{ (balloon). The reaction mixture was stirred at 90 °C for 48 hours. After cooling down to room temperature, the residue was analyzed by TLC and GC-MS. NO 2a was detected.}
\end{align*}
\]

(6) Reaction catalyzed by copper(I)-acetylide

\[
\begin{align*}
&\text{Mix } 1c \text{ (48.7 mg, 0.32 mmol), copper(I)-acetylide } 8 \text{ (used as a catalyst, 17.2 mg, 0.08 mmol), TMSN}_3 \text{ (92.2 mg, 0.80 mmol), NO CuBr (0 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O}_2 \text{ (balloon). The reaction mixture was stirred at 90 °C for 48 hours. After cooling down to room}
\end{align*}
\]
temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to afford 49.4 mg (75%, Z/E = 63:37) of 2c. The yield is competent with the reaction employing CuBr (20 mol%) as a catalyst (entry 3 of Table 2 in Text).

(7) Preparation of 1a-1-d₁

According to the literature¹, 1a (0.58 g, 4 mmol) and dry THF (5 mL) was added to a sealed flask via a syringe under argon. nBuLi (2.5 M hexane solution; 2.0 mL, 1.25 equiv.) was added dropwise at -78 °C, and the reaction mixture was stirred for 1 h at -30 °C. D₂O (99.9%-d; 10 mL) was carefully added to the lithium acetylide solution at -78 °C, and the reaction mixture was stirred for 30 min at the same temperature. After dilution with diethyl ether (15 mL), the mixture was washed with HCl (2 M, 10 mL) and extracted with diethyl ether (10 mL x 3). The combined organic phases were dried (MgSO₄) and concentrated in vacuo. 1a-1-d₁ was obtained by flash chromatography on a short silica gel (0.47g, 81%, > 99% D).

(8) Deuterium labelling experiments with 1a-1-d₁

Mix 1a-1-d₁ (58.1 mg, 0.40 mmol), TMSN₃ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O₂ (balloon). The reaction mixture was stirred at 90 °C for 48 hours. After cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to afford 43.2 mg (69%, Z/E = 65:35) of 2a. NO deuterium was detected in the product.
Preparation of \(1a-3,3-d_2\)

According to the reported procedure,\(^\text{12}\) LiAlD\(_4\) (0.42 g, 10 mmol) was added to a solution of \textit{ethyl 3-phenylpropanoate} (1.78 g, 10 mmol, in 12 mL dry Et\(_2\)O) by dropwise under argon at room temperature. The mixture was stirred until the reaction was completed (TLC monitoring). After careful addition of D\(_2\)O to the reaction mixture, the white solid was filtered off and the solvent carefully evaporated to dryness and then the residue obtained was purified by flash chromatography on silica gel to give 1.32 g of the pure dideuterated alcohol (96% for the first step).

Next, pyridine (1.58 g, 20 mmol) was added dropwise to the dideuterated alcohol (1.32 g, 9.6 mmol) and tosyl chloride (2.86 g, 15 mmol) in CH\(_2\)Cl\(_2\) at room temperature. After being stirred for 24 h at room temperature, the reaction mixture was poured into saturated NH\(_4\)Cl. Usual work up and column purification afforded 1,1-dideuterio hydrocinnamyl tosylate (2.39 g, 85% yield for the second step).

Then, a solution of 1,1-dideuterio hydrocinnamyl tosylate (1.96 g, 6.7 mmol) in DMSO (6 mL) was added dropwise to a solution of lithium acetylide ethylenediamine complex (0.78 g, 8.7 mmol) in DMSO (6 mL) at room temperature. The resulting dark brown solution was stirred for 3 h and then 30 mL of ice-water was added. After adjusting pH to 1 by HCl (1 M) and extracting with diethyl ether (10 mL x 3), The combined organic phases were dried (MgSO\(_4\)) and concentrated in vacuo. \(1a-3,3-d_2\) was obtained by flash chromatography on a short silica gel (0.10 g, 7% for three steps, > 99% D).

Deuterium labelling experiments with \(1a-3,3-d_2\)

Mix \(1a-3,3-d_2\) (14.6 mg, 0.10 mmol), TMSN\(_3\) (23.1 mg, 0.20 mmol), CuBr (2.9
mg, 0.02 mmol), Py (15.8 mg, 0.20 mmol) and NaOAc (8.2 mg, 0.10 mmol) in PhCl (0.5 mL) under O₂ (balloon). The reaction mixture was stirred at 90 °C for 48 hours. After cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to afford 7.3 mg (46%, Z/E = 64:36) of 2a-d₂. To our surprise, nearly 100% incorporation of deuterium at the both α and β positions of the nitrile was observed.

(11) Intermolecular kinetic isotopic experiment

Mix 1a (28.8 mg, 0.20 mmol), 1a-3,3-d₂ (29.2 mg, 0.20 mmol), TMSN₃ (92.2 mg, 0.80 mmol), CuBr (11.5 mg, 0.08 mmol), Py (63.2 mg, 0.80 mmol) and NaOAc (32.8 mg, 0.40 mmol) in PhCl (2.0 mL) under O₂ (balloon). The reaction mixture was stirred at 90 °C for 2 hours. After cooling down to room temperature and concentrating in vacuum, the residue was analyzed by ¹H-NMR. The calculated k_H/k_D is 2.2.
Computational Methods

All the DFT calculations were carried out with the GAUSSIAN 09 series of programs. Density functional theory B3LYP with a standard 6-31G(d) basis set (SDD basis set for Cu atom) was used for geometry optimizations (keyword 5D was used in the calculations). The vibrational frequencies were computed at the same level to check whether each optimized structure is an energy minimum or a transition state and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298 K. IRC calculations were used to confirm that the transition states found from the optimization calculations connect the related reactants and products. Single-point energies were obtained at the B3LYP level using 6-311+G(d,p) basic set (SDD basis set for Cu atom) based on the structures obtained on the gas-phase. Solvation energies were evaluated by a self-consistent reaction field (SCRF) using the CPCM model, where UFF radii were used. The reported energies are Gibbs free energies in PhCl solution ($\Delta G_{\text{sol}}$).
To further unravel the mechanism, the density functional theory (DFT) calculation investigation was carried out (Figure S1). After the reasonable Cu-catalyzed azide-alkyne cycloaddition (CuAAC), the formed triazole intermediate INT-a undergoes ring-opening reaction through transition state TS-a with an activation free energy of 28.7 kcal/mol to afford INT-b. Although this is an endergonic process by 25.7 kcal/mol, the following oxidation of imine motif by molecular oxygen exergonic by 28.4 kcal/mol, delivering the stable α-diazonitrile INT1. See text for the details of the following processes.

Figure S1  DFT-computed energy profiles.
## Computed Energies of All Stationary Points

**Table S12**  Sum of electronic and zero-point energies (E, in a.u.), sum of electronic and thermal enthalpies (H, in a.u.), sum of electronic and thermal free energies (G, in a.u.), thermal correction to Gibbs free energy (TCGFE, in Hartree), and total free energy in solution (Eₗₜ, in Hartree, solvent = PhCl).

<table>
<thead>
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<td>INT-a</td>
<td>-765.733472</td>
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<td>-765.778674</td>
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<td>INT-b</td>
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<td>-765.672390</td>
<td>-765.735482</td>
<td>0.145851</td>
<td>-766.066212</td>
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<tr>
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<td>-150.309523</td>
<td>-150.332809</td>
<td>-0.016204</td>
<td>-150.370488</td>
</tr>
<tr>
<td>HO₂CuPy</td>
<td>-596.517148</td>
<td>-596.506550</td>
<td>-596.554771</td>
<td>0.069743</td>
<td>-596.771284</td>
</tr>
<tr>
<td>INT1</td>
<td>-319.515380</td>
<td>-319.507790</td>
<td>-319.546183</td>
<td>0.058613</td>
<td>-319.709329</td>
</tr>
<tr>
<td>TS1</td>
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<td>-319.460992</td>
<td>-319.502777</td>
<td>0.051775</td>
<td>-319.662595</td>
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<tr>
<td>INT2</td>
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<td>-209.955363</td>
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<td>-109.511814</td>
<td>-109.533568</td>
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<tr>
<td>E-TS2</td>
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<td>-209.949091</td>
<td>-209.983590</td>
<td>0.045818</td>
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<td>Z-TS2</td>
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<td>-209.950060</td>
<td>-209.984948</td>
<td>0.045645</td>
<td>-210.109881</td>
</tr>
<tr>
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[a] Computed at the B3LYP(gas)/SDD-6-31G(d) level.

[b] Computed at the B3LYP (CPCM)/SDD-6-311+G(d,p)// B3LYP(gas)/SDD-6-31G(d) level.
## Coordinates of All Stationary Points

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S37
References


$^1$H NMR and $^{13}$C NMR Spectra of Products

![NMR Spectra](Image)

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\[\text{CN}\]
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Z-2I

![Chemical Structure](image)

[Chemical structure image]

Z-2m
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$4b$
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