Supporting Information

Direct Acylation and Alkynylation of Hydrocarbons via Synergistic Decatungstate Photo-HAT/Nickel Catalysis

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1. General Information

Nuclear magnetic resonance (NMR) spectroscopy measurements were carried out at room temperature. $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR, HSQC and HMBC experiments were carried out using Bruker ADVANCE III (600 MHz) or JNM-ECZ400S/L1 (400 MHz) spectrometers. Chemical shifts (δ) are reported in ppm relative to the residual solvent peak with corresponding coupling constants (J) in Hertz (Hz) and multiplicities (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet and combinations of these and app.: apparent multiplicities).

Gas chromatography was determined with a SHIMADZU Nexis GC 2030 gas chromatography instrument with a FID detector. High-resolution mass spectra (HRMS) were recorded on Thermo Fisher Orbitrap Elite mass spectrometer. The photoreaction instrument (WPTEC-1020L) was purchased from WATTCAS, China.

Materials and Methods:

Commercially available reagents and ligands were purchased from Sigma Aldrich, Alfa Aesar, and Strem Chemicals and unless otherwise stated were used without further purification. NiBr$_2$DME, NiI$_2$ and Ni(OAc)$_2$ were bought from Strem Chemicals. All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere. Solvents were purchased in HPLC quality, degassed by purging thoroughly with argon and dried over 4 Å activated molecular sieves. More sensitive compounds were stored in a desiccator or in a glove-box if required. Reactions were monitored by thin layer chromatography (TLC) using glass 0.25 mm silica gel plates. Compounds were visualized by UV-light at 254 nm and by dipping the plates in an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (200-400 mesh).
2. General Procedure

2.1 Synthesis of ketones via direct and selective acylation of hydrocarbons

An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with NiBr₂•dtbbpy (0.002 mmol, 1.0 mol%), tetrabutylammonium decatungstate (0.004 mmol, 2.0 mol%), acyl chlorides (0.2 mmol, 1.0 equiv.), hydrocarbons (2.0 mmol, 10.0 equiv.), anhydrous K₃PO₄ (0.48 mmol, 2.4 equiv.) and dry MeCN (1.0 mL) in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 2 W 390 nm LED lamp (WATTCAS: WP-TEC-1020LC) at 25 °C for 8 hours. The resulting mixture was diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with EtOAc/hexane to afford the corresponding ketone products.

2.2 Synthesis of amides via direct and selective acylation of hydrocarbons

An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with NiCl₂•dtbbpy (0.004 mmol, 2.0 mol%), tetrabutylammonium decatungstate (0.004 mmol, 2.0 mol%), carbamic chloride (0.2 mmol, 1.0 equiv.), hydrocarbons (2.0 mmol, 10.0 equiv.), anhydrous K₃PO₄ (0.4 mmol, 2.0 equiv.) and dry MeCN (1.0 mL) in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp (WATTCAS: WP-TEC-1020LC) at 25 °C for 36 hours. The resulting mixture was
diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with EtOAc/hexane to afford the corresponding amide products.

### 2.3 Synthesis of esters via direct and selective acylation of hydrocarbons

An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with NiBr$_2$ (0.02 mmol, 10 mol%), dtbbpy (0.03 mmol, 15 mol%), tetrabutylammonium decatungstate (0.004 mmol, 2.0 mol%), chloroformates (0.2 mmol, 1.0 equiv.), hydrocarbons (2.0 mmol, 10.0 equiv.), anhydrous K$_3$PO$_4$ (0.4 mmol, 2.0 equiv.) and dry MeCN (1.0 mL) in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp (WATTCAS: WP-TEC-1020LC) at 25°C for 24 hours. The resulting mixture was diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with EtOAc/hexane to afford the corresponding ester products.

### 2.4 Synthesis of alkyl-substituted alkynes via direct and selective alkynylation of hydrocarbons

An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with NiBr$_2$•dtbbpy (0.02 mmol, 10 mol%), tetrabutylammonium decatungstate (0.004 mmol, 2.0 mol%), chloroformates (0.2 mmol, 1.0 equiv.), hydrocarbons (2.0 mmol, 10.0 equiv.), anhydrous K$_3$PO$_4$ (0.4 mmol, 2.0 equiv.) and dry MeCN (1.0 mL) in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp (WATTCAS: WP-TEC-1020LC) at 5°C for 12 hours. The resulting mixture was diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with EtOAc/hexane to afford the corresponding alkynyl products.
mmol, 2 mol%), alkynyl bromides (0.2 mmol, 1.0 equiv.), anhydrous K$_2$HPO$_4$ (0.3 mmol, 1.5 equiv.), hydrocarbon (2.0 mmol, 10.0 equiv.) and dry MeCN (1.0 mL) in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 6 W 390 nm LED lamp (WATTCAS: WP-TEC-1020LC) at 5 °C for 12 hours. The resulting mixture was diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. Solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with EtOAc/hexane to afford the corresponding alkyne products.

2.5 Synthesis of alkyl-substituted alkynes via direct and selective alkynylation of ethers

An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with Ni(acac)$_2$ (0.02 mmol, 10 mol%), dtbbpy (0.03 mmol, 15 mol%), PC1 (0.02 mmol, 10 mol%), alkynyl bromides (0.2 mmol, 1.0 equiv.), anhydrous Na$_2$CO$_3$ (0.4 mmol, 2.0 equiv.) and ether (1.0 mL) as both C-H partners and solvent in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp (WATTCAS: WP-TEC-1020LC) at 25 °C for 48 hours. The resulting mixture was diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. Solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with EtOAc/hexane to afford the corresponding alkyne products.
3. Optimization of Reaction Conditions

Table S1: Optimization of the reaction conditions for C(sp³)-H alkylation of hydrocarbons.

<table>
<thead>
<tr>
<th>entry</th>
<th>Power value of LED lamp (W)</th>
<th>yield of 34 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
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<tr>
<td>3</td>
<td>6</td>
<td>65</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>59</td>
</tr>
</tbody>
</table>
Table S2: optimization of the equivalents of Ni and TBADT, concentration for C(sp³)–H alkynylation of hydrocarbons with alkynyl bromides

<table>
<thead>
<tr>
<th>entry</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>yield of 34 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>2</td>
<td>0.5</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>2</td>
<td>1.0</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>2</td>
<td>0.5</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>1</td>
<td>0.5</td>
<td>64</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>2</td>
<td>2</td>
<td>62</td>
</tr>
</tbody>
</table>
Table S3: optimization of the base for C(sp³)−H alkynylation of hydrocarbons with alkynyl bromides

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>entry</th>
<th>Base</th>
<th>Eq.</th>
<th>yield of 34 (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K₃PO₄</td>
<td>2.0</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>K₂HPO₄</td>
<td>2.0</td>
<td>86</td>
</tr>
<tr>
<td>3</td>
<td>Na₂CO₃</td>
<td>2.0</td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td>K₂HPO₄</td>
<td>1.5</td>
<td>96(76)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>K₂HPO₄</td>
<td>1.1</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>K₂HPO₄&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.5</td>
<td>67(57)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>GC yield, <sup>b</sup>isolated yield, <sup>c</sup>This reaction was performed at 25 °C.
Table S4: Optimization of the Reaction Conditions

![Reaction Scheme]

<table>
<thead>
<tr>
<th>entry</th>
<th>nickel catalyst</th>
<th>Power value of LEDs (W)</th>
<th>yield of 3 (%)(^b)</th>
<th>yield of 4 (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L.1 NiBr(_2)</td>
<td>10</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>L.2 NiBr(_2)</td>
<td>10</td>
<td>45</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>L.3 NiBr(_2)</td>
<td>10</td>
<td>45</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>L.4 NiBr(_2)</td>
<td>10</td>
<td>42</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>L.5 NiBr(_2)</td>
<td>10</td>
<td>trace</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>L.2 NiCl(_2)</td>
<td>10</td>
<td>trace</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>L.2 NiI(_2)</td>
<td>10</td>
<td>39</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>L.2 NiOAc(_2)·4\text{H}_2\text{O}</td>
<td>10</td>
<td>44</td>
<td>15</td>
</tr>
<tr>
<td>9</td>
<td>L.2 NiBr(_2)·dme</td>
<td>10</td>
<td>62</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>Ni(L.2)Br(_2)</td>
<td>10</td>
<td>66</td>
<td>7</td>
</tr>
<tr>
<td>11</td>
<td>Ni(L.2)Br(_2)</td>
<td>6</td>
<td>68</td>
<td>5</td>
</tr>
<tr>
<td>12</td>
<td>Ni(L.2)Br(_2)</td>
<td>2</td>
<td>78</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>13(^d)</td>
<td>Ni(L.2)Br(_2)</td>
<td>2</td>
<td>83 (71)(^c)</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>14(^d,e)</td>
<td>Ni(L.2)Br(_2)</td>
<td>2</td>
<td>69</td>
<td>6</td>
</tr>
<tr>
<td>15(^d)</td>
<td>-</td>
<td>2</td>
<td>no reaction</td>
<td></td>
</tr>
<tr>
<td>16(^d,f)</td>
<td>Ni(L.2)Br(_2)</td>
<td>2</td>
<td>no reaction</td>
<td></td>
</tr>
<tr>
<td>17(^d,g)</td>
<td>Ni(L.2)Br(_2)</td>
<td>2</td>
<td>no reaction</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Reaction conditions: 1 (2 mmol), 2 (0.2 mmol), [Ni]/L (10 mol%), TBADT (2 mol%), K\(_3\)PO\(_4\) (0.48 mmol) in MeCN (0.5 mL) at 25 °C under irradiation of LEDs (X W, 390 nm) for 8 hours. \(^b\)Yields determined by GC analysis using adamantane as an internal standard. \(^c\)Isolated yield. \(^d\)1 mol% Ni(L.2)Br\(_2\) was used. \(^e\)5 equivalents of cyclohexane were used. \(^f\)Without TBADT. \(^g\)Without light.
4. Mechanistic studies

4.1 UV-VIS absorption spectra

The UV-visible absorption spectra for TBADT in MeCN ($10^{-4}$ M) is shown above.

4.2 Emission spectra

The emission spectra for TBADT irradiated under 320 nm light in MeCN ($10^{-5}$ M) is shown above.
5. Characterization Data of Products

Cyclohexyl(phenyl)methanone (3)

\[
\text{Chemical Formula: } C_{13}H_{16}O \\
\text{Exact Mass: } 188.120^1
\]

3 was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and benzoyl chloride (0.2 mmol, 28.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain 3 as colorless oil (28.9 mg, 71% yield).

The NMR data matched those reported in the literature.$^1$

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.97-7.91 (m, 2H), 7.56-7.52 (m, 1H), 7.48-7.42 (m, 2H), 3.26 (tt, $J = 11.4, 3.3$ Hz, 1H), 1.96-1.81 (m, 4H), 1.79-1.70 (m, 1H), 1.56-1.45 (m, 2H), 1.45-1.35 (m, 2H), 1.31-1.24 (m, 1H);

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 204.0, 136.5, 132.8, 128.7, 128.4, 45.8, 29.5, 26.1, 26.0.

Cyclohexyl(p-tolyl)methanone (6)

\[
\text{Chemical Formula: } C_{14}H_{16}O \\
\text{Exact Mass: } 202.1358
\]

6 was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain 6 as colorless oil (32.2 mg, 73% yield).

The NMR data matched those reported in the literature.$^2$

\[513\]
$^1$H NMR (600 MHz, CDCl$_3$) δ 7.85 (d, $J = 8.2$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 3.24 (tt, $J = 11.6$, 3.3 Hz, 1H), 2.40 (s, 3H), 1.92-1.81 (m, 4H), 1.78-1.69 (m, 1H), 1.53-1.45 (m, 2H), 1.44-1.34 (m, 2H), 1.31-1.24 (m, 1H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 203.7, 143.6, 133.9, 129.4, 128.5, 45.6, 29.6, 26.1, 26.0, 21.7.

**Cyclohexyl(4-methoxyphenyl)methanone (7)**

![Chemical Structure](image)

7 was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-methoxybenzoyl chloride (0.2 mmol, 34.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain 7 as colorless oil (28.8 mg, 66% yield).

The NMR data matched those reported in the literature.$^1$

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.96-7.89 (m, 2H), 6.97-6.89 (m, 2H), 3.86 (s, 3H), 3.21 (tt, $J = 11.6$, 3.2 Hz, 1H), 1.92-1.80 (m, 4H), 1.77-1.70 (m, 1H), 1.55-1.45 (m, 2H), 1.43-1.34 (m, 2H), 1.31-1.22 (m, 1H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 202.6, 163.3, 130.6, 129.4, 113.8, 55.6, 45.4, 29.7, 26.1, 26.1.

**Cyclohexyl(4-fluorophenyl)methanone (8)**

![Chemical Structure](image)

8 was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2
mmol, 168.0 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-fluorobenzoyl chloride (0.2 mmol, 31.7 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain 8 as colorless oil (29.7 mg, 72% yield).

The NMR data matched those reported in the literature.$^1$

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.00-7.94 (m, 2H), 7.15-7.08 (m, 2H), 3.21 (tt, $J = 11.6$, 3.2 Hz, 1H), 1.90-1.81 (m, 4H), 1.76-1.71 (m, 1H), 1.53-1.44 (m, 2H), 1.43-1.34 (m, 2H), 1.29-1.24 (m, 1H);

$^{19}$F NMR (565 MHz, CDCl$_3$) δ -106.00 (m);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 202.3, 165.6 (d, $J = 254.0$ Hz), 132.7 (d, $J = 2.9$ Hz), 130.9 (d, $J = 9.2$ Hz), 115.7 (d, $J = 21.8$ Hz), 45.6, 29.4, 25.9, 25.8.

**Cyclohexyl(3-methoxyphenyl)methanone (9)**

![Chemical structure of 9](image)

Chemical Formula: C$_{14}$H$_{19}$C$_2$

Exact Mass: 218.1307

9 was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 3-methoxybenzoyl chloride (0.2 mmol, 34.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain 9 as colorless oil (27.9 mg, 64% yield).

The NMR data matched those reported in the literature.$^1$

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.54-7.50 (m, 1H), 7.49-7.44 (m, 1H), 7.36 (t, $J = 7.9$ Hz, 1H), 7.11-7.07 (m, 1H), 3.85 (s, 3H), 3.23 (tt, $J = 11.5$, 3.3 Hz, 1H), 1.90-1.82 (m, 4H), 1.76-1.72 (m, 1H), 1.53-1.45 (m, 2H), 1.43-1.35 (m, 2H), 1.29-1.24 (m, 1H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 203.8, 159.9, 137.8, 129.5, 120.8, 119.0, 112.8, 55.4, 45.8, 29.5, 26.0, 25.9.

**Cyclohexyl(3,5-dimethylphenyl)methanone (10)**
10 was prepared according to general procedure 2.1 using NiBr₂•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K₃PO₄ (0.48 mmol, 101.8 mg) and 3,5-dimethylbenzoyl chloride (0.2 mmol, 33.7 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain 10 as colorless oil (27.2 mg, 66% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.53 (s, 2H), 7.18 (s, 1H), 3.24 (tt, J = 11.5, 3.3 Hz, 1H), 2.37 (s, 6H), 1.90-1.81 (m, 4H), 1.77-1.70 (m, 1H), 1.53-1.44 (m, 2H), 1.44-1.35 (m, 2H), 1.31-1.23 (m, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 204.3, 138.1, 136.5, 134.3, 125.9, 45.6, 29.4, 25.9, 25.8, 21.2;


Cyclohexyl(2-fluorophenyl)methanone (11)

11 was prepared according to general procedure 2.1 using NiBr₂•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K₃PO₄ (0.48 mmol, 101.8 mg) and 2-fluorobenzoyl chloride (0.2 mmol, 31.7 mg) and was purified by silica gel column chromatography (PE/EtOAc = 100/1) to obtain 11 as colorless oil (12.8 mg, 31% yield).

The NMR data matched those reported in the literature.³
\(^1\text{H}\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.76-7.70 (m, 1H), 7.51-7.44 (m, 1H), 7.24-7.19 (m, 1H), 7.14-7.08 (m, 1H), 3.15-3.08 (m, 1H), 1.97-1.91 (m, 2H), 1.84-1.78 (m, 2H), 1.73-1.68 (m, 1H), 1.45-1.34 (m, 4H), 1.27-1.23 (m, 1H); 

\(^1^9\text{F}\) NMR (565 MHz, CDCl\(_3\)) \(\delta\) -111.69 (m); 

\(^{13}\text{C}\) NMR (151 MHz, CDCl\(_3\)) \(\delta\) 202.9 (d, \(J = 4.2\) Hz), 161.1 (d, \(J = 253.1\) Hz), 133.8 (d, \(J = 8.8\) Hz), 130.8 (d, \(J = 2.9\) Hz), 126.1 (d, \(J = 13.6\) Hz), 124.4 (d, \(J = 3.6\) Hz), 116.4 (d, \(J = 23.8\) Hz), 50.1 (d, \(J = 6.1\) Hz), 28.8, 26.0, 25.8.

**Cyclohexyl(furan-2-yl)methanone (12)**

\[
\text{Chemical Formula C}_{11}\text{H}_{14}\text{O}_2 \\
\text{Exact Mass} \ 178.0994
\]

12 was prepared according to general procedure 2.1 using NiBr\(_2\)•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K\(_3\)PO\(_4\) (0.48 mmol, 101.8 mg) and furan-2-carbonyl chloride (0.2 mmol, 26.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain 12 as colorless oil (15.3 mg, 43% yield).

The NMR data matched those reported in the literature.\(^4\)

\(^1\text{H}\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.60-7.55 (m, 1H), 7.18 (dd, \(J = 3.5, 0.8\) Hz, 1H), 6.52 (dd, \(J = 3.5, 1.7\) Hz, 1H), 3.06 (tt, \(J = 11.7, 3.3\) Hz, 1H), 1.91-1.80 (m, 4H), 1.75-1.69 (m, 1H), 1.55-1.46 (m, 2H), 1.40-1.32 (m, 2H), 1.30-1.25 (m, 1H); 

\(^{13}\text{C}\) NMR (151 MHz, CDCl\(_3\)) \(\delta\) 193.0, 152.3, 146.1, 117.0, 112.1, 46.3, 28.9, 25.8, 25.7.

**(4-chlorophenyl)(cyclohexyl)methanone (13)**
13 was prepared according to general procedure 2.1 using NiBr$_2$·dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-chlorobenzoyl chloride (0.2 mmol, 35.0 mg) and was purified by silica gel column chromatography (PE/EtOAc = 100/1) to obtain 13 as colorless oil (29.8 mg, 67% yield).

The NMR data matched those reported in the literature.$^5$

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.00-7.78 (m, 2H), 7.53-7.35 (m, 2H), 3.20 (tt, $J = 11.5, 3.2$ Hz, 1H), 1.94-1.80 (m, 4H), 1.80-1.71 (m, 1H), 1.54-1.42 (m, 2H), 1.42 -1.32 (m, 2H), 1.31-1.21 (m, 1H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 202.6, 139.1, 134.6, 129.7, 128.9, 45.6, 29.3, 25.9, 25.8.

cyclohexyl(4-(trifluoromethyl)phenyl)methanone (14)

14 was prepared according to general procedure 2.1 using NiBr$_2$·dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-(trifluoromethyl)benzoyl chloride (0.2 mmol, 41.7 mg) and was purified by silica gel column chromatography (PE/EtOAc = 100/1) to obtain 14 as colorless oil (17.9 mg, 35% yield).

The NMR data matched those reported in the literature.$^1$
$^1$H NMR (600 MHz, CDCl$_3$) δ 8.06-7.99 (m, 2H), 7.76-7.69 (m, 2H), 3.24 (tt, $J = 11.4, 3.3$ Hz, 1H), 1.92-1.83 (m, 4H), 1.78-1.72 (m, 1H), 1.55-1.44 (m, 2H), 1.44-1.35 (m, 2H), 1.30-1.25 (m, 1H);

$^{19}$F NMR (565 MHz, CDCl$_3$) δ -63.08(s);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 202.9, 139.1, 134.0 (q, $J = 32.7$ Hz), 128.5, 125.6 (q, $J = 3.7$ Hz), 123.6 (q, $J = 272.6$ Hz), 45.9, 29.2, 25.8, 25.7.

**Cyclooctyl($p$-tolyl)methanone (15)**

![Chemical structure of cyclooctyl($p$-tolyl)methanone (15)](image)

Chemical Formula: $C_{16}H_{22}O$

Exact Mass: 230.167

15 was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclooctane (2 mmol, 224.0 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain 15 as colorless oil (33.0 mg, 69% yield).

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.84 (d, $J = 8.2$ Hz, 2H), 7.25 (d, $J = 7.9$ Hz, 2H), 3.46 (tt, $J = 8.8, 3.5$ Hz, 1H), 2.41 (s, 3H), 1.88-1.81 (m, 2H), 1.80-1.70 (m, 4H), 1.69-1.63 (m, 3H), 1.63-1.53 (m, 5H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 204.2, 143.4, 133.9, 129.3, 128.4, 44.8, 29.1, 26.7, 26.6, 25.6, 21.6;

HRMS: (ESI) calcd for C$_{16}$H$_{23}$O$^+$/[M+H]$^+$ 217.1743; found 217.1736.

**Cyclopentyl($p$-tolyl)methanone (16)**

![Chemical structure of cyclopentyl($p$-tolyl)methanone (16)](image)

Chemical Formula: $C_{13}H_{16}O$

Exact Mass: 188.1201
16 was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclopentane (2 mmol, 140.0 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain 16 as colorless oil (20.7 mg, 66% yield).

The NMR data matched those reported in the literature.$^6$

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.88 (d, $J = 8.2$ Hz, 2H), 7.25 (d, $J = 7.9$ Hz, 2H), 3.74-3.65 (m, 1H), 2.41 (s, 3H), 1.96-1.85 (m, 4H), 1.77-1.69 (m, 2H), 1.69-1.61 (m, 2H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 202.5, 143.4, 134.5, 129.2, 128.6, 46.3, 30.1, 26.4, 21.6.

((1S,4R)-Bicyclo[2.2.1]heptan-2-yl)(p-tolyl)methanone (17)

17 was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), (1s,4s)-bicyclo[2.2.1]heptane (2 mmol, 192.4 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain 17 as colorless oil (26.6 mg, 60% yield).

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.86 (d, $J = 8.2$ Hz, 2H), 7.26-7.22 (m, 2H), 3.19 (dd, $J = 8.9, 5.5$ Hz, 1H), 2.52-2.48 (m, 1H), 2.40 (s, 3H), 2.34 (s, 1H), 2.03-1.97 (m, 1H), 1.65-1.55 (m, 2H), 1.50-1.44 (m, 1H), 1.44-1.39 (m, 2H), 1.33-1.27 (m, 1H), 1.17-1.11 (m, 1H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 201.2, 143.4, 134.2, 129.3, 128.7, 49.5, 41.2, 36.4, 36.3, 33.8, 29.9, 29.2, 21.7;
HRMS: (ESI) calcd for $\text{C}_{15}\text{H}_{19}\text{O}^{+}[\text{M+H}]^+$ 215.1430; found 215.1428.

2-phenyl-1-(p-tolyl)ethan-1-one (18)

\[
\text{Chemical Formula C}_{15}\text{H}_{14}\text{O} \\
\text{Exact Mass: 210.1045}
\]

18 was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), toluene (2.0 mmol, 184.3 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain 18 as colorless oil (15.0 mg, 35% yield).

The NMR data matched those reported in the literature.$^7$

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.95-7.88 (m, 2H), 7.36-7.29 (m, 2H), 7.29-7.23 (m, 5H), 4.26 (s, 2H), 2.40 (s, 3H);

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 197.4, 144.1, 134.9, 134.2, 129.6, 129.5, 128.9, 128.8, 126.9, 45.6, 21.8.

(tetrahydrofuran-2-yl)(p-tolyl)methanone (19)

\[
\text{Chemical Formula C}_{12}\text{H}_{14}\text{O}_2 \\
\text{Exact Mass: 190.0994}
\]

19 was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), tetrahydrofuran (2 mmol, 144.2 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain 19 as colorless oil (22.3 mg, 57% yield).

The NMR data matched those reported in the literature.$^8$
\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.89 (d, \(J = 8.2\) Hz, 2H), 7.27-7.25 (m, 2H), 5.24 (dd, \(J = 8.5, 5.8\) Hz, 1H), 4.04 (dt, \(J = 8.3, 6.8\) Hz, 1H), 3.97 (dt, \(J = 8.2, 6.7\) Hz, 1H), 2.41 (s, 3H), 2.32-2.24 (m, 1H), 2.16-2.07 (m, 1H), 2.00-1.93 (m, 2H);

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 198.5, 144.3, 132.7, 129.4, 129.0, 80.0, 69.5, 29.5, 25.8, 21.8.

(1,4-dioxan-2-yl)(\(p\)-tolyl)methanone (20)

\[
\text{Chemical Formula: } C_{13}H_{15}O_3 \\
\text{Exact Mass: } 206.0943
\]

20 was prepared according to general procedure 2.1 using NiBr\(_2\)-dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), 1,4-dioxane (2 mmol, 176.2 mg), anhydrous K\(_3\)PO\(_4\) (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain 20 as colorless oil (26.6 mg, 61% yield).

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.89 (d, \(J = 8.3\) Hz, 2H), 7.29-7.25 (m, 2H), 4.97 (dd, \(J = 9.5, 2.9\) Hz, 1H), 4.08 (dd, \(J = 11.8, 2.9\) Hz, 1H), 4.00-3.95 (m, 1H), 3.92-3.86 (m, 1H), 3.81-3.76 (m, 1H), 3.74-3.67 (m, 2H), 2.42 (s, 3H);

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 195.5, 144.8, 132.4, 129.5, 129.0, 77.6, 68.4, 66.9, 66.5, 21.9.

HRMS: (ESI) calcd for C\(_{12}\)H\(_{15}\)O\(_3\)[M+H]\(^+\) 207.1016; found 207.1014.

(4-bromotetrahydro-2\(H\)-pyran-2-yl)(\(p\)-tolyl)methanone (21)

\[
\text{Chemical Formula: } C_{13}H_{15}BrO_2 \\
\text{Exact Mass: } 282.0255
\]
21 was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), 4-bromotetrahydro-2H-pyran (2.0 mmol, 330.1 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain 21 as colorless oil (30.6 mg, 54% yield).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.88 (d, $J$ = 8.3 Hz, 2H), 7.29-7.25 (m, 2H), 5.29 (dd, $J$ = 10.1, 2.6 Hz, 1H), 4.83-4.77 (m, 1H), 4.16-4.09 (m, 1H), 4.05-3.99 (m, 1H), 2.41 (s, 3H), 2.35-2.28 (m, 1H), 2.26-2.17 (m, 2H), 2.01-1.95 (m, 1H);

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 197.0, 144.7, 132.1, 129.5, 129.1, 74.6, 63.7, 49.3, 37.1, 34.2, 21.9;

HRMS: (ESI) calcd for C$_{13}$H$_{16}$BrO$_2$ $^{[M+H]}$ 283.0823; found 283.0325.

2-(tert-butoxy)-1-(p-tolyl)ethan-1-one (22)

22 was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), 2-methoxy-2-methylpropane (2.0 mmol, 176.4 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain 22 as colorless oil (26.4 mg, 64% yield).

The NMR data matched those reported in the literature.$^9$

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J$ = 8.2 Hz, 2H), 7.26-7.23 (m, 2H), 4.63 (s, 2H), 2.40 (s, 3H), 1.27 (s, 9H);

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 196.9, 144.1, 133.0, 129.3, 128.4, 74.6, 66.3, 27.6, 21.8.
**2-ethoxy-1-(p-toly1)propan-1-one (23)**

![Chemical Structure](https://example.com/structure.png)

**Chemical Formula**: C₁₀H₁₆O₂  
**Exact Mass**: 192.1150

23 was prepared according to general procedure 2.1 using NiBr₂·dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), ethoxyethane (2.0 mmol, 148.2 mg), anhydrous K₃PO₄ (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain 23 as colorless oil (9.6 mg, 27% yield).

The NMR data matched those reported in the literature.¹⁰

¹H NMR (600 MHz, CDCl₃) δ 7.99 (d, J = 8.2 Hz, 2H), 7.27-7.25 (m, 2H), 4.65 (q, J = 6.9 Hz, 1H), 3.54 (dq, J = 9.1, 7.0 Hz, 1H), 3.47 (dq, J = 9.0, 7.0 Hz, 1H), 2.41 (s, 3H), 1.48 (d, J = 6.9 Hz, 3H), 1.21 (t, J = 7.0 Hz, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 200.9, 144.3, 132.4, 129.4, 129.1, 79.3, 65.3, 21.8, 19.2, 15.5.

**Tert-butyl 2-(4-methylbenzoyl)pyrrolidine-1-carboxylate (24)**

![Chemical Structure](https://example.com/structure.png)

**Chemical Formula**: C₁₇H₂₃NO₃  
**Exact Mass**: 289.1678

24 was prepared according to general procedure 2.1 using NiBr₂·dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), tert-butyl pyrrolidine-1-carboxylate (1.0 mmol, 171.2 mg), anhydrous K₃PO₄ (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain 24 as colorless oil (26.5 mg, 45% yield); a 3:2 mixture of rotamers.

The NMR data matched those reported in the literature.¹¹
**Tert-butyl methyl(2-oxo-2-(p-tolyl)ethyl)carbamate (25)**

![Chemical Structure of 25](image)

25 was prepared according to general procedure **2.1** using NiBr₂•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), tert-butyl dimethylcarbamate (1.0 mmol, 145.2 mg), anhydrous K₃PO₄ (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain 25 as colorless oil (35.8 mg, 69% yield); a 1.2:1 mixture of rotamers.

**1H NMR (600 MHz, CDCl₃)** δ 7.86-7.80 (m, 2H), 7.29-7.22 (m, 2H), 4.65 (s, 1.1H), 4.55 (s, 0.9H), 2.96 (s, 1.35H), 2.92 (s, 1.65H), 2.41 (s, 1.35H), 2.40 (s, 1.65H), 1.48 (s, 5H), 1.37 (s, 4H);

**13C NMR (151 MHz, CDCl₃)** δ 194.9, 194.5, 156.4, 155.9, 144.5, 144.4, 132.91, 132.88, 129.6, 129.5, 128.1, 127.9, 80.1, 80.0, 55.7, 55.1, 35.7, 35.8, 28.5, 28.3, 21.8.

HRMS: (ESI) calcd for C₁₅H₂₁NO₃⁺[M+H]⁺ 264.1594; found 264.1601.

**N-methyl-N-(2-oxo-2-phenylethyl)acetamide (26)**
26 was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), N,N-dimethylacetamide (2.0 mmol, 174.2 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain 26 as colorless oil (15.7 mg, 41% yield); a 4.7:1 mixture of rotamers.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.88-7.80 (m, 2H), 7.27-7.24 (m, 2H), 4.82 (s, 1.65H), 4.72 (s, 0.35H), 3.09 (s, 2.5H), 2.99 (s, 0.5H), 2.43 (s, 0.5H), 2.40 (s, 2.5H), 2.19 (s, 2.5H), 1.98 (s, 0.5H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 194.1, 193.1, 171.6, 171.5, 145.3, 144.6, 132.8, 132.3, 129.8, 129.5, 128.2, 128.0, 57.0, 54.0, 37.4, 35.3, 21.9, 21.8, 21.5, 21.3;

HRMS: (ESI) calcld for C$_{12}$H$_{16}$NO$_2$+[M+H]$^+$ 206.1176; found 206.1170.

3-(4-methylbenzoyl)cyclopentan-1-one (27)

27 was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclopentanone (2.0 mmol, 168.2 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain 27 as colorless oil (19.9 mg, 47% yield).

The NMR data matched those reported in the literature.$^{12}$
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J = 8.2$ Hz, 2H), 7.32-7.27 (m, 2H), 4.14-4.06 (m, 1H), 2.74-2.65 (m, 1H), 2.48-2.43 (m, 1H), 2.43 (s, 3H), 2.42-2.37 (m, 1H), 2.37-2.32 (m, 1H), 2.31-2.24 (m, 1H), 2.20-2.12 (m, 1H);

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 217.2, 200.0, 144.6, 133.2, 129.7, 128.7, 43.1, 41.2, 37.5, 27.2, 21.8.

3-(4-methylbenzoyl)cyclohexan-1-one (28)

![Chemical structure of 3-(4-methylbenzoyl)cyclohexan-1-one (28)](image)

Chemical Formula: C$_{14}$H$_{16}$O$_2$

Exact Mass: 216.1150

28 was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexanone (2.0 mmol, 196.3 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain 28 as colorless oil (29.7 mg, 68% yield, r.r. = 3:2).

The NMR data matched those reported in the literature.$^{12}$

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J = 8.2$ Hz, 0.8H), 7.85 (d, $J = 8.3$ Hz, 1.2H), 7.31-7.27 (m, 2H), 3.85-3.75 (m, 0.6H), 3.69 (tt, $J = 10.2$, 3.8 Hz, 0.4H), 2.75-2.69 (m, 0.6H), 2.61-2.51 (m, 0.9H), 2.50-2.44 (m, 1.1H), 2.43-2.36 (m, 4.4H), 2.24-2.19 (m, 1H), 2.13-2.00 (m, 2H), 1.89-1.80 (m, 1H);

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 210.6, 210.4, 200.1, 144.5, 144.3, 132.9, 129.7, 129.6, 128.6, 128.5, 45.2, 43.3, 42.7, 41.1, 40.1, 29.0, 28.6, 25.0, 21.8.

(1,1-dioxidotetrahydrothiophen-3-yl)(p-tolyl)methanone (29)
was prepared according to general procedure 2.1 using NiBr$_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), tetrahydrothiophene 1,1-dioxide (2.0 mmol, 240.3 mg), anhydrous K$_3$PO$_4$ (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain 29 as colorless oil (25.8 mg, 53% yield).

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.85 (d, $J = 8.3$ Hz, 2H), 7.34-7.30 (m, 2H), 4.35-4.23 (m, 1H), 3.52-3.42 (m, 1H), 3.30-3.21 (m, 2H), 3.17-3.10 (m, 1H), 2.60-2.50 (m, 1H), 2.44 (s, 3H), 2.41-2.33 (m, 1H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 196.3, 145.5, 132.2, 130.0, 128.8, 52.5, 50.8, 41.8, 25.9, 21.9;

HRMS: (ESI) calcd for C$_{12}$H$_{14}$O$_3$S$^+$[M+H]$^+$ 239.0736; found 239.0733.

$N$, $N$-diphenylcyclohexanecarboxamide (31)

was prepared according to general procedure 2.2 using NiCl$_2$•dtbbpy (0.004 mmol, 1.6 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K$_3$PO$_4$ (0.4 mmol, 84.8 mg) and diphenylcarbamic chloride (0.2 mmol, 46.3 mg) and was purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain 31 as colorless oil (34.1 mg, 61% yield).

The NMR data matched those reported in the literature.$^{13}$
$^{1}$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.42–7.31 (m, 5H), 7.28–7.20 (m, 5H), 2.38 (tt, $J$ = 11.6, 3.4 Hz, 1H), 1.86–1.76 (m, 2H), 1.73–1.68 (m, 2H), 1.65–1.53 (m, 3H), 1.26–1.17 (m, 1H), 1.07–0.95 (m, 2H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 176.7, 143.1, 129.6, 128.9, 126.7, 42.3, 29.4, 25.6, 25.5.

**Isobutyl cyclohexanecarboxylate (33)**

![Chemical Structure](image)

Chemical Formula: $C_{11}H_{20}O_2$
Exact Mass: 184.1463

33 was prepared according to general procedure 2.3 using NiBr$_2$ (0.02 mmol, 4.4 mg), dtbbpy (0.03 mmol, 8.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K$_3$PO$_4$ (0.4 mmol, 84.8 mg) and isobutyl carbonochloridate (0.2 mmol, 27.3 mg) and was purified by silica gel column chromatography (PE/EtOAc = 100/1) to obtain 33 as colorless oil (14.4 mg, 39% yield).

The NMR data matched those reported in the literature.$^{14}$

$^{1}$H NMR (600 MHz, CDCl$_3$) $\delta$ 3.81 (d, $J$ = 6.6 Hz, 2H), 2.27 (tt, $J$ = 11.3, 3.7 Hz, 1H), 1.91–1.85 (m, 3H), 1.74–1.68 (m, 2H), 1.63–1.58 (m, 1H), 1.45–1.37 (m, 2H), 1.29–1.16 (m, 3H), 0.89 (d, $J$ = 6.7 Hz, 6H);

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 176.1, 70.1, 43.3, 29.0, 27.8, 25.8, 25.4, 19.0.

**(cyclohexylethynyl)triisopropylsilane (34)**

![Chemical Structure](image)

Chemical Formula: $C_{17}H_{30}Si$
Exact Mass: 264.2273

34 was prepared according to general procedure 2.4 using NiBr$_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2
mmol, 168.0 mg), anhydrous K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE) to obtain 34 as colorless oil (40.3 mg, 76% yield).

The NMR data matched those reported in the literature.$^{15}$

$^1$H NMR (600 MHz, CDCl$_3$) δ 2.50-42 (m, 1H), 1.80-1.70 (m, 4H), 1.53-1.44 (m, 3H), 1.39-1.28 (m, 3H), 1.13-1.03 (m, 21H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 113.6, 79.5, 32.7, 29.8, 26.0, 24.5, 18.6, 11.3

(cyclohexylethynyl)benzene (35)

35 was prepared according to general procedure 2.4 using NiBr$_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) and (bromoethynyl)benzene (0.2 mmol, 36.2 mg) and was purified by silica gel column chromatography (PE) to obtain 35 as colorless oil (18.8 mg, 51% yield).

The NMR data matched those reported in the literature.$^{16}$

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.41-7.38 (m, 2H), 7.29-7.23 (m, 3H), 2.62-2.55 (m, 1H), 1.92-1.86 (m, 2H), 1.79-1.74 (m, 2H), 1.57-1.51 (m, 3H), 1.39-1.32 (m, 3H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 131.6, 128.2, 127.4, 124.1, 94.5, 80.5, 32.7, 29.7, 26.0, 24.9.

1-(cyclohexylethynyl)-4-methoxybenzene (36)

36 was prepared according to general procedure 2.4 using NiBr$_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2
mmol, 168.0 mg), anhydrous K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) and 1-(bromoethynyl)-4-methoxybenzene (0.2 mmol, 42.2 mg) and was purified by silica gel column chromatography (PE) to obtain 36 as colorless oil (26.9 mg, 63% yield).

The NMR data matched those reported in the literature.$^{17}$

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.35-7.31 (m, 2H), 6.83-6.78 (m, 2H), 3.79 (s, 3H), 2.59-2.53 (m, 1H), 1.90-1.84 (m, 2H), 1.79-1.72 (m, 2H), 1.55-1.48 (m, 3H), 1.37-1.30 (m, 3H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 158.9, 132.9, 116.3, 113.7, 92.8, 80.1, 55.2, 32.8, 29.7, 25.9, 24.9.

**methyl 4-(cyclohexylethynyl)benzoate (37)**

![Chemical Structure](image)

**Chemical Formula**: $C_{16}H_{18}O_2$

**Exact Mass**: 242.1307

37 was prepared according to general procedure 2.4 using NiBr$_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) and methyl 4-(bromoethynyl)benzoate (0.2 mmol, 47.8 mg) and was purified by silica gel column chromatography (PE/EtOAc = 100/1) to obtain 37 as colorless oil (22.3 mg, 46% yield).

The NMR data matched those reported in the literature.$^{17}$

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.96-7.92 (m, 2H), 7.47-7.39 (m, 2H), 3.90 (s, 3H), 2.66-2.56 (m, 1H), 1.92-1.86 (m, 2H), 1.78-1.73 (m, 2H), 1.58-1.50 (m, 3H), 1.39-1.30 (m, 3H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 166.7, 131.5, 129.3, 129.0, 128.7, 97.9, 80.0, 52.1, 32.5, 29.7, 25.8, 24.8.

tert-butyl((1-(cyclohexylethynyl)cyclohexyl)oxy)dimethylsilane (38)
38 was prepared according to general procedure 2.4 using NiBr$_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) and ((1-(bromoethynyl)cyclohexyl)oxy)(tert-butyl)dimethylsilane (0.2 mmol, 63.5 mg) and was purified by silica gel column chromatography (PE) to obtain 38 as colorless oil (51.5 mg, 80% yield).

$^1$H NMR (600 MHz, CDCl$_3$) δ 2.45-2.33 (m, 1H), 1.84-1.76 (m, 2H), 1.75-1.68 (m, 4H), 1.66-1.57 (m, 3H), 1.55-1.49 (m, 3H), 1.48-1.37 (m, 4H), 1.35-1.25 (m, 4H), 0.87 (s, 9H), 0.16 (s, 6H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 89.0, 84.5, 69.2, 41.5, 32.8, 29.1, 25.9, 25.9, 25.5, 25.0, 23.0, 18.1, -2.8.

HRMS: (ESI) calcd for C$_{20}$H$_{37}$OSi$^+[M+H]^+$ 321.2608; found 321.2600.

tert-butyl((3-cyclohexyl-1,1-diphenylprop-2-yn-1-yl)oxy)dimethylsilane (39)

39 was prepared according to general procedure 2.4 using NiBr$_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) and ((3-bromo-1,1-diphenylprop-2-yn-1-yl)oxy)(tert-butyl)dimethylsilane (0.2 mmol, 80.3 mg) and was purified by silica gel column chromatography (PE) to obtain 39 as colorless oil (41.5 mg, 51% yield).

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.60-7.57 (m, 4H), 7.28-7.24 (m, 4H), 7.20-7.17 (m, 2H), 2.56-2.50 (m, 1H), 1.94-1.87 (m, 2H), 1.77-1.73 (m, 2H), 1.58-1.53 (m, 3H), 1.37-1.31 (m, 3H), 0.97 (s, 9H), 0.02 (s, 6H);
$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 147.5, 127.7, 126.8, 126.0, 93.2, 82.9, 75.4, 32.5, 29.4, 26.1, 25.8, 25.1, 18.5, -3.1.

HRMS: (APCI) calcd for C$_{27}$H$_{37}$OSi$^{+}$[M+H]$^+$ 405.2608; found 405.2608.

2-(3-cyclohexylprop-2-yn-1-yl)-2-methylcyclopentane-1,3-dione (40)

![Chemical Structure](image)

Chemical Formula: C$_{16}$H$_{20}$O$_2$
Exact Mass: 232.1463

40 was prepared according to general procedure 2.4 using NiBr$_2$·dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) and 2-(3-bromoprop-2-yn-1-yl)-2-methylcyclopentane-1,3-dione (0.2 mmol, 45.8 mg) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain 40 as colorless oil (23.0 mg, 50% yield).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 2.77 (s, 4H), 2.41 (d, 2H), 2.26-2.20 (m, 1H), 1.73-1.67 (m, 2H), 1.64-1.59 (m, 2H), 1.51-1.44 (m, 1H), 1.31-1.20 (m, 5H), 1.07 (s, 3H);

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 216.0, 87.3, 74.2, 55.7, 36.1, 32.8, 28.8, 25.8, 25.7, 24.8, 18.6.

HRMS: (ESI) calcd for C$_{15}$H$_{21}$O$_2^{+}$[M+H]$^+$ 233.1536; found 233.1538.

(cyclopentylethynyl)triisopropylsilane (41)

![Chemical Structure](image)

Chemical Formula: C$_{16}$H$_{30}$Si
Exact Mass: 250.2117

41 was prepared according to general procedure 2.4 using NiBr$_2$·dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclopentane (2 mmol, 140.3 mg), anhydrous K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) and
(bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE) to obtain 41 as colorless oil (32.5 mg, 65% yield).

The NMR data matched those reported in the literature.\textsuperscript{15}

\[\text{H NMR (600 MHz, CDCl}_3\text{) } \delta \ 2.70-2.64 \text{ (m, 1H), 1.93-1.86 (m, 2H), 1.76-1.70 (m, 2H), 1.67-1.61 (m, 2H), 1.57-1.53 (m, 2H), 1.09-1.02 (m, 21H);} \]

\[\text{C NMR (151 MHz, CDCl}_3\text{) } \delta \ 114.1, 79.0, 34.2, 31.2, 24.9, 18.6, 11.3.\]

(cyclooctylethynyl)triisopropylsilane (42)

42 was prepared according to general procedure 2.4 using NiBr$_2$\textsuperscript{•}dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclooctane (2 mmol, 224.4 mg), anhydrous K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE) to obtain 42 as colorless oil (24.5 mg, 42% yield).

The NMR data matched those reported in the literature.\textsuperscript{15}

\[\text{H NMR (600 MHz, CDCl}_3\text{) } \delta \ 2.65-2.60 \text{ (m, 1H), 1.89-1.83 (m, 2H), 1.79-1.73 (m, 2H), 1.73-1.65 (m, 3H), 1.55-1.51 (m, 4H), 1.50-1.46 (m, 3H), 1.07-1.04 (m, 21H);} \]

\[\text{C NMR (151 MHz, CDCl}_3\text{) } \delta \ 114.5, 79.4, 31.7, 31.2, 27.5, 25.4, 24.4, 18.7, 11.3.\]

N-methyl-N-(3-(triisopropylsilyl)prop-2-yn-1-yl)acetamide (43)

43 was prepared according to general procedure 2.4 using NiBr$_2$\textsuperscript{•}dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), N,N-dimethylacetamide (2.0 mmol, 174.2 mg), anhydrous K$_2$HPO$_4$ (0.3 mmol, 52.3 mg) and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by
silica gel column chromatography (PE/EtOAc = 10/1) to obtain 43 as colorless oil (27.3 mg, 51% yield); a 1.2:1 mixture of rotamers.

The NMR data matched those reported in the literature.\textsuperscript{18}

\begin{align*}
\textsuperscript{1}H \text{ NMR} & (600 \text{ MHz, CDCl}_3) \delta 4.29 (s, 1.1H), 4.06 (s, 0.9H), 3.07 (s, 1.7H), 2.99 (s, 1.3H), 2.16 (s, 1.3H), 2.09 (s, 1.7H), 1.05 (s, 3H), 1.05 (s, 18H); \\
\textsuperscript{13}C \text{ NMR} & (151 \text{ MHz, CDCl}_3) \delta 170.5, 170.1, 102.2, 101.2, 86.0, 85.0, 41.3, 36.7, 34.7, 33.1, 21.7, 21.4, 18.5, 18.5, 11.1, 11.0.
\end{align*}

triisopropyl((tetrahydrofuran-2-yl)ethynyl)silane (44)

\begin{center}
\begin{tikzpicture}
\node at (0,0) {$\text{C}_3$};
\node at (0.5,0) {$\equiv$};
\node at (1,0) {$\text{Si}$};
\node at (0.5,-0.5) {$\equiv$};
\node at (0,0.5) {$\equiv$};
\end{tikzpicture}
\end{center}

Chemical Formula: $\text{C}_{15}\text{H}_{25}\text{OSi}$

Exact Mass: 252.1909

44 was prepared according to general procedure 2.5 using Ni(acac)$_2$ (0.02 mmol, 5.1 mg), dtbbpy (0.03 mmol, 8.0 mg), 4-(4-methoxybenzoyl)benzonitrile (0.02 mmol, 4.7 mg), anhydrous Na$_2$CO$_3$ (0.4 mmol, 42.0 mg), tetrahydrofuran (1 mL) as sovlen and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain 44 as colorless oil (41.9 mg, 83% yield).

The NMR data matched those reported in the literature.\textsuperscript{18}

\begin{align*}
\textsuperscript{1}H \text{ NMR} & (600 \text{ MHz, CDCl}_3) \delta 4.62 (dd, J = 7.3, 4.6 \text{ Hz, 1H}), 3.97-3.94 (m, 1H), 3.84-3.80 (m, 1H), 2.17-2.11 (m, 1H), 2.06-1.97 (m, 2H), 1.92-1.86 (m, 1H), 1.07-1.05 (m, 21H); \\
\textsuperscript{13}C \text{ NMR} & (151 \text{ MHz, CDCl}_3) \delta 107.8, 85.0, 68.6, 67.5, 33.7, 25.1, 18.6, 11.1.
\end{align*}

((1,4-dioxan-2-yl)ethynyl)triisopropylsilane (45)

\begin{center}
\begin{tikzpicture}
\node at (0,0) {$\text{O}$};
\node at (0.5,0) {$\equiv$};
\node at (1,0) {$\text{Si}$};
\node at (0.5,-0.5) {$\equiv$};
\end{tikzpicture}
\end{center}

Chemical Formula: $\text{C}_{15}\text{H}_{25}\text{C}_2\text{Si}$

Exact Mass: 268.1859
45 was prepared according to general procedure 2.5 using Ni(acac)$_2$ (0.02 mmol, 5.1 mg), dtbbpy (0.03 mmol, 8.0 mg), 4-(4-methoxybenzoyl)benzonitrile (0.02 mmol, 4.7 mg), anhydrous Na$_2$CO$_3$ (0.4 mmol, 42.0 mg), 1,4-dioxane (1 mL) as sovlent and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain 45 as colorless oil (17.2 mg, 32% yield).

The NMR data matched those reported in the literature.$^{18}$

$^1$H NMR (600 MHz, CDCl$_3$) δ 4.37 (dd, $J = 8.3$, 2.9 Hz, 1H), 3.92-3.88 (m, 1H), 3.84 (dd, $J = 11.5$, 2.9 Hz, 1H), 3.69-3.66 (m, 3H), 3.59 (dd, $J = 11.5$, 8.3 Hz, 1H), 1.07-1.06 (m, 21H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 102.5, 87.9, 70.6, 66.5, 66.3, 65.6, 18.5, 11.0.

(benzo[d][1,3]dioxol-2-yethynyl)triisopropylsilane (46)

Chemical Formula: C$_{16}$H$_{26}$O$_2$Si
Exact Mass: 302.1702

46 was prepared according to general procedure 2.5 using Ni(acac)$_2$ (0.02 mmol, 5.1 mg), dtbbpy (0.03 mmol, 8.0 mg), 4-(4-methoxybenzoyl)benzonitrile (0.02 mmol, 4.7 mg), anhydrous Na$_2$CO$_3$ (0.4 mmol, 42.0 mg), benzo[d][1,3]dioxole (1 mL) as sovlent and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain 46 as colorless oil (21.8 mg, 36% yield).

The NMR data matched those reported in the literature.$^{18}$

$^1$H NMR (600 MHz, CDCl$_3$) δ 6.85 (s, 4H), 6.58 (s, 1H), 1.08-1.07 (m, 21H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 146.7, 121.8, 108.9, 99.6, 98.1, 90.9, 18.4, 10.9.

(3-(tert-butoxy)prop-1-yn-1-yl)triisopropylsilane (47)
47 was prepared according to general procedure 2.5 using Ni(acac)₂ (0.02 mmol, 5.1 mg), dtbbpy (0.03 mmol, 8.0 mg), 4-(4-methoxybenzoyl)benzonitrile (0.02 mmol, 4.7 mg), anhydrous Na₂CO₃ (0.4 mmol, 42.0 mg), 2-methoxy-2-methylpropane (1 mL) as sovlent and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain 47 as colorless oil (22.1 mg, 41% yield).

The NMR data matched those reported in the literature.¹⁸

¹H NMR (600 MHz, CDCl₃) δ 4.14 (s, 2H), 1.25 (s, 9H), 1.08-1.05 (m, 21H);

¹³C NMR (151 MHz, CDCl₃) δ 106.2, 85.4, 74.6, 51.2, 27.8, 18.6, 11.2.

(3,4-dimethoxybut-1-yn-1-yl)triisopropylsilane (48)

48 was prepared according to general procedure 2.5 using Ni(acac)₂ (0.02 mmol, 5.1 mg), dtbbpy (0.03 mmol, 8.0 mg), 4-(4-methoxybenzoyl)benzonitrile (0.02 mmol, 4.7 mg), anhydrous Na₂CO₃ (0.4 mmol, 42.0 mg), 1,2-dimethoxyethane (1 mL) as sovlent and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain 48 as colorless oil (22.7 mg, 42% yield).

The NMR data matched those reported in the literature.¹⁸

¹H NMR (600 MHz, CDCl₃) δ 4.22 (dd, J = 8.0, 3.4 Hz, 1H), 3.61-3.53 (m, 2H), 3.47 (s, 3H), 3.41 (s, 3H), 1.08-1.06 (m, 21H);

¹³C NMR (151 MHz, CDCl₃) δ 103.0, 88.1, 75.0, 71.0, 59.2, 56.5, 18.5, 11.1.
6. Synthetic Applications

![Chemical Structure](image)

To the solution of 34 (211.6 mg, 0.8 mmol) in THF (2.0 mL) and 2 mL TBAF (1.0 M in THF) was added under Ar atmosphere, and was stirred at room temperature for 2 h. Saturated NH₄Cl aqueous solution (10 mL) was added to the reaction mixture, and the product was extracted with AcOEt (10 mL × 3). The combined extracts were washed by brine (10 mL), dried over Na₂SO₄ and concentrated under reduced pressure to give the terminal alkyne, which was used in the next step without further purification.

The terminal alkyne was dissolved in acetone (2.0 mL). Then, AgNO₃ (13.6 mg, 0.1 equiv.), NBS (156.6 mg, 1.1 equiv.) were added. The mixture was stirred at room temperature for 4 h. After the reaction was completed, concentrated the mixture and purified by chromatography on silica gel (PE) to afford the bromide alkyne 50 as colorless liquid (116.7 mg, 78% yield).

The NMR data matched those reported in the literature.¹⁹

¹H NMR (600 MHz, CDCl₃) δ 2.45-2.34 (m, 1H), 1.83-1.74 (m, 2H), 1.73-1.64 (m, 2H), 1.53-1.41 (m, 3H), 1.34-1.26 (m, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 84.4, 37.7, 32.3, 30.1, 25.8, 24.8.
An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with NiBr$_2$•dtbbpy (9.8 mg, 0.02 mmol), tetrabutylammonium decatungstate (14.0 mg, 0.004 mmol), 50 (37.4 mg, 0.2 mmol), anhydrous K$_2$HPO$_4$ (50 mg, 0.3 mmol), cyclohexane (168 mg, 2.0 mmol) and dry MeCN (1.0 mL) in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 6 W 390 nm LED lamp at 5 °C for 12 hours. The resulting mixture was diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. Solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (PE) to afford 51 as colorless liquid (26.3 mg, 69% yield).

The NMR data matched those reported in the literature.$^{20}$

$^1$H NMR (600 MHz, CDCl$_3$) δ 2.38-2.29 (m, 2H), 1.82-1.73 (m, 4H), 1.72-1.65 (m, 4H), 1.53-1.44 (m, 2H), 1.45-1.35 (m, 4H), 1.33-1.23 (m, 6H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 84.5, 33.2, 29.0, 26.0, 24.9.
An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with Ni(acac)$_2$ (5.6 mg, 0.02 mmol), dtbbpy (7.7 mg, 0.03 mmol), PC1 (5.6 mg, 0.02 mmol), 50 (37.4 mg, 0.2 mmol), anhydrous Na$_2$CO$_3$ (42.3 mg, 0.4 mmol) and THF (1.0 mL) as both C-H partners and solvent in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp at 25 °C for 48 hours. The resulting mixture was diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. Solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (PE/EA = 50/1) to afford 52 as colorless liquid (20.3 mg, 57% yield).

$^1$H NMR (600 MHz, CDCl$_3$) δ 4.56 (ddd, $J$ = 7.3, 5.7, 1.8 Hz, 1H), 3.97-3.92 (m, 1H), 3.80-3.74 (m, 1H), 2.42-2.34 (m, 1H), 2.15-2.09 (m, 1H), 2.04-1.98 (m, 1H), 1.94-1.86 (m, 2H), 1.80-1.74 (m, 2H), 1.72-1.67 (m, 2H), 1.52-1.47 (m, 1H), 1.44-1.38 (m, 2H), 1.30-1.25 (m, 3H);

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 89.3, 79.8, 68.5, 67.6, 33.7, 32.6, 29.1, 25.9, 25.4, 24.9;

HRMS: (ESI) calcd for C$_{12}$H$_{19}$O$^+$$[M+H]$$^+$ 179.1430; found 179.1424.
7. NMR Spectra

3
52

\[ \text{Diagram of a molecule} \]

\[ \text{Diagram of another molecule} \]
8. References


