Supporting Information for

Development of a Storable Triazinone-Based Reagent for O-p-Methoxybenzylolation under Mild Heating Conditions

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1. Reaction condition screening

Table S1. Solvent screening for \(O\)-\(p\)-methoxybenzylation of 5a with 1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield of 6a (%)(^a)</th>
<th>5a:6a ratio(^b)</th>
<th>6a:7 ratio(^b)</th>
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<tbody>
<tr>
<td>1</td>
<td>DMF</td>
<td>17</td>
<td>—</td>
<td>83:17</td>
<td>11:89</td>
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<tr>
<td>2(^d)</td>
<td>EtOAc</td>
<td>100</td>
<td>17</td>
<td>82:18</td>
<td>12:88</td>
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<tr>
<td>3</td>
<td>DCE</td>
<td>40</td>
<td>—</td>
<td>71:29</td>
<td>18:82</td>
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<tr>
<td>4</td>
<td>MeCN</td>
<td>17</td>
<td>—</td>
<td>72:28</td>
<td>18:82</td>
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<tr>
<td>5</td>
<td>toluene</td>
<td>25</td>
<td>31</td>
<td>64:36</td>
<td>21:79</td>
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<td>PhCF(_3)</td>
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<td>40</td>
<td>58:42</td>
<td>28:72</td>
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<tr>
<td>7</td>
<td>1,4-dioxane</td>
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<td>22</td>
<td>70:30</td>
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<tr>
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<td>DMSO</td>
<td>10</td>
<td>nd(^c)</td>
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<td>49</td>
<td>48:52</td>
<td>36:64</td>
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\(^a\)Calculated from \(^1\)H NMR spectroscopic analysis by using an internal standard. \(^b\)Calculated from \(^1\)H NMR spectroscopic analysis. \(^c\)Not determined. \(^d\)The reaction was carried out at reflux temperature. \(^e\)Not detected. Alcohol 2a was recovered in 65% yield along with \(p\)-methoxybenzaldehyde.
Table S2. O-p-Methoxybenzylolation of 5g with 1 in the presence of additives.

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>I (equiv)</th>
<th>Additive (mol%)</th>
<th>Concentration (M)</th>
<th>Time (h)</th>
<th>Recovered 5g (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Recovered 6g (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Recovered 1 (%)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>7 (%)&lt;sup&gt;c&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>–</td>
<td>0.6</td>
<td>8</td>
<td>5</td>
<td>67&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2</td>
<td>40</td>
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<tr>
<td>2</td>
<td>2.0</td>
<td>DTBP&lt;sup&gt;d&lt;/sup&gt; (100)</td>
<td>0.6</td>
<td>10.5</td>
<td>6</td>
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<td>pyridine (10)</td>
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<td>3.0</td>
<td>pyridine (5)</td>
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<td>66</td>
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<tr>
<td>5</td>
<td>3.5</td>
<td>pyridine (1)</td>
<td>1.0</td>
<td>11</td>
<td>nd&lt;sup&gt;e&lt;/sup&gt;</td>
<td>82</td>
<td>4</td>
<td>54</td>
</tr>
</tbody>
</table>

<sup>a</sup>Calculated from <sup>1</sup>H NMR spectroscopic analysis unless otherwise noted. <sup>b</sup>Yield based on I. <sup>c</sup>Isolated yield. <sup>d</sup>2,6-Di-tert-butylpyridine. <sup>e</sup>Not detected.
2. Experimental procedure and characterization data for products

**General Information.** NMR spectra were recorded on a JEOL JNM-ECS400 spectrometer [$^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz)]. Chemical shifts for $^1$H NMR are reported in parts per million (δ) relative to tetramethylsilane as the internal standard. Coupling constant (J) are reported in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet. Chemical shifts for $^{13}$C NMR are reported in parts per million (δ) relative to the solvent (CDCl₃, δ 77.16). IR spectra were recorded on a Horiba FT-720 FREEEXACT-II spectrophotometer and were reported in wavenumbers (cm⁻¹). Mass spectra were measured on JMS-T100TD (DART-MS). Analytical thin layer chromatography (TLC) was performed using glass plates precoated with 0.25 mm silica gel impregnated with a fluorescent indicator (254 nm). Preparative TLC separations were performed using glass plates precoated with 0.25 or 0.50 mm silica gel impregnated with a fluorescent indicator (254 nm). Flash chromatography was performed using silica gel (spherical, neutral, 40–100 mesh) or diol-functionalized silica gel (Fuji Silysia Chromatorex DIOL MB100-40/75). Recycling preparative HPLC was performed with Japan Analytical Industry LC-928 equipped with GPC columns Jaigel-1H and 2H. Reagents were commercial grades and were used without any purification unless otherwise noted. Dehydrated 1,4-dioxane was purchased from commercial sources. MeNO₂ was purchased from commercial sources and distilled over calcium hydride before use. $^{n}$Bu₄NOTs was prepared from $^{n}$Bu₄NBr by ion-exchange resin. All reactions sensitive to oxygen or moisture were conducted under a nitrogen atmosphere. DSC analysis for 1 was carried out on a heat-flux DSC (SHIMADZU DSC-60 plus) apparatus under nitrogen flow, in the range of 25–200 °C (10 °C/min heating rate). The samples were placed in sealed aluminum pans. An empty aluminum pan was used as reference. The data collection and the analysis was performed using SHIMADZU TA-60WS thermal analyzer and its program package.

**2-tert-Butyl-4-chloro-6-phenoxy-1,3,5-triazine (2).**

\[
\begin{align*}
\text{Cl} & \quad \text{N} \quad \text{N} \quad \text{O} \\
& \quad \text{tert-Butyl chloride (8.79 mL, 80.0 mmol) was added to a slurry of Mg (2.14 g, 88.0 mmol) and iodine (a catalytic amount) in THF (80 mL). The mixture was heated to reflux for 3 h and then cooled to room temperature. The mixture was added to a suspension of cyanuric chloride (7.38 g, 40.0 mmol) and copper iodide (381 mg, 2.00 mmol) in THF (40 mL) at 0 °C over 80 min. After 2 h, a solution of phenol (3.76 g, 40.0 mmol) and $^{i}$Pr₂EtN (9.29 mL, 53.3 mmol) in THF (24.2 mL) was added at 0 °C. The reaction mixture was warmed to room temperature and stirred for 50 min. A solution of phenol (1.88 g, 20.0 mmol) and $^{i}$Pr₂EtN (4.64 mL, 26.7 mmol) in THF (12.1 mL) was added. The reaction mixture was heated to 40 °C for 18 h. A solution of phenol (5.65}
\end{align*}
\]
g, 60.0 mmol) and Pr₂EtN (13.9 mL, 80.0 mmol) in THF (25.0 mL) was added. The reaction mixture was heated to reflux for 2 h and then cooled to room temperature. The reaction mixture was diluted with EtOAc (150 mL), washed with aqueous HCl (1 M, 100 mL) and brine (150 mL), dried (Na₂SO₄), and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, EtOAc:hexane = 19:1) to afford a white solid (8.37 g, 79%). Mp 71–72 °C. ¹H NMR (CDCl₃): δ 7.44 (t, J = 7.8 Hz, 2H), 7.30 (t, J = 7.8 Hz, 1H), 7.19 (d, J = 7.8 Hz, 2H), 1.33 (s, 9H). ¹³C NMR (CDCl₃): δ 190.9, 172.5, 171.1, 151.6, 129.7, 126.4, 121.4, 40.1, 28.6. Anal. Calcd for C₁₃H₁₄ClN₃O: C, 59.21; H, 5.35; N, 15.93. Found: C, 59.17; H, 5.31; N, 15.92. HRMS (DART-TOF): [M + H]⁺ calcd for C₁₃H₁₅ClN₃O, 264.0904; found, 264.0911. IR (KBr): 1552, 1508, 1417, 1394, 1281, 1188, 997, 887, 823, 766, 694 cm⁻¹.

4-tert-Butyl-6-phenoxy-1,3,5-triazin-2(1H)-one (3).

N-Methylmorpholine (3.80 mL, 34.3 mmol) was added to a solution of sodium acetate (5.11 g, 62.3 mmol) and 2-tert-butyl-4-chloro-6-phenoxy-1,3,5-triazine (8.22 g, 31.2 mmol) in 2-propanol (226 mL) and H₂O (41.6 mL) at room temperature. After 1 h, the reaction mixture was concentrated under reduced pressure. Aqueous HCl (0.1 M, 380 mL) was added. A precipitate was filtered and washed with H₂O to afford a white solid (7.06 g, 92%). Mp 226–228 °C. ¹H NMR (CDCl₃): δ 12.14 (br s, 1H), 7.44–7.37 (m, 2H), 7.29–7.23 (m, 1H), 7.22–7.17 (m, 2H), 1.40 (s, 9H). ¹³C NMR (CDCl₃): δ 180.8, 171.4, 159.4, 151.6, 129.6, 126.2, 121.7, 38.1, 27.8. Anal. Calcd for C₁₃H₁₅N₃O₂: C, 63.66; H, 6.16; N, 17.13. Found: C, 63.26; H, 6.07; N, 17.02. HRMS (DART-TOF): [M + H]⁺ calcd for C₁₃H₁₆N₃O₂, 246.1242; found, 246.1250. IR (KBr): 3170, 3107, 3068, 2978, 1685, 1601, 1576, 1550, 1493, 1375, 1354, 1201, 806, 764 cm⁻¹.

4-tert-Butyl-6-phenoxy-1-propargyl-1,3,5-triazin-2(1H)-one (4).

Propargyl bromide (5.93 mL, 79.3 mmol) and Pr₂EtN (13.8 mL, 79.3 mmol) were added to a suspension of 4-tert-butyl-6-phenoxy-1,3,5-triazin-2(1H)-one (7.78 g, 31.7 mmol) in toluene (79.3 mL) at room temperature. The mixture was heated to 80 °C for 13 h and then cooled to room temperature. The reaction mixture was diluted with EtOAc (80 mL), washed with aqueous citric
acid (10% w/w, 100 mL) and brine (100 mL), dried (Na$_2$SO$_4$), and filtered. The filtrate was concentrated under reduced pressure.

The residue was purified by column chromatography (silica gel, EtOAc:hexane = 3:7) to afford an yellowish solid (7.70 g, 86%). Mp: 108–110 °C. $^1$H NMR (CDCl$_3$): $\delta$ 7.46 (t, $J = 7.6$ Hz, 2H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.23 (d, $J = 7.6$ Hz, 2H), 4.93 (d, $J = 2.3$ Hz, 2H), 2.34 (t, $J = 2.3$ Hz, 1H), 1.17 (s, 9H). $^{13}$C NMR (CDCl$_3$): $\delta$ 187.2, 161.3, 155.6, 151.0, 129.6, 126.9, 121.4, 76.5, 72.7, 40.0, 32.1, 28.1. Anal. Calcd for C$_{16}$H$_{17}$N$_3$O$_2$: C, 67.83; H, 6.05; N, 14.83. Found: C, 67.88; H, 6.12; N, 14.76. HRMS (DART-TOF): [M + H]$^+$ calcd for C$_{16}$H$_{18}$N$_3$O$_2$, 284.1399; found, 284.1388. IR (KBr): 3246, 1699, 1610, 1502, 1473, 1437, 1284, 1190, 984, 762 cm$^{-1}$.

4-tert-Butyl-6-(p-methoxybenzyloxy)-1-propargyl-1,3,5-triazin-2(1H)-one (1).

$\text{O\text{-OMe}}$

$p$-Anisyl alcohol (724 µL, 5.82 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (948 µL, 6.35 mmol) were added to a solution of 4-tert-butyl-6-phenoxy-1-propargyl-1,3,5-triazin-2(1H)-one (1.50 g, 5.29 mmol) in CH$_2$Cl$_2$ (10.6 mL) at 0 °C. The reaction mixture was stirred for 2 h at 0 °C and then directly purified by column chromatography (dion-functionalized silica gel, CHCl$_3$:hexane = 2:1) followed by recrystallization from Et$_2$O to afford a crystalline solid (1.48 g, 86%). Mp 106–108 °C. $^1$H NMR (CDCl$_3$): $\delta$ 7.42 (d, $J = 8.7$ Hz, 2H), 6.92 (d, $J = 8.7$ Hz, 2H), 5.50 (s, 2H), 4.72 (d, $J = 2.3$ Hz, 2H), 3.83 (s, 3H), 2.21 (t, $J = 2.3$ Hz, 1H), 1.33 (s, 9H). $^{13}$C NMR (CDCl$_3$): $\delta$ 186.7, 161.3, 160.3, 155.8, 130.7, 126.2, 114.2, 76.7, 72.2, 71.5, 55.4, 40.0, 31.5, 28.5. Anal. Calcd for C$_{18}$H$_{21}$N$_3$O$_3$: C, 66.04; H, 6.47; N, 12.84. Found: C, 66.01; H, 6.43; N, 12.82. HRMS (DART-TOF): [M + H]$^+$ calcd for C$_{18}$H$_{22}$N$_3$O$_3$, 328.1661; found, 328.1677. IR (KBr): 3251, 1699, 1601, 1514, 1496, 1286, 1246, 1113, 1032, 814 cm$^{-1}$.

Compound 1 was stored at room temperature (25–30 °C) under open air for 20 days to examine its stability. No decomposition was detected by $^1$H NMR spectroscopic analysis (Figure S1).
Figure S1. Stability of 1 at room temperature under open air.
Isolation of coproducts from the $O$-$p$-methoxybenzylation reaction of 5a with 1.

Compound 1 (589.3 mg, 1.80 mmol) was added to a solution of 5a (122.6 µL, 0.90 mmol) and $^t$Bu$_4$NOTs (74.5 mg, 0.18 mmol) in MeNO$_2$/1,4-dioxane (4:1, 1.50 mL) at room temperature. The reaction mixture was heated to 50 °C for 7 h and then cooled to room temperature. The reaction mixture was filtered through silica gel (EtOAc as an eluent). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, EtOAc:hexane = 2:3 to 5:5) and preparative TLC (EtOAc:hexane = 5:5) to give 7 (204.4 mg, 35% based on 1) and 7 (242.0 mg, 65% based on 1).

6-tert-Butyl-1-($p$-methoxybenzylxoy)-3-propargyl-1,3,5-triazin-2,4-dione (7)

White solid. mp: 150–151 °C. $^1$H NMR (CDCl$_3$): $\delta$ 6.99 (d, $J$ = 8.7 Hz, 2H), 6.87 (d, $J$ = 8.7 Hz, 2H), 5.30 (s, 2H), 4.65 (d, $J$ = 2.3 Hz, 2H), 3.78 (s, 3H), 2.20 (t, $J$ = 2.3 Hz, 1H), 1.44 (s, 9H). $^{13}$C NMR (CDCl$_3$): $\delta$ 173.0, 159.1, 153.3, 151.0, 127.4, 126.6, 114.4, 77.1, 71.6, 55.3, 49.5, 39.9, 31.8, 29.4. Anal. Calcd for C$_{18}$H$_{21}$N$_3$O$_3$: C, 66.04; H, 6.47; N, 12.84. Found: C, 65.99; H, 6.59; N, 12.75. HRMS (DART-TOF): [M + H]$^+$ calcd for C$_{18}$H$_{22}$N$_3$O$_3$, 328.1661; found, 328.1670. IR (KBr): 3246, 1739, 1684, 1579, 1516, 1417, 1400, 1252, 1182, 1022, 796 cm$^{-1}$.

6-tert-Butyl-3-propargyl-1,3,5-triazin-2,4-dione (10)

White solid. mp: 181–183 °C. $^1$H NMR (CDCl$_3$): $\delta$ 10.86 (br, s, 1H), 4.69 (d, $J$ = 2.3 Hz, 2H), 2.22 (t, $J$ = 2.3 Hz, 1H), 1.40 (s, 9H). $^{13}$C NMR (CDCl$_3$): $\delta$ 174.0, 154.7, 151.6, 76.9, 71.7, 38.1, 30.9, 27.5. Anal. Calcd for C$_{10}$H$_{13}$N$_3$O$_2$: C, 57.96; H, 6.32; N,
20.28. Found: C, 57.66; H, 6.26; N, 20.05. HRMS (DART-TOF): [M + H]+ calcd for C<sub>10</sub>H<sub>14</sub>N<sub>3</sub>O<sub>2</sub>, 208.1086; found, 208.1086. IR (KBr): 3269, 1749, 1676, 1655, 1595, 1496, 1431, 1344, 1003, 800 cm<sup>-1</sup>.

**General procedure for O-p-methoxybenzylolation of an alcohol using 1.**

Compound 1 (196.4 mg, 0.60 mmol) was added to a solution of 5b (21.3 µL, 0.30 mmol) and nBu<sub>4</sub>NOTs (24.8 mg, 0.060 mmol) in MeNO<sub>2</sub>/1,4-dioxane (4:1, 0.50 mL) at room temperature. The mixture was heated to 50 °C for 7 h and then cooled to room temperature. The reaction mixture was diluted with EtOAc (10 mL), washed with saturated aqueous NaHCO<sub>3</sub> (10 mL) and brine (10 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, toluene:hexane = 1:1 to hexane to EtOAc:hexane = 1:19) followed by preparative TLC (EtOAc:hexane = 1:19) to afford 6b (63.7 mg, 87%) as a colorless oil.

**p-Methoxybenzyl 3-phenylpropyl ether (6a)<sup>1</sup>**

![Image of p-Methoxybenzyl 3-phenylpropyl ether (6a)]

Compound 1 (196.4 mg, 0.60 mmol) was added to a solution of 5a (21.3 µL, 0.30 mmol) and nBu<sub>4</sub>NOTs (24.8 mg, 0.060 mmol) in MeNO<sub>2</sub>/1,4-dioxane (4:1, 0.50 mL) at room temperature. The reaction mixture was heated to 50 °C for 7 h, cooled to room temperature, and filtered through silica gel (EtOAc as an eluent). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, toluene:hexane = 1:1 to hexane to EtOAc:hexane = 1:19) and preparative TLC (EtOAc:hexane = 1:19) to afford a colorless oil (69.1 mg, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.31–7.23 (m, 4H), 7.21–7.14 (m, 3H), 6.92–6.85 (m, 2H), 4.44 (s, 2H), 3.81 (s, 3H), 3.46 (t, <i>J</i> = 6.4 Hz, 2H). 13C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.3, 142.1, 130.8, 129.4, 128.6, 128.4, 125.8, 113.9, 72.7, 69.3, 55.4, 32.5, 31.5; LRMS (DART-TOF): 274 ([M + NH<sub>4</sub>]+).

**2-Bromoethyl p-methoxybenzyl ether (6b)<sup>2</sup>**

![Image of 2-Bromoethyl p-methoxybenzyl ether (6b)]

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.31–7.25 (m, 2H), 6.92–6.85 (m, 2H), 4.52 (s, 2H), 3.81 (s, 3H), 3.76 (t, <i>J</i> = 6.4 Hz, 2H), 3.47 (t, <i>J</i> = 6.4 Hz, 2H). 13C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.5, 129.9, 129.5, 114.0, 72.9, 69.7, 55.4, 30.7. HRMS (DART-TOF): [M + NH<sub>4</sub>]+ calcd for C<sub>16</sub>H<sub>17</sub>BrNO<sub>2</sub>, 262.0443; found, 262.0446.
6-(tert-Butyldimethysilyloxy)hexyl p-methoxybenzyl ether (6c)

![Chemical structure](image)

Compound 1 (190.7 mg, 0.583 mmol) was added to a solution of 5c (67.7 mg, 0.291 mmol) and nBu₄NOTs (24.0 mg, 0.058 mmol) in MeNO₂/1,4-dioxane (4:1, 0.49 mL) at room temperature. The reaction mixture was heated to 50 °C for 7 h and then cooled to room temperature. The reaction mixture was diluted with EtOAc (10 mL), washed with saturated aqueous NaHCO₃ (10 mL) and brine (10 mL), dried (MgSO₄), and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, EtOAc:hexane = 1:19) and preparative TLC (EtOAc:hexane = 1:19) to afford a colorless oil (90.7 mg, 88%). ¹H NMR (400 MHz, CDCl₃): δ 7.26 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.59 (t, J = 6.4 Hz, 2H), 3.43 (t, J = 6.4 Hz, 2H), 1.67–1.56 (m, 2H), 1.56–1.45 (m, 2H), 1.42–1.27 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 159.2, 130.9, 129.3, 113.9, 72.6, 70.3, 63.4, 55.4, 33.0, 29.9, 26.2, 26.1, 25.8, 18.5, –5.1. LRMS (DART-TOF): 370 ([M + NH₄]⁺).

p-Methoxybenzyl (2-trimethylsilyl)ethyl ether (6d)

![Chemical structure](image)

Compound 1 (196.4 mg, 0.60 mmol) was added to a solution of 5d (42.7 µL, 0.30 mmol) and nBu₄NOTs (24.8 mg, 0.060 mmol) in MeNO₂/1,4-dioxane (4:1, 0.50 mL) at room temperature. The reaction mixture was heated to 50 °C for 7 h and then cooled to room temperature. The reaction mixture was diluted with EtOAc (10 mL), washed with saturated aqueous NaHCO₃ (10 mL) and brine (10 mL), dried (Na₂SO₄), and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, EtOAc:hexane = 1:19) and preparative TLC (EtOAc:hexane = 1:19) to afford a colorless oil (59.9 mg, 84%). ¹H NMR (CDCl₃): δ 7.29–7.23 (m, 2H), 6.90–6.85 (m, 2H), 4.41 (s, 2H), 3.80 (s, 3H), 3.58–3.51 (m, 2H), 1.02–0.94 (m, 2H), 0.01 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 159.2, 131.0, 129.3, 113.9, 72.6, 70.3, 63.4, 55.4, 33.0, 29.9, 26.2, 26.1, 25.8, 18.4, –1.2; LRMS (DART-TOF): 256 ([M + NH₄]⁺).

p-Methoxybenzyl (1-phenylethyl) ether (6e)

![Chemical structure](image)

Compound 1 (196.4 mg, 0.60 mmol) was added to a solution of 5d (42.7 µL, 0.30 mmol) and nBu₄NOTs (24.8 mg, 0.060 mmol) in MeNO₂/1,4-dioxane (4:1, 0.50 mL) at room temperature. The reaction mixture was heated to 50 °C for 7 h and then cooled to room temperature. The reaction mixture was diluted with EtOAc (10 mL), washed with saturated aqueous NaHCO₃ (10 mL) and brine (10 mL), dried (Na₂SO₄), and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, EtOAc:hexane = 1:19) and preparative TLC (EtOAc:hexane = 1:19) to afford a colorless oil (59.9 mg, 84%). ¹H NMR (CDCl₃): δ 7.29–7.23 (m, 2H), 6.90–6.85 (m, 2H), 4.41 (s, 2H), 3.80 (s, 3H), 3.58–3.51 (m, 2H), 1.02–0.94 (m, 2H), 0.01 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 159.2, 131.0, 129.3, 113.9, 72.6, 70.3, 63.4, 55.4, 33.0, 29.9, 26.2, 26.1, 25.8, 18.4, –1.2; LRMS (DART-TOF): 256 ([M + NH₄]⁺).
Compound 1 (196.4 mg, 0.60 mmol) was added to a solution of 5e (36.3 µL, 0.30 mmol) and nBu₄N OTs (24.8 mg, 0.060 mmol) in MeNO₂/1,4-dioxane (4:1, 0.50 mL) at room temperature. The reaction mixture was heated to 50 °C for 7 h and then cooled to room temperature. The reaction mixture was diluted with EtOAc (10 mL), washed with saturated aqueous NaHCO₃ (10 mL) and brine (10 mL), dried (Na₂SO₄), and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, toluene:hexane = 1:1 to 2:1) to afford a colorless oil (64.7 mg, 89%). ¹H NMR (CDCl₃): δ 7.40–7.33 (m, 4H), 7.33–7.26 (m, 1H), 7.26–7.19 (m, 2H), 6.90–6.83 (m, 2H), 4.48 (q, J = 6.4 Hz, 1H), 4.38, 4.22 (ABq, JAB = 11.4 Hz, 2H), 3.79 (s, 3H), 1.46 (d, J = 6.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 159.2, 143.9, 130.8, 129.4, 128.6, 127.6, 126.5, 113.9, 77.0, 70.0, 55.4, 24.4. HRMS (DART-TOF): [M + NH₄]⁺ calcd for C₁₆H₂₂NO₂, 260.1651; found, 260.1663.

2-Methyl-4-phenylbutan-2-yl p-methoxybenzyl ether (6f)⁴

²-Methyl-4-phenylbutan-2-yl p-methoxybenzyl ether (6f)⁴

Compound 1 (196.4 mg, 0.60 mmol) was added to a solution of 5f (50.8 µL, 0.30 mmol) and nBu₄N OTs (24.8 mg, 0.060 mmol) in MeNO₂/1,4-dioxane (4:1, 0.50 mL) at room temperature. The reaction mixture was heated to 50 °C for 7 h and then cooled to room temperature. The reaction mixture was diluted with EtOAc (10 mL), washed with saturated aqueous NaHCO₃ (10 mL) and brine (10 mL), dried (Na₂SO₄), and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, toluene:hexane = 1:1 to 2:1 to toluene) and preparative TLC (EtOAc:hexane = 1:9) to afford a colorless oil (63.8 mg, 75%). ¹H NMR (CDCl₃): δ 7.33–7.25 (m, 4H), 7.23–7.15 (m, 3H), 6.91–6.85 (m, 2H), 4.40 (s, 2H), 3.80 (s, 3H), 2.76–2.68 (m, 2H), 1.92–1.83 (m, 2H), 1.32 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 159.0, 143.0, 131.9, 128.9, 128.47, 128.44, 125.8, 113.9, 74.9, 63.5, 55.4, 42.4, 30.5, 25.9. HRMS (DART-TOF): [M + NH₄]⁺ calcd for C₁₉H₂₆NO₂, 302.2120; found, 302.2129.

trans-2-[(p-Methoxybenzyl)oxy)methyl]-3-phenyloxirane (6g)⁶

trans-2-[(p-Methoxybenzyl)oxy)methyl]-3-phenyloxirane (6g)⁶

Compound 1 (196.4 mg, 0.60 mmol) was added to a solution of 5g (45.6 mg, 0.304 mmol) and nBu₄N OTs (25.1 mg, 0.061 mmol) in MeNO₂/1,4-dioxane (4:1, 0.51 mL) at room temperature. The reaction mixture was heated to 50 °C for 7 h and then cooled to room temperature. The reaction mixture was diluted with EtOAc (10 mL), washed with saturated aqueous NaHCO₃ (10
mL) and brine (10 mL), dried (Na$_2$SO$_4$), and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, EtOAc:hexane = 1:19) followed by recycling preparative HPLC to afford a colorless oil (55.1 mg, 67%). $^1$H NMR (CDCl$_3$): $\delta$ 7.38–7.23 (m, 7H), 6.92–6.86 (m, 2H), 4.57, 4.54 (ABq, $J_{AB} = 11.4$ Hz, 2H), 3.83 (dd, $J = 11.5$, 3.2 Hz, 1H), 3.81 (s, 3H), 3.78 (d, $J = 2.3$ Hz, 1H), 3.60 (dd, $J = 11.5$, 5.5 Hz, 1H), 3.24 (ddd, $J = 5.5$, 3.2, 2.3 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.4, 137.0, 130.0, 129.6, 128.6, 128.4, 125.8, 114.0, 73.2, 69.7, 61.3, 56.0, 55.4. LRMS (DART-TOF): 271 ([M + H]$^+$).

**O-p-Methoxybenzylolation of 5g and 5b in one flask.**

Compound 1 (753 mg, 2.30 mmol) was added to a solution of 5b (27.2 µL, 0.384 mmol), 5g (57.6 mg, 0.384 mmol), pyridine (0.6 µL, 7.7 µmol), and $^4$Bu$_4$NOTs (63.5 mg, 0.153 mmol) in MeNO$_2$/1,4-dioxane (4:1, 0.77 mL) at room temperature. The reaction mixture was heated to 60 °C for 3.5 h and then cooled to room temperature. The reaction mixture was diluted with EtOAc (15 mL), washed with saturated aqueous NaHCO$_3$ (15 mL), dried (MgSO$_4$), and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, EtOAc:hexane = 1:19) followed by recycling preparative HPLC to afford 6b (83.8 mg, 89%, colorless oil) and 6g (59.9 mg, 74%, colorless oil).

**O-p-Methoxybenzylolation of 6a on a 3 mmol scale.**

Compound 1 (1.964 g, 6.00 mmol) was added to a solution of 5a (409 µL, 3.00 mmol) and $^4$Bu$_4$NOTs (248 mg, 0.600 mmol) in MeNO$_2$/1,4-dioxane (4:1, 5.0 mL) at room temperature. The mixture was heated to 50 °C for 7 h and then cooled to room temperature. The reaction mixture was diluted with EtOAc (50 mL), washed with saturated aqueous NaHCO$_3$ (50 mL) and brine (50 mL), dried (Na$_2$SO$_4$), and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (twice, EtOAc:hexane = 1:19 followed by toluene) and preparative TLC (EtOAc:hexane = 1:19) to afford a colorless oil (663 mg, 86%).

**Thermal decomposition of 1.**

Compound 1 (9.9 mg, 0.030 mmol) was heated to 120 °C for 30 min without a solvent under a nitrogen atmosphere, and then cooled to room temperature. The crude material (10.0 mg) was analyzed by $^1$H NMR spectroscopy.
3. References


4. $^1$H and $^{13}$C NMR spectra

2-tert-Butyl-4-chloro-6-phenoxy-1,3,5-triazine (2)

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
4-tert-Butyl-6-phenoxy-1,3,5-triazin-2(1H)-one (3)

$^1$H NMR (CDCl$_3$, 600 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
4-tert-Butyl-6-phenoxy-1-propargyl-1,3,5-triazin-2(1H)-one (4)

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
4-tert-Butyl-6-(p-methoxybenzyl)oxy)-1-propargyl-1,3,5-triazin-2-one (1)

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
6-tert-Butyl-1-(p-methoxybenzyloxy)-3-propargyl-1,3,5-triazin-2,4(1H,3H)-dione (7)

$^1$H NMR (CDCl$_3$, 400 MHz)

![NMR Spectrum Image]
$^{13}$C NMR (CDCl$_3$, 100 MHz)

![C NMR spectrum](image-url)
6-tert-Butyl-3-propargyl-1,3,5-triazin-2,4(1H,3H)-dione (10)

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
$p$-Methoxybenzyl 3-phenylpropyl ether (6a)

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
2-Bromoethyl \( p \)-methoxybenzyl ether (6b)

\(^1H\) NMR (CDCl\(_3\), 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
6-(tert-Butyldimethylsilyloxy)hexyl p-methoxybenzyl ether (6c)

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
$p$-Methoxybenzyl (2-Trimethylsilyl)ethyl ether (6d)

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)

TMS

[Chemical structure diagram]
$p$-Methoxybenzyl (1-phenylethyl) ether (6e)

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
2-Methyl-4-phenylbutan-2-yl \( p \)-methoxybenzyl ether (6f)

\(^1\text{H NMR (CDCl}_3\), 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)
trans-2-[(p-Methoxybenzyloxy)methyl]-3-phenyloxirane (6g)

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)