Electronic Supplementary Information for
Zn-Catalyzed hydrohydrzination of propargylamides with BocNHNH₂: a novel entry into 1,2,4-triazine core
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Contents:

Experimental procedures, results of optimization experiments and characterization data for compounds 8a-q, 9a, 10a-q
Copies of ¹H and ¹³C spectra

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General
All reactions were conducted in oven-dried glassware in atmosphere of nitrogen. Melting points were measured with a Buchi B-520 melting point apparatus and were not corrected. Analytical thin-layer chromatography was carried out on Silufol UV-254 silica gel plates using appropriate mixtures of ethyl acetate and hexane. Compounds were visualized with short-wavelength UV light. $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker MSL-300 spectrometers in DMSO-D6-$_d_6$ using TMS as an internal standard. Mass spectra were recorded using Shimadzu LCMS-2020 system with electron impact (EI) ionization. All and reagents and solvents were obtained from commercial sources and used without purification.

Summary of optimization experiments

- **Screening of solvents**

\[
\text{BocNHNNH}_2 \quad \text{Zn(OTf)}_2 \quad \text{reflux} \quad \text{9a}
\]

Table S1. Solvent screening results.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Starting material present</th>
<th>Reaction time (h)</th>
<th>Formation of 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>-</td>
<td>4</td>
<td>+</td>
</tr>
<tr>
<td>benzene</td>
<td>-</td>
<td>8</td>
<td>+</td>
</tr>
<tr>
<td>MeCN</td>
<td>+</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>+</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>THF</td>
<td>+</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>DMF</td>
<td>+</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>MeOH</td>
<td>+</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Xylene (110 °C)</td>
<td>-</td>
<td>4</td>
<td>+</td>
</tr>
</tbody>
</table>

- **Screening of catalysts**

\[
\text{BocNHNH}_2 \quad \text{reflux} \quad \text{9a}
\]
Table S2. Catalyst screening results.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Starting material present</th>
<th>Catalyst mol. %</th>
<th>Reaction time (h)</th>
<th>Formation of 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(OTf)$_2$</td>
<td>-</td>
<td>25</td>
<td>4</td>
<td>+</td>
</tr>
<tr>
<td>Cu(OTf)$_2$</td>
<td>-</td>
<td>25</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>LiOTf</td>
<td>+</td>
<td>25</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Sc(OTf)$_3$</td>
<td>+</td>
<td>25</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Gd(OTf)$_3$</td>
<td>+</td>
<td>25</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Yb(OTf)$_3$</td>
<td>+</td>
<td>25</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>-</td>
<td>100</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>Zn(OTf)$_2$</td>
<td>-</td>
<td>25</td>
<td>4</td>
<td>+</td>
</tr>
<tr>
<td>none</td>
<td>+</td>
<td>n/a</td>
<td>48</td>
<td>-</td>
</tr>
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</table>

- Screening of oxidants

\[ \text{9a} \xrightarrow{\text{oxidant conditions}} \text{10} \]

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Conditions</th>
<th>Reaction time (h)</th>
<th>9 present in the reaction mixture</th>
<th>Formation of 10a</th>
<th>Isolated yield (%)</th>
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</thead>
<tbody>
<tr>
<td>Air</td>
<td>toluene, reflux</td>
<td>8</td>
<td>+</td>
<td>+</td>
<td>11</td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>CH$_2$Cl$_2$, r. t.</td>
<td>12</td>
<td>-</td>
<td>+</td>
<td>32</td>
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<tr>
<td>DDQ</td>
<td>CH$_2$Cl$_2$, r. t.</td>
<td>12</td>
<td>-</td>
<td>+</td>
<td>42</td>
</tr>
<tr>
<td>K$_3$[Fe(CN)$_6$]</td>
<td>Benzene/aq. NaOH, r. t.</td>
<td>12</td>
<td>-</td>
<td>+</td>
<td><strong>77</strong></td>
</tr>
<tr>
<td>KMnO$_4$/SiO$_2$</td>
<td>CH$_2$Cl$_2$, r. t.</td>
<td>0.5</td>
<td>-</td>
<td>+</td>
<td>56</td>
</tr>
<tr>
<td>Pd/C</td>
<td>benzene, reflux</td>
<td>3</td>
<td>+</td>
<td>-</td>
<td>0</td>
</tr>
</tbody>
</table>
General procedure 1 (exemplified by preparation of benzoic acid propargylamide, 8a): 

\[
\text{\begin{center}
\includegraphics[width=0.2\textwidth]{benzoic_acid_propargylamide}
\end{center}}
\]

To a solution of benzoic acid (5.0 g, 40 mmol) in CH\(_2\)Cl\(_2\) (100 mL) N,N-carbonyldiimidazole (CDI, 7.13 g, 44 mmol) was added and the mixture was stirred at r. t. for 30 min. Propargylamide (2.42 g, 44 mmol) was added dropwise and the stirring continued for 18 h. The reaction mixture was successively washed with 5% aqueous citric acid (2 x 50 mL) and 10% aqueous K\(_2\)CO\(_3\) (2 x 50 mL). The organic phase was dried over anhydrous Na\(_2\)SO\(_4\), filtered, concentrated in vacuo and further dried under high vacuum to provide analytically pure 8a (6.23 g, 39 mmol, 98%) as pale yellow crystals; m. p. 103 – 105 °C; \(^1\)H NMR (300 MHz, DMSO-d\(_6\)) \(\delta\) 8.90 (s, 1H, NH), 7.86 (d, \(J = 7.2\) Hz, 2H, Ph 2,6-H), 7.59 – 7.41 (m, 3H, Ph 3,4,5-H), 4.06 (dd, \(J_1 = 5.5\) Hz, \(J_2 = 2.4\) Hz, 2H, CH\(_2\)), 3.10 (s, 1H, CH).

Compounds 8b-q were prepared in an analogous manner and on approximately the same scale and are all either literature-described or commercially available compounds. Hence only \(^1\)H NMR was used as the means to characterize these starting materials.

**Isonicotic acid propargylamide (8b):** 

\[
\text{\begin{center}
\includegraphics[width=0.2\textwidth]{isonicotic_acid_propargylamide}
\end{center}}
\]

Yield 2.7 g (17.0 mmol, 71%); pale-yellow crystals, m. p. 140 – 142 °C; \(^1\)H NMR (300 MHz, DMSO-d\(_6\)) \(\delta\) 9.27 (s, 1H, NH), 8.73 (d, \(J = 5.5\) Hz, 2H, Py 2,6-H), 7.76 (d, \(J = 5.5\) Hz, 2H, Py 3,5-H), 4.08 (dd, \(J_1 = 5.2\) Hz, \(J_2 = 2.1\) Hz, 2H, CH\(_2\)), 3.17 (s, 1H, CH).

**Nicotinic acid propargylamide (8c):** 

\[
\text{\begin{center}
\includegraphics[width=0.2\textwidth]{nicotinic_acid_propargylamide}
\end{center}}
\]

Yield 3.11 g (19.0 mmol, 81%); pale-yellow crystals, m. p. 85 – 87 °C; \(^1\)H NMR (300 MHz, DMSO-d\(_6\)) \(\delta\) 9.15 (s, 1H, NH), 9.00 (d, \(J = 1.7\) Hz, 1H, Py 2-H), 8.71 (dd, \(J_1 = 4.7\) Hz, \(J_2 = 1.3\) Hz, 2H, CH\(_2\)), 3.17 (s, 1H, CH).

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\(^1\) Chachignon, H. *et al.* *J. Org. Chem.* 2015, 80, 5287-5295;


\(^3\) Bai, H. *et al.* *MedChemComm* 2015, 6, 418-424.
Hz, 1H, Py 6-H), 8.25 – 8.15 (m, 1H, Py 4-H), 7.51 (dd, $J_1$ = 7.8 Hz, $J_2$ = 4.8 Hz, 1H, Py 5-H), 4.08 (dd, $J_1$ = 5.4 Hz, $J_2$ = 2.4 Hz, 2H, CH₂), 3.16 (t, $J = 2.3$ Hz, 1H, CH).

3-Fluorobenzoic acid propargylamide (8d):

Yield 1.98 g (11.0 mmol, 79%); pale-yellow crystals, m.p. 120 – 122 °C; $^1$H NMR (300 MHz, DMSO-d₆) $\delta$ 9.02 (t, $J = 5.3$ Hz, 1H, NH), 7.67 (d, $J = 7.7$ Hz, 1H, Ph 6-H), 7.64 – 7.56 (m, 1H, Ph 5-H), 7.49 (td, $J_1$ = 8.0 Hz, $J_2$ = 85.9 Hz, 1H, Ph 4-H), 7.36 (td, $J_1$ = 8.4 Hz, $J_2$ = 2.3 Hz, 1H, Ph 2-H), 4.02 (dd, $J_1$ = 5.5 Hz, $J_2$ = 82.5 Hz, 2H, CH₂), 3.10 (t, $J = 2.4$ Hz, 1H, CH).

4-Bromobenzoic acid propargylamide (8e):

Yield 3.90 g (16.0 mmol, 66%), pale-yellow crystals, m.p. 168 – 170 °C; $^1$H NMR (300 MHz, DMSO-d₆) $\delta$ 9.02 (t, $J = 5.4$ Hz, 1H, NH), 7.80 (d, $J = 8.5$ Hz, 2H Ph 2,6-H), 7.68 (d, $J = 8.5$ Hz, 2H, Ph 3,5-H), 4.05 (dd, $J_1$ = 5.5 Hz, $J_2$ = 2.5 Hz, 2H, CH₂), 3.12 (t, $J = 2.4$ Hz, 1H, CH).

Thiophene-2-carboxylic acid propargylamide (8f):

Yield 5.8 g (35.0 mmol, 90%), pale-yellow crystals, m.p. 109 – 111 °C; $^1$H NMR (300 MHz, CDCl₃) $\delta$: 7.57 (dd, $J_1$ = 3.7 Hz, $J_2$ = 0.8 Hz, 1H, Thieryl 3-H), 7.51 (d, $J = 5.0$ Hz, 1H, Thieryl 5-H), 7.09 (dd, $J_1$ = 4.9 Hz, $J_2$ = 3.8 Hz, 1H, Thieryl 4-H), 6.30 (s, 1H, NH), 4.25 (dd, $J_1$ = 5.1 Hz, $J_2$ = 2.5 Hz, 2H, CH₂), 2.29 (t, $J = 2.5$ Hz, 1H, CH).

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Thiophene-3-carboxylic acid propargylamide (8g):

Yield 6.34 g (38.0 mmol, 98%), pale-yellow crystals, m.p. 105 – 107 °C; ^1H NMR (300 MHz, CDCl$_3$) δ 7.92 (s, 1H), 7.42 (d, $J = 5.0$ Hz, 1H), 7.36 (dd, $J_1 = 4.9$ Hz, $J_2 = 3.0$ Hz, 1H), 6.30 (s, 1H), 4.24 (s, 2H), 2.29 (t, $J = 2.4$ Hz, 1H).

Cyclohexanecarboxylic acid propargylamide (8h):

Yield 3.54 g (21.0, 91%), pale-yellow crystals, m.p. 102 – 104 °C; ^1H NMR (300 MHz, CDCl$_3$) δ 5.76 (s, 1H, NH), 4.05 (dd, $J_1 = 5.1$ Hz, $J_2 = 2.6$ Hz, 2H, CH$_2$), 2.23 (t, $J = 2.6$ Hz, 1H, CH), 2.11 (tt, $J = 11.7$, 3.5 Hz, 1H, Cyclohexyl CH), 1.93 – 1.74 (m, 4H, Cyclohexyl), 1.72 – 1.62 (m, 1H, Cyclohexyl), 1.53 – 1.36 (m, 2H, Cyclohexyl), 1.35 – 1.16 (m, 3H, Cyclohexyl).

3-Methylbenzoic acid propargylamide (8i):

Yield 5.3 g (31.0 mmol, 79%), pale-yellow crystals, m.p. 50 – 52 °C; ^1H NMR (300 MHz, CDCl$_3$) δ 7.43 - 7.20 (3m, 4H, Ph 4 CH), 5.96 (s, 1H, NH), 4.25 (dd, $J_1 = 5.2$ Hz, $J_2 = 2.5$ Hz, 2H, CH$_2$), 2.47 (s, 3H, CH$_3$), 2.29 (t, $J = 2.5$ Hz, 1H, CH).

Adamantane-1-carboxylic acid propargylamide (8j):

7 CAS 124750-66-9; UORSY Building Block Library Catalog # BBV-32711101.


Yield 3.5 g (16.0 mmol, 95%), pale-yellow crystals, m.p. 115 – 117 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.76 (s, 1H, NH), 4.04 (dd, $J_1$ = 5.0 Hz, $J_2$ = 2.6 Hz, 2H, CH$_2$), 2.23 (t, $J$ = 2.6 Hz, 1H, CH), 2.12 – 2.00 (m, 3H, Ad 3,5,7-CH), 1.92 – 1.84 (m, 6H, Ad 2,8,9-CH$_2$), 1.81 – 1.65 (m, 6H, Ad 4,6,10-CH$_2$).

**Cyclopropanecarboxylic acid propargylamide (8k)$^{11}$:**

Yield 5.04 g (41.0 mmol, 70%), pale-yellow crystals, m.p. 64 – 66 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.21 (s, 1H, NH), 4.07 (s, 2H, CH$_2$), 2.24 (t, $J$ = 2.4 Hz, 1H, CH), 1.52 – 1.32 (m, 1H, Cyclopropyl CH), 1.10 – 0.91 (m, 2H, Cyclopropyl CH$_2$), 0.90 – 0.67 (m, 2H, Cyclopropyl CH$_2$).

**2-Methoxybenzoic acid propargylamide (8l)$^{12}$:**

Yield 4.95 g (24.0 mmol, 69%), white crystals, m.p. 40 – 42 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.22 (dd, $J_1$ = 7.8 Hz, $J_2$ = 1.8 Hz, 1H, Ph 6-H), 8.10 (s, 1H, NH), 7.52 – 7.40 (m, 1H, Ph 4-H), 7.08 (t, $J$ = 7.5 Hz, 1H, Ph 5-H), 6.98 (d, $J$ = 8.3 Hz, 1H, Ph 3-H), 4.27 (dd, $J_1$ = 5.1 Hz, $J_2$ = 2.5 Hz, 2H, CH$_2$), 3.98 (s, 3H, OCH$_3$), 2.26 (t, $J$ = 2.5 Hz, 1H, CH).

**Phenylacetic acid propargylamide (8m)$^{13}$:**

Yield 3.4 g (20.0 mmol, 91%), pale-yellow crystals, m.p. 80 – 82 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.42 – 7.24 (m, 5H, Ph), 5.74 (s, 1H, NH), 4.02 (dd, $J_1$ = 5.3 Hz, $J_2$ = 2.5 Hz, 2H, CH$_2$), 3.61 (s, 2H, Ph-CH$_2$), 2.20 (t, $J$ = 2.5 Hz, 1H, CH).

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Cyclopentanecarboxylic acid propargylamide (8n): 

Yield 2.98 g (20.0 mmol, 76%), pale-yellow crystals, m.p. 100 – 102 °C. \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 5.65 (s, 1H, NH), 4.07 (dd, \(J_1 = 5.0\) Hz, \(J_2 = 2.5\) Hz, 2H, CH\(_2\)), 2.63 – 2.45 (m, 1H, Cyclopentyl CH), 2.24 (t, \(J = 2.5\) Hz, 1H, CH), 1.95 – 1.47 (2m, 8H, Cyclopentyl 4CH\(_2\)).

Lauric acid propargylamide (8o): 

Yield 1.3 g (5.0 mmol, 37%), pale-yellow crystals, m.p. 84 – 86 °C; \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.21 (t, \(J = 5.1\) Hz, 1H, NH), 3.82 (dd, \(J_1 = 5.5\) Hz, \(J_2 = 2.5\) Hz, 2H, CH\(_2\)), 3.07 (t, \(J = 2.5\) Hz, 1H, CH), 2.05 (t, \(J = 7.4\) Hz, 2H, Undecyl 1-CH\(_2\)), 1.54 – 1.40 (m, 2H, Undecyl 2-CH\(_2\)), 1.23 (s, 16H, Undecyl 3,4,5,6,7,8,9,10-CH\(_2\)), 0.85 (t, \(J = 6.6\) Hz, 3H, Undecyl CH\(_3\)).

(3-Fluoropheny)acetic acid propargylamide (8p): 

Yield 3.54 g (19.0 mmol, 95%), pale-yellow crystals, m.p. 66 – 68 °C; \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.39 – 7.28 (m, 1H, Ph 5-H), 7.09 – 6.95 (m, 3H, Ph 2,4,6-H), 5.93 (d, \(J = 61.0\) Hz, 1H, NH), 4.02 (dd, \(J_1 = 5.2\), \(J_2 = 2.5\) Hz, 2H, CH\(_2\)), 3.57 (s, 2H, Ph-CH\(_2\)), 2.22 (t, \(J = 2.5\) Hz, 1H, CH).

Cyclopent-3-enecarboxylic acid propargylamide (8q): 

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\(^{16}\) CAS 1250077-77-0. UORSY Building Blocks Catalog Number BBV-32710884.

\(^{17}\) CAS 1342644-38-5. UORSY Building Blocks Catalog Number BBV-39215052.
Yield 3.41 g (19.0 mmol, 72%), off-white crystals, m.p. 105 – 107 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 5.70 (s, 3H, NH, Cyclopentenyl 1,2-CH), 4.08 (dd, \(J_1 = 5.2\) Hz, \(J_2 = 2.5\) Hz, 2H, CH\(_2\)), 3.07 – 2.89 (m, 1H, Cyclopentenyl 4-CH), 2.65 (d, \(J = 8.0\) Hz, 4H, Cyclopentenyl 2CH\(_2\)), 2.25 (t, \(J = 2.5\) Hz, 1H, CH).

6-Methyl-3-phenyl-2,5-dihydro-1,2,4-triazine (9a).

![Chemical structure](image)

To a solution of 8a (1 g, 6.29 mmol) in toluene (40 mL) BocNHNH\(_2\) (0.83 g, 6.29 mmol) and Zn(OTf)\(_2\) (0.57 g, 1.57 mmol) were added. The resulting mixture was heated at reflux for 4 h and then cooled down to r. t. It was poured into 10% aqueous K\(_2\)CO\(_3\) (100 mL) and extracted with ethyl acetate (3 x 50 mL). The combined organic extracts were dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel using 0-3% gradient of methanol in chloroform to obtain 0.421 g (2.31 mmol, 37%) of the title compound as pale-yellow crystals, m.p. 56-58 °C (decomp.); \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 8.53 – 8.48 (m, 1H, NH), 7.74 – 7.68 (m, 2H, Ph 2,6-H), 7.48 – 7.37 (m, 3H, Ph 3,4,5-H), 3.95 (s, 2H, CH\(_2\)), 2.03 (s, 3H, CH\(_3\)); \(^13\)C NMR (75 MHz, CDCl\(_3\)) δ 154.88 (Dihydrotriazine 3-C), 145.86 (Dihydrotriazine 6-C), 132.72 (Ph 1-C), 130.86 (Ph 4-C), 128.76 (Ph 3,5-C), 126.38 (Ph 2,6-C), 47.58 (Dihydrotriazine CH\(_2\)), 20.39 (CH\(_3\)). The product is markedly unstable to afford further characterization.

**General procedure to obtain compounds 10a-r:** The respective propargylamide 8 (1.26 mmol) in dry toluene (15 mL) was treated with BocNHNH\(_2\) (6, 1.26 mmol) and Zn(OTf)\(_2\) (0.32 mmol). The resulting mixture was heated under reflux in the atmosphere of argon for 4 h and then cooled down to r. t. Aqueous solution (10 mL) containing K\(_3\)[Fe(CN)\(_6\)] (0.62 g, 1.89 mmol) and NaOH (0.13 g, 3.15 mmol) was added. The resulting biphasic mixture was vigorously stirred overnight. The organic phase was separated, dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel using and appropriate gradient of ethyl acetate in hexane as eluent to provide analytically pure 1,2,4-triazines 10 in yields indicated.

6-Methyl-3-phenyl-1,2,4-triazine (10a)

![Chemical structure](image)
Yield 0.173 g (1.01 mmol, 80%). Pale-yellow crystals, mp = 65 – 67 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.54 (s, 1H, Tr), 8.53 – 8.47 (m, 2H, Ph 2,6-H), 7.59 – 7.49 (m, 3H, Ph 3,4,5-H), 2.76 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 162.13 (Tr 3-C), 156.30 (Tr 6-C), 149.28 (Tr 5-C), 134.84 (Ph 1-C), 131.40 (Ph 4-C), 128.85 (Ph 3,5-C), 127.98 (Ph 2,6-C), 19.41 (CH₃); HRMS (ESI) m/z calcd for C₁₀H₁₀N₃ [M+H⁺] 172.0869, found 172.0865.

6-Methyl-3-pyridin-4-y1-1,2,4-triazine (10b)

Yield 0.071 g (0.41 mmol, 33%), pale yellow crystals m.p. 112 – 114 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.84 (d, J = 5.56 Hz, 2H, Py 2,6-H), 8.63 (s, 1H, Tr), 8.40 (dd, J = 4.61, 1.54 Hz, 2H, Py 3,5-H), 2.82 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 160.38 (Tr 3-C), 157.94 (Tr 6-C), 150.24 (Tr 5-C), 149.50 (Py 2,5-C), 142.68 (Py 4-C), 121.78 (Py 3,5-C), 19.59 (CH₃); HRMS (ESI) m/z calcd for C₉H₉N₄ [M+H⁺] 173.0821, found 173.0814.

6-Methyl-3-pyridin-3-y1-1,2,4-triazine (10c)

Yield 0.080 g (0.47 mmol, 37%), pale-yellow crystals, m.p. 109 – 111 °C; ¹H NMR (300 MHz, CDCl₃): δ 9.73 (s, 1H, Py 2-H), 8.88 (d, J = 8.01 Hz, 1H, Py 6-H), 8.81 (d, J = 3.94 Hz, 1H, Py4-H), 8.61 (s, 1H, Tr), 7.62 – 7.50 (m, 1H, Py 5-H), 2.81 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 160.34 (Tr 3-C), 157.31 (Tr 6-C), 151.08 (Py 2-C), 149.41 (Py 6-C), 148.64 (Tr 5-C), 136.10 (Py 4-C), 131.17 (Py 3-C), 124.04 (Py 5-C), 19.50 (CH₃); HRMS (ESI) m/z calcd for C₉H₉N₄ [M+H⁺] 173.0821, found 173.0824

3-(3-Fluorophenyl)-6-methyl-1,2,4-triazine (10d)

Yield 0.09 g (0.48 mmol, 42%), pale-yellow crystals, m.p. 57 – 59 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.56 (s, 1H, Tr), 8.32 (dt, J₁ = 7.87 Hz, J₂ = 1.19 Hz, 1H, Ph 6-H), 8.27 – 8.16 (m, 1H, Ph 2-H), 7.51 (td, J₁ = 8.05 Hz, J₂ =5.79 Hz, 1H, Ph 5-H), 7.27 – 7.20 (m, 1H, Ph 4-H), 2.78 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 163.22 (d, J = 245.75 Hz, Ph 3-C), 161.15 (d, J = 3.21
Hz, Tr 3-C), 156.75 (Tr 6-C), 149.30 (Tr 5-C), 137.14 (d, J = 8.09 Hz, Ph 1-C), 130.40 (d, J = 7.99 Hz, Ph 5-C), 123.62 (d, J = 2.99 Hz, Ph6-C), 118.31 (d, J = 21.36 Hz, Ph 4-C), 114.86 (d, J = 23.67 Hz, Ph 2-C), 19.41 (CH₃); HRMS (ESI) m/z calcd for C₁₀H₆FN₃ [M+H⁺] 190.0775, found 190.0774.

3-(4-Bromophenyl)-6-methyl-1,2,4-triazine (10e)

![Image of 3-(4-Bromophenyl)-6-methyl-1,2,4-triazine](image)

Yield 0.123 g (0.49 mmol, 58%), pale-yellow crystals, m.p. 149 – 151 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.54 (s, 1H, Tr), 8.39 (d, J = 8.59 Hz, 2H, Ph 2,6-H), 7.66 (d, J = 8.56 Hz, 2H, Ph 3,5-H), 2.76 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ161.41 (Tr 3-C), 156.54 (Tr 6-C), 149.28 (Tr 5-C), 133.78 (Ph 1-C), 132.09 (Ph 2,6-C), 129.50 (Ph 3,5-C), 126.30 (Ph 6-C), 19.43 (CH₃); HRMS (ESI) m/z calcd for C₁₀H₆BrN₃ [M+H⁺] 249.9974, found 249.9970.

6-Methyl-3-thiophen-2-yl-1,2,4-triazine (10f)

![Image of 6-Methyl-3-thiophen-2-yl-1,2,4-triazine](image)

Yield 0.051 g (0.28 mmol, 23%), pale-yellow crystals, m.p. 112 – 114 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.46 (s, 1H, tr), 8.15 (dd, J₁ = 3.71 Hz, J₂ = 1.07 Hz, 1H, Thiethyl 3-H), 7.57 (dd, J₁ = 4.99 Hz, J₂ = 1.07 Hz, 1H, Thiethyl 5-H), 7.21 (dd, J₁ = 4.93 Hz, J₂ = 3.79 Hz, 1H, Thiethyl 4-H), 2.74 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 159.61 (Tr 6-C), 155.62 (Tr 3-C), 149.31 (Tr 5-C), 139.47 (Thiethyl 2-C), 130.80 (Thiethyl 3-C), 129.90 (Thiethyl 5-C), 128.50 (Thiethyl 4-C), 19.35 (CH₃); HRMS (ESI) m/z calcd for C₈H₅NS [M+H⁺] 178.0433, found 178.0427.

6-Methyl-3-thiophen-3-yl-1,2,4-triazine (10g)

![Image of 6-Methyl-3-thiophen-3-yl-1,2,4-triazine](image)

Yield 0.131 g (0.74 mmol, 61%), pale-yellow crystals, m.p. 83 – 85 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.50 (s, 1H, Tr), 8.42 (dd, J₁ = 3.07 Hz, J₂ = 1.19 Hz, 1H, Thiethyl 2-H), 8.00 (dd, J₁ = 5.09 Hz, J₂ = 1.19 Hz, 1H, Thiethyl 5-H), 7.45 (dd, J₁ = 5.09 Hz, J₂ = 3.08 Hz, 1H, Thiethyl 4-H), 2.74 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ159.60 (Tr 3-C), 155.74 (Tr 6-C), 149.34 (Tr 5-
C), 138.30 (Thienyl 2-C), 128.59 (Thienyl 5-C), 127.00 (Thienyl 4-C), 126.64 (Thienyl 3-C), 19.43 (CH3); HRMS (ESI) m/z calcd for C8H8N3S [M+H+] 178.0433, found 178.0427.

3-Cyclohexyl-6-methyl-1,2,4-triazine (10h)

Yield 0.133 g (0.73 mmol, 61%), pale-yellow crystals, m.p. 63 – 65 °C; 1H NMR (300 MHz, CDCl3): δ 8.43 (s, 1H, Tr), 3.09 (tt, J1 = 11.76 Hz, J2 = 3.46 Hz, 1H, Cyclohexyl CH), 2.69 (s, 3H, CH3), 2.11 - 1.97 (m, 2H, Cyclohexyl CH2), 1.95 – 1.83 (m, 2H, Cyclohexyl CH2), 1.57 - 1.23 (m, 2H, Cyclohexyl CH2), 1.56 – 1.24 (m, 4H, Cyclohexyl CH2); 13C NMR (75 MHz, CDCl3): δ 171.01 (Tr 3-C), 155.98 (Tr 6-C), 149.24 (Tr 5-C), 45.11 (Cyclohexyl 1-C), 31.61 (Cyclohexyl 2,6-C), 26.10 (Cyclohexyl 3,5-C), 25.85 (Cyclohexyl 4-C), 19.25 (CH3); HRMS (ESI) m/z calcd for C10H16N3 [M+H+] 178.1338, found 178.1333.

6-Methyl-3-(2-methylphenyl)-1,2,4-triazine (10i)

Yield 0.104 g (0.55 mmol, 47%), yellow oil; 1H NMR (300 MHz, CDCl3): δ 8.58 (s, 1H, Tr), 7.95 – 7.85 (m, 1H, Ph 6-H), 7.45 – 7.31 (m, 3H, Ph 3,4,5-H), 2.77 (s, 3H, Tr-CH3), 2.59 (s, 3H, Ph-CH3); 13C NMR (75 MHz, CDCl3): δ 165.03 (Tr 3-C), 155.60 (Tr 6-C), 148.81 (Tr 5-C), 137.84 (Ph 2-C), 135.01 (Ph 6-C), 131.51 (Ph 1-C), 130.66 (Ph 3-C), 130.17 (Ph 4-C), 126.10 (Ph 5-C), 21.24 (Ph-CH3), 19.37 (Tr-CH3); HRMS (ESI) m/z calcd for C11H12N3 [M+H+] 186.1025, found 186.1022.

3-Adamantyl-6-methyl-1,2,4-triazine (10j)

Yield 0.131 g (0.57 mmol, 62%), pale-yellow crystals, m.p. 92 – 94 °C; 1H NMR (300 MHz, CDCl3): δ 8.43 (s, 1H, Tr), 2.68 (s, 3H, CH3), 2.13 (s, 9H, Ad 2,8,9-CH, 3,5,7-CH2), 1.81 (s, 6H, Ad 4,6,10-CH2); 13C NMR (75 MHz, CDCl3): δ172.82 (Tr 3-C), 155.58 (Tr 6-C), 149.01 (Tr 5-
C), 40.89 (Ad 2,8,9-C), 39.91 (Ad 1-C), 36.61 (Ad 4,6,10-C), 28.44 (Ad 3,5,7-C), 19.26 (CH3); HRMS (ESI) m/z calcd for C14H20N3 [M+H+] 230.1651, found 230.1647.

3-Cyclopropyl-6-methyl-1,2,4-triazine (10k)

Yield 0.072 g (0.52 mmol, 32%), yellow oil; 1H NMR (300 MHz, CDCl3): δ 8.30 (s, 1H, Tr), 2.64 (s, 3H, CH3), 2.50 – 2.38 (m, 1H, Cyclopropyl CH), 1.19 – 1.12 (m, 4H, Cyclopropyl 2CH2); 13CNMR (75 MHz, CDCl3): δ 168.95 (Tr 3-C), 155.39 (Tr 6-C), 149.15 (Tr 5-C), 19.12 (CH3), 16.00 (Cyclopropyl 1-C), 10.73 (Cyclopropyl 2,3-C); HRMS (ESI) m/z calcd for C7H10N3 [M+H+] 136.0869, found 136.0864.

3-(2-Methoxyphenyl)-6-methyl-1,2,4-triazine (10l)

Yield 0.073 g (0.35 mmol, 35%), amorphous solid; 1H NMR (300 MHz, CDCl3) δ 8.59 (s, 1H, Tr), 7.79 (dd, J1 = 7.60 Hz, J2 = 1.78 Hz, 1H, Ph 6-H), 7.53 – 7.45 (m, 1H, Ph 3-H), 7.15 – 7.05 (m, 2H, Ph 4,5-H), 3.88 (s, 3H, OCH3), 2.77 (s, 3H, CH3); 13C NMR (75 MHz, CDCl3) δ 163.62 (Ph 2-C), 157.91 (Tr 3-C), 155.77 (Tr 6-C), 148.76 (Tr 5-C), 131.83 (Ph 6-C), 131.81 (Ph 4-C), 125.35 (Ph 1-C), 120.82 (Ph 5-C), 111.96 (Ph 3-C), 56.03 (OCH3), 19.44 (CH3); HRMS (ESI) m/z calcd for C11H12N3O [M+H+] 202.0974, found 202.0982.

3-Benzyl-6-methyl-1,2,4-triazine (10m)

Yield 0.083 g (0.43 mmol, 37%), yellow oil; 1H NMR (300 MHz, CDCl3): δ 8.40 (s, 1H, Tr), 7.42 – 7.18 (m, 5H, Ph), 4.42 (s, 2H, CH2), 4.42 (s, 2H), 2.66 (s, 3H, CH3); 13C NMR (75 MHz, CDCl3): δ 166.83 (Tr 3-C), 156.26 (Tr 6-C), 149.66 (Tr 5-C), 137.36 (Ph 1-C), 129.19 (Ph 3,5-C), 128.65 (Ph 2,6-C), 126.88 (Ph 4-C), 43.25 (CH2), 19.24 (CH3); HRMS (ESI) m/z calcd for C11H12N3 [M+H+] 186.1025, found 186.1032.
3-Cyclopentyl-6-methyl-1,2,4-triazine (10n)

Yield 0.092 g (0.55 mmol, 42%), yellow oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 8.43\) (s, 1H, Tr), 3.63 – 3.49 (m, 1H, Cyclopentyl CH), 2.69 (s, 3H, CH\(_3\)), 2.23 – 1.69 (3m, 8H, Cyclopentyl 4CH\(_2\)); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 171.20\) (Tr 3-C), 155.88 (Tr 6-C), 149.38 (Tr 5-C), 46.33 (Cyclopentyl 1-C), 32.92 (Cyclopentyl 2,5-C), 26.09 (Cyclopentyl 3,4-C), 19.26 (CH\(_3\)); HRMS (ESI) \(m/z\) calcd for C\(_9\)H\(_{14}\)N\(_3\) [M+H\(^+\)] 164.1182, found 164.1184.

6-Methyl-3-undecyl-1,2,4-triazine (10o)

Yield 0.062 g (0.35 mmol, 29%), pale-yellow crystals, m.p, 59 – 61 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 8.43\) (s, 1H, Tr), 3.15 – 3.02 (m, 2H, Undecyl 1-CH\(_2\)), 2.69 (s, 3H, Tr-CH\(_3\)), 1.91 – 1.78 (m, 2H, Undecyl 2-CH\(_2\)), 1.56 – 1.17 (m, 16H, Undecyl 3,4,5,6,7,8,9,10-CH\(_2\)), 0.91 – 0.85 (m, 3H, Undecyl CH\(_3\)); \(^13\)C NMR (75 MHz, DMSO) \(\delta 168.24\) (Tr 3-C), 155.88 (Tr 6-C), 149.26 (Tr 5-C), 36.83 (Undecyl 1-C), 31.91 (Undecyl 9-C), 29.61 (Undecyl 7-C), 29.50 (Undecyl 3-C), 29.38 (Undecyl 4-C), 29.34 (Undecyl 5,7-C), 29.26 (Undecyl 6-C), 28.52 (Undecyl 6-C), 22.69 (Undecyl 10-C), 19.25 (Tr CH\(_3\)), 14.12 (Undecyl CH\(_3\)); HRMS (ESI) \(m/z\) calcd for C\(_{13}\)H\(_{28}\)N\(_3\) [M+H\(^+\)] 250.2277, found 250.2289.

3-(3-Fluorobenzyl)-6-methyl-1,2,4-triazine (10p)

Yield 0.092 g (0.44 mmol, 42%), yellow oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 8.40\) (s, 1H, Tr), 7.28 – 7.19 (m, 1H, Ph 6-H), 7.12 (d, \(J = 7.68\) Hz, 1H, Ph 2-H), 7.09 – 7.03 (m, 1H, Ph 5-H), 6.94 – 6.85 (m, 1H, Ph 4-H), 4.38 (s, 2H, CH\(_2\)), 2.65 (s, 3H, CH\(_3\)); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 166.29\) (Tr 3-C), 162.83 (d, \(J = 24.607\) Hz, Ph 3-C), 156.48 (Tr 6-C), 149.68 (Tr 5-C), 139.64 (d, \(J = 7.58\) Hz, Ph 1-C), 130.07 (d, \(J = 8.32\) Hz, Ph 5-C), 124.87 (d, \(J = 2.86\) Hz, Ph 6-C), 116.14 (d, \(J = 21.61\) Hz, Ph 2-C), 113.83 (d, \(J = 21\) Hz, Ph 4-C), 42.87 (d, \(J = 1.53\) Hz, CH\(_2\)), 19.25 (CH\(_3\)); HRMS (ESI) \(m/z\) calcd for C\(_{11}\)H\(_{11}\)FN\(_3\) [M+H\(^+\)] 204.0931, found 204.0942.
3-Cyclopent-3-enyl-6-methyl-1,2,4-triazine (10q)

Yield 0.091 g (0.56 mmol, 42%), yellow oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.42 (s, 1H, Tr), 5.74 (s, 2H, Cyclopentenyl 1,2-CH), 4.10 – 3.88 (m, 1H, Cyclopentenyl 4-CH), 2.97 – 2.69 (m, 4H, Cyclopentenyl 2CH$_2$), 2.66 (s, 3H, CH$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.97 (Tr 3-C), 156.03 (Tr 6-C), 149.53 (Tr 5-C), 129.29 (Cyclopentenyl 1,2-C), 43.56 (Cyclopentenyl 4-C), 39.05 (Cyclopentenyl 3,5-C), 19.24 (CH$_3$); HRMS (ESI) $m/z$ calcd for C$_9$H$_{12}$N$_3$ [M+H$^+$] 162.1025, found 162.1032.
Compound 8a:

Compound 8b:
Compound 8c:

Compound 8d:
Compound 8e:

![Chemical structure of Compound 8e](image)

Compound 8f:

![Chemical structure of Compound 8f](image)
Compound 8g:

![Compound 8g NMR spectrum](image)

CDCl3 7926

Compound 8h:

![Compound 8h NMR spectrum](image)

CDCl3 8747
Compound 8i:

Compound 8j:
Compound **8k:**

![NMR spectrum of compound 8k](image)

Compound **8l:**

![NMR spectrum of compound 8l](image)
Compound 8m:

Compound 8n:
Compound 8o:

Compound 8p:
Compound **8q**: 

[Chemical structure image]  

Chemical shift values: 2.94, 2.98, 3.01, 4.08, 1.04.
Compound 9a:
Compound 10a:
Compound 10b:
Compound 10c:
Compound 10d:
Compound 10e:
Compound 10g:

CDC13 8339

CDC13 8356
Compound 10h:
Compound 10i:

[Chemical structure image]

CDCl$_3$ 8514

[Graph image]

Compound 8554:

[Chemical structure image]

CDCl$_3$ 8554

[Graph image]
Compound **10k**: 

![NMR spectrum of Compound 10k in CDCl3 8544](image1)

![NMR spectrum of Compound 10k in CDCl3 8557](image2)
Compound 10l:
Compound 10m:
Compound 10n:
Compound 10o:
Compounds 10p:
Compound 10q: