A General Approach to Selective Functionalization of 1,2,4-Triazines Using Organometallics in Palladium-Catalyzed Cross-Coupling and Addition Reactions

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Abstract: A selective way to obtain disubstituted 1,2,4-triazines in good yields by combining addition reactions and palladium-catalyzed cross-coupling reactions of organometallics with 3-methylsulfanyl-1,2,4-triazine is described.

Key words: 1,2,4-triazines, palladium, cross-coupling, selective addition, organometallics, catalysis

1,2,4-Triazine derivatives, especially aryl 1,2,4-triazines, are well known in therapeutic chemistry as antifungal,1 or antitumoral,1 in agronomy as insecticides2 and in selective complexation as metallic cations ligands.3 Many of them were prepared by cyclization of the triazine ring. 4+2 Atom combination of 1,2-dicarbonyl compounds with amidrazones is the most frequently described synthesis of aryl or hetaryl substituted 1,2,4-triazines.4 Unfortunately, both cyano and diketone precursors are sometimes difficult to synthesize. Furthermore, diketones have to be symmetrical to avoid mixture of isomeric triazines and to obtain better yields.5

Another way to prepare those substituted triazines is the direct functionalization of a triazine ring by carbon-carbon bond formation.6 Indeed, Yamanaka et al.7 have described the addition of phenylmagnesium bromide on 1,2,4-triazines to form 5-phenyl-, 5,6-diphenyl- and 3,5,6-triphenyl-1,2,4-triazines, subsequently. This study also showed that the relative reactivity of positions 3, 5 and 6 of the 1,2,4-triazine ring with Grignard reagents is controlled. Indeed, the most active position is position 5 and the least active is position 3 (Scheme 1).

At this stage, we thought it would be interesting to be able to supervise the functionalization order on the 1,2,4-triazine ring. Therefore, the reactivity of readily available 3-methylsulfanyl-1,2,4-triazine (1)8 was investigated with different organometallics: organolithium reagents, Grignard reagents, boronic acids, organostannanes and organozinc reagents. This paper describes a suitable choice of organometallics for the selective introduction of a wide range of substituents at C-3, C-5 and C-6 positions. The best combination between addition and palladium-catalyzed cross-coupling to obtain 3,5-diaryl-1,2,4-triazines is also reported. We first tried the addition reactions of organolithium reagents on 3-methylsulfanyl-1,2,4-triazine (1). The results are summarized in Table 1.

As expected, the addition of 1.25 equivalents of aryllithium to 1 led to 5-substituted compounds and a further oxidation step gave 5-aryl-1,2,4-triazines 2–4 in good yields (Table 1). Although the oxidation into furyl derivative 3 and pyridinyl derivative 4 with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) gave byproducts, the use of milder oxidant MnO2 was successful.

According to the literature, Grignard reagents react with heteroaromatic thiouthers in palladium or nickel-catalyzed cross-coupling reactions.9,10 We attempted palladium catalyzed cross-coupling reaction conditions on 3-methylsulfanyl-1,2,4-triazine (1) (Table 2, entry 1). No coupled product 6 was observed and only the addition compound, 2,5-dihydro-5-(p-methoxyphenyl)-3-methylsulfanyl-1,2,4-triazine (5) was isolated. A further oxidation step with 1.25 equivalents of DDQ gave quantitatively the 5-(p-methoxyphenyl)-3-methylsulfanyl-1,2,4-triazine (7). A control experiment showed that the palladium catalyst is useless and triazine 5 was isolated in 85% yield without any transition metal (Table 2, entry 2).

To summarize, regarding Grignard reagents, the C-5 position of the 1,2,4-triazine ring is more reactive towards addition reaction than the C-3 position towards transition metal catalyzed cross-coupling reaction.

We were then curious to evaluate the behavior of 3-methylsulfanyl-5-substituted-1,2,4-triazine towards palladium- or nickel-catalyzed cross-coupling reactions. When 5-(2-furyl)-3-methylsulfanyl-1,2,4-triazine (3) was treat-
ed with 1.2 equivalents of \( p \)-methoxyphenylmagnesium bromide in THF with 10 mol% \( \text{PdCl}_2(\text{dpf}) \) for 24 hours, we isolated a mixture of C-6 addition product \( 8 \) (7%) and C-3 coupled product \( 9 \) (20%) (Table 3, entry 1). With \( \text{NiCl}_2(\text{dppe}) \), a few traces of \( 8 \) were observed (Table 3, entry 2). Although, few palladium catalysts were tested [\( \text{Pd}([\text{PPh}_3])_2, \text{PdCl}_2(\text{PPh}_3)_2, \text{Pd}_{\text{db}a}/\text{AsPh}_3 \)], none was selective towards cross-coupling reaction.

However, when 5-(2-furyl)-3-methylsulfanyl-1,2,4-triazine \( 3 \) was treated without catalyst with 2.4 equivalents of \( p \)-methoxyphenylmagnesium bromide in THF for 24 hours, only the addition product \( 8 \) was isolated in 45% yields (Table 3, entry 3). Treatment of non aromatic compound \( 8 \) with 1.25 equivalents of \( \text{DDQ} \) led quantitatively to 5-(2-furanyl)-6-(\( p \)-methoxyphenyl)-3-methylsulfanyl-1,2,4-triazine \( 10 \).

Considering the lack of selectivity of the transition metal catalyzed reaction, we thought it would be interesting to use non-nucleophilic organometallics.

Recently, Liebeskind and Srogl indicated\(^{11,12} \) that heteroaromatic thioether-boronic acid cross-coupling mediated by copper (I) carboxylates would be feasible. Indeed, this method has been successfully reported for 3-methylsulfanyl-1,2,4-triazines \( 1 \).\(^{13} \) Various 3-aryl-1,2,4-triazines were obtained in good yields using palladium-catalyzed cross-coupling reactions between boronic acids and 3-methylsulfanyl-1,2,4-triazine \( 1 \) in the presence of copper (I) methylsalicylate (CuMeSal) as cofactor (Scheme 2). The reactions were typically carried out at 55–60 °C in THF using 5–10 mol% of \( \text{Pd}([\text{PPh}_3])_2, 2.2 \) equivalents of boronic acid and 2.2 equivalents of CuMeSal. No addition product was observed.

Considering the advantages of using trialkylorganotin species [they are readily available (especially alkenyl and heteroaromatic stannanes)],\(^{14} \) we investigated this strategy on heteroaromatic stannanes.\(^{15} \) Many vinyl and arylstannanes were coupled in excellent yields using 2.2

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**Table 1** Addition Reactions of Aryllithium Reagents with 3-Methylsulfanyl-1,2,4-triazine \( 1 \)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time (h)</th>
<th>Oxidation conditions</th>
<th>Products</th>
<th>Yield (%) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>1.25 equiv DDQ, toluene, r.t., 24 h</td>
<td><img src="image1" alt="Reaction" /></td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>2(^b)</td>
<td>10 equiv MnO(_2), CH(_2)Cl(_2), r.t., 24 h</td>
<td><img src="image2" alt="Reaction" /></td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>10 equiv MnO(_2), CH(_2)Cl(_2), r.t., 24 h</td>
<td><img src="image3" alt="Reaction" /></td>
<td>70</td>
</tr>
</tbody>
</table>

\(^{a}\) Yields after column chromatography.
\(^{b}\) Reaction was performed in Et\(_2\)O instead of THF.

**Table 2** Attempt to Palladium and Nickel-Catalyzed Cross-Coupling of \( p \)-Methoxyphenylmagnesium Bromide with \( 1 \)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>5 (%)(^a)</th>
<th>6 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{PdCl}_2(\text{dpf}) )</td>
<td>73</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>–</td>
<td>85</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^{a}\) Isolated after column chromatography.
equivalents of organostannanes, 2.2 equivalents of Cu-
Br·Me2S with 5–10 mol% of Pd(PPh3)4, in refluxing THF
or DME (Scheme 3). No addition product was observed.

We were then interested in organozinc compounds. They
are versatile reagents for metal catalyzed cross-coupling
reactions and are compatible with many functional
groups.16 Furthermore, with the growing interest for the
Negishi reaction (among others for the synthesis of bi-
hetaryl compounds),17 many organozinc derivatives are
commercially available or their synthesis is described in
the literature.18

On the basis of recent results of Casalnuovo and
Angiolelli19 on palladium-catalyzed cross-coupling reac-
tions of benzylzinc reagents with methylthio azaheterocy-
cles, 3-methylsulfanyl-1,2,4-triazine (1) was treated with
two equivalents of benzylzinc bromide in THF using 10
mol% of Pd(PPh3)4 (Table 4, entry 1). Surprisingly, we
exclusively isolated the addition product 11 in 73%
yields. The presence of the catalyst is not necessary since
compound 11 was isolated in 60% yield when the reaction
was conducted without palladium (Table 4, entry 2). The
oxidation of the unstable dihydro compound 11 with ten
equivalents of MnO2 led to 13 in 28% yields (Scheme 4).

We also tested palladium-catalyzed cross-coupling reac-
tions between phenylzinc bromide and 3-methylsulfanyl-
1,2,4-triazine (1) under similar conditions. In this case 3-
phenyl-1,2,4-triazine (12) was isolated in 30% yield
(Table 4, entry 3) probably due to the lower nucleophilic
phenylzinc reagent.

At this stage, we investigated whether the original func-
tionalization order (C-5, C-6 and C-3) of the 1,2,4-triazine
ring towards nucleophiles could be deliberately modified
using different organometallics species.

We examined two pathways to obtain regioselectively
3,5-disubstituted-1,2,4-triazines starting from 3-methyl-
sulfanyl-1,2,4-triazine (1):

Pathway 1: addition reaction + cross-coupling reaction
Pathway 2: cross-coupling reaction + addition reaction
As summarized in Table 5, addition products 3, 4 and 7 were coupled with \( p \)-methoxyphenyl boronic acid in the presence of palladium and CuMeSal, \(^{13} \) to afford 3,5-disubstituted-1,2,4-triazines 9, 14 and 15, respectively, in good yields (pathway 1). In the case of 3-(\( p \)-methoxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazine (14), 3.2 equivalents of CuMeSal were necessary to observe complete cross-coupling reaction probably because of complexation of copper in the coordination site N-C-C-N of the starting material 4.

Table 5 Description of the Cross-Coupling Reaction of 3-Methylsulfanyl-1,2,4-triazine (1) with Boronic Acids and Organostannanes in the Presence of Copper (I) and a Catalytic Amount of Pd(PPh\(_3\))\(_4\) (THF for 48 h)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar-ZnBr</th>
<th>Time(h)</th>
<th>Catalyst</th>
<th>Products</th>
<th>Yield (%)</th>
<th>a</th>
</tr>
</thead>
</table>
| 1     | \[
\begin{array}{c}
\text{C}_6\text{H}_{12}\text{ZnBr} \\
\end{array}
\] | 48      | Pd(PPh\(_3\))\(_4\) | 9         | 73        |    |
| 2     | \[
\begin{array}{c}
\text{C}_6\text{H}_{12}\text{ZnBr} \\
\end{array}
\] | 48      | /               | 11        | 60        |    |
| 3     | \[
\begin{array}{c}
\text{C}_6\text{H}_{12}\text{ZnBr} \\
\end{array}
\] | 2       | Pd(PPh\(_3\))\(_4\) | 12        | 30\(^{b}\) |    |

\(^{a}\) Isolated yields after column chromatography.
\(^{b}\) Reaction was performed with 20 mol\% of Pd(PPh\(_3\))\(_4\).

The same 3,5-disubstituted-1,2,4-triazines 9, 14 and 15 were also isolated when the coupled product 6\(^{13,15}\) was treated with selected aryllithiums and Grignard reagents (pathway 2).

To sum up, the functionalization order of the 1,2,4-triazine ring can be easily modified (Scheme 5): position 3 can be first substituted followed by position 5 or position 5 can be first substituted followed by position 3, both of them leading to similar yields.

In conclusion, we have extended addition reactions on 1,2,4-triazines to organolithiums and benzylzinc reagents. Furthermore, 3-methylsulfanyl-1,2,4-triazine (1) was successfully coupled with boronic acids and organostannanes in the presence of copper (I) and a catalytic amount of Pd(PPh\(_3\))\(_4\).

With all those new functionalization tools combined with Yamanaka’s results,\(^{7}\) one can regioselectively functionalize the 1,2,4-triazine ring to obtain 5-aryl-, 3-aryl-, 3,5-diaryl-, 5,6-diaryl- and 3,5,6-triaryl-1,2,4-triazines (Scheme 6).

\(^1\)H NMR and \(^{13}\)C NMR spectra were recorded on a Bruker Avance 250 MHz spectrometer. \(^1\)H NMR spectra are reported as follows: chemical shifts in ppm (\( \delta \)) downfield from TMS as an internal standard, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), integration and coupling constants spectra (Hz). \(^{13}\)C NMR spectra reported in ppm (\( \delta \)) relative to the central line of triplet for CDCl\(_3\) at 77 ppm. IR spectra were recorded on a Perkin-Elmer FT PARAGON 1000PC spectrometer.
and absorption are reported in cm\(^{-1}\). HRMS (CI) were acquired on a ThermoFinnigan-MAT instrument 95 XL Analytical spectrometer. Melting points, uncorrected values, were measured on a Büchi 510 instrument. Microanalyses were taken on a ThermoFinnigan Flash EA1112 CHNS/O + MAS apparatus. Analytical TLC was performed on 0.2 mm precoated Kieselgel 60 F\(_{254}\) (Merck) plates. THF and 1,2-dimethoxyethane (DME) were distilled over sodium and benzophenone before use. 3-Methylsulfanyl-1,2,4-triazine (1) was prepared according to the literature. 8 Compounds 6 and 12 were described in previous papers. 13,15 All other compounds used were commercially available.

Addition of Organolithium Derivatives; Typical Procedure
To a solution of 3-methylsulfanyl-1,2,4-triazine (1) (100 mg, 0.79 mmol) in anhyd THF (3 mL) cooled to \(-78^\circ\text{C}\) under Ar was added dropwise phenyllithium (2 M, 500 \(\mu\)L, 1.25 equiv). The reaction mixture was kept at this temperature for 3 h and then was allowed to warm to r.t. over a period of 2 h. The reaction was quenched with a sat. solution of NH\(_4\)Cl and extracted twice with Et\(_2\)O. The crude product was dissolved in toluene (7 mL) under Ar and 2,3-dichloro-5,6-dicyanoquinone (188 mg, 1.25 equiv) was added by portion. After stirring for 1 h at r.t., the reaction mixture was filtrated on celite and the filtrate was diluted with a sat. solution of K\(_2\)CO\(_3\) and extracted with CH\(_2\)Cl\(_2\). Purification by flash chromatography (silica gel, petroleum ether–EtOAc, 90:10) afforded aromatic product 2 (96 mg, 60% yield) as a pale yellow solid.

3-Methylsulfanyl-5-phenyl-1,2,4-triazine (2)\(^6,8\) Yields 60%; pale yellow solid; mp 97–99 °C (lit.\(^8\) mp 99–100 °C).

IR (NaCl): 1597, 1538, 1501, 1237, 761, 663 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\)):
\[\delta = 9.37 (s, 1\ H), 8.15 (dd, J = 1.6, 7.9\ Hz, 2\ H), 7.61-7.55 (m, 3\ H), 2.73 (s, 3\ H).\]

\(^13\)C NMR (CDCl\(_3\)):
\[\delta = 173.9, 154.6, 142.0, 133.2, 132.8, 129.5 (2 \times C), 127.8 (2 \times C), 13.9.\]

3-(2-Furanyl)-3-methylsulfanyl-1,2,4-triazine (3)
Purified by flash chromatography (silica gel, petroleum ether–EtOAc, 70:30). Yield: 66%; yellow solid; mp 108–110 °C (lit.\(^{20}\) mp 88–90 °C).

IR (KBr): 1490, 1253, 1107, 767 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\)):
\[\delta = 9.22 (s, 1\ H), 7.71 (m, 1\ H), 7.46 (d, J = 3.4\ Hz, 1\ H), 6.65 (dd, J = 2.3, 3.7\ Hz, 1\ H), 2.69 (s, 3\ H).\]

\(^13\)C NMR (CDCl\(_3\)):
\[\delta = 173.7, 149.1, 147.6, 146.1, 140.5, 116.9, 113.7, 14.2.\]

Addition of Organomagnesium Derivatives; Typical Procedure
To a solution of 3-methylsulfanyl-1,2,4-triazine (1) (200 mg, 1.57 mmol) in anhyd THF (5 mL) under Ar was added dropwise p-methoxyphenylmagnesium bromide (0.5 M, 500 \(\mu\)L, 1.2 equiv) at r.t. The reaction mixture was stirred for 20 h, was then diluted with a sat. solution of NH\(_4\)Cl and extracted twice with CH\(_2\)Cl\(_2\). Purification by flash chromatography (silica gel, petroleum ether–EtOAc, 90:10) afforded non-aromatic product 5 (314 mg, 85% yield) as a pale yellow solid.

3-Methylsulfanyl-5-(pyridin-2-yl)-1,2,4-triazine (4)
Purified by flash chromatography (silica gel, petroleum ether–EtOAc–Et\(_3\)N, 90:10:0.1). Yield: 70%; yellow solid; mp 128–130 °C.

IR (KBr): 1533, 1507, 1469, 1311, 1301, 1234 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\)):
\[\delta = 9.95 (s, 1\ H), 8.79–8.76 (m, 1\ H), 8.51 (d, J = 7.9\ Hz, 1\ H), 7.89 (td, J = 1.8, 7.9\ Hz, 1\ H), 7.48 (ddd, J = 1.2, 4.9, 7.9\ Hz, 1\ H), 2.77 (s, 3\ H).\]

\(^13\)C NMR (CDCl\(_3\)):
\[\delta = 173.5, 153.2, 151.7, 150.1, 142.7, 137.4, 126.6, 123.0, 14.1.\]

HRMS (CI): \([M + H]^+\) calcd for C\(_9\)H\(_9\)N\(_4\)S: 205.0548; found: 205.0542.

Table 5 Different Combinations Between Addition Reaction and Cross-Coupling Reaction Starting with 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>(\text{Ar}_1)-M(_1)</th>
<th>(\text{Ar}_2)-M(_2)</th>
<th>Products, Yields (pathway 1/pathway 2) (%)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="Pathway_1" alt="Diagram" /></td>
<td><img src="Pathway_2" alt="Diagram" /></td>
<td>9, 44:17</td>
</tr>
<tr>
<td>2</td>
<td>14, 55:55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>15, 55:47</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Isolated after column chromatography.

Addition of Organolithium Derivatives; Typical Procedure
To a solution of 3-methylsulfanyl-1,2,4-triazine (I) (100 mg, 0.79 mmol) in anhyd THF (3 mL) cooled to \(-78^\circ\text{C}\) under Ar was added dropwise propylium bromide (2 M, 500 \(\mu\)L, 1.25 equiv). The reaction mixture was kept at this temperature for 3 h and then was allowed to warm to r.t. over a period of 2 h. The reaction was quenched with a sat. solution of NH\(_4\)Cl and extracted twice with Et\(_2\)O. The crude product was dissolved in toluene (7 mL) under Ar and 2,3-dichloro-5,6-dicyanoquinone (188 mg, 1.25 equiv) was added by portion. After stirring for 1 h at r.t., the reaction mixture was filtrated on celite and the filtrate was diluted with a sat. solution of K\(_2\)CO\(_3\) and extracted with CH\(_2\)Cl\(_2\). Purification by flash chromatography (silica gel, petroleum ether–EtOAc, 90:10) afforded aromatic product 2 (96 mg, 60% yield) as a pale yellow solid.

5-(2-Furanyl)-3-methylsulfanyl-1,2,4-triazine (3)
Purified by flash chromatography (silica gel, petroleum ether–EtOAc, 70:30). Yield: 66%; yellow solid; mp 83–85 °C (lit.\(^{20}\) mp 88–90 °C).

IR (KBr): 1490, 1253, 1107, 767 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\)):
\[\delta = 9.22 (s, 1\ H), 7.71 (m, 1\ H), 7.46 (d, J = 3.4\ Hz, 1\ H), 6.65 (dd, J = 2.3, 3.7\ Hz, 1\ H), 2.69 (s, 3\ H).\]

\(^13\)C NMR (CDCl\(_3\)):
\[\delta = 173.7, 149.1, 147.6, 146.1, 140.5, 116.9, 113.7, 14.2.\]

Addition of Organomagnesium Derivatives; Typical Procedure
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5-Benzyl-2,5-dihydro-3-methylsulfanyl-1,2,4-triazine (11)  
Yield: 60%; orange oil.  
IR (NaCl): 3019, 1215, 771 cm\(^{-1}\).  
\(^{1}H\) NMR (CDCl\(_3\)): \(\delta = 7.09\) (br s, 1 H, NH), 7.34–7.21 (m, 5 H), 6.64 (d, \(J = 3.4\) Hz, 1 H), 3.98 (dd, \(J = 2.0, 6.5, 8.2\) Hz, 1 H), 3.09–3.03 (dd, \(J = 6.4, 13.5\) Hz, 1 H), 2.95–2.86 (dd, \(J = 6.4, 13.5\) Hz, 1 H), 2.44 (s, 3 H).  
\(^{13}C\) NMR (CDCl\(_3\)): \(\delta = 154.8, 141.3, 137.6, 129.6\) (2 \(\times\) C), 128.5 (2 \(\times\) C), 126.6, 55.9, 38.9, 13.7.

5-Benzyl-3-methylsulfanyl-1,2,4-triazine (13)  
Yield: 28%; brown oil.  
IR (NaCl): 3241, 3160, 3056, 3003, 1725, 1677, 1530, 1142 cm\(^{-1}\).  
\(^{1}H\) NMR (CDCl\(_3\)): \(\delta = 8.21\) (s, 1 H), 7.40–7.25 (m, 5 H), 4.29 (s, 2 H), 2.67 (s, 3 H).  
\(^{13}C\) NMR (CDCl\(_3\)): \(\delta = 156.5, 149.0, 143.6, 134.7, 129.6\) (2 \(\times\) C), 129.2 (2 \(\times\) C), 128.8, 39.6, 14.1.

Palladium-Catalyzed Cross-Coupling Reaction with Boronic Acids  
To a mixture of 5-substituted-3-methylsulfanyl-1,2,4-triazine (0.393 mmol, 1.0 equiv), CuMeSal (0.867 mmol, 2.2 equiv), boronic acid (0.867 mmol, 2.2 equiv) in anhyd THF (3 mL) under Ar, was added Pd(PPh\(_3\))\(_2\) (23 mg, 0.02 mmol, 5\% mol). The reaction was stirred for 5 h at 50 \(^\circ\)C. The mixture was quenched with a Na\(_2\)CO\(_3\) solution (2 N, 5 mL) and extracted with CH\(_2\)Cl\(_2\) (3 \(\times\) 5 mL). The combined organic phases were washed with a Na\(_2\)CO\(_3\) solution (2 N, 15 mL) and water, dried over MgSO\(_4\) and concentrated in vacuo. The products were purified by column chromatography on silica gel.

5-(2-Furanyl)-3-(5-pyridinyl)-1,2,4-triazine (14)  
Purified by flash chromatography (silica gel, petroleum ether–EtOAc, 90:10). Yield: 80%; yellow solid; mp 139–141 \(^\circ\)C.
IR (KBr): 1606, 1510, 1498, 1252, 1167 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\)): \(\delta = 9.42\) (s, 1 H), 8.57 (d, \(J = 9.0\) Hz, 2 H), 8.20 (d, \(J = 9.0\) Hz, 2 H), 7.04 (d, \(J = 9.0\) Hz, 4 H), 3.88 (s, 3 H), 3.78 (s, 3 H).

\(^1^3\)C NMR (CDCl\(_3\)): \(\delta = 163.2, 162.9, 162.6, 130.1\) (2 \(\times\) C), 129.3 (2 \(\times\) C), 127.8, 126.1, 114.8 (2 \(\times\) C), 114.2 (2 \(\times\) C), 55.6, 55.5.

HRMS (Cl): \(m/z\) [M + H\(^+\)] calcd for C\(_{17}\)H\(_{16}\)N\(_3\)O\(_2\): 294.1243; found: 294.1238.

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References


