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**o-Benzenedisulfonimide as a Reusable Brønsted Acid Catalyst for Hetero-Michael Reactions**

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**Keywords:** Brønsted acid; conjugate addition; homogeneous catalysis; Michael reaction; recyclable catalyst

**Abstract**

The hetero-Michael reactions between various oxygen, sulphur and nitrogen nucleophiles and α,β-unsaturated compounds were carried out in the presence of catalytic amounts of *o*-benzenedisulfonimide as Brønsted acid organocatalyst. The reaction conditions were very mild and the yields of target products were good. The catalyst was easily recovered and purified, ready to be used in further reactions. This ability grants economic and ecological advantages.

**Introduction**
The conjugate addition of oxygen, nitrogen and sulphur nucleophiles to unsaturated carbonyl compounds by Michael reaction is one of the most advantageous and easy methods for the forming of C-O, C-N and C-S bonds in organic synthesis.\cite{1}

In fact β-amino\cite{2a,b} and β-oxy carbonyl groups\cite{2a,c} are important functionalities presents in numerous natural organic compounds such as alkaloids and polyketides. β-Amino carbonyl compounds are also the key intermediates for the synthesis of amino alcohol and β-amino acid derivatives which possess various biological activities.\cite{3} Moreover, thio-Michael addition has emerged as one of the most powerful tools for C-S bond formation;\cite{4} in fact thio-Michael addition provides a widespread synthetic utility in many organic processes\cite{5a-c} and in the synthesis of medicinally important compounds.\cite{5d}

Many different catalysts have been applied in hetero-Michael additions\cite{1} and, in particular, a number of Lewis acids.\cite{6} The main disadvantages of many of these methods are the harsh reaction conditions, the relatively long reaction times, the low selectivity and often the use of toxic, corrosive and expensive catalysts in high loading. Moreover their recovery and reuse is often impossible. To overcome this, hetero-Michael additions have been successfully performed in acidic ionic liquids (2-hydroxyethylammonium formate,\cite{7a} 1-(4-sulfobutyl)piridinium sulfate,\cite{7b} ethyl-n-butylphosphonium tosylate,\cite{7c} N-methyl-2-pyrrolidonium dihydrogen phosphate\cite{7d}) and very recently it has been reported that 1,4-addition of anilines to Michael acceptors proceeds easily in protic solvents\cite{8a} or in water\cite{8b} without any catalyst. Moreover it was also reported that the aza-Michael reaction between various aliphatic amines and Michael acceptors furnished the Michael adducts in good to excellent yield, without any solvent or catalysts.\cite{8c}

The use of Brønsted acids as homogeneous catalysts is less widespread. Spencer\cite{9a} tested a number of Brønsted acid in aza, oxa and thia-Michael additions obtaining the best results using Tf$_2$NH; Shen\cite{9b} used TfOH as catalyst in an intramolecular oxa-Michael addition and Goswani\cite{9c} used 15% aqueous HCl in the Michael addition between acrylates and fullerenol in the presence of an ammonium salt as phase transfer catalyst. Furthermore, the literature shows the use of some Brønsted acids as heterogeneous catalysts
We have recently reported the use of o-benzenedisulfonimide\textsuperscript{[11a]} (1, Figure 1) in catalytic amounts as a safe, non-volatile and non-corrosive Brønsted acid in several acid-catalyzed organic reactions.\textsuperscript{[11b]} The catalyst, that belongs to a high acidity (pk_a = -4.1 at 20 °C),\textsuperscript{[11a]} was easily recovered and purified, ready to be used in further reactions, with economic and ecological advantages.

\textbf{Figure 1.} o-Benzenedisulfonimide

\textbf{Results and Discussion}

In this paper we wish to propose the use of 1 as a reusable Brønsted acid catalyst for the hetero-Michael addition reactions between oxygen 2, sulphur 3 or nitrogen 4 nucleophiles and several \(\alpha,\beta\)-unsaturated compounds 5–9 (Scheme 1).

\textbf{Scheme 1.} o-Benzenedisulfonimide 1 as a catalyst for hetero-Michael reactions

Initially, in order to optimize the reaction conditions, the model reaction between methyl vinyl ketone (5) and benzyl alcohol (2a) at r.t. and in the presence of 1 as catalyst was studied under different conditions. As reported in Table 1 (entries 1–4), polar, slightly polar solvents or H\(_2\)O were tested but the best results were obtained in solvent-free reaction conditions (entries 5–7). The effect of the catalytic amount of 1 was also studied. So, in the best conditions, an excellent yield (92%) of Michael adduct 10a was achieved in a short reaction time (1 h) under solvent-free conditions and in the presence of 5 mol % of 1 (entry 7).

\textbf{Table 1.} Trial reactions between 2a and 5

Furthermore, 1 was recovered in excellent yields (89%) by simply evaporating the aqueous washings under reduced pressure. The recovered 1 was reused as the catalyst in another five
consecutive runs between 2a and 5. The results are listed in Table 2. The yields of 10a and the recovery of 1 were always good throughout the course of the different runs.

**Table 2. Consecutive runs with recovered 1**

The high yield, short reaction time and simplicity of the procedure encouraged us to further exploit the generality and the scope of this reaction, catalyzed by 1, using other alcohols 2 and other nucleophiles like thiols 3. The results are collected in Table 3. The Michael addition of various alcohols 2b–e to 5 produced the corresponding adducts 10b–e in excellent yields (Table 3, entries 2–5). On the other hand, no reactions occurred when less reactive phenols 2f, g were used (Table 3, entries 6, 7). Also, the reaction of aliphatic or aromatic thiols 3a–e with 5 gave the corresponding adducts 11a–e in very high yields without any by-product (Table 3, entries 8–12). It must be stressed that thiols can react without a catalyst.\[4c\] However, the reaction time was longer. (Table 3, entry 13)

**Table 3. Hetero-Michael reaction between 5 and alcohols 2 or thiols 3**

In order to explore the synthetic usefulness of 1 in oxa-Michael and thia-Michael reactions further, we also investigated the reactions of four other types of α,β unsaturated compounds 6–9 with selected 2 or 3. The reaction between 2a and 6 furnished 10h in very good yields (Table 4; entry 1). However, it must be stressed that the reactions of the weak nucleophile 2a with 7–9 did not proceed at all, even at 50 °C (Table 4; entries 2–4). Thiols 3a and 3e reacted easily at r.t. or when heated to 50 °C with 6 and 7 (Table 4; entries 5–7), whereas no results were obtained with 8 and 9 (Table 4; entries 8–9). All these examples demonstrate the usefulness and the simplicity of this method since it requires mild reaction conditions and short reaction times; the target products are obtained in good yields and good selectivity and the absence of by-products is observed.

**Table 4: Hetero-Michael reaction between 6–9 and alcohol 2a or thiols 3a, 3e.**
In order to further expand the scope of our work, we decided to study the aza-Michael addition too. To start, we tested the reaction between 4a and 5 as reported in Table 5. First of all, it was necessary to cool at 0 °C (Table 5, entry 2) to minimize the formation of two by-products, namely imine 13a (that formed as a result of nucleophilic attack of 4a on the carbonyl group of 5) and adducts 14a (that formed as a result of the further nucleophilic attack of 12a on 5; Table 5, entry 1). On the contrary, no side products were detected using the less nucleophilic aniline 4e (Table 5, entry 6). Also the reaction of other aliphatic amines 4b–d gave the corresponding Michael adducts 12 b–d in good yields and short reaction times (Table 5, entries 3–5).

Table 5: Hetero-Michael reaction between 5 and amines 4

Finally, amines 4a, b, e, stronger nucleophiles than 2 or 3, reacted easily at r.t. or at 50 °C with 6–9 (Table 6; entries 1–3, 6, 8–10) producing the adduct 12f–l in good yields. It must be stressed that the reactions between 4a, b and 9 furnished the immines 15a, b that derived from Michael adducts after the loss of nitromethane (Table 6; entries 11–12).

Table 6: Hetero-Michael reaction between 6–9 and amines 4a, b, e.

In the literature it is reported that the aza-Michael reaction proceeds without any catalyst, reacting various aliphatic amines with a number of Michael acceptors. For example, the reaction between benzyl amine and methyl acrylate furnishes after 18 hours at r.t. a mixture of mono and di-Michael adducts (in total 90% yield). On the contrary, aniline does not react in these conditions. In the light of these, performing the reaction between 4a, e and 7 without 1 we obtained about the same results reported in the literature (Table 6; entries 4, 7). From our experimental data it was evident that the presence of catalyst 1 significantly accelerated the reaction between 4a and 7 (Table 6, entry 3), allowed the reaction between 7 and weaker nucleophile 4e (Table 6, entry 6) and prevented the formation of the di-adduct. It is reasonable to assume to have a protonation of amine 4a by strong acid 1, with the formation of ammonium salt 16. Despite this, 4a and 7 reacted very fast. So, we
prepared the ammonium salt 16 and used it as a catalyst in the reaction between 4a and 7. We obtained the Michael adduct 12h with a yield and time comparable to those obtained for the reaction performed with 1 (Table 6; entry 5). In the light of these, it can be assumed that 16 transfers a proton on the carbonyl group of the Michael acceptor 7. The stable intermediate 17 reacts very easily with 4a to give 12h (Scheme 2). However, due to the high stability of the cation 17, the direct protonation of 7 by 1 can not be excluded, even in the presence of 4a. Finally, the absence of the possible di-adduct \(N,N\text{-bis(2-ethoxycarbonylethyl)}\text{benzylamine}\) could be explained by the higher rate, in the presence of a catalyst, of the reaction between 4a and 7. Clearly, also in all the other aza-Michael reactions conducted with aliphatic amines, it could be assumed that ammonium salt of 1 acts as a catalyst, activating the Michael acceptors.

Scheme 2. Aza-Michael reaction catalyzed by 16

In conclusion, in this paper the synthetic usefulness of o-benzenedisulfonimide (1) as a catalyst in hetero-Michael reactions has been demonstrated. The advantages of the method are mild solvent-free reaction conditions, stoichiometric reagent ratios, catalytic amount of the readily available and easy-handling Brønsted acid catalyst. Furthermore, in comparison with other catalysts extensively used for hetero-Michael reactions, 1 turned out to be a safe, non-volatile, non-corrosive and bench-stable catalyst. A further valuable aspect of the use of 1 is its easy recovery in high yield from the reaction mixture, due to its complete solubility in water, and its reuse without loss of catalytic activity in other reactions.

Experimental

4-Benzylxybutan-2-one (10a): representative procedure for the preparation of Michael adducts 10, 11, 12: o-Benzenedisulfonimide (1; 5 mol %; 55 mg, 0.25 mmol) was added to a mixture of benzyl alcohol (2a; 0.54 g, 5 mmol) and methyl vinyl ketone (5; 0.36 g, 5 mmol) The
mixture was stirred at r.t. The reaction was monitored by GC and GC-MS until the complete disappearance of 2a and 5 (1 hours). The reaction mixture was poured into Et₂O-H₂O (50 ml, 1:1). The aqueous layer was separated and extracted with Et₂O (2 x 50 ml). The combined organic extracts were washed with H₂O (2 x 50 ml), dried over Na₂SO₄. After solvent removal under reduced pressure, the crude residue was the virtually pure (GC, GC-MS, ¹H NMR, ¹³C NMR) title compound 10a. The aqueous layer and aqueous washings were collected and evaporated under reduced pressure. After removal of the water, virtually pure (¹H NMR) o-benzenedisulfonimide (1) was recovered (49 mg, 89 % yield).

The recovered 1 was employed in other five catalytic cycles under the conditions above described, reacting with 2a and 5; Table 2 reported the yields of 10a and the yields of recovered 1.

Supplementary Material: General experimental details; physical and spectral data of the products 10,11,12; preparation, physical and spectral data of product 16; more details for Tables 5 and 6.

Acknowledgments

This work was supported by the University of Torino.

References


**Figure 1.** *o*-Benzenedisulfonimide
Scheme 1. o-Benzenedisulfonimide 1 as a catalyst for hetero-Michael reactions
Scheme 2. Aza-Michael reaction catalyzed by 16
Table 1. Trial reactions between 2a and 5

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>1 mol-%</th>
<th>Time (h)</th>
<th>Yield (%) of 10a&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeCN</td>
<td>5</td>
<td>24</td>
<td>42&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5</td>
<td>6</td>
<td>90&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>5</td>
<td>24</td>
<td>35&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>5</td>
<td>24</td>
<td>Traces&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>neat</td>
<td>1</td>
<td>5</td>
<td>87&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>neat</td>
<td>2</td>
<td>3</td>
<td>89&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>7</td>
<td>neat</td>
<td>5</td>
<td>1</td>
<td>92&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yields refer to the pure products.

<sup>b</sup>After 24 h, unreacted 2a and 5 were detected by GC and GC-MS. Nevertheless, the reaction was stopped and the crude residue, purified in a silica gel chromatography column, (eluent: PE/Et<sub>2</sub>O 9.8:0.2), afforded pure 10a.

<sup>c</sup>On the GC, GC-MS and NMR analyses, the crude residue was the virtually pure 10a.

<sup>d</sup>After 24 h, unreacted 2a and 5 were detected by GC and GC-MS. Only weak traces of 10a were detected.
### Table 2. Consecutive runs with recovered 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time (h)</th>
<th>Yield (%) of 10a&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Recovery (%) of 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>92&lt;sup&gt;b&lt;/sup&gt;</td>
<td>89,49 mg&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>85</td>
<td>86,42 mg&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>85</td>
<td>86,42 mg&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>82</td>
<td>81,34 mg&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
<td>83</td>
<td>79,27 mg&lt;sup&gt;g&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>2.5</td>
<td>80</td>
<td>74,20 mg</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yields refer to the pure products.

<sup>b</sup>The reaction was performed with 5 mmol of 2a and 5 and 5 mol-% of 1 (55 mg, 0.25 mmol).

<sup>c</sup>Recovered 1 was used as a catalyst in entry 2.

<sup>d</sup>Recovered 1 was used as catalyst in entry 3.

<sup>e</sup>Recovered 1 was used as a catalyst in entry 4.

<sup>f</sup>Recovered 1 was used as a catalyst in entry 5.

<sup>g</sup>Recovered 1 was used as catalyst in entry 6.
Table 3. Hetero-Michael reaction between 5 and alcohols 2 or thiols 3

\[
\begin{align*}
\text{RXH} & \quad + \quad \overset{\text{1}}{\text{5}} \quad \rightarrow \quad \text{RX} \quad \overset{\text{1}}{\text{2}} \\
\text{2: } X= \text{ O} & \quad \text{3: } X= \text{ S} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Products and Yields</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bn; 2a</td>
<td>10a; 92(^{c})</td>
<td>r.t.</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>nBu; 2b</td>
<td>10b; 85(^{c})</td>
<td>r.t.</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>sBu; 2c</td>
<td>10c; 88(^{c})</td>
<td>r.t.</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>tBu; 2d</td>
<td>10d; 82(^{c})</td>
<td>r.t.</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>Cy; 2e</td>
<td>10e; 84(^{c})</td>
<td>r.t.</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>Ph; 2f</td>
<td>10f; -</td>
<td>50</td>
<td>24</td>
</tr>
<tr>
<td>7</td>
<td>4-MeOC(_6)H(_4); 2g</td>
<td>10g; -</td>
<td>50</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
<td>Bn; 3a</td>
<td>11a; 87(^{c})</td>
<td>r.t.</td>
<td>0.5</td>
</tr>
<tr>
<td>9</td>
<td>nBu; 3b</td>
<td>11b; 91(^{c})</td>
<td>r.t.</td>
<td>0.5</td>
</tr>
<tr>
<td>10</td>
<td>sBu; 3c</td>
<td>11c; 85(^{c})</td>
<td>r.t.</td>
<td>0.5</td>
</tr>
<tr>
<td>11</td>
<td>tBu; 3d</td>
<td>11d; 82(^{c})</td>
<td>r.t.</td>
<td>0.5</td>
</tr>
<tr>
<td>12</td>
<td>Ph; 3e</td>
<td>11e; 92(^{d})</td>
<td>r.t.</td>
<td>0.5</td>
</tr>
</tbody>
</table>
All the reactions were performed with 5 mol-% of 1; the reactants are in equimolar amounts (5 mmol).

Yields refer to the pure and isolated products.

On the GC, GC-MS and NMR analyses, the crude residues were the virtually pure hetero-Michael adducts 10,11.

The crude residue was purified in a silica gel chromatography column (eluent: PE/Et₂O 9.8:0.2).

The reaction was performed without catalyst 1.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactants</th>
<th>Products and Yields (%)$^{a,b}$</th>
<th>Temp.(°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BnOH 2a</td>
<td>BnO 6 82$^c$</td>
<td>r.t</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>BnOH 2a</td>
<td>7</td>
<td>50</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>BnOH 2a</td>
<td>8</td>
<td>50</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>BnOH 2a Ph</td>
<td>9</td>
<td>50</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 4. Hetero-Michael reaction between 6–9 and alcohol 2a or thiols 3a, 3e
All the reactions were performed with 5 mol-% of 1; the reactants are in a equimolar amounts (5 mmol).

Yields refer to the pure and isolated products.

On the GC, GC-MS and NMR analyses, the crude residues were the virtually pure hetero-Michael adducts 10, 11.
Table 5. Hetero-Michael reaction between 5 and amines 4
\[
\text{RNH}_2 \quad + \quad \text{\text{O}} \quad \text{5} \quad \xrightarrow{1} \quad \text{RNH} \quad \text{12}
\]

\[
\left( \text{\text{O}} \quad \text{13} \quad \text{NR} \right) \quad \left( \text{\text{O}} \quad \text{14} \right)
\]

| Entry | R     | Products and Yields (%)
|-------|-------|------------------------|
| 1     | Bn; 4a| 12a; 85
| 2     | Bn; 4a| 12b; 82
| 3     | nBu; 4b| 12b; 82
| 4     | sBu; 4c| 12c; 82
| 5     | tBu; 4d| 12d; 77
| 6     | Ph; 4e| 12e; 89

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>r.t</td>
<td>0.5</td>
</tr>
<tr>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>r.t.</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^{a}\text{All the reactions were performed with 5 mol-% of 1; the reactants are in equimolar amounts (5 mmol).}\)

\(^{b}\text{Yields refer to the pure and isolated products.}\)

\(^{c}\text{On the GC and GC-MS analyses of the crude residue, three products were detected: 12a, 13a and 14a. However, it was impossible to separate them by chromatography column.}\)

\(^{d}\text{On the GC and GC-MS analyses of the crude residues, weak traces of compounds 13 and 14 were detected. The crude residues, purified in a silica gel chromatography column (eluent: PE/Et}_2\text{O 9.8:0.2), afforded pure compounds 12.}\)

\(^{e}\text{The crude residues were purified in a silica gel chromatography column (eluent: PE/Et}_2\text{O 9.8:0.2). For more details see also Supplementary Material.}\)
<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactants</th>
<th>Products and Yields (%)&lt;sup&gt;a,b&lt;/sup&gt;</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BnNH&lt;sub&gt;2&lt;/sub&gt; 4a 6</td>
<td>BnNH&lt;sub&gt;2&lt;/sub&gt; 12f</td>
<td>86&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0</td>
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<tr>
<td>2</td>
<td>PhNH&lt;sub&gt;2&lt;/sub&gt; 4e 6</td>
<td>PhNH&lt;sub&gt;2&lt;/sub&gt; 12g</td>
<td>82&lt;sup&gt;d&lt;/sup&gt;</td>
<td>r.t.</td>
</tr>
<tr>
<td>3</td>
<td>BnNH&lt;sub&gt;2&lt;/sub&gt; 4a 7</td>
<td>BnNH&lt;sub&gt;2&lt;/sub&gt; 12h</td>
<td>80&lt;sup&gt;c&lt;/sup&gt;</td>
<td>r.t.</td>
</tr>
<tr>
<td>4</td>
<td>4a 7&lt;sup&gt;e&lt;/sup&gt;</td>
<td>-</td>
<td>r.t.</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>4a 7&lt;sup&gt;e&lt;/sup&gt; 12h</td>
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<td>r.t.</td>
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<td>7</td>
<td>4e 7&lt;sup&gt;e&lt;/sup&gt;</td>
<td>-</td>
<td>50</td>
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</tr>
<tr>
<td>8</td>
<td>BnNH&lt;sub&gt;2&lt;/sub&gt; 4a 8</td>
<td>BnNH&lt;sub&gt;2&lt;/sub&gt; 12j</td>
<td>82&lt;sup&gt;c&lt;/sup&gt;</td>
<td>r.t.</td>
</tr>
<tr>
<td>9</td>
<td>nBuNH&lt;sub&gt;2&lt;/sub&gt; 4b 8</td>
<td>nBuNH&lt;sub&gt;2&lt;/sub&gt; 12k</td>
<td>85&lt;sup&gt;c&lt;/sup&gt;</td>
<td>50</td>
</tr>
</tbody>
</table>
All the reactions were performed with 5 mol-% of 1; the reactants are in equimolar amounts (5 mmol).

Yields refer to the pure and isolated products.

On the GC, GC-MS and NMR analyses, the crude residues were the virtually pure hetero-Michael adducts 12.

The crude residues were purified in a silica gel chromatography column; eluent: PE-Et₂O (9.8:0.2).

The reaction was performed without catalyst 1.

On the GC and GC-MS analyses of the crude residue, two products were detected: 12h and N,N-bis(2-ethoxycarbonylethyl)benzylamine. However, it was impossible to separate them by chromatography column.

The reaction was performed using the benzylammonium salt 16 as catalyst (5 mol-%; 81.5 mg).

On the GC and GC-MS analyses of the crude residue two products were detected: N-benzylideneaniline (15e) and N-(1-phenyl-2-nitroethyl)aniline. However, it was impossible to separate them by chromatography column. For more details see also Supplementary Material.