Highly Chemoselective Rearrangement of 3-Aryloxaziridines to Nitrones or Amides

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Received 27 April 2009; revised 8 June 2009

Abstract: An efficient method for the chemoselective ring-opening rearrangement of 3-aryloxaziridines by using silver triflate alone to afford nitrones, or in the presence of a simple Brønsted acid to yield amides, has been developed. Silver triflate plays an important role in both transformations.

Key words: oxaziridines, rearrangement, chemoselectivity, nitrones, amides

Oxaziridines have three different bonds (C–N, C–O, N–O) in one highly strained three-membered ring. This unique structure has gained wide application in a variety of transformations, among which electrophilic oxygenation and amination have been intensively studied and further developed into a series of asymmetric transformations. In addition, the ring-opening rearrangement of oxaziridines has also drawn attention. It can not only yield diversely useful compounds via different bond cleavages, but also provide insights into the strength and reactivity of different bonds under various reaction conditions, which can direct the further transformations of oxaziridines. Oxaziridines can undergo ring-opening rearrangement either via C–O bond cleavage to produce nitrones or via N–O bond cleavage to afford amides. The chemoselectivity is greatly affected by the substitution pattern in the oxaziridines. For example, under thermal or acidic conditions, 3-aryloxaziridines afford nitrones, while 3-alkyloxaziridines give amide products. Different catalytic systems have also been applied to achieve highly chemoselective products. For 3-aryloxaziridines, it has been reported that aluminum trichloride can catalyze nitrone formation, while manganese or rhodium complexes can catalyze amide formation; however, a simple and convenient method for the chemoselective ring-opening rearrangement of oxaziridines is still lacking. Here, we report a general and efficient method to fulfill this purpose, by simply controlling the reaction conditions. Starting from 3-aryloxaziridines and using silver triflate as the catalyst, oxaziridine was heated in anhydrous 1,2-dichloroethane (DCE) at 70 °C with 20 mol% iron(III) chloride as the catalyst (Table 1, entry 1). Only a trace amount of the corresponding nitro product was formed, while most of the starting material was decomposed into 4-methoxybenzaldehyde. Following this result, a series of other Lewis acids was tested, among which 20 mol% zinc chloride or aluminum trichloride showed good activity with moderate to good yield (Table 1, entries 2 and 3); however, several copper salts, such as copper(II) chloride, copper(II) acetate and copper(II) triflate, gave even worse results than iron(III) chloride (Table 1, entries 4–6), and oxaziridine was almost completely decomposed to 4-methoxybenzaldehyde, which indicated the poor stability of 1a in the presence of Lewis acids at high temperature. The best result was obtained when 10 mol% silver triflate was used, which afforded nitrone 2a with a 91% isolated yield (Table 1, entry 7). The yield remained unaffected when the catalyst loading of silver triflate was reduced to 5 mol%, however, the yield was greatly decreased when the catalyst loading was further reduced to 1 mol% (Table 1, entries 8 and 9). The reaction proceeds slowly at room temperature, giving a relatively poor conversion even after a prolonged reaction time (Table 1, entry 10). It is worth mentioning that with copper(II) chloride as the catalyst, oxaziridine gave the amide product via N–O bond cleavage in 36% yield, instead of nitrone 2a. With Nitrones are important and versatile synthetic intermediates in organic synthesis; for example, they can undergo [3+2]-cycloaddition reactions with alkenes to produce isoxazolines, which are important precursors for a variety of biologically important compounds, such as β-amino acids, alkaloids, etc. Considering the importance of nitro structures, the simple ring-opening rearrangement of oxaziridines to yield nitrones is highly desired; however, besides the above-mentioned literature, methods for this direct transformation are still quite limited. More recently, it has been found that under different Lewis acid catalysis, N-sulfonyloxaziridines can act as the precursor of nitrones to produce isoxazolines with styrenes via [3+2] cycloaddition. Inspired by this result we decided to further explore the catalytic abilities of more simple and general Lewis acids toward this transformation.

3-(4-Methoxyphenyl)-2-(2-phenylethyl)oxaziridine (1a), which was easily prepared by epoxidation of the corresponding imine using m-chloroperoxybenzoic acid, was chosen as the substrate to conduct our initial investigation. Thus, oxaziridine 1a was heated in anhydrous 1,2-dichloroethane (DCE) at 70 °C with 20 mol% iron(III) chloride as the catalyst (Table 1, entry 1). Only a trace amount of the corresponding nitro product 2a was formed, while most of the starting material was decomposed into 4-methoxybenzaldehyde. Following this result, a series of other Lewis acids was tested, among which 20 mol% zinc chloride or aluminum trichloride showed good activity with moderate to good yield (Table 1, entries 2 and 3); however, several copper salts, such as copper(II) chloride, copper(II) acetate and copper(II) triflate, gave even worse results than iron(III) chloride (Table 1, entries 4–6), and oxaziridine was almost completely decomposed to 4-methoxybenzaldehyde, which indicated the poor stability of 1a in the presence of Lewis acids at high temperature. The best result was obtained when 10 mol% silver triflate was used, which afforded nitrone 2a with a 91% isolated yield (Table 1, entry 7). The yield remained unaffected when the catalyst loading of silver triflate was reduced to 5 mol%, however, the yield was greatly decreased when the catalyst loading was further reduced to 1 mol% (Table 1, entries 8 and 9). The reaction proceeds slowly at room temperature, giving a relatively poor conversion even after a prolonged reaction time (Table 1, entry 10). It is worth mentioning that with copper(II) chloride as the catalyst, oxaziridine gave the amide product via N–O bond cleavage in 36% yield, instead of nitrone 2a. With
this unexpected chemoselectivity switch, we decided to develop an efficient method for amide formation. We turned our initial attention to simple Brønsted acids, which have been found to be capable of promoting oxygen atom transfer from oxaziridines onto sulfides.\textsuperscript{13}

Therefore, following the standard reaction conditions applied to nitrone formation, several Brønsted acids were tested. The results showed that the acidity had a strong effect on the outcome of the rearrangement of oxaziridine 1a. When the more acidic trifluoromethanesulfonic acid or trifluoroacetic acid catalyst was used, only nitrone product 2a was obtained in moderate yield, along with the formation of a small amount of 4-methoxybenzaldehyde (Table 2, entries 1 and 2); however, when the less acidic acetic acid was used, the amide 3a became the major product, albeit in low yield (Table 2, entry 3). Increasing the amount of acetic acid was useful to gain a better yield of amide 3a (Table 2, entries 4 and 5), however, the decomposition of oxaziridine 1a into 4-methoxybenzaldehyde was also accelerated (1a was completely consumed under the conditions of both entries 4 and 5). In our above-mentioned results, the decomposition of oxaziridine 1a had been greatly inhibited by the efficient formation of nitrone 2a with silver triflate catalyst. Therefore, we decided to test the effect of silver triflate catalyst on amide formation.

The use of 5 mol\% silver triflate with 20 mol\% acetic acid made the rearrangement more complicated, with the formation of both nitrone 2a and amide 3a (Table 2, entry 6); however, when the amount of acetic acid was increased to 50 mol\%, the most satisfactory result was obtained and amide 3a was exclusively afforded in 78\% isolated yield (Table 2, entry 7). A control experiment showed that both nitrone 2a and amide 3a could be obtained in poor yield, without any chemoselectivity, under thermal conditions (Table 2, entry 8). This result indicated that our reaction system was not only able to accelerate the reactivity but also to give a good control in the chemoselectivity for the ring-opening rearrangement of oxaziridine 1a.

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**Table 1** Lewis Acid Catalyzed Rearrangement of Oxaziridine 1a to Nitrone 2a\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Catalyst Amount (mol%)</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Yield* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FeCl\textsubscript{3}</td>
<td>20</td>
<td>70</td>
<td>3</td>
<td>&lt;8\textsuperscript{c}</td>
</tr>
<tr>
<td>2</td>
<td>ZnCl\textsubscript{2}</td>
<td>20</td>
<td>70</td>
<td>3</td>
<td>65\textsuperscript{c}</td>
</tr>
<tr>
<td>3</td>
<td>AlCl\textsubscript{3}</td>
<td>20</td>
<td>70</td>
<td>3</td>
<td>86</td>
</tr>
<tr>
<td>4</td>
<td>CuCl\textsubscript{2}</td>
<td>20</td>
<td>70</td>
<td>3</td>
<td>&lt;5\textsuperscript{d}</td>
</tr>
<tr>
<td>5</td>
<td>Cu(OAc)\textsubscript{2}</td>
<td>20</td>
<td>70</td>
<td>3</td>
<td>&lt;5\textsuperscript{d}</td>
</tr>
<tr>
<td>6</td>
<td>Cu(OTf)\textsubscript{2}</td>
<td>10</td>
<td>70</td>
<td>3</td>
<td>&lt;5\textsuperscript{d}</td>
</tr>
<tr>
<td>7</td>
<td>AgOTf</td>
<td>10</td>
<td>70</td>
<td>1.5</td>
<td>91</td>
</tr>
<tr>
<td>8</td>
<td>AgOTf</td>
<td>5</td>
<td>70</td>
<td>1.5</td>
<td>91</td>
</tr>
<tr>
<td>9</td>
<td>AgOTf</td>
<td>1</td>
<td>70</td>
<td>6</td>
<td>52</td>
</tr>
<tr>
<td>10</td>
<td>AgOTf</td>
<td>5</td>
<td>r.t.</td>
<td>12</td>
<td>22\textsuperscript{c}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reactions were carried out on 0.5-mmol scale with the indicated amount of catalyst in anhydrous DCE (4 mL) for the indicated time.

\textsuperscript{b} Isolated yield unless otherwise stated.

\textsuperscript{c} Yield was determined by \textsuperscript{1}H NMR spectroscopy.

\textsuperscript{d} The corresponding amide product via N–O bond cleavage was formed in 36\% NMR yield.

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**Table 2** Brønsted Acid Promoted Chemoselective Rearrangement of Oxaziridine 1a to Amide 3a\textsuperscript{a,b,c}

<table>
<thead>
<tr>
<th>Entry</th>
<th>AgOTf (mol%)</th>
<th>Brønsted acid (mol%)</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Yield (%) of 2a</th>
<th>Yield (%) of 3a</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>–</td>
<td>TIOH (20)</td>
<td>70</td>
<td>6</td>
<td>52</td>
<td>n.d.</td>
</tr>
<tr>
<td>2</td>
<td>–</td>
<td>TFA (20)</td>
<td>70</td>
<td>6</td>
<td>48</td>
<td>n.d.</td>
</tr>
<tr>
<td>3</td>
<td>–</td>
<td>AcOH (20)</td>
<td>70</td>
<td>6</td>
<td>n.d.</td>
<td>37</td>
</tr>
<tr>
<td>4</td>
<td>–</td>
<td>AcOH (50)</td>
<td>70</td>
<td>6</td>
<td>n.d.</td>
<td>53</td>
</tr>
<tr>
<td>5</td>
<td>–</td>
<td>AcOH (100)</td>
<td>70</td>
<td>2</td>
<td>n.d.</td>
<td>58</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>AcOH (20)</td>
<td>70</td>
<td>6</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>AcOH (50)</td>
<td>70</td>
<td>2</td>
<td>n.d.</td>
<td>78\textsuperscript{d}</td>
</tr>
<tr>
<td>8</td>
<td>–</td>
<td>–</td>
<td>70</td>
<td>6</td>
<td>11</td>
<td>27</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reactions were carried out on 0.5-mmol scale, with the indicated amount of AgOTf and Brønsted acid in anhydrous DCE (4 mL).

\textsuperscript{b} All yields were determined by \textsuperscript{1}H NMR spectroscopy unless otherwise stated.

\textsuperscript{c} n.d. = not detected.

\textsuperscript{d} Isolated yield.
With the optimized conditions in hand, we further investigated the substrate scope for both transformations. Starting from alkylamines and different aromatic aldehydes, a series of substituted 3-aryloxaziridines was easily prepared. In terms of the silver triflate catalyzed C–O bond cleavage transformation, a strong electronic effect was shown. Reactions of substrates with strong electron-donating groups at the para position of the 3-aryl ring run smoothly and fast (Table 3, entries 1–3, 6 and 7), while reaction of the substrate with a weak electron-donating group was less efficient (Table 3, entry 5). Substitution at the ortho position made this transformation less efficient (Table 3, entry 4), while the meta-substituted substrate gave a relatively low yield (Table 3, entry 9). The substitution pattern at the N-position was also tested, and substrates with more bulky alkyl groups gave better yields (Table 3, entries 8 and 10). We have also tested for the formation of amides under the conditions of a combination of silver triflate catalyst and 0.5 equivalents of acetic acid. Generally, except for the formation of a small amount of the corresponding benzaldehyde, the N–O bond could be chemoselectively cleaved to afford the amides without nitrone formation, and the substrate scope showed very similar trends to nitrone formation (Table 3, formation of 3). This similarity indicated that the silver triflate catalyst, as the same factor applied in both transformations, plays the dominant role in both transformations.

We have also considered the possible reaction pathways for this chemoselective rearrangement of 3-aryloxaziridines. For nitrone formation, the silver triflate catalyst would coordinate with the oxygen atom in the oxaziridine three-membered ring to lower the activation barrier for the rearrangement to proceed via C–O bond breakage. For amide formation, we assume that in the presence of acetic acid, the relatively weak N–O bond in the oxaziridine ring would be cleaved by O-protonation, to afford an oxonium intermediate via a 1,2-H shift from C to N. This intermediate would then undergo deprotonation to afford the amide product. Silver triflate may have a role in accelerating the N–O bond cleavage by coordinating with the oxygen atom, or in stabilizing the oxonium intermediate. Further investigations to understand the mechanism are underway.

In summary, we have developed a simple and efficient method for the chemoselective ring-opening rearrangement of 3-aryloxaziridines. By applying silver triflate as the catalyst, nitrones can be efficiently afforded and, with the addition of 0.5 equivalents of acetic acid to the system, the chemoselectivity can be completely switched from the C–O bond to N–O bond cleavage, to yield amides exclusively.

### Table 3 The Chemoselective Rearrangement of 3-Aryloxaziridines 1 to Nitrones 2a or Amides 3b

<table>
<thead>
<tr>
<th>Entry</th>
<th>1</th>
<th>R1</th>
<th>R2</th>
<th>Conditions A</th>
<th>Conditions B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>(CH2)2Ph</td>
<td>4-MeOC6H4</td>
<td>1.5</td>
<td>2a: 91</td>
</tr>
<tr>
<td>2</td>
<td>1b</td>
<td>(CH2)2Ph</td>
<td>4-Tol</td>
<td>2</td>
<td>2b: 67</td>
</tr>
<tr>
<td>3</td>
<td>1c</td>
<td>(CH2)2Ph</td>
<td>4-(H2C=CHCH2O)C6H4</td>
<td>2</td>
<td>2c: 67</td>
</tr>
<tr>
<td>4</td>
<td>1d</td>
<td>(CH2)2Ph</td>
<td>2-MeOC6H4</td>
<td>6</td>
<td>2d: 69</td>
</tr>
<tr>
<td>5</td>
<td>1e</td>
<td>(CH2)2Ph</td>
<td>4-PhC6H4</td>
<td>6</td>
<td>2e: 34</td>
</tr>
<tr>
<td>6</td>
<td>1f</td>
<td>(CH2)2C6H4-Cp-F</td>
<td>4-MeOC6H4</td>
<td>2</td>
<td>2f: 77</td>
</tr>
<tr>
<td>7</td>
<td>1g</td>
<td>(CH2)2Ph</td>
<td>4-MeOC6H4</td>
<td>2</td>
<td>2g: 68</td>
</tr>
<tr>
<td>8</td>
<td>1h</td>
<td>s-Bu</td>
<td>2-MeOC6H4</td>
<td>1.5</td>
<td>2h: 94</td>
</tr>
<tr>
<td>9</td>
<td>1i</td>
<td>s-Bu</td>
<td>3-MeOC6H4</td>
<td>6</td>
<td>2i: 26</td>
</tr>
<tr>
<td>10</td>
<td>1j</td>
<td>t-Bu</td>
<td>2-MeOC6H4</td>
<td>2.5</td>
<td>2j: 80</td>
</tr>
</tbody>
</table>

*a Nitrones were afforded under conditions A, in which reactions were carried out on 0.5-mmol scale with AgOTf (5 mol%) in anhydrous DCE (4 mL).
*b Amides were afforded under conditions B, in which reactions were carried out on 0.5-mmol scale with AgOTf (5 mol%) and AcOH (0.25 mmol) in anhydrous DCE (4 mL).
*c Isolated yield.
*d In all cases the yield based on conversion was greater than 90%.
*e The corresponding benzaldehyde was always detected as a byproduct in less than 10% conversion.
All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. All reagents were obtained commercial and were used without further purification unless otherwise noted. 1,2-Dichloroethane was purchased from Acros and was used directly without further purification. The petroleum ether (PE) used refers to the fraction boiling in the range 60–90 °C. The starting materials were synthesized according to known procedures.14–17 IR spectra were recorded on a Thermo Nicolet Nexus 670 FTIR instrument. 

Silver Triflate Catalyzed Rearrangement of Oxaziridines 1 to Nitrones 2 (Table 3, Conditions A); General Procedure

To a DCE soln (4 mL) containing AgOTf (6.5 mg, 0.025 mmol) in a Schlenk tube under N2, a 3-aryloxaziridine 1a–j (0.5 mmol) was added at r.t. The reaction mixture was then heated at 70 °C until the starting material was completely consumed, as monitored by TLC. The reaction mixture was purified by flash chromatography to directly afford the corresponding nitron 2a–j.

**C-(4-Methoxyphenyl)-N-(2-phenylethyl)nitrone (2a)**

Colorless crystals (recrystallized from PE–CH2Cl2); mp 71–72 °C.

IR (KBr): 3067, 1607, 1459, 1226, 1150, 1081 cm–1.


1H NMR (300 MHz, CDCl3): δ = 9.28 (d, J = 8.1 Hz, 1 H), 7.67 (s, 1 H), 7.38–7.19 (m, 6 H), 7.03 (t, J = 7.2 Hz, 1 H), 6.85 (d, J = 8.1 Hz, 1 H), 4.14 (t, J = 7.5 Hz, 2 H), 3.79 (s, 3 H), 3.32 (t, J = 7.2 Hz, 2 H).

13C NMR (75 MHz, CDCl3): δ = 160.0, 137.8, 134.3, 132.7, 130.5, 128.8, 128.6, 126.8, 123.4, 118.0, 114.5, 68.7, 68.1, 34.0.

MS (EI, 70 eV): m/z = 281 [M+]．


**C-(1,1-Biphenyl-4-yl)-N-(2-phenylethyl)nitrone (2e)**

Colorless crystals (recrystallized from PE–CH3Cl); mp 122–123 °C.

IR (KBr): 3067, 1607, 1459, 1260, 1150, 1081 cm–1.


**N-(2-Fluorophenyl)-C-(4-methoxyphenyl)nitrone (2h)**

Colorless crystals (recrystallized from PE–CH3Cl); mp 80–81 °C.

IR (KBr): 3209, 1604, 1507, 1273, 1178, 1160, 1027 cm–1.

1H NMR (300 MHz, CDCl3): δ = 8.16 (d, J = 9.0 Hz, 2 H), 7.72–7.16 (m, 2 H), 7.05 (s, 1 H), 6.97–6.90 (m, 4 H), 4.05 (t, J = 6.9 Hz, 2 H), 3.84 (s, 3 H), 3.27 (t, J = 6.9 Hz, 2 H).

13C NMR (75 MHz, CDCl3): δ = 163.3, 161.0, 160.1, 134.5, 133.5, 133.4, 130.5, 130.3, 130.2, 123.1, 115.5, 115.3, 113.8, 67.9, 55.3, 33.0.

MS (EI, 70 eV): m/z = 273 [M+].


**C-(4-Methoxyphenyl)-N-(2-phenylethyl)nitrone (2d)**

Colorless liquid.

IR (KBr): 3206, 1667, 1387, 1248, 1002 cm–1.

1H NMR (300 MHz, CDCl3): δ = 9.28 (d, J = 8.1 Hz, 1 H), 7.67 (s, 1 H), 7.38–7.19 (m, 6 H), 7.03 (t, J = 7.2 Hz, 1 H), 6.85 (d, J = 8.1 Hz, 1 H), 4.14 (t, J = 7.5 Hz, 2 H), 3.79 (s, 3 H), 3.32 (t, J = 7.2 Hz, 2 H).

13C NMR (75 MHz, CDCl3): δ = 165.9, 137.8, 131.5, 129.3, 128.8, 128.7, 126.7, 120.7, 119.4, 109.8, 68.7, 55.5, 34.2.

MS (EI, 70 eV): m/z = 255 [M+].

HRMS (EI): m/z [M+] calcd for C16H17NO2: 255.1264; found: 255.1264.

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Chemoselective Rearrangement of 3-Aryloxaziridines

Silver Triflate/Acetic Acid Catalyzed Rearrangement of Oxaaziridines 1 to Amides 3 (Table 3, Conditions B); General Procedure

To a DCE soln (4 mL) containing AgOTf (6.5 mg, 0.025 mmol) in a Schlenk tube under N₂, a 3-aryloxaziridine 1a–j (0.5 mmol) and AcOH (15 µL, 0.25 mmol) were added at r.t. The reaction mixture was then heated at 70 °C until the starting material was completely consumed, as monitored by TLC. The reaction mixture was purified by flash chromatography to directly afford the corresponding amide 3a–j.

4-Methoxy-N-(2-phenylethyl)benzamide (3a)†
Colorless crystals (recrystallized from PE–CH₂Cl₂); mp 116–117 °C.
IR (KBr): 3329, 1642, 1551, 1330, 1037 cm⁻¹.
1H NMR (300 MHz, CDCl₃): δ = 7.66 (d, J = 6.9 Hz, 2 H), 7.34–7.22 (m, 5 H), 6.89 (d, J = 9.2 Hz, 2 H), 6.11 (br s, 1 H), 3.83 (s, 3 H), 3.70 (td, J = 6.9, 5.9 Hz, 2 H), 2.92 (t, J = 6.9 Hz, 2 H).
13C NMR (75 MHz, CDCl₃): δ = 166.9, 162.1, 139.0, 128.8, 128.7, 128.6, 126.8, 126.5, 113.7, 55.3, 41.0, 35.8.
MS (EI, 70 eV): m/z = 255 [M⁺].

4-Methyl-N-(2-phenylethyl)benzamide (3b)‡
Colorless crystals (recrystallized from PE–CH₂Cl₂); mp 76–77 °C.
IR (KBr): 3335, 1642, 1544, 1324, 1027 cm⁻¹.
1H NMR (300 MHz, CDCl₃): δ = 7.59 (d, J = 6.3 Hz, 2 H), 7.35–7.18 (m, 7 H), 6.17 (br s, 1 H), 3.73–3.67 (m, 2 H), 2.92 (t, J = 6.9 Hz, 2 H), 2.37 (s, 3 H).
13C NMR (75 MHz, CDCl₃): δ = 167.4, 141.8, 139.0, 131.8, 129.2, 129.8, 128.7, 126.8, 126.5, 41.0, 35.7, 21.4.
MS (EI, 70 eV): m/z = 239 [M⁺].

4-Allyloxy-N-(2-phenylethyl)benzamide (3c)
Colorless crystals (recrystallized from PE–CH₂Cl₂); mp 181–182 °C.
IR (KBr): 3395, 1652, 1538, 1185, 1018 cm⁻¹.
1H NMR (300 MHz, CDCl₃): δ = 7.77–7.57 (m, 6 H), 7.47–7.22 (m, 8 H), 6.22 (br s, 1 H), 3.77–3.71 (m, 2 H), 2.95 (t, J = 7.2 Hz, 2 H).
13C NMR (75 MHz, CDCl₃): δ = 167.1, 144.2, 140.0, 138.9, 133.3, 128.9, 128.8, 127.9, 127.9, 127.2, 127.2, 126.6, 41.1, 35.7.
MS (EI, 70 eV): m/z = 301 [M⁺].
HRMS (EI): m/z [M⁺] calcd for C₂₁H₁₈NO: 301.1467; found: 301.1463.

N-(4-Fluorophenethyl)-1,1'-biphenylyl-4-carboxamide (3e)§
Colorless crystals (recrystallized from PE–CH₂Cl₂); mp 138–139 °C.
IR (KBr): 3351, 1633, 1544, 1507, 1182, 1024 cm⁻¹.
1H NMR (300 MHz, CDCl₃): δ = 7.69 (d, J = 6.9 Hz, 2 H), 7.15–7.01 (m, 2 H), 7.01–6.86 (m, 4 H), 6.27 (br s, 1 H), 3.82 (s, 3 H), 3.68–3.61 (m, 2 H), 2.88 (t, J = 7.2 Hz, 2 H).
13C NMR (75 MHz, CDCl₃): δ = 167.0, 163.2, 162.1, 160.0, 134.7, 134.6, 130.2, 130.1, 128.6, 126.7, 115.5, 115.2, 113.7, 55.3, 41.1, 34.9.
MS (EI, 70 eV): m/z = 273 [M⁺].
4-Methoxy-N-(3-phenylpropyl)benzamide (3g)

Colorless crystals (recrystallized from PE–CH2Cl2); mp 88–89 °C.

IR (KBr): 3266, 1639, 1535, 1248, 1034 cm–1.


MS (EI, 70 eV): 137 [M-NO2] and 93 [M-NO2-CH3].

1H NMR (300 MHz, CDCl3): δ = 8.20 (d, J = 6.9 Hz, 1 H), 7.67 (br s, 1 H), 7.10–6.95 (m, 2 H), 4.19–4.10 (m, 1 H), 3.86 (s, 3 H), 1.63–1.53 (m, 2 H), 0.97 (t, J = 7.5 Hz, 3 H).

13C NMR (75 MHz, CDCl3): δ = 166.7, 159.8, 136.6, 129.5, 118.4, 117.4, 112.3, 55.4, 47.1, 29.8, 20.5, 10.4.

MS (EI, 70 eV): m/z = 269 [M+].

HRMS (EI): m/z = 207 [M+].

Acknowledgment

Financial support from The Science and Technology Commission of Shanghai Municipality is gratefully acknowledged.

References


