C-Imidoylation of esters, sulfones, sulfoxides, amides and nitro compounds

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Abstract
C-Imidoylation of esters, sulfones, sulfoxides, amides, and nitro compounds with N-imidoylbenzotriazoles 1a–g gives β-enaminoesters 2a–d, β-iminosulfones 6a–c, β-enaminosulfoxides 7a–c, β-iminoamides 9a–d, and α-nitroamines 10a–c respectively in yields averaging 60%.

Keywords: Imidoylation, β-enaminoesters, β-iminosulfones, iminosulfoxides, β-iminoamides, α-nitroimines

Introduction
C-Acylations of activated CH groups are familiar reactions for many classes of compounds including alkanecarboxylic esters,1a–b alkyl sulfones2a and sulfoxides,2b and aliphatic nitro compounds.3a–b By contrast there are only limited reports of analogous C-imidoylation reactions although C-imidoylated products are useful for the preparation of natural products such as apo-β-erythroidine,4a and (+/-)-lupinine,4b terpenes,4c 2,2’-bis-imidazoles4d for receptors, supramolecular architectures, and seleno-imidates4e (Figure 1). Radical-mediated group-transfer imidoylation has been widely applied in synthetic and theoretical studies of organometallic compounds.4g
We reasoned that N-imidoylbenzotriazoles could enable efficient C-imidoylation, by analogy with the many applications of N-acylbenzotriazoles in C-acylation. We now disclose simple procedures for the imidoylation at carbon of esters, sulfoxides, amides, and nitro compounds via deprotonation in the presence of a strong base followed by treatment with imidoylbenzotriazoles 1a–g.

The imidoylbenzotriazoles 1 are important stable alternatives to the corresponding imidoyl chlorides. Major synthetic strategies utilized for the preparation of the imidoylbenzotriazoles 1 include reaction of secondary amides with: (i) benzotriazole and POCl₃ in the presence of triethylamine; (ii) triphenylphosphine and 1-chlorobenzotriazole; or (iii) 1,1′-sulfinyldibenzo[d]triazole. Imidoylbenzotriazoles 1a–g were prepared in good yields (50–90%) from the reaction of a secondary amide (1 equiv.), oxalyl chloride (1 equiv.) and benzotriazole (2 equiv.) in the presence of pyridine (Scheme 1). The crude products were washed with aqueous sodium carbonate and were chromatographed on basic alumina (EtOAc/Hex.) to give pure imidoylbenzotriazoles 1a–g.

\[ R^3\text{HN} + \text{(COCl)}_2 \rightarrow R^3\text{HN} \]

**Scheme 1**

**C-Imidoylation of esters**

**Figure 1.** Apo-β-erythroidine, (+/-)-lupinine, 2,2’-biimidazoles, and selenoimidates.
The β-Enaminoesters 2a–d were prepared in 77–88% yield from the reaction of the corresponding ester enolate with imidoylbenzotriazoles 1 (Scheme 3, Table 1). Published C-imidoylations of esters 2 (Scheme 2) include; (i) efficient reactions with ester enolates, but these are limited to fluorinated imidoyl chlorides;8a–c (ii) reaction of malonic esters with alkyl carboximidates, alkyl carboximidothioates, or carboximidic chlorides,9a (iii) a single reaction of an isocyanoide with a cyanoester sulfide;9b or, (iv), one example of the condensation of ethyl cyanoacetate with bis-(imidoyl)chloride.9c Alternative access to compounds 2 is given by amination of β-ketoesters (no yields are mentioned).10

**Preparations of β-enaminoesters 2a–d from imidoylbenzotriazoles (1a,b).** The imidoylbenzotriazoles 1a,b were reacted with the enolates generated from the corresponding esters 3a–d by treatment with potassium tert-butoxide at room temperature (Scheme 3). Treatment of 2 equiv. of the ester enolates 3a–d with 2.5 equiv. of potassium tert-butoxide in THF at room temperature, followed by 1 equiv. of imidoylbenzotriazoles 1a,b, afforded the β-enaminoesters 2a–d in excellent yields (Table 1) with reduced times. If less potassium tert-butoxide was used the reaction was incomplete.

![Chemical structure](image)

**Scheme 2**

Elemental analysis and NMR spectral data support the structural assignments of the novel products 2a–d. The 1H-NMR spectra of β-enaminoesters 2a–d reveal a broad signal at 11.25–11.40 ppm which is assigned to the N-H proton. Thus, the structures of 2a–d have a double bond between the ester and the imidoyl carbons (Scheme 3). Attempted C-imidoylation of esters 3c,d using imidoylbenzotriazole 1g gave only the imidoyl esters 4a,b (73% average yield) (Scheme 3).

**Table 1. Preparation of β-enaminoesters 2a–d**

<table>
<thead>
<tr>
<th></th>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>Product</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>Ph</td>
<td>Me</td>
<td>Me</td>
<td>p-Tol</td>
<td>88</td>
</tr>
<tr>
<td>3b</td>
<td>Naphthyl</td>
<td>Me</td>
<td>Me</td>
<td>p-Tol</td>
<td>85</td>
</tr>
</tbody>
</table>
### Scheme 3

**C-Imidoylation of sulfones**

Previous successful imidoylations of sulfones by imidoyl chlorides are limited to fluorinated imidoyl chlorides and aryl methyl sulfones \((R^1=H, R^3=Ar, Alk)\). Other reports of C-imidoylations of sulfones describe analytical and spectral data, but the products were not characterized fully. Other than forming a C–C bond between imidoyl chlorides and sulfones, compound 6 can be prepared by the reaction of linear \(\beta\)-ketoalkyl sulfones with simple amines. However, linear \(\beta\)-ketoalkyl sulfones are of limited stability, which dramatically affects the yields. We have now prepared the \(\beta\)-iminosulfones 6a–c in 75–97% yield by the reaction of imidoylbenzotriazoles 1a,f with sulfones 5a,b (Scheme 4, Table 2).

### Scheme 4

**Preparations of \(\beta\)-iminosulfones 6a–c from imidoylbenzotriazoles (1a,f).** Treatment of the sulfones 5a,b (2 equiv.) with potassium tert-butoxide (2.5 equiv.) (6a,c) or n-BuLi (1.1 equiv.) (6b) in THF followed by an imidoylbenzotriazoles 1a,f afforded the \(\beta\)-iminosulfones 6a–c (Scheme 4). The progress of the reaction was monitored by TLC. Upon completion of the reaction, water was added and the organic layer was separated then chromatographed to give pure \(\beta\)-iminosulfones 6a–c in 53–97% yields (Table 2). The novel \(\beta\)-iminosulfones 6a–c were characterized by NMR and elemental analysis. In the \(^1\)H-NMR spectra a signal in the region 4.30–5.16 is assigned to the proton attached to the carbon between the sulfone- and the imidoyl groups. In the case of 6c, both the imine and the enamine tautomers formed in a 53:47 ratio.
Table 2. Preparation of β-iminosulfones 4a–c

<table>
<thead>
<tr>
<th>Reagent</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>R&lt;sup&gt;3&lt;/sup&gt;</th>
<th>R&lt;sup&gt;4&lt;/sup&gt;</th>
<th>Product</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Ph</td>
<td>Ph</td>
<td>Me</td>
<td>p-Tol</td>
<td>6a</td>
<td>97</td>
</tr>
<tr>
<td>1g</td>
<td>Ph</td>
<td>Ph</td>
<td>Furyl</td>
<td>p-Tol</td>
<td>6b</td>
<td>53</td>
</tr>
<tr>
<td>1c</td>
<td>Ph</td>
<td>Ph</td>
<td>Bn</td>
<td>p-Tol</td>
<td>6c</td>
<td>65</td>
</tr>
</tbody>
</table>

C-Imidoylation of sulfoxides

Reported imidoylations of the sulfoxides 3 include (i) reaction of fluorinated imidoyl chlorides with methylsulfinyl carbanion (but yields were greatly influenced by the nature of the methylsulfinyl carbanion),<sup>12a–c</sup> and (ii) reactions of unstable nitriles with methylsulfinyl carbanion (R<sup>1</sup>=H) (Scheme 5).<sup>13</sup> We prepared the β-enaminsulfoxides 7a–c in 48–78% yield from the reaction of imidoylbenzotriazoles 1e–g with sulfoxides (Scheme 6, Table 3).

![Scheme 5](image)

Scheme 5

Preparations of β-enaminsulfoxides 7a–c from imidoylbenzotriazoles (1e–g). Potassium tert-butoxide (2 equiv.) or n-BuLi (1.1 equiv.) (in the case of 7b) was added to the sulfoxide (2 equiv.) in THF at room temperature followed by imidoylbenzotriazole (1 equiv.). Upon completion, the reaction mixture was hydrolyzed with water and extracted with chloroform. After workup, the residue was purified by flash column chromatography on silica to afford pure β-enaminsulfoxides 7a–c (Scheme 6, Table 3). Compound 7a, isolated in good yield, existed only in a single tautomeric structure; the N-H proton could be observed at 7.2 ppm. However in the cases of both 7b and 7c the imine and the enamine tautomers (30:70 ratio) exist in equilibrium, with the N-H protons appearing at ca 7.6 ppm.

![Scheme 6](image)

Scheme 6
Table 3. Preparation of β-enaminosulfoxides 7a–c

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>R⁴</th>
<th>Product</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>Ph</td>
<td>Ph</td>
<td>7a</td>
<td>78</td>
</tr>
<tr>
<td>H</td>
<td>Me</td>
<td>Furyl</td>
<td>p-Tol</td>
<td>7b</td>
<td>48</td>
</tr>
<tr>
<td>H</td>
<td>Me</td>
<td>p-Tol</td>
<td>4-MeOC₆H₄</td>
<td>7c</td>
<td>71</td>
</tr>
</tbody>
</table>

C-Imidoylation of amides

C-Imidoylation of amides is apparently unexplored: no report of the preparation of a β-iminoamide by C–C bond formation has been located. A single example of the preparation of an α-iminoamide by the reaction of an imidoyl chloride with a carbamoylsilane under palladium(0) catalysis was reported recently.¹⁴ β-Iminoamides 9a–d have now been prepared in 51–75% yield by the reaction of imidoarylbenzotriazoles 1a,c,e,g with amides 8a–c (Scheme 7, Table 4).

Preparations of β-iminoamides 7a–d from imidoarylbenzotriazoles (1a,c,e,g). Deprotonation of the amide was carried out using n-BuLi, after which imidoarylbenzotriazole was added to the reaction mixture. The pure β-imino-amides 9a–d (Scheme 7, Table 4) were obtained in 48–75% yield. NMR data prove that we had obtained the imine tautomers of compounds 9a–d. There was no evidence of the N-H proton, but a singlet assigned to the proton on the α-carbon was seen around 3.6 ppm. The two Et groups of 9a,c showed different signals in the H-NMR, indicating restricted rotation around the Et₂N–CO bond. The structures of the novel compounds 9a–d were supported by elemental analysis.

Scheme 7

Table 4. Preparation of β-iminoamides 9a–d

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>R⁴</th>
<th>Product</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>Et</td>
<td>Me</td>
<td>p-Tol</td>
<td>9a</td>
<td>51</td>
</tr>
<tr>
<td>Ph</td>
<td>Et</td>
<td>Furyl</td>
<td>p-Tol</td>
<td>9b</td>
<td>48</td>
</tr>
<tr>
<td>Ph</td>
<td>Et</td>
<td>Bn</td>
<td>p-Tol</td>
<td>9c</td>
<td>75</td>
</tr>
<tr>
<td>Ph</td>
<td>Et</td>
<td>p-Tol</td>
<td>4-MeOC₆H₄</td>
<td>9d</td>
<td>69</td>
</tr>
</tbody>
</table>
C-Imidoylation of nitro compounds

A single example of C-imidoylation of a nitro compound involved ethyl nitroacetate and an imidoyl chloride (Scheme 8).\textsuperscript{15} So far, no general procedure for C-imidoylation of nitro compounds has been reported. It was suggested on infrared and NMR spectral evidence that the imidoylation product arose from the rearrangement of the N-nitroenamine shown (Scheme 8).\textsuperscript{16}

We have now prepared \( \alpha \)-nitroenamines \textbf{10a–c} in 34–60\% yield by the reaction of imidoylbenzotriazoles \textbf{1a,c,e} with nitroethane (Scheme 9, Table 5).

\begin{center}
\textbf{Scheme 8}
\end{center}

\textbf{Preparations of \( \alpha \)-nitroenamines \textbf{10a–c} from imidoylbenzotriazoles (1a,c,e).} Potassium tert-butoxide was added to nitroethane at room temperature followed by imidoylbenzotriazoles \textbf{1a,c,e} in DMSO. Purification of the crude product gave pure \( \alpha \)-nitroenamines \textbf{10a–c} (Scheme 9, Table 5). Compounds \textbf{10a–c} were isolated as the enamine tautomeric structure, as indicated by the N-H peak in the 7.2–7.7 region of the \( ^1 \text{H} \) NMR spectra. Elemental analysis was also used to further verify the identities of the novel \textbf{10a–c}.

\begin{center}
\textbf{Scheme 9}
\end{center}

\textbf{Table 5. Preparation of \( \alpha \)-nitroenamines \textbf{10a–c}}

<table>
<thead>
<tr>
<th>( R^3 )</th>
<th>( R^4 )</th>
<th>Product</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>( p )-Tol</td>
<td>\textbf{10a}</td>
<td>60</td>
</tr>
<tr>
<td>( p )-Tol</td>
<td>4-OMeC(_6)H(_4)</td>
<td>\textbf{10b}</td>
<td>34</td>
</tr>
<tr>
<td>Bn</td>
<td>( p )-Tol</td>
<td>\textbf{10c}</td>
<td>50</td>
</tr>
</tbody>
</table>
**Tautomeric structures of products**

These imidoylation products are potentially tautomeric with alternative imine or enamine structures. Throughout this paper, compounds have been designated as the predominant form in solution; these forms are easily identified by NMR analysis. The enamine form predominates for the imidoylated products 2a–d of esters, 7a–c of sulfoxides, and 10a–c of nitro compounds. However, the imidoylated products 6a–c of sulfones, and 9a–d of amides exist in the imide form. We have located no previous discussion of the tautomerism of the products of imidoylation of esters, sulfones, sulfoxides, amides and nitro compounds in the literature. In the references cited in the present paper, some structures were represented in the imino-form\(^{11a-b, 12a, 14}\) and others in the enamino-form\(^{8a-c}\) evidence of the structure assignment was provided via NMR analysis.

In the present work, we utilized NMR to assign the precise tautomeric structure of each product. The position of tautomeric equilibrium is classified by consideration of the common cation 11 formed by the two forms 12 and 13. Thus a strongly inductively electron-withdrawing substituent X in 11 is expected to increase the acidity of the \(\alpha\)-proton; mesomeric electron withdrawal by contrast will increase the acidity of the NH\(_{2}\) proton because of increased interaction in 13. This helps to explain the preference of the enamine form for esters 2, sulfoxides 7 and nitro compounds 10, but of the imine form for sulfones 6 and amides 9.

![NMR diagram]

**Conclusions**

A simple and straightforward method for the C-imidoylation of esters, sulfones, sulfoxides, amides, and nitro compounds was established using the imidoylbenzotriazoles 1a–i. The imidoylated products 2a–d, 6a–c, 7a–c, 9a–d, and 10a–c were easily isolated in 34–97%, average 80 %, yield.

**Experimental Section**

**General Procedures.** Melting points were determined on a hot-stage apparatus and are uncorrected. NMR spectra were recorded in CDCl\(_3\), or DMSO-\(d_6\) with TMS as the internal standard for \(^1\)H-(300 MHz) or a solvent as the internal standard for \(^13\)C- NMR (75 MHz).
Column chromatography was conducted on silica gel (200–425 mesh) or on basic alumina (60–325 mesh). Microwave heating was carried out with a single-mode cavity Discover Microwave Synthesizer (CEM Corporation, NC).

**General procedure for the preparation of β-enaminoesters 2a–d**

To a stirred solution of the corresponding ester (1.2 mmol) and potassium tert-butoxide (1.5 mmol) in THF (20 mL) was added (0.6 mmol) of 1. The mixture was stirred at room temperature for 1–2 hours. Progress of the reaction was monitored by TLC. After the reaction was complete, water (20 mL) was added to the reaction mixture which was then extracted with dichloromethane (3x30 mL). The combined extracts were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the remaining residue was purified by gradient column chromatography on silica gel (ethyl acetate/hexanes) to give pure β-enaminoesters 2a–d.

**Methyl 3-[(4-methylphenyl)imino]-2-phenylbutanoate (2a).** Recrystallized from EtOAc–hexanes to give white microcrystals (88%), mp 94–95 °C; ¹H NMR δ 11.21 (br. s, 1H), 7.27–7.10 (m, 5H), 7.05 (d, J = 8.2 Hz, 2H), 6.93 (d, J = 8.2 Hz, 2H), 3.59 (s, 1H), 3.53 (s, 3H), 2.24 (s, 3H), 1.67 (s, 3H); ¹³C NMR δ 170.4, 158.1, 138.3, 136.8, 134.8, 132.0, 129.6, 127.9, 126.2, 125.1, 50.8, 41.1, 20.8, 18.4. Anal. Calcd for C₁₈H₁₉NO₂: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.62; H, 6.94; N, 4.81.

**Methyl 2-(1-naphthyl)-3-(4-toluidino)-2-butenoate (2b).** Recrystallized from EtOAc–hexanes to give white microcrystals (85%), mp 111–112 °C; ¹H NMR δ 11.25 (br. s, 1H), 7.85–7.82 (m, 1H), 7.78–7.75 (m, 1H), 7.72–7.69 (m, 1H), 7.41–7.35 (m, 3H), 7.28–7.25 (m, 1H), 7.05 (d, J = 8.2 Hz, 2H), 6.99 (d, J = 8.2 Hz, 2H), 3.42 (s, 3H), 2.24 (s, 3H), 1.53 (s, 3H); ¹³C NMR δ 170.8, 158.8, 136.8, 135.8, 134.9, 133.8, 133.8, 129.6, 129.6, 128.3, 127.2, 125.8, 125.6, 125.5, 125.1, 95.9, 50.8, 50.8, 20.8, 18.0. Anal. Calcd for C₂₂H₂₁NO₂: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.54; H, 6.50; N, 4.35.

**Isopropyl 3-(4-toluidino)-2-butenoate (2c).** Yellow oil (82%); ¹H NMR δ 11.32 (br. s, 1H), 7.08 (d, J = 8.1 Hz, 2H), 6.65 (d, J = 8.1 Hz, 2H), 5.18 (d, 1H), 2.30 (s, 3H), 1.78 (s, 3H), 1.30 (d, J = 6.2 Hz, 6H); ¹³C NMR δ 160.4, 144.3, 131.8, 129.5, 120.9, 115.7, 67.4, 58.8, 37.9, 22.6, 20.8. Anal. Calcd for C₁₄H₁₉NO₂: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.57; H, 8.08; N, 9.04.

**Methyl 3-isobutylamino-2-butenoate (2d).** Yellow oil (78%); ¹H NMR δ 11.40 (br. s, 1H), 5.42 (s, 1H), 3.00 (t, J = 6.3 Hz, 2H), 1.92 (s, 3H), 1.71–1.64 (m, 1H), 1.18 (s, 3H), 0.84 (d, J = 6.7 Hz, 6H); ¹³C NMR δ 170.0, 155.9, 47.0, 31.9, 29.7, 28.4, 23.4, 20.1.

**Isopropyl N-(4-methylphenyl)-2-furancarboximidoate (4a).** Colorless oil (79%); ¹H NMR δ 7.32 (s, 1H), 7.09 (d, J = 8.0 Hz, 2H), 6.69 (d, J = 8.0 Hz, 2H), 6.23–6.21 (m, 1H), 5.97–5.96 (m, 1H), 5.35–5.31 (m, 1H), 2.33 (s, 3H), 1.42 (d, J = 6.2 Hz, 6H); ¹³C NMR δ 148.6, 146.2, 143.2, 132.0, 129.7, 120.0, 116.1, 111.0, 103.3, 68.4, 21.8, 20.8. Anal. Calcd for C₁₅H₁₇NO₂: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.26; H, 7.38; N, 5.78.

**Methyl N-(4-methylphenyl)-2-furancarboximidoate (4b).** Colorless oil (67%); ¹H NMR δ 7.33 (s, 1H), 7.10 (d, J = 8.1 Hz, 2H), 6.71 (d = 8.1 Hz, 2H), 6.24–6.23 (m, 1H), 5.96–5.95 (m, 1H), 3.96 (s, 3H), 2.33 (m, 3H); ¹³C NMR δ 149.8, 145.8, 143.3, 143.2, 132.3, 129.7, 120.0,
General procedure for the preparation of β-iminosulfones 6a and 6c
To a stirred solution of the corresponding sulfone (1.2 mmol) and potassium tert-butoxide (1.5 mmol) in THF (20 mL) was added (0.6 mmol) of 1. The mixture was stirred at room temperature for 7–10 hours. Progress of the reaction was monitored by TLC. After the reaction was complete, water (20 mL) was added to the reaction mixture which was then extracted with dichloromethane (3x30 mL). The combined extracts were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the remaining residue was purified by gradient column chromatography on silica gel (ethyl acetate/hexanes) to give pure β-iminosulfones 6a and 6c.

4-Methyl-N-[1-methyl-2-phenyl-2-(phenylsulfonyl)ethylidene]aniline (6a). Colorless oil (97%); 1H NMR δ 7.50 (d, J = 7.8 Hz, 2H), 7.36–7.14 (m, 8H), 6.89 (d, J = 8.1 Hz, 2H), 6.54 (d, J = 8.1 Hz, 2H), 5.16 (s, 1H), 2.31 (s, 3H), 2.16 (s, 3H); 13C NMR δ 156.4, 144.8, 135.4, 134.0, 132.6, 130.3, 129.8, 129.7, 128.7, 128.5, 127.0, 124.3, 115.2, 53.5, 41.9, 34.6. Anal. Calcd for C22H21NO2S: C, 72.70; H, 5.82; N, 3.85. Found: C, 72.25; H, 5.87; N, 3.89.

N-[1-Benzyl-2-phenyl-2-(phenylsulfonyl)-1-ethenyl]-N-(4-methylphenyl)amine (6c). Yellow oil (65%); 1H NMR δ (mixture of tautomers) 9.66 (s, 0.61H), 7.71–7.682 (m, 1.54H), 7.61–7.51 (m, 2.78H), 7.44–7.33 (m, 5.38H), 7.29–7.17 (m, 5.48H), 7.14–7.05 (m, 6.51H), 7.00 (d, J = 8.1 Hz, 2.22H), 6.95 (d, J = 6.9 Hz, 2.22H), 6.86–6.84 (m, 2.70H), 6.74–6.72 (m, 1.9H), 6.63 (d, J = 8.1 Hz, 1.6H), 5.10 (s, 0.54H), 3.70–3.38 (m, 0.86H), 3.42 (s, 2H), 2.32 (s, 2.1H), 2.28 (s, 2.8H); 13C NMR δ 163.9, 154.4, 146.8, 142.5, 137.8, 137.0, 136.4, 135.7, 134.7, 133.7, 133.4, 133.2, 132.4, 130.9, 130.1, 129.7, 129.6, 129.5, 129.2, 129.1, 128.9, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.0, 126.9, 126.1, 126.3, 118.7, 115.2, 107.4, 112.2, 74.1, 39.9, 35.9, 20.9, 20.8. HRMS (EI) Calcd for C28H25NO2S (M+Na)⁺: 462.1498. Found: 462.1487.

Procedure for the preparation of 6b
To (0.50 mmol) of benzylphenylsulfone in 15 mL THF at -78 °C was added (0.55 mmol) n-BuLi dropwise over a period of 15 min. The mixture was warmed to -20 C, stirred for 1 h at this temperature and re-cooled to -78 °C. A solution of 1g (0.5 mmol) in 10 mL THF was added to the mixture over a period of 15 min. The mixture was stirred for 1 h at -78 C, then warmed to room temperature and stirred overnight. The mixture was quenched with 20 mL saturated NH4Cl then extracted with (3x25 mL) dichloromethane. The organic layer was dried over magnesium sulfate, concentrated and chromatographed on silica gel (EtOAc/hexanes gradient) to give 6b.

N-[1-(2-Furyl)-2-phenyl-2-(phenylsulfonyl)ethylidene]-N-(4-methylphenyl)amine (6b). Yellow gum (53%); 1H NMR δ 7.58–7.52 (m,1 H), 7.39–7.33 (m, 4 H), 7.22–7.14 (m, 3H), 7.01–6.95 (m, 5H), 6.76 (d, J = 8.1 Hz, 2H), 6.35 (d, J = 7.8 Hz, 2H), 6.24 (s, 1H), 2.15 (s, 3H); 13C NMR δ 144.3, 143.7, 139.5, 138.6, 136.7, 136.4, 134.4, 133.3, 130.9, 130.3, 129.4, 128.7, 128.6, 128.4, 128.2, 127.9, 118.6, 77.2, 20.6. Anal. Calcd for C50H44N2O7S2.0.5 HCl: C, 69.23; H, 5.00; N, 3.23. Found: C, 68.84; H, 5.28; N, 2.95.
General procedure for the preparation of β-iminosulfoxides 7a and 7c
To a stirred solution of the corresponding sulf oxide (0.7 mmol) and THF (10 mL), t-BuOK (0.7 mmol) was added at room temperature and the reaction mixture was stirred for 15 min. A solution of 1 (0.35 mmol) in THF (2 mL) was added slowly by syringe, and the mixture was allowed to react for 1.5–3 h at room temperature (TLC control). The reaction mixture was hydrolyzed with water (10–15 mL) and extracted with chloroform. The aqueous phase was acidified to pH 6–7 by addition of hydrochloric acid and extracted with chloroform. Combined organic layers were dried over anhydrous magnesium sulfate, filtered and evaporated under vacuum. The residue was purified by flash column chromatography on silica using hexanes/EtOAc (9/1) as an eluent to give pure β-iminosulfoxides 7a and 7c.

N-[1,2-Diphenyl-2-(phenylsulfinyl)ethylidene]aniline (7a). Colorless oil (78%); \(^1\)H NMR δ 7.84 (d, \(J = 7.3\) Hz, 5H), 7.65 (d, \(J = 8.2\) Hz, 4H), 7.55–7.44 (m, 5H), 7.37 (t, \(J = 7.8\) Hz, 4H), 7.16 (t, \(J = 7.4\) Hz, 2H), 4.30 (s, 1H); \(^{13}\)C NMR δ 165.7, 148.8, 137.9, 135.0, 133.7, 132.6, 131.8, 130.8, 129.1, 128.8, 128.7, 128.6, 127.0, 124.6, 120.2, 62.8. Anal. Calcd for C\(_{26}\)H\(_{21}\)NOS: C, 78.95; H, 5.35; N, 3.54. Found: C, 79.24; H, 5.62; N, 6.08.

N-(4-Methoxyphenyl)-N-[1-(4-methylphenyl)-2-(methylsulfinyl)-1-ethenyl]amine (7c). Recrystallized from EtOAc/Hexane to give white crystals (71%), mp 137–139 °C; \(^1\)H NMR δ (mixture of isomers 57:43) 7.74 (d, \(J = 8.1\) Hz, 2H), 7.58 (br. s, 1H), 7.51 (d, \(J = 8.7\) Hz, 2H), 7.25 (d, \(J = 9.0\) Hz, 2H), 7.15 (d, \(J = 8.1\) Hz, 2H), 6.97 (d, \(J = 8.1\) Hz, 2H), 6.90 (d, \(J = 9.0\) Hz, 2H), 6.69 (d, \(J = 9.0\) Hz, 2H), 6.57 (d, \(J = 8.7\) Hz, 2H), 3.79 (s, 3H), 3.71 (s, 2.3H), 2.40 (s, 3H), 2.26 (s, 2.33H), 1.61 (s, 6H), 1.41 (s, 1H), 1.27 (s, 1H); \(^{13}\)C NMR δ 166.0, 157.7, 156.5, 155.2, 142.2, 139.9, 139.1, 132.5, 132.0, 131.1, 129.5, 129.4, 128.5, 126.9, 122.3, 122.0, 114.2, 114.0, 80.5, 77.2, 55.5, 55.4, 28.3, 28.4, 21.5, 21.3. Anal. Calcd for C\(_{17}\)H\(_{19}\)NO\(_2\)S: C, 67.74; H, 6.35; N, 4.65. Found: C, 67.22; H, 6.69; N, 4.58.

Procedure for the preparation of 7b
To (0.40 mmol) dimethyl sulfoxide in 15 mL THF -78 °C was added (0.44 mmol) n-BuLi dropwise over a period of 15 min. The mixture was warmed to -20 °C, stirred for 1 h at this temperature and cooled to -78 °C. A solution of 1g (0.40 mmol) in 10 mL THF was added to the mixture over a period of 15 min. The mixture was stirred for 1 h at -78 °C, then warmed to room temperature and stirred overnight. The mixture was quenched with 20 mL saturated NH\(_4\)Cl then extracted with (3x25 mL) dichloromethane. The organic layer was dried over magnesium sulfate, concentrated, and chromatographed on silica gel (EtOAc/hexanes gradient) to give 7b.

N-[1-(2-Furyl)-2-(methylsulfinyl)-1-ethenyl]-N-(4-methylphenyl)amine (7b). (48%); \(^1\)H NMR δ (mixture of isomers 60:40) 7.62–7.61 (m, 1H), 7.41–7.40 (m, 0.61H), 7.18–7.13 (m, 4.29H), 6.77 (d, \(J = 8.1\) Hz, 2H), 6.64 (d, \(J = 8.1\) Hz, 1.34H), 6.59–6.57 (m, 1H), 6.32–6.28 (m, 0.6H), 5.78 (d, \(J = 3.6\) Hz, 0.59H), 4.53–3.99 (m, 2H), 2.82 (s, 1.86H), 2.50 (s, 3H), 2.36 (s, 1.96 H), 2.35 (s, 3H); \(^{13}\)C NMR δ 152.2, 150.5, 149.5, 148.8, 146.8, 146.5, 145.6, 143.8, 134.2, 133.6, 130.3, 129.8, 120.0, 117.6, 117.1, 115.2, 112.4, 112.3, 61.1, 53.9, 39.4, 39.3, 21.0, 20.9. Anal. Calcd for C\(_{28}\)H\(_{32}\)N\(_2\)O\(_5\)S\(_2\): C, 62.20; H, 5.97; N, 5.18. Found: C, 62.93; H, 6.07; N, 5.21.
General procedure for the preparation of β-iminoamides 9a–d
To (0.8 mmol) of the corresponding amide in 15 mL THF at -78 °C was added (0.88 mmol) n-BuLi dropwise over a period of 15 minutes. The mixture was warmed to -20 °C, stirred for 1 h at this temperature, and then re-cooled to -78 °C. A solution of 1 (0.8 mmol) in 10 mL THF was added to the mixture over a period of 15 min. The reaction mixture was stirred for 2 hrs at -78 °C, then warmed to room temperature overnight. The mixture was quenched with 20mL saturated NH_4Cl then extracted with (3x50mL) dichloromethane. The organic layer was dried over anhydrous magnesium sulfate, concentrated under vacuum, and chromatographed on silica gel (EtOAc/hexanes gradient) to give pure β-iminoamides 9a–d.

N,N-Diethyl-3-([4-methylphenyl]imino]-2-phenylbutanamide hydrochloride (9a).
Colorless oil (51%); ^1H NMR δ 7.31 (d, J = 8.4 Hz, 2H), 7.23–7.13 (m, 5H), 6.97 (d, J = 8.2 Hz, 2H), 3.61 (s, 1H), 3.30 (q, J = 7.1 Hz, 2H), 3.88 (q, J = 7.1 Hz, 2H), 1.98 (s, 3H), 1.06–0.98 (m, 6H); ^13C NMR δ 170.2, 168.8, 135.7, 135.2, 133.3, 129.1, 128.5, 126.6, 120.0, 119.7, 42.3, 40.6, 40.1, 24.0, 20.6, 14.0, 12.8. Anal. Calcd for C_{42}H_{53}ClN_4O_2: C, 74.04; H, 7.84; N, 8.22. Found: C, 73.82; H, 8.08; N, 8.46.

N,N-Diethyl-3-([2-furyl]-3-(4-toluidino)-2-phenyl-3-propenamide hydrochloride (9b).
Colorless oil (48%); ^1H NMR δ 7.65–7.62 (m, 2H), 7.42–7.40 (m, 3H), 7.30–7.26 (m, 1H), 7.09 (d, J = 8.1 Hz, 2H), 6.70 (d, J = 8.1 Hz, 2H), 6.52 (s, 1H), 6.23–6.21 (m, 2H), 6.50 (s, 1H), 3.41–3.35 (m, 4H), 2.33 (s, 3H), 1.15–1.05 (m, 6H); ^13C NMR δ 167.8, 148.4, 145.5, 143.9, 135.4, 132.2, 129.6, 128.9, 128.8, 128.7, 120.1, 116.7, 111.0, 74.4, 41.8, 40.9, 20.9, 13.7, 12.9. HRMS (EI) Calcd for C_{24}H_{26}N_2O_2: 375.2067. Found: 375.2063.

N,N-Diethyl-3-[([4-methylphenyl]imino]-2,4-diphenylbutanamide hydrochloride (9c).
Colorless oil (75%); ^1H NMR δ 7.80 (br. s, 1H), 7.34–7.22 (m, 12H), 7.05 (d, J = 8.2 Hz, 1H), 3.71 (s, 3H), 3.67 (s, 1H), 3.40 (q, J = 7.1 Hz, 2H), 3.30 (q, J = 7.1 Hz, 2H), 2.27 (s, 2H), 1.15–1.05 (m, 6H); ^13C NMR δ 170.2, 169.2, 135.3, 134.7, 133.7, 133.9, 129.3, 128.9, 127.8, 126.6, 119.9, 44.4, 42.3, 40.8, 40.1, 20.7, 14.1, 12.8. Anal. Calcd for C_{27}H_{31}N_2OCl: C, 74.55; H, 6.95; N, 6.44. Found: C, 74.49; H, 7.47; N, 5.80.

N,N-Diethyl-3-([4-methoxyanilino]-3-(4-methylphenyl)-2-phenyl-2-propenamide hydrochloride (9d).
Pale yellow solid (69%), mp 130–131 °C; ^1H NMR δ 7.64–7.61 (m, 2H), 7.43–7.22 (m, 4H), 6.99 (d, J = 8.1 Hz, 2H), 6.73–6.6 (m, 4H), 6.54 (s, 1H), 3.74 (s, 3H), 3.43–3.32(m, 4H), 2.26 (s, 3H), 1.14–1.06 (m, 6H); ^13C NMR δ 168.2, 158.3, 152.5, 141.4, 140.0, 138.2, 135.7, 129.7, 128.7, 128.69, 128.5, 127.9, 122.3, 114.0, 74.4, 55.3, 41.8, 40.8, 21.4, 13.7, 12.9. Anal. Calcd for C_{27}H_{30}N_2O_2.0.5HCl: C, 74.93; H, 7.10; N, 6.47. Found: C, 74.82; H, 7.32; N, 6.23.

General procedure for the preparation of α-nitroimines 10a–c
To the corresponding nitro compound (1.2 mmol) was added potassium tert-butoxide (1.5 mmol) at room temperature followed by 1 (0.6 mmol) in DMSO (10 mL). The mixture was heated and stirred at 50 °C for 5 hours. Progress of the reaction was monitored by TLC. Upon the completion of the reaction, HCl or acetic acid was used to acidify the reaction mixture. The organic layer was then extracted with dichloromethane (3x30 mL). The combined extracts were
dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the remaining residue was purified by gradient column chromatography on silica gel (ethyl acetate/hexanes) to give pure α-nitroimines 10a–c.

4-Methyl-N-[1-methyl-2-nitropropylidene]aniline (10a). Colorless oil (60%); $^{1}$H NMR δ 7.71 (br. d, 1H), 7.30 (d, $J = 8.2$ Hz, 2H), 7.01 (d, $J = 8.1$ Hz, 2H), 2.32 (s, 3H), 2.22 (s, 3H), 2.06 (s, 3H); $^{13}$C NMR δ 168.6, 135.4, 133.7, 129.3, 120.0, 70.4, 24.3, 20.8, 16.3. Anal. Calcd for C$_{22}$H$_{30}$N$_{4}$O$_{5}$: C, 61.38; H, 7.02; N, 13.01. Found: C, 61.96; H, 7.28; N, 11.32.

N-(4-Methoxyphenyl)-N-[1-(4-methylphenyl)-2-nitro-1-propenyl]amine (10b). Yellow oil (34%); $^{1}$H NMR δ 7.14 (d, $J = 8.1$ Hz, 2H), 7.06 (d, $J = 8.1$ Hz, 2H), 6.72–6.62 (m, 5H), 3.71 (s, 3H), 2.35 (s, 3H), 1.98 (s, 3H); $^{13}$C NMR δ 157.4, 152.8, 139.9, 129.8, 129.5, 129.2, 128.6, 125.6, 114.0, 55.3, 29.7, 21.4. Anal. Calcd for C$_{34}$H$_{36}$N$_{4}$O$_{7}$·0.5H$_{2}$O: C, 66.43; H, 6.23; N, 9.11. Found: C, 66.84; H, 6.45; N, 9.69.

N-[{(Z)-1-Benzyl-2-nitro-1-propenyl]-N-(4-methylphenyl)amine (10c). Yellow oil (50%); $^{1}$H NMR δ 7.37–7.26 (m, 8H), 7.07 (d, $J = 8.4$ Hz, 2H), 3.73 (s, 2H), 2.28 (s, 3H), 1.25 (s, 3H); $^{13}$C NMR δ 168.9, 135.0, 134.5, 134.0, 129.7, 129.5, 129.3, 129.1, 127.5, 119.9, 44.7, 29.7, 20.8. Anal. Calcd for C$_{17}$H$_{18}$N$_{2}$O$_{2}$: C, 72.32; H, 6.43; N, 9.92. Found: C, 71.98; H, 6.62; N, 9.86.

References


