Supporting Information

Direct Electrochemical Imidation of Aliphatic Amines via Anodic Oxidation

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Contents:

Experimental Section S2-S10
Characterization data of all products S10-S15
NMR Spectra of all products S15-S35
HPLC spectra of all products S36-S45
General Remarks: $^1$H NMR and $^{13}$C NMR were recorded on a Bruker AC-300 FT ($^1$H: 300 MHz, $^{13}$C: 75 MHz) using TMS as internal reference. The chemical shifts ($\delta$) and coupling constants ($J$) were expressed in ppm and Hz respectively. Infrared samples were recorded on a Perkin-Elmer 2000 FTIR spectrometer. HPLC analysis was carried out on an Agilent 1100 series HPLC with a multiple wavelength detector. Chiralpak OD columns was purchased from Daicel Chemical Industries, LTD. Hexane: 2-propanol = 80:20, flow rate = 0.45 mL/min, $T = 23^\circ$C, UV = 254 nm.

1. Experimental Section.

Instruments: The instrument for electrolysis is dual display potentiostat (CJS-292) (made in China). Cyclic voltammetric (CV) experiments were carried out with a CHI400A system (USA CH Instruments) in a conventional three-electrode cell in the presence of supporting electrolyte. The anode electrode is Pt (1.0 × 1.0 cm$^2$) or a graphite (diameter 0.5 cm) while the cathode electrode is graphite (diameter 0.5 cm). A saturated calomel electrode (SCE) were used as the reference electrode. CH$_3$CN and CH$_2$Cl$_2$ were distilled from CaH$_2$. Et$_3$N, THF, hexane and 1, 4-dioxane were distilled from sodium/benzophenone. CCl$_4$ and CHCl$_3$ were dried over calcium chloride and distilled. Caution: Azides and diazoalkanes may be hazardous and/or explosive.

Representative procedures for imidation of tertiary amines: An undivided cell was equipped with a magnet stirrer, two graphite electrode both as the working electrode and the counter electrode respectively. In the electrolytic cell a solution of TsN$_3$ (0.2 mmol), tertiary amine (0.4 mmol), Bu$_4$NPF$_6$ (0.3 mmol) in CH$_3$CN (6 mL) was added. In addition, for the safety, a gas tube was installed in the electrolytic cell and the terminal of this gas tube was inserted in the excess solution of benzoic acid (1.22 g, 10 mmol, benzoic acid dissolved in CH$_3$CN) in a two-neck flask. One of the two necks was equipped with a buffer balloon for the safe. The electrolyte was allowed to stir and the electrolysis was carried out at a constant current of 4 mA (electrode square 1.6 cm$^2$) at ambient temperature ($25\pm1^\circ$C) for 3 h until the quantity of the electricity 2.2 F/mol was passed. Upon completion of the reaction, the solvent was removed with a rotary evaporator. The residue was washed with anhydrous ether (3 × 10 mL) and the insoluble Bu$_4$NPF$_6$ was filtered and dried for next use. The filtrate was combined and the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel. The schematic diagram is listed as follows:

Representative procedures for imidation of secondary amines: An undivided cell was
equipped with a magnet stirrer, two graphite electrode both as the working electrode and the counter electrode respectively. In this cell a solution of TsN₃ (0.2 mmol), secondary amine (0.6 mmol), Bu₄NPF₆ (0.3 mmol) in CH₃CN (6 mL) was added. The electrolyte was allowed to stir and the electrolysis was carried out at a constant current of 6 mA (electrode square 1.6 cm²) at ambient temperature (25±1°C) for 3 h until the quantity of the electricity 3.4 F/mol was passed. Upon completion of the reaction, the solvent was removed with a rotary evaporator. The residue was washed with anhydrous ether (3×10 mL) and the insoluble Bu₄NPF₆ was filtered and dried for next use. The filtrate was combined and the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (Ditto for the handling of diazoalkanes).

**Representative procedures for imidation of primary amines:** An undivided cell was equipped with a magnet stirrer, two graphite electrode both as the working electrode and the counter electrode respectively. In this cell a solution of TsN₃ (0.2 mmol), primary amine (1.0 mmol), Bu₄NPF₆ (0.3 mmol) in CHCl₃ (6 mL) was added. The electrolyte was allowed to stir and the electrolysis was carried out at a constant current of 7 mA (electrode square 1.6 cm²) at ambient temperature (25±1°C) for 3 h until the quantity of the electricity 3.9 F/mol was passed. Upon completion of the reaction, the solvent was removed with a rotary evaporator. The residue was washed with anhydrous ether (3×10 mL) and the insoluble Bu₄NPF₆ was filtered and dried for next use. The filtrate was combined and the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (Ditto for the handling of diazoalkanes).

**Experimental details for the capture of radical cation A:**

An undivided cell was equipped with a magnet stirrer, two graphite electrode both as the working electrode and the counter electrode respectively. In this cell a solution of triethylamine (5 mmol), Bu₄NPF₆ (0.3 mmol) in CHCl₃ (6 mL) was added. The electrolyte was allowed to stir and the electrolysis was carried out at a constant current of 4 mA (electrode square 1.6 cm²) at ambient temperature (25±1°C) for 0.5 h. Then the electrolyte was frozen by liquid nitrogen. The EPR measurements were performed with a Braker Elexys X-band (9.7 GHz) E580 EPR spectrometer at room temperature (Ditto for the handling of diazoalkanes).

The X-band EPR measurement was conducted at room temperature and the result was shown in Figure 1. The characterized g-value of the radical was 2.0022. The EPR simulation demonstrated that the magnetic interactions between the unpaired electron and one ¹⁴N and six equivalent ¹H (see A in Scheme 1) gave rise to the resolved isotropic hyperfine constants, ¹⁴N (43.69 MHz) and ¹H (30.98 MHz) displayed in Figure 1.

**Experimental details for the measurement of CV of Et₃N:**

The cyclic voltammetry (CV) of Et₃N was measured in 0.05 M n-Bu₄NPF₆/CH₃CN. As shown in
Figure S1 (Supporting Information, SI), the value of +1.60 V (vs SCE) in trace b (green) indicated the oxidation potential of Et₃N in acetonitrile while trace a (red) showed that blank solution was not electroactive in the potential window of interest.

**Figure S1.** Cyclic voltammetry (CV) curves of a) 0.05 M n-Bu₄NPF₆/CH₃CN (red), b) 1mmol Et₃N, 0.05 M n-Bu₄NPF₆/CH₃CN (green), recorded at a glassy carbon electrode (diameter 4.0 mm), Scan rate: 100 mV s⁻¹, at room temperature.

**Experimental details for the optimization of the reaction conditions:**

The optimization of the reaction conditions was achieved by screening different solvents and electrodes, as shown in Table S1. When the platinum anode was replaced with a graphite anode, the reaction yield was hexane, and H₂O hardly gave the desired product and the use of MeOH and THF afforded the product with poor yields (Table S1, entries 8-14). In comparison with acetonitrile, the solvent CHCl₃ gave almost the same yield under the same condition while CH₂Cl₂ gave a moderate yield (Table S1, entries 3-7). Therefore CH₃CN and CHCl₃ should be the best solvents. Taking all factors into the consideration, the standard reaction condition was established as follows: CH₃CN as the solvent, Bu₄NPF₆ as the electrolyte, graphite as both anode and cathode.

**Table S1.** Synthesis of sulfonyl amidine under various conditions

\[
\begin{align*}
\text{Ph-SO₂N₃} + \text{N} & \xrightarrow{-e^-} \text{Ph-SO₂N-N}
\end{align*}
\]
<table>
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<tr>
<th>entry</th>
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<th>anode</th>
<th>cathode</th>
<th>yield(%)</th>
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<tr>
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</tr>
<tr>
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<td>CH₂Cl₂</td>
<td>Pt</td>
<td>C</td>
<td>45</td>
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<td>CH₂Cl₂</td>
<td>C</td>
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<td>Pt</td>
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<td>1,4-dioxane</td>
<td>C</td>
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<td>C</td>
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</tr>
<tr>
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<td>hexane</td>
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<td>C</td>
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<tr>
<td>14</td>
<td>H₂O</td>
<td>C</td>
<td>C</td>
<td>trace</td>
</tr>
</tbody>
</table>

* Reaction conditions: the mixture of 0.2 mmol of TsN₃, 0.4 mmol of triethylamine, 0.3 mmol Bu₄NPF₆ and 6 mL of solvent was stirred and electrolyzed with constant current of 4 mA at room temperature for 3 h. * Isolated yield based on TsN₃. * Reaction conditions: the mixture of 0.2 mmol of TsN₃, 0.4 mmol of triethylamine, 0.3 mmol KNO₃ and 6 mL of H₂O was stirred and electrolyzed with constant current of 20 mA at room temperature for 3 h.

Experimental details for the investigation of reaction mechanism:

The electrolysis of TsN₃ and Et₃N was performed separately. After electrolysis of TsN₃ alone for 3 h, Et₃N was added and stirred for 1 h. Afterwards, TsN₃ could be recovered with a yield of 98% and no product was detected. In the parallel electrolysis of Et₃N for 3 h, the solution color was changed from colorless into yellow. When TsN₃ was added to this yellow solution and the mixture was stirred for 1 h, the corresponding sulfonyl amidine was obtained with a yield of 88%. These results showed that only Et₃N was electroactive substrate in this reaction.

Experimental details for the capture of enamine:

![Scheme S1](https://doi.org/10.1039/C8CS00861D)

An undivided cell was equipped with a magnet stirrer, two graphite electrode both as the working electrode and the counter electrode respectively. In this cell a solution of triethylamine (5 mmol), Bu₄NPF₆ (0.3 mmol) in CH₃CN (6 mL) was electrolyzed. The electrolyte was allowed to stir and the electrolysis was carried out at a constant current of 4 mA (electrode square 1.6 cm²) at ambient temperature (25±1°C) for 2 h. Then 2, 4-dinitrobenzenedihydrazine (0.100g, 0.5 mmol) was added and the reaction was quenched with 0.1 N and extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with brine, dried over sodium sulfate. The filtrate was concentrated under reduced pressure. The residue was washed with anhydrous ether (3×10 mL) and the insoluble Bu₄NPF₆ was filtered and dried for next use. The filtrate was combined and the
solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel.

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta$ = 11.16 (s, 0.43 H), 11.03 (s, 0.95 H), 9.20-9.00 (m, 0.89 H), 8.40-8.20 (m, 1.22 H), 8.00-7.85 (m, 1.25 H), 7.70-7.40 (m, 1.05 H), 7.20-7.00 (m, 0.41 H), 2.14 (d, $J$ = 5.4 Hz, 3 H), 2.08 (d, $J$ = 5.7 Hz, 1.5 H).

Figure S2

Experimental details for the capture of CH$_2$N$_2$:
Caution: Azides and diazoalkanes may be hazardous and/or explosive. An undivided cell was equipped with a magnet stirrer, two graphite electrodes both as the working electrode and the counter electrode respectively. In this cell a solution of TsN₃ (2 mmol), tertiary amine (4 mmol), Bu₄NPF₆ (0.3 mmol) in CH₃CN (6 mL) was added. In addition, for the safety, a gas tube was installed in the electrolytic cell and the terminal of this gas tube was inserted in the excess solution of benzoic acid (1.22 g, 10 mmol, benzoic acid dissolved in CH₃CN) in a two-neck flask. One of the two necks was equipped with a buffer balloon for the safe. The electrolyte was allowed to stir and the electrolysis was carried out at a constant current of 4 mA (electrode square 1.6 cm²) at ambient temperature (25±1°C) for 4 h. Upon completion of the reaction, the solvent was removed with a rotary evaporator. The residue was washed with anhydrous ether (3×10 mL). The filtrate was combined and the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel.

¹H-NMR (CDCl₃, 300 MHz, ppm): δ = 8.10-7.90 (m, 2 H), 7.60-7.50 (m, 1 H), 7.50-7.40 (m, 2 H), 3.92 (s, 3 H).
A representative mechanism for imidation of cyclic tertiary amine:

The mechanism of imidation of cyclic tertiary amine was also proposed as shown in Scheme S3. First, N-methylpiperidine is oxidized to form iminium ion E through the same route as triethylamine. It is easier for the cyclic hydrogen to be eliminated to produce iminium ion.\textsuperscript{7a,8h} Then, iminium ion E is attacked by sulfonyle azide (nucleophile) with the release of one molecule of \(\text{N}_2\) (Scheme S3, SI). At the cathode, the proton produced at the anode is reduced to hydrogen.

\begin{equation}
\text{Anode:} \quad \text{N-methylpiperidine} \rightarrow \text{iminium ion E} \rightarrow \text{imidation product}
\end{equation}

\begin{equation}
\text{Cathode:} \quad 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2
\end{equation}

Scheme S3. Proposed mechanism for imidation of cyclic tertiary amine.

Experimental details for the measurement of CV of Et\(_2\)NH:
The cyclic voltammetry (CV) of Et₂NH was measured in 0.05 M n-Bu₄NPF₆/CH₃CN. As shown in Figure S4 (Supporting Information, SI), the value of +1.80 V (vs SCE) in trace b (green) indicated the oxidation potential of Et₂NH in acetonitrile while trace a (red) showed that blank solution was not electroactive in the potential window of interest.

**Figure S4.** Cyclic voltammetry (CV) curves of a) 0.05 M n-Bu₄NPF₆/CH₃CN (red), b) 1 mmol Et₂NH, 0.05 M n-Bu₄NPF₆/CH₃CN (green), recorded at a glassy carbon electrode (diameter 4.0 mm), Scan rate: 100 mV s⁻¹, at room temperature.

**Experimental details for the capture of ethylamine:**

An undivided cell was equipped with a magnet stirrer, two graphite electrode both as the working electrode and the counter electrode respectively. In this cell a solution of benzaldehyde (0.5 mmol), diethylamine (5 mmol), Bu₄NPF₆ (0.3 mmol) in CH₃CN (6 mL) was electrolyzed. The electrolyte was allowed to stir and the electrolysis was carried out at a constant current of 6 mA (electrode square 1.6 cm²) at ambient temperature (25±1°C) for 4 h. Then the electrolyte was characterized by GC-MS.
2. Characterization data of all products.

**General Remarks:** $^1$H NMR and $^{13}$C NMR were recorded on a Bruker AC-300 FT ($^1$H: 300 MHz, $^{13}$C: 75 MHz) using TMS as internal reference. The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz respectively. Infrared samples were recorded on a Perkin-Elmer 2000 FTIR spectrometer.

**(E)-N, N-diethyl-N’-tosylformimidamide**

![Chemical structure](image)

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): δ = 8.14 (s, 1 H), 7.75 (d, J = 8.4 Hz, 2 H), 7.25 (d, J = 8.4 Hz, 2 H), 3.60-3.32 (m, 4 H), 2.39 (s, 3 H), 1.31-1.20 (t, J = 7.2 Hz, 3 H), 1.20-1.10 (t, J = 7.2 Hz, 3 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): δ = 158.1, 142.4, 139.9, 129.4, 126.5, 47.2, 41.1, 29.8, 21.6, 14.6, 12.2; IR (liquid film, cm$^{-1}$): ν = 2978, 2937, 1610, 1451, 1345, 1298, 1283, 1148, 1087, 955, 875, 817, 768, 674.

**(E)-N, N-diethyl-N’-(phenylsulfonyl)formimidamide**

![Chemical structure](image)

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): δ = 8.16 (s, 1 H), 8.00-7.80 (m, 2 H), 7.60-7.40 (m, 3 H),
3.60-3.32 (m, 4 H), 1.30-1.24 (t, \( J = 7.2 \) Hz, 3 H), 1.20-1.10 (t, \( J = 7.2 \) Hz, 3 H); \(^{13}\)C-NMR (CDCl\(_3\), 75 MHz, ppm): \( \delta = 158.3, 131.8, 128.9, 128.8, 126.5, 47.2, 41.1, 14.6, 12.2 \); IR (liquid film, cm\(^{-1}\)): \( \nu = 2978, 2938, 1612, 1447, 1345, 1299, 1149, 1088, 955, 875, 819, 770, 723, 690.\)

**(E)-N, N-diethyl-N’-(4-methoxyphenylsulfonyl)formimidamide**

![Chemical Structure](image)

\(^{1}\)H-NMR (CDCl\(_3\), 300 MHz, ppm): \( \delta = 8.14 (s, 1 \text{ H}), 7.81 (d, \( J = 9.0 \) Hz, 2 H), 6.92 (d, \( J = 9.0 \) Hz, 2 H), 3.84 (s, 3 H), 3.53-3.30 (m, 4 H), 1.30-1.20 (t, \( J = 7.2 \) Hz, 3 H), 1.20-1.10 (t, \( J = 7.2 \) Hz, 3 H); \(^{13}\)C-NMR (CDCl\(_3\), 75 MHz, ppm): \( \delta = 158.0, 128.5, 113.9, 55.6, 47.3, 41.2, 14.6, 12.2 \); IR (liquid film, cm\(^{-1}\)): \( \nu = 2977, 2939, 1612, 1499, 1452, 1346, 1290, 1257, 1146, 1090, 1025, 955, 877, 768, 676.\)

**(E)-N’-(4-bromophenylsulfonyl)-N, N-diethylformimidamide**

![Chemical Structure](image)

\(^{1}\)H-NMR (CDCl\(_3\), 300 MHz, ppm): \( \delta = 8.13 (s, 1 \text{ H}), 7.75 (d, \( J = 8.4 \) Hz, 2 H), 7.59 (d, \( J = 8.4 \) Hz, 2 H), 3.53-3.30 (m, 4 H), 1.30-1.20 (t, \( J = 7.2 \) Hz, 3 H), 1.20-1.10 (t, \( J = 7.2 \) Hz, 3 H); \(^{13}\)C-NMR (CDCl\(_3\), 75 MHz, ppm): \( \delta = 158.2, 132.0, 128.1, 47.3, 41.2, 14.6, 12.2 \); IR (liquid film, cm\(^{-1}\)): \( \nu = 2977, 2938, 1611, 1449, 1344, 1302, 1271, 1147, 1086, 877, 770, 740.\)

**(E)-N, N-diethyl-N’-(4-nitrophenylsulfonyl)formimidamide**

![Chemical Structure](image)

\(^{1}\)H-NMR (CDCl\(_3\), 300 MHz, ppm): \( \delta = 8.31 (d, \( J = 9.0 \) Hz, 2 H), 8.16 (s, 1 H), 8.07 (d, \( J = 9.0 \) Hz, 2 H), 3.55-3.32 (m, 4 H), 1.33-1.25 (t, \( J = 7.2 \) Hz, 3 H), 1.20-1.10 (t, \( J = 7.2 \) Hz, 3 H); \(^{13}\)C-NMR (CDCl\(_3\), 75 MHz, ppm): \( \delta = 158.5, 127.8, 124.1, 47.6, 41.4, 14.6, 12.2 \); IR (liquid film, cm\(^{-1}\)): \( \nu = 2980, 2940, 1613, 1528, 1449, 1345, 1295, 1150, 1086, 957, 881, 853, 732, 686.\)

**(E)-N, N-diethyl-N’-(2-nitrophenylsulfonyl)formimidamide**

![Chemical Structure](image)

\(^{1}\)H-NMR (CDCl\(_3\), 300 MHz, ppm): \( \delta = 8.30-8.20 (m, 1 \text{ H}), 8.11 (s, 1 \text{ H}), 7.80-7.60 (m, 3 \text{ H}), 3.60-3.32 (m, 4 \text{ H}), 1.39-1.29 (t, \( J = 7.2 \) Hz, 3 H), 1.20-1.10 (t, \( J = 7.2 \) Hz, 3 H); \(^{13}\)C-NMR (CDCl\(_3\), 75 MHz, ppm): \( \delta = 160.0, 132.8, 132.1, 130.9, 124.1, 47.5, 41.4, 14.5, 12.2 \); IR (liquid film, cm\(^{-1}\)): \( \nu = 2979, 2939, 1615, 1540, 1344, 1309, 1154, 1121, 880, 772, 607.\)

**(E)-N,N-diethyl-N’-(3-nitrophenylsulfonyl)formimidamide**

![Chemical Structure](image)

\(^{1}\)H-NMR (CDCl\(_3\), 300 MHz, ppm): \( \delta = 8.30-8.20 (m, 1 \text{ H}), 8.11 (s, 1 \text{ H}), 7.80-7.60 (m, 3 \text{ H}), 3.60-3.32 (m, 4 \text{ H}), 1.39-1.29 (t, \( J = 7.2 \) Hz, 3 H), 1.20-1.10 (t, \( J = 7.2 \) Hz, 3 H); \(^{13}\)C-NMR (CDCl\(_3\), 75 MHz, ppm): \( \delta = 160.0, 132.8, 132.1, 130.9, 124.1, 47.5, 41.4, 14.5, 12.2 \); IR (liquid film, cm\(^{-1}\)): \( \nu = 2979, 2939, 1615, 1540, 1344, 1309, 1154, 1121, 880, 772, 607.\)
(E)-N’-(2,5-dibromophenylsulfonyl)-N,N-diethylformimidamide

1H-NMR (CDCl3, 300 MHz, ppm): δ = 8.39 (s, 1 H), 8.29 (s, 1 H), 7.56-7.40 (m, 2 H), 3.60-3.40 (m, 4 H), 1.40-1.29 (t, J = 7.2 Hz, 3 H), 1.25-1.10 (t, J = 7.2 Hz, 3 H); 13C-NMR (CDCl3, 75 MHz, ppm): δ = 160.2, 136.3, 135.9, 133.5, 121.6, 47.5, 41.5, 14.7, 12.1; IR (liquid film, cm⁻¹): v = 2978, 2937, 1614, 1445, 1343, 1303, 1153, 1023, 956, 880, 882, 766, 611, 592.

(E)-N’-(((1R,4R)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methylsulfonyl)-N,N-diethylformimidamide

1H-NMR (CDCl3, 300 MHz, ppm): δ = 8.05 (s, 1 H), 3.55-3.41 (m, 4 H), 3.41-3.35 (m, 1 H), 3.10-2.90 (m, 1 H), 2.75-2.55 (m, 1 H), 2.40-2.20 (m, 1 H), 2.10-1.96 (m, 2 H), 1.95-1.80 (m, 1 H), 1.80-1.60 (m, 1 H), 1.50-1.35 (m, 1 H), 1.35-1.25 (t, J = 7.2 Hz, 3 H), 1.25-1.10 (t, J = 7.2 Hz, 3 H), 1.15 (s, 3 H), 0.85 (s, 3 H); 13C-NMR (CDCl3, 75 MHz, ppm): δ = 158.8, 58.6, 50.8, 48.1, 47.0, 42.8, 42.7, 40.8, 27.1, 24.8, 20.1, 19.8, 14.5, 12.1; IR (liquid film, cm⁻¹): v = 2966, 2887, 1744, 1613, 1454, 1352, 1304, 1127, 955, 873, 766.

(E)-N,N-diethyl-N’-(thiophen-2-ylsulfonyl)formimidamide

1H-NMR (CDCl3, 300 MHz, ppm): δ = 8.15 (s, 1 H), 7.62-7.53 (m, 1 H), 7.50-7.45 (m, 1 H), 7.05-7.00 (m, 1 H), 3.60-3.40 (m, 4 H), 1.40-1.25 (t, J = 7.2 Hz, 3 H), 1.23-1.10 (t, J = 7.2 Hz, 3 H); 13C-NMR (CDCl3, 75 MHz, ppm): δ = 158.4, 130.6, 130.4, 127.0, 47.4, 41.3, 14.6, 12.2; IR (liquid film, cm⁻¹): v = 2977, 2938, 1611, 1451, 1341, 1298, 1133, 1088, 1014, 876, 672.

(E)-N,N-dipropyl-N’-tosylformimidamide
$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta = 8.15$ (s, 1 H), 7.75 (d, $J = 8.4$ Hz, 2 H), 7.25 (d, $J = 8.4$ Hz, 2 H), 3.40-3.20 (m, 4 H), 2.39 (s, 3 H), 1.68-1.50 (m, 4 H), 1.00-0.80 (m, 6 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta = 159.0, 129.4, 126.5, 54.4, 48.0, 22.1, 21.6, 20.1, 11.3, 11.0$; IR (liquid film, cm$^{-1}$): $\nu = 2964, 2931, 1607, 1451, 1343, 1297, 1147, 1087, 909, 877, 674$.

(E)-N,N-diisopropyl-N'-tosylformimidamide

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta = 8.25$ (s, 1 H), 7.75 (d, $J = 8.4$ Hz, 2 H), 7.25 (d, $J = 8.4$ Hz, 2 H), 4.60-4.40 (m, 1 H), 3.80-3.50 (m, 1 H), 2.39 (s, 3 H), 1.31 (d, $J = 6.9$ Hz, 6 H), 1.21 (d, $J = 6.9$ Hz, 6 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta = 156.5, 129.4, 126.4, 48.6, 48.0, 23.7, 21.6, 19.8$; IR (liquid film, cm$^{-1}$): $\nu = 2976, 2933, 1602, 1341, 1282, 1146, 1088, 891, 839, 670$.

(E)-4-methyl-N-(1-methylpyrrolidin-2-ylidene)benzenesulfonamide

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta = 7.81$ (d, $J = 8.4$ Hz, 2 H), 7.24 (d, $J = 8.4$ Hz, 2 H), 3.50-3.40 (t, $J = 7.2$ Hz, 2 H), 3.10-3.00 (t, $J = 7.8$ Hz, 2 H), 2.97 (s, 3 H), 2.39 (s, 3 H), 2.20-2.00 (m, 2 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta = 170.0, 142.1, 140.7, 129.3, 126.6, 51.8, 32.1, 30.8, 21.6, 19.1$; IR (liquid film, cm$^{-1}$): $\nu = 2927, 1600, 1492, 1301, 1281, 1144, 1091, 1007, 902, 813, 670, 606, 580, 558$.

(E)-N-(1-ethylpiperidin-2-ylidene)-4-methylbenzenesulfonamide

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta = 7.81$ (d, $J = 8.4$ Hz, 2 H), 7.26 (d, $J = 8.4$ Hz, 2 H), 3.60-3.40 (m, 2 H), 3.38-3.10 (t, $J = 6.0$ Hz, 2 H), 3.10-3.00 (t, $J = 6.0$ Hz, 2 H), 2.40 (s, 3 H), 1.80-1.70 (m, 4 H), 1.18-1.00 (t, $J = 7.2$ Hz, 3 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta = 165.3, 141.7, 129.8, 129.2, 126.6, 126.3, 48.3, 45.7, 28.7, 22.4, 21.5, 19.7, 11.5$; IR (liquid film, cm$^{-1}$): $\nu = 2937, 2871, 1562, 1482, 1261, 1141, 1093, 1066, 935, 815, 671, 584, 554$.

(E)-4-methyl-N-(1-methylpiperidin-2-ylidene)benzenesulfonamide

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta = 7.82$ (d, $J = 7.8$ Hz, 2 H), 7.24 (d, $J = 7.8$ Hz, 2 H), 3.40-3.30 (m, 2 H), 3.03 (s, 3 H), 2.39 (s, 3 H), 1.90-1.60 (m, 6 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz,
ppm): $\delta = 166.1, 141.8, 141.5, 129.6, 129.2, 126.6, 126.4, 50.9, 38.5, 28.7, 22.3, 21.4, 19.8$; IR (liquid film, cm$^{-1}$): $\nu = 2950, 2870, 1571, 1483, 1273, 1142, 1089, 962, 823, 675$.

(Z/E)-N,N-dipropyl-N'-tosylformimidamide

![Chemical structure](image)

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta = 8.15$ (s, 0.59 H), 7.81 (d, $J = 8.4$ Hz, 0.69 H), 7.75 (d, $J = 8.4$ Hz, 1.14 H), 7.30-7.20 (m, 1.83 H), 3.40-3.20 (m, 4 H), 2.39 (s, 3 H), 1.80-1.40 (m, 4 H), 1.00-0.70 (m, 6 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta = 169.0, 162.9, 159.0, 142.3, 139.9, 129.7, 129.4, 129.1, 129.0, 126.5, 126.4, 54.4, 50.7, 49.3, 47.9, 24.4, 23.4, 22.2, 21.5, 20.1, 11.9, 11.4; IR (liquid film, cm$^{-1}$): $\nu = 2965, 2935, 2876, 1670, 1609, 1545, 1297, 1283, 1147, 1087, 878, 676$.

(Z/E)-N,N-dibutyl-N'-tosylformimidamide

![Chemical structure](image)

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta = 8.13$ (s, 0.82 H), 7.82 (d, $J = 8.4$ Hz, 0.32 H), 7.75 (d, $J = 8.4$ Hz, 1.61 H), 7.30-7.20 (m, 1.94 H), 3.50-3.20 (m, 4 H), 2.36 (s, 3 H), 1.70-1.40 (m, 4 H), 1.40-1.10 (m, 4 H), 1.00-0.80 (m, 6 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta = 158.8, 142.3, 140.0, 129.3, 129.0, 126.4, 126.1, 52.4, 47.1, 46.0, 30.8, 28.8, 21.5, 20.2, 20.0, 19.7, 13.8, 13.7, 13.6; IR (liquid film, cm$^{-1}$): $\nu = 2958, 2932, 2872, 1672, 1608, 1458, 1348, 1298, 1147, 1088, 892, 814$.

(Z/E)-N-ethyl-N-methyl-N'-tosylformimidamide

![Chemical structure](image)

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta = 8.18$ (s, 0.68 H), 8.09 (s, 0.36 H), 7.80-7.70 (m, 2 H), 7.25 (d, $J = 7.2$ Hz, 2 H), 3.50-3.30 (m, 2 H), 3.08 (s, 1 H), 2.98 (s, 2 H), 2.40 (s, 3 H), 1.28-1.20 (t, 2 H), 1.20-1.10 (m, 1 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta = 158.7, 158.5, 142.5, 142.4, 139.8, 139.7, 129.3, 126.3, 126.5, 49.6, 43.1, 38.9, 33.2, 21.6, 13.9, 11.3; IR (liquid film, cm$^{-1}$): $\nu = 2977, 2935, 1617, 1343, 1297, 1282, 1147, 1086, 905, 888, 673$.

(Z/E)-N-propyl-N'-tosylpropionimidamide

![Chemical structure](image)

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta = 8.25$ (s, 0.39 H), 7.85-7.70 (m, 2.04 H), 7.30-7.20 (m, 2.22
H), 5.90 (s, 0.57 H), 3.35-3.20 (m, 2 H), 2.92-2.80 (m, 1 H), 2.40 (s, 3 H), 2.40-2.30 (m, 1 H),
1.70-1.50 (m, 2.19 H), 1.30-1.20 (m, 1.87 H), 1.20-1.10 (m, 1.37 H) 1.00-0.90 (m, 1.46 H)
0.90-0.80 (m, 1.85 H); $^1$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta$ = 169.7, 169.6, 142.7, 142.0, 141.3,
140.0, 129.4, 129.2, 126.4, 126.3, 45.5, 43.7, 27.5, 26.9, 23.1, 21.8, 21.6, 21.5, 11.5, 11.4, 11.2,
10.4; IR (liquid film, cm$^{-1}$): $\nu$ = 3313, 2966, 2934, 2877, 1558, 1271, 1142, 1088, 953, 694.
HRMS calc. C$_{13}$H$_{20}$N$_2$O$_2$S (M$^+$): 268.1245. Found: 268.1250.

(Z/E)-N-butyl- N'-tosylbutyrimidamide

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta$ = 8.20 (s, 0.35 H), 7.85-7.70 (m, 1.87 H), 7.30-7.20 (m, 2.28
H), 5.67 (s, 0.43 H), 3.40-3.20 (m, 1.86 H), 2.80-2.60 (m, 0.97 H), 2.43 (s, 2.87 H), 2.30-2.20 (m,
0.88 H), 1.80-1.45 (m, 4.57 H), 1.45-1.35 (m, 0.96 H), 1.35-1.20 (m, 1.00 H) 1.10-0.80 (m, 5.97
H); $^1$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta$ = 168.7, 168.5, 142.6, 141.9, 141.4, 140.0, 129.3, 129.2,
126.4, 43.7, 41.8, 36.2, 35.3, 31.9, 30.7, 21.6, 21.5, 20.8, 20.2, 19.9, 19.7, 13.9, 13.8, 13.7; IR
(liquid film, cm$^{-1}$): $\nu$ = 3331, 2960, 2932, 2873, 1651, 1556, 1334, 1267, 1142, 1089, 814, 695.
HRMS calc. C$_{15}$H$_{24}$N$_2$O$_2$S (M$^+$): 296.1558. Found: 296.1553.

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