Electronic Supplementary Information

Electro-oxidative coupling of Bunte salts with aryldiazonium tetrafluoroborates: A benign access to unsymmetrical sulfoxides

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1. Electrochemical Apparatus / Electrode Materials:

All the reactions and cyclic voltammetric (CV) investigations were performed using an IKA ElectraSyn 2.0 system [Figure S1]. The graphite (SK-50) electrode (8 x 52.5 x 2 mm), platinum electrode (8 x 52.5 x 2 mm), glassy carbon electrode, and Ag/AgCl reference electrode were used as furnished in the Electrochemistry Kit by the IKA India Private Limited.

![Figure S1. IKA ElectraSyn 2.0 System](image.png)

2. Cyclic Voltammetry Study:

The cyclic voltammetry was recorded at room temperature using glassy carbon as working electrode, Pt as counter electrode, and Ag/AgCl as reference electrode with $\text{Bu}_4\text{NBF}_4$ (0.1M) as supporting electrolyte in DMF: H$_2$O (9:1 v/v) at a scan rate of 100 mV s$^{-1}$ by the IKA ElectraSyn 2.0. The concentration of both the benzyl thiosulfate salt (1a) and 4-fluorobenzenediazonium tetrafluoroborate (2d) was maintained to be 10 mM for the cyclic voltammetry investigations.
Figure S2: (a) CV of \textsuperscript{4}Bu\textsubscript{4}NBF\textsubscript{4} (0.1M) in DMF: H\textsubscript{2}O at a scan rate of 100 mVs\textsuperscript{−1} vs Ag/AgCl. (b) CV of benzyl thiosulfate salt (1a) using 0.1M \textsuperscript{4}Bu\textsubscript{4}NBF\textsubscript{4} / DMF: H\textsubscript{2}O at a scan rate of 100 mVs\textsuperscript{−1} vs Ag/AgCl. (c) CV of 4-fluorobenzenediazonium tetrafluoroborate (2d) in 0.1M \textsuperscript{4}Bu\textsubscript{4}NBF\textsubscript{4} / DMF: H\textsubscript{2}O at a scan rate of 100 mVs\textsuperscript{−1} vs Ag/AgCl. (d) CV of the mixture of 1a with 2d in 0.1M \textsuperscript{4}Bu\textsubscript{4}NBF\textsubscript{4} / DMF: H\textsubscript{2}O at a scan rate of 100 mVs\textsuperscript{−1} vs Ag/AgCl.
3. Copies of $^1$H, $^{19}$F, and $^{13}$C Spectra of the Products 3

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl₃)

$^{13}$C NMR (126 MHz, CDCl₃)
$^{19}$F NMR (471 MHz, CDCl$_3$)

\[ \text{Compound 3k} \]

$^1$H NMR (500 MHz, CDCl$_3$)

\[ \text{Compound 3l} \]
$^{13}$C NMR (126 MHz, CDCl$_3$)

$^{19}$F NMR (471 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

13C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl₃)

$^{13}$C NMR (126 MHz, CDCl₃)
$^{19}$F NMR (471 MHz, CDCl$_3$)

$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (126 MHz, CDCl$_3$)
4. HRMS Data of TEMPO Adduct 4 and 5:

**Adduct 4**

![Spectrum of TEMPO Adduct 4](image)

\[ [M+Na]^+ = 302.1543 \]

**Adduct 5**

![Spectrum of TEMPO Adduct 5](image)

\[ [M+H]^+ = 248.2007 \]
5. Crystallographic Data.

Crystal of compound 3d was grown by slow evaporation of a solution of the compound in CHCl₃. All the measurements were obtained on Oxford Xcalibar Diffractometer system (model of the instrument – Xcalibar™ E).

Figure S3. View of the molecular structure of 3d.
Table T1. Crystallographic data for compound 3d.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Crystallized from</td>
<td>CHCl₃</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₁₄H₁₂Cl₂OS</td>
</tr>
<tr>
<td>Formula weight [g mol⁻¹]</td>
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<tr>
<td>Crystal colour, habit</td>
<td>White, block</td>
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<tr>
<td>Crystal dimensions (mm)</td>
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<tr>
<td>Temperature [K]</td>
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<tr>
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<tr>
<td>Space group</td>
<td>P2₁/n</td>
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<tr>
<td>a/Å</td>
<td>5.7326(5)</td>
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<tr>
<td>b/Å</td>
<td>16.7916(19)</td>
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<tr>
<td>c/Å</td>
<td>14.3441(12)</td>
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<tr>
<td>α/°</td>
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<tr>
<td>β/°</td>
<td>92.205(9)</td>
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<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>V[Å³]</td>
<td>1379.7(2)</td>
</tr>
<tr>
<td>Z</td>
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</tr>
<tr>
<td>Dx [g/cm³]</td>
<td>1.4404</td>
</tr>
<tr>
<td>μ (MoKα) [mm⁻¹]</td>
<td>5.515</td>
</tr>
<tr>
<td>F(000)</td>
<td>621.6</td>
</tr>
<tr>
<td>Radiation</td>
<td>Cu Kα (λ = 1.54184)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>8.12 to 144.66</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-6 ≤ h ≤ 7, -18 ≤ k ≤ 20, -17 ≤ l ≤ 14</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>5008</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2644 [R_int = 0.0538, R_sigma = 0.0769]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.017</td>
</tr>
<tr>
<td>Final R indexes [I&gt;=2σ (I)]</td>
<td>R₁ = 0.0749, wR₂ = 0.1869</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.1063, wR₂ = 0.2285</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.74/-0.46</td>
</tr>
</tbody>
</table>