Late-Stage Sulfoximidation of Electron-Rich Arenes by Photoredox Catalysis

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1. General Information

Commercially available reagents and solvents were purchased from Alfa Aesar, abcr, Acros Organics, Merck and Sigma-Aldrich, and were used without further purification. Reactions were performed in Biotage® microwave reaction vials (2 – 5 mL or 10 – 20 mL) equipped with a stir bar and a cap with septum under argon or oxygen atmosphere. The reaction mixtures were irradiated either in a Tectrion photoreactor (8 x 8 W; 8 LED rows, each 6 single LEDs; 455 – 465 nm; operation temperature 37 °C), by two Kessil Aquarium lamps A160WE Tuna Blue (40 W each, 460 nm) in a PhotoRedOx Duo photoreactor by HepatoChem (operation temperature 37 °C) or in a Penn OC photoreactor m1 (4 x 1.1 W, 450 nm, LED intensity 100%, cooling fan 5200 rpm, stirrer 600 rpm). The reactions were monitored by UPLC-MS analysis with a Waters Acquity UPLC-MS system with Single Quad and ELS detector; column: Acquity UPLC BEH C18 (1.7 µm, 2.1 x 50 mm); eluent A: water (with additive of 0.2 vol% aqueous ammonia (32%)); eluent B: acetonitrile; gradient: 1 – 100% B (2.0 min); flow: 0.8 mL/min. Chromatographic purification of crude products was achieved either by flash column chromatography on an Isolera™ Spektra System with ACI™ and Assist (ISO-4EV) using Biotage® SNAP Ultra cartridges or by high-pressure liquid chromatography (HPLC) using a LABOMATIC HD-3000 HPLC pump equipped with a Chromatorex C18 (10 µm, 125 mm x 30 mm) column and an AZURA UVD 2.1S UV Detector. For HPLC, a solvent mixture of water (with additive of 0.1 vol% aqueous ammonia (25%)) and acetonitrile was used (flow rate of 150.0 mL/min over 7.5 min (gradient 5.5 min, 100% acetonitrile 2.0 min)). Thin-layer chromatography (TLC) was performed on aluminium-backed silica gel 60 F254 plates; with visualization under UV light (254 nm) or by staining with potassium permanganate solution and subsequent heating. 1H NMR and 13C NMR spectra were recorded on a Bruker Ascend 600 MHz, a Bruker UltraShield 500 MHz, or a Bruker UltraShield 600 MHz spectrometer and were internally referenced to residual protic solvent signals (DMSO-d6: δ (ppm) = 2.50 and 39.51, CD3CN: δ (ppm) = 1.94 and 1.3/118.3, CDCl3: δ (ppm) = 7.26 and 77.2). In the case of 19F NMR, C6F6 was added as internal standard (-162.9 ppm). Data for 1H NMR are reported as follows: chemical shift δ in ppm (multiplicity, coupling constant J in Hz, number of protons). Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad or combinations thereof. Chemical shift δ in ppm is reported for 13C NMR. In addition, TMS in a CDCl3 solution was added as internal reference in the case of 13C spectra resulting in a small CDCl3 solvent peak. NMR spectra were assigned using information ascertained from DEPT, COSY, HECOTR, COLOC and NOESY experiments. High-resolution mass spectra (HRMS) were recorded on a WATERS XEVO G2XS Tof or an Agilent Tof 6230 by electron impact (EI) or electrospray ionization (ESI) techniques. Melting points were recorded on a Büchi B-540 melting point apparatus using open glass capillaries.
2. Preparation of Nucleophiles

Sulfoximines were synthesized according to a literature known procedure (Lohier, J.-F.; Glachet, T.; Marzag, H.; Gaumont, A.-C.; Reboul, V. Chem. Commun. 2017, 53, 2064-2067) and were used as obtained after purification. Sulfonimidamide 30 was synthesized by a literature known procedure (Izzo, F.; Schäfer, M.; Stockman, R.; Lücking, U. Chem. Eur. J. 2017, 23, 15189-15193). The synthesis of $\text{S,\text{S}}$-dimethyl sulfodiimide (28) is reported in the literature (Frings, M.; Bolm, C.; Blum, A.; Gnamm, C. Eur. J. Med. Chem. 2017, 126, 225-245). $\text{S,\text{S}}$-dimethyl sulfoximine (2) was purchased from commercial sources.

3. General Procedures

3.1 General Screening Procedure:

To a microwave vial equipped with a stir bar were added diphenyl ether (1, 20.0 mg, 0.117 mmol, 1.0 eq), $\text{S,\text{S}}$-dimethyl sulfoximine (2, 21.9 mg, 0.235 mmol, 2.0 eq), photocatalyst (0.05 eq), co-oxidant (0.2 eq, if required) and oxidant (1.1 eq, if required), then the vial was closed with a cap. The solvent or the solvent mixture was added and the reaction mixture was sparged with oxygen or argon. The reaction mixture was subsequently irradiated in an inhouse-designed Tectrion photoreactor for parallel reaction screening (8 x 8 W; 8 LED rows, each 6 single LEDs; 455 – 465 nm; operation temperature 37 °C). A solution of 4-methoxybenzonitrile as internal standard (0.1 M in DMSO, 1.0 eq) was added to each reaction mixture, of which a sample was then analyzed by UPLC-MS.

3.2 Screening of Reaction Parameters

Table S1. Screening using DDQ as photocatalyst

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<th></th>
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<tbody>
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<td>1</td>
<td>2</td>
<td>1</td>
<td>MeCN</td>
<td>0.33 M</td>
<td>90</td>
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<td>9</td>
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<td>0%</td>
</tr>
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<td>2</td>
<td>5</td>
<td>1</td>
<td>MeCN</td>
<td>0.6 M</td>
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<td>1</td>
<td>7</td>
<td>0</td>
<td>0%</td>
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<tr>
<td>3</td>
<td>5</td>
<td>1</td>
<td>DCE</td>
<td>0.6 M</td>
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<td>7</td>
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<td>0%</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>2</td>
<td>MeCN</td>
<td>0.2 M</td>
<td>85</td>
<td>0</td>
<td>15</td>
<td>0</td>
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<td>0.2 M</td>
<td>83</td>
<td>3</td>
<td>14</td>
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<td>0%</td>
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*a* UV area at 220 nm. *b* Yield by UPLC-MS (4-methoxybenzonitrile as internal standard).
Table S2. Screening of photocatalysts

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<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>SM</th>
<th>Byproducts</th>
<th>Standard</th>
<th>Desired</th>
<th>Yield</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium BF₄⁻</td>
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<td>6</td>
<td>12</td>
<td>72</td>
<td>96%</td>
</tr>
<tr>
<td>2</td>
<td>9-Mesityl-2,7-dimethyl-10-phenylacridinium BF₄⁻</td>
<td>0</td>
<td>14</td>
<td>13</td>
<td>73</td>
<td>90%</td>
</tr>
<tr>
<td>3</td>
<td>9-Mesityl-10-phenylacridinium BF₄⁻</td>
<td>14</td>
<td>18</td>
<td>13</td>
<td>55</td>
<td>68%</td>
</tr>
<tr>
<td>4</td>
<td>9-Mesityl-1,3,6,8-tetramethoxy-10-phenylacridinium BF₄⁻</td>
<td>85</td>
<td>2</td>
<td>13</td>
<td>0</td>
<td>0%</td>
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<td>5</td>
<td>Ru(bpz)₃(PF₆)₂</td>
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<td>13</td>
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<td>0%</td>
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<td>6</td>
<td>2,4,6-Triphenylpyrylium BF₄⁻</td>
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<td>4</td>
<td>13</td>
<td>28</td>
<td>34%</td>
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<td>7</td>
<td>9,10-Dicyanoanthracene</td>
<td>81</td>
<td>6</td>
<td>13</td>
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<td>0%</td>
</tr>
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<td>8</td>
<td>Chloranil</td>
<td>65</td>
<td>6</td>
<td>12</td>
<td>17</td>
<td>23%</td>
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<td>9</td>
<td>Thioxanthone</td>
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<td>0%</td>
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<td>10</td>
<td>Methylene blue</td>
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<td>13</td>
<td>0</td>
<td>0%</td>
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<td>4C20PN</td>
<td>53</td>
<td>39</td>
<td>8</td>
<td>0</td>
<td>0%</td>
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<tr>
<td>12</td>
<td>[Ir(dF(CF₃)ppy)(dtbpy)]PF₆</td>
<td>84</td>
<td>3</td>
<td>13</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>13</td>
<td>[Ir(dF(CF₃)ppy)(dtbpy)]PF₆</td>
<td>85</td>
<td>2</td>
<td>13</td>
<td>0</td>
<td>0%</td>
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Table S3. Screening of solvents

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<th>Solvent</th>
<th>SM</th>
<th>Byproducts</th>
<th>Standard</th>
<th>Desired</th>
<th>Yield</th>
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<tbody>
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<td>1</td>
<td>9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium BF₄⁻</td>
<td>TFE</td>
<td>82</td>
<td>5</td>
<td>13</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>2</td>
<td>9-Mesityl-2,7-dimethyl-10-phenylacridinium BF₄⁻</td>
<td>TFE</td>
<td>84</td>
<td>3</td>
<td>13</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>3</td>
<td>9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium BF₄⁻</td>
<td>MeOH</td>
<td>32</td>
<td>4</td>
<td>12</td>
<td>52</td>
<td>69%</td>
</tr>
<tr>
<td>4</td>
<td>9-Mesityl-2,7-dimethyl-10-phenylacridinium BF₄⁻</td>
<td>MeOH</td>
<td>42</td>
<td>4</td>
<td>12</td>
<td>42</td>
<td>56%</td>
</tr>
<tr>
<td>5</td>
<td>9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium BF₄⁻</td>
<td>MeCN</td>
<td>15</td>
<td>13</td>
<td>11</td>
<td>61</td>
<td>89%</td>
</tr>
<tr>
<td>6</td>
<td>9-Mesityl-2,7-dimethyl-10-phenylacridinium BF₄⁻</td>
<td>MeCN</td>
<td>15</td>
<td>9</td>
<td>12</td>
<td>64</td>
<td>85%</td>
</tr>
<tr>
<td>7</td>
<td>9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium BF₄⁻</td>
<td>DMA</td>
<td>79</td>
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<td>12</td>
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<td>0%</td>
</tr>
<tr>
<td>8</td>
<td>9-Mesityl-2,7-dimethyl-10-phenylacridinium BF₄⁻</td>
<td>DMA</td>
<td>82</td>
<td>6</td>
<td>12</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>9</td>
<td>9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium BF₄⁻</td>
<td>DMSO</td>
<td>80</td>
<td>8</td>
<td>12</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>10</td>
<td>9-Mesityl-2,7-dimethyl-10-phenylacridinium BF₄⁻</td>
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<td>87</td>
<td>0</td>
<td>13</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>11</td>
<td>9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium BF₄⁻</td>
<td>DMF</td>
<td>56</td>
<td>18</td>
<td>10</td>
<td>16</td>
<td>26%</td>
</tr>
<tr>
<td>12</td>
<td>9-Mesityl-2,7-dimethyl-10-phenylacridinium BF₄⁻</td>
<td>DMF</td>
<td>74</td>
<td>7</td>
<td>12</td>
<td>7</td>
<td>9%</td>
</tr>
<tr>
<td>13</td>
<td>9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium BF₄⁻</td>
<td>dioxane</td>
<td>41</td>
<td>17</td>
<td>12</td>
<td>30</td>
<td>40%</td>
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<td>14</td>
<td>9-Mesityl-2,7-dimethyl-10-phenylacridinium BF₄⁻</td>
<td>dioxane</td>
<td>53</td>
<td>9</td>
<td>12</td>
<td>26</td>
<td>35%</td>
</tr>
<tr>
<td>15</td>
<td>9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium BF₄⁻</td>
<td>THF</td>
<td>57</td>
<td>15</td>
<td>11</td>
<td>17</td>
<td>25%</td>
</tr>
<tr>
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<td>9-Mesityl-2,7-dimethyl-10-phenylacridinium BF₄⁻</td>
<td>THF</td>
<td>68</td>
<td>11</td>
<td>12</td>
<td>9</td>
<td>12%</td>
</tr>
<tr>
<td>17</td>
<td>9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium BF₄⁻</td>
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<td>12</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>18</td>
<td>9-Mesityl-2,7-dimethyl-10-phenylacridinium BF₄⁻</td>
<td>DMI</td>
<td>25</td>
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<td>4</td>
<td>0</td>
<td>0%</td>
</tr>
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<td>9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium BF₄⁻</td>
<td>DMPU</td>
<td>18</td>
<td>26</td>
<td>3</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>20</td>
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<td>DMPU</td>
<td>18</td>
<td>22</td>
<td>3</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>21</td>
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<td>13</td>
<td>11</td>
<td>44</td>
<td>64%</td>
</tr>
<tr>
<td>22</td>
<td>9-Mesityl-2,7-dimethyl-10-phenylacridinium BF₄⁻</td>
<td>DME</td>
<td>30</td>
<td>30</td>
<td>9</td>
<td>31</td>
<td>55%</td>
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*a UV area at 220 nm. b Yield by UPLC-MS (4-methoxybenzonitrile as internal standard).
Table S4. Screening of solvent mixtures

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<tr>
<th>entry</th>
<th>solvent mix (2:1)</th>
<th>SM&lt;sup&gt;a&lt;/sup&gt;</th>
<th>byproducts&lt;sup&gt;a&lt;/sup&gt;</th>
<th>standard&lt;sup&gt;a&lt;/sup&gt;</th>
<th>desired&lt;sup&gt;a&lt;/sup&gt;</th>
<th>yield&lt;sup&gt;a&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>1</td>
<td>DCE/TFE</td>
<td>72</td>
<td>11</td>
<td>17</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>2</td>
<td>DCE/McOH</td>
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<td>7</td>
<td>14</td>
<td>71</td>
<td>81%</td>
</tr>
<tr>
<td>3</td>
<td>DCE/McCN</td>
<td>0</td>
<td>12</td>
<td>14</td>
<td>74</td>
<td>85%</td>
</tr>
<tr>
<td>4</td>
<td>DCE/DMA</td>
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<td>5</td>
<td>13</td>
<td>43</td>
<td>53%</td>
</tr>
<tr>
<td>5</td>
<td>DCE/DMSO</td>
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<td>13</td>
<td>28</td>
<td>34%</td>
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<tr>
<td>6</td>
<td>DCE/DMF</td>
<td>8</td>
<td>12</td>
<td>12</td>
<td>68</td>
<td>91%</td>
</tr>
<tr>
<td>7</td>
<td>DCE/dioxane</td>
<td>0</td>
<td>14</td>
<td>12</td>
<td>74</td>
<td>99%</td>
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<td>8</td>
<td>DCE/THP</td>
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<td>13</td>
<td>74</td>
<td>91%</td>
</tr>
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<td>9</td>
<td>DCE/DME</td>
<td>33</td>
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<td>5</td>
<td>0</td>
<td>0%</td>
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<tr>
<td>10</td>
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<td>20</td>
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<td>0%</td>
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<tr>
<td>11</td>
<td>DCE/DME</td>
<td>0</td>
<td>14</td>
<td>13</td>
<td>73</td>
<td>90%</td>
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<tr>
<td>12</td>
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<td>20</td>
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<td>6</td>
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<td>45%</td>
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<td>13</td>
<td>DCE/TFT</td>
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<td>87%</td>
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<td>14</td>
<td>DCE/hexane</td>
<td>0</td>
<td>13</td>
<td>14</td>
<td>73</td>
<td>83%</td>
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<sup>a</sup> UV area at 220 nm. <sup>b</sup> Yield by UPLC-MS (4-methoxybenzonitrile as internal standard).
Table S5. Screening of additives and oxidants

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<th>entry</th>
<th>catalyst</th>
<th>additive (0.2 eq)</th>
<th>oxidant</th>
<th>solvent</th>
<th>SM(^{a})</th>
<th>byproducts(^{a})</th>
<th>standard(^{a})</th>
<th>desired(^{a})</th>
<th>Yield(^{a})</th>
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<tr>
<td>1</td>
<td>B</td>
<td>–</td>
<td>O(_2)</td>
<td>DCE</td>
<td>0</td>
<td>4</td>
<td>14</td>
<td>82</td>
<td>94%</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>–</td>
<td>TEMPO</td>
<td>DCE</td>
<td>38</td>
<td>12</td>
<td>11</td>
<td>39</td>
<td>57%</td>
</tr>
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<td>3</td>
<td>B</td>
<td>4-oxo-TEMPO</td>
<td>O(_2)</td>
<td>DCE</td>
<td>7</td>
<td>13</td>
<td>12</td>
<td>68</td>
<td>91%</td>
</tr>
<tr>
<td>4</td>
<td>A</td>
<td>4-hydroxy-TEMPO</td>
<td>O(_2)</td>
<td>DCE</td>
<td>5</td>
<td>12</td>
<td>12</td>
<td>71</td>
<td>95%</td>
</tr>
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<td>O(_2)</td>
<td>DCE</td>
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<td>14</td>
<td>13</td>
<td>73</td>
<td>90%</td>
</tr>
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<td>O(_2)</td>
<td>DCE</td>
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<td>36</td>
<td>10</td>
<td>8</td>
<td>13%</td>
</tr>
<tr>
<td>7</td>
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<td>Na(_2)S(_2)O(_5)</td>
<td>O(_2)</td>
<td>DCE</td>
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<td>4</td>
<td>14</td>
<td>72</td>
<td>82%</td>
</tr>
<tr>
<td>8</td>
<td>A</td>
<td>K(_2)S(_2)O(_5)</td>
<td>O(_2)</td>
<td>DCE</td>
<td>12</td>
<td>7</td>
<td>14</td>
<td>67</td>
<td>77%</td>
</tr>
<tr>
<td>9</td>
<td>B</td>
<td>(NH(_4))(_2)S(_2)O(_5)</td>
<td>O(_2)</td>
<td>DCE</td>
<td>10</td>
<td>7</td>
<td>14</td>
<td>69</td>
<td>79%</td>
</tr>
<tr>
<td>10</td>
<td>A</td>
<td>–</td>
<td>Na(_2)S(_2)O(_5)</td>
<td>DCE</td>
<td>75</td>
<td>7</td>
<td>13</td>
<td>6</td>
<td>7%</td>
</tr>
<tr>
<td>11</td>
<td>B</td>
<td>–</td>
<td>K(_2)S(_2)O(_5)</td>
<td>DCE</td>
<td>76</td>
<td>4</td>
<td>14</td>
<td>6</td>
<td>7%</td>
</tr>
<tr>
<td>12</td>
<td>A</td>
<td>–</td>
<td>(NH(_4))(_2)S(_2)O(_5)</td>
<td>DCE</td>
<td>73</td>
<td>5</td>
<td>13</td>
<td>9</td>
<td>11%</td>
</tr>
<tr>
<td>13</td>
<td>A</td>
<td>BrCCl(_3)</td>
<td>O(_2)</td>
<td>DCE</td>
<td>8</td>
<td>7</td>
<td>16</td>
<td>69</td>
<td>69%</td>
</tr>
<tr>
<td>14</td>
<td>A</td>
<td>Ph(OAc)(_2)</td>
<td>O(_2)</td>
<td>DCE</td>
<td>10</td>
<td>20</td>
<td>15</td>
<td>55</td>
<td>59%</td>
</tr>
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<td>15</td>
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<td>Mesl(OAc)(_2)</td>
<td>O(_2)</td>
<td>DCE</td>
<td>10</td>
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<td>92%</td>
</tr>
<tr>
<td>16</td>
<td>A</td>
<td>1,4-benzoquinone</td>
<td>O(_2)</td>
<td>DCE</td>
<td>8</td>
<td>8</td>
<td>12</td>
<td>72</td>
<td>96%</td>
</tr>
<tr>
<td>17</td>
<td>A</td>
<td>dibenzoyl peroxide</td>
<td>O(_2)</td>
<td>DCE</td>
<td>16</td>
<td>5</td>
<td>15</td>
<td>64</td>
<td>68%</td>
</tr>
<tr>
<td>18</td>
<td>A</td>
<td>–</td>
<td>BrCCl(_3)</td>
<td>DCE</td>
<td>52</td>
<td>6</td>
<td>14</td>
<td>28</td>
<td>32%</td>
</tr>
<tr>
<td>19</td>
<td>A</td>
<td>–</td>
<td>Ph(OAc)(_2)</td>
<td>DCE</td>
<td>36</td>
<td>49</td>
<td>8</td>
<td>7</td>
<td>14%</td>
</tr>
<tr>
<td>20</td>
<td>A</td>
<td>–</td>
<td>Mesl(OAc)(_2)</td>
<td>DCE</td>
<td>36</td>
<td>51</td>
<td>7</td>
<td>6</td>
<td>14%</td>
</tr>
<tr>
<td>21</td>
<td>A</td>
<td>–</td>
<td>1,4-benzoquinone</td>
<td>DCE</td>
<td>38</td>
<td>15</td>
<td>11</td>
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<td>52%</td>
</tr>
<tr>
<td>22</td>
<td>A</td>
<td>–</td>
<td>dibenzoyl perox.</td>
<td>DCE</td>
<td>55</td>
<td>11</td>
<td>14</td>
<td>20</td>
<td>23%</td>
</tr>
<tr>
<td>23</td>
<td>A</td>
<td>TEMPO</td>
<td>BrCCl(_3)</td>
<td>DCE</td>
<td>70</td>
<td>2</td>
<td>13</td>
<td>15</td>
<td>18%</td>
</tr>
<tr>
<td>24</td>
<td>A</td>
<td>TEMPO</td>
<td>Ph(OAc)(_2)</td>
<td>DCE</td>
<td>23</td>
<td>49</td>
<td>7</td>
<td>21</td>
<td>48%</td>
</tr>
<tr>
<td>25</td>
<td>A</td>
<td>TEMPO</td>
<td>Mesl(OAc)(_2)</td>
<td>DCE</td>
<td>26</td>
<td>53</td>
<td>7</td>
<td>14</td>
<td>32%</td>
</tr>
<tr>
<td>26</td>
<td>A</td>
<td>TEMPO</td>
<td>1,4-benzoquinone</td>
<td>DCE</td>
<td>38</td>
<td>23</td>
<td>10</td>
<td>29</td>
<td>46%</td>
</tr>
<tr>
<td>27</td>
<td>A</td>
<td>TEMPO</td>
<td>dibenzoyl perox.</td>
<td>DCE</td>
<td>42</td>
<td>12</td>
<td>12</td>
<td>34</td>
<td>45%</td>
</tr>
<tr>
<td>28</td>
<td>A</td>
<td>TEMPO</td>
<td>Na(_2)S(_2)O(_5)</td>
<td>DCE</td>
<td>29</td>
<td>5</td>
<td>11</td>
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<td>80%</td>
</tr>
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<td>A</td>
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<td>K(_2)S(_2)O(_5)</td>
<td>DCE</td>
<td>27</td>
<td>5</td>
<td>11</td>
<td>57</td>
<td>83%</td>
</tr>
<tr>
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<td>A</td>
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<td>(NH(_4))(_2)S(_2)O(_5)</td>
<td>DCE</td>
<td>27</td>
<td>6</td>
<td>11</td>
<td>56</td>
<td>81%</td>
</tr>
<tr>
<td>31</td>
<td>A</td>
<td>TEMPO</td>
<td>BrCCl(_3)</td>
<td>DCE</td>
<td>70</td>
<td>1</td>
<td>13</td>
<td>16</td>
<td>20%</td>
</tr>
<tr>
<td>32</td>
<td>A</td>
<td>TEMPO</td>
<td>Ph(OAc)(_2)</td>
<td>DCE</td>
<td>24</td>
<td>65</td>
<td>6</td>
<td>5</td>
<td>13%</td>
</tr>
<tr>
<td>33</td>
<td>A</td>
<td>TEMPO</td>
<td>Mesl(OAc)(_2)</td>
<td>DCE</td>
<td>26</td>
<td>66</td>
<td>6</td>
<td>2</td>
<td>5%</td>
</tr>
<tr>
<td>34</td>
<td>A</td>
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<td>1,4-benzoquinone</td>
<td>DCE</td>
<td>40</td>
<td>37</td>
<td>7</td>
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<td>37%</td>
</tr>
<tr>
<td>35</td>
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<td>TEMPO</td>
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<td>DCE</td>
<td>42</td>
<td>22</td>
<td>12</td>
<td>24</td>
<td>32%</td>
</tr>
<tr>
<td>36</td>
<td>A</td>
<td>TEMPO</td>
<td>Na(_2)S(_2)O(_5)</td>
<td>DCE</td>
<td>37</td>
<td>1</td>
<td>12</td>
<td>50</td>
<td>67%</td>
</tr>
<tr>
<td>37</td>
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<td>TEMPO</td>
<td>K(_2)S(_2)O(_5)</td>
<td>DCE</td>
<td>31</td>
<td>2</td>
<td>11</td>
<td>56</td>
<td>81%</td>
</tr>
<tr>
<td>38</td>
<td>A</td>
<td>TEMPO</td>
<td>(NH(_4))(_2)S(_2)O(_5)</td>
<td>DCE</td>
<td>44</td>
<td>6</td>
<td>11</td>
<td>39</td>
<td>57%</td>
</tr>
<tr>
<td>39</td>
<td>A</td>
<td>–</td>
<td>TEMPO (_d)</td>
<td>DCE</td>
<td>53</td>
<td>19</td>
<td>11</td>
<td>17</td>
<td>25%</td>
</tr>
<tr>
<td>40</td>
<td>B</td>
<td>TEMPO</td>
<td>K(_2)S(_2)O(_5)</td>
<td>MeOH</td>
<td>63</td>
<td>4</td>
<td>12</td>
<td>21</td>
<td>28%</td>
</tr>
<tr>
<td>41</td>
<td>B</td>
<td>TEMPO</td>
<td>K(_2)S(_2)O(_5)</td>
<td>TFE</td>
<td>82</td>
<td>5</td>
<td>13</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>42</td>
<td>B</td>
<td>TEMPO</td>
<td>K(_2)S(_2)O(_5)</td>
<td>MeCN</td>
<td>52</td>
<td>2</td>
<td>12</td>
<td>34</td>
<td>45%</td>
</tr>
<tr>
<td>43</td>
<td>B</td>
<td>TEMPO</td>
<td>K(_2)S(_2)O(_5)</td>
<td>DMA</td>
<td>84</td>
<td>3</td>
<td>13</td>
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<td>0%</td>
</tr>
<tr>
<td>44</td>
<td>B</td>
<td>TEMPO</td>
<td>K(_2)S(_2)O(_5)</td>
<td>DMSO</td>
<td>86</td>
<td>0</td>
<td>14</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>45</td>
<td>B</td>
<td>TEMPO</td>
<td>K(_2)S(_2)O(_5)</td>
<td>dioxane</td>
<td>65</td>
<td>0</td>
<td>13</td>
<td>22</td>
<td>27%</td>
</tr>
<tr>
<td>46</td>
<td>B</td>
<td>TEMPO</td>
<td>K(_2)S(_2)O(_5)</td>
<td>DME</td>
<td>61</td>
<td>0</td>
<td>13</td>
<td>26</td>
<td>32%</td>
</tr>
</tbody>
</table>

\(^{a}\) UV area at 220 nm. \(^{b}\) 1 atm. \(^{c}\) 1.1 eq. argon atmosphere. \(^{d}\) 2.2 eq. argon atmosphere. \(^{e}\) Yield by UPLC-MS (4-methoxybenzonitrile as internal standard).

Catalyst A and B (A = 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium BF\(_4\), B = 9-mesityl-2,7-dimethyl-10-phenylacridinium BF\(_4\))
3.3 Photoredox Catalytic Synthesis of Sulfoximines

**General Experimental Procedure Using an O₂-Atmosphere (conditions A):**

To a microwave vial equipped with a stir bar was added the substrate (1.0 eq), sulfoximine (2.0 eq), photocatalyst (0.05 eq) and TEMPO (0.2 eq), then the vial was closed with a septum cap. The solvent was added and the mixture was sparged with oxygen. The reaction mixture was subsequently irradiated in a Hepatochem PhotoRedOx Duo photoreactor and two Kessil LED lamps (each 40 W, A160WE) or a PennOC photoreactor m1 (450 nm). For the reaction work-up, the mixture was either directly evaporated or half-saturated aqueous NaHCO₃ solution was added followed by extraction (5xEtOAc, Na₂SO₄). Purification was performed using an automated Isolera™ Spektra System or preparative HPLC as described below.

**General Experimental Procedure Using a Stoichiometric Oxidant (conditions B):**

To a microwave vial equipped with a stir bar were added the substrate (1.0 eq), sulfoximine (2.0 eq, 5 eq in the case of example 17), photocatalyst (0.05 eq), TEMPO (0.2 eq) and peroxodisulfate salt (1.1 eq), then the vial was closed with a septum cap. The solvent was added and the mixture was sparged with argon. The reaction mixture was subsequently irradiated in a Hepatochem PhotoRedOx Duo photoreactor and two Kessil LED lamps (each 40 W, A160WE) or a PennOC photoreactor m1 (450 nm). For the reaction work-up, the mixture was either directly evaporated or half-saturated aqueous NaHCO₃ solution was added followed by extraction (5xEtOAc, Na₂SO₄). Purification was performed using an automated Isolera™ Spektra System or preparative HPLC as described below.

**Diphenyl ether 4 and 4’**

\[
\begin{align*}
4 & \quad 4' \\
\end{align*}
\]

Prepared by the general procedure A outlined above using diphenyl ether (1, 120 mg, 0.705 mmol, 1.0 eq), S,S-dimethyl sulfoximine (2, 131 mg, 1.41 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 20.2 mg, 35.3 µmol, 0.05 eq) and TEMPO (22.0 mg, 0.141 mmol, 0.2 eq) in 1,2-dichloroethane (7 mL). The reaction mixture in a microwave vial equipped with an oxygen-filled balloon was irradiated by two Kessil lamps in a PhotoRedOx Duo photoreactor for 40 h. The crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 24 CV) to yield product 4 (109 mg, 0.418 mmol, 59%) and 4’ (23.0 mg, 88.0 µmol, 12%).

**Compound 4:**

Yellow solid, **melting point:** 75.7-77.7 °C.

\[\text{^1H NMR (500 MHz, DMSO-d}_6\text{):} \quad \delta \text{ (ppm)} = 7.36 - 7.32 \text{ (m, 2H),} 7.06 \text{ (tt,} \ J = 7.4, 1.1 \text{ Hz, 1H),} 6.96 - 6.92 \text{ (m, 4H),} 6.88 \text{ (dt,} \ J = 9.2, 3.2 \text{ Hz, 2H),} 3.20 \text{ (s, 6H).}\]
\(^{13}\text{C NMR (101 MHz, DMSO-}\text{d}_6\text{)}: \delta (\text{ppm}) = 157.9, 150.1, 142.3, 129.9, 123.8, 122.6, 120.2, 117.5, 41.4.\)\n

Compound 4':

Yellow wax

\(^1\text{H NMR (600 MHz, DMSO-}\text{d}_6\text{)}: \delta (\text{ppm}) = 7.33 – 7.26 (m, 2H), 7.17 (dd, \textbf{J} = 7.6, 1.5 Hz, 1H), 7.05 (td, \textbf{J} = 7.4, 1.9 Hz, 1H), 7.00 (tt, \textbf{J} = 7.4, 1.0 Hz, 1H), 6.97 – 6.91 (m, 2H), 6.85 – 6.82 (m, 2H), 3.02 (s, 6H).\)

\(^{13}\text{C NMR (151 MHz, DMSO-}\text{d}_6\text{)}: \delta (\text{ppm}) = 158.4, 148.6, 138.3, 129.5, 124.9, 123.8, 121.9, 121.8, 121.6, 116.7, 41.8.\)


Diphenyl ether 5 and 5'

\[
\text{\includegraphics[width=0.3\textwidth]{diphenyl_ether.png}}
\]

Prepared by the general procedure A outlined above using diphenyl ether (1, 150 mg, 0.881 mmol, 1.0 eq), \(S,S\)-diphenyl sulfoximine (2, 383 mg, 1.76 mmol, 2.0 eq), 9-mesityl-3,6-di-\textit{tert}-butyl-10-phenylacridinium tetrafluoroborate (3, 25.3 mg, 44.1 \(\mu\text{mol}, 0.05 \text{ eq}) and TEMPO (27.5 mg, 0.176 mmol, 0.2 eq) in 1,2-dichloroethane (9 mL). The reaction mixture was irradiated in a Penn photoreactor for 14 h. The crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 35\% ethyl acetate in hexanes over 15 CV) to yield regioisomer 5 (84.2 mg, 0.218 mmol, 25\%) and regioisomer 5' (51.7 mg, 0.134 mmol, 15\%).

Compound 5:

Yellow oil

\(^1\text{H NMR (500 MHz, DMSO-}\text{d}_6\text{)}: \delta (\text{ppm}) = 8.06 – 8.04 (m, 4H), 7.66 – 7.63 (m, 2H), 7.62 – 7.58 (m, 4H), 7.34 – 7.30 (m, 2H), 7.08 – 7.04 (m, 3H), 6.90 – 6.86 (m, 2H), 6.84 – 6.82 (m, 2H).\)

\(^{13}\text{C NMR (101 MHz, DMSO-}\text{d}_6\text{)}: \delta (\text{ppm}) = 157.5, 150.7, 140.6, 140.2, 133.3, 129.9, 129.8, 128.3, 124.6, 122.8, 119.9, 117.7.\)

Compound 5’:

Colourless oil, solidified slowly to a white solid, **melting point**: 75.1-78.0 °C

**1H NMR (600 MHz, DMSO-**\(_d_6\)**): \(\delta\) (ppm) = 7.71 – 7.68 (m, 4H), 7.57 (tt, \(J = 7.2, 1.1\) Hz, 2H), 7.50 – 7.47 (m, 4H), 7.45 – 7.42 (m, 2H), 7.12 – 7.09 (m, 2H), 7.07 – 7.05 (m, 1H), 6.99 – 6.92 (m, 4H).

**13C NMR (151 MHz, DMSO-**\(_d_6\)**): \(\delta\) (ppm) = 158.4, 147.8, 140.0, 137.0, 133.2, 129.7, 129.6, 127.9, 125.3, 123.5, 122.6, 122.6, 121.8, 116.0.

**HRMS (ESI)**: calc. for C\(_{24}\)H\(_{20}\)NO\(_2\)S \[M+H\]^+: 386.1209, found: 386.1213.

Chlorodiphenyl ether 6

Prepared by the general procedure A outlined above using 1-chloro-4-phenoxybenzene (150 mg, 0.733 mmol, 1.0 eq), S,S-dimethyl sulfoximine (2, 137 mg, 1.47 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenlacridinium tetrafluoroborate (3, 21.0 mg, 36.6 \(\mu\)mol, 0.05 eq) and TEMPO (22.9 mg, 0.147 mmol, 0.2 eq) in 1,2-dichloroethane (7 mL). The reaction mixture in a microwave vial equipped with an oxygen-filled balloon was irradiated by two Kessil lamps in a PhotoRedOx Duo photoreactor for 40 h. After evaporation of the reaction mixture the crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 30 CV) to yield product 6 (114 mg, 0.384 mmol, 52%) and compound 6’ and 6’’ (35.1 mg, 0.119 mmol, 16%) as an inseparable 7:3 mixture of regioisomers. While the assignment of 6’ was possible, the identity of 6’’ is based on the observation of a 1,2,4-substitution pattern in the NMR data and the regioselectivity observed with other substrates.

Compound 6:

Yellow solid, **melting point**: 96.0-98.0 °C.

**1H NMR (600 MHz, DMSO-**\(_d_6\)**): \(\delta\) (ppm) = 7.40 – 7.36 (m, 2H), 6.96 – 6.93 (m, 4H), 6.92 – 6.89 (m, 2H), 3.20 (s, 6H).

**13C NMR (151 MHz, DMSO-**\(_d_6\)**): \(\delta\) (ppm) = 156.9, 149.5, 142.8, 129.7, 126.2, 123.7, 120.4, 119.0, 41.5.

**HRMS (ESI)**: calc. for C\(_{14}\)H\(_{15}\)Cl\(_{35/37}\)NO\(_2\)S \[M+H\]^+: 296.0506/298.0477, found: 296.0508/298.0478.

Compound 6’ and 6’’ (7:3 mixture of regioisomers):

Colourless oil

**1H NMR (600 MHz, DMSO-**\(_d_6\)**): \(\delta\) (ppm) = 7.35 – 7.28 (m, 2H), 7.21 – 7.16 (m, 1H), 7.09 – 7.06 (m, 1H), 7.05 – 6.99 (m, 0.7 H), 6.97 – 6.91 (m, 1.3 H), 6.88 – 6.81 (m, 2 H), 3.08 (s, 1.7 H), 3.04 (s, 4.3 H).
$^{13}$C NMR (151 MHz, DMSO-$d_6$): $\delta$ (ppm) = 158.1 (minor), 157.3 (major), 148.0 (major), 147.7 (minor), 139.9 (minor), 138.5 (major), 129.6 (minor), 129.2 (major), 128.21 (minor), 125.4 (major), 125.3 (minor), 123.7 (major), 122.7 (minor), 122.6 (minor), 122.2 (major), 121.9 (major), 121.3 (minor), 118.1 (major), 116.9 (minor), 41.9 (minor), 41.8 (major).

HRMS (ESI): calc. for C$_{14}$H$_{15}$Cl$_{35/37}$NO$_2$S [M+H]$^+$: 296.0506/298.0477, found: 296.0515/298.0486.

Chlorodiphenyl ether 7

Prepared by the general procedure A outlined above using 1-chloro-4-phenoxybenzene (150 mg, 0.733 mmol, 1.0 eq), S,S-diethyl sulfoximine (178 mg, 1.47 mmol, 2.0 eq), 9-mesityl-3,6-di-$tert$-butyl-10-phenylacridinium tetrafluoroborate (3, 21.0 mg, 36.6 µmol, 0.05 eq) and TEMPO (22.9 mg, 0.147 mmol, 0.2 eq) in 1,2-dichloroethane (7 mL). The reaction mixture in a microwave vial equipped with an oxygen-filled balloon was irradiated by two Kessil lamps in a PhotoRedOx Duo photoreactor for 40 h. After evaporation of the reaction mixture the crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 21 CV) to yield product 7 (119 mg, 0.365 mmol, 50%) and compound 7’ and 7” (33.6 mg, 0.104 mmol, 14%) as an inseparable mixture of regioisomers. While the assignment of 7’ was possible, the identity of 7” is based on the observation of a 1,2,4-substitution pattern in the NMR data and the regioselectivity observed with other substrates.

Compound 7:

Yellow oil

$^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ (ppm) = 7.40 – 7.36 (m, 2 H), 6.99 – 6.92 (m, 4 H), 6.91 – 6.85 (m, 2 H), 3.28 (q, $J = 7.6$ Hz, 4 H), 1.25 (t, $J = 7.4$ Hz, 6 H).

$^{13}$C NMR (151 MHz, DMSO-$d_6$): $\delta$ (ppm) = 157.0, 149.3, 142.9, 129.7, 126.2, 123.8, 120.4, 119.0, 44.9, 7.44.

HRMS (ESI): calc. for C$_{16}$H$_{19}$Cl$_{35/37}$NO$_2$S [M+H]$^+$: 324.0820/326.0790, found:324.0826/326.0797.

Compound 7’ and 7” (7:3 mixture of regioisomers):

Colourless oil

$^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ (ppm) = 7.33 – 7.25 (m, 2 H), 7.22 – 7.17 (m, 1 H), 7.07 (td, $J = 7.2$, 1.5 Hz, 0.7 H), 7.04 – 6.97 (m, 1.3 H), 6.95 – 6.90 (m, 1 H), 6.84 – 6.77 (m, 2 H), 3.23 – 3.02 (m, 4 H), 1.06 (t, $J = 7.6$ Hz, 6 H).

$^{13}$C NMR (151 MHz, DMSO-$d_6$): $\delta$ (ppm) = $^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ ppm 158.1 (minor), 157.3 (major), 147.3 (major), 146.9 (minor), 140.3 (minor), 138.8 (major), 129.5 (minor), 129.1 (major), 128.4 (minor), 125.6 (major), 125.0 (major), 123.2 (major), 122.3 (minor), 118.1 (major), 116.9 (minor), 41.9 (minor), 41.8 (major).
Note: One carbon signal of the minor isomer is overlapping.

**HRMS (ESI):** calc. for C_{16}H_{19}Cl^{35/37}NO_{2}S [M+H]^+ : 324.0820/326.0790, found:324.0826/326.0799.

**Bromodiphenyl ether 8**

Prepared by the general procedure A outlined above using 1-bromo-4-phenoxybenzene (150 mg, 0.602 mmol, 1.0 eq), S,S-dimethyl sulfoximine (2, 112 mg, 1.20 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 17.3 mg, 30.1 µmol, 0.05 eq) and TEMPO (18.8 mg, 0.120 mmol, 0.2 eq) in 1,2-dichloroethane (6 mL). The reaction mixture in a microwave vial equipped with an oxygen-filled balloon was irradiated by two Kessil lamps in a PhotoRedOx Duo photoreactor for 40 h. After evaporation of the reaction mixture the crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 30 CV) to yield product 8 (102 mg, 0.299 mmol, 50%) and compound 8’ and 8” (32.6 mg, 95.8 µmol, 16%) as an inseparable 2:1 mixture of regioisomers. While the complete assignment of 8’ was possible, the identity of 8” is based on the observation of a 1,2,4-substitution pattern in the NMR data and the regioselectivity observed with other substrates.

**Compound 8:**

Yellow solid, melting point: 68.8-71.2 °C.

\[^1\text{H} \text{NMR (600 MHz, DMSO-d}_6\text{): }\delta (\text{ppm}) = 7.53 - 7.48 (m, 2 H), 6.98 - 6.87 (m, 6 H), 3.20 (s, 6 H)\]

\[^{13}\text{C NMR (151 MHz, DMSO-d}_6\text{): }\delta (\text{ppm}) = 157.4, 149.4, 142.8, 132.6, 123.7, 120.4, 119.4, 114.0, 41.5.\]

**HRMS (ESI):** calc. for C_{14}H_{15}Br^{79/81}NO_{2}S [M+H]^+ : 340.0001/341.9981, found: 340.0000/341.9980.

**Compound 8’ and 8” (2:1 mixture of regioisomers):**

Colourless oil

\[^1\text{H} \text{NMR (600 MHz, DMSO-d}_6\text{): }\delta (\text{ppm}) = 7.47 - 7.42 (m, 1.3 H), 7.33 - 7.28 (m, 1 H), 7.19 (dd, J = 8.0, 1.5 Hz, 0.7 H), 7.11 - 7.06 (m, 1 H), 7.06 - 6.98 (m, 1 H), 6.94 (td, J = 8.0, 1.5 Hz, 0.7 H), 6.91 (d, J = 8.4 Hz, 0.3 H), 6.88 - 6.84 (m, 0.7 H), 6.80 - 6.75 (m, 1.3 H), 3.07 (s, 2 H), 3.04 (s, 4 H).\]

\[^{13}\text{C NMR (151 MHz, DMSO-d}_6\text{): }\delta (\text{ppm}) = 157.9 (minor), 157.8 (major), 148.2 (minor), 147.9 (major), 140.2 (minor), 138.5 (major), 132.1 (major), 129.6 (minor), 125.5 (major), 124.3 (minor), 123.7 (major), 123.1 (minor), 122.2 (minor), 122.0 (major), 121.9 (major), 118.6 (major), 117.0...\]
(minor), 116.3 (minor), 113.0 (major), 41.9 (minor), 41.8 (major). **Note:** One carbon signal of the minor isomer is overlapping.

**HRMS (ESI):** calc. for C_{14}H_{15}Br^{79/81}NO_{2}S [M+H]^+: 340.0001/341.9981, found: 340.0007/341.9986.

**Benzofuran 9**

Prepared by the general procedure A outlined above using dibenzofuran (110 mg, 0.654 mmol, 1.0 eq), S,S-dimethyl sulfoximine (2, 122 mg, 1.31 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 18.8 mg, 32.7 µmol, 0.05 eq) and TEMPO (20.4 mg, 0.131 mmol, 0.2 eq) in 1,2-dichloroethane (7 mL). The reaction mixture in a microwave vial equipped with an oxygen-filled balloon was irradiated by two Kessil lamps in a PhotoRedOx Duo photoreactor for 40 h. After evaporation of the reaction mixture the crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 19 CV, 0 to 10% methanol in ethyl acetate over 10 CV) to yield regioisomer 9 (85.0 mg, 0.328 mmol, 50%), regioisomer 9' (17.8 mg, 68.6 µmol, 11%) and regioisomer 9'' (8.20 mg, 31.6 µmol, 5%).

**Compound 9:**

Yellow solid, **melting point:** 124.7-127.2 °C

{^1}H NMR (500 MHz, DMSO-\textit{d}6): δ (ppm) = 7.99 (d, J = 7.6 Hz, 1 H), 7.90 (d, J = 8.3 Hz, 1 H), 7.61 (d, J = 8.0 Hz, 1 H), 7.40 (td, J = 7.7, 1.4 Hz, 1 H), 7.36 - 7.31 (m, 1 H), 7.18 (d, J = 1.9 Hz, 1 H), 6.99 (dd, J = 8.3, 1.9 Hz, 1 H), 3.29 (s, 6 H).

{^13}C NMR (126 MHz, DMSO-\textit{d}6): δ (ppm) = 156.7, 155.3, 146.8, 125.9, 124.1, 122.9, 121.2, 120.1, 118.6, 116.2, 111.2, 104.4, 41.5.

**HRMS (ESI):** calc. for C_{14}H_{14}NO_{2}S [M+H]^+: 260.0740, found: 260.0745.

**Compound 9':**

Yellow oil

{^1}H NMR (500 MHz, DMSO-\textit{d}6): δ (ppm) = 8.26 (dd, J = 7.6, 1.0 Hz, 1 H), 7.61 (d, J = 8.3 Hz, 1 H), 7.45 - 7.41 (m, 1 H), 7.37 - 7.28 (m, 2 H), 7.17 (d, J = 7.6 Hz, 1 H), 7.03 (d, J = 7.6 Hz, 1 H), 3.40 (s, 6 H).

{^13}C NMR (126 MHz, DMSO-\textit{d}6): δ (ppm) = 156.6, 154.8, 142.8, 127.9, 126.1, 124.2, 123.0, 122.6, 117.2, 114.0, 110.8, 103.6, 41.8.

**HRMS (ESI):** calc. for C_{14}H_{14}NO_{2}S [M+H]^+: 260.0740, found: 260.0745.

S12
Compound 9**:  
Yellow oil  

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) = 8.08 (dd, \(J = 8.0, 1.0\) Hz, 1 H), 7.66 – 7.61 (m, 2 H), 7.52 (d, \(J = 8.6\) Hz, 1 H), 7.50 – 7.46 (m, 1 H), 7.35 (td, \(J = 7.6, 1.0\) Hz, 1 H), 7.08 (dd, \(J = 8.6, 2.2\) Hz, 1 H), 3.23 (s, 6 H).  

\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) = 155.9, 150.9, 141.8, 127.3, 124.1, 123.8, 122.7, 121.1, 113.8, 111.8, 111.6, 41.4.  


Biphenyl 10  

Prepared by the general procedure A outlined above using biphenyl (150 mg, 0.973 mmol, 1.0 eq), \(S,S\)-dimethyl sulfoximine (2, 181 mg, 1.95 mmol, 2.0 eq), 9-mesityl-3,6-di-\(\text{tert}\)-butyl-10-phenyl-acridinium tetrafluoroborate (3, 27.9 mg, 48.6 \(\mu\)mol, 0.05 eq) and TEMPO (30.4 mg, 0.195 mmol, 0.2 eq) in 1,2-dichloroethane (10 mL). The reaction mixture in a microwave vial equipped with an oxygen-filled balloon was irradiated by two Kessil lamps in a PhotoRedOx Duo photoreactor for 38 h. After evaporation of the reaction mixture the crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 36 CV) to yield product 10 (153 mg, 0.622 mmol, 64\%) and 10’ (32.0 mg, 0.130 mmol, 13\%).  

Compound 10:  
Slightly yellow solid, melting point: 144.3-145.9 °C.  

\(^1\)H NMR (600 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) = 7.59 (dd, \(J = 8.4, 1.1\) Hz, 2 H), 7.52 – 7.48 (m, 2 H), 7.41 (t, \(J = 7.6\) Hz, 2 H), 7.29 (t, \(J = 7.2\) Hz, 1 H), 7.00 – 7.04 (m, 2 H), 3.24 (s, 6 H).  

\(^{13}\)C NMR (151 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) = 146.1, 140.1, 132.4, 128.9, 127.3, 126.6, 126.0, 122.6, 41.6.  


Compound 10’:  
Yellow solid, melting point: 107.3-109.1 °C.  

\(^1\)H NMR (600 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) = 7.53 – 7.49 (m, 2 H), 7.35 (t, \(J = 7.6\) Hz, 2 H), 7.26 (s, 1 H), 7.27 – 7.22 (m, 1 H), 7.20 – 7.15 (m, 1 H), 6.99 – 6.94 (m, 1 H), 3.10 (s, 6 H).
$^{13}$C NMR (151 MHz, DMSO-$d_6$): δ (ppm) = 143.2, 140.4, 135.0, 130.5, 129.6, 128.0, 127.5, 126.2, 121.9, 121.3, 41.6.

HRMS (ESI): calc. for C$_{14}$H$_{16}$NOS [$M+H]^+$: 246.0947, found: 246.0958.

Mesitylene 11

Prepared by the general procedure A outlined above using mesitylene (75.0 mg, 0.624 mmol, 1.0 eq), $S_S$-methylphenyl sulfoximine (194 mg, 1.25 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 17.9 mg, 31.2 µmol, 0.05 eq) and TEMPO (19.5 mg, 0.125 mmol, 0.2 eq) in 1,2-dichloroethane (6 mL). The reaction mixture in a microwave vial equipped with an oxygen-filled balloon was irradiated by two Kessil lamps in a PhotoRedOx Duo photoreactor for 20 h. After evaporation of the reaction mixture the crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 60% ethyl acetate in hexanes over 25 CV) to yield product 11 (69.2 mg, 0.253 mmol, 41%).

Yellow oil

$^1$H NMR (600 MHz, DMSO-$d_6$): δ (ppm) = 8.06 − 8.03 (m, 2 H), 7.73 − 7.66 (m, 1 H), 7.66 − 7.62 (m, 2 H), 6.75 (s, 2 H), 3.20 (s, 3 H), 2.17 (s, 6 H), 2.15 (s, 3 H).

$^{13}$C NMR (151 MHz, DMSO-$d_6$): δ (ppm) = 141.5, 138.5, 133.2, 132.9, 131.0, 129.3, 128.7, 127.2, 43.2, 20.3, 19.7.

HRMS (ESI): calc. for C$_{16}$H$_{20}$NOS [$M+H]^+$: 274.1260, found: 274.1269.

Benzylated nitrile 12

Prepared by the general procedure A outlined above using [2-(benzyloxy)phenyl]acetonitrile (130 mg, 0.582 mmol, 1.0 eq), $S_S$-dimethyl sulfoximine (2, 108 mg, 1.16 mmol, 2.0 eq),
9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 16.7 mg, 29.1 µmol, 0.05 eq) and TEMPO (18.2 mg, 0.116 mmol, 0.2 eq) in 1,2-dichloroethane (6 mL). The reaction mixture in a microwave vial equipped with an oxygen-filled balloon was irradiated by two Kessil lamps in a PhotoRedOx Duo photoreactor for 20 h. After evaporation of the reaction mixture the crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 8 CV, then 0 to 10% methanol in ethyl acetate over 8 CV) to yield product 12 (110 mg, 0.350 mmol, 60%).

Yellow solid, melting point: 118.4-120.0 °C.

1H NMR (600 MHz, DMSO-d6): δ (ppm) = 7.50 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 7.3 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 6.97 (d, J = 8.8 Hz, 1H), 6.95 (d, J = 2.7 Hz, 1H), 6.86 (dd, J = 8.4, 2.7 Hz, 1H), 5.10 (s, 2H), 3.83 (s, 2H), 3.16 (s, 6H).

13C NMR (151 MHz, DMSO-d6): δ (ppm) = 150.4, 139.5, 137.2, 128.4, 127.8, 127.4, 124.1, 122.7, 119.9, 119.0, 113.2, 69.7, 41.3, 18.2.


Benzylated nitrile 13

Prepared by the general procedure A outlined above using [2-(benzyloxy)phenyl]acetonitrile (130 mg, 0.582 mmol, 1.0 eq), 1-iminohexahydro-1λ6-thiopyran-1-oxide (155 mg, 1.16 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 16.7 mg, 29.1 µmol, 0.05 eq) and TEMPO (18.2 mg, 0.116 mmol, 0.2 eq) in 1,2-dichloroethane (6 mL). The reaction mixture in a microwave vial equipped with an oxygen-filled balloon was irradiated by two Kessil lamps in a PhotoRedOx Duo photoreactor for 25 h. After evaporation of the reaction mixture the crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 10 CV) to yield product 13 (115 mg, 0.324 mmol, 56%).

Yellow solid, melting point: 107.5-112.0 °C.

1H NMR (600 MHz, DMSO-d6): δ (ppm) = 7.50 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 8.0 Hz, 1H), 6.99 – 6.95 (m, 2 H), 6.89 (dd, J = 8.8, 2.7 Hz, 1H), 5.09 (s, 2 H), 3.83 (s, 2 H), 3.32 – 3.27 (m, 2 H), 3.22 – 3.14 (m, 2 H), 1.94 – 1.82 (m, 4 H), 1.68 – 1.59 (m, 1 H), 1.59 – 1.50 (m, 1 H).

13C NMR (151 MHz, DMSO-d6): δ (ppm) = 150.3, 139.1, 137.2, 128.4, 127.8, 127.4, 124.2, 122.9, 119.9, 119.0, 113.2, 69.7, 50.0, 23.9, 23.0, 18.2.
HRMS (ESI): calc. for C_{20}H_{23}N_{2}O_{2}S [M+H]^+ : 355.1475, found: 355.1479.

Benzonitrile 14

\[
\begin{align*}
\end{align*}
\]

Prepared by the general procedure A outlined above using 2-(benzyloxy)benzonitrile (130 mg, 0.621 mmol, 1.0 eq), S,S-dimethyl sulfoximine (2, 116 mg, 1.24 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 17.8 mg, 31.1 µmol, 0.05 eq) and TEMPO (19.4 mg, 0.124 mmol, 0.2 eq) in 1,2-dichloroethane (6 mL). The reaction mixture in a microwave vial equipped with an oxygen-filled balloon was irradiated by two Kessil lamps in a PhotoRedOx Duo photoreactor for 20 h. After evaporation of the reaction mixture the crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 36 CV, then 0 to 10% methanol in ethyl acetate over 7 CV) to yield product 14 (39.0 mg, 0.130 mmol, 21%).

Yellow Solid, melting point: 131.8-135.0 °C.

\[\text{^1H NMR (600 MHz, DMSO-d_6): } \delta (ppm) = 7.46 (d, J = 7.2 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.20 - 7.15 (m, 3H), 5.20 (s, 2H), 3.20 (s, 6H).\]

\[\text{^13C NMR (151 MHz, DMSO-d_6): } \delta (ppm) = 154.5, 139.9, 136.4, 129.3, 128.6, 128.1, 127.6, 126.0, 116.5, 114.7, 101.1, 70.2, 41.4.\]

HRMS (ESI): calc. for C_{16}H_{17}N_{2}O_{2}S [M+H]^+: 301.1005, found: 301.1014.

Resorcinol 15

\[
\begin{align*}
\end{align*}
\]

Prepared by the experimental procedure A outlined above using 2'-bromo-2,6-dimethoxybiphenyl (150 mg, 0.512 mmol, 1.0 eq), S,S-dimethyl sulfoximine (2, 238 mg, 2.56 mmol, 5.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 14.7 mg, 25.6 µmol, 0.05 eq) and TEMPO (16.0 mg, 0.102 mmol, 0.2 eq) in 1,2-dichloroethane (5 mL). The reaction mixture was
irradiated in a Penn photoreactor for 14 h. The crude product was purified by HPLC (15 to 55% acetonitrile in water) to yield product 15 (58.8 mg, 0.153 mmol, 30%).

Yellow solid, melting point: 164.8-167.0 °C.

\[ ^1H \text{ NMR } (500 \text{ MHz, DMSO-}d_6): \delta \text{ (ppm) } = 7.64 \text{ (dd, } J = 8.0, 1.3 \text{ Hz, 1H), } 7.38 \text{ (td, } J = 7.3, 1.3 \text{ Hz, 1H), } 7.25 \text{ (td, } J = 7.9, 1.6 \text{ Hz, 1H), } 7.22 \text{ (dd, } J = 7.6, 1.6 \text{ Hz, 1H), } 7.05 \text{ (d, } J = 8.6 \text{ Hz, 1H), } 6.69 \text{ (d, } J = 8.9 \text{ Hz, 1H), } 3.60 \text{ (s, 3H), } 3.48 \text{ (s, 3H), } 3.18 \text{ (s, 3H), } 3.16 \text{ (s, 3H).} \]

\[ ^{13}C \text{ NMR } (101 \text{ MHz, DMSO-}d_6): \delta \text{ (ppm) } = 151.7, 151.2, 136.6, 132.0, 131.88, 131.86, 128.8, 127.1, 124.5, 124.3, 123.8, 106.6, 59.4, 55.7, 41.7, 41.6. \]

HRMS (ESI): calc. for C\textsubscript{16}H\textsubscript{19}Br\textsuperscript{79/81}NO\textsubscript{3}S [M+H]+: 384.0264/386.0243, found: 384.0248/386.0228.

Quinoline 16

Prepared by the general procedure B outlined above using 6-methoxyquinoline (150 mg, 0.942 mmol, 1.0 eq), S,S-dimethyl sulfoximine (2, 439 mg, 4.71 mmol, 5.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 27.0 mg, 47.1 µmol, 0.05 eq), TEMPO (29.4 mg, 0.188 mmol, 0.2 eq) and sodium peroxodisulfate (247 mg, 1.04 mmol, 1.1 eq) in 1,2-dichloroethane (9 mL). The reaction mixture was irradiated by two Kessil lamps in a PhotoRedOx Duo photoreactor for 40 h. The crude product was purified by HPLC (25 to 100% acetonitrile in water) to yield product 16 (116 mg, 0.461 mmol, 49%).

Brownish solid, melting point: 126.3-128.8 °C.

\[ ^1H \text{ NMR } (600 \text{ MHz, DMSO-}d_6): \delta \text{ (ppm) } = 8.70 \text{ (dd, } J = 4.0, 1.7 \text{ Hz, 1H), } 8.60 \text{ (dd, } J = 8.4, 1.5 \text{ Hz, 1H), } 7.66 \text{ (d, } J = 9.5 \text{ Hz, 1H), } 7.63 \text{ (d, } J = 9.2 \text{ Hz, 1H), } 7.39 \text{ (dd, } J = 8.6, 4.0 \text{ Hz, 1H), } 3.90 \text{ (s, 3H), } 3.27 \text{ (s, 6H).} \]

\[ ^{13}C \text{ NMR } (101 \text{ MHz, DMSO-}d_6): \delta \text{ (ppm) } = 148.4, 148.1, 144.2, 132.7, 127.4, 126.7, 123.7, 123.3, 120.3, 118.3, 56.5, 43.8. \]

HRMS (ESI): calc. for C\textsubscript{12}H\textsubscript{15}N\textsubscript{2}O\textsubscript{2}S [M+H]+: 251.0854, found: 251.0856.
Clofibrate derivative 17

Prepared by the general procedure B outlined above using Clofibrate (150.0 mg, 0.618 mmol, 1.0 eq), S,S-dimethyl sulfoximine (2, 288 mg, 3.09 mmol, 5.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 17.7 mg, 30.9 µmol, 0.05 eq), TEMPO (19.3 mg, 123 µmol, 0.2 eq) and ammonium peroxodisulfate (155 mg, 0.680 mmol, 1.1 eq) in 1,2-dichloroethane (6 mL). The reaction mixture was irradiated in a Penn photoreactor for 22 h. After evaporation of the reaction mixture the crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 30 CV) to yield product 17 (63.1 mg, 0.189 mmol, 31%) and 17’ (3.0 mg, 8.9 µmol, 1%).

Compound 17:  
Slightly pink oil

\[ \delta = 6.99 (d, J = 2.5 \text{ Hz}, 1 \text{ H}), 6.85 (d, J = 8.6, 2.5 \text{ Hz}, 1 \text{ H}), 6.76 (d, J = 8.6 \text{ Hz}, 1 \text{ H}), 4.16 (q, J = 7.6 \text{ Hz}, 2 \text{ H}), 3.19 (s, 6 \text{ H}), 1.46 (s, 6 \text{ H}), 1.20 (t, J = 7.3 \text{ Hz}, 3 \text{ H}) \]

\[ \delta = 173.4, 147.7, 140.2, 126.4, 123.2, 121.9, 120.9, 79.9, 60.8, 42.0, 24.7, 14.0 \]

HRMS (ESI): calc. for C\textsubscript{14}H\textsubscript{21}Cl\textsuperscript{35/37}NO\textsubscript{4}S \([M+H]^+\): 334.0874/336.0845, found: 334.0883/336.0856.

Compound 17’:  
Slightly pink oil

\[ \delta = 7.21 (d, J = 8.4 \text{ Hz}, 1 \text{ H}), 6.67 (d, J = 2.7 \text{ Hz}, 1 \text{ H}), 6.34 (dd, J = 8.8, 3.1 \text{ Hz}, 1 \text{ H}), 4.16 (q, J = 7.2 \text{ Hz}, 2 \text{ H}), 3.23 (s, 6 \text{ H}), 1.50 (s, 6 \text{ H}), 1.19 (t, J = 6.5 \text{ Hz}, 4 \text{ H}) \]

\[ \delta = 173.0, 154.0, 143.6, 129.7, 120.5, 112.8, 112.4, 78.9, 61.1, 41.8, 25.0, 13.9 \]

HRMS (ESI): calc. for C\textsubscript{14}H\textsubscript{21}Cl\textsuperscript{35/37}NO\textsubscript{4}S \([M+H]^+\): 334.0874/336.0845, found: 334.0879/336.0852.
Fenofibrate derivative 18

![Fenofibrate derivative 18](image)

Prepared by the general procedure B outlined above using Fenofibrate (200 mg, 0.554 mmol, 1.0 eq), S,S-dimethyl sulfoximine (2, 103 mg, 1.11 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 15.9 mg, 27.7 µmol, 0.05 eq), TEMPO (17.3 mg, 0.111 mmol, 0.2 eq) and sodium peroxodisulfate (145 mg, 0.610 mmol, 1.1 eq) in 1,2-dichloroethane (6 mL). The reaction mixture was irradiated in a Penn photoreactor for 18 h. The crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 17 CV) to yield product 18 (60.1 mg, 0.133 mmol, 24%) as an inseparable 5:1 regioisomeric mixture.

Yellow oil

\[ ^1H \text{NMR (major regioisomer, 600 MHz, DMSO-}d_6\text{): } \delta \text{ (ppm) = 7.72} - 7.69 \text{ (m, 2 H), 7.62} - 7.59 \text{ (m, 2 H), 7.40} \text{ (d, } J = 2.3 \text{ Hz, 1 H), 7.28} \text{ (dd, } J = 8.8, 2.3 \text{ Hz, 1 H), 6.75} \text{ (d, } J = 8.8 \text{ Hz, 1 H), 4.98} \text{ (spt, } J = 6.1 \text{ Hz, 1 H), 3.18} \text{ (s, 6 H), 1.57} \text{ (s, 6 H), 1.17} \text{ (d, } J = 6.1 \text{ Hz, 6 H).} \]

\[ ^{13}C \text{NMR (major regioisomer, 151 MHz, DMSO-}d_6\text{): } \delta \text{ (ppm) = 193.5, 172.6, 153.4, 137.0, 136.7, 136.5, 131.2, 130.0, 128.6, 126.3, 124.7, 116.8, 79.5, 68.7, 42.1, 24.9, 21.3.} \]

HRMS (ESI): calc. for C_{22}H_{27}NO_5S [M+H]^+: 452.1293/454.1263, found: 452.1297/454.1274.

Roflumilast derivative 19

![Roflumilast derivative 19](image)

Prepared by the general procedure A outlined above using Roflumilast (150 mg, 0.372 mmol, 1.0 eq), S,S-dimethyl sulfoximine (2, 69.3 mg, 0.744 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 10.7 mg, 18.6 µmol, 0.05 eq) and TEMPO (11.6 mg, 74.4 µmol, 0.2 eq) in 1,2-dichloroethane (4 mL). The reaction mixture was irradiated in a Penn photoreactor for 14 h. The crude product was purified by HPLC (30 to 70% acetonitrile in water) to yield product 19 (94.5 mg, 0.191 mmol, 51%).

White solid, melting point: 189.7-191.1 °C.
$^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ (ppm) = 11.59 (s, 1H), 8.69 (s, 2H), 7.71 (s, 1H), 7.22 (t, $J = 74.0$ Hz, 1H), 7.15 (s, 1H), 3.87 (d, $J = 6.9$ Hz, 2H), 3.48 (s, 6H), 1.25 – 1.18 (m, 1H), 0.58 – 0.55 (m, 2H), 0.37 – 0.34 (m, 2H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$): $\delta$ (ppm) = 162.1, 148.0, 143.7, 143.2 (t, $J = 3.0$ Hz, 1C), 141.4, 139.3, 129.3, 120.5, 116.7 (t, $J = 258.6$ Hz, 1C), 116.6, 112.8, 73.5, 41.7, 10.1, 3.1.

$^{19}$F NMR (471 MHz, C$_6$F$_6$ as internal standard, DMSO-$d_6$): $\delta$ (ppm) = -81.66 (d, $J = 73.0$ Hz).

HRMS (ESI): calc. for C$_{19}$H$_{20}^{35}$Cl$_2$F$_2$N$_3$O$_4$S $[M+H]^+$: 494.0514/496.0485, found: 494.0515/496.0489.

The regiochemistry of the product can be completely assigned from different observations in the 1D and 2D NMR data. At first, protons 3 and 7 appear as singlets resulting from para-orientation. If the sulfoximine group would be connected to carbon 3 or 7, the resulting two aromatic protons of the core would be in ortho- or meta-position to each other generating two doublets with a coupling constant between 2-9 Hz. Furthermore, based on NOESY experiments shown below proton 3 can be determined by its strong coupling to protons 4 and 5 (marked in red). The strong interaction of protons 6 and 2 (marked in blue) confirms the ortho-orientation of the sulfoximine and the amide functionality. Furthermore, proton 3 shows a strong signal with the carbonyl C-atom in the COLOC experiment (marked in purple), whereas no signal is observed for proton 7. Consequently, the sulfoximine group cannot be connected to carbon 3 or 7 and has to be connected to carbon 8 (all 2D spectra are depicted on the next pages).
NOESY data of 19 (DMSO-d$_6$)
COLOC data of 19 (DMSO-\textit{d}_6)
HETCOR data of 19 (DMSO-d$_6$)

Roflumilast derivative 20

Prepared by the general procedure A outlined above using Roflumilast (150 mg, 0.372 mmol, 1.0 eq), S,S-diethyl sulfoximine (90.2 mg, 0.744 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 10.7 mg, 18.6 µmol, 0.05 eq) and TEMPO (11.6 mg, 74.4 µmol, 0.2 eq) in 1,2-dichloroethane (4 mL). The reaction mixture was irradiated in a Penn photoreactor for 14 h. The crude product was purified by column chromatography (SNAP Ultra 25 g, 0 to 100% ethyl acetate in hexanes over 30 CV) to yield product 20 (121 mg, 0.231 mmol, 62%).

Slightly yellow solid, melting point: 133.0-135.0 °C.

$^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ (ppm) = 11.59 (s, 1H), 8.70 (s, 2H), 7.72 (s, 1H), 7.23 (s, 1H), 7.20 (t, $J = 74.1$ Hz, 1H), 3.87 (d, $J = 7.0$ Hz, 2H), 3.59 (q, $J = 7.3$ Hz, 4H), 1.28 (t, $J = 7.5$ Hz, 6H), 1.25 – 1.19 (m, 1H), 0.58 – 0.54 (m, 2H), 0.38 – 0.33 (m, 2H).

$^{13}$C NMR (101 MHz, DMSO-d$_6$): $\delta$ (ppm) = 162.2, 148.0, 143.8, 143.2 (t, $J = 3.0$ Hz, 1C), 141.2, 139.8, 129.6, 120.2, 116.6 (t, $J = 258.6$ Hz, 1C), 116.4, 113.2, 73.4, 45.5, 10.1, 6.9, 3.1.
\[^{19}\text{F} \text{NMR (471 MHz, C}_6\text{F}_6 \text{ as internal standard, DMSO-d}_6\)]\(\delta\) (ppm) = -81.74 (d, \(J = 74.4 \text{ Hz}\)).

**HRMS (ESI):** calc. for C_{21}H_{34}\text{Cl}_2\text{F}_2\text{N}_3\text{O}_4\text{S} \([M+H]^+\): 522.0827/524.0798, found: 522.0831/524.0805.

The regiochemistry was determined by 2D NMR experiments in analogy to compound 19.

**Roflumilast derivative 21**

![Diagram of compound 21]

Prepared by the general procedure A outlined above using Roflumilast (150 mg, 0.372 mmol, 1.0 eq), 1-iminothiopyran-1-oxide (99.1 mg, 0.744 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 10.7 mg, 18.6 µmol, 0.05 eq) and TEMPO (11.6 mg, 74.4 µmol, 0.2 eq) in 1,2-dichloroethane (4 mL). The reaction mixture was irradiated in a Penn photoreactor for 14 h. The crude product was purified by column chromatography (SNAP Ultra 25 g, 0 to 100% ethyl acetate in hexanes over 30 CV) to yield product 21 (105 mg, 0.197 mmol, 53%).

Slightly yellow solid, **melting point:** 159.1-161.3 °C.

\[^{1}\text{H} \text{NMR (500 MHz, DMSO-d}_6\)]\(\delta\) (ppm) = 11.67 (s, 1H), 8.72 (s, 2H), 7.71 (s, 1H), 7.22 (t, \(J = 74.1 \text{ Hz}, 1H\)), 7.16 (s, 1H), 3.87 (d, \(J = 7.0 \text{ Hz}, 2H\)), 3.65 – 3.51 (m, 4H), 1.98 – 1.83 (m, 4H), 1.67 – 1.54 (m, 2H), 1.25 – 1.18 (m, 1H), 0.59 – 0.54 (m, 2H), 0.37 – 0.33 (m, 2H).

\[^{13}\text{C} \text{NMR (101 MHz, DMSO-d}_6\)]\(\delta\) (ppm) = 162.3, 148.1, 143.7, 143.2 (t, \(J = 3.0 \text{ Hz}, 1C\)), 141.1, 139.1, 129.7, 120.3, 116.6, 113.0, 73.5, 50.3, 23.3, 22.5, 10.1, 3.1.

\[^{19}\text{F} \text{NMR (471 MHz, C}_6\text{F}_6 \text{ as internal standard, DMSO-d}_6\)]\(\delta\) (ppm) = -81.72 (d, \(J = 74.4 \text{ Hz}\)).

**HRMS (ESI):** calc. for C_{22}H_{34}\text{Cl}_2\text{F}_2\text{N}_3\text{O}_4\text{S} \([M+H]^+\): 534.0827/536.0798, found: 534.0834/536.0807.

The regiochemistry was determined by 2D NMR experiments in analogy to compound 19.
Roflumilast derivative 22

![Structure of Roflumilast derivative 22](image)

Prepared by the general procedure A outlined above using Roflumilast (150 mg, 0.372 mmol, 1.0 eq), S,S-methylphenyl sulfoximine (115 mg, 0.744 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 10.7 mg, 18.6 µmol, 0.05 eq) and TEMPO (11.6 mg, 74.4 µmol, 0.2 eq) in 1,2-dichloroethane (4 mL). The reaction mixture was irradiated in a Penn photoreactor for 14 h. The crude product was purified by column chromatography (SNAP Ultra 50 g, 0 to 50% ethyl acetate in hexanes over 30 CV) to yield product 22 (118 mg, 0.211 mmol, 57%).

Yellow oil

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ (ppm) = 11.73 (s, 1H), 8.73 (s, 2H), 8.00 – 7.97 (m, 2H), 7.76 – 7.72 (m, 1H), 7.70 – 7.65 (m, 3H), 6.93 (t, $J = 74.4$ Hz, 1H), 6.79 (s, 1H), 3.86 – 3.77 (m, 2H), 3.73 (s, 3H), 1.19 – 1.13 (m, 1H), 0.55 – 0.49 (m, 2H), 0.34 – 0.28 (m, 2H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$): $\delta$ (ppm) = 162.1, 148.0, 144.0, 142.4 (t, $J = 3.0$ Hz, 1C), 141.5, 138.3, 137.1, 134.1, 129.9, 129.6, 128.3, 121.1, 116.3, 116.1 (t, $J = 259.6$ Hz, 1C), 113.8, 73.3, 45.2, 10.0, 3.0.

$^{19}$F NMR (471 MHz, C$_6$F$_6$ as internal standard, DMSO-$d_6$): -81.70 (dd, $J = 165.9$, 74.4 Hz, 1 F), -82.67 (dd, $J = 164.5$, 75.8 Hz, 1 F).


The regiochemistry was determined by 2D NMR experiments in analogy to compound 19.
Difenoconazol derivative 23

![Chemical structure of 23](image)

2:1 mixture of diastereomer, 93:7 mixture of regioisomers

Prepared by the general procedure A outlined above using Difenoconazol Pestanal® (2:1 mixture of diastereomers, 200 mg, 0.492 mmol, 1.0 eq), S,S-dimethyl sulfoximine (2, 91.7 mg, 0.985 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 14.1 mg, 24.6 µmol, 0.05 eq), TEMPO (15.4 mg, 98.5 µmol, 0.2 eq) in acetonitrile (5 mL). The reaction mixture was irradiated in a Penn photoreactor for 21 h. The crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 27 CV; 0 to 100% methanol in ethyl acetate over 10 CV) to yield product 23 (2:1 mixture of diastereomers, 88.6 mg, 0.178 mmol, 36%) accompanied by a minor inseparable isomeric compound (7% by NMR).

Yellow gluey oil

**Note:** The $^1$H-NMR shifts are reported as observed for a 2:1 mixture of two diastereomers.

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ (ppm) = 8.40 − 8.37 (m, 1 H), 7.89 − 7.84 (m, 1 H), 7.43 − 7.35 (m, 1 H), 7.23 − 7.19 (m, 1 H), 7.10 − 7.05 (m, 1 H), 6.98 (dd, $J = 8.6, 2.5$ Hz, 1 H), 6.92 − 6.87 (m, 1 H), 6.77 − 6.69 (m, 1 H), 4.81 − 4.64 (m, 2 H), 4.14 − 3.98 (m, 1 H), 3.92 − 3.87 (m, 1H), 3.19 − 3.12 (m, 1 H), 3.11 − 3.05 (m, 6 H), 1.12 − 1.03 (m, 3 H).

**Note:** Most $^{13}$C-NMR shifts could be assigned to the major and minor diastereomer. Nevertheless a full assignment of all signals was not possible due to the close proximity of the chemical shifts, especially between 120-135 ppm. The chemical shifts are therefore reported as observed.

$^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ (ppm) = 159.0 (major), 158.9 (minor), 150.74 (minor), 150.65 (major), 146.2 (major), 146.1 (minor), 145.3 (major), 145.2 (minor), 140.15 (major), 140.12 (minor), 131.8 (major), 131.6, 130.4, 129.6, 129.5, 129.3 (major), 129.2, 123.52 (minor), 123.48 (major), 122.35 (major), 122.28 (minor), 121.3 (both), 118.8, 118.5 (major), 118.2, 114.4 (major), 114.3 (minor), 106.7 (major), 106.6 (minor), 73.5, 72.5, 70.7, 53.8 (major), 53.8 (minor), 41.9, 41.8, 17.9 (minor), 17.7 (major).

**HRMS (ESI):** calc. for C$_{21}$H$_{23}$Cl$_2$N$_4$O$_4$S $[M+H]^+$: 497.0812, found: 497.0821.
Esfenvalerate derivative 24

Prepared by the general procedure A outlined above using Esfenvalerate Pestanal® (180 mg, 0.429 mmol, 1.0 eq), S,S-dimethyl sulfoximine (2, 79.9 mg, 0.857 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylenediamidinium tetrafluoroborate (3, 12.3 mg, 21.4 µmol, 0.05 eq) and TEMPO (13.4 mg, 85.7 µmol, 0.2 eq) in acetonitrile (4 mL). The reaction mixture was irradiated in a Penn photoreactor for 18 h. The crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 50 CV) to yield product 24 (1:1 mixture of epimers, 93.2 mg, 0.182 mmol, 43%) and product 24' (1:1 mixture of epimers, 20.1 mg, 39.3 µmol, 9%).

Compound 24:
Brownish oil

$^1$H NMR (1:1 mixture of epimers, 600 MHz, CD$_3$CN): $\delta$ (ppm) = 7.41 (t, $J$ = 8.0 Hz, 0.5 H), 7.38 − 7.25 (m, 4.5 H), 7.20 (d, $J$ = 7.6 Hz, 0.5 H), 7.12 (d, $J$ = 7.6 Hz, 0.5 H), 7.04 (dd, $J$ = 8.0, 2.3 Hz, 0.5 H), 6.92 − 6.87 (m, 2 H), 6.36 (s, 0.5 H), 3.36 (d, $J$ = 10.3 Hz, 1 H), 3.10 (s, 3 H), 2.35 − 2.25 (m, 1 H), 1.02 (d, $J$ = 6.5 Hz, 1.5 H), 0.95 (d, $J$ = 6.9 Hz, 1.5 H).

$^{13}$C NMR (1:1 mixture of epimers, 151 MHz, CD$_3$CN): $\delta$ (ppm) = 172.64, 172.59, 160.13, 160.11, 151.04, 150.99, 143.9 (2C), 137.0 (2C), 134.62, 134.55, 133.99, 133.95, 131.71, 131.64, 131.2, 129.6 (2C), 125.36, 125.35, 122.4, 122.2, 121.7 (2C), 120.0, 119.9, 117.3, 117.2, 117.1, 117.0, 64.0, 63.8, 60.0, 58.9, 42.3 (2C), 32.8, 32.7, 21.4 (2C), 20.2, 20.1.


Compound 24':
Brownish oil

$^1$H NMR (1:1 mixture of epimers, 600 MHz, CD$_3$CN): $\delta$ (ppm) = 7.41 − 7.25 (m, 5 H), 7.24 − 7.21 (m, 1 H), 7.16 − 7.12 (m, 1.5 H), 7.08 − 6.99 (m, 2.5 H), 6.96 − 6.90 (m, 1.5 H), 6.87 (t, $J$=1.9 Hz, 0.5 H), 6.33 (s, 0.5 H), 6.30 (s, 0.5 H), 3.34 (t, $J$ = 9.9 Hz, 1 H), 2.88 (d, $J$ = 5.0 Hz, 3 H), 2.85 (d, $J$=2.67 Hz, 3 H), 2.23 - 2.35 (m, 1 H), 1.02 (d, $J$ = 6.5 Hz, 1.5 H), 0.95 (d, $J$ = 6.5 Hz, 1.5 H), 0.70 (d, $J$ = 6.9 Hz, 1.5 H), 0.68 (d, $J$=6.9 Hz, 1.5 H).

$^{13}$C NMR (1:1 mixture of epimers, 151 MHz, CD$_3$CN): $\delta$ (ppm) = 173.07, 173.0, 160.97, 160.96, 149.6 (2C), 139.81, 139.78, 137.37, 137.36, 134.6, 134.5, 134.34, 134.30, 131.73, 131.67, 131.52, 131.51, 130.01, 129.98, 127.12, 127.11, 125.68, 125.67, 123.9, 123.84, 123.81 (2C), 121.9, 121.8, 119.6, 119.5, 117.7, 117.5, 116.6, 116.5, 64.5, 64.3, 59.3, 59.2, 43.0, 42.9, 33.3, 33.0, 21.8, 21.7, 20.52, 20.47.

Prepared by the general procedure A outlined above using Esfenvalerate Pestanal® (180 mg, 0.429 mmol, 1.0 eq), S,S-methylphenyl sulfoximine (133 mg, 0.857 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 12.3 mg, 21.4 µmol, 0.05 eq) and TEMPO (13.4 mg, 85.7 µmol, 0.2 eq) in acetonitrile (4 mL). The reaction mixture was irradiated in a Penn photoreactor for 20 h. The crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 40 CV) to yield product 25 (2:1 mixture of epimers, 94.2 mg, 0.164 mmol, 38%) and product 25’ (d.r. 5:1 regarding stereocenter 1, d.r. 1:1 regarding stereocenter 2, 13.1 mg, 22.8 µmol, 5%).

Compound 25:

Colourless oil

Note: For this regioisomer, just two diastereomers were observed in the 1H- and 13C-NMR which resulted from epimerization next to the nitrile. The diastereomers resulting from the introduction of a racemic sulfoximine seem to overlap.

1H NMR (1:2 mixture of epimers, 600 MHz, CD3CN): δ (ppm) = 7.98 – 7.95 (m, 2 H), 7.68 – 7.64 (m, 1 H), 7.61 – 7.57 (m, 2 H), 7.23 (s, 5 H), 7.18 (d, J = 8.01 Hz, 0.7 H), 7.10 (d, J = 7.63 Hz, 0.3 H), 6.98 – 6.91 (m, 3.7 H), 6.87 – 6.84 (m, 0.3 H), 6.81 – 6.74 (m, 2 H), 6.33 (s, 0.7 H), 6.30 (s, 0.3 H), 3.37 – 3.30 (m, 1 H), 3.24 (s, 3 H), 2.34 – 2.22 (m, 1 H), 1.01 (d, J = 6.48 Hz, 1 H), 0.93 (dd, J = 6.48, 2.29 Hz, 2 H), 0.69 (d, J = 6.87 Hz, 1 H), 0.67 (d, J = 6.87 Hz, 2 H)

13C NMR (1:2 mixture of epimers, 151 MHz, CD3CN): δ (ppm) = 172.6 (minor), 172.5 (major), 159.84 (major), 159.81 (minor), 151.0 (major), 150.9 (minor), 143.4 (both), 140.28 (both), 136.94 (both), 134.6 (major), 134.5 (minor), 134.3 (both), 133.94 (major), 133.89 (minor), 131.7 (major), 131.6 (minor), 131.11 (major), 131.07 (minor), 130.5 (both), 129.59 (minor), 129.57 (major), 125.30 (major), 125.28 (minor), 122.4 (major), 122.27 (minor), 121.4 (both), 120.1 (major), 120.0 (minor), 117.3, 117.2, 117.1, 117.02, 116.99, 63.9 (major), 63.8 (minor), 58.9 (minor), 58.8 (minor), 46.1 (both), 32.7 (minor), 32.6 (major), 21.31 (minor), 21.30 (major), 20.13 (minor), 20.11 (major). Note: Most 13C-NMR shifts could be assigned to the major and minor epimer. Nevertheless a full assignment of all signals was not possible due to the close proximity of the chemical shifts. The chemical shifts are therefore reported as observed.


Compound 25’:

Colourless oil
Note: For this regioisomer, 4 diastereomers were observed in the $^1$H- and $^{13}$C-NMR which resulted from epimerization next to the nitrile (d.r. 5:1) and the introduction of a racemic sulfoximine (d.r. 1:1). For clarity the NMR data is just reported for the major two diastereomers.

$^1$H NMR (600 MHz, CD$_3$CN): $\delta$ (ppm) = 7.69 – 7.64 (m, 2 H), 7.63 – 7.59 (m, 1 H), 7.51 – 7.45 (m, 2 H), 7.44 – 7.39 (m, 1 H), 7.35 – 7.31 (m, 2 H), 7.30 – 7.26 (m, 2 H), 7.20 – 7.17 (m, 1 H), 7.16 – 7.13 (m, 1 H), 7.05 – 7.00 (m, 3 H), 6.99 – 6.93 (m, 2 H), 6.38 (s, 0.5 H), 6.37 (s, 0.5 H), 3.33 (d, $J$ = 5.34 Hz, 1 H), 3.32 (d, $J$ = 5.34 Hz, 1 H), 3.05 (s, 1.5 H), 3.04 (s, 1.5 H), 2.34 – 2.21 (m, 1 H), 0.93 (d, $J$ = 6.87 Hz, 3 H), 0.66 (dd, $J$ = 6.87, 1.14 Hz, 3 H).

$^{13}$C NMR (151 MHz, CD$_3$CN): $\delta$ (ppm) = 172.58, 172.57, 160.34, 160.33, 148.91, 148.90, 140.38, 140.36, 139.11, 139.07, 136.9, 134.36, 134.35, 134.34, 133.9, 131.5, 131.1, 130.35, 130.32, 129.61, 129.04, 129.03, 126.62, 126.59, 125.00, 124.97, 123.5, 123.4, 123.3, 121.74, 121.71, 119.18, 119.16, 117.2, 117.1, 116.4, 116.3, 64.07, 64.06, 58.9, 45.4, 45.3, 32.60, 32.59, 21.4, 20.1. Note: A full assignment of all signals was not possible due to the close proximity of the chemical shifts. The chemical shifts are therefore reported as observed.

HRMS (ESI): calc. for C$_{32}$H$_{30}$Cl$_3$N$_2$O$_4$S $^+$: 573.1609/575.1580, found: 573.1619/575.1603.

$\alpha$-Cypermethrin derivative 26:

![Chemical structure of 26]

Prepared by the general experimental procedure A outlined above $\alpha$-Cypermethrin Pestanal® (140 mg, 0.336 mmol, 1.0 eq), S,S-dimethyl sulfoximine (2, 62.7 mg, 0.673 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 9.6 mg, 16.8 µmol, 0.05 eq), TEMPO (10.5 mg, 67.3 µmol, 0.2 eq) in acetonitrile (3 mL). The reaction mixture was irradiated in a Penn photoreactor for 19 h. The crude product was purified first by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 40 CV) to yield product 26 (84.5 mg, 0.167 mmol, 50%) and product 26’ (12.5 mg, 24.6 µmol, 7%).

Compound 26:

Yellow oil

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ (ppm) = 7.38 (t, $J$ = 7.6 Hz, 1 H), 7.20 (d, $J$ = 7.6 Hz, 1 H), 7.12 – 7.07 (m, 3 H), 7.03 (dd, $J$ = 7.6, 1.9 Hz, 1 H), 6.96 – 6.91 (m, 2 H), 6.35 (s, 1 H), 6.18 (d, $J$ = 8.8 Hz, 1 H), 3.17 (s, 6 H), 2.16 (t, $J$ = 8.4 Hz, 1 H), 1.91 (d, $J$ = 8.4 Hz, 1 H), 1.25 (s, 3 H), 1.21 (s, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ (ppm) = 168.5, 159.0, 150.9, 141.5, 133.5, 130.5, 124.8, 123.7, 122.0, 121.5, 120.7, 119.3, 116.9, 116.0, 62.3, 42.1, 33.5, 31.0, 28.8, 28.2, 14.8.

HRMS (ESI): calc. for C$_{24}$H$_{25}$Cl$_3$N$_2$O$_4$S $^{+}$: 529.0726/531.0696, found: 529.0737/531.0716.
Compound 26:

Yellow oil

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) = 7.34 (t, $J = 8.0$ Hz, 1 H), 7.31 (d, $J = 8.0$ Hz, 1 H), 7.16 – 7.09 (m, 2 H), 7.07 – 7.00 (m, 3 H), 6.97 (dd, $J = 8.4$, 2.3 Hz, 1 H), 6.33 (s, 1 H), 6.17 (d, $J = 8.8$ Hz, 1 H), 3.01 (s, 3 H), 2.99 (s, 3 H), 2.16 (t, $J = 8.8$ Hz, 1 H), 1.90 (d, $J = 8.0$ Hz, 1 H), 1.25 (s, 3 H), 1.19 (s, 3 H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ (ppm) = 168.5, 159.4, 148.6, 137.2, 133.3, 130.3, 125.8, 125.2, 123.6, 123.3, 122.11, 122.06, 120.8, 118.5, 116.1, 115.9, 62.4, 42.5, 42.3, 33.5, 31.0, 28.8, 28.2, 14.8.


Triasulfuron derivative 27

Prepared by the general procedure A outlined above using Triasulfuron Pestanal$^\circledR$ (150 mg, 0.373 mmol, 1.0 eq), S,S-diphenyl sulfoximine (162 mg, 0.747 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-pheny lacridinium tetrafluoroborate (3, 10.7 mg, 18.7 µmol, 0.05 eq) and TEMPO (11.7 mg, 74.7 µmol, 0.2 eq) in acetonitrile (4 mL). The reaction mixture was irradiated in a Penn photoreactor for 14 h. The crude product was purified first by HPLC (50 to 100% acetonitrile in water), then by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 10 CV) to yield product 27 (33.9 mg, 54.9 µmol, 15%).

Yellow oil

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ (ppm) = 12.34 (s, 1 H), 10.98 (s, 1 H), 8.10 – 8.06 (m, 4 H), 7.67 – 7.63 (m, 3 H), 7.63 – 7.59 (m, 4 H), 7.30 (dd, $J = 8.9$, 2.9 Hz, 1 H), 7.08 (d, $J = 8.9$ Hz, 1 H), 4.28 – 4.24 (m, 2 H), 3.97 (s, 3 H), 3.80 – 3.74 (m, 2 H), 2.46 (s, 3 H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$): $\delta$ (ppm) = 176.9, 170.7, 168.2, 149.3, 139.9, 137.9, 133.4, 131.9, 129.8, 128.3, 127.9, 122.2, 115.0, 69.1, 53.8, 42.8, 24.9.

Diimide 29

Prepared by the general procedure A outlined above using diphenyl ether (1, 120 mg, 0.705 mmol, 1.0 eq), S,S-dimethyl sulfondiimide (28, 195 mg, 2.115 mmol, 3.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 20.2 mg, 35.3 µmol, 0.05 eq) and TEMPO (22.0 mg, 141 µmol, 0.2 eq) in 1,2-dichloroethane (7 mL). The reaction mixture in a microwave vial equipped with an oxygen-filled balloon was irradiated by two Kessil lamps in a PhotoRedOx Duo photoreactor for 20 h. The crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 17 CV; 0 to 30% methanol in ethyl acetate over 17 CV) to yield product 29 (105 mg, 0.404 mmol, 57%) and 29’ (25.4 mg, 97.6 µmol, 14%).

Compound 29:
Brown solid, melting point: 113.0-118.0 °C.

$^1$H NMR (500 MHz, DMSO-_$d_6$): $\delta$ (ppm) = 7.37 - 7.28 (m, 2 H), 7.07 - 6.98 (m, 3 H), 6.92 - 6.88 (m, 2 H), 6.86 - 6.82 (m, 2 H), 3.18 (s, 6 H), 3.08 (br s, 1 H).

$^{13}$C NMR (151 MHz, DMSO-_$d_6$): $\delta$ (ppm) = 158.3, 148.6, 144.3, 129.8, 123.3, 122.2, 120.2, 117.1, 44.8.

HRMS (ESI): calc. for C$_{14}$H$_{17}$N$_2$OS [M+H]$^+$: 261.1056, found: 261.1066.

Compound 29’:
Brown solid, melting point: 102.5-106.6 °C.

$^1$H NMR (600 MHz, DMSO-_$d_6$): $\delta$ (ppm) = 7.36 - 7.28 (m, 2 H), 7.07 - 7.25 (m, 2 H), 7.03 - 6.96 (m, 2 H), 6.90 (dd, J = 7.3, 1.9 Hz, 1 H), 6.85 - 6.81 (m, 3 H), 2.99 (s, 6 H), 2.87 (br s, 1 H).

$^{13}$C NMR (151 MHz, DMSO-_$d_6$): $\delta$ (ppm) = 158.5, 148.9, 139.8, 129.4, 124.6, 124.0, 121.5, 121.3, 120.6, 116.6, 45.3.

HRMS (ESI): calc. for C$_{14}$H$_{17}$N$_2$OS [M+H]$^+$: 261.1056, found: 261.1065.
Sulfonimidamide 31

Prepared by the general procedure A outlined above using diphenyl ether (1, 120 mg, 0.705 mmol, 1.0 eq), sulfonimidamide 30 (316 mg, 2.115 mmol, 2.0 eq), 9-mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (3, 20.2 mg, 35.3 µmol, 0.05 eq) and TEMPO (22.0 mg, 141 µmol, 0.2 eq) in 1,2-dichloroethane (7 mL). The reaction mixture in a microwave vial equipped with an oxygen-filled balloon was irradiated by two Kessil lamps in a PhotoRedOx Duo photoreactor for 40 h. The crude product was purified by column chromatography (SNAP Ultra 10 g, 0 to 100% ethyl acetate in hexanes over 21 CV) to yield product 31 (82.3 mg, 0.210 mmol, 30%) and 31’ (25.6 mg, 65.2 µmol, 9%).

Compound 31:

Yellow oil

$^1$H NMR (600 MHz, DMSO-$d_6$): δ (ppm) = 7.94 − 7.91 (m, 2 H), 7.72 − 7.69 (m, 1 H), 7.67 − 7.63 (m, 2 H), 7.38 − 7.32 (m, 2 H), 7.17 − 7.13 (m, 2 H), 7.09 − 7.06 (m, 1 H), 6.96 − 6.91 (m, 4 H), 3.00 − 2.89 (m, 4 H), 1.52 − 1.38 (m, 4 H), 1.35 − 1.28 (m, 2 H).

$^{13}$C NMR (151 MHz, DMSO-$d_6$): δ ppm = 157.7, 150.6, 139.7, 135.7, 132.7, 129.9, 129.2, 127.5, 124.5, 122.7, 120.0, 117.6, 47.0, 24.9, 23.0.

HRMS (ESI): calc. for C$_{23}$H$_{25}$N$_2$O$_2$S [M+H]$^+$: 393.1631, found: 393.1641.

Compound 31’:

Yellow oil

$^1$H NMR (600 MHz, DMSO-$d_6$): δ (ppm) = 7.62 − 7.58 (m, 1 H), 7.49 − 7.42 (m, 4 H), 7.36 − 7.32 (m, 3 H), 7.13 − 7.08 (m, 2 H), 7.05 − 6.98 (m, 2 H), 6.87 (dd, $J$ = 8.77, 1.14 Hz, 2 H), 2.83 − 2.70 (m, 4 H), 1.44 − 1.33 (m, 4 H), 1.29 − 1.22 (m, 2 H).

$^{13}$C NMR (151 MHz, DMSO-$d_6$): δ ppm = $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ ppm 158.4, 147.6, 136.1, 135.6, 132.6, 129.5, 128.9, 127.3, 125.2, 123.8, 122.5, 122.4, 121.6, 115.7, 46.7, 24.8, 22.9.

HRMS (ESI): calc. for C$_{23}$H$_{25}$N$_2$O$_2$S [M+H]$^+$: 393.1631, found: 393.1635
4. $^1$H- and $^{13}$C-NMR Data
7:3 regioisomeric mixture

6''6'

7.3 regioisomeric mixture
$7:3$ regioisomeric mixture

Chemical Shift (ppm): 7.31, 7.29, 6.80, 6.79, 3.17, 3.16, 3.13, 3.12, 3.10, 3.07, 1.07, 1.06

$7'$

$7''$

$S$
2:1 regioisomeric mixture

Chemical Shift (ppm)
10

Chemical Shift (ppm): 7.60, 7.50, 7.51, 7.49, 7.40, 7.00

Chemical Shift (ppm): 146.07, 140.14, 132.36, 128.86, 127.31, 126.56, 126.00

Chemical Shift (ppm): 7.00, 3.24, 14.01, 13.23, 12.88, 12.73, 12.65, 12.60, 12.56, 12.51

Chemical Shift (ppm): 41.55, 79.01, 79.01
Chemical Shift (ppm)
Chemical Shift (ppm)

(5:1 regioisomeric mixture)
2:1 mixture of diastereomer, 93:7 mixture of regioisomers