Transition Metal-Free, Chemoselective Arylation of Thioamides Yielding Aryl Thioimidates or N-Aryl Thioamides

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1 General information
All reactions were carried out in non-dried glassware unless otherwise stated. Toluene, THF, acetonitrile, CH$_2$Cl$_2$ and DMF were dried using VAC purification system, stored under argon, and over activated 4Å molecular sieved, when needed. tBuOLi, tBuONa, tBuOK were stored under argon in a desiccator. All diaryliodonium salts were synthesized according to procedures described in Section 2.1. Thioamides were synthesized according to protocols in literature (Section 2.2), except for pyrrolidine-2-thione, thiobenzamide, N,N-dimethylthioacetamide, and 2-mercaptopypyridine which were purchased. mCPBA (77% active oxidant) was purchased from commercial supplier, and dried at rt on high vacuum for 3-4 h, and titrated by iodometric titration prior to use. TIOH was stored and handled under argon, using Hamilton syringes and oven-dried metal syringes. All other solvents and reagents were purchased from commercial suppliers and used without further purification. Anhydrous toluene was degassed using the freeze-thaw method.
TLC analysis was performed on pre-coated silica gel 60 F$_{254}$ plates using UV light and phosphomolybdic acid stain (solution in EtOH). Column chromatography was conducted by flash column chromatography using 40-60 µm, 230-400 mesh, 60Å silica gel as stationary phase. Alternatively, automated flash system Teledyne ISCO CombiFlash Rf 200 with RediSep Rf columns was used. Melting points were measured using a STUART SMP3 and are reported uncorrected. All NMR spectra were recorded using a 400 MHz Bruker AVANCE II with a BBO probe at 298 K using CDCl$_3$, CD$_3$OD or DMSO-d$_6$ as solvents. Chemical shifts are given in ppm either relative to tetramethylnsilane (TMS) as internal standard or to the residual solvent peak (1H NMR: CDCl$_3$ δ 7.26; CD$_3$OD 3.31; DMSO-d$_6$ 2.50, CD$_3$CN 1.93; 13C NMR: CDCl$_3$ δ 77.16; CD$_3$OD 49.00, DMSO-d$_6$ 39.52) with multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, hept = heptet, m = multiplet, app = apparent), coupling constants (in Hz) and integration. High resolution mass analyses were obtained using a Bruker microTOF ESI or APCI. GC-MS analyses were performed using a Shimadzu GC-2010 Plus gas chromatograph (column HP-5MS 30 m x 0.25 mm x 0.25 uM) connected to a GCMS-QP2020 mass spectrometer. Analytical data is given if the compound is novel or not fully characterized in the literature.
2 Synthesis of Starting Materials

2.1 Synthesis of Thioamides and Thiolactams

Thioamides 1a-1d were synthesized according to a literature procedure. The analytical data matched those previously reported for 1a, 1b-1c, and 1d.

Thioamide 1e, 1f and 1g were synthesized from a corresponding amide according to a literature procedure. The analytical data for 1e and 1g matched those previously reported.

Thioamide 1h was synthesized according to a literature procedure. 1h: 1H NMR (400 MHz, CDCl3) δ 8.98 (s, 1H), 7.80–7.59 (m, 2H), 7.55–7.44 (m, 2H), 7.44–7.32 (m, 2H), 1.49 (s, 9H). 13C NMR (101 MHz, CDCl3) δ 203.7, 149.1, 142.2, 131.6, 128.1, 127.1, 83.5, 27.9. HRMS (ESI): calcd for C12H10NNaS [M+Na]+: 256.1130; found 256.1130.

Thioamide 1i was synthesized according to a literature procedure. 1i: 1H NMR (400 MHz, CDCl3) δ 8.98 (s, 1H), 7.80–7.59 (m, 2H), 7.55–7.44 (m, 2H), 7.44–7.32 (m, 2H), 1.49 (s, 9H). 13C NMR (101 MHz, CDCl3) δ 203.7, 149.1, 142.2, 131.6, 128.1, 127.1, 83.5, 27.9. HRMS (ESI): calcd for C12H10NO2S [M-H]: 236.0751; found 236.0751.
2.2 Synthesis of Diaryliodonium Salts 2
The general methods developed in our group were used for synthesis of diaryliodonium salts featured in the arylation of thioamides (Table S1). No precautions were taken to avoid air or moisture. In unsymmetric diaryliodonium salts, the substrates should be selected such that an aryl group with electron-withdrawing substituents is introduced as the ArI, and the other aryl group as ArH. See Table S2 for synthetic details and references to analytical data.

Table S1. General methods to synthesize diaryliodonium salts

<table>
<thead>
<tr>
<th>Method</th>
<th>Reaction</th>
<th>Conditions</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;9&lt;/sup&gt;</td>
<td>R&lt;sub&gt;1&lt;/sub&gt;-&lt;i&gt;I&lt;/i&gt; + R&lt;sub&gt;2&lt;/sub&gt;-&lt;i&gt;I&lt;/i&gt;</td>
<td>mCPBA (1.1 equiv) TIOH (2-3 equiv) CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; temp., time</td>
<td>R&lt;sub&gt;1&lt;/sub&gt;-&lt;i&gt;OTf&lt;/i&gt;</td>
</tr>
<tr>
<td>2&lt;sup&gt;10&lt;/sup&gt;</td>
<td>R&lt;sub&gt;1&lt;/sub&gt;-&lt;i&gt;I&lt;/i&gt;</td>
<td>mCPBA (1.1 equiv) TIOH (2 equiv) CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; temp., time</td>
<td>R&lt;sub&gt;1&lt;/sub&gt;-&lt;i&gt;OTf&lt;/i&gt;</td>
</tr>
<tr>
<td>3&lt;sup&gt;11&lt;/sup&gt;</td>
<td>R&lt;sub&gt;1&lt;/sub&gt;-&lt;i&gt;N&lt;/i&gt; + R&lt;sub&gt;1&lt;/sub&gt;-&lt;i&gt;RR&lt;/i&gt;</td>
<td>mCPBA (1.75 equiv) TIOH (4 equiv) CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; 60 °C, 30 min</td>
<td>R&lt;sub&gt;1&lt;/sub&gt;-&lt;i&gt;OTf&lt;/i&gt;</td>
</tr>
<tr>
<td>4&lt;sup&gt;10&lt;/sup&gt;</td>
<td>R&lt;sub&gt;1&lt;/sub&gt;-&lt;i&gt;I&lt;/i&gt; + R&lt;sub&gt;2&lt;/sub&gt;-&lt;i&gt;I&lt;/i&gt;</td>
<td>mCPBA (1.1 equiv) TsOH·H&lt;sub&gt;2&lt;/sub&gt;O (1.1 equiv) CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; temp., time</td>
<td>R&lt;sub&gt;1&lt;/sub&gt;-&lt;i&gt;OTs&lt;/i&gt;</td>
</tr>
<tr>
<td>5&lt;sup&gt;9&lt;/sup&gt;</td>
<td>4 + R&lt;sub&gt;1&lt;/sub&gt;-&lt;i&gt;I&lt;/i&gt;</td>
<td>mCPBA (3-4 equiv) TIOH (4-5 equiv) CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; temp., time</td>
<td>R&lt;sub&gt;1&lt;/sub&gt;-&lt;i&gt;OTf&lt;/i&gt;</td>
</tr>
<tr>
<td>6&lt;sup&gt;11&lt;/sup&gt;</td>
<td>4 + R&lt;sub&gt;1&lt;/sub&gt;-&lt;i&gt;I&lt;/i&gt;</td>
<td>mCPBA (3-4 equiv) TsOH·H&lt;sub&gt;2&lt;/sub&gt;O (4 equiv) CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; temp., time</td>
<td>R&lt;sub&gt;1&lt;/sub&gt;-&lt;i&gt;OTf&lt;/i&gt;</td>
</tr>
<tr>
<td>7&lt;sup&gt;12&lt;/sup&gt;</td>
<td>(2 equiv) + I&lt;sub&gt;2&lt;/sub&gt;</td>
<td>mCPBA (3 equiv) TsOH·H&lt;sub&gt;2&lt;/sub&gt;O (2 equiv) CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; temp., time</td>
<td>R&lt;sub&gt;1&lt;/sub&gt;-&lt;i&gt;OTs&lt;/i&gt;</td>
</tr>
<tr>
<td>8&lt;sup&gt;10&lt;/sup&gt;, 13</td>
<td>F&lt;sub&gt;3&lt;/sub&gt;C-&lt;i&gt;I&lt;/i&gt;</td>
<td>mCPBA (1 equiv) TsOH·H&lt;sub&gt;2&lt;/sub&gt;O (1 equiv) TFE, 40 °C, 1 h</td>
<td>F&lt;sub&gt;3&lt;/sub&gt;C-&lt;i&gt;OTs&lt;/i&gt;</td>
</tr>
</tbody>
</table>
Anion exchange:

NaX (85 mmol) was dissolved in H₂O (100 mL). Diaryliodonium salt (3.4 mmol) was dissolved in CH₂Cl₂ (20 mL) and washed 5 times with 20 mL of the prepared aqueous solution. The organic layer was concentrated without drying. To the crude was added Et₂O, and the mixture was stirred at rt or at 0 °C until precipitation occurred. The solid was filtered and washed with Et₂O, followed by drying under vacuum. The method was used to exchange BF₄⁻ to OTs using NaOTs, and OTs to OTf using NaOTf.

**Table S2.** Synthesized diaryliodonium salts.

<table>
<thead>
<tr>
<th>Ar₂IX</th>
<th>Method</th>
<th>Acid (equiv)</th>
<th>Temp. [°C]</th>
<th>Time</th>
<th>Yield [%]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Ar₂I - OTf" /></td>
<td>1</td>
<td>3</td>
<td>Acid addition at 0 °C, then run at rt</td>
<td>1.5 h</td>
<td>95</td>
<td>9</td>
</tr>
<tr>
<td><img src="image" alt="NC" /></td>
<td>1</td>
<td>2</td>
<td>Acid addition at 0 °C, then run at rt</td>
<td>17 h</td>
<td>79</td>
<td>15</td>
</tr>
<tr>
<td><img src="image" alt="O₂N" /></td>
<td>1</td>
<td>2</td>
<td>Acid addition at 0 °C, then run at rt</td>
<td>17 h</td>
<td>88</td>
<td>15</td>
</tr>
<tr>
<td><img src="image" alt="Ar₂I - OTf" /></td>
<td>1</td>
<td>2</td>
<td>Acid addition at 0 °C, then run at rt</td>
<td>1 h</td>
<td>78</td>
<td>9</td>
</tr>
<tr>
<td><img src="image" alt="Br" /></td>
<td>1</td>
<td>3</td>
<td>Acid addition at 0 °C, then run at rt</td>
<td>3 h</td>
<td>90</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>r.t.</td>
<td>1</td>
<td>66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2f</td>
<td>COOMe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1) 0 °C</td>
<td>2) 40 °C</td>
<td>10 min + 3 h</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>2g</td>
<td>Acid addition at 0 °C, then run at rt</td>
<td>30 min + 30 min</td>
<td>89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2h</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2i</td>
<td>Acid addition at 0 °C, then run at rt; 2) 0 °C</td>
<td>50 min + 50 min</td>
<td>68</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2j</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2l</td>
<td>Acid addition at 0 °C, then run at rt</td>
<td>2 h</td>
<td>43</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2m</td>
<td>Acid addition at 0 °C, then run at rt</td>
<td>1.5 h</td>
<td>31</td>
<td></td>
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</tr>
<tr>
<td>2n</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2o</td>
<td>TsOH·H₂O (4), TIOH (2)</td>
<td>rt</td>
<td>20 h, 1 h</td>
<td>57</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**

- 9
- 10
- 14
- 16
- 17
To a stirred solution of 2,4-dichloroiodobenzene (100 µL, 0.737 mmol) and mCPBA (0.810 mmol, 160 mg, 87% active oxidant) in CH₂Cl₂ (8 mL) was added TsOH·H₂O (210 mg, 1,105 mmol) portion wise at room temperature. The mixture was warmed at 40 °C for 5 min. After that anisole (88 µL, 0.810 mmol) was added to the solution at r.t, followed by stirring the reaction for 2 h at rt. Then the solution was concentrated to dryness, added Et₂O (ca 4 mL) and stirred on ice-bath. The precipitation was filtrated and washed with Et₂O to yield white solid as product (312 mg, 77%). ¹H NMR (400 MHz, CD₃OD) δ 8.34 (d, J = 8.6 Hz, 1H), 8.12–8.06 (m, 2H), 7.86 (d, J = 2.3 Hz, 1H), 7.71–7.66 (m, 2H), 7.47 (dd, J = 8.6, 2.3 Hz, 1H), 7.24–7.19 (m, 2H), 7.09–7.04 (m, 2H), 3.84 (s, 3H), 2.36 (s, 3H) ppm. ¹³C NMR (101 MHz, CD₃OD) δ 163.3, 142.2, 140.2, 140.1, 139.0, 137.9, 137.3, 130.1, 130.1, 128.4, 125.5, 117.5, 115.9, 103.6, 54.9, 19.9 ppm. HRMS (ESI): calcd for C₁₃H₁₀Cl₂IO [M-OTs]⁺: 378.9148; found 378.9151.
3 Optimization of the Arylation of Thioamides

3.1 Screening of Reaction Conditions

Extensive optimization studies were performed. Base, anions and solvents were screened at rt. (Tables S3-S5). The stoichiometry and concentration effects are detailed in Table S6. The addition of aryne traps (furan or piperidine), and radical trap (DPE) excluded radical or aryne mechanisms (Table S6). The temperature was finally varied in Table S7.

![Chemical structure](image)

Table S3. Base screening in toluene at r.t. (X = OTf)

<table>
<thead>
<tr>
<th>Salt (equiv)</th>
<th>Base (equiv)</th>
<th>solvent</th>
<th>Temp. [°C]</th>
<th>Time [h]</th>
<th>Yield 3a [%]a</th>
<th>Recovered thioamide 1a [%]a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>-</td>
<td>toluene</td>
<td>rt</td>
<td>24</td>
<td>n.o.</td>
<td>Quant.</td>
</tr>
<tr>
<td>2.0</td>
<td>NaH (1.5)</td>
<td>toluene</td>
<td>rt</td>
<td>24</td>
<td>25b</td>
<td>61</td>
</tr>
<tr>
<td>2.0</td>
<td>NaH (1.5)</td>
<td>toluene</td>
<td>rt</td>
<td>24</td>
<td>34</td>
<td>43</td>
</tr>
<tr>
<td>1.5</td>
<td>NaH (1.5)</td>
<td>toluene</td>
<td>rt</td>
<td>24</td>
<td>39</td>
<td>49</td>
</tr>
<tr>
<td>1.5</td>
<td>NaH (1.5)</td>
<td>toluene</td>
<td>rt</td>
<td>16</td>
<td>40</td>
<td>29</td>
</tr>
<tr>
<td>1.5</td>
<td>NaH (1.1)</td>
<td>toluene</td>
<td>rt</td>
<td>16</td>
<td>27</td>
<td>33</td>
</tr>
<tr>
<td>1.5</td>
<td>NaH (1.5)</td>
<td>toluene</td>
<td>rt</td>
<td>1</td>
<td>6</td>
<td>94</td>
</tr>
<tr>
<td>1.5</td>
<td>NaOrBu (1.5)</td>
<td>toluene</td>
<td>rt</td>
<td>1</td>
<td>27</td>
<td>43</td>
</tr>
<tr>
<td>1.5</td>
<td>NaOrBu (1.2)</td>
<td>toluene</td>
<td>rt</td>
<td>1</td>
<td>29</td>
<td>45</td>
</tr>
<tr>
<td>1.5</td>
<td>NaOrBu (1.1)</td>
<td>toluene</td>
<td>rt</td>
<td>1</td>
<td>22</td>
<td>48</td>
</tr>
<tr>
<td>1.5</td>
<td>nBuLi (1.2)</td>
<td>toluene</td>
<td>rt</td>
<td>1</td>
<td>20</td>
<td>72</td>
</tr>
<tr>
<td>1.5</td>
<td>NaOrBu (1.2)</td>
<td>toluene</td>
<td>rt</td>
<td>16</td>
<td>28</td>
<td>39</td>
</tr>
<tr>
<td>1.5</td>
<td>tBuOK (1.2)</td>
<td>toluene</td>
<td>rt</td>
<td>16</td>
<td>27</td>
<td>33</td>
</tr>
<tr>
<td>1.5</td>
<td>LiOrBu (1.2)</td>
<td>toluene</td>
<td>rt</td>
<td>16</td>
<td>40</td>
<td>26</td>
</tr>
<tr>
<td>1.5</td>
<td>Et3N (1.2)</td>
<td>toluene</td>
<td>rt</td>
<td>16</td>
<td>3</td>
<td>Quant.</td>
</tr>
<tr>
<td>1.5</td>
<td>TMG (1.2)</td>
<td>toluene</td>
<td>rt</td>
<td>16</td>
<td>39</td>
<td>58</td>
</tr>
<tr>
<td>1.5</td>
<td>NH3 in MeOH (excess)</td>
<td>toluene</td>
<td>rt</td>
<td>16</td>
<td>6</td>
<td>89</td>
</tr>
<tr>
<td>1.5</td>
<td>NH3 (25% aq., excess)</td>
<td>toluene</td>
<td>rt</td>
<td>16</td>
<td>34</td>
<td>26</td>
</tr>
<tr>
<td>1.5</td>
<td>NaOH (1.2)</td>
<td>toluene</td>
<td>rt</td>
<td>16</td>
<td>34</td>
<td>39</td>
</tr>
<tr>
<td>1.5</td>
<td>Na2CO3 (1.2)</td>
<td>toluene</td>
<td>rt</td>
<td>16</td>
<td>traces</td>
<td>95</td>
</tr>
<tr>
<td>1.5</td>
<td>Cs2CO3 (1.2)</td>
<td>toluene</td>
<td>rt</td>
<td>16</td>
<td>4</td>
<td>86</td>
</tr>
</tbody>
</table>

a Isolated yields
b Reaction was run under argon atmosphere
n.o. – not observed; n.d. – not determined; TMG – 1,1,3,3-tetramethylguanidine

Table S4. Diaryliodonium counterion (X) screening in toluene at rt.

<table>
<thead>
<tr>
<th>Counter -ion X</th>
<th>Salt (equiv)</th>
<th>Base (equiv)</th>
<th>solvent</th>
<th>Temp. [°C]</th>
<th>Time [h]</th>
<th>Yield 3a [%]a</th>
<th>Recovered thioamide 1a [%]a</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTf</td>
<td>1.5</td>
<td>NaOrBu (1.2)</td>
<td>toluene</td>
<td>rt</td>
<td>1</td>
<td>29</td>
<td>45</td>
</tr>
<tr>
<td>OTs</td>
<td>1.5</td>
<td>NaOrBu (1.2)</td>
<td>toluene</td>
<td>rt</td>
<td>1</td>
<td>29</td>
<td>48</td>
</tr>
<tr>
<td>Br</td>
<td>1.5</td>
<td>NaOrBu (1.2)</td>
<td>toluene</td>
<td>rt</td>
<td>1</td>
<td>29</td>
<td>28</td>
</tr>
<tr>
<td>BF3</td>
<td>1.5</td>
<td>NaOrBu (1.2)</td>
<td>toluene</td>
<td>rt</td>
<td>1</td>
<td>25</td>
<td>57</td>
</tr>
<tr>
<td>PF6</td>
<td>1.5</td>
<td>NaOrBu (1.2)</td>
<td>toluene</td>
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a Isolated yields
Table S5. Solvent screening at rt. (X = OTf)

<table>
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<tr>
<th>Salt (equiv)</th>
<th>Base (equiv)</th>
<th>solvent</th>
<th>Temp. [°C]</th>
<th>Time [h]</th>
<th>Yield 3a [%]</th>
<th>Recovered thioamide 1a [%]</th>
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<td>1.5</td>
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a Isolated yields

Table S6. Screening for reagent loading, concentration effect and additives (X = OTf)

<table>
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<tr>
<th>Additive (equiv)</th>
<th>Salt (equiv)</th>
<th>Base (equiv)</th>
<th>solvent</th>
<th>Temp. [°C]</th>
<th>Time [h]</th>
<th>Yield 3a [%]</th>
<th>Recovered thioamide 1a [%]</th>
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<td>LiOrBu (1.5)</td>
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<td>16</td>
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<td>LiOrBu (1.2)</td>
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<td>1</td>
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<td>n.d.</td>
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</tbody>
</table>

a Isolated yields
b 1H NMR of the crude reaction mixture showed no evidence of formed Diels-Alder adducts. Low yield could be explained by high loading of furane that can interfere with the reaction outcome via other mechanisms.
c 1H NMR yield was determined with 1,3,5-trimethoxybenzene as internal standard. No arylated piperidine was observed in crude 1H NMR.
n.d. – not determined

Table S7. Temperature and reaction time screening, X = OTf

<table>
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<tr>
<th>Salt (equiv)</th>
<th>Base (equiv)</th>
<th>solvent</th>
<th>Temp. [°C]</th>
<th>Time [h]</th>
<th>Yield 3a [%]</th>
<th>Recovered thioamide 1a [%]</th>
</tr>
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<tr>
<td>1.1</td>
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<td>rt</td>
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<td>71</td>
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3.2 Effect of the Counterion in Diaryliodonium Salts

A preliminary comparison of counterions OTf, OTs, Br, PF₆, BF₄ and TFA was performed in the optimization (Table S4). The superiority of the commonly used OTf over BF₄ was further confirmed by reactions at 80 °C under our optimized conditions (Scheme S1).

![Scheme S1. Effect of the counterion X.](image)

A considerable increase in yield was detected when the effects of the counterion X (here BF₄ vs OTf) and the dummy group (here anisyl) work in favour of the expected product 3e (Scheme S2).

![Scheme S2. Combined effect of counterion X and dummy group.](image)
3.3 Effect of Degassing the Toluene

Towards the end of the project, we discovered a positive effect on the reaction yield upon degassing the toluene. Especially the yields of 3b, 3h, and 3r increased considerably as well as thioimidates 3s, 3a, 3o, 3p (Scheme S3). The positive effect included both electron rich (e.g. 3p) or electron deficient aryl transfer (e.g. 3b). The yields of some thioimidates were, on the other hand, almost not affected by the degassed solvent (e.g. 3j, 3k, 3l, 3m). Surprisingly, 3c even gave a somewhat lower yield compared to reactions in non-degassed toluene. The reason behind the general yield increase was not explored, but degassing is presumed to suppress desulfurization and hydrolysis processes of the formed thioimidates.

Scheme S3. Effect of degassed toluene on the yield of thioimidates 3.
4 Chemoselectivity Studies

Byproducts often form in the synthesis of symmetric diaryliodonium salts with either two electron withdrawing or two electron donating aryl groups. Unsymmetric diaryliodonium salts are often easier to synthesize, as the electronic properties can be better matched to get good reactivity, as exemplified in Figure S1. Furthermore, the preparation cost can be considerably decreased when a precious aryl group should be introduced, or when a substitution pattern that cannot be reached by electrophilic aromatic substitution (Methods 1-8) is desired, as boronic acids (Method 9) can be avoided.

**Figure S1.** Ease of synthesis of symmetric and unsymmetric iodonium salts.

Unsymmetric iodonium salts are highly useful reagents when one aryl group is chemoselectively transferred to the nucleophile. The chemoselectivity can depend both on the sterics and electronics, and under transition metal-free reaction conditions, the more electron deficient aryl is preferably transferred.\(^\text{10, 12, 19}\) Ortho-substituted aryl groups are often preferred in the ligand coupling, a feature that is referred to as the "ortho-effect".\(^\text{20}\) Considering these aspects and the nature of the nucleophile, the non-transferable aryl moiety or the "dummy group" can be specifically chosen to aid the transfer of the desired aryl to the nucleophile under metal-free conditions.\(^\text{21}\) In this project, we have employed the three dummy groups depicted in Figure S2. The phenyl group is used in reactions where a strongly electron withdrawing aryl group should be transferred, e.g. NO\(_2\) and CN. Complete chemoselectivity is often not reached with the Ph dummy in transfer of aryl groups with weaker EWG substituents, such as CF\(_3\) and halides, for which the anisyl dummy is suitable. The latter dummy can also be used in transfer of aryl groups with weakly EDG substituents. The TMP dummy is suitable in transfer of EDG aryls, and salts with a TMP dummy sometimes give superior yields in synthesis or arylations compared to the corresponding anisyl salts.\(^\text{22}\)

**Figure S2.** Employed dummy groups.

We observed a considerable ortho-effect for the S-arylation of thioamides, as exemplified in Scheme S4. The arylation with mesityl(phenyl)iodonium triflate (2f) delivered a mixture of mesitylated and phenylated products 3n and 3a in a 86:14 ratio and overall yield of 84% in favor of 3n, with 16% of thioamide 1a recovered. In comparison, a reaction with symmetric dimesityliodonium triflate 2n gave 73% yield under the same conditions, i.e. 3n was formed in similar yields with both salts.
Scheme S4. Chemoselectivity study.

To achieve complete chemoselectivity, we investigated the anisyl as group as dummy by comparing arylations of 1a with a symmetric 2e and an unsymmetric p-Br salt 2i (Scheme S5). Indeed, employment of the anisyl salt 2i increased the yield considerably compared to the symmetric salt 2e, giving 3j in 55% and 40% respectively. The observed chemoselectivity with the unsymmetric salt was also good, with < 5% of 3p isolated. (Product 3p can be obtained in 69% with the symmetric dianisyliodonium triflate 2o.)

Scheme S5. Comparison of symmetric and unsymmetric salts.
5 Structure Analysis of Thioimidates 3

5.1 Determination of the Z/E–Ratio
Throughout the optimization and scope studies, the major product was isolated together with an inseparable minor product by column chromatography. While the thioamides can easily hydrolyze to the corresponding amides, such species were not formed according to comparison with literature NMR data.

Schmidt and coworkers reported the synthesis of thioimidates from indazolium salts and thiophenols, and observed the products to be an Z:E mixture with ratios up to 5:1. The extra set of signals for the N-CH₃ of the E isomer in ¹H and ¹³C NMR spectra were shifted upfield from the major Z isomer. Single-crystal X-ray analysis confirmed the Z configuration of the imine bond.

The NMR data of the major and minor products formed in the synthesis of acyclic aryl thioimidates 3a-3s, 3v are in agreement with the formation of Z- and E-isomers. The minor E-isomer was observed as an extra set of NMR signals upfield for the methylene signals in N-CH₂-Ph. This hypothesis was also supported by NOESY analysis that did not show any correlation between the methylene and the aromatic backbone, which would be expected for the E isomer. The Z:E ratios were determined by integrating the methylene signals N-CH₂-Ph for both isomers in the ¹H NMR spectrum of the isolated product and ranged from 86:14 up to 96:4. The ratios stayed constant independent of the reaction conditions (various solvents, bases and reaction temperatures). The minor isomer is not fully characterized due to overlapping of signals in the aromatic area. Thioimdate 3o, furnished with a bulky S-aryl moiety, gave the lowest Z:E ratio of 86:14 (Scheme S6).

Scheme S6. E and Z isomers of thioimdate 3o.

As the Z:E ratio of 3o was lower than for the other thioimidates 3, the carbonyl group S-C=N was also observable for the minor isomer (Figure S3). The shifts of the carbonyl group of both the major (162.59 ppm) and minor (165.00 ppm) counterpart are observable in the thioimidate area, which is high field from a thioamide carbonyl region (203 ppm).
Figure S3. $^1$H and $^{13}$C NMR of thioimidate 3o.

Other thioimidates 3a-3s, 3v have been analyzed in analogy with 3o (Figure S4). No significant alterations in the Z:E ratios were detected when the arylation was run at room temperature or elevated temperature. Compounds 3w, 3x, 3y and 4b only gave one set of signals by NMR analysis.
5.2 Hydrolysis of Thioimidate

In order to further confirm the formation of S-arylated thioimidates, product 3c was subjected to hydrolysis under acidic conditions (Scheme S7). Two major products were isolated and identified as the corresponding amide and p-NO₂ thiophenol, which are both reported compounds (¹H,¹³C NMR spectra shown in Figure S5).

![Scheme S7. Hydrolysis of thioimidate 3c](image)
5.3 S/N-Arylation Products of Thioamides 1e, 1f and Pyrrolidine-2-thione

In general, the acyclic thioamides delivered S-arylated products with no observed N-arylations. The exceptions were alkyl thioamides 1e and 1f. Thioamide 1e gave the S-arylated 3t as major product with a minor N-arylated product 4t in 43% overall yield (Scheme S8). No E/Z-mixture was detected, only one set of signals was observed for both products in $^1$H and $^{13}$C NMR analysis. The carbonyl signal in $^{13}$C NMR for thioimidate 3t is at 167.8 ppm, whereas the carbonyl signal in 4t is at 214.0 ppm, which is characteristic for a thioamide. For a similar thioamide ($t$Bu instead of $i$Pr),

Figure S5. $^1$H and $^{13}$C NMR spectra for amide and thiophenol from hydrolysis of 3c.
the reported carbonyl signal is at 217.0 ppm. The ratio of $S:N$-arylation (87:13) is assessed by $^1$H NMR integration as shown from $-CH$-iPr signals at 2.60 ppm (3t) and 2.84 ppm (4t). A substantial shift is also seen for the $-CH_2$-Ph protons at 4.73 ppm (3t) and 5.61 ppm (4t), for the reported $t$Bu thioamide the corresponding signals are at 5.65 ppm. Thioamide 1f bearing cyclo-hexyl instead on i-Pr followed suit, giving a $S:N$ mixture 5:1 of arylation products in 32% yield (3u). On the other hand, 1g with linear $n$-hexyl substitution, gave only traces of arylation products, with mostly starting material 1g recovered (29%) along with the corresponding amide (51%), indicating that the alkylated thioamide is much more prone to hydrolysis compared to arylated substrates.

Scheme S8. $^1$H and $^{13}$C NMR of $N$- and $S$-arylated products of thioamide 1e. A reported $t$Bu thioamide is shown as comparison. Interestingly, reactions with thiolactams gave predominantly $N$-arylated products. Pyrrolidine-2-thione gave a mixture of $N$-arylated 4a (major) and $S$-arylated product 3aa (minor) (Scheme S9), which matches the literature data on 4a. The products were difficult to separate by flash chromatography and were thus isolated together. The $N:S$ ratio was measured from the crude reaction mixture ($N:S$ 1.5:1) after evaporation of toluene. Some of minor isomer was lost during purification, giving $N:S$
2:1 for the isolated 4a,3aa mixture. The isolated mixture of 4a and 3aa was investigated by GC-MS, which showed two major signals with the same mass (Figure S6). The N/S mixture was observed also under different reaction conditions, e.g., at room temperature, at 0 °C and after shorter and longer reaction times.

Scheme S9. $^1$H, $^{13}$C NMR of the N/S mixture from arylation of pyrrolidine-2-thione.
Figure S6. GC-MS analysis of the N/S mixture from arylation of pyrrolidine-2-thione. Isoquinoline-1-thione delivered the N-arylated thiolactam 4b in high yields already at room temperature (Scheme S10). In this case, the yield can be further improved by adding the base to a stirred solution of thiolactam and 2c in toluene after 5 min. This effect was not observed for other substrates. LiO(CH$_3$)$_3$ gave 76-95% isolated yield of 4b, and NaO(CH$_3$)$_3$ gave 81%, whereas reactions with K$_2$CO$_3$ only resulted in recovered starting material [conditions: Ph$_2$IO Tf (1.1 equiv), K$_2$CO$_3$ (1.1 equiv), 80 °C, 1 h].
Scheme S10. Arylation of isoquinoline-1-thione.
6 Preliminary Mechanistic Studies

We have recently published a mechanistic study of O-arylations with diaryliodonium salts, based on experimental techniques and calculations. We demonstrated that reactions under basic conditions can result in aryne formation already at room temperature. We used two approaches to identify arynes:

1) arylations with EDG-substituted iodonium salts (e.g. para-alkyl) gives regioisomers when arynes are involved.

2) furan was added as an aryne trap, resulting in cycloaddition products in the presence of arynes.

Preliminary mechanistic investigations in the arylation of thioamides revealed that arynes could not be identified using the approaches above. Furthermore, addition of radical scavengers (piperidine and 1,1-diphenylethylene, respectively) had negligible effect on the reaction outcome (see Table S6). Hence both an aryne pathway and a radical mechanism can be excluded.

We have previously studied the mechanisms in arylation of other nucleophiles with two nucleophilic atoms (enolates and nitrite) using a combination of experimental and theoretical techniques. Those studies revealed the possibility of two different intermediates that could be converted to product via different types of ligand coupling, either with a 3-membered TS or with a larger TS. We have been unable to observe intermediates in any arylations by NMR due to the heterogeneous reactions, apart from in a recently described synthesis of Phenoxazine, where the T-shaped intermediate was stable to workup.

Based on previous studies, we propose that the reaction proceeds by deprotonation and ligand exchange to provide T-shaped intermediate A and/or B (Scheme S11). I-N intermediate A could form the S-arylated thioimidate 3 via a [2,3] rearrangement, whereas I-S intermediate B would undergo a [1,2] rearrangement to yield 3. Alternatively, intermediates A and B could yield N-aryl thioamide 4 through [1,2] and [2,3] rearrangement, respectively.

Scheme S11. Mechanistic possibilities.
7 Synthesis of Aryl Thioimidates 3

7.1 General Procedure for Arylation of Thioamides
Thioamide 1 (0.12 mmol, 1 equiv), diaryliodonium salt 2 (1.1 equiv) and LiO\textsubscript{t}Bu (1.1 equiv) were weighed into an oven dried 4 mL microwave vial. The reaction vessel was evacuated and backfilled with argon three times, and the solids were then dissolved in degassed, anhydrous toluene (1.9 mL) under argon. The reaction was stirred at 80 °C for 1 h. After that the reaction mixture was brought to room temperature, and transported directly onto a silica gel column with a small amount of CH\textsubscript{2}Cl\textsubscript{2}. The mixture was purified by flash column chromatography (2% EtOAc in pentane or Et\textsubscript{2}O in pentane).

7.2 Synthetic Details and Analytical Data

Phenyl (Z)-N-benzylbenzimidothioate (3a)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2a as yellow oil, Z:E ratio 93:7. (Z) isomer: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.67–7.62 (m, 2H), 7.53–7.48 (m, 2H), 7.34–7.29 (m, 1H), 7.25 (m, 5H), 7.19–7.14 (m, 3H), 5.04 (bs, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 161.5, 139.6, 138.2, 132.6, 132.6, 129.5, 129.1, 128.9, 128.4, 127.89, 127.8, 127.4, 126.8, 58.6. Characteristic signals for (E) isomer: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 4.56 (s, 2H, N-C\textsubscript{6}H\textsubscript{5}Ph); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 167.1, 56.9 ppm. HRMS (ESI): calcd C\textsubscript{20}H\textsubscript{18}N\textsubscript{2}S [M+H]\textsuperscript{+}: 304.1154, found 304.1153.

4-Cyanophenyl (Z)-N-benzylbenzimidothioate (3b)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2b as beige oil, Z:E ratio 92:8. (Z) isomer: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.75–7.65 (m, 2H), 7.47–7.34 (m, 6H), 7.32–7.20 (m, 6H), 5.03 (s, 2H) ppm. \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 158.0, 140.2, 138.94, 137.6, 132.3, 131.3, 130.4, 129.2, 128.6, 128.3, 127.8, 127.4, 126.8, 58.6. Characteristic signals for (E) isomer: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 4.53 (s, 2H, N-C\textsubscript{6}H\textsubscript{5}Ph); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 164.8, 57.12. HRMS (ESI): calcd C\textsubscript{21}H\textsubscript{17}N\textsubscript{2}O\textsubscript{2}S [M+H]\textsuperscript{+}: 329.1107, found 329.1105.

4-Nitrophenyl (Z)-N-benzylbenzimidothioate (3c)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2c as yellow oil, Z:E ratio 92:7. (Z) isomer: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.99 (app.d, 2H), 7.76 (app.d, 2H), 7.47–7.34 (m, 6H), 7.32–7.20 (m, 6H), 5.03 (s, 2H) ppm. \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 157.5, 146.2, 142.6, 138.8, 137.5, 130.9, 130.5, 129.2, 128.5, 128.3, 127.8, 127.1, 118.3, 110.4, 59.4. Characteristic signals for (E) isomer: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 4.56 (s, 2H, N-C\textsubscript{6}H\textsubscript{5}Ph); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 164.5, 57.2. HRMS (ESI): calcd C\textsubscript{20}H\textsubscript{17}N\textsubscript{2}O\textsubscript{2}S [M+H]\textsuperscript{+}: 349.1005, found 349.1003.
4-(Trifluoromethoxy)phenyl (Z)-N-benzylbenzimidothioate (3d)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2r as yellow oil, Z:E ratio 89:11. (Z) isomer: 1H NMR (400 MHz, CDCl3) δ 7.61–7.55 (m, 2H), 7.50–7.45 (m, 2H), 7.43–7.36 (m, 2H), 7.34–7.28 (m, 1H), 7.27–7.21 (m, 5H), 7.03–6.97 (m, 2H), 5.02 (s, 2H). 13C NMR (101 MHz, CDCl3) δ 160.8, 148.7, 139.5, 137.9, 134.2, 131.5, 129.8, 129.2, 128.7, 128.1, 128.0, 127.1, 123.0 (q, J = 258.3 Hz), 121.5, 58.9. Characteristic signals for (E) isomer: 1H NMR (400 MHz, CDCl3) δ 4.54 (s, 2H, N-CH2-Ph). HRMS (ESI): calcd C21H17F3NOS [M+H]+: 388.0977, found 388.0975.

4-(Trifluoromethyl)phenyl (Z)-N-benzylbenzimidothioate (3e)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2h as yellow oil, Z:E ratio 92:8. (Z) isomer: 1H NMR (400 MHz, CDCl3) δ 7.72–7.67 (m, 2H), 7.44 (m, 2H), 7.40–7.34 (m, 4H), 7.32–7.21 (m, 6H), 5.03 (s, 2H). 13C NMR (101 MHz, CDCl3) δ 159.2, 139.3, 138.2, 137.9, 135.1, 131.6, 130.3, 129.3, 128.7, 128.3, 128.0, 127.1, 125.9 (q, J = 3.7 Hz), 123.9 (q, J = 272.1 Hz), 59.3. Characteristic signals for (E) isomer: 1H NMR (400 MHz, CDCl3) δ 4.53 (s, 2H, N-CH2-Ph). 13C NMR (101 MHz, CDCl3) δ 57.1. HRMS (ESI): calcd C21H17F3NS [M+H]+: 372.1028, found 372.1028.

3-(Trifluoromethyl)phenyl (Z)-N-benzylbenzimidothioate (3f)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2q as yellow oil, Z:E ratio 88:12. (Z) isomer: 1H NMR (400 MHz, CDCl3) δ 7.60–7.53 (m, 2H), 7.45 (dd, J = 7.2, 1.7 Hz, 3H), 7.40–7.32 (m, 4H), 7.32–7.26 (m, 1H), 7.24–7.16 (m, 4H), 5.01 (s, 2H). 13C NMR (101 MHz, CDCl3) δ 160.2, 139.2, 137.6, 135.5 (q, J = 0.9 Hz), 134.2, 131.3 (q, J = 32.5 Hz), 129.8, 129.2, 129.1, 128.5, 128.0, 127.9, 126.9, 124.0 (q, J = 3.7 Hz), 123.4 (q, J = 272.9 Hz), 58.9. Characteristic signals for (E) isomer: 1H NMR (400 MHz, CDCl3) δ 4.51 (s, 2H, N-CH2-Ph). 13C NMR (101 MHz, CDCl3) δ 56.9. HRMS (ESI): calcd C21H17F3NS [M+H]+: 372.1028, found 372.1016. The isolated 3f contained ca 5% 4-iodoanisole, the yield 50% is calculated from the isolated mixture. Characteristic signal for 4-iodoanisole: 1H NMR (400 MHz, CDCl3) δ 3.71 (s, 3H, OCH3).

2-Fluorophenyl (Z)-N-benzylbenzimidothioate (3g)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2s as yellow oil, Z:E ratio 92:8. (Z) isomer: 1H NMR (400 MHz, CDCl3) δ 7.57–7.53 (m, 2H), 7.50–7.45 (m, 2H), 7.41–7.35 (m, 2H), 7.32–7.25 (m, 2H), 7.21–7.11 (m, 4H), 6.97–6.92 (m, 1H), 6.91–6.86 (m, 1H), 5.04 (s, 2H). 13C NMR (101 MHz, CDCl3) δ 162.6, 160.6 (d, J = 93.5 Hz), 139.6, 138.0, 135.6, 130.5 (d, J = 7.9 Hz), 129.6, 128.9, 128.6, 128.1, 127.9, 127.0, 124.6 (d, J = 3.9 Hz), 119.9 (d, J = 18.2 Hz), 115.9 (d, J = 22.6 Hz), 58.8. Characteristic signals for (E) isomer: 1H NMR (400 MHz, CDCl3) δ 4.51 (s, 2H, N-CH2-Ph). 13C NMR (101 MHz, CDCl3) δ 57.1. HRMS (ESI): calcd C20H17F3NOS [M+H]+: 322.1060, found 322.1062.
Methyl (Z)-2-[(benzylimino)(phenyl)methyl]thio)benzoate (3b)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2g as beige oil, Z:E ratio 96:4. (Z) isomer: 1H NMR (400 MHz, CDCl₃) δ 7.89–7.83 (m, 1H), 7.81–7.75 (m, 2H), 7.50–7.42 (m, 2H), 7.35 (m, 2H), 7.30–7.20 (m, 4H), 7.15 (dd, J = 7.1, 4.3, 2.0 Hz, 2H), 7.11–7.07 (m, 1H), 5.05 (s, 2H), 3.95 (s, 3H). 13C NMR (101 MHz, CDCl₃) δ 166.7, 160.2, 139.6, 138.4, 136.0, 132.2, 131.9, 131.1, 130.1, 130.0, 129.1, 128.4, 128.0, 127.9, 126.8, 126.2, 59.2, 52.4. Characteristic signals for (E) isomer: 1H NMR (400 MHz, CDCl₃) δ 4.48 (s, 2H, N=CH₂-Ph), 3.78 (s, 3H, COOC₃H₅). HRMS (ESI): calcd C₂₂H₂₂NO₂S [M+H]+: 362.1209, found 362.1207.

4-Azidophenyl (Z)-N-benzybenzimidothioate (3i)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2l as yellow oil, Z:E ratio 90:10. (Z) isomer: 1H NMR (400 MHz, CDCl₃) δ 7.57–7.52 (m, 2H), 7.48–7.42 (m, 2H), 7.40–7.33 (m, 2H), 7.30–7.25 (m, 2H), 7.23–7.16 (m, 4H), 6.82–6.75 (m, 2H), 4.99 (s, 2H). 13C NMR (101 MHz, CDCl₃) δ 161.5, 139.6, 139.5, 137.9, 134.4, 129.6, 129.1, 128.5, 128.5, 127.9, 126.9, 119.5, 58.5. Characteristic signals for (E) isomer: 1H NMR (400 MHz, CDCl₃) δ 4.50 (s, 2H, N=CH₂-Ph). HRMS (ESI): calcd C₂₀H₁₄N₂S [M+H]+: 345.1168, found 345.1169.

The isolated 3i contained ca 5% TMP-I, the yield 45% is calculated from the isolated mixture. Characteristic signal for TMP-I: 1H NMR (400 MHz, CDCl₃) δ 6.09 (s, 2H), 3.77 (s, 6H, OCH₃).

4-Bromophenyl (Z)-N-benzybenzimidothioate (3j)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2e or 2l as yellow oil, Z:E ratio 91:9. (Z) isomer: 1H NMR (400 MHz, CDCl₃) δ 7.64–7.56 (m, 2H), 7.46–7.42 (m, 2H), 7.39–7.33 (m, 2H), 7.30–7.20 (m, 6H), 7.10–7.03 (m, 2H), 4.99 (s, 2H). 13C NMR (101 MHz, CDCl₃) δ 160.5, 139.4, 137.8, 133.8, 132.0, 131.8, 129.8, 129.1, 128.5, 128.0, 127.9, 126.9, 121.7, 58.8. Characteristic signals for (E) isomer: 1H NMR (400 MHz, CDCl₃) δ 4.51 (s, 2H, N=CH₂-Ph). HRMS (ESI): calcd C₂₀H₁₃BrNS [M+H]+: 382.0260, found 382.0261.

2,4-Dichlorophenyl (Z)-N-benzybenzimidothioate (3k)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2k as yellow oil in 56% yield, Z:E ratio 93:7. (Z) isomer: 1H NMR (400 MHz, CDCl₃) δ 7.64–7.56 (m, 2H), 7.48–7.43 (m, 2H), 7.41–7.34 (m, 2H), 7.31–7.14 (m, 6H), 6.99 (dd, J = 8.4, 2.2 Hz, 1H), 5.03 (s, 2H). 13C NMR (101 MHz, CDCl₃) δ 159.7, 139.3, 137.7, 137.1, 135.5, 134.5, 130.6, 129.9, 129.7, 128.9, 128.5, 127.9, 127.9, 127.4, 126.9, 58.9. Characteristic signals for (E) isomer: 1H NMR (400 MHz, CDCl₃) δ 4.51 (s, 2H, N=CH₂-Ph). 13C NMR (101 MHz, CDCl₃) δ 56.9. HRMS (ESI): calcd C₂₀H₁₁Cl₂NS [M+H]+: 372.0375, found 372.0376.

A parallel reaction gave the isolated 3k contaminated with ca 32% 4-iodoanisole, the yield 75% for 3k was calculated from the isolated mixture. Characteristic signal for 4-iodoanisole: 1H NMR (400 MHz, CDCl₃) δ 3.76 (s, 3H, OCH₃) ppm.

p-Tolyl (Z)-N-benzybenzimidothioate (3l)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2d as beige waxy solid in 75% yield, Z:E ratio 93:7. (Z) isomer: 1H NMR (400 MHz, CD₃OD) δ 7.44–7.40 (m,
4-(tert-Butyl)phenyl (Z)-N-benzylbenzimidothioate (3m)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2m as yellow oil in 66% yield, Z:E ratio 92:8. (Z) isomer: 1H NMR (400 MHz, CDCl$_3$) δ 7.61–7.56 (m, 2H), 7.45 (m, 2H), 7.40–7.33 (m, 2H), 7.30–7.24 (m, 1H), 7.21–7.11 (m, 7H), 4.97 (s, 2H), 1.21 (s, 9H). 13C NMR (101 MHz, CDCl$_3$) δ 167.7, 164.0, 139.7, 139.2, 134.9, 130.8, 130.5, 130.1, 129.6, 129.1, 128.8, 128.1, 59.1, 21.0. Characteristic signals for (E) isomer: 1H NMR (400 MHz, CDCl$_3$) δ 4.43 (s, 2H, N–C$_2$H$_5$–Ph). HRMS (ESI): calcd C$_{23}$H$_{22}$NS [M+H]$^+$: 318.1311, found 318.1313.

Mesityl (Z)-N-benzylbenzimidothioate (3n)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2n or 2f as yellow oil in 73% yield, Z:E ratio 91:9. (Z) isomer: 1H NMR (400 MHz, CDCl$_3$) δ 7.54–7.49 (m, 2H), 7.47–7.43 (m, 2H), 7.43–7.37 (m, 2H), 7.30 (t, J = 7.3 Hz, 1H), 7.22–7.13 (m, 3H), 6.79 (s, 2H), 4.98 (s, 2H), 2.40 (s, 6H), 2.19 (s, 3H). 13C NMR (101 MHz, CDCl$_3$) δ 163.3, 141.4, 140.1, 138.7, 138.5, 129.4, 129.2, 128.5, 128.2, 128.1, 127.6, 127.5, 126.8, 125.9, 58.5, 34.5, 31.1. Characteristic signals for (E) isomer: 1H NMR (400 MHz, CDCl$_3$) δ 4.51 (s, 2H, N–C$_2$H$_5$–Ph). HRMS (ESI): calcd C$_{28}$H$_{26}$NS [M+H]$^+$: 360.1780, found 360.1780.

3-Bromo-2,4,6-trimethylphenyl (Z)-N-benzylbenzimidothioate (3o)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2p as beige oil, in 80% yield, Z:E ratio 86:14. (Z) isomer: 1H NMR (400 MHz, CDCl$_3$) δ 7.50–7.44 (m, 2H), 7.44–7.31 (m, 4H), 7.31–7.22 (m, 1H), 7.21–7.08 (m, 3H), 6.82 (s, 1H), 4.95 (s, 2H), 2.60 (s, 3H), 2.31 (s, 3H), 2.26 (s, 3H). 13C NMR (101 MHz, CDCl$_3$) δ 162.6, 140.9, 140.2, 139.7, 139.1, 138.0, 130.0, 129.5, 129.4, 128.4, 127.9, 127.5, 126.8, 125.6, 57.9, 24.0, 23.6, 22.1. Characteristic signals for (E) isomer: 1H NMR (400 MHz, CDCl$_3$) δ 4.46 (s, 2H, N–C$_2$H$_5$–Ph), 2.67 (s, 3H, CH$_3$), 2.43 (s, 3H, CH$_3$), 2.41 (s, 3H, CH$_3$). HRMS (ESI): calcd C$_{28}$H$_{25}$BrNS [M+H]$^+$: 424.0729, found 424.0715.

4-Methoxymethyl (Z)-N-benzylbenzimidothioate (3p)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2o as beige waxy solid in 69% yield, Z:E ratio 91:9. (Z) isomer: 1H NMR (400 MHz, CDCl$_3$) δ 7.56–7.42 (m, 4H), 7.41–7.32 (m, 2H), 7.31–7.21 (m, 1H), 7.21–7.11 (m, 5H), 6.73–6.58 (m, 2H), 4.97 (s, 2H), 3.70 (s, 3H). 13C NMR (101 MHz, CDCl$_3$) δ 163.1, 150.8, 139.8, 138.2, 135.0, 129.2, 128.9, 128.4, 127.9, 127.7, 126.8, 122.6, 114.5, 58.2, 55.2. Characteristic signals for (E) isomer: 1H NMR (400 MHz, CDCl$_3$) δ 4.50 (s, 2H, N–C$_2$H$_5$–Ph), 3.80 (s, 3H, OCH$_3$). HRMS (ESI): calcd C$_{27}$H$_{28}$NOS [M+H]$^+$: 334.1260, found 334.1258.
Pyridin-3-yl (Z)-N-benzylbenzimidothioate (3q)
Synthesized according to the general procedure using thioamide 1a and diaryliodonium salt 2j as yellow oil in 53% yield, Z:E ratio 87:13. (Z) isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.46 (dd, $J$ = 2.3, 0.9 Hz, 1H), 8.32 (dd, $J$ = 4.8, 1.6 Hz, 1H), 7.57–7.50 (m, 2H), 7.48–7.43 (m, 3H), 7.40–7.33 (m, 3H), 7.31–7.26 (m, 1H), 7.23–7.15 (m, 2H), 7.02 (ddd, $J$ = 8.0, 4.8, 0.8 Hz, 1H), 5.03 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.1, 152.7, 148.3, 139.9, 139.2, 137.4, 130.1, 129.8, 129.1, 128.5, 128.1, 127.9, 126.9, 123.5, 58.8. Characteristic signals for (E) isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.72 (m, 1H), 8.55 (m, 1H), 7.75 (m, 2H), 7.65 (m, 2H), 8.1, 127.9, 126.9, 123.5, 58.8. HRMS (ESI): calcd C$_{20}$H$_{17}$N$_2$S [M+H]$^+$: 305.1107, found 305.1113. The yield 53% is calculated from an isolated mixture of 3q and the corresponding amide, which is the product of hydrolysis of 3q. Characteristic signals for the corresponding amide: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (m, 2H), 6.52 (bs, 1H, NH$_2$), 4.64 (d, $J$ = 5.7 Hz, 2H). Compound 3q seems to be more prone to hydrolysis than other isolated thioimidates 3, and even when NMR analysis is carried out directly after isolation, the corresponding amide signals are always observed. Also, the amide signals increase over time.

Phenyl (Z)-N-benzyl-4-((trifluoromethyl)benzimidothioate (3r)
Synthesized according to the general procedure using thioamide 1b and diaryliodonium salt 2a as yellow oil in 73% yield, Z:E ratio 96:4. (Z) isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72–7.65 (m, 2H), 7.48–7.41 (m, 4H), 7.41–7.35 (m, 2H), 7.33–7.26 (m, 1H), 7.23–7.18 (m, 2H), 7.14 (dp, $J$ = 4.4, 1.5 Hz, 3H), 5.00 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.5, 141.5, 139.3, 132.8, 131.7, 131.2 (q, $J$ = 32.6 Hz), 129.4, 129.2, 128.5, 127.9, 127.9, 127.0, 124.8 (q, $J$ = 3.8 Hz), 123.8 (q, $J$ = 272.4 Hz), 58.8. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.81. Characteristic signals for (E) isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.46 (s, 2H, N-CH$_2$-Ph). HRMS (ESI): calcd C$_{21}$H$_{17}$F$_3$NS [M+H]$^+$: 372.1028, found 372.1034.

Phenyl (Z)-N-benzyl-4-methoxybenzimidothioate (3s)
Synthesized according to the general procedure using thioamide 1c and diaryliodonium salt 2a as yellow oil in 71% yield, Z:E ratio 95:5. (Z) isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72–7.61 (m, 2H), 7.47–7.40 (m, 2H), 7.38–7.32 (m, 2H), 7.29–7.19 (m, 3H), 7.18–7.10 (m, 3H), 6.79–6.67 (m, 2H), 4.98 (s, 2H), 3.73 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.8, 160.1, 139.9, 133.3, 131.9, 131.0, 130.8, 128.9, 128.4, 127.9, 127.0, 126.7, 113.2, 58.7, 55.2. Characteristic signals for (E) isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.54 (s, 2H, N-CH$_2$-Ph), 3.81 (s, 3H, OCH$_3$). HRMS (ESI): calcd C$_{20}$H$_{18}$NSO$^+$: 334.1260, found 334.1262.

Phenyl (Z)-N-benzyl-2-methylpropanimidothioate (3t)
Synthesized according to the general procedure using thioamide 1e and diaryliodonium salt 2a as beige oil in 45% yield, S:N ratio 6:1. Major isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53–7.47 (m, 2H), 7.42–7.31 (m, 6H), 7.28–7.23 (m, 2H), 4.73 (s, 2H), 2.60 (hept, $J$ = 6.7 Hz, 1H), 1.10 (d, $J$ = 6.7 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.8, 140.1, 134.9, 131.5, 129.3, 128.6, 128.3, 127.5, 126.5, 56.4, 35.4, 21.3. Minor isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40–7.21 (m, 9H, signals overlapping with aromatic signals of major product), 6.90 (m, 1H), 5.61 (s, 1H), 2.84 (hept, $J$ = 6.6 Hz, 1H), 1.17
(Z)-Phenyl N-benzylecyclohexanecarbimidothioate (3u)

Synthesized according to the general procedure using thioamide 1f and diaryliodonium salt 2a as beige oil in 32% yield; S:N ratio 5:1. **Major isomer:** ¹H NMR (400 MHz, CDCl₃) δ 7.42–7.34 (m, 2H), 7.30–7.19 (m, 6H), 7.17–7.12 (m, 2H), 4.61 (s, 2H), 2.11 (tt, J = 11.5, 3.3 Hz, 1H), 1.75–1.65 (m, 2H), 1.60–1.48 (m, 2H), 1.46–1.34 (m, 3H), 1.10–0.95 (m, 5H), 0.89–0.76 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 134.1, 130.9, 129.9, 129.1. HRMS (ESI): calcd [M+Na]⁺: 270.1311, found 270.1309.

Phenyl (Z)-N-hexylbenzimidothioate (3v)

Synthesized according to the general procedure using thioamide 1d and diaryliodonium salt 2a as beige oil in 58% yield, Z:E ratio 95:5. **(Z) isomer:** ¹H NMR (400 MHz, CDCl₃) δ 7.56–7.44 (m, 2H), 7.23–7.14 (m, 5H), 7.13–7.04 (m, 3H), 3.77 (t, J = 6.9 Hz, 2H), 1.89–1.74 (m, 2H), 1.57–1.41 (m, 2H), 1.40–1.32 (m, 4H), 1.00–0.88 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.03, 140.29, 135.00, 131.71, 129.36, 128.77, 128.43, 127.63, 126.65, 56.67, 45.62, 31.87, 26.23, 26.02. Characteristic signals for **minor isomer:** ¹H NMR (400 MHz, CDCl₃) δ 5.49, 2.34. ¹³C NMR (101 MHz, CDCl₃) δ 67.61, 65.18, 132.7, 132.6, 132.5, 131.5, 130.4, 128.7, 128.2, 128.1, 127.9, 127.8, 127.5, 127.2, 55.1, 31.7, 30.6, 27.3, 22.8, 14.1. Characteristic signals for **(E) isomer:** ¹H NMR (400 MHz, CDCl₃) δ 3.26 (t, 2H, N-CH₂). HRMS (ESI): calcd C₁₃H₁₂NS [M+H]⁺: 310.1624, found 310.1625.

Phenyl (Z)-N-((tert-butoxycarbonyl)benzimidothioate (3w)

Synthesized according to the general procedure using thioamide 1h and diaryliodonium salt 2a as orange oil in 78% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.68–7.59 (m, 2H), 7.50–7.42 (m, 2H), 7.41–7.34 (m, 1H), 7.33–7.26 (m, 5H), 1.39 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 160.2, 138.3, 132.8, 132.7, 129.1, 128.9, 128.7, 127.8, 127.2, 55.1, 31.7, 30.6, 27.3, 22.8, 14.1. HRMS (ESI): calcd C₁₃H₁₉NNaO₃S [M+Na]⁺: 336.1029, found 336.1026.

2,4-Dichlorophenyl (Z)-N-((tert-butoxycarbonyl)benzimidothioate (3x)

Synthesized according to the general procedure using thioamide 1h and diaryliodonium salt 2k as yellow oil in 72%. ¹H NMR (400 MHz, CDCl₃) δ 7.67–7.61 (m, 2H), 7.48 (d, J = 8.3 Hz, 1H), 7.44–7.38 (m, 2H), 7.37–7.31 (m, 2H), 7.18 (dd, J = 8.3, 2.2 Hz, 1H), 1.39 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 168.3, 159.4, 138.9, 137.4, 136.3, 135.8, 131.5, 130.2, 128.5, 128.4, 127.8, 82.7, 28.0. HRMS (ESI): calcd C₁₉H₁₁Cl₂NNaO₂S [M+Na]⁺: 404.0249, found 404.0251.

2-[(4-Nitrophenyl)thio]pyridine (3y)
Synthesized according to the general procedure using pyridine-2-thiol and diaryliodonium salt 2c as yellow oil in 78% yield. Analytical data is in agreement with data reported in literature.\[^{33}\] 1H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.51 (d, \(J = 4.9\) Hz, 1H), 8.18 (d, \(J = 8.3\) Hz, 2H), 7.62 (m, 3H), 7.30 (d, \(J = 7.9\) Hz, 1H), 7.18 (m, 1H). \[^{13}\]C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 156.6, 150.4, 146.9, 142.3, 137.3, 131.8, 124.8, 121.4, 121.9.

1-Phenylpyrrolidine-2-thione\[^{39}\] (4a)
Synthesized according to the general procedure using pyrrolidine-2-thione and diaryliodonium salt 2a as yellow waxy solid. N:S ratio 2:1. \[^{4a}\] 1H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.53–7.49 (m, 2H), 7.48–7.42 (m, 2H), 7.36–7.30 (m, 1H), 4.12 (m, 2H), 3.24 (m, 2H), 2.31–2.17 (m, 2H). \[^{13}\]C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 202.9, 140.7, 129.5, 129.3, 125.1, 58.9, 46.5, 20.9. Minor isomer: 1H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60–7.30 (m, 5H, signals overlapping with major isomer), 3.86 (m, 2H), 2.57 (m, 2H), 1.93 (m, . 2H). \[^{13}\]C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 173.2, 140.7, 134.9, 129.5, 124.9, 61.8, 38.8, 23.1. HRMS (ESI): calcd C\(_{10}\)H\(_{10}\)NNaS [M+Na]\(^+\): 200.0504, found 200.0507.

2-(4-Nitrophenyl)-3,4-dihydroisoquinoline-1(2H)-thione (4b)
Synthesized according to the general procedure using thioamide 1i and diaryliodonium salt 2c as yellow waxy solid in 78% yield. \[^{4b}\] 1H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.61 (dd, \(J = 8.0, 1.3\) Hz, 1H), 8.39–8.31 (m, 2H), 7.59–7.52 (m, 2H), 7.50 (td, \(J = 7.5, 1.3\) Hz, 1H), 7.38 (m, 1H), 7.22 (m, 1H), 4.04–3.95 (m, 2H), 3.21 (t, \(J = 6.5\) Hz, 2H). \[^{13}\]C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 194.9, 152.8, 146.7, 133.8, 132.9, 132.8, 132.6, 128.2, 127.6, 127.0, 125.3, 52.2, 28.6. HRMS (ESI): calcd C\(_{15}\)H\(_{10}\)NNaS [M+H]\(^+\): 307.0512, found 307.0508.

8 References


9 Copies of NMR Spectra
$^1$H NMR, CDCl$_3$, 400 MHz

1a
$^{13}$C NMR, CDCl$_3$, 101 MHz

**$1b$**

- 197.51 ppm
- 144.60 ppm
- 144.59 ppm
- 125.54 ppm
- 125.51 ppm
- 125.47 ppm
- 125.43 ppm
- 77.3 ppm
- 72.0 ppm
- 71.2 ppm
- 51.12 ppm
$^{19}$F NMR (376 MHz, CDCl$_3$)
$^1$H NMR, CDCl₃, 400 MHz
$^{13}$C NMR, CDCl$_3$, 101 MHz
$	ext{^1H NMR, CDCl$_3$, 400 MHz}$
$^{13}$C NMR, CDCl$_3$, 101 MHz

![Chemical structure](image)
$^{1}$H NMR, CDCl$_3$, 400 MHz

$\begin{align*}
\text{H}_2\text{C} & \quad \text{S} \\
\text{CH}_3 & \quad \text{NH} \\
\text{CH}_3 & \quad \text{Ph}
\end{align*}$

1e
$^{13}$C NMR, CDCl$_3$, 101 MHz

![Chemical structure of compound le](image)
$^1$H NMR, CDCl$_3$, 400 MHz
$^{13}$C NMR, CDCl$_3$, 101 MHz
$^{1}$H NMR, CDCl$_3$, 400 MHz

$^{1}$h
$^{13}$C NMR, CDCl$_3$, 101 MHz

1h
$^1$H NMR, CDCl$_3$, 400 MHz

1i
$^{13}$C NMR, CDCl$_3$, 101 MHz

![Chemical Structure](image)
$^{13}$C NMR, CDCl$_3$, 101 MHz

$2k$
$^1$H NMR, CDCl$_3$, 400 MHz

3a

93:7 mixture of Z:E
$^{13}$C NMR, CDCl$_3$, 101 MHz

93:7 mixture of Z:E
$^1$H NMR, CDCl$_3$, 400 MHz

$3b$

92:8 mixture of Z:E

(Z:E) ratio
92:8
$^{13}$C NMR, CDCl$_3$, 101 MHz

3b
92:8 mixture of Z:E
$^{1}$H NMR, CDCl$_3$, 400 MHz

92:8 mixture of Z:E

(Z:E) ratio 92:8
$^{13}$C NMR, CDCl$_3$, 101 MHz

![Chemical Structure] $3e$

92:8 mixture of Z:E
\[ (Z:E) \text{ ratio} \]

89:11

\[ 3 \text{d} \]

89:11 mixture of Z:E

{\text{H NMR, CDCl₃, 400 MHz}}

\[ f_1 \text{ (ppm)} \]

\[ \begin{align*}
7.57 & \quad 7.55 \\
7.46 & \quad 7.45 \\
7.39 & \quad 7.37 \\
7.30 & \quad 7.28 \\
7.32 & \quad 7.29 \\
7.22 & \quad 7.23 \\
7.22 & \quad 7.22 \\
7.23 & \quad 7.21 \\
7.20 & \quad 7.20 \\
6.99 & \quad 6.97 \\
\end{align*} \]
13C NMR, CDCl3, 101 MHz

89:11 mixture of Z:E
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$

\[ \text{OCF}_3 \]

\[ \text{3d} \]

89:11 mixture of Z:E
$^1$H NMR, CDCl$_3$, 400 MHz

92:8 mixture of Z:E
$^1$H NMR, CDCl$_3$, 101 MHz

![Chemical Structure](image)

$^1$C NMR, CDCl$_3$, 101 MHz

92:8 mixture of Z:E
$^{19}$F NMR (376 MHz, CDCl$_3$)

92:8 mixture of Z:E
$^1$H NMR, CDCl$_3$, 400 MHz

3f

88:12 mixture of $Z:E$
$^{13}$C NMR, CDCl$_3$, 101 MHz

88:12 mixture of Z:E
$^{19}$F NMR (376 MHz, CDCl$_3$)

3f

88:12 mixture of Z:E
$^1$H NMR, CDCl$_3$, 400 MHz

92:8 mixture of Z:E
$^{13}$C NMR, CDCl$_3$, 101 MHz

3g
92:8 mixture of Z:E
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$

92:8 mixture of Z:E
$^1$H NMR, CDCl$_3$, 400 MHz

3h

96:4 mixture of Z:E

(Z:E) ratio
96:4
$^{13}$C NMR, CDCl$_3$, 101 MHz

96:4 mixture of Z:E
$^1$H NMR, CDCl$_3$, 400 MHz

90:10 mixture of Z:E

(Z:E) ratio
90:10
$^{13}$C NMR, CDCl$_3$, 101 MHz

90:10 mixture of Z:E
$^{1}$H NMR, CDCl$_3$, 400 MHz

$\text{Br}$

91:9 mixture of $Z:E$
$^{13}$C NMR, CDCl$_3$, 101 MHz

3j

91:9 mixture of Z:E
$^1$H NMR, CDCl$_3$, 400 MHz

3k

93:7 mixture of Z:E
$^{13}$C NMR, CDCl$_3$, 101 MHz

3k

93:7 mixture of Z:E
$^1$H NMR, MeOD$_3$, 400 MHz

93:7 mixture of Z:E
$^{13}$C NMR, MeOD, 101 MHz

93:7 mixture of Z:E
$^1$H NMR, CDCl$_3$, 400 MHz

92:8 mixture of Z:E
$^{13}$C NMR, CDCl$_3$, 101 MHz

92:8 mixture of Z:E
$^1$H NMR, CDCl$_3$, 400 MHz

91:9 mixture of Z:E
$^{13}$C NMR, CDCl$_3$, 101 MHz

91:9 mixture of Z:E
$^1$H NMR, CDCl$_3$, 400 MHz

30

86:14 mixture of Z:E

(Z/E)-ratio 86:14
$^{13}$C NMR, CDCl$_3$, 101 MHz

86:14 mixture of Z:E
$^1$H NMR, CDCl$_3$, 400 MHz

3p

91:9 mixture of Z:E

(Z:E) ratio
91:9
$^{13}$C NMR, CDCl$_3$, 101 MHz

$3p$

91:9 mixture of Z:E
(Z:E) ratio 87:13

$^{1}$H NMR, CDCl$_3$, 400 MHz

3q

87:13 mixture of Z:E
$^{13}$C NMR, CDCl$_3$, 101 MHz

87:13 mixture of Z:E
$\text{Z:E ratio}$

96:4

$^1\text{H NMR, CDCl}_3, \text{400 MHz}$

$3r$

96:4 mixture of Z:E
$^{13}$C NMR, CDCl$_3$, 101 MHz

3r

96:4 mixture of Z:E
$^{19}$F NMR (376 MHz, CDCl$_3$)

![NMR spectrum diagram]
\[ 3s \]

95:5 mixture of Z:E

\(^1\text{H} \text{NMR, CDCl}_3, 400 \text{ MHz} \]
$^{13}$C NMR, CDCl$_3$, 101 MHz

95:5 mixture of Z:E
$^1$H NMR, CDCl$_3$, 400 MHz

3t
15:85 mixture of N- and S-arylation
$^{13}$C NMR, CDCl$_3$, 101 MHz

3t  
15:85 mixture of  
N- and S-arylation
$\text{C NMR, CDCl}_3, 101 \text{ MHz}$
(Z:E) ratio
95:5

$^1$H NMR, CDCl$_3$, 400 MHz

95:5 mixture of Z:E
$^{13}$C NMR, CDCl$_3$, 101 MHz

95:5 mixture of Z:E
$^1$H NMR, CDCl$_3$, 400 MHz

3w
$^{13}$C NMR, CDCl$_3$, 101 MHz

![Chemical structure](image)
$^{13}$C NMR, CDCl$_3$, 101 MHz

3x
\[ \text{\textsuperscript{1}H NMR, CDCl}_3, 400 \text{ MHz} \]

4a

N:S ratio 67:33
\( ^{13}\text{C NMR, CDCl}_3, 101\text{ MHz} \)

4a \((N)\)  

(S)
$^{13}$C NMR, CDCl$_3$, 101 MHz

4b