Supporting Information

Ligand-Enabled Gold-Catalyzed C(sp$^2$)–N Cross-Coupling Reactions of Aryl Iodides with Amines

Manjur O. Akram, Avishek Das, Indradweep Chakrabarty and Nitin T. Patil*

Scheme: 2.5 mol % [Au(I)]
1.1 equiv AgSbF$_6$
MeOH, 80 °C
12-24 h

- Directing group free
- Moisture and air tolerance
- Late stage functionalization
- Broad functional group tolerance
- Large scale synthesis
- Application to indolines/carbazoles

[Au(I)]
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1. General information:

1.1 Practical considerations:

All reactions were carried out in oven-dried vials or reaction vessels with magnetic stirring under nitrogen atmosphere, unless otherwise specified. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccator. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV at 254 nm for UV active materials. Further visualization was achieved by staining in KMnO₄ and charring on a hot plate. Solvents were removed in vacuum and heated with a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in pet ether and equilibrated with the appropriate solvent mixture prior to use. The elution was assisted by applying pressure with an air pump.

1.2 Instrumentation:

Melting points were uncorrected and recorded using digital Buchi Melting Point Apparatus B-540. ¹H NMR and ¹³C NMR spectra were recorded in Bruker AVANCE III 400 and 500 MHz NMR spectrometers at 25 °C unless mentioned otherwise spectrometers using TMS as an internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ¹H NMR signals are designated as s (singlet), br. s (broad singlet), d (doublet), dd (doublet of doublet), ddd (doublet of doublet of doublet), ddt (doublet of doublet of triplet), t (triplet), q (quartet), m (multiplet) etc. HRMS (ESI) data were recorded on a Bruker MicroTOF-Q-II spectrometer. Single crystal X-ray diffraction measurements were performed with Bruker APEX-II CCD instrument.

1.3 Materials:

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF was distilled from Na/benzophenone under an atmosphere of N₂. DMSO, MeCN, DCM, 1,4-dioxane and acetone were dried using standard protocol under N₂. Gold, silver salts and deuterated solvents were purchased from Sigma-Aldrich and stored under nitrogen atmosphere.
2. **Optimization of the reaction conditions:**

At the outset, we utilized \( p \)-nitroaniline \( 2a \), given its major acidity compared to other amines (\( pK_a = 20.9 \) in DMSO), and Iodobenzene (\( 1a \)) as model substrates to test our hypothesis. When 1 equiv of \( 1a \) and 1 equiv of \( 2a \) was treated with 5 mol\% (MeDalPhos)Au(I)Cl (\( L_1 \text{Au(I)Cl} \)), 1 equiv of \( \text{AgSbF}_6 \) as a halide scavenger in 1,4-dioxane and stirred at 80 °C for 12 h (entry 1); to our delight, the cross-coupled product \( 3a \) was obtained in 23% yields with the recovered starting materials in quantitative amount. The details of the optimization studies are given below.

2.1 **Control experiments:**\(^{[a]}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Variation of the ‘standard conditions’</th>
<th>Yield (%)[^{[b]}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>without ( \text{Au-1} ) cat</td>
<td>NR</td>
</tr>
<tr>
<td>3</td>
<td>without ( \text{AgSbF}_6 )</td>
<td>NR</td>
</tr>
<tr>
<td>4</td>
<td>5 mol% MeDalPhos instead ( \text{Au-1} )</td>
<td>NR</td>
</tr>
</tbody>
</table>

\(^{[a]}\)Reaction conditions: 0.10 mmol \( 1a \), 0.10 mmol \( 2a \), 5 mol\% \( \text{Au-1} \), 1 equiv \( \text{AgSbF}_6 \), 1,4-dioxane (0.1 M), \( \text{N}_2 \), 80 °C, 12 h. \(^{[b]}\)Isolated yields. NR = No reaction.

2.2 **Screening of base:**\(^{[a]}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Yield (%)[^{[b]}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{K}_2\text{CO}_3 )</td>
<td>NR</td>
</tr>
<tr>
<td>2</td>
<td>( \text{K}_3\text{PO}_4 )</td>
<td>23</td>
</tr>
<tr>
<td>Entry</td>
<td>Solvent</td>
<td>Yield (%)[^b]</td>
</tr>
<tr>
<td>-------</td>
<td>-----------</td>
<td>---------------</td>
</tr>
<tr>
<td>1</td>
<td>DCM</td>
<td>&lt;5</td>
</tr>
<tr>
<td>2</td>
<td>DCE</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>THF</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>toluene</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>MeCN</td>
<td>11</td>
</tr>
<tr>
<td>6</td>
<td>DMF</td>
<td>51</td>
</tr>
<tr>
<td>7</td>
<td>DMSO</td>
<td>32</td>
</tr>
<tr>
<td>8</td>
<td>MeOH</td>
<td>89</td>
</tr>
<tr>
<td>9</td>
<td>acetone</td>
<td>NR</td>
</tr>
<tr>
<td>10</td>
<td>CF$_3$CH$_2$OH</td>
<td>NR</td>
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</table>

[^a] Reaction conditions: 0.10 mmol 1a, 0.10 mmol 2a, 5 mol% Au-1, 1 equiv AgSbF$_6$, solvent (0.1 M), N$_2$, 80 ºC, 12 h. [^b] Isolated yields. NR = No reaction.

### 2.3 Screening of solvent:[^a]

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AgOTf</td>
<td>89</td>
</tr>
<tr>
<td>2</td>
<td>AgTf$_2$</td>
<td>84</td>
</tr>
<tr>
<td>3</td>
<td>AgBF$_4$</td>
<td>89</td>
</tr>
</tbody>
</table>

[^a] Reaction conditions: 0.10 mmol 1a, 0.10 mmol 2a, 5 mol% Au-1, 1 equiv AgSbF$_6$, solvent (0.1 M), N$_2$, 80 ºC, 12 h. [^b] Isolated yields. NR = No reaction.
| 4 | AgPF₆ | 84 |
| 5 | AgOTs | 79 |
| 6 | AgOAc | 75 |
| 7 | NaBARF | NR |

[a] Reaction conditions: 0.10 mmol 1a, 0.10 mmol 2a, 5 mol% Au-1, 1 equiv halide scavengers, MeOH (0.1 M), N₂, 80 °C, 12 h. [b] Isolated yields. NR = No reaction.

### 2.5 Effect of AgSbF₆ loading:

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>x</th>
<th>Yield (%) [b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>91</td>
</tr>
<tr>
<td>2</td>
<td>1.1</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td>1.2</td>
<td>98</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 0.10 mmol 1a, 0.10 mmol 2a, 5 mol% Au-1, x equiv AgSbF₆, MeOH (0.1 M), N₂, 80 °C, 12 h. [b] Isolated yields.

### 2.6 Effect of Au-1 loading:

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>x</th>
<th>Yield (%) [b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5</td>
<td>98</td>
</tr>
<tr>
<td>2[c]</td>
<td>1</td>
<td>89</td>
</tr>
<tr>
<td>3[c]</td>
<td>0.5</td>
<td>51</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 0.10 mmol 1a, 0.10 mmol 2a, 5 mol% Au-1, x equiv AgSbF₆, MeOH (0.1 M), N₂, 80 °C, 12 h. [b] Isolated yields. [c] Reaction was stirred for 24 h.
2.7 Screening of various gold(I) catalysts.\textsuperscript{[a]}

![Reaction scheme]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Gold cat (Au)</th>
<th>Yield (%)\textsuperscript{[b]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Au-2</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>Au-3</td>
<td>51</td>
</tr>
<tr>
<td>3</td>
<td>Au-4</td>
<td>79</td>
</tr>
<tr>
<td>4</td>
<td>Au-5</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} \textbf{Reaction conditions}: 0.10 mmol 1a, 0.10 mmol 2a, 2.5 mol% Au, 1.1 equiv AgSbF$_6$, MeOH (0.1 M), N$_2$, 80 °C, 12 h. \textsuperscript{[b]} Isolated yields.
2.8  Screening of bases in the cross-coupling reaction of iodobenzene (1a) and aniline (2l):

In order to justify the unsatisfactory outcome for less acidic amines (4l, 4m, 4x and 4y) and to find a comprehensive solution it was needed to improve the previous set of reaction conditions. To start with, less acidic aniline 2l (pK$_a$ = 30.6 in DMSO) was used as a model substrate along with electronically neutral iodobenzene (1a) and bases were screened.

![Chemical diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K$_2$CO$_3$</td>
<td>NR</td>
</tr>
<tr>
<td>2</td>
<td>K$_3$PO$_4$</td>
<td>23</td>
</tr>
<tr>
<td>3</td>
<td>NaOMe</td>
<td>NR</td>
</tr>
<tr>
<td>4</td>
<td>KO'Bu</td>
<td>NR</td>
</tr>
<tr>
<td>5</td>
<td>NEt$_3$</td>
<td>NR</td>
</tr>
<tr>
<td>6</td>
<td>N,N-Diisopropylethylamine</td>
<td>NR</td>
</tr>
<tr>
<td>7</td>
<td>1,8-Bis(dimethylamino)naphthalene</td>
<td>NR</td>
</tr>
<tr>
<td>8</td>
<td>1,1,3,3-Tetramethylguanidine</td>
<td>NR</td>
</tr>
<tr>
<td>9</td>
<td>1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU)</td>
<td>NR</td>
</tr>
<tr>
<td>10</td>
<td>1,2,2,6,6-Pentamethylpiperidine</td>
<td>30</td>
</tr>
<tr>
<td>11</td>
<td>2,6-Lutidine</td>
<td>36</td>
</tr>
<tr>
<td>12</td>
<td>2,6-Di-tert-butylpyridine</td>
<td>47</td>
</tr>
<tr>
<td>13$^c$</td>
<td>2,6-Di-tert-butylpyridine</td>
<td>53</td>
</tr>
<tr>
<td>14$^d$</td>
<td>2,6-Di-tert-butylpyridine</td>
<td>47</td>
</tr>
</tbody>
</table>

$^{[a]}$Reaction conditions: 0.10 mmol 1a, 0.10 mmol 2l, 5 mol% Au-1, 1.1 equiv AgSbF$_6$, 1 equiv base, 1,4-dioxane (0.1 M), N$_2$, 80 ºC, 12 h. $^{[b]}$Isolated yields. $^{[c]}$1.5 Equiv of 2,6-Di-tert-butylpyridine was used. $^{[d]}$2.0 Equiv of 2,6-Di-tert-butylpyridine was used. NR = No reaction.
3. General procedures:

3.1 Synthesis of ancillary (P,N)-ligands (L₁-L₅):

Ancillary (P,N)-ligands L₁ and L₄ were purchased from commercial sources, whereas, L₂, L₃, L₅ were prepared by literature known procedures.

3.2 Synthesis of gold(I) catalysts:

- **Representative procedure**: To a solution of Me₂SAuCl (147 mg, 0.5 mmol) in anhydrous DCM (5 mL); L₂ (153 mg, 0.5 mmol) was added slowly at −20 ºC under nitrogen and stirred for 6 h at room temperature. After completion of the reaction, the solvent was evaporated and the crude reaction mixture was crystallized with DCM/diethyl ether at 0 ºC. The resulting crystalline solid was isolated by filtration and washed with cold diethyl ether and dried under vacuum to achieve Au-2 in quantitative yield (224 mg, 83%). Gold catalysts Au-1, Au-3, Au-4 and Au-5 were also prepared by this procedure. The structures of these catalysts were confirmed by X-ray crystallography.

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Characterization Data:

**Compound Au-2:** 224 mg, yield: 83%; **physical appearance:** off white solid, **mp:** 196-198 °C; ¹H NMR: \((500 \text{ MHz}, \text{CD}_2\text{Cl}_2)\) δ = 7.64-7.58 (m, 4 H), 7.58-7.51 (m, 3 H), 7.51-7.46 (m, 4 H), 7.46-7.42 (m, 1 H), 7.21-7.15 (m, 1 H), 6.90-6.82 (m, 1 H), 2.41 (s, 6 H); ¹³C NMR: \((125 \text{ MHz}, \text{CD}_2\text{Cl}_2)\) δ = 181.7 (d, \(J = 8.18\) Hz), 157.9 (d, \(J = 14.53\) Hz), 157.2 (d, \(J = 6.36\) Hz), 156.8 (d, \(J = 1.82\) Hz), 155.0 (d, \(J = 2.72\) Hz), 153.7 (d, \(J = 62.67\) Hz), 152.6 (d, \(J = 11.81\) Hz), 151.1 (d, \(J = 69.03\) Hz), 149.5 (d, \(J = 9.99\) Hz), 148.1 (d, \(J = 5.45\) Hz), 69.4; ³¹P NMR: \((162 \text{ MHz}, \text{CD}_2\text{Cl}_2)\) δ = 24.8; HRMS: (ESI) calcld 560.0580 for C\(_{20}\)H\(_{20}\)AuClNP [M + Na]? found 560.0553.

**Compound Au-3:** 255 mg, yield: 93%; **physical appearance:** white solid, **mp:** 174-176 °C; ¹H NMR: \((500 \text{ MHz}, \text{CD}_2\text{Cl}_2)\) δ = 7.80-7.74 (m, 1 H), 7.59-7.53 (m, 1 H), 7.51-7.45 (m, 1 H), 7.31 (t, \(J = 7.5\) Hz, 1 H), 2.65 (s, 6 H), 2.54-2.43 (m, 2 H), 2.18-2.10 (m, 2 H), 1.88-1.83 (m, 2 H), 1.75-1.70 (m, 2 H), 1.69-1.64 (m, 2 H), 1.58-1.46 (m, 2 H), 1.43-1.36 (m, 2 H), 1.35-1.20 (m, 6 H); ¹³C NMR: \((125 \text{ MHz}, \text{CD}_2\text{Cl}_2)\) δ = 159.6 (d, \(J = 3.63\) Hz), 137.5 (d, \(J = 11.81\) Hz), 133.5 (d, \(J = 1.82\) Hz), 126.5 (d, \(J = 10.90\) Hz), 125.5 (d, \(J = 5.45\) Hz), 125.1 (d, \(J = 55.40\) Hz), 47.5, 36.5 (d, \(J = 34.51\) Hz), 31.9 (d, \(J = 4.54\) Hz), 30.5, 27.0 (d, \(J = 5.45\) Hz), 26.9 (d, \(J = 3.63\) Hz), 26.3 (d, \(J = 1.82\) Hz); ³¹P NMR: \((162 \text{ MHz}, \text{CD}_2\text{Cl}_2)\) δ = 48.0; HRMS: (ESI) calcld 550.1699 for C\(_{20}\)H\(_{32}\)AuClNP [M + H]? found 550.1684.
Compound Au-4: 301 mg, yield: 87%; physical appearance: white solid, mp: >250 °C; \(^1\)H NMR: (500 MHz, CD\(_2\)Cl\(_2\)) \(\delta = 7.82-7.75\) (m, 1 H), 7.61-7.53 (m, 2 H), 7.34-7.26 (m, 1 H), 2.85-2.80 (m, 2 H), 2.79-2.72 (m, 2 H), 2.63-2.53 (m, 2 H), 2.26-2.19 (m, 6 H), 2.14-2.08 (m, 6 H), 1.99 (dd, \(J = 3.1, 6.0\) Hz, 6 H), 1.91-1.85 (m, 1 H), 1.72-1.65 (m, 12 H), 1.61-1.55 (m, 3 H), 1.39-1.29 (m, 1 H); \(^{13}\)C NMR: (125 MHz, CD\(_2\)Cl\(_2\)) \(\delta = 161.5\) (d, \(J = 6.36\) Hz), 135.7, 132.9, 127.2 (d, \(J = 5.45\) Hz), 125.0 (d, \(J = 2.72\) Hz), 122.5, 56.7, 47.7 (d, \(J = 3.63\) Hz), 42.4 (d, \(J = 23.62\) Hz), 36.9, 29.4 (d, \(J = 9.99\) Hz), 25.8, 24.8; \(^{31}\)P NMR: (162 MHz, CD\(_2\)Cl\(_2\)) \(\delta = 54.10\); HRMS: (ESI) calcd 694.2638 C\(_{31}\)H\(_{44}\)AuClNP \([M + H]^+\) found 694.2637.

Compound Au-5: 319 mg, yield: 93%; physical appearance: off white solid, mp: 206 °C (decomposition); \(^1\)H NMR: (500 MHz, CD\(_2\)Cl\(_2\)) \(\delta = 8.63-8.54\) (m, 1 H), 7.95-7.89 (m, 1 H), 7.70 (dt, \(J = 1.8, 7.7\) Hz, 1 H), 7.60-7.53 (m, 2 H), 7.44 (ddd, \(J = 1.2, 5.0, 7.7\) Hz, 1 H), 7.33-7.28 (m, 1 H), 7.27 (td, \(J = 1.2, 7.7\) Hz, 1 H), 2.23-2.18 (m, 6 H), 2.17-2.12 (m, 6 H), 2.03-1.97 (m, 6 H), 1.71-1.67 (m, 12 H); \(^{13}\)C NMR: (125 MHz, CD\(_2\)Cl\(_2\)) \(\delta = 160.6\) (d, \(J = 6.36\) Hz), 149.5, 137.0, 135.3 (d, \(J = 2.72\) Hz), 133.1 (d, \(J = 7.26\) Hz), 131.1 (d, \(J = 1.82\) Hz), 127.5 (d, \(J = 6.36\) Hz), 125.6, 124.5, 124.1, 123.5, 43.2 (d, \(J = 24.52\) Hz), 42.7 (d, \(J = 2.72\) Hz), 36.8, 29.4 (d, \(J = 9.99\) Hz); \(^{31}\)P NMR: (162 MHz, CD\(_2\)Cl\(_2\)) \(\delta = 62.08\); HRMS: (ESI) calcd 688.2169 for C\(_{31}\)H\(_{38}\)AuCINP \([M + H]^+\) found 688.2146.

- X-ray crystallography:

<table>
<thead>
<tr>
<th>ORTEP diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Au-2" /></td>
</tr>
</tbody>
</table>

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511
3.3 Synthesis of starting materials:

3.3.1 Synthesis of iodo-(hetero)arenes:

The statistics given in the following table provides the information for accessing the iodo-(hetero)arenes. The experimental procedures and data for the newly synthesized iodo-(hetero)arenes is also provided in this section.
Iodo-(hetero)arenes

<table>
<thead>
<tr>
<th>Sources</th>
</tr>
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<tbody>
<tr>
<td>Commerically available</td>
</tr>
<tr>
<td>Prepared by literature known procedures</td>
</tr>
<tr>
<td>Not reported in the literature. Prepared by literature known procedures</td>
</tr>
</tbody>
</table>

- **Synthesis of compound 1am:**

\[
\begin{align*}
\text{S}_1 & \quad \text{S}_2 \\
\text{Ph} & \quad 5 \text{ mol\% AuCl, DCE} \\
\text{N}_2, 80 \degree \text{C, 12 h} & \quad 1am
\end{align*}
\]

To a solution of \(\text{S}_1\)\(^{[6]}\) (105 mg, 0.4 mmol) and \(\text{S}_2\)\(^{[7]}\) (82 mg, 0.4 mmol) in DCE (4.0 mL) \(\text{AuCl}\) (5 mg, 5 mol%) was added under nitrogen atmosphere and stirred at 80 °C for 12 h. After consumption of starting materials as monitored by TLC, the reaction mixture was directly loaded on silica gel column and eluted with MeOH/DCM to afford **1am**. **Characterization data:** \(R_f\): 0.40 (pet. ether/EtOAc = 70/30); 141 mg, yield: 78%; **physical appearance:** yellow solid, **mp:** 206–208 °C; \(^1\text{H NMR: (500 MHz, DMSO-d}_6\) \(\delta = 9.25\ (d, J = 5.0 \text{ Hz, 1 H}), 7.91\ (d, J = 2.1 \text{ Hz, 1 H}), 7.88 - 7.74\ (m, 2 H), 7.49 - 7.45\ (m, 2 H), 7.44 - 7.39\ (m, 2 H), 7.39 - 7.33\ (m, 4 H), 7.32 - 7.29\ (m, 1 H), 5.93\ (d, J = 8.7 \text{ Hz, 1 H}), 5.75\ (s, 1 H); \(^{13}\text{C NMR: (125 MHz, DMSO-d}_6\) \(\delta = 160.4, 143.6, 141.3, 141.0, 135.2, 134.3, 131.9, 129.2, 129.2, 128.4, 128.2, 125.8, 125.7, 123.4, 120.0, 118.9, 116.9, 82.2, 67.1, 54.9; HRMS (ESI) calcd 451.0302 for C\(_{22}\)H\(_{13}\)IN\(_2\)O [M + H]\(^+\) found 451.0298.  

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\(^{[6]}\) Compound \(\text{S}_1\) is prepared by literature known method, see: Zhu, Y. P.; Fei, Z.; Liu, M. C.; Jia, F. C.; Wu, A. *X. Org. Lett.* 2013, 15, 378.

• Synthesis of compound 1an:

To a dried screw-capped vial equipped with magnetic stir bar, S₃[^8] (239 mg, 1.0 mmol), p-iodophenol (1h, 220 mg, 1.0 mmol), p-TSA·H₂O (17 mg, 0.1 mmol, 10 mol%) and DCE (10 mL) were added under nitrogen atmosphere. The reaction vial was fitted with a cap and allowed to stir at 80 °C for 24 h. After consumption of starting materials as monitored by TLC, the reaction mixture was directly loaded on silica gel column and eluted with pet. ether/EtOAc to afford S₄ as white solid. Characterization data: Rf: 0.60 (pet. ether/EtOAc = 70/30); 396 mg, yield: 90%; physical appearance: white solid, mp: 192-194 °C; ^1H NMR: (500 MHz, DMSO-d₆) δ = 9.88 (s, 1 H), 7.41 (dd, J = 2.2, 8.5 Hz, 1 H), 7.38 - 7.30 (m, 6 H), 7.16 - 7.13 (m, 1 H), 7.08 - 7.02 (m, 2 H), 6.92 (d, J = 2.3 Hz, 1 H), 6.53 (d, J = 8.4 Hz, 1 H), 3.14 (s, 3 H); ^13C NMR: (125 MHz, DMSO-d₆) δ = 177.2, 155.1, 144.0, 138.1, 137.8, 136.9, 132.3, 131.1, 128.4, 128.3, 128.2, 127.7, 125.3, 122.0, 118.3, 108.5, 80.5, 58.7, 26.5; HRMS: (ESI) calcd 464.0118 for C₂₁H₁₆INO₂ [M + Na]^+ found 464.0139.

To a solution of S₄ (220 mg, 0.5 mmol) and triethylamine (279 μL, 2.0 mmol) in DCM (5 mL); triflic anhydride (109 μL, 0.65 mmol) was added slowly at 0 °C under nitrogen atmosphere. The reaction mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was then quenched with water (10 mL) and diluted with DCM (10 mL). The organic layer was dried over Na₂SO₄, removed under reduced pressure and the resulting residue was purified by column chromatography (silica gel, pet. ether/EtOAc) to afford 1an. Characterization data: Rf: 0.50 (pet. ether/EtOAc = 95/05); 211 mg, yield: 74%; physical appearance: white solid, mp: 150-152 °C; ^1H NMR: (500 MHz, CDCl₃) δ = 7.68 (dd, J = 2.2, 8.8 Hz, 1 H), 7.51 - 7.28 (m, 7 H), 7.15 - 7.11 (m, 1 H), 7.09 - 7.04 (m, 2 H), 6.95 (d, J = 7.9 Hz, 1 H), 3.23 (s, 3 H); ^13C NMR: (125 MHz, CDCl₃) δ = 176.4, 148.6, 143.8, 141.0, 138.4, 137.2, 136.7, 129.6, 129.2, 128.7, 128.5, 125.8, 122.6, 121.7, 121.6, 118.1 (q, J = 320.62 Hz), 109.3, 92.0, 59.1, 26.7; ^19F NMR

(376 MHz, CDCl$_3$) $\delta = -73.82$; HRMS: (ESI) calcd 573.9791 for C$_{22}$H$_{15}$F$_3$INO$_4$S [M + H]$^+$ found 573.9796.

- **Synthesis of compound 1ao:**

A solution of tBuONO (185 µL, 1.56 mmol) in acetonitrile (2 mL) was added drop wise to a suspension of S$_5$[9] (390 mg, 1.29 mmol) and $p$-TSA·H$_2$O (444 mg, 2.58 mmol) in acetonitrile (13 mL) at 0 °C. The mixture was further stirred at 0 °C for 1 h. Then a saturated aqueous solution of potassium iodide (539 mg, 3.245 mmol) was added to the mixture and stirred at rt for 2 h. The reaction mixture was then poured into a saturated aqueous solution of Na$_2$S$_2$O$_3$ and extracted with (3 × 10 mL) of EtOAc. After the mixture was dried over Na$_2$SO$_4$, the solvent was evaporated and the residue was purified by column chromatography on silica gel using pet. ether/EtOAc as eluent to afford compound 1ao. **Characterization data:** $R_f$: 0.60 (pet. ether/EtOAc = 80/20); 358 mg, yield: 68%; **physical appearance:** white solid, mp: 76-78 °C; $^1$H NMR: (500 MHz, DMSO-d$_6$) $\delta = 7.93$ (d, $J = 8.9$ Hz, 1 H), 7.78 - 7.70 (m, 1 H), 7.68 - 7.61 (m, 2 H), 7.59 - 7.48 (m, 1 H), 7.24 - 7.20 (m, 2 H), 6.27 (s, 1 H), 2.59 (s, 3 H), 2.36 (s, 3 H); $^{13}$C NMR: (125 MHz, DMSO-d$_6$) $\delta = 145.0, 138.4, 136.3, 136.0, 132.1, 131.9, 129.9, 129.8, 128.7, 126.3, 116.2, 108.4, 87.6, 21.5, 15.6; HRMS: (ESI) calcd 433.9682 for C$_{16}$H$_{14}$INO$_2$S [M + Na]$^+$ found 433.9680.

- **Synthesis of compound 1au:**

A solution of 4-iodobenzenesulfonyl chloride (S$_7$, 227 mg, 0.75 mmol) in dichloromethane (2 mL) was slowly added to a solution of dehydroabietylamine (S$_6$, 143 mg, 0.5 mmol) and triethylamine (279 µL, 2.0 mmol) in dichloromethane (5 mL) at 0 °C. The reaction mixture was

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then warmed to room temperature and stirred for 6 h. After completion of the reaction it was quenched with water (10 mL) and extracted with dichloromethane (3 × 10 mL). The organic layer was dried over Na₂SO₄, removed under reduced pressure and the resulting residue was purified by column chromatography (silica gel, pet. ether/EtOAc) to afford 1a.

**Characterization data:** 

**Rf:** 0.30 (pet. ether/EtOAc = 95/05); 199 mg, yield: 72%; **physical appearance:** white solid, **mp:** 180-182 °C; **¹H NMR:** (500 MHz, CDCl₃) δ = 7.87 - 7.80 (m, 2 H), 7.59 - 7.52 (m, 2 H), 7.19 - 7.12 (m, 1 H), 7.03 - 6.96 (m, 1 H), 6.88 (s, 1 H), 4.69 - 4.58 (m, 1 H), 2.94 - 2.75 (m, 4 H), 2.72 - 2.62 (m, 1 H), 2.32 - 2.22 (m, 1 H), 1.76 - 1.61 (m, 4 H), 1.50 - 1.44 (m, 1 H), 1.39 - 1.31 (m, 2 H), 1.25 - 1.22 (m, 6 H), 1.21 - 1.17 (m, 3 H), 0.90 (s, 3 H); **¹³C NMR:** (125 MHz, CDCl₃) δ = 146.8, 145.7, 139.8, 138.4, 134.5, 128.4, 126.8, 124.1, 123.9, 99.9, 53.8, 44.8, 38.2, 37.3, 36.9, 35.8, 33.4, 29.7, 25.1, 24.0, 23.9, 18.7, 18.6, 18.4; **HRMS:** (ESI) calcd 552.1428 for C₂₆H₃₄INO₂S [M + H]+ found 552.1417.

**3.3.2 Synthesis of amines:**

<table>
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<td>Commercially available</td>
</tr>
<tr>
<td>2ab, 2ac, 2af, 2ag, 2p, 2w, 2x, 2ai</td>
<td>Prepared by literature known procedures</td>
</tr>
</tbody>
</table>
3.4 General procedure for the gold catalyzed C(sp²)−N cross-coupling reactions:

An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with the aryl iodide (1, 0.1 mmol), amine (2, 0.1 mmol), MeDalPhosAuCl (Au-1, 2.5 mol%, 0.0025 mmol) and MeOH (0.1 M). The resulting reaction mixture was then cooled to 0 °C and AgSbF₆ (0.11 mmol) was added and allowed to stir at 80 °C for 12-16 h. After completion of the reaction, it was diluted with DCM (10 mL), filtered through a small pad of celite, concentrated and subsequently purified by column chromatography (silica gel) with appropriate solvent systems to afford the C(sp²)−N cross-coupled products (3 and 4).

Characterization Data:

**Compound 3a:[10]** R_f: 0.60 (pet. ether/EtOAc = 70/30); 21 mg, yield: 98%; physical appearance: yellow solid, mp: 132-134 °C; ¹H NMR: (500 MHz, CDCl₃) δ = 8.19-8.07 (m, 2 H), 7.45-7.35 (m, 2 H), 7.25-7.20 (m, 2 H), 7.20-7.14 (m, 1 H), 6.98-6.93 (m, 2 H), 6.36 (br. s., 1 H); ¹³C NMR: (125 MHz, CDCl₃) δ = 150.2, 139.7, 139.5, 129.7, 126.2, 124.6, 121.9, 113.7.

**Compound 3b:[11]** R_f: 0.30 (pet. ether/EtOAc = 80/20); 23 mg, yield: 99%; physical appearance: yellow solid, mp: 187-189 °C; ¹H NMR: (500 MHz, CDCl₃) δ = 8.20-8.06 (m, 2 H), 7.45-7.35 (m, 2 H), 7.26-7.21 (m, 2 H), 7.21-7.14 (m, 1 H), 7.00-6.91 (m, 2 H), 6.46 (br. s., 1 H); ¹³C NMR: (125 MHz, CDCl₃) δ = 160.0 (d, J = 245.23 Hz), 150.7, 139.8, 135.3 (d, J = 3.63 Hz), 126.3, 124.9 (d, J = 8.17 Hz), 116.6 (d, J = 22.71 Hz), 113.2; ¹⁹F NMR (376 MHz, CDCl₃) δ = −116.63.

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Compound 3c: $R_f$: 0.60 (pet. ether/EtOAc = 70/30); 22 mg, yield: 89%; physical appearance: yellow solid, mp: 178-181 °C; $^1H$ NMR: (500 MHz, CDCl₃) $\delta$ = 8.23-8.09 (m, 2 H), 7.42-7.33 (m, 2 H), 7.23-7.11 (m, 2 H), 7.00-6.88 (m, 2 H), 6.34-6.13 (m, 1 H); $^{13}C$ NMR: (125 MHz, CDCl₃) $\delta$ = 149.7, 140.2, 138.2, 129.8, 129.7, 126.2, 123.1, 113.9; HRMS: (ESI) calcd 249.0425 for C₁₂H₉ClN₂O₂ [M + H]$^+$ found 249.0446.

Compound 3d: $R_f$: 0.40 (pet. ether/EtOAc = 80/20); 27 mg, yield: 93%; physical appearance: yellow solid, mp: 158-161 °C; $^1H$ NMR: (500 MHz, CDCl₃) $\delta$ = 8.22-8.06 (m, 2 H), 7.56-7.45 (m, 2 H), 7.17-7.05 (m, 2 H), 6.98-6.91 (m, 2 H), 6.28 (br. s., 1 H); $^{13}C$ NMR: (125 MHz, CDCl₃) $\delta$ = 149.5, 140.2, 138.7, 132.7, 126.2, 123.2, 117.1, 114.0.

Compound 3e: $R_f$: 0.50 (pet. ether/EtOAc = 80/20); 22 mg, yield: 65%; physical appearance: yellow solid, mp: 137-139 °C; $^1H$ NMR: (500 MHz, CDCl₃) $\delta$ = 8.20-8.07 (m, 2 H), 7.74-7.59 (m, 2 H), 7.04-6.91 (m, 4 H), 6.31 (br. s., 1 H); $^{13}C$ NMR: (125 MHz, CDCl₃) $\delta$ = 149.3, 140.2, 139.5, 138.7, 126.2, 123.3, 114.2, 87.3; HRMS: (ESI) calcd 339.9703 for C₁₂H₉IN₂O₂ [M]$^+$ found 339.9724.

Compound 3f: $R_f$: 0.60 (pet. ether/EtOAc = 70/30); 34 mg, yield: 94%; physical appearance: yellow solid, mp: 130-133 °C; $^1H$ NMR: (500 MHz, CDCl₃) $\delta$ = 8.21-8.13 (m, 2 H), 7.34-7.23 (m, 5 H), 7.06-6.98 (m, 2 H), 6.37 (s, 1 H); $^{13}C$ NMR: (125 MHz, CDCl₃) $\delta$ = 148.8, 145.1, 140.8, 140.4, 126.2, 122.8, 122.1, 114.7 (carbon for –CF₃ did not appear); $^{19}F$ NMR (376 MHz, CDCl₃) $\delta$ = −72.71; HRMS: (ESI) calcd 385.0076 for C₁₃H₉F₃N₂O₃S [M + Na]$^+$ found 385.0095.

Compound 3g: \( R_f \): 0.30 (pet. ether/EtOAc = 70/30); 37 mg, yield: 96%; physical appearance: yellow solid, mp: 140-142 °C; \(^1\)H NMR: (500 MHz, CDCl\(_3\)) \( \delta = 8.16-8.07 \) (m, 2 H), 7.81-7.68 (m, 2 H), 7.40-7.30 (m, 2 H), 7.15-7.08 (m, 2 H), 7.01-6.96 (m, 2 H), 6.96-6.90 (m, 2 H), 6.44 (s, 1 H), 2.47 (s, 3 H); \(^{13}\)C NMR: (125 MHz, CDCl\(_3\)) \( \delta = 149.4, 145.6, 145.5, 140.2, 138.6, 132.2, 129.8, 128.5, 126.2, 123.7, 122.2, 114.1, 21.7; \) HRMS: (ESI) calcd 407.0672 for C\(_{19}\)H\(_{16}\)N\(_2\)O\(_5\)S \([M + Na]^+\) found 407.0680.

Compound 3h:\(^{13}\) \( R_f \): 0.50 (pet. ether/EtOAc = 80/20); 22 mg, yield: 97%; physical appearance: yellow solid, mp: 130-132 °C; \(^1\)H NMR: (500 MHz, CDCl\(_3\)) \( \delta = 8.16-8.07 \) (m, 2 H), 7.23-7.18 (m, 2 H), 7.16-7.12 (m, 2 H), 6.92-6.84 (m, 2 H), 6.24 (br. s., 1 H), 2.37 (s, 3 H); \(^{13}\)C NMR: (125 MHz, CDCl\(_3\)) \( \delta = 150.8, 139.4, 136.7, 134.8, 130.3, 126.3, 122.7, 113.2, 20.9.

Compound 3i:\(^{14}\) \( R_f \): 0.60 (pet. ether/EtOAc = 70/30); 23 mg, yield: 94%; physical appearance: yellow solid, mp: 137-139 °C; \(^1\)H NMR: (500 MHz, CDCl\(_3\)) \( \delta = 8.15-8.03 \) (m, 2 H), 7.21-7.12 (m, 2 H), 7.01-6.91 (m, 2 H), 6.83-6.73 (m, 2 H), 6.17 (br. s., 1 H), 3.84 (s, 3 H); \(^{13}\)C NMR: (125 MHz, CDCl\(_3\)) \( \delta = 157.4, 151.7, 139.1, 132.0, 126.3, 125.5, 115.0, 112.6, 55.5.

Compound 3j: \( R_f \): 0.40 (pet. ether/EtOAc = 70/30); 15 mg, yield: 65%; physical appearance: red solid, mp: 169-172 °C; \(^1\)H NMR: (500 MHz, DMSO-d\(_6\)) \( \delta = 9.41 \) (s, 1 H), 9.00 (s, 1 H), 8.06-7.99 (m, 2 H), 7.09-7.02 (m, 2 H), 6.85-6.77 (m, 4 H); \(^{13}\)C NMR: (125 MHz, DMSO-d\(_6\)) \( \delta 

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S19
= 154.5, 152.6, 136.8, 130.8, 126.3, 124.5, 116.0, 112.0; HRMS: (ESI) calcd 253.0584 for C_{12}H_{10}N_{2}O_{3} [M + Na]^+ found 253.0576.

**Compound 3k**: R_f: 0.70 (pet. ether/EtOAc = 70/30); 34 mg, yield: 89%; **physical appearance**: yellow solid, mp: 71-73 °C; ^1H NMR: [500 MHz, CDCl$_3$/DMSO-$d_6$ (4:1)] δ = 9.68 (br. s., 1 H), 8.53 (br. s., 1 H), 7.93 (d, J = 9.2 Hz, 2 H), 7.58 (d, J = 8.2 Hz, 2 H), 7.20-7.12 (m, 2 H), 7.07-7.00 (m, J = 8.9 Hz, 2 H), 7.00-6.90 (m, J = 8.5 Hz, 2 H), 6.90-6.76 (m, 2 H), 2.30 (s, 3 H); ^13C NMR: [125 MHz, CDCl$_3$/DMSO-$d_6$ (4:1)] δ = 150.6, 142.6, 137.8, 136.4, 136.2, 133.0, 128.9, 126.5, 125.5, 121.9, 121.5, 112.6, 20.9; HRMS: (ESI) calcd 384.1013 for C$_{19}$H$_{17}$N$_3$O$_4$S [M + H]^+ found 384.1007.

**Compound 3m**: R_f: 0.40 (pet. ether/EtOAc = 70/30); 24 mg, yield: 93%; **physical appearance**: red solid, mp: 86-88 °C; ^1H NMR: (500 MHz, DMSO-$d_6$) δ = 9.97 (s, 1 H), 8.28-8.13 (m, 4 H), 7.40-7.31 (m, 4 H); ^13C NMR: (125 MHz, DMSO-$d_6$) δ = 147.6, 140.5, 125.8, 117.1; HRMS: (ESI) calcd 260.0666 for C$_{12}$H$_9$N$_3$O$_4$ [M + H]^+ found 260.0667.

**Compound 3n**: R_f: 0.20 (pet. ether/EtOAc = 70/30); 23 mg, yield: 90%; **physical appearance**: yellow solid, mp: 140-142 °C; ^1H NMR: (500 MHz, CDCl$_3$) δ = 8.24-8.16 (m, 2 H), 8.02-7.95 (m, 2 H), 7.25-7.21 (m, 2 H), 7.18-7.13 (m, 2 H), 2.60 (s, 3 H); ^13C NMR: (125 MHz, CDCl$_3$) δ = 196.5, 147.8, 144.6, 141.3, 132.0, 130.5, 126.1, 118.3, 116.0, 26.4.

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**Compound 3o**:

\[ R_f: 0.50 \text{ (pet. ether/EtOAc = 70/30); 24 mg, yield: 84%; physical appearance: yellow solid, mp: 180-182 °C; } ^1H \text{ NMR: (500 MHz, CDCl}_3) \delta = 8.25-8.13 \text{ (m, 2 H), 8.11-8.00} \text{ (m, 2 H), 7.25-7.17} \text{ (m, 2 H), 7.17-7.08} \text{ (m, 2 H), 6.55} \text{ (s, 1 H), 4.38} \text{ (q, } J = 7.1 \text{ Hz, 2 H), 1.41} \text{ (t, } J = 7.1 \text{ Hz, 3 H); } ^13C \text{ NMR: (125 MHz, CDCl}_3) \delta = 166.0, 148.1, 144.2, 141.1, 131.5, 126.1, 125.1, 118.6, 115.6, 60.9, 14.4; HRMS: (ESI) calcd 309.0846 for } C_{15}H_{14}N_2O_4 [M + Na]^+ \text{ found 309.0858. [Note: 1,4-Dioxane was used as a solvent as transesterification occurs in MeOH with the } –\text{CO}_2\text{Et groups to furnish a mixture of esters.}

**Compound 3p**:

\[ R_f: 0.60 \text{ (pet. ether/EtOAc = 70/30); 22 mg, yield: 95%; physical appearance: yellow solid, mp: 114-116 °C; } ^1H \text{ NMR: (500 MHz, CDCl}_3) \delta = 8.19-8.11 \text{ (m, 2 H), 7.34} \text{ (dt, } J = 6.4, 8.2 \text{ Hz, 1 H), 7.04-7.00} \text{ (m, 2 H), 7.00-6.97} \text{ (m, 1 H), 6.94} \text{ (td, } J = 2.3, 10.2 \text{ Hz, 1 H), 6.88-6.81} \text{ (m, 1 H), 6.43} \text{ (br. s., 1 H); } ^13C \text{ NMR: (125 MHz, CDCl}_3) \delta = 163.5 \text{ (d, } J = 246.14 \text{ Hz), 149.2, 141.4} \text{ (d, } J = 9.99 \text{ Hz), 140.4, 130.9} \text{ (d, } J = 9.99 \text{ Hz), 126.2, 116.5} \text{ (d, } J = 3.63 \text{ Hz), 114.5, 110.9} \text{ (d, } J = 20.89 \text{ Hz), 108.1} \text{ (d, } J = 23.62 \text{ Hz); } ^19F \text{ NMR (376 MHz, CDCl}_3) \delta = –110.90; \text{ HRMS: (ESI) calcd 255.0540 for } C_{12}H_9FN_2O_2 [M + Na]^+ \text{ found 255.0541.}

**Compound 3q**:

\[ R_f: 0.60 \text{ (pet. ether/EtOAc = 70/30); 24 mg, yield: 97%; physical appearance: yellow solid, mp: 115-117 °C; } ^1H \text{ NMR: (500 MHz, CDCl}_3) \delta = 8.23-8.06 \text{ (m, 2 H), 7.34-7.28} \text{ (m, 1 H), 7.22} \text{ (t, } J = 2.1 \text{ Hz, 1 H), 7.16-7.07} \text{ (m, 2 H), 7.05-6.95} \text{ (m, 2 H), 6.37} \text{ (br. s., 1 H); } ^13C \text{ NMR: (125 MHz, CDCl}_3) \delta = 149.2, 141.0, 140.4, 135.3, 130.7, 126.2, 124.3, 121.2, 119.3, 114.4; \text{ HRMS: (ESI) calcd 271.0245 for } C_{12}H_9ClN_2O_2 [M + Na]^+ \text{ found 271.0254.}

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16 Sapountzis, I.; Knochel, P. *Synlett* 2004, 955.
Compound 3r: R$_f$: 0.70 (pet. ether/EtOAc = 70/30); 27 mg, yield: 93%; physical appearance: yellow solid, mp: 140-142 °C; $^1$H NMR: (500 MHz, CDCl$_3$) δ = 8.24-8.08 (m, 2 H), 7.42-7.34 (m, 1 H), 7.32-7.21 (m, 2 H), 7.15 (td, J = 1.9, 7.6 Hz, 1 H), 7.04-6.95 (m, 2 H), 6.31 (br. s., 1 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) δ = 149.1, 141.2, 140.5, 131.0, 127.3, 126.2, 124.1, 123.3, 119.8, 114.4; HRMS: (ESI) calcd 314.9740 for C$_{12}$H$_9$BrN$_2$O$_2$ [M + Na]$^+$ found 314.9723.

Compound 3s: R$_f$: 0.70 (pet. ether/EtOAc = 70/30); 19 mg, yield: 56%; physical appearance: yellow solid, mp: 151-153 °C; $^1$H NMR: (500 MHz, CDCl$_3$) δ = 8.17-8.14 (m, 2 H), 7.60-7.55 (m, 1 H), 7.49 (td, J = 1.4, 7.8 Hz, 1 H), 7.20-7.17 (m, 1 H), 7.13-7.09 (m, 1 H), 6.99-6.96 (m, 2 H), 6.25 (br. s., 1 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) δ = 149.1, 141.0, 140.5, 133.3, 131.1, 130.1, 126.2, 120.5, 114.3, 94.8; HRMS: (ESI) calcd 340.9781 for C$_{12}$H$_9$IN$_2$O$_2$ [M + H]$^+$ found 340.9755.

Compound 3t: R$_f$: 0.70 (pet. ether/EtOAc = 70/30); 34 mg, yield: 94%; physical appearance: yellow solid, mp: 78-80 °C; $^1$H NMR: (500 MHz, CDCl$_3$) δ = 8.19-8.15 (m, 2 H), 7.45 (t, J = 8.2 Hz, 1 H), 7.23 (ddt, J = 0.8, 1.4, 8.2 Hz, 1 H), 7.14 (t, J = 2.3 Hz, 1 H), 7.08-7.05 (m, 2 H), 7.04-7.00 (m, 1 H), 6.62 (s, 1 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) δ = 150.2, 148.5, 142.0, 140.8, 131.2, 126.2, 120.1, 118.7 (q, J = 320.62 Hz), 116.1, 114.9 (q, J = 320.62 Hz), 113.3; $^{19}$F NMR (376 MHz, CDCl$_3$) δ = −72.78; HRMS: (ESI) calcd 385.0076 for C$_{13}$H$_9$F$_3$N$_2$O$_5$S [M + Na]$^+$ found 385.0068.
Compound 3u: Rf: 0.30 (pet. ether/EtOAc = 70/30); 35 mg, yield: 91%; physical appearance: yellow solid, mp: 126-129 °C; ¹H NMR: (500 MHz, CDCl₃) δ = 8.16-8.02 (m, 2 H), 7.81-7.70 (m, 2 H), 7.37 (d, J = 8.2 Hz, 2 H), 7.31-7.23 (m, 1 H), 7.11-7.03 (m, 1 H), 6.92 (t, J = 2.2 Hz, 1 H), 6.90-6.86 (m, 2 H), 6.78-6.68 (m, 1 H), 6.65-6.52 (m, 1 H), 2.49 (s, 3 H); ¹³C NMR: (125 MHz, CDCl₃) δ = 150.2, 148.9, 145.7, 141.1, 140.2, 132.1, 130.5, 129.9, 128.4, 126.0, 119.3, 117.4, 114.6, 114.4, 21.7; HRMS: (ESI) calcd 407.0672 for C₁⁹H₁₆N₂O₅S [M + Na]⁺ found 407.0670.

Compound 3v: Rf: 0.50 (pet. ether/EtOAc = 80/20); 21 mg, yield: 92%; physical appearance: yellow solid, mp: 124-126 °C; ¹H NMR: (500 MHz, CDCl₃) δ = 8.13-8.06 (m, 2 H), 7.29-7.23 (m, 1 H), 7.03-6.95 (m, 3 H), 6.94-6.90 (m, 2 H), 6.29 (br. s., 1 H), 2.35 (s, 3 H); ¹³C NMR: (125 MHz, CDCl₃) δ = 150.3, 148.9, 145.7, 141.1, 140.2, 132.1, 130.5, 129.9, 128.4, 126.0, 119.3, 113.6, 21.4; HRMS: (ESI) calcd 251.0791 for C₁₃H₁₂N₂O₂ [M + Na]⁺ found 251.0805.

Compound 3w: Rf: 0.50 (pet. ether/EtOAc = 70/30); 21 mg, yield: 86%; physical appearance: yellow solid, mp: 101-103 °C; ¹H NMR: (500 MHz, CDCl₃) δ = 8.16-8.09 (m, 2 H), 7.29 (t, J = 8.2 Hz, 1 H), 7.00-6.96 (m, 2 H), 6.83-6.79 (m, 1 H), 6.76 (t, J = 2.3 Hz, 1 H), 6.74-6.70 (m, 1 H), 6.39 (br. s., 1 H), 3.82 (s, 3 H); ¹³C NMR: (125 MHz, CDCl₃) δ = 160.7, 150.0, 140.8, 139.8, 130.5, 126.2, 114.0, 113.9, 109.7, 107.6, 55.3.

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Compound 3x: \[ R_f: 0.60 \text{ (pet. ether/EtOAc = 80/20); 18 mg, yield: 64\%}; \] physical appearance: yellow solid, mp: 134-136 °C; \[ ^1H \text{ NMR: (500 MHz, CDCl}_3\] \[ \delta = 8.21-8.12 \text{ (m, 2 H), 7.54-7.48 \text{ (m, 1 H), 7.48-7.43 \text{ (m, 1 H), 7.43-7.37 \text{ (m, 2 H), 7.05-6.98 \text{ (m, 2 H), 6.48 \text{ (br. s., 1 H)}}; ^{13}C \text{ NMR: (125 MHz, CDCl}_3\] \[ \delta = 149.0, 140.6, 140.4, 132.2 \text{ (q, J = 32.70 Hz), 130.3, 128.7 \text{ (q, J = 272.48 Hz), 126.2, 124.1 \text{ (d, J = 0.91 Hz), 120.7 \text{ (q, J = 3.63 Hz), 117.7 \text{ (q, J = 4.54 Hz), 114.5; ^{19}F \text{ NMR (376 MHz, CDCl}_3\] \[ \delta = -62.88; HRMS: (ESI) \text{ calcd 283.0689 for C}_{13}H_9F_3N_2O_2 [M + H]^+ \text{ found 283.0694.}} \]

![Chemical Structure](image)

Compound 3y: \[ R_f: 0.40 \text{ (pet. ether/EtOAc = 70/30); 24 mg, yield: 94\%}; \] physical appearance: yellow solid, mp: 144-146 °C; \[ ^1H \text{ NMR: (500 MHz, CDCl}_3\] \[ \delta = 8.20-8.09 \text{ (m, 2 H), 7.80 \text{ (t, J = 2.1 Hz, 1 H), 7.71 \text{ (td, J = 1.4, 7.6 Hz, 1 H), 7.49 \text{ (t, J = 7.8 Hz, 1 H), 7.47-7.42 \text{ (m, 1 H), 7.04-6.96 \text{ (m, 2 H), 6.66-6.49 \text{ (m, 1 H), 2.63 \text{ (s, 3 H)}}; ^{13}C \text{ NMR: (125 MHz, CDCl}_3\] \[ \delta = 197.6, 149.4, 140.3, 138.6, 138.6, 130.0, 126.2, 125.6, 124.3, 120.6, 114.2, 26.7; HRMS: (ESI) \text{ calcd 279.0740 for C}_{14}H_{12}N_2O_3 [M + Na]^+ \text{ found 279.0750.}} \]

![Chemical Structure](image)

Compound 3z: \[ R_f: 0.40 \text{ (pet. ether/EtOAc = 70/30); 24 mg, yield: 88\%}; \] physical appearance: yellow solid, mp: 142-144 °C; \[ ^1H \text{ NMR: [500 MHz, CDCl}_3/DMSO-d_6 \text{ (4:1)] \delta = 9.34 \text{ (s, 1 H), 8.14-8.01 \text{ (m, 2 H), 7.83-7.74 \text{ (m, 1 H), 7.67-7.59 \text{ (m, 1 H), 7.52-7.41 \text{ (m, 2 H), 7.14-7.02 \text{ (m, 2 H), 3.85 \text{ (s, 3 H)}}; ^{13}C \text{ NMR: [125 MHz, CDCl}_3/DMSO-d_6 \text{ (4:1)] \delta = 165.7, 149.9, 140.6, 138.5, 130.8, 129.5, 125.8, 124.3, 123.3, 120.5, 113.6, 51.9; HRMS: (ESI) \text{ calcd 295.0689 for C}_{14}H_{12}N_2O_4 [M + Na]^+ \text{ found 295.0670.}} \]

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Compound 3aa: \(^{21}\) R\(_f\) 0.60 (pet. ether/EtOAc = 80/20); 20 mg, yield: 83\%; physical appearance: yellow solid, mp: 182-184 °C; \(^1\)H NMR: (500 MHz, CDCl\(_3\)) δ = 8.14-8.10 (m, 2 H), 6.94-6.91 (m, 2 H), 6.85-6.83 (m, 2 H), 6.83-6.80 (m, 1 H), 6.22 (br. s., 1 H), 2.33 (s, 6 H); \(^1^3\)C NMR: (125 MHz, CDCl\(_3\)) δ = 150.4, 139.5, 139.3, 126.5, 126.2, 119.7, 113.6, 21.3.

Compound 3ab: R\(_f\) 0.60 (pet. ether/EtOAc = 80/20); 33 mg, yield: 94\%; physical appearance: yellow solid, mp: 145-147 °C; \(^1\)H NMR: (500 MHz, CDCl\(_3\)) δ = 8.26-8.20 (m, 2 H), 7.65-7.60 (m, 2 H), 7.60-7.56 (m, 1 H), 7.13-7.09 (m, 2 H), 6.65 (s, 1 H); \(^1^3\)C NMR: (125 MHz, CDCl\(_3\)) δ = 147.7, 141.9, 141.6, 133.3 (q, J = 33.61 Hz), 126.3, 123.0 (q, J = 272.48 Hz), 119.4 (q, J = 3.63 Hz), 116.7 (quin, J = 4.54 Hz), 115.7; \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) δ = –63.18; HRMS: (ESI) calcd 351.0563 for C\(_{14}\)H\(_8\)F\(_6\)N\(_2\)O\(_2\) [M + H]\(^+\) found 351.0550.

Compound 3ac: R\(_f\) 0.60 (pet. ether/EtOAc = 80/20); 16 mg, yield: 65\%; physical appearance: yellow solid, mp: 139-142 °C; \(^1\)H NMR: (500 MHz, CDCl\(_3\)) δ = 8.21-8.14 (m, 2 H), 7.47 (ddd, J = 1.7, 6.0, 7.9 Hz, 2 H), 7.31-7.27 (m, 1 H), 7.10-7.04 (m, 3 H), 6.42 (br. s., 1 H); \(^1^3\)C NMR: (125 MHz, CDCl\(_3\)) δ = 148.7, 140.8, 136.8, 130.4, 127.7, 126.1, 125.7, 124.6, 120.9, 115.1; HRMS: (ESI) calcd 271.0245 for C\(_{12}\)H\(_9\)ClN\(_2\)O\(_2\) [M + Na]\(^+\) found 271.0223.

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**Compound 3ad:** $R_f$: 0.60 (pet. ether/EtOAc = 80/20); 20 mg, yield: 69%; **physical appearance:** yellow solid, mp: 143-145 °C; $^1$H NMR: (500 MHz, CDCl$_3$) $\delta$ = 8.22-8.12 (m, 2 H), 7.68-7.60 (m, 1 H), 7.48-7.43 (m, 1 H), 7.36-7.31 (m, 1 H), 7.07-6.99 (m, 3 H), 6.40 (br. s., 1 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta$ = 148.8, 140.8, 138.0, 133.6, 128.4, 126.1, 125.1, 121.2, 116.4, 115.0; HRMS: (ESI) calcd 314.9740 for C$_{12}$H$_9$BrN$_2$O$_2$ [M + Na]$^+$ found 314.9721.

**Compound 3ae:** $R_f$: 0.40 (pet. ether/EtOAc = 80/20); 22 mg, yield: 61%; **physical appearance:** yellow solid, mp: 78-81 °C; $^1$H NMR: (500 MHz, CDCl$_3$) $\delta$ = 8.20-8.14 (m, 2 H), 7.55-7.50 (m, 1 H), 7.45-7.40 (m, 1 H), 7.40-7.36 (m, 1 H), 7.29-7.24 (m, 1 H), 6.99-6.95 (m, 2 H), 6.24 (s, 1 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta$ = 148.7, 142.3, 141.1, 133.0, 129.4, 126.1, 125.8, 124.2, 123.0, 118.6 (q, $J = 320.62$ Hz), 114.8; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = -73.39; HRMS: (ESI) calcd 385.0076 for C$_{13}$H$_9$F$_3$N$_2$O$_5$S [M + Na]$^+$ found 385.0056.

**Compound 3af:** $R_f$: 0.40 (pet. ether/EtOAc = 80/20); 24 mg, yield: 63%; **physical appearance:** yellow solid, mp: 104-106 °C; $^1$H NMR: (500 MHz, CDCl$_3$) $\delta$ = 8.09-8.03 (m, 2 H), 7.69-7.63 (m, 2 H), 7.40-7.36 (m, 1 H), 7.29-7.25 (m, 1 H), 7.17 (dd, $J = 0.7$, 8.6 Hz, 2 H), 7.14 (dd, $J = 1.5$, 8.2 Hz, 1 H), 7.07 (ddd, $J = 1.5$, 7.2, 8.4 Hz, 1 H), 6.79-6.75 (m, 2 H), 6.52 (s, 1 H), 2.31 (s, 3 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta$ = 148.9, 145.9, 141.3, 140.3, 133.1, 131.7, 129.8, 128.3, 127.9, 125.8, 124.7, 124.4, 122.5, 114.2, 21.6; HRMS: (ESI) calcd 385.0853 for C$_{19}$H$_{16}$N$_2$O$_5$S [M + H]$^+$ found 385.0874.

**Compound 3ag:** $R_f$: 0.60 (pet. ether/EtOAc = 90/10); 18 mg, yield: 79%; **physical appearance:** yellow solid, mp: 109-111 °C; $^1$H NMR: (500 MHz, CDCl$_3$) $\delta$ = 8.16-8.07 (m, 2
H), 7.33-7.30 (m, 1 H), 7.30-7.24 (m, 2 H), 7.23-7.15 (m, 1 H), 6.77-6.70 (m, 2 H), 6.00 (br. s., 1 H), 2.26 (s, 3 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta$ = 151.3, 139.4, 137.5, 133.2, 131.5, 127.2, 126.3, 126.2, 124.7, 113.1, 17.9; HRMS: (ESI) calcd 251.0791 for C$_{13}$H$_{12}$N$_2$O$_2$ [M + Na]$^+$ found 251.0772.

**Compound 3ah:**$^{[22]}$ $R_f$: 0.40 (pet. ether/EtOAc = 80/20); 16 mg, yield: 66%; physical appearance: yellow solid, mp: 98-100 °C; $^1$H NMR: (500 MHz, CDCl$_3$) $\delta$ = 8.21-8.08 (m, 2 H), 7.44-7.37 (m, 1 H), 7.13-7.07 (m, 1 H), 7.02-6.95 (m, 2 H), 6.54 (br. s., 1 H), 3.90 (s, 3 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta$ = 150.4, 149.6, 139.9, 129.0, 126.1, 124.0, 120.8, 119.6, 114.2, 111.2, 55.6; HRMS: (ESI) calcd 267.0740 for C$_{13}$H$_{12}$N$_2$O$_3$ [M + Na]$^+$ found 267.0735.

**Compound 3ai:** $R_f$: 0.60 (pet. ether/EtOAc = 70/30); 19 mg, yield: 66%; physical appearance: yellow solid, mp: 90-92 °C; $^1$H NMR: (500 MHz, CDCl$_3$) $\delta$ = 9.92 (s, 1 H), 8.23-8.15 (m, 2 H), 8.10-8.02 (m, 1 H), 7.55-7.51 (m, 1 H), 7.51-7.45 (m, 1 H), 7.27-7.23 (m, 2 H), 6.99 (ddd, $J = 1.4$, 6.9, 8.0 Hz, 1 H), 4.39 (q, $J = 7.2$ Hz, 2 H), 1.43 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta$ = 168.1, 147.8, 144.0, 141.3, 134.0, 131.9, 125.8, 120.6, 117.4, 116.8, 115.8, 61.3, 14.2; HRMS: (ESI) calcd 309.0846 for C$_{15}$H$_{14}$N$_2$O$_4$ [M + Na]$^+$ found 309.0861. [Note: 1,4-Dioxane was used as a solvent as transesterification occurs in MeOH with the –CO$_2$Et groups to furnish a mixture of esters]

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Compound 3aj: \( R_f: 0.50 \) (pet. ether/EtOAc = 70/30); 51 mg, yield: 87%; **physical appearance**: thick red liquid; \( ^1H \) NMR: (500 MHz, CDCl\(_3\)) \( \delta = 8.32-8.21 \) (m, 4 H), 8.01 (s, 2 H), 7.84 (d, \( J = 8.2 \) Hz, 2 H), 7.49-7.42 (m, 2 H), 7.36-7.30 (m, 4 H), 7.27-7.20 (m, 4 H), 7.02 (s, 2 H), 3.40 (s, 6 H); \( ^{13}C \) NMR: (125 MHz, CDCl\(_3\)) \( \delta = 148.5, 148.1, 140.7, 132.9, 130.9, 130.0, 127.1, 126.2, 126.0, 125.6, 125.4, 124.9, 115.5, 114.7, 61.0; **HRMS**: (ESI) calcd 609.1745 for C\(_{34}\)H\(_{26}\)N\(_4\)O\(_6\) [M + Na]\(^+\) found 609.1717.

Compound 3ak: \[^{10}R_f: 0.70\) (pet. ether/EtOAc = 70/30); 25 mg, yield: 95%; **physical appearance**: yellow solid, mp: 169-172 °C; \( ^1H \) NMR: (500 MHz, CDCl\(_3\)) \( \delta = 8.14-8.07 \) (m, 2 H), 7.98-7.91 (m, 2 H), 7.82 (dd, \( J = 1.2, 7.9 \) Hz, 1 H), 7.59-7.54 (m, 1 H), 7.54-7.50 (m, 2 H), 7.50-7.47 (m, 1 H), 6.80-6.74 (m, 2 H), 6.43 (br. s., 1 H); \( ^{13}C \) NMR: (125 MHz, CDCl\(_3\)) \( \delta = 152.0, 139.5, 135.1, 134.8, 129.6, 128.7, 126.9, 126.7, 126.6, 126.2, 125.9, 122.3, 122.2, 113.4.

Compound 3am: \( R_f: 0.50 \) (pet. ether/EtOAc = 70/30); 37 mg, yield: 80%; **physical appearance**: yellow solid, mp: 88-90 °C; \( ^1H \) NMR: (500 MHz, DMSO-d\(_6\)) \( \delta = 9.21 \) (d, \( J = 4.9 \) Hz, 1 H), 9.08 (s, 1 H), 8.05-7.97 (m, 2 H), 7.91-7.74 (m, 2 H), 7.56 (d, \( J = 2.7 \) Hz, 1 H), 7.50-7.46 (m, 2 H), 7.45-7.41 (m, 1 H), 7.38-7.32 (m, 4 H), 7.00 (dd, \( J = 2.7, 8.9 \) Hz, 1 H), 6.88-6.79 (m, 2 H), 6.16 (d, \( J = 8.9 \) Hz, 1 H), 5.75 (br. s., 1 H); \( ^{13}C \) NMR: (125 MHz, DMSO-d\(_6\)) \( \delta = 161.4, 151.0, 141.8, 140.0, 137.6, 134.9, 132.5, 132.5, 132.1, 129.2, 128.3, 128.1, 126.5, 126.4, 126.2, 126.0, 125.9, 125.6, 123.6, 123.5, 119.9, 112.7, 67.3; **HRMS**: (ESI) calcd 461.1608 for C\(_{28}\)H\(_{20}\)N\(_4\)O\(_3\) [M + H]\(^+\) found 461.1605.
Compound 3an: $R_f$: 0.60 (pet. ether/EtOAc = 70/30); 56 mg, yield: 96%; physical appearance: yellow solid, mp: 198 °C (decomposition); $^1$H NMR: (500 MHz, DMSO-d$_6$) $\delta$ = 9.49 (s, 1 H), 8.07-8.03 (m, 2 H), 7.49-7.26 (m, 8 H), 7.21-7.19 (m, 1 H), 7.15-7.10 (m, 2 H), 7.04-7.01 (m, 2 H), 6.81 (d, $J$ = 2.6 Hz, 1 H), 3.17 (s, 3 H); $^{13}$C NMR: (125 MHz, DMSO-d$_6$) $\delta$ = 175.9, 149.2, 143.3, 142.5, 139.9, 138.9, 137.8, 135.1, 129.6, 129.2, 128.7, 128.2, 125.9, 125.6, 122.6, 122.6, 121.2, 121.2, 120.1, 117.7 (q, $J$ = 320.62 Hz), 114.4, 109.6, 59.0, 26.5; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = –74.00; HRMS: (ESI) calcd 606.0917 for C$_{28}$H$_{20}$F$_3$N$_3$O$_6$S [M + Na]$^+$ found 606.0899.

Compound 3ao: $R_f$: 0.50 (pet. ether/EtOAc = 70/30); 33 mg, yield: 78%; physical appearance: thick yellow liquid; $^1$H NMR: (500 MHz, CDCl$_3$) $\delta$ = 8.17 (d, $J$ = 8.9 Hz, 1 H), 8.10 (d, $J$ = 9.3 Hz, 2 H), 7.70 (d, $J$ = 8.4 Hz, 2 H), 7.32-7.22 (m, 3 H), 7.13-7.06 (m, 1 H), 6.87 (d, $J$ = 9.3 Hz, 2 H), 6.33 (s, 1 H), 6.35 (s, 1 H), 2.62 (s, 3 H), 2.39 (s, 3 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta$ = 151.1, 145.0, 139.3, 138.8, 136.1, 135.1, 134.3, 130.7, 130.0, 126.4, 126.3, 119.5, 115.5, 114.0, 113.1, 109.2, 21.6, 15.7; HRMS: (ESI) calcd 444.0988 for C$_{22}$H$_{19}$N$_3$O$_4$S [M + Na]$^+$ found 444.0983.

Compound 3aq: $^{[23]}$ $R_f$: 0.40 (pet. ether/EtOAc = 60/40); 10 mg, yield: 38%; physical appearance: yellow solid, mp: 178-180 °C; $^1$H NMR: (500 MHz, DMSO-d$_6$) $\delta$ = 9.67 (s, 1 H), 8.81 (d, $J$ = 2.7 Hz, 1 H), 8.19 (d, $J$ = 2.9 Hz, 1 H), 8.18-8.13 (m, 2 H), 8.00-7.95 (m, 1 H), 7.95-7.90 (m, 1 H), 7.64 (ddd, $J$ = 1.6, 6.8, 8.4 Hz, 1 H), 7.61-7.55 (m, 1 H), 7.30-7.23 (m, 2 H); $^{13}$C

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NMR: (125 MHz, DMSO-d$_6$) $\delta = 149.9, 146.2, 144.0, 138.9, 134.2, 128.6, 128.1, 127.6, 127.3, 127.2, 126.1, 121.4, 114.3$.

**Compound 3ar:** $R_f$: 0.50 (pet. ether/EtOAc = 70/30); 26 mg, yield: 93%; **physical appearance:** yellow solid, mp: 193 °C (decomposition); $^1$H NMR: (500 MHz, DMSO-d$_6$) $\delta = 9.93-9.70$ (m, 1 H), 8.89 (d, $J = 2.6$ Hz, 1 H), 8.55-8.44 (m, 1 H), 8.21-8.13 (m, 2 H), 7.93-7.86 (m, 1 H), 7.65-7.55 (m, 2 H), 7.34-7.25 (m, 2 H), 2.73 (s, 3 H); $^{13}$C NMR: (125 MHz, DMSO-d$_6$) $\delta = 149.2, 142.9, 139.5, 138.7, 134.8, 133.4, 129.9, 128.9, 128.2, 126.1, 125.8, 125.6, 114.8, 17.4; HRMS: (ESI) calcd 280.1081 for C$_{16}$H$_{13}$N$_3$O$_2$ [M + H]$^+$ found 280.1093.

**Compound 3as:** $R_f$: 0.60 (pet. ether/EtOAc = 70/30); 25 mg, yield: 94%; **physical appearance:** yellow solid, mp: 162-164 °C; $^1$H NMR: (500 MHz, DMSO-d$_6$) $\delta = 9.60$ (br. s., 1 H), 9.01-8.82 (m, 1 H), 8.38 (dd, $J = 0.4$, 8.3 Hz, 1 H), 8.22-8.05 (m, 2 H), 7.76 (d, $J = 7.5$ Hz, 1 H), 7.68-7.53 (m, 3 H), 7.43 (d, $J = 9.2$ Hz, 2 H); $^{13}$C NMR: (125 MHz, DMSO-d$_6$) $\delta = 150.0, 148.9, 140.0, 138.7, 136.7, 136.5, 128.8, 126.8, 125.7, 122.2, 121.6, 115.8, 115.2; HRMS: (ESI) calcd 266.0924 for C$_{15}$H$_{11}$N$_3$O$_2$ [M + H]$^+$ found 266.0930.

**Compound 3at:** $R_f$: 0.60 (pet. ether/EtOAc = 80/20); 37 mg, yield: 93%; **physical appearance:** thick yellow liquid; $^1$H NMR: (500 MHz, CDCl$_3$) $\delta = 8.32$-8.21 (m, 4 H), 8.01 (s, 2 H), 7.84 (d, $J = 8.2$ Hz, 2 H), 7.49-7.42 (m, 2 H), 7.36-7.30 (m, 4 H), 7.27-7.20 (m, 4 H), 7.02 (s, 2 H), 3.40 (s, 6 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta = 165.6, 148.3, 144.3, 140.9, 131.4, 126.1, 125.4,
Compound 3au: Rf 0.40 (pet. ether/EtOAc = 60/40); 49 mg, yield: 87%; physical appearance: yellow solid, mp: 118-120 °C; **1H NMR:** (500 MHz, DMSO-d6) δ = 9.64 (s, 1 H), 8.19-8.12 (m, 2 H), 7.79-7.71 (m, 2 H), 7.42 (t, J = 7.0 Hz, 1 H), 7.39-7.34 (m, 2 H), 7.28-7.23 (m, 2 H), 7.14 (d, J = 8.2 Hz, 1 H), 6.99-6.89 (m, 1 H), 6.89-6.77 (m, 1 H), 2.89-2.80 (m, 1 H), 2.76 (dd, J = 6.9, 13.7 Hz, 2 H), 2.37 (dd, J = 6.7, 13.3 Hz, 1 H), 2.30-2.20 (m, 1 H), 1.74-1.63 (m, 2 H), 1.60-1.49 (m, 3 H), 1.43 (dt, J = 4.3, 13.5 Hz, 1 H), 1.30-1.17 (m, 3 H), 1.17-1.13 (m, 6 H), 1.11 (s, 3 H), 0.81 (s, 3 H); **13C NMR:** (125 MHz, DMSO-d6) δ = 148.9, 147.1, 144.9, 144.1, 139.3, 134.5, 133.8, 128.2, 126.3, 125.9, 123.8, 123.4, 118.4, 115.3, 52.7, 43.1, 37.9, 36.8, 36.6, 35.1, 32.9, 29.1, 25.0, 24.0, 23.9, 18.7, 18.1, 18.0; **HRMS:** (ESI) calcd 562.2734 for C32H39N3O4S [M + H]+ found 562.2721.

Compound 3av: Rf 0.40 (pet. ether/EtOAc = 80/20); 44 mg, yield: 66%; physical appearance: thick yellow liquid; **1H NMR:** (500 MHz, CDCl3) δ = 8.21-8.08 (m, 2 H), 7.38-7.35 (m, 1 H), 7.09 (s, 1 H), 6.88-6.81 (m, 2 H), 6.10 (s, 1 H), 5.65 (dd, J = 1.6, 3.3 Hz, 1 H), 3.01-2.90 (m, 2 H), 2.37 (ddd, J = 3.4, 6.3, 14.9 Hz, 2 H), 2.32-2.27 (m, 1 H), 2.17-2.10 (m, 1 H), 2.03-1.97 (m, 1 H), 1.93-1.88 (m, 1 H), 1.81 (dt, J = 6.3, 11.3 Hz, 1 H), 1.72-1.58 (m, 3 H), 1.58-1.42 (m, 2 H), 1.04 (s, 3 H); **13C NMR:** (125 MHz, CDCl3) δ = 158.9, 149.7, 141.7, 141.1, 140.5, 136.0, 129.7, 126.2, 122.7, 118.6 (q, J = 321.36 Hz), 118.5 (q, J = 320.20 Hz), 114.5, 113.9, 53.4, 44.9, 44.3, 35.9, 32.5, 28.8, 28.3, 26.2, 25.6, 15.3; **19F NMR** (376 MHz, CDCl3) δ = 75.4, 75.3; **HRMS:** (ESI) calcd 671.0951 for C26H24F6N2O8S2 [M + H]+ found 671.0949.
Compound 3aw: $R_f$ 0.40 (pet. ether/EtOAc = 60/40); 44 mg, yield: 81%; physical appearance: thick yellow liquid; $^1$H NMR: ($500$ MHz, CDCl$_3$) $\delta$ = 8.23-8.17 (m, 2 H), 7.82-7.76 (m, 2 H), 7.27-7.23 (m, 2 H), 7.22-7.17 (m, 3 H), 7.10 (s, 1 H), 6.83 (d, $J$ = 2.7 Hz, 1 H), 6.72 (dd, $J$ = 2.7, 8.5 Hz, 1 H), 2.89-2.82 (m, 2 H), 2.54-2.47 (m, 1 H), 2.37-2.32 (m, 1 H), 2.28-2.22 (m, 1 H), 2.19-2.10 (m, 1 H), 2.09-2.05 (m, 1 H), 2.03-1.97 (m, 1 H), 1.96-1.91 (m, 1 H), 1.65-1.56 (m, 2 H), 1.55-1.40 (m, 4 H), 0.90 (s, 3 H); $^{13}$C NMR: ($125$ MHz, CDCl$_3$) $\delta$ = 220.8, 171.3, 147.4, 147.0, 146.1, 141.8, 138.8, 138.5, 130.5, 128.1, 126.5, 126.0, 122.4, 119.2, 117.6, 116.8, 60.4, 50.3, 47.9, 44.0, 37.8, 35.8, 31.5, 29.3, 26.1, 25.6, 21.5, 13.8; HRMS: (ESI) calcd 569.1717 for C$_{30}$H$_{30}$N$_2$O$_6$S [M + Na]$^+$ found 569.1709.

Compound 3ax: $R_f$ 0.50 (pet. ether/EtOAc = 80/20); 55 mg, yield: 82%; physical appearance: yellow solid, mp: 144-146 °C; $^1$H NMR: ($500$ MHz, CDCl$_3$) $\delta$ = 8.27-8.22 (m, 2 H), 8.22-8.17 (m, 2 H), 7.29-7.25 (m, 2 H), 7.16-7.10 (m, 2 H), 6.81 (br. s., 1 H), 2.62 (br. s., 2 H), 2.12 (s, 3 H), 2.08 (s, 3 H), 2.04 (s, 3 H), 1.87-1.73 (m, 2 H), 1.63 (br. s., 1 H), 1.54 (tt, $J$ = 6.7, 13.3 Hz, 2 H), 1.47-1.35 (m, 4 H), 1.34-1.20 (m, 11 H), 1.18-1.06 (m, 6 H), 0.91-0.85 (m, 12 H); $^{13}$C NMR: ($125$ MHz, CDCl$_3$) $\delta$ = 164.8, 149.5, 147.9, 145.1, 141.1, 140.6, 140.1, 140.1, 126.9, 126.0, 125.1, 123.7, 123.2, 118.5, 117.6, 115.9, 75.1, 39.4, 37.5, 37.4, 37.4, 37.3, 32.8, 28.0, 24.8, 24.8, 24.4, 24.2, 23.5, 22.7, 22.6, 21.0, 20.6, 19.7, 19.7, 19.6, 13.1, 12.2, 11.8; HRMS: (ESI) calcd 671.4418 for C$_{42}$H$_{58}$N$_2$O$_5$ [M + H]$^+$ found 671.4405.
Compound 3ay: RF 0.50 (pet. ether/EtOAc = 60/40); 43 mg, yield: 96%; physical appearance: thick yellow liquid; $^1$H NMR: (500 MHz, CDCl$_3$) $\delta =$ 8.14-8.07 (m, 2 H), 7.43-7.28 (m, 5 H), 7.11 (s, 4 H), 6.94-6.90 (m, 2 H), 6.46 (br. s., 1 H), 3.75 (s, 3 H), 3.16 (dd, $J$ = 5.6, 14.0 Hz, 1 H), 3.07 (dd, $J$ = 6.2, 14.0 Hz, 1 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta =$ 171.9, 155.6, 150.0, 139.7, 138.6, 136.1, 131.9, 130.5, 128.5, 128.2, 128.1, 126.2, 121.8, 113.7, 67.0, 54.8, 52.4, 37.6; HRMS: (ESI) calcd 472.1479 for C$_{24}$H$_{23}$N$_3$O$_6$ [M + Na]$^+$ found 472.1502.

Compound 4a:[$^{24}$] RF 0.70 (pet. ether/EtOAc = 70/30); 17 mg, yield: 76%; physical appearance: white solid, mp: 104-106 °C; $^1$H NMR: (500 MHz, CDCl$_3$) $\delta =$ 7.89-7.83 (m, 2 H), 7.20-7.14 (m, 2 H), 7.13-7.08 (m, 2 H), 6.96-6.91 (m, 2 H), 6.07 (br. s., 1 H), 2.53 (s, 3 H), 2.36 (s, 3 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta =$ 196.3, 149.1, 137.8, 133.4, 130.6, 130.1, 128.5, 121.6, 113.8, 26.1, 20.8.

Compound 4b:[$^{25}$] RF 0.50 (pet. ether/EtOAc = 80/20); 21 mg, yield: 93%; physical appearance: thick colourless liquid; $^1$H NMR: (500 MHz, CDCl$_3$) $\delta =$ 7.59-7.56 (m, 1 H), 7.44 (td, $J$ = 1.3, 7.7 Hz, 1 H), 7.32 (t, $J$ = 7.9 Hz, 1 H), 7.20 (ddd, $J$ = 1.1, 2.4, 8.1 Hz, 1 H), 7.16-7.10 (m, 2 H), 7.06-7.00 (m, 2 H), 5.76 (br. s., 1 H), 2.58 (s, 3 H), 2.33 (s, 3 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta =$ 198.3, 144.6, 139.4, 138.3, 131.9, 130.0, 129.4, 120.7, 120.1, 119.6, 115.6, 26.7, 20.7; HRMS: (ESI) calcd 226.1226 for C$_{15}$H$_{15}$NO [M + H]$^+$ found 226.1242.

Compound 4c: \cite{26} R_f: 0.60 (pet. ether/EtOAc = 90/10); 18 mg, yield: 80%; physical appearance: white solid, mp: 40-42 °C; \textsuperscript{1}H NMR: \textsuperscript{500} MHz, CDCl\textsubscript{3} δ = 10.49 (br. s., 1 H), 7.82 (td, J = 0.8, 8.1 Hz, 1 H), 7.29 (ddt, J = 0.8, 6.7, 8.9 Hz, 1 H), 7.23-7.12 (m, 5 H), 6.71 (ddd, J = 1.2, 6.9, 8.1 Hz, 1 H), 2.66 (s, 3 H), 2.37 (s, 3 H); \textsuperscript{13}C NMR: \textsuperscript{125} MHz, CDCl\textsubscript{3} δ = 201.1, 148.6, 137.5, 134.5, 133.9, 132.5, 129.9, 123.7, 118.6, 116.0, 113.9, 28.1, 20.9.

Compound 4d: R_f: 0.60 (pet. ether/EtOAc = 80/20); 21 mg, yield: 92%; physical appearance: yellow solid, mp: 90-92 °C; \textsuperscript{1}H NMR: \textsuperscript{500} MHz, CDCl\textsubscript{3} δ = 7.77 (t, J = 2.3 Hz, 1 H), 7.69-7.62 (m, 1 H), 7.36-7.31 (m, 1 H), 7.24-7.20 (m, 1 H), 7.20-7.16 (m, J = 8.4 Hz, 2 H), 7.10-7.05 (m, 2 H), 5.89 (br. s., 1 H), 2.36 (s, 3 H); \textsuperscript{13}C NMR: \textsuperscript{125} MHz, CDCl\textsubscript{3} δ = 149.3, 145.9, 138.1, 133.3, 130.2, 129.9, 121.1, 120.9, 114.0, 109.4, 20.8; HRMS: (ESI) calcd 229.0972 for C\textsubscript{13}H\textsubscript{12}N\textsubscript{2}O\textsubscript{2} [M + H]\textsuperscript{+} found 229.0976.

Compound 4e: \cite{27} R_f: 0.60 (pet. ether/EtOAc = 80/20); 16 mg, yield: 70%; physical appearance: yellow solid, mp: 62-64 °C; \textsuperscript{1}H NMR: \textsuperscript{500} MHz, CDCl\textsubscript{3} δ = 9.46 (br. s., 1 H), 8.20 (dd, J = 1.7, 8.7 Hz, 1 H), 7.38-7.31 (m, 1 H), 7.25-7.22 (m, 2 H), 7.19-7.14 (m, 3 H), 6.74 (ddd, J = 1.4, 7.0, 8.5 Hz, 1 H), 2.39 (s, 3 H); \textsuperscript{13}C NMR: \textsuperscript{125} MHz, CDCl\textsubscript{3} δ = 143.7, 135.9, 135.7, 135.6, 130.3, 126.6, 124.8, 117.1, 115.9, 21.0; HRMS: (ESI) calcd 251.0791 for C\textsubscript{13}H\textsubscript{12}N\textsubscript{2}O\textsubscript{2} [M + Na]\textsuperscript{+} found 251.0778.

Compound 4f: Rf: 0.60 (pet. ether/EtOAc = 90/10); 20 mg, yield: 96%; physical appearance: yellow solid, mp: 102-104 °C; 1H NMR: (500 MHz, CDCl₃) δ = 7.50-7.41 (m, 2 H), 7.21-7.14 (m, J = 8.2 Hz, 2 H), 7.11-7.05 (m, 2 H), 6.94-6.87 (m, 2 H), 6.16-5.99 (m, 1 H), 2.36 (s, 3 H); 13C NMR: (125 MHz, CDCl₃) δ = 148.7, 137.2, 134.0, 133.7, 130.1, 122.0, 120.0, 114.3, 100.8, 20.8; HRMS: (ESI) calcd 209.1073 for C₁₄H₁₂N₂ [M + H]+ found 209.1087.

[Note: 1,4-Dioxane was used as a solvent, as –CN converts –CO₂Me in presence of MeOH under the standard reaction conditions]

Compound 4g: Rf: 0.60 (pet. ether/EtOAc = 80/20); 20 mg, yield: 96%; physical appearance: yellow solid, mp: 62-65 °C; 1H NMR: (500 MHz, CDCl₃) δ = 7.31-7.26 (m, 1 H), 7.20-7.18 (m, 1 H), 7.18-7.14 (m, 2 H), 7.14-7.11 (m, 1 H), 7.09 (td, J = 1.3, 7.6 Hz, 1 H), 7.06-7.01 (m, 2 H), 5.77 (br. s., 1 H), 2.35 (s, 3 H); 13C NMR: (125 MHz, CDCl₃) δ = 145.4, 138.2, 133.1, 130.2, 130.1, 122.9, 120.9, 119.9, 119.1, 117.9, 113.1, 20.8. [Note: 1,4-Dioxane was used as a solvent, as –CN converts –CO₂Me in presence of MeOH under the standard reaction conditions]

Compound 4h: Rf: 0.60 (pet. ether/EtOAc = 90/10); 18 mg, yield: 87%; physical appearance: white solid, mp: 64-66 °C; 1H NMR: (500 MHz, CDCl₃) δ = 7.54-7.44 (m, 1 H), 7.37-7.32 (m, 1 H), 7.22-7.16 (m, 2 H), 7.13-7.07 (m, 3 H), 6.84-6.76 (m, 1 H), 6.28 (br. s., 1 H), 2.36 (s, 3 H); 13C NMR: (125 MHz, CDCl₃) δ = 148.0, 137.0, 134.3, 133.9, 132.9, 130.2, 122.6, 118.6, 117.7, 113.5, 97.7, 20.9; HRMS: (ESI) calcd 209.1073 for C₁₄H₁₂N₂ [M + H]+ found 209.1090. [Note: 1,4-Dioxane was used as a solvent, as –CN converts –CO₂Me in presence of MeOH under the standard reaction conditions]

Compound 4i: \[^{[31]}\] Rf: 0.70 (pet. ether/EtOAc = 80/20); 22 mg, yield: 91%; **physical appearance**: white solid, mp: 100-102 °C; \(^1\)H NMR: (500 MHz, CDCl\(_3\)) \(\delta = 7.94-7.87\) (m, 2 H), 7.19-7.14 (m, 2 H), 7.11-7.07 (m, 2 H), 6.94-6.91 (m, 2 H), 6.00 (br. s., 1 H), 3.88 (s, 3 H), 2.35 (s, 3 H); \(^{13}\)C NMR: (125 MHz, CDCl\(_3\)) \(\delta = 167.0, 148.8, 138.0, 133.1, 131.5, 130.0, 121.3, 120.5, 113.9, 51.6, 20.8\). [Note: 4-Aminobenzoic acid was used as a coupling partner]

Compound 4j: \[^{[32]}\] Rf: 0.70 (pet. ether/EtOAc = 70/30); 21 mg, yield: 87%; **physical appearance**: white solid, mp: 76-78 °C; \(^1\)H NMR: (500 MHz, CDCl\(_3\)) \(\delta = 7.71-7.62\) (m, 1 H), 7.54 (td, \(J = 1.3, 7.7\) Hz, 1 H), 7.29 (t, \(J = 7.9\) Hz, 1 H), 7.19 (ddd, \(J = 1.1, 2.5, 8.1\) Hz, 1 H), 7.16-7.09 (m, 2 H), 7.06-7.01 (m, 2 H), 5.73 (br. s., 1 H), 3.90 (s, 3 H), 2.33 (s, 3 H); \(^{13}\)C NMR: (125 MHz, CDCl\(_3\)) \(\delta = 167.2, 144.4, 139.5, 131.7, 131.3, 130.0, 129.3, 121.1, 120.5, 119.5, 117.2, 52.1, 20.7\); HRMS: (ESI) calcd 242.1176 for C\(_{15}\)H\(_{15}\)NO\(_2\) [M + H]\(^+\) found 242.1178. [Note: 3-Aminobenzoic acid was used as a coupling partner]

Compound 4k: \[^{[33]}\] Rf: 0.40 (pet. ether/EtOAc = 70/30); 16 mg, yield: 71%; **physical appearance**: white solid, mp: 196-198 °C; \(^1\)H NMR: (500 MHz, DMSO-d\(_6\)) \(\delta = 13.00\) (br. s., 1 H), 9.55 (br. s., 1 H), 7.88 (dd, \(J = 1.7, 7.9\) Hz, 1 H), 7.35 (ddd, \(J = 1.8, 7.0, 8.6\) Hz, 1 H), 7.19-7.15 (m, 2 H), 7.15-7.07 (m, 3 H), 6.73 (ddd, \(J = 1.1, 7.0, 8.0\) Hz, 1 H), 2.28 (s, 3 H); \(^{13}\)C NMR: (125 MHz, DMSO-d\(_6\)) \(\delta = 170.0, 147.7, 137.7, 134.2, 132.5, 131.8, 129.9, 122.2, 116.8, 113.3, 111.9, 20.4\); HRMS: (ESI) calcd 228.1019 for C\(_{14}\)H\(_{13}\)NO\(_2\) [M + H]\(^+\) found 228.1028. [Note: 2-
Aminobenzoic acid was used as a coupling partner. However, the esterification did not occur probably due to steric reasons.

**Compound 4l:**[^34] R$_f$: 0.50 (pet. ether/EtOAc = 95/05); 4 mg, yield: 22%; **physical appearance:** white solid, mp: 68-70 ºC; $^1$H NMR: (500 MHz, CDCl$_3$) $\delta$ = 7.28-7.22 (m, 2 H), 7.12-7.09 (m, 2 H), 7.06-7.00 (m, 4 H), 6.92-6.87 (m, 1 H), 5.62 (br. s., 1 H), 2.32 (s, 3 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta$ = 143.9, 140.3, 130.9, 129.8, 129.3, 120.3, 118.9, 116.9, 20.7.

**Compound 4n:** R$_f$: 0.70 (pet. ether/EtOAc = 90/10); 14 mg, yield: 57%; **physical appearance:** red solid, mp: 50-52 ºC; $^1$H NMR: (500 MHz, CDCl$_3$) $\delta$ = 9.33 (br. s., 1 H), 7.94-7.88 (m, 1 H), 7.25-7.22 (m, 2 H), 7.17-7.13 (m, 4 H), 2.39 (s, 3 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta$ = 154.3, 152.4, 140.7 (d, $J$ = 0.91 Hz), 135.9 (d, $J$ = 4.54 Hz), 131.8 (d, $J$ = 8.17 Hz), 130.4, 124.7, 124.4 (d, $J$ = 23.61 Hz), 117.5 (d, $J$ = 7.26 Hz), 111.7 (d, $J$ = 26.34 Hz), 21.0; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = -125.50; **HRMS:** (ESI) calcd 269.0697 for C$_{13}$H$_{11}$FN$_2$O$_2$ [M + Na]$^+$ found 269.0692.

**Compound 4o:** R$_f$: 0.40 (pet. ether/EtOAc = 99/01); 22 mg, yield: 72%; **physical appearance:** red solid, mp: 110-112 ºC; $^1$H NMR: (500 MHz, CDCl$_3$) $\delta$ = 9.42 (br. s., 1 H), 8.41-8.30 (m, 1 H), 7.40 (dd, $J$ = 2.4, 9.2 Hz, 1 H), 7.26-7.22 (m, 2 H), 7.16-7.13 (m, 2 H), 7.03 (d, $J$ = 9.2 Hz, 1 H), 2.39 (s, 3 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) $\delta$ = 142.8, 138.4, 136.3, 135.3, 133.0, 130.5, 128.7, 124.9, 117.7, 108.1, 21.0; **HRMS:** (ESI) calcd 307.0077 for C$_{13}$H$_{11}$BrN$_2$O$_2$ [M + H]$^+$ found 307.0078.

**Compound 4p:** \( R_f \): 0.70 (pet. ether/EtOAc = 90/10); 19 mg, yield: 79%; **physical appearance:** red solid, \( mp \): 72-74 °C; \(^1\)H NMR: (500 MHz, CDCl\(_3\)) \( \delta = 9.35 \) (br. s., 1 H), 8.00 (s, 1 H), 7.24-7.20 (m, 2 H), 7.20-7.17 (m, 1 H), 7.15 (d, \( J = 8.4 \) Hz, 2 H), 7.12-7.05 (m, 1 H), 2.38 (s, 3 H), 2.29 (s, 3 H); \(^{13}\)C NMR: (125 MHz, CDCl\(_3\)) \( \delta = 141.5, 137.1, 136.3, 135.2, 132.6, 130.2, 126.8, 125.7, 124.3, 116.0, 20.9, 20.0;\) **HRMS:** (ESI) calcd 265.0947 for C\(_{14}\)H\(_{14}\)N\(_2\)O\(_2\) [M + Na]\(^+\) found 265.0952.

**Compound 4q:** \( R_f \): 0.50 (pet. ether/EtOAc = 90/10); 18 mg, yield: 70%; **physical appearance:** red solid, \( mp \): 78-80 °C; \(^1\)H NMR: (500 MHz, CDCl\(_3\)) \( \delta = 9.34 \) (br. s., 1 H), 7.63 (d, \( J = 3.1 \) Hz, 1 H), 7.23-7.19 (m, 2 H), 7.18-7.12 (m, 3 H), 7.05 (dd, \( J = 3.0, 9.4 \) Hz, 1 H), 3.82 (s, 3 H), 2.37 (s, 3 H); \(^{13}\)C NMR: (125 MHz, CDCl\(_3\)) \( \delta = 150.9, 138.8, 136.4, 135.1, 132.3, 130.2, 126.3, 124.1, 117.7, 106.7, 55.8, 20.9;\) **HRMS:** (ESI) calcd 281.0897 for C\(_{14}\)H\(_{14}\)N\(_2\)O\(_3\) [M + Na]\(^+\) found 281.0893.

**Compound 4r:** \( R_f \): 0.60 (pet. ether/EtOAc = 80/20); 22 mg, yield: 85%; **physical appearance:** yellow solid, \( mp \): 104-106 °C; \(^1\)H NMR: (500 MHz, CDCl\(_3\)) \( \delta = 7.83 \) (dd, \( J = 2.4, 8.9 \) Hz, 1 H), 7.72 (d, \( J = 2.4 \) Hz, 1 H), 7.25-7.18 (m, 2 H), 7.17-7.09 (m, 2 H), 7.02 (d, \( J = 9.0 \) Hz, 1 H), 6.70 (br. s., 1 H), 4.00 (s, 3 H), 2.37 (s, 3 H); \(^{13}\)C NMR: (125 MHz, CDCl\(_3\)) \( \delta = 145.6, 141.3, 138.4, 136.5, 134.5, 130.2, 122.6, 119.1, 108.9, 105.4, 56.0, 20.9;\) **HRMS:** (ESI) calcd 281.0897 for C\(_{14}\)H\(_{14}\)N\(_2\)O\(_3\) [M + Na]\(^+\) found 281.0902.
**Compound 4s:** Rf: 0.30 (pet. ether/EtOAc = 70/30); 22 mg, yield: 94%; **physical appearance:** red solid, mp: 132-134 °C; **$^1$H NMR:** (500 MHz, DMSO-d$_6$) $\delta = 13.00$ (br. s., 1 H), 9.55 (br. s., 1 H), 7.88 (dd, $J = 1.7$, 7.9 Hz, 1 H), 7.35 (ddd, $J = 1.8$, 7.0, 8.6 Hz, 1 H), 7.19-7.15 (m, 2 H), 7.15-7.07 (m, 3 H), 6.73 (ddd, $J = 1.1$, 7.0, 8.0 Hz, 1 H), 2.28 (s, 3 H); **$^{13}$C NMR:** (125 MHz, DMSO-d$_6$) $\delta =$ 140.6, 139.0, 138.3, 131.6, 130.0, 129.4, 128.5, 128.0, 127.0, 123.7, 119.1, 118.2, 20.4; **HRMS:** (ESI) calcd 235.1230 for C$_{16}$H$_{14}$N$_2$ [M + H]$^+$ found 235.1246.

![Compound 4s](image)

**Compound 4t:** Rf: 0.40 (pet. ether/EtOAc = 80/20); 26 mg, yield: 91%; **physical appearance:** thick yellow liquid; **$^1$H NMR:** (500 MHz, DMSO-d$_6$) $\delta = 9.01$ (s, 1 H), 7.67-7.60 (m, 1 H), 7.54-7.48 (m, 2 H), 7.44 (d, $J = 8.2$ Hz, 1 H), 7.37-7.32 (m, 1 H), 7.23 (d, $J = 2.0$ Hz, 1 H), 7.21-7.11 (m, 4 H), 6.83-6.74 (m, 1 H), 2.29 (s, 3 H); **$^{13}$C NMR:** (125 MHz, DMSO-d$_6$) $\delta =$ 190.6, 151.5, 146.4, 142.6, 137.9, 135.3, 133.9, 132.0, 129.9, 129.3, 126.3, 123.1, 122.8, 121.0, 120.5, 113.0, 106.0, 20.4; **HRMS:** (ESI) calcd 286.1226 for C$_{20}$H$_{15}$NO [M + H]$^+$ found 286.1215.

![Compound 4t](image)

**Compound 4u:** Rf: 0.60 (pet. ether/EtOAc = 80/20); 16 mg, yield: 53%; **physical appearance:** yellow solid, mp: 193-195 °C; **$^1$H NMR:** (500 MHz, CDCl$_3$) $\delta =$ 8.37-8.32 (m, 1 H), 7.88 (dd, $J =$ 0.9, 2.4 Hz, 1 H), 7.71 (ddd, $J =$ 1.7, 7.0, 8.6 Hz, 1 H), 7.50-7.47 (m, 1 H), 7.45-7.40 (m, 2 H), 7.37 (ddd, $J =$ 1.1, 7.0, 8.1 Hz, 1 H), 7.15-7.11 (m, 2 H), 7.07-7.02 (m, 2 H), 5.79 (s, 1 H), 2.34 (s, 3 H); **$^{13}$C NMR:** (125 MHz, CDCl$_3$) $\delta =$ 177.0, 156.2, 150.7, 140.6, 139.9, 134.5, 131.6, 130.1, 126.7, 125.2, 123.5, 122.5, 121.4, 119.0, 118.9, 117.9, 111.4, 20.7; **HRMS:** (ESI) calcd 302.1176 for C$_{20}$H$_{15}$NO$_2$ [M + H]$^+$ found 302.1184.

![Compound 4u](image)
**Compound 4v**: $R_f$: 0.70 (pet. ether/EtOAc = 80/20); 14 mg, yield: 46%; physical appearance: white solid, $\text{mp}$: 46-48 °C; $^1\text{H NMR}$: (500 MHz, CDCl$_3$) $\delta$ = 7.71-7.62 (m, 1 H), 7.54 (td, $J$ = 1.3, 7.7 Hz, 1 H), 7.29 (t, $J$ = 7.9 Hz, 1 H), 7.19 (ddd, $J$ = 1.1, 2.5, 8.1 Hz, 1 H), 7.16-7.09 (m, 2 H), 7.06-7.01 (m, 2 H), 5.73 (br. s., 1 H), 3.90 (s, 3 H), 2.33 (s, 3 H); $^{13}\text{C NMR}$: (125 MHz, CDCl$_3$) $\delta$ = 164.9, 146.6, 141.0, 139.1, 137.4, 132.6, 129.2, 128.6, 127.2, 123.0, 119.7, 100.8, 51.2, 20.6; HRMS: (ESI) calcd 308.1394 for C$_{18}$H$_{17}$N$_3$O$_2$ [M + H]$^+$ found 308.1408.

![4w](image)

**Compound 4w**: $^{[35]}$ $R_f$: 0.50 (pet. ether/EtOAc = 90/10); 25 mg, yield: 92%; physical appearance: white solid, $\text{mp}$: 90-92 °C; $^1\text{H NMR}$: (500 MHz, CDCl$_3$) $\delta$ = 7.15-7.05 (m, 2 H), 6.77 (d, $J$ = 8.4 Hz, 2 H), 5.37 (br. s., 1 H), 2.32 (s, 3 H); $^{13}\text{C NMR}$: (125 MHz, CDCl$_3$) $\delta$ = 139.5, 131.8, 129.7, 117.1, 20.6 (carbon of pentafluoroaniline did not appear); $^{19}\text{F NMR}$ (376 MHz, CDCl$_3$) $\delta$ = −150.3 to −150.4 (m, 2F), −163.0 to −163.1 (m, 2F), −164.7 to −164.9 (m, 1F); HRMS: (ESI) calcd 274.0650 for C$_{13}$H$_8$F$_5$N [M + H]$^+$ found 274.0634.

![4w](image)

**Compound 4z**: $^{[36]}$ $R_f$: 0.30 (pet. ether/EtOAc = 70/30); 16 mg, yield: 91%; physical appearance: white solid, $\text{mp}$: 68-70 °C; $^1\text{H NMR}$: (500 MHz, CDCl$_3$) $\delta$ = 7.53-7.45 (m, 2 H), 7.21-7.14 (m, 2 H), 3.84 (t, $J$ = 7.0 Hz, 2 H), 2.60 (t, $J$ = 8.1 Hz, 2 H), 2.33 (s, 3 H), 2.19-2.12 (m, 2 H); $^{13}\text{C NMR}$: (125 MHz, CDCl$_3$) $\delta$ = 174.0, 136.9, 134.1, 129.3, 120.0, 48.9, 32.6, 20.8, 18.0; HRMS: (ESI) calcd 176.1070 for C$_{11}$H$_{13}$NO [M + H]$^+$ found 176.1083.

![4z](image)

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Compound 4aa.\textsuperscript{[37]} R\textsubscript{f}: 0.30 (pet. ether/EtOAc = 70/30); 12 mg, yield: 68%; physical appearance: white solid, mp: 70-72 °C; \textsuperscript{1}H NMR: (500 MHz, CDCl\textsubscript{3}) \( \delta = 7.45-7.39 \) (m, 2 H), 7.22-7.15 (m, 2 H), 4.49-4.44 (m, 2 H), 4.05-4.01 (m, 2 H), 2.34 (s, 3 H); \textsuperscript{13}C NMR: (125 MHz, CDCl\textsubscript{3}) \( \delta = 155.3, 135.7, 133.7, 129.5, 118.3, 61.2, 45.3, 20.7 \); HRMS: (ESI) calcd 200.0682 for C\textsubscript{10}H\textsubscript{11}NO\textsubscript{2} [M + Na]\textsuperscript{+} found 200.0691.

\[ \text{Compound 4ab.} \textsuperscript{[38]} R\textsubscript{f}: 0.50 \text{ (pet. ether/EtOAc = 70/30); 16 mg, yield: 72%; physical appearance: white solid, mp: 134-136 °C; } \textsuperscript{1}H NMR: (500 MHz, CDCl\textsubscript{3}) \( \delta = 7.96-7.90 \) (m, 1 H), 7.77-7.72 (m, 2 H), 7.60 (dt, \( J = 1.3, 7.4 \) Hz, 1 H), 7.54-7.49 (m, 2 H), 7.26-7.22 (m, 2 H), 4.84 (s, 2 H), 2.37 (s, 3 H); \textsuperscript{13}C NMR: (125 MHz, CDCl\textsubscript{3}) \( \delta = 167.4, 140.1, 137.0, 134.2, 133.3, 131.9, 129.7, 128.3, 124.1, 122.6, 119.6, 50.9, 20.9 \); HRMS: (ESI) calcd 224.1070 for C\textsubscript{15}H\textsubscript{13}NO [M + H]\textsuperscript{+} found 224.1076. \]

Compound 4ad.\textsuperscript{[39]} R\textsubscript{f}: 0.60 (pet. ether/EtOAc = 80/20); 16 mg, yield: 76%; physical appearance: white solid, mp: 153-155 °C; \textsuperscript{1}H NMR: (500 MHz, CDCl\textsubscript{3}) \( \delta = 7.91-7.85 \) (m, 2 H), 7.80 (br. s., 1 H), 7.58-7.52 (m, 3 H), 7.52-7.46 (m, 2 H), 7.24-7.13 (m, 2 H), 2.35 (s, 3 H); \textsuperscript{13}C NMR: (125 MHz, CDCl\textsubscript{3}) \( \delta = 165.6, 135.3, 135.1, 134.2, 131.7, 129.6, 128.8, 127.0, 120.3, 20.9. \]

\[ \text{Compound 4ae.} \]

Compound 4ae: R_f: 0.40 (pet. ether/EtOAc = 80/20); 21 mg, yield: 73%; physical appearance: white solid, mp: 231-233 °C; ^1H NMR: (500 MHz, DMSO-d$_6$) δ = 10.22 (s, 1 H), 7.93-7.87 (m, 2 H), 7.77-7.71 (m, 2 H), 7.68-7.59 (m, 2 H), 7.20-7.11 (m, 2 H), 2.28 (s, 3 H); ^13C NMR: (125 MHz, DMSO-d$_6$) δ = 164.3, 136.4, 134.1, 132.8, 131.3, 129.7, 129.0, 125.2, 120.4, 20.5; HRMS: (ESI) calcd 311.9994 for C$_{14}$H$_{12}$BrNO [M + Na]$^+$ found 311.9967.

![4ae](image)

Compound 4af: R_f: 0.40 (pet. ether/EtOAc = 80/20); 23 mg, yield: 80%; physical appearance: white solid, mp: 142-144 °C; ^1H NMR: (500 MHz, DMSO-d$_6$) δ = 10.37 (s, 1 H), 7.74-7.68 (m, 1 H), 7.63-7.58 (m, 2 H), 7.56-7.52 (m, 1 H), 7.51-7.46 (m, 1 H), 7.44-7.38 (m, 2 H), 7.18-7.13 (m, J = 8.4 Hz, 2 H), 2.28 (s, 3 H); ^13C NMR: (125 MHz, DMSO-d$_6$) δ = 165.6, 139.2, 136.5, 132.7, 132.7, 131.1, 129.1, 128.8, 127.7, 119.6, 119.0, 20.5; HRMS: (ESI) calcd 290.0175 for C$_{14}$H$_{12}$BrNO [M + H]$^+$ found 290.0197.

![4af](image)

Compound 4ag: R_f: 0.50 (pet. ether/EtOAc = 80/20); 10 mg, yield: 57%; physical appearance: white solid, mp: 94-96 °C; ^1H NMR: (500 MHz, CDCl$_3$) δ = 7.44-7.38 (m, J = 8.5 Hz, 2 H), 7.25 (br. s., 1 H), 7.14-7.10 (m, J = 8.4 Hz, 2 H), 2.50 (spt, J = 6.9 Hz, 1 H), 2.31 (s, 3 H), 1.25 (d, J = 6.9 Hz, 6 H); ^13C NMR: (125 MHz, CDCl$_3$) δ = 175.1, 135.5, 133.7, 129.4, 119.9, 36.6, 20.8, 19.6; HRMS: (ESI) calcd 178.1226 for C$_{11}$H$_{15}$NO [M + H]$^+$ found 178.1248.

![4ag](image)

Compound 4ah: R_f: 0.40 (pet. ether/EtOAc = 70/30); 12 mg, yield: 58%; physical appearance: white solid, mp: 72-74 °C; ^1H NMR: (500 MHz, CDCl$_3$) δ = 9.07 (br. s., 1 H), 7.49-7.38 (m, 2 H), 7.25-7.13 (m, J = 8.4 Hz, 2 H), 7.14-7.09 (m, J = 8.3 Hz, 2 H), 7.08-7.04 (m, 1 H), 6.95-6.87 (m, J = 8.3 Hz, 2 H), 2.50 (s, 3 H), 1.25 (d, J = 6.9 Hz, 6 H); ^13C NMR: (125 MHz, CDCl$_3$) δ = 175.1, 135.5, 133.7, 129.4, 119.9, 36.6, 20.8, 19.6; HRMS: (ESI) calcd 178.1226 for C$_{11}$H$_{15}$NO [M + H]$^+$ found 178.1248.

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H), 7.18-7.08 (m, 2 H), 3.80 (s, 3 H), 3.48 (s, 2 H), 2.32 (s, 3 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) δ = 170.3, 162.6, 134.8, 134.2, 129.4, 120.2, 52.6, 41.4, 20.8; HRMS: (ESI) calcd 230.0788 for C$_{11}$H$_{13}$NO$_3$ [M + Na]$^+$ found 230.0811.

**Compound 4ai:** $R_f$: 0.60 (pet. ether/EtOAc = 80/20); 29 mg, yield: 90%; **physical appearance:** white solid, mp: 98-100 °C; $^1$H NMR: (500 MHz, CDCl$_3$) δ = 7.63-7.54 (m, 4 H), 7.09-7.03 (m, 2 H), 7.00-6.91 (m, 2 H), 6.67 (s, 1 H), 2.29 (s, 3 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) δ = 138.0, 136.0, 133.1, 132.3, 130.0, 128.8, 128.0, 122.7, 20.9; HRMS: (ESI) calcd 325.9845 for C$_{13}$H$_{12}$BrNO$_2$S [M + H]$^+$ found 325.9863.

**Compound 4aj:**$^{[43]}$ $R_f$: 0.40 (pet. ether/EtOAc = 80/20); 23 mg, yield: 88%; **physical appearance:** white solid, mp: 102-104 °C; $^1$H NMR: (500 MHz, CDCl$_3$) δ = 7.68-7.61 (m, 2 H), 7.25-7.20 (m, 2 H), 7.05-7.01 (m, 2 H), 6.98-6.94 (m, 2 H), 6.74 (s, 1 H), 2.38 (s, 3 H), 2.27 (s, 3 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) δ = 143.7, 136.1, 135.3, 133.7, 129.8, 129.6, 127.3, 122.3, 21.5, 20.8 HRMS: (ESI) calcd 284.0716 for C$_{14}$H$_{15}$NO$_2$S [M + Na]$^+$ found 284.0740.

**Compound 4ak:**$^{[44]}$ $R_f$: 0.20 (pet. ether/EtOAc = 80/20); 24 mg, yield: 82%; **physical appearance:** white solid, mp: 178-181 °C; $^1$H NMR: (500 MHz, CDCl$_3$) δ = 8.32-8.22 (m, 2 H), 7.95-7.87 (m, 2 H), 7.11-7.06 (m, 2 H), 6.99-6.93 (m, 2 H), 6.67 (s, 1 H), 2.31 (s, 3 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) δ = 150.2, 144.7, 136.8, 132.5, 130.2, 128.5, 124.2, 123.1, 20.9; HRMS: (ESI) calcd 315.0410 for C$_{13}$H$_{12}$N$_2$O$_4$S [M + Na]$^+$ found 315.0426.

Compound 4al: R_f: 0.50 (pet. ether/EtOAc = 70/30); 16 mg, yield: 86%; physical appearance: white solid, mp: 98-101 °C; \(^1\)H NMR: (500 MHz, CDCl\(_3\)) \(\delta = 7.19-7.12\) (m, 4 H), 6.60 (br. s., 1 H), 2.99 (s, 3 H), 2.34 (s, 3 H); \(^{13}\)C NMR: (125 MHz, CDCl\(_3\)) \(\delta = 135.6, 133.9, 130.2, 121.6, 39.1, 20.8\).

Compound 4an: R_f: 0.60 (pet. ether/EtOAc = 70/30); 26 mg, yield: 82%; physical appearance: white solid, mp: 172-174 °C; \(^1\)H NMR: (500 MHz, CDCl\(_3\)) \(\delta = 7.79-7.73\) (m, 2 H), 7.67 (br. s., 1 H), 7.55-7.48 (m, 2 H), 7.20-7.13 (m, 4 H), 7.12-7.06 (m, 2 H), 7.02-6.96 (m, 2 H), 5.93 (s, 1 H), 2.35 (d, \(J = 4.4\) Hz, 6 H); \(^{13}\)C NMR: (125 MHz, CDCl\(_3\)) \(\delta = 165.1, 147.8, 138.3, 135.7, 133.7, 133.0, 130.0, 129.5, 128.7, 125.3, 121.0, 120.1, 114.6, 20.9, 20.8\); HRMS: (ESI) calcld 317.1648 for C\(_{21}\)H\(_{20}\)N\(_2\)O [M + H]^+ found 317.1642.

Compound 4ao: R_f: 0.60 (pet. ether/EtOAc = 70/30); 31 mg, yield: 88%; physical appearance: white solid, mp: 150-152 °C; \(^1\)H NMR: (500 MHz, DMSO-d\(_6\)) \(\delta = 9.81\) (s, 1 H), 8.61 (s, 1 H), 7.54-7.46 (m, 2 H), 7.14-7.10 (m, 2 H), 7.05-6.99 (m, 4 H), 6.99-6.90 (m, 4 H), 2.25 (s, 3 H), 2.18 (s, 3 H); \(^{13}\)C NMR: (125 MHz, DMSO-d\(_6\)) \(\delta = 148.5, 138.2, 135.6, 132.7, 131.4, 129.8\).

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129.4, 128.7, 127.4, 120.3, 120.1, 113.3, 20.4, 20.3; **HRMS** (ESI) calcd 353.1318 for C_{20}H_{20}N_{2}O_{2}S C_{20}H_{20}N_{2}O_{2}S [M + H]^+ found 353.1299.

**3.5 General procedure for the gold-catalyzed C(sp²)−N cross-coupling reactions in presence of base (2,6-di-tert-butylpyridine):**

An oven-dried screw-cap vial, equipped with a stir bar, was loaded with the aryl iodide (1, 0.1 mmol), amine (2, 0.1 mmol), MeDalPhosAuCl (Au-I, 5 mol%, 0.005 mmol) and MeOH (0.1 M). Then resulting reaction mixture was then cooled to 0 °C; 2,6-di-tert-butylpyridine (0.15 mmol) and AgSbF₆ (0.11 mmol) was added subsequently. The reaction mixture was then allowed to stir at 80 °C for 16 h. After completion of the reaction, it was then diluted with DCM, filtered through a small pad of celite, concentrated and subsequently purified by column chromatography (silica gel) with appropriate solvent systems to afford the C(sp²)−N cross-coupled products.

**Compound 5a:**[47] R_f: 0.50 (pet. ether/EtOAc = 95/05); 9 mg, yield: 53%; **physical appearance:** white solid, **mp:** 48-50 °C; **¹H NMR:** (500 MHz, CDCl₃) δ = 7.33-7.27 (m, 4 H), 7.14-7.08 (m, 4 H), 7.00-6.93 (m, 2 H), 5.86-5.62 (m, 1 H); **¹³C NMR:** (125 MHz, CDCl₃) δ = 143.1, 129.3, 121.0, 117.8.

**Compound 5b:**[48] R_f: 0.50 (pet. ether/EtOAc = 80/20); 18 mg, yield: 85%; **physical appearance:** white solid, **mp:** 78-80 °C; **¹H NMR:** (500 MHz, CDCl₃) δ = 7.95-7.81 (m, 2 H), 7.40-7.32 (m, 2 H), 7.24-7.16 (m, 2 H), 7.10 (tt, J = 1.3, 7.4 Hz, 1 H), 7.06-6.95 (m, 2 H), 6.12 (br. s., 1 H), 2.54 (s, 3 H); **¹³C NMR:** (125 MHz, CDCl₃) δ = 196.4, 148.3, 140.6, 130.6, 129.5, 129.0, 123.4, 120.7, 114.4, 26.1.

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Compound 5c:[49] Rf: 0.40 (pet. ether/EtOAc = 95/05); 15 mg, yield: 63%; physical appearance: pale yellow liquid; $^1$H NMR: (500 MHz, CDCl$_3$) δ = 7.48 (d, $J$ = 8.7 Hz, 2 H), 7.37-7.31 (m, 2 H), 7.19-7.13 (m, 2 H), 7.12-7.01 (m, 3 H), 5.93 (br. s., 1 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) δ = 146.8, 141.1, 129.6, 126.7 (q, $J$ = 3.90 Hz), 125.6 (q, $J$ = 271.80 Hz), 122.9, 121.6 (q, $J$ = 33.81 Hz), 120.0, 115.3; $^{19}$F NMR (376 MHz, CDCl$_3$) δ = −280.95.

Compound 5e:[50] Rf: 0.30 (pet. ether/EtOAc = 90/10); 23 mg, yield: 85%; physical appearance: thick yellow liquid; $^1$H NMR: (176 MHz, CDCl$_3$) δ = 8.17-8.06 (m, 2 H), 7.46-7.38 (m, 2 H), 7.20-7.12 (m, 2 H), 6.95-6.87 (m, 2 H), 6.25 (br. s., 1 H), 1.35 (s, 9 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) δ = 150.6, 148.0, 139.4, 136.6, 126.6, 126.3, 122.0, 113.3, 34.5, 31.3; HRMS: (ESI) calcd 271.1441 for C$_{16}$H$_{18}$N$_2$O$_2$ [M + H]$^+$ found 271.1440.

Compound 5f: Rf: 0.40 (pet. ether/EtOAc = 90/10); 16 mg, yield: 52%; physical appearance: yellow solid, mp: 142-144 ºC; $^1$H NMR: (500 MHz, CDCl$_3$) δ = 8.17-8.07 (m, 2 H), 7.43-7.32 (m, 2 H), 7.23-7.17 (m, 2 H), 7.14 (tt, $J$ = 1.1, 7.4 Hz, 1 H), 7.11-7.00 (m, 4 H), 6.90-6.83 (m, 2 H), 6.20 (s, 1 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) δ = 157.1, 154.6, 150.9, 139.6, 134.5, 129.9, 126.3, 124.6, 123.5, 120.0, 118.8, 113.1; HRMS: (ESI) calcd 307.1077 for C$_{18}$H$_{14}$N$_2$O$_3$ [M + H]$^+$ found 307.1089.

**Compound 5g**: R$_f$: 0.40 (pet. ether/EtOAc = 80/20); 27 mg, yield: 88%; **physical appearance**: yellow solid, mp: 111-113 °C; $^1$H NMR: (500 MHz, CDCl$_3$) δ = 8.24-8.01 (m, 2 H), 7.44-7.34 (m, 2 H), 7.32 (t, J = 8.1 Hz, 1 H), 7.18-7.13 (m, 1 H), 7.11-7.03 (m, 2 H), 7.00-6.92 (m, 3 H), 6.84 (t, J = 2.3 Hz, 1 H), 6.80-6.75 (m, 1 H), 6.38 (br. s., 1 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) δ = 158.8, 156.5, 149.5, 141.1, 140.0, 130.7, 129.9, 126.2, 123.8, 119.3, 115.7, 114.2, 114.1, 111.3; HRMS: (ESI) calcd 307.1077 for C$_{18}$H$_{14}$N$_2$O$_3$ [M + H]$^+$ found 307.1073.

**Compound 5h**: R$_f$: 0.40 (pet. ether/EtOAc = 80/20); 8 mg, yield: 41%; physical appearance: yellow liquid; $^1$H NMR: (500 MHz, CDCl$_3$) δ = 8.13-8.05 (m, 2 H), 6.55-6.50 (m, 2 H), 4.47 (br. s., 1 H), 3.24-3.20 (m, 2 H), 1.68-1.62 (m, 2 H), 1.49-1.42 (m, 2 H), 0.99 (t, J = 7.4 Hz, 3 H); $^{13}$C NMR: (125 MHz, CDCl$_3$) δ = 153.4, 137.8, 126.5, 110.9, 43.1, 31.2, 20.1, 13.8.

### 3.6 Representative procedure for the large scale synthesis:

An oven-dried Schlenk tube was equipped with a stirring bar, filled with 1-bromo-4-iodobenzene (1d, 564 mg, 2 mmol), 4-nitroaniline (2a, 276 mg, 2.0 mmol), Au-1 (33 mg, 2.5 mol%), MeOH (20 mL) were added. The resulting reaction mixture was then cooled to 0 °C and AgSbF$_6$ (0.11 mmol) was added subsequently. The reaction mixture was then allowed to stir at 80 °C for 24 h. The crude reaction mixture was then diluted with DCM and filtered through a small pad of celite, concentrated and subsequently purified by column chromatography (silica gel) with pet. ether/EtOAc as eluent to afford the C(sp$^2$)−N cross-coupled products 3d (507 mg, 87%). Following the same procedure compound 3k was also accessed from 4-iodophenyl trifluoromethanesulfonate (1k) with equal efficiency (614 mg, 85%).

![Reaction Scheme](image)

### 3.7 Usefulness of the reaction:

3.7.1 Indolinones synthesis via domino C-N cross-coupling and lactamization reactions:

Representative procedure: An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with 2-iodophenylacetic acid (1ay, 0.1 mmol), 4-nitroaniline (2a, 0.1 mmol), 2.5 mol% MeDalPhosAuCl (Au-1) in MeOH (0.1 M). The resulting reaction mixture was then cooled to 0 °C and AgSbF₆ (0.11 mmol) was added subsequently and allowed to stir at 80 °C for 24 h. The crude reaction mixture was then diluted with DCM and filtered through a small pad of celite, concentrated and subsequently purified by column chromatography (silica gel) with pet. ether/EtOAc as eluent to afford the cross-coupled product 6a in 89% yields. Following the similar procedure compound 6b was also accessed in 86% yield.

- Characterization data:

Compound 6a: Rf: 0.50 (pet. ether/EtOAc = 70/30); 23 mg, yield: 91%; physical appearance: white solid, mp: 150-152 °C; ¹H NMR: (500 MHz, CDCl₃) δ = 8.45-8.35 (m, 2 H), 7.73-7.66 (m, 2 H), 7.40-7.34 (m, 1 H), 7.30-7.24 (m, 1 H), 7.19-7.13 (m, 1 H), 6.94 (d, J = 7.9 Hz, 1 H), 3.77 (s, 2 H); ¹³C NMR: (125 MHz, CDCl₃) δ = 173.9, 146.3, 143.4, 140.4, 128.0, 126.5, 125.1, 124.9, 124.2, 123.7, 109.4, 36.0; HRMS: (ESI) calcd 255.0764 for C₁₄H₁₀N₂O₃ [M + H]⁺ found 255.0771.
Compound 6b: Rf: 0.40 (pet. ether/EtOAc = 60/40); 19 mg, yield: 76%; physical appearance: white solid, mp: 120-122 °C; ¹H NMR: (500 MHz, CDCl₃) δ = 8.16-8.11 (m, 2 H), 7.62-7.54 (m, 2 H), 7.38-7.31 (m, 1 H), 7.27-7.23 (m, 1 H), 7.15-7.10 (m, 1 H), 6.89 (d, J = 7.9 Hz, 1 H), 3.75 (s, 2 H), 2.66 (s, 3 H); ¹³C NMR: (125 MHz, CDCl₃) δ = 197.0, 174.2, 144.2, 138.8, 136.2, 129.7, 127.9, 126.2, 124.9, 124.3, 123.3, 109.5, 36.1, 26.7; HRMS: (ESI) calcd 252.1019 for C₁₆H₁₃NO₂ [M + H]⁺ found 252.1039.

3.7.2 Carbazoles synthesis via domino C-N and C-C cross-coupling reactions:

Representative procedure: To a screw-cap vial containing a stir bar, 1,2-di-iodobenzene (1az, 0.1 mmol), p-nitroaniline (2a, 0.1 mmol), 5 mol% MeDalPhosAuCl (Au-1) were added in MeOH (0.1 M). The resulting reaction mixture was then cooled to 0 °C and 2.2 equiv of AgSbF₆ (0.22 mmol) was added subsequently and stirred at 80 °C for 24 h. The crude reaction mixture was then diluted with DCM and filtered through a small pad of celite, concentrated and subsequently purified by column chromatography (silica gel) with pet. ether/EtOAc as eluent to afford the cross-coupled product 6c was obtained in 85% yields. The reaction is believed to proceed via the consecutive C(sp²)−N and C(sp²)-C(sp³) reaction sequence. Following the similar procedure compounds 6d-6f were also accessed in excellent yields.

- Characterization data
Compound 6c: [52] $R_f$: 0.40 (pet. ether/EtOAc = 80/20); 18 mg, yield: 85%; physical appearance: yellow solid, mp: 200-203 °C; $^1H$ NMR: (500 MHz, DMSO-$d_6$) $\delta$ = 12.06 (s, 1 H), 9.16 (d, $J$ = 2.3 Hz, 1 H), 7.63 (d, $J$ = 9.0 Hz, 1 H), 7.61-7.58 (m, 1 H), 7.54-7.49 (m, 1 H), 7.31-7.26 (m, 1 H); $^{13}C$ NMR: (125 MHz, DMSO-$d_6$) $\delta$ = 143.3, 141.0, 139.8, 127.3, 122.5, 122.2, 121.3, 121.2, 120.3, 117.4, 111.9, 111.1.

![Compound 6c](image)

Compound 6d: [53] $R_f$: 0.40 (pet. ether/EtOAc = 80/20); 21 mg, yield: 93%; physical appearance: white solid, mp: 174-177 °C; $^1H$ NMR: (500 MHz, CDCl$_3$) $\delta$ = 8.85-8.81 (m, 1 H), 8.41 (br. s., 1 H), 8.16-8.12 (m, 2 H), 7.49-7.45 (m, 2 H), 7.43 (d, $J$ = 8.5 Hz, 1 H), 7.31 (ddd, $J$ = 2.7, 5.4, 7.9 Hz, 1 H), 4.00 (s, 3 H); $^{13}C$ NMR: (125 MHz, CDCl$_3$) $\delta$ = 167.9, 142.3, 139.9, 127.4, 126.6, 126.5, 123.3, 123.1, 121.4, 120.6, 120.3, 110.9, 110.1, 51.9.

![Compound 6d](image)

Compound 6e: [52] $R_f$: 0.40 (pet. ether/EtOAc = 80/20); 18 mg, yield: 86%; physical appearance: pale yellow solid, mp: 158-160 °C; $^1H$ NMR: (500 MHz, CDCl$_3$) $\delta$ = 8.75 (dd, $J$ = 0.8, 1.8 Hz, 1 H), 8.50 (br. s., 1 H), 8.16-8.12 (m, 1 H), 8.10 (dd, $J$ = 1.8, 8.5 Hz, 1 H), 7.51-7.47 (m, 2 H), 7.45 (dd, $J$ = 0.8, 8.5 Hz, 1 H), 7.34-7.29 (m, 1 H), 2.74 (s, 3 H); $^{13}C$ NMR: (125 MHz, CDCl$_3$) $\delta$ = 197.9, 142.4, 140.0, 129.4, 126.7, 126.6, 123.4, 123.1, 121.9, 120.6, 120.4, 111.0, 110.3, 26.7.

![Compound 6e](image)

Compound 6f: $R_f$: 0.60 (pet. ether/EtOAc = 80/20); 17 mg, yield: 78%; physical appearance: yellow solid, mp: 194 °C (decomposition); $^1H$ NMR: (500 MHz, DMSO-$d_6$) $\delta$ = 12.29 (s, 1 H),

9.35 (s, 1 H), 8.84 (td, J = 0.9, 8.0 Hz, 1 H), 8.74-8.67 (m, 1 H), 8.26-8.16 (m, 1 H), 7.83-7.76 (m, 2 H), 7.71 (ddd, J = 1.4, 6.9, 8.3 Hz, 1 H), 7.63 (ddd, J = 1.1, 7.1, 8.3 Hz, 1 H), 7.45-7.38 (m, 1 H); ¹³C NMR: (125 MHz, DMSO-d₆) δ = 140.9, 139.9, 138.1, 132.4, 128.9, 127.4, 127.2, 125.8, 124.1, 123.4, 123.2, 121.1, 120.6, 120.2, 112.9; HRMS: (ESI) calcd 219.0917 for C₁₅H₁₀N₂ [M + H]⁺ found 219.0923.

4. Proposed mechanistic rationale and control experiments:

4.1 Plausible mechanism:

To substantiate the intermediacy of putative Au(III)-aryl intermediates (B, C and D) as competent catalytic intermediates, few control experiments were performed.

4.2 Identification of gold-intermediates B and C by ³¹P and ¹⁹F NMR studies:

First, to prove the intermediacy of Au(III)-aryl intermediates B and C we monitored the stoichiometric reaction by NMR. To start with, the Au(III)-aryl intermediate I was prepared and characterized by ¹H and ³¹P and ¹⁹F NMR following the procedure described by Amgoune, Bourissou and co-workers. It was then subjected with 1 equiv of 4-nitroaniline (2a) in presence of 1 equiv of AgSbF₆ and heated at 80 °C for 30 min (Figure 1). The intermediate I was consumed (confirmed by ³¹P and ¹⁹F NMR) to form 3b in 39% GC yield along with some unidentified side products.[24] However, intermediate I was not consumed in the absence of AgSbF₆ (confirmed by ³¹P and ¹⁹F NMR), with no formation of 3a (GC analysis). This unequivocally confirmed that the putative Au(III)-aryl intermediate C, generated from B by the action of Ag⁺.
**Figure 1**: $^{19}$F and $^{31}$P NMR studies for the identification of gold-intermediates B and C.

**Procedure for the NMR experiments**: In a glovebox, a NMR tube was charged with AgSbF$_6$ (6.9 mg, 0.02 mmol) in CD$_2$Cl$_2$ (0.3 mL). The NMR tube was then cooled to $-78$ °C outside of the glovebox. Next, a solution of MeDalphosAuCl (Au-1, 13 mg, 0.02 mmol) and 4-fluoriodobenzene (2.3 μL, 0.02 mmol) in CD$_2$Cl$_2$ (0.3 mL) was added to the NMR tube slowly. The tube was gently shaken and allowed to warm to RT for 15 min. The formation of the Au(III) complex I was monitored and confirmed by $^1$H and $^{31}$P and $^{19}$F NMR. **NMR data**: $^1$H NMR: (500 MHz, CD$_2$Cl$_2$) $\delta = 8.03$ - 7.94 (m, 2 H), 7.93 - 7.87 (m, 1 H), 7.78 - 7.72 (m, 1 H), 7.51 - 7.42 (m, 2 H), 7.16 - 7.09 (m, 2 H), 3.51 (s, 6 H), 2.31 - 2.23 (m, 6 H), 2.13 - 2.03 (m, 12 H), 1.83 - 1.70 (m, 12 H); $^{31}$P NMR: (162 MHz, CD$_2$Cl$_2$) $\delta = 76.1$; $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) $\delta = 115.5$.

In a glovebox, another NMR tube was charged with AgSbF$_6$ (6.9 mg, 0.02 mmol) and 2a (2.8 mg, 0.02 mmol) in CD$_2$Cl$_2$ (0.2 mL). The NMR tube was then cooled to $-78$ °C outside of the glovebox and reaction mixture of intermediate I was slowly added via syringe. The tube was then gently shaken and allowed to warm to 80 °C for 30 min. After 30 min it was cooled to room
temperature and NMR was recorded. Intermediate I was fully consumed as confirmed by $^{31}$P NMR and $^{19}$F NMR (see Figure 1) for the formation of product 3b in 39% yield (determined by GC using biphenyl as an internal standard). However, when the same procedure was followed in the absence of AgSbF$_6$, we didn’t observe any product formation (see Figure 1).

4.3 Identification of gold-intermediate D:

Next, to substantiate the intermediacy of Au(III)-intermediate D, we sought to investigate the reaction through mass spectrometry; as all efforts in the isolation and characterization of these highly reactive reaction intermediates failed. First, the intermediate I was treated with different sets of amines in presence of 1 equiv of AgSbF$_6$ and heated at 80 ºC for 10 min; the putative intermediates IIa and IIb were detected in ESI-HRMS (Figure 2), which disappeared completely after 1 h along with the formation of the respective cross-coupled products. This eventually attests the high-valent Au(III)-intermediate D as a putative intermediate; from which the reductive elimination is taking place. When the similar experiments were performed with more acidic phthalimide and succinamide, we also detected II-c and II-d in ESI-HRMS. However, both II-c and II-d were not consumed to provide the corresponding cross-coupled products even after 1 h at 80 ºC. This indicates the difficulty of relatively acidic amines to undergo the reductive elimination (4ac and 4am).
Representative procedure for the ESI-HRMS studies: In a glovebox, a screw cap vial was charged with AgSbF$_6$ (6.9 mg, 0.02 mmol) in dry CD$_2$Cl$_2$ (0.2 mL). The vial was then cooled to $-78 \, ^\circ$C and subsequently, a solution of MeAlphosAuCl (Au-1, 13 mg, 0.02 mmol) and 4-fluoriodobenzene (2.3 μL, 0.02 mmol) in dry CD$_2$Cl$_2$ (0.2 mL) was added slowly via a syringe. The reaction mixture was then stirred at 80 °C. After a mentioned time intervals (10 min and 1 h), an aliquot (50 μL) of the reaction mixture was taken, diluted in 1:10 ratio with MeOH, and monitored via ESI-HRMS.
5. **NMR data:**

\[ \begin{align*}
\text{DICHLOROMETHANE-d2} & : \\
7.62 & 7.61 & 7.59 & 7.59 & 7.50 & 7.49 & 7.48 & 7.48 & 7.43 & 7.18 & 6.87 & 6.85 & 5.32 & 2.41 \\
\end{align*} \]

\[ \begin{align*}
\text{CHLOROFORM-d} & : \\
181.76 & 181.69 & 157.95 & 157.25 & 156.80 & 155.04 & 155.02 & 153.43 & 152.60 & 152.51 & 149.49 & 148.11 & 77.43 & 77.22 & 77.00 & 76.78 & 76.57 & 69.40 \\
\end{align*} \]
$^{31}$P NMR (162 MHz), $CD_2Cl_2$
$^3$P NMR (162 MHz). CD$_2$Cl$_2$
$^{31}$P NMR (162 MHz), CD$_2$Cl$_2$
$^{31}$P NMR (162 MHz), CD$_2$Cl$_2$
\textbf{CHLOROFORM-d}

\textbf{1H NMR (500 MHz), CDCl$_3$}

\textbf{13C NMR (125 MHz), CDCl$_3$}
$^{19}\text{F NMR (376 MHz), CDCl}_3$
$^{1}$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
Chemical Shift (ppm)

CHLOROFORM-d

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

$^{13}$C NMR (125 MHz), CDCl$_3$
$^{19}F$ NMR (376 MHz), CDCl$_3$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
$^{19}$F NMR (376 MHz), CDCl$_3$
\[ ^1H \text{ NMR (500 MHz), CDCl}_3 \]

\[ ^{13}C \text{ NMR (125 MHz), CDCl}_3 \]
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$

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

$^{13}$C NMR (125 MHz), CDCl$_3$
$^{1}$H NMR (500 MHz), CDCl$_3$:DMSO-d$_6$ (4:1)

$^{13}$C NMR (125 MHz), CDCl$_3$:DMSO-d$_6$ (4:1)
$^1$H NMR (500 MHz), DMSO-d$_6$

$^{13}$C NMR (125 MHz), DMSO-d$_6$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
\[ ^{19}\text{F} \text{NMR (376 MHz, CDCl}_3 \]
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$

Chemical Shift (ppm)

CHLOROFORM-d

8.19 8.18 8.17 8.16 7.46 7.45 7.43 7.14 7.14 7.07 7.07 7.06 7.06 7.03 6.62 1.72 0.01
$^{19}$F NMR (376 MHz), CDCl$_3$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
**$^1$H NMR (500 MHz), CDCl$_3$**

- Chemical Shifts (ppm):
  - 8.14, 8.13, 8.13, 8.11, 8.11, 7.31, 7.29, 7.28, 6.99, 6.98, 6.97, 6.82, 6.76, 6.76, 6.73, 6.39, 3.82, 1.66, 0.01

**$^{13}$C NMR (125 MHz), CDCl$_3$**

- Chemical Shifts (ppm):
  - 160.73, 149.96, 140.77, 139.78, 130.45, 126.16, 113.98, 113.91, 109.71, 107.59, 77.25, 77.00, 76.75, 55.33
$^{1}H$ NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
$^{19}$F NMR (376 MHz), CDCl$_3$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
Chemical Shift (ppm)

$^{19}$F NMR (376 MHz), CDCl$_3$
**1H NMR (500 MHz), CDCl₃**

- Chemical Shifts:
  - 8.19
  - 8.18
  - 8.17
  - 7.48
  - 7.48
  - 7.47
  - 7.46
  - 7.46
  - 7.27
  - 7.06
  - 7.06
  - 7.05
  - 7.04
  - 6.42
  - 1.56

**13C NMR (125 MHz), CDCl₃**

- Chemical Shifts:
  - 148.70
  - 140.82
  - 136.76
  - 130.38
  - 127.70
  - 126.07
  - 125.69
  - 124.59
  - 120.90
  - 115.08
  - 77.25
  - 77.00
  - 76.75

*3ac*
**1H NMR (500 MHz), CDCl3**

- Chemical Shifts:
  - 8.19
  - 8.18
  - 8.16
  - 7.66
  - 7.65
  - 7.64
  - 7.46
  - 7.45
  - 7.44
  - 7.34
  - 7.27
  - 7.05
  - 7.03
  - 7.02
  - 6.40
  - 1.56

**13C NMR (125 MHz), CDCl3**

- Chemical Shifts:
  - 148.78
  - 140.80
  - 137.97
  - 133.59
  - 128.40
  - 126.09
  - 125.11
  - 121.24
  - 116.40
  - 115.03
  - 77.25
  - 77.00
  - 76.75
$^{1}H$ NMR (500 MHz), CDCl$_3$

$^{13}C$ NMR (125 MHz), CDCl$_3$
\[ ^1H \text{NMR (500 MHz), CDCl}_3 \]

\[ ^13C \text{NMR (125 MHz), CDCl}_3 \]
$^{19}$F NMR (376 MHz), CDCl$_3$
**$^1$H NMR (500 MHz), CDCl$_3$**

**$^{13}$C NMR (125 MHz), CDCl$_3$**
Chemical Shift (ppm)

O\textsubscript{2}N

\textsuperscript{1}H NMR (500 MHz), CDCl\textsubscript{3}

\textsuperscript{13}C NMR (125 MHz), CDCl\textsubscript{3}
$^1$H NMR (500 MHz), DMSO-d$_6$

$^{13}$C NMR (125 MHz), DMSO-d$_6$
$^{19}$F NMR (376 MHz), DMSO-$d_6$
$^{1}H$ NMR (500 MHz), DMSO-$d_6$

$^{13}C$ NMR (125 MHz), DMSO-$d_6$
$^1$H NMR (500 MHz), DMSO-$d_6$

$^{13}$C NMR (125 MHz), DMSO-$d_6$
$^{19}$F NMR (376 MHz), CDCl$_3$
**Chemical Shift (ppm)**

- **CHLOROFORM-d**
  - 8.21
  - 8.19
  - 7.80
  - 7.78
  - 7.26
  - 7.24
  - 7.21
  - 7.20
  - 7.19
  - 7.17
  - 6.83

- **3aw**
  - 5.52
  - 3.79
  - 2.05

**1H NMR (500 MHz), CDCl₃**

- 2.03
- 1.04
- 1.01
- 0.87
- 1.01

**13C NMR (125 MHz), CDCl₃**

- 220.84
- 171.25
- 146.08
- 138.83
- 77.26
- 50.34
- 44.03
- 31.45
- 21.02
- 13.78
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
Chemical Shift (ppm)

1H NMR (500 MHz), CDCl₃

13C NMR (125 MHz), CDCl₃
$^{1}H$ NMR (500 MHz), CDCl$_3$

$^{13}C$ NMR (125 MHz), CDCl$_3$
\[
{^1}H \text{ NMR (500 MHz), CDCl}_3
\]

\[
{^{13}}C \text{ NMR (125 MHz), CDCl}_3
\]
Chemical Shift (ppm)

**H NMR (500 MHz), CDCl₃**

**13C NMR (125 MHz), CDCl₃**
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
$^1$H NMR (500 MHz), DMSO-$d_6$

$^{13}$C NMR (125 MHz), DMSO-$d_6$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
$^{19}$F NMR (375 MHz), CDCl$_3$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
$^{1}\text{H NMR (500 MHz), DMSO-d}_6$

$^{13}\text{C NMR (125 MHz), DMSO-d}_6$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
$^{19}$F NMR (375 MHz), CDCl$_3$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
$^1$H NMR (500 MHz), DMSO-d$_6$

$^{13}$C NMR (125 MHz), DMSO-d$_6$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
4ai

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

4.00 2.02 0.01 0.38 3.00

$^{13}$C NMR (125 MHz), CDCl$_3$

98.04 36.32 33.12 32.25 32.07 27.98 22.72 77.25 77.00 76.75 20.85
$^{1}$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
\[ \text{CHLOROFORM-d} \]

\[ {^1}\text{H NMR (500 MHz), CDCl}_3 \]

\[ {^{13}}\text{C NMR (125 MHz), CDCl}_3 \]
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (176 MHz), CDCl$_3$
$^{19}$F NMR (376 MHz), CDCl$_3$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
$^1$H NMR (500 MHz), CDCl$_3$

$^{13}$C NMR (125 MHz), CDCl$_3$
\[ ^1\text{H NMR (500 MHz), CDCl}_3 \]

\[ ^1\text{C NMR (125 MHz), CDCl}_3 \]
Chemical Shift (ppm)

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

![NMR spectrum diagram]

**$^{13}$C NMR (125 MHz), CDCl$_3$**

![NMR spectrum diagram]
Chemical Shift (ppm)

$^{31}$P NMR (162 MHz), CD$_2$Cl$_2$

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