KO'Bu-Promoted Transition-Metal-Free Transamidation of Primary and Tertiary Amides with Amines

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1.0 General information: All solvents and reagents were purified by standard techniques reported in Armarego, W. L. F., Chai, C. L. L., Purification of Laboratory Chemicals, 5th edition, Elsevier, 2003; or used as supplied from commercial sources (Sigma-Aldrich Corporation® unless stated otherwise). All reactions were generally carried out under inert atmosphere unless otherwise noted. TLC was performed on Merck Kieselgel 60 F254 plates, and spots were visualized under UV light. Products were purified by column chromatography on silica gel (100-200 mesh, Merck). $^1$H and $^{13}$C NMR spectra were recorded on either Brüker AVANCE 500 (500 MHz and 125 MHz), JEOL 400 (400 MHz and 100 MHz), or Brüker AVANCE 300 (300 MHz and 75 MHz) instruments using deuterated solvents as detailed and at ambient probe temperature (300 K). Chemical shifts are reported in parts per million (ppm) and are referred to the residual solvent peak. The following notations are used: singlet (s); doublet (d); triplet (t); quartet (q); multiplet (m); broad (br). Coupling constants are quoted in Hertz and are denoted as $J$. Mass spectra were recorded on a Micromass® Q-Tof (ESI) spectrometer. EPR spectra was recorded at room temperature on EPR spectrometer operated at Magnettech GmbH MiniScope MS400 spectrometer (equipped with a TC H03 temperature controller), where the microwave frequency was measured with an FC400 frequency counter.
2.0 Procedures for transamidation of amides with amines

2.1. Transamidation of amides with amines (GP-1): To a mixture of amine 1 (1.0 equiv) and amide 2 (10 equiv), KO'Bu (1.5 equiv) was added. The mixture was stirred in a sealed tube and the progress of the reaction was monitored by TLC visualized with UV short wavelength followed by iodine or ninhydrin stain. After completion, the mixture was diluted with water (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic phases were washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude residue was then purified by column chromatography on silica gel with ethylacetate–hexane (20/80 to 40/60) to obtain the desired amides (3, 5 and 7).

2.2. Representative procedure for transamidation of p-anisidine: To the mixture of p-anisidine 1a (200 mg, 1.62 mmol, 1.0 equiv) and dry DMF 2a (1.3 mL, 16.2 mmol, 10.0 equiv) in a flame-dried sealed tube fitted with magnetic stir bar was added KO'Bu (273 mg, 2.43 mmol, 1.5 equiv). The resulting mixture was stirred at room temperature for 2 h under nitrogen atmosphere, and the progress of the reaction was monitored by TLC. After completion, the mixture was diluted with water (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic phases were washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude residue was then purified by column chromatography on silica gel with ethylacetate–hexane (30:70) to obtain the desired corresponding amide 3a in 97% yield (237 mg, 0.97 mmol) as a brown liquid.

2.3. Transamidation of cyclopropyl amine (GP-2): To a mixture of cyclopropyl amine (1 equiv) and amide 2 (10 equiv), KO'Bu (1.5 equiv) was added. The mixture was stirred and heated at 80 °C in a sealed tube. The progress of the reaction was monitored by TLC visualized with UV short wavelength followed by iodine or ninhydrin stain. After completion, the mixture was diluted with water (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic phases were washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude residue was then purified by column chromatography on silica gel with ethylacetate–hexane (20/80 to 40/60) to obtain pure products (6a-b).

2.4. Transamidation of p-anisidine using DMF as a reagent: To a mixture of p-anisidine 1a (1.0 equiv) and KO’Bu (1.5 equiv) in toluene or THF, DMF 2a (1-4 equiv) was added. The mixture was stirred in a sealed tube and the progress of the reaction was monitored by TLC.
visualized with UV short wavelength followed by iodine or ninhydrin stain. After completion, the mixture was diluted with water (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The crude residue was then purified by column chromatography on silica gel with ethylacetate–hexane (20/80 to 40/60) to obtain the desired amide 3a.

**Table S1.** Transamidation of amine 1a using DMF as the formylating agent.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base (% mol)</th>
<th>Reagent (% mol)</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>1.</td>
<td>KO'Bu (150)</td>
<td>DMF (100)</td>
<td>Toluene</td>
<td>47</td>
</tr>
<tr>
<td>2.</td>
<td>KO'Bu (150)</td>
<td>DMF (200)</td>
<td>Toluene</td>
<td>61</td>
</tr>
<tr>
<td>3.</td>
<td>KO'Bu (150)</td>
<td>DMF (300)</td>
<td>Toluene</td>
<td>80</td>
</tr>
<tr>
<td>4.</td>
<td>KO'Bu (150)</td>
<td>DMF (400)</td>
<td>Toluene</td>
<td>80</td>
</tr>
<tr>
<td>5.</td>
<td>KO'Bu (150)</td>
<td>DMF (100)</td>
<td>THF</td>
<td>44</td>
</tr>
<tr>
<td>6.</td>
<td>KO'Bu (150)</td>
<td>DMF (200)</td>
<td>THF</td>
<td>52</td>
</tr>
<tr>
<td>7.</td>
<td>KO'Bu (150)</td>
<td>DMF (300)</td>
<td>THF</td>
<td>65</td>
</tr>
<tr>
<td>8.</td>
<td>KO'Bu (150)</td>
<td>DMF (400)</td>
<td>THF</td>
<td>67</td>
</tr>
</tbody>
</table>

3.0 **Electron Paramagnetic Resonance (EPR) experiments:** The formation of radical species during the transamidation process was investigated using electron paramagnetic resonance (EPR) spectroscopy. The sample was taken out into a small tube and then analyzed by EPR spectrophotometer. EPR spectra was recorded at room temperature on EPR spectrometer operated at Magnettech GmbH MiniScope MS400 spectrometer (equipped with a TC H03 temperature controller), where the microwave frequency was measured with an FC400 frequency counter. The EPR spectra was recorded for the reaction mixture containing p-anisidine (1 mmol) and KO'Bu (1.5 mmol) after stirring in DMF (0.8 mL) for 1 h (Figure S1). The hyperfine EPR spectrum is suggestive of an electron-transfer process between KO'Bu and amine.
Figure S1. The electron paramagnetic resonance (EPR) spectrum of the reaction mixture comprising of $p$-anisidine (1 mmol), KO'Bu (1.5 mmol) in DMF (0.8 mL) after stirring for 1 h at rt.

4.0 ESI-MS analysis of radical quenching experiments:
Figure S2. ESI-MS spectra of KO'Bu mediated transamidation of amine with DMF in the presence of (a) TEMPO and (b) galvinoxyl radicals show the intermediate amine radical is quenched by radical scavengers.

5.0 Analytical data of compounds:

N-(4-Methoxyphenyl)formamide (3a): Using the general procedure GP-1, compound 1a (200 mg, 1.62 mmol) and KO'Bu (273 mg, 2.43 mmol) provided compound 3a (237 mg, 97%) as a brown liquid. A mixture of rotamers is observed; $^1$H NMR (400 MHz, DMSO-$d_6$):

Major rotamer: $\delta$ 9.99 (s, 1H), 8.19 (d, $J = 2.0$ Hz, 1H), 7.49 (d, $J = 9.0$ Hz, 2H), 6.91–6.84 (m, 2H), 3.70 (s, 3H); Minor rotamer: $\delta$ 9.92 (d, $J = 11.1$ Hz, 1H), 8.57 (d, $J = 11.1$ Hz, 1H), 7.10 (d, $J = 8.9$ Hz, 2H), 6.91–6.84 (m, 2H), 3.70 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): Major rotamer: $\delta$ 163.0, 159.5, 131.9, 121.1, 114.4, 55.7; Minor rotamer: $\delta$
156.5, 155.9, 131.7, 120.2, 115.1, 55.6; HRMS (ESI) calcd for $\text{C}_8\text{H}_9\text{NNaO}_2\text{[M+Na]}^+$: 174.0531; Found: 174.0528.

**N-(3-Methoxyphenyl)formamide (3b):** Using the general procedure GP-1, compound 1b (64 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 3b (72 mg, 95%) as a brown liquid. A mixture of rotamers is observed; $^1\text{H}$ NMR (500 MHz, DMSO-$d_6$). Major rotamer: $\delta$ 10.00 (s, 1H), 8.20 (d, $J = 2.0$ Hz, 1H), 7.53–7.48 (m, 2H), 6.92–6.87 (m, 3H), 3.72 (s, 3H); Minor rotamer: $\delta$ 9.94 (d, $J = 11.2$ Hz, 1H), 8.59 (d, $J = 11.1$ Hz, 1H), 7.14–7.10 (m, 1H), 3.72 (s, 3H); $^{13}\text{C}$ NMR (125 MHz, DMSO-$d_6$) Major Rotamer: $\delta$ 158.9, 155.4, 131.3, 120.6, 113.9, 55.1; Minor rotamer: $\delta$ 162.4, 156.0, 131.2, 119.7, 114.6, 55.2; HRMS (ESI) calcd for $\text{C}_8\text{H}_9\text{NNaO}_2\text{[M+Na]}^+$: 174.0531; Found: 174.0529.

**N-(3,5-Dimethoxyphenyl)formamide (3c):** Using the general procedure GP-1, compound 1c (76 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 3c (81 mg, 90%) as a brown solid. A mixture of rotamers is observed; $^1\text{H}$ NMR (300 MHz, DMSO-$d_6$): Major rotamer: $\delta$ 10.11 (s, 1H), 8.24 (d, $J = 1.9$ Hz, 1H), 6.82 (d, $J = 2.3$ Hz, 2H), 6.25–6.22 (m, 2H), 3.71 (s, 6H); Minor rotamer: $\delta$ 10.02 (d, $J = 10.9$ Hz, 1H), 8.82 (d, $J = 10.9$ Hz, 1H), 6.38 (d, $J = 2.2$ Hz, 2H), 3.72 (s, 3H); $^{13}\text{C}$ NMR (75 MHz, DMSO-$d_6$): Major roamer: $\delta$ 161.4, 160.5, 140.6, 98.4, 96.4, 55.9; Minor rotamer: $\delta$ 163.4, 161.9, 141.0, 96.6, 96.2, 56.1; HRMS (ESI) calcd for $\text{C}_9\text{H}_{12}\text{NO}_3\text{[M+H]}^+$: 182.0817; Found: 182.0815.

**N-(2-Ethylphenyl)formamide (3d):** Using the general procedure GP-1, compound 1d (64 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 3d (67 mg, 84%) as a brown solid. A mixture of rotamers is observed; $^1\text{H}$ NMR (300 MHz, DMSO-$d_6$): Major rotamer: 9.52 (s, 1H), 8.27 (d, $J = 2.0$ Hz, 1H), 7.69 (dd, $J = 7.8$, 1.5 Hz, 1H), 7.26–
7.04 (m, 5H), 2.64–2.52 (m, 3H), 1.10 (td, \(J = 7.5, 3.4\) Hz, 5H); Minor rotamer: \(\delta 9.72\) (d, \(J = 10.2\) Hz, 1H), 8.33 (d, \(J = 10.7\) Hz, 1H), 7.26–7.04 (m, 5H, merged with major rotamer), 2.64–2.52 (m, 3H, merged with major rotamer), 1.10 (td, \(J = 7.5, 3.4\) Hz, 5H, merged with major rotamer); \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)): Major rotamer: \(\delta 160.6, 135.9, 129.3, 126.6, 125.6, 124.1, 24.3, 14.9\); Minor rotamer: \(\delta 164.4, 137.2, 135.4, 129.6, 127.3, 126.4, 123.4, 24.1, 14.8\); HRMS (ESI) calcd for \(C_{9}H_{11}NNaO\) [M+Na]+: 172.0783; Found: 172.0781.

\(N\)-(2-Hydroxy-4-methylphenyl)formamide (3f): Using the general procedure GP-1, compound If (62 mg, 0.5 mmol) and KO\(^{t}\)Bu (168 mg, 0.75 mmol) provided compound 3f (49 mg, 65%) as a brown solid. A mixture of rotamers is observed; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): Major rotamer: \(\delta 9.80\) (s, 1H), 9.48 (s, 1H), 8.22 (d, \(J = 2.0\) Hz, 1H), 7.84 (d, \(J = 8.1\) Hz, 1H), 6.68 (dd, \(J = 10.0, 2.0\) Hz, 1H), 6.56 (dd, \(J = 8.3, 2.0\) Hz, 1H), 2.18 (s, 3H); Minor rotamer: \(\delta 9.65\) (s, 1H), 9.16 (d, \(J = 11.3\) Hz, 1H), 8.40 (d, \(J = 11.3\) Hz, 1H), 6.97 (d, \(J = 7.9\) Hz, 1H), 6.89–6.80 (m, 1H), 2.18 (s, 3H, merge with major rotamer); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): Major rotamer: \(\delta 159.7, 146.6, 133.4, 123.4, 120.7, 119.9, 115.7, 20.6\); Minor rotamer: \(\delta 163.4, 149.0, 134.9, 122.6, 122.1, 119.4, 117.9, 116.6, 21.3\); HRMS (ESI) calcd for \(C_{8}H_{9}NNaO_{2}\) [M+Na]+: 174.0531; Found: 174.0530.

\(N\)-(2-Hydroxyphenyl)formamide (3g): Using the general procedure GP-1, compound Ig (55 mg, 0.5 mmol) and KO\(^{t}\)Bu (168 mg, 0.75 mmol) provided compound 3g (44 mg, 64%) as a brown solid. A mixture of rotamers is observed; \(^1\)H NMR (300 MHz, ): Major rotamer: \(\delta 9.93\) (s, 1H), 9.54 (s, 1H), 8.25 (d, \(J = 2.0\) Hz, 1H), 7.99 (dd, \(J = 8.0, 1.5\) Hz, 1H), 6.91–6.81 (m, 2H), 6.73 (ddd, \(J = 8.6, 5.7, 2.0\) Hz, 1H); Minor rotamer: \(\delta 9.78\) (s, 1H), 9.23 (d, \(J = 11.3\) Hz, 1H), 8.49 (d, \(J = 11.2\) Hz, 1H), 7.10 (dd, \(J = 7.9, 1.5\) Hz, 2H), 6.99–6.91 (m, 1H); \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)): Major rotamer: \(\delta 160.6, 147.3, 126.5, 125.9, 122.3, 119.5, 115.6\);
Minor rotamer: δ 164.0, 149.5, 126.0, 124.7, 121.3, 120.0, 116.6; HRMS (ESI) calcd for C$_7$H$_7$NNaO$_2$ [M+Na]$^+$: 160.0374; Found: 160.0372.

*N-(4-Bromo-2-methylphenyl)formamide (3h):* Using the general procedure GP-1, compound 1h (93 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 3h (94 mg, 88%) as a yellow solid. A mixture of rotamers is observed; $^1$H NMR (400 MHz, DMSO-$d_6$):

Major rotamer: δ 9.61 (s, 1H), 8.28 (d, $J = 1.9$ Hz, 1H), 7.73 (d, $J = 8.6$ Hz, 1H), 7.42 (d, $J = 2.4$ Hz, 1H), 7.34 (dd, $J = 8.6$, 2.6 Hz, 1H), 2.20 (s, 3H); Minor rotamer: δ 9.74 (d, $J = 10.6$ Hz, 1H), 8.39 (d, $J = 10.7$ Hz, 1H), 7.17 (d, $J = 8.5$ Hz, 1H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): Major rotamer: δ 159.8, 135.0, 133.08, 132.7, 128.8, 124.3, 17.3; Minor rotamer: δ 163.4, 136.7, 133.1, 131.9, 129.3, 123.5, 116.3, 17.4; HRMS (ESI) calcd for C$_8$H$_9$BrNO [M+H]$^+$: 213.9867; Found: 213.9866.

*N-phenylformamide (3i):* Using the general procedure, GP-1, compound 1i (47 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 3i (57 mg; 94%) as a colorless solid. A mixture of rotamers is observed: $^1$H NMR (400 MHz, DMSO-$d_6$): Major Rotamer: δ 10.22 (s, 1H), 8.26 (d, $J = 2.0$ Hz, 1H), 7.65–7.58 (m, 2H), 7.16 (m, 2.6 Hz, 3H); Minor Rotamer: 10.12 (d, $J = 12.0$ Hz, 1H) 8.70 (d, $J = 11.0$ Hz, 1H), 7.21 (d, $J = 5.0$ Hz, 1H) 7.16 (m, 2.6 Hz, 3H merged with major rotamer); $^{13}$C NMR (100 MHz, DMSO-$d_6$): Major Rotamer: δ 159.4, 120.9, 120.8, 115.5, 115.2; Minor Rotamer: δ 162.6, 156.9, 134.6, 119.5, 119.4, 116.0, 115.8; HRMS (ESI) calcd for C$_7$H$_8$NO [M+H]$^+$: 122.0606; Found: 122.0605.

*N-([1,1'-Biphenyl]-2-yl)formamide (3j):* Using the general procedure GP-1, compound 1j (85 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 3j (79 mg, 80%) as a white solid. A mixture of rotamers is observed: $^1$H NMR (400 MHz, DMSO-$d_6$): Major Rotamer: δ
9.33 (s, 1H), 8.16 (q,  J = 4.3 Hz, 1H), 7.87 (d,  J = 8.0 Hz, 1H), 7.51–7.43 (m, 3H), 7.37 (ddt,  J = 16.3, 7.6, 4.2 Hz, 7H), 7.31–7.18 (m, 2H). Minor Rotamer: δ 9.51 (d,  J = 11.0 Hz, 1H), 7.51–7.43 (m, 3H merged with major rotamer), 7.37 (ddt,  J = 16.3, 7.6, 4.2 Hz, 7H merged with major rotamer), 7.31–7.18 (m, 2H merged with major rotamer); 13C NMR (100 MHz, DMSO-d6): Minor rotamer: δ 160.4, 138.3, 133.9, 130.4, 129.0, 128.6, 127.8, 127.4, 125.2, 124.3, 124.2; Minor Rotamer: δ 163.7, 138.5, 134.5, 134.3, 130.9, 129.2, 128.5, 127.2, 126.1,124.3; HRMS (ESI) calcd for C13H12NO [M+H]+: 198.0915; Found: 198.0915.

**N-(3-Bromophenyl)formamide (3k):** Using the general procedure GP-1, compound 1k (85 mg, 0.5 mmol) and KOtBu (168 mg, 0.75 mmol) provided compound 3k (87 mg, 87%) as a yellow solid. A mixture of rotamers is observed; 1H NMR (400 MHz, DMSO-d6): Major rotamer: δ 10.36 (s, 1H), 8.30 (d,  J = 1.9 Hz, 1H), 7.94 (t,  J = 1.8 Hz, 1H), 7.49 (dt,  J = 7.2, 2.1 Hz, 1H), 7.30–7.25 (m, 3H); Minor rotamer: δ 10.23 (d,  J = 10.9 Hz, 1H), 8.84 (d,  J = 10.8 Hz, 1H), 7.44 (q,  J = 1.5 Hz, 1H), 7.32 (s, 1H), 7.24–7.19 (m, 1H); 13C NMR (100MHz, DMSO-d6): Major rotamer: δ 159.9, 139.7, 130.9, 126.2, 121.5, 117.9; Minor rotamer: δ 162.5, 140.2, 131.3, 126.1, 122.2, 119.7, 116.1; HRMS (ESI) calcd for C7H6BrNNaO [M+Na]+: 221.9530; Found: 221.9528.

**N-(4-Bromophenyl)formamide (3l):** Using the general procedure GP-1, compound 1l (85 mg, 0.5 mmol) and KOtBu (168 mg, 0.75 mmol) provided compound 3l (85 mg, 85%) as a yellow solid. A mixture of rotamers is observed; 1H NMR (500 MHz, DMSO-d6): Major rotamer: δ 10.29 (s, 1H), 8.27 (d,  J = 1.9 Hz, 1H), 7.57–7.52 (m, 2H), 7.49–7.45 (m, 3H); Minor rotamer: δ 10.19 (d,  J = 10.8 Hz, 1H), 8.77 (d,  J = 10.9 Hz, 1H), 7.49–7.45 (m, 3H merged with minor rotamer), 7.14 (d,  J = 8.8 Hz, 1H); 13C NMR (125 MHz, DMSO-d6): Major rotamer: δ 162.4, 137.51, 131.6, 121.1, 115.2; Minor rotamer: δ 159.7, 137.8,
132.1, 119.4, 115.4; HRMS (ESI) calcd for C$_7$H$_6$BrNNaO [M+Na]$^+$: 221.9530; Found: 221.9528.

**N-(2-Iodophenyl)formamide (3m):** Using the general procedure GP-1, compound **1m** (109 mg, 0.5 mmol) and KOtBu (168 mg, 0.75 mmol) provided compound **3m** (105 mg, 85%) as a brown solid. A mixture of rotamers is observed; $^1$H NMR (400 MHz, DMSO-$d_6$): Major rotamer: δ 9.53 (s, 1H), 8.34 (d, $J$ = 2.3 Hz, 1H), 7.89 (dd, $J$ = 7.9, 1.5 Hz, 1H), 7.78 (dd, $J$ = 8.1, 1.6 Hz, 1H), 7.41–7.33 (m, 1H), 6.98–6.94 (m, 1H); Minor rotamer: δ 9.65 (d, $J$ = 9.4 Hz, 1H), 7.78 (dd, $J$ = 8.1, 1.6 Hz, 1H, merged with major rotamer), 7.41–7.33 (m, 1H, merged with major rotamer), 7.04 (d, $J$ = 7.5 Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): Major rotamer: δ 160.3, 139.1, 138.5, 128.7, 126.9, 124.6; HRMS (ESI) calcd for C$_7$H$_6$INNaO [M+Na]$^+$: 269.9391; Found: 269.9390.

**N-(4-Bromo-2-fluorophenyl)formamide (3n):** Using the general procedure GP-1, compound **1n** (95 mg, 0.5 mmol) and KOtBu (168 mg, 0.75 mmol) provided compound **3n** (94 mg, 87%) as a brown solid. A mixture of rotamers is observed; $^1$H NMR (300 MHz, DMSO-$d_6$): Major rotamer: δ 10.23 (s, 1H), 8.32 (d, $J$ = 1.7 Hz, 1H), 8.08 (t, $J$ = 8.6 Hz, 1H), 7.61 (dd, $J$ = 10.6, 2.2 Hz, 1H), 7.41–7.33 (m, 1H); Minor rotamer: δ 10.11 (d, $J$ = 12 Hz, 1H), 8.56 (d, $J$ = 10.8 Hz, 1H), 7.61 (dd, $J$ = 10.6, 2.2 Hz, 1H, merged with major rotamer), 7.41–7.33 (m, 1H, merged with major rotamer); $^{13}$C NMR (75 MHz, DMSO-$d_6$): Major rotamer: δ 160.7, 128.2, 128.2, 125.7, 124.4, 119.5, 119.2; HRMS (ESI) calcd for C$_7$H$_5$BrFNNaO [M+Na]$^+$: 239.9436; Found: 239.9435.
**N-(2-Bromo-5-fluorophenyl)formamide (3o):** Using the general procedure GP-1, compound 1o (95 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 3o (95 mg, 88%) as a brown solid. A mixture of rotamers is observed: $^1$H NMR (300 MHz, DMSO-$d_6$): Major rotamer: $\delta$ 9.85 (s, 1H), 8.38 (d, $J = 1.6$ Hz, 1H), 8.00 (dd, $J = 11.1$, 3.1 Hz, 1H), 7.75–7.67 (m, 1H), 7.05–6.96 (m, 1H); Minor rotamer: $\delta$ 9.85 (s, 1H, merged with minor rotamer), 8.51 (d, $J = 9.8$ Hz, 1H), 7.45 (d, $J = 10.1$ Hz, 1H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): Major rotamer: $\delta$ 161.5, 134.6, 134.5, 113.5, 113.2, 110.7, 110.4; Minor rotamer: $\delta$ 163.3, 160.1, 137.6, 137.4, 108.7; HRMS (ESI) calcd for C$_7$H$_5$BrFNNaO [M+Na]$^+$: 239.9436; Found: 239.9432.

**N-(4-Acetylphenyl)formamide (3p):** Using the general procedure GP-1, compound 1p (68 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 3p (69 mg, 85%) as a white solid. A mixture of rotamers is observed: $^1$H NMR (400 MHz, DMSO-$d_6$): Major Rotamer: $\delta$ 10.53 (s, 1H), 8.35 (d, $J = 1.8$ Hz, 1H), 7.98–7.92 (m, 2H), 7.74–7.68 (m, 2H), 2.53 (s, 3H); Minor Rotamer: $\delta$ 10.45 (d, $J = 10.7$ Hz, 1H), 8.98 (d, $J = 10.8$ Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 1H), 2.53 (s, 3H merged with major rotamer); $^{13}$C NMR (125 MHz, DMSO-$d_6$): Major Rotamer: $\delta$ 196.4, 160.1, 142.3, 132.1, 129.9, 129.5, 118.5, 116.3, 26.4; HRMS (ESI) calcd for C$_9$H$_9$NNaO$_2$[M+Na]$^+$: 186.0531; Found: 186.0530.

**N-(3,5-Bis(trifluoromethyl)phenyl)formamide (3q):** Using the general procedure GP-1, compound 1q (115 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 3q (98 mg, 76%) as a white solid. A mixture of rotamers is observed: $^1$H NMR (500 MHz, DMSO-$d_6$): Major rotamer: $\delta$ 10.82 (s, 1H), 8.45 (d, $J = 1.7$ Hz, 1H), 8.26 (s, 2H), 7.81 (s, 1H); Minor rotamer: $\delta$ 10.56 (d, $J = 10.56$ Hz, 1H), 9.05 (d, $J = 8$ Hz, 1H), 7.90 (s, 1H), 7.75 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): Major Rotamer: $\delta$ 160.7,
139.9, 131.3, 131.0, 131.0, 130.7, 118.9, 116.4; Minor rotamer: δ 162.8, 140.8, 127.1, 124.4, 121.7, 117.1, 116.3, 116.0; HRMS (ESI) calcd for C$_9$H$_5$F$_6$NNaO [M+Na]$^+$: 280.0173; Found: 280.0173.

**N-(2-Cyanophenyl)formamide (3r):** Using the general procedure GP-1, compound 1r (59 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 3r (61 mg, 84%) as a colorless solid. A mixture of rotamers is observed: $^1$H NMR (500 MHz, DMSO-$d_6$): Major rotamer: δ 10.38 (s, 1H), 8.37 (s, 1H), 7.94 (d, $J$ = 8.3 Hz, 1H), 7.83 (d, $J$ = 7.9 Hz, 1H), 7.75–7.64 (m, 2H), 7.34 (t, $J$ = 7.7 Hz, 1H); Minor rotamer: δ10.47 (s, 1H), 8.57 (d, $J$ = 10.2 Hz, 1H), 7.58 (d, $J$ = 8.1 Hz, 1H), 7.48 (d, $J$ = 8.2 Hz, 1H); $^{13}$C NMR (125 MHz, DMSO-$d_6$): Major rotamer: δ 160.4, 139.2, 133.9, 133.2, 125.2, 123.4, 116.4, 104.5; HRMS (ESI) calcd for C$_8$H$_6$N$_2$NaO [M+Na]$^+$: 169.0377; Found: 169.0375.

**N-(4-Cyanophenyl)formamide (3s):** Using the general procedure GP-1, compound 1s (59 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 3s (61 mg, 83%) as a colorless solid. A mixture of rotamers is observed: $^1$H NMR (400 MHz, DMSO-$d_6$): Major rotamer: δ 10.63 (s, 1H), 8.36 (d, $J$ = 1.8 Hz, 1H), 7.85–7.71 (m, 5H); Minor rotamer: δ10.52 (d, $J$ = 10.4 Hz, 1H), 8.99 (d, $J$ = 10.6 Hz, 1H), 7.85–7.71 (m, 5H merged with major rotamer), 7.37 (d, $J$ = 8.3 Hz, 1H); $^{13}$C NMR (125 MHz, DMSO-$d_6$): Major rotamer: δ 159.2, 134.5, 132.5, 124.8, 121.7, 118.3; Minor rotamer: δ 161.2, 139.7, 133.8, 125.4, 116.3, 101.9; HRMS (ESI) calcd for C$_8$H$_6$N$_2$NaO [M+Na]$^+$: 169.0377; Found: 169.0374.

**N-(4-Nitrophenyl)formamide (3t):** Using the general procedure GP-1, compound 1t (76 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 3t (42 mg, 50%) as yellow solid. A mixture of rotamers is observed: $^1$H NMR (300 MHz, DMSO-$d_6$):
Major rotamer: \( \delta 10.80 \) (s, 1H), 8.40 (d, \( J = 1.7 \text{ Hz}, 1H \)), 8.21 (t, \( J = 8.8 \text{ Hz}, 3H \)), 7.81 (dd, \( J = 9.2, 2.2 \text{ Hz}, 2H \)), 7.42 (d, \( J = 8.7 \text{ Hz}, 1H \)); Minor rotamer: \( \delta 10.69 \) (d, \( J = 10.8 \text{ Hz}, 1H \)), 10.54 (s, 1H), 9.04 (d, \( J = 10.5 \text{ Hz}, 1H \)), 8.21 (t, \( J = 8.8 \text{ Hz}, 3H \), merged with minor rotamer); \(^{13}\)C NMR (75 MHz, DMSO-\( d_6 \)): Major rotamer: \( \delta 160.9, 144.6, 142.9, 125.5, 125.3, 119.4, 118.9 \); HRMS (ESI) calcd for C\(_7\)H\(_6\)N\(_2\)NaO\(_3\) [M+Na]$: 189.0276; Found: 189.0272.

\( N,N'-(1,2\text{-Phenylene})\text{diformamide\ (3u): Using the general procedure GP-1, compound 1u (55 mg, 0.5 mmol) and KO'Bu (336 mg, 1.5 mmol) provided compound 3u (60 mg, 64%) as a brown solid. A mixture of rotamers is observed; \(^1\)H NMR (500 MHz, DMSO-\( d_6 \)): Major rotamer: \( \delta 9.56 \) (s, 2H), 8.27 (d, \( J = 1.9 \text{ Hz}, 3H \)), 7.67–7.65 (m, 2H), 7.24–7.15 (m, 4H); Minor rotamer: \( \delta 9.80 \) (s, 1H), 9.36 (d, \( J = 11.0 \text{ Hz}, 1H \)), 8.39 (d, \( J = 10.8 \text{ Hz}, 1H \)), 7.71 (dd, \( J = 7.8, 1.8 \text{ Hz}, 1H \)), 7.32 (dd, \( J = 7.6, 1.9 \text{ Hz}, 1H \)), 7.24–7.15 (m, 4H merged with major rotamer); \(^{13}\)C NMR (100 MHz, DMSO-\( d_6 \)): Major rotamer: \( \delta 160.3, 129.4, 125.2, 124.3, 124.1, 123.0 \); Minor rotamer: \( \delta 163.4, 163.3, 129.7, 129.5, 125.7, 125.6, 122.7 \); HRMS (ESI) calcd for C\(_8\)H\(_8\)N\(_2\)NaO\(_2\) [M+Na]$: 187.0483; Found: 187.0483.

\( N,N'-(4\text{-Chloro-1,2-phenylene})\text{diformamide (3v): Using the general procedure GP-1, compound 1v (71mg, 0.5 mmol) and KO'Bu (336 mg, 1.5 mmol) provided compound 3v (64 mg, 65%) as a brown solid. A mixture of rotamers is observed; \(^1\)H NMR (500 MHz, DMSO-\( d_6 \)): Major rotamer: \( \delta 9.70 \) (d, \( J = 23.8 \text{ Hz}, 2H \)), 8.33–8.26 (m, 2H), 7.88 (d, \( J = 2.5 \text{ Hz}, 1H \)), 7.65 (d, \( J = 8.6 \text{ Hz}, 1H \)), 7.27–7.22 (m, 2H); Minor rotamer: \( \delta 9.87 \) (d, \( J = 44.4 \text{ Hz}, 1H \)), 9.49 (t, \( J = 13.5 \text{ Hz}, 1H \)), 8.48 (t, \( J = 12.5 \text{ Hz}, 1H \)), 8.36 (d, \( J = 10.7 \text{ Hz}, 1H \)), 7.95 (d, \( J = 2.4 \text{ Hz}, 1H \)), 7.50 (d, \( J = 2.4 \text{ Hz}, 1H \)), 7.36 (d, \( J = 8.5 \text{ Hz}, 1H \)); \(^{13}\)C NMR (100 MHz, DMSO-\( d_6 \)): Major rotamer: \( \delta 160.4, 160.4, 131.2, 129.0, 127.5, 126.0, 124.6 \),
122.6; Minor rotamer: δ 163.3, 125.3, 125.1, 124.8, 123.0; HRMS (ESI) calcd for C₈H₇ClN₂NaO₂ [M+Na⁺]: 221.0093; Found: 221.0095.

**N-(Pyridin-4-yl)formamide (3w):** Using the general procedure GP-1, compound 1w (47 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 3w (41 mg, 82%) as a brown solid. A mixture of rotamers is observed; ¹H NMR (400 MHz, DMSO-d₆): Major rotamer: δ 10.58 (s, 1H), 8.51 – 8.34 (m, 4H), 7.54 (d, J = 5.7 Hz, 2H); Minor rotamer: δ 10.45 (d, J = 10.7 Hz, 1H), 9.06 (d, J = 11.0 Hz, 1H), 8.51–8.34 (m, 4H, merged with major rotamer), 7.20 (d, J = 5.5 Hz, 1H); ¹³C NMR (100 MHz, DMSO-d₆): Major rotamer: δ 162.9, 161.3, 151.0, 145.1, 113.8, 111.6; HRMS (ESI) calcd for C₆H₇N₂O [M+H⁺]: 123.0558; Found: 123.0555.

**N-(4-Bromo-2-fluorophenyl)formamide (3x):** Using the general procedure GP-1, compound 1x (72 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 3x (68 mg, 84%) as a brown solid. A mixture of rotamers is observed; ¹H NMR (300 MHz, DMSO-d₆): Major rotamer: δ 10.73 (s, 1H), 8.92 (dd, J = 4.2, 1.7 Hz, 1H), 8.65 (dd, J = 7.6, 1.4 Hz, 1H), 8.58 (d, J = 1.9 Hz, 1H), 8.39 (dd, J = 8.3, 1.7 Hz, 1H), 7.72–7.53 (m, 3H); ¹³C NMR (75 MHz, DMSO-d₆): Major rotamer: δ 161.5, 149.5, 137.1, 134.7, 128.5, 127.5, 122.7, 117.4; HRMS (ESI) calcd for C₁₀H₈N₂O [M+Na⁺]: 195.0534; Found: 195.0532.

**N-Hexadecylformamide (3y):** Using the general procedure GP-1, compound 1y (120 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 3y (110 mg, 82%) as a white solid. A mixture of rotamers is observed; ¹H NMR (300 MHz, DMSO-d₆): Major rotamer: δ 7.95 (d, J = 1.7 Hz, 1H), 3.06–2.99 (m, 2H), 1.51–1.31 (m, 3H), 1.21 (s, 30H), 0.91–0.77 (m, 3H); ¹³C NMR (75 MHz, DMSO-d₆): Major rotamer: δ 161.5,
37.7, 31.9, 29.6, 29.6, 29.3, 26.9, 22.7, 14.6; HRMS (ESI) calcd for C_{17}H_{35}NNaO[M+Na]^+: 292.2616; Found: 292.2612.

**N- Allylformamide (3z):** Using the general procedure **GP-1**, compound 1z (28 mg, 0.5 mmol) and KO’Bu (168 mg, 0.75 mmol) provided compound 3z (28 mg, 65%) as a yellow liquid. A mixture of rotamers is observed; \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): Major rotamer: \(\delta 9.75\) (d, \(J = 31.2\) Hz, 2H), 8.03 (s, 1H), 7.91 (d, \(J = 1.7\) Hz, 1H), 6.69–6.55 (m, 2H), 5.23 (dq, \(J = 13.7, 6.7\) Hz, 1H), 4.74 (m, 1H); Minor rotamer: \(\delta 8.28\) (d, \(J = 10.7\) Hz, 1H), 8.18 (d, \(J = 11.1\) Hz, 1H), 6.50–6.30 (m, 1H), 5.03 (dq, \(J = 13.5, 6.7\) Hz, 1H), 4.56 (dq, \(J = 8.9, 7.1\) Hz, 1H);

\(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)): Major rotamer: \(\delta 159.4, 122.7, 106.8, 15.4\); Minor rotamer: \(\delta 158.8, 121.0, 108.6, 11.8\); HRMS (ESI) calcd for C_{4}H_{7}NNaO[M+Na]^+: 108.0425; Found: 108.0423.

**N-(4-Methoxyphenyl)acetamide (5a):** Using the general procedure **GP-1**, compound 1a (69 mg, 0.5 mmol) and KO’Bu (168 mg, 0.75 mmol) provided compound 5a (72 mg, 87%) as a brown solid; \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta 9.77\) (s, 1H), 7.49–7.43 (m, 2H), 6.88 – 6.83 (m, 2H), 3.70 (s, 3H), 2.00 (s, 3H); \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)): \(\delta 167.8, 155.1, 132.5, 120.6, 113.8, 55.2, 23.8\); HRMS (ESI) calcd for C_{9}H_{11}NNaO_{2}[M+Na]^+: 188.0687; Found: 188.0686.

**N-(3,5-Dimethoxyphenyl)acetamide (5c):** Using the general procedure **GP-1**, compound 1c (81 mg, 0.5 mmol) and KO’Bu (168 mg, 0.75 mmol) provided compound 5c (82 mg, 84%) as a white solid; \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta 9.84\) (s, 1H), 6.80 (d, \(J = 2.3\) Hz, 2H), 6.17 (t, \(J = 2.3\) Hz, 1H), 3.68 (s, 6H), 1.99 (s, 3H); \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)): \(\delta 168.9, 161.0, 141.5, 97.9, 95.5, 55.6, 24.7\); HRMS (ESI) calcd for C_{10}H_{13}NNaO_{3}[M+Na]^+: 218.0793; Found: 218.0792.
**N-(2-Ethylphenyl)acetamide (5d):** Using the general procedure GP-1, compound 1d (64 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 5d (65 mg, 80%) as a brown solid; 

\[
\text{\textsuperscript{1}H NMR (300 MHz, DMSO-\textit{d}_6): } \delta 9.26 (s, 1H), 7.32 (dd, \textit{J} = 7.2, 2.1 Hz, 1H), 7.22 (dd, \textit{J} = 6.6, 2.6 Hz, 1H), 7.13 (m, 2H), 2.66–2.54 (m, 2H), 1.13–1.07 (m, 3H);
\]

\[
\text{\textsuperscript{13}C NMR (75 MHz, DMSO-\textit{d}_6)} \delta 169.0, 138.4, 136.3, 129.0, 126.6, 126.4, 126.1, 24.3, 23.8, 14.8;
\]

HRMS (ESI) calcd for C\textsubscript{10}H\textsubscript{13}NNaO [M+Na]\textsuperscript{+}: 186.0894; Found: 186.0891.

**N-(4-Bromo-2-methylphenyl)acetamide (5h):** Using the general procedure GP-1, compound 1h (93 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 5h (93 mg, 82%) as a brown solid; 

\[
\text{\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): } \delta 9.30 (s, 1H), 7.52–7.34 (m, 2H), 7.31 (dd, \textit{J} = 8.7, 2.4 Hz, 1H), 2.18 (s, 3H), 2.04 (s, 3H);
\]

\[
\text{\textsuperscript{13}C NMR (100 MHz, DMSO-\textit{d}_6)} \delta 168.2, 135.9, 134.0, 132.5, 128.6, 126.5, 116.8, 23.2, 17.5;
\]

HRMS (ESI) calcd for C\textsubscript{9}H\textsubscript{10}BrNNaO [M+Na]\textsuperscript{+}: 249.9843; Found: 249.9840.

**N-Phenylacetamide (5i):** Using the general procedure GP-1, compound 1i (47 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 5i (59 mg, 87%) as a white solid; 

\[
\text{\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): } \delta 9.89 (s, 1H), 7.54 (d, \textit{J} = 8.3 Hz, 2H), 7.26 (t, \textit{J} = 8.0 Hz, 2H), 7.00 (t, \textit{J} = 7.4 Hz, 1H), 2.01 (s, 3H);
\]

\[
\text{\textsuperscript{13}C NMR (125 MHz, DMSO-\textit{d}_6)} \delta 168.1, 139.2, 128.5, 122.8, 119.0, 23.8;
\]

HRMS (ESI) calcd for C\textsubscript{8}H\textsubscript{10}NO [M+H]\textsuperscript{+}: 136.0762; Found: 136.0762.

**N-(Naphthalen-2-yl)acetamide (5j):** Using the general procedure GP-1, compound 1j (85 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 5j (79 mg, 85%) as a white solid; 

\[
\text{\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): } \delta 9.91 (s, 1H), 8.06 (d, \textit{J} = 5.9 Hz, 1H), 7.92 (d, \textit{J} = 8.7 Hz, 1H), 7.74 (d, \textit{J} = 8.2 Hz, 1H), 7.67 (d, \textit{J} = 7.4 Hz, 1H), 7.56 – 7.43 (m, 3H), 2.17 (s, 3H);
\]

\[
\text{\textsuperscript{13}C NMR (100 MHz, DMSO-\textit{d}_6): } \delta 168.9, 133.6, 128.0,
127.6, 125.9, 125.7, 125.5, 125.0, 122.7, 121.5, 23.4; HRMS (ESI) calcd for C_{12}H_{11}NNaO [M+Na]^+: 208.0738; Found: 208.0735.

*N-(2-Bromophenyl)acetamide (5i)*: Using the general procedure GP-1, compound 1i' (85mg, 0.5 mmol) and KOtBu (168 mg, 0.75 mmol) provided compound 5i'(86 mg 81%) as a yellow solid; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 9.44 (s, 1H), 7.67–7.56 (m, 2H), 7.34 (td, \(J = 7.7, 1.4\) Hz, 1H), 7.11 (td, \(J = 7.7, 1.6\) Hz, 1H), 2.06 (s, 3H); \(^{13}\)C NMR (100MHz, DMSO-\(d_6\)): \(\delta\) 168.4, 136.4, 132.5, 127.8, 127.1, 126.8, 117.8 , 23.2; HRMS (ESI) calcd for C_{8}H_{8}BrNNaO [M+Na]^+: 235.9687; Found: 235.9686.

*N-(2-Bromo-5-fluorophenyl)acetamide (5o)*: Using the general procedure GP-1, compound 1o (95mg, 0.5 mmol) and KOtBu (168 mg, 0.75 mmol) provided compound 5o (85 mg, 82%) as a brown solid; \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta\) 9.48 (s, 1H), 7.69–7.58 (m, 2H), 7.06–6.97 (m, 1H), 2.11 (s, 3H); \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 169.5, 163.2, 156.0, 138.5, 138.3, 134.3, 134.2, 114.2, 113.9, 113.8, 113.4, 24.0; HRMS (ESI) calcd for C_{8}H_{7}BrFNNaO [M+Na]^+: 253.9592; Found: 253.9590.

*N-(4-Acetylphenyl)acetamide (5p)*: Using the general procedure GP-1, compound 1p (68 mg, 0.5 mmol) and KOtBu (168 mg, 0.75 mmol) provided compound 5p (73 mg, 81%) as a white solid. \(^1\)H NMR (300 MHz, Chloroform-\(d\)): \(\delta\) 7.94–7.88 (m, 2H), 7.84 (s, 1H), 7.62 (d, \(J = 8.5\) Hz, 2H), 2.57 (s, 3H), 2.21 (s, 3H); \(^{13}\)C NMR (75 MHz, Chloroform-\(d\)): \(\delta\) 197.1, 168.7, 142.3, 132.7, 129.7, 118.8, 26.4, 24.7; HRMS (ESI) calcd for C_{10}H_{11}NNaO_{2} [M+Na]^+: 200.0678; Found: 200.0677.

*N-(3,5-Bis(trifluoromethyl)phenyl)acetamide (5q)*: Using the general procedure GP-1, compound 1q (115mg, 0.5 mmol) and KOtBu (168 mg, 0.75 mmol) provided compound 5q (108 mg, 80%) as a brown solid; \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\)
10.59 (s, 1H), 8.24 (s, 2H), 7.72 (s, 1H), 2.12 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ 169.3, 141.0, 130.8 (d, $J$ = 32.5 Hz), 130.5, 124.5, 121.8, 118.5, 115.7, 24.0; HRMS (ESI) calcd for C$_{10}$H$_7$F$_6$NNaO [M+Na]$^+$: 294.0329; Found: 294.0325.

$N$-(2-Cyanophenyl)acetamide (5r): Using the general procedure GP-1, compound 1r (59 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 5r (64 mg, 80%) as a white solid; $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 10.17 (s, 1H), 7.80 (dd, $J$ = 7.8, 1.5 Hz, 1H), 7.73–7.65 (m, 1H), 7.57 (dd, $J$ = 8.3, 1.2 Hz, 1H), 7.34 (td, $J$ = 7.6, 1.2 Hz, 1H), 2.09 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ 168.6, 140.3, 133.7, 133.1, 125.5, 125.4, 116.8, 23.1; HRMS (ESI) calcd for C$_{9}$H$_8$N$_2$NaO [M+Na]$^+$: 183.0534; Found: 183.0530.

$N$-(4-Cyanophenyl)acetamide (5s): Using the general procedure GP-1, compound 1s (59 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 5s (64 mg, 80%) as a white solid; $^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ 10.36 (s, 1H), 7.75 (s, 4H), 2.09 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ 169.1, 143.4, 133.2, 119.0, 118.9, 104.6, 24.1; HRMS (ESI) calcd for C$_{9}$H$_8$N$_2$NaO [M+Na]$^+$: 183.0534; Found: 183.0530.

$N$-(4-Nitrophenyl)acetamide (5t): Using the general procedure GP-1, compound 1t (76 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 5t (43 mg, 47%) as a yellow solid; $^1$H NMR (300 MHz, DMSO-d$_6$): $\delta$ 10.50 (s, 1H), 8.23–8.19 (m, 2H), 7.85–7.80 (m, 2H), 2.12 (s, 3H); $^{13}$C NMR (75 MHz, DMSO-d$_6$): $\delta$ 169.9, 146.0, 125.5, 119.1, 24.8; HRMS (ESI) calcd for C$_{8}$H$_8$N$_2$NaO$_3$ [M+Na]$^+$: 203.0436; Found: 203.0432.

$N$-(Pyridin-4-yl)acetamide (5w): Using the general procedure GP-1, compound 1w (47 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 5w (54 mg, 78%) as a brown solid; $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 10.32 (s, 1H), 8.44–8.36 (m, 1H), 7.85–7.80 (m, 2H), 2.12 (s, 3H); $^{13}$C NMR (75 MHz, DMSO-d$_6$): $\delta$ 169.9, 146.0, 125.5, 119.1, 24.8; HRMS (ESI) calcd for C$_{8}$H$_8$N$_2$NaO$_3$ [M+Na]$^+$: 203.0436; Found: 203.0432.
7.58–7.50 (m, 1H), 2.09 (s, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 169.6, 150.2, 145.7, 113.0, 24.1; HRMS (ESI) calcd for C$_7$H$_8$N$_2$NaO [M+Na]$^+$: 159.0534; Found: 159.0530.

$N$-(Pyridin-2-yl)acetamide ($5w'$): Using the general procedure GP-1, compound 1w' (47mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 5w' (56 mg, 82%) as a brown solid; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 10.47 (s, 1H), 8.29 (d, $J = 4.9$ Hz, 1H), 8.07 (d, $J = 8.3$ Hz, 1H), 7.75 (m, $J = 7.9$, 1H), 7.12–7.03 (m, 1H), 2.09 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 169.2, 152.1, 147.8, 138.0, 119.1, 113.3, 23.8; HRMS (ESI) calcd for C$_7$H$_8$N$_2$NaO [M+Na]$^+$: 159.0534; Found: 159.0533.

$N$-(Quinolin-8-yl)acetamide ($5x$): Using the general procedure GP-1, compound 1x (72 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 5x (73 mg, 79%) as a brown solid; $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 10.08 (s, 1H), 8.90 (dd, $J = 4.2$, 1.7 Hz, 1H), 8.59 (dd, $J = 7.6$, 1.5 Hz, 1H), 8.37 (dd, $J = 8.3$, 1.7 Hz, 1H), 7.65–7.52 (m, 3H), 2.26 (s, 3H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 169.5, 149.4, 138.6, 137.1, 135.2, 128.4, 127.5, 122.6, 122.3, 117.2, 25.1; HRMS (ESI) calcd for C$_{11}$H$_{10}$N$_2$NaO [M+Na]$^+$: 209.0691; Found: 209.0690.

$N$-(Prop-1-en-1-yl)acetamide (6a): Using the general procedure GP-2, compound 1a (57 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 6a (37 mg, 75%, E/Z=10:1) as a yellow liquid; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 9.46–9.10 (m, 1H), 6.54–6.48 (m, 1H), 4.66–4.57 (m, 1H), 1.93 (s, 3H), 1.60 (dd, $J = 7.1$, 1.7 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 167.4, 122.4, 104.0, 22.4, 11.2; HRMS (ESI) calcd for C$_5$H$_9$NNaO [M+Na]$^+$: 122.1208; Found: 122.1206.
**N-(Prop-1-en-1-yl)benzamide (6b'):** Using the general procedure GP-2, compound 1b’ (57mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 6b (E/Z = 1:1).

E-isomer 6b’ (23 mg, 35%) was obtained as a white solid; \(^1H\) NMR (400 MHz, DMSO-\(d_6\)): \(\delta 10.14 (d, J = 9.6 \text{ Hz, 1H}), 7.88 (dt, J = 7.1, 1.4 \text{ Hz, 2H}), 7.59–7.51 (m, 1H), 7.48 (dd, J = 8.2, 6.6 \text{ Hz, 2H}), 6.82 (ddt, J = 13.1, 9.7, 1.7 \text{ Hz, 1H}), 5.44 (dq, J = 13.7, 6.7 \text{ Hz, 1H}), 1.67 (dd, J = 6.8, 1.7 \text{ Hz, 3H}); \(^13C\) NMR (75 MHz, DMSO-\(d_6\)): \(\delta 164.0, 134.3, 132.1, 128.9, 128.0, 125.0, 108.5, 15.7\); HRMS (ESI) calcd for C\(_{10}\)H\(_{11}\)NNaO \([\text{M+Na}]^+\): 184.0738; Found: 184.0740.

Z-isomer 6b'' (24 mg, 35%) as white solid; \(^1H\) NMR (400 MHz, DMSO-\(d_6\)): \(\delta 9.60 (d, J = 9.7 \text{ Hz, 1H}), 7.97–7.77 (m, 2H), 7.64–7.52 (m, 1H), 7.48 (dd, J = 8.2, 6.7 \text{ Hz, 2H}), 6.72 (td, J = 9.3, 1.7 \text{ Hz, 1H}), 4.93–4.77 (m, 1H), 1.72 (dd, J = 7.1, 1.7 \text{ Hz, 3H}); \(^13C\) NMR (75 MHz, DMSO-\(d_6\)): \(\delta 165.5, 134.6, 132.1, 128.8, 128.4, 123.4, 108.0, 12.2\). HRMS (ESI) calcd for C\(_{10}\)H\(_{11}\)NNaO \([\text{M+Na}]^+\): 184.0735; Found: 184.0735.

**2,2,2-Trifluoro-N-(4-methoxyphenyl)acetamide (7a):** Using the general procedure GP-1, compound 1a (64mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 7a (95 mg, 87%) as a brown solid; \(^1H\) NMR (400 MHz, DMSO-\(d_6\)): \(\delta 11.11 (s, 1H), 7.56 (d, J = 9.0 \text{ Hz, 2H}), 6.97 (d, J = 9.1 \text{ Hz, 2H}), 3.75 (s, 3H); \(^13C\) NMR (75 MHz, DMSO-\(d_6\)): \(\delta 157.5, 154.8\) (q, J = 36.7 Hz), 129.7, 123.3, 118.4, 114.7, 55.9; HRMS (ESI) calcd for C\(_9\)H\(_8\)F\(_3\)NaNO\(_2\)[M+Na]^+: 242.0405; Found: 242.0403.

**2,2,2-Trifluoro-N-phenylacetamide (7b):** Using the general procedure GP-1, compound 1i (64 mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 7b (80 mg, 85%) as a white solid; \(^1H\) NMR (400 MHz, DMSO-\(d_6\)): \(\delta 11.23 (s, 1H), 7.65 (d, J = 7.5 \text{ Hz, 2H}), 7.40 (t, J = 7.9 \text{ Hz, 2H}), 7.22 (t, J = 7.4 \text{ Hz, 1H}); \(^13C\) NMR (125 MHz, DMSO-
$d_6$: $\delta$ 154.4 (q, $J = 37.1$ Hz), 154.2, 136.5, 128.8, 125.5, 121.0, 114.5; HRMS (ESI) calcd for C$_9$H$_8$F$_3$NaNO$_2$[M+Na]$^+$: 242.0405; Found: 242.0403.

**N-phenylbenzamide (7c):** Using the general procedure GP-1, compound 1i (64mg, 0.5 mmol) and KO'Bu (168 mg, 0.75 mmol) provided compound 7c (84 mg, 85%) as a white solid; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 10.23 (s, 1H), 7.94 (d, $J = 7.0$ Hz, 2H), 7.77 (d, $J = 8.7$ Hz, 1H), 7.63–7.47 (m, 3H), 7.34 (t, $J = 7.9$ Hz, 2H), 7.09 (t, $J = 7.3$ Hz, 1H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 166.1, 139.7, 135.6, 132.1, 129.2, 129.0, 128.2, 124.2, 120.9; HRMS (ESI) calcd for C$_{13}$H$_{12}$NO[M+H]$^+$: 198.0918; Found: 198.0918.
6.0 NMR spectra of all compounds:

$^1$H and $^{13}$C NMR of 3a:
$^1$H and $^{13}$C NMR of 3b:
$^{1}H$ and $^{13}C$ NMR of 3c:
$^{1}H$ and $^{13}C$ NMR of 3d:
$^1$H and $^{13}$C NMR of 3f:
\(^1\)H and \(^{13}\)C NMR of 3g:
$^1$H and $^{13}$C NMR of 3h:
$^1$H and $^{13}$C NMR of 3i:
$^1$H and $^{13}$C NMR of 3j:
$^{1}H$ and $^{13}C$ NMR of 3k:
$^{1}H$ and $^{13}C$ NMR of 3i:

\[
\begin{align*}
\text{NHCHO} & \quad \text{NHCHO} \\
\text{Br} & \quad \text{Br}
\end{align*}
\]
$^1\text{H}$ and $^{13}\text{C}$ NMR of 3m:
$^{1}H$ and $^{13}C$ NMR of 3n:
$^1$H and $^{13}$C NMR of 3o:
$^1$H and $^{13}$C NMR of 3p:
$^1$H and $^{13}$C NMR of 3q:
$^{1}H$ and $^{13}C$ NMR of 3r:

![NMR Spectrum Image]

NHCHO

CN

![NMR Spectrum Image]
$^1$H and $^{13}$C NMR of 3s:

\[
\begin{align*}
\text{NHCHO} & \quad \text{CN} \\
\text{CN} & \\
\end{align*}
\]
$^1$H and $^{13}$C NMR of 3t:
$^1$H and $^{13}$C NMR of 3u:

![NMR Spectrum](image)

![NMR Spectrum](image)
$^1$H and $^{13}$C NMR of 3v:
$^{1}H$ and $^{13}C$ NMR of 3w:

![NMR spectra](image)

NHCHO

NHCHO

2.0  11.5  11.0  10.5  10.0  9.5  9.0  8.5  8.0  7.5  7.0  6.5  6.0  5.5  5.0  4.5  4.0  3.5  3.0  2.5  2.0  1.5  1.0  0.5  0.0  0.0

150  180  170  160  150  140  130  120  110  100  90  80  70  60  50  40  30  20  10  0
$^1$H and $^{13}$C NMR of 3x:
$^1$H and $^{13}$C NMR of 3y:

\[ \text{NHCHO} \]

\[ \text{NHCHO} \]
$^{1}H$ and $^{13}C$ NMR of 3z:

\[
\text{NHCHO}
\]
$^1$H and $^{13}$C NMR of 5a:
$^1$H and $^{13}$C NMR of 5c:
$^1$H and $^{13}$C NMR of 5d:
$^1$H and $^{13}$C NMR of 5h:
$^1$H and $^{13}$C NMR of 5i:
$^{1}H$ and $^{13}C$ NMR of 5j:
$^1$H and $^{13}$C NMR of 5'I:

\[ \text{NHOCH}_3 \]

\[ \text{Br} \]

\[ \text{NHOCH}_3 \]

\[ \text{Br} \]
$^1$H and $^{13}$C NMR of 5o:
$^1$H and $^{13}$C NMR of 5p:
$^1$H and $^{13}$C NMR of 5q:

![NMR Spectra](image-url)
$^1$H and $^{13}$C NMR of 5r:
$^1H$ and $^{13}C$ NMR of 5s:
$^1$H and $^{13}$C NMR of 5t:
**1H and 13C NMR of 5w:**
$^1$H and $^{13}$C NMR of 5w':

![Chemical Structure](image)

![NMR Spectrum](image)
$^1$H and $^{13}$C NMR of 5x:

![NMR spectra of 5x with chemical structures and peaks indicating the positions of protons and carbons.](image-url)
$^1$H and $^{13}$C NMR of 6a:
$^1$H and $^{13}$C NMR of 6b":
$^1$H and $^{13}$C NMR of 6b'':
$^1$H and $^{13}$C NMR of 7a:
$^1$H and $^{13}$C NMR of 7b:
$^1$H and $^{13}$C NMR of 7c: