Supporting Information

for

Sulfonium Salts as Alkylating Agents for Palladium Catalyzed Direct ortho Alkylation of Anilides and Aromatic Ureas

by

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General
Unless otherwise indicated, starting materials were obtained from commercial suppliers, and were used without further purification.

Analytical thin-layer chromatography (TLC) was performed on Merck DC pre coated TLC plates with 0.25 mm Kieselgel 60 F$_{254}$. Visualization was performed with a 254 nm UV lamp.

The $^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded on a Bruker Avance-250 in CDCl$_3$, DMSO-$d_6$ and CD$_3$CN. Solvents’ residual proton peaks were used as standards. Chemical shifts ($\delta$) are reported in ppm, coupling constants ($J$) are reported in Hertz (Hz). Splitting patterns are designated as s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), h (heptet), hept (heptet) and m (multiplet).

Conversions for the optimization studies were determined by gas chromatography with an Agilent 5890 Gas Chromatograph (30 m x 0.25 mm column with 0.25 µm HP-5MS coating, He carrier gas) with FID detector. GC-(EI-MS) spectrometry was obtained on an Agilent 6890N Gas Chromatograph (30 m x 0.25 mm column with 0.25 µm HP-5MS coating, He carrier gas) and Agilent 5973 Mass Spectrometer (Ion source: EI+, 70eV, 230 °C, interface 300 °C).

All melting points were measured on Büchi 501 apparatus and are uncorrected.

IR spectra were obtained from the solid products using ATR on a Bruker Alpha FT-IR (from 4000 cm$^{-1}$ to 375 cm$^{-1}$) or a Mettler Toledo ReactIR 15 with AgX DiComp probe (6 mm x 1.5 m Fiber (Silver Halide)) and MCT detector (from 3000 cm$^{-1}$ to 650 cm$^{-1}$).

High-resolution mass spectra were acquired on an Agilent 6230 time-of-flight mass spectrometer equipped with a Jet Stream electrospray ion source in positive ion mode. Injections of 0.1-0.3 µl were directed to the mass spectrometer at a flow rate 0.5 ml/min (70% acetonitrile-water mixture, 0.1 % formic acid), using an Agilent 1260 Infinity HPLC system.

Preparation of starting materials

Synthesis of formic esters for the preparation of sulfonium salts
Method A: Simple esterification with alcohol, formic acid and sulphuric acid for the preparation of methyl formate and propyl formate.

A 100 mL round bottom flask was charged with 4.5 mL formic acid (85% aqueous solution, 100 mmol, 1.0 equiv), 50 mL propanol or methanol (0.7-1.2 mol, 7-12 equiv) and 6 mL sulphuric acid (98%, 0.11 mol) was added. The solution was refluxed for four hours. Then the condenser was replaced for a Vigreux column and the product was distilled (at atm. pressure, 72-75 °C for propyl formate and 33-38 °C for methyl formate). We got the product as a 75% solution in propanol and an 80% solution in methanol. The esters were used without further purification.
**Method B:** Esterification with acetic formic anhydride for the preparation of phenethyl formate.

1. \[ \text{HOC} \bigg( \text{Na} \bigg) \oplus \text{Cl} \rightarrow \text{HOC} \bigg( \text{CH}_3 \bigg) \]

2. \[ \text{HOC} \bigg( \text{CH}_3 \bigg) \bigg( \text{HOC} \bigg) \]

8.2 g (120 mmol, 1.2 equiv) sodium formate was measured into a 100 mL round bottom flask. 8.8 mL abs. ether was added. Then 7.1 mL acetyl chloride (100 mmol, 1.0 equiv) was added. The mixture was stirred at room temperature overnight. After 16 h, the sodium chloride was filtered off, washed with ether. The acetic formic anhydride was used as a solution in ether.

A 100 mL round bottom flask was charged with 7.2 mL 2-phenylethanol (60 mmol, 1.0 equiv) and 25 mL abs. ether. 8.4 mL triethylamine (60 mmol, 1.0 equiv) was added and finally acetic formic anhydride solution was added dropwise (29 mL solution, ca. 100 mmol, 1.6 equiv). The mixture was stirred at room temperature for 3 hours. After the reaction was completed, the mixture was washed with sat. NaHCO₃ and water, dried over MgSO₄. Ether was evaporated, and the crude product was distilled at reduced pressure 65-70 °C. The product was obtained as a colourless liquid (6.3 g, yield: 70%), containing 18% phenylethyl acetate. The product was used without further purification.

**Synthesis of the N-aryl amide and N-aryl urea derivatives**

Substituted N-aryl amides were synthesized by standard acylation processes.

A 100 mL round bottom flask was equipped with stirring bar and charged with 15 mmol aryl amine and 40 mL of dichloromethane or ethyl acetate as solvent. A reflux condenser is replaced. The mixture was cooled to 0 °C.

**Method A:** (3a – 3m, for N-acetylation) Acetic anhydride (1.05 equiv. 15.75 mmol to 1.5 equiv. 23 mmol) added in small portions and allowed to warm up to room temperature. The reaction mixture stirred until all the starting materials reacted (1-8 hours), monitored by TLC.

**Method B:** (3n – 3q, for pivalamides, benzamides and phenacetamides) Triethyl amine (1.05 equiv. 15.75 mmol or 1.1 equiv. 16.5 mmol) added and the solution cooled to 0 °C. Subsequently, a solution of acyl chloride (1.05 equiv. 15.75 mmol or 1.1 equiv. 16.5 mmol in
15 mL solvent) added to the amine solution in small portions and allowed to warm up to room temperature. The reaction mixture stirred until all the starting materials reacted (1-4 hours), monitored by TLC. The precipitated white triethyl amine hydrochloride were filtered off.

The reaction mixture extracted twice with sat. NaHCO₃ solution and once with brine. The organic phase solution was dried over MgSO₄ and evaporated in rotary evaporator. The crude product was purified by crystallization.

Substituted N-aryl urea derivatives were synthesized by the following methods:

**Method A:**¹ (5e, 5g)

\[
\begin{align*}
\text{R} & \quad \text{Et}_2\text{O}, 25 \degree \text{C}, 1-16 \text{ h} \\
\text{NH} & \quad \text{R}^2
\end{align*}
\]

A 50 mL round-bottom flask was equipped with stirring bar and charged with amine derivatives (5 mmol) in 4.5 mL diethyl ether. The solution of aryl isocyanate (5 mmol in 4.5 mL diethyl ether) was added slowly to the solution at 25 °C and the reaction was stirred for 1-16 hours. The precipitate was filtered and washed with diethyl ether and dried under vacuum to give the product.

The reaction mixture extracted twice with sat. NaHCO₃ solution and once with brine. The organic phase solution was dried over MgSO₄ and evaporated in rotary evaporator. The crude product was purified by crystallization.

**Method B:**² (5a, 5b, 5d)

\[
\begin{align*}
\text{R} & \quad \text{N} \quad \text{O} \\
\text{Et}_2\text{O}, 0-25 \degree \text{C}, 24 \text{ h} \\
\text{NH} & \quad \text{R}^2
\end{align*}
\]

To a solution of aniline derivatives (5 mmol) in dichloromethane (5 mL), triethylamine (10 mmol) was added and the reaction mixture was allowed to cool at 0 °C. Dimethylcarbamoyl chloride (20 mmol) was added dropwise to the reaction mixture via syringe. The mixture was stirred for 24 h at 25 °C. The reaction mixture was poured onto crushed ice and extracted with ethyl acetate, washed with 2N HCl and brine, dried over MgSO₄ and evaporated under reduced pressure. The crude product was purified by recrystallization from EtOAc.
Method C: $^3$ (5c, 5f)

A 100 mL round-bottom flask was equipped with stirring bar, charged with aniline derivatives (10 mmol) in 20 mL anhydrous tetrahydrofuran and cooled to 0 °C. Pyridine (12.5 mmol) and phenyl chloroformate (10.3 mmol) were added to the solution at 0 °C and stirred for 5 minutes, then 1-3 hours at 25 °C. The reaction mixture was diluted with ethyl acetate, washed with 1M HCl, water, saturated NaHCO$_3$ solution and brine, dried over MgSO$_4$ and evaporated under reduced pressure. The crude product was purified by recrystallization from ethyl acetate.

A 100 mL round-bottom flask was equipped with stirring bar, charged with carbamate derivatives (4 mmol) and amine HCl salt (4.5 mmol). Dimethyl sulfoxide (8 mL) and triethylamine (4.6 mmol) were added to the mixture and the reaction was stirred for 1-3 hours at 25 °C. The reaction mixture was diluted with ethyl acetate, washed with water (2x), 1M HCl, water, 1M NaOH and brine, dried over MgSO$_4$ and evaporated under reduced pressure. The crude product was purified by recrystallization from EtOAc.

**General conditions for the preparation of sulfonium salts**

**Method A:** $^4$ (2a – 2d)

A 20 mL screw capped vial was charged with 3.68 g dibenzothiophene (20.0 mmol, 1 equiv) and alkyl formate (40.0 mmol, 2 equiv). The mixture was stirred vigorously on ice bath and then 10 mL trifluoromethanesulfonic acid (120 mmol, 6 equiv) was added dropwise. The mixture was stirred over night at room temperature. After a night the mixture became a clear solution. The mixture was poured into water (200 mL) and extracted with dichloromethane (3 x 200 mL). The solution was concentrated under reduced pressure to 20 mL and poured into ether (370 mL). The product precipitated as white oil which crystallized easily after scratching and cooling in a refrigerator. The product was filtered and washed with ether, dried on air or under vacuum. The preparations were carried out in 2 mmol to 50 mmol scales.
Dibenzothiophenium triflates:

2a: S-methyldibenzothiophenium triflate: The product is a white solid. 7.62 g, yield: 88 %. Mp.: 132 °C; \( R_t = 0.31 \) (dichloromethane:methanol = 10:1); \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta \) 8.50 (d, 2H, \( J = 8.0 \) Hz), 8.10 (d, 2H, \( J = 7.7 \) Hz), 7.85 (td, 2H, \( J_1 = 7.6 \) Hz, \( J_2 = 1.1 \) Hz), 7.72 (td, 2H, \( J_1 = 7.8 \) Hz, \( J_2 = 1.3 \) Hz), 3.56 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\( d_6 \)): \( \delta \) 138.5, 135.0, 127.0, 123.0, 122.0, 62.1; IR (ATR): 3048, 1446, 1254, 1151, 1027, 754, 636, 516, 416 cm\(^{-1}\).

2b: S-ethylidibenzothiophenium triflate: The product is a white solid. 6.40 g, yield: 89 %. Mp.: 104 °C; \( R_t = 0.41 \) (dichloromethane:methanol = 10:1); \(^1\)H NMR (250 MHz, DMSO-\( d_6 \)): \( \delta \) 8.38-8.32 (m, 2H), 8.05-8.00 (m, 2H), 7.55-7.48 (m, 4H), 4.32 (q, 2H, \( J = 7.02 \) Hz), 1.30 (t, 3H, \( J = 7.02 \) Hz); \(^{13}\)C NMR (62.5 MHz, DMSO-\( d_6 \)): \( \delta \) 138.5, 135.0, 127.0, 124.7, 123.0, 122.0, 72.7, 15.2; IR (ATR) 1448, 1258, 1150, 1029, 755 cm\(^{-1}\); HRMS calcd for C\(_{14}\)H\(_{13}\)S\(^+\) [M-OTf]\(^+\) 213.0732 found 213.0733.

2c: S-propyldibenzothiophenium triflate: The product is a white solid. 225 mg, yield: 30 %. Mp.: 97 °C; \( R_t = 0.44 \) (dichloromethane:methanol = 10:1); \(^1\)H NMR (250 MHz, DMSO-\( d_6 \)): \( \delta \) 8.37-8.34 (m, 2H), 8.03-8.00 (m, 2H), 7.53-7.49 (m, 4H), 4.22 (t, 2H, \( J = 6.48 \) Hz), 1.67 (h, 2H, \( J = 7.06 \) Hz), 0.89 (t, 3H, \( J = 7.36 \) Hz); \(^{13}\)C NMR (62.5 MHz, DMSO-\( d_6 \)): \( \delta \) 138.5, 135.0, 127.0, 124.7, 123.0, 122.0, 77.6, 22.5, 9.6; IR (ATR): 3071, 3024, 1447, 1266, 1222, 1148, 1032, 757, 632, 516 cm\(^{-1}\); HRMS calcd for C\(_{15}\)H\(_{15}\)S\(^+\) [M-OTf]\(^+\) 227.0889 found 227.0889.
**2d: S-phenethyldibenzothiophenium triflate:** The product is a white solid. 270 mg, yield: 68%. Mp.: 107 °C; R_{f} = 0.5 (dichloromethane:methanol = 10:1); \(^{1}\)H NMR (250 MHz, CDCl\(_3\)): \(\delta\) 8.25 (d, 2H, \(J = 7.87\) Hz), 8.07 (d, 2H, \(J = 7.61\) Hz), 7.82 (t, 2H, \(J = 7.41\) Hz), 7.65 (t, 2H, \(J = 7.54\) Hz), 7.11-7.00 (m, 5H), 4.26 (t, 2H, \(J = 7.55\) Hz), 2.77 (t, 2H, \(J = 7.37\) Hz); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 138.5, 136.4, 135.0, 129.0, 128.5, 127.0, 126.8, 124.7, 123.0, 122.0, 76.4, 35.2; IR (ATR): 2977, 1447, 1253, 1222, 1147, 1026, 754, 507, 419 cm\(^{-1}\); HRMS calcd for C\(_{20}\)H\(_{17}\)S\([\text{M-OTf}]^{+}\) 289.1045 found 289.1060.

**Method B:** \(^{6}\) (2e – 2g)

![Reaction Scheme](image)

A 20 mL screw capped vial with septa was charged with 550 mg dibenzothiophene (3 mmol, 1 equiv) and 584 mg silver tetrafluoroborate (3 mmol, 1 equiv). The atmosphere of the vial was eliminated and filled with argon three times. 12 mL abs. 1,2-dichloroethane was added. Finally other alkyl iodide (18 mmol, 6 equiv) was added dropwise. The yellow silver iodide precipitate appears immediately. The mixture was stirred overnight at room temperature. The mixture was filtered, the filtrate was washed with dichloromethane and acetonitrile. The filtrate was evaporated until the solution started to be cloudy (2-3 mL), then was poured in 80 mL ether. The product precipitated as white crystals. After cooling in a refrigerator for an hour, the product was filtered, washed with ether and dried under vacuum. The preparations were carried out in 1 mmol to 4 mmol scales.

**Dibenzothiophenium tetrafluorborates:**

![Reaction Scheme](image)

**2e: S-methyldibenzothiophenium tetrafluoroborate:** \(^{6}\) The product is a white solid. 682 mg, yield: 79%. Mp.: 150-153 °C; R_{f} = 0.46 (dichloromethane:methanol = 10:1); \(^{1}\)H NMR (250 MHz, CD\(_3\)CN): \(\delta\) 8.29-8.22 (m, 4H), 7.92 (t, 2H, \(J = 7.4\) Hz), 7.76 (t, 2H, \(J = 7.5\) Hz), 3.31 (s,
3H); \(^{13}\)C NMR (62.5 MHz, CD\(_3\)CN): \(\delta\) 140.3, 135.0, 132.1, 131.7, 128.6, 125.3, 35.0; IR (ATR) 3094, 3023, 2934, 1419, 1034, 756, 508, 418 cm\(^{-1}\);

2f: \(S\)-ethyldibenzothiophenium tetrafluoroborate: The product is a white solid. 143 mg, yield: 48%. Mp.: 114-118 °C; \(R_f\) = 0.45 (dichloromethane:methanol = 10:1); \(^1\)H NMR (250 MHz, CD\(_3\)CN): \(\delta\) 8.28 (d, 2H, \(J = 7.6\) Hz), 8.19 (d, 2H, \(J = 7.8\) Hz), 7.93 (t, 2H, \(J = 7.4\) Hz), 7.77 (t, 2H, \(J = 7.4\) Hz), 3.89 (q, 2H, \(J = 6.9\) Hz), 0.84 (t, 3H, \(J = 7.0\) Hz); \(^{13}\)C NMR (62.5 MHz, CD\(_3\)CN): \(\delta\) 141.4, 135.1, 132.1, 129.0, 128.1, 125.2, 45.9, 7.4; IR (ATR) 3078, 2973, 1448, 1265, 1048, 1036, 1010, 761, 519, 423 cm\(^{-1}\).

2g: \(S\)-(2-ethoxy-2-oxoethyl)dibenzothiophenium tetrafluoroborate: The product is a white solid. 1.23 g, yield: 86%. Mp.: 108-109 °C; \(R_f\) = 0.51 (dichloromethane:methanol = 10:1); \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 8.38-8.33 (m, 2H), 8.06-8.01 (m, 2H), 7.55-7.48 (m, 4H), 5.04 (s, 2H), 4.24 (q, 2H, \(J = 7.1\) Hz), 1.24 (t, 3H, \(J = 7.1\) Hz); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 168.3, 138.5, 135.0, 127.1, 124.7, 123.0, 122.0, 70.3, 62.0, 13.9; IR (ATR) 3006, 2950, 1723, 1314, 1192, 1055, 1015, 747, 521, 484 cm\(^{-1}\); HRMS calcd for C\(_{16}\)H\(_{15}\)O\(_2\)S\(^+\) [M-BF\(_4\)]\(^+\) 271.0787 found 271.0796.

**Optimization of the reaction conditions**

**Solvent effect**

A 4 mL screw capped vial was charged with 0.8 mg palladium acetate (0.00375 mmol; 0.075 equiv), and 7.5 mg 3’-methylacetanilide (0.05 mmol, 1equiv). 0.5 mL abs. 1,2-dichloroethane was added, then 19.3 \(\mu\)L trifluoroacetic acid (0.25 mmol, 5equiv). Finally 21 mg \(S\)-methyldibenzothiophenium triflate (0.06 mmol, 1.2 equiv) was added. The reaction mixture was stirred at 50 °C for the appropriate time.
The amount of palladium acetate
A 4 mL screw capped vial was charged with 0.6 or 0.8 or 1.1 mg palladium acetate (0.0025 or 0.00375 or 0.005 mmol; 0.05 or 0.075 or 0.1 equiv), and 7.5 mg 3’-methylacetanilide (0.05 mmol, 1.0 equiv). 0.5 mL abs. 1,2-dichloroethane was added, then 19.3 µL trifluoroacetic acid (0.25 mmol, 5 equiv). Finally 21 mg S-methyldibenzothiophenium triflate (0.06 mmol, 1.2 equiv) was added. In one case 12.0 mg (0.06 mmol, 1.2 equiv) copper(II)acetate monohydrate was also added. The reaction mixture was stirred at 50 °C for the appropriate time.

<table>
<thead>
<tr>
<th>solvent</th>
<th>GC-yield %</th>
</tr>
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<tbody>
<tr>
<td>1,2-dichloroethane</td>
<td>78%</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>76%</td>
</tr>
<tr>
<td>toluene</td>
<td>79%</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>53%</td>
</tr>
<tr>
<td>methanol</td>
<td>0%</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>0%</td>
</tr>
<tr>
<td>acetone</td>
<td>0%</td>
</tr>
</tbody>
</table>

The effects of other transition metals
A 4 mL screw capped vial was charged with 0.8 mg palladium acetate (0.00375 mmol; 0.075 equiv), with 8.3 mg 3’-methoxyacetanilide (0.05 mmol, 1 equiv), and 0.06 mmol copper salt or other additive. 0.5 mL 1,2-dichloroethane was added, then 19.3 µL trifluoroacetic acid (0.25 mmol, 5 equiv). Finally 22 mg S-ethyl dibenzothiophenium triflate (0.06 mmol, 1.2 equiv) was added. The reaction mixture was stirred at 50 °C for 16 h.
Copper(II) acetate monohydrate seemed to be an effective additive, other metals and oxidants, do not have a positive effect or these retard the reaction. Manganese(III) acetate caused a homocoupling of the acetanilide.  

### Procedure for getting back dibenzothiophene

Dibenzothiophene was recovered during the process of the chromatographic purification of the alkylated products. Dibenzothiophene was regained with 188 mg, 85% (4c), 154 mg, 70% (4k), 219 mg, 99% (6a), 187 mg, 85% (6d). Purification was checked by GC and $^1$H NMR measurements.

### General procedure for the preparation of ortho-alkylated amide derivatives (products of the C-H activation)

A 20 mL screw capped vial was charged with 22 mg palladium acetate (0.1 mmol; 0.1 equiv), with 1 mmol N-aryl amide or N-aryl urea (1.0 mmol, 1 equiv) and 240 mg copper(II) acetate monohydrate (1.2 mmol). 10 mL abs. 1,2-dichloroethane, then 385 µL trifluoroacetic acid (5 mmol, 5 equiv) was added. Finally 1.2 mmol dibenzo thiophenium triflate (1.2 mmol, 1.2 equiv) was added. The mixture was stirred for 5-16 hours at 50 °C. (For the solvent, we used 1,2-
dichloroethane, distilled from calcium carbide. Acidic decomposition contaminants in the solvent retard the C-H activation.) Work up and purification: The reaction mixture was concentrated onto celite. Purification of the mixture by chromatography on silica gel with hexane – ethyl acetate eluent afforded the product. In some cases ethyl acetate solution of the product was washed with aqueous ammonia and water to eliminate copper salt contaminant. The preparations were carried out in 0.5 mmol or 1 mmol scales.

4a: 2'-methylacetanilide: \(^8\) Reaction time: 12 h. The product is an off-white solid. 51 mg, yield: 68%. Mp.: 99-101 °C; \(R_f = 0.38\) (hexane:ethyl acetate = 1:2); \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 9.27 (s, 1H), 7.40-7.37 (m, 1H), 7.20-7.02 (m, 3H), 2.19 (s, 3H), 2.05 (s, 3H); \(^13\)C NMR (62.5 Hz, DMSO-\(d_6\)) \(\delta\) 168.1, 136.4, 131.4, 130.1, 125.8, 124.91, 124.88, 23.2, 17.8.; MS (EI, 70 eV): \(m/z\) (%): 149(41[M+]), 107(100), 106(99), 91(6), 77(25), 51(8); IR (ATR) 2919, 1653, 1527, 1458, 1368, 1271, 755, 699 cm\(^{-1}\).

4b: 2',6'-dimethylacetanilide: \(^9\) Reaction time: 16 h. The product is a pale yellow solid. 70 mg, yield: 43%. Mp.: 187-192 °C; \(R_f = 0.35\) (hexane:ethyl acetate = 1:2); \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 9.22 (s, 1H), 7.05 (s, 3H), 2.13 (s, 6H), 2.04 (s, 3H); \(^13\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 167.8, 135.4, 135.1, 127.6, 126.2, 22.6, 18.1; MS (EI, 70 eV): \(m/z\) (%): 149 (45 [M+]), 148 (4), 121 (100), 120 (54), 106 (53), 91 (17), 77 (16); IR (ATR) 2919, 2852, 1647, 1532, 1465, 1370, 1301, 963, 766, 700 cm\(^{-1}\).
**4c: 2',5'-dimethylacetanilide:** Reaction time: 5 h. The product is an off-white solid. 146 mg, yield: 89%. Mp.: 132-135 °C; R\_f = 0.43 (hexane:ethyl acetate = 1:2); \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 9.21 (s, 1H), 7.21 (s, 1H), 7.06 (d, 1H, \(J = 7.6\) Hz), 6.87 (d, 1H, \(J = 7.4\) Hz), 2.24 (s, 3H), 2.14 (s, 3H), 2.04 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 168.1, 136.3, 134.8, 130.0, 128.4, 125.6, 125.5, 23.3, 20.6, 17.4; MS (EI, 70 eV): \(m/z\) (%): 163(46 [M\^+]\)), 121(100), 120(52), 106(63), 91(31), 77(29), 65(10); IR (ATR) 1655, 1538, 1290, 1200, 807, 718 cm\(^{-1}\).

**4d: 5'-methoxy-2'-methylacetanilide:** Reaction time: 16 h. The product is a brown solid. 121 mg, yield: 68 %. Mp.: 80-87 °C; R\_f = 0.34 (hexane:ethyl acetate = 1:2); \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 9.19 (s, 1H), 7.09-7.06 (m, 2H), 6.64 (dd, 2H, \(J_1 = 8.24\) Hz, \(J_2 = 2.00\) Hz), 3.68 (s, 3H), 2.11 (s, 3H), 2.04 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 168.0, 157.1, 137.1, 130.4, 122.6, 110.1, 110.0, 54.8, 23.2, 16.8; MS (EI, 70 eV): \(m/z\) (%): 179(68[M\^+]\)), 137(100), 136(86), 122(15), 106(23), 93(40), 77(22), 66(14); IR (ATR) 1657, 1532, 1502, 1454, 1200, 1163, 1038, 797, 703 cm\(^{-1}\).

**4e: 5'-fluoro-2'-methylacetanilide:** Reaction time: 16 h. The product is a white solid. 30 mg, yield: 18 %. Mp.:111-115 °C; R\_f = 0.51 (hexane:ethyl acetate = 1:2); \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 9.29 (s, 1H), 7.43 (dd, 1H, \(J_1 = 11.15\) Hz, \(J_2 = 2.47\) Hz), 7.22-7.16 (m, 1H), 6.87 (td, 1H, \(J_1 = 8.32\) Hz, \(J_2 = 2.63\) Hz), 2.18 (s, 3H), 2.08 (s, 3H); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 168.5, 160.1 (d, \(J = 240\) Hz), 137.8 (d, \(J = 10.6\) Hz), 131.2 (d, \(J = 9.0\) Hz), 126.1, 110.9 (d, \(J = 17.0\) Hz), 110.6 (d, \(J = 20.7\) Hz), 23.4, 17.1; MS (EI, 70 eV): \(m/z\) (%): 164 (22 [M\^+]\)), 125 (100), 124 (81), 107 (10), 77 (11); IR (ATR): 3268, 1654, 1600, 1524, 1487, 1369, 1283, 1253, 1158, 863, 811, 713, 612, 552, 460 cm\(^{-1}\).
**4f: 5’-chloro-2’-methylacetanilide:** Reaction time: 16 h. The product is a pale yellow solid. 84 mg, yield: 46 %. Mp.: 129-133 °C; Rt = 0.49 (hexane:ethyl acetate = 1:2); \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta\) 7.70 (s, 1H), 7.47 (s, 1H), 7.06-6.98 (m, 2H), 2.14 (s, 6H); \(^1^3\)C NMR (62.5 MHz, CDCl\(_3\)): \(\delta\) 168.9, 136.7, 131.8, 131.4, 128.0, 125.3, 123.6, 24.1, 17.4; MS (EI, 70 eV): \(m/z\) (%): 183(30[M\(^+\)]), 141(100), 140(39), 106(63), 104(11), 89(7), 77(41), 63(9); IR (ATR) 1653, 1522, 1405, 1278, 863, 803, 706, 650 cm\(^{-1}\); HRMS calcd for C\(_9\)H\(_{11}\)ClNO \([M+H]^+\) 184.0524 found 184.0522.

**4g: 5’-bromo-2’-methylacetanilide:** Reaction time: 6 h. The product is a white solid. 29 mg, yield: 13 %. Mp.: 155-156 °C; Rt = 0.46 (hexane:ethyl acetate = 1:2); \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 9.33 (s, 1H), 7.72 (s, 1H), 7.25-7.14 (m, 2H), 2.17 (s, 3H), 2.07 (s, 3H); \(^1^3\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 168.5, 138.1, 132.0, 130.0, 127.2, 126.6, 117.9, 23.4, 17.4; MS (EI, 70 eV): \(m/z\) (%): 227(48[M\(^+\)]), 185(100), 106(83), 104(26), 89(9), 77(34), 63(9); IR (ATR) 1651, 1522, 1476, 1399, 1278, 997, 861, 802, 695 cm\(^{-1}\); HRMS calcd for C\(_9\)H\(_{11}\)BrNO \([M+H]^+\) 228.0019 found 228.0025.

**4h: 2’,4’-methylacetanilide:** \(^1^2\) Reaction time: 6 h. The product is a pale yellow solid. 94 mg, yield: 56%. Mp.: 115-118 °C; Rt = 0.34 (hexane:ethyl acetate = 1:2); \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 9.20 (s, 1H), 7.23 (d, 1H, \(J = 7.92\) Hz), 6.99-6.92 (m, 2H), 2.23 (s, 3H), 2.14 (s, 3H), 2.02 (s, 3H); \(^1^3\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 168.0, 133.9, 133.8, 131.4, 130.6, 126.2, 124.9, 23.1, 20.3, 17.7; MS (EI, 70 eV): \(m/z\) (%): 163(59[M\(^+\)]), 121(100), 120(71), 106(66), 100(100), 99(44), 95(100), 94(100), 93(49), 92(54), 77(100), 63(56), 52(45), 51(100), 41(42), 39(42), 38(42), 37(42), 36(42), 35(42), 34(42), 33(42), 32(42), 31(42), 30(42), 29(42), 28(42), 27(42), 26(42), 25(42), 24(42), 23(42), 22(42), 21(42), 20(42), 19(42), 18(42), 17(42), 16(42), 15(42), 14(42), 13(42), 12(42), 11(42), 10(42), 9(42), 8(42), 7(42), 6(42), 5(42), 4(42), 3(42), 2(42), 1(42).
91(28), 77(26), 65(10); IR (ATR) 2919, 1646, 1530, 1443, 1368, 1301, 1200, 811, 727 cm⁻¹.

4i: 4'-isopropyl-2'-methylacetanilide: Reaction time: 12 h. The product is a pale grey solid. 127 mg, yield: 66%. Mp.: 108-111 °C; Rf = 0.43 (hexane:ethyl acetate = 1:2); ¹H NMR (250 MHz, DMSO-d₆): δ 9.21 (s, 1H), 7.25 (d, 1H, J = 8.01 Hz), 7.05-6.99 (m, 2H), 2.82 (hept, 1H, J = 6.77 Hz), 2.16 (s, 3H), 2.03 (s, 3H), 1.18 (d, 6H, J = 6.81 Hz); ¹³C NMR (62.5 MHz, DMSO-d₆): δ 168.1, 145.1, 134.2, 131.6, 128.0, 125.2, 123.6, 32.9, 23.9, 23.2, 18.0; MS (EI, 70 eV): m/z (%): 191 (38 [M⁺]), 176(18), 149(11), 134(100), 119(8), 106(5), 91(8), 77(8); IR (ATR) 2957, 1651, 1534, 1312, 874, 833, 727 cm⁻¹; HRMS calcd for C₁₂H₁₈NO⁺ [M+H]⁺ 192.1383 found 192.1386.

4j: 4'-methoxy-2'-methylacetanilide: Reaction time: 10 h. The product is a green solid. 91 mg, yield 51%. Mp.: Rf = 0.26 (hexane:ethyl acetate = 1:2); ¹H NMR (250 MHz, DMSO-d₆): δ 9.18 (s, 1H), 7.16 (d, 1H, J = 8.11 Hz), 6.75-6.67 (m, 2H), 3.69 (s, 3H), 2.12 (s, 3H), 1.98 (s, 3H); ¹³C NMR (62.5 MHz, DMSO-d₆): δ 156.1, 133.3, 128.9, 126.2, 114.6, 110.5, 54.5, 22.5, 17.5; MS (EI, 70 eV): m/z (%): 179(53[M⁺]), 137(47), 136(29), 122(100), 93(48), 77(15); IR (ATR) 2919, 1728, 1642, 1530, 1500, 1197, 1148, 796, 725 cm⁻¹.
4k: *N*-mesitylacamide: Reaction time: 16 h. The product is a pale green solid. 57 mg, yield: 32%. Mp.: 198-203 °C; *R*~f~ = 0.31 (hexane:ethyl acetate = 1:2); $^1$H NMR (250 MHz, DMSO-$d_6$): $\delta$ 9.11 (s, 1H), 6.84 (s, 2H), 2.21 (s, 3H), 2.08 (s, 6H), 2.01 (s, 3H); $^{13}$C NMR (62.5 MHz, DMSO-$d_6$): $\delta$ 167.7, 135.0, 134.6, 132.6, 128.0, 22.4, 20.3, 17.8; MS (EI, 70 eV): $m/z$ (%): 177(49[M$^+$]), 135(100), 134(58), 120(66), 91(19), 77(9); IR (ATR) 2921, 1644, 1540, 1290, 1200, 863, 718 cm$^{-1}$; HRMS calcd for C$_{11}$H$_{16}$NO$^+$ [M+H]$^+$ 178.1226 found 178.1235.

4l: 4'-chloro-2',5'-dimethylacetanilide: Reaction time: 16 h. The product is a white solid. 110 mg, yield: 56%. Mp.: 177-178 °C; *R*~f~ = 0.46 (hexane:ethyl acetate = 1:2); $^1$H NMR (250 MHz, DMSO-$d_6$): $\delta$ 9.29 (s, 1H), 7.39 (s, 1H), 7.24 (s, 1H), 2.25 (s, 3H), 2.15 (s, 3H), 2.04 (s, 3H); $^{13}$C NMR (62.5 MHz, DMSO-$d_6$): $\delta$ 168.3, 135.4, 132.5, 131.1, 130.0, 128.9, 127.3, 23.3, 19.2, 17.1; MS (EI, 70 eV): $m/z$ (%): 197(46[M$^+$]), 155(100), 120(47), 91(32), 77(10); IR (ATR) 1653, 1525, 1389, 981, 878, 712, 680 cm$^{-1}$; HRMS calcd for [M+H]$^+$ C$_{10}$H$_{13}$ClNO$^+$ 198.0680 found 198.0680.

4m: 4’,5’-dimethoxy-2’-methylacetanilide: Reaction time: 16 h. The product is a pale yellow solid. 150 mg, yield: 72%. Mp.: 138-139 °C; *R*~f~ = 0.18 (hexane:ethyl acetate = 1:2); $^1$H NMR (250 MHz, DMSO-$d_6$): $\delta$ 9.17 (s, 1H), 6.93 (s, 1H), 6.78(s, 1H), 3.72-3.68 (m, 6H), 2.10 (s, 3H), 1.97 (s, 3H), 1.89 (s, 3H); MS (EI, 70 eV): $m/z$ (%): 238(100), 195(13), 167(14), 103(15), 91(25); IR (ATR) 1644, 1524, 1389, 1280, 1058, 878, 718 cm$^{-1}$; HRMS calcd for [M+H]$^+$ C$_{12}$H$_{15}$NO$_3^+$ 240.0980 found 240.0991.
$^{13}$C NMR (62.5 MHz, DMSO-$d_6$): $\delta$ 168.0, 146.3, 146.1, 129.0, 124.0, 113.6, 110.2, 55.62, 55.57, 23.0, 17.3; MS (EI, 70 eV): $m/z$ (%): 209(94[M$^+$]), 166(23), 152(100), 124(37), 122(21), 109(14), 93(9), 80(12), 68(7); IR (ATR) 1651, 1515, 1221, 1117, 857 cm$^{-1}$; HRMS calcd for C$_{11}$H$_{16}$NO$_3^+$ [M+H]$^+$ 210.1125 found 210.1127.

4n: 2',5'-dimethylpivalanilide: Reaction time: 6 h. The product is a white solid. 173 mg, yield: 84%. Mp: 97-99 $^\circ$C; $R_f$ = 0.48 (hexane:ethyl acetate = 4:1); $^1$H NMR (250 MHz, DMSO-$d_6$): $\delta$ 8.81 (s, 1H), 7.10-6.91 (m, 3H), 2.25 (s, 3H), 2.10 (s, 3H), 1.23 (s, 9H); $^1$H NMR (62.5 MHz, DMSO-$d_6$): $\delta$ 176.2, 136.4, 134.8, 130.5, 129.8, 127.3, 126.3, 38.6, 27.4, 20.4, 17.2; MS (EI, 70 eV): $m/z$ (%): 205(100[M$^+$]), 162(14), 148(14), 121(61), 106(21), 91(27), 77(26), 57(69); IR (ATR) 1652, 1532, 1475, 1292, 1187, 805, 669 cm$^{-1}$; HRMS calcd for C$_{13}$H$_{20}$NO$^+$ [M+H]$^+$ 206.1539 found 206.1547.

4o: 5'-methoxy-2'-methylpivalanilide: Reaction time: 8 h. The product was isolated as a mixture of the starting material (3'-methoxypivalanilide) and the product (5'-methoxy-2'-methylpivalanilide) as a grey solid. 165 mg. The rate of starting material and product is 46% / 54% according to $^1$H NMR. $R_f$ = 0.58 (hexane:ethyl acetate = 2:1);

MS (EI, 70 eV): $m/z$ (%): 221(100[M$^+$]), 178(11), 164(19), 137(59), 121(12), 106(9), 93(32), 77(15), 57(94).

HRMS calcd for C$_{13}$H$_{20}$NO$_2^+$ [M+H]$^+$ 222.1489 found 222.1492.
4p: \textit{N-}(2,5-\textit{dimethylphenyl})benzamide: \textsuperscript{16} Reaction time: 5 h. The product is a white solid. 189 mg, yield: 84%. Mp.: 159-162 °C; \textit{Rf} = 0.36 (hexane:ethyl acetate = 4:1); \textsuperscript{1}H NMR (250 MHz, DMSO-\textit{d}_6): \delta 9.83 (s, 1H), 7.99-7.96 (m, 2H), 7.59-7.50 (m, 3H), 7.17-7.13 (m, 2H), 7.00-6.97 (m, 1H), 2.28 (s, 3H), 2.19 (s, 3H); \textsuperscript{13}C NMR (62.5 MHz, DMSO-\textit{d}_6): \delta 165.2, 136.2, 135.0, 134.6, 131.5, 130.5, 130.1, 128.4, 127.6, 127.1, 126.6, 20.5, 17.5; MS (EI, 70 eV): \textit{m/z} (%) 225(18[M\textsuperscript{+}]), 120(13), 105(100), 91(5), 77(41); IR (ATR) 3237, 2919, 1635, 1523, 1306, 1292, 803, 709, 695, 653, 600, 459 cm\textsuperscript{-1}; HRMS calcd for [M+H\textsuperscript{+}]\textsubscript{C}_{15}H_{16}NO\textsuperscript{+} 226.1226 found 226.1228.

4q: \textit{N-}(2,5-\textit{dimethylphenyl})-2-phenylacetamide: Reaction time: 5 h. The product is a white solid. 201 mg, yield: 84%. Mp.: 165-167 °C; \textit{Rf} = 0.29 (hexane:ethyl acetate = 4:1); \textsuperscript{1}H NMR (250 MHz, DMSO-\textit{d}_6): \delta 9.43 (s, 1H), 7.38-7.19 (m, 6H), 7.08-7.05 (m, 1H), 6.90-6.87 (m, 1H), 3.66 (s, 2H), 2.23 (s, 3H), 2.11 (s, 3H); \textsuperscript{13}C NMR (62.5 MHz, DMSO-\textit{d}_6): \delta 169.0, 136.3, 136.0, 134.9, 130.1, 129.0, 128.6, 128.3, 126.5, 125.9, 125.6, 42.8, 20.6, 17.4; MS (EI, 70 eV): \textit{m/z} (%) 239(26[M\textsuperscript{+}]), 147(14), 121(100), 106(14), 91(62), 77(12), 65(14); IR (ATR) 3254, 3027, 2919, 1655, 1532, 1494, 1411, 1343, 1192, 807, 698, 584, 444 cm\textsuperscript{-1}; HRMS calcd for [M+H\textsuperscript{+}]\textsubscript{C}_{16}H_{18}NO\textsuperscript{+} 240.1383 found 240.1384.

6a: 1,1-\textit{dimethyl}-3-(\textit{o-tolyl})urea: \textsuperscript{17} Reaction time: 6 h. The product is a white solid. 101 mg, yield: 57%. Mp.: 149-152 °C; \textit{Rf} = 0.31 (hexane:ethyl acetate = 1:2); \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}): \delta 7.68 (d, 1H, \textit{J} = 8.0 Hz), 7.20-7.13 (m, 2H), 7.02-6.96 (m, 1H), 6.15 (s, 1H), 3.01 (s, 6H), 2.23 (s, 3H); \textsuperscript{13}C NMR (62.5 MHz, CDCl\textsubscript{3}): \delta 156.0, 137.3, 130.3, 128.5, 126.8, 123.8,
122.7, 36.5, 17.9; MS (EI, 70 eV): unable to record EI-MS spectra, IR (ATR) 1637, 1484, 1372, 1249, 902, 746 cm\(^{-1}\).

6b: \(N'-(2,5\text{-dimethylphenyl})-N,N\text{-dimethylurea}\): Reaction time: 16 h. The product is a dark oil. 145 mg, yield: 75%. \(R_t = 0.32\) (hexane:ethyl acetate = 1:2); \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 7.67 (s, 1H), 7.02-7.00 (m, 2H), 6.83-6.80 (m, 1H), 2.89 (s, 6H), 2.21 (s, 3H), 2.09 (s, 3H); \(^13\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 137.6, 134.2, 129.4, 129.3, 126.0, 124.6, 35.9, 20.3, 17.1; MS (EI, 70 eV): \(m/z\) (%): 192 (50 [M\(^+\)]), 147(19), 132(8), 120(18), 104(4), 91(21), 77(20), 72(100), 65(6); IR (ATR) 1674, 1633, 1530, 1495, 1191, 1133, 798, 721 cm\(^{-1}\); HRMS calcd for [M+H]\(^+\) \(C_{11}H_{17}N_2O^+\) 193.1335 found 193.1343.

6c: \(N'-(5\text{-chloro-2-methyphenyl}),N,N\text{-dimethylurea}\): Reaction time: 16 h. The product was isolated as a dark green oil. It was washed with ammonia solution (15%) and water. The product is a brown solid. 142 mg, yield: 67 %. Mp.: 96-99 °C; \(R_t = 0.46\) (hexane:ethyl acetate = 1:2); \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 7.78 (s, 1H), 7.40-7.39 (m, 1H), 7.18 (d, 1H, \(J = 8.1\) Hz), 7.07-7.03 (m, 1H), 2.93 (s, 6H), 2.16 (s, 3H); \(^13\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 155.8, 139.7, 131.4, 130.8, 129.6, 124.3, 123.5, 36.2, 17.3; MS (EI, 70 eV): unable to record EI-MS spectra, the product decomposes to its isocyanate; IR (ATR) 2923, 2854, 1633, 1516, 1501, 1368, 1252, 1182, 802, 761, 654 cm\(^{-1}\); HRMS calcd for [M+H]\(^+\) \(C_{10}H_{14}ClN_2O^+\) 213.0789 found 213.0799.

6d: 3-(2-methoxy-6-methylphenyl)-1,1-dimethylurea: Reaction time: 16 h. The product is a white solid. 101 mg, yield: 48%. Mp.: 102-103 °C; \(R_t = 0.16\) (hexane:ethyl acetate = 1:2); \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 7.37 (s, 1H), 7.07 (t, 1H, \(J = 7.9\) Hz), 6.84-6.77 (m, 2H), 3.72
6e: \( N'-(2\text{-methylnaphtyl})-N,N\text{-dimethylurea} \): Reaction time: 16 h. The product is a yellow solid. 119 mg, yield: 54%. Mp.: 130-133 °C; \( R_f = 0.27 \) (hexane:ethyl acetate = 1:2); \( ^1\text{H} \) NMR (250 MHz, DMSO-\( d_6 \)): \( \delta \) 8.14 (s, 1H), 7.89-7.87 (m, 2H), 7.76-7.73 (m, 1H), 7.49-7.39 (m, 3H), 3.01 (s, 6H), 2.33 (s, 3H); \( ^{13}\text{C} \) NMR (62.5 MHz, DMSO-\( d_6 \)): \( \delta \) 156.7, 133.1, 133.07, 132.3, 131.7, 128.6, 127.6, 125.8, 125.7, 124.8, 123.4, 36.3, 18.2; MS (EI, 70 eV): \( m/z \) (%): 226(7[M+]), 183(99), 153(100), 127(67), 76(46); IR (ATR): 3296, 2922, 1641, 1521, 1487, 1366, 1247, 1190, 866, 738, 477 cm\(^{-1}\); HRMS calcd for \( C_{14}H_{17}N_2O^+ \) [M+H]^+ 229.1335 found 229.1334.

6f: \( N'\text{-2-(3\text{-methylnaphtyl})-N,N\text{-dimethylurea}} \): Reaction time: 16 h. The product is a white solid. 141 mg, yield: 62%. Mp.: 112-115 °C; \( R_f = 0.32 \) (hexane:ethyl acetate = 1:2); \( ^1\text{H} \) NMR (250 MHz, DMSO-\( d_6 \)): \( \delta \) 7.92-7.69 (m, 5 H), 7.40 (s, 2H), 2.97 (s, 6H), 2.37 (s, 3H); \( ^{13}\text{C} \) NMR (62.5 MHz, DMSO-\( d_6 \)): \( \delta \) 156.4, 137.0, 132.6, 132.0, 130.6, 127.8, 126.8, 126.6, 125.1, 124.7, 121.9, 36.2, 18.2; MS (EI, 70 eV): unable to record EI-MS spectra, the product decomposes to its isocyanate; IR (ATR): 3292, 2922, 1641, 1521, 1487, 1366, 1247, 1190, 866, 738, 477 cm\(^{-1}\); HRMS calcd for \( C_{14}H_{17}N_2O^+ \) [M+H]^+ 229.1335 found 229.1340.
6g: N-(2,5-dimethylphenyl)morpholine-4-carboxamide: Reaction time: 16 h. The product is a white solid. 181 mg, yield: 77%. Mp.: 180-181 °C; $R_f = 0.29$ (hexane:ethyl acetate = 1:2); $^1$H NMR (250 MHz, DMSO-$d_6$): $\delta$ 7.99 (s, 1H), 7.06-7.01 (m, 2H), 6.87-6.84 (m, 1H), 3.60 (t, 4H, $J = 4.66$ Hz), 3.40 (t, 4H, $J = 4.66$ Hz), 2.24 (s, 3H), 2.11 (s, 3H); $^{13}$C NMR (62.5 MHz, DMSO-$d_6$): $\delta$ 155.8, 137.5, 134.7, 129.9, 129.8, 126.6, 125.3, 66.0, 44.3, 20.5, 17.5; MS (EI, 70 eV): $m/z$ (%): 235(42), 147(100), 125(41), 106(40), 77(40); IR (ATR): 3292, 2964, 2851, 1640, 1493, 1247, 1113, 870, 806, 575 cm$^{-1}$; HRMS calcd for C$_{13}$H$_{19}$N$_2$O$_2$ $[M+H]^+$ 235.1441 found 235.1448.

8a: 2’-ethyl-5’-methoxyacetanilide: Reaction time: 8 h. The product is a yellow solid. 80 mg, yield: 41%. Mp.: 108-112 °C; $R_f = 0.43$ (hexane:ethyl acetate = 1:2); $^1$H NMR (250 MHz, DMSO-$d_6$): $\delta$ 9.22 (s, 1H), 7.10 (d, 1H, $J = 8.4$ Hz), 7.01 (s, 1H), 6.72-6.69 (m, 1H), 3.70 (s, 3H), 2.51 (q, 2H, $J = 7.4$ Hz), 2.05 (s, 3H), 1.08 (t, 3H, $J = 7.5$ Hz); $^{13}$C NMR (62.5 MHz, DMSO-$d_6$): $\delta$ 168.4, 157.2, 136.6, 129.3, 129.0, 111.2, 110.8, 55.0, 23.3, 23.0, 14.5; MS (EI, 70 eV): $m/z$ (%): 193(20), 178(9), 150(39), 136(100), 119(3), 106(6), 93(8), 77(8), 65(6); IR (ATR) 2955, 2919, 1653, 1493, 1262, 1038, 844, 721 cm$^{-1}$; HRMS calcd for C$_{11}$H$_{16}$NO$_2$ $[M+H]^+$ 194.1176 found 194.1175.

8b: 2’-ethyl-5’-methylacetanilide: Reaction time: 16 h. The product is an off-white solid. 125 mg, yield: 71%. Mp.: 103-110 °C; $R_f = 0.49$ (hexane:ethyl acetate = 1:2); $^1$H NMR (250 MHz, DMSO-$d_6$): $\delta$ 9.21 (s, 1H), 7.14-7.07 (m, 2H), 6.94-6.91 (m, 1H), 2.50 (m, 2H), 2.23 (s, 3H), 2.03 (s, 3H), 1.08 (m, 3H); $^{13}$C NMR (62.5 MHz, DMSO-$d_6$): $\delta$ 168.3, 135.5, 134.74, 134.69, 128.2, 126.5, 126.1, 23.4, 23.1, 20.5, 14.3; MS (EI, 70 eV): $m/z$ (%): 177(18), 143(36), 134(36), 125(100), 112(44), 106(35), 93(15), 77(8), 65(4), 57(3), 43(3).
120(100), 91(17), 77(12), 65(7); IR (ATR) 2960, 1655, 1540, 1294, 826, 725 cm\(^{-1}\); HRMS calcd for C\(_{11}\)H\(_{16}\)NO\(^+\) [M+H]\(^+\) 178.1226 found 178.1233.

8c: 5'-methyl-2'-propylacetanilide: Reaction time: 6 h. The product is an off-white solid. 116 mg, yield: 61 %. Mp.: 147-149 °C; R\(_f\) = 0.55 (hexane:ethyl acetate = 1:2); \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta\) 7.53 (s, 1H), 7.07-6.91 (m, 3H), 2.50 (t, 2H, \(J = 7.24\) Hz), 2.31 (s, 3H), 2.18 (s, 3H), 1.63-1.55 (m, 2H), 0.96 (t, 3H, \(J = 7.11\) Hz); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 168.3, 135.7, 134.8, 133.2, 129.1, 126.7, 125.9, 32.4, 23.1, 22.7, 20.5, 13.8; MS (EI, 70 eV): \(m/z\) (%): 191(30[M\(^+\)]), 176(6), 162(8), 148(25), 132(13), 120(100), 118(8), 91(19) 77(11); IR (ATR) 2962, 1648, 1536, 1292, 823, 794, 725, 707 cm\(^{-1}\); HRMS calcd for C\(_{12}\)H\(_{18}\)NO\(^+\) [M+H]\(^+\) 192.1383 found 192.1384.

8d: N'-(2-ethyl-5-methylphenyl)-N,N-dimethylurea: Reaction time: 16 h. The product is a white solid. 153 mg, yield: 80 %. Mp.: 82-83 °C; R\(_f\) = 0.37 (hexane:ethyl acetate = 1:2); \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 7.67 (s, 1H), 7.08-7.01 (m, 2H), 6.92-6.88 (m, 1H), 2.91 (s, 6H), 2.52 (q, 2H, \(J = 7.53\) Hz), 2.24 (s, 3H), 1.09 (t, 3H, \(J = 7.55\) Hz); \(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)): \(\delta\) 156.6, 137.3, 135.8, 134.5, 127.8, 127.4, 125.5, 36.2, 23.4, 20.5, 14.0; MS (EI, 70 eV): \(m/z\) (%): 206(7[M\(^+\)]), 161(16), 134(27), 72(100); IR (ATR): 3248, 2917, 2862, 1627, 1528, 1369, 1283, 1183, 813, 752, 599 cm\(^{-1}\); HRMS calcd for C\(_{12}\)H\(_{19}\)N\(_2\)O\(^+\) [M+H]\(^+\) 207.1492 found 207.1499.

8e: N'-(2-phenethyl-5-methylphenyl)-N,N-dimethylurea: Reaction time: 16 h. The product is a white solid. 169 mg, yield: 60 %. Mp.: 147-148 °C; R\(_f\) = 0.44 (hexane:ethyl acetate =
1:2; ¹H NMR (250 MHz, DMSO-d₆): δ 7.76 (s, 1H), 7.31-7.25 (m, 2H), 7.21-7.14 (m, 3H), 7.10-7.02 (m, 2H), 6.91-6.88 (m, 1H), 2.92 (s, 6H), 2.78 (s, 4H), 2.25 (s, 3H); ¹³C NMR (62.5 MHz, DMSO-d₆): δ 156.7, 142.1, 137.4, 134.9, 134.1, 128.9, 128.3, 128.2, 127.8, 125.7, 125.6, 36.2, 35.6, 33.1, 20.5; MS (EI, 70 eV): unable to record EI-MS spectra, the product decomposes to its isocyanate; IR (ATR): 3253, 3024, 2923, 1634, 1493, 1371, 1268, 1199, 864, 808, 757, 699, 613, 523, 389 cm⁻¹; HRMS calcd for C₁₈H₂₃N₂O⁺ [M+H]+ 283.1805 found 283.1810.

8f: ethyl 2-(2-acetamido-4-methoxyphenyl)acetate: Reaction time: 16 h. The product is a pale yellow solid. 67 mg, 53%. Mp.: 108-109 °C; Rᵣ = 0.43 (hexane:ethyl acetate = 1:2); ¹H NMR (250 MHz, DMSO-d₆): δ 9.34 (s, 1H), 7.14 (d, 1H, J = 8.4 Hz), 7.00-6.99 (m, 1H), 6.72 (dd, 1H, J₁ = 8.3 Hz, J₂ = 1.9 Hz), 4.04 (q, 2H, J = 7.0 Hz), 3.72 (s, 3H), 3.60 (s, 2H), 2.00 (s, 3H), 1.16 (t, 3H, J = 7.1 Hz); ¹³C NMR (62.5 MHz, DMSO-d₆): δ 171.2, 168.2, 158.2, 137.6, 131.5, 121.0, 111.0, 110.6, 60.1, 55.1, 36.2, 23.3, 14.1; MS (EI, 70 eV): m/z (%): 251(9[M⁺]), 208(6), 178(13), 163(94), 148(8), 136(100), 93(15), 77(9), 65(8); IR (ATR) 2919, 1728, 1655, 1495, 1255, 1025, 848, 712 cm⁻¹; HRMS calcd for C₁₃H₁₈NO⁺ [M+H]+ 252.1230 found 252.1240.

8g: ethyl 2-(2-acetamido-4-methylphenyl)acetate: Reaction time: 6 h. The product is a white solid. 210 mg, yield: 89%. Mp.: 144-146 °C; Rᵣ = 0.48 (hexane:ethyl acetate = 1:2); ¹H NMR (250 MHz, DMSO-d₆): δ 9.34 (s, 1H), 7.16-7.10 (m, 2H), 6.95 (d, 1H, J = 7.4 Hz), 4.04 (q, 2H, J = 7.1 Hz), 3.61 (s, 2H), 2.26 (s, 3H), 2.00 (s, 3H), 1.16 (t, 3H, J = 7.1 Hz); ¹³C NMR (62.5 MHz, DMSO-d₆): δ 171.0, 168.1, 136.4, 130.5, 126.4, 126.2, 126.0, 60.1, 36.7, 23.1, 20.6, 14.1; IR (ATR) 1728, 1655, 1541, 1296, 1154, 1035, 716 cm⁻¹; HRMS calcd for C₁₃H₁₈NO₃⁺ [M+H]+ 236.1281 found 236.1289.
References
NMR spectra

2a: S-methyldibenzo thiophenium triflate
2b: S-ethyldibenzothiophenium triflate:
2c: S-propyldibenzothiophenium triflate:
2d: S-phenethyldibenzothiophenium triflate:
2e: S-methyldibenzothiophenium tetrafluoroborate:
2f: S-ethyl dibenzothiophenium tetrafluoroborate:
2g: S-(2-ethoxy-2-oxoethyl)dibenzothiophenium tetrafluoroborate:
4a: 2'-methylacetanilide:
4b: 2',6'-dimethylacetanilide:
4c: 2’,5’-dimethylacetanilide:
4d: 5’-methoxy-2’-methylacetanilide:
4e: 5'-fluoro-2'-methylacetanilide:
4f: 5'-chloro-2'-methylacetnailide:
4g: 5'-bromo-2'-methylacetanilide:
4h: 2',4’-methylacetanilide:
4i: 4'-isopropyl-2'-methylacetanilide:
4j: 4’-methoxy-2’-methylacetanilide:
4k: N-mesitylacetamide:
4l: 4’-chloro-2’,5’-dimethylacetanilide:
4m: 4',5'-dimethoxy-2'-methylacetanilide:
4n: 2',5'-dimethylpivalanilide:
40: mixture of 5'-methoxy-2'-methylpivalanilide and 3'-methoxypivalanilide:
4p: N-(2,5-dimethylphenyl)benzamide:
4q: N-(2,5-dimethylphenyl)-2-phenylacetamide:
6a: 1,1-dimethyl-3-(o-tolyl)urea:
6b: *N*-((2,5-dimethylphenyl)-*N*,*N*-dimethylurea:
6c: \( N'-(5\text{-chloro-2-methyphenyl})_2N,N\text{-dimethylurea} \):
6d: 3-(2-methoxy-6-methylphenyl)-1,1-dimethylurea:
6e: \( \text{N'}-(2\text{-methylnaphtyl})-\text{N},\text{N}-\text{dimethylurea:} \)
6f: $N'$-2-(3-methylnaphtyl)-$N,N'$-dimethylurea:
6g: N-(2,5-dimethylphenyl)morpholine-4-carboxamide:
8a: 2’-ethyl-5’-methoxyacetanilide:
8b: 2'-ethyl-5'-methylacetanilide:
8c: 5’-methyl-2’-propylacetanilide:
8d: \( N'(2\text{-ethyl-5-methylphenyl})\cdot N,N\text{-dimethylurea}: \)
8e: N'-{(2-phenethyl-5-methylphenyl)-N,N-dimethylurea:}
8f: ethyl 2-(2-acetamido-4-methoxyphenyl)acetate:
8g: ethyl 2-(2-acetamido-4-methylphenyl)acetate: