SYNTHESIS OF 1,2-DICARBONYLS FROM FIVE-MEMBERED CYCLIC ENAMINES AND ARYGLYOXAL HYDRATES UNDER METAL-FREE CONDITIONS

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Abstract – An efficient and practical protocol for O₂-enabled oxidative 1,2-dicarbonylation of five-membered cyclic enamines with arylglyoxal hydrates is developed, producing 32 examples of functionalized 1,2-dicarboxyls in good to excellent yields. Notable features of this transformation include wide substrate scope, excellent yields and metal-free conditions as well as O₂ from air as the green oxidant with H₂O as sole by-product.

INTRODUCTION

1,2-Dicarbonyl functionalities are important structural moieties that occur widely in natural products and drug molecules such as licoagrodione, mansonone F, Indibulin, which contain the antimicrobial, antiproliferative, anticancer activity, respectively (Figure 1). Furthermore, 1,2-dicarbonyl compounds can serve as versatile intermediates for the construction of complex molecules.

Consequently, in the past decades, numerous synthetic methodologies for the construction of this important unit have been developed, realizing the 1,2-dicarbonylation of pyridine, indolizine, imidazotriazine and other skeletons (Figure 2). However, most of these described methods suffer from limitations such as long reaction time, metal catalysts, and stoichiometric oxidants. Therefore, there
is still a need to develop general and simple methods for the synthesis of 1,2-dicarbonyls from inexpensive starting materials and cheap sources of oxygen under metal-free conditions.

As important 1,3-bidonors, five-membered cyclic enamines have been extensively applied to the synthesis of heterocycles.13 On the other hand, arylglyoxal hydrates,14 possessing two electrophilic centers, have been constructed diverse heterocyclic skeletons by our group such as oxazoloindoles,14b pyrazolopyridines,14e naphthyridines,14f-g and azafluorenones.14h Herein, we report an efficient and practical protocol for O2-enabled oxidative 1,2-dicarbonylation of five-membered cyclic enamines with arylglyoxal hydrates as 1,2-dicarbonyl source (Figure 3). The present protocol features wide substrate scope, excellent yields and metal-free conditions as well as O2 from air as green oxidant, together with H2O as sole by-product.

**RESULTS AND DISCUSSION**

Our investigation was initiated by evaluating the reaction of 4-(phenylamino)furan-2(5H)-one 1a with 2,2-dihydroxy-1-(4-methoxyphenyl)ethanone 2a. Representative datas were summarized in Table 1.
Firstly, the reaction was tested under a variety of different solvents such as EtOH, 1,2-dichloroethane (DCE), ethyl acetate (EA), benzene, tetrahydrofuran (THF), 1,4-dioxane and MeCN. It was found that the reaction could proceed at 100 °C using EtOH as a solvent, giving the expected product 3a with a poor yield of 18% (entry 1). The use of benzene as the solvent completely suppressed the reaction process (entry 2). A higher yield was observed when exchanging EtOH for DCE (21%), EA (25%), 1,4-dioxane (34%), THF (53%) or MeCN (65%) (entries 3-7). Of these solvents, the latter MeCN gave the best result, in which a 65% yield was obtained (entry 7). Next, the reaction temperature was investigated. The higher reaction temperature is beneficial for this reaction (entries 8-10). When increasing the reaction temperature to 120 °C, the reaction gave 76% yield of 3a. Further increase in the reaction temperature to 130 °C made the reaction system slightly complex, affording a slightly decreased yield (71%, entry 10). Moreover, the identical reaction was investigated under O$_2$ (1.0 atm) conditions, but the yield of product 3a could not be improved, suggesting that O$_2$ from air is enough to oxidize hydroxyl group into carbonyl functionality. In addition, the reaction was conducted at 120 °C under conventional heating for 10 h to provide 3a in 55% yield (entry 12).

Table 1. Optimization for the Synthesis of Product 3a$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Yield/%$^{b}$</th>
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<tr>
<td>1</td>
<td>EtOH</td>
<td>100</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
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<td>100</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>THF</td>
<td>100</td>
<td>53</td>
</tr>
<tr>
<td>6</td>
<td>1,4-dioxane</td>
<td>100</td>
<td>34</td>
</tr>
<tr>
<td>7</td>
<td>MeCN</td>
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<td>110</td>
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<td>9</td>
<td>MeCN</td>
<td>120</td>
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</tr>
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<td>10</td>
<td>MeCN</td>
<td>130</td>
<td>71</td>
</tr>
<tr>
<td>11</td>
<td>MeCN</td>
<td>120</td>
<td>76$^c$</td>
</tr>
<tr>
<td>12</td>
<td>MeCN</td>
<td>120</td>
<td>55$^d$</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: all the reactions were performed with 1a (0.5 mmol), 2a (0.5 mmol), solvent (2.0 mL) in the sealed reaction tube under air conditions. $^b$Isolated yield. $^c$O$_2$ (1.0 atm) conditions. $^d$Conventional heating for 10 h.

With the established optimal conditions, we then set out to explore the scope of this reaction by examining a variety of structurally diverse 4-(arylamino)furan-2(5H)-one 1 with arylglyoxal hydrates
2. As illustrated in Scheme 1, the influence of substituents in the phenyl ring (Ar\textsuperscript{1} moiety) of 4-(arylamino)furan-2(5\textit{H})-one 1 was investigated by employing different aryl groups bearing both

![Scheme 1. Substrate Scope for Synthesis of 3a-3x](image-url)
electron-poor (such as Me) and electron-rich (such as F, Cl and Br) groups. Notably, substituents at 3 and 4 position, and dissubstituents at 3, 4 and 3, 5 positions of the aromatic ring were found to have no influence on the course of the reaction. Next, we turned our attention to investigate the electronic properties of Ar² moiety of arylglyoxal hydrates 2. Substrates 2 carrying both electron-donating groups (EDG) groups and electron-withdrawing (EWG) all worked well to provide the corresponding products 3 in moderate to excellent yields.

After our success with 1,2-dicarbonyl derivatives 3a-3x, we attempted to explore the scope of this reaction using 3-(arylamino)cyclopent-2-enone to replace 4-(arylamino)furan-2(5H)-one. To our delight, different substituents resided at the phenyl ring (Ar¹) and (Ar²) were compatible. Both electron-rich and electron-poor groups worked well to provide the desired products 3y-3bb in yields ranging from 73% to 86%. It is worth mentioning that when the Ar² is 2-thienyl, it did not hamper the reaction progress, giving the corresponding products 3cc-3ff smoothly (Scheme 2).

The structural elucidations were unambiguously determined by their IR, NMR, and HRMS spectroscopic analysis. The structures of 3m and 3t were further confirmed by X-ray diffraction analysis (Figure 4 and Figure 5).
As shown in Scheme 3, several control reactions were carried out so as to understand the mechanism of this transformation. The desired product 1-(4-methoxyphenyl)-2-(2-oxo-4-(phenylamino)-2,5-dihydrofuran-3-yl)ethane-1,2-dione 3a was not observed under Ar conditions (Scheme a), indicating that O₂ play a key role in the success of this reaction. The preformed 3-(1-hydroxy-2-(4-methoxyphenyl)-2-oxoethyl)-4-(phenylamino)furan-2(5H)-one was reacted under standard conditions, providing 3a in 76% yield (Scheme b).
Based on our above results, a plausible reaction mechanism is presented in Scheme 4. Five-membered cyclic enamine 1 is subjected with arylglyoxal hydrate 2 to give access to intermediate A, then the intermediate A was oxidized by O₂ to get product 3. The structure of intermediate A was unequivocally confirmed by X-ray diffraction analysis (Figure 6).

Scheme 4. Mechanism Hypothesis for Forming 3

![Scheme 4](image)

Figure 6. The ORTEP Drawing of Intermediate A

In order to explore whether the reaction can be applied to gram-scale, the following experiments were carried out. As shown in Figure 7, 10 mmol 4-(phenylamino)furan-2(5H)-one 1a and 10 mmol 2,2-dihydroxy-1-(4-methoxyphenyl)ethanone 2a were treated under optimal conditions, then 2.56 g 1-(4-methoxyphenyl)-2-(2-oxo-4-(phenylamino)-2,5-dihydrofuran-3-yl)ethane-1,2-dione 3a was obtained.

![Figure 7](image)
CONCLUSION

In summary, we have established a new and versatile protocol for the synthesis of various 1,2-dicarbonyl derivatives in moderate to excellent yield with a broad substrate scopes. This transformation use O2 as an ideal oxidant and produce H2O as the only by-product, which is environmentally friendly. Further investigations to understand the mechanism of this reaction and their applications in other organic reactions are ongoing in our laboratory.

EXPERIMENTAL

Microwave irradiation was carried out with Initiator 2.5 Microwave synthesizers obtained from Biotage, Uppsala, Sweden. The reaction temperatures were measured by an infrared detector during microwave heating.

Example for the synthesis of 3a: In a typical experiment procedure, 4-(phenylamino)furan-2(5H)-one 1a (0.5 mmol) and 2,2-dihydroxy-1-(4-methoxyphenyl)ethanone 2a (0.5 mmol) were introduced in a 30-mL reaction vial, then MeCN (2.0 mL) was successively added. Subsequently, the mixture was stirred at 120 °C under microwave radiation condition for 30 min. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and diluted with cold water, then extracted with EtOAc. The extract was washed with 10% aq. Na2S2O3 solution, dried over anhydrous Na2SO4 and evaporation. The residue was purified by column chromatography to afford the pure product 3a.

1-(4-Methoxyphenyl)-2-(2-oxo-4-(phenylamino)-2,5-dihydrofuran-3-yl)ethane-1,2-dione (3a) A yellow solid; 76% yield; Mp 205-207 °C; IR (KBr, ν, cm⁻¹): 3197, 1755, 1683, 1633, 1599, 1422, 1379, 1264, 1156; ¹H NMR (400 MHz, DMSO-d6) (δ, ppm): 11.32 (s, 1H, NH), 7.84 (d, 2H, J = 8.8 Hz, ArH), 7.50-7.47 (m, 4H, ArH), 7.41-7.37 (m, 1H, ArH), 7.13 (d, 2H, J = 8.8 Hz, ArH), 5.16 (s, 2H, CH2), 3.88 (s, 3H, OCH3); ¹³C NMR (100 MHz, DMSO-d6) (δ, ppm): 192.1, 190.5, 173.2, 170.5, 164.6, 137.2, 131.9, 130.0, 128.1, 126.1, 124.5, 115.0, 94.9, 66.8, 56.2; HRMS (ESI): m/z calcd for: C₁₉H₁₄NO₅, 336.0872 [M-H]⁻; found: 336.0876.

1-(4-((4-Fluorophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)-2-phenylethane-1,2-dione (3b) A pink solid; 75% yield; Mp 235-236 °C; IR (KBr, ν, cm⁻¹): 3189, 1758, 1645, 1637, 1629, 1510, 1255; ¹H NMR (400 MHz, DMSO-d6) (δ, ppm): 11.32 (s, 1H, NH), 7.88 (d, 2H, J = 7.2 Hz, ArH), 7.75 (t, 1H, J = 7.2 Hz, ArH), 7.62 (t, 2H, J = 7.6 Hz, ArH), 7.57-7.54 (m, 2H, ArH), 7.34 (t, 2H, J = 8.8 Hz, ArH), 5.09 (s, 2H, CH2); ¹³C NMR (100 MHz, DMSO-d6) (δ, ppm): 193.7, 190.0, 173.6, 170.8, 161.5 (¹JC=CF = 243.6 Hz), 135.0, 133.6 (¹JC=CF = 2.9 Hz), 133.2, 129.6, 129.5, 127.4 (²JC=CF = 8.8 Hz), 116.7 (²JC=CF = 22.7 Hz), 94.9, 66.8; HRMS (ESI): m/z calcd for: C₁₈H₁₁FNO₄, 324.0672 [M-H]⁻; found: 324.0676.

1-(4-((4-Fluorophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)-2-(p-tolyl)ethane-1,2-dione (3c) A pale yellow solid; 78% yield; Mp 249-250 °C; IR (KBr, ν, cm⁻¹): 3232, 1758, 1672, 1636, 1509, 1387, 1263,
1160; $^1$H NMR (400 MHz, DMSO-$d_6$) ($\delta$, ppm): 11.30 (s, 1H, NH), 7.77 (d, 2H, $J = 8.4$ Hz, ArH), 7.57-7.54 (m, 2H, ArH), 7.42 (d, 2H, $J = 8.0$ Hz, ArH), 7.34 (t, 2H, $J = 8.8$ Hz, ArH), 5.08 (s, 2H, CH$_2$), 2.42 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, DMSO-$d_6$) ($\delta$, ppm): 193.3, 190.2, 173.5, 170.7, 161.5 ($^1$J$_{CF} = 243.6$ Hz), 145.7, 133.6 ($^3$J$_{CF} = 2.8$ Hz), 130.8, 130.2, 129.6, 127.4 ($^3$J$_{CF} = 8.8$ Hz), 116.7 ($^2$J$_{CF} = 22.7$ Hz), 94.9, 66.7, 21.8; HRMS (ESI): $m/z$ calcd for: C$_{19}$H$_{13}$FNO$_4$, 338.0829 [M-H]$^-$; found: 338.0831.

1-(4-((4-Fluorophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)-2-(4-methoxyphenyl)ethane-1,2-dione (3d) A pale yellow solid; 74% yield; Mp 205-206 °C; IR (KBr, v, cm$^{-1}$): 3236, 1766, 1668, 1651, 1516, 1392, 1263, 1151; $^1$H NMR (400 MHz, DMSO-$d_6$) ($\delta$, ppm): 11.29 (s, 1H, NH), 7.83 (d, 2H, $J = 8.8$ Hz, ArH), 7.57-7.53 (m, 2H, ArH), 7.33 (t, 2H, $J = 8.8$ Hz, ArH), 7.13 (d, 2H, $J = 7.2$ Hz, ArH), 5.08 (s, 2H, CH$_2$), 3.88 (s, 3H, OCH$_3$); $^{13}$C NMR (100 MHz, DMSO-$d_6$) ($\delta$, ppm): 192.2, 190.4, 173.5, 170.6, 164.6, 161.4 ($^1$J$_{CF} = 243.5$ Hz), 133.6 ($^3$J$_{CF} = 2.9$ Hz), 131.9, 127.3 ($^3$J$_{CF} = 8.7$ Hz), 126.1, 116.7 ($^2$J$_{CF} = 22.7$ Hz), 115.0, 94.9, 66.7, 56.2; HRMS (ESI): $m/z$ calcd for: C$_{19}$H$_{13}$FNO$_4$, 338.0778 [M-H]$^-$; found: 338.0779.

1-(4-((4-Chlorophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)-2-phenylethane-1,2-dione (3e) A white solid; 82% yield; Mp 218-220 °C; IR (KBr, v, cm$^{-1}$): 3225, 1757, 1670, 1636, 1621, 1487, 1373, 1258, 1158; $^1$H NMR (400 MHz, DMSO-$d_6$) ($\delta$, ppm): 11.35 (s, 1H, NH), 7.88 (d, 2H, $J = 7.2$ Hz, ArH), 7.75 (t, 1H, $J = 7.6$ Hz, ArH), 7.61 (t, 1H, $J = 8.0$ Hz, ArH), 7.57-7.52 (m, 4H, ArH), 5.15 (s, 2H, CH$_2$); $^{13}$C NMR (100 MHz, DMSO-$d_6$) ($\delta$, ppm): 193.7, 190.1, 173.3, 170.7, 136.2, 135.0, 133.1, 132.5, 129.9, 129.6, 129.5, 126.7, 95.2, 66.9; HRMS (ESI): $m/z$ calcd for: C$_{18}$H$_{11}$ClNO$_4$, 340.0377 [M-H]$^-$; found: 340.0381.

1-(4-((4-Chlorophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)-2-(3,4-dichlorophenyl)ethane-1,2-dione (3f) A pale yellow solid; 71% yield; Mp 230-232 °C; IR (KBr, v, cm$^{-1}$): 3238, 1753, 1689, 1656, 1639, 1517, 1162; $^1$H NMR (400 MHz, DMSO-$d_6$) ($\delta$, ppm): 11.38 (s, 1H, NH), 8.04 (d, 1H, $J = 1.6$ Hz, ArH), 7.91 (d, 1H, $J = 8.4$ Hz, ArH), 7.85-7.83 (m, 1H, ArH), 7.57-7.51 (m, 4H, ArH), 5.15 (s, 2H, CH$_2$); $^{13}$C NMR (100 MHz, DMSO-$d_6$) ($\delta$, ppm): 191.7, 188.5, 173.4, 170.8, 138.1, 136.1, 133.2, 132.9, 132.6, 132.3, 130.7, 129.9, 129.4, 126.7, 95.1, 67.2; HRMS (ESI): $m/z$ calcd for: C$_{18}$H$_{12}$Cl$_2$NO$_4$, 407.9597 [M-H]$^-$; found: 407.9599.

1-(4-Chlorophenyl)-2-(4-((3,5-dichlorophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)ethane-1,2-dione (3g) A white solid; 75% yield; Mp 225-227 °C; IR (KBr, v, cm$^{-1}$): 3216, 1768, 1651, 1641, 1627, 1518, 1170; $^1$H NMR (400 MHz, DMSO-$d_6$) ($\delta$, ppm): 11.37 (s, 1H, NH), 7.87 (d, 2H, $J = 8.4$ Hz, ArH), 7.71-7.65 (m, 5H, ArH), 5.23 (s, 2H, CH$_2$); $^{13}$C NMR (100 MHz, DMSO-$d_6$) ($\delta$, ppm): 192.5, 189.5, 173.4, 170.6, 140.1, 139.6, 135.0, 131.7, 131.2, 129.9, 127.8, 124.0, 95.7, 67.1; HRMS (ESI): $m/z$ calcd for: C$_{18}$H$_{12}$Cl$_2$NO$_4$, 407.9597 [M-H]$^-$; found: 407.9600.

1-(4-((3,5-Dichlorophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)-2-(p-toly)ethane-1,2-dione (3h) A white solid; 80% yield; Mp 216-218 °C; IR (KBr, v, cm$^{-1}$): 3240, 1759, 1676, 1643, 1628, 1523, 1167; $^1$H
NMR (400 MHz, DMSO-d$_6$) ($\delta$, ppm): 11.33 (s, 1H, NH), 7.75 (d, 2H, $J = 8.0$ Hz, ArH), 7.66 (s, 3H, ArH), 7.42 (d, 2H, $J = 7.6$ Hz, ArH), 5.22 (s, 2H, CH$_2$), 2.42 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, DMSO-d$_6$) ($\delta$, ppm): 193.1, 190.4, 173.3, 170.5, 145.8, 139.6, 135.0, 130.6, 130.2, 129.6, 127.7, 123.9, 95.7, 67.0, 21.8; HRMS (ESI): $m/z$ calc for: C$_{18}$H$_{12}$Cl$_2$NO$_4$, 388.0144 [M-H]; found: 388.0147.

1-(4-((4-Bromophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)-2-phenylethane-1,2-dione (3i) A brown solid; 78% yield; Mp 190-191 °C; IR (KBr, $\nu$, cm$^{-1}$): 3233, 1749, 1677, 1646, 1628, 1507, 1158; $^1$H NMR (400 MHz, DMSO-d$_6$) ($\delta$, ppm): 11.34 (s, 1H, NH), 7.89-7.87 (m, 2H, ArH), 7.75 (t, 1H, $J = 7.6$ Hz, ArH), 7.69 (d, 2H, $J = 8.8$ Hz, ArH), 7.61 (t, 2H, $J = 7.6$ Hz, ArH), 7.47 (d, 2H, $J = 8.8$ Hz, ArH), 5.16 (s, 2H, CH$_2$); $^{13}$C NMR (100 MHz, DMSO-d$_6$) ($\delta$, ppm): 193.7, 190.1, 173.2, 170.6, 136.6, 135.0, 133.1, 132.8, 129.6, 129.5, 126.9, 19.5, 67.0; HRMS (ESI): $m/z$ calc for: C$_{18}$H$_{11}$BrNO$_4$, 383.9872 [M-H]; found: 383.9873.

1-(4-((4-Bromophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)-2-(4-fluorophenyl)ethane-1,2-dione (3j) A pale yellow solid; 73% yield; Mp 198-200 °C; IR (KBr, $\nu$, cm$^{-1}$): 3196, 1752, 1676, 1639, 1596, 1504, 1390, 1259, 1152; $^1$H NMR (400 MHz, DMSO-d$_6$) ($\delta$, ppm): 11.35 (s, 1H, NH), 7.98-7.94 (m, 2H, ArH), 7.69 (d, 2H, $J = 8.8$ Hz, ArH), 7.45 (t, 4H, $J = 8.8$ Hz, ArH), 5.15 (s, 2H, CH$_2$); $^{13}$C NMR (100 MHz, DMSO-d$_6$) ($\delta$, ppm): 192.2, 189.7, 173.3, 170.7, 166.2 ($^3$J$_{CF}$ = 252.4 Hz), 136.6, 132.8, 132.5 ($^3$J$_{CF}$ = 9.9 Hz), 129.9 ($^3$J$_{CF}$ = 2.6 Hz), 126.9, 120.9, 116.9 ($^3$J$_{CF}$ = 22.1 Hz), 95.2, 67.0; HRMS (ESI): $m/z$ calc for: C$_{18}$H$_{10}$BrFNO$_4$, 401.9777 [M-H]; found: 401.9779.

1-(4-((4-Bromophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)-2-(4-chlorophenyl)ethane-1,2-dione (3k) A pale yellow solid; 82% yield; Mp 202-204 °C; IR (KBr, $\nu$, cm$^{-1}$): 3290, 1771, 1695, 1646, 1628, 1579, 1388; $^1$H NMR (400 MHz, DMSO-d$_6$) ($\delta$, ppm): 11.35 (s, 1H, NH), 7.89 (d, 2H, $J = 8.4$ Hz, ArH), 7.70 (d, 2H, $J = 3.2$ Hz, ArH), 7.68 (d, 2H, $J = 3.6$ Hz, ArH), 7.46 (d, 2H, $J = 8.8$ Hz, ArH), 5.15 (s, 2H, CH$_2$); $^{13}$C NMR (100 MHz, DMSO-d$_6$) ($\delta$, ppm): 192.6, 189.4, 173.3, 170.7, 140.0, 136.6, 132.8, 131.8, 131.2, 129.9, 127.0, 121.0, 95.2, 67.0; HRMS (ESI): $m/z$ calc for: C$_{18}$H$_{10}$BrClNO$_4$, 417.9482 [M-H]; found: 417.9485.

1-(4-Bromophenyl)-2-(4-((4-bromophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)ethane-1,2-dione (3l) A yellow solid; 84% yield; Mp 190-192 °C; IR (KBr, $\nu$, cm$^{-1}$): 3193, 1759, 1685, 1635, 1620, 1587, 1398, 1253, 1154; $^1$H NMR (400 MHz, DMSO-d$_6$) ($\delta$, ppm): 11.36 (s, 1H, NH), 7.85-7.79 (m, 4H, ArH), 7.68 (d, 2H, $J = 8.8$ Hz, ArH), 7.46 (d, 2H, $J = 8.8$ Hz, ArH), 5.16 (s, 2H, CH$_2$); $^{13}$C NMR (100 MHz, DMSO-d$_6$) ($\delta$, ppm): 192.9, 189.4, 173.3, 170.7, 136.6, 132.9, 132.8, 132.1, 131.3, 129.3, 127.0, 121.0, 95.2, 67.1; HRMS (ESI): $m/z$ calc for: C$_{18}$H$_{10}$Br$_2$NO$_4$, 463.8956 [M-H]; found: 463.8959.

1-(4-((4-Bromophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)-2-(p-tolyl)ethane-1,2-dione (3m) A white solid; 78% yield; Mp 246-247 °C; IR (KBr, $\nu$, cm$^{-1}$): 3213, 1760, 1671, 1632, 1572, 1487, 1261, 1158; $^1$H NMR (400 MHz, DMSO-d$_6$) ($\delta$, ppm): 11.32 (s, 1H, NH), 7.77 (d, 2H, $J = 8.0$ Hz, ArH), 7.68 (d,
2H, J = 8.4 Hz, ArH), 7.46 (d, 2H, J = 8.8 Hz, ArH), 7.41 (d, 2H, J = 8.0 Hz, ArH), 5.15 (s, 2H, CH2), 2.42 (s, 3H, CH3); 13C NMR (100 MHz, DMSO-d6) (δ, ppm): 193.2, 190.3, 173.2, 170.5, 145.7, 136.7, 132.8, 130.7, 130.2, 129.6, 126.9, 120.9, 95.2, 66.9, 21.8; HRMS (ESI): m/z calcd for: C19H13BrNO4, 398.0028 [M-H]; found: 398.0030.

1-(4-((3-Bromophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)-2-phenylethane-1,2-dione (3n) A yellow solid; 80% yield; Mp 208-209 °C; IR (KBr, ν, cm⁻¹): 3232, 1766, 1679, 1651, 1574, 1482, 1267, 1163; 1H NMR (400 MHz, DMSO-d6) (δ, ppm): 11.35 (s, 1H, NH), 7.87 (d, 2H, J = 7.6 Hz, ArH), 7.77-7.73 (m, 2H, ArH), 7.64-7.59 (m, 3H, ArH), 7.53 (d, 1H, J = 8.0 Hz, ArH), 7.45 (t, 1H, J = 8.0 Hz, ArH), 5.18 (s, 2H, CH2); 13C NMR (100 MHz, DMSO-d6) (δ, ppm): 193.6, 190.1, 173.3, 170.6, 138.8, 135.0, 133.1, 131.8, 131.0, 129.6, 129.5, 127.7, 123.9, 122.3, 95.3, 67.0; HRMS (ESI): m/z calcd for: C18H11BrNO4, 383.9872 [M-H]; found: 383.9875.

1-(4-((3-Bromophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)-2-(4-fluorophenyl)ethane-1,2-dione (3o) A yellow solid; 74% yield; Mp 179-180 °C; IR (KBr, ν, cm⁻¹): 3232, 1768, 1674, 1630, 1578, 1503, 1260; 1H NMR (400 MHz, DMSO-d6) (δ, ppm): 11.36 (s, 1H, NH), 7.97-7.94 (m, 2H, ArH), 7.77 (s, 1H, ArH), 7.60 (d, 1H, J = 8.0 Hz, ArH), 7.52 (d, 1H, J = 8.0 Hz, ArH), 7.48-7.43 (m, 3H, ArH), 5.18 (s, 2H, CH2); 13C NMR (100 MHz, DMSO-d6) (δ, ppm): 192.2, 189.7, 173.4, 170.6, 166.2 (1JC = 252.6 Hz), 138.7, 132.5 (1JC = 9.9 Hz), 131.8, 131.0, 129.9 (1JC = 2.7 Hz), 127.7, 123.9, 122.3, 116.9 (1JC = 22.3 Hz), 95.3, 67.0; HRMS (ESI): m/z calcd for: C18H10BrFNO4, 401.9777 [M-H]; found: 401.9780.

1-(4-((3-Bromophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)-2-(p-tolyl)ethane-1,2-dione (3p) A purple solid; 72% yield; Mp 186-188 °C; IR (KBr, ν, cm⁻¹): 3231, 1749, 1689, 1642, 1578, 1479, 1252, 1151; 1H NMR (400 MHz, DMSO-d6) (δ, ppm): 11.32 (s, 1H, NH), 7.76 (d, 3H, J = 8.0 Hz, ArH), 7.59 (d, 1H, J = 8.0 Hz, ArH), 7.52 (d, 1H, J = 8.4 Hz, ArH), 7.47-7.41 (m, 3H, ArH), 5.18 (s, 2H, CH2), 2.42 (s, 3H, CH3); 13C NMR (100 MHz, DMSO-d6) (δ, ppm): 193.2, 190.4, 173.3, 170.5, 145.8, 138.8, 131.8, 131.0, 130.7, 130.2, 129.6, 127.7, 123.8, 122.3, 95.3, 66.9, 21.8; HRMS (ESI): m/z calcd for: C19H13BrNO4, 398.0028 [M-H]; found: 398.0031.

1-(4-((3-Bromophenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)-2-(4-methoxyphenyl)ethane-1,2-dione (3q) A pale yellow solid; 77% yield; Mp 175-177 °C; IR (KBr, ν, cm⁻¹): 3245, 1737, 1683, 1622, 1572, 1474, 1254, 1154; 1H NMR (400 MHz, DMSO-d6) (δ, ppm): 11.31 (s, 1H, NH), 7.82 (d, 2H, J = 8.8 Hz, ArH), 7.77 (s, 1H, ArH), 7.59 (d, 1H, J = 8.0 Hz, ArH), 7.52 (d, 1H, J = 7.6 Hz, ArH), 7.44 (t, 1H, J = 8.0 Hz, ArH), 7.13 (d, 2H, J = 8.8 Hz, ArH), 5.17 (s, 2H, CH2), 3.88 (s, 3H, OCH3); 13C NMR (100 MHz, DMSO-d6) (δ, ppm): 192.1, 190.5, 173.3, 170.4, 164.6, 138.9, 131.9, 131.7, 130.9, 127.6, 126.1, 123.7, 122.3, 115.0, 95.4, 66.8, 56.2; HRMS (ESI): m/z calcd for: C19H13BrNO4, 413.9977 [M-H]; found: 413.9980.

1-(4-((3-Bromo-4-methylphenyl)amino)-2-oxo-2,5-dihydrofuran-3-yl)-2-(4-fluorophenyl)ethane-1,2-
dione (3r) A white solid; 75% yield; Mp 208-209 °C; IR (KBr, ν, cm⁻¹): 3196, 1749, 1673, 1623, 1600, 1557, 1261; ¹H NMR (400 MHz, DMSO-d₆) (δ, ppm): 11.31 (s, 1H, NH), 7.97-7.94 (m, 2H, ArH), 7.77 (d, 1H, J = 1.6 Hz, ArH), 7.47-7.43 (m, 4H, ArH), 5.14 (s, 2H, CH₂), 2.38 (s, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-d₆) (δ, ppm): 192.2, 189.6, 173.4, 170.7, 166.2 (¹JC = 252.4 Hz), 137.5, 136.2, 132.5 (¹JCₐ = 9.8 Hz), 132.0, 129.9 (¹JCₐ = 2.7 Hz), 128.4, 124.6, 124.1, 116.9 (¹JCₐ = 22.2 Hz), 95.1, 66.9, 22.4; HRMS (ESI): m/z calcd for: C₁₉H₁₂BrFNO₄, 415.9934 [M-H]; found: 415.9936.

1-(4-{(3-Bromo-4-methylphenylamino)-2-oxo-2,5-dihydrofuran-3-yl}-2-(4-methoxyphenyl)ethane-1,2-dione (3s) A pale yellow solid; 79% yield; Mp 231-233 °C; IR (KBr, ν, cm⁻¹): 3188, 1756, 1665, 1599, 1476, 1355, 1254, 1160; ¹H NMR (400 MHz, DMSO-d₆) (δ, ppm): 11.27 (s, 1H, NH), 7.83 (d, 2H, J = 8.8 Hz, ArH), 7.77 (d, 1H, J = 1.6 Hz, ArH), 7.47-7.41 (m, 2H, ArH), 7.13 (d, 2H, J = 8.8 Hz, ArH), 5.14 (s, 2H, CH₂), 3.88 (s, 3H, OCH₃), 2.38 (s, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-d₆) (δ, ppm): 192.1, 190.5, 173.3, 170.5, 164.6, 137.4, 136.3, 132.0, 131.9, 128.3, 126.1, 124.6, 124.0, 115.0, 95.1, 66.7, 56.2, 22.4; HRMS (ESI): m/z calcd for: C₂₀H₁₅BrNO₅, 428.0134 [M-H]; found: 428.0138.

1-(2-Oxo-4-{(p-tolylamino)-2,5-dihydrofuran-3-yl}-2-phenylethane-1,2-dione (3t) A yellow solid; 82% yield; Mp 241-243 °C; IR (KBr, ν, cm⁻¹): 3238, 1767, 1688, 1630, 1595, 1398, 1246, 1134; ¹H NMR (400 MHz, DMSO-d₆) (δ, ppm): 11.29 (s, 1H, NH), 7.88-7.86 (m, 2H, ArH), 7.74 (t, 1H, J = 7.6 Hz, ArH), 7.61 (t, 2H, J = 8.0 Hz, ArH), 7.37 (d, 2H, J = 8.4 Hz, ArH), 7.29 (d, 2H, J = 8.4 Hz, ArH), 5.13 (s, 2H, CH₂), 2.35 (s, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-d₆) (δ, ppm): 193.7, 190.0, 173.2, 170.7, 137.7, 134.9, 134.7, 133.2, 130.4, 129.6, 129.5, 124.5, 124.4, 94.7, 66.9, 21.0; HRMS (ESI): m/z calcd for: C₁₉H₁₄FNO₄, 320.0923 [M-H]; found: 320.0926.

1-(4-Fluorophenyl)-2-(2-oxo-4-{(p-tolylamino)-2,5-dihydrofuran-3-yl)ethane-1,2-dione (3u) A yellow solid; 77% yield; Mp 193-195 °C; IR (KBr, ν, cm⁻¹): 3234, 1759, 1686, 1635, 1595, 1398, 1254, 1154; ¹H NMR (400 MHz, DMSO-d₆) (δ, ppm): 11.30 (s, 1H, NH), 7.98-7.94 (m, 2H, ArH), 7.45 (t, 2H, J = 8.8 Hz, ArH), 7.37 (d, 2H, J = 8.4 Hz, ArH), 7.29 (d, 2H, J = 8.4 Hz, ArH), 5.13 (s, 2H, CH₂), 2.35 (s, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-d₆) (δ, ppm): 192.3, 189.5, 173.2, 170.7, 166.1 (¹JC = 252.3 Hz), 137.8, 134.7, 132.5 (¹JCₐ = 9.8 Hz), 130.4, 130.0 (¹JCₐ = 2.7 Hz), 124.5, 116.9 (¹JCₐ = 22.2 Hz), 94.7, 66.9, 21.0; HRMS (ESI): m/z calcd for: C₁₉H₁₃FNO₄, 338.0829 [M-H]; found: 338.0830.

1-(4-Chlorophenyl)-2-(2-oxo-4-{(p-tolylamino)-2,5-dihydrofuran-3-yl)ethane-1,2-dione (3v) A yellow solid; 78% yield; Mp 214-215 °C; IR (KBr, ν, cm⁻¹): 3237, 1769, 1663, 1621, 1562, 1391, 1238, 1169; ¹H NMR (400 MHz, DMSO-d₆) (δ, ppm): 11.31 (s, 1H, NH), 7.89 (d, 2H, J = 8.4 Hz, ArH), 7.69 (d, 2H, J = 8.4 Hz, ArH), 7.37 (d, 2H, J = 8.4 Hz, ArH), 7.29 (d, 2H, J = 8.4 Hz, ArH), 5.13 (s, 2H, CH₂), 2.35 (s, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-d₆) (δ, ppm): 192.7, 189.3, 173.2, 170.8, 139.9, 137.8, 134.7, 131.9, 131.3, 130.4, 129.9, 124.5, 94.7, 67.0, 21.0; HRMS (ESI): m/z calcd for: C₁₉H₁₃ClNO₄, 354.0533 [M-H]; found: 354.0533.
1-(3,4-Dichlorophenyl)-2-(2-oxo-4-(p-tolylamino)-2,5-dihydrofuran-3-yl)ethane-1,2-dione (3w) A white solid; 71% yield; Mp 186-187 °C; IR (KBr, ν, cm⁻¹): 3213, 1759, 1674, 1633, 1604, 1573, 1388, 1238, 1162; ¹H NMR (400 MHz, DMSO-d₆) (δ, ppm): 11.32 (s, 1H, NH), 8.04 (d, 1H, J = 2.0 Hz, ArH), 7.91 (d, 1H, J = 8.4 Hz, ArH), 7.85-7.83 (m, 1H, ArH), 7.37 (d, 2H, J = 8.4 Hz, ArH), 7.29 (d, 2H, J = 8.4 Hz, ArH), 5.13 (s, 2H, CH₂), 2.35 (s, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-d₆) (δ, ppm): 191.7, 188.4, 173.3, 170.9, 138.0, 137.9, 134.7, 133.3, 132.9, 132.3, 130.7, 130.4, 129.4, 124.5, 94.7, 67.1, 21.0; HRMS (ESI): m/z calcd for: C₁₉H₁₁₂Cl₂NO₄, 388.0144 [M-H]⁻; found: 388.0146.

1-(2-Oxo-4-(p-tolylamino)-2,5-dihydrofuran-3-yl)-2-(p-tolyl)ethane-1,2-dione (3x) A brown solid; 84% yield; Mp 203-205 °C; IR (KBr, ν, cm⁻¹): 3227, 1761, 1682, 1651, 1513, 1376, 1241, 1160; ¹H NMR (400 MHz, DMSO-d₆) (δ, ppm): 11.28 (s, 1H, NH), 7.76 (d, 2H, J = 8.4 Hz, ArH), 7.41 (d, 2H, J = 8.0 Hz, ArH), 7.37 (d, 2H, J = 8.4 Hz, ArH), 7.29 (d, 2H, J = 8.4 Hz, ArH), 5.12 (s, 2H, CH₂), 2.42 (s, 3H, CH₃), 2.35 (s, 3H, CH₃); ¹³C NMR (100 MHz, DMSO-d₆) (δ, ppm): 193.3, 190.2, 173.2, 170.6, 145.7, 137.7, 134.7, 130.8, 130.4, 129.1, 126.4, 94.7, 66.8, 21.8, 21.0; HRMS (ESI): m/z calcd for: C₂₀H₁₈NO₄, 334.1080 [M-H]⁻; found: 334.1082.

1-(2-(3,5-Dichlorophenyl) amino)-5-oxocyclopent-1-en-1-yl)-2-(p-tolyl)ethane-1,2-dione (3y) A brown solid; 78% yield; Mp 192-194 °C; IR (KBr, ν, cm⁻¹): 3275, 1759, 1666, 1598, 1567, 1513, 1372, 1318; ¹H NMR (400 MHz, DMSO-d₆) (δ, ppm): 11.41 (s, 1H, NH), 7.71-7.67 (m, 5H, ArH), 7.39 (d, 2H, J = 8.0 Hz, ArH), 2.97-2.94 (m, 2H, CH₂), 2.41 (s, 3H, CH₃), 2.30-2.27 (m, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-d₆) (δ, ppm): 199.9, 193.7, 191.3, 181.6, 145.2, 139.9, 134.8, 131.0, 130.0, 129.4, 127.6, 124.9, 110.8, 33.3, 26.8, 21.8; HRMS (ESI): m/z calcd for: C₂₀H₁₄BrNO₃, 386.0351 [M-H]⁻; found: 386.0355.

1-(4-Bromophenyl)-2-(5-oxo-2-(p-tolylamino)cyclopent-1-en-1-yl)ethane-1,2-dione (3z) A brown solid; 77% yield; Mp 185-187 °C; IR (KBr, ν, cm⁻¹): 3188, 1731, 1748, 1704, 1692, 1682, 1601, 1583, 1565, 1516, 1472, 1417; ¹H NMR (400 MHz, DMSO-d₆) (δ, ppm): 11.40 (s, 1H, NH), 7.81 (d, 2H, J = 8.4 Hz, ArH), 7.75 (d, 2H, J = 8.0 Hz, ArH), 7.39 (d, 2H, J = 8.4 Hz, ArH), 7.30 (d, 2H, J = 8.0 Hz, ArH), 2.89-2.88 (m, 2H, CH₂), 2.35 (s, 3H, CH₃), 2.30-2.27 (m, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-d₆) (δ, ppm): 199.9, 193.4, 190.0, 181.4, 137.6, 134.8, 132.7, 132.6, 131.1, 130.2, 128.7, 125.2, 110.0, 33.3, 26.9, 21.1; HRMS (ESI): m/z calcd for: C₂₀H₁₅BrNO₃, 396.0238 [M-H]⁻; found: 396.0239.

1-(2-((4-Methoxyphenyl)amino)-5-oxocyclopent-1-en-1-yl)-2-phenylethane-1,2-dione (3aa) A brown solid; 82% yield; Mp 188-190 °C; IR (KBr, ν, cm⁻¹): 3218, 1697, 1651, 1606, 1553, 1521, 1401, 1373, 1316; ¹H NMR (400 MHz, DMSO-d₆) (δ, ppm): 11.34 (s, 1H, NH), 7.82 (d, 2H, J = 7.2 Hz, ArH), 7.70 (t, 1H, J = 6.8 Hz, ArH), 7.58 (t, 2H, J = 7.2 Hz, ArH), 7.44 (d, 2H, J = 8.4 Hz, ArH), 7.05 (d, 2H, J = 8.4 Hz, ArH), 3.81 (s, 3H, OCH₃), 2.84 (s, 2H, CH₂), 2.27 (s, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-d₆) (δ, ppm): 199.8, 194.3, 190.7, 181.6, 158.9, 134.5, 133.6, 130.2, 129.4, 129.3, 127.0, 114.9, 109.9, 55.9, 33.3,
1-(2-((4-Methoxyphenyl)amino)-5-oxocyclopent-1-en-1-yl)-2-(p-toly)ethane-1,2-dione (3bb) A brown solid; 86% yield; Mp 173-175 °C; IR (KBr, ν, cm⁻¹): 3227, 1693, 1677, 1618, 1599, 1569, 1514, 1479, 1424, 1382, 1321; ¹H NMR (400 MHz, DMSO-δ₆) (δ, ppm): 8.15 (s, 1H, NH), 7.14 (d, 2H, J = 8.8 Hz, ArH), 7.44 (d, 2H, J = 8.8 Hz, ArH), 7.78 (d, 2H, J = 8.0 Hz, ArH), 7.38 (d, 2H, J = 8.8 Hz, ArH), 3.81 (s, 3H, OCH₃), 2.85-2.83 (m, 2H, CH₂), 2.04 (s, 3H, CH₃), 2.28-2.25 (m, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-δ₆) (δ, ppm): 199.7, 193.9, 190.9, 181.6, 158.9, 145.1, 131.2, 130.2, 130.0, 129.4, 126.9, 114.9, 109.9, 55.9, 33.3, 26.6, 21.8; HRMS (ESI): m/z calcd for: C₂₁H₁₈NO₄, 348.1236 [M-H]⁻; found: 348.1237.

1-(5-Oxo-2-(phenylamino)cyclopent-1-en-1-yl)-2-(thiophen-2-yl)ethane-1,2-dione (3ce) A brown solid; 73% yield; Mp 170-172 °C; IR (KBr, ν, cm⁻¹): 3275, 1760, 1698, 1667, 1597, 1557, 1513, 1413, 1373, 1342, 1318; ¹H NMR (400 MHz, DMSO-δ₆) (δ, ppm): 11.45 (s, 1H, NH), 8.15 (d, 1H, J = 4.4 Hz, ArH), 7.66 (d, 1H, J = 3.2 Hz, ArH), 7.51 (m, 4H, J = 4.0 Hz, ArH), 7.42-7.39 (m, 1H, ArH), 7.23 (t, 1H, J = 4.0 Hz, ArH), 7.30-7.20 (m, 2H, CH₂), 2.31-2.28 (m, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-δ₆) (δ, ppm): 199.5, 188.8, 186.8, 181.8, 140.4, 137.4, 136.6, 135.8, 129.8, 129.4, 128.0, 125.4, 109.5, 33.5, 26.8; HRMS (ESI): m/z calcd for: C₁₇H₁₂NO₂S, 310.0538 [M-H]⁻; found: 310.0539.

1-(2-((4-Chlorophenyl)amino)-5-oxocyclopent-1-en-1-yl)-2-(thiophen-2-yl)ethane-1,2-dione (3dd) A white solid; 75% yield; Mp 172-174 °C; IR (KBr, ν, cm⁻¹): 3217, 1752, 1735, 1684, 1652, 1611, 1567, 1513, 1491, 1475, 1410, 1355, 1321; ¹H NMR (400 MHz, DMSO-δ₆) (δ, ppm): 11.41 (s, 1H, NH), 8.16-8.14 (m, 1H, ArH), 7.66-7.65 (m, 1H, ArH), 7.58-7.53 (m, 4H, ArH), 7.28-7.26 (m, 1H, ArH), 2.90-2.87 (m, 2H, CH₂), 2.31-2.28 (m, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-δ₆) (δ, ppm): 199.5, 188.8, 186.8, 181.8, 140.3, 136.6, 136.4, 135.8, 132.4, 129.7, 129.4, 127.5, 109.8, 33.4, 26.8; HRMS (ESI): m/z calcd for: C₁₇H₁₁ClNO₂S, 344.0148 [M-H]⁻; found: 344.0149.

1-(5-Oxo-2-(p-tolylamino)cyclopent-1-en-1-yl)-2-(thiophen-2-yl)ethane-1,2-dione (3ee) A brown solid; 75% yield; Mp 175-177 °C; IR (KBr, ν, cm⁻¹): 3223, 1680, 1655, 1619, 1570, 1511, 1474, 1410, 1355, 1320; ¹H NMR (400 MHz, DMSO-δ₆) (δ, ppm): 11.39 (s, 1H, NH), 8.14 (d, 1H, J = 4.4 Hz, ArH), 7.66 (d, 1H, J = 2.8 Hz, ArH), 7.39 (d, 2H, J = 8.4 Hz, ArH), 7.30 (d, 2H, J = 8.0 Hz, ArH), 7.27 (t, 1H, J = 4.0 Hz, ArH), 7.30-0.87 (m, 2H, CH₂), 2.36 (s, 3H, CH₃), 2.30-2.27 (m, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-δ₆) (δ, ppm): 199.4, 188.7, 186.8, 181.8, 140.4, 137.5, 136.5, 135.8, 134.9, 130.3, 129.4, 125.2, 109.4, 33.5, 26.7, 21.1; HRMS (ESI): m/z calcd for: C₁₈H₁₄NO₃S, 324.0695 [M-H]⁻; found: 324.0697.

1-(2-((4-Methoxyphenyl)amino)-5-oxocyclopent-1-en-1-yl)-2-(thiophen-2-yl)ethane-1,2-dione (3ff) A brown solid; 74% yield; Mp 163-165 °C; IR (KBr, ν, cm⁻¹): 3282, 1713, 1681, 1589, 1576, 1528, 1376, 1323; ¹H NMR (400 MHz, DMSO-δ₆) (δ, ppm): 11.31 (s, 1H, NH), 8.14 (d, 1H, J = 4.8 Hz, ArH), 7.65 (d, 1H, J = 3.2 Hz, ArH), 7.43 (d, 2H, J = 8.4 Hz, ArH), 7.27 (t, 1H, J = 4.0 Hz, ArH), 7.04 (d, 2H, J = 8.8 Hz, ArH))
Hz, ArH), 3.81 (s, 3H, OCH₃), 2.83 (s, 2H, CH₂), 2.29-2.26 (m, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-δ₆) (δ, ppm): 199.8, 194.3, 190.7, 181.6, 158.9, 134.5, 133.6, 130.2, 129.4, 129.3, 127.0, 114.9, 109.9, 55.9, 33.3, 26.7; HRMS (ESI): m/z calcd for: C₁₈H₁₄NO₄S, 340.0644 [M-H]; found: 340.0648.

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REFERENCES AND NOTES


15. Crystal data for 3m (CCDC: 2231949): C_{19}H_{14}BrNO_4, Mr = 400.22, Monoclinic, a = 10.9020(8) Å, b = 6.2300(5) Å, c = 25.290(2) Å, U = 1668.5(2) Å^3, T = 293(2) K, space group P2(1)/c, Z = 4, 8126 reflections measured, 2943 unique (R_{int} = 0.1963) which were used in all calculation. The final wR(F_2) was 0.1296 (all data).

16. Crystal data for 3t (CCDC: 2231948): C_{19}H_{15}NO_4, Mr = 321.32, Monoclinic, a = 11.0238(9) Å, b = 5.9101(4) Å, c = 24.313(2) Å, U = 1568.4(2) Å^3, T = 298(2) K, space group P2(1)/c, Z = 4, 7459 reflections measured, 2725 unique (R_{int} = 0.0315) which were used in all calculation. The final wR(F_2) was 0.1094 (all data).

17. Crystal data for intermediate A (CCDC: 2232494): C_{18}H_{13}BrClNO_4, Mr = 422.65, Monoclinic, a = 25.531(2) Å, b = 11.3558(11) Å, c = 12.1460(12) Å, U = 3478.4(6) Å^3, T = 293(2) K, space group C2/c, Z = 8, 9003 reflections measured, 3077 unique (R_{int} = 0.1907) which were used in all calculation. The final wR(F_2) was 0.2132 (all data).