Supporting Information for


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1. General Considerations:

All reagents and solvents were used as received from commercial sources unless otherwise noted. All experiments were carried out in a round bottom flask or Schlenk tube equipped with a stirring bar. Aluminium plates precoated with silica gel 60 PF254, 0.25 mm or 0.5 mm, were utilized for thin-layer chromatography (TLC) to monitor the progress of a reaction. Visualization of the developed TLC plate was performed by irradiation with UV light. Column chromatographic purifications were carried out on flash silica gel (240−400 mesh) using ethyl acetate, acetone, DCM and petroleum ether as eluents. The $^1$H and $^{13}$C NMR spectra were recorded on 400/500 MHz and 100/125 MHz NMR spectrometers respectively, in CDCl$_3$ or DMSO-$d_6$. Chemical shifts were reported as $\delta$ values from standard peaks. The multiplicities of signals are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quint. (quintet), m (multiplet). Coupling constants ($J$) are reported in hertz. Melting points are uncorrected. High-resolution mass spectrometry (HRMS) was performed on a TOF/Q-TOF mass spectrometer. The substrate cyclopropane-1,1-dicarboxylic acid 7 was prepared using known literature procedure. The dianilides 5y and 5z were prepared as per the literature procedure.

2. Experimental Procedures:

1] General Experimental Procedure for the Synthesis of Dianilides 5a-s, 5w, 5x:

An oven dried two-neck round bottom flask was charged with cyclopropane-1,1-dicarboxylic acid 7 (1.54 mmol, 1 equiv.) and thionyl chloride (5 ml) under argon. After overnight stirring at refluxing condition (90 °C), the excess of thionyl chloride was removed by distillation, yielding the dichloride 7' as an yellow oil. The product was used in the next step without further purification.

To the solution of cyclopropane-1,1-dicarboxylic acid 7' (1.54 mmol, 1 equiv.) in THF (10 ml), the solution of amines 6a-u (3.85 mmol, 2.5 equiv.) and triethyl amine (4.62 mmol, 3 equiv.) in THF (5 ml) was added dropwise at 0 °C temperature with vigorous stirring. Combination of these two solutions caused the precipitation of triethylamine hydrochloride as a finely dispersed powder. After two hours stirring at room temperature, the reaction mixture was diluted with water (15 mL) and extracted with EtOAc (3 x 30 mL). The organic layer was separated and washed with brine solution once and dried over anhydrous Na$_2$SO$_4$. Evaporation of the solvent under vacuo to dryness followed by the purification of the crude product using column chromatography pet ether: ethyl acetate in 1:4 provided the expected dianilides 5a-s, 5w, 5x in very good yields.

The known dianilides 5a-d, 5g, 5i-k, 5m, 5o, 5q-r, 5w were prepared by the same procedure and their structure was confirmed by comparing their analytical data with the reported literature.
Synthesis of Dianilides 5t-u:

![Image of chemical reaction]

The intermediate 10 was prepared by following the reported procedure and used for the next step directly.\(^4\) Similarly, dianilides 5t and 5u were synthesized following the reported procedure by slightly modifying the coupling reagent.\(^5\)

Synthesis of Dianilides 5v:

![Image of chemical reaction]

Dianilide 5v was synthesized by treatment of triflic anhydride with the dianilide 5u using known literature procedure.\(^5\)

Experimental Procedure for the Synthesis of dianilide 11:

![Image of chemical reaction]

An oven dried pressure tube was charged with sodium methoxide (5.8 mg, 0.11 mmol, 1.5 equiv.) under argon atmosphere. Dry methanol (0.7 ml, 0.1 M) followed by the thiophenol (7.9 mg, 0.07 mmol, 1 equiv.) was added and the reaction mixture was kept for 30 min. at room temperature before adding the dianilide 5a (20 mg, 0.07 mmol, 1 equiv.). After stirring the reaction mixture at 120 °C for the completion of the reaction (monitored by TLC, approx. 12h), the solvent was evaporated and the residue was mixed with water (5 ml) and EtOAc (5 ml). The aqueous part was extracted with EtOAc (3 x 5 ml) and the combined organic layers were dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The resulting crude mixture was purified by flash column chromatography using pet ether: ethyl acetate (4:1) to provide pure sulfide compound 11 in 81% (16.6 mg) yield as a colorless sticky solid.
Table 1: Optimization of Reaction Conditions to obtain 3a

<table>
<thead>
<tr>
<th>Sr. no</th>
<th>Conditions</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>KMnO₄ (2.5 equiv.)</td>
<td>acetone</td>
<td>60</td>
<td>24</td>
<td>NR</td>
</tr>
<tr>
<td>2.</td>
<td>CuBr₂ (20 mol%), O₂</td>
<td>DMSO</td>
<td>120</td>
<td>24</td>
<td>NR</td>
</tr>
<tr>
<td>3.</td>
<td>[Mes-acr]+BF₄⁻ (1 mol%)</td>
<td>HFIP</td>
<td>25</td>
<td>24</td>
<td>NR</td>
</tr>
<tr>
<td>4.</td>
<td>PIDA (1 equiv.)</td>
<td>HFIP</td>
<td>40</td>
<td>16</td>
<td>30 (43)²</td>
</tr>
<tr>
<td>5.</td>
<td>PIDA (1 equiv.)</td>
<td>HFIP</td>
<td>70</td>
<td>16</td>
<td>24</td>
</tr>
<tr>
<td>6.</td>
<td>PIDA (1.5 equiv.)</td>
<td>HFIP</td>
<td>70</td>
<td>16</td>
<td>30</td>
</tr>
<tr>
<td>7.</td>
<td>PIDA (2 equiv.)</td>
<td>HFIP</td>
<td>70</td>
<td>16</td>
<td>40</td>
</tr>
<tr>
<td>8.</td>
<td>PhIO (2 equiv.)</td>
<td>HFIP</td>
<td>70</td>
<td>16</td>
<td>38</td>
</tr>
<tr>
<td>9.</td>
<td>PIFA (2 equiv.)</td>
<td>HFIP</td>
<td>70</td>
<td>16</td>
<td>15</td>
</tr>
<tr>
<td>10.</td>
<td>PIDA (2 equiv.)</td>
<td>DMF/MeOH/THF/IPA/MeOH/DCE/BuOH</td>
<td>70</td>
<td>16</td>
<td>NR</td>
</tr>
<tr>
<td>11.</td>
<td>PIDA (2 equiv.)</td>
<td>ACN</td>
<td>70</td>
<td>16</td>
<td>56 (74)²</td>
</tr>
<tr>
<td>12.</td>
<td>PhIO (2 equiv.)</td>
<td>ACN</td>
<td>70</td>
<td>16</td>
<td>41 (64)²</td>
</tr>
<tr>
<td>13.</td>
<td>PhIO (20 mol%), m-CPBA (1.2 equiv.)</td>
<td>ACN</td>
<td>25</td>
<td>12</td>
<td>44</td>
</tr>
<tr>
<td>14.</td>
<td>PhIO (20 mol%), Oxone (3 equiv.)</td>
<td>HFIP</td>
<td>70</td>
<td>17</td>
<td>NR</td>
</tr>
<tr>
<td>15.</td>
<td>PIDA (2 equiv.), HFIP (3 equiv.)</td>
<td>MeOH</td>
<td>70</td>
<td>16</td>
<td>24</td>
</tr>
<tr>
<td>16.</td>
<td>PIDA (2 equiv.), HFIP (3 equiv.)</td>
<td>toluene</td>
<td>70</td>
<td>16</td>
<td>34</td>
</tr>
<tr>
<td>17.</td>
<td>PIDA (2 equiv.), HFIP (3 equiv.)</td>
<td>ACN</td>
<td>70</td>
<td>16</td>
<td>68 (72)²</td>
</tr>
<tr>
<td>18.</td>
<td>PIDA (2 equiv.)</td>
<td>HFIP:MeOH (1:1)</td>
<td>70</td>
<td>16</td>
<td>37</td>
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<tr>
<td>19.</td>
<td>PIDA (2 equiv.)</td>
<td>HFIP:toluene (1:1)</td>
<td>70</td>
<td>16</td>
<td>20</td>
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<tr>
<td>20.</td>
<td>PIDA (2 equiv.), under argon</td>
<td>HFIP:heptane (1:1)</td>
<td>70</td>
<td>16</td>
<td>38</td>
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<tr>
<td>21.</td>
<td>PIDA (2 equiv.), under argon</td>
<td>HFIP:hexane (1:1)</td>
<td>70</td>
<td>16</td>
<td>30</td>
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<tr>
<td>22.</td>
<td>PIDA (2 equiv.), under argon</td>
<td>HFIP: ACN (1:1)</td>
<td>70</td>
<td>16</td>
<td>61 (75)²</td>
</tr>
<tr>
<td>23.</td>
<td>PIDA (2 equiv.), under argon</td>
<td>Dry ACN</td>
<td>70</td>
<td>16</td>
<td>87 (92)²</td>
</tr>
<tr>
<td>24.</td>
<td>PIDA (2 equiv.), under argon, 4A'MS</td>
<td>ACN</td>
<td>70</td>
<td>16</td>
<td>61 (74)²</td>
</tr>
<tr>
<td>25.</td>
<td>PIDA (2 equiv.), under argon, 3A'MS</td>
<td>ACN</td>
<td>70</td>
<td>16</td>
<td>63 (71)²</td>
</tr>
<tr>
<td>26.</td>
<td>PhIO (2 equiv.), under argon</td>
<td>Dry ACN</td>
<td>70</td>
<td>16</td>
<td>23</td>
</tr>
<tr>
<td>27.</td>
<td>IBX (2 equiv.), under argon</td>
<td>Dry ACN</td>
<td>70</td>
<td>16</td>
<td>NR</td>
</tr>
<tr>
<td>28.</td>
<td>DMP (2 equiv.), under argon</td>
<td>Dry ACN</td>
<td>70</td>
<td>16</td>
<td>NR</td>
</tr>
<tr>
<td>29.</td>
<td>PhI (20 mol%), m-CPBA (3 equiv.)</td>
<td>Dry ACN</td>
<td>70</td>
<td>16</td>
<td>26</td>
</tr>
<tr>
<td>30.</td>
<td>PhI (20 mol%), Oxone (3 equiv.)</td>
<td>Dry ACN</td>
<td>70</td>
<td>16</td>
<td>NR</td>
</tr>
</tbody>
</table>

²Reaction conditions: 5a (20 mg, 1.0 equiv.), Oxidant in solvent (0.1 M, 0.7 ml). ³Isolated yield. *Yield in the parentheses is based on the recovered starting material.
II] General Experimental Procedure for the Preparation of Pyrazolidine-3,5-dione Derivatives 3a-z:

To an oven dried Schlenk tube containing dianilide 5a-z, 11 (50 mg, 1 equiv.) and diacetoxyiodobenzene (2 equiv.) under argon was added dry acetonitrile (0.1 M). The reaction mixture was placed in a preheated oil bath at 70 °C and stirred for 16 hours. After completion of the reaction (TLC) it was cooled to room temperature and the solvent was evaporated on a rotatory evaporator. The residue was purified by flash silica gel column chromatography using a gradient of pet ether: ethyl acetate (4:1 to 3:2) to afford the corresponding pyrazolidine-3,5-dione derivatives 2, 3a-z in good to excellent yield.

III] Typical Experimental Procedure for the Preparation of Representative Product 3a:

To an oven dried Schlenk tube containing dianilide 5a (50 mg, 0.18 mmol, 1 equiv.) and diacetoxyiodobenzene (115 mg, 0.36 mmol, 2 equiv.) was added dry acetonitrile (1.8 ml, 0.1 M). The reaction mixture was placed on preheated oil bath at 70 °C and stirred for 16 hours. After completion of the reaction (TLC) it was cooled to room temperature and the solvent was evaporated on a rotatory evaporator. The residue was purified by flash silica gel column chromatography using a gradient of pet ether: ethyl acetate (6:1) to afford the corresponding pyrazolidine-3,5-dione derivative 3a as a white solid in 87% yield (43.2 mg) and in based on the recovery of starting material 92% yield.
IV] Gram Scale Experimental Procedure for the Preparation of Representative Product 3a:

To an oven dried Schlenk tube containing dianilide 5a (1 gm, 3.6 mmol, 1 equiv.) and diacetoxyiodobenzene (2.3 g, 7.14 mmol, 2 equiv.) was added dry acetonitrile (36 ml, 0.1 M). The reaction mixture was placed on preheated oil bath at 70 °C and stirred for 24 hours. After completion of the reaction (TLC) it was cooled to room temperature and the solvent was evaporated on a rotatory evaporator. The residue was purified by flash silica gel column chromatography using a gradient of pet ether: ethyl acetate (6:1) to afford the corresponding pyrazolidine-3,5-dione derivative 3a as a white solid in 63% yield (0.626 g) and in based on the recovery of starting material 67 % yield.

V] Synthesis of G-25671 (2):

An oven dried two-neck round bottom flask was charged with sodium methoxide (14.6 mg, 0.27 mmol, 1.5 equiv.) under argon atmosphere. Dry methanol (1.8 ml, 0.1 M) followed by the thiophenol (19.8 mg, 0.18 mmol, 1 equiv.) was added and the reaction mixture was kept for 30 min at room temperature before adding the key intermediate 3a (50 mg, 0.18 mmol, 1 equiv.). After the completion of the reaction (monitored by TLC, approx. 2h), the solvent was evaporated and the residue was mixed with water (5 ml) and EtOAc (5 ml). The aqueous part was extracted with EtOAc (3 x 5 ml) and the combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The resulting crude mixture was purified using flash column chromatography pet ether: ethyl acetate (4:1 to 1:1) to provide pure sulfide compound 2 in 88% (61.4 mg) as a colorless to solid.
3. Characterization Data of Compounds:

\[ \text{N,N'}-\text{bis(3,5-Dimethylphenyl)cyclopropane-1,1-dicarboxamide (5e)} \]

![Structure of 5e](image)

- Reaction time: 2h; Rf: 0.3 (1:4, EtOAc: Pet. ether); White solid; Mp = 185-187 °C; 485.9 mg, 94% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.87 (brs, 2H), 7.16 (s, 4H), 6.79 (s, 2H), 2.31 (s, 12H), 1.61 (s, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.7, 138.7, 137.1, 126.5, 118.4, 29.6, 21.3, 17.0; HRMS (ESI-TOF) m/z: [M+H]\(^+\) calcd for C\(_{21}\)H\(_{25}\)N\(_2\)O\(_2\) 337.1911, found 337.1895.

\[ \text{N,N'}-\text{bis(4-Isopropylphenyl)cyclopropane-1,1-dicarboxamide (5f)} \]

![Structure of 5f](image)

- Reaction time: 2h; Rf: 0.5 (1:4, EtOAc: Pet. ether); White solid; Mp = 130-132 °C; 520.8 mg, 93% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.96 (brs, 2H), 7.42 (d, \(J = 8.5\) Hz, 4H), 7.20 (d, \(J = 8.4\) Hz, 4H), 2.89 (septet, \(J = 6.9\) Hz, 2H), 1.61 (s, 4H), 1.25 (s, 6H), 1.23 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.8, 145.6, 134.9, 126.9, 120.8, 33.6, 29.6, 24.0, 17.0; HRMS (ESI-TOF) m/z: [M+H]\(^+\) calcd for C\(_{23}\)H\(_{29}\)O\(_2\)N\(_2\)I 565.2224, found 565.2224.

\[ \text{N,N'}-\text{bis(4-Iodophenyl)cyclopropane-1,1-dicarboxamide (5h)} \]

![Structure of 5h](image)

- Reaction time: 2h; Rf: 0.4 (2:3, EtOAc: Pet. ether); Brown solid; Mp = 195-197 °C; 703.9 mg, 86% yield; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 10.09 (brs, 2H), 7.63 (d, \(J = 8.8\) Hz, 4H), 7.46 (d, \(J = 8.7\) Hz, 4H), 1.43 (s, 4H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 168.1, 138.8, 137.1, 122.5, 87.2, 32.1, 15.4; HRMS (ESI-TOF) m/z: [M+H]\(^+\) calcd for C\(_{17}\)H\(_{15}\)O\(_2\)N\(_2\)I 532.9217, found 532.9210.

\[ \text{N,N'}-\text{bis(3,4-Dichlorophenyl)cyclopropane-1,1-dicarboxamide (5l)} \]

![Structure of 5l](image)

- Reaction time: 2h; Rf: 0.4 (2:3, EtOAc: Pet. ether); Yellowish solid; Mp = 213-215 °C; 531.2 mg, 83% yield; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 10.28 (brs, 2H), 8.11-7.95 (m, 2H), 7.56-7.54 (m, 4H), 1.44 (s, 4H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 168.0, 139.2, 130.7, 130.4, 124.9, 121.5, 120.2, 32.4, 15.4; HRMS (ESI-TOF) m/z: [M+H]\(^+\) calcd for C\(_{17}\)H\(_{15}\)O\(_2\)Cl\(_4\) 416.9726, found 416.9723.
**N,N’-bis(4-Nitrophenyl)cyclopropane-1,1-dicarboxamide (5n)**

Reaction time: 2h; Rf: 0.2 (3:2, EtOAc:Methanol); White solid; Mp = 265-267 °C; 296 mg, 52% yield; \(^1\)H NMR (400 MHz, DMSO-\(\text{d}_6\)) \(\delta\) 10.61 (brs, 2H), 8.27-8.16 (m, 4H), 7.92-7.86 (m, 4H), 1.51 (s, 4H); \(^{13}\)C NMR (100 MHz, DMSO-\(\text{d}_6\)) \(\delta\) 168.5, 145.4, 142.5, 124.8, 119.9, 33.1, 15.8; HRMS (ESI-TOF) m/z: [M–H]\(^+\) calcd for C\(_{17}\)H\(_{13}\)O\(_6\)N\(_4\) 369.0830, found 369.0846.

**N,N’-bis(4-Acetylphenyl)cyclopropane-1,1-dicarboxamide (5p)**

Reaction time: 2h; Rf: 0.4 (4:1, EtOAc:Pet. ether); Yellow solid; Mp = 213-215 °C; 336 mg, 60% yield; \(^1\)H NMR (400 MHz, DMSO-\(\text{d}_6\)) \(\delta\) 10.32 (brs, 2H), 7.92 (d, \(J = 8.8\) Hz, 4H), 7.78 (d, \(J = 8.8\) Hz, 4H), 2.53 (s, 6H), 1.50 (s, 4H); \(^{13}\)C NMR (100 MHz, DMSO-\(\text{d}_6\)) \(\delta\) 196.6, 168.3, 143.4, 131.9, 129.2, 119.4, 32.5, 26.4, 15.6; HRMS (ESI-TOF) m/z: [M+H]\(^+\) calcd for C\(_{21}\)H\(_{21}\)O\(_4\)N\(_2\) 365.1496, found 365.1494.

**N,N’-bis(3,5-Dimethoxyphenyl)cyclopropane-1,1-dicarboxamide (5s)**

Reaction time: 2h; Rf: 0.4 (3:7, EtOAc:Pet. ether); White solid; Mp = 195-197 °C; 480 mg, 78% yield; \(^1\)H NMR (400 MHz, DMSO-\(\text{d}_6\)) \(\delta\) 9.90 (brs, 2H), 6.91 (d, \(J = 2.1\) Hz, 4H), 6.22 (t, \(J = 2.3\) Hz, 2H), 3.70 (s, 12H), 1.43 (s, 4H); \(^{13}\)C NMR (100 MHz, DMSO-\(\text{d}_6\)) \(\delta\) 168.2, 160.3, 140.6, 98.6, 95.8, 55.1, 32.0, 15.3; HRMS (ESI-TOF) m/z: [M+H]\(^+\) calcd for C\(_{21}\)H\(_{25}\)O\(_6\)N\(_2\) 401.1707, found 401.1704.

**N-(4-Bromophenyl)-N-(p-tolyl)cyclopropane-1,1-dicarboxamide (5t)**

Reaction time: 15h; Rf: 0.4 (1:4, EtOAc: Pet. ether); White solid; Mp = 220-222 °C; 73% yield over two steps from 7; \(^1\)H NMR (400 MHz, DMSO-\(\text{d}_6\)) \(\delta\) 10.17 (brs, 1H), 9.88 (brs, 1H), 7.60 (d, \(J = 7.9\) Hz, 2H), 7.46 (d, \(J = 7.9\) Hz, 4H), 7.10 (d, \(J = 7.9\) Hz, 2H), 2.25 (s, 3H), 1.45 (s, 4H); \(^{13}\)C NMR (100 MHz, DMSO-\(\text{d}_6\)) \(\delta\) 168.4, 167.9, 138.2, 136.2, 132.6, 131.3, 128.8, 122.3, 120.6, 115.2, 31.5, 20.4, 15.5; HRMS (ESI-TOF) m/z: [M+H]\(^+\) calcd for C\(_{18}\)H\(_{18}\)BrN\(_2\)O\(_2\) 373.0546, found 373.0553.
**N-(4-Bromophenyl)-N-(4-hydroxyphenyl)cyclopropane-1,1-dicarboxamide (5u)**

Reaction time: 15h; Rf: 0.6 (1:19, MeOH: DCM); White solid; Mp = 162-164 °C; 63% yield over two steps; **1H NMR (400 MHz, DMSO-d6)** δ 10.27 (brs, 1H), 9.66 (brs, 1H), 9.21 (broad s, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 6.68 (d, J = 8.0 Hz, 2H), 1.44 (s, 4H); **13C NMR (100 MHz, DMSO-d6)** δ 168.4, 167.8, 153.8, 138.2, 131.3, 130.1, 122.6, 122.2, 115.1, 114.8, 31.1, 15.5; **HRMS (ESI-TOF) m/z:** [M+H]+ calcd for C17H16BrN2O3 375.0339, found 375.0333.

**4-(1-((4-Bromophenyl)carbamoyl)cyclopropane-1-carboxamido)phenyl trifluoromethanesulfonate (5v)**

Reaction time: 12h; Rf: 0.4 (1:4, EtOAc: Pet. ether); White solid; Mp = 135-137 °C; 60.8 mg, 90% yield; **1H NMR (400 MHz, DMSO-d6)** δ 10.28 (brs, 1H), 10.10 (brs, 1H), 7.79 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.56-7.36 (m, 4H), 1.45 (s, 4H); **13C NMR (100 MHz, DMSO-d6)** δ 168.2, 167.9, 144.4, 139.4, 138.3, 131.3, 122.3, 121.8, 121.6, 118.3 (q, J = 320.4 Hz, CF3), 115.2, 32.0, 15.4; **HRMS (ESI-TOF) m/z:** [M+H]+ calcd for C18H15BrF3N2O5S 506.9832, found 506.9832.

**N,N’-Dipropylcyclopropane-1,1-dicarboxamide (5x)**

Reaction time: 2h; Rf: 0.5 (2:3, EtOAc:Pet. ether); White solid; Mp = 48-50 °C; 254.4 mg, 78% yield; **1H NMR (400 MHz, CDCl3)** δ 7.11 (broad s, 2H), 3.25-3.17 (m, 4H), 1.58-1.48 (m, 4H), 1.35 (s, 4H), 0.92 (t, J = 7.4 Hz, 6H); **13C NMR (100 MHz, CDCl3)** δ 170.7, 41.5, 28.2, 22.6, 16.1, 11.4; **HRMS (ESI-TOF) m/z:** [M+H]+ calcd for C11H21O2N2 213.1598, found 213.1600.

**N,N’-Diphenyl-2-(2-(phenylthio)ethyl)malonamide (11)**

Reaction time: 12h; Rf: 0.3 (1:4, EtOAc: Pet. ether); colorless sticky solid; 16.6 mg, 81% yield; **1H NMR (200 MHz, CDCl3)** δ 9.07 (broad s, 2H), 7.56 (d, J = 7.6 Hz, 4H), 7.36-7.31 (m, 6H), 7.23-7.13 (m, 5H), 3.74 (t, J = 7.5 Hz, 1H), 3.06 (t, J = 7.0 Hz, 2H), 2.39 (q, J = 7.1 Hz, 2H); **13C NMR (100 MHz, CDCl3)** δ 168.7, 137.2, 134.8, 129.9, 129.05, 129.01, 126.6, 124.9, 120.3, 54.7, 32.5, 31.7; **HRMS (ESI-TOF) m/z:** [M+H]+ calcd for C23H15N2O3S 391.1475, found 391.1475.
5,6-Diphenyl-5,6-diazaspiro[2.4]heptane-4,7-dione (3a)

Reaction time: 16h; Rf: 0.5 (1:4, EtOAc:Pet. ether); White solid; Mp = 163-165 °C; 43.2 mg, 87% yield; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.41-7.30 (m, 8H), 7.22-7.15 (m, 2H), 1.92 (s, 4H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.2, 136.4, 128.9, 126.5, 122.2, 26.9, 21.8; HRMS (ESI-TOF) m/z: [M+H]\(^+\)calcd for C\(_{17}\)H\(_{15}\)O\(_2\)N\(_2\) 279.1128, found 279.1126.

5,6-Di-p-tolyl-5,6-diazaspiro[2.4]heptane-4,7-dione (3b)

Reaction time: 16h; Rf: 0.6 (1:4, EtOAc: Pet. ether); White solid; Mp = 160-162 °C; 44.2 mg, 89% yield; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.24 (d, \(J = 8.4\) Hz, 4H), 7.13 (d, \(J = 8.4\) Hz, 4H), 2.29 (s, 6H), 1.89 (s, 4H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.2, 136.5, 133.8, 129.5, 122.6, 26.8, 21.5, 21.0; HRMS (ESI-TOF) m/z: [M+H]\(^+\)calcd for C\(_{19}\)H\(_{19}\)O\(_2\)N\(_2\) 307.1441, found 307.1435.

5,6-Di-m-tolyl-5,6-diazaspiro[2.4]heptane-4,7-dione (3c)

Reaction time: 16h; Rf: 0.6 (1:4, EtOAc: Pet. ether); Thick oil; 23.3 mg, 47% yield (brsm-52%); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.24 (s, 2H), 7.20 (t, \(J = 7.8\) Hz, 2H), 7.12 (d, \(J = 8.3\) Hz, 2H), 6.99 (d, \(J = 7.5\) Hz, 2H), 2.33 (s, 6H), 1.90 (s, 4H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.3, 138.9, 136.4, 128.7, 127.4, 123.3, 119.4, 26.9, 21.7, 21.4; HRMS (ESI-TOF) m/z: [M+H]\(^+\)calcd for C\(_{19}\)H\(_{19}\)O\(_2\)N\(_2\) 307.1441, found 307.1438.

5,6-bis(3,4-Dimethylphenyl)-5,6-diazaspiro[2.4]heptane-4,7-dione (3d)

Reaction time: 16h; Rf: 0.4 (1:4, EtOAc: Pet. ether); White solid; Mp = 127-129 °C; 35.3 mg, 71% yield; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.20 (d, \(J = 1.3\) Hz, 2H), 7.09-6.99 (m, 4H), 2.22 (s, 6H), 2.18 (s, 6H), 1.87 (s, 4H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.4, 137.3, 135.4, 134.1, 129.9, 124.3, 120.2, 26.8, 21.4, 19.9, 19.3; HRMS (ESI-TOF) m/z: [M+H]\(^+\)calcd for C\(_{21}\)H\(_{23}\)O\(_2\)N\(_2\) 335.1754, found 335.1756.

5,6-bis(3,5-Dimethylphenyl)-5,6-diazaspiro[2.4]heptane-4,7-dione (3e)

Reaction time: 16h; Rf: 0.5 (1:4, EtOAc: Pet. ether); White Solid; Mp = 172-174 °C; 36.8 mg, 74% yield; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.99 (s, 4H), 6.82 (s, 2H), 2.27 (s, 12H), 1.87 (s, 4H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.5, 138.6, 136.4, 128.6, 120.5, 26.8, 21.5, 21.3; HRMS (ESI-TOF) m/z: [M+H]\(^+\)calcd for C\(_{21}\)H\(_{23}\)O\(_2\)N\(_2\) 335.1754, found 335.1755.
5,6-bis(4-isopropylphenyl)-5,6-diazaspiro[2.4]heptane-4,7-dione (3f)

Reaction time: 16h; Rf: 0.4 (1:4, EtOAc:Pet. ether); White solid; Mp = 80-82 °C; 34.8 mg, 70% yield; 
\[ ^1H \text{NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.29 (d, \( J = 8.5 \) Hz, 4H), 7.18 (d, \( J = 8.4 \) Hz, 4H), 2.86 (septate, \( J = 6.9 \) Hz, 2H), 1.89 (s, 4H), 1.21 (s, 6H), 1.19 (s, 6H); 
\[ ^13C \text{NMR (100 MHz, CDCl}_3 \] \( \delta \) 171.4, 147.2, 134.1, 126.9, 122.3, 33.6, 26.9, 23.8, 21.7; HRMS (ESI-TOF) m/z: [M+H]+calcd for C\(_{23}\)H\(_{27}\)O\(_2\)N\(_2\) 363.2067, found 363.2069.

5,6-bis(4-(tert-Butyl)phenyl)-5,6-diazaspiro[2.4]heptane-4,7-dione (3g)

Reaction time: 16h; Rf: 0.6 (1:4, EtOAc:Pet. ether); White solid; Mp = 145-147 °C; 41.3 mg, 83% yield; 
\[ ^1H \text{NMR (500 MHz, CDCl}_3 \] \( \delta \) 7.35 (d, \( J = 8.2 \) Hz, 4H), 7.30 (d, \( J = 8.5 \) Hz, 4H), 1.89 (s, 4H), 1.27 (s, 18H); 
\[ ^13C \text{NMR (125 MHz, CDCl}_3 \] \( \delta \) 171.5, 149.4, 133.9, 125.8, 121.8, 34.5, 31.2, 26.8, 21.7; HRMS (ESI-TOF) m/z: [M+H]+calcd for C\(_{25}\)H\(_{31}\)O\(_2\)N\(_2\)I 391.2385, found 391.2385.

5,6-bis(4-Iodophenyl)-5,6-diazaspiro[2.4]heptane-4,7-dione (3h)

Reaction time: 16h; Rf: 0.4 (1:4, EtOAc:Pet. ether); White solid; Mp = 207-209 °C; 
47.8 mg, 96% yield; 
\[ ^1H \text{NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.66 (d, \( J = 8.9 \) Hz, 4H), 7.10 (d, \( J = 8.9 \) Hz, 4H), 1.94 (s, 4H); 
\[ ^13C \text{NMR (100 MHz, CDCl}_3 \] \( \delta \) 171.0, 138.1, 136.0, 123.6, 91.1, 26.8, 22.4; HRMS (ESI-TOF) m/z: [M+H]+calcd for C\(_{17}\)H\(_{13}\)O\(_2\)N\(_2\)I\(_2\) 530.9061, found 530.9064.

5,6-bis(4-Bromophenyl)-5,6-diazaspiro[2.4]heptane-4,7-dione (3i)

Reaction time: 16h; Rf: 0.4 (1:4, EtOAc:Pet. ether); Brown solid; Mp = 183-185 °C; 
43.8 mg, 88% yield; 
\[ ^1H \text{NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.52-7.42 (m, 4H), 7.26-7.21 (m, 4H), 1.94 (s, 4H); 
\[ ^13C \text{NMR (100 MHz, CDCl}_3 \] \( \delta \) 171.0, 135.3, 132.2, 123.5, 120.0, 26.8, 22.4; HRMS (ESI-TOF) m/z: [M+H]+calcd for C\(_{17}\)H\(_{13}\)O\(_2\)N\(_2\)Br\(_2\) 434.9338, found 434.9333.

5,6-bis(4-Chlorophenyl)-5,6-diazaspiro[2.4]heptane-4,7-dione (3j)

Reaction time: 16h; Rf: 0.3 (1:4, EtOAc:Pet. ether); Yellow solid; Mp = 162-164 °C; 42.8 mg, 86% yield; 
\[ ^1H \text{NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.40-7.19 (m, 8H), 1.94 (s, 4H); 
\[ ^13C \text{NMR (100 MHz, CDCl}_3 \] \( \delta \) 171.1, 134.7, 132.2, 129.2, 123.2, 26.8, 22.3; HRMS (ESI-TOF) m/z: [M+H]+calcd for C\(_{17}\)H\(_{13}\)O\(_2\)Cl\(_2\) 347.0349, found 347.0346.
5,6-bis(3-Chlorophenyl)-5,6-diazaspiro[2.4]heptane-4,7-dione (3k)

![Chemical structure image]

Reaction time: 16h; Rf: 0.3 (1:4, EtOAc: Pet. ether); Thick oil; 27.8 mg, 56% yield (brsm-83%); 1H NMR (400 MHz, CDCl3) δ 7.44 (t, J = 1.9 Hz, 2H), 7.32-7.26 (m, 2H), 7.25-7.17 (m, 4H), 1.96 (s, 4H); 13C NMR (100 MHz, CDCl3) δ 171.2, 137.5, 134.9, 130.1, 126.9, 122.1, 119.8, 26.8, 22.5; HRMS (ESI-TOF) m/z: [M+H]+calcld for C13H11O2N2Cl2 347.0349, found 347.0348.

5,6-bis(3,4-Dichlorophenyl)-5,6-diazaspiro[2.4]heptane-4,7-dione (3l)

![Chemical structure image]

Reaction time: 16h; Rf: 0.3 (1:4, EtOAc: Pet. ether); White solid; Mp = 175-177 °C; 29.4 mg, 59% yield; 1H NMR (400 MHz, CDCl3) δ 7.54 (d, J = 2.5 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.18 (dd, J = 8.8 & 2.5 Hz, 2H), 1.98 (s, 4H); 13C NMR (100 MHz, CDCl3) δ 171.1, 135.5, 133.3, 130.8, 130.7, 123.6, 120.7, 26.7, 22.9; HRMS (ESI-TOF) m/z: [M+H]+calcld for C17H10O2N2Cl2 414.9569, found 414.9562.

5,6-bis(4-Fluorophenyl)-5,6-diazaspiro[2.4]heptane-4,7-dione (3m)

![Chemical structure image]

Reaction time: 16h; Rf: 0.4 (1:4, EtOAc: Pet. ether); White solid; Mp = 110-112 °C; 27.8 mg, 56% yield; 1H NMR (400 MHz, CDCl3) δ 7.38-7.29 (m, 4H), 7.09-7.00 (m, 4H), 1.93 (s, 4H); 13C NMR (100 MHz, CDCl3) δ 171.3, 160.9 (d, J = 247.2 Hz), 132.1 (d, J = 3.1 Hz), 124.4 (d, J = 8.4 Hz), 116.0 (d, J = 22.9 Hz), 26.7, 22.0; HRMS (ESI-TOF) m/z: [M+H]+calcld for C17H10O2N2Cl2 315.0940, found 315.0939.

5,6-bis(4-Acetylphenyl)-5,6-diazaspiro[2.4]heptane-4,7-dione (3p)

![Chemical structure image]

Reaction time: 16h; Rf: 0.4 (2:3, EtOAc: Pet. ether); Thick oil; 19.9 mg (100 mg scale), 20% yield (brsm-29%); 1H NMR (400 MHz, CDCl3) δ 8.00-7.90 (m, 4H), 7.55-7.39 (m, 4H), 2.56 (s, 6H), 2.0 (s, 4H); 13C NMR (100 MHz, CDCl3) δ 196.6, 171.2, 150.9, 140.2, 134.8, 129.4, 121.1, 27.0, 26.5, 22.8; HRMS (ESI-TOF) m/z: [M+H]+calcld for C21H10O2N2 363.1339, found 363.1341.

5,6-bis(4-Methoxyphenyl)-5,6-diazaspiro[2.4]heptane-4,7-dione (3q)

![Chemical structure image]

Reaction time: 16h; Rf: 0.4 (1:1, EtOAc: Pet. ether); White solid; Mp = 185-187 °C; 32.8 mg (100 mg scale), 33% yield; 1H NMR (400 MHz, CDCl3) δ 7.26 (d, J = 9.0 Hz, 4H), 6.84 (d, J = 9.0 Hz, 4H), 3.76 (s, 6H), 1.89 (s, 4H); 13C NMR (100 MHz, CDCl3) δ 171.2, 158.3, 128.9, 125.2, 114.2, 55.4, 26.8, 21.3; HRMS (ESI-TOF) m/z: [M+H]+calcld for C19H10O2N2 339.1339, found 339.1344.
5,6-Bis(4-Ethoxyphenyl)-5,6-diazaspiro[2.4]heptane-4,7-dione (3r)

Reaction time: 16h; Rf: 0.3 (1:9, Acetone:Pet. ether); Brown solid; Mp = 158-160 °C; 28.8 mg (100 mg scale), 29% yield (brsm-35%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.26-7.20 (m, 4H), 6.85-6.79 (m, 4H), 3.97 (q, \(J = 7.0\) Hz, 4H), 1.88 (s, 4H), 1.38 (t, \(J = 6.9\) Hz, 6H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.2, 157.8, 128.7, 125.3, 114.7, 63.6, 26.8, 21.2, 14.7; HRMS (ESI-TOF) m/z: [M+H]\(^+\)calcd for C\(_{21}\)H\(_{23}\)O\(_4\)N\(_2\) 367.1652, found 367.1647.

5,6-Bis(3,5-Dimethoxyphenyl)-5,6-diazaspiro[2.4]heptane-4,7-dione (3s)

Reaction time: 16h; Rf: 0.4 (2:3, EtOAc:Pet. ether); White solid; Mp = 173-175 °C; 24.9 mg (100 mg scale), 25% yield (brsm-30%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.57 (d, \(J = 2.3\) Hz, 4H), 6.30 (t, \(J = 2.2\) Hz, 2H), 3.73 (s, 12H), 1.90 (s, 4H); 13C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.3, 160.9, 138.3, 100.8, 98.8, 55.5, 27.0, 22.0; HRMS (ESI-TOF) m/z: [M+H]\(^+\)calcd for C\(_{21}\)H\(_{23}\)O\(_6\)N\(_2\) 399.1555, found 399.1555.

5-(4-Bromophenyl)-6-(p-tolyl)-5,6-diazaspiro[2.4]heptane-4,7-dione (3t)

Reaction time: 16h; Rf: 0.5 (1:4, EtOAc; Pet. ether); White solid; Mp = 140-142 °C; 35.8 mg, 72% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.45 (d, \(J = 8.5\) Hz, 2H), 7.36-7.06 (m, 6H), 2.31 (s, 3H), 1.92 (s, 4H); 13C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.3, 171.0, 136.8, 135.3, 133.8, 132.0, 129.7, 123.7, 122.4, 119.7, 26.8, 21.9, 21.0; HRMS (ESI-TOF) m/z: [M+H]\(^+\)calcd for C\(_{18}\)H\(_{16}\)BrN\(_2\)O\(_2\) 504.9675, found 504.9693.

4,4-Dimethyl-1,2-diphenylpyrazolidine-3,5-dione (3z)

Reaction time: 16h; Rf: 0.4 (1:4, EtOAc; Pet. ether); colorless sticky solid; 9.5 mg (20 mg scale), 48% yield (brsm-72%); \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) 7.37-7.30 (m, 8H), 7.23-7.16 (m, 2H), 1.52 (s, 6H); GC-MS m/z: [M]\(^+\)calcd for C\(_{17}\)H\(_{18}\)N\(_2\)O\(_2\) 280.3, found 280.3.

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1,2-Diphenyl-4-(2-phenylthio)ethyl)pyrazolidine-3,5-dione (2)²

Reaction time: 2h; Rf: 0.6 (3:7, EtOAc:Pet. ether); White solid; Mp = 100-102 ºC (lit.³ Mp = 110-113 ºC); 61.4 mg (50 mg scale), 88% yield;

¹H NMR (400 MHz, CDCl₃) δ 7.36-7.23 (m, 12H), 7.23-7.11 (m, 3H), 3.64 (t, J = 6.3 Hz, 1H), 3.22 (t, J = 7.1 Hz, 2H), 2.37 (q, J = 6.7 Hz, 2H);

¹³C NMR (100 MHz, CDCl₃) δ 169.6, 135.7, 134.7, 129.9, 129.0, 128.9, 126.8, 126.5, 122.6, 44.4, 30.3, 27.0;

HRMS (ESI-TOF) m/z: [M+H]⁺calcd for C₂₃H₂₁O₂N₂S 389.1318, found 389.1315.
4. References:


5. Copies of $^1$H NMR and $^{13}$C NMR Spectra:
$^1$H NMR, 400 MHz

$^{13}$C NMR, 100 MHz
$^1$H NMR, 400 MHz

Chemical Shift (ppm)

DMSO-d$_6$

$^1$C NMR, 100 MHz

Chemical Shift (ppm)

DMSO-d$_6$
\(^1\)H NMR, 400 MHz

\[^1\]C NMR, 100 MHz
$^1$H NMR, 400 MHz

$^1$H NMR, 400 MHz

$^{13}$C NMR, 100 MHz

$^{13}$C NMR, 100 MHz
$^1$H NMR, 400 MHz

$^1$C NMR, 100 MHz
$^1$H NMR, 400 MHz

$^{13}$C NMR, 100 MHz
$^1$H NMR, 400 MHz

$^1$C NMR, 100 MHz

CHLOROFORM-d

5x

Chemical Shift (ppm)
$^{1}H$ NMR, 200 MHz

$^{13}C$ NMR, 100 MHz
$^{1}H$ NMR, 400 MHz

$^{13}$C NMR, 100 MHz
$^1$H NMR, 400 MHz

$^{13}$C NMR, 100 MHz
**$^1$H NMR, 400 MHz**

![Chemical Shift (ppm)](image1.png)

**$^{13}$C NMR, 100 MHz**

![Chemical Shift (ppm)](image2.png)

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S37
$^1$H NMR, 400 MHz

$^{13}$C NMR, 100 MHz
$\text{1}^1\text{H NMR, 400 MHz}$

$\text{1}^3\text{C NMR, 100 MHz}$
$^1$H NMR, 400 MHz

$^{13}$C NMR, 100 MHz
$^1$H NMR, 400 MHz

$^1$C NMR, 100 MHz

3t
$^1$H NMR, 400 MHz

$^{13}$C NMR, 100 MHz
$^1$H NMR, 200 MHz

CHLOROFORM-d

Chemical Shift (ppm)

6.01
2.01
8.00

3z