Facile Synthesis of Benzo[d]azol-2(3H)-ones Using 2-Phenoxy carbonyl-4,5-dichloropyridazin-3(2H)-one as Green CO Source

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Table of contents

1. Condition screening for synthesis of 10 ................................................................. S2
2. Condition screening for synthesis of 11a ............................................................. S3
3. General experimental information ............................................................................. S6
4. Procedure for preparation of 3a-3g and their analytical data ..................................... S6
5. Procedure for preparation of 5a-5e and their analytical data ..................................... S9
6. Procedure for preparation of 11a-11c and their analytical data ................................. S11
7. References............................................................................................................. S13
1. Condition screening for synthesis of 10

1.1. Solvent screening for synthesis of 10

A mixture of 2-phenoxy carbonyl-4,5-dichloropyridazin-3(2H)-one (2a, 2.2 equiv, 758 mg), 2,2’-dithiodianiline (7, 1 equiv, 300 mg), and solvent (5 mL) was stirred at room temperature (or at reflux condition) until 7 was consumed by TLC monitoring. The reaction mixture was cooled to room temperature. The resulting precipitate was filtered off and then washed with dichloromethane. After evaporating the solvent under reduced pressure, the residue was recrystallized from ethanol. The resulting crystals were filtered and dried in air to give compound 10. Table S1 summarizes the results.

Table S1. Solvent screening for synthesis of 10

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Condition</th>
<th>Time (h)</th>
<th>10 (Yield, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-Hexane</td>
<td>reflux</td>
<td>2</td>
<td>72</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>reflux</td>
<td>1</td>
<td>91</td>
</tr>
<tr>
<td>3</td>
<td>Chloroform</td>
<td>reflux</td>
<td>2</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>Ethyl acetate</td>
<td>reflux</td>
<td>2</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>Acetic acid</td>
<td>rt</td>
<td>3</td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td>Acetic acid</td>
<td>reflux</td>
<td>0.5</td>
<td>73</td>
</tr>
<tr>
<td>7</td>
<td>Tetrahydrofuran</td>
<td>reflux</td>
<td>2</td>
<td>86</td>
</tr>
<tr>
<td>8</td>
<td>Dichloromethane</td>
<td>reflux</td>
<td>11</td>
<td>87</td>
</tr>
<tr>
<td>9</td>
<td>Acetonitrile</td>
<td>reflux</td>
<td>2</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td>Water</td>
<td>reflux</td>
<td>2</td>
<td>69</td>
</tr>
</tbody>
</table>

2,2'-Dithiodianiline (7, 1 equiv.) and 2a (2.2 equiv.) in solvent (5 mL).

Isolated yield.

Intermediate 9 remained.

Unknown by-product was formed.
1.2. Optimization of reaction conditions for synthesis of 10 from 7 and 2a in acetic acid

A mixture of 2-phenoxy carbonyl-4,5-dichloropyridazin-3(2H)-one (2a, 2.2 equiv, 758 mg or 2.5 equiv, 673 mg), 2,2'-dithiodianiline (7, 1 equiv, 300 mg) and acetic acid (5 mL) was stirred at room temperature (or reflux temperature) until 7 was consumed by TLC monitoring. The precipitate was filtered off and then washed with dichloromethane. After evaporating the solvent under reduced pressure, the residue was recrystallized from ethanol. The resulting crystals were filtered and dried in air to give compound 10. Table S2 summarizes the results.

<table>
<thead>
<tr>
<th>Entry</th>
<th>2 (equiv.)</th>
<th>Condition</th>
<th>Time (h)</th>
<th>10 (Yield, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.2</td>
<td>reflux</td>
<td>0.5</td>
<td>73(^c)</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>reflux</td>
<td>0.5</td>
<td>74(^c)</td>
</tr>
<tr>
<td>3</td>
<td>2.2</td>
<td>rt</td>
<td>3</td>
<td>80(^c)</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>rt</td>
<td>1.5</td>
<td>91</td>
</tr>
</tbody>
</table>

\(^a\)2,2'-Dithiodianiline (7, 1 equiv) and 2a in AcOH (5 mL).

\(^b\)Isolated yields.

\(^c\)Unknown by-product was formed.

\(^d\)Intermediate 9 remained.

2. Condition screening for synthesis of 11a

2.1. Synthesis of benzo[d]thiazol-2(3H)-one (11a) with 7 and 2a

A mixture of 2-phenoxy carbonyl-4,5-dichloropyridazin-3(2H)-one (2a, 2.5 equiv, 678 mg),
2,2’-dithiodianiline (7, 1 equiv, 300 mg), and acetic acid (5 mL) was stirred at room temperature until 7 was consumed by TLC monitoring. After adding zinc powder (5 equiv, 395 mg), the mixture was refluxed for 1 h. After cooling to room temperature, the resulting precipitate was filtered, and then washed with dichloromethane. After evaporating the solvent under reduced pressure, the residue was transferred to an open-bed silica gel column (3 × 10 cm). The column was eluted with dichloromethane/ethyl acetate (10:1, v/v). Fractions containing compound 11a were combined and evaporated under reduced pressure to give compound 11a. Table S3 summarizes the results.

Table S3. Optimization of zinc equivalents for one-pot synthesis of 11

<table>
<thead>
<tr>
<th>Entry</th>
<th>Zinc (Equiv)</th>
<th>Time (h, step i/ii)</th>
<th>11a (Yield, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>2.5 (1.5/1)</td>
<td>52c</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>2.5 (1.5/1)</td>
<td>93</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>1.5 (1.5/0)</td>
<td>-d</td>
</tr>
</tbody>
</table>

2,2'-Dithiodianiline (7, 1 equiv) and 2a (2.5 equiv) in AcOH (5mL).
Isolated yields.
Intermediate 10 remained.
The main product was compound 10.

2.2. Synthesis of benzo[d]thiazol-2(3H)-one (11a) using 2-aryloxy (or alkoxy)carbonyl-4,5-dichloropyridazin-3(2H)-ones 2

A mixture of 2-aryloxy (or alkoxy)carbonyl-4,5-dichloropyridazin-3(2H)-one (2, 2.5 equiv), 2,2’-dithiodianiline (7, 1 equiv, 300 mg) and acetic acid (5 mL) was stirred at room temperature (or at reflux condition) until 3 was consumed by TLC monitoring. After adding zinc powder (5 equiv, 395 mg), the mixture was refluxed for 0.5 h (or 5h for 2e). After cooling to room temperature, the resulting precipitate was filtered off and washed with
dichloromethane. After evaporating the solvent under reduced pressure, the residue was transferred to an open-bed silica gel column (3 × 10 cm). The column was eluted with dichloromethane/ethyl acetate (10:1, v/v). Fractions containing compound 11a were combined and evaporated under reduced pressure to give compound 11a. Table S4 summarizes the results.

Table S4. Screening of aryloxy (or alkoxy) carbonyl-4,5-dichloropyridazin-3(2H)-ones 2 for synthesis of benzo[d]thiazol-2(3H)-onea

<table>
<thead>
<tr>
<th>Entry</th>
<th>2, R</th>
<th>Conditions: step i/ii (Time, h, steps i/ii)</th>
<th>11a (Yield, %)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2a Ph</td>
<td>rt/reflux (2.5:2/0.5)</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>2b (p-Cl)Ph</td>
<td>rt/reflux (2.5:2/0.5)</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>2c (p-Me)Ph</td>
<td>rt/reflux (3.5:3/0.5)</td>
<td>82</td>
</tr>
<tr>
<td>4</td>
<td>2d (p-OMe)Ph</td>
<td>reflux/reflux (4.5:4/0.5)</td>
<td>46c</td>
</tr>
<tr>
<td>5</td>
<td>2e (p-NO2)Ph</td>
<td>reflux/reflux (10:5/5)</td>
<td>tracec</td>
</tr>
<tr>
<td>6</td>
<td>2f Me</td>
<td>rt/reflux (8.5:8/0.5)</td>
<td>65c</td>
</tr>
<tr>
<td>7</td>
<td>2g Et</td>
<td>rt/reflux (8.5:8/0.5)</td>
<td>76</td>
</tr>
<tr>
<td>8</td>
<td>2h PhCH2</td>
<td>reflux/reflux (4.5:4/0.5)</td>
<td>81</td>
</tr>
</tbody>
</table>

a2,2'-Dithiodianiline (7, 1 equiv) and compounds 2 (2.5 equiv) in AcOH (5 mL) with zinc (5 equiv).
bIsolated yields.
cUnknown by-product was formed.
3. General experimental information

Melting points were determined with a capillary apparatus and uncorrected. NMR spectra were recorded on a 300 MHz spectrometer (Bruker) with chemical shift values reported in δ units (ppm) relative to an internal standard (TMS). IR spectra were obtained on a Varian 640-IR spectrophotometer. Mass spectra were recorded under electron ionization (EI). Thin-layer chromatography (TLC) analyses were performed using pre-coated silica gel plates. The open-bed chromatography was carried out on silica gel 60 (70-230 mesh, Merck) using gravity flow. The column was packed with slurries made from the elution solvent. Chemicals were purchased from the Aldrich, TCI or Alfa Aeser chemical company. Solvent was dried by molecular sieve 4Å or anhydrous magnesium sulfate. 2-Alkoxycarbonyl-4,5-dichloropyridazin-3(2H)-ones 2 were synthesized according to the literature procedures.1

4. Procedure for preparation of 3a-3g and their analytical data

4.1. Base screening for synthesis of benzo[d]oxazol-2(3H)-one (3a)

A mixture of 2-phenoxycarbonyl-4,5-dichloropyridazin-3(2H)-one (2a, 1.2 equiv, 940 mg), 2-aminophenol (1a, 1 equiv, 300 mg), and toluene (5 mL) was stirred at reflux temperature until 1a was consumed by TLC monitoring. After adding base (1 equiv), the mixture was refluxed until the intermediate was consumed by TLC monitoring. After cooling to room temperature, the resulting precipitate was filtered off and washed with tetrahydrofuran. The solvent was evaporated under reduced pressure. The residue was transferred to an open-bed silica gel column (3 × 10 cm). The column was eluted with n-hexane/tetrahydrofuran (3:1, v/v). Fractions containing compound 3a were combined and evaporated under reduced pressure to give compound 3a. Table 1 summarizes the results.
4.2. Solvent screening for synthesis of benzo[d]oxazol-2(3H)-one (3a)

A mixture of 2-phenoxy carbonyl-4,5-dichloropyridazin-3(2H)-one (2a, 1.2 equiv, 940 mg), 2-aminophenol (1a, 1 equiv, 300 mg) and solvent (5 mL) was stirred at reflux condition until 1a was consumed by TLC monitoring. After adding sodium bicarbonate (1 equiv, 231 mg), the mixture was refluxed until the intermediate was consumed by TLC monitoring. After cooling to room temperature, the resulting precipitate was filtered off and washed with tetrahydrofuran. The solvent was evaporated under reduced pressure. The residue was transferred to an open-bed silica gel column (3 × 10 cm). The column was eluted with n-hexane/tetrahydrofuran (3:1, v/v). Fractions containing compound 3a were combined and evaporated under reduced pressure to give compound 3a. Table 2 summarizes the results.

4.3. Synthesis of benzo[d]oxazol-2(3H)-ones 3

A mixture of 2-phenoxy carbonyl-4,5-dichloropyridazin-3(2H)-one (2a, 1.2 equiv), compounds (1, 1 equiv, 300 mg) and toluene (5 mL) was stirred at reflux condition until 1 was consumed by TLC monitoring. After adding sodium bicarbonate (1 equiv), the mixture was refluxed until the intermediate was consumed by TLC monitoring. After cooling to room temperature, the resulting precipitate was filtered off and washed with tetrahydrofuran. The solvent was evaporated under reduced pressure. The resulting residue was transferred to an open-bed silica gel column (3 × 10 cm). The column was eluted with n-hexane/tetrahydrofuran (3:1, v/v). Fractions containing compounds 3 were combined and evaporated under reduced pressure to give compounds 3. Table 3 summarizes the results.

4.3.1. Benzo[d]oxazol-2(3H)-one (3a). Yield: 340 mg, 92%; White solid; mp 140 °C (lit.2)
IR (KBr) 3215, 1772, 1733, 1480, 1398, 1307, 1253, 1147, 1009, 944, 739, 718, 701, 574 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ 7.10-7.26 (m, 3H), 9.87 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆) δ 110.17, 110.25, 122.76, 124.23, 129.42, 143.90, 156.23; HRMS (m/z): [M]+ calcd for C₇H₅NO₂ 135.0320. Found: 135.0319.

4.3.2. 6-Chlorobenzo[d]oxazol-2(3H)-one (3b). Yield: 225 mg (64%); White solid; mp 193-194 °C (lit.³ 194-195 °C); IR (KBr) 3274, 3083, 1781, 1731, 1479, 1392, 1301, 1261, 943, 917, 854, 813, 711, 592 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ 7.10 (d, 1H, J=9.0 Hz), 7.20 (dd, 1H, J₁=9.0, J₂=1.9 Hz) 7.47 (d, 1H, J=1.9 Hz) 11.84 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆) δ 110.14, 110.65, 123.58, 125.74, 129.42, 143.74, 154.14; HRMS (m/z): [M]+ calcd for C₇H₄ClNO₂ 168.9931. Found: 168.9931.

4.3.3. 6-Methylbenzo[d]oxazol-2(3H)-one (3c). Yield: 353 mg (97%); White solid; mp 145-146 °C (lit.⁴ 144-146 °C); IR (KBr) 3257, 3081, 2915, 1776, 1737, 1625, 1498, 1398, 1301, 1267, 1178, 1101, 931, 852, 815, 707, 601, 568 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ 2.32 (s, 3H), 6.96 (t, 2H, J=9.7 Hz), 7.11 (s, 1H), 11.45 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆) δ 20.83, 109.26, 109.92, 123.96, 127.81, 131.28, 143.42, 154.53; HRMS (m/z): [M]+ calcd for C₈H₇NO₂ 149.0477. Found: 149.0476.

4.3.4. 5-Chlorobenzo[d]oxazol-2(3H)-one (3d). Yield: 327 mg (92%); White solid; mp 192 °C (lit.² 193-194 °C); IR (KBr) 3224, 3154, 3054, 1979, 1770, 1617, 1479, 1363, 1299, 1259, 1151, 1105, 962, 921, 844, 804, 692, 590, 549, 416 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ 7.10-7.15 (m, 2H), 7.31 (d, 1H, J=9.3 Hz), 11.77 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆) δ 109.76, 110.72, 121.44, 127.71, 131.64, 142.05, 154.24; HRMS (m/z): [M]+ calcd for C₇H₄ClNO₂ 168.9931. Found: 168.9930.

4.3.5. 5-Methylbenzo[d]oxazol-2(3H)-one (3e). Yield: 350 mg (96%); White solid; mp 131-133 °C (lit.⁵ 130-131 °C); IR (KBr) 3266, 3041, 1781, 1735, 1498, 1457, 1328, 1259, 1172,
956, 929, 796, 676 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ 2.32 (s, 3H), 6.86-6.90 (m, 2H), 7.14 (d, 1H, J=9.0 Hz), 11.51 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆) δ 20.83, 108.97, 110.03, 122.01, 130.21, 133.06, 141.26, 154.56; HRMS(m/z): [M]^+ calcd for C₈H₇NO₂ 149.0477. Found: 149.0478.

4.3.6. 5-Nitrobenzo[d]oxazol-2(3H)-one (3f). Yield: 312 mg (89%); Light yellow solid; mp 230 °C (lit.² 230-231 °C); IR (KBr) 3149, 3116, 3081, 2964, 1774, 1745, 1521, 1483, 1465, 1346, 1267, 1151, 1068, 960, 921, 889, 825, 748, 713, 688, 597 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ 7.36 (d, 1H, J=9.0 Hz), 7.45 (dd, 1H, J₁=9.0, J₂=2.3 Hz), 7.93 (d, 1H, J=9.0 Hz), 10.51 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆) δ 111.32, 111.60, 124.45, 125.41, 132.12, 142.65, 154.15; HRMS(m/z): [M]^+ calcd for C₇H₄N₂O₄ 180.0171. Found: 180.0172.

4.3.7. 5-Methoxybenzo[d]oxazol-2(3H)-one (3g). Yield: 313 mg (88%); White solid; mp 168-170 °C (lit.³ 170-172 °C); IR (KBr) 3276, 3253, 1764, 1629, 1502, 1469, 1301, 1257, 1195, 1170, 1024, 929, 858, 757, 622 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ 3.75 (s, 3H), 6.66 (m, 2H), 7.18 (d, 1H, J=9.7 Hz), 11.58 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆) δ 30.33, 55.58, 96.20, 106.70, 109.75, 131.01, 137.29, 156.04; HRMS(m/z): [M]^+ calcd for C₈H₇NO₃ 165.0426. Found: 165.0427

5. Procedure for preparation of 5a-5e and their analytical data

5.1. Solvent screening for synthesis of benzo[d]imidazol-2(3H)-one (5a)

A mixture of 2-phenoxy carbonyl-4,5-dichloropyridazin-3(2H)-one (2a, 1.2 equiv, 949 mg), 1,2-phenylenediamine (4a, 1 equiv, 300 mg), and solvent (10 mL) was stirred at reflux condition until amide intermediate was consumed by TLC monitoring. After cooling to room temperature, the resulting precipitate was filtered off and washed the solvent was evaporated under reduced pressure. The residue was transferred to an open-bed silica gel column (3 × 7
cm). The column was eluted with \( n \)-hexane/tetrahydrofuran (1:2, v/v). Fractions containing compound 5a were combined and evaporated under reduced pressure to give compound 5a. Table 4 summarizes the results.

5.2. Synthesis of benzo[d]imidazol-2(3H)-ones 5

A mixture of 2-phenoxycarbonyl-4,5-dichloropyridazin-3(2H)-one (2a, 1.2 equiv), compounds 4 (1 equiv, 300 mg) and toluene (10 mL) was stirred at reflux condition until amide intermediate was consumed by TLC monitoring. After cooling to room temperature, the resulting precipitate was filtered off and the solvent was evaporated under reduced pressure. The residue was transferred to an open-bed silica gel column (3 × 7 cm). The column was eluted with \( n \)-hexane/tetrahydrofuran (1:2, v/v). Fractions containing compounds 5 were combined and evaporated under reduced pressure to give compounds 5. Table 5 summarizes the results.

5.2.1. Benzo[d]imidazol-2(3H)-one (5a). Yield: 335 mg (90%); White solid; mp 320-322 °C (lit.\(^6\) 305-308 °C); IR (KBr) 3178, 3114, 3027, 2910, 2807, 2726, 1743, 1483, 1361, 1270, 1197, 1027, 736, 703, 597 cm\(^{-1}\); \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 6.91 (s, 4H), 10.56 (s, 2H); \(^13\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 108.42, 113.27, 120.49, 126.96, 129.63, 130.24, 155.28; HRMS(m/z): [M\(^+\)] calcd for C\(_7\)H\(_6\)N\(_2\)O 134.0480. Found: 134.0480.

5.2.2. 5-Fluoro-1H-benzo[d]imidazol-2(3H)-one (5b). Yield: 252 mg (70%); White solid; mp 300 °C (lit.\(^7\) 300 °C); IR (KBr) 3149, 3051, 1768, 1621, 1466, 1312, 1289, 1101, 847 cm\(^{-1}\); \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 6.81 (m, 3H), 10.65 (s, 1H), 10.76 (s, 1H); \(^13\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 106.36, 108.88, 117.85, 126.01, 130.029, 130.48, 155.71; HRMS(m/z): [M\(^+\)] calcd for C\(_7\)H\(_5\)FN\(_2\)O 152.0386. Found: 152.0385.
5.2.3. 5-Chloro-1H-benzo[d]imidazol-2(3H)-one (5c). Yield: 317 mg (89%); White solid; mp 324-326 °C (lit. 324-328 °C); IR (KBr) 3061, 3026, 1780, 1489, 1321, 1248, 1160, 796 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ 6.98-6.89 (m, 3H), 10.76 (s, 2H); ¹³C NMR (75 MHz, DMSO-d₆) δ 108.48, 109.55, 120.17, 124.56, 128.69, 130.87, 155.21; HRMS(m/z): [M]⁺ calcd for C₇H₅ClN₂O 168.0090. Found: 168.0091.

5.2.4. 5-Nitro-1H-benzo[d]imidazol-2(3H)-one (5d). Yield: 302 mg (86%); Light yellow solid; mp 308-309 °C (lit. 308 °C); IR (KBr) 3094, 1756, 1626, 1331, 1256, 1179, 856, 627 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ 7.11 (d, 1H, J=9.7 Hz), 7.72 (d, 1H, J=2.3 Hz), 7.96 (dd, J₁=9.7, J₂=2.3 Hz, 1H), 11.24 (s, 1H), 11.41 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆) δ 103.55, 108.01, 117.70, 129.68, 135.74, 141.09, 155.48; HRMS(m/z): [M]⁺ calcd for C₇H₅N₃O₃ 179.0331. Found: 179.0331.

5.2.5. 5-Methyl-1H-benzo[d]imidazol-2(3H)-one (5e). Yield: 342 mg (94%); White solid; mp 295-297 °C (lit. 297-300 °C); IR (KBr) 3237, 1765, 1612, 1309, 1278, 1162, 825, 549 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ 2.27 (s, 3H), 6.80-6.71 (m, 3H), 10.43 (s, 1H), 10.47 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆) δ 21.08, 108.16, 109.03, 120.84, 127.45, 129.31, 155.49; HRMS(m/z): [M]⁺ calcd for C₈H₈N₂O 148.0637. Found: 148.0637.

6. Procedure for preparation of 11a-11c and their analytical data


A mixture of 2-phenoxy carbonyl-4,5-dichloropyridazin-3(2H)-one (2a, 1.2 equiv), compounds 6 (1 equiv, 300 mg) and acetic acid (5 mL) was stirred at room temperature (for 11a) or at reflux condition (for 11b-11c) until 6 was consumed by TLC monitoring. After adding zinc powder (5 equiv), the mixture was refluxed for 0.5 hour. After cooling to room temperature, the resulting precipitate was filtered off and washed with dichloromethane (for S11
S12

or tetrahydrofuran (for 11b-11c), the solvent was evaporated under reduced pressure. The resulting residue was transferred to an open-bed silica gel column (3 × 10 cm). The column was eluted with dichloromethane/ethyl acetate (10:1, v/v). Fractions containing compounds 11 were combined and evaporated under reduced pressure to give compounds 11.

Table 6 summarizes the results.

6.1.1. Benzo[d]thiazol-2(3H)-one (11a). Yield: 341 mg (93%); Light yellow solid; mp 138-139 °C (lit.10 139-141 °C); IR (KBr) 3307, 3154, 3108, 3054, 3946, 2881, 2823, 2740, 2674, 1680, 1592, 1463, 1413, 1214, 1222, 742, 701, 642 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ 7.10-7.15 (m, 2H), 7.26-7.31 (m, 1H), 7.55-7.58 (m, 1H), 11.89 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆) δ 111.44, 122.56, 122.66, 123.23, 126.38, 136.27, 169.98; HRMS(m/z): [M]+ calcd for C₇H₅NOS 151.0092. Found: 151.0091.

6.1.2. 5-Chlorobenzo[d]thiazol-2(3H)-one (11b). Yield: 377 mg (82%); Blue-gray solid; mp 234-235 °C (lit.2 240-241 °C); IR (KBr) 3066, 3010, 2923, 2821, 1738, 1743, 1596, 1463, 1301, 121, 1079, 842, 794, 752, 715, 653 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ 7.67 (d, 1H, J=9.0 Hz), 7.83 (s, 1H), 7.98 (d, 1H, J=9.0 Hz), 8.0 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆) δ 111.16, 122.39, 124.23, 130.76, 137.42, 170.06; HRMS(m/z): [M]+ calcd for C₇H₄ClNOS 184.9702. Found: 184.9702.

6.1.3. 5-(Trifluoromethyl)benzo[d]thiazol-2(3H)-one (11c). Yield: 165 mg (58%); Light yellow solid; mp 204 °C; IR (KBr) 3094, 3028, 2989, 2875, 2763, 1696, 1841, 1465, 1384, 1335, 1237, 1173, 1119, 1079, 1053, 937, 887, 819, 772, 749, 703, 646, 460 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ 7.34 (s, 1H), 7.33 (d, 1H, J=9.0 Hz), 7.84 (d, 1H, J=9.0 Hz), 12.23 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆) δ 108.02, 108.08, 119.38, 119.43, 124.16, 128.06, 137.19, 170.22; HRMS(m/z): [M]+ calcd for C₈H₄F₃NOS 218.9966. Found: 218.9967.
7. References

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