Copper catalyzed three-component synthesis of benzothiazolones from o-iodoanilines, DMF, and potassium sulfide

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1) General Information

NMR spectra of the products 2 and 4b–4g were obtained using Bruker Avance-500 instruments, calibrated to TMS (1H NMR spectra) and CD(H)Cl3 (13C NMR spectra) as the internal reference (0.00 ppm for 1H NMR spectra and 77.00 ppm for 13C NMR spectra). NMR spectra of the product 4h–4k was recorded using Bruker Avance-500 instruments, calibrated to residual DMSO-d6 as the internal reference (2.50 ppm for 1H NMR spectra and 40.00 ppm for 13C NMR spectra). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). Melting points were measured uncorrected. Reactions were monitored by thin-layer chromatography or GC-MS analysis. Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh). Unless otherwise noted, all reactions were run under nitrogen atmosphere.

2) Synthesis of Starting Materials

Preparation of 1a and 3b-3g:

\[
\begin{align*}
\text{NH}_2\begin{array}{c} R_1 \\
\end{array} & + \text{CH}_3\text{I} & \xrightarrow{\text{K}_2\text{CO}_3, \text{DMF}, \text{rt}} & \begin{array}{c} \text{NH} \\
\end{array} \begin{array}{c} R_1 \\
\end{array}
\end{align*}
\]

To a solution of the corresponding o-iodoaniline (1.2 equiv) and iodomethane (2 mmol) in DMF (10 mL) was added K₂CO₃ (2 equiv). The resulting mixture was stirred at room temperature for 36 h. Water (10 mL) was added to the reaction mixture. The resulting solution was extracted with diethyl ether (3 × 10 mL). The organic layers were combined and washed with water to remove any remaining DMF and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent.

Preparation of 1b-1e, 1l-1o and 1q:
To a schlenk tube were added 1,2-iodobenzene (3 mmol), the corresponding amine (1.5 equiv), Pd(OAc)$_2$ (0.5 mol%), DPEphos (0.75 mol%), NaOtBu (1.5 equiv) and toluene (8 mL). The resulting mixture was stirred 100 °C for 24h. The reaction mixture was filtered by a crude column with ethyl acetate as eluent, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to provide the desired product.

**Preparation of 1f-1k:**

To a schlenk tube were added o-iodoaniline (1.2 equiv), the corresponding benzyl bromide (2 mmol), NaHCO$_3$ (2 equiv), and EtOH (10 mL). The resulting mixture was stirred at room temperature for overnight. After completion of the reaction, the reaction mixture was filtered by a crude column with ethyl acetate as eluent, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to provide the desired product.

**3) Typical Procedures**

To a schlenk tube were added o-haloanilines (0.3 mmol), K$_2$S (3 equiv), CuBr$_2$ (10 mol%), and DMF (2 mL). Then under the protection of nitrogen, the mixture was stirred at 120 °C (oil bath temperature) for the indicated time until complete
consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted in ethyl acetate, and washed with water. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na$_2$SO$_4$ and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 15:1) to afford the desired product.

4) Experiments of investigating the reaction mechanism

\[
\begin{align*}
(1) & \quad \text{NH}_2\text{SH} \xrightarrow{\text{CuBr}_2 \ (10 \text{ mol\%})} \text{DMF, 120 °C, 15 h}} & \quad \text{SH} \quad \text{N} \quad \text{O} \quad \text{NH}_2 \\
(2) & \quad \text{NH}_2\text{SH} + \text{K}_2\text{S} \xrightarrow{\text{CuBr}_2 \ (10 \text{ mol\%})} \text{DMF, 120 °C, 15 h}} & \quad \text{SH} \quad \text{N} \quad \text{O} \quad \text{NH}_2 \\
(3) & \quad \text{NH}_2\text{SH} + \text{K}_2\text{S} \xrightarrow{\text{DMF}} \text{DMF, 120 °C, 15 h}} & \quad \text{SH} \quad \text{N} \quad \text{O} \\
(4) & \quad \text{NH}_2\text{SH} + \text{S} \xrightarrow{\text{NEt}_3, \text{DMF}} \text{DMF, 120 °C, 15 h}} & \quad \text{SH} \quad \text{N} \quad \text{O} \\
(5) & \quad \text{K}_2\text{S} + \text{H}_2\text{O} \xrightarrow{\text{DMF}} \text{DMF, 120 °C, 15 h}} & \quad \text{S} \\

\text{Scheme 1} \quad \text{2-Aminobenzenethiol React with DMF}
\]

\[
\begin{align*}
(1) & \quad \text{NH}_2\text{SH} \xrightarrow{\text{CO} \ (1 \text{ atm})} \text{DMSO, 120 °C, 15 h}} & \quad \text{SH} \quad \text{N} \quad \text{O} \\
(2) & \quad \text{NH}_2\text{SH} + \text{K}_2\text{S} \xrightarrow{\text{CO} \ (1 \text{ atm})} \text{DMSO, 120 °C, 15 h}} & \quad \text{SH} \quad \text{N} \quad \text{O} \\

\text{Scheme 2} \quad \text{2-Aminobenzenethiol React with CO}
\]
Firstly, 2-aminothiophenol was treated with DMF in the presence of CuBr₂, and there was no benzothiazolone product found in the reaction mixture (scheme 1, eq 1). Importantly, when K₂S was added in the above experiment, 48% of benzothiazolone was obtained (scheme 1, eq 2). Surprised, 46% of benzothiazolone was given in the absence of CuBr₂ in the above reaction (scheme 1, eq 3). For these results we inferred that K₂S played a key role in carbonylation reaction, and that copper catalyst are not involved in carbonylation reaction. Owing to a small amount of sulfur observed in the experiment 2 and 3, we assume it is not K₂S but sulfur that promoted the carbonylation process.⁴ In order to prove our hypothesis, the reaction 2-aminothiophenol with sulfur was run in DMF, and 78% benzothiazolone was afforded (scheme 1, eq 4). Subsequently, we found that 13% of sulfur was afforded when K₂S and equivalent H₂O reacted in DMF (scheme 1, eq 5). Finally, 2-aminothiophenol was treated with CO in DMSO, no product benzothiazolone was found in the reaction mixture (scheme 2, eq 1). Similarly, when K₂S was added in this reaction, 41% of benzothiazolone was isolated (scheme 2, eq 2). These results proved the above results again.

5) Characterization Data

3-methylbenzo[d]thiazol-2(3H)-one (2a):⁵ Pale yellow solid, isolated yield 77% (38.1 mg); mp: 69.7-70.7 °C; ¹H NMR (500 MHz, CDCl₃) δ: 7.42 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 7.33 (td, J = 7.8 Hz, 1.0 Hz, 1H), 7.17 (td, J = 7.8 Hz, 1.0 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 3.45 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 170.00, 137.65, 126.31, 123.15, 122.48, 122.45, 110.36, 28.92; IR (KBr): 1679 (C=O) cm⁻¹.
3-propylbenzo[d]thiazol-2(3H)-one (2b): Pale yellow oil, isolated yield 68% (39.4 mg); $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.42 (dd, $J = 8.0$ Hz, 1.0 Hz, 1H), 7.31 (td, $J = 8.0$ Hz, 1.0 Hz, 1H), 7.15 (td, $J = 7.8$ Hz, 1.0 Hz, 1H), 7.04 (d, $J = 8.5$ Hz, 1H), 3.91 (t, $J = 7.5$ Hz, 2H), 1.81-1.74 (m, 2H), 0.99 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 169.87, 137.13, 126.16, 122.86, 122.73, 122.55, 110.54, 44.24, 20.89, 11.18; IR (KBr): 1685 (C=O) cm$^{-1}$.

3-pentylbenzo[d]thiazol-2(3H)-one (2c): Pale yellow oil, isolated yield 71% (46.9 mg); $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.42 (dd, $J = 7.5$ Hz, 1.0 Hz, 1H), 7.31 (td, $J = 7.8$ Hz, 1.0 Hz, 1H), 7.15 (td, $J = 7.8$ Hz, 1.0 Hz, 1H), 7.04 (d, $J = 8.5$ Hz, 1H), 3.93 (t, $J = 7.5$ Hz, 2H), 1.76-1.71 (m, 2H), 1.38-1.36 (m, 4H), 0.90 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 169.79, 137.11, 126.16, 122.84, 122.77, 122.55, 110.51, 42.76, 28.83, 27.23, 22.28, 13.86; IR (KBr): 1679 (C=O) cm$^{-1}$; HRMS (ESI, m/z) calcd for [C$_{12}$H$_{15}$NOS]H$^+$: 222.0947; found 222.0947.

3-octylbenzo[d]thiazol-2(3H)-one (2d): Pale yellow oil, isolated yield 81% (64.0 mg); $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.41 (dd, $J = 7.5$ Hz, 1.0 Hz, 1H), 7.31 (td, $J = 7.8$ Hz, 1.0 Hz, 1H), 7.14 (td, $J = 7.5$ Hz, 1.0 Hz, 1H), 7.04 (d, $J = 8.0$ Hz, 1H), 3.93 (t, $J = 7.5$ Hz, 2H), 1.76-1.70 (m, 2H), 1.38-1.26 (m, 10H), 0.87 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 169.77, 137.12, 126.16, 122.84, 122.78, 122.56, 110.52, 42.80, 31.68, 29.16, 29.07, 27.54, 26.75, 22.54, 14.01; IR (KBr): 1679 (C=O) cm$^{-1}$.

3-(2-methoxyethyl)benzo[d]thiazol-2(3H)-one (2e): yellow oil, isolated yield 62% (38.9 mg); $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.40 (dd, $J = 7.5$ Hz, 1.0 Hz, 1H), 7.29 (td, $J = 7.8$ Hz, 1.0 Hz, 1H), 7.13 (td, $J = 7.5$ Hz, 1.0 Hz, 1H), 7.04 (d, $J = 8.0$ Hz, 1H), 3.92 (t, $J = 7.5$ Hz, 2H), 1.76-1.71 (m, 2H), 1.38-1.36 (m, 4H), 0.90 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 169.79, 137.11, 126.16, 122.84, 122.78, 122.56, 110.52, 42.80, 31.68, 29.16, 29.07, 27.54, 26.75, 22.54, 14.01; IR (KBr): 1679 (C=O) cm$^{-1}$.

3-(2-methoxyethyl)benzo[d]thiazol-2(3H)-one (2e): yellow oil, isolated yield 62% (38.9 mg); $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.40 (dd, $J = 7.5$ Hz,
1.0 Hz, 1H), 7.30 (td, J = 7.8 Hz, 1.0 Hz, 1H), 7.19-7.13 (m, 2H), 4.13 (t, J = 5.8 Hz, 2H), 3.68 (t, J = 5.5 Hz, 2H), 3.33 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 170.13, 137.48, 126.17, 122.98, 122.45, 122.36 111.18, 69.80, 58.98, 42.72; IR (KBr): 1679 (C=O) cm$^{-1}$; HRMS (ESI, m/z) calcd for [C$_{10}$H$_{11}$NO$_2$S]H$: 210.0583$; found 210.0581.

3-benzylbenzo[d]thiazol-2(3H)-one (2f):$^5$ yellow solid, isolated yield 52% (37.7 mg); mp: 83.3-84.1 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.40 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 7.32-7.24 (m, 5H), 7.19 (td, J = 8.0 Hz, 1.0 Hz, 1H), 7.11 (td, J = 7.5 Hz, 1.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 5.13 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 170.22, 136.88, 135.05, 128.81, 127.81, 127.04, 126.26, 123.17, 122.52 (2C), 111.19, 46.09; IR (KBr): 1665 (C=O) cm$^{-1}$.

3-(4-methylbenzyl)benzo[d]thiazol-2(3H)-one (2g): yellow solid, isolated yield 53% (40.7 mg); mp: 66.2-67.3 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.39 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 7.21-7.17 (m, 3H), 7.12-7.08 (m, 3H), 6.96 (d, J = 8.0 Hz, 1H), 5.09 (s, 2H), 2.29 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 170.21, 137.55, 136.93, 132.04, 129.46, 127.08, 126.22, 123.10, 122.52, 122.47, 111.21, 45.90, 21.02; IR (KBr): 1662 (C=O) cm$^{-1}$; HRMS (ESI, m/z) calcd for [C$_{15}$H$_{13}$NOS]H$: 256.0791$; found 256.0791.

3-(4-chlorobenzyl)benzo[d]thiazol-2(3H)-one (2h):$^7$ yellow solid, isolated yield 61% (50.3 mg); mp: 79.5-80.6 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.43 (dd, J = 7.5 Hz, 1.0 Hz, 1H), 7.30-7.27 (m, 2H), 7.24-7.20 (m, 3H), 7.14 (td, J =
7.5 Hz, 1.0 Hz, 1H), 6.92 (dd, J = 8.0 Hz, 0.5 Hz, 1H), 5.10 (s, 2H); $^{13}\text{C}$ NMR (125 MHz, CDCl$_3$) δ: 170.24, 136.63, 133.75, 133.60, 129.04, 128.50, 126.36, 123.38, 122.68, 122.55, 111.01, 45.47; IR (KBr): 1669 (C=O) cm$^{-1}$.

3-(naphthalen-2-ylmethyl)benzo[d]thiazol-2(3H)-one (2i): yellow solid, isolated yield 54% (47.4 mg); mp: 108.9-110.1 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.79-7.75 (m, 3H), 7.70 (s, 1H), 7.45-7.43 (m, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.15 (td, J = 7.8 Hz, 1.0 Hz, 1H), 7.08 (td, J = 7.5 Hz, 1.0 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 5.27 (s, 2H); $^{13}\text{C}$ NMR (125 MHz, CDCl$_3$) δ: 170.34, 136.89, 133.16, 132.81, 132.52, 128.84, 127.71, 127.64, 126.37, 126.28, 126.11, 125.94, 124.82, 123.21, 122.53 (2C), 111.26, 46.33; IR (KBr): 1685 (C=O) cm$^{-1}$; HRMS (ESI, m/z) calcd for [C$_{18}$H$_{13}$NOS]$^+$: 292.0791; found 292.0792.

3-(furan-2-ylmethyl)benzo[d]thiazol-2(3H)-one (2j): yellow oil, isolated yield 58% (40.2 mg); $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.41 (dd, J = 7.5 Hz, 0.5 Hz, 1H), 7.34 (dd, J = 2.0 Hz, 0.5 Hz, 1H), 7.30 (td, J = 7.8 Hz, 1.0 Hz, 1H), 7.24(t, J = 6.0 Hz, 1H), 7.15 (td, J = 7.5 Hz, 1.0 Hz, 1H), 6.36 (d, J = 3.5 Hz, 1H), 6.31 (dd, J = 3.5 Hz, 2.0 Hz, 1H), 5.10 (s, 2H); $^{13}\text{C}$ NMR (125 MHz, CDCl$_3$) δ: 169.82, 148.59, 142.62, 136.74, 126.30, 123.26, 122.51, 122.43, 111.07, 110.55, 109.06, 39.02; IR (KBr): 1682 (C=O) cm$^{-1}$; HRMS (ESI, m/z) calcd for [C$_{12}$H$_9$NO$_2$S]$^+$: 232.0427; found 232.0427.

3-(1-phenylethyl)benzo[d]thiazol-2(3H)-one (2k): yellow oil, isolated yield 42% (32.1 mg); $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.40-7.38 (m, 1H),
7.34-7.33 (m, 4H), 7.29-7.27 (m, 1H), 7.06-7.04 (m, 2H), 6.73-6.71 (m, 1H), 6.14-6.09 (m, 1H), 1.90 (d, J = 7.5 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 170.18, 138.58, 135.89, 128.74, 127.58, 126.46, 125.72, 122.65, 122.62, 122.51, 112.75, 51.81, 16.17; IR (KBr): 1665 (C=O) cm$^{-1}$; HRMS (ESI, m/z) calcd for [C$_{15}$H$_{13}$NOS]$^+$: 256.0791; found 256.0793.

**3-(3,4-dimethoxyphenethyl)benzo[d]thiazol-2(3H)-one (2l):** yellow solid, isolated yield 71% (67.2 mg); mp: 83.9-85.0 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.41 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 7.27 (td, J = 8.0 Hz, 1.0 Hz, 1H), 7.13 (td, J = 7.8 Hz, 1.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.80-6.75 (m, 2H), 6.67 (d, J = 1.5 Hz, 1H), 4.13 (t, J = 7.5 Hz, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 2.96 (t, J = 8.0 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 169.64, 148.89, 147.80, 136.83, 130.03, 126.14, 122.89, 122.49, 122.46, 120.65, 111.90, 111.30, 110.41, 55.78, 55.72, 44.19, 33.24; IR (KBr): 1672 (C=O) cm$^{-1}$; HRMS (ESI, m/z) calcd for [C$_{17}$H$_{17}$NO$_3$S]$^+$: 316.1002; found 316.1000.

**3-phenethylbenzo[d]thiazol-2(3H)-one (2m):** yellow solid, isolated yield 79% (60.5 mg); mp: 85.8-86.7 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.40 (d, J = 7.5 Hz, 1H), 7.30-7.25 (m, 3H), 7.23-7.21 (m, 3H), 7.13 (t, J = 7.5 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 4.13 (t, J = 8.0 Hz, 2H), 3.00 (t, J = 8.0 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 169.64, 137.52, 136.79, 128.70, 128.62 (2C), 126.76, 126.18, 122.91, 122.58, 110.36, 44.09, 33.73; IR (KBr): 1669 (C=O) cm$^{-1}$. 

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3-(4-fluorophenethyl)benzo[d]thiazol-2(3H)-one (2n):
yellow oil, isolated yield 80% (65.5 mg); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.41 (dd, $J = 7.5$ Hz, 0.5 Hz, 1H), 7.28 (td, $J = 7.8$ Hz, 1.5 Hz, 1H), 7.17-7.12 (m, 3H), 6.96 (t, $J = 9.0$ Hz, 3H), 4.12 (t, $J = 7.8$ Hz, 2H), 2.99 (t, $J = 7.5$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 169.68, 161.76 (d, $J = 243.5$ Hz), 136.73, 133.22 (d, $J = 2.9$ Hz), 130.20 (d, $J = 7.9$ Hz), 126.22, 123.00, 122.65, 122.59, 115.46 (d, $J = 21.0$ Hz), 110.30, 44.03, 32.91; IR (KBr): 1675 (C=O) cm$^{-1}$; HRMS (ESI, m/z) calcd for [C$_{15}$H$_{12}$FNOS]H$^+$: 274.0696; found 274.0700.

3-(2-(thiophen-2-yl)ethyl)benzo[d]thiazol-2(3H)-one (2o):
yellow solid, isolated yield 77% (60.3 mg); mp: 82.8-83.8 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.41 (dd, $J = 8.0$ Hz, 1.0 Hz, 1H), 7.27 (td, $J = 8.0$ Hz, 1.0 Hz, 1H), 7.15-7.12 (m, 2H), 6.95 (d, $J = 8.0$ Hz, 1H), 6.90 (dd, $J = 5.0$ Hz, 3.5 Hz, 1H), 6.84 (d, $J = 2.5$ Hz, 1H), 4.17 (t, $J = 7.5$ Hz, 2H), 3.24 (t, $J = 7.8$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 169.70, 139.35, 136.75, 127.09, 126.26, 125.76, 124.25, 123.01, 122.62, 122.56, 110.27, 44.12, 27.75; IR (KBr): 1672 (C=O) cm$^{-1}$; HRMS (ESI, m/z) calcd for [C$_{13}$H$_{11}$NOS$_2$]H$^+$: 262.0355; found 262.0355.

benzo[d]thiazol-2(3H)-one (2p):$^9$ Pale yellow solid, isolated yield 75% (34.0 mg); mp: 134.5-135.3 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 10.44 (s, 1H), 7.39 (d, $J = 7.5$ Hz, 1H), 7.27 (t, $J = 7.5$ Hz, 1H), 7.18 (d, $J = 8.0$ Hz, 1H), 7.14 (t, $J = 7.8$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 173.37, 135.50, 126.49, 123.88, 123.20, 122.42, 111.88; IR (KBr): 1665 (C=O) cm$^{-1}$.
3-phenylbenzo[d]thiazol-2(3H)-one (2q): \(^5\) yellow oil, isolated yield 24\% (16.4 mg); \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ: 7.58-7.55 (m, 2H), 7.51-7.48 (m, 1H), 7.47-7.45 (m, 1H), 7.42-7.40 (m, 2H), 7.22-7.16 (m, 2H), 6.80-6.78 (m, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ: 169.66, 138.23, 134.82, 129.98, 129.61, 129.18, 127.86, 126.27, 123.54, 122.52, 111.78; IR (KBr): 1695 (C=O) cm\(^{-1}\).

6-fluoro-3-methylbenzo[d]thiazol-2(3H)-one (4b): \(^10\) yellow solid, isolated yield 78\% (42.8 mg); mp: 91.9-92.9 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ: 7.18 (dd, \(J = 7.5\) Hz, 2.5 Hz, 1H), 7.05 (td, \(J = 8.8\) Hz, 2.5 Hz, 1H), 6.97 (dd, \(J = 9.0\) Hz, 4.5 Hz, 1H), 3.44 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ: 169.41, 158.93 (d, \(J = 241.1\) Hz), 133.92, 123.60 (d, \(J = 10.0\) Hz), 113.45 (d, \(J = 23.8\) Hz), 110.91 (d, \(J = 8.4\) Hz), 109.84 (d, \(J = 26.8\) Hz), 29.12; IR (KBr): 1679 (C=O) cm\(^{-1}\).

6-chloro-3-methylbenzo[d]thiazol-2(3H)-one (4c): \(^11\) Pale yellow solid, isolated yield 83\% (49.6 mg); mp: 107.7-108.6 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ: 7.39 (d, \(J = 2.0\) Hz, 1H), 7.28 (dd, \(J = 8.5\) Hz, 2.0 Hz, 1H), 6.95 (d, \(J = 9.0\) Hz, 1H), 3.43 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ: 169.26, 136.17, 128.43, 124.66, 123.83, 122.20, 111.08, 29.07; IR (KBr): 1682 (C=O) cm\(^{-1}\).

5-chloro-3-methylbenzo[d]thiazol-2(3H)-one (4d): \(^11\) Pale yellow solid, isolated yield 77\% (46.1 mg); mp: 104.2-104.9 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ: 7.32 (d, \(J = 8.0\) Hz, 1H), 7.14 (dd, \(J = 8.0\) Hz, 1.5 Hz, 1H), 7.03 (d, \(J = 1.5\) Hz, 1H), 3.43 (s, 3H); mp: 103.2-103.9 °C; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ: 169.84, 138.55,
132.33, 123.24, 123.19, 120.70, 110.77, 29.06; IR (KBr): 1685 (C=O) cm⁻¹.

6-bromo-3-methylbenzo[d]thiazol-2(3H)-one (4e): Pale yellow solid, isolated yield 55% (40.3 mg); mp: 116.6-117.8 °C; ¹H NMR (500 MHz, CDCl₃) δ: 7.53 (d, J = 1.5 Hz, 1H), 7.43 (dd, J = 8.5 Hz, 1.5 Hz, 1H), 6.90 (d, J = 8.5 Hz, 1H), 3.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 169.22, 136.65, 124.97, 124.28, 115.54, 111.52, 29.08; IR (KBr): 1679 (C=O) cm⁻¹.

3-methyl-6-(trifluoromethyl)benzo[d]thiazol-2(3H)-one (4f): yellow solid, isolated yield 72% (50.5 mg); mp: 51.6-52.7 °C; ¹H NMR (500 MHz, CDCl₃) δ: 7.69 (s, 1H), 7.59 (d, J = 8.5 Hz, 1H), 7.13 (d, J = 8.5 Hz, 1H), 3.49 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 169.62, 140.16, 125.55 (q, J = 32.8 Hz), 123.85 (q, J = 270.4 Hz), 123.66 (q, J = 3.8 Hz), 123.12, 119.73 (q, J = 3.6 Hz), 110.18, 29.20; IR (KBr): 1685 (C=O) cm⁻¹; HRMS (ESI, m/z) calcd for [C₉H₆F₃NOS]⁺: 234.0195; found 234.0195.

3,6-dimethylbenzo[d]thiazol-2(3H)-one (4g): Pale yellow solid, isolated yield 75% (40.3 mg); mp: 68.5-70.0 °C; ¹H NMR (500 MHz, CDCl₃) δ: 7.21 (s, 1H), 7.11 (d, J = 8.5 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 3.41 (s, 3H), 2.37 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 169.89, 135.41, 132.93, 127.02, 122.65, 122.34, 110.04, 28.86, 20.96; IR (KBr): 1669 (C=O) cm⁻¹.

6-bromobenzoc[d]thiazol-2(3H)-one (4h): Pale yellow solid, isolated yield 53% (36.6 mg); mp: 229.8-230.8 °C; ¹H NMR (500 MHz, DMSO-d₆) δ: 11.98 (s, 1H), 7.81 (d, J = 2.0 Hz, 1H), 7.42 (dd, J = 8.5 Hz, 2.0 Hz, 1H), 7.04 (d, J = 1.5 Hz, 1H); ¹³C NMR (125 MHz, DMSO-d₆) δ: 170.23, 136.13, 129.69, 126.10,
125.51, 114.51, 113.66; IR (KBr): 1672 (C=O) cm\(^{-1}\).

6-(trifluoromethyl)benzo[\textit{d}]thiazol-2(3H)-one (4i):\(^9\) Pale yellow solid, isolated yield 73\% (47.9 mg); mp: 130.9-131.8 °C; \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\): 12.28 (s, 1H), 8.01 (s, 1H), 7.58 (d, \(J = 8.5\) Hz, 1H), 7.25 (d, \(J = 8.5\) Hz, 1H); \(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta\): 170.77, 140.13, 124.89, 124.80 (q, \(J = 270.1\) Hz), 124.08 (q, \(J = 3.8\) Hz), 123.67 (q, \(J = 32.0\) Hz), 120.71 (q, \(J = 3.9\) Hz), 112.21; IR (KBr): 1722 (C=O) cm\(^{-1}\).

2-oxo-2,3-dihydrobenzo[\textit{d}]thiazole-6-carbonitrile (4j):\(^{15}\) Pale yellow solid, isolated yield 14\% (7.4 mg); mp: above 230 °C; \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\): 12.41 (s, 1H), 8.13 (d, \(J = 1.5\) Hz, 1H), 7.72 (dd, \(J = 8.5\) Hz, 1.5 Hz, 1H), 7.24 (d, \(J = 8.0\) Hz, 1H); \(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta\): 170.54, 140.73, 131.31, 127.33, 125.09, 119.31, 112.61, 105.23; IR (KBr): 1689 (C=O) cm\(^{-1}\).

6-methylbenzo[\textit{d}]thiazol-2(3H)-one (4k):\(^9\) Pale yellow solid, isolated yield 70\% (34.7 mg); mp: 166.3-167.4 °C; \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\): 11.74 (s, 1H), 7.32 (s, 1H), 7.06 (d, \(J = 8.0\) Hz, 1H), 6.99 (d, \(J = 8.0\) Hz, 1H), 2.28 (s, 3H); \(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta\): 170.46, 134.48, 132.32, 127.60, 123.77, 123.12, 111.72, 21.12; IR (KBr): 1655 (C=O) cm\(^{-1}\).

6) References


6) Scanned $^1$H NMR and $^{13}$C NMR Spectra of All New Compounds
$\text{O} \quad \text{N}$

**Figure 1:**

- **Structure 2o:**
  - Chemical structure of compound 2o.

**Figure 2:**

- **Structure 2p:**
  - Chemical structure of compound 2p.