Electronic supplementary information for

Regulable Cross-Coupling of Alcohols and Benzothiazoles via Noble-Metal-Free Photocatalyst under Visible Light

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1. Experimental section

1) General information

All chemicals, unless otherwise noted, were purchased from commercial sources and were used without further purification. Unless stated otherwise, all reactions were carried out under nitrogen atmosphere. The substrates were synthesized according to the literature methods\(^1\). Irradiation with visible light was performed using blue LEDs (\(\lambda = 450 \pm 10\) nm) illumination instruments (The instruments were designed by ourselves and the actual output power density of the LEDs at 0.5 cm distance is 33.70 mW/cm\(^2\) detected by CEL-NP2000-10 (Beijing Ceau Light Co. Ltd., China) light power meter). For irradiation, the material of the reaction vessel is common glass; the distance from the light source is about 0.5 cm.

The nuclear magnetic resonance spectra were recorded on the Bruker Ascend\(^\text{TM}\) 400 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal standard. High resolution mass spectra were recorded using a Q Exactive mass spectrometer (Thermo Fisher Scientific, USA).
2) Preparation of 2-2- substituted benzothiazole

\[ \text{R} + \text{NH}_2 \xrightarrow{\text{ONO}} \text{THF (10 mL)} \rightarrow \text{R} \]

6.5 mmol 2.2 equiv. 2a

Scheme S1. Synthesis of benzothiazoles.

Substituted benzothiazoles (9a, 14a, 15a, 16a) were not commercially available: 7a, 8a were prepared following a procedure previously reported\(^1\)-\(^2\) in the literature (Scheme S1). In particular, a 50 mL round-bottom flask was charged with 10 mL of freshly distilled THF and the chosen 2-aminobenzothiazole derivative (6.5 mmol, 0.65 M). Stirring was applied and isoamyl nitrite (1.9 mL, 14.3 mmol, 2.2 equiv., \(\rho = 0.872 \text{ g/mL}\)) was added dropwise. The resulting mixture was then refluxed, depending on the substrate, for a period of time ranging from 1 to 6 hours. The solution was then poured into a mixture of ice and water, then the aqueous phase was extracted with ethyl acetate (3×30 mL). Organic phases were combined and washed with brine, dried on Na\(_2\)SO\(_4\), filtered, then solvent was removed under reduced pressure. Purification was performed by means of column chromatography (SiO\(_2\); n-hexane/ethyl acetate 95:5). Products were obtained with yields ranging from 52% to 76% (see above).

9a, 14a, 15a, 16a were prepared according to the above procedure.
3) General procedure for the reactions

The benzothiazoles substrates (0.2 mmol, 1.1 eq.), ethyl alcohol (1 mL, 85.0 equiv.), 5 mol% Esoin Y and 0.6 equiv. Fe$_2$(SO$_4$)$_3$ were dissolved in 4.0 mL DCE in a 15 mL reaction tube equipped with magnetic stirring bar, the reaction tube was sealed, and the resulting mixture was degassed with nitrogen for 15 min, then the reaction tube was irradiated by blue LEDs (λ = 450 ± 10 nm) at room temperature for 8-36 h. After reaction, the solvent was removed by rotary evaporation and purified by column chromatography on silica gel using petroleum ether/ethyl acetate (200:3) as the eluent.
4) Optimization of the reaction conditions

Table S1. Substrate ratio effect

<table>
<thead>
<tr>
<th>Entry</th>
<th>a / b (equiv.)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1/10</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>1/25</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>1/50</td>
<td>58</td>
</tr>
<tr>
<td>5</td>
<td>1/85</td>
<td>99</td>
</tr>
</tbody>
</table>

Yields of isolated products.

Table S2. LED light effect

<table>
<thead>
<tr>
<th>Entry</th>
<th>LED light</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3W 380 nm</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>3W 450 nm</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>3W 510 nm</td>
<td>0</td>
</tr>
</tbody>
</table>

Yields of isolated products.

Table S3. Solvent effect

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent (4 mL)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeCN</td>
<td>41</td>
</tr>
<tr>
<td>2</td>
<td>1,4-Dioxane</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>DCE</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>DMF</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>DMSO</td>
<td>0</td>
</tr>
</tbody>
</table>

Yields of isolated products.
Table S4. \( \text{Fe}_2(\text{SO}_4)_3 \) effect

\[
\text{Ar, 4% EY, Fe}_2(\text{SO}_4)_3, \text{DCE, 450 nm}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>( \text{Fe}_2(\text{SO}_4)_3 ) (mg)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>63</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>45</td>
</tr>
</tbody>
</table>

Yields of isolated products.

Table S5. Optimization studies for the synthesis of acylation products

\[
\text{Air, 4% EY, Fe}_2(\text{SO}_4)_3, \text{DCE, 450 nm}
\]

<table>
<thead>
<tr>
<th>entry</th>
<th>a/b</th>
<th>Eosin Y (mol %)</th>
<th>( \text{Fe}_2(\text{SO}_4)_3 )</th>
<th>solvent (0.2 M)</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/10</td>
<td>2</td>
<td>0.6 equiv.</td>
<td>DCE</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>1/40</td>
<td>2</td>
<td>0.6 equiv.</td>
<td>DCE</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>1/80</td>
<td>2</td>
<td>0.6 equiv.</td>
<td>DCE</td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td>1/80</td>
<td>2</td>
<td>0.6 equiv.</td>
<td>DMSO</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>1/80</td>
<td>2</td>
<td>0.6 equiv.</td>
<td>DMF</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>1/80</td>
<td>2</td>
<td>0.6 equiv.</td>
<td>MeCN</td>
<td>35</td>
</tr>
<tr>
<td>7</td>
<td>1/80</td>
<td>-</td>
<td>0.6 equiv.</td>
<td>DCE</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>1/80</td>
<td>2</td>
<td>-</td>
<td>DCE</td>
<td>trace</td>
</tr>
<tr>
<td>9a</td>
<td>1/80</td>
<td>2</td>
<td>0.6 equiv.</td>
<td>DCE</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) Yields of isolated products. \(^b\) Without light.
5) Radical-trapping experiment

\[
\begin{align*}
\text{a1} + \begin{array}{c}
\text{Ar, 4\% EY, 0.6 equiv. Fe}_2(\text{SO}_4)_3 \n\end{array} \rightarrow \text{c1} \quad \text{b1}\n\text{DCE, 450 nm} \quad \text{trace detected by HRMS}\n\end{align*}
\]

found: 202.1803

Benzothiazole a1 (0.2 mmol), ethanol b1 (1.0 mL), 2 mol% Eosin Y, 60 mol% Fe$_2$(SO$_4$)$_3$ and TEMPO (0.4 mmol) were dissolved in 4.0 mL DCE in a 15 mL reaction tube equipped with a magnetic stirring bar, the tube was sealed and degassed with nitrogen for 15 min, and then the reaction tube was irradiated with blue LED ($\lambda = 450\pm10$ nm) at room temperature.
6) Quenching experiments

Figure S1. Photoluminescence quenching spectra of EY (Eosin Y) (1.0 x 10^{-5} M) by 1a and EtOH, in Ar or air atmosphere, and inset figures shows the Stern-Volmer plots. (A) EY + 1a in Ar, (B) EY with iron salt (EY@Fe) + 1a in Ar, (C) EY + EtOH in Ar, (D) EY@Fe + 1a in Ar, (E) EY + 1a in air, (F) EY@Fe + 1a in air, (G) EY + EtOH in air, (H) EY@Fe + EtOH in air.

Table S6. Quenching constants with different additive in EY solvent

<table>
<thead>
<tr>
<th>Entry</th>
<th>ATM</th>
<th>EY solvent</th>
<th>Quencher</th>
<th>K (M^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ar</td>
<td>EY</td>
<td>1a</td>
<td>10.9 ± 0.1</td>
</tr>
<tr>
<td>2</td>
<td>Ar</td>
<td>EY</td>
<td>EtOH</td>
<td>8.1 ± 0.1</td>
</tr>
<tr>
<td>3</td>
<td>Ar</td>
<td>EY + iron salt</td>
<td>1a</td>
<td>172.8 ± 1.1</td>
</tr>
<tr>
<td>4</td>
<td>Ar</td>
<td>EY + iron salt</td>
<td>EtOH</td>
<td>18.9 ± 0.6</td>
</tr>
<tr>
<td>5</td>
<td>Air</td>
<td>EY</td>
<td>1a</td>
<td>9.9 ± 0.2</td>
</tr>
<tr>
<td>6</td>
<td>Air</td>
<td>EY</td>
<td>EtOH</td>
<td>4.1 ± 0.1</td>
</tr>
<tr>
<td>7</td>
<td>Air</td>
<td>EY + iron salt</td>
<td>1a</td>
<td>20.8 ± 0.3</td>
</tr>
<tr>
<td>8</td>
<td>Air</td>
<td>EY + iron salt</td>
<td>EtOH</td>
<td>7.3 ± 0.5</td>
</tr>
</tbody>
</table>

General procedure: The fluorescence quenching experiments were measured with excitation at 450 nm. A degassed MeCN solution of 1×10^{-5} M EY and 3.0×10^{-1} M 1a respectively were prepared. The experiments were conducted in 1.25 cm x 1.25 cm x 4.5 cm quartz cuvette at room temperature. Appropriate volume (the whole solution volume change < 5% ) of the quencher 1a or EtOH was respectively injected to the MeCN solution (3 mL) of 1×10^{-5} M EY in the sealed quartz cuvette by microsyringe. For the EY solution with iron salt additive, 10 mg ferric sulfate solid was added.
7) Transformation Cycle of Eosin Y

Scheme S2. The chemical structure of Eosin Y and its HAT cycles with alcohol and aldehyde to form alkyl radicals.
8) References


2. Characterization data of the products

2-ethylbenzo[d]thiazole (1c)

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 7.97 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 7.9$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 1H), 7.34 (t, $J = 8.0$ Hz, 1H), 3.15 (q, $J = 7.6$ Hz, 2H), 1.47 (t, $J = 7.6$ Hz, 3H).
$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 173.57, 153.28, 135.07, 125.88, 124.62, 122.50, 121.50, 27.77, 13.80.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_9$H$_{10}$NS: 164.0534, found: 164.0534.

2-propylbenzo[d]thiazole (2c)

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 7.99 (s, 1H), 7.85 (s, 1H), 7.45 (t, $J = 7.4$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 3.08 (s, 2H), 1.98 – 1.86 (m, 2H), 1.06 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 125.81, 124.64, 122.53, 121.51, 36.31, 23.04, 13.73.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{10}$H$_{12}$NS: 178.0690, found: 178.0690.

2-butylbenzo[d]thiazole (3c)

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 7.97 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 7.9$ Hz, 1H), 7.47 – 7.41 (m, 1H), 7.37 – 7.30 (m, 1H), 3.16 – 3.07 (m, 2H), 1.90 – 1.83 (m, 2H), 1.54 – 1.42 (m, 2H), 0.97 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 172.41, 153.26, 135.14, 125.85, 124.61, 122.50, 121.47, 34.06, 31.78, 22.31, 13.76.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{11}$H$_{14}$NS: 192.0847, found: 192.0854.

2-pentylbenzo[d]thiazole (4c)

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 7.97 (d, $J = 8.1$ Hz, 1H), 7.84 (d, $J = 7.9$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.35 (t, $J = 7.5$ Hz, 1H), 3.11 (t, $J = 7.7$ Hz, 2H), 1.88 (q, $J = 7.4$ Hz, 2H), 1.41 (s, 4H), 0.91 (t, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 172.55, 153.24, 135.16, 125.91, 124.66, 122.52, 121.53, 34.38, 31.38, 29.50, 22.44, 14.02.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{12}$H$_{15}$NS: 206.1003, found: 206.1013.
2-hexylbenzo[d]thiazole (5c)

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 7.96 (s, 1H), 7.84 (d, $J$ = 7.9 Hz, 1H), 7.45 (t, $J$ = 7.7 Hz, 1H), 7.35 (t, $J$ = 7.6 Hz, 1H), 3.16 – 3.07 (m, 2H), 1.88 (p, $J$ = 7.6 Hz, 2H), 1.44 (p, $J$ = 6.6 Hz, 2H), 1.27 (s, 4H), 0.88 (t, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 172.49, 153.17, 135.10, 125.85, 124.61, 122.47, 121.46, 34.35, 31.80, 29.72, 29.12, 22.63, 14.07.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{13}$H$_{17}$NS: 220.1115, found: 220.1108.

2-heptylbenzo[d]thiazole (6c)

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 7.97 (d, $J$ = 8.1 Hz, 1H), 7.84 (d, $J$ = 7.9 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.34 (t, $J$ = 7.6 Hz, 1H), 3.15 – 3.09 (m, 2H), 1.91 – 1.85 (m, 2H), 1.35 (ddd, $J$ = 20.6, 18.2, 5.5 Hz, 8H), 0.88 (t, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 172.50, 153.21, 135.12, 125.86, 124.62, 122.49, 121.48, 34.36, 31.67, 29.74, 29.14, 28.97, 22.61, 14.06.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{14}$H$_{19}$NS: 234.1316, found: 234.1319.

2-octylbenzo[d]thiazole (7c)

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 7.97 (d, $J$ = 8.1 Hz, 1H), 7.84 (d, $J$ = 7.9 Hz, 1H), 7.44 (t, $J$ = 8.2 Hz, 1H), 7.34 (t, $J$ = 7.6 Hz, 1H), 3.16 – 3.05 (m, 2H), 1.88 (p, $J$ = 7.6 Hz, 2H), 1.44 (p, $J$ = 7.0, 6.5 Hz, 2H), 1.33 – 1.23 (m, 8H), 0.88 (t, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 172.45, 153.25, 135.13, 125.83, 124.62, 122.49, 121.46, 34.37, 31.81, 29.73, 29.26, 29.18, 29.13, 22.64, 14.08.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{15}$H$_{21}$NS: 248.1473, found: 248.1464.

2-isopropylbenzo[d]thiazole (9c)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, $J$ = 8.1 Hz, 1H), 7.85 (d, $J$ = 8.0 Hz, 1H), 7.45 (t, $J$ = 7.7 Hz, 1H), 7.34 (t, $J$ = 7.6 Hz, 1H), 3.43 (p, $J$ = 6.9 Hz, 1H), 1.48 (d, $J$ = 6.9 Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 178.76, 153.13, 134.71, 125.91, 124.65, 122.62, 121.61, 34.15, 22.98.

HRMS (ESI-TOF) (m/z) for [M+Na]$^+$ calculated for C$_{10}$H$_{11}$NS: 178.0646, found: 178.0654.
2-(sec-butyl)benzo[d]thiazole (10c)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm = 7.88 (d, $J = 8.1$ Hz, 1H), 7.70 (d, $J = 7.9$ Hz, 1H), 7.31 (t, $J = 8.0$ Hz, 1H), 7.19 (t, $J = 7.5$ Hz, 1H), 3.08 (h, $J = 6.9$ Hz, 1H), 1.78 (dd, $J = 14.2$, 6.9 Hz, 1H), 1.65 (dq, $J = 13.9$, 7.1 Hz, 1H), 1.32 (d, $J = 6.9$ Hz, 3H), 0.85 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm = 177.74, 153.12, 134.68, 124.53, 122.59, 121.52, 41.05, 30.59, 20.68, 11.82.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{11}$H$_{13}$NS: 192.0847, found: 192.0843.

2-(pentan-3-yl)benzo[d]thiazole (11c)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm = 7.99 (d, $J = 8.0$ Hz, 1H), 7.85 (dd, $J = 7.9$, 0.4 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.38 – 7.31 (m, 1H), 3.00 (tt, $J = 8.5$, 5.8 Hz, 1H), 1.90 – 1.79 (m, 4H), 0.93 (t, $J = 7.4$ Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm = 176.86, 153.07, 134.74, 125.73, 124.53, 122.62, 121.54, 48.72, 28.94, 11.90.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{12}$H$_{16}$NS: 206.1003, found: 206.1008.

2-cyclopentylbenzo[d]thiazole (12c)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm = 7.97 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 7.9$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.33 (t, $J = 7.6$ Hz, 1H), 3.56 (p, $J = 8.1$ Hz, 1H), 2.32 – 2.20 (m, 2H), 2.00 – 1.83 (m, 4H), 1.80 – 1.70 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm = 177.29, 153.14, 134.80, 125.90, 124.61, 122.51, 121.55, 44.83, 34.14, 25.66.

HRMS (ESI-TOF) (m/z) for [M+Na]$^+$ calculated for C$_{12}$H$_{13}$NS: 204.0802, found: 204.0806.

2-cyclohexylbenzo[d]thiazole (13c)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm = 7.97 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 7.6$ Hz, 1H), 7.47 – 7.39 (m, 1H), 7.35 – 7.27 (m, 1H), 3.09 (tt, $J = 11.7$, 3.6 Hz, 1H), 2.20 (dd, $J = 13.3$, 2.1 Hz, 2H), 1.92 – 1.83 (m, 2H), 1.80 – 1.72 (m, 1H), 1.63 (ddd, $J = 24.6$, 12.3, 3.1 Hz, 2H), 1.50 – 1.37 (m, 2H), 1.36 – 1.24 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm = 177.57, 153.14, 134.56, 125.79, 124.50, 122.57, 121.55, 43.45, 33.43, 26.08, 25.81.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{13}$H$_{16}$NS: 218.1003, found: 218.1002.
**2-cycloheptylbenzo[d]thiazole (14c)**

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm = 7.96 (d, \(J = 8.1\) Hz, 1H), 7.83 (d, \(J = 7.9\) Hz, 1H), 7.47 – 7.39 (m, 1H), 7.36 – 7.29 (m, 1H), 3.35 – 3.21 (m, 1H), 2.22 (dd, \(J = 8.8, 5.1\) Hz, 2H), 1.87 (dt, \(J = 13.0, 4.9\) Hz, 4H), 1.73 – 1.57 (m, 6H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) ppm = 178.71, 153.02, 134.69, 125.78, 124.49, 122.54, 121.51, 45.52, 35.37, 28.08, 26.55.

HRMS (ESI-TOF) (m/z) for [M+H]^+ calculated for C\(_{14}\)H\(_{18}\)NS: 232.1160, found: 232.1165.

**2-(tetrahydro-2H-pyran-4-yl)benzo[d]thiazole (15c)**

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm = 7.99 (d, \(J = 8.1\) Hz, 1H), 7.87 (d, \(J = 7.8\) Hz, 1H), 7.50 – 7.42 (m, 1H), 7.40 – 7.33 (m, 1H), 4.16 – 4.06 (m, 2H), 3.58 (t, \(J = 12.8\) Hz, 2H), 3.42 – 3.30 (m, 1H), 2.05 (ddd, \(J = 29.3, 24.7, 12.1\) Hz, 4H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) ppm = 175.35, 153.06, 134.51, 126.01, 124.81, 122.73, 121.62, 67.51, 40.50, 32.83.

HRMS (ESI-TOF) (m/z) for [M+H]^+ calculated for C\(_{12}\)H\(_{14}\)NS: 220.0796, found: 220.0796.

**7-chloro-2-ethylbenzo[d]thiazole (16c)**

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm = 7.72 (dd, \(J = 8.0, 0.9\) Hz, 1H), 7.46 (dd, \(J = 7.8, 0.9\) Hz, 1H), 7.26 (t, \(J = 7.9\) Hz, 1H), 3.20 (q, \(J = 7.6\) Hz, 2H), 1.47 (t, \(J = 7.6\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) ppm = 175.00, 150.21, 136.52, 127.25, 126.15, 125.14, 120.07, 27.98, 14.07.

HRMS (ESI-TOF) (m/z) for [M+H]^+ calculated for C\(_9\)H\(_9\)ClNS: 198.0144, found: 198.0151.

**6-chloro-2-ethylbenzo[d]thiazole (17c)**

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm = 7.85 (d, \(J = 8.7\) Hz, 1H), 7.79 (d, \(J = 1.9\) Hz, 1H), 7.39 (dd, \(J = 8.7, 2.0\) Hz, 1H), 3.13 (q, \(J = 7.6\) Hz, 2H), 1.46 (t, \(J = 7.6\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) ppm = 174.04, 151.81, 136.52, 127.25, 126.15, 125.14, 120.07, 27.74, 13.62.

HRMS (ESI-TOF) (m/z) for [M+H]^+ calculated for C\(_9\)H\(_8\)ClNS: 198.0144, found: 198.0141.

**5-chloro-2-ethylbenzo[d]thiazole (18c)**

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm = 7.85 (d, \(J = 8.7\) Hz, 1H), 7.79 (d, \(J = 1.9\) Hz, 1H), 7.39 (dd, \(J = 8.7, 2.0\) Hz, 1H), 3.13 (q, \(J = 7.6\) Hz, 2H), 1.46 (t, \(J = 7.6\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) ppm = 174.04, 151.81, 136.52, 127.25, 126.15, 125.14, 120.07, 27.74, 13.62.

HRMS (ESI-TOF) (m/z) for [M+H]^+ calculated for C\(_9\)H\(_8\)ClNS: 198.0144, found: 198.0141.
$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 7.85 (d, $J = 8.7$ Hz, 1H), 7.79 (d, $J = 1.9$ Hz, 1H), 7.39 (dd, $J = 8.7$, 2.0 Hz, 1H), 3.13 (q, $J = 7.6$ Hz, 2H), 1.46 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 174.05, 151.83, 136.27, 130.52, 126.64, 123.22, 121.10, 27.74, 13.62.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_9$H$_9$ClNS: 198.0144, found: 198.0148.

4-chloro-2-ethylbenzo[d]thiazole (19c)

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 7.72 (dd, $J = 8.0$, 0.9 Hz, 1H), 7.46 (dd, $J = 7.8$, 0.9 Hz, 1H), 7.26 (t, $J = 7.9$ Hz, 1H), 3.20 (q, $J = 7.6$ Hz, 2H), 1.47 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 174.98, 150.19, 136.50, 127.23, 126.14, 125.12, 120.05, 27.98, 14.07.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_9$H$_8$ClNS: 198.0141, found: 198.0147.

7-bromo-2-ethylbenzo[d]thiazole (20c)

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 7.92 – 7.86 (m, 1H), 7.47 (dd, $J = 7.7$, 0.5 Hz, 1H), 7.31 (t, $J = 8.0$ Hz, 1H), 3.14 (q, $J = 7.6$ Hz, 2H), 1.47 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 173.86, 153.11, 137.96, 127.45, 127.07, 121.33, 113.86, 27.87, 13.70.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_9$H$_9$BrNS: 241.9639, found: 241.9647.

5-bromo-2-ethylbenzo[d]thiazole (21c)

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 8.11 (d, $J = 1.6$ Hz, 1H), 7.69 (d, $J = 8.5$ Hz, 1H), 7.45 (dd, $J = 8.5$, 1.8 Hz, 1H), 3.14 (q, $J = 7.6$ Hz, 2H), 1.46 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 154.49, 133.88, 127.73, 125.46, 122.53, 119.47, 27.83, 13.68.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_9$H$_8$BrNS: 241.9639, found: 241.9647.

2-ethyl-5-fluorobenzo[d]thiazole (22c)

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 7.96 (d, $J = 8.9$ Hz, 1H), 7.71 (s, 1H), 7.31 (s, 1H), 3.16 (q, $J = 7.6$ Hz, 2H), 1.48 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 176.21, 161.73 (d, $J = 242.7$ Hz), 154.29, 130.41, 122.10 (d, $J = 9.7$ Hz), 113.24 (d, $J = 24.9$ Hz), 108.79 (d, $J = 23.7$ Hz), 27.90, 13.69.
**F NMR** (377 MHz, CDCl$_3$) δ ppm = -116.46.

**HRMS** (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_9$H$_9$FNS: 182.0440, found: 182.0437.

![2-ethylbenzo[d]thiazole-6-carbonitrile (23c)]

**H NMR** (400 MHz, CDCl$_3$) δ ppm = 8.18 (d, $J = 1.2$ Hz, 1H), 8.03 (d, $J = 8.5$ Hz, 1H), 7.70 (dd, $J = 8.5$, 1.6 Hz, 1H), 3.20 (q, $J = 7.6$ Hz, 2H), 1.50 (t, $J = 7.6$ Hz, 3H).

**C NMR** (101 MHz, CDCl$_3$) δ ppm = 129.18, 126.29, 123.31, 108.24, 28.03, 13.49.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{10}$H$_{10}$NS: 189.0486, found: 189.0486.

![2-ethyl-4-methylbenzo[d]thiazole (24c)]

**H NMR** (400 MHz, CDCl$_3$) δ ppm = 7.66 (dd, $J = 5.3$, 3.9 Hz, 1H), 7.23 (dd, $J = 6.3$, 3.0 Hz, 2H), 3.16 (q, $J = 7.6$ Hz, 2H), 2.73 (s, 3H), 1.46 (t, $J = 7.6$ Hz, 3H).

**C NMR** (101 MHz, CDCl$_3$) δ ppm = 172.32, 152.62, 134.99, 132.43, 126.45, 124.43, 118.88, 27.88, 18.46, 14.07.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{10}$H$_{12}$NS: 178.0690, found: 178.0697.

![2-ethyl-5,6-dimethylbenzo[d]thiazole (25c)]

**H NMR** (400 MHz, CDCl$_3$) δ ppm = 7.73 (s, 1H), 7.57 (s, 1H), 3.11 (q, $J = 7.6$ Hz, 2H), 2.37 (d, $J = 5.9$ Hz, 6H), 1.45 (t, $J = 7.6$ Hz, 3H).

**C NMR** (101 MHz, CDCl$_3$) δ ppm = 172.38, 152.03, 134.99, 133.92, 122.72, 121.44, 27.66, 20.12, 20.01, 13.80.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{11}$H$_{14}$NS: 192.0847, found: 192.0846.

![2-ethyl-6-(trifluoromethoxy)benzo[d]thiazole (26c)]

**H NMR** (400 MHz, CDCl$_3$) δ ppm = 7.96 (d, $J = 8.9$ Hz, 1H), 7.71 (s, 1H), 7.31 (s, 1H), 3.16 (q, $J = 7.6$ Hz, 2H), 1.48 (t, $J = 7.6$ Hz, 3H).

**C NMR** (101 MHz, CDCl$_3$) δ ppm = 174.09, 151.83, 136.27, 130.53, 126.65, 123.22, 121.12, 13.64.

**F NMR** (377 MHz, CDCl$_3$) δ ppm = -58.07.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{10}$H$_{8}$F$_3$NOS: 248.0357, found: 203.0358.
methyl 2-ethylbenzo[d]thiazole-6-carboxylate (27c)

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 8.57 (d, $J = 1.3$ Hz, 1H), 8.12 (dd, $J = 8.5$, 1.6 Hz, 1H), 7.98 (d, $J = 8.5$ Hz, 1H), 3.96 (s, 3H), 3.17 (t, $J = 7.6$ Hz, 2H), 1.49 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 166.67, 156.22, 135.02, 127.15, 126.49, 123.72, 122.18, 28.02, 13.59.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{11}$H$_{11}$NO$_2$S: 222.0583, found: 222.0584.

4-(benzo[d]thiazol-2-yl)butan-1-ol (28c)

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 7.96 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 7.9$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 3.70 (t, $J = 6.3$ Hz, 2H), 3.16 (t, $J = 7.5$ Hz, 2H), 2.15 (s, 1H), 2.04 – 1.94 (m, 2H), 1.78 – 1.66 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 172.04, 153.10, 135.06, 125.95, 124.75, 122.48, 121.49, 62.10, 33.81, 31.99, 25.67.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{11}$H$_{14}$NOS: 208.0796, found: 208.0789.

4-(benzo[d]thiazol-2-yl)pentan-1-ol (29c) 5-(benzo[d]thiazol-2-yl)pentan-2-ol (29c') (29c and 29c' are the compounds that we had not been isolated, because their polarities are basically the same.)

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 7.96 (d, $J = 8.1$ Hz, 1H), 7.83 (dd, $J = 7.7$, 4.3 Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 1H), 7.33 (t, $J = 7.6$ Hz, 1H), 3.64 (t, $J = 6.4$ Hz, 1H), 3.36 – 3.28 (m, 1H), 3.14 (t, $J = 7.5$ Hz, 1H), 2.38 (s, 1H), 2.04 – 1.80 (m, 2H), 1.63 (ddt, $J = 33.0$, 16.0, 7.9 Hz, 2H), 1.46 (d, $J = 6.9$ Hz, 2H), 1.20 (d, $J = 6.2$ Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 177.79, 172.13, 153.08, 152.88, 135.04, 134.57, 125.94, 125.90, 124.74, 124.70, 122.55, 122.47, 121.57, 121.49, 67.38, 62.32, 39.15, 38.45, 34.01, 33.67, 30.34, 25.59, 23.55, 21.32.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{12}$H$_{18}$NOS: 222.0908, found: 222.0913.

1-(benzo[d]thiazol-2-yl)ethan-1-one (1d)

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm = 8.19 (d, $J = 8.4$ Hz, 1H), 7.98 (d, $J = 8.1$ Hz, 1H), 7.61 – 7.51 (m, 2H), 2.83 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm = 193.14, 166.50, 153.58, 137.44, 127.70, 126.98, 125.45, 122.45, 26.16.
HRMS (ESI-TOF) (m/z) for [M+H]^+ calculated for C_9H_7NOS: 178.0321, found: 178.0322.

![Structure of 1-(benzo[d]thiazol-2-yl)propan-1-one (2d)]

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) δ ppm = 8.18 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.61 – 7.49 (m, 2H), 3.31 (q, J = 7.3 Hz, 2H), 1.30 (t, J = 7.3 Hz, 3H).

\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) δ ppm = 196.08, 166.42, 153.63, 137.25, 127.64, 127.00, 125.42, 122.50, 32.15, 7.94.

HRMS (ESI-TOF) (m/z) for [M+H]^+ calculated for C_{10}H_9NOS: 192.0478, found: 192.0485.

![Structure of 1-(benzo[d]thiazol-2-yl)butan-1-one (3d)]

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) δ ppm = 8.18 (d, J = 8.7 Hz, 1H), 7.98 (d, J = 8.6 Hz, 1H), 7.60 – 7.50 (m, 2H), 3.26 (t, J = 7.3 Hz, 2H), 1.86 (p, J = 7.4 Hz, 2H), 1.05 (t, J = 7.4 Hz, 3H).

\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) δ ppm = 195.57, 166.69, 153.63, 137.29, 127.65, 126.99, 125.43, 122.50, 40.55, 17.55, 13.85.

HRMS (ESI-TOF) (m/z) for [M+H]^+ calculated for C_{11}H_{11}NOS: 206.0634, found: 206.0640.

![Structure of 1-(benzo[d]thiazol-2-yl)pentan-1-one (4d)]

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) δ ppm = 8.19 (d, J = 7.9 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.61 – 7.50 (m, 2H), 3.28 (t, J = 7.5 Hz, 2H), 1.80 (p, J = 7.5 Hz, 2H), 1.46 (h, J = 7.4 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H).

\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) δ ppm = 195.73, 166.70, 153.64, 137.31, 127.65, 126.99, 125.44, 122.50, 38.40, 26.11, 22.43, 13.97.

HRMS (ESI-TOF) (m/z) for [M+H]^+ calculated for C_{12}H_{13}NOS: 220.0791, found: 220.0793.

![Structure of 1-(benzo[d]thiazol-2-yl)hexan-1-one (5d)]

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) δ ppm = 8.18 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.54 (dt, J = 20.8, 7.1 Hz, 2H), 3.27 (t, J = 7.5 Hz, 2H), 1.81 (q, J = 7.3 Hz, 2H), 1.44 – 1.35 (m, 4H), 0.92 (t, J = 6.9 Hz, 3H).

\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) δ ppm= 195.70, 166.70, 153.65, 137.31, 127.62, 126.97, 125.44, 122.49, 38.62, 31.43, 23.72, 22.52, 14.00.

HRMS (ESI-TOF) (m/z) for [M+H]^+ calculated for C_{13}H_{15}NOS: 234.0908, found: 234.0911.
1-(benzo[d]thiazol-2-yl)heptan-1-one (6d)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm = 8.19 (d, $J = 7.7$ Hz, 1H), 7.98 (d, $J = 7.8$ Hz, 1H), 7.61 – 7.50 (m, 2H), 3.27 (t, $J = 7.4$ Hz, 2H), 1.81 (p, $J = 7.4$ Hz, 2H), 1.47 – 1.40 (m, 2H), 1.34 (dt, $J = 7.3$, 3.7 Hz, 4H), 0.90 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm = 195.73, 166.71, 153.65, 137.32, 127.63, 126.97, 125.44, 122.49, 38.68, 31.64, 28.94, 24.00, 22.57, 14.11.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{14}$H$_{17}$NOS: 248.1104, found: 248.1104.

1-(benzo[d]thiazol-2-yl)octan-1-one (7d)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm = 8.19 (d, $J = 8.1$ Hz, 1H), 7.98 (d, $J = 7.8$ Hz, 1H), 7.55 (dt, $J = 20.2$, 7.2 Hz, 2H), 3.27 (t, $J = 7.4$ Hz, 2H), 1.82 (q, $J = 7.3$ Hz, 2H), 1.44 – 1.39 (m, 2H), 1.31 – 1.28 (m, 6H), 0.89 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm = 195.74, 166.71, 153.69, 137.32, 127.63, 126.97, 125.44, 122.49, 38.67, 31.74, 29.23, 24.04, 22.68, 14.15.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{15}$H$_{19}$NOS: 262.1260, found: 262.1263.

1-(6-chlorobenzo[d]thiazol-2-yl)ethan-1-one (8d)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm = 8.09 (d, $J = 8.8$ Hz, 1H), 7.95 (d, $J = 2.0$ Hz, 1H), 7.53 (dd, $J = 8.8$, 2.0 Hz, 1H), 2.81 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm = 192.87, 166.96, 152.09, 138.58, 130.48, 128.11, 126.27, 122.05, 26.16.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{9}$H$_{6}$ClNOS: 211.9931, found:211.9927.

1-(4-chlorobenzo[d]thiazol-2-yl)ethan-1-one (9d)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm = 7.87 (d, $J = 8.1$ Hz, 1H), 7.59 (d, $J = 7.7$ Hz, 1H), 7.45 (t, $J = 7.9$ Hz, 1H), 2.87 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm = 193.10, 167.06, 150.70, 138.92, 130.43, 128.21, 127.21, 121.03, 26.14.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{9}$H$_{6}$ClNOS:211.9931, found:211.9935.
1-(6-bromobenzo[d]thiazol-2-yl)ethan-1-one (10d)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm = 8.12 (d, $J = 1.8$ Hz, 1H), 8.03 (d, $J = 8.8$ Hz, 1H), 7.67 (dd, $J = 8.8, 1.8$ Hz, 1H), 2.81 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm = 192.88, 166.92, 152.39, 138.98, 130.78, 126.54, 125.06, 121.98, 26.17.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{10}$H$_7$BrNOS: 255.9428, found: 255.9428.

1-(5-bromobenzo[d]thiazol-2-yl)ethan-1-one (11d)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm = 8.33 (d, $J = 1.7$ Hz, 1H), 7.83 (d, $J = 8.6$ Hz, 1H), 7.62 (dd, $J = 8.6, 1.8$ Hz, 1H), 2.81 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm = 192.87, 167.96, 154.67, 136.17, 130.90, 128.17, 123.54, 120.63, 26.18.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{10}$H$_7$BrNOS: 255.9427.

1-(5-fluorobenzo[d]thiazol-2-yl)ethan-1-one (12d)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm = 7.92 (dd, $J = 8.9, 5.0$ Hz, 1H), 7.85 (dd, $J = 9.1, 2.5$ Hz, 1H), 7.32 (td, $J = 8.8, 2.5$ Hz, 1H), 2.82 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm = 192.94, 168.81, 160.88, 154.51, 133.03, 123.34, 117.12, 116.87, 111.19, 110.96, 26.18.

$^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ ppm = -114.04.

HRMS (ESI-TOF) (m/z) for [M+H]$^+$ calculated for C$_{10}$H$_7$FNOS: 196.0228, found: 196.0228.

1-(4-methylbenzo[d]thiazol-2-yl)ethan-1-one (13d)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm = ppm = 7.78 (d, $J = 8.0$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 7.35 (d, $J = 7.2$ Hz, 1H), 2.83 (s, 3H), 2.80 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm = 193.48, 165.17, 153.19, 137.56, 135.85, 127.76, 127.22, 119.79, 26.08, 18.21.

HRMS (ESI-TOF) (m/z) for [M+Na]$^+$ calculated for C$_{10}$H$_9$NOS: 214.0298, found: 214.0298.

1-(6-methylbenzo[d]thiazol-2-yl)ethan-1-one (14d)

1
\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta \text{ ppm} = 8.06 \text{ (d, } J = 8.5 \text{ Hz, 1H), 7.76 (s, 1H), 7.39 (d, } J = 8.4 \text{ Hz, 1H), 2.81 (s, 3H), 2.53 (s, 3H).} \]

\[ \text{\textsuperscript{13}C NMR (101 MHz, CDCl}_3\text{) } \delta \text{ ppm} = 193.29, 165.59, 151.81, 138.47, 128.95, 124.98, 122.05, 77.39, 26.19, 21.88. \]

**HRMS (ESI-TOF) (m/z) for [M+Na]^+ calculated for C\textsubscript{10}H\textsubscript{9}NOS: 192.0438, found: 192.0438.**

![1-(5,6-dimethylbenzo[d]thiazol-2-yl)ethan-1-one (15d)]

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{) } \delta \text{ ppm} = 7.94 \text{ (s, 1H), 7.72 (s, 1H), 2.80 (s, 3H), 2.42 (d, } J = 2.6 \text{ Hz, 6H).} \]

\[ \text{\textsuperscript{13}C NMR (101 MHz, CDCl}_3\text{) } \delta \text{ ppm} = 193.29, 165.48, 152.51, 138.06, 136.71, 135.22, 125.26, 122.15, 26.19, 20.33. \]

**HRMS (ESI-TOF) (m/z) for [M+H]^+ calculated for C\textsubscript{11}H\textsubscript{11}NOS: 206.0634, found: 206.0636.**

![1-(6-(trifluoromethoxy)benzo[d]thiazol-2-yl)ethan-1-one (16d)]

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{) } \delta \text{ ppm} = 8.20 \text{ (d, } J = 9.0 \text{ Hz, 1H), 7.84 (s, 1H), 7.45 (d, } J = 9.0 \text{ Hz, 1H), 2.83 (s, 3H).} \]

\[ \text{\textsuperscript{13}C NMR (101 MHz, CDCl}_3\text{) } \delta \text{ ppm} = 192.73, 167.66, 151.93, 148.37, 138.39, 126.62, 121.02, 114.49, 29.74, 26.12. \]

\[ \text{\textsuperscript{19}F NMR (377 MHz, CDCl}_3\text{) } \delta \text{ ppm} = -57.88. \]

**HRMS (ESI-TOF) (m/z) for [M+H]^+ calculated for C\textsubscript{10}H\textsubscript{6}F\textsubscript{3}NO\textsubscript{2}S: 262.0144, found:262.0145**
3. NMR spectra for the products

$^1$H NMR spectrum of compound 1c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 1c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 2c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 2c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 3c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 3c in CDCl$_3$ (101 MHz):
\( ^1H \) NMR spectrum of compound 4c in CDCl\(_3\) (400 MHz): 

\[ \text{Diagram of } ^1H \text{ NMR spectrum} \]

\( ^{13}C \) NMR spectrum of compound 4c in CDCl\(_3\) (101 MHz): 

\[ \text{Diagram of } ^{13}C \text{ NMR spectrum} \]
$^1$H NMR spectrum of compound 5c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 5c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 6c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 6c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 7c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 7c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 9c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 9c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 10c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 10c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 11c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 11c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 12c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 12c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 13c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 13c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 14c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 14c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 15c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 15c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 16c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 16c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 17c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 17c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 18c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 18c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 19c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 19c in CDCl$_3$ (101 MHz):
\(^1\)H NMR spectrum of compound 20c in CDCl\(_3\) (400 MHz):

\(^{13}\)C NMR spectrum of compound 20c in CDCl\(_3\) (101 MHz):
$^1$H NMR spectrum of compound 21c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 21c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 22c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 22c in CDCl$_3$ (101 MHz):
$^{19}$F NMR spectrum of compound 22c in CDCl$_3$ (101 MHz):
$^{1}$H NMR spectrum of compound 23c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 23c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 24c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 24c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 25c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 25c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 26c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 26c in CDCl$_3$ (101 MHz):
$^{19}$F NMR spectrum of compound 26c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 27c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 27c in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 28c in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 28c in CDCl$_3$ (101 MHz):
\textbf{'H NMR} spectrum of compound 29c and 29c' in CDCl\textsubscript{3} (400 MHz):

\begin{figure}
\centering
\includegraphics[width=\textwidth]{hnmr_spectrum.png}
\end{figure}

\textbf{\textsuperscript{13}C NMR} spectrum of compound 29c and 29c' in CDCl\textsubscript{3} (101 MHz):

\begin{figure}
\centering
\includegraphics[width=\textwidth]{cnmr_spectrum.png}
\end{figure}
$^1$H NMR spectrum of compound 1d in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 1d in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 2d in CDCl$_3$ (400 MHz):

\[
\begin{align*}
\text{f1 (ppm)} & \\
3.11 & 2.07 & 2.05 & 0.99 & 1.00 & \\
\end{align*}
\]

$^{13}$C NMR spectrum of compound 2d in CDCl$_3$ (101 MHz):

\[
\begin{align*}
\text{f1 (ppm)} & \\
7.94 & 32.15 & 122.50 & 125.42 & 127.00 & 127.64 & 137.25 & 153.63 & 166.42 & 196.08 & 221.5 & 754
\end{align*}
\]
$^1$H NMR spectrum of compound 3d in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 3d in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 4d in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 4d in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 5d in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 5d in CDCl$_3$ (101 MHz):
**1H NMR spectrum of compound 6d in CDCl₃ (400 MHz):**

![1H NMR spectrum](image)

**13C NMR spectrum of compound 6d in CDCl₃ (101 MHz):**

![13C NMR spectrum](image)
$^1$H NMR spectrum of compound 7d in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 7d in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound **8d** in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound **8d** in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 9d in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 9d in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound $10d$ in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound $10d$ in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 11d in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 11d in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 12d in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 12d in CDCl$_3$ (101 MHz):
$^{19}$F NMR spectrum of compound 12d in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 13d in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 13d in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 14d in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 14d in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 15d in CDCl$_3$ (400 MHz):

$^{13}$C NMR spectrum of compound 15d in CDCl$_3$ (101 MHz):
$^1$H NMR spectrum of compound 16d in CDCl$_3$ (400 MHz):

13C NMR spectrum of compound 16d in CDCl$_3$ (101 MHz):
$^{19}$F NMR spectrum of compound 16d in CDCl$_3$ (101 MHz):