TBHP-Mediated Oxidative Thiolation of an sp³ C-H Bond Adjacent to a Nitrogen Atom

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(A) Typical Experimental Procedure

(a) Typical Experimental Procedure for TBHP-Oxidative Thiolation of an sp³ C-H Bond adjacent to a Nitrogen Atom or an Oxygen Atom:

To a Schlenk tube were added disulfide 1 (0.2 mmol), TBHP (0.8 mmol), 4 Å molecular sieve (100 mg) and 2 (2 mL). Then the tube was charged with argon, and 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 brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na₂SO₄ and concentrated in vacuo, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the product.

(b) Screening Optimal Conditions

Table S1. Screening Optimal Conditions[^a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidant (mmol)</th>
<th>Additive (mg)</th>
<th>T (°C)</th>
<th>Isolated yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DDQ (0.8)</td>
<td>—</td>
<td>120</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>TBHP (0.8)</td>
<td>—</td>
<td>120</td>
<td>77</td>
</tr>
<tr>
<td>3</td>
<td>TBHP (0.8)</td>
<td>—</td>
<td>150</td>
<td>78</td>
</tr>
<tr>
<td>4</td>
<td>TBHP (0.8)</td>
<td>—</td>
<td>100</td>
<td>41</td>
</tr>
<tr>
<td>5</td>
<td>MCBPA (0.8)</td>
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<td>120</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>OIBA (0.8)</td>
<td>—</td>
<td>120</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>Ph(OAc)₂ (0.8)</td>
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<td>120</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>K₂S₂O₇ (0.8)</td>
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<td>120</td>
<td>trace</td>
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<tr>
<td>9</td>
<td>TBHP (1.2)</td>
<td>—</td>
<td>120</td>
<td>78</td>
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<tr>
<td>10</td>
<td>TBHP (0.4)</td>
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<td>120</td>
<td>72</td>
</tr>
<tr>
<td>11</td>
<td>TBHP (0.8)</td>
<td>4Å MS (100)</td>
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<td>86</td>
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<tr>
<td>12[^b]</td>
<td>TBHP (0.8)</td>
<td>4Å MS (100)</td>
<td>120</td>
<td>71</td>
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<tr>
<td>13[^b]</td>
<td>TBHP (0.8)</td>
<td>4Å MS (100)</td>
<td>120</td>
<td>87</td>
</tr>
<tr>
<td>14[^b]</td>
<td>TBHP (0.8)</td>
<td>4Å MS (100)</td>
<td>120</td>
<td>87</td>
</tr>
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<td>4Å MS (100)</td>
<td>120</td>
<td>51</td>
</tr>
<tr>
<td>16[^b]</td>
<td>TBHP (0.8)</td>
<td>—</td>
<td>120</td>
<td>85</td>
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<tr>
<td>17[^b]</td>
<td>TBHP (0.8)</td>
<td>—</td>
<td>120</td>
<td>trace</td>
</tr>
<tr>
<td>18[^b]</td>
<td>TBHP (0.8)</td>
<td>—</td>
<td>120</td>
<td>trace</td>
</tr>
</tbody>
</table>

[^a] Reaction conditions: 1a (0.2 mmol), 2a (2 mL, 21.5 mmol), and oxidant for 12 h. TBHP (70% in water solution). 4Å MS = 4Å molecular sieve.[^b] 2a (1 mL, 10.8 mmol).[^c] 2a (3 mL, 31.3 mmol).[^d] In dark.[^e] K₂CO₃ (0.8 mmol) was added.[^f] K₂CO₃ (0.1 mmol) was added.[^g] CuI (5 mol%) was added.[^h] FeCl₃ (5 mol%) was added.
(B) Analytical data for 3-27

Notably, there is the signal duplication in the NMR spectra of the purified products 4–12 and 14, and the reason is because these products have rotamers.

**N-Methyl-N-(phenylthiomethyl)acetamide (3)**

Light-yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.38-7.42 (m, 2H), 7.16-7.28 (m, 3H), 4.81 and 4.57 (2×s, 2H), 2.92 and 2.90 (2×s, 3H), 1.95 and 1.57 (2×s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 170.7 and 170.6, 134.9 and 133.9, 132.4 and 131.5, 129.3 and 129.0, 128.9 and 127.2, 57.8 and 51.7, 35.1 and 32.8, 21.7 and 20.6; IR (KBr, cm$^{-1}$): 2914, 2846, 1651, 1489, 1393, 1258, 1013, 743, 692; LRMS (EI, 70 eV) m/z (%): 195 (M$^+$, 5), 86 (100); HRMS (ESI) for C$_{10}$H$_{13}$NOS (M+H)$^+$: calcd. 196.0791, found 196.0796.

**N-Methyl-N-(p-tolylthiomethyl)acetamide (4)**

Light-yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.28-7.30 (m, 2H), 7.07 and 7.02 (2×d, J = 7.8 Hz, 2H), 4.76 and 4.53 (2×s, 2H), 2.91 and 2.89 (2×s, 3H), 2.27 and 2.24 (2×s, 3H), 1.94 and 1.56 (2×s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 170.6, 139.3 and 135.1, 137.5 and 132.2, 130.2 and 130.1, 129.7 and 128.6, 57.9 and 52.3, 35.2 and 32.7, 21.7 and 21.1, 21.0 and 20.6; IR (KBr, cm$^{-1}$): 2917, 2855, 1651, 1488, 1393, 1258, 1013, 808, 675; LRMS (EI, 70 eV) m/z (%): 209 (M$^+$, 8), 124 (16), 86 (100); HRMS (ESI) for C$_{11}$H$_{15}$NOS (M+H)$^+$: calcd. 210.0947, found 210.0951.

**N-((4-Methoxyphenylthio)methyl)-N-methylacetamide (5)**

Light-yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.32-7.35 (m, 2H), 6.75-6.80 (m, 2H), 4.69 and 4.48 (2×s, 2H), 3.73 and 3.71 (2×s, 3H), 2.90 and 2.89 (2×s, 3H), 1.93 and 1.53 (2×s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 170.6, 160.5 and 159.6, 137.0 and 134.8, 124.0 and 122.5, 114.8 and 114.5, 58.1 and 55.2, 55.3 and 53.1, 35.2 and 32.6, 21.7 and 20.5; IR (KBr, cm$^{-1}$): 2923, 2834, 1634, 1590, 1493, 1393, 1243, 1016, 828; LRMS (EI, 70 eV) m/z (%): 225 (M$^+$, 11), 86 (100); HRMS (ESI) for C$_{11}$H$_{15}$NO$_2$S (M+H)$^+$: calcd. 226.0896, found 226.0899.
\textbf{\textit{N-((4-Chlorophenylthio)methyl)-N-methylacetamide (6)}}

Light-yellow oil; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\): 7.34 and 7.32 (2×d, \(J = 8.5\) Hz, 2H), 7.24 and 7.18 (2×d, \(J = 8.5\) Hz, 2H), 4.80 and 4.57 (2×s, 2H), 2.93 and 2.89 (2×s, 3H), 1.96 and 1.64 (2×s, 3H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\): 170.8 and 170.4, 136.1 and 135.4, 133.3 and 132.7, 132.3 and 130.8, 129.5 and 129.0, 57.8 and 51.6, 35.0 and 32.9, 21.8 and 20.7; IR (KBr, cm\textsuperscript{-1}): 2917, 2849, 1651, 1474, 1392, 1258, 1092, 1011, 817; LRMS (EI, 70 eV) m/z (%): 229 (M\textsuperscript{+}, 2), 86 (100); HRMS (ESI) for C\textsubscript{10}H\textsubscript{12}ClNOS (M+H\textsuperscript{+}): calcd. 230.0401, found 230.0406.

\textbf{\textit{N-((4-Bromophenylthio)methyl)-N-methylacetamide (7)}}

Light-yellow oil; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\): 7.47 and 7.40 (2×d, \(J = 8.5\) Hz, 2H), 7.32-7.36 (m, 2H), 4.88 and 4.65 (2×s, 2H), 3.01 and 2.97 (2×s, 3H), 2.03 and 1.73 (2×s, 3H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\): 170.8 and 170.4, 136.3 and 133.1, 132.9 and 131.6, 132.6 and 123.5, 132.0 and 121.3, 57.7 and 51.4, 35.1 and 32.9, 21.8 and 20.8; IR (KBr, cm\textsuperscript{-1}): 2917, 2850, 1645, 1472, 1389, 1255, 1090, 1006, 813; LRMS (EI, 70 eV) m/z (%): 273 (M\textsuperscript{+}, 2), 275 (M\textsuperscript{+}+2, 2), 86 (100); HRMS (ESI) for C\textsubscript{10}H\textsubscript{12}BrNOS (M+H\textsuperscript{+}): calcd. 273.9896, found 273.9898.

\textbf{\textit{N-((4-Fluorophenylthio)methyl)-N-methylacetamide (8)}}

Light-yellow oil; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\): 7.36-7.41 (m, 2H), 6.97 and 6.91 (2×t, \(J = 8.3\) Hz, 2H), 4.74 and 4.54 (2×s, 2H), 2.92 and 2.89 (2×s, 3H), 1.93 and 1.58 (2×s, 3H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\): 170.6 and 170.4, 163.7 and 161.7 (2×d, \(J = 247.5\) Hz, 1C), 137.1 and 134.3 (2×d, \(J = 8.3\) Hz, 1C), 128.6 and 127.4 (2×d, \(J = 3.4\) Hz, 1C), 116.4 and 115.9 (2×d, \(J = 21.7\) Hz, 1C), 57.9 and 52.4, 35.0 and 32.6, 21.6 and 20.5; IR (KBr, cm\textsuperscript{-1}): 2915, 2848, 1651, 1489, 1393, 1259, 1219, 1013, 830, 815; LRMS (EI, 70 eV) m/z (%): 213 (M\textsuperscript{+}, 3), 86 (100); HRMS (ESI) for C\textsubscript{10}H\textsubscript{12}FNOS (M+H\textsuperscript{+}): calcd. 214.0696, found 214.0702.

\textbf{\textit{N-((3-Fluorophenylthio)methyl)-N-methylacetamide (9)}}
Light-yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.09-7.24 (m, 3H), 6.98 and 6.84 (2×t, $J = 7.9$ Hz, 1H), 4.82 and 4.62 (2×s, 2H), 2.93 and 2.88 (2×s, 3H), 1.96 and 1.70 (2×s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 170.7 and 170.4, 162.5 and 162.4 (2×d, $J = 247.9$ Hz, 1C), 136.2 and 134.6 (2×d, $J = 7.7$ Hz, 1C), 130.5 and 130.1 (2×d, $J = 8.4$ Hz, 1C), 129.9 and 126.4 (2×d, $J = 3.0$ Hz, 1C), 120.8 and 117.6 (2×d, $J = 22.1$ Hz, 1C), 115.7 and 113.9 (2×d, $J = 21.0$ Hz, 1C), 57.4 and 51.2, 35.0 and 32.8, 21.6 and 20.6; IR (KBr, cm$^{-1}$): 2914, 2846, 1645, 1577, 1473, 1393, 1260, 1214, 876, 780, 680; LRMS (EI, 70 eV) m/z (%): 213 (M$^+$, 2), 86 (100); HRMS (ESI) for C$_{10}$H$_{12}$FNOS (M+H)$^+$: calcd. 214.0696, found 214.0702.

Methyl 2-((N-methylacetamido)methylthio)benzoate (10)

Light-yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.90 and 7.80 (2×d, $J = 7.6$ Hz, 1H), 7.19-7.60 (m, 3H), 4.98 and 4.82 (2×s, 2H), 3.94 and 3.92 (2×s, 3H), 3.05 and 3.00 (2×s, 3H), 2.08 and 1.86 (2×s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 171.1 and 171.0, 167.5 and 167.1, 138.0 and 134.5, 134.0 and 132.4, 131.8 and 130.9, 130.3 and 129.4, 128.8 and 127.8, 125.4 and 125.2, 56.7 and 52.1, 52.4 and 49.5, 34.9 and 33.3, 21.9 and 20.7; IR (KBr, cm$^{-1}$): 2949, 2846, 1711, 1644, 1432, 1395, 1245, 1085, 1015, 744; LRMS (ESI, 70 eV) m/z (%): 253 (M$^+$, 4), 86 (100); HRMS (ESI) for C$_{12}$H$_{15}$NO$_3$S (M+H)$^+$: calcd. 254.0845, found 254.0850.

N-(Benzylthiomethyl)-N-methylacetamide (11)

Light-yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.23-7.28 (m, 5H), 4.36 and 4.08 (2×s, 2H), 3.84 and 3.82 (2×s, 2H), 2.92 and 2.82 (2×s, 3H), 2.06 and 1.97 (2×s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 171.1 and 170.7, 137.1 and 137.0, 129.5 and 129.4, 128.8 and 128.6, 127.8 and 127.5, 59.1 and 54.3, 43.9 and 43.3, 35.6 and 33.1, 21.7 and 21.4; IR (KBr, cm$^{-1}$): 2920, 2850, 1651, 1390, 1256, 1015, 765, 698; LRMS (EI, 70 eV) m/z (%): 209 (M$^+$, 9), 86 (100); HRMS (ESI) for C$_{11}$H$_{15}$NOS (M+H)$^+$: calcd. 210.0947, found 210.0946.

N-Methyl-N-((2-methylfuran-3-ylthio)methyl)acetamide (12)
Light-yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.24 and 7.19 (2×d, $J = 1.7$ Hz, 1H), 6.27 and 6.26 (2×d, $J = 1.7$ Hz, 1H), 4.52 and 4.37 (2×s, 2H), 2.94 and 2.90 (2×s, 3H), 2.26 and 2.23 (2×s, 3H), 1.96 and 1.70 (2×s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 170.5 and 170.3, 156.9 and 155.3, 141.1 and 140.6, 115.5 and 115.1, 108.6 and 107.5, 56.9 and 52.5, 35.3 and 32.6, 21.7 and 20.5, 11.6 and 11.5; IR (KBr, cm$^{-1}$): 2917, 2837, 1651, 1495, 1393, 1249, 1224, 1013, 888, 733; LRMS (EI, 70 eV) m/z (%): 199 (M$^+$, 6), 86 (100); HRMS (ESI) for C$_9$H$_{13}$NO$_2$S (M+H)$^+$: calcd. 200.0740, found 200.0745.

N-Methyl-N-(phenylthiomethyl)formamide (13)

Light-yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.95 and 7.52 (2×s, 1H), 7.24-7.46 (m, 5H), 4.81 and 4.54 (2×s, 2H), 2.95 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 162.2 and 161.4, 134.2 and 133.1, 131.6 and 131.2, 129.3 and 128.9, 128.8 and 127.2, 56.8 and 48.1, 33.2 and 28.7; IR (KBr, cm$^{-1}$): 2925, 2856, 1653, 1487, 1395, 1013, 763, 672; LRMS (EI, 70 eV) m/z (%): 181 (M$^+$, 6), 72 (100); HRMS (ESI) for C$_9$H$_{11}$NOS (M+H)$^+$: calcd. 182.0634, found 182.0638.

S-Phenyl dimethylcarbamothioate (14)

Light-yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.48-7.50 (m, 2H), 7.37-7.39 (m, 3H), 3.08 (s, 3H), 3.02 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 166.9, 135.7, 129.1, 128.9, 128.8, 36.9; LRMS (EI, 70 eV) m/z (%): 181 (M$^+$, 5), 72 (100); HRMS (ESI) for C$_9$H$_{11}$NOS (M+H)$^+$: calcd. 182.0634, found 182.0639.

1-(Phenylthiomethyl)pyrrolidin-2-one (15) and 1-methyl-5-(phenylthio)pyrrolidin-2-one (16)

15/16 = 1:6.7; Light-yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.41-7.43 (m, 2H), 7.32-7.36 (m, 3H), 7.27-7.30 (m, 3H), 7.23-7.25 (m, 2H), 4.80 (m, 1H), 4.76 (s, 2H), 3.43 (t, $J = 7.1$ Hz, 2H), 2.97 (s, 3H), 3.45-2.51 (m, 1H), 2.29 (t, $J = 7.1$ Hz, 2H), 2.15-2.20 (m, 1H), 2.07-2.11 (m, 1H), 1.93-2.06 (m, 2H), 1.64-1.71 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 174.7, 174.4, 135.0, 133.9, 130.9, 130.5,
129.2, 128.9, 127.1, 125.3, 69.4, 46.7, 45.8, 30.7, 29.0, 27.9, 26.3, 17.5; IR (KBr, cm⁻¹): 2916, 2848, 1695, 1437, 1395, 1260, 1115, 694; LRMS (EI, 70 eV) m/z (%): 207 (M⁺, 1), 110 (28), 98 (100); HRMS (ESI) for C₁₁H₁₃NOS (M+H)⁺: calcd. 208.0791, found 208.0796.

1-(p-Tolylthiomethyl)pyrrolidin-2-one (17) and 1-methyl-5-(p-tolylthio)pyrrolidin-2-one (18)

17/18 = 1:5.7; Light-yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.26 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 8.1 Hz, 2H), 7.02 (d, J = 8.1 Hz, 2H), 4.66 (m, 1H), 4.64 (s, 2H), 3.36 (t, J = 7.0 Hz, 2H), 2.91 (s, 3H), 2.37 (m, 1H), 2.27 (s, 3H), 2.24 (s, 3H), 2.21 (t, J = 7.0 Hz, 2H), 2.10 (m, 1H), 1.96 (m, 1H), 1.92 (m, 2H), 1.56 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 174.8, 174.5, 139.4, 137.5, 135.5, 131.7, 130.0, 129.8, 128.5, 126.6, 69.5, 47.3, 45.9, 30.8, 29.1, 26.3, 21.1, 21.0, 17.6; IR (KBr, cm⁻¹): 2911, 2850, 1682, 1418, 1392, 1259, 1105, 812, 670; LRMS (EI, 70 eV) m/z (%): 221 (M⁺, 2), 124 (19), 98 (100); HRMS (ESI) for C₁₂H₁₅NOS (M+H)+: calcd. 222.0947, found 222.0952.

Benzo[d]thiazole (19)

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 8.99 (s, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 154.2, 152.5, 133.5, 126.4, 125.7, 123.4, 121.9; LRMS (EI, 70 eV) m/z (%): 135 (M⁺, 100).

2-Propylbenzo[d]thiazole (20)

Light-yellow oil; ¹H NMR (300 MHz, CDCl₃) δ: 7.97 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 7.9, 1H), 7.42 (t, J = 7.6, 1H), 7.30 (t, J = 7.5, 1H), 3.07 (t, 2H), 1.89 (m, 2H), 1.04 (t, 3H); ¹³C NMR (75 MHz, CDCl₃) δ: 172.1, 153.2, 135.1, 125.8, 124.6, 122.5, 121.4, 36.2, 23.1, 13.7; IR (KBr, cm⁻¹): 3062, 2958, 2873, 1518, 1443, 1164, 756, 652; LRMS (EI, 70 eV) m/z (%): 177 (M⁺, 9), 149 (100).

2-Phenylbenzo[d]thiazole (21)
Colorless solid, mp 111.4-111.9 °C (uncorrected); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 8.13-8.09 (m, 3H), 7.92 (d, \(J = 7.6\) Hz, 1H), 7.53-7.49 (m, 4H), 7.40 (t, \(J = 7.0\) Hz, 1H); \(^1^3\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\): 168.1, 154.1, 135.1, 133.6, 131.0, 129.0, 127.6, 126.3, 125.2, 123.2, 121.6; IR (KBr, cm\(^{-1}\)): 3061, 1897, 1597, 1306, 1228, 1067, 958, 756, 684, 552; LRMS (EI, 70 eV) m/z (%): 211 (M\(^+\), 100).

6-methoxybenzo[d]thiazole (22)

Yellow solid, mp 57.3 °C (uncorrected); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 8.75 (s, 1H), 7.93 (d, \(J = 8.9\), 1H), 7.31 (d, \(J = 2.4\), 1H), 7.04 (dd, \(J = 8.9\), \(J = 2.4\), 1H), 3.81 (s, 3H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 158.0, 151.4, 147.8, 135.0, 128.5, 123.9, 115.8, 103.9, 55.8; LRMS (ESI, 70 eV) m/z (%): 165 (M\(^+\), 100), 150 (70), 122 (76).

4-methylbenzo[d]thiazole (23)

Yellow oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 8.90 (s, 1H), 7.71 (d, \(J = 7.4\), 1H), 7.24-7.27 (m, 2H), 2.72 (s, 3H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 152.7, 152.5, 133.5, 133.4, 126.6, 125.4, 119.3, 18.3; LRMS (ESI, 70 eV) m/z (%): 149 (M\(^+\), 100), 121 (36).

5,6-dimethylbenzo[d]thiazole (24)

Yellow solid, mp 55.1 °C (uncorrected); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 8.88 (s, 1H), 7.91 (s, 1H), 7.71 (s, 1H), 2.42 (s, 3H), 2.41 (s, 3H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 152.8, 152.0, 135.5, 135.1, 131.1, 123.6, 121.7, 20.3, 20.2; LRMS (ESI, 70 eV) m/z (%): 163 (M\(^+\), 94), 148 (100).

6-fluorobenzo[d]thiazole (25)

Yellow solid, mp 41.2 °C (uncorrected); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 8.96 (s, 1H), 8.09 (dd, \(J = 8.9\), \(J = 4.8\), 1H), 7.63 (d, \(J = 8.1\), 1H), 7.27 (m, 1H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 160.7 (d, \(J = 244.5\), 1C), 153.5 (d, \(J = 3.33\), 1C), 149.9, 134.7 (d, \(J = 11.3\), 1C), 124.5 (d, \(J = 9.45\), 1C), 114.9 (d, \(J = 24.8\), 1C), 107.8 (d, \(J = 26.6\), 1C); LRMS (ESI, 70 eV) m/z (%): 153 (M\(^+\), 100), 126 (47).
6-chlorobenzo[d]thiazole (26)

Yellow solid, mp 43.3 °C (uncorrected); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 8.89 (s, 1H), 7.96 (d, $J$ = 8.7, 1H), 7.84 (d, $J$ = 2.0, 1H), 7.39 (dd, $J$ = 8.7, $J$ = 2.0, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 154.3, 151.7, 134.9, 131.6, 127.0, 124.3, 121.4; LRMS (ESI, 70 eV) m/z (%): 171 (M$^+$ + 2, 35), 169 (M$^+$, 100).

$N$-((5-Amino-3-cyano-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-1H-pyrazol-4-ylthio)methyl)-$N$-methylacetamide (27)

Light-yellow solid, mp 84.3-86.7 °C (uncorrected); $^1$H NMR (500 MHz, C$_3$D$_6$O) $\delta$: 7.95 and 7.93 (2×s, 1H), 6.10 and 5.96 (2×s, 2H), 4.56 and 4.49 (2×s, 2H), 3.02 and 2.86 (2×s, 3H), 1.88 and 1.79 (2×s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 171.1 and 170.2, 150.8 and 150.6, 150.6, 136.5 and 136.4, 135.5 and 135.3, 134.3 (q, $J$ = 34.4, 1C), 132.4 and 132.3, 126.2 and 126.1, 122 (q, $J$ = 272.3, 1C), 112.8 and 112.3, 93.4 and 92.3, 57.1 and 52.8, 36.0 and 33.1, 21.7 and 21.0; IR (KBr, cm$^{-1}$): 3288, 2927, 2853, 1622, 1557, 1393, 1317, 1175, 1138, 1099, 881, 817; LRMS (EI, 70 eV) m/z (%): 437 (M$^+$, 1), 352 (2), 255 (3), 86 (73); HRMS (ESI) for C$_{13}$H$_{12}$Cl$_2$F$_3$N$_5$OS (M+H)$^+$: calcd. 438.0164, found 438.0171.

(C) References


(D) Spectra

N-methyl-N-(phenylthiomethyl)acetamide (3)
N-methyl-N-(p-tolylthiomethyl)acetamide (4)
N-methyl-N-(p-tolylthiomethyl)acetamide (4)
N-((4-methoxyphenylthio)methyl)-N-methylacetamide (5)
N-((4-methoxyphenylthio)methyl)-N-methylacetamide (5)
N-((4-chlorophenylthio)methyl)-N-methylacetamide (6)
N-((4-chlorophenylthio)methyl)-N-methylacetamide (6)
N-((4-bromophenylthio)methyl)-N-methylacetamide (7)
N-((4-bromophenylthio)methyl)-N-methylacetamide (7)
N-((4-fluorophenylthio)methyl)-N-methylacetamide (8)
N-((4-fluorophenylthio)methyl)-N-methylacetamide (8)
N-((3-fluorophenylthio)methyl)-N-methylacetamide (9)
N-((3-fluorophenylthio)methyl)-N-methylacetamide (9)
Methyl 2-((N-methylacetamido)methylthio)benzoate (10)
N-(benzylthiomethyl)-N-methylacetamide (11)
N-(benzylthiomethyl)-N-methylacetamide (11)
N-methyl-N-((2-methylfuran-3-ylthio)methyl)acetamide (12)
N-methyl-N-((2-methylfuran-3-ylthio)methyl)acetamide (12)
N-methyl-N-(phenylthiomethyl)formamide (13)
S-phenyl dimethylcarbamothioate (14)
1-(phenylthiomethyl)pyrrolidin-2-one (15) and 1-methyl-5-(phenylthio)pyrrolidin-2-one (16)
1-(phenylthiomethyl)pyrrolidin-2-one (15) and 1-methyl-5-(phenylthio)pyrrolidin-2-one (16)
1-(p-tolylthiomethyl)pyrrolidin-2-one (17) and 1-methyl-5-(p-tolylthio)pyrrolidin-2-one (18)
1-(p-tolylthiomethyl)pyrrolidin-2-one (17) and 1-methyl-5-(p-tolylthio)pyrrolidin-2-one (18)
benzo[d]thiazole (19)
benzo[d]thiazole (19)
2-propylbenzo[d]thiazole (20)
2-propylbenzo[d]thiazole (20)
2-phenylbenzo[d]thiazole (21)
2-phenylbenzo[d]thiazole (21)
6-methoxybenzo[d]thiazole (22)
6-methoxybenzod[\(d\)]thiazole (22)
4-methylbenzo[d]thiazole (23)
4-methylbenzo[d]thiazole (23)
5,6-dimethylbenzo[d]thiazole (24)
5,6-dimethylbenzo[d]thiazole (24)
6-fluorobenzo[d]thiazole (25)
6-fluorobenzod[thiazole (25)
6-chlorobenzodithiazole (26)
6-chlorobenz[d]thiazole (26)
N-((5-amino-3-cyano-1-(2,6-dichloro-4-((trifluoromethyl)phenyl)-1H-pyrazol-4-ylthio)methyl)-N-methylacetamide (27)
N-((5-amino-3-cyano-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-1H-pyrazol-4-ylthio)methyl)-N-methylacetamide (27)