Electronic Supplementary Information

Investigation of Facet Effects on the Catalytic Activity of Cu$_2$O Nanocrystals for Efficient Regioselective Synthesis of 3,5-Disubstituted Isoxazoles

Kaushik Chanda, Sourav Rej and Michael H. Huang*

Department of Chemistry and Frontier Research Center on Fundamental and Applied Sciences of Matters, National Tsing Hua University, Hsinchu 30013, Taiwan

Experimental section

Chemicals

Anhydrous copper (II) chloride (CuCl$_2$; 97%) and hydroxylamine hydrochloride (NH$_2$OH·HCl; 99%) were purchased from Aldrich. Sodium hydroxide (98.2%) and sodium dodecyl sulfate (SDS; 100%) were acquired from Mallinckrodt. All chemicals were used as received without further purification along with deionized water for all solution preparations. Commercially available reagents were used for the [3+2] cycloaddition reactions.

Synthesis of Cu$_2$O nanocubes and rhombic dodecahedra

The synthetic method described here is adopted from our previously reported procedure.$^{14}$ For the synthesis of Cu$_2$O nanocrystals with cubic and rhombic dodecahedral shapes, 8.92 and 6.95 ml of deionized water were added respectively to sample vials. The volume of water added to each vial was adjusted in such a manner that after the addition of NH$_2$OH·HCl, total volume of the final solution is 10 mL. The sample vials were placed in a water bath set at 30–32 ºC. Then 0.5 mL of 0.1 M CuCl$_2$ solution and 0.087 g of SDS powder were added to the vials with vigorous stirring. When the solution became clear, 0.18 mL of 1.0 M NaOH solution was added and shaken for ~10 s. The solution turned light blue immediately, due to the formation of threadlike Cu(OH)$_2$ precipitate. Finally, 0.40 and 2.37 mL of 0.1 M NH$_2$OH·HCl were quickly injected in 5 s for the synthesis of nanocubes and rhombic dodecahedra, respectively. After stirring for 20 s, the solutions were kept in the water bath for 1 h for nanocrystal growth. The concentrations of Cu$^{2+}$ ions and SDS surfactant in the final solution are 1.0 × 10$^{-3}$ M and 3.0 × 10$^{-2}$ M, respectively. The reaction mixtures were centrifuged at 5000 rpm for 3 min. After decanting the top solution, the precipitate was washed with 6 mL of 1:1 volume ratio of water and ethanol for three times to remove unreacted chemicals and SDS surfactant. The final washing step used 5 mL of ethanol, and the precipitate was dispersed in 0.6 mL of
ethanol for storage and analysis.

**Synthesis of Cu$_2$O octahedra**

The synthetic procedure used for making octahedral Cu$_2$O nanocrystals is based on our reported procedure with a slight modification in the volume of NH$_2$OH·HCl solution added.$^{15}$ First, 9.02 ml of deionized water was added to a sample vial. The sample vial was placed in a water bath set at 30–32 °C. Next, 0.1 mL of 0.1 M CuCl$_2$ and 0.2 mL of 1.0 M NaOH solution were added and the vial was shaken for ~10 s. Then 0.087 g of SDS powder was introduced with vigorous stirring. Finally, 0.68 mL of 0.2 M NH$_2$OH·HCl was quickly injected. After stirring for 20 s, the solution was kept in the water bath for 2 h for nanocrystal growth. The concentrations of Cu$^{2+}$ ions and SDS surfactant in the final solution are 1.0 × 10$^{-3}$ M and 3.0 × 10$^{-2}$ M. The reaction mixture was centrifuged at 3500 rpm for 2 min. After decanting the top solution, the precipitate was washed with 6 mL of 1:1 volume ratio of water and ethanol for three times to remove unreacted chemicals and SDS surfactant. The final washing step used 5 mL of ethanol, and the precipitate was dispersed in 0.6 mL of ethanol for storage and analysis.

**Turnover frequency calculations**

Since surface copper atoms are considered to be the active catalytic sites, we define TOF as moles of products formed / (moles of total surface copper atoms × reaction time). The surface copper atom area density for a particular lattice plane can be calculated by determining the number of surface copper atoms within a chosen area. The chosen areas are shown in Figure S4. Here the unit cell parameter $a$ is taken as 4.267 Å. For the (100) plane with the area shown in panel a of Figure S4, the surface copper atom density is $32 / (4 \times 4.267 \times 4 \times 4.267) = 0.1098 \text{ Å}^{-2}$, or 10.98 nm$^{-2}$. For the (111) plane with the area shown in panel c of Figure S4, a total of 36 surface copper atoms are counted from line 1 to line 8. The surface copper atom density is $36 / (4\sqrt{2} \times 4.267 \times 2\sqrt{6} \times 4.267 / 2) = 0.1427 \text{ Å}^{-2}$, or 14.27 nm$^{-2}$. For the (110) plane with the area shown in panel e of Figure S4, the surface copper atom density is $32 / (4 \times 4.267 \times 4\sqrt{2} \times 4.267) = 0.0776 \text{ Å}^{-2}$, or 7.76 nm$^{-2}$.

All catalysts have approximately the same total surface area of 0.0028 m$^2$ or 2.8 × 10$^{15}$ nm$^2$. For nanocubes, this surface area contains $(10.98 \times 2.8 \times 10^{15}) / 6.023 \times 10^{23}$, or 5.104 × 10$^{-8}$, mole of surface Cu atoms. For octahedra and rhombic dodecahedra, this area contains 6.634 × 10$^{-8}$ and 3.608 × 10$^{-8}$ mole of surface Cu atoms, respectively.

For the reaction shown in Table 1 (1a to product 3aa), 0.050 g of 1a was used for each case. The molecular weight of 1a is 200.57 g/mole and that of 3aa is 266.25
Moles of product 3aa formed can be calculated from the percent product yield. For the nanocubes, weight of 3aa produced = \((266.25/200.57 \times 0.050) \times 0.82 = 0.0544\) g or \(2.04 \times 10^{-4}\) mol. For the octahedra, weight of 3aa produced = \((266.25/200.57 \times 0.050) \times 0.89 = 0.0590\) g or \(2.22 \times 10^{-4}\) mol. For the rhombic dodecahedra, it is \(0.06305\) g or \(2.37 \times 10^{-4}\) mol.

TOF of nanocubes = \(2.04 \times 10^{-4}\) mol / \((5.104 \times 10^{-8}\) mol \times 7 h\) = \(571\) h\(^{-1}\).

TOF of octahedra = \(2.22 \times 10^{-4}\) mol / \((6.634 \times 10^{-8}\) mol \times 5 h\) = \(669\) h\(^{-1}\).

TOF of rhombic dodecahedra = \(2.37 \times 10^{-4}\) mol / \((3.608 \times 10^{-8}\) mol \times 2 h\) = \(3338\) h\(^{-1}\).

**Fig. S1** Size distribution histograms of Cu\(_2\)O (a) nanocubes, (b) octahedra, and (c) rhombic dodecahedra.

**Table S1.** Average particle sizes and their relative standard deviations.

<table>
<thead>
<tr>
<th>Shape</th>
<th>Average Particle Size</th>
<th>Relative Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubes</td>
<td>241 (\pm) 20 nm</td>
<td>8%</td>
</tr>
<tr>
<td>Octahedra</td>
<td>427 (\pm) 123 nm</td>
<td>29%</td>
</tr>
<tr>
<td>Rhombic dodecahedra</td>
<td>268 (\pm) 17 nm</td>
<td>6%</td>
</tr>
</tbody>
</table>
Fig. S2  XRD patterns of the synthesized Cu$_2$O nanocubes, octahedra, and rhombic dodecahedra. A standard diffraction pattern of Cu$_2$O is also given (JCPDS card no. 77-0199 for cuprite Cu$_2$O with a lattice constant $a_0$ of 4.26 Å). Due to random orientation of the nanocubes, the (200) peak intensity is not enhanced. Octahedra display an exceptionally strong (111) reflection peak because of their {111} facets. Rhombic dodecahedra show enhanced (110) and (220) peaks as a result of their {110} faces.
Fig. S3  FT-IR spectra of the synthesized Cu$_2$O (a) nanocubes, (b) octahedra, and (c) rhombic dodecahedra.

Fig. S4  Possible mechanism for the Cu$_2$O-catalyzed [3 + 2] cycloaddition addition.
Spectral Data of Synthesized Compounds from Table 2

3-(4-Nitrophenyl)-5-phenylisoxazole (3aa)

![Chemical Structure of 3aa](image)

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.33 (d, $J = 8.8$ Hz, 2H), 8.03 (d, $J = 8.8$ Hz, 2H), 7.83 (d, $J = 7.6$ Hz, 2H), 7.51-7.48 (m, 3H), 6.88 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.5, 161.2, 148.7, 135.2, 130.7, 129.2, 127.7, 126.9, 125.9, 124.2, 97.5; MS (EI) $m/z$: 266 (M$^+$); HRMS (EI, m/z) calcd for C$_{15}$H$_{10}$N$_2$O$_3$: $m/z$ 266.0691; Found 266.0693 (M$^+$).

3-(4-Methoxyphenyl)-5-phenylisoxazole (3ba)

![Chemical Structure of 3ba](image)

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.81 (dd, $J = 8.0$, 1.5 Hz, 2H), 7.78 (dd, $J = 6.8$, 2.0 Hz, 2H), 7.48-7.43 (m, 3H), 6.97 (dd, $J = 6.8$, 2.0 Hz, 2H), 6.76 (s, 1H), 3.85 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.1, 162.6, 161.0, 130.1, 128.9, 128.2, 127.6, 125.8, 121.7, 114.3, 97.2, 55.4; MS (EI) $m/z$: 251 (M$^+$); HRMS (EI, m/z) calcd for C$_{16}$H$_{13}$NO$_2$: $m/z$ 251.0946; Found 251.0938 (M$^+$).

5-(4-Methoxyphenyl)-3-(4-nitropheny)isoxazole (3ab)

![Chemical Structure of 3ab](image)

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.32 (d, $J = 8.9$ Hz, 2H), 8.02 (d, $J = 8.9$ Hz, 2H), 7.76 (d, $J = 8.8$ Hz, 2H), 6.99 (d, $J = 8.8$ Hz, 2H), 7.51-7.48 (m, 3H), 6.75 (s, 1H), 3.86 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.5, 161.5, 161.1, 148.6, 135.4, 127.5, 124.5, 124.2, 119.7, 114.5, 96.1, 55.4; MS (EI) $m/z$: 296 (M$^+$); HRMS (EI, m/z) calcd for C$_{16}$H$_{12}$N$_2$O$_4$: $m/z$ 296.0797; Found 296.0801 (M$^+$).
3,5-Diphenylisoxazole (3ca)

![Structure](image)

$^{1}$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.86-7.82 (m, 5H), 7.48-7.44 (m, 5H), 6.82 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.4, 162.9, 130.2, 130.0, 129.1, 129.0, 128.9, 127.5, 126.8, 125.8, 97.5; MS (EI) m/z: 221 (M$^+$); HRMS (EI, m/z) calcd for C$_{15}$H$_{11}$NO: m/z 221.0841; Found 221.0842 (M$^+$).

5-(4-Methoxyphenyl)-3-phenylisoxazole (3cb)

![Structure](image)

$^{1}$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.84 (dd, $J$ = 7.5, 1.5 Hz, 2H), 7.76 (d, $J$ = 8.6 Hz, 2H), 7.48-7.44 (m, 3H), 6.98 (d, $J$ = 8.6 Hz, 2H), 6.69 (s, 1H), 3.85 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.4, 162.9, 161.1, 129.9, 129.3, 128.9, 127.5, 126.8, 120.3, 114.4, 96.1, 55.4; MS (EI) m/z: 251 (M$^+$); HRMS (EI, m/z) calcd for C$_{16}$H$_{13}$NO$_2$: m/z 251.0946; Found 251.0939 (M$^+$).

5-(3-Chlorophenyl)-3-phenylisoxazole (3cc)

![Structure](image)

$^{1}$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.85-7.81 (m, 2H), 7.80 (t, $J$ = 1.6 Hz, 1H), 7.71-7.70 (m, 1H), 7.47-7.45 (m, 3H), 7.41-7.40 (m, 2H), 6.84 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 168.9, 163.1, 135.1, 130.2, 130.1, 129.0, 128.9, 128.8, 126.8, 125.9, 123.9, 98.3; MS (EI) m/z: 255 (M$^+$); HRMS (EI, m/z) calcd for C$_{15}$H$_{10}$ClNO: m/z 255.0451; Found 255.0456 (M$^+$).
3-(4-Methylphenyl)-5-phenyloxazole (3ca)

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \begin{array}{c}
\text{N} \quad \text{O} \\
\text{C} \quad \text{H}_3
\end{array}
\end{array}
\]

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.71 (dd, $J = 8.1$, 1.5 Hz, 2H), 7.74 (d, $J = 8.5$ Hz, 2H), 7.48-7.43 (m, 3H), 7.26 (dd, $J = 8.1$, 1.5 Hz, 2H), 6.79 (s, 1H), 2.39 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.2, 162.9, 140.2, 130.2, 129.6, 128.9, 127.6, 126.3, 125.8, 97.4, 21.4; MS (EI) $m/z$: 235 (M$^+$); HRMS (EI, m/z) calcd for C$_{16}$H$_{13}$NO: $m/z$ 235.0997; Found 235.0990 (M$^+$).

5-(3-Chlorophenyl)-3-p-tolyloxazole (3dc)

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \begin{array}{c}
\text{N} \quad \text{O} \\
\text{Cl}
\end{array}
\end{array}
\]

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.83 (t, $J = 1.4$ Hz, 1H), 7.71 (d, $J = 8.0$ Hz, 2H), 7.68 (dt, $J = 6.0$, 1.4 Hz, 1H), 7.38 (dd, $J = 5.0$, 3.6 Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 6.79 (s, 1H), 2.39 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 168.6, 162.9, 140.3, 134.9, 130.3, 130.1, 129.6, 129.0, 126.6, 125.9, 125.8, 123.8, 98.2, 21.4; MS (EI) $m/z$: 269 (M$^+$); HRMS (EI, m/z) calcd for C$_{16}$H$_{12}$ClNO: $m/z$ 269.0607; Found 269.0600 (M$^+$).

5-(4-Methoxyphenyl)-3-p-tolyloxazole (3db)

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \begin{array}{c}
\text{N} \quad \text{O} \\
\text{OCH}_3
\end{array}
\end{array}
\]

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.75 (dd, $J = 6.8$, 1.8 Hz, 2H), 7.73 (dd, $J = 8.0$, 0.5 Hz, 2H), 7.25 (dd, $J = 8.0$, 0.5 Hz, 2H), 6.96 (dd, $J = 6.8$, 1.8 Hz, 2H), 6.66 (s, 1H), 3.84 (s, 3H), 2.39 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.2, 162.9, 161.0, 140.0, 129.6, 127.4, 126.7, 126.7, 126.4, 120.4, 114.4, 96.0, 55.4, 21.4; MS (EI) $m/z$: 265 (M$^+$); HRMS (EI, m/z) calcd for C$_{17}$H$_{15}$NO$_2$: $m/z$ 265.1103; Found 265.1098 (M$^+$).
3-(2-Bromophenyl)-5-(4-methoxyphenyl)isoxazole (3eb)

![Chemical structure of 3-(2-Bromophenyl)-5-(4-methoxyphenyl)isoxazole (3eb)](image)

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J = 8.5$ Hz, 2H), 7.67 (t, $J = 8.6$ Hz, 2H), 7.49 (t, $J = 7.5$ Hz, 1H), 7.29 (t, $J = 7.5$ Hz, 1H), 6.98 (d, $J = 8.5$ Hz, 2H), 6.81 (s, 1H), 3.86 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 169.6, 162.9, 161.1, 13.6, 130.9, 130.7, 127.6, 127.5, 122.3, 120.3, 114.4, 95.5, 55.4; MS (EI) $m/z$: 330 (M$^+$); HRMS (EI, m/z) calcd for C$_{16}$H$_{12}$BrNO$_2$: m/z 329.0051; Found 329.0054 (M$^+$).

3-(2-Bromophenyl)-5-(3-chlorophenyl)isoxazole (3ec)

![Chemical structure of 3-(2-Bromophenyl)-5-(3-chlorophenyl)isoxazole (3ec)](image)

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 0.9$ Hz, 1H), 7.75-7.72 (m, 1H), 7.72 (d, $J = 8.1$ Hz, 1H), 7.70 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.44-7.42 (m, 3H), 7.35 (dt, $J = 7.4$, 0.9 Hz, 1H), 6.99 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 168.1, 163.1, 135.1, 133.7, 131.5, 131.3, 131.2, 130.4, 130.2, 128.9, 127.7, 125.9, 123.9, 122.4, 101.7; MS (EI) $m/z$: 334 (M$^+$); HRMS (EI, m/z) calcd for C$_{15}$H$_9$ClBrNO: m/z 332.9556; Found 332.9554 (M$^+$).

3,5-Bis(4-methoxyphenyl)isoxazole (3bb)

![Chemical structure of 3,5-Bis(4-methoxyphenyl)isoxazole (3bb)](image)

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.76 (dd, $J = 8.8$, 2.0 Hz, 2H), 7.73 (dd, $J = 8.8$, 2.0 Hz, 2H), 6.96 (dd, $J = 8.8$, 2.0 Hz, 2H), 6.95 (dd, $J = 8.8$, 2.0 Hz, 2H), 6.63 (s, 1H), 3.84 (s, 3H), 3.83 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.1, 162.5, 161.0, 160.9, 128.1, 127.4, 121.7, 120.4, 14.3, 114.2, 95.9, 55.4, 55.3; MS (EI) $m/z$: 281 (M$^+$); HRMS (EI, m/z) calcd for C$_{17}$H$_{13}$NO$_3$: m/z 281.1052; Found 281.1050 (M$^+$).
5-(3-Chlorophenyl)-3-(4-methoxyphenyl)isoxazole (3bc)

\[ \text{H}_3\text{CO} \begin{array}{c} \text{N} \\
\rightarrow \\
\text{O} \\
\text{Cl} \end{array} \]

\(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) 7.76 (d, \(J = 8.7\) Hz, 3H), 7.61 (m, 1H), 7.37 (d, \(J = 4.6\) Hz, 2H), 6.95 (d, \(J = 8.7\) Hz, 2H), 6.75 (s, 1H), 3.83 (s, 3H); \(^{13}\text{C NMR} (150 \text{ MHz, CDCl}\(_3\)) \delta\) 168.6, 162.6, 161.1, 134.9, 130.3, 130.1, 129.0, 128.2, 125.8, 123.8, 121.2, 114.3, 98.0, 55.3; MS (EI) \(m/z\): 285 (M\(^+\)); HRMS (EI, \(m/z\)) calcd for C\(_{16}\)H\(_{12}\)ClNO\(_2\): \(m/z\) 285.0557; Found 285.0565 (M\(^+\)).

3-(2-Bromo-6-methoxyphenyl)-5-(3-chlorophenyl)isoxazole (3fc)

\[ \text{H}_3\text{CO} \begin{array}{c} \text{N} \\
\rightarrow \\
\text{O} \\
\text{Cl} \end{array} \]

\(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) 7.81-7.80 (m, 1H), 7.71 (dt, \(J = 4.3, 1.6\) Hz, 1H), 7.55 (d, \(J = 8.8\) Hz, 2H), 7.688 (dd, \(J = 8.8, 3.0\) Hz, 1H), 3.82 (s, 3H); \(^{13}\text{C NMR} (150 \text{ MHz, CDCl}\(_3\)) \delta\) 168.1, 163.1, 158.9, 135.1, 130.8, 130.4, 130.2, 128.9, 125.9, 123.9, 117.8, 116.0, 112.5, 101.7, 55.7; MS (EI) \(m/z\): 364 (M\(^+\)); HRMS (EI, \(m/z\)) calcd for C\(_{16}\)H\(_{11}\)BrClNO\(_2\): \(m/z\) 362.9662; Found 362.9664 (M\(^+\)).

3-(2-Bromo-6-methoxyphenyl)-5-(4-methoxyphenyl)isoxazole (3fb)

\[ \text{H}_3\text{CO} \begin{array}{c} \text{N} \\
\rightarrow \\
\text{O} \\
\text{OCH}_3 \end{array} \]

\(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) 7.75 (dd, \(J = 6.8, 2.0\) Hz, 2H), 7.53 (d, \(J = 8.8\) Hz, 1H), 7.21 (d, \(J = 3.1\) Hz, 1H), 6.96 (dd, \(J = 6.8, 2.0\) Hz, 2H), 6.84 (dd, \(J = 8.8, 3.1\) Hz, 1H), 6.82 (s, 1H), 3.84 (s, 3H), 3.80 (s, 3H); \(^{13}\text{C NMR} (150 \text{ MHz, CDCl}\(_3\)) \delta\) 169.6, 162.9, 161.1, 158.8, 134.3, 131.2, 127.4, 120.2, 117.5, 115.9, 114.4, 112.5, 99.4, 55.6, 55.4; MS (EI) \(m/z\): 360 (M\(^+\)); HRMS (EI, \(m/z\)) calcd for C\(_{17}\)H\(_{14}\)BrNO\(_3\): \(m/z\) 359.0157; Found 359.0154 (M\(^+\)).
3-(2-Bromo-6-methoxyphenyl)-5-(trimethylsilyl)isoxazole (3fe)

![](image)

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J = 8.8$ Hz, 1H), 7.14 (d, $J = 3.1$ Hz, 1H), 6.83 (s, 1H), 6.80 (dd, $J = 8.8$, 3.1 Hz, 1H), 3.78 (s, 3H), 0.36 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 177.8, 160.7, 158.7, 134.1, 131.2, 117.3, 116.1, 113.7, 112.5, 55.5, -1.94; MS (EI) $m/z$: 326 (M$^+$); HRMS (EI, m/z) calcd for C$_{13}$H$_{16}$BrNO$_2$Si: $m/z$ 325.0134; Found 325.0132 (M$^+$).

(3-(2-Bromo-6-methoxyphenyl)isoxazol-5-yl)methanol (3fd)

![](image)

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.52 (d, $J = 8.8$ Hz, 1H), 7.15 (d, $J = 3.1$ Hz, 1H), 6.84 (dd, $J = 8.8$, 3.1 Hz, 1H), 6.69 (s, 1H), 4.82 (t, $J = 3.0$ Hz, 2H), 3.80 (s, 3H), 2.31 (brs, OH); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.0, 162.7, 159.1, 134.5, 131.1, 117.9, 116.3, 112.7, 103.6, 56.8, 55.9; MS (EI) $m/z$: 284 (M$^+$); HRMS (EI, m/z) calcd for C$_{11}$H$_{10}$BrNO$_3$: $m/z$ 282.9844; Found 282.9848 (M$^+$).

Spectral Data of Compounds from Table 3

3-(4-Methoxyphenyl)isoxazol-5-yl)methanol (3bd)

![](image)

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.66 (d, $J = 8.8$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 6.45 (s, 1H), 4.74 (s, 2H), 3.81 (s, 3H), 3.10 (brs, OH); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.8, 162.0, 161.9, 128.2, 121.2, 114.3, 99.7, 56.4, 55.3; MS (EI) $m/z$: 205 (M$^+$); HRMS (EI, m/z) calcd for C$_{11}$H$_{11}$NO$_3$: $m/z$ 205.0739; Found 205.0734 (M$^+$).
3-(Phenyl)isoxazol-5-yl)methanol (3cd)

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[Phenyl]-N-O-\text{OH}
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$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.73-7.71 (m, 2H), 7.41-7.39 (m, 3H), 6.51 (s, 1H), 4.75 (s, 2H), 3.56 (brs, OH); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 172.2, 162.4, 130.1, 128.9, 128.6, 126.7, 100.0, 56.3; MS (EI) $m/z$: 175 (M$^+$); HRMS (EI, m/z) calcd for C$_{10}$H$_9$NO$_2$: $m/z$ 175.0633; Found 175.0639 (M$^+$).

3-(4-Methylphenyl)isoxazol-5-yl)methanol (3dd)

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H$_3$C-\[Phenyl]-N-O-\text{OH}
```

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.60 (dd, $J = 8.1$, 1.5 Hz, 2H), 7.22 (dd, $J = 8.1$, 1.5 Hz, 2H), 6.48 (s, 1H), 4.76 (s, 2H), 3.70 (brs, OH), 2.39 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.9, 162.4, 140.2 129.6, 126.6, 125.8, 99.9, 56.4, 21.3; MS (EI) $m/z$: 189 (M$^+$); HRMS (EI, m/z) calcd for C$_{11}$H$_{11}$NO$_2$: $m/z$ 189.0790; Found 189.0799 (M$^+$).

(3-(2-Bromophenyl)isoxazol-5-yl)methanol (3ed)

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Br-\[Phenyl]-N-O-\text{OH}
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$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.62 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.55 (dd, $J = 7.6$, 1.7 Hz, 1H), 7.35 (dt, $J = 7.6$, 1.2 Hz, 1H), 7.26 (dd, $J = 8.0$, 1.7 Hz, 1H), 6.62 (s, 1H), 4.76 (s, 2H), 4.00 (brs, OH); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.3, 162.3, 133.5, 131.1, 131.0, 129.9, 127.5, 122.1, 103.2, 56.1; MS (EI) $m/z$: 254 (M$^+$); HRMS (EI, m/z) calcd for C$_{10}$H$_8$BrNO$_2$: $m/z$ 252.9738; Found 252.9742 (M$^+$).
3-(4-Methoxyphenyl)-5-(trimethylsilyl)isoxazole (3be)

![Structure of 3be]

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.73 (dd, $J = 6.8, 2.0$ Hz, 2H), 6.93 (dd, $J = 6.8, 2.0$ Hz, 2H), 6.67 (s, 1H), 3.81 (s, 3H), 0.35 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 178.4, 160.7, 160.3, 128.3, 121.6, 114.2, 110.2, 55.2, -1.96; MS (EI) m/z: 247 (M$^+$); HRMS (EI, m/z) calcd for C$_{13}$H$_{17}$NO$_2$Si: m/z 247.1029; Found 247.1026 (M$^+$).

3-(2-Bromo-6-methoxyphenyl)-5-(trimethylsilyl)isoxazole (3fe)

![Structure of 3fe]

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J = 8.8$ Hz, 1H), 7.14 (d, $J = 3.1$ Hz, 1H), 6.83 (s, 1H), 6.80 (dd, $J = 8.8, 3.1$ Hz, 1H), 3.78 (s, 3H), 0.36 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 177.8, 160.7, 158.7, 134.1, 131.2, 117.3, 116.1, 113.7, 112.5, 55.5, -1.94; MS (EI) m/z: 326 (M$^+$); HRMS (EI, m/z) calcd for C$_{13}$H$_{16}$BrNO$_2$Si: m/z 325.0134; Found 325.0132 (M$^+$).

(3-(2-Bromo-6-methoxyphenyl)isoxazol-5-yl)methanol (3fd)

![Structure of 3fd]

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.52 (d, $J = 8.8$ Hz, 1H), 7.15 (d, $J = 3.1$ Hz, 1H), 6.84 (dd, $J = 8.8, 3.1$ Hz, 1H), 6.69 (s, 1H), 4.82 (t, $J = 3.0$ Hz, 2H), 3.80 (s, 3H), 2.31 (brs, OH); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.0, 162.7, 159.1, 134.5, 131.1, 117.9, 116.3, 112.7, 103.6, 56.8, 55.9; MS (EI) m/z: 284 (M$^+$); HRMS (EI, m/z) calcd for C$_{11}$H$_{10}$BrNO$_3$: m/z 282.9844; Found 282.9848 (M$^+$).
3-(4-Nitrophenyl)-5-(trimethylsilyl)isoxazole (3ae)

\[
\text{O}_2\text{N} \quad \text{N-O} \quad \text{SiMe}_3
\]

\(^1\text{H}\) NMR (600 MHz, CDCl\(_3\)) \(\delta 8.29\ (d, J = 8.9\ \text{Hz}, 2\text{H}), 7.99\ (d, J = 8.9\ \text{Hz}, 2\text{H}), 6.79\ (s, 1\text{H}), 0.38\ (s, 9\text{H}); \(^{13}\text{C}\) NMR (150 MHz, CDCl\(_3\)) \(\delta 180.3, 159.1, 148.5, 127.8, 124.5, 123.5, 110.6, -1.94\); MS (EI) \(m/z\): 262 (M\(^+\)); HRMS (EI, m/z) calcd for C\(_{12}\)H\(_{14}\)N\(_2\)O\(_3\)Si: \(m/z\) 262.0774; Found 262.0776 (M\(^+\)).

Ethyl-3-phenylisoxazole-5-carboxylate (3cf)

\[
\begin{align*}
\text{N-O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{align*}
\]

\(^1\text{H}\) NMR (600 MHz, CDCl\(_3\)) \(\delta 7.80-7.78\ (m, 2\text{H}), 7.44-7.42\ (m, 3\text{H}), 7.22\ (s, 1\text{H}), 4.42\ (q, J = 7.2\ \text{Hz}, 2\text{H}), 1.39\ (t, J = 7.2\ \text{Hz}, 3\text{H}); \(^{13}\text{C}\) NMR (150 MHz, CDCl\(_3\)) \(\delta 164.1, 162.8, 156.7, 130.4, 129.3, 128.9, 126.7, 107.2, 62.2, 14.0\); MS (EI) \(m/z\): 217 (M\(^+\)); HRMS (EI, m/z) calcd for C\(_{12}\)H\(_{11}\)NO: \(m/z\) 217.0739; Found 217.0740 (M\(^+\)).

3-Phenyl-5-propylisoxazole (3cg)

\[
\begin{align*}
\text{N-O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{align*}
\]

\(^1\text{H}\) NMR (600 MHz, CDCl\(_3\)) \(\delta 7.83-7.76\ (m, 2\text{H}), 7.42-7.41\ (m, 3\text{H}), 6.27\ (s, 1\text{H}), 2.75\ (t, J = 7.5\ \text{Hz}, 2\text{H}), 1.78-1.74\ (m, 2\text{H}), 1.00\ (t, J = 7.5\ \text{Hz}, 3\text{H}); \(^{13}\text{C}\) NMR (150 MHz, CDCl\(_3\)) \(\delta 174.0, 162.3, 129.7, 128.8, 128.6, 126.7, 98.8, 28.7, 20.9, 13.6\); MS (EI) \(m/z\): 187 (M\(^+\)); HRMS (EI, m/z) calcd for C\(_{12}\)H\(_{13}\)NO: \(m/z\) 187.0997; Found 187.0990 (M\(^+\)).
$^1$H NMR spectrum of compound 3aa in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3aa in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3ba in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3ba in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3ab in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3ab in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3ca in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3ca in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3cb in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3cb in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3cc in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3cc in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3da in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3da in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3dc in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3dc in CDCl$_3$ in 150 MHz
\(^1\)H NMR spectrum of compound 3db in CDCl\(_3\) in 600 MHz

\(^{13}\)C NMR spectrum of compound 3db in CDCl\(_3\) in 150 MHz
$^1$H NMR spectrum of compound 3eb in CDCl₃ in 600 MHz

$^{13}$C NMR spectrum of compound 3eb in CDCl₃ in 150 MHz
$^1$H NMR spectrum of compound 3ec in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3ec in CDCl$_3$ in 150 MHz
$^{1}$H NMR spectrum of compound 3bb in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3bb in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3bc in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3bc in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3fc in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3fc in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3fb in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3fb in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3bd in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3bd in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3cd in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3cd in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3dd in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3dd in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3ed in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3ed in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3be in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3be in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3fe in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3fe in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3fd in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3fd in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3ae in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3ae in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3cf in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3cf in CDCl$_3$ in 150 MHz
$^1$H NMR spectrum of compound 3cg in CDCl$_3$ in 600 MHz

$^{13}$C NMR spectrum of compound 3cg in CDCl$_3$ in 150 MHz