Supporting Information
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Silver-Catalyzed intramolecular C (5)-H Acyloxylation of 1, 4-disubstituted 1, 2, 3-triazoles

Yaowen Liu,* Wensheng Zhang, b Kai Xie, a Yubo Jiang a,*

a Faculty of Science, Kunming University of Science and Technology, Kunming 650500, China.
b School of Science and Technology, Jiaozuo Teachers’ College, Jiaozuo 454001, China.
Email address: ybjiang@kmust.edu.cn.

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General:

$^1$H and $^{13}$C NMR spectra were recorded with a Bruker ACF400 spectrometer (400 MHz) in CDCl$_3$ with TMS as an internal standard. All reactions were monitored by TLC with HuanghaiGF 254 silica gel coated plates. Column chromatography was carried out using 300–400 mesh silica gel at medium pressure. Infrared spectra were taken on a Bruker Vertex Series FTIR (KBr) and are reported in reciprocal centimeters (cm$^{-1}$). Melting points were obtained using a Büchi melting point apparatus and are uncorrected. HRMS spectra were recorded on Waters Micromass Premier Q-TOF spectrometer.

General Procedures for the substrates.

![Chemical reaction diagram](image)

The hydrazoates 3 (1mmol) and the terminal alkynes 4 (1.1mmol), CuI (0.05mmol), NaAsc (2mmol) and DMF-H$_2$O (5mL-0.5mL) were added to the above system at room temperature. After 8h, the mixture was treated with H$_2$O (5mL) and extracted with EtOAc (5 × 15 mL) and the combined organic layer was washed with brine (3 × 15 mL), dried over Na$_2$SO$_4$ and concentrated under reduced pressure to afford the 1, 4-disubstituted 1, 2, 3-triazoles 1.

General Procedures for the Target Products.

![Chemical reaction diagram](image)

1, 4-disubstituted 1, 2, 3-triazoles 1 (0.3 mmol), AgNO$_3$ (5.1 mg, 0.03mmol), KOAc (88.3mg, 0.9mmol), (NH$_4$)$_2$S$_2$O$_8$ (205.4mg, 0.9mmol), and EtOAc/H$_2$O (1:1, v:v, 12 mL) were sequentially added to a 25mL flask. Then the flask was stirred at room temperature for 24 h. After consumption of the 1, 4-disubstituted 1, 2, 3-triazoles monitored by TLC analysis, H$_2$O (15 mL) was added to the mixture and extracted with EtOAc (5 × 15 mL). The combined organic layer was washed with brine (3 × 5 mL), dried with Na$_2$SO$_4$, and concentrated under reduced pressure to afford the crude product. Purification by column chromatography on silica gel with EtOAc-PE (1:8) afforded the desired product 2.

Spectral Data of the Compounds

3-Phenyl-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2a):
White solid (61mg, 78% yield); Mp. 178-180°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.33 (t, $J$ = 7.9 Hz, 2H), 8.05 (d, $J$ = 7.6 Hz, 2H), 8.02 – 7.96 (m, 1H), 7.65 (t, $J$ = 7.7 Hz, 1H), 7.48 (t, $J$ = 7.7 Hz, 2H), 7.36 (t, $J$ = 7.4 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 155.8, 141.2, 137.7, 135.2, 131.7, 131.4, 128.8, 128.7, 128.4, 128.3, 125.5, 115.4, 110.1. HRMS (ESI) m/z [M + H$^+$]: calcd for C$_{15}$H$_{10}$N$_3$O$_2$: 264.0773, found: 264.0768; IR (KBr): 3664, 3075, 1774, 1611, 1507, 1436, 1379, 1323, 1229, 1133, 1005, 759, 689, 501 cm$^{-1}$.

3-(p-Tolyl)-5H-benzo[1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2b):

White solid (64mg, 78% yield); Mp. 166-168°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.26 (dd, $J$ = 13.4, 4.9 Hz, 2H), 7.91 (ddd, $J$ = 12.3, 9.4, 4.7 Hz, 3H), 7.62 – 7.51 (m, 1H), 7.24 – 7.18 (m, 2H), 2.33 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 155.9, 141.0, 138.3, 137.7, 135.4, 131.5, 129.6, 128.8, 128.7, 125.5, 125.4, 115.5, 110.2, 21.3. HRMS (ESI) m/z [M + H$^+$]: calcd for C$_{16}$H$_{12}$N$_3$O$_2$: 278.0930, found: 278.0932; IR (KBr): 3672, 3060, 2960, 1760, 1600, 1482, 1379, 1263, 1095, 1010, 803, 754, 669, 450 cm$^{-1}$.

3-(o-Tolyl)-5H-benzo[1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2c):

Yellow solid (58mg, 70% yield); Mp. 163-164°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.27 (dd, $J$ = 23.2, 8.1 Hz, 2H), 7.93 (t, $J$ = 7.8 Hz, 1H), 7.58 (t, $J$ = 7.7 Hz, 1H), 7.52 (d, $J$ = 6.4 Hz, 1H), 7.24 (d, $J$ = 11.7 Hz, 3H), 2.45 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 155.9, 141.7, 137.7, 137.0, 135.4, 131.4, 130.9, 129.5, 129.4, 128.8, 128.6, 126.9, 125.9, 115.4, 110.2, 20.7. HRMS (ESI) m/z [M + H$^+$]: calcd for C$_{16}$H$_{12}$N$_3$O$_2$: 278.0930, found: 278.0932; IR (KBr): 3678, 3070, 2962, 1766, 1607, 1477, 1376, 1257, 1097, 1015, 803, 754, 669, 450 cm$^{-1}$.

3-(m-Tolyl)-5H-benzo[1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2d):

White solid (63mg, 76% yield); Mp. 171-173°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.34 (t, $J$ = 8.4 Hz, 2H), 8.00 (dd, $J$ = 11.5, 4.2 Hz, 1H), 7.92 – 7.81 (m, 2H), 7.65 (t, $J$ = 7.7 Hz, 1H), 7.37 (t, $J$ = 7.7 Hz, 1H), 7.18 (d, $J$ = 7.5 Hz, 1H), 2.43 (d, $J$ = 10.5 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ = 155.9, 141.2, 138.6, 137.6, 135.3, 131.4, 129.1, 128.8, 128.7, 128.6, 128.2, 126.0, 122.6, 115.4, 110.1, 21.5. HRMS (ESI) m/z [M + H$^+$]: calcd for C$_{16}$H$_{12}$N$_3$O$_2$: 278.0930, found: 278.0932; IR (KBr): 3675, 2922, 1769, 1611, 1508, 1140, 1227, 1137, 922, 874, 750, 677 cm$^{-1}$.
3-(2-Methoxyphenyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2e):

White solid (59mg, 67% yield); Mp. 183-184°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.32\) (d, \(J = 8.1\) Hz, 1H), 8.27 (d, \(J = 7.9\) Hz, 1H), 7.96 (t, \(J = 7.8\) Hz, 1H), 7.73 (d, \(J = 7.5\) Hz, 1H), 7.63 – 7.58 (m, 1H), 7.39 (t, \(J = 7.9\) Hz, 1H), 7.07 (dd, \(J = 13.3\), 5.9 Hz, 1H), 7.01 (d, \(J = 8.4\) Hz, 1H), 3.92 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 156.6, 137.4, 136.7, 131.1, 130.2, 130.0, 128.7, 128.4, 121.1, 120.7, 117.2, 115.2, 111.9, 111.2, 110.2, 55.6.\)

HRMS (ESI) m/z [M + H\(^{+}\)]: calcd for C\(_{16}\)H\(_{12}\)N\(_{3}\)O\(_{3}\): 294.0879, found: 294.0882; IR (KBr): 3661, 2938, 1767, 1681, 1594, 1498, 1378, 1253, 1169, 1014, 679 cm\(^{-1}\).

3-(2-Fluorophenyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2f):

White solid (45mg, 53% yield); Mp. 192-193°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.37\) (dd, \(J = 18.7, 8.1\) Hz, 2H), 8.06 – 7.97 (m, 1H), 7.92 (td, \(J = 7.5, 1.6\) Hz, 1H), 7.67 (t, \(J = 7.7\) Hz, 1H), 7.48 – 7.36 (m, 1H), 7.34 – 7.17 (m, 3H).\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 155.8, 137.7, 135.3, 132.1, 130.6, 130.5, 129.7, 129.6, 128.8, 124.5, 124.4, 116.3, 116.1, 115.5, 110.3.\)

HRMS (ESI) m/z [M + H\(^{+}\)]: calcd for C\(_{15}\)H\(_{13}\)FN\(_{3}\)O\(_{2}\): 282.0679, found: 282.0682; IR (KBr): 3661, 3069, 2921, 1775, 1592, 1508, 1443, 1382, 1226, 1148, 1102, 996, 871, 753, 674, 553 cm\(^{-1}\).

3-(4-Fluorophenyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2g):

White solid (49mg, 58% yield); Mp. 175-177°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 8.36\) (dd, \(J = 11.5, 8.2\) Hz, 2H), 8.06 (dd, \(J = 8.7, 5.4\) Hz, 2H), 8.02 (t, \(J = 7.8\) Hz, 1H), 7.67 (t, \(J = 7.7\) Hz, 1H), 7.20 (t, \(J = 8.7\) Hz, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 156.6, 137.8, 135.2, 131.5, 128.8, 127.9, 127.4, 127.3, 124.6, 116.1, 115.9, 115.5, 110.1.\)

HRMS (ESI) m/z [M + H\(^{+}\)]: calcd for C\(_{15}\)H\(_{13}\)FN\(_{3}\)O\(_{2}\): 282.0679, found: 282.0682; IR (KBr): 3678, 3436, 3330, 2923, 1771, 1610, 1508, 1453, 1377, 1225, 1148, 998, 849, 752, 672, 594, 515 cm\(^{-1}\).

3-(4-Chlorophenyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2h):

White solid (44mg, 50% yield); Mp. 178-180°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.35\) (dd, \(J = 7.0, 6.2\) Hz, 2H), 8.02 (dd, \(J = 12.7, 4.8\) Hz, 3H), 7.67 (t, \(J = 7.8\) Hz, 1H), 7.44 (t, \(J = 7.7\) Hz, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 155.7, 141.3, 137.8, 135.2, 134.2, 131.5, 129.2, 128.9, 127.7, 126.9, 126.7, 115.5, 110.0.\)

HRMS (ESI) m/z [M + H\(^{+}\)]: calcd for C\(_{15}\)H\(_{9}\)ClN\(_{3}\)O\(_{2}\): 298.0383, found: 298.0385; IR (KBr): 3665, 2922, 1773, 1612, 1505, 1375, 1229, 1089, 1000, 836, 750, 674, 499 cm\(^{-1}\).

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3-(4-Bromophenyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2i):

Yellow solid (49mg, 48% yield); Mp. 201-203°C; 1H NMR (400 MHz, CDCl3) δ = 8.53 – 8.23 (m, 2H), 8.17 – 7.82 (m, 3H), 7.80 – 7.52 (m, 3H). 13C NMR (100 MHz, CDCl3) δ = 155.7, 141.4, 137.8, 135.2, 132.1, 131.8, 131.5, 129.8, 127.3, 127.0, 122.3, 115.5, 110.0. HRMS (ESI) m/z [M + H⁺]: calcd for C15H9BrN3O2: 341.9878, found: 341.9880; IR (KBr): 3664, 3084, 1781, 1617, 1506, 1438, 1385, 1238, 1136, 1068, 998, 831, 750, 677, 507 cm⁻¹.

7-Methyl-3-phenyl-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2j):

White solid (62mg, 75% yield); Mp. 156-158°C; 1H NMR (400 MHz, CDCl3) δ = 8.17 (d, J = 8.3 Hz, 1H), 8.09 – 7.95 (m, 3H), 7.72 (d, J = 8.4 Hz, 1H), 7.43 (dd, J = 16.5, 8.9 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 2.47 (s, 3H). 13C NMR (100 MHz, CDCl3) δ = 156.1, 139.3, 138.6, 133.2, 131.2, 131.1, 128.9, 128.5, 128.2, 125.5, 115.4, 21.2. HRMS (ESI) m/z [M + H⁺]: calcd for C16H12N3O2: 278.0930, found: 278.0932; IR (KBr): 3066, 2924, 1768, 1613, 1513, 1385, 1321, 1243, 1163, 1033, 893, 839, 765, 693, 503 cm⁻¹.

9-Methyl-3-phenyl-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2k):

White solid (59mg, 72% yield); Mp. 153-155°C; 1H NMR (400 MHz, CDCl3) δ = 8.15 (d, J = 58.4 Hz, 3H), 7.80 (s, 1H), 7.42 (d, J = 48.7 Hz, 4H), 2.99 (s, 3H). 13C NMR (100 MHz, CDCl3) δ = 156.4, 141.4, 140.8, 134.1, 131.0, 129.4, 129.0, 128.8, 128.5, 128.2, 128.0, 125.5, 111.1, 22.3. HRMS (ESI) m/z [M + H⁺]: calcd for C16H12N3O2: 278.0930, found: 278.0932; IR (KBr): 3084, 2924, 2862, 1771, 1590, 1499, 1369, 1321, 1259, 1134, 1013, 911, 756, 696 cm⁻¹.

8-Fluoro-3-phenyl-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2l):

Yellow solid (46mg, 55% yield); Mp. 195-197°C; 1H NMR (400 MHz, CDCl3) δ = 8.36 (ddd, J = 11.2, 8.9, 5.6 Hz, 1H), 8.21 (d, J = 7.4 Hz, 1H), 8.14 – 7.99 (m, 1H), 7.79 – 7.63 (m, 1H), 7.63 – 7.30 (m, 4H). 13C NMR (100 MHz, CDCl3) δ = 156.1, 134.7, 130.8, 128.9, 128.7, 128.5, 125.6, 119.0, 118.8, 117.1, 116.8, 103.4, 103.1. HRMS (ESI) m/z [M + H⁺]: calcd for C15H9FN3O2: 282.0679, found: 282.0683; IR (KBr): 3072, 2924, 2856, 1771, 1612, 1485, 1429, 1371, 1322, 1262, 1171, 1133, 1007, 890, 766, 695, 657, 507 cm⁻¹.

7-Methyl-3-(p-tolyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2m):
Yellow solid (66mg, 76% yield); Mp. 197-199°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) = 8.23 (d, \(J = 8.4\) Hz, 1H), 8.11 (s, 1H), 7.96 (d, \(J = 8.1\) Hz, 2H), 7.79 (dd, \(J = 8.3, 1.5\) Hz, 1H), 7.29 (d, \(J = 8.1\) Hz, 2H), 2.54 (s, 3H), 2.41 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) = 156.2, 139.2, 138.6, 138.2, 133.2, 131.1, 129.5, 125.6, 125.4, 115.3, 109.9, 21.3, 21.2. HRMS (ESI) m/z [M + H\(^+\)]: calcd for C\(_{17}\)H\(_{14}\)N\(_3\)O\(_2\): 292.1086, found: 292.1089; IR (KBr): 3661, 3077, 1772, 1619, 1516, 1103,823, 469 cm\(^{-1}\).

**9-Methyl-3-(p-tolyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2n):**

Yellow solid (61mg, 70% yield); Mp. 192-193°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) = 8.21 (t, \(J = 7.1\) Hz, 2H), 8.14 (d, \(J = 7.8\) Hz, 1H), 7.74 (d, \(J = 7.5\) Hz, 1H), 7.54 (t, \(J = 7.7\) Hz, 1H), 7.33 (d, \(J = 8.1\) Hz, 2H), 2.60 (s, 3H), 2.46 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) = 158.5, 145.5, 143.1, 137.7, 137.6, 131.6, 131.1, 129.9, 129.5, 129.2, 126.4, 125.4, 118.4, 21.8, 17.0. HRMS (ESI) m/z [M + H\(^+\)]: calcd for C\(_{17}\)H\(_{14}\)N\(_3\)O\(_2\): 292.1086, found: 292.1089; IR (KBr): 3666, 3075, 1775, 1612, 1500, 1109,820, 465 cm\(^{-1}\).

**7,9-Dimethyl-3-(p-tolyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2o):**

Yellow solid (65mg, 72% yield); Mp. 158-160°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) = 8.21 (d, \(J = 8.3\) Hz, 2H), 7.93 (d, \(J = 10.3\) Hz, 1H), 7.56 (s, 1H), 7.33 (d, \(J = 8.2\) Hz, 2H), 2.56 (s, 3H), 2.48 (s, 3H), 2.46 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) = 158.8, 145.3, 140.7, 138.9, 137.4, 133.5, 131.1, 129.5, 129.2, 126.7, 126.2, 125.4, 118.2, 22.6, 21.8, 21.4. HRMS (ESI) m/z [M + H\(^+\)]: calcd for C\(_{18}\)H\(_{16}\)N\(_3\)O\(_2\): 306.1243, found: 306.1245; IR (KBr): 2922, 2857, 1746, 1669, 1602, 1459, 1375, 1321, 1235, 1154, 993, 869, 771, 471 cm\(^{-1}\).

**8-Fluoro-3-(p-tolyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2p):**

White solid (51mg, 58% yield); Mp. 179-181°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) = 8.41 – 8.29 (m, 1H), 8.06 – 7.86 (m, 3H), 7.36 – 7.24 (m, 3H), 2.40 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) = 155.2, 138.4, 134.8, 134.7, 129.6, 128.8, 125.4, 125.2, 124.2, 117.0, 116.7, 103.4, 103.1, 21.3. HRMS (ESI) m/z [M + H\(^+\)]: calcd for C\(_{16}\)H\(_{11}\)FN\(_3\)O\(_2\): 296.0835, found: 296.0837; IR (KBr): 3666, 3071, 1776, 1614, 1484, 1322, 1261, 1232, 1122, 1006, 824, 663, 509, 450 cm\(^{-1}\).

**3-(4-Fluorobenzyl)-7-methyl-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazin-5-one(2q):**

White solid (62mg, 71% yield); Mp. 198-200°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) = 7.96 (dd, \(J = 8.6, 5.4\) Hz, 2H), 7.71 (dd, \(J = 7.4, 5.4\) Hz, 2H), 7.11 (dd, \(J = 16.6, 8.1\) Hz, 3H), 2.47 (s, 3H). \(^{13}\)C NMR
(100 MHz, CDCl₃) δ = 155.9, 139.4, 138.7, 131.1, 129.7, 127.3, 127.2, 125.8, 116.0, 115.8, 115.3, 21.2. HRMS (ESI) m/z [M + H⁺]: calcd for C₁₆H₁₁FN₃O₂: 296.0835, found: 296.0836; IR (KBr): 3068, 2923, 2856, 1776, 1584, 1508, 1384, 1311, 1233, 1158, 1094, 1025, 892, 835, 755, 691, 591, 515 cm⁻¹.

3-Pentyl-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazin-5-one (2r):

White solid (47mg, 61% yield); Mp. 59-61°C; ¹H NMR (400 MHz, CDCl₃) δ = 8.31 (dd, J = 5.1, 3.6 Hz, 2H), 8.03 – 7.90 (m, 1H), 7.67 – 7.56 (m, 1H), 2.86 – 2.71 (m, 2H), 1.82 – 1.73 (m, 2H), 1.41 – 1.35 (m, 4H), 0.91 (dd, J = 9.4, 4.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 156.3, 142.0, 137.5, 135.4, 131.4, 129.7, 128.4, 115.2, 110.3, 31.3, 28.0, 23.6, 22.3, 13.9. HRMS (ESI) m/z [M + H⁺]: calcd for C₁₄H₁₆N₂O₂: 258.1243, found: 258.1245; IR (KBr): 3666, 2927, 2861, 1774, 1693, 1613, 1517, 1448, 1379, 1228, 1144, 1003, 754, 678 cm⁻¹.

¹H and ¹³C NMR spectra of the compounds