Supporting Information

Copper(II)-catalyzed oxidative [3 + 2] cycloaddition reactions of secondary amines with α-diazo compounds: facile and efficient synthesis of 1,2,3-triazoles

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I. General Information

All reactions were performed in dried glassware. Solvents (DMF) were commercial and were dried prior to use. The α-diazo compounds were prepared according to the previous method reported.¹ Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Chromatography was carried on flash silica gel (300-400 mesh). All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). The ¹H NMR spectra were recorded at 500 MHz in CDCl₃ and the ¹³C NMR spectra were recorded at 125 MHz in CDCl₃ with TMS as internal standard. All coupling constants (J values) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). The compound 3a was glued on a glass fiber. Data were collected at 293 K using graphite-monochromated Mo Ka radiation (λ = 0.71073Å) and IP technique in the range 2.19° < θ < 27.48°. Empirical absorption correction was applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F² using the SHELXS 97 crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps.

II. General Procedure for the Preparation of 3 (3a as Example):

\[
\begin{array}{c}
\text{R}^1\text{O} \quad \text{N} \quad \text{R}^3
\\ \text{N}^2 \quad \text{O} \quad \text{R}^2
\\ \text{CuBr}_2 \ (30 \text{ mol\%}), \text{O}_2 \ (1 \text{ atm})
\\ \text{DBU} \ (3.0 \text{ eq.}), \text{DMF}, \text{rt}
\\ \text{R}^1\text{O} \quad \text{N} \quad \text{R}^3
\\ \text{N}^2 \quad \text{O} \quad \text{R}^2
\end{array}
\]

Glycine derivative 1a (0.2 mmol, 38.6 mg), ethyl diazoacetate 2a (1.0 mmol, 0.11 mL), DBU (0.6 mmol, 0.09 mL), CuBr2 (0.06 mmol, 13.4 mg) and dry DMF (1.5 mL) were added to a 10 mL Schlenk tube equipped with a magnetic stir bar. Subsequently, the reaction mixture was stirred under an oxygen atmosphere (oxygen balloon) at room temperature for 10 h. After 1a was consumed (monitored by TLC), the reaction mixture was poured into water (20.0 mL) and extracted with CH2Cl2 (3×10 mL). The combined organic extracts were dried over anhydrous MgSO4, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by chromatography (silica gel, petroleum ether/ethyl acetate = 10/2, V/V) to give 3a (51 mg, 84%) as a light yellow solid.

**Diethyl 1-p-tolyl-1H-1,2,3-triazole-4,5-dicarboxylate (3a):**

![Structure of 3a]

White solid; mp 53–55 °C; 1H NMR (500 MHz, CDCl3) δ: 1.27 (t, \( \text{J} = 7.0 \text{ Hz}, 3\text{H} \)), 1.43 (t, \( \text{J} = 7.0 \text{ Hz}, 3\text{H} \)), 2.45 (s, 3H), 4.37 (q, \( \text{J} = 7.0 \text{ Hz}, 2\text{H} \)), 4.47 (q, \( \text{J} = 7.0 \text{ Hz}, 2\text{H} \)), 7.33 (d, \( \text{J} = 7.5 \text{ Hz}, 2\text{H} \)), 7.42 (d, \( \text{J} = 8.0 \text{ Hz}, 2\text{H} \)); 13C NMR (125 MHz, CDCl3) δ: 13.7, 14.2, 21.2, 61.8, 63.2, 124.1 (2C), 130.1 (2C), 132.7, 133.1, 138.7, 140.8, 159.1, 159.8; HRMS (ESI-TOF) Calcd for C13H18N3O4\(^+\) ([M + H]+): 304.1292. Found 304.1286.

**Diethyl 1-(4-methoxyphenyl)-1H-1,2,3-triazole-4,5-dicarboxylate (3b):**
White solid; mp 43–45 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.27 (t, $J$ = 7.0 Hz, 3H), 1.43 (t, $J$ = 7.0 Hz, 3H), 3.88 (s, 3H), 4.36 (q, $J$ = 7.0 Hz, 2H), 4.46 (q, $J$ = 7.0 Hz, 2H), 7.02 (d, $J$ = 8.5 Hz, 2H), 7.45 (d, $J$ = 8.5 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 13.8, 14.2, 55.6, 61.8, 63.2, 114.6 (2C), 125.9 (2C), 128.4, 132.8, 138.6, 159.1, 159.8, 161.0; HRMS (ESI-TOF) Calcd for C$_{13}$H$_{18}$N$_3$O$_5$ $^+$ ([M + H$^+$]): 320.1241. Found 320.1242.

Diethyl 1-(3-methoxyphenyl)-1$H$-1,2,3-triazole-4,5-dicarboxylate (3c):

Yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.28 (t, $J$ = 7.0 Hz, 3H), 1.43 (t, $J$ = 7.0 Hz, 3H), 3.86 (s, 3H), 4.38 (q, $J$ = 7.0 Hz, 2H), 4.47 (q, $J$ = 7.0 Hz, 2H), 7.08 (s, 1H), 7.10 (d, $J$ = 8.5 Hz, 2H), 7.43 (t, $J$ = 8.0 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 13.7, 14.1, 55.6, 61.8, 63.3, 109.9, 116.1, 116.3, 130.3, 132.7, 136.4, 138.6, 159.0, 159.6, 160.3; HRMS (ESI-TOF) Calcd for C$_{13}$H$_{18}$N$_3$O$_5$ $^+$ ([M + H$^+$]): 320.1241. Found 320.1241..

Diethyl 1-m-tolyl-1$H$-1,2,3-triazole-4,5-dicarboxylate (3d):

Yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.27 (t, $J$ = 7.0 Hz, 3H), 1.43 (t, $J$ = 7.0 Hz, 3H), 2.44 (s, 3H), 4.37 (q, $J$ = 7.0 Hz, 2H), 4.47 (q, $J$ = 7.0 Hz, 2H), 7.31 (d, $J$ = 7.5 Hz, 1H) 7.35-7.37 (m, 2H), 7.41 (d, $J$ = 7.5 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 13.7, 14.2, 21.3, 61.8, 63.2, 121.2, 124.9, 129.3, 131.2, 132.7, 135.5, 138.7, 139.9, 159.1, 159.8; HRMS (ESI-TOF) Calcd for
Diethyl 1-o-tolyl-1H-1,2,3-triazole-4,5-dicarboxylate (3e):

Yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.14 (t, $J = 7.0$ Hz, 3H), 1.44 (t, $J = 7.0$ Hz, 3H), 2.11 (s, 3H), 4.26 (q, $J = 7.0$ Hz, 2H), 4.49 (q, $J = 7.0$ Hz, 2H), 7.27 (d, $J = 7.5$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.39 (d, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 13.6, 14.2, 17.2, 61.9, 62.9, 126.7, 126.8, 131.0, 131.2, 133.3, 134.7, 135.4, 138.7, 158.1, 159.9; HRMS (ESI-TOF) Calcd for C$_{15}$H$_{18}$N$_3$O$_4$ $^+$ ([M + H]$^+$): 304.1292. Found 304.1286.

Diethyl 1-phenyl-1H-1,2,3-triazole-4,5-dicarboxylate (3f):

Yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.26 (t, $J = 7.0$ Hz, 3H), 1.43 (t, $J = 7.0$ Hz, 3H), 4.37 (q, $J = 7.0$ Hz, 2H), 4.47 (q, $J = 7.0$ Hz, 2H), 7.54 (d, $J = 6.0$ Hz, 5H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 13.7, 14.2, 61.9, 63.3, 124.4 (2C), 129.6 (2C), 130.5, 132.7, 135.6, 138.8, 159.0, 159.8; HRMS (ESI-TOF) Calcd for C$_{14}$H$_{16}$N$_3$O$_4$ $^+$ ([M + H]$^+$): 290.1135. Found 290.1130.

Diethyl 1-(4-chlorophenyl)-1H-1,2,3-triazole-4,5-dicarboxylate (3g):

The reaction was performed at 80 °C following the general procedure described above and 3g was isolated as a white solid: mp 40–42 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.30 (t, $J = 7.0$ Hz, 3H),
1.43 (t, J = 7.0 Hz, 3H), 4.38 (q, J = 7.0 Hz, 2H), 4.47 (q, J = 7.0 Hz, 2H), 7.52 (d, J = 6.0 Hz, 4H);

$^{13}$C NMR (125 MHz, CDCl$_3$) δ: 13.7, 14.1, 61.9, 63.4, 125.7, 129.8, 132.5, 134.0, 136.6, 139.1, 158.7, 159.6; HRMS (ESI-TOF) Calcd for C$_{14}$H$_{15}$ClN$_3$O$_4$ $^+$ ([M + H]$^+$): 324.0746. Found 324.0726.

**Diethyl 1-(thiophen-3-yl)-1H-1,2,3-triazole-4,5-dicarboxylate (3h):**

Red oil; $^1$H NMR (500 MHz, CDCl$_3$) δ: 1.33 (t, J = 7.0 Hz, 3H), 1.42 (t, J = 7.0 Hz, 3H), 4.42 (q, J = 7.0 Hz, 2H), 4.46 (q, J = 7.0 Hz, 2H), 7.35 (dd, J = 1.4 Hz, 1H), 7.48 (dd, J = 3.5 Hz, 2Hz, 1H), 7.65 (dd, J = 1.2 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 13.7, 14.1, 61.8, 63.4, 119.9, 123.1, 126.9, 132.4, 133.2, 138.4, 159.1, 159.6; Calcd for C$_{12}$H$_{14}$N$_3$O$_4$S$^+$ ([M + H]$^+$): 296.0700. Found 296.0688.

**Diethyl 1-(naphthalen-2-yl)-1H-1,2,3-triazole-4,5-dicarboxylate (3i):**

The reaction was performed at 60 °C following the general procedure described above and 3i was isolated as a red oil. $^1$H NMR (500 MHz, CDCl$_3$) δ: 1.25 (t, J = 7.0 Hz, 3H), 1.45 (t, J = 7.0 Hz, 3H), 4.36 (q, J = 7.0 Hz, 2H), 4.49 (q, J = 7.0 Hz, 2H), 7.61-7.63 (m, 3H), 7.94 (t, J = 9.0 Hz, 2H), 8.01 (d, J = 8.5 Hz, 1H), 8.05 (d, J = 2.0 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 13.7, 14.2, 61.9, 63.3, 121.5, 123.4, 127.6, 127.8, 127.9, 128.4 (2C), 129.8, 132.7, 132.9, 133.5, 138.8, 159.1, 159.8; HRMS (ESI-TOF) Calcd for C$_{18}$H$_{18}$N$_3$O$_4$ $^+$ ([M + H]$^+$): 340.1292. Found 340.1278.

**Diethyl 1-(naphthalen-1-yl)-1H-1,2,3-triazole-4,5-dicarboxylate (3j):**
The reaction was performed at 60 °C following the general procedure described as above and 3j was isolated as a red oil. $^1$H NMR (500 MHz, CDCl$_3$) δ: 0.91 (t, $J = 7.0$ Hz, 3H), 1.46 (t, $J = 7.0$ Hz, 3H), 4.11 (q, $J = 7.0$ Hz, 2H), 4.52 (q, $J = 7.0$ Hz, 2H), 7.28 (d, $J = 8.5$ Hz, 1H), 7.52-7.61 (m, 4H), 7.97 (d, $J = 7.5$ Hz, 1H), 8.08 (d, $J = 7.5$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 13.4, 14.2, 62.0, 62.8, 124.7, 124.9, 127.2, 128.1, 128.2, 129.2, 131.4, 131.9, 133.9, 134.3, 138.8, 158.0, 159.9; HRMS (ESI-TOF) Calcd for C$_{18}$H$_{18}$N$_3$O$_4$ $^+$ ([M + H]$^+$): 340.1292. Found 340.1282.

Diethyl 1-phenethyl-1$H$-1,2,3-triazole-4,5-dicarboxylate (3k):

Yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) δ: 1.36 (t, $J = 7.0$ Hz, 3H), 1.41 (t, $J = 7.0$ Hz, 3H), 3.20 (t, $J = 7.5$ Hz, 2H), 4.33 (q, $J = 7.0$ Hz, 2H), 4.42 (q, $J = 7.0$ Hz, 2H), 4.84 (t, $J = 7.5$ Hz, 2H), 7.11 (d, $J = 7.0$ Hz, 2H), 7.24-7.31 (m, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 13.8, 14.1, 36.7, 51.4, 61.7, 62.7, 127.1, 128.6, 128.7 (4C), 136.3 (2C), 158.4, 160.1; HRMS (ESI-TOF) Calcd for C$_{16}$H$_{20}$N$_3$O$_4$ $^+$ ([M + H]$^+$): 318.1448. Found 318.1433.

Ethyl 5-(methylcarbamoyl)-1-$p$-tolyl-1$H$-1,2,3-triazole-4-carboxylate (3l):

White solid; mp 103−105 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 1.47 (t, $J = 7.0$ Hz, 3H), 2.43 (s, 3H), 2.94 (d, $J = 4.5$ Hz, 3H), 4.50 (q, $J = 7.0$ Hz, 2H), 7.31 (t, $J = 9.0$ Hz, 4H), 9.22 (br s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 14.0, 21.2, 26.3, 62.7, 125.3 (2C), 129.5 (2C), 134.4, 134.5, 136.2,
Ethyl 5-(dimethylcarbamoyl)-1-p-tolyl-1H-1,2,3-triazole-4-carboxylate (3m):

![Structure](image)

White solid; mp 177–179 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.42 (t, $J = 7.0$ Hz, 3H), 2.43 (s, 3H), 2.78 (s, 3H), 3.09 (s, 3H), 4.43 (q, $J = 7.0$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.50 (d, $J = 8.5$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 14.2, 21.2, 39.4, 37.6, 61.6, 123.2 (2C), 130.3 (2C), 133.1, 135.4, 136.9, 140.6, 159.5, 160.0; HRMS (ESI-TOF) Calcd for C$_{15}$H$_{19}$N$_4$O$_3$ $^+$ ([M + H]$^+$): 303.1452. Found 303.1458.

Ethyl 4-benzoyl-1-p-tolyl-1H-1,2,3-triazole-5-carboxylate (3n):

![Structure](image)

Yellow solid; mp 93–95 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.20 (t, $J = 7.0$ Hz, 3H), 2.46 (s, 3H), 4.31 (q, $J = 7.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.54 (t, $J = 7.5$ Hz, 2H), 7.65 (t, $J = 8.0$ Hz, 1H), 8.31 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 13.6, 21.3, 63.0, 124.4 (2C), 128.5 (2C), 130.0 (2C), 130.5 (2C), 132.5, 133.2, 133.7, 136.1, 140.8, 146.5, 159.0, 185.5; HRMS (ESI-TOF) Calcd for C$_{19}$H$_{18}$N$_3$O$_3$ $^+$ ([M + H]$^+$): 336.1343. Found 336.1348.

Ethyl 4-benzoyl-1-(thiophen-3-yl)-1H-1,2,3-triazole-5-carboxylate (3o):

![Structure](image)

Red oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.25 (t, $J = 7.0$ Hz, 3H), 4.37 (q, $J = 7.0$ Hz, 2H), 7.41 (dd,
$J = 1.5, 3.5 \text{ Hz}, 1\text{H}$), 7.48-7.55 (m, 3H), 7.64 (t, $J = 7.5 \text{ Hz}, 1\text{H}$), 7.72 (d, $J = 2.0 \text{ Hz}, 1\text{H}$), 8.31 (d, $J = 7.5 \text{ Hz}, 2\text{H}$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 13.6, 63.2, 120.2, 123.4, 126.7, 128.5, 130.5 (2C), 132.3 (2C), 133.3, 133.7, 136.0, 146.3, 159.1, 185.2; HRMS (ESI-TOF) Calcd for C$_{16}$H$_{14}$N$_3$O$_3$S$^+$ ([M + H]$^+$): 328.0750. Found 328.0759.

**Ethyl 4-benzoyl-1-(4-chlorophenethyl)-1H-1,2,3-triazole-5-carboxylate (3p):**

![Chemical Structure](image)

Yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.08 (t, $J = 7.0 \text{ Hz}, 3\text{H}$), 3.25 (t, $J = 7.0 \text{ Hz}, 2\text{H}$), 4.15 (q, $J = 7.0 \text{ Hz}, 2\text{H}$), 4.94 (t, $J = 7.5 \text{ Hz}, 2\text{H}$), 7.09 (d, $J = 8.0 \text{ Hz}, 2\text{H}$), 7.27 (d, $J = 8.0 \text{ Hz}, 2\text{H}$), 7.50 (t, $J = 7.5 \text{ Hz}, 2\text{H}$), 7.62 (t, $J = 7.5 \text{ Hz}, 1\text{H}$), 7.96 (d, $J = 7.5 \text{ Hz}, 2\text{H}$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 13.3, 36.1, 51.1, 62.5, 128.5 (2C), 128.7 (2C), 128.9, 130.1 (2C), 130.3 (2C), 133.1, 133.8, 134.9, 136.5, 147.2, 158.2, 186.8; HRMS (ESI-TOF) Calcd for C$_{20}$H$_{19}$ClN$_3$O$_3$ $^+ ([M + H]^+)$: 384.1109. Found 384.1101.

**4-Benzoyl-N-methyl-1-p-tolyl-1H-1,2,3-triazole-5-carboxamide (3q):**

![Chemical Structure](image)

White solid; mp 174–176 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 2.45 (s, 3H), 2.96 (t, $J = 5.5 \text{ Hz}, 3\text{H}$), 7.34 (d, $J = 8.5 \text{ Hz}, 2\text{H}$), 7.39 (d, $J = 8.5 \text{ Hz}, 2\text{H}$), 7.50-7.57 (m, 2H), 7.66-7.72 (m, 1H), 8.24 (d, $J = 7.5 \text{ Hz}, 2\text{H}$), 9.34 (br s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 21.3, 26.4, 119.7, 125.3 (2C), 128.4 (2C), 128.8, 129.6 (2C), 130.8, 131.3(2C), 134.1, 140.3, 143.1, 157.1, 189.4; HRMS (ESI-TOF) Calcd for C$_{18}$H$_{17}$N$_4$O$_2$ $^+ ([M + H]^+)$: 321.1346. Found 321.1332.

**4-Benzoyl-N,N-dimethyl-1-p-tolyl-1H-1,2,3-triazole-5-carboxamide (3r):**

![Chemical Structure](image)
White solid; mp 171–173 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 2.44 (s, 3H), 2.81 (s, 3H), 7.34 (d, $J = 8.5$ Hz, 2H), 7.52-7.56 (m, 4H), 7.64 (t, $J = 7.0$ Hz, 1H), 8.48 (d, $J = 7.5$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 21.2, 34.9, 37.5, 123.2 (2C), 128.4 (2C), 130.3 (2C), 130.7 (2C), 133.2, 133.5, 136.1, 136.4, 140.6, 144.4, 160.2, 185.3; HRMS (ESI-TOF) Calcd for C$_{19}$H$_{19}$N$_4$O$_2$ ($[M + H]^+$): 335.1503. Found 335.1500.

**Ethyl 4-(4-methoxybenzoyl)-1-p-tolyl-1H-1,2,3-triazole-5-carboxylate (3s):**

Yellow solid; mp 160–162 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 1.20 (t, $J = 7.5$ Hz, 3H), 2.46 (s, 3H), 3.90 (s, 3H), 4.32 (q, $J = 7.0$ Hz, 2H), 7.01 (dd, $J = 7, 2.0$ Hz, 2H), 7.35 (d, $J = 8.5$ Hz, 2H), 7.47 (d, $J = 8.5$ Hz, 2H), 8.35 (dd, $J = 7, 2.0$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 13.6, 21.3, 55.5, 63.0, 113.8 (2C), 124.4 (2C), 129.1, 130.0 (2C), 132.3, 133.0 (2C), 133.2, 140.7, 146.9, 159.2, 164.1, 183.8; HRMS (ESI-TOF) Calcd for C$_{20}$H$_{20}$N$_3$O$_4^+$ ($[M + H]^+$): 366.1448. Found 366.1454.

**N,N-Dimethyl-4-(4-methylbenzoyl)-1-p-tolyl-1H-1,2,3-triazole-5-carboxamide (3t):**

Yellow solid; mp 195–197 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 2.42-2.44 (d, 6H), 2.80 (s, 3H), 3.11 (s, 3H), 7.31-7.34 (m, 4H), 7.54 (d, $J = 8.5$ Hz, 2H), 8.41 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 21.2, 21.7, 34.9, 37.5, 123.2 (2C), 129.1 (2C), 130.3 (2C), 130.8 (2C), 133.1, 133.5, 136.3, 140.5, 144.5, 160.3, 184.7; HRMS (ESI-TOF) Calcd for C$_{20}$H$_{21}$N$_4$O$_2^+$ ([M + H]$^+$): 349.1659. Found 349.1661.
4-(4-Chlorobenzoyl)-N,N-dimethyl-1-p-tolyl-1H-1,2,3-triazole-5-carboxamide (3u):

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{O} \\
\text{N}
\end{array}
\]

Yellow solid; mp 172–174 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 2.45 (s, 3H), 2.80 (s, 3H), 3.13 (s, 3H), 7.34 (d, \(J = 8\) Hz, 2H), 7.51-7.55 (m, 4H), 8.48 (d, \(J = 8.5\) Hz, 2H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 21.2, 34.9, 37.5, 123.2 (2C), 128.8 (2C), 130.4 (2C), 132.1 (2C), 133.0, 134.3, 136.5, 140.1, 140.7, 144.1, 160.1, 183.8; HRMS (ESI-TOF) Calcd for C\(_{19}\)H\(_{18}\)ClN\(_4\)O\(_2\)\(^+\) ([M + H]\(^+\]): 369.1113. Found 369.1120.

\(N,N\)-Dimethyl-4-(thiophene-2-carbonyl)-1-p-tolyl-1H-1,2,3-triazole-5-carboxamide (3v):

\[
\begin{array}{c}
\text{S} \\
\text{O} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{O} \\
\text{N}
\end{array}
\]

Yellow solid; mp 192–194 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 2.44 (s, 3H), 2.82 (s, 3H), 3.13 (s, 3H), 7.25 (dd, \(J = 5.0, 4.0\) Hz, 1H), 7.33 (d, \(J = 8.5\) Hz, 2H), 7.54 (d, \(J = 8.5\) Hz, 2H), 7.78 (dd, \(J = 5.0, 1.0\) Hz, 1H), 8.78 (dd, \(J = 3.5, 1.0\) Hz, 1H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 21.2, 34.9, 37.5, 123.2 (2C), 128.5, 130.3 (2C), 133.1, 135.4, 135.7, 136.5, 140.6, 142.1, 143.6, 159.9, 176.9; HRMS (ESI-TOF) Calcd for C\(_{17}\)H\(_{17}\)N\(_4\)O\(_2\)S\(^+\) ([M + H]\(^+\]): 341.1067. Found 341.1066.
III. Crystal ORTEP Drawing of Compound 3a:

![ORTEP drawing of 3a](image-url)
IV. Copies of $^1$H NMR and $^{13}$C NMR spectra of compounds 3:

Figure 1. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3a.
Figure 2. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3b.
Figure 3. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3c.
Figure 4. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3d.
Figure 5. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3e.
Figure 6. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3f.
Figure 7. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3g.
Figure 8. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3h.
Figure 9. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3i.
Figure 10. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3j.
Figure 11. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3k.
Figure 12. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3l.
Figure 13. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3m.
Figure 14. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3n.
Figure 15. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3o.
Figure 16. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3p.
Figure 17. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3q.
Figure 18. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3r.
Figure 19. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3s.
Figure 20. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3t.
Figure 21. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3u.
Figure 22. $^1$H- (upper) and $^{13}$C-NMR (lower) spectra of compound 3v.