Supporting materials

An efficient and recyclable heterogeneous catalytic system for the synthesis of 1,2,4-triazoles using air as the oxidant

Xu Meng, Chaoying Yu and Peiqing Zhao*

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R China. Fax:+96 931 8277008; Tel: +86 931 4968688; E-mail: zhaopq@licp.cas.cn

Table of Contents

General information and procedure-------------------------------S2-S3
Spectrum data of products-------------------------------------S4-S15
Copy of $^1$H NMR and $^{13}$C NMR spectra for products----------S16-S50
General information: All reagents were purchased from commercial suppliers and used without further purification. Metal salts and catalyst supports were commercially available and were used directly. All experiments were carried out under air. Flash chromatography was carried out with Merck silica gel 60 (230-400 mesh). Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection. $^1$H NMR and $^{13}$C NMR (400 and 100 MHz respectively) spectra were recorded in CDCl$_3$ or d-DMSO. Chemical shifts ($\delta$) are reported in ppm using TMS as internal standard, and spin-spin coupling constants ($J$) are given in Hz.

Preparation of CuO$_x$-ZnO/Al$_2$O$_3$-TiO$_2$

Support Al$_2$O$_3$-TiO$_2$ powder (8g) was added to a 250 mL round-bottom flask. A solution of Cu(NO$_3$)$_2$-3H$_2$O (1.205g) and Zn(NO$_3$)$_2$-6H$_2$O (1.462g) in deionized water (100 mL) was added to Al$_2$O$_3$-TiO$_2$ powder, and additional deionized water (50 mL) was added to wash down the sides of the flask. Then the flask was submerged into an ultrasound bath for 3h at room temperature. After that, the water was distilled under reduced pressure on a rotary evaporator at 90 °C for more than 2h. Subsequently, the white powder was dried into an oven under the condition of increasing the temperature from 25 °C to 110 °C within 1h and keeping the temperature for another 5h. Finally, the dried white...
powder was calcined under the condition of increasing the temperature from 25 °C to 350 °C within 1h and keeping the temperature for 2 more hours.

**Characterization of Cu-Zn/Al-Ti**

The Inductive Coupled Plasma Optical Emission Spectrum (ICP-OES) showed that the contents of catalyst and support are as below:

Catalyst: Cu% = 3.25%, Zn%=3.40%, BET surface area: 97 m²/g, pore volume (BJH Adsorption): 0.312 cm³/g, pore size (BJH Adsorption): 112.373 Å.

Support: Ti%=24%, Al%=76%

**General procedure for Cu-Zn/Al-Ti-catalyzed cyclization**

Cu-Zn/Al-Ti (24 mg, 1.6 mol%), 2-aminopyridine (0.72 mmol), benzonitrile (0.6 mmol) and DCB (0.6 mL) were added to a flask with a bar. The flask was stirred at 140 °C for indicated time under air. After cooling to room temperature, the mixture was diluted with ethyl acetate and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography (petroleum/ethyl acetate = 3/2 as eluent) to yield corresponding product. The identity and purity of the products was confirmed by ¹H and ¹³C NMR spectroscopic analysis.
Spectrum data of the products

2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (3a)\(^1\)

\[
\text{White solid, isolated yield 83\%.} \quad ^1\text{H NMR (400MHz, CDCl}_3\text{): } \delta = 8.56 (d, 1H, J = 6.8 Hz), 8.29-8.26 (m, 2H), 7.73 (d, 1H, J = 8.8 Hz), 7.51-7.44(m, 4H), 6.98-6.94(m, 1H); \quad ^{13}\text{C NMR (100MHz, CDCl}_3\text{): } \delta = 164.1, 151.6, 130.7, 130.2, 129.4, 128.6, 128.2, 127.2, 116.3, 113.5.
\]

2-(4-chlorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (3b)\(^1\)

\[
\text{White solid, isolated yield 93\%.} \quad ^1\text{H NMR (400MHz, CDCl}_3\text{): } \delta = 8.58-8.56 (m, 1H), 8.22-8.19 (m, 2H), 7.74-7.72 (m, 1H), 7.51(t, 1H, J = 1.6 Hz), 7.47-7.44 (m, 2H), 7.01(t, 1H, J = 1.2 Hz); \quad ^{13}\text{C NMR (100MHz, CDCl}_3\text{): } \delta = 163.2, 151.7, 136.1, 129.7, 129.3, 128.9, 128.6, 128.3, 116.4, 113.8.
\]

2-(3-chlorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (3c)\(^1\)

\[
\text{White solid, isolated yield 86\%.} \quad ^1\text{H NMR (400MHz, CDCl}_3\text{): } \delta = 8.57 (d, 1H, J = 6.8 Hz), 8.28 (s, 1H), 8.16-8.14 (m, 1H), 7.73 (d, 1H, J = 8.8 Hz), 7.52-7.43 (m, 1H), 7.40(t, 2H, J = 4.8 Hz), 7.01(t, 1H, J = 6.8 Hz); \quad ^{13}\text{C}
\]
NMR (100MHz, CDCl$_3$): $\delta = 162.9$, 161.7, 134.8, 132.6, 130.1, 130.0, 129.8, 128.4, 127.4, 125.4, 116.5, 113.9.

2-(2-chlorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (3d)$^{[1]}$

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

White solid, isolated yield 44%. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 8.62$ (d, 1H, J = 6.8 Hz), 7.99-7.96 (m, 1H), 7.77 (d, 1H, J = 9.2 Hz), 7.52-7.49 (m, 2H), 7.37-7.34 (m, 2H), 7.02-6.99 (m, 1H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 162.7$, 150.8, 133.1, 132.1, 130.6, 130.5, 129.9, 129.5, 128.4, 126.7, 116.6, 113.8.

2-(2-bromophenyl)-[1,2,4]triazolo[1,5-a]pyridine (3e)$^{[1]}$

\[
\begin{array}{c}
\text{N} \\
\text{N}
\end{array}
\begin{array}{c}
\text{Br}
\end{array}
\]

White solid, isolated yield 35%. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 8.65$-8.62 (m, 1H), 7.89-7.87 (m, 1H), 7.79 (d, 1H, J = 8.8 Hz), 7.54-7.50 (m, 1H), 7.43-7.39 (m, 1H), 7.31-7.25 (m, 1H), 7.05-7.01 (m, 1H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 163.7$, 150.8, 140.5, 133.9, 132.2, 130.7, 129.6, 128.4, 127.3, 122.1, 116.7, 113.8.

2-(4-(trifluoromethyl)phenyl)-[1,2,4]triazolo[1,5-a]pyridine (3f)$^{[1]}$

\[
\begin{array}{c}
\text{N} \\
\text{N}
\end{array}
\begin{array}{c}
\text{CF}_3
\end{array}
\]

White solid, isolated yield 92%. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 8.60$ (d, 1H, J = 6.8 Hz), 8.39 (d, 2H, J = 8.4 Hz), 7.78-7.73 (m, 3H), 7.56-7.51 (m, 1H), 7.07-7.03 (m, 1H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 162.8$, 151.8,
134.2, 131.9, 131.6, 129.9, 128.5, 127.6, 125.7, 125.6, 122.7, 116.7, 114.1.

2-(3-(trifluoromethyl)phenyl)-[1,2,4]triazolo[1,5-a]pyridine (3g)[1]

![Molecule](image)

White solid, isolated yield 82%. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 8.59$ (d, 1H, $J = 6.0$ Hz), 8.56 (s, 1H), 8.45 (d, 1H, $J = 8.0$ Hz), 7.76 (d, 1H, $J = 8.8$ Hz), 7.71 (d, 1H, $J = 6.8$ Hz), 7.60 (t, 1H, $J = 6.0$ Hz), 7.53 (t, 1H, $J = 4.8$ Hz), 7.02 (t, 1H, $J = 6.8$ Hz); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 162.8$, 151.7, 131.6, 130.4, 129.9, 129.2, 128.4, 126.6, 126.5, 124.2, 124.1, 116.5, 114.0.

2-(4-fluorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (3h)[1]

![Molecule](image)

White solid, isolated yield 84%. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 8.56$ (d, 1H, $J = 7.2$ Hz), 8.27-8.23 (m, 2H), 7.51-7.47 (m, 1H), 7.18-7.14 (m, 1H), 7.73-7.71 (m, 2H), 7.01-6.97 (m, 1H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 165.3$, 163.3, 162.8, 151.7, 129.6, 129.3, 129.2, 128.3, 127.0, 126.9, 116.3, 115.8, 115.6, 113.6.

2-(4-methoxyphenyl)-[1,2,4]triazolo[1,5-a]pyridine (3i)[1]

![Molecule](image)

White solid, isolated yield 66%. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 8.53$ (q,
1H, J = 7.6 Hz), 8.20 (q, 2H, J = 8.8 Hz), 7.68 (q, 1H, J = 8.8 Hz), 7.46-7.42 (m, 1H), 6.99 (q, 2H, J = 9.2 Hz), 6.95-6.91 (m, 1H); $^{13}$C NMR (100MHz, CDCl$_3$): δ = 164.1, 161.2, 151.7, 129.4, 128.8, 128.2, 123.4, 116.1, 114.1, 113.3, 55.3.

2-(3-methoxyphenyl)-[1,2,4]triazolo[1,5-a]pyridine (3j)$^{[1]}$

![Chemical structure](image)

White solid, isolated yield 52%. $^1$H NMR (400MHz, CDCl$_3$): δ = 8.83-8.51 (m, 1H), 7.86-7.84 (m, 1H) 7.79-7.78 (m, 1H), 7.68 (q, 1H, J = 8.8), 7.43-7.33 (m, 2H), 6.98-6.95 (m, 1H), 6.92-6.88 (m, 1H), 3.86 (s, 3H); $^{13}$C NMR (100MHz, CDCl$_3$): δ = 161.8, 159.8, 151.4, 131.9, 129.6, 129.4, 128.1, 119.6, 116.6, 116.2, 113.5, 111.6, 113.5, 111.6, 55.2.

2-(3,5-dimethoxyphenyl)-[1,2,4]triazolo[1,5-a]pyridine (3k)$^{[2]}$

![Chemical structure](image)

White solid, isolated yield 49%. $^1$H NMR (400MHz, CDCl$_3$): δ = 8.57 (d, 1H, J = 6.8 Hz), 7.74 (d, 1H, J = 8.8 Hz), 7.50-7.47 (m, 3H), 7.00-7.96 (m, 1H), 7.43-7.33 (m, 2H), 6.56(t, 1H, J = 2.4 Hz), 3.88 (s, 6H); $^{13}$C NMR (100MHz, CDCl$_3$): δ = 164.1, 161.1, 151.6, 132.6, 129.6, 128.3, 116.4, 113.7, 104.9, 103.4, 55.6.

2-(benzo[d][1,3]dioxol-5-yl)-[1,2,4]triazolo[1,5-a]pyridine (3l)$^{[2]}$
White solid, isolated yield 68%. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 8.53$ (d, 1H, J = 6.8 Hz), 7.82 (q, 1H, J = 9.6 Hz), 7.72-7.67 (m, 2H), 7.47-7.43 (m, 1H), 6.95 (t, 1H, J = 6.4 Hz), 6.90 (d, 1H, J = 8.0 Hz), 6.01 (s, 2H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 163.9, 151.6, 149.2, 147.9, 129.4, 128.2, 124.8, 121.7, 116.1, 113.4, 108.5, 107.5, 101.3.$

2-m-tolyl-[1,2,4]triazolo[1,5-a]pyridine (3m)$^{[1]}$

White solid, isolated yield 70%. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 8.57$ (d, 1H, J = 6.8 Hz), 8.12-8.08 (m, 2H), 7.73 (d, 1H, J = 8.8 Hz), 7.48-7.44 (m, 1H), 7.40-7.36 (m, 1H), 7.37 (d, 1H, J= 9.2 Hz), 6.97-6.93 (m, 1H), 2.44 (s, 3H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 164.2, 151.5, 138.3, 130.8, 130.5, 129.8, 128.5, 128.2, 127.8, 124.3, 116.2, 113.5, 21.3.$

2-o-tolyl-[1,2,4]triazolo[1,5-a]pyridine (3n)$^{[1]}$

White solid, isolated yield 57%. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 8.62$ (d, 1H, J = 6.8 Hz), 8.05 (d, 1H, J = 9.6 Hz), 7.79-7.76 (m, 1H), 7.53-7.49 (m, 1H), 7.35-7.31 (m, 3H), 7.26-7.99 (m, 1H), 2.72 (s, 3H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 165.2, 150.9, 137.7, 131.3, 130.3, 130.1, 129.4, 129.3, 128.3, 125.8, 116.4, 113.4, 21.7.$

2-(4-(1H-imidazol-1-yl)phenyl)-[1,2,4]triazolo[1,5-a]pyridine (3o)
Yellow solid, isolated yield 65%. \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 8.61\) (d, J = 6.8 Hz, 1H), 8.40 (d, J = 8.4 Hz, 2H), 8.02 (s, 1H), 7.79 (m, 2H), 7.52 (m, 4H), 7.05 (m, 1H); \(^{13}\)C NMR (100MHz, CDCl\(_3\)): \(\delta = 163.0, 151.8, 134.1, 130.0, 129.8, 128.9, 128.4, 121.4, 116.5, 113.9\).

**2-(pyridin-4-yl)-[1,2,4]triazolo[1,5-a]pyridine (3p)** \(^1\)

White solid, isolated yield 80%. \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 8.73\) (s, 2H), 8.61-8.58 (m, 1H), 8.12-8.10 (m, 2H), 7.78-7.75 (m, 1H), 7.56-7.51 (m, 1H), 7.07-7.03 (m, 1H); \(^{13}\)C NMR (100MHz, CDCl\(_3\)): \(\delta = 161.9, 151.7, 150.4, 138.2, 129.9, 128.5, 121.3, 116.8, 114.3\).

**2-(pyridin-3-yl)-[1,2,4]triazolo[1,5-a]pyridine (3q)** \(^1\)

White solid, isolated yield 85%. \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 9.49\) (s, 1H), 8.69-8.67 (m, 1H), 8.59 (d, 1H, J= 6.8 Hz), 8.52-8.49 (m, 1H), 7.75 (d, 1H, J = 8.8 Hz), 7.54-7.50 (m, 1H), 7.42-7.38 (m, 1H), 7.02 (t, 1H, J = 6.0 Hz); \(^{13}\)C NMR (100MHz, CDCl\(_3\)): \(\delta = 161.9, 151.7, 150.9, 148.8, 134.5, 129.9, 128.4, 126.9, 123.6, 116.6, 114.0\).

**2-(5-chloropyridin-3-yl)-[1,2,4]triazolo[1,5-a]pyridine (3r)** \(^3\)
White solid, isolated yield 80%. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 9.22$ (s, 1H), 8.56 (d, 1H, J = 6.8 Hz), 8.45-8.43 (m, 1H), 7.72 (d, 1H, J = 8.8 Hz), 7.54-7.50 (m, 1H), 7.40 (d, 1H, J = 8.4 Hz), 7.05-7.01 (m, 1H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 160.8, 152.6, 151.6, 148.5, 137.1, 130.0, 128.4, 125.8, 124.2, 116.5, 114.2$.

2-(thiophen-3-yl)-[1,2,4]triazolo[1,5-a]pyridine (3s)$^{[1]}$

White solid, isolated yield 71%. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 8.55$ (d, 1H, J = 6.8 Hz), 8.13-8.12 (m, 1H), 7.79-7.78 (m, 1H), 7.70 (d, 1H, J = 5.2 Hz), 7.49-7.45 (m, 1H), 7.41-7.39 (m, 1H), 6.98-6.95 (m, 1H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 160.8, 151.4, 132.8, 129.6, 128.2, 126.6, 126.3, 125.6, 116.2, 113.5$.

2-(furan-3-yl)-[1,2,4]triazolo[1,5-a]pyridine (3t)$^{[3]}$

White solid, isolated yield 80%. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 8.55$ (d, 1H, J = 6.8 Hz), 8.13-8.12 (m, 1H), 7.79-7.78 (m, 1H), 7.70 (d, 1H, J = 5.2 Hz), 7.49-7.45 (m, 1H), 7.41-7.39 (m, 1H), 6.98-6.95 (m, 1H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 159.1, 151.4, 143.8, 142.8, 129.6, 128.1, 118.1, 116.0, 113.5, 109.1$.

(E)-2-styryl-[1,2,4]triazolo[1,5-a]pyridine (3w)
White solid, isolated yield 85%. $^1$H NMR (400MHz, CDCl$_3$): $\delta =$ 8.53-8.51 (m, 1H), 7.84 (d, 1H, J = 8.4 Hz), 7.69 (d, 1H, J = 8.8 Hz), 7.60 (d, 2H, J = 8.0 Hz), 7.49-7.46 (m, 1H), 7.39 (t, 2H, J = 7.2 Hz), 7.33 (d, 1H, J = 7.2 Hz), 7.247-7.206 (m, 1H), 6.99-6.05 (m, 1H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta =$ 163.6, 151.3, 136.4, 136.1, 129.7, 128.8, 128.7, 128.1, 127.2, 117.5, 116.1, 113.4.

2-(pyrimidin-2-yl)-[1,2,4]triazolo[1,5-a]pyridine (3y)

White solid, isolated yield 85%. $^1$H NMR (400MHz, CDCl$_3$): $\delta =$ 8.95 (d, J = 4.8 Hz, 2H), 8.49 (d, J = 8.4 Hz, 1H), 8.37-8.36 (m, 1H), 7.80 (t, J = 1.6 Hz, 1H), 7.50 (t, J = 4.8 Hz, 1H), 7.12-7.08 (m, 1H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta =$ 160.1, 157.7, 157.3, 150.8, 148.2, 138.5, 128.8, 120.3, 114.3.

8-methyl-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (3aa) $^{[1]}$

White solid, isolated yield 88%. $^1$H NMR (400MHz, CDCl$_3$): $\delta =$ 8.44 (d, 1H, J = 6.8 Hz), 8.31-8.28 (t, 2H), 7.51-7.45 (m, 3H), 7.26-7.23 (m, 1H), 6.87 (t, 1H, J = 6.8 Hz), 2.68 (s, 3H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta =$ 163.6, 152.1, 130.9, 129.8, 128.6, 128.1, 127.3, 126.9, 125.8, 113.4, 16.9.
7-methyl-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (3ab) \(^{[1]}\)

![7-methyl-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (3ab)](image)

White solid, isolate yield 86\%. \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 8.42\) (d, 1H, J = 6.8 Hz), 8.26-8.23 (m, 2H), 7.49-7.43 (m, 4H), 6.78 (m, 1H), 2.45 (s, 3H); \(^{13}\)C NMR (100MHz, CDCl\(_3\)): \(\delta = 164.1, 151.8, 140.9, 130.9, 129.9, 128.6, 127.2, 127.1, 116.0, 114.9, 21.5\).

2-phenyl-6-(trifluoromethyl)-[1,2,4]triazolo[1,5-a]pyridine (3ac)\(^{[1]}\)

![2-phenyl-6-(trifluoromethyl)-[1,2,4]triazolo[1,5-a]pyridine (3ac)](image)

White solid, isolated yield 90\%. \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 8.93\) (d, 1H, J = 0.8 Hz), 8.28-8.26 (m, 2H), 7.83 (d, 1H, J = 9.6 Hz), 7.66-7.63 (m, 1H), 7.51-7.48 (m, 3H); \(^{13}\)C NMR (100MHz, CDCl\(_3\)): \(\delta = 166.1, 152.2, 130.7, 129.9, 128.8, 127.5, 127.2, 127.1, 125.8, 125.7, 117.0\).

6-nitro-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (3ad)

![6-nitro-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (3ad)](image)

Yellow solid, isolated yield 85\%. \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 9.63-9.62\) (m, 1H), 8.31-8.28 (m, 3H), 7.82 (t, J = 5.6 Hz, 1H), 7.52 (d, J = 3.2 Hz, 3H); \(^{13}\)C NMR (100MHz, CDCl\(_3\)): \(\delta = 167.9, 152.9, 137.6, 131.2, 129.5, 128.9, 127.8, 127.7, 124.1, 115.6\).

3,5-diphenyl-1H-1,2,4-triazole (4a)\(^{[1]}\)
White solid, isolated yield 81%. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 8.06-8.03 (m, 4H), 7.44-7.43 (m, 6H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ = 159.6, 130.0, 128.9, 126.5.

3-(4-chlorophenyl)-5-phenyl-1H-1,2,4-triazole (4b)$^{[1]}$

White solid, isolated yield 85%. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 8.01-7.98 (m, 3H), 7.94-7.92 (m, 1H), 7.39-7.37 (m, 5H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ = 159.6, 130.0, 129.0, 128.9, 128.8, 128.7, 127.8, 126.5, 126.4.

3-(4-methoxyphenyl)-5-phenyl-1H-1,2,4-triazole (4c)$^{[1]}$

White solid, isolated yield 71%. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 13.93 (s, 1H), 7.91-7.81 (m, 4H), 7.29-7.23 (m, 3H), 6.75-6.72 (m, 2H), 3.74 (s, 3H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ = 160.9, 134.0, 129.6, 128.6, 127.9, 126.4, 120.7, 116.5, 114.1, 55.2.

3-(4-nitrophenyl)-5-phenyl-1H-1,2,4-triazole (4d)$^{[4]}$
Yellow solid, isolated yield 65%. $^1$H NMR (400MHz, DMSO-$d_6$): $\delta =$ 14.86 (s, 1H), 8.33 (d, J = 8.8 Hz, 4H), 8.11 (d, J = 7.2 Hz, 2H), 7.57 (d, J = 6.0 Hz, 3H); $^{13}$C NMR (100MHz, DMSO-$d_6$): $\delta =$ 159.8, 156.7, 152.9, 147.6, 133.4, 130.4, 129.0, 126.8, 126.2, 124.1, 113.4.

4-(5-phenyl-1H-1,2,4-triazol-3-yl)pyridine (4e)$^{[1]}$

White solid, isolated yield 78%. $^1$H NMR (400MHz, DMSO-$d_6$): $\delta =$ 8.76 (d, J = 5.2 Hz, 2H), 8.13 (d, J = 8.8 Hz, 2H), 8.03 (d, J = 5.6 Hz, 2H), 7.61-7.54 (m, 3H); $^{13}$C NMR (100MHz, DMSO-$d_6$): $\delta =$ 162.4, 157.1, 150.2, 137.2, 131.1, 130.1, 128.9, 128.1, 120.0.

5-methyl-3-phenyl-1H-1,2,4-triazole (4f)$^{[1]}$

White solid, isolated yield 79%. $^1$H NMR (400MHz, CDCl$_3$): $\delta =$ 13.23 (s, 1H), 8.00-7.93 (m, 2H), 7.38-7.36 (m, 3H), 2.44 (s, 3H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta =$ 160.4, 155.9, 132.2, 129.9, 128.7, 127.3, 126.4, 12.1.

3-(4-chlorophenyl)-5-methyl-1H-1,2,4-triazole (4g)$^{[1]}$

White solid, isolated yield 80%. $^1$H NMR (400MHz, CDCl$_3$): $\delta =$ 7.94 (d, 2H, J = 8.4 Hz), 7.39 (d, 2H, J = 8.4 Hz), 2.48 (s, 3H); $^{13}$C NMR
(100MHz, CDCl$_3$): $\delta = 161.9, 154.3, 135.4, 128.9, 128.7, 127.6, 12.4$.

3-(4-methoxyphenyl)-5-methyl-1H-1,2,4-triazole (4h)$^{[1]}$

![Chemical Structure](HN N NOMe)

White solid, isolated yield 64%. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 7.91$ (d, 2H, J = 9.2 Hz), 6.88 (d, 2H, J = 8.8 Hz), 3.78 (s, 3H), 2.42 (s, 3H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 160.1, 152.8, 133.9, 127.6, 116.4, 113.8, 55.2, 40.7$.

5-methyl-3-o-tolyl-1H-1,2,4-triazole (4i)$^{[1]}$

![Chemical Structure](HN N N)

White solid, isolated yield 45%. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 7.32$-7.18 (m, 4H), 2.51 (s, 3H), 2.38 (s, 3H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 160.3, 155.7, 136.8, 131.0, 129.4, 128.8, 20.9, 12.5$.

Reference:


Copy of the spectrums