Electronic Supplementary Material (ESI) for Dalton Transactions.

Sustainable catalyst for efficient triazole synthesis: immobilized triazine-based copper-NNN pincer complex on TiO_2

Mitra Esfandiari,[a,b] Gholamhossein Mohammadnezhad,*[a] Oluseun Akintola,[b] Felix Otto,[c] Torsten Fritz,[c] Winfried Plass*[b]

[a] *Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Islamic Republic of Iran*

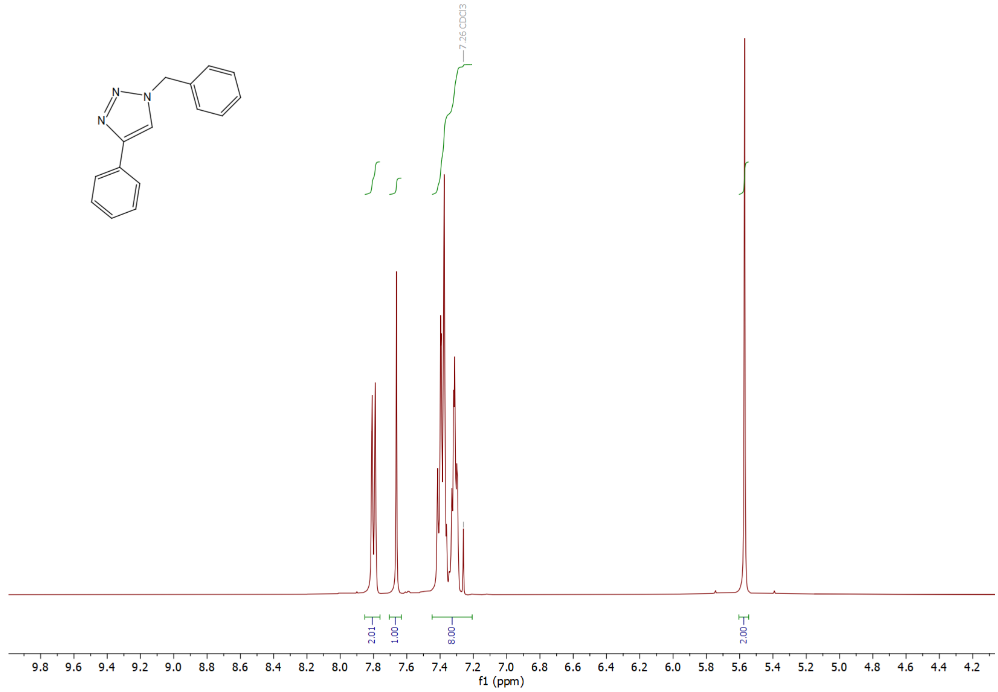
[b] *Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, Humboldtstraße 8, 07743 Jena, Germany*

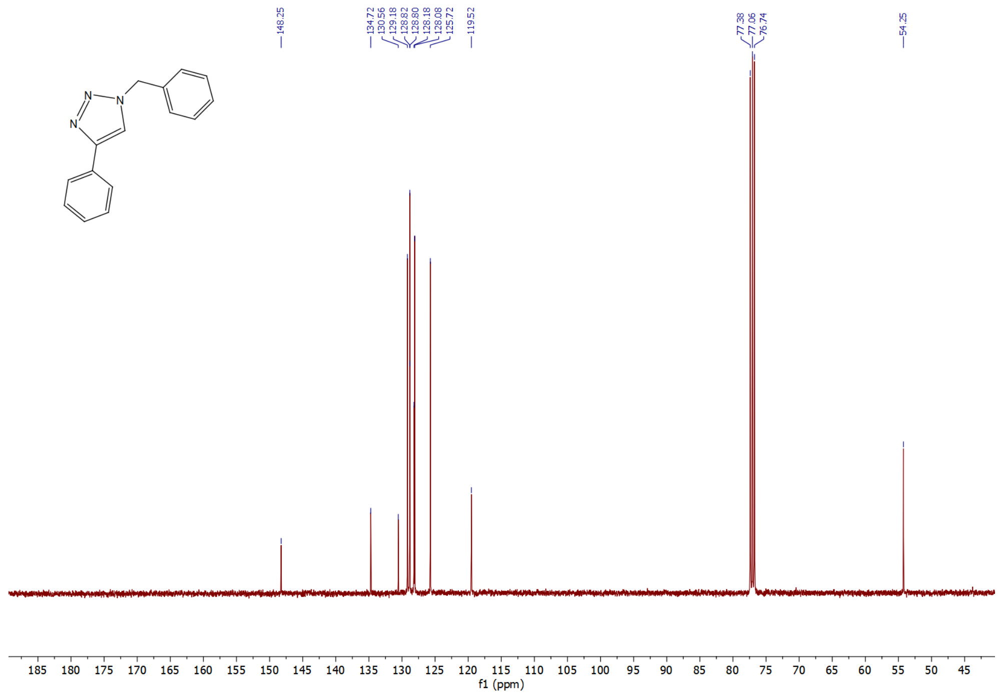
[c] *Institute of Solid State Physics, Friedrich Schiller University Jena, Helmholtzweg 5, 07743 Jena, Germany*

Electronic Supplementary Information (ESI)

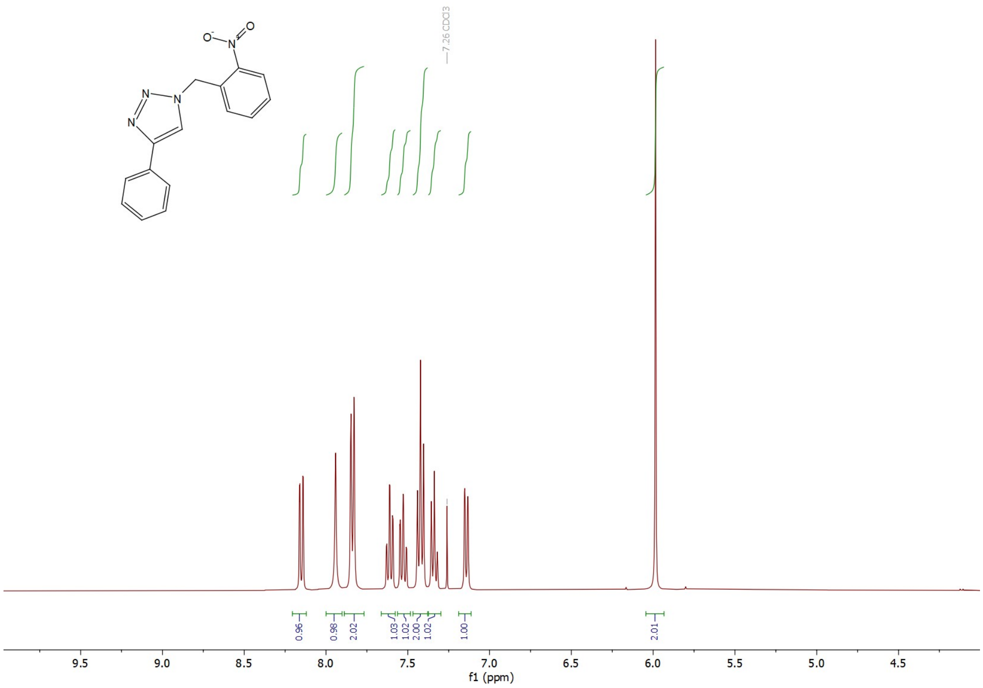
Characterization of triazoles derivates:

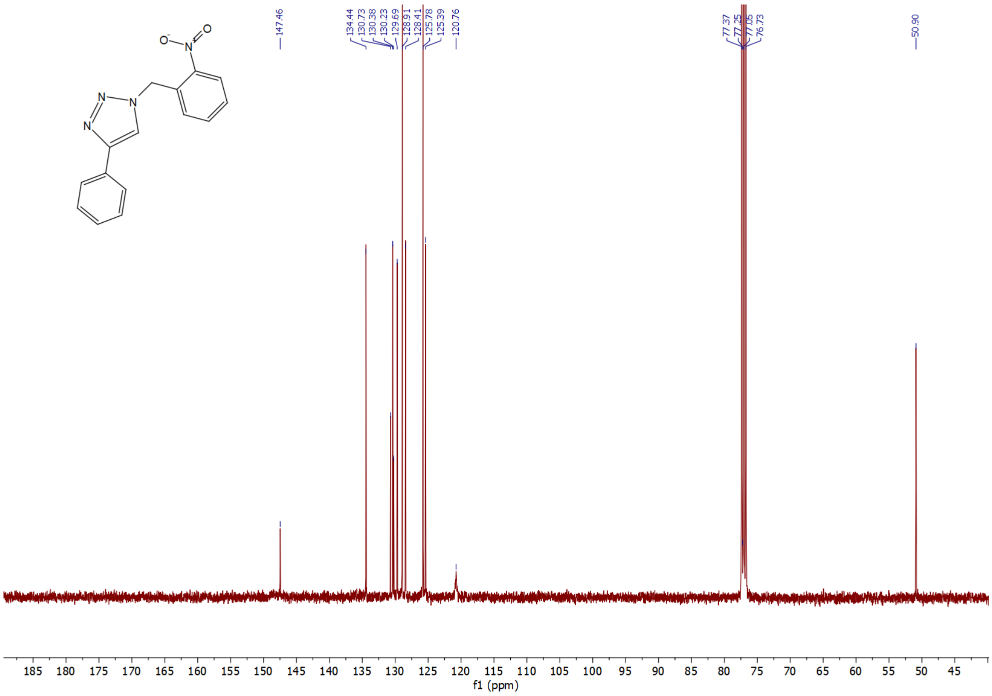
1-benzyl-4-phenyl-1H-1,2,3-triazole (3a): White solid (crystal). Mp: 127-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.57 (s, 2 H), 7.23–7.42 (m, 8 H), 7.66 (s, 1 H), 7.80 (d, J = 7.2, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 54.2, 119.5, 125.7, 128.1, 128.2, 128.8, 129.2, 130.5, 134.6, 148.3 ppm. FT-IR (KBr): $\tilde{\nu}$ = 3141, 1494, 1469, 1449, 1359, 1224, 1075, 1049, 766, 693 cm^{-1}.



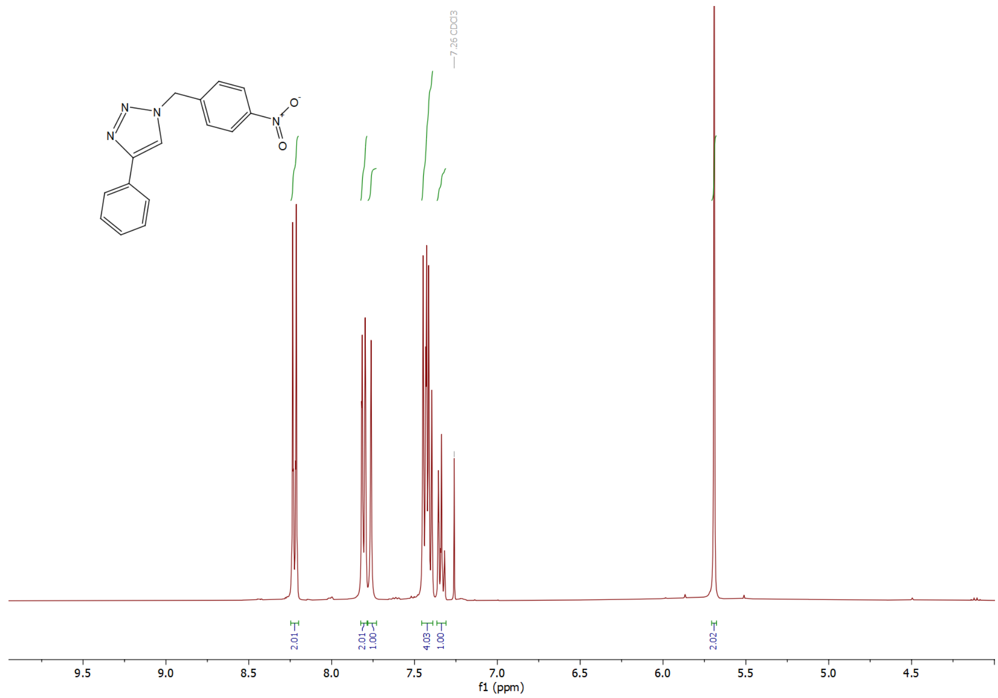


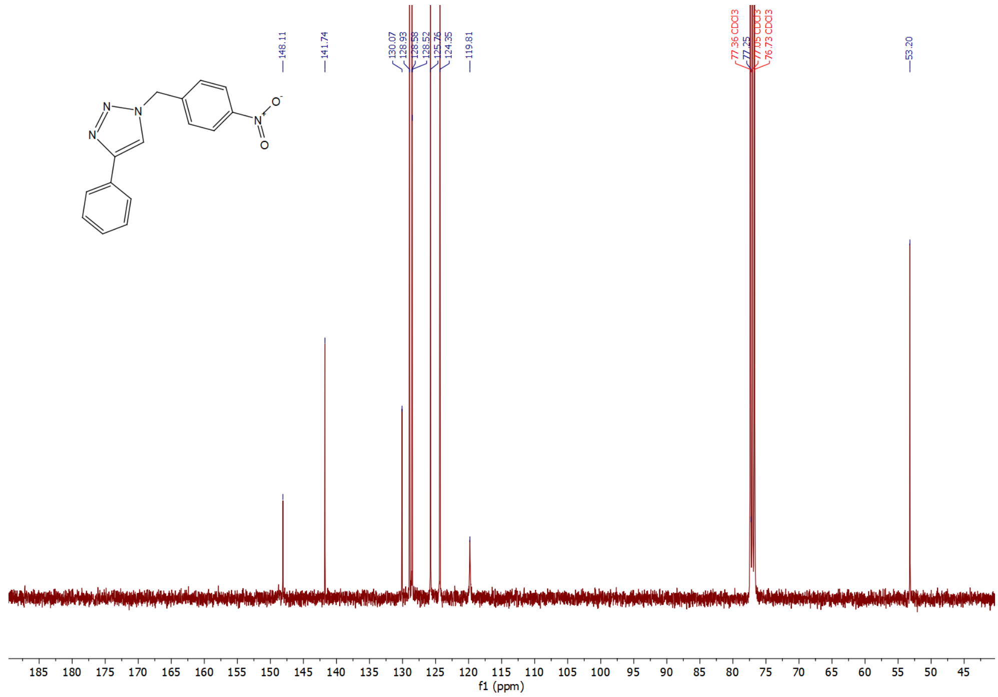
1-(2-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (3b): Yellow solid. Mp: 145–147 °C. ^{1}H NMR (400 MHz,$CDCl_3$): δ = 5.98 (s, 2 H), 7.14 (d, J = 7.5 Hz, 1 H), 7.33 (t, J = 7.5 Hz, 1 H), 7.42 (dd, J_{av} = 7.5 Hz, 2 H), 7.52 (dd, J_{av} = 7.7 Hz, 1 H), 7.61 (dd, J_{av} = 7.6 Hz, 1 H), 7.87 (d, J = 7.1 Hz, 2 H), 7.95 (s, 1 H), 8.15 (d, J = 8.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.9, 120.7, 125.4, 125.8, 128.4, 128.9, 129.7, 130.2, 130.4, 130.7, 134.4, 147.5 ppm. FT-IR (KBr): $\tilde{\nu}$ = 3091, 1604, 1527, 1463, 1340, 1222, 1205, 1074, 1049, 977, 863, 791, 762, 730, 687, 600 cm^{-1}.



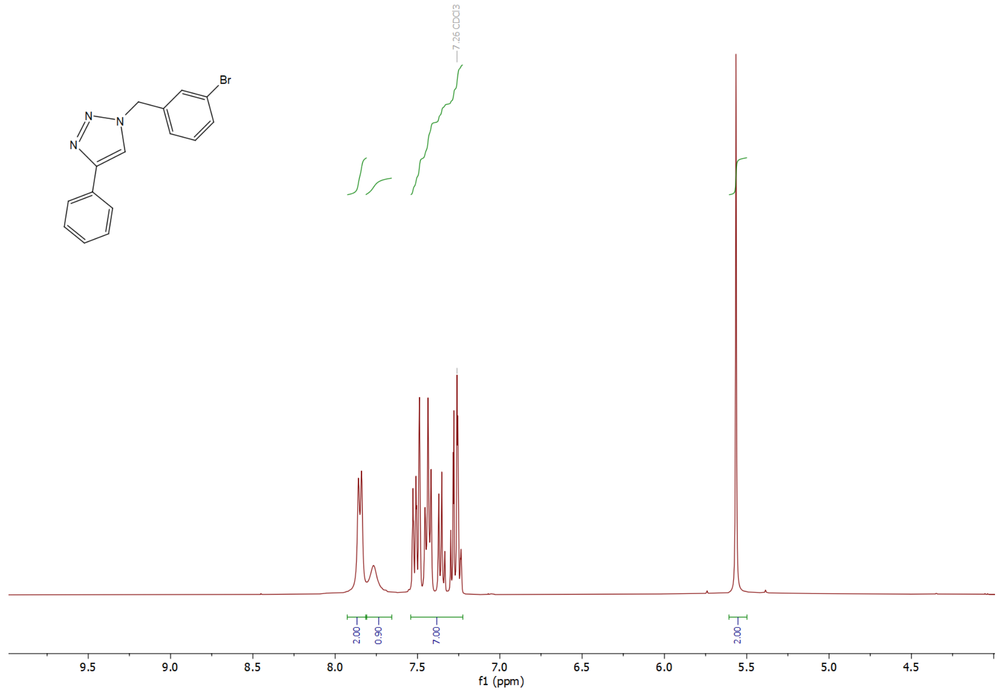


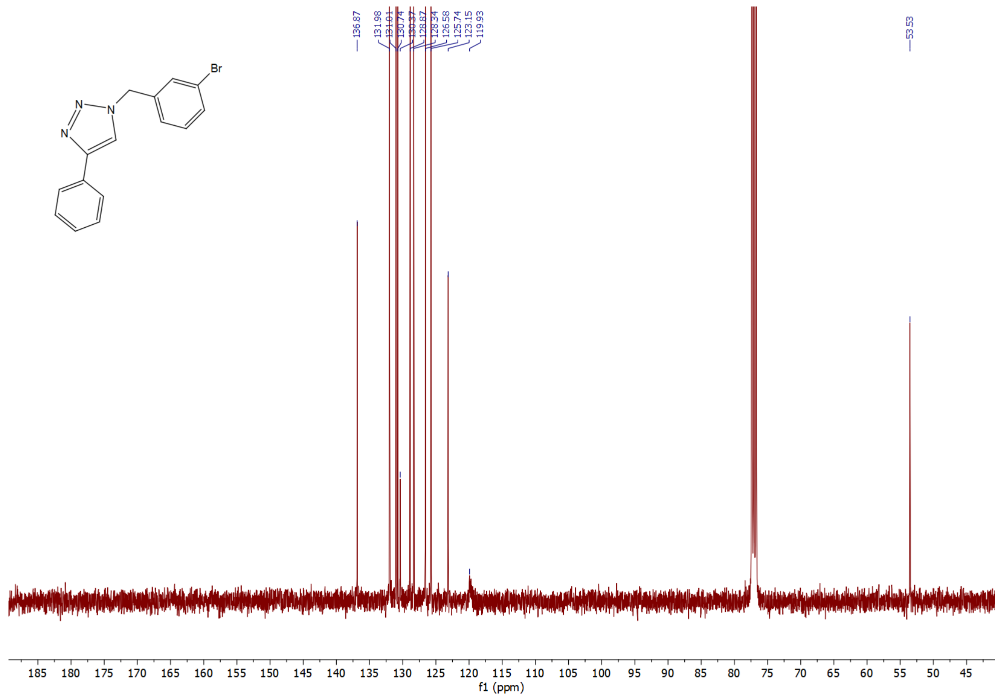
1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (3c): Yellow solid. Mp: 156–158 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.70 (s, 2 H), 7.30–7.46 (m, 1 H), 7.40–7.46 (m, 4 H), 7.76 (s, 1 H), 7.80 (d, J = 7.2 Hz, 2 H), 8.22 (d, J = 8.7 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.2, 119.8, 124.4, 125.8, 128.5, 128.6, 128.9, 130.1, 141.7, 148.1 ppm. FT-IR (KBr): $\tilde{\nu}$ = 3127, 1609, 1516, 1348, 1073, 861, 765, 514 cm^{-1}.



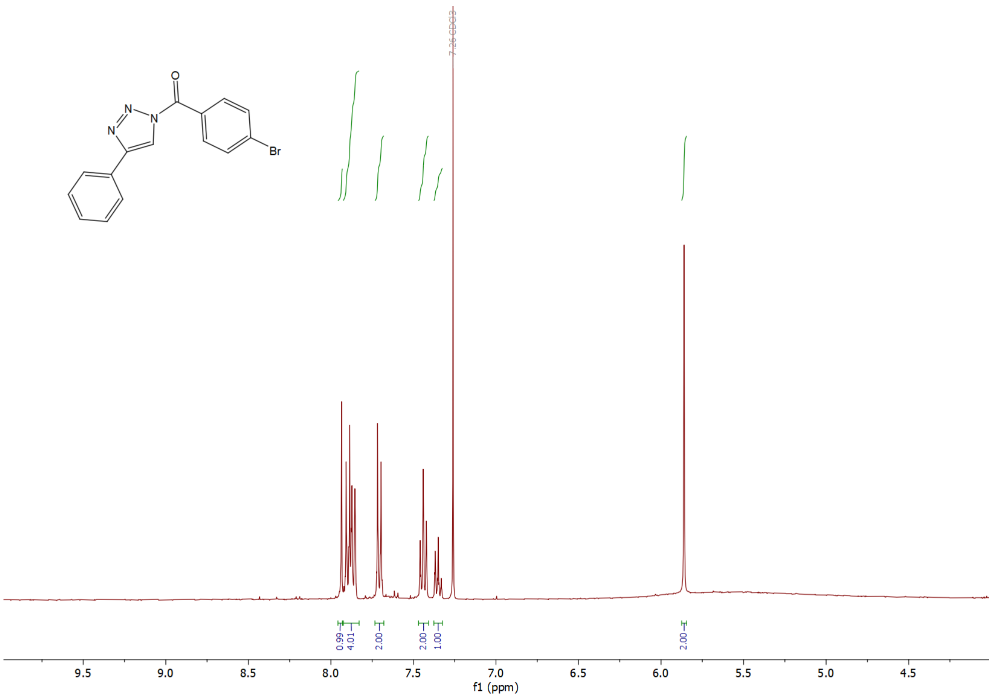


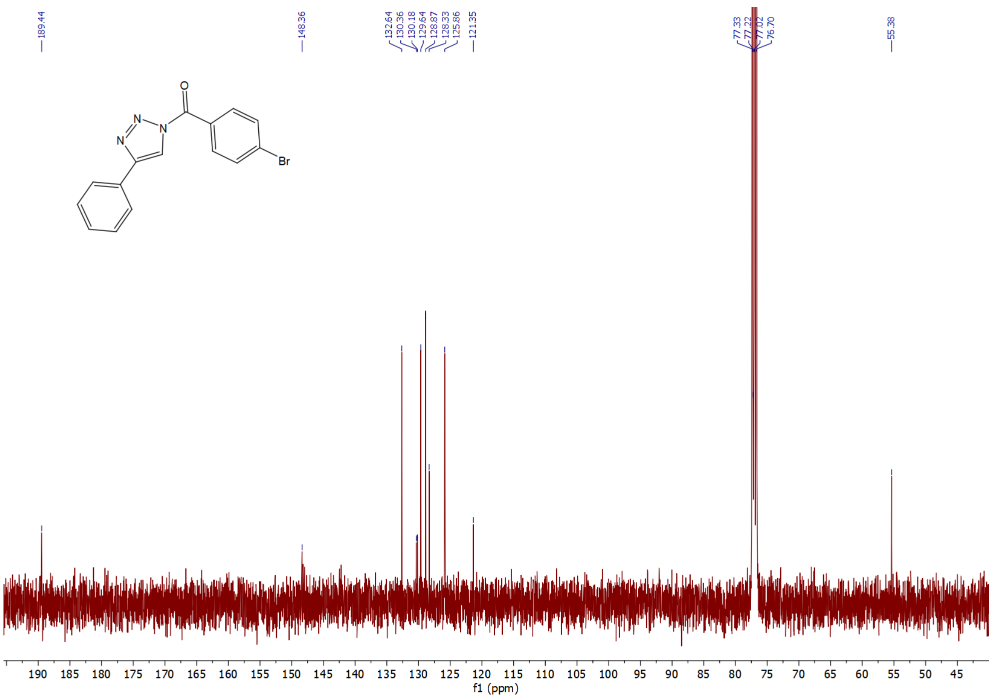
1-(3-bromobenzyl)-4-phenyl-1H-1,2,3-triazole (3d): Pale yellow solid. Mp: 88–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.56 (s, 2 H), 7.21–7.55 (m, 7 H), 7.76 (s, 1 H), 7.82 (d, J = 7.3, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.5, 119.9, 123.1, 125.7, 126.6, 128.3, 128.9, 130.4, 130.7 131.1, 132.0, 136.9 ppm. FT-IR (KBr): $\tilde{\nu}$ = 3084, 1460, 1432, 1222, 1046, 766, 693 cm^{-1}.



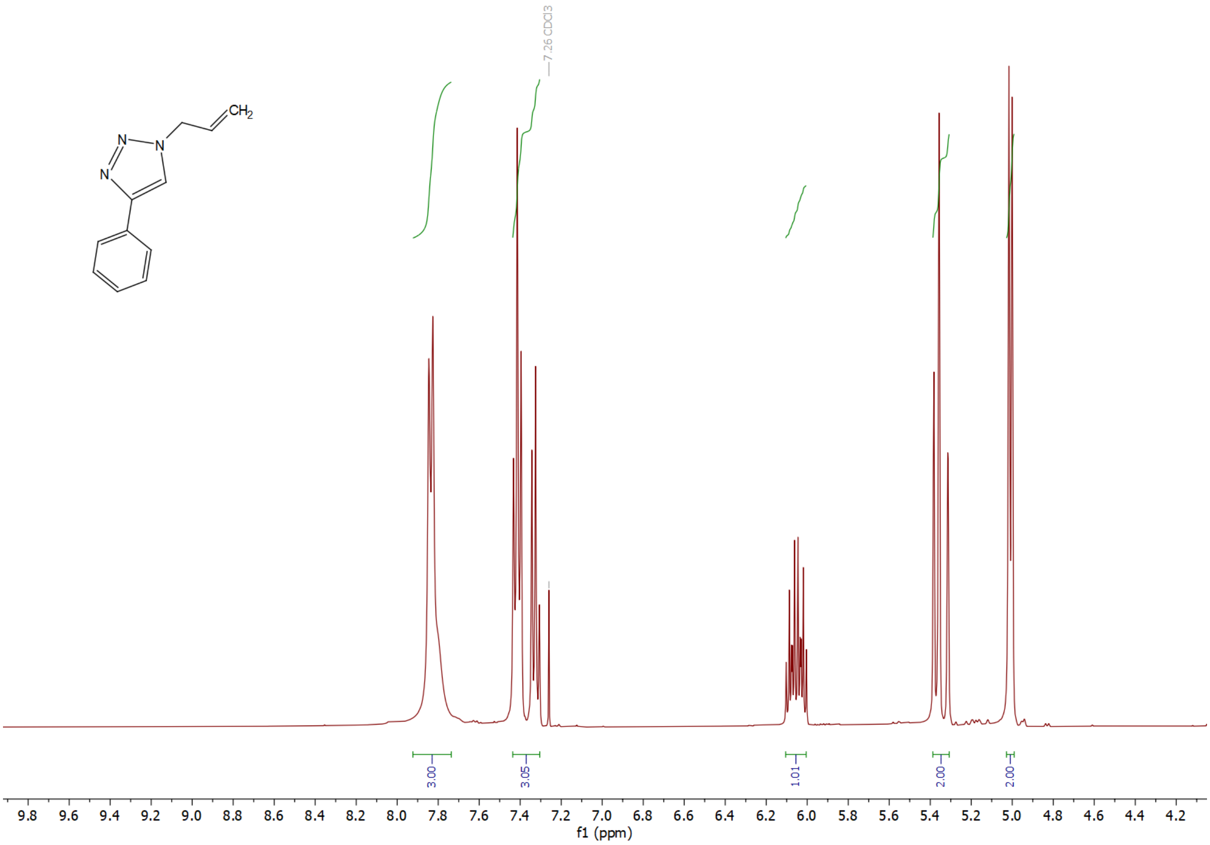


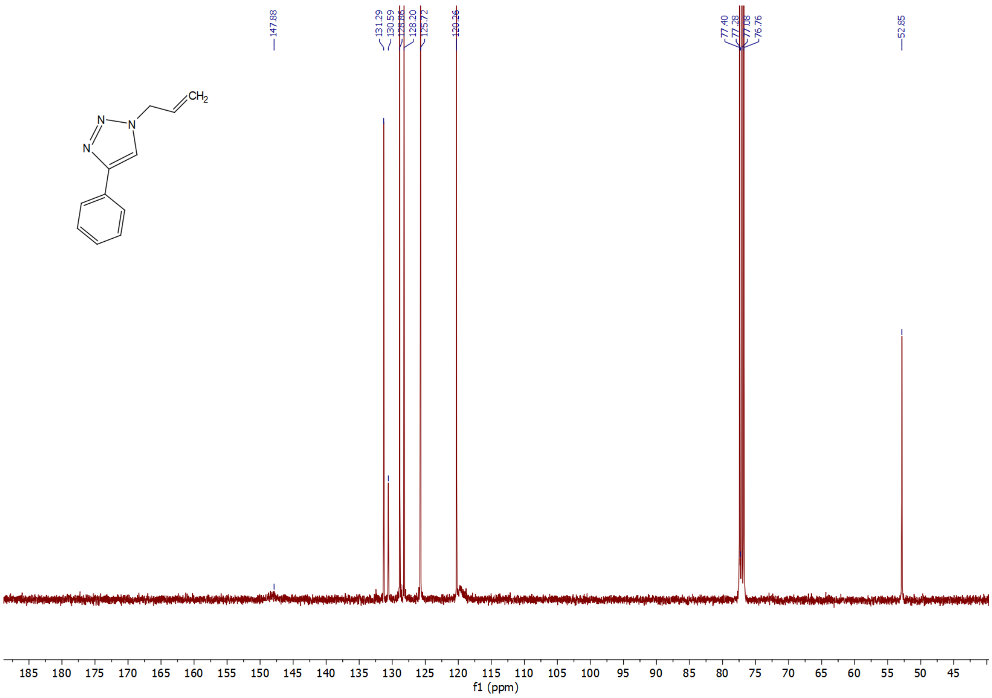
1-(4-Bromophenyl)-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-ethanone (3e): Orange solid. Mp: 178−180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.8x (s, 2 H), 7.34 (t, J = 7.2 Hz, 1 H), 7.44 (dd, J_{av} = 7.6 Hz, 2 H), 7.73 (d, J = 8.0 Hz, 2 H), 7.82–7.92 (m, 4 H), 7.93 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 121.4, 125.9, 128.3, 128.9, 129.6, 130.2, 130.4, 132.6, 148.4, 189.4 ppm. FT-IR (KBr): $\tilde{\nu}$ = 3142, 2936, 1709, 1582, 1229, 847, 762, 562 cm^{-1}.





(Allyl)-2-(4-phenyl-1H-1,2,3-triazole (3f): White solid. Mp: 56–57 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.95–5.06 (m, 2 H), 5.27–5.42 (m, 2 H), 5.98–6.10 (m, 1 H), 7.30–7.47 (m, 3 H), 7.71–7.94 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.8, 120.3, 125.7, 128.2, 128.9, 130.6, 131.3, 147.9 ppm. FT-IR (KBr): $\tilde{\nu}$ = 3130, 2972, 1645, 1449, 1240, 1015, 995, 908 cm^{-1}.





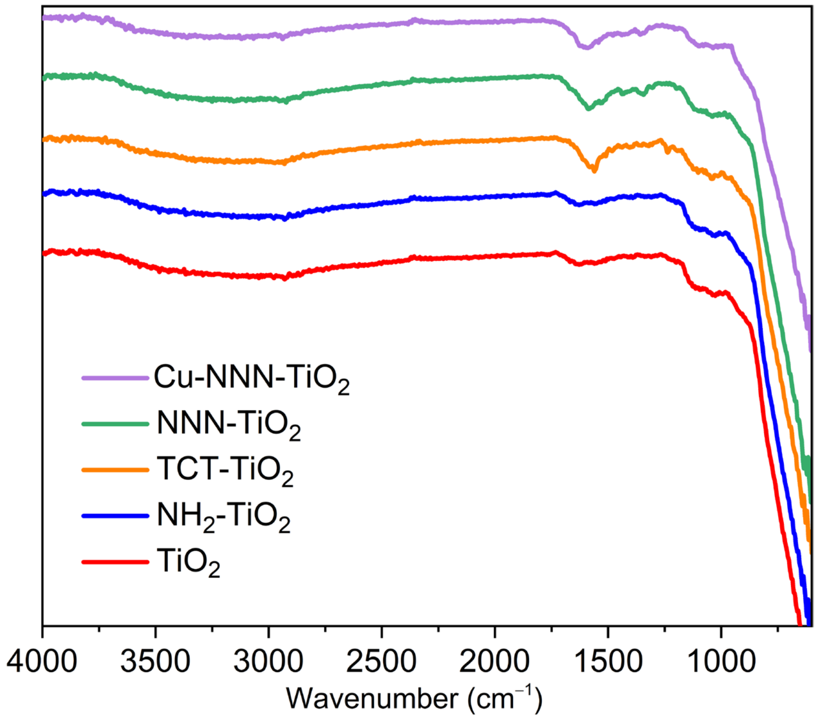


Fig. S1 FTIR spectra of the products of all steps in the immobilization of the NNN-pincer complex on TiO_2.

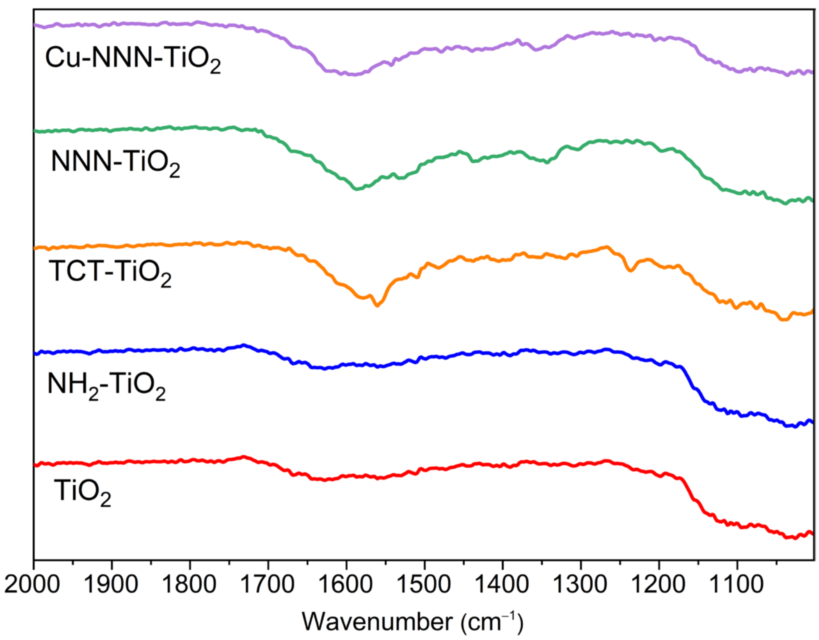


Fig. S2 FTIR spectra of the products of all steps in the immobilization of the NNN-pincer complex on TiO_2 in the range 1000–2000 cm^{-1}.

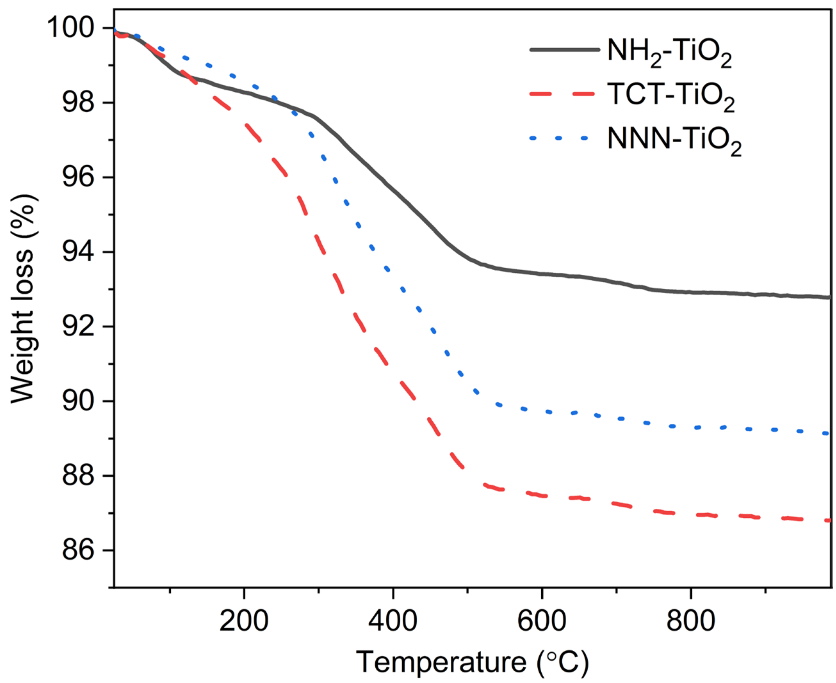


Fig. S3 TGA curves of the products of all steps in the immobilization of the NNN-pincer complex on TiO_2.

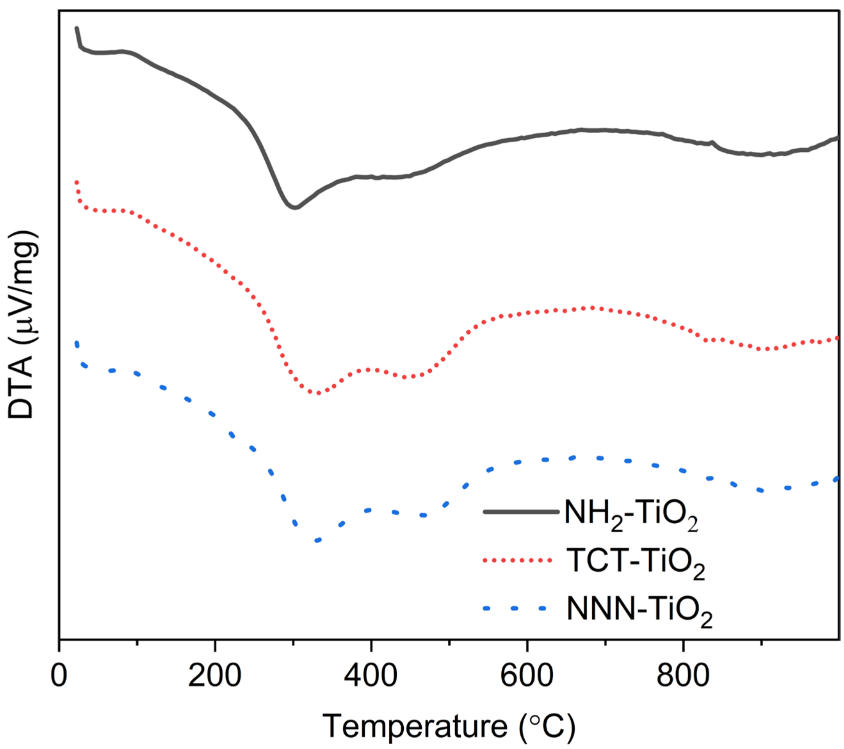


Fig. S4 Differential thermal analysis (DTA) curves of the products of all steps in the immobilization of the NNN-pincer complex on TiO_2.

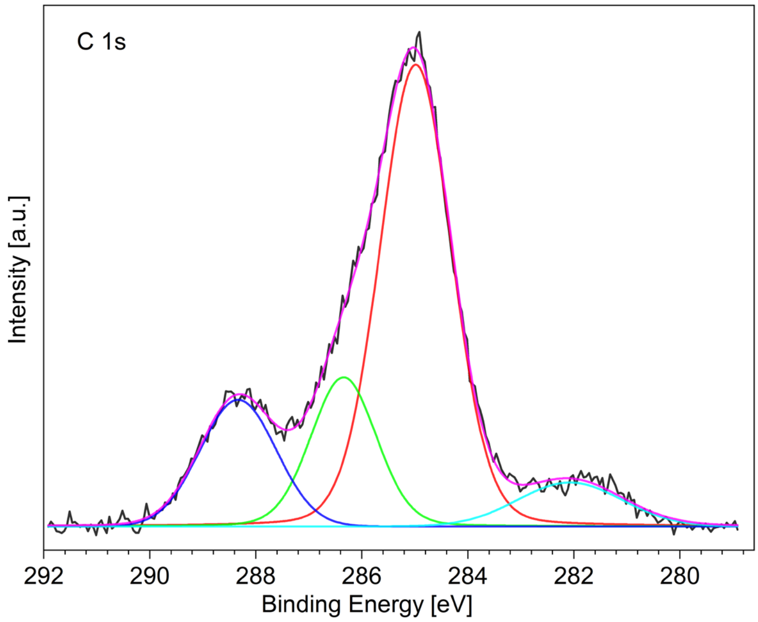


Fig. S5 High-resolution XPS of C 1*s* for Cu-NNN-TiO_2 (Black curve: measured spectrum; colored curves: fitted peaks); the peak at around 282 eV is considered an artifact of the measurement.

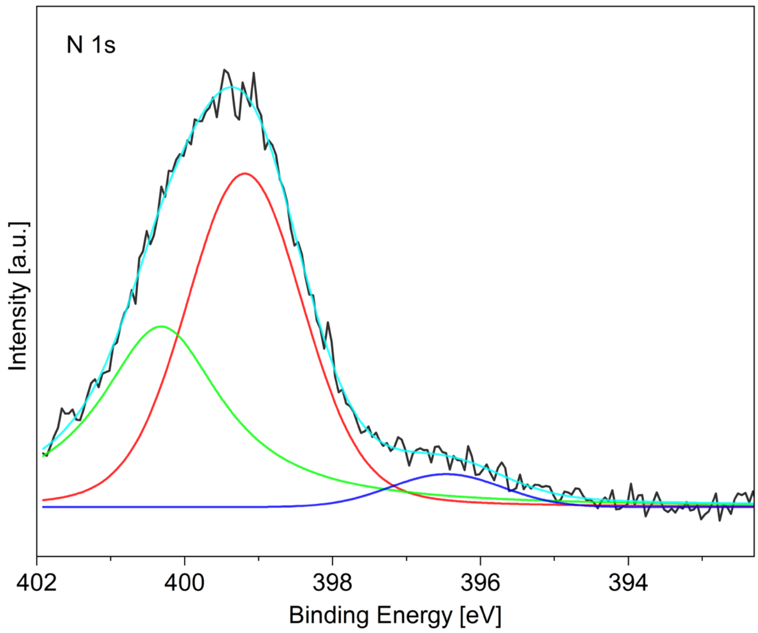


Fig. S6 High-resolution XPS spectra of N 1*s* for Cu-NNN-TiO_2 (Black curve: measured spectrum; colored curves: fitted peaks).

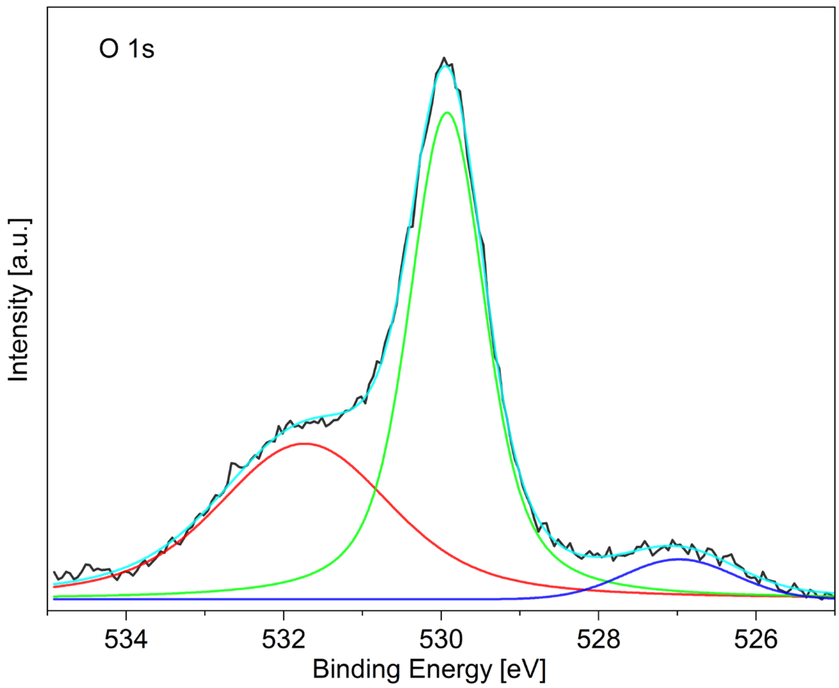


Fig. S7 High-resolution XPS spectra of O 1*s* for Cu-NNN-TiO_2 (Black curve: measured spectrum; colored curves: fitted peaks).

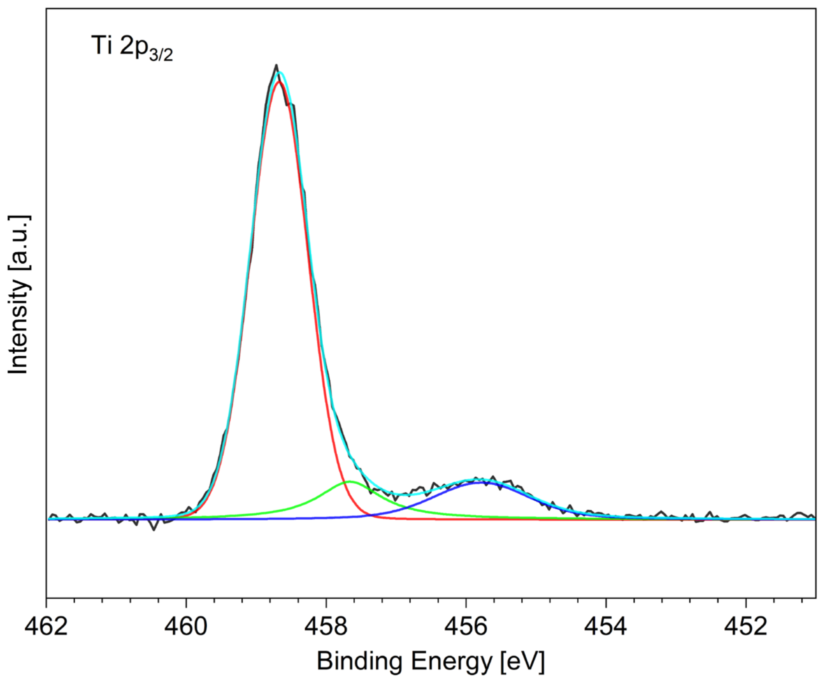


Fig. S8 High-resolution XPS spectra of Ti 2$p_{3/2}$ for Cu-NNN-TiO_2 (Black curve: measured spectrum; colored curves: fitted peaks).

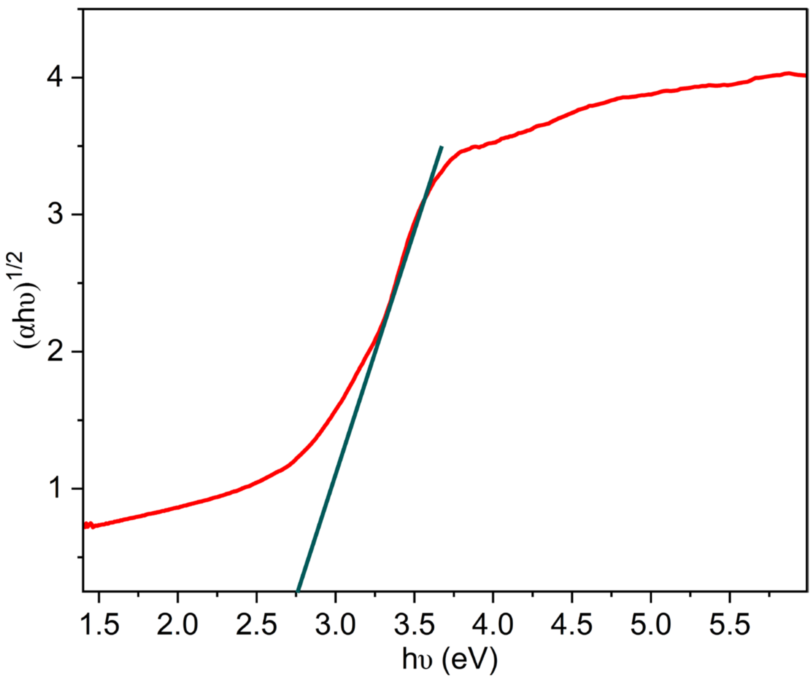


Fig. S9 Tauc plot for Cu-NNN-TiO_2.

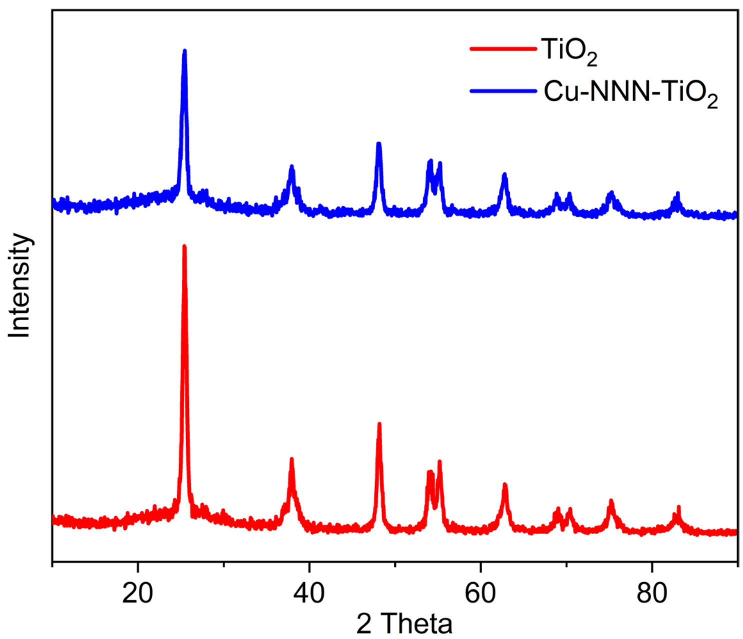


Fig. S10 XRD pattern of TiO_2 and Cu-NNN-TiO_2.

Table S1 Summary of sorption parameters obtained for TiO_2 and Cu-NNN-TiO_2

	TiO_2	Cu-NNN-TiO_2
*a*BET	64 m^2/g	47 m^2/g
Pore volume	0.37 cm^3/g	0.22 cm^3/g
Modal Pore width	21.4 nm	21.4 nm
Mean Pore width	22.8 nm	19.2 nm

Table S2 Summary of consistency criteria derived from fitting BET surface areas on TiO_2 and Cu-NNN-TiO_2

	TiO_2	**Cu-NNN-TiO_2**
P/Po range	0.13–0.27	0.13–0.28
C	42.59	29.44
V_m (cm^3/g)	16.84	12.24
$^{1}/_{(\sqrt{C}+1)}$	0.133	0.156
P/P_0 (V_m)	0.132	0.156
*a*BET (m^2/g)	64	47
R	0.9999	0.9999