Supplementary Information

Clay supported Cu (II) catalyst: An efficient, heterogeneous and recyclable catalyst for synthesis of 1,4-disubstituted 1,2,3-triazoles from alloxan derived terminal alkyne and substituted azides using click chemistry approach

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S1. Characterizations of clay-Cu(II) catalyst

Clay-Cu(II) catalyst^[24] was prepared according to the reported method. A calculated amount of aqueous copper oligomer to form a 10% copper deposition on to Montmorillonite KSF and the system was stirred for 15 h followed by filtration and several washing with distilled water. The cake so formed was dried at room temperature, kept overnight in air oven at 110 °C and then powdered and calcined at 425 °C for 3 h. The calcined product is referred to as clay-Cu(II) catalyst and the catalyst so formed was used in the experiments without further activation. Other catalysts with 20 and 5 % loading of Cu were also prepared in the same way. Catalyst was characterized using temperature programmed reduction studies and SEM analysis.

The H₂ TPR curves of catalyst showed three reduction peaks (as shown in Fig. S1.1), a major peak centered at 225 °C, small broad by diffused shoulder at 370 °C and a small broad peak at 540 °C, which indicated stepwise reduction. The large signal peak at 225 °C can be attributed to the reduction of highly dispersed small CuO particles which are easily reducible and that at 370 °C is assigned to the reduction of bulk CuO species supported on Montmorillonite-KSF clay. The small broad peak at 540 °C is attributed to reduction of CuAl₂O₄ spinel corresponding to some copper species in the clay pores. The presence of the spinel indicates that there is a strong interaction between the catalyst and the support.^[36,37] Since the intensity of the peak representing the reduction of highly dispersed fine CuO particles is highest, this suggests that the highly dispersed CuO species are dominating and are responsible for the catalytic activity.

Figure S1.1. TPR curve of Clay-Cu(II) catalyst

Further, in order to study the surface morphology, SEM analysis of the sample was carried out using electron microscope with voltage 20.0 KV. The SEM images of the clay-Cu(II) catalyst before and after the reaction are shown in Fig. S1.2.

The SEM image of the clay-Cu(II) catalyst is shown in Fig. S1.2, showing the presence of coarse surface (thus elevated surface area). It is therefore clear that the catalyst is able to adsorb substrate and/ or reagent to a great extent. Further, it is observed that CuO particles are randomly distributed over the support surface. It is noted that CuO layer formed in clay-Cu(II) catalyst is composed of several aggregates of CuO particles rather than a continuous film. The change of surface area of clay-Cu(II) catalyst before and after reaction are illustrated in Fig. S1.2(a) and S1.2(b).

Figure S1.2. Sem images of Clay-Cu(II) catalysts before(a) and after(b) reaction

XPS spectra was recorded by VG ESCA LAB MK II spectrometer using Al K α (1486.6 eV) radiation from an X-ray source operated at 12 kV, 10mA. Samples were degassed for several hours in XPS chamber to minimize air contamination.

Fig. S1.3 shows the high resolution narrow X-ray photoelectron spectra (XPS) for fresh clay supported Cu(II) catalyst and clay-Cu(II) catalyst treated with sodium azide, recorded to know the oxidation state of Cu after treating with sodium azide. As observed in Fig. S1.3a, binding energy peaks at 935.6 eV and 955.3 eV can be attributed to 2p $_{3/2}$ and 2p $_{1/2}$ spin-orbit split-doublets, respectively, which are characteristic of Cu in +2 oxidation state. On the other hand, when clay-Cu(II) was treated with sodium azide (Fig. S1.3b), in addition to the binding energy peaks (935.9 eV, and 955.5 eV), an additional set of binding energy peaks at 933.0 eV, and 952.7 eV are also observed, which clearly indicates that Cu is present in both +1 and +2 oxidation states.^[39,40] These results concluded that Cu(II) gets partially reduced to Cu(I) state after treatment with NaN $_3$, and thus is present as Cu(II)/Cu(I) mixed valency dinuclear species.

Figure S1.3. High resolution X-ray photoelectron spectra (XPS) of (a) Fresh clay supported Cu(II) catalyst; (b) Clay-Cu(II) catalyst treated with sodium azide

S2 Spectral data for newly synthesized substituted triazole derivatives are given below (6a-6n):

1,3-bis((1-(4-hydroxybenzyl)-1H-1,2,3-triazole-4-yl)methyl)pyrimidine-2,4,5,6(1H,3H)-tetraone (6a)

Green solid, yield: 96%; m.p.188-190 °C; IR (KBr, ν , cm^{-1}); 3440, 3064, 2921, 2806, 1726, 1630, 1609, 1470, 1132, 1024. ^1H NMR (400 MHz, DMSO-d_6) δ : 4.65 (s, 4H, $2\times\text{CH}_2$), 4.97 (s, 4H, $2\times\text{CH}_2$), 5.56 (s, 2H, OH), 7.05 (d, 4H, $J = 8.0$ Hz, Ar-H), 7.32 (d, 4H, $J = 8.0$ Hz, Ar-H), 8.1 (s, 2H, triazole-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ : 47.7, 56.8, 116.3, 122.5, 125.3, 127.9, 128.7, 129.9, 130.5, 131.8, 150.4, 155.1, 158.3, 173.3. ESI-MS: 516 $[\text{M}+\text{H}]^+$; Anal. Calcd. For $\text{C}_{24}\text{H}_{20}\text{N}_8\text{O}_6$: C, 55.81; H, 3.90; N, 21.70%. Found: C, 55.96; H, 4.05; N, 21.56%.

1,3-bis((1-(2-methylbenzyl)-1H-1,2,3-triazole-4-yl)methyl)pyrimidine-2,4,5,6(1H,3H)-tetraone (6b)

Dark green solid, yield: 95%; m.p.205-208 °C; IR (KBr, ν , cm^{-1}); 3066, 2960, 2930, 2866, 1720, 1635, 1612, 1467, 1142, 1030. ^1H NMR (400 MHz, DMSO-d_6) δ : 2.33 (s, 6H, $2\times\text{CH}_3$), 4.67 (s, 4H, $2\times\text{CH}_2$), 5.02 (s, 4H, $2\times\text{CH}_2$), 7.13 (t, 4H, $J = 8.5$ Hz, Ar-H), 7.54 (d, 4H, $J = 8.5$ Hz, Ar-H), 7.89 (s, 2H, triazole-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ : 32.7, 51.0, 53.7, 120.8, 122.7, 125.1, 128.8, 129.8, 131.1, 139.6, 150.2, 155.8, 172.5. ESI-MS: 512 $[\text{M}+\text{H}]^+$; Anal. Calcd. For $\text{C}_{26}\text{H}_{24}\text{N}_8\text{O}_4$: C, 60.93; H, 4.72; N, 21.86%. Found: C, 60.81; H, 4.86; N, 21.94%.

1,3-bis((1-(4-chlorobenzyl)-1H-1,2,3-triazole-4-yl)methyl)pyrimidine-2,4,5,6(1H,3H)-tetraone (6c)

Dark green solid, yield: 94%; m.p.188-192 °C; IR (KBr, ν , cm^{-1}); 3062, 2932, 2810, 1725, 1628, 1608, 1471, 1123, 1028, 724. ^1H NMR (400 MHz, DMSO-d_6) δ : 4.63 (s, 4H, $2\times\text{CH}_2$), 5.03 (s, 4H, $2\times\text{CH}_2$), 7.08 (d, 4H, $J = 8.0$ Hz, Ar-H), 7.37 (d, 4H, $J = 8.0$ Hz, Ar-H), 7.67 (s, 2H, triazole-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ : 46.0, 57.2, 123.1, 126.6, 127.5, 129.3, 130.9, 131.4, 132.8, 133.7, 135.1, 150.4, 158.7, 172.9. ESI-MS: 553.5 $[\text{M}+\text{H}]^+$; Anal. Calcd. For $\text{C}_{24}\text{H}_{18}\text{Cl}_2\text{N}_8\text{O}_4$: C, 52.09; H, 3.28; N, 20.25%. Found: C, 52.22; H, 3.12; N, 20.09%.

1,3-bis((1-(4-methoxybenzyl)-1H-1,2,3-triazole-4-yl)methyl)pyrimidine-2,4,5,6(1H,3H)-tetraone (6d)

Dark green solid, yield: 96%; m.p.196-198 °C; IR (KBr, ν , cm^{-1}); 3058, 2925, 2816, 1730, 1631, 1610, 1465, 1250, 1128, 1024. ^1H NMR (400 MHz, DMSO-d_6) δ : 3.89 (s, 6H, phenyl- OCH_3), 4.61 (s, 4H, $2\times\text{CH}_2$), 5.01 (s, 4H, $2\times\text{CH}_2$), 6.99 (d, 4H, $J = 8.0$ Hz, Ar-H), 7.28 (d, 4H, $J = 8.0$ Hz, Ar-H), 7.84 (s, 2H, triazole-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ : 45.8, 55.6, 57.8, 112.5, 118.0, 123.3, 129.1, 129.8, 131.6, 132.4, 139.8, 149.0, 158.5, 173.4. ESI-MS: 544 $[\text{M}+\text{H}]^+$; Anal. Calcd. For $\text{C}_{26}\text{H}_{24}\text{N}_8\text{O}_6$: C, 57.35; H, 4.44; N, 20.58%. Found: C, 57.45; H, 4.58; N, 20.49%.

1,3-bis((1-(2-hydroxybenzyl)-1H-1,2,3-triazole-4-yl)methyl)pyrimidine-2,4,5,6(1H,3H)-tetraone (6e)

Dark green solid, yield: 95%; m.p.190-193 °C; IR (KBr, ν , cm^{-1}); 3450, 3072, 2920, 2806, 1726, 1630, 1613, 1468, 1132, 1031. ^1H NMR (400 MHz, DMSO-d_6) δ : 4.58 (s, 4H, $2\times\text{CH}_2$), 4.88 (s, 4H, $2\times\text{CH}_2$), 5.51 (s, 2H, $2\times\text{OH}$), 7.13 (d, 4H, $J = 8.5$ Hz, Ar-H), 7.45 (t, 4H, $J = 8.5$ Hz, Ar-H), 7.65 (s, 2H, triazole-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ : 46.1, 50.3, 115.1, 119.8, 120.9, 123.2, 128.4, 130.3, 131.5, 157.1, 158.8, 173.0. ESI-MS: 516 $[\text{M}+\text{H}]^+$; Anal. Calcd. For $\text{C}_{24}\text{H}_{20}\text{N}_8\text{O}_6$: C, 55.81; H, 3.90; N, 21.70%. Found: C, 55.89; H, 3.71; N, 21.79%.

1,3-bis((1-(4-methylbenzyl)-1H-1,2,3-triazole-4-yl)methyl)pyrimidine-2,4,5,6(1H,3H)-tetraone (6f)

Dark green solid, yield: 95%; m.p.202-206 °C; IR (KBr, ν , cm^{-1}); 3066, 2965, 2928, 2863, 1724, 1628, 1611, 1471, 1138, 1019. ^1H NMR (400 MHz, DMSO-d_6) δ : 2.41 (s, 6H, $2\times\text{CH}_3$), 4.63 (s, 4H, $2\times\text{CH}_2$), 4.92 (s, 4H, $2\times\text{CH}_2$), 7.13 (d, 4H, $J = 8.0$ Hz, Ar-H), 7.37 (d, 4H, $J = 8.0$ Hz, Ar-H), 7.66 (s, 2H, triazole-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ : 20.7, 46.5, 57.8, 123.3, 127.5, 128.6, 130.7, 132.9, 135.2, 150.4, 155.9, 158.3, 173.9. ESI-MS: 512 $[\text{M}+\text{H}]^+$; Anal. Calcd. For $\text{C}_{26}\text{H}_{24}\text{N}_8\text{O}_4$: C, 60.93; H, 4.72; N, 21.86%. Found: C, 60.71; H, 4.85; N, 22.04%.

1,3-bis((1-benzyl-1H-1,2,3-triazole-4-yl)methyl)pyrimidine-2,4,5,6(1H,3H)-tetraone (6g)

Dark green solid, yield: 94%; m.p.198-201 °C; IR (KBr, ν , cm^{-1}); 3061, 2934, 2804, 1726, 1631, 1614, 1469, 1133, 1027. ^1H NMR (400 MHz, DMSO-d_6) δ : 4.61 (s, 4H, $2\times\text{CH}_2$), 4.97 (s, 4H, $2\times\text{CH}_2$), 7.27-7.42 (m, 10H, Ar-H), 8.20 (s, 2H, triazole-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ : 46.2, 57.5, 122.8, 125.4, 128.4, 128.8, 128.9, 129.8, 150.6, 156.5, 172.3. ESI-MS: 485 $[\text{M}+\text{H}]^+$; Anal. Calcd. For $\text{C}_{24}\text{H}_{20}\text{N}_8\text{O}_4$: C, 59.50; H, 4.16; N, 23.13%. Found: C, 59.62; H, 4.02; N, 23.26%.

1,3-bis((1-(4-(2-hydroxyethyl)benzyl)-1H-1,2,3-triazole-4-yl)methyl)pyrimidine-2,4,5,6(1H,3H)-tetraone (6h)

Dark green solid, yield: 95%; m.p.194-197 °C; IR (KBr, ν , cm^{-1}); 3440, 3068, 2921, 2805, 1725, 1629, 1610, 1472, 1120, 1032. ^1H NMR (400 MHz, DMSO-d_6) δ : 3.66 (t, $J = 2.2$ Hz, 4H, CH_2), 4.64 (s, 4H, $2\times\text{CH}_2$), 4.92 (s, 4H, $2\times\text{CH}_2$), 5.28 (s, 2H, $2\times\text{OH}$), 7.0 (d, 4H, $J = 8.0$ Hz, Ar-H), 7.28 (d, 4H, $J = 8.0$ Hz, Ar-H), 7.55 (s, 2H, triazole-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ : 29.2, 32.0, 46.3, 57.3, 61.4, 123.3, 126.1, 126.9, 128.2, 130.8, 133.2, 135.6, 150.3, 158.7, 172.5. ESI-MS: 572 $[\text{M}+\text{H}]^+$; Anal. Calcd. For $\text{C}_{28}\text{H}_{28}\text{N}_8\text{O}_6$: C, 58.73; H, 4.93; N, 19.57%. Found: C, 58.89; H, 5.09; N, 19.42%.

1,3-bis((1-(4-bromobenzyl)-1H-1,2,3-triazole-4-yl)methyl)pyrimidine-2,4,5,6(1H,3H)-tetraone (6i)

Dark green solid, yield: 93%; m.p.190-192 °C; IR (KBr, ν , cm^{-1}); 3080, 2934, 2816, 1719, 1632, 1608, 1468, 1142, 1030, 660. ^1H NMR (400 MHz, DMSO-d_6) δ : 4.61 (s, 4H, $2\times\text{CH}_2$), 5.01 (s,

4H, 2×CH₂), 7.23 (d, 4H, *J* = 8.0 Hz, Ar-H), 7.47 (d, 4H, *J* = 8.0 Hz, Ar-H), 7.56 (s, 2H, triazole-H). ¹³C NMR (100 MHz, DMSO-d₆) δ: 46.0, 57.1, 119.7, 122.9, 129.7, 130.9, 131.4, 134.7, 150.8, 158.4, 174.2. ESI-MS: 642 [M+H]⁺; Anal. Calcd. For C₂₄H₁₈Br₂N₈O₄: C, 44.88; H, 2.82; N, 17.45%. Found: C, 44.98; H, 2.69; N, 17.61%.

1,3-bis((1-(4-nitrobenzyl)-1H-1,2,3-triazole-4-yl)methyl)pyrimidine-2,4,5,6(1H,3H)-tetraone (6j)

Dark green solid, yield: 95%; m.p.196-198 °C; IR (KBr, ν, cm⁻¹); 3074, 2923, 2812, 1728, 1635, 1606, 1552, 1471, 1348, 1137, 1025. ¹H NMR (400 MHz, DMSO-d₆) δ: 4.62 (s, 4H, 2×CH₂), 4.98 (s, 4H, 2×CH₂), 7.25 (d, 4H, *J* = 8.5 Hz, Ar-H), 7.48 (d, 4H, *J* = 8.5 Hz, Ar-H), 7.64 (s, 2H, triazole-H). ¹³C NMR (100 MHz, DMSO-d₆) δ: 46.0, 57.6, 121.9, 123.3, 129.1, 129.8, 130.5, 141.2, 144.7, 150.5, 158.5, 172.6. ESI-MS: 574 [M+H]⁺; Anal. Calcd. For C₂₄H₁₈N₁₀O₈: C, 50.18; H, 3.16; N, 24.38%. Found: C, 49.95; H, 3.28; N, 24.50%.

1,3-bis((1-(2-chlorobenzyl)-1H-1,2,3-triazole-4-yl)methyl)pyrimidine-2,4,5,6(1H,3H)-tetraone (6k)

Dark green solid, yield: 94%; m.p.203-205 °C; IR (KBr, ν, cm⁻¹); 3077, 2921, 2806, 1723, 1631, 1610, 1466, 1130, 1029, 726. ¹H NMR (400 MHz, DMSO-d₆) δ: 4.64 (s, 4H, 2×CH₂), 4.95 (s, 4H, 2×CH₂), 7.28 (t, 4H, *J* = 8.0 Hz, Ar-H), 7.52 (d, 4H, *J* = 8.0 Hz, Ar-H), 7.63 (s, 2H, triazole-H). ¹³C NMR (100 MHz, DMSO-d₆) δ: 46.5, 50.7, 122.8, 126.3, 127.2, 128.6, 130.1, 130.9, 131.7, 135.4, 137.8, 150.7, 158.9, 172.4. ESI-MS: 553 [M+H]⁺; Anal. Calcd. For C₂₄H₁₈Cl₂N₈O₄: C, 52.09; H, 3.28; N, 20.25%. Found: C, 52.27; H, 3.09; N, 20.37%.

1,3-bis((1-(2-bromobenzyl)-1H-1,2,3-triazole-4-yl)methyl)pyrimidine-2,4,5,6(1H,3H)-tetraone (6l)

Dark green solid, yield: 92%; m.p.193-195 °C; IR (KBr, ν, cm⁻¹); 3080, 2934, 2816, 1719, 1634, 1612, 1467, 1142, 1030, 665. ¹H NMR (400 MHz, DMSO-d₆) δ: 4.65 (s, 4H, 2×CH₂), 4.95 (s, 4H, 2×CH₂), 7.19 (t, 4H, *J* = 8.5 Hz, Ar-H), 7.46 (d, 4H, *J* = 8.5 Hz, Ar-H), 7.57 (s, 2H, triazole-H). ¹³C NMR (100 MHz, DMSO-d₆) δ: 46.3, 57.3, 155.8, 123.1, 128.5, 130.9, 131.6, 132.3, 150.2, 158.6, 160.3, 174.5. ESI-MS: 520 [M+H]⁺; Anal. Calcd. For C₂₄H₁₈F₂N₈O₄: C, 55.39; H, 3.49; N, 21.53%. Found: C, 55.12; H, 3.35; N, 21.38%.

1,3-bis((1-(4-(2-methoxyethyl)benzyl)-1H-1,2,3-triazole-4-yl)methyl)pyrimidine-2,4,5,6(1H,3H)-tetraone (6m)

Dark green solid, yield: 95%; m.p.198-200 °C; IR (KBr, ν, cm⁻¹); 3070, 2967, 2925, 2873, 2808, 1720, 1628, 1608, 1472, 1257, 1135, 1027. ¹H NMR (400 MHz, DMSO-d₆) δ: 3.03 (s, 6H, 2×OCH₃), 3.51 (t, *J* = 5.4 Hz, 4H, 2×CH₂), 4.19 (t, *J* = 5.4 Hz, 4H, 2×CH₂), 4.63 (s, 4H, 2×CH₂), 5.06 (s, 4H, 2×CH₂), 7.07 (d, 4H, *J* = 8.5 Hz, Ar-H), 7.36 (d, 4H, *J* = 8.5 Hz, Ar-H), 7.55 (s, 2H, triazole-H). ¹³C NMR (100 MHz, DMSO-d₆) δ: 27.5, 31.8, 35.7, 46.4, 57.6, 60.1, 122.7, 127.4, 130.3, 133.6, 135.4,

150.5, 158.2, 169.6. ESI-MS: 601 $[M+H]^+$; Anal. Calcd. For $C_{30}H_{32}N_8O_6$: C, 59.99; H, 5.37; N, 18.66%. Found: C, 60.15; H, 5.52; N, 18.79%.

1,3-bis((1-(2-methoxybenzyl)-1H-1,2,3-triazole-4-yl)methyl)pyrimidine-2,4,5,6(1H,3H)-tetraone (6n)

Dark green solid, yield: 96%; m.p. 195-198 °C; IR (KBr, ν , cm^{-1}): 3043, 2975, 2920, 2868, 2812, 1724, 1631, 1609, 1470, 1250, 1135, 1026. ^1H NMR (400 MHz, DMSO-d_6) δ : 3.94 (s, 6H, $2\times\text{OCH}_3$), 4.65 (s, 4H, $2\times\text{CH}_2$), 4.98 (s, 4H, $2\times\text{CH}_2$), 7.03 (t, 4H, $J = 8.5$ Hz, Ar-H), 7.42 (d, 4H, $J = 8.5$ Hz, Ar-H), 7.58 (s, 2H, triazole-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ : 46.5, 50.8, 57.6, 111.7, 120.3, 123.1, 125.3, 126.9, 129.4, 150.3, 158.6, 173.4. ESI-MS: 544 $[M+H]^+$; Anal. Calcd. For $C_{26}H_{24}N_8O_6$: C, 57.35; H, 4.44; N, 20.58%. Found: C, 57.52; H, 4.57; N, 20.41%.

S3. ^1H and ^{13}C NMR spectra of triazole derivatives **6a-6n**

400 MHz ^1H NMR Spectra of Compound 6a

100 MHz ^{13}C NMR Spectra of Compound 6a

400 MHz ¹H NMR Spectra of Compound 6b

100 MHz ¹³C NMR Spectra of Compound 6b

400 MHz ^1H NMR Spectra of Compound 6c

100 MHz ^{13}C NMR Spectra of Compound 6c

400 MHz ^1H NMR Spectra of Compound 6d

100 MHz ^{13}C NMR Spectra of Compound 6d

400 MHz ^1H NMR Spectra of Compound 6g

100 MHz ^{13}C NMR Spectra of Compound 6g

400 MHz ¹H NMR Spectra of Compound 6h

100 MHz ¹³C NMR Spectra of Compound 6h

400 MHz ^1H NMR Spectra of Compound 6k

100 MHz ^{13}C NMR Spectra of Compound 6k

400 MHz ^1H NMR Spectra of Compound 6l

100 MHz ^{13}C NMR Spectra of Compound 6l