Supplementary Information For:

Highly Active Urea-Functionalized Zr(IV)-UiO-67 Metal-Organic Framework as Hydrogen Bonding Heterogeneous Catalyst for Friedel-Crafts Alkylation

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Characterization of H$_2$L linker:

In order to characterize the H$_2$L linker molecule, we have performed both $^1$H and $^{13}$C NMR experiments in DMSO-d$_6$. The spectra are shown in Figure S1 and S2, Supporting Information. From the $^1$H NMR spectrum, it can be observed that there are peaks for eight protons. The $^{13}$C NMR spectrum shows that there are peaks for eight different carbon atoms. Therefore, both the $^1$H and $^{13}$C NMR spectra clearly indicated that the H$_2$L linker has been synthesized successfully in its pure form. $^1$H-NMR (400 MHz, DMSO-d$_6$): $\delta = 9.12$ (s, 2H, NH), 7.72 (m, 4H), 7.62 (t, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta = 167.18, 164.12, 140.77, 133.05, 131.99, 130.24, 125.23, 122.29$ ppm.

Figure S1. $^1$H NMR spectrum of the H$_2$L linker in DMSO-d$_6$. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta = 9.12$ (s, 2H, NH), 7.72 (m, 4H), 7.62 (t, 2H) ppm.
Figure S2. $^{13}$C NMR spectrum of the H$_2$L linker in DMSO-d$_6$. $^{13}$C NMR (100 MHz, DMSO-d$_6$): \( \delta = 167.18, 164.12, 140.77, 133.05, 131.99, 130.24, 125.23, 122.29 \) ppm.

Figure S3. FT-IR spectra of (a) H$_2$L linker, (b) as-synthesized 1, (c) activated 1’ and (d) 1’ after 4th catalytic cycle.
**Figure S4.** Pawley fit for the XRPD pattern of as-synthesized 1. Blue lines and red dots denote calculated and observed patterns, respectively. The peak positions and difference plot are displayed at the bottom ($R_p = 6.85$, $R_{wp} = 9.38$).

**Figure S5.** $^1$H NMR spectrum of digested 1' (digestion by adding CsF in D$_2$O) in D$_2$O. $^1$H NMR (400 MHz, D$_2$O): $\delta = 7.59$ (d, 2H), 7.50 (d, 2H,), 7.39 (d, 2H) ppm.
Figure S6. $^{13}$C NMR spectrum of digested 1′ (digestion by adding CsF in D$_2$O) in D$_2$O. $^{13}$C NMR (100 MHz, D$_2$O): $\delta = 173.52, 138.51, 137.13, 130.68, 129.33, 128.63, 125.07, 121.11$ ppm.

Figure S7. TG curves of as-synthesized 1 (black) and thermally activated 1′ (red) recorded in an argon atmosphere in the temperature range of 25-700 °C with a heating rate of 10 °C min$^{-1}$. 
Figure S8. XRRD patterns of 1’ after stirring in different solvents: (a) 1’ (activated), (b) 1’ after stirring in water, (c) 1’ after stirring in glacial acetic acid and (d) 1’ after stirring in 1M HCl.

Figure S9. N\textsubscript{2} adsorption (solid circle) and desorption (empty circle) isotherms of 1’ measured at –196 °C.
Figure S10. FE-SEM images of 1′ before catalysis.

Figure S11. FE-SEM images of 1′ after catalysis.
Figure S12. EDX spectrum of 1′ before catalysis. Inset: complete image of EDX mapping of 1′ before catalysis.

Figure S13. EDX elemental mapping of 1′ before catalysis.
Figure S14. EDX spectrum of $1'$ after catalysis. Inset: complete image of EDX mapping of $1'$ after catalysis.

Figure S15. EDX elemental mapping of $1'$ after catalysis.
Figure S16. GC-MS trace of 3-(2-nitro-1-phenylethyl)-1H-indole.

Figure S17. $^1$H-NMR spectrum of 3-(2-nitro-1-phenylethyl)-1H-indole.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.68$ (s, 1H), 7.42 (d, $J = 7.8$ Hz, 1H), 7.28 (d, $J = 13.5$ Hz, 5H), 7.23 (d, $J = 1.9$ Hz, 1H), 7.15 (t, $J = 7.5$ Hz, 1H), 7.04 (t, $J = 7.4$ Hz, 1H), 6.95 (s, 1H), 5.15 (t, $J = 7.8$ Hz, 1H), 5.01 (dd, $J = 12.3$, 7.7 Hz, 1H), 4.89 (dd, $J = 11.6$, 9.2 Hz, 1H).
Figure S18. GC-MS trace of 1-methyl-3-(2-nitro-1-phenylethyl)-1H-indole.

Figure S19. $^1$H-NMR spectrum of 1-methyl-3-(2-nitro-1-phenylethyl)-1H-indole.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.37$ (d, $J = 7.8$ Hz, 1H), 7.28 – 7.21 (m, 4H), 7.19 (s, 1H), 7.17 – 7.09 (m, 2H), 6.99 (t, $J = 7.2$ Hz, 1H), 6.77 (s, 1H), 5.09 (t, $J = 7.8$ Hz, 1H), 4.95 (dd, $J = 12.1, 7.6$ Hz, 1H), 4.89 – 4.80 (m, 1H), 3.64 (s, 3H).
Figure S20. GC-MS trace of 2-methyl-3-(2-nitro-1-phenylethyl)-1H-indole.

![GC-MS trace of 2-methyl-3-(2-nitro-1-phenylethyl)-1H-indole]

Figure S21. ^1^H-NMR spectrum of 2-methyl-3-(2-nitro-1-phenylethyl)-1H-indole.

^1^H NMR (400 MHz, CDCl₃): δ = 7.69 (s, 1H), 7.25 (d, J = 7.5 Hz, 1H), 7.21 – 7.11 (m, 4H), 7.11 – 7.02 (m, 2H), 6.97 (t, J = 7.3 Hz, 1H), 6.90 (t, J = 6.9 Hz, 1H), 5.06 (dd, J = 17.3, 8.4 Hz, 2H), 4.96 (dd, J = 17.1, 10.7 Hz, 1H), 2.14 (s, 3H).
Figure S22. GC-MS trace of 5-methyl-3-(2-nitro-1-phenylethyl)-1H-indole.

Figure S23. $^1$H-NMR spectrum of 5-methyl-3-(2-nitro-1-phenylethyl)-1H-indole.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.97$ (s, 1H), 7.36 – 7.27 (m, 4H), 7.25 – 7.15 (m, 3H), 6.98 (dd, $J = 29.2$, 11.0 Hz, 2H), 5.15 (d, $J = 8.0$ Hz, 1H), 5.03 (d, $J = 7.4$ Hz, 1H), 4.97 – 4.83 (m, 1H), 2.37 (s, 3H).
Figure S24. GC-MS trace of 5-methoxy-3-(2-nitro-1-phenylethyl)-1H-indole.

Figure S25. $^1$H-NMR spectrum of 5-methoxy-3-(2-nitro-1-phenylethyl)-1H-indole.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.92$ (s, 1H), 7.21 (s, 4H), 7.15 (d, $J = 3.2$ Hz, 1H), 7.08 (d, $J = 9.2$ Hz, 1H), 6.83 (s, 1H), 6.74 (s, 2H), 5.02 (t, $J = 7.7$ Hz, 1H), 4.95 – 4.87 (m, 1H), 4.80 (dd, $J = 12.0$, 8.6 Hz, 1H), 3.66 (s, 3H).
Figure S26. GC-MS trace of 5-chloro-3-(2-nitro-1-phenylethyl)-1H-indole.

Figure S27. $^1$H-NMR spectrum of 5-chloro-3-(2-nitro-1-phenylethyl)-1H-indole.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.18$ (s, 1H), 7.36 (s, 1H), 7.27 (s, 5H), 7.18 (d, $J = 8.4$ Hz, 1H), 7.09 (d, $J = 8.3$ Hz, 1H), 6.99 (s, 1H), 5.08 (t, $J = 7.6$ Hz, 1H), 5.02 – 4.91 (m, 1H), 4.87 (dd, $J = 11.6$, 8.2 Hz, 1H).
Figure S28. GC-MS trace of 5-bromo-3-(2-nitro-1-phenylethyl)-1H-indole.

Figure S29. $^1$H-NMR spectrum of 5-bromo-3-(2-nitro-1-phenylethyl)-1H-indole.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.10 (s, 1H), 7.46 (s, 1H), 7.20 (dt, $J = 8.3, 7.2$ Hz, 6H), 7.11 (d, $J = 8.6$ Hz, 1H), 6.95 (s, 1H), 5.03 (t, $J = 7.8$ Hz, 1H), 4.92 (dd, $J = 12.3, 8.1$ Hz, 1H), 4.82 (dd, $J = 12.4, 8.0$ Hz, 1H).
**Figure S30.** GC-MS trace of 5-nitro-3-(2-nitro-1-phenylethyl)-1H-indole.

**Figure S31.** GC-MS trace of 2-(2-nitro-1-phenylethyl)-1H-pyrrole.
Figure S32. $^1$H-NMR spectrum of 2-(2-nitro-1-phenylethyl)-1H-pyrrole.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.80$ (s, 1H), 7.25 (dd, $J = 12.7$, 6.3 Hz, 3H), 7.15 (d, $J = 6.9$ Hz, 2H), 6.60 (s, 1H), 6.05 (d, $J = 33.2$ Hz, 2H), 4.90 (dd, $J = 11.5$, 7.2 Hz, 1H), 4.85 – 4.78 (m, 1H), 4.72 (dd, $J = 10.8$, 7.6 Hz, 1H).

Figure S33. GC-MS trace of N,N-dimethyl-4-(2-nitro-1-phenylethyl)aniline.
Figure S34. $^1$H-NMR spectrum of N,N-dimethyl-4-(2-nitro-1-phenylethyl)aniline.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.19$ (d, $J = 6.2$ Hz, 2H), 7.13 (d, $J = 6.5$ Hz, 3H), 6.98 (d, $J = 7.3$ Hz, 2H), 6.56 (d, $J = 7.9$ Hz, 2H), 4.81 (d, $J = 3.2$ Hz, 2H), 4.71 (d, $J = 7.0$ Hz, 1H), 2.79 (s, 6H).

Figure S35. Density functional theory pore-size distribution of compound 1′ as determined from its N$_2$ adsorption isotherms at -196 °C.
Table S1. Unit cell parameters of as-synthesized Zr-Uio-67-urea obtained by indexing its XRPD pattern. The obtained values were compared with those of the previously reported un-functionalized and functionalized Zr-Uio-67 MOFs.

<table>
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References: