Ligand-free *N*-arylation of heterocycles using metal-organic framework [Cu(INA)$_2$] as an efficient heterogeneous catalyst

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Supporting Information

Synthesis of MOFs

1. Cu$_3$(BTC)$_2$: The procedure to prepare Cu$_3$(BTC)$_2$ was similar to that previously reported [1, 2]. In a typical preparation, a solid mixture of Cu(NO$_3$)$_2$.3H$_2$O (0.438 g, 1.81 mmol) and 1,3,5-benzenetricarboxylic acid (H$_3$BTC) (0.236 g, 1.12 mmol) was dissolved in a mixture of DMF (3 mL), ethanol (4 mL) and water (2 mL) in a 20 mL vial. The vial was heated at 85 ^{o}C in an isothermal oven for 24 h, yielding light blue crystals. After cooling the vial to room temperature, the solid product was obtained by decanting with mother liquor and washed with DMF (3 x 8 mL). Solvent exchange was then carried out with ethanol (3 x 8 mL) at room temperature. The product was then dried under vacuum at 170 ^{o}C for 6 h, yielding 0.285 g of Cu$_3$(BTC)$_2$ in the form of deep purple crystals (84% based on 1,3,5-benzenetricarboxylic acid).

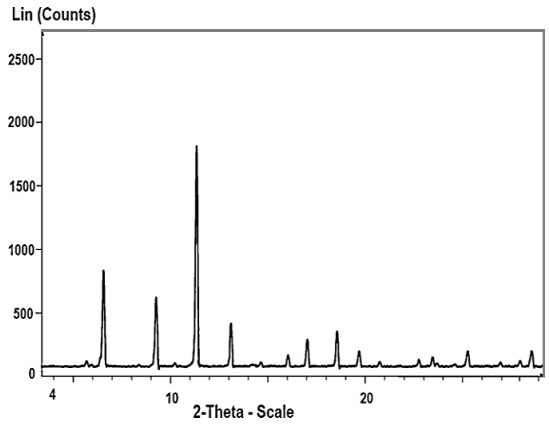

Fig S1. X – ray powder diffractogram of the $Cu_3(BTC)_2$

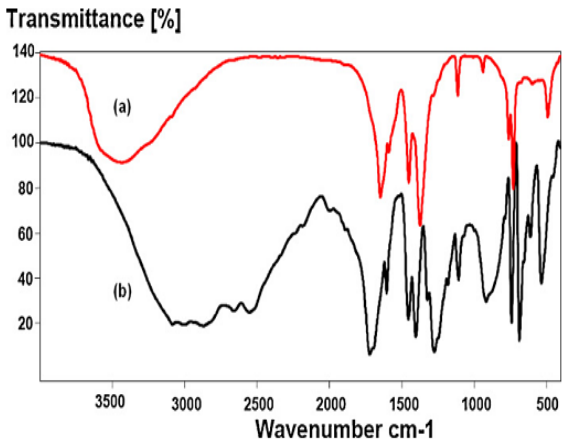

Fig S2. FT – IR spectra of the $Cu_3(BTC)_2$ (a) and 1,3,5-benzenetricarboxylic acid (b)

2. $Cu_2(BDC)_2(BPY)$: The $Cu_2(BDC)_2(BPY)$ was prepared according to literature procedure [3]. A solid mixture of $Cu(NO_3)_2.3H_2O$ (0.105 g, 0.4 mmol), 1,4-benzenedicarboxylic acid (H_2BDC) (0.068 g, 0.4 mmol), and 4,4'-bipyridine (BPY) (0.062 g, 0.4 mmol) was dissolved in DMF (30 mL). The resulting solution was then distributed in four 20 mL vials. The vials were heated at 120 ^oC in an isothermal oven for 24 h, yielding light blue crystals. After cooling the vials to room temperature, the solid product was obtained by decanting with mother liquor and washed with DMF (3 x 10 mL). Solvent exchange was then carried out with methanol (3 x 10 mL) at room temperature. The product was then dried under vacuum at 120 ^oC for 6 h, yielding 0.184 g of $Cu_2(BDC)_2(BPY)$ (75% based on 1,4-benzenedicarboxylic acid).

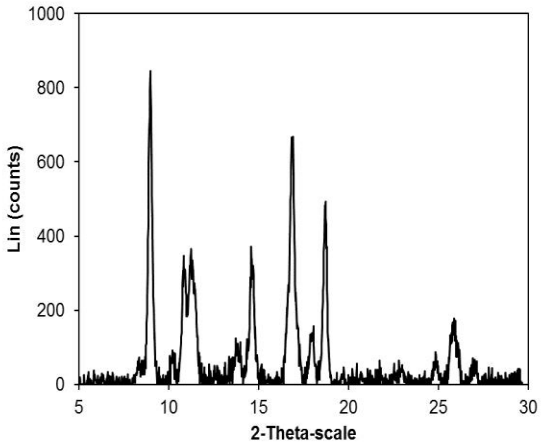

Fig S3. X – ray powder diffractogram of the $Cu_2(BDC)_2(BPY)$

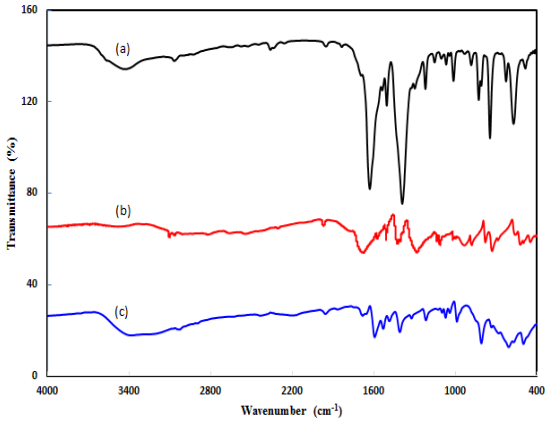

Fig S4. FT – IR spectra of the $Cu_2(BDC)_2(BPY)$ (a), 4,4'-Bipyridine (b), and 1,4-Benzenedicarboxylic acid (c)

3. $Cu_2(BDC)_2(DABCO)$: The $Cu_2(BDC)_2(DABCO)$ was prepared according to literature procedures [4, 5-7]. In a typical preparation, a mixture of H_2BDC (H_2BDC = 1,4-benzenedicarboxylic acid; 0.506 g, 3.1 mmol), DABCO (DABCO = 1,4-diazabicyclo[2.2.2]octane; 0.188 g, 1.67 mmol), and $Cu(NO_3)_2 \cdot 3H_2O$ (0.8 g, 3.3 mmol) was dissolved in DMF (mL). The mixture was stirred for 2 h, and the resulting solution was then distributed to eight 10 ml vials. The vials were heated at 120 ^oC in an isothermal oven for 48 h, forming blue crystals. After cooling the vials to room temperature, the solid product was removed by decanting with mother liquor and washed with DMF (3 x 10 mL). Solvent exchange was carried out with methanol (3 x 10 mL) at room temperature. The product was then dried at 140 ^oC for 6 h under vacuum, yielding 0.57 g of the metal-organic framework $Cu_2(BDC)_2(DABCO)$ as light blue crystals (66% based on 1,4-benzenedicarboxylic acid).

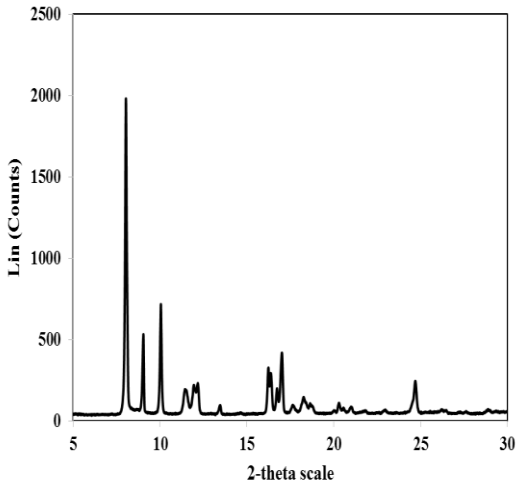

Fig S5. X – ray powder diffractogram of the $Cu_2(BDC)_2(DABCO)$

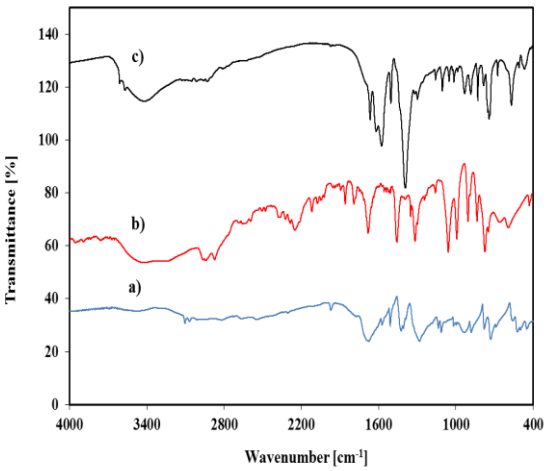

Fig S6. FT – IR spectra of of 1,4-diazabicyclo[2.2.2]octane (a), 1,4-benzenedicarboxylic acid (b), and the $Cu_2(BDC)_2(DABCO)$ (c)

Elemental analysis of the $Cu(INA)_2$ with ICP - MS indicated an atomic copper about 19.26%.

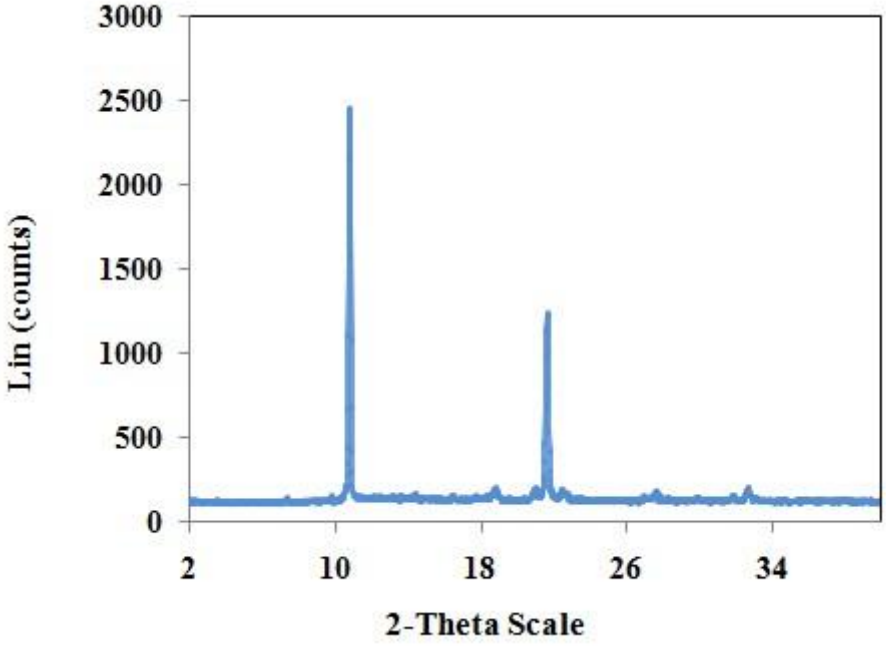

Fig. S7. X-ray powder diffractograms of the $Cu(INA)_2$

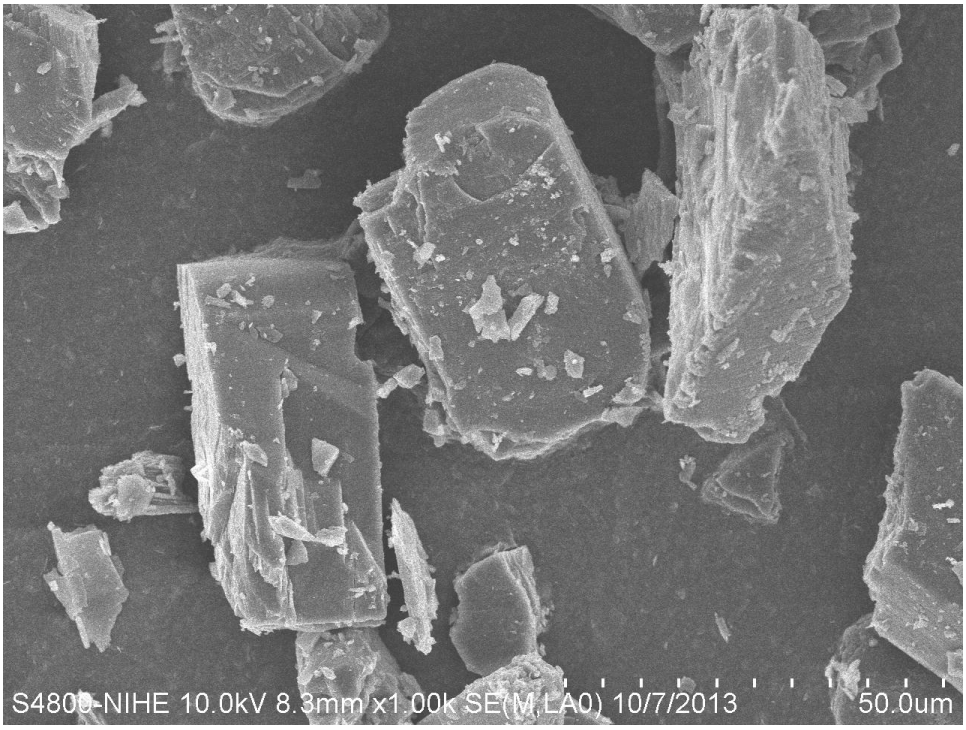

Fig. S8. SEM micrograph of the $Cu(INA)_2$.

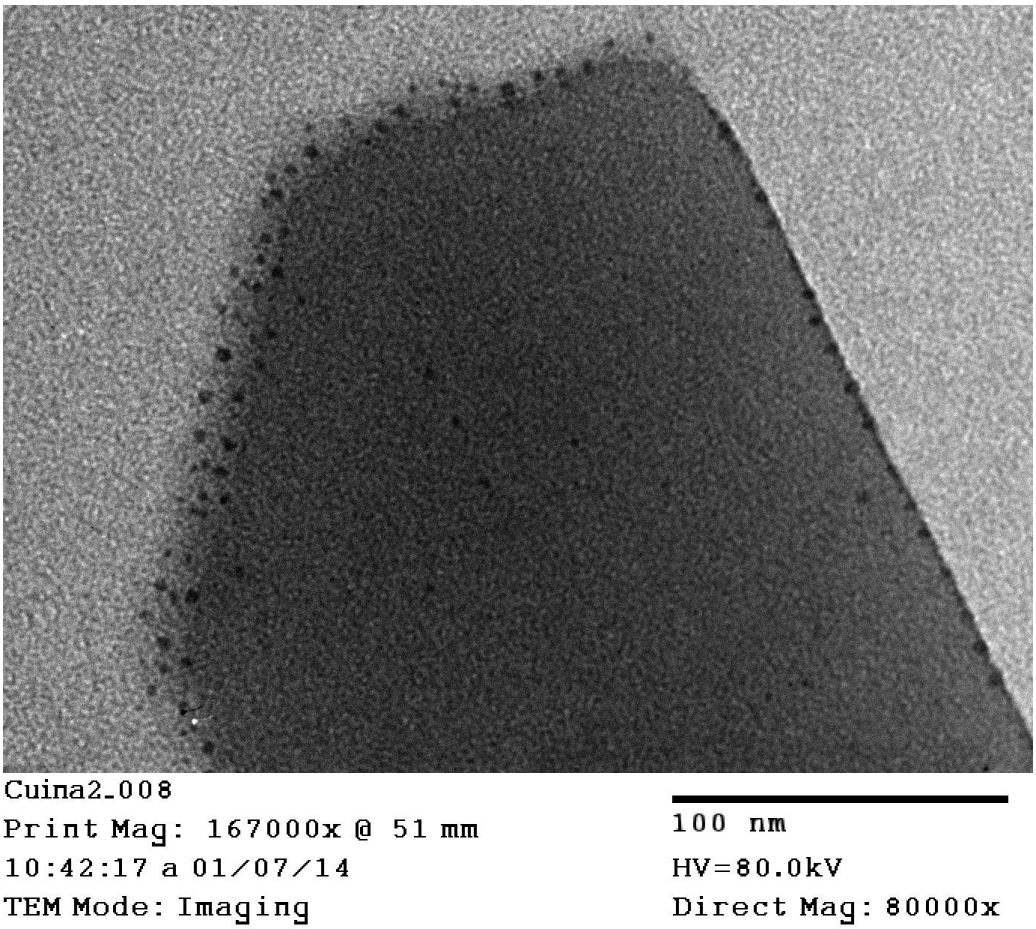

Fig. S9. TEM micrograph of the $Cu(INA)_2$.

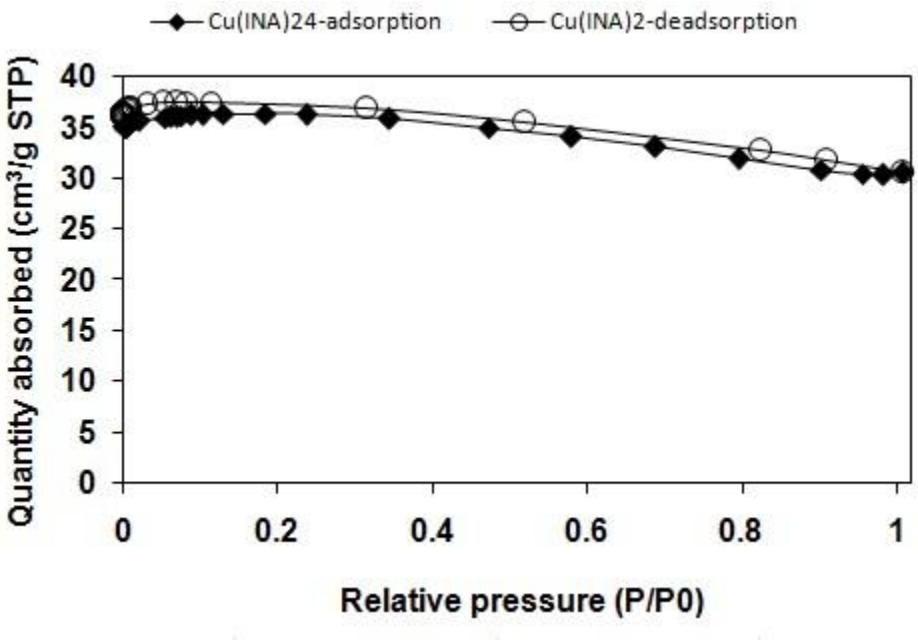

Fig. S10. Nitrogen adsorption/desorption isotherm of the $Cu(INA)_2$. Adsorption data are shown as tetragons and desorption data as circles

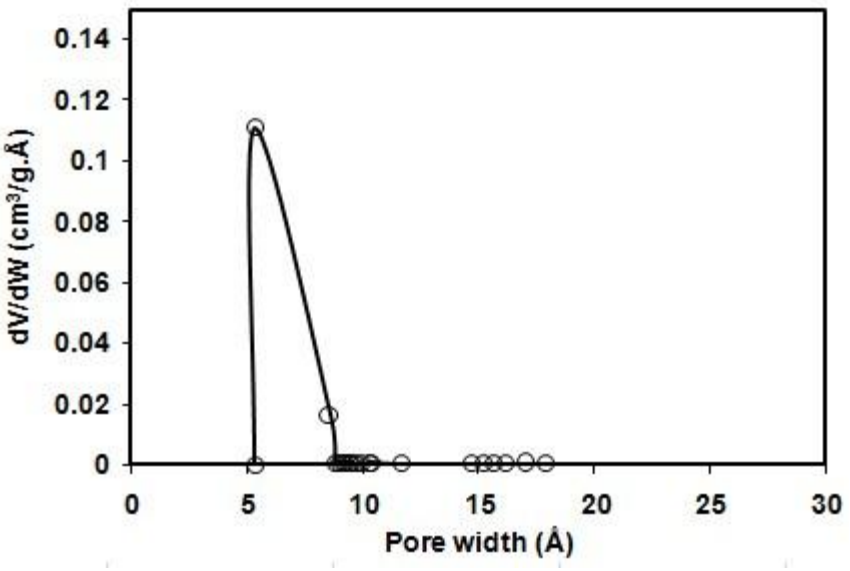

Fig. S11. Pore size distribution of the $Cu(INA)_2$

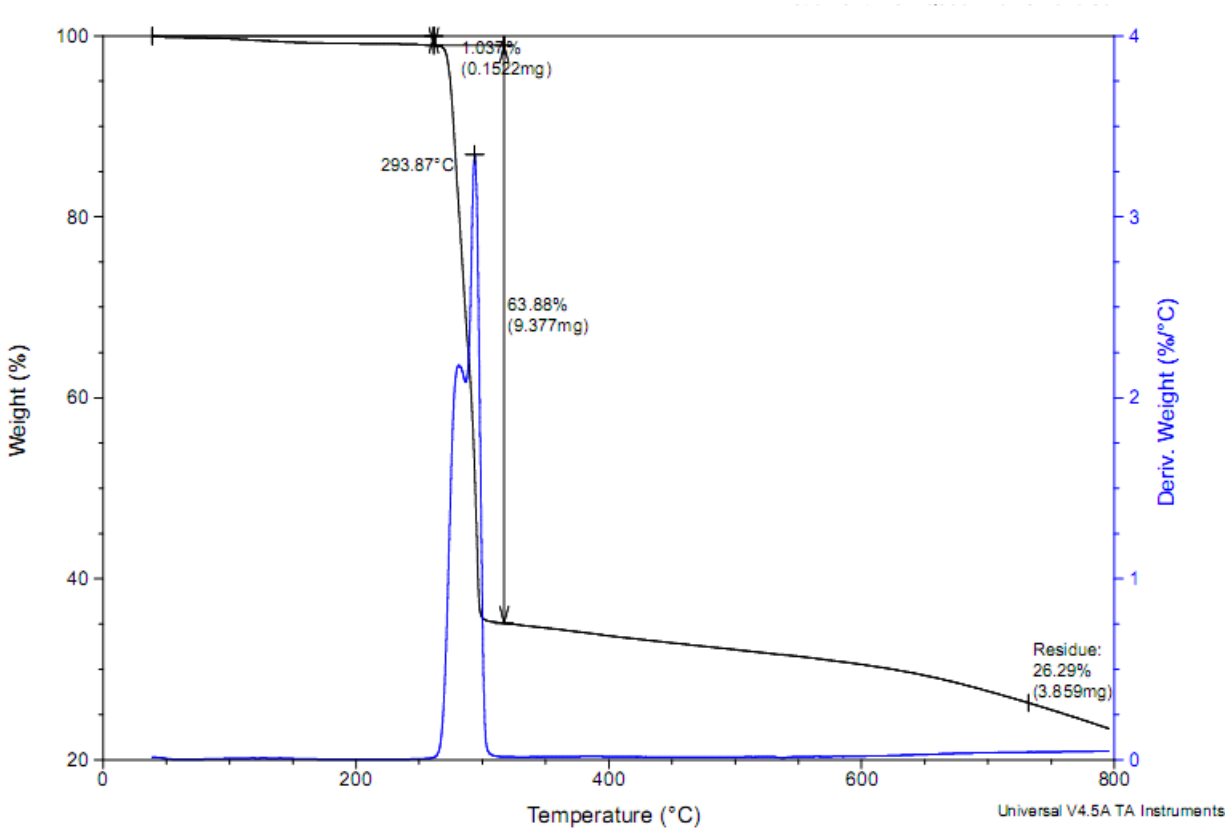

Fig. S12. TGA analysis of the $Cu(INA)_2$

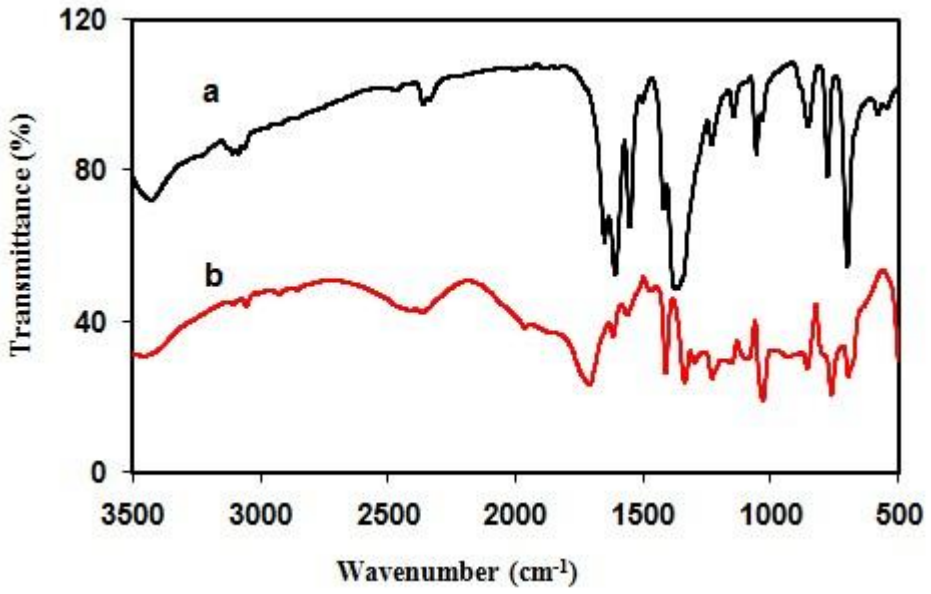

Fig. S13. FT-IR spectra of the $Cu(INA)_2$ (a) and isonicotinic acid (b)

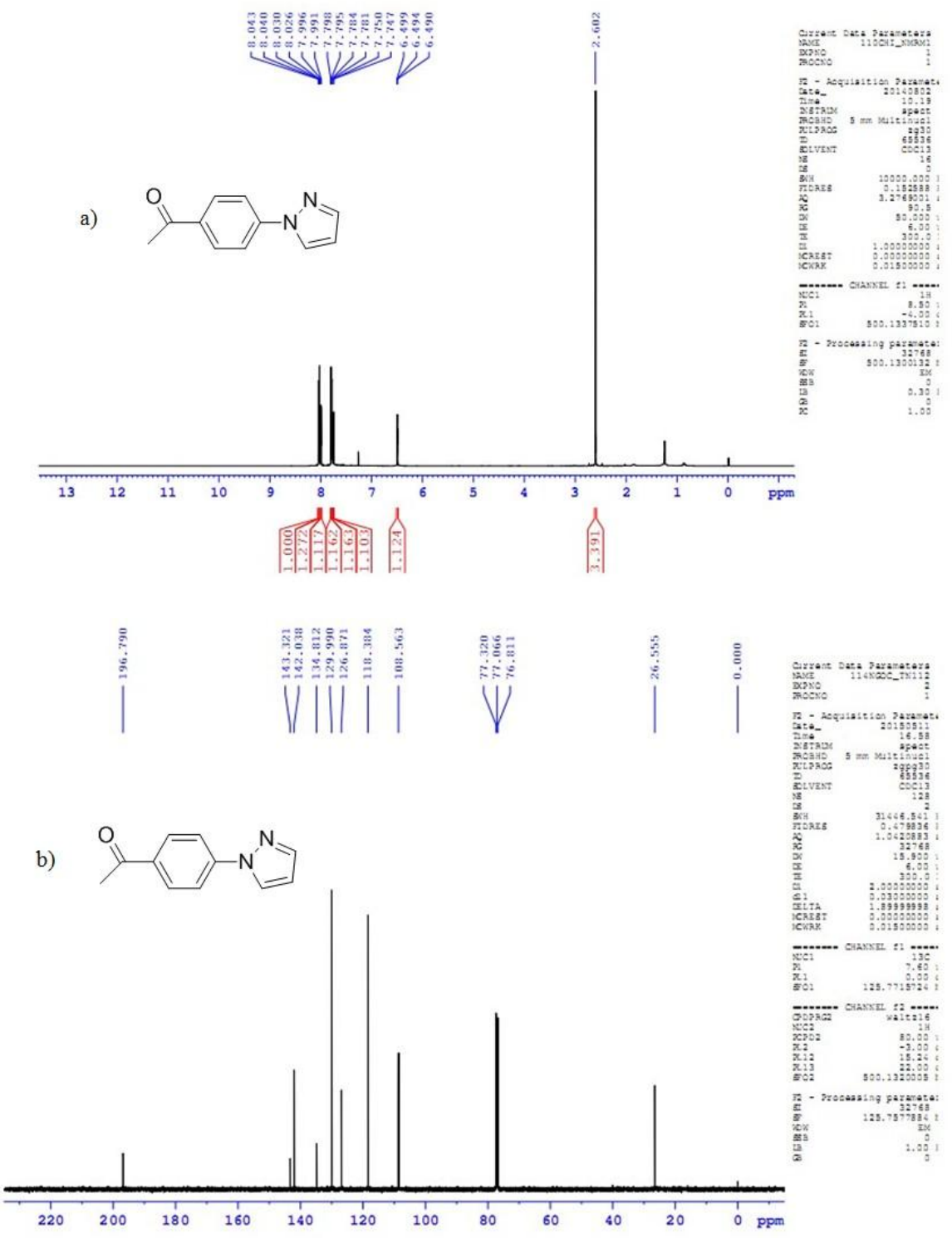

Fig S14. ^{1}H NMR a) and ^{13}C NMR spectra b) of 1-(4-(1H-pyrazol-1-yl)phenyl)ethanone in $CDCl_3$

1-(4-(1H-pyrazol-1-yl)phenyl)ethanone. 4'-iodoacetophenone (492 mg, 2.0 mmol), pyrazole (204 mg, 3 mmol), $Cu(INA)_2$ (0.03 g, 5 mol%), DMA (4 mL), K_3PO_4 (848 mg, 2 eq.). After chromatography (ethyl acetate/hexane = 1: 2), 324 mg brown liquid was obtained (87 %). R_f = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 8.04 (d, *J* = 8.5 Hz, 2H), 7.99 (d, *J* = 2.5 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 1.5 Hz, 1H), 6.49 (t, *J* = 4.5 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): *δ* = 196.7, 143.3, 142.0, 134.8, 129.9, 126.8, 118.3, 108, 26.5..

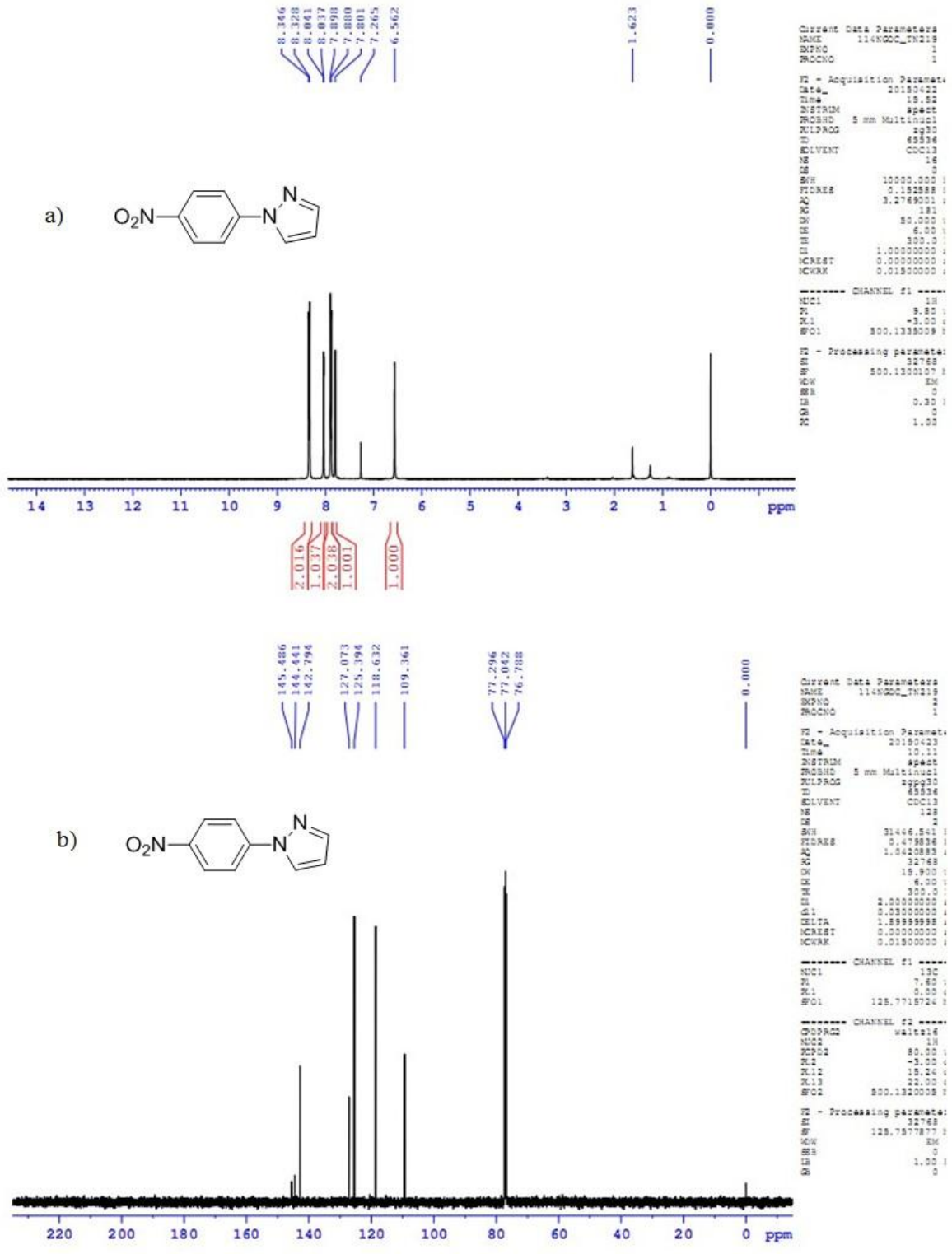

Fig S15. ^{1}H NMR a) and ^{13}C NMR spectra b) of 1-(4-nitrophenyl)-1H-pyrazole in $CDCl_3$

1-(4-nitrophenyl)-1H-pyrazole. 1-iodo-4-nitrobenzene (596 mg, 2.0 mmol), pyrazole (272 mg, 3 mmol) , $Cu(INA)_2$ (0.03 g, 5 mol%), DMA (4 mL), K_3PO_4 (848 mg, 2 eq.). After chromatography (ethyl acetate/hexane = 1: 4), 328 mg brown liquid was obtained (87 %). R_f = 0.5^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 8.34 (d, *J* = 9 Hz, 2H), 8.04 (d, *J* = 2.5 Hz, 1H), 7.89 (d, *J* = 9 Hz, 2H), 7.8 (s, 1H), 6.52 (s, 1H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 145.5, 144.4, 142.7, 127.0, 125.3, 118.6, 109, 3.

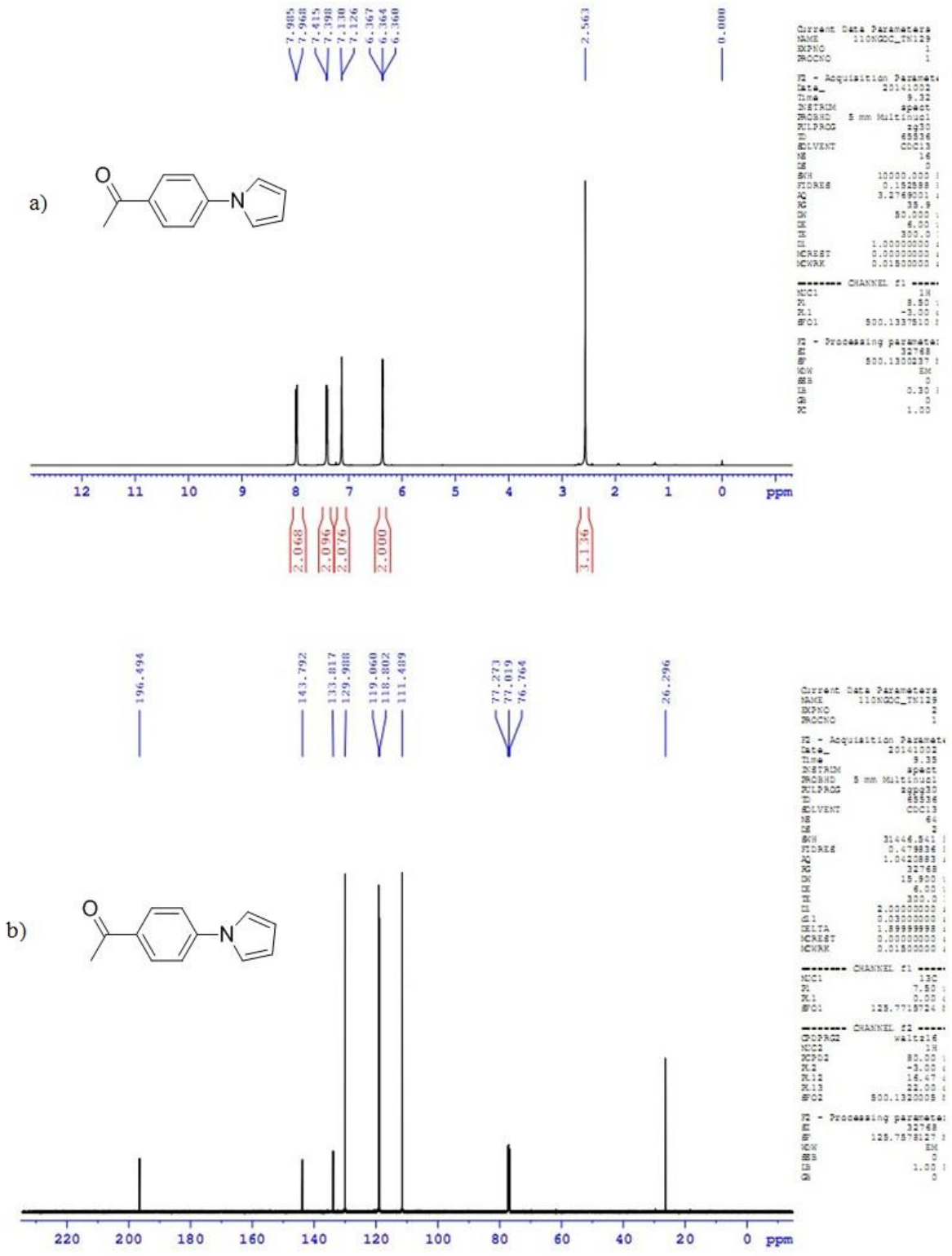

Fig S16. ^{1}H NMR a) and ^{13}C NMR spectra b) of 1-(4-(1H-pyrrol-1-yl)phenyl)ethanone in $CDCl_3$

1-(4-(1H-pyrrol-1-yl)phenyl)ethanone. 4'-iodoacetophenone (592 mg, 2.0 mmol), pyrole (200 mg, 3 mmol) , $Cu(INA)_2$ (0.03 g, 5 mol%), DMA (4 mL), K_3PO_4 (848 mg, 2 eq.). After chromatography (ethyl acetate/hexane = 1: 4), 307 mg brown liquid was obtained (83 %). R_f = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.98 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 2 Hz, 2H), 6.36 (t, *J* = 3.5 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): *δ* = 196.4, 143.7, 133.8, 129.9, 119.0, 118.8, 111.4, 26.2.

References

1. L. T. L. Nguyen, T. T. Nguyen, K. D. Nguyen, N. T. S. Phan, *App. Catal. A* **2012**, *425-426*, 44-52. (2)
2. D. Britt, D. Tranchemontagne, O. M. Yaghi, *PNASS* **2008**, *33*, 11623-11627. (3)
3. Y. Sakata, S. Furukawa, M. Kondo, K. Hirai, N. Horike, Y. Takashima, H. Uehara, N. Louvain, M. Meiliknov, T. T. Suruoka, S. Isoda, W. Kosaka, O. Sakata, S. Kitagawa, *Science* **2013**, *339*, 193-196. (4)
4. K. Tan, N. Nijem, P. Canepa, Q. Gong, J. Li, T. Thonhauser, Y. J. Chaba, *Chem. Mater.* **2012**, *24*, 3153-3167. (5)
5. P. Mishra, S. Edubilli, B. Mandal, S. Gumma, *Micropor. Mesopor. Mater.* **2013**, *169*, 75-80. (9)
6. K. Seki, W. Mori, *J. Phys. Chem. B* **2002**, *106*, 1380-1385. (10)
7. S. Achmann, G. Hagen, M. Hämmerle, I. Malkowsky, C. Kiener, R. Moos, *Chem. Eng. Technol.* **2010**, *33*, 275-280. (11)