

Wheel-Shaped Copper Containing Polyoxotungstate as an Efficient Catalyst in Three-Component Synthesis of 1,2,3-Triazoles

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Supporting Information

1. General Methods and Materials: All POMs catalyst were prepared according to the literature¹⁻⁵. All common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. Elemental analyses were carried out on a Perkin-Elmer 7300 DV and Leco, CHNS-932 elemental analyzer. Infrared spectra (KBr pellets) were recorded on a JASCO, FT/IR-6300 instrument. ¹H and ¹³C NMR were recorded on a Bruker (400 and 100 MHz; 296 K) using CDCl₃ as the solvent with TMS as an internal reference. UV-vis spectra were recorded on JASCO V-670 UV-vis spectrophotometer (190-2700 nm). X-ray diffraction data (XRD) were obtained on a D8 Advanced Bruker using Cu K α radiation ($2\theta = 10-80^\circ$).

2. Synthesis methods of Cu containing POMs

2.1. Synthesis of Na₄K₅[K₃Cu₃(NO₃)(A- α -PW₉O₃₄)₂]¹

Na₂WO₄·2H₂O (5 g, 15.2 mmol) and Na₂HPO₄ (0.24 g, 1.7 mmol) were dissolved in 100 mL H₂O then (0.31 g, 1.01 mmol) Cu(NO₃)₂·6H₂O was added. The pH was adjusted to 7.5 by drop wise addition of 6 M HCl, and a green solution formed. The produced green solution heated at 90 °C for 1 h and then allowed to cool to room temperature. KCl (0.6 g, 8.0 mmol) was added, and the

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solution was kept at room temperature. After several weeks, dark green crystals were formed (yield 70% based on W). IR (KBr): 1099, 1063, 1045, 945, 873, 810, 743, 641 (cm^{-1}).

2.2. Synthesis of $\text{K}_{28}\text{Li}_5[\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}]\cdot 92\text{H}_2\text{O}^2$

60 g (1 mol) of glacial acetic acid, 21 g (0.5 mol) of lithium hydroxide, 21 g (0.5 mol) of lithium chloride, and 28 g of $\text{K}_{12}[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]\cdot 24\text{H}_2\text{O}$ were successively dissolved in 950 mL of water. The solution was left in a closed flask. After 1 day, white needles appeared and the crystallization has been continued for several days. After one week, the crystals were collected by suction filtration on a coarse frit and air dried for 3 days (Yield: 33%).

The P-O bands are at 1140, 1090, and 1020 cm^{-1} (KBr) in the IR spectrum.

2.3. Synthesis of $\text{K}_7\text{Na}_3[\text{Cu}_4(\text{PW}_9\text{O}_{34})_2]^3$

$\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.62 g, 3.6 mmol) was dissolved in 12 mL of water. To this solution, 5.0 g (1.8 mmol) of solid Δ -PW9 was added with stirring until all the Δ -PW9 was dissolved. Addition of KCl (0.66 g, 8.8 mmol) to this light green solution, resulted in the precipitation of a pale green product. This product was stirred for 10 min and then heated under hot water (60 °C) or on a steam bath for brief periods (1-5 min) until the bulk of the precipitated solid had redissolved. The slightly cloudy solution was centrifuged for about 5 min to remove the fine blue suspension. The clear light green supernatant was removed and allowed to crystallize at room temperature. Pale green crystalline cubes began to form immediately and continued to crystallize for 6-12 h. The yield was (27%).

IR (KBr): $\bar{\nu} = 1085, 1033, 975, 947, 932, 865, 821 \text{ cm}^{-1}$.

2.4. Synthesis of $\text{K}_4[\gamma\text{-H}_2\text{SiW}_{10}\text{O}_{36}\text{Cu}_2(\mu\text{-}1,1\text{-N}_3)_2]^4$

CuCl_2 (0.67 mmol, two equivalents with respect to $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$) in water (20 mL) was added to a suspension of $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot 12\text{H}_2\text{O}$ (0.335 mmol) in water (20 mL). After 1 min, NaN_3 (1.75 mmol, 5.2 equivalents with respect to $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$) in water (20 mL) was added, followed

by the immediate addition of KCl (26.20 mmol) in water (20 mL). The pH of the mixture was adjusted to 6.0 with 1.0 M aqueous HNO₃ solution, followed by stirring for 20 min at room temperature. The green precipitate of **1** was collected by filtration and washed with an excess amount of water (0.78 g, 64% yield based on K₈[γ -SiW₁₀O₃₆] \cdot 12H₂O).

In the IR spectrum a strong band at 2077 cm⁻¹ assigned to the asymmetric stretching vibration of the azido ligands. IR (KBr): $\bar{\nu}$ = 2077, 995, 958, 914, 893, 874, 809, 692, 550, 512, 470, 459 cm⁻¹.

2.5. Synthesis of β -K₁₀[SiW₉O₃₇{(Cu(H₂O))₃}]⁵

To a solution of copper(II) acetate (3.0 g, 15 mmol) in 0.5 mol dm⁻³ sodium acetate (pH 6.5, 150 cm³) was added β -SiW₉ (12.8 g, 4.5 mmol). An initially formed blue precipitate redissolved to form a green solution. After cation-exchange treatment, a solution of KCl (4 g) in water (12 cm³) was added. A green oil was formed that upon stirring changed to a green solid. The latter was recrystallized from water to yield green crystals (7.8 g). The main vibrational frequencies in IR (KBr): $\bar{\nu}$ = 997, 957, 897, 788, 660, 539, 438 cm⁻¹.

2.6. Synthesis of K₁₂Li₁₃[Cu₂₀Cl(OH)₂₄(H₂O)₁₂(P₈W₄₈O₁₈₄)] \cdot 22H₂O (Cu₂₀ POM)⁶

A sample of CuCl₂ \cdot 2H₂O (0.60 mmol) was dissolved in a 1M LiCH₃COO buffer solution (20 mL) at pH 6.0, then K₂₈Li₅[H₇P₈W₄₈O₁₈₄] \cdot 92H₂O (0.025 mmol) was added. This solution was heated to 80 °C for 1 h and after cooling to room temperature it was filtered. The filtrate was allowed to evaporate at room temperature. After 1–2 days a blue crystalline product started to appear. Evaporation was allowed to continue until the solution level had approached the solid product, which was then collected by filtration and air-dried. Yield: 30%. IR: $\bar{\nu}$ = 1136(sh), 1121(s), 1080(s), 1017(m), 979(sh), 950(sh), 932(s), 913(sh), 830(sh), 753(s), 683(s), 570(sh), 525(w) cm⁻¹.

Elemental analysis data for $\text{K}_{12}\text{Li}_{13}[\text{Cu}_{20}\text{Cl}(\text{OH})_{24}(\text{H}_2\text{O})_{12}(\text{P}_8\text{W}_{48}\text{O}_{184})]$: Calcd.: K: 3.2, Li: 0.6, W: 59.2, Cu: 8.5, P: 1.7; found: K: 3.35, Li: 0.71, W: 60.1, Cu: 8.3, P: 1.6 (Figures S1-S5).

3. General procedure for the three-component synthesis of 1,2,3-triazoles

A 10 mL glass vessel was charged with Cu_{20}POM catalyst (10 μmol), sodium ascorbate (10 mol %), an alkyne (0.5 mmol), sodium azide (0.5 mmol), and an alkyl halide (0.5 mmol) in a mixture of water and *tert*-butyl alcohol (2:1; 3 mL). The reaction vessel was stirred at room temperature for 2–4h and the color of reaction mixture was changed from blue to yellow during the progress of reaction. After completion of the reaction, colorless triazole product was precipitated (Figures S6–S12). The products were quantitatively recovered by simple extraction with ethyl acetate (3 \times 2 mL). The organic layer was separated, dried over MgSO_4 and concentrated under reduced pressure to give the corresponding 1,2,3-triazole. Purification of the obtained triazoles were accomplished by a recrystallization process (EtOAc:*n*-hexane). All of the products were known and characterized by comparison their spectral data with authentic samples.

The reaction with benzyl bromide and phenyl acetylene was used for investigation the recyclability. Upon the completion of the reaction, the mixture was diluted with H_2O /ethyl acetate (1:1.6 mL), then the aqueous phase was separated and this operation was repeated three times. After removing the solvent by evaporation and drying the catalyst, the cycloaddition reaction was performed with the recovered catalyst. This catalyst could be reused three times without any significant loss of activity.

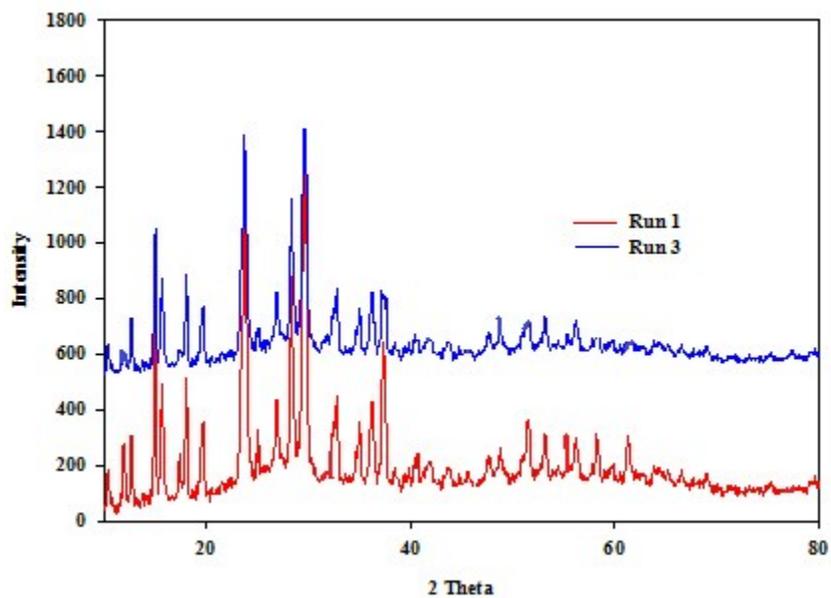


Figure S1. The XRD pattern of Cu_{20} POM in Run 1 (red) and recovered in run 3 (blue).

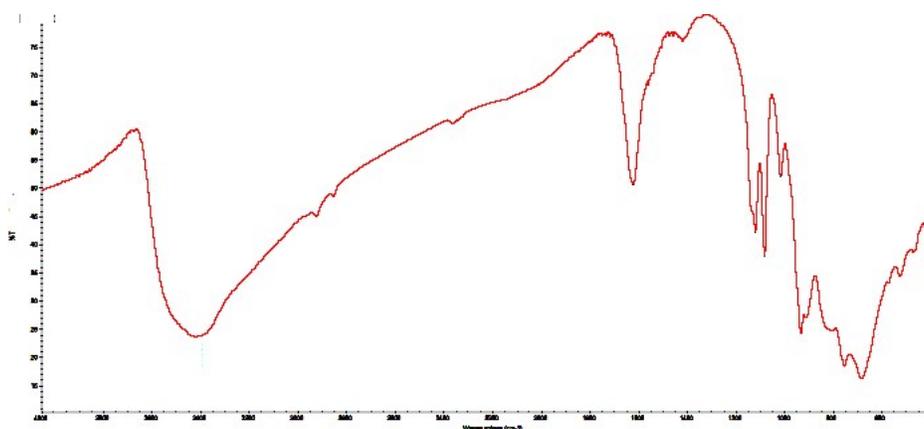


Figure S2. FT-IR Spectrum of Cu_{20} POM

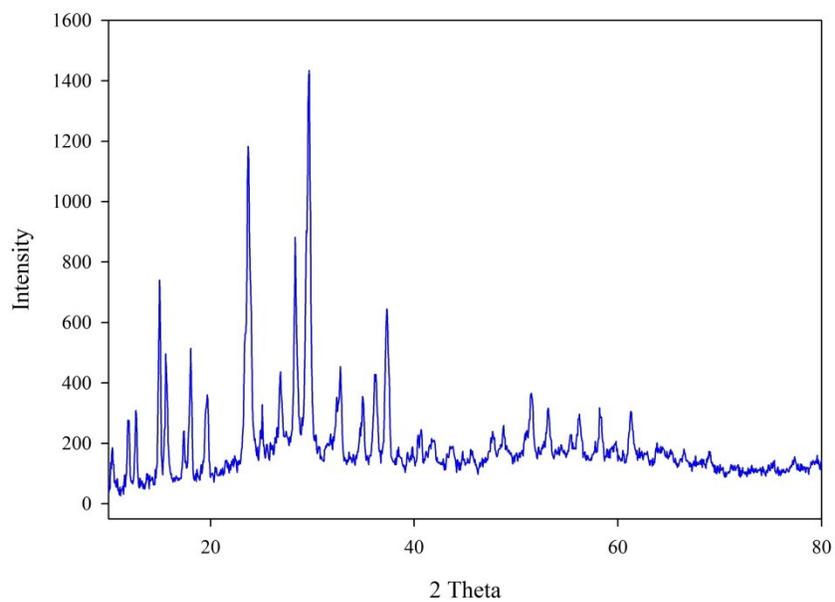


Figure S3. XRD pattern of Cu₂₀ POM

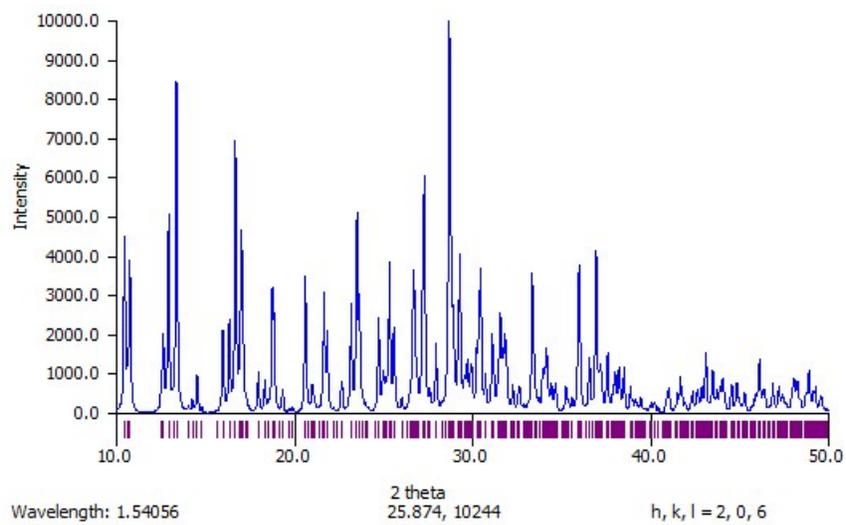


Figure S4. Simulated XRD pattern of Cu₂₀ POM

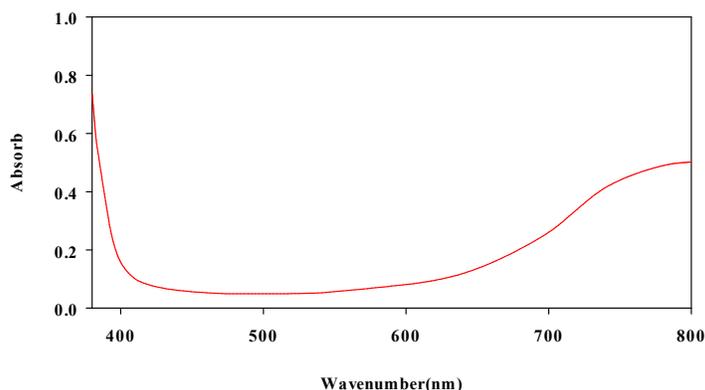


Figure S5. UV-vis spectrum of Cu₂₀ POM solution

¹H and ¹³C NMR data of isolated compounds: NMR data are in agreement with the literature references^{7–10}.

1-Benzyl-4-phenyl-1H-1,2,3-triazole: Colorless solid; ¹H NMR (400 MHz, CDCl₃): δ: 7.80 (d, 2H), 7.65 (s, 1H), 7.31–7.40 (m, 8H), 5.57 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ: 54.41, 119.48, 125.65, 128.10, 128.09, 128.74, 129.08, 134.59, 148.15.

1-Benzyl-4-propyl-1H-1,2,3-triazole: Light yellow liquid oil; ¹H NMR (400 MHz, CDCl₃): δ: 0.94–1.01 (t, 3H), 1.63–1.77 (m, 2H), 2.64–2.75 (t, 2H), 5.53 (s, 2H), 7.24–7.30 (m, 2H, ArH), 7.33–7.45 (m, 4H, ArH). ¹³C NMR (100 MHz, CDCl₃) δ: 13.47, 22.34, 27.36, 53.59, 120.51, 127.60, 128.23, 128.69, 134.77, 148.26.

1-(2-Chlorobenzyl)-4-phenyl-1H-1,2,3-triazole: White solid; ¹H NMR (400 MHz, CDCl₃): δ: 5.75 (s, 2H), 7.24–7.39 (m, 4H, ArH), 7.40–7.50 (m, 3H, ArH), 7.81 (s, 1H, ArH), 7.82–7.89 (d, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃) δ: 52.06, 119.88, 123.30, 125.91, 127.72, 128.77, 128.82, 129.06, 131.05, 130.27, 132.28, 133.01, 148.17.

1-(4-Nitrobenzyl)-4-phenyl-1H-1,2,3-triazole: Yellowish solid, ¹H NMR (400 MHz, CDCl₃): δ: 5.73 (s, 2H), 7.34–7.41 (t, 1H, ArH), 7.41–7.52 (m, 4H, ArH), 7.79 (s, 1H, ArH), 7.81–7.89 (d,

2H, ArH,), 8.20–8.32 (d, 2H, ArH). ^{13}C NMR (CDCl_3) δ : 13.9, 22.4, 25.5, 28.8, 29.2, 31.4, 52.8, 120.7, 124.0, 124.1, 127.7, 128.3, 142.0, 147.8, 149.4.

1-(4-Bromobenzyl)-4-hexyl-1H-1,2,3-triazole: White solid · ^1H NMR (400 MHz, CDCl_3): δ : 7.42–7.40 (d, $J = 8.42$ Hz 2H), 7.12 (s, 1H), 7.005 (m, 2H), 5.36 (s, 2H), 2.62–2.38 (t, 2H), 1.59–1.40 (m, 2H), 1.25–1.15 (m, 6H), 0.80–0.77 (t, 3H). ^{13}C NMR (CDCl_3) δ : 149.1, 133.9, 132.1, 129.4, 128.7, 122.6, 120.4, 53.1, 31.4, 29.2, 28.8, 25.6, 22.4, 13.9 ppm.

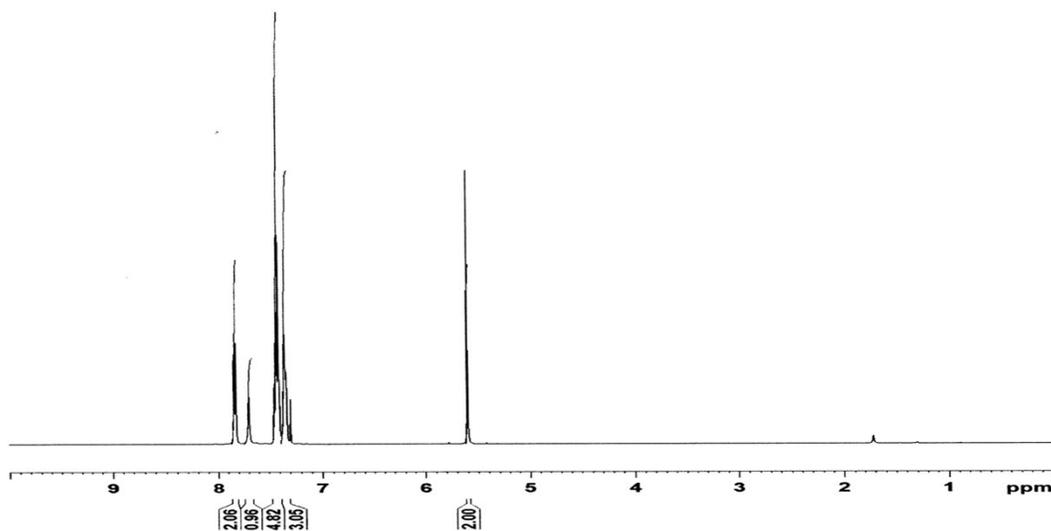


Figure S6. ^1H NMR spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole

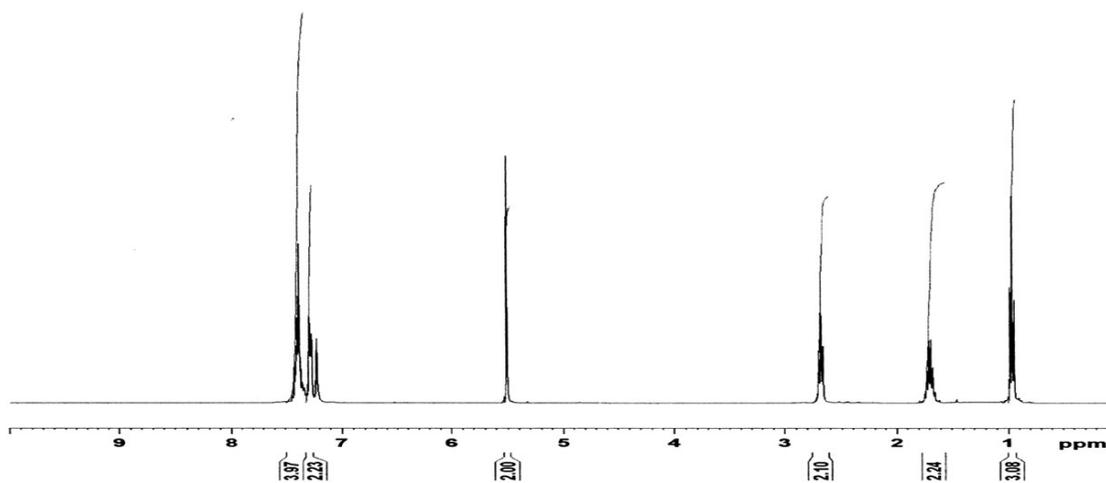


Figure S7. ^1H NMR spectrum of 1-Benzyl-4-propyl-1H-1,2,3-triazole

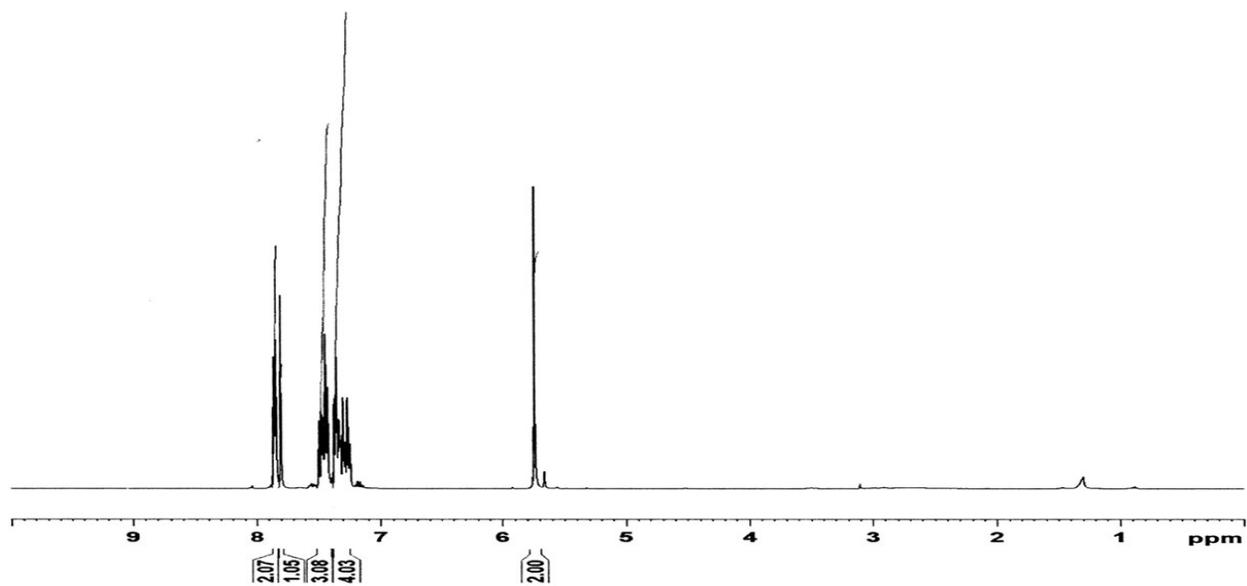


Figure S8. 1-(2-Chlorobenzyl)-4-phenyl-1H-1,2,3-triazole

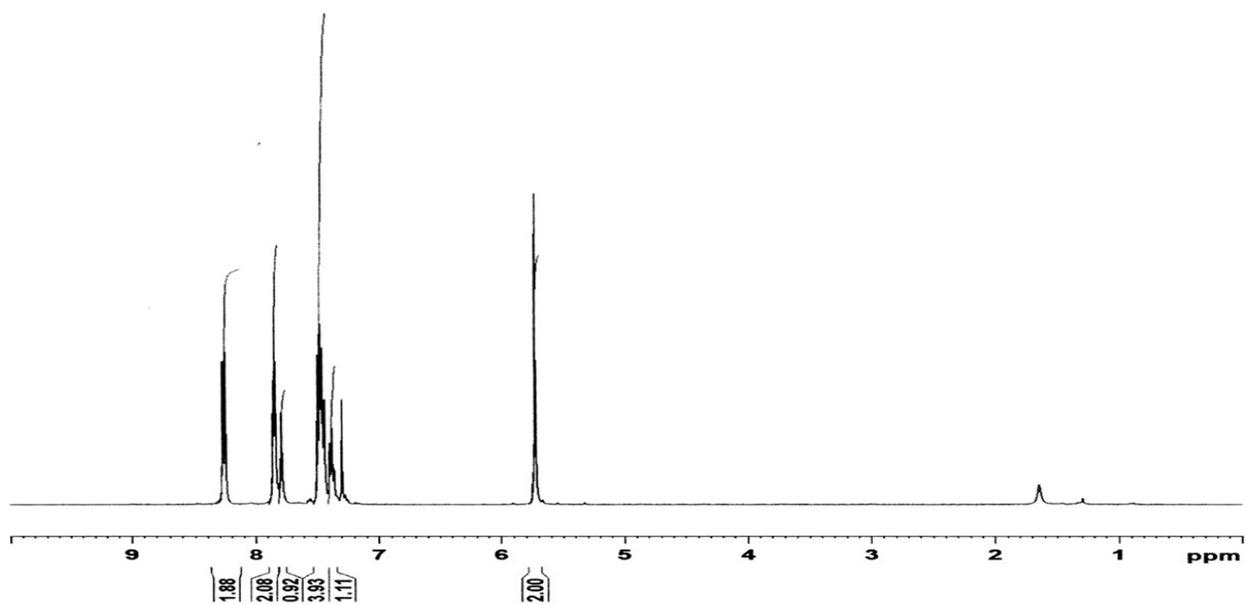


Figure S9. 1-(4-Nitrobenzyl)-4-phenyl-1H-1,2,3-triazole

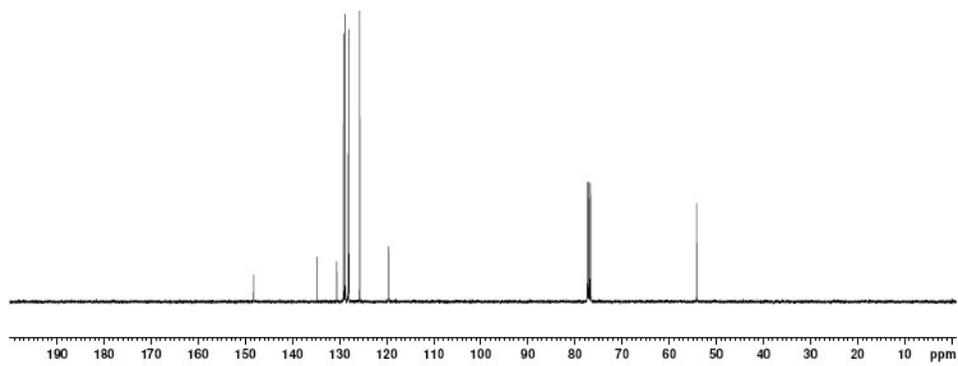


Figure S10. ¹³C NMR spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole

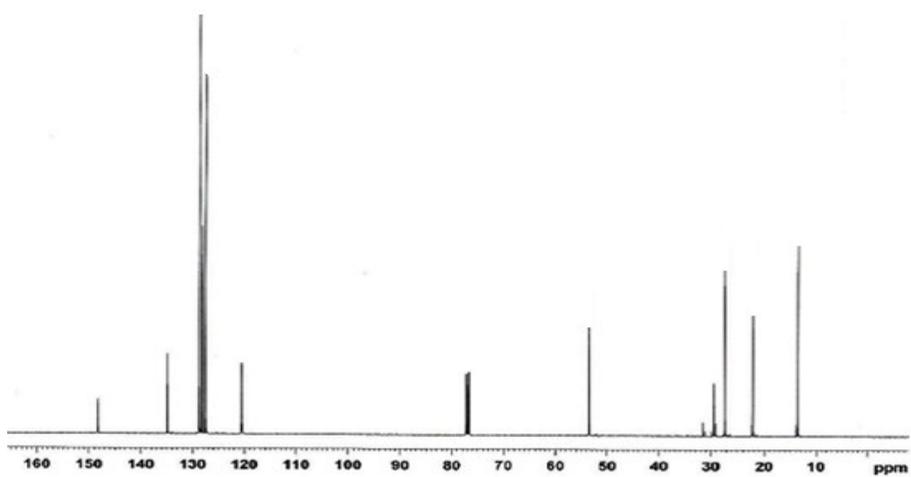


Figure S11. ¹³C NMR spectrum of 1-Benzyl-4-propyl-1H-1,2,3-triazole

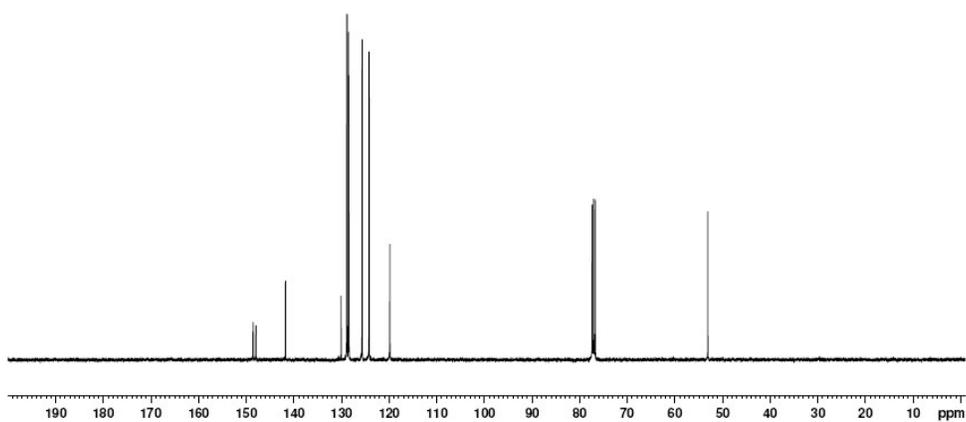


Figure S12. ¹³C NMR spectrum of 1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole

References

1. M. R. Farsani, B. Yadollahi, H. A. Rudbari, A. Amini, T. Caradoc-Davis and J. R. Price, *Inorg. Chem. Commun.*, 2014, **43**, 39-44.
2. R. Contant, *Inorg. Synth.*, 1990, **27**, 110-111.
3. R. G. Finke, M. W. Droegge and P. J. Domaille, *Inorg. Chem.*, 1987, **26**, 3886-3896.
4. K. Yamaguchi, K. Kamata, S. Yamaguchi, M. Kotani and N. Mizuno, *J. Catal.*, 2008, **258**, 121-30.
5. J. Liu, F. Ortéga, P. Sethuraman, D. E. Katsoulis, C. E. Costello and M. T. Pope, *J. Chem. Soc., Dalton Trans.*, 1992, 1901-1906.
6. S. S. Mal and U. Kortz, *Angew. Chem. Int. Ed.*, 2005, **44**, 3777-3780
7. C. Shao, X. Wang, Q. Zhang, S. Luo, J. Zhao and Y. Hu, *J. Org. Chem.*, 2011, **76**, 6832-6836.
8. X. Meng, X. Xu, T. Gao and B. Chen, *Eur. J. Org. Chem.*, 2010, 5409-5414.
9. S. Chassaing, A. S. S. Sido, A. Alix, M. Kumarraja, P. Pale and J. Sommer, *Chem. Eur. J.*, 2008, **14**, 6713-6721.
10. A. N. Prasad, B. M. Reddy, E-Y. Jeong and S-E. Park, *RSC Adv.*, 2014, **4**, 29772-781.