Electronic Supplementary Information

The binuclear Cu(I)complex as novel catalyst towards direct synthesis of N–2–aryl–substituted–1,2,3–triazoles from chalcones

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Table of Contents

Materials and methods

All chemicals were purchased from Sigma-Aldrich Chemicals, USA and Merck Chemicals, India, and used without further purification. Solvents were purified by standard methods. Thin layer chromatography (TLC) was performed on Merck Kieselgel 60 GF_{254} plates (thickness 0.25 mm). Visualization was performed with a 254 nm UV lamp and by staining in I_2 chamber. All the reactions were carried out under an open atmosphere using oven-dried glassware.

Physico-chemical measurements

C, H and N contents were determined on an Exeter Analytical Inc. CHN Analyzer (Model CE–440). The copper content in the complex was analyzed gravimetrically as CuSCN after decomposing the organic matter with a mixture of conc. HNO_3 and HCl and by employing the standard literature procedure.[1] ^{1}H, ^{13}C and ^{31}P NMR spectra of the compounds were recorded in DMSO-d_6 on a JEOL AL-300 FT-NMR multinuclear spectrometer. Chemical shifts were reported in parts per million (ppm) using tetramethylsilane (TMS) as an internal standard. All exchangeable protons were confirmed by addition of D_2O. Infrared spectra were recorded in KBr on a Varian 3100 FT-IR spectrophotometer in 4000–400 cm^{-1} region.

Crystal structure determination

Single crystal X–ray diffraction data of H_2bioh ligand and its Cu(I) complex was obtained at 295(2) K, on a Oxford Diffraction Gemini diffractometer equipped with CrysAlis Pro., using a graphite mono-chromated Mo Kα (λ = 0.71073 Å) radiation source. The structure was solved by direct methods (SHELXL–97) and refined against all data by full matrix least-square on F2 using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included in the refinement at geometrically ideal position and refined with a riding model.[2, 3] The MERCURY package and ORTEP–3 for Windows program were used for generating structures.[4, 5]

Fig. S1. ^{1}H NMR spectra of the ligand (H_2bioh).

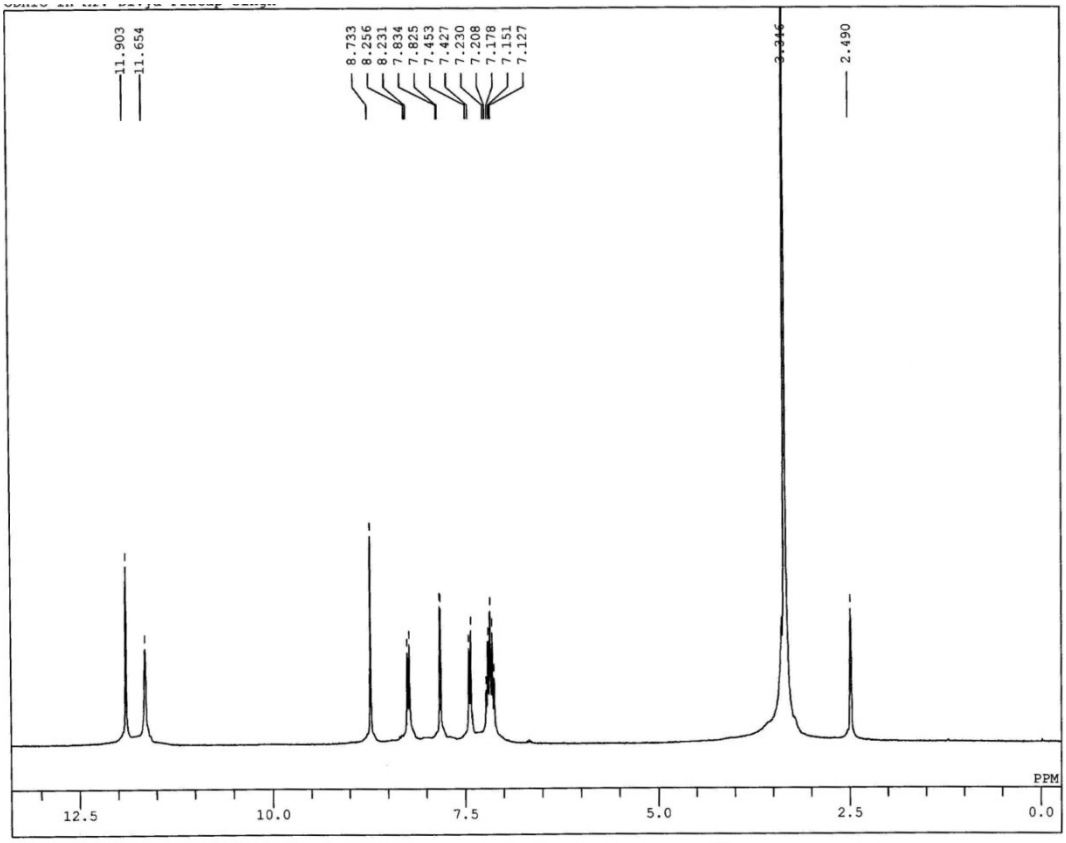


Fig. S2. ^{1}H NMR spectra of Cu(I) complex.

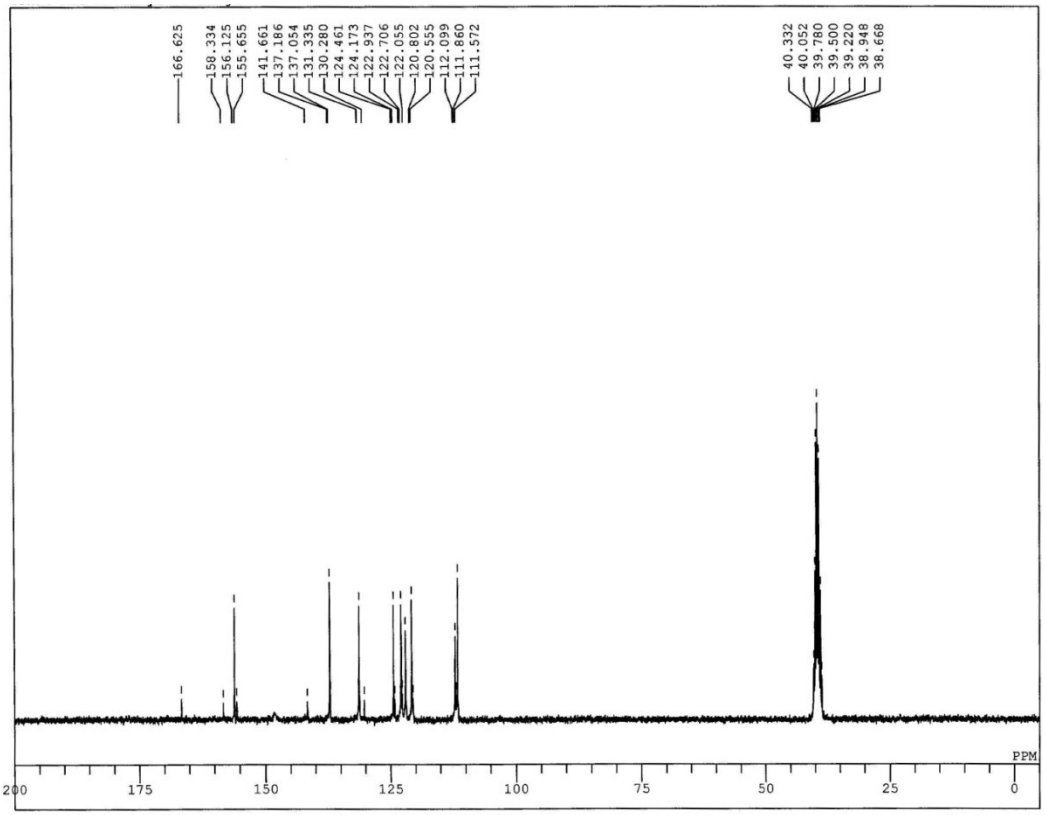


Fig. S3. ^{13}C NMR spectra of the ligand (H_2bioh).

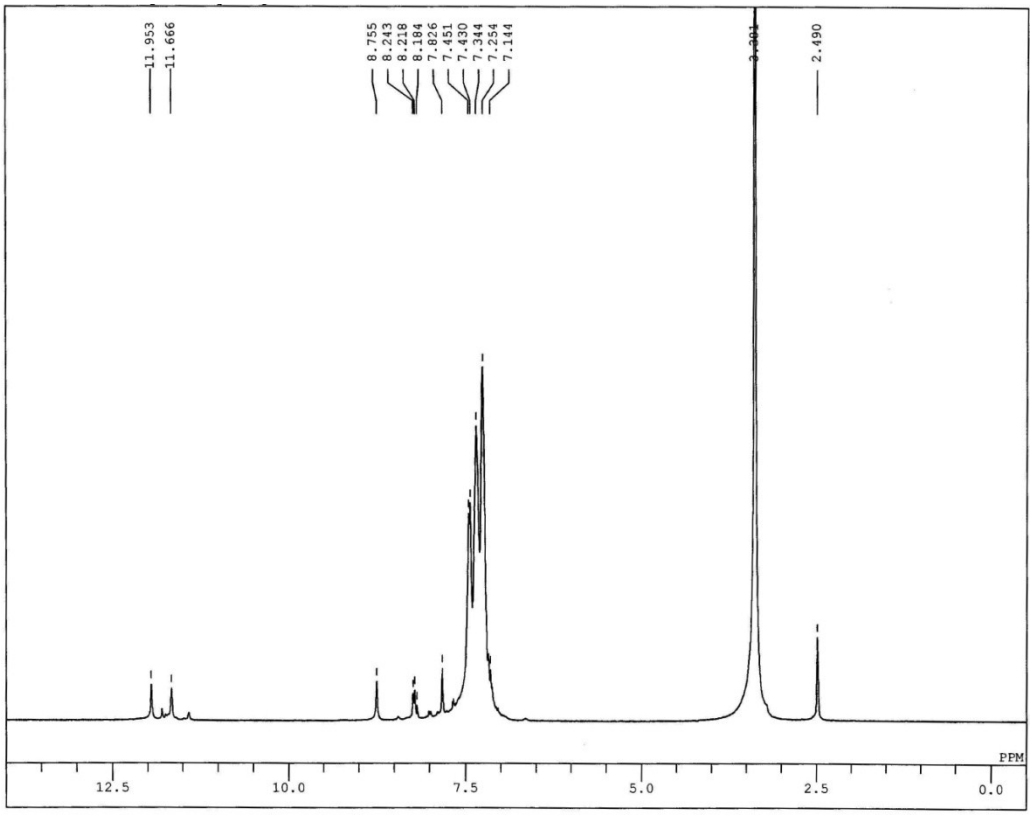


Fig. S4. ^{13}C NMR spectra of Cu(I) complex.

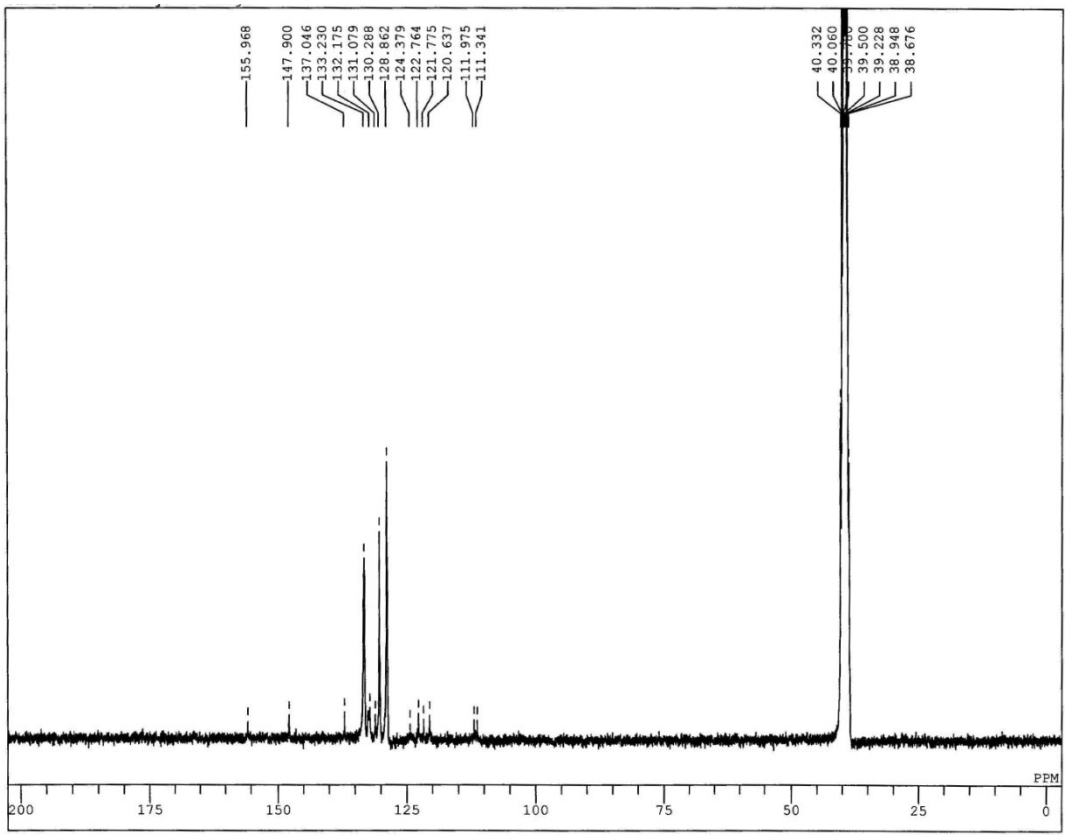


Fig. S5. Diagram showing inter-molecular H–bonding interactions in the H_2bioh.

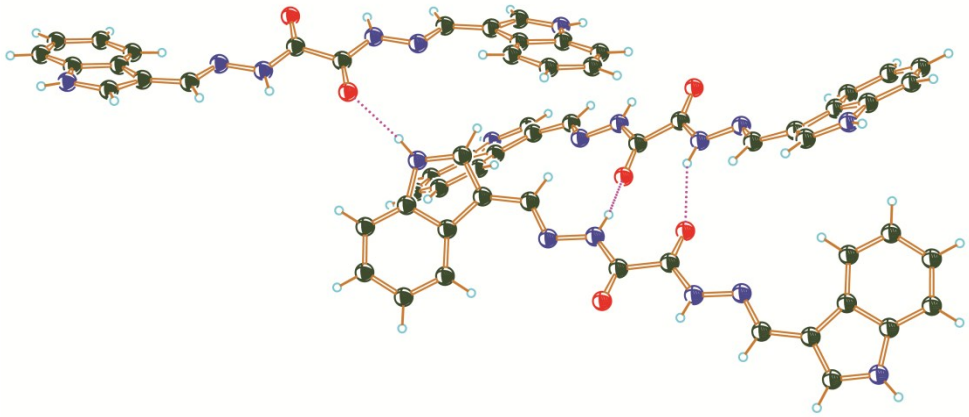


Fig. S6. Diagram of $[Cu_2(H_2bioh)(PPh_3)_4]\cdot(NO_3)_2(CH_3OH)_2$ complex forming supra-molecular architecture along 'c'-axis.

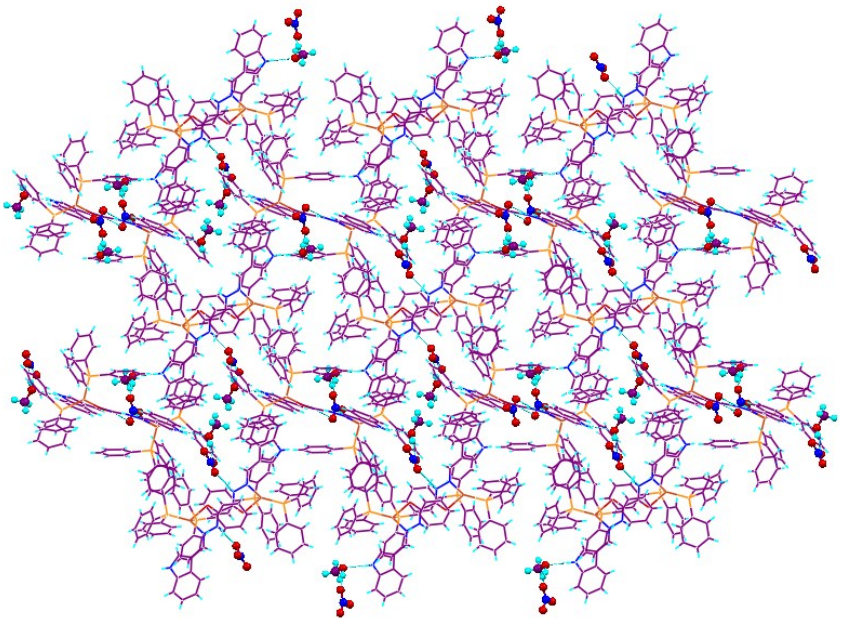


Table S1 Crystallographic data for H_2bioh and $[Cu_2(H_2bioh)(PPh_3)_4]\cdot(NO_3)_2(CH_3OH)_2$

	H_2bioh	$[Cu_2(H_2bioh)(PPh_3)_4]\cdot(NO_3)_2(CH_3OH)_2$
Empirical Formula	$C_{20}H_{16}N_6O_2$	$C_{94}H_{82}Cu_2N_8O_{10}P_4$
Formula weight	372.39	1734.64
Temp, K	293(2)	293(2)
λ (Å)	0.71073	0.71073
Crystal system	orthorhombic	Monoclinic
Space group	Pbcn	P 21/c
a (Å)	18.537(2)	12.5570(14)
b (Å)	10.3318(16)	21.963(2)
c (Å)	9.9527(10)	16.5060(18)
α (º)	90°	90°
β (º)	90°	103.072(10)°
γ (º)	90°	90°
V (Å^3)	1906.1(4)	4434.3(8)
Z	4	2
D_{calc} (g/cm^3)	1.2977(3)	1.299
μ (mm^{-1})	0.089	0.614
F(000)	776.0	1800
Crystal size (mm)	0.20x 0.18x 0.16	0.38 x 0.37 x 0.36
θ range for data collection (º)	3.59 to 29.13	3.14 - 29.22
No. of reflections collected	5521	23291
No. of independent reflections (R_{int})	2222 (0.0490)	10283 (0.0373)
Number of data/restraints/ parameters	2222 / 0 / 127	10283 / 0 / 538
Goodness-of-fit on F^2	1.053	1.014
R_1, wR_2 [a,b] [(I>2σ(I))]	0.0684, 0.0973	0.0565, 0.1172
R_1, wR_2 [a,b] (all data)	0.1502, 0.1237	0.1073, 0.1413
Largest difference in peak and hole (e.Å^{-3})	0.155 and -0.199	0.397 and -0.296

[a] $R_1 = \Sigma||F_o| - |Fc||\Sigma|F_o|$.

[b] $R_2 = [\Sigma w(|F^2_o| - |F^2_c|)^2/\Sigma w|F^2_o|^2]^{1/2}$

Table S2 Selected bond lengths (Å) and angles (°)

	H_4bioh	$[Cu_2(H_2bioh)(PPh_3)_4]\cdot(NO_3)_2(CH_3OH)_2$
Bond length		
O(1)-C(10)	1.236(2)	1.228(3)
N(2)-C(9)	1.285(3)	1.294(3)
N(2)-N(3)	1.390(2)	1.398(3)
N(3)-C(10)	1.319(2)	1.325(4)
C(2)-C(9)	1.425(3)	1.426(4)
N(1)-C(1)	1.346(3)	1.357(4)
N(1)-C(8)	1.376(3)	1.386(4)
Cu(1)-O(1)		2.197(18)
Cu(1)-N(2)		2.076(2)
Cu(1)-P(1)		2.235(9)
Cu(1)-P(2)		2.288(9)
Bond angles		
O(1)-C(10)-N(3)	125.21(19)	125.1(2)
C(10)-N(3)-N(2)	120.38(17)	117.3(2)
C(9)-N(2)-N(3)	113.67(19)	113.9(2)
N(2)-C(9)-C(2)	122.6(2)	124.5(3)
C(1)-C(2)-C(3)	106.0(2)	106.9(2)
C(9)-C(2)-C(3)	131.2(2)	123.6(3)
C(1)-N(1)-C(8)	109.5(2)	108.7(3)
C(10)-O(1)-Cu(1)		107.97(17)
C(9)-N(2)-Cu(1)		136.12(19)
N(3)-N(2)-Cu(1)		109.99(17)
N(2)-Cu(1)-O(1)		77.77(8)
O(1)-Cu(1)-P(1)		115.72(6)
O(1)-Cu(1)-P(2)		92.51(6)
N(2)-Cu(1)-P(1)		122.38(7)
N(2)-Cu(1)-P(2)		111.90(7)
P(1)-Cu(1)-P(2)		122.24(3)

Table S3 Hydrogen bond parameters [Å and °] in H_2bioh

D−H···A	D−H	H···A	D···A	< (DHA)
N(1)−H(1A)···O(1)	0.86	2.10	2.920(3)	159
N(3)−H(3A)···O(1)	0.86	2.34	2.696(2)	105
N(3)−H(3A)···O(1)	0.86	2.09	2.882	153

1-x,-y,-z; 1/2-x,1/2-y,1/2+z; x,-y,1/2+z

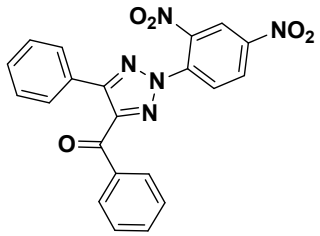
Hydrogen bond parameters [Å and °] in $[Cu_2(H_2bioh)(PPh_3)_4]\cdot(NO_3)_2(CH_3OH)_2$

D−H···A	D−H	H···A	D···A	< (DHA)
N(1)−H(1A)···O(2)	0.86	1.96	2.790(4)	163
O(2)−H(2A)···O(3)	0.82	1.95	2.759(5)	169
N(3)−H(3A)···O(3)	0.96(3)	2.52(3)	3.232(4)	131(2)
N(3)−H(3A)···O(4)	0.96(3)	1.99(3)	2.909(4)	160(3)
C(9)−H(9)···O(4)	0.93	2.43	3.257(4)	149
C(14)−H(14)···O(4)	0.93	2.55	3.474(6)	171
C(28)−H(28)···O(1)	0.93	2.56	3.459(4)	164
C(40)−H(40)···O(4)	0.93	2.58	3.337(5)	139

-1/2+x,1/2-y,-1/2+z; -1/2+x,1/2-y,1/2+z
3/2-x,1/2+y,1/2-z; 1/2-x,1/2+y,1/2-z

Spectral data for some representative products:

(2-(2,4-dinitrophenyl)-5-phenyl-2*H*-1,2,3-triazol-4-yl)(phenyl)methanone (4a):



^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.67 (s, 1H), 8.66–8.56 (m, 1H), 8.55–8.52 (m, 1H), 8.35–8.02 (m, 1H), 8.07–8.04 (m, 2H), 7.85–7.83 (m, 2H), 7.68–7.63 (m, 1H), 7.55–7.45 (m, 1H), 7.45 (br s, 2H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.98, 162.0, 152.2, 146.4, 145.3, 142.5, 136.2, 134.9, 134.2, 130.4, 130.2, 128.8, 128.6, 127.8, 127.2, 125.3, 120.8 ppm.

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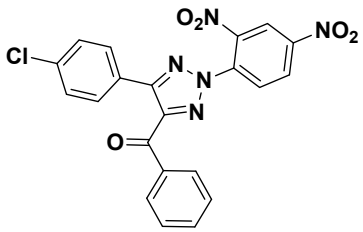
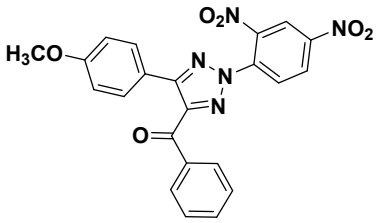


^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.67 (s, 1H), 8.66–8.54 (m, 1H), 8.34–8.32 (m, 1H), 8.06–8.04 (m, 2H), 7.83–7.80 (m, 2H), 7.69–7.64 (m, 1H), 7.55–7.50 (m, 2H), 7.42–7.26 (m, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.67, 158.99, 151.29, 146.5, 145.0, 142.5, 136.4, 136.0, 134.8, 134.3, 131.5, 130.4, 130.2, 128.9, 128.6, 127.2, 126.3, 125.4, 121.8, 121.2, 120.8 ppm.

(2-(2,4-dinitrophenyl)-5-(4-methoxyphenyl)-2H-1,2,3-triazol-4-yl)(phenyl)methanone (4g):



^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.68 (s, 1H), 8.59–8.56 (m, 1H), 8.38–8.35 (m, 1H), 8.08–8.05 (m, 2H), 7.86–7.83 (m, 2H), 7.67–7.64 (m, 1H), 7.56–7.51 (m, 2H), 6.99–6.96 (m, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.1, 161.2, 152.1, 146.3, 144.9, 136.3, 134.9, 134.1, 130.5, 130.4, 128.6, 127.1, 125.1, 120.8, 120.2, 114.1, 55.3 ppm.

References

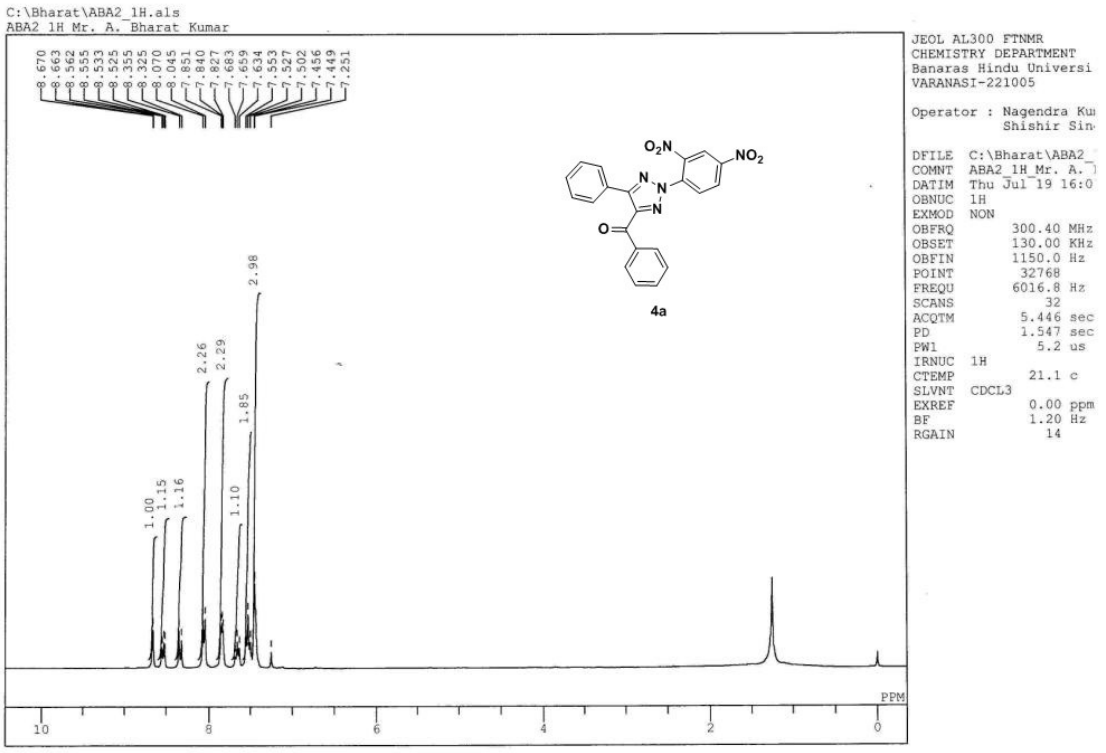
[1] G. H. Jeffery, J. Bassett, J. Mendham, R. C. Denney, *Vogel's Textbook of Quantitative Chemical Analyses*, fifth ed., Longman, Amsterdam, 1989.

[2] G. M. Sheldrick, Acta Crystallogr. Sect. A: Found. Crystallogr. 64 (2008) 112–122.

[3] G. M. Sheldrick, SHELXL–97, Program for Crystal Structure Refinement, University of Gottingen, Germany, 1997.

[4] I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson, R. Taylor, Acta Crystallogr. Sect. B, 58 (2002) 389.

[5] L. J. Farrugia, J. Appl. Crystallogr., 30 (1997) 565–566.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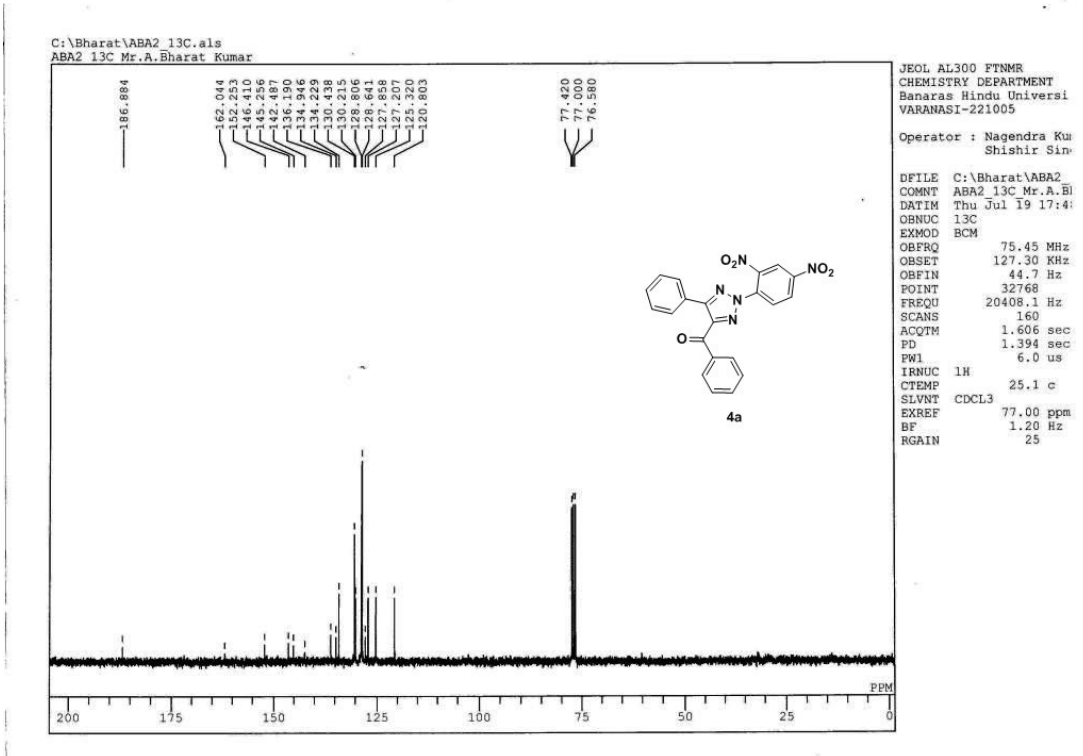
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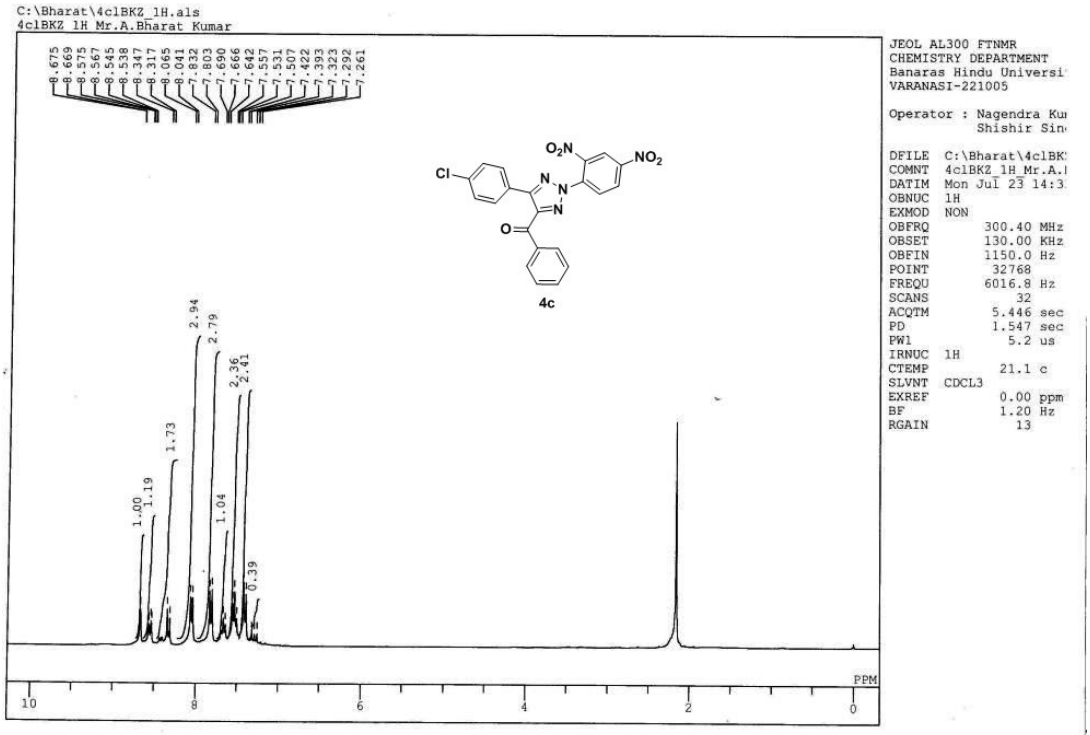
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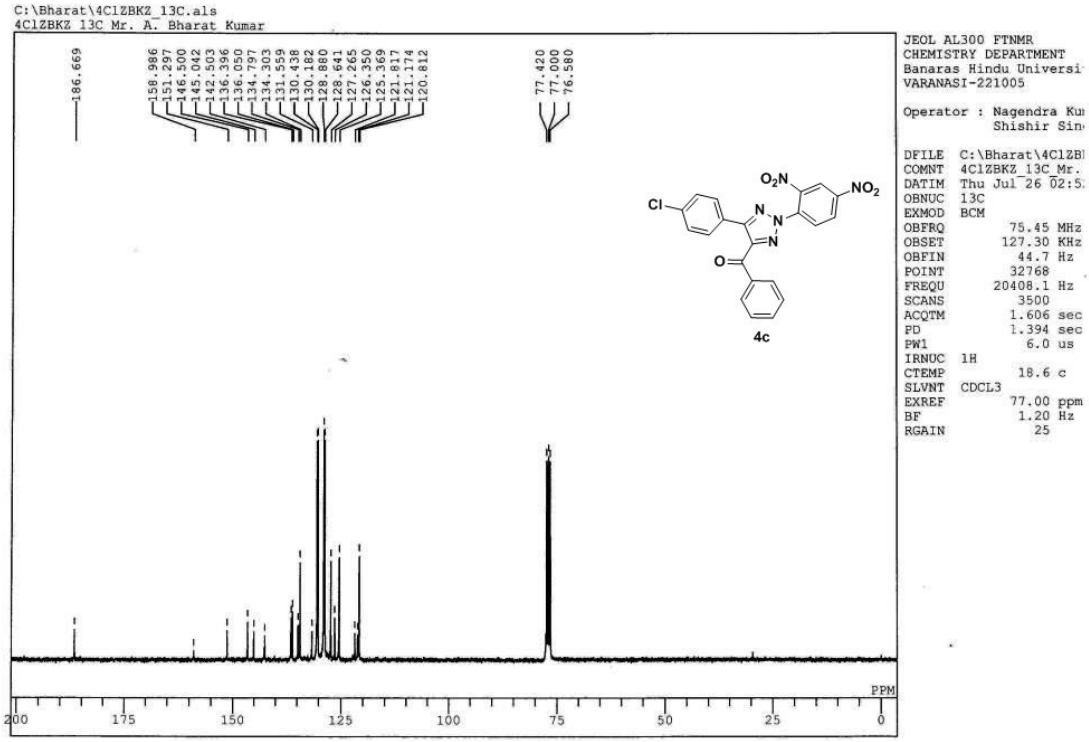
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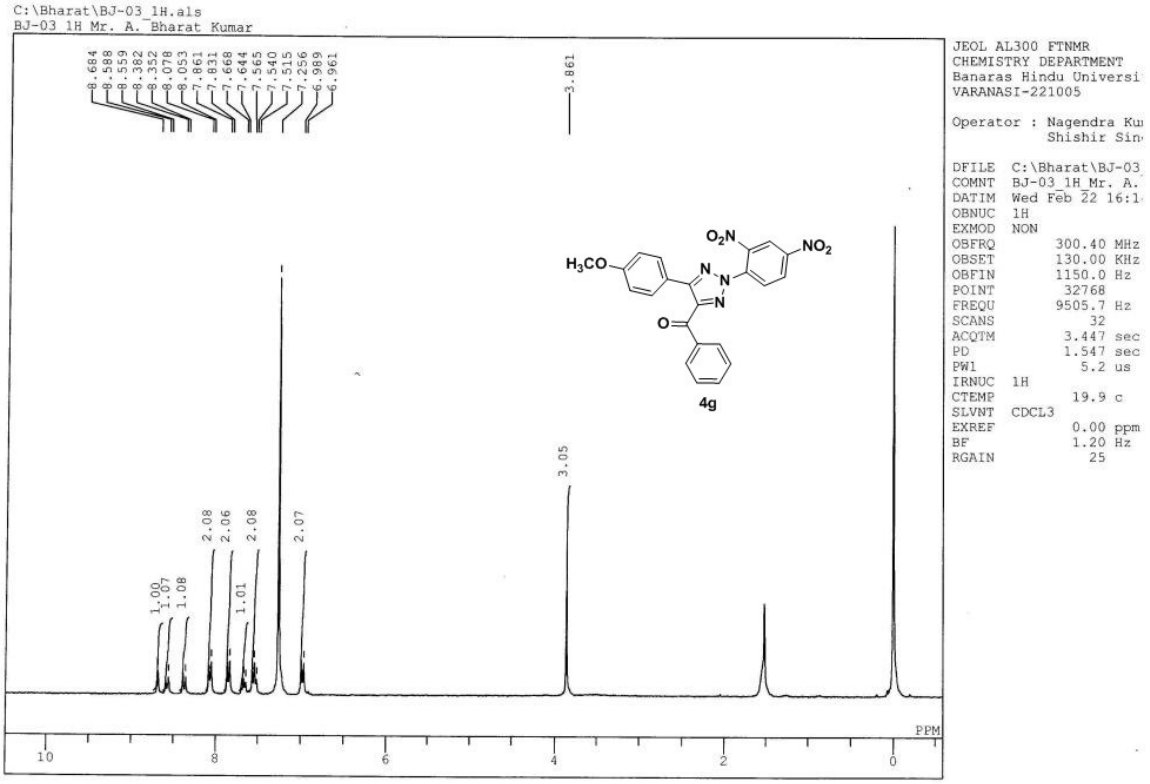
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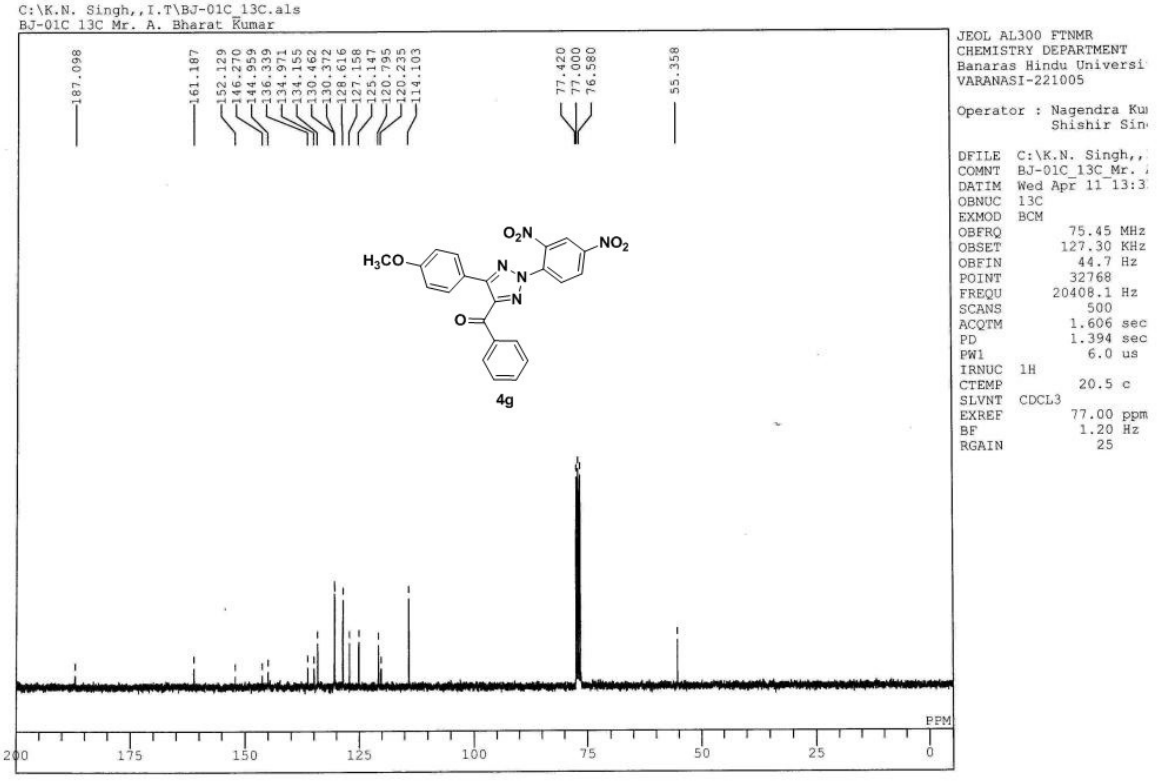
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ACQTM 1.606 sec
PD 1.394 sec
PW1 6.0 us
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25