Supplementary data

On water synthesis of pyran-chromenes *via* multicomponent reactions catalyzed by fluorescent t-ZrO2 nanoparticles

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Materials: All the chemicals and reagents used in this work have been purchased from Sigma Aldrich without out further purification. The solvents were purchased from Himedia Pvt. Ltd. and distilled before use. Deionised water was used wherever required.

ESI-1. Method for the preparation of *t*-ZrO_2 nanoparticles:

t-ZrO_2 nanoparticles (NPs) have been synthesized by dissociation of $ZrO_2Cl_2.8H_2O$ in a basic medium (pH~10) at low temperature without adding any stabiliser. For synthesizing *t*-ZrO_2 NPs, 40 ml 0.05M NaOH solution in distilled water was added in 100 ml 0.005M solution of $ZrO_2Cl_2.8H_2O$ in methanol-water (1:1) drop by drop over 30 minutes at constant temperature (5 ^oC) with continuous stirring. The mixture was then stirred for 1 hour. Subsequently, the sol solution was aged at 100 ^oC for 24 hours with continuous stirring. After that, the solids were separated by centrifugation and washed with dilute solution of NH_4NO_3 until negative test for chloride ion followed by washed with de-ionized water (4x20 ml) and ethanol (2x10 ml). As prepared solids were dried well and then calcined at 500 ^oC for 4 hours. The formation of nano-sized *t*-ZrO_2 particles was confirmed by powder XRD, HRTEM, SEM and UV-Vis studies.

ESI-2. Characterization of *t*-ZrO_2 nanoparticles:

a) Size distribution of *t*-ZrO_2 nanoparticles by HRTEM:

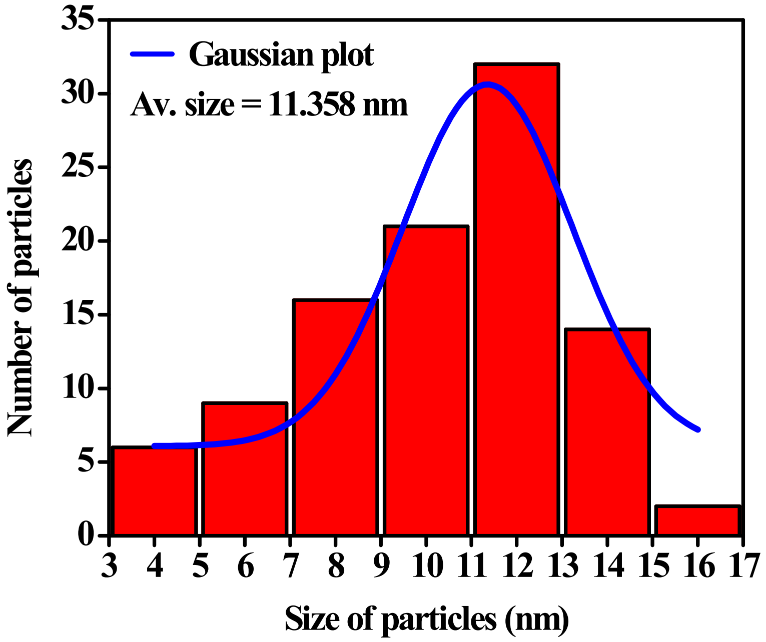


Fig. S1. Size distribution histogram of *t*-ZrO_2 NPs by HRTEM analysis over 100 particles.

b) EDX analysis of fresh *t*-ZrO_2 nanoparticles:

	Wt% of Zr	**Wt% of O**	**Wt% ratio (Zr:O)**	**Av. %age of oxygen vacancies**
Expected	74.03	25.97	2.85	~2.52
EDX result (Av.)	76.55	23.45	3.26	

ESI-3. Method for the preparation and characterization of *m*-ZrO_2 nanoparticles:

a) Method for the preparation of *m*-ZrO_2 nanoparticles:

m-ZrO_2 nanoparticles (NPs) have been synthesized by dissociation of $ZrO_2Cl_2.8H_2O$ in a basic medium (pH~10) at low temperature without adding any stabiliser following the above mentioned procedure (ESI-1) and calcined at 800 ^oC for 4 hours. The formation of m-ZrO2 NPs were confirmed by powder XRD analysis and the results were in good agreement with that of our previous report in Green Chemistry, 2015, 17, 2859 (The spectra was not given here).

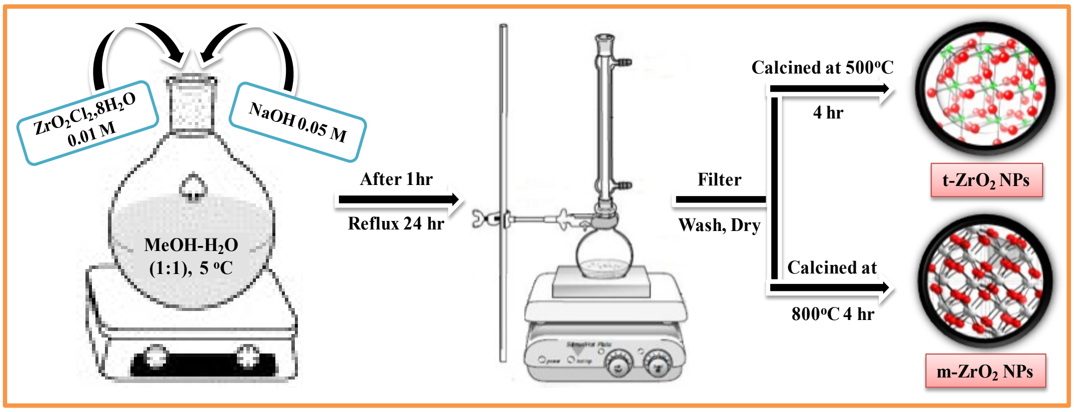


Fig. S2. Schematic representation for the synthesis of tetragonal (*t*) and monoclinic (*m*) ZrO_2 nanoparticles.

ESI-4. Experimental procedure for the synthesis of 2-Amino-3-cyano-4-phenyl-4H-benzo[*h*]chromene:

A mixture of the benzaldehyde (1 mmol, 106 mg), malononitrile (1 mmol, 66 mg), 1-naphthol (1 mmol, 144 mg) and *t*-ZrO_2 catalyst (10 mmol%, 12 mg) was refluxed in 5 mL water for 30 minutes indicated by TLC. After the completion of the reaction, the solid product along with catalyst were separated by simple filtration and then dissolve in hot ethanol and subjected to filtration to separate the catalyst. The separated catalyst was then washed with ethyl acetate and hot methanol. Pure yellow crystals were obtained through slow evaporation of the filtrate. Finally, the crystalline compounds were washed with ethanol to produce pure 2-amino-3-cyano-4-phenyl-4H-benzo[*h*]chromene (1a) (yield = 92%, 274 mg) as yellow solid (M.P = 205-207°C). Further the formation of the compound confirmed by ^{1}HNMR study. ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 4.71 (2H, s, NH_2), 4.85 (1H, s, CH). 7.06 (1H, d, J_{HH} = 8.5 Hz, Ar), 7.16 -7.32 (5H, m, Ar). 7.46 -7.64 (3H, m, Ar). 7.78 (1H, d, J_{HH} = 7.5 Hz, Ar), 8.14 (1H, d, J_{HH} = 7.5 Hz, Ar) ppm. These values are well accordance with the values reported in the literature.

ESI-5. Reusability study of *t*-ZrO_2 nanoparticles:

a) Powder XRD of reused *t*-ZrO_2 nanoparticles:

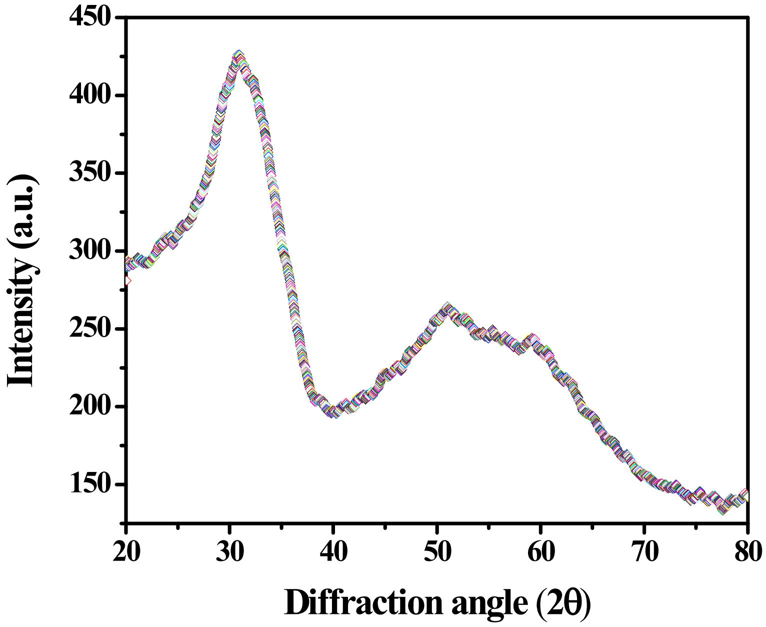


Fig. S3 Powder XRD pattern of t-ZrO2 nanoparticles after 10th cycle.

b) Fluorescence study of reused *t*-ZrO_2 nanoparticles:

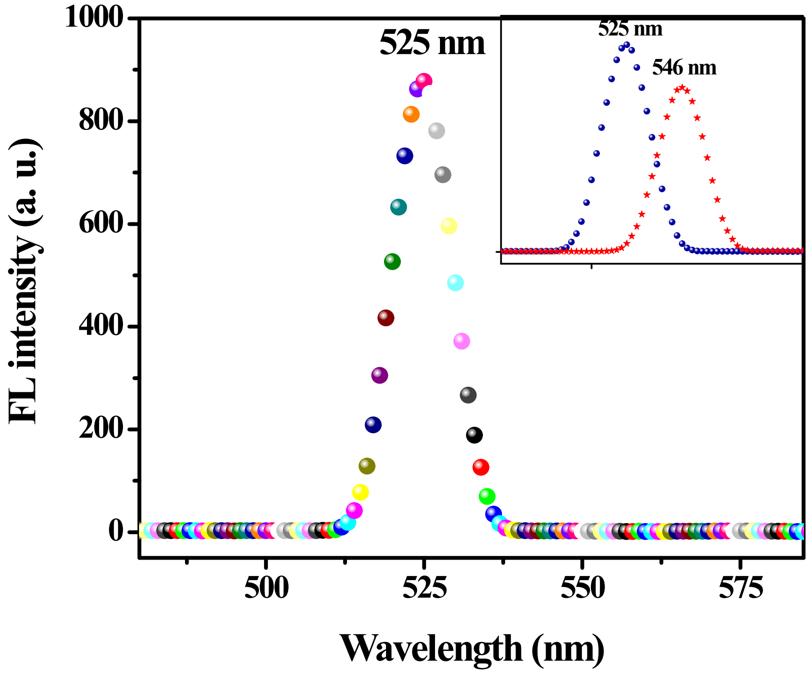


Fig. S4 Fluorescence spectrum of t-ZrO2 nanoparticles in water after 10th cycle ($\lambda_{excitation}$ = 260 nm).

c) Atomic Absorption Spectroscopic analysis of fresh and reused *t*-ZrO_2 nanoparticles:

Table 1 Wt percentage of Zr content in different run.

Run	**Wt % of Zr**
Fresh	**75.98**
1	**75.93**
5	**75.42**
10	**74.63**

d) FT-IR study of product obtained by using recycled ZrO_2 NPs:

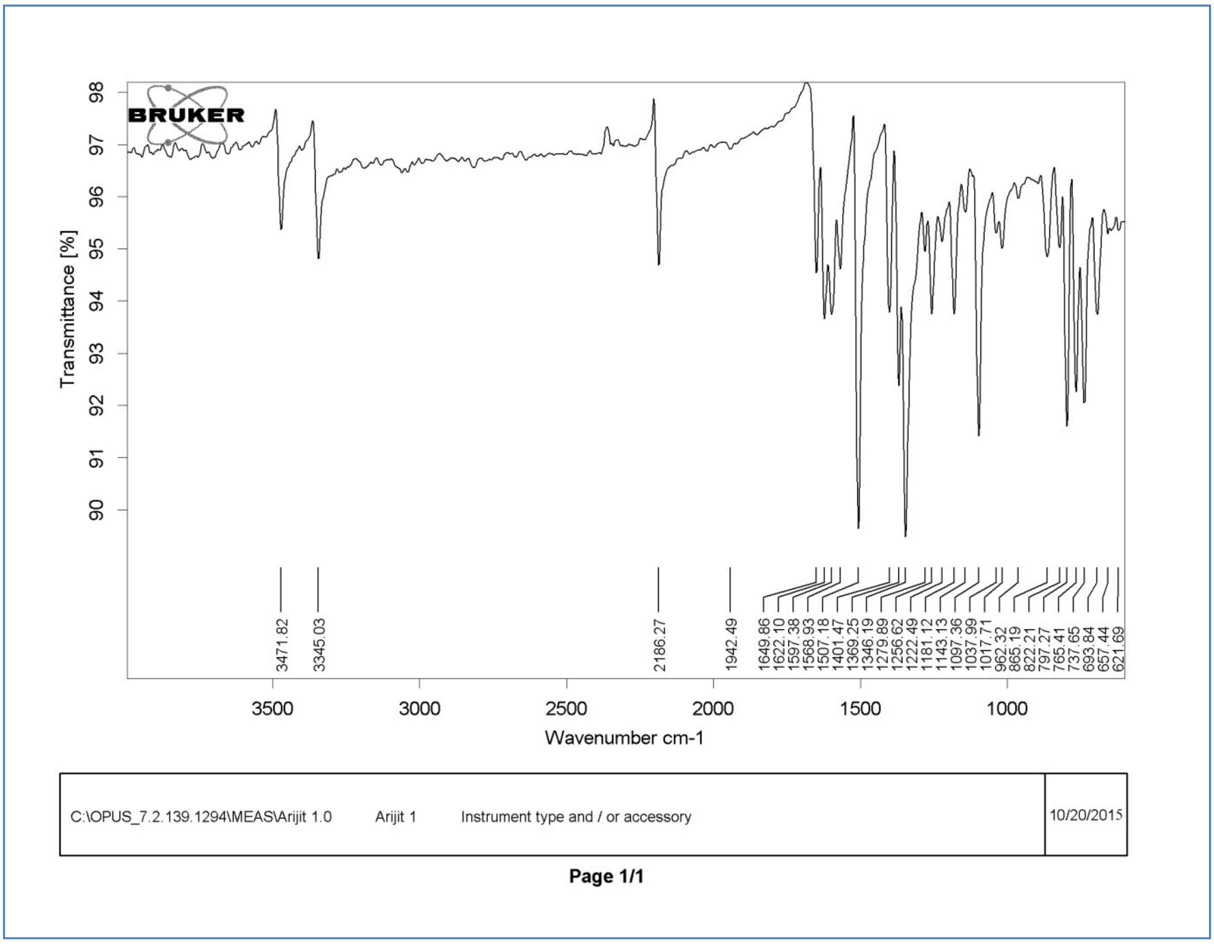


Fig. S5: FT-IR spectra of 2-amino-3-cyano-4-phenyl-4H-benzo[h]chromene using recycled ZrO_2 NPs.

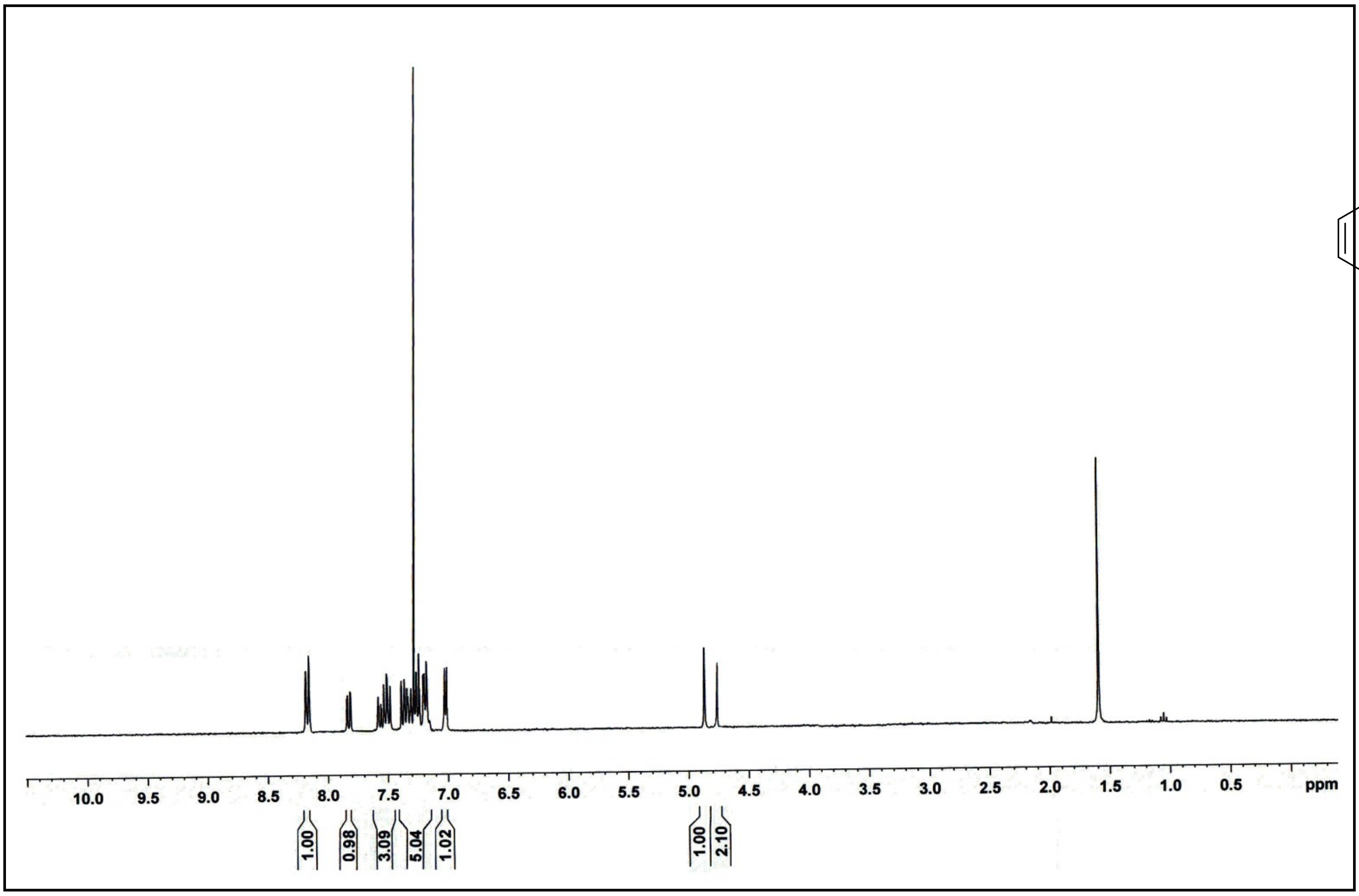
ESI-6. Experimental procedure for the synthesis of 2-amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile:

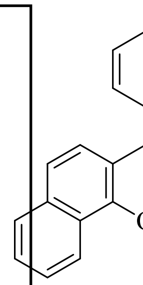
A mixture of the benzaldehyde (1 mmol, 106 mg), malononitrile (1 mmol, 66 mg), 4-hydroxycoumarin (1 mmol, 162 mg) and *t*-ZrO_2 catalyst (10 mmol%, 12 mg) was refluxed in 5 mL water for 30 minutes indicated by TLC. After the completion of the reaction, the solid product along with catalyst were separated by simple filtration and then dissolve in hot ethanol and subjected to filtration to separate the catalyst. The separated catalyst was then washed with ethyl acetate and hot methanol. Pure white crystals were obtained after slow evaporation of the filtrate. Finnaly, the crystalline compound was washed with ethanol to get pure 2-amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (3a) (yield = 92%, 291 mg). Further, the formation of the compound was confirmed by melting point determination and ^{1}HNMR study. White solid, M.P. = 255–257, ^{1}H NMR (500 MHz, DMSO-d_6) δ = 4.45 (1H, s, CH), 7.20-7.30 (3H, m, Ar), 7.31-7.37 (2H, m, Ar), 7.39 (2H, br s, NH_2), 7.46-7.52 (2H, m, Ar), 7.73 (1H, t, J = 7.5 Hz, Ar), 7.91 (1H, d, J = 7.0 Hz, Ar) ppm.

ESI-7. Experimental procedure for the synthesis of 10,10-dimethyl-7-phenyl-10,11-dihydrochromeno[4,3-*b*]chromene-6,8(7*H*,9*H*)-dione:

A mixture of the benzaldehyde (1 mmol, 106 mg), malononitrile (1 mmol, 66 mg), 5,5-dimethyl-1,3-cyclohexanedione (1 mmol, 140 mg) and *t*-ZrO_2 catalyst (10 mmol%, 12 mg) was refluxed in 5 mL water for 25 minutes indicated by TLC. After the completion of the reaction, the solid product along with catalyst were separated by simple filtration and then dissolve in hot ethanol and subjected to filtration to separate the catalyst. The separated catalyst was then washed with ethyl acetate and hot methanol. Pure white crystals were obtained after slow evaporation of the filtrate. Finally, the crystalline compound was washed with ethanol to get the pure 10,10-dimethyl-7-phenyl-10,11-dihydrochromeno[4,3-*b*]chromene-6,8(7*H*,9*H*)-dione (4a) (yield = 91%, 339 mg). Further, the formation of the compound was confirmed by melting point determination and ^{1}HNMR study. White solid, M.P. = 227–229, ^{1}H NMR (500 MHz, DMSO-d_6) δ = 0.90 (3H, s, CH_3), 1.01 (3H, s, CH_3), 2.36-2.62 (2H, m, CH_2), 4.84 (1H, s, CH), 7.10-7.22 (3H, m, Ar), 7.31-7.40 (4H, m, Ar), 7.50 (1H, t, J = 7.2 Hz, Ar), 7.89 (1H, d, J = 7.5 Hz, Ar) ppm.

ESI-8. Representative ^{1}HNMR copies of compounds: The NMR spectra were recorded in 500 or 400 MHz Bruker instrument and $CDCl_3$ or DMSO-d_6 were used as solvent.





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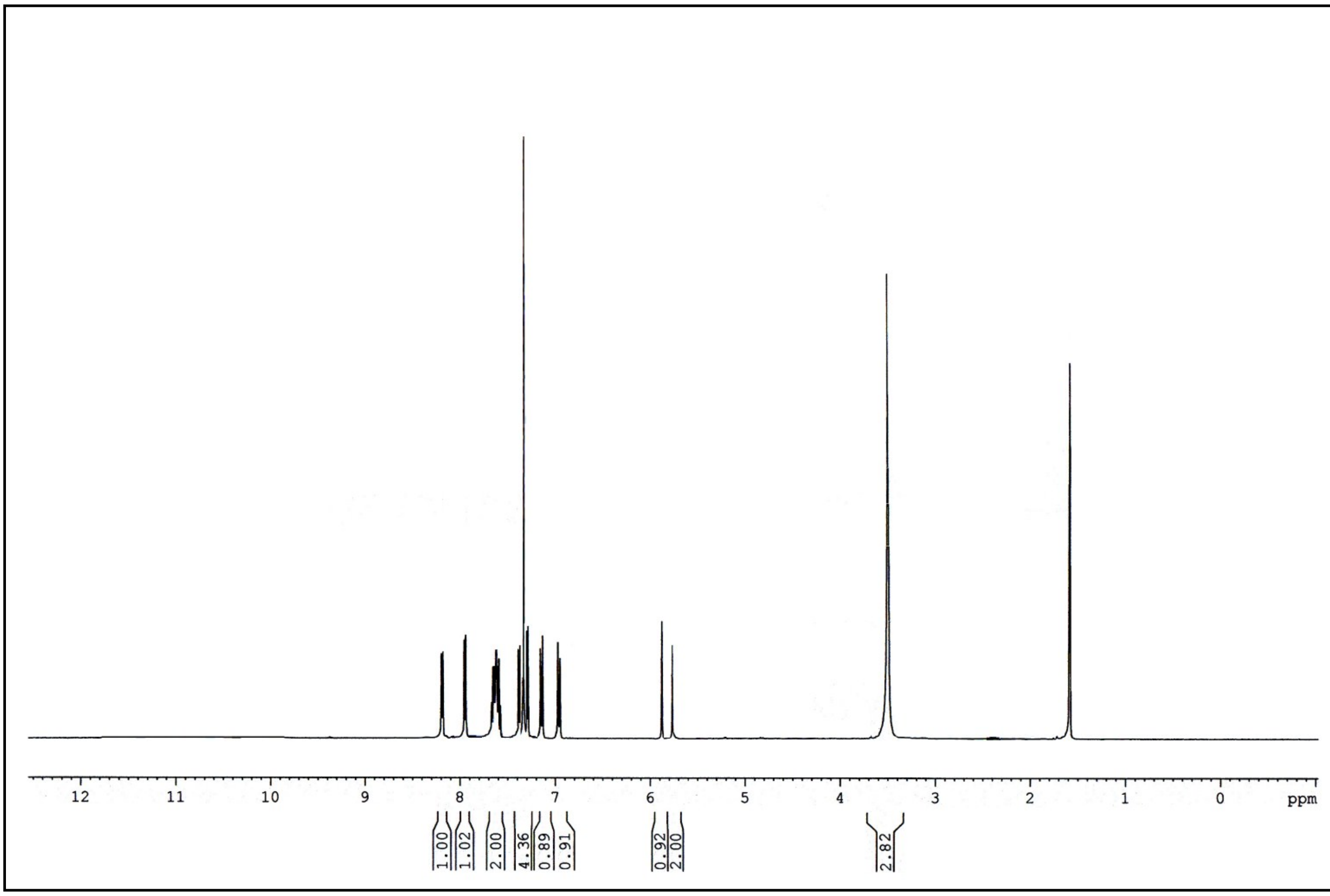

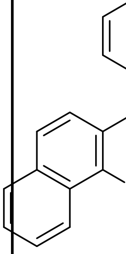

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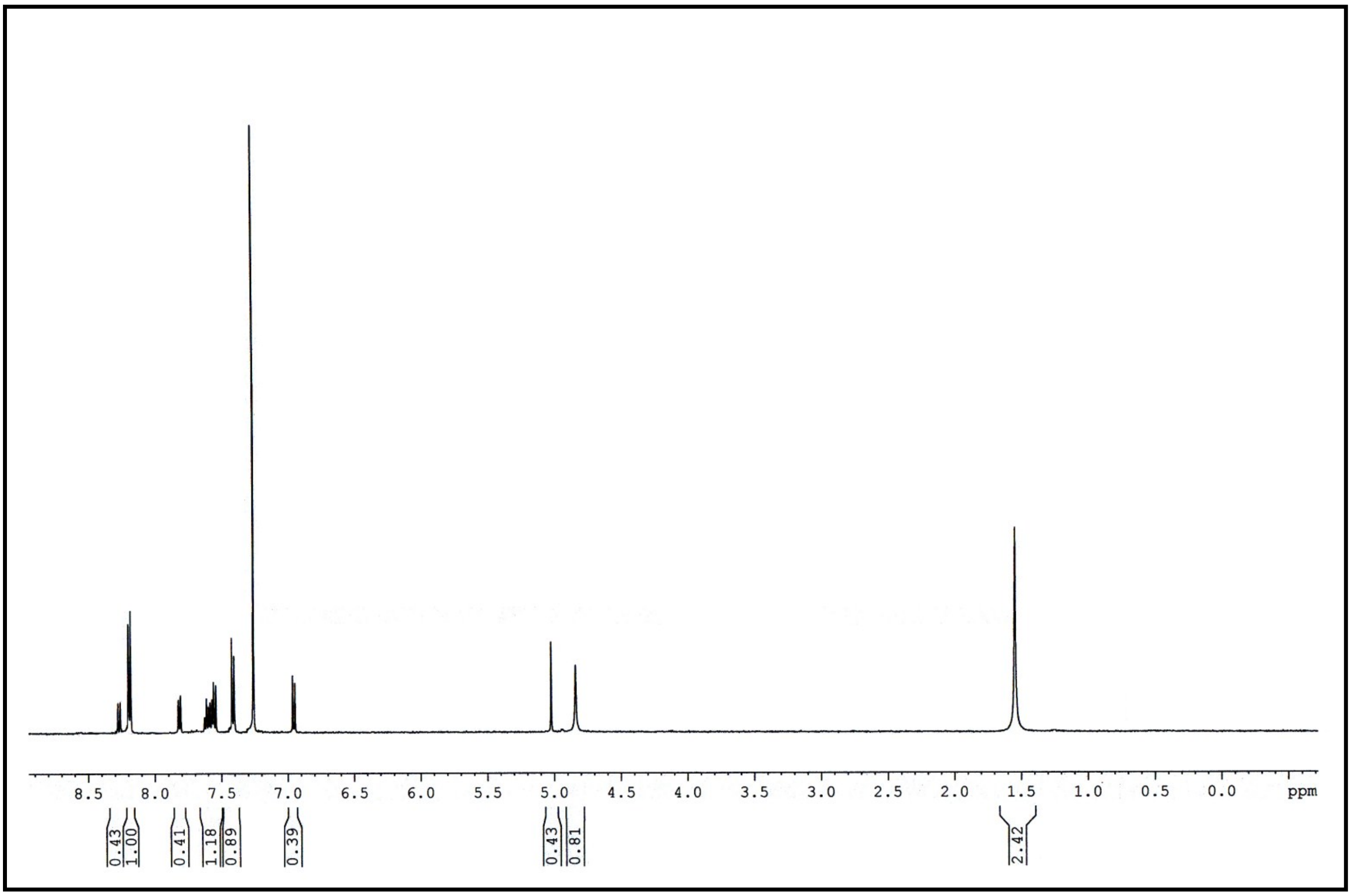
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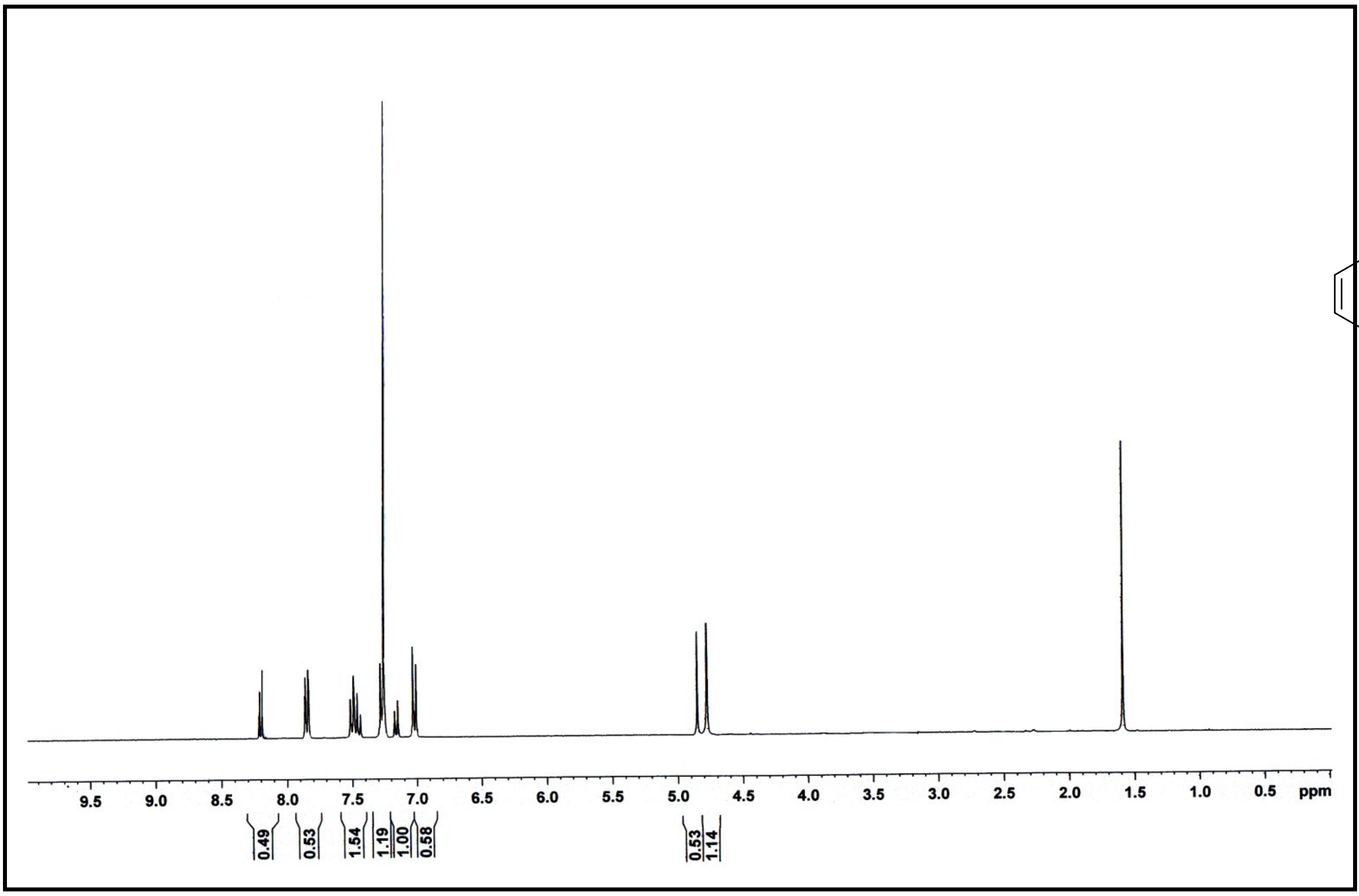
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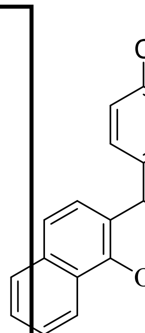

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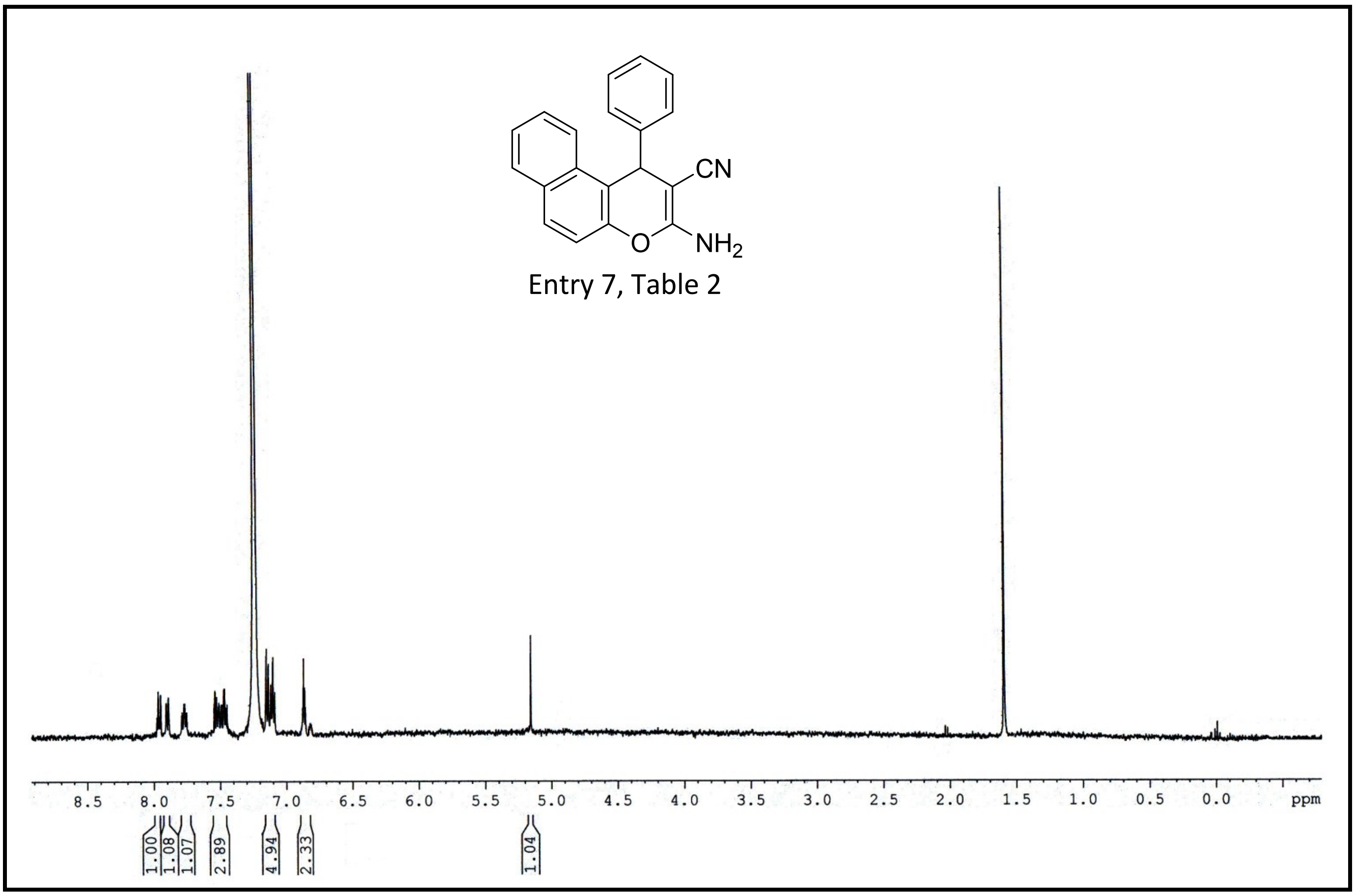
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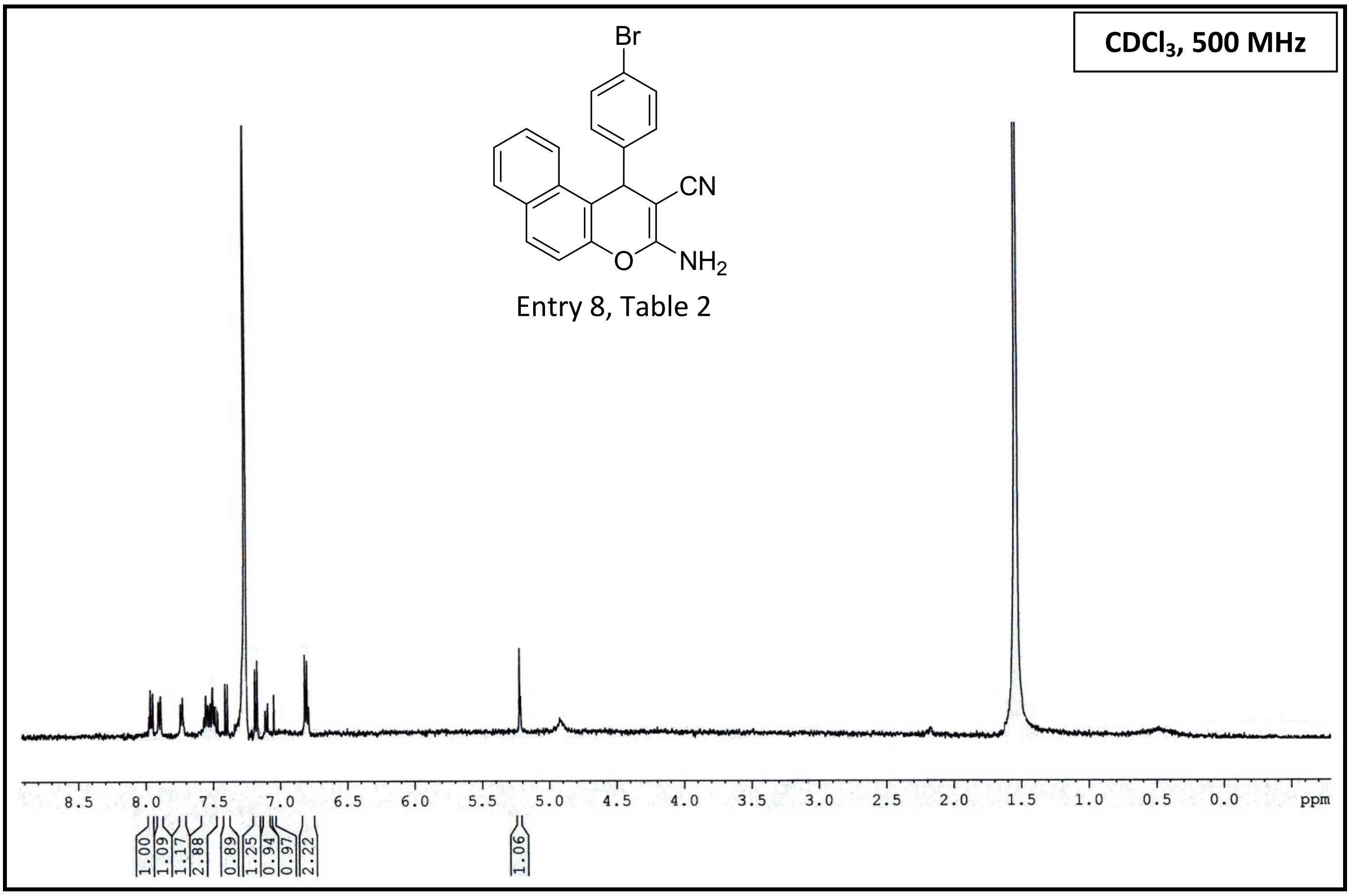

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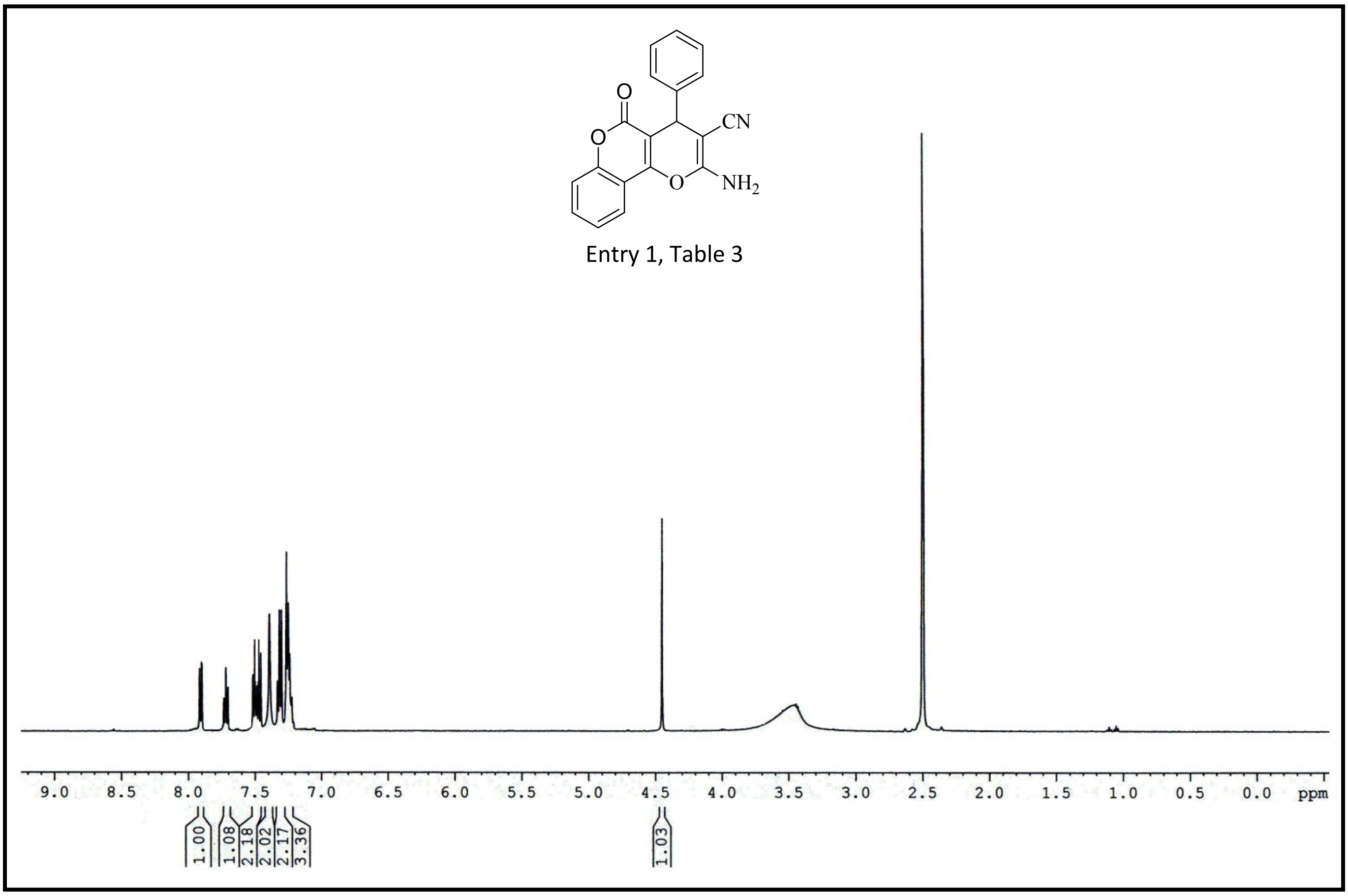

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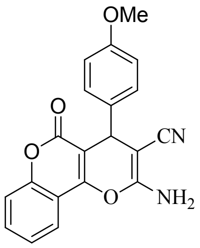

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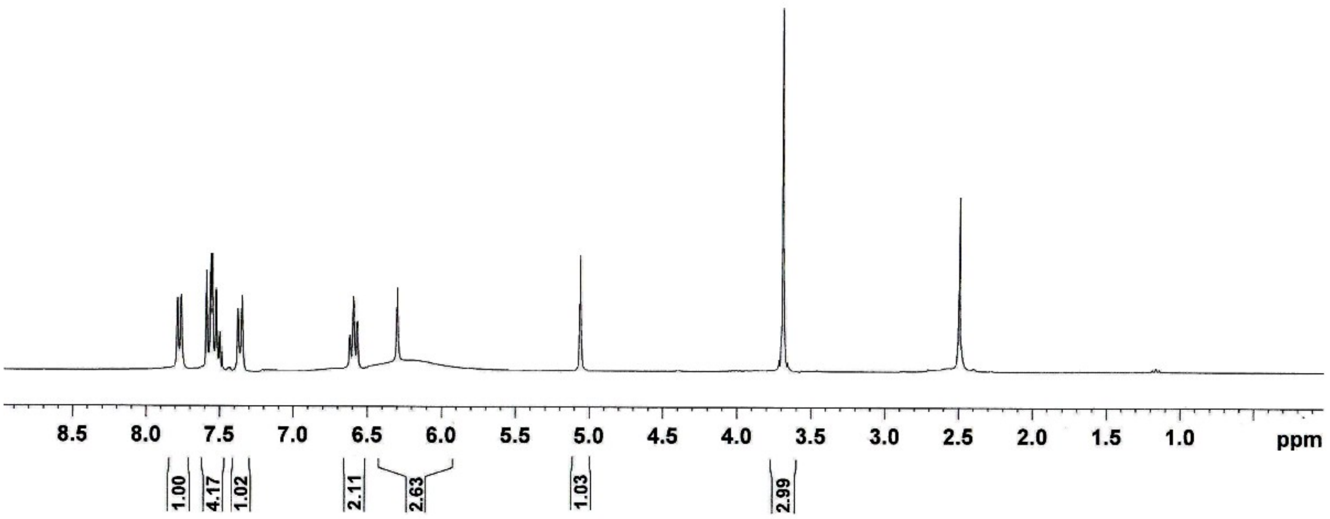

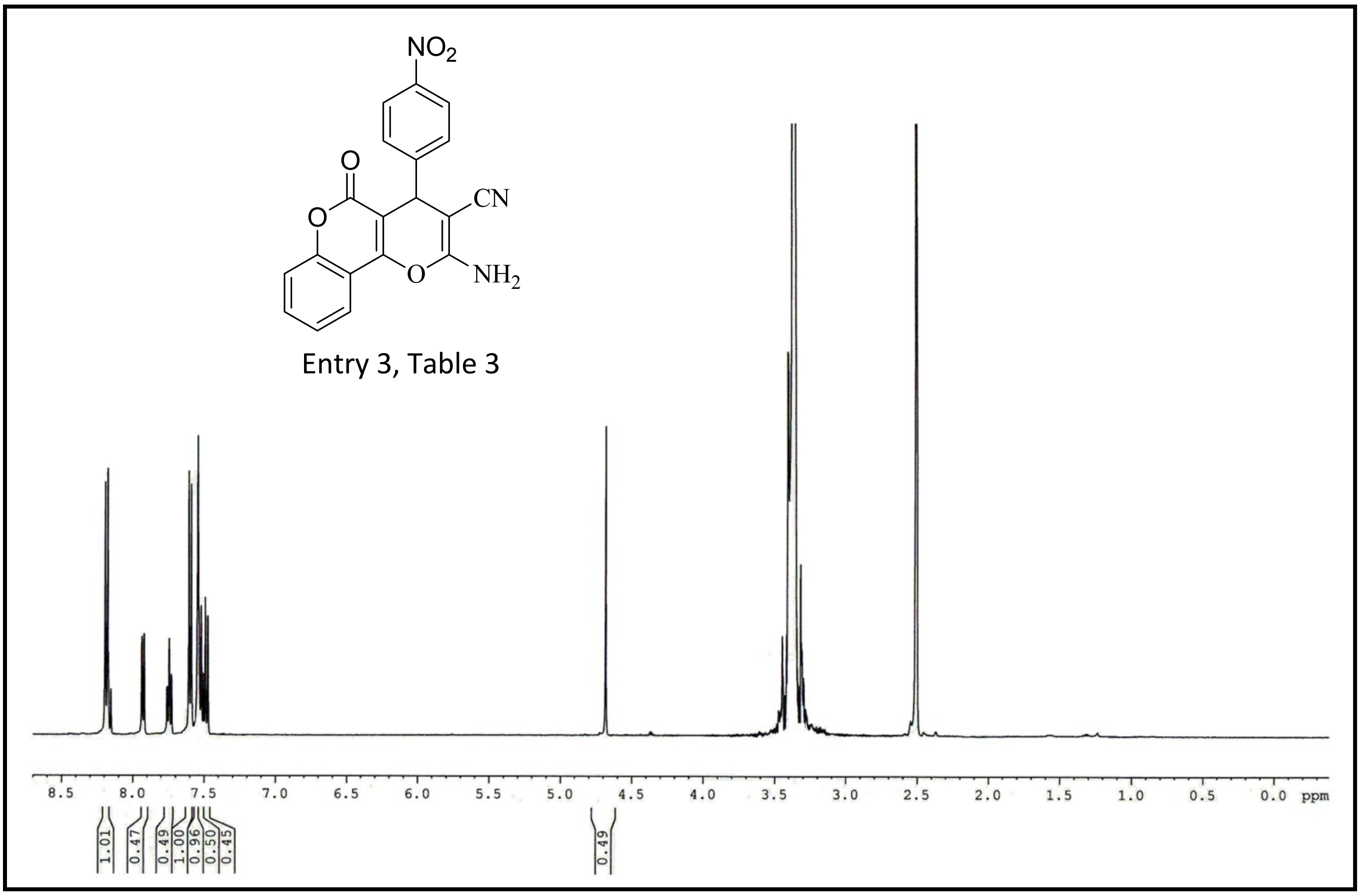

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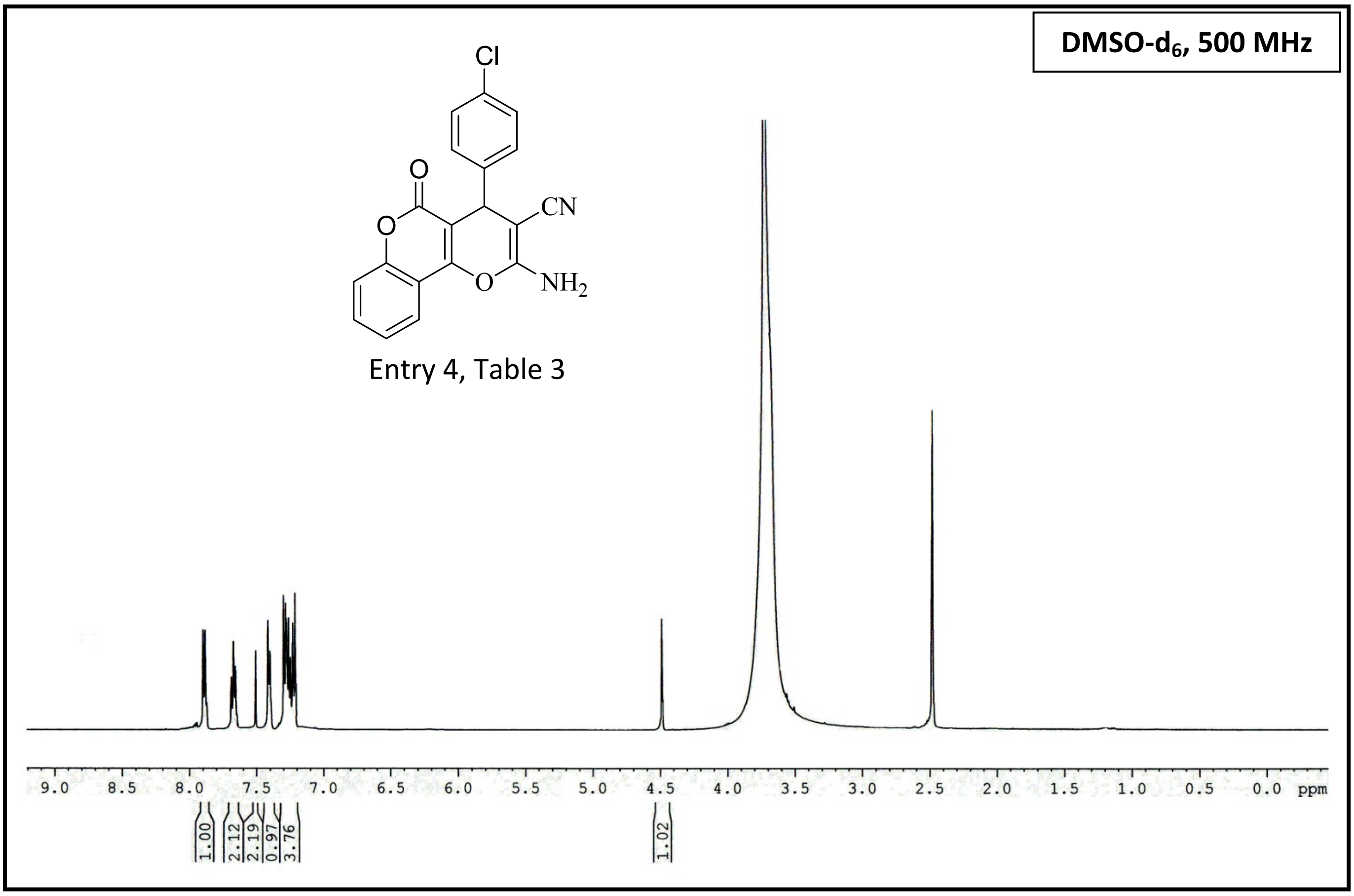
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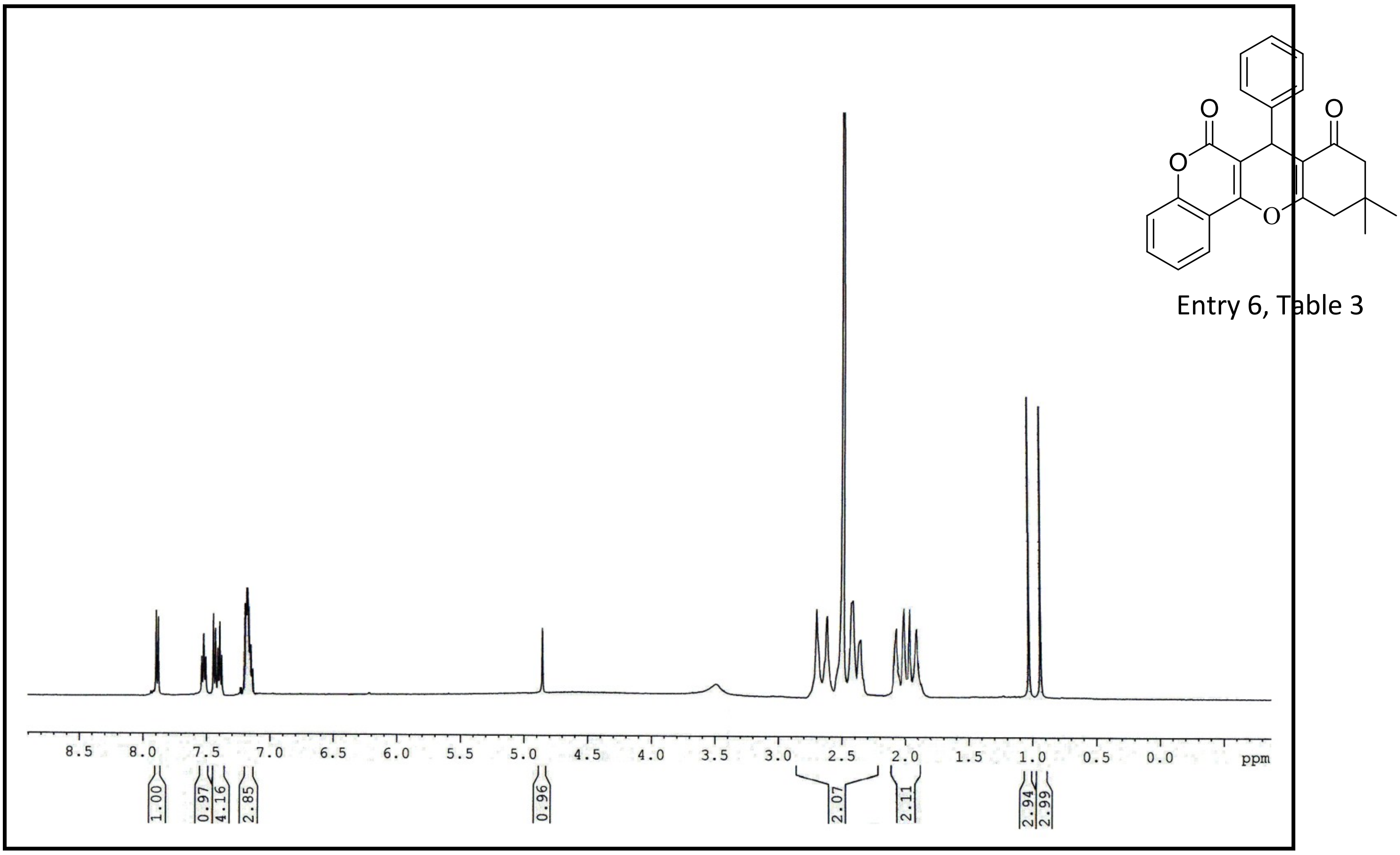

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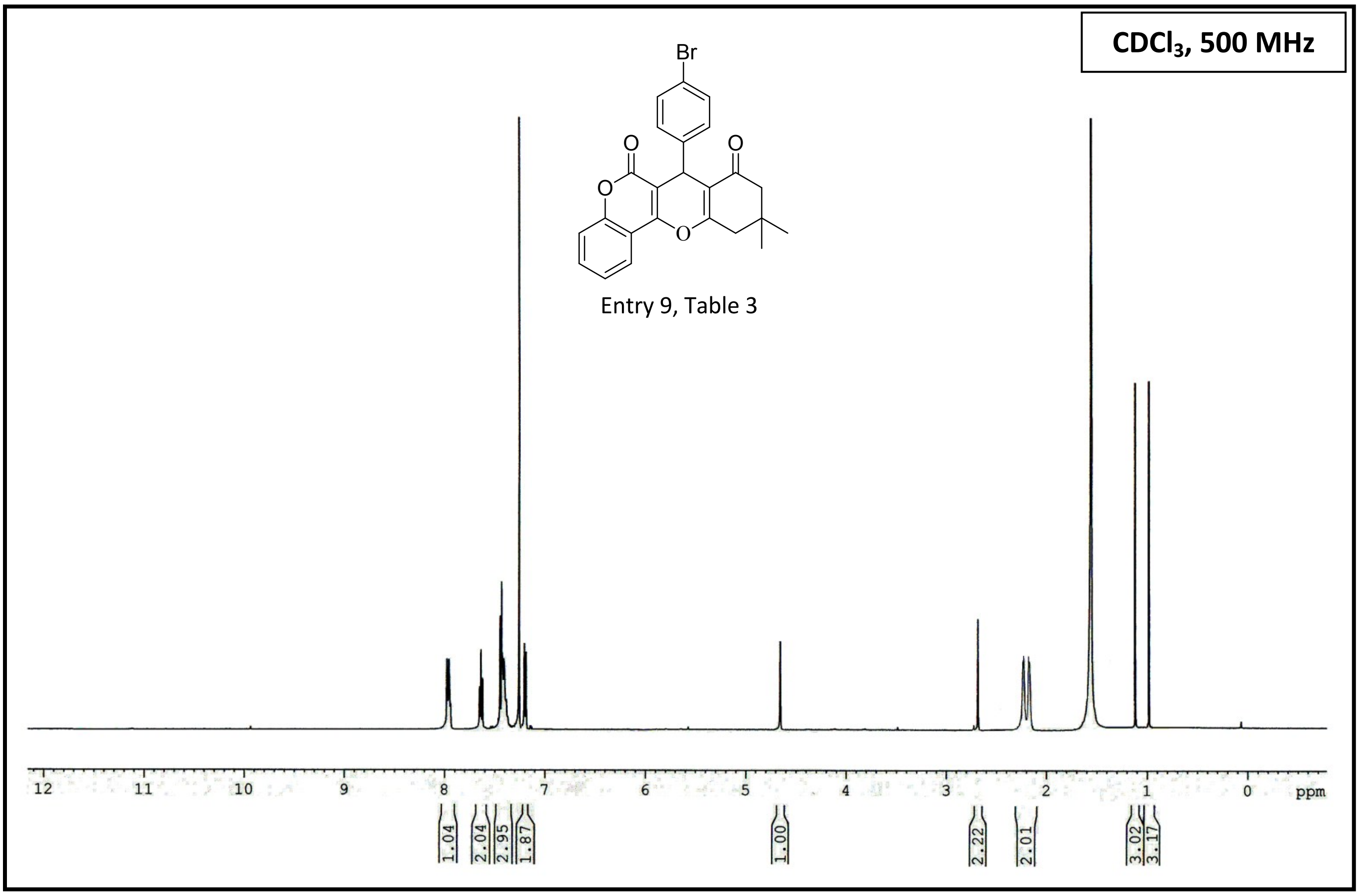
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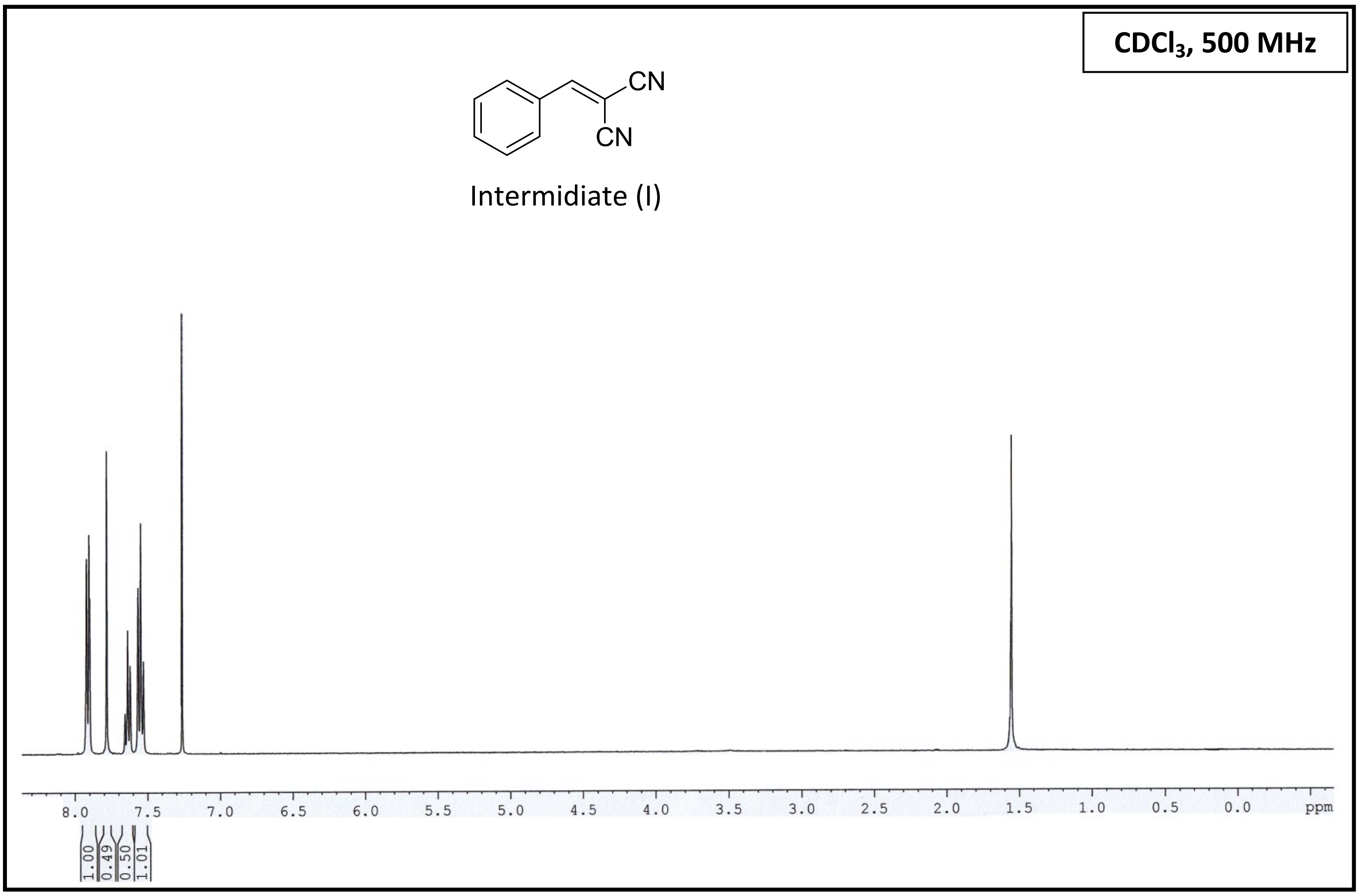
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CN
Intermidiate (I)
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