

Supplementary Information

Converting CO₂ into heterocyclic compounds under accelerated performance through Fe₃O₄ grafted ionic liquid catalysts

Niraj K. Vishwakarma,^{*,1} Shikha Singh,² Sambhav Vishwakarma,³ Ajay Kumar Shahi,¹ Vijay Kumar Patel,⁴ Shiva Kant⁵ and Sanjeev Kumar Mahto^{*,1}

¹*School of Biomedical Engineering, Indian Institute of Technology (Banaras Hindu University), Varanasi-221105, India*

²*Department of Chemical Engineering, Indian Institute of Technology (Banaras Hindu University), Varanasi-221105, India*

³*Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi-221105, India*

⁴*Department of Chemistry, K. P. College, Murliganj (a constituent College of Bhupendra Narayan Mandal University), Madhepura, Bihar, India*

⁵*Department of Materials Science and Engineering, Indian Institute of Technology Kanpur, Kanpur-208016, India*

Synthesis of 6-allyl-1,8-diazobicyclo[5.4.0]undec-7-ene (A-DBU): The A-DBU was synthesized according to reported method.¹ A clean and dried three necked 250 mL round bottom flask, equipped with magnetic bar, was dried with heat blow and flushed with nitrogen gas. To it, DBU (0.5 g, 3.28 mmol) was dissolved in 75 mL dry THF and vessel temperature was maintained up to -78 °C using liquid nitrogen/acetone mixture. *n*-Butyl lithium (2.2 mL, 3.52 mmol) was added dropwise for 5 min under stirring. The solution was kept at this temperature for 1 h under vigorously stirring. A solution of allyl chloride (0.28 g, 3.66 mol) in 10 mL anhydrous THF was added dropwise using a syringe pump with a flow rate of 250 ml/min to the reaction mixture. After complete addition, the reaction mixture was stirred for additional 3 h at room temperature. The reaction was quenched by addition of methanol (5 mL). The mixture was concentrated by evaporating the solvent under vacuum. The presence of alkene protons peak at 5.8-5.9 ppm (1H) and 5.1-5.2 ppm (2H) in ¹H NMR spectra confirmed the synthesis of A-DBU. Yield was calculated using ¹H NMR spectra and was 89%. The product was used as crude because only allyl functionalized DBU, not DBU, can react with -SH group of mercaptosilane grafted Fe₃O₄ *via* thio-ene click reaction.

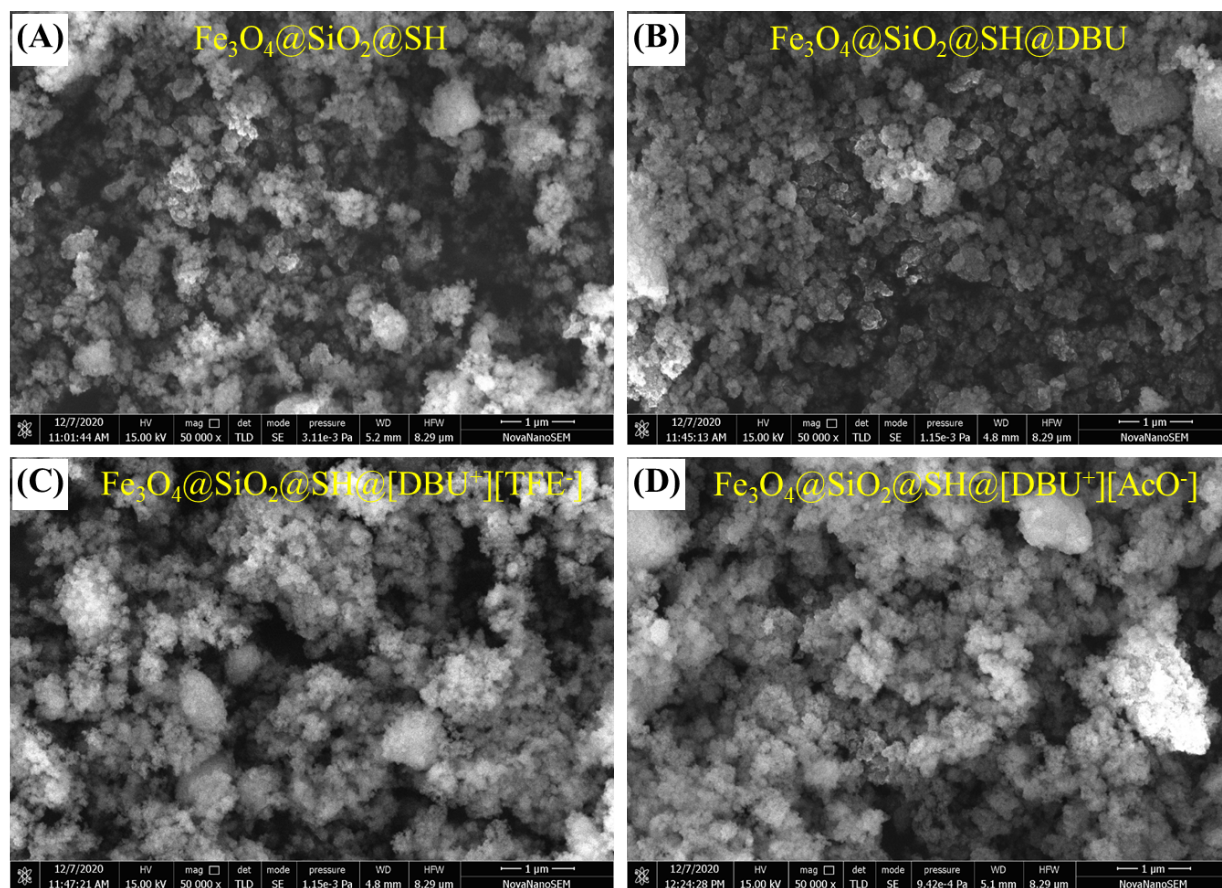


Figure S1. High resolution SEM images of (A) $\text{Fe}_3\text{O}_4@\text{SH}$, (B) $\text{Fe}_3\text{O}_4@\text{DBU}$, (C) $\text{Fe}_3\text{O}_4@[HDBU^+][TFE^-]$ and (D) $\text{Fe}_3\text{O}_4@[HDBU^+][AcO^-]$.

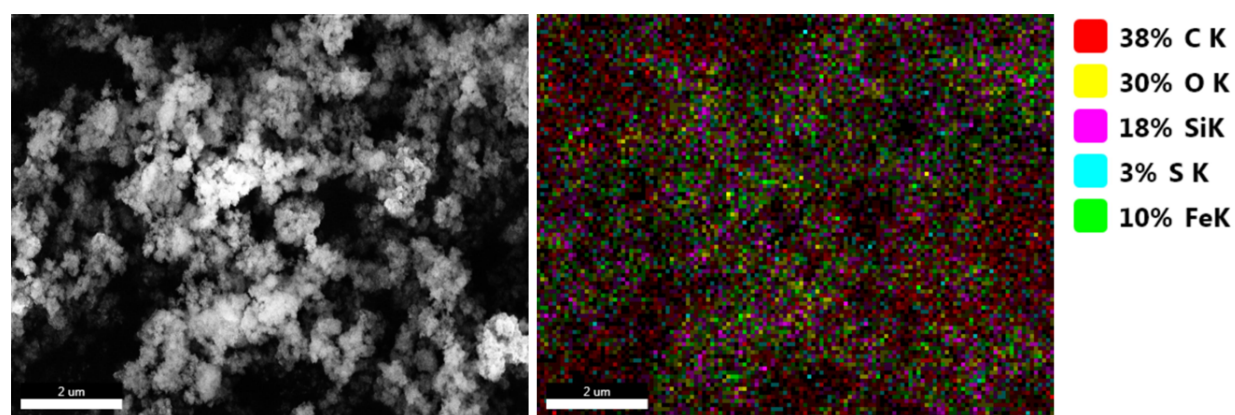


Figure S2. SEM images of $\text{Fe}_3\text{O}_4@\text{SH}$ and elemental EDX-mapping.

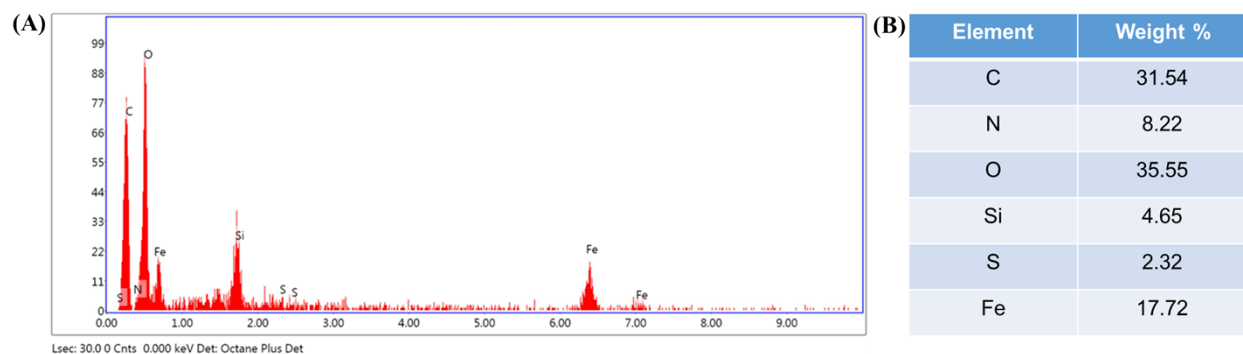


Figure S3. (A) EDX spectra of $\text{Fe}_3\text{O}_4@\text{DBU}$ and (B) the corresponding weight % elemental data.

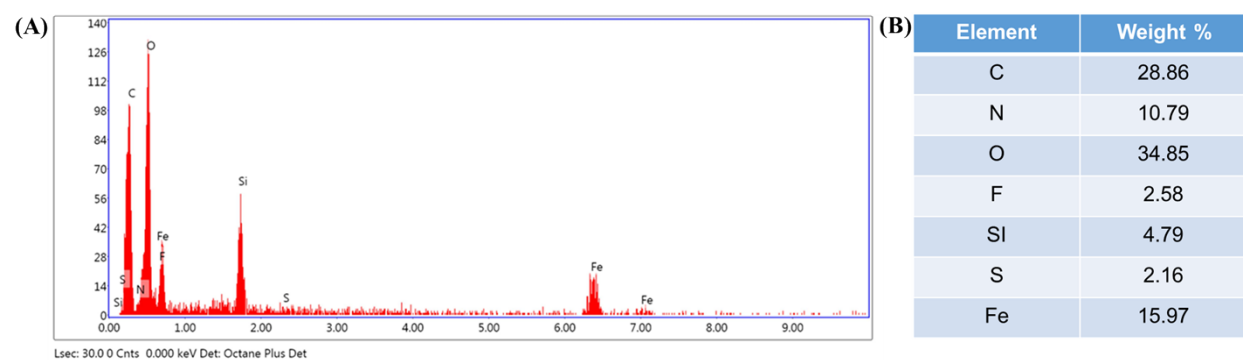


Figure S4. (A) EDX spectra of $\text{Fe}_3\text{O}_4@[\text{HDBU}^+][\text{TFE}^-]$ and (B) the corresponding weight % elemental data.

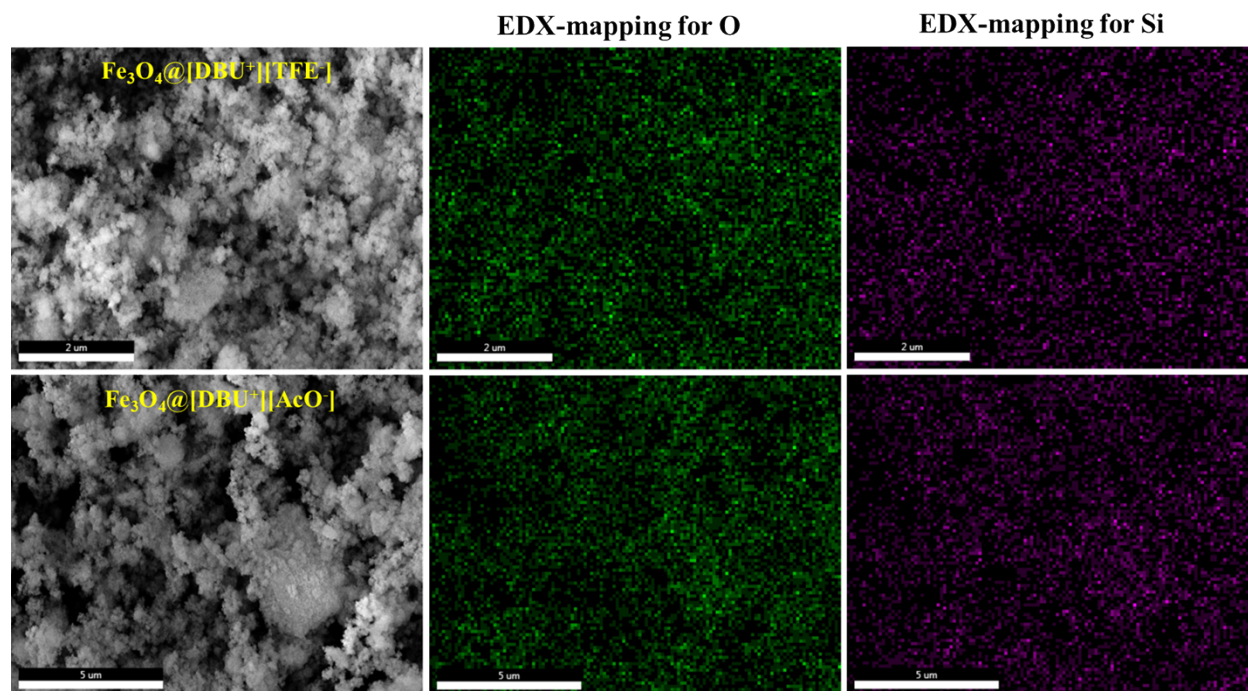


Figure S5. SEM images of $\text{Fe}_3\text{O}_4@[\text{HDBU}^+][\text{TFE}^-]$ and $\text{Fe}_3\text{O}_4@[\text{HDBU}^+][\text{AcO}^-]$ MNPs and corresponding EDX-mapping of oxygen and silicon.

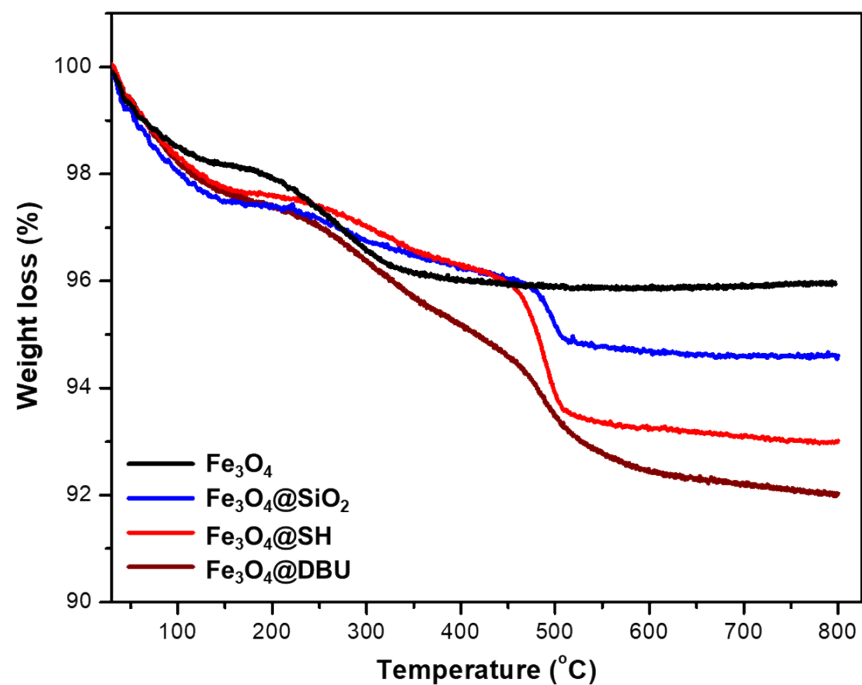


Figure S6: TGA curves of Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SH and Fe₃O₄@DBU.

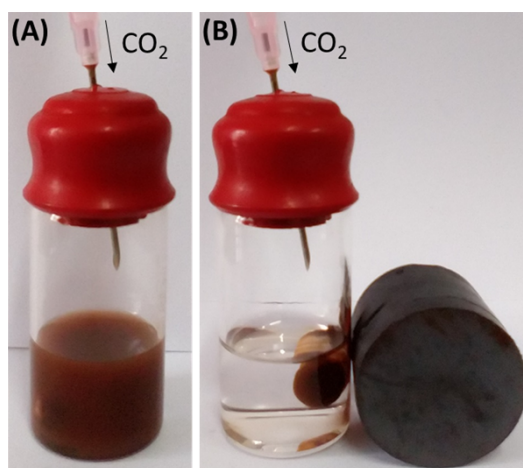


Figure S7. Image of (A) Fe₃O₄@[HDBU⁺][TFE⁻] dispersed catalyst in reaction medium and (B) separation of catalyst under external magnetic field.

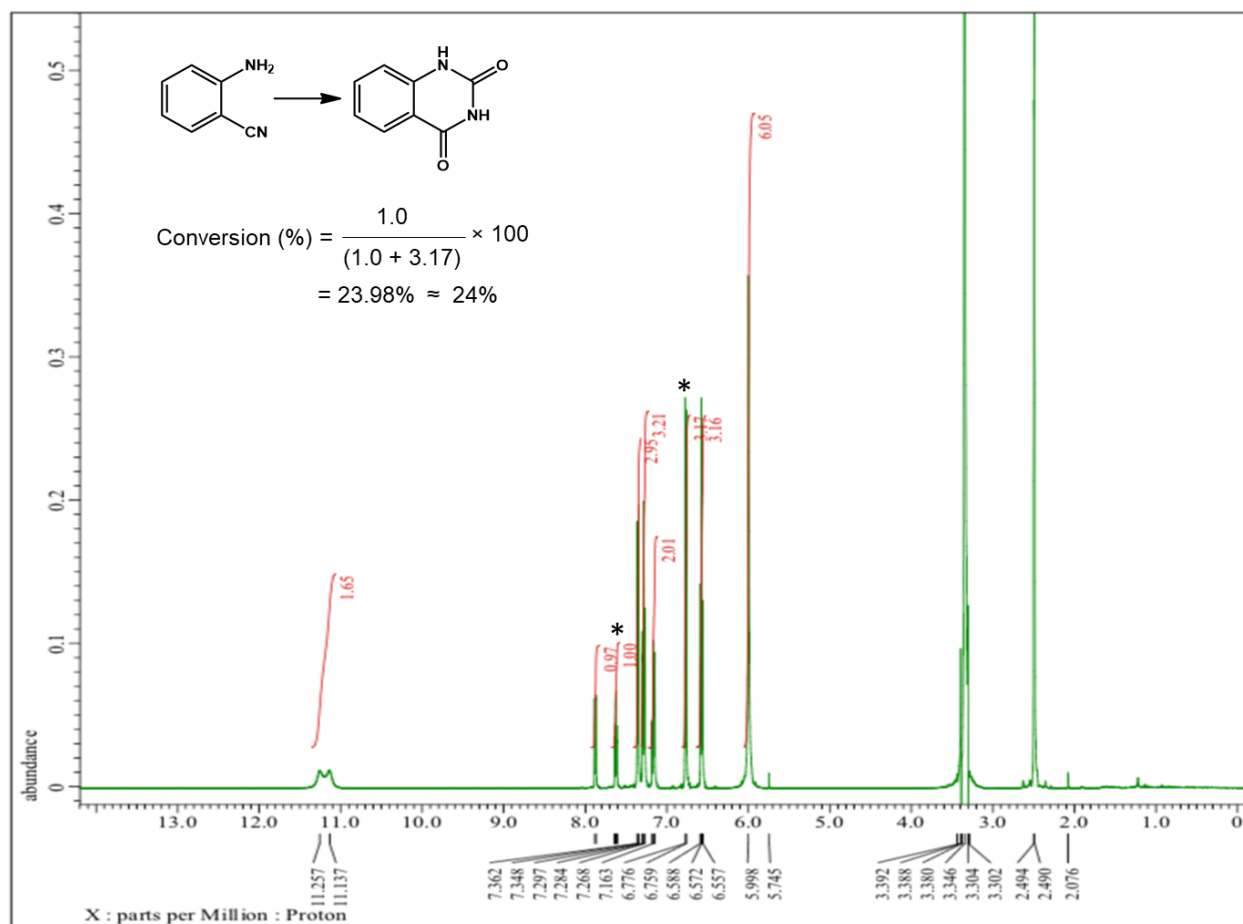


Figure S8. ¹H NMR spectra for conversion of 2-aminobenzonitrile to quinazolidione in DMSO-*d*₆ after evaporating DCM. Reaction condition: Fe₃O₄@[HDBU⁺][TFE⁻] (35 mg), 2-aminobenzonitrile (59 mg, 0.5 mmol), DCM, room temperature (Table 1, Entry 3). Peak at 7.62 ppm (1H) of product and peak at 6.75 ppm (1H) of reactant was used to calculate conversion.

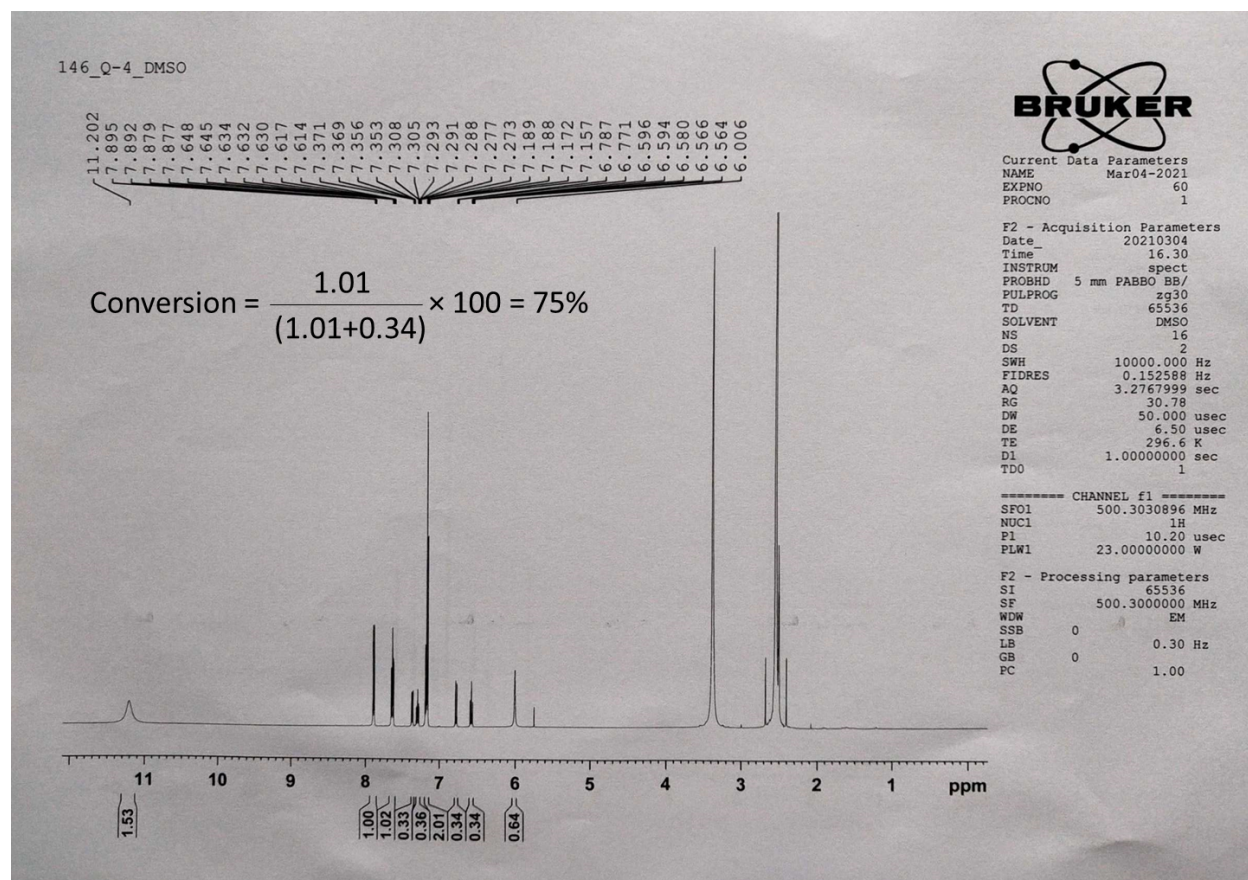


Figure S9. ^1H NMR spectra for conversion of 2-aminobenzonitrile to quinazolidione in $\text{DMSO-}d_6$. Reaction condition: $\text{Fe}_3\text{O}_4@[\text{HDBU}^+][\text{TFE}^-]$ (35 mg), 2-aminobenzonitrile (59 mg, 0.5 mmol), DMSO , room temperature (Table 1, Entry 8). Peak at 7.62 ppm (1H) of product and peak at 6.75 ppm (1H) of reactant were used to calculate conversion.

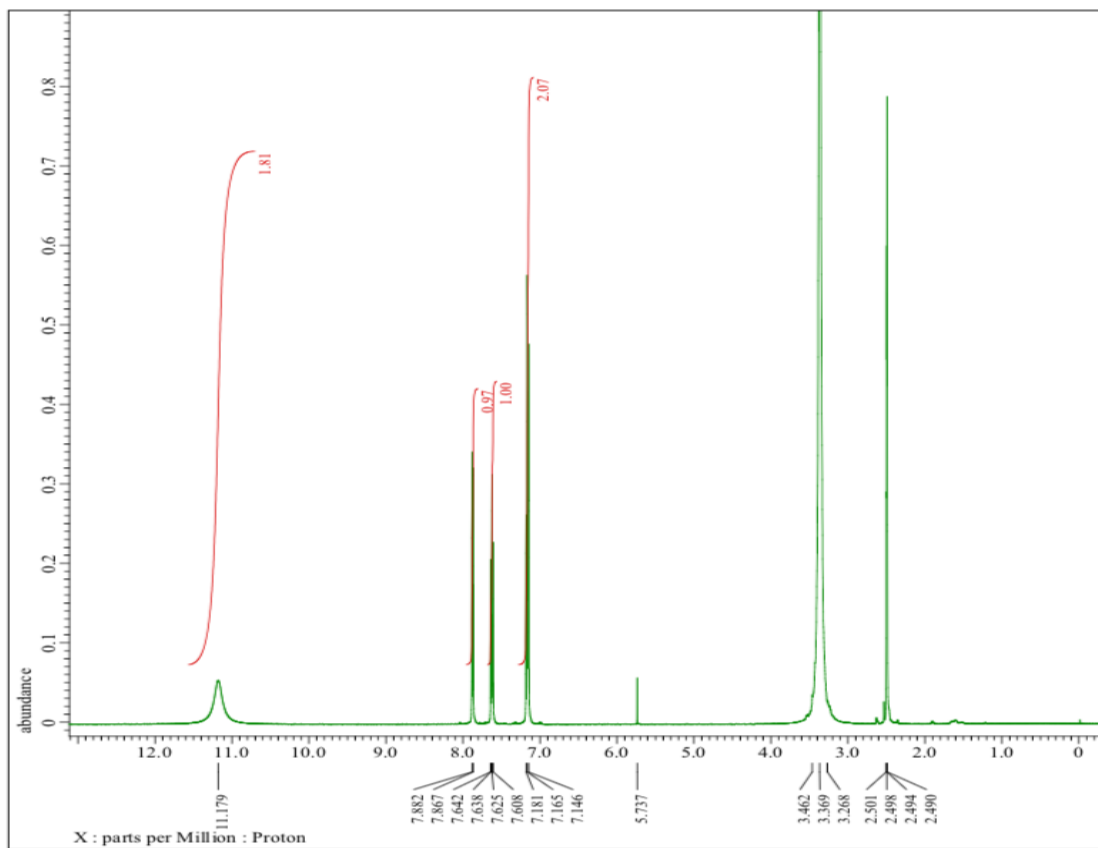


Figure S10. ¹H NMR spectra of purified product quinazoline-2,4-(1H,3H)-diones.

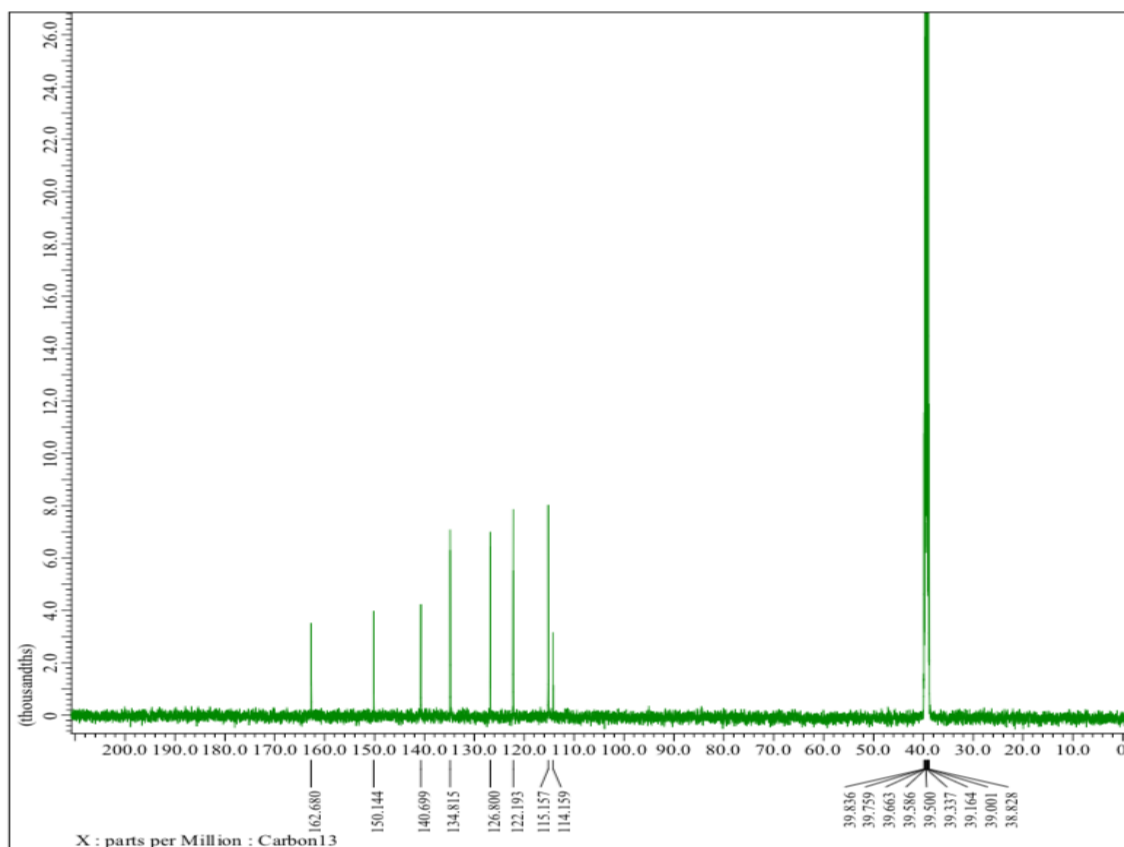
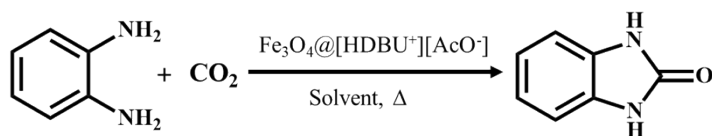


Figure S11. ^{13}C NMR spectra of purified product quinazoline-2,4-(1*H*,3*H*)-diones.

Table S1: Fe₃O₄@[HDBU⁺][AcO⁻] catalyzed carbonylation of *o*-phenylenediamine with CO₂.^a



Entry	Solvent	Temperature (°C)	Time (h)	Yield (%) ^b
1	Toluene	RT	36	0
2	Benzene	RT	36	0
3	DMF	RT	36	0
4	DMSO	RT	36	<5
5	DCM	RT	36	0
6	THF	RT	36	0
7	ACN	RT	36	0
8	THF	60	12	18
9	DMSO	60	12	66
10	DMSO	60	15	91

^aReactions conditions: *o*-phenylenediamine (54 mg, 0.5 mmol), catalyst Fe₃O₄@[HDBU⁺][AcO⁻] (35 mg), solvent (5 mL), CO₂ (99.9%) (1 atm, using balloon). ^bYield determined by ¹H NMR spectra in DMSO-*d*₆ (Figure S12).

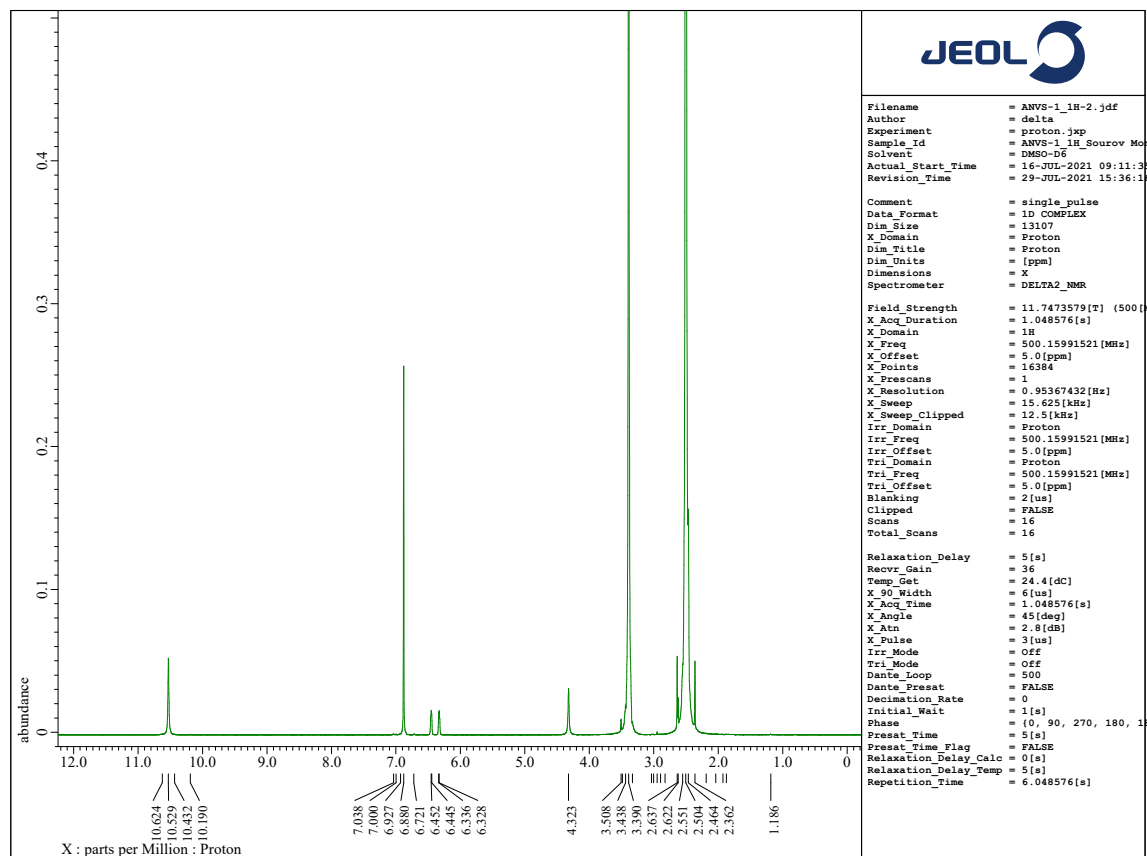


Figure S12. ^1H NMR spectra for conversion of *o*-phenylenediamine to benzimidazolone in $\text{DMSO-}d_6$. Reaction condition: $\text{Fe}_3\text{O}_4@[\text{HDBU}^+][\text{AcO}^-]$ (35 mg), *o*-phenylenediamine (54 mg, 0.5 mmol), DMSO , room temperature. Peak at 6.88 ppm (4H) of benzimidazolone and peak at 6.25-6.50 ppm (4H) of *o*-phenylenediamine were used to calculate conversion.

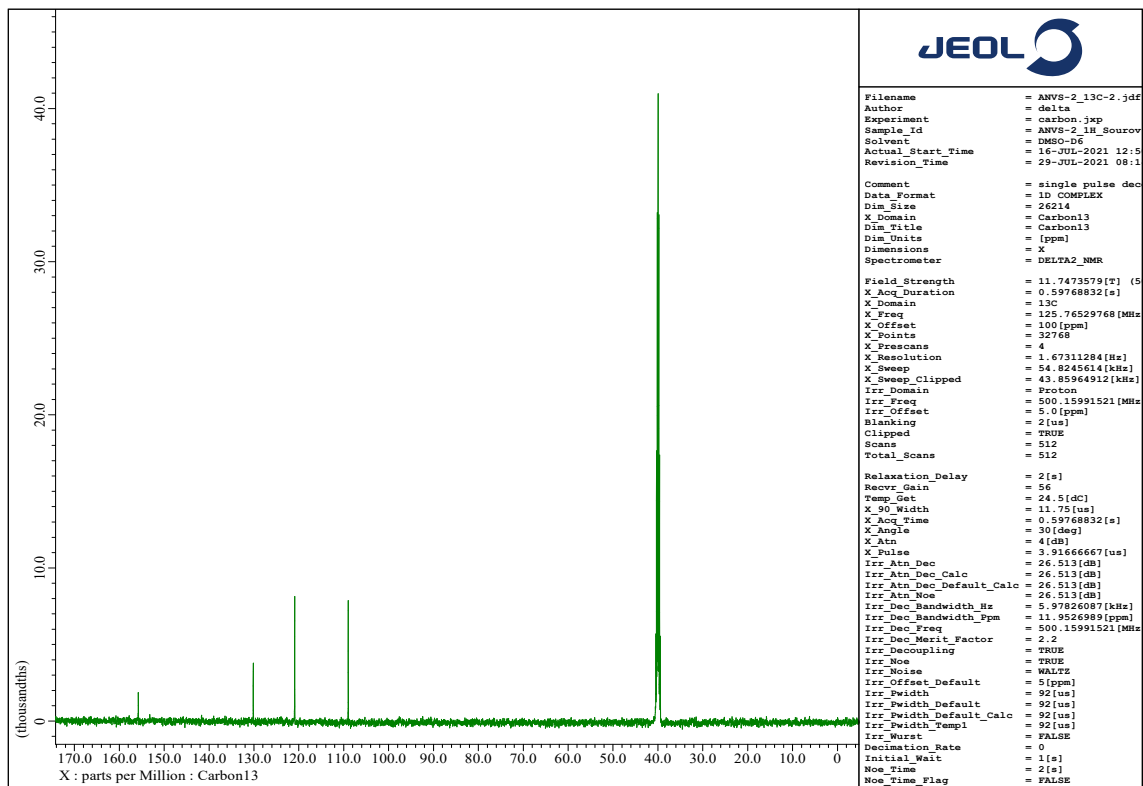


Figure S14. ^{13}C NMR spectra of purified benzimidazolone.

References

1. Niraj K. Vishwakarma, Ajay K. Singh, Yoon-Ho Hwang, Dong-Hyeon Ko, Jin-Oh Kim, A. Giridhar Babu & Dong-Pyo Kim, *Nature Communications* **2017**, 8:14676