Supplementary Information (SI) for Materials Horizons.

Supporting Information

Binary Cu/Boron Enhanced Graphene Quantum Dot as a Biomimetic Nanocatalyst for Trp Catabolism to Indole-3-aldehyde: Mechanism and Specificity

Morteza Hasani[1] and Hamid R. Kalhor[*1,2]

[1]Biochemistry and Chemical Biology Research Laboratory, Chemistry Department, Sharif University of Technology, Tehran, Iran; Phone: +982166165315; Email: *kalhor@sharif.edu*; Fax: +982166029165; PO Box: 11365-11155.

[2] Institute for Convergence Science & Technology, Sharif University of Technology, Tehran, Iran

Synthesis of Cu-NPs:

10 mmol of citric acid (1.92 g) and 1 mmol of $CuCl_2.2H_2O$ (0.17 g) were dissolved in 50 mL of distilled water. The solution was heated at 160 °C for 6 h. The precipitate was dissolved in 3 mL of distilled water and dialyzed against distilled water using a 2 KD bag and for 6 h. Next, the dialyzed solution was dried by freeze drying to collect the intended nanoparticles.

Synthesis of B-NPs:

10 mmol of citric acid (1.92 g) and 10 mmol of boric acid (0.61 g) were dissolved in 50 mL of distilled water. The solution was heated at 160 °C for 4 h. The precipitate was dissolved in 3 mL of distilled water and dialyzed against distilled water using a 2 KD bag and for 3 h. Next, the dialyzed solution was dried by freeze drying to collect the intended nanoparticles.

Synthesis of C-NPs:

10 mmol of citric acid (1.92 g) were dissolved in 50 mL of distilled water. The solution was heated at 160 °C for 4 h. The precipitate was dissolved in 3 mL of distilled water and dialyzed against distilled water using a 2 KD bag and for 3 h. Next, the dialyzed solution was dried by freeze drying to collect the intended nanoparticles.

Synthesis of M/B-NPs:

20 mmol of citric acid (3.84 g), 20 mmol of boric acid (1.22 g), and 2 mmol of various metal salts including $FeCl_2$ (0.25 g), $NiCl_2.6H_2O$ (0.47 g), $MnCl_2.4H_2O$ (0.40 g), $ZnCl_2.H_2O$ (0.30 g) and $CoCl_2.6H_2O$ (0.47 g) were dissolved in 50 mL of distilled water. The mixture was shaken and gently heated until a uniformly dissolved solution was obtained. The solution was heated at 155 °C for 3 h. The as-obtained solid was dissolved in 3 mL of distilled water and dialyzed against distilled water using a 2 KD bag and for 3 h. Next, the dialyzed solution was dried by freeze drying.

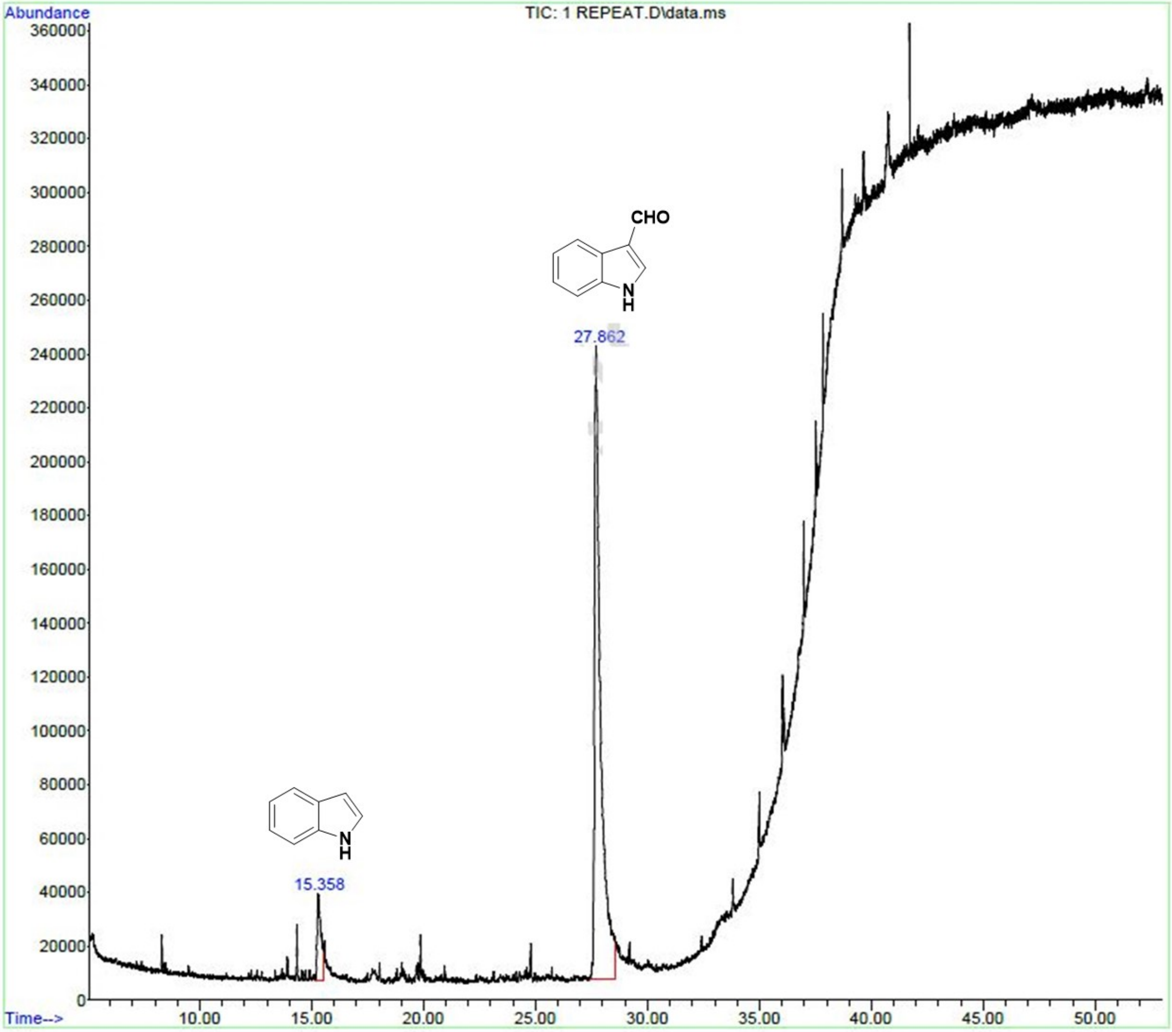


Figure S1. The GC-MS result of the initial benchmark reaction.

Evaluation the effect of various scavengers in the model reaction

1 mmol of Trp (0.204 g) and 0.01 g of Cu/B-GQD in the presence of catalytic amount of NaOH and 1 mmol of scavengers were dissolved in 2 mL of H_2O. To this solution was added 80 µL of H_2O_2 (30% w/w) and the solution was stirred at 37°C and for 10 h. Reaction was then stopped by adding 2 mL of H_2O and 2 mL of ethyl acetate. The reaction was then extracted three times with ethyl acetate to pull organic moieties into ethyl acetate. The reaction was monitored by TLC using a 1:1 ratio of hexane to ethyl acetate do detect any possible product in the reaction mixture.

Trp mimetic catabolism after 1h:

1 mmol of Trp (0.204 g) and 0.02 g of Cu/B-GQD in the presence of catalytic amount of KOH were dissolved in a 1:1 ratio of water to acetonitrile with a total volume of 2 mL. To this solution was added 80 µL of H_2O_2 (30% w/w) and the solution was stirred at 37°C and for 1 h (Caution: upon starting the reaction, the transformation progresses exothermically with severe bubbling). After, the reaction was quenched by adding 2 mL of H_2O. The reaction was extracted three times with ethyl acetate to pull organic moieties into ethyl acetate layer. The organic layer was separated from aqueous phase and then it was completely dried over Na_2SO_4. The dried organic phase was analyzed by GC-MS to detect any possible intermediate in the reaction mixture. As a result, in addition to indole-3-carbaldehyde, indole-3-acetonitrile was also detected in the reaction mixture.

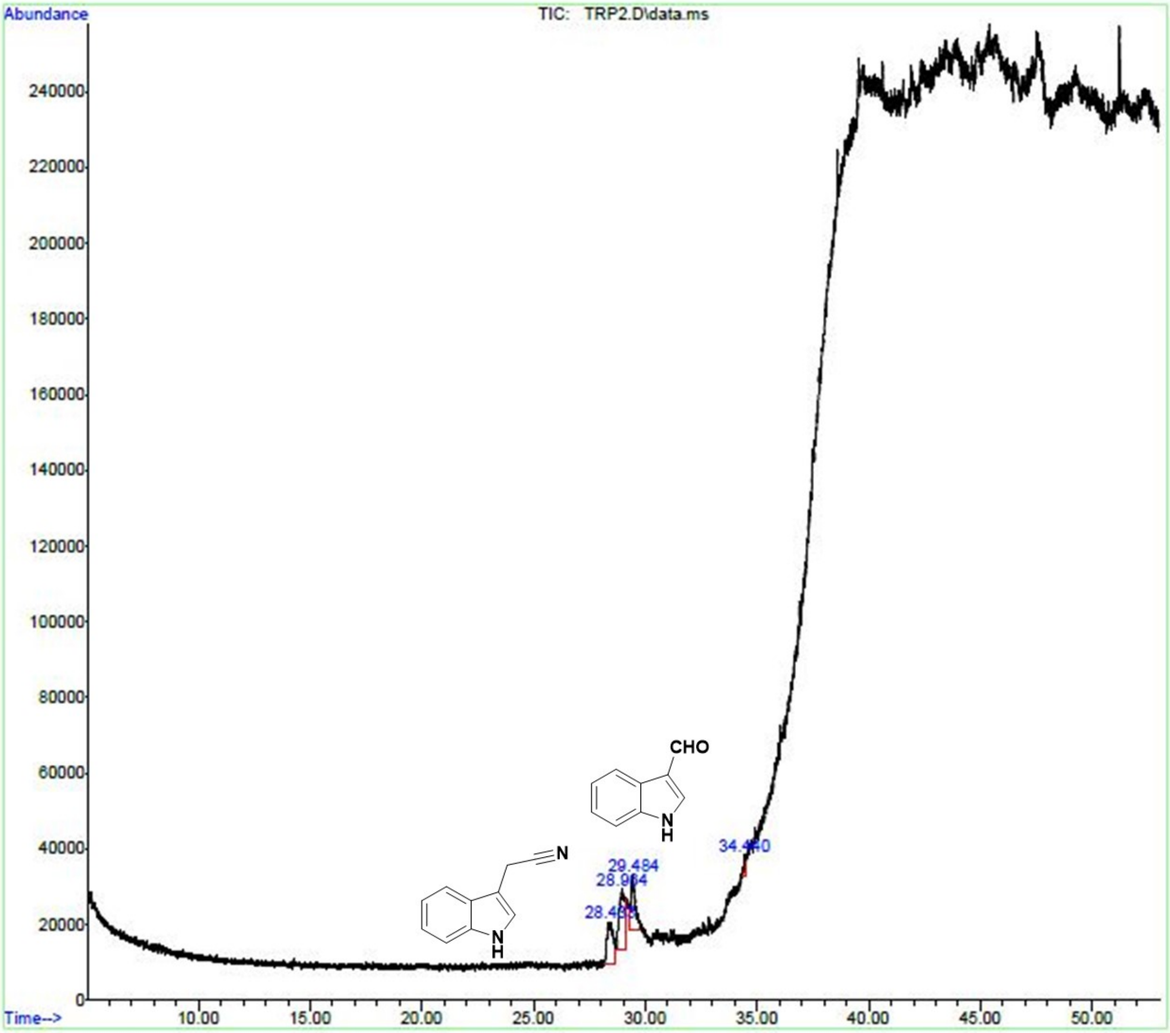


Figure S2. The GC-MS result of the Trp conversion after 1h.

Phenylalanine conversion under the optimized reaction conditions:

1 mmol of Phe (0.165 g) and 0.02 g of Cu/B-GQD in the presence of catalytic amount of KOH were dissolved in a 1:1 ratio of water to acetonitrile (total volume 2 mL). To this solution was added 80 µL of H_2O_2 (30% w/w) and the solution was stirred at 37°C and for 3 h. After, the reaction was quenched by adding 2 mL of H_2O. The reaction was extracted three times with ethyl acetate to pull organic moieties into ethyl acetate layer. The organic layer was separated from aqueous phase and then it was completely dried over Na_2SO_4. The dried organic phase was analyzed by GC-MS to study the progress of the reaction and detect the products formed during the reaction. As a result, benzeneacetamide was detected in the reaction mixture.

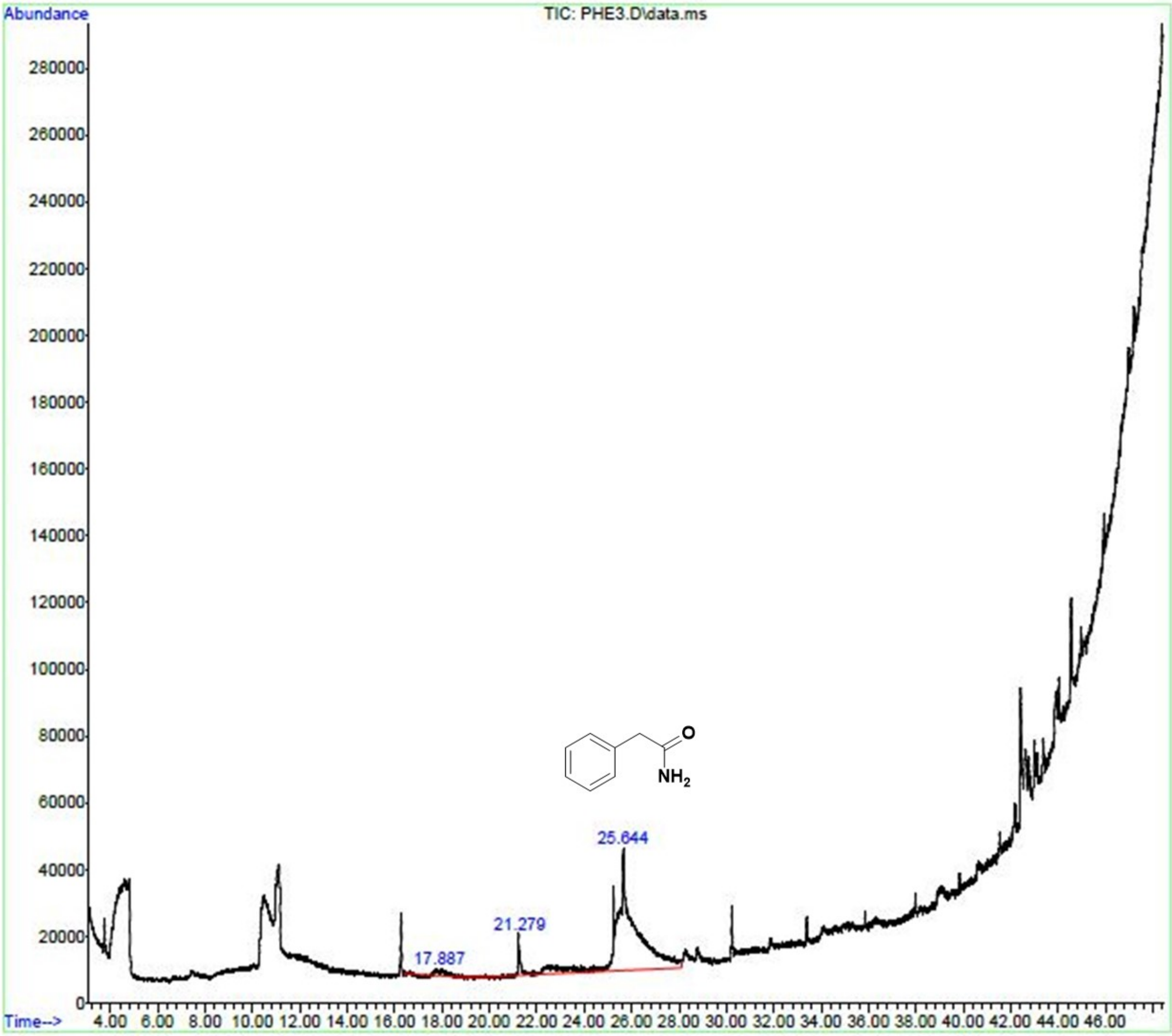


Figure S3. The GC-MS result of the optimized reaction with phenylalanine.

Phenylalanine conversion (overnight):

1 mmol of Phe (0.165 g) and 0.02 g of Cu/B-GQD in the presence of catalytic amount of KOH were dissolved in a 1:1 ratio of water to acetonitrile with a total volume of 2 mL. To this solution was added 80 µL of H_2O_2 (30% w/w) and the solution was stirred at 37°C and for overnight. After, the reaction was quenched by adding 2 mL of H_2O. The reaction was extracted three times with ethyl acetate to pull organic moieties into ethyl acetate layer. The organic layer was separated from aqueous phase and then it was completely dried over Na_2SO_4. The dried organic phase was analyzed by GC-MS to study the progress of the reaction and detect the

products formed during the reaction. As a result, benzaldehyde was detected in the reaction mixture.

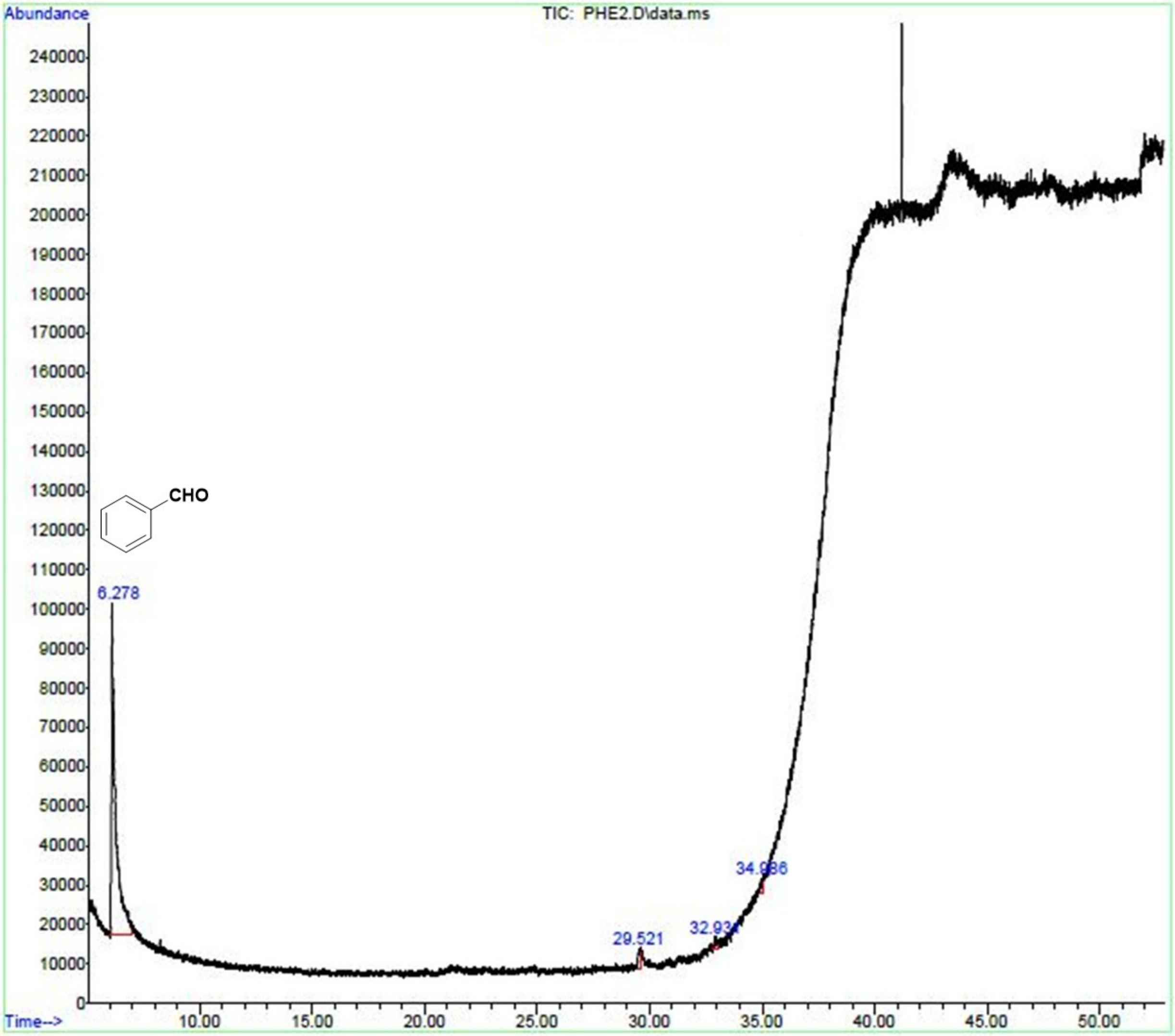


Figure S4. The GC-MS result of the phenylalanine conversion overnight.

Phenylalanine conversion (9h):

1 mmol of Phe (0.165 g) and 0.02 g of Cu/B-GQD in the presence of catalytic amount of KOH were dissolved in a 1:1 ratio of water to acetonitrile (total volume 2 mL). To this solution was added 80 µL of H_2O_2 (30% w/w) and the solution was stirred at 37°C and for 9h. After, the reaction was quenched by adding 2 mL of H_2O. The reaction was extracted three times with ethyl acetate to pull organic moieties into ethyl acetate layer. The organic layer was separated from aqueous phase and then it was completely dried over Na_2SO_4. The dried organic phase was

analyzed by GC-MS to study the progress of the reaction and detect the products formed during the reaction. As a result, benzaldehyde, benzeneacetamide, and 2-hydroxy-2-phenylacetamide (mandelamide) were detected in the reaction mixture.

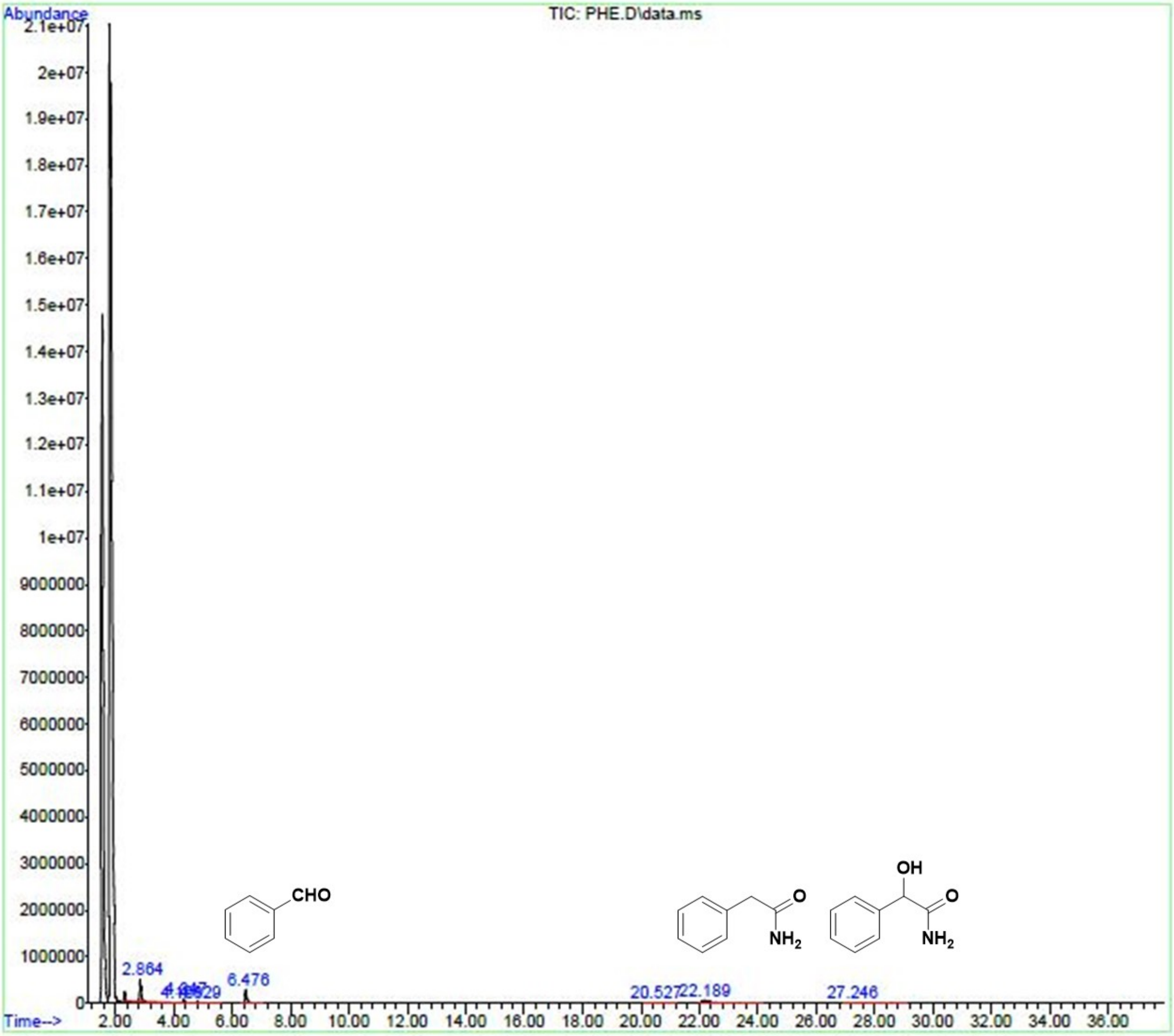


Figure S5. The GC-MS result of the phenylalanine conversion (9h).

Tyrosine conversion with the optimized reaction conditions:

1 mmol of Tyr (0.181 g) and 0.02 g of Cu/B-GQD in the presence of catalytic amount of KOH were dissolved in a 1:1 ratio of water to acetonitrile with a total volume of 2 mL. To this solution was added 80 µL of H_2O_2 (30% w/w) and the solution was stirred at 37°C and for 3 h. After, the reaction was quenched by adding 2 mL of H_2O. The reaction was extracted three times with ethyl acetate to pull organic moieties into ethyl acetate layer. The organic layer was separated from

aqueous phase and then it was completely dried over Na_2SO_4. Thin layer chromatography was used to trace the reaction.

Mechanistic experiments with tryptamine, phenylacetic acid, benzaldehyde, and toluene:

1 mmol of each substrate and 0.02 g of Cu/B-GQD in the presence of catalytic amount of KOH were dissolved in a 1:1 ratio of water to acetonitrile with a total volume of 2 mL. To this solution was added 80 µL of H_2O_2 (30% w/w) and the solution was stirred at 37°C and for 3 h. After, the reaction was quenched by adding 2 mL of H_2O. The reaction was extracted three times with ethyl acetate to pull organic moieties into ethyl acetate layer. The organic layer was separated from aqueous phase and then it was completely dried over Na_2SO_4. Thin layer chromatography was used to trace the reaction.

Recyclability of Cu/B-GQD:

1 mmol of Trp (0.204 g) and 0.02 g of Cu/B-GQD, in the presence of a catalytic amount of KOH, were dissolved in a 1:1 mixture of water and acetonitrile to a total volume of 2 mL. To this solution, 80 µL of H_2O_2 (30% w/w) was added, and the mixture was stirred at 37°C for 3 h. In the recycling experiment, the reaction was extracted by 4 mL of ethyl acetate. The aqueous layer (containing water-soluble catalyst) was then collected and used for the next run under the same conditions. The recycling test was repeated three times. Reusing the catalyst 3 times resulted in only a 9% drop in the reaction yield.

Benzonitrile conversion to benzamide:

1 mmol of benzonitrile (0.103 mL) and 0.02 g of Cu/B-GQD in the presence of catalytic amount of KOH were dissolved in a 1:1 ratio of water to acetonitrile with a total volume of 2 mL. After, the reaction was quenched by adding 2 mL of H_2O. The reaction was extracted three times with ethyl acetate to pull organic moieties into ethyl acetate layer. The organic layer was separated from aqueous phase and then it was completely dried over Na_2SO_4. Thin layer chromatography was used to

trace the reaction. Benzamide was isolated by preparative TLC plate (20×20 cm) in a mobile phase of 2:1 mixture of n-hexane to ethyl acetate.

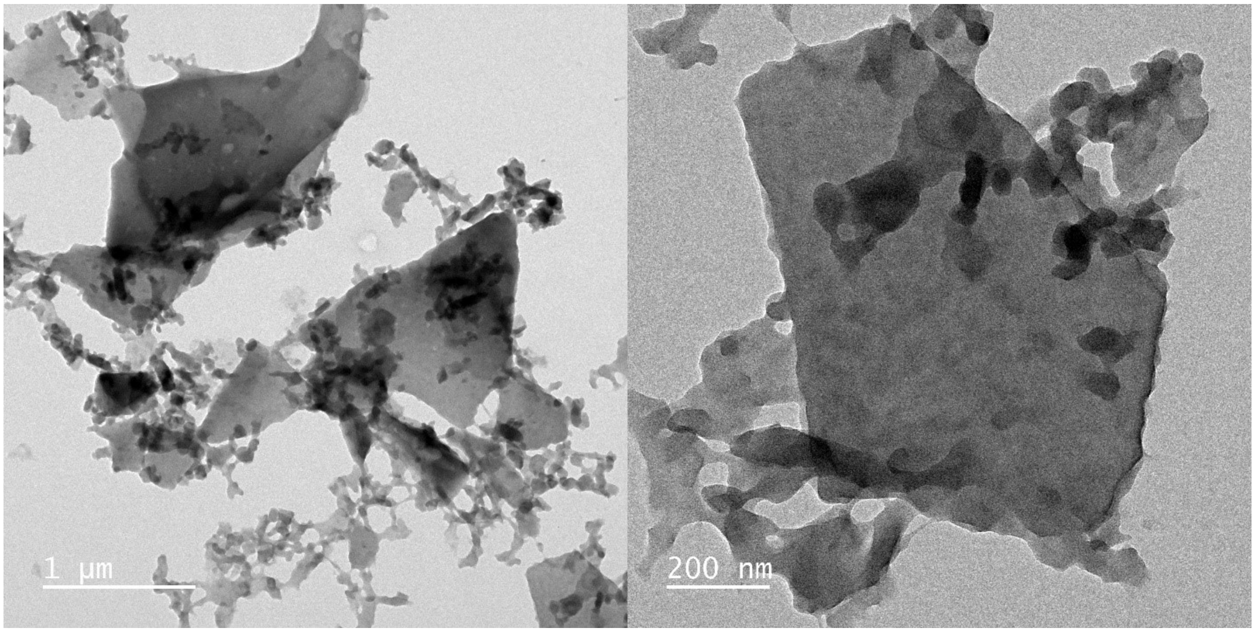
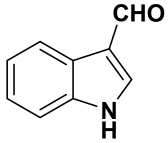


Figure S6. TEM image of Cu/B-GQD

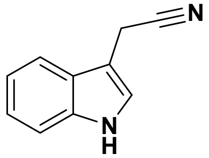
Spectra Data

Indole-3-aldehyde



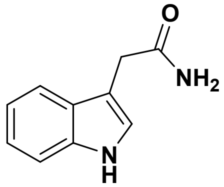
1HNMR (DMSO-d, 400 MHz): δ 12.30 (br, 1H), 9.93 (s, 1H), 8.30 (s, 1H), 8.10 (d, 1H, *J* = 6.88 Hz), 7.53 (d, 1H, *J* = 7.48 Hz), 7.28-7.20 (m, 2H). MS Calcd m/z 145.1, found 145.1. The data was same as reported in literature[1].

Indole-3-acetonitrile



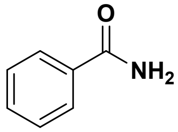
1HNMR (DMSO-d, 400 MHz): δ 11.16 (s, 1H), 7.61 (d, 1H, *J* = 4.12 Hz), 7.44 (d, 1H, *J* = 4.12 Hz), 7.37 (s, 1H), 7.19-7.14 (m, 1H), 7.11-7.06 (m, 1H), 4.06 (s, 2H). Anal. calcd. for $C_{10}H_8N_2$: C, 76.90; H, 5.16; N, 17.94. found: C, 76.98; H, 5.45; N, 18.10. The NMR spectrum was same as reported in literature[2].

Indole-3-acetamide



1HNMR (DMSO-d, 400 MHz): δ 10.90 (s, 1H), 7.61 (d, 1H, *J* = 7.76 Hz), 7.39 (d, 2H, *J* = 8.08 Hz), 7.23 (s. 1H), 7.12 (t, 1H, *J* = 7.76 Hz), 7.03 (t, 1H, *J* = 7.32 Hz). 6.94 (s, 1H), 3.53 (s, 2H). Anal. calcd. for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N, 16.08. found: C, 68.97; H, 5.96; N, 16.17. The NMR spectrum was same as reported in literature[3].

Benzamide



1HNMR (DMSO-d, 400 MHz): δ 8.01 (s, 1H), 7.89 (d, 2H, *J* = 7.2 Hz), 7.52 (t, 1H, *J* = 7.2 Hz), 7.47-7.41 (m, 3H). 13C{1H} NMR (DMSO-d, 100MHz): δ 168.3, 134.6, 131.7, 128.6, 127.9. The NMR spectrum was same as reported in literature[3].

Copies of NMR spectra

Figure S7. HNMR (DMSO-d, 400 MHz) image of indole-3-aldehyde.

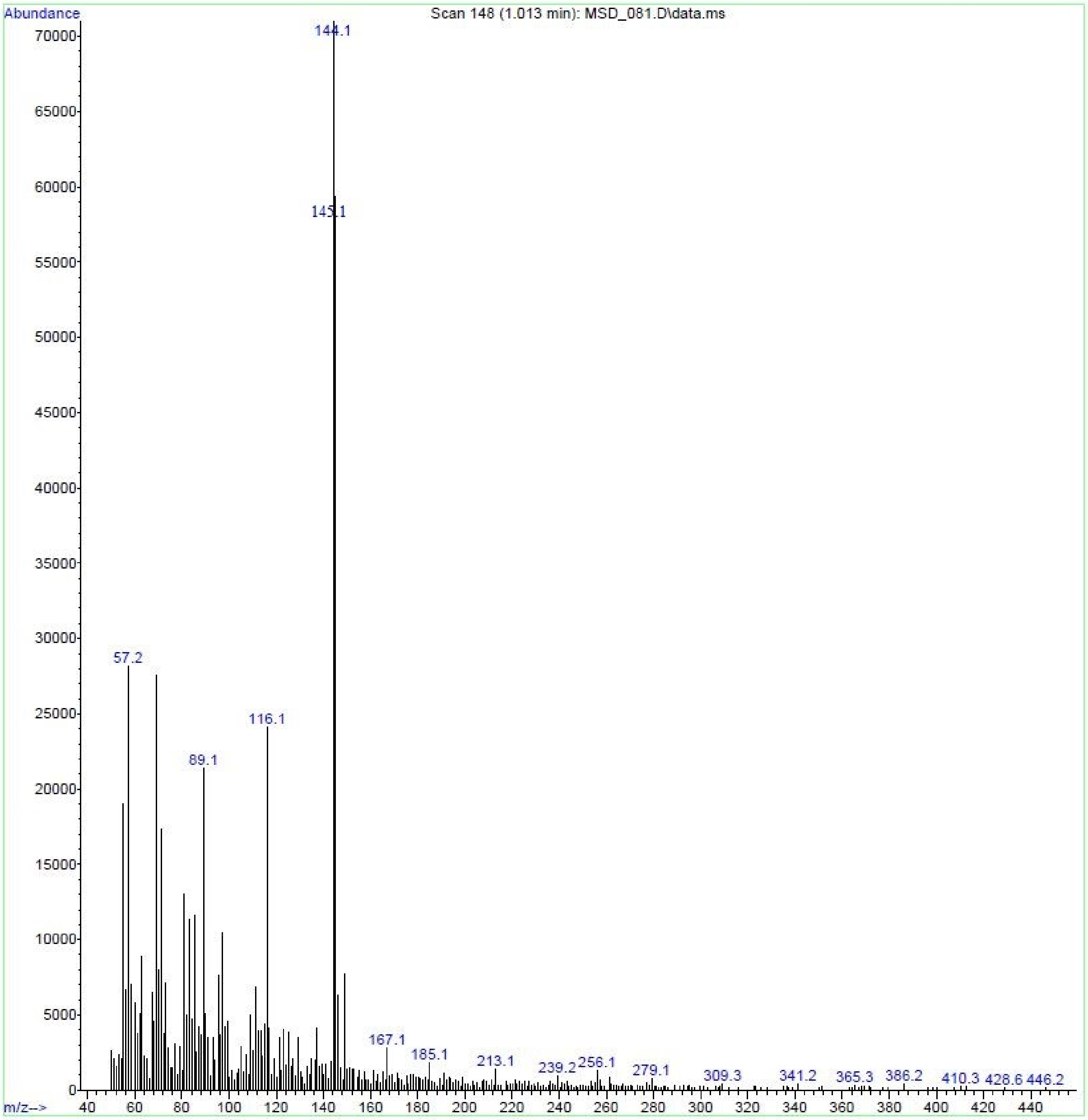

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Figure S8. Mass spectrum of indole-3-aldehyde.

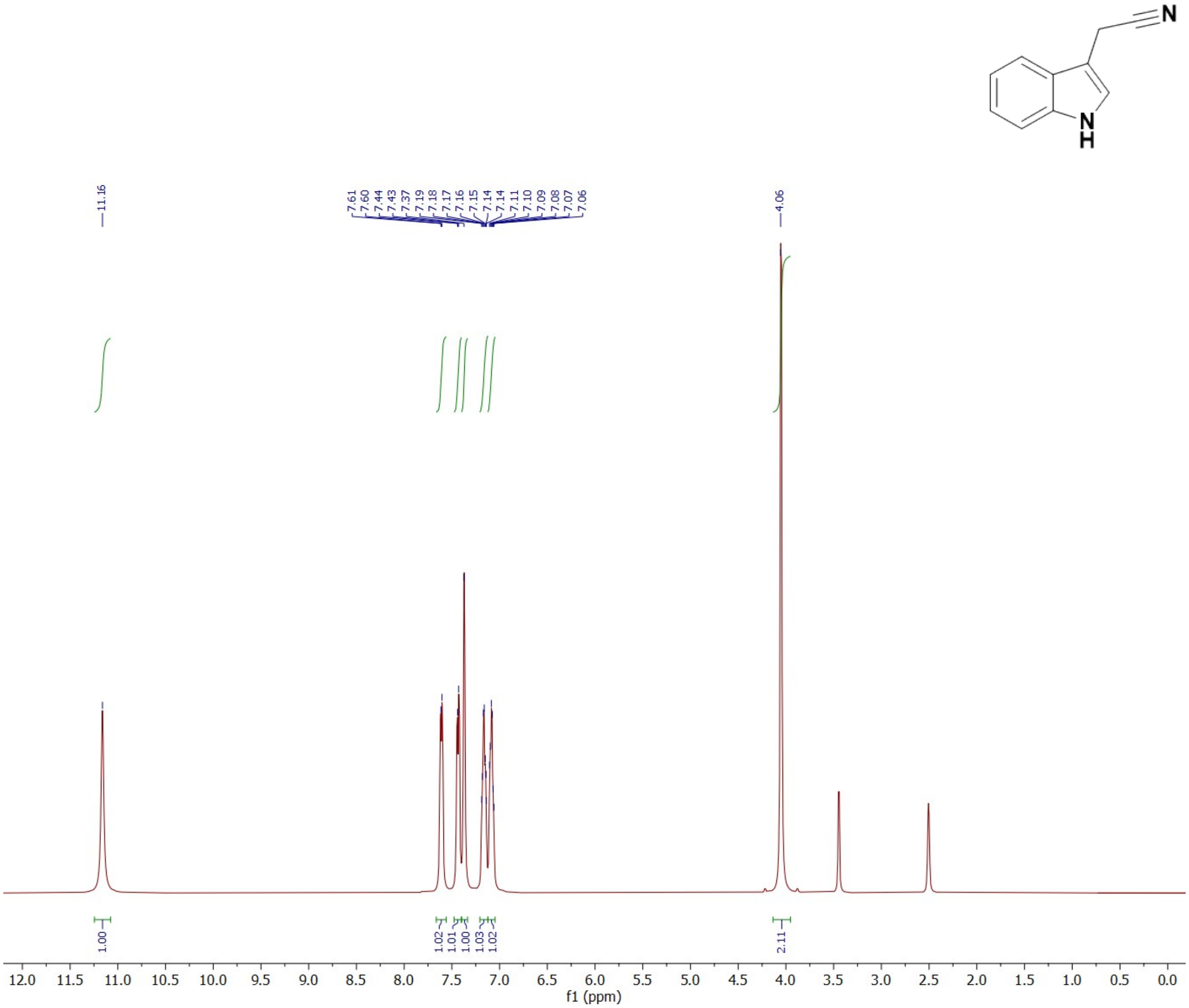

Figure S9. HNMR (DMSO-d, 400 MHz) image of indole-3-acetonitrile.

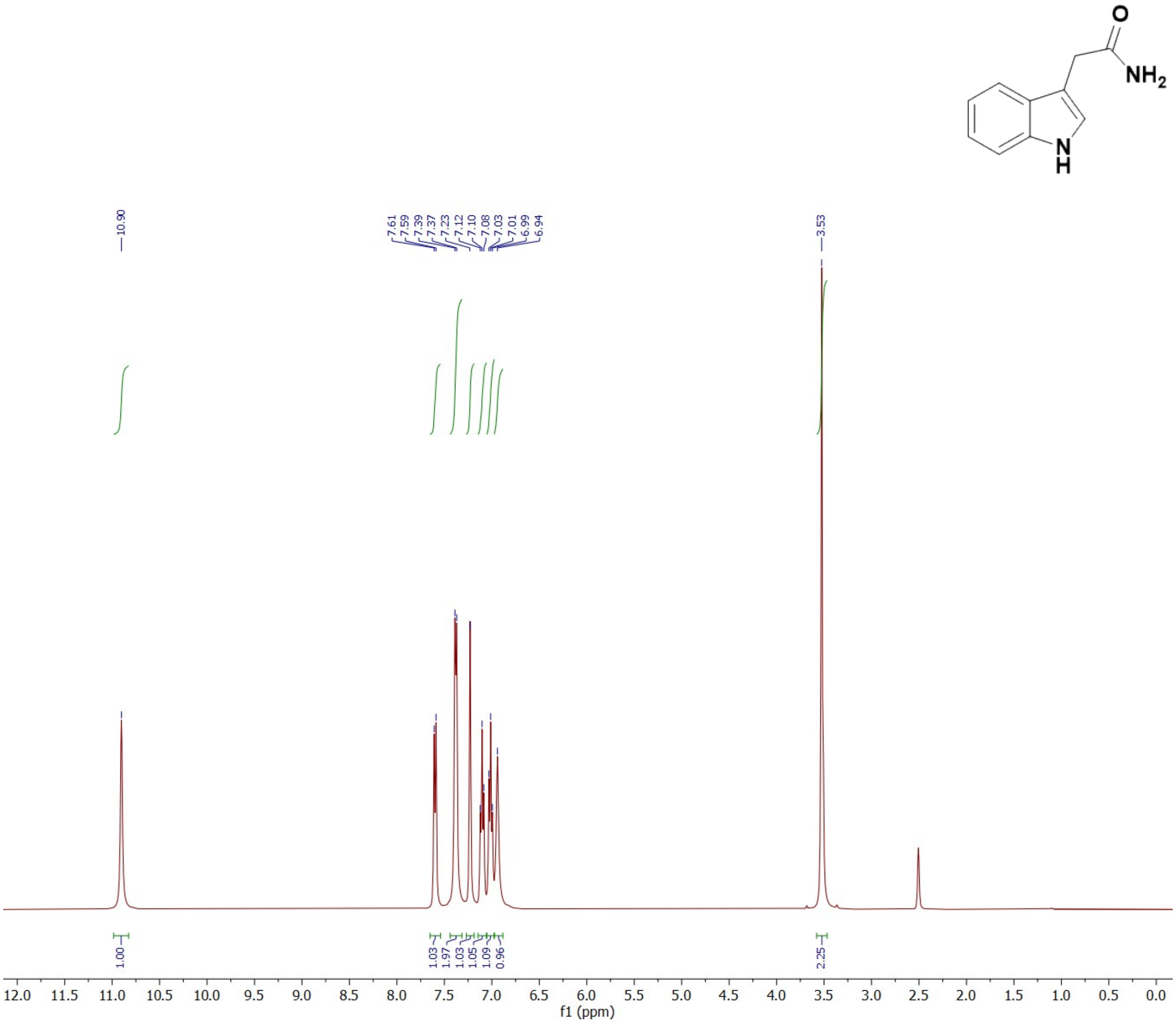

Figure S10. HNMR (DMSO-d, 400 MHz) image of indole-3-acetoamide.

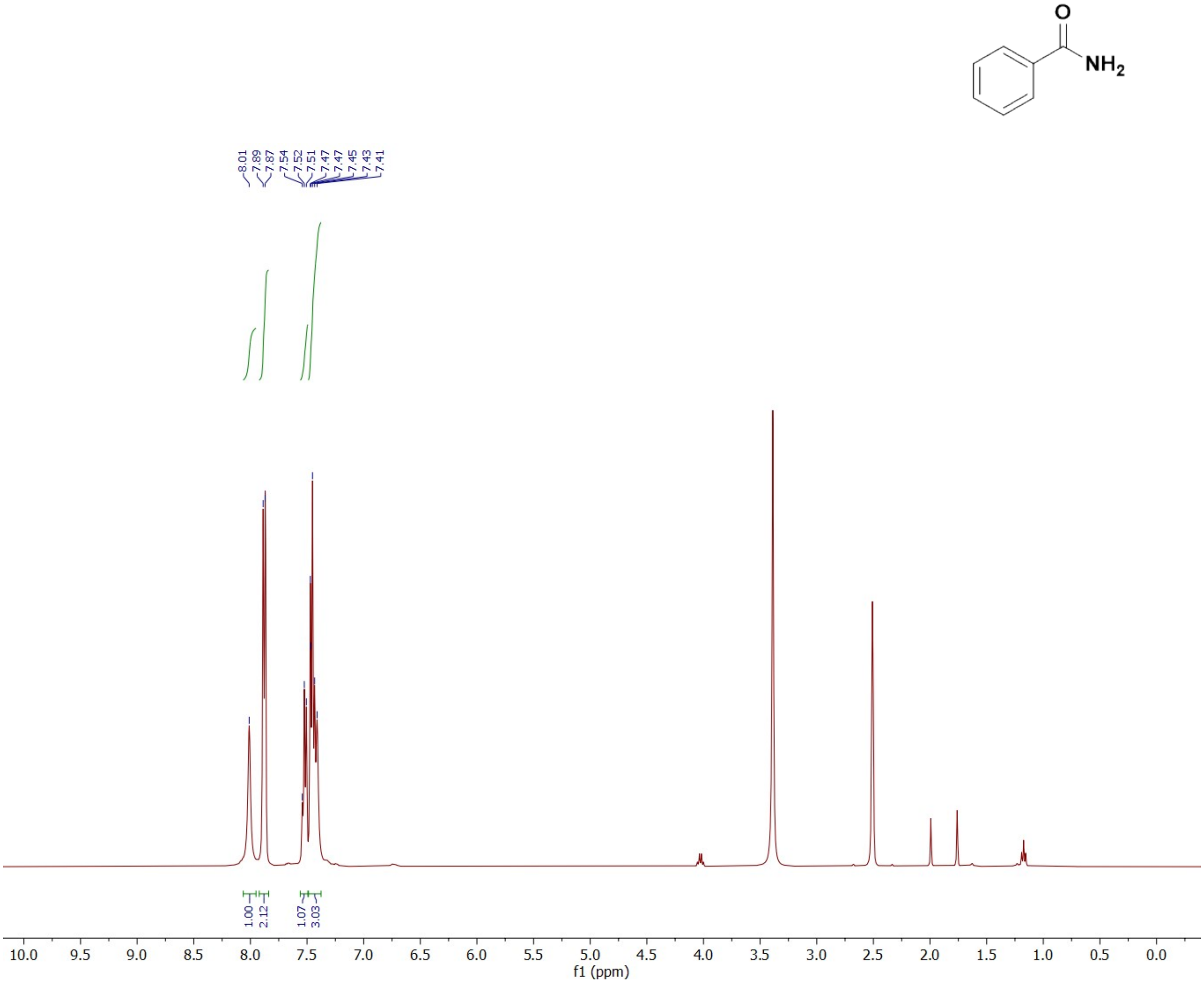

Figure S11. HNMR (DMSO-d, 400 MHz) image of benzamide.

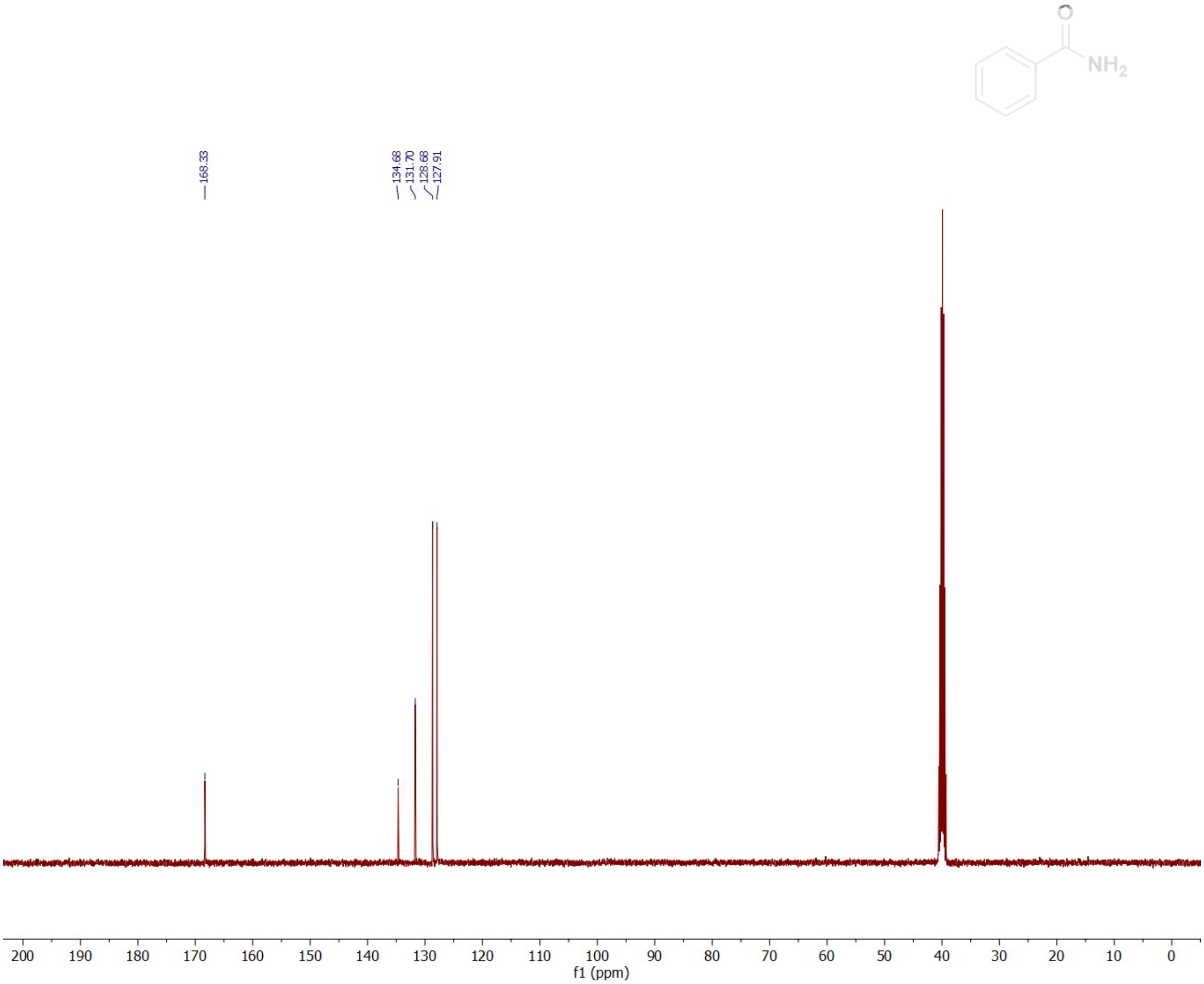

Figure S12. CNMR (DMSO-d, 400 MHz) image of benzamide.

References

1. Lin, D.-Z.; Huang, J.-M., Synthesis of 3-Formylindoles via Electrochemical Decarboxylation of Glyoxylic Acid with an Amine as a Dual Function Organocatalyst. *Organic Letters* **2019,** *21* (15), 5862-5866.
2. Liu, C.; Cai, Z.; Luo, J.; Wu, L.; He, L., Arynes Promoted Dehydrosulfurization of Thioamides: Access to Nitriles and Diaryl Sulfides. *Organic Letters* **2024,** *26* (36), 7678-7682.
3. Li, X.-Y.; Kang, J.-X.; Han, H.; Ma, Y.-N.; Liu, Z.; Chen, X., Rapid Synthesis of Primary Amides Using Ammonia Borane. *The Journal of Organic Chemistry* **2025,** *90* (4), 1720-1726.