Supplementary Information (SI) for Catalysis Science & Technology.

Preparation of CuCo/NH_2-MIL-101(Fe) nanocomposite for photocatalytic synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones and 1-amidoalkyl-2-naphthols

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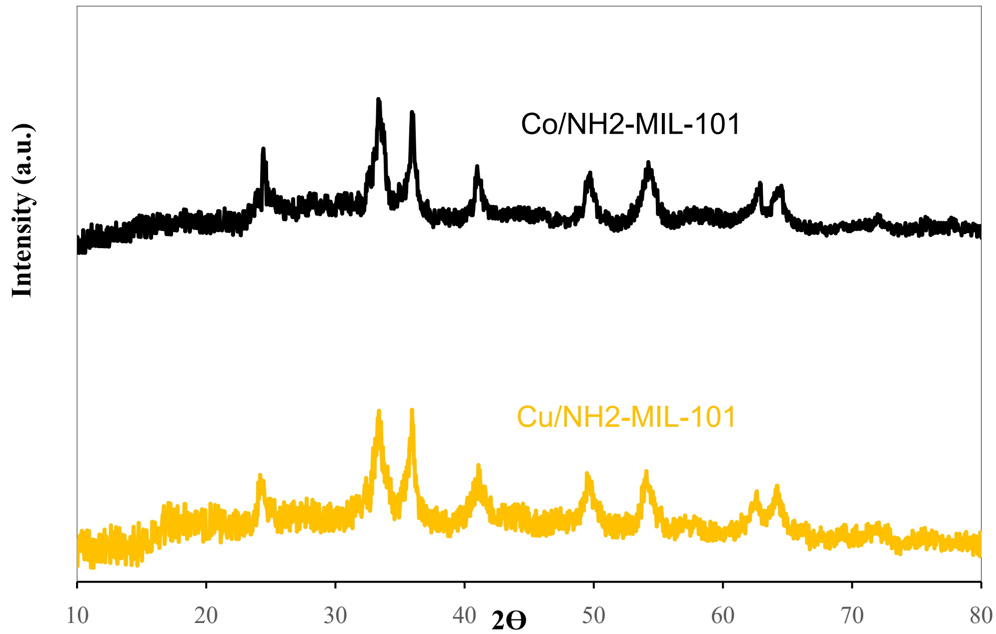


Figure S1. XRD patterns of Co/NH_2-MIL-101 and Cu/NH_2-MIL-101.

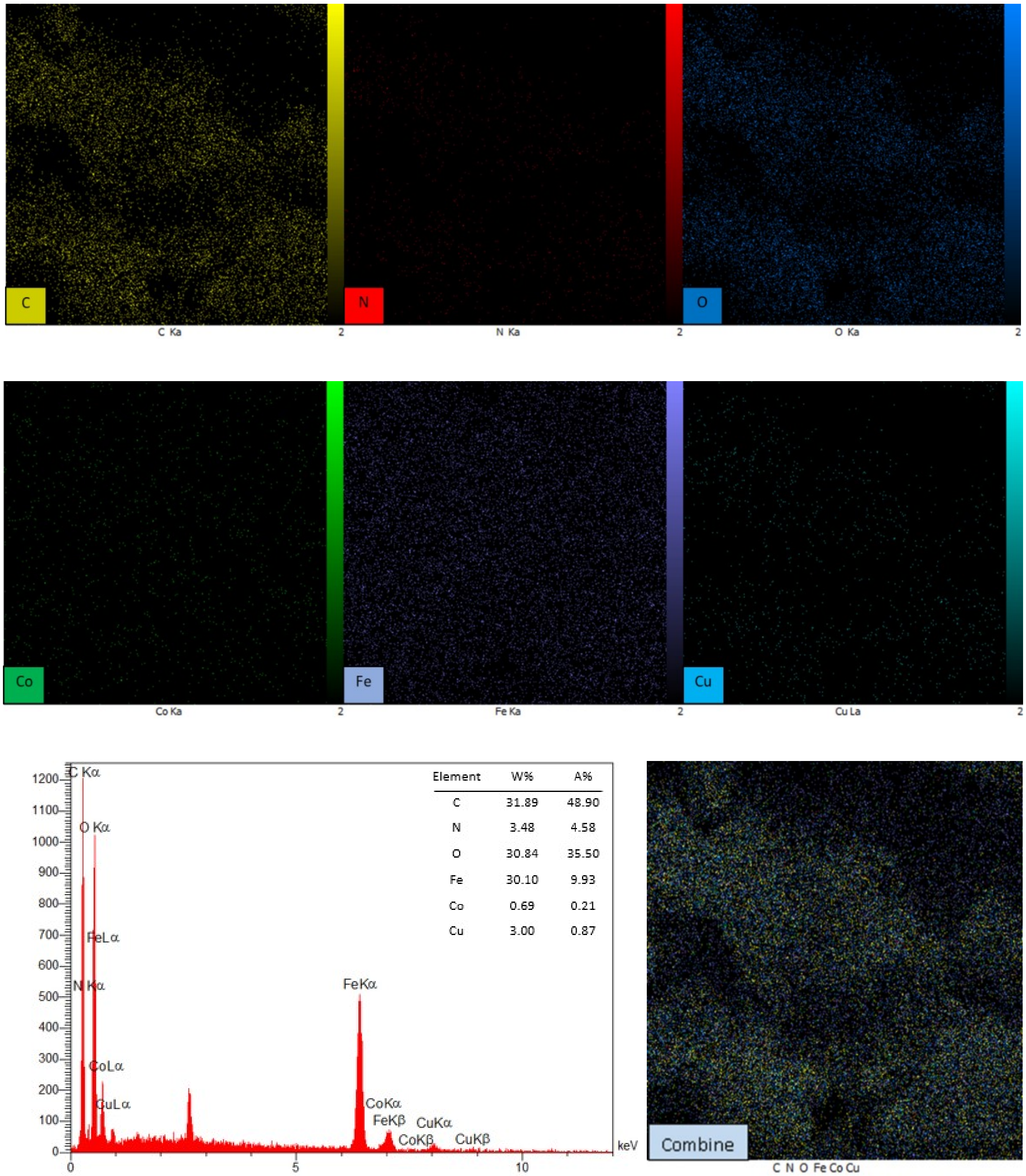


Figure S2. Elemental mapping and EDX spectrum for a specific region of CuCo/NH_2-MIL-101.

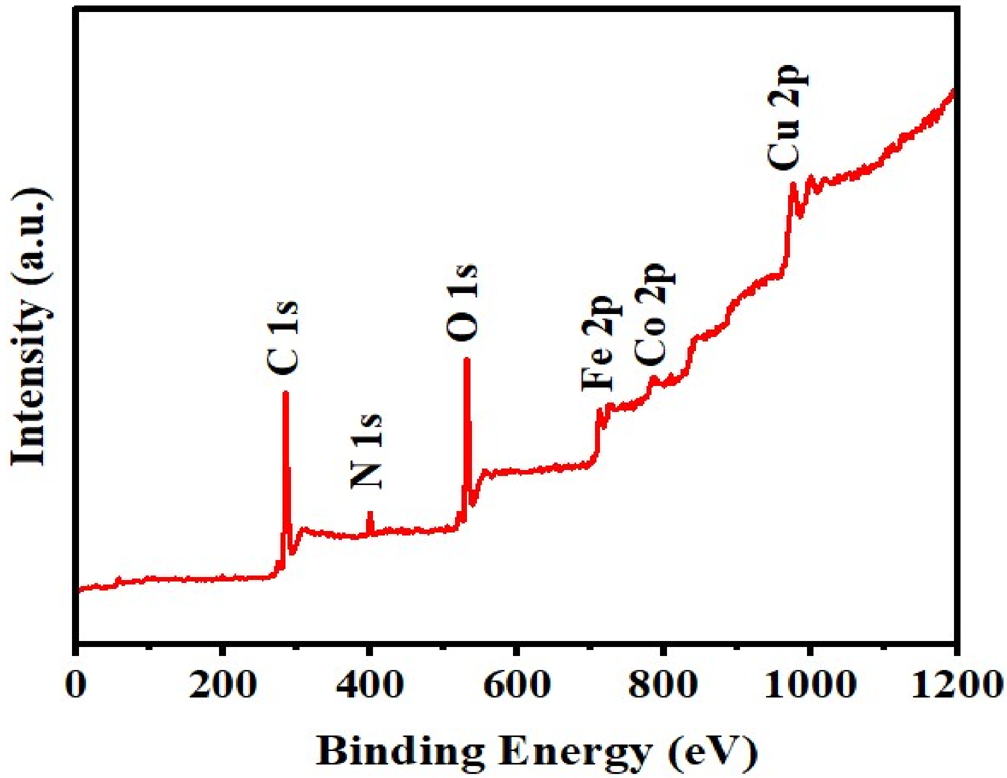


Figure S3. XPS survey of CuCo/NH_2-MIL-101(Fe).

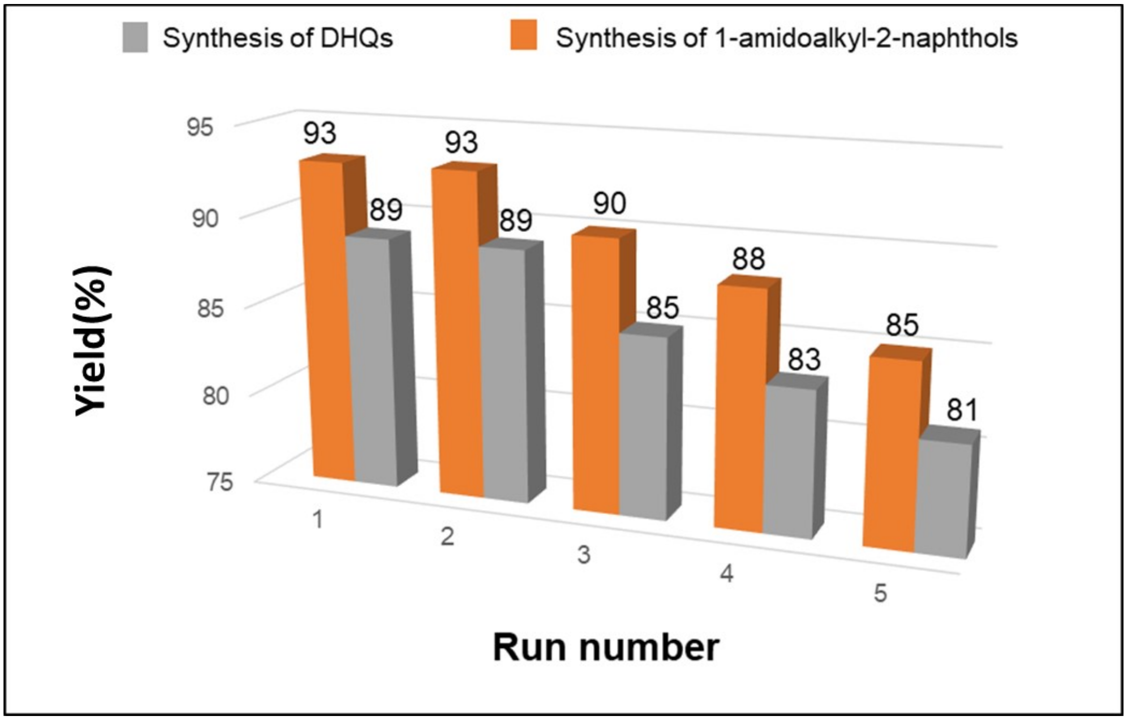


Figure S4. Reusability of the photocatalyst for the synthesis of 2-phenyl-2,3-dihydroquinazolin-4(1*H*)-ones (DHQs) and 1-amidoalkyl-2-naphthols.

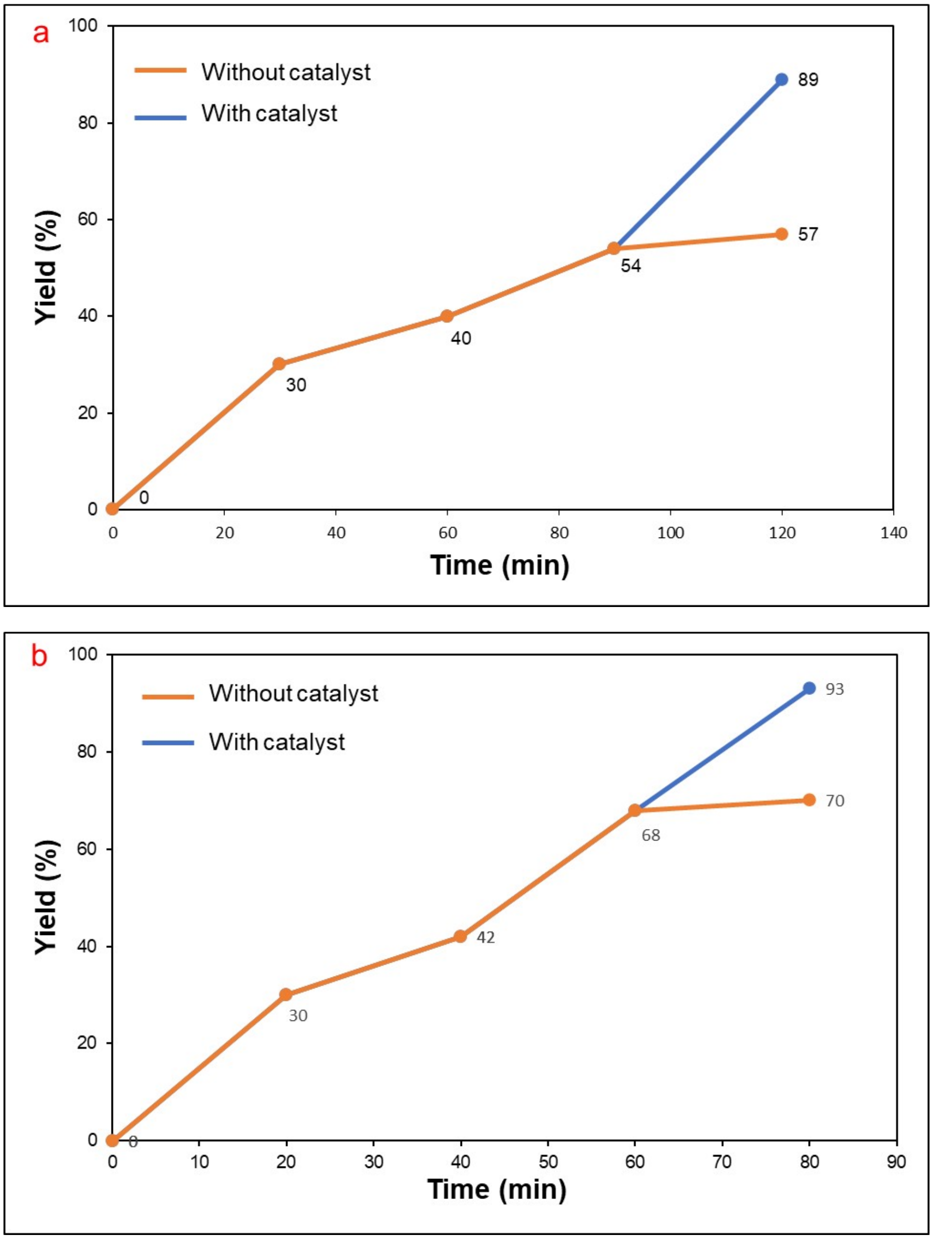


Figure S5. Hot filtration test of the photocatalyst for the synthesis of (a) 2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one and (b) 1-amidoalkyl-2-naphthol.

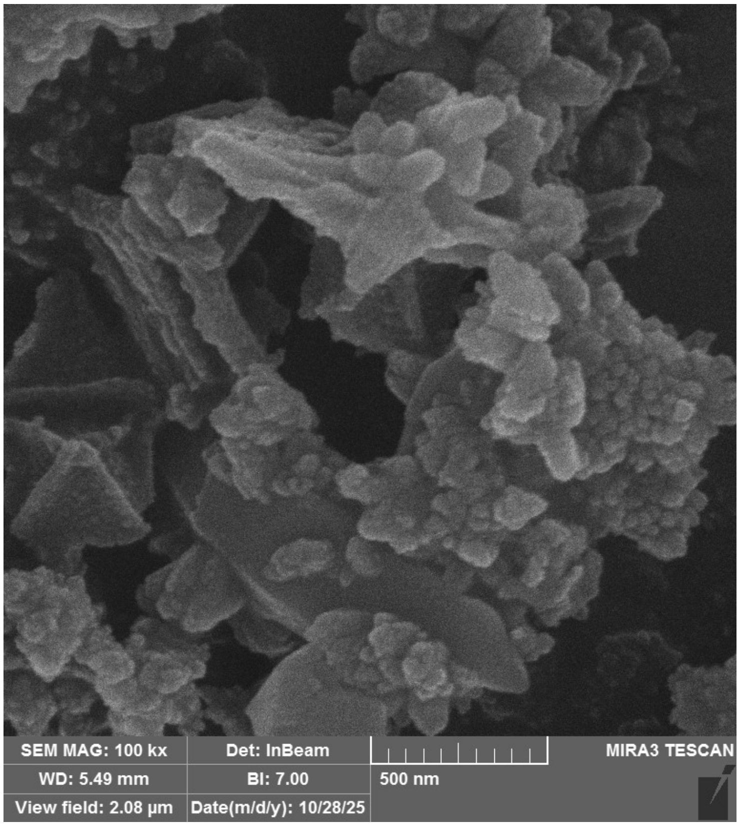


Figure S6. SEM image of the reused CuCo/NH_2-MIL-101.

Table S1. Performance of CuCo/NH_2-MIL-101 in the synthesis of 2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one compared to the reported catalytic systems.

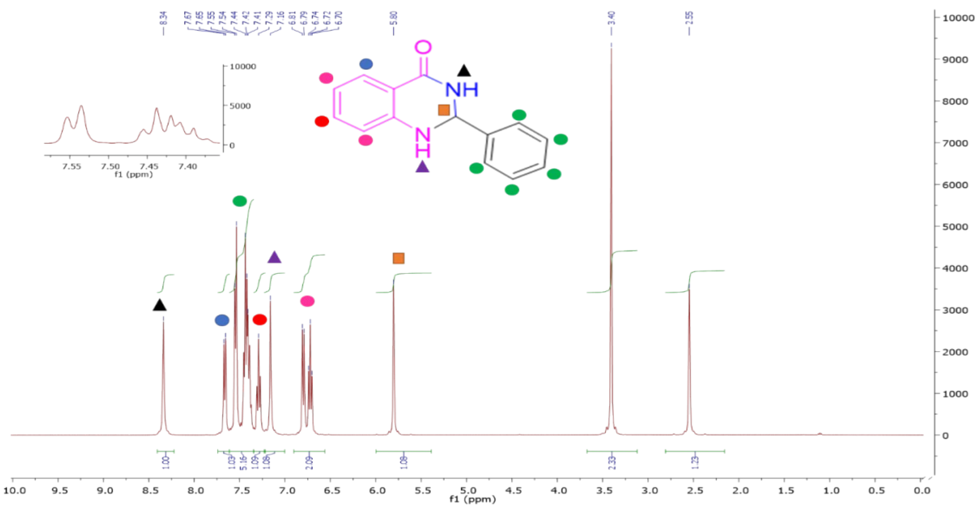
Entry	Catalyst (loading)	Conditions	Solvent	Time (h)	Yield (%)	Ref
1	Urea-rich POP (0.02 g)	100 °C	-	1	85	1
2	Hydroxypatite NPs (0.05 g)	110 °C	H_2O	1	95	2
3	β-Cyclodextrin (10 mol%)	90 °C	-	1	90	3
4[a]	MOF(Zr)/rGO (0.02 g)	55 °C	EtOH	0.5	95	4
5[a]	MOF(Nd) (10 mol%)	25 °C	CH_3CN	24	100	5
6[a]	MOFCu) (5.0 mol %)	70 °C/N_2	MeOH	12	79	6
7[a]	MOF(In) (0.004 g, 1 mol %)	reflux/air	EtOH	10	99	7
8[a]	α-Chymotrypsin (0.36 mol%)	LED (18 W)/37 °C	MeOH	2	96	8
9	CuCo/NH_2-MIL101 (0.02 g)	LED (200 W)/35 °C	EtOH	2	89	This work

[a] 2-Aminobenzamide.

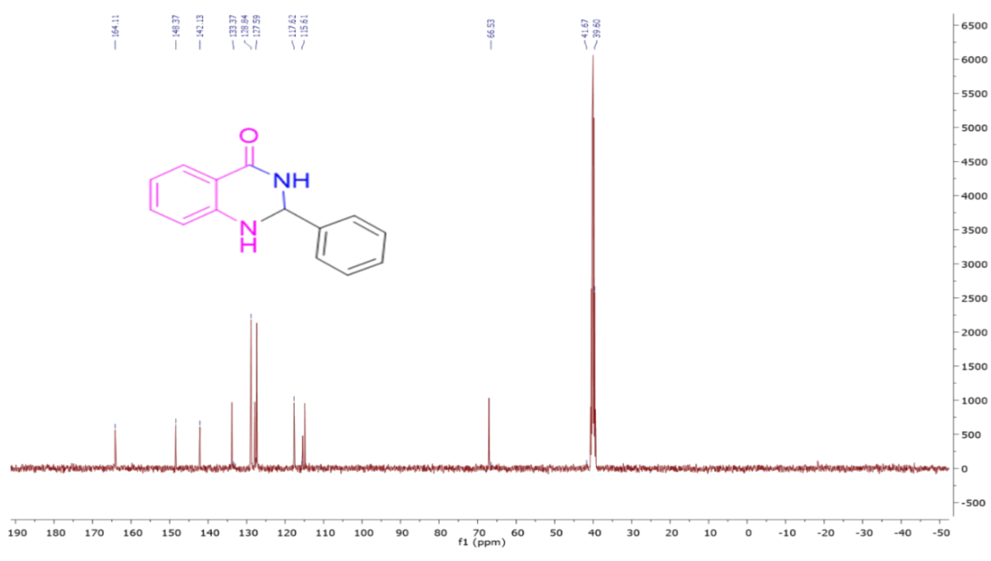
Table S2. Performance of CuCo/MIL-101-NH_2 in the synthesis of *N*-((2-hydroxynaphthalen-1-yl)(phenyl)methyl)benzamide compared to the reported catalytic systems.

Entry	Catalyst (loading)	Conditions	Solvent	Time (min)	Yield (%)	Ref
1	Fe_3O_4@SiO_2@K10 NPs (0.08 mg)	70 °C	-	25	96	9
2	ZS-1 Zeolite (0.05 mg)	110 °C	-	30	95	10
3	MSNs-HPZ-SO_3H (0.01 g)	120 °C	-	95	84	11
4	Nano-$BF_3 \cdot SiO_2$ (0.02 g)	80 °C	EtOAc	50	95	12
5	Cu@Ag−CeO_2/chitosan (0.01 g)	100 °C	-	15	98	13
6	MIL101(Cr)/phosphotungstic acid (5.1 mol%)	130 °C	-	5	92	14
7	MOF(Cu/Ag)/MCM-41 (0.1 g)	130 °C	-	10	93	15
8	CdS-Fe_3O_4 (0.03 g)	Hg lamp (400 W)/82 °C	CH_3CN	90	93	16
9	CuCo/NH_2-MIL-101 (0.02 g)	LED (200 W)/35 °C	EtOH	80	93	This work

Spectral Data

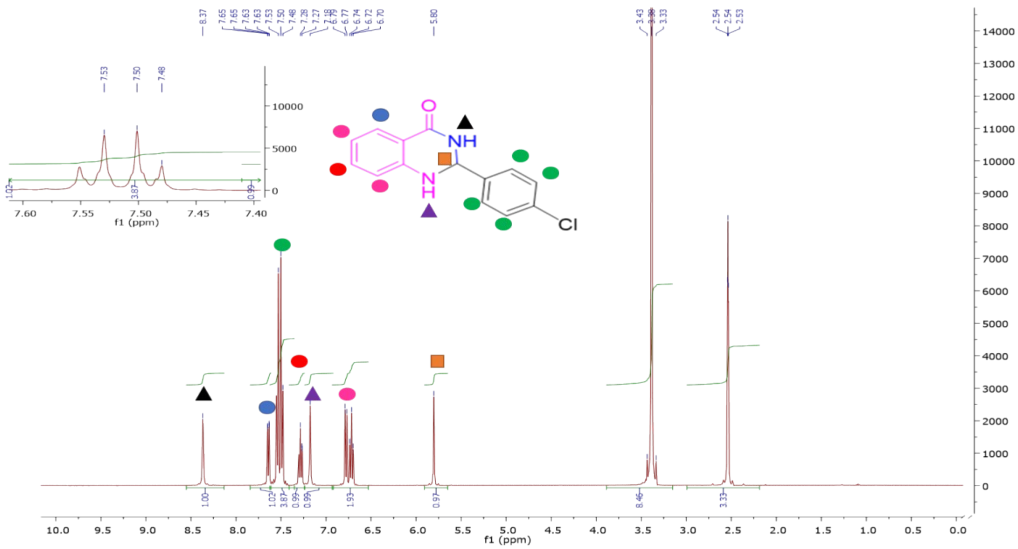


^{1}H NMR (400 MHz, DMSO-d_6) δ 8.34 (s, 1H), 7.67–7.65 (d, J = 7.7 Hz, 1H), 7.55–7.54 (m, 5H), 7.44–7.41 (s, 1H), 7.16 (s, 1H), 6.81–6.70 (m, 2H), 5.80 (s, 1H).

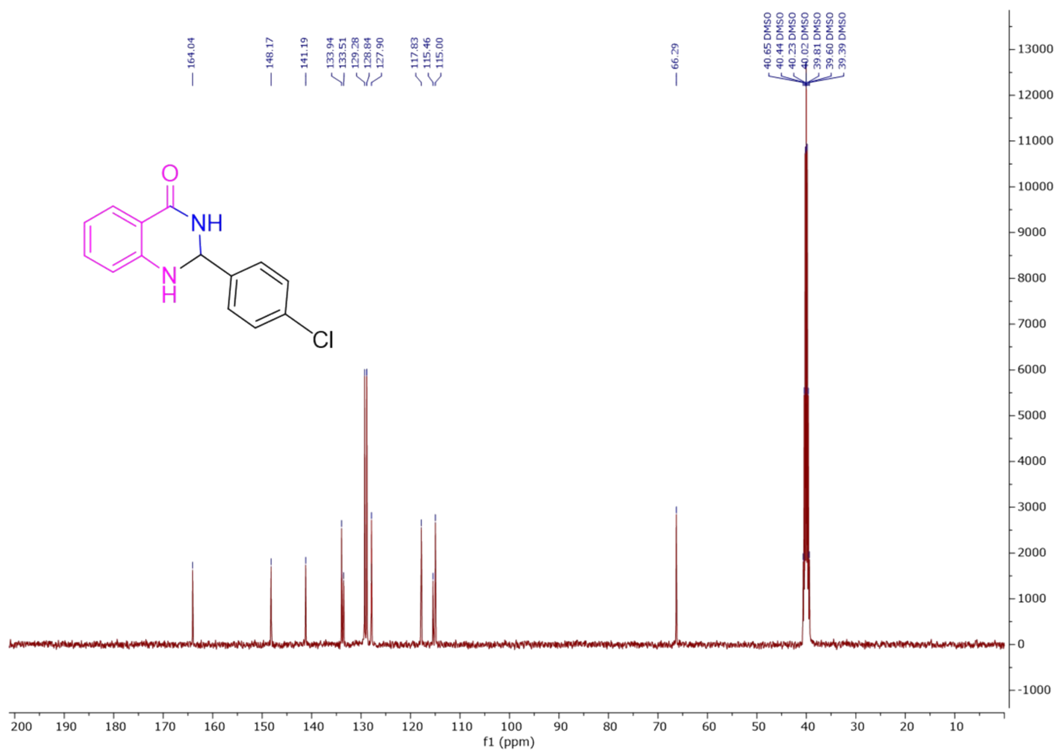


^{13}C NMR (100 MHz, DMSO-d_6) δ 164.1, 148.3, 142.1, 133.3, 128.8, 127.5, 117.6, 115.6, 66.5.

Figure A1. ^{1}H and ^{13}C NMR of 2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one.

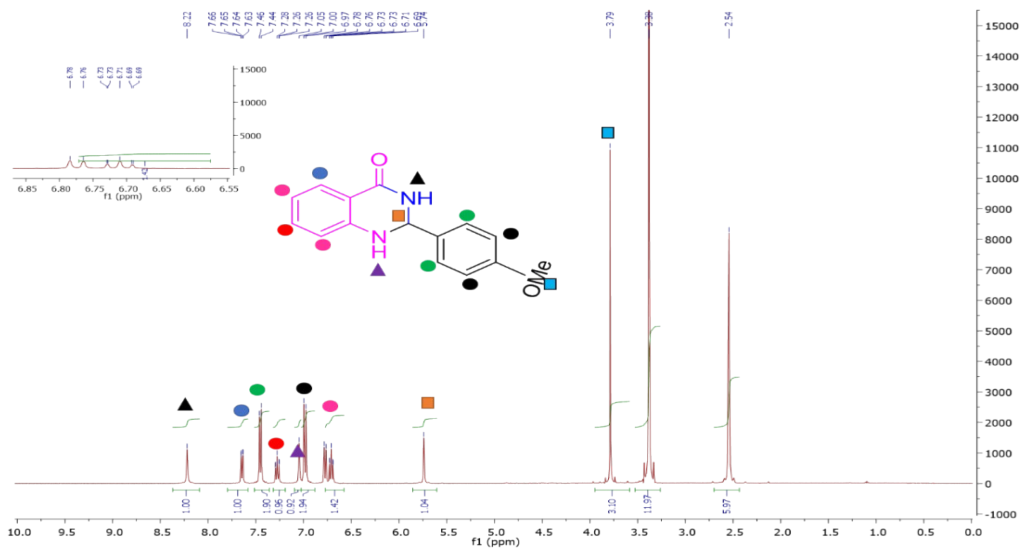


[1]H NMR (400 MHz, DMSO-d_6) δ 8.37 (s, 1H), 7.65–7.63 (dd, J = 7.7, 1.1 Hz, 1H), 7.53–7.48 (q, 4H), 7.28–7.27 (m, 1H), 7.18 (s, 1H), 6.79–6.70 (m, 2H), 5.80 (s, 1H).

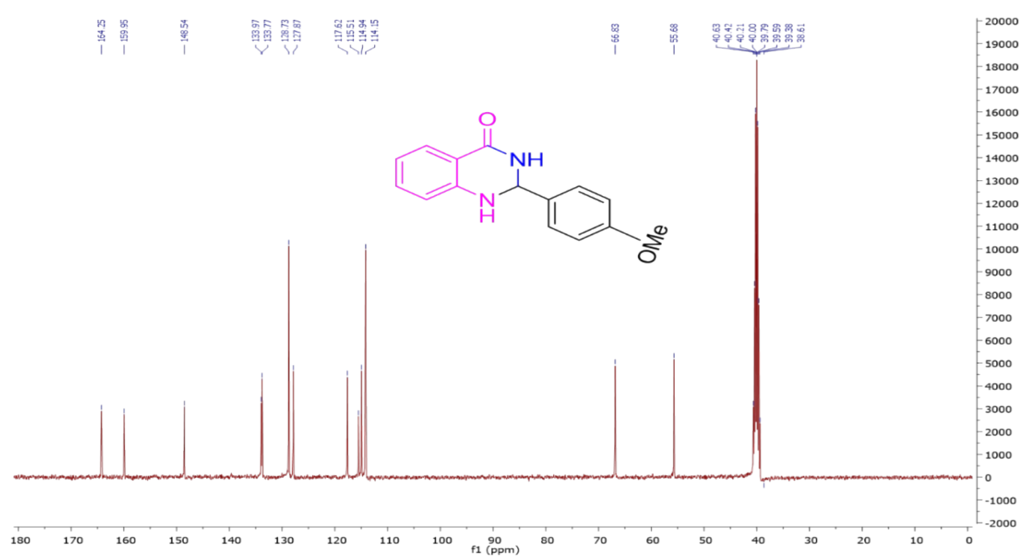


[13]C NMR (100 MHz, DMSO-d_6) δ 164.04 ,148.1, 141.1, 133.9, 133.5, 129.2, 128.8, 127.9, 117.8, 115.0, 66.2.

Figure A2. [1]H and [13]C NMR of 2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1H)-one.

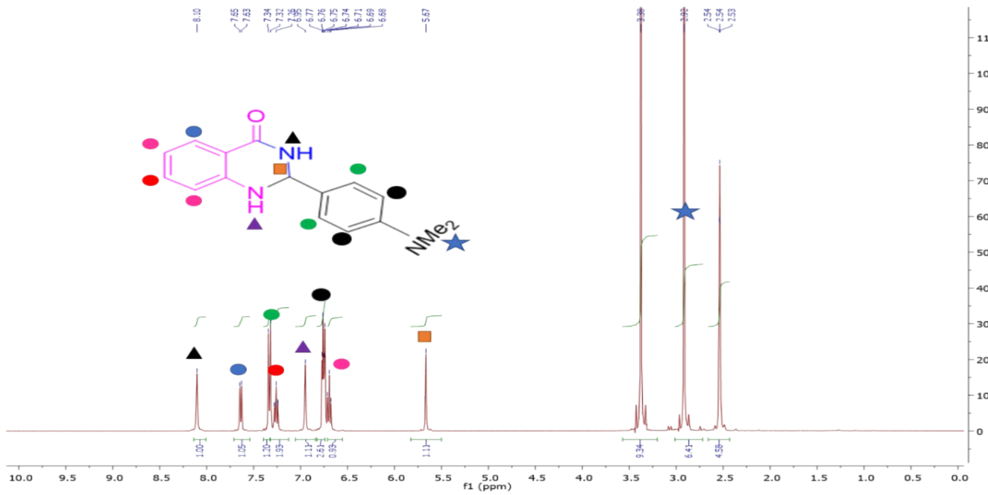


[1]H NMR (400 MHz, DMSO-d_6) δ 8.22 (s, 1H), 7.66–7.63 (d, 1H), 7.46–7.44 (d, 2H), 7.28–7.26 (t, 1H), 7.05 (s, 1H), 7.0–6.97 (dd, J = 20.0, 8.7 Hz, 2H), 6.78–6.69 (ddd, J = 19.7, 17.2, 9.8 Hz, 1H), 5.74 (s, 3H).

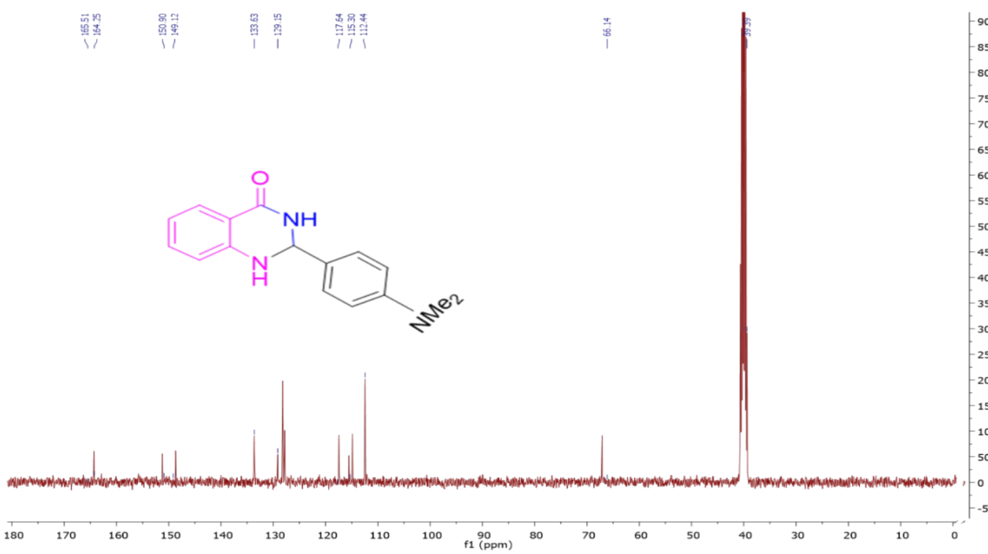


[13]C NMR (100 MHz, DMSO-d_6) δ 164.2, 159.9, 148.5, 133.9, 133.7, 128.7, 127.8, 117.6, 115.5, 114.9, 114.1, 66.8, 55.6.

Figure A3. [1]H NMR and [13]C NMR of 2-(4-methoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one.

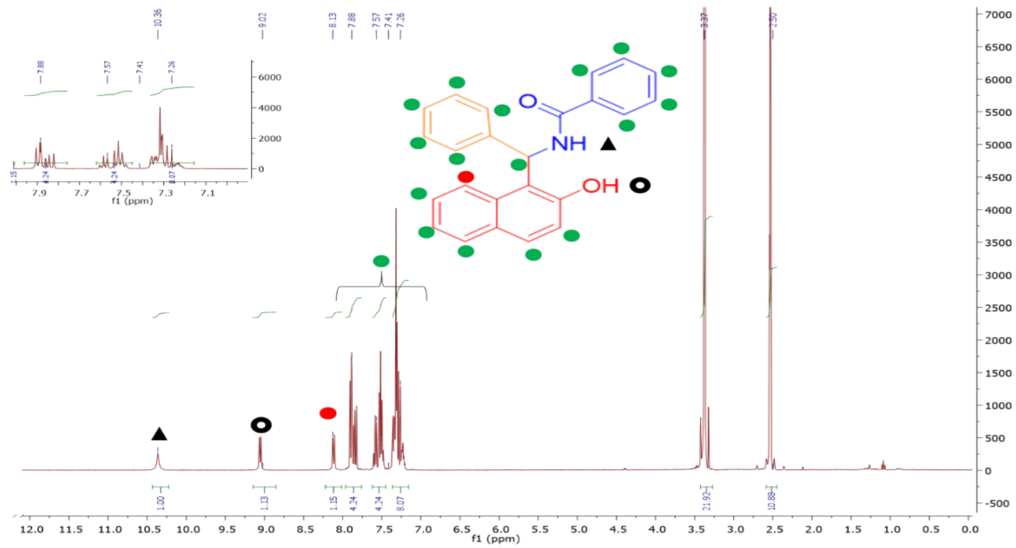


[1]H NMR (400 MHz, DMSO-d_6) δ 8.10 (s, 1H), 7.65–7.63 (d, J = 6.9 Hz, 1H), 7.34–7.32 (d, J = 8.7 Hz, 1H), 7.26–6.95 (m, 2H), 6.95 (s, 1H), 6.77–6.75 (dd, J = 8.3, 3.7 Hz, 3H), 6.74–6.68 (m, 1H), 5.67 (s, 1H), 2.92 (s, 6H).

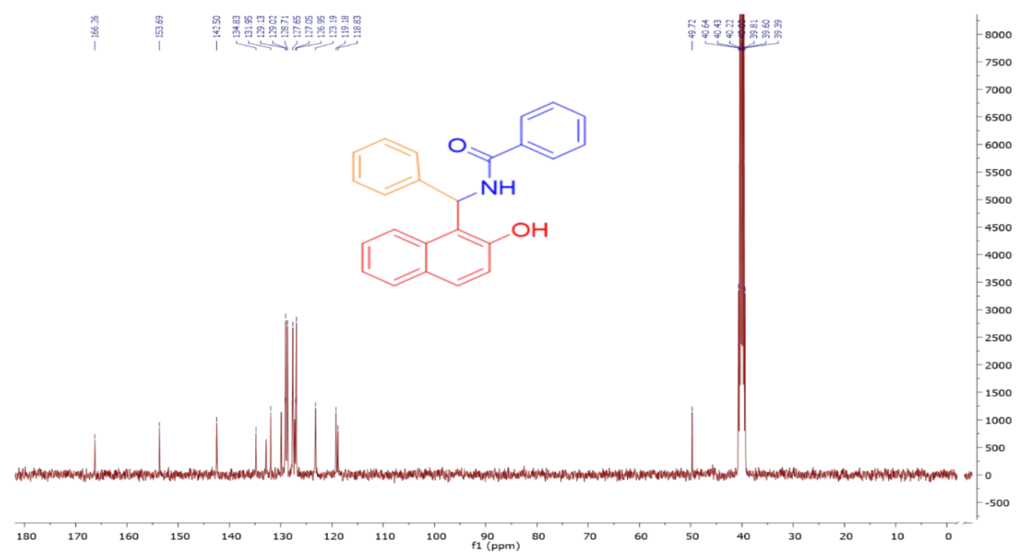


[13]C NMR (100 MHz, DMSO-d_6) δ 165.5, 164.2, 150.9, 149.1, 133.6, 129.1, 117.6, 115.3, 112.4, 66.1.

Figure A4. [1]H NMR and [13]C NMR of 2-(4-(dimethylamino)phenyl)-2,3-dihydroquinazolin-4(1*H*)-one.

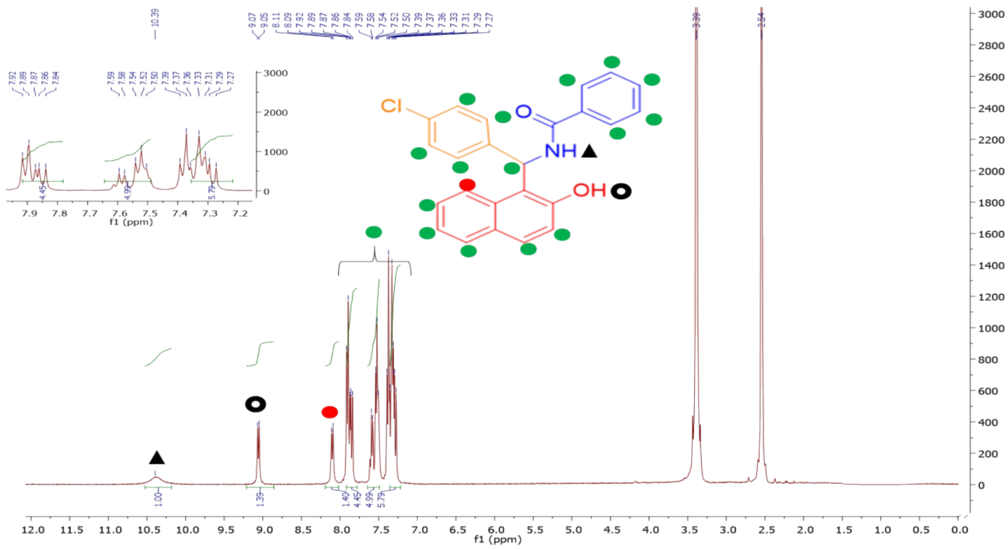


^{1}H NMR (400 MHz, DMSO-d_6) δ 10.36 (s, 1H), 9.02 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 8.6 Hz, 1H), 8.00–7.76 (m, J = 24.8, 11.1, 5.0 Hz, 4H), 7.65–7.45 (m, 4H), 7.40–7.06 (m, 8H).

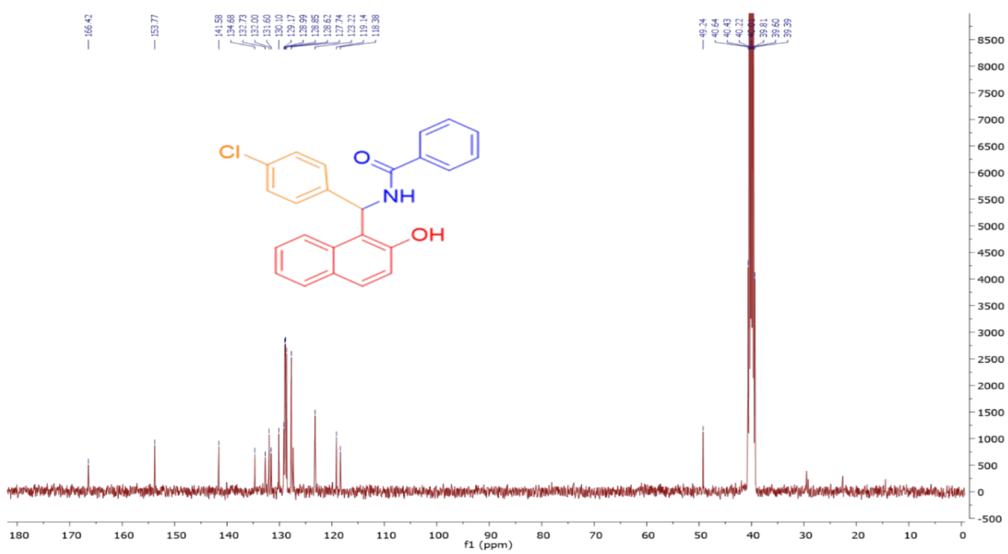


^{13}C NMR (100 MHz, DMSO-d_6) δ 166.2, 153.6, 142.5, 134.8, 131.9, 129.1, 129, 128.7, 127.6, 127, 126.9, 123.1, 119.1, 118.8, 49.7.

Figure A5. ^{1}H NMR and ^{13}C NMR of *N*-((2-hydroxynaphthalen-1-yl)(phenyl)methyl)benzamide.

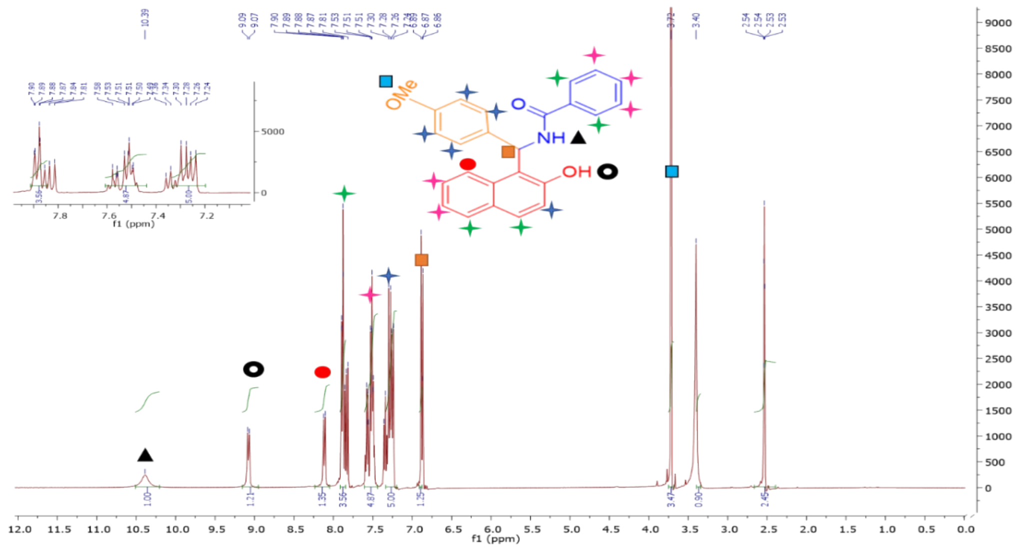


^{1}H NMR (400 MHz, DMSO-d_6) δ 10.39 (s, 1H), 9.07–9.05 (d, J = 8.3 Hz, 1H), 8.11–8.09 (d, J = 8.6 Hz, 1H), 7.92–7.84 (m, 4H), 7.59–7.50 (m, 5H), 7.39–7.27 (ddd, J = 22.7, 14.2, 8.7 Hz, 6H).

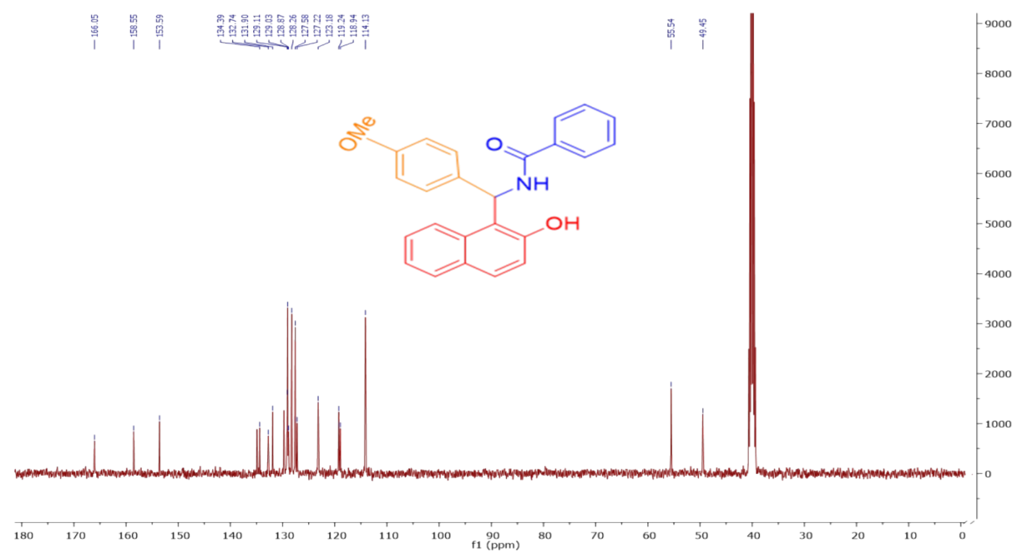


^{13}C NMR (100 MHz, DMSO-d_6) δ 166.4, 153.7, 141.5, 134.6, 132.7, 132, 131.6, 130.1, 129.1, 128.9, 128.8, 128.6, 127.7, 123.2, 119.1, 118.3, 49.2.

Figure A6. ^{1}H and ^{13}C NMR of *N*-((4-chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl) benzamide.

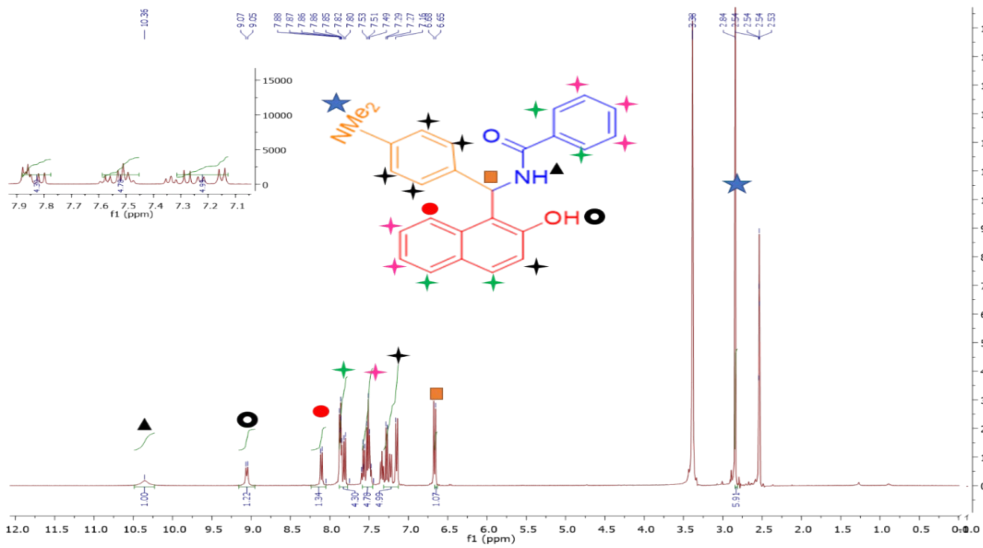


^{1}H NMR (400 MHz, DMSO-d_6) δ 10.39 (s, 1H), 9.08–9.07 (d, 1H), 7.90–7.89 (d, J = 8.7 Hz, 1H), 7.88–7.81 (m, 4H), 7.58–7.49 (m, 5H), 7.36–7.24 (m, 5H), 6.87 (s, 1H), 3.72 (s, 3H).

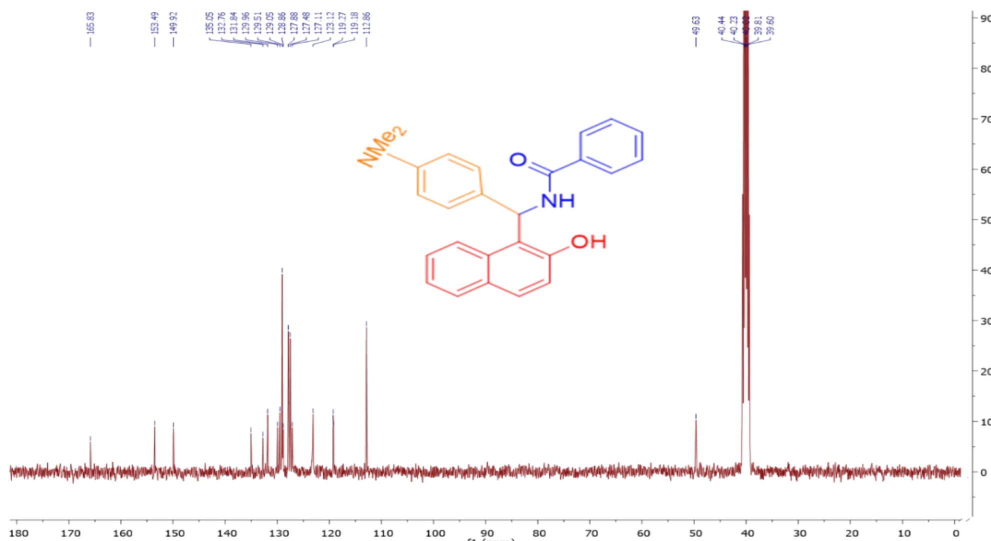


^{13}C NMR (100 MHz, DMSO-d_6) δ 166, 158.5, 153.5, 134.3, 132.7, 131.9, 129.1, 129, 128.8, 128.2, 127.5, 127.2, 123.1, 119.2, 118.9, 114.1, 55.5, 49.4.

Figure A7. ^{1}H NMR and ^{13}C NMR of *N*-((4-methoxy)(2-hydroxynaphthalen-1-yl)methyl) benzamide.



^{1}H NMR (400 MHz, DMSO-d_6) δ 10.36 (s, 1H), 9.07 (d, J = 8.6 Hz, 1H), 9.05 (d, J = 14.2 Hz, 1H), 7.88–7.80 (ddd, J = 40.3, 17.9, 12.2 Hz, 4H), 7.53–7.49 (m, 5H), 7.29–7.16 (m, 5H), 6.68–6.65 (d, J = 8.9 Hz, 1H), 2.84 (s, 6H).



^{13}C NMR (100 MHz, DMSO-d_6) δ 165.8, 153.4, 149.9, 135, 132.7, 131.8, 129.9, 129.5, 129, 128.8, 127.8, 127.4, 127.1, 123.1, 119.2, 119.1, 112.8, 49.6.

Figure A8. ^{1}H NMR and ^{13}C NMR of *N*-((4-(dimethylamino)phenyl)(2-hydroxynaphthalen-1-yl)methyl) benzamide.

References

1. Zarei, N.; Yarie, M.; Torabi, M.; Zolfigol, M. A. Urea-Rich Porous Organic Polymer as a Hydrogen Bond Catalyst for Knoevenagel Condensation Reaction and Synthesis of 2,3-Dihydroquinazolin-4(1H)-ones. *RSC Adv.* **2024**, *14*, 1094–1105.

2. Razavi, N.; Akhlaghinia, B. Hydroxyapatite Nanoparticles (HAP NPs): A Green and Efficient Heterogeneous Catalyst for Three-Component One-Pot Synthesis of 2,3-Dihydroquinazolin-4(1H)-one Derivatives in Aqueous Media. *New J. Chem.* **2016**, *40*, 447–457.

3. Mitra, B.; Chandra Pariyar, G.; Ghosh, P. β-Cyclodextrin: A Supramolecular Catalyst for Metal-Free Approach Towards the Synthesis of 2-Amino-4,6-diphenylnicotinonitriles and 2,3-Dihydroquinazolin-4(1H)-one. *RSC Adv.* **2021**, *11*, 1271–1281.

4. Kumar, G.; Mogha, N. K.; Masram, D. T. Zr-Based Metal–Organic Framework/Reduced Graphene Oxide Composites for Catalytic Synthesis of 2,3-Dihydroquinazolin-4(1H)-one Derivatives. *ACS Appl. Nano Mater.* **2021**, *4*, 2682–2693.

5. Liu, Y.; Zhao, P.; Duan, C.; He, C. Three-Dimensional Neodymium Metal–Organic Framework for Catalyzing the Cyanosilylation of Aldehyde and the Synthesis of 2,3-Dihydroquinazolin-4(1H)-one Derivatives. *Inorg. Chem.* **2023**, *62*, 10359–10368.

6. Xia, Q.; Zhang, S.; Zhang, Y.; Bai, R.; Li, S.; Zhang, J.; Chen, X. Few-Layered Metal–Organic Framework Nanosheets as Catalysts for the Synthesis of 2,3-Dihydroquinazolinone and Propargylamines. *ACS Appl. Nano Mater.* **2021**, *4*, 12108–12118.

7. Jeevananthan, V.; Senadi, G. C.; Muthu, K.; Arumugam, A.; Shanmugan, S. Construction of Indium(III)–Organic Framework Based on a Flexible Cyclotriphosphazene-Derived Hexacarboxylate as a Reusable Green Catalyst for the Synthesis of Bioactive Aza-Heterocycles. *Inorg. Chem.* **2024**, *63*, 5446–5463.

8. Jin, L.; Le, Z.; Fan, Q.; Yang, J.; Zhang, C.; Li, Q.; Xie, Z. Fast Quinazolinone Synthesis by Combining Enzymatic Catalysis and Photocatalysis. *Photochem. Photobio. Sci.* **2023**, *22*, 525–534.

9. Patil, S. M.; Tandon, R.; Tandon, N.; Singh, I.; Bedre, A.; Gade, V. Magnetite-Supported Montmorillonite (K10) (nanocat-Fe-Si-K10): An Efficient Green Catalyst for Multicomponent Synthesis of Amidoalkyl Naphthol. *RSC Adv.* **2023**, *13*, 17051–17061.

10. Dipake, S. S.; Gadekar, S. P.; Thombre, P. B.; Lande, M. K.; Rajbhoj, A. S.; Gaikwad, S. T. ZS-1 Zeolite as a Highly Efficient and Reusable Catalyst for Facile Synthesis of 1-Amidoalkyl-2-naphthols Under Solvent-Free Conditions. *Catal. Lett.* **2022**, *152*, 755–770.

11. Nasresfahani, Z.; Kassaee, M. Z.; Eidi, E. Homopiperazine Sulfamic Acid Functionalized Mesoporous Silica Nanoparticles (MSNs-HPZ-SO_3H) as an Efficient Catalyst for One-Pot Synthesis of 1-Amidoalkyl-2-naphthols. *New J. Chem.* **2016**, *40*, 4720–4726.

12. Mirjalili, B. F.; Bamoniri, A.; Rahmati, L. One-pot Synthesis of 1-Amidoalkyl-2-naphthols Catalyzed by Nano-$BF_3 \cdot SiO_2$. *Arab. J. Chem.* **2019**, *12*, 2216–2223.

13. Mahajan, A.; Mahajan, A.; Kuznetsov, A.; Gupta, M. Cu@Ag–CeO_2/Chitosan Nanocomposite: Green Catalyst for Synthesis of 4-Arylidene-isoxazolidinones and Amidoalkyl Naphthols with Density Functional Theory and Antimicrobial Studies. *ACS Sust. Chem. Eng.* **2024**, *12*, 3419–3438.

14. Bromberg, L.; Diao, Y.; Wu, H.; Speakman, S. A.; Hatton, T. A. Chromium(III) Terephthalate Metal Organic Framework (MIL-101): HF-Free Synthesis, Structure, Polyoxometalate Composites, and Catalytic Properties. *Chem. Mater.* **2012**, *24*, 1664–1675.

15. El-Yazeed, W. S. A.; Ahmed, A. I. Monometallic and Bimetallic Cu–Ag MOF/MCM-41 Composites: Structural Characterization and Catalytic Activity. *RSC Adv.* **2019**, *9*, 18803–18813.

16. Sun, C.; Mao, S.; Yu, D.; Xue, M.; Sun, X. Synthesis, Characterization, and Photocatalytic Application of Cadmium(II) Sulfide-Magnetite in One-Pot Multi-Component Synthesis of Some 1-Amidoalkyl-2-naphthols. *J. Mol. Struct.* **2024**, *1312*, 138451.