Supporting Information

Functionalized graphene oxide by 4-amino-3-hydroxy-1-naphthalenesulfonic acid as a heterogeneous nanocatalyst for one-pot synthesis of tetraketone and tetrahydrobenzo[*b*]pyran derivatives under green conditions

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Experimental

2.1 Materials

$NaNO_3$ (98+%) was purchased from Sigma-Aldrich. Graphite flakes (99.8%), H_2SO_4 (98%), potassium permanganate ($KMnO_4$, 98.5%), HCl (37%), H_2O_2 (30%), acetic anhydride, 4-amino-3-hydroxy-1-naphthalenesulfonic acid (96%), dimedone, 1,3- cyclohexanedione, benzaldehyde derivatives, malononitrile, DMF and EtOH (96%) were purchased from Merck. Distilled water was used in all required steps of reactions or purification.

2.2 Instrument

The XRD pattern was collected by a D8 advance Bruker with Cu Ka radiation (λ = 1.54050 Å). FESEM images, EDX and EDX mapping were taken by FESEM TESCAN-MIRA3. Atomic force microscopy, AFM (Full PLUS ،Brisk, ARA Research) was used to visualize the surface morphology of the sample. FTIR spectroscopy was performed on a 1720-X Perkin Elmer. TGA-DTA analysis was performed by SPA-503 BAHR. ^1H NMR spectroscopy was carried out on a Bruker DRX-500 at 500 MHz using $CDCl_3$ and DMSO as solvent and TMS as an internal standard at room temperature ($CDCl_3$: ^1H: δ=7.26 ppm).

2.3 Synthesis of GO

The GO was synthesized via the modified Hummers' method. The mixture of graphite (1.0 g) and $NaNO_3$ (0.5 g) was added to the concentrated sulfuric acid solution (23.0 ml, 98%) and stirred while the reaction temperature was kept below 4 ℃. Then, $KMnO_4$ (3.0 g) was added at 20 ℃ and the stirring of the mixture was continued for 2 h until the reaction was complete. To avoid a sudden increase in the reaction temperature, due to the exothermic nature of the reaction, $KMnO_4$ was slowly added to the mixture. After that, distilled water (46.0 ml) was slowly added to the reaction mixture at a temperature of 96 °C. In the next step, distilled water (140.0 ml) was added and finally, hydrogen peroxide (10.0 ml, 30% v/v) was added until the color of the mixture turned to yellow. Then the obtained mixture was allowed to rest for 24 h, and it was washed with HCl (5%) solution and distilled water so all the impurities were washed and removed. Finally, GO was dried in a 60 ℃ oven.

2.4 Synthesis of 4-Amino-3-hydroxy-1-naphthalenesulfonic acid Functionalized Graphene Oxide (GO-ANSA, 1)

DMF (20.0 ml) and GO (200.0 mg) were added to a round-bottom flask and dispersed with an ultrasonic probe to separate the GO sheets. Afterward, Ac_2O (0.4 ml) was added to the sonicated solution and the obtained mixture was placed in an ultrasonic bath for 2.0 h. Then, ANSA (0.4 g) and Et_3N (0.35 ml) were added, and the mixture was stirred at 80 ℃ for 48 h. At the end of the reaction, sulfuric acid (0.1 ml) was added to the mixture. Then, the obtained residue was filtered using filter paper and washed with THF and EtOH. Finally, the obtained black powder was dried at ambient temperature for 4 h.

2.5 General procedure for the synthesis of tetraketone (4) and tetrahydrobenzo[*b*]pyran (6) derivatives catalysed by GO-ANSA as nanocatalyst

For the synthesis of tetraketone derivatives **4**, aldehydes derivative (**2,** 1.0 mmol), enolizable compounds (**3**, 2.0 mmol), GO-ANSA (**1**, 15.0 mg), as a nanocatalyst, and EtOH (3.0 ml) were added to a 10 ml flask under reflux conditions and the mixture was stirred. The progress of the reaction was followed by TLC (n-Hexane: EtOAc, 1:3). After the completion of the reaction, the mixture was filtered to remove the catalyst from the reaction mixture. Then, recrystallization with EtOH was performed to obtain the pure products. The products were identified by measurement of the melting point as well as FTIR and ^1H NMR spectral data. The results are reported in **Table 2**.

For the synthesis of tetrahydrobenzo[*b*]pyran derivatives, aldehydes derivative (**2**, 1.0 mmol), malononitrile (**5**, 1.0 mmol), enolizable compounds (**3**, 1.0 mmol), GO-ANSA (**1**, 10.0 mg) as a nanocatalyst and EtOH (3.0 ml), as solvent, were added to a 10 ml round-bottom flask equipped with a magnetic stirring and reflux condenser. The progress of the reaction was monitored by TLC (n-Hexane: EtOAc, 1:3). After the completion of the reaction, the mixture was filtered and recrystallization with EtOH was done to obtain the pure products **6**.

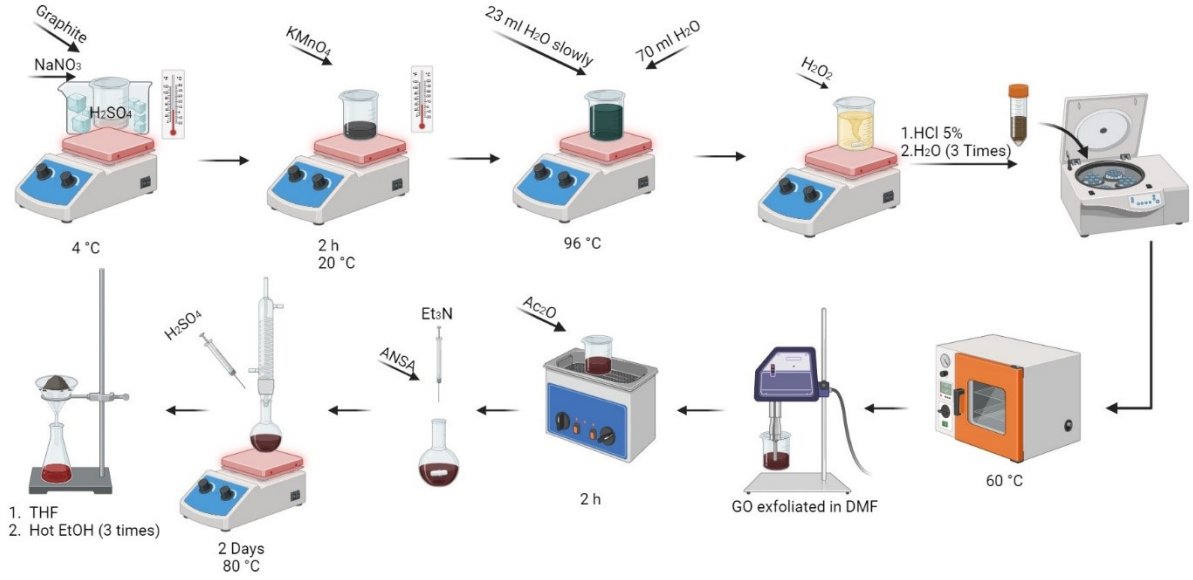


Figure 1. Procedures for synthesis of GO according to modified Hummers' method and the preparation of GO-ANSA (**1**).

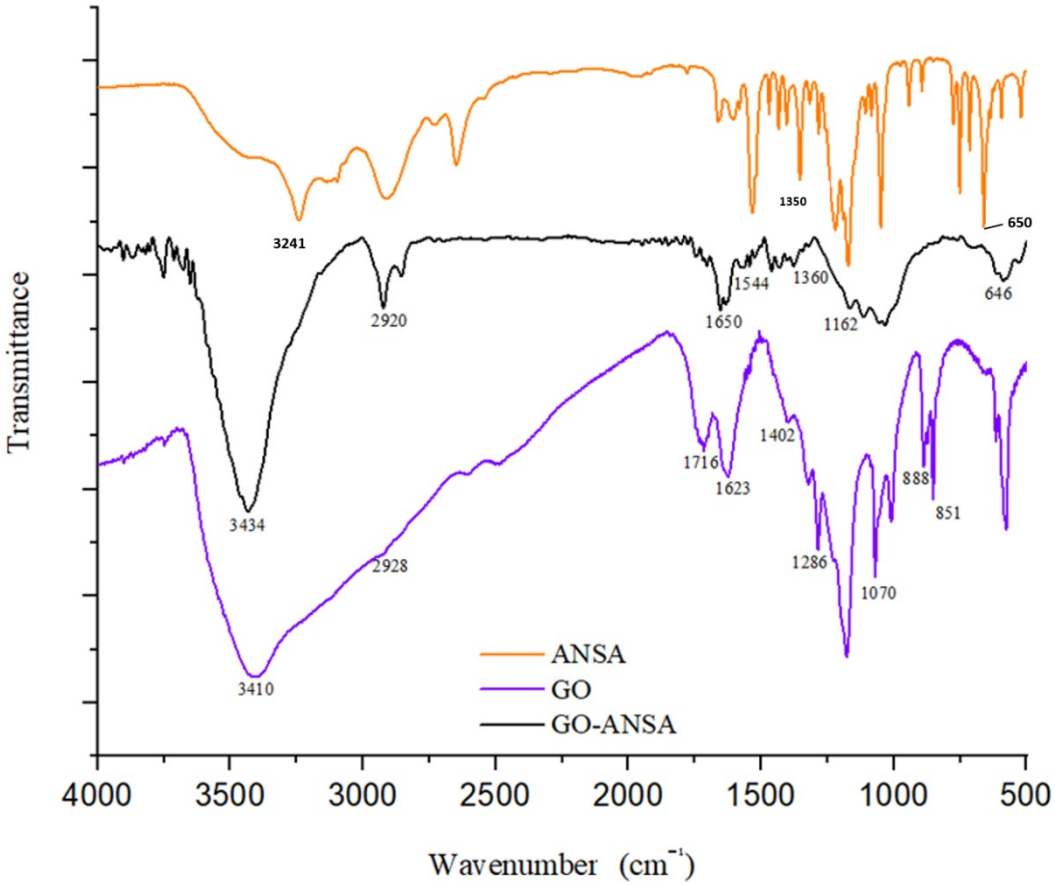
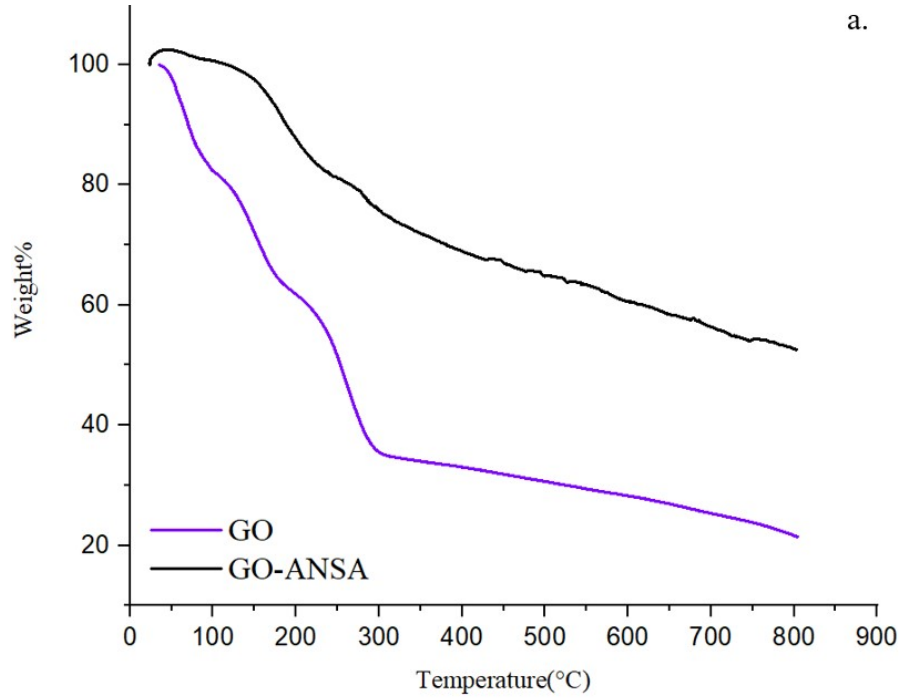


Figure 2. FT-IR spectra of GO, ANSA, and GO-ANSA (**1**).

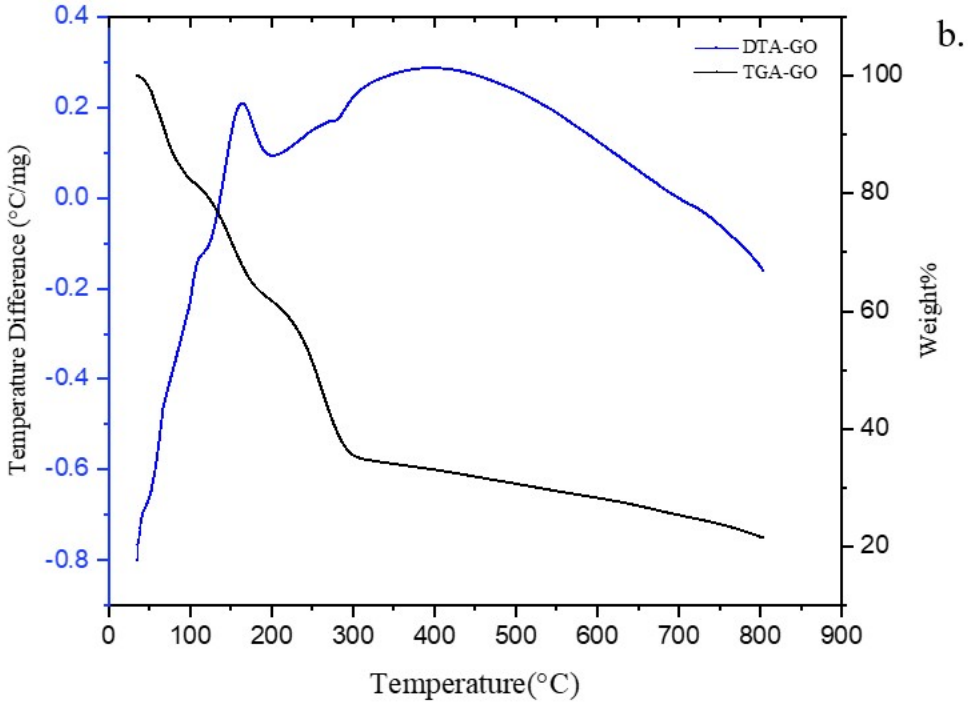
	Peak Position (cm^{-1})	Functional Group	Vibration Mode	Ref.
GO	**3410**	Alcohols & Carboxylic acid (-OH)	Stretching	1
	2928	CH_2 (sp^2)	Stretching (asymmetric)	1
	1716	Carboxylic acid (C=O)	Stretching	2
	1623	C=C	Stretching	2
	1402	Alcohols (C-OH)	Bending	2
	1286	Epoxide (C-O-C) & Phenols (C-O)	Stretching	1,2
	1178-1070	2° & 3°Alcohols (C-O)	Stretching	3
	851-888	CH	Bending (out of plane)	1
GO-ANSA (1)	**3434**	Alcohols (-OH) & Amides (NH)	Stretching	1,4
	2920	CH_2 (sp^2)	Stretching (asymmetric)	1
	1650	2° Amides (C=O)	Stretching	4
	1544	2° Amides (C-N) & (N-H)	Stretching/ Bending	4
	1360	Sulfonic acid (S=O)	Stretching (asymmetric)	5
	1162	Sulfonic acid (S=O)	Stretching(symmetric)	5
	646	Sulfonic acid (S-O)	Stretching	5

Table 1 Characteristic vibrational modes and their energies of GO and GO-ANSA (**1**).

a.


Weight%
Temperature(°C)
GO
GO-ANSA

b.


Temperature Difference (°C/mg)
Weight%
Temperature(°C)
DTA-GO
TGA-GO

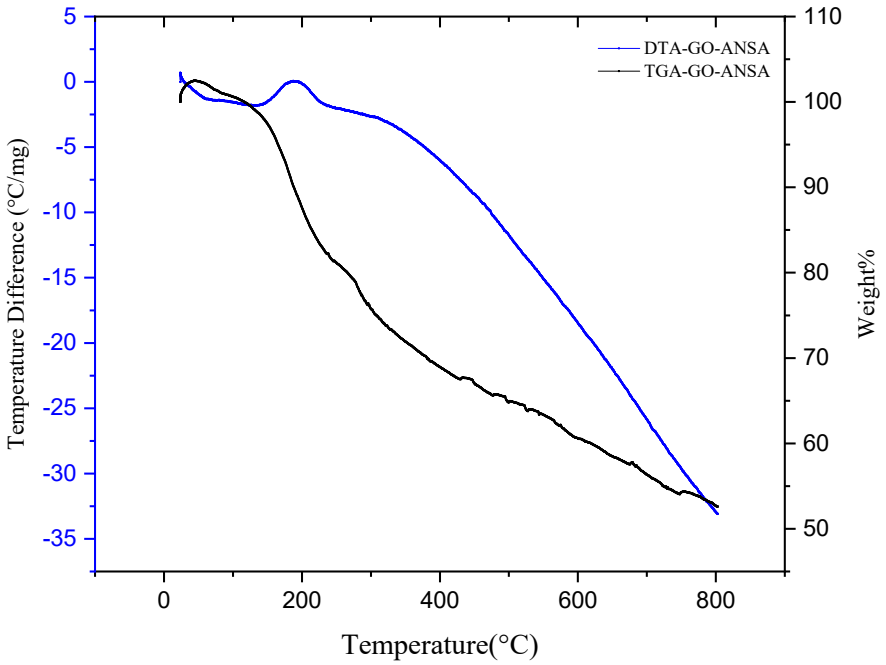
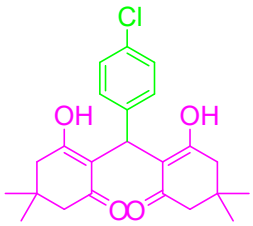
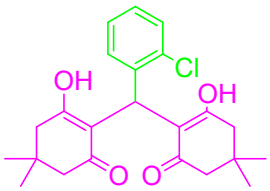


Figure 3. The TGA-DTA analysis a) TGA of GO-ANSA (**1**) and GO b) TGA-DTA for GO c) TGA-DTA for GO-ANSA.

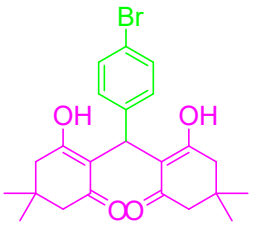
Structure of tetraketone (4a-p) and tetrahydrobenzo[b]pyran (6a-k) derivatives



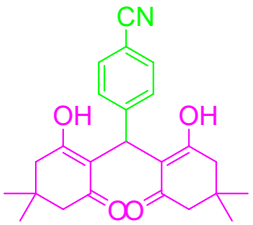
4a



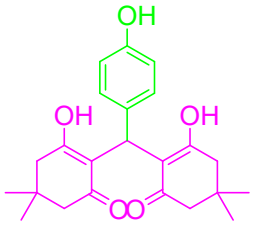
4b



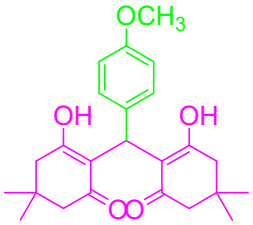
4c



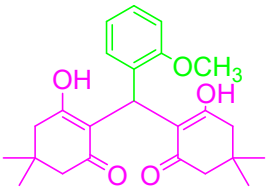
4d



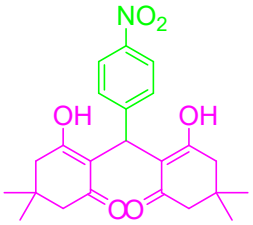
4e



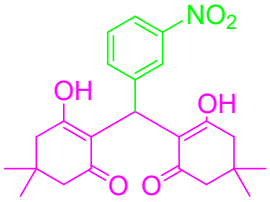
4f



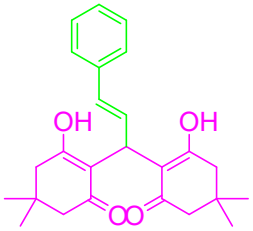
4g



4h



4i



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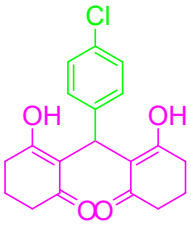
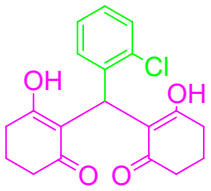
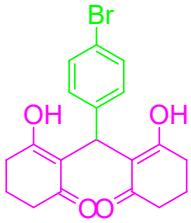


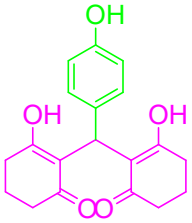
4k



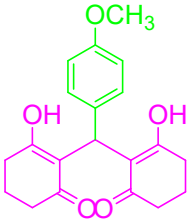
4l



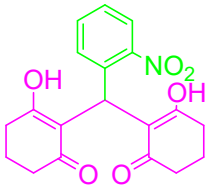
4m



4n



4o



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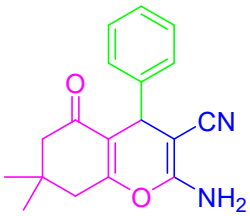
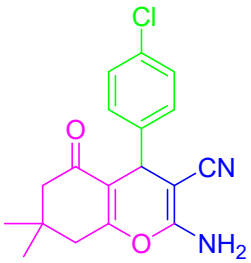
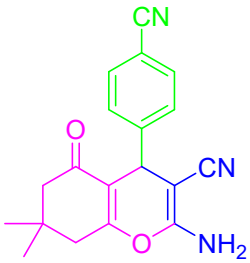


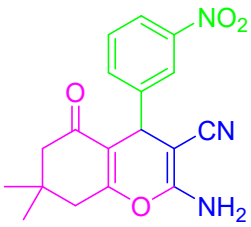
6a



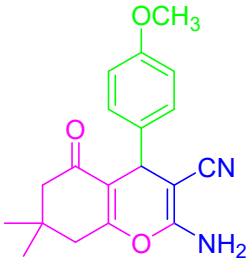
6b



6c



6d



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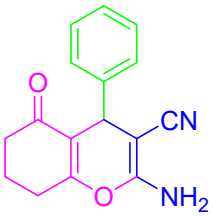
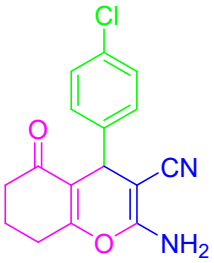
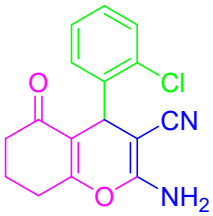


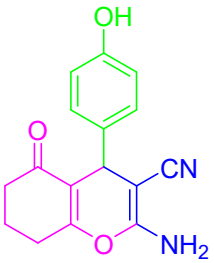
6f



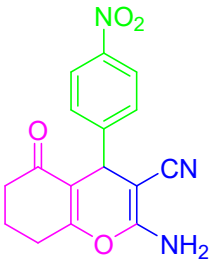
6g



6h



6i



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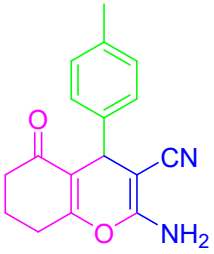


6k

FT-IR spectra of the products 4a and 4g

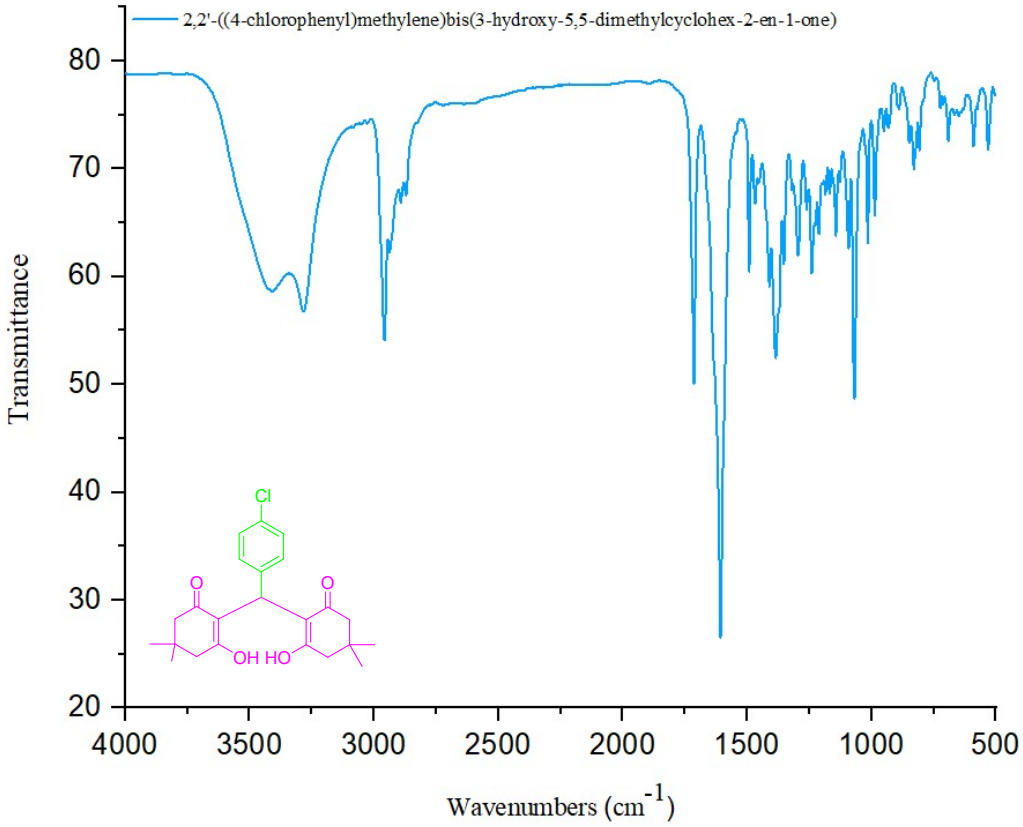


Figure 4. FT-IR spectra of the 2,2'-((4-chlorophenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (**4a**).

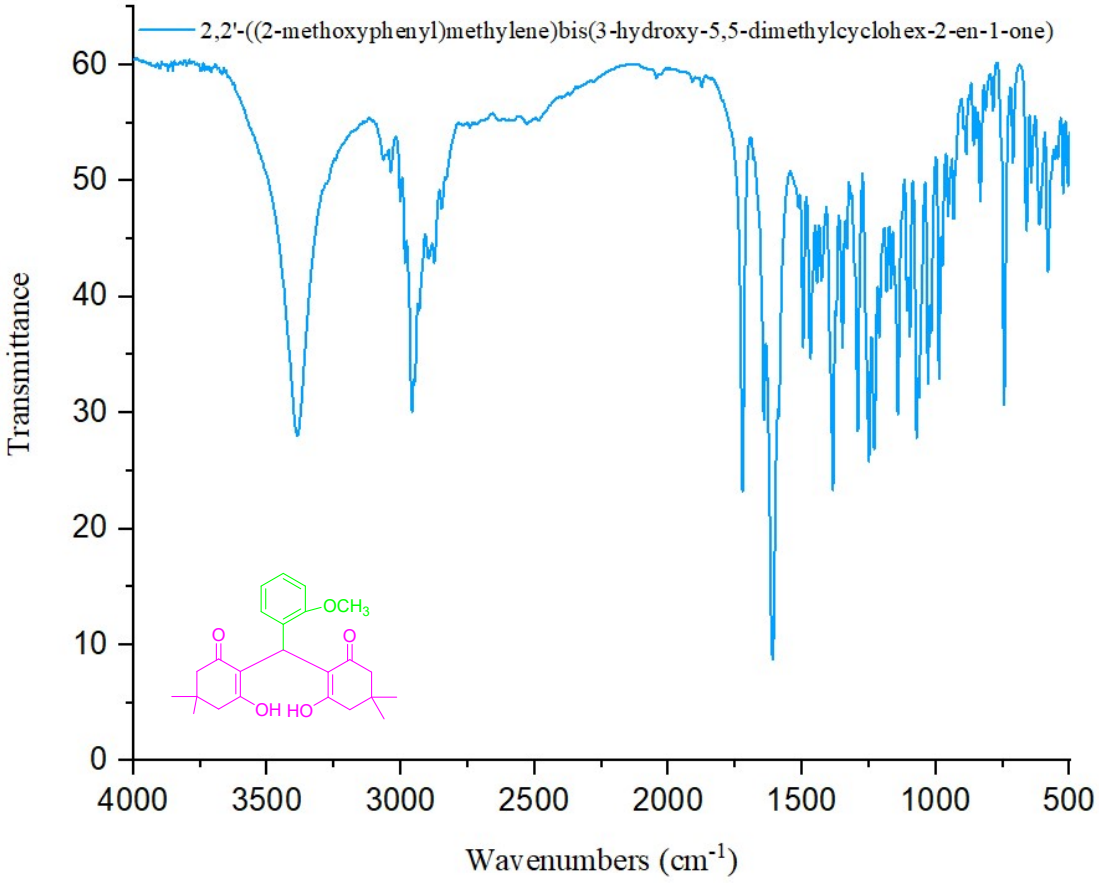
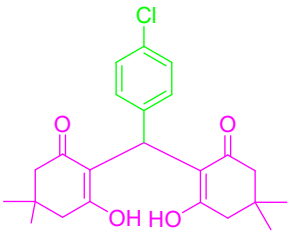
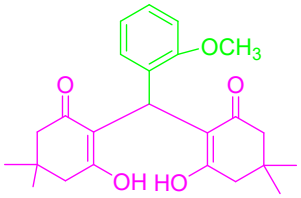


Figure 5. FT-IR spectra of the 2,2'-((2-methoxyphenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (**4g**).

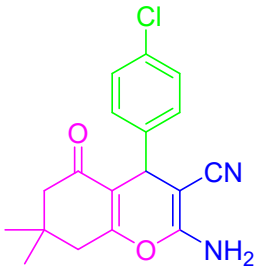
Spectroscopic characterization of the products 4a, 4g, 6b, and 6c.



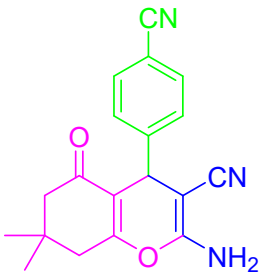
2,2'-((4-chlorophenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (4a, Figure 6). ; white solid; m.p 140-142 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.1 (s, 6H), 1.22 (s, 6H), 2.3-2.5 (m, 8H), 5.47 (s, 1H), 7.0 (d, 2H), 7.28 (d, 2H), 11.87 (brs, 2H).



2,2'-((2-methoxyphenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (4g, Figure 7). ; white solid; m.p 179-181 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.09 (m, 6H); 1.30 (s, 6H); 2.58 (d, 4H); 3.38 (d, 4H); 3.76 (m, 3H); 5.62 (s, 1H); 6.84-6.94 (m, 2H) ; 7.24-7.32 (m, 2H).



2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6b, Figure 8): white solid; m.p 210-212 ℃; 1H NMR (500 MHz, DMSO-d_6) δ (ppm): 7.39 – 7.30 (m, 2H), 7.21 – 7.12 (m, 2H), 7.07 (s, 2H), 4.19 (s, 1H), 3.37– 3.28 (m, 2H), 2.50 (d, J = 17.1 Hz, 4H), 2.25 (d, J = 16.1 Hz, 1H), 2.10 (d, J = 16.1 Hz, 1H), 1.03 (s,3H), 0.94 (s, 3H).



2-amino-4-(4-cyanophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6b, Figure 9): white solid; m.p 211 ℃; 1H NMR (500 MHz, DMSO-d_6) δ (ppm): 7.77 (d, J = 7.7 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 7.15 (s, 2H), 4.29 (s,1H), 2.53 (s, 2H), 2.25 (d, J = 16.0 Hz, 1H), 2.11 (d, J = 16.1 Hz, 1H), 1.03 (s, 3H), 0.95 (s, 3H).

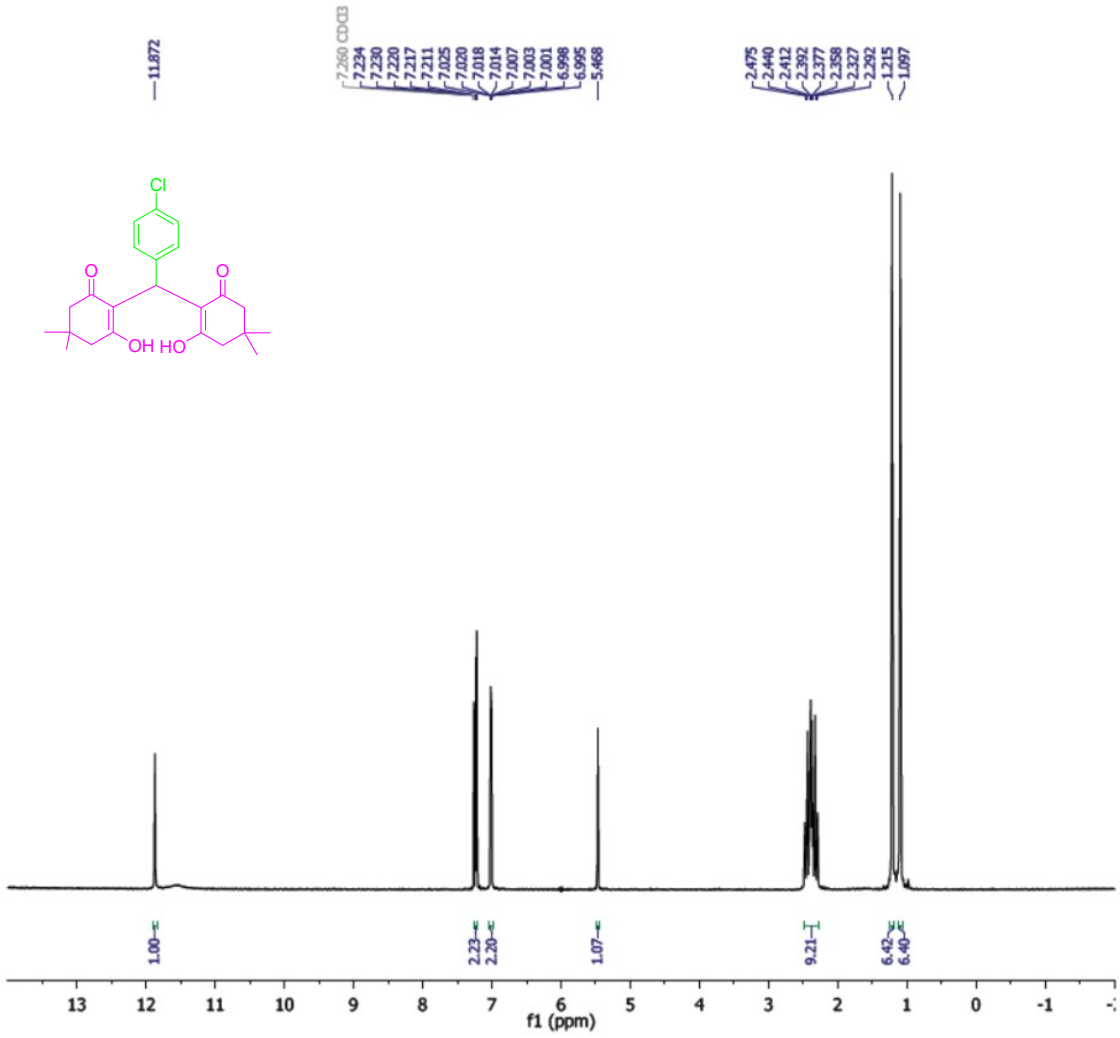


Figure 6. ^{1}H NMR spectra of the 2,2'-((4-chlorophenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (**4a**).

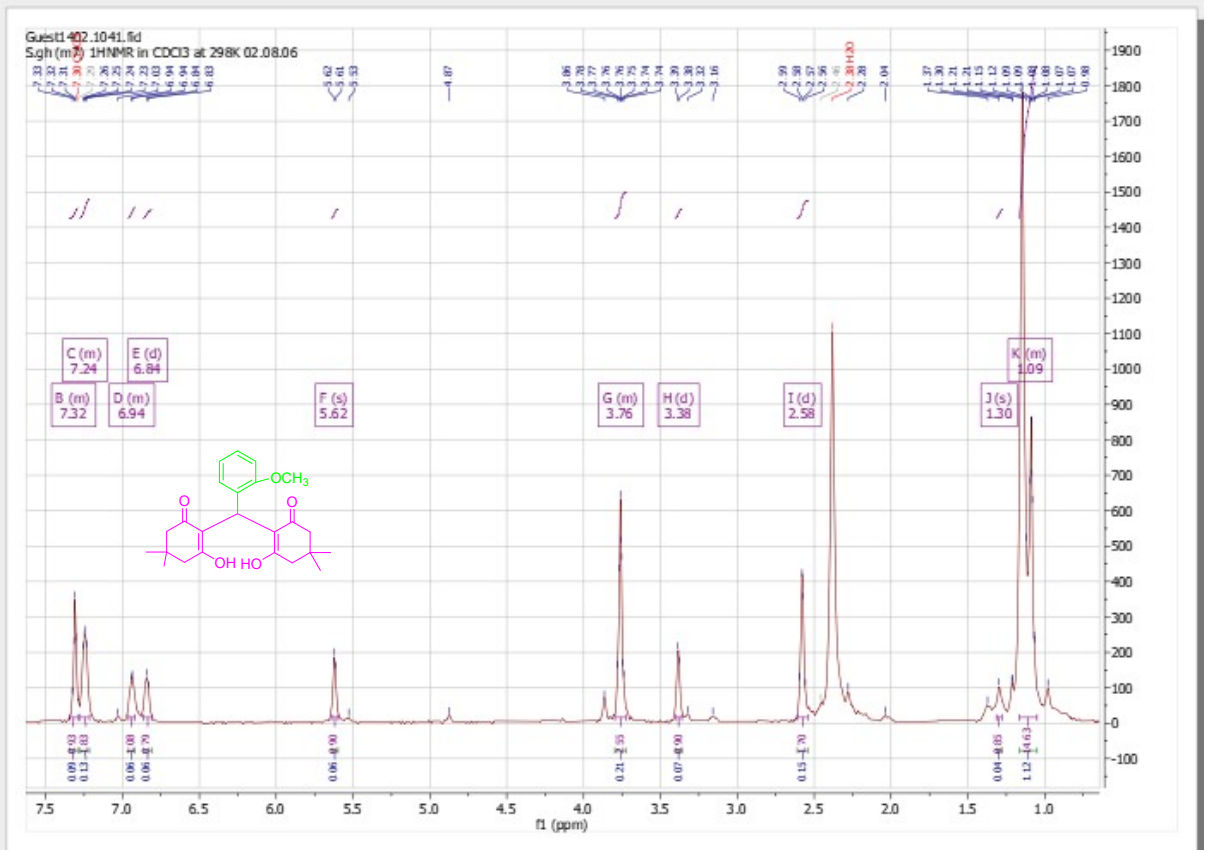


Figure 7. ^{1}H NMR spectra of the 2,2'-((2-methoxyphenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one) (**4g**).

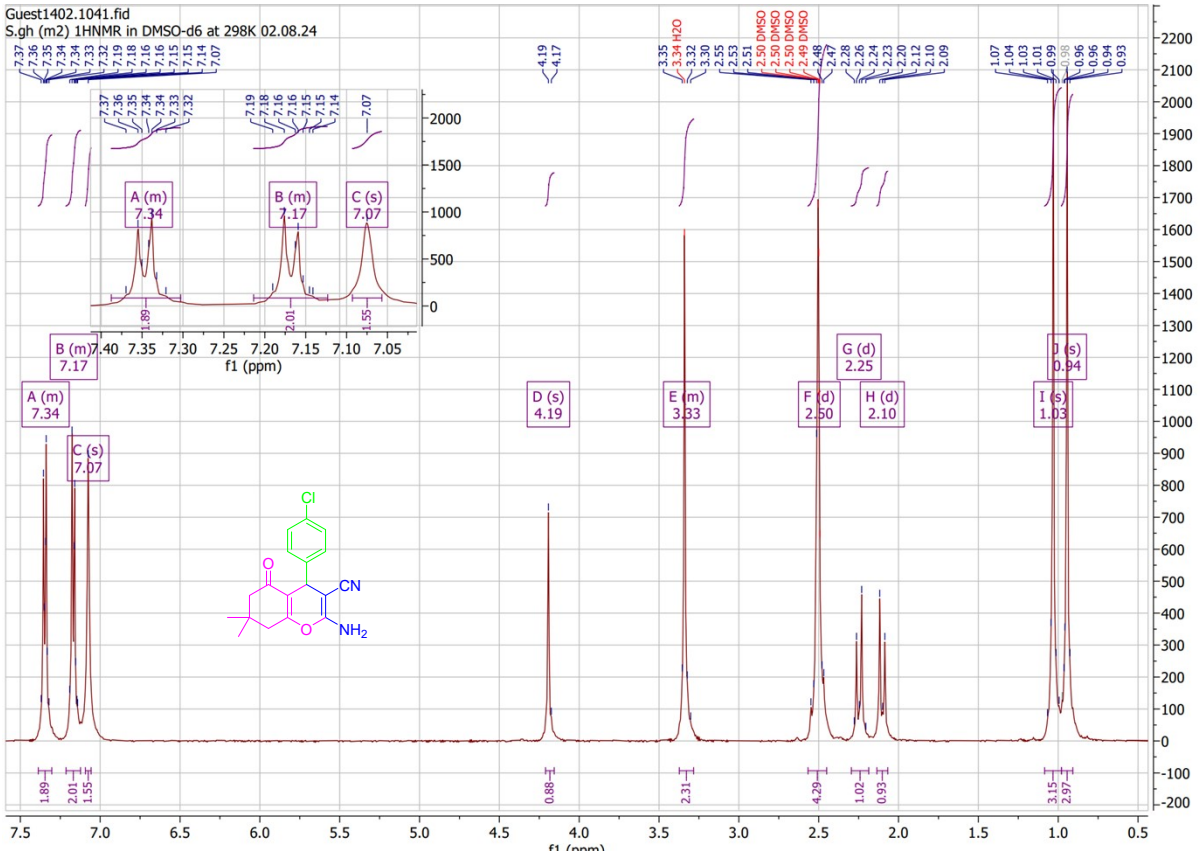


Figure 8. ^{1}H NMR spectra of the 2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6b**).

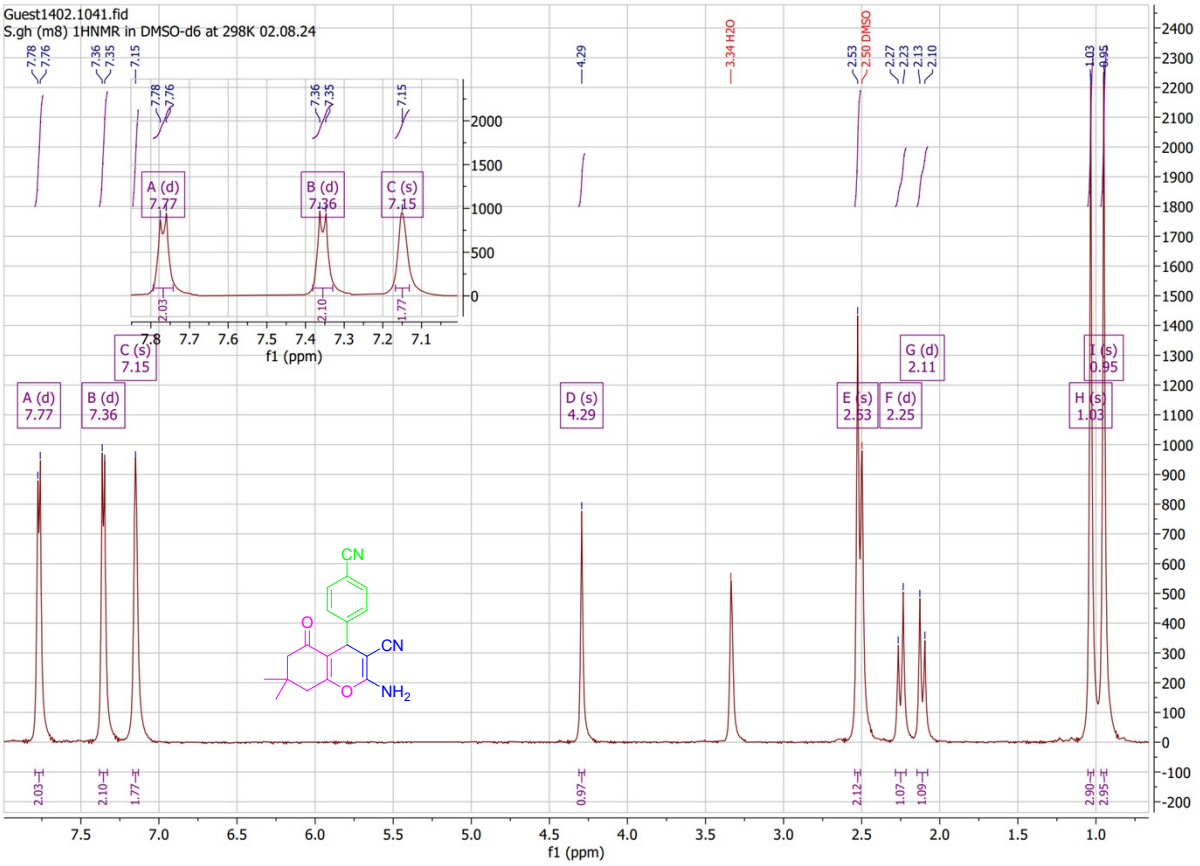


Figure 9. ^{1}H NMR spectra of the 2-amino-4-(4-cyanophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6c**).

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