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Synthesis and characterization of a novel Fe_3O_4@SiO_2-BenzIm-Fc[Cl]/BiOCl nano-composite and its efficient catalytic activity in the ultrasound-assisted synthesis of diverse chromene analogs

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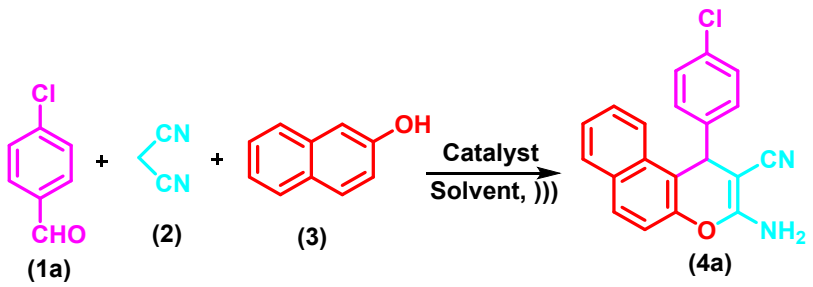
Table 1. Optimization of the reaction conditions for the synthesis of **4a**, using Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl as catalyst[a].



Entry	Catalyst amount (mg)	Ultrasound power (W)	Solvent (v/v)	Time (min)	Yield (%)
1	-	50	EtOH	60	10
2	5	50	EtOH	30	80
3	10	50	EtOH	20	88
4	15	50	EtOH	20	86
5	10	50	EtOH:H_2O (4:1)	20	92
6	**10**	**50**	**EtOH:H_2O (3:2)**	**15**	**96**
7	10	50	EtOH:H_2O (2:3)	25	90
8	10	30	EtOH:H_2O (3:2)	30	85
9	10	40	EtOH:H_2O (3:2)	20	90
10	10	60	EtOH:H_2O (3:2)	15	94

[a]Reaction conditions: 4-chlorobenzaldehyde (1 mmol), malononitrile (1.1 mmol) and 2-naphthol (1 mmol), catalyst, solvent, ultrasound irradiation.

Materials and Apparatus

The chemical reagents used in synthesis were purchased from Merck and Sigma–Aldrich CO. Melting points were determined with a MEL-TEMP model 1202D and are uncorrected. FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer as KBr disks. The ^{1}H NMR spectra were recorded with a Bruker Spectrospin Avance 400 spectrometer with DMSO-d_6 as solvent

and TMS as internal standard. ^{13}C NMR spectra were determined on the same instrument at 100 MHz. All chemical shifts were reported as d (ppm) and coupling constants (*J*) are given in Hz. Elementary analyses (C, H, N) were performed on a Vario EL III analyzer. X-ray diffraction patterns of samples were taken on Siemens D500 X-ray powder diffraction diffractometer (CuK radiation, λ= 1.5406 Å). FE-SEM images of the products visualized by a TESCAN MIRA3 Field Emission Scanning Electron Microscope. A multiwave ultrasonic generator (Sonicator 3200; Bandelin, MS 73, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 10-60 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level.

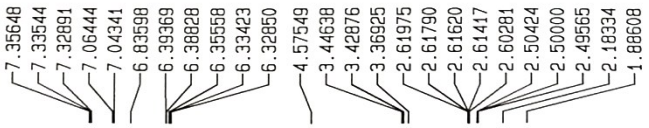
General procedure for the synthesis of 2-amino-4H-chromenes derivatives under ultrasound irradiation

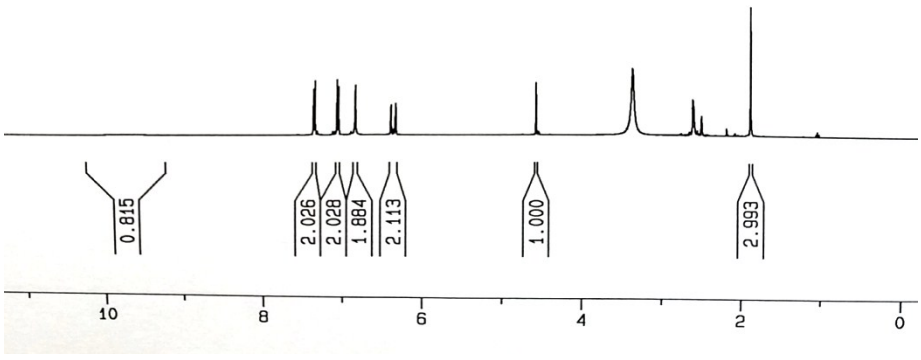
To a mixture of an aldehyde (1 mmol), malononitrile (1.1 mmol) and an appropriate C-H acid 3, 5, 7, 9 or 11 (1 mmol) in ethanol:water (3:2, 5 mL) was added Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl (10 mg), and was sonicated at ambient temperature. When the reaction was completed [monitored by thin layer chromatography (TLC), using *n*-hexane/ethyl acetate (3:1) as eluent], the catalyst was separated using an external magnet and the reaction mixture was cooled and the precipitate was filtered, washed and dried. The crude product was crystallized from ethanol. The structures of new compounds 12a-f were characterized by IR, ^1H NMR, ^{13}C NMR and CHN analysis.

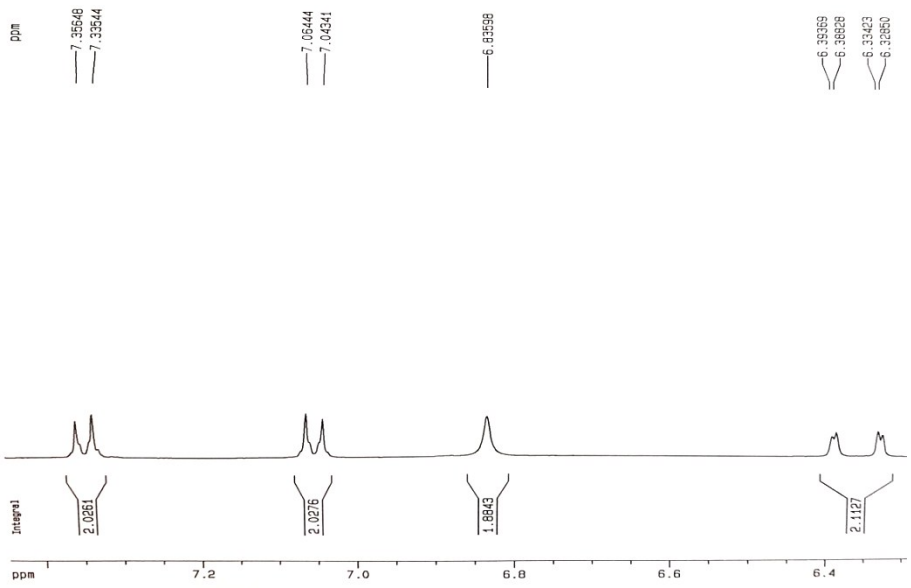
2-Amino-4-(4-chlorophenyl)-7-hydroxy-5-methyl-4*H*-chromene-3-carbonitrile (12a):

Cream powder; m.p 256-258 ^oC ; FT-IR(KBr): 3443, 3351, 3319, 3190, 3028, 2941, 2871, 2073, 1648, 1551 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 1.88 (s, 3H, CH_3), 4.57 (s, 1H, methin-H),

6.33 (d, 1H, *J*=2.2 Hz, Ar-H), 6.39 (d, 1H, *J*=2.2 Hz, Ar-H), 6.83 (bs, 2H, NH_2), 7.05 (d, 2H, *J*=8.4 Hz, Ar-H), 7.34 (d, 2H, *J*=8.4 Hz, Ar-H), 9.68 (bs, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.8, 37.7, 57.5, 100.3, 111.9, 113.9, 120.5, 128.2, 128.5, 128.8, 130.9, 137.8, 144.7, 149.9, 156.9, 159.8 ppm; Anal. Calc. for $C_{17}H_{13}ClN_2O_2$ (%): C, 65.29; H, 4.19; N, 8.96; found: C, 65.02; H, 4.21; N, 8.94.



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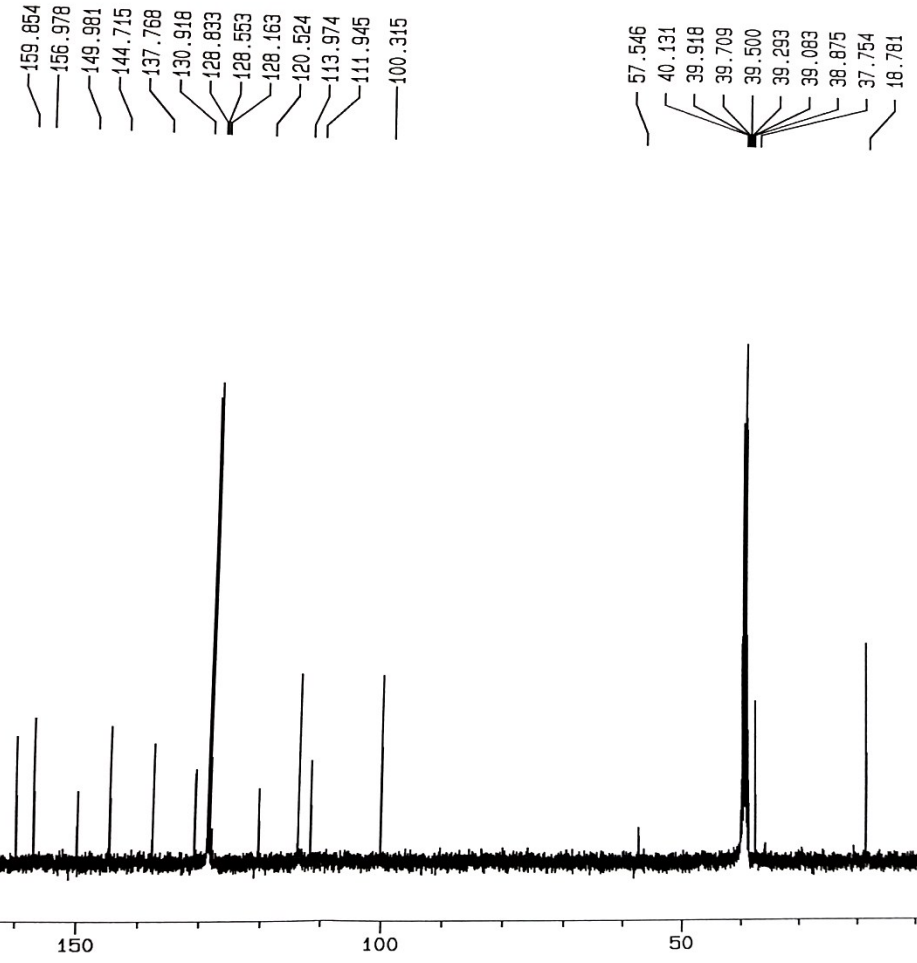
6.4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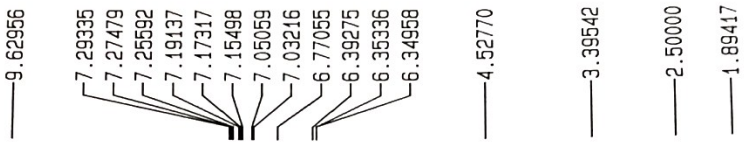
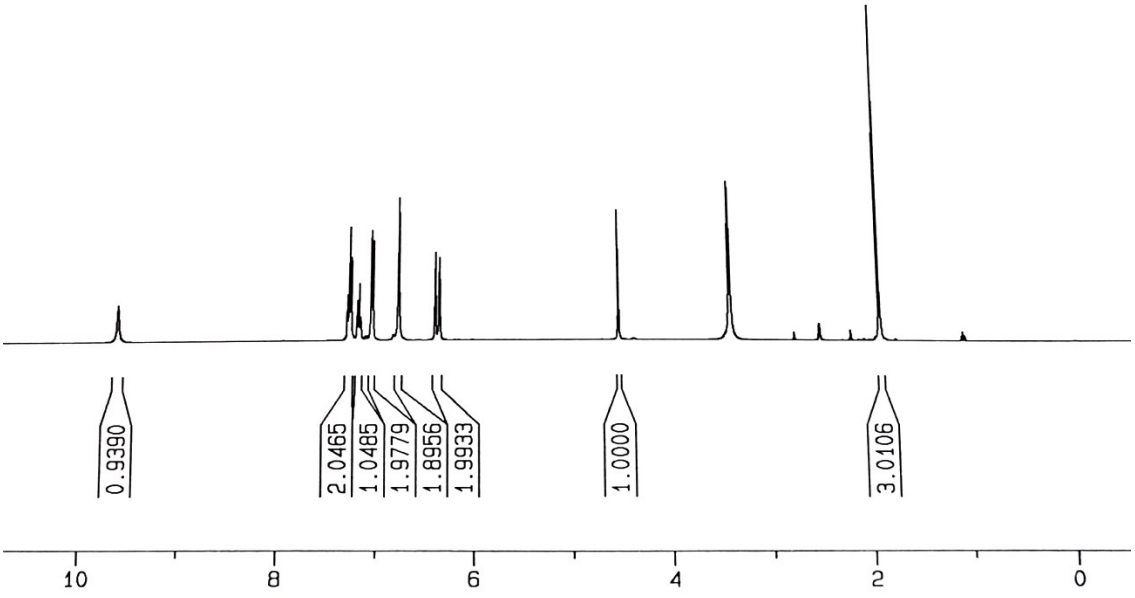
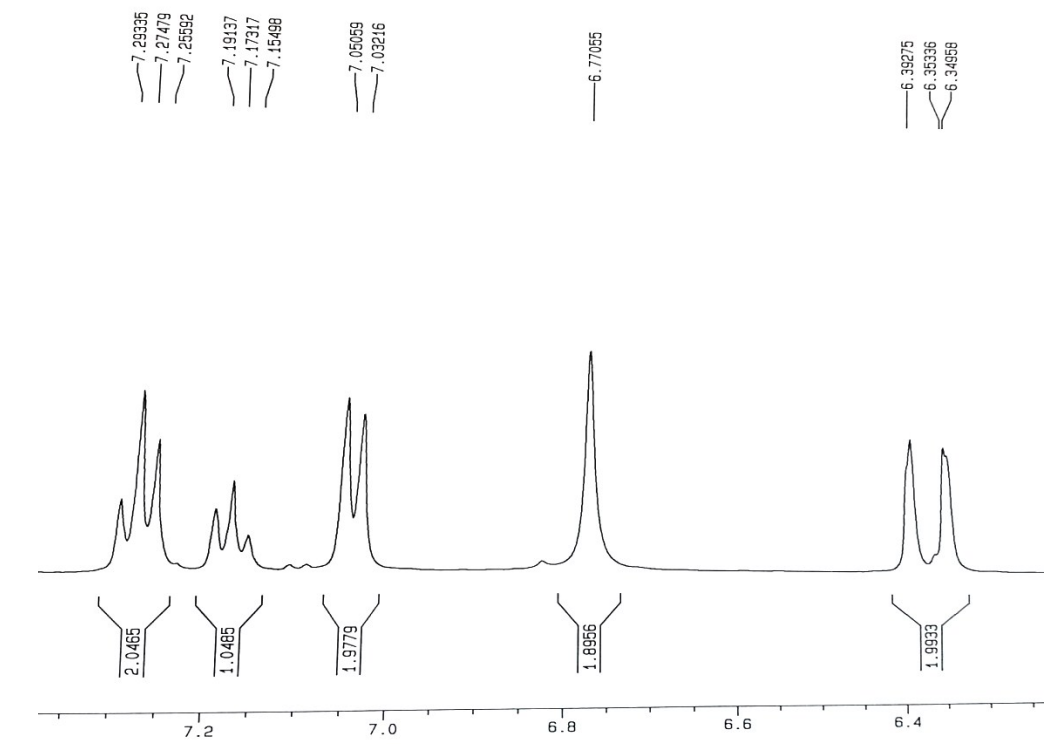
39.293
39.083
38.875
37.754
18.781
150
100
50
0

2-Amino-7-hydroxy-5-methyl-4-phenyl-4*H*-chromene-3-carbonitrile (12b):

Cream powder; m.p 283-285 ^{o}C ; FT-IR(KBr): 3501, 3408, 3333, 3213, 2867, 2074, 1646, 1553 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.89 (s, 3H, CH_3), 4.53 (s, 1H, methin-H), 6.35 (s, 1H, Ar-H), 6.39 (s, 1H, Ar-H), 6.77 (bs, 2H, NH_2), 7.04 (d, 2H, J=7.4 Hz, Ar-H), 7.15-7.29 (m, 3H, Ar-H), 9.63 (bs, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.8, 38.5, 58.1, 100.3, 112.5, 113.9, 120.7, 126.4, 126.9, 128.5, 137.7, 145.7, 150.1, 156.8, 159.8 ppm; Anal. Calc. for $C_{17}H_{14}N_2O_2$ (%): C, 73.37; H, 5.07; N, 10.07; found: C, 73.12; H, 5.08; N, 10.04.



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6.6
6.4


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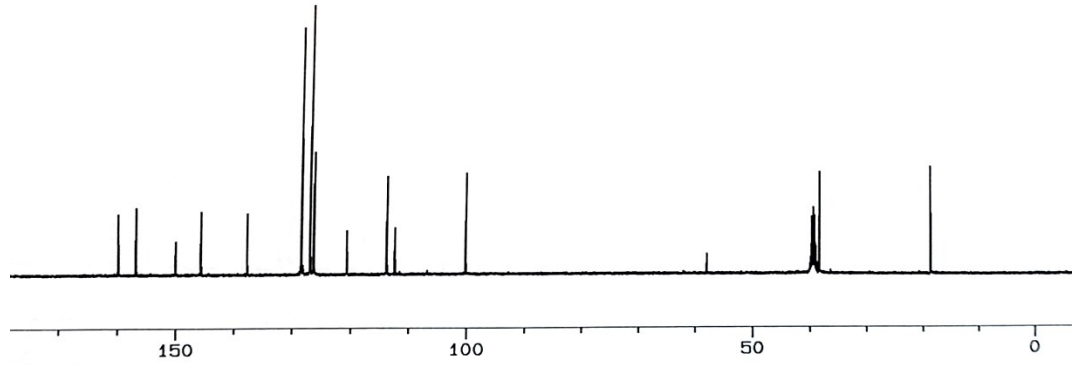
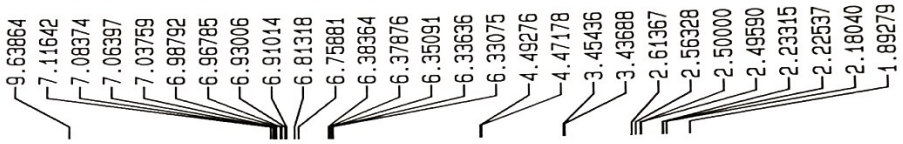
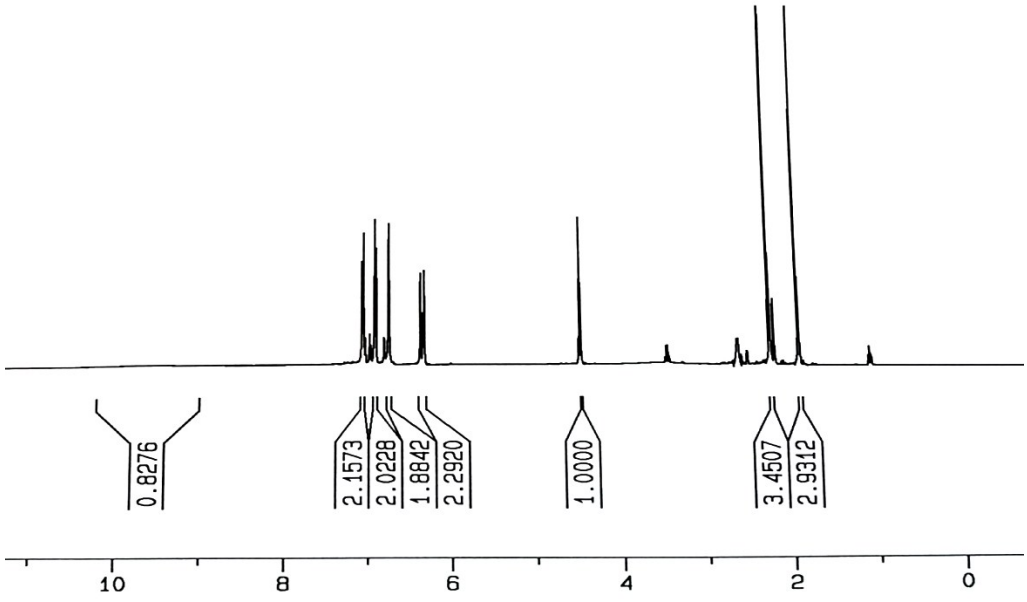
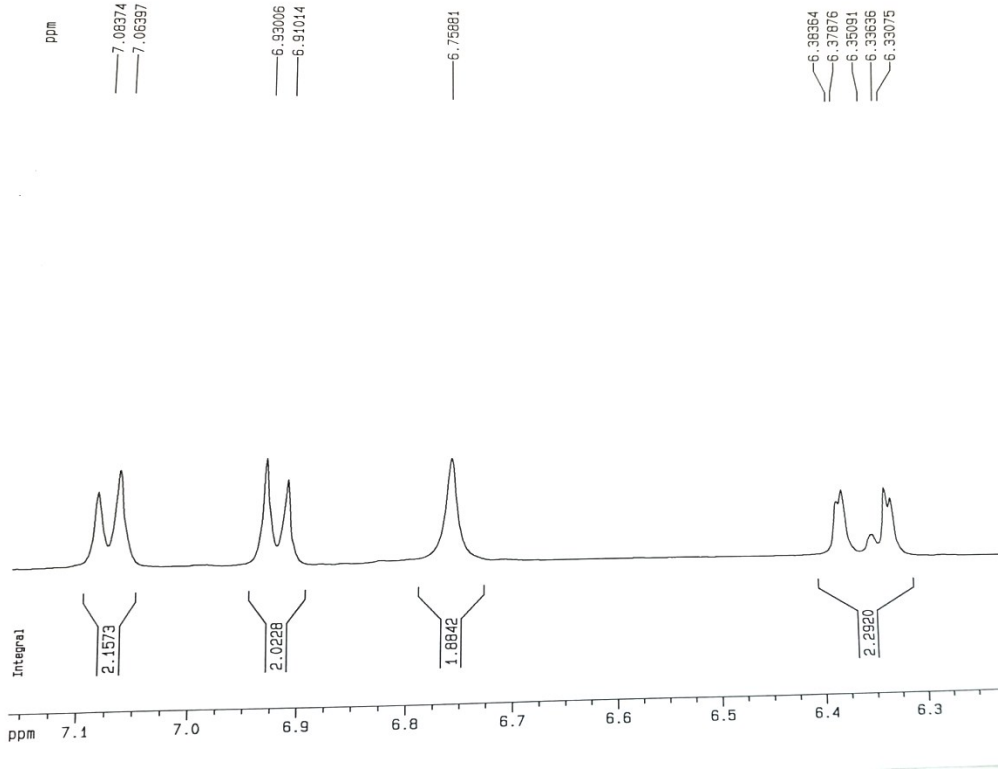

150
100
50
0

2-Amino-7-hydroxy-5-methyl-4-(*p*-tolyl)-4*H*-chromene-3-carbonitrile (12c):

Light yellow powder; m.p 236-238 ^{o}C ; FT-IR(KBr): 3492, 3395, 3366, 3219, 3030, 2953, 2876, 2079, 1646, 1564 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.89 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 4.47 (s, 1H, methin-H), 6.33 (d, 1H, *J*=2.2 Hz, Ar-H), 6.38 (d, 1H, *J*=2.2 Hz, Ar-H), 6.76 (bs, 2H, NH_2), 6.92 (d, 2H, *J*=7.9 Hz, Ar-H), 7.07 (d, 2H, *J*=7.9 Hz, Ar-H), 9.64 (bs, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.8, 20.6, 38.1, 58.2, 100.2, 112.6, 113.8, 120.7, 126.8, 126.9, 128.7, 129.1, 135.4, 137.7, 142.7, 150.0, 156.7, 159.8 ppm; Anal. Calc. for $C_{18}H_{16}N_2O_2$ (%): C, 73.95; H, 5.52; N, 9.58; found: C, 73.71; H, 5.55; N, 9.54.



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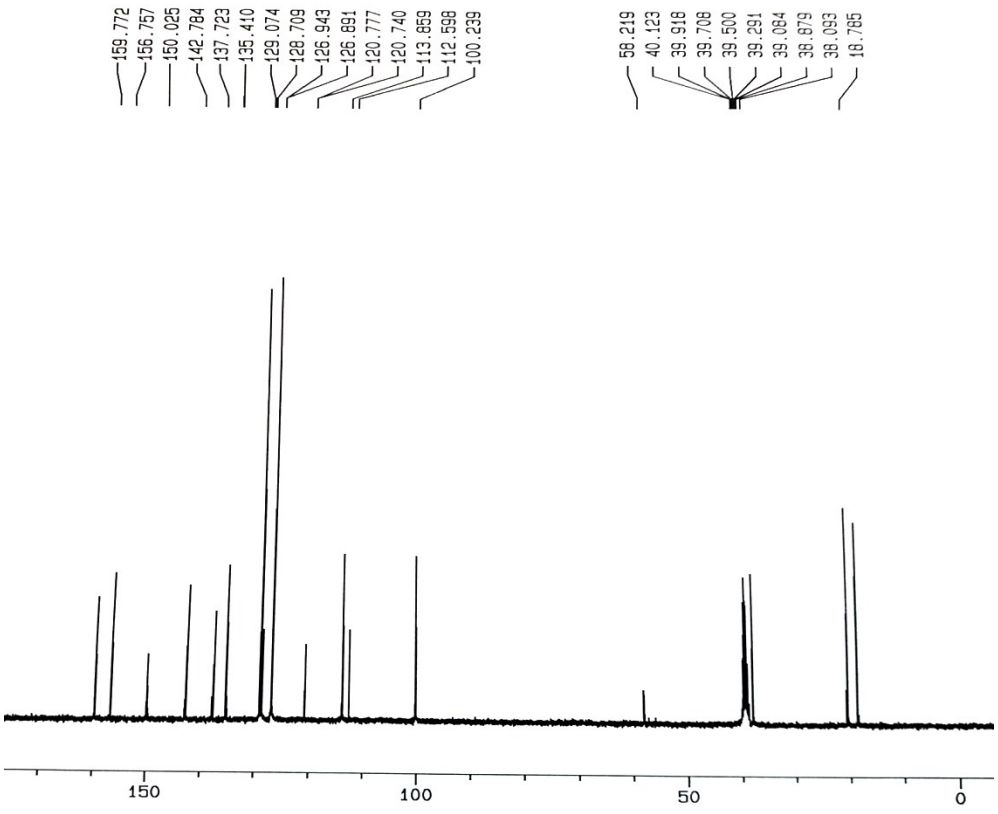
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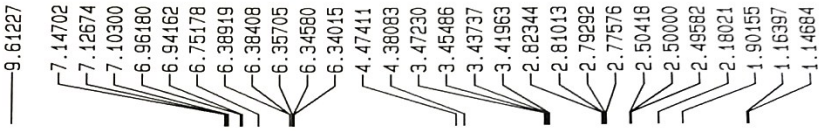
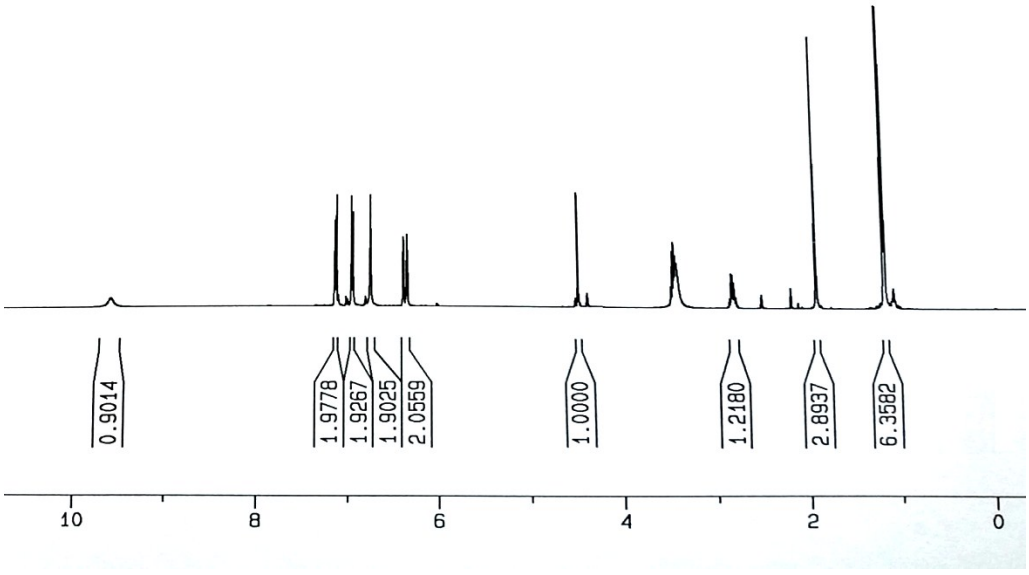
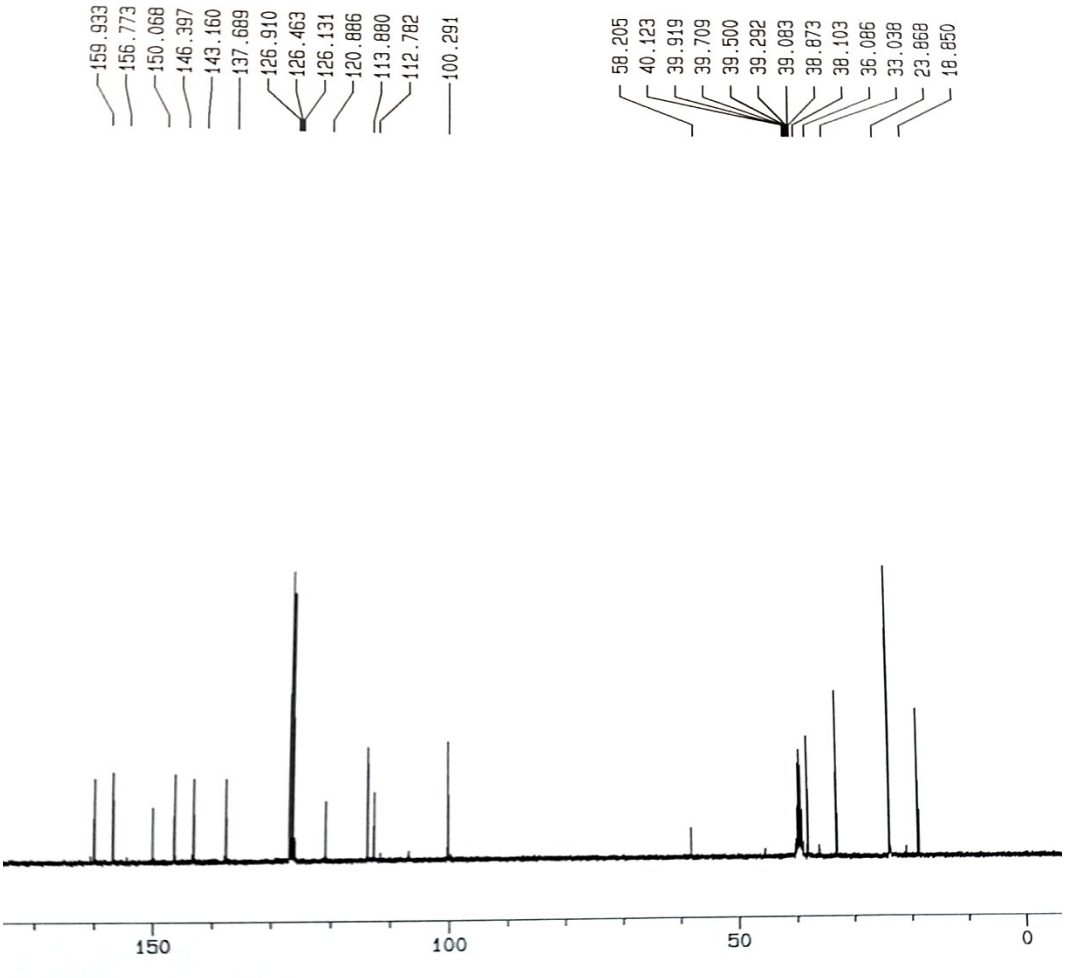
39.500
39.291
39.084
38.879
38.093
18.785
150
100
50
0

2-amino-7-hydroxy-4-(4-isopropylphenyl)-5-methyl-4*H*-chromene-3-carbonitrile (12d):

Light yellow powder; m.p 241-243 ^{o}C ; FT-IR(KBr): 3451, 3336, 3207, 3117, 2957, 2876, 2081, 1642, 1574 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.15 (d, 6H, J=6.8 Hz, 2×CH_3), 1.90 (s, 3H, CH_3), 2.77-2.84 (m, 1H, CH), 4.47 (s, 1H, methin-H), 6.34 (d, 1H, J=2.2 Hz, Ar-H), 6.38 (d, 1H, J=2.2 Hz, Ar-H), 6.75 (bs, 2H, NH_2), 6.95 (d, 2H, J=8.1 Hz, Ar-H), 7.13 (d, 2H, J=8.1 Hz, Ar-H), 9.61 (bs, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.8, 23.8, 33.0, 38.1, 58.2, 100.3, 112.8, 113.9, 120.9, 126.1, 126.5, 126.9, 137.7, 143.2, 150.1, 156.8, 159.9 ppm; Anal. Calc. for $C_{20}H_{20}N_2O_2$ (%):C, 74.98; H, 6.29; N, 8.74; found: C, 74.73; H, 6.31; N, 8.70.

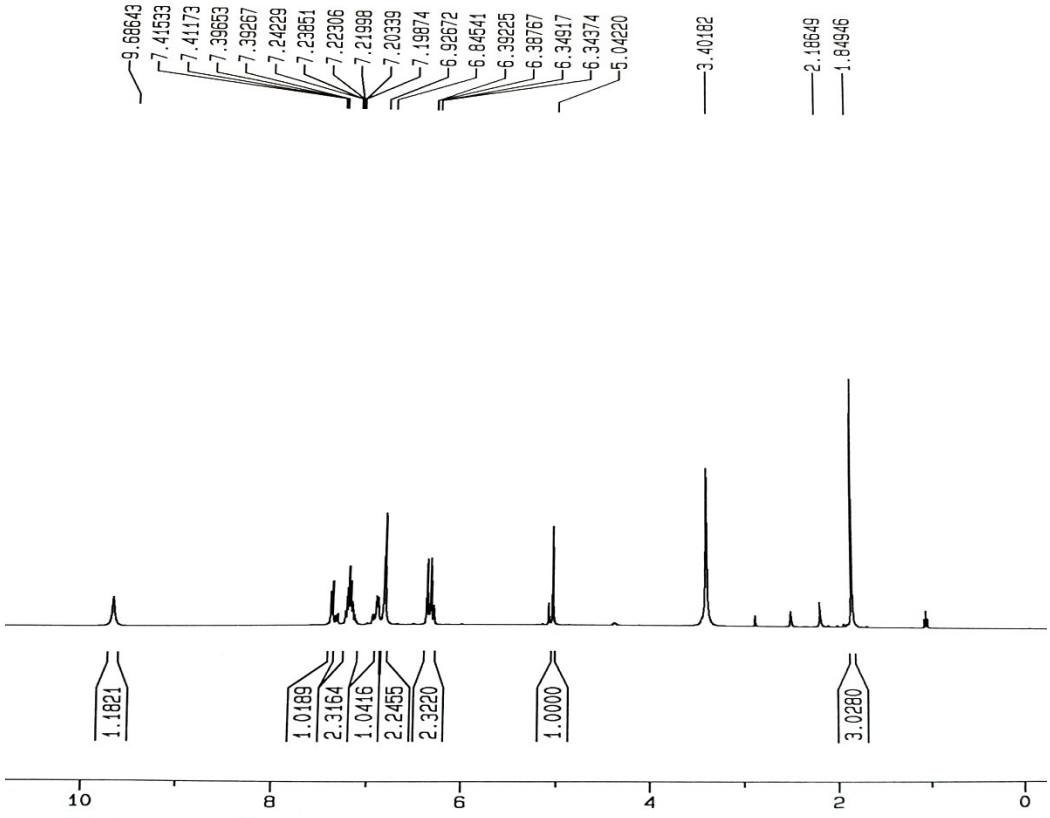






2-Amino-4-(2-chlorophenyl)-7-hydroxy-5-methyl-4*H*-chromene-3-carbonitrile (12e):

Cream powder; m.p 270-272 ^{o}C ; FT-IR(KBr): 3500, 3394, 3332, 3219, 2972, 2188, 1650, 1464 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.85 (s, 3H, CH_3), 5.04 (s, 1H, methin-H), 6.32-6.39 (m, 2H, Ar-H), 6.84 (bs, 2H, NH_2), 6.92 (d, 1H, J=6.2 Hz, Ar-H), 7.17-7.26 (m, 2H, Ar-H), 7.40 (dd, 1H, J=7.5 Hz, J=1.4 Hz, Ar-H), 9.68 (bs, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.6, 20.9, 56.3, 100.3, 111.8, 113.9, 120.1, 127.9, 128.2, 129.3, 130.2, 131.5, 137.7, 142.7, 150.3, 157.0, 160.2 ppm; Anal. Calc. for $C_{17}H_{13}ClN_2O_2$ (%): C, 65.29; H, 4.19; N, 8.96; found: C, 65.03; H, 4.22; N, 8.92.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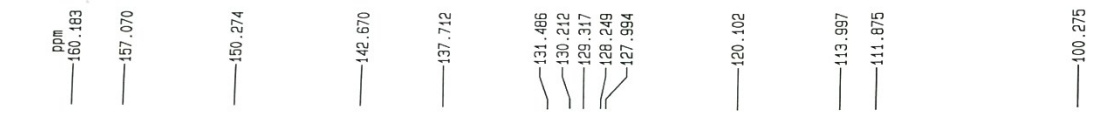
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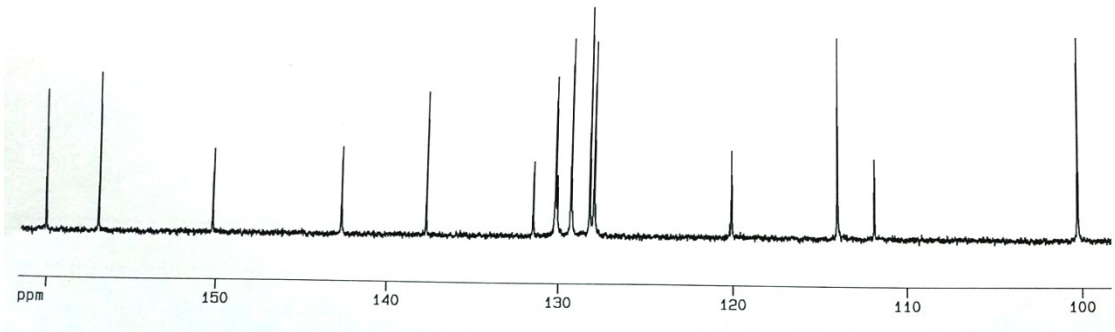
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140
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120
110
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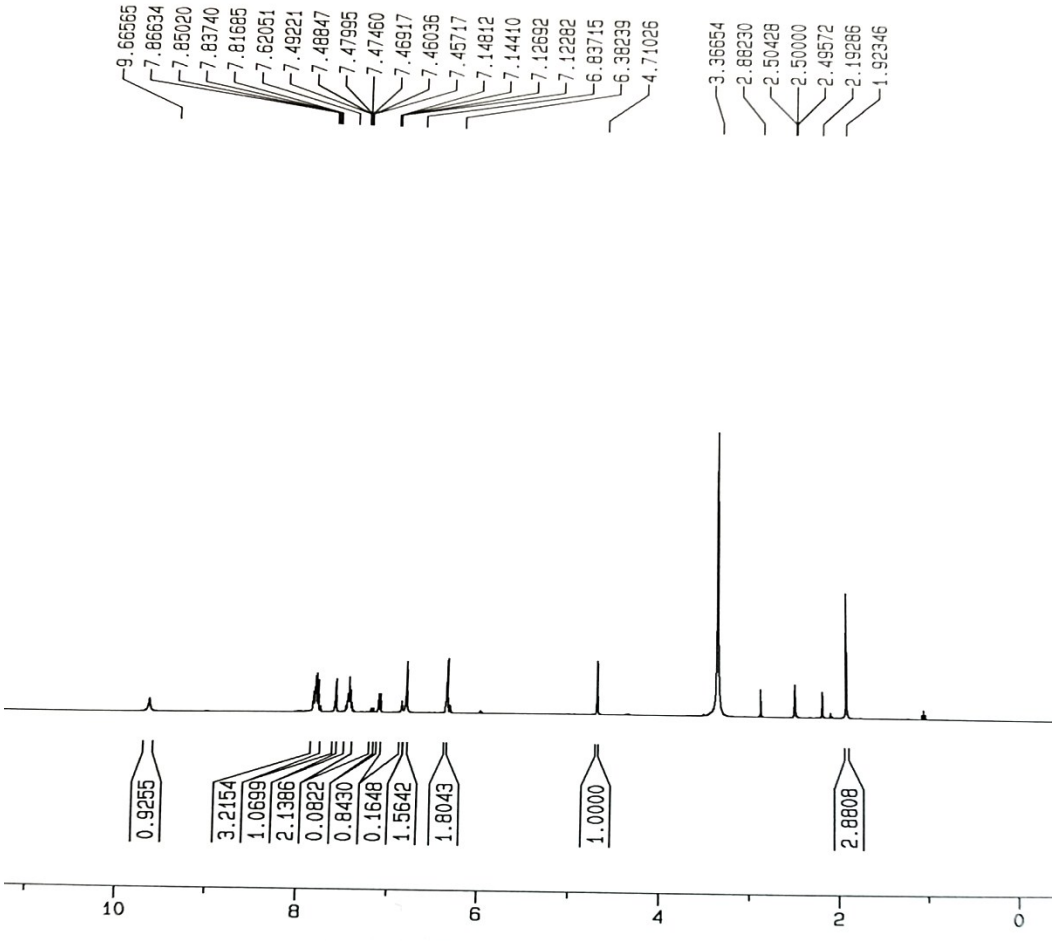
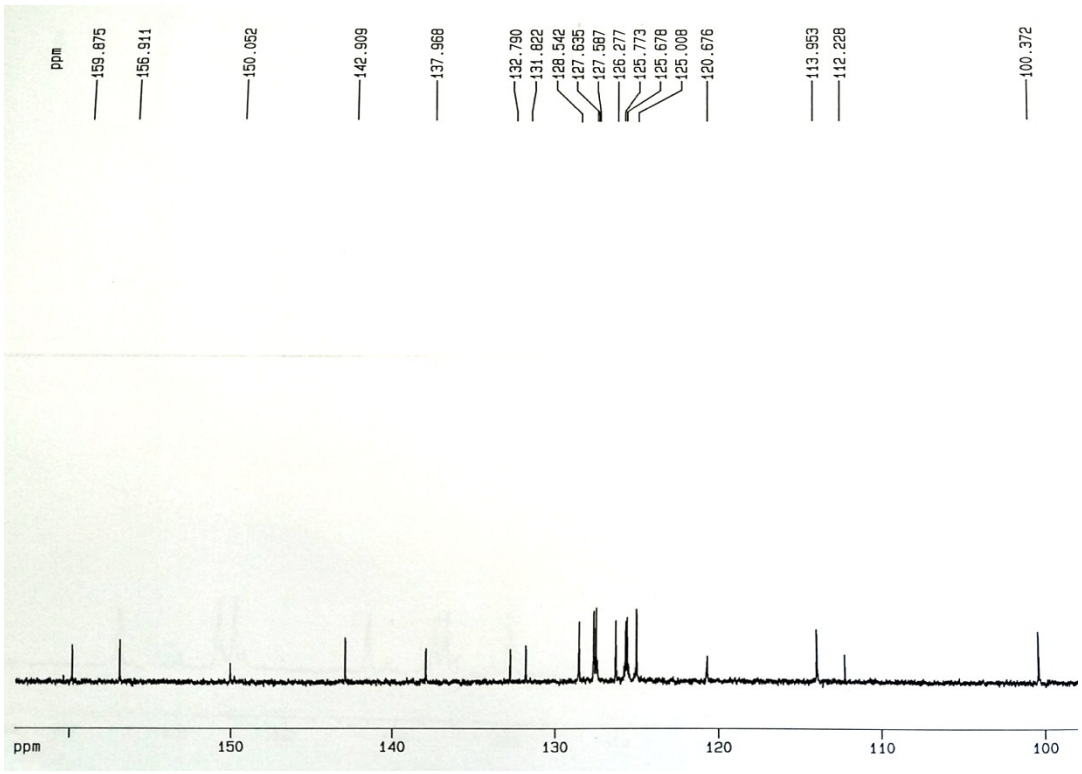
2-Amino-7-hydroxy-5-methyl-4-(naphthalen-2-yl)-4*H*-chromene-3-carbonitrile (12f):

Light yellow powder; m.p 272-274 ^{o}C ; FT-IR(KBr): 3490, 3399, 3319, 3206, 2923, 2074, 1642, 1497 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.92 (s, 3H, CH_3), 4.71 (s, 1H, methin-H), 6.35-6.38 (m, 2H, Ar-H), 6.84 (bs, 2H, NH_2), 7.14 (dd, 1H, J=8.5 Hz, J=1.6 Hz, Ar-H), 7.44-7.51 (m, 2H, Ar-H), 7.62 (s, 1H, Ar-H), 7.78-7.86 (m, 3H, Ar-H), 9.66 (bs, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.8, 38.7, 57.8, 100.4, 112.2, 113.9, 120.7, 125.0, 125.6, 125.7, 126.3, 127.5, 127.6, 128.5, 131.8, 132.8, 137.9, 142.9, 150.0, 156.9, 159.9 ppm; Anal. Calc. for $C_{21}H_{16}N_2O_2$ (%): C, 76.81; H, 4.91; N, 8.53; found: C, 76.58; H, 4.94; N, 8.50.

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