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Sodium Benzenesulfinates: Novel and Effective Organo Catalyst for Three Component Synthesis 5,6,7,8-Tetrahydro-4*H*-chromene Derivatives Under Ultrasound Irradiation

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Abstract: Sodium benzenesulfinates, as a new organo catalyst, can be used to synthesize tetrahydro-4*H*-chromene derivatives by three component reaction of cyclic β-dicarbonyl compounds, malononitrile, and aromatic aldehydes, in H_2O/EtOH, under ultrasound irradiation at room temperature. Inexpensiveness, stability and the potential of being easily obtained can be noted as preponderance of these catalysts. Furthermore, high conversions, short reaction times and cleaner reaction profiles are some of the advantages of this method. Moreover, H_2O/EtOH (7:3) was selected as a green solvent.

Keywords: Sodium benzenesulfinates, tetrahydro-4*H*-chromene derivatives, three component reactions, ultrasound irradiation, cyclic β-dicarbonyl compounds, aromatic aldehydes.

INTRODUCTION

Ultrasound irradiation has been increasingly used in organic synthesis in the last three decades as a green synthetic approach for accelerating organic chemical reactions [1-3]. Moreover, formation of unadulterated products in high yields, easier manipulation and waste minimization are some prominent features of this approach [4, 5]. More recently, ultrasonic irradiation has been used in the click chemistry [6], synthesis of benzotriazoles and 1-acylbenzotriazoles [7] and multicomponent reactions (MCRs) [8] as a clean, practical and of use protocol.

MCRs are highly flexible and supply the opportunity of building up complex molecules with exceptional synthetic efficiency, frequently with high stereoselectivity, from simple and easily available substrates [9-11]. In fact, development of MCRs can lead to new efficient synthetic methodologies to afford many small organic compounds in the field of new organic, bioorganic, and medicinal chemistry [12-14]. Hence, MCRs are considered as a vital technique in the synthesis of many important heterocyclic compounds such as tetrahydro-4*H*-chromene derivatives nowadays.

Tetrahydro-4*H*-chromenes have recently attracted attention as an important class of heterocyclic compounds in the field of drugs and pharmaceuticals due to their useful biological and pharmacological properties. These compounds are widely used as anticancer [15], antimalarial [16], antileishmanial [17], antibacterial [18], antifungal [19], antianaphylactic [20], antiallergenic [21], diuretic [22] and hypotensive [23] agents. They can also be used as cognitive enhancers for the treatment of neurodegenerative diseases such as Alzheimer's disease, amyotrophic lateral sclerosis, Huntington's disease, Parkinson's disease, AIDS associated diseases [24].

Due to the important properties of tetrahydro-4*H*-chromene derivatives, considerable attention has been focused on the development of environmentally friendly procedures to synthesize tetrahydro-4*H*-chromenes, by three component reaction of cyclic β-dicarbonyl compounds, malononitrile and aromatic aldehydes. Various catalytic systems such as potassium phthalimide-*N*-oxyl (POPINO) [25], $CaCl_2$ under ultrasonic irradiation [26], high surface area MgO [27], tetrabutylammonium bromide [28], *N,N*-dimethylaminoethylbenzyldimethylammonium chloride [29], diammonium hydrogen phosphate (DAHP) [30], K_3PO_4 [31], Na_2CO_3 under grinding [32], SiO_2 nanoparticles [33], methanesulfonic acid [34] and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [35] have been used. Each of these methods has its own merits, but the use of toxic organic solvents, expensive catalysts, containing transition metals, difficult work up, high reaction times, and low yields are drawbacks of these procedures. Thus, the exploitation of a simple and green synthesis of tetrahydro-4*H*-chromene derivatives is desirable to remove these restrictions.

Sodium benzenesulfinates (SBSs) have been used in many organic reactions as traceless linkers [36] and as nucleophiles [37]. SBSs have been never used as catalysts in the synthesis of heterocyclic compounds *via* three component reaction. Hence, we make our minds up to synthesize tetrahydro-4*H*-chromene derivatives in H_2O/EtOH by using inexpensive and commercially available SBSs as catalysts under ultrasound irradiation at room temperature.

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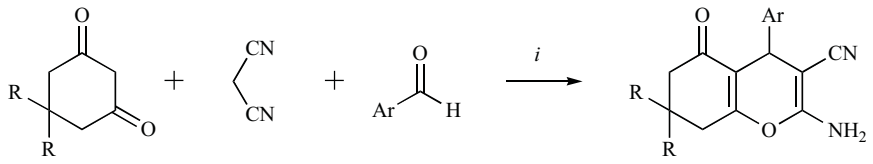


1a (R = Me) **1b** (R = H) **2** **3a-r** **4a-z,a'-g'**

i: H_2O/EtOH, 4-chloroSBS (10 mol%), ultrasound irradiation at room temperature

Scheme 1.

Table 1. Optimization of the model reaction between dimedone (1a), malononitrile (2), and benzaldehyde (3a Ar = C_6H_5).

Entry	Solvent	Catalyst	Catalyst (mol%)	Time (min)	Yield (%)
1	H_2O/EtOH	4-chloroSBS	10	8	93
2	H_2O	4-chloroSBS	10	12	89
3	EtOH	4-chloroSBS	10	10	90
4	Ethyl acetate	4-chloroSBS	10	30	82
5	Acetonitrile	4-chloroSBS	10	28	83
6	Toluene	4-chloroSBS	10	70	65
7	H_2O/EtOH	SBS	10	18	91
8	H_2O/EtOH	4-methylSBS	10	25	88
9	H_2O/EtOH	4-chloroSBS	8	10	90
10	H_2O/EtOH	4-chloroSBS	6	18	86
11	H_2O/EtOH	4-chloroSBS	4	30	84

RESULTS AND DISCUSSION

In the present work and in continuing our interest in the synthesis of heterocyclic compounds by three component reaction [38], we report the synthesis of 5,6,7,8-tetrahydro-4*H*-chromene derivatives **4a-x,a'-g'** by three component reaction of dimedone (**1a**) or 1,3-cyclohexanedione (**1b**), malononitrile (**2**) and aromatic aldehydes (**3a-r**) in H_2O/EtOH by using SBSs as new and effective organo catalyst under ultrasound irradiation at room temperature (Scheme **1**).

To optimize the conditions, the reaction between dimedone (**1a**), malononitrile (**2**), and benzaldehyde (**3a** Ar = C_6H_5) was chosen as a model. When this three component reaction was carried out in the presence of 4-chloroSBS (10 mol%), in H_2O/EtOH (7:3), under ultrasound irradiation at room temperature, 2-amino-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4*H*-chromene-3-carbonitrile (**4a**) was obtained in 93% yield within 8 min. This reaction was also carried out in different solvents such as H_2O, EtOH, ethyl acetate, acetonitrile and toluene, and the best results in terms of reaction time and yield of the desired product **4a** were obtained when the reaction was conducted in H_2O/EtOH (Table **1**, entries 1-6). Moreover SBS and 4-methylSBS were used as a catalyst (Table **1**, entries 7-8). Decreasing the catalyst loading from 10 to 4 mol% significantly lowered the yield of the reaction (Table **1**, entries 9-11). The best catalyst loading was found in 10 mol%, which gave an excellent yield of **4a** after only 8 min.

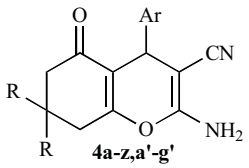
According to rely on our collected data, we decided to apply this method for synthesizing 5,6,7,8-tetrahydro-4*H*-chromene derivatives by using three component reaction of dimedone (**1a**) or 1,3-cyclohexanedione (**1b**), malononitrile (**2**) and aromatic aldehydes (**3a-r**), in H_2O/EtOH, under ultrasound irradiation at room temperature, in the presence of 4-chloroSBS (Table **2**).

According to the literature [36], condensation of SBSs, aromatic aldehydes (**3a-r**) and dimedone (**1a**), or 1,3-cyclohexanedione (**1b**), provided **I**. Subsequent coupling of **I** with malononitrile (**2**) gave the expected products **4a-z,a'-g'** (5,6,7,8-tetrahydro-4*H*-chromene derivatives) (Scheme **2**).

CONCLUSION

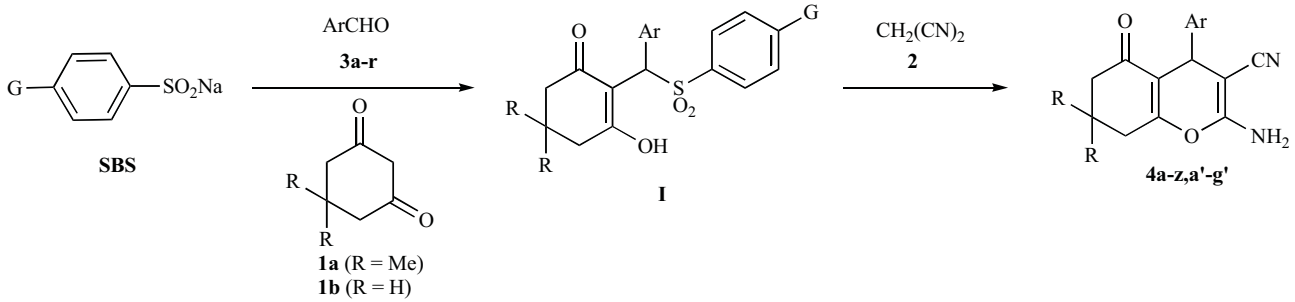
In summary, we have reported the use of SBSs as a new and effective organo catalyst for three component reaction of dimedone (**1a**) or 1,3-cyclohexanedione (**1b**), malononitrile (**2**), and aromatic aldehydes (**3a-r**), which leads to the synthesis of 5,6,7,8-tetrahydro-4*H*-chromene derivatives (**4a-z,a'-g'**). These reactions were carried out in H_2O/EtOH under ultrasound irradiation at room temperature. High yields, operational simplicity, clean reaction conditions in comparison with existing methods are advantages of this procedure that make it a useful practical process for the synthesis of these compounds.

Table 2. Three component reactions of dimedone (1a), or 1,3-cyclohexanedione (1b), malononitrile (2), and aromatic aldehydes (3a-r).



4a-z,a'-g'

Product	R	Ar	Time (min)	Yield (%)	Mp Observed (°C)	Mp Reported (°C)
4a	CH_3	C_6H_5	8	93	231-232	234-236 [25]
4b	CH_3	4-ClC_6H_4	6	94	215-217	216-218 [25]
4c	CH_3	2-ClC_6H_4	7	94	210-212	214-215 [25]
4d	CH_3	2,4-$Cl_2C_6H_3$	5	95	175-178	178-179 [27]
4e	CH_3	4-BrC_6H_4	6	93	221-222	222-224 [26]
4f	CH_3	2-BrC_6H_4	7	93	108-110	——
4g	CH_3	4-FC_6H_4	6	94	207-210	208-211 [25]
4h	CH_3	4-$NO_2C_6H_4$	5	94	181-182	180-182 [25]
4i	CH_3	3-$NO_2C_6H_4$	7	93	213-216	217-219 [25]
4j	CH_3	2-$NO_2C_6H_4$	6	94	214-217	215-217 [27]
4k	CH_3	4-$CH_3C_6H_4$	10	92	218-220	219-221 [25]
4l	CH_3	4-$CH_3OC_6H_4$	12	91	200-202	201-203 [25]
4m	CH_3	2-$CH_3OC_6H_4$	12	92	231-233	231-232 [26]
4n	CH_3	4-HOC_6H_4	15	90	225-228	226-228 [25]
4o	CH_3	4-$(CH_3)_2NC_6H_4$	17	90	208-210	210-212 [25]
4p	CH_3	2-furanyl	13	91	221-222	220-222 [25]
4q	CH_3	2-thienyl	15	90	227-229	226-228 [25]
4r	CH_3	3-pyridinyl	10	92	206-207	——
4s	H	C_6H_5	10	92	230-231	229-231 [27]
4t	H	4-ClC_6H_4	7	93	223-226	225-227 [27]
4u	H	2-ClC_6H_4	8	93	195-197	197-199 [26]
4v	H	2,4-$Cl_2C_6H_3$	6	94	220-222	221-223 [27]
4w	H	4-BrC_6H_4	8	93	248-250	——
4x	H	2-BrC_6H_4	10	92	215-217	——
4y	H	4-$NO_2C_6H_4$	6	94	234-237	235-237 [27]
4z	H	3-$NO_2C_6H_4$	9	92	200-202	201-203 [27]
4a'	H	2-$NO_2C_6H_4$	7	94	200-202	——
4b'	H	4-$CH_3C_6H_4$	13	92	223-225	224-226 [26]
4c'	H	4-$CH_3OC_6H_4$	15	90	189-191	190-192 [27]
4d'	H	4-HOC_6H_4	20	89	256-258	257-259 [26]
4e'	H	2-furanyl	15	90	237-239	——
4f'	H	2-thienyl	17	89	210-211	——
4g'	H	3-pyridinyl	12	91	229-230	——



Scheme 2.

EXPERIMENTAL

Melting points were measured on an Electrothermal-9100 apparatus and are uncorrected. IR spectra were recorded on a Bruker FT-IR Tensor 27 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. ^{13}C NMR spectra were recorded on the same instrument at 100 MHz using TMS as an internal standard. Elemental analyses were performed using a Heracus CHN-O-Rapid analyzer.

Typical Procedure for the Preparation of 2-Amino-4-aryl-5,6,7,8-tetrahydro-5-oxo-4*H*-chromene-3-carbonitriles 4a-z,a'-g'

A mixture of dimedone (**1a**) or 1,3-cyclohexanedione (**1b**) (2 mmol), malononitrile (**2**) (2 mmol), aromatic aldehydes (**3a-r**) (2 mmol), and 4-chloroSBS (10 mol%) in H_2O/EtOH (7:3) was refluxed for the reported time in Table **2** (the progress of the reaction being monitored by TLC using hexane / ethyl acetate as an eluent). After completion of the reaction, the reaction mixture was poured into ice-cold H_2O; the crude product was filtered, dried and recrystallized from EtOH.

2-Amino-4-(2-bromophenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (4f)

Yellow powder; IR (KBr, ν_{max}/cm^{-1}): 3440, 3328 (NH_2), 2192 (CN), 1683 (C=O), 1590, 1542 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 7.83-7.02 (m, 6H, CH-Ar, NH_2), 4.69 (s, 1H, CH), 2.32 (d, $^2J_{HH}$= 8.0 Hz, CH), 2.22 (d, $^2J_{HH}$= 7.9 Hz, CH), 2.05 (d, $^2J_{HH}$= 7.9 Hz, CH), 1.89 (d, $^2J_{HH}$= 8.0 Hz, CH), 1.02 (s, 3H, CH_3), 0.96 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6) δ_{ppm}: 197.72 (C=O), 160.22, 144.97, 137.58, 135.58, 134.24, 131.47, 130.04, 129.66, 124.36, 113.76 (CN), 70.00 (C3), 58.80 (CH_2), 51.60 (CH_2), 36.67 (CH), 33.63 (CMe_2), 33.35 (CH_3), 30.05 (CH_3). Anal. calcd. for $C_{18}H_{17}BrN_2O_2$: C, 57.92; H, 4.59; N, 7.51%. Found: C, 57.64; H, 4.37; N, 7.24%.

2-Amino-4-(2-furanyl)- 5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (4p)

Yellow powder; IR (KBr, ν_{max}/cm^{-1}): 3408, 3328 (NH_2), 2192 (CN), 1680 (C=O), 1600, 1555 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 7.46 (d, $^3J_{HH}$= 3.9 Hz, furan H-5'), 7.07 (s, 2H, NH_2), 6.30-6.04 (m, 2H, furan H-3',4'), 4.30 (s, 1H, H-4), 2.47 (d, $^2J_{HH}$= 7.9 Hz, CH), 2.40 (d, $^2J_{HH}$= 7.9 Hz, CH), 2.27 (d, $^2J_{HH}$= 8.0 Hz, CH), 2.15 (d, $^2J_{HH}$= 8.0 Hz, CH), 1.03 (s, 3H, CH_3), 0.97 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6) δ_{ppm}: 198.14 (C-5), 163.22 (C-2), 160.92 (C-8a), 157.34 (furan C-2'), 143.35 (furan C-5'), 135.21 (C-4a), 131.12 (furan C-4'), 123.78 (furan C-3'), 112.05 (CN), 77.68 (C-3), 57.01 (C-6), 51.51 (C-8), 33.41 (C-4), 30.59 (C-7), 30.02 (CH_3), 28.16 (CH_3). Anal. calcd. for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85%. Found: C, 67.23; H, 5.45; N, 9.64%.

2-Amino-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(2-thienyl)-4H-chromene-3-carbonitrile (4q)

White powder; IR (KBr, ν_{max}/cm^{-1}): 3392, 3328 (NH_2), 2192 (CN), 1673 (C=O), 1596, 1539 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 7.30 (d, $^3J_{HH}$= 4.0 Hz, CH-Ar), 7.10 (s, 2H, NH_2), 6.88-6.84 (m, 2H, CH-Ar), 4.51 (s, 1H, CH), 2.45 (d, $^2J_{HH}$= 8.0 Hz, CH), 2.40 (d, $^2J_{HH}$= 8.0 Hz, CH), 2.28 (d, $^2J_{HH}$= 7.9 Hz, CH), 2.13 (d, $^2J_{HH}$= 7.9 Hz, CH), 1.02 (s, 3H, CH_3), 0.95 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6) δ_{ppm}: 197.58 (C=O), 164.10, 160.54, 150.88, 128.41, 125.99, 125.60, 121.20, 114.56 (CN), 68.42 (C3), 59.73 (CH_2), 51.51 (CH_2), 33.33 (CH), 32.04 (CMe_2), 30.25 (CH_3), 28.10 (CH_3). Anal. calcd. for $C_{16}H_{16}N_2O_2S$: C, 63.98; H, 5.37; N, 9.33%. Found: C, 63.72; H, 5.18; N, 9.14%.

2-Amino-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(3-pyridinyl)-4H-chromene-3-carbonitrile (4r)

White powder; IR (KBr, ν_{max}/cm^{-1}): 3392, 3312 (NH_2), 2192 (CN), 1680 (C=O), 1596, 1574 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 8.37 (s, 2H, NH_2), 7.52-7.10 (m, 4H, CH-Ar), 4.22 (s, 1H, CH), 2.47 (d, $^2J_{HH}$= 8.0 Hz, CH), 2.39 (d, $^2J_{HH}$= 7.9 Hz, CH), 2.22 (d, $^2J_{HH}$= 7.9 Hz, CH), 2.09 (d, $^2J_{HH}$= 8.0 Hz, CH), 1.01 (s, 3H, CH_3), 0.92 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6) δ_{ppm}: 197.33 (C=O), 164.21, 160.22, 150.30, 149.44, 141.66, 136.36, 125.30, 121.10, 113.43 (CN), 67.08 (C3), 58.98 (CH_2), 51.53 (CH_2), 35.04 (CH), 33.42 (CMe_2), 29.85 (CH_3), 28.52 (CH_3). Anal. calcd. for $C_{17}H_{17}N_3O_2$: C, 69.14; H, 5.80; N, 14.23%. Found: C, 68.92; H, 5.63; N, 14.04%.

2-Amino-4-(4-bromophenyl)-5,6,7,8-tetrahydro-5-oxo-4H-chromene-3-carbonitrile (4w)

White powder; IR (KBr, ν_{max}/cm^{-1}): 3424, 3344 (NH_2), 2192 (CN), 1680 (C=O), 1593, 1539 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 7.44 (d, $^3J_{HH}$= 4.0 Hz, CH-Ar), 7.10 (d, $^3J_{HH}$= 3.9 Hz, CH-Ar), 7.04 (s, 2H, NH_2), 4.15 (s, 1H, CH), 2.47-1.93 (m, 6H, 3CH_2).^{13}C NMR (100 MHz, DMSO-d_6) δ_{ppm}: 197.89 (C=O), 166.05, 160.06, 145.82, 132.79, 131.10, 124.54, 121.20, 114.92 (CN), 59.24 (C3), 37.89 (CH), 36.70 (CH_2), 28.08 (CH_2), 21.37 (CH_2). Anal. calcd.

for $C_{16}H_{13}BrN_2O_2$: C, 55.67; H, 3.80; N, 8.12%. Found: C, 55.48; H, 3.63; N, 7.91%.

2-Amino-4-(2-bromophenyl)-5,6,7,8-tetrahydro-5-oxo-4H-chromene-3-carbonitrile (4x)

Yellow powder; IR (KBr, ν_{max}/cm^{-1}): 3472, 3328 (NH_2), 2192 (CN), 1680 (C=O), 1593, 1545 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 7.51-7.08 (m, 4H, ArH), 7.05 (s, 2H, NH_2), 4.69 (s, 1H, H-4), 2.27-1.94 (m, 6H, H_2-6-8). ^{13}C NMR (100 MHz, DMSO-d_6) δ_{ppm}: 197.12 (C-5), 166.58 (C-2), 160.05 (C-8a), 145.09 (phenyl C-1'), 134.16 (phenyl C-3'), 131.46 (phenyl C-6'), 129.98 and 129.75 (phenyl C-4',5'), 124.32 (phenyl C-2'), 120.75 and 114.77 (C-4a, CN), 58.67 (C-3), 37.93 (C-4), 36.57 (C-6), 28.10 (C-8), 21.42 (C-7). Anal. calcd. for $C_{16}H_{13}BrN_2O_2$: C, 55.67; H, 3.80; N, 8.12%. Found: C, 55.46; H, 3.65; N, 7.94%.

2-Amino-5,6,7,8-tetrahydro-4-(2-nitrophenyl)-5-oxo-4H-chromene-3-carbonitrile (4a')

Yellow powder; IR (KBr, ν_{max}/cm^{-1}): 3408, 3344 (NH_2), 2192 (CN), 1680 (C=O), 1593, 1523 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 7.78-7.36 (m, 4H, CH-Ar), 7.15 (s, 2H, NH_2), 4.91 (s, 1H, CH), 2.48-1.82 (m, 6H, $3CH_2$).^{13}C NMR (100 MHz, DMSO-d_6) δ_{ppm}: 197.88 (C=O), 166.22, 160.66, 150.54, 140.59, 134.99, 132.01, 129.38, 125.24, 120.73, 114.86 (CN), 58.04 (C3), 37.54 (CH), 31.73 (CH_2), 27.96 (CH_2), 21.30 (CH_2). Anal. calcd. for $C_{16}H_{13}N_3O_4$: C, 61.73; H, 4.21; N, 13.50%. Found: C, 61.54; H, 4.04; N, 13.33%.

2-Amino-4-(2-furanyl)-5,6,7,8-tetrahydro-5-oxo-4H-chromene-3-carbonitrile (4e')

Brown powder; IR (KBr, ν_{max}/cm^{-1}): 3408, 3328 (NH_2), 2192 (CN), 1680 (C=O), 1596, 1587 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 7.45 (d, $^3J_{HH}$= 4.0 Hz, CH-Ar), 7.05 (s, 2H, NH_2), 6.28-6.02 (m, 2H, CH-Ar), 4.30 (s, 1H, CH), 2.47-1.93 (m, 6H, $3CH_2$).^{13}C NMR (100 MHz, DMSO-d_6) δ_{ppm}: 197.31 (C=O), 166.75, 160.88, 157.41, 143.37, 121.01, 113.07 (CN), 112.01, 106.71, 56.93 (C3), 37.80 (CH), 30.58 (CH_2), 28.10 (CH_2), 21.36 (CH_2). Anal. calcd. for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93%. Found: C, 65.42; H, 4.56; N, 10.76%.

2-Amino-5,6,7,8-tetrahydro-5-oxo-4-(2-thienyl)-4H-chromene-3-carbonitrile (4f')

White powder; IR (KBr, ν_{max}/cm^{-1}): 3424, 3344 (NH_2), 2192 (CN), 1680 (C=O), 1596, 1580 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 7.29 (d, $^3J_{HH}$= 3.9 Hz, CH-Ar), 7.11 (s, 2H, NH_2), 6.88-6.83 (m, 2H, CH-Ar), 4.51 (s, 1H, CH), 2.48-1.85 (m, 6H, $3CH_2$).^{13}C NMR (100 MHz, DMSO-d_6) δ_{ppm}: 197.02 (C=O), 165.89, 160.62, 150.87, 128.44, 125.96, 125.58, 121.25, 115.70 (CN), 59.50 (C3), 37.86 (CH), 31.94 (CH_2), 28.04 (CH_2), 21.37 (CH_2). Anal. calcd. for $C_{14}H_{12}N_2O_2S$: C, 61.75; H, 4.44; N, 10.29%. Found: C, 61.54; H, 4.27; N, 10.10%.

2-Amino-5,6,7,8-tetrahydro-5-oxo-4-(3-pyridinyl)-4H-chromene-3-carbonitrile (4g')

White powder; IR (KBr, ν_{max}/cm^{-1}): 3360, 3312 (NH_2), 2192 (CN), 1664 (C=O), 1580, 1542 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm}: 8.38 (s, 2H, NH_2), 7.53-7.09 (m, 2H, CH-Ar), 4.21 (s, 1H, CH), 2.47-1.92 (m, 6H, $3CH_2$).^{13}C NMR (100 MHz, DMSO-d_6) δ_{ppm}: 197.36 (C=O), 166.48, 160.15, 150.29, 149.38, 141.71, 136.36, 125.23, 121.14, 114.40 (CN), 58.92 (C3), 37.86 (CH), 34.96 (CH_2), 28.11 (CH_2), 21.35 (CH_2). Anal. calcd. for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.72%. Found: C, 67.19; H, 4.75; N, 15.53%.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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