Journal of Fluorine Chemistry 141 (2012) 11–15

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

A facile and efficient synthesis of 2-amino-3-cyano-4*H*-chromenes and tetrahydrobenzo[*b*]pyrans using 2,2,2-trifluoroethanol as a metal-free and reusable medium

Samad Khaksar *, Ahmad Rouhollahpour, Saeed Mohammadzadeh Talesh

Department of Chemistry, Ayatollah Amoli Branch, Islamic Azad University, Amol, Iran

ARTICLE INFO

Article history:
Received 18 January 2012
Received in revised form 13 May 2012
Accepted 14 May 2012
Available online 23 May 2012

Keywords:
Fluorinated solvent
Malononitrile
Resorcinol
Metal-free

ABSTRACT

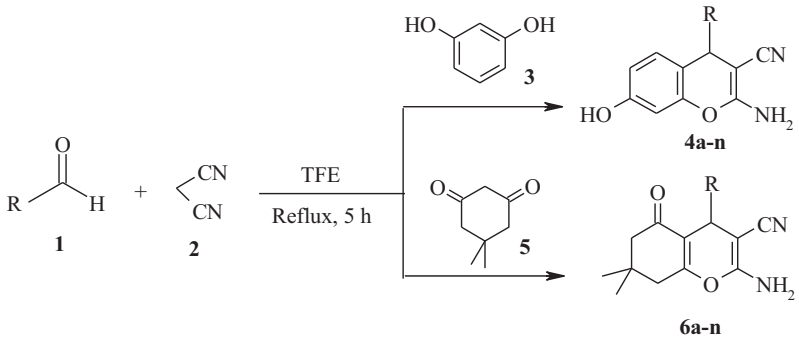
A highly efficient one-pot three-component regioselective synthesis of 2-amino-3-cyano-4*H*-chromene and tetrahydrobenzo[*b*]pyran derivatives has been developed by annulation of aldehydes, malononitrile, and resorcinol or dimedone under reflux conditions in 2,2,2-trifluoroethanol without the use of a catalyst or any other additive.

1. Introduction

Pyran annulated heterocyle derivatives represent an important class of oxygen-containing heterocycles being the main components of many natural occurring products, and are widely employed as cosmetics, pigments [1], and potential biodegradable agrochemicals [2] and exhibit a wide spectrum of biological activities [3–12]. 4*H*-Pyran can also serve as useful building blocks in the generation of a variety of natural products showing molluscicidal, antibacterial, anticancer, antitubercular, antimicrobial, anti-coagulant, antiallergic, antibiotic, hypolipidemic, and immunomodulating activities [13–20]. In addition, they can be used as cognitive enhancers, for the treatment of neurodegenerative disease, including Alzheimer's disease, amyotrophic lateral sclerosis, Huntington's disease, Parkinson's disease, AIDS associated dementia and Down's syndrome as well as for the treatment of schizophrenia and myoclonus [21]. Hence, an easy access to pyran derivatives is highly desirable as they possess unique pharmacological properties. The most straightforward synthesis of this heterocyclic system involves a three-component coupling of aromatic aldehyde, malononitrile and activated phenol. Traditionally, this reaction was catalyzed by a basic catalyst such as piperidine [22]. In view of the great importance of pyran derivatives, in recent years efforts have been made in developing new methodologies for the synthesis of these compounds. A variety of reagents, such as ionic liquids [23], hexadecyltrimethyl ammonium bromide [24], Mg/La mixed metal oxides [25], Cu(II) oxymetasilicate [26], cetyltrimethylammonium bromide [27], organic bases [28,29], MgO [30], tetrabutylammonium fluoride [31], silica nanoparticle [32] and DBU under microwave-irradiation [33] have been employed to achieve the synthesis of these molecules. Recently, the electrochemical synthesis of benzopyrans has been reported *via* three component reaction in the presence of NaBr as an electrolyte [34]. These methods, however, suffer from drawbacks such as unsatisfactory yields, acidic or basic catalysts, extended reaction times, elevated temperatures, tedious work-up, anhydrous organic solvents and the use of stoichiometric and/or relatively expensive reagents. Moreover, the main disadvantage of almost all existing methods is that the catalysts are destroyed in the work-up procedure and cannot be recovered or reused. Therefore, the search continues for a better catalyst for the synthesis of pyrans in terms of operational simplicity, reusability, economic viability, and greater selectivity. The use of fluorinated solvent, as chemical reaction media in place of conventional volatile organic solvents, has grown dramatically in recent years [35–50]. Fluorinated alcohols possess interesting physiochemical properties, which include lower boiling points and higher melting points than their non-fluorinated counterparts, high polarity, strong hydrogen bond donation properties and the ability to solvate water. Due to the current challenges for developing environmentally benign synthetic processes and in continuation of

* Corresponding author. Fax: +98 121 2517071.
E-mail addresses: S.khaksar@iauamol.ac.ir, samadkhaksar@yahoo.com (S. Khaksar).

0022-1139/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jfluchem.2012.05.014



Scheme 1. Synthesis of pyran annulated heterocycles.

our interest in the application of fluorinated solvents for various organic transformations [51–56] we report a new, convenient, mild and efficient procedure for the synthesis of pyran annulated heterocyles, which are obtained through one-pot three-component condensation reaction of aldehydes, malononitrile, and resorcinol as well as condensation of aldehydes, malononitrile, and cyclic 1,3-diketones under reflux conditions in 2,2,2-trifluoroethanol without the use of a catalyst or any other additives (Scheme 1).

2. Results and discussion

In an initial endeavor, the reaction was carried out by simply mixing benzaldehyde, malononitrile and resorcinol (Table 1, entry 1) in trifluoroethanol and refluxing the resulting mixture for 5 h. The corresponding substituted 2-amino-4*H*-chromene **4a** was obtained in high yield (90%). Encouraged by this success, we extended this reaction to a range of aldehydes **1a**–**o** under similar conditions to furnish the respective substituted 2-amino-4*H*-chromene **4a**–**o** in good yields. The results are summarized in Table 1.

As shown in Table 1, aromatic aldehydes carrying either electron-donating or electron-withdrawing substituents reacted efficiently giving excellent yields (Table 1, entries 2–12). It is noteworthy to mention that the structural variation of the aldehyde and substituents on the aromatic ring did not show any obvious effect on this conversion, because the desired products were obtained in high yields in relatively short reaction times. The experimental procedure is very efficient, convenient, rapid and has the ability to tolerate a variety of other functional groups, such as methoxyl, amino, nitro, and halides under these reaction conditions. Furthermore, acid sensitive aldehydes [57,58] worked well without any decomposition or polymerization under these reaction conditions (entries 10, 11 and 14). However aliphatic aldehydes did not undergo condensation under this reaction condition.

The present protocol was extended using dimedone and the reaction of benzaldehyde, malononitrile, and dimedone was carried out under similar reaction conditions. The desired product 6a was obtained in 90% yield. The reaction of other aromatic aldehydes substituted with Cl, Br, F, Me, NO_2, and MeO was also performed with dimedone and malononitrile, the desired products 6b–k were isolated in good yields (Table 2, entries 2–11).

The reaction of trans-cinnamaldehyde with malononitrile and dimedone was performed and the product **6l** was obtained in good yield (entry 12). Interestingly, aliphatic aldehydes were also suitable for this transformation (Table 1, entries 13 and 14) giving moderate yield. The result using HFIP at reflux condition was similar to that in TFE.

The mechanism of this reaction can be seen as sequential reactions involving Knoevenagel reaction, Michael addition and an intra-molecular cyclization that may take place in the formation of the final product. The probable mechanism is given in Scheme 2.

Although there is no solid evidence to support the catalytic mechanism of TFE in the reaction, it is surely reasonable to propose that the reactions carried out in fluorinated alcohols are

Table 1
Synthesis of 2- amino-4*H*-chromenes derivatives in TFE.

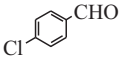
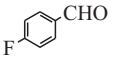
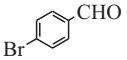
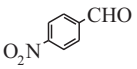
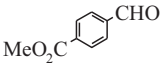
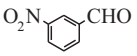
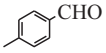
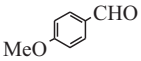
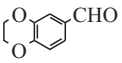
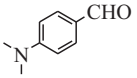
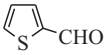
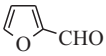
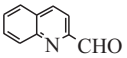
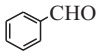
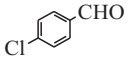
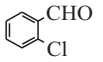
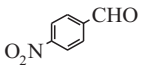
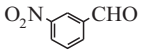
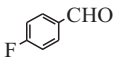
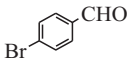
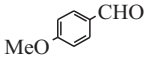
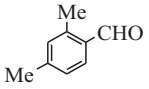
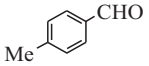
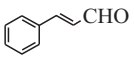
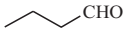
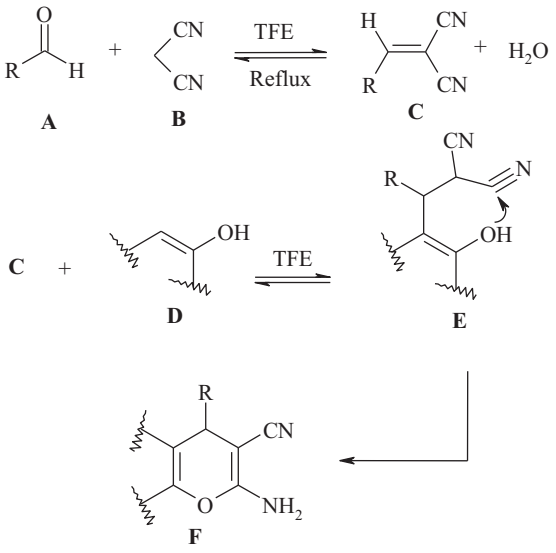
Entry	Aldehyde	Product	**4** yield (%) Ref.
1		**4a**	90 [33]
2		**4b**	95 [33]
3		**4c**	96 [33]
4		**4d**	95 [33]
5		**4e**	93 [33]
6		**4f**	92 [33]
7		**4g**	90 [33]
8		**4h**	90 [33]
9		**4i**	88 [33]
10		**4j**	90 [34]
11		**4k**	90 [27]
12		**4l**	85 [34]
13		**4m**	90 [34]
14		**4n**	80 [34]
15		**4o**	90 [34]

Table 2
Synthesis of tetrahydrobenzo[*b*]pyran derivatives in TFE.

Entry	Aldehyde	Product	**4** yield (%) Ref.
1		**6a**	90 [32]
2		**6b**	95 [32]
3		**6c**	85 [32]
4		**6d**	90 [32]
5		**6e**	92 [32]
6		**6f**	90 [31]
7		**6g**	90 [31]
8		**6h**	80 [31]
9		**6i**	85 [32]
10		**6j**	80 [31]
11		**6k**	90 [31]
12		**6l**	90 [31]
13		**6m**	80 [32]
14		**6n**	80 [32]

acid-catalyzed. The weak Brønsted acidity (pK_a = 12.4 for TFE and 9.3 for HFIP) and strong ionizing power may be relevant to its unique role in this transformation. The polarity effect and hydrogen bond donor ability might not be important in this case. Actually the hydrogen bond donating ability of these solvents drops as temperature rises owing to the fact that hydrogen-bond formation is exothermic [59,60]. Although fluorinated alcohols is known to have a remarkable stabilizing effect for cationic species due to its high polarizability and low nucleophilicity, the synthesis of pyrans does not go through a discrete carbocation intermediate. The polar transition state of the reaction could be stabilized well by the high ionizing solvent TFE.

Interestingly, the reaction did not proceed to completion when either ethanol or water alone was used as solvent, even at reflux conditions. This method not only affords the products in excellent yields but also avoids the problems associated with catalyst cost, handling, safety, and pollution. One of the major advantages of this protocol is the isolation and purification of the products, which have been achieved by simple filtration and crystallization of the crude products. After the reaction, TFE can be easily separated (by distillation) and reused without decrease in its activity. For example, the reaction of benzaldehyde, malononitrile and dimedone afforded the corresponding tetrahydrobenzo[*b*]pyran derivative in 90%, 90%, 90%, 88% and 88% isolated yield over five cycles.



Scheme 2. Plausible mechanism for the formation of pyran annulated heterocyclic compounds.

When we carried out the reaction in TFE at room temperature, the reaction proceeded very slowly to give very poor yields.

3. Conclusions

In summary, we have developed efficient synthesis 2-amino-4*H*-chromene and tetrahydrobenzo[*b*]pyran derivatives *via* one-pot condensation of aldehydes, malononitrile and resorcinol or dimedone in TFE without using any catalyst or additives. In contrast to the existing methods using potentially hazardous catalysts/additives, this new method offers the following competitive advantages: (i) avoiding the use of any base, metal or Lewis acid catalyst (ii) short reaction time, (iii) ease of product isolation/purification by non-aqueous work-up, (iv) high chemoselectivity, (v) no side reaction, and (vi) low costs and simplicity in process and handling. The recovered TFE can be reusable.

4. Experimental

4.1. General procedure for the preparation of 2-amino-3-cyano-4H-chromenes

Aldehyde (1 mmol), resorcinol (1 mmol) and malononitrile (1 mmol) were dissolved in TFE (2 mL) and was refluxed for the stipulated time. The progress of the reaction is monitored by TLC. After completion of the reaction, the corresponding solid product **4** was obtained through simple filtering, and recrystallized from ethanol to yield the highly pure 2-amino-4*H*-chromene derivatives. The physical data (mp, IR, NMR) of known compounds were found to be identical with those reported in the literature [27,33,34].

4.2. General procedure for the preparation of tetrahydrobenzo[b]pyrans

Aldehyde (1 mmol), dimedone (1 mmol) and malononitrile (1 mmol) were dissolved in TFE (2 mL) and was refluxed for 5 h. After completion of the reaction as indicated by TLC, the products were isolated by filtration (for solid products) or after selective evaporation of the TFE (for liquid products) to yield the highly pure tetrahydrobenzo[*b*]pyran derivatives. The physical data (mp, IR,

NMR) of known compounds were found to be identical with those reported in the literature [31,32].

Spectroscopic data for selected examples are shown below:

2-Amino-3-cyano-7-hydroxy-4-phenyl-4H-chromene (4a). Light yellow solid, mp: 231–233 °C. IR (KBr): 3428, 3217, 2190, 1650, 1580 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 4.61 (s, 1H), 6.85 (br s, 2H, NH_2), 6.40–7.31 (m, 8H), 9.68 (br s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 42.3, 56.2, 102.1, 112.3, 113.7, 120.5, 126.6, 127.3, 128.5, 129.8, 146.3, 148.8, 157.1, 160.2.

2-Amino-3-cyano-7-hydroxy-4-(4-bromophenyl)-4H-chromene (4d). Light yellow solid, mp: 224–226 °C. IR (KBr): 3471, 3337, 2194, 1641, 1578 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 4.64 (s, 1H), 6.90 (br s, 2H, NH_2), 6.40–7.84 (m, 7H), 9.71 (br s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 41.2, 56.3, 102.6, 112.0, 113.7, 120.2, 121.4, 130.1, 130.3, 132.1, 147.2, 149.5, 157.8, 160.5.

2-Amino-3-cyano-7-hydroxy-4-(3-nitrophenyl)-4H-chromene (4g). Yellow solid, mp: 169–170 °C. IR (KBr): 3440, 3345, 2192, 1650, 1585 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 4.85 (s, 1H), 7.05 (br s, 2H, NH_2), 6.45–8.10 (m, 7H), 9.78 (br s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 42.1, 58.3, 102.4, 111.9 112.7, 120.2, 121.1, 123.7, 128.2, 129.6, 131.4, 133.4, 139.3, 148.7, 149.0, 157.5, 160.3.

2-Amino-3-cyano-7-hydroxy-4-(2-fluorophenyl)-4H-chromene (4h). Yellow solid, mp: 200–202 °C. IR (KBr): 3424, 3333, 2190, 1651, 1587 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 4.87 (s, 1H), 6.85 (br s, 2H, NH_2), 6.38–7.25 (m, 7H), 9.69 (br s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 41.5, 54.5, 102.2, 112.4, 115.5 (d, $^2J_{C-F}$ = 22.0 Hz), 115.8, 120.4, 124.7, 128.8 (d, $^3J_{C-F}$ = 8.4 Hz), 129.5, 129.8, 132.7, 149.1, 157.2, 160.6 (d, $^1J_{C-F}$ = 246.1 Hz).

2-Amino-3-cyano-7-hydroxy-4-(4-methylphenyl)-4H-chromene (4i). Yellow solid, mp: 184–186 °C. IR (KBr): 3409, 3332, 2194, 1656, 1589 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 2.24 (s, 3H), 4.56 (s, 1H), 6.81 (br s, 2H, NH_2), 6.38–7.10 (m, 7H), 9.66 (br s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.5, 42.2, 56.4, 102.1, 112.3, 113.8, 120.6, 127.2, 129.5, 129.8, 135.6, 143.4, 148.7, 156.9, 160.1.

2-Amino-3-cyano-7-hydroxy-4-(4-methoxyphenyl)-4H-chromene (4j). Yellow solid, mp: 110–112 °C. IR (KBr): 3424, 3333, 2190, 1651, 1587 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 3.51 (s, 3H), 4.53 (s, 1H), 6.84 (br s, 2H, NH_2), 6.43–7.21 (m, 7H), 9.63 (br s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 41.3, 55.8, 56.0, 102.2, 112.3, 113.5, 120.6, 126.4, 129.7, 136.5, 142.0, 148.4, 152.7, 156.8, 160.4.

2-Amino-3-cyano-7-hydroxy-4-(4-dimethylaminophenyl)-4H-chromene (4k). Yellow solid, mp: 193–195 °C. IR (KBr): 3415, 3330, 2190, 1654, 1585 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 2.84 (s, 6H), 4.46 (s, 1H), 6.77 (br s, 2H, NH_2), 6.37–6.97 (m, 7H), 9.66 (br s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 41.2, 42.2, 56.8, 101.9, 112.1, 112.5, 114.4, 120.7, 127.8, 129.8, 134.1, 148.7, 149.2, 156.7, 159.9.

2-Amino-3-cyano-7-hydroxy-4-(2-thienyl)-4H-chromene (4 m). Yellow solid, mp: 204–205 °C. IR (KBr): 3422, 3332, 2193, 1653, 1568 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 4.97 (s, 1H), 6.91 (br s, 2H, NH_2), 6.38–7.35 (m, 6H), 9.76 (br s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 41.4, 56.4, 102.2, 112.4, 113.4, 120.5, 124.0, 125.0, 126.7, 129.8, 148.5, 151.5, 157.4, 160.3.

2-Amino-3-cyano-7-hydroxy-4-(2-furyl)-4H-chromene (4n). Yellow solid, mp: 189–191 °C. IR (KBr): 3420, 3331, 2193, 1651, 1589 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 4.75 (s, 1H), 6.92 (br s, 2H, NH_2), 6.13–7.50 (m, 6H), 9.74 (br s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 39.4, 53.2, 102.3, 105.4, 110.2, 111.0, 112.2, 120.3, 129.5, 142.3, 149.1, 156.9, 157.3, 160.9.

2-Amino-3-cyano-7-hydroxy-4-(quinoline-2-yl)-4H-chromene (4o). Yellow solid, mp: 199–201 °C. IR (KBr): 3428, 3338, 2192, 1633, 1560. ^1H NMR (400 MHz DMSO-d_6): δ = 4.65 (s, 1H), 6.39–6.49 (m, 3H), 6.89 (br s, 2H, NH_2), 7.09–7.22 (m, 6H), 9.70 (br s, 1H, OH). ^{13}C NMR (100 MHz DMSO-d_6): δ = 40.2, 56.6, 102.6, 112.8, 113.9, 115.6, 115.8, 116.2, 116.5, 121.0, 129.6, 129.7, 130.3, 131.4, 131.5, 143.0, 149.2, 155.7, 157.6, 160.6.

2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6a**). White solid; mp: 234–235 °C; ^1H NMR (400 MHz, DMSO-d_6): δ = 0.96 (s, 3H), 1.05 (s, 3H), 2.11 (d, J = 16.2 Hz, 1H), 2.25 (d, J = 16.2 Hz, 1H), 2.51 (s, 2H), 4.18 (s, 1H), 6.98 (s, 2H), 7.13–7.21 (m, 3H), 7.28 (t, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 26.7, 28.4, 31.7, 35.5, 38.6, 49.9, 58.2, 112.7, 119.7, 126.5, 127.1, 128.3, 144.7, 158.4, 162.4, 195.6.

2-Amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6b**). White solid; mp: 215–216 °C; ^1H NMR (400 MHz, DMSO-d_6): δ = 0.95 (s, 3H), 1.03 (s, 3H), 2.10 (d, J = 16.2 Hz, 1H), 2.24 (d, J = 16.2 Hz, 1H), 2.50 (s, 2H), 4.20 (s, 1H), 7.17 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.05 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 26.8, 28.3, 31.9, 35.1, 40.1, 49.9, 57.9, 112.3, 119.6, 128.3, 129.1, 132.1, 143.8, 158.5, 162.6, 195.8.

2-Amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6c**). White solid; mp: 191–192 °C; ^1H NMR (400 MHz, DMSO-d_6): δ = 0.95 (s, 3H), 1.02 (s, 3H), 2.10 (d, J = 16.2 Hz, 1H), 2.25 (d, J = 16.2 Hz, 1H), 2.50 (s, 2H), 4.21 (s, 1H), 7.02 (s, 1H), 7.10 (t, J = 8.8 Hz, 2H), 7.14–7.22 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 27.3, 28.8, 32.2, 35.4, 50.4, 58.6, 113.1, 115.4, 115.5, 120.2, 129.4, 129.5, 141.4, 141.4, 159.1, 160.1, 162.5, 163.1, 196.1.

2-Amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6d**). Yellow solid; mp: 151–152 °C; ^1H NMR (400 MHz,DMSO-d_6): δ = 0.95 (s, 3H), 1.04 (s, 3H), 2.12 (d, J = 15.6 Hz, 1H), 2.26 (d, J = 15.6 Hz, 1H), 2.50 (s, 2H), 4.37 (s, 1H), 7.17 (s, 2H), 7.44 (d, J = 8.2 Hz, 2H), 8.17 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 26.9, 28.2, 34.8, 35.6, 49.9, 57.1, 112.1, 119.3, 123.6, 128.6, 146.3, 152.2, 158.7, 163.1, 195.8.

2-Amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**6i**). Yellow solid; mp: 200–202 °C; ^1H NMR (400 MHz, DMSO-d_6): δ = 0.95 (s, 3H), 1.04 (s, 3H), 2.09 (d, J = 16.2 Hz, 1H), 2.24 (d, J = 16.2 Hz, 1H), 2.51 (s, 2H), 3.72 (s, 1H), 4.13 (s, 1H), 6.84 (d, J = 8.1 Hz, 2H), 6.94 (s, 2H), 7.06 (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 26.8, 28.4, 31.7, 34.8, 50.1, 54.9, 58.5, 112.9, 113.6, 119.7, 128.2, 136.8, 158.1, 158.5, 162.1, 195.6.

Acknowledgment

This research is supported by the Islamic Azad University, Ayatollah Amoli Branch.

References

[1] G.P. Ellis, in: A. Weissberger, E.C. Taylor (Eds.), The Chemistry of Heterocyclic Compounds Chromenes, Chromanes and Chromones, John Wiley, New York, NY, 1977, p. 11e139 (Chapter II).
[2] E.A. Hafez, M.H. Elnagdi, A.G.A. Elagemey, F.M.A.A. El-Taweel, Heterocycles 26 (1987) 903–907.
[3] M.M. Khafagy, A.H.F.A. El-Wahas, F.A. Eid, A.M. El-Agrody, Farmaco 57 (2002) 715–722.
[4] W.P. Smith, L.S. Sollis, D.P. Howes, C.P. Cherry, D.I. Starkey, N.K. Cobley, Journal of Medicinal Chemistry 41 (1998) 787–797.
[5] A.G. Martinez, L.J. Marco, Bioorganic and Medicinal Chemistry Letters 7 (1997) 3165–3170.
[6] K. Hiramoto, A. Nasuhara, K. Michiloshi, T. Kato, K. Kikugawa, Mutation Research 395 (1997) 47–56.
[7] G. Bianchi, A. Tava, Agricultural and Biological Chemistry 51 (1987) 2001–2002.
[8] S.J. Mohr, M.A. Chirigos, F.S. Fuhrman, J.W. Pryor, Cancer Research 35 (1975) 3750–3754.
[9] F. Eiden, F. Denk, Archiv der Pharmazie Weinheim Ger. (Archiv der Pharmazie) 324 (1991) 353–354.
[10] G.R. Green, J.M. Evans, A.K. Vong, in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Eds.), Comprehensive Heterocyclic Chemistry II, vol. 5, Pergamon Press, Oxford, 1995, p. 469.

[11] D.M. Pore, K.A. Undale, B.B. Dongare, U.V. Desai, Catalysis Letters 132 (2009) 104–108.
[12] L.Q. Yu, F. Liu, Q.D. You, Organic Preparations and Procedures International 41 (2009) 77–82.
[13] F.M. Abdelrazeka, P. Metza, E.K. Farragb, Archiv der Pharmazie Pharmaceutical and Medicinal Chemistry 337 (2004) 482–485.
[14] N.M.A. El-Rahmana, A.A. El-Kateba, M.F. Mady, Synthetic Communications 37 (2007) 3961–3970.
[15] M. Darbarwar, V. Sundarmurthy, Synthesis (1982) 337–340.
[16] L. Bonsignore, G. Loy, D. Secci, A. Calignano, European Journal of Medical Chemistry 28 (1993) 517–520.
[17] C.N. O'Callaghan, T.B.H. McMurry, Journal of Chemical Research (1995) 214–215.
[18] N.R. Kamdar, D.D. Haveliwala, P.T. Mistry, S.K. Patel, European Journal of Medical Chemistry 45 (2010) 5056–5063.
[19] W. Kemnitzer, S. Kasibhatla, S. Jiang, H. Zhang, J. Zhao, S. Jia, L. Xu, C. Crogan-Grundy, R. Denis, N. Barriault, L. Vaillancourt, S. Charron, J. Dodd, G. Attardo, D. Labrecque, S. Lamothe, H. Gourdeau, B. Tseng, J. Drewea, S.X. Caia, Bioorganic and Medicinal Chemistry Letters 15 (2005) 4745–4751.
[20] L.L. Andreani, E. Lapi, Bollettino Chimico Farmaceutico 99 (1960) 583–586.
[21] C.S. Konkoy, D.B. Fick, S.X. Cai, N.C. Lan, J.F.W. Keana, PCT Int. Appl. WO 0075123, 2000 (Chem. Abstr., 134 (2001) 29313a).
[22] (a) F.F. Abdel-Latif, Indian Journal of Chemistry 29B (1990) 664–666;
(b) A.G.A. Elagamey, F.M.A.A. El-Taweel, Indian Journal of Chemistry 29B (1990) 885–886;
(c) J. Bioxham, C.P. Dell, C.W. Smith, Heterocycles 38 (1994) 399–408.
[23] Y. Peng, G. Song, Catalysis Communications 8 (2007) 111–114.
[24] T.S. Jin, L.B. Liu, Y. Zhao, T.S. Li, Synthetic Communications 35 (2005) 1859–1861.
[25] N.S. Babu, N. Pasha, K.T.V. Rao, P.S.S. Prasad, N. Lingaiah, Tetrahedron Letters 49 (2008) 2730–2733.
[26] M.M. Heravi, Y.S. Beheshtiha, Z. Pirnia, S. Sadjadi, M. Adibi, Synthetic Communications 39 (2009) 3663–3667.
[27] T.S. Jin, J.C. Xiao, S.J. Wang, T.S. Li, Ultrasonics Sonochemistry 11 (2004) 393–397.
[28] N. Martin, C. Seoane, J.L. Soto, Tetrahedron 44 (1988) 5861–5868.
[29] V.D. Dyachenko, Russian Journal of General Chemistry 76 (9) (2006) 282–291.
[30] (a) M. Seifi, H. Sheibani, Catalysis Letters 126 (2008) 275–279;
(b) K. Gong, H.L. Wang, J. Luo, Z.L. Liu, Journal of Heterocyclic Chemistry 46 (2009) 1145–1150.
[31] S. Gao, C.H. Tsai, C.T.C.-F. Yao, Tetrahedron 64 (2008) 9143–9149.
[32] S. Banerjee, A. Horn, H. Khatri, G. Sereda, Tetrahedron Letters 52 (2011) 1878–1881.
[33] D.S. Raghuvanshi, K.N. Singh, Arkivoc (2010) 305–317.
[34] S. Makarem, A.A. Mohammadi, A.R. Fakhari, Tetrahedron Letters 49 (2008) 7194–7196.
[35] I.A. Shuklov, N.V. Dubrovina, A. Børner, Synthesis (2007) 2925–2943.
[36] J.-P. Bégué, D. Bonnet-Delpon, B. Crousse, Synlett (2004) 18–29.
[37] M. Westermaier, H. Mayr, Organic Letters 8 (2006) 4791–4794.
[38] M.O. Ratnikov, V.V. Tumanov, W.A. Smit, Angewandte Chemie International Edition 47 (2008) 9739–9742.
[39] M. Westermaier, H. Mayr, Chemistry: A European Journal 14 (2008) 1638–1647.
[40] K. De, J. Legros, B. Crousse, D. Bonnet-Delpon, Journal of Organic Chemistry 74 (2009) 6260–6265.
[41] N. Nishiwaki, R. Kamimura, K. Shono, T. Kawakami, K. Nakayama, K. Nishino, T. Nakayama, K. Takahashi, A. Nakamura, T. Hosokawa, Tetrahedron Letters 51 (2010) 3590–3592.
[42] J. Choy, S. Jaime-Figueroa, T. Lara-Jaime, Tetrahedron Letters 51 (2010) 2244–2246.
[43] Y. Kuroiwa, S. Matsumura, K. Toshima, Synlett (2008) 2523–2525.
[44] H. Tanabe, J. Ichikawa, Chemistry Letters 39 (2010) 248–249.
[45] M. Yokota, D. Fujita, J. Ichikawa, Organic Letters 9 (2007) 4639–4642.
[46] R. Ben-Daniel, S.P. de Visser, S. Shaik, R. Neumann, Journal of the American Chemical Society 125 (2003) 12116–12117.
[47] S. Kobayashi, H. Tanaka, H. Amii, K. Uneyama, Tetrahedron 59 (2003) 1547–1552.
[48] K. Neimann, R. Neumann, Organic Letters 2 (2000) 2861–2863.
[49] K.S. Ravikumar, Y.M. Zhang, J.P. Bégué, D. Bonnet-Delpon, European Journal of Organic Chemistry (1998) 2937–2940.
[50] J. Legros, B. Crousse, D. Bonnet-Delpon, J.P. Bégué, European Journal of Organic Chemistry (2002) 3290–3293.
[51] A. Heydari, S. Khaksar, M. Tajbakhsh, Synthesis 19 (2008) 3126–3130.
[52] A. Heydari, S. Khaksar, M. Tajbakhsh, Tetrahedron Letters 50 (2009) 77–80.
[53] A. Heydari, S. Khaksar, M. Tajbakhsh, H.R. Bijanzadeh, Journal of Fluorine Chemistry 130 (2009) 609–614.
[54] A. Heydari, S. Khaksar, M. Tajbakhsh, H.R. Bijanzadeh, Journal of Fluorine Chemistry 131 (2010) 106–110.
[55] S. Khaksar, A. Heydari, M. Tajbakhsh, S.M. Vahdat, Journal of Fluorine Chemistry 131 (2010) 1377–1381.
[56] M. Tajbakhsh, R. Hosseinzadeh, H. Alinezhad, S. Ghahari, A. Heydari, S. Khaksar, Synthesis (2011) 490–496.
[57] M. Willot, J.Ch. Chen, J. Zhu, Synlett (2009) 577–580.
[58] (a) M. De Paolis, A. Chiaroni, J. Zhu, Chemical Communications (2003) 2896–2897;
(b) X. Chen, J. Chen, M. De Paolis, J. Zhu, Journal of Organic Chemistry 70 (2005) 4397–4408.
[59] J. Lu, J.S. Brown, C.L. Liotta, C.A. Eckert, Chemical Communications (2001) 665–666.
[60] A.V. Iogansen, Spectrochimica Acta: A 55 (1999) 1585–1612.