Asian Journal of Chemistry Vol. 20, No. 7 (2008), 5145-5152

One-Pot Synthesis of Benzochromene Derivatives Catalyzed by KF-Al_2O_3 with Grinding

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An efficient and convenient approach to the condensation reaction of naphthol, aromatic aldehydes and malono-nitrile using KF-Al_2O_3 as catalyst with grinding at room temperature (without any solvent) is described. This method provides several advantages such as neutral condition, simple work-up procedure, high yields and reduced environmental impact.

Key Words: Benzochromene derivatives, Aromatic aldehydes, Naphthol, Malononitrile, Grinding method.

INTRODUCTION

It is known that substituted benzochromene and their derivatives is a kind of very useful compound[1]. They have attracted strong interest[2] due to their useful biological and pharmacological properties, such as anticoagulant, spasmolytic, diuretic, antianaphylactin, anticancer, *etc.* In addition, they also constitute a structural unit of a series of natural products[3] and they are versatile intermediates in synthesis[4]. Furthermore, these compounds can be employed as cosmetics, pigments[5] and utilized as potential biodegradable agrochemicals[6]. In several years, many synthetic methods for preparation of these compounds have been reported using base or amide as catalysts[7]. However, each of the above methods has its own merit, while some of these methods have not been entirely satisfactory owing to cumbersome experimental conditions such as requiring an organic solvent, higher temperatures, long reaction times, lower yields and effluent pollution. Consequently, there is scope for further renovation toward mild conditions, increased of variation of the substituents in the components and better yields. The grinding method is used more and more frequently in organic synthesis[8]. Compared with traditional methods, proposed method is more convenient and easily controlled. A great number of organic reactions can be carried

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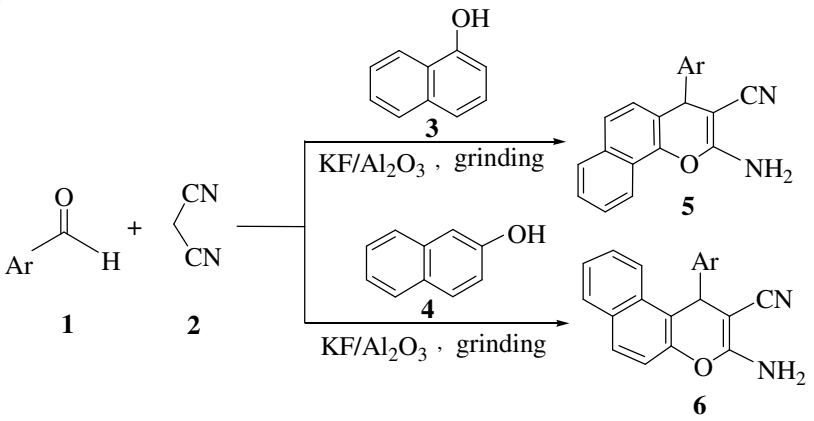
out in higher yields, shorter times or milder conditions by the grinding method. It can even set off some reactions that cannot be carried out under traditional conditions. Herein, the condensation of naphthol, aromatic aldehydes and malononitrile using KF-Al_2O_3 as catalyst under solvent-free conditions by the grinding method at room temperature is reported. This is an efficient synthetic method, not only preserves the simplicity and is carried out without any solvent, but also consistently give the corresponding products in good to excellent yields (**Scheme-I**).



Scheme-I

EXPERIMENTAL

^{1}H NMR spectra were measured on a Bruker Advance (400 MHz) spectrometer using TMS as internal standard and DMSO-d_6 as solvent. IR spectra were recorded on a Bio-Rad FTS-40 spectrometer (KBr). Elemental analyses were determined using Perkin-Elmer 2400 II elemental analyzer. All products were characterized by comparison of their melting points, melting points are uncorrected.

Preparation of KF/Al_2O_3: KF/Al_2O_3 was prepared by dissolving 32.5 g of KF·$2H_2O$ in 100 mL water and adding 30 g basic Al_2O_3 (100-200 mesh). The mixture was stirred at 70-75 °C for 2 h. The water was removed under reduced pressure. The resulting free flowing power was dried at 110 °C for 4 h and finally stored in a desiccator until used. The content of KF is about 40 %.

General procedure for synthesis of benzochromene derivatives: Aromatic aldehyde **1** (2 mmol), malononitrile (**2**) (2 mmol), naphthol (**3** or **4**) (2 mmol) and KF-Al_2O_3 (200 mg) were added to a mortar. The mixture was ground by mortar and pestle at room temperature for 20 min and was kept at room temperature in a desiccator for a period (16-24 h). The completion of the reaction was monitored by TLC (eluent ethyl acetate-petroleum ether).

After completion of the reaction, the mixture was dissolved in ethyl acetate, the catalyst was removed by filtration and washed with ethyl acetate. The majority solvent was evaporated under reduced pressure and the remained solution was poured into H_2O (50 mL). The precipitate was filtered and washed with EtOH, affording the crude product. The crude product was purified by recrystallization from ethanol (95 %) to pure product **5** or **6**. Data of compounds are shown below:

2-Amino-3-cyano-4-phenyl-7,8-benzochromene (5a): IR (KBr, ν_{max}, cm^{-1}): 3452, 3308, 3020, 2932, 2205, 1656, 1600, 1572, 1450, 1372, 1267, 1100, 1022, 810, 744. ^{1}H NMR (DMSO-d_6): δ 4.90 (s, 1H, CH), 7.10 (s 2H, NH_2), 7.07-7.12 (m, 5H, ArH), 7.56-7.66 (m, 4H, ArH), 7.94 (d, 1H, *J* = 8.4 Hz, ArH), 8.23 (d, 1H, *J* = 8.4 Hz, ArH) ppm. Anal. calcd. (%) for $C_{20}H_{14}N_2O$: C 80.52, H 4.73, N 9.39; found C 80.57, H 4.68, N 9.41.

2-Amino-4-(2-chlorophenyl)-3-cyano-7,8-benzochromene (5b): IR (KBr, ν_{max}, cm^{-1}): 3474, 3320, 2918, 2196, 1660, 1594, 1400, 1360, 1272, 1180, 1042, 806, 750. ^{1}H NMR (DMSO-d_6): δ 5.40 (s, 1H, CH), 7.02 (d, 1H, *J* = 8.4 Hz, ArH), 7.12 (s, 2H, NH_2), 7.21-7.30 (m, 4H, ArH), 7.54-7.66 (m, 3H, ArH), 7.86 (d, 1H, *J* = 8.4 Hz, ArH), 8.24 (d, 1H, *J* = 8.4 Hz, ArH) ppm. Anal. calcd. (%) for $C_{20}H_{13}ClN_2O$: C 72.18, H 3.94, N 8.42; found C 72.15, H 4.01, N 8.45.

2-Amino-4-(4-chlorophenyl)-3-cyano-7,8-benzochromene (5c): IR (KBr, ν_{max}, cm^{-1}): 3460, 3324, 2916, 2194, 1668, 1600, 1572, 1490, 1404, 1372, 1274, 1190, 1016, 806, 760. ^{1}H NMR (DMSO-d_6): δ 5.18 (s, 1H, CH), 7.02 (d, 1H, *J* = 8.4 Hz, ArH), 7.12 (s, 2H, NH_2), 7.28 (d, 2H, *J* = 8.4 Hz, ArH), 7.36 (d, 2H, *J* = 8.4 Hz, ArH), 7.54-7.66 (m, 3H, ArH), 7.87 (d, 1H, *J* = 8.4 Hz, ArH), 8.24 (d, 1H, *J* = 8.4 Hz, ArH) ppm. Anal. calcd. (%) for $C_{20}H_{13}ClN_2O$: C 72.18, H 3.94, N 8.42; found C 72.22, H 3.91, N 8.51.

2-Amino-4-(2,4-dichlorophenyl)-3-cyano-7,8-benzochromene (5d): IR (KBr, ν_{max}, cm^{-1}): 3458, 3330, 2918, 2192, 1664, 1603, 1490, 1374, 1284, 1190, 1048, 960, 810, 760. ^{1}H NMR (DMSO-d_6): δ 5.40 (s, 1H, CH), 7.02 (d, 1H, *J* = 8.4 Hz, ArH), 7.21 (s, 2H, NH_2), 7.28-7.32 (m, 2H, ArH), 7.38 (s, 1H, ArH), 7.56-7.68 (m, 3H, ArH), 7.88 (d, 1H, *J* = 8.4 Hz, ArH), 8.24 (d, 1H, *J* = 8.4 Hz, ArH) ppm. Anal. calcd. (%) for $C_{20}H_{12}Cl_2N_2O$: C 65.41, H 3.29, N 7.63; found C 65.43, H 3.24, N 7.67.

2-Amino-3-cyano-4-(4-nitrophenyl)-7,8-benzochromene (5e): IR (KBr, ν_{max}, cm^{-1}): 3460, 3334, 2196, 1664, 1600, 1576, 1500, 1346, 1270, 1194, 1100, 770. ^{1}H NMR (DMSO-d_6): δ 5.32 (s, 1H, CH), 7.05 (d, 1H, *J* = 8.4 Hz, ArH), 7.28 (s, 2H, NH_2), 7.50-7.72 (m, 3H, ArH), 7.52 (d, 2H, *J* = 8.4 Hz, ArH), 7.90 (d, 1H, *J* = 8.4 Hz, ArH), 8.15 (d, 2H, *J* = 8.4 Hz, ArH), 8.27 (d, 1H, *J* = 8.4 Hz, ArH) ppm. Anal. calcd. (%) for $C_{20}H_{13}N_3O_3$: C 69.97, H 3.79, N 12.24; found C 70.04, H 3.82, N 12.29.

2-Amino-3-cyano-4-(4-methylphenyl)-7,8-benzochromene (5f): IR (KBr, ν_{max}, cm^{-1}): 3416, 3292, 2915, 2190, 1664, 1580, 1420, 1384, 1276, 1024, 764. ^{1}H NMR (DMSO-d_6): δ 2.24 (s, 3H, CH_3), 4.86 (s, 1H, CH), 7.02 (d, 1H, *J* = 8.4 Hz, ArH), 7.06-7.08 (m, 4H, ArH), 7.12 (s, 2H, NH_2), 7.54-7.64 (m, 3H, ArH), 7.94 (d, 1H, ArH), 8.23 (d, 1H, *J* = 8.4 Hz, ArH) ppm. Anal. calcd. (%) for $C_{21}H_{16}N_2O$: C 80.75, H 5.16, N 8.97; found C 80.82, H 5.13, N 9.03.

2-Amino-3-cyano-4-(4-methoxyphenyl)-7,8-benzochromene (5g): IR (KBr, ν_{max}, cm^{-1}): 3414, 3316, 2920, 2186, 1658, 1504, 1402, 1374, 1260, 1170, 1024, 804, 760. ^{1}H NMR (DMSO-d_6): δ 3.72 (s, 3H, CH_3O), 4.87 (s, 1H, CH), 6.88-6.94 (m, 4H, ArH), 7.02 (d, 1H, *J* = 8.4 Hz, ArH), 7.12 (m, 2H, NH_2), 7.54-7.66 (m, 3H, ArH), 7.88 (d, 1H, *J* = 8.4 Hz, ArH), 8.24 (d, 1H, *J* = 8.4 Hz, ArH) ppm. Anal. calcd. (%) for $C_{21}H_{16}N_2O_2$: C 76.81, H 4.91, N 8.53; found C 76.78, H 4.96, N 8.61.

2-Amino-3-cyano-4-(3,4-methylenedioxyphenyl)-7,8-benzochromene (5h): IR (KBr, ν_{max}, cm^{-1}): 3428, 3318, 2914, 2194, 1670, 1576, 1490, 1404, 1380, 1256, 1190, 1040, 806, 770. ^{1}H NMR (DMSO-d_6): δ 4.84 (s, 1H, CH), 5.97 (s, 2H, OCH_2O), 6.74-6.84 (m, 3H, ArH), 7.02 (d, 1H, *J* = 8.4 Hz, ArH), 7.12 (s, 2H, NH_2), 7.55-7.65 (m, 3H, ArH), 7.88 (d, 1H, *J* = 8.4 Hz, ArH), 8.22 (d, 1H, *J* = 8.4 Hz, ArH) ppm. Anal. calcd. (%) for $C_{21}H_{14}N_2O_3$: C 73.68, H 4.12, N 8.18; found C 73.65, H 4.17, N 8.27.

2-Amino-3-cyano-4-phenyl-5,6-benzochromene (6i): IR (KBr, ν_{max}, cm^{-1}): 3432, 3330, 2185, 1640, 1590, 1518, 1412, 1236, 1186, 1028, 805, 746. ^{1}H NMR (DMSO-d_6): δ 5.21 (s, 1H, CH), 7.02 (s, 2H, NH_2), 7.10-7.20 (m, 3H, ArH), 7.22-7.26 (m, 2H, ArH), 7.32 (d, 1H, *J* = 8.4 Hz, ArH), 7.40-7.46 (m, 2H, ArH), 7.84 (d, 1H, *J* = 8.4 Hz, ArH), 7.90-7.92 (m, 2H, ArH) ppm. Anal. calcd. (%) for $C_{20}H_{14}N_2O$: C 80.52, H 4.73, N 9.39; found C 80.62, H 4.79, N 9.45.

2-Amino-4-(2-chlorophenyl)-3-cyano-5,6-benzochromene (6j): IR (KBr, ν_{max}, cm^{-1}): 3454, 3340, 2186, 1654, 1590, 1518, 1406, 1224, 1092, 1043, 806, 746. ^{1}H NMR (DMSO-d_6): δ 5.42 (s, 1H, CH), 7.02-7.10 (d, 1H, ArH), 7.12 (s, 2H, NH_2), 7.18-7.21 (m, 2H, ArH), 7.34 (d, 1H, *J* = 8.4 Hz, ArH), 7.40-7.50 (m, 3H, ArH), 7.64 (d, 1H, *J* = 8.4 Hz, ArH), 7.92 (d, 1H, *J* = 8.4 Hz, ArH), 7.98 (d, 1H, *J* = 8.4 Hz, ArH). Anal. calcd. (%) for $C_{20}H_{13}ClN_2O$: C 72.18, H 3.94, N 8.42; found C 72.25, H 3.96, N 8.48.

2-Amino-4-(4-chlorophenyl)-3-cyano-5,6-benzochromene (6k): IR (KBr, ν_{max}, cm^{-1}): 3426, 3324, 2194, 1640, 1586, 1408, 1246, 1220, 1100, 1022, 830, 812, 750. ^{1}H NMR (DMSO-d_6): δ 5.36 (s, 1H, CH), 7.08 (s, 2H, NH_2), 7.20 (d, 1H, *J* = 8.4 Hz, ArH), 7.24 (d, 1H, *J* = 8.4 Hz, ArH), 7.32-7.35 (m, 3H, ArH), 7.42-7.47 (m, 2H, ArH), 7.82 (d, 1H, *J* = 8.4 Hz, ArH), 7.90-7.98 (m, 2H, ArH) ppm. Anal. calcd. (%) for $C_{20}H_{13}ClN_2O$: C 72.18, H 3.94, N 8.42; found C 72.27, H 3.98, N 8.47.

2-Amino-4-(2,4-dichlorophenyl)-3-cyano-5,6-benzochromene (6l): IR (KBr, ν_{max}, cm^{-1}): 3462, 3324, 2198, 1660, 1590, 1516, 1466, 1408, 1238, 1190, 1086, 1046, 846, 806, 748. ^{1}H NMR (DMSO-d_6): d 5.62 (s, 1H, CH), 7.02 (d, 1H, *J* = 8.4 Hz, ArH), 7.12 (s, 2H, NH_2), 7.26-7.36 (m, 2H, ArH), 7.42-7.52 (m, 2H, ArH), 7.56 (d, 1H, *J* = 8.4 Hz, ArH), 7.64 (s, 1H, ArH), 7.92-7.98 (m, 2H, ArH) ppm. Anal. calcd. (%) for $C_{20}H_{12}Cl_2N_2O$: C 65.41, H 3.29, N 7.63; found C 65.49, H 3.27, N 7.68.

2-Amino-3-cyano-4-(4-methylphenyl)-5,6-benzochromene (6m): IR (KBr, ν_{max}, cm^{-1}): 3425, 3348, 2178, 1640, 1589, 1404, 1226, 1076, 830, 750. ^{1}H NMR (DMSO-d_6): δ 2.21 (s, 3H, CH_3), 5.25 (s, 1H, CH), 6.98 (s, 2H, NH_2), 7.06-7.08 (m, 4H, ArH), 7.30 (d, 1H, *J* = 8.4 Hz, ArH), 7.42-7.46 (m, 2H, ArH), 7.82 (d, 1H, *J* = 8.4 Hz, ArH), 7.91-7.94 (m, 2H, ArH) ppm. Anal. calcd. (%) for $C_{21}H_{16}N_2O$: C 80.75, H 5.16, N 8.97; found C 80.68, H 5.13, N 8.89.

2-Amino-3-cyano-4-(4-methoxyphenyl)-5,6-benzochromene (6n): IR (KBr, ν_{max}, cm^{-1}): 3426, 3350, 2192, 1654, 1590, 1516, 1390, 1232, 1184, 1026, 805, 758. ^{1}H NMR (DMSO-d_6): δ 3.68 (s, 3H, OCH_3), 5.24 (s, 1H, CH), 6.86 (d, 2H, *J* = 8.4 Hz, ArH), 6.94 (s, 2H, NH_2), 7.10 (d, 2H, *J* = 8.4 Hz, ArH), 7.32 (d, 1H, *J* = 8.4 Hz, ArH), 7.42-7.44 (m, 2H, ArH), 7.84 (d, 1H, *J* = 8.4 Hz, ArH), 7.90-7.94 (m, 2H, ArH) ppm. Anal. calcd. (%) for $C_{21}H_{16}N_2O_2$: C 76.81, H 4.91, N 8.54; found C 76.78, H 5.02, N 8.62.

2-Amino-3-cyano-4-(3,4-methylenedioxyphenyl)-5,6-benzochromene (6o): (KBr, ν_{max}, cm^{-1}): 3434, 3330, 2190, 1654, 1596, 1510, 1482, 1406, 1284, 1080, 1042, 926, 804, 750. ^{1}H NMR (DMSO-d_6): δ 5.24 (s, 1H, CH), 5.92 (s, 2H, OCH_2O), 6.76 (m, 2H, ArH), 6.82 (d, 1H, *J* = 8.4 Hz, ArH), 7.02 (s, 2H, NH_2), 7.32 (d, 1H, *J* = 8.4 Hz, ArH), 7.40-7.48 (m, 2H, ArH), 7.86-7.94 (m, 3H, ArH) ppm. Anal. calcd. (%) for $C_{21}H_{14}N_2O_3$: C 73.68, H 4.12, N 8.18; found C 73.71, H 4.17, N 8.26.

RESULTS AND DISCUSSION

The aromatic aldehyde (**1**), malononitrile (**2**) and naphthol (**3** or **4**) were ground by mortar and pestle catalyzed by KF-Al_2O_3 without solvent at room temperature for 20 min and was kept at room temperature in a desiccator. The reaction mixture was extracted with ethyl acetate. The majority solvent was evaporated under reduced pressure after and the remained solution was poured into H_2O and get the crude product. The crude product was purified by recrystallization by ethanol, the product **5** or **6** was obtained. The results are summarized in Table-1.

To study the generality of this process, several examples illustrating this method for the synthesis of benzochromene derivatives were studied. The effect of electron deficiency and the nature of substituents on the aromatic ring did not show strongly obvious effect in terms of yields under this

TABLE-1
SYNTHESIS OF BENZOCHROMENE DERIVATIVES CATALYZED BY KF-AL_2O_3 WITH GRINDING METHOD

Entry	Ar	Naphthol	Lay away time (h)	Product	Yield (%)*	m.p. (ºC)	
						Found	Reported[9]
1	C_6H_5 **1a**	1-Naphthol	18	**5a**	86	216-218	218-219
2	2-ClC_6H_4 **1b**	1-Naphthol	18	**5b**	89	248-250	251-253
3	4-ClC_6H_4 **1c**	1-Naphthol	16	**5c**	90	238-240	243-244
4	2,4-$Cl_2C_6H_3$ **1d**	1-Naphthol	16	**5d**	92	218-220	221-223
5	4-$NO_2C_6H_4$ **1e**	1-Naphthol	16	**5e**	94	236-238	239-241
6	4-$CH_3C_6H_4$ **1f**	1-Naphthol	22	**5f**	86	198-200	205-206
7	4-$CH_3OC_6H_4$ **1g**	1-Naphthol	22	**5g**	85	192-195	195-197
8	3,4-$OCH_2OC_6H_3$ **1h**	1-Naphthol	20	**5h**	87	248-250	252-254
9	C_6H_5 **1i**	2-Naphthol	24	**6i**	76	284-286	288-289
10	2-ClC_6H_4 **1j**	2-Naphthol	24	**6j**	83	270-272	273-274
11	4-ClC_6H_4 **1k**	2-Naphthol	24	**6k**	84	222-224	224-226
12	2,4-$Cl_2C_6H_3$ **1l**	2-Naphthol	24	**6l**	86	255-257	258-260
13	4-$CH_3C_6H_4$ **1m**	2-Naphthol	24	**6m**	74	266-268	270-272
14	4-$CH_3OC_6H_4$ **1n**	2-Naphthol	24	**6n**	73	196-198	200-202
15	3,4-$OCH_2OC_6H_3$ **1o**	2-Naphthol	24	**6o**	78	272-274	276-277

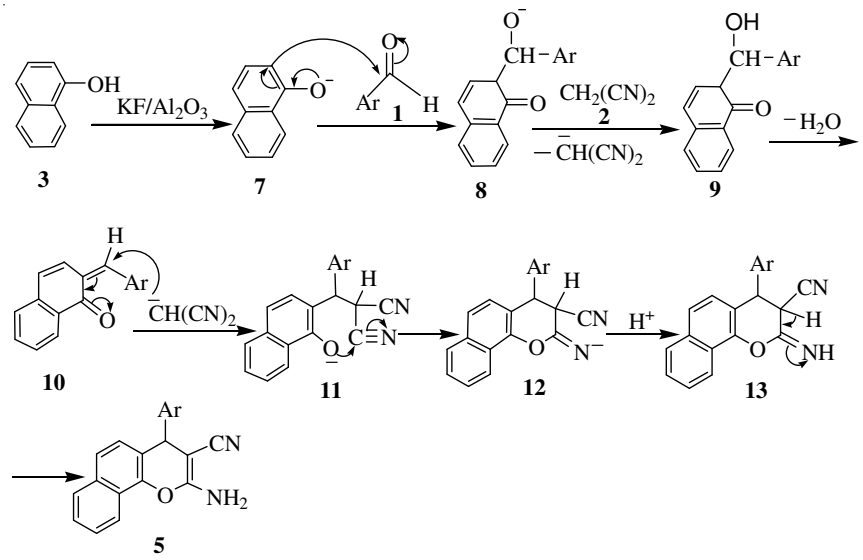
*Yields refer to isolated products.

reaction conditions. The three-component cyclocondensation reaction proceeded smoothly under this condition to give the corresponding product **5** or **6** in higher yields. Benzaldehyde and other aromatic aldehydes containing electron-withdrawing groups (such as nitro group, halide) or electron-donating groups (such as methyl, methoxy and methylenedioxy) were employed and reacted well to give the corresponding benzochromene derivatives in good to excellent yields.

The reaction of 1-naphthol or 2-naphthol with an aromatic aldehyde and malononitrile gave different experimental results. For example, 4-chlorobenzaldehyde reacted with malononitrile and 1-naphthol or 2-naphthol with grinding method to give the corresponding compounds **5c** (90 %) and **6k** (84 %), respectively. When 4-methoxybenzaldehyde was treated with malononitrile and 1-naphthol or 2-naphthol under the same conditions, the isolated yield of corresponding compounds were **5g** (85 %) and **6n** (73 %). It is concluded that 1-naphthol exhibits higher reactivity than 2-naphthol.

The possible following mechanism is proposed to account for the reaction[9]. Firstly aromatic aldehyde **1** was condensed with 1-naphthol **3** to afford the intermediate **10** (**1** + **3** → **7** → **8** → **9** → **10**). Then the intermediate **10** reacted with malononitrile **2** *via* Michael addition reaction to give addition product **11**. After that the intermediate **11** was cyclized by the nucleophilic attack of OH group on the cyano (CN) moiety and gave the intermediate

13 (**11** → **12** → **13**). Finally the expected product **5** was afforded by isomerization (**13** → **5**) (**Scheme-II**).



Scheme-II

In conclusion, a general and highly efficient procedure for the preparation of benzochromene derivatives catalyzed by KF-Al_2O_3 with grinding method is described. In addition, it is possible to apply the tenets of green chemistry to the generation of biologically interesting products with grinding method which are less expensive and less toxic than those with organic solvents. Moreover, the procedure offers several advantages including high yields, operational simplicity, cleaner reactions, minimal environmental impact which makes it a useful and attractive process for the synthesis of these compounds.

ACKNOWLEDGEMENTS

This project was supported by the National Natural Science Foundation of China, Educational Ministry of China, Educational Department of Hebei Province, Science and Technology Commission of Hebei Province.

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(*Received*: 24 May 2007; *Accepted*: 9 April 2008) AJC-6512