I.A.U
Karaj branch

Journal of
A p p l ied
C hemical
R esearch
jacr.kiau.ac.ir

Journal of Applied Chemical Research, 16, 4, 22-34 (2023)

Fe_3O_4@SiO_2/Kit-6 as a Magnetic Nano-Catalyst for the Synthesis of New Coumarin Fused Pyrrole Derivatives

Elham Sadr, Hossein Anaraki-Ardakani*, Soheil Sayyahi, Farzaneh Hosseini

Department of Chemistry, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

(Received 14 Feb. 2023; Final revised received 17 May 2023)

Abstract

A series of new coumarin fused pyrrole derivatives were successfully synthesized through a one-pot multi-component reaction between 4-aminocoumarin, aryl glyoxals, and amides (thioacetamide) in the presence of Fe_3O_4@SiO_2/Kit-6 in ethanol under reflux conditions. Further advantages to this synthesis include excellent yields, mild reaction conditions, atom economy, environment-friendly, magnetically reusable catalyst, and no need for chromatographic separations.

Keywords: Coumarin fused pyrrole, 4-aminocoumarin, Aryl glyoxals, Multi-component reaction.

**Corresponding author*: *Hossein Anaraki-Ardakani, Department of Chemistry, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran. Email: Hosseinanaraki@yahoo.com.*

Introduction

Coumarin and its derivatives are an important class of heterocyclic compounds, which constitute the key core of various natural products [1, 2]. The application of coumarin derivatives as bioactive molecules against different kinds of diseases has gained great interest from medicinal chemists. Coumarin derivatives demonstrate a wide spectrum of biological activities such as anticancer, anticoagulant, anti-HIV, antimalarial, and anti-inflammatory, and are usually associated with low toxicity [3-6].

Pyrrole derivatives are five-membered ring nitrogen-containing heterocyclic compounds and distributed structural units in a variety of natural and biologically important molecules such as porphyrins, bile pigments, coenzymes, and alkaloids [7,8].

Coumarin fused pyrrole derivatives comprise important classes of marine natural products, some of which display remarkable biological and pharmacological properties. The structure of some biologically important coumarin fused pyrrole derivatives are shown in Figure.1. For example compound A was also found to be efficient against tumor angiogenesis which is a key step for spreading out cancer cells [9].

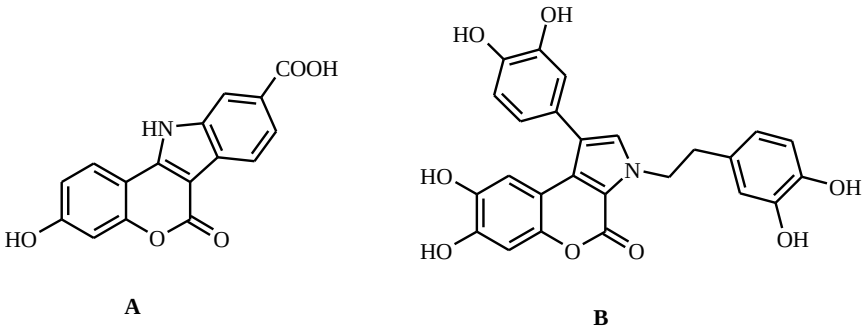
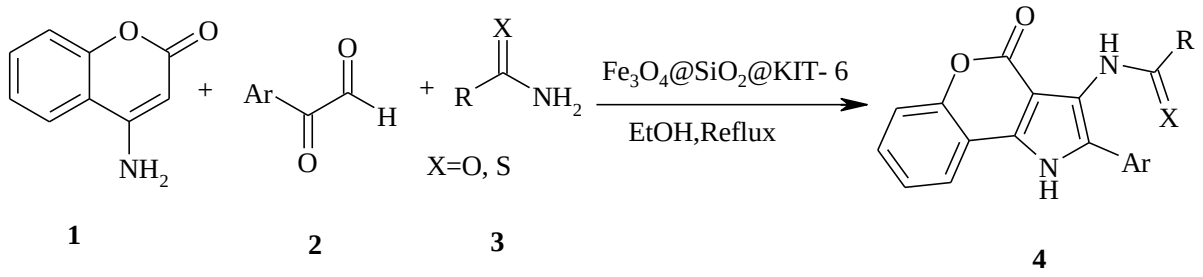


Figure 1. The structure of some biologically important coumarin fused pyrrole derivatives.

Modern synthetic design demands high efficiency in terms of minimization of synthetic steps together with maximization of complexity [10]. One of the ways to fulfill these goals is the development and use of multi-component reactions (MCRs) which consist of several simultaneous bond-forming reactions and allow the highly efficient synthesis of complex molecules starting from simple substrates in a one-pot manner [11-13]. The use of heterogeneous catalysts with recyclability and reusability potential adds value to the one-pot reactions involving MCRs [14]. Furthermore, the use of magnetic nanoparticles (MNPs) as support in heterogeneous catalysis is a growing field of research. In this area, MNPs appear as ultimate nano support due to their ease of recovery [15, 16]. Fe_3O_4 NPs for their strong magnetic properties, high chemical stability, abundance, effortless

preparation via co-precipitation and low toxicity is the most common MNPs that have been more extensively studied as the core magnetic support by researchers [17, 18]. It should be mentioned that pure Fe_3O_4 MNPs, with a high surface area to volume ratio, are highly chemically active and suffer from an inherent instability [19]. They are very sensitive to oxidation and tend to aggregate spontaneously when exposed to acids and aqueous solutions. To overcome the above mentioned limitations, the surface of MNPs must be covered by a protective agent such as silica, polymer, or carbon [20-23]. Among different supported MNPs, Kit-6 mesoporous silica-supported Fe_3O_4 MNPs (Fe_3O_4@SiO_2@Kit-6) has also emerged as powerful catalyst because it has preferable properties such as small dimensions, uniform porosity, high chemical stability, and easy magnetic separability [24–28].

Considering the above reports and in continuation of our research at developing green and eco-friendly multi-component reactions [29-30], herein we report Fe_3O_4@SiO_2@Kit-6 nanoparticles as a highly efficient and heterogeneous catalyst for the synthesis of coumarin-fused pyrrole derivatives by a three-component condensation of 4-aminocoumarin, aryl glyoxals, and amides (thioacetamide). (Scheme 1).



1 **2** **3** **4**

Scheme 1. Synthesis of coumarin-fused pyrrole derivatives using Fe_3O_4@SiO_2@Kit-6

Experimental

Melting points were determined with an electrothermal 9100 apparatus. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^1H and ^{13}C NMR spectra were recorded on Bruker DRX-400 Avance spectrometer at a solution in $CDCl_3$using TMS as an internal standard. The chemicals used in this work were purchased from fluka (Buchs, Switzerland) and were used without further purification. SEM was obtained using a Mira III.

Preparation of Fe_3O_4@SiO_2@Kit-6 nanoparticles

Fe_3O_4@SiO_2-Kit-6 was used as a catalyst in this work prepared by literature procedure, which has been developed by Shariati et al. [31]. The IR, XRD, SEM, and EDS images for the synthesized nanocomposite have been presented previously in the published article [24]. The SEM image shows that the nanocomposite has a uniform and spherical shape with diameters smaller than 55 nm (Figure 2).

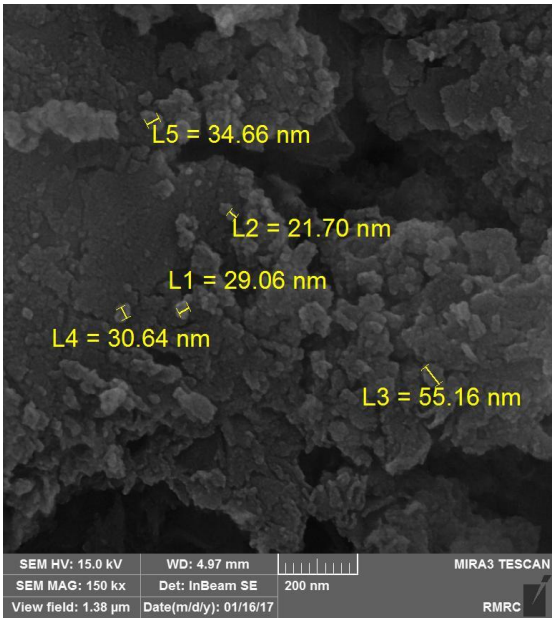


Figure 2. FESEM images of the Fe_3O_4@SiO_2-Kit-6.

General procedure

A mixture of aryl glyoxal (1 mmol), 4-aminocoumarin (1 mmol), amides (thioacetamide) (1 mmol), and Fe_3O_4@SiO_2-Kit-6 nanoparticle (0.05g) in 10 ml ethanol was stirred and heated in reflux condition for the appropriate amount of time (3–4 h)[32]. The reaction progress was monitored by TLC (EtOAc/hexane, 1:٢). The catalyst was collected with an external magnet, and the reaction mixture was then heated to obtain the crude product. After the purification process of the crude product by recrystallization from ethanol/acetone (v/v= 3:2), the corresponding compounds were obtained.

Results and discussion

Aryglyoxals **2** was prepared by the reaction between their corresponding acetophenone and SeO_2 according to the reported procedures [33].

Firstly, to optimize the reaction conditions, the model reaction was carried out by using 4-aminocoumarin, 4-chlorophenyl glyoxal, and acetamide under various reaction conditions, and the results are listed in Table 1.

Table 1. Optimization of the reaction conditions for the synthesis of *N*-(2-(4-chlorophenyl)-1,4-dihydro-4-oxochromeno[4,3-b]pyrrol-3-yl)acetamide (**4a**) [a].

Entry	Catalyst	Catalyst (g)	Time(h)	Yield[b] (%)
1	Non	-	4	trace
2	SiO_2 bulk	0.06	4	25
3	SiO_2 NPs	0.06	4	30
4	Fe_3O_4 NPs	0.06	4	25
5	Fe_3O_4@SiO_2	0.06	4	35
6	Fe_3O_4@SiO_2@Kit-6	0.06	4	60
7	Fe_3O_4@SiO_2@Kit-6	0.05	3	80

[a] Reaction conditions: 4-aminocoumarin (1.0 mmol), 4-chloro-phenyl glyoxal (1.0 mmol), acetamide (1.1 mmol), in ethanol under reflux condition.

We examined this reaction in the presence of various catalysts in hand including SiO_2, Fe_3O_4, Fe_3O_4@SiO_2, and Fe_3O_4@SiO_2@Kit-6 nanoparticles, (Table 1). It was shown that the Fe_3O_4@SiO_2@Kit-6 nanoparticle was the most efficient of all tested catalysts (Table 1, entry 7). However, no product was formed in the absence of the catalyst (Table 1, entry 1).

To improve the yield of the target product, the test reaction was carried out in presence of various solvents such as acetone, acetonitrile, water, tetrahydrofuran (THF), methanol, ethanol at reflux temperature, and the results are presented in Table 2. As can be seen from this table, in the presence of ethanol the products were obtained in high yields.

Table 2. Solvent effect on the reaction between 4-aminocoumarin (1eq), 4-chloro-phenyl glyoxal (1 eq) and acetamide (1 eq) catalyzed by Fe_3O_4@SiO_2@Kit-6.

Entr	Solvent	Temp(^{0}C)	Time(h)	Yield(%)
1	Solvent- free	100	4	50
2	H_2O	Reflux	4	55
3	Acetone	Reflux	5	50
4	Acetonitrile	Reflux	5	50
5	THF	Reflux	5	55
6	Methanol	Reflux	4	65
7	Ethanol	Reflux	3	80

Afterward, optimization of catalyst amounts was carried out in the model study by using different amounts of Fe_3O_4@SiO_2@Kit-6. A higher yield was obtained by increasing the amount of catalyst from 0.03 g to 0.07 g. However, a further increase of the molar amount of the catalyst from 0.05g to 0.07 did not significantly increase the yield of the product (Figure 3). Hence, the optimum concentration of Fe_3O_4@SiO_2@Kit-6 NPs was chosen 0.05g in the model reaction.

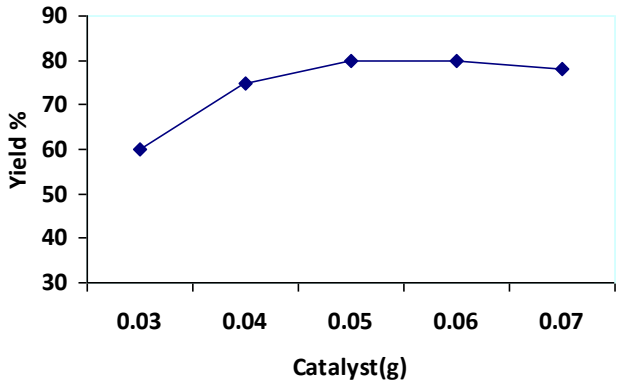


Figure 3. Influence of the amount of the catalyst on the model reaction.

To study the scope of the reaction, a series of aryl glyoxals and a series of amides (thioacetamide) were employed. The results are shown in Table 3. In all cases, the aromatic ring of the aryl glyoxal substituted with either electron-donating or electron-withdrawing groups underwent the reaction smoothly and gave the products good yields. It could also be concluded that the aromatic ring of the

aryl glyoxal bearing electron-withdrawing groups required a shorter time and gave higher yields (Table 3).

Table 3. The three-component reaction of 4-aminocoumarin, aryl glyoxals, and amides (thioacetamide) catalyzed by Fe_3O_4@SiO_2@Kit-6.

Entry	Ar	R	X	Time (h)	Yield(%)[a]	m.p. °C
4a	4-chlorophenyl	CH_3	O	3	80	248
4b	4-methylphenyl	CH_3	O	3.5	78	240
4c	2-naphthalenyl	CH_3	O	3.5	78	248
4d	4-methylpheny	CH_3	S	4	75	243
4e	2-naphthalenyl	CH_3	S	4	78	237
4f	2-naphthalenyl	C_6H_5	O	3.5	72	249
4g	2-thiophenyl	C_6H_5	O	3.3	75	244

[a] Isolated Yield

N-(2-(4-chlorophenyl)-1,4-dihydro-4-oxochromeno[4,3-b]pyrrol-3-yl)acetamide (**4a**)

Yellow powder, m.p. 248 °C; IR (KBr): 3410, 3220, 1680, 1650 cm^{-1}; ^1H NMR (250 MHz, d_6-DMSO): δ = 2.10(3H, s, CH_3), 7.23-8.44(9H, m, arom, and NH), 11.47 (1H, s, NH); ^{13}C NMR (62.90 MHz, d_6-DMSO): δ = 21.22, 102.83, 112.39, 118.20, 120.39, 121.99, 125.47, 126.16, 128.21, 129.33, 129.80, 130.39, 131.96, 140.56, 144.51, 157.80, 168.96. Anal. Calcd. for $C_{19}H_{13}ClN_2O_3$: C, 64.69; H, 3.71; N, 7.94 %. Found: C, 64.74; H, 3.79; N, 7.82; %.

N-(1,4-dihydro-4-oxo-2-p-tolylchromeno[4,3-b]pyrrol-3-yl)acetamide (**4b**)

Yellow powder, m.p. 240°C; IR (KBr): 3403, 3220, 1690, 1676 cm^{-1}; ^1H NMR (250 MHz, d_6-DMSO): δ = 2.07 (3H, s, CH_3), 2.30 (3H, s, CH_3), 7.23-9.02 (9H, m, arom and NH), 11.46 (1H, s, NH); ^{13}C NMR (62.90 MHz, d_6-DMSO): δ = 21.12, 22.25, 103.20, 112.20, 115.21, 118.22, 120.37,

123.00, 125.52, 126.12,126.98, 129.83, 130.54, 131.95, 136.56, 140.52, 152.55, 169.52. Anal. Calcd. for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.43%. Found: C, 72.41; H, 4.65; N, 8.55 %.

N-(1,4-dihydro-2-(naphthalen-3-yl)-4-oxochromeno[4,3-b]pyrrol-3-yl)acetamide (**4c**)

Yellow powder, m.p. 248 °C; IR (KBr): 3403, 3205, 1694, 1678 cm^{-1}; ^1H NMR (250 MHz, d_6-DMSO): δ = 2.04 (3H, s, CH_3), 7.39-9.29 (12H, m, arom, and NH), 11.23 (1H, s, NH); ^{13}C NMR (62.90 MHz, d_6-DMSO): δ = 22.25, 101.86, 110.06, 115.15, 118.30, 120.15, 123.15, 125.11, 125.59, 127.01, 128.02, 129.07, 129.42, 130.12, 132.75, 134.63, 141.72, 152.69, 158.86, 168.86. Anal. Calcd. for $C_{23}H_{16}N_2O_3$: C, 74.99; H, 4.38; N, 7.60%. Found: C, 74.82; H, 4.26; N, 7.78 %.

N-(1,4-dihydro-4-oxo-2-p-tolylchromeno[4,3-b]pyrrol-3-yl)ethanethioamide(**4d**)

Yellow powder, m.p. 243 °C; IR (KBr): 3412, 3180, 1681, 1664 cm^{-1}; ^1H NMR (250 MHz, d_6-DMSO): δ = 1.95(3H, s, CH_3), 2.26(3H, s, CH_3), 7.39-9.27(9H, m, arom, and NH), 11.21(1H, s, NH); ^{13}C NMR (62.90 MHz, d_6-DMSO): δ = 21.93, 23.53, 101.86, 115.12, 118.22, 120.13, 123.70, 125.09, 125.57, 126.99, 126.98, 128.00, 129.06, 132.71, 134.62, 141.69, 152.68, 192.44. Anal. Calcd. for $C_{20}H_{16}N_2O_2S$: C, 68.94; H, 4.63; N, 8.04; S, 9.20 %. Found: C, 68.81; H, 4.52; N, 8.32; S, 9.31 %.

N-(1,4-dihydro-2-(naphthalen-3-yl)-4-oxochromeno[4,3-b]pyrrol-3-yl)ethanethioamide (**4e**)

Yellow powder, m.p. 237 °C; IR (KBr): 3405, 3211, 1686, 1678 cm^{-1}; ^1H NMR (250 MHz, d_6-DMSO): δ = 2.29 (3H, s, CH_3), 7.22-9.02 (12H, m, arom, and NH), 11.01(1H, s, NH); ^{13}C NMR (62.90 MHz, d_6-DMSO): δ = 22.24, 101.82, 111.62, 115.23, 118.20, 120.36, 123.00,123.96, 125.48, 126.14, 128.96, 129.80, 130.52, 131.96, 136.54, 140.54,142,11 152.56, 158.94, 191.23. Anal. Calcd. for $C_{23}H_{16}N_2O_2S$: C, 71.85; H, 4.19; N, 7.29; S, 8.34%. Found: C, 71.74; H, 4.22; N, 7.40; S, 8.45%.

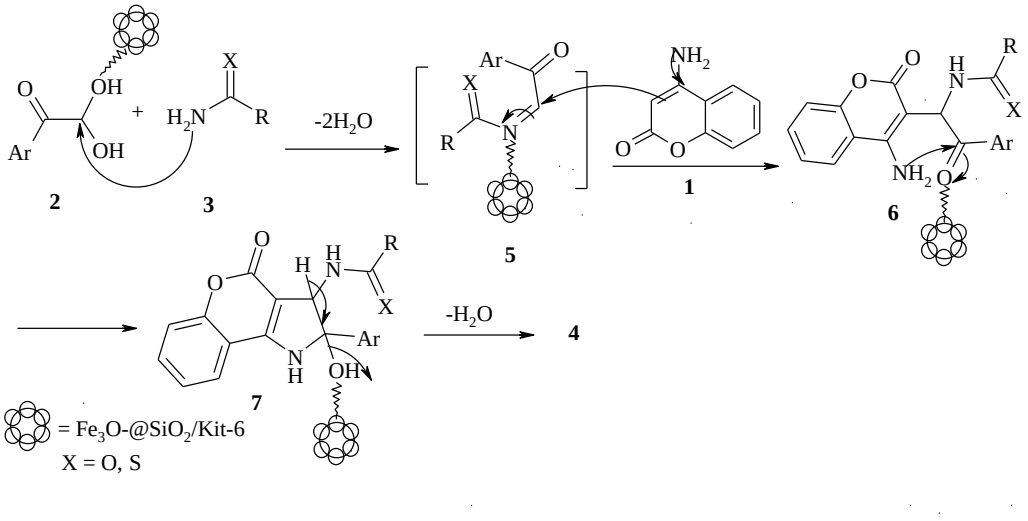
N-(1,4-dihydro-2-(naphthalen-3-yl)-4-oxochromeno[4,3-b]pyrrol-3-yl)benzamide (**4f**)

Yellow powder, m.p. 249 °C; IR (KBr): 3403, 3221, 1689, 1676 cm^{-1}; ^1H NMR (250 MHz, d_6-DMSO): δ = 7.14-9.29 (17H, m, arom and NH), 11.25 (1H, s, NH); ^{13}C NMR (62.90 MHz, d_6-DMSO): δ = 101.82, 112.72, 115.12, 118.29, 120.14, 123.13, 125.09, 125.60, 127.02, 128.02 129.06, 129.42, 130.17, 132.71, 134.60, 141.68, 152.66, 159.66, 175.12. Anal. Calcd. for $C_{28}H_{18}N_2O_3$: C, 78.13; H, 4.21; N, 6.51%. Found: C, 78.32; H, 4.42; N, 6.64%.

N-(1,4-dihydro-4-oxo-2-(thiophen-2-yl)chromeno[4,3-b]pyrrol-3-yl)benzamide (**4g**)

Yellow powder, m.p. 244 °C; IR (KBr): 3409, 3214, 1691, 1678 cm^{-1}; ^1H NMR (250 MHz, d_6-DMSO): δ = 7.10-9.29 (13H, m, arom, and NH), 11.21(1H, s, NH); ^{13}C NMR (62.90 MHz, d_6-DMSO): δ = 103.02, 115.03, 115.85, 117.47,118.26, 122.74, 122.91, 124.41, 124.69, 125.57, 128.33, 130.02, 132.25, 133.59, 139.78, 140.54, 152.63, 155.13, 157.05, 158.64, 163.09. Anal. Calcd. for $C_{22}H_{14}N_2O_3S$: C, 68.38; H, 3.65; N, 7.25; S, 8.30%. Found: C, 68.41; H, 3.73; N, 7.37; S, 8.42%.

A possible mechanism for the formation of the products **4a-g** is proposed in Scheme 2. Initially, aryl glyoxal **2** reacts with amides **3** in the presence of Fe_3O_4@SiO_2-Kit-6 as the catalyst to provide corresponding imine **5**. The next attack of 4-aminocoumarin **1** to imine **5** provides intermediate **6**, which undergoes intermolecular cyclization to afford intermediate **7** that subsequently loses water to produce final product **4**.



Scheme 2. Suggested pathway for the formation of compounds **4a-g**

The reusability of the catalyst was tested in the synthesis of coumarin-fused pyrrole derivatives, as shown in Figure 4. The catalyst was recovered after each run, washed with ethanol, dried in an oven at 90 ºC for 25 min before use, and tested for its activity in the subsequent run. The catalyst was tested for 3 runs. It was seen that the catalyst displayed very good reusability (Figure 4).

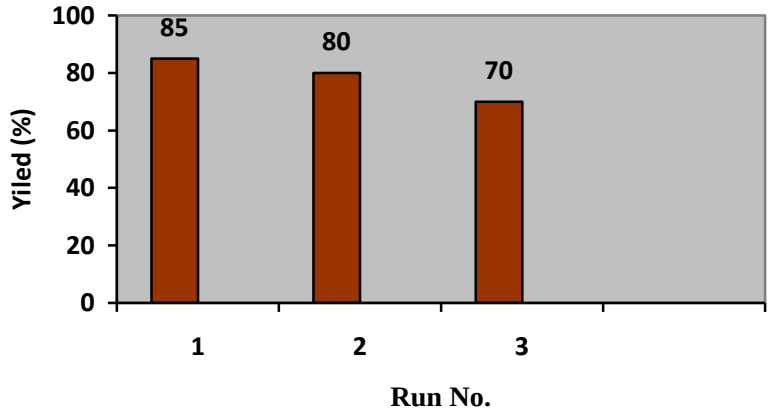


Figure 4. Catalyst recycling experiment

Conclusions

In summary, we have tried to develop an efficient procedure for the synthesis of new coumarin fused pyrrole derivatives in high yields *via* a one-pot three-component reaction between 4-aminocoumarin, aryl glyoxals and amides (thioacetamide) in the presence of a catalytic amount of Fe_3O_4@SiO_2-Kit-6 nanocomposite in ethanol. The most important advantage of this protocol is that the materials used for this protocol are readily accessible. Furthermore, this method offers several advantages including a high yield of products, recyclability of the catalyst and the products being purified without resorting to chromatography.

References

1. Murray R, McKinnie S, Moore B, George Meroterpenoid natural products from *Streptomyces* bacteria – the evolution of chemoenzymatic syntheses. Nat Prod Rep. 2020;,37: 1334-1366

2. Lacy A, O'kennedy R. Studies on coumarins and coumarin-related compounds to determine their therapeutic role in the treatment of cancer. Current pharmaceutical design. 2004;10(30):3797-811.

3. Patil AD, Freyer AJ, Eggleston DS, Haltiwanger RC, Bean MF, Taylor PB, et al. The inophyllums, novel inhibitors of HIV-1 reverse transcriptase isolated from the Malaysian tree, Calophyllum inophyllum Linn. Journal of medicinal chemistry. 1993;36(26):4131-8.

4. Guilet D, Hélesbeux J-J, Séraphin D, Sévenet T, Richomme P, Bruneton J. Novel Cytotoxic 4-Phenylfuranocoumarins from Calophyllum d ispar. Journal of natural products. 2001;64(5):563-8.

5. Emami S, Dadashpour S. Current developments of coumarin-based anti-cancer agents in medicinal chemistry. European Journal of Medicinal Chemistry. 2015;102:611-30.

6. Keri RS, Sasidhar B, Nagaraja BM, Santos MA. Recent progress in the drug development of coumarin derivatives as potent antituberculosis agents. European journal of medicinal chemistry. 2015;100:257-69.

7. Jones G, Gilow HM, Low J. Regioselective photoaddition of pyrroles and aliphatic carbonyl compounds. A new synthesis of 3 (4)-substituted pyrroles. The Journal of Organic Chemistry. 1979;44(16):2949-51.

8. DL B. Boyce CW. Labroli MA. Sehon CA. Jin Q. J Am Chem Soc. 1999;121:54.

9. Yang X, Jing L, Chen Z. An efficient method for one-pot synthesis of 3-alkoxy-substituted chromeno [4, 3-b] pyrrol-4 (1 H)-one derivatives. Chemistry of Heterocyclic Compounds. 2018;54:1065-9.

10. Trost BM. The atom economy—a search for synthetic efficiency. Science. 1991;254(5037):1471-7.

11. Bienayme H, Hulme C, Oddon G, Schmidt P. Chem. sEur. J. 2000;6:3321.

12. Heidarpour M, Kiani M, Anaraki-Ardakani H, Rezaei P, Ghaleh SP, Ahmadi R, et al. New magnetic nanocomposite Fe_3O_4@ Saponin/Cu (II) as an effective recyclable catalyst for the synthesis of aminoalkylnaphthols via Betti reaction. Steroids. 2022:109170.

13. Orru RV, de Greef M. Recent advances in solution-phase multicomponent methodology for the synthesis of heterocyclic compounds. Synthesis. 2003;2003(10):1471-99.

14. Climent MJ, Corma A, Iborra S. Homogeneous and heterogeneous catalysts for multicomponent reactions. RSC advances. 2012;2(1):16-58.

15. Astruc D, Lu F, Aranzaes JR. Nanoparticles as recyclable catalysts: the frontier between homogeneous and heterogeneous catalysis. Angewandte Chemie International Edition. 2005;44(48):7852-72.

16. Lim CW, Lee IS. Magnetically recyclable nanocatalyst systems for the organic reactions. Nano Today. 2010;5(5):412-34.

17. Zheng X, Luo S, Zhang L, Cheng J-P. Magnetic nanoparticle supported ionic liquid catalysts for CO 2 cycloaddition reactions. Green Chemistry. 2009;11(4):455-8.

18. Ma C, Shao H, Zhan S, Hou P, Zhang X, Chai Y, et al. Bi-phase dispersible Fe_3O_4@ Au core–shell multifunctional nanoparticles: Synthesis, characterization and properties. Composite Interfaces. 2019;26(6):537-49.

19. Rossi LM, Costa NJ, Silva FP, Wojcieszak R. Magnetic nanomaterials in catalysis: advanced catalysts for magnetic separation and beyond. Green Chemistry. 2014;16(6):2906-33.

20. Koli RR, Phadatare MR, Sinha BB, Sakate DM, Ghule AV, Ghodake GS, et al. Gram bean extract-mediated synthesis of Fe3O4 nanoparticles for tuning the magneto-structural properties that

influence the hyperthermia performance. Journal of the Taiwan Institute of Chemical Engineers. 2019;95:357-68.

21. Gill CS, Price BA, Jones CW. Sulfonic acid-functionalized silica-coated magnetic nanoparticle catalysts. Journal of Catalysis. 2007;251(1):145-52.

22. Samiei Z, Soleimani-Amiri S, Azizi Z. Fe $_3$ O $_4$@ C@ OSO $_3$ H as an efficient, recyclable magnetic nanocatalyst in Pechmann condensation: green synthesis, characterization, and theoretical study. Molecular Diversity. 2021;25:67-86.

23. Zeinali S, Fekri LZ, Nikpassand M, Varma RS. Greener syntheses of coumarin derivatives using magnetic nanocatalysts: recent advances. Topics in Current Chemistry. 2023;381(1):1.

24. Nikpassand M, Fekri LZ, Sahrapeima S, Shariati S. Synthesis of bis coumarinyl methanes using Fe3O4@ SiO2@ KIT-6 as an efficient and reusable catalyst. Letters in Organic Chemistry. 2016;13(8):578-84.

25. Fekri LZ, Maleki R. KIT-6 Mesoporous silica-coated magnetite nanoparticles: A highly efficient and easily reusable catalyst for the synthesis of benzo [d] imidazole derivatives. Journal of Heterocyclic Chemistry. 2017;54(2):1167-71.

26. Nikpassand M, Fekri LZ, Nabatzadeh M. Fe3O4@ SiO2@ KIT-6 as an Efficient and Reusable Catalyst for the Synthesis of Novel Derivatives of 3, 3'-((Aryl-1-phenyl-1H-pyrazol-4-yl) methylene) bis (1H-indole). Combinatorial Chemistry & High Throughput Screening. 2017;20(6):533-8.

27. Nikpassand M, Fekri LZ, Sanagou S. Green synthesis of 2-hydrazonyl-4-phenylthiazoles using KIT-6 mesoporous silica coated magnetite nanoparticles. Dyes and Pigments. 2017;136:140-4.

28. Abdolmohammadi S, Shariati S, Fard NE, Samani A. Aqueous-Mediated green synthesis of novel spiro [indole-quinazoline] derivatives using kit-6 mesoporous silica coated Fe3O4 nanoparticles as catalyst. Journal of Heterocyclic Chemistry. 2020;57(7):2729-37.

29. Heidarpour M, Anaraki-Ardakani H, Hasanzadeh N, Rayatzadeh A. Efficient synthesis of β-aminoketones catalyzed by Fe_3O_4@ quillaja sapogenin/Ni (II) as a novel magnetic nano-catalyst. Applied Organometallic Chemistry. 2020;34(10):e5834.

30. Kiani M, Anaraki-Ardakani H, Hasanzadeh N, Rayatzadeh A. Fe_3O_4@ saponin/Cd: a novel magnetic nano-catalyst for the synthesis of β-aminoketone derivatives. Journal of the Iranian Chemical Society. 2020;17(9):2243-56.

31. Khabazipour M, Shariati S, Safa F. SBA and KIT-6 mesoporous silica magnetite nanoparticles: Synthesis and characterization. Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry. 2016;46(5):759-65.

32. Saha M, Pradhan K, Das AR. Facile and eco-friendly synthesis of chromeno [4, 3-b] pyrrol-4 (1H)-one derivatives applying magnetically recoverable nano crystalline $CuFe_2O_4$ involving a domino three-component reaction in aqueous media. RSC advances. 2016;6(60):55033-8.

33. Khalili B, Jajarmi P, Eftekhari-Sis B, Hashemi MM. Novel one-pot, three-component synthesis of new 2-alkyl-5-aryl-(1 H)-pyrrole-4-ol in water. The Journal of organic chemistry. 2008;73(6):2090-5.