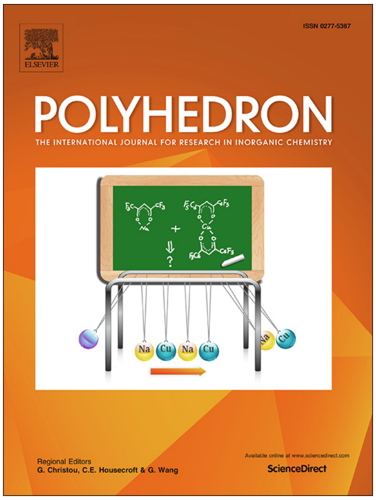

Fe_3O_4@SiO_2@$(BuSO_3H)_3$ Synthesis as a new efficient nanocatalyst and its application in the synthesis of heterocyclic [3.3.3] propellane derivatives

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Fe_3O_4@SiO_2@$(BuSO_3H)_3$ Synthesis as a new efficient nanocatalyst and its application in the synthesis of heterocyclic [3.3.3] propellane derivatives

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Abstract

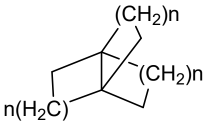
The acidic agent ($BuSO_3H$) coated on core-shell Fe_3O_4 nanomagnetic particles was successfully designed and synthesized. It was characterized and confirmed by different techniques such as FT-IR spectroscopy, scanning electron microscopy vibrating sample magnetometer, X-Ray diffraction, energy dispersive X-ray and Thermogravimetric analysis. The application of Fe_3O_4@SiO_2@$(BuSO_3H)_3$ as an efficient catalyst in the synthesis of propellane derivatives was evaluated by the domino reaction of acenaphthenequinone, malono derivatives, primary amines and β-ketoester derivatives under the solvent-free condition at 60 ˚C.

Keywords: Magnetic nanocatalyst, Fe_3O_4@SiO_2@$(BuSO_3H)_3$, [3.3.3] Propellane, Domino reaction, Multicomponent reaction

1. Introduction

In recent years, the use of green chemistry rules including reduction of by-product and waste, reducing energy utilization, application of solvent-free conditions and the use of non-toxic stating materials is more important [1-3]. The application of hybrid organic and inorganic materials as heterogeneous catalysts in chemistry is one of the advantages of green chemistry. Recently, among various heterogeneous catalysts, the modification of Fe_3O_4 nanoparticles with organic and inorganic compounds attracted very attention [4-6]. Fe_3O_4 nanoparticles have special properties including easy synthesis, low cost, nontoxicity, high stability, easy separation by external magnetic and high surface-area [7,8]. Fe_3O_4 nanoparticles were applied in different fields such as sensor, drug delivery, and as a catalyst in the multicomponent reaction [9-11]. So, we decided to use the Fe_3O_4 nanoparticle as a magnetic core, and then it was modified by organic and inorganic reagents to creat the $Fe_3O_4@SiO_2@(BuSO_3H)_3$ as an efficient nanomagnetic catalyst.

In the 1930s during studies on the Diels–Alder reaction, the first propellanes were prepared [12-14]. Among the organic compounds, propellane compounds have tricyclic structure whit a C-C band in common in three rings (Scheme 1) [15]. According to scheme 1, when (n) in the structure is equal to one, three-membered rings under angular pressure are formed [16]. Propellanes, due to their presence in the different structure including natural and unnatural products, medicinal compounds and polymers were attracted many attentions in nowadays [17].



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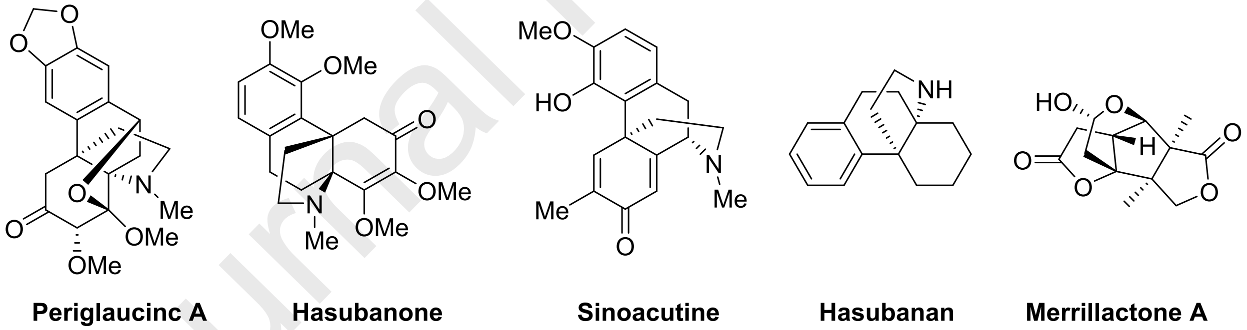
Scheme 1. The general structure of propellane.

As shown in Scheme 2, propellane derivatives exist in a great part of the natural compound structures such as Periglaucinc A [18], Hasubanone alkaloids [19], Sinoacutine [20], Hasubanan[21] and Merrilactone A [22]



Periglaucinc A **Hasubanone** **Sinoacutine** **Hasubanan** **Merrillactone A**

Scheme 2. Typical natural products with propellane skeleton.

Therefore, according to the green chemistry roles, multi-component reactions, are a useful method in medicinally, pharmacologically and chemistry science [23-24]. Subsequently, they were applied in the synthesis of biological and pharmacological compounds because this method is green and eco-friendly [25-27]. Recently, the synthesis of propellane compounds became very interesting for many researchers [18, 28-31]. Therefore, according to our previous research in the context of multicomponent reactions [32-39], in this work, it is reported the efficient, green, eco-friendly and simple method for synthesis of [3.3.3] propellane derivatives via domino reaction of acenaphthoquinone, malononitrile, β-keto ester and anilines under solvent condition in the presence of $Fe_3O_4@SiO_2@(BuSO_3H)_3$ at 60 ˚C. The advantages of this work are including green conditions, the use of available materials, the high yield products, the low reaction times, the simple purification, the easy separation of catalyst from mixture reaction by an external magnet and the reusability of catalyst.

2. Experimental

All material and methods were introduced in the supporting information. Nanomagnetic particles Fe_3O_4, $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2Pr\text{-}NH(CH_2)_2NH_2$ were obtained according to the reported articles in literature [40- 42].

2.1. *Synthesis of $Fe_3O_4@SiO_2@(BuSO_3H)_3$*

For the synthesis of nanomagnetic catalyst, the mixture of $Fe_3O_4@SiO_2(CH_2)_3NH(CH_2)_2NH_2$ (1 gr) and dry toluene (25 ml) was sonicated for 1 h, and then 1,4-butane sultone (5 ml) was added to this colloidal solution. The reaction mixture was refluxed for 36 h, and then, the nanomagnetic catalyst separated by an external magnet, and washed with dichloromethane, and dried at room temperature.

2.2. *General procedure for the synthesis of [3.3.3] propellane*

For the synthesis of [3,3,3] propylene, initially, acenaphtoqinone (1.0 mmol, 0.16 gr) and malononitrile (1 mmol, 0.66 gr) in the presence *of* $Fe_3O_4@SiO_2@(BuSO_3H)_3$ (0.01 gr) under solvent-free conditions were stirred at 60 ˚C for ten minutes. Afterward, 4-Cl-aniline (1 mmol, 0.12 gr) and *β*-ketoester (1 mmol, 0.12 ml) were added the mixture reaction and the reaction continued under solvent-free conditions at 60 ˚C. The progression of the reaction was followed by TLC using ethyl acetate: hexane (8: 2) ratio as solvent. After completion of the reaction, the reaction mixture was dissolved in hot ethanol, and then the nano magnetic catalyst separated using an external magnet from the aqueous solution, and then, The pure sediment of the product was obtained. The obtained products were characterized using melting point and FT-IR spectra and the new compounds were charecterizied by the ^1H and ^{13}C NMR spectra.

1. Ethyl (6bR,9aR)-11-amino- 7-(4-bromophenyl)-10 -cyano-8-methyl-7H-6b,9a-(epoxyetheno) acenaphtho [1,2-b]pyrrole-9-carboxylate (6g)

White solid; **m.p.** 216-218 ˚C; **IR (KBr, ν, cm^{-1}):** 3467, 3316, 3255, 3195, 3056, 2978, 2931, 2196, 1680, 1658, 1598, 1489, 1423, 1381, 1323, 1252, 1236, 1198, 1130, 1092, 1069, 1010, 954, 830 and 809. **^{1}H NMR (500 MHz, DMSO-d$_6$): δ (ppm)=** 1.44-146 (t, 3H, Me), 2.09 (s, 3H, Me), 4.22-4.37 (m, 2H, CH_2), 6.52-6.53 (d, 1 H, Ar), 7.26-7.27 (d, 1H, Ar), 7.30 (s, 2H, NH_2), 7.39-7.42 (t, 1H, Ar), 7.64-7.66 (t, 1H, Ar), 7.71-7.73 (d, 2H, Ar), 7.78-7.79 (d, 1H, Ar), 7.84-7.86 (t, 2H, Ar).). **^{13}C NMR (125 MHz, DMSO-d$_6$): δ (ppm)=** 13.96, 14.93, 59.43, 59.49, 70.88, 106.38, 114.91, 119.16, 119.70, 120.51, 121.66, 124.10, 126.71, 128.32, 129.47, 131.13, 132.20, 133.00, 136.24, 136.71, 136.80, 144.49, 157.39, 166.22, 167.88.

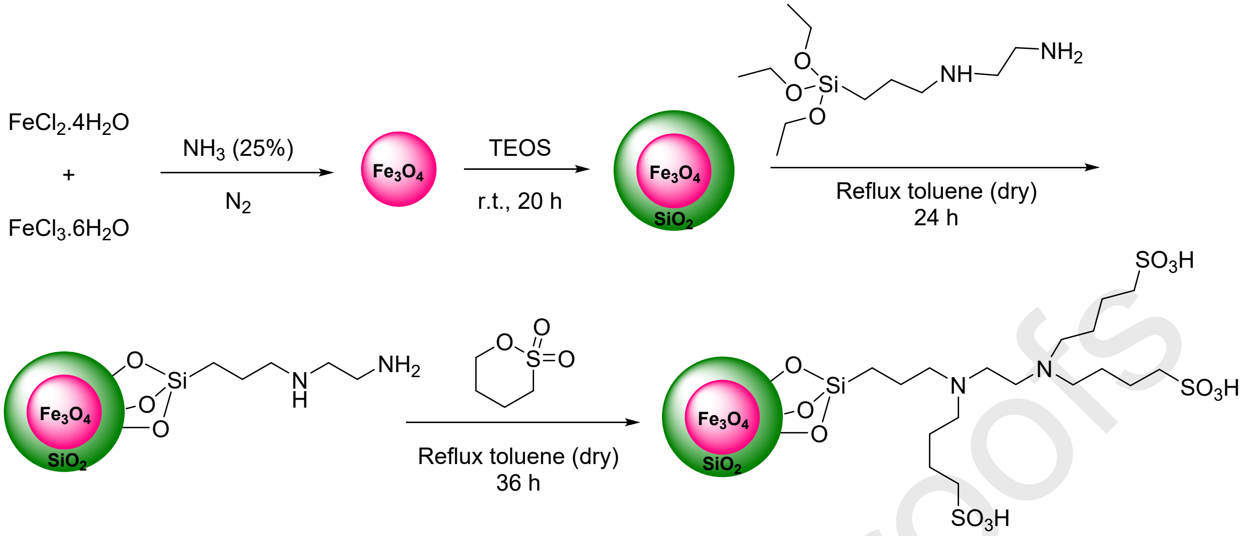
2. Ethyl (6bR,9aR)-11- amino -10- cyano-8-methyl-7- phenyl- 7H-6b,9a- (epoxyetheno) acenaphtho [1,2-b] pyrrole-9-carboxylate (6h)

White solid; **m.p.** 202-204 ˚C; **IR (KBr, ν, cm^{-1}):** 3420, 3306, 3192, 3062, 2978, 2931, 2182, 1657, 1634, 1592, 1487, 1494, 1456, 1423, 1399, 1382, 1367, 1339, 1260, 1233, 1199, 1146, 1122, 1087, 1066, 1007, 950, 928, 885, 728 and 757. **^{1}H NMR (500 MHz, DMSO-d$_6$): δ (ppm)=** 1.43-1.46 (t, 3H, Me), 2.09 (s, 3H, Me), 4.22-4.37 (m, 2H, CH_2), 6.39-6.40 (d, 1H, Ar), 7.27 (s, 2H, NH_2), 7.34-7.37 (t, 1H, Ar), 7.47-7.54 (m, 3H, Ar), 7.62-7.66 (t, 1 H, Ar), 7.78-7.80 (d, 1H, Ar), 7.83-7.87 (m, 2H, Ar).). **^{13}C NMR (125 MHz, DMSO-d$_6$): δ (ppm)=** 14.02, 14.06, 59.39, 59.48, 70.75, 106.82, 115.16, 119.26, 119.66, 120.47, 124.02, 126.58, 128.07, 128.77, 129.22, 129.43, 130.00, 132.18, 136.76, 136.84, 136.97, 144.70, 157.80, 166.29, 167.94.

3. Results and discussion

3.1. Preparation of catalyst

Nanomagnetic particles Fe_3O_4 were obtained from the reaction of $FeCl_3 \cdot 6H_2O$, $FeCl_2 . 4H_2O$ and ammonia solution (25%) in the water at in 100 °C under nitrogen atmosphere. After core-shell structure of nanomagnetic particles were synthesized by tetraethyl orthosilicate in room temperature. Afterward, the core-shell structure ($Fe_3O_4@SiO_2$) was modified by N-(3-triethoxysilylpropyl)ethylenediamine. In the next step, the amine groups on the surface of magnetic nanoparticles were functionalized by 1,4-butane saltone and finally, the nanocatalyst was prepared (Scheme 3).



Scheme 3. Synthesis of $Fe_3O_4@SiO_2@(BuSO_3H)_3$**.**

3.2. Characterization of the catalyst

3.1.1. FT-IR analysis

The FT-IR spectra of the Fe_3O_4, $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2@PrNH(CH_2)_2NH_2$ and $Fe_3O_4@SiO_2@(BuSO_3H)_3$ were shown in Figure 1. All bands at around 574 cm^{-1} are ascribed to Fe-O vibrations. The weak bands at around 800 cm^{-1} related to the SiO_4 groups. The strong absorbent bands around the area 1080 cm^{-1}, were attributed to the Si-O-Si groups. The absorbent peak in the 2931 cm^{-1} was indicated the C–H stretching vibrations of alkyl groups. The broad peak in the 3442 cm^{-1} was related to the various groups including SO_3H and OH agent in the silica shell.

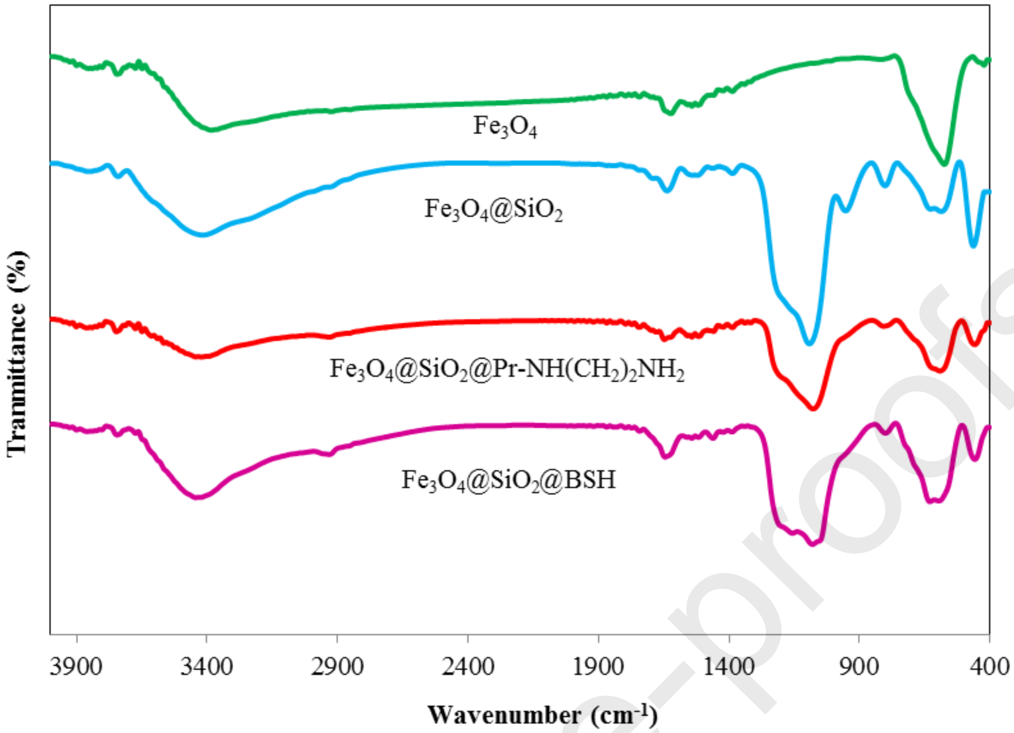


Fig. 1. FT-IR spectra of Fe_3O_4 (a), $Fe_3O_4@SiO_2$ (b), $Fe_3O_4@SiO_2@Pr\text{-}NH(CH_2)_2NH_2$ (c) and $Fe_3O_4@SiO_2@(BuSO_3H)_3$

3.1.2. XRD analysis

As shown in Figure 2, the X-ray diffraction (XRD) pattern of Fe_3O_4 (a) and $Fe_3O_4@SiO_2@BSH$ (b) were displayed. The various peaks at $2\theta = 18^\circ$, 30.12°, 35.56°, 43.26°, 53.56°, 57.24°, 62.8°, and 74.34°, correspond to the different planes including (111), (220), (311), (400), (422), (511), (440) and (622). According to Figure 2, both nanoparticles including Fe_3O_4 and $Fe_3O_4@SiO_2@(BuSO_3H)_3$ have the same pattern which demonstrates the successful nanoparticles synthesis.

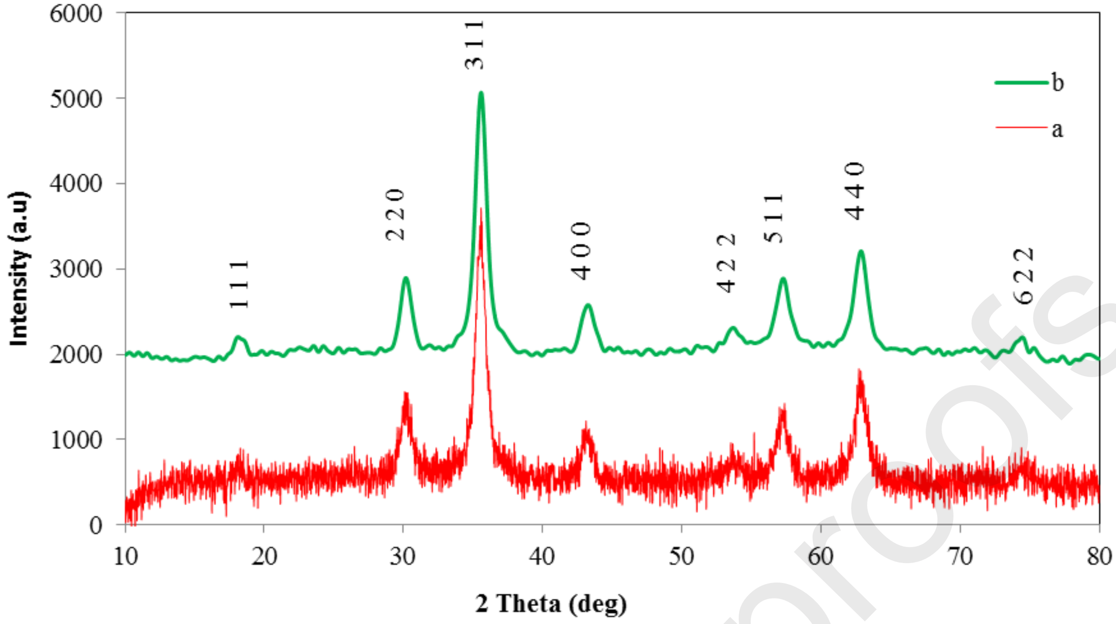
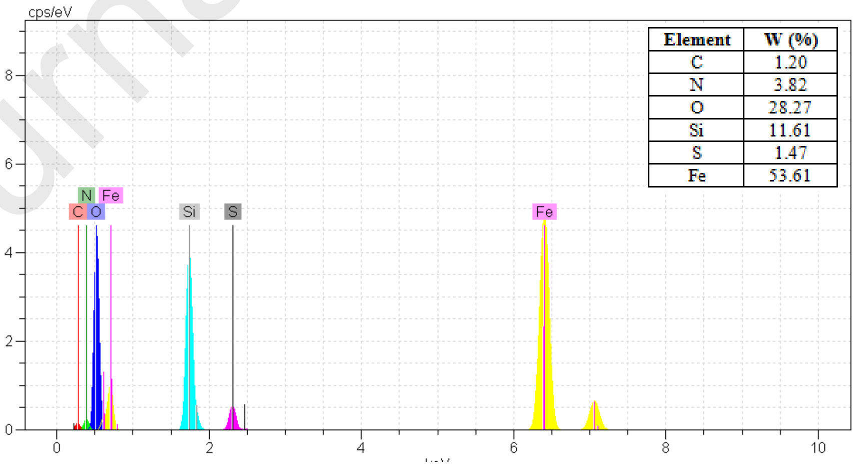


Fig. 2. XRD pattern of Fe_3O_4 and Fe_3O_4@SiO_2@$(BuSO_3H)_3$.

3.1.3. Energy Dispersive X-ray Spectroscopy (EDX) analysis

The EDX spectrum of the Fe_3O_4@SiO_2@$(BuSO_3H)_3$ showed in Figure 3. The presence of different elements, including C, N, O, Si, S, Fe was demonstrated in the Fe_3O_4@SiO_2@$(BuSO_3H)_3$ nanocatalyst. According to Figure 4, the SEM image of the Fe_3O_4@SiO_2@$(BuSO_3H)_3$ nanoparticles are spherical with average size 60-80 nm.



Element	W (%)
C	1.20
N	3.82
O	28.27
Si	11.61
S	1.47
Fe	53.61

Fig. 3. EDX spectrum of Fe_3O_4@SiO_2@BSH.

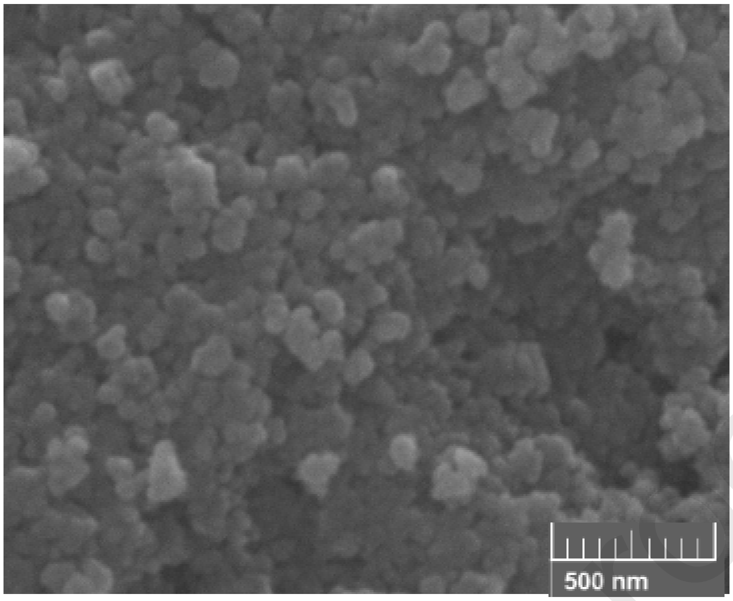


Fig. 4. SEM image of $Fe_3O_4@SiO_2@(BuSO_3H)_3$.

3.1.4. Thermogravimetric analysis (TGA)

The thermogravimetric analysis was investigated for $Fe_3O_4@SiO_2@Pr\text{-}NH(CH_2)_2NH_2$ and $Fe_3O_4@SiO_2@(BuSO_3H)_3$ catalyst at the room temperature to 1000 ˚C under air atmosphere. As shown in Figure 4, the weight loss of 7 % and 9 % in the range 20-200 ˚C related to the loss of the adsorbed water on the surface of $Fe_3O_4@SiO_2@Pr\text{-}NH(CH_2)_2NH_2$ and $Fe_3O_4@SiO_2@(BuSO_3H)_3$ respectively. According to Figure 5, with the increase of the hydrophilic group (SO_3H) on the surface of the nanocatalyst, the surface water percentage was increased. Also, the weight loss of organic part in the nanoparticles in the range of 200-550 °C is around 8.5 % and 17.5 % for $Fe_3O_4@SiO_2@Pr\text{-}NH(CH_2)_2NH_2$ and $Fe_3O_4@SiO_2@(BuSO_3H)_3$. The amount of the grafted organic compound was evaluated to be about 0.60 mmol g^{-1}.

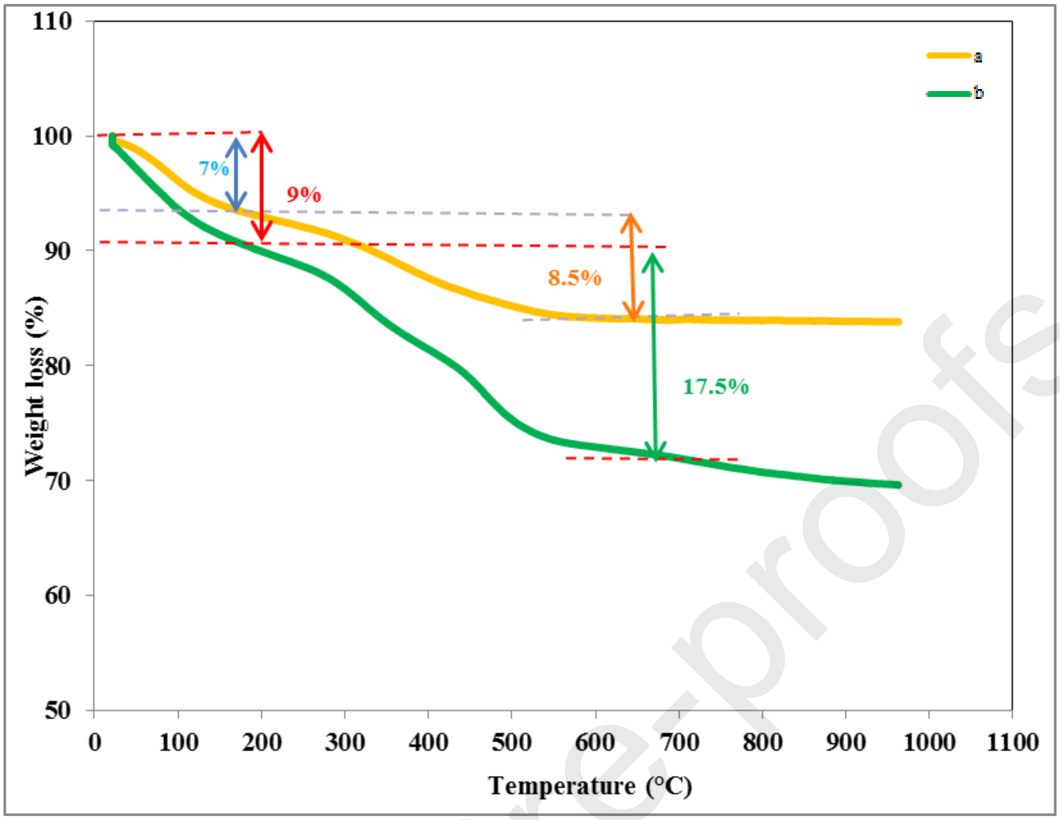


Fig. 5. Thermogravimetric analysis of a) $Fe_3O_4@SiO_2@Pr\text{-}NH(CH_2)_2NH_2$ and b) $Fe_3O_4@SiO_2@(BuSO_3H)_3$

3.1.5. Magnetic properties of nanomagnetic particles (VSM)

The magnetic properties of nanoparticles including Fe_3O_4, $Fe_3O_4@SiO_2$, and $Fe_3O_4@SiO_2@(BuSO_3H)_3$ were investigated by vibrating sample magnetometer (VSM) at room temperature. As shown in Figure 6, the magnetization behavior of Fe_3O_4, $Fe_3O_4@SiO_2$, and $Fe_3O_4@SiO_2@(BuSO_3H)_3$ is respectively equal to 60 emu/gr, 48 emu/gr, and 33 emu/gr.

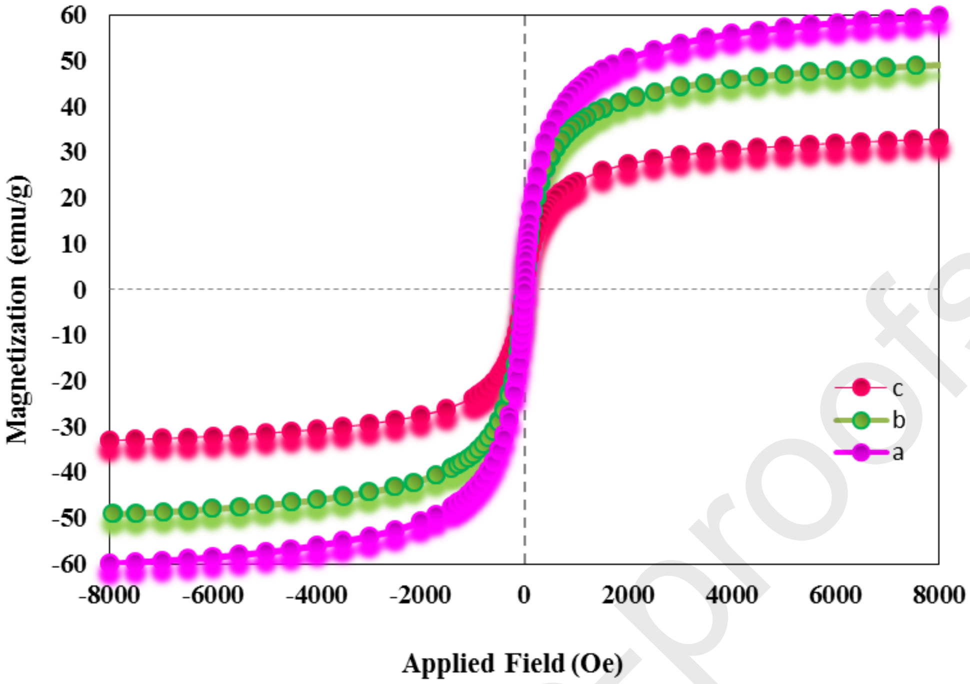
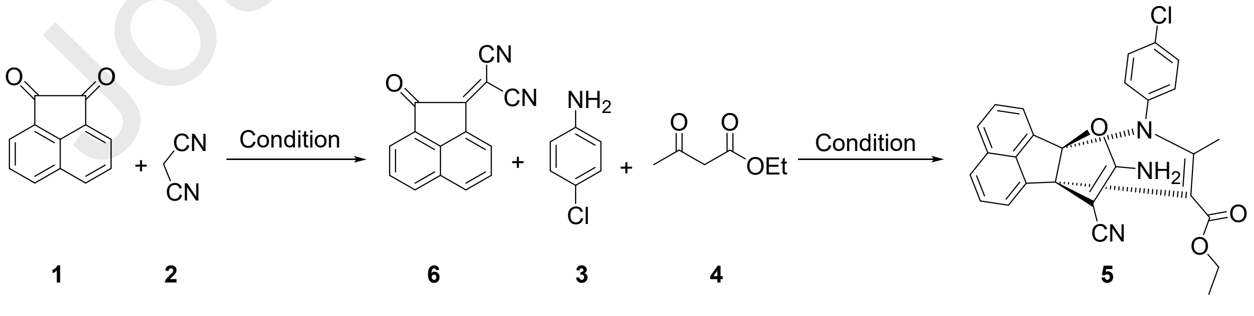


Fig. 6. Magnetization curves of a) Fe_3O_4, b) $Fe_3O_4@SiO_2$, and c) $Fe_3O_4@SiO_2@(BuSO_3H)_3$

3.3. Synthesis of [3.3.3] propellane by $Fe_3O_4@SiO_2@(BuSO_3H)_3$ as a catalyst

Initially, the catalytic activity of the $Fe_3O_4@SiO_2@(BuSO_3H)_3$ nanoparticles was studied in the reaction model for the synthesis of [3.3.3] propellane **5a** (Scheme 4). Various conditions including solvent-free systems, reflux in EtOH, H_2O, H_2O: EtOH (1:1) and without catalyst were studied. As shown in Table 1, among different conditions, the best results were obtained under domino reaction and solvent-free condition at 60 ˚C in the presence of $Fe_3O_4@SiO_2@(BuSO_3H)_3$ catalyst.

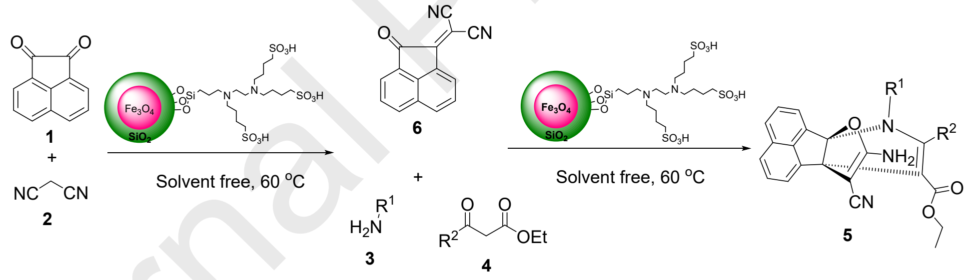


Scheme 4. Synthesis [3.3.3]propellane **5a** as a model of reaction

Table 1 The reaction conditions optimization in the synthesis of [3.3.3] propellane **5a**.

Entry	Catalyst (gr)	Solvent	Condition	Time (h)	Yield (%)
1	-	-	rt.	5	-
2	Fe_3O_4@SiO_2@BSH (0.01gr)	EtOH	Reflux	4	70
3	Fe_3O_4@SiO_2@BSH (0.01 gr)	H_2O	Reflux	6	40
4	Fe_3O_4@SiO_2@BSH (0.01 gr)	EtOH:H_2O (1:1)	Reflux	4	55
5	Fe_3O_4@SiO_2@BSH (0.08 gr)	-	60 °C	55 min	91
6	Fe_3O_4@SiO_2@BSH (0.01 gr)	-	60 °C	40 min	92
7	Fe_3O_4@SiO_2@BSH (0.01 gr)	-	90 °C	40 min	70

In order to further study of catalytic activity Fe_3O_4@SiO_2@$(BuSO_3H)_3$ nanoparticles in this work, various [3.3.3] propellane derivatives were synthesized successfully under the solvent-free condition in 60 °C (Scheme 5). According to the obtained results in table 2, all products were synthesized in a short time and excellent yield. The structure of new products was determined by melting point, IR, ^1H NMR, and ^{13}C NMR spectra.



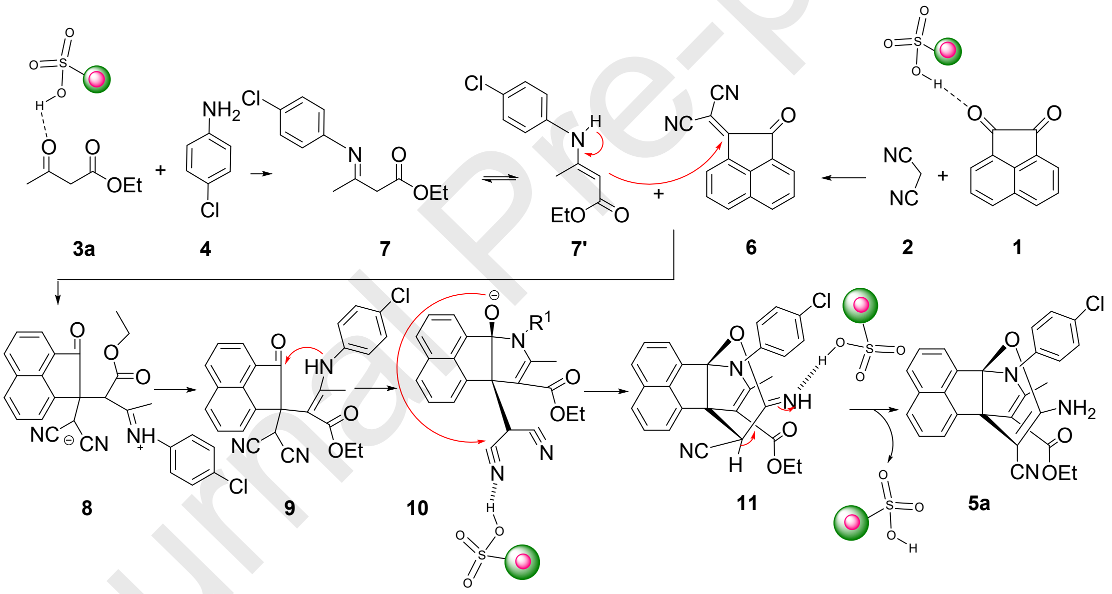
Scheme 5. Synthesis [3.3.3] propellane derivatives **5a-h**.

Table 2 The synthesis of [3.3.3] propellane derivatives **5a-h**.

Entry	R¹	R²	Time (min)	Yield (%)	m.p. (˚C)	m.p. (˚C) [Ref.]
1	4-Cl C_6H_4	Me	40	90	245-247	251-253 [28]
2	Benzyl	C_6H_5	35	91	232-234	247-249 [28]
3	Et	Me	30	93	247-250	250-252 [28]
4	Butyl	Me	30	93	248-250	247-249 [28]
5	Benzyl	Me	35	92	250-252	249-251 [28]

6	4-BrC$_6$H$_4$	Me	40	91	216-218	**New**
7	C$_6$H$_5$	Me	35	93	202-204	**New**

The plausible mechanism for synthesis of [3.3.3] propellane **5a** in the presence of Fe$_3$O$_4$@SiO$_2$@(BuSO$_3$H)$_3$ as a catalyst was shown in (Scheme 6). Malononitrile **2** attacks to the carbonyl group of acenaphthoquinone **1** via a Knoevenagel reaction to generate intermediate **6**. The nucleophilic addition 4-chloro aniline **4** to beta keto ester **3a** gave intermediate **7** which was reacted with intermediate **6** via Michael addition to produce intermediate **8**. Via proton transfer, the compound **8** was converted to the intermediate **9**, which produced propellane **5a** subsequently via the intramolecular cyclization attack of the nitrogen atom, the intramolecular O-cyclization, and then tautomerization.



Scheme 6. Proposed mechanism for the synthesis of [3.3.3] propellane **5a**.

The recyclability of Fe$_3$O$_4$@SiO$_2$@(BuSO$_3$H)$_3$ nanoparticles was measured in the synthesis of [3.3.3]propellan **5a** under the optimized conditions. Therefore, the nanocatalyst was washed several times with hot ethanol, distilled water, and diluted sulfonic acid solution. Then the nanocatalyst dried at room temperature. As showed in table 3, Fe$_3$O$_4$@SiO$_2$@(BuSO$_3$H)$_3$ was reused four times for model reaction.

Table 3 Recyclability of Fe$_3$O$_4$@SiO$_2$@(BuSO$_3$H)$_3$

Entry	Time (min)	Yield (%)
1	40	90
2	40	89
3	40	85
4	40	83

According to table 4, we compared the effect of $Fe_3O_4@SiO_2@(BuSO_3H)_3$ with *tri*-ethylamine (Et_3N) as a catalyst as the reaction model. This work in compared with the previous method has various advantages including, great yields, high purity products, shorter reaction time. One of the most important benefits this work applied that the nanomagnetic catalyst that is easily separated from the reaction mixture by the external magnet.

Table 4

Comparison of different conditions in the synthesis of compound **5a**.

Entry	Catalyst	Solvent	Condition	Time (h)	Yield (%)
1	Et_3N	EtOH	r.t.	2.7	77 [28]
2	$Fe_3O_4@SiO_2@(BuSO_3H)_3$	-	60	40 min	90

4. Conclusion

In this work, we prepared $Fe_3O_4@SiO_2@(BuSO_3H)_3$, and characterized using FT-IR, XRD, TGA, VSM, SEM, and EDX analyses, and then it was used as a new nanocatalyst in the synthesis of [3.33] propellanes. This catalyst has different advantages such as eco-friendly efficient, green reaction conditions, short reaction times, an excellent yield of products, simple separation of the catalyst by using external magnet from the reaction mixture.

Acknowledgments

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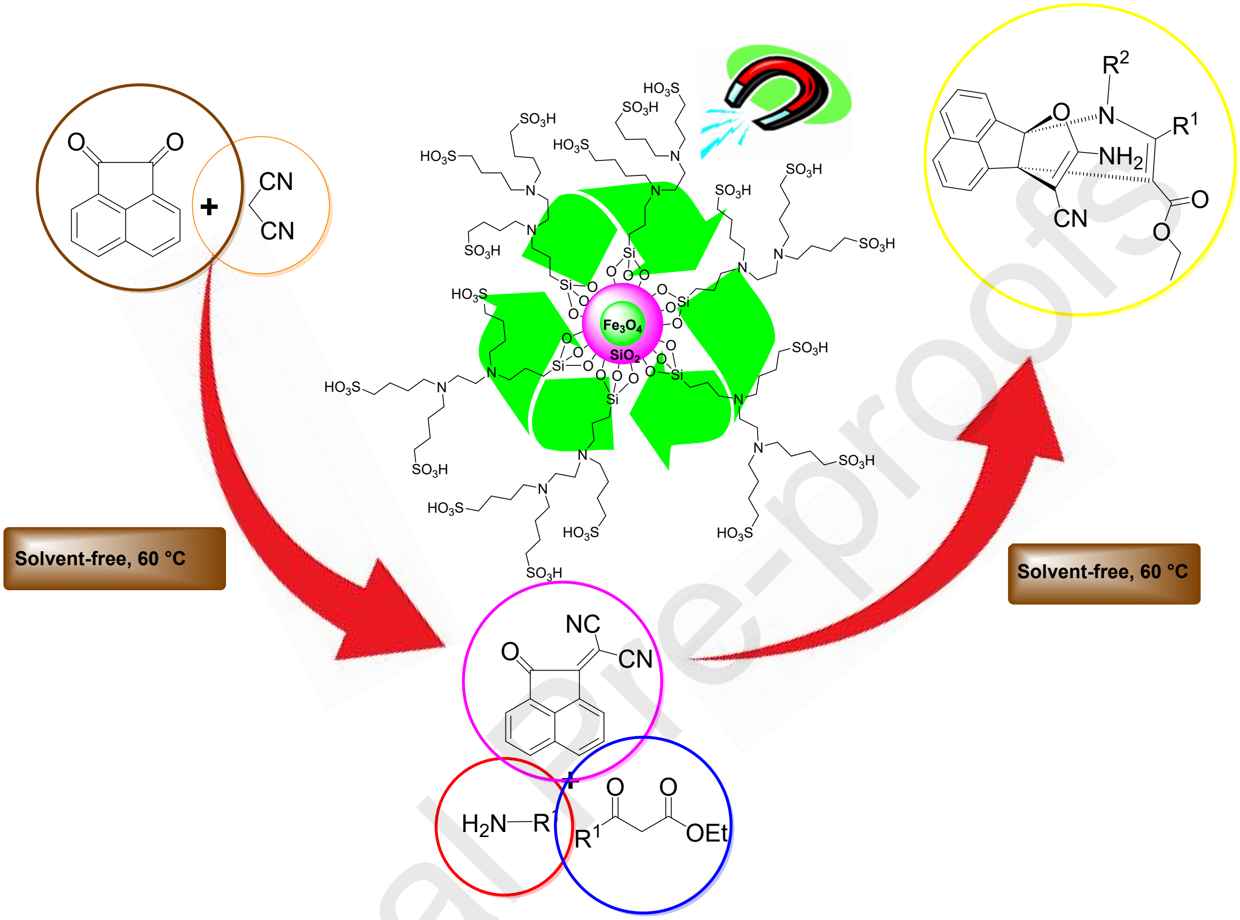
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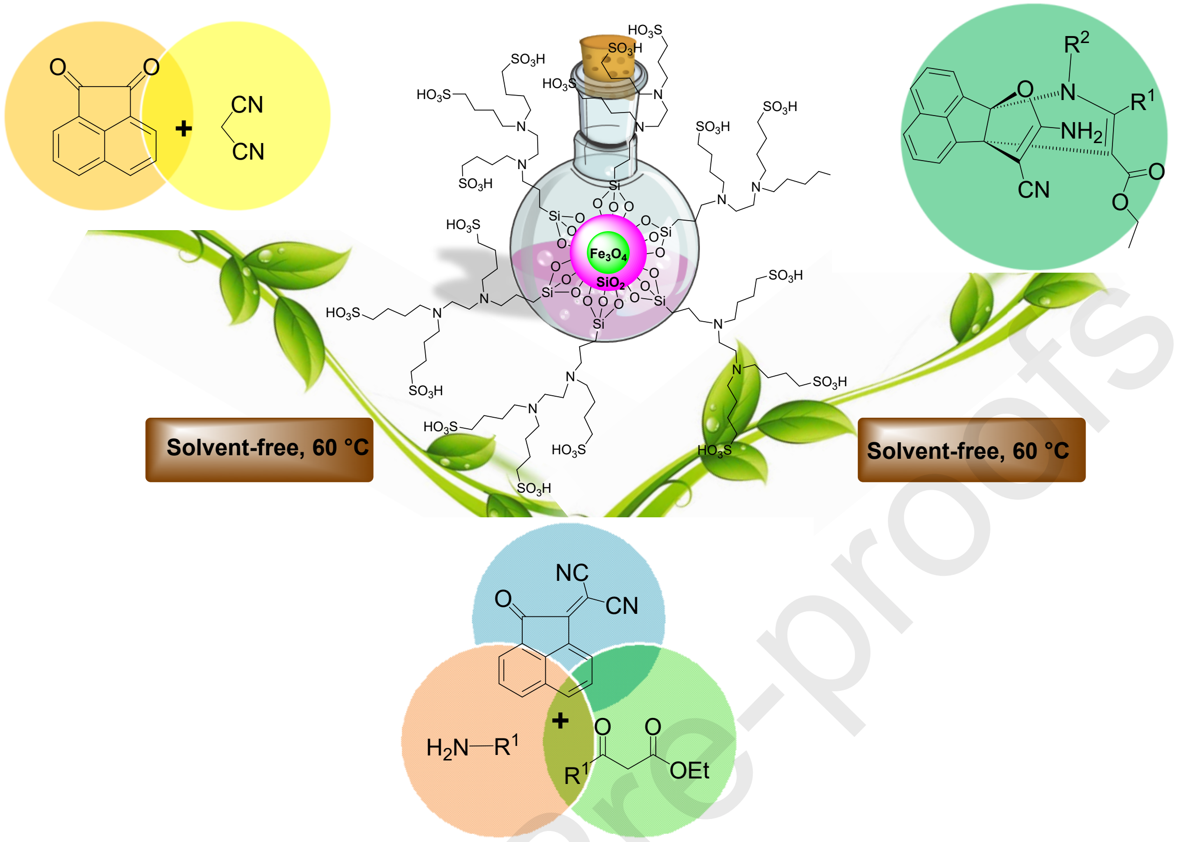
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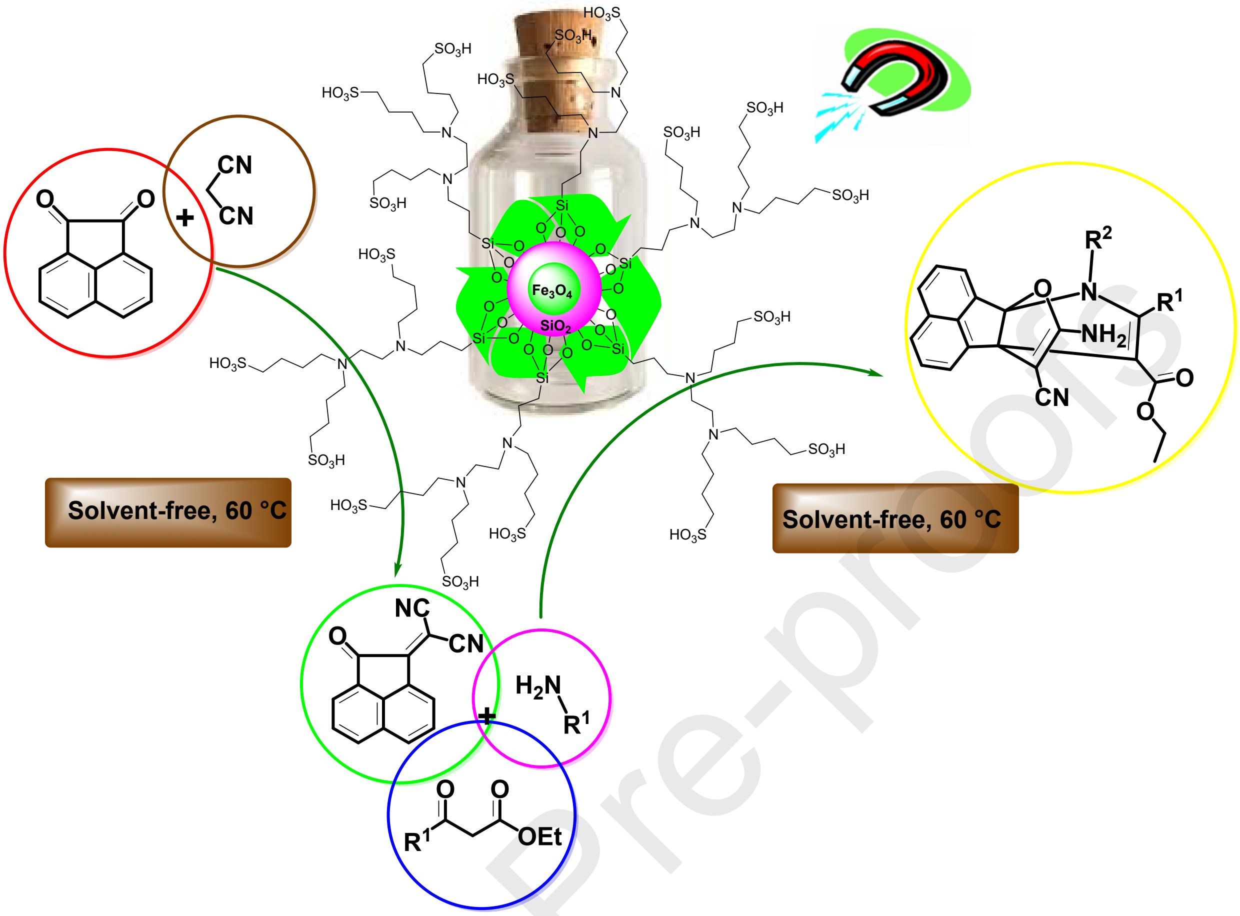
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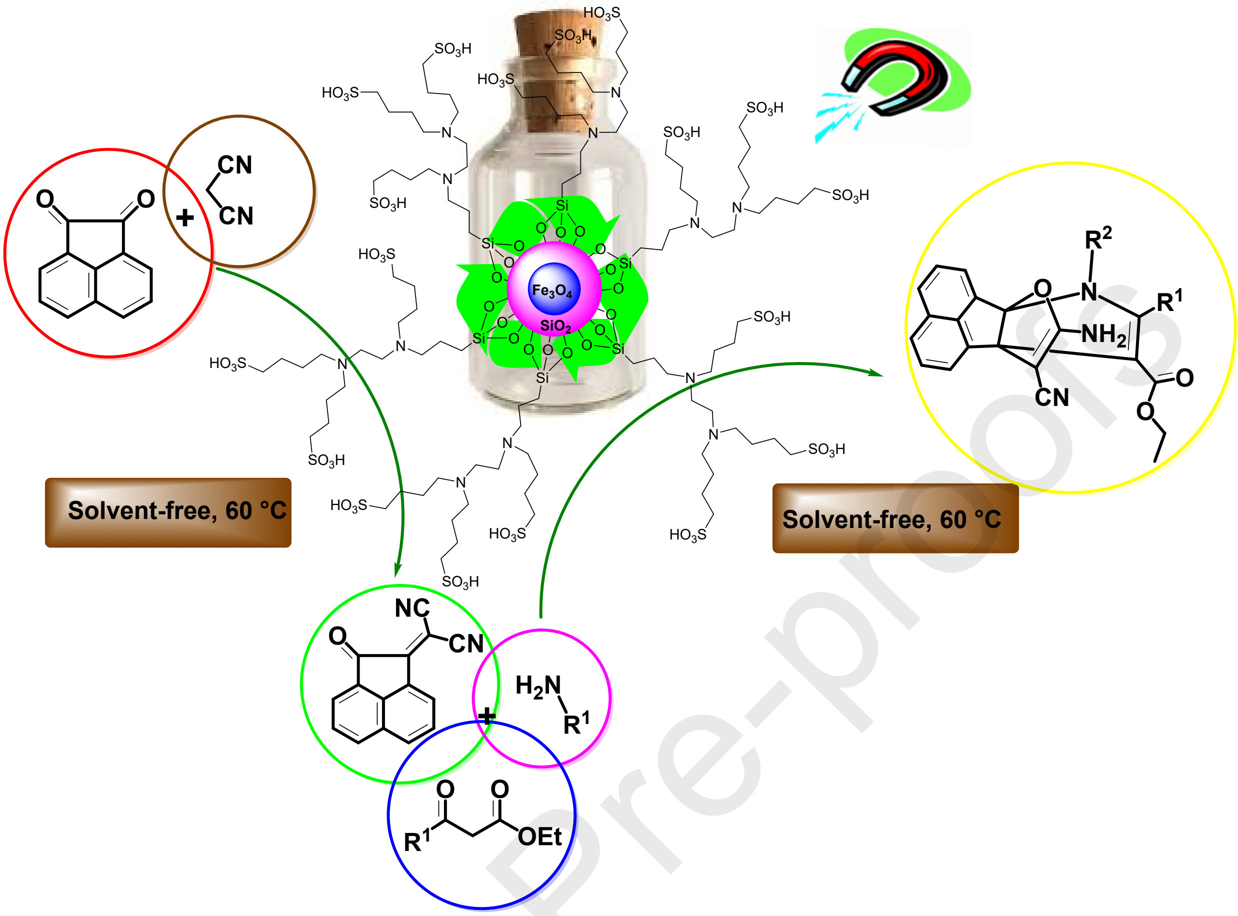
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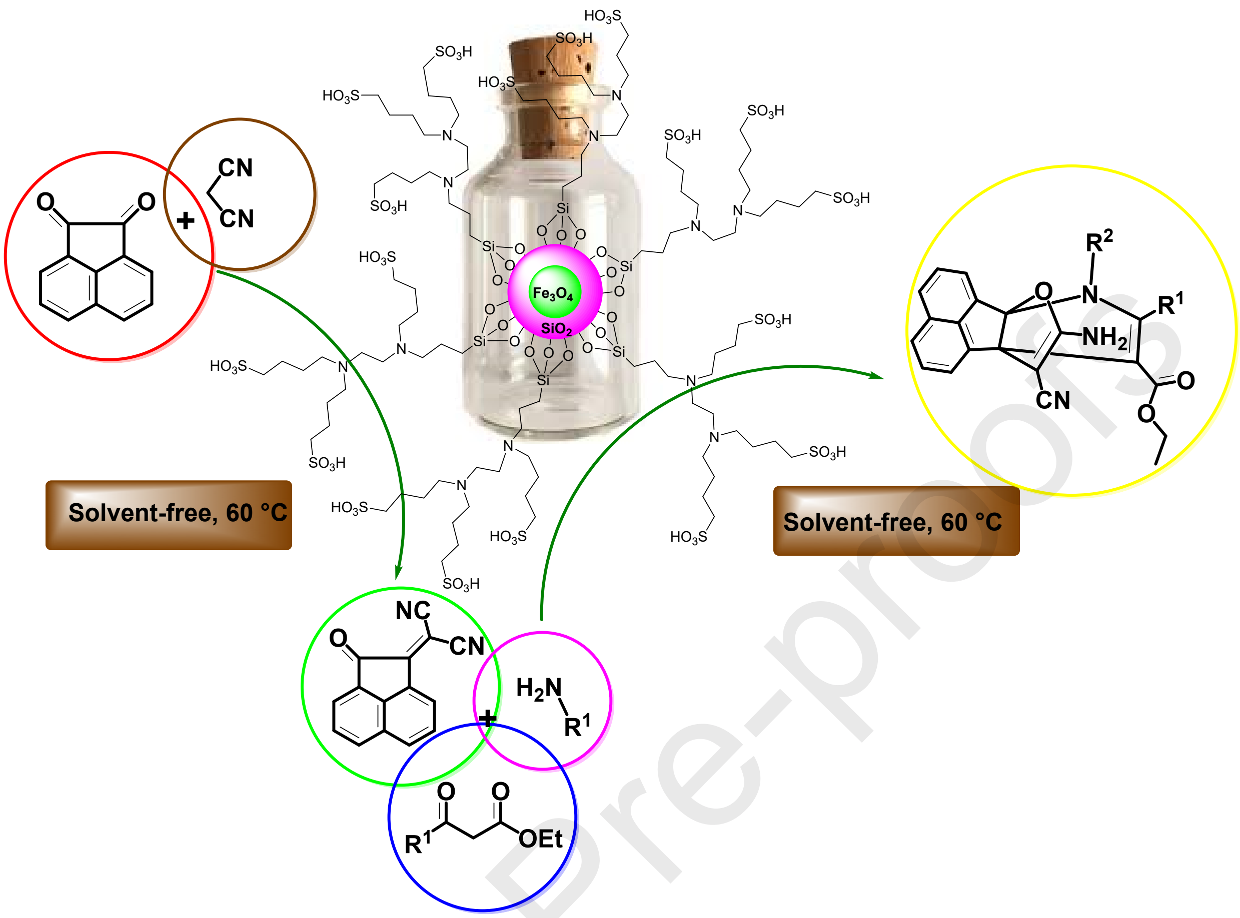
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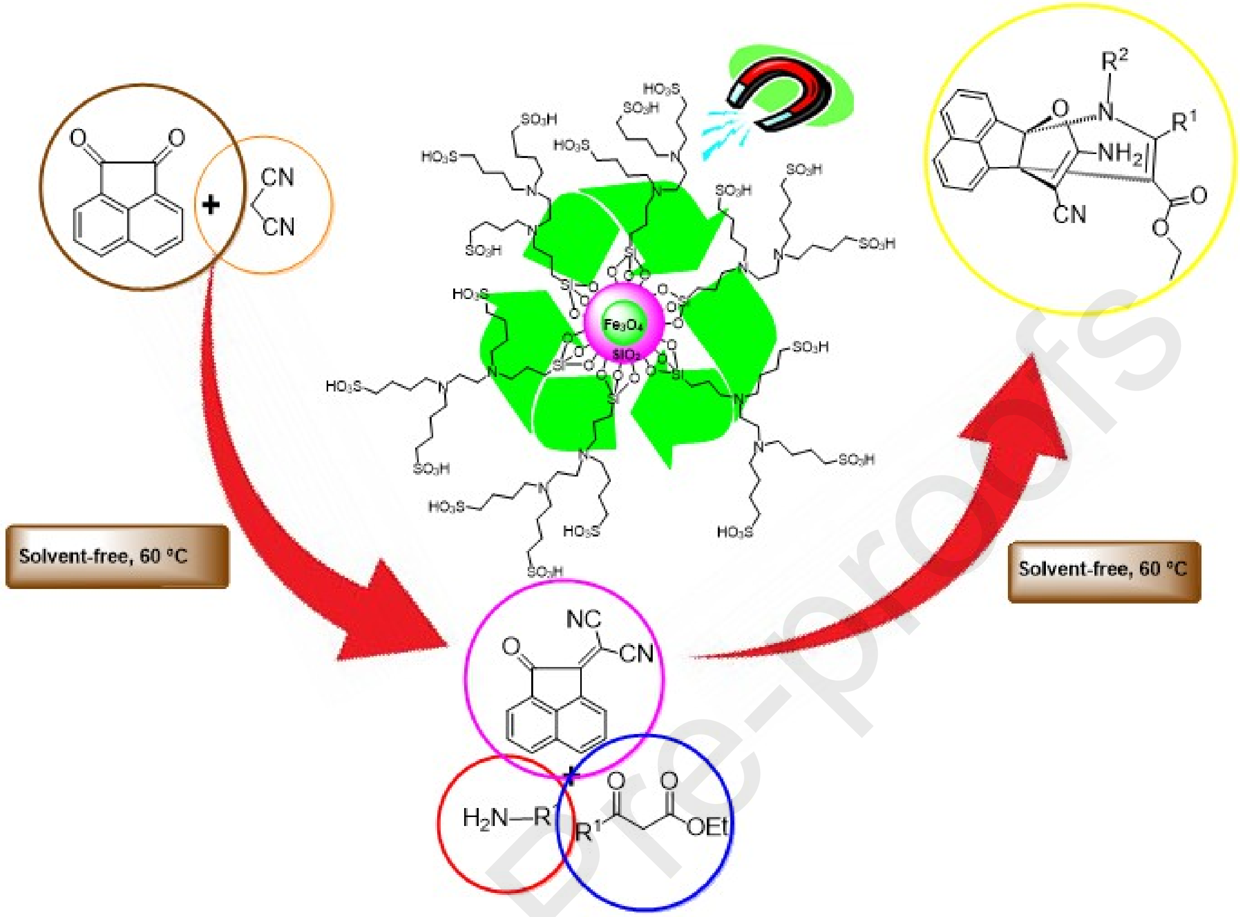

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