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CATALYSIS

The Modified Clay as a New and Eco-Friendly Catalyst for the Knoevenagel Reaction

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Abstract—This work aims the synthesis of substituted alkenes via Knoevenagel condensation using the clay collected from the Agadir region and modified by KF as a heterogeneous catalyst (KF-modified clay). In this context, the influence of various parameters on the reaction yield was studied, and the reuse of catalyst was carried out. The results obtained show that KF-modified clay is very effective for the preparation of substituted alkenes giving excellent yields (87–99%) and in very short times (between 2–4 s and 8 min) under mild and heterogeneous conditions. In addition, the recycling of our catalyst indicates that our material can be reused several times without losing its catalytic activity.

Keywords: heterogeneous catalysts, Knoevenagel reaction, clay modified, substituted alkenes

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INTRODUCTION

The Knoevenagel reaction remains the most frequently used method for the synthesis of C=C double bonds in organic chemistry [1, 2]. This condensation occurs between the aldehydes and the ketones reacting with the methylene compounds which become active in the presence of a weak base and thus makes it possible to obtain α, β-unsaturated dicarbonyl compounds accompanied by the formation of water molecules.

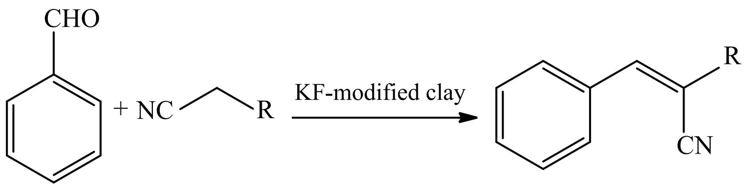
In recent years, Knoevenagel products have received significant interest because of their use in the preparation of polymers [3], coumarin derivatives [4], cosmetic products [5], perfumes [6], and pharmaceutical chemicals [7].

Recently, several homogeneous and heterogeneous catalysts have been developed for the synthesis of substituted alkenes such as K_3PO_4 [8], zeolite [9], poly(vinyl chloride) supported tetraethylenepentamine [10], amino-functionalized mesoporous silica [11], anion-exchange resins [12], guanidinium group [13], task-specific ionic liquid [14], MgO/ZrO_2 [15], modified SBA-1 materials [16], Niobium (V) chloride [7], and lipoprotein lipase [17]. Hence the need to research and develop efficient, alternative, more environmentally friendly methods.

Nowadays, one of the priority axes of research in organic chemistry concerns the development of alternative and more respectful methods for the environment compared to conventional reactions.

In this study, we have established a simple, efficient and economical method for the preparation of substituted alkenes by the condensation of benzaldehyde with malononitrile or ethyl cyanoacetate (Scheme 1) using KF modified clay [18] as new catalyst under the mild reaction conditions. Indeed, we optimized the reaction

Scheme 1. General reaction scheme of Knoevenagel condensation.



conditions as the effect of catalyst amount and solvent, thus, we expanded the reaction with other aromatic benzaldehyde substrates.

EXPERIMENTAL

General. All commercial reagents were purchased from Aldrich. All solvents were distilled before use. Nuclear magnetic resonance spectra of ^{1}H NMR were recorded on a Bruker apparatus. IR spectra were performed on a JASCO 4100 spectrometer, absorption bands ν are expressed in cm^{-1}. The thin-layer chromatography was carried out on silica plates from ALBET. The revelation was realized using the CAUTION Ultra-Violet lamp (254 and 365 nm). Melting points were measured with a Kofler bench, type Wagner & Munz HEIZBANK.

General procedure for the synthesis of substituted alkenes. The synthesis of substituted alkenes was realized by introducing into a flask an equimolar mixture of aromatic aldehyde and malononitrile or ethyl cyanoacetate in methanol by adding 20 mg of KF-modified clay as a heterogeneous catalyst. The mixture is stirred at room temperature. The condensation reaction is monitored by thin-layer chromatography (eluent = 9 mL of hexane and 1 mL of ethyl acetate), the revelation is carried out using (utilizing, employing, through) a UV lamp. At the end of the reaction, the product precipitates. The latter is taken up in dichloromethane (2 × 10 mL). The filtrate is dried over Na_2SO_4 and the solvent is evaporated at reduced pressure. The product obtained is purified by recrystallization from ethanol.

2-(Phenylmethylene)malononitrile ($3a_a$): mp 81–83 °C, 99% yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, 2H, H_{Ar}), 7.81 (s, 1H, $H_{C=C}$), 7.59 (m, 3H, H_{Ar}); FTIR (ATR, cm^{-1}) 3060 (C–H_{Ar}), 2976 (C–H_{alkene}), 2212 (C≡N), 1572 (C=C_{alkene}), 1447 (C=C_{Ar}).

2-(4-Methoxyphenylmethylene)-malononitrile ($3a_b$): mp 108–110°C, 94% yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, 2H, H_{Ar}), 7.6 (s, 1H, $H_{C=C}$), 6.9 (d, 2H, H_{Ar}), 3.87 (s, 3H, CH_3); FTIR (ATR, cm^{-1}) 3088 (C–H_{Ar}), 2942 (C–H_{alkene}), 2803 (C–H_{CH3}), 2198 (C≡N), 1524 (C=C_{alkene}), 1414 (C=C_{Ar}), 998 (C–O_{ether}).

2-(4-Methylphenylmethylene)-malononitrile ($3a_c$): mp: 129–131°C, 95% yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.8 (d, 2H, HAr), 7.65 (s, 1H, HC=C), 7.3 (d, 2H, HAr), 2.4 (s, 3H, CH3); FTIR (ATR, cm^{-1}) 3182 (C–HAr), 3018 (C–H_{alkene}), 2846 (C–H_{CH3}), 2195 (C≡N), 1565 (C=C_{alkene}), 1421 (C=CAr).

2-(4-Chlorophenylmethylene)-malononitrile ($3a_d$): mp 157–159°C, 97% yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, 2H, H_{Ar}), 7.65 (s, 1H, HC=C), 7.49 (d, 2H, H_{Ar}); FTIR (ATR, cm^{-1}) 3081 (C–H_{Ar}), 2949 (C–H_{alkene}), 2204 (C≡N), 1704 (C=C_{alkene}), 1475 (C=C_{Ar}).

Scheme 2. Optimization for the synthesis of **$3a_a$** and **$3b_a$**.

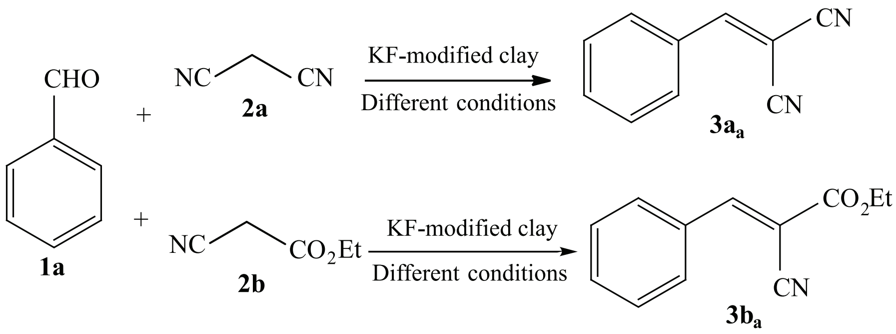


Table 1. Effect of KF-modified clay amount on the yield of 2-(phenylmethylene)-malononitrile and ethyl (*E*)-2-cyano-3-phenyl-2-propenoate[a]

Entry no.	Products	Quantity, mg	*t,* min	Yield, %[b]
1	**$3a_a$**	10	3	90
2	**$3a_a$**	20	3	99
3	**$3a_a$**	30	3	99
4	**$3a_a$**	40	3	97
5	**$3b_a$**	10	8	84
6	**$3b_a$**	20	8	91
7	**$3b_a$**	30	8	90
8	**$3b_a$**	40	8	90

[a] Reaction condition: benzaldehyde (1 mmol), malononitrile or ethyl cyanoacetate (1 mmol), room temperature, solvent: CH_3OH.
[b] Isolated yields.

2-(3-Nitrophenylmethylene)-malononitrile ($3a_e$): mp 112–114°C, 93% yield, ^1H NMR (300 MHz, $CDCl_3$) δ 8.59 (s, 1H, HC=C), 8.41 (d, 1H, HAr), 8.26 (d, 1H, HAr), 7.8 (s, 1H, HAr), 7.72 (t, 1H, HAr); FTIR (ATR, cm^{-1}) 3123 (C–HAr), 2935 (C–H_{alkene}), 2170 (C≡N), 1565–1467 (C=C_{alkene}, C=C_{Ar}), 1329 (C–NO_2 Ar).

Ethyl (*E*)-2-cyano-3-phenyl-2-propenoate ($3b_a$). mp 47–49°C, 91% yield; ^1H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 1H, HC=C), 8.01 (d, 2H, HAr), 7.55 (m, 3H, HAr), 4.41 (q, 2H, CH_2), 1.41 (t, 3H, CH_3); FTIR (ATR, cm^{-1}) 3046–2845 (C–HAr, C–H_{alkene}, C–H_{CH3}, C–H_{CH2}), 2198 (C≡N), 1684 (C=O), 1572 (C=C_{alkene}), 1450 (C=C_{Ar}), 1182 (C–O_{ester}).

Ethyl (*E*)-2-cyano-3-(4-methoxyphenyl)-2-propenoate ($3b_b$): mp 79–81°C, 87% yield, ^1H NMR (300 MHz, $CDCl_3$) δ 8.2 (s, 1H, HC=C), 8.03 (d, 2H, H_{Ar}), 7.01(d, 2H, H_{Ar}), 4.38 (q, 2H, CH_2), 3.91 (s, 3H, CH_3), 1.42 (t, 3H, CH_3); FTIR (ATR, cm^{-1}) 3080-2886 (C–H_{Ar}, C–H_{alkene}, C–H_{CH3}, C–H_{CH2}), 2198 (C≡N), 2212 (C≡N), 1700 (C=O), 1579–1440 (C=C_{alkene}, C=CAr), 1162 (C–O_{ester}), 1000 (C–O_{ether}).

Ethyl (*E*)-2-cyano-3-(4-methylphenyl)-2-propenoate ($3b_c$): mp 92–94°C, 89% yield, ^1H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 1H, HC=C), 7.91 (d, 2H, H_{Ar}), 7.34 (d, 2H, H_{Ar}), 4.4 (q, 2H, CH_2), 2.45 (s, 3H, CH_3), 1.42 (t, 3H, CH_3); FTIR (ATR, cm^{-1}) 3060–3845 (C–H_{Ar}, C–H_{alkene}, C–H_{CH3}, C–H_{CH2}), 2191 (C≡N), 1684 (C=O), 1544 (C=C_{alkene}), 1467 (C=C_{Ar}), 1204 (C–O_{ester}).

Ethyl (*E*)-3-(4-chlorophenyl)-2-cyano-2-propenoate ($3b_d$): mp 87–89°C, 90% yield, ^1H NMR (300 MHz, $CDCl_3$) δ 8.23 (s, 1H, HC=C), 7.96 (d, 2H, H_{Ar}), 7.51 (d, 2H, H_{Ar}), 4.41 (q, 2H, CH_2), 1.42 (t, 3H, CH_3); FTIR (ATR, cm^{-1}) 3081–2851 (C–HAr, C–H_{alkene}, C–H_{CH3}, C–H_{CH2}), 2233 (C≡N), 1621 (C=O), 1558 (C=C_{alkene}), 1440 (C=C_{Ar}), 1190 (C–O_{ester}).

Ethyl (*E*)-3-(4-Nitrophenyl)-2-cyano-2-propenoate ($3b_e$): mp 129–131°C, 87% yield, ^1H NMR (300 MHz, $CDCl_3$) δ 8.71 (s, 1H, H_{Ar}), 8.44 (2d in coincidence, 2H, H_{Ar}), 8.33 (s, 1H, HC=C), 7.7 (t, 1H, H_{Ar}), 4.44 (q, 2H, CH_2), 1.44 (t, 3H, CH_3); FTIR (ATR, cm^{-1}) 3074 (C–H_{Ar}), 2991–2928 (C–H_{alkene}, C–H_{CH3}), 2858 (C–H_{CH2}), 2204 (C≡N), 1711 (C=O), 1517 (C=C_{alkene}), 1475 (C=CAr), 1078 (C–O_{ester}).

RESULTS AND DISCUSSION

The effect of the catalyst amount is a major factor affecting the yield of the Knoevenagel condensation. For this reason, we have studied the effect of the amount of catalyst on the yield of the products obtained during the condensation of benzaldehyde (1 mmol) with malononitrile (1 mmol) or ethyl cyanoacetate (1 mmol) in methanol at room temperature and varying the amount of the catalyst from 10 to 40 mg (Table 1, Scheme 2). The results gathered in Table 1 show that increasing the catalyst amount from 10 to 20 mg results in an increase in the yield of the desired product from 90 to 99% after 3 min for the malononitrile substrate (entries 1 and 2, Table 1) and from 84 to 91% after 8 min for the cyanoacetate ethyl substrate (entries 5 and 6, Table 1). An amount of KF-modified clay greater than 20 mg does not influence the yield of the condensation reaction of benzaldehyde with the two substrates (entries 3, 4, 7б and 8, Table 1). From these results, it can be concluded that 20 mg is the optimal catalytic amount for this condensation.

To concretize the solvent effect on the Knoevenagel condensation in the presence of our catalyst, the reaction was carried out by reacting 1 mmol of benzaldehyde with 1 mmol of malononitrile or ethyl cyanoacetate as shown in Scheme 2 and keeping the same catalyst amount (20 mg). The reaction is carried out at room temperature and in various solvents. All the results found are grouped in Table 2. Analysis of these results indicates that the reaction appears to proceed more rapidly in polar solvents such as methanol (dipole moment $\mu = 1.71$), ethanol ($\mu = 1.74$), and acetonitrile ($\mu = 3.45$) with 99, 90, and 88%, respectively, after 3 min for the condensation

Table 2. Influence of solvent on the yield of 2-(phenylmethylene)malononitrile and ethyl (*E*)-2-cyano-3-phenyl-2-propenoate[a]

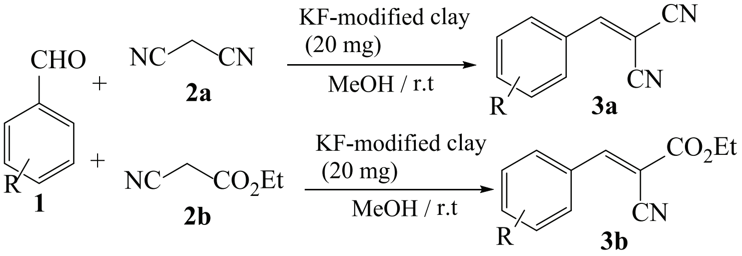
Entry	Products	Solvents	*t*, min	Yield, [b]
1	$\mathbf{3a_a}$	CH_3OH	3	99
2	$\mathbf{3a_a}$	EtOH	3	90
3	$\mathbf{3a_a}$	CH_3CN	3	88
4	$\mathbf{3a_a}$	H_2O	3	7
5	$\mathbf{3a_a}$	$CHCl_3$	3	6
6	$\mathbf{3a_a}$	CH_2Cl_2	3	4
7	$\mathbf{3a_a}$	Petroleum ether	–	–
8	$\mathbf{3b_a}$	CH_3OH	8	91
9	$\mathbf{3b_a}$	EtOH	8	84
10	$\mathbf{3b_a}$	CH_3CN	8	79
11	$\mathbf{3b_a}$	H_2O	8	8
12	$\mathbf{3b_a}$	$CHCl_3$	8	7
13	$\mathbf{3b_a}$	CH_2Cl_2	8	4
14	$\mathbf{3b_a}$	Petroleum ether	–	–

[a] Reaction condition: benzaldehyde (1 mmol), malononitrile or ethyl cyanoacetate (1 mmol), room temperature, catalyst amount 20 mg.
[b] Isolated yields.

of benzaldehyde with malononitrile (entries 1, 2 and 3, Table 2), and 91, 84, and 79% after 8 min in the case of using the cyanoacetate ethyl substrate (entries 8, 9 and 10, Table 2), with a preference for protic solvents. For moderately polar solvents as chloroform ($\mu = 1.15$) and dichloromethane ($\mu = 1.55$), the yields obtained are low for the same duration of the reaction (entries 5, 6, 12, and 13, Table 2). We note that the reaction gave lower yields for the two condensations in water (entries 4 and 11, Table 2) which is very polar ($\mu = 1.80$) and this may be due to the non-solubility of reagents in this solvent as well as a possible interaction of the latter with our catalyst. From these results, it can be concluded that only protic solvents characterized by high polarity solubilize the reactants and promote this condensation [19].

In order to expand the reaction to other reagents, we have carried out the condensation of 1 mmol of substituted benzaldehyde with 1 mmol of malononitrile or ethyl cyanoacetate under conditions previously optimized (20 mg of KF-modified clay in methanol). The results obtained are summarized in Table 3. We note that excellent yields were obtained for both condensations. The kinetics of the reaction involved

Table 3. Effect of other benzaldehyde substrates on the yield of reactions[a]

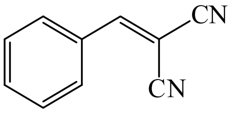
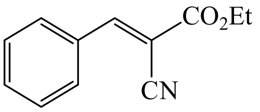
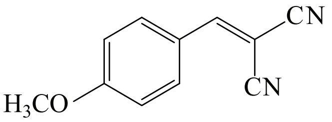
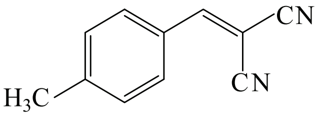
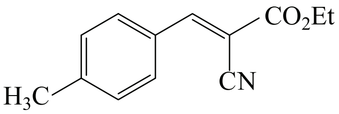
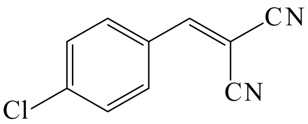
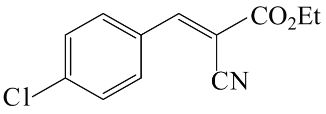
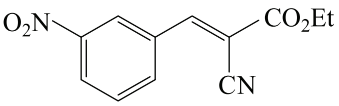


R = H (**a**), OCH_3 (**b**), CH_3 (**c**), Cl (**d**), NO_2 (**e**).

Entry	R	Products	Time	Yield, %[b]	mp, °C	mp, °C, references
1	H	$\mathbf{3a_a}$	3 min	99	81–83	83–83.5 [10]
2	4-OCH_3	$\mathbf{3a_b}$	2–4 s	94	108–110	113–115 [10]
3	4-CH_3	$\mathbf{3a_c}$	2–4 s	95	129–131	134.5–135 [22]
4	4-Cl	$\mathbf{3a_d}$	2–4 s	97	157–159	162–163 [10]
5	3-NO_2	$\mathbf{3a_e}$	1 min	93	112–114	100–101 [23]
6	H	$\mathbf{3b_a}$	8 min	91	47–49	50–51 [10]
7	4-OCH_3	$\mathbf{3b_b}$	5 min	87	79–81	80–81 [10]
8	4-CH_3	$\mathbf{3b_c}$	5 min	89	92–94	90–92 [8]
9	4-Cl	$\mathbf{3b_d}$	5 min	90	87–89	89.5–90.5 [22]
10	3-NO_2	$\mathbf{3b_e}$	8 min	87	129–131	129–131 [24]

[a] Reaction condition: Various aromatic aldehydes (1 mmol), malononitrile or ethyl cyanoacetate (1 mmol), catalyst amount= 20 mg, solvent: CH_3OH, room temperature.
[b] Isolated yields.

Table 4. Comparison with other heterogeneous catalysts

Products synthesized	Catalyst	Solvent	T, °C	Time	R, %	References
	PVC-TEPA	EtOH	Reflux	1 h	75	[10]
	C/Z-30/70	EtOH	Reflux	50 min	82	[25]
	Modified clay	MeOH	r. t	3 min	99	In this study
	PVC-TEPA	EtOH	Reflux	2.5 h	80	[10]
	C/Z-30/70	EtOH	Reflux	75 min	78	[25]
	Modified clay	MeOH	r. t	8 min	91	In this study
	PVC-TEPA	EtOH	Reflux	1 h	91	[10]
	Chitosan	EtOH	40	6 h	89	[26]
	Modified clay	MeOH	r. t	2-4 s	94	In this study
	C/Z-30/70	EtOH	Reflux	60 min	78	[25]
	Modified clay	MeOH	r. t	2-4 s	95.2	In this study
	C/Z-30/70	EtOH	Reflux	90 min	72	[25]
	Modified clay	MeOH	r. t	5 min	89.05	In this study
	PVC-TEPA	EtOH	Reflux	1h	90	[10]
	C/Z-30/70	EtOH	Reflux	60 min	81	[25]
	Chitosan	EtOH	40	6h	85	[26]
	Modified clay	MeOH	r. t	2-4 s	97	In this study
	C/Z-30/70	EtOH	Reflux	60 min	78	[25]
	Modified clay	MeOH	r. t	5 min	90	In this study
	C/Z-30/70	EtOH	Reflux	45 min	83	[25]
	Modified clay	MeOH	r. t	8 min	87	In this study

are very rapid for the *para*-substituted benzaldehyde, which varies from the instantaneous for the first series (entries 2 to 4, Table 3) to a few minutes for the second (entries 7 to 9, Table 3). The difference noted for the yields of all the reactions is rather due to the recovery and purification of the product and not to the state at the end of the reaction since they are all complete. We also note that the electron-donating groups (by the inductive or mesomeric effect) have a very positive effect on the reaction rate. These effects increase the electronic charge around the oxygen atom of the carbonyl group. We deduce that the first intervention of the aldehyde in the reaction is done through this oxygen atom. On the other hand, it can be noticed that the reactivity of malononitrile is faster than that of ethyl cyanoacetate. This can be attributed to the fact that the CN group is more attractive than the CO_2Et group, which makes the proton of the methylene group more acidic in the case of malononitrile than in the case of ethyl cyanoacetate [20, 21].

The reuse of modified clay was carried out after condensation of 1 mmol of benzaldehyde with 1 mmol of malononitrile in the presence of 20 mg of KF-modified clay at room temperature. After each reaction, the catalyst was recovered by simple filtration and washed successively with acetone and ether for 30 min and dried at 80°C for 8 h [18]. The catalyst is then reused in successive cycles under the same operating conditions. The results obtained are grouped in Fig. 1. We note from Fig. 1 that the yield of compound **3a$_a$** remains constant

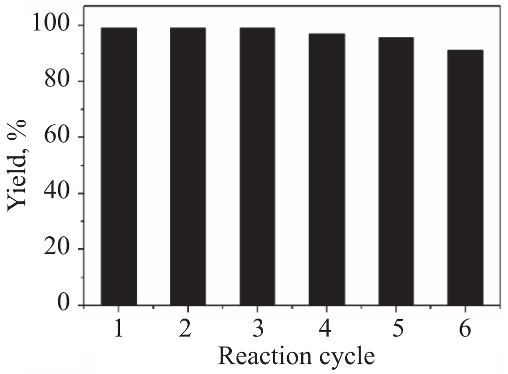


Fig. 1. Reusability of KF-modified clay for the synthesis of compound **3a$_a$**.

at 99% during the first three cycles. From the fourth to the sixth cycle, we observe a no significant decrease in the yield (from 99 to 91%). This slight decrease can be due either to the saturation of the active sites on catalyst surface or to their partial disappearance. These results are encouraging; indeed our catalyst is recyclable and can be used several times without losing much its catalytic efficiency and reusable for up to six cycles.

In the literature, several studies have investigated the Knoevenagel reaction using different catalysts. Table 4 regroups the essential experimental data for some of this work. Comparing the results obtained in this work with those of our study, shows that our catalyst has better catalytic efficiency, which results in very short reaction time, low reaction temperatures (room temperature), excellent yields, as well as the reuse of the catalyst without significant loss of its catalytic efficiency.

CONCLUSION

The Knoevenagel reaction was carried out by condensing various aromatic aldehydes with malononitrile or ethyl cyanoacetate at room temperature in methanol in the presence of KF-modified clay as a heterogeneous catalyst. All the obtained results are encouraging since the desired products have been isolated with excellent yields and in reaction times ranging from seconds to a few minutes. In addition, the catalytic activity of our catalyst remains profitable until at least 6 cycles with a slight decrease in yield (the total loss is 8%). The general process involved in this condensation is very simple, convenient, effective and does not involve any hazardous chemicals during the synthesis of alkenes, which makes it respectful of the environment.

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CONFLICT OF INTEREST

The authors declared no conflict of interest

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