



## Original Research Article

# Evaluation of reaction of aza Michael catalyzed by raw red clay of Adrar-Algeria zone, under solvent-free conditions, and at room temperature

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### ARTICLE INFORMATION

Received: 23 March 2019

Received in revised: 20 May 2020

Accepted: 02 September 2019

Available online: 01 April 2020

DOI: [10.26655/jmchemsci.2020.2.7](https://doi.org/10.26655/jmchemsci.2020.2.7)

### KEYWORDS

Raw Clay  
Amines; Alkenes  
Environment  
Adrar  
Aza-Michael

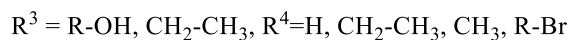
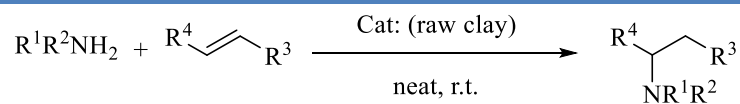
### ABSTRACT

This work was conducted to evaluate catalytic efficiency of red clay of Adrar-Algeria zone as an effective green catalyst on the Aza Michael reaction. The Aza-Michael reaction is the addition of amine to  $\alpha, \beta$ -unsaturated alkene was carried out using raw red clay from the Adrar-Algeria area as a catalyst to synthesize the new carbon-carbon or carbon-heteroatom bond containing products. The reaction was carried out with favorable conditions, ambient temperature, without solvent, and the protocol likes the environment, so that the synthesized products provide high yields and excellent chemo selectivity.

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Journal of Medicinal and Chemical Sciences: <http://www.jmchemsci.com/>

### Graphical Abstract



## Introduction

Clays are crystalline porous materials that have been used in many separation processes [1-6] such as in extracting oxygen from the air or separating the Orth, Meta, and para isomers of xylene from a mixture [7-15]. These processes exploit the properties of adsorption selectivity of in the molecular sieves [16-20]. Also, clays are among the polides [21], which are used in catalyst industries [22-26]. Their fields of application are vast, industrial, sanitary, and environmental. These polides are used in heterogeneous catalysis.

The use of heterogeneous catalysts for organic synthesis is growing rapidly on homogeneous catalytic systems due to their high stability, ease of handling, recovery and reuse, non-corrosive character, persistent long-term catalytic activity duration, and environmentally friendly [27].

Recently, we reported several organic transformations catalyzed by clay, such as a solid support acid catalyst [28-29]. It has a low production cost, easy to prepare in laboratory, and can be stored for a long time without significant loss of catalytic activity. However, in the research study, we evaluated the raw clay of the Adrarwillaya zone - Algeria as a catalyst in a green synthesis and effective, based on the Aza-Michael reaction [30].

Many methods have been described in the literature for synthesis of  $\beta$ -amino, ketones, esters or nitriles. Among the various synthesis

methods [31-33], the most frequently used is the conjugated addition of amines, on  $\alpha$ ,  $\beta$ -unsaturated ketones or esters or nitriles, called Aza-Michael reaction [34-37]. In general, the Michael addition-1, 4 reaction requires basic conditions or very specific conditions [38-39]. The short reaction time, very good chemo selectivity, high efficiency, the ease of purification of the products [40], the use of an inexpensive and reusable catalyst, are the main characteristics of this protocol.

## Materials and methods

A practical method was developed for the addition of aliphatic or aromatic amines to alkenes, catalyzed by acids or alkalis, which is called Aza-Michael reaction. In an Erlenmeyer Meyer we add (5 mmol, 1eq) alkenes on (6 mmol, 1.2 equivalents) of amines and during stirring of the mixture we add (0.100 mg) of our catalyst the raw clay, the reaction is without solvent, and at room temperature, we followed the reaction by TLC platelets, until the appearance of the compound after filtered, and washed with dichloromethane, and remove excess amine and excess of the starting reagents by evaporation in a rotary evaporator, and analyzes the products obtained by <sup>1</sup>HNMR.

### *Characterization of our catalyst the natural clay of Adrar-Algeria*

The physical properties of the Adrar's natural clay catalyst is shown in Table 1.

**Table 1.** Physical properties of the studied catalysts.

Parameters	Value	Parameters (obtained at the laboratory level of Bechar clays)	Les valeurs
PH	3,6	Moistdensity	1,92 t /m <sup>3</sup>
Humidity	2,14%	Dry density	1,87 t /m <sup>3</sup>
Swelling index	1,04%	Saturation level	17%
		Liquiditylimit (WI)	75%

That the results revealed that, the clay type contains a large presence of acid where the pH value was 3.6. The corresponding saturation rate was 17% with a small amount of water depending on the humidity value (2.14%) with a wet and dry density of 1.92 t/m<sup>3</sup>. On the other hand, there is a small IG inflation of 1.06% and liquidity value of 75%.

#### *Chemical properties of Adrar's natural clay catalyst*

The chemical properties were obtained according to the Béchar geotechnical laboratory: Insoluble: 90.86% present the crystalline compounds.

Carbonate: 09.86%

Sulfate: traces

The results of the chemical analysis of the natural clay sample are presented in [Table 2](#).

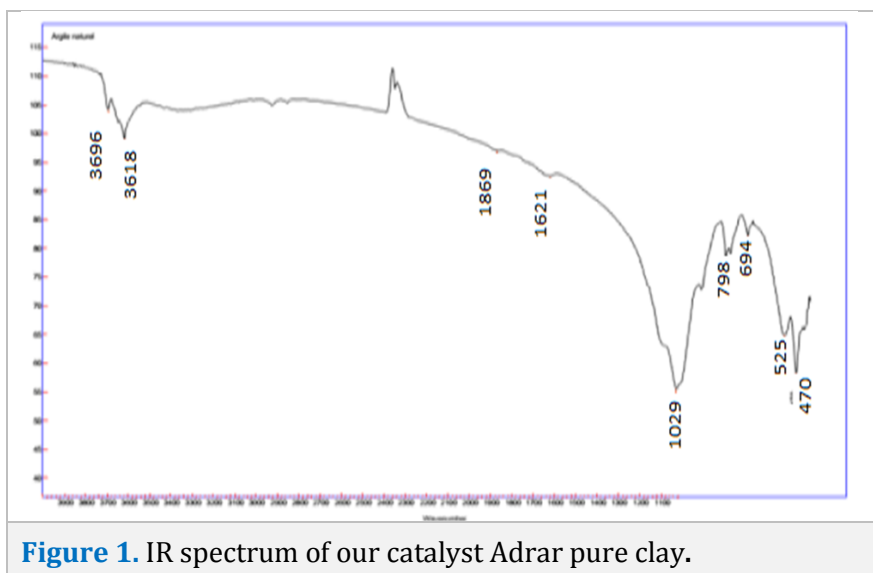
**Table 2.** Results of chemical analyzes of Adrar's natural clay.

Chemical compound % mass.	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Cl	F
	62,86	15,17	7,24	1,65	0,99	0,58	3,52	0,309	0,05

It was found that the predominant constituents of this clay are silica and alumina. The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio is 4.14. This is explained by the high content of free silica. Some authors present relate to the degree of purity of a clay, especially when its value varies between 2 and 5.5 [89]. In particular, the presence of trace oxides such as MgO, CaO, Na<sub>2</sub>O, and K<sub>2</sub>O. The presence of a remarkable amount (3.52%) of K<sub>2</sub>O revealed the presence of an illite phase.

Appearance of MgO in the sample may indicate the presence of smectite and a small amount of dolomite in the carbonate-rich clay [89]. Fe<sub>2</sub>O<sub>3</sub> content of the natural clay sample was found to be 7.24%, being the dominant form of iron, iron bound to the silicate lattice (96% of total iron) and the remainder occurred in the form of free iron oxides

#### *FTIR characterization*



**Figure 1.** IR spectrum of our catalyst Adrar pure clay.

The IR spectra of the sample are in agreement with data from the clay materials literature Jana Madejov, and the spectra show smaller bands around 3696 and 3618 cm<sup>-1</sup> which are attributed to elongation of hydroxyl bonds (OH)

1869 cm<sup>-1</sup> characteristic with carbonate CO<sub>3</sub>-2

1621 cm<sup>-1</sup> which is attributed to H-O-H deformation vibrations of water molecules

The widest and widest band located between 900-1200 cm<sup>-1</sup> and centered at 1029 cm<sup>-1</sup> corresponds to the valence vibrations of the Si-

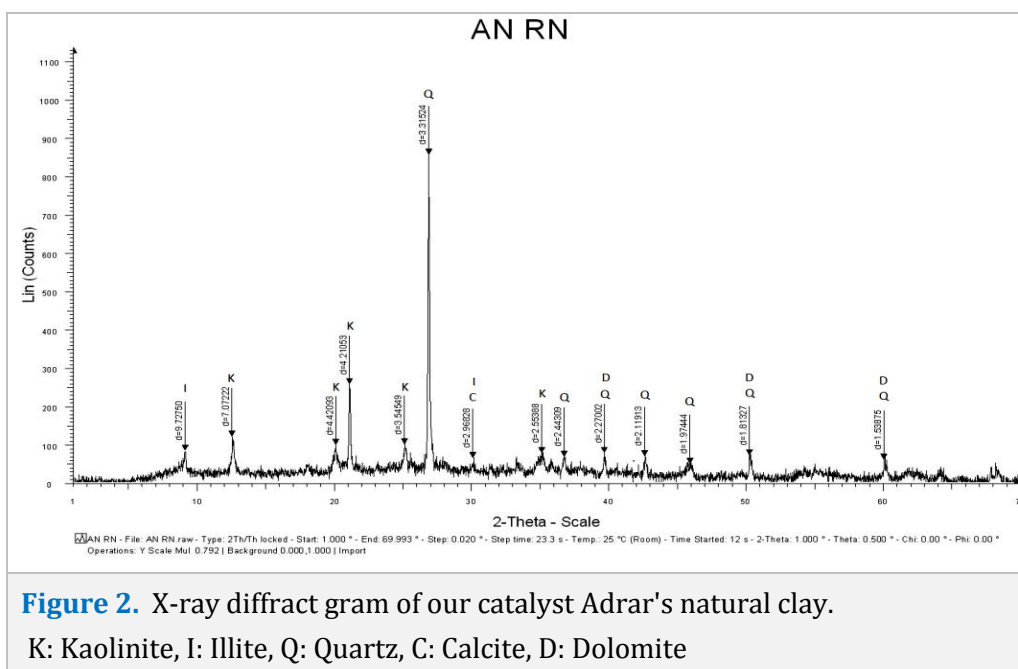
O bond 798cm<sup>-1</sup> pair Al-O and Si-O outside the planes attributed to the impurity of Silica and Quartz.

The 798 cm<sup>-1</sup> band is attributed to Si-O-Al stretching vibrations

The bands centered at 694, 525 and 470 cm<sup>-1</sup> are respectively attributed to the deformation vibrations of the Al-OH-Al and Si-O-Al bonds.

#### XRD Characterization

X-ray diffraction pattern of natural clay is shown in [Figure 2](#).



The preliminary examination of the diffractogram of natural clay reveals the presence of the following minerals: Kaolinite (K), Illite (I), Quartz (Q), Dolomite (D) and Calcite (C). The major crystalline phases contained in this natural clay are composed of

the following minerals: Kaolinite (K) and Illite (I). The dominant clay mineral is Kaolinite, characterized by an intense peak at ( $d = 4.21 \text{ \AA}$ ,  $2\theta = 21.093$ ) and a series of peaks of varying intensities presented in the following [Table](#):

**Table 3.** Diffraction angle and inter-reticular distances of clay phases.

	Kaolinite					Illite	
2θ (°)	12,537	20,075	21,093	25,153	35,143	9,096	30,114
d (Å°)	7,072	4,420	4,210	3,545	2,553	9,727	2,968

Crystalline impurities (non-clay minerals) consist mainly of quartz, calcite and dolomite (Table 4).

Table 4. Diffraction angle and inter-reticular distances of impurities.							
	<b>Quartz</b>						
<b>2θ (°)</b>	26,865	36,772	40,029	42,675	46,013	50,321	60,133
<b>d (Å°)</b>	3,315	2,44	2,270	2,119	1,974	1,813	1,538
	<b>Dolomite</b>			<b>Calcite</b>			
<b>2θ (°)</b>	40,029	50,321	60,133	30,114			
<b>d (Å°)</b>	2,27	1,813	1,538	2,968			

From these results it can be shown that this natural clay is comparable to that of type 7 A °, which is a Kaolinite

### Results and discussion

From these raw Adrar Clay analysis results we have carried out our work of testing the catalytic efficiency of our Catalyst raw clay from

Adrar - Algeria, with a cost effective and efficient method able to satisfy the objective of Aza-Michael addition, nucleophilic addition of a carbanion on an α, β-unsaturated carbonyl compound, for the synthesis of a variety of nitrogen-containing products, bioactive natural products, antibiotics, and chiral auxiliaries, and the formation of CC or C-heteroatom bonds.

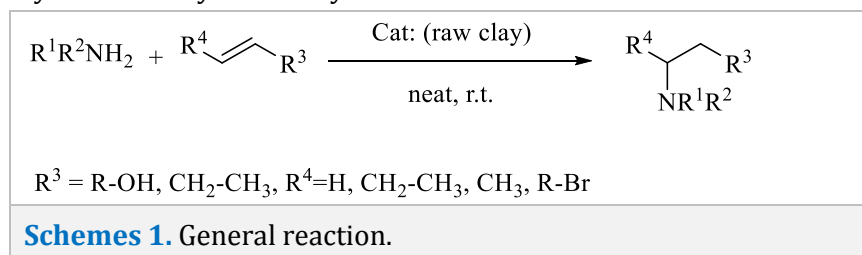

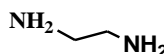
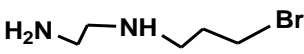
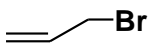
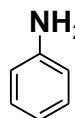
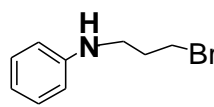
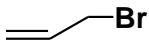
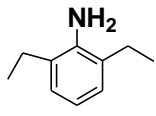
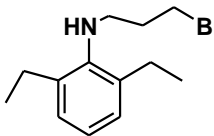


Table 5. shows the addition of Aza-Michael 1, 4 of a series of amines on an, α, β-unsaturated alkene, of Allyl bromide catalyzed by crude red Clay of the Adrar-Algeria zone. Dry medium without solvent, and at room temperature.

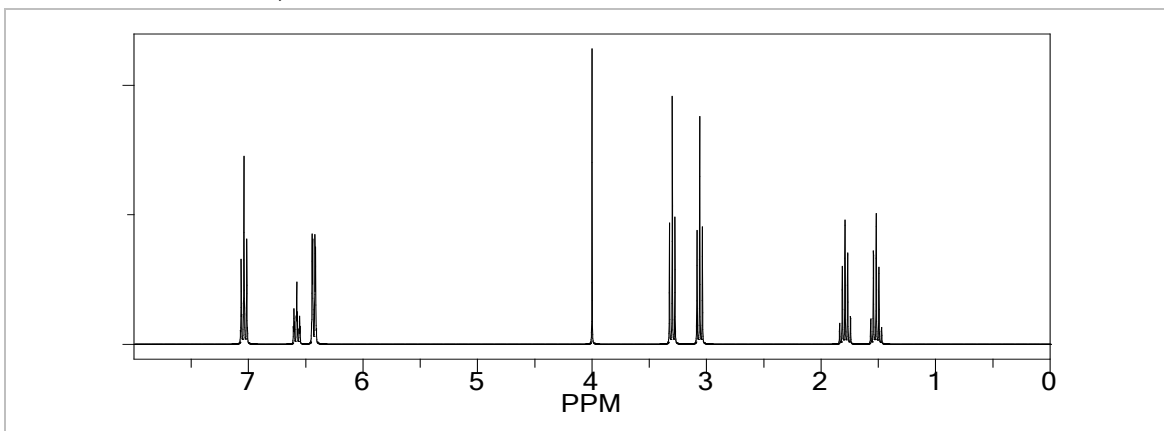
Entry	Alkenes	Amines	Product	Time (mn)	Yield (%)	Catalyst
01				20	97	RawClay
02				20	96	RawClay
03				20	94	RawClay

## Conclusion

According to these excellent results, we can conclude that the use of an inexpensive and reusable catalyst such as Red Clay of the Adrar-Algeria zone, to synthesize the new Carbon-Carbon or Carbon-Heteroatom bond containing products according to the recommendations of the reaction Aza Michael, of addition of amines

to  $\alpha$ ,  $\beta$ -unsaturated alkenes, is satisfying the objective. The reaction was solvent free, with short time, at room temperature, with excellent chemical selectivity, high product yields and easy purification, are the main features of this elegant protocol.

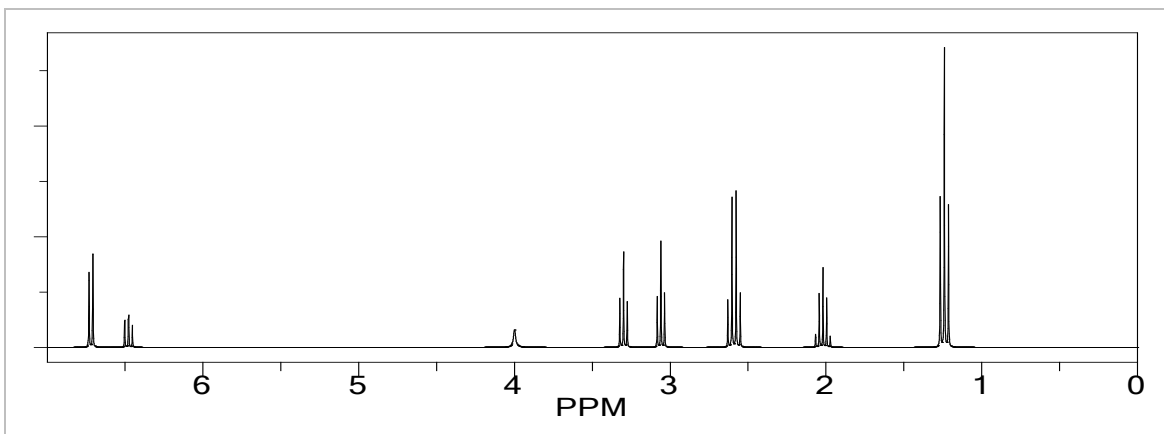
## Spectral data



### Product 01

RF= 0.69 (Hexane-EtoAc): 2/1

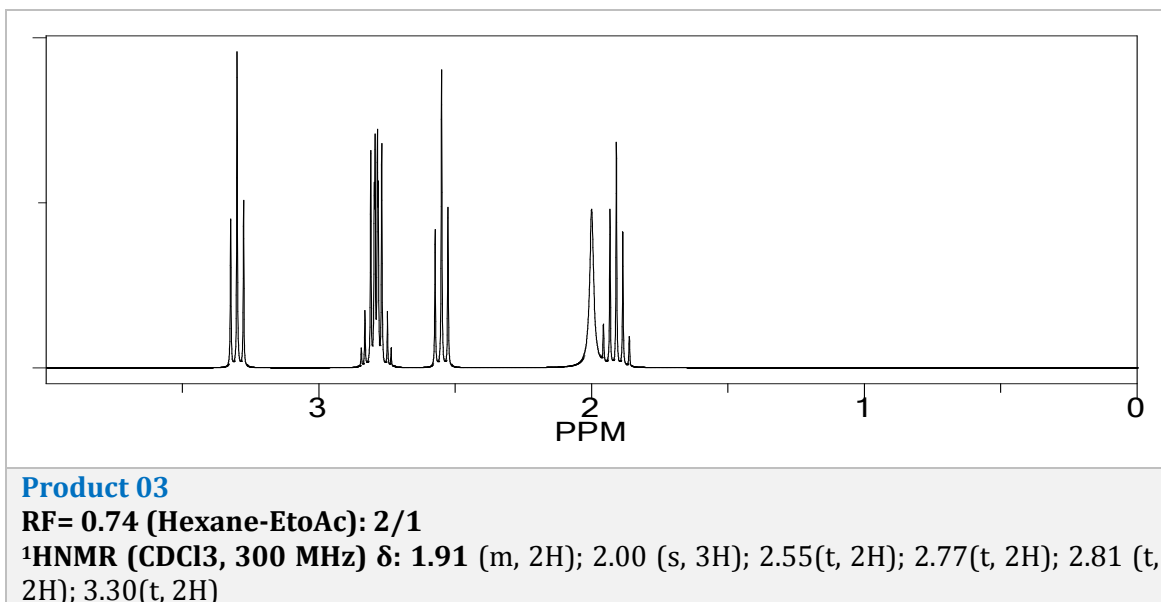
<sup>1</sup>HNMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 1-1.52 (t, 2H); 1.79 (m, 2H); 3.30(t, 2H); 4.00(s, 1H); 6.34 (d, 2H); 6.58(t, 1H); 7.04(m, 2H)



### Product 02

RF= 0.66 (Hexane-EtoAc): 2/1

<sup>1</sup>HNMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 1.24 (s, 6H); 2.02 (m, 2H); 2.59(q, 4H); 3.06(q, 2H); 3.30 (t, 2H); 4.0(s, 1H); 6.48(t, 2H); 6.72(d, 4H)



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**How to cite this manuscript:** Elmeliani M'hammed<sup>a,\*</sup>, Djafri Fatiha<sup>a</sup>, Djafri Ayada<sup>b</sup>, Belbali Djeloul<sup>c</sup>. Evaluation of Reaction of Aza Michael Catalyzed by Raw Red Clay of Adrar-Algeria Zone, under Solvent-Free Conditions, and at Room Temperature. *Journal of Medicinal and Chemical Sciences*, 2019, 3(2), 154-161. DOI: [10.26655/jmchemsci.2020.2.7](https://doi.org/10.26655/jmchemsci.2020.2.7)