Supplementary Material

The role of the catalyst on the reactivity and mechanism in the Diels-Alder cycloaddition step of the Povarov reaction for the synthesis of a biological active quinoline derivative. An experimental and theoretical investigations

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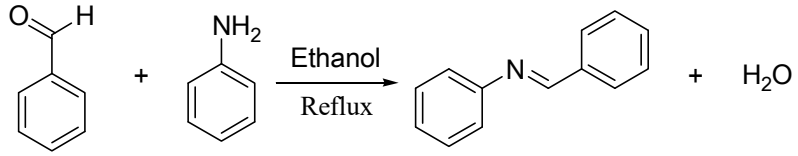
S6. Figure S1. Maps of the ASD of the radical radical cations of the allyl alcohol with isovalue=0.008 together with the nucleophilic and electrophilic indices

Procedure for the synthesis of imine 2

In a single-neck flask of 100 ml, we have introduced an equimolecular quantity of bnezaldehyde and aniline (0.05 mol**)** which were dissolved in an anhydrous ethanol. Then, we placed the flask in a water bath under magnetic stirring and refluxing solvent during 30 minutes. After that, we put the flask in a cold water bath for a few times until the mixture crystallized, then we added to it 5ml of ethanol (solvent). In order to purify the obtained product, we have putted again the reactive mixture in a hot water bath to dissolve the mixture. After dissolving the mixture, we have put it in a cold water bath for recrystallization. After that, we have added 5ml of ethanol, leading to obtain a heterogeneous mixture, which we purify it by vacuum filtration. At the end, the obtained product was dried in the oven.



Scheme S1. Synthesis of imine **2.**

Spectroscopic analysis of quinoline derivative

The UV-visible spectrum of the crude product shows two adsorption bands in 230 and 249nm corresponding to electronic transitions $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$, respectively, accounts for the presence of a C=C and C=N bond, in which this last is attributed to the mesmeric effect ($N-C=C \leftrightarrow {}^{+}N=C-C^{-}$).

The IR spectrum of the prepared quinoline derivative showed an absorption bands at 1600, 1311, 1454 and 3364 cm^{-1} characterising the C=C, C−N, C−O and N−H absorption, confirming the formation of the desired cyclic structure.

The ^{1}H NMR spectrum of the prepared quinoline derivative **5** makes it possible to determine its structure from the chemical shifts. This spectrum shows two multiplets at 7.29 and 6.8 ppm attributed to the protons of the phenyl ring and the quinoline one, respectively. In addition, the proton linked to the nitrogen atom resonates at 4ppm as doublets indicate that it couples with neighboring protons, where the coupling constant is 7Hertz. Moreover, the signals for the two protons neighboring the nitrogen and oxygen atoms appear at 1.28ppm as a multiplets. The protons of methylene group were observed at 1.87ppm and finally, the proton of the methyl group appears at 0.18ppm.

General techniques

All reactions were carried out in dried reaction glassware. The temperatures of the reaction are reported as the temperature of the hot plate used. The commercial products were obtained from Sigma Aldrich, Alfa Aesar and were typically used without further purification. The spectra of ^{1}H NMR were recorded on a Bruker AC 200 250 MHz. Chemical shifts (δ) are expressed on parts per million (ppm) relative to external reference TMS. Coupling constants (J) are given in

Hertz. The NMR spectra were performed in $CDCl_3$ and referenced to the residual peak of $CHCl_3$ at δ_H=7.26 ppm for ^1H. Infrared spectra (IR) were recorded with a spectrometer Shimadzu-FTIR 8400S, using KBr for the solid imine **2** and CCl_4 as a solvent for the liquid quinoline **5**. Ultraviolet spectra (UV) were realized using Double beam UV-visible spectrophotometer 190 - 900 nm, with ethanol as a reference. All the reactions were monitored by thin-layer chromatography (TLC) on silica gel 60 F_{254} TLC plates; the revelation was attended up with UV light, and a colored solution of potassium permanganate solution followed by simple heating. Petroleum ether and ethyl acetate were used as eluent for TLC.

General procedure for the synthesis of quinoline 5 using Lewis acid catalyst

An equimolecular amount (0.0125mol) of the previously prepared imine **2**, alkene **1** and catalyst were introduced on single-neck flask of 100 ml and dissolved in 25ml of anhydrous diethylether under stirring during 48 hours. The reaction evolution was monitored by TLC. After completion of the reaction, a 10ml of NaOH (10%) solution was added to the reaction mixture in order to eliminate the catalyst. After, we have obtained a homogenous solution, in which the organic layer was separated from aqueous one using decanting flask. The obtained organic layer was then dried by adding $MgSO_4$, and then filtrated through vacuum filtration, and finally, the solvent was evaporated under reduced pressure giving the crude product as yellow brown oil.

General procedure for the synthesis of quinoline 5 using Brönsted acid catalyst

First, we prepare a solution of catalyst by putting 1ml of acetic acid or chlorydric acid in a beaker then we add 10ml of ethanol. Then, we take 1ml of this solution and we introduce it in a flask of 100ml. Secondly, we add a solution prepared from 1ml of aniline in 10ml acetonitrile. After 10minutes, we add another solution of 1.02ml of benzaldehyde in 10ml of acetonitrile and let the reaction mixture under stirring. After that, we introduce to the flask another solution composed of 1.17ml of ethylvinylether dissolved in 10ml of acetonitrile and let the reaction mixture under stirring in room temperature during two nights. After, we add a 40ml of saturated sodium bicarbonate aqueous solution. An extraction of the obtained mixture using ethyl acetate (20ml*3) then dried the obtained organic layer by $MgSO_4$ salt. The filtration of heterogenous mixture and solvent evaporation of the filtrate allow us to obtain the desired product as yellow brown oil. The reported yields were determined based on the isolated pure products.

Table S1. Global CDFT reactivity properties calculated, in eV, of allyl alcohol.

	HOMO	LUMO	μ	η	ω	N
Allyl alcohol	-6.86	0.47	-3.10	7.16	0.67	2.44

Table S2. Total energies, in gas phase of the stationary points for the Povarov reaction of the imine **2** with alkene **1.**

System	E(a.u)
Imine 2	-556.769554
Alkene 1	-232.441637
TS1-mn	-789.148088
TS1-mx	-789.149583
TS1-on	-789.139074

TS1-ox	-789.13625
P1-mn	-789.203841
P1-mx	-789.206703
P1-on	-789.207938
P1-ox	-789.206809

Table S3. Total energies, in gas phase of the stationary points for the Povarov reaction of the $AlCl_3$:imine complex **3** with alkene **1.**

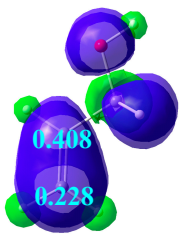
System	E(a.u)
Imine 3	-2180.04848
Alkene 1	-232.441637
TS2-mn	-2412.46719
TS2-mx	-2412.46592
TS2-on	-2412.44155
TS2-ox	-2412.43917
P2-mn	-2412.49771
P2-mx	-2412.50572
P2-on	-2412.50657
P2-ox	-2412.50115

Table S4. Total energies, in gas phase of the separated reactants, TSs of the first step and cycloadducts for the Povarov reaction of the H^+:imine complex **4** with alkene **1.**

System	E(a.u)
Imine 4	-557.157186
Alkene 1	-232.441637
TS3-mn	-789.763892
TS3-mx	-789.759769
TS3-on	-789.753531
TS3-ox	-789.753535
P3-mn	-789.618193
P3-mx	-789.617852
P3-on	-789.617066
P3-ox	-789.621486

Table S5. Total energies, in gas phase of the intermediates and TSs of the second step for the Povarov reaction of the H^+:imine complex **4** with alkene **1.**

Intermediates	E(a.u)	2nd TSs	E(a.u)
Int-mn	-789.791314	**TS3-2mn**	-789.769476
Int-mx	-789.789525	**TS3-2mx**	-789.769499
Int-on	-789.777917	**TS3-2on**	-789.540553
Int-ox	-789.776236	**TS3-2ox**	-789.545707



allyl alcohol $^{\cdot+}$

Figure S1. Maps of the ASD of the radical radical cations of the allyl alcohol with isovalue=0.008 together with the nucleophilic and electrophilic indices.