

Synthesis of electron-poor *N*-Vinylimidazole derivatives catalyzed by Silica nanoparticles under solvent-free conditions

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ABSTRACT: Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and acetylenic esters, by NH-acids such as azathioprine, imidazole or theophylline leads to the formation of vinyltriphenylphosphonium salts, which undergo a Michael addition reaction with a conjugate base to produce phosphorus ylides. Silica nanoparticles (silica NPs were prepared by thermal decomposition of rice hulls) was found to catalyze the conversion of the phosphorus ylides to electron-poor *N*-vinyl imidazoles in solvent-free conditions under thermal (90 °C, 30 min) conditions. It may be speculated that the polar amphoteric surface (OH groups of the silica NPs) facilitates the interaction of adsorbed weak acidic and basic components due to stabilization of the corresponding transition states and intermediates by H-bonding. It seems that the interactions with the neighboring silanol groups are plausible factors in the rate acceleration. Participation of two proximate silanol groups (one as an H-bond donor and the other as an H-bond acceptor) in the reaction mechanism also seems to be plausible.

Keywords: Acetylenic Esters; *N*-Vinyl Imidazole; Phosphorus ylides; Silica nanoparticles; Solvent-free conditions; Vinyltriphenylphosphonium salts.

INTRODUCTION

Imidazole chemistry currently attracts considerable attention, where the imidazole derivatives are widely applied as *N*-ligand coordinating transition metals [1, 2]. The application of imidazoles in medicinal chemistry [3] or chemistry of natural products/alkaloids [4, 5] or of 1,3-disubstituted imidazole salts as ionic liquids [6, 7] are also well known.

1-Vinylimidazole is employed as a copolymer in the production of cationic polymers for various uses. Alkylimidazoles are used as hardeners for epoxy resins

and for polyurethanes [8]. Less important uses for alkyl- and arylimidazoles include photography and dyes [8].

In recent years, nanoparticles (NPs) have attracted tremendous attention in catalysis because of their improved efficiency under mild and environmentally benign conditions in the context of ecological (Green) synthesis [9, 10]. Due to their enormously large and highly reactive surface area, NPs have potential to exhibit superior catalytic activity in comparison to bulk counterparts [11, 12].

-Additions of nucleophiles to the vinyl group of vinylic phosphonium salts leading to the formation of new alkylidenephosphoranes have attracted much attention as a very convenient and synthetically useful method in organic synthesis [13]. Organophosphorus

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compounds have been extensively used in organic synthesis as useful reagents as well as ligands of a number of transition metal catalysts [14]. Phosphorus ylides are a class of a special type of zwitterions, which bear strongly nucleophilic electron-rich carbanions. The electron distribution around the P⁺-C⁻ bond and its consequent chemical implications had been probed and assessed through theoretical, spectroscopic, and crystallographic investigations [13-16]. In recent years, we have established a one-pot method for the synthesis of stabilized phosphorus ylides [17-28].

In this article, we wish to report a simple and practical procedure for the preparation of electron-poor *N*-vinyl imidazole derivatives from acetylenic esters and azathioprine or imidazole or theophylline and triphenylphosphine in the presence of silica nanoparticles (silica NPs, ca. 42 nm) in high yields.

EXPERIMENTAL

Starting materials and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. The methods used to follow the reactions are TLC and NMR, which indicated that there is no side product. M.P. were measured with an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ¹H- and ¹³C-NMR spectra were measured (CDCl₃) with a BRUKER DRX-250 AVANCE spectrometer at 250.0 and 62.5 MHz, respectively. Flash chromatography columns were prepared with Merck silica gel powder.

A heterogeneous mixture of acetylenic ester (1 mmol) and silica nanoparticles (0.1 g), were added to a heterogeneous mixture of triphenylphosphine (1 mmol), imidazole derivative (1 mmol), and silica nanoparticles (0.2 g), then the heterogeneous mixture were heated (without stirring) in an oven at 90°C for 30 min. After completion of the reaction, flash column chromatography (petroleum ether/ethyl acetate) of the residue gave *N*-vinyl imidazole Derivative 4. The structures of the isolated products were confirmed by IR, ¹H, and ¹³C NMR spectroscopy.

Selected data for methyl-2-{6-[(1-methyl-4-nitro-1H-imidazol-5-yl)sulfanyl]-7H-purin-7-yl} acrylate (4a).

Viscous yellow oil; Yield: 80%. IR(neat)(_{max}, cm⁻¹): 3123, 2923, 1738, 1646 and 1192. ¹H NMR (CDCl₃)_H: 3.76 (s, 3 H, CH₃), 3.89 (s, 3 H, OCH₃), 6.42 and 6.75 (2 d, 2H, ²J_{HH} = 1.0 Hz, =CH₂), 7.76 and 8.24 (2 s, 2 H, CH=N

of imidazole), 8.59 (s, 1 H, CH=N of pyrimidine). ¹³C NMR (CDCl₃)_C: 33.21 (CH₃), 53.36 (OCH₃), 125.19 (=CH₂), 138.03 and 143.94 (2 CH of imidazole), 152.54 (CH of pyrimidine), 116.51, 130.57, 138.03, 150.35 and 157.04 (6 C), 162.24 (C=O of ester).

Selected data for ethyl (Z)-2-{6-[(1-methyl-4-nitro-1H-imidazol-5-yl)sulfanyl]-7H-purin-7-yl}-3-phenyl-2-propenoate (4b).

Viscous yellow oil; Yield: 87%. IR (Neat) (_{max}, cm⁻¹): 3115, 2930, 1723, 1646, 1269 and 1207. ¹H NMR (CDCl₃)_H: 1.31 (t, 3 H, ³J_{HH} = 7.0 Hz, CH₃ of OEt), 3.75 (s, 3 H, CH₃), 4.33 (q, 2 H, ³J_{HH} = 7.0 Hz, OCH₂ of OEt), 6.90 (d, 2 H, ³J_{HH} = 7.3 Hz, arom), 7.22-7.37 (m, 5 H, arom), 7.76 (s, 1 H, =CH), 7.90 and 8.16 (2 s, 2 H, CH=N of imidazole), 8.53 (s, 1 H, CH=N of pyrimidine). ¹³C NMR (CDCl₃)_C: 14.17 and 33.29 (2 CH₂), 62.58 (OCH₂ of OEt), 121.29 (CH of vinyl), 129.29, 129.80 and 130.83 (5 CH of Ph), 141.13 and 144.07 (2 CH of imidazole), 152.76 (CH of pyrimidine), 116.87, 129.29, 131.49, 138.00, 150.35 and 157.01 (7 C), 163.00 (C=O of ester).

Selected Data for Methyl 2-(1,3-dimethyl-2,6-dioxo-1,3,3,6-tetrahydro-7H-purin-7-yl) acrylate (4c).

Colorless crystals. Yield: 97%. m.p. 160-163 °C. IR (KBr) (_{max}, cm⁻¹): 2953, 1707, 1669, 1453, 1230. ¹H NMR (CDCl₃)_H: 3.36, 3.60 (2s, 6H, 2CH₃); 3.86 (1s, 3H, OCH₃); 5.99-6.51 (d of d, 2H, ²J_{HH} = 1Hz, =CH₂); 7.63 (1s, 1H, imidazol). ¹³C NMR (CDCl₃)_C: 28.07 and 29.66 (2CH₃); 53.23 (OCH₃); 107.94, 133.39 and 148.74 (3C); 123.69 (=CH₂); 140.95 (CH imidazol); 151.60 and 154.47 (2C=O of amide); 162.33(C=O of ester).

Selected data for Ethyl 2-(1,3-dimethyl-2,6-dioxo-1,3,3,6-tetrahydro-7H-purin-7-yl) acrylate (4d).

Colorless crystals. Yield: 95%; m.p. 143-146 °C. IR (KBr) (_{max}, cm⁻¹): 2984, 1715, 1676, 1453, 1230. ¹H NMR (CDCl₃)_H: 1.27 (1t, 3H, ³J_{HH} = 7.25 Hz, CH₃); 3.38, 3.62 (2s, 6H, 2CH₃); 4.29 (q, 2H, ³J_{HH} = 7 Hz, OCH₂); 5.99-6.52 (d of d, 2H, ²J_{HH} = 1Hz, =CH₂); 7.63 (1s, 1H, imidazol). ¹³C NMR (CDCl₃)_C: 14.04, 28.07 and 29.66 (3CH₃); 62.55 (OCH₂); 107.97, 133.62 and 148.73 (3C); 123.42 (=CH₂); 141 (CH imidazol); 151.64 and 154.46 (2C=O of amide); 161.82 (C=O of ester).

Selected data for ethyl (Z,E)-2-(1,3-dimethyl-2,6-dioxo-1,3,3,6-tetrahydro-7H-purin-7-yl)-3-phenyl-2-peropenoate (4e).

Colorless crystals. Yield: 97 %; m.p: 145-148 °C. IR (KBr) (_{max}, cm⁻¹): 2946, 1707, 1661, 1453, 1269. ¹H NMR

(CDCl₃, %E = 40 and %Z = 60) for Z: $\delta_{\text{H}} = 1.28$ (1t, 3H, $^3J_{\text{HH}} = 7$ Hz, CH₃); 3.31 and 3.58 (2s, 6H, 2CH₃); 4.29 (q, 2H, $^3J_{\text{HH}} = 7$ Hz, OCH₂); 6.93 (d, 2H, $^3J_{\text{HH}} = 7.25$ Hz, arom); 7.20-7.29 (m, 3H, arom); 7.40 (1s, 1H, imidazol); 7.89 (1s, 1H, =CH); ¹³C NMR (CDCl₃) for Z: $\delta_{\text{C}} = 14.13, 27.95$ and 29.91 (3CH₃); 62.28 (OCH₂); 129.11, 129.70, 130.90, 138.66 and 141.19 (7CH); 107.39, 123.77, 131.06 and 148.68 (5C); 151.64 and 154.24 (2C=O of amide); 163.10 (C=O of ester). ¹H NMR (CDCl₃, %E = 40 and %Z = 60) for E: $\delta_{\text{H}} = 1.59$ (1t, 3H, $^3J_{\text{HH}} = 7.25$ Hz, CH₃); 3.40 and 3.65 (2s, 6H, 2CH₃); 4.25 (q, 2H, $^3J_{\text{HH}} = 7$ Hz, OCH₂); 7.30 (1s, 1H, =CH); 7.34-7.77 (m, 5H, arom); 7.81 (1s, 1H, imidazol); ¹³C NMR (CDCl₃) for E: $\delta_{\text{C}} = 13.55, 28.07$ and 29.90 (3CH₃); 62.02 (OCH₂); 128.38, 129.70, 131.98, 132.14 and 141.58 (7CH); 107.96, 125.96, 137.02 and 148.75 (4C); 151.61 and 154.50 (2C=O of amide); 162.75 (C=O of ester).

Selected data for Dimethyl (Z,E)-2-(1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydro-7H-purin-7-yl)butenedioate (4f).

Viscous yellow oil, Yield: 90% IR (Neat) (ν_{max} , cm⁻¹): 3115, 2953, 1715, 1669, 1230 and 1276. ¹H NMR (CDCl₃, %E = 21 and %Z = 79) for Z: $\delta_{\text{H}} = 3.32$ and 3.60 (2s, 6H, 2CH₃), 3.69 and 3.83 (2s, 6H, 2OCH₃), 7.67 (1s, 1H, =CH), 7.11 (1s, 1H, imidazol). ¹³C NMR (CDCl₃) for Z: $\delta_{\text{C}} = 28.03$ and 30.03 (2CH₃), 52.67 and 53.88 (2OCH₃), 102.84, 134.19 and 148.47 (3C), 125.43 (=CH), 142.44 (CH imidazol), 151.57 and 154.55 (2C=O of amid), 162.14 and 162.80 (2C=O of ester). ¹H NMR (CDCl₃, %E = 21 and %Z = 79) for E: $\delta_{\text{H}} = 3.35$ and 3.58 (2s, 6H, 2CH₃), 3.78 and 3.83 (2s, 6H, 2OCH₃), 6.64 (1s, 1H, =CH), 7.72 (1s, 1H, imidazol). ¹³C NMR (CDCl₃) for E: $\delta_{\text{C}} = 28.26$ and 30.03 (2CH₃), 52.72 and 53.64 (2OCH₃), 104.02, 134.19 and 148.47 (3C), 123.03 (=CH), 141.11 imidazol), 151.57 and 154.55 (2C=O of amid), 162.14 and 162.80 (2C=O of ester).

Selected data for ethyl (Z)-2-(1H-imidazol-1-yl)-3-phenyl-2-propenoate (4g).

White crystals; Yield: 98%, mp: 90-92 °C. IR (KBr) (ν_{max} , cm⁻¹): 2969, 1712, 1643, 1257 and 1211. ¹H NMR (CDCl₃) $\delta_{\text{H}} = 1.35$ (t, 3H, $^3J_{\text{HH}} = 7.0$ Hz, CH₃ of OEt), 4.33 (q, 2H, $^3J_{\text{HH}} = 7.0$ Hz, OCH₂ of OEt), 6.89 and 7.29 (2d, 2H, CH=CH of imidazole), 7.25-7.35 (m, 5H, arom), 7.44 (s, 1H, =CH), 7.85 (s, 1H, =CH of imidazole). ¹³C NMR (CDCl₃) $\delta_{\text{C}} = 14.17$ (CH₃), 62.14 (OCH₂ of OEt), 119.37, 130.06 and 138.15 (3 CH of imidazole), 125.12 (CH of vinyl), 128.99, 130.06 and 130.92, (5 CH of Ph), 131.27 and 137 (2C), 163.78 (C=O of ester).

RESULTS AND DISCUSSION

Silica NPs were prepared by thermal decomposition of rice hulls [29-31]. The results from XRD showed that the sample was silica NPs as indicated by broadened peaks around $2\theta = 22$ (Fig. 1). The morphology and grain size of the silica NPs was investigated by scanning electron microscopy (SEM) (Fig. 2).

Silica NPs were found to catalyze the formation of N-vinyl imidazole derivatives **4** (X or Y) from triphenylphosphine **1** and acetylenic esters **2**, by NH-acids (azathioprine, imidazole and theophylline) **3** under solvent-free conditions in high yields (Fig. 3 and Table 1). We have also used silica-gel powder instead of silica NPs in this reaction, but the reaction times and the amounts of used silica gel powder as catalyst were very high [27, 28]. The use of just 0.3 g of silica NPs (per mmol of reactants) was sufficient to push the reaction forward. Higher amounts of silica NPs (0.4 g) did not improve the result to a great extent (Table 2).

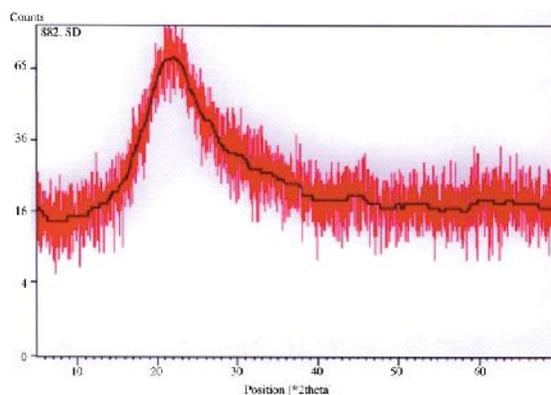


Fig. 1: X-ray diffraction pattern of the synthesized silica nanoparticles.

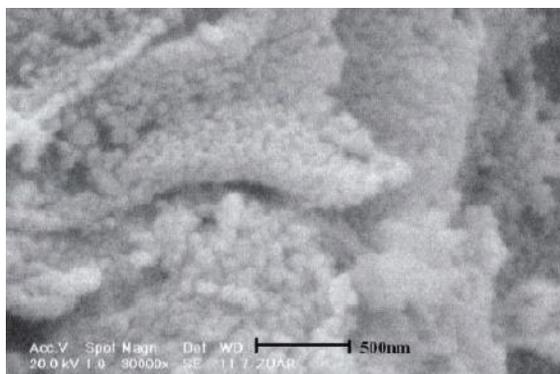
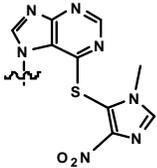
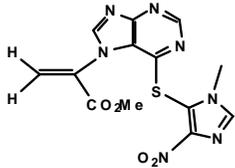
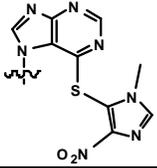
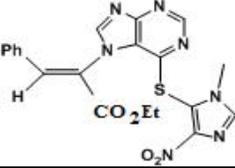
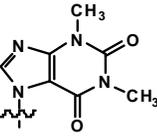
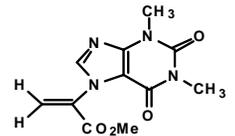
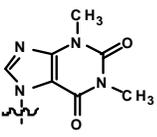
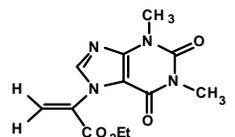
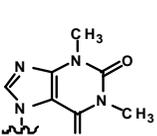
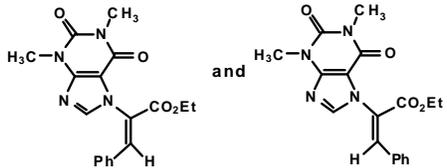
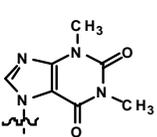
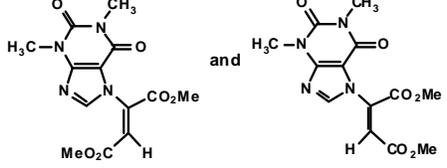
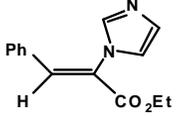


Fig. 2: SEM of the synthesized silica nanoparticles.

Table 1: Synthesis of *N*-vinyl imidazole derivatives 4 from acetylenic esters in the presence of silica nanoparticles.^{a)} (See Fig. 3).

4	Z	E ₁	E ₂	Product	% Yield ^{ab}
a		H	CO ₂ Me		80
b		Ph	CO ₂ Et		87
c		H	CO ₂ Me		97
d		H	CO ₂ Et		95
e		Ph	CO ₂ Et		97
f		CO ₂ Me	CO ₂ Me		90
g		Ph	CO ₂ Et		98

^{a)} cf. Fig. 3; 0.3 g SiO₂ NPs/mmol reactants were applied.^{b)} Yield of isolated 4.

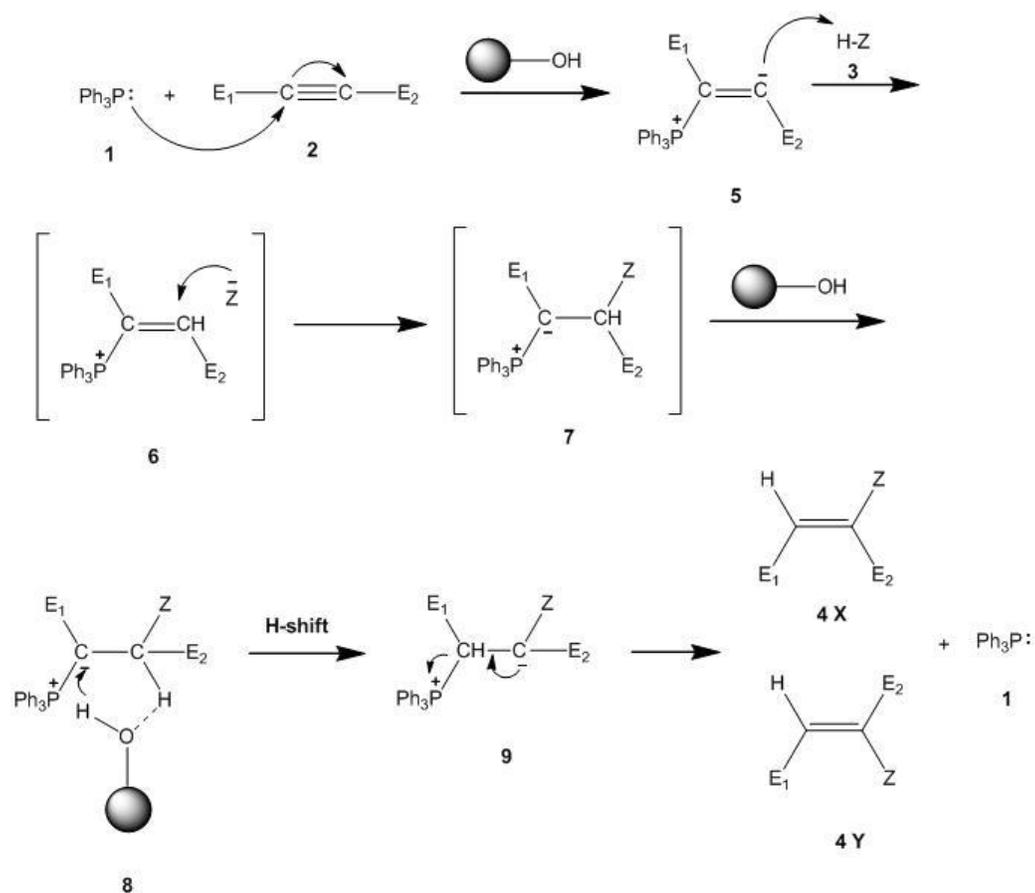


Fig. 4: Proposed mechanism for the preparation of *N*-vinyl imidazole derivatives 4 (X or Y) from acetylenic esters 2 and imidazoles 3 in the presence of silica nanoparticles.

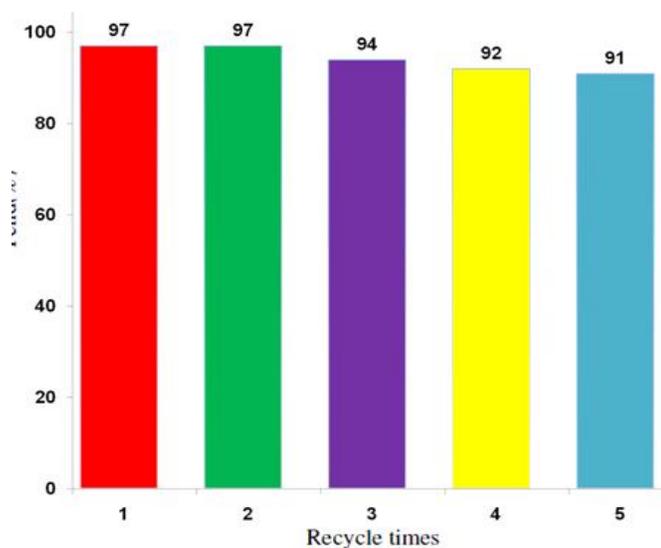


Fig. 5: Recycle of the catalyst.

Table 3: Selected physical and spectral data for *N*-vinyl imidazole derivatives 4 (See Fig. 3 and Experimental section).

4	Physical data	IR (max, cm ⁻¹)	¹ H NMR (CDCl ₃) _H (ppm)	¹³ C NMR (CDCl ₃) _C (ppm)
a	Viscous yellow oil	(Neat): 3123, 2923, 1738, 1646 and 1192.	3.76 (s, 3 H, CH ₃), 3.89 (s, 3 H, OCH ₃), 6.42 and 6.75 (2 d, 2H, ³ J _{HH} = 1.0 Hz, =CH ₂), 7.76 and 8.24 (2 s, 2 H, CH=N of imidazole), 8.59 (s, 1 H, CH=N of pyrimidine).	33.21 (CH ₃), 53.36 (OCH ₃), 125.19 (=CH ₂), 138.03 and 143.94 (2 CH of imidazole), 152.54 (CH of pyrimidine), 116.51, 130.57, 138.03, 150.35 and 157.04 (6 C), 162.24 (C=O of ester).
b	Viscous yellow oil	(Neat): 3115, 2930, 1723, 1646, 1269 and 1207.	1.31 (t, 3 H, ³ J _{HH} = 7.0 Hz, CH ₃ of OEt), 3.75 (s, 3 H, CH ₃), 4.33 (q, 2 H, ³ J _{HH} = 7.0 Hz, OCH ₂ of OEt), 6.90 (d, 2 H, ³ J _{HH} = 7.3 Hz, arom), 7.22-7.37 (m, 5 H, arom), 7.76 (s, 1 H, =CH), 7.90 and 8.16 (2 s, 2 H, CH=N of imidazole), 8.53 (s, 1 H, CH=N of pyrimidine).	14.17 and 33.29 (2 CH ₃), 62.58 (OCH ₂ of OEt), 121.29 (CH of vinyl), 129.29, 129.80 and 130.83 (5 CH of Ph), 141.13 and 144.07 (2 CH of imidazole), 152.76 (CH of pyrimidine), 116.87, 129.29, 131.49, 138.00, 150.35 and 157.01 (7 C), 163.00 (C=O of ester).
c	Colorless crystals, m.p. 160-163 °C.	(KBr): 2953, 1707, 1669, 1453, 1230.	3.36, 3.60 (2s, 6H, 2CH ₃); 3.86 (1s, 3H, OCH ₃); 5.99-6.51 (d of d, 2H, ² J _{HH} = 1Hz, =CH ₂); 7.63 (1s, 1H, imidazol).	28.07 and 29.66 (2CH ₃); 53.23 (OCH ₃); 107.94, 133.39 and 148.74 (3C); 123.69 (=CH ₂); 140.95 (CH imidazol); 151.60 and 154.47 (2C=O of amide); 162.33(C=O of ester).
d	Colorless crystals, m.p. 143-146 °C.	(KBr): 2984, 1715, 1676, 1453, 1230.	1.27 (1t, 3H, ³ J _{HH} = 7.25 Hz, CH ₃); 3.38, 3.62 (2s, 6H, 2CH ₃); 4.29 (q, 2H, ³ J _{HH} = 7 Hz, OCH ₂); 5.99-6.52 (d of d, 2H, ² J _{HH} = 1Hz, =CH ₂); 7.63 (1s, 1H, imidazol).	14.04, 28.07 and 29.66 (3CH ₃); 62.55 (OCH ₂); 107.97, 133.62 and 148.73 (3C); 123.42 (=CH ₂); 141 (CH imidazol); 151.64 and 154.46 (2C=O of amide); 161.82 (C=O of ester).
e	Colorless crystals, m.p. 145-148 °C.	(KBr): 2946, 1707, 1661, 1453, 1269.	(% E = 40 and % Z = 60) for E: 1.59 (1t, 3H, ³ J _{HH} = 7.25 Hz, CH ₃); 3.40 and 3.65 (2s, 6H, 2CH ₃); 4.25 (q, 2H, ³ J _{HH} = 7 Hz, OCH ₂); 7.30(1s, 1H, =CH); 7.34-7.77 (m, 5H, arom); 7.81 (1s, 1H, imidazol);	for Z: c = 14.13, 27.95 and 29.91 (3CH ₃); 62.28 (OCH ₂); 129.11, 129.70, 130.90, 138.66 and 141.19 (7CH); 107.39, 123.77, 131.06 and 148.68 (5C); 151.64 and 154.24 (2C=O of amide); 163.10 (C=O of ester). for E: c = 13.55, 28.07 and 29.90 (3CH ₃); 62.02 (OCH ₂); 128.38, 129.70, 131.98, 132.14 and 141.58 (7CH); 107.96, 125.96, 137.02 and 148.75 (4C); 151.61 and 154.50 (2C=O of amide); 162.75 (C=O of ester).
f	Viscous yellow oil	(Neat): 3115, 2953, 1715, 1669, 1230 and 1276.	(% E = 21 and % Z = 79) for Z: <i>H</i> = 3.32 and 3.60 (2s, 6H, 2CH ₃), 3.69 and 3.83 (2s, 6H, 2OCH ₃), 7.67 (1s, 1H, =CH), 7.11 (1s, 1H, imidazol). for E: <i>H</i> = 3.35 and 3.58 (2s, 6H, 2CH ₃), 3.78 and 3.83 (2s, 6H, 2OCH ₃), 6.64 (1s, 1H, =CH), 7.72 (1s, 1H, imidazol).	for Z: c: 28.03 and 30.03 (2CH ₃), 52.67 and 53.88 (2OCH ₃), 102.84, 134.19 and 148.47 (3C), 125.43 (=CH), 142.44 (CH imidazol), 151.57 and 154.55 (2C=O of amid), 162.14 and 162.80 (2C=O of ester). for E: c = 28.26 and 30.03 (2CH ₃), 52.72 and 53.64 (2OCH ₃), 104.02, 134.19 and 148.47 (3C), 123.03 (=CH), 141.11 imidazol), 151.57 and 154.55 (2C=O of amid), 162.14 and 162.80 (2C=O of ester).
g	White crystals, mp: 90-92 °C.	(KBr): 2969, 1712, 1643, 1257 and 1211.	1.35 (t, 3 H, ³ J _{HH} = 7.0 Hz, CH ₃ of OEt), 4.33 (q, 2 H, ³ J _{HH} = 7.0 Hz, OCH ₂ of OEt), 6.89 and 7.29 (2 d, 2 H, CH=CH of imidazole), 7.25-7.35 (m, 5 H, arom), 7.44 (s, 1 H, =CH), 7.85 (s, 1 H, =CH of imidazole).	14.17 (CH ₃), 62.14 (OCH ₂ of OEt), 119.37, 130.06 and 138.15 (3 CH of imidazole), 125.12 (CH of vinyl), 128.99, 130.06 and 130.92, (5 CH of Ph), 131.27 and 137 (2 C), 163.78 (C=O of ester).

CONCLUSION

In conclusion, we have developed a convenient and one-pot for preparing electron-poor imidazoles in the presence of silica NPs. The ease of workup and high yields of products make this procedure a useful addition to modern synthetic methods. Furthermore, this solvent-free reaction has many advantages: reduced pollution, low costs, and simplicity in process and handling. These factors may be important, especially in industry.

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