SUPPLEMENTARY INFORMATION

Dicalcium phosphate dehydrate DCPD as a highly efficient and reusable catalyst for Knoevenagel condensation

Zakaria Benzekri^a, Kamal El Mejdoub^b, Said Boukhris^{a*}, Brahim Sallek^b, Brahim Lakhrissi^b,

Abdelaziz Souizi^a

^a Laboratoire de Chimie Organique, Organométallique et Théorique. Faculté des Sciences, Université Ibn Tofaïl,, 14000 Kenitra, Morocco

^b Laboratoire d'Agroressources et Génie des Procédés. Faculté des Sciences, Université Ibn Tofaïl,, 14000 Kenitra, Morocco

Corresponding author e-mail: nsboukhris@yahoo.com

Table of Contents

Section	Page No.
1. Experimental section	2
1.1 General experimental details	2
1.2 General procedure for the synthesis of catalyst (DCPD)	2
1.2 Typical procedure for the Knoevenagel reaction	2-3
2. Spectroscopic characterization data	3-5
3. ¹H NMR and ¹³C NMR spectra of all the products	6-17

1. Experimental

1.1 General experimental details

All reactions were monitored by TLC on silica gel plates (Fluka Kieselgel 60 F₂₅₄). The products were purified by recrystallization in ethanol. Melting points were taken on a KOFER hot stage apparatus and are uncorrected. FT-IR spectra were recorded using KBr pellets on a Tensor-27 infrared spectrometer and absorptions were reported as wave numbers (cm⁻¹). ¹H NMR and ¹³C NMR spectra were recorded on a Bruker 300-MHz spectrometer in CDCl₃ using TMS as an internal reference (chemical shift in δ ppm). Mass spectra were recorded on a Thermo DSQII-Focus mass spectrometer.

1.2 General procedure for the synthesis of catalyst (DCPD)

Dicalcium phosphate dihydrate (DCPD) was prepared by mixing 50 mL of a 0.3M solution of ammonium di-hydrogenophosphate ((NH₄)H₂PO₄) with 50 mL of a 0.5M solution calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O) at room temperature. After 2 hours of maturation. The precipitate was collected by vacuum filtration, washed with deionized water and freeze dried overnight.

1.3 Typical procedure for the Knoevenagel reaction

A 10 mL round bottomed flask was charged with the carbonyl compound (1 mmol), active methylene compound (1 mmol), **DCPD** (0.01 g, 5.8 × 10⁻² mmol) and ethanol (3 mL). The reaction mixture was stirred at room temperature for 10 min (or 3 min at reflux). Progress of the reaction was monitored by TLC, using *n*-hexane–EtOAc (5:1) as eluent. After completion of the reaction, 5 mL of water was added and the mixture was extracted three times with dichloromethane. The catalyst was removed by filtration and washed with ethanol-H₂O. The solid product was obtained after solvents were removed under vacuum. The product **3a** was purified through recrystallisation from ethanol.

The DCPD could be recycled after vaporizing water-ethanol. The recycled DCPD could be used repeatedly under the same reaction conditions.

The products prepared **3** are known compounds^[47, 50-51] and were confirmed by comparing the IR, ¹H NMR, ¹³C NMR and mass spectral data with authentic samples reported in the literature. The spectral data of all products are given below:

2. Spectroscopic characterization data

2-(4-chlorophenylmethylene) malononitrile (3a)

Colorless solid, mp 158-159°C (lit.^[50] 159-160°C); IR (KBr) ν : 2222, 1585. ¹H NMR (300 MHz, DMSO-d₆) δ : 7.67 (d, 2H, J = 8.7 Hz, ArH), 7.92 (d, 2H, J = 8.7 Hz, ArH), 8.49 (s, 1H, C=CH). ¹³C NMR (300 MHz, DMSO-d₆) δ : 160.5, 139.5, 132.5, 131.6, 130.1, 114.4, 113.4, 82.7. MS: m/z 188 [M]⁺.

2-(phenylmethylene) malononitrile (3b)

Colorless solid, mp 80-81°C (lit.^[50] 80-81°C); IR (KBr) ν : 2225, 1560. ¹H NMR (300 MHz, DMSO-d₆) δ : 7.57-7.70 (m, 3H, ArH), 7.59 (d, 2H, J = 7.2 Hz, ArH), 8.50 (s, 1H, C=CH). ¹³C NMR (300 MHz, DMSO-d₆) δ : 155.7, 134.8, 131.7, 131.6, 130.9, 129.9, 114.6, 113.5, 82.0.

2-(p-tolylmethylene) malononitrile (3c)

White solid, mp 118-119°C (lit.^[51] 118-120°C); IR (KBr) ν : 2222, 1593. ¹H NMR (300 MHz, DMSO-d₆) δ : 2.37 (s, 3H), 7.38 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 8.39 (s, 1H, C=CH). ¹³C NMR (300 MHz, DMSO-d₆) δ : 161.6, 146.1, 131.1, 130.5, 129.1, 114.8, 113.8, 80.3, 21.5. MS: m/z 168 [M]⁺.

2-(4-nitrophenylmethylene) malononitrile (3d)

Yellow solid, mp 161-162°C (lit.^[51] 160-161°C); IR (KBr) ν : 2225, 1600. ¹H NMR (300 MHz, DMSO-d₆) δ : 8.11 (d, J = 8.7 Hz, 2H), 8.29 (d, J = 8.7 Hz, 2H), 8.67 (s, 1H, C=CH). ¹³C NMR (300 MHz, DMSO-d₆) δ : 159.7, 150.1, 137.1, 131.9, 124.8, 114.0, 112.9, 82.4.

Methyl-3-(4-chlorophenyl)-2-cyanoacrylate (3e)

White solid, mp 120-121°C (lit.^[47] 119.2-121.5°C); IR (KBr) ν : 2230, 1720. ¹H NMR (300 MHz, DMSO-d₆) δ : 3.84 (t, 3H, OCH₃), 7.65 (d, 2H, J = 8.4 Hz, ArH), 8.04 (d, 2H, J = 8.4 Hz, ArH), 8.38 (s, 1H, C=CH). ¹³C NMR (300 MHz, DMSO-d₆) δ : 162.5, 154.2, 138.5, 132.5, 130.6, 129.9, 115.8, 103.4, 53.8.

Methyl-2-cyano-3-phenylacrylate (3f)

White solid, mp 84-85°C (lit.^[47] 83.9-85.4°C); IR (KBr) ν : 2235, 1725. ¹H NMR (300 MHz, DMSO-d₆) δ : 3.84 (t, 3H, CH₃), 7.54-7.65 (m, 3H, ArH), 8.03 (d, 2H, J = 8.4 Hz, ArH), 8.38 (s, 1H, C=CH). ¹³C NMR (300 MHz, DMSO-d₆) δ : 162.8, 155.6, 133.9, 131.7, 131.6, 129.8, 115.0, 102.8, 53.8.

Methyl-2-cyano-3-(4-nitrophenyl) acrylate (3g)

Yellow solid, mp 172-173°C (lit.^[47] 171.6-173.8°C); IR (KBr) ν : 2232, 1722. ¹H NMR (300 MHz, DMSO-d₆) δ : 3.88 (s, 3H, CH₃), 8.19 (d, 2H, J = 7.1 Hz, ArH), 8.34 (d, 2H, J = 7.1 Hz, ArH), 8.48 (s, 1H, C=CH). ¹³C NMR (300 MHz, DMSO-d₆) δ : 162.1, 153.1, 149.8, 137.6, 132.1, 131.0, 124.4, 115.1, 107.0, 53.9.

Ethyl-3-(4-chlorophenyl)-2-cyanoacrylate (3h)

Colorless solid, mp 89-90°C (lit.^[50] 89-90°C); IR (KBr) ν : 2230, 1725. ¹H NMR (300 MHz, DMSO-d₆) δ : 1.28 (t, 3H, J = 7.2 Hz, CH₃), 4.29 (q, 2H, J = 7.2 Hz, CH₂), 7.61 (d, 2H, J = 8.7 Hz, ArH), 8.00 (d, 2H, J = 8.7 Hz, ArH), 8.33 (s, 1H, C=CH). ¹³C NMR (300 MHz, DMSO-d₆) δ : 162.0, 154.0, 138.5, 132.8, 130.5, 129.8, 115.7, 103.5, 62.9, 14.3. MS: m/z 235 [M]⁺.

Ethyl-2-cyano-3-phenylacrylate (3i)

Colorless solid, mp 45-46°C (lit.^[50] 46-47°C); IR (KBr) ν : 2235, 1720. ¹H NMR (300 MHz, DMSO-d₆) δ : 1.38 (t, 3H, J = 7.2 Hz, CH₃), 4.29 (q, 2H, J = 7.2 Hz, CH₂), 7.56-7.69 (m, 3H, ArH), 7.92 (d, 2H, J = 7.2 Hz, ArH), 8.50 (s, 1H, C=CH). ¹³C NMR (300 MHz, DMSO-d₆) δ : 162.0, 154.0, 134.8, 131.7, 130.9, 129.9, 115.7, 103.5, 62.9, 14.3.

Ethyl-2-cyano-3-p-tolylacrylate (3j)

White solid, mp 91-92°C (lit.^[51] 90-91°C); IR (KBr) ν : 2235, 1730. ¹H NMR (300 MHz, DMSO-d₆) δ : 1.31 (t, J = 7.2 Hz, 3H), 2.37 (s, 3H), 4.34 (q, J = 7.4 Hz, 2H), 7.79 (d, J = 7.7 Hz, 2H), 7.90 (d, J = 7.2 Hz, 2H), 8.05 (s, 1H). ¹³C NMR (300 MHz, DMSO-d₆) δ : 163.0, 155.5, 144.9, 131.4, 130.4, 129.1, 116.2, 101.2, 63.1, 14.3, 21.3. MS: m/z 215 [M]⁺.

Ethyl-2-cyano-3-(4-nitrophenyl) acrylate (3k)

Yellow solid, mp 168-169°C (lit.^[50] 170-171°C); IR (KBr) ν : 2230, 1720. ¹H NMR (300 MHz, DMSO-d₆) δ : 1.28 (t, 3H, J = 7.2 Hz, CH₃), 4.29 (q, 2H, J = 7.2 Hz, CH₂), 7.62 (d, 2H, J = 8.4 Hz, ArH), 8.02 (d, 2H, J = 8.4 Hz, ArH), 8.30 (s, 1H, C=CH). ¹³C NMR (300 MHz, DMSO-d₆) δ : 162.0, 154.0, 138.4, 132.8, 130.6, 129.9, 115.8, 103.6, 62.9, 14.4.

3. ^1H NMR and ^{13}C NMR spectra of all the products

^1H NMR spectrum of 2-(4-chlorophenylmethylene) malononitrile **3a** (DMSO- d_6).

¹³C NMR spectrum of 2-(4-chlorophenylmethylene) malononitrile **3a** (DMSO-d₆).

¹H NMR spectrum of 2-(phenylmethylene) malononitrile **3b** (DMSO-d₆).

^{13}C NMR spectrum of 2-(phenylmethylene) malononitrile **3b** (DMSO- d_6).

^1H NMR spectrum of 2-(p-tolylmethylene) malononitrile **3c** (DMSO- d_6).

^{13}C NMR spectrum of 2-(4-nitrophenylmethylene) malononitrile **3d** (DMSO- d_6).

^1H NMR spectrum of methyl-3-(4-chlorophenyl)-2-cyanoacrylate **3e** (DMSO- d_6).

^{13}C NMR spectrum of methyl-3-(4-chlorophenyl)-2-cyanoacrylate **3e** (DMSO- d_6).

^1H NMR spectrum of methyl-2-cyano-3-phenylacrylate **3f** (DMSO- d_6).

^{13}C NMR spectrum of methyl-2-cyano-3-phenylacrylate **3f** (DMSO- d_6).

^{13}C NMR spectrum of methyl-2-cyano-3-(4-nitrophenyl) acrylate **3g** (DMSO- d_6)

^1H NMR spectrum of ethyl-3-(4-chlorophenyl)-2-cyanoacrylate **3h** (DMSO- d_6).

¹³C NMR spectrum of ethyl-3-(4-chlorophenyl)-2-cyanoacrylate **3h** (DMSO-d₆).

^1H NMR spectrum of ethyl-2-cyano-3-phenylacrylate **3i** (DMSO- d_6).

^{13}C NMR spectrum of ethyl-2-cyano-3-phenylacrylate **3i** (DMSO- d_6).

^1H NMR spectrum of ethyl-2-cyano-3-p-tolylacrylate **3j** (DMSO- d_6)

¹³C NMR spectrum of ethyl-2-cyano-3-p-tolylacrylate **3j** (DMSO-d₆)

^{13}C NMR spectrum of ethyl-2-cyano-3-(4-nitrophenyl) acrylate **3k** (DMSO- d_6).