Supporting information of:

Amine-functionalized Ionic Liquid Based Mesoporous Organosilica as Highly Efficient Nanocatalyst for the Knoevenagel Condensation

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Contents:

1. General information

The following chemicals were commercially available and used as received: tetramethoxysilane (TMOS), 3-aminopropyl-trimethoxysilane, pluronic P123, KCl, HCl, ethyl cyanoacetate, and all applied aromatic aldehydes (Merck and Fluka). All solvents were purified and dried using standard procedures. Liquid NMR was obtained on a DMX-400 MHz Bruker Advance instrument using $CDCl_3$ as solvent and TMS as internal standard. Nitrogen adsorption-desorption analyses were performed using a Belsorp-BEL, Inc. analyzer at 77 K. Prior to the measurements, the materials were degassed at 373 K for 12 h. The surface areas were calculated by BET method and the pore size distributions were calculated using BJH method. Powder X-ray diffraction (PXRD) pattern of the material was obtained by XRD-diffractometer (X'pert, Philips). Transmission electron microscopy (TEM) images were taken on a FEI Tecnai 12 BioTWIN microscope operated at 150 kV. The thermal gravimetric analysis (TGA) was measured by NETZSCH STA 409 PC/PG from room temperature to 800 °C. The morphology of the material was taken by scanning electron microscopy on a Philips, XL30 microscope. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed using a Brucker-Vector 22.

2. Preparation of PMO-IL-NH$_2$ nanostructure

Preparation of aminopropyl containing ionic liquid based PMO (PMO-IL-NH$_2$) was achieved by simultaneous hydrolysis and co-condensation of tetramethoxysilane (TMOS), 1,3-bis(trimethoxysilylpropyl)imidazolium chloride and 3-aminopropyl-trimethoxysilane in the presence of pluronic P123 under acidic conditions.[1, 2] In a typical procedure, pluronic P123 (2 g) was added to a solution containing deionized water (11.7 g), HCl (2M, 50 g) and potassium chloride (12.2 g) while stirring at 40 °C. After complete dissolution of surfactant, a mixture of tetramethoxysilane (19 mmol), 1,3-bis(trimethoxysilylpropyl)imidazolium chloride (1.8 mmol) and 3-aminopropyl-trimethoxysilane (1.5 mmol) was added to reaction vessel and stirred at the same temperature for 24 h. The mixture was then heated at 100 °C under static conditions for 72 h. After that, the obtained material was filtered, washed with deionized water and dried at room temperature. The removal of surfactant was achieved by a Soxhlet apparatus using ethanol for 48 h. The final material was dried at 70 °C for 12 h and denoted as PMO-IL-NH$_2$.

3. General procedure for the Knoevenagel condensation using PMO-IL-NH$_2$ nanocatalyst:

Aldehyde (1 mmol), ethyl cyanoacetate (1 mmol) and catalyst (0.5 mol%) were added in a flask and stirred vigorously at room temperature. The progress of the reaction was monitored *via* TLC. After completion of the reaction; 5 mL of warm ethanol was added to the reaction vessel and the mixture was hotly filtered and completely washed with ethanol. Pure products were obtained after recrystallization in a mixture of hexane/ethanol solvents or isolated the residue by column chromatography on silica.

4. General procedure for the recovery of PMO-IL-NH$_2$ nanocatalyst in the Knoevenagel reaction:

For this, in a flask containing benzaldehyde (1 mmol) and ethyl acetoacetate (1 mmol), 0.5 mol% of PMO-IL-NH$_2$ catalyst was added and the mixture was magnetically stirred at room temperature. The reaction progress was monitored by TLC. After completion of the reaction, hot ethanol (5 mL) was added and the obtained solution was hotly filtered and washed with ethanol. The recovered catalyst was then washed and reused at the same conditions as the first run for at least 8 times and gave corresponding Knoevenagel product in high yield and selectivity.

5. Procedure for the determination of loading of amine groups in the PMO-IL-NH$_2$

The basic property of the PMO-IL-NH$_2$ was determined with acid–base titration test.[3] For this, the PMO-IL-NH$_2$ material (0.1 g) was degassed in vacuum at 140 °C for 1.5 h and then suspended in decarbonized potassium chloride (0.1 M, 50 mL) solution under an argon atmosphere. The obtained mixture was then titrated with a HCl solution (0.005 M) and the pH was recorded as a function of the volume of titrate added. The loading of amine basic sites were calculated from the amount of HCl added to obtain a pH of 7.0. This demonstrated that the loading of amine groups is 0.25 mmol NH$_2$/g solid.
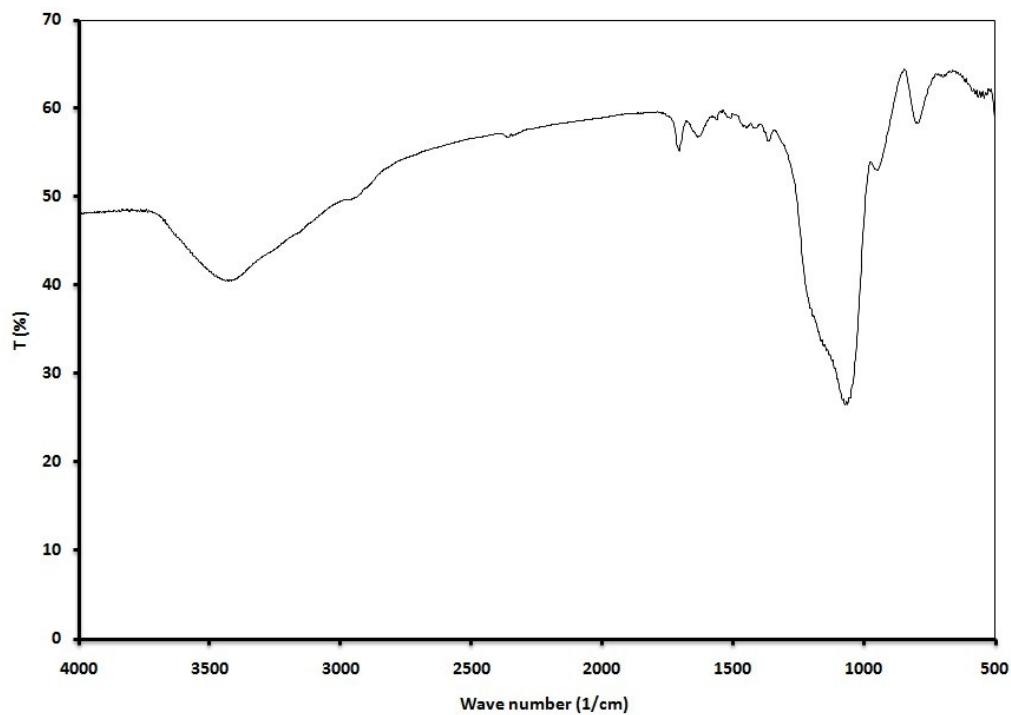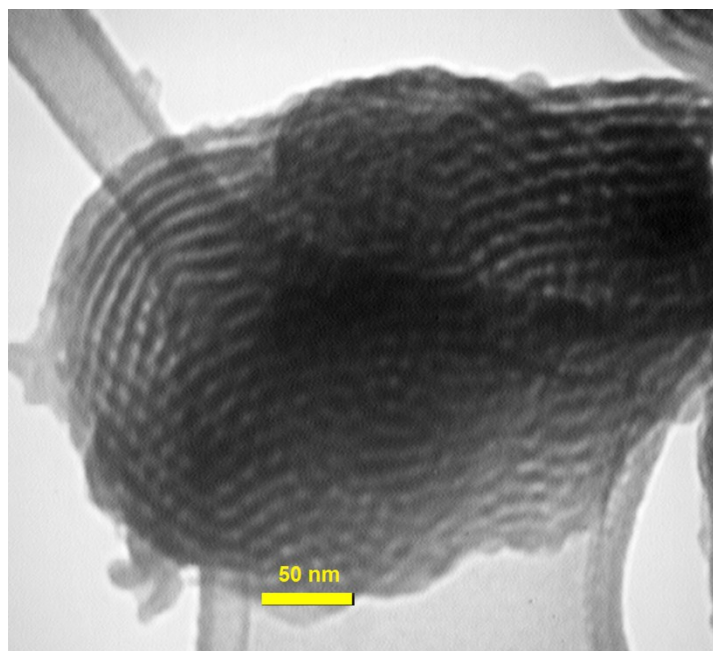
Figure 1S. DRIFT spectrum of PMO-Il-NH$_2$

Figure 2S. TEM image of the recovered PMO-IL-NH$_2$ nanocatalyst after 9th reaction cycle

Table 1S. Reusability of the PMO-IL-NH$_2$ nanocatalyst in the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate

Run	Time (h)	Yield (%)	TON
1	1.5	96	192
2	2	94	188
3	2.5	90	180
4	2.5	90	180
5	3	88	176
6	3	88	176
7	3.5	86	172
8	3.5	84	168
9	3.5	82	164

Table 2S. Structural parameters of PMO-IL-NH$_2$ and recovered PMO-IL-NH$_2$ after fifth cycle (RPMO-IL-NH$_2$) determined from nitrogen sorption experiments

Sample	BET surface area (m^2 g^{-1})	Pore diameter (nm)	Pore volume (cm^3 g^{-1})
PMO-IL-NH$_2$	596	9.1	1.12
RPMO-IL-NH$_2$	438	7.1	0.9

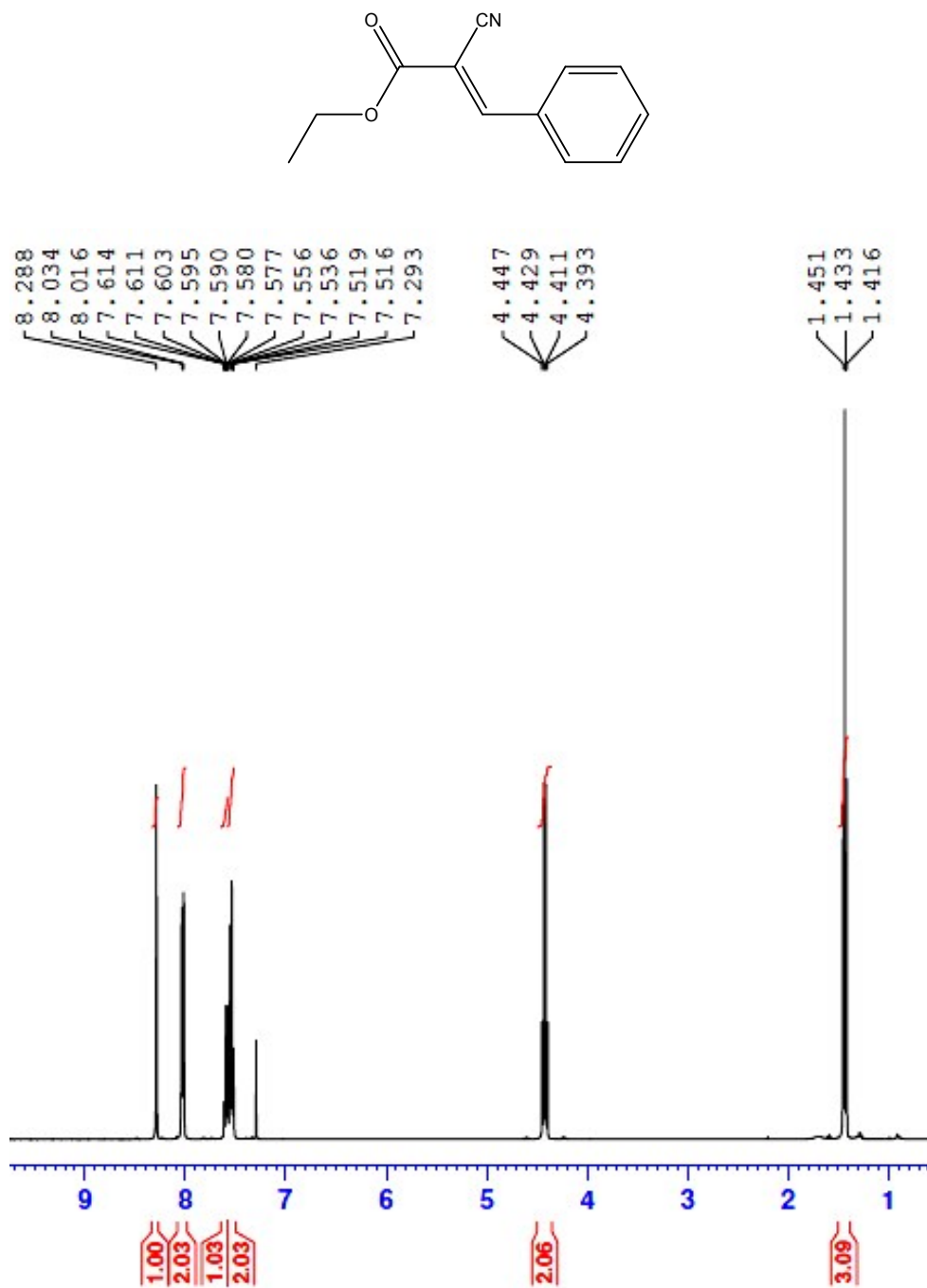**The IR, ¹H-NMR and ¹³C-NMR results of some Knoevenagel products are as following:**

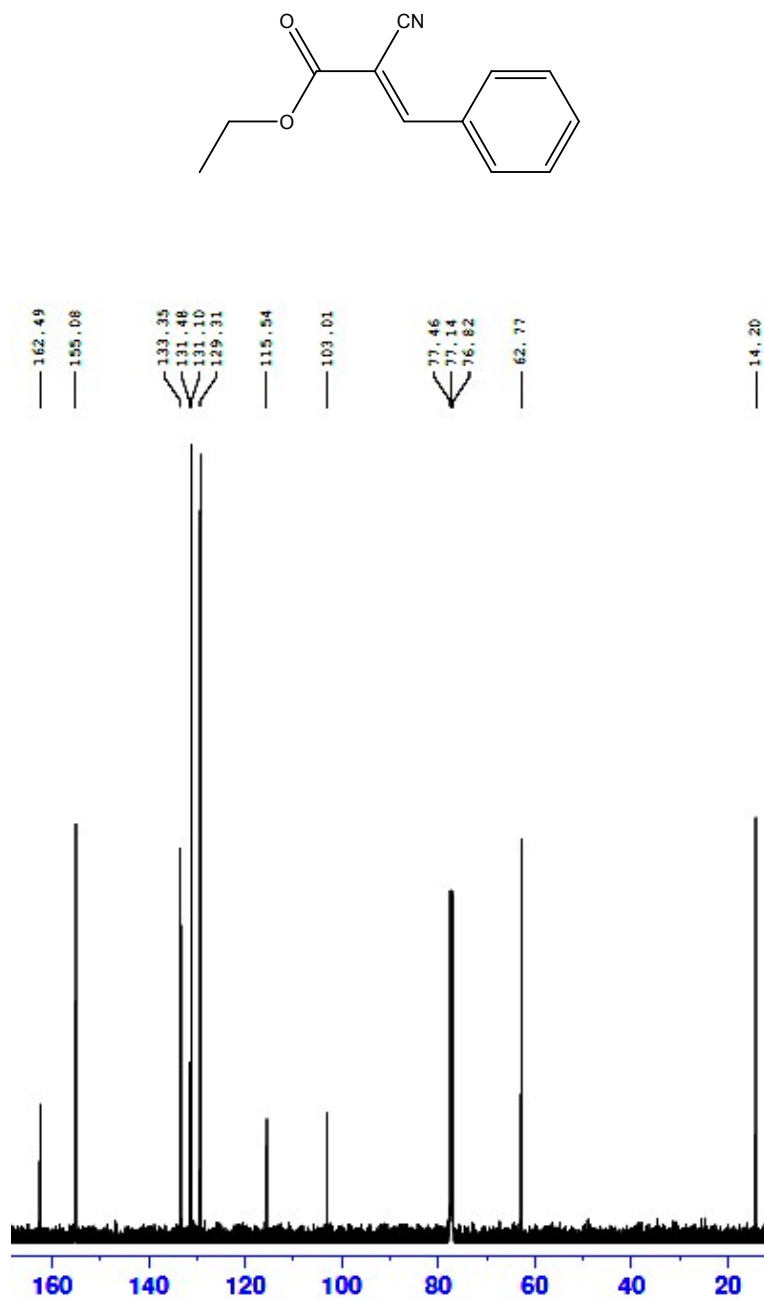**Figure 3S.** ¹H-NMR-spectrum of (*E*)-ethyl 2-cyano-3-phenylacrylate

Figure 4S. ^{13}C-NMR-spectrum of (*E)-ethyl 2-cyano-3-phenylacrylate*

(E)-ethyl 2-cyano-3-phenylacrylate:

IR: (KBr, cm[-1]), 3002.58 (C-H, Stretching, sp[2]), 2940.89 (C-H, Stretching, sp[3]), 2223.45 (CN), 1727.88 (C=O ester), 1606.34 (C=C), 1444-15720 (C=C, Ar).
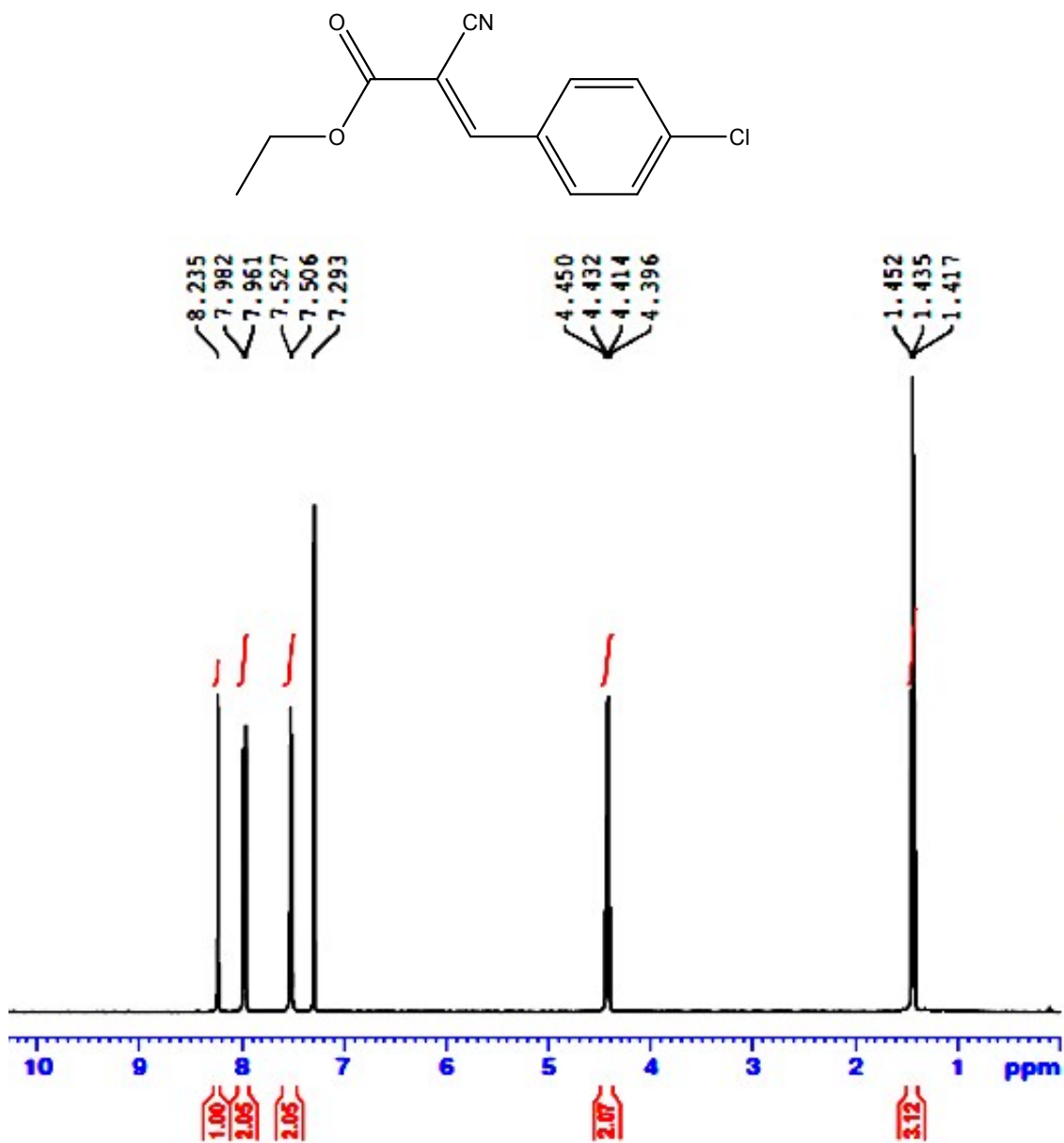
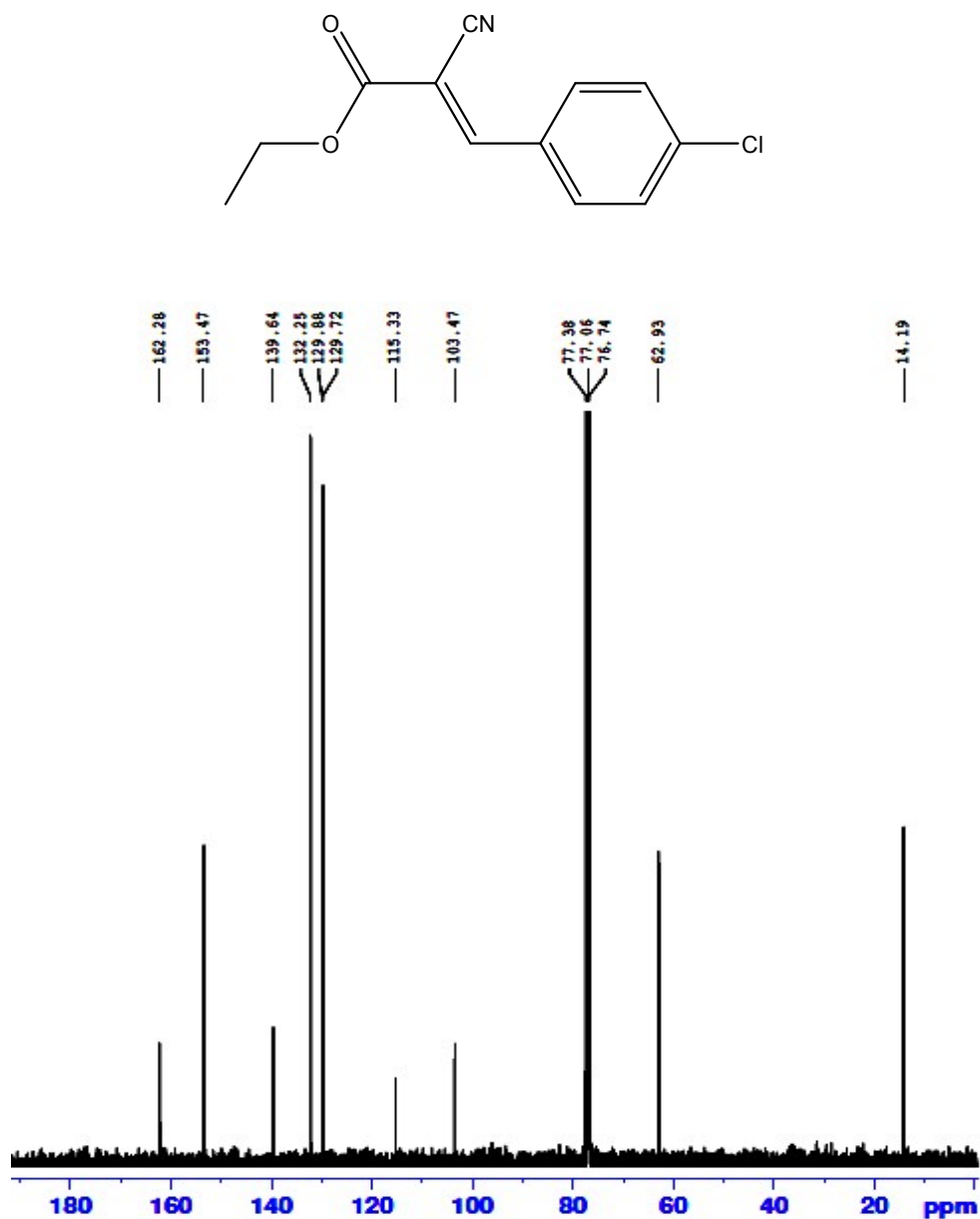**Figure 5S.** ¹H-NMR-spectrum of *(E)-ethyl 3-(4-chlorophenyl)-2-cyanoacrylate*

Figure 6S. ^{13}C-NMR-spectrum of *(E)-ethyl 3-(4-chlorophenyl)-2-cyanoacrylate*

(E)-ethyl 3-(4-chlorophenyl)-2-cyanoacrylate:

IR: (KBr, cm[-1]), 3422 (C-H, Stretching, sp[2]), 2954.3 (C-H, Stretching, sp[3]), 2223.4 (CN), 1723 (C=O, ester), 1411-1612 (C=C, Ar), 1199 (C-O, ester), 1082 (Ar-Cl).
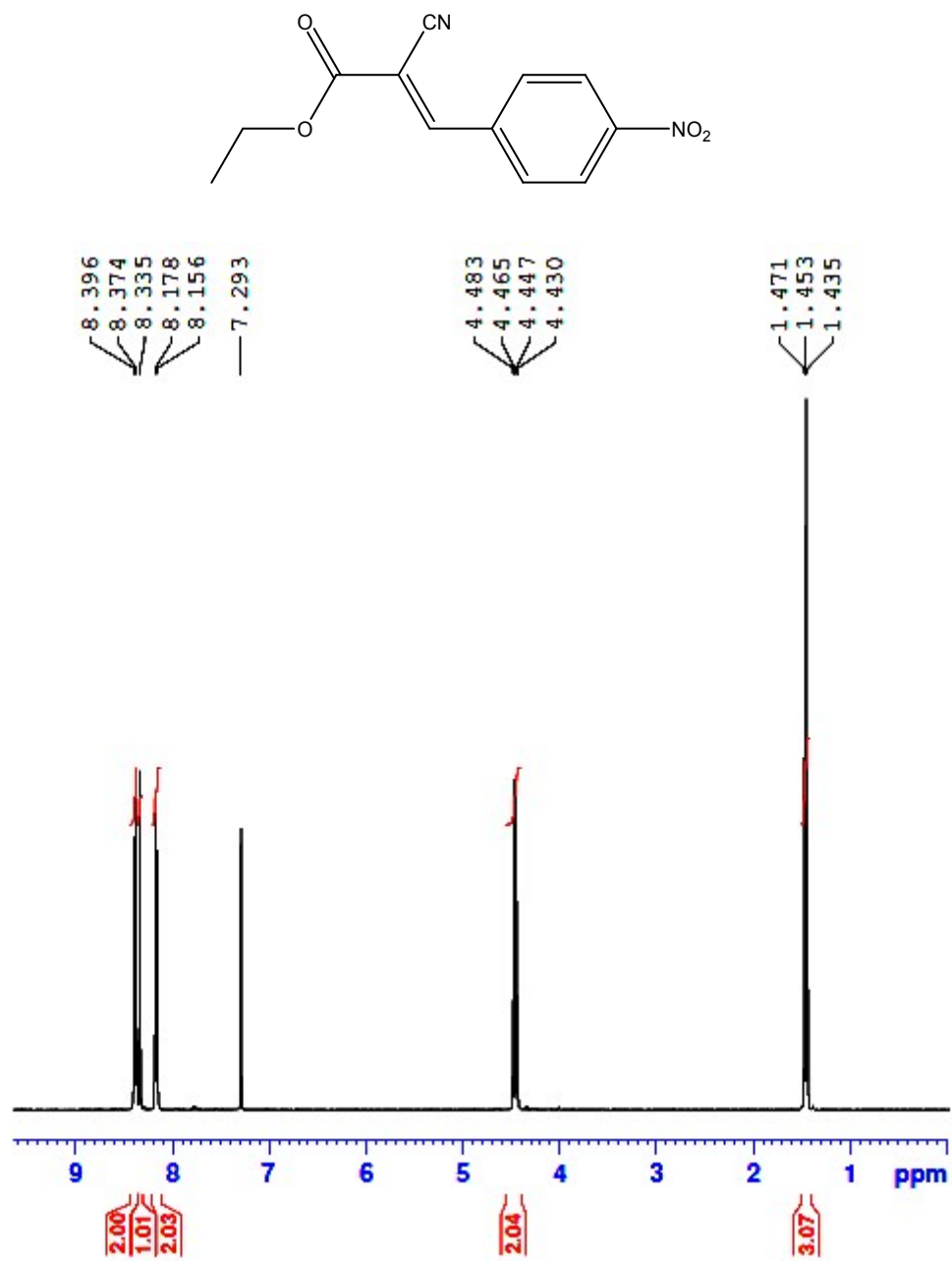
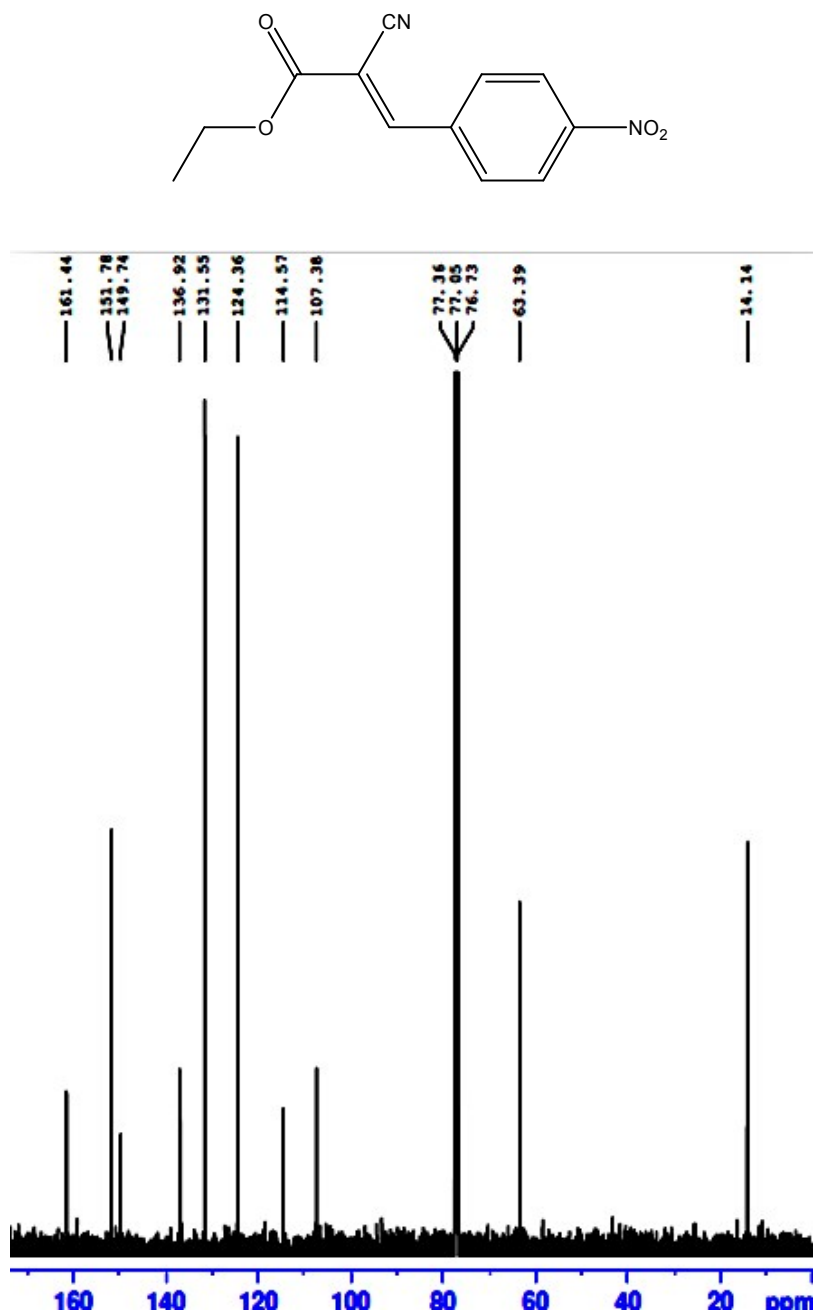**Figure 7S.** ^{1}H-NMR-spectrum of *(E)-ethyl 2-cyano-3-(4-nitrophenyl)acrylate*

Figure 8S. ^{13}C-NMR-spectrum of *(E)-ethyl 2-cyano-3-(4-nitrophenyl)acrylate*

(E)-ethyl 2-cyano-3-(4-nitrophenyl)acrylate:

IR: (KBr, cm^{-1}), 3098 (C-H, Stretching, sp^2), 2992 (C-H, Stretching, sp^3), 2226 (CN), 1722 (C=O, ester), 1512, 1265 (NO$_2$), 1415-1616 (C=CAr), 1007 (C-O, ester).
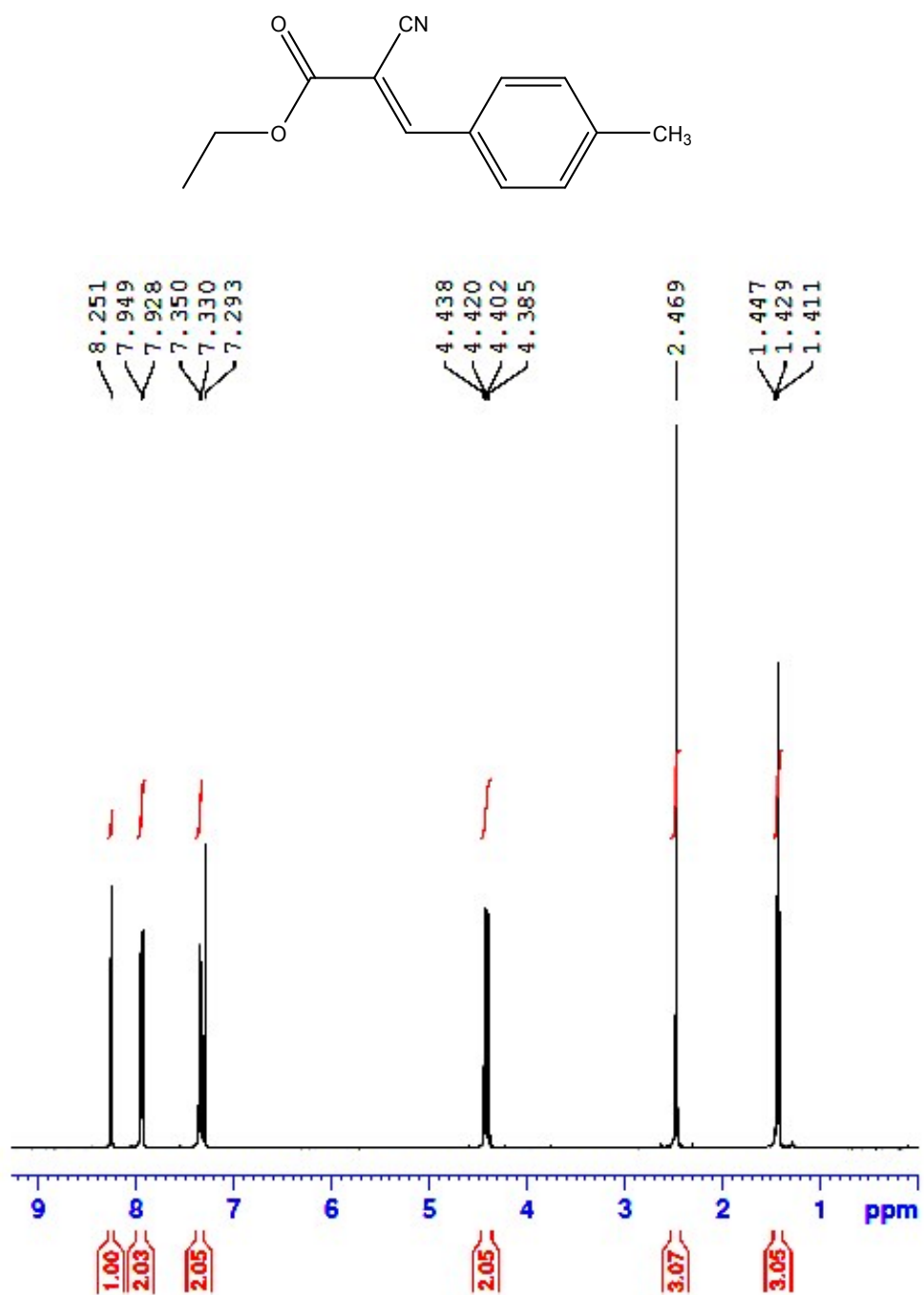
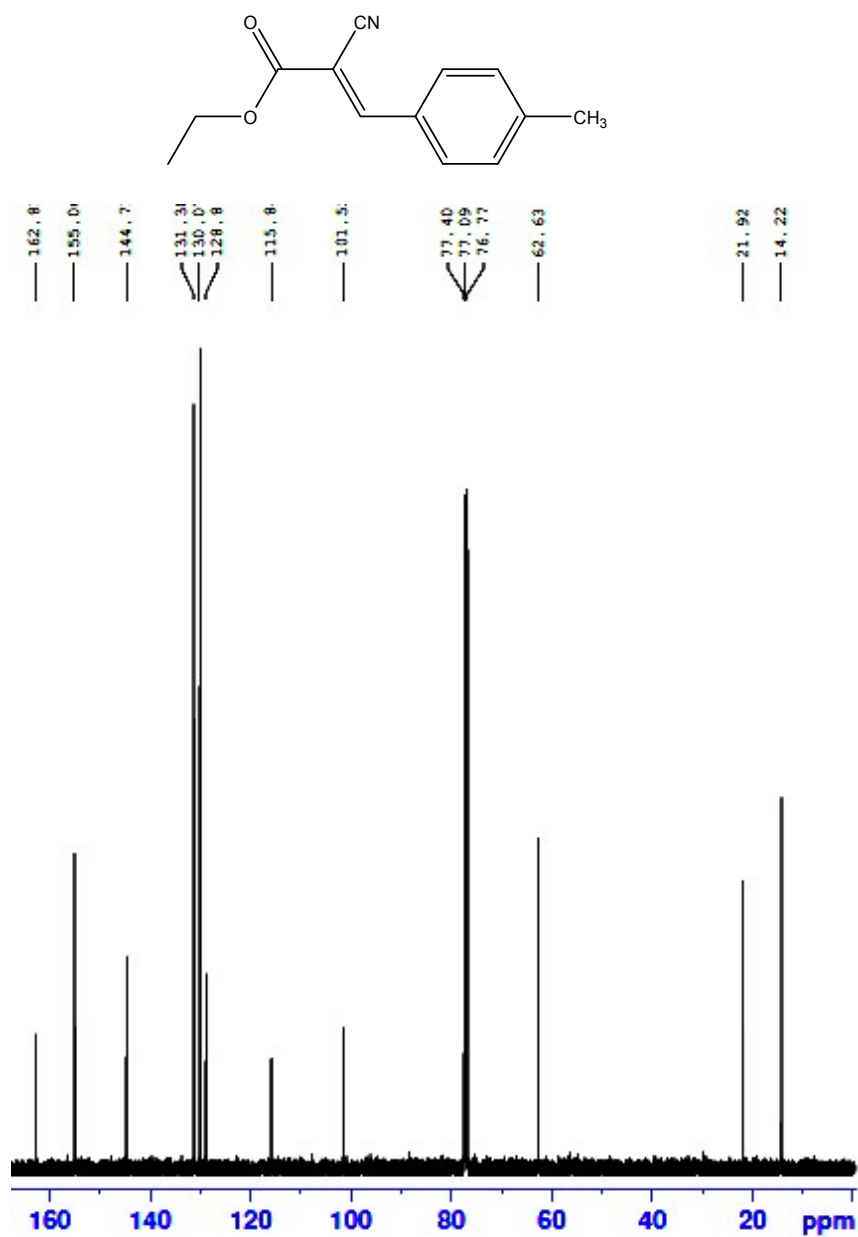**Figure 9S.** ¹H-NMR-spectrum of *(E)-ethyl 2-cyano-3-p-tolylacrylate*

Figure 10S. ^{13}C-NMR-spectrum of *(E)-ethyl 2-cyano-3-p-tolylacrylate*

(E)-ethyl 2-cyano-3-p-tolylacrylate:

IR: (KBr, cm[-1]): 3089 (C-H, Stretching, sp[2]), 2965 (C-H, Stretching, sp[3]), 2216 (CN), 1728 (C=O, ester), 1448- 1601 (C=C-Ar), 1094 (C-O, ester).

References:

1. D. Elhamifar, B. Karimi, J. Rastegar, M. H. Banakar, *ChemCatChem*, **2013**, 5, 2218-2224.

2. D. Elhamifar, B. Karimi, A. Moradi, J. Rastegar, *ChemPlusChem* **2014**, *79*, 1147–1152.

3. S. van Dommele, K. P. de Jong, J. H. Bitter *Chem. Commun.* **2006**, 4859–4861