

Isocyanurate-Based periodic mesoporous organosilica (PMO-ICS): a highly efficient and recoverable nanocatalyst for the one-pot synthesis of substituted imidazoles and benzimidazoles

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Experimental Section

General

All chemicals were purchased from Merck or Aldrich and used as received except for benzaldehyde which a fresh distilled sample was used. field emission scanning electron microscopy (FESEM) images was obtained using Sigma instrument of Zeiss company, Germany. The BET specific surface area of the catalyst was obtained using an equipment ASAP 2020TM micromeritics. Thermal gravimetric analysis (TGA) was performed by means of Bahr company STA 504 instrument. transmission electron microscopy (TEM) images were recorded using EM10C-100 KV of Zeiss company, Germany. XRD analysis was performed using STOE-Thata-Thata. FTIR spectra were recorded as KBr pellets on a Shimadzu FT IR-8400S spectrometer. Melting points were determined using an Electrothermal 9100 apparatus and are uncorrected. ¹H NMR (500 MHz) spectra were obtained using a Bruker DRX-500 AVANCE spectrometer in CDCl₃ at ambient temperature. Analytical TLC was carried out using Merck 0.2 mm silica gel 60 F-254 Al-plates. All the products are known compounds and were identified by comparison of their physical and spectroscopic and analytical data with authentic samples.

General procedure for the synthesis of PMO-ICS (1)

The synthesis of PMO-ICS (1) has been achieved using known procedure described by Jaroniec and his co-workers.³⁵ In a typical experiment, 2.0 g of Pluronic P123 (Aldrich, average Mw \cong 5800 Dalton) was dissolved in a mixture of 15 mL of deionized water and 60 g of 2 M HCl solution. Then, 0.01 mol (3.08 g) of tris [3-trimethoxysilyl] propyl] isocyanurate (ICS, Aldrich) and 0.03 mol tetraethoxysilane (TEOS, 3.12 g) was added dropwise into that solution. The obtained mixture was stirred at the constant rate and room temperature for 20 h. The mixture was aged at 100 °C for 48 h without stirring. The solid was filtered off and washed thoroughly with hot EtOH/H₂O (60 mL of EtOH 96% and 2 mL of 12 M HCl) using a soxhlet apparatus for 72 h to remove the surfactant molecules. The obtained white powder was dried in air at 100 °C overnight.

General procedure for synthesis of 2,4,5-trisubstituted imidazole derivatives (5a-t)

In a 5 mL round-bottomed flask, benzoin (2, 1 mmol), aldehyde 3 (1 mmol), ammonium acetate (4, 2.5 mmol) and 20 mg PMO-ICS (1) were added to EtOH 96% (2 mL). The obtained mixture was stirred at reflux conditions for times indicated in Table 2. After completion of the reaction monitored by TLC (eluent: EtOAc: n-hexane), EtOH (3 mL) was added and the obtained mixture was heated and filtered off to separate the solid catalyst 1. Water was added dropwise to the filtrate at 50 °C to give pure crystals of the desired products 5a-t in 74–98% yields based on the starting aldehyde. The separated catalyst was suspended in EtOAc (1mL) for 30 min and the filtered. The obtained white powder was heated in an oven at 70 °C for 1 h and reused for successive runs.

General procedure for synthesis of Benzimidazole Derivatives (7a-s)

In a 5 mL round-bottomed flask, 1,2-phenylenediamine (6, 1 mmol), aldehyde 3 (1 mmol), and PMO-ICS (1, 20 mg) were added to EtOH 96% (2 mL). The obtained mixture was stirred at reflux conditions for times indicated in Table 3. After completion of the reaction, monitored by TLC (eluent: EtOAc: n-hexane) EtOH (3 mL) was added and the obtained mixture was heated and filtered off to separate the solid catalyst 1. Water was added dropwise to the filtrate at 50 °C to give pure crystals of the desired products 7a-s in 83–99% yields based on the starting aldehyde. The separated catalyst was suspended in EtOAc (1mL) for 30 min and the filtered. The obtained white powder was heated in an oven at 70 °C for 1 h and reused for successive runs.

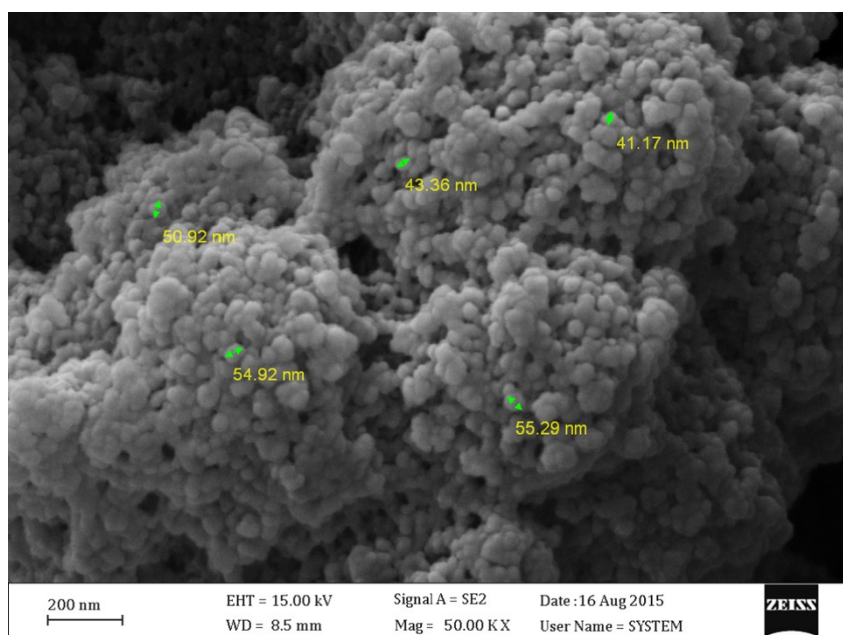


Fig. 1 Scanning electron microscopy (SEM) image of PMO-ICS nanocatalyst.

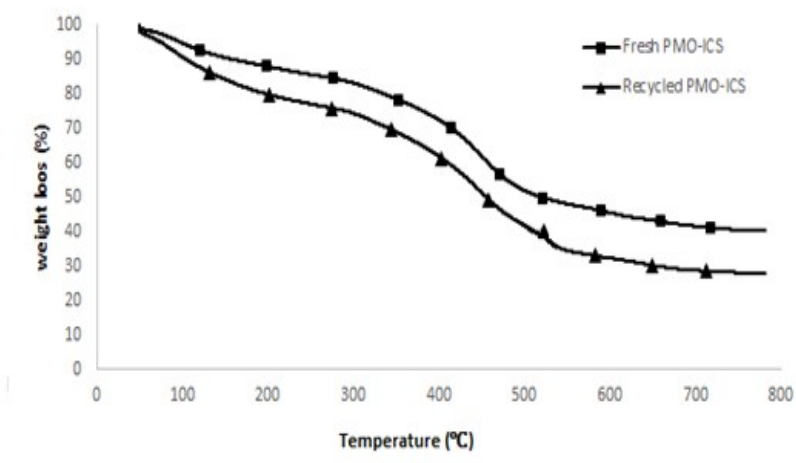


Fig. 2 Thermal gravimetric analysis (TGA) of the fresh PMO-ICS (1) (■) and recycled PMO-ICS (1) (▲) nanocatalyst.

Thermogravimetric analysis (TGA) of PMO-ICS (1) showed the thermal stability about 470 °C for the isocyanurate bridging containing organics which have been incorporated into the silica framework.

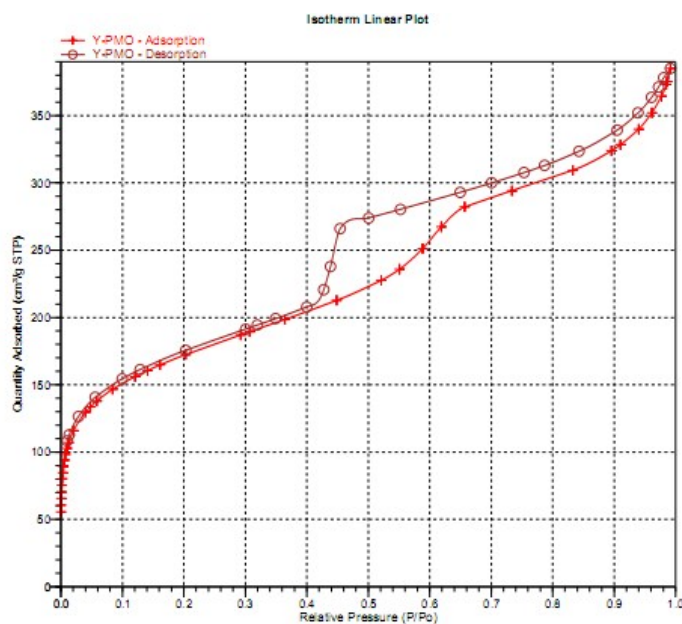


Fig. 3 BET analysis of PMO-ICS nanocatalyst.

BET analysis of PMO-ICS (**1**) showed specific surface area close to 570 m²/g, pore size \approx 4.1 and volume pore \approx 5 nm.

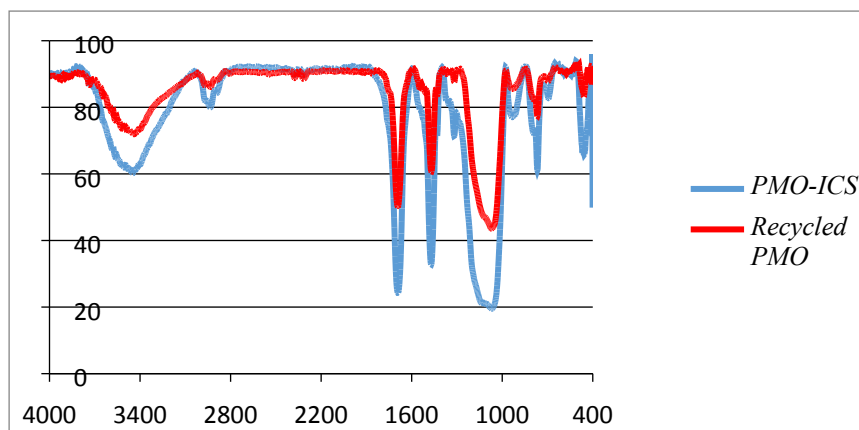


Fig. 4 FT IR spectra of fresh PMO-ICS nanocatalyst (blue line) and recycled PMO-ICS nanocatalyst.

The IR spectrum of PMO-ICS (**1**) shows the presence of organic functional groups in the material framework (See ESI). Indeed, the bands observed at 2935 and 2850 cm⁻¹ are assigned to C–H stretching of aliphatic moieties. Moreover, the signals appeared at 1689 and 1471 cm⁻¹ are attributed to the stretching vibrations of the isocyanurate ring. On the other hand, PMO-ICS (**1**) showed bands at 1120, 1070 and 935 cm⁻¹ corresponding to asymmetric and symmetric vibrations of Si–O–Si (siloxane) bonds, respectively. The strong and broad signal appeared about 3334 cm⁻¹ is attributed to O–H bonds of silanol groups.

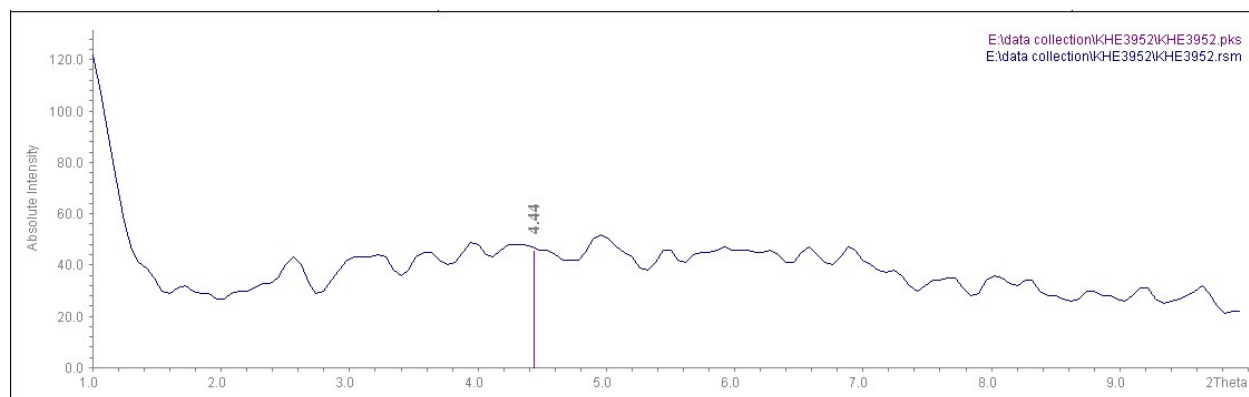


Fig. 5 X-ray powder diffraction (PXRD) of PMO-ICS.

2-(4-chlorophenyl)-4,5-diphenyl-4,5-dihydro-1H-imidazole(5a, Table 2, Entry 1). M P 263-265 ° C; ¹H NMR (500MHz, DMSO-d₆): 12.71 (s, 1H), 8.10 (d, J = 8.43Hz, 2H), 7.52 (d, J= 8.357 Hz, 2H), 7.48 (t, J= 6.56 Hz, 4H), 7.42 (d of d, J= 7.32 Hz, 4H), 7.36 (t, J= 7.75 Hz, 2H); FTIR (KBr, cm⁻¹): 3421.48, 3060.82, 1602.74, 1442.66.

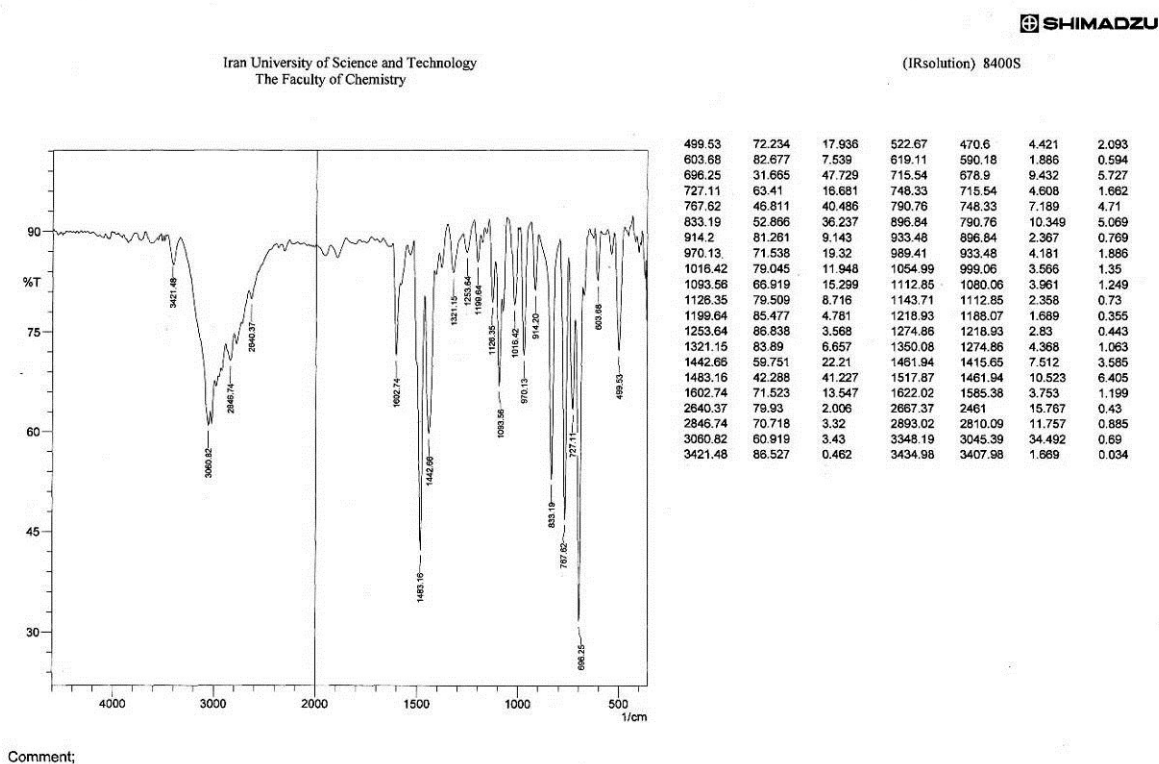
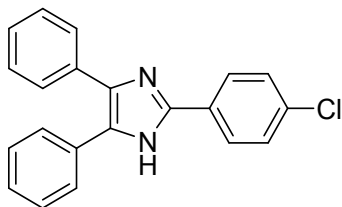


Fig. 6 FT IR spectrum of 2-(4-chlorophenyl)-4,5-diphenyl-4,5-dihydro-1H-imidazole(5a, Table 2, Entry 1).

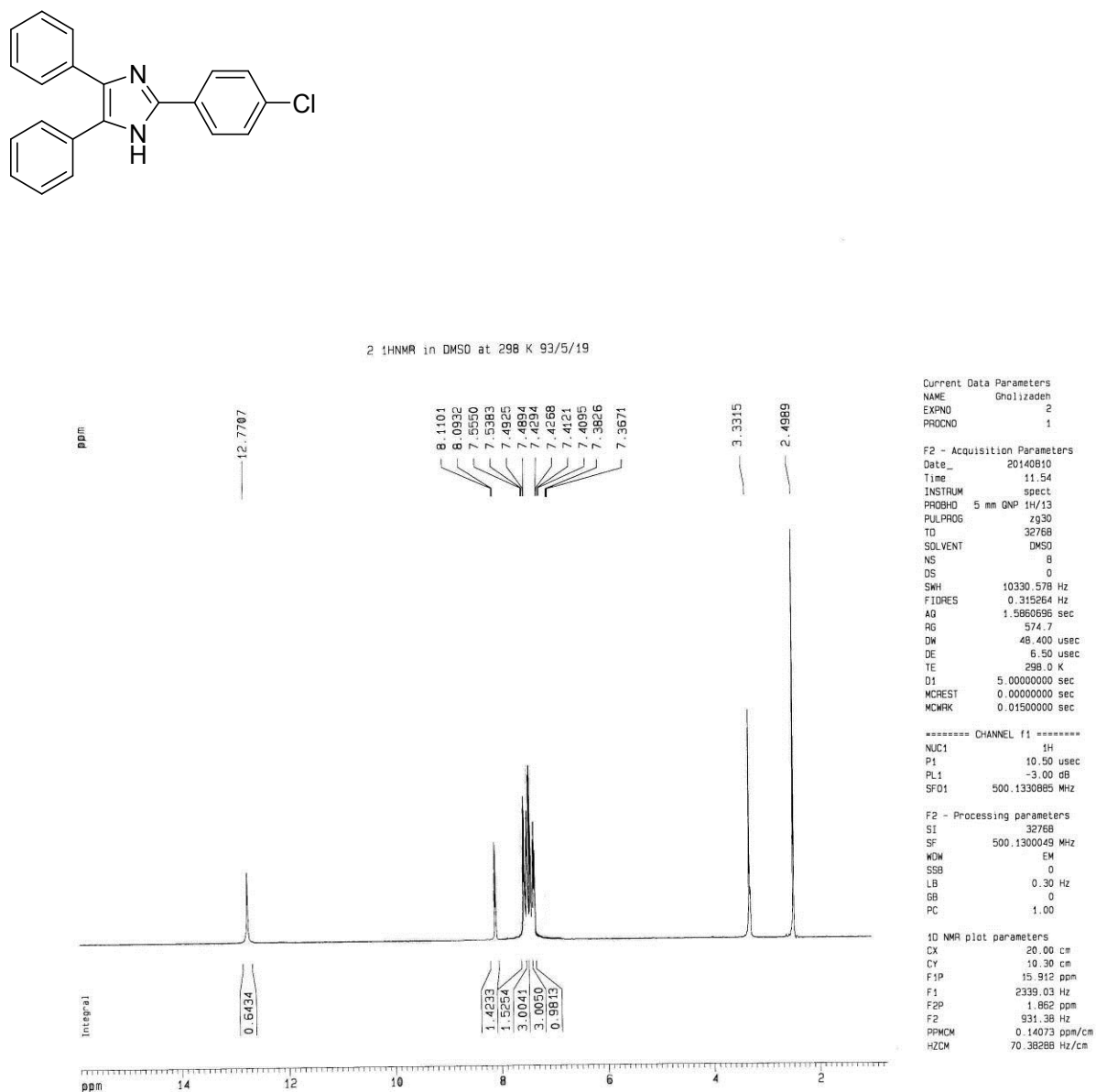


Fig. 7 ¹H NMR spectrum of 2-(4-chlorophenyl)-4,5-diphenyl-4,5-dihydro-1H-imidazole (5a, Table 2, Entry 1).

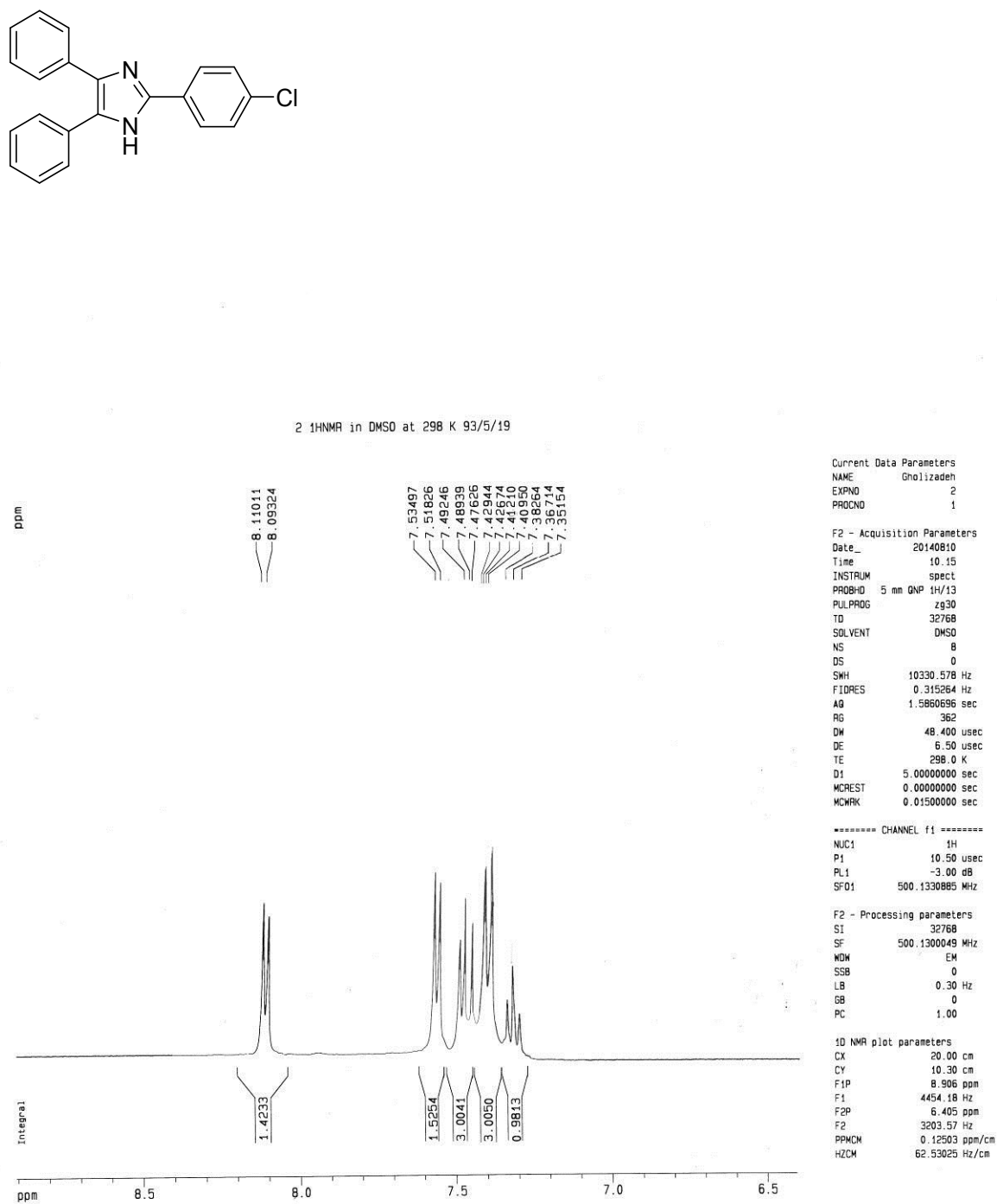


Fig. 8 ¹H NMR spectrum (expanded aromatic region) of 2-(4-chlorophenyl)-4,5-diphenyl-4,5-*H*-imidazole (**5a**, Table 2, Entry 1).