

Simultaneous Immobilization of Palladium and Phase Transfer Catalyst Matrix on Silica Nanoparticles: Application as A Recoverable Catalyst for the Heck Reaction in Pure Water

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General

(3-Iodopropyl)trimethoxysilane was synthesized from (3-chloropropyl)trimethoxysilane (MERCK) and NaI in refluxing dry acetone for 24 hours. Palladium chloride (99%, reagent plus) was purchased from Sigma-Aldrich. Triphenyl phosphine, NaHCO₃ and aryl halides were purchased from Merck. NMR spectra were recorded on a Bruker Avance DPX spectrometer (¹H NMR 400 or 300 MHz) in CDCl₃ with tetramethylsilane (TMS) as the internal standard. UV-vis spectra were recorded on a Jasco V-570 UV-vis-NIR Spectrometer and Jasco ARN-475 accessory for diffuse reflectance purpose. Transmission electron microscopy (TEM) images were obtained by TEM, Philips CM10. Palladium content of the catalyst was measured by an AAS; Perkin-Elmer 2380 atomic absorption spectrophotometer.

Preparation of triphenyl(3-trimethoxysilylpropyl)phosphonium iodide (1): In a well-dried 100 mL round bottom flask, to a solution of triphenyl phosphine (1.311 g, 5 mmol) in dry toluene (30 mL), (3-iodopropyl)trimethoxysilane (1.450 g, 5 mmol) was added and then system was filled with argon three times and refluxed for 24 h under an argon atmosphere. The reaction process was monitored by TLC (80:20, hexane: EtOAc). After completion of reaction, the resulting two phase reaction mixture was then allowed to cool to room temperature and the organic layer was separated from the phosphonium salt layer. The resulting glassy pale yellow material was then thoroughly washed with dry toluene under gentle heating (1 × 10 mL) and Et₂O (3 × 5 mL) and finally dried under vacuum (640 mmHg) for 1 h at 40 °C (80%, 2.2 g, 4 mmol). The spectral data for compound **1** is as follows:

¹H NMR (400 MHz; CDCl₃; SiMe₄): δ = 1.030-1.068 (t, 2H, *J* = 7.6 Hz), 1.672-1.711 (m, 2H), 3.459 (s, 9H), 3.640-3.712 (m, 2H), 7.620-7.753 (m, 15H). FT-IR (KBr) ν_{max}/cm⁻¹: 3065 (C-H phenyl ring), 2964 (CH₂-propyl), 1587 and 1486 (C-H phenyl), 746 and 690 (C-H OOP). Anal. Calc. for C₂₄H₃₀IO₃PSi: C, 52.18; H, 5.47. Found: C, 52.25; H, 5.52.

Preparation of phosphonium salt-Pd complex (2): In a well-dried 100 mL round bottom flask equipped with magnetic stirrer bar, to a CHCl₃ (40 mL) solution of **1** (2.2 g, 4 mmol) was added PdCl₂ (44.5 mg, 0.25 mmol) and then the system was evacuated and refilled with argon. The mixture was then allowed to react with stirring at reflux temperature for 1 h under an argon

atmosphere. The system was then allowed to cool to room temperature to afford a dark red-purple complex solution (Fig. 1s).

Preparation of phosphonium-Pd complex /PTC matrix immobilized on Silicananoparticles:

Silica nanoparticles with the size of about 12 nm were synthesized according to the previously reported procedure.¹ Silica nanoparticles were reactivated by heating with aqueous 5 M HCl with vigorous stirring overnight. The activated silica was separated by centrifugation (6000rpm, 10 min), washed thoroughly with distilled water and dried in 150 °C overnight before undergoing chemical surface modification. The above solution containing 4mmol of **1** was added to a suspension of nano-silica (10 g) in dry CHCl₃ (60 mL) under argon atmosphere. The resulting mixture was refluxed for 5 h. After cooling, the solid materials were filtered off and the residue was Soxhlet extracted with CHCl₃ overnight and then dried in oven at 80 °C to give palladium complex/PTC matrix immobilized on silica nanoparticles as a purple solid (Figure 1s). The final material has a Palladium loading of 0.024mmol g⁻¹ determined by atomic absorption spectroscopy.

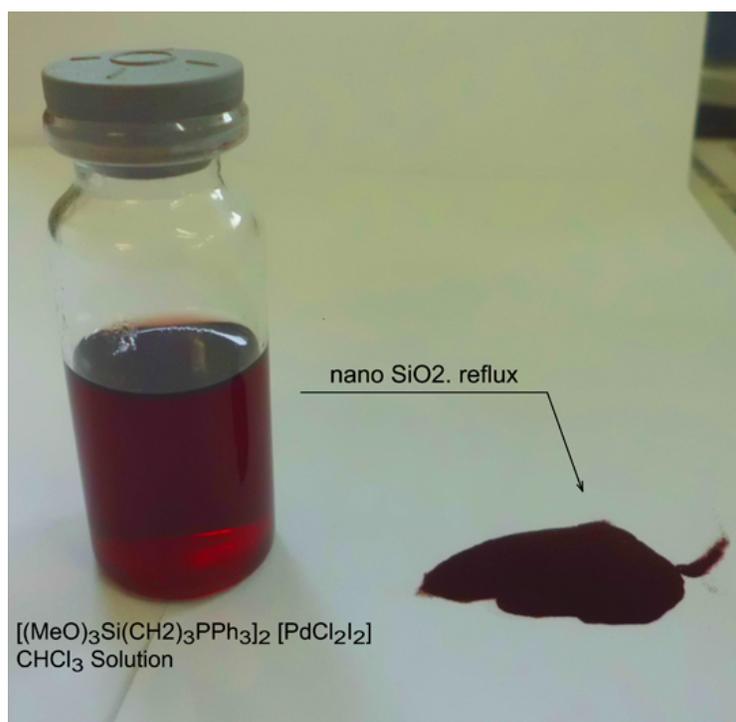


Fig. 1S

General experimental procedure for the Heck reaction: In a 3 mL stainless steel flask equipped with magnetic stirrer bar, the aryl halide (1 mmol) was mixed with methylacrylate (1mmol), NaHCO₃ (1.5 mmol) and catalyst (5 mg). The reactor was then filled with water and heated to 130 °C in an oil bath. After 5 hours, the reaction was cooled to room temperature and the catalyst was removed by centrifugation. The reaction mixture was then extracted with EtOAc (3 × 5 mL). The organic layers were combining together and dried over anhydrous CaCl₂. The solvent was

evapoated under reduced pressure to give the corresponding products. In most cases, the purity of products was analyzed by GC to be more than 95% without any chromatographic purification. Other products were purified by column chromatography (80:20, hexane: EtOAc).

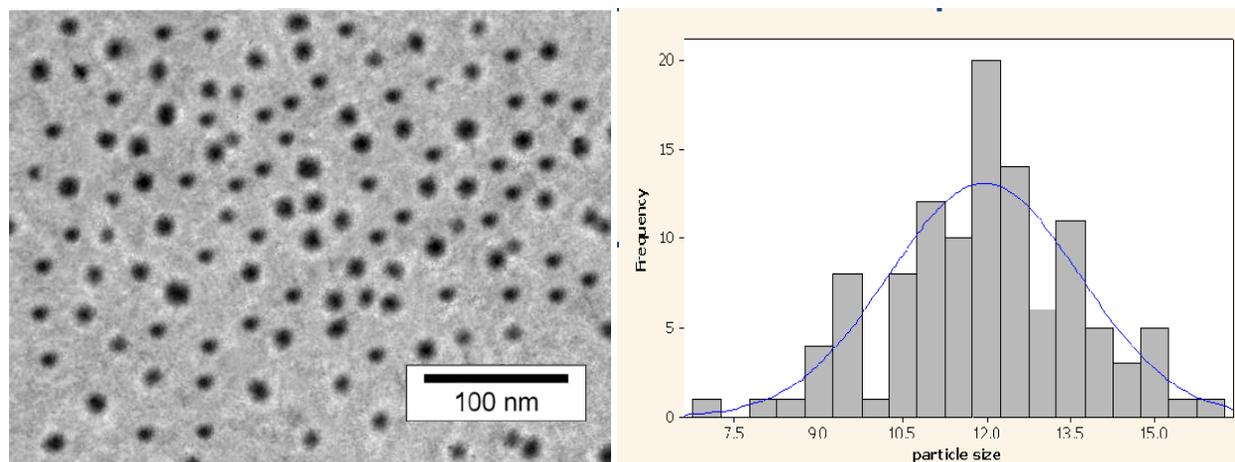


Fig. 2S TEM image of the Silica nanoparticles supported Pd/PTC, which shows the size distribution of the particles to be around 12 nm.

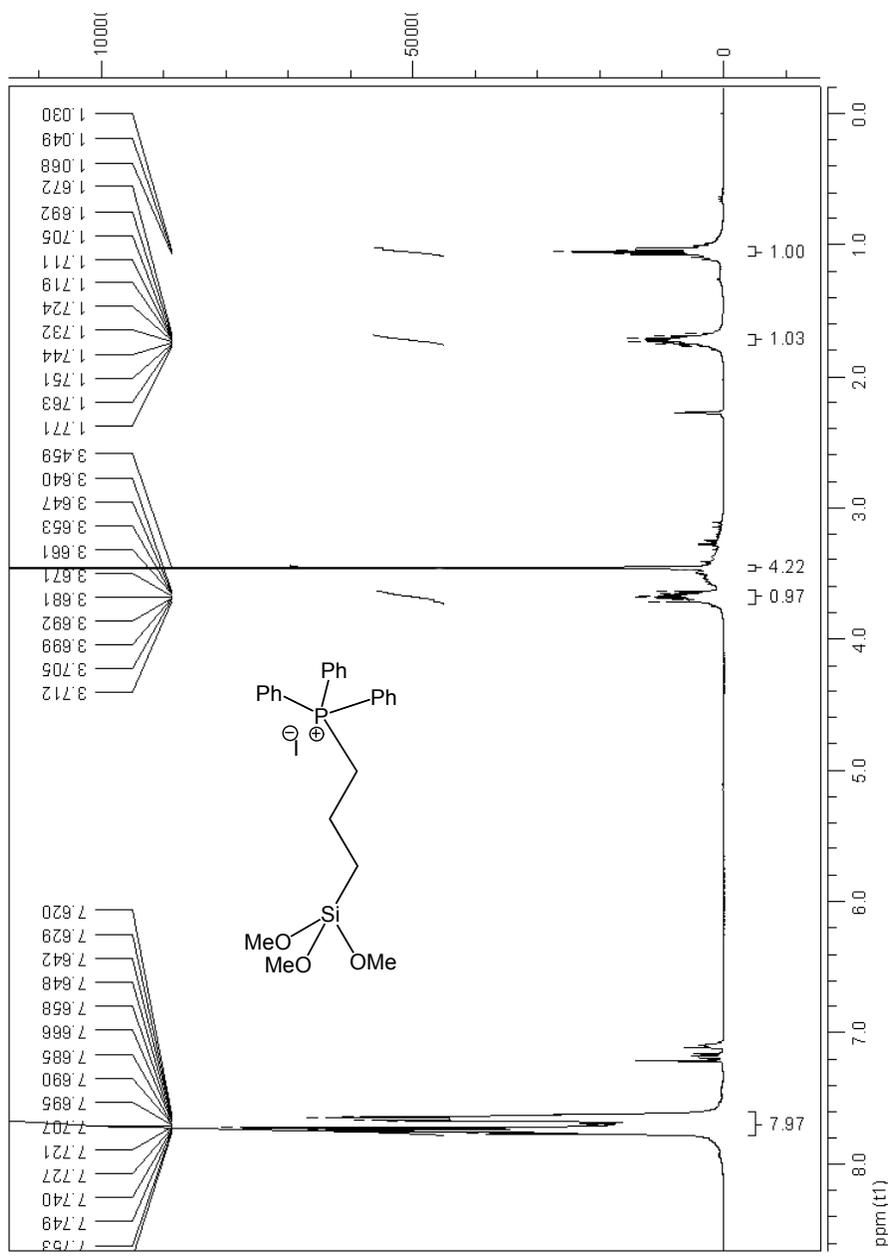


Fig. 3S

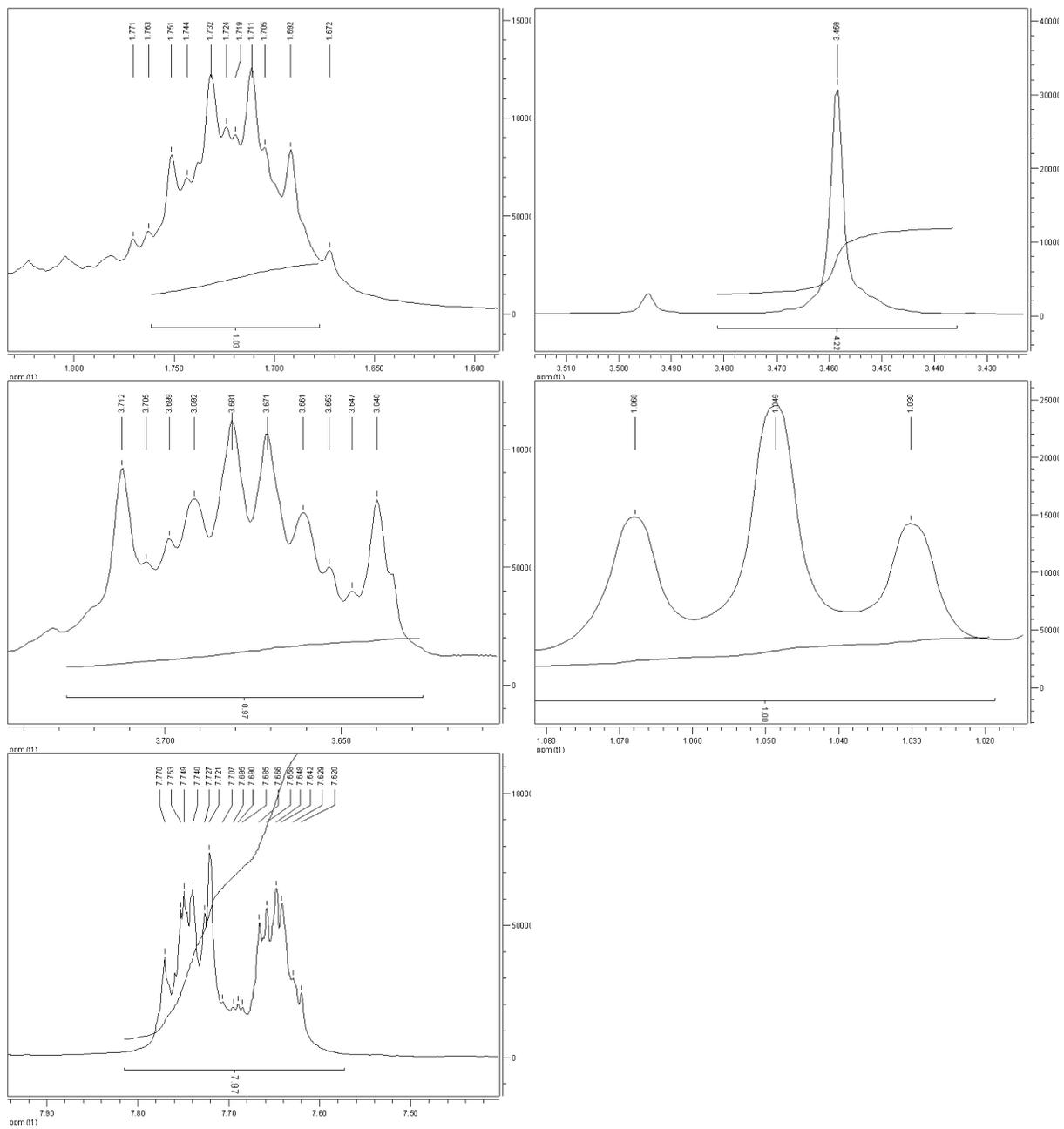


Fig. 4S

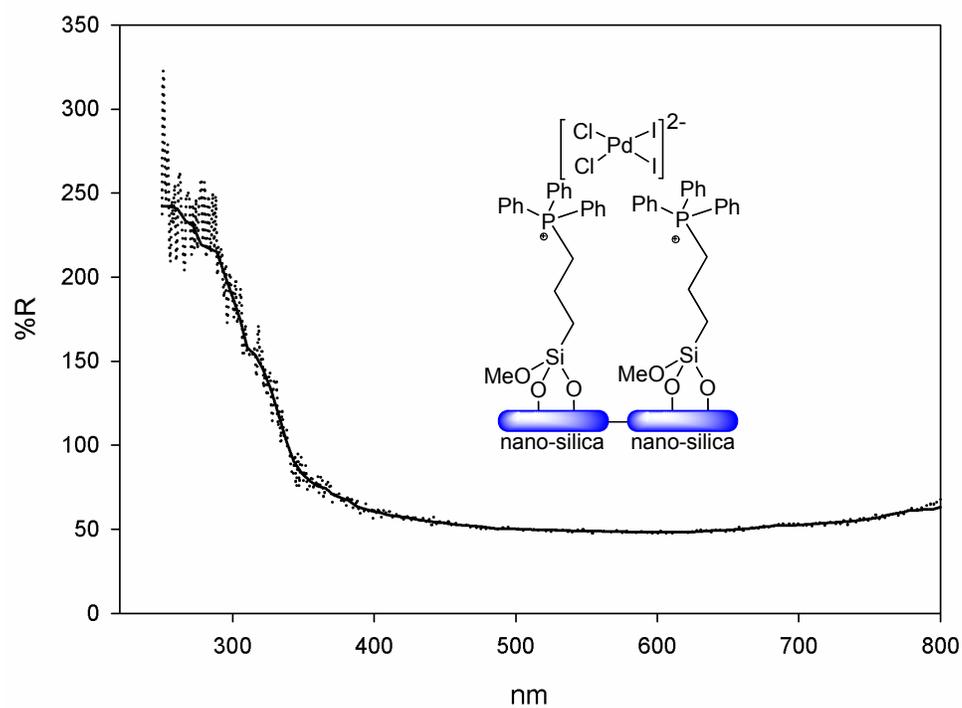


Fig. 5S DR UV-vis spectra of Pd supported on SiO₂ nanoparticles

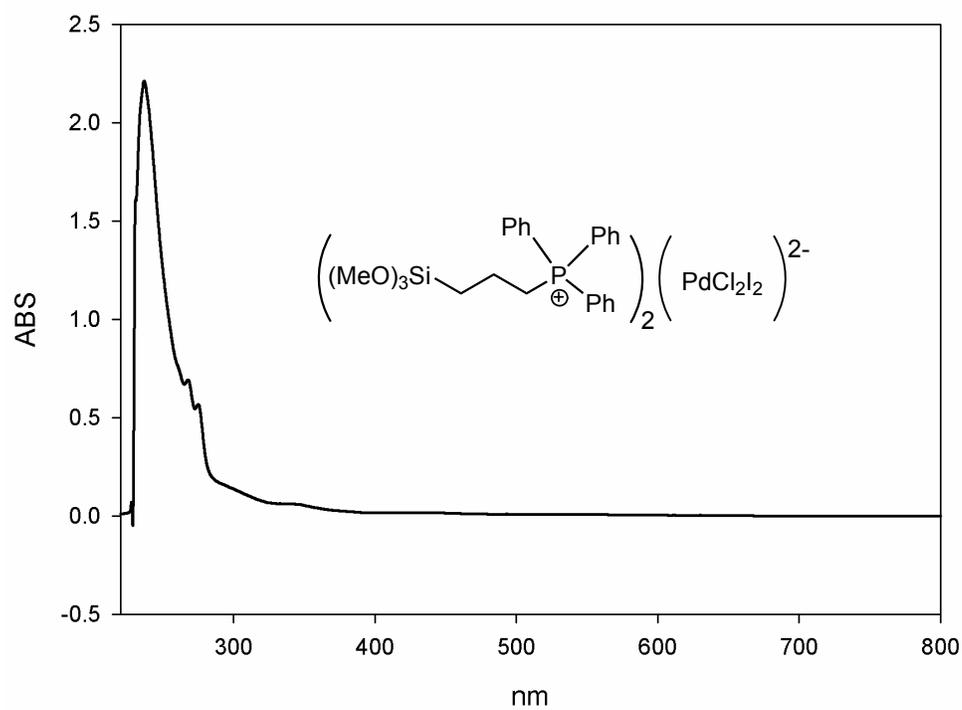


Fig. 6S UV-vis spectra of quaternary phosphonium -Pd complex **2** before immobilization on silica nanoparticles.

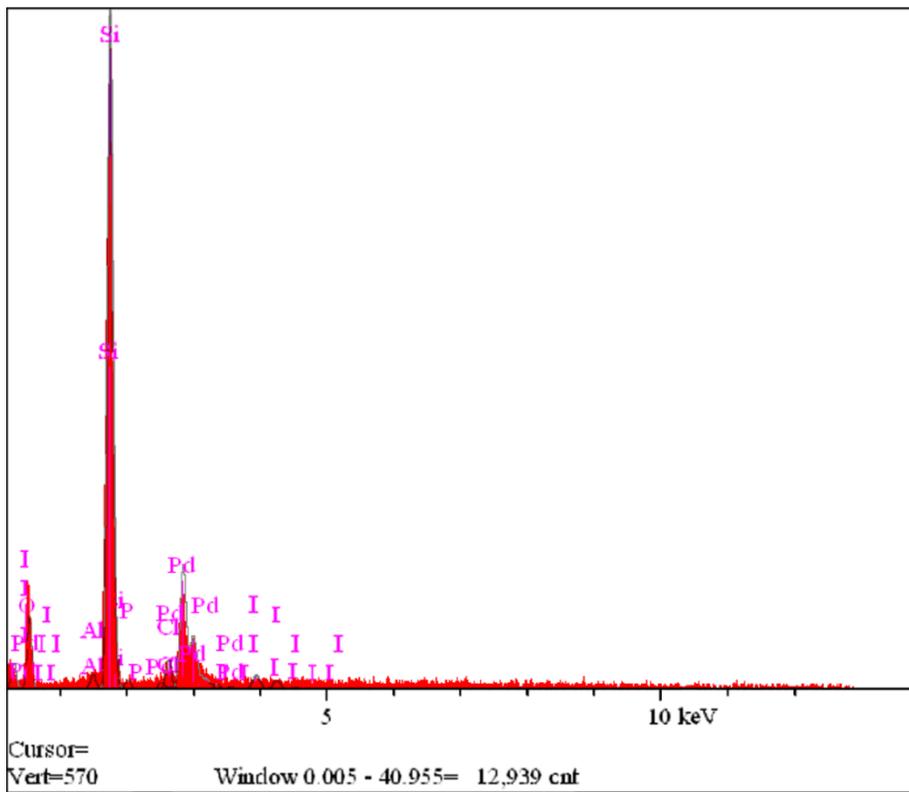


Fig. 7S SEM-EDX spectrum of Pd/PTC matrix immobilized on silica nanoparticles

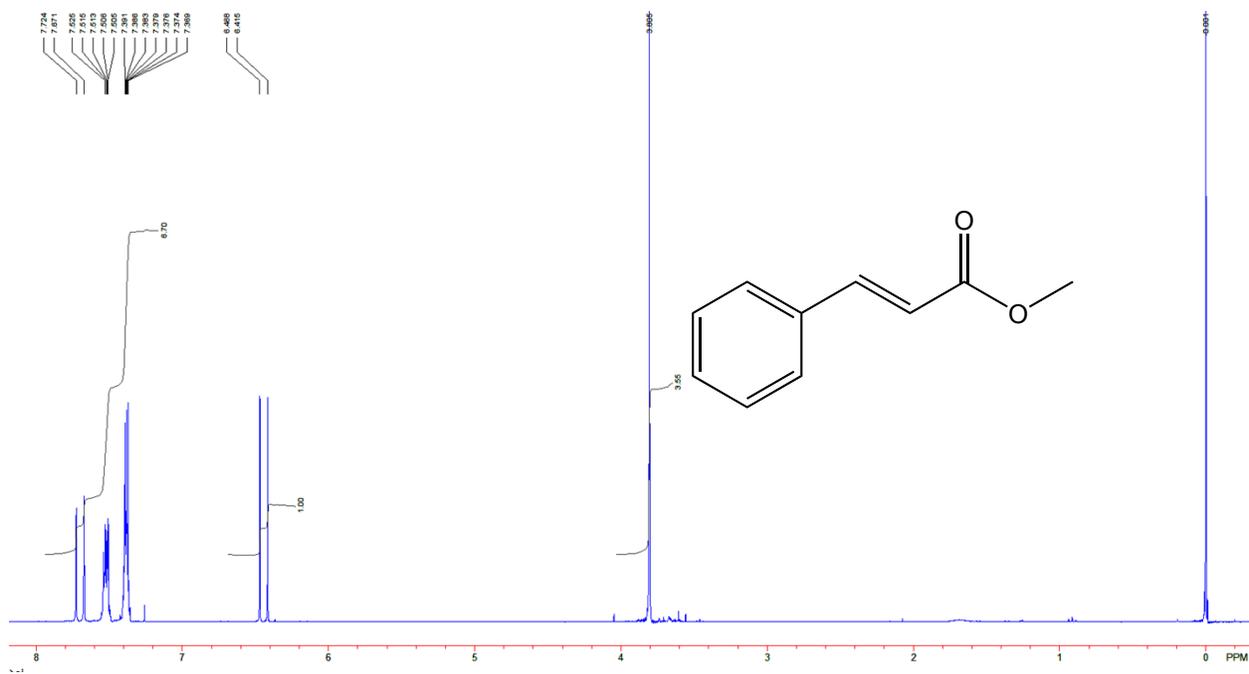


Fig. 8S

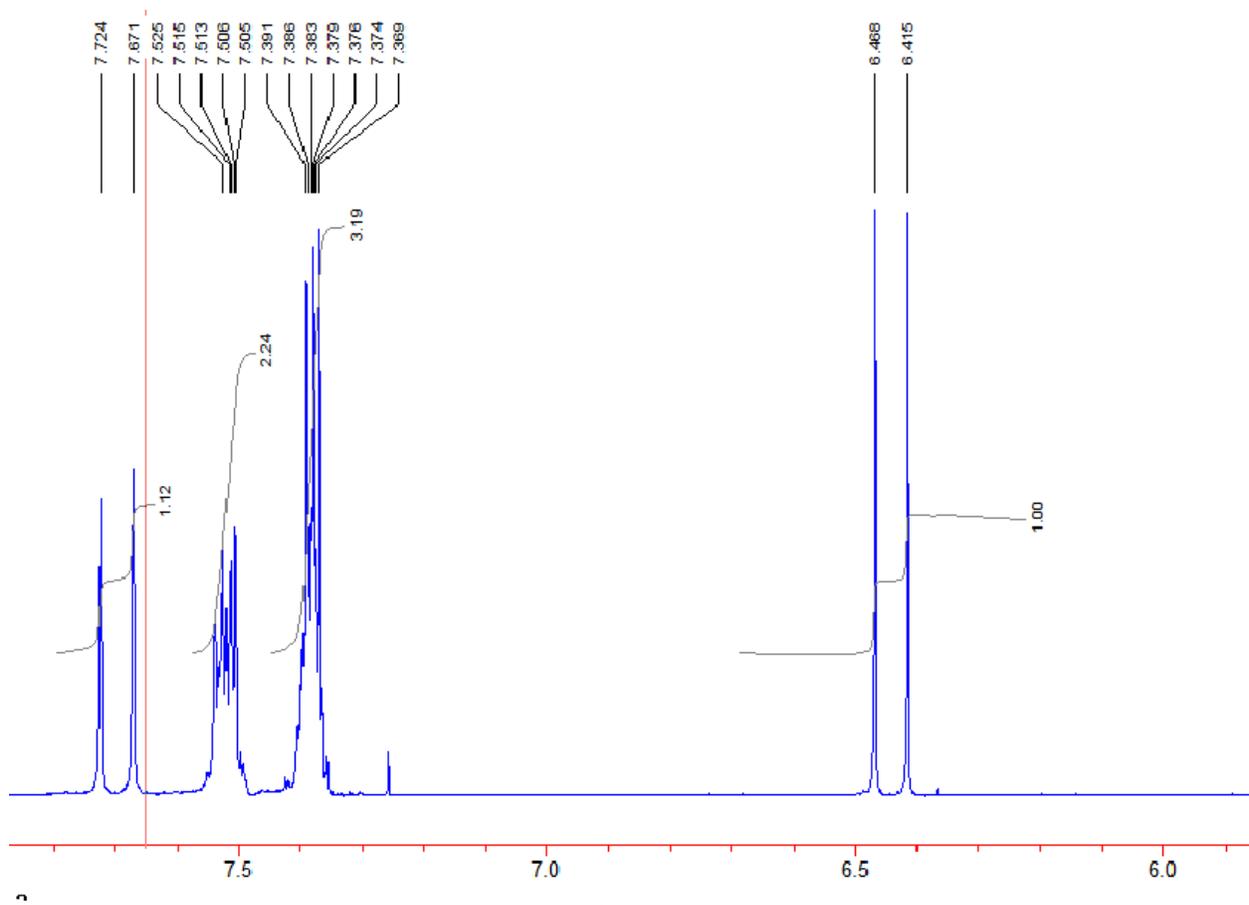


Fig. 9S

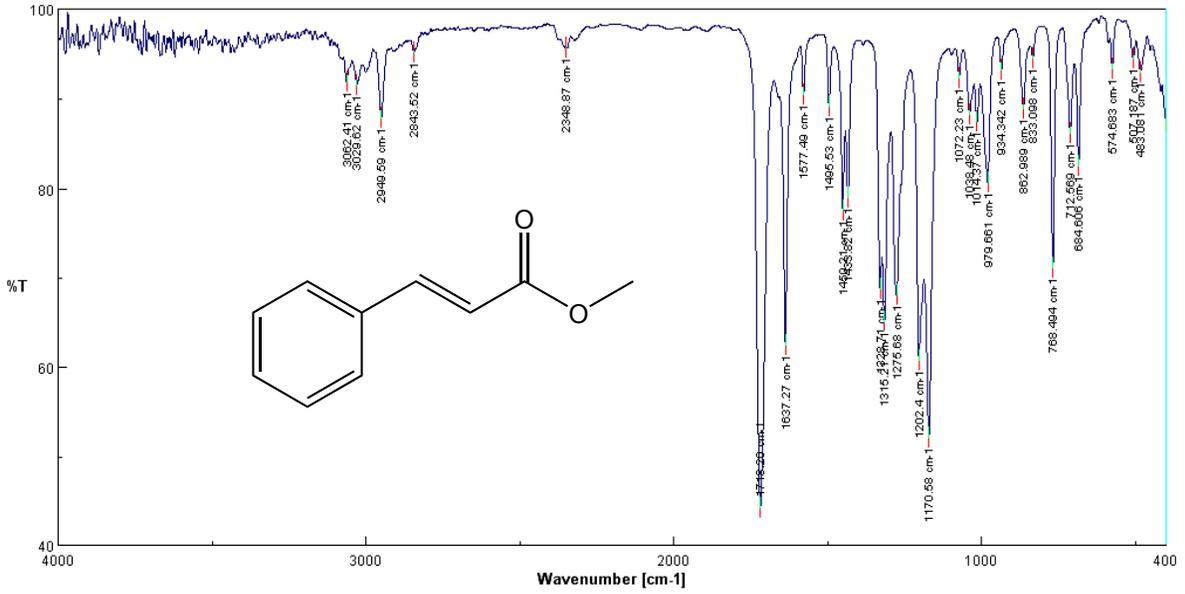


Fig. 10S

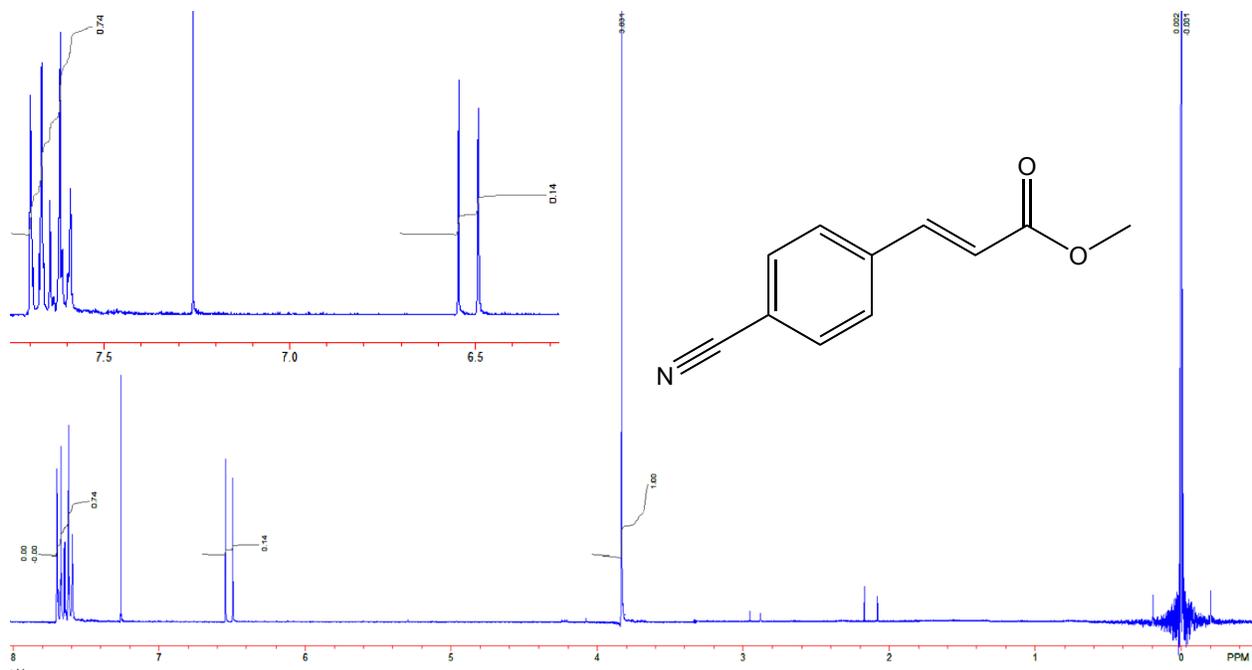


Fig. 11S

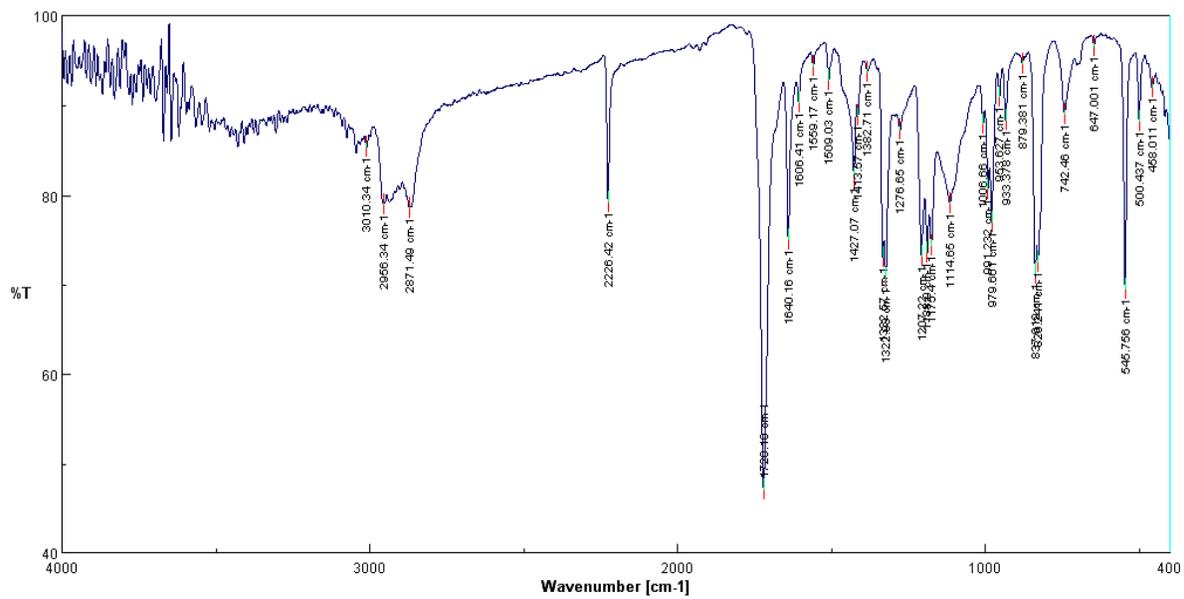


Fig. 12S

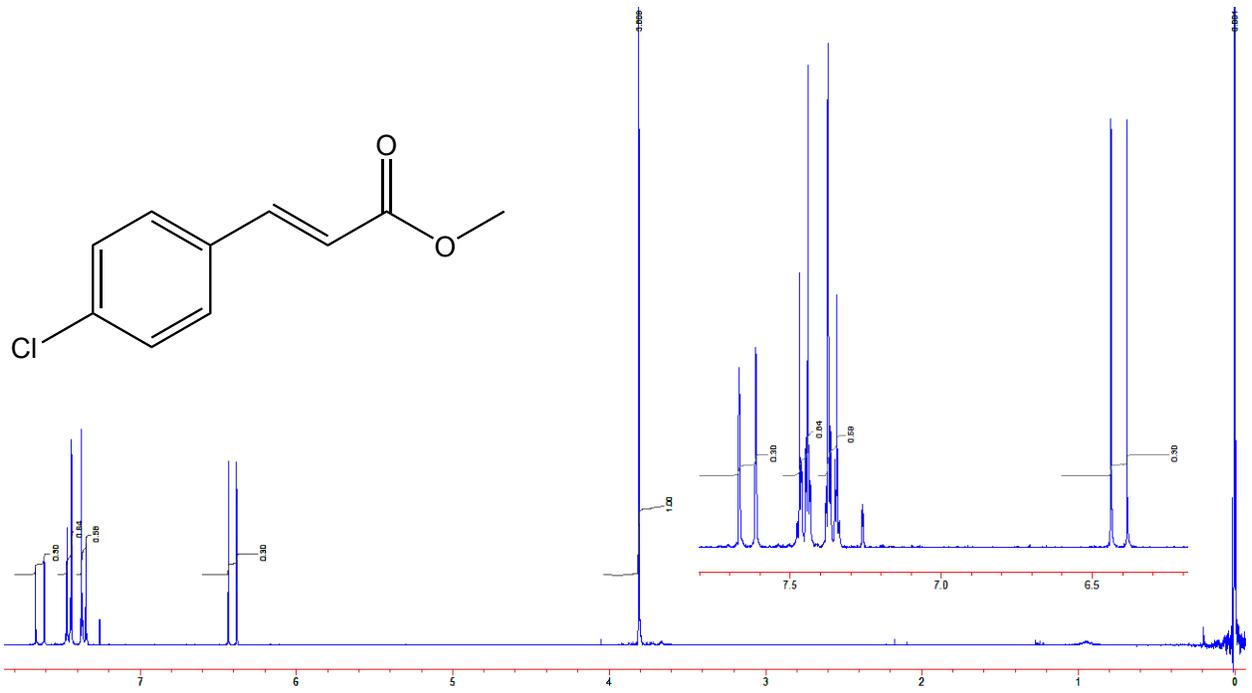


Fig. 13S

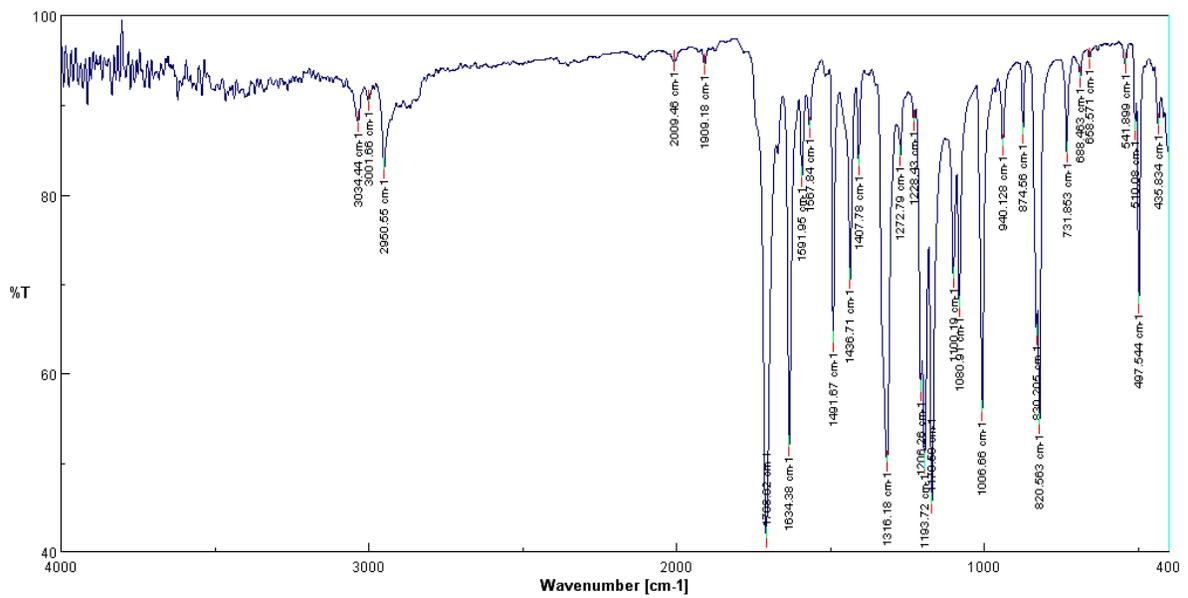


Fig. 14S

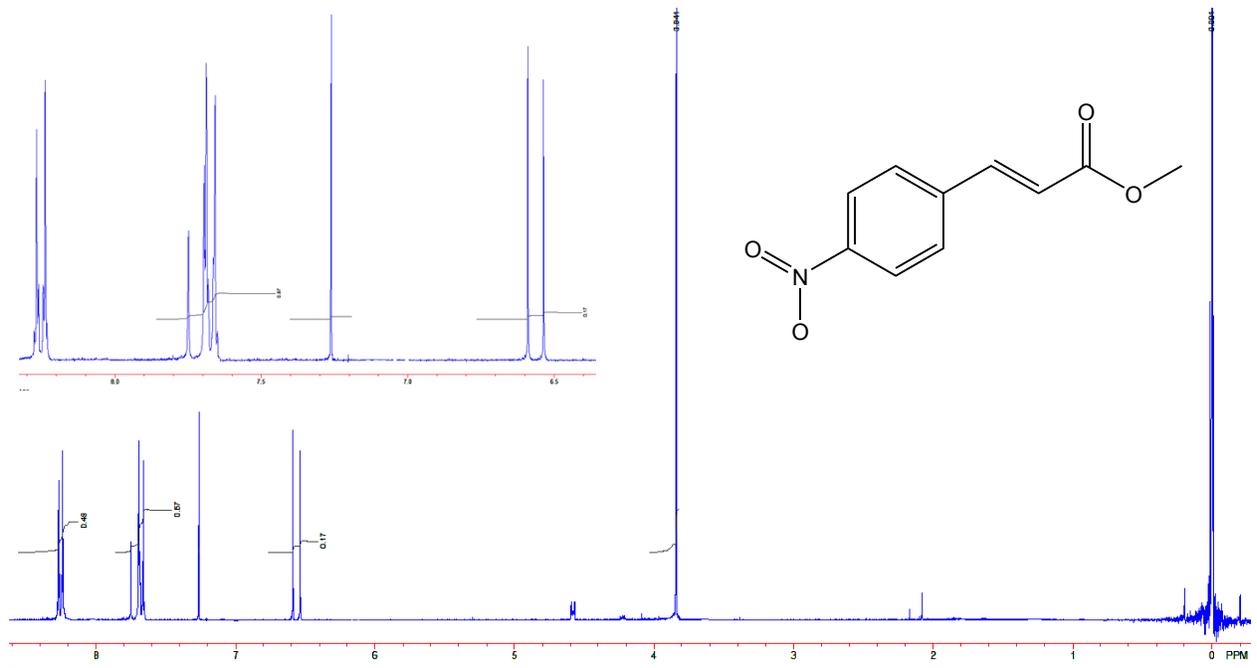


Fig. 15S

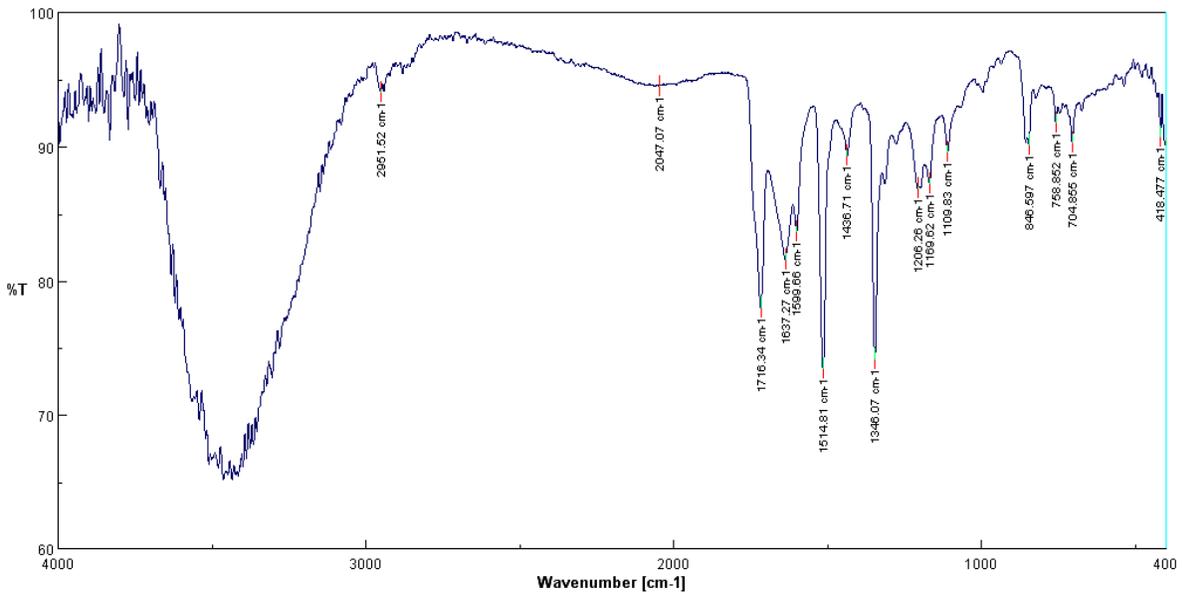


Fig. 16S

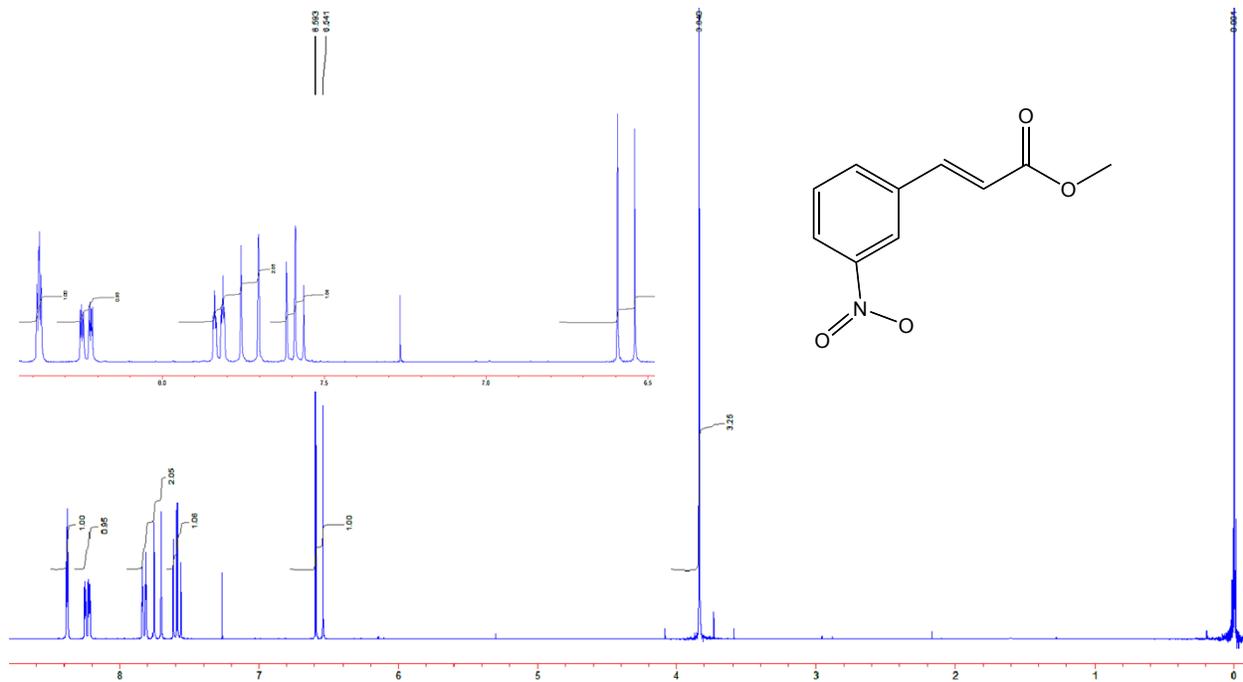


Fig. 17S

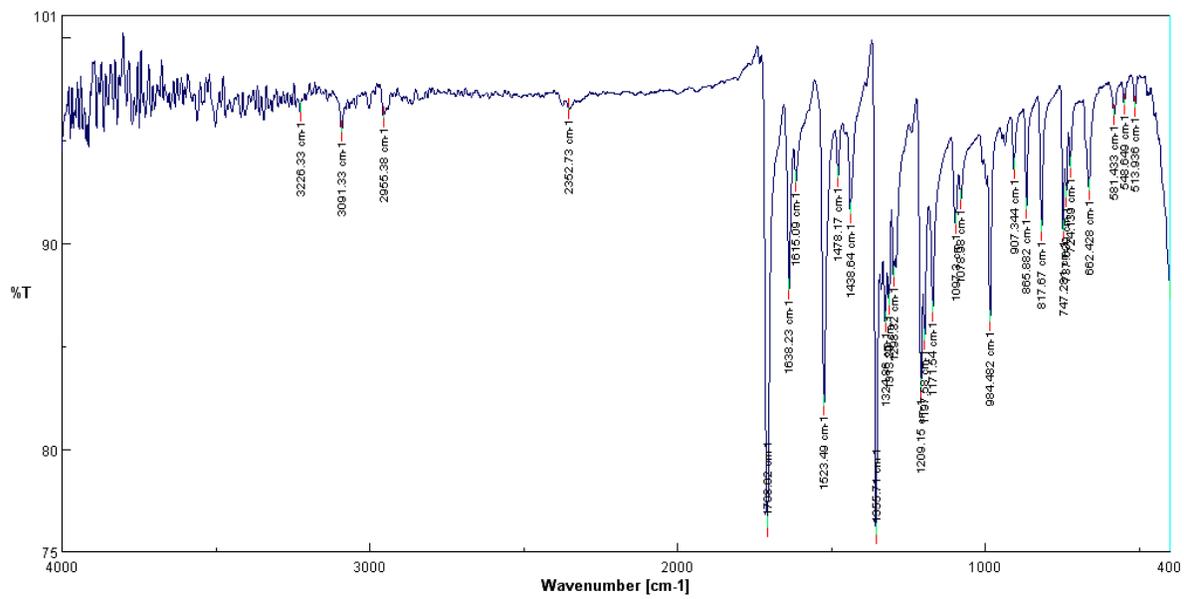


Fig. 18S

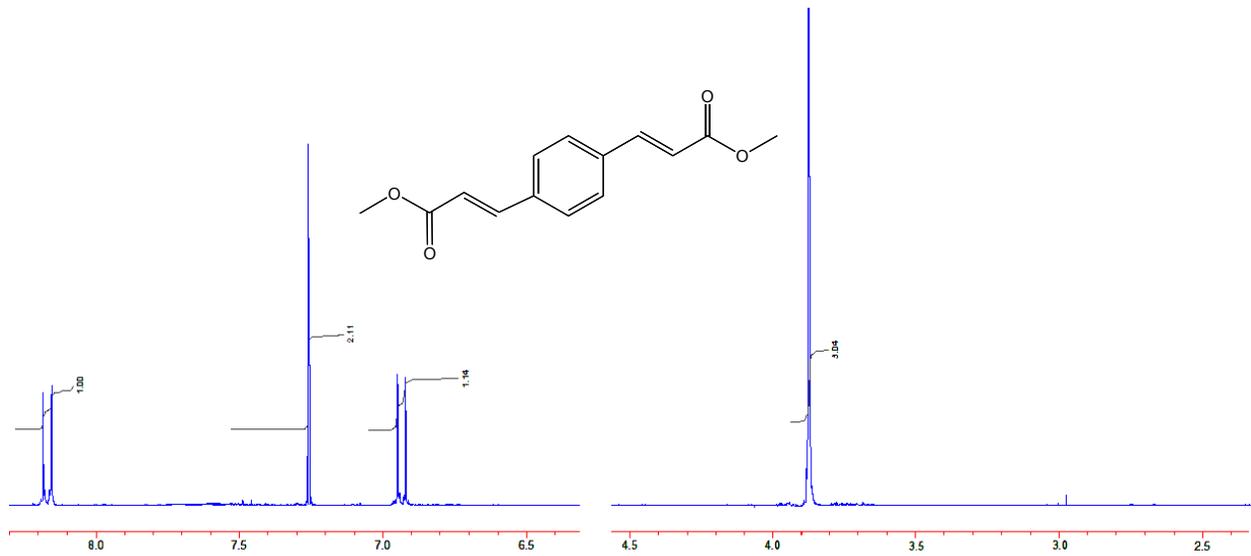


Fig. 19S

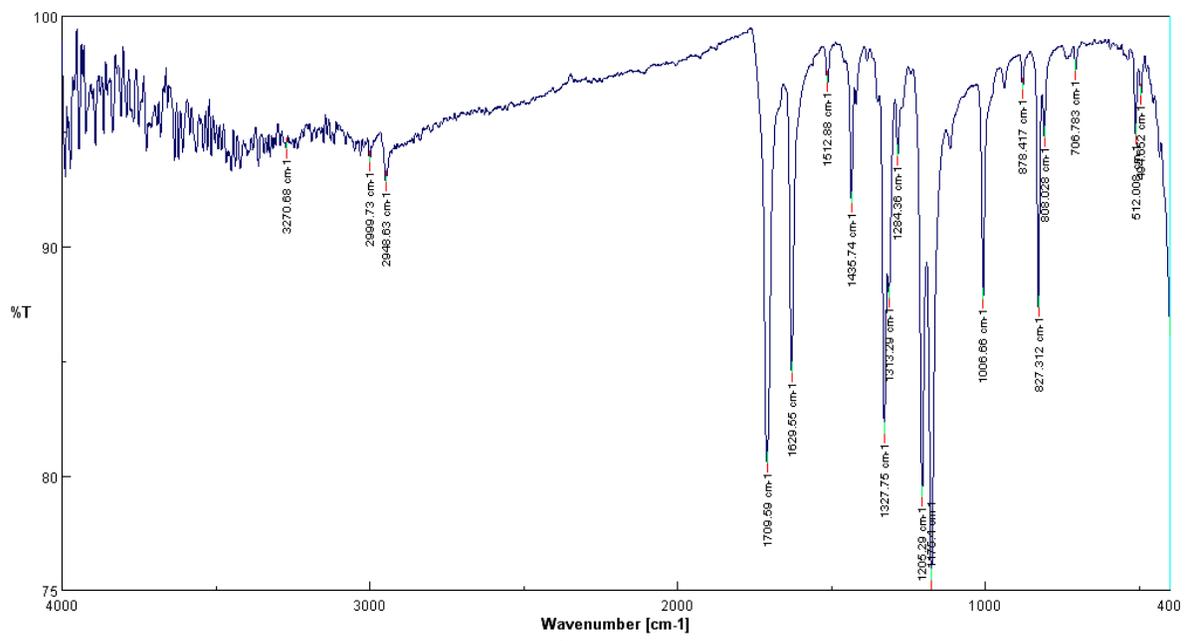


Fig. 20S

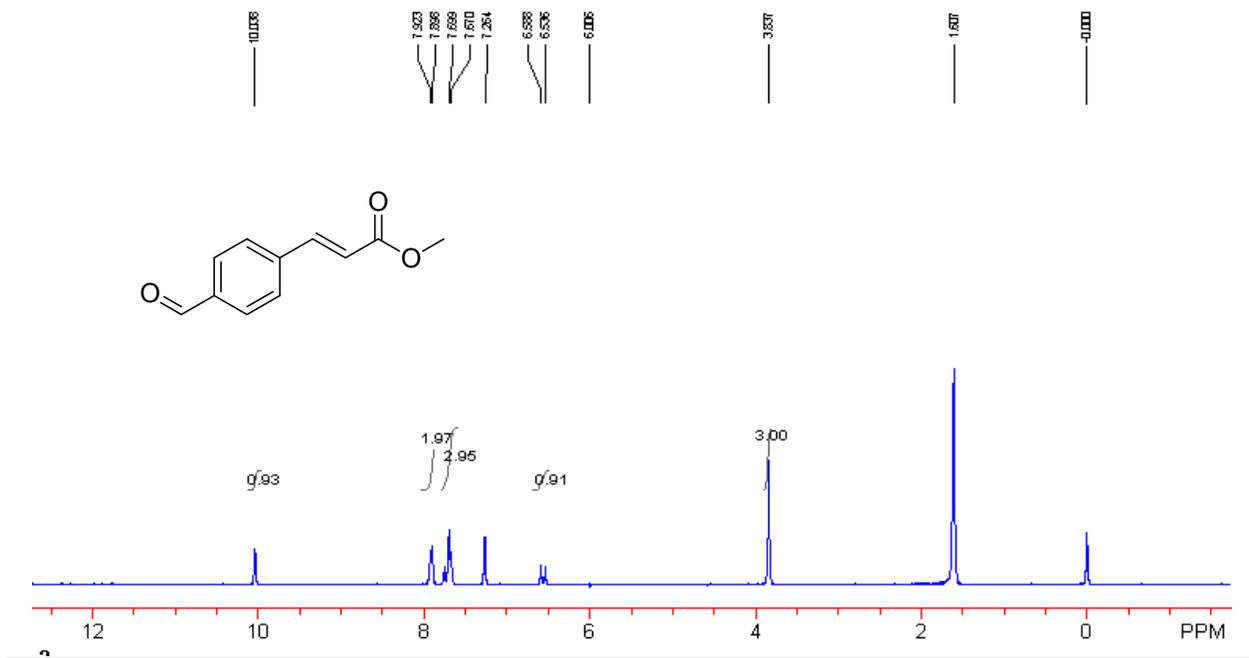


Fig. 21S



Fig. 22S

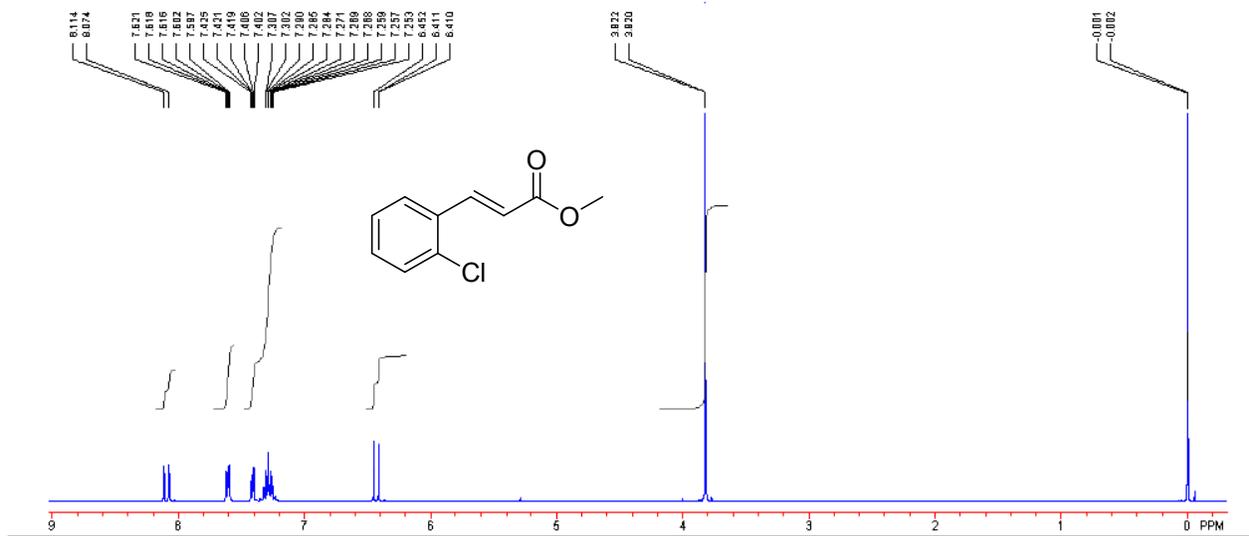


Fig. 23S

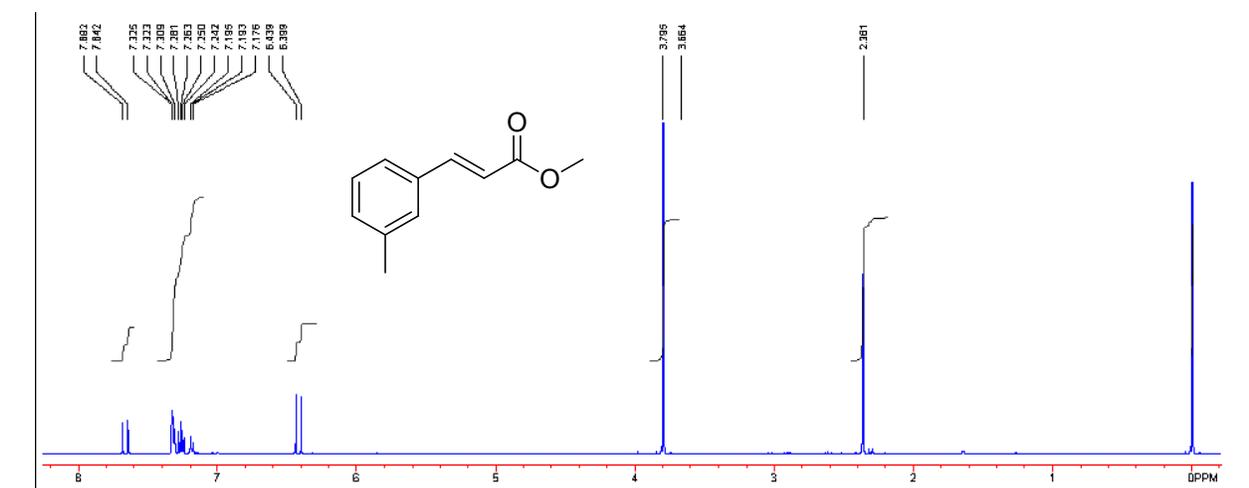


Fig. 24S

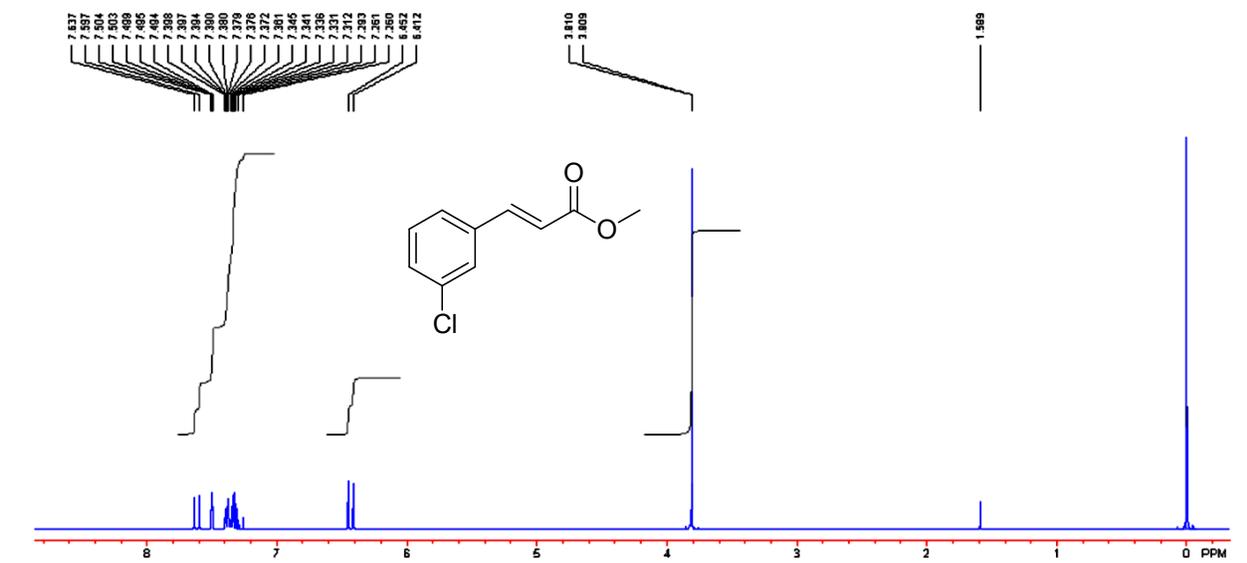


Fig. 25S

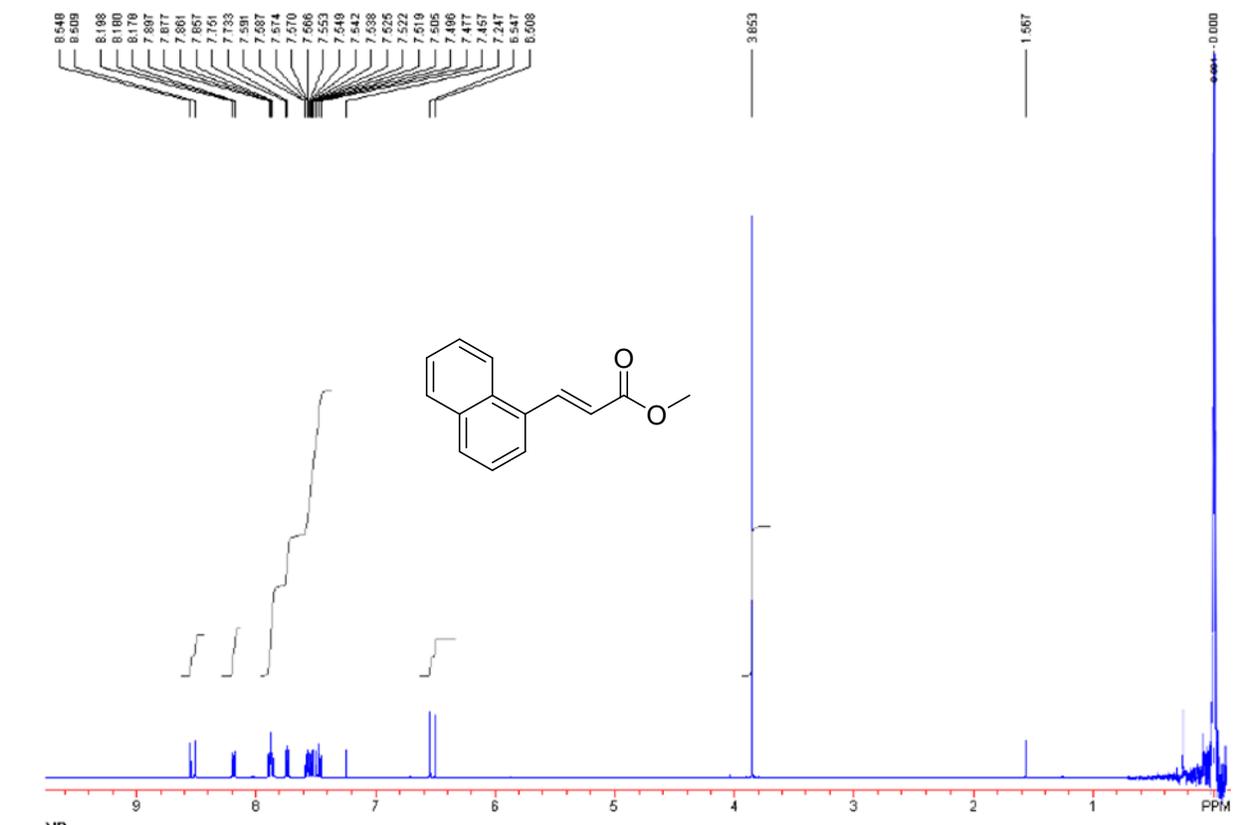


Fig. 26S

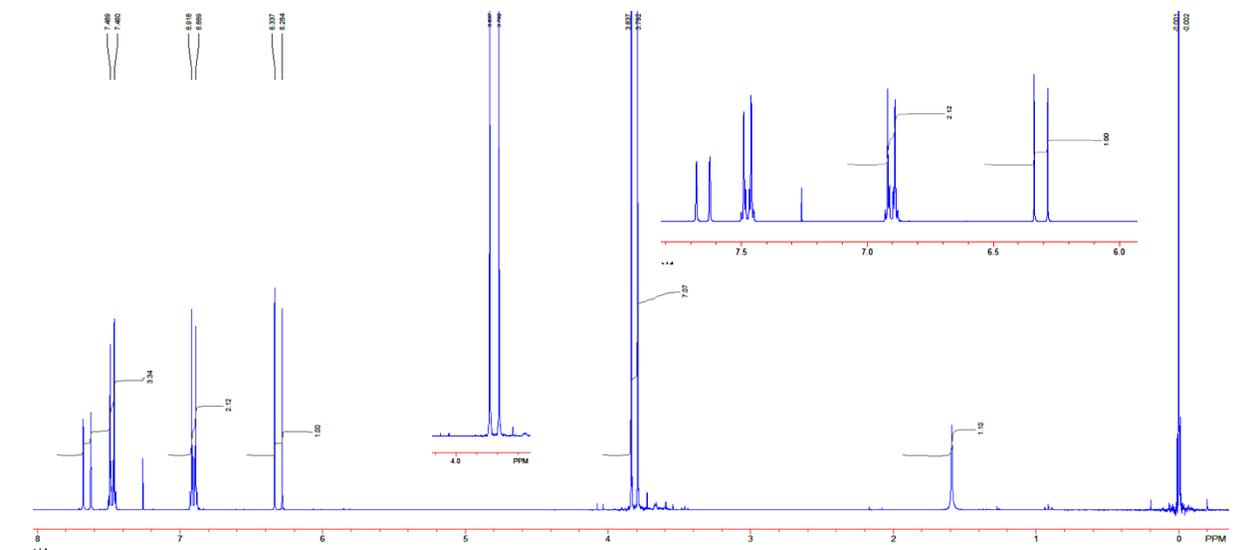


Fig. 27S

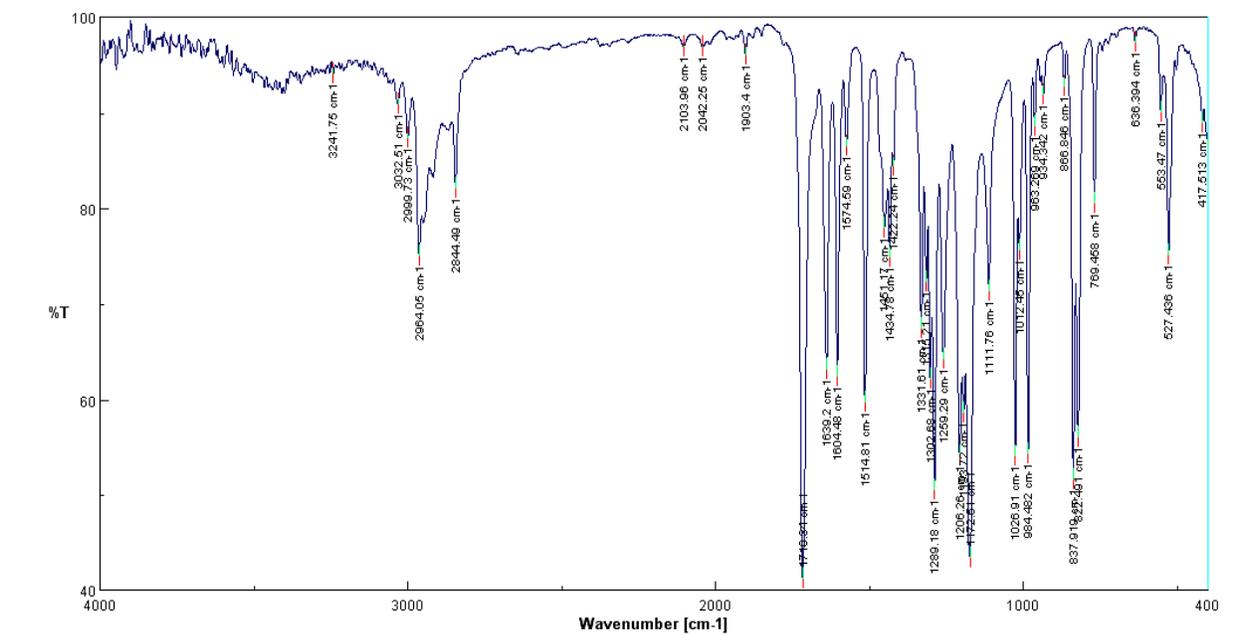


Fig. 28S

1. W. Stöber, A. Fink and E. Bohn, *Journal of Colloid and Interface Science*, 1968, **26**, 62-69.