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Supporting Information

Palladium Catalyst Supported on *N*-Aminoguanidine Functionalized Magnetic Graphene Oxide as a Robust Water-Tolerance and Versatile Nanocatalyst

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Experimental Section

Preparation of graphene oxide

Graphene oxide (GO) was prepared from graphite using modified Hummer's method.[1]

Briefly, 2 g $KMnO_4$ was gently added to a continuous stirring solution of graphite powder (1 g) and 50 mL H_2SO_4 98% in an ice bath. The rate of addition was carefully controlled to avoid a sudden increase of mixture temperature. The reaction mixture was stirred for 2 h at < 10 °C, followed by another 1 h at 35 °C. Then the mixture was diluted with deionized water (50 mL) in an ice bath and the temperature was kept below 100 °C. After 1 h, the mixture was further diluted with deionized water (150 mL). Afterwards, H_2O_2 30% (10 mL) was added to the mixture. The resulting solid was centrifuged and washed thoroughly with 5% aq. HCl and then, neutralized with deionized water. Finally the product was dried at 60 °C for 24 h.

Preparation of magnetic graphene oxide (MGO)

The MGO was constructed by co-precipitation of Fe^{3+} and Fe^{2+} in the presence of GO.[2] A solution of GO (50 mg) was dispersed in water (40 mL) via sonication for 45 min. Then a solution of $FeCl_3$ (1 g) and $FeCl_2$ (375 mg) in 50 mL deionized water was added to the later solution. The temperature was raised to 85 °C and the pH was increased to 10 by adding ammonia solution 30% and the stirred for 45 min. Then the solution was cooled to r. t., and the obtained precipitate was centrifuged at 6000 rpm for 10 min and washed thoroughly with deionized water and dried at 60 °C for 24 h.

Preparation of aminoguanidine functionalized magnetic graphene oxide (AGu@MGO)

To produce the aminoguanidine functionalized magnetic graphene oxide (AGu@MGO) nanosheets, first the surface of MGO with DEG (diethylene glycol) was modified. To attach DEG, the required carboxylic acid groups were introduced by taking 50 mg of MGO in deionized water (~4 mg/ml) and sonicating it for 1 h and then, 50 ml NaOH 1 M was added to it and sonicated again for 3 h. Then the solution was neutralized with HCl, filtered and then rinsed.[3]

Afterwards, 50 mg of the modified MGO was homogenized in 70 ml deionized water by ultrasonication for 10 min. Next, 10 mg of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and 8 mg of N-hydroxysuccinnimide (NHS) were added into the obtained solution. The mixture was stirred for 1 h and homogenized by ultrasonication for 30 min. Then, 2.5 mmol of H_2N-DEG-OTs was added into the suspension and sonicated for 30 min. Then, the reaction was stirring at 90°C for 1 h. The obtained OTs-DEG-MGO was purified by magnetic decantation and washed with water. At the end, 50 mg of OTs-DEG-MGO, 2.5 mmol of aminoguanidine hydrochloride (AGu. HCl), and 2.0 g of sodium carbonate in 50 mL DMF were stirred at 90 °C overnight. The obtained solid was separated by a magnet. The product was successively washed with deionized water to neutralize and then was dried under vacuum at 60°C for 24 h to give aminoguanidine functionalized magnetic graphene oxide (AGu@MGO) nanosheets.

Preparation of Pd nanoparticles supported on aminoguanidine functionaized graphene oxide (Pd@AGu@MGO)

1 mmol of $PdCl_4{}^{2-}$ was added to a solution of AGu@MGO (100 mg) in dry acetone and was stirred at 40 °C for 24 h under inert atmosphere. Then, the final product, which named as Pd@AGu@MGO was separated by centrifugation, washed thoroughly with EtOH and diethyl ether, and dried under vacuum at r. t. for 12 h.

General procedure for Heck reaction

Aryl halide (1.0 mmol), alkene (1.1 mmol), K_2CO_3 (2.0 mmol) and catalytic amount of Pd@AGu@MGO (10 mg) was stirred in EtOH: H_2O (1:1) (3.0 ml) at r.t. and the reaction progress was monitored by TLC. At the end, the catalyst was removed by magnet. The liquid was poured into distilled water (20 ml) and the product was extracted with ethyl acetate. The organic layer was dried with Na_2SO_4. Then the organic layer was evaporated and the column chromatography on silica gel using *n*-hexane:ethyl acetate (5:1) as eluent gave the purified products. The recovered catalyst was washed with water and EtOH, and dried at r. t. and used for next runs. The catalyst recycling test was performed in the reaction between bromobenzene and n-butyl acrylate according to the above procedure.

General procedure for Suzuki reaction

Aryl halide (1.0 mmol), aryl boronic acid (1.1 mmol), K_2CO_3 (2.0 mmol) and the catalytic amount of of Pd@AGu@MGO (10 mg) was stirred in H_2O (3.0 ml) at r.t. and then, the reaction progress was monitored by TLC. After the reaction, the catalyst was separated from mixture by a magnet device. Then, the residual mixture was poured into distilled water (20 ml) and extracted with ethyl acetate. The organic layer was washed with brine, dried by anhydrous Na_2SO_4, and filtered. Next, the solvent was evaporated and the product was purified by column chromatography on silica gel using a mixture of *n*-hexane:ethyl acetate (5:1) as eluent.

Catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP)

Nanocatalyst (0.1 mg) of was added to a solution containing 2.5 mL of fresh $NaBH_4$ (1.2 M) and 10 mL aq. solution of 3.4 mmol 4-NP and stirred. The color of the solution was faded as the reaction proceeded. To monitor the progress of the reaction, UV-vis spectra were recorded at short intervals (a few seconds). This procedure was repeated for blank experiments to show that the reactions do not proceed without the catalyst.

References

[1] W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* **1958**, *80*, 1339-1339.

[2] M. Z. Kassaee, E. Motamedi, M. Majdi, *Chem. Eng. J.* **2011**,*172*, 540– 549.

[3] Z. Liu, J. T. Robinson, X. Sun, H. Dai, *J. Am. Chem. Soc.* **2008**, *130*, 10876–10877.

Characterization of Nanocatalyst

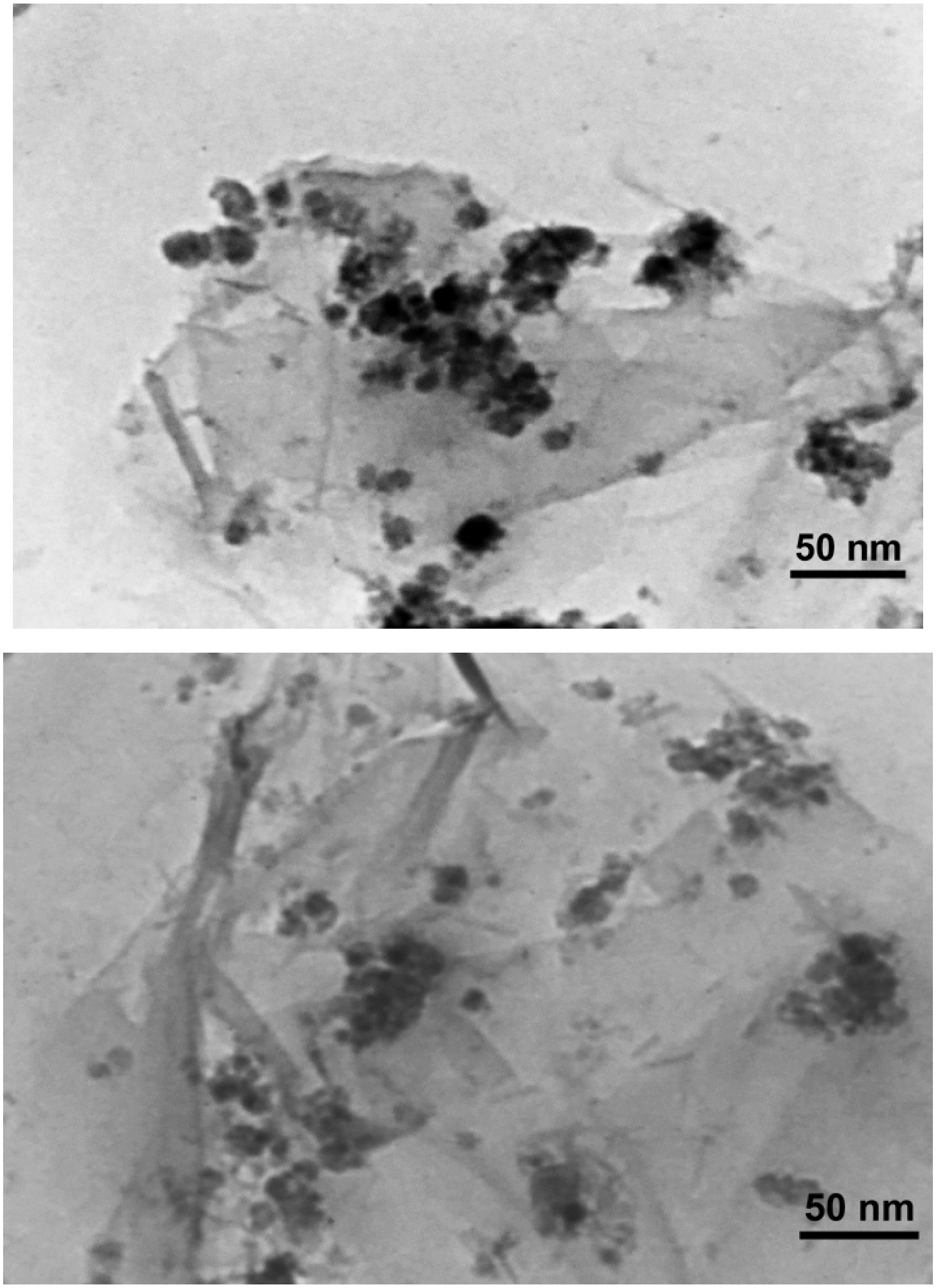


Figure 1. TEM image of AGu@MGO nanosheets.

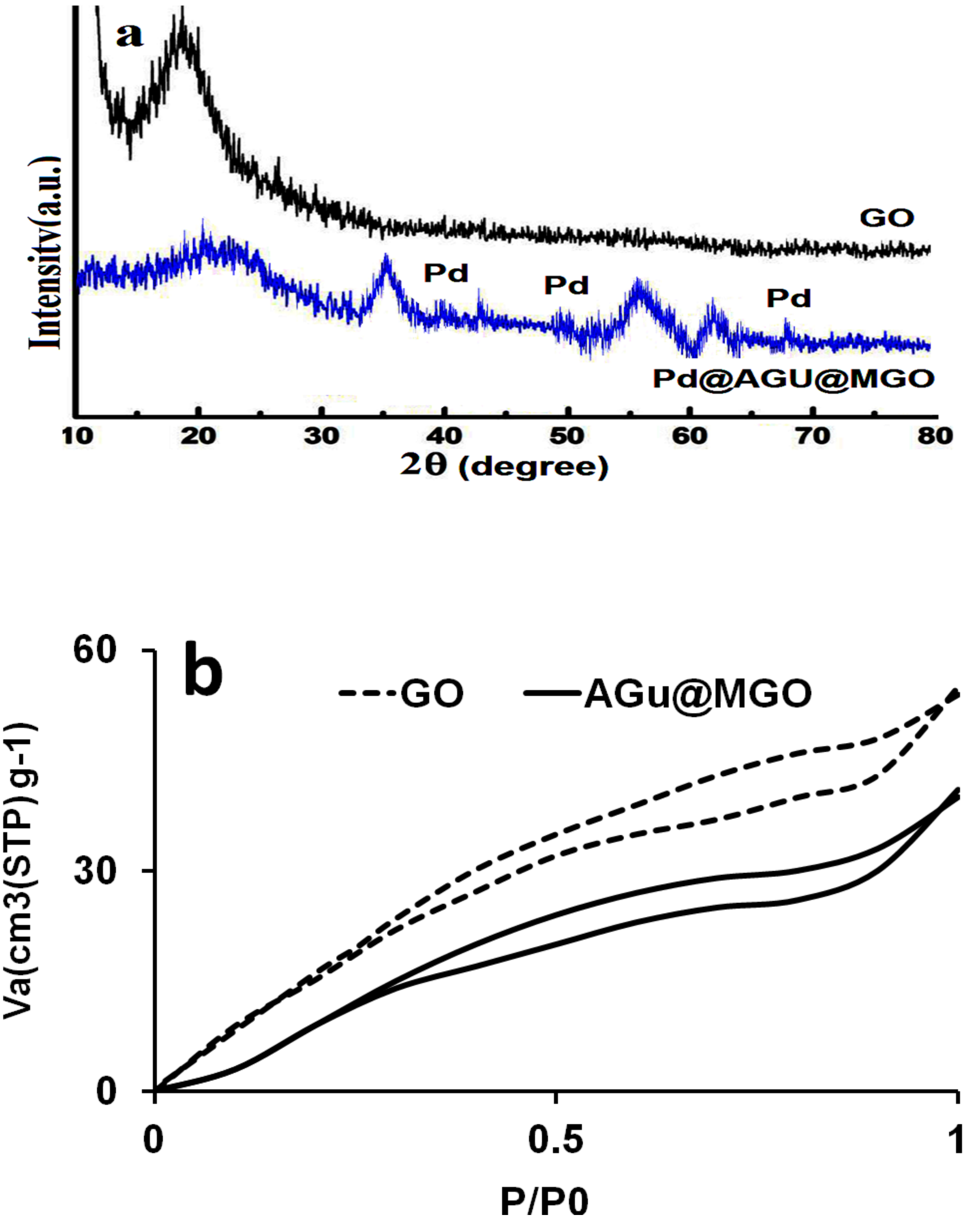


Figure 2. (a) XRD pattern of GO and Pd@AGu@MGO nanosheets; and (b) N_2 adsorption-desorption isotherm of Go and AGu@MGO.

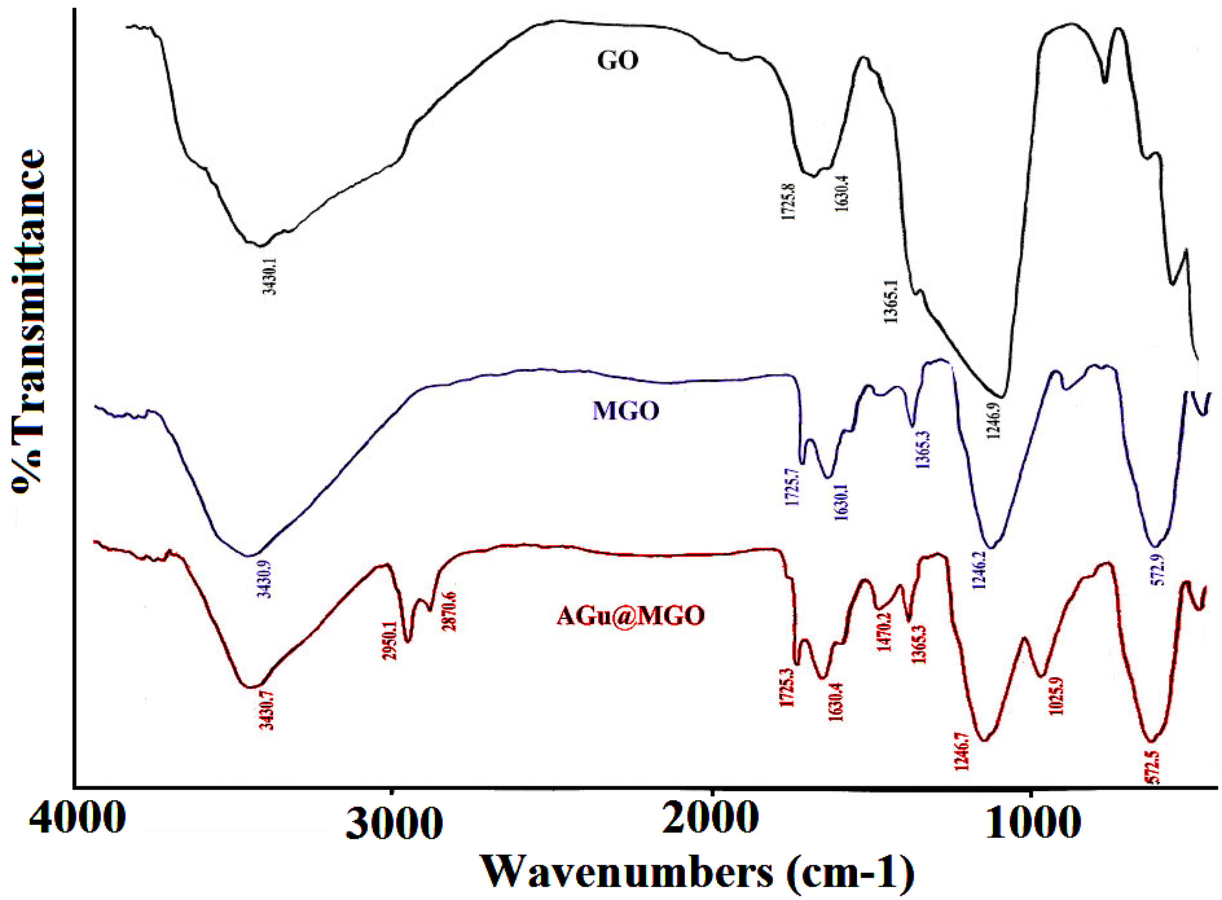


Figure 3. FTIR spectra of Go, MGO, and AGu@MGO

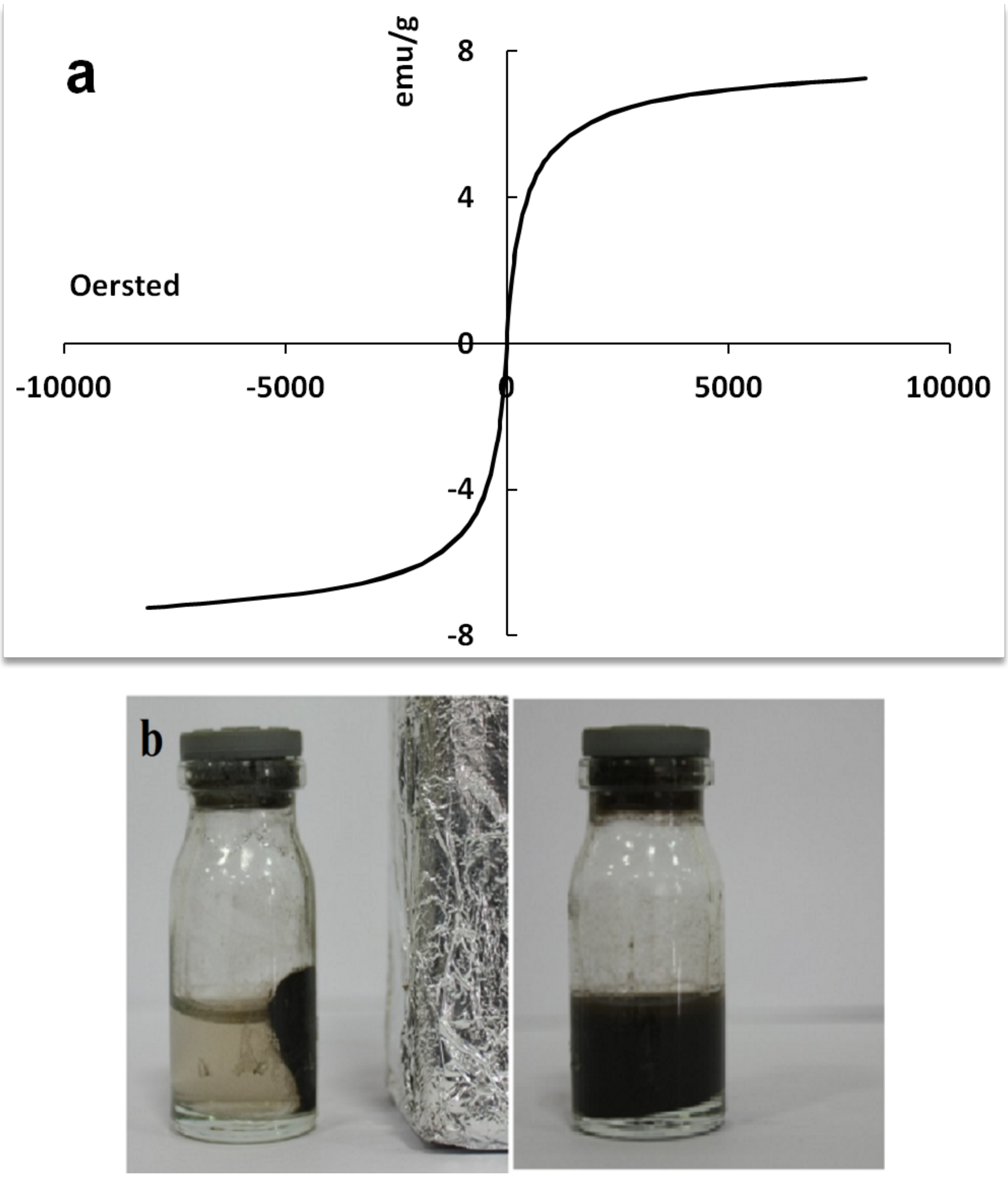
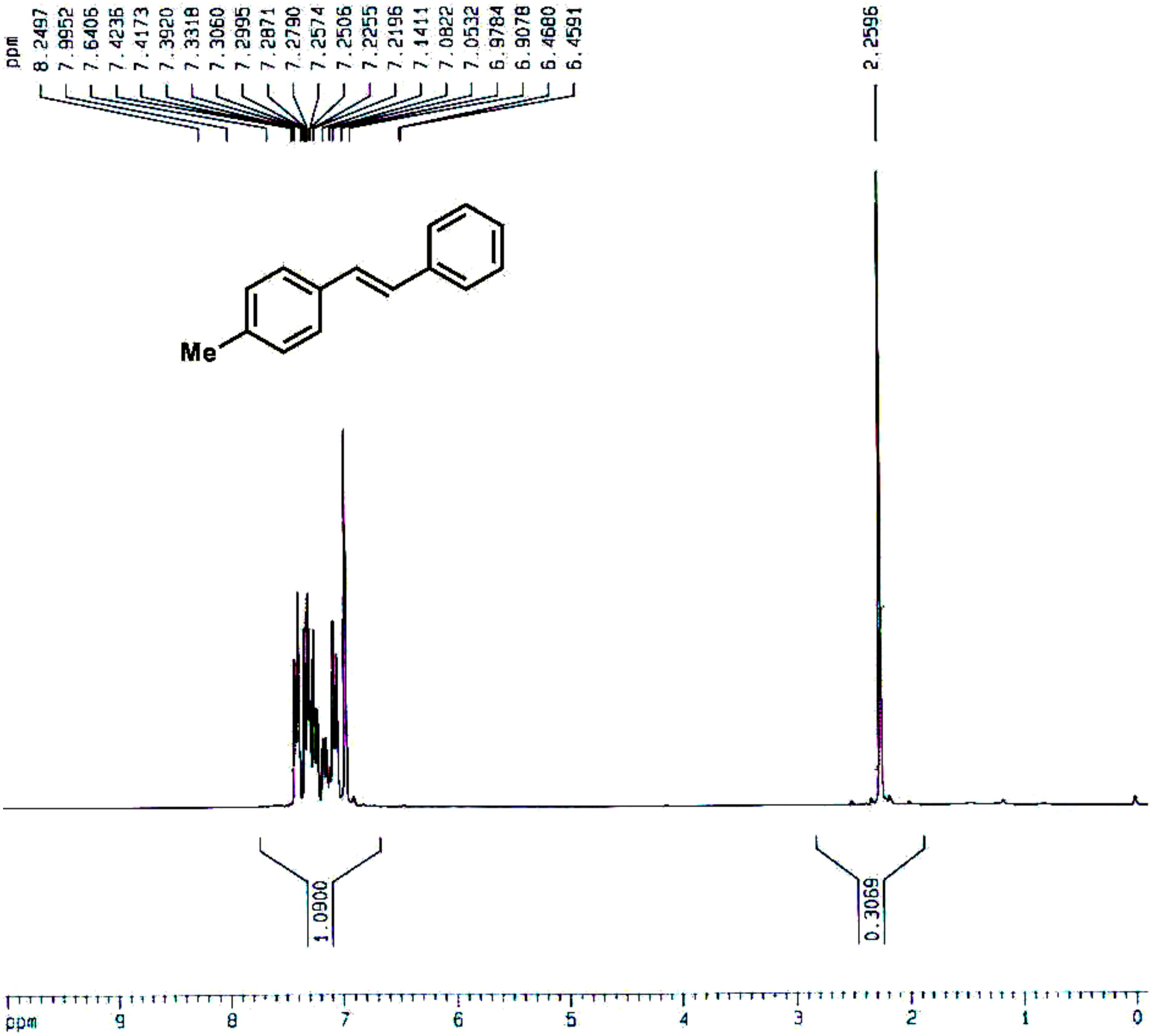


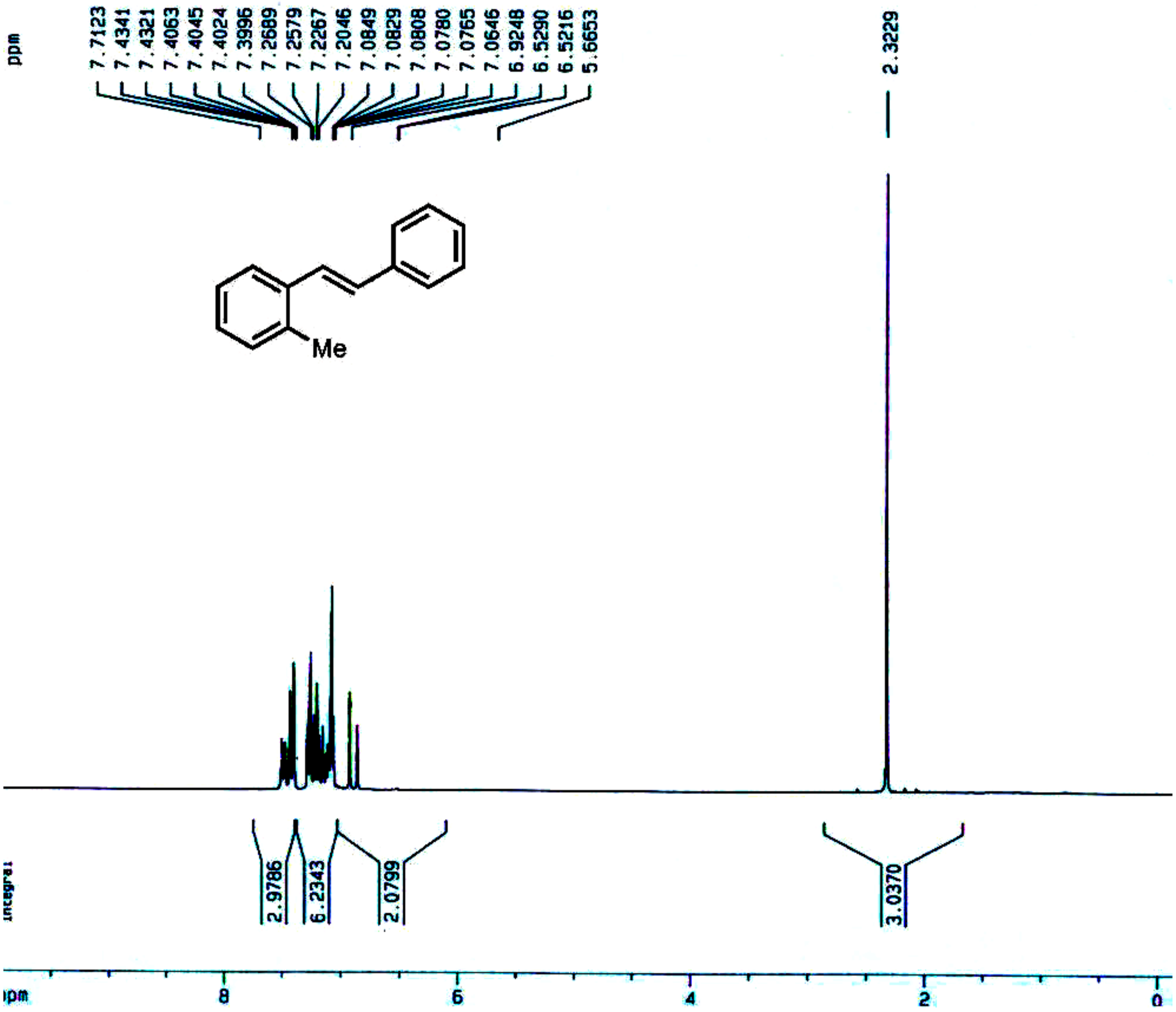
Figure 4. a) The VSM of AGu@MGO nanosheets, and b) magnetic separation of Pd@AGu@MGO nanosheets.

¹HNMR Spectra of the selected products

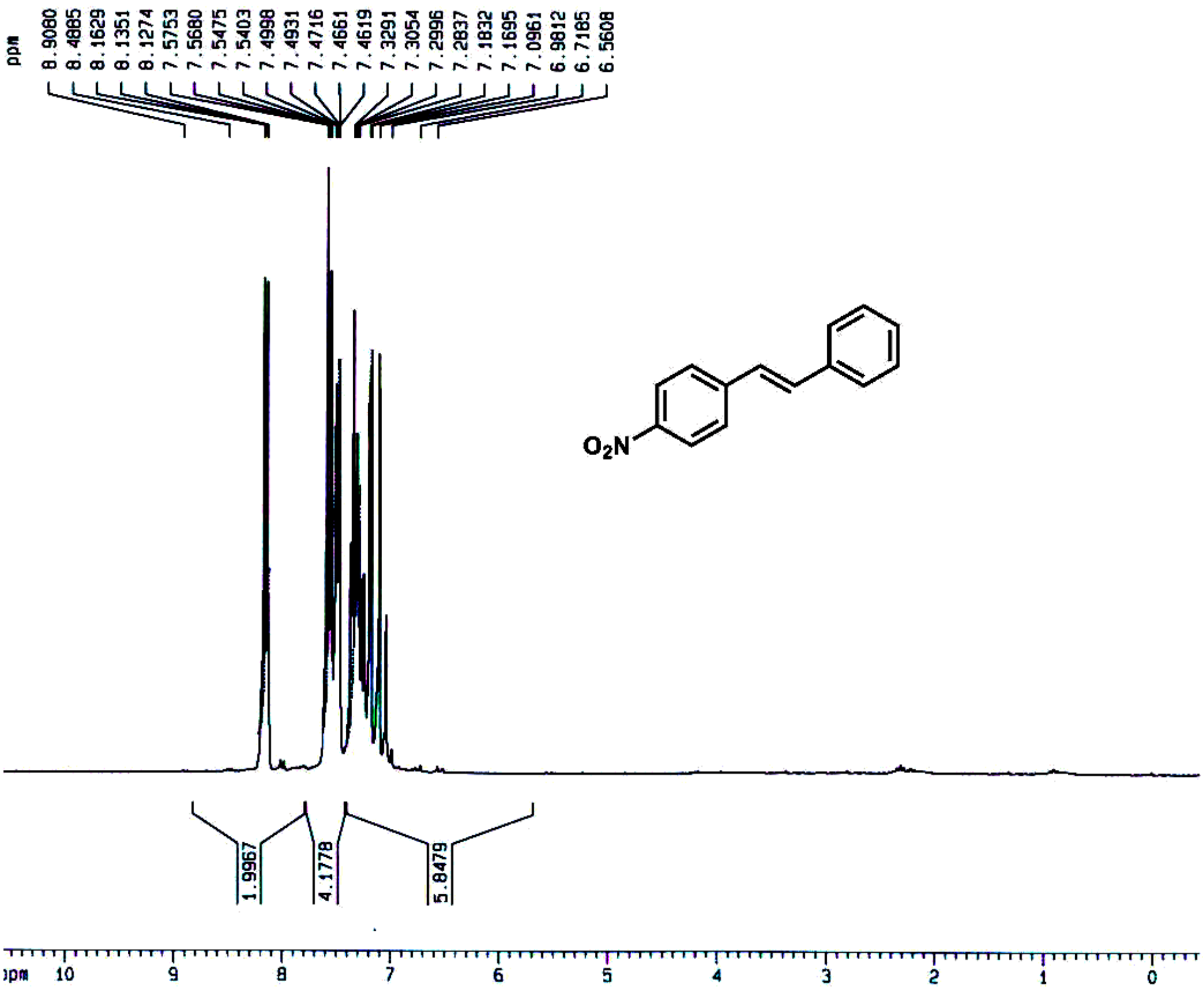
a) Heck Reaction



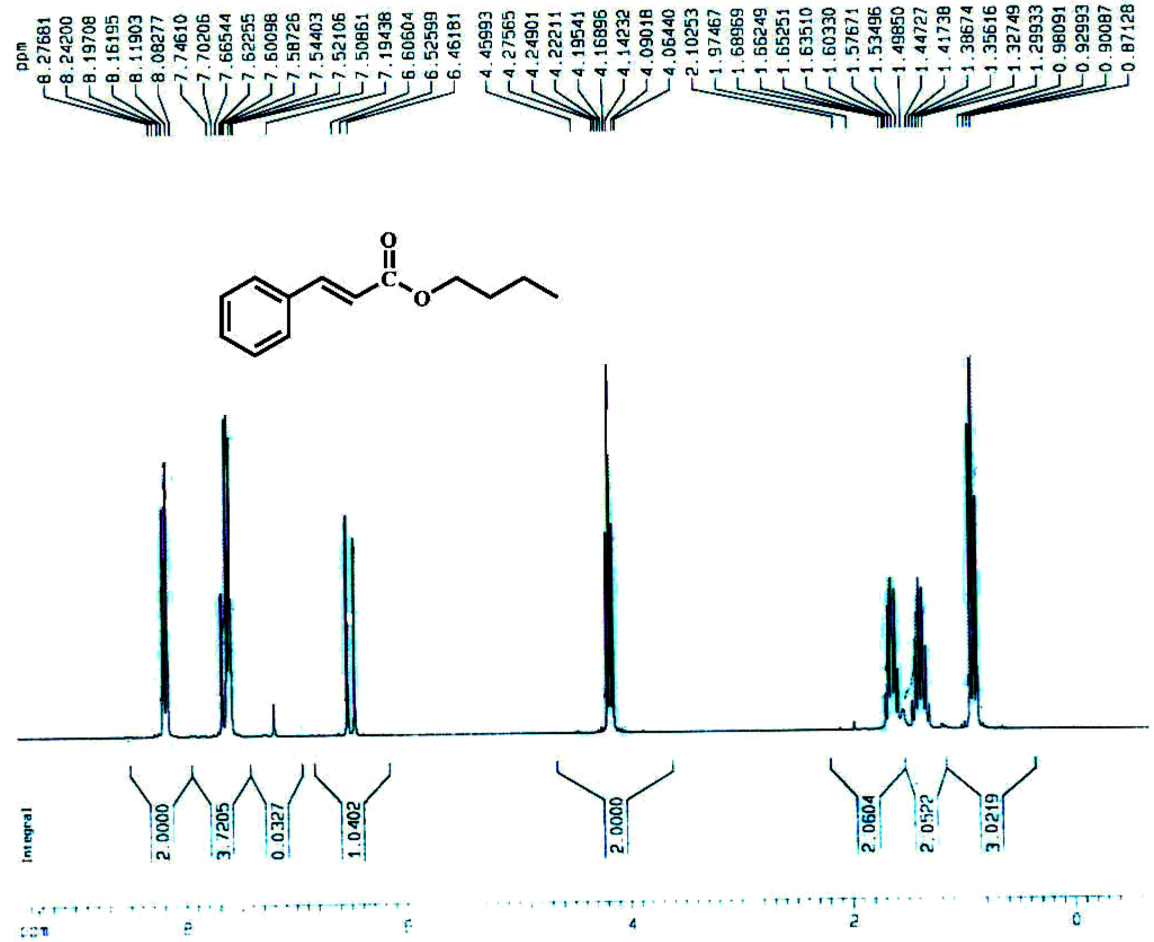
¹HNMR spectrum of **(E)-4-Methylstilbene**



^{1}HNMR spectrum of **(E)-2-Methylstilbene**

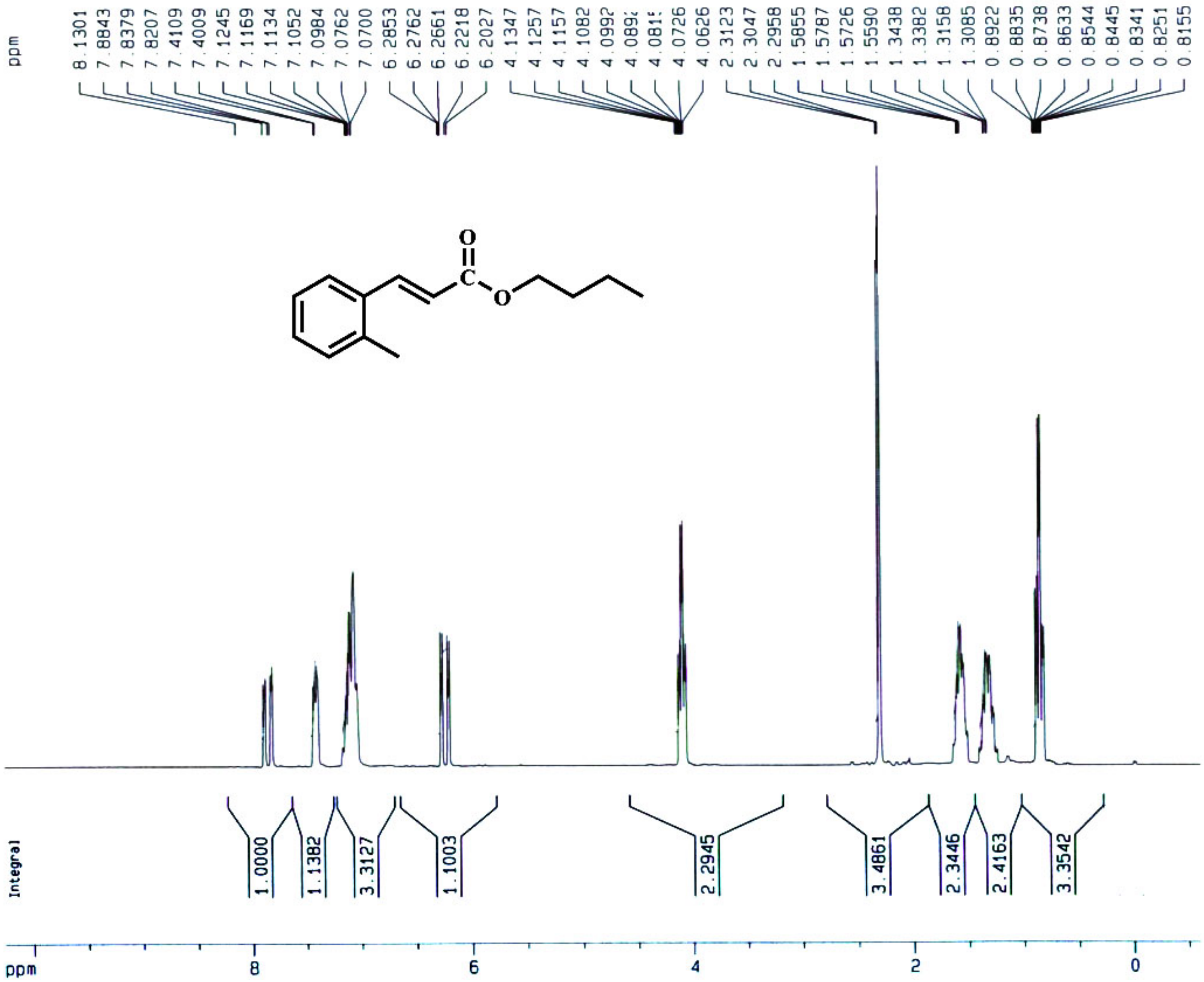


^{1}HNMR spectrum of **(E)-4-Nitrostilbene**



^{1}HNMR spectrum of **n-Butyl (E)-cinnamate**

^{1}HNMR spectrum of **n-Butyl (E)-3-(4-methylphenyl)prop-2-enoate**



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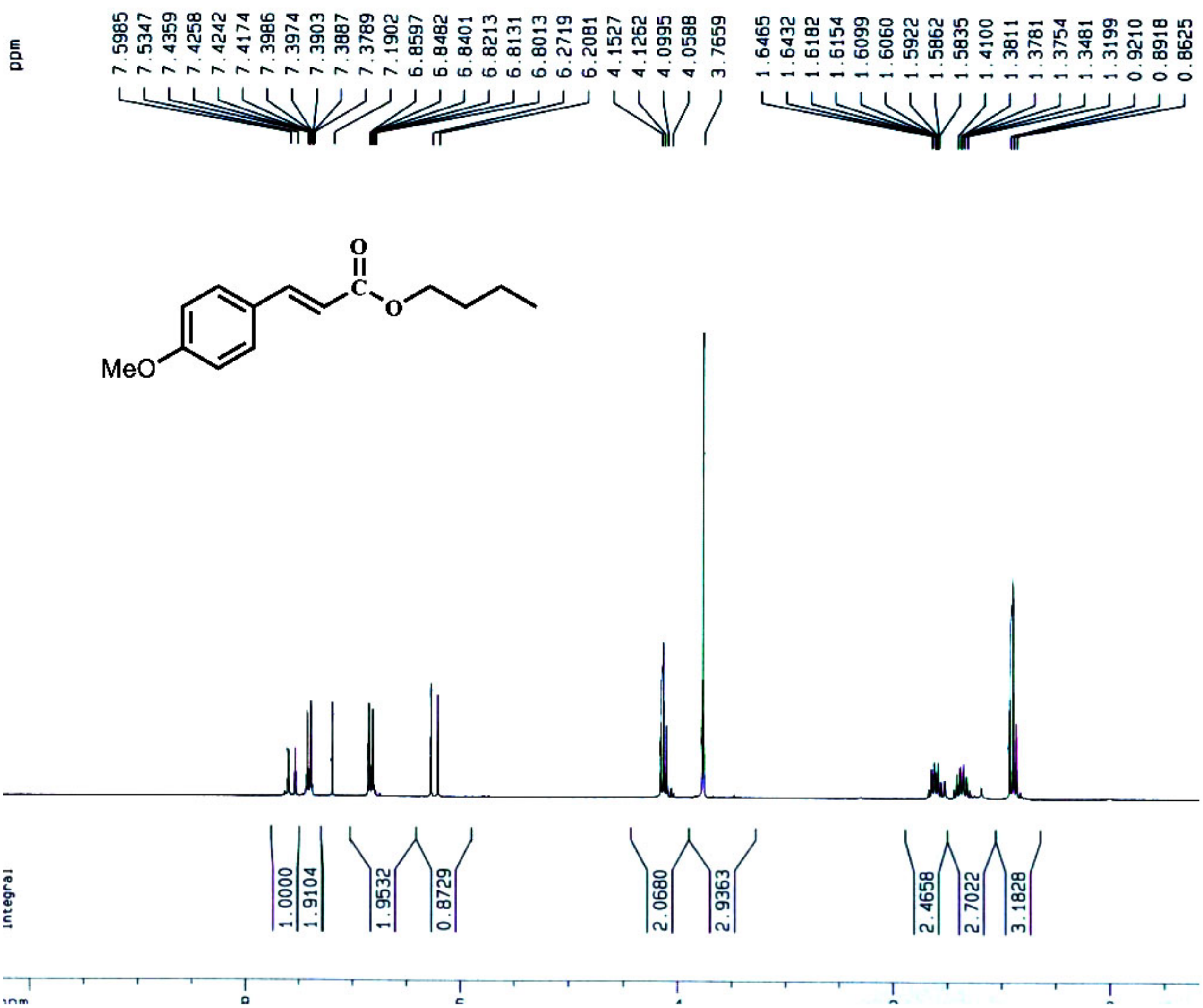
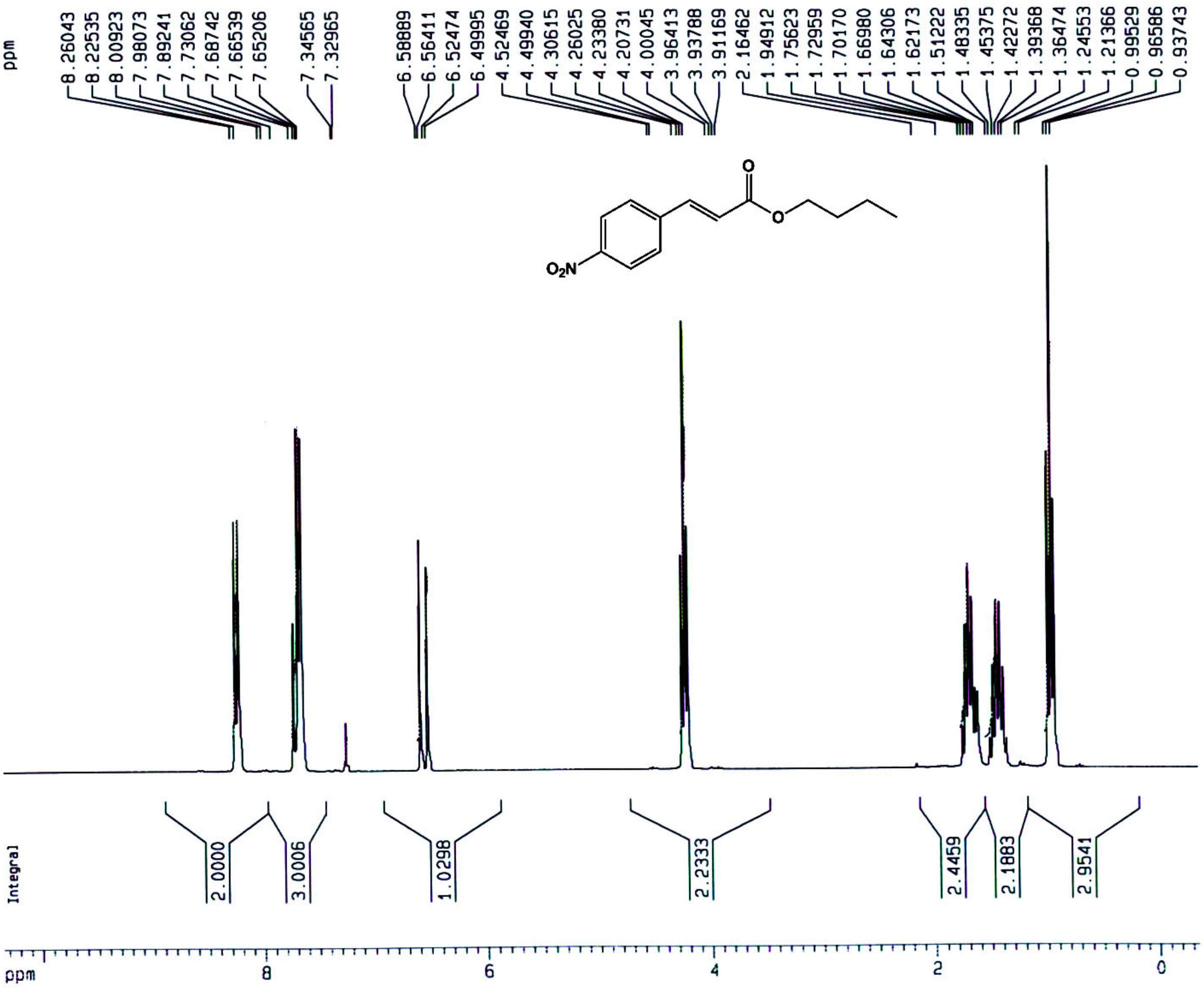
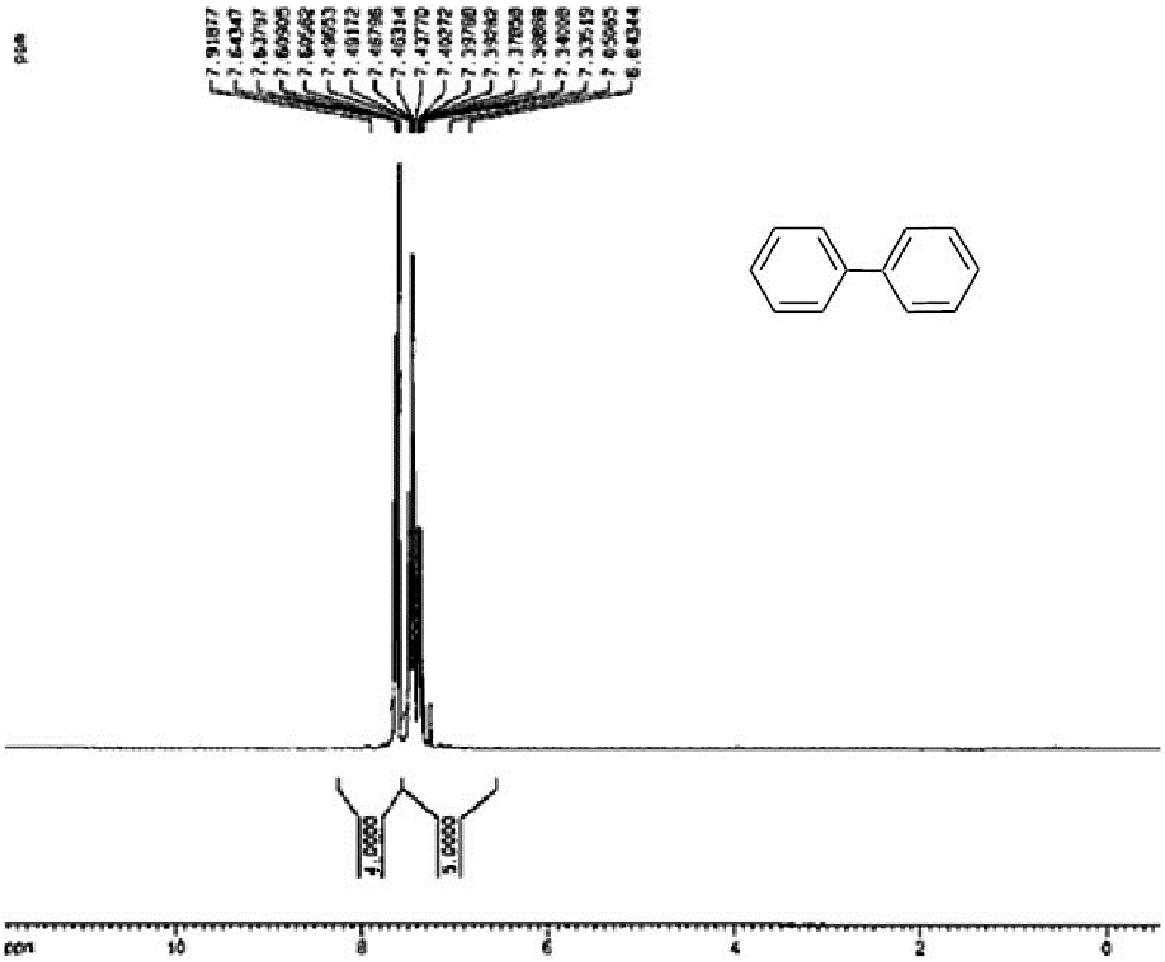


^{1}HNMR spectrum of **n-Butyl (E)-3-(4-methoxyphenyl)prop-2-enoate**



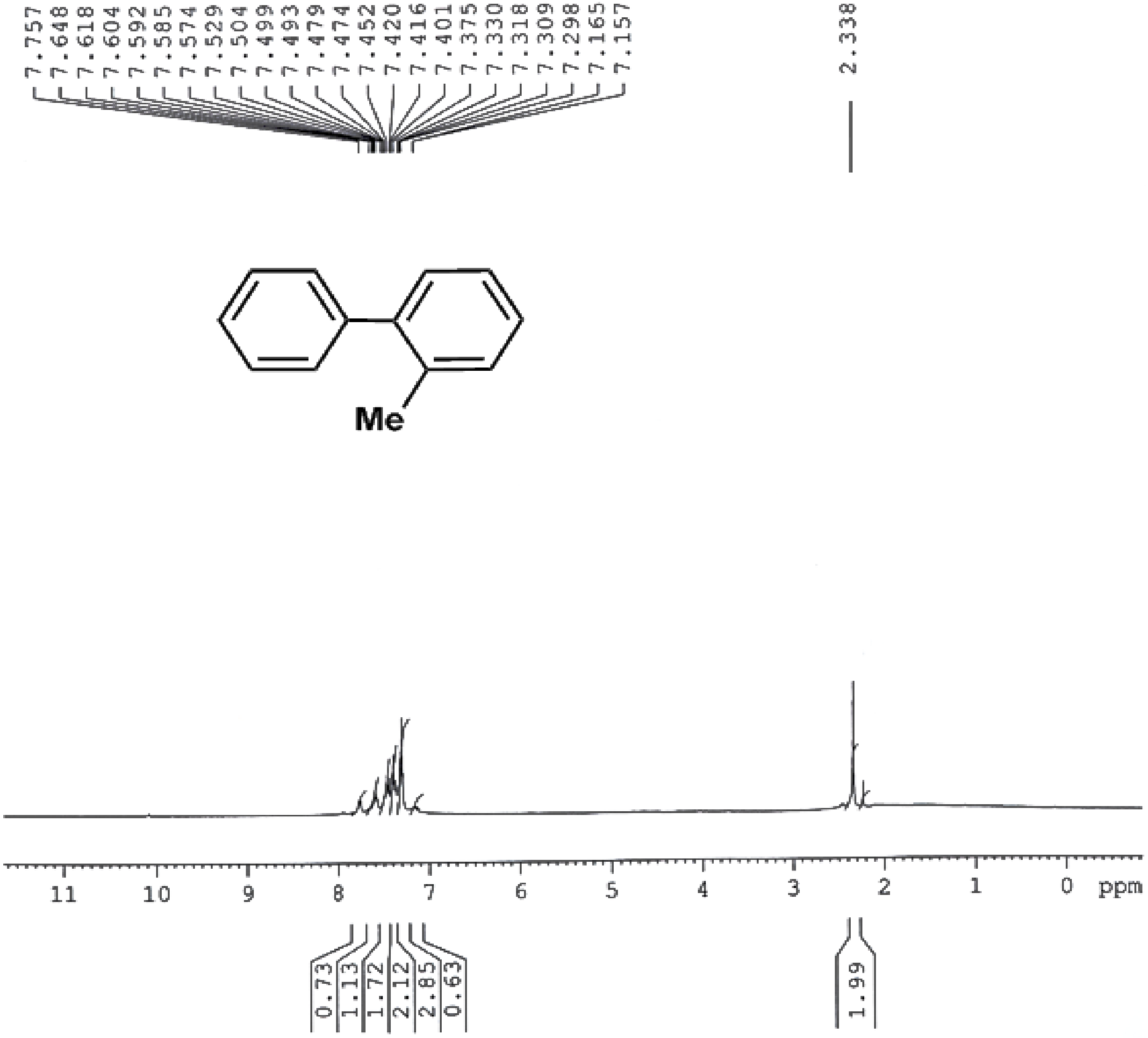
^{1}HNMR spectrum of **n-Butyl (E)-3-(4-nitrophenyl)prop-2-enoate**

b) Suzuki Reaction



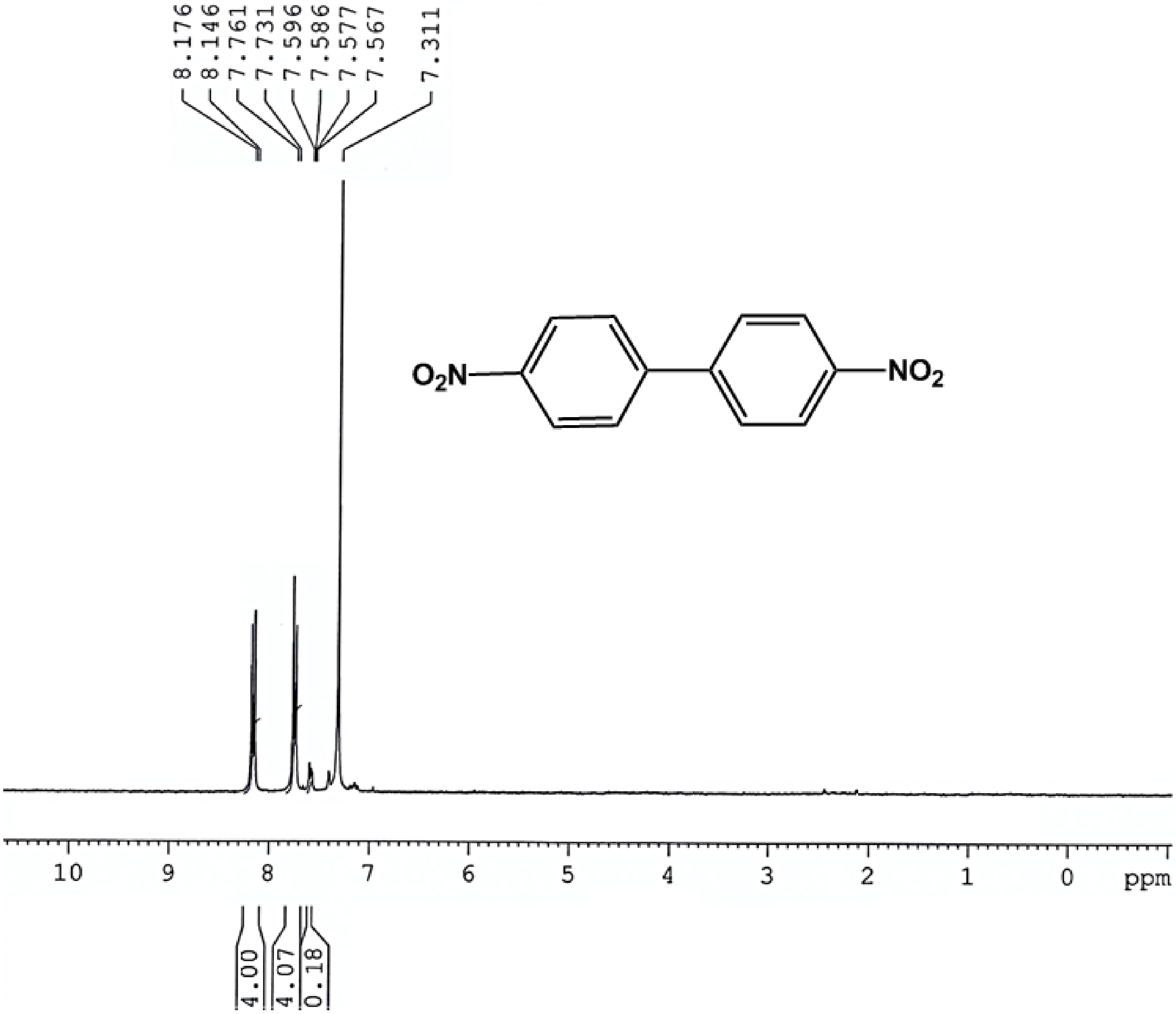
^{1}HNMR spectrum of **1,1'-biphenyl**

^{1}HNMR spectrum of **4-methoxy-1,1'-biphenyl**



^{1}HNMR spectrum of **2-Methyl-1,1'-biphenyl**

^{1}HNMR spectrum of **4-Nitro-1,1'-biphenyl**



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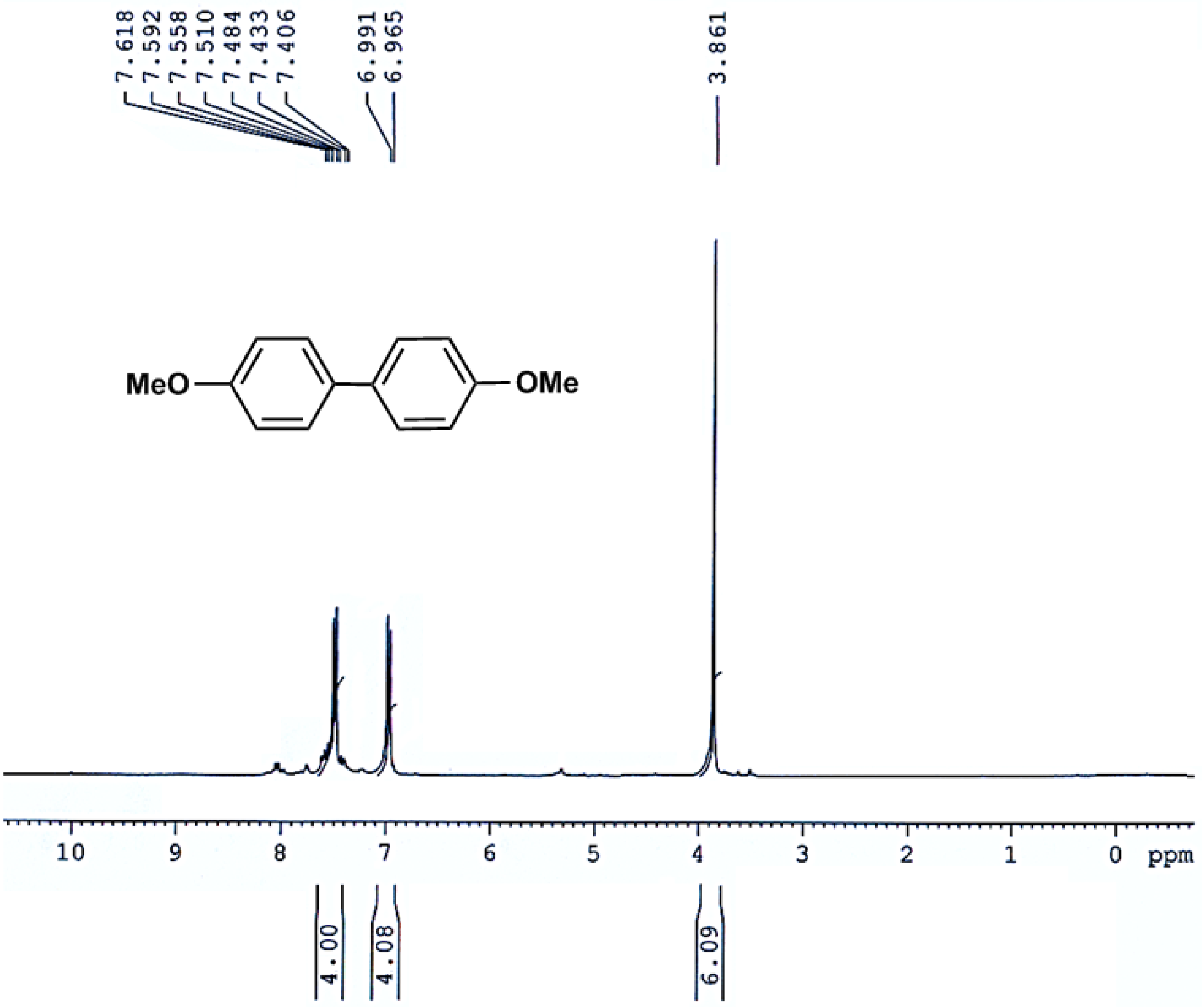
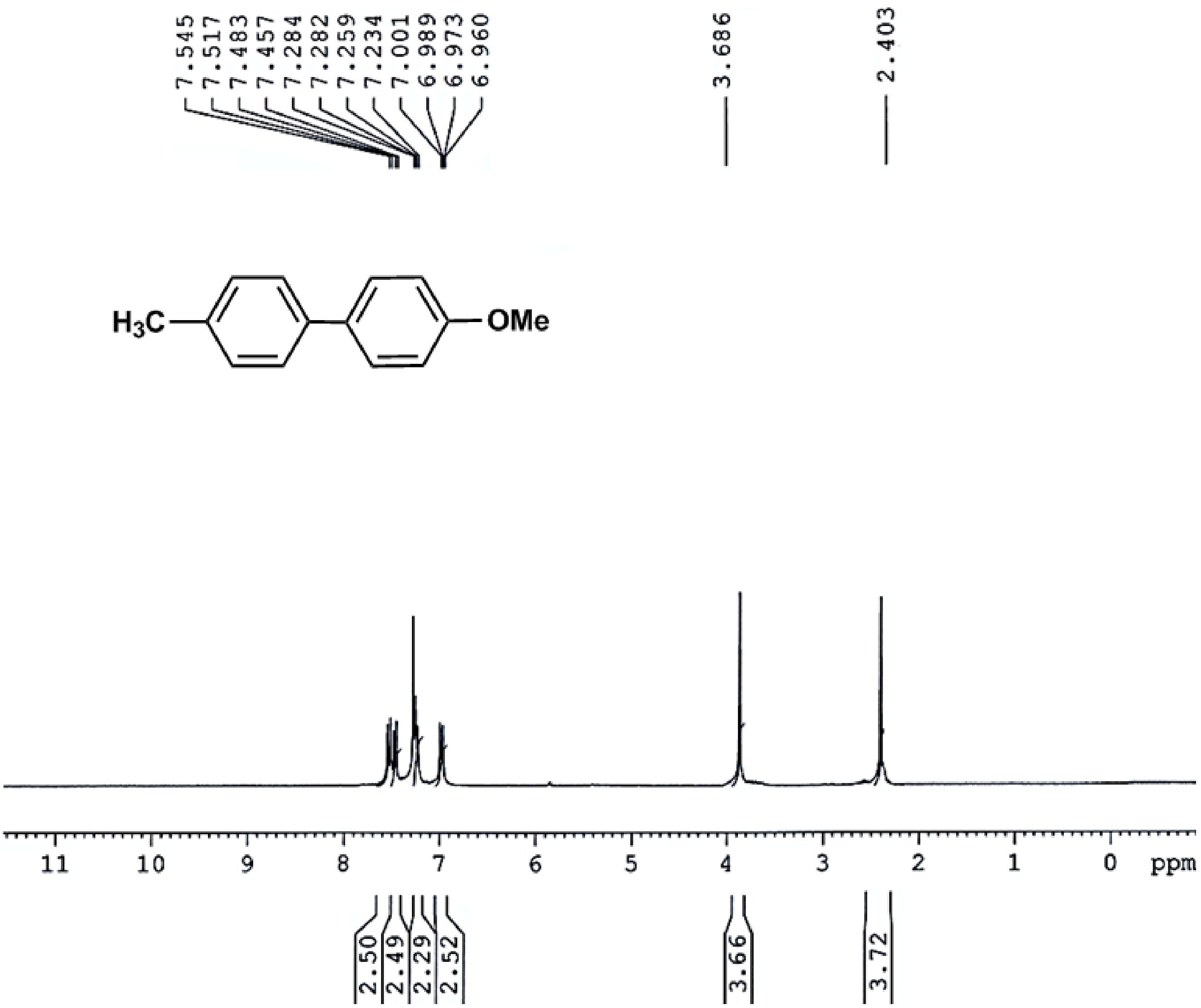
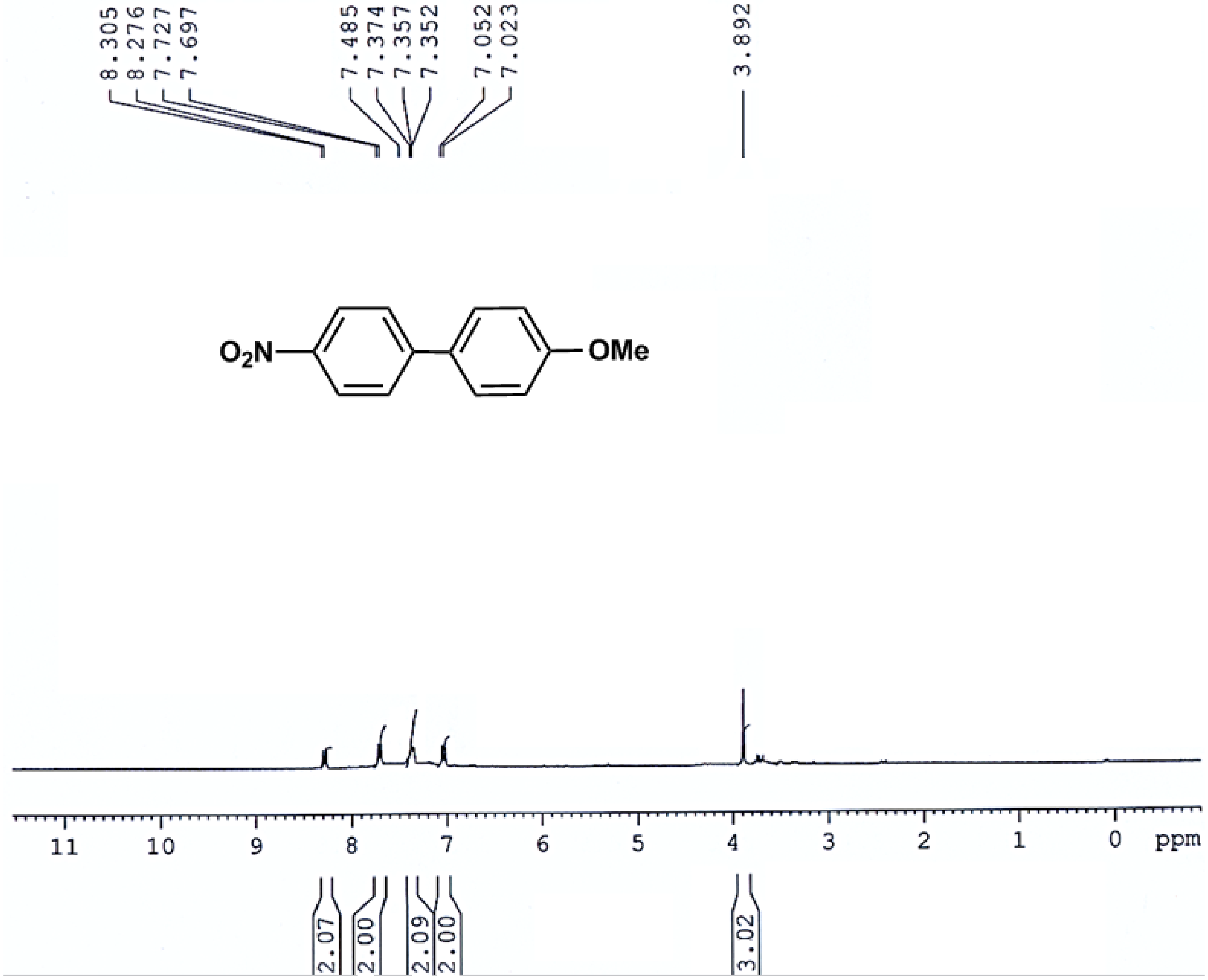


^{1}HNMR spectrum of **4,4'-Dimethoxy-1,1'-biphenyl**



^{1}HNMR spectrum of **4'-Methoxy-4-methyl-1,1'-biphenyl**



^{1}HNMR of spectrum **4'-Methoxy-4-nitro-1,1'-biphenyl**