SUPPORTING INFORMATION

A simple and facile Heck-type arylation of alkenes with diaryliodonium salts using magnetically recoverable catalyst

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1. General Information

The reagents were obtained commercially and used without further purification. The preparation of diaryliodonium salts were carried out according to the literature procedures mentioned in the manuscript. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz NMR spectrometer using TMS as the internal standard. Chemical shifts are given in parts per million (d) and coupling constants (J) in Hz. MS data was obtained on Hewlett Packard HP 5973 quadrupole Mass Selective Detector with interface for 6890 series GC. Thin-layer chromatography (TLC) was performed on silica gel 60 F254 precoated glass plates.

2. Experimental Procedures

2.1. Procedure for the catalyst preparation

Preparation of magnetic nano-ferrites

The magnetic nano-ferrites were prepared by dissolving 13.9 g of $FeSO_4.7H_2O$ and 20 g of $Fe_2(SO_4)_3$ in 500 mL water. To this stirring solution was slowly added ammonium hydroxide (25%) to adjust the solution pH to 10. The stirring was further continued for 1 h while maintaining the temperature at 60 ^{o}C. The precipitated nano-ferrites were separated using an external magnet. The separated nanoparticles were washed with water till the solution pH was neutral. It was then dried under vacuum for 2 h at 60 ^{o}C.

Dopamine functionalization of magnetic nanoparticles

2 g of nano-ferrites prepared by the above method were dispersed in water (25 mL) by sonicating for 0.5 h. A solution of dopamine hydrochloride (2 g) in 5 mL of water was added to the aqueous suspension of nano-ferrites and further sonicated for 2 h. The dopamine functionalized nano-ferrites were isolated by centrifugation and was washed with acetone followed by drying under vacuum at 60 ^{o}C for 2 h.

Preparation of [Fe_3O_4-Dopa-Pd] catalyst

The amine functionalized nano-ferrites (1 g) were stirred in methanol (25 mL) at room temperature. To the above stirring suspension was slowly added $PdCl_2$ (200 mg) and further stirred for 10 min. A 25% NH_4OH solution was added slowly to adjust the pH of the mixture to 9 and stirred for further 24 h. The synthesized magnetic nano-catalyst was retrieved using an external magnet and washed with acetone for three times followed by drying under vacuum at 60 ^{o}C for 2 h.

2.2. General Procedure for Heck-type arylation reaction

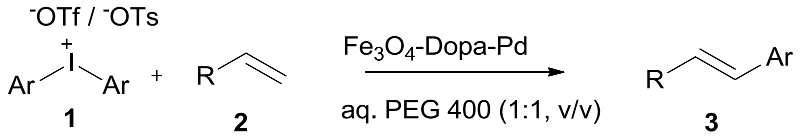
The diaryliodonium salt (1.0 mmol), alkene (1.1 mmol), 50 mg (4.8 mol %) of [Fe-Dopa-Pd] catalyst with aqueous PEG-400 (1:1, v/v, 3 mL) is subjected to ultrasonication (1-5 min) (cycle: 20 sec pulse and 10 sec pause) on high intensity sonicator. Upon completion of the reaction, as indicated by TLC, the reaction mixture is diluted with water and the crude product is extracted using ethyl acetate. The organic layer is dried over anhydrous Na_2SO_4 and purified by passing through silica gel column to afford the products (**3a-m**).

3. Heck-type arylation of alkenes at room temperature

The Heck-type arylation of alkenes was also carried out by stirring at room temperature for up to 12 hours. This room temperature procedure, however, was not applicable to all substrates. The successful reactions at room temperature appeared to be cleaner with slightly improved yields.

3.1. General Procedure for the reaction at room temperature: The diaryliodonium salt (1.0 mmol), alkene (1.1 mmol), 50 mg (4.8 mol %) of [Fe-Dopa-Pd] catalyst with aqueous PEG-400 (1:1, v/v, 3 mL) is stirred at room temperature for up to 12 hours. Upon completion of the reaction, as indicated by TLC, the reaction mixture is diluted with water and the crude product is extracted using ethyl acetate. The organic layer is dried over anhydrous Na_2SO_4 and purified by passing through silica gel column to afford the products.

Table S3. Room temperature Heck-type arylation of alkenes.



S.No.	Ar	R	Product	Yield (%)
1	C_6H_5	$-COCH_3$	3a	92
2	C_6H_5	$-CO_2n$Bu	3c	85
3	C_6H_5	$-CH_2OH$	3f	50
4	4-*t*-BuC_6H_4	$-CH_2OAc$	3l	85
5	4-OMeC_6H_4	$-CH_2OAc$	3m	82

4. TEM image of the recovered [Fe_3O_4-Dopa-Pd] catalyst.

After the reaction is complete, the catalyst was recovered by using an external magnet and washed with acetone followed by drying in vacuum oven. The TEM analysis demonstrated that the catalyst morphology and size remains unchanged upon reuse (Figure S1)

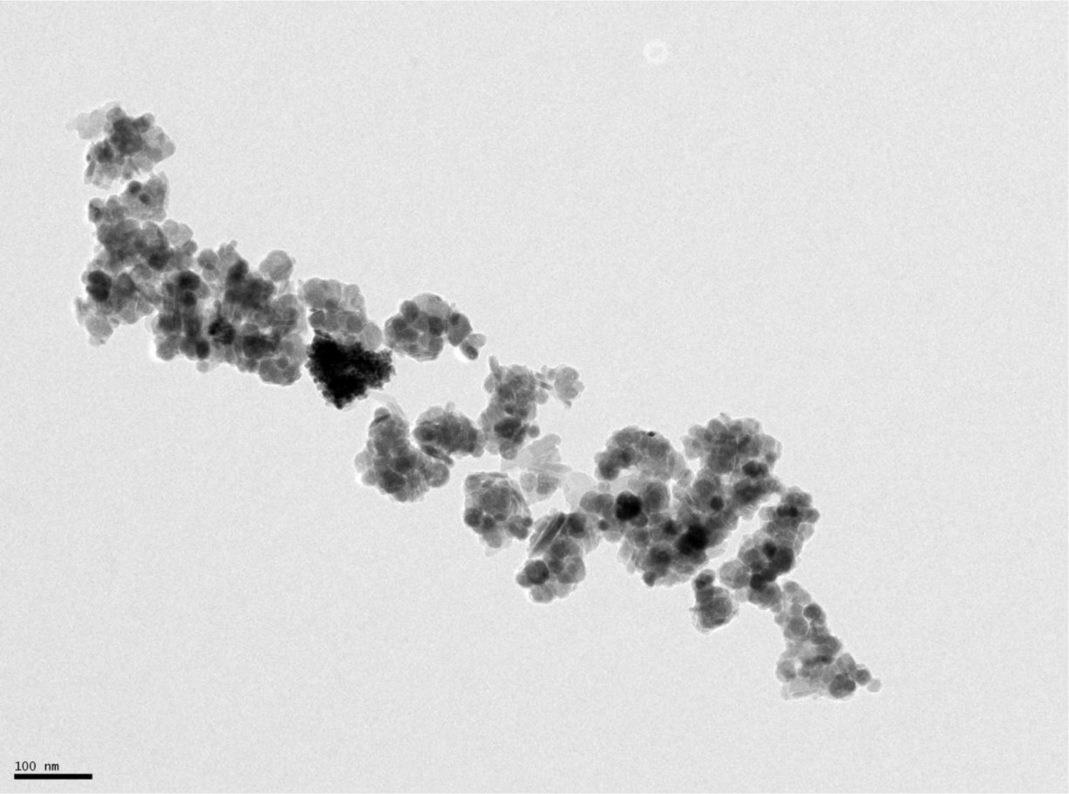
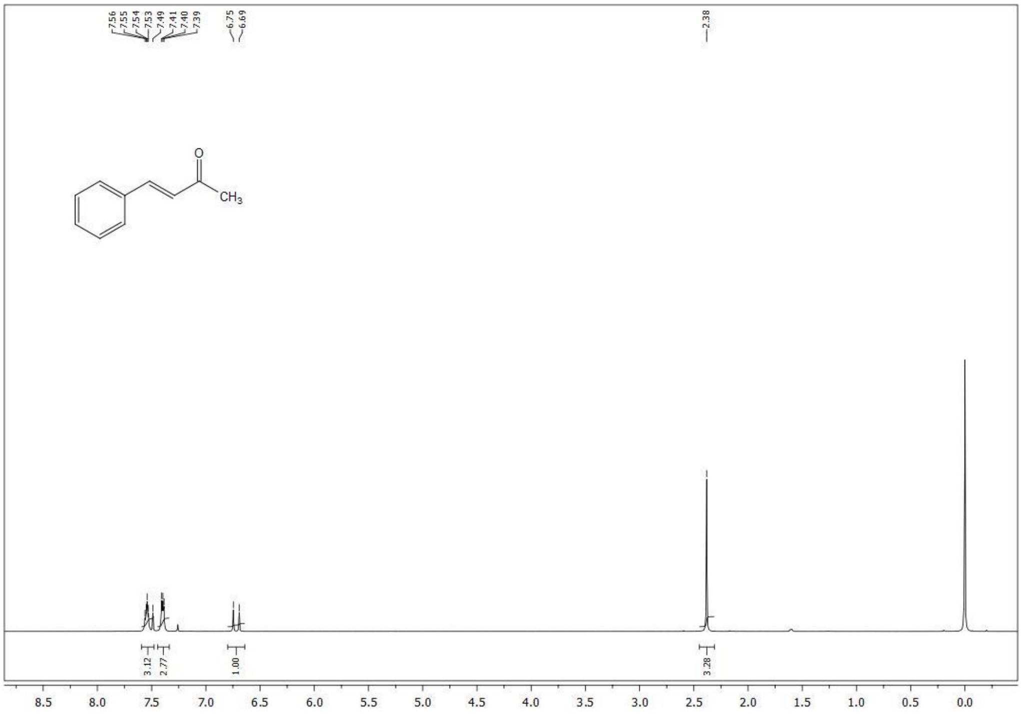
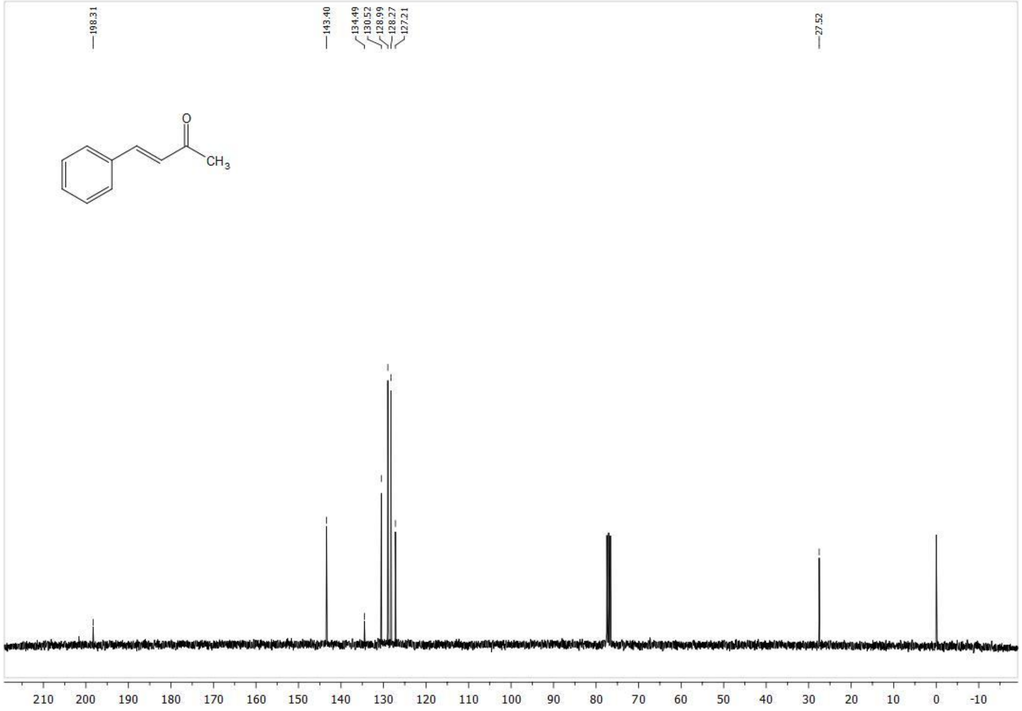


Figure S1. TEM image of the recovered [Fe_3O_4-Dopa-Pd] catalyst.

^{1}H & ^{13}C NMR spectra

(*E*)-4-Phenylbut-3-en-2-one (3a):





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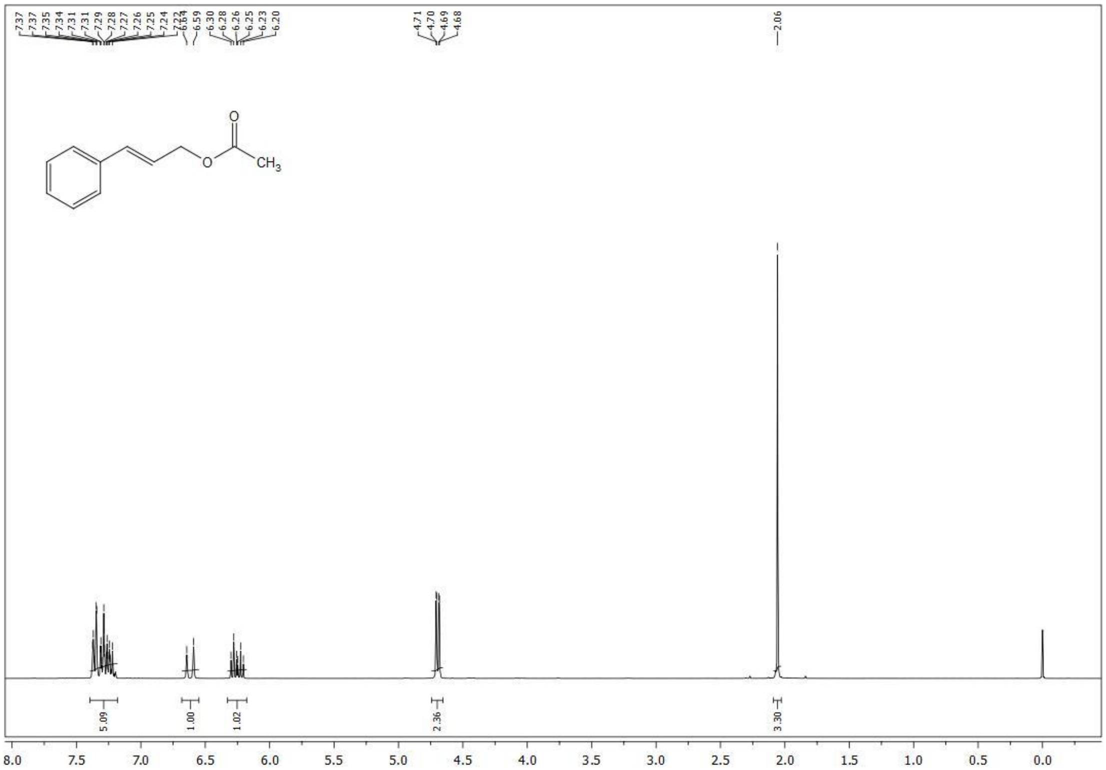
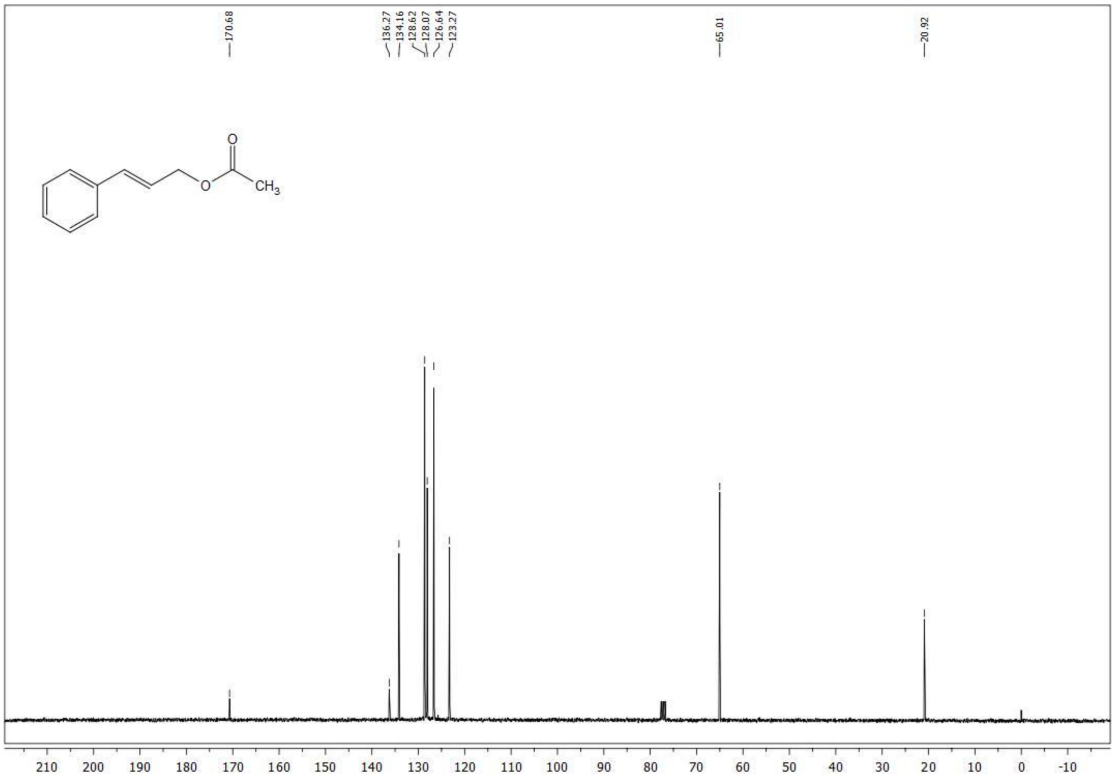
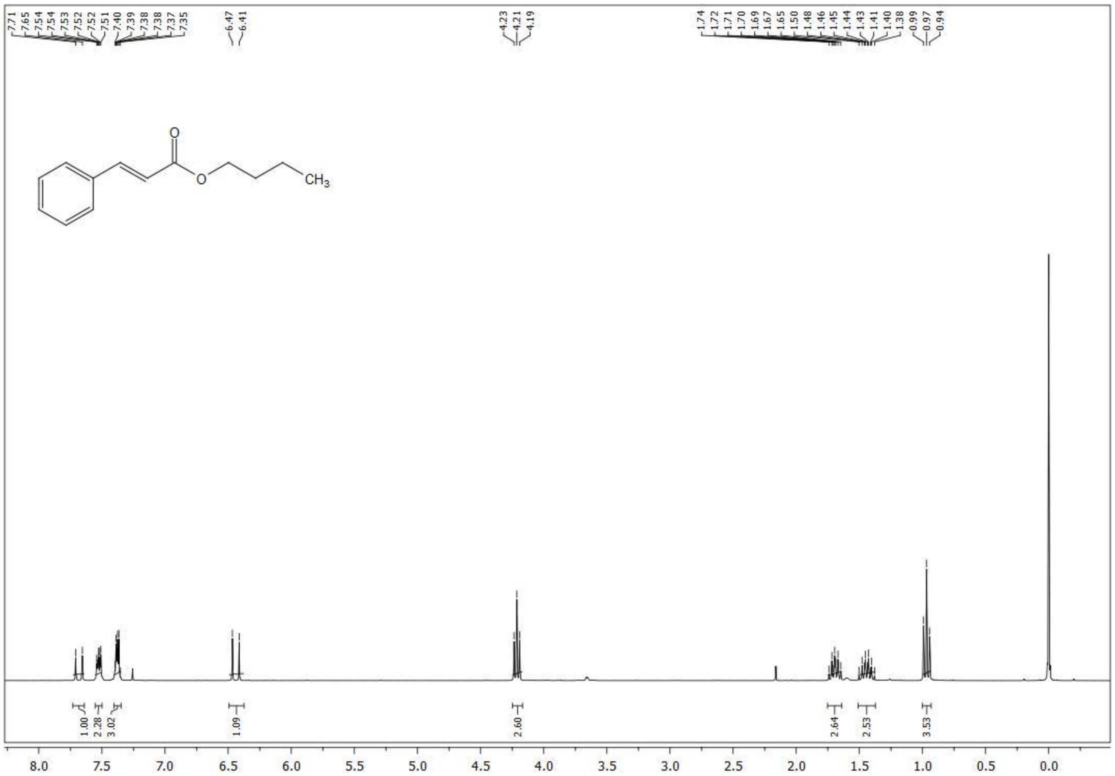
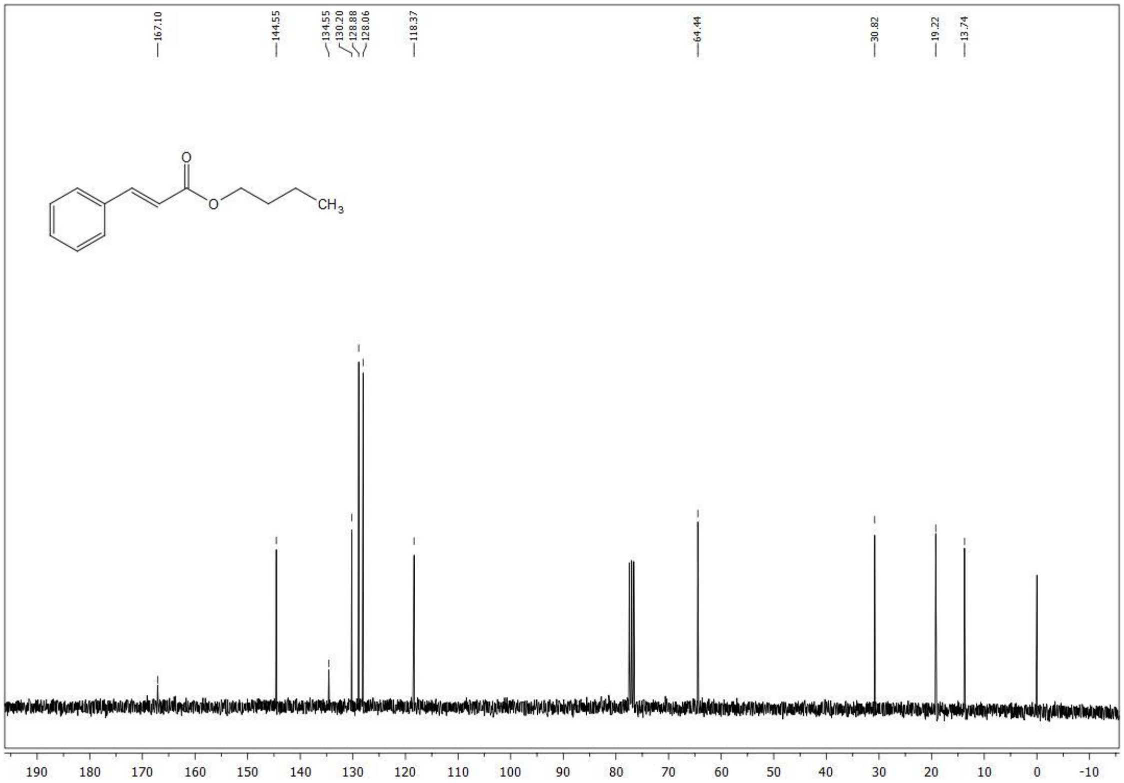


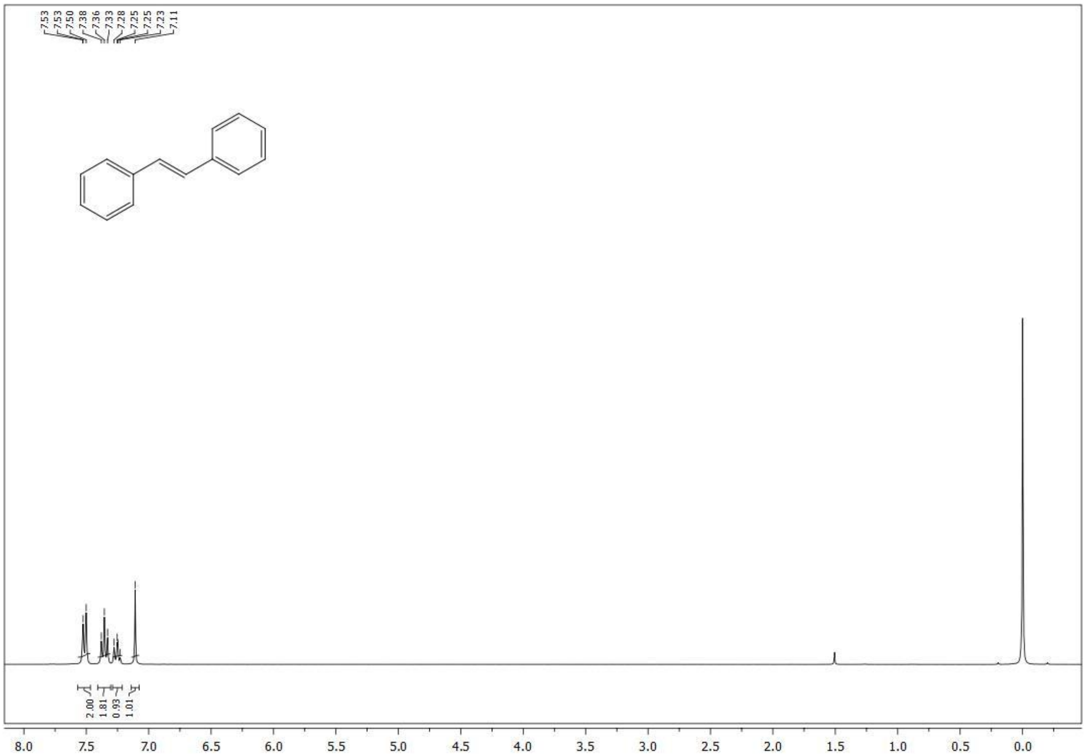


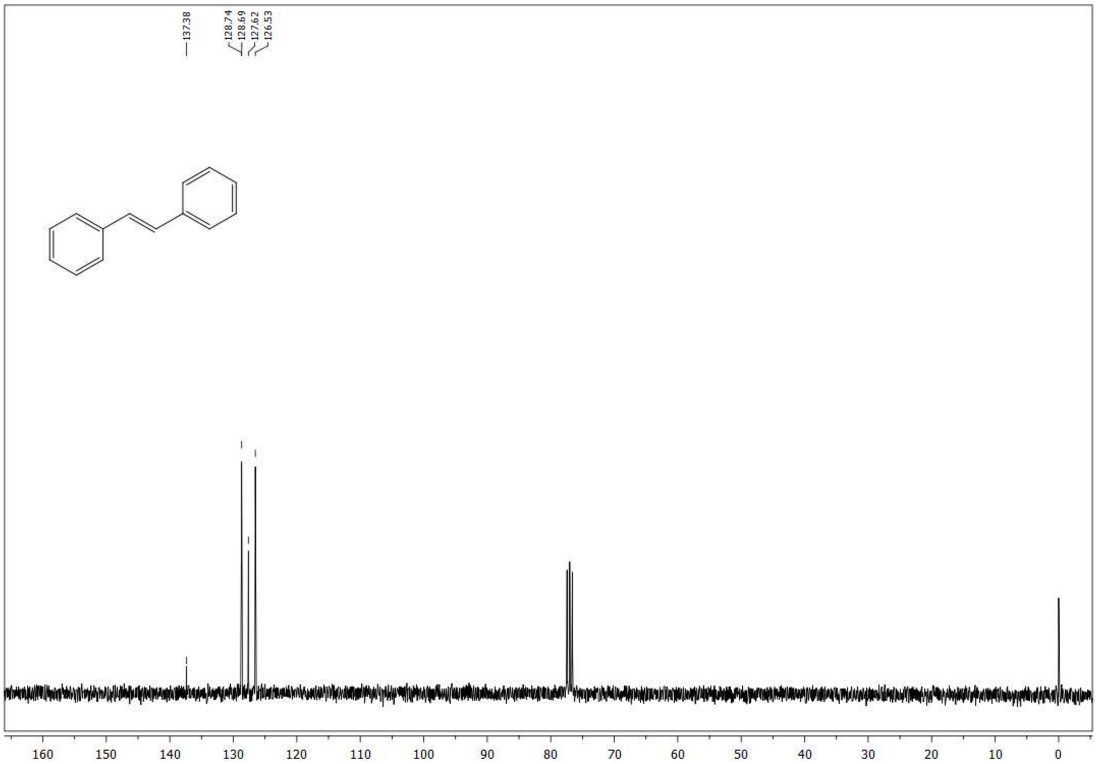
Butyl cinnamate (3c):



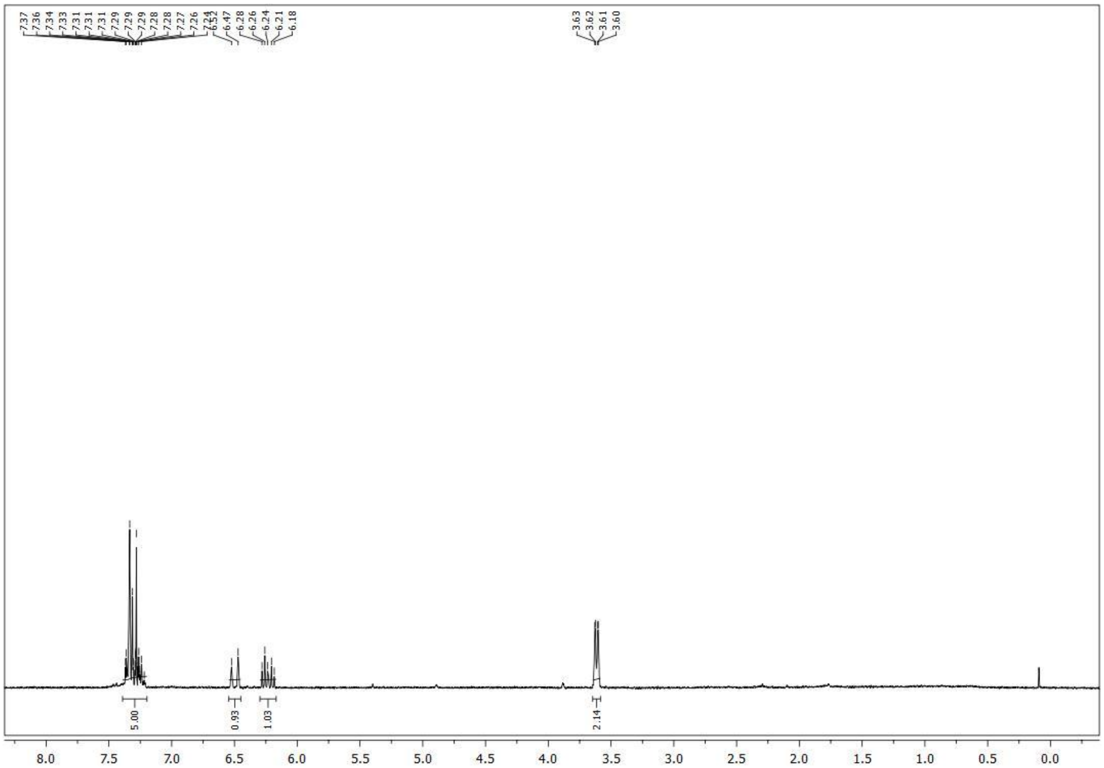


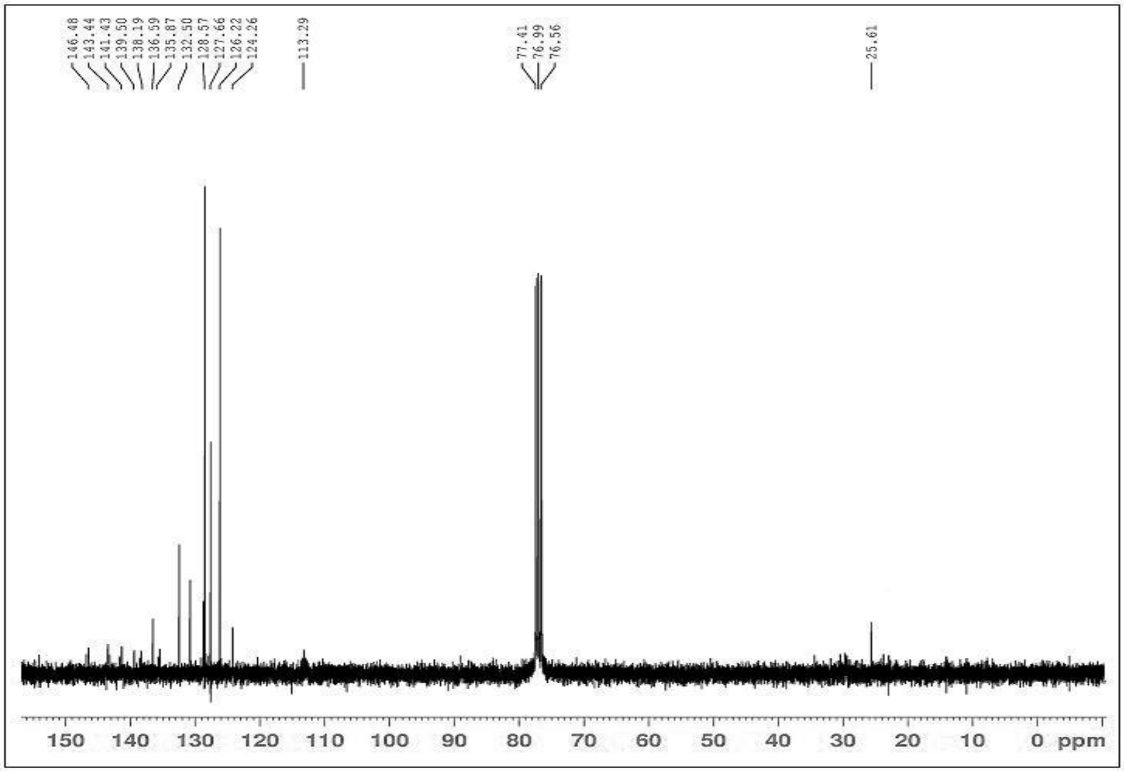
(*E*)-1,2-Diphenylethene (3d):





1-Cinnamyl-2,3,4,5,6-pentafluorobenzene (3e):





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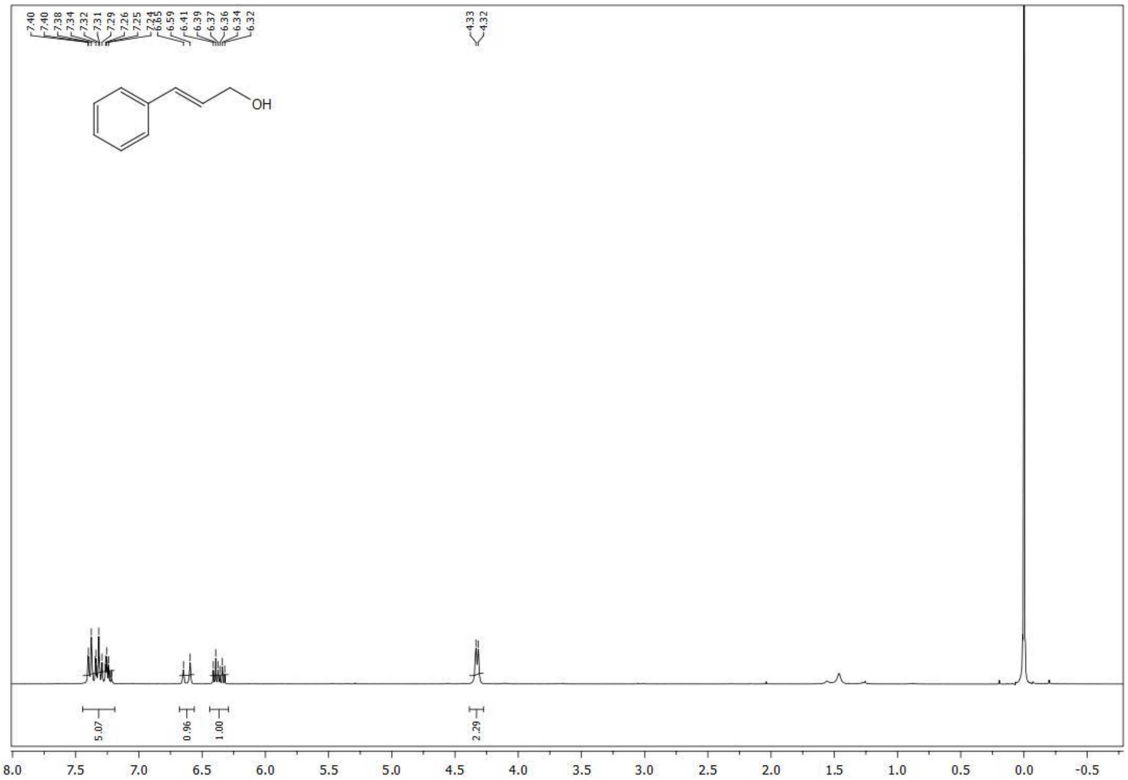
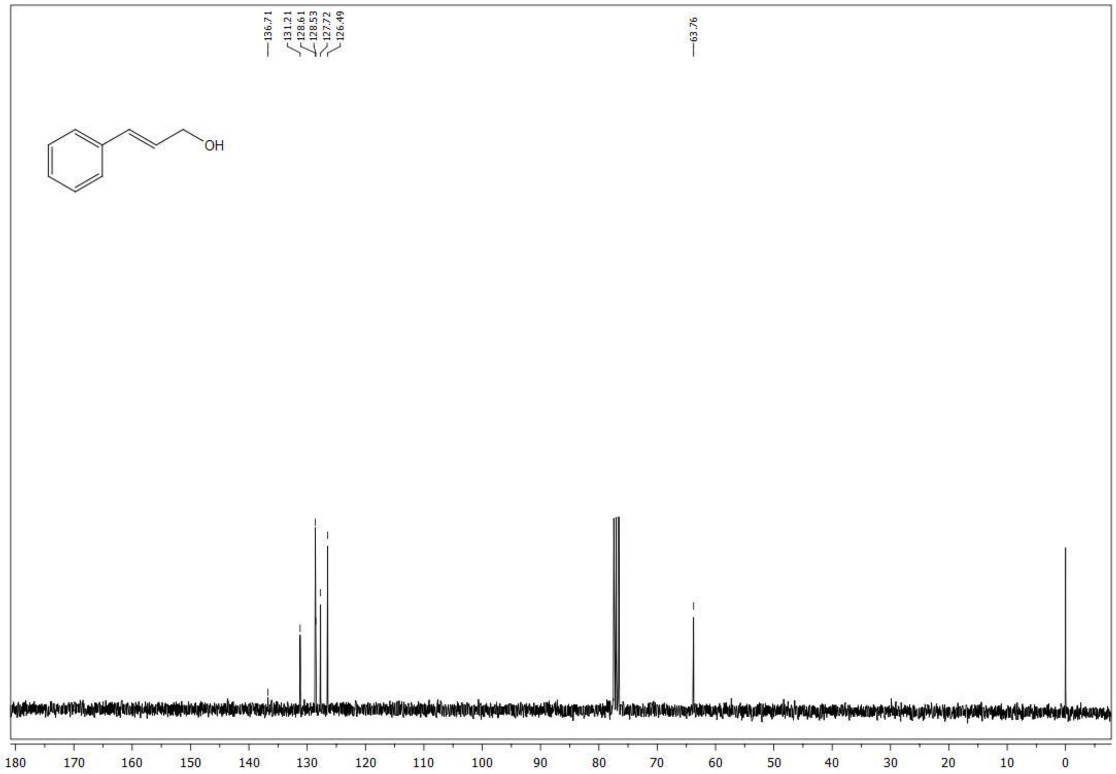
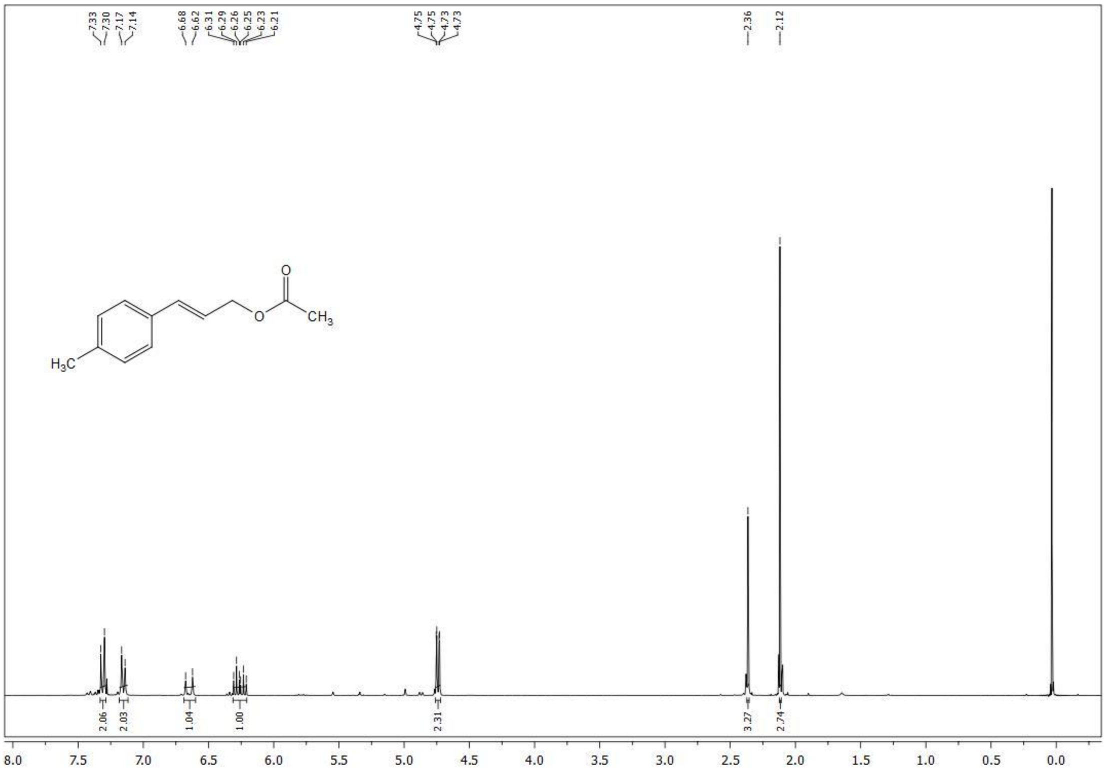
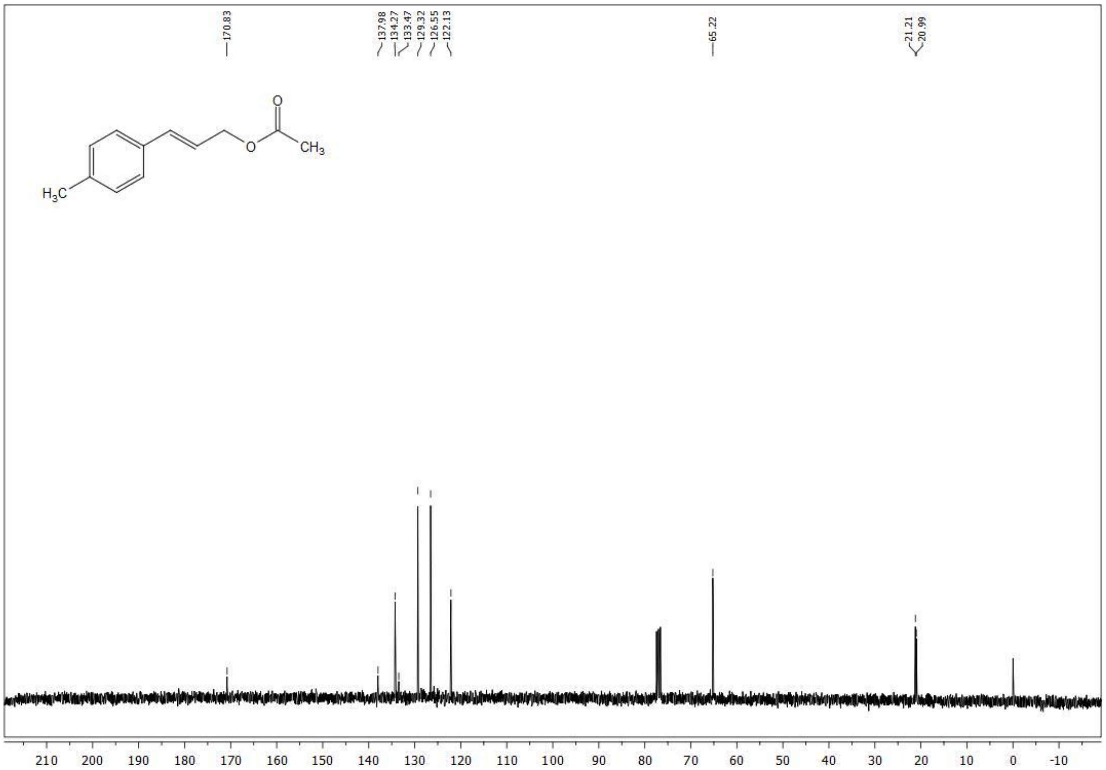


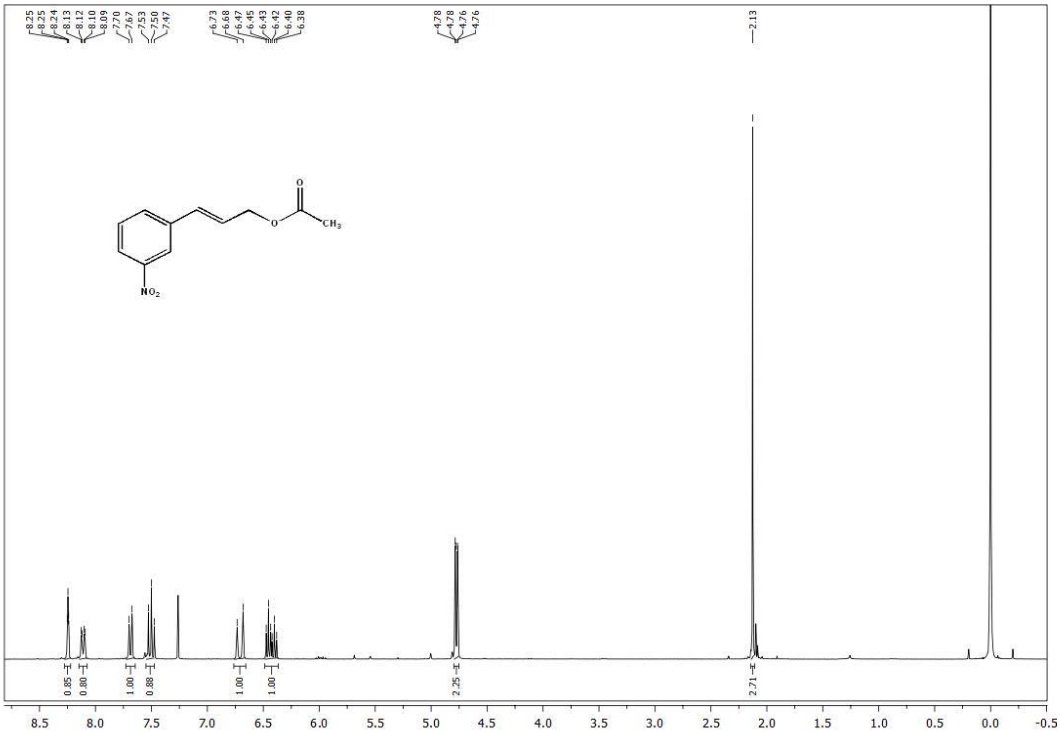


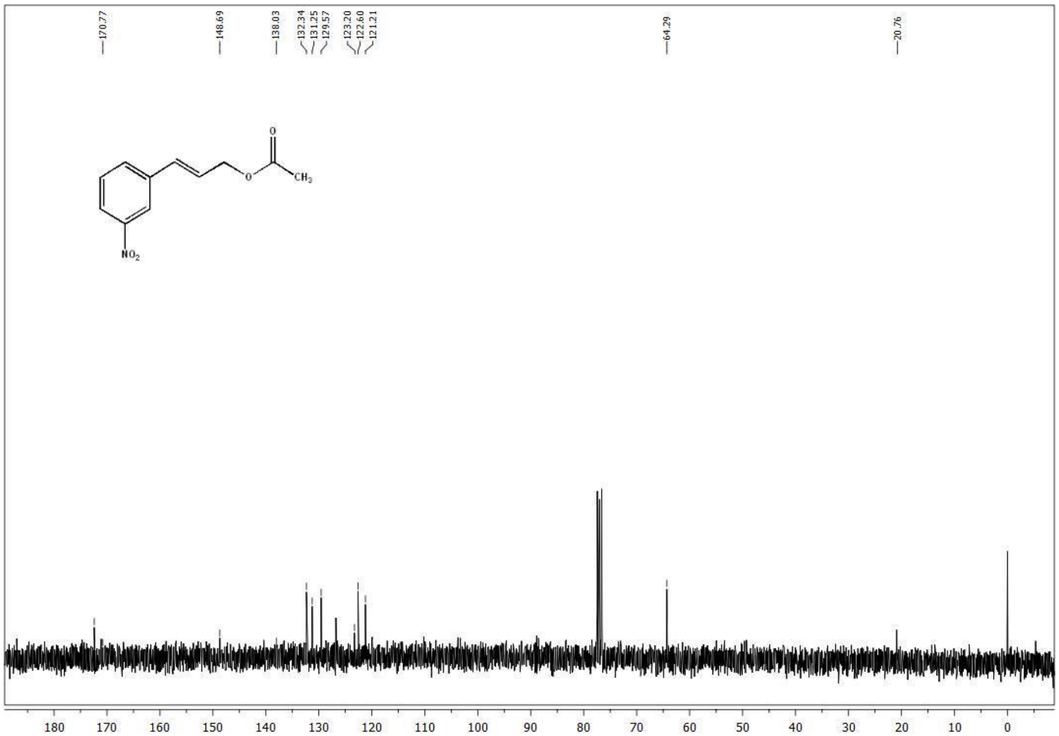
(*E*)-3-(*p*-Tolyl)allyl acetate (3g):



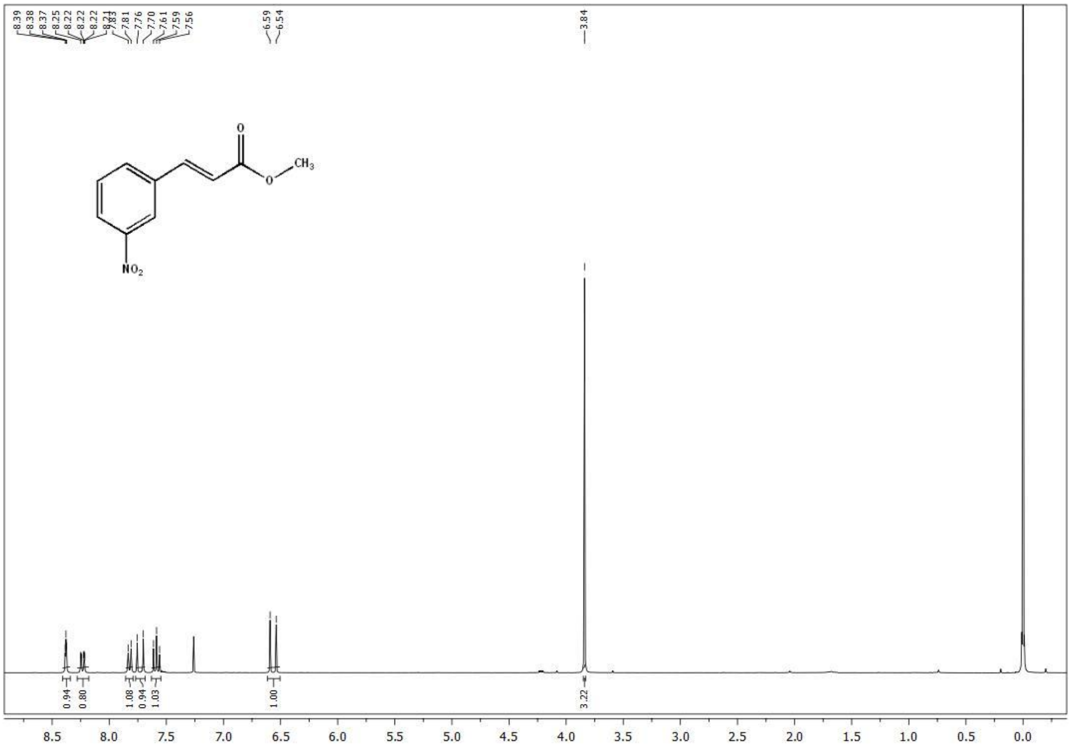


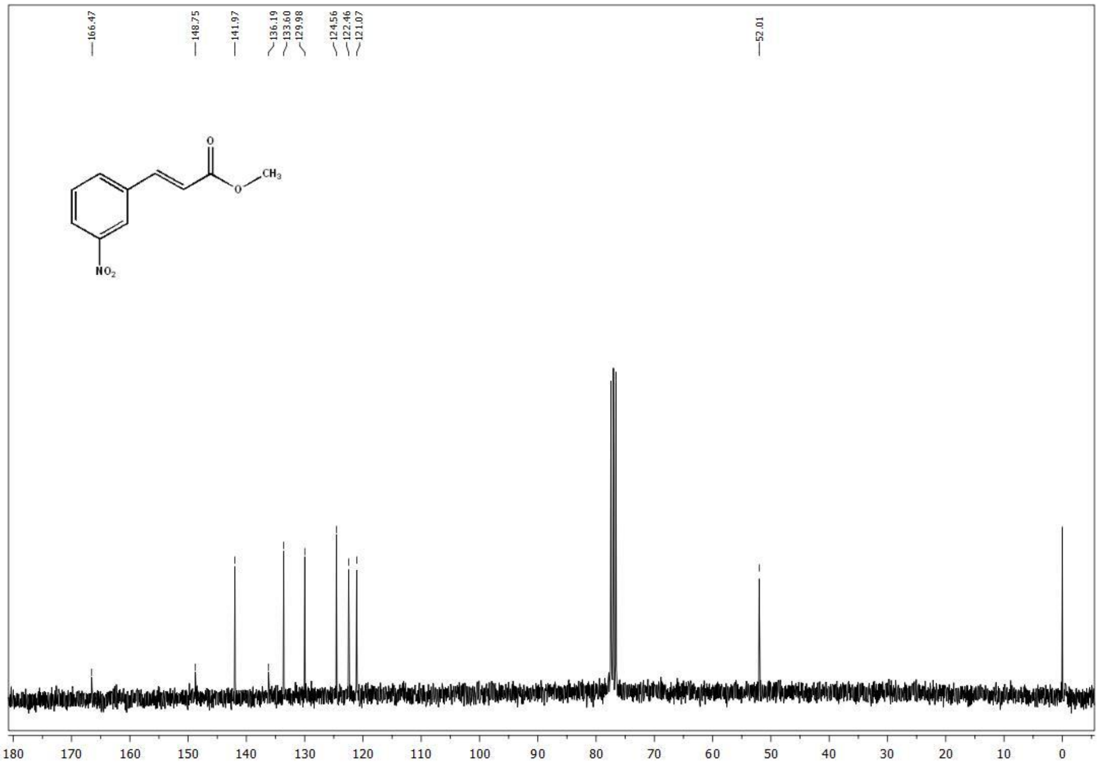
(*E*)-3-(3-Nitrophenyl)allyl acetate (3h):



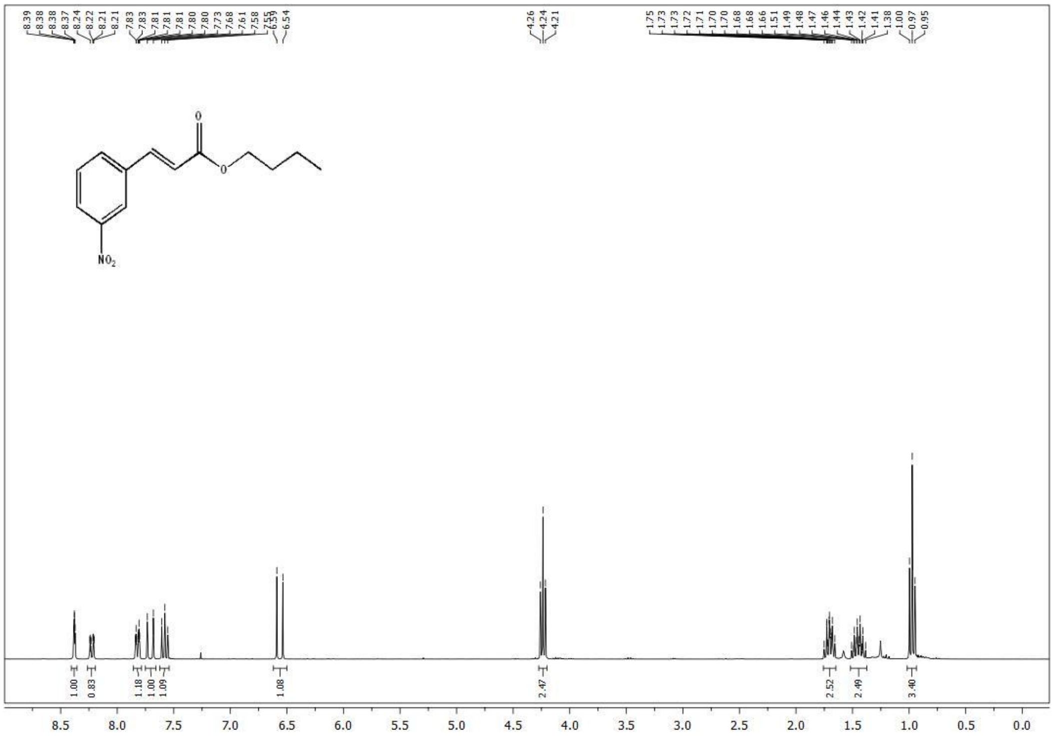


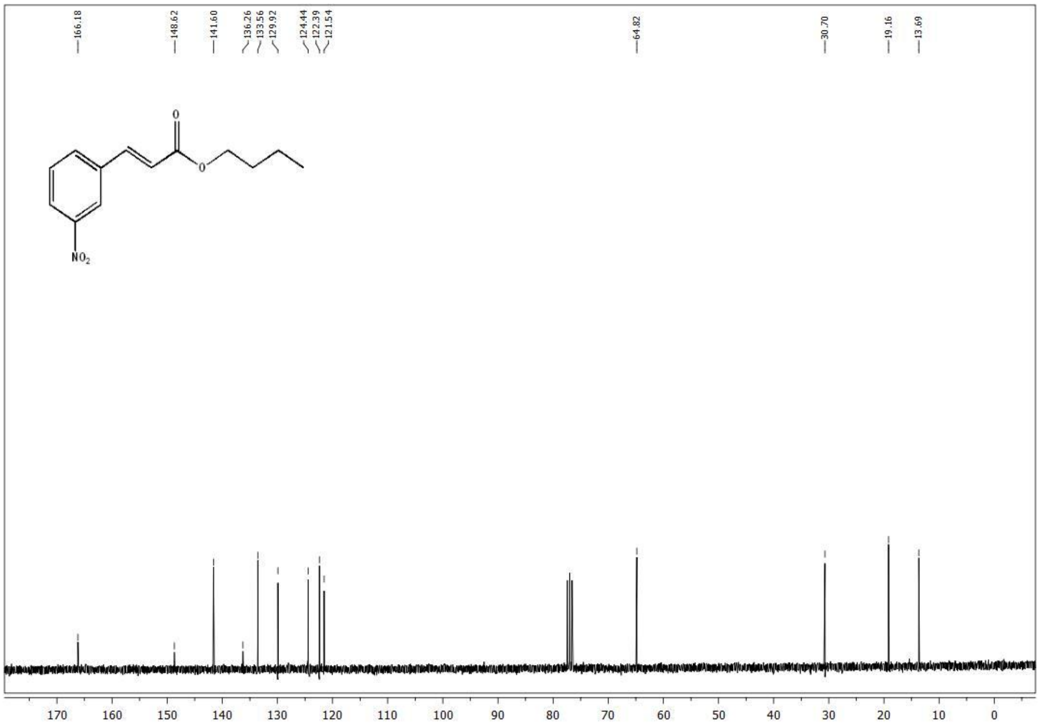
(*E*)-Methyl 3-(3-nitrophenyl)acrylate (3i):



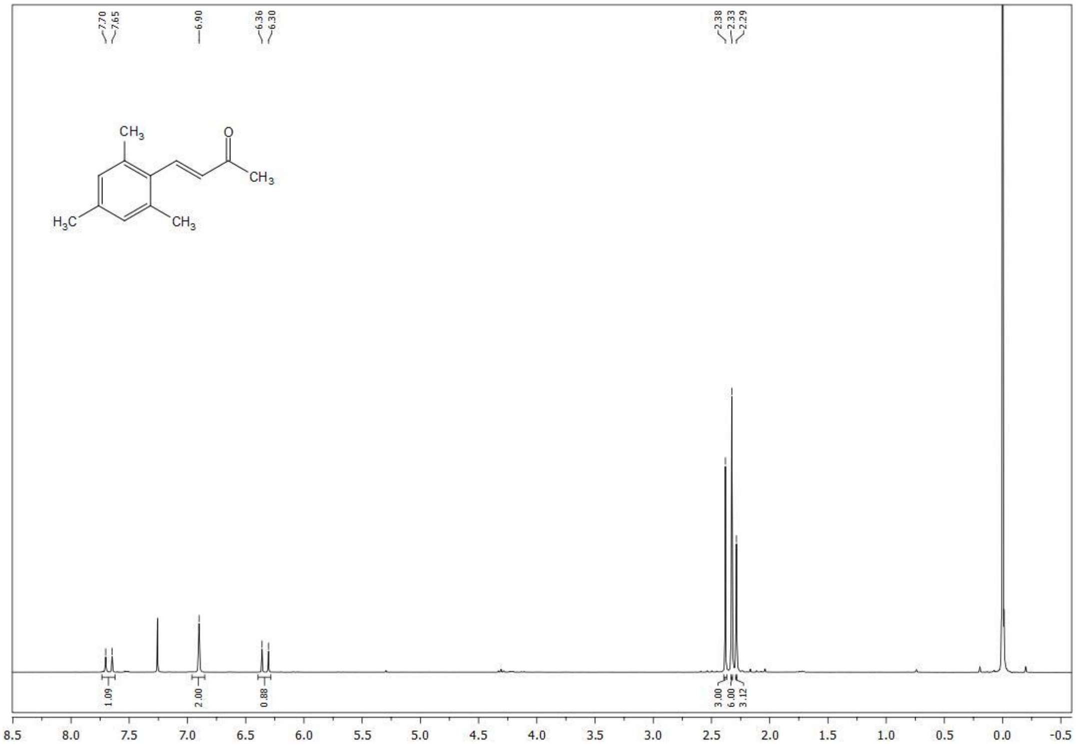


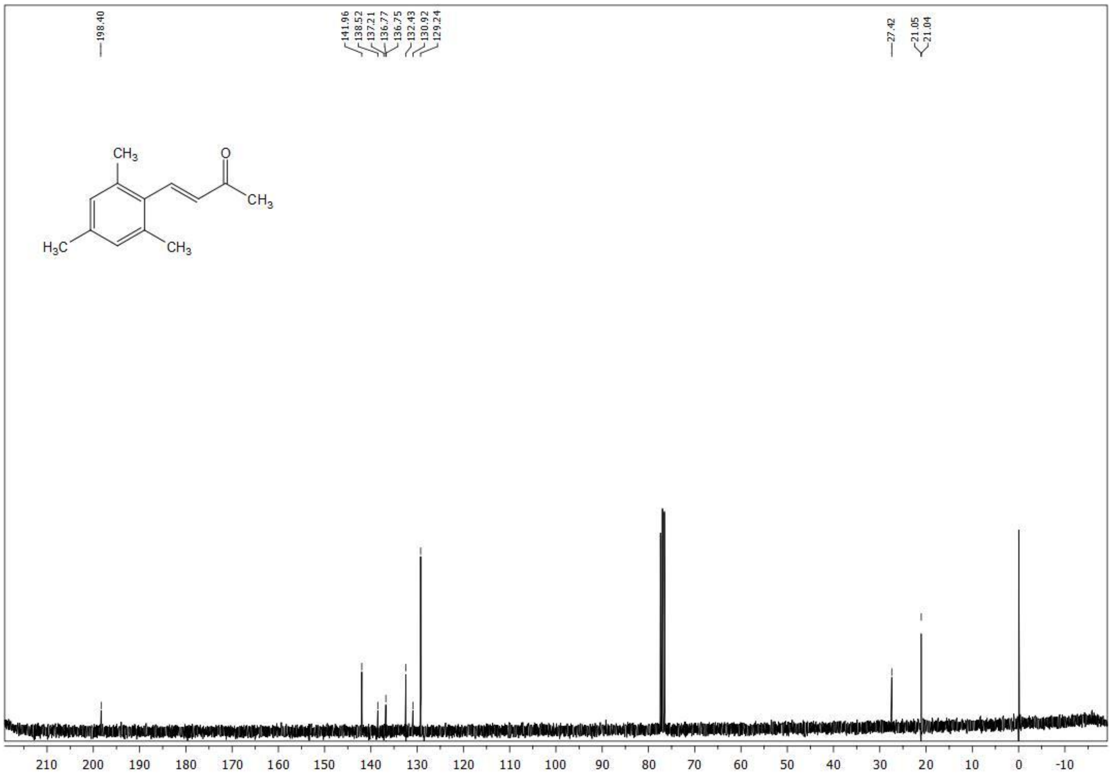
(*E*)-Butyl 3-(3-nitrophenyl)acrylate (3j):



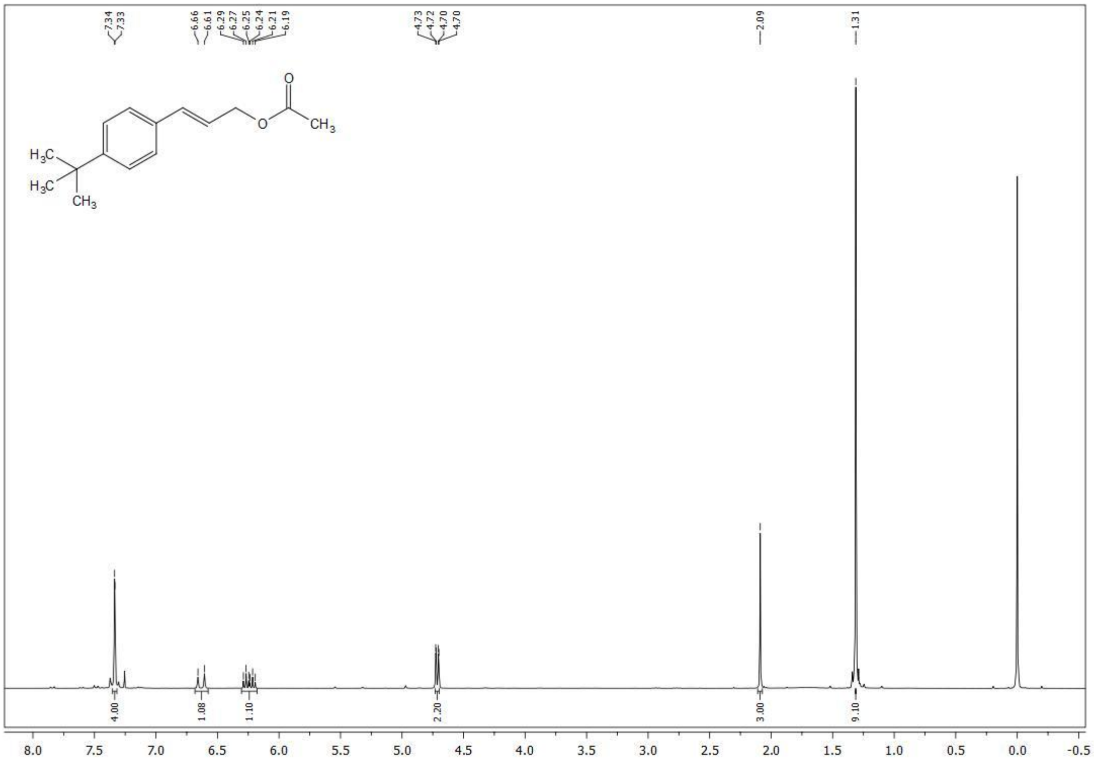


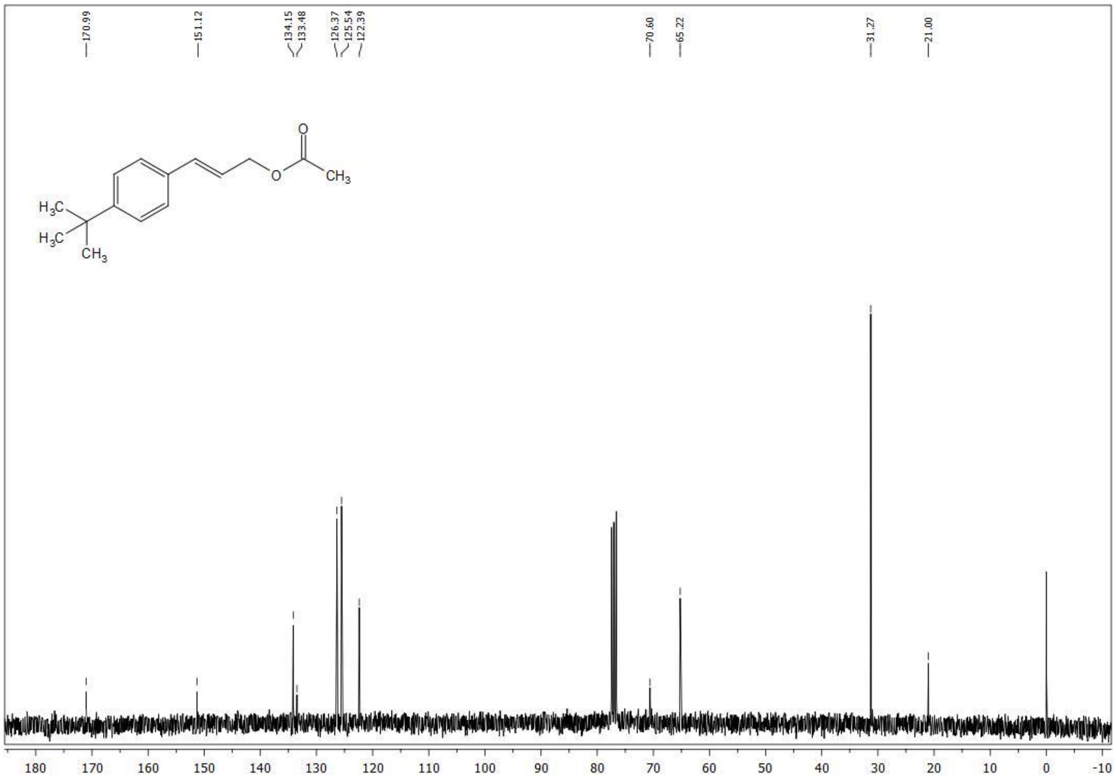
(*E*)-4-Mesitylbut-3-en-2-one (3k):





(*E*)-3-(4-(*tert*-Butyl)phenyl)allyl acetate (3l):





(*E*)-3-(4-Methoxyphenyl)allyl acetate (3m):