

Electronic Supplementary Information

for

Trace Amount Pd(ppm)-Catalyzed Sonogashira, Heck and Suzuki Cross-Coupling Reactions Based on Synergistic Interaction with an Asymmetric Conjugated Pyridinespirofluorene

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Materials and methods

All catalysis coupling reactions were carried out under air atmosphere. All other synthetic reactions were performed by using standard Schlenk techniques utilizing a double-manifold vacuum system with high purity nitrogen flow. Poly(ethylenimine) (abbreviated as PEI) was purchased from Aldrich Chemical Company. All solutions were prepared with doubly-distilled water. Triethylamine was dried over KOH and distill under N₂ prior to use. CH₂Cl₂, MeOH and DMF were dried using a solvent purification system and degassed prior to use. Other solvents were best available commercial quality and used as received. All other reagents were of analytical grade and used as received without further purification.

Physical measurements

Infra-red spectra were recorded on a Nicolet Avatar FTIR spectrophotometer in the range 4000-400 cm⁻¹. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained from solutions in CDCl₃ using a Bruker AVANCE 400 spectrometer. UV-vis absorption spectra were recorded on a quartz slide using a Lambda35 spectrophotometer (Perkin Elmer, USA). AFM images were taken on a single-crystal silicon slide using a Veeco Multimode NS3A-02NanoscopeIII atomic force microscope with silicon tips. Height images of the films were recorded using tapping-mode AFM. High-resolution X-ray photoelectron spectra (XPS) were collected at a takeoff angle of 45° using PHI Quantum 2000 scanning ESCA microprobe (Physical Electronics, USA) with an Al α X-ray line (1486.6 eV). Analysis of Pd content was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using Ultima. SEM images

were taken with FEI SIRION-100 field-emission scanning electron microscope. Fluorescence spectra were collected by the FLS920 fluorescence spectrometer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Focus X-ray diffractometer using CuK α radiation..

Synthesis of 2-bromine-2',7,7'-tri(4-pyridyl)-9,9'-spirobifluorene (1)

2,2',7,7'-tetrabromo-9,9'-spirobi[fluorene] (3.0 mmol), pyridine-4-boronic acid (9.0 mmol), K₂CO₃ (40 mmol), Pd(PPh₃)₄ (0.3 mmol) were dissolved in toluene/EtOH/H₂O (80/30/20 mL). The reaction mixture was refluxed under N₂ for 48h, cooled to the room temperature, and then extracted with CH₂Cl₂ for three times. The organic phase was dried with anhydrous MgSO₄, concentrated, and purified by column chromatography (EtOAc) to afford the compound **1** as a yellow solid (36%). IR (KBr): 3428(m), 3026(w), 2919(w), 1594(s), 1544(w), 1463(m), 1406(m), 1251(w), 1218(w), 1118(w), 1068(w), 1004(w), 991(m), 810(s), 616 (s) cm⁻¹. ¹H NMR: (CDCl₃, 400MHz): 8.49-8.53(m, 6H), 7.97-8.04 (d, 3H), 7.76-7.82(m, 1H), 7.71-7.75(dd, 3H); 7.56-7.58(d, 1H); 7.33-7.37(m, 6H); 7.01-7.02(d, 3H); 6.92-6.93(s, 1H). ¹³CNMR (CDCl₃, 100MHz): 149.9, 149.1, 148.7, 147.7, 141.8, 139.9, 138.4, 131.7, 127.5, 127.4, 122.5, 122.0, 121.5, 121.3, 121.1, 60.43. ES(+)-MS: 628.3 [M + 2H]²⁺, 626.2 [M].

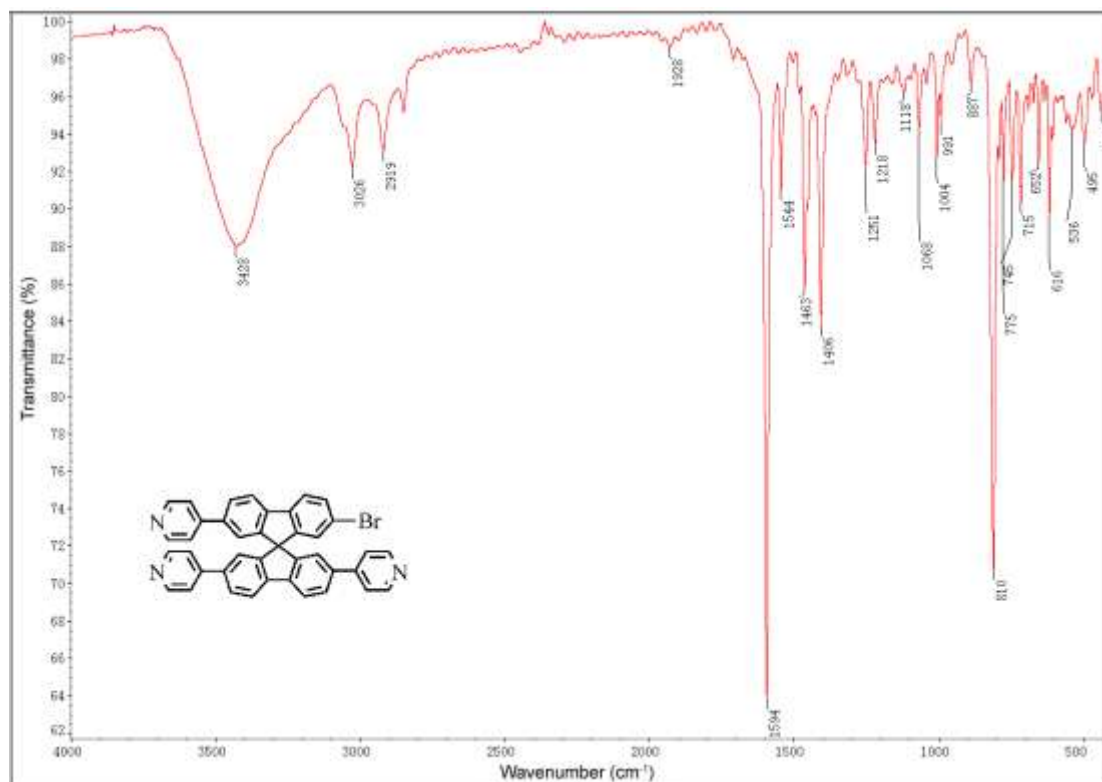


Figure S1. FTIR spectrum of **1** ligand

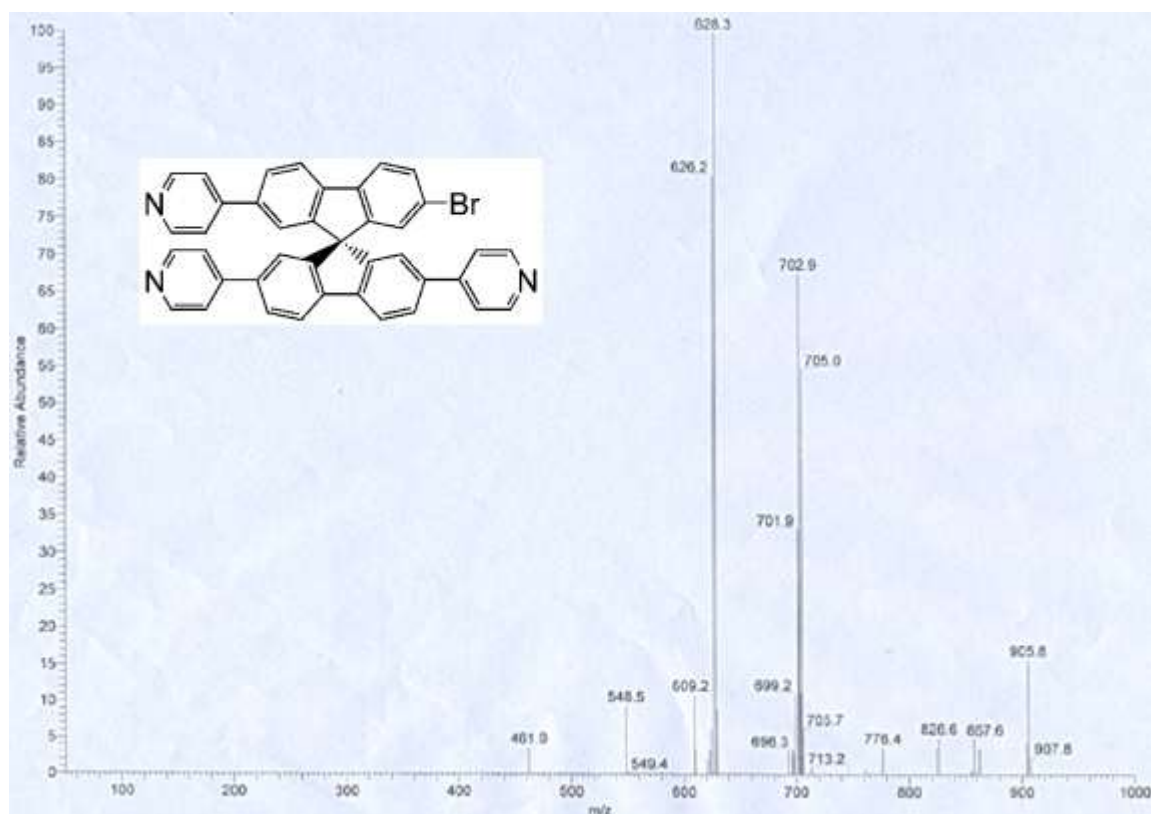
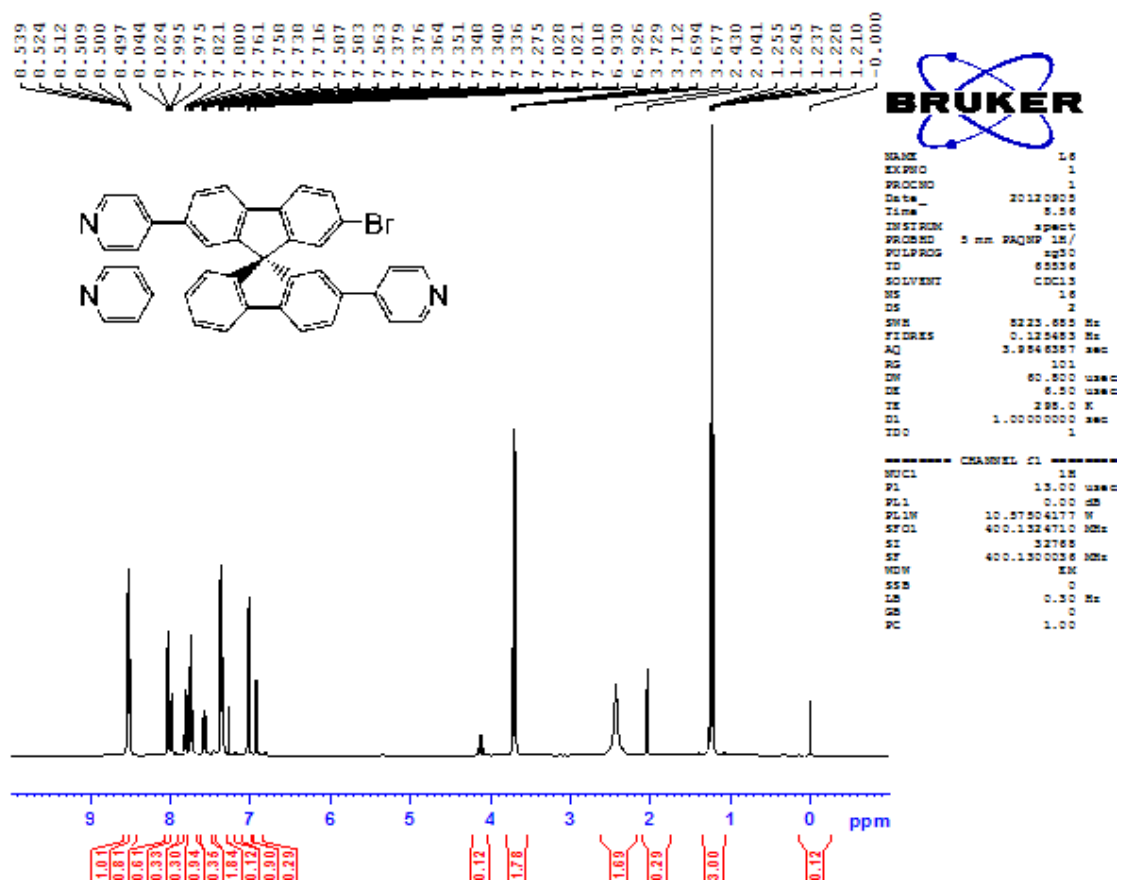


Figure S2. Mass spectrogram of 1 ligand



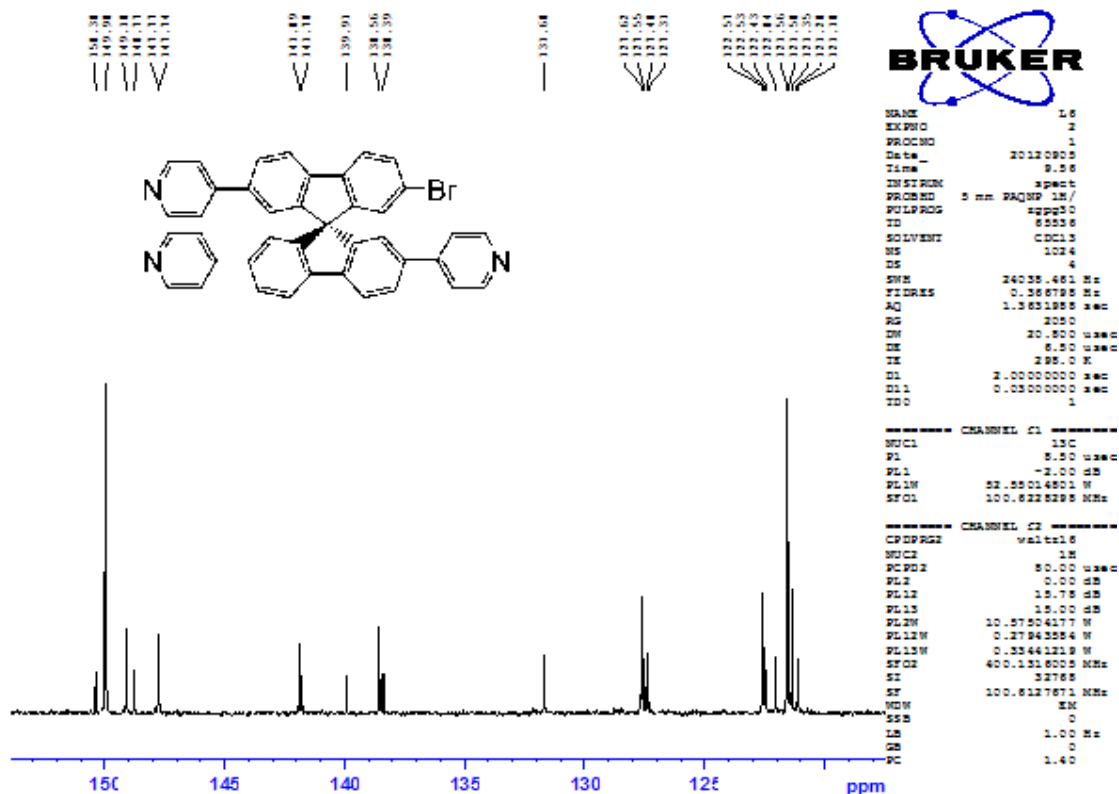


Figure S4. ^{13}C NMR spectrum of **1**.

Preparation of Nanoparticles (NPs)

Nanoparticles were prepared as followed: PdCl_2 aqueous solution was added to the EtOH solution of compound **1** ($\text{Pd}:\mathbf{1} = 1:1$ /mol), and the mixture was stirred at room temperature for 1.0 hours. After that the mixture was transferred to teflon autoclave, heated to 50°C for 4h. The suspension was centrifuged to get $\text{PdCl}_2/\mathbf{1}$ nanocomposite, washed with H_2O and EtOH.

Layer-by-Layer assembly of multilayer films

The quartz plate was treated with Piranha solution (7:3 v/v, $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$) at 80°C for 40 min followed by washing several times with water. Further purification was carried out by immersion in a $\text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{NH}_4\text{OH}$ (5:1:1) (V/V/V) bath at 70°C for 20 min. Then the slides were immersed in Poly(ethylenimine) (PEI, MW = 60 000, 10wt% aqueous solution) solution for 20 min. After that the slides were alternately immersed into PdCl_2 aqueous solution (5.0 mM) and ethanol solution of **1** (5.0 mM) for 30 min. The substrates were washed with deionized water and dried with nitrogen gas at a room temperature after each immersion. By repeating this cycle covalent bonded multilayer thin film was fabricated onto a quartz plate and growth was monitored by

UV–visible spectroscopy and scanning electron microscopy (SEM). Film morphology was studied by atomic force microscopy (AFM).

Analysis of Pd content in PEI-(Pd²⁺/I)₁₀ multilayer films

The quartz slide coated with PEI-(Pd²⁺/I)₁₀ was immersed into a NaOH aqueous solution (0.5 mM, 25 mL); when the quartz slide exhibited no absorbance monitored by UV-vis spectra, indicating the PEI-(Pd²⁺/I)₁₀ multilayer film was completely desorbed into the aqueous solution, which was used for analysis of Pd content. The amount of Pd was determined as 0.47 ppm (ICP) in the solution. In other words, the amount of Pd in PEI-(Pd²⁺/I)₁₀ multilayer film is 11.75 μg (11.0 × 10⁻⁶ mol%). Once the Pd(II) catalysts are desorbed into the solution, they cannot be recovered and re-deposited onto the solid slide, which can be confirmed by UV-vis spectra. When the UV-vis spectra showed no absorbance of the multilayer film, it suggested that all the Pd ions of the multilayer film were desorbed into the mixture. Therefore, the amount of Pd catalyst in PEI-(Pd²⁺/I)₁₀ film is 11.0 × 10⁻⁶ mol%.

Atomic force microscopy images

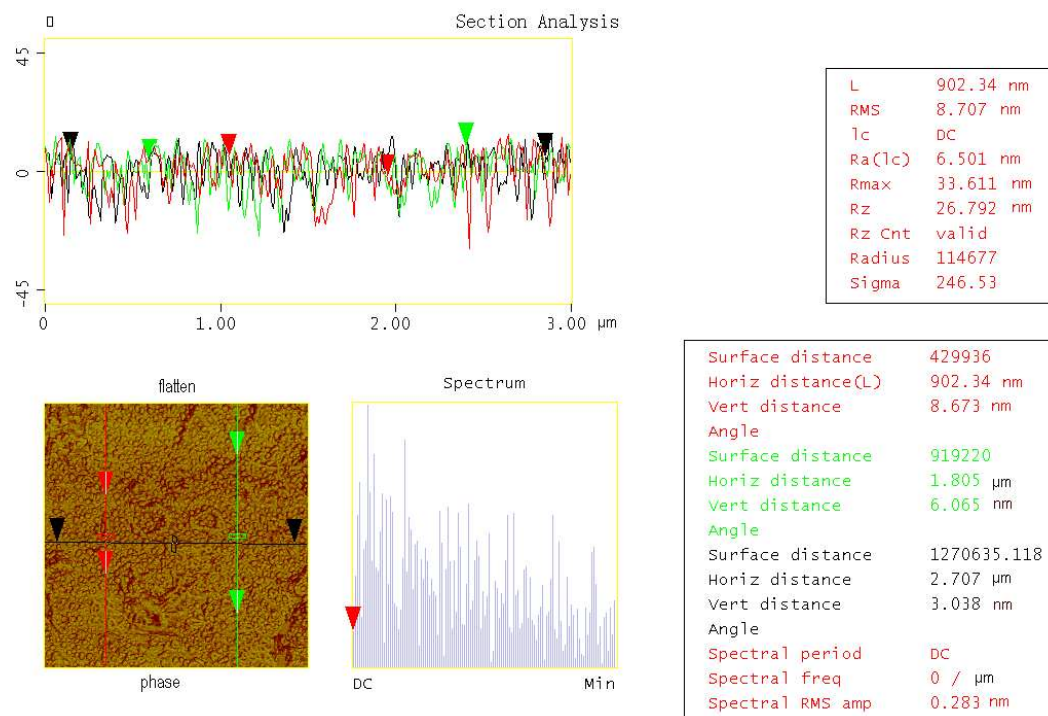


Fig. S5. The phase flat view of film (Pd²⁺/I)₅ (Scan area 3.0 x 3.0 μm², RMS = 8.7 nm, R_{max} = 33.6 nm).

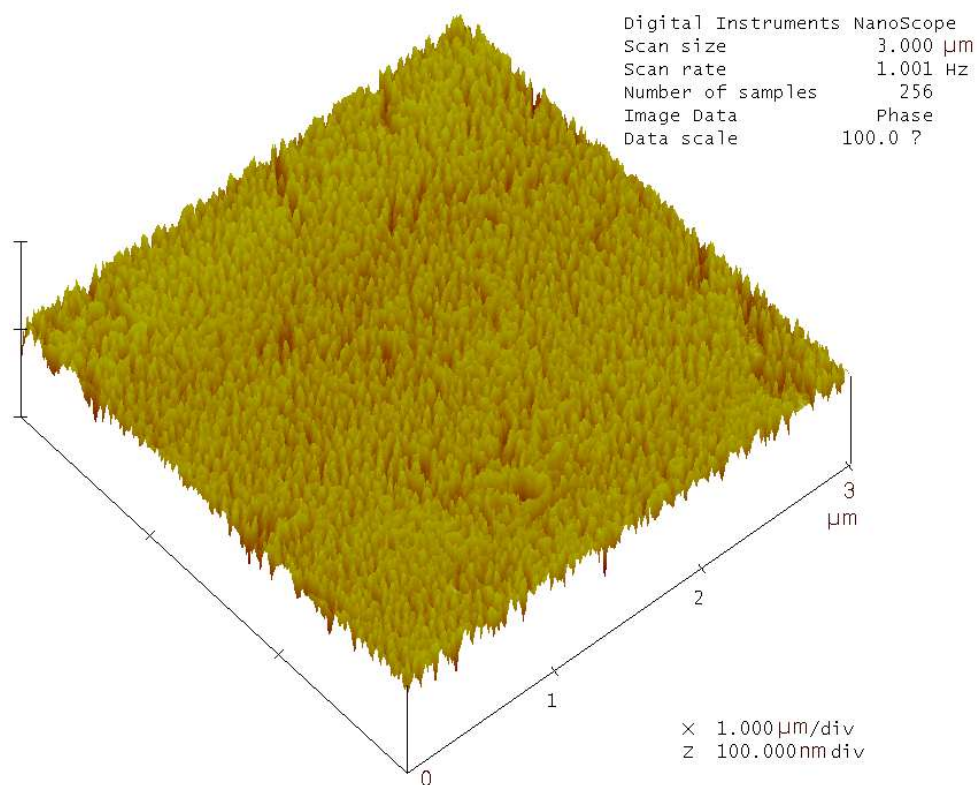


Fig. S6. The stereoscopic graphics of film $(\text{Pd}^{2+}/\mathbf{1})_5$ (Scan area $3.0 \times 3.0 \mu\text{m}^2$).

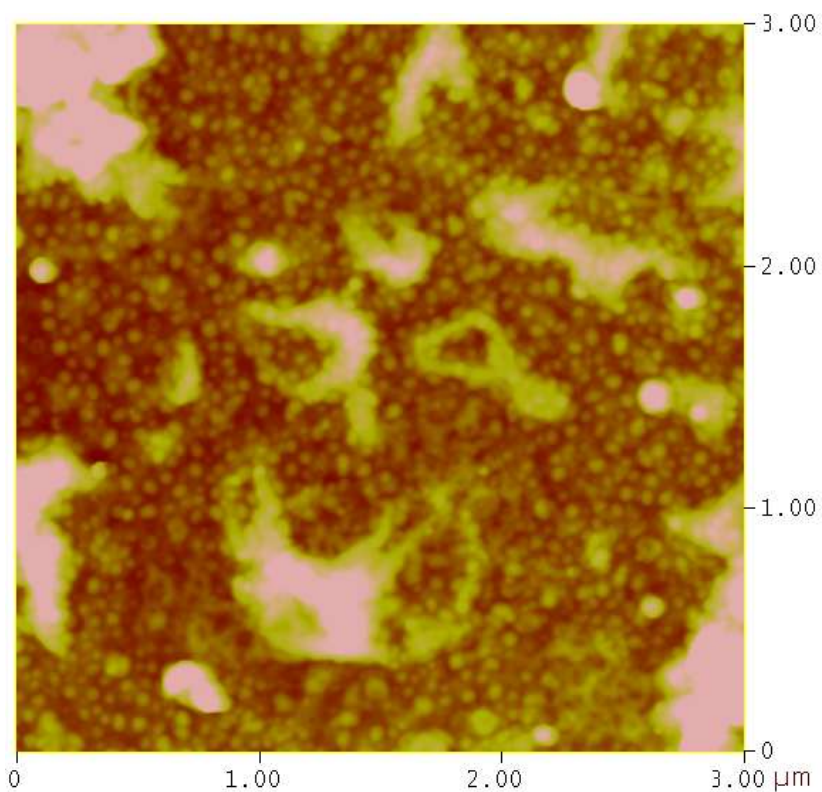


Fig. S7. The typical height image of of film $(\text{Pd}^{2+}/\mathbf{1})_5$ (Scan area $3.0 \times 3.0 \mu\text{m}^2$)

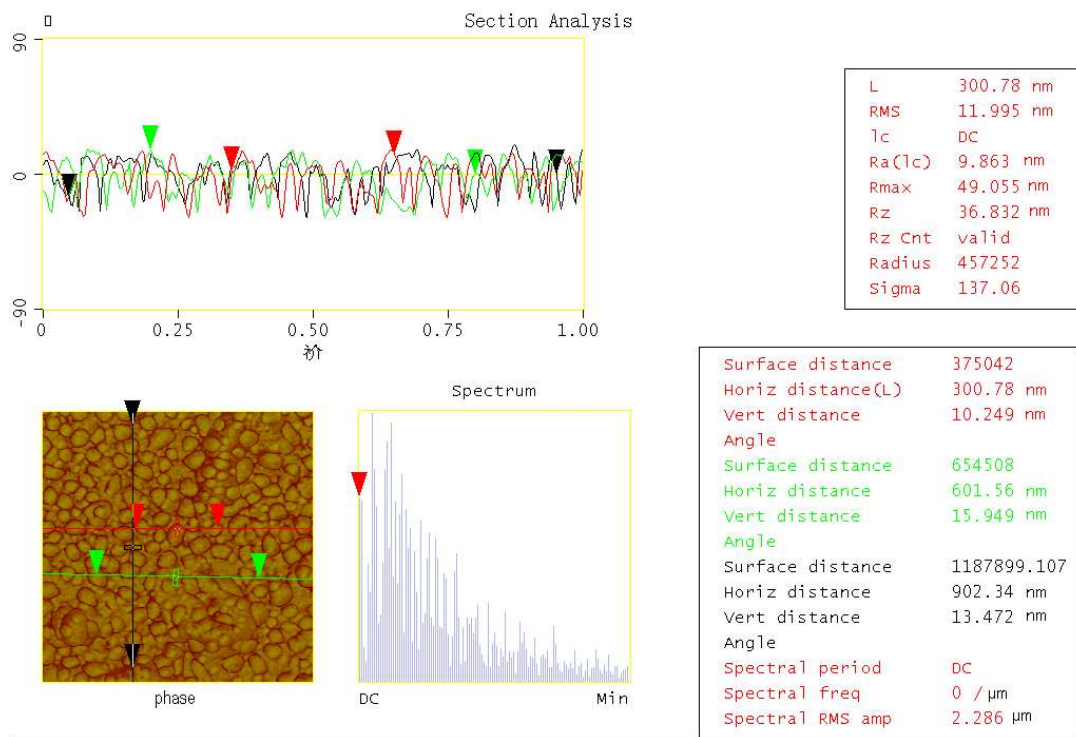


Fig. S8. The phase flat view of film $(\text{Pd}^{2+}/\mathbf{1})_{10}$ (Scan area $1.0 \times 1.0 \mu\text{m}^2$, $\text{RMS} = 11.99 \text{ nm}$, $R_{\text{max}} = 49.05 \text{ nm}$).

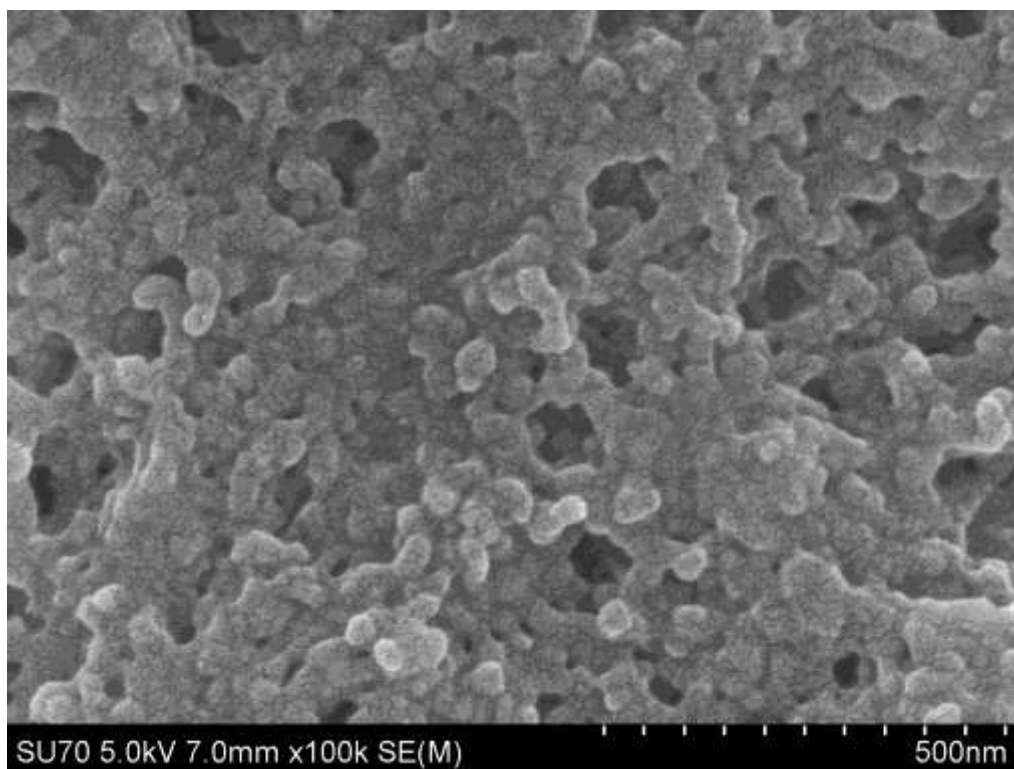


Fig. S9. SEM image of film $(\text{Pd}^{2+}/\mathbf{1})_{10}$. The delamination-like deposition microstructures, larger block-like peaks and deep hollows are shown on the film surface.

General experimental procedure for the coupling reaction

For Suzuki reaction: aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), K_2CO_3 (3.0 mmol), EtOH (3.0 mL), H_2O (4.0 mL) and the catalyst were combined in a 20 mL round-bottomed flask. The reaction mixture was magnetically stirred and the temperature was maintained properly with an oil bath. After reaction was completed, the reaction mixture was cooled to room temperature and extracted by ethyl acetate, the combined organic phase was wash with saturated brine, dried by anhydrous Na_2SO_4 , and the solvent was removed under reduced pressure, and purified by column chromatography on silica to give the product.

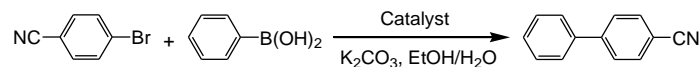
For Heck reaction: in a typical reaction, bromobenzene (1.0 mmol), styene (1.2 mmol), Na_2CO_3 (2.0 mmol), *N,N*-dimethylformamide (DMF, 6.0mL) and the catalyst were charged in a round-bottomed flask. The reaction mixture was heated to 140°C for 24h. The others process were similar to the Suzuki reaction.

For Sonogashira reaction: the aryl halide (1.0 mmol), alkyne (1.1 mmol), K_2CO_3 (2.0 mmol) and the catalyst were put in a 20 mL round-bottomed flask equipped with 6.0 mL EtOH, then the reaction mixture were heated to 80°C with stirring for 6h. The others process were similar to the Suzuki reaction.

Recycling Experiments

The multilayer film PEI-(PdCl₂/1)₁₀ as a Pd-catalyst cistern was used for the Suzuki coupling reaction in air atmosphere by the following procedure. The quartz slide coated with (PdCl₂/1)₁₀ multilayer was immersed into a solution of aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), K_2CO_3 (3.0 mmol) in 7.0 mL of H_2O /EtOH (4:3 / v) in air atmosphere. The mixture was stirred for 30 min at 50°C, the quartz slide was removed from the mixture. Then the mixture reacted for a further 20h at 50°C. After the reaction, the mixture was extracted three times with ethyl acetate (10 mL). The water phase was recycled as the reaction medium and the same coated quartz slide was immersed into the next reaction mixture. In the second cycle, the mixture was stirred for 30 min, the quartz slide was again removed from the reaction mixture and the mixture was allowed to react for 20h. By repeating this produces, we studied the catalyst property of the thin film, in which recycling of the solvent was very important for the yields and environmental protection.

Table S1. Suzuki cross-coupling of 4-bromobenzonitrile with phenyl-boronic acid using **1, PdCl₂, PdCl₂/**1** nanoparticles, PEI-(PdCl₂/**1**)₁₀ film and PdCl₂/bpy nanoparticles as catalysts (bpy = 4,4'-bipyridine).^a**



Entry	Runs	Catalyst	Yield(%)
1	1 st	1 ^b	0
2	1 st	PdCl ₂ ^b	28
3	1 st	PdCl ₂ /bpy NPs ^b	51
4	2 nd	PdCl ₂ /bpy NPs	<5
5	1 st	PdCl ₂ / 1 NPs ^b	100
6	2 nd	PdCl ₂ / 1 NPs	48
7	1 st	(PdCl ₂ / 1) ₁₀ film ^c	100
8	2 nd	(PdCl ₂ / 1) _{10-x} film	99
9	3 rd	(PdCl ₂ / 1) _{10-x} film	100
10	4 th	(PdCl ₂ / 1) _{10-x} film	97
11	5 th	(PdCl ₂ / 1) _{10-x} film	89
12	6 th	(PdCl ₂ / 1) _{10-x} film	86
13	7 th	(PdCl ₂ / 1) _{10-x} film	81
14	8 th	(PdCl ₂ / 1) _{10-x} film	93
15	9 th	(PdCl ₂ / 1) _{10-x} film	83
16	10 th	(PdCl ₂ / 1) _{10-x} film	72
17	11 th	(PdCl ₂ / 1) _{10-x} film	44
18	12 th	(PdCl ₂ / 1) _{10-x} film	<9

^a General procedure: 1.0 mmol of aryl halide, 1.2 mmol of arylboronic acid, 3.0 mmol of K₂CO₃, in H₂O/EtOH (4:3) under ambient atmosphere at 50°C for 20h. ^b Catalyst 3.0 mol%. ^c 11.0 x 10⁻⁶ mol%

Desorption of Pd content from PEI-(Pd²⁺/**1**)₁₀ multilayer film

In order to determine whether the catalytic active species of Pd-**1** complexes was gradually released from the multilayer film, we carried out the following tests: The quartz slide coated with (PdCl₂/**1**)₁₀ multilayers was immersed in a mixed solution of K₂CO₃, EtOH and H₂O for each interval of 30 minutes, respectively, to study the release behavior of Pd-**1** complex. UV-vis spectra were used to monitor the absorbance change of films (Fig. S5). A obvious decrease of the absorbance at 340 nm was observed for the first 180 min due to the desorption of the multilayers, and the absorbance slowly decreases in the subsequent measurement. The UV-vis spectra above exhibited that the desorption was not completely uniform, but close to be linear, which validated that (PdCl₂/**1**)₁₀ multilayer could release the Pd-**1** species mostly in a layer-by-layer manner in each cycle step.

Powder diffraction of complex **1**, (PdCl₂/**1**)_n films and PdCl₂-**1** NPs

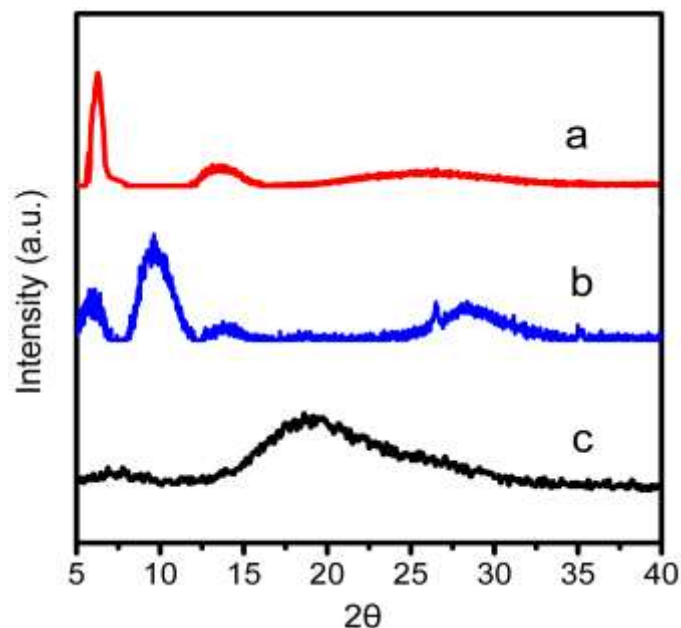


Fig. S10. PXRD patterns. (a) PEI-(PdCl₂/**1**)₁₀ film; (b) PdCl₂-**1** NPs and (c) complex **1**.

Analysis of the fragments discharged from the film by UV-vis and fluorescent spectra.

The absorption spectra of **1** exhibited two broad absorption bands 200 ~ 270 nm (maximum peak centered at 227 nm) and 270 ~ 400 nm (maximum peak centered at 312 and 337 nm) in the solid state (Fig. S11); and maximum peak centered at 220, 310 and 326 nm in the solution of EtOH/H₂O (v:v, 1:1) at room temperature (Fig. S12). The similar absorptions were observed with maximum peak centered at 201, 218, 313 and 327 nm for PdCl₂/**1** NPs; 200, 224, 310 and 329 nm for fragment materials discharged from the film in the solution of EtOH/H₂O (Fig. S13, S14). The weak absorption peaks resulted from very low concentration of the fragments or particles. The absorption band of 200 ~ 270 nm could be attributed to the π - π^* transition and electron transfer transition; the absorption 270 ~ 400 nm assigned to intraligand $n \rightarrow \pi^*$ transition. UV-vis absorption spectra above indicate that the fragment materials released from the film were mainly composed of the Pd-**1** compositions or its nanoparticulates, in which the slight differences of UV-vis absorption might result from the quantum effect of the nanoparticulates or solvent effect. The reasoning above was also notarized by the fluorescence emission spectra of the related samples (Fig. S15-17). The fluorescence emission spectra of the fractures released from the film

resembled ones of PdCl₂-**1** NPs or compound **1** very much in the solution of EtOH/H₂O, but the blue shift occurred due to the nanometer size effect of the nanoparticles.

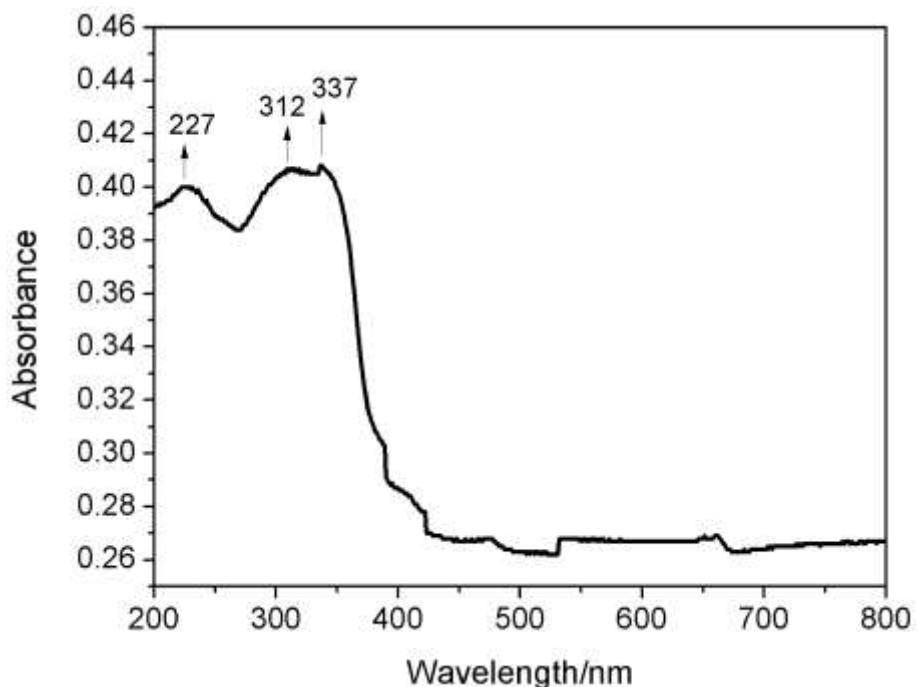


Fig. S11. UV-vis absorption spectra of **1** in the solid state at room temperature

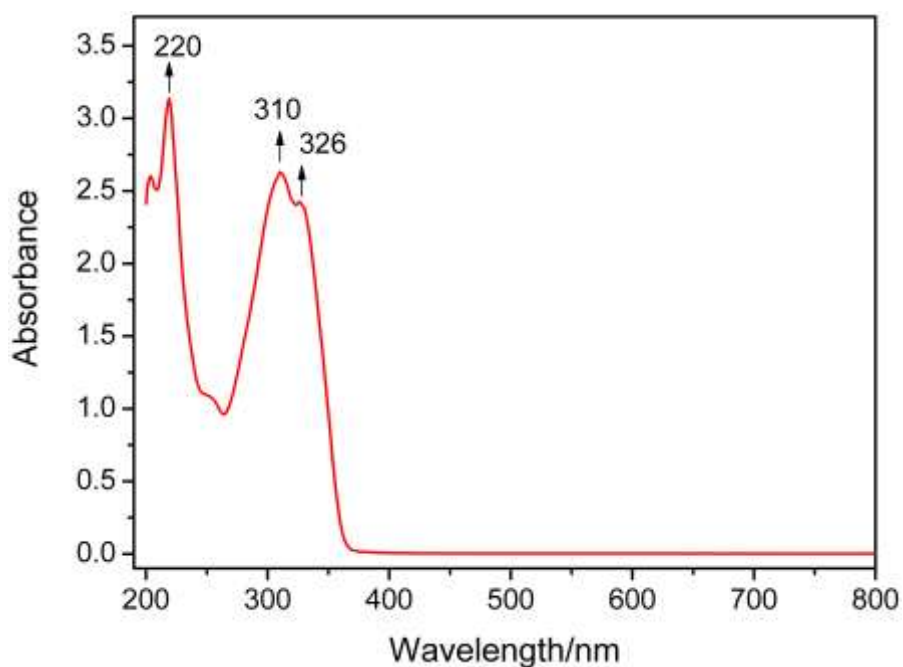


Fig. S12. UV-vis absorption spectra of **1** in the solution of EtOH/H₂O (v:v, 1:1) at room temperature.

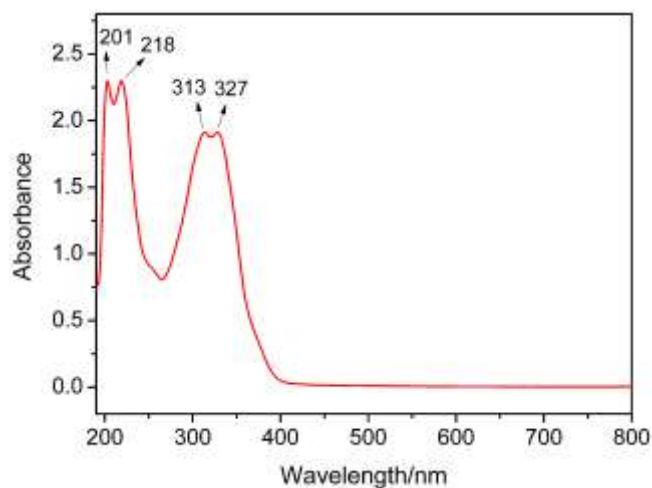


Fig. S13. UV-vis absorption spectra of Pd-1 NPs in the solution of EtOH/H₂O (v:v, 1:1) at room temperature.

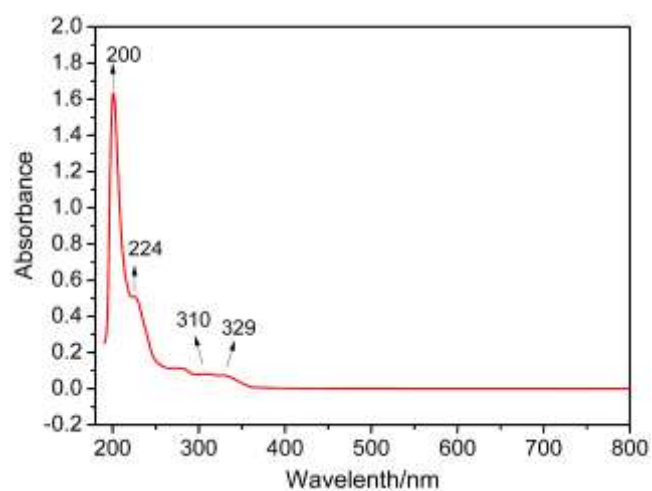


Fig. S14. UV-vis absorption spectra of fragments discharged from the film in the solution of EtOH/H₂O (v:v, 1:1) at room temperature.

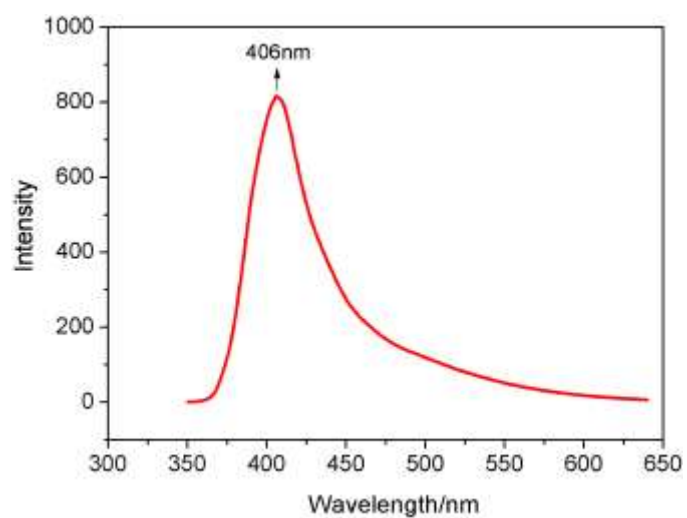


Fig. S15. The photoluminescent spectra of **1** in the solution of EtOH/H₂O (v:v, 1:1) at room temperature (λ_{ex} =330nm).

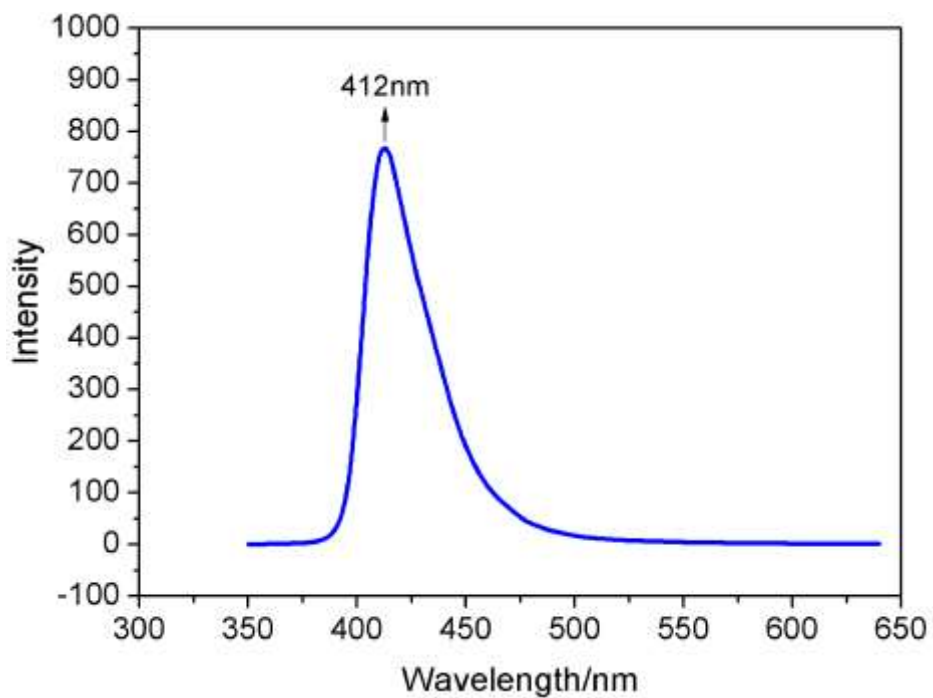


Fig. S16. The photoluminescent spectra of PdCl₂-1 NPs in the solution of EtOH/H₂O (v:v, 1:1) at room temperature (λ_{ex} =330nm).

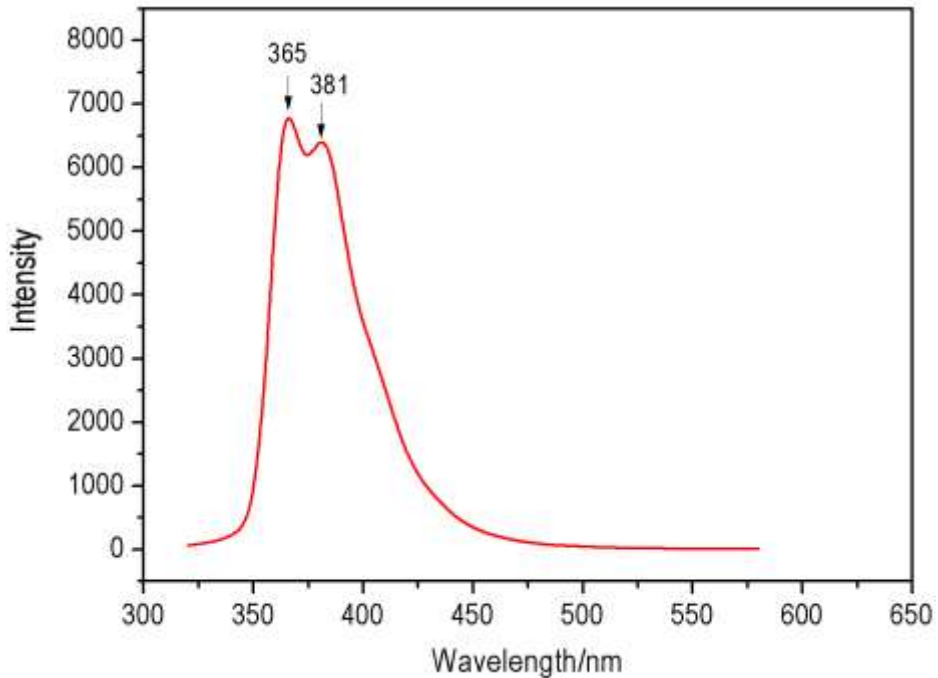
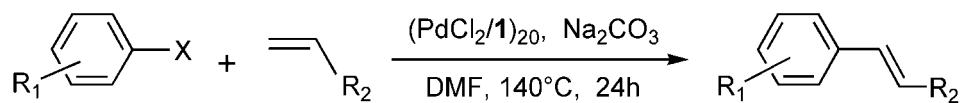


Fig. S17. The photoluminescent spectra of fractures released from the (PdCl₂/1)₁₀ film in the solution of EtOH/H₂O (v:v, 1:1) at room temperature (λ_{ex} =300nm).

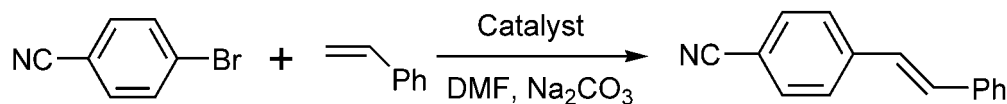
Table S2 Heck reactions of aryl halides with olefins using (Pd/1)₂₀ films loaded solid slides as the catalysts.



Entry	R ₁	X	R ₂	Yield (%)
1	H	Br	Ph	93
2	4-CN	Br	Ph	95
3	4-COMe	Br	Ph	90
4	4-CF ₃	Br	Ph	91
5	4-OMe	Br	Ph	87
6	H	Br	CO ₂ ^t Bu	62

General procedure: 1.0 mmol of aryl halide, 1.2 mmol of olefin and 2.0 mmol of Na₂CO₃ in 6.0 mL DMF at 140 °C for 24 h in air atmosphere.

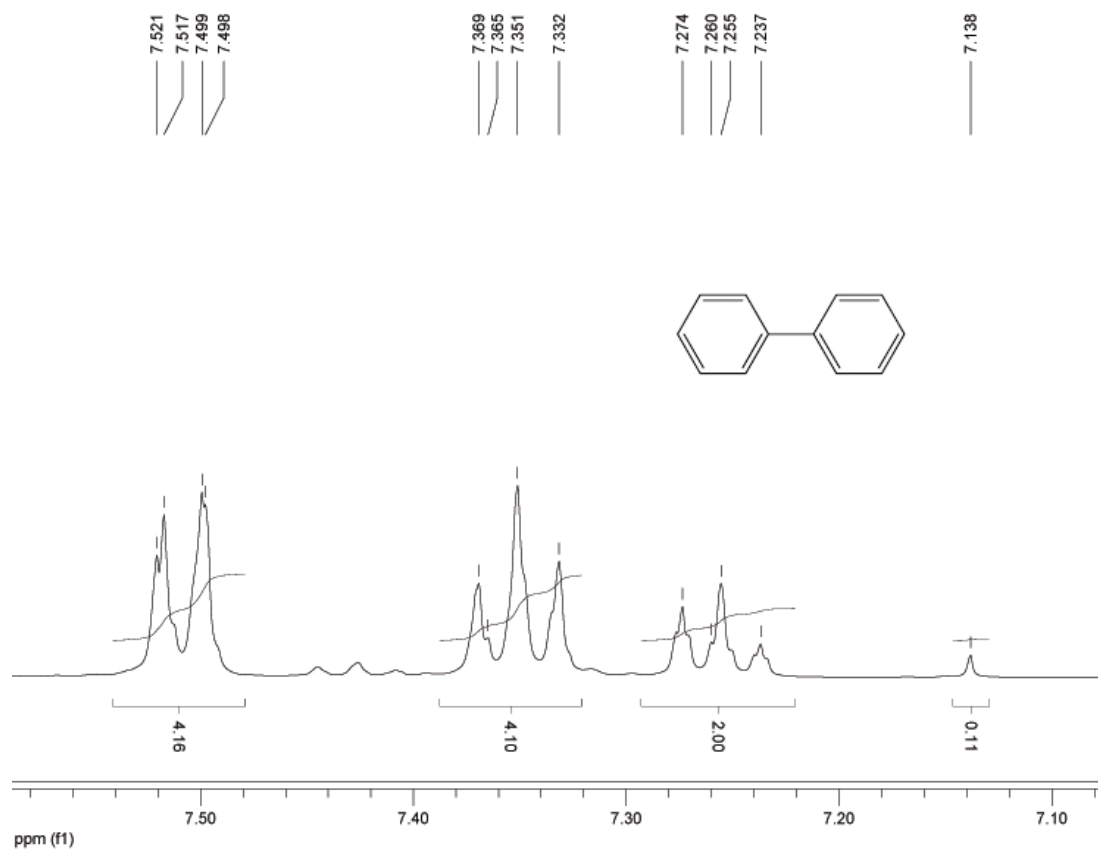
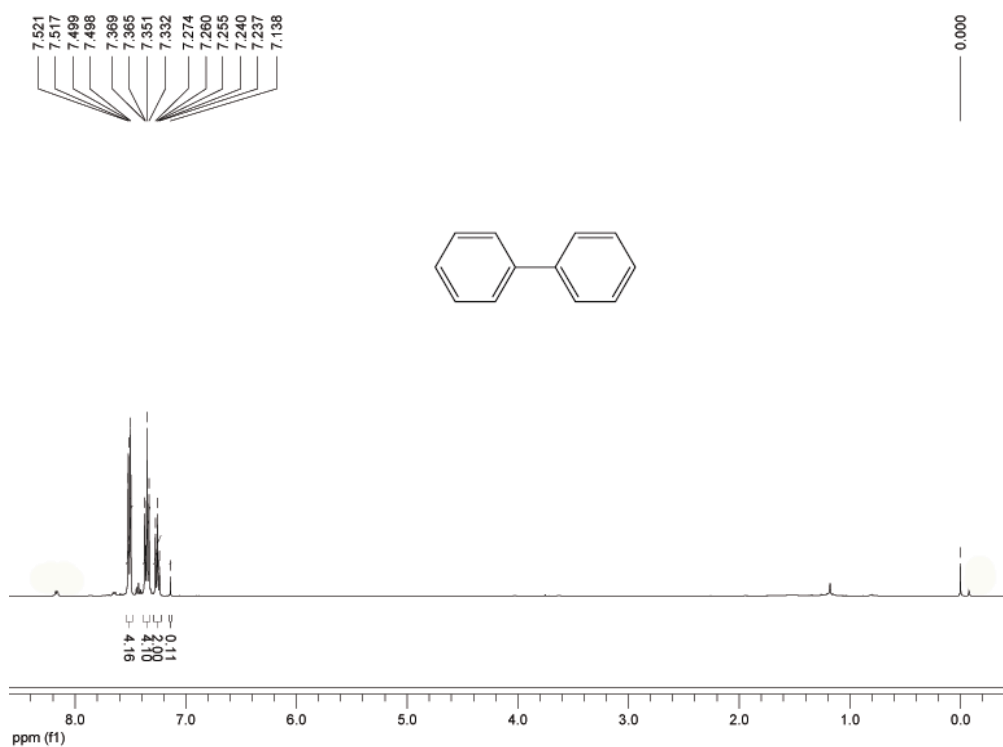
Table S3 Heck reactions of aryl halides with styrene using Pd-1 NPs loaded solid slides as the catalysts.

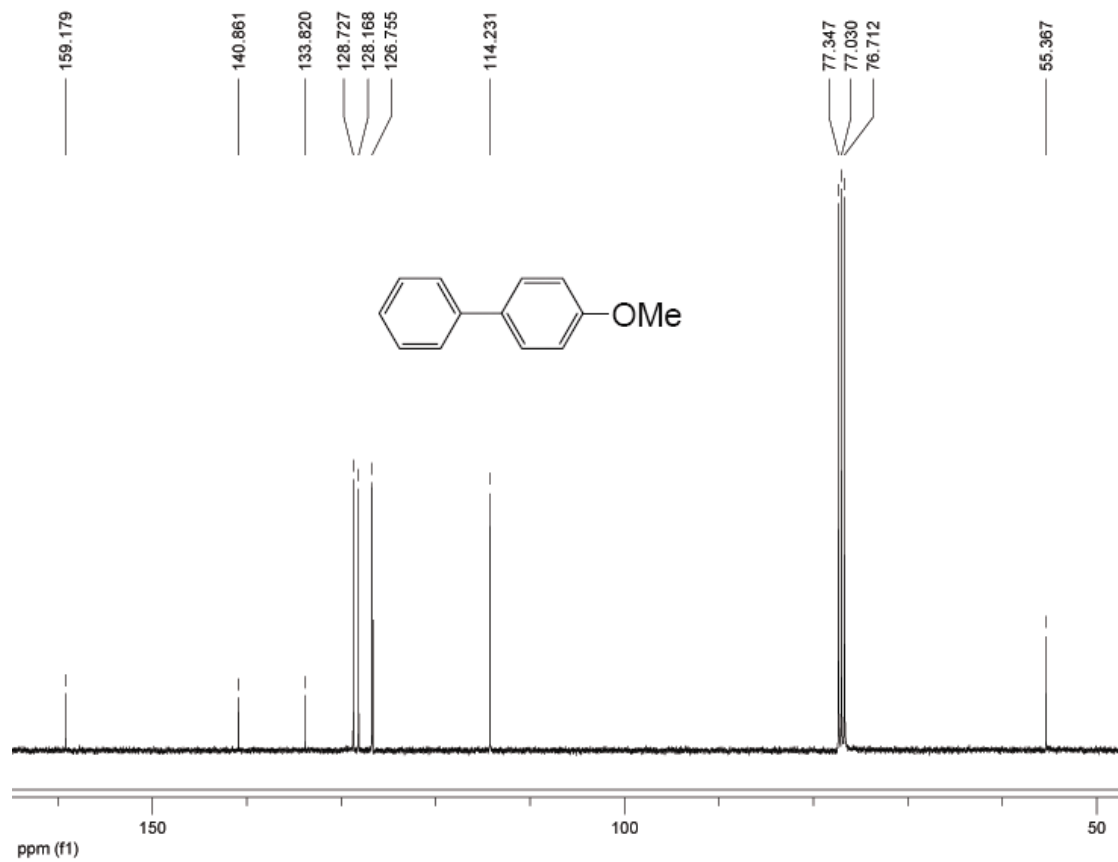
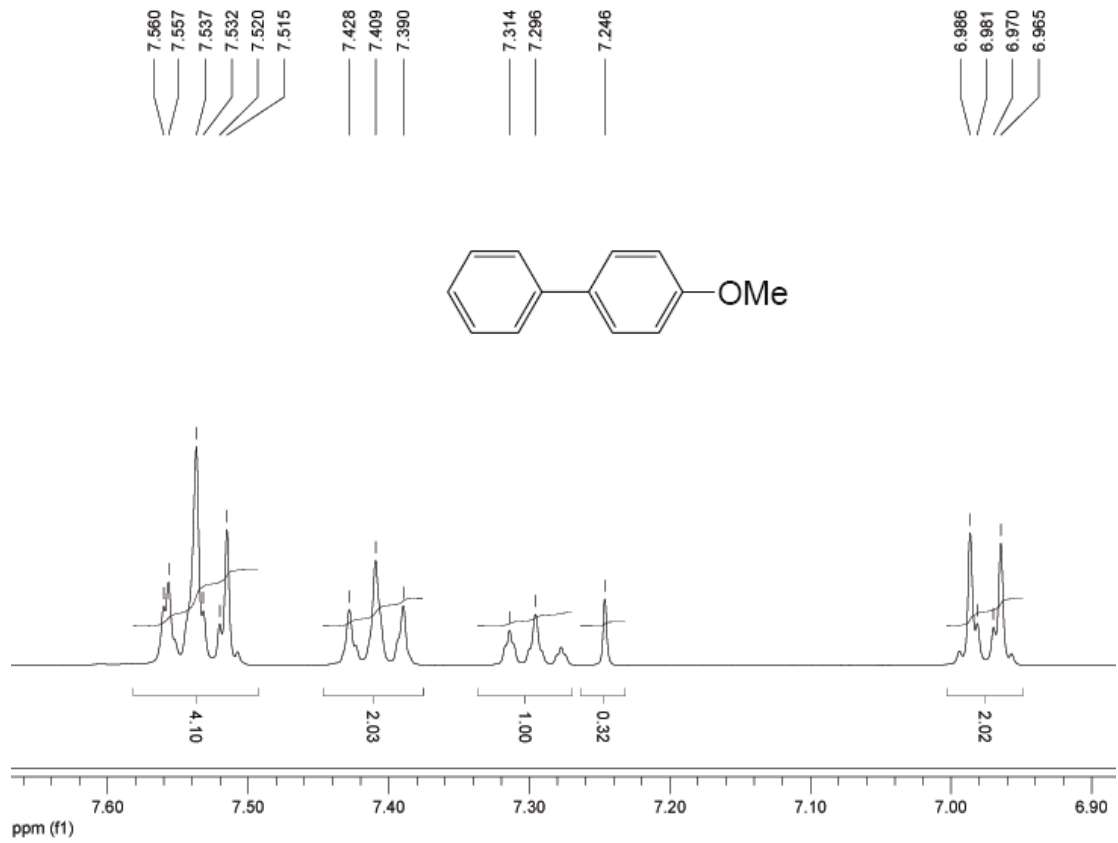


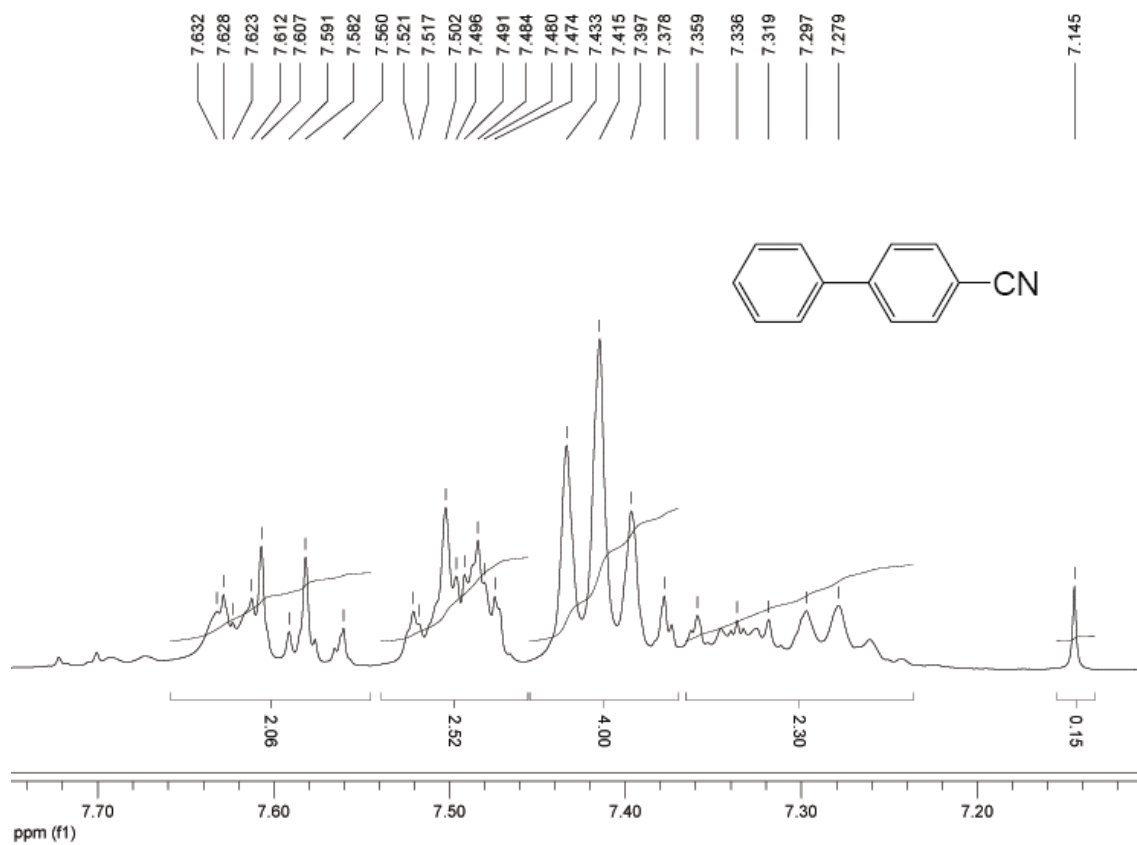
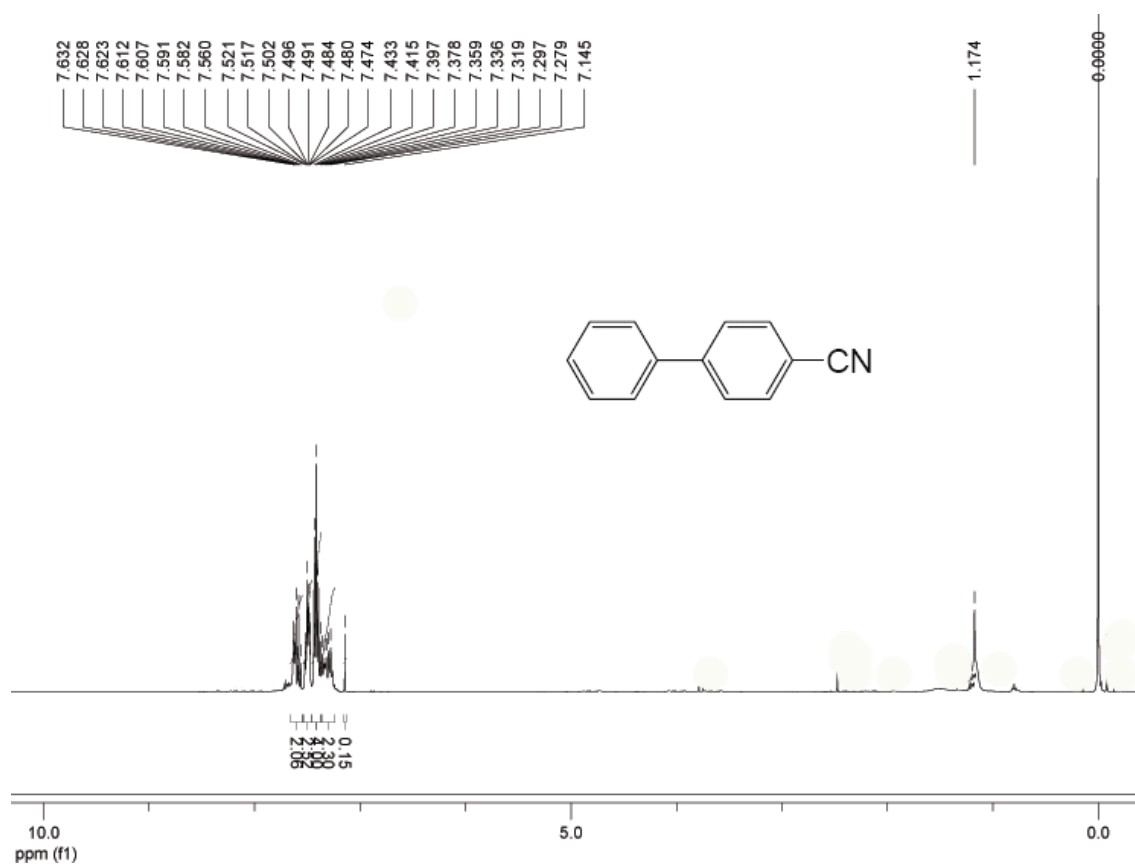
Entry	Catalyst loading	T/°C	Time/h	Yield (%)
1	1%	140	24	47
2	5%	140	24	78
3	10%	140	24	83

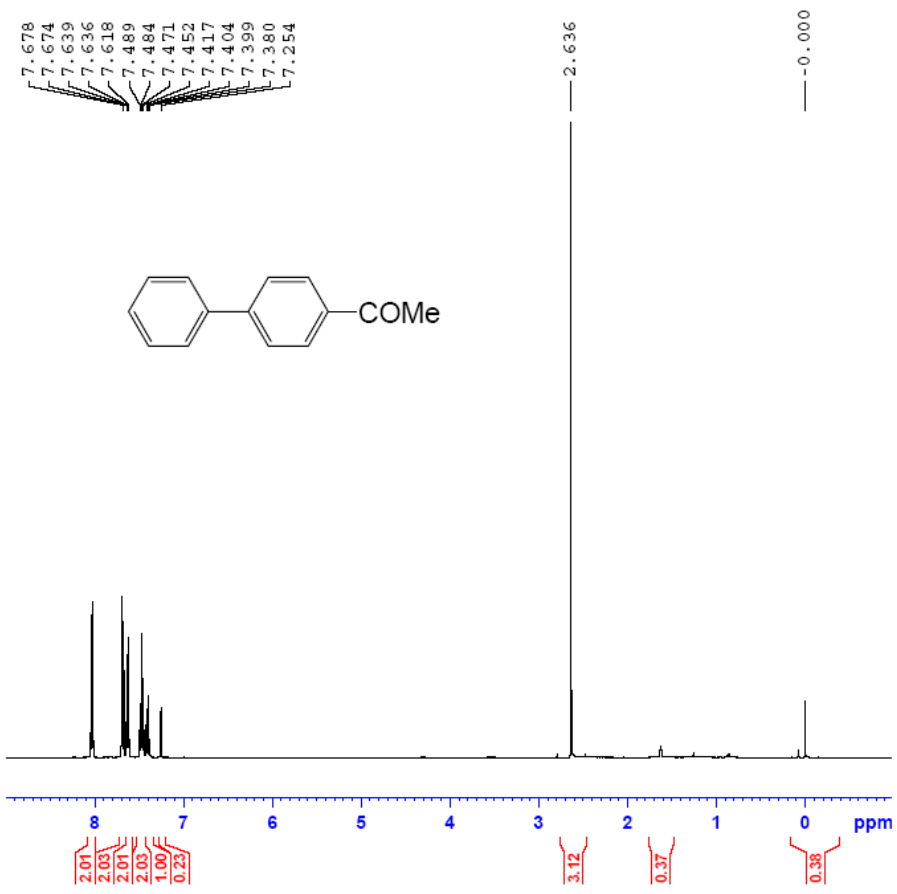
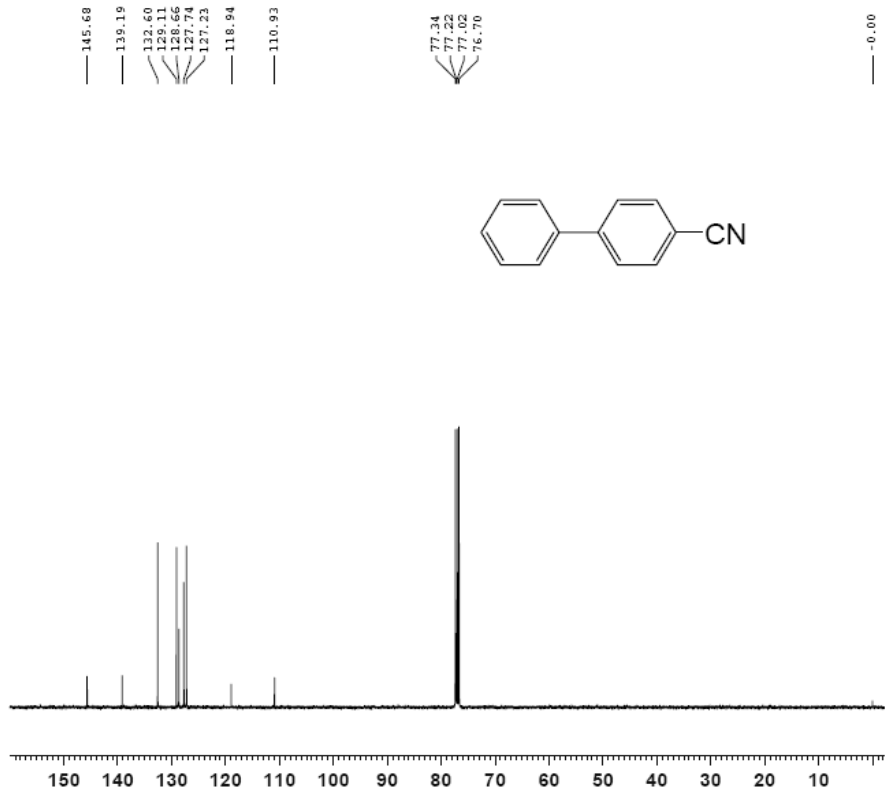
General procedure: 1.0 mmol of aryl halide, 1.2 mmol of styrene and 2.0 mmol of Na₂CO₃ in 6.0 mL DMF at 140 °C for 24 h in air atmosphere.

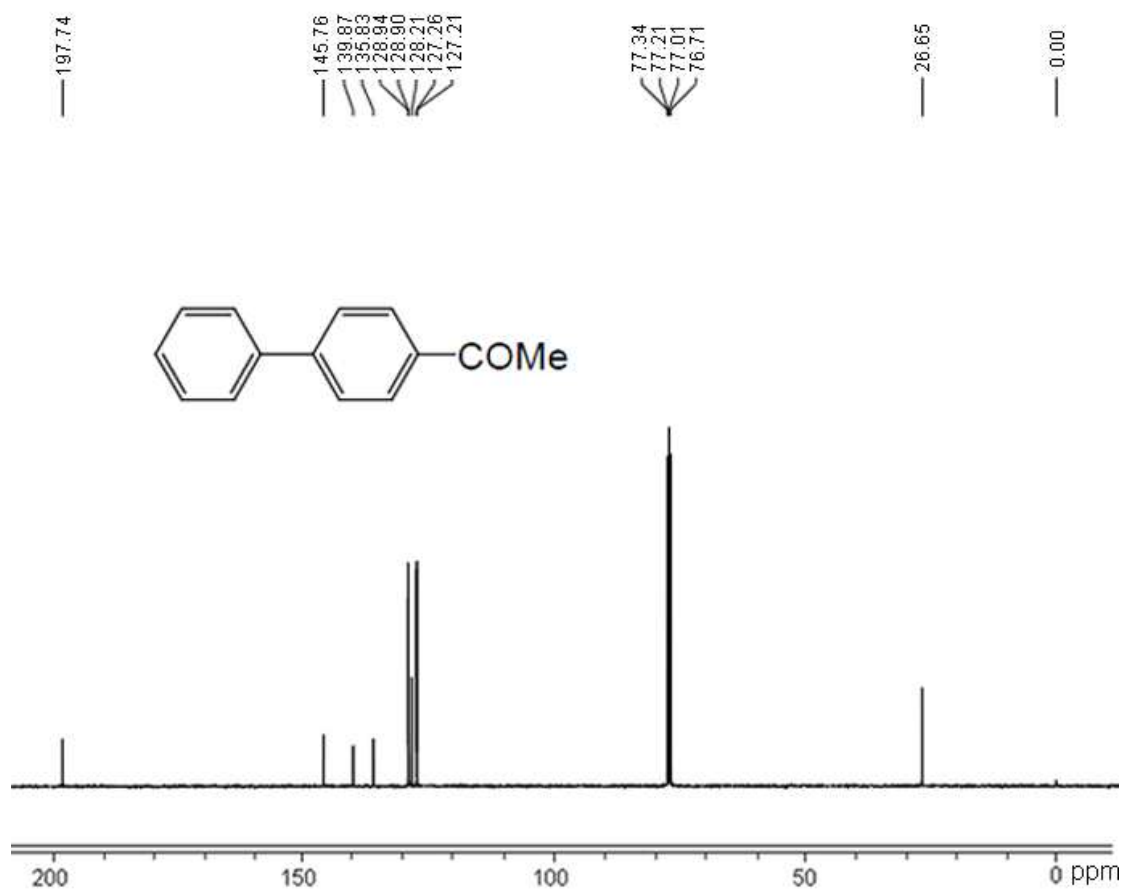
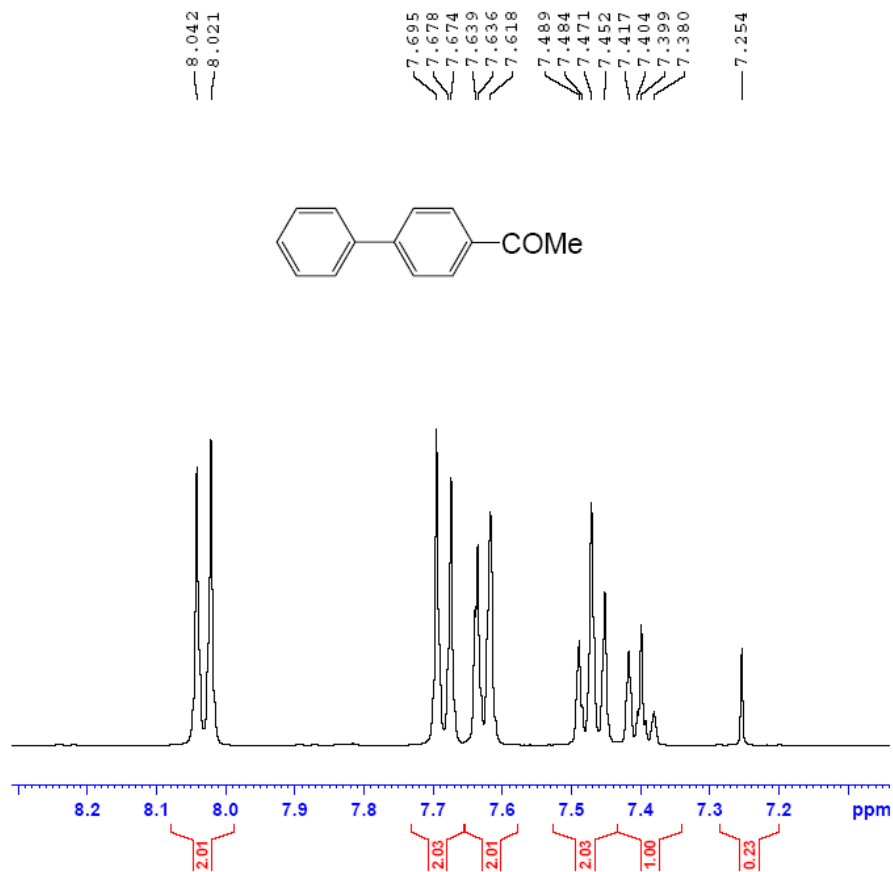
Suzuki reactions:
¹H NMR and ¹³C NMR Spectra of the products

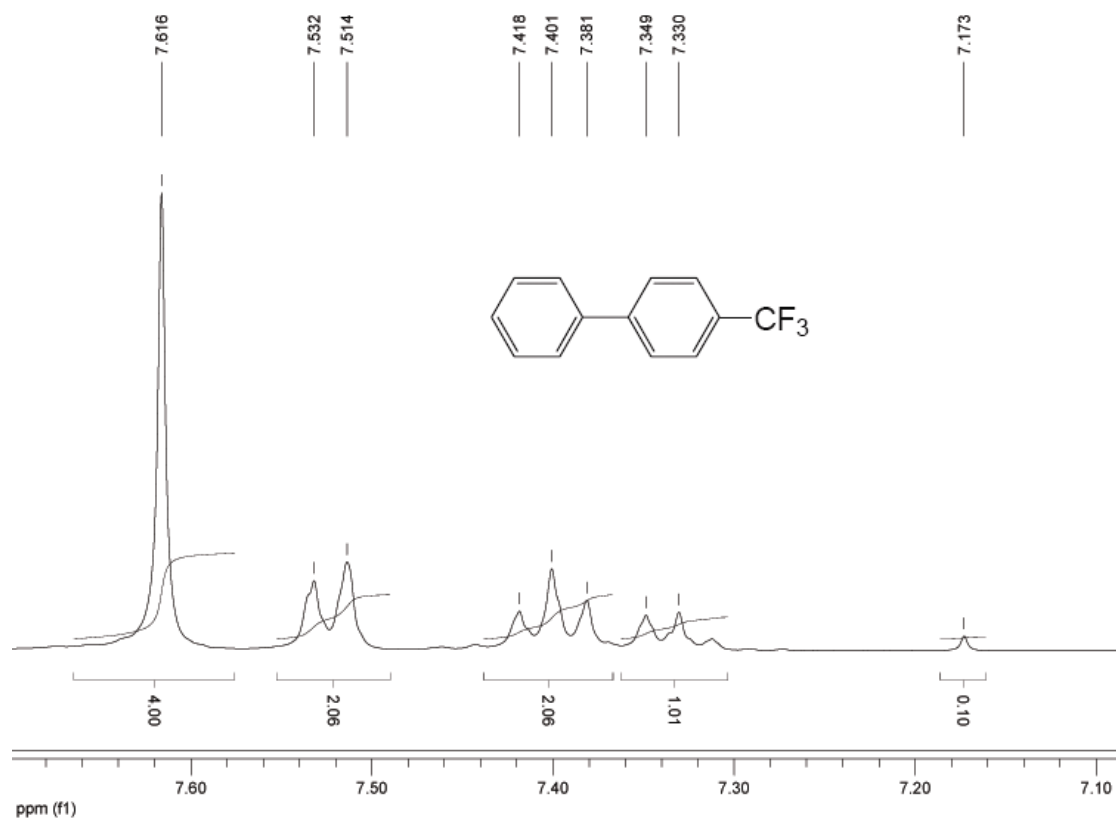
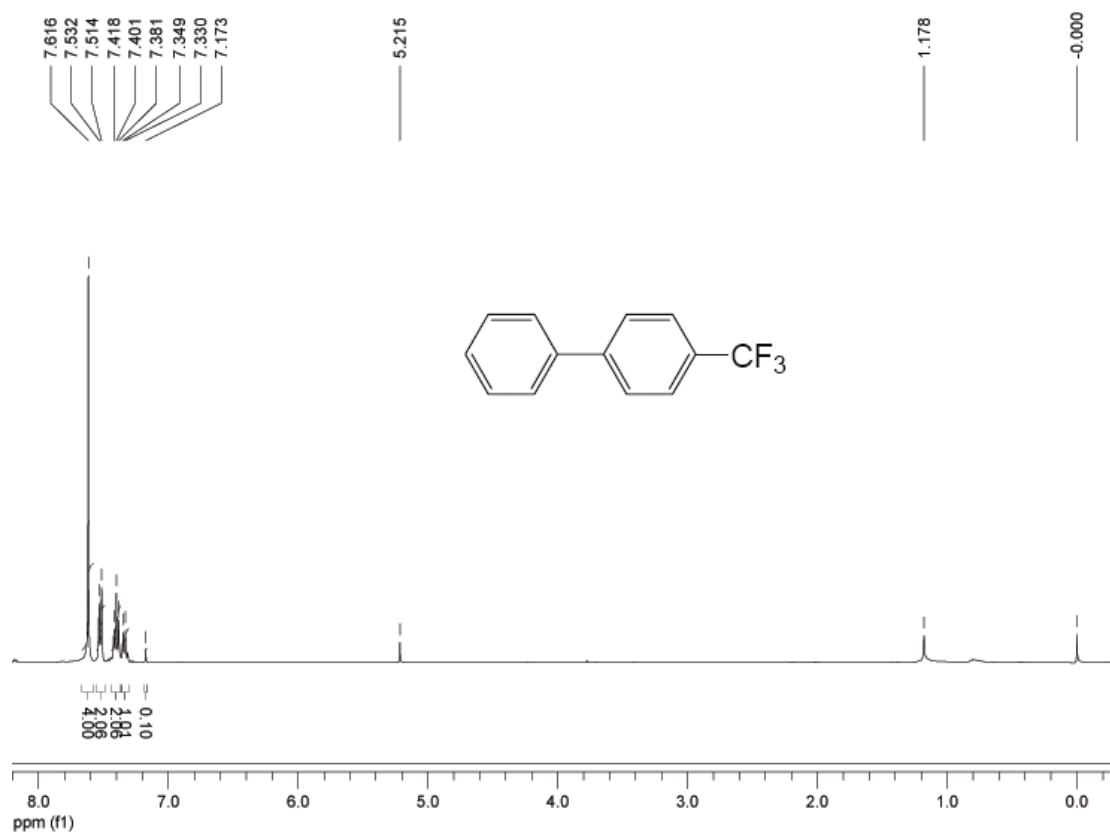


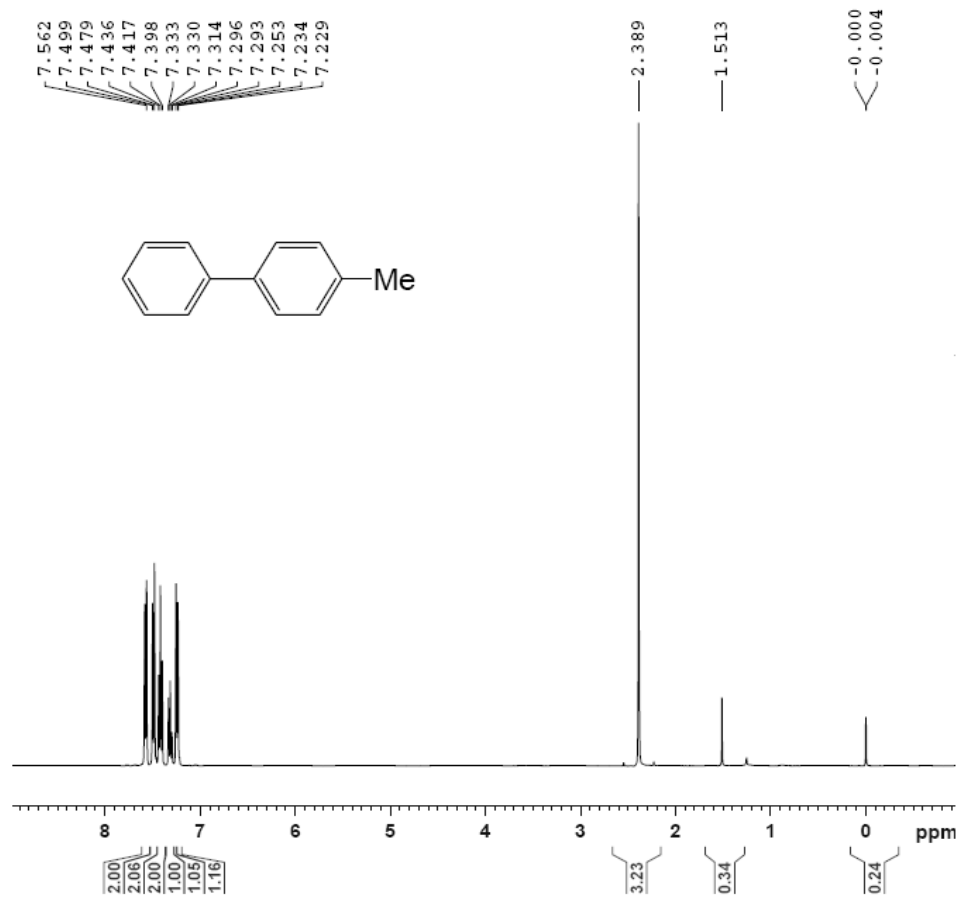
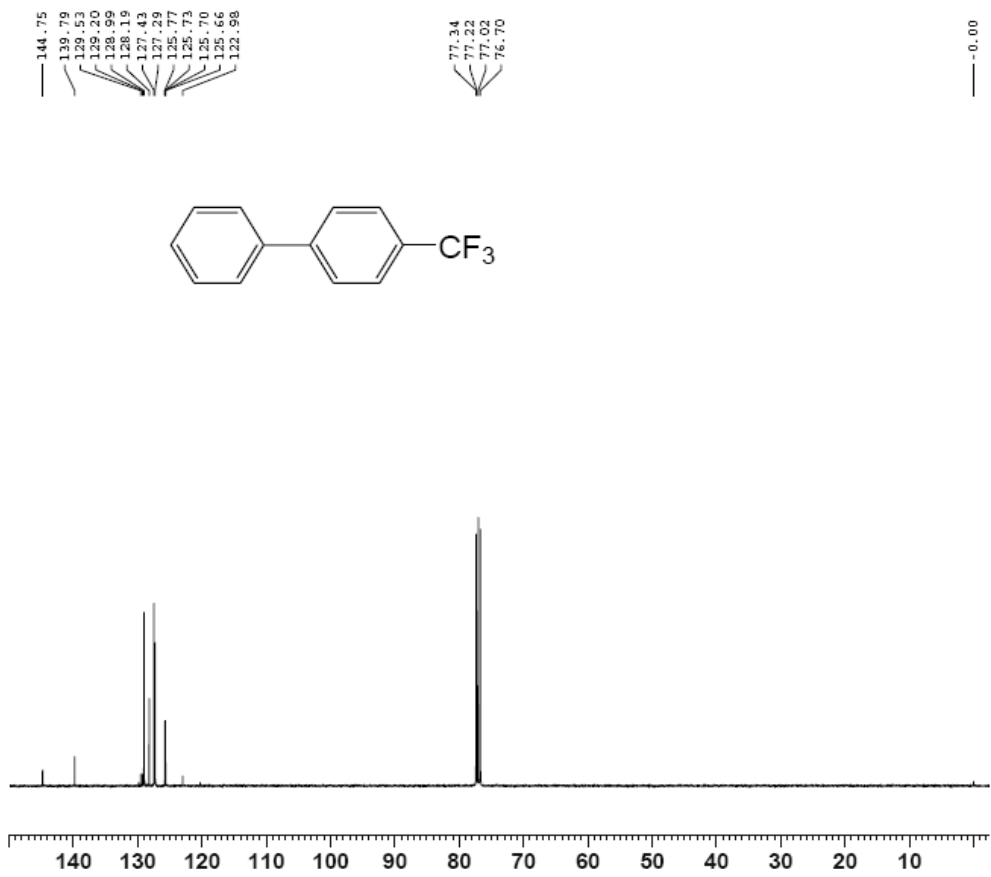












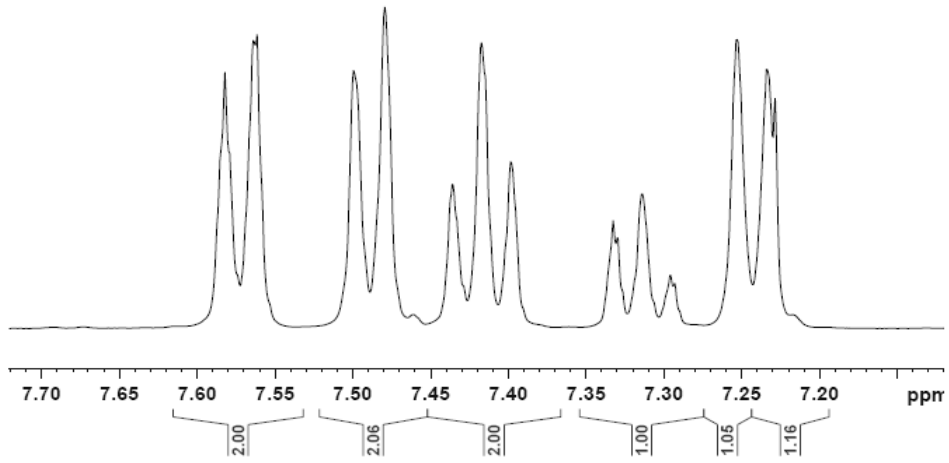
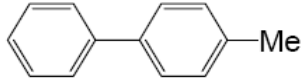
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7.564
7.562

7.499
7.479

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7.417
7.398

7.333
7.330
7.314
7.296
7.293

7.253
7.234
7.229



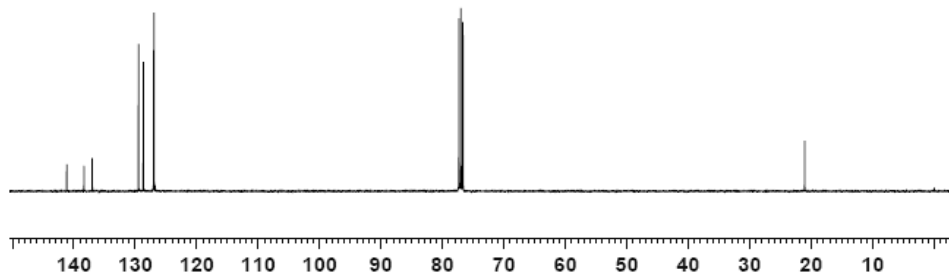
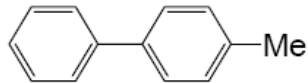
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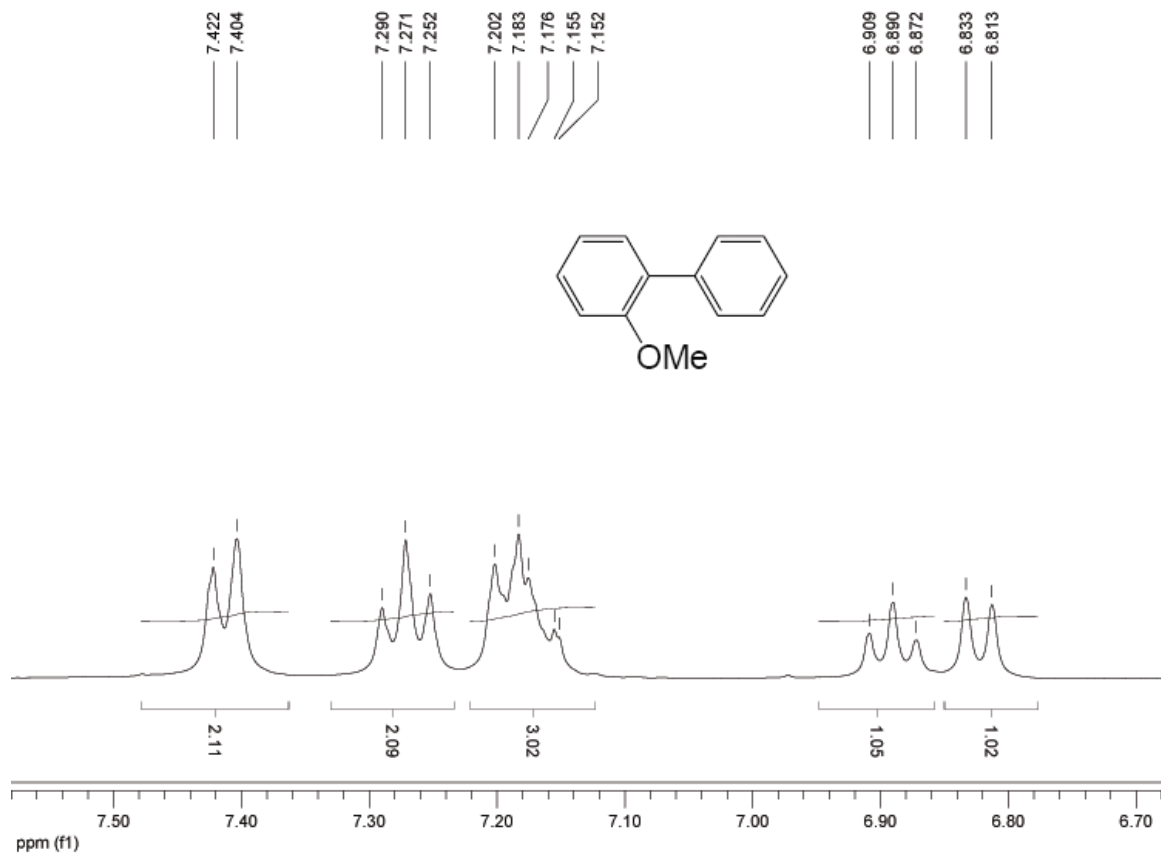
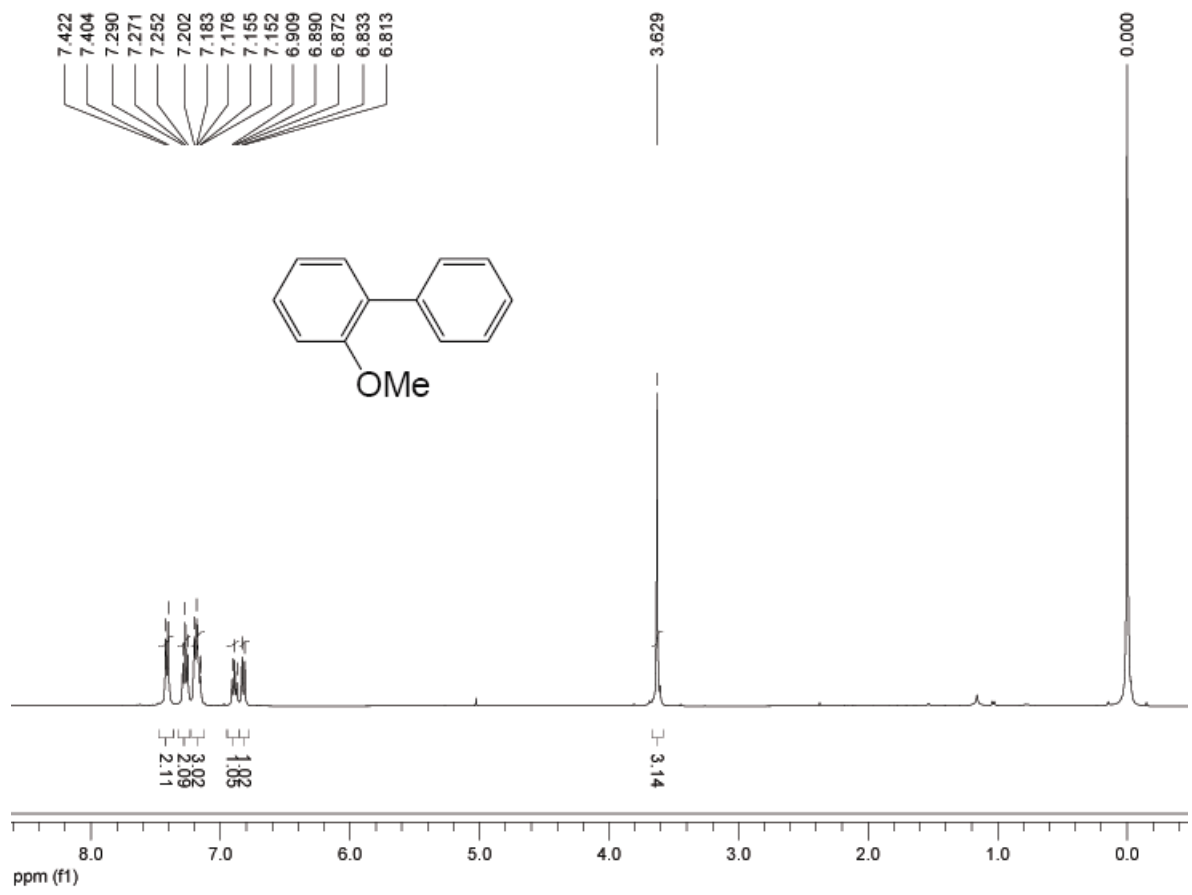
129.47
128.70
126.99
126.97
126.80

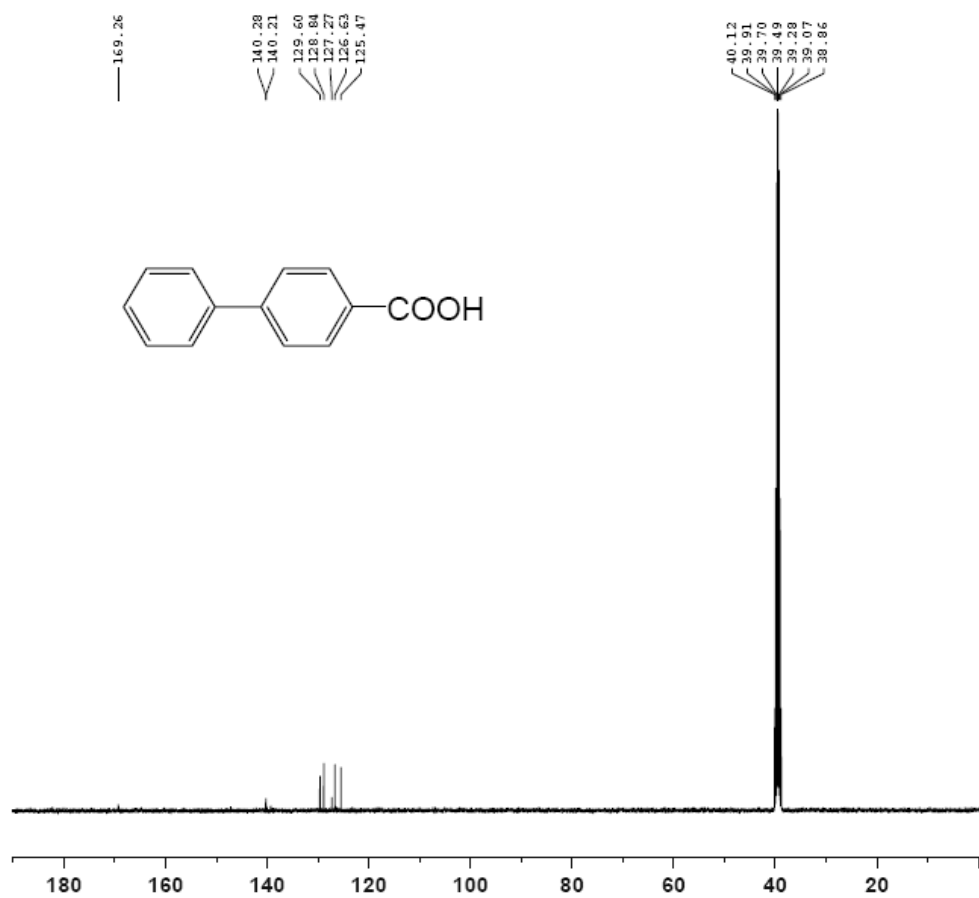
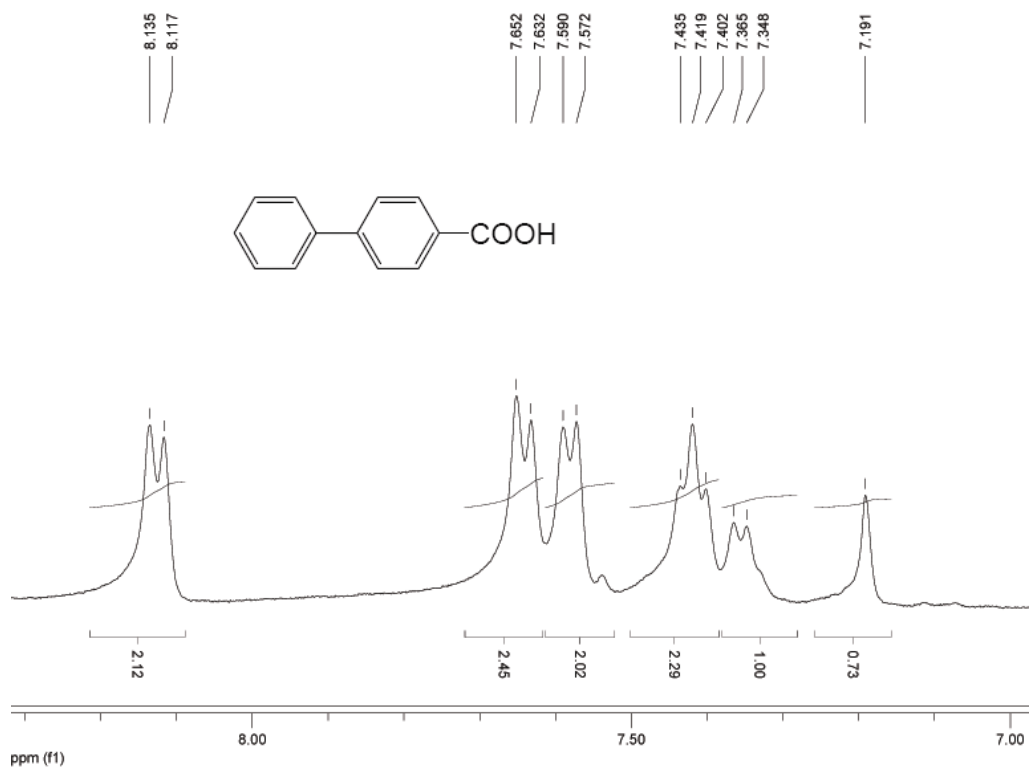
77.33
77.21
77.01
76.69

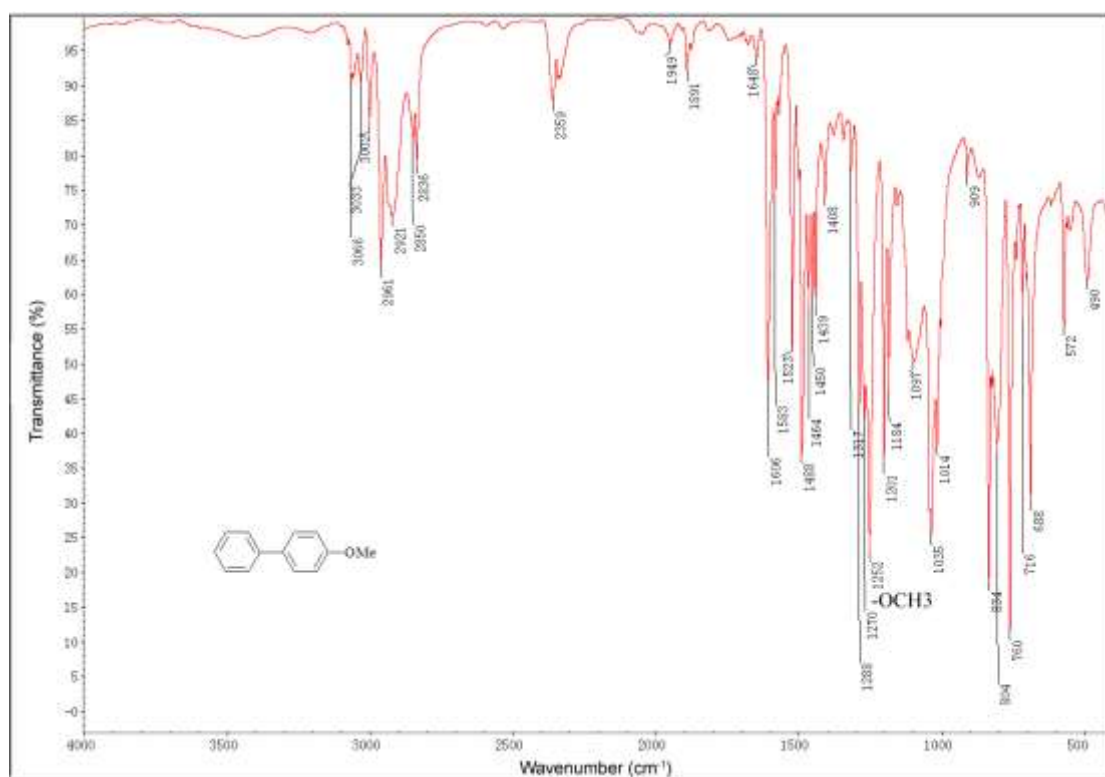
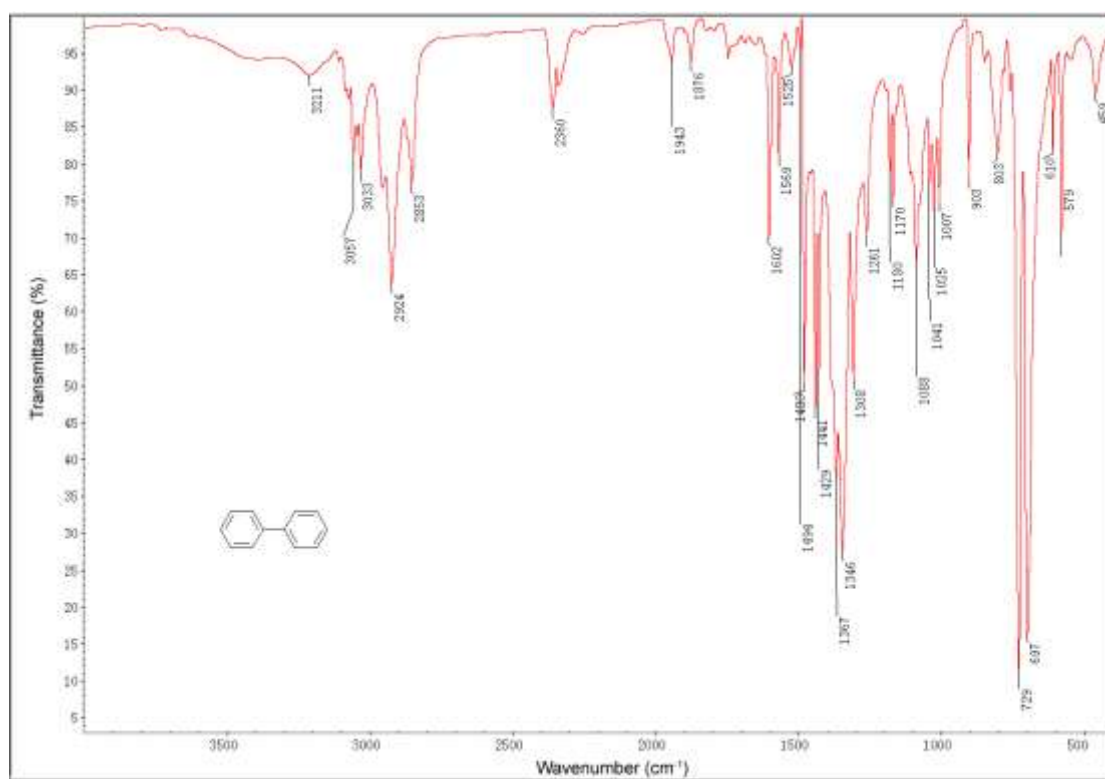
21.08

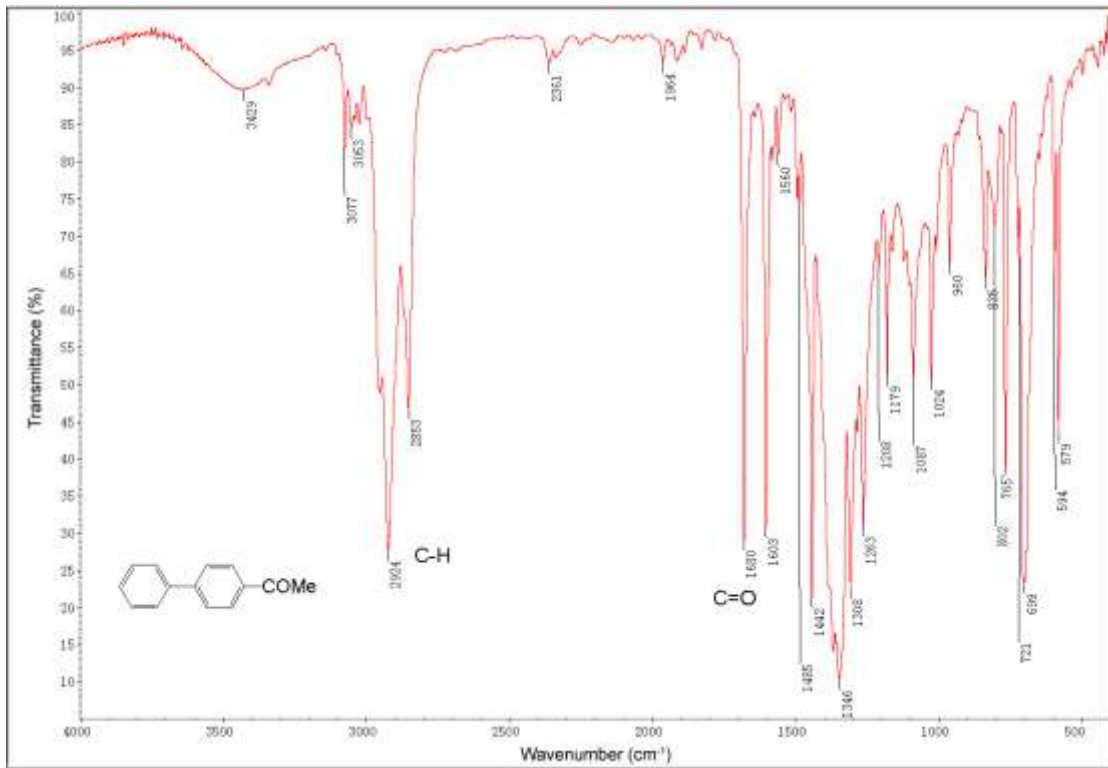
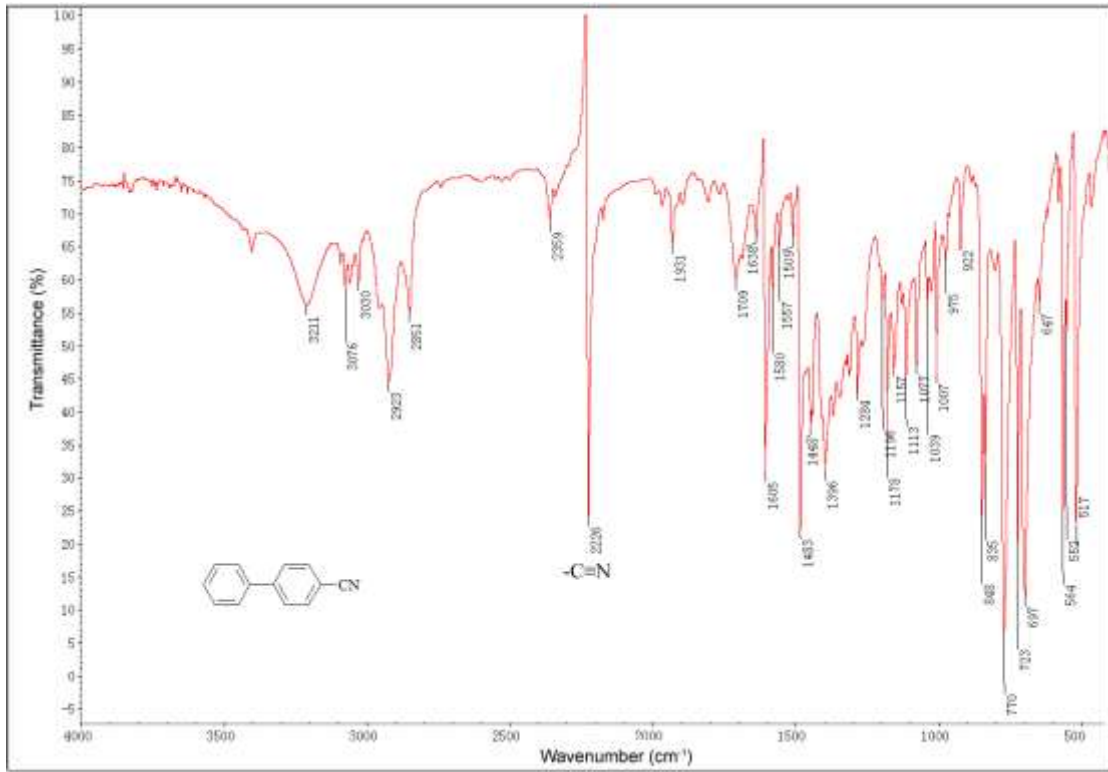
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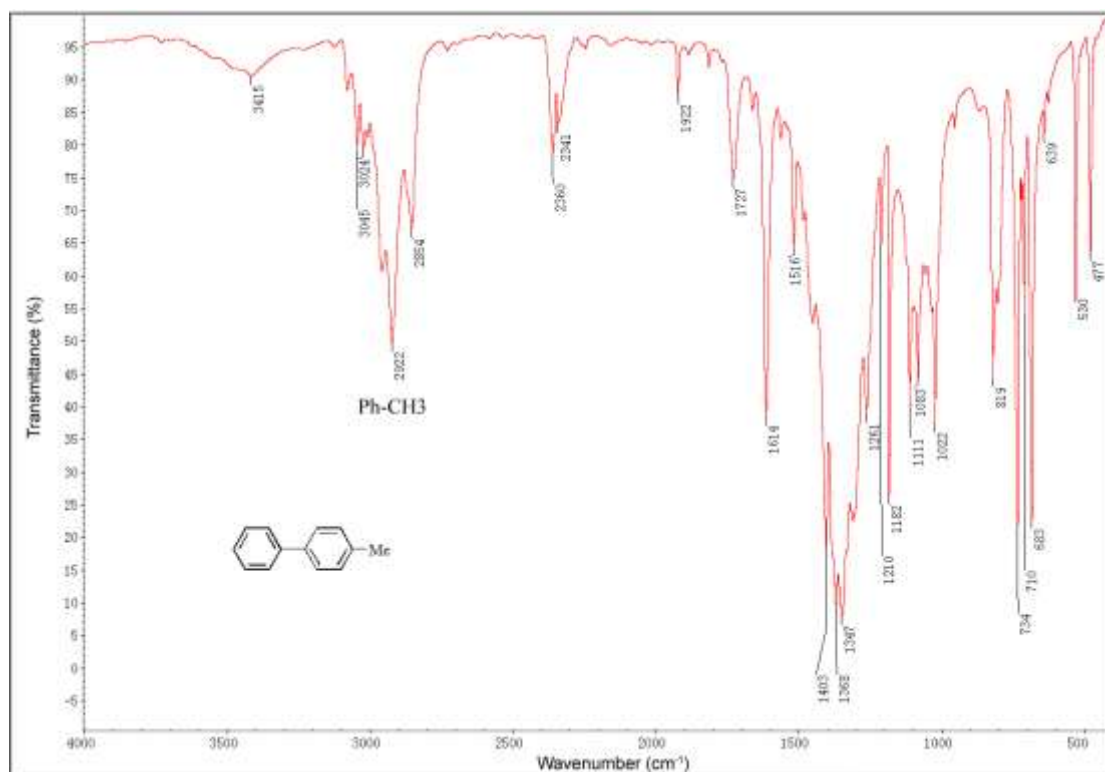
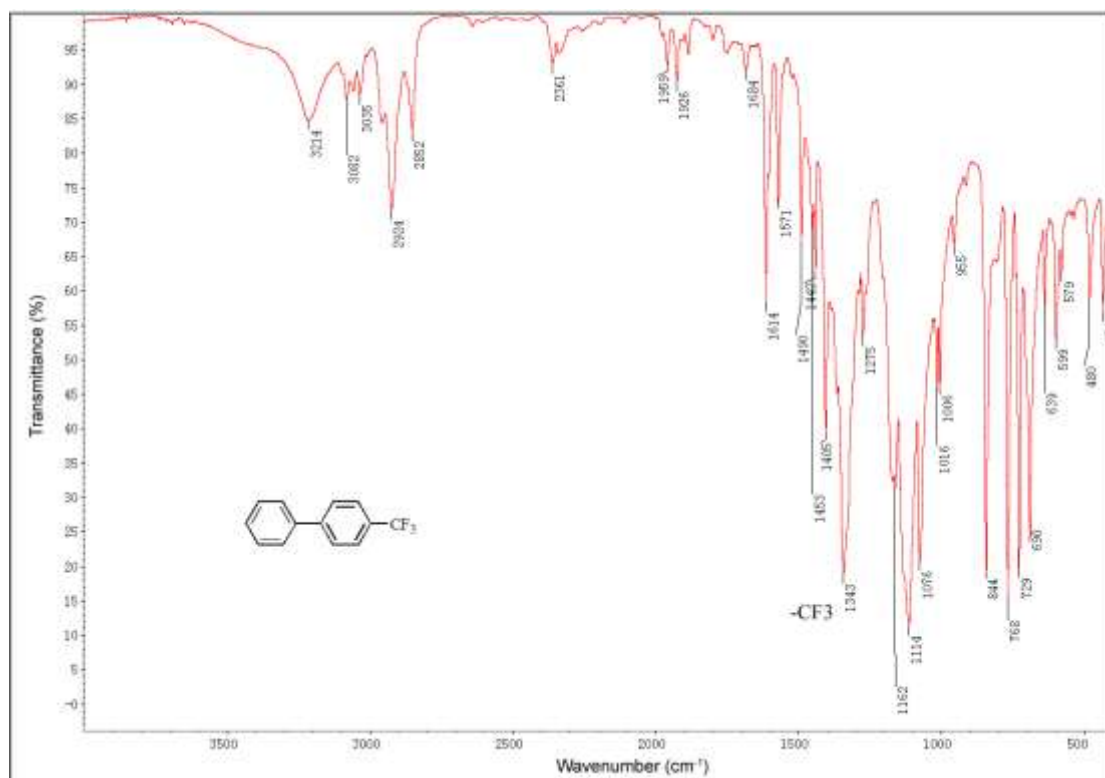


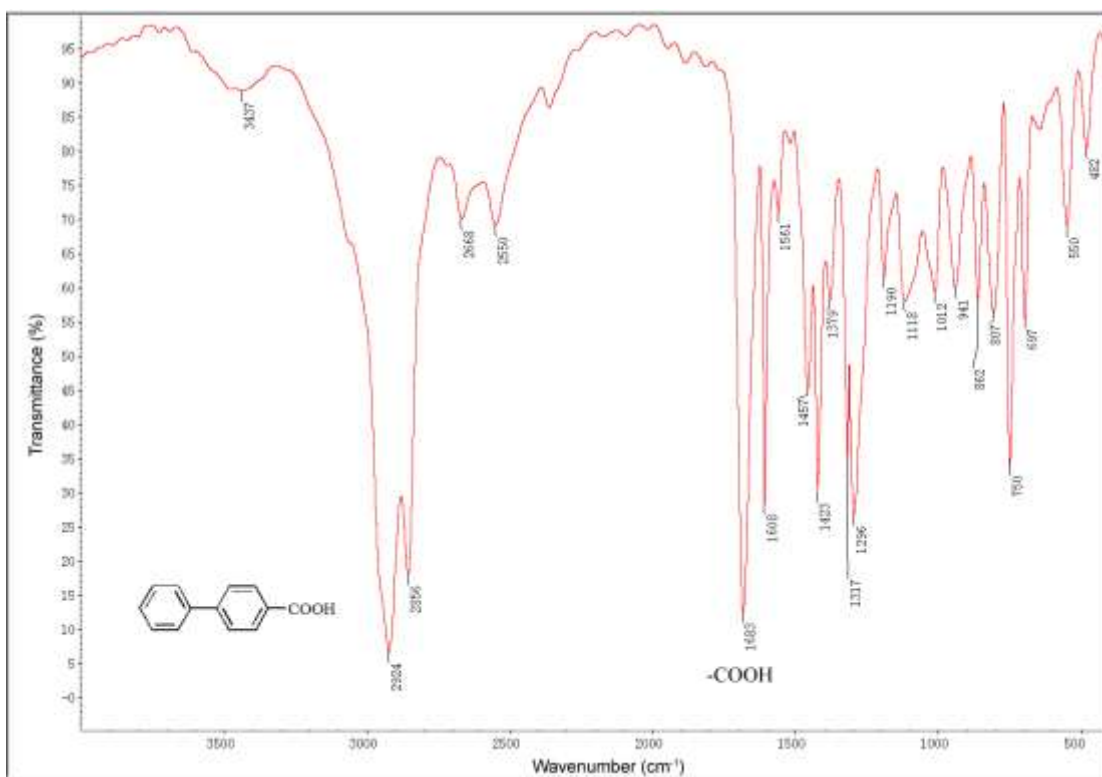
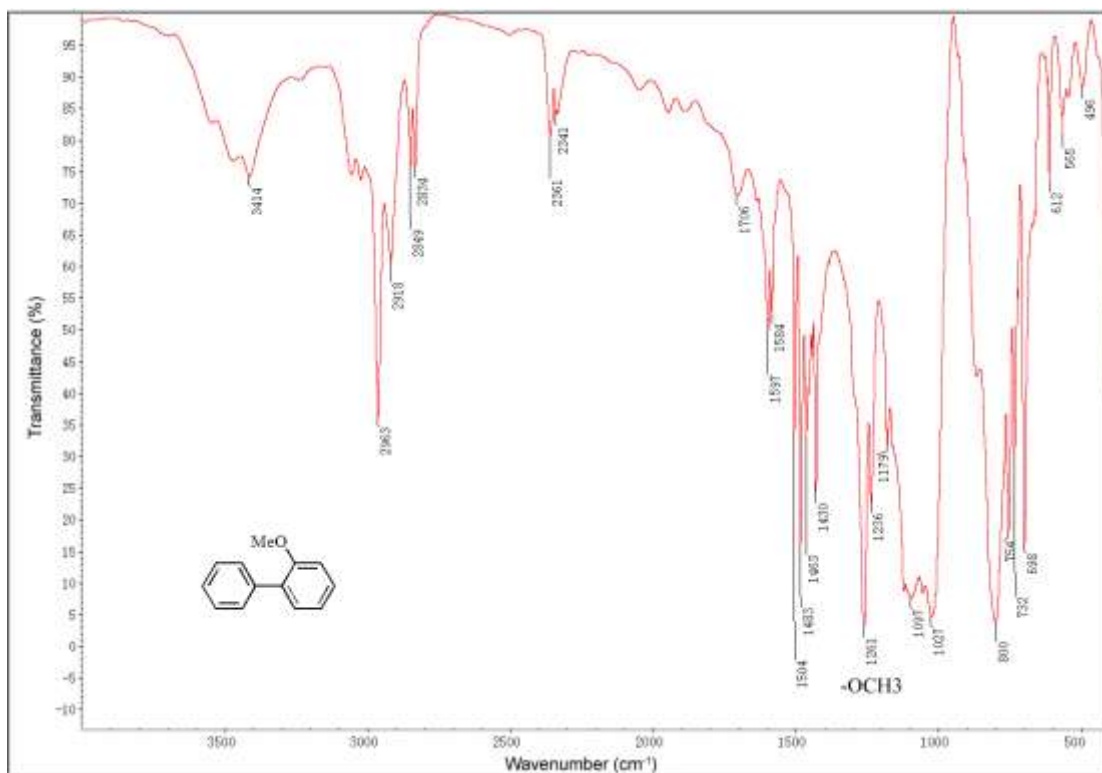




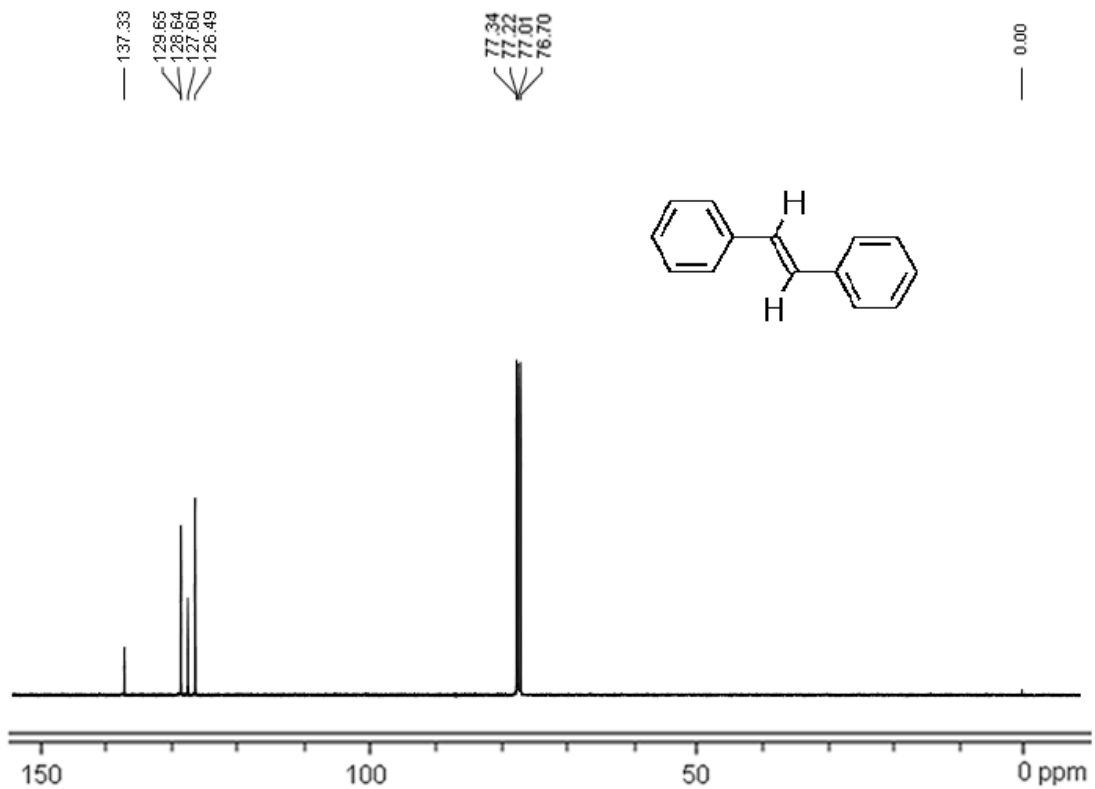
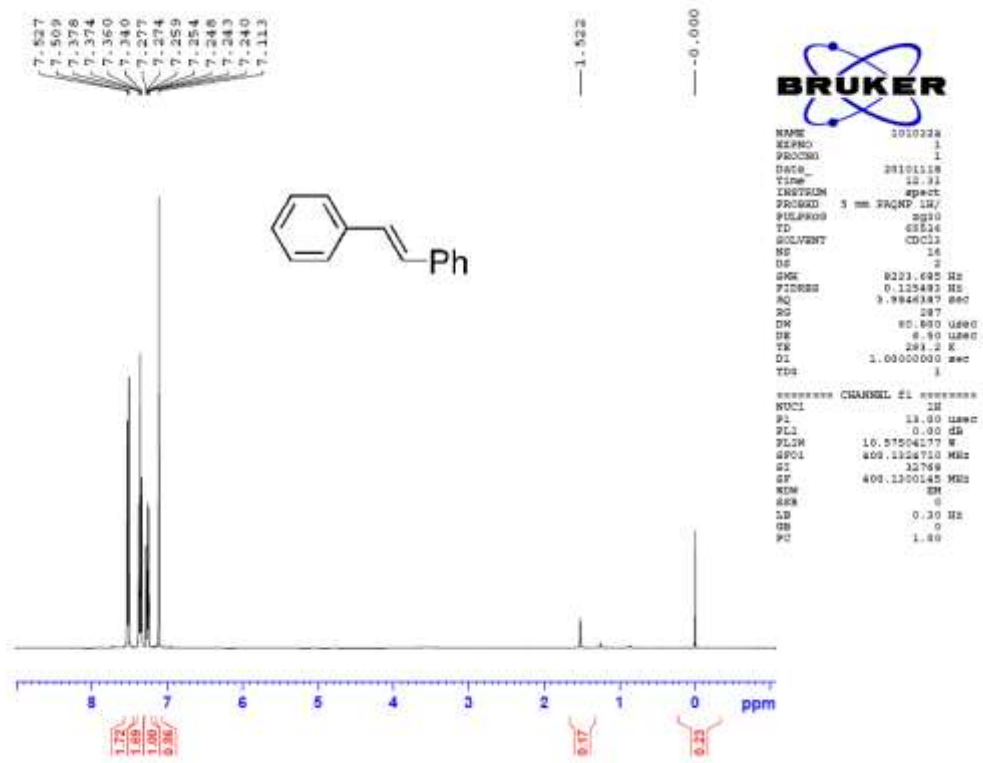


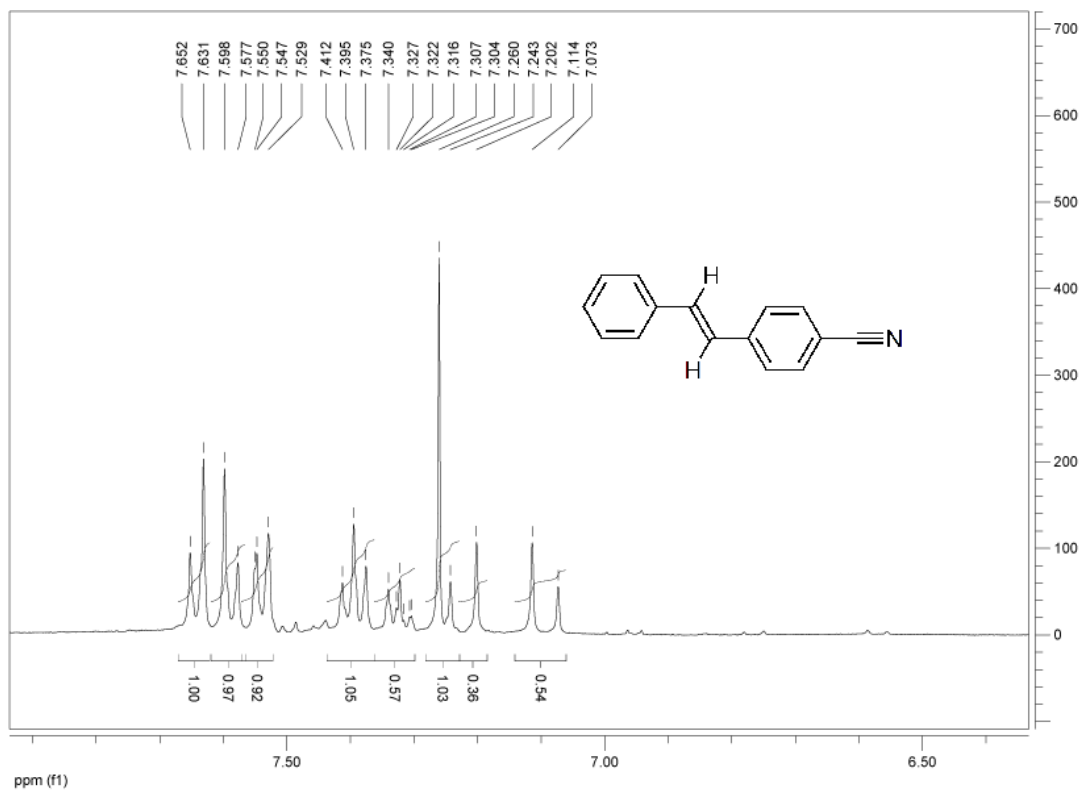
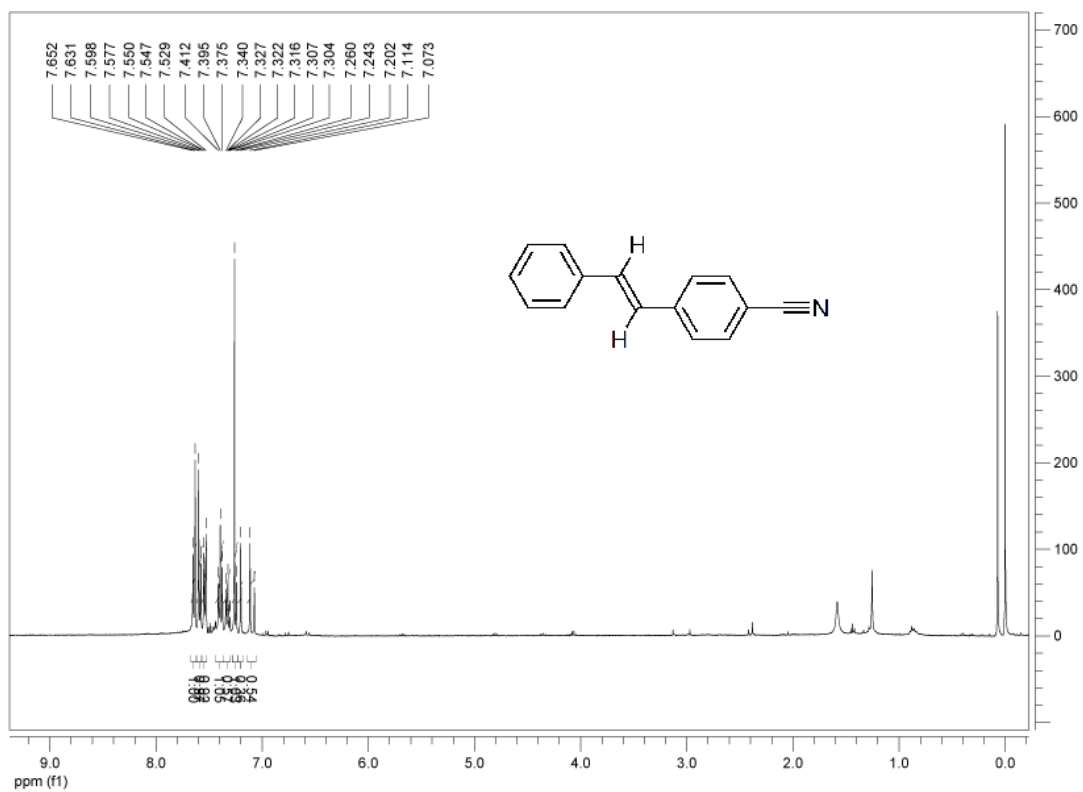


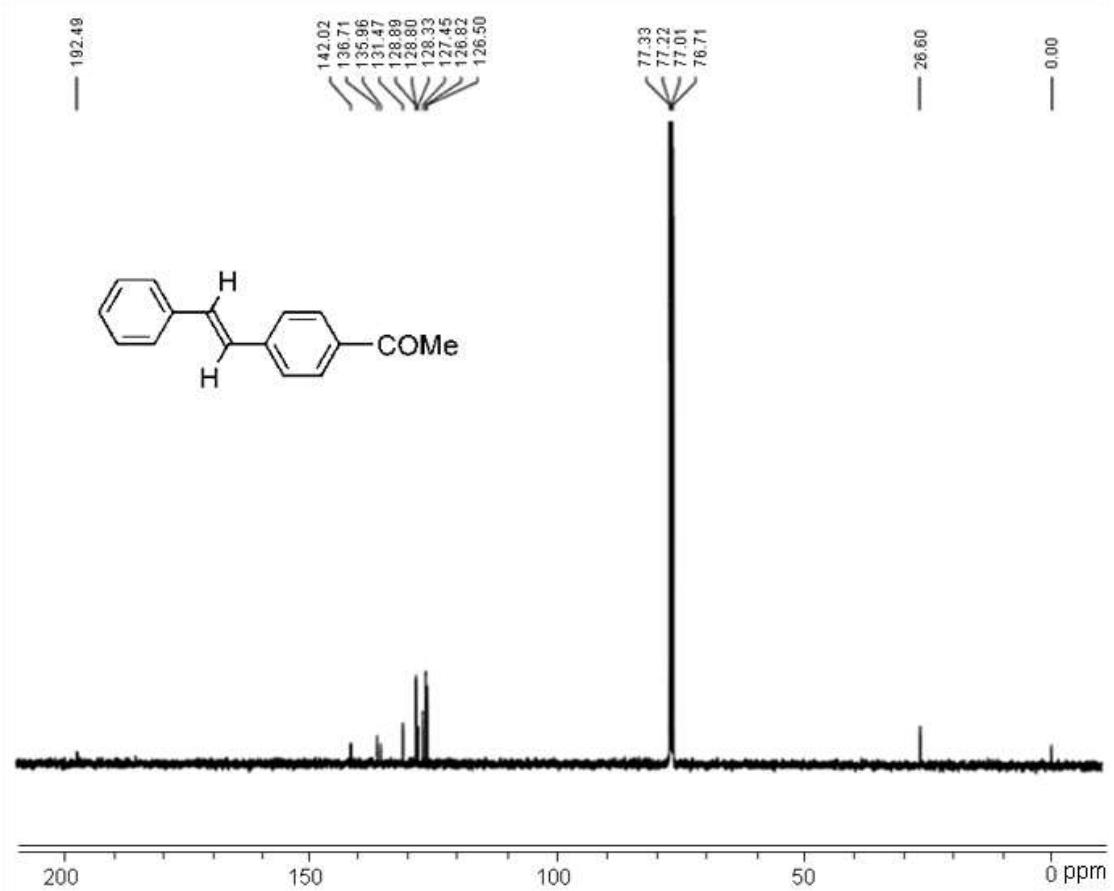
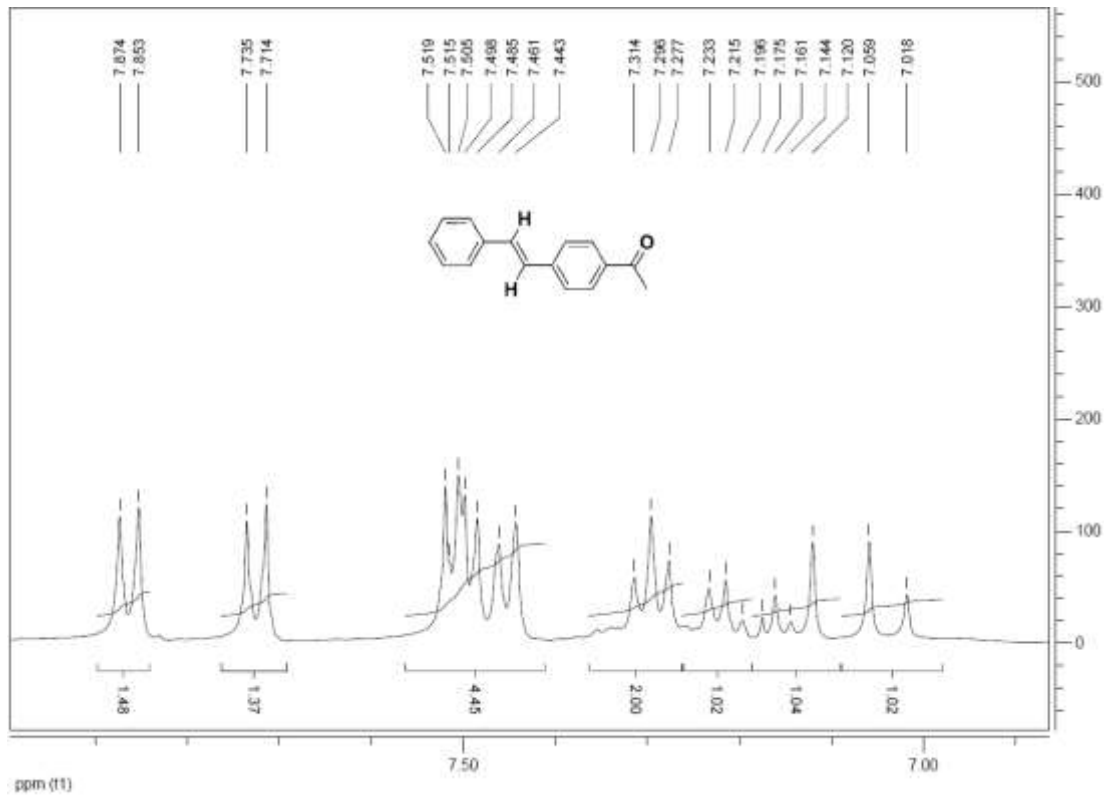


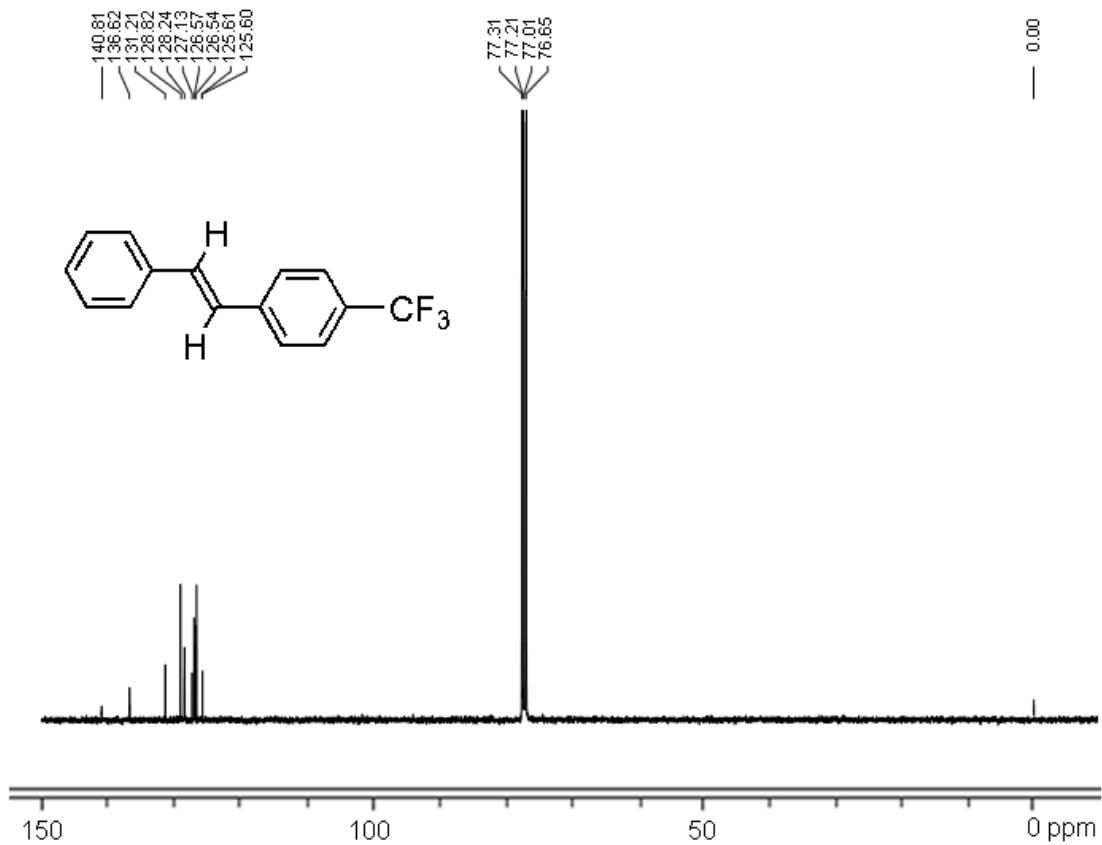
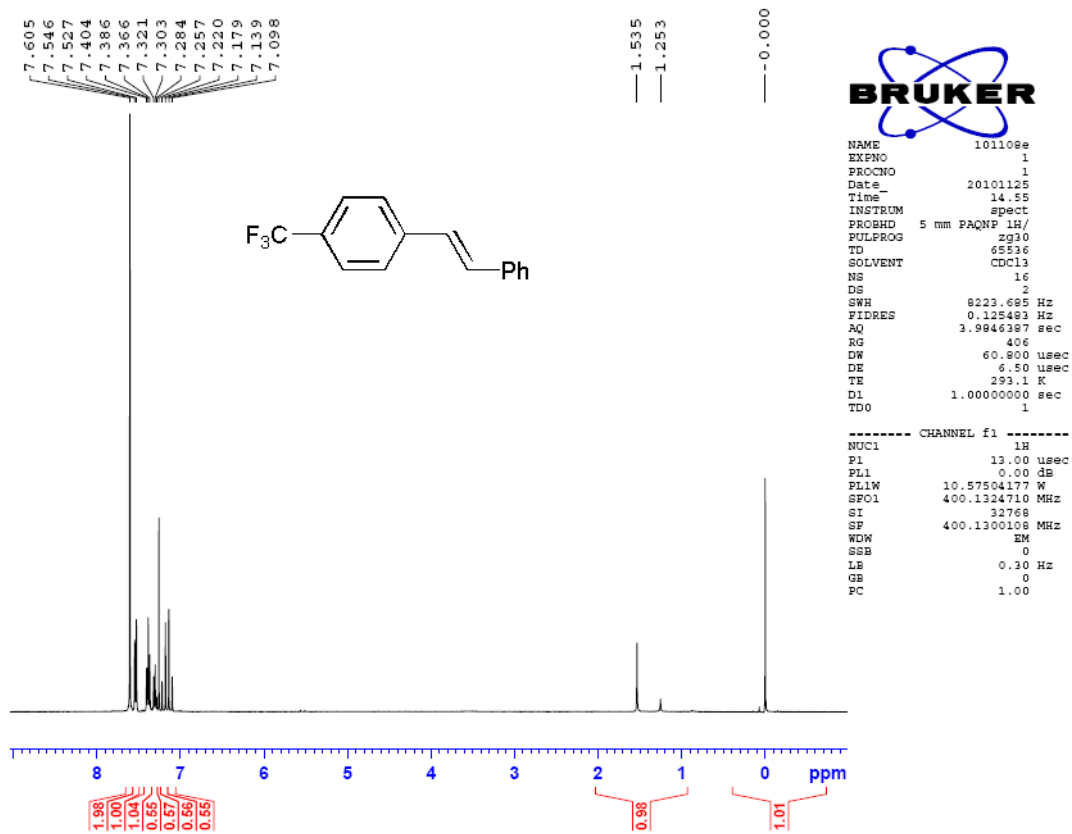


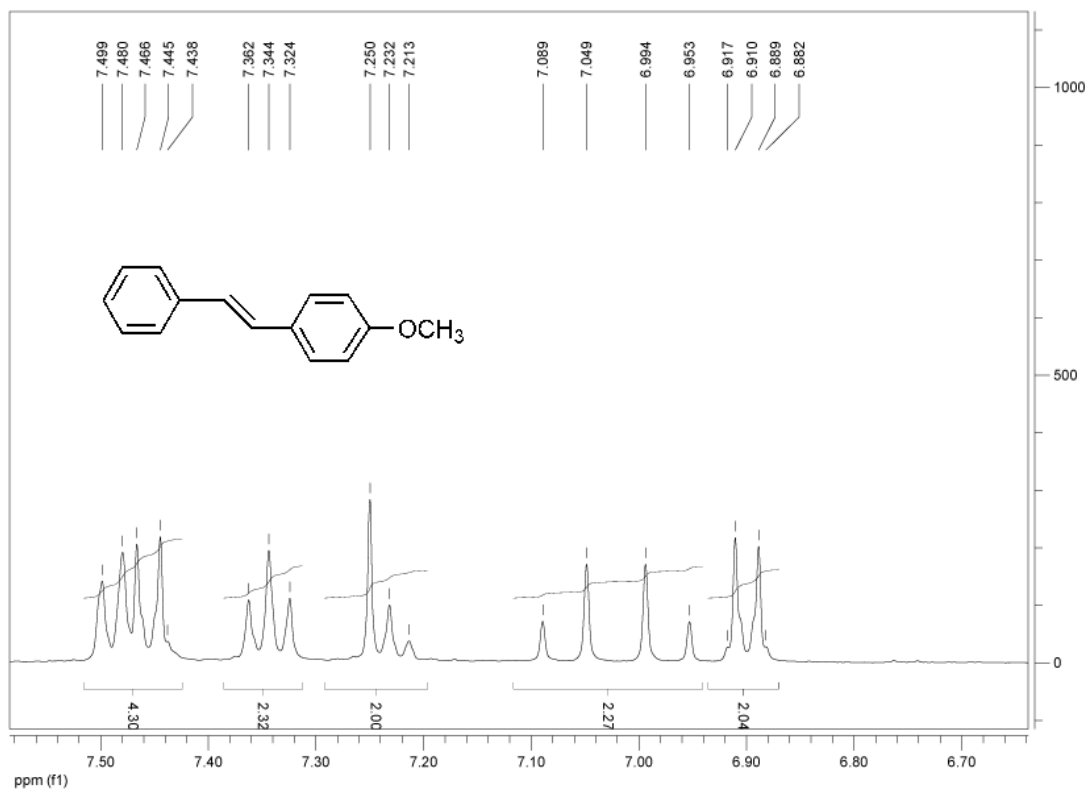
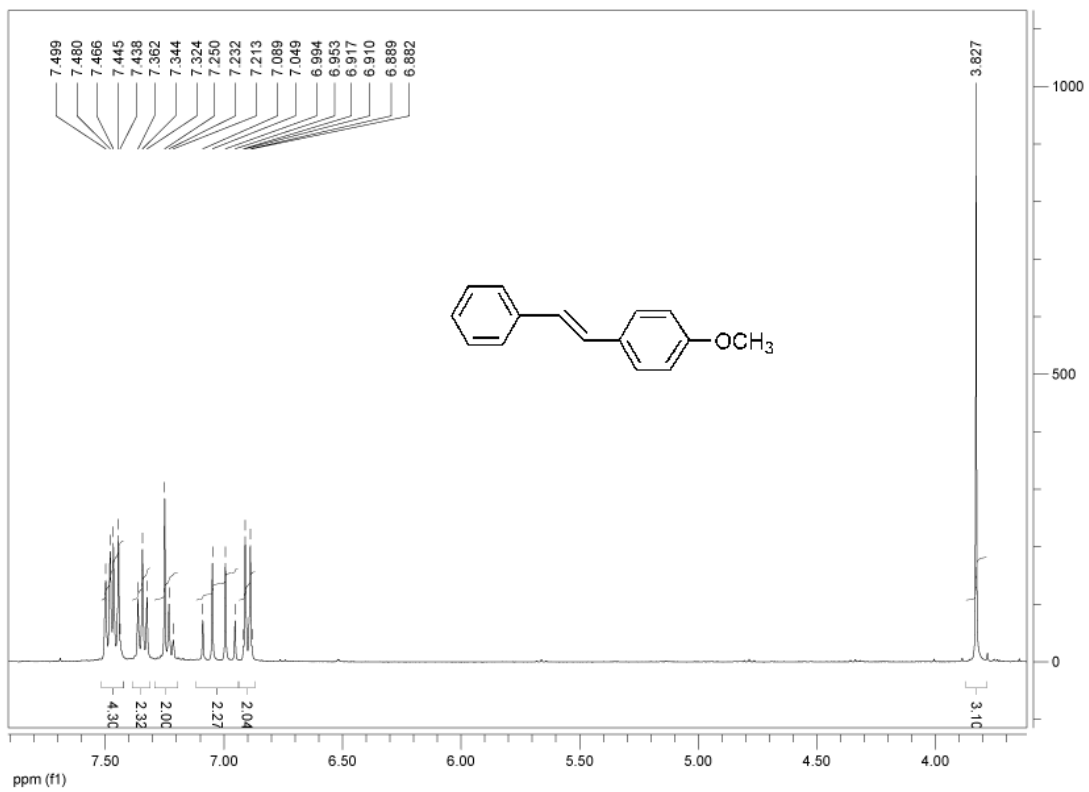
Heck reaction:

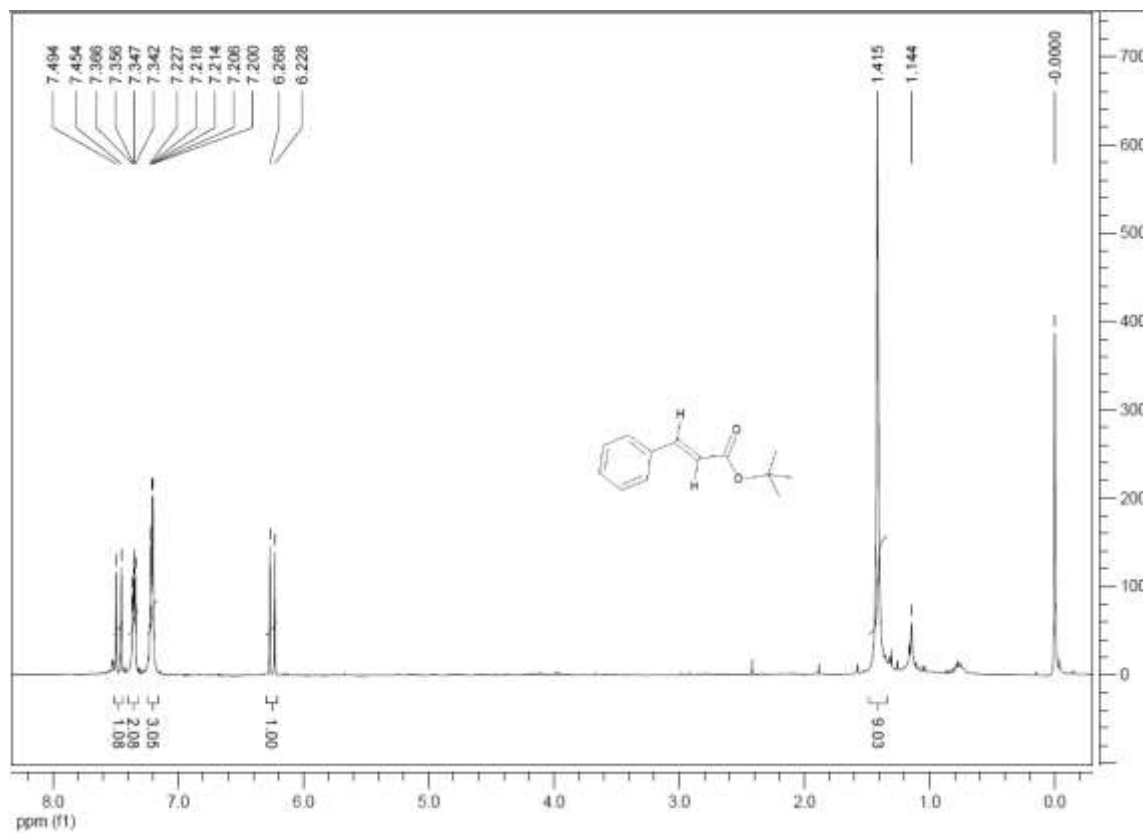
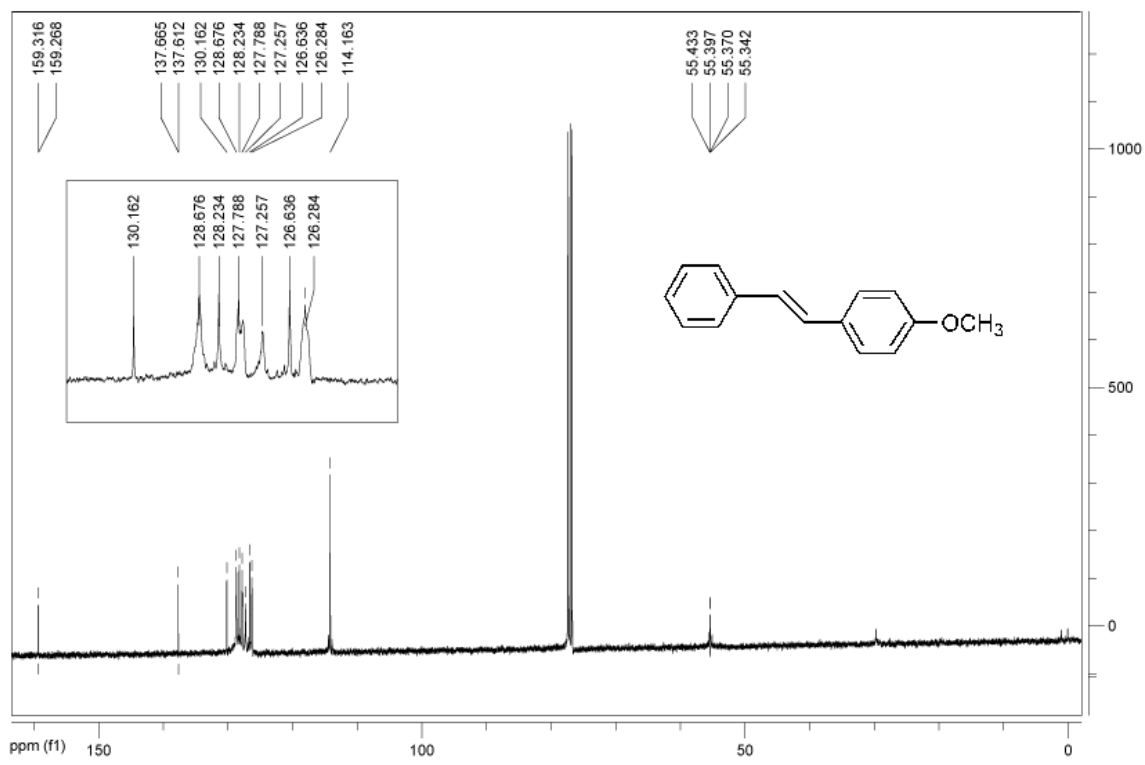


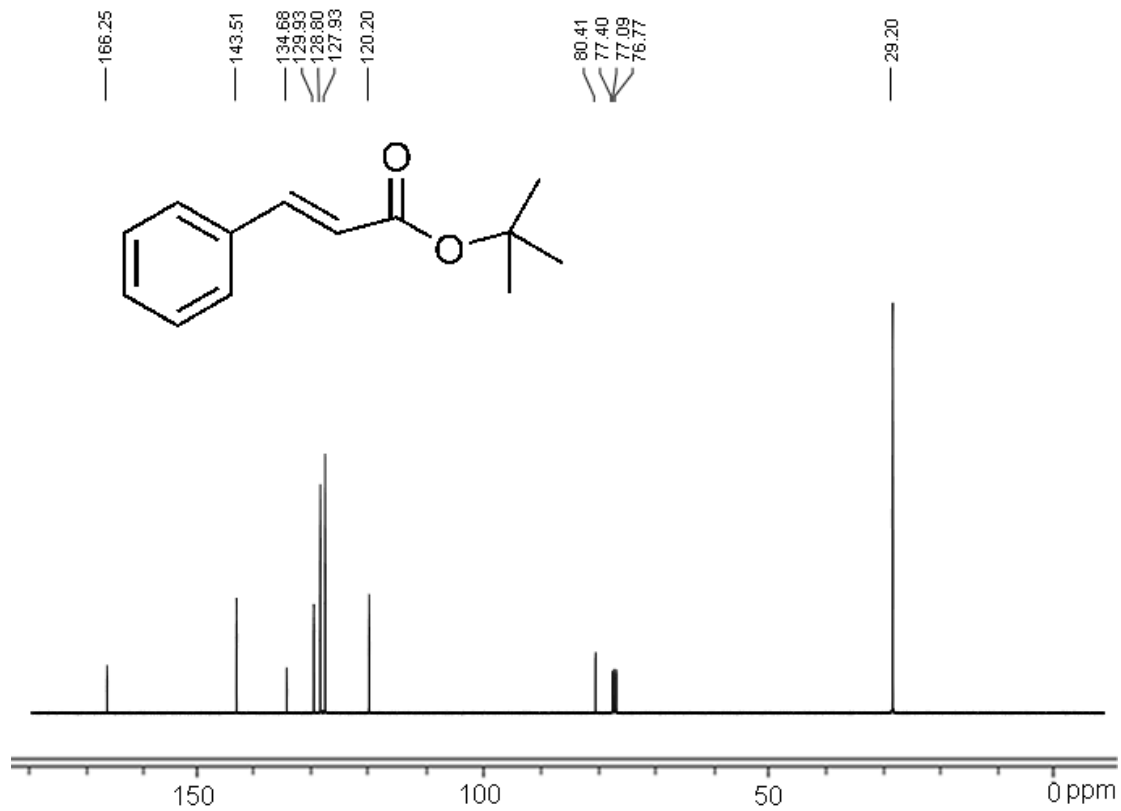
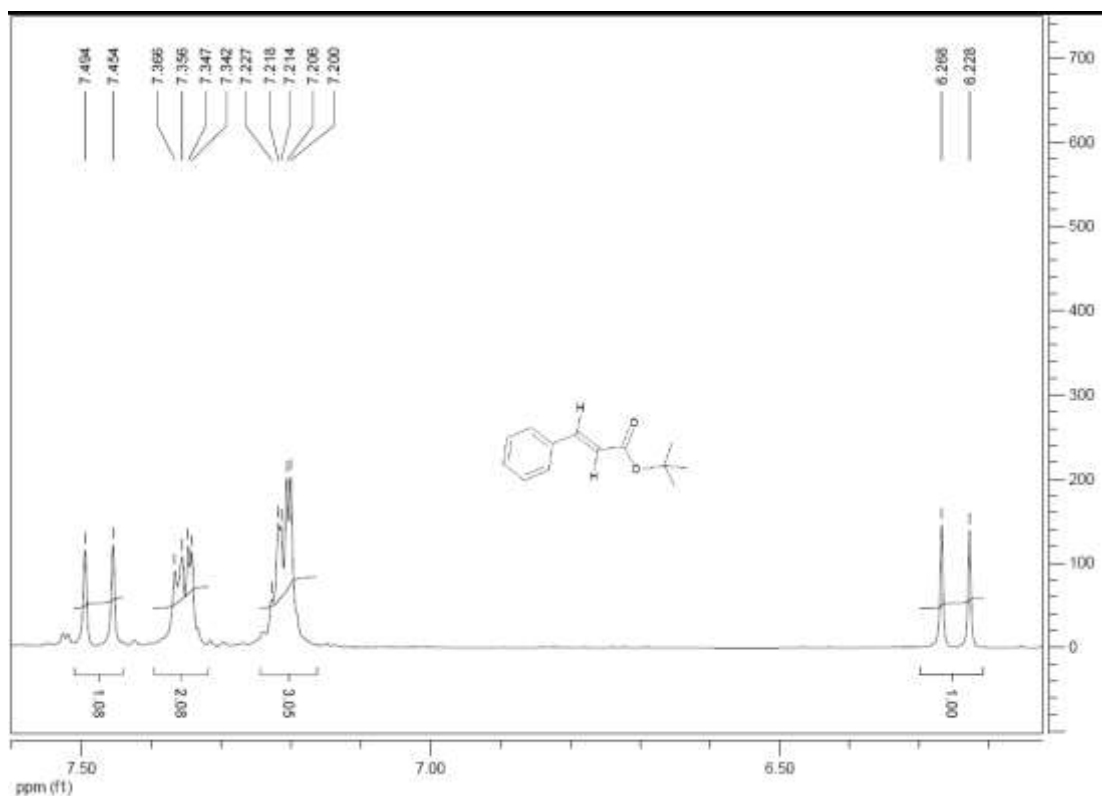


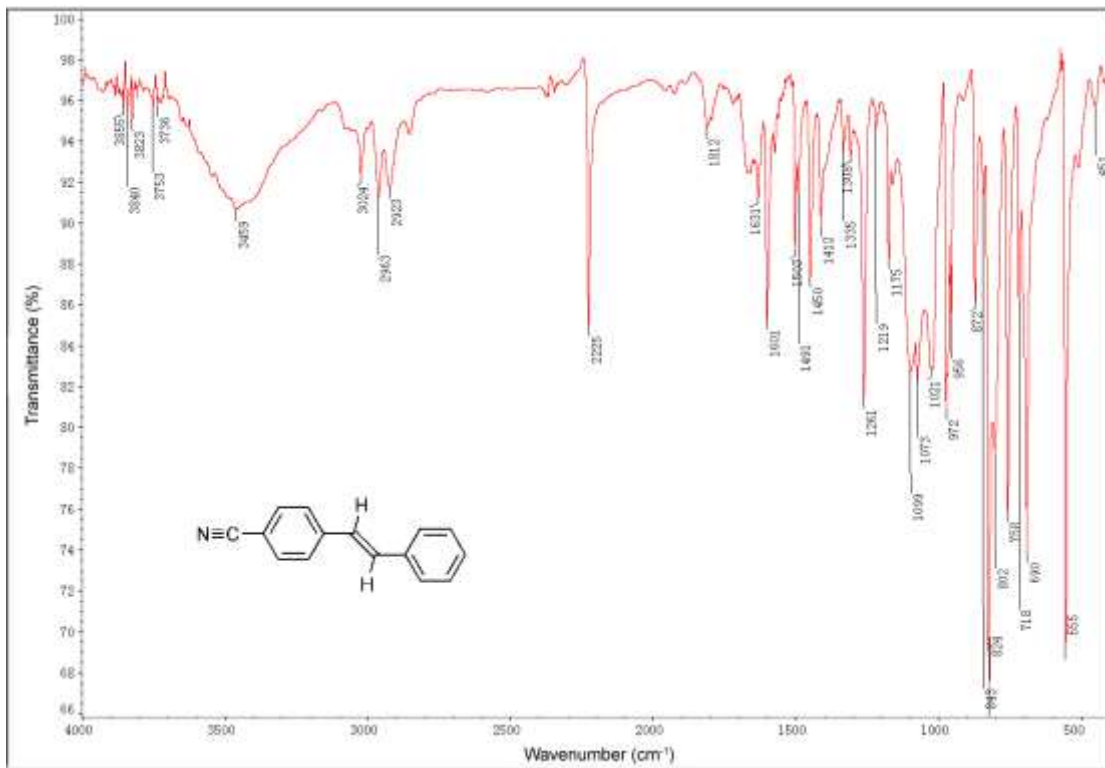
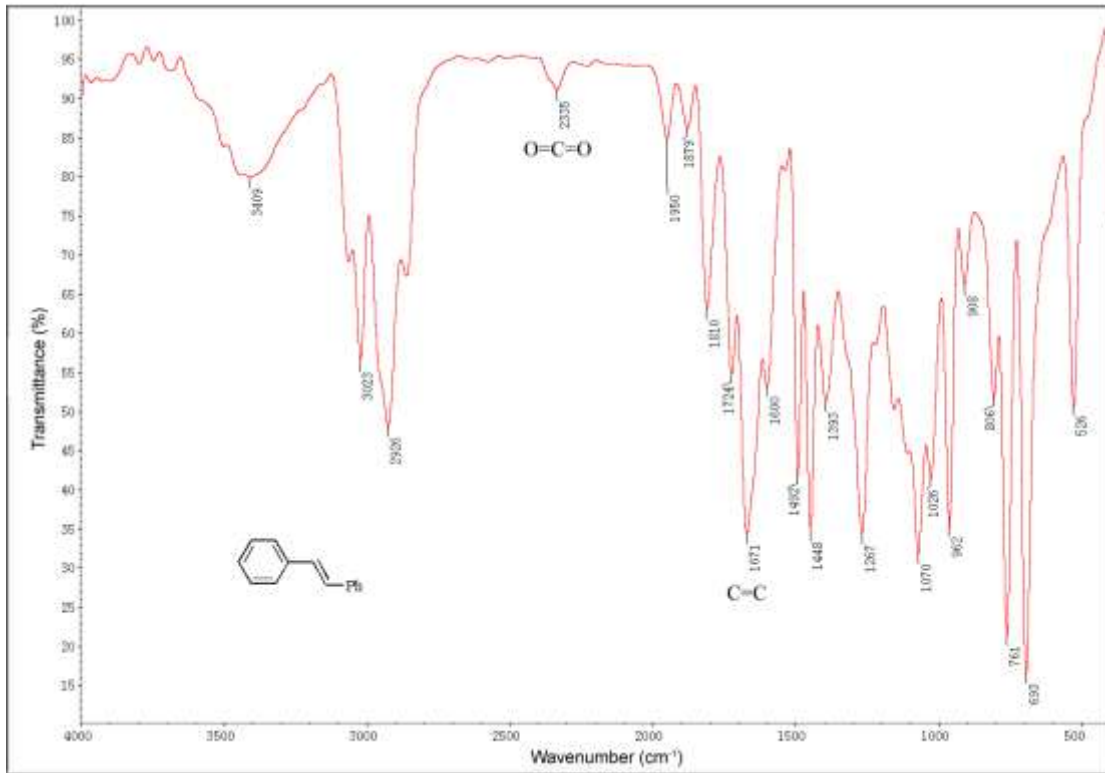


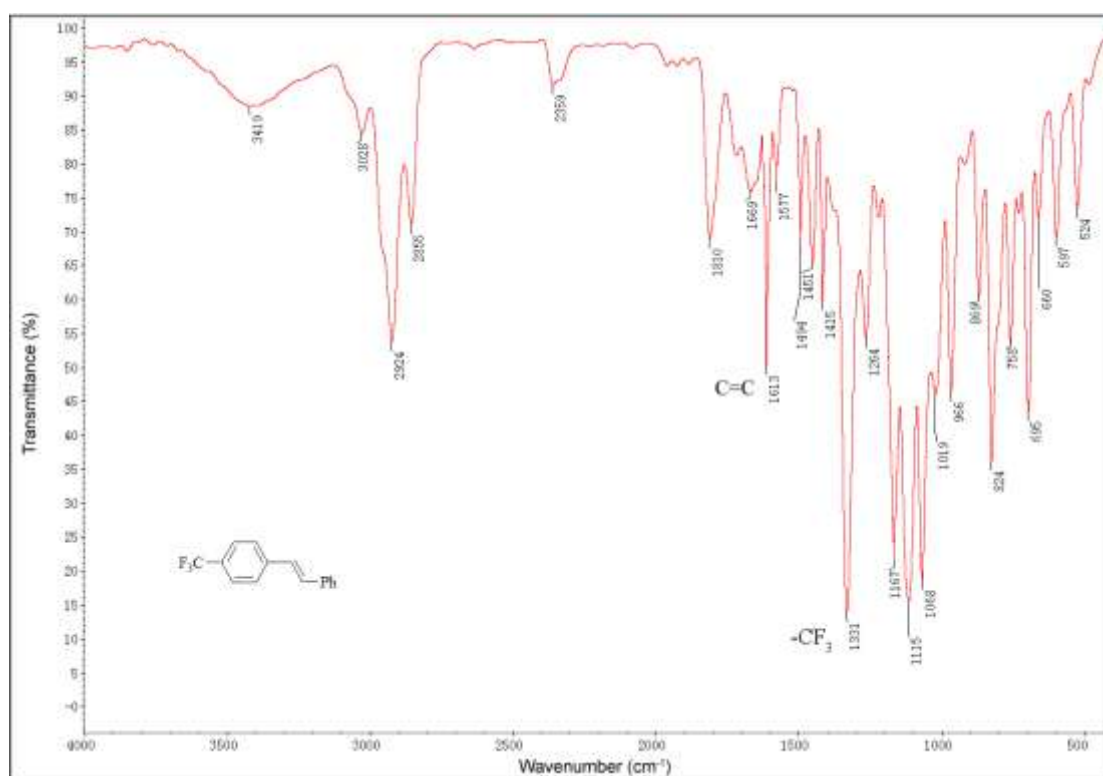
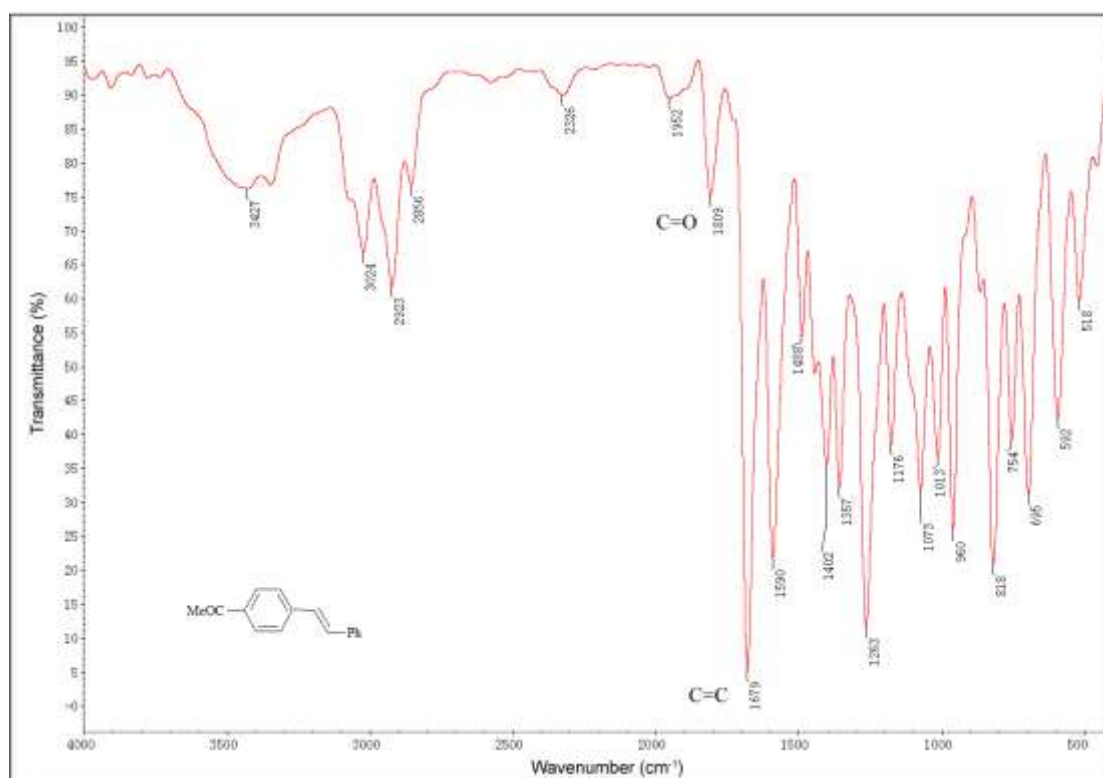


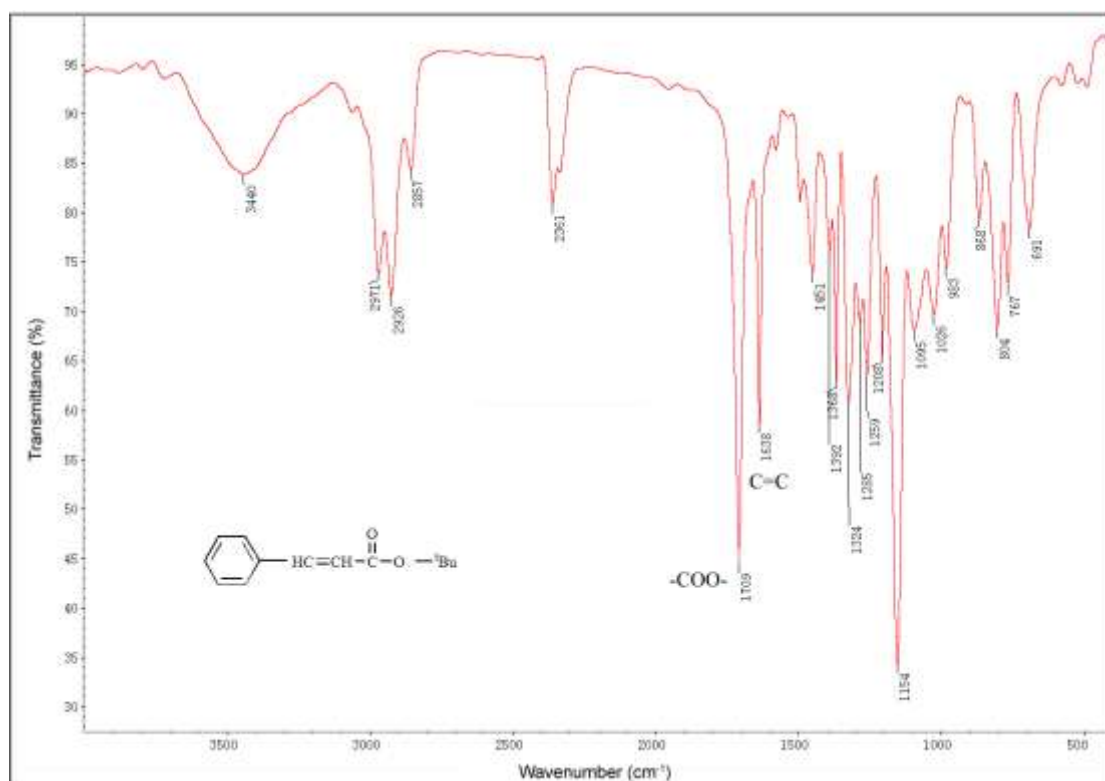
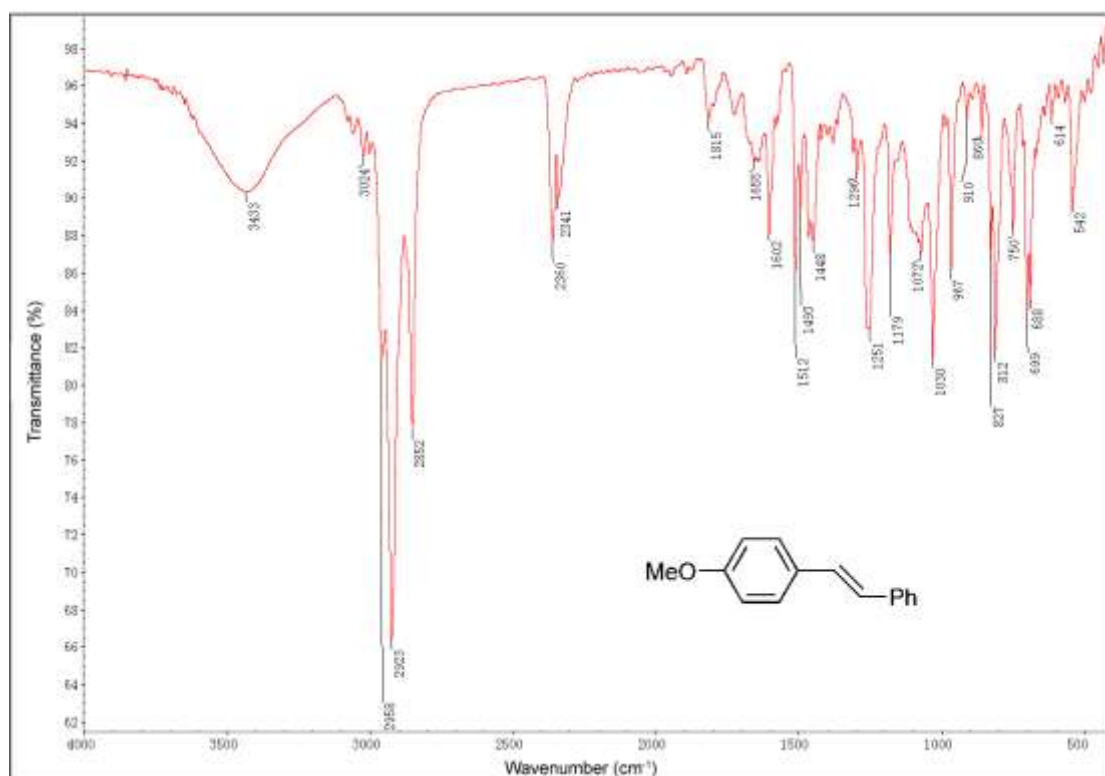












Sonogashira reaction

