

Supporting Information

Assembly of a Multilayer Film and Catalytic Application in Suzuki Cross-coupling Reaction Based on Synergistic Effect of a Conjugated Organometallic Pyridyl Pt(C≡C)₂ Moieties with Palladium

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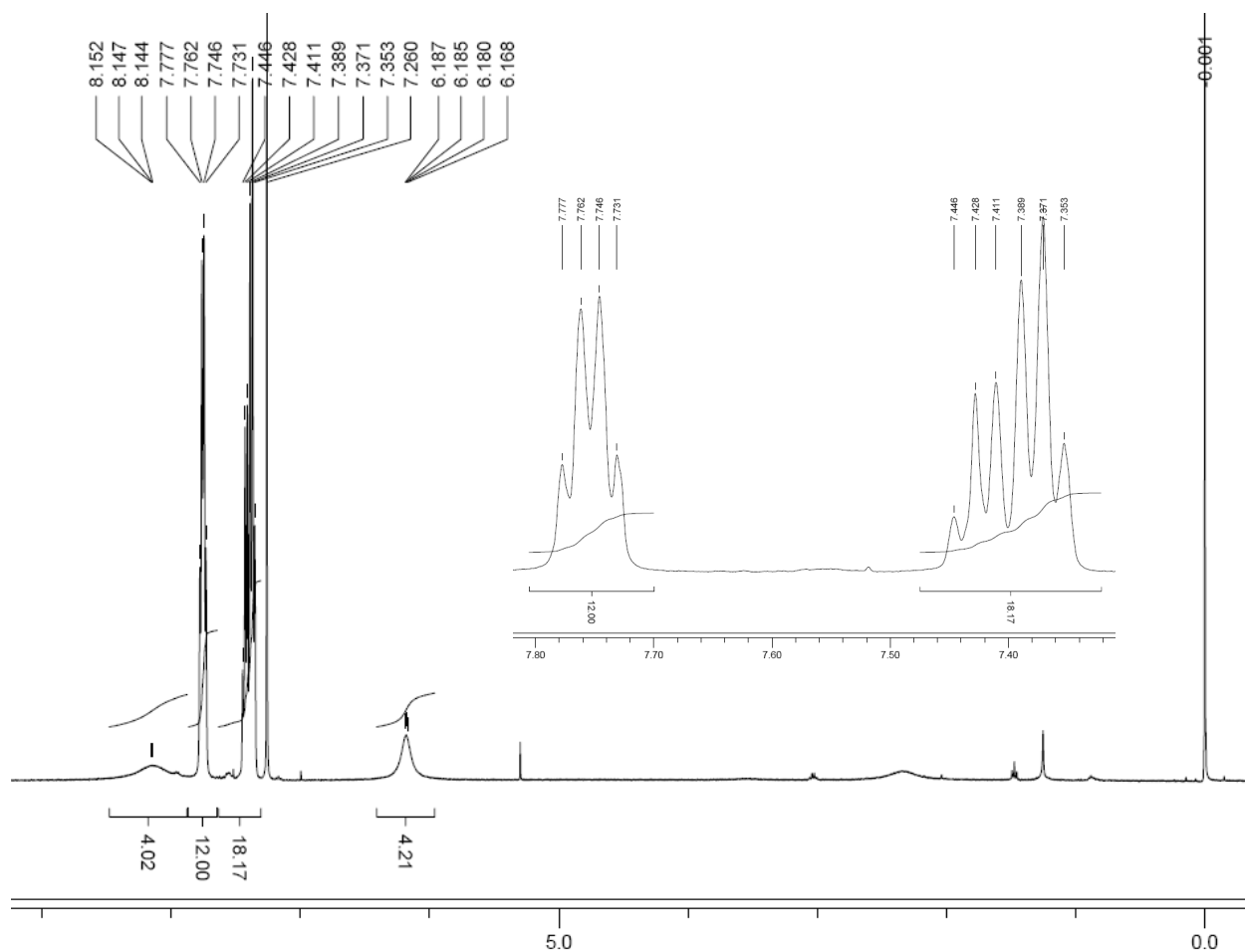


Fig. S1. ¹H NMR of compound 1.



Fig. S2. ^{31}P NMR of compound **1**.

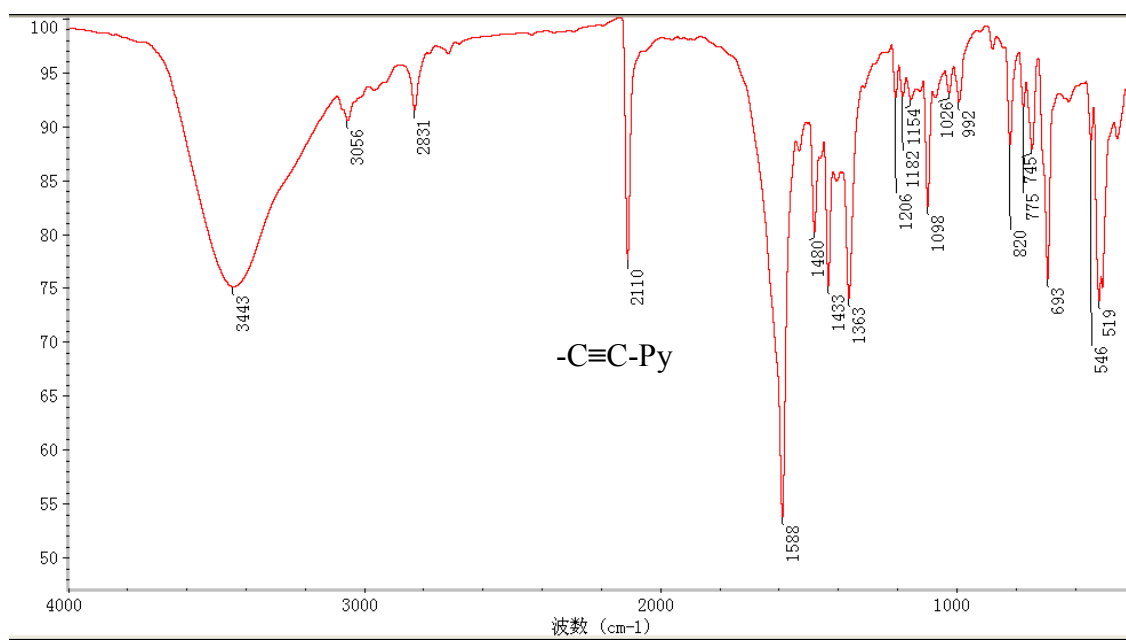


Fig. S3. IR spectrum for **1**.

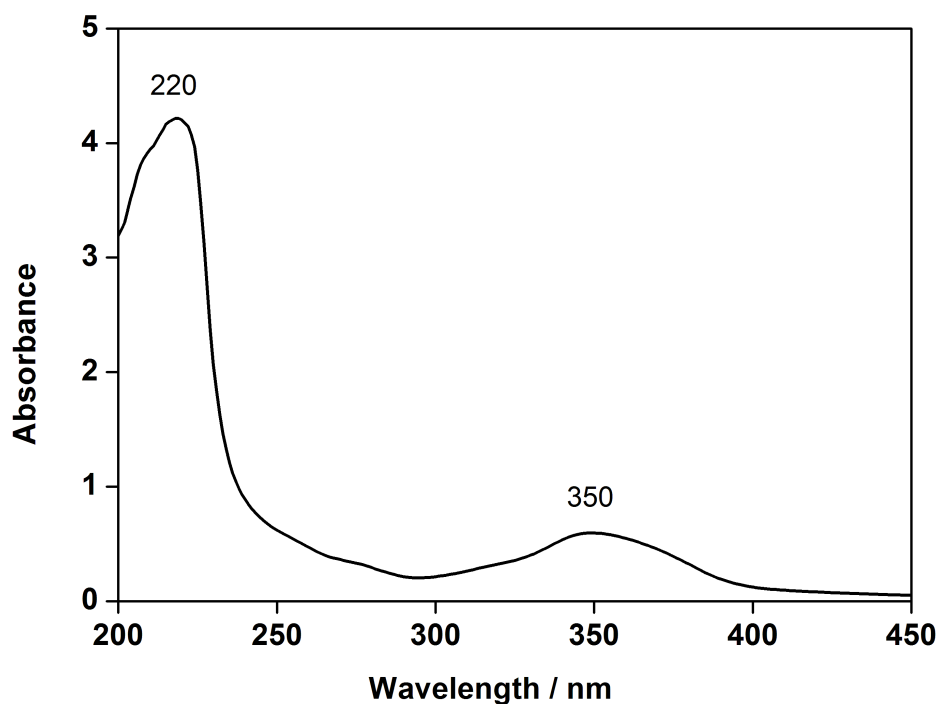


Fig. S4. UV-vis absorption spectrum of **1** at room temperature.

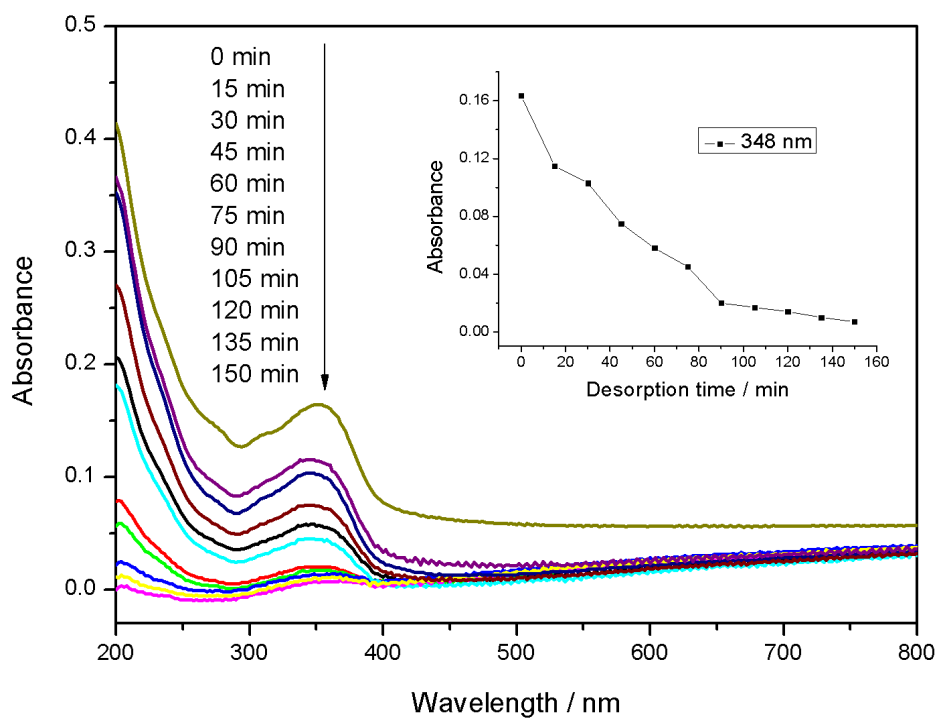


Fig. S5. UV-vis spectra of $(\text{PdCl}_2/\mathbf{1})_{10}$ multilayer at different desorption time. Inset: decrease in the absorbance at 348 nm as a function of the desorption time.

Desorption of Pd content from $\text{PEI}-(\text{Pd}^{2+}/\mathbf{1})_{10}$ multilayer film

In order to determine whether the catalyst was functioning in a homogeneous solution phase, we carried out the following tests: The quartz slide coated with $(\text{PdCl}_2/\mathbf{1})_{10}$ multilayers was immersed a mixed solution of K_2CO_3 , EtOH and H_2O for each interval

of 15 minutes, respectively, to study the release behavior of Pd-1 complex. UV-vis spectra were used to monitor the change of films (Fig. S5). A obvious decrease of the absorbance at 348 nm was observed for the first 15 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 be completely uniform, but close to be linear, which validated that $(\text{PdCl}_2/1)_{10}$ multilayer could release the Pd-1 species mostly in a layer-by-layer manner in each cycle step.

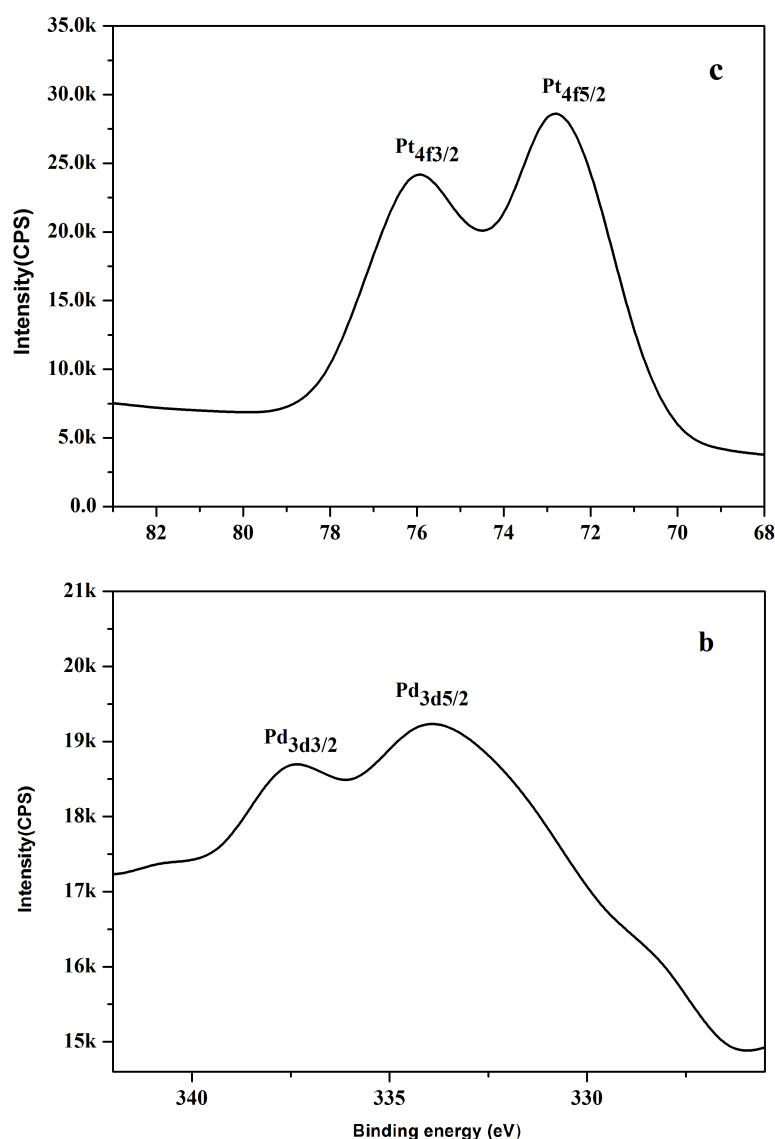


Fig. S6. XPS view of the films $(\text{PdCl}_2/1)_{10}$ deposited on the single crystal silicon substrates. (b) Pd_{3d}. (c) Pt_{4f}.

X-ray photoelectron spectroscopy (XPS) analysis

XPS measurements were carried out to identify the element composition of the

multilayer films deposited on the single crystal silicon substrates. As expected, the survey spectra of the multilayer film showed the existence of C_{1s} (284.6 eV), Cl_{2p} (200.3 eV), N_{1s} (398.8 eV), O_{1s} (531.9 eV), P_{2s} (189.1 eV), P_{2p} (133.5 eV), Pd_{3d} (334.5 eV), Pt_{4p} (519.6 eV), Pt_{4d} (315.8 eV), Pt_{5s} (102.4 eV), Pt_{4f} (74.5 eV), and Si_{2s} (152.7eV), which were consistent with characteristic peaks of the corresponding elements (Fig. 5a). The shoulders of the Pd_{3d} and Pt_{4d} peaks on the low binding energy region were ascribed to satellite peaks. Photoelectrons with energies of 337.4 eV (Pd_{3d3/2}), 333.8 eV (Pd_{3d5/2}), 75.9 eV (Pt_{4f3/2}) and 72.8 eV (Pt_{4f5/2}) were observed in the spectra (Fig. 5b and 5c), indicating the Pd(II) and Pt(II) oxidation state in the (Pd²⁺/1)_n multilayer. The 152.7eV peak (Si_{2s}) came from the silicon substrate.

Experimental section

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. NMR spectra were obtained from solutions in CDCl₃ using Bruker DRX-400 spectrometers. 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. 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). Height images of the films were recorded using tapping-mode AFM. Analysis of Pd content was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using Ultima.

Synthesis of *trans*-[Pt(C \equiv CPy)₂(PPh₃)₂] (**1**)

Trans-[Pt(PPh₃)₂Cl₂] (0.50g, 0.632 mmol) was suspended in dry DMF (5 mL), CH₂Cl₂ (10 mL) and NHEt₂ (10 mL), to which was added 4-ethynylpyridine·HCl (0.195g, 1.40 mmol) with stirring. CuI (12.50 mg, 0.065 mmol) as catalyst was added to the above solution and refluxed overnight, resulting in a pale grey precipitate. The solution color changed from white to red and dark-red. The solvent was removed and filtered and washed with water, hexane and Et₂O, and air dried to give a pale grey crude product (0.459 g, yield 78.6 %). Recrystallization from CH₂Cl₂ and Et₂O afforded colorless needle-like crystals. Anal. Calcd. (%) for C₅₀H₃₈N₂P₂Pt (Mr = 923.89): C, 65.00; H, 4.15; N, 3.03. Found: C, 64.20; H, 4.07; N, 3.03. ¹H NMR (CDCl₃): δ 6.18 (br., 4H, Py), 7.35 ~ 7.78 (m, 30H, PPh₃), 8.15 (br, 4H, Py). ³¹P NMR (CDCl₃): δ 18.73 (J_{Pt-P} = 2600 Hz, PPh₃). ES(+)-MS (m/z) = 924.2, [M + H]⁺. IR (Nujol): ν (C \equiv C) 2110 cm⁻¹.

X-ray crystallography

Data collection for **1** was performed on a Bruker-AXS diffractometer equipped with a graphite monochromated Mo-K α radiation (λ = 0.71073 Å) at 293K. All absorption corrections were applied using the SADABS program. The structure was solved by direct methods, the metal atom was located from the *E*-map, and other non-hydrogen atoms were derived from the successive difference Fourier Syntheses. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were generated geometrically and refined with isotropic thermal parameters. The structure was refined on *F*² by full-matrix least-squares using the SHELXTL-97 program package. The crystallographic data of **1** were listed in Table S1 and the selected bond lengths and angles in Table S2. Crystallographic data (excluding structure factors) for **1** have been deposited at the Cambridge Crystallographic Data Center as supplementary publications. CCDC-900608 for **1** contains the crystallographic data for this paper. The

data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; E-mail: deposit@ccdc.cam.ac.uk].

Table S1. Crystal Data and Structure Refinement for **1**.

Identification code	1
Empirical formula	C ₅₀ H ₃₈ N ₂ P ₂ Pt
Formula weight	923.85
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, <i>P2(1)/c</i>
<i>a</i> / Å	12.0599(12)
<i>b</i> / Å	22.474(2)
<i>c</i> / Å	7.8012(8)
α / °	90
β / °	101.5980(10)
γ / °	90
Volume / Å ³	2071.2(4)
<i>Z</i> , Calculated density / Å ³	2, 1.481
Absorption coefficient / mm ⁻¹	3.501
<i>F</i> (000)	920
Crystal size / mm	0.24 x 0.6 x 0.6
Theta range for data collection / °	1.72 to 27.52
Reflections collected / unique	17791 / 4744 [<i>R</i> (int) = 0.0387]
Completeness to theta = 27.52°	99.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	4744 / 2 / 250
Goodness-of-fit on <i>F</i> ²	1.177
Final <i>R</i> indices [<i>I</i> > 2sigma(<i>I</i>)]	<i>R</i> 1 = 0.0276, <i>wR</i> 2 = 0.0717
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0354, <i>wR</i> 2 = 0.0755
Largest diff. peak and hole	0.519 and -1.017 eÅ ⁻³

Table S2. All bond lengths (Å) and angles (°) for complex **1**.

Pt(1)-C(19)#1	1.999(7)	C(8)-C(9)	1.406(12)
Pt(1)-C(19)	1.999(8)	C(9)-C(10)	1.366(15)
Pt(1)-P(1)	2.3165(17)	C(10)-C(11)	1.390(19)
Pt(1)-P(1)#1	2.3165(17)	C(11)-C(12)	1.395(14)
P(1)-C(1)	1.822(8)	C(13)-C(14)	1.390(11)
P(1)-C(13)	1.825(8)	C(13)-C(18)	1.391(11)
P(1)-C(7)	1.827(7)	C(14)-C(15)	1.384(12)
N(1)-C(23)	1.30(2)	C(15)-C(16)	1.385(15)
N(1)-C(25)	1.32(2)	C(16)-C(17)	1.374(15)
C(1)-C(6)	1.390(11)	C(17)-C(18)	1.387(12)
C(1)-C(2)	1.391(11)	C(19)-C(20)	1.195(11)
C(2)-C(3)	1.390(11)	C(20)-C(21)	1.434(12)
C(3)-C(4)	1.368(13)	C(21)-C(24)	1.373(14)
C(4)-C(5)	1.406(14)	C(21)-C(22)	1.401(14)
C(5)-C(6)	1.346(12)	C(22)-C(23)	1.366(16)
C(7)-C(12)	1.386(11)	C(24)-C(25)	1.405(19)
C(7)-C(8)	1.406(12)		
C(19)#1-Pt(1)-C(19)	180.0(7)	N(1)-C(23)-C(22)	124.6(14)
C(19)#1-Pt(1)-P(1)	91.6(2)	C(12)-C(7)-P(1)	122.3(6)
C(19)-Pt(1)-P(1)	88.4(2)	C(8)-C(7)-P(1)	118.0(6)
C(19)#1-Pt(1)-P(1)#1	88.4(2)	C(7)-C(8)-C(9)	118.5(9)
C(19)-Pt(1)-P(1)#1	91.6(2)	C(10)-C(9)-C(8)	121.4(10)
P(1)-Pt(1)-P(1)#1	180.00(8)	C(9)-C(10)-C(11)	119.8(9)
C(1)-P(1)-C(13)	105.4(4)	C(10)-C(11)-C(12)	120.0(11)
C(1)-P(1)-C(7)	104.3(3)	C(7)-C(12)-C(11)	120.3(9)
C(13)-P(1)-C(7)	104.2(3)	C(14)-C(13)-C(18)	119.1(8)
C(1)-P(1)-Pt(1)	111.1(2)	C(14)-C(13)-P(1)	122.5(6)
C(13)-P(1)-Pt(1)	113.3(2)	C(18)-C(13)-P(1)	118.4(6)
C(7)-P(1)-Pt(1)	117.4(2)	C(15)-C(14)-C(13)	120.2(9)
C(23)-N(1)-C(25)	116.7(12)	C(14)-C(15)-C(16)	120.0(9)
C(6)-C(1)-C(2)	119.5(7)	C(17)-C(16)-C(15)	120.3(9)
C(6)-C(1)-P(1)	121.1(6)	C(16)-C(17)-C(18)	119.7(9)
C(2)-C(1)-P(1)	119.4(6)	C(17)-C(18)-C(13)	120.6(9)
C(3)-C(2)-C(1)	119.9(8)	C(20)-C(19)-Pt(1)	177.5(8)
C(4)-C(3)-C(2)	120.2(8)	C(19)-C(20)-C(21)	174.5(10)
C(3)-C(4)-C(5)	119.2(8)	C(24)-C(21)-C(22)	116.5(9)
C(6)-C(5)-C(4)	121.0(9)	C(24)-C(21)-C(20)	123.2(10)
C(5)-C(6)-C(1)	120.2(8)	C(22)-C(21)-C(20)	120.2(9)
C(12)-C(7)-C(8)	119.8(7)	C(23)-C(22)-C(21)	119.6(12)
N(1)-C(25)-C(24)	124.2(14)	C(21)-C(24)-C(25)	118.3(13)

Symmetry codes: #1 -x+1, -y, -z+2.

Layer-by-Layer assembly of multilayer films

The quartz sheets were cleaned with a mixture solution (H_2SO_4 / 30 % H_2O_2 = 7:3; Caution: this solution is an extremely dangerous oxidizing agent and should be handled with care using appropriate personal protection), and thoroughly rinsed with distilled water. Further purification was carried out by immersion in a H_2O / H_2O_2 / NH_4OH (5:1:1) (V/V) bath for 30 min at 70 °C. The clean quartz sheets were first immersed in PEI solution for 10 min. Then the sheets were deposited into PdCl_2 solution (5.0 mmol / L) for 30 min. The sheets coated with PEI-Pd^{2+} were immersed in compound *trans*- $\text{Pt}(\text{C}\equiv\text{CPy})_2(\text{PPh}_3)_2$ ethanol aqueous solution for 30 min. By repeating the two steps, $\text{PEI-(Pd}^{2+}/[\text{Pt}(\text{C}\equiv\text{CPy})_2(\text{PPh}_3)_2])_n$ films were prepared. Between each immersion step, the substrates were washed with water and dried with nitrogen stream at room temperature.

Analysis of Pd content in $\text{PEI-(Pd}^{2+}/\mathbf{1})_{10}$ multilayer films

The quartz slide coated with $\text{PEI-(Pd}^{2+}/\mathbf{1})_{10}$ 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 $\text{PEI-(Pd}^{2+}/\mathbf{1})_{10}$ multilayer film was completely desorbed into the aqueous solution, which was used for analysis of Pd content. The amount of Pd was determined as 0.28 ppm (ICP) in the solution. In other words, the amount of Pd in $\text{PEI-(Pd}^{2+}/\mathbf{1})_{10}$ multilayer film is 7.0 μg (6.6×10^{-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 $\text{PEI-(Pd}^{2+}/\mathbf{1})_{10}$ film is 6.6×10^{-6} mol%.

Suzuki reaction procedure of the films as catalysts

In the typical Suzuki reaction, the 15 mL vessels were loaded with aryl halide (1.0 mmol), arylboronic acid (1.05 mmol), K_2CO_3 (3.0 mmol), and the catalyst of

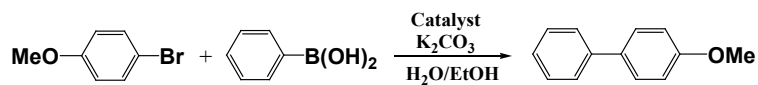
(Pd²⁺/1)₁₀ films loaded quartz slides (size 25 × 12 × 1 mm) in H₂O-EtOH solution of 7 mL (4:3, V/V). The reaction mixtures were heated to 50 or 100 °C for different reactions under ambient atmosphere. The reaction mixtures were cooled to room temperature, the aqueous phases were separated and extracted with EtOAc (10 mL) for three time. The combined organic phases were washed with saturated brine, dried over anhydrous Na₂SO₄. After removal of the solvent, the residues were purified by column chromatography on silica gel using ethyl acetate and petroleum ether mixture to afford the purity product. ¹H NMR (400 MHz) spectra were recorded in CDCl₃ solution.

Table S3. Suzuki Cross-coupling Reactions of Aryl Halides with Arylboronic Acids Using (PdCl₂/1)₁₀ Films as Catalysts.

Entry	R ₁ -Ar-X	R ₂ -Ar-B(OH) ₂	Time, hour	Product	Yield(%)
1			50°C, 4h		98
2			50°C, 4h		99
3			50°C, 4h		98
4			50°C, 4h		95
5			50°C, 4h		38
6			100°C, 24h		86
7			50°C, 4h		92
8			50°C, 4h		95
9			50°C, 4h		91

General procedure: 1.0 mmol of aryl halide, 1.05 mmol of arylboronic acid, 3.0 mmol of K₂CO₃, in H₂O / EtOH (4:3, V/V) under ambient atmosphere. TON = mol product / mol Pd.

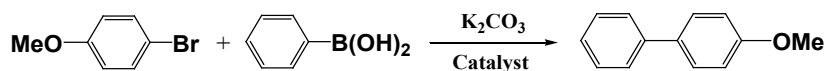
Table S4. Suzuki cross-coupling of 4-methoxyaryl bromide with phenylboronic acid using **1**, PdCl₂, PdCl₂/**1** precipitate, PEI-(PdCl₂/**1**)₁₀ film and (PdCl₂/bpy)₁₀ film as catalyst (bpy = 4,4'-bipyridine).



Entry	Run	Catalysts	Yield
1	5 th	(PdCl ₂ / 1) _{10-x} film	68 %
2	6 th	(PdCl ₂ / 1) _{10-x} film	35 %
3	7 th	(PdCl ₂ / 1) _{10-x} film	23 %
4	8 th	(PdCl ₂ / 1) _{10-x} film	<8 %

^a General procedure: 1.0 mmol of PhBr, 1.05 mmol of PhB(OH)₂, 3.0 mmol of K₂CO₃, in H₂O/EtOH (4:3) at 50 °C under ambient atmosphere for 10 h. ^b Catalyst 3.0 mol%.

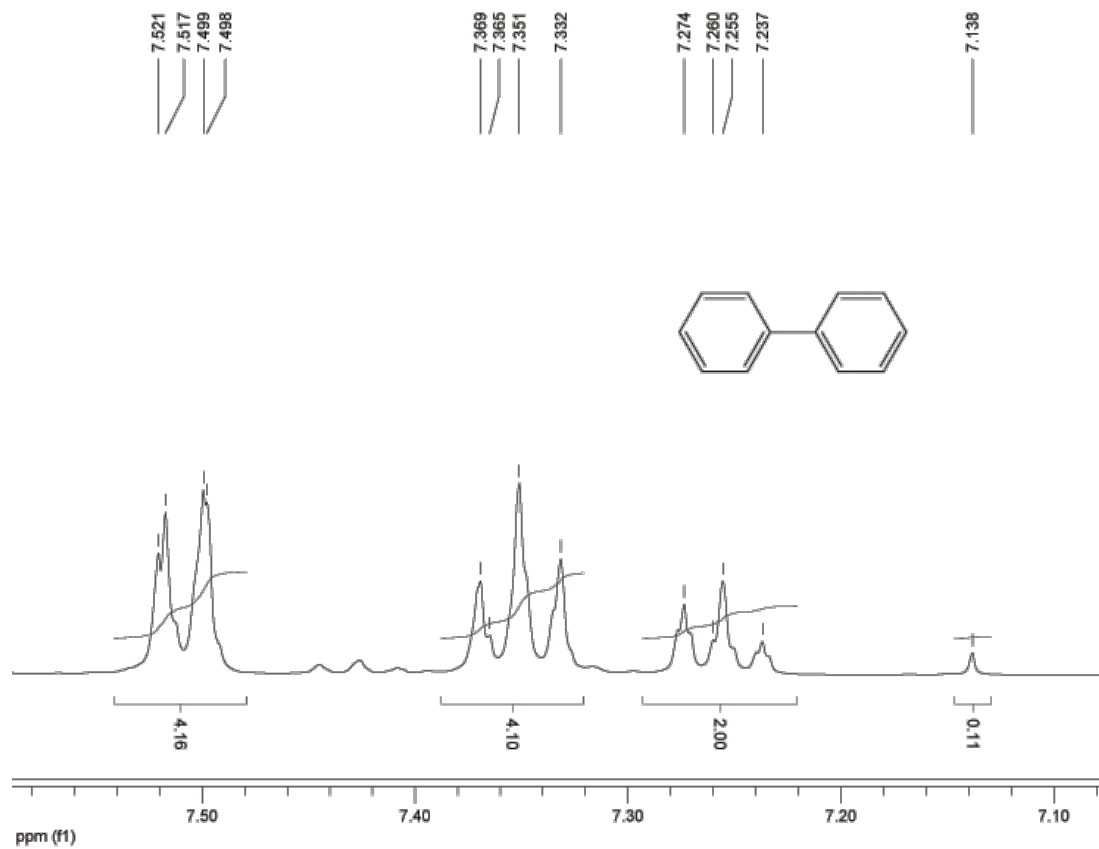
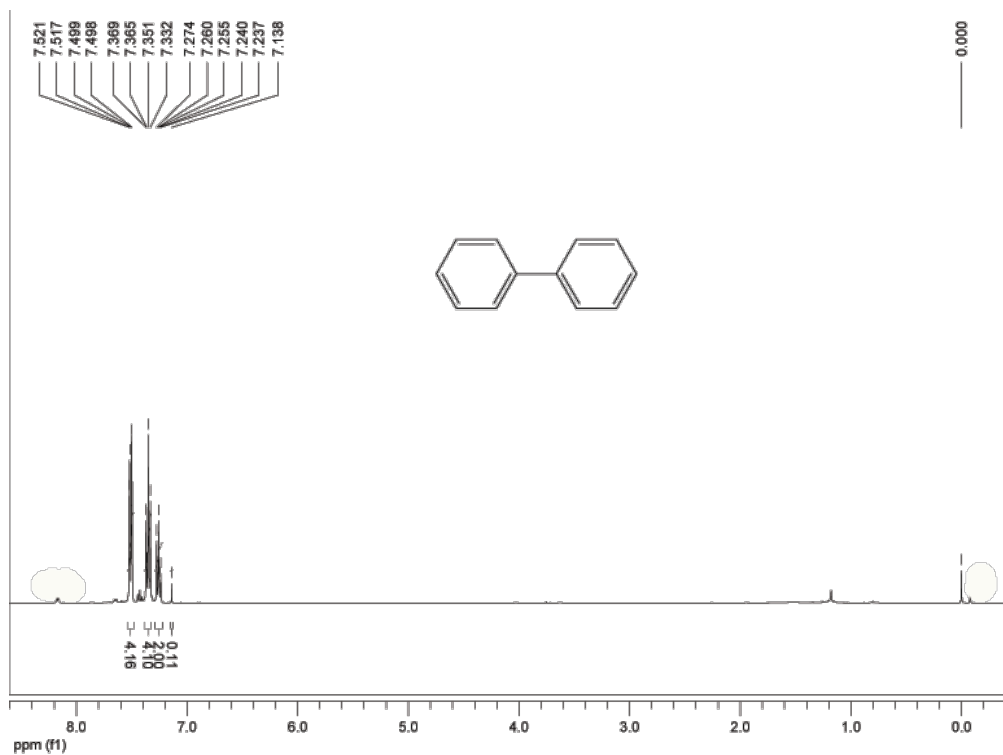
Table S5. Suzuki cross-coupling of 4-methoxyaryl bromide and phenylboronic acid in the solvents of Dimethylformamide (DMF) or 1,2-dimethoxyethane (DME) using (PdCl₂/**1**)₁₀ film as catalyst.

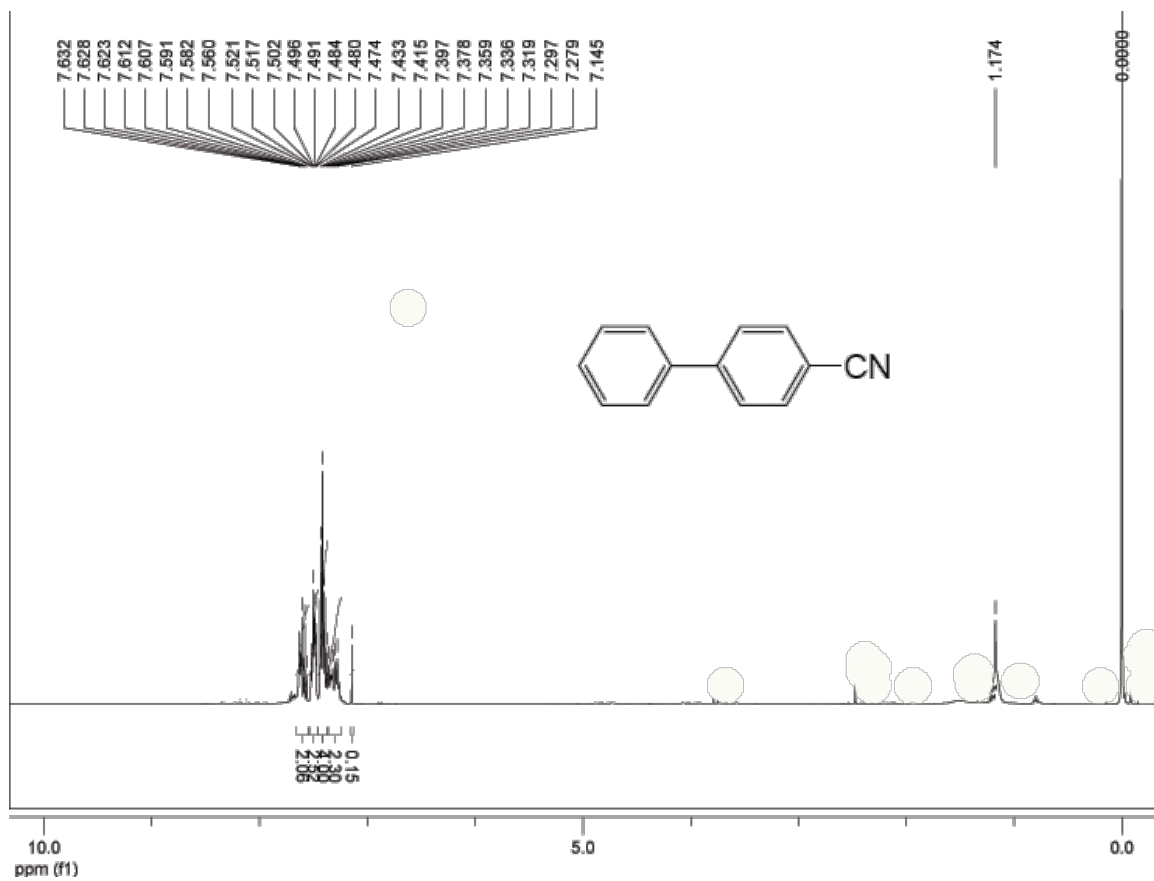
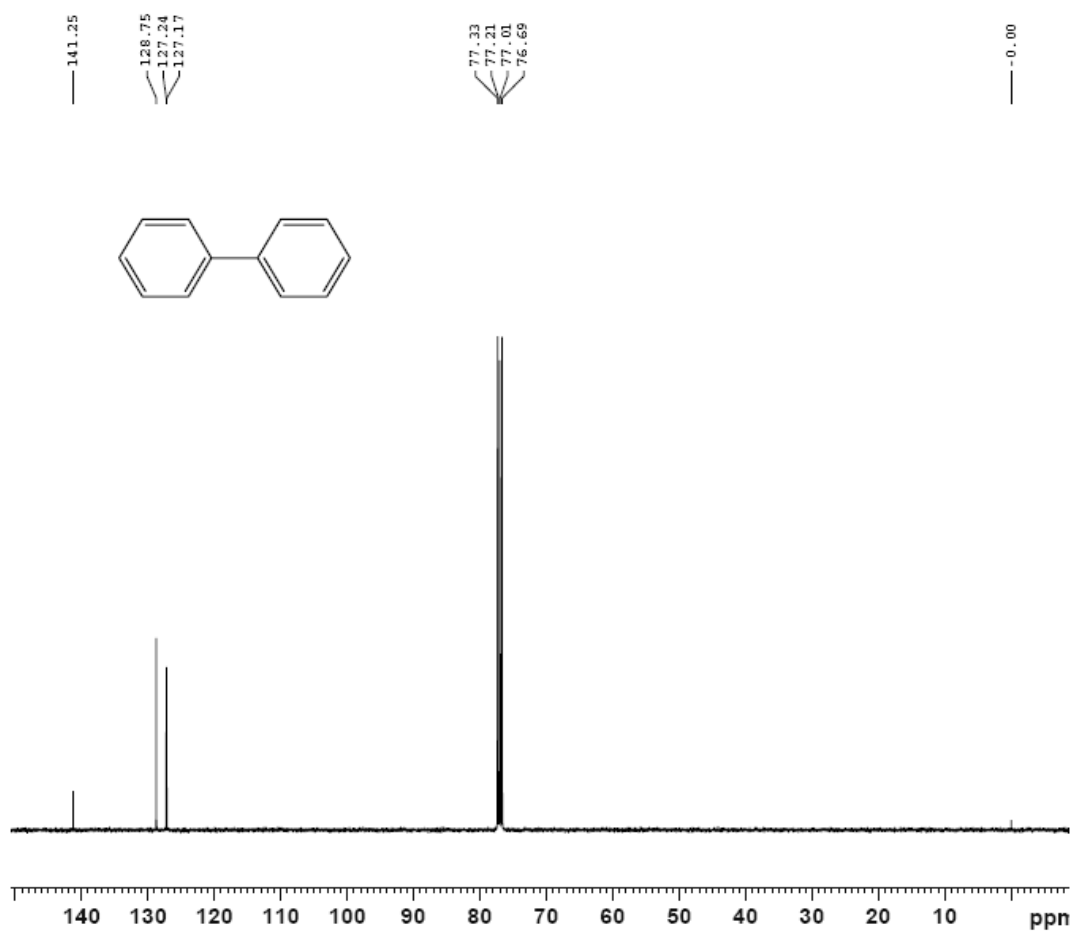


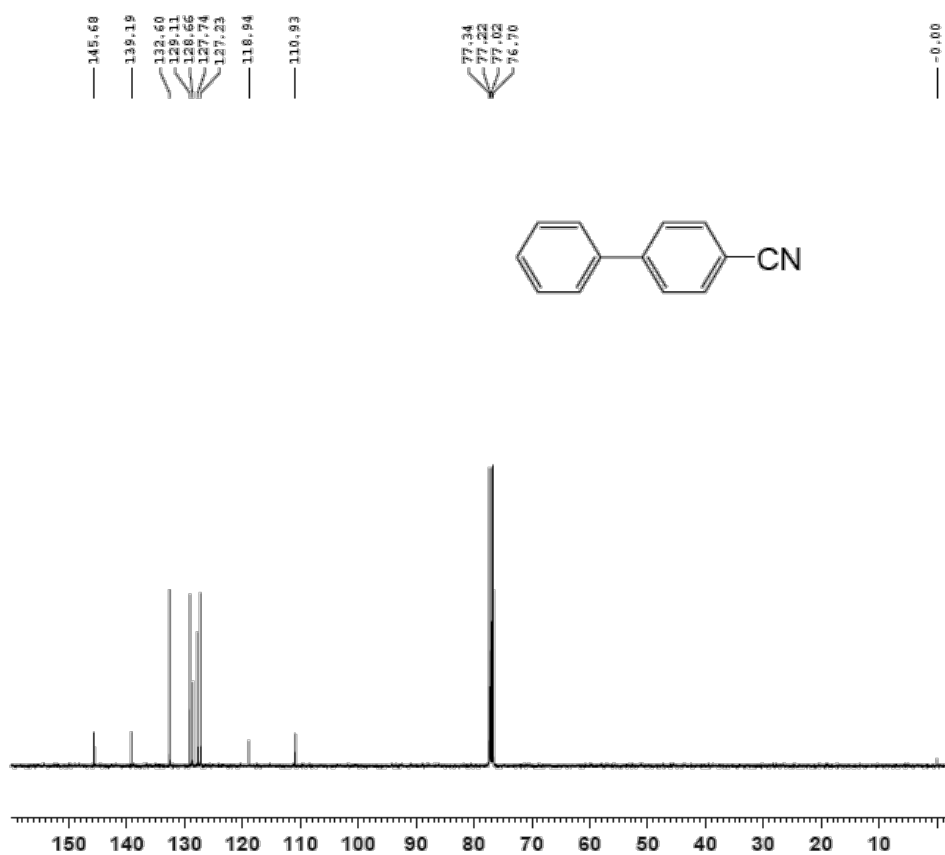
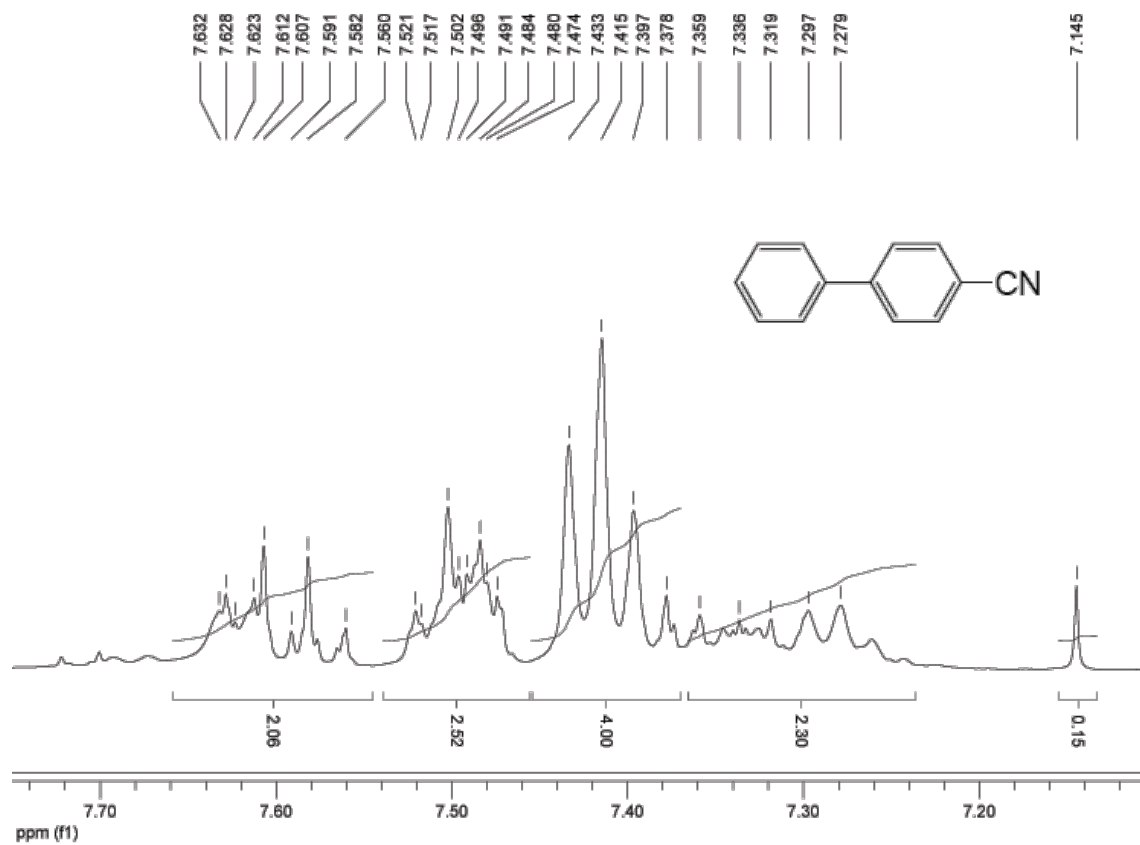
Entry	Catalysts	Solvents	Yield
1	(PdCl ₂ / 1) ₁₀ film	DMF	72 %
2	(PdCl ₂ / 1) ₁₀ film	DME	69 %

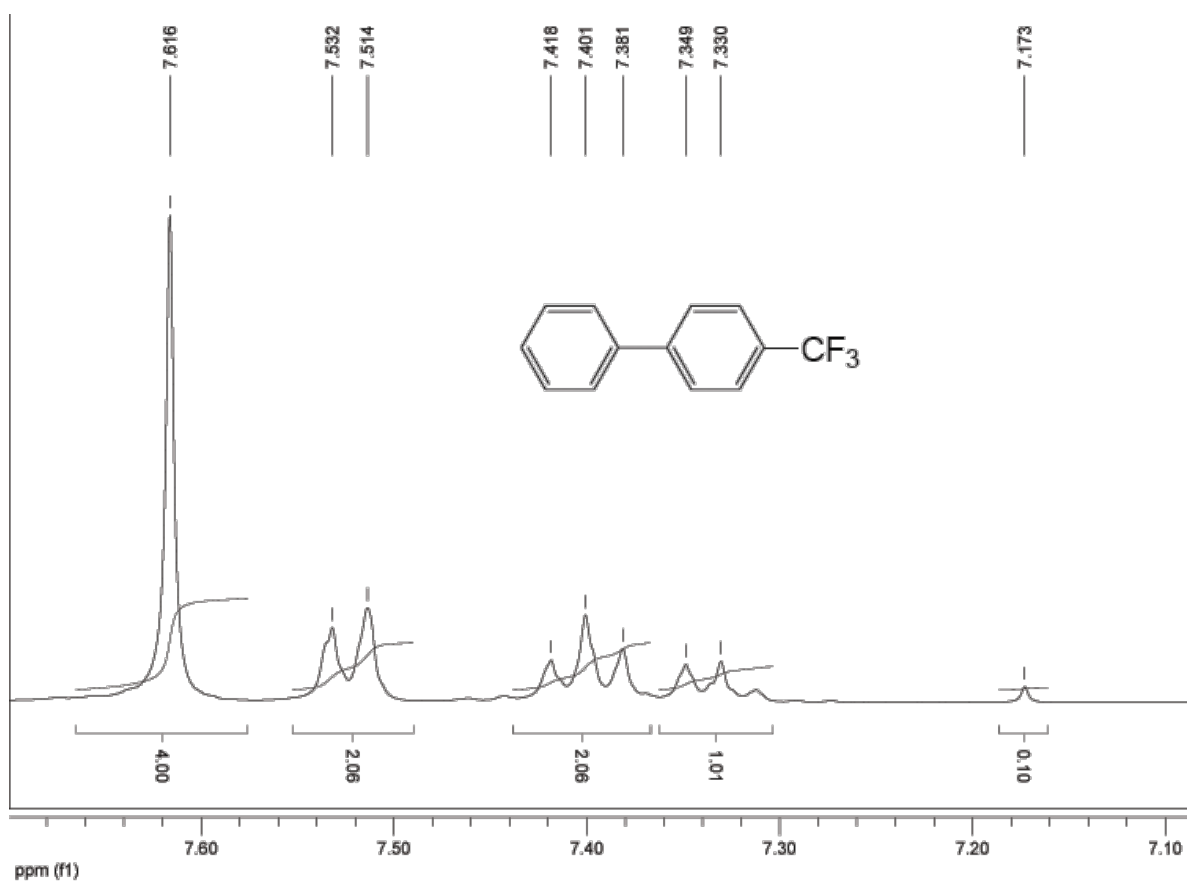
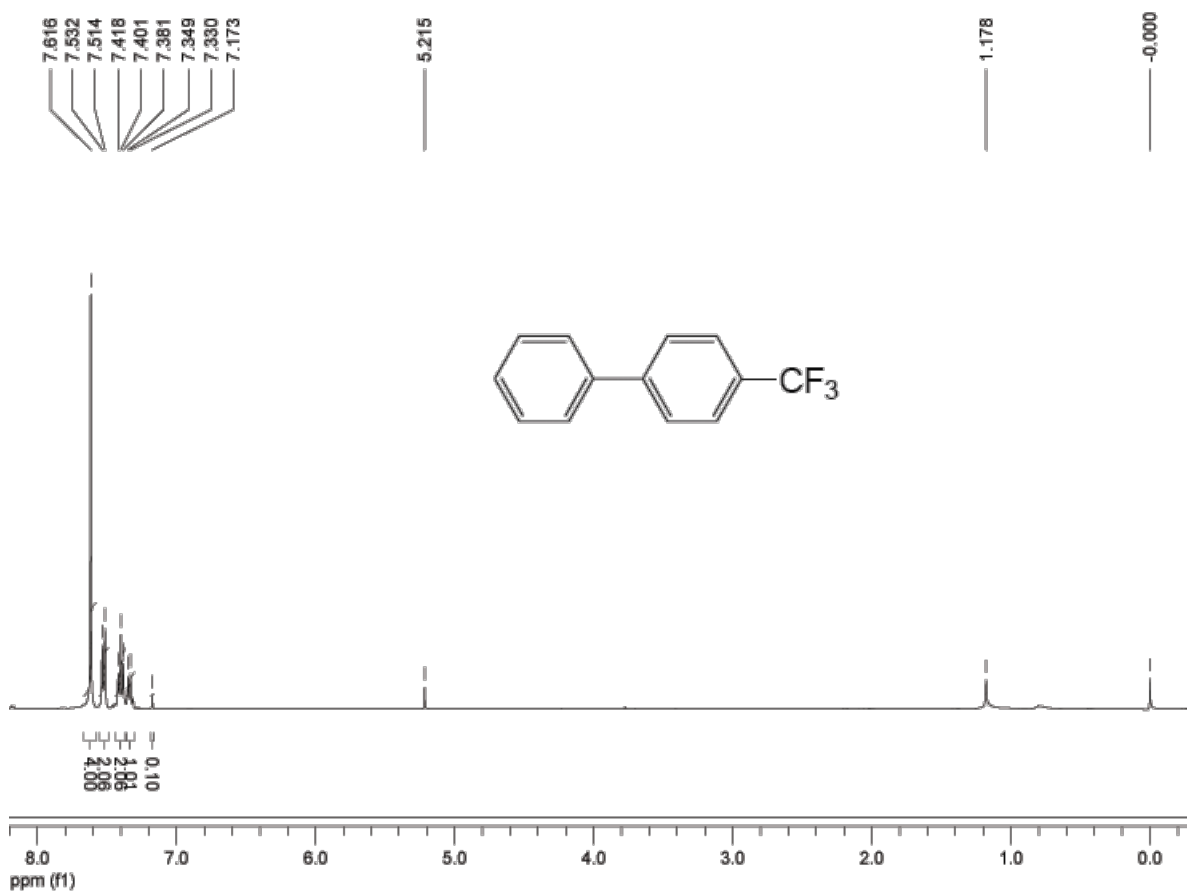
General procedure: 1.0 mmol of PhBr, 1.05 mmol of PhB(OH)₂, 3.0 mmol of K₂CO₃, at 50 °C under ambient atmosphere for 10 h.

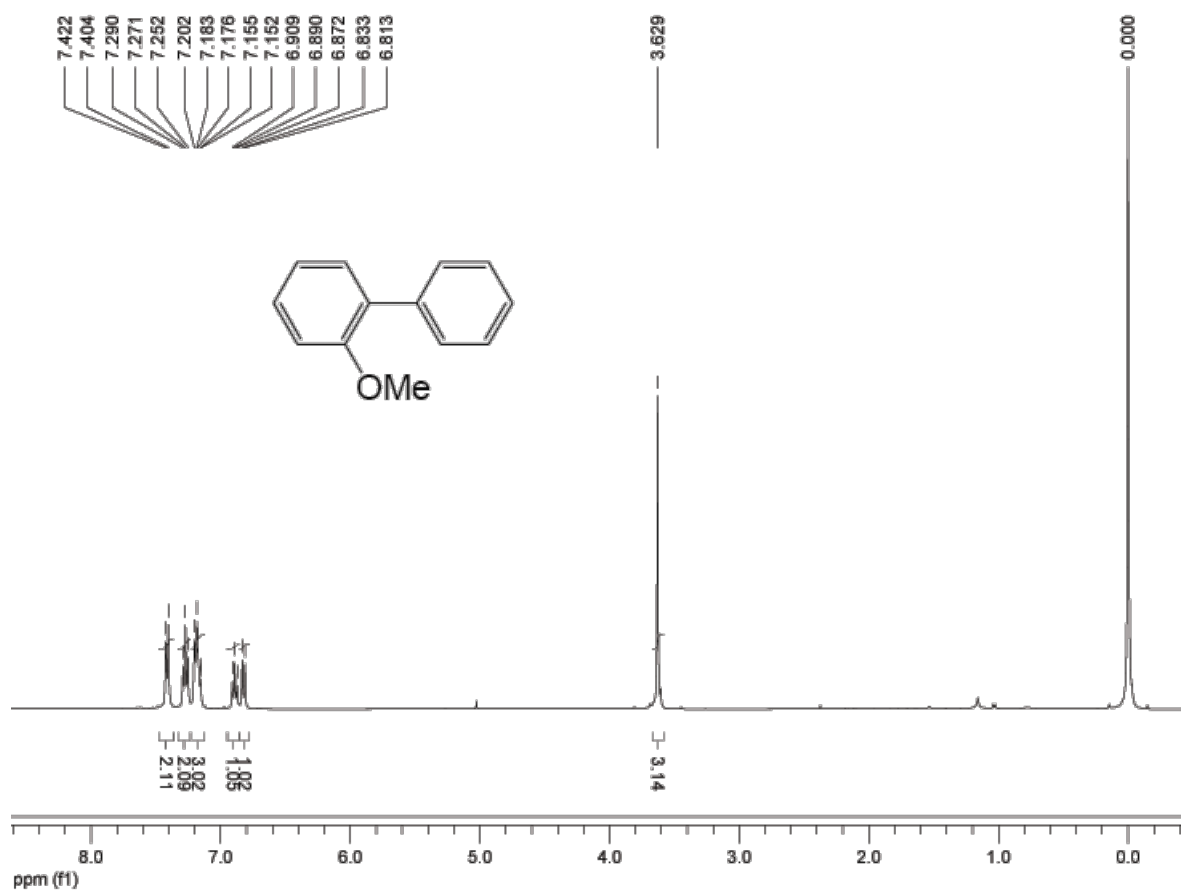
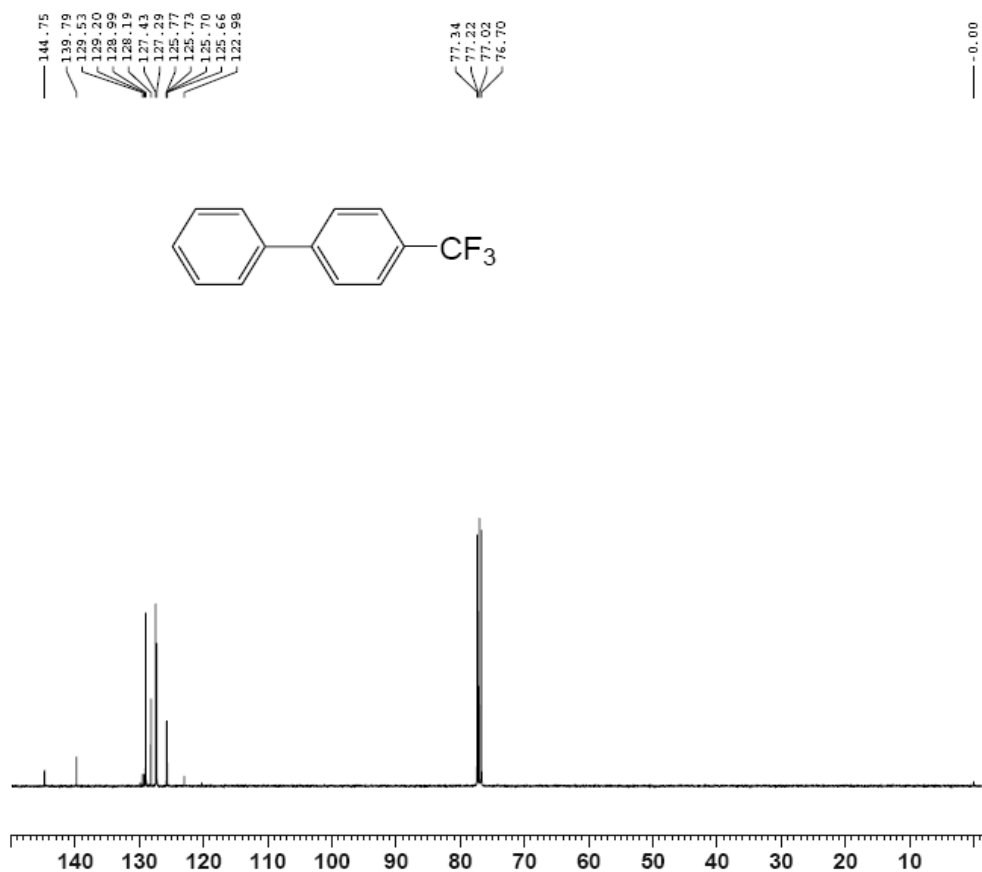
^1H NMR and ^{13}C NMR Spectra of the products

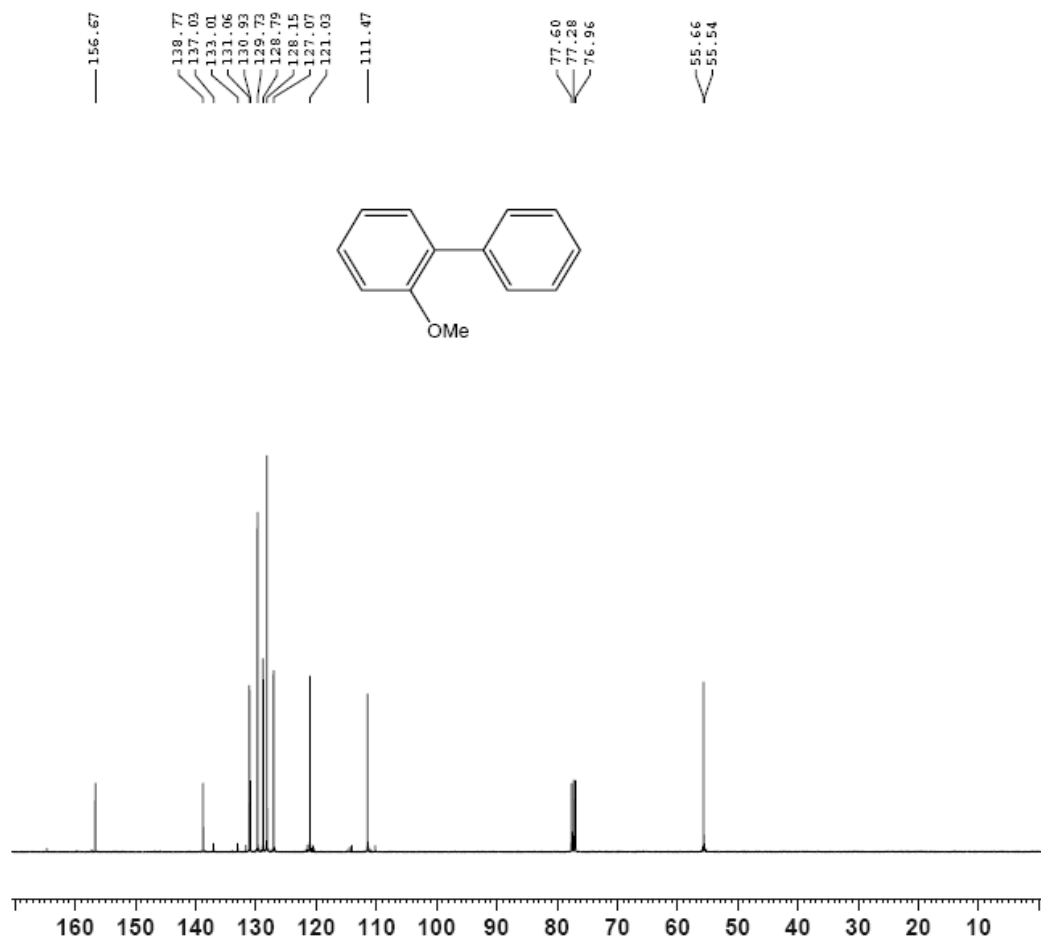
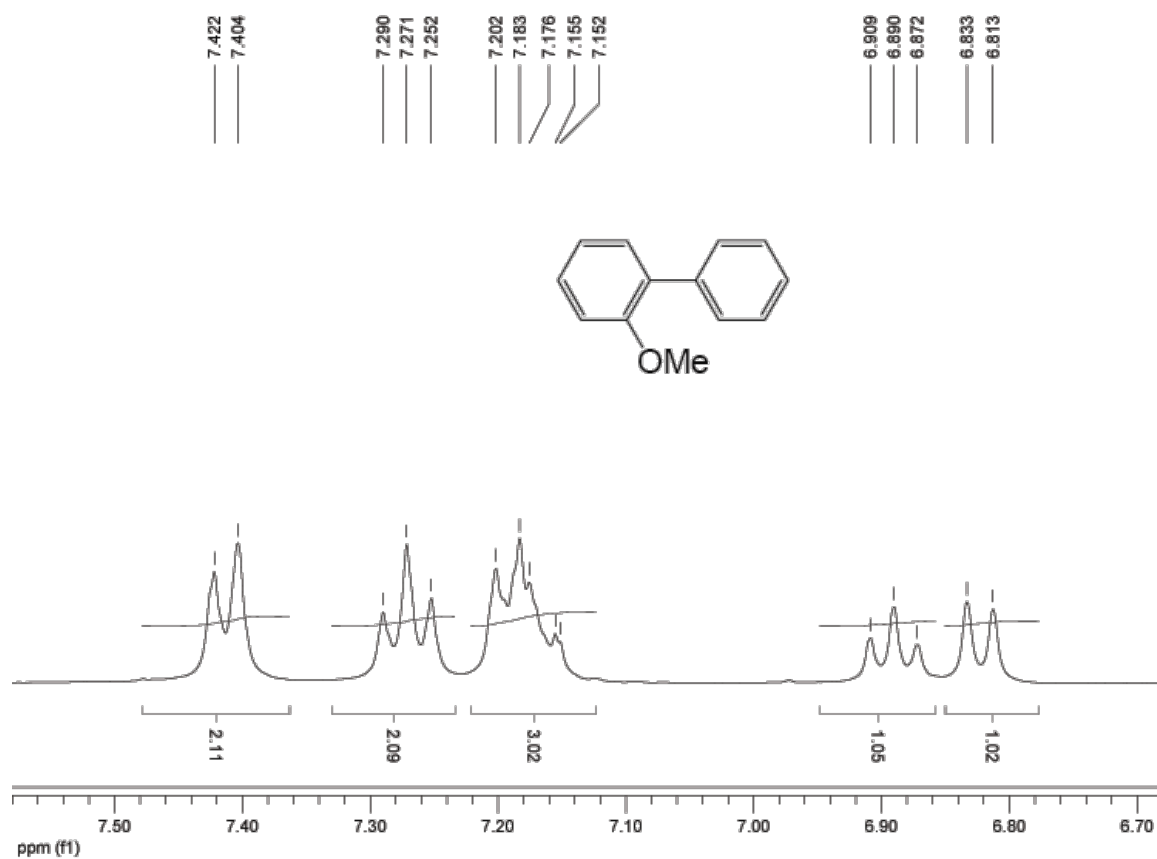


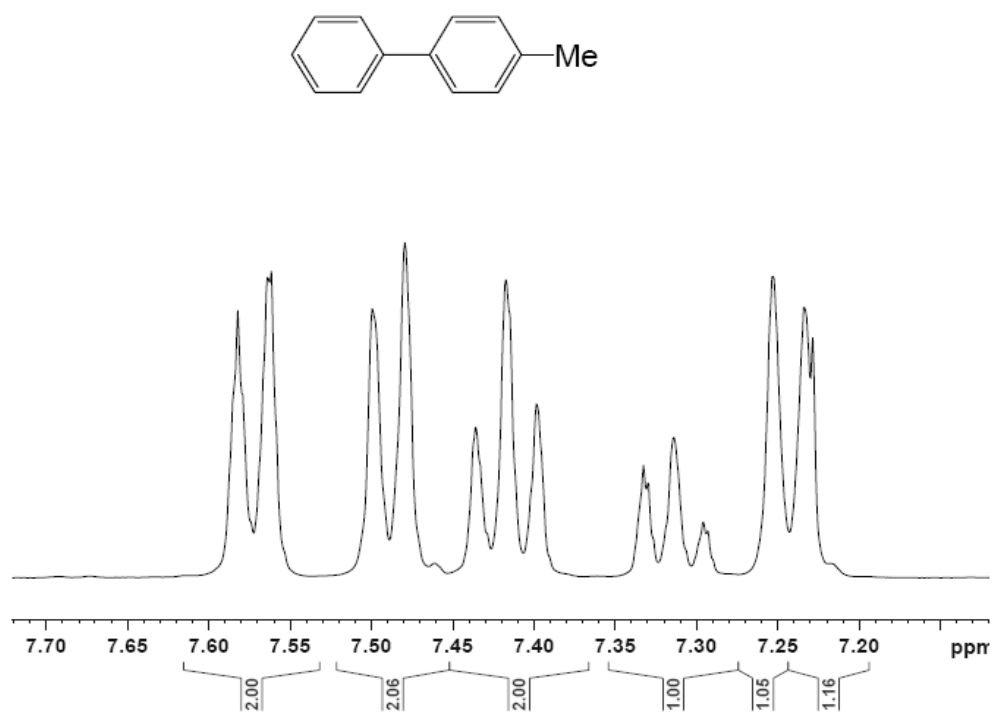
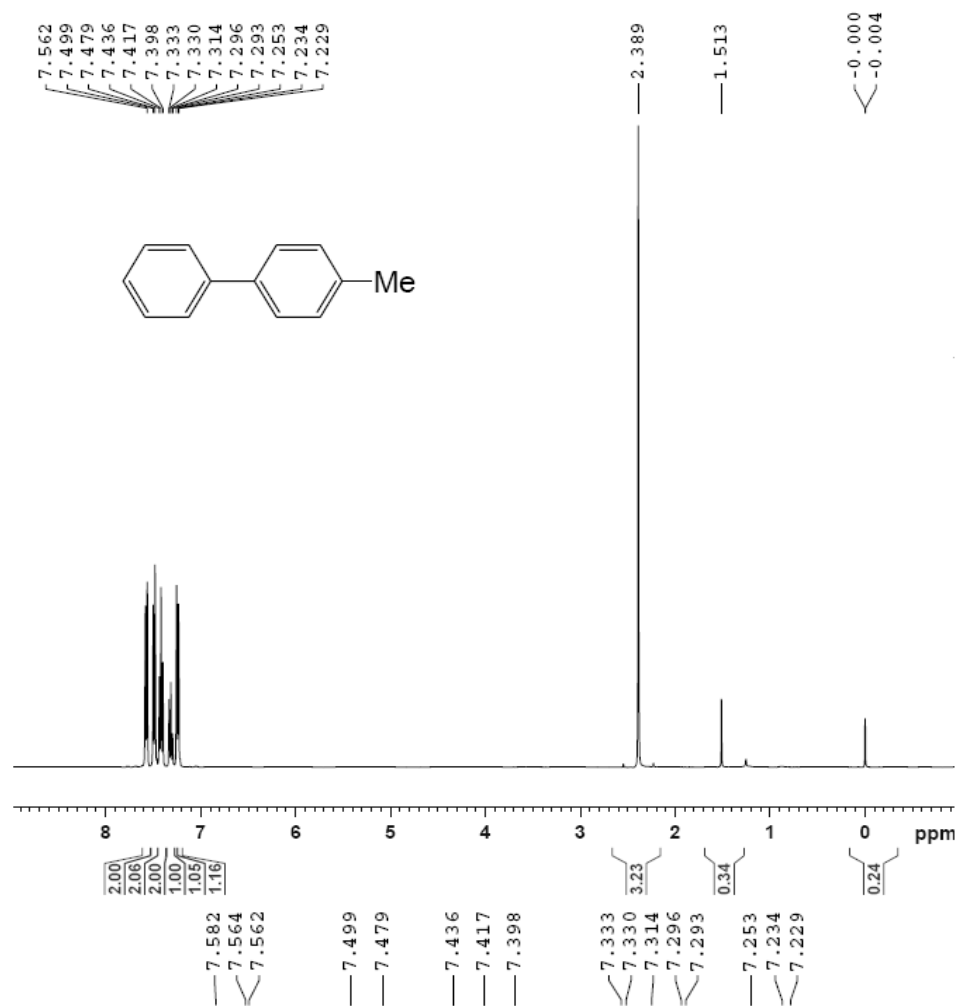


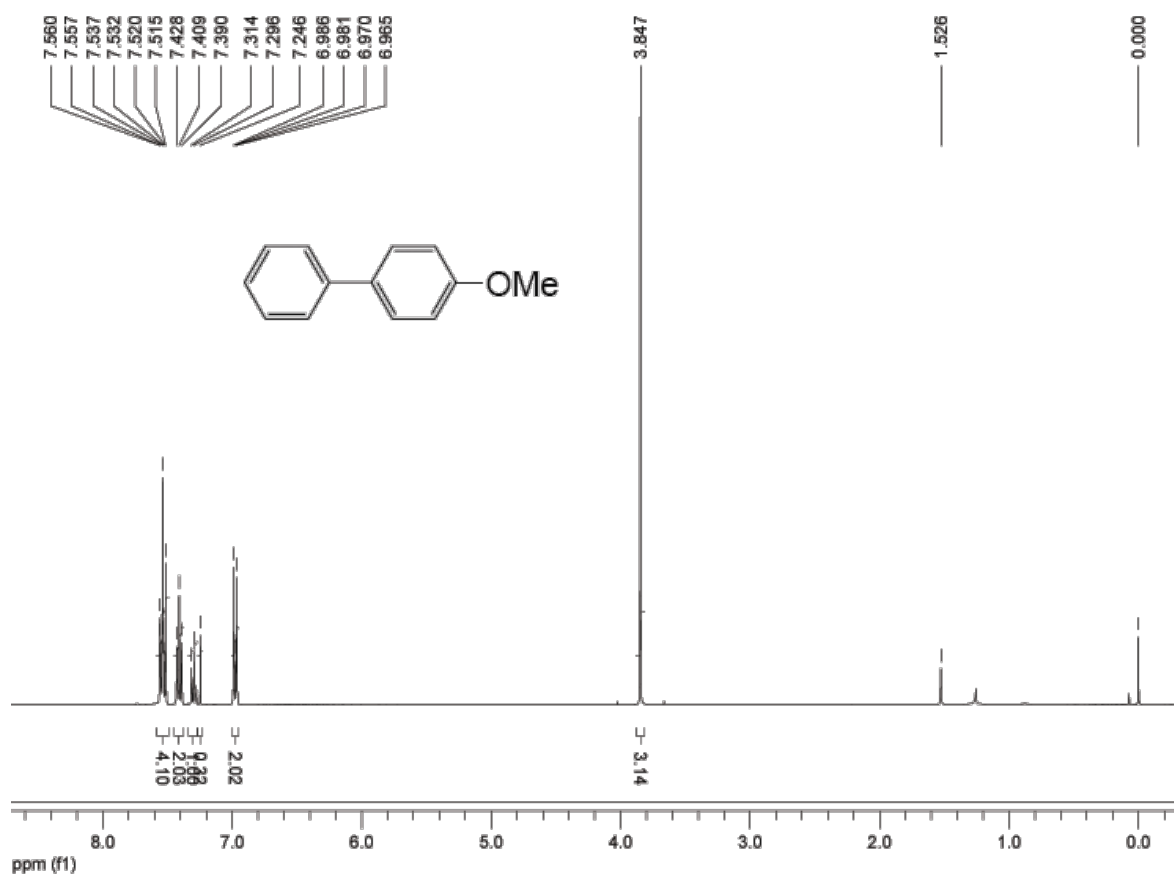
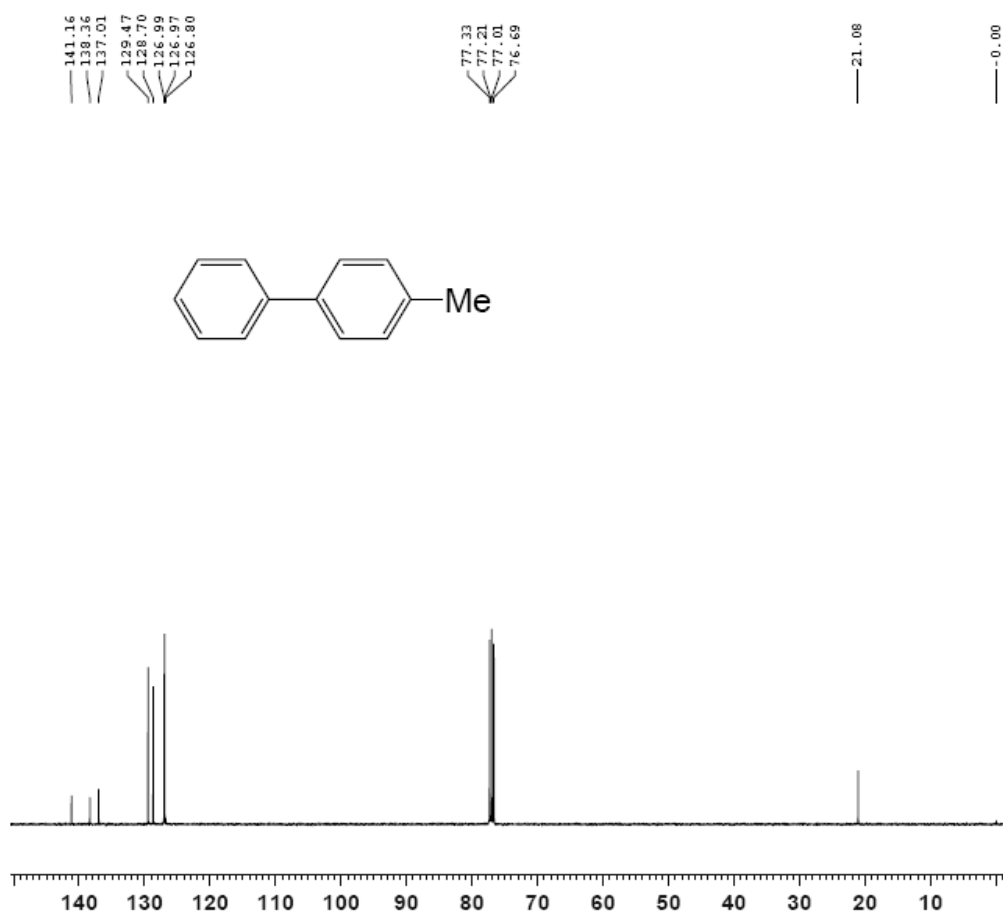


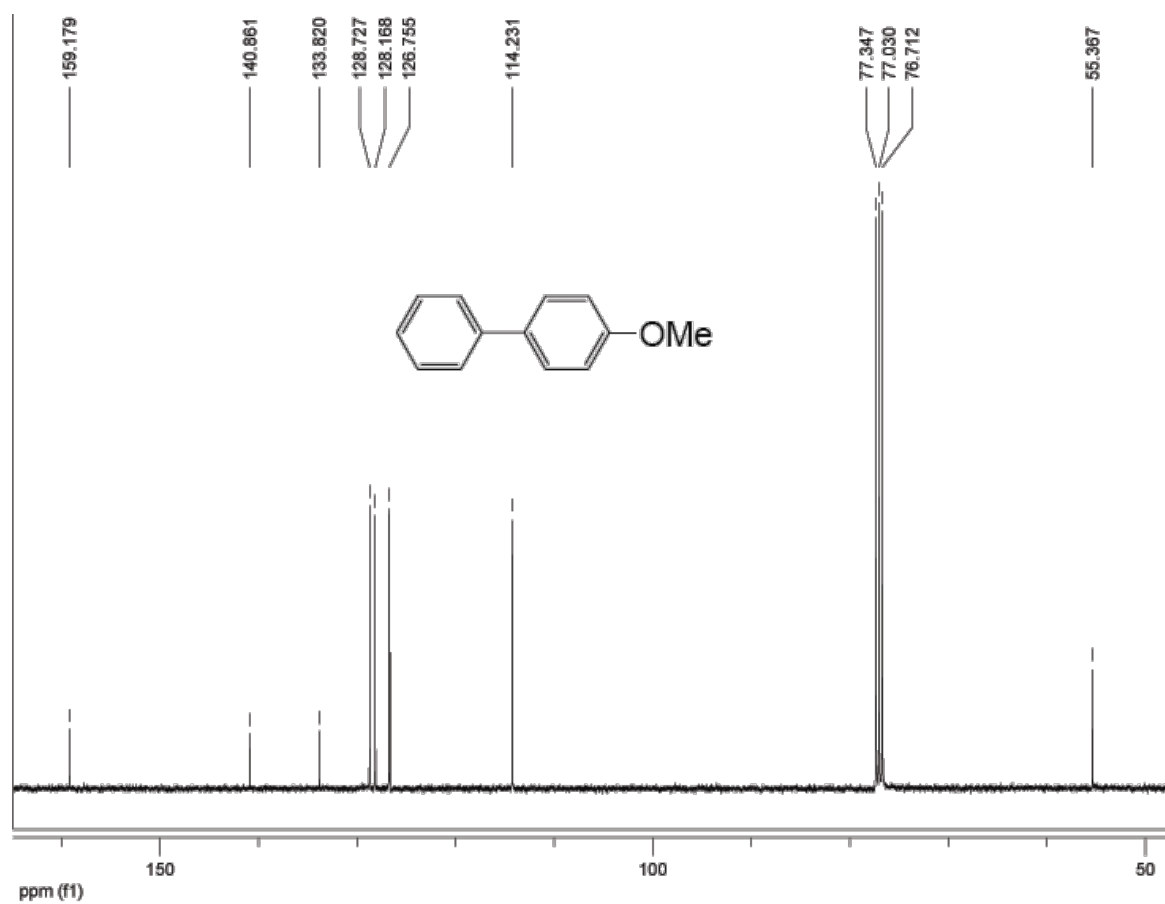
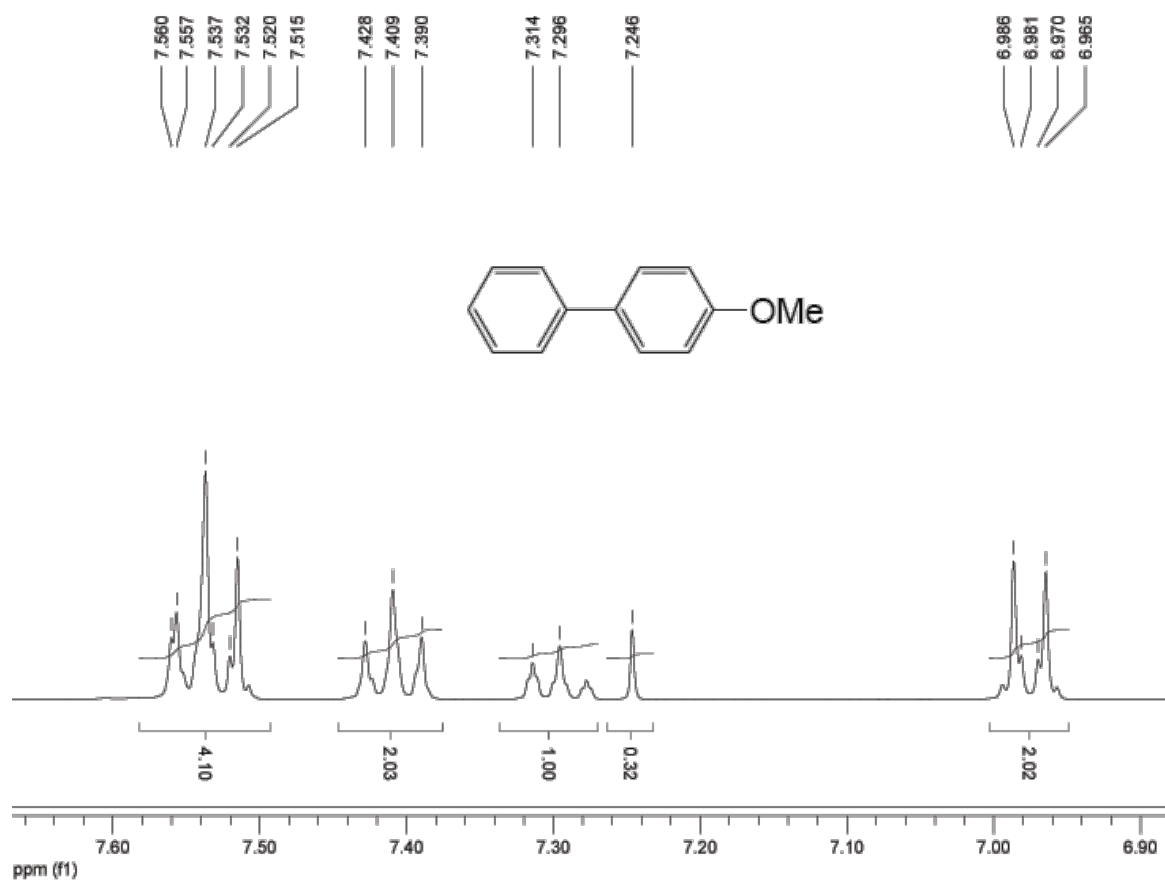


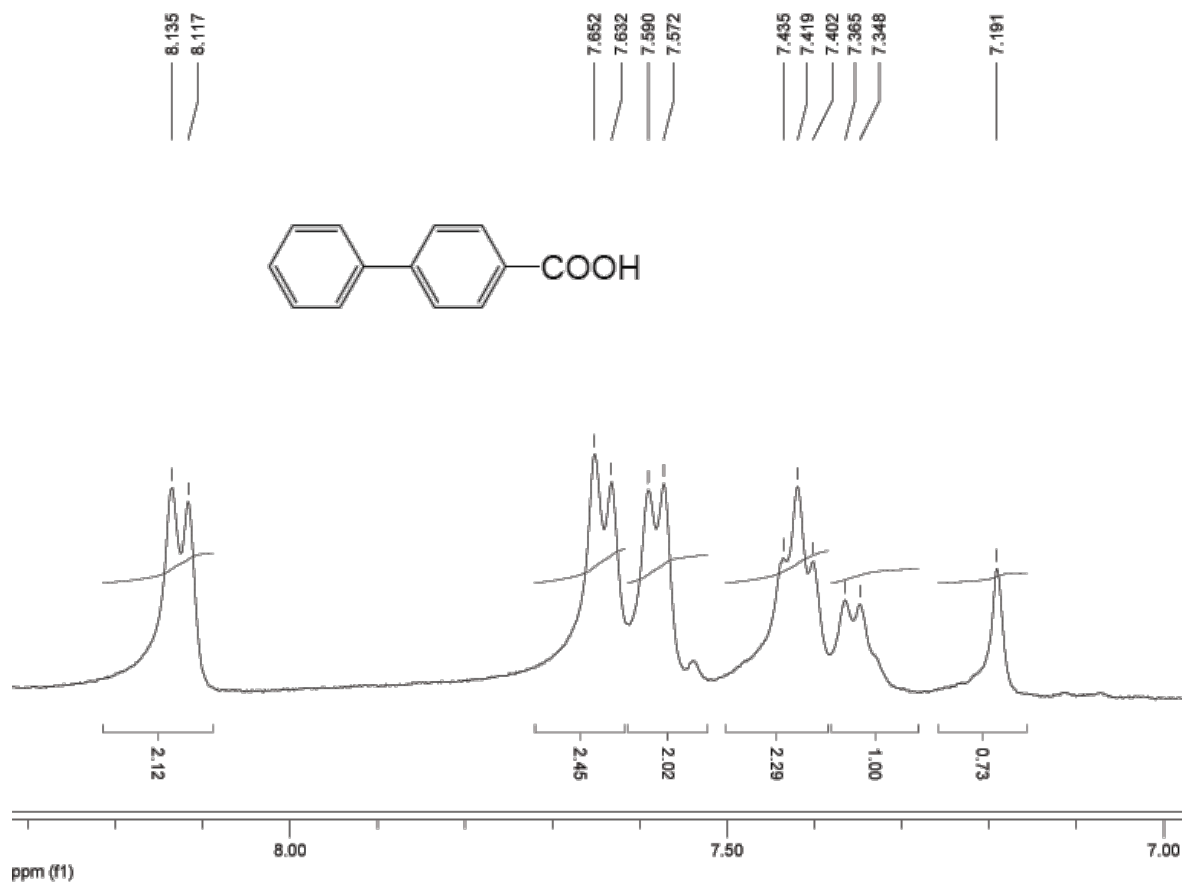
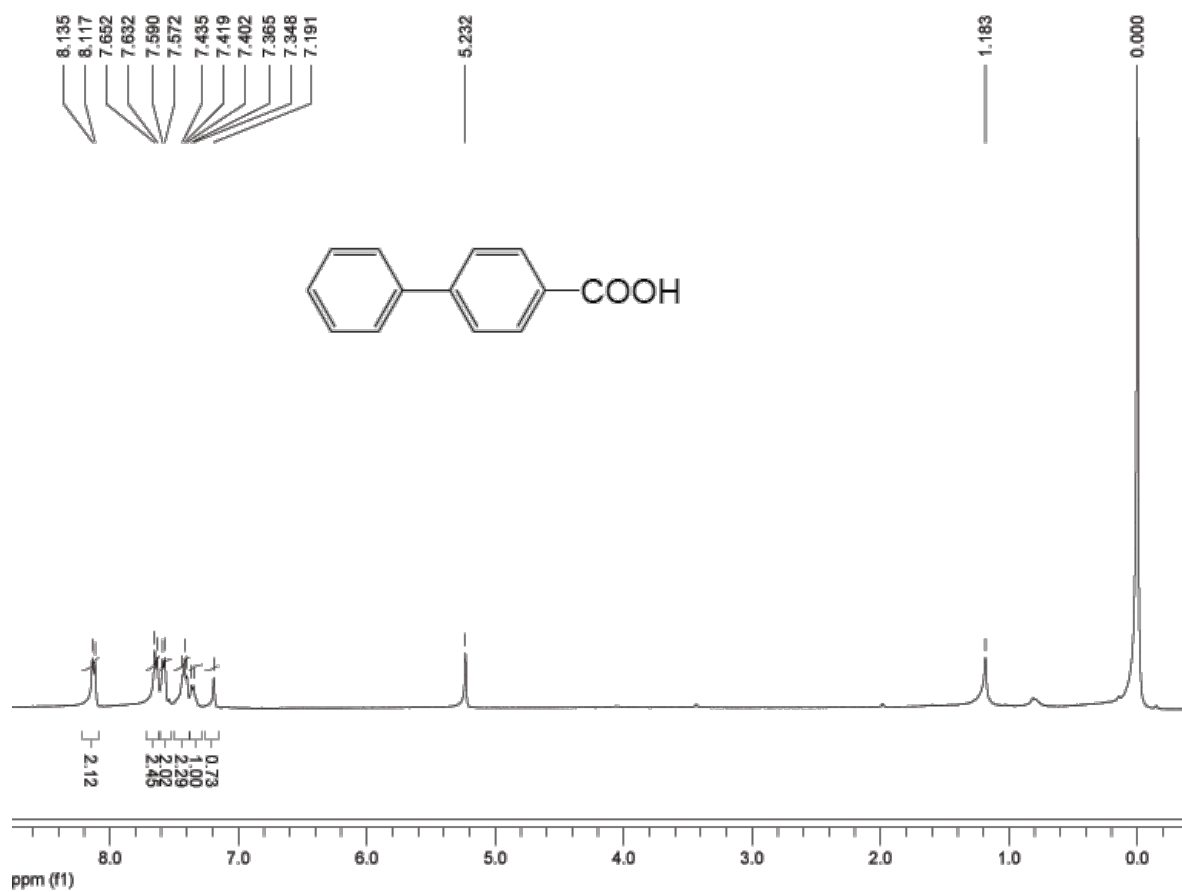


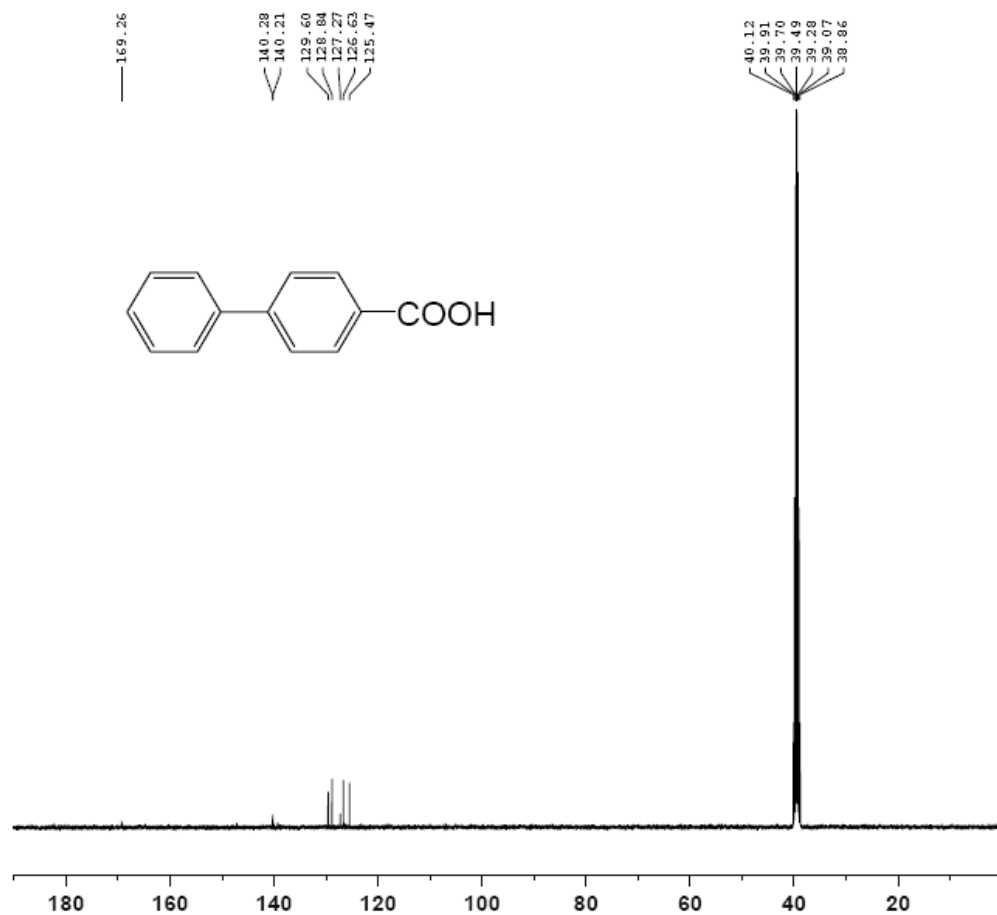












IR Spectra of the products

