

## Supplementary Information

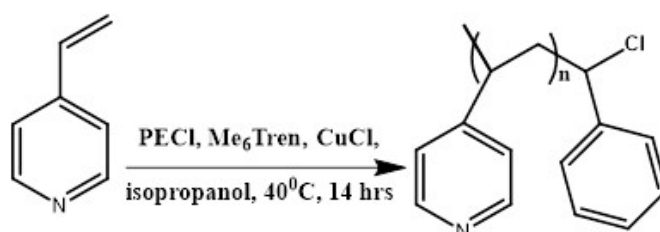
### **Palladium nanoparticle implanted polymer membrane for reusable dip-catalysis of diverse C-C and C-heteroatom (O/S/N) coupling reactions**

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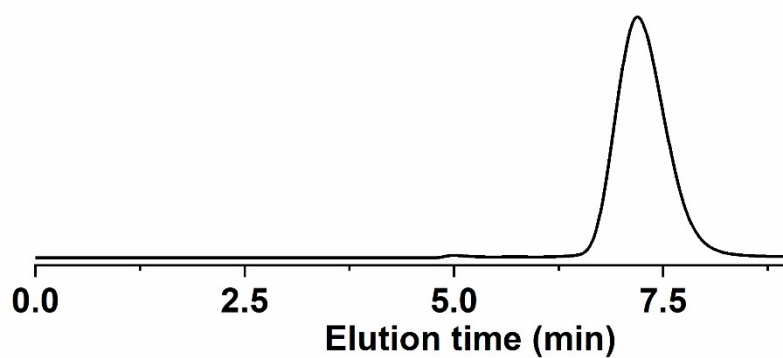
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#### **Preparation of Poly(4-vinyl pyridine) (P4VP):**

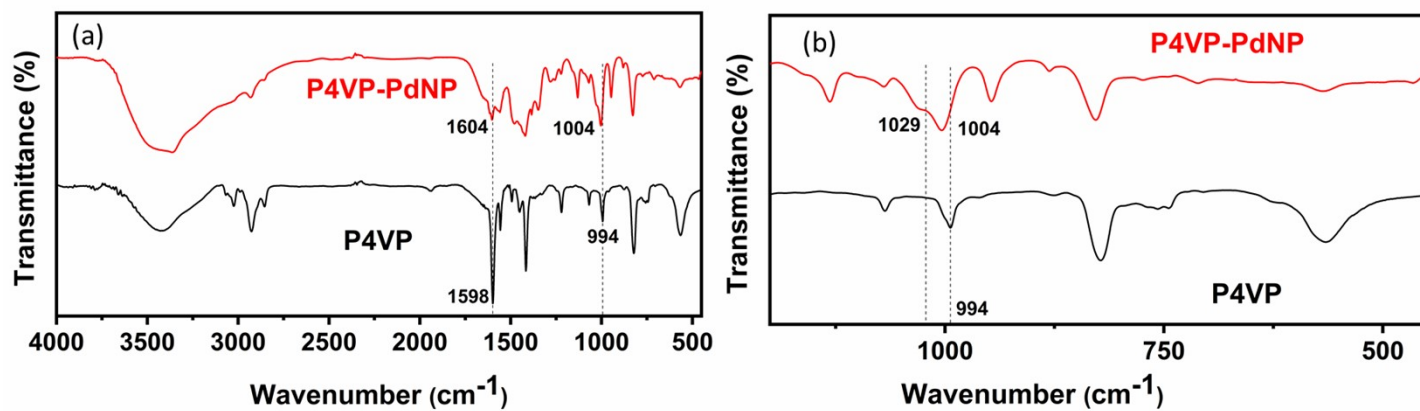
P4VP was prepared by atom transfer radical polymerization of 4VP in 2-propanol with PECl as the initiator and CuCl / tris[2-(dimethylamino)ethyl]amine (Me<sub>6</sub>-TREN) as catalyst at 40 °C. CuCl (0.0487 mmol, 4.82 mg) and a stir bar were first loaded into a dry schlenk flask. To remove oxygen, the flask was sealed with a rubber septum, evacuated, and backfilled with argon atmosphere for several cycles. Using a degassed syringe, degassed isopropanol (3ml), 4-vinyl pyridine (1 ml, 9.28 mmol), and Me<sub>6</sub>-TREN (0.0487 mmol, 11.21mg) were added to the reaction mixture. The sealed flask was then immersed in a 40°C oil bath. After 14 hours, the initiator 1-phenyl ethyl chloride (0.0487 mmol, 6.80 mg) was added. The polymer was recovered and purified by precipitation in hexane and subsequently passing chloroform solution of the polymer through basic alumina column. The molecular weight of the polymer was measured by GPC. The molecular weight of the polymer as determined by GPC (DMF as solvent) was  $M_n = 18,502$  with PDI=1.5.



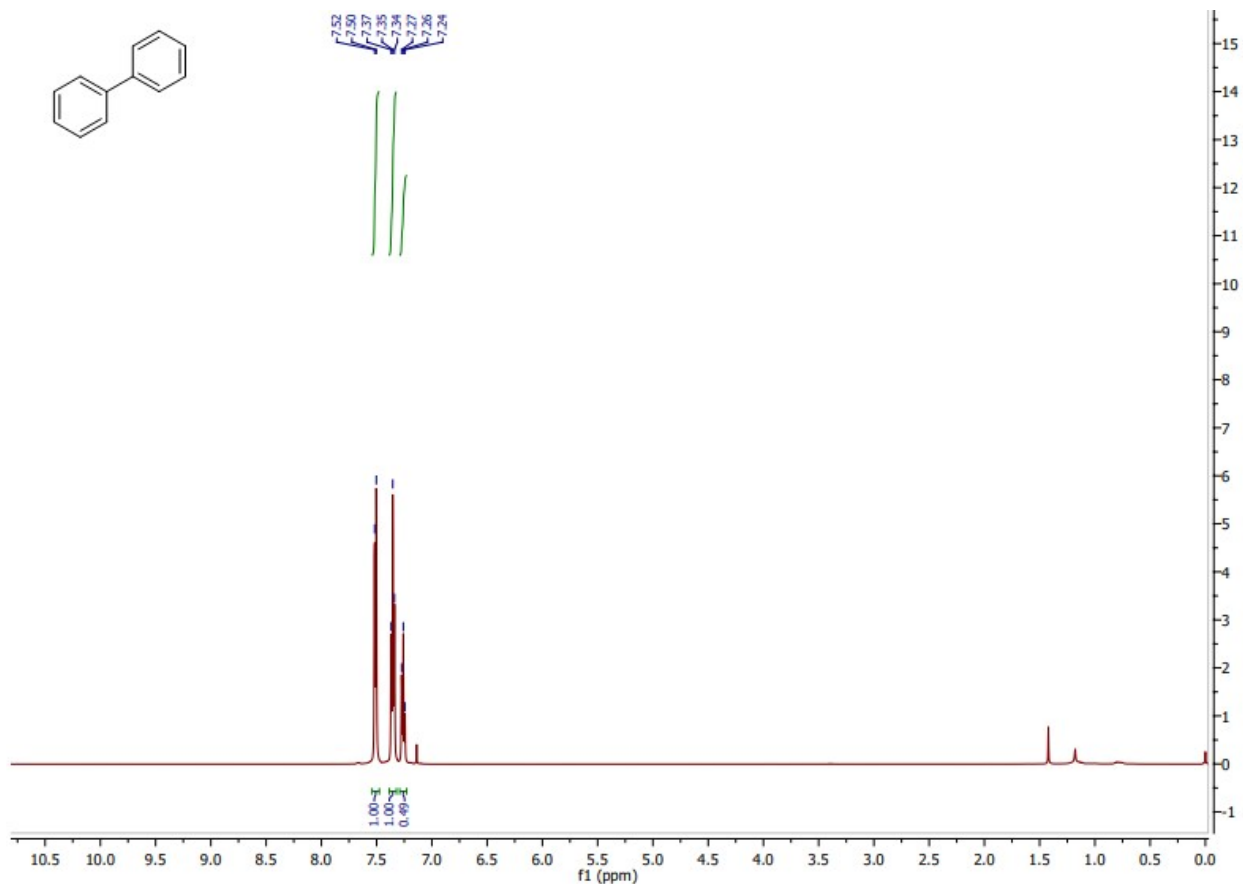
**Figure S1.** Reaction scheme for synthesis of P4VP through ATRP



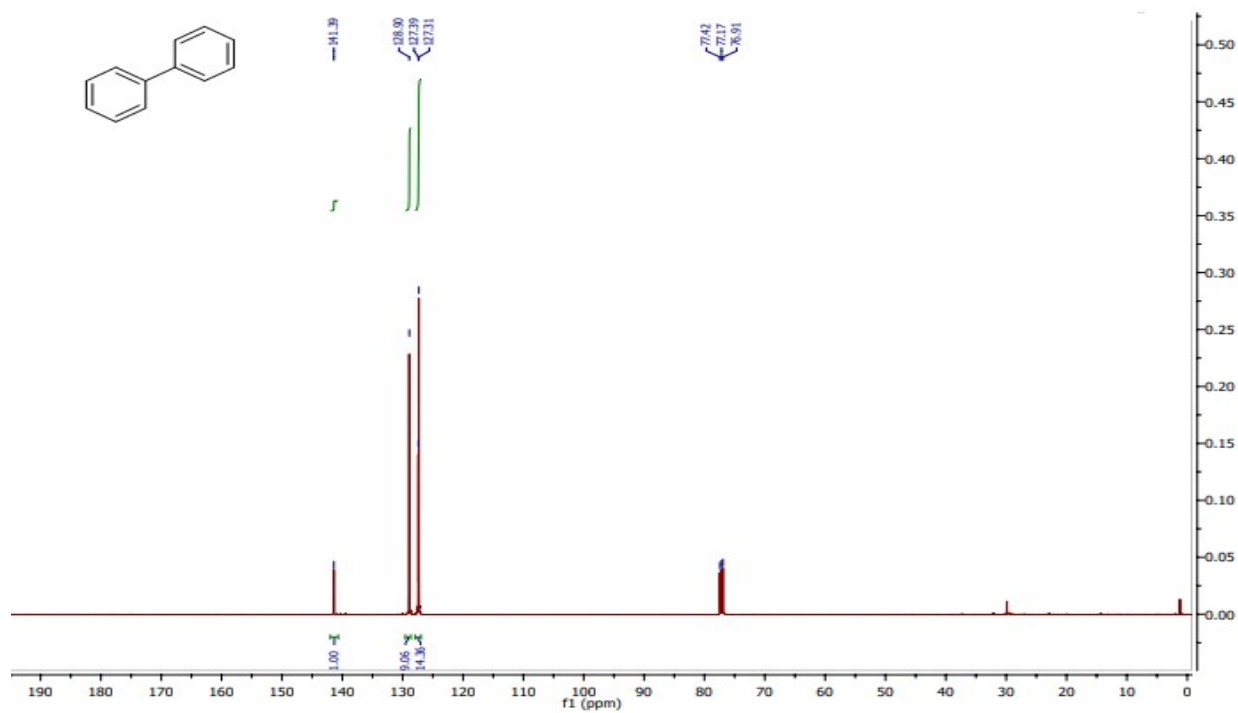
**Figure S2.** GPC trace of synthesized P4VP.



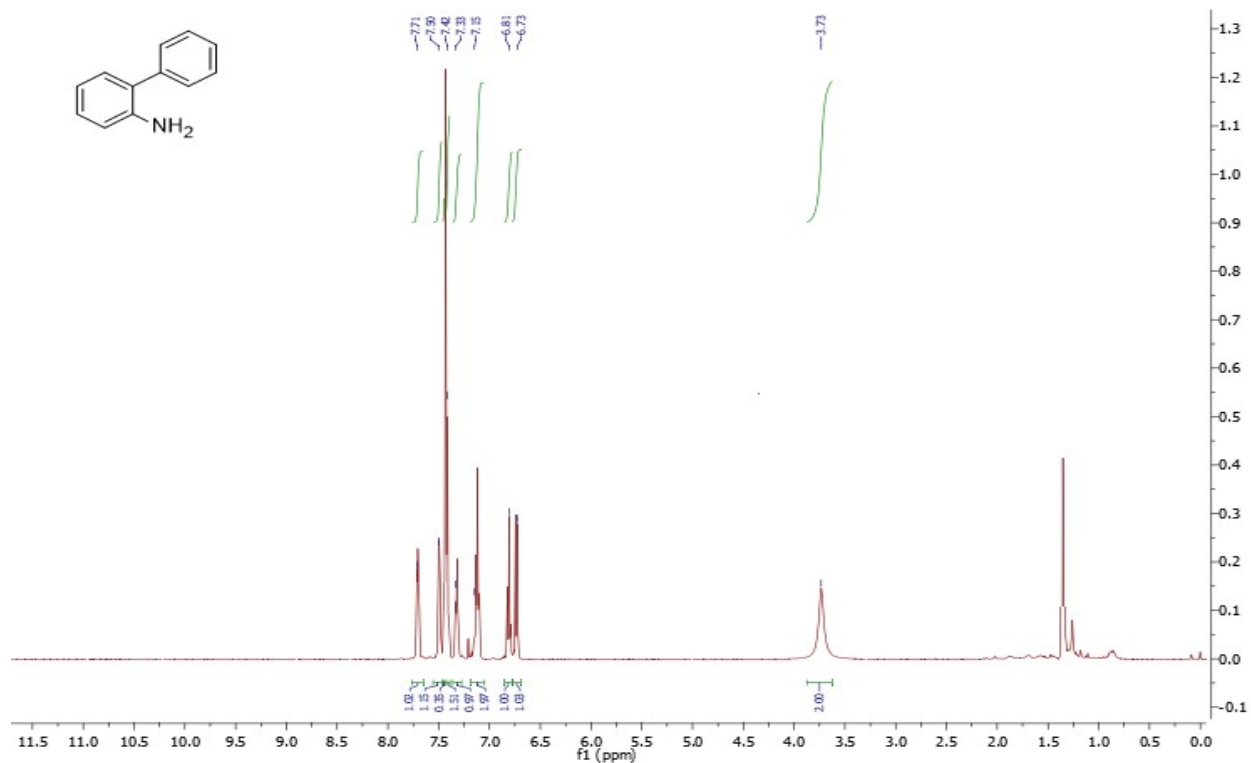
**Figure S3** FTIR spectra of P4VP and P4VP-PdNP layer (a) full range 4000-450 cm<sup>-1</sup> (b) 1200 - 450 cm<sup>-1</sup>.



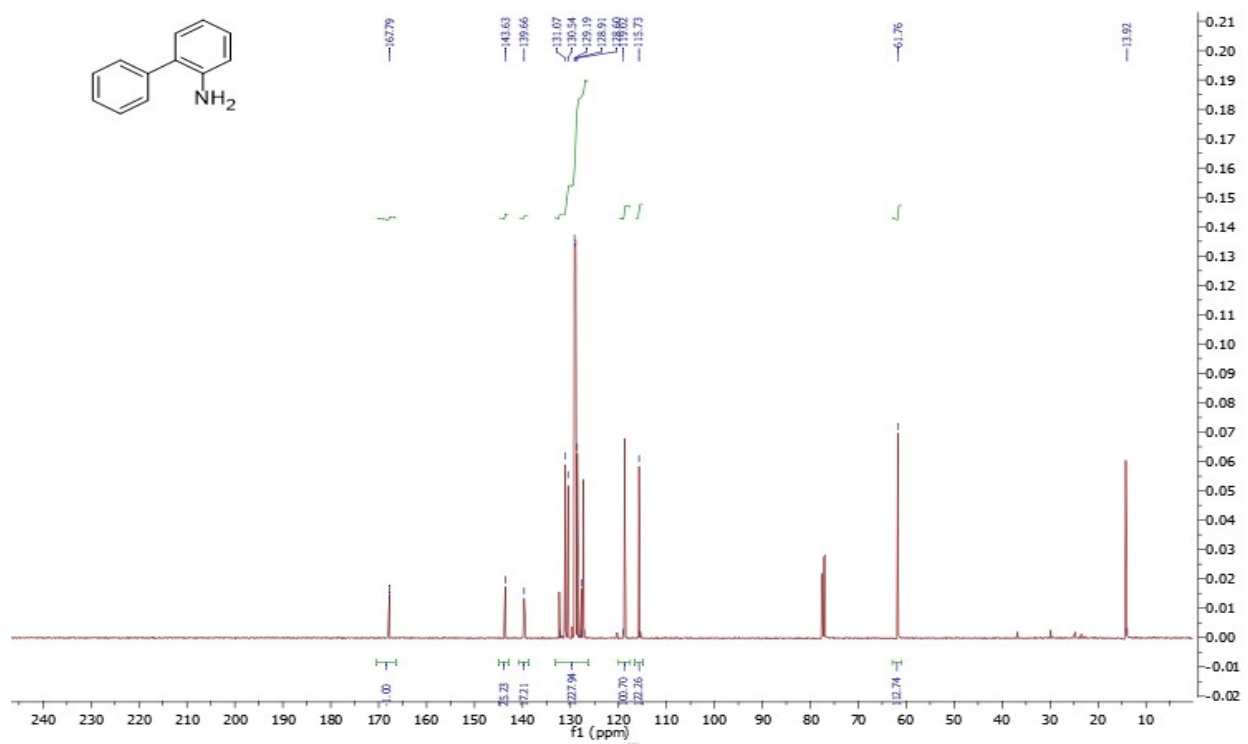
**Figure S4.**  $^1\text{H}$  NMR spectra of biphenyl compound by Suzuki-Miyaura cross-coupling reaction



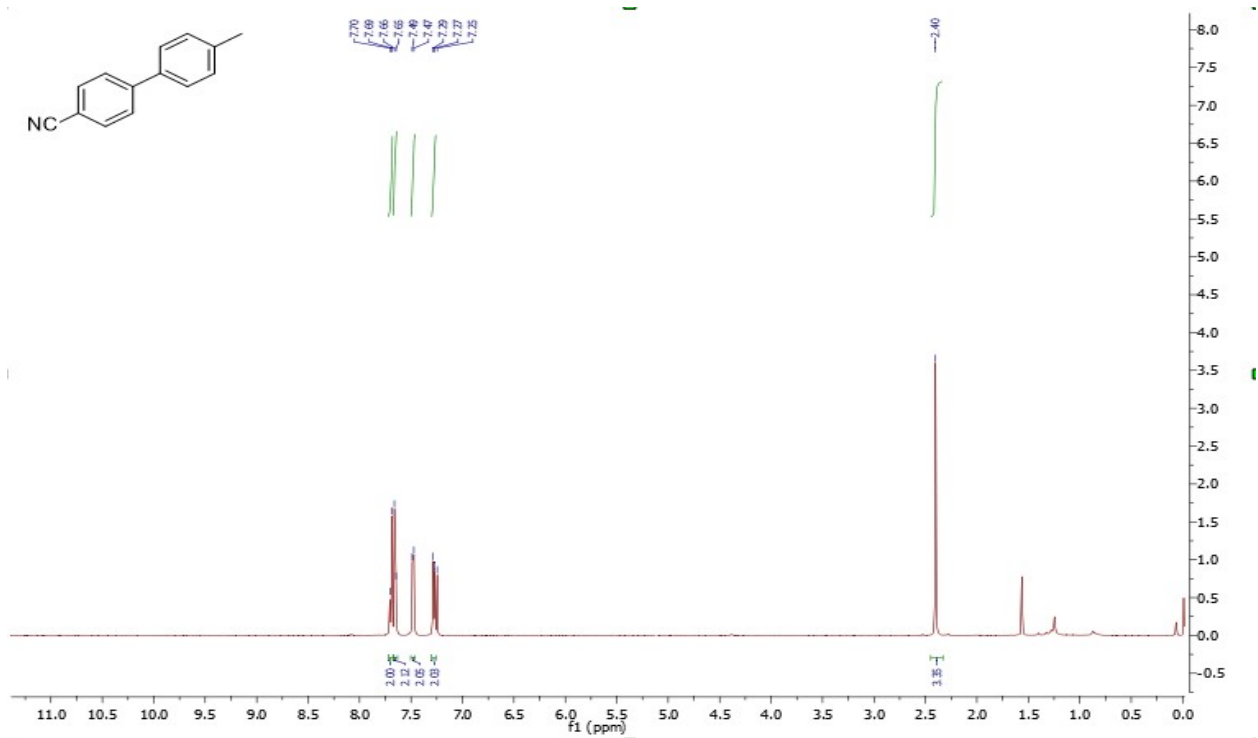
**Figure S5.**  $^{13}\text{C}$  NMR spectra of biphenyl compound by Suzuki-Miyaura cross-coupling reaction



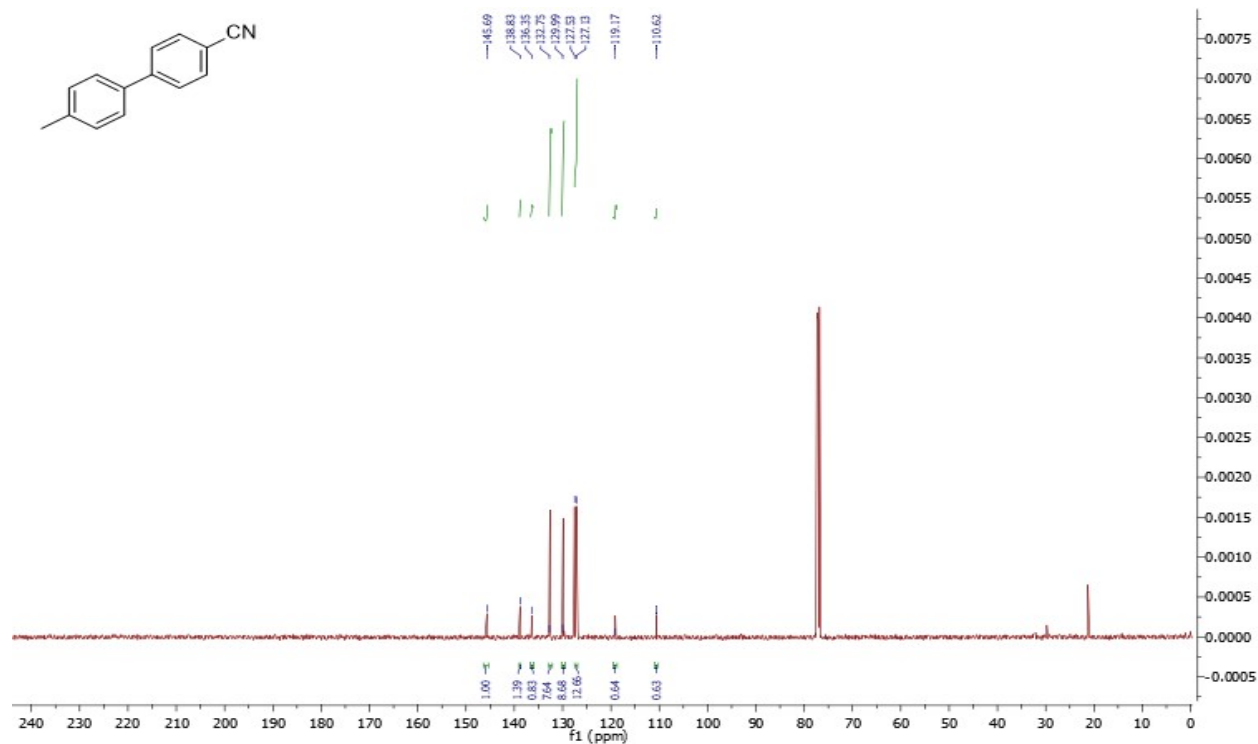
**Figure S6.** <sup>1</sup>H NMR spectra of 2-aminobiphenyl compound by Suzuki-Miyaura cross-coupling reaction



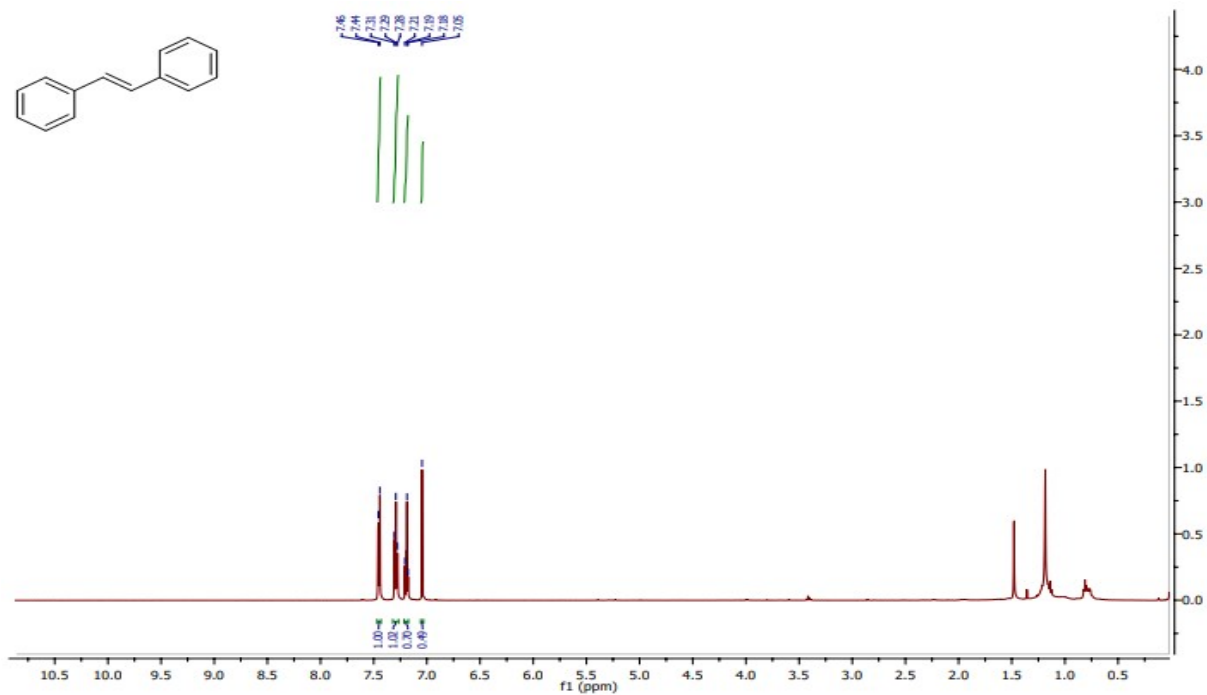
**Figure S7.** <sup>13</sup>C NMR spectra of 2-aminobiphenyl compound by Suzuki-Miyaura cross-coupling reaction



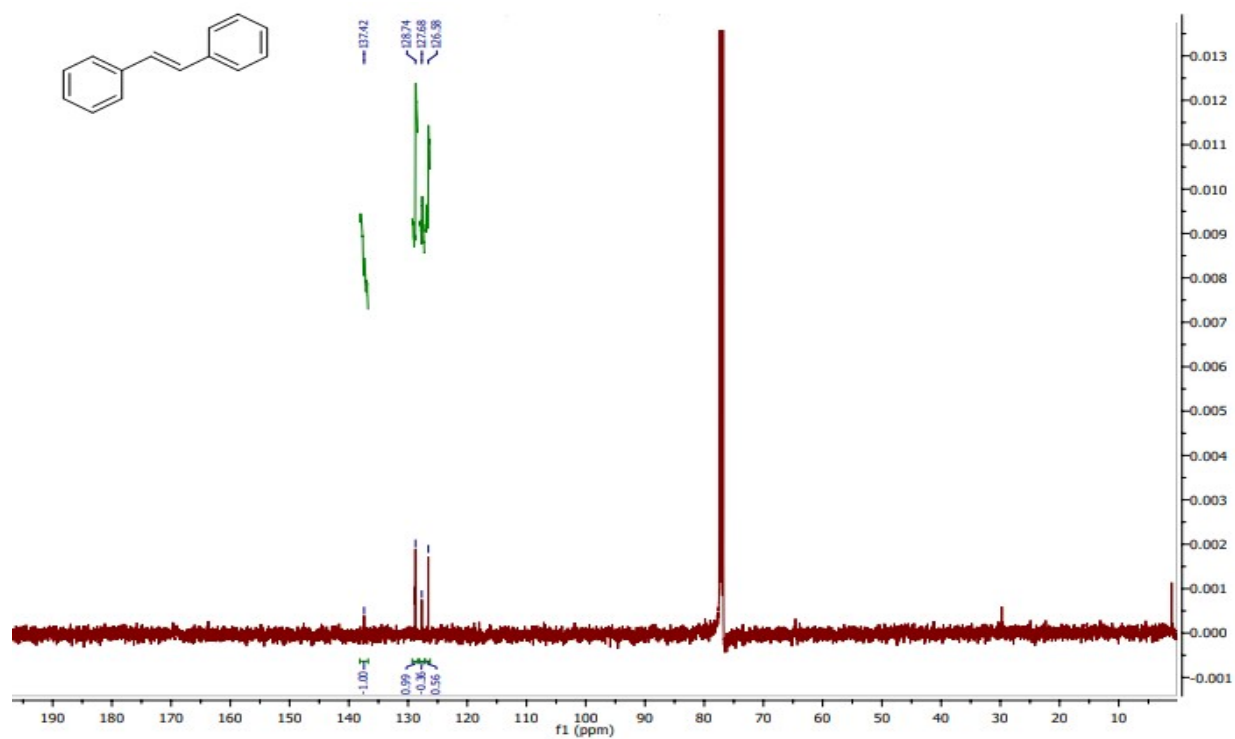
**Figure S8.** <sup>1</sup>H NMR spectra of 4-cyano-4-methylbiphenyl compound by Suzuki-Miyaura cross-coupling reaction.



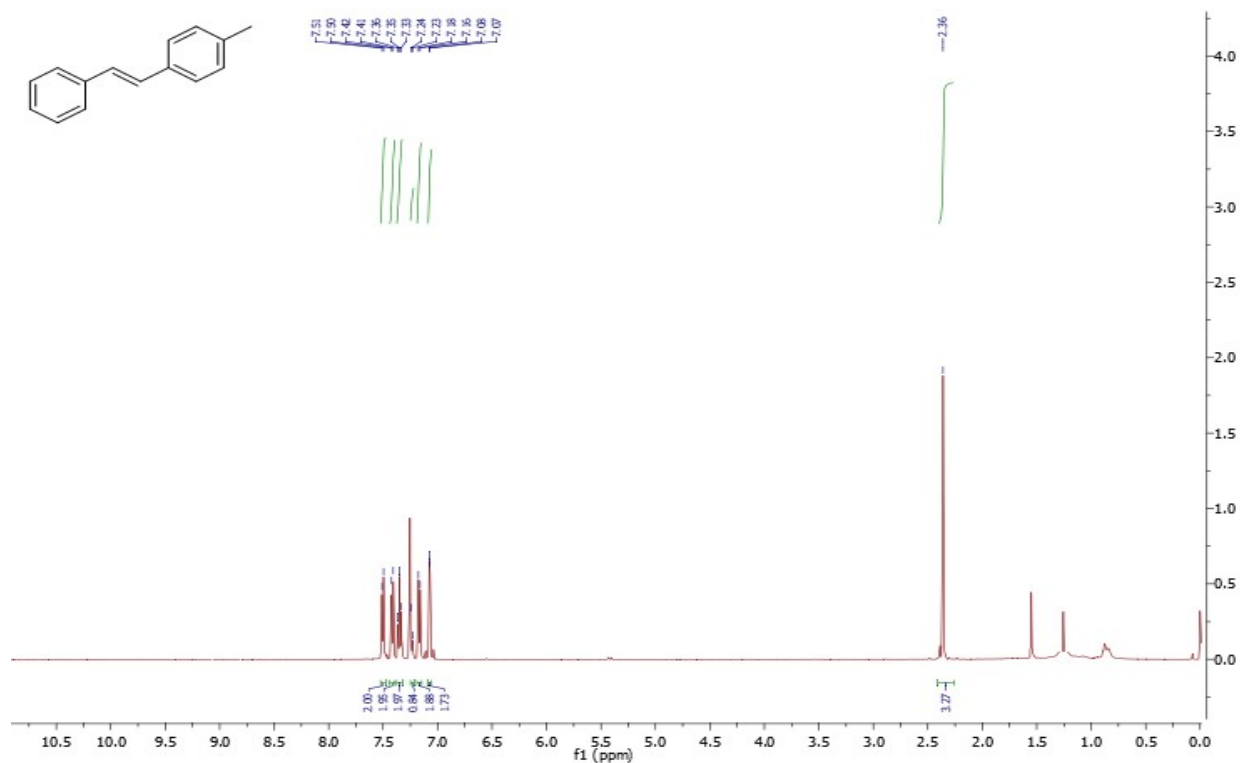
**Figure S9.** <sup>13</sup>C NMR spectra of 4-cyano-4-methylbiphenyl compound by Suzuki-Miyaura cross-coupling reaction



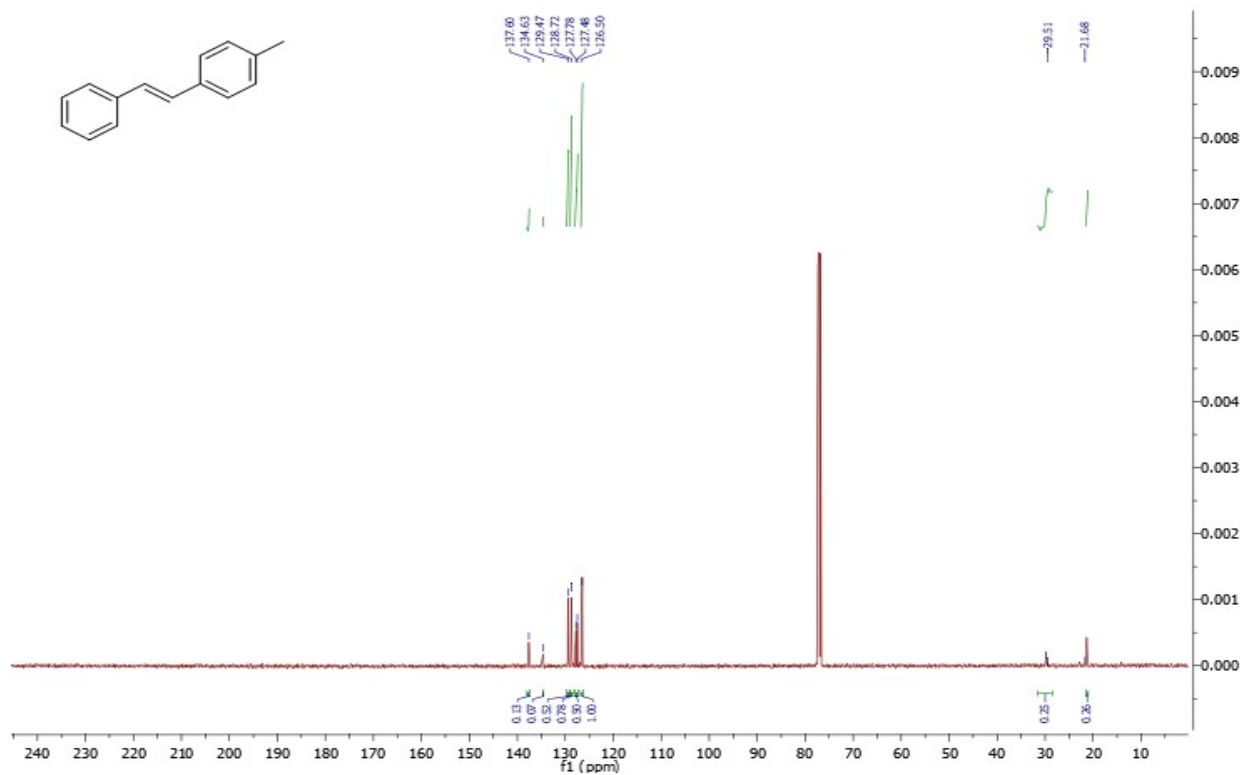
**Figure S10.** <sup>1</sup>H NMR spectra of Stilbene compound by Heck coupling reaction.



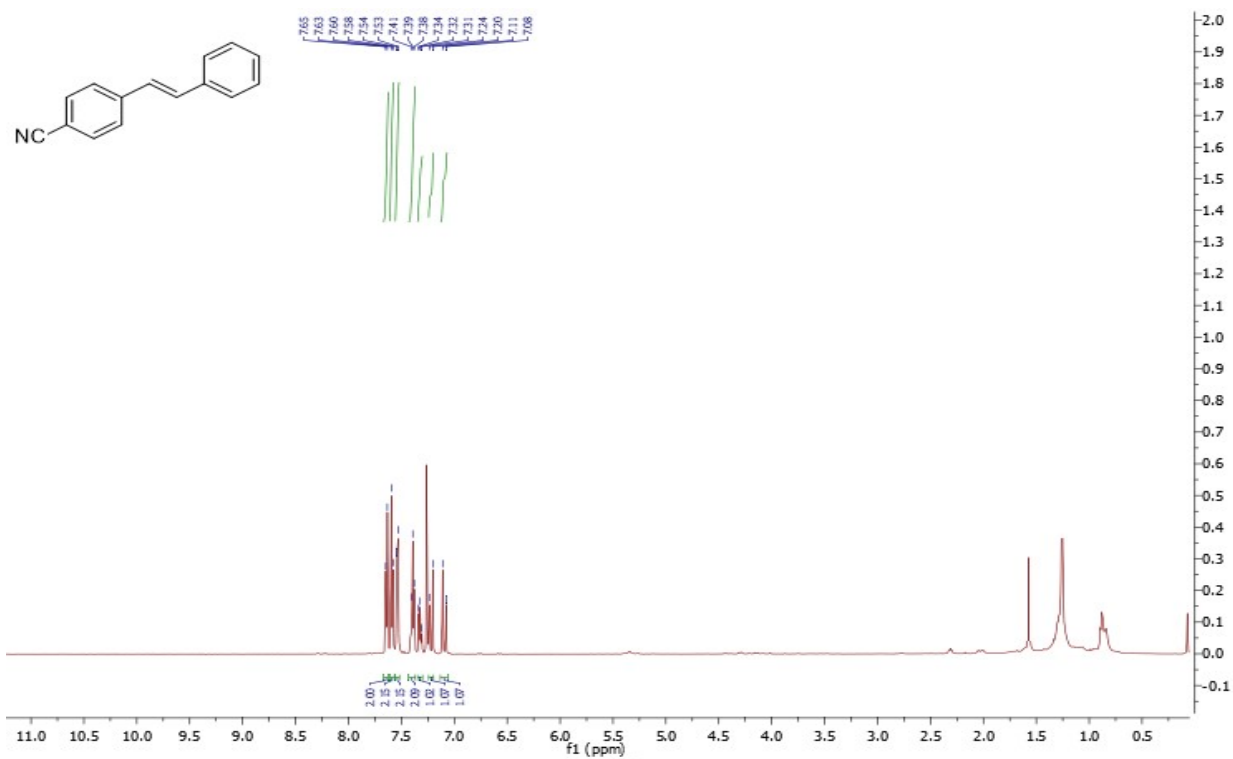
**Figure S11.** <sup>13</sup>C NMR spectra of Stilbene compound by Heck coupling reaction.



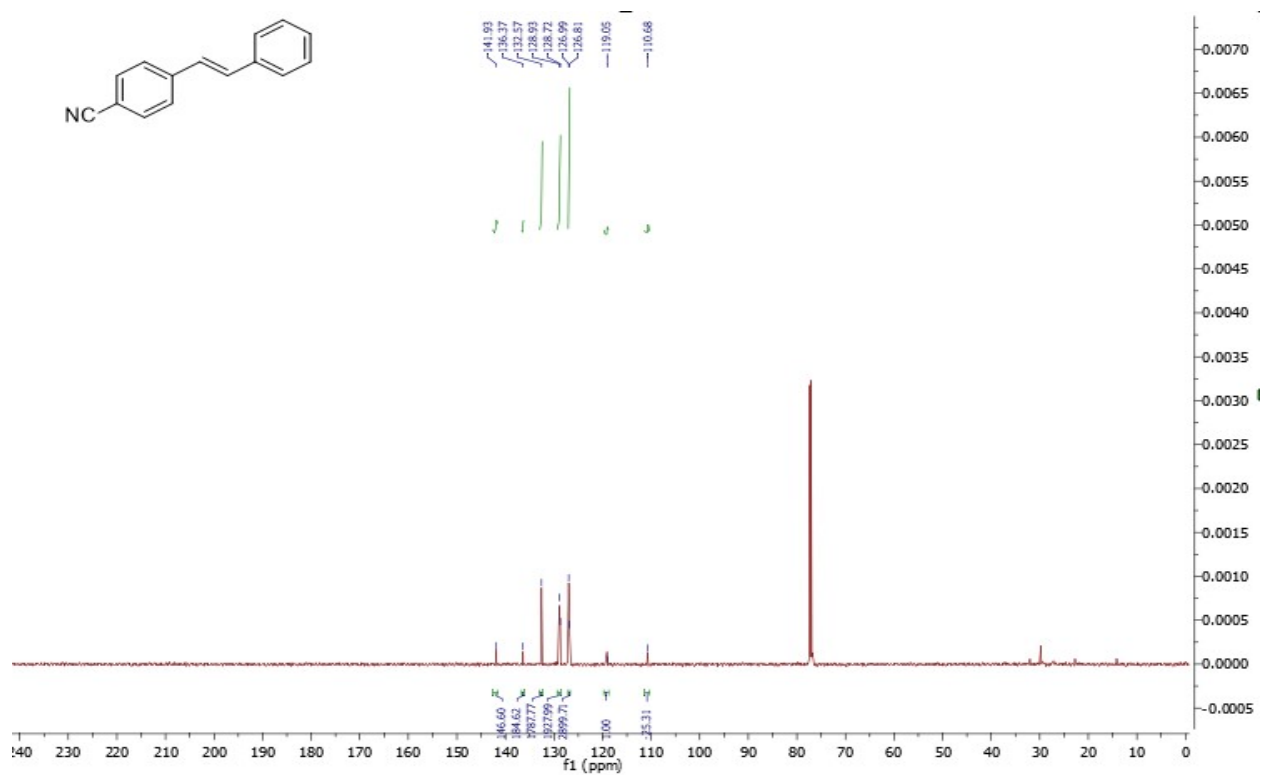
**Figure S12.** <sup>1</sup>H NMR spectra of 4-Methylstilbene compound by Heck coupling reaction.



**Figure S13.** <sup>13</sup>C NMR spectra of 4-Methylstilbene compound by Heck coupling reaction.

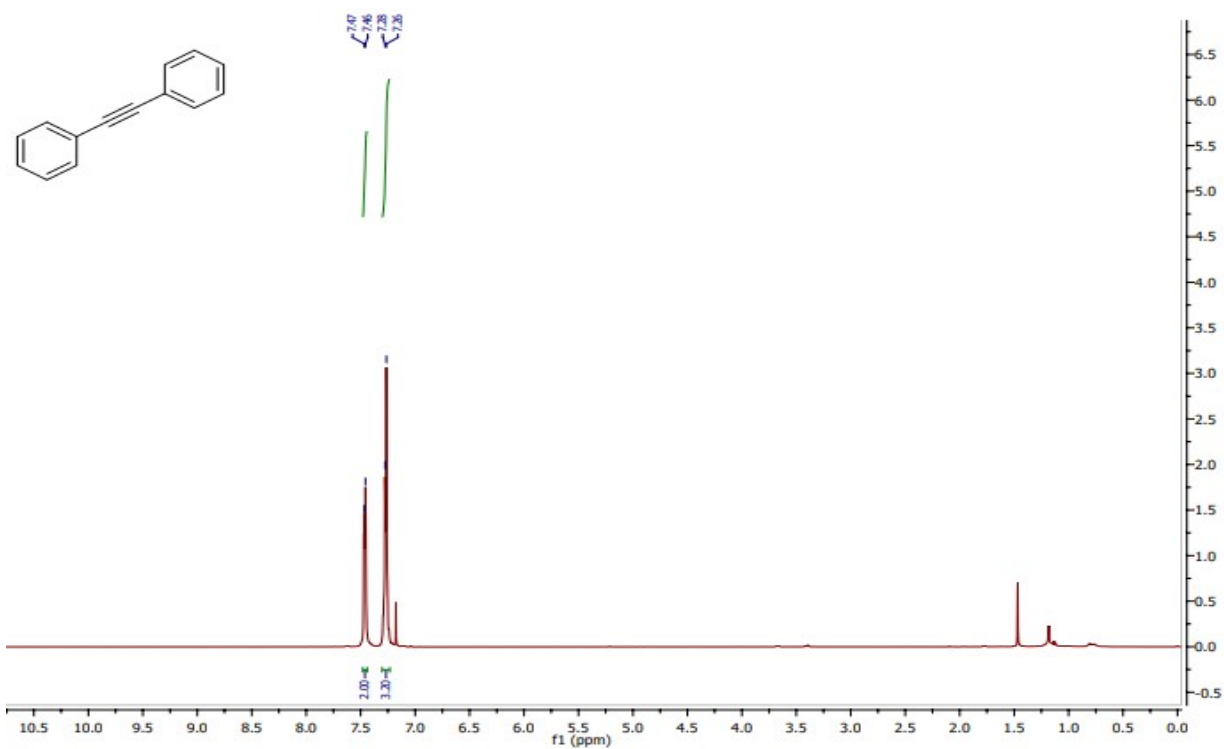


**Figure S14.** <sup>1</sup>H NMR spectra of 4-Cyanostilbene compound by Heck coupling reaction.

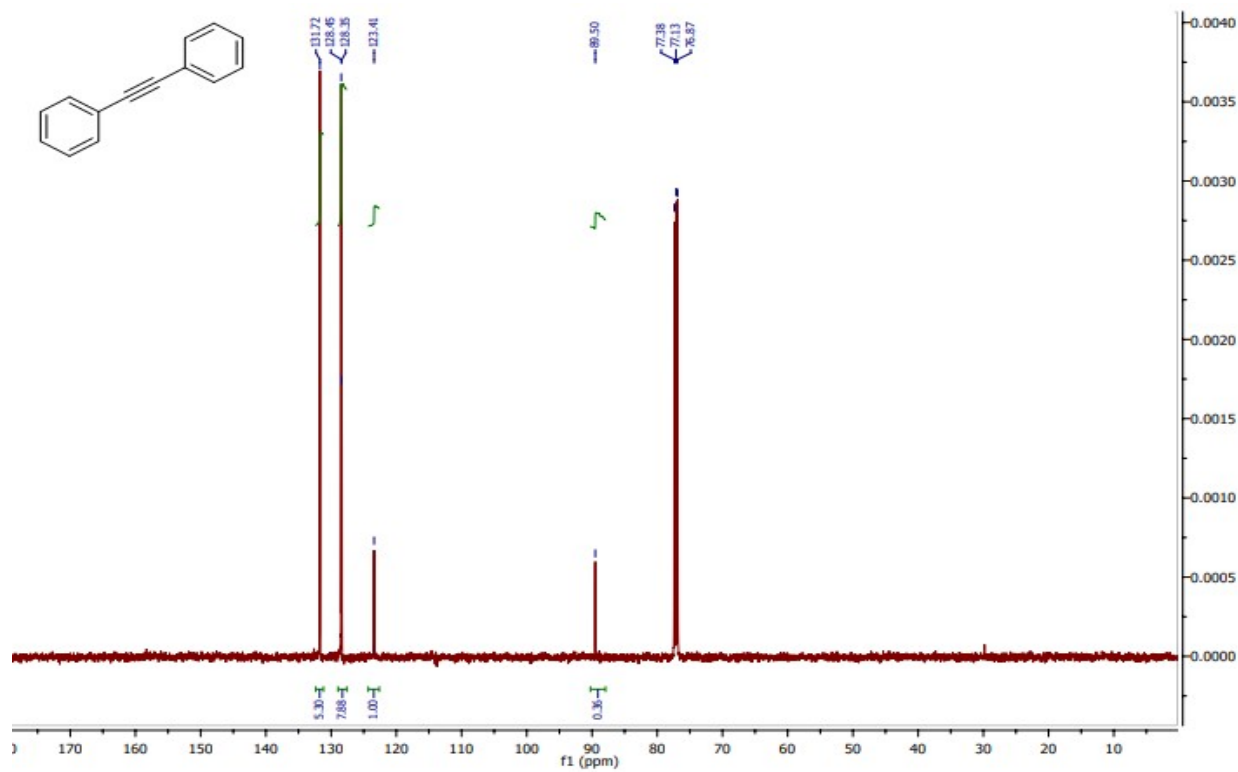


**Figure S15.** <sup>13</sup>C NMR spectra of 4-Cyanostilbene compound by Heck coupling reaction.

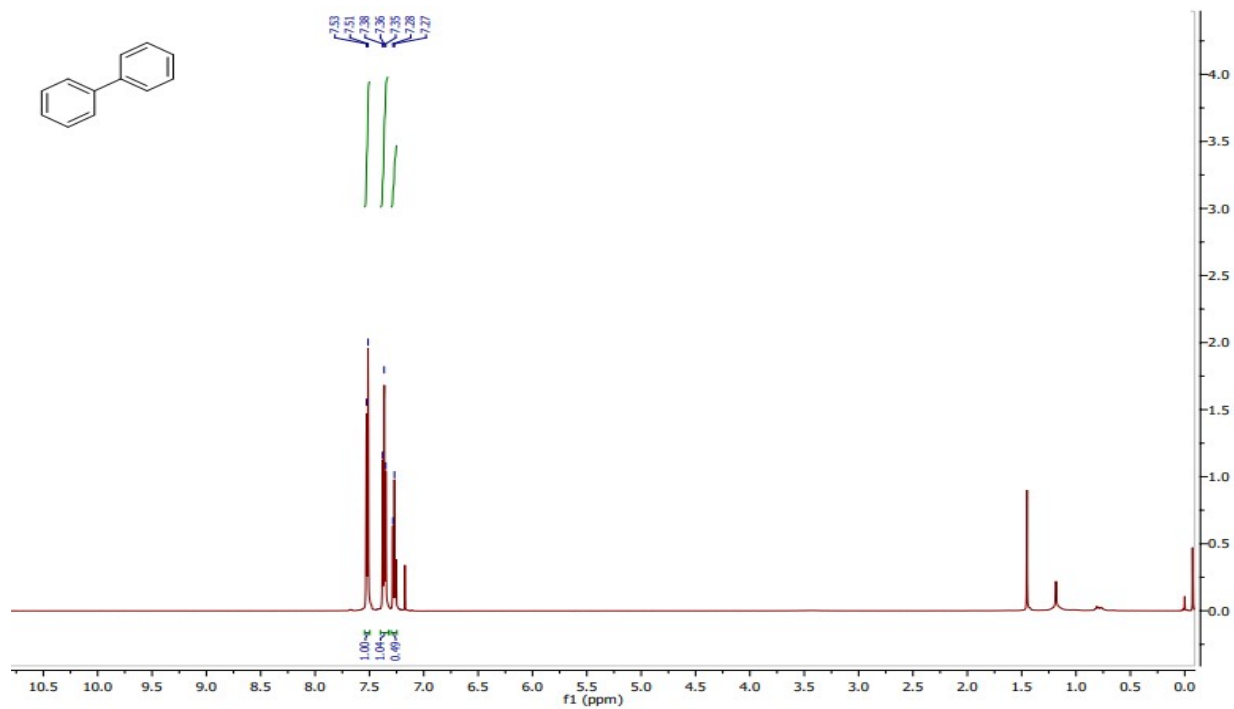




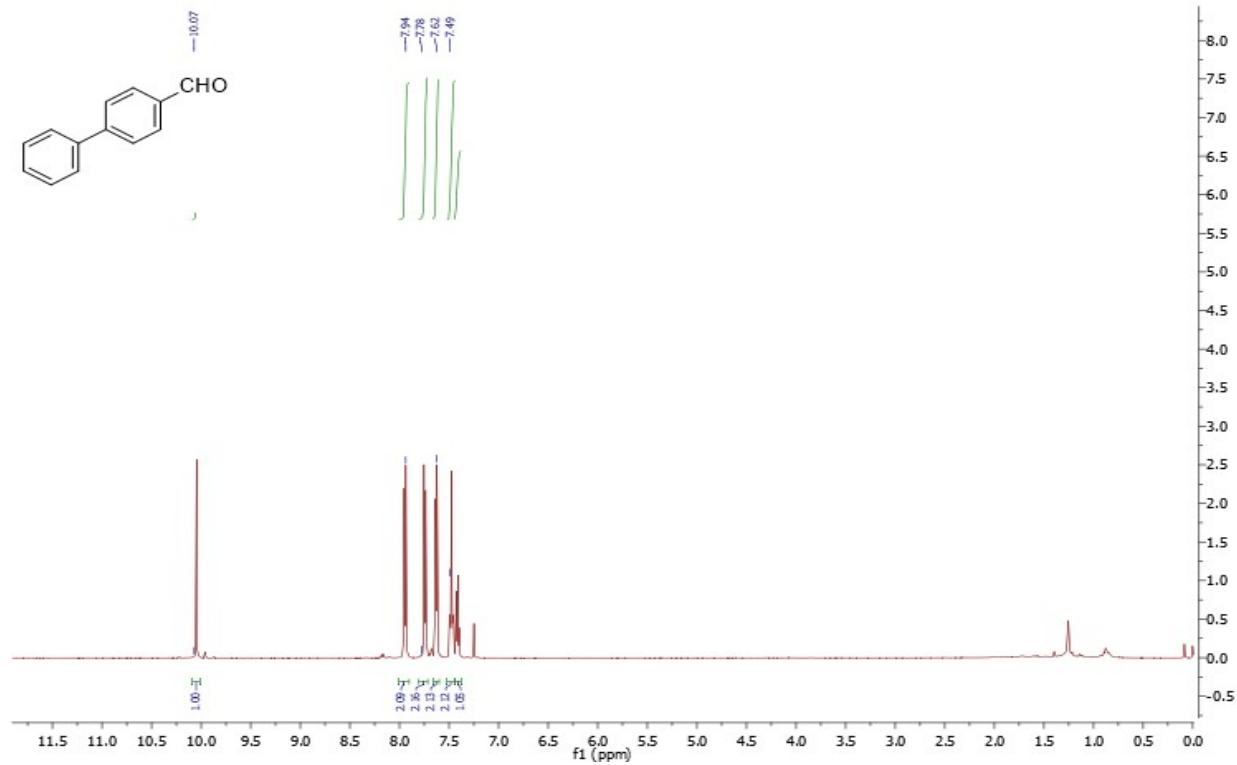
**Figure S16.** <sup>1</sup>H NMR spectra of diphenyl acetylene compound by Sonagashira coupling reaction.



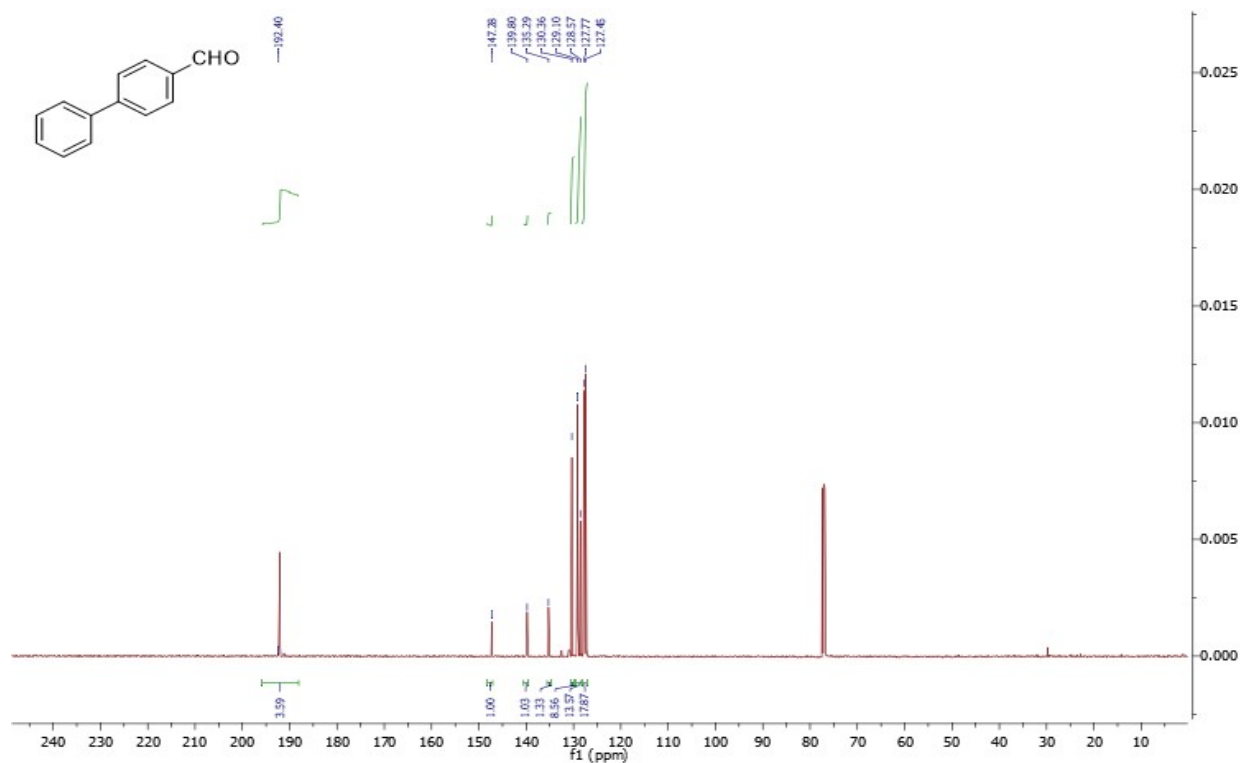
**Figure S17.** <sup>13</sup>C NMR spectra of diphenylacetylene compound by Sonagashira coupling reaction.



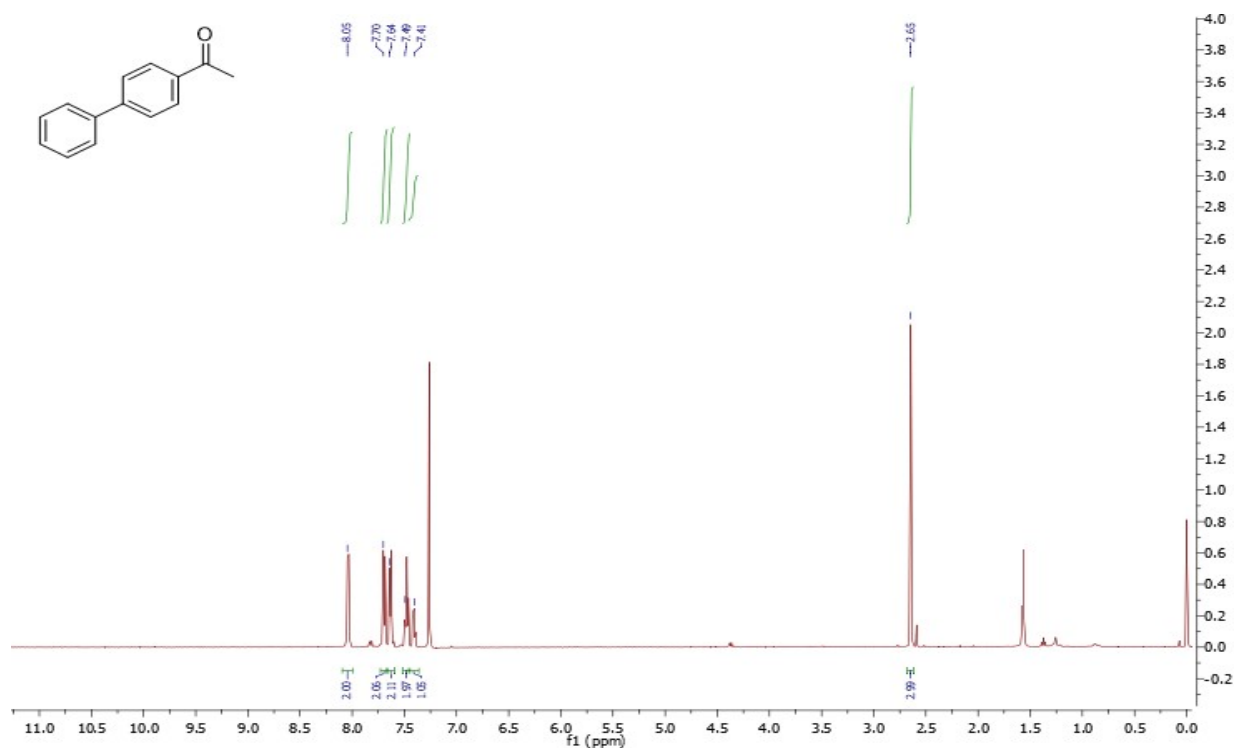
**Figure S18.**  $^1\text{H}$  NMR spectra of biphenyl compound by Stille coupling.



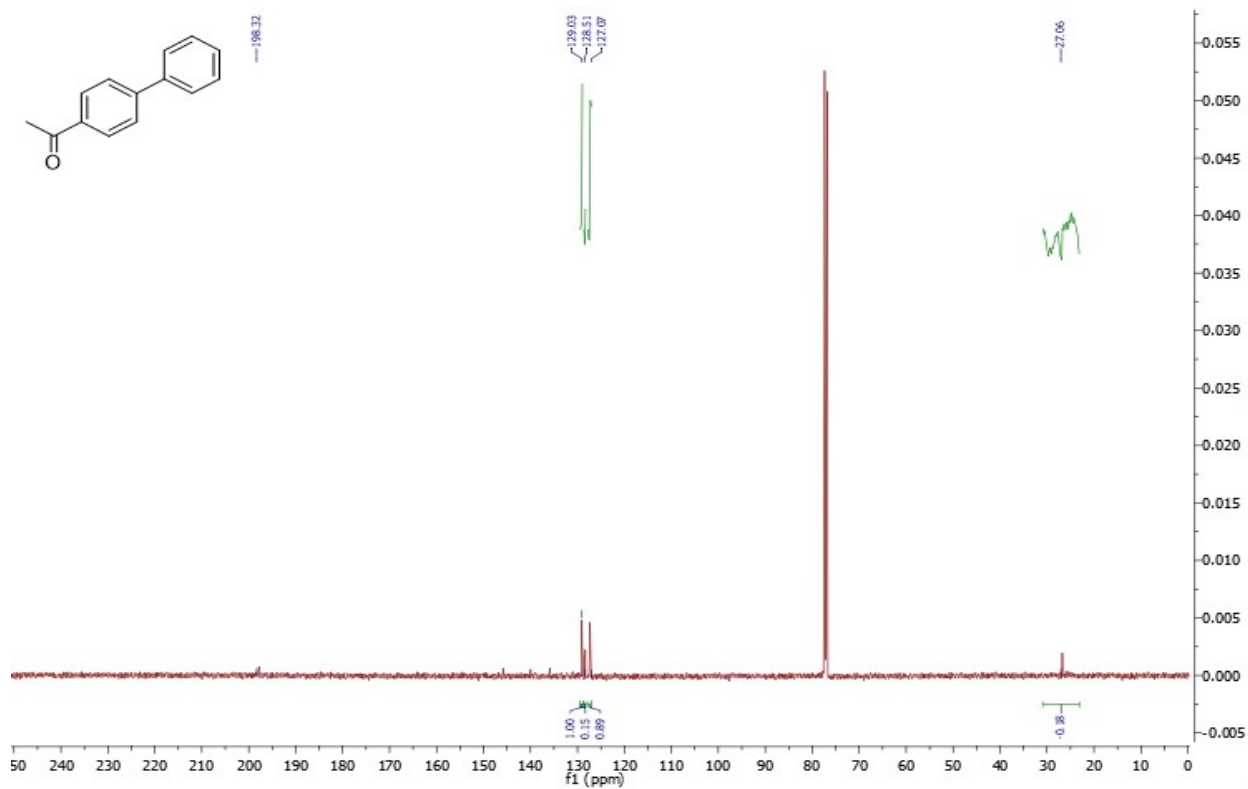
**Figure S19.**  $^1\text{H}$  NMR spectra of Biphenyl-4-carboxaldehyde compound by Stille coupling.



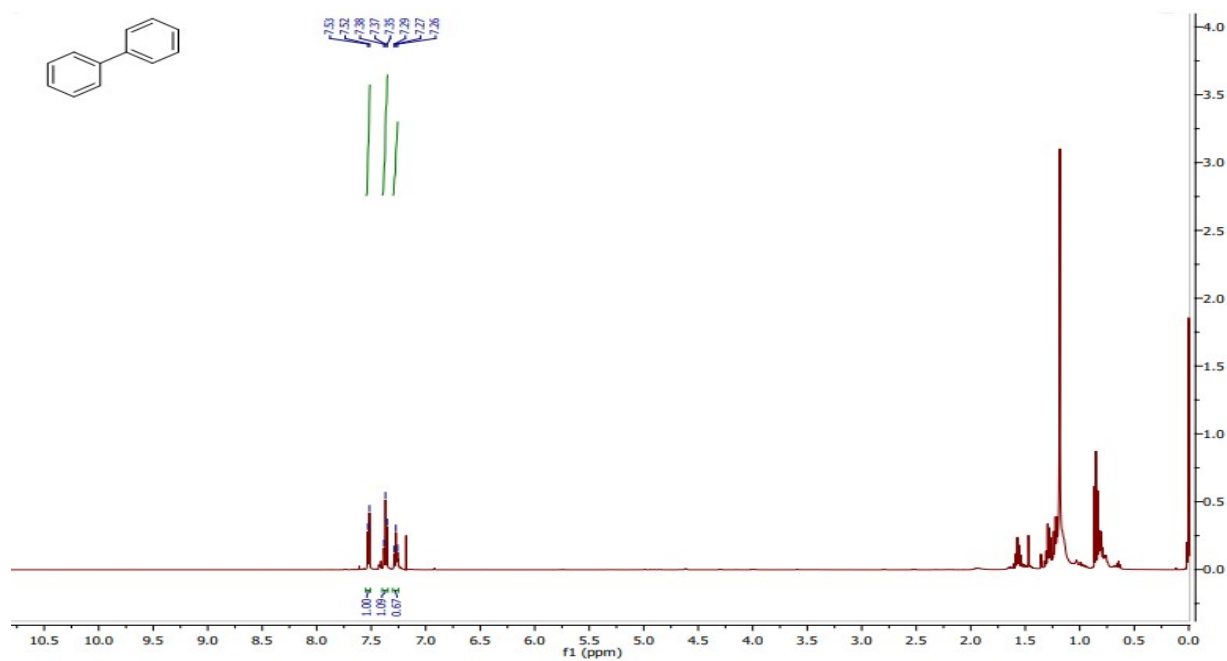
**Figure S20.**  $^{13}\text{C}$  NMR spectra of Biphenyl-4-carboxaldehyde compound by Stille coupling.



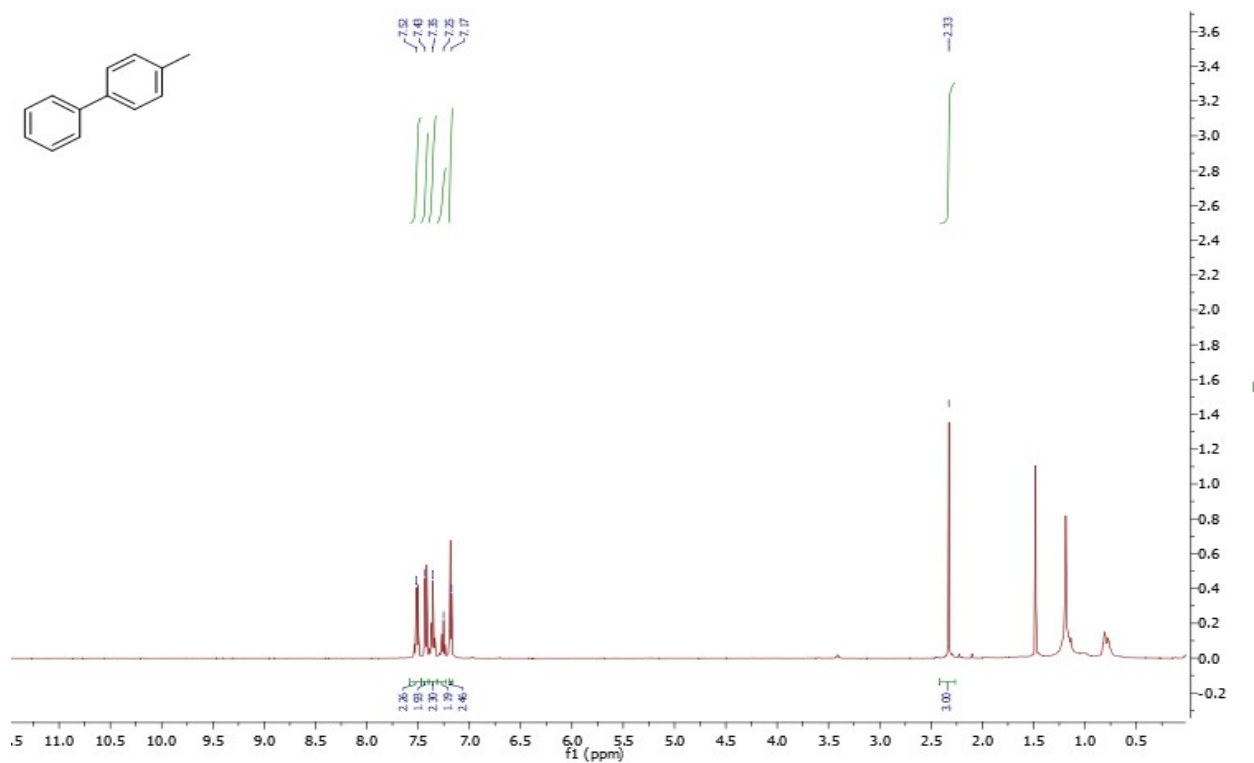
**Figure S21.**  $^1\text{H}$  NMR spectra of 4-Acetylbiphenyl compound by Stille coupling.



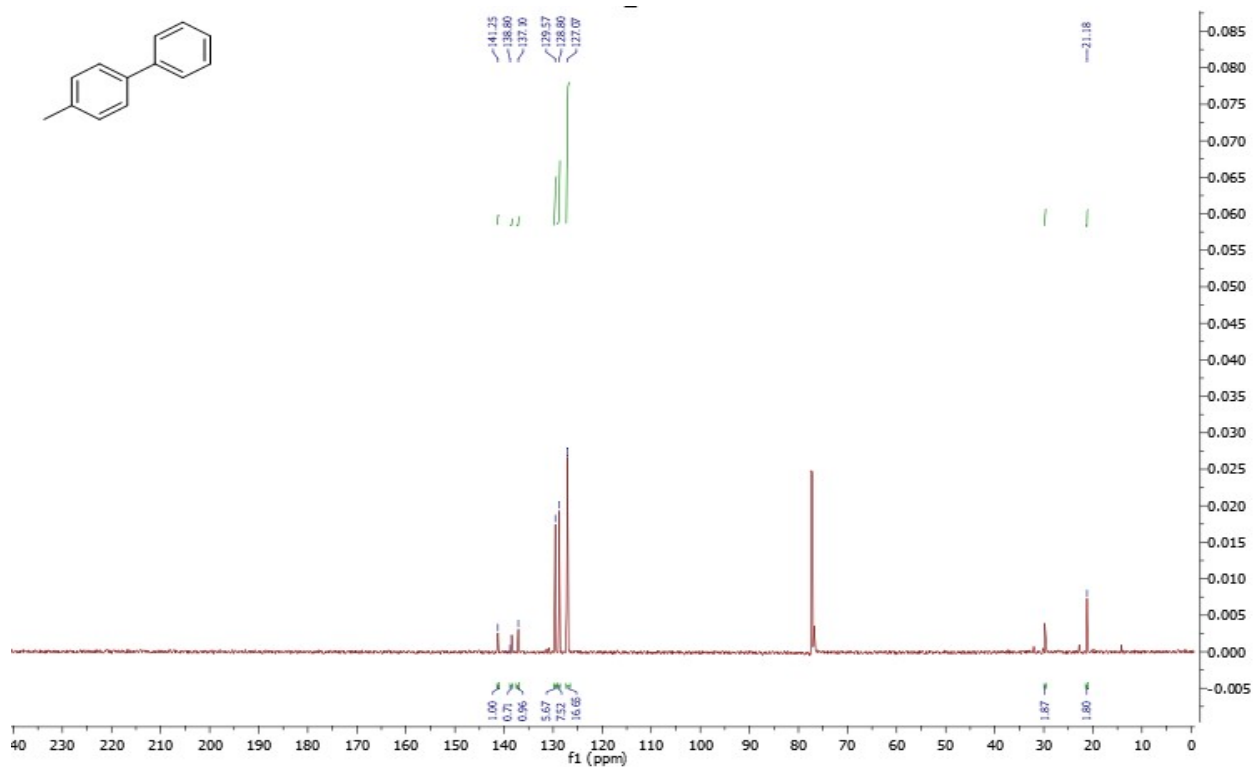
**Figure S22.**  $^{13}\text{C}$  NMR spectra of 4-Acetylbiphenyl compound by Stille coupling.



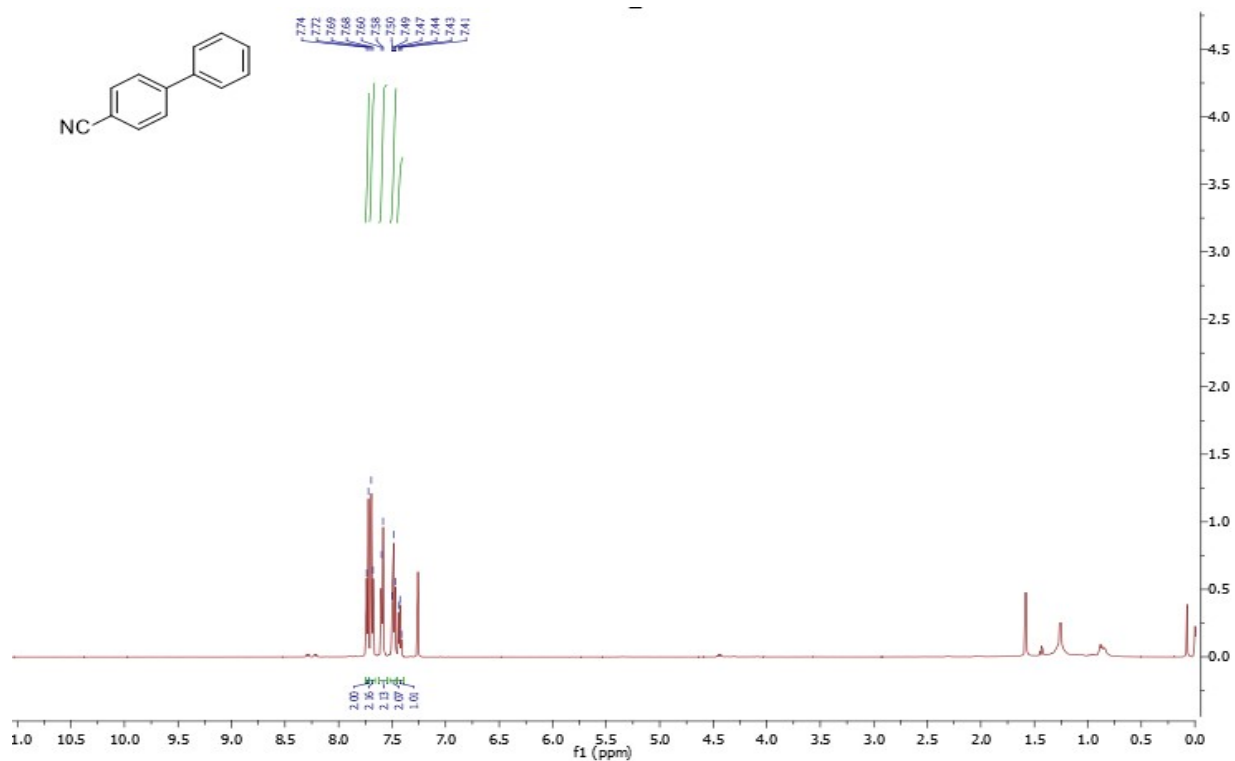
**Figure S23.**  $^1\text{H}$  NMR spectra of biphenyl compound by Hiyama coupling reaction.



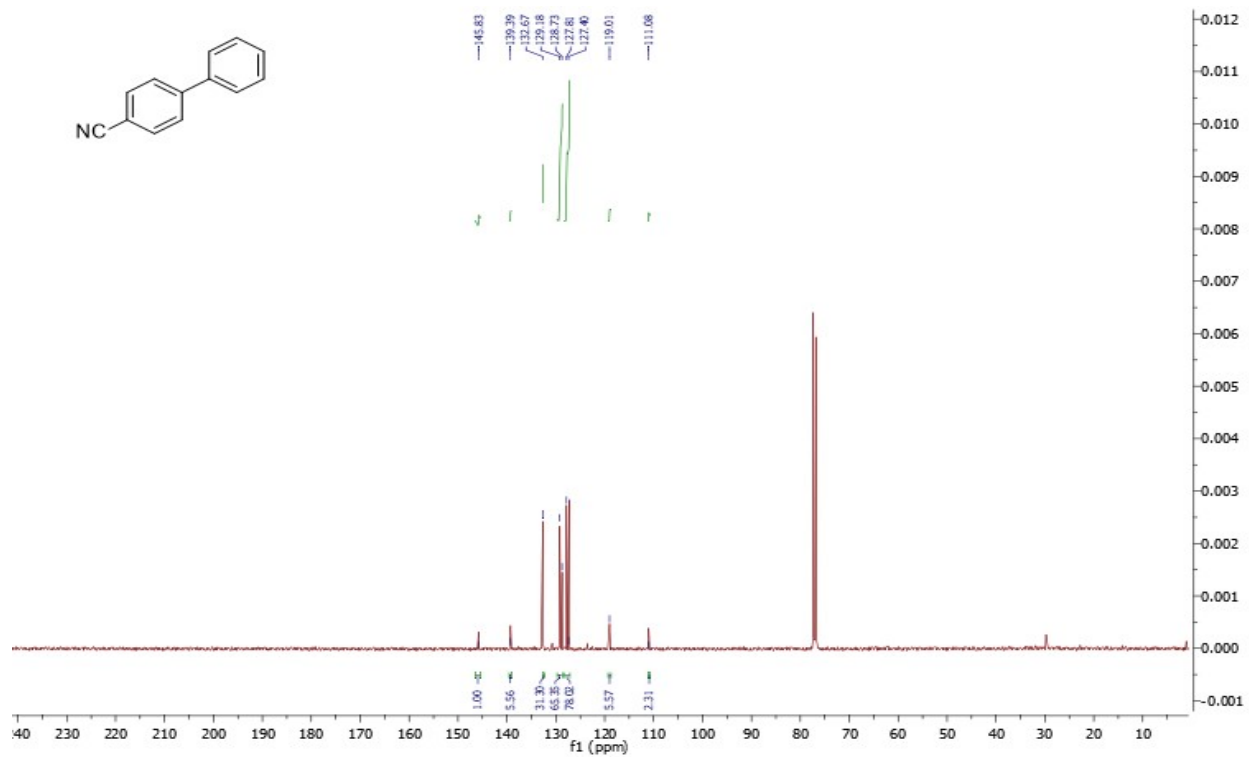
**Figure S24.** <sup>1</sup>H NMR spectra of 4-Methylbiphenyl compound by Hiyama coupling reaction.



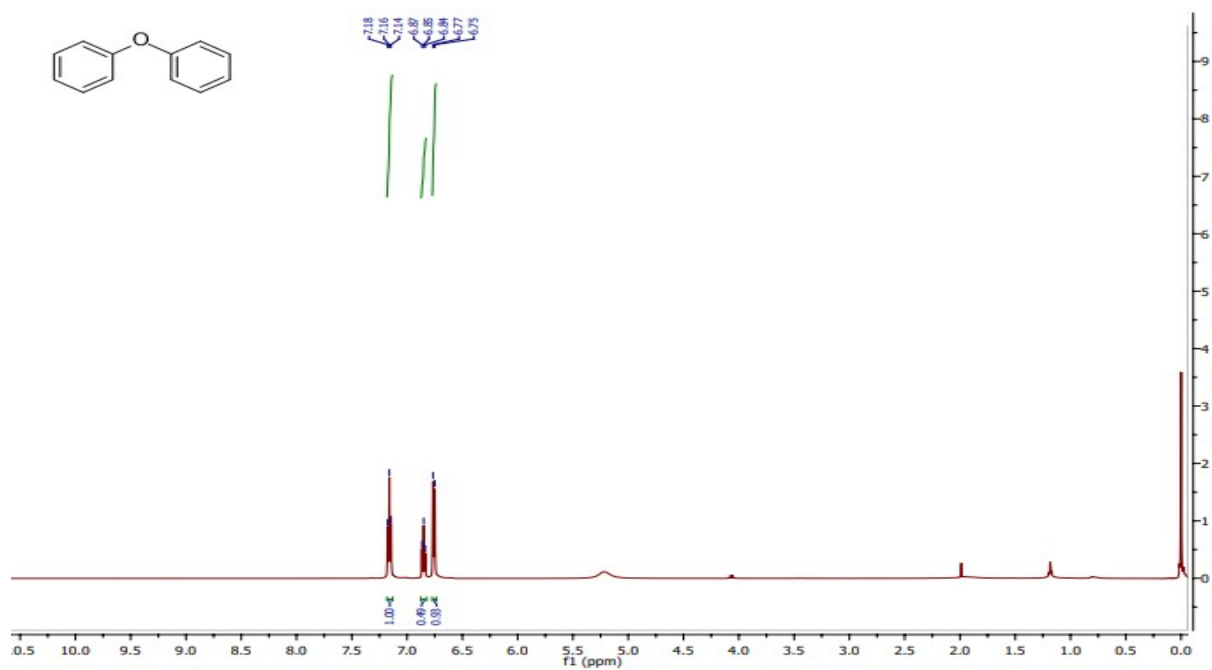
**Figure S25.** <sup>13</sup>C NMR spectra of 4-Methylbiphenyl compound by Hiyama coupling reaction.



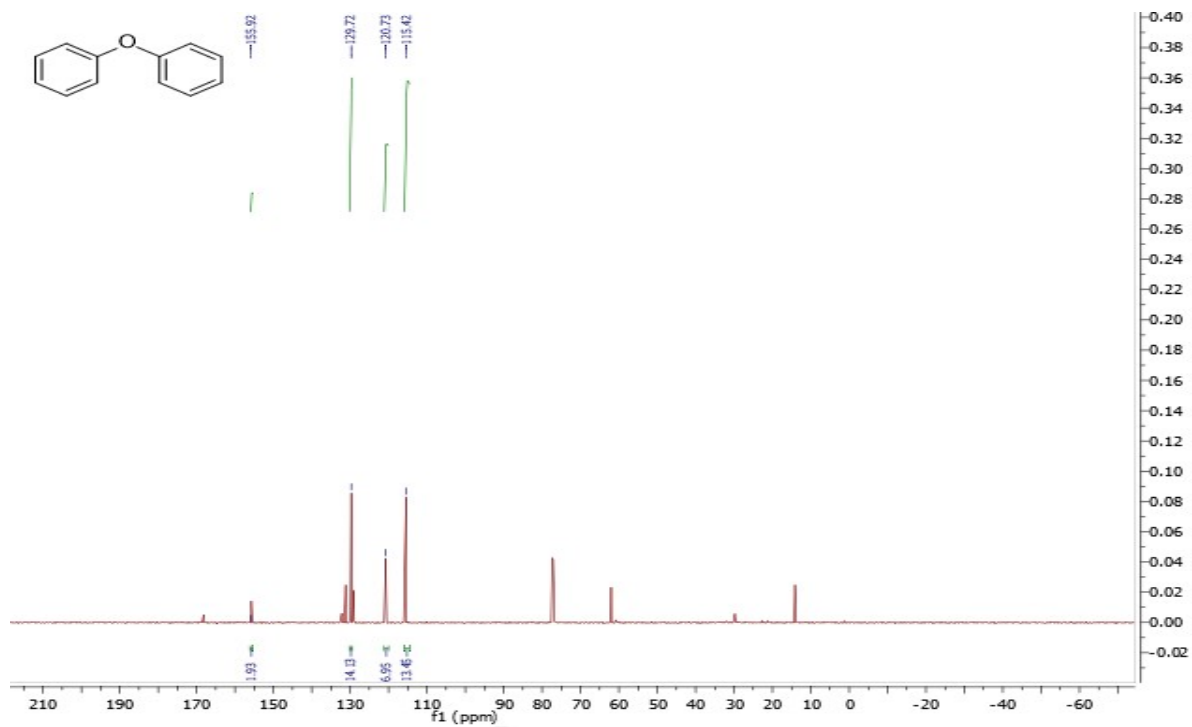
**Figure S26.** <sup>1</sup>H NMR spectra of 4-Cyanobiphenyl compound by Hiyama coupling reaction.



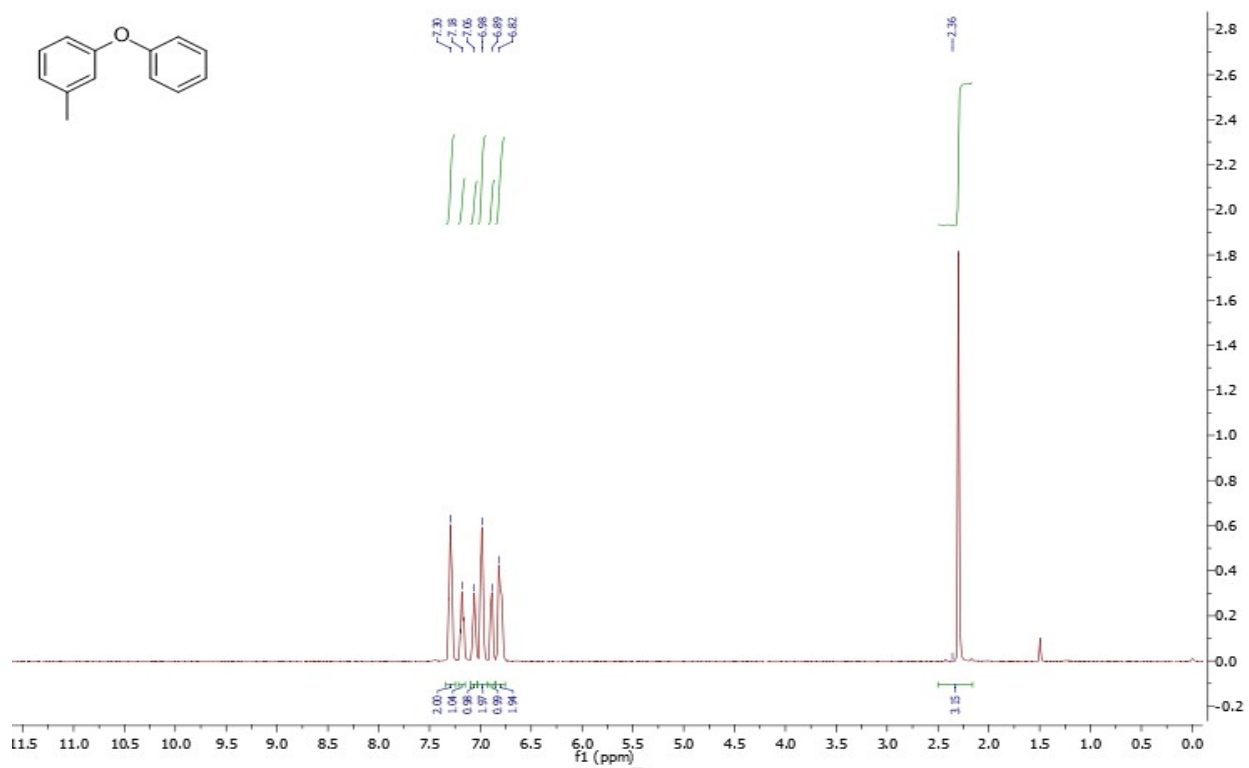
**Figure S27.** <sup>13</sup>C NMR spectra of 4-Cyanobiphenyl compound by Hiyama coupling reaction.



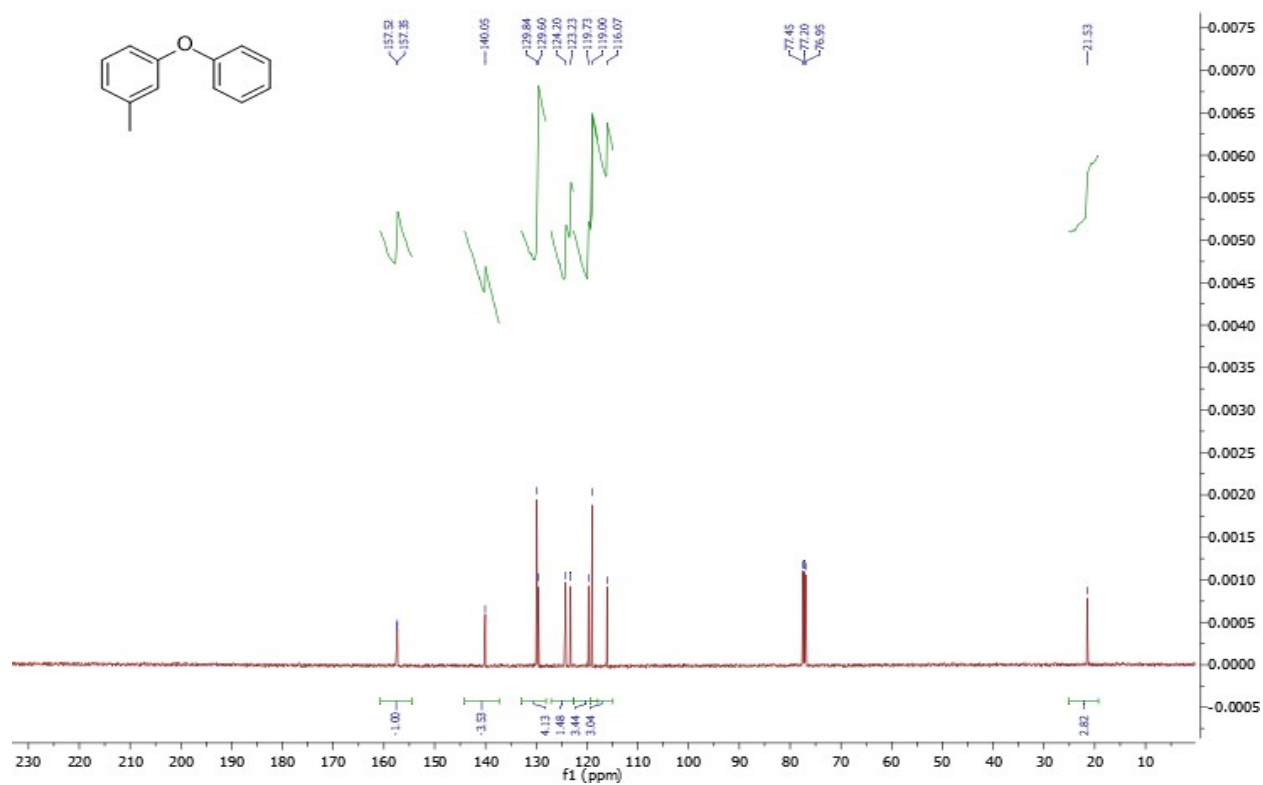
**Figure S28.** <sup>1</sup>H NMR spectra of diphenyl ether compound by Ullmann type reaction.



**Figure S29.** <sup>13</sup>C NMR spectra of diphenyl ether compound by Ullmann type reaction.

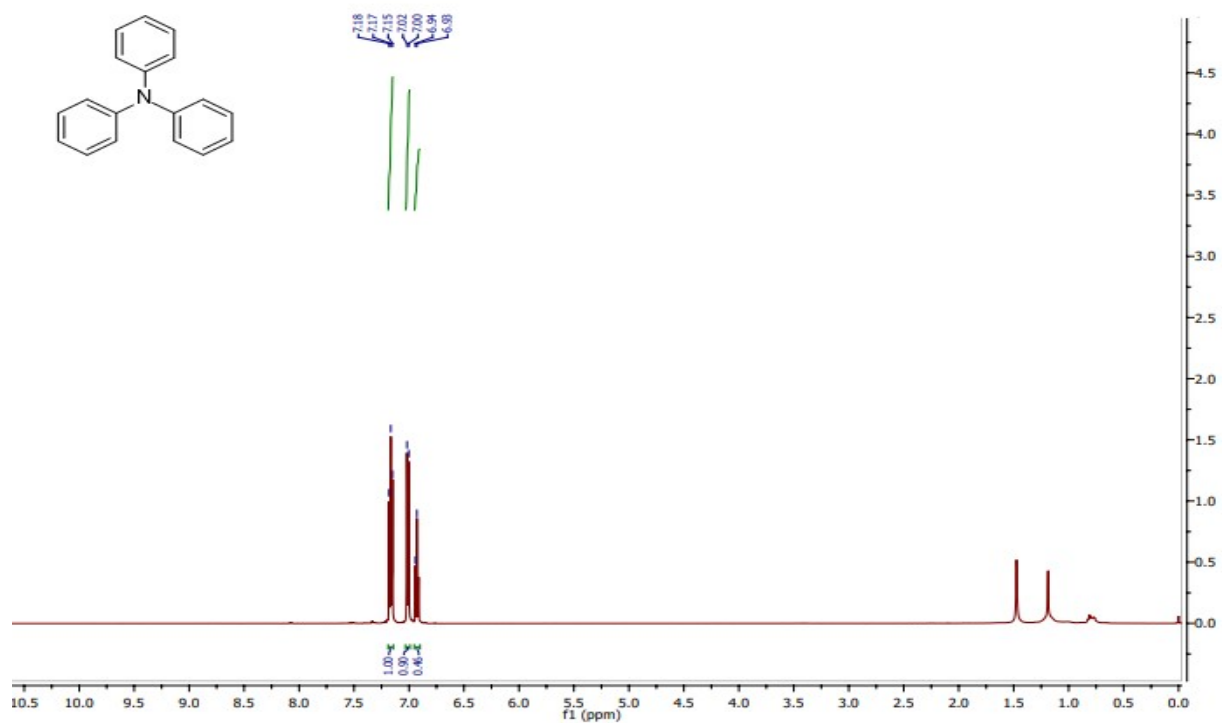


**Figure S30.** <sup>1</sup>H NMR spectra of 3-Phenoxytoluene compound by Ullmann type reaction.

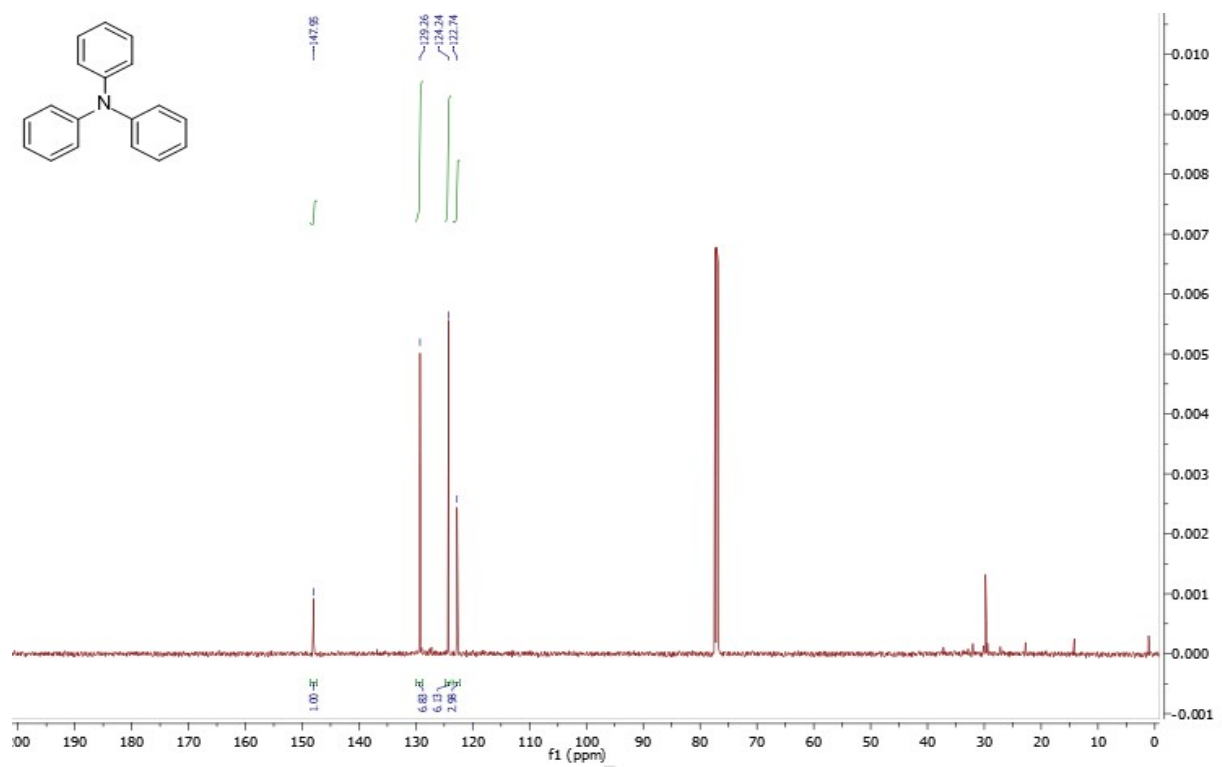


**Figure S31.** <sup>13</sup>C NMR spectra of 3-Phenoxytoluene compound by Ullmann type reaction.

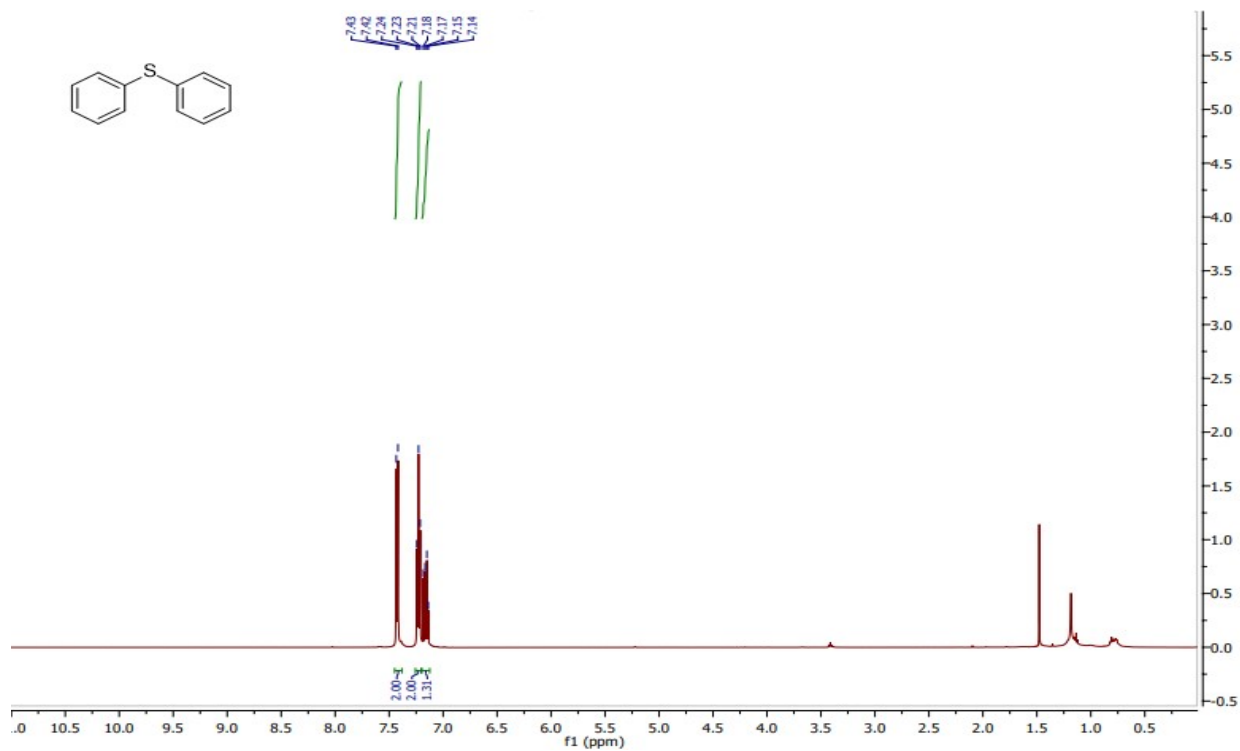




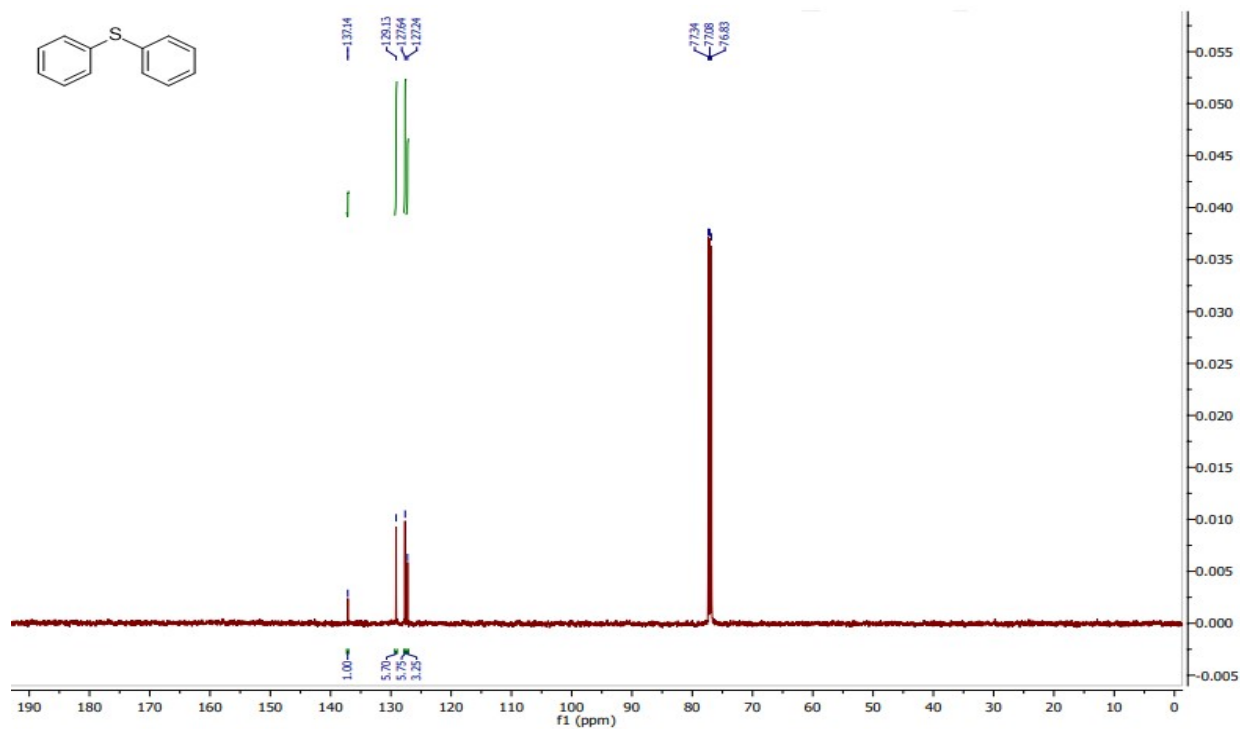
**Figure S32.** <sup>1</sup>H NMR spectra of triphenylamine compound by Buchwald Hartwig coupling



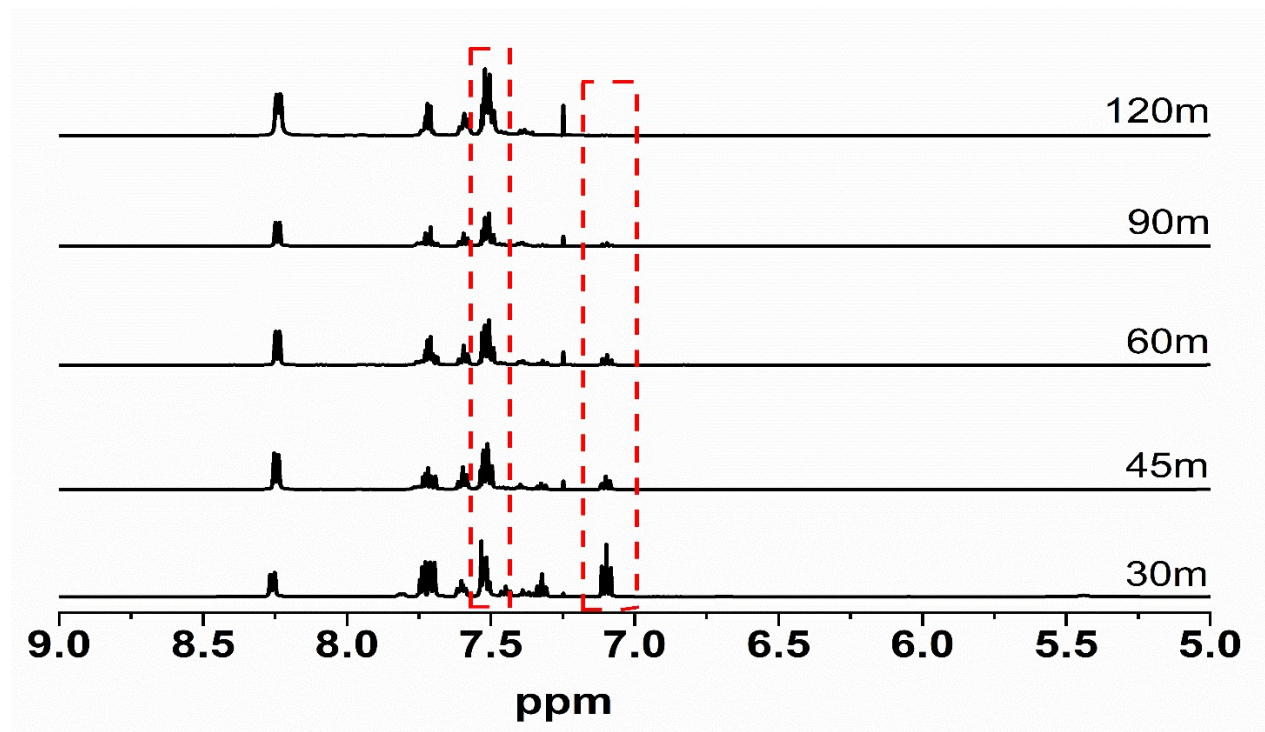
**Figure S33.** <sup>13</sup>C NMR spectra of triphenylamine compound by Buchwald Hartwig coupling reaction



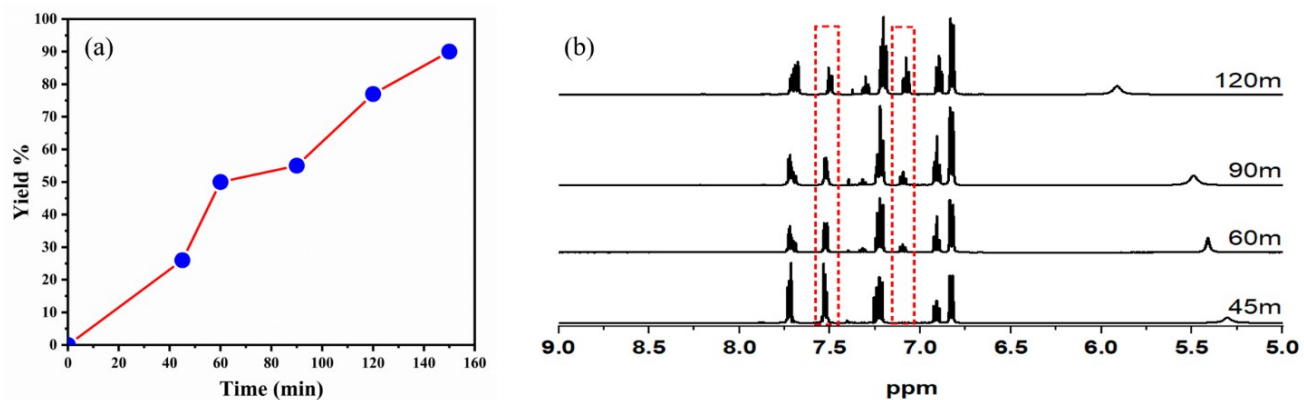
**Figure S34.** <sup>1</sup>H NMR spectra of diphenyl sulfide compound by C-S coupling reaction



**Figure S35.** <sup>13</sup>C NMR spectra of diphenyl sulfide compound by C-S coupling reaction



**Figure S36.** <sup>1</sup>H NMR spectra of the Suzuki-Miyaura reaction mixture at different time intervals that shows decrease in the intensity of proton signal of iodobenzene ( $\delta = 7.09$  ppm) and increase in the intensity of proton signal ( $\delta = 7.51$  ppm).



**Figure S37.** (a) % yield vs time plot of Ullmann type reaction. Reaction conditions: Phenol, Iodobenzene,  $K_2CO_3$ , EtOH,  $90\text{ }^\circ\text{C}$ . (b)  $^1\text{H}$  NMR spectra of the reaction mixture at different time intervals. The reaction yields are calculated from NMR study of the reaction mixture at different times of the reaction by comparing the intensity of the proton signal at position  $\delta = 7.50$  ppm of iodobenzene and the intensity of the proton at  $\delta = 7.15$  ppm of diphenyl ether.

### Calculation of Turn Over Number and Turn Over Frequency

For measuring turn over number, we have prepared the catalytic membrane with desired amount of Pd (50 nmol) by drop casting on nylon membrane ( $4\text{ cm}^2$ ). This membrane was utilized for catalysis to calculate TON by similar experiment. The reaction was carried out by dipping the membrane in a reaction mixture of 1 mmol Iodobenzene, 1.1 mmol Phenylboronic acid, and 2 mmol  $K_2CO_3$ , in 3 ml ethanol solvent. The turn over number (TON) and turn over frequency (TOF) of the reaction were calculated as below:

TON = Number of moles of reactant consumed / Number of moles of catalyst

TOF = TON/time of reaction

#### For Suzuki – Miyaura reaction:

TON = 1 mmol / 35 nmol

$$= 2.8 \times 10^4$$

TOF = TON/time =  $2.8 \times 10^4 / 9000\text{ s}^{-1} = 3.11\text{ s}^{-1}$

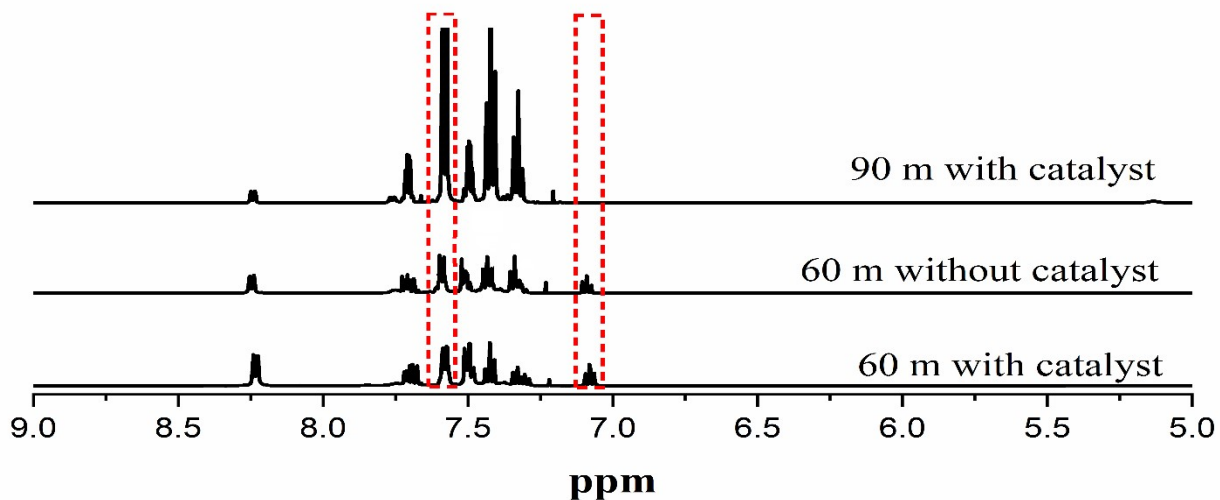
#### For Ullmann reaction:

TON = 1 mmol / 50 nmol

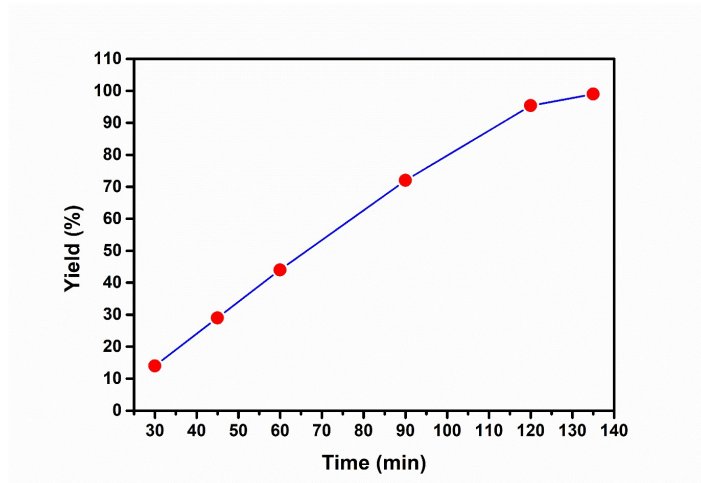
$$= 2 \times 10^4$$

TOF =  $2 \times 10^4 / 10800\text{ s}^{-1} = 1.85\text{ s}^{-1}$

**Dip-catalyst stability study:**



**Figure S38.** <sup>1</sup>H NMR spectra of the Suzuki-Miyaura reaction mixture at different time intervals with and without catalyst showing the stability of the catalyst. Here we compare the intensity of two peaks at  $\delta = 7.09$  ppm and  $\delta = 7.59$  ppm. The peak intensity at  $\delta = 7.09$  ppm and  $\delta = 7.59$  ppm remains almost the same in the absence of the catalyst showing very little leaching of Pd. But with reinsertion of the dip-catalyst the intensity of both the peaks changes (peak at  $\delta = 7.09$  ppm disappears while intensity of peak at  $\delta = 7.59$  ppm is maximum).



**Figure S39.** Progress of the Suzuki–Miyaura reaction of phenylboronic acid with iodobenzene in ethanol using  $K_2CO_3$  as the base and P4VP-PdNP composite membrane as catalyst after 10 rounds of recycling.

Reaction	Reactant Conc.	Catalyst Conc.(nmol)	Time (in h)	TON	TOF in $s^{-1}$
Suzuki	1 mmol	24.8	5.30	$4.0 \times 10^4$	2.42
		37.2	3	$2.6 \times 10^4$	2.40
		50.0	2.15	$2.0 \times 10^4$	2.96

Table S1 comparison of the catalytic activity of PdNP based “dip catalysis” reported in the earlier literature

Catalytic system based on Pd nanoparticle	Reactions performed	Different type reactions performed using single catalytic system (total no.)	Maximum Turnover number (TON), Turn over frequency (TOF), Number of cycles (NOC) performed	Reference

PVA-PdNP	Suzuki–Miyaura, Heck and Sonogashira coupling reactions	3	TON: 1667 TOF: 1102 h <sup>-1</sup> NOC: 30	1
Cellulose-PdNP	Suzuki-Miyaura cross-coupling, C5-arylation of 2-substituted Thiophenes,	2	..... NOC: 15	2
Pd nanoparticle-embedded Bacterial cellulose	Suzuki–Miyaura reaction	1	TOF: 60.3 h <sup>-1</sup> NOC: 26	3
PdNP-PS-b-PAA	Suzuki–Miyaura reaction	1		4
PdNP-polyacrylic acid (PAA) or polyvinyl alcohol (PVA) and CNT	Reduction of nitrophenol	1	NOC: 08	5
Pyrenyl Graphdiyne Supported Pd Nanoparticle	Reduction of 4-Nitrophenol	1	NOC: 06	6
PdNP-Jute Stem	Hydrogenation of numerous styrenyl and unfunctionalized olefins	1	TOF: 4938 h <sup>-1</sup> NOC: 36	7
Palladium Nanoparticle-loaded Cellulose Paper	Oxidative homocoupling of arylboronic acids, Suzuki cross-coupling reaction, and nitro to amine reduction	3	TON: 5808 NOC: 11	8
PdNP-P4VP membrane	Suzuki-Miyaura, Sonagashira, Stille, Negishi, Heck, Ullmann, Hartwig and C-S coupling reaction	8	TON $\geq$ X10 <sup>4</sup> and TOF: 3.11s <sup>-1</sup> NOC: up to 10 cycles were performed	This work

## References:

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