

**Supplementary information for:**

## **Recyclable palladium-graphene nanocomposite catalysts containing ionic polymers: efficient Suzuki coupling reactions**

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## Experimental Section

### Synthesis of pyrene-functionalized PDMAEMA-*b*-PPEGMEMA ionic block polymer.

According to the typical atom transfer radical polymerization (ATRP) technique, the reagents CuCl (0.75 mmol, 77.7 mg), dNbpy (1.5 mmol, 0.64 mg), 2-(dimethylamino)ethyl methacrylate (DMAEMA) (18.8 mmol, 3.2 mL), anisole (10.5 mL), and a solution of 2-EBP (0.6 mmol, 0.9 mL, 700 mM in toluene) were sequentially added. The reaction mixture was stirred at 80 °C for 14 h, and around 97% conversion was observed. According to an in-situ process, poly(ethylene glycol) methyl ether methacrylate (PEGMEMA) monomer (18.8 mmol, 8.97 mL) was sequentially injected into the unpurified PDMAEMA solution and then the reaction was stirred for 16 h, yielding around 97% conversion. For its purification, the reaction solution was quenched upon cooling to -78 °C immediately using liquid nitrogen and then diluted with 30 mL of THF. This solution was passed through an aluminium oxide column with extra THF. After concentration of collected solution under reduced pressure, the solution was dropped into hexane. Thereafter, precipitates were separated from the liquid by a decantation process. The obtained precipitates were dissolved in THF and then the precipitation process was repeated 3 cycles. Finally obtained PDMAEMA-*b*-PPEGMEMA block copolymer was dried at RT for 48 h, yielding MW: 19k and MWD: 1.09. The obtained resulting product was functionalized with an addition of pyrene moiety into PDMAEMA block through the Menshutkin reaction. For this, 0.5 g of PDMAEMA-*b*-PPEGMEMA was dissolved in DMF (9.6 mL) and then 1-(bromomethyl)pyrene (0.39 mM, 0.116g) was added to the prepared solution. The reaction was completed after heating the reaction mixture at 60 °C for 24 h, yielding pyrene-functionalized PDMAEMA-*b*-PPEGMEMA ionic block polymer with 14 pyrene units per chain in over 95% yield. Purification was performed by precipitation in 200 mL of hexane after removal of DMF and then dissolving in THF. The resulting product, pyrene-functionalized poly(dimethylaminoethyl methacrylate)-*b*-poly[(ethylene glycol) methyl ether methacrylate] (Py-PDMAEMA-*b*-PPEGMEMA) ionic block copolymers, were dried at RT for 48 h under reduced pressure. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, δ) (ppm): 7.9-8.4 (broad, pyrene), 5.2-5.7 (broad, 2H, NCH<sub>2</sub>pyrene), 4.2-4.8 (broad, 2H, OCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Pyrene), 4 (t, 2H, OCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 3.4-3.8 (broad, 4H, CH<sub>2</sub>CH<sub>2</sub>O) 3.36 (s, 3H, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 2.5 (t, 2H, OCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 2.3 (s, 6H, OCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 1.6-2.1 (broad, 2H, CH<sub>2</sub>CCH<sub>3</sub> backbone), 0.7-1.3 (broad, 3H, CH<sub>2</sub>CCH<sub>3</sub> backbone).

### ***Synthesis of graphene oxide (GO).***

GO dispersion was prepared by the oxidative exfoliation of graphite powder (Sigma Aldrich, Graphite flakes), following modified Hummer's method. Briefly, 1 g of graphite powder was oxygenated in 40 mL H<sub>2</sub>SO<sub>4</sub>, while stirring for 15 min, which was followed by slow adding of 3.5 g potassium permanganate under an ice bath. The mixture was then continuously stirred for 24 h at 35 °C. After completion oxygenation, the excess amount of deionized water and 35% H<sub>2</sub>O<sub>2</sub> were added to the mixture. The obtained yellow mixture was thoroughly filter washed with 1 M HCl solution and deionized water and re-dispersed in 1 L of deionized water. The monolayer exfoliation was achieved by the sonication of the washed GO dispersion in water bath ultrasonicator. Subsequent purification was performed by dialysis and centrifugation to remove ionic impurities and unexfoliated graphite oxides. A predetermined amount of the concentrated dispersion was diluted in deionized water to prepare the GO dispersions with a desired composition.

### ***Synthesis of reduced graphene oxide (rGO).***

Reduced graphene oxide (rGO) was synthesized through a high temperature thermal annealing of freeze-dried GO in temperature controlled furnace. First, the freeze-dried GO was placed in quartz tube and placed into the furnace at 100 °C for 1 hr. Then, the furnace temperature was increased with the rate of 10 °C/min up to 1000 °C and kept for 1 hour. Thereafter, the furnace temperature was allowed to cool down to room temperature and rGO powder was collected from quartz tube. All the reactions were performed under continuous flow of Ar gas.

### **Calculation of the average crystalline size**

The average crystalline size of Pd NPs in Pd-IPG was calculated by the relation of Scherrer equation:

$$D_s = \frac{K\lambda}{\beta_{hkl}\cos\theta} \quad (\text{S1})$$

where  $D$  is crystalline size,  $K$  is shape factor (0.9),  $\lambda$  is wavelength of  $\text{CuK}\alpha$  radiation, and  $\beta_{hkl}$  is full width of half maximum (FWHM).

**Table S1.** Structural parameters of Pd-IPG.

Catalyst	$2\theta$	$d$ (nm)	$\beta_{hkl}$	FWHM (rad)	$D_S^{[a]}$ (nm)	$D_{STEM}^{[b]}$ (nm)
Pd-IPG	39.5	0.22	(111)	0.02670	8.4	Large numbers (3-5 nm), Small numbers (15-30 nm)

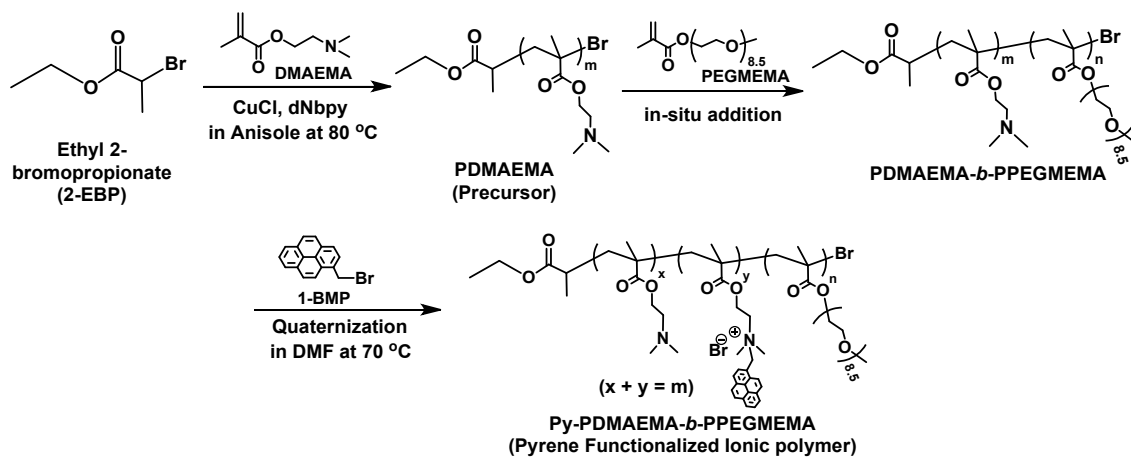
<sup>[a]</sup>  $D_S$  was deduced from the relation of Scherrer formula. <sup>[b]</sup>  $D_{STEM}$  was measured by using STEM images.

**Table S2.** Catalytic performances and reaction conditions of various Pd-based heterogeneous catalysts in the Suzuki coupling reaction of iodobenzene with phenylboronic acid.

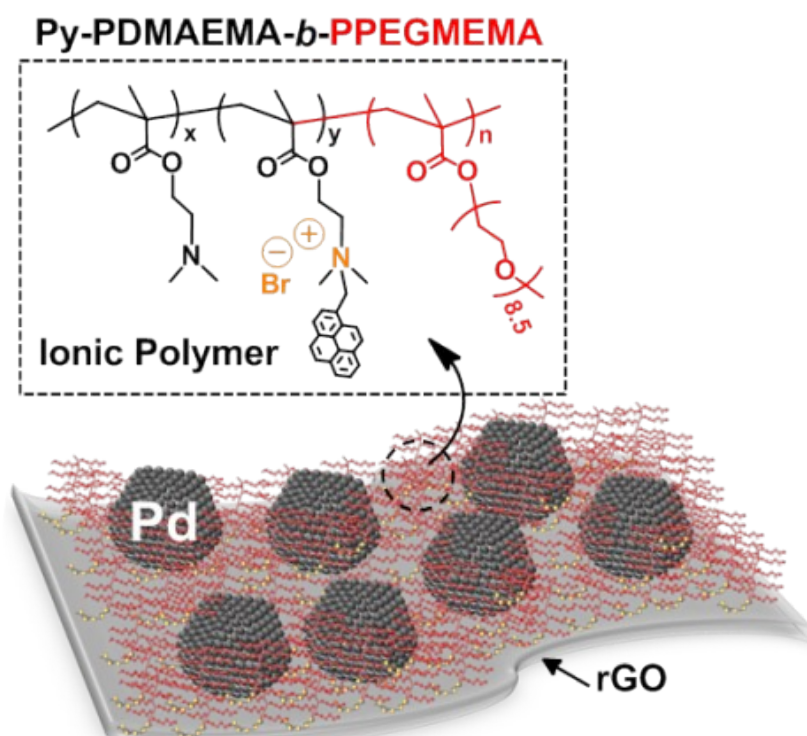
Entry	Catalyst	Solvent	Base	Temperature (°C)	Time (h)	Yield <sup>[a]</sup> (%)	TOF <sup>[b]</sup> (h <sup>-1</sup> )	Ref.
1	Pd NPs	H <sub>2</sub> O	Na <sub>2</sub> CO <sub>3</sub>	80	24.0	97	40	1
2	Pd-Fe <sub>3</sub> O <sub>4</sub>	DME-H <sub>2</sub> O (3:1)	Na <sub>2</sub> CO <sub>3</sub>	Reflux	24.0	99	41	2
3	Pd/Polymer colloids	DMF-H <sub>2</sub> O (1:1)	K <sub>2</sub> CO <sub>3</sub>	50	1.5	97	645	3
4	Silica@Pd-ZnMOF	EtOH	K <sub>3</sub> PO <sub>4</sub>	80	2.0	92	79	4
5	Pd-CNT	DMF	Na <sub>2</sub> CO <sub>3</sub>	110	24.0	94	13	5
6	Pd/SiC-CNT	EtOH-H <sub>2</sub> O (4:1)	K <sub>3</sub> PO <sub>4</sub>	60	1.0	98	350	6
7	Pd/CNT-graphene	EtOH-H <sub>2</sub> O (1:1)	K <sub>2</sub> CO <sub>3</sub>	60	0.25	>99	799	7
8	Pd-Fe <sub>3</sub> O <sub>4</sub> @C	EtOH	K <sub>2</sub> CO <sub>3</sub>	Reflux	1.0	100	325	8
9	Pd-rGO	EtOH-H <sub>2</sub> O (1:1)	NaOH	60	3.0	92	61	This Work
10	Pd-IPG	EtOH-H <sub>2</sub> O (1:1)	NaOH	60	1.0	99	990	This Work

<sup>[a]</sup> GC yield was calculated by using anisole as an internal standard. <sup>[b]</sup> TOF value was calculated using the equation as follows

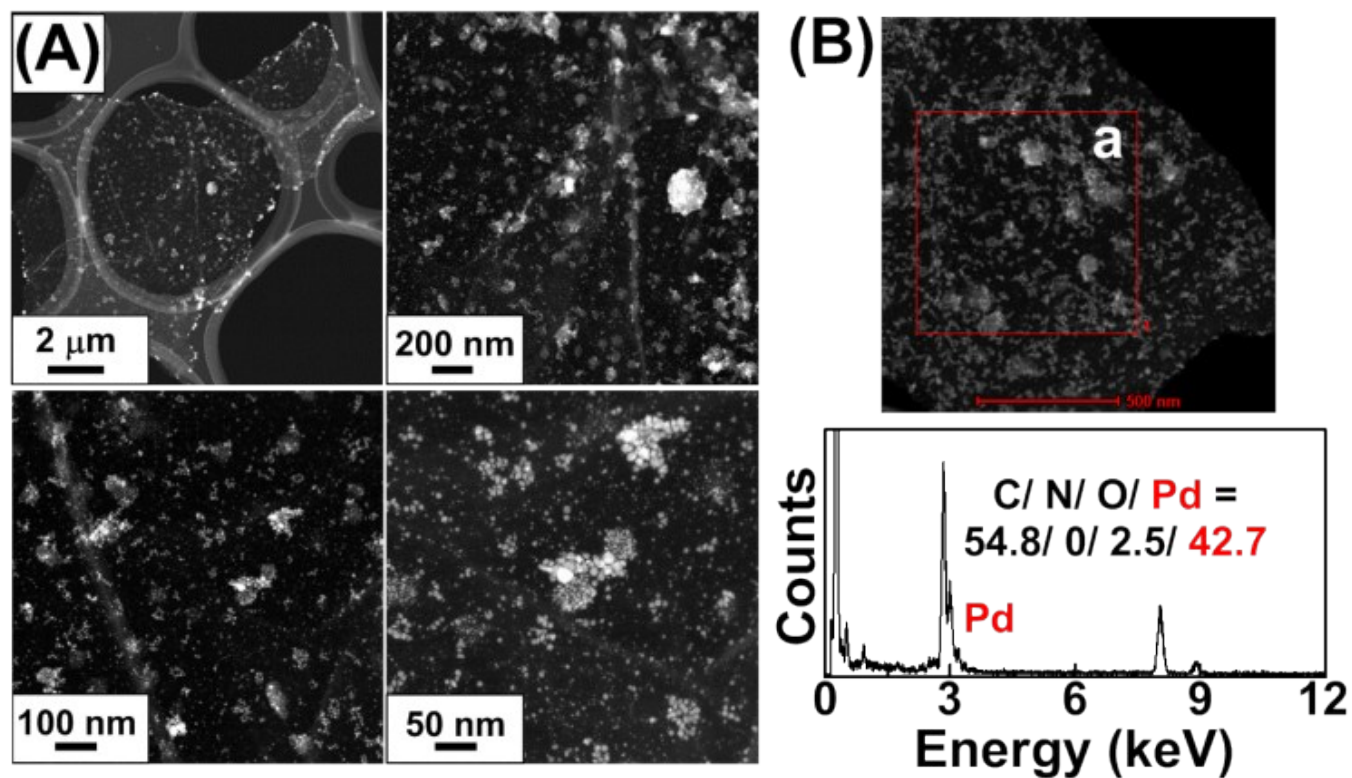
$$\text{TOF} = \frac{M_{\text{Sub}} \times \text{Yield}(\%)}{M_{\text{cat}} \times \text{Yield}(\%)}$$



**Scheme S1.** Synthesis of pyrene functionalized PDMAEMA-*b*-PPEGMEMA ionic polymer.

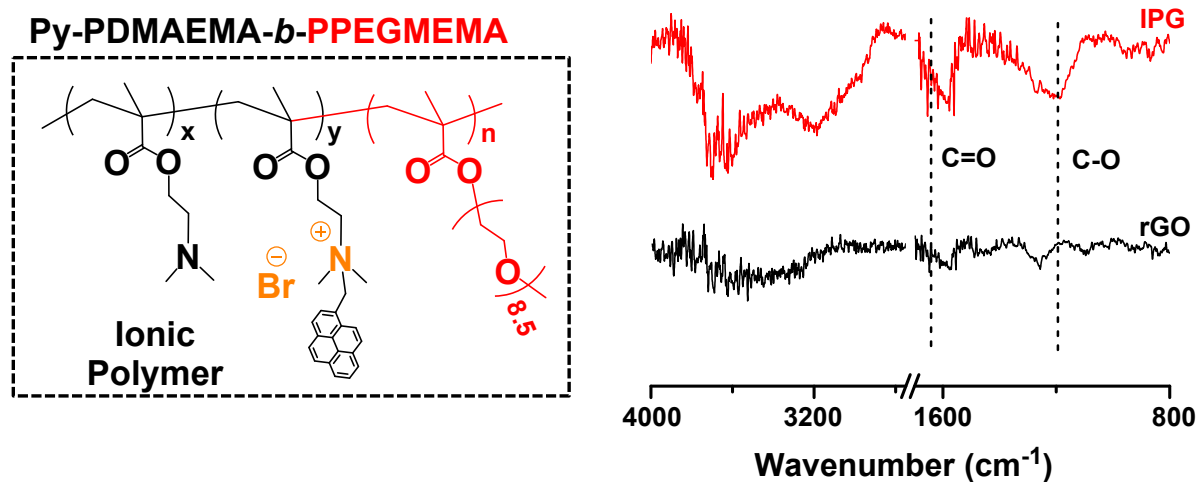


**Scheme S2.** Illustration of the Pd-IPG nanocomposite catalyst with the chemical structure of pyrene functionalized poly(dimethylaminoethyl methacrylate)-*b*-poly[(ethylene glycol) methyl ether methacrylate] (Py-PDMAEMA-*b*-PPEGMEMA) ionic polymer on the rGO support.



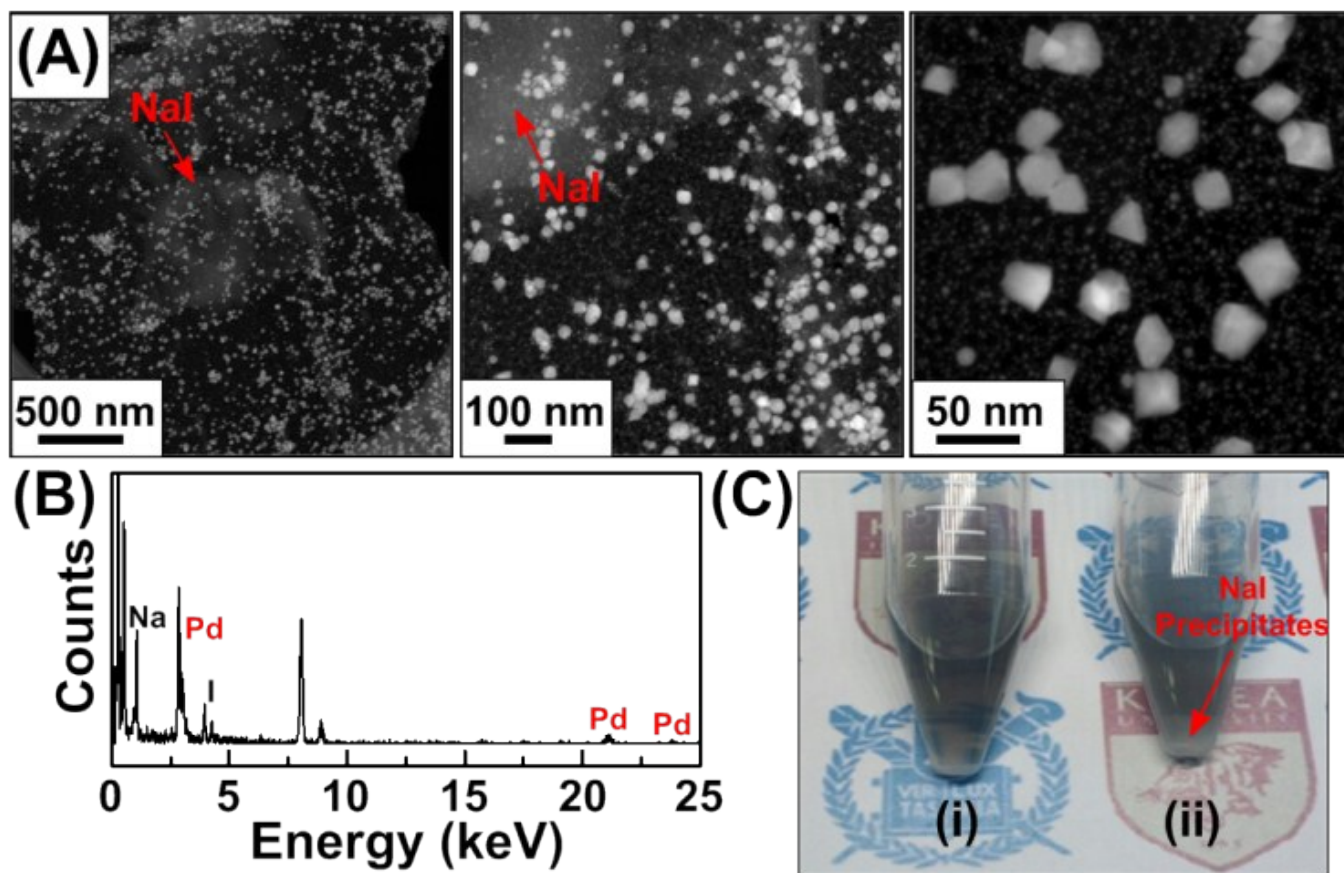
**Fig. S1** (A) Representative STEM images and (B) STEM-EDX spectrum of Pd-rGO scanned on the region marked on inset a.

The STEM images of Pd-rGO showed relatively aggregated and partially decorated Pd NPs on the rGO support (Fig. S1A). The content of Pd NPs in Pd-rGO (42.7 wt.%) was almost similar to that of Pd-IPG (49.7 wt.%).



**Fig. S2** The chemical structure of the pyrene-functionalized PDMAEMA-*b*-PPEGMEMA ionic polymer (left). FT-IR spectra of rGO and IPG (right).

We have obtained the FT-IR spectra of rGO and IPG to confirm the ionic polymer doping on the rGO surface. We found highly increased adsorption peaks corresponding to C-O stretch (1050-1300 cm<sup>-1</sup>), which is originated from the long ethylene oxide groups in the PPEGMEMA block corroborating the presence of the ionic polymers onto the rGO. From this investigation, we can confirm the presence of ionic polymers on the rGO surface.



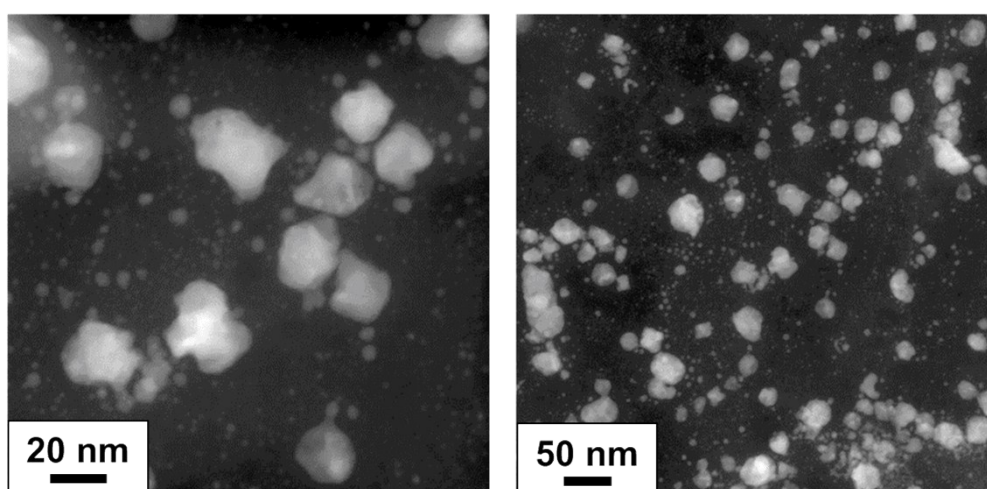
**Fig. S3** (A) Representative STEM images and (B) STEM-EDX spectrum of Pd-IPG after ten repeated reaction cycles. (C) Photograph of the reaction solutions with Pd-IPG (i) before and (ii) after the recycle test (ten cycles).



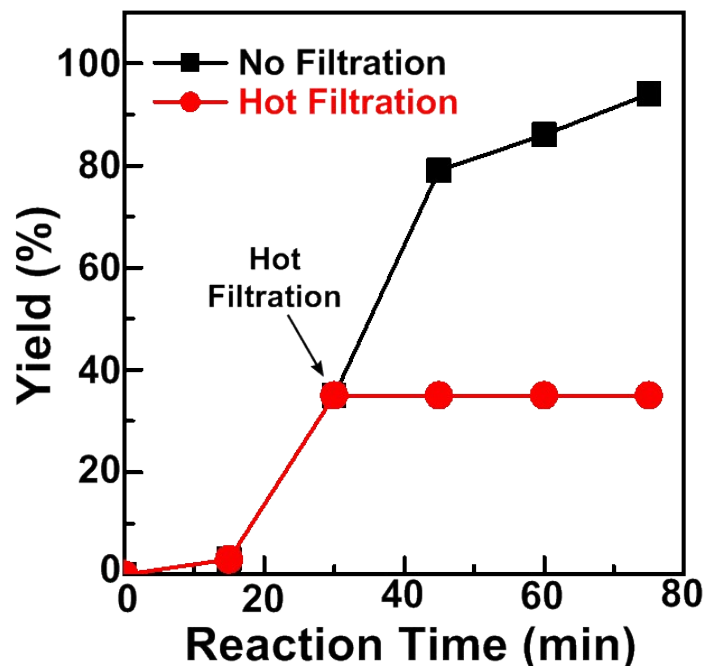
**Table S3.** Recyclability tests of Pd-IPG for the Suzuki coupling reaction of iodobenzene with phenylboronic acid under optimized conditions.<sup>[a]</sup>

Runs	11th	12th	13th	14th	15th	16th	17th	18th	19th	20th
Yield (%)	99	96	98	95	89	91	87	97	99	98
Time (h)	1	1	1	1	1	1	1	1.5	1.5	1.5

[a] Reaction conditions : Pd-IPG (0.1 mol%), Iodobenzen (0.1 mmol), Phenylboronic acid (0.12 mmol), base (0.2 mmol), and solvent (0.8 mL) at 60 °C under air.



**Fig. S4** Representative STEM images of the Pd-IPG after 20 repeated reaction cycles.



**Fig. S5** Yields of the Suzuki coupling reactions between iodobenzene and phenylboronic acid with and without hot-filtration (the reaction was catalyzed by Pd-IPG and performed under the optimized conditions).

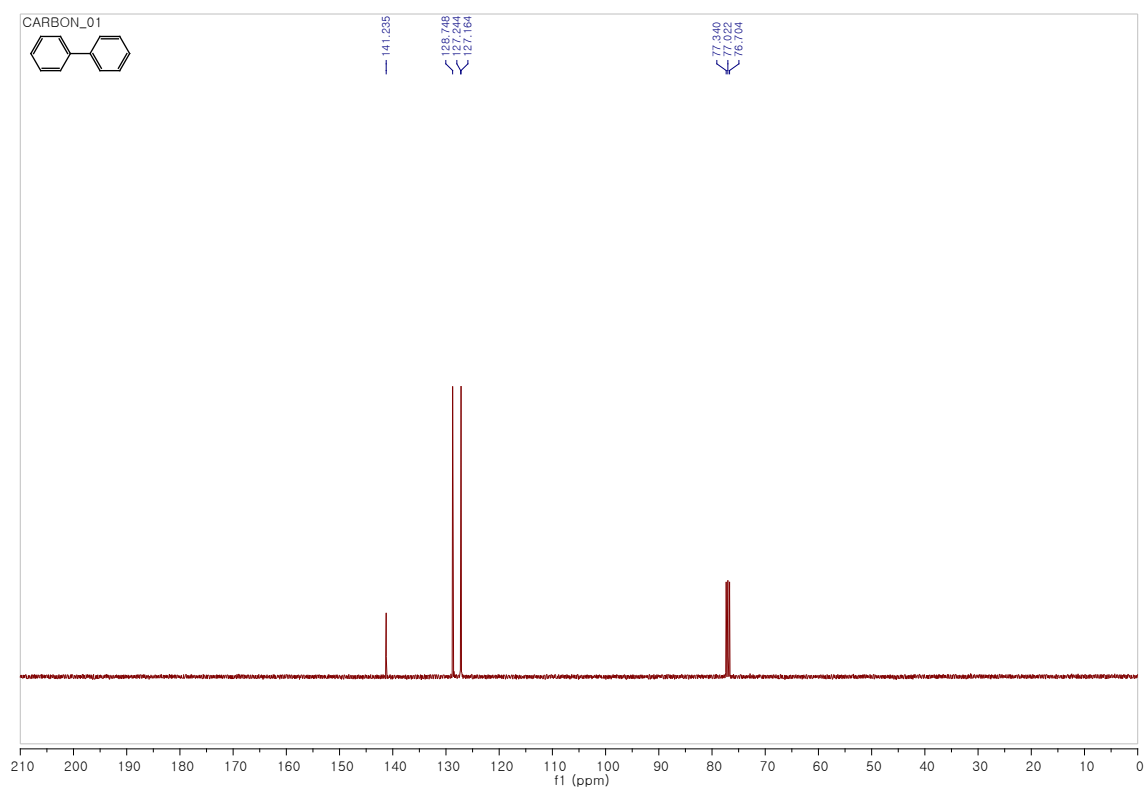
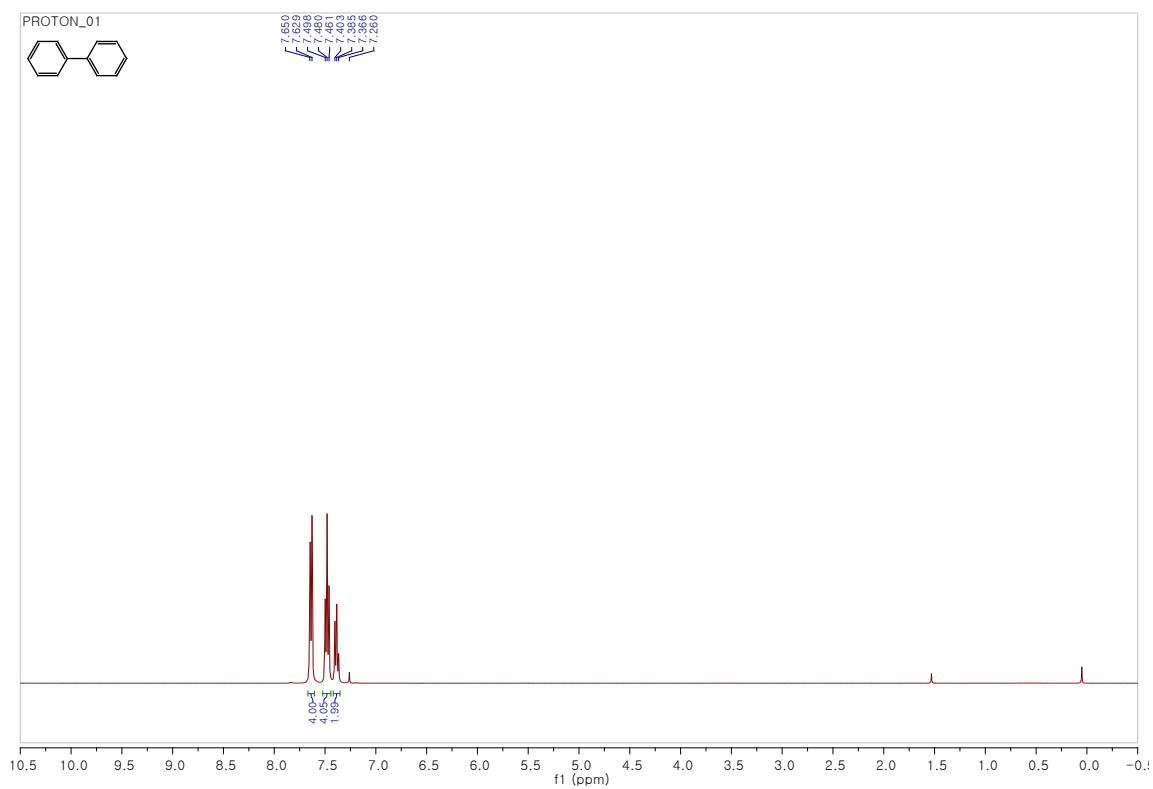
We examined the yields of the product biphenyl according to the Suzuki reaction every 15 minutes. At 15 min, the yield was very low (3%). There may be an induction period when a part of the Pd NPs from the Pd-IPG catalyst system leaches out into the solution and gets trapped alongside the ionic polymer species as an active Pd species.

## References

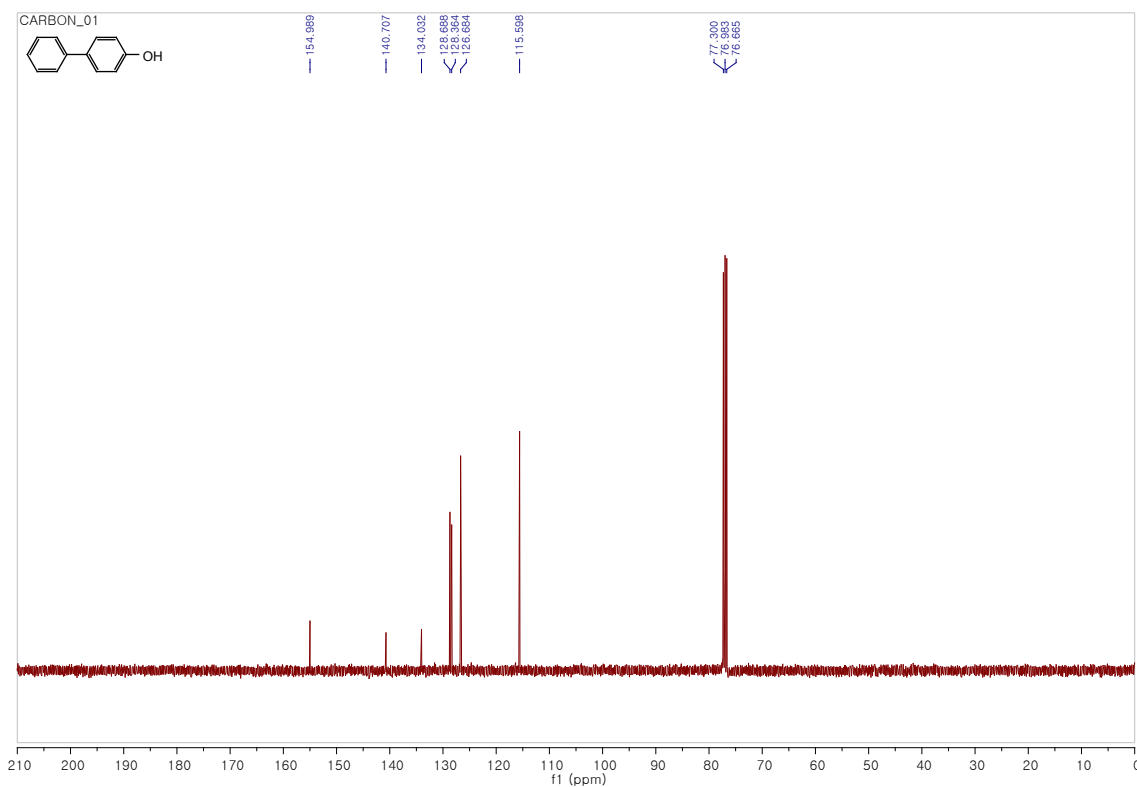
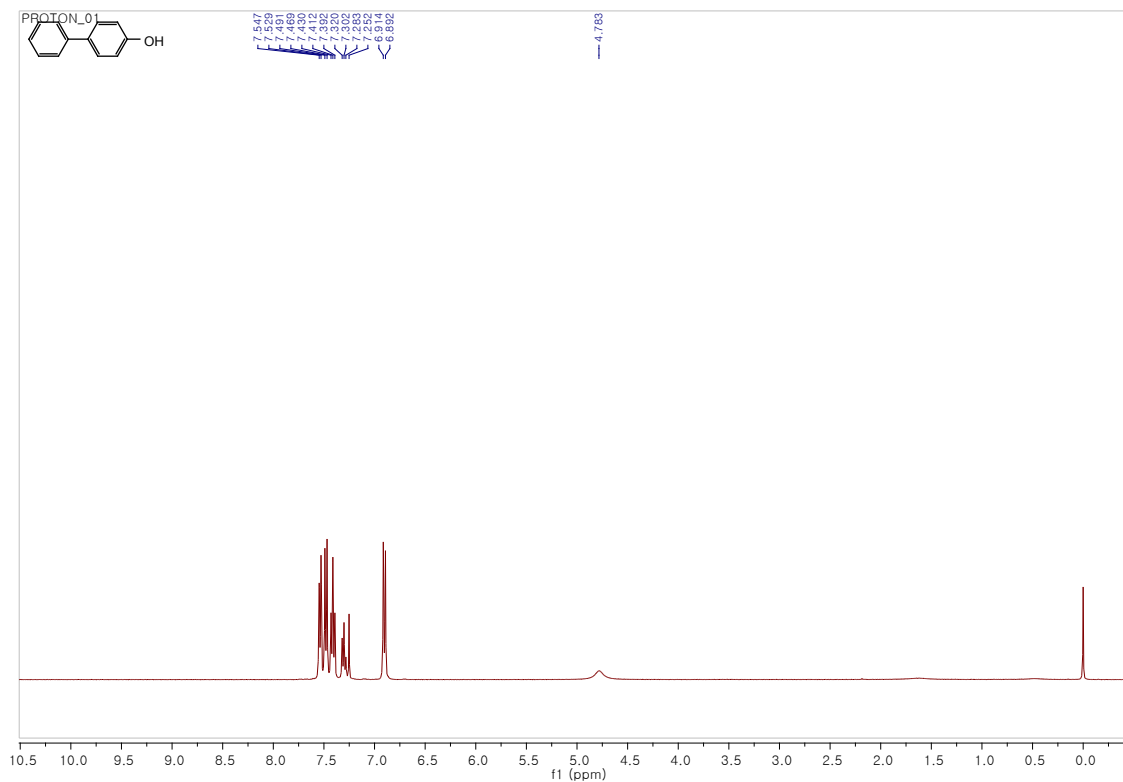
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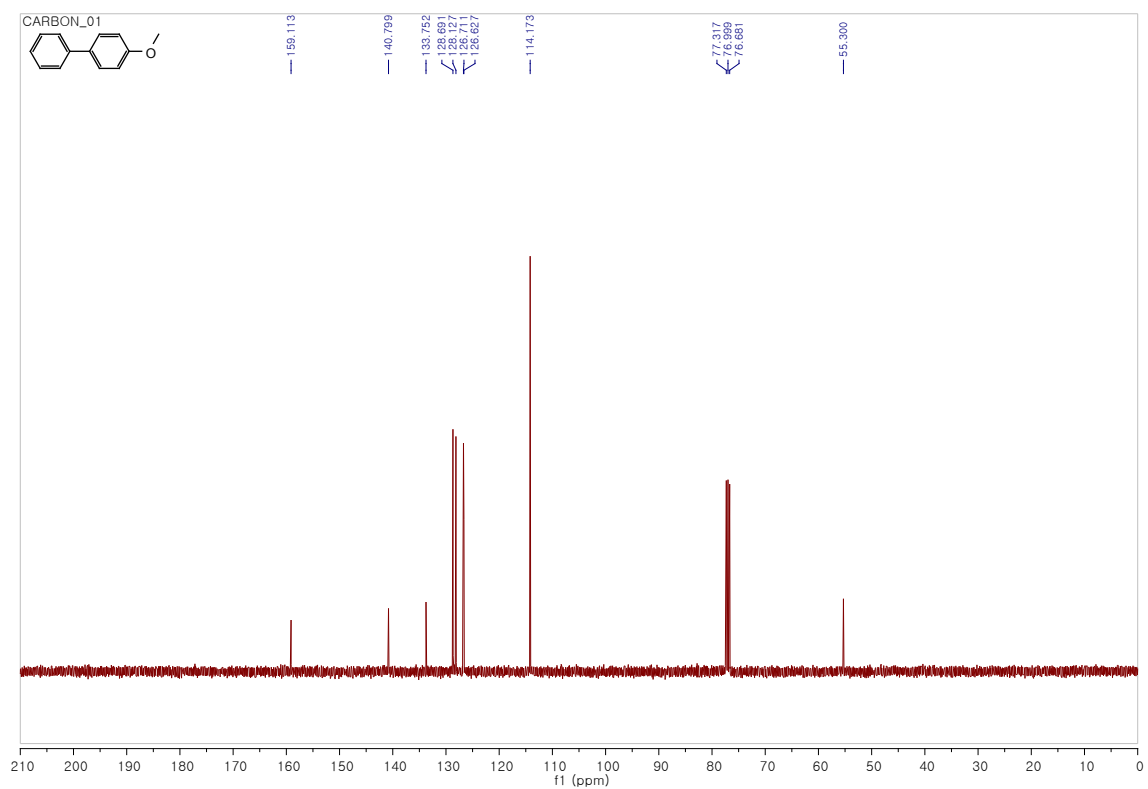
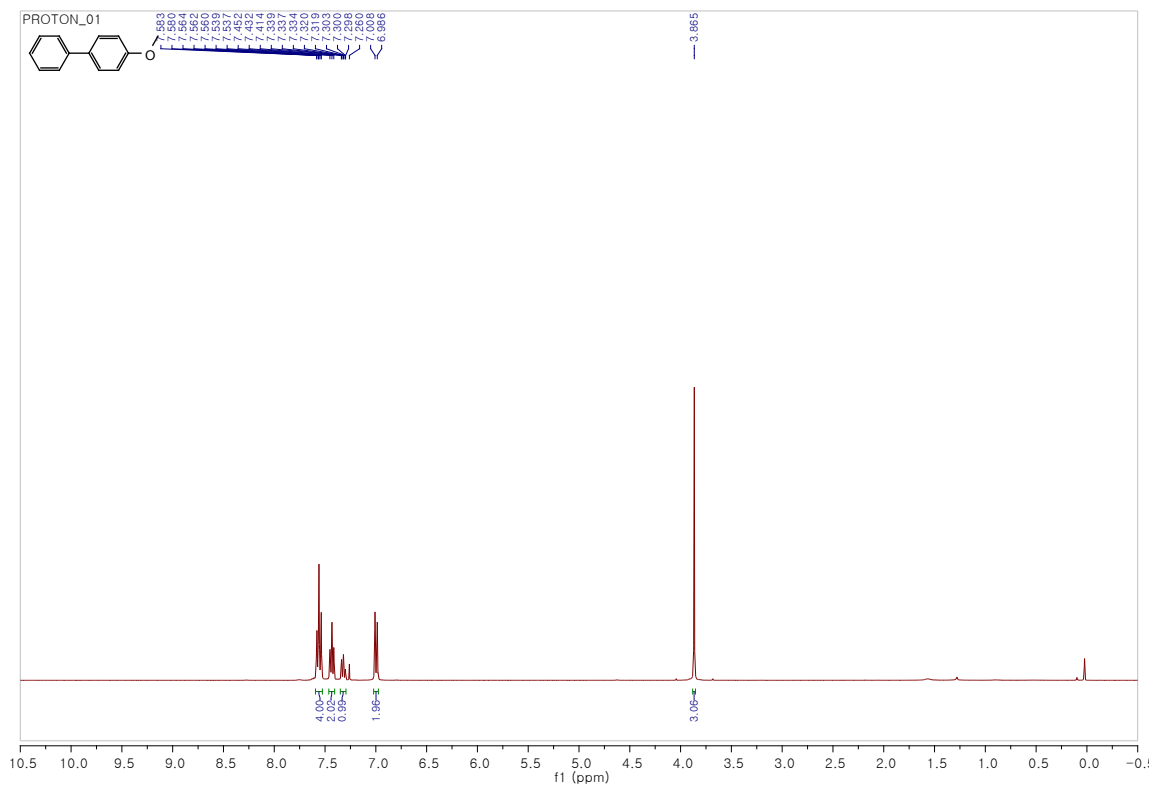
## Characterization data of coupling products



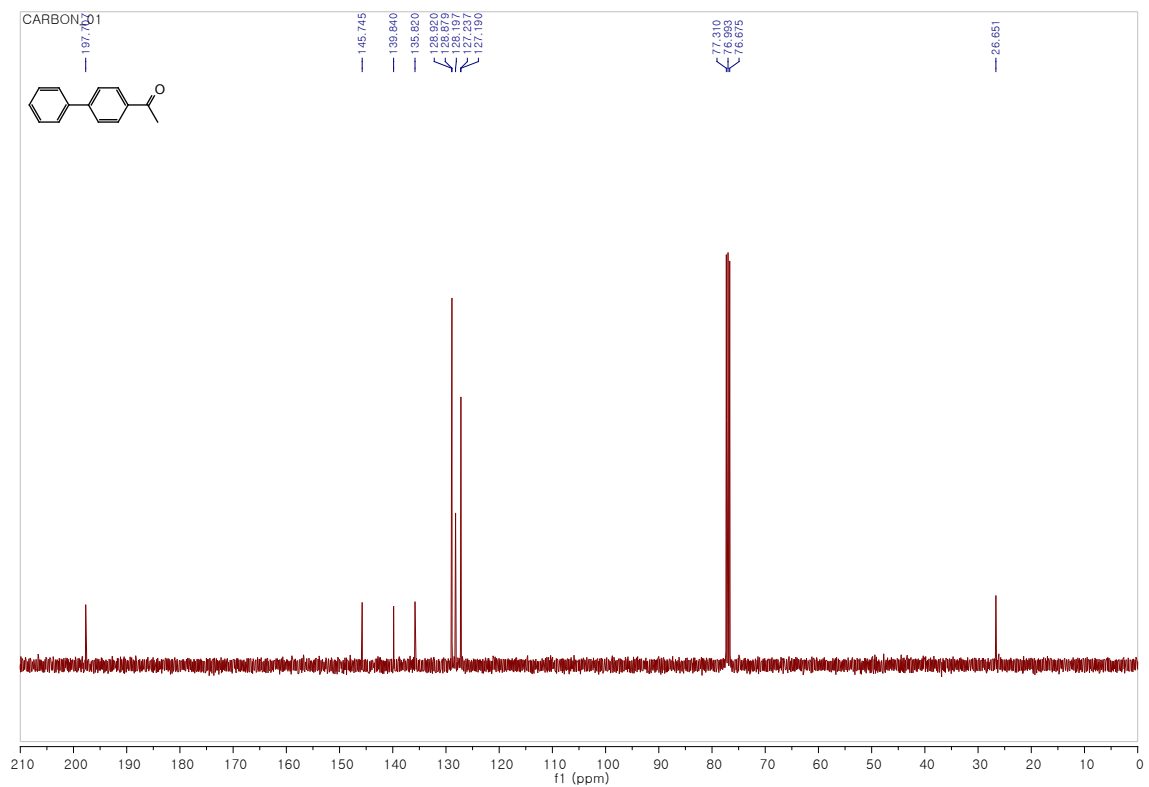
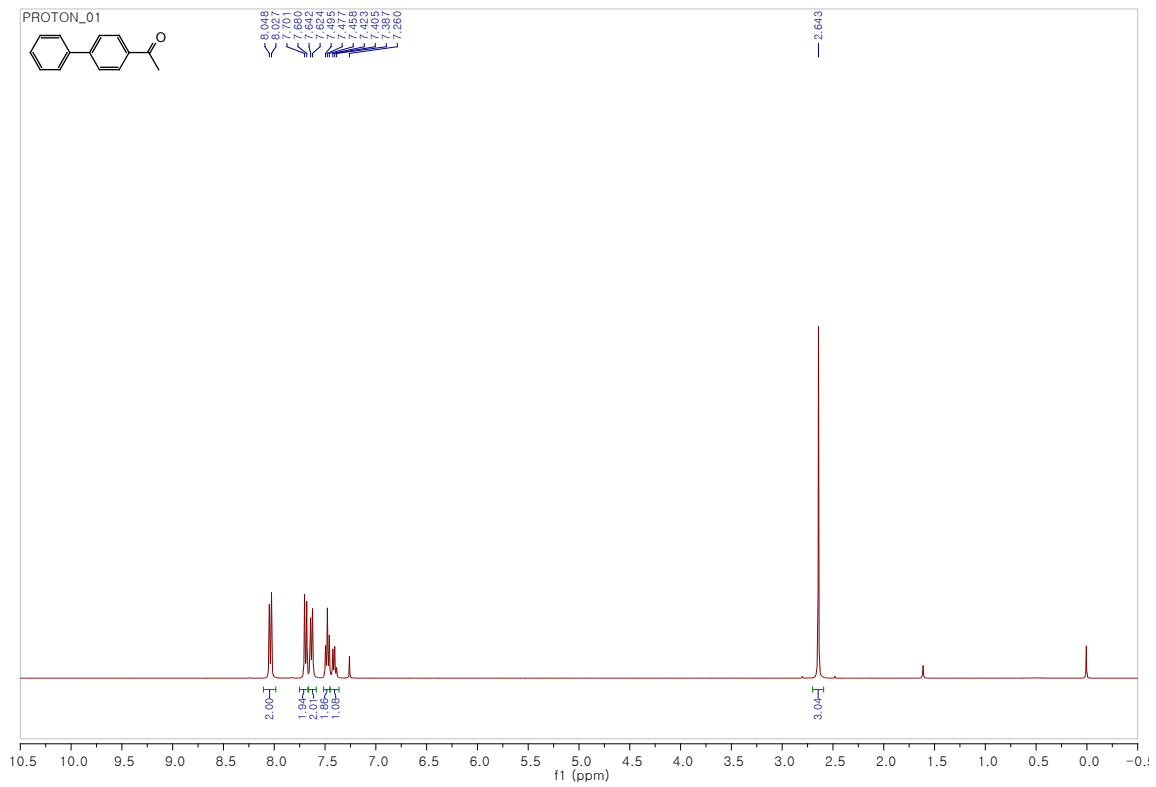
**Biphenyl** :  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.64 (d,  $J = 8.4$  Hz, 4H), 7.49 (t,  $J = 7.2$  Hz, 4H), 7.39 (t,  $J = 7.2$  Hz, 2H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  141.3, 128.75, 127.24, 127.16.



**4-Phenylphenol** :  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.54 (d,  $J = 7.2$  Hz, 2H), 7.48 (d,  $J = 8.8$  Hz, 2H), 7.41 (t,  $J = 7.6$  Hz, 2H), 7.30 (t,  $J = 7.2$  Hz, 2H), 6.90 (d,  $J = 8.8$  Hz, 1H), 4.78 (s, 1H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  155.0, 140.7, 134.0, 128.7, 128.4, 126.7, 126.7, 115.6.



**4-Methoxybiphenyl** :  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.54-7.59 (m, 4H), 7.43 (t,  $J = 8.0$  Hz, 2H), 7.30-7.34 (m, 1H), 7.00 (d,  $J = 8.8$  Hz, 2H), 3.87 (s, 3H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.



**4-Acetylbiphenyl** :  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  8.04 (d,  $J = 8.4$  Hz, 2H), 7.69 (d,  $J = 8.4$  Hz, 2H), 7.63 (d,  $J = 7.2$  Hz, 2H), 7.48 (t,  $J = 7.2$  Hz, 2H), 7.41 (t,  $J = 7.2$  Hz, 1H), 2.64 (s, 3H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  197.7, 145.7, 139.8, 128.9, 128.9, 128.2, 127.2, 127.2, 26.7.