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Supporting Information

Polystyrene-Cross-Linking Triphenylphosphine on Porous Monolith: Enhanced Catalytic Activity for Aryl Chloride Cross-Coupling in Biphasic Flow

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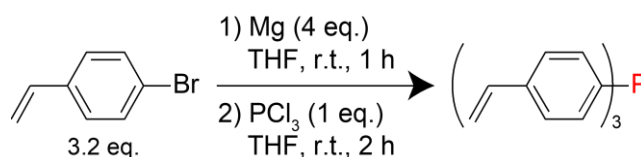
1. Generals

The samples for field emission scanning electron microscopy (FE-SEM) analysis were coated with platinum (approx. 4 nm thickness) using an JEOL JFC-1600 auto fine coater (JEOL Ltd., Tokyo, Japan). FE-SEM analysis was performed on a Hitachi SU8000 microscopy (Hitachi High-Technologies Corporation, Tokyo, Japan). Mercury intrusion porosimetry analysis was performed on a Micromeritics AutoPoreIV9520 (Micromeritics Instrument Co., Norcross, GA, USA). Fourier transform-infrared (FT-IR) spectra were recorded on a JASCO FT/IR 620 spectroscopy at room temperature in vacuum with 4 cm⁻¹ spectral resolution and 32 scans. Solution nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECZ400S spectroscopy, operating at 400, 101, and 162 MHz for ¹H, ¹³C, and ³¹P NMR, respectively. Chemical shifts values for ¹H, ¹³C, and ³¹P NMR spectra were referenced to Me₄Si, the residual solvent, and 85% H₃PO₄, respectively. Cross polarized magic angle spinning (CP/MAS) NMR spectra were recorded on a Bruker AVANCE III 500 spectroscopy (Bruker Co., Billerica, MA, USA), operating at 203 MHz for ³¹P NMR. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was performed on a Seiko Instruments SPS-1700 HVR spectroscopy (Seiko Instruments Inc., Chiba, Japan). The samples for transmission electron microscopy (TEM) analysis were prepared by placing a drop of THF suspension of monoliths onto a carbon-coated copper grid and allowing THF to be evaporated under air. TEM analysis was performed on a Philips FEI Tecnai 20 (Philips FEI, Hillsboro, OR, USA) with accelerating voltage of 200 kV. High-performance liquid chromatography (HPLC) analyses were performed on a JASCO LC-2000Plus system equipped with a JASCO DG-980-50 degasser, a JASCO PU-980 pump, a Kanto Chemical Mightysil RP-18 GP 250-4.6 column (Kanto Chemical Co., Tokyo, Japan), a JASCO UV-2077Plus UV detector, and a JASCO CO-2065Plus column oven (JASCO Co., Tokyo, Japan). Acetonitrile/water (80:20 v/v) containing trifluoroacetic acid (0.1 vol%) was employed as a mobile phase in the HPLC measurements. In continuous-flow setup, SGE glass gas-tight syringe (SGE Analytical Science Pty. Ltd., Melbourne, Australia), which was mounted on YMC YSP-101 syringe pump (YMC Co. Ltd., Kyoto, Japan), and Krone KDM-30 pressure gauge (Krone Co., Tokyo, Japan) were connected to column in a thermo-controlled incubator with PTFE or PFA tubing (0.75 mm inner diameter). For residence time distribution (RTD) studies, a FLOM VI-11 injection valve (FLOM Co., Tokyo, Japan) with a 10 µL loop, an Ocean Optics USB2000+ ultraviolet-visible (UV-Vis) spectrometer, an Ocean Optics tungsten halogen light source, and an Ocean Optics FIA-Z-SMA-TEF Z-type flow cell (Ocean Optics Inc., Dunedin, FL, USA) were included in continuous-flow setup. For continuous-flow catalysis, two syringe pumps were used to deliver THF and aqueous phase, which were mixed through PTFE T-shaped mixer. Thin-layer chromatography analyses were performed on aluminum sheers bearing 0.17–0.22 mm layer of Merck Silica gel 60F₂₅₄. Merck silica gel 60 (40–63 µm, neutral, Merck Co., Darmstadt, Germany) was used for column chromatography.

All solvents for preparation of polymer and catalytic reactions were degassed by sonication for > 30 min before use. Materials were obtained from commercial suppliers unless otherwise noted. 4-*tert*-butylstyrene (>99% GC purity, stabilized with 4-*tert*-butylcatechol, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) and divinylbenzene (3- and 4- mixture, contains ethylvinylbenzene and ethylbenzene, >80% GC purity, stabilized with 4-*tert*-butylcatechol, Sigma-Aldrich Co., St. Louis, MO, USA) were purified using basic alumina column. 2,2'-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from MeOH. PCl_3 was purified by distillation under nitrogen atmosphere before use.

2. Synthesis of Tris(4-Vinylphenyl)phosphane

Scheme S1. Synthesis of Tris(4-Vinylphenyl)phosphane^[1]

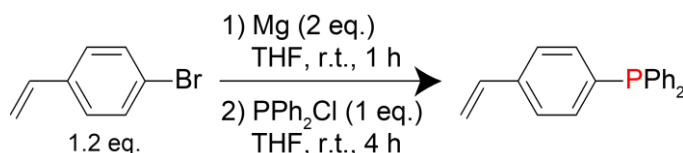


Threefold cross-linkable triphenylphosphine (TPP) was synthesized according to the previous reports (Scheme S1). Mg turnings (2.40 g, 100 mmol, 4 eq) were placed in a 300-mL round-bottom flask equipped with a magnetic stirring bar. After addition of anhydrous THF, 80 mL) under N_2 , *p*-bromostyrene (14.64 g, 80 mmol, 3.2 eq) was slowly added to the flask followed by stirring at room temperature for 1 h. Next, PCl_3 (3.43 g, 25 mmol, 1 eq) was added to the solution in ice water bath over 0.5 h followed by stirring at room temperature for 4 h. Quenching with aq. NH_4Cl , the mixture was extracted with Et_2O . The organic layer was washed with water, dried over MgSO_4 , filtered, and concentrated. The residue was purified by silica gel chromatography (hexane/ EtOAc 97:3 v/v) to give desired product as white solids (4.82 g, 57% yield).

¹H NMR (CDCl_3): δ 5.27 (d, J = 11.0 Hz, 3H), 5.77 (d, J = 17.4 Hz, 3H), 6.70 (dd, J = 17.4, 11.0 Hz, 3H), 7.23–7.38 (m, 12H). ¹³C NMR (CDCl_3): δ 114.85 (3C), 126.44 (d, $J_{\text{C-P}}$ = 7.1 Hz, 6C), 134.00 (d, $J_{\text{C-P}}$ = 19.2 Hz, 6C), 136.45 (3C), 136.72 (d, $J_{\text{C-P}}$ = 10.1 Hz, 3C), 138.07 (3C). ³¹P NMR (CDCl_3): δ -6.21.

3. Synthesis of 4-(Diphenylphosphino)styrene

Scheme S2. Synthesis of 4-(Diphenylphosphino)styrene^[1]



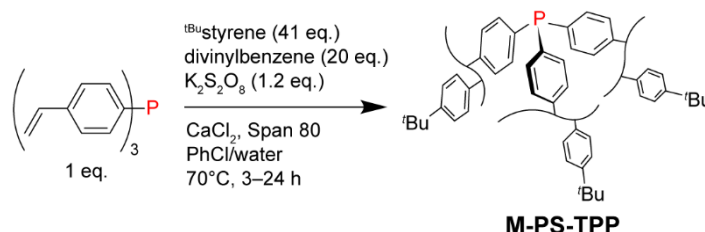
Single-point-graftable TPP was synthesized according to the previous reports (Scheme S2). Mg turnings (0.14 g, 6.0 mmol, 2 eq) were placed in a 50-mL round-bottom flask equipped with a magnetic stirring bar. After addition of anhydrous THF (3.6 mL) under N_2 , *p*-

bromostyrene (0.66 g, 3.6 mmol, 1.2 eq) was slowly added to the flask followed by stirring at room temperature for 1 h. Next, PPh₂Cl (0.66 g, 3.0 mmol, 1 eq) was added to the solution in ice water bath over 0.5 h followed by stirring at room temperature for 4 h. Quenching with aq. NH₄Cl, the mixture was extracted with Et₂O. The organic layer was washed with water, dried over MgSO₄, filtered and concentrated. The residue was purified by silica gel chromatography (hexane/EtOAc 97:3 v/v) to give MPP as white solids (0.813 g, 94% yield).

¹H NMR (CDCl₃): δ 5.27 (d, *J* = 11.0 Hz, 1H), 5.77 (d, *J* = 17.8 Hz, 1H), 6.70 (dd, *J* = 17.6, 10.7 Hz, 1H), 7.24–7.39 (m, 14H). ¹³C NMR (CDCl₃): δ 114.80, 126.43 (d, *J*_{C-P} = 6.8 Hz, 2C), 128.65 (d, *J*_{C-P} = 6.8 Hz, 4C), 128.88 (2C), 133.86 (d, *J*_{C-P} = 19.1 Hz, 4C), 134.08 (d, *J*_{C-P} = 19.1 Hz, 2C), 136.53, 136.88 (d, *J*_{C-P} = 10.6 Hz), 137.30 (d, *J*_{C-P} = 10.6 Hz, 2C), 138.08. ³¹P NMR (CDCl₃): δ -5.14.

4. Synthesis of M-PS-TPP

Scheme S3. Synthesis of **M-PS-TPP** in the Presence of HIPE Template^[2]



A solution of tris(4-vinylphenyl)phosphane (5.5 mg, 0.016 mmol, 1 eq.), 4-*tert*-butylstyrene (106.0 mg, 0.66 mmol, 41 eq.), divinylbenzene (42.0 mg, 0.32 mmol, 20 eq.), and Span 80 (0.061 mL) in chlorobenzene (0.19 mL) was placed in a glass vial (21.00 mm inner diameter) equipped with a magnetic stirring bar (~20 mm) (Scheme S3). The organic phase was degassed by three freeze-pump-thaw cycles. Separately, CaCl₂ (36.9 mg, 0.33 mmol) and K₂S₂O₈ (5.2 mg, 0.019 mmol, 1.2 eq.) was dissolved in water (3.3 mL). The aqueous phase was degassed by nitrogen bubbling for > 0.5 h. Under vigorous stirring of organic phase (500 rpm), the initiator-containing aqueous phase was added dropwise using syringe. The ratio of organic phase to aqueous phase was 10:90 v/v. After addition of aqueous phase, stirring was further continued for 5 min to give HIPE.

For characterization of **M-PS-TPP**, HIPE was incubated in the vial at 70°C for various time (3–24 h) after removing stirring bar. Carefully crushing the vial, the resulting cylindrical polymer was washed successively by immersion in THF/water (2:1 v/v) and THF for > 1 day each. Using calipers, the diameter (*d*) and length (*L*) of swollen **M-PS-TPP** was measured to estimate a swelling volume. The **M-PS-TPP** showed swelling behavior in THF (*d* = 21.97 mm) and THF/water (*d* = 21.40 mm), which were larger than inner diameter of glass vial (21.00 mm) used as mold. The yield of **M-PS-TPP** was determined after drying under vacuum at room temperature overnight, to give a white solid polymer (120.2–143.0 mg, 78–93 wt% dry yield) (Table S1). The amount of TPP moiety incorporated ([P]) was 0.11 mmol g⁻¹ based on feed ratio of monomers. The internal structure of the dried **M-PS-TPP** were observed

using FE-SEM (Figure S1). In 6–24 h of polymerization time, no significant difference of yield and macroporous structure for **M-PS-TPP** was observed. For further experiment, the polymerization time was fixed to be 6 h.

Table S1. Yields and Swelling Volume of **M-PS-TPP**^a

entry	Polymerization time (h)	Yield (mg)	Swelling volume ^b (mL g ⁻¹)
1	3	120.2 (78 wt%)	31.1
2	6	141.5 (92 wt%)	26.2
3	9	142.2 (93 wt%)	26.1
4	12	138.7 (90 wt%)	28.4
5	24	143.0 (93 wt%)	26.9

^aConditions: tris(4-vinylphenyl)phosphane (0.016 mmol, 1 eq.), 4-*tert*-butylstyrene (0.66 mmol, 41 eq.), divinylbenzene (0.32 mmol, 20 eq.), Span 80 (0.061 mL), chlorobenzene (0.19 mL), CaCl₂ (0.33 mmol), K₂S₂O₈ (0.019 mmol, 1.2 eq.), water (3.3 mL), organic phase/aqueous phase 10:90 v/v, 70°C, 3–24 h.

^bMeasured after immersion in THF for > 1 day using calipers.

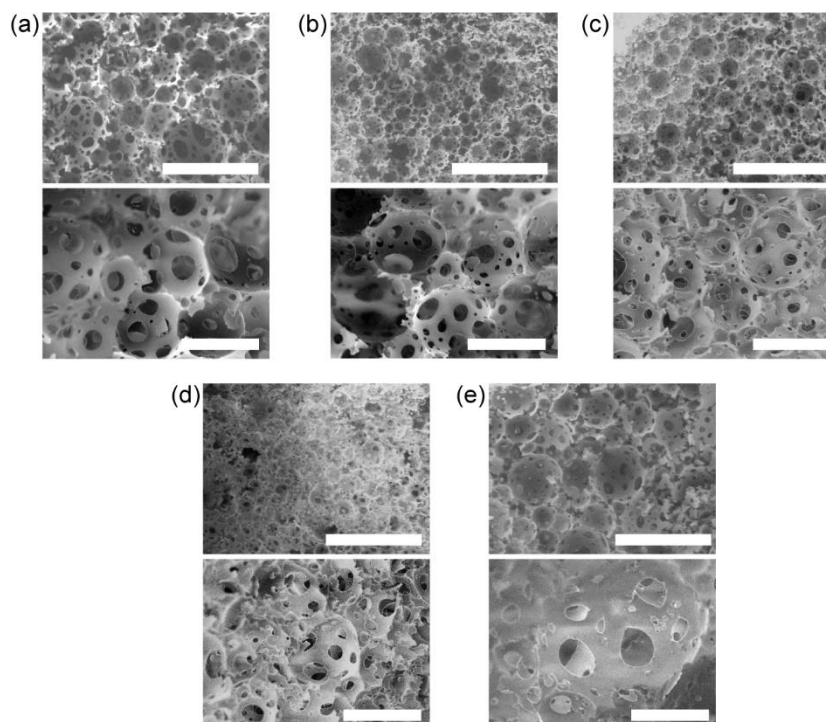
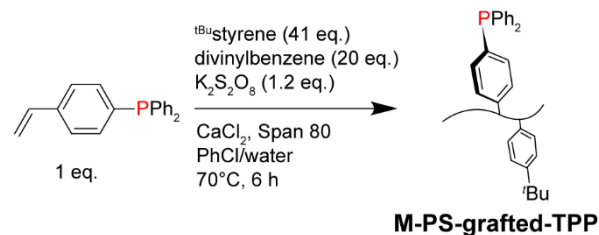


Figure S1. FE-SEM images of **M-PS-TPP** prepared with different polymerization time. (a) 3 h, (b) 6 h, (c) 9 h, (d) 12 h, and (e) 24 h. Scale bars: 100 (upper) and 20 μm (bottom).

5. Synthesis of M-PS-grafted-TPP

Scheme S4. Synthesis of **M-PS-grafted-TPP** in the Presence of HIPE Template^[2]



A solution of 4-(Diphenylphosphino)styrene (4.6 mg, 0.016 mmol, 1 eq.), 4-*tert*-butylstyrene (106.0 mg, 0.66 mmol, 41 eq.), divinylbenzene (42.0 mg, 0.32 mmol, 20 eq.), and Span 80 (0.061 mL) in chlorobenzene (0.19 mL) was placed in a glass vial (21.00 mm inner diameter) equipped with a magnetic stirring bar (~20 mm) (Scheme S4). The organic phase was degassed by three freeze-pump-thaw cycles. Separately, CaCl_2 (36.9 mg, 0.33 mmol) and $\text{K}_2\text{S}_2\text{O}_8$ (5.2 mg, 0.019 mmol, 1.2 eq.) was dissolved in water (3.3 mL). The aqueous phase was degassed by nitrogen bubbling for > 0.5 h. Under vigorous stirring of organic phase (500 rpm), the initiator-containing aqueous phase was added dropwise using syringe. The ratio of organic phase to aqueous phase was 10:90 v/v. After addition of aqueous phase, stirring was further continued for 5 min to give HIPE.

For characterization of **M-PS-grafted-TPP**, HIPE was incubated in the vial at 70°C for 6 h after removing stirring bar. Carefully crushing the vial, the resulting cylindrical polymer was washed successively by immersion in THF/water (2:1 v/v) and THF for > 1 day each. Using calipers, the d and L of swollen **M-PS-grafted-TPP** was measured. The **M-PS-grafted-TPP** showed swelling behavior in THF ($d = 22.00$ mm) and THF/water ($d = 21.44$ mm), which were larger than inner diameter of glass vial (21.00 mm) used as mold. The dry yield of **M-PS-grafted-TPP** was determined after drying under vacuum at room temperature overnight, to give a white solid polymer (132.5 mg, 87 wt% dry yield). The amount of TPP moiety incorporated ($[\text{P}]$) was 0.11 mmol g^{-1} based on feed ratio of monomers. The FE-SEM observation of **M-PS-grafted-TPP** was indicative of formation of window and void structures in monolithic material (Figure S2).

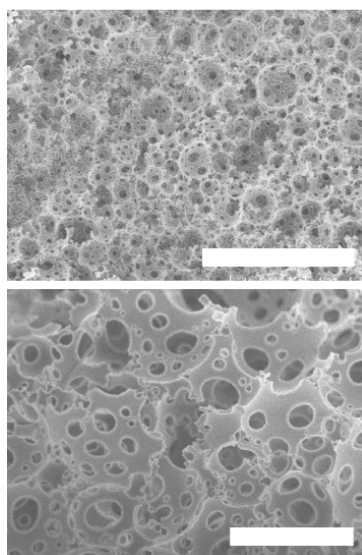


Figure S2. FE-SEM images of **M-PS-grafted-TPP**. Scale bars: 100 (upper) and 20 μm (bottom).

6. Mercury Intrusion Porosimetry Test for Monolith Before and After Loading of Pd

Mercury intrusion tests were conducted to determine the pore sizes and porosities of monolith before and after loading of Pd (Table S2, Figures S3 and S4).

Table S2. Mode Pore Sizes, Specific Surface Areas, and Porosities of Monolith^a

Monolith	1 st -mode pore size (nm)	2 nd -mode pore size (nm)	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	Porosity (%)
M-PS-TPP	10690	3600	6	81
M-PS-TPP-Pd	10690	3610	5	82
M-PS-grafted-TPP	8360	3040	10	88
M-PS-grafted-TPP-Pd	7420	3000	11	87

^aDetermined by mercury intrusion porosimetry for dry sample.

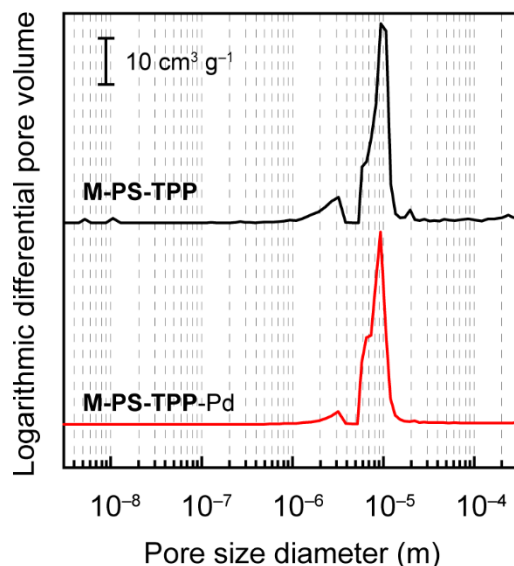


Figure S3. Pore size distributions of **M-PS-TPP** (black line) and **M-PS-TPP-Pd** (Pd/P 1:2, red line) in dry state.

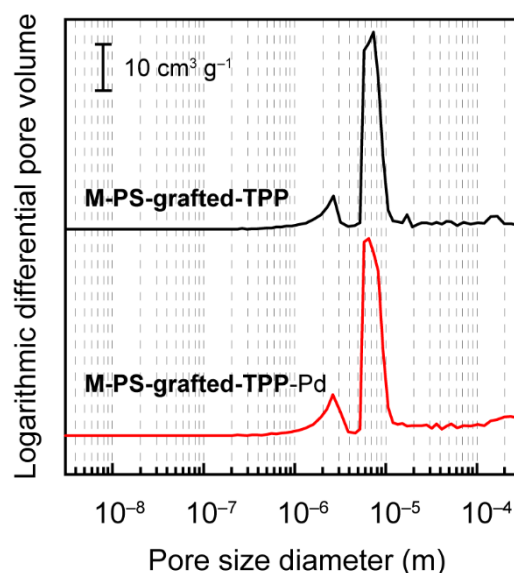


Figure S4. Pore size distributions of **M-PS-grafted-TPP** (black line) and **M-PS-grafted-TPP-Pd** (Pd/P 1:2, red line) in dry state.

7. FT-IR Studies for Monolith Before and After Loading of Pd

FT-IR studies of monolith were conducted using FT-IR spectroscopy (Figure S5). All spectra showed peaks for benzene skeleton stretching, C–H out-of-plane bending, and in-plane bending vibration at 1600–1450, 1200–950, and 900–650 cm^{-1} , respectively.^[3] It was also seen that all the monoliths showed strong peaks at 830 cm^{-1} , which were assignable to CH out-of-plane vibration for para-disubstituted benzene.^[4] The peaks corresponding to P–Ph linkage (1450–1425 and 1010–990 cm^{-1})^[5] and their low wavenumber shifts^[6] were not observed due to low feed ratios of TPP.

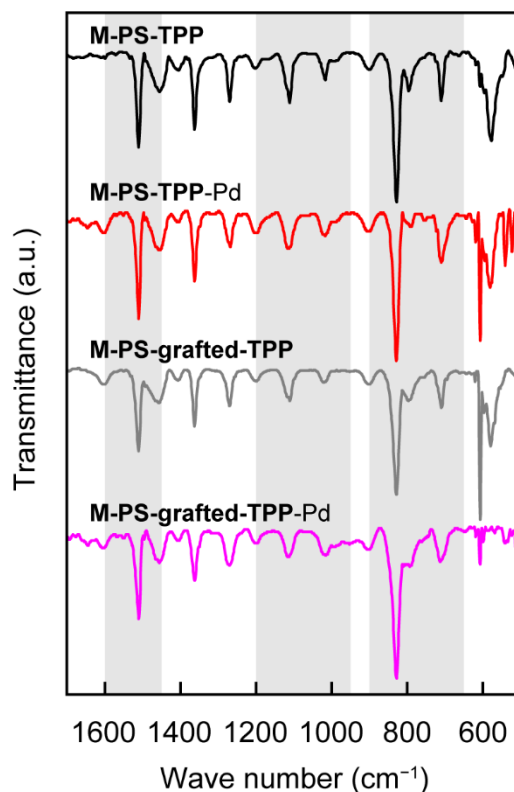


Figure S5. FT-IR spectra of monoliths before and after loading of Pd.

8. ^{31}P CP/MAS NMR Studies for Reactions of TPP-supporting Monolith and $[\text{PdCl}_2(\text{PhCN})_2]$

The dried **M-PS-TPP** ($[\text{P}]$ 0.11 mmol g^{-1} , 200.0 mg , 0.022 mmol) was grinded into powder using pestle and mortar, then placed in a glass vial. $[\text{PdCl}_2(\text{PhCN})_2]$ (4.2 mg , 0.011 mmol , Pd/P 1:2) was dissolved in degassed THF (11 mL), and this Pd solution was added to the vial. The mixture was stirred at room temperature for $> 1 \text{ h}$. The molar ratio of Pd to P was 1:2. The suspension was filtered, washed with THF, and dried in vacuo at room temperature overnight to give yellow powder. From ICP-AES analyses for the filtrate, all the Pd added was loaded on **M-PS-TPP** to give 0.05 mmol g^{-1} of Pd loading ($[\text{Pd}]$). The powder before and after loading of Pd were analyzed using ^{31}P CP/MAS NMR spectroscopy (Figure S6). For **M-PS-grafted-TPP**, the ^{31}P CP/MAS NMR analyses were also performed (Figure S7).

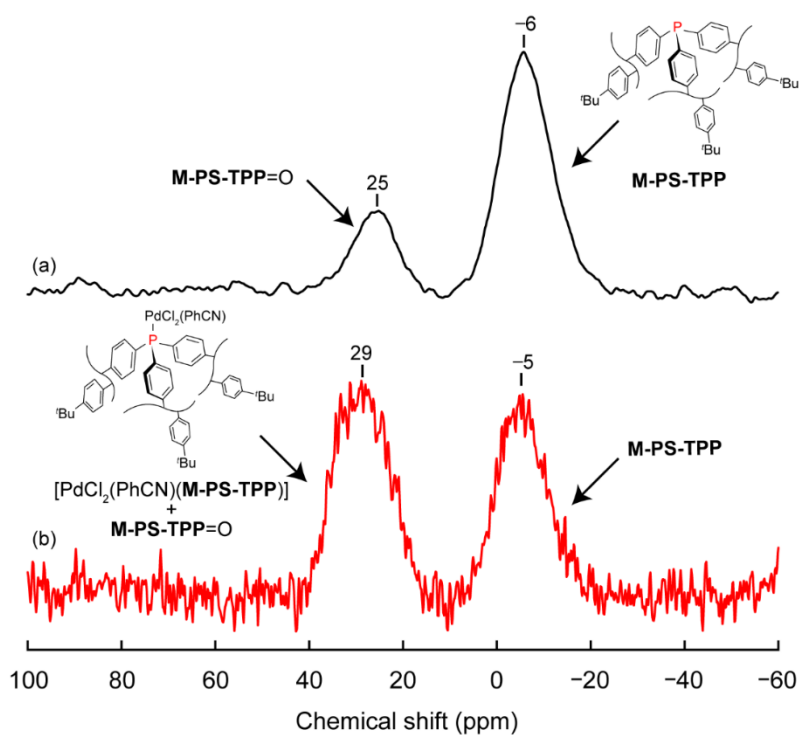


Figure S6. ^{31}P CP/MAS NMR spectra obtained from **M-PS-TPP** (a) before and (b) after reactions with $[\text{PdCl}_2(\text{PhCN})_2]$ (Pd/P 1:2).

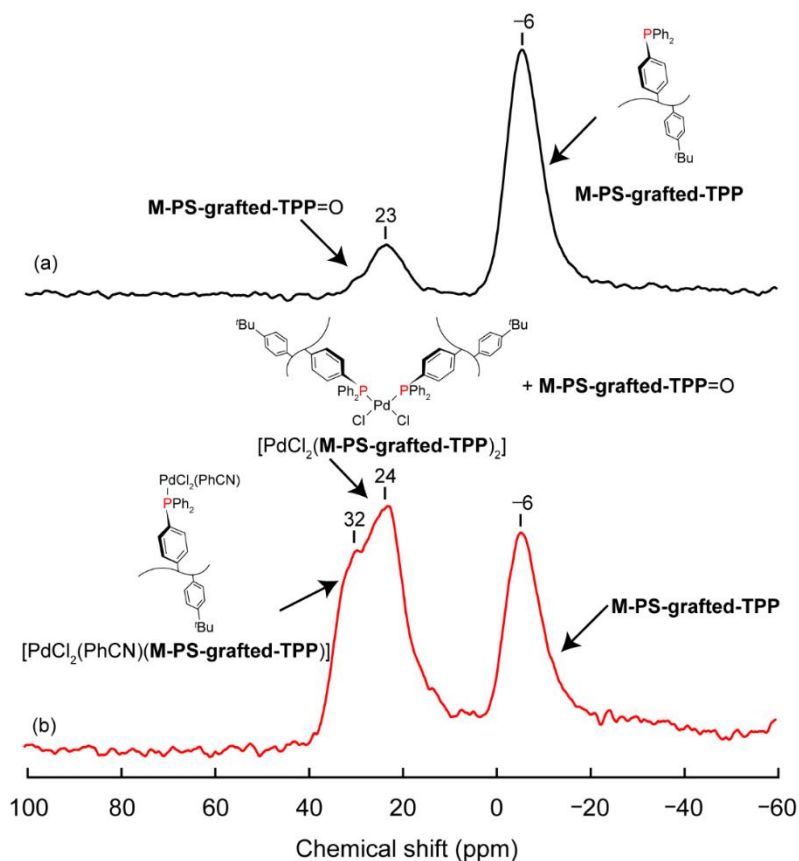


Figure S7. ^{31}P CP/MAS NMR spectra obtained from **M-PS-grafted-TPP** before (a) and after (b) reactions with $[\text{PdCl}_2(\text{PhCN})_2]$ (Pd/P 1:2).

9. Preparation and Permeability of Monolith Column in Continuous-Flow System

Stainless-steel tube (4.4 mm inner diameter) with different length (2.5, 5.0, or 10.0 cm) was filled with HIPE using syringe and sealed at the ends with septa. After incubation at 70°C for 6 h, the seals were removed, and the L of monolith column within stainless-steel column was measured using calipers. The monolith column was provided with fittings and attached to a syringe pump. Superficial linear velocity (u) and residence time (τ) in the column were defined as follows:

$$u = \frac{Q}{\pi d^2/4} \quad (1)$$

$$\tau = \frac{L}{u} \quad (2)$$

where Q is flow rate of feed. THF/water (2:1 v/v) and THF were successively permeated through the column for wash (2.5 h each, $\tau = 0.50$ h). At various u ($\tau = 0.25, 0.50, 1.00, 1.50$, or 2.00 h), the pressure losses were monitored for more than 48 h. The Darcy's permeabilities (k_D) of monolith columns were estimated as follows:

$$k_D = \frac{\mu L u}{\Delta P} \quad (3)$$

where μ and ΔP are viscosity^[7] of feed and pressure loss, respectively. The ΔP through monolith columns were proportional to u (Figures S8 and S9). The k_D of monolith columns for each mobile phase were estimated (Table S3).

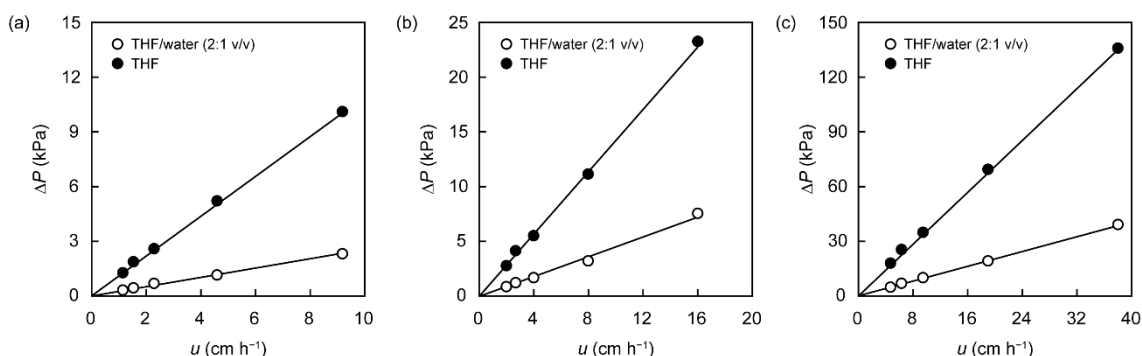


Figure S8. Pressure loss v.s. flow rate diagram through **M-PS-TPP** with L of (a) 2.3, (b) 4.0, and (c) 9.5 cm.

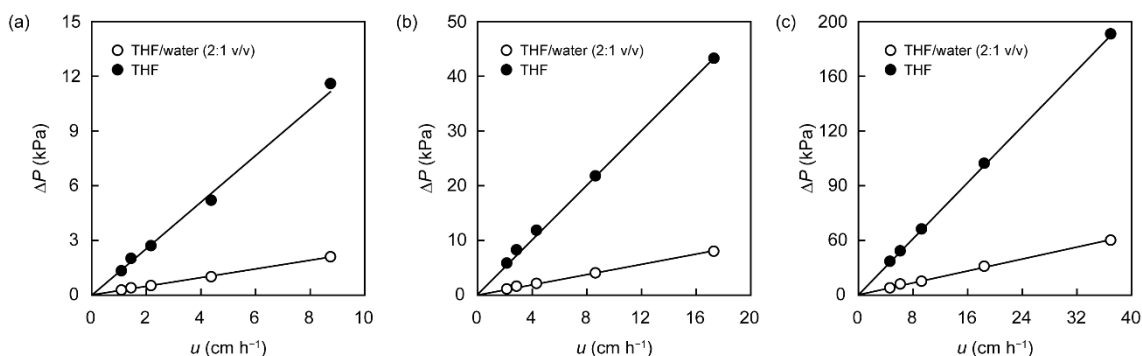


Figure S9. Pressure loss v.s. flow rate diagram through **M-PS-grafted-TPP** with L of (a) 2.2, (b) 4.0, and (c) 9.5 cm.

(b) 4.3, and (c) 9.2 cm.

Table S3. k_D of Monolith Column for Mobile Phase^a

Monolith	L (mm)	k_D (m ²)	
		THF/water ^b	THF
M-PS-TPP	2.3	3.4×10^{-13}	2.8×10^{-14}
	4.0	3.3×10^{-13}	3.8×10^{-14}
	9.5	3.5×10^{-13}	3.6×10^{-14}
M-PS-grafted-TPP	2.2	3.4×10^{-13}	2.3×10^{-14}
	4.3	3.5×10^{-13}	2.3×10^{-14}
	9.2	3.1×10^{-13}	2.4×10^{-14}

^aEstimated using Darcy's equation.

^bVolume ratio was 2:1 v/v.

10. RTD Studies for Pulse Tracer Injection into M-PS-TPP Column

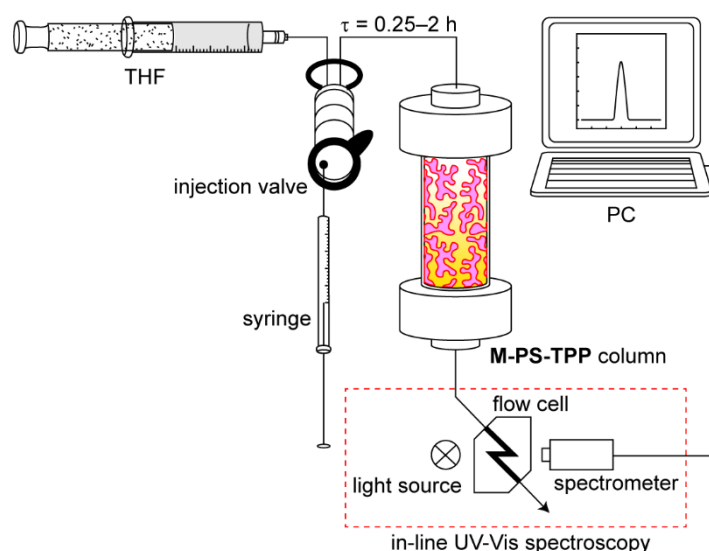


Figure S10. Continuous-flow setup for RTD studies using in-line UV-Vis spectroscopy.

M-PS-TPP column ($d = 4.4$ mm, $L = 4.5$ cm) was provided with fittings and attached to a syringe pump, UV-Vis spectrometer, deuterium halogen light source, and Z-type flow cell (Figure S10).^[8] As mobile phase, THF was permeated through the column, then methyl red in ethanol (1 g L^{-1} , $10 \text{ } \mu\text{L}$) as pulse tracer was injected into the THF stream. At various u ($\tau = 0.25, 0.50, 1.00, 1.50$, or 2.00 h), UV-vis absorbance at 475 nm wavelength at each time (t) was measured to monitor the concentration of methyl red in the eluent ($C(t)$). RTD function ($E(t)$), the mean residence time ($\bar{\tau}$) were defined as follows:

$$E(t) = \frac{C(t)}{\int_0^\infty C(t) dt} \quad (4)$$

$$\bar{\tau} = \int_0^{\infty} tE(t) dt \quad (5)$$

In order to facilitate the comparison of the results obtained under different flow condition (different τ), dimensionless time (θ) and dimensionless RTD function ($E(\theta)$) were employed as follows:

$$\theta = \frac{t}{\tau} \quad (6)$$

$$E(\theta) = \bar{\tau}E(t) \quad (7)$$

The narrow and high $E(\theta)$ curves were observed for **M-PS-TPP** column under all the flow conditions, which were repeated at least three times in each run (Figure S11).

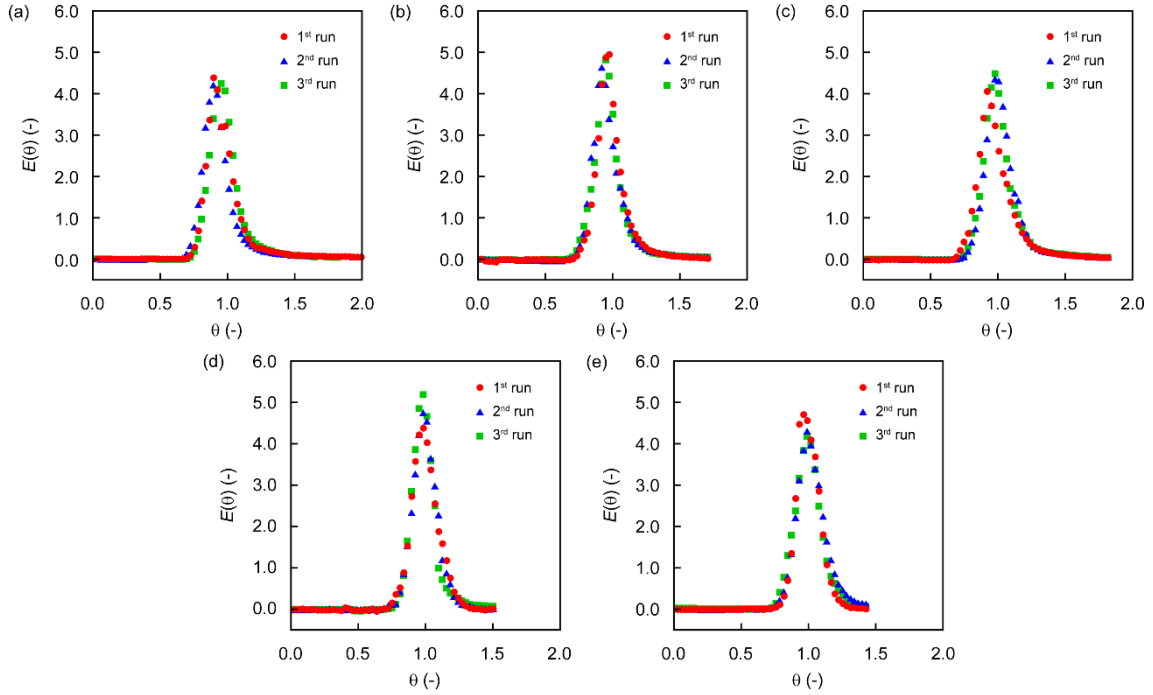


Figure S11. Dimensionless residence time distribution function v.s. dimensionless time diagram for a pulse injection of methyl red in ethanol (1 g L^{-1} , $10 \mu\text{L}$) into a THF stream through **M-PS-TPP** column ($L = 4.5 \text{ cm}$) at residence time of (a) 0.25 , (b) 0.50, (c) 1.00, (d) 1.50, and (e) 2.00 h.

For parametric RTD analysis, the dimensionless variance (σ^2) are further introduced as follows:

$$\sigma^2 = \int_0^{\infty} (1 - \theta)^2 E(\theta) d\theta \quad (8)$$

σ^2 were determined at various u ($\tau = 0.25, 0.50, 1.00, 1.50$, or 2.00 h) for **M-PS-TPP** column (Table S4). A σ^2 approaching to 0 suggests an ideal plug flow, while a σ^2 close to 1 indicates severe longitudinal mixing due to non-uniform velocity distribution and diffusion.^[9] The obtained σ^2 in RTD experiments were 0.010–0.024, demonstrating that **M-PS-TPP** system provided an excellent flow behavior close to plug-flow condition. From the elution volume of methyl red, the total porosity of **M-PS-TPP** column (ε_T) was calculated as follows:^[10]

$$\varepsilon_T = \frac{\text{elution volume of non-retained pulse tracer}}{\text{geometrical volumes of empty column}} \times 100 \quad (8)$$

In the tested flow conditions, the ε_T were 91–98% featuring full accessibility of small molecules in **M-PS-TPP** column.

Table S4. σ^2 and ε_T for **M-PS-TPP** Column under Different Flow Conditions^a

τ (h)	u (cm h ⁻¹)	σ^2 (-)	ε_T (%)
0.25	18.0	0.024 ± 0.003	91 ± 2
0.50	9.0	0.020 ± 0.003	98 ± 1
1.00	4.5	0.023 ± 0.003	95 ± 2
1.50	3.0	0.010 ± 0.002	93 ± 0
2.00	2.3	0.012 ± 0.004	93 ± 2

^aConditions: **M-PS-TPP** column (d = 4.4 mm, L = 4.5 cm), methyl red in ethanol (1 g L⁻¹, 10 μ L) as pulse tracer, THF as mobile phase, r.t.

11. Flow Suzuki-Miyaura Cross-Coupling Reaction in Biphasic Solvent System

Suzuki-Miyaura cross-coupling reaction of aryl chloride under continuous-flow mode was realized using **M-PS-TPP**-Pd column (Scheme 1c). [PdCl₂(PhCN)₂] (0.005 mol L⁻¹) in THF was permeated through **M-PS-TPP** column (τ = 2.00 h). The molar ratio of Pd to P was 1:2, controlled by total elution volume of feed solution. After completion of the permeation, the column was washed by permeation of THF to afford **M-PS-TPP**-Pd (2.5 h, τ = 0.50 h). 4-Chlorotoluene (0.50 mol L⁻¹, 1 eq.) and phenylboronic acid (0.75 mol L⁻¹, 1.5 eq.) in THF, and K₃PO₄ (3.00 mol L⁻¹, 3 eq.) in water were separately prepared. Tetra-*n*-butylammonium bromide (TBAB, 0.025 mol L⁻¹, 0.05 eq.) was dissolved in the THF phase with aryl substrates if needed. These solutions were loaded into syringes and attached to syringe pumps. Two syringe pumps were used to deliver the feed substrate solutions at controlled flow rate of THF-phase (Q_{THF}) and water-phase (Q_{water}). The ratio of Q_{THF} to Q_{water} was 2:1. The two substrate solutions were pumped and mixed via T-shaped mixer. The mixture was continuously permeated through the **M-PS-TPP**-Pd column. In continuous-flow catalysis, τ was calculated based on the total flow rate of THF-phase and water-phase substrate solutions ($Q = Q_{\text{THF}} + Q_{\text{water}}$, Eq. 1 and 2). The elution from the column was continuously collected, and the THF-phase was analyzed using HPLC. Turnover number (TON) were defined as follows:

$$\text{TON} = \frac{\text{total amount of 4-methylbiphenyl produced}}{\text{moles of Pd loaded}} \quad (9)$$

After run, THF/water (2:1 v/v) and THF was successively permeated through the column for washing. The eluent from the column was diluted in aqueous solution of HCl (1 mol L⁻¹) and analyzed using ICP-AES.

12. TEM Observation of Pd-Loaded Monoliths before and after Reaction

The Pd-loaded monoliths ([Pd] 0.05 mmol g⁻¹) before and after long-term run (34 h time on stream) was observed using TEM (Figures S12a,b and S13a,b). The number average of

Pd diameters were determined counting 200 numbers of Pd aggregates, which gave 5.1 ± 2.7 and 9.1 ± 3.6 nm for **M-PS-TPP-Pd** and **M-PS-grafted-TPP-Pd**, respectively (Figures 12c and 13c).

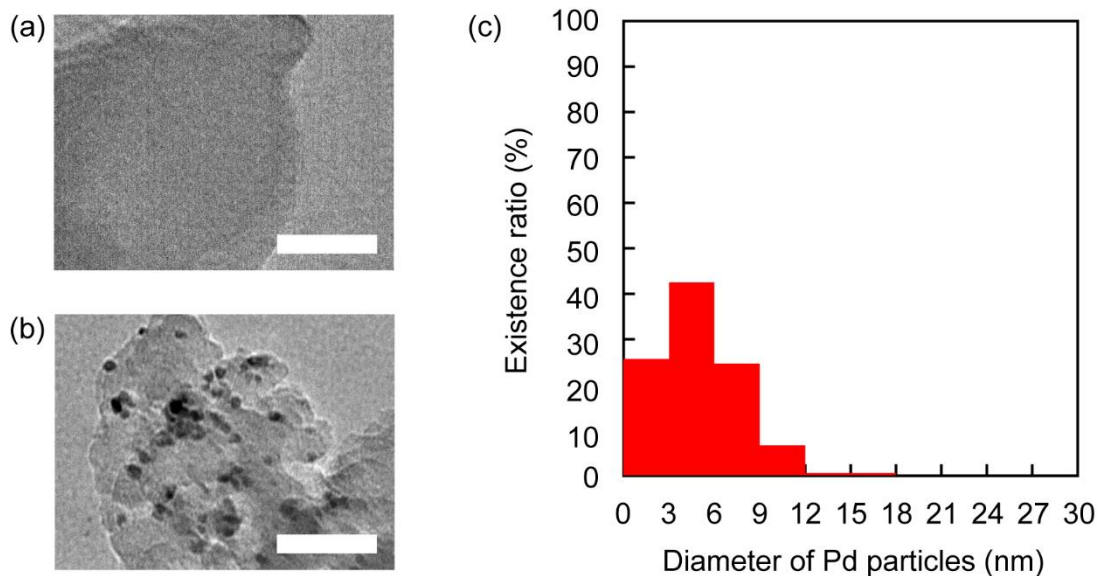


Figure S12. TEM images of **M-PS-TPP-Pd** (a) before and (b) after run. Scale bars: 50 nm. (c) Size distribution of Pd particles loaded on **M-PS-TPP-Pd**.

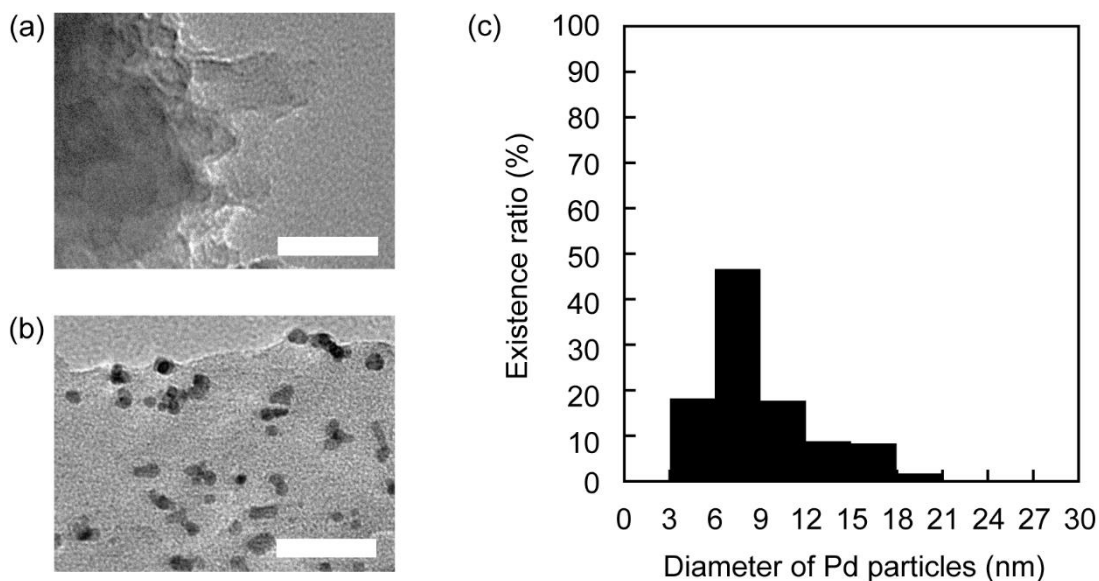
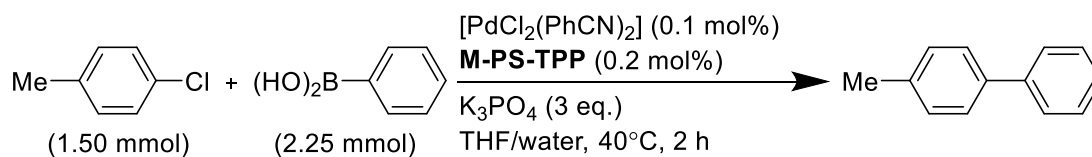


Figure S13. TEM images of **M-PS-grafted-TPP-Pd** (a) before and (b) after run. Scale bars: 50 nm. (c) Size distribution of Pd particles loaded on **M-PS-grafted-TPP-Pd**.

13. Batch Suzuki-Miyaura Cross-Coupling Reaction in Biphasic Solvent System

Scheme S5. Pd-Catalyzed Suzuki-Miyaura Cross-Coupling Reaction in Batch System



M-PS-TPP ([P] 0.11 mmol g⁻¹, 27.3 mg, 0.0030 mmol, 0.2 mol%) was placed in a glass vial (21.0 mm inner diameter). A solution of [PdCl₂(PhCN)₂] (0.58 mg, 0.0015 mmol, 0.1 mol%, Pd/P 1:2) in THF (1.5 mL) was added to the vial followed by magnetic stirring for 1 h (500 rpm). 4-chlorotoluene (189.9 mg, 1.5 mmol, 1 eq.) and phenylboronic acid (274.3 mg, 2.25 mmol, 1.5 eq.) in THF (1.5 mL in total), and K₃PO₄ (955.2 mg, 4.5 mmol, 3 eq.) in water (1.5 mL in total) were added successively. TBAB (24.2 mg, 0.075 mmol, 5 mol%) was dissolved in the THF phase with aryl substrates if needed. The reaction mixture was incubated at 40°C for 2.00 h with magnetic stirring (0, 250, or 500 rpm). A small aliquot was taken out from the THF phase, then analyzed using HPLC to determine a yield of 4-methylbiphenyl (Scheme S5, Figure S14).

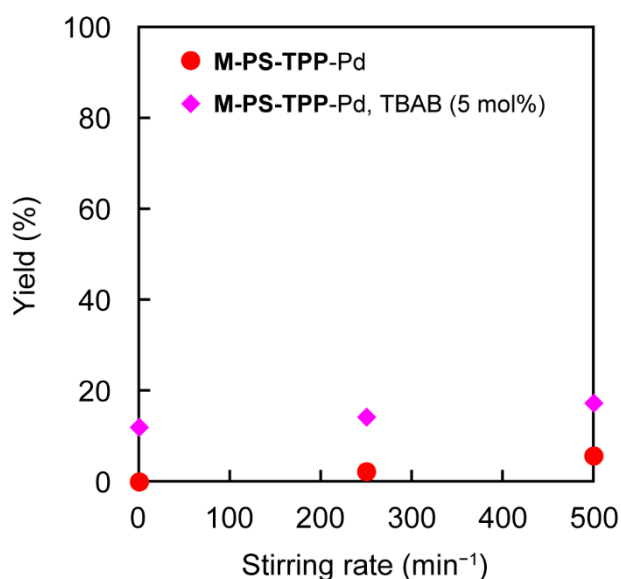


Figure S14. Effects of stirring rate and TBAB on yield of 4-methylbiphenyl in batch Suzuki-Miyaura cross-coupling reaction using biphasic solvent. Conditions: 4-chlorotoluene (1.5 mmol, 1 eq.), phenylboronic acid (2.25 mmol, 1.5 eq.), and TBAB (0.075 mmol, 5 mol%) in THF (3.0 mL in total), K₃PO₄ (4.5 mmol, 3 eq.) in water (1.5 mL in total), THF phase/water phase 2:1 v/v, [PdCl₂(PhCN)₂] (0.0015 mmol, 0.1 mol%), **M-PS-TPP** (0.0030 mmol, 0.2 mol%), 40°C, 2.00 h.

14. References

- [1] (a) T. Iwai, T. Harada, K. Hara, M. Sawamura, *Angew. Chem.* **2013**, *125*, 12548–12552; *Angew. Chem. Int. Ed.* **2013**, *52*, 12322–12326; (b) Y. B. Zhou, C. Y. Li, M. Lin, Y. J. Ding, Z. P. Zhan, *Adv. Synth. Catal.* **2015**, *357*, 2503–2508.
- [2] N. R. Cameron, D. C. Sherrington, *J. Mater. Chem.* **1997**, *7*, 2209–2212.
- [3] Corbrjidge, D. E. C. *J. Appl. Chem.* **1956**, *6*, 456–465.
- [4] Yang, J. C.; Jablonsky, M. J.; Mays, J. W. *Polymer* **2002**, *43*, 5125–5132.
- [5] Li, H., Zhang, F., Wan, Y., Lu, Y. *J. Phys. Chem. B* **2006**, *110*, 22942–22946.
- [6] El-Hefny, N. E.; Daoud, J. A. *J. Phys. Sci.* **2013**, *24*, 35–47.

- [7] T. M. Aminabhavi, B. Gopalakrishna, *J. Chem. Eng. Data* **1995**, 40, 856–861.
- [8] Sans, V.; Karbass, N.; Burguete, M. I.; García-Verdugo, E.; Luis, S. V. *RSC Adv.* **2012**, 2, 8721–8728.
- [9] Puaux, J. P.; Bozga, G.; Ainser, A. *Chem. Eng. Sci.* **2000**, 55, 1641–1651.
- [10] Urban, J.; Eeltink, S.; Jandera, P.; Schoenmakers, P. J. *J. Chromatogr. A* **2008**, 1182, 161–168.

15. NMR Spectra

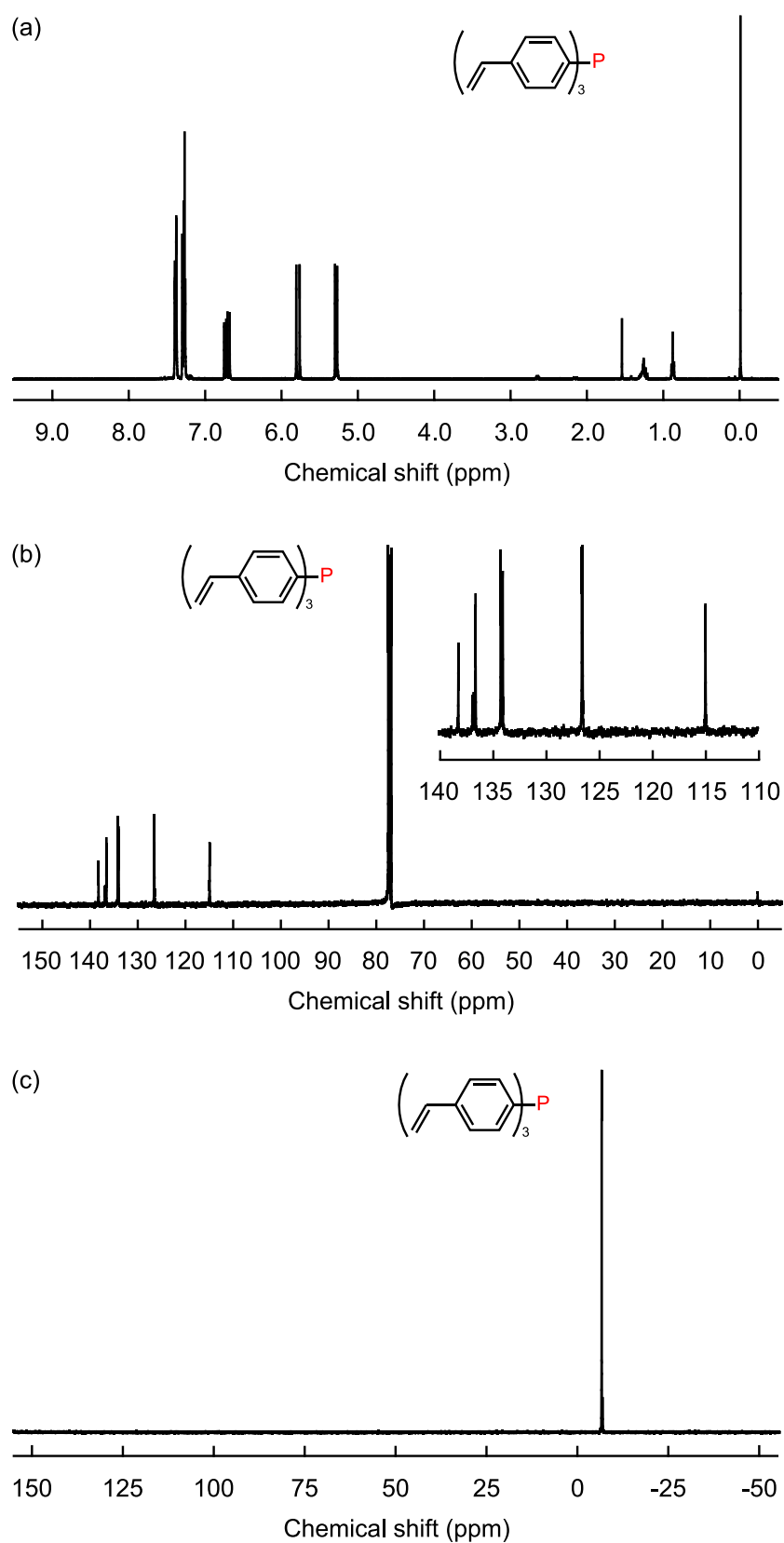


Figure S15. (a) ^1H , (b) ^{13}C , and (c) ^{31}P solution NMR spectra of tris(4-vinylphenyl)phosphane.

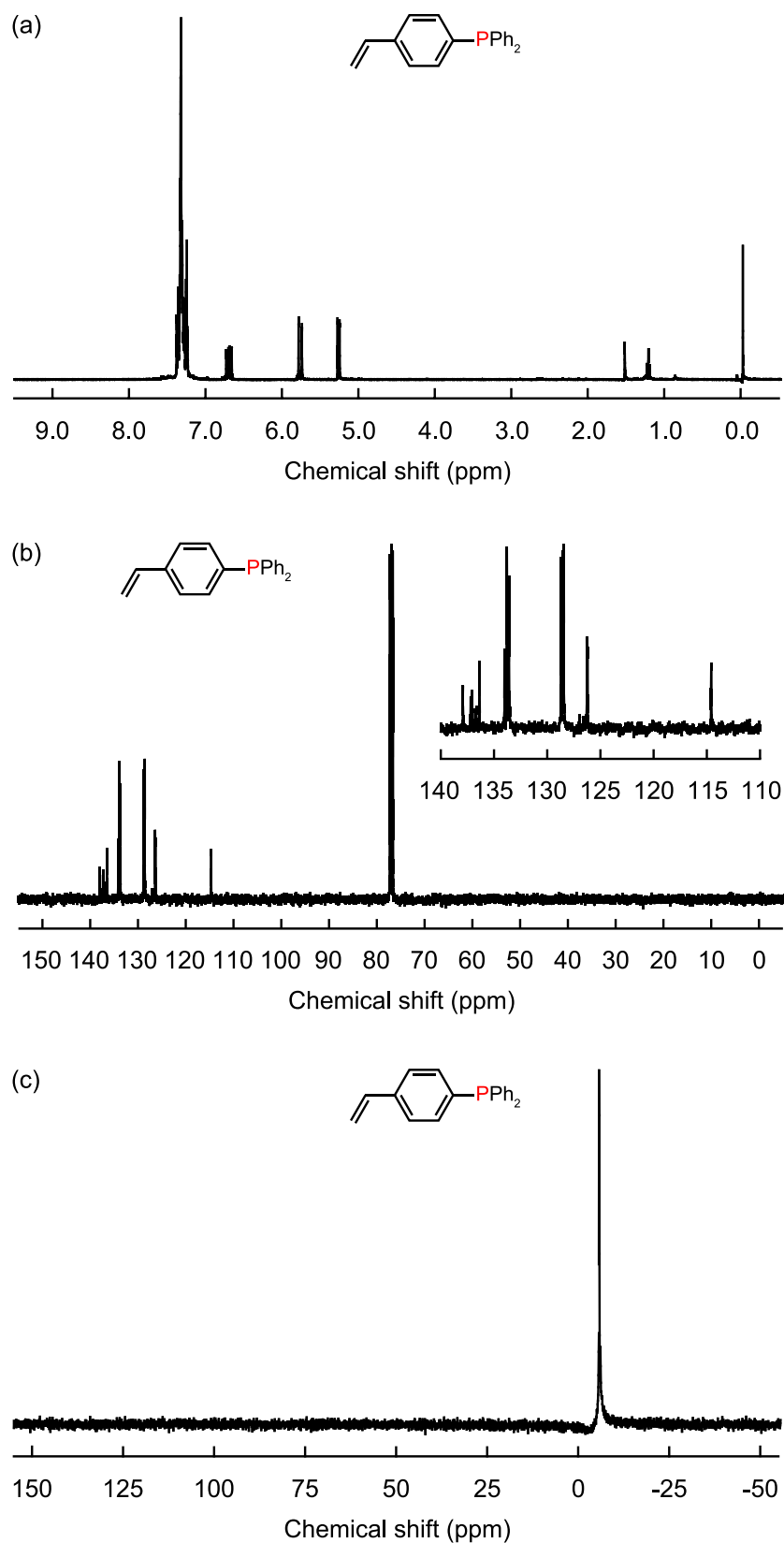


Figure S16. (a) ^1H , (b) ^{13}C , and (c) ^{31}P solution NMR spectra of (4-diphenylphosphino)-styrene.