

A new homogeneous polymer support based on syndiotactic polystyrene and its application in palladium-catalyzed Suzuki–Miyaura cross-coupling reactions

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Soluble syndiotactic polystyrene-supported triphenylphosphine (sPS–TPP) was synthesized by reacting borylated syndiotactic polystyrene with (4-bromophenyl)diphenylphosphine. A palladium catalyst, supported on sPS–TPP, effectively catalyzed Suzuki–Miyaura coupling reactions of aryl halides under homogeneous conditions. The polymer-supported palladium complex was recovered *quantitatively* by adding an equal volume of poor solvent to the polymer, and coupling products could be easily isolated by evaporating the solvents. The recovered polymer complex was reused several times without significant loss of activity.

Introduction

Homogeneous catalysts display better efficiency and higher selectivity than their heterogeneous counterparts, but tedious and time-consuming purification steps are required to remove homogeneous catalysts from the reaction mixture, making recovery and recycling difficult.¹ Since the introduction of the Merrifield resin for peptide synthesis, cross-linked polystyrene-supported catalysts have been adopted for numerous organic reactions to facilitate product purification and catalyst recovery.² Catalysts have also been supported on insoluble materials such as activated carbon,³ zeolite,⁴ metal oxide,⁵ insoluble polymer resin,⁶ and mesoporous silica nano particles.⁷ Despite the advantage of convenient separation, however, heterogeneous catalysts generally have slow diffusion rates, difficult characterizations, and lower activity owing to the nature of heterogeneous reaction conditions.⁸ It is also generally known that heterogeneous catalysis exhibits a lower degree of selectivity compared to the homogeneous counterpart, even though some exceptions of more selective heterogeneous catalysts have been found.⁹

Soluble polymer supports have been studied as a way to overcome the problems of insoluble supports. Soluble polymer supports allow expeditious transfer of solution-based synthetic protocols, circumventing the extensive optimization process often required in heterogeneous reactions. After the addition of an appropriate poor solvent, the polymer support can be

precipitated and filtered, allowing its expeditious recovery. Thus, these soluble polymer supports offer the advantage of use under homogeneous conditions and convenient catalyst separation.

Among the soluble polymer supports, oligomeric poly(ethylene glycol) (PEG, $M_n = 3\text{--}5\text{ kg mol}^{-1}$),¹⁰ oligomeric polyethylene (PE, $M_n \approx 3\text{ kg mol}^{-1}$),¹¹ and non-cross-linked atactic polystyrene (aPS)¹² are the most common supports used in organic synthesis and combinatorial chemistry. These supports have drawbacks that need to be addressed, however. For example, because PEG is soluble in water, it is unsuitable for organic reactions that involve aqueous work-up. In addition, PEG and PE are end-functionalized polymer supports, therefore, they have only modest loading capacity—typically less than 0.3 mmol g^{-1} for PEG and 0.1 mmol g^{-1} for PE. aPS is difficult to recover in high yield *via* the precipitation method and often needs membrane filtration.¹³ Thus, studies of recovery yield of soluble polymer supports have often been omitted.¹⁴

Herein we report a new type of soluble polymer support derived from crystalline syndiotactic polystyrene (sPS). Although various loading capacities can be achieved in aPS by changing functional group levels in the side chain of the polymer, the addition of excess cold poor solvent or membrane filtration is required to recover the atactic polymer in high yield and it often causes non-quantitative recovery on precipitation. Compared to aPS, sPS and functionalized sPS show a more restrictive solubility profile because of their high stereoregular configuration of phenyl rings along the polymer main chain and the resulting tendency toward crystallization.¹⁵ We theorized that this solubility *versus* recovery relationship of crystalline polymer—a well-known phenomenon in polymer chemistry—could lead to better recovery yield of the polymer support when precipitated with a poor solvent.

Recently, we reported a controlled functionalization of sPS *via* an iridium-catalyzed activation/borylation of aromatic C–H bonds. The functionalization allowed the introduction of a pinacolboronate ester [B(pin)] group in a quantity of up to 42 mol%.¹⁶ While working on the functionalization of sPS

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† Electronic supplementary information (ESI) available: Experimental details of recycling experiment on sPS-supported catalyst without addition of fresh Cs_2CO_3 , analytical data for the characterization of the isolated coupled products, and the spectral data of TPP–Br, sPS–TPP, and the isolated coupled products are reported. See DOI: 10.1039/b913060h

($M_n = 48.6 \text{ kg mol}^{-1}$, $M_w/M_n = 2.90$), we found that a functionalized sPS such as pinacolboronate ester-functionalized sPS [sPS-B(pin)] (50 mg) can be recovered *quantitatively* as a fine powder when dissolved in a good solvent (CHCl_3 , 2.5 mL) and precipitated by adding an *equal volume* of poor solvent (methanol, 2.5 mL) (Fig. 1a). To compare the solubility/recovery difference of sPS and aPS, we also did the same recovery experiment with borylated atactic polystyrene [aPS-B(pin)] (50 mg). The recovery yield of sPS-B(pin) was over 99%, whereas aPS-B(pin) was recovered only ~55% as a sticky solid under the same condition (Fig. 1b).

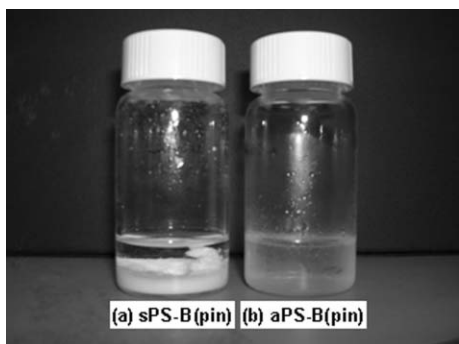
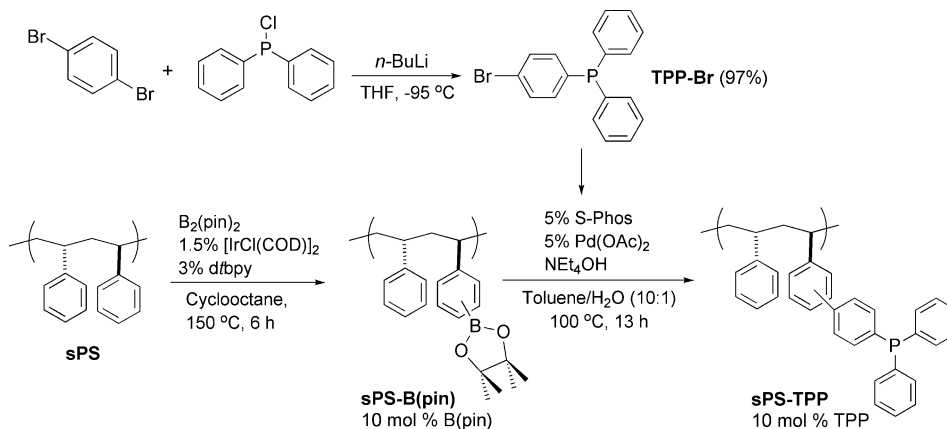


Fig. 1 Precipitation results of (a) sPS-B(pin) and (b) aPS-B(pin) after being dissolved in CHCl_3 and precipitated by adding an *equal volume* of CH_3OH .

Developing a controlled functionalization of sPS has allowed us to prepare sPS supports of variable loading capacity without sacrificing molecular weight and recovery yield. In this report, we describe the first example of an sPS-supported palladium catalyst and its use in Suzuki–Miyaura cross-coupling reactions. Because triphenylphosphine (TPP) is a widely used ligand in carbon–carbon bond forming coupling reactions and other soluble polymer supports,¹⁷ we decided to synthesize sPS-supported TPP (sPS–TPP; Scheme 1) and investigate its catalytic activity and reusability in palladium-catalyzed Suzuki–Miyaura cross-coupling reactions of aryl halides and aryl boronic acid.¹⁸ Recently there has been considerable interest in developing heterogeneous catalyst systems¹⁹ and recoverable homogeneous catalysts^{13,20} for Suzuki–Miyaura reactions.



Scheme 1 Synthesis of syndiotactic polystyrene-supported triphenylphosphine (sPS–TPP).

Results and discussion

As shown in Scheme 1, (4-bromophenyl)diphenylphosphine (TPP–Br) was synthesized in 97% yield from the reaction of 1,4-dibromobenzene and chlorodiphenylphosphine in THF. We prepared 10 mol% functionalized sPS–B(pin) *via* iridium-catalyzed C–H borylation according to a literature method.¹⁶ TPP was immobilized to sPS *via* the Suzuki–Miyaura coupling reaction of TPP–Br and sPS–B(pin), and the immobilized polymer support, sPS–TPP, was fully characterized using NMR spectroscopy.

The successful incorporation of the TPP moiety was confirmed in the ^{31}P NMR spectrum, which revealed a resonance at -5.0 ppm (Fig. 2c). The ^{31}P NMR spectrum did not show any resonance that could have resulted from aryl phosphine oxide. In addition, the ^1H NMR spectrum of sPS–TPP showed two new resonances at 7.34 and 7.51 ppm, which correlate to the phenyl groups of the attached TPP moiety (see Electronic Supplementary Information†). The phosphine loading level of sPS–TPP determined by ^1H NMR was 0.71 mmol g^{-1} (*i.e.*, 10 mol%). Unlike that of end-functionalized polymer supports,²¹ this loading capacity can be easily tuned by adjusting the

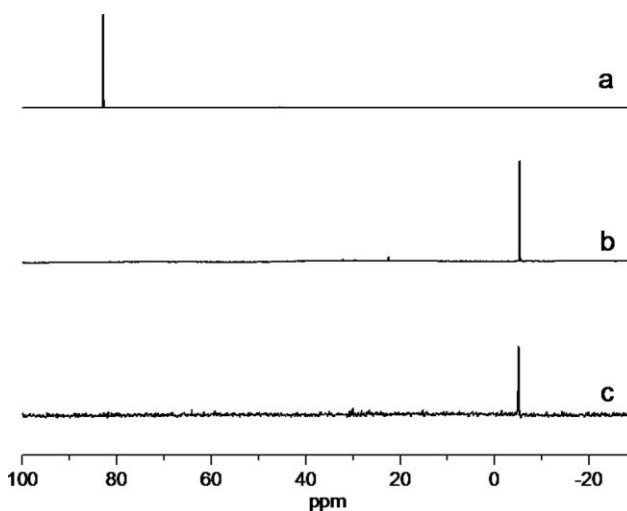
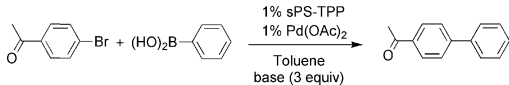


Fig. 2 ^{31}P NMR spectra of (a) chlorodiphenylphosphine ($\delta = 82.8 \text{ ppm}$), (b) TPP–Br ($\delta = -5.3 \text{ ppm}$), and (c) sPS–TPP ($\delta = -5.0 \text{ ppm}$).

Table 1 Effect of base on the sPS-TPP-supported Suzuki–Miyaura reactions of 4-bromoacetophenone and phenylboronic acid^a


Entry	Base	Time/h	Temp/°C	Conv. ^b (%)
1	Cs ₂ CO ₃	1	110	99
2	K ₃ PO ₄	1	110	92
3	K ₂ CO ₃	1	110	94
4	NEt ₄ OH	1	110	18
5	NaOH	1	110	91
6	NaOtBu	1	110	52

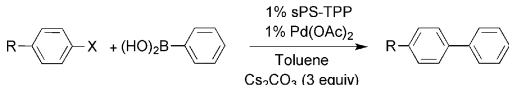
^a 4-Bromoacetophenone (0.044 mmol), phenylboronic acid (0.066 mmol), sPS-TPP (1 mol%), Pd(OAc)₂ (1 mol%), toluene (1 mL). ^b Conversion to coupled product determined using GC-MS.

pinacolboronate ester concentration in the C–H borylation step without affecting the solubility and recovery of the polymer.

sPS-TPP is readily soluble in common organic solvents including toluene, THF, dioxane, diglyme, DME, DMF, DMA, CH₂Cl₂, and CHCl₃ when heated gently; it is insoluble in hexane, diethyl ether, and methanol. Unlike aPS support, which requires the addition of excess cold poor solvent (*e.g.*, 10-fold volume of –30 °C methanol) for polymer recovery in high yield, support with sPS-TPP requires only the addition of an equal volume of methanol for quantitative precipitation of the polymer.

The catalyst activity of the soluble polymer-supported ligand was tested for the Suzuki–Miyaura coupling reactions of aryl bromides and chlorides with phenylboronic acid. The coupling of 4-bromoacetophenone (1 equiv.) and phenylboronic acid (1.5 equiv.) in toluene was performed as a model reaction under varying reaction conditions using a palladium catalyst generated *in situ* from the complexation of sPS-TPP (1 mol%) and Pd(OAc)₂ (1 mol%) (Table 1). Among the six different bases tested (Cs₂CO₃, K₃PO₄, K₂CO₃, NEt₄OH, NaOH, and NaOtBu), Cs₂CO₃ gave the highest conversion (99%) within 1 h (Table 1, entry 1). Thus, Cs₂CO₃ was selected as the base for polymer-catalyzed Suzuki–Miyaura reactions of various aryl halides with phenylboronic acid (Table 2).

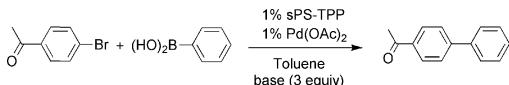
As shown in Table 2, Suzuki–Miyaura reactions of both electron-rich and electron-deficient aryl bromides proceed with high yields at 70 °C under homogeneous conditions. As expected, the reaction rates of electron-deficient aryl bromides were faster than those of electron-rich aryl bromides (entries 4, 6 and 8). Hence, the cross-coupling reactions of electron-rich aryl bromides required a slightly longer reaction time (*i.e.*, 4 h) to achieve over 80% yield (entries 10, 12 and 14). When conducted at 110 °C, all aryl bromides except for *p*-(*N,N*-dimethylamino)phenyl bromide afforded more than 99% conversion within 1 h and their products could be conveniently isolated by simple precipitation of the sPS-TPP-supported palladium catalyst and removal of the supported catalyst (entries 1, 3, 5, 7, 9, 11 and 13). Aryl chlorides are known to be much less reactive when TPP is used as a ligand.²² Although the sPS-TPP-supported palladium catalyst furnished the Suzuki–Miyaura reaction products of aryl chlorides, it did so in low yields even after 24 h at 110 °C (11–28%; Table 2, entries 17–19).

Table 2 sPS-TPP-supported Suzuki–Miyaura reactions of aryl halides with phenylboronic acid^a


Entry	R	X	Temp/°C	Time/h	Yield ^b (Conv. ^c) (%)
1	H	Br	110	1	96 (99)
2	H	Br	70	1	84 (93)
3	COCH ₃	Br	110	1	95 (99)
4	COCH ₃	Br	70	1	84 (94)
5	CF ₃	Br	110	1	93 (99)
6	CF ₃	Br	70	1	82 (93)
7	CHO	Br	110	1	94 (99)
8	CHO	Br	70	1	83 (95)
9	CH ₃	Br	110	1	91 (99)
10	CH ₃	Br	70	4	82 (90)
11	CH ₂ OH	Br	110	1	96 (99)
12	CH ₂ OH	Br	70	4	79 (89)
13	OCH ₃	Br	110	1	93 (99)
14	OCH ₃	Br	70	4	81 (87)
15	NMe ₂	Br	110	1	82 (88)
16	NMe ₂	Br	70	4	11 (20)
17	H	Cl	110	24	11 (20)
18	CHO	Cl	110	24	28 (41)
19	COCH ₃	Cl	110	24	17 (25)

^a Aryl bromide or aryl chloride (0.88 mmol), phenylboronic acid (1.32 mmol), sPS-TPP (1 mol%), Pd(OAc)₂ (1 mol%), toluene (2 mL).

^b Isolated yield obtained by column chromatography. ^c Conversion to coupled product determined using GC-MS.

Table 3 Recovery/recycling of sPS-TPP-supported palladium catalyst in Suzuki–Miyaura reactions and the leaching of palladium^a


Cycle ^b	1st	2nd	3rd	4th	5th
Conversion (%) ^c	99	96	99	98	66
Yield of product (%) ^d	96	96	97	95	— ^e
Purity (%) ^f	> 99	> 99	> 99	> 99	— ^e
Recovery yield of polymer support (%) ^g	99	98	98	99	99
Leaching of Pd (%) ^h	0.6	0.5	0.4	0.4	0.4

^a 4-Bromoacetophenone (14.2 mmol), phenylboronic acid (21.3 mmol), sPS-TPP (1 mol%), and Pd(OAc)₂ (1 mol%) at 110 °C for 1 h.

^b No additional Pd(OAc)₂ was added in the recycling experiments.

^c Conversion to coupled product determined using GC-MS based on an average of two experiments. ^d Isolated yield of product based on an average of two experiments. ^e Not measured. ^f Purity of product determined from ¹H NMR spectrum. ^g Recovered yield (weight%) of polymer support when precipitated by adding methanol and washed with H₂O. ^h Percentage of original Pd leached into the product solution.

Because we could recover sPS-TPP quantitatively by adding methanol, we performed the recycling experiment with the sPS-TPP-supported palladium catalyst (Table 3). After filtering the base and polymer-supported catalyst in the first run, we evaporated the volatile liquid from the filtrate and retrieved pure coupled product in 96% isolated yield. No additional purification process such as column chromatography was necessary. Washing the filtered solids with water removed the base and allowed measurement of the recovered polymer support. As shown in Table 3, the recovery yield of the polymer support is quantitative in each

cycle, demonstrating the great potential of the soluble support for use as a recoverable catalyst or reagent. The recovered polymer-supported catalyst was reused for the next cycle with fresh Cs_2CO_3 (see Table 3). Or alternatively, the filtered solid (*i.e.*, a mixture of polymer-supported catalyst and base) can be reused for the next cycle without adding fresh base.²³

The recycled sPS-supported palladium catalyst did not show any loss of catalytic activity up to a fourth cycle.²⁴ When we investigated the leaching of the palladium into the product solution after precipitation of the polymer support, however, we found that a very small percentage of the total amount of the original palladium species was lost to the product solution in each cycle [0.6%, 0.5%, 0.4%, 0.4%, and 0.4%, measured using inductively-coupled plasma atomic emission spectroscopy (ICP-AES)].²⁵ Considering the initial loading of $\text{Pd}(\text{OAc})_2$ in the first run of the reaction (1 mol%) and the convenience of product purification (just precipitation and filtration), the amount of palladium found in the product is very small (an average of 46 ppm of palladium in each cycle).

Conclusion

In summary, a soluble sPS-supported phosphine ligand was prepared by reaction of sPS-B(pin) with TPP-Br. The loading of the polymer support can be easily tuned by changing the boronate ester concentration in the C-H borylation of sPS. The sPS-TPP-supported palladium catalyst showed excellent catalytic activity in Suzuki-Miyaura coupling of aryl halides. Moreover, it could be recovered quantitatively through a simple precipitation/filtration process and reused multiple times without significant loss of activity.

Experimental

(4-Bromophenyl)diphenylphosphine (TPP-Br)²⁶

A solution of 1,4-dibromobenzene (3.00 g; 12.7 mmol) in THF (75 mL) was cooled to -95°C using a toluene/liquid nitrogen bath under a nitrogen atmosphere. *n*-BuLi (8.10 mL of 1.6 M in hexane; 12.7 mmol) was added slowly and the resulting solution was stirred at -95°C . After 1 h, chlorodiphenylphosphine (2.81 g; 12.7 mmol) was added. The solution was allowed to warm to room temperature, stirred overnight, and filtered through a short plug of Celite. The filtrate was evaporated under reduced pressure, and the remaining solid was extracted with hexane (300 mL) and filtered through a short plug of silica gel. Evaporation of the solvent from the filtrate afforded a pure, moderately air-stable white solid (4.21 g; 97% yield). δ_{H} (400 MHz, CDCl_3 , Me_4Si) 7.45 (dd, 2H, $J = 1.2$ and 8.0 Hz), 7.36–7.32 (m, 6H), 7.31–7.26 (m, 4H), 7.15 (dd, 2H, $J = 6.9$ and 8.0 Hz). δ_{C} (100 MHz, CDCl_3 , Me_4Si) 136.6 (d, C_5 , $J = 10.5$ Hz), 136.5 (d, C_4 , $J = 12.7$ Hz), 135.2 (d, C_3 , $J = 20.2$ Hz), 133.7 (d, C_6 , $J = 19.4$ Hz), 131.6 (d, C_2 , $J = 7.5$ Hz), 129.0 (s, C_8), 128.6 (d, C_7 , $J = 6.7$ Hz), 123.4 (s, C_1). δ_{P} (161.82 MHz, CDCl_3 , 85% H_3PO_4) -5.32 (s).

Preparation of sPS-supported triphenylphosphine (sPS-TPP).

In a nitrogen-filled glovebox, sPS-B(pin) [500 mg; 0.470 mmol B(pin)], (4-bromophenyl)diphenylphosphine [1.30 g; 3.79 mmol; 8 equiv. based on the amount of boron concentration of

sPS-B(pin)], $\text{Pd}(\text{OAc})_2$ [5.3 mg; 0.024 mmol; 5 mol% based on the amount of boron concentration of sPS-B(pin)], S-Phos [11.0 mg; 0.0240 mmol; 5 mol% based on the amount of boron concentration of sPS-B(pin)], toluene (10 mL), and a magnetic stirring bar were placed in a vial. The vial was capped with a Teflon-lined septum and removed from the glovebox. NET_4OH solution [0.6 mL of 35% solution; 1.42 mmol; 3 equiv. based on the amount of boron concentration of sPS-B(pin)] and water (1 mL) were added to the vial. The vial was placed in an oil bath at 100°C for 13 h. After cooling, the reaction mixture was diluted with chloroform (50 mL), dried with magnesium sulfate, and filtered through a short plug of Celite. The filtrate was concentrated using a rotary evaporator to approximately 7 mL, and methanol (7 mL) was added to precipitate polymer. The precipitated polymer was filtered and dried under vacuum at 60°C for 12 h (589 mg; 103% yield based on polymer weight). δ_{H} (400 MHz, CDCl_3 , Me_4Si) 1.29 (2H, CH_2 of sPS main chain), 1.80 (1H, CH of sPS main chain), 6.53 (2H, H_c and H_g of C_6H_5 in sPS side chain), 7.05 (3H, H_d , H_e , and H_f of C_6H_5 in sPS side chain), 7.34 (14H, $H_{2,3,5,6,8,9,10}$ of triphenylphosphine moiety in the polymer), 7.51 (2H, H_{11} of triphenylphosphine moiety in the polymer). δ_{C} (100 MHz, CDCl_3 , Me_4Si) 145.2 (C_c of C_6H_5 in sPS side chain), 137.3 (d, C_7 , $J = 10.5$ Hz), 133.7 (d, C_8 , $J = 18.7$ Hz), 128.7 (s, C_{10}), 128.5 (d, C_9 , $J = 7.5$ Hz), 127.9 (C_e of C_6H_5 in sPS side chain), 127.7 (C_d of C_6H_5 in sPS side chain), 125.6 (C_f of C_6H_5 in sPS side chain), 43.9 (CH_2 of sPS main chain), 40.6 (CH of sPS main chain). δ_{P} (161.82 MHz, CDCl_3 , 85% H_3PO_4) -5.04 (s).

General procedure of sPS-support-catalyzed Suzuki-Miyaura cross-coupling in Table 2. In a nitrogen-filled glovebox, aryl halide (0.880 mmol; 1 equiv.), phenylboronic acid (161 mg; 1.32 mmol; 1.5 equiv.), $\text{Pd}(\text{OAc})_2$ (2.0 mg; 0.0088 mmol; 1 mol% based on the amount of aryl halide), Cs_2CO_3 (860 mg; 2.64 mmol; 3 equiv.), and a magnetic stirring bar were placed in a vial. sPS-TPP (12.4 mg; 0.00880 mmol TPP; 1 mol% based on the amount of aryl halide) and toluene (2 mL) were placed in another vial. Both vials were capped with Teflon-lined septa and removed from the glovebox. sPS-TPP was dissolved in toluene by applying gentle heat. The sPS-TPP solution was transferred to the aryl halide solution using a syringe, and the reaction mixture was stirred in an oil bath under the specified conditions in Table 2 (70 and 110°C for aryl bromide and 110°C for aryl chloride). The reaction mixture was cooled to room temperature, diluted with chloroform (2 mL), and filtered through a short plug of Celite. The filtrate was concentrated by a rotary evaporator to approximately 2 mL, and methanol (2 mL) was added to precipitate the polymer. The precipitated polymer was removed by filtration through a short plug of Celite. The filtrate was dried under vacuum and analyzed using GC-MS to check conversion of the coupled product. Isolation by column chromatography afforded the pure product.

Recycling experiment of sPS-supported catalyst in Table 3.

In a nitrogen-filled glovebox, 4-bromoacetophenone (2.83 g; 14.2 mmol; 1 equiv.), phenylboronic acid (2.60 g; 21.3 mmol; 1.5 equiv.), Cs_2CO_3 (13.9 g; 42.6 mmol; 3 equiv.), $\text{Pd}(\text{OAc})_2$ (31.8 mg; 0.142 mmol; 1 mol%), sPS-TPP (184 mg; 0.142 mmol TPP; 1 mol%), toluene (33 mL), and a magnetic stirring bar were placed in a 250 mL flask. The flask was removed from

the glovebox and placed in an oil bath at 110 °C for 1 h. The reaction mixture was cooled to room temperature, filtered, and washed with hot toluene (100 mL). The filtered solid, which contains base and polymer-supported palladium catalyst, was washed with additional hot toluene (20 mL × 2) and dried under vacuum. The filtrate was concentrated by a rotary evaporator to approximately 10 mL, and methanol (10 mL) was added to precipitate the remaining polymer support which was collected by centrifugation (~30 mg of polymer was recovered). Although the remaining polymer precipitated quantitatively with the addition of 10 mL of methanol, additional methanol (300 mL) was added to the toluene/methanol solution in order to prevent co-precipitation of the product with the polymer during centrifugation—because the solubility of the product in methanol for the centrifugation process was found to be ~10 mg mL⁻¹ and the expected weight of the product was 2.78 g, it was necessary to add 300 mL of methanol to prevent co-precipitation of the product. After removal of the precipitated polymer, evaporation of the centrifuged methanol solution afforded pure product (96% yield), which was analyzed by ¹H and ¹³C NMR spectroscopy to check the purity, and subjected to ICP-AES to determine the amount of leached palladium. The polymer recovered from the centrifugation was dried, combined with the initially filtered base and polymer-supported palladium catalyst mixture, and washed with water (400 mL) to remove the base. The resulting brownish polymer solid was filtered, washed with water (50 mL × 2) and methanol (10 mL × 1), and dried under vacuum. The weight percent of the brownish polymer relative to the initial weight of sPS–TPP is provided as the recovery yield of polymer support in Table 3. Fresh Cs₂CO₃ (3 equiv.), 4-bromoacetophenone (2.83 g; 14.2 mmol; 1 equiv.), phenylboronic acid (2.60 g; 21.3 mmol; 1.5 equiv.), and toluene (33 mL) were added to the recovered polymer support, and they were used for the next run.

Acknowledgements

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- See Electronic Supplementary Information for detailed procedures for the alternative recycling experiment†.
- It appears that the sPS–TPP–Pd complex was gradually deactivated over the course of recycling work-up procedure (*i.e.*, precipitation of the polymer support with methanol and washing with water to remove the base). The total amount of palladium leached out during the recycling was not significant; 0.023 mol% (2.3% × 1 mol%) over the five cycles. Thus, the loss of palladium due to leaching will not be a major culprit that causes the loss of catalytic activity. A similar deactivation of palladium-phosphine complex supported on cross-linked polystyrene has been reported. See C. A. Parrish and S. L. Buchwald, *J. Org. Chem.*, 2001, **66**, 3820.
- In the ICP-AES experiment, we also discovered that the synthesized sPS–TPP contained a small quantity of palladium (0.37 wt%) possibly due to the coordination of palladium to the phosphine during sPS–TPP synthesis. However, the 1 mol% sPS–TPP alone, although it contains 0.045 mol% of residual palladium, could not catalyze Suzuki–Miyaura coupling reactions of aryl bromide even at 110 °C and only starting materials were observed.
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