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Selective Syntheses of Mono- and Diphosphanyltriazines as Novel Ligands for Transition Metal Catalysts

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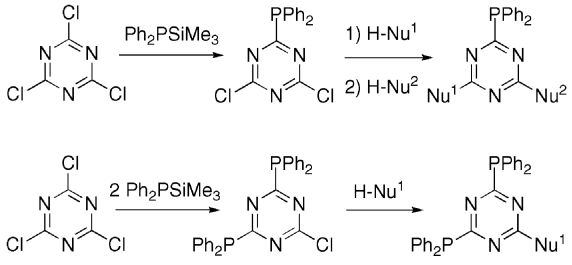
1,3,5-Triazines bearing one, two or three diphenylphosphanyl group(s) were selectively synthesized from cyanuric chloride by the one-pot step-by-step addition of silylphosphane and other nucleophiles. Mono- and diphosphanyltriazines with a variety of substituents on the triazine ring could be easily prepared in good yields. The Pd complexes of mono- and diphosphanyltriazine were isolated, and the crystal structures were determined. Polymer-supported and water-soluble ligands were prepared. The Mizorogi–Heck reaction and the Suzuki–Miyaura coupling reaction using the phosphanyltriazine-Pd catalysts are described.

Introduction

The synthesis of organophosphorus compounds have received much attention due to their essential roles in various fields of chemistry, especially as ligands in transition-metal catalysis.[1] However, the synthesis of organophosphanes with various functional groups still has many difficulties due to limitations in P–C bond formation.[1] One of the promising ways to prepare such functional phosphanes is to use a suitable multifunctional, reactive linker, which connects functional side-chains with the phosphane parts. 1,3,5-Triazine should be advantageous as such a linker because there are plenty of synthetic examples of triazine derivatives prepared by the step-by-step addition of nucleophiles to cyanuric chloride[2] as potential building blocks in materials chemistry.[3] In addition, Hoge et al. recently reported the synthesis and properties of tris-triazinophosphane derivatives prepared from chlorotriazine derivatives and tris(trimethylsilyl)phosphane [$P(SiMe_3)_3$].[4] This result clearly indicated that phosphanyltriazines could be accessed by P–C bond formation using a silylphosphane. However, there is no practical synthesis of 1,3,5-triazines bearing phosphane groups by the selective and stepwise addition of phosphane functionalities to cyanuric chloride.[5]

We have developed some synthetic reactions of organophosphanes by using a silylphosphane as a P source.[6] Therefore, we have tried to apply cyanuric chloride as a reactive linker for functional phosphane synthesis, by developing a procedure for stepwise substitutions by silylphosphanes and other nucleophiles, as shown in Scheme 1.



Scheme 1. Step-by-step syntheses of functional phosphanes with a triazine core.

Herein, we wish to report a novel synthesis of phosphanyltriazines by the one-pot, stepwise addition of silylphosphane and other nucleophiles. The formation of their Pd complexes and the application in the catalytic reaction are also described.

Results and Discussion

We attempted the selective substitution of three chlorines on cyanuric chloride by a silylphosphane in the initial stage of the research. We treated cyanuric chloride **1** with 1.0, 2.2 or 4.5 equiv. of (trimethylsilyl)diphenylphosphane (**2**) and monitored each reaction by ^{31}P NMR spectroscopy. Due to the distinct difference in the reactivities between the substitution steps, we accomplished the selective substitution with one, two or three phosphane group(s) simply by changing the amount of the nucleophile, as shown in Figure 1. Since

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the intermediate phosphanyltriazines were too unstable to isolate, we identified these intermediates by their FABMS spectra and NMR spectra. Silylphosphane **2** was the best suited for the present selective substitution; other phosphorus nucleophiles, such as lithium diphenylphosphide ($LiPPh_2$) and diphenylphosphane (Ph_2PH), could not accomplish the controlled mono- and disubstitution.[7]

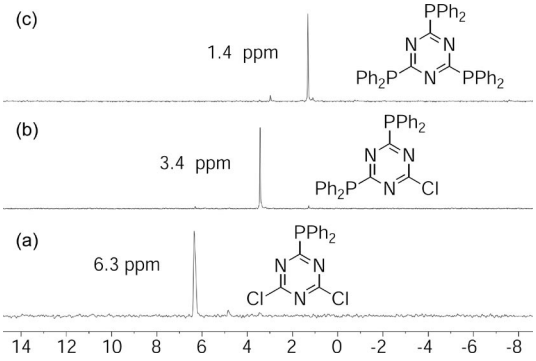
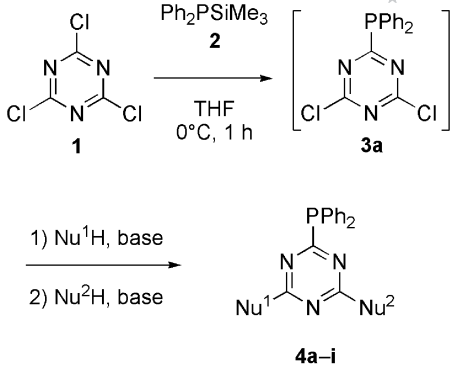


Figure 1. ^{31}P NMR spectra of the reaction mixture of cyanuric chloride and (a) silylphosphane (1.0 equiv.); (b) silylphosphane (2.2 equiv.) or (c) silylphosphane (4.5 equiv.) in THF.

To convert the unstable intermediates to more stable derivatives, we performed further substitutions by other nucleophiles before isolation. We conducted the syntheses of mono-phosphane-substituted 1,3,5-triazines by the reaction of cyanuric chloride with 1.1 equiv. of silylphosphane **2** in THF at 0 °C. We then reacted the intermediate dichloride **3a** with amines and/or alcohols in the presence of an adequate base to give amino- and/or alkoxy-substituted phosphanyltriazines **4a**–**i**. The results are shown in Table 1 and Scheme 2.

When we treated an excess of amine with **3a**, the symmetrically substituted diaminophosphanyltriazines formed in good yields (Table 1, Entries 1 and 3–5). In addition to the primary and secondary amines, we also applied an aqueous solution of a small amine (Table 1, Entries 3 and 4). Diisopropylethylamine (DIPEA) was the best-suited base for this substitution when we used an equimolar amount of the amine.[8] In this case, each step of the substitution by two moles of amine were also highly selective. Thus, we could also prepare asymmetrically substituted diaminophosphanyltriazines by the stepwise addition of a silylphosphane and



Scheme 2.

two amines (Table 1, Entry 7). We also incorporated alkoxy substituents by the reaction of **3a** with an alcohol as a solvent (Table 1, Entry 8) or with an equimolar amount of alcohol in the presence of CsF in DMF (Table 1, Entry 9). Since only one alkoxy group was incorporated into **3a** in the absence of CsF, we could prepare triazine **4i** with P, O and N substituents in one pot in good selectivity (Table 1, Entry 10).

We obtained bis(phosphane)-substituted 1,3,5-triazines in good yield by the reaction of **1** with 2.2 equiv. of silylphosphane **2** in THF, followed by substitution with an amine or an alcohol. The results are shown in Table 2 and Scheme 3.

Table 2. Selective synthesis of diphosphanyltriazines.

Entry	NuH	Base	Conditions	Product	Yield [%][a]
1	morpholine	–[b]	r.t., 3 h	**5a**	87
2	morpholine	DIPEA	r.t., 3 h	**5a**	87
3	$nBuNH_2$	–[b]	r.t., 1 h	**5b**	55
4	NH_3[c]	–[b]	r.t., 1.5 h	**5c**	87
5	$PhCHMeNH_2$	DIPEA	r.t., 1.5 h	**5d**	63
6	CH_3OH	DIPEA	r.t., 5 h	**5e**	68
7	$Ph(CH_2)_3OH$	CsF, DIPEA	r.t., 15 h	**5f**	63

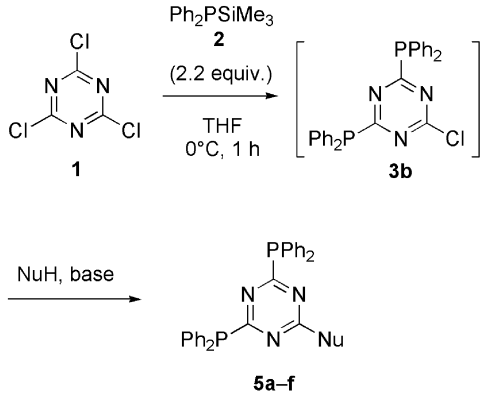
[a] Isolated yield. [b] An excess amount of amine was used. [c] Aqueous solution was used.

Phosphanyltriazines have multiple sites for interaction with transition metals through both the organophosphane part(s) and the Ns on the triazine ring. Thus, the intricate behavior of their complex formation has been forecasted.[9]

Table 1. Selective synthesis of mono-phosphanyltriazines.

Entry	Nu^1H	Nu^2H	Base	Conditions	Product	Yield [%][a]
1	morpholine	–[b]	–[b]	r.t., 1 h	**4a**	57
2	morpholine	–	DIPEA	r.t., 1 h	**4a**	85
3	Me_2NH[c]	–[b]	–[b]	r.t., 2.5 h	**4b**	64
4	NH_3[c]	–[b]	–[b]	r.t., 4 d	**4c**	49
5	$nBuNH_2$	–[b]	–[b]	r.t., 1.5 h	**4d**	74
6	$PhMeCHNH_2$	–[b]	DIPEA	r.t., 1.5 h	**4e**	50
7	morpholine	Et_2NH	DIPEA	r.t., 2 h	**4f**	76
8	CH_3OH	–	DIPEA	r.t., 5 h	**4g**	55
9[d]	$Ph(CH_2)_3OH$	–	CsF, DIPEA	r.t., 14 h	**4h**	66
10	$Ph(CH_2)_2OH$	morpholine	DIPEA	r.t., 10 h	**4i**	68

[a] Isolated yield. [b] An excess amount of nucleophile and/or amine was used. [c] Aqueous solution was used. [d] DMF was used instead of THF in the latter step.



Scheme 3.

Indeed, various complexes were formed depending on both the ligand structure and the metal/ligand (M/L) ratio, especially the metal/P ratio. We note that we observed simple complex formation when we reacted Pd^{II} and phosphanyltriazine **4a** or **5c** in an adequate Pd/P ratio (1:2 for **4a** and 1:1 for **5c**). In both cases, ^{31}P NMR showed a single signal around 30 ppm, which indicated the formation of a P-Pd complex. Complexes Pd/**4a** and Pd/**5c** gave single crystals suitable for X-ray crystallographic analyses.[10] The ORTEP drawings are shown in Figures 2 and 3, respectively. The P atoms are coordinated to Pd in both complexes in accordance with the NMR results. Two triazine rings are parallel to each other at a distance of about 3.6 Å. We note that the Pd in both complexes had a *cis* orientation in a square planar configuration; two ligand molecules behave formally as bidentate ligands probably due to the π-interaction of the two triazine rings. Thus, bis-phosphane ligand **5c** gave the bridging dinuclear complex due to the orientation of the two phosphanyl groups, whereas mono-phosphane ligand **4a** exclusively gave the *cis* complex.

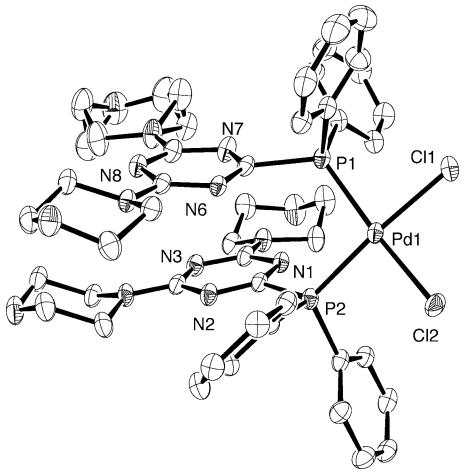


Figure 2. ORTEP drawing of complex Pd-**4a** (30% probability for thermal ellipsoids; one of the independent Pd complex molecules is shown; hydrogen atoms are omitted for clarity; one of the morpholine ring has disordered conformations.).

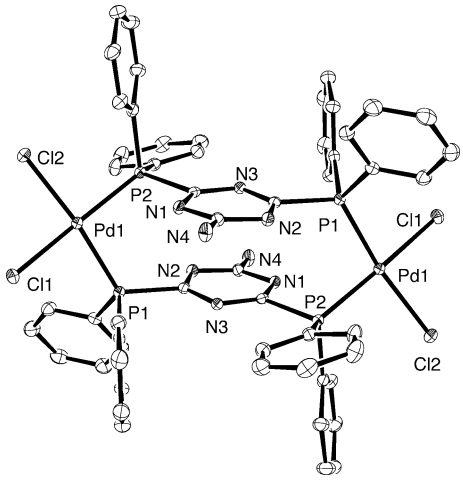


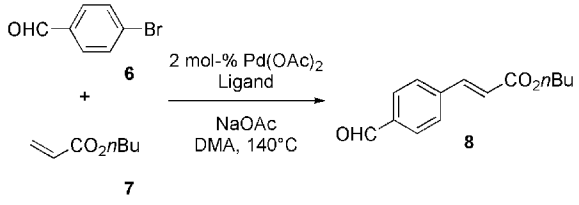
Figure 3. ORTEP drawing of complex Pd-**5c** (30% probability for thermal ellipsoids; hydrogen atoms and solvent molecules are omitted for clarity.).

We applied phosphanyltriazine **4a** to the Mizorogi–Heck reaction as a model ligand. The coupling reactions under several conditions are summarized in Table 3. The coupling reaction of **6** with butyl acrylate proceeded quite smoothly (Scheme 4).

Table 3. Phosphanyltriazine-Pd-catalyzed Mizorogi–Heck reaction.[a]

Entry	Pd/P	Ligand	Time [min]	Conversion [%][b]
1	1:4	**4a**	30	100
2	1:2	**4a**	5	97
3	1:1	**4a**	5	96
4	1:4	**4d**	60	82
5	1:4	**5a**	60	100

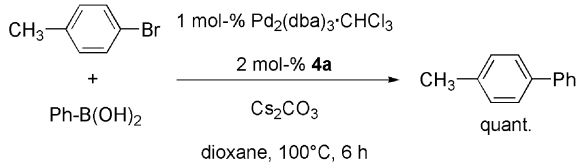
[a] Reactions were conducted by using 2 mol-% $Pd(OAc)_2$ in DMA at 140 °C. NaOAc was used as a base. [b] Determined by ^1H NMR spectroscopy.



Scheme 4.

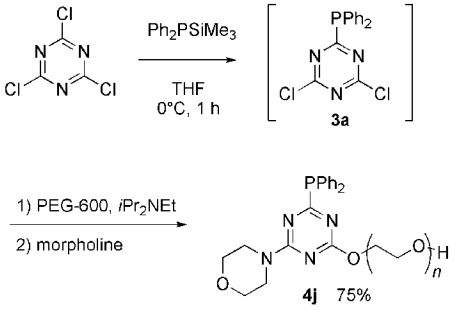
The activity of the catalyst strongly depended on the Pd/ligand. In the case of Pd/P = 1:2, the initial rate of the catalytic reaction was quite high; the reaction completed within 5 min. However, the turn over number (TON) was as high as 7000.[11] In contrast, when we used Pd/P = 1:4, the initial rate was slower than in the former case. However, the TON reached up to 18000.[11] These results were much better than those of the reaction using the triarylphosphane-Pd catalysts [PPh_3: 4 h, 86%; P(*o*-Tol)$_3$: 1.5 h, 92%]. This suggests that the triazine rings in the ligand have positive effects for both the reactivity and the stability of the catalyst.

The phosphanyltriazine-Pd catalysts are also effective in Suzuki–Miyaura coupling reactions (Scheme 5). The coupling of phenylboronic acid with *p*-bromotoluene proceeded smoothly under the usual coupling conditions to give the coupling product in excellent yield.

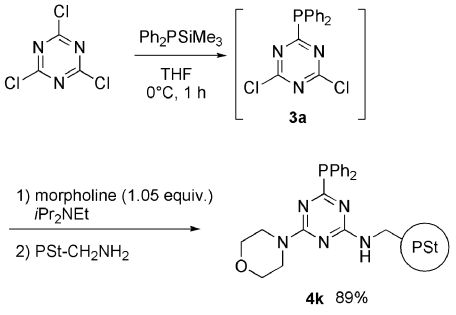


Scheme 5.

We note that the properties and efficiency of the catalyst are easily tunable since the present synthesis allows for the preparation of phosphanyltriazines bearing a variety of substituents with functionality, such as water-soluble chains or a solid support, as shown below (Scheme 6 and Scheme 7).

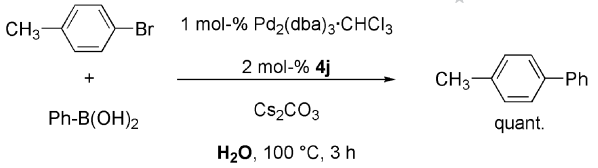


Scheme 6. Phosphanyltriazine ligand with a PEG side chain.



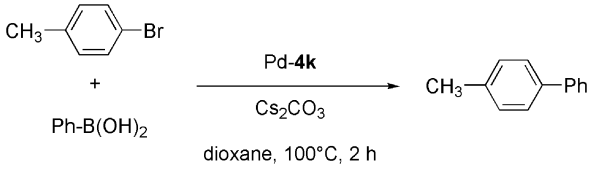
Scheme 7. Phosphanyltriazine ligands on a solid support.

The tunable solubility was well-demonstrated by the properties of PEG-phosphanyltriazine **4j**; it was soluble in both water and most organic solvents. We tuned the solubility by changing the length of the PEG chain and the substituent on the other site. The tuned ligand **4j** worked well in the Pd-catalyzed cross coupling in water (Scheme 8).



Scheme 8. PEG–phosphanyltriazine-Pd-catalyzed Suzuki–Miyaura coupling in water.

Polymer-supported phosphanyltriazine **4k** was also a good ligand for the Suzuki–Miyaura coupling. After the reaction was complete, we recovered the PSt-supported **4k**-Pd catalyst simply by filtration, washing with solvent, drying and reusing it in the next reaction. We reused it five times without loss of reactivity. However, reusing it more than five times caused a remarkable decrease in reactivity (Scheme 9, Table 4). The further effects of the substituents on the phosphanyltriazines and the property tuning of the supported ligands are still under investigation.



Scheme 9.

Table 4. Repetitive use of polymer-supported, phosphanyltriazine-Pd catalyst in a Suzuki–Miyaura coupling reaction.[a]

Entry	Run	Reuse[b]	Time [h]	Yield [%][c]
1	1	0	2	>99
2	2	1	2	>99
3	3	2	2	>99
4	4	3	2	>99
5	5	4	2	98
6	6	5	2	76
7	7	6	2	43

[a] Reactions were conducted by using 5 mol-% Pd-**4k** in dioxane at 100 °C. Cs_2CO_3 was used as a base. [b] The polystyrene-supported catalyst was recovered by filtration. The recovered catalyst was washed and dried before the next use. [c] Determined by ^1H NMR spectroscopy.

Conclusions

A simple and straightforward synthesis of phosphanyltriazines with one or two phosphane group(s) and other substituent(s) has been developed. Several types of 1,3,5-triazines with P, N and O substituents were synthesized, and the Pd complex of those phosphanyltriazines could be prepared by mixing a Pd source and the ligand in an adequate ratio. The phosphanyltriazine was successfully applied as a ligand to the Pd-catalyzed Mizorogi–Heck reaction and Suzuki–Miyaura coupling reaction. The properties of the phosphanyltriazine could be tuned by introducing a func-

tional side chain, which was well-demonstrated by the synthesis and application of the PEG-connected and the PSt-supported phosphanyltriazines.

Experimental Section

General: (Trimethylsilyl)diphenylphosphane (**2**) was prepared from Ph_3P, Li and TMSCl in THF. The other chemicals were purchased and purified prior to use. Experimental procedures and characterization data (^1H, ^{13}C, and ^{31}P NMR and MS) are reported below.

General Procedure for the Synthesis of Monophosphanyltriazine 4: To a THF solution of cyanuric chloride (**1**) was added silylphosphane **2** (1.0–1.1 equiv.) at 0 °C under Ar. After the mixture was stirred for 1 h, the solvent and TMSCl formed were removed under reduced pressure. THF, DIPEA (2.5 equiv. when used) and the nucleophilic reagent (2.0–2.5 equiv. or an excess amount) were added to the residue, and then the mixture was stirred for 1 h. After THF was removed, water was added, and the product was extracted twice with $CHCl_3$. The extraction should be done as soon as possible to avoid oxidation of the desired phosphane. The extract was dried and evaporated, and the crude product was then purified with column chromatography on silica gel to give the pure products **4a** (85% yield, 1.37 g from 3.72 mmol of **1**), **4b** (64% yield, 796 mg from 3.55 mmol of **1**), **4c** (49% yield, 504 mg from 3.52 mmol of **1**), **4d** (74% yield, 2.22 g from 7.36 mmol of **1**), **4e** (50% yield, 884 mg from 3.51 mmol of **1**), **4f** (76% yield, 298 mg from 0.93 mmol of **1**), **4g** (55% yield, 665 mg from 3.72 mmol of **1**), **4h** (66% yield, 312 mg from 0.89 mmol of **1**) and **4i** (68% yield, 297 mg from 0.93 mmol of **1**).

Typical Procedure for the Synthesis of Diphosphanyltriazine 5: To a THF solution of cyanuric chloride (**1**) was added silylphosphane **2** (2.1–2.5 equiv.) at room temp. under Ar. After the mixture was stirred for 1 h, the solvent and TMSCl formed were removed under reduced pressure. THF and an amine (2.5–5.3 equiv.) were added to the residue, and the mixture was then stirred for 1–3 h. After THF was removed, water was added, and the product was extracted twice with $CHCl_3$. The extraction should be done as soon as possible to avoid oxidation of the desired phosphane. The extract was dried and evaporated, and the crude product was then purified with column chromatography on silica gel to give the pure products **5a** (87% yield, 413 mg from 0.89 mmol of **1**), **5b** (66% yield, 1.35 g from 3.65 mmol of **1**), **5c** (87% yield, 706 mg from 1.74 mmol of **1**), **5d** (63% yield, 555 mg from 1.55 mmol of **1**), **5e** (68% yield, 289 mg from 0.89 mmol of **1**) and **5f** (63% yield, 268 mg from 0.89 mmol of **1**).

Physical Data for 4 and 5

2-(Diphenylphosphanyl)-4,6-dimorpholino-1,3,5-triazine (4a): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.40–3.90 (br., 16 H, -N-CH_2-CH_2-O-), 7.28–7.36 (m, 6 H, arom.), 7.50–7.58 (m, 4 H, arom.) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 43.3 (4 C, CH_2-N), 66.6 (4 C, CH_2-O), 127.8 (d, $^3J_{C,P}$ = 7.6 Hz, 4 C, *meta*-C), 128.7 (s, 2 C, *para*-C), 134.6 (d, $^2J_{C,P}$ = 19.2 Hz, 4 C, *ortho*-C), 135.2 (d, $^1J_{C,P}$ = 6.9 Hz, 2 C, *ipso*-C), 163.2 (d, $^3J_{C,P}$ = 8.5 Hz, 2 C, triazine-4,6), 183.3 (d, $^3J_{C,P}$ = 16.4 Hz, 1 C, triazine-2) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = –0.50 ppm. FABMS: 436 $[M + H]^+$.

4,6-Bis(dimethylamino)-2-(diphenylphosphanyl)-1,3,5-triazine (4b): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.90–3.12 (br., 12 H, CH_3-N), 7.28–7.34 (m, 6 H, arom.), 7.53–7.60 (m, 4 H, arom.) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 35.8 (br., 4 C, N-CH_3), 127.8 (d, $^3J_{C,P}$ = 7.4 Hz, 4 C, *meta*-C), 128.5 (s, 2 C, *para*-C), 134.8 (d, $^2J_{C,P}$ = 19.0 Hz, 4 C, *ortho*-C), 135.9 (d, $^1J_{C,P}$ = 7.5 Hz, 2 C, *ipso*-C), 163.8 (d, $^3J_{C,P}$ = 9.0 Hz, 2 C, triazine-4,6), 182.0 (d, $^3J_{C,P}$ = 19.0 Hz, 1 C, triazine-2) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = –1.20 ppm. FABMS: 353 $[M + H]^+$.

4,6-Diamino-2-(diphenylphosphanyl)-1,3,5-triazine (4c): ^1H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 6.63 (br., 4 H, NH_2), 7.30–7.36 (m, 6 H, arom.), 7.40–7.48 (m, 4 H, arom.) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 128.8 (d, $^3J_{C,P}$ = 7.6 Hz, 4 C, *meta*-C), 129.4 (s, 2 C, *para*-C), 135.0 (d, $^2J_{C,P}$ = 19.9 Hz, 4 C, *ortho*-C), 136.1 (d, $^1J_{C,P}$ = 7.5 Hz, 2 C, *ipso*-C), 166.0 (d, $^3J_{C,P}$ = 9.0 Hz, 2 C, triazine-4,6), 183.4 (d, $^1J_{C,P}$ = 19.4 Hz, 1 C, triazine-2) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]DMSO, 25 °C): δ = –2.40 ppm. FABMS: 296 $[M + H]^+$.

4,6-Bis(butylamino)-2-(diphenylphosphanyl)-1,3,5-triazine (4d): ^1H NMR (400 MHz, [D$_6$]DMSO, 100 °C): δ = 0.85 (t, J = 7.3 Hz, 6 H, -CH_3), 1.26 (sextet, J = 7.3 Hz, 4 H, -CH_2-CH$_3$), 1.44 (quintet, J = 7.2 Hz, 4 H, -CH$_2$-CH_2-CH$_2$-), 3.18 (q, J = 6.0 Hz, 4 H, NH-CH_2-), 6.45–6.55 (br., 2 H, NH), 7.28–7.34 (m, 6 H, arom.), 7.47–7.55 (m, 4 H, arom.) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]DMSO, 100 °C): δ = 13.8 (2 C, -CH_3), 19.9 (2 C, -CH_2-CH$_3$), 31.8 (2 C, -CH$_2$-CH_2-CH$_2$-), 41.0 (2 C, N-CH_2-), 128.3 (d, $^3J_{C,P}$ = 7.5 Hz, 4 C, *meta*-C), 129.0 (s, 2 C, *para*-C), 134.7 (d, $^2J_{C,P}$ = 19.7 Hz, 4 C, *ortho*-C), 136.6 (d, $^1J_{C,P}$ = 9.3 Hz, 2 C, *ipso*-C), 165.0 (d, $^3J_{C,P}$ = 9.1 Hz, 2 C, triazine-4,6), 182.5 (d, $^1J_{C,P}$ = 17.0 Hz, 1 C, triazine-2) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]DMSO, 100 °C): δ = –0.50 ppm. FABMS: 409 $[M + H]^+$.

2-(Diphenylphosphanyl)-4,6-bis[(*R*)-1-phenylethylamino]-1,3,5-triazine (4e): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.25–1.55 (m, 6 H, -CH_3), 4.85–5.55 (m, 2 H, -CHPh), 7.00–8.00 (m, 10 H, arom.) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, mixture of rotamers): δ = 22.5 (2 C, -CH_3), 49.7–51.0 (m, 2 C, -CH-Ph), 126.1, 127.0, 128.0–128.8 (m), 128.5, 129.0, 131.7–132.5 (m), 134.5–135.1 (m), 143.8–144.3 (m), 163.7 (d, $^3J_{C,P}$ = 8.2 Hz, 2 C, triazine-4,6), 183.1 (d, $^1J_{C,P}$ = 13.4 Hz, 1 C, triazine-2) ppm. $^{31}P\{^1H\}$ NMR: δ = –0.51 ppm. FABMS: 504 $[M + H]^+$.

6-(Diethylamino)-2-(diphenylphosphanyl)-4-morpholino-1,3,5-triazine (4f): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.92 (t, J = 6.8 Hz, 3 H), 1.17 (t, J = 6.8 Hz, 3 H, -CH_3), 3.35 (q, J = 6.8 Hz, 2 H, -CH_2-CH$_3$), 3.47 (q, J = 6.8 Hz, 2 H, -CH_2-CH$_3$), 3.65 (br., 4 H, CH_2-N), 3.67 (br., 4 H, CH_2-O), 7.27–7.34 (m, 6 H, arom.), 7.52–7.59 (m, 4 H, arom.) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 12.9 (1 C, -CH_3), 13.3 (1 C, -CH_3), 41.2 (1 C, -CH_2-CH$_3$), 41.6 (1 C, -CH_2-CH$_3$), 43.4 (2 C, -CH_2-N), 66.8 (2 C, -CH_2-O), 127.8 (d, $^3J_{C,P}$ = 7.5 Hz, 4 C, *meta*-C), 128.6 (s, 2 C, *para*-C), 134.8 (d, $^2J_{C,P}$ = 19.2 Hz, 4 C, *ortho*-C), 135.7 (d, $^1J_{C,P}$ = 7.1 Hz, 2 C, *ipso*-C), 162.7 (d, $^3J_{C,P}$ = 7.8 Hz, 1 C, triazine-4), 163.5 (d, $^3J_{C,P}$ = 9.7 Hz, 1 C, triazine-6), 182.6 (d, $^1J_{C,P}$ = 18.3 Hz, 1 C, triazine-2) ppm. $^{31}P\{^1H\}$ NMR: δ = –0.91 ppm. FABMS: 422 $[M + H]^+$.

2-(Diphenylphosphanyl)-4,6-dimethoxy-1,3,5-triazine (4g): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.90 (s, 6 H, -CH_3), 7.35–7.41 (m, 6 H, arom.), 7.52–7.57 (m, 4 H, arom.) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 55.2 (2 C, -O-CH_3), 128.4 (d, $^3J_{C,P}$ = 8.0 Hz, 4 C, *meta*-C), 129.5 (s, 2 C, *para*-C), 133.5 (d, $^1J_{C,P}$ = 5.4 Hz, 2 C, *ipso*-C), 134.9 (d, $^2J_{C,P}$ = 20.1 Hz, 4 C, *ortho*-C), 171.1 (d, $^3J_{C,P}$ = 7.6 Hz, 2 C, Tiazine-4,6), 190.3 (d, $^1J_{C,P}$ = 5.1 Hz, 1 C, triazine-2) ppm. $^{31}P\{^1H\}$ NMR: δ = 2.50 ppm. FABMS: 326 $[M + H]^+$.

2-(Diphenylphosphanyl)-4,6-bis(3-phenylpropyloxy)-1,3,5-triazine (4h): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.99 (tt, J = 7.7,

6.5 Hz, 4 H, -CH_2-CH_2-CH_2-), 2.67 (t, J = 7.7 Hz, 4 H, -CH_2-Ph), 4.25 (t, J = 6.5 Hz, 4 H, -CH_2-O), 7.12–7.28 (m, 10 H, arom.), 7.30–7.37 (m, 6 H, arom.), 7.51–7.56 (m, 4 H, arom.) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 30.1 (2 C, -CH_2-CH_2-CH_2-), 32.0 (2 C, -CH_2-Ph), 67.6 (2 C, -CH_2-O), 126.1 (s, 2 C, -CH_2-Ph: *para*-C), 128.44 (d, $^3J_{C,P}$ = 8.8 Hz, 4 C, P-Ph: *meta*-C), 128.48 (s, 8 C, -CH_2-Ph: *ortho*, *meta*-C), 129.5 (s, 2 C, -P-Ph: *para*-C), 133.7 (d, $^1J_{C,P}$ = 5.6 Hz, 2 C, -P-Ph: *ipso*-C), 134.9 (d, $^2J_{C,P}$ = 20.0 Hz, 4 C, P-Ph: *ortho*-C), 141.2 (s, 2 C, -CH_2-Ph: *ipso*-C), 170.8 (d, $^3J_{C,P}$ = 7.7 Hz, 2 C, Tiazine-4,6), 190.1 (d, $^1J_{C,P}$ = 5.7 Hz, 1 C, triazine-2) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 2.46 ppm. FABMS: 534 $[M + H]^+$.

2-(Diphenylphosphanyl)-4-morpholino-6-(2-phenylethoxy)-1,3,5-triazine (4i): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.96 (t, J = 7.6 Hz, 2 H, -CH_2-Ph), 3.55–3.85 (br., 8 H, -N-CH_2-CH_2-O-), 4.40 (t, J = 7.6 Hz, 2 H, PhCH_2-CH_2-O), 7.08–7.29 (m, 5 H, arom.), 7.30–7.37 (m, 6 H, arom.), 7.51–7.57 (m, 4 H, arom.) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 35.2 (1 C, -O-CH_2-CH_2-Ph), 43.5 (1 C, -CH_2-N-), 43.9 (1 C, -CH_2-N-), 66.58 (1 C, -NCH_2-CH_2-O-), 66.63 (1 C, -NCH_2-CH_2-O-), 67.8 (1 C, PhCH_2-CH_2-O-), 126.5 (s, 1 C, -CH_2-Ph: *para*-C), 128.2 (d, $^3J_{C,P}$ = 7.8 Hz, 4 C, P-Ph: *meta*-C), 128.5 (s, 2 C, -CH_2-Ph: *meta*-C), 129.0 (s, 2 C, -CH_2-Ph: *ortho*-C), 129.2 (s, 2 C, -P-Ph: *para*-C), 134.5 (d, $^1J_{C,P}$ = 6.2 Hz, 2 C, -P-Ph: *ipso*-C), 134.9 (d, $^2J_{C,P}$ = 19.7 Hz, 4 C, P-Ph: *ortho*-C), 137.6 (s, 1 C, -CH_2-Ph: *ipso*-C), 164.5 (d, $^3J_{C,P}$ = 7.5 Hz, 1 C, triazine-4), 169.2 (d, $^3J_{C,P}$ = 8.9 Hz, 1 C, triazine-6), 186.6 (d, $^1J_{C,P}$ = 11.1 Hz, 1 C, triazine-2) ppm. $^{31}P\{^1H\}$ NMR: δ = 1.02 ppm. FABMS: 471 $[M + H]^+$.

6-(PEG-600)-Substituted 2-(Diphenylphosphanyl)-4-morpholino-1,3,5-triazine (4j): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.55–3.82 (br., -N-CH_2-CH_2-O-, O-CH_2-CH_2-O-), 4.34 (br. t, 2 H, -OH), 7.24–7.58 (m, 10 H, arom.) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 0.89 ppm. FABMS: 895 $[M]^+$ (n = 12).

2,4-Bis(diphenylphosphanyl)-6-morpholino-1,3,5-triazine (5a): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.54 (br. s, 8 H, -N-CH_2-CH_2-O-), 7.20–7.33 (m, 12 H, arom.), 7.42–7.47 (m, 8 H, arom.) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 43.1 (2 C, -CH_2-N-), 66.4 (2 C, -CH_2-O-), 128.0 (d, $^3J_{C,P}$ = 7.8 Hz, 8 C, *meta*-C), 128.8 (s, 4 C, *para*-C), 134.4 (d, $^1J_{C,P}$ = 6.7 Hz, 4 C, *ipso*-C), 134.7 (d, $^2J_{C,P}$ = 19.5 Hz, 8 C, *ortho*-C), 160.7 (t, $^3J_{C,P}$ = 6.4 Hz, 1 C, triazine-6), 183.5 (dd, $^1J_{C,P}$ = 8.4, 5.5 Hz, 2 C, triazine-2,4) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 0.18 ppm. FABMS: 535 $[M + H]^+$.

6-(Butylamino)-2,4-bis(diphenylphosphanyl)-1,3,5-triazine (5b): ^1H NMR (400 MHz, [D_6]DMSO, 25 °C): δ = 0.74 (t, J = 7.4 Hz, 3 H, -CH_3), 1.08 (sextet, J = 7.6 Hz, 2 H, -CH_2-CH_3), 1.20–1.30 (m, 2 H, -CH_2-CH_2-CH_2-), 2.97 (q, J = 6.7 Hz, 2 H, -N-CH_2-), 7.28–7.44 (m, 20 H, arom.), 8.01 (t, J = 6.0 Hz, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D_6]DMSO, 25 °C): δ = 14.0 (1 C, -CH_3), 19.9 (1 C, -CH_2-CH_3), 31.0 (1 C, -CH_2-CH_2-CH_2-), 40.6 (1 C, N-CH_2-), 128.7 (d, $^3J_{C,P}$ = 7.7 Hz, 4 C, *meta*-C), 128.9 (d, $^3J_{C,P}$ = 7.9 Hz, 4 C, *meta*-C), 129.5 (s, 2 C, *para*-C), 129.6 (s, 2 C, *para*-C), 134.7 (d, $^1J_{C,P}$ = 6.2 Hz, 2 C, *ipso*-C), 134.87 (d, $^2J_{C,P}$ = 19.5 Hz, 4 C, *ortho*-C), 134.98 (d, $^1J_{C,P}$ = 6.5 Hz, 2 C, *ipso*-C), 134.99 (d, $^2J_{C,P}$ = 20.0 Hz, 4 C, *ortho*-C), 162.1 (t, $^3J_{C,P}$ = 7.6 Hz, 1 C, triazine-6), 182.6 (dd, $J_{C,P}$ = 6.3, 11.4 Hz, 1 C, triazine-2/4), 183.3 (dd, $J_{C,P}$ = 4.9, 11.3 Hz, 1 C, triazine-2/4) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, [D_6]DMSO, 25 °C): δ = –1.53, –1.41 ppm. FABMS: 521 $[M + H]^+$.

6-Amino-2,4-bis(diphenylphosphanyl)-1,3,5-triazine (5c): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.42 (br., 2 H, NH_2), 7.23–7.44 (m, 20 H, arom.) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 128.2 (d, $^3J_{C,P}$ = 8.0 Hz, 8 C, *meta*-C), 129.1 (s, 4 C, *para*-C), 134.1 (d, $^1J_{C,P}$ = 6.5 Hz, 4 C, *ipso*-C), 134.8 (d, $^2J_{C,P}$ = 19.8 Hz, 8 C, *ortho*-C), 163.3 (t, $^3J_{C,P}$ = 7.8 Hz, 1 C, triazine-6), 184.5 (dt, $J_{C,P}$ = 11.2, 7.0 Hz, 2 C, triazine-2,4) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 0.35 ppm. FABMS: 465 $[M + H]^+$.

2,4-Bis(diphenylphosphanyl)-6-[(*R*)-1-phenylethylamino]-1,3,5-triazine (5d): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.33 (d, J = 7.2 Hz, 3 H, -CH_3), 4.86 (quintet, J = 7.2 Hz, 1 H, CH), 5.52 (br. d, J = 8 Hz, 1 H, NH), 7.02 (dd, J = 5.6, 1.6 Hz, 2 H, arom.), 7.18–7.45 (m, 23 H, arom.) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.9 (1 C, -CH_3), 50.0 (1 C, CH), 126.1 (s, 2 C, phenethyl-*ortho*-C), 127.1 (s, 1 C, phenethyl-*para*-C), 128.00 (d, $^3J_{C,P}$ = 14.0 Hz, 2 C, *meta*-C), 128.06 (d, $^3J_{C,P}$ = 6.9 Hz, 4 C, *meta*-C), 128.2 (s, 2 C, *para*-C), 128.4 (s, 2 C, phenethyl-*meta*-C), 128.8 (d, $^2J_{C,P}$ = 12.5 Hz, 2 C, *meta*-C), 129.0 (s, 2 C, *para*-C), 134.2 (d, $^1J_{C,P}$ = 6.0 Hz, 3 C, *ipso*-C), 134.3 (d, $^1J_{C,P}$ = 7.3 Hz, 1 C, *ipso*-C), 134.6 (d, $^2J_{C,P}$ = 18.8 Hz, 2 C, *ortho*-C), 134.75 (d, $^1J_{C,P}$ = 19.1 Hz, 2 C, *ortho*-C), 134.78 (d, $^1J_{C,P}$ = 19.9 Hz, 2 C, *ortho*-C), 134.9 (d, $^1J_{C,P}$ = 19.5 Hz, 2 C, *ortho*-C), 143.0 (s, 1 C, phenethyl-*ipso*-C), 161.4 (t, $^3J_{C,P}$ = 6.5 Hz, 1 C, triazine-6), 183.4 (dd, $J_{C,P}$ = 7.6, 6.2 Hz, 1 C, triazine-2/4), 184.3 (dd, $J_{C,P}$ = 8.2, 5.0 Hz, 1 C, triazine-2/4) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 0.58, 0.05 ppm. FABMS: 569 $[M + H]^+$.

2,4-Bis(diphenylphosphanyl)-6-methoxy-1,3,5-triazine (5e): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.74 (s, 3 H, -OCH_3), 7.24–7.48 (m, 20 H, arom.) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 54.7 (1 C, -O-CH_3), 128.2 (d, $^3J_{C,P}$ = 8.1 Hz, 8 C, *meta*-C), 129.1 (s, 4 C, *para*-C), 133.4 (d, $^1J_{C,P}$ = 5.7 Hz, 4 C, *ipso*-C), 134.7 (d, $^2J_{C,P}$ = 19.9 Hz, 8 C, *ortho*-C), 167.4 (t, $^3J_{C,P}$ = 6.3 Hz, 1 C, triazine-6), 187.2 (dd, $J_{C,P}$ = 4.2, 2.9 Hz, 2 C, triazine-2,4) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 1.83 ppm. FABMS: 480 $[M + H]^+$.

2,4-Bis(diphenylphosphanyl)-6-(3-phenylpropyloxy)-1,3,5-triazine (5f): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.91 (tt, J = 8.0, 6.8 Hz, 2 H, -CH_2C$H_2$$CH_2$-), 2.59 (t, J = 8.0 Hz, 2 H, -CH_2Ph), 4.15 (t, J = 6.8 Hz, 2 H, -CH_2-O), 7.08–7.46 (m, 25 H, arom.) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ = 29.9 (1 C, -CH_2C$H_2$$CH_2$-), 31.9 (1 C, -C$H_2$-Ph), 67.4 (1 C, -O-C$H_2$-), 125.9 (s, 1 C, -$CH_2$-Ph: *para*-C), 128.3 (d, $^3J_{C,P}$ = 8.1 Hz, 8 C, P-Ph: *meta*-C), 128.4 (s, 4 C, -CH_2-Ph: *ortho*, *meta*-C), 129.2 (s, 4 C, -P-Ph: *para*-C), 134.6 (d, $^1J_{C,P}$ = 5.8 Hz, 4 C, -P-Ph: *ipso*-C), 134.8 (d, $^2J_{C,P}$ = 19.9 Hz, 8 C, P-Ph: *ortho*-C), 141.1 (s, 1 C, -CH_2-Ph: *ipso*-C), 167.2 (t, $^3J_{C,P}$ = 6.7 Hz, 1 C, triazine-6), 187.2 (t, $J_{C,P}$ = 4.0 Hz, 2 C, triazine-2,4) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 1.76 ppm. FABMS: 480 $[M + H]^+$.

Procedure for the Preparation of the Pd-4a Complex: $PdCl_2(CH_3CN)_2$ (50 mg, 0.19 mmol) and phosphanyltriazine **4a** (0.52 mmol) were dissolved in THF (7.5 mL) at room temp. under Ar. After the mixture was stirred for 1 h, it was concentrated in vacuo. The yellow solid residue was then recrystallized from CH_2Cl_2/Et_2O to give the single crystal of the Pd-**4a** suitable for X-ray analysis.

Procedure for the Preparation of the Pd-5c Complex: $PdCl_2(CH_3CN)_2$ (106 mg, 0.41 mmol) and diphosphanyltriazine **5c** (0.43 mmol) were dissolved in CH_2Cl_2 (10 mL) at room temp. under Ar. After the mixture was stirred for 1 h, the precipitate formed was collected by filtration. The yellow solid was then recrystallized from DMF/Et_2O to give the single crystal of the Pd-**5c** complex suitable for X-ray analysis.

Typical Procedure for the Mizorogi–Heck Reaction Using Pd-4a: Aryl halide **6** (0.50 mmol), NaOAc (0.55 mmol), $Pd(OAc)_2$ (0.01 mmol, 2 mol-%) and phosphane ligand **4a** (0.04 mmol, 8 mol-

%) were mixed in DMA (1 mL) at room temp. under Ar for 20 min. To the mixture, butyl acrylate **7** (0.70 mmol) was added, and the mixture was stirred for 10 min at room temp. and 1 h at 140 °C. The conversion of the reaction was determined by ^{1}H NMR by using a portion of the reaction mixture.

Typical Procedure for the Suzuki–Miyaura Coupling Reaction in Aqueous Media Using Pd-4j: *p*-Bromotoluene (0.41 mmol), phenylboronic acid (0.61 mmol), Cs_2CO_3 (0.81 mmol), $Pd_2(dba)_3$·$CHCl_3$ (0.0041 mmol) and phosphane ligand **4j** (0.016 mmol) were mixed in water (2 mL) at room temp. under Ar for 30 min and at 100 °C for 3 h. The product was extracted with ethyl acetate, dried and concentrated. The residue was purified by chromatography on silica gel to afford the coupling product (69 mg, 100%).

Procedure for the Suzuki–Miyaura Coupling Reaction by Polymer-Supported Catalyst: *p*-Bromotoluene (1.00 mmol), phenylboronic acid (1.50 mmol), Cs_2CO_3 (2.00 mmol), $Pd_2(dba)_3$·$CHCl_3$ (0.05 mmol) and phosphane ligand **4k** (0.40 mmol) were mixed in dioxane (1 mL) at 100 °C under Ar for 3 h. The conversion of the reaction was determined by ^{1}H NMR by using a portion of the reaction mixture. After the reaction was complete, the catalyst was filtered off and washed three times with water and acetone. The collected solid was dried in vacuo for 2 h before the next use. The recovered catalyst was mixed with the substrates and base as above for reuse.

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[10] CCDC-719707 (for Pd-**4a**) and -719708 (for Pd-**5c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] TONs were calculated from the reactions using 0.002 mol-% of Pd catalyst.

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