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Borane-Protecting Strategy for Hydrosilylation of Phosphorus-Containing Olefins

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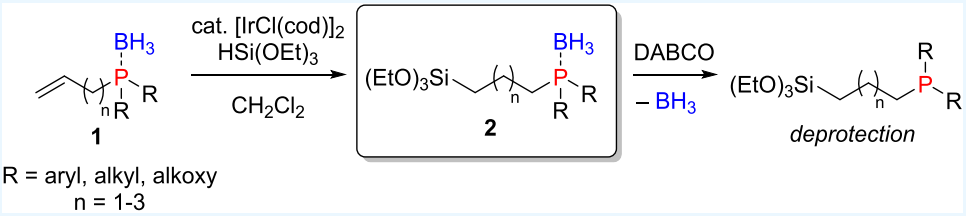


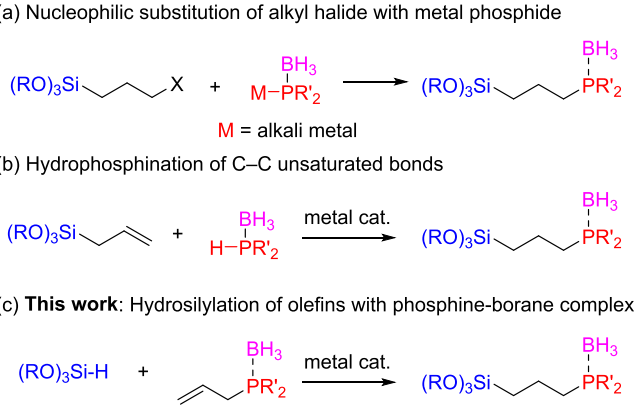
ABSTRACT: Ir-catalyzed hydrosilylation of the alkenyl phosphine borane complex **1** was achieved to give the corresponding products **2**. Because the phosphino group coordinates with metals and is unstable under aerobic conditions, the formation of the corresponding borane adduct was effective not only to promote the target hydrosilylation but also to keep **1** stable under aerobic conditions. The removal of coordinated borane from **2** was readily performed with the treatment by 1,4-diazabicyclo[2.2.2]octane to apply to further transformations. The immobilization and following deprotection of **2** on the surface of mesoporous silica were also examined.

INTRODUCTION

The considerable value of the actions of phosphines in organic synthesis such as metal ligands, reducing agents, and useful reactants has been established.[1] Immobilization of such useful phosphine functionalities upon solid materials is also attractive toward the application of heterogeneous catalysts and metal trapping agents.[2] Owing to the good affinity of organosilicon functionality with inorganic materials, such as silicas and aluminas, bifunctional compounds bearing alkoxy silyl groups and phosphino groups have been utilized for their immobilization on inorganic surfaces.[3] Typical construction of such bifunctional structures has been realized by a C−P bond-forming process between various phosphorus reactants and organosilanes, such as the nucleophilic substitution of alkyl halide with metal phosphide[3] (Scheme 1a) and the catalytic hydrophosphination of the C−C unsaturated bonds[4] (Scheme 1b). Alternatively, we aimed to access the target structures based on the C−Si bond formation. Transition-metal-catalyzed hydrosilylation of olefins is one of the most common strategies to obtain via the C−Si bond formation of various useful organosilicon compounds.[5]

Although hydrosilylation reactions have matured substantially since the discovery of conventional platinum catalysts, the challenging issue still lies in the development of catalysts that effectively achieve hydrosilylation of olefins with coordinating functional groups, which might cause suppression of their catalytic activity.[6] Hydrosilylation of olefins with a series of heteroatoms, such as oxygen,[7] nitrogen,[8] and sulfur,[9] has been well performed by finding efficient transition-metal catalysts. However, despite their broad utility, because of their strong coordinating ability to metal catalysts as well as their reduced stability toward oxidation to phosphine oxide, hydrosilylation of olefins bearing a phosphino group rarely has been documented.[10] We devised the use of an appropriate protecting method to maintain phosphorus atoms intact under

Scheme 1. Synthesis of Bifunctional Compounds with Alkoxy Silyl and Phosphino Groups



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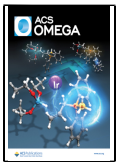
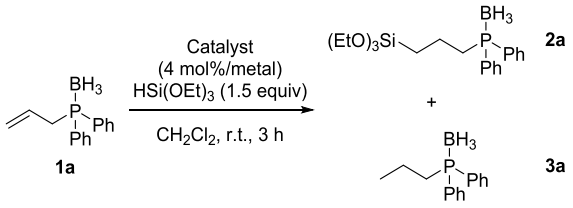


Table 1. Catalyst Screening for Hydrosilylation of 1a[a]



entry	catalyst	% conv. (1a)[b]	% yield (2a)[b]	% yield (3a)[b]
1	Speier's	15	7	7
2	Karstedt's	54	14	12
3	$[RhCl(cod)]_2$	6	n.d.	<5
4	$[IrCl(cod)]_2$	>99	88	<5
5	$[IrOMe(cod)]_2$	25	4	10
6	$[Ir(cod)_2]BF_4$	18	n.d.	7
7[c]	$[IrCl(cod)]_2$	18	n.d.	<5
8[d]	$[IrCl(cod)]_2/PPh_3$	7	n.d.	n.d.
9[e]	$[IrCl(cod)]_2$	36	10	<5
10[f]	$[IrCl(cod)]_2$	>99	84	10

[a]Reaction conditions: catalyst (4 mol % metal), **1a** (0.5 mmol), triethoxysilane (0.75 mmol) in dichloromethane (2.0 mL), r.t., 3 h. [b]Determined by ^{1}H NMR spectroscopy with hexamethyldisiloxane (0.5 mmol) as an internal standard. [c]Allyldiphenylphosphine was used instead of **1a**. Products **2a** and **3a** should be without borane protection. [d]Performed with triphenylphosphine (20 mol %). [e]Performed with 1.0 equiv of triethoxysilane (0.5 mmol). [f]Performed with 1.0 equiv of TEMPO (0.5 mmol).

hydrosilylation conditions. One of the reliable candidates is the employment of phosphine borane complexes, expanding the powerful utility of phosphines in organic synthesis.[11] Protection of phosphine moieties is readily performed with the treatment by borane-dimethyl sulfide or borane-tetrahydrofuran complexes, and the removal protocols of coordinating borane have been well established to form the free phosphines.[12] Herein, we report iridium-catalyzed hydrosilylation[9,13] of olefins with phosphine borane complexes (Scheme 1c). The removal of coordinating borane and further transformations of the hydrosilylated products were also examined.

RESULTS AND DISCUSSION

Initially, we sought to discover an appropriate candidate for the metal catalyst (4 mol % metal) for the model reaction of allyldiphenylphosphine borane complex (**1a**) and triethoxysilane (Table 1). The starting compound **1a** was prepared through a one-pot reaction comprising the protection of chlorodiphenylphosphine with a borane-dimethyl sulfide complex and the substitution reaction with an allyl Grignard reagent (see the Experimental Section). The hydrosilylation reaction of **1a** using conventional platinum catalysts, such as Speier's catalyst or Karstedt's catalyst, resulted in the formation of the target compound **2a** in low yields (Table 1, entries 1 and 2). Instead, we observed the reduction of **1a** to give **3a** as a major side product along with other unidentified byproducts. Therefore, we next moved on to examine other transition-metal catalysts. Because our group has investigated Rh(I)[14] and Ir(I)[9a] catalysis for hydrosilylation of olefins, the reaction with $[RhCl(cod)]_2$ or $[IrCl(cod)]_2$ was tested (Table 1, entries 3 and 4). Gratifyingly, the iridium-catalyzed reaction furnished **2a** in an 88% yield with suppression of the production of **3a** (Table 1, entry 4; Figure S1), whereas the rhodium-catalyzed reaction did not provide the desired product (Table 1, entry 3). Furthermore, the reaction with other Ir catalysts such as $[Ir(OMe)(cod)]_2$ or $[Ir(cod)_2]BF_4$ resulted in poorer yields and selectivity (Table 1, entries 5 and 6). To ensure the necessity of the borane complex, the reaction of allyldiphenylphosphine with $[IrCl(cod)]_2$ was conducted under an atmosphere of argon, and no desired product was observed (Table 1, entry 7). In addition, the catalytic activity of $[IrCl(cod)]_2$ was dramatically suppressed in the presence of triphenylphosphine, which is one of the most common phosphine ligands (Table 1, entry 8). These results supported the importance of the protection of the phosphino group with borane for iridium-catalyzed hydrosilylation of allyl phosphorus compounds. A satisfactory yield could not be achieved with 1.0 equiv of hydrosilane (Table 1, entry 9). The addition of TEMPO gave almost the same results, which could rule out a reaction mechanism via radical pathways (Table 1, entry 10).

We optimized the reaction conditions after screening the effects of deviations from standard conditions for time, reaction temperature, ratios of substrates, amounts of catalyst loading, and solvent used (see Table S1). With the optimized reaction conditions in hand, we checked the scope of hydrosilylation of allyl phosphorus-borane complex **1** bearing various substituents on the phosphorus atom (Table 2). Products **2** were obtained as a pure form after chromatography on silica gel. For example, compound **2a** was isolated in a 74% yield. Concerning the position of aromatic substituents, the reaction of **1b** and **1c** with *p*-tolyl and 3,5-xylyl groups proceeded smoothly to afford **2b** and **2c** in 59 and 70% yields, respectively. Moreover, the reaction of **1d**, which contains a bulky 2,4,6-mesityl group also proceeded without problems to give **2d** in a 74% yield. The electron-donating 3,5-dimethyl-4-methoxyphenyl ring was tolerated to furnish **2e** in a 97% yield.[15] Because the trialkylphosphines act as highly electron-donating, yet oxidatively unstable ligands,[16] we next studied the hydrosilylation of **1** with a trialkylphosphine-borane complex. While the reaction of **1f** with the isopropyl group resulted in a moderate 26% yield, the reaction of **1g**−**i** with larger alkyl substituents such as cyclopentyl, cyclohexyl, and *tert*-butyl proceeded to give **2g**−**i** in a 72−85% yield. We tested **1j** with diethylphosphite moiety to obtain **2j** in a 31% yield. Several alkenyl groups other than the allyl group were

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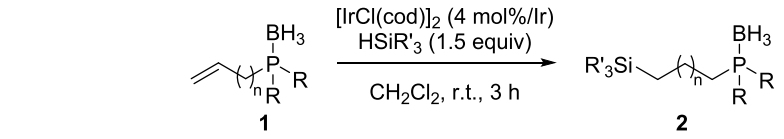
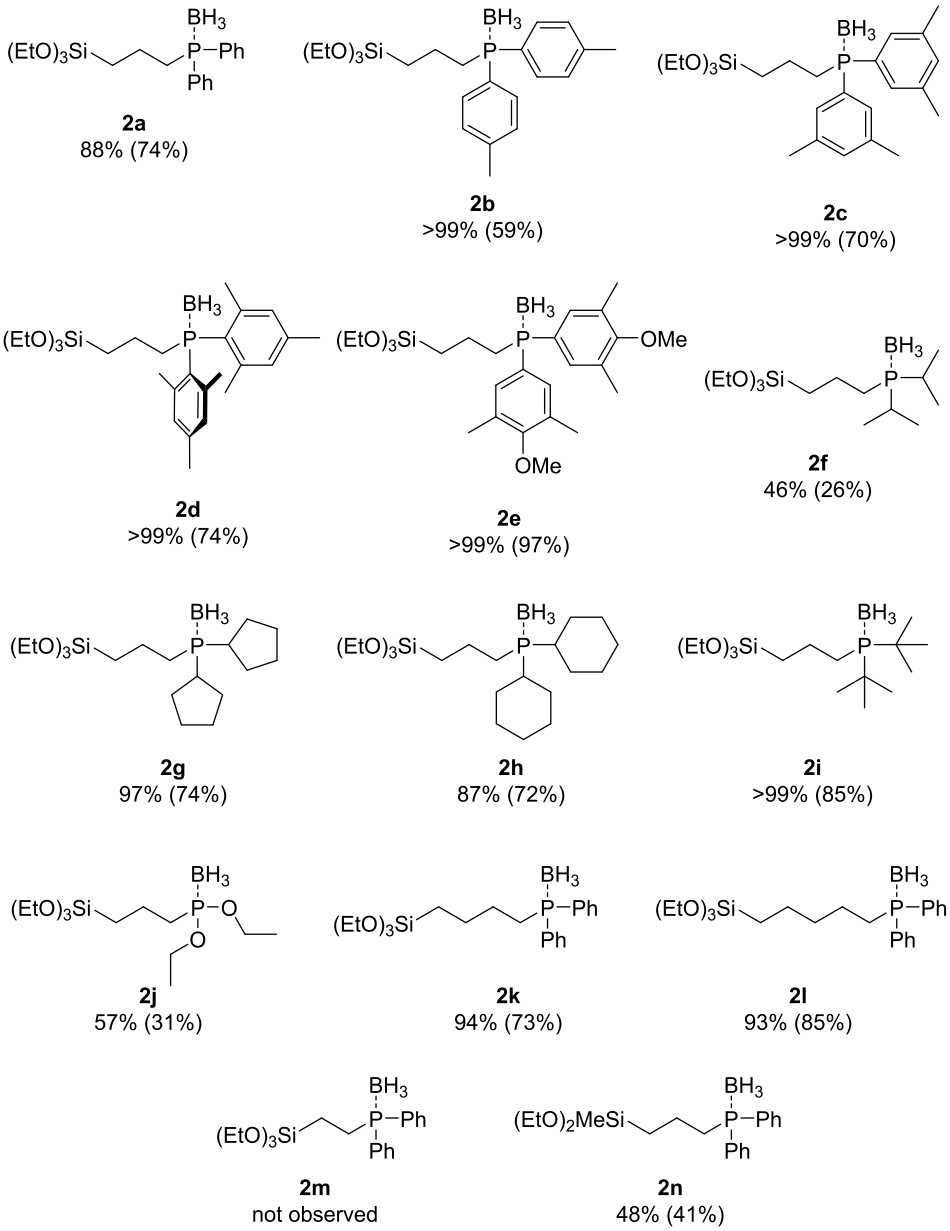
Table 2. Scope of Substrate[a]





[a]Reaction conditions: $[IrCl(cod)]_2$ (2 mol %), **1** (0.5 mmol), triethoxysilane (0.75 mmol) in dichloromethane (2.0 mL), r.t., 3 h. Yield was determined by ^1H NMR spectroscopy with hexamethyldisiloxane (0.5 mmol) as an internal standard. The isolated yield is shown in parentheses.

examined, and the corresponding products **2k** and **2l** were obtained in good yields from **1k** with the 1-butenyl and **1l** with 1-pentenyl groups. In contrast, the reaction of vinyl diphenylphosphine borane (**1m**) did not proceed, probably due to the steric hindrance. As another hydrosilane, the reaction of **1a** with methyldiethoxysilane was also successful to give **2n** in a 41% yield.

According to the literature,[12] the deprotection of borane complex from **2a** was conducted with the treatment by 1,4-diazabicyclo[2.2.2] octane (DABCO) in toluene at room temperature to afford **4** in a 90% yield (Scheme 2a). In combination with the treatment by hydrogen peroxide or elemental sulfur, the in situ transformation of **4** proceeded to give phosphine oxide **5a** and phosphine sulfide **5b**, which are useful as extractants,[17] flame retardants,[18] metal ligands,[19] and organocatalysts[20] (Scheme 2b).

We also performed a gram-scale reaction of **1a** (5 mmol) with triethoxysilane to furnish 1.43 g of **2a** in a 71% yield (Scheme 3a). With the borane-protecting silane-coupling agent in large quantity, the immobilization of mesoporous silica,

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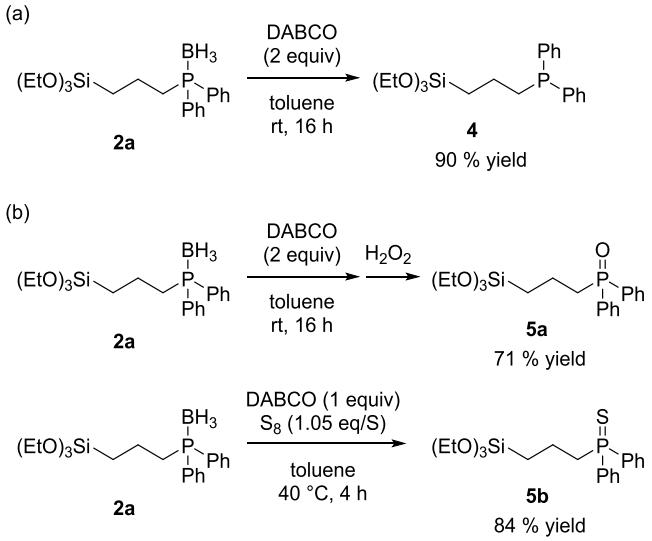
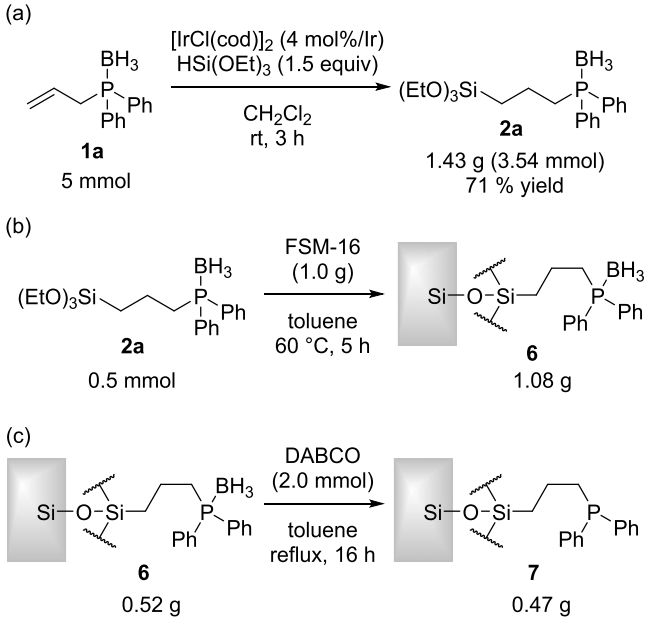
Scheme 2. (a) Borane Deprotection of 2a. (b) In Situ Transformation of 2a



Scheme 3. (a) Gram-Scale Synthesis of 2a. (b) Immobilization of 2a on FSM-16. (c) Borane Deprotection of Immobilized 2a



FSM-16,[21] was examined (Scheme 3b). The treatment of **2a** (0.5 mmol) with FSM-16 (1.0 g) in toluene at 60 °C gave functionalized mesoporous silica **6**. Subsequently, the removal of a coordinating borane from **6** (0.52 g) was conducted with DABCO (2.0 mmol) to provide **7** with free phosphine (Scheme 3c).

The phosphorus species on the surfaces of **6** and **7** was analyzed with solid-state ^{31}P CP/MAS NMR (Figure 1). The NMR spectrum of **6** and **7** showed signals at 12.3 and −18.5 ppm, which are almost consistent with preimmobilized analogs **2a** (15.5 ppm, $CDCl_3$) and **4** (−17.1 ppm, C_6D_6), respectively. This observation indicated that immobilization and deprotection of **2a** proceeded cleanly on the silica surface. The infrared spectra of **6** and **7** also showed that the characteristic B−H stretching band at 2385 cm^{-1} in **6** completely

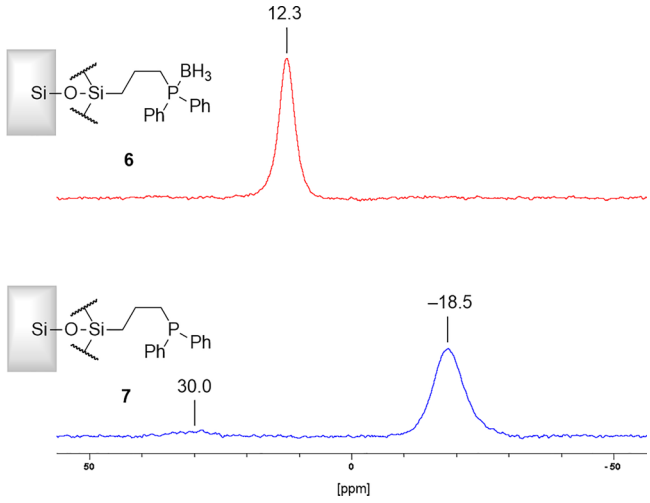


Figure 1. ^{31}P CP/MAS NMR spectra of **2a** immobilized on **6** and **7**.

disappeared in **7** (Figure S2).[22] Although the immobilization of silane-coupling agents bearing free phosphines significantly suffers from undesired oxidation reactions on phosphorus,[23] the present method with borane protection could almost suppress the formation of phosphine oxide, which was observed around 30.0 ppm in the solid-state ^{31}P CP/MAS NMR spectrum to allow for more precise synthesis of solid-state phosphorus compounds.

Hydrosilylation reaction of functionalized olefins by [IrCl(cod)]$_2$ has been reported previously,[9a,13,24] and the present reactions are supposed to follow a similar mechanism.

CONCLUSIONS

In summary, we achieved hydrosilylation of the alkenyl phosphorus compound **1**, enabled by the strategy using a borane complex to protect the phosphorus atom from coordinating with metal atoms. [IrCl(cod)]$_2$ was found to be an effective catalyst for the target hydrosilylation of **1** with triethoxysilane to furnish **2**, which was readily purified by silica gel chromatography and sufficiently stable under aerobic conditions. The deprotection of borane from **2** could be performed using a conventional method by treatment with DABCO. As an application to material chemistry, we demonstrated the immobilization of **2a** on a silica surface. The borane deprotection of silica-supported phosphorus-borane complex in **6** was successfully applied to the synthesis of pure solid-state phosphorus compound **7** without undesirable oxidation. The major advantage of the present hydrosilylation over previous methods is the ability to introduce multiple alkoxy silyl groups at once to phosphine boranes containing multiple olefins. Such compounds can be used as precursors for the mesoporous organosilica (PMO)[25] synthesis, and our research group is actually investigating the possibility of using them to report in the future.

EXPERIMENTAL SECTION

General Information. All experiments were performed under an argon atmosphere using Schlenk techniques or a glovebox unless otherwise noted. CH_2Cl_2 toluene and Et_2O were purchased from Wako Pure Chemical Industries, Ltd., as "super dehydrated" and used as received. FSM-16 was kindly donated from Taiyo Kagaku Co. Ltd. Other reagents were purchased from commercial suppliers and used without further

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purification. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra (^{1}H, 600 MHz; ^{13}C, 150 MHz; ^{31}P, 243 MHz) were recorded on a Bruker AVANCE III HD 600 spectrometer. Chemical shifts are reported in δ (ppm) and referenced to the residual solvent signals for ^{1}H and ^{13}C and 85% H_3PO_4 for ^{31}P as external standards. Solid-state ^{31}P CP/MAS NMR spectra were recorded on a Bruker AVANCE II+ 400 spectrometer using a 4 mm diameter ZrO_2 rotor (^{31}P, 162 MHz), and the rotation frequency was set to 12.5 kHz. Standard ramped cross-polarization (CP) was used to transfer polarization from the ^{1}H nuclei to the nucleus of interest (^{31}P), and the CP contact time was set to 5 ms. SPINAL-64 ^{1}H heteronuclear decoupling was applied during acquisition. ^{31}P chemical shifts were referenced to H_3PO_4 at 0 ppm using $(NH_4)_2HPO_3$ as an external standard (−1.6 ppm). High-resolution ESI mass spectra were obtained on a Bruker micrOTOF II. Column chromatography was performed with silica gel (Kanto Chemical Co., Inc. Silica gel 60 N, 100−210 μm). GPC chromatography was performed on a YMC multiple preparative HPLC LC-forte/R with YMC-GPC T4000-40 and T2000-40 as GPC columns. FT-IR spectra were measured on a Bruker α FT-IR Spectrometer. Elemental analyses were performed with a Yanaco CHN CORDER MT-6 instrument.

General Procedure for Catalyst Screening for Hydrosilylation of 1a (Table 1). In a test tube with a PTFE screw cap, a catalyst (0.01 mmol/metal) was equipped. CH_2Cl_2 (2.0 mL), **1a** (120.0 mg, 0.5 mmol), and triethoxysilane (136.9 μL, 0.75 mmol) were successively added to the test tube. The resulting mixture was stirred at room temperature for 3 h. Then, hexamethyldisiloxane (105 μL, 0.5 mmol) was added to the crude mixture to determine the yield of **2a** by ^{1}H NMR spectroscopy.

Allyldiphenylphosphine Borane (1a).[26] To a solution of chlorodiphenylphosphine (10.0 mL, 54 mmol) in Et_2O (50 mL), dimethyl sulfide borane (2.0 M in Et_2O, 32.5 mL, 65 mmol) was added dropwise at 0 °C. The reaction mixture was stirred for 1 h at room temperature. After cooling at 0 °C, allylmagnesium bromide (2.0 M in Et_2O, 32.5 mL, 65 mmol) was then added dropwise to the mixture. After stirring for 18 h at room temperature, the reaction mixture was quenched with saturated NH_4Cl solution and the aqueous phase was extracted with CH_2Cl_2. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: hexane/EtOAc = 40/60) afforded **1a** in a 75% yield (9.7 g) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69−7.66 (m, 4H), 7.50−7.43 (m, 6H), 5.78 (m, 1H), 5.11 (m, 1H), 5.06 (m, 1H), 3.06 (dd, J = 12.5, 7.4 Hz, 2H), 1.36−0.62 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 132.4 (d, $^{2}J_{C,P}$ = 8.9 Hz), 131.3 (d, $^{4}J_{C,P}$ = 2.3 Hz), 128.9 (d, $^{1}J_{C,P}$ = 54.1 Hz), 128.8 (d, $^{3}J_{C,P}$ = 9.9 Hz), 128.3 (d, $^{2}J_{C,P}$ = 5.2 Hz), 120.4 (d, $^{3}J_{C,P}$ = 10.9 Hz), 31.9 (d, $^{1}J_{C,P}$ = 31.9 Hz). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 15.6 (m). HRMS (ESI): m/z calcd for $[C_{30}H_{32}BP_2]^+$ (2M − BH_3 − H): 465.2072; found, 465.2084.

Allyldi(*p*-tolyl)phosphine Borane (1b). Compound **1b** was prepared from chlorodi(*p*-tolyl)phosphine (0.50 g, 2 mmol) by the procedure for the preparation of **1a**. Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 92/8) afforded **1b** in a 40% yield (0.22 g) as a colorless oil (97% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62−7.57 (m, 4H), 7.29−7.23 (m, 4H), 5.80 (m, 1H), 5.11 (m, 1H), 5.09 (m, 1H), 3.05 (dd, J = 12.6, 7.2 Hz, 2H), 2.38 (s, 6H), 1.44−0.68 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 141.6 (d, $^{4}J_{C,P}$ = 2.3 Hz), 132.4 (d, $^{2}J_{C,P}$ = 9.0 Hz), 129.6. (d, $^{3}J_{C,P}$ = 10.2 Hz), 128.6 (d, $^{2}J_{C,P}$ = 4.9 Hz), 125.7 (d, $^{1}J_{C,P}$ = 56.4 Hz), 120.2 (d, $^{3}J_{C,P}$ = 11.0 Hz), 32.1 (d, $^{1}J_{C,P}$ = 35.9 Hz), 21.5. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 14.0 (m). HRMS (ESI): m/z calcd for $[C_{34}H_{40}BP_2]^+$ (2M − BH_3 − H): 521.2699; found, 521.2680.

Allyldi(3,5-dimethylphenyl)phosphine Borane (1c). Compound **1c** was prepared from chlorobis(3,5-dimethylphenyl)phosphine (0.50 g, 1.8 mmol) by the procedure for the preparation of **1a**. Purification by column chromatography on silica gel (eluent: hexane) afforded **1c** in a 37% yield (0.22 g) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 (d, J = 11.4 Hz, 4H), 7.09 (s, 2H), 5.76 (m, 1H), 5.10 (m, 1H), 5.06 (m, 1H), 3.01 (dd, J = 12.8, 7.4 Hz, 2H), 2.32 (s, 12H), 1.32−0.56 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 138.3 (d, $^{3}J_{C,P}$ = 10.3 Hz), 133.0 (d, $^{4}J_{C,P}$ = 2.4 Hz), 129.9 (d, $^{2}J_{C,P}$ = 8.9 Hz), 128.72 (d, $^{1}J_{C,P}$ = 53.8 Hz), 128.69 (d, $^{2}J_{C,P}$ = 5.0 Hz), 120.0 (d, $^{3}J_{C,P}$ = 11.0 Hz), 31.9 (d, $^{1}J_{C,P}$ = 35.6 Hz), 21.3. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 14.4 (m). HRMS (ESI): m/z calcd for $[C_{19}H_{26}BP_2Na]^+$ (M + N a): 319.1761; found, 319.1767.

Allyldimesitylphosphine Borane (1d). To a solution of chlorodimesitylphosphine (0.85 g, 2.8 mmol) in Et_2O (50 mL) cooled at 0 °C, allylmagnesium bromide (2.0 M in Et_2O, 1.7 mL, 3.4 mmol) was added dropwise. The resulting mixture was warmed up to room temperature and stirred for 18 h. After cooling at 0 °C again, dimethyl sulfide borane (2.0 M in Et_2O, 1.7 mL, 3.4 mmol) was then added dropwise to the mixture. After the additional 1 h at room temperature, the reaction was quenched with saturated NH_4Cl solution and the aqueous phase was extracted with CH_2Cl_2. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: hexane/EtOAc = 90/10) afforded **1d** in a 20% yield (0.19 g) as a white solid (97% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.79 (d, J = 3.0 Hz, 4H), 5.53 (m, 1H), 4.99−4.92 (m, 2H), 3.38 (dd, J = 11.6, 7.5 Hz, 2H), 2.27 (s, 12H), 2.24 (s, 6H), 1.76−0.92 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 141.5 (d, $^{2}J_{C,P}$ = 8.1 Hz), 140.0 (d, $^{4}J_{C,P}$ = 2.3 Hz), 130.9 (d, $^{3}J_{C,P}$ = 8.6 Hz), 129.2 (d, $^{2}J_{C,P}$ = 4.7 Hz), 126.4 (d, $^{1}J_{C,P}$ = 49.7 Hz), 120.4 (d, $^{3}J_{C,P}$ = 11.9 Hz), 35.8 (d, $^{1}J_{C,P}$ = 33.8 Hz), 23.3 (d, $^{3}J_{C,P}$ = 4.6 Hz), 20.9. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 15.8 (m). HRMS (ESI): m/z calcd for $[C_{21}H_{28}P]^+$ (M − BH_3 + H): 311.1923; found, 311.1934.

Allyldi(3,5-dimethyl-4-methoxyphenyl)phosphine Borane (1e). Compound **1e** was prepared from bis(3,5-dimethyl-4-methoxyphenyl)chlorophosphine (0.59 mL, 2 mmol) by the procedure for the preparation of **1a**. Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 67/33) afforded **1e** in a 45% yield (0.32 g) as a colorless oil (95% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (d, J = 10.5 Hz, 4H), 5.76 (m, 1H), 5.11 (m, 1H), 5.08 (m, 1H), 3.73 (s, 6H), 2.98 (dd, J = 12.8, 7.4 Hz, 2H), 2.29 (s, 12 H), 1.42−0.48 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 159.5 (d, $^{4}J_{C,P}$ = 2.7 Hz), 132.9 (d, $^{2}J_{C,P}$ = 9.6 Hz), 131.6 (d, $^{3}J_{C,P}$ = 11.0 Hz), 128.7 (d, $^{2}J_{C,P}$ = 5.1 Hz), 123.6 (d, $^{1}J_{C,P}$ = 56.0 Hz), 120.0 (d, $^{3}J_{C,P}$ = 11.0 Hz), 59.6, 32.2 (d, $^{1}J_{C,P}$ = 36.1 Hz), 16.3. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 12.6 (m). HRMS (ESI): m/z calcd for

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$[C_{21}H_{27}O_2PNa]^+$ (M − BH_3 + Na): 365.1641; found, 365.1635.

Allyldiisopropylphosphine Borane (1f). Compound **1f** was prepared from diisopropylchlorophosphine (0.31 mL, 2 mmol) by the procedure for the preparation of **1d**. Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 90/10) afforded **1f** in a 35% yield (0.12 g) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.85 (m, 1H), 5.17 (m, 1H), 5.15 (m, 1H), 2.48 (m, 2H), 2.04 (m, 2H), 1.22−1.16 (m, 12H), 0.70 to −0.09 (m, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 130.1 (d, $^2J_{C,P}$ = 6.3 Hz), 119.0 (d, $^3J_{C,P}$ = 9.2 Hz), 26.0 (d, $^1J_{C,P}$ = 30.3 Hz), 21.5 (d, $^1J_{C,P}$ = 32.1 Hz), 17.01 (d, $^2J_{C,P}$ = 6.7 Hz), 17.00 (d, $^2J_{C,P}$ = 8.2 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 31.6 (m). HRMS (ESI): *m*/*z* calcd for $[C_{18}H_{44}B_2P_2Na]^+$ (2M + Na): 367.3003; found, 367.3000.

Allyldicyclopentylphosphine Borane (1g).[27] Compound **1g** was prepared from dicyclopentylchlorophosphine (0.38 mL, 2 mmol) by the procedure for the preparation of **1a**. Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 90/10) afforded **1g** in a 34% yield (0.15 g) as a colorless oil (92% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.81 (m, 1H), 5.19−5.11 (m, 2H), 2.48 (m, 2H), 2.05 (m, 2H), 1.90−1.50 (m, 16H), 0.72 to −0.15 (m, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 129.7 (d, $^2J_{C,P}$ = 7.9 Hz), 119.0 (d, $^3J_{C,P}$ = 8.6 Hz), 32.3 (d, $^1J_{C,P}$ = 34.4 Hz), 28.8 (d, $^1J_{C,P}$ = 31.8 Hz), 27.9 (d, $^3J_{C,P}$ = 2.1 Hz), 27.8, 26.5 (d, $^2J_{C,P}$ = 9.0 Hz), 26.0 (d, $^2J_{C,P}$ = 8.6 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 28.0 (m). HRMS (ESI): *m*/*z* calcd for $[C_{26}H_{52}B_2P_2Na]^+$ (2M + Na): 471.3632; found, 471.3638.

Allyldicyclohexylphosphine Borane (1h).[28] Compound **1h** was prepared from dicyclohexylchlorophosphine (0.44 mL, 2 mmol) by the procedure for the preparation of **1a**. Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 95/5) afforded **1h** in a 59% yield (0.30 g) as a white solid (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.83 (m, 1H), 5.18−5.11 (m, 2H), 2.47 (ddt, *J* = 11.7, 7.6, 1.2 Hz, 2H), 1.92−1.65 (m, 12H), 1.48−1.32 (m, 4H), 1.30−1.15 (m, 6H), 0.84 to −0.79 (m, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 130.4 (d, $^2J_{C,P}$ = 6.2 Hz), 118.9 (d, $^3J_{C,P}$ = 9.2 Hz), 31.3 (d, $^1J_{C,P}$ = 31.4 Hz), 26.9 (d, $^2J_{C,P}$ = 6.4 Hz), 26.83 (d, $^2J_{C,P}$ = 7.3 Hz), 26.79, 26.7 (d, $^3J_{C,P}$ = 1.1 Hz), 26.0 (d, $^3J_{C,P}$ = 1.0 Hz), 25.8 (d, $^1J_{C,P}$ = 30.7 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 23.7 (m). HRMS (ESI): *m*/*z* calcd for $[C_{15}H_{30}BPNa]^+$ (M + Na): 275.2073; found, 275.2063.

Allyldi(*tert*-butyl)phosphine Borane (1i). Compound **1i** was prepared from di(*tert*-butyl)chlorophosphine (1.9 mL, 10 mmol) by the procedure for the preparation of **1d**. Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 90/10) afforded **1i** in a 73% yield (1.47 g) as a colorless oil (93% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.02 (m, 1H), 5.15 (m, 1H), 5.12 (m, 1H), 2.54 (ddt, *J* = 11.9, 7.1, 1.3 Hz, 2H), 1.26 (d, *J* = 12.5 Hz, 18H), 0.78−0.04 (m, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 132.3 (d, $^2J_{C,P}$ = 3.8 Hz), 118.2 (d, $^3J_{C,P}$ = 9.8 Hz), 32.5 (d, $^1J_{C,P}$ = 25.6 Hz), 28.0, 25.0 (d, $^1J_{C,P}$ = 28.7 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 43.1 (m). HRMS (ESI): *m*/*z* calcd for $[C_{22}H_{49}BP_2Na]^+$ (2M − BH_3 + Na): 409.3299; found, 409.3292.

Allyldiethoxyphosphine Borane (1j).[29] Compound **1j** was prepared from diethyl chlorophosphite (0.29 mL, 2 mmol) by the procedure for the preparation of **1a**. Purification by GPC chromatography (eluent: CH_2Cl_2) afforded **1j** in a 60% yield (0.21 g) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.76 (m, 1H), 5.24−5.16 (m, 2H), 4.13−3.97 (m, 4H), 2.60 (dd, *J* = 11.9, 7.6 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 6H), 0.82−0.06 (m, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 127.0 (d, $^2J_{C,P}$ = 5.0 Hz), 120.3 (d, $^3J_{C,P}$ = 11.5 Hz), 63.4 (d, $^2J_{C,P}$ = 4.5 Hz), 36.0 (d, $^1J_{C,P}$ = 68.5 Hz), 16.5 (d, $^3J_{C,P}$ = 5.5 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 143.3 (m). HRMS (ESI): *m*/*z* calcd for $[C_{14}H_{32}BO_4P_2]^+$ (2M − BH_3 − H): 337.1866; found, 337.1867.

3-Butenyldiphenylphosphine Borane (1k).[30] To a suspension of Mg (1.0 g, 41 mmol) in Et_2O (40 mL), 4-bromo-1-butene (3.0 mL, 30 mmol) was added dropwise at room temperature. After stirring for 1 h, chlorodiphenylphosphine (3.6 mL, 20 mmol) was added dropwise at 0 °C. The resulting mixture was warmed up to room temperature and stirred for 18 h. After cooling at 0 °C again, dimethyl sulfide borane (2.0 M in Et_2O, 12 mL, 24 mmol) was then added dropwise to the mixture. After the additional 1 h at room temperature, the reaction was quenched with saturated NH_4Cl solution and the aqueous phase was extracted with CH_2Cl_2. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: hexane/EtOAc = 50/50) afforded **1k** in an 80% yield (4.06 g) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71−7.64 (m, 4H), 7.53−7.40 (m, 6H), 5.82 (m, 1H), 5.04 (m, 1H), 4.98 (m, 1H), 2.33−2.22 (m, 4H), 1.45−0.62 (m, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 137.4 (d, $^3J_{C,P}$ = 15.3 Hz), 132.2 (d, $^2J_{C,P}$ = 9.0 Hz), 131.2 (d, $^4J_{C,P}$ = 2.4 Hz), 129.3 (d, $^1J_{C,P}$ = 54.7 Hz), 128.9 (d, $^3J_{C,P}$ = 9.8 Hz), 115.3, 27.1 (d, $^2J_{C,P}$ = 0.7 Hz), 25.0 (d, $^1J_{C,P}$ = 36.4 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 16.0 (m). HRMS (ESI): *m*/*z* calcd for $[C_{32}H_{36}BP_2]^+$ (2M − BH_3 − H): 493.2385; found, 493.2361.

4-Pentenyldiphenylphosphine Borane (1l).[31] Compound **1l** was prepared from diphenylchlorophosphine (3.6 mL, 20 mmol) by the procedure for the preparation of **1k**. Grignard reagent was prepared from Mg (1.0 g, 41 mmol) and 5-bromo-1-pentene (3.6 mL, 30 mmol) in Et_2O (40 mL). Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 80/20) afforded **1l** in a 6% yield (0.3 g) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71−7.62 (m, 4H), 7.52−7.41 (m, 6H), 5.72 (m, 1H), 5.03-4.97 (m, 2H), 2.27−2.10 (m, 4H), 1.63 (m, 2H), 1.36−0.60 (m, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 137.3, 132.2 (d, $^2J_{C,P}$ = 9.0 Hz), 131.1 (d, $^4J_{C,P}$ = 2.4 Hz), 129.6 (d, $^1J_{C,P}$ = 54.6 Hz), 128.8 (d, $^3J_{C,P}$ = 9.8 Hz), 115.9, 34.8 (d, $^2J_{C,P}$ = 14.2 Hz), 25.0 (d, $^2J_{C,P}$ = 37.2 Hz), 22.2. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 16.0 (m). HRMS (ESI): *m*/*z* calcd for $[C_{17}H_{22}BPNa]^+$ (M + Na): 291.1447; found, 291.1445.

Diphenylvinylphosphine Borane (1m).[32] Compound **1l** was prepared from diphenylchlorophosphine (3.6 mL, 20 mmol) and vinylmagnesium bromide (1.0 M in THF, 30.0 mL, 30 mmol) by the procedure for the preparation of **1d**. Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 40/60) afforded **1m** in a 49% yield (2.23 g) as a colorless oil (>99% purity).

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^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72−7.60 (m, 4H), 7.55−7.41 (m, 6H), 6.58 (ddd, J = 18.3, 14.3, 12.1 Hz, 1H), 6.27 (ddd, J = 39.5, 12.1, 1.3 Hz, 1H), 6.11 (ddd, J = 20.0, 18.3, 1.3 Hz, 1H), 1.48−0.63 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 135.2 (d, $^2J_{C,P}$ = 4.6 Hz), 132.6 (d, $^2J_{C,P}$ = 9.5 Hz), 131.3 (d, $^4J_{C,P}$ = 2.3 Hz), 128.93 (d, $^1J_{C,P}$ = 58.4 Hz), 128.86 (d, $^3J_{C,P}$ = 10.1 Hz), 128.3 (d, $^1J_{C,P}$ = 54.0 Hz). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 15.4 (m). HRMS (ESI): m/z calcd for $[C_{14}H_{16}BPNa]^+$ (M + Na): 249.0977; found, 249.0980.

General Procedure for Iridium-Catalyzed Hydrosilylation of Allyl Phosphine Borane Complex 2 (Table 2). In a test tube with a PTFE screw cap, $[IrCl(cod)]_2$ (6.7 mg, 0.01 mmol) was equipped. CH_2Cl_2 (2.0 mL), **1** (0.5 mmol), and triethoxysilane (136.9 μL, 0.75 mmol) were successively added to the test tube. The resulting mixture was stirred at room temperature for 3 h. Then, hexamethyldisiloxane (105 μL, 0.5 mmol) was added to the crude mixture to determine the yield of **2** by ^{1}H NMR spectroscopy. After the removal of volatile in vacuo, the crude mixture was directly purified by column chromatography on silica gel or GPC chromatography to obtain the target compound (**2**).

Diphenyl[3-(triethoxysilyl)propyl]phosphine Borane (2a). Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 84/16) afforded **2a** in a 74% yield (150.3 mg) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70−7.63 (m, 4H), 7.49−7.40 (m, 6H), 3.76 (q, J = 7.0 Hz, 6H), 2.29 (m, 2H), 1.67 (m, 2H), 1.32−0.61 (m, 3H), 1.17 (t, J = 7.0 Hz, 9H), 0.73 (t, J = 7.9 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 132.2 (d, $^2J_{C,P}$ = 8.9 Hz), 131.0 (d, $^4J_{C,P}$ = 2.3 Hz), 129.7 (d, $^1J_{C,P}$ = 54.4 Hz), 128.8 (d, $^3J_{C,P}$ = 9.8 Hz), 58.4, 28.4 (d, $^1J_{C,P}$ = 35.7 Hz), 18.3, 16.9, 12.2 (d, $^2J_{C,P}$ = 13.5 Hz). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 15.5 (m). HRMS (ESI): m/z calcd for $[C_{21}H_{34}BO_3PSiNa]^+$ (M + Na): 427.2004; found, 427.2013.

Di(*p*-tolyl)[3-(triethoxysilyl)propyl]phosphine Borane (2b). Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 90/10) afforded **2b** in a 59% yield (127.4 mg) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55−7.52 (m, 4H), 7.23−7.21 (m, 4H), 3.76 (q, J = 7.0 Hz, 6H), 2.36 (s, 6H), 2.24 (m, 2H), 1.65 (m, 2H), 1.39−0.54 (m, 3H), 1.18 (t, J = 7.0 Hz, 9H), 0.73 (t, J = 7.9 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 141.3 (d, $^4J_{C,P}$ = 2.4 Hz), 132.1 (d, $^2J_{C,P}$ = 9.2 Hz), 129.5 (d, $^3J_{C,P}$ = 10.1 Hz), 126.5 (d, $^1J_{C,P}$ = 56.3 Hz), 58.4, 28.4 (d, $^1J_{C,P}$ = 36.1 Hz), 21.3, 18.3, 16.9, 12.2 (d, $^2J_{C,P}$ = 13.5 Hz). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 13.8 (m). HRMS (ESI): m/z calcd for $[C_{23}H_{38}BO_3PSiNa]^+$ (M + Na): 455.2318; found, 455.2312.

Di(3,5-dimethylphenyl)[3-(triethoxysilyl)propyl]-phosphine Borane (2c). Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 95/5) afforded **2c** in a 70% yield (161.6 mg) as a white solid (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 (m, 4H), 7.07 (s, 2H), 3.77 (q, J = 7.0 Hz, 6H), 2.32 (s, 12H), 2.24 (m, 2H), 1.65 (m, 2H), 1.36−0.58 (m, 3H), 1.18 (t, J = 7.0 Hz, 9H), 0.74 (t, J = 7.9 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 138.3 (d, $^3J_{C,P}$ = 10.2 Hz), 132.8 (d, $^4J_{C,P}$ = 2.3 Hz), 129.7 (d, $^2J_{C,P}$ = 8.9 Hz), 129.5 (d, $^1J_{C,P}$ = 54.2 Hz), 58.4, 28.6 (d, $^1J_{C,P}$ = 36.2 Hz), 21.5, 18.3, 16.9, 12.2 (d, $^2J_{C,P}$ = 13.5 Hz). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 14.2 (m). HRMS (ESI): m/z calcd for $[C_{25}H_{41}BO_3PSi]^+$ (M − H): 459.2655; found, 459.2643.

Dimesityl[3-(triethoxysilyl)propyl]phosphine Borane (2d). Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 90/10) afforded **2d** in a 74% yield (180.6 mg) as a white solid (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.78 (d, J = 2.8 Hz, 4H), 3.71 (q, J = 7.0 Hz, 6H), 2.61 (m, 2H), 2.27 (s, 12H), 2.22 (s, 6H), 1.76−0.99 (m, 3H), 1.42 (m, 2H), 1.13 (t, J = 7.0 Hz, 9H), 0.70 (t, J = 7.9 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 141.6 (d, $^2J_{C,P}$ = 8.2 Hz), 139.8 (d, $^4J_{C,P}$ = 2.2 Hz), 130.9 (d, $^3J_{C,P}$ = 8.4 Hz), 126.7 (d, $^1J_{C,P}$ = 50.3 Hz), 58.3, 33.3 (d, $^1J_{C,P}$ = 34.6 Hz), 23.2 (d, $^3J_{C,P}$ = 4.8 Hz), 20.8, 18.24, 18.21, 12.4 (d, $^2J_{C,P}$ = 15.6 Hz). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 16.7 (m). HRMS (ESI): m/z calcd for $[C_{27}H_{43}O_3PSiNa]^+$ (M − BH_3 + Na): 497.2611; found, 497.2602.

Di(3,5-dimethyl-4-methoxyphenyl)[3-(triethoxysilyl)-propyl]phosphine Borane (2e). Purification by GPC chromatography (eluent: CH_2Cl_2) afforded **2e** in a 97% yield (254.8 mg) as a white solid (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27 (d, J = 10.5 Hz, 4H), 3.77 (q, J = 7.0 Hz, 6H), 3.72 (s, 6H), 2.27 (s, 12H), 2.20 (m, 2H), 1.63 (m, 2H), 1.40−0.54 (m, 3H), 1.18 (t, J = 7.0 Hz, 6H), 0.73 (t, J = 7.9 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 159.4 (d, $^4J_{C,P}$ = 2.6 Hz), 132.6 (d, $^2J_{C,P}$ = 9.6 Hz), 131.5 (d, $^3J_{C,P}$ = 10.8 Hz), 124.4 (d, $^1J_{C,P}$ = 56.2 Hz), 59.5, 58.4, 28.6 (d, $^1J_{C,P}$ = 36.5 Hz), 18.2, 16.9, 16.2, 12.1 (d, $^2J_{C,P}$ = 13.5 Hz). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 12.4 (m). HRMS (ESI): m/z calcd for $[C_{27}H_{45}BO_5PSi]^+$ (M − H): 519.2867; found, 519.2847.

Diisopropyl[3-(triethoxysilyl)propyl]phosphine Borane (2f). Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 90/10) afforded **2f** in a 26% yield (42.9 mg) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.81 (q, J = 7.0 Hz, 6H), 1.98 (m, 2H), 1.72−1.67 (m, 4H), 1.22 (t, J = 7.0 Hz, 9H), 1.20−1.13 (m, 12H), 0.73 (t, J = 7.2 Hz, 2H), 0.61 to −0.04 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 58.4, 22.5 (d, $^1J_{C,P}$ = 30.1 Hz), 21.7 (d, $^1J_{C,P}$ = 32.9 Hz), 18.3, 17.5 (d, $^2J_{C,P}$ = 1.5 Hz), 17.2, 17.0 (d, $^2J_{C,P}$ = 1.6 Hz), 12.8 (d, $^2J_{C,P}$ = 11.6 Hz). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 31.2 (m). HRMS (ESI): m/z calcd for $[C_{15}H_{38}BO_3PSiNa]^+$ (M + Na): 359.2316; found, 359.2324.

Dicyclopentyl[3-(triethoxysilyl)propyl]phosphine Borane (2g). Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 90/10) afforded **2g** in a 74% yield (194.2 mg) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.81 (q, J = 7.0 Hz, 6H), 2.02 (m, 2H), 1.88−1.48 (m, 20H), 1.22 (t, J = 7.0 Hz, 9H), 0.71 (m, 2H), 0.60 to −0.06 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 58.4, 32.8 (d, $^1J_{C,P}$ = 35.1 Hz), 28.0 (d, $^3J_{C,P}$ = 1.3 Hz), 27.8, 26.4 (d, $^2J_{C,P}$ = 8.8 Hz), 26.1 (d, $^2J_{C,P}$ = 8.5 Hz), 25.6 (d, $^1J_{C,P}$ = 32.0 Hz), 18.3, 17.1 (d, $^3J_{C,P}$ = 2.6 Hz), 12.7 (d, $^2J_{C,P}$ = 11.3 Hz). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 26.3 (m). HRMS (ESI): m/z calcd for $[C_{19}H_{42}BO_3PSiNa]^+$ (M + Na): 411.2630; found, 411.2644.

Dicyclohexyl[3-(triethoxysilyl)propyl]phosphine Borane (2h). Purification by GPC chromatography (eluent: CH_2Cl_2) afforded **2h** in a 72% yield (150.0 mg) as a white solid (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.82 (q, J = 7.0 Hz, 6H), 1.99−1.76 (m, 8H), 1.75−1.59 (m, 8H), 1.43−1.15 (m, 10H), 1.22 (t, J = 7.0 Hz, 9H), 0.71 (t, J = 7.4 Hz, 2H), 0.65 to −0.09 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 58.4, 31.6 (d, $^1J_{C,P}$ = 32.4 Hz), 26.954 (d, $^2J_{C,P}$ = 10.0 Hz), 26.952, 26.92 (d, $^2J_{C,P}$ = 10.8 Hz), 26.7, (d, $^3J_{C,P}$ = 2.3 Hz), 26.0 (d, $^4J_{C,P}$ = 0.9

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Hz), 22.4 (d, $^{1}J_{C,P}$ = 30.5 Hz), 18.3, 17.6 (d, $^{3}J_{C,P}$ = 1.3 Hz), 12.7 (d, $^{2}J_{C,P}$ = 11.7 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 23.8 (m). HRMS (ESI): m/z calcd for $[C_{21}H_{44}O_3PSi]^+$ (M − BH_3 + H): 403.2792; found, 403.2784.

Di(*tert*-butyl)[3-(triethoxysilyl)propyl]phosphine Borane (2i). Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 90/10) afforded **2i** in an 85% yield (154.7 mg) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.82 (q, J = 7.0 Hz, 6H), 1.80 (m, 2H), 1.67 (m, 2H), 1.24 (d, J = 12.3 Hz, 18H), 0.73 (t, J = 7.6 Hz, 2H), 0.69−0.03 (m, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 58.4, 32.0 (d, $^{1}J_{C,P}$ = 26.9 Hz), 27.9 (d, $^{2}J_{C,P}$ = 0.8 Hz), 21.1 (d, $^{1}J_{C,P}$ = 27.8 Hz), 19.0, 18.3, 12.8 (d, $^{2}J_{C,P}$ = 12.1 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 43.2 (m). HRMS (ESI): m/z calcd for $[C_{17}H_{42}BO_3PSiNa]^+$ (M + Na): 387.2630; found, 387.2639.

Diethoxy[3-(triethoxysilyl)propyl]phosphine Borane (2j). Purification by GPC chromatography (eluent: CH_2Cl_2) afforded **2j** in a 31% yield (52.9 mg) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.05 (m, 2H), 3.98 (m, 2H), 3.80 (q, J = 7.0 Hz, 6H), 1.79 (m, 2H), 1.69 (m, 2H), 1.27 (t, J = 7.1 Hz, 6H), 1.20 (t, J = 7.1 Hz, 9H), 0.79−0.11 (m, 3H), 0.71 (m, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 62.9 (d, $^{2}J_{C,P}$ = 4.8 Hz), 58.4, 32.8 (d, $^{1}J_{C,P}$ = 54.2 Hz), 18.3, 16.5 (d, $^{3}J_{C,P}$ = 5.6 Hz), 15.5, 11.8 (d, $^{2}J_{C,P}$ = 13.1 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 147.2 (m). HRMS (ESI): m/z calcd for $[C_{13}H_{33}BO_5PSi]^+$ (M − H): 339.1925; found, 339.1935.

Diphenyl[4-(triethoxysilyl)butyl]phosphine Borane (2k). Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 84/16) afforded **2k** in a 73% yield (152.7 mg) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72−7.65 (m, 4H), 7.54−7.43 (m, 6H), 3.80 (q, J = 7.0 Hz, 6H), 2.22 (m, 2H), 1.63-1.48 (m, 4H), 1.40−0.61 (m, 3H), 1.22 (t, J = 7.0 Hz, 9H), 0.63 (m, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 132.2 (d, $^{2}J_{C,P}$ = 8.9 Hz), 131.1 (d, $^{4}J_{C,P}$ = 2.3 Hz), 129.7 (d, $^{1}J_{C,P}$ = 54.5 Hz), 128.8 (d, $^{3}J_{C,P}$ = 9.7 Hz), 58.4, 26.3, 25.4 (d, $^{1}J_{C,P}$ = 36.9 Hz), 24.6 (d, $^{2}J_{C,P}$ = 14.9 Hz), 18.3, 10.1. $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 15.9 (m). HRMS (ESI): m/z calcd for $[C_{22}H_{36}BO_3PSiNa]^+$ (M + Na): 441.2161; found, 441.2169.

Diphenyl[5-(triethoxysilyl)pentyl]phosphine Borane (2l). Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 84/16) afforded **2l** in an 85% yield (184.8 mg) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68−7.63 (m, 4H), 7.50−7.40 (m, 6H), 3.79 (q, J = 7.0 Hz, 6H), 2.19 (m, 2H), 1.51 (m, 2H), 1.35−1.34 (m, 4H), 1.33−0.52 (m, 3H), 1.20 (t, J = 7.0 Hz, 9H), 0.59 (m, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 132.1 (d, $^{2}J_{C,P}$ = 8.9 Hz), 131.1 (d, $^{4}J_{C,P}$ = 2.4 Hz), 129.7 (d, $^{1}J_{C,P}$ = 54.5 Hz), 128.8 (d, $^{3}J_{C,P}$ = 9.7 Hz), 58.3, 34.6 (d, $^{3}J_{C,P}$ = 13.7 Hz), 25.7 (d, $^{2}J_{C,P}$ = 36.8 Hz), 22.3 (d, $^{1}J_{C,P}$ = 49.3 Hz), 18.3, 10.2. $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 15.9 (m). HRMS (ESI): m/z calcd for $[C_{23}H_{38}BO_3PSiNa]^+$ (M + Na): 455.2318; found, 455.2325.

Diphenyl[3-(diethoxymethylsilyl)propyl]phosphine Borane (2n). Purification by column chromatography on silica gel (eluent: hexane/AcOEt = 84/16) afforded **2n** in a 41% yield (77.6 mg) as a colorless oil (91% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73−7.62 (m, 4H), 7.52−7.40 (m, 6H), 3.70 (q, J = 7.0 Hz, 4H), 2.27 (m, 2H), 1.63 (m, 2H), 1.41−0.65 (m, 3H), 1.16 (t, J = 7.0 Hz, 6H), 0.71 (m, 2H), 0.06 (s, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 132.2 (d, $^{2}J_{C,P}$ = 9.0 Hz), 131.1 (d, $^{4}J_{C,P}$ = 2.4 Hz), 129.7 (d, $^{1}J_{C,P}$ = 54.4 Hz), 128.8 (d, $^{3}J_{C,P}$ = 9.7 Hz), 58.2, 28.7 (d, $^{1}J_{C,P}$ = 35.4 Hz), 18.4, 17.0, 15.9 (d, $^{2}J_{C,P}$ = 12.8 Hz), −4.8. $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 15.4 (m). HRMS (ESI): m/z calcd for $[C_{20}H_{32}BO_2PSiNa]^+$ (M + Na): 397.1898; found, 397.1906.

Diphenyl[3-(triethoxysilyl)propyl]phosphine (4).[33] In a test tube with a PTFE screw cap, DABCO (56.0 mg, 0.5 mmol) was equipped. Toluene (2.5 mL) and **2a** (100.0 mg, 0.25 mmol) were successively added to the test tube. The resulting mixture was stirred at room temperature for 16 h. After the removal of volatile in vacuo, the crude mixture was directly purified by column chromatography on silica gel (eluent: hexane/AcOEt = 84/16) to obtain **4** in a 90% yield (87.8 mg) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, C_6D_6): δ 7.48−7.45 (m, 4H), 7.09−7.02 (m, 6H), 3.75 (q, $^{2}J_{H,H}$ = 7.0 Hz, 6H), 2.12 (m, 2H), 1.81 (m, 2H), 1.12 (t, $^{2}J_{H,H}$ = 7.0 Hz, 9H), 0.89 (m, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, C_6D_6): δ 140.0 (d, $^{1}J_{C,P}$ = 14.6 Hz), 133.2 (d, $^{2}J_{C,P}$ = 18.5 Hz), 128.6 (d, $^{3}J_{C,P}$ = 6.4 Hz), 128.5, 58.5, 32.0 (d, $^{1}J_{C,P}$ = 12.5 Hz), 20.2 (d, $^{3}J_{C,P}$ = 17.9 Hz), 18.6, 12.8 (d, $^{2}J_{C,P}$ = 12.4 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6): δ −17.1. HRMS (ESI): m/z calcd for $[C_{21}H_{32}O_3PSi]^+$ (M + H): 391.1853; found, 391.1850.

Diphenyl[3-(triethoxysilyl)propyl]phosphine Oxide (5a).[34] In a test tube with a PTFE screw cap, DABCO (56.0 mg, 0.5 mmol) was equipped. Toluene (2.5 mL) and **2a** (100.0 mg, 0.25 mmol) were successively added to the test tube. The resulting mixture was stirred at room temperature for 16 h. Then, H_2O_2 (30%, 60.0 μL) was added to the mixture. After stirring for 1 h at room temperature, the aqueous phase was extracted with EtOAc. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: EtOAc) afforded **5a** in a 71% yield (72.4 mg) as a colorless oil (95% purity).

^{1}H NMR (600 MHz, C_6D_6): δ 7.85−7.77 (m, 4H), 7.06−7.02 (m, 6H), 3.72 (q, J = 7.0 Hz, 6H), 2.19 (m, 2H), 2.01 (m, 2H), 1.11 (t, J = 7.0 Hz, 9H), 0.82 (t, J = 7.9 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, C_6D_6): δ 135.4 (d, $^{1}J_{C,P}$ = 95.0N Hz), 131.2 (d, $^{4}J_{C,P}$ = 2.2 Hz), 131.1 (d, $^{2}J_{C,P}$ = 8.9 Hz), 128.6 (d, $^{3}J_{C,P}$ = 11.2 Hz), 58.5, 33.0 (d, $^{1}J_{C,P}$ = 70.5 Hz), 18.5, 16.1 (d, $^{3}J_{C,P}$ = 3.7 Hz), 12.4 (d, $^{2}J_{C,P}$ = 12.8 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6): δ 27.7. HRMS (ESI): m/z calcd for $[C_{21}H_{32}O_4PSi]^+$ (M + H): 407.1802; found, 407.1822.

Diphenyl[3-(triethoxysilyl)propyl]phosphine Sulfide (5b). In a test tube with a PTFE screw cap, DABCO (56.0 mg, 0.5 mmol) and S_8 (16.5 mg, 0.065 mmol) were equipped. Toluene (2.5 mL) and **2a** (200.0 mg, 0.5 mmol) were successively added to the test tube. The resulting mixture was stirred at 40 °C for 4 h. After cooling to room temperature, the reaction mixture was treated with pH2 buffer solution (0.5 M H_2SO_4 and 1.5 M Na_2SO_4 aqueous solution),[35] and then the aqueous phase was extracted with EtOAc. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: hexane/toluene = 84/16) afforded **5b** in an 84% yield (176.5 mg) as a colorless oil (>99% purity).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86−7.78 (m, 4H), 7.50−7.41 (m, 6H), 3.76 (q, J = 7.0 Hz, 6H), 2.54 (m, 2H), 1.78 (m, 2H), 1.17 (t, J = 7.0 Hz, 9H), 0.74 (t, J = 7.9 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 133.1 (d, $^{1}J_{C,P}$ = 79.0

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Hz), 131.3 (d, $^{4}J_{C,P}$ = 2.8 Hz), 131.1 (d, $^{2}J_{C,P}$ = 10.0 Hz), 128.6 (d, $^{3}J_{C,P}$ = 11.8 Hz), 58.4, 35.2 (d, $^{1}J_{C,P}$ = 55.1 Hz), 18.3, 16.2 (d, $^{3}J_{C,P}$ = 2.1 Hz), 11.5 (d, $^{2}J_{C,P}$ = 16.1 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 42.0. HRMS (ESI): m/z calcd for $[C_{21}H_{32}O_3PSSi]^+$ (M + H): 423.1574; found, 423.1581.

Immobilization of 2a on FSM-16 (Scheme 3b). A two-neck flask connected to a condenser was charged with a stir bar and FSM-16 (1.0 g). Toluene (25 mL) and **2a** (202.2 mg, 0.5 mmol) were successively added to the flask. The resulting suspension was vigorously stirred at 60 °C for 5 h. The suspension was then filtered and washed with toluene using a Soxhlet extractor. The material was dried under reduced pressure to give functionalized mesoporous silica **6** (1.08 g).

Anal. Found: C, 10.03; H 1.43.

Removal of Coordinating Borane from 6 (Scheme 3c). A two-neck flask connected to a condenser was charged with a stir bar, **6** (0.52 g), and DABCO (224.3 mg, 2.0 mmol). Toluene (20 mL) was added to the flask, and then the resulting suspension was vigorously stirred at reflux temperature for 16 h. The suspension was then filtered and washed with toluene using a Soxhlet extractor. The material was dried under reduced pressure to give functionalized mesoporous silica **7** (0.47 g).

Anal. Found: C, 10.69; H 1.09.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c07161.

Optimization of the reaction conditions (Table S1); identification of main product **2a** and byproduct **3a** by crude NMR (Figure S1); infrared spectra of the functionalized mesoporous silica **6** and **7** (Figure S2); and copies of ^{1}H, ^{13}C, and ^{31}P NMR spectra (Figures S3−S31) (PDF)

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Notes

The authors declare no competing financial interest.

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