Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Pd-Bisphosphine Complex and Organic Functionalities Immobilized on the Same SiO_2 Surface: Detailed Characterization and Its Use as an Efficient Catalyst for Allylation

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Contents

Experimental Section

NMR measurements

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ with an AVANCE 400 spectrometer (Bruker) operating at 400.0, 100.6, and 161.9 MHz, respectively. An AVANCE 500 spectrometer (Bruker) was also used, operating at 500.1 and 125.8 MHz for ^{1}H and ^{13}C, respectively. Solid-state ^{13}C, ^{29}Si, and ^{31}P MAS NMR spectra [MAS rate = 5 kHz (^{13}C and ^{29}Si), 14 kHz (^{31}P)] were recorded with an AVANCE III spectrometer (Bruker) operating at 100.6, 79.5, and 161.9 MHz, respectively. Cross-polarization (CP) contact time in ^{13}C and ^{29}Si CP/MAS NMR measurements was 1.0 and 2.0 ms, respectively. The accumulation number and delay time were around 20000 and 20 s (^{13}C), 10000 and 15 s (^{29}Si), and 6000 and 10 s (^{31}P) respectively. Adamantane (δ 38.52 and 29.47 ppm), hexamethylcyclotrisiloxane (δ -9.66 ppm), and NH_4-H_2PO_4 (δ 1.00 ppm) were used as external standards for the calibration of chemical shifts.

XPS measurements

XPS analyses were performed on an ESCA1700R system equipped with a dual Mg/Al X-ray source and a hemispherical analyzer operating in fixed analyzer transmission mode. Spectra were obtained using a pass energy of 58.7 eV; an $Al_{K\alpha}$ X-ray source was operated at 350 W and 14 kV. Excess charges on the samples were neutralized by argon ion sputtering. The analysis area was 0.8×2 mm. The working pressure in the analyzing chamber was less than 1×10^{-7} Pa. Spectra were acquired in the Pd 3d, P 2p, O 1s, N 1s, C 1s, Si 2p, and Cl 2p regions. The C 1s peak at a binding energy (BE) of 285 eV was taken as an internal reference.

XAFS data acquisition

XAFS was measured in transmission mode at the BL7 of the Kyusyu Synchrotron Light Research Center (Proposal number: 1504037F, SAGA-LS, Saga, Japan). The electron storage ring was operated at 1.4 GeV-137 mA. Synchrotron radiation from the storage ring was monochromatized with a Si (220) channel-cut crystals. Ionization chambers filled with Ar gas and Kr were used as detectors monitoring incident X-rays (I_0) and transmitted one (I), respectively. The angle of the monochromator was calibrated using Pd foil, with the inflection point at the edge set to 24352.6 eV.

XAFS spectra were analyzed by using Athena and Altemis[1], and REX2000 (for curve-fitting analysis, Rigaku. Co. Japan). The backscattering amplitude and phase shift of Pd-P/Cl were extracted from the $PdCl_2(PPh_3)_2$ complex.

A goodness of curve fit was estimated using the following equation.

$$R_{factor} = \sqrt{\frac{k^n \chi_{exp}(k) - k^n \chi_{cf}(k)}{k^n \chi_{experimental}(k)}}$$

where $\chi_{exp}(k), \chi_{cf}(k)$ are the experimental data, curve-fitted data (theoretical), respectively.

[1] (a) Ravel, B.; Newville, M. *Syncrotron Rad*. **2005**, *12*, 537. (b) Newville, J. *Syncrotron Rad*. **2001**, *8*, 322.

Materials

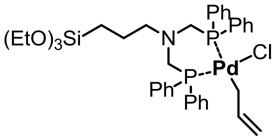
Aerosil® 300 (NIPPON AEROSIL Co.) was used as the SiO_2 source. SiO_2 was treated at 120 °C under vacuum before use. Unless otherwise noted, all other materials were purchased from Wako Pure Chemicals, Tokyo Kasei Co., Kanto Kagaku Co., and

Aldrich Inc. and used without further purification. In the catalytic reactions, 1,3,5-triisopropylbenzene was used as an internal standard.

Preparation of Catalyst

Preparation of PP-Pd complex

Treatment of the diphosphine ligand (0.50 mmol) with a solution of [PdCl(η^3-allyl)]$_2$ (Pd: 0.50 mmol) in THF (4 mL) at room temperature for 4 h afforded the desired Pd-bisphosphine complex (PP-Pd).



PP-Pd

δ(^{1}H) (500.1MHz, CDCl$_3$) 0.40(t, *J*=8.0Hz, 2H), 1.19(t, *J*=7.0Hz, 9H), 1.53(quint, *J*=7.9Hz, 2H), 2.64(t, *J*=7.5Hz, 2H), 3.86(br, 4H), 3.78(q, *J*=7.0Hz, 6H), 4.01(br, 4H), 5.59(quint, *J*=10.4Hz, 1H), 7.25-7.87 (m, 20H); δ(^{13}C) (125.8MHz, CDCl$_3$) 7.94(s), 18.43(s), 18.95(s), 54.12(t, *J*=19.8), 58.52(s), 65.56(t, *J*=10.4), 70.70(t, *J*=16.6), 119.17(t, *J*=6.6), 128.50(t, *J*=4.9Hz), 130.29(s), 133.35(t, *J*=5.5Hz); δ(^{31}P) (202.3MHz, CDC$_3$) 3.06. HRMS (ESI, [M-Cl]$^+$) calcd for $C_{38}H_{50}NO_3P_2PdSi$: 764.2078; found: 764.2057.

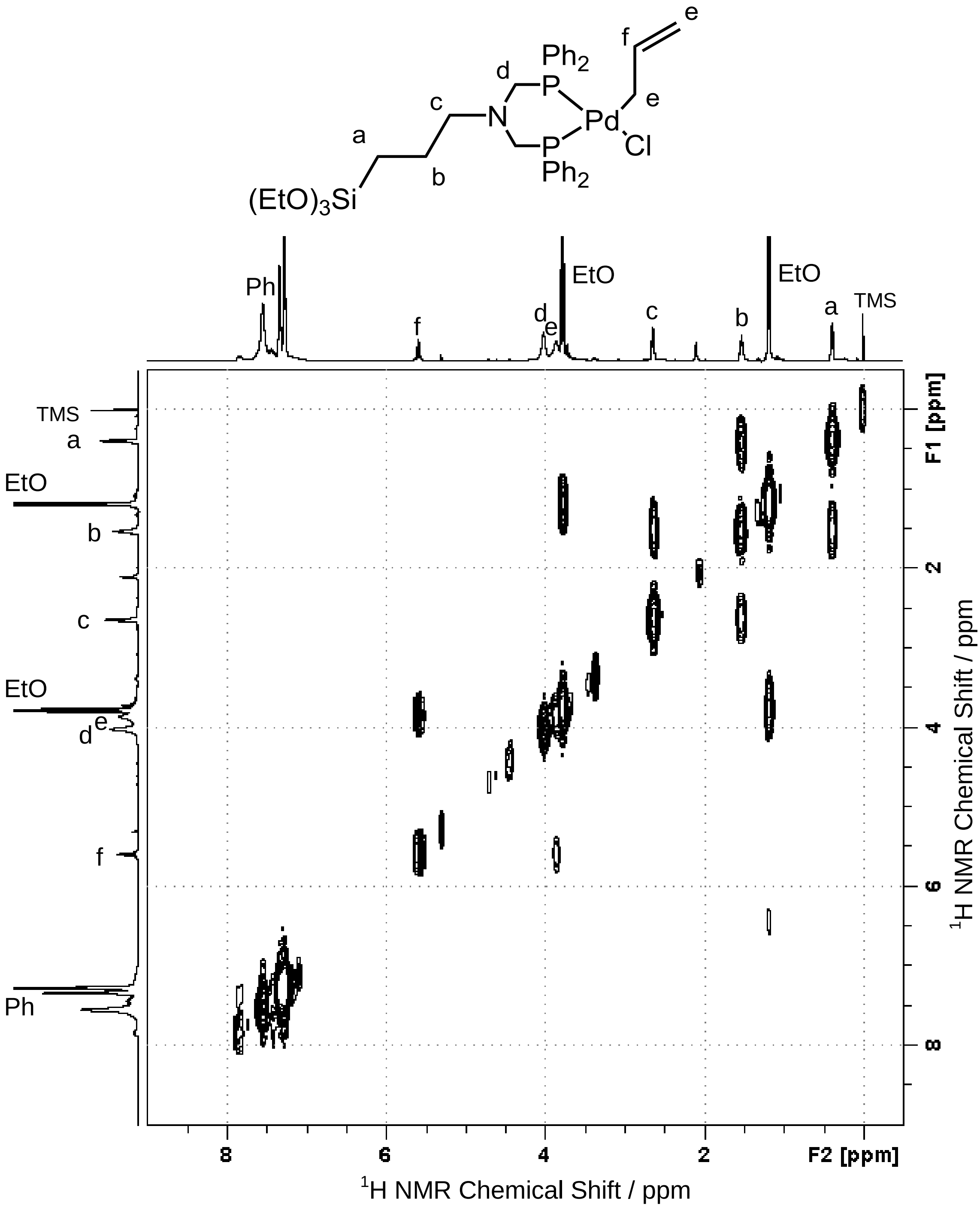


Figure S1. ^{1}H-^{1}H COSY NMR spectrum for diphosphine/Pd

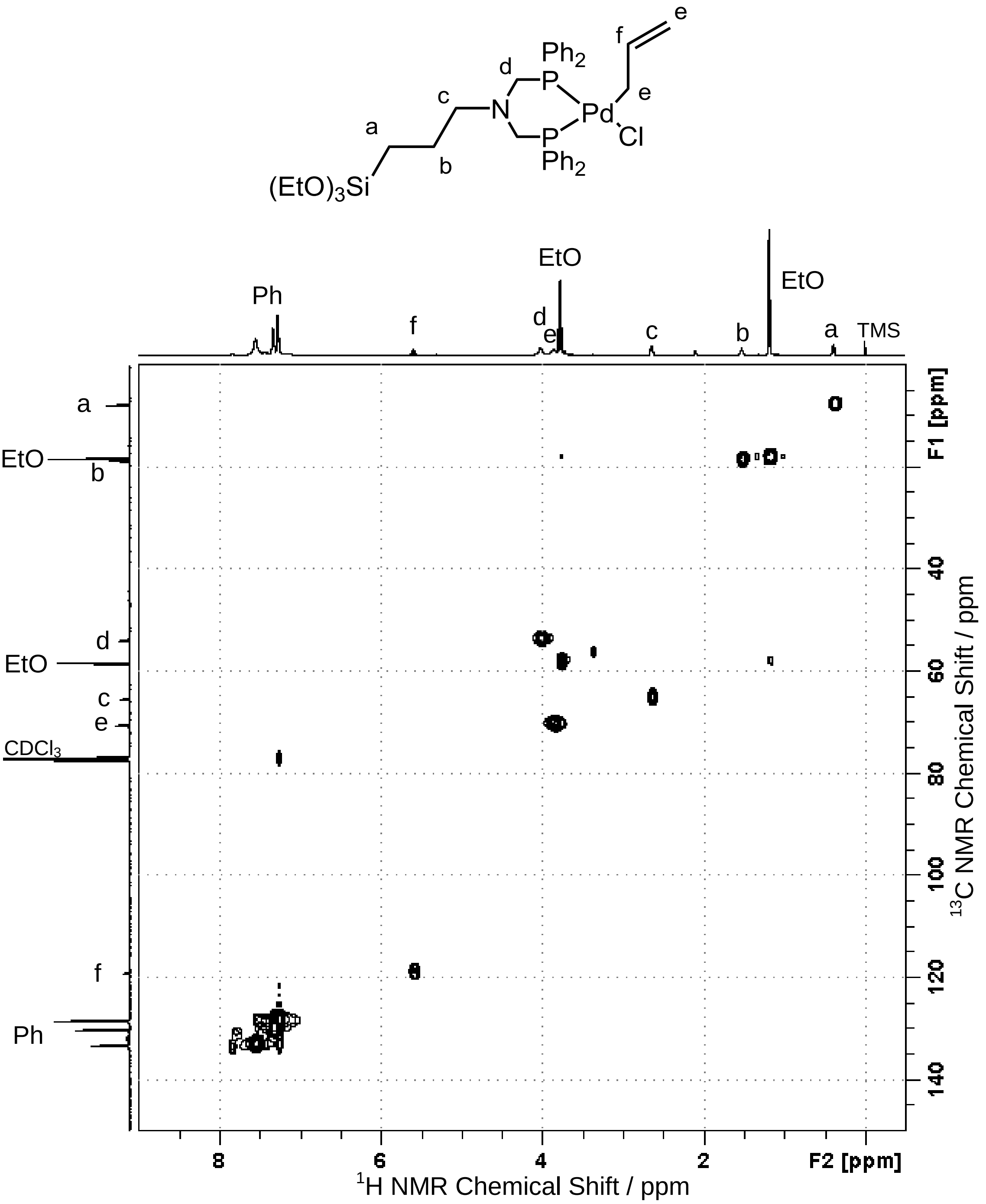


Figure S2. ^{1}H – ^{13}C HSQC NMR spectrum for diphosphine/Pd

Preparation of SiO_2/PP-Pd

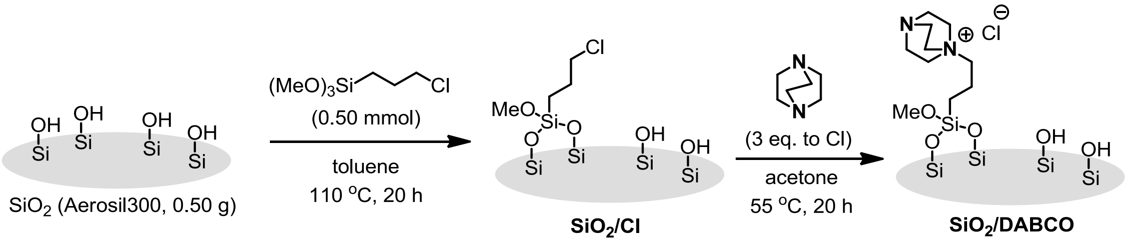
SiO_2 (Aerosil® 300, SiO_2 content: >99.9%) was pretreated by drying at 120 °C for 3 h under vacuum. Dried SiO_2 (0.30 g) was treated with a solution of PP-Pd (0.050 mmol) in toluene (10 mL) at 50 °C for 20 h. The resulting mixture was filtered, washed with toluene, and dried under vacuum, affording SiO_2/PP-Pd.

Preparation of SiO_2/Me/PP-Pd and SiO_2/Hex/PP-Pd

SiO_2 (Aerosil® 300, SiO_2 content: >99.9%) was pretreated by drying at 120 °C for 3 h under vacuum. Dried SiO_2 (0.50 g) was treated with methyltrimethoxysilane (0.50 mmol) in toluene (10 mL) at 110 °C for 20 h. Toluene was removed by vacuum evaporation, affording SiO_2/Me. The SiO_2/Me (0.30 g) was treated with a solution of PP-Pd (0.050 mmol) in toluene (10 mL) at 50 °C for 20 h. The resulting mixture was filtered, washed with toluene, and dried under vacuum, affording SiO_2/Me/PP-Pd. In the case of SiO_2/Hex/PP-Pd, *n*-hexyltrimethoxysilane was used as a silane-coupling agent.

Preparation of SiO_2/DABCO/PP-Pd

SiO_2 (Aerosil® 300, SiO_2 content: >99.9%) was pretreated by drying at 120 °C for 3 h under vacuum. Dried SiO_2 (0.50 g) was placed in a round-bottom flask and treated with a solution of 3-chloropropyltrimethoxysilane (0.50 mmol, 9.9×10^{-2} g) in toluene (10 mL) at 110 °C for 20 h. Toluene was removed by vacuum evaporation, affording SiO_2/Cl. An acetone solution of 1,4-diazabicyclo[2.2.2]octane (DABCO) (1.50 mmol of DABCO, 10 mL) was then added to SiO_2/Cl. The resulting slurry was heated at 55 ^{o}C for 20 h, then the solid was filtered, washed with acetone, and dried under vacuum, affording SiO_2/DABCO (Scheme S1). The SiO_2/DABCO (0.30 g) was treated with a solution of PP-Pd (0.050 mmol) in toluene (10 mL) at 50 °C for 20 h. The resulting mixture was filtered, washed with toluene, and dried under vacuum, affording SiO_2/DABCO/PP-Pd.



Scheme S1. Preparation of SiO_2-supported DABCO (SiO_2/DABCO).

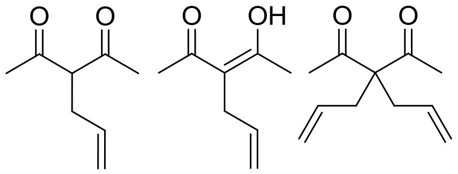
Catalytic Reaction Procedures

The Tsuji-Trost reaction using a silica-supported Pd catalyst

The silica-supported Pd catalyst (3.0 μmol), toluene (2.0 mL), K_2CO_3 (0.25 mmol), ethyl acetoacetate (**1**) (0.50 mmol), and allyl methyl carbonate (1.25 mmol) were placed in a Pyrex glass reactor. The resulting mixture was stirred vigorously for 60 min at 70 °C under Ar. The products were confirmed by GC-MS and NMR. Yields and conversions were determined by ^{1}H NMR analysis of a reaction mixture aliquot in $CDCl_3$ solution. All products were identified by comparison with reported data.

^{1}H NMR data and references are as follows:

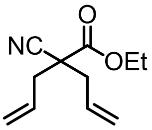
Table 5, entry 1



^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 6H [enol, di]), 2.18 (s, 6H [keto]), 2.58-2.61 (m, 2H [keto]), 2.65 (d, *J* = 7.3Hz, 2H [di]), 2.98-3.00 (m, 1H [enol]) 3.73 (t, *J* = 7.4Hz, 1H[keto]), 4.98-5.14 (m, 2H), 5.49-5.56 (m, 1H [di]), 5.65-5.74 (m, 1H [keto]), 5.81-5.87 (m, 1H [enol])

Ref: H. Noda, K. Motokura, A. Miyaji, T. Baba, *Adv. Synth. Catal.* **2013**, *355*, 973

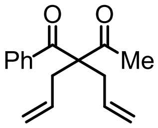
Table 5, entry 3



^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.1 Hz, 3H), 2.53-2.57 (m, 2H), 2.63-2.67 (m, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 5.23-5.27 (m, 4H), 5.77-5.84 (m, 2H)

Ref: M. Lamberto, J. D. Kilburn, *Tetrahedron Lett.* **2008**, *49*, 6364.

Table 5, entry 4



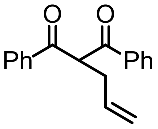
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.10 (s, 3H), 2.77-2.85 (m, 4H), 4.98-5.02 (m, 4H), 5.45-5.53 (m, 2H), 7.41-7.44 (m, 2H), 7.53-7.56 (m, 1H), 7.79-7.81(m, 2H)

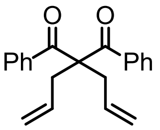
^{13}C NMR (100 MHz, CDCl3) δ 28.0, 36.1, 68.5, 119.5, 128.7, 128.9, 131.8, 133.2, 136.4, 197.9, 206.6.

MS (EI) *m*/*z* (%): 241(M^+-H), 199(M^+-$COCH_3$), 159, 122, 105, 77, 43(100).

HRMS calcd for $C_{16}H_{18}O_2$+Na: 265.1199; found: 265.1200.

Table 5, entry 5

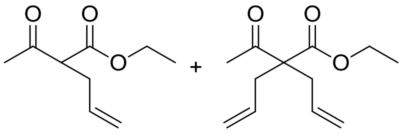




^{1}H NMR (500 MHz, $CDCl_3$) δ 2.89-2.91 (m, 2H [mono]), 2.99 (d, *J* = 7.3 Hz, 4H [di]), 4.91-5.06 (m, 4H [di]), 5.05-5.14 (m, 2H [mono]), 5.29-5.33 (m, 1H [mono]), 5.47-5.55 (m, 2H [di]), 5.86-6.00 (m, 1H [mono]), 7.34-7.37 (m, 4H [di]), 7.48-7.49 (m, 4H [mono], 2H [di]), 7.58-7.61 (m, 2H [mono]), 7.86-7.87 (m, 4H [di]), 7.97-7.99 (m, 4H [di])

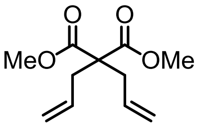
Ref: F. Nahra, Y. Macé, A. Boreux, F. Billard, O. Riant, *Chem. Eur. J.* **2014**, *20*, 10970; X. Zhao, D. Liu, H. Guo, Y. Liu, W. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 19354.

Table 5, entry 6



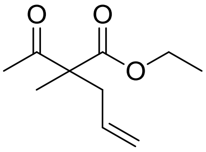
^{1}H NMR (400 MHz, CDCl$_3$) mono: δ 1.26 (t, *J* = 7.1Hz, 3H), 2.22 (s, 3H), 2.58 (quint, *J* = 3.9Hz, 2H), 3.50 (t, *J* = 7.4Hz, 1H), 4.19 (q, *J* = 7.1Hz, 2H), 5.02-5.11 (m, 2H), 5.68-5.78 (m, 1H); di: δ 2.12 (s, 3H); 5.56-5.63 (m, 2H)
Ref: K. Motokura, K. Saitoh, H. Noda, Y. Uemura, W.-J. Chun, A. Miyaji, S. Yamaguchi, T. Baba, *ChemCatChem* **2016**, *8*, 331.

Table 5, entry 7



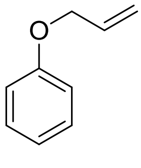
^{1}H NMR (500 MHz, CDCl$_3$) δ 2.64 (d, *J* = 7.4 Hz, 4H), 3.72 (s, 6H), 5.09-5.13 (m, 4H), 5.61-5.69 (m, 2H)
Ref: T. Yang, L. Lu, Q. Shen, *Chem Commun.* **2015**, *51*, 5479.

Table 5, entry 8



^{1}H NMR (400 MHz, CDCl$_3$) δ 1.25-1.36 (m, 6H), 2.16 (s, 3H), 2.48-2.67 (m, 2H), 4.20 (q, *J* = 7.1Hz, 2H), 5.08-5.13 (m, 2H), 5.61-5.71 (m, 1H)
Ref: H. Noda, K. Motokura, A. Miyaji, T. Baba, *Adv. Synth. Catal.* **2013**, *355*, 973

Table 5, entry 9



^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57-4.59 (m, 2H), 5.31-5.49 (m, 2H), 6.06-6.16 (m, 1H), 6.95-7.01 (m, 3H), 7.30-7.35 (m, 2H)

Ref: H. Noda, K. Motokura, A. Miyaji, T. Baba, *Adv. Synth. Catal.* **2013**, *355*, 973

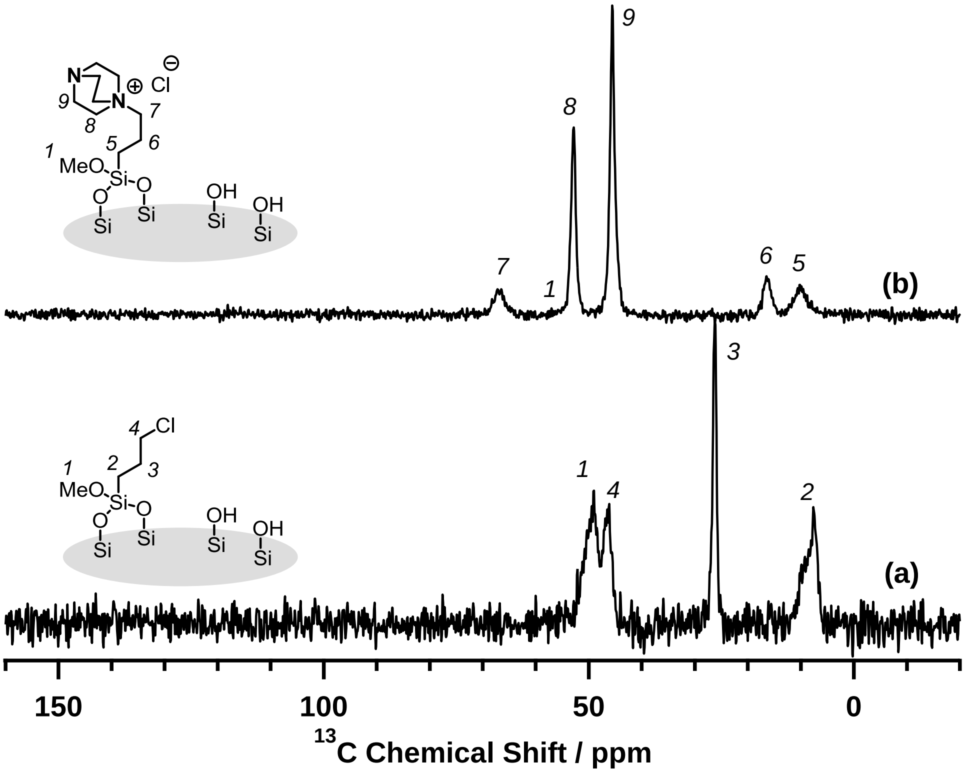


Figure S3. ^{13}C CP/MAS NMR spectra for (a) SiO_2/Cl and (b) SiO_2/DABCO

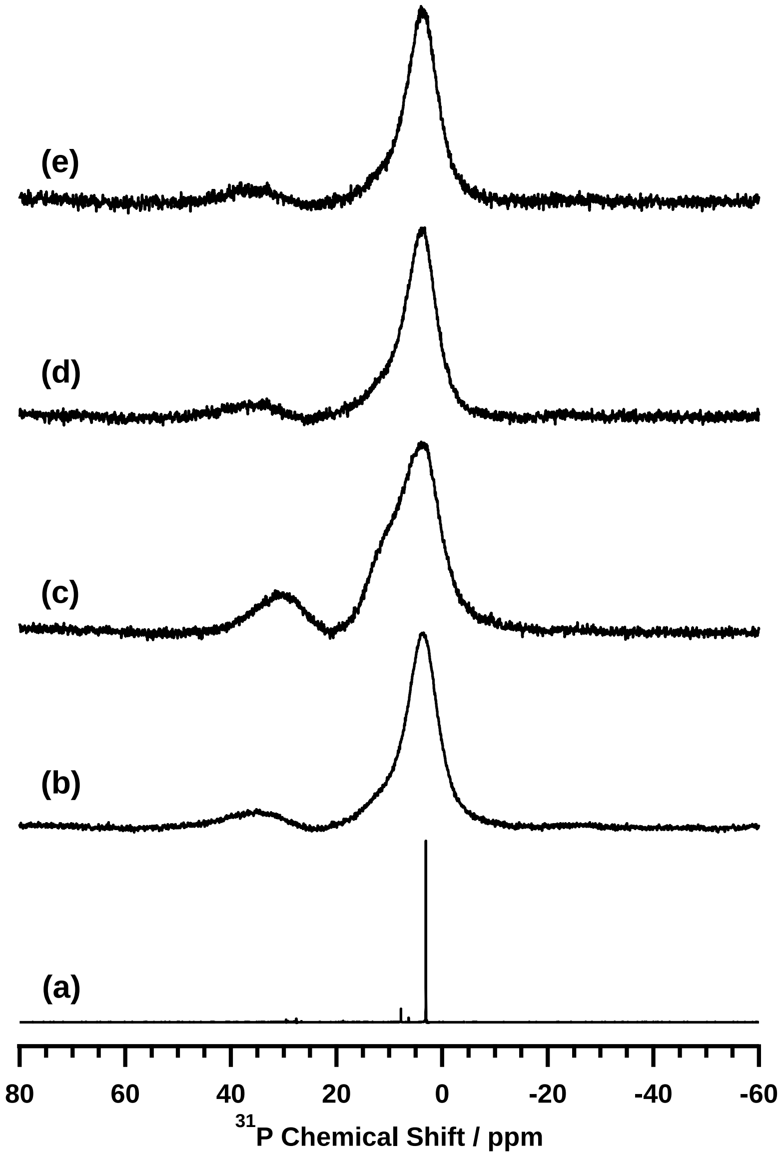


Figure S4. (a) ^{31}P NMR spectrum of PP-Pd in $CDCl_3$ solution, and ^{31}P MAS NMR spectra for (b) SiO_2/PP-Pd, (c) SiO_2/DABCO/PP-Pd, (d) SiO_2/Me/PP-Pd, and (e) SiO_2/Hex/PP-Pd.

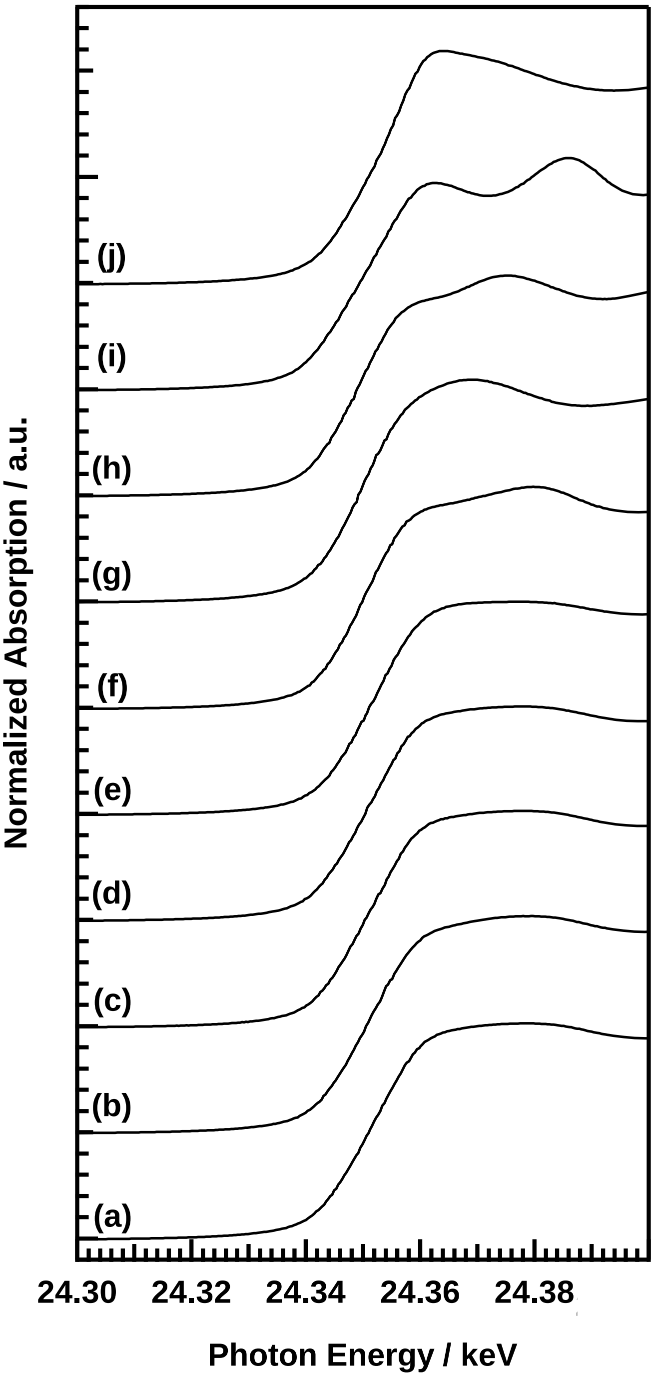


Figure S5. Pd K-edge XANES spectra of (a) SiO_2/PP-Pd, (b) SiO_2/DABCO/PP-Pd, (c) SiO_2/Me/PP-Pd, (d) SiO_2/Hex/PP-Pd, (e) PP-Pd THF solution, (f) $Pd^{II}Cl_2(PPh_3)_2$, (g) $[Pd^{II}Cl(\eta^3\text{-allyl})]_2$, (h) $Pd^0(PPh_3)_4$, (i) Pd^0 foil, and (j) $Pd^{II}O$.

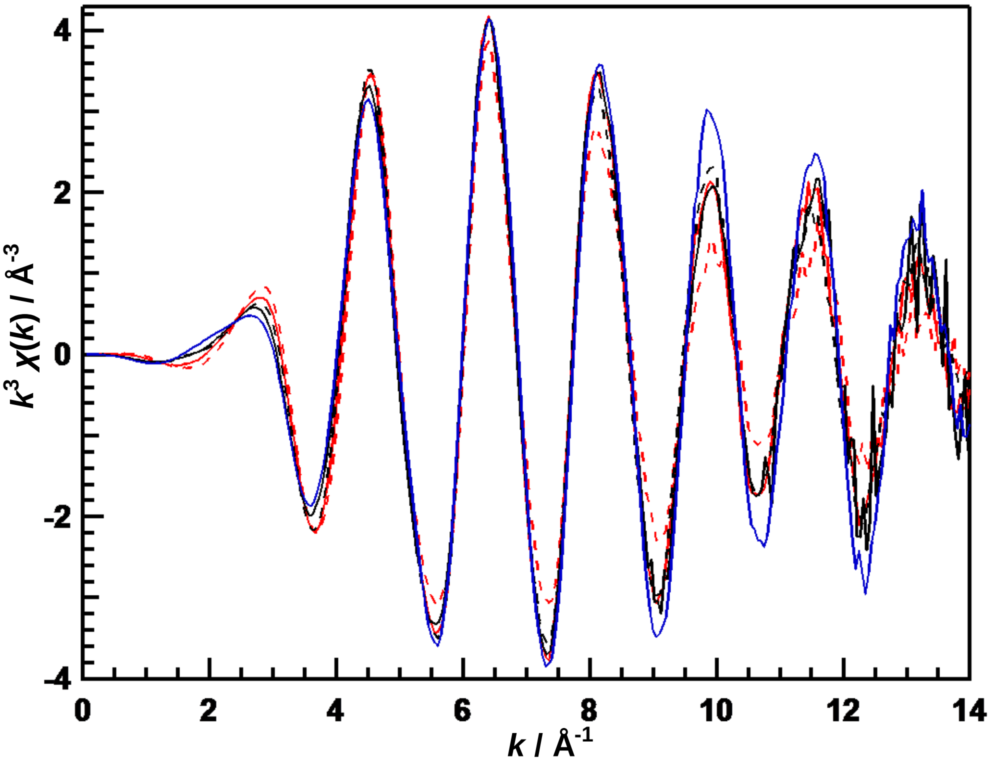


Figure S6. EXAFS spectra of SiO_2/DABCO/PP-Pd (red dash line), SiO_2/PP-Pd (red solid line), SiO_2/Me/PP-Pd (black solid line), SiO_2/Hex/PP-Pd (black dash line), and the THF solution of the homogeneous PP-Pd complex (blue solid line).

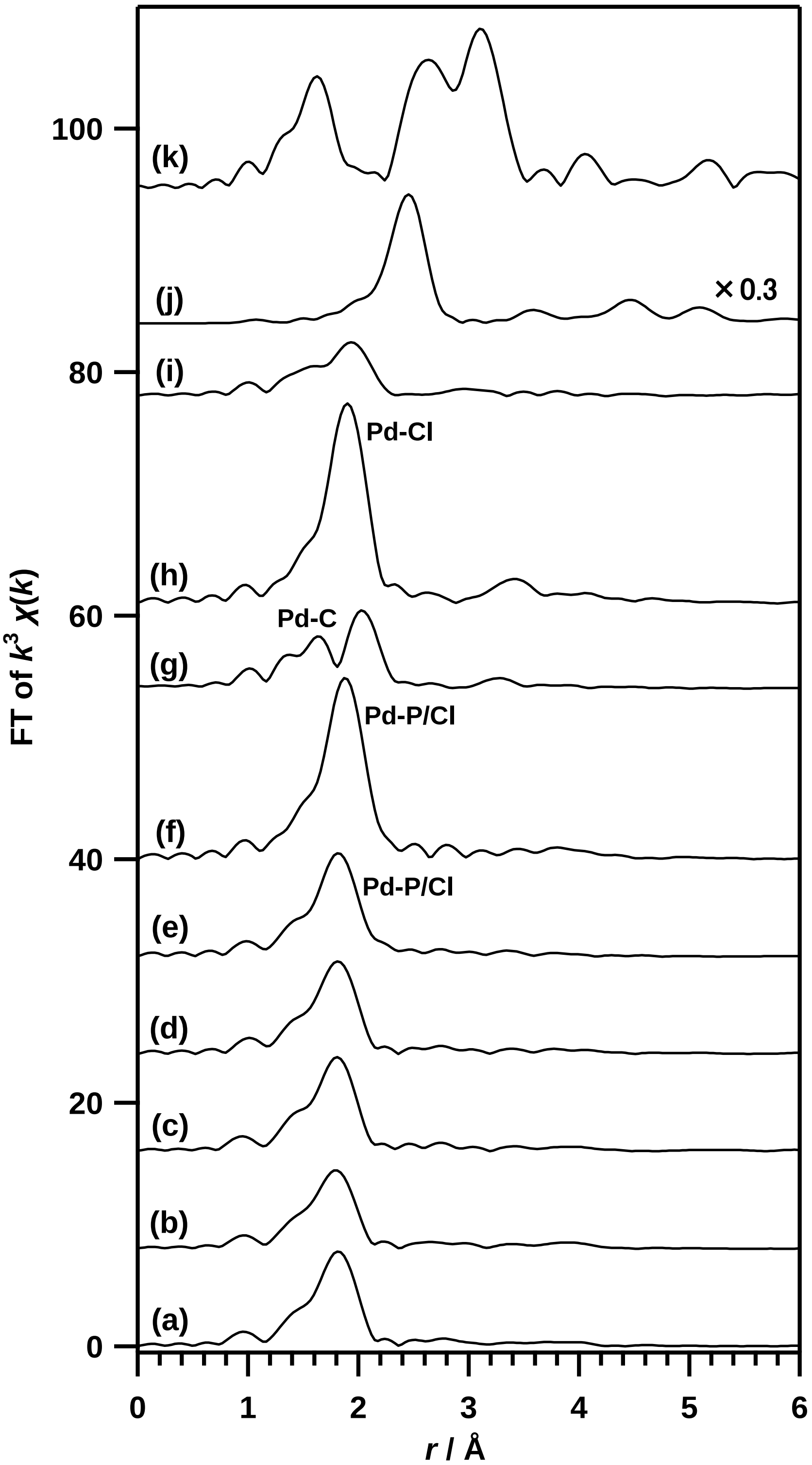


Figure S7. FT of k^3-weighted Pd K-edge EXAFS spectra of (a) SiO_2/PP-Pd, (b) SiO_2/DABCO/PP-Pd, (c) SiO_2/Me/PP-Pd, (d) SiO_2/Hex/PP-Pd, (e) THF solution of homogeneous PP-Pd complex, (f) $Pd^{II}Cl_2(PPh_3)_2$, (g) $[Pd^{II}Cl(\eta^3\text{-allyl})]_2$, (h) $Pd^{II}Cl_2$, (i) $Pd^0(PPh_3)_4$, (j) Pd^0 foil, and (k) $Pd^{II}O$.