Supporting Information

Confirmation of Suzuki-Miyaura Cross-coupling Reaction Mechanism through Synthetic Architecture of Nanocatalysts

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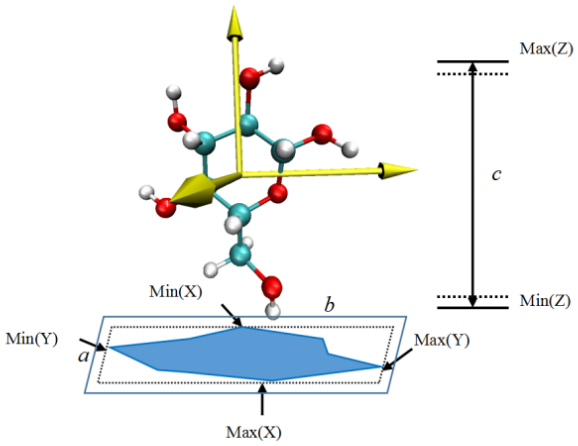


$a = Max(X) - Min(X) + Radius(A1) + Radius(A2)$
$b = Max(Y) - Min(Y) + Radius(B1) + Radius(B2)$
$c = Max(Z) - Min(Z) + Radius(C1) + Radius(C2)$

A1,A2,B1,B2,C1,C2 are boundary atoms

Figure S1. Illustration of the computational method.

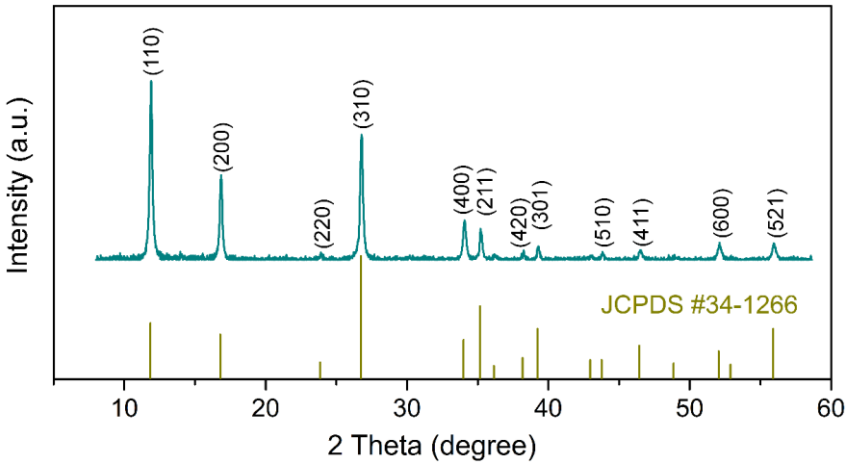


Figure S2. XRD pattern of β-FeOOH spindles.

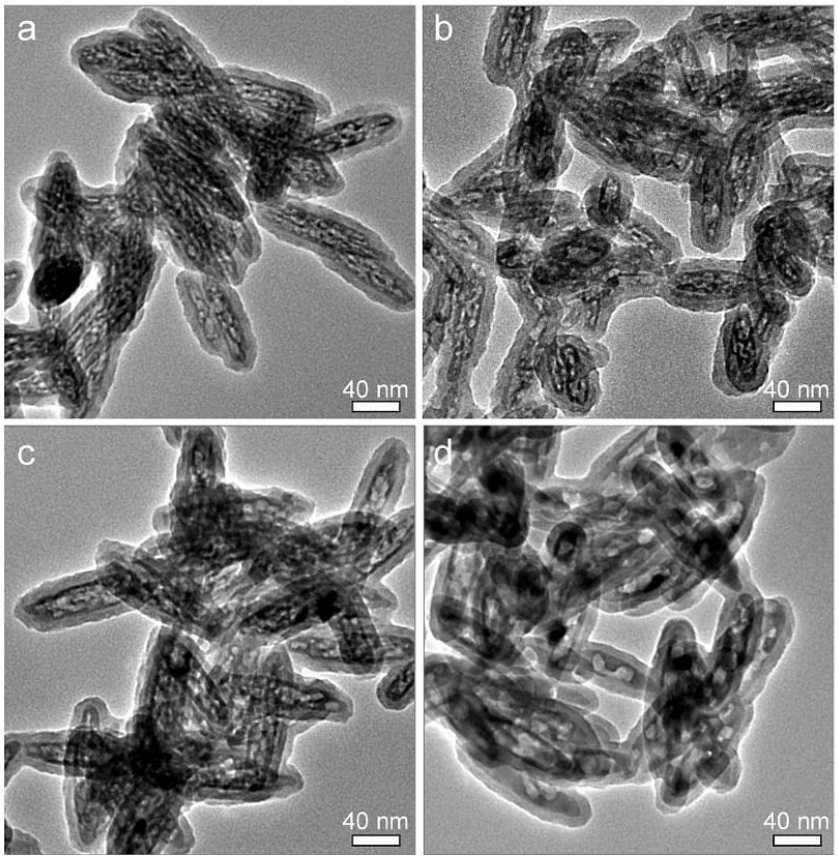


Figure S3. TEM images of $Pd/FeO_x@SiO_2$ calcined at different temperatures: (a) 500°C, (b) 600°C, (c) 700°C, and (d) 800°C.

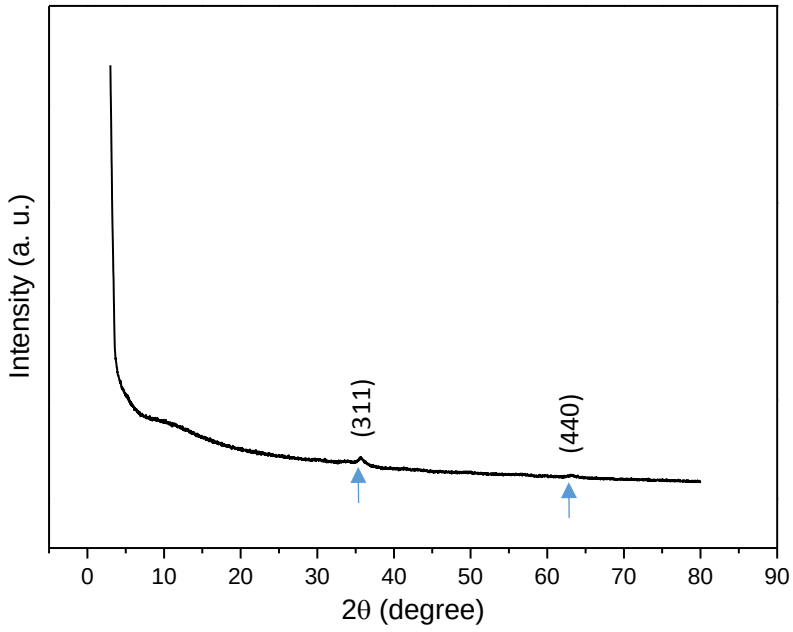


Figure S4. XRD pattern of $Pd/FeO_x@SiO_2$-600. The FeO_x phase is essentially amorphous. However, the tiny peaks marked with arrows can be assigned to (311) and (440) reflections of spinel oxide Fe_3O_4.

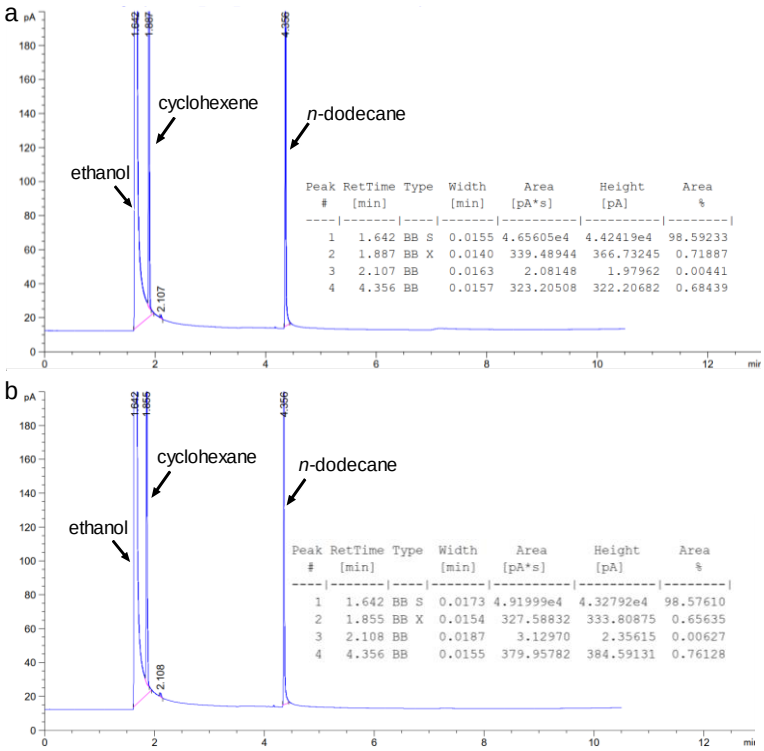


Figure S5. GC chromatograms of cyclohexene hydrogenation using Pd/FeO_x@SiO_2-600 as catalyst: (a) before reaction (at time = 0), and (b) after reaction (120 min). Reaction conditions: 1 mmol of cyclohexene, 10 mL of ethanol, 0.1 mL of *n*-dodecane (as internal standard), H_2 flow (30 mL·min^{-1}), 120 min at room temperature and atmospheric pressure. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280 °C, and oven at 70-280 °C with the ramp rate of 20 °C/min.

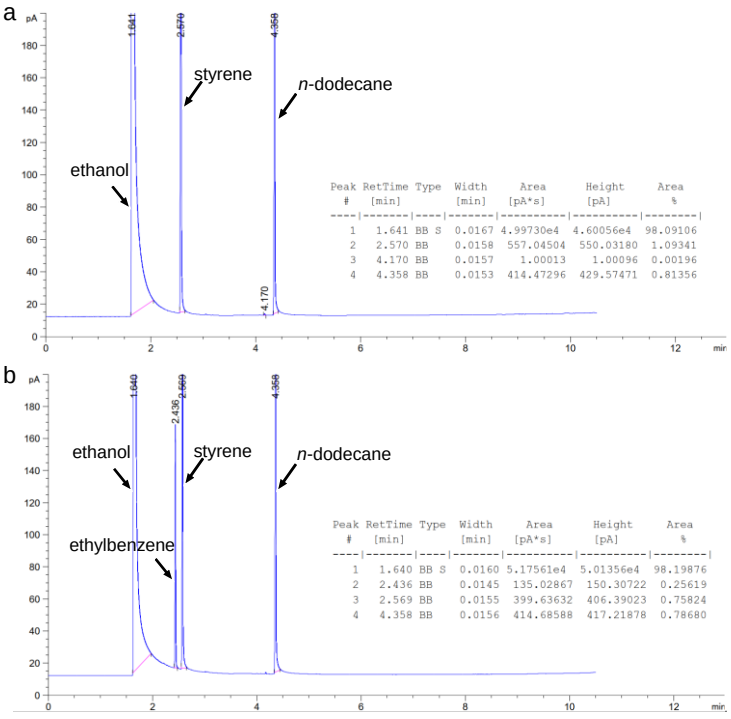


Figure S6. GC chromatograms of styrene hydrogenation using Pd/FeO_x@SiO_2-600 as catalyst: (a) before reaction (at time = 0), and (b) after reaction (120 min). Reaction conditions: 1 mmol of styrene, 10 mL of ethanol, 0.1 mL of *n*-dodecane (as internal standard), H_2 flow (30 mL·min^{-1}), 120 min at room temperature and atmospheric pressure. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280 °C, and oven at 70-280 °C with the ramp rate of 20 °C/min.

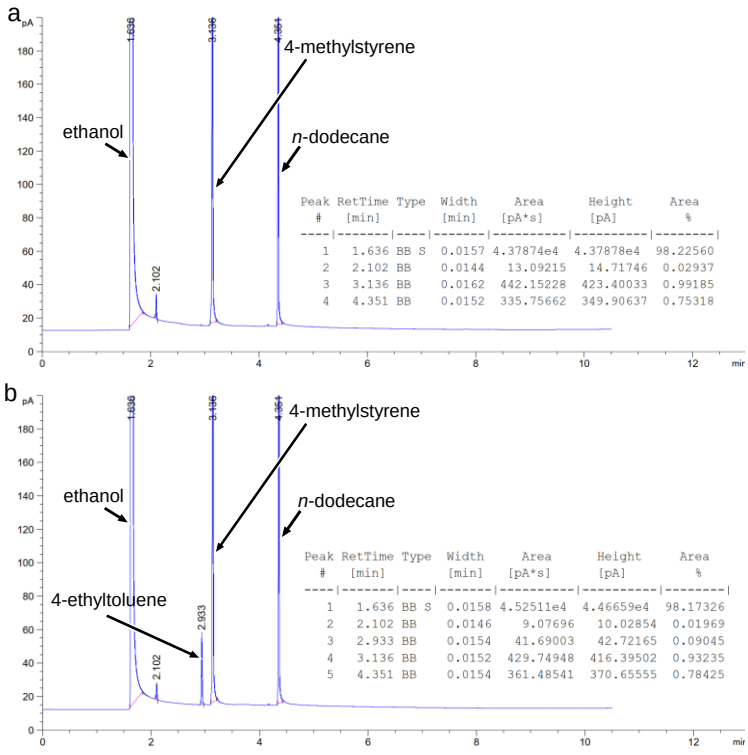


Figure S7. GC chromatograms of 4-methylstyrene hydrogenation using Pd/FeO_x@SiO_2-600 as catalyst: (a) before reaction (at time = 0), and (b) after reaction (120 min). Reaction conditions: 1 mmol of 4-methylstyrene, 10 mL of ethanol, 0.1 mL of *n*-dodecane (as internal standard), H_2 flow (30 mL·min^{-1}), 120 min at room temperature and atmospheric pressure. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280 °C, and oven at 70-280 °C with the ramp rate of 20 °C/min.

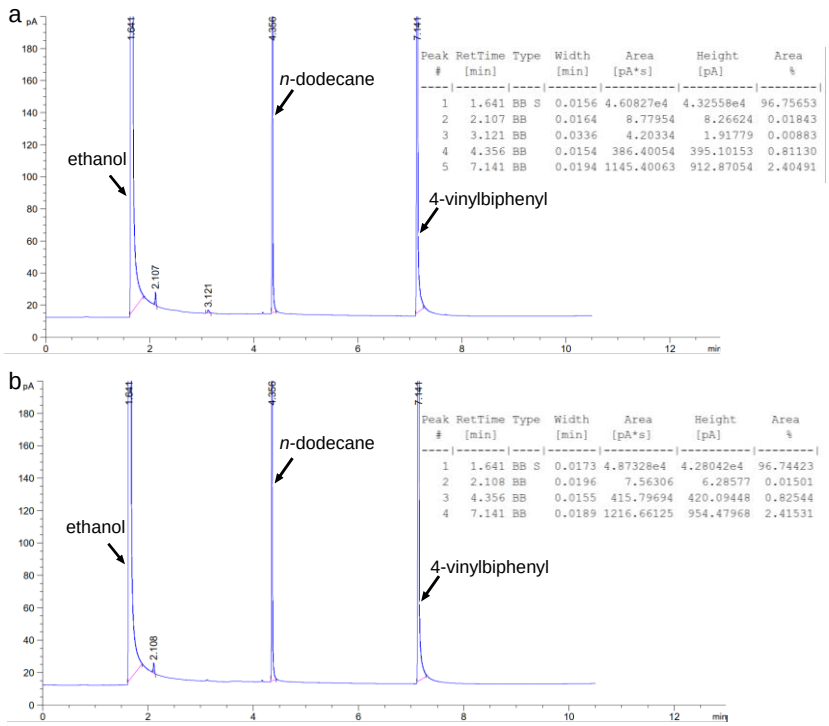


Figure S8. GC chromatograms of 4-vinylbiphenyl hydrogenation using Pd/FeO_x@SiO_2-600 as catalyst: (a) before reaction (at time = 0), and (b) after reaction (120 min). Reaction conditions: 1 mmol of 4-vinylbiphenyl, 10 mL of ethanol, 0.1 mL of *n*-dodecane (as internal standard), H_2 flow (30 mL·min^{-1}), 120 min at room temperature and atmospheric pressure. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280 °C, and oven at 70-280 °C with the ramp rate of 20 °C/min.

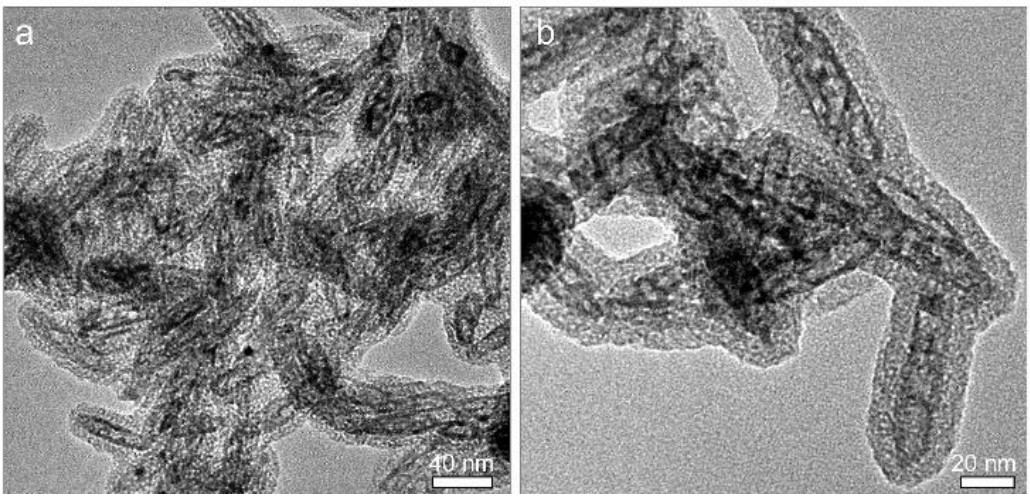


Figure S9. TEM images at different magnifications (a, b) of Pd/FeO_x@*m*SiO_2 sample in which the silica shell is mesoporous (*m*SiO_2).

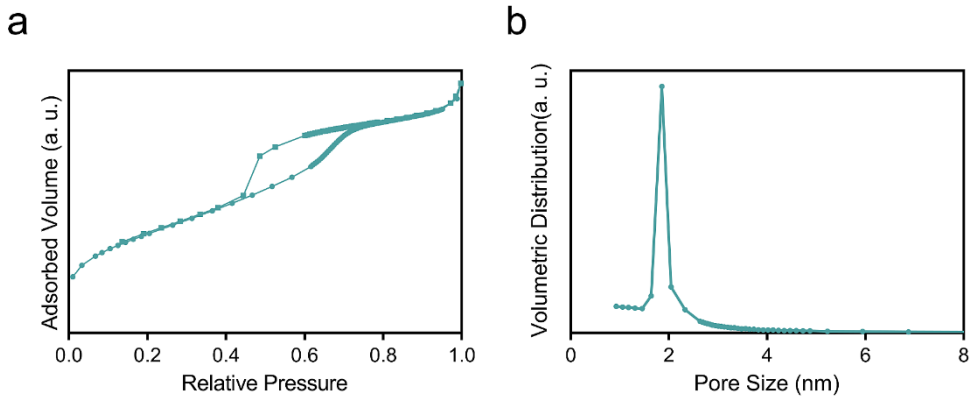


Figure S10. (a) Isothermal nitrogen adsorption-desorption loop and (b) corresponding pore size distribution of Pd/FeO_x@*m*SiO_2 sample in which the silica shell is mesoporous (*m*SiO_2).

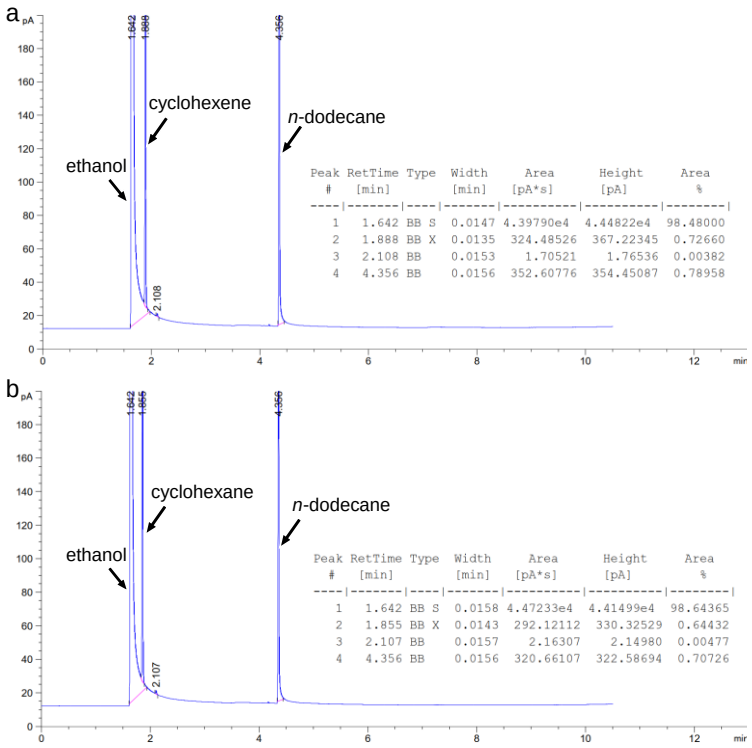


Figure S11. GC chromatograms of cyclohexene hydrogenation using Pd/FeO_x@*m*SiO_2 as catalyst: (a) before reaction (at time = 0), and (b) after reaction (60 min). Reaction conditions: 1 mmol of cyclohexene, 10 mL of ethanol, 0.1 mL of *n*-dodecane (as internal standard), H_2 flow (30 mL·min^{-1}), 60 min at room temperature and atmospheric pressure. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280 °C, and oven at 70-280 °C with the ramp rate of 20 °C/min.

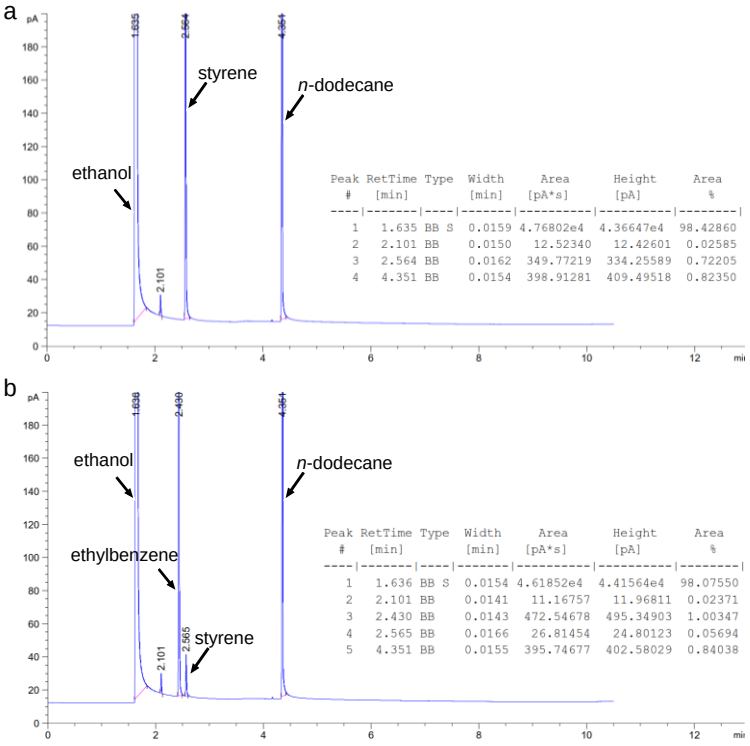


Figure S12. GC chromatograms of styrene hydrogenation using Pd/FeO_x@*m*SiO_2 as catalyst: (a) before reaction (at time = 0), and (b) after reaction (60 min). Reaction conditions: 1 mmol of styrene, 10 mL of ethanol, 0.1 mL of *n*-dodecane (as internal standard), H_2 flow (30 mL·min^{-1}), 60 min at room temperature and atmospheric pressure. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280 °C, and oven at 70-280 °C with the ramp rate of 20 °C/min.

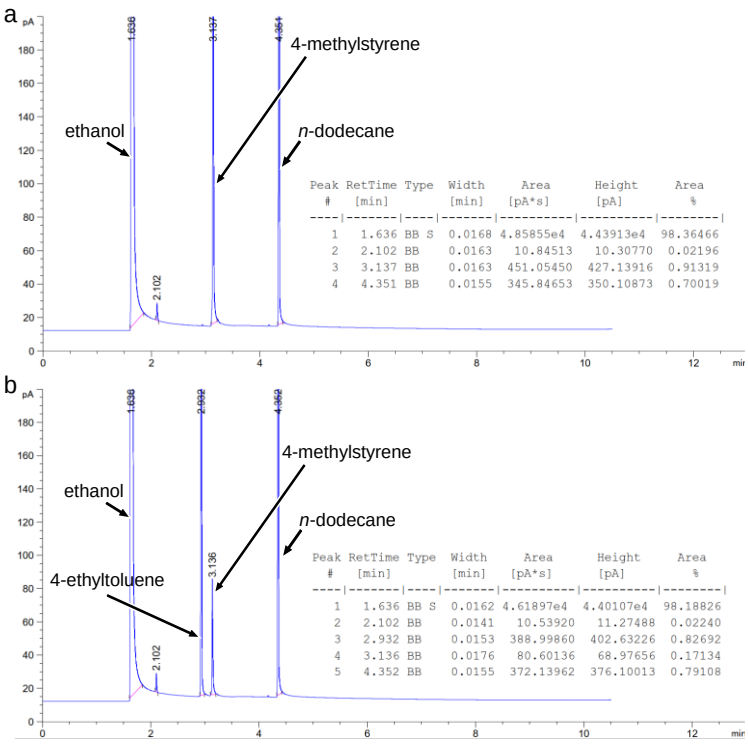


Figure S13. GC chromatograms of 4-methylstyrene hydrogenation using Pd/FeO_x@*m*SiO_2 as catalyst: (a) before reaction (at time = 0), and (b) after reaction (60 min). Reaction conditions: 1 mmol of 4-methylstyrene, 10 mL of ethanol, 0.1 mL of *n*-dodecane (as internal standard), H_2 flow (30 mL·min^{-1}), 60 min at room temperature and atmospheric pressure. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280 °C, and oven at 70-280 °C with the ramp rate of 20 °C/min.

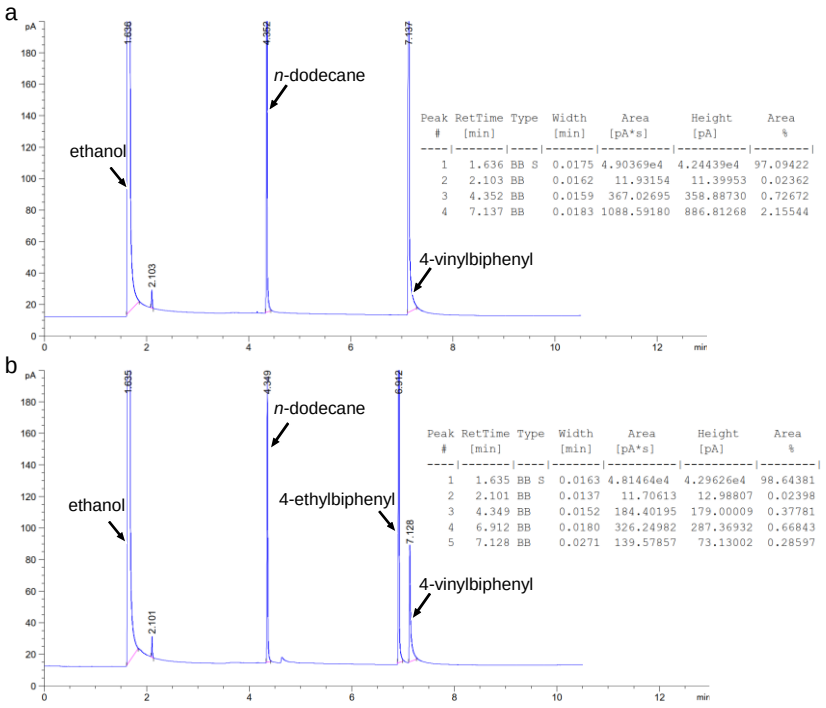


Figure S14. GC chromatograms of 4-vinylbiphenyl hydrogenation using Pd/FeO_x@*m*SiO_2 as catalyst: (a) before reaction (at time = 0), and (b) after reaction (60 min). Reaction conditions: 1 mmol of 4-vinylbiphenyl, 10 mL of ethanol, 0.1 mL of *n*-dodecane (as internal standard), H_2 flow (30 mL·min^{-1}), 60 min at room temperature and atmospheric pressure. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280 °C, and oven at 70-280 °C with the ramp rate of 20 °C/min.

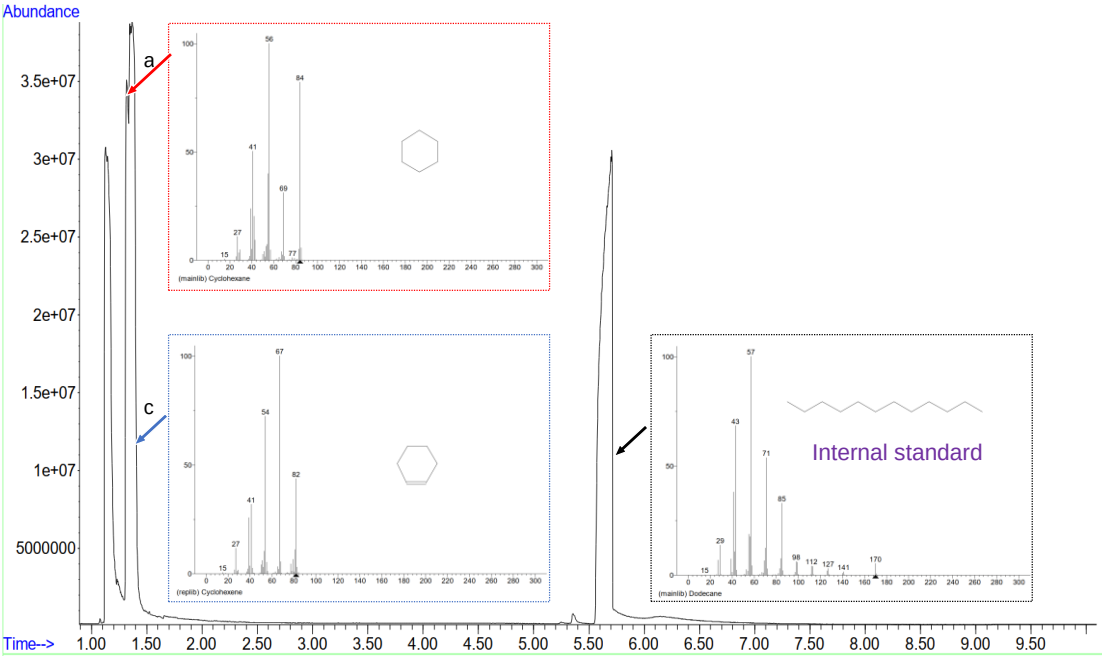


Figure S15. GC-MS chromatogram of cyclohexene hydrogenation using Pd/FeO_x@*m*SiO_2 as catalyst after reaction for 30 min. Reaction conditions: 1 mmol of cyclohexene, 10 mL of ethanol, 0.1 mL of *n*-dodecane (as internal standard), H_2 flow (30 mL·min^{-1}), 30 min at room temperature and atmospheric pressure. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280 °C, and oven at 70-240 °C with the ramp rate of 20 °C/min.

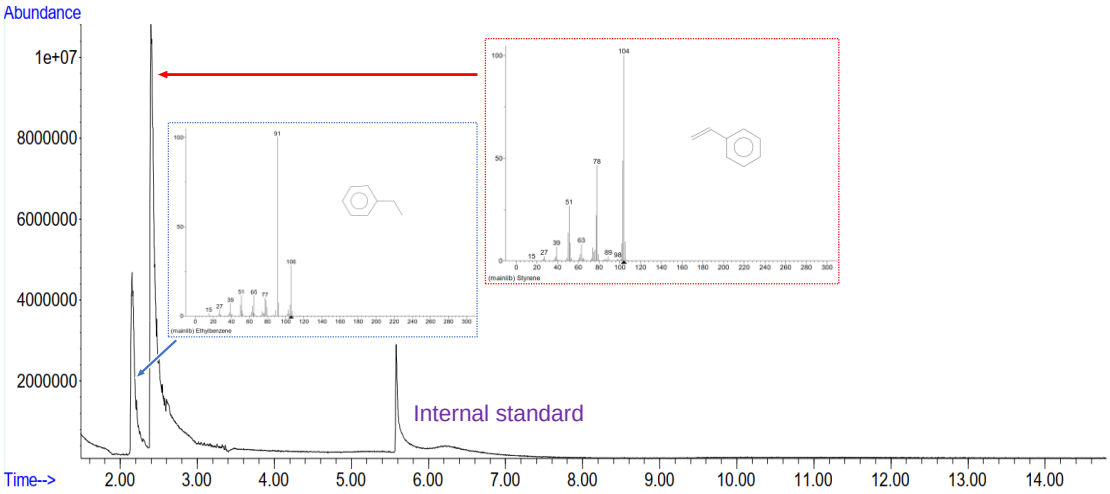


Figure S16. GC-MS chromatogram of styrene hydrogenation using Pd/FeO_x@*m*SiO_2 as catalyst after reaction for 30 min. Reaction conditions: 1 mmol of styrene, 10 mL of ethanol, 0.1 mL of *n*-dodecane (as internal standard), H_2 flow (30 mL·min^{-1}), 30 min at room temperature and atmospheric pressure. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280 °C, and oven at 70-280 °C with the ramp rate of 25 °C/min and hold at 280 °C for 5 min.

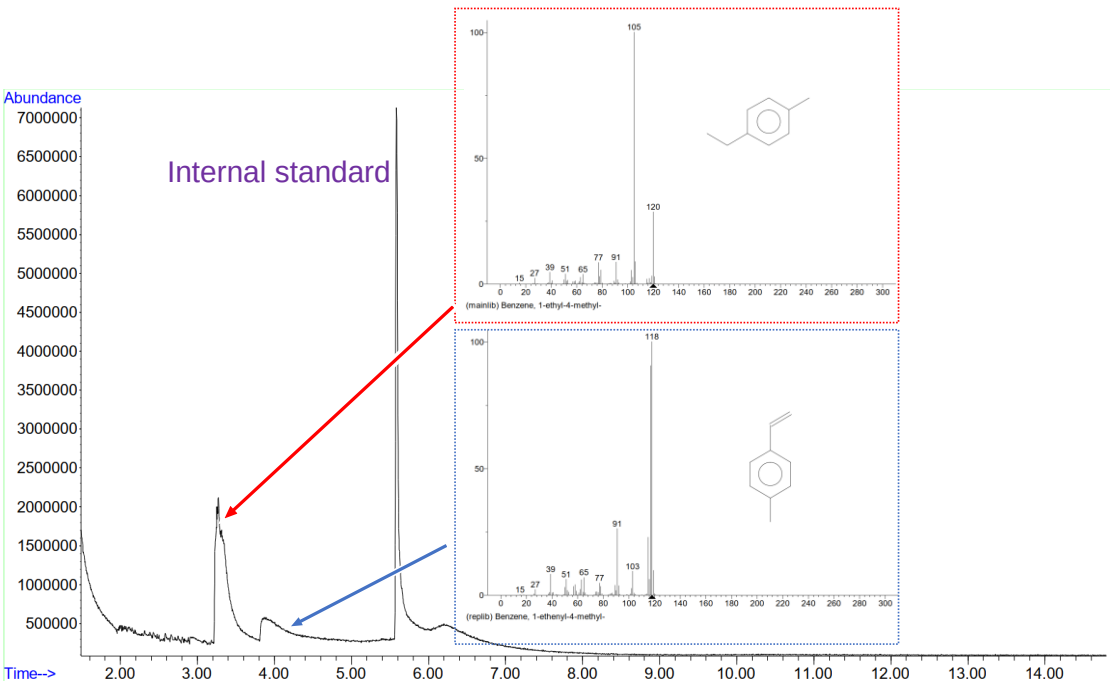


Figure S17. GC-MS chromatogram of 4-methylstyrene hydrogenation using Pd/FeO_x@*m*SiO_2 as catalyst after reaction for 60 min. Reaction conditions: 1 mmol of 4-methylstyrene, 10 mL of ethanol, 0.1 mL of *n*-dodecane (as internal standard), H_2 flow (30 mL·min^{-1}), 60 min at room temperature and atmospheric pressure. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280 °C, and oven at 70-280 °C with the ramp rate of 25 °C/min and hold at 280 °C for 5 min.

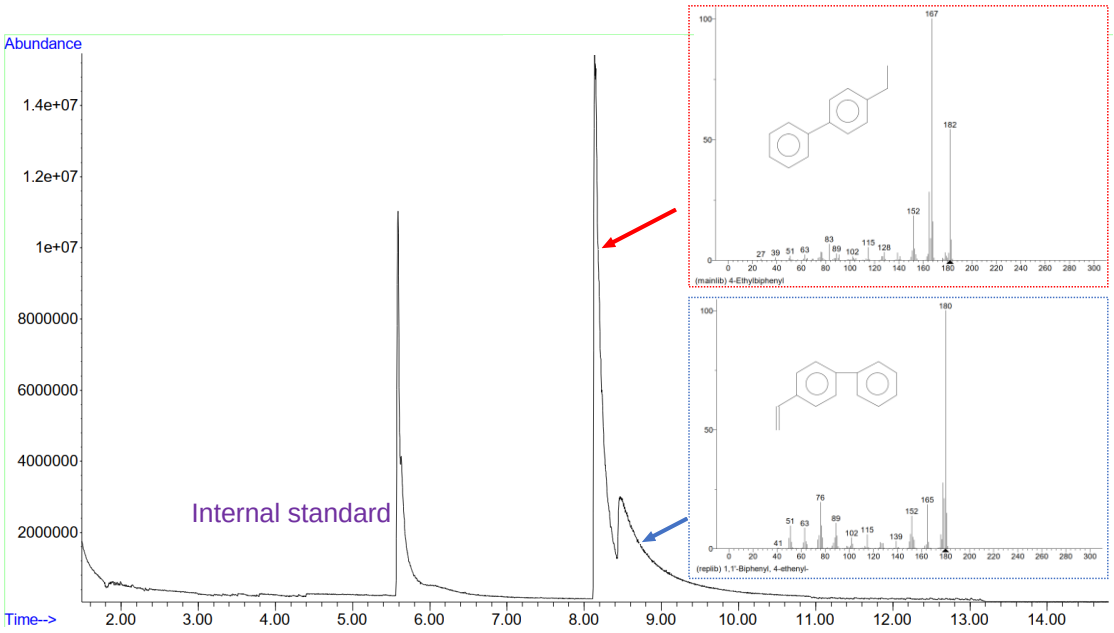


Figure S18. GC-MS chromatogram of 4-vinylbiphenyl hydrogenation using Pd/FeO_x@*m*SiO_2 as catalyst after reaction for 60 min. Reaction conditions: 1 mmol of 4-vinylbiphenyl, 10 mL of ethanol, 0.1 mL of *n*-dodecane (as internal standard), H_2 flow (30 mL·min^{-1}), 60 min at room temperature and atmospheric pressure. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280 °C, and oven at 70-280 °C with the ramp rate of 25 °C/min and hold at 280 °C for 5 min.

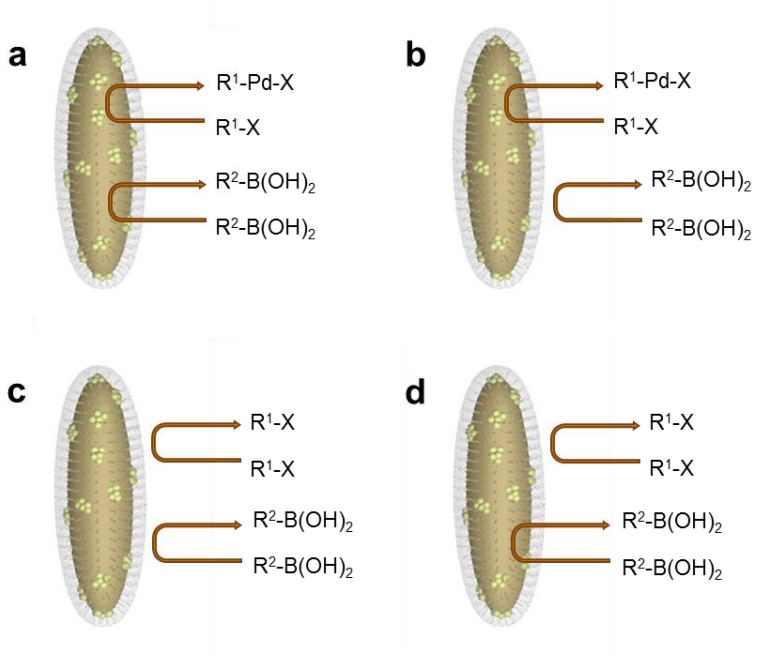


Figure S19. Size selective cross-coupling reactions: (a) both R^1-X and R^2-$B(OH)_2$ are small, (b) R^1-X is small but R^2-$B(OH)_2$ is large, (c) both R^1-X and R^2-$B(OH)_2$ are large, and (d) R^1-X is large but R^2-$B(OH)_2$ is small, where R^1 and R^2 are aryl functional groups of aryl halides and arylboronic acids, respectively (Table S3). Pd atoms or cations are represented by small light olive spheres; FeO_x support of solid Pd is illustrated as spindle-like core with cider color; and microporous silica shell in gray is depicted as the outmost layer on the Pd/FeO_x core; the soluble base used in the reaction is not indicated above.

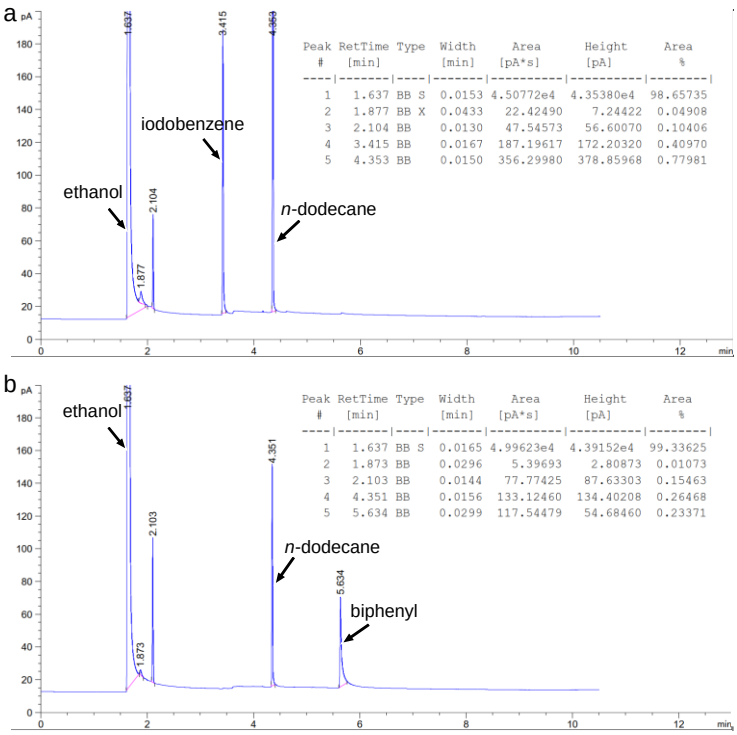
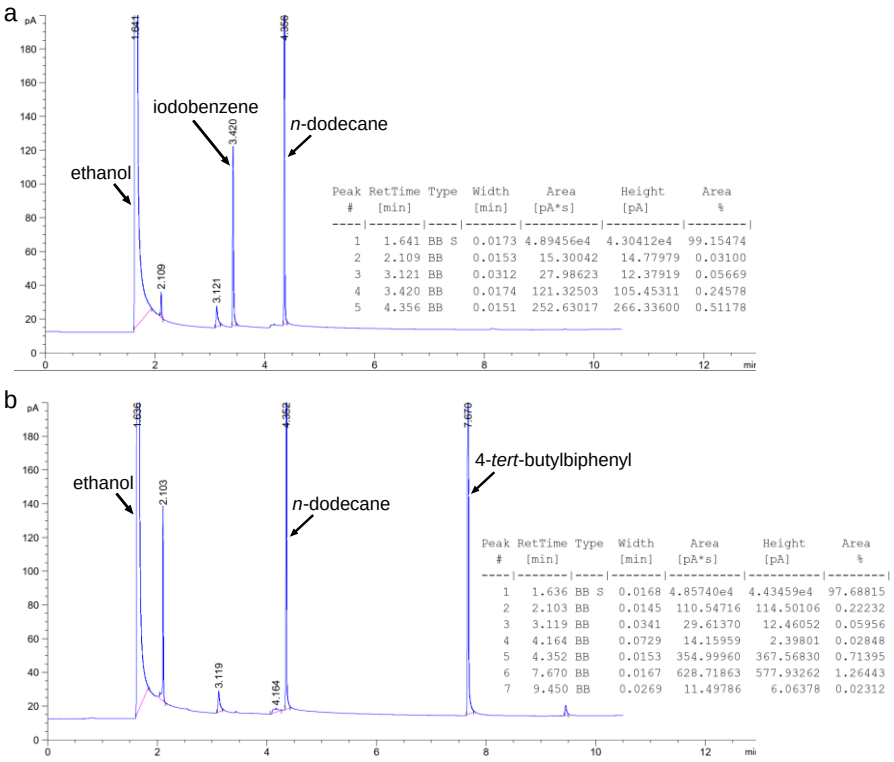


Figure S20. GC chromatograms of Suzuki coupling reaction between iodobenzene and phenylboronic acid using Pd/FeO_x@SiO_2-600 as catalyst: (a) before reaction (at time = 0), and (b) after reaction (120 min). Reaction conditions: 0.5 mmol of iodobenzene, 1 mmol of phenylboronic acid, 0.1 mL of *n*-dodecane (as an internal standard for GC), 2 mmol of K_2CO_3, 120 min at 85 °C. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280°C, and oven at 70-280 °C with the ramp rate of 20°C/min. The product was also analyzed by NMR (Figure S23).



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.641	BB S	0.0173	4.89456e4	4.30412e4	99.15474
2	2.109	BB	0.0153	15.30042	14.77979	0.03100
3	3.121	BB	0.0312	27.98623	12.37919	0.05669
4	3.420	BB	0.0174	121.32503	105.45311	0.24578
5	4.356	BB	0.0151	252.63017	266.33600	0.51178

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.636	BB S	0.0168	4.85740e4	4.43459e4	97.68815
2	2.103	BB	0.0145	110.54716	114.50106	0.22232
3	3.119	BB	0.0341	29.61370	12.46052	0.05956
4	4.164	BB	0.0729	14.15959	2.39801	0.02848
5	4.352	BB	0.0153	354.99960	367.56830	0.71395
6	7.670	BB	0.0167	628.71863	577.93262	1.26443
7	9.450	BB	0.0269	11.49786	6.06378	0.02312

Figure S21. GC chromatograms of Suzuki coupling reaction between iodobenzene and 4-*tert*-butylphenylboronic acid using Pd/FeO_x@SiO_2-600 as catalyst: (a) before reaction (at time = 0), and (b) after reaction (120 min). Reaction conditions: 0.5 mmol of iodobenzene, 1 mmol of 4-*tert*-butylphenylboronic acid, 0.1 mL of *n*-dodecane (as an internal standard for GC), 2 mmol of K_2CO_3, 120 min at 85 °C. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280°C, and oven at 70-280 °C with the ramp rate of 20°C/min. The product was also analyzed by NMR (Figure S24).

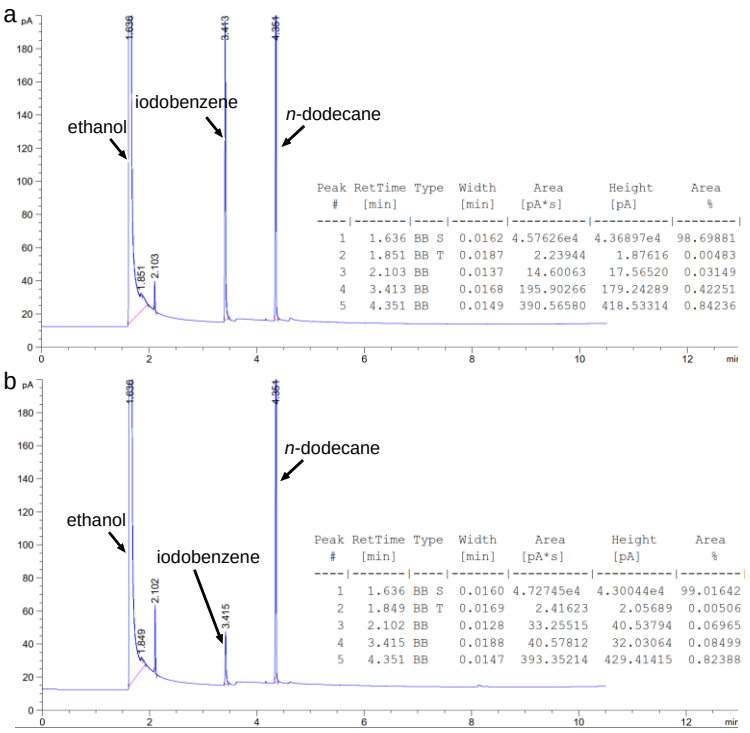


Figure S22. GC chromatograms of Suzuki coupling reaction between iodobenzene and 4-benzyloxyphenylboronic acid using Pd/FeO_x@SiO_2-600 as catalyst: (a) before reaction (at time = 0), and (b) after reaction (120 min). Reaction conditions: 0.5 mmol of iodobenzene, 1 mmol of 4-benzyloxyphenylboronic acid, 0.1 mL of *n*-dodecane (as an internal standard for GC), 2 mmol of K_2CO_3, 120 min at 85 °C. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280°C, and oven at 70-280 °C with the ramp rate of 20°C/min. Due to its low solubility and high boiling point, the product for this reaction was not detected under our GC setting. The product was then analyzed by NMR (Figure S25).

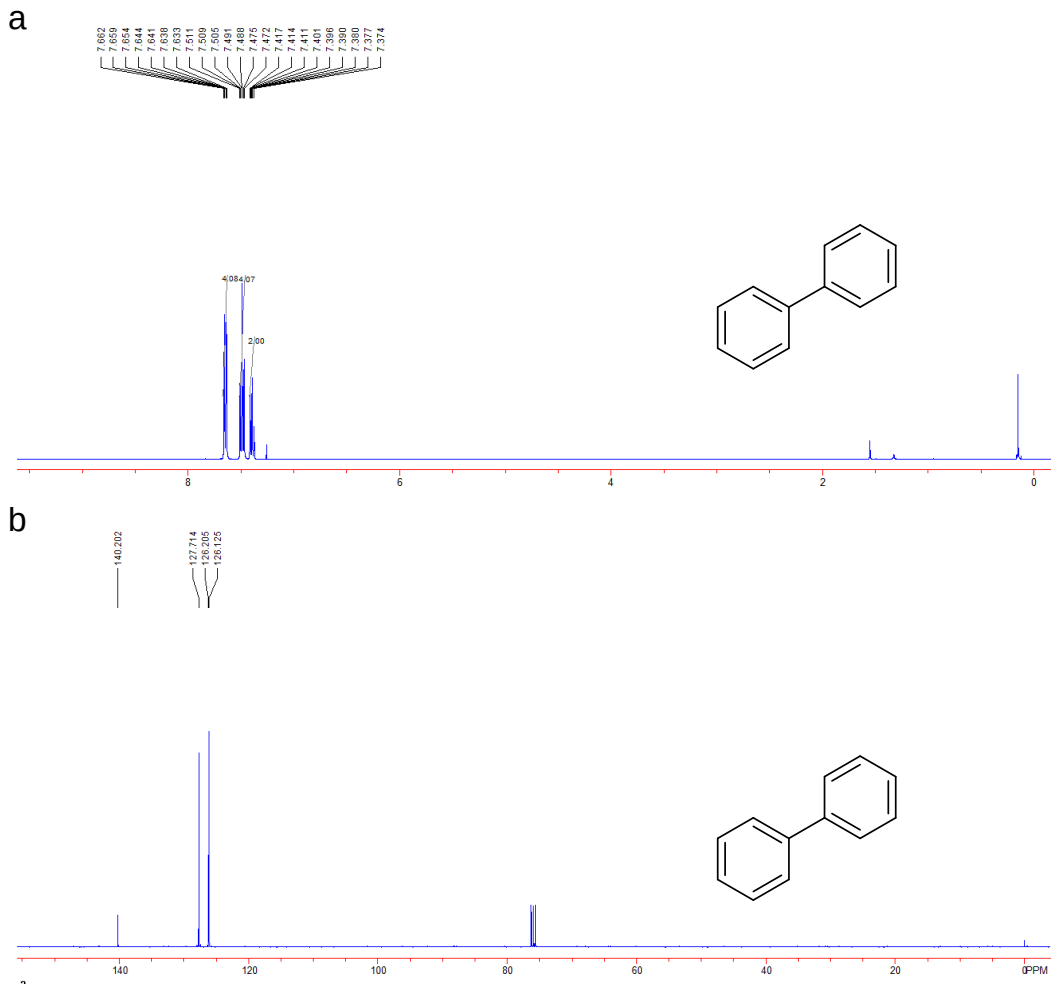


Figure S23. Spectroscopic data of the products for the reaction between iodobenzene and phenylboronic acid. a) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66-7.63 (m, 4H), 7.51-7.47 (m, 4H), 7.41-7.37 (dt, J = 8 Hz, J = 1 Hz, 2H). b) **^{13}C NMR (100 MHz, $CDCl_3$)** δ 140.2, 127.7, 126.2, 126.1.

Comments: ^{1}H NMR spectra were recorded on Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuterium incorporation as the internal standard ($CDCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dt = double triplet; dd = double doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm). All the NMR characterizations were conducted under the same conditions in this work.

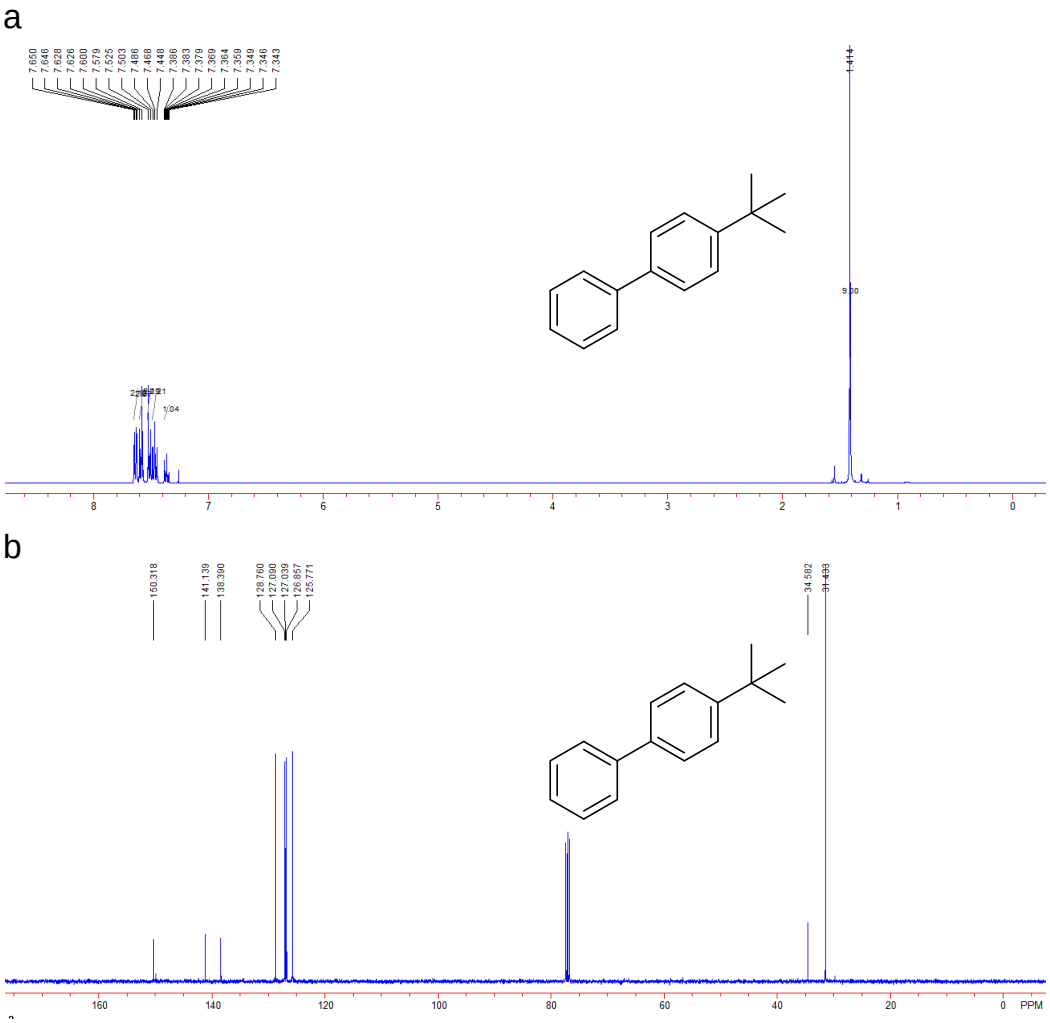


Figure S24. Spectroscopic data of the product for the reaction between iodobenzene and 4-*tert*-butylphenylboronic acid. (a) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65-7.62 (dd, J = 8 Hz, J = 1 Hz, 2H), 7.60-7.58 (d, J = 8 Hz, 2H), 7.52-7.50 (d, J = 8 Hz, 2H), 7.48-7.44 (t, J = 8 Hz, 2H), 7.38-7.34 (dt, J = 8 Hz, J = 1 Hz, 1H), 1.41 (s, 9H). (b) **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.3, 141.1, 138.3, 128.7, 127.1, 127.0, 126.8, 125.7, 34.5, 31.4.

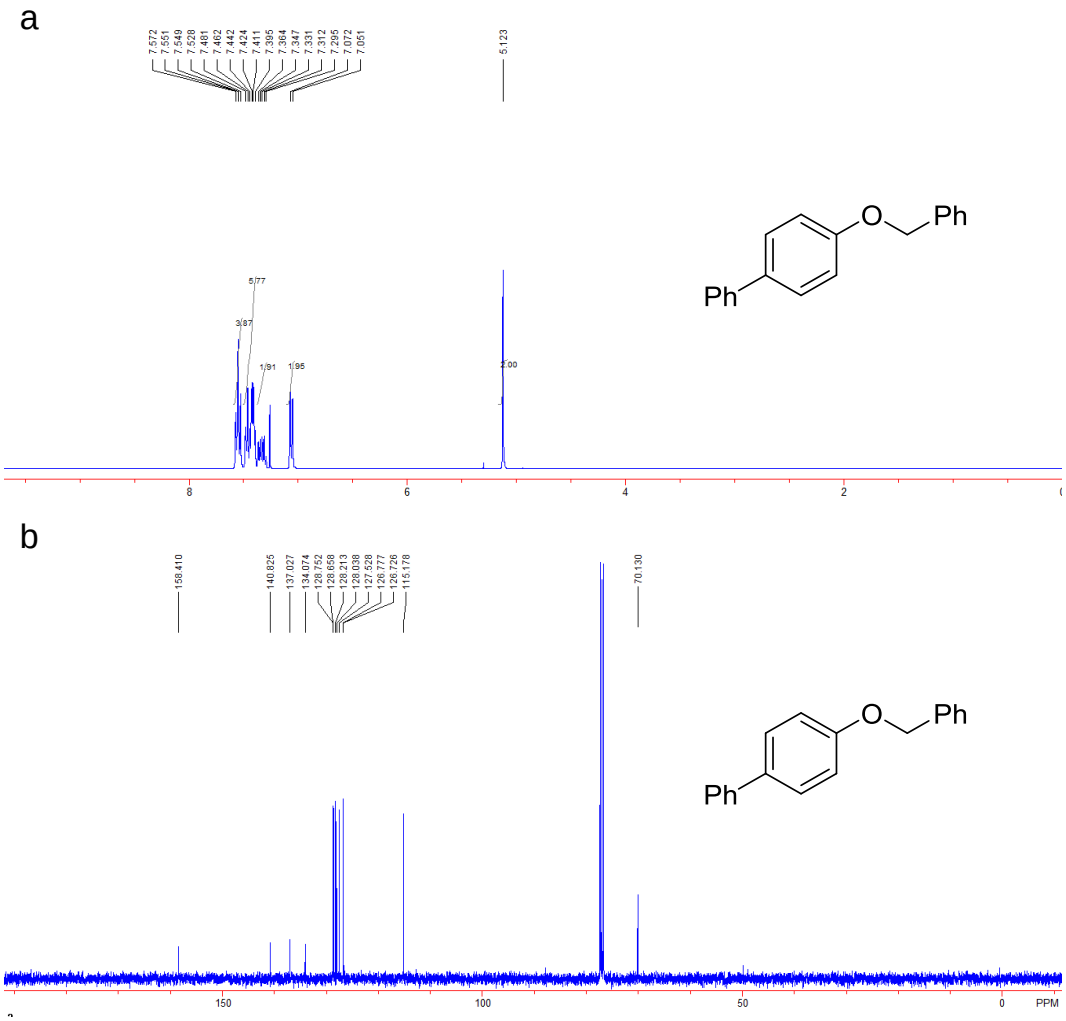


Figure S25. Spectroscopic data of the product for the reaction between iodobenzene and 4-benzyloxyphenylboronic acid. (a) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57-7.52 (t, *J* = 8 Hz, 4H), 7.48-7.39 (m, 6H), 7.36-7.29 (m, 2H), 7.07-7.05 (d, *J* = 8 Hz, 2H), 5.12 (s, 2H). (b) **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.4, 140.8, 137.0, 134.0, 128.7, 128.6, 128.2, 128.0, 127.5, 126.8, 126.7, 115.1, 70.1.

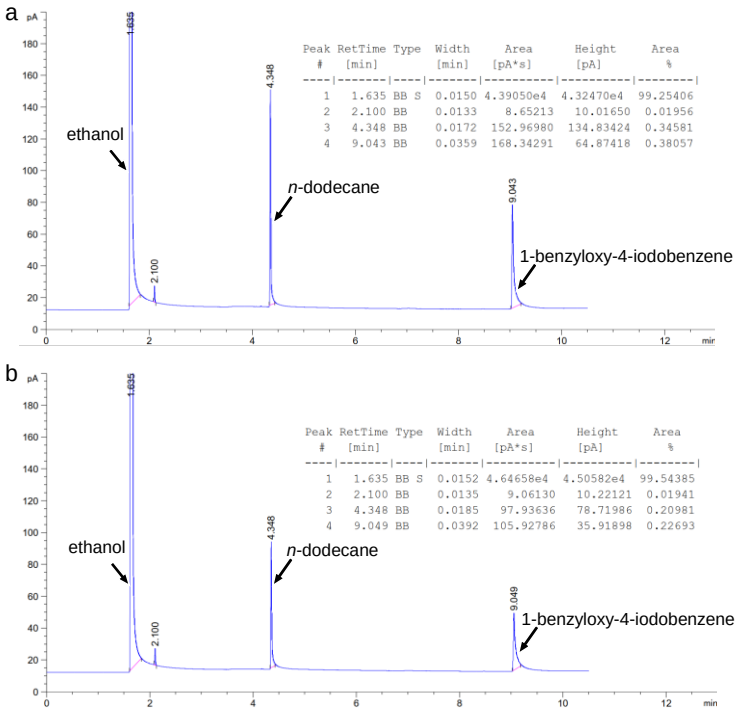


Figure S26. GC chromatograms of Suzuki coupling reaction between 1-benzyloxy-4-iodobenzene and 4-benzyloxyphenylboronic acid using $Pd/FeO_x@SiO_2$-600 as catalyst: (a) before reaction (at time = 0), and (b) after reaction (60 min). Reaction conditions: 0.5 mmol of 1-benzyloxy-4-iodobenzene, 1 mmol of 4-benzyloxyphenylboronic acid, 0.1 mL of *n*-dodecane (as an internal standard for GC), 2 mmol of K_2CO_3, 60 min at 85 °C. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280°C, and oven at 70-280 °C with the ramp rate of 20°C/min.

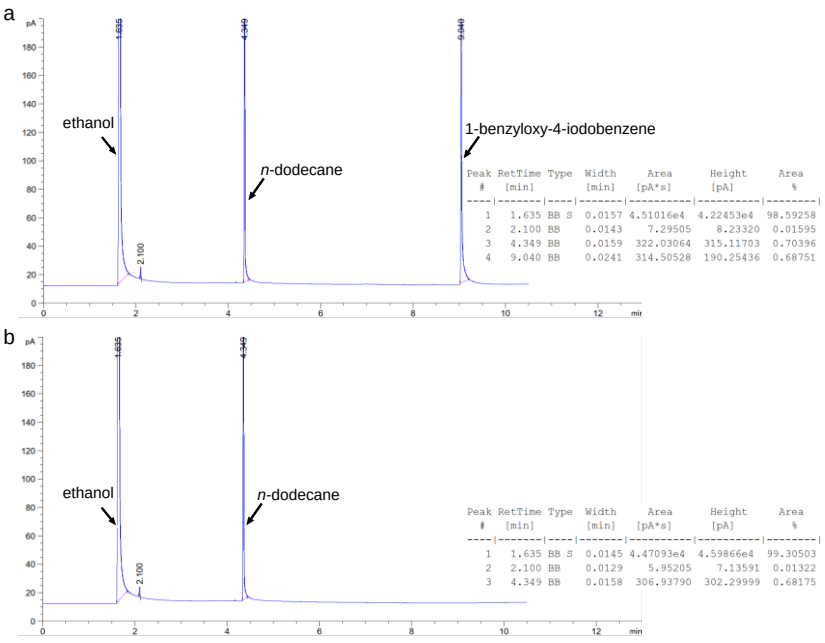


Figure S27. GC chromatograms of Suzuki coupling reaction between 1-benzyloxy-4-iodobenzene and 4-benzyloxyphenylboronic acid using Pd/C as catalyst: (a) before reaction (at time = 0), and (b) after reaction (60 min). Reaction conditions: 0.5 mmol of 1-benzyloxy-4-iodobenzene, 1 mmol of 4-benzyloxyphenylboronic acid, 0.1 mL of *n*-dodecane (as an internal standard for GC), 2 mmol of K_2CO_3, 60 min at 85 °C. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280°C, and oven at 70-280 °C with the ramp rate of 20°C/min. Due to its high boiling point, the product for this reaction was not detected under our GC setting.

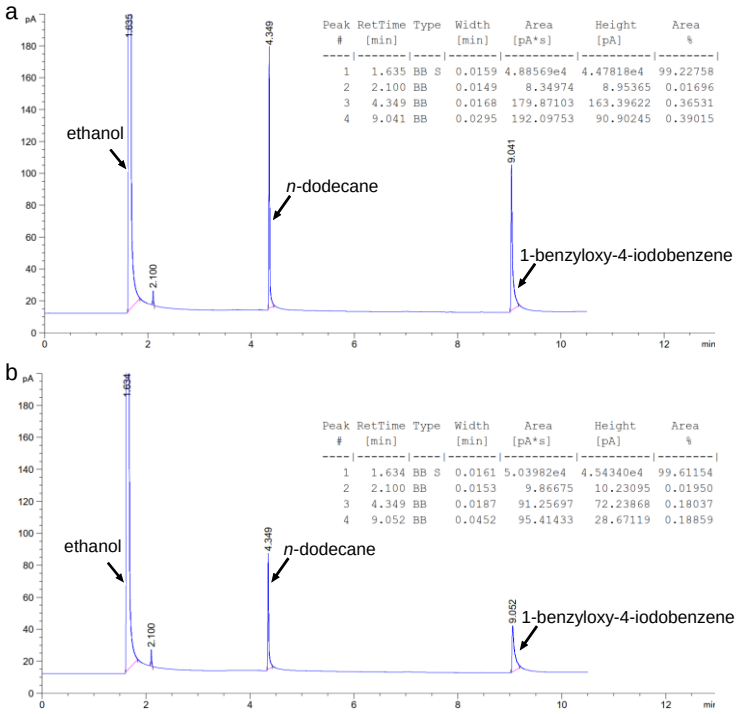


Figure S28. GC chromatograms of Suzuki coupling reaction between 1-benzyloxy-4-iodobenzene and phenylboronic acid using Pd/FeO_x@SiO_2-600 as catalyst: (a) before reaction (at time = 0), and (b) after reaction (60 min). Reaction conditions: 0.5 mmol of 1-benzyloxy-4-iodobenzene, 1 mmol of phenylboronic acid, 0.1 mL of *n*-dodecane (as an internal standard for GC), 2 mmol of K_2CO_3, 60 min at 85 °C. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280°C, and oven at 70-280 °C with the ramp rate of 20°C/min.

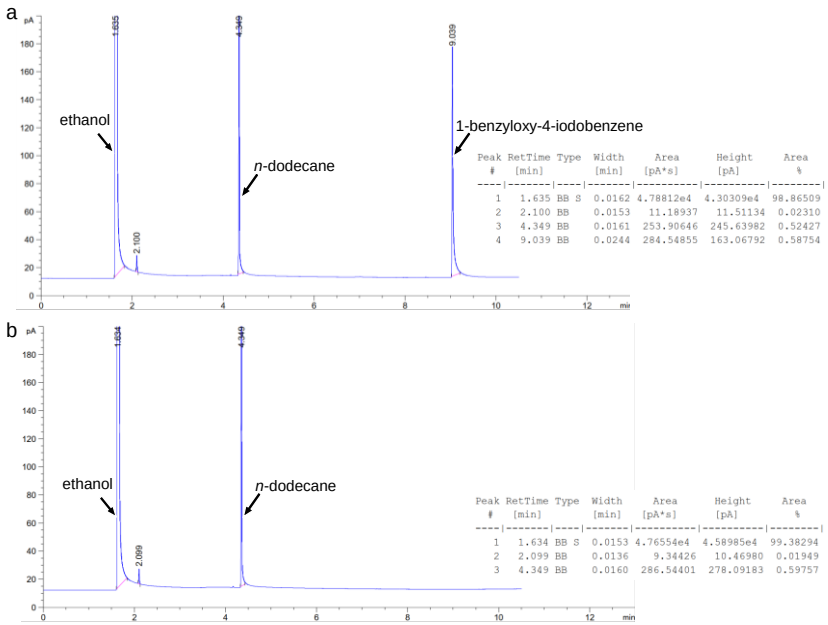


Figure S29. GC chromatograms of Suzuki coupling reaction between 1-benzyloxy-4-iodobenzene and phenylboronic acid using Pd/C as catalyst: (a) before reaction (at time = 0), and (b) after reaction (60 min). Reaction conditions: 0.5 mmol of 1-benzyloxy-4-iodobenzene, 1 mmol of phenylboronic acid, 0.1 mL of *n*-dodecane (as an internal standard for GC), 2 mmol of K_2CO_3, 60 min at 85 °C. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280°C, and oven at 70-280 °C with the ramp rate of 20°C/min. Due to its high boiling point, the product for this reaction was not detected under our GC setting.

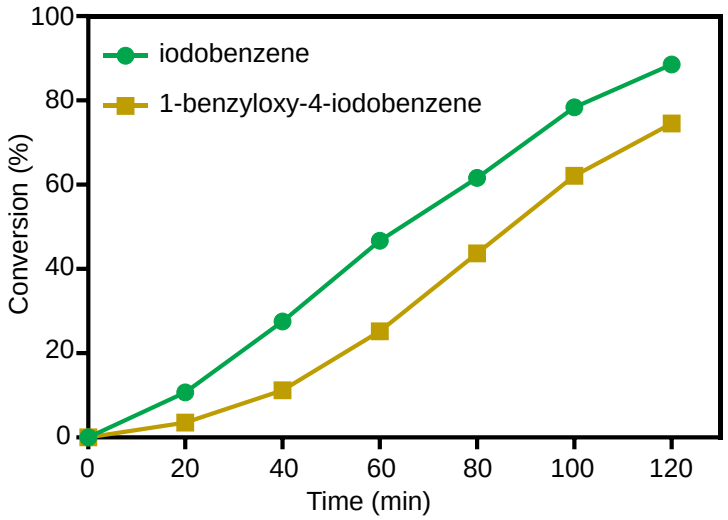


Figure S30. Catalytic performances of Suzuki-Miyaura cross-coupling reactions between iodobenzene and phenylboronic acid (green curve) and 1-benzyloxy-4-iodobenzene and phenylboronic acid (golden yellow curve) over Pd/FeO_x@SiO_2-600. Reaction conditions: iodobenzene (0.5 mmol), 1-benzyloxy-4-iodobenzene (0.5 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2 mmol), and ethanol (10 mL); reaction temperature at 85 ^oC under atmospheric condition.

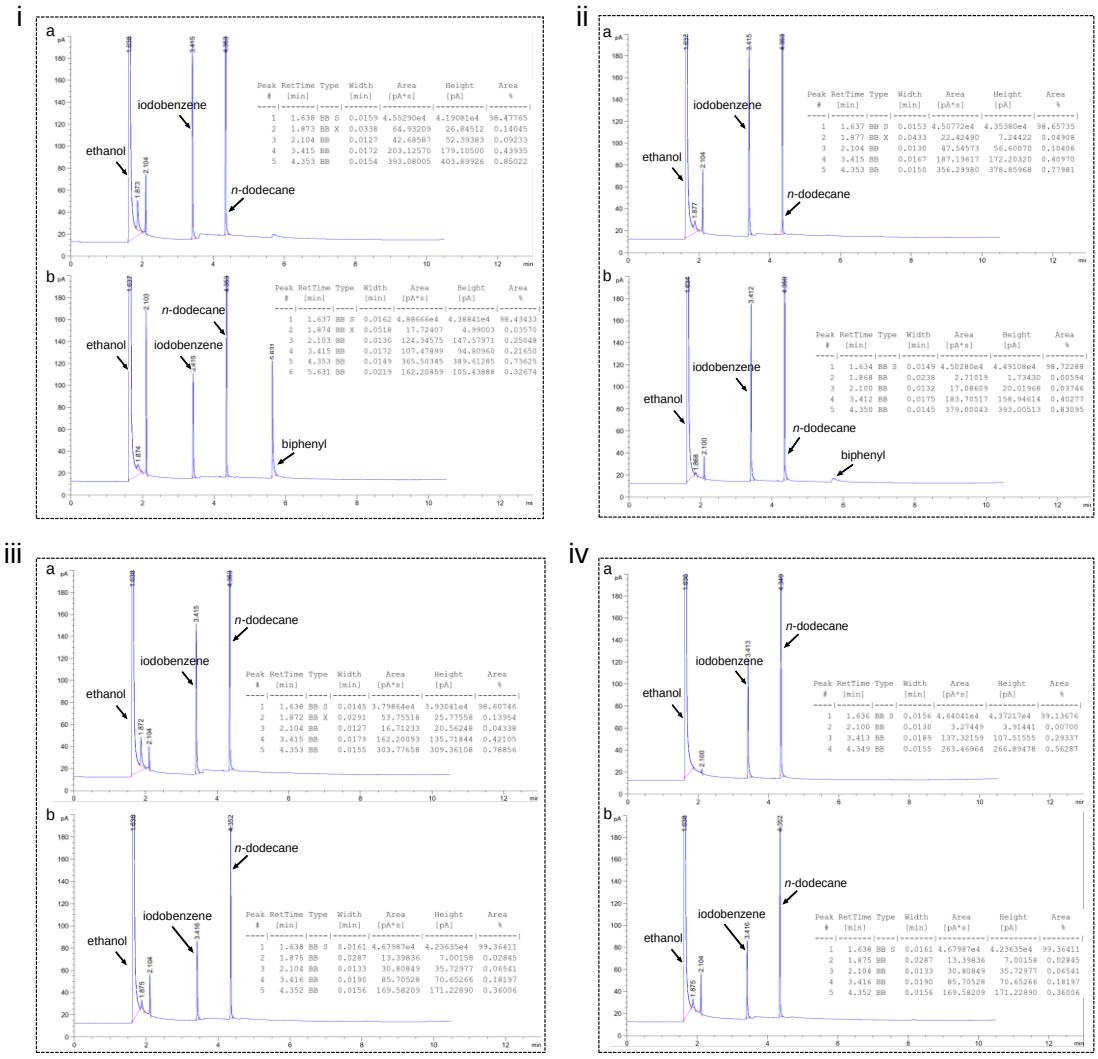


Figure S31. GC chromatograms of recycle tests of $Pd/FeO_x@SiO_2$-600 in the reaction between iodobenzene and phenylboronic acid: (i) 1 time, (ii) 2 times, (iii) 3 times, and (iv) 4 times; (a) before reaction (at time = 0), and (b) after reaction (50 min). Reaction conditions: 0.5 mmol of iodobenzene, 1 mmol of phenylboronic acid, 0.1 mL of *n*-dodecane (as an internal standard for GC), 2 mmol of K_2CO_3, 85 °C; refer to Figure 3c in the main text for further information on the reaction. Reaction time was set at 50 min in each recycle experiment. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280°C, and oven at 70-280 °C with the ramp rate of 20°C/min.

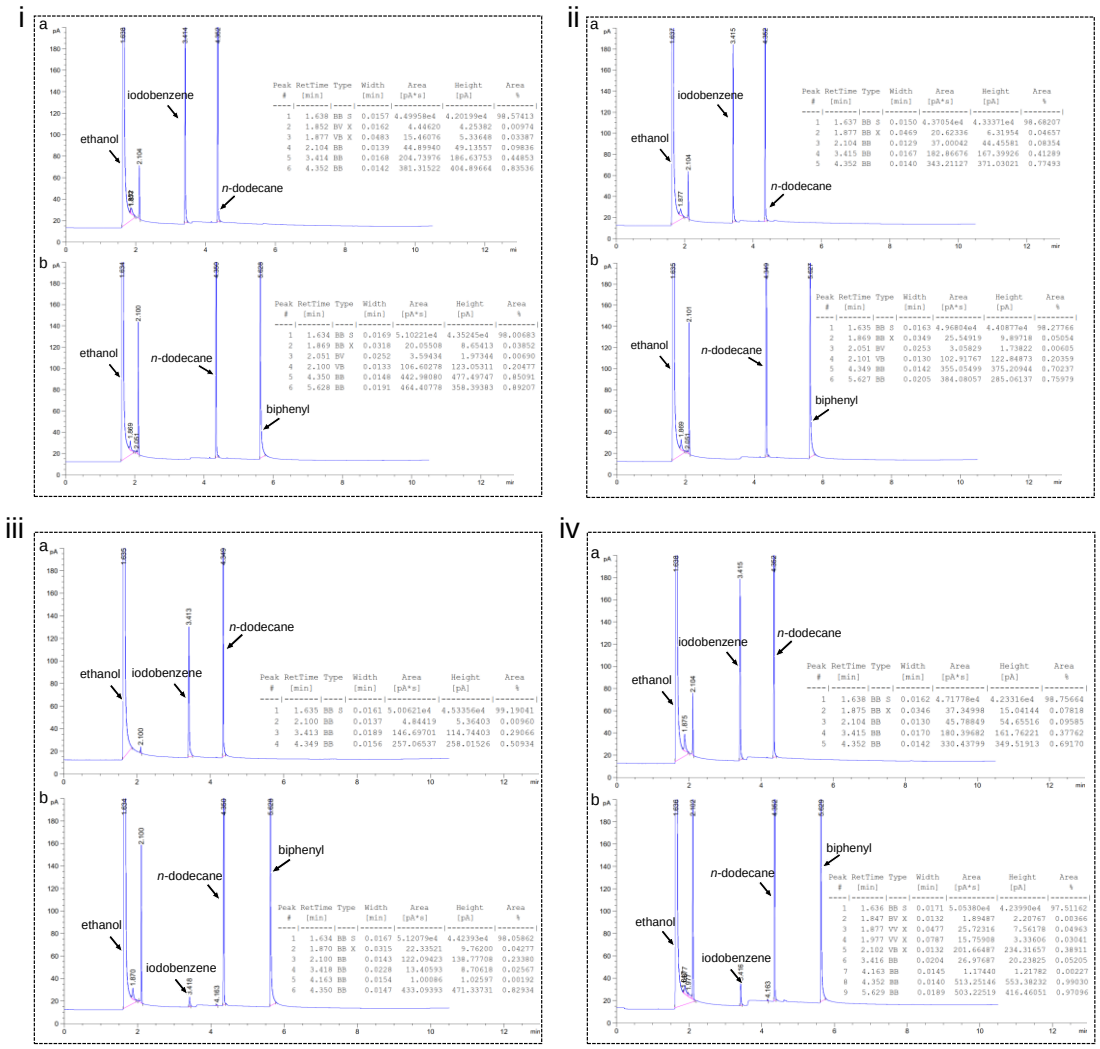


Figure S32. GC chromatograms of recycle tests of $Pd/FeO_x@SiO_2$-600 in the reaction between iodobenzene and phenylboronic acid: (i) 1 time, (ii) 2 times, (iii) 3 times, and (iv) 4 times; (a) before reaction (at time = 0), and (b) after reaction (120 min). Reaction conditions: 0.5 mmol of iodobenzene, 1 mmol of phenylboronic acid, 0.1 mL of *n*-dodecane (as an internal standard for GC), 2 mmol of K_2CO_3, 85 °C; refer to Figure 3d in the main text for further information on the reaction. Reaction time was set at 120 min in each recycle experiment. GC operating conditions: inlet temperature at 250 °C, FID temperature at 280°C, and oven at 70-280 °C with the ramp rate of 20°C/min.

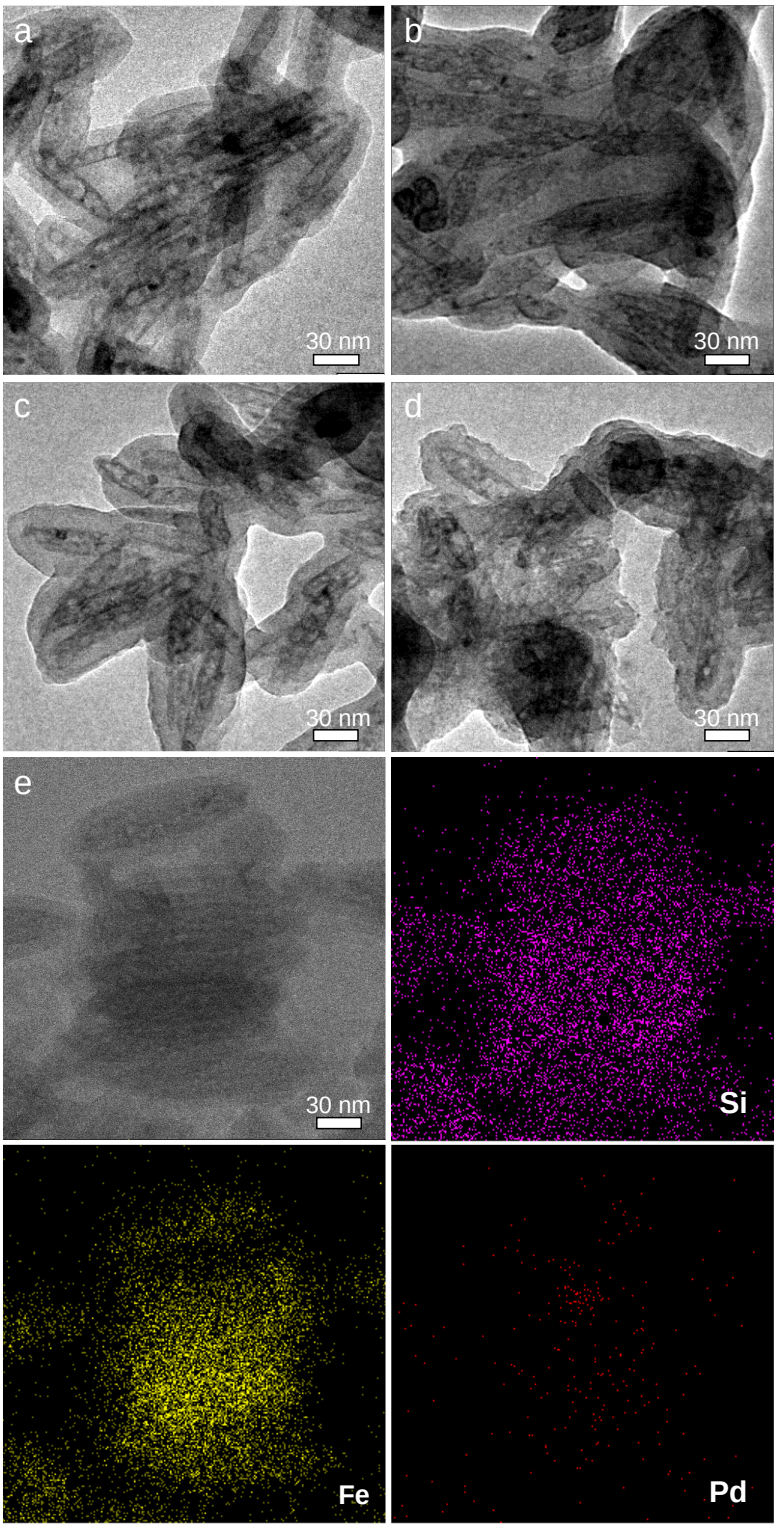


Figure S33. TEM images of Pd/FeO_x@SiO_2-600 after it was recycled for: (a) 1 time, (b) 2 times, (c) 3 times, and (d) 4 times; and (e) EDX elemental mapping images of Pd/FeO_x@SiO_2-600 after recycled for 4 times; refer to Figure 3c in the main text for further information on the reaction. Reaction time was set at 50 min in each recycle experiment (also see Figure 3c in the main text).

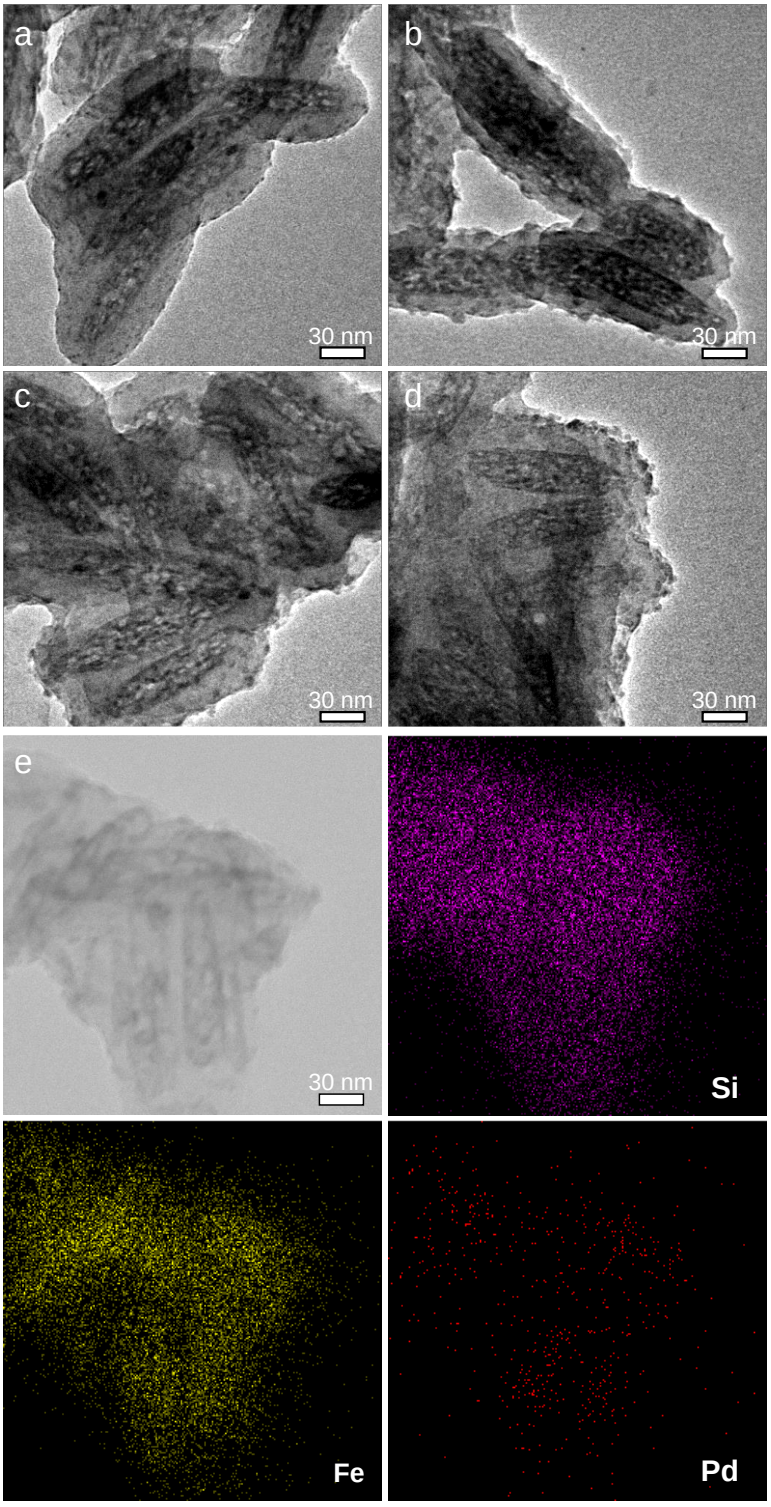


Figure S34. TEM images of Pd/FeO_x@SiO_2-600 after it was recycled for: (a) 1 time, (b) 2 times, (c) 3 times, and (d) 4 times; and (e) EDX elemental mapping images of Pd/FeO_x@SiO_2-600 after recycled for 4 times; refer to Figure 3d in the main text for further information on the reaction. Reaction time was set at 120 min in each recycle experiment (also see Figure 3d in the main text).

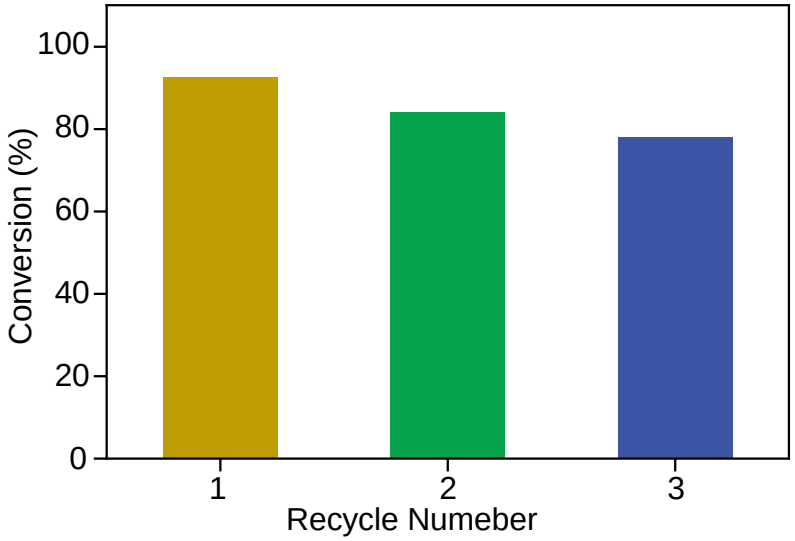


Figure S35. Recycle test of the leaching solution in the reaction between iodobenzene and phenylboronic acid. Reaction conditions: iodobenzene (0.5 mmol), phenylboronic acid (1.0 mmol), K_2CO_3 (2 mmol), ethanol (~10 mL); reaction temperature at 85 ^oC under atmospheric conditions. Each experimental run (recycle number 1, 2, and 3) was stopped after 120 min of the reaction.

Detailed reaction process and comments: After reaction for 50 min between iodobenzene and phenylboronic acid, the mixture was centrifuged at 10000 rpm for 10 min (similar to the procedure of the first experimental run of Figure 3c in the main text). The clear upper liquid was carefully filtered through a membrane filter into a 25 mL round-bottom flask. This liquid is named as "the leaching solution" for the three recycle experiments reported above, in which iodobenzene (0.5 mmol), phenylboronic acid (1.0 mmol), and K_2CO_3 (2 mmol) were added to the leaching solution from the previous one; each reaction run was stopped after 120 min of the reaction.

Supporting Tables:

Table S1. The dimensions of several molecules estimated by our method compared to experimental results.

Molecule	Urea	Gly	Glycol	Glycerol	Acetamide	Formamide
Results	3.4×5.0×5.5 Å^3	3.4×5.1×6.8 Å^3	4.0×4.4×6.0 Å^3	4.0×5.3×7.9 Å^3	3.4×5.3×5.6 Å^3	3.4×4.0×5.3 Å^3
Benchmark	3.6×5.2×5.4 Å^3	3.7×5.1×7.1 Å^3	3.7×4.7×6.3 Å^3	4.8×5.1×7.8 Å^3	3.8×5.2×5.4 Å^3	3.4×4.4×5.4 Å^3

Table S2. Structural property of the sample Pd/β-FeOOH@SiO_2 and Pd/FeO_x@SiO_2 after calcined at different temperatures.

Sample	Pd/β-FeOOH@SiO_2	Pd/FeO_x@SiO_2-500	Pd/FeO_x@SiO_2-600	Pd/FeO_x@SiO_2-700	Pd/FeO_x@SiO_2-800
BET surface area (m^2 g^{-1})	442.1	280.6	183.1	79.1	46.3
Pore volume (cm^3 g^{-1})	0.208	0.138	0.083	0.022	0.014

Table S3. Dimensions of reactants and products.

Reactants	Dimensions	Product	Dimensions
cyclohexene	6.3×5.7×4.5 Å^3	cyclohexane	6.2×6.2×3.9 Å^3
styrene	8.5×6.0×4.0 Å^3	ethylbenzene	8.5×6.1×3.6 Å^3
4-methylstyrene	9.8×6.0×3.4 Å^3	4-ethyltoluene	9.9×6.0×3.4 Å^3
4-vinylbiphenyl	12.0×5.7×3.4 Å^3	4-ethylbiphenyl	12.0×5.8×3.4 Å^3
iodobenzene	8.5×5.9×4.0 Å^3	biphenyl	10.3×5.8×3.8 Å^3
phenylboronic acid	8.4×6.2×3.4 Å^3	4-*tert*-butylbiphenyl	12.3×6.0×5.9 Å^3
4-tert-butylphenylboronic acid	10.8×6.0×5.8 Å^3		
4-benzyloxyphenylboronic acid	14.8×6.3×3.0 Å^3		
1-benzyloxy-4-iodobenzene	14.8×5.8×3.0 Å^3		

Table S4. Summary of Pd content in leaching solution based on ICP-MS analysis.

Sample	Pd content (ppb) in solution
$Pd/FeO_x@SiO_2$-600 [a]	141
$Pd/FeO_x@SiO_2$-600 [b]	27

Notes: (a) After reaction for 50 min in Suzuki coupling reaction between iodobenzene and phenylboronic acid (equivalent to the first run of Figure 3c in the main text), and (b) after reaction for 120 min in Suzuki coupling reaction between iodobenzene and phenylboronic acid (equivalent to the first run of Figure 3d in the main text).

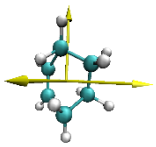
Comments: After reaction, the mixture was centrifuged at 10000 rpm for 10 min. The clear upper layer was carefully filtered through a membrane filter. After evaporation of the solvent, the sample was treated with aqua regia and analyzed by ICP-MS.

Table S5. Summary of Pd contents (based on ICP-OES analysis) in fresh $Pd/FeO_x@SiO_2$-600 and in spent catalyst $Pd/FeO_x@SiO_2$-600 with different reaction times.

Sample	Pd content (wt%) in sample
Fresh $Pd/FeO_x@SiO_2$-600	0.85
Spent $Pd/FeO_x@SiO_2$-600 [a]	0.76
Spent $Pd/FeO_x@SiO_2$-600 [b]	0.82

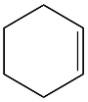
Notes: (a) After reaction for 50 min in Suzuki coupling reaction between iodobenzene and phenylboronic acid (equivalent to the first run of Figure 3c in the main text), and (b) after reaction for 120 min in Suzuki coupling reaction between iodobenzene and phenylboronic acid (equivalent to the first run of Figure 3d in the main text).

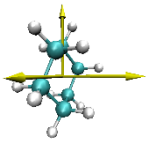
Calculated Molecular Dimensions:



cyclohexene

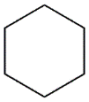
6.3×5.7×4.5 Å^3

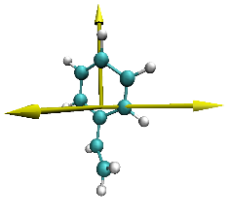




cyclohexane

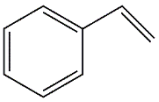
6.2×6.2×3.9 Å^3

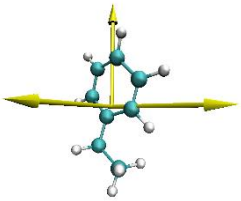




styrene

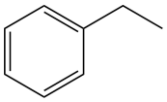
8.5×6.0×4.0 Å^3

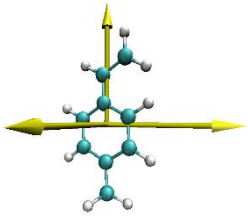




ethylbenzene

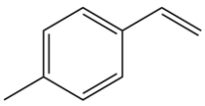
8.5×6.1×3.6 Å^3

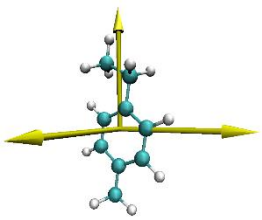




4-methylstyrene

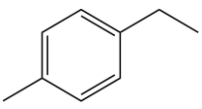
9.8×6.0×3.4 Å^3

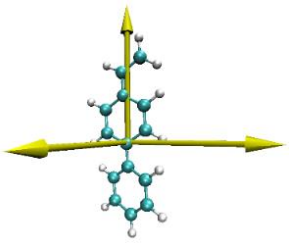




4-ethyltoluene

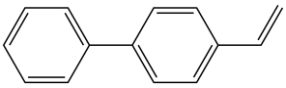
9.9×6.0×3.4 Å^3

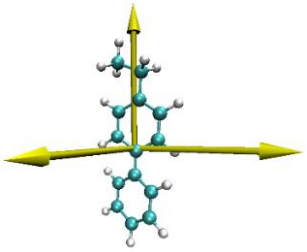




4-vinylbiphenyl

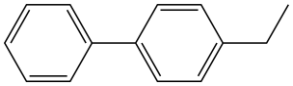
12.0× 5.7×3.4 Å^3

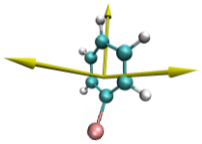




4-ethylbiphenyl

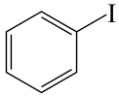
12.0×5.8×3.4 Å^3

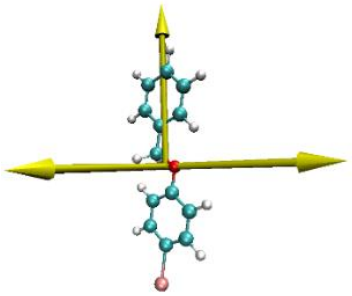




iodobenzene

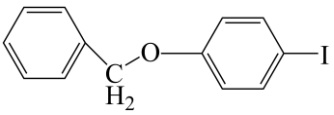
8.5×5.9×4.0 Å^3

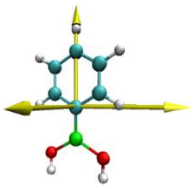




1-benzyloxy-4-iodobenzene

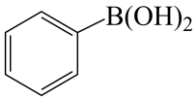
14.8×5.8×3.0 Å^3

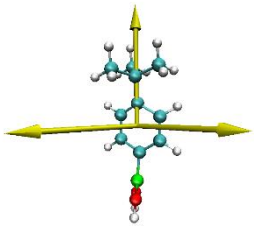




phenylboronic acid

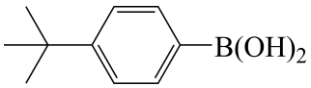
8.4×6.2×3.4 Å^3

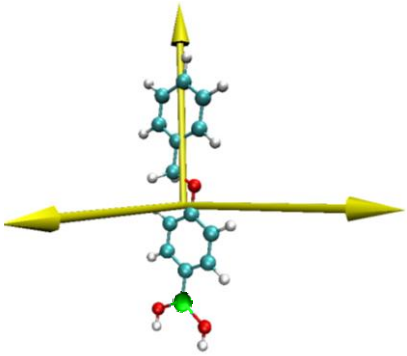




4-tert-butylphenylboronic acid

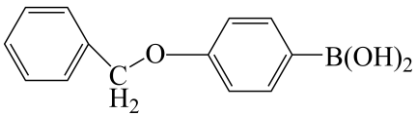
10.8×6.0×5.8 Å^3

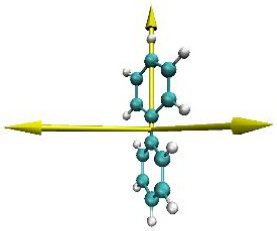




4-benzyloxyphenylboronic acid

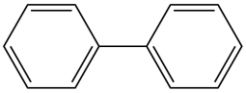
14.8×6.3×3.0 Å^3

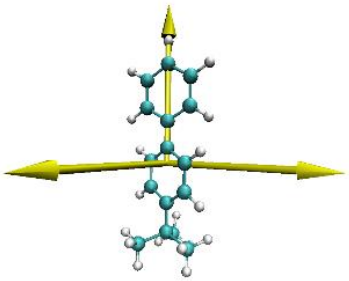




biphenyl

10.3×5.8×3.8 Å^3





4-tert-butylbiphenyl

12.3×6.0×5.9 Å^3