Electronic Supplementary Information

A triazine-based covalent organic framework-palladium hybrid for one-pot silicon-based cross-coupling of silanes and aryl iodides

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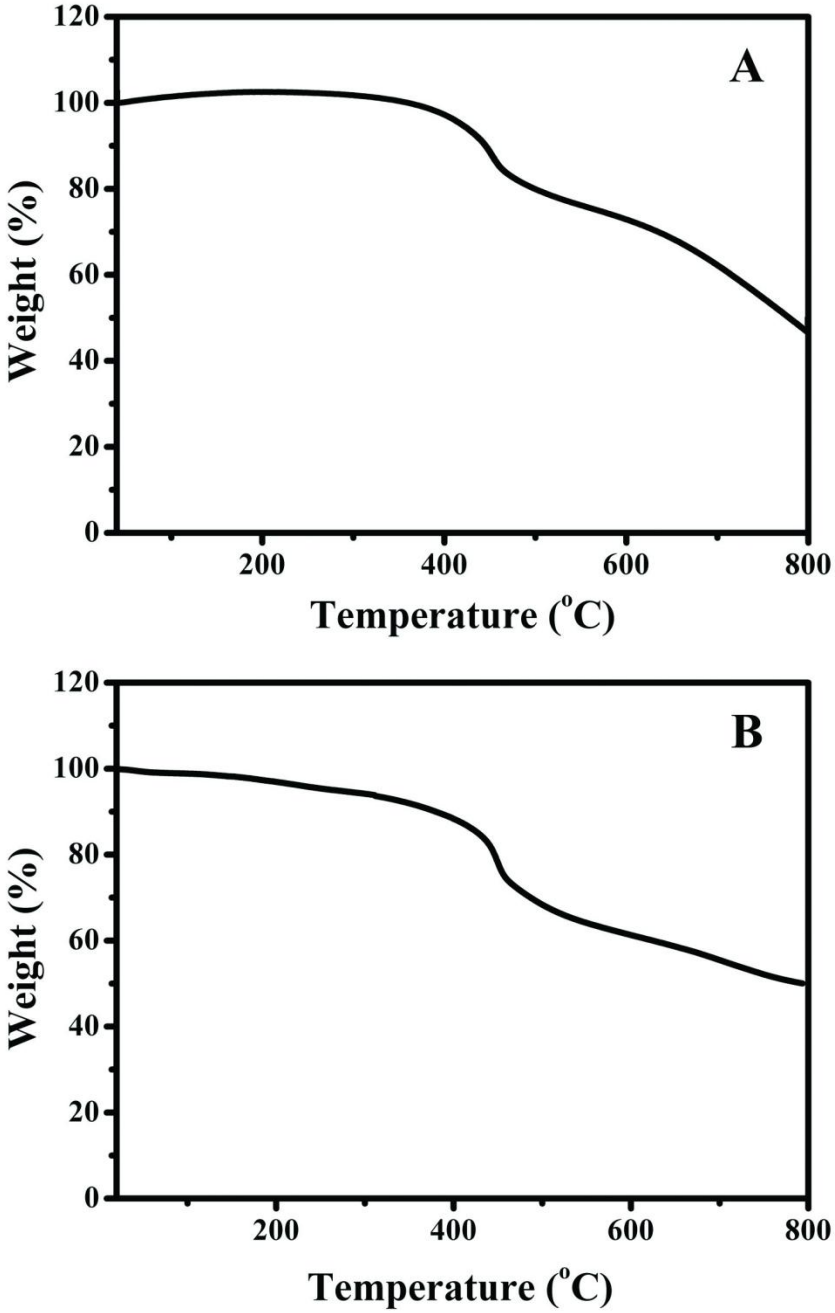


Figure S1. Thermogravimetric analysis (TGA) data of (A) **COF-SDU1** and (B) **Pd(II)/COF-SDU1**.

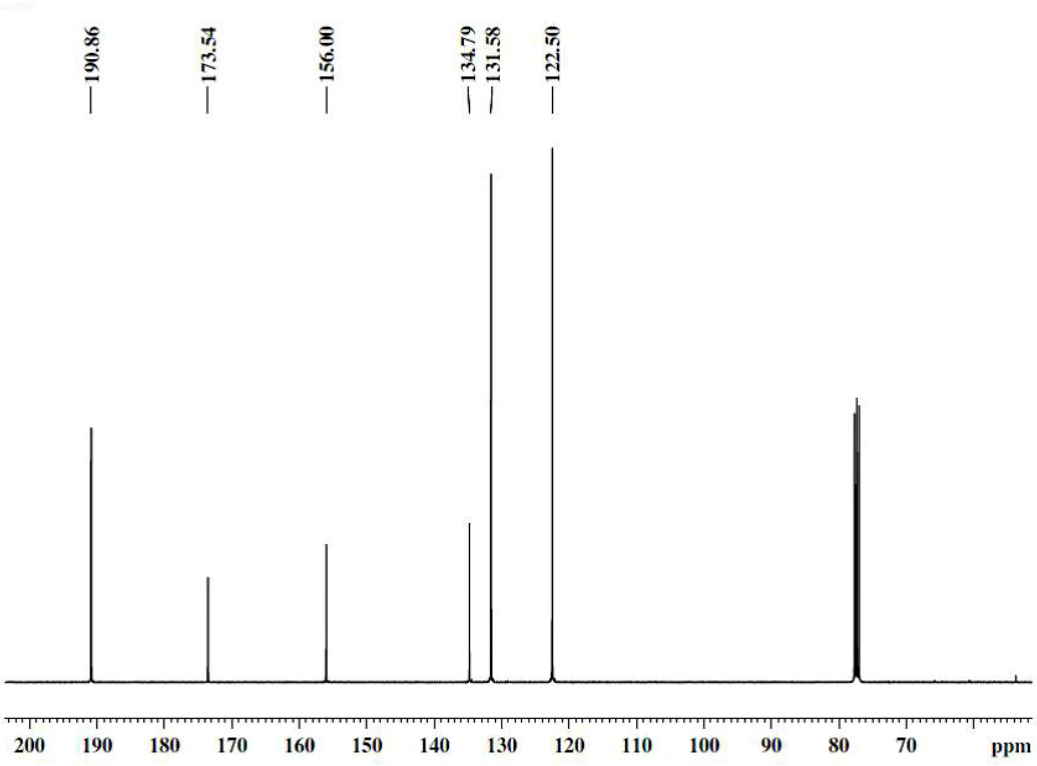


Figure S2. ^{13}C CP/MAS NMR spectrum of trif.

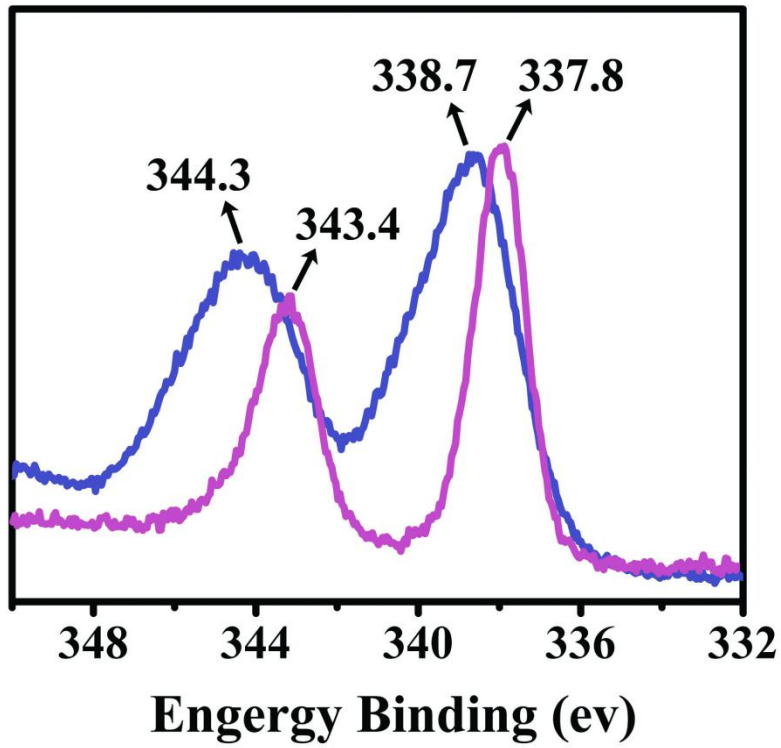


Figure S3. XPS spectrum of **$Pd(OAc)_2$** (bule line) and **Pd(II)/COF-SDU1** (pink line).

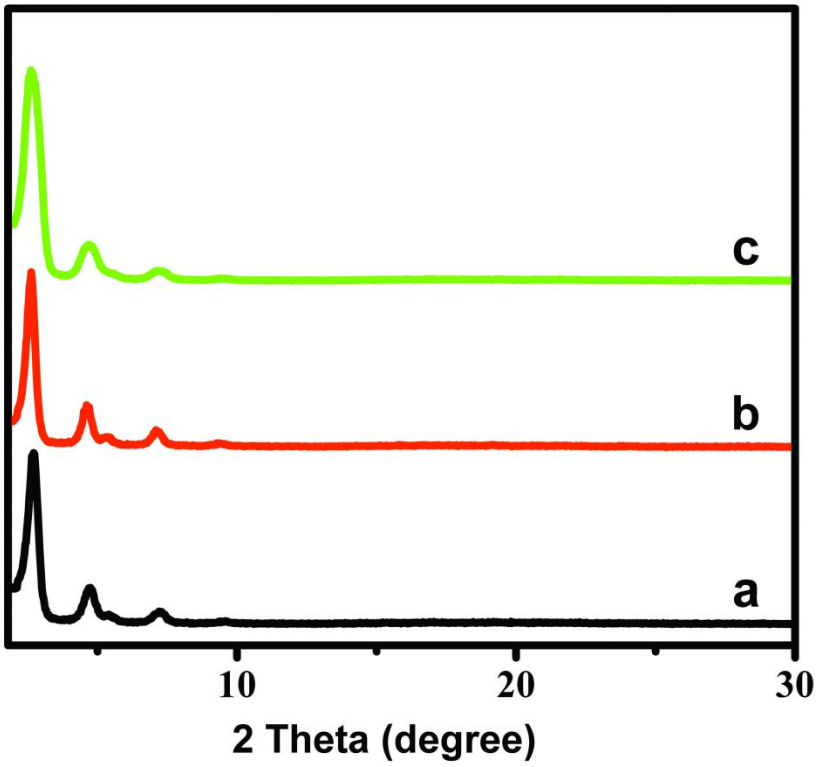


Figure S4. PXRD patterns of **Pd(II)/COF-SDU1** (a) before reused, (b) after reused first time and (c) three times.

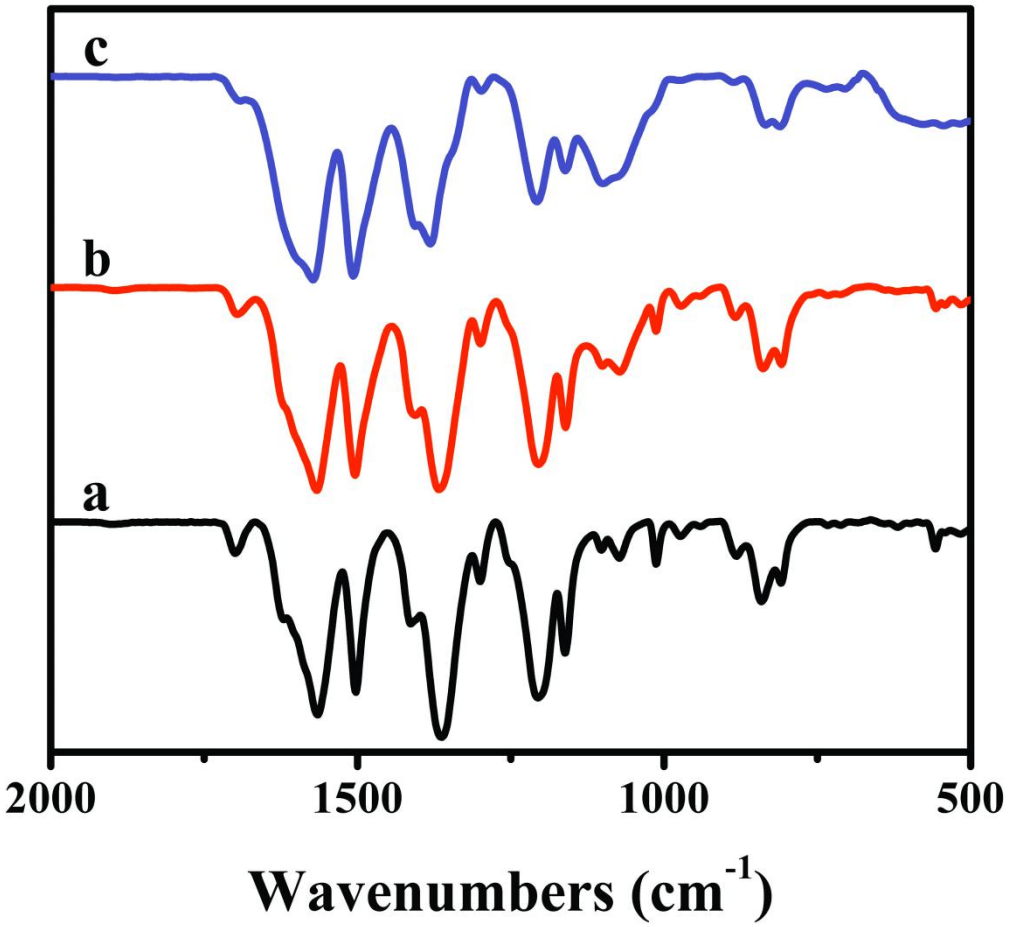
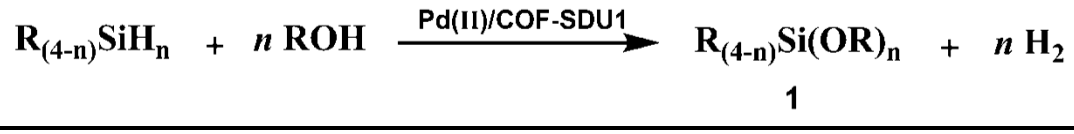


Figure S5. Fourier transforms infrared (FT-IR) spectra of **Pd(II)/COF-SDU1** (a) before reused, (b) after reused first time and (c) three times in the region of 500-2000 cm^{-1} with 2 cm^{-1} resolution.

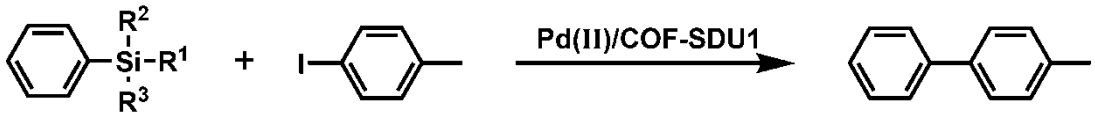
Table S1 Catalytic activity test of **Pd(II)/COF-SDU1** towards oxidation of organosilanes to organo(alkoxy)silanes or organosilanols.



Entry	$R_{(4-n)}SiH_n$	ROH	**1**	t (h)[a]	Yield (%)[b,c]
1	$PhSiH_3$	H_2O	**1a**	2	97.8
2	Me_2PhSiH	H_2O	**1b**	2	97.3
3	Ph_2SiH_2	H_2O	**1c**	2	97.1
4	$PhSiH_3$	CH_3OH	**1d**	3	98.0
5	$PhSiH_3$	C_2H_5OH	**1e**	3	97.0

[a] Reaction conditions: $R_{(4-n)}SiH_n$ (1 mmol), ROH (5 mmol), **Pd(II)/COF-SDU1** (20 mg, 8.5■10^{-3} mmol of Pd) and THF (2 mL), room temperature. [b] Isolated yield. [c] The values are the average of two independent experiments.

Table S2 Catalytic activity test of **Pd(II)/COF-SDU1** towards silicon-based cross-coupling reaction of the organo(alkoxy)silanes or organosilanols with aryl iodides.



Entry	R^1	R^2	R^3	t (h) [a]	Yield (%)[b,c]
1	OCH_3	OCH_3	OCH_3	7	97.8
2	OCH_3	CH_3	CH_3	18	58.1
3	OH	CH_3	CH_3	18	66.5

[a] Reaction conditions: organo(alkoxy)silanes or organosilanols (1 mmol), aryl halides (1.1 mmol), **Pd(II)/COF-SDU1** (20 mg, 8.5■10^{-3} mmol of Pd), TBAF (3 mmol) and THF (2 mL), 80 ^{o}C. [b] Isolated yield. [c] The values are the average of two independent experiments.

NMR signals:[1-6]

Phenylsilanetriol (1a): ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.74-7.55 (m, 2H), 7.42-7.24 (m, 3H).

Dimethylphenylsilanol (1b): ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.64-7.60 (m, 2H), 7.46-7.37 (m, 3H), 3.15 (bs, 1H), 0.41 (s, 6H).

Diphenylsilanediol (1c): ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.73-7.70 (m, 4H), 7.49-7.33 (m, 6H), 2.17 (bs, 2H).

Phenyltrimethoxylsilane (1d): ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.71-7.69 (m, 2H), 7.46-7.40 (m, 3H), 3.65 (s, 9H).

Phenyltriethoxylsilane (1e): ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.70-7.66 (m, 2H), 7.40-7.30 (m, 3H), 3.90-3.83 (q, J = 6.9 Hz, 6H), 1.25-1.20 (t, J = 7.2 Hz, 9H).

4-methyl-bipheny (2a): ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.53-7.49 (m, 2H), 7.44-7.41 (m, 2H), 7.40-7.32 (m, 2H), 7.28-7.22 (m, 1H), 7.19-7.15 (m, 2H), 2.33-2.32 (d, J = 3.0 Hz, 3H). R_f = 0.5 (100% petroleum ether).

2-methyl-bipheny (2b): ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.37-7.32 (m, 2H), 7.29-7.24 m, 3H), 7.21-7.16 (m, 4H), 2.20 (s, 3H). R_f = 0.5 (100% petroleum ether).

4-methoxy-biphenyl (2c): ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.57-7.51 (m, 4H), 7.44-7.39 (m, 2H), 7.33-7.28 (m, 1H), 7.01-6.56 (m, 2H), 3.86 (s, 3H). R_f = 0.5 (100% petroleum ether).

4-fluoro-bipheny (2d): ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.51-7.41 (m, 4H), 7.40-7.25 (m, 3H), 7.09-7.02 (m, 2H). R_f = 0.5 (100% petroleum ether).

4-hydroxy-bipheny (2e): ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.57-7.53 (m, 2H), 7.51-7.47 (m, 2H), 7.45-7.39 (m, 2H), 7.34-7.28 (m, 1H), 6.94-6.89 (m, 2H). R_f = 0.5 (petroleum ether/*n*-hexane 1:1).

4-nitro-biphenyl (2f): ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.33-8.28 (m, 2H), 7.77-7.72 (m, 2H), 7.65-7.61 (m, 2H), 7.53-7.42 (m, 3H). R_f = 0.5 (petroleum ether/ethyl acetate 1:1).

References:

1. J. John, E. Gravel, A. Hagége, H. Li, T. Gacoin, and E. Doris, *Angew. Chem. Int. Ed.* 2011, **50**, 7533-7536.

2. M. Shibata, R.Horie and W. Yoneta, *Polymer*, 2010, **51**, 5764-5770.

3. A. S. Manoso , C. Ahn , A. Soheili , C. J. Handy , R. Correia , W. M. Seganish, and P. DeShong, *J. Org. Chem.*, 2004, **69**, 8305-8314.

4. L. Bai and J. Wang, *Adv. Synth. Catal.* 2008, **350**, 315-320.

5. D. A. Watson, M. Su, G. Teverovskiy, Y. Zhang, J. G. Fortanet, T. Kinzel and S. L. Buchwald, Science, 2009, **325**, 1661-1664.

6. P. D. Stevens, J. Fan, H. M. R. Gardimalla, M. Yen and Y.Gao, *Org. Lett.*, 2005, **7**, 2085-2088.