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Molecular Engineered Palladium Single Atom Catalyst with M-C_1N_3 Subunit for Suzuki Coupling

Jia Liu,[1,2,#] Zhongxin Chen,[1,#] Cuibo Liu,[1,3,#] Bao Zhang,[2] Yonghua Du,[4] Chen-Fei Liu,[1] Lu Ma,[4] Shibo Xi,[5] Runlai Li,[1] Xiaoxu Zhao,[1] Jingting Song,[1,6] Xin Zhi Sui,[2] Wei Yu,[1] Ling Miao,[2,*] Jianjun Jiang,[2] Ming Joo Koh,[1,*] Kian Ping Loh[1,*]

Methods

Synthesis of N-confused porphyrin precursors. 5,10,15,20-Tetraphenylporphyrin (TPP), N-confused, 5,10,15,20-tetraphenylporphyrin (NCTPP), metallo-TPP and metallo-NCTPP were provided by *PorphyChem* (www.porphychem.com) with a purity of > 99%. Alternatively, TPP can be easily synthesized by refluxing pyrole and benzaldehyde in propanoic acid;[1] NCTPP was synthesized by refluxing pyrole and benzaldehyde with the addition of methanesulfonic acid in CH_2Cl_2;[2] Metallo-TPP (or metallo-NCTPP) was synthesized by refluxing the corresponding metal precursor (*e.g.* $PdCl_2$) and TPP (or NCTPP) in benzonitrile (or $CHCl_3$).[3-4] Crude product was purified by column chromatography and recrystallization in CH_2Cl_2.

Synthesis of Pd SACs. Pd-N_4-SAC (or Pd-N_3C_1-SAC) was prepared by grinding a mixture of 10 mg of Pd-TPP (or Pd-NCTPP) and 200 mg of glutamic acid with 500 mg of nano MgO powder for 30 mins.The mixture was then placed in a tube furnace and heated to 600 ^oC for 2 h at a heating rate of 3 ^oC min^{-1} under Argon and then cooled to room temperature. MgO was removed by washing in 0.5 M H_2SO_4 at 80 ^oC for 24 h, followed by repeated washing with DI water, acetone and finally dried at 80 ^oC in vaccum for 24 h.

Suzuki coupling using Pd SACs. Suzuki coupling was carried out in a 10 mL Schlenk tube with Pd SAC catalyst (1 mol% according to Pd), 0.1 mmol of iodobenzene, 0.35 mmol of phenylboronic acid, 0.3 mmol of K_2CO_3 and 0.5 mL of dimethoxyethane (DME) at 100 °C for 24 h.[5] Upon the competion of reaction, the mixture was diluted with water and extracted with DCM. The crude product was analyzed by gas chromatography-mass spectrometry (GC-MS). For Suzuki coupling with bromobenzene (0.1 mmol), the mixture was kept at 110 °C for 24 h with a lower dosage of phenylboronic acid (0.2 mmol).

DFT calculations. The first-principles calculations were performed with density functional theory (DFT) as implemented in Vienna *ab-initio* Simulation Package (VASP).[6,7] The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) format,[8] the projectoraugmented wave (PAW) method[9] and a plane-wave basis with the kinetic cut-off energy of 500 eV is used are employed in all calculations. Pd-N_4-SAC (or Pd-N_3C_1-SAC) surface was modelled with one atomic layer containing a 6 × 6 unit cell. During geometry optimization, the atoms in the Pd SACs and the adsorbates were allowed to relax until the force acting each atom was less than 0.02 eV $Å^{-1}$. To avoid the artificial interactions along the Z-direction between its periodic images, a vacuum space of at least 20 Å was employed.

Material characterization. The following equipment were used: STEM/EDS (JEOL ARM200F equipped with ASCOR probe corrector, Oxford X-Max 100TLE, at 80 kV), SEM (JEOL JSM-6701F), TEM (JEM 2010F, 200 kV), XPS (AXIS UltraDLD, monochromatic Al K_a), TGA (Discovery 5500), UV-Vis (Shimadzu UV-3600), NMR (Bruker AV400), ICP-OES (Perkin Elmer Avio 500, ppm level accuracy), AFM (Dimension Fast Scan), BET (Quantachrome Autosorb-iQ), FT-IR (Varian 3100), GC-MS (Agilent 5975 C inert MSD with triple-axis detector), MS (Bruker MicroTOF-QII). XANES/EXAFS: 100 mg of sample was first ground into fine powder using a mortar and pestle before being pressed into a 10 mm pellet. For Pd *K*-edge XAS, measurements were carried out in the National Synchrotron Light Source II at Brookhaven National Laboratory. Data analysis and simulation were carried out on Athena, Artemis, and Hephaestus (Version 0.9.23).[10]XPS fitting. For Pd_{3d}, the FWHM is constrained at ~ 1.5 eV, the area ratio and the distance between $Pd_{3d\ 3/2}$ and $Pd_{3d\ 5/2}$ are kept at 0.667 and ~ 5.3 eV, with a 30%/70% Lorentzian-Gaussian shape; for C_{1s} and N_{1s}, the FWHM is constrained at ~ 1.5 eV (except for 2 ~ 2.5 eV for the small tailing from the π^* satellite or graphitic N), with a 100% Gaussian shape. The peak assignment in C_{1s} and N_{1s} are determined from the literature and kept constant for all samples.

References:

[1] D P. Arnold, *J. Chem. Edu*. 1988, *65*, 1111.

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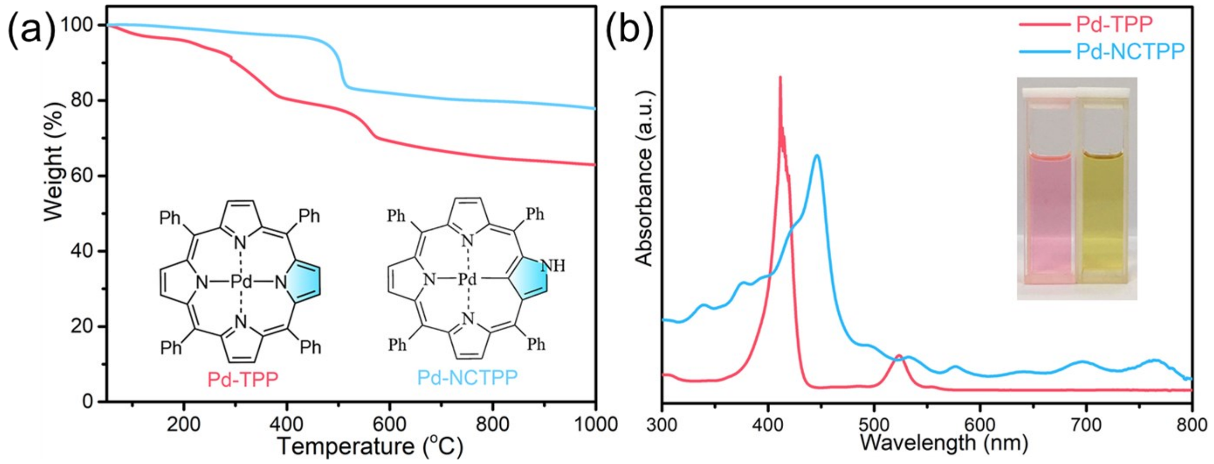


Figure S1. (a) TGA curves of Pd-TPP and Pd-NCTPP in N_2 at 10 °C min^{-1}. Inset shows the chemical structures; (b) UV-Vis spectra of Pd-TPP and Pd-NCTPP. Inset shows the digital photo of Pd-TPP (left) and Pd-NCTPP (right).

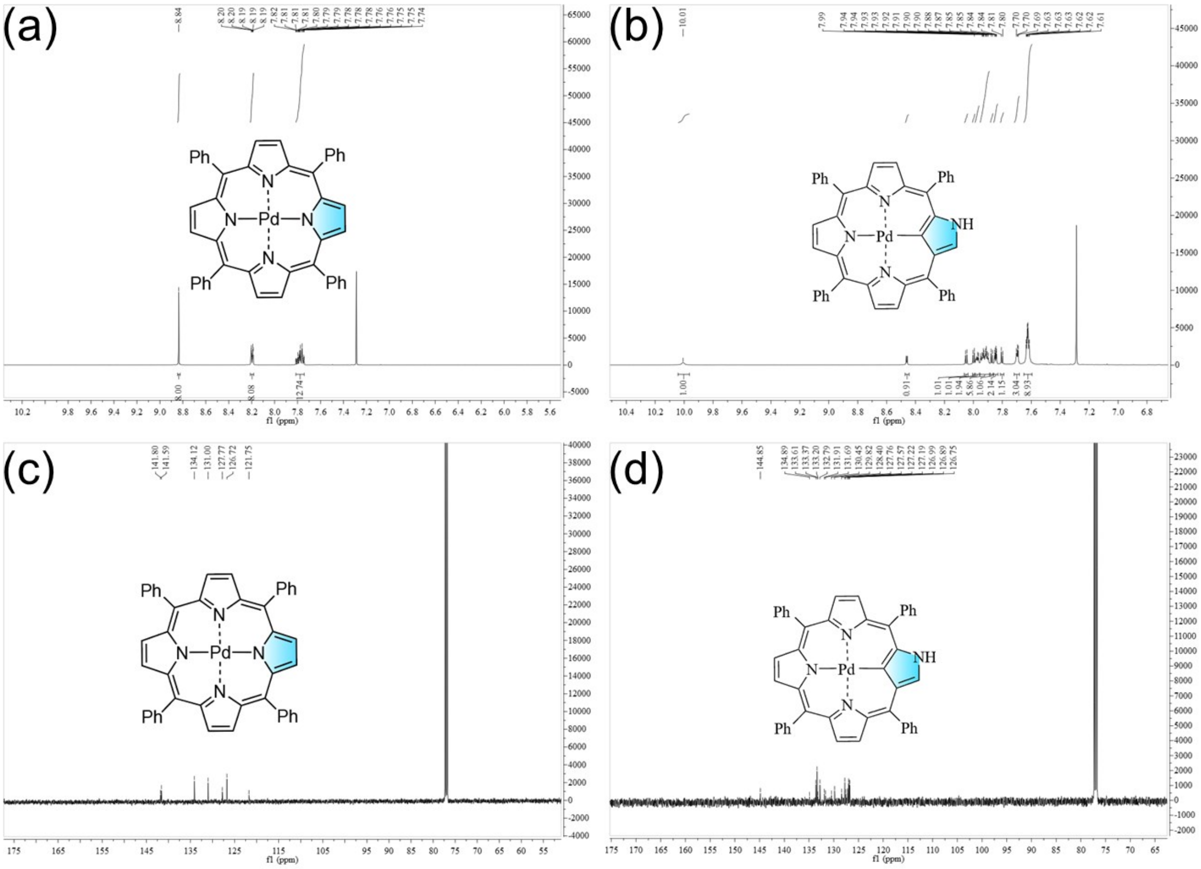


Figure S2. NMR spectra of Pd-TPP and Pd-NCTPP. **TPP ^{1}H NMR** (500 MHz, $CDCl_3$) δ [ppm] 8.84 (s, 8H), 8.21 - 8.18 (m, 8H), 7.81 - 7.74 (m, 12H); **^{13}C NMR** (500 MHz, $CDCl_3$) δ [ppm] 141.8, 141.6, 134.1, 131.0, 127.8, 126.7, 121.8; **NCTPP. ^{1}H NMR** (500 MHz, $CDCl_3$)

δ [ppm] 10.01 (s, 1H), 8.46 (d, *J* = 3.6 Hz, 1H), 8.05 (d, *J* = 5.1 Hz, 1H), 8.00 (d, *J* = 4.9 Hz, 1H), 7.97 (d, *J* = 2.2 Hz, 2H), 7.95 - 7.89 (m, 6H), 7.87 (d, *J* = 4.9 Hz, 1H), 7.85 (dd, *J* = 5.0, 2.0 Hz, 2H), 7.80 (d, *J* = 5.0 Hz, 1H), 7.72 - 7.68 (m, 3H), 7.62 (td, *J* = 4.1, 1.5 Hz, 9H); **^{13}C NMR** (500 MHz, $CDCl_3$) δ [ppm] 144.9, 134.9, 133.6, 133.4, 133.2, 132.8, 131.9, 131.7, 130.4, 129.8, 128.4, 127.8, 127.6, 127.2, 127.1, 127.0, 126.9, 126.8.

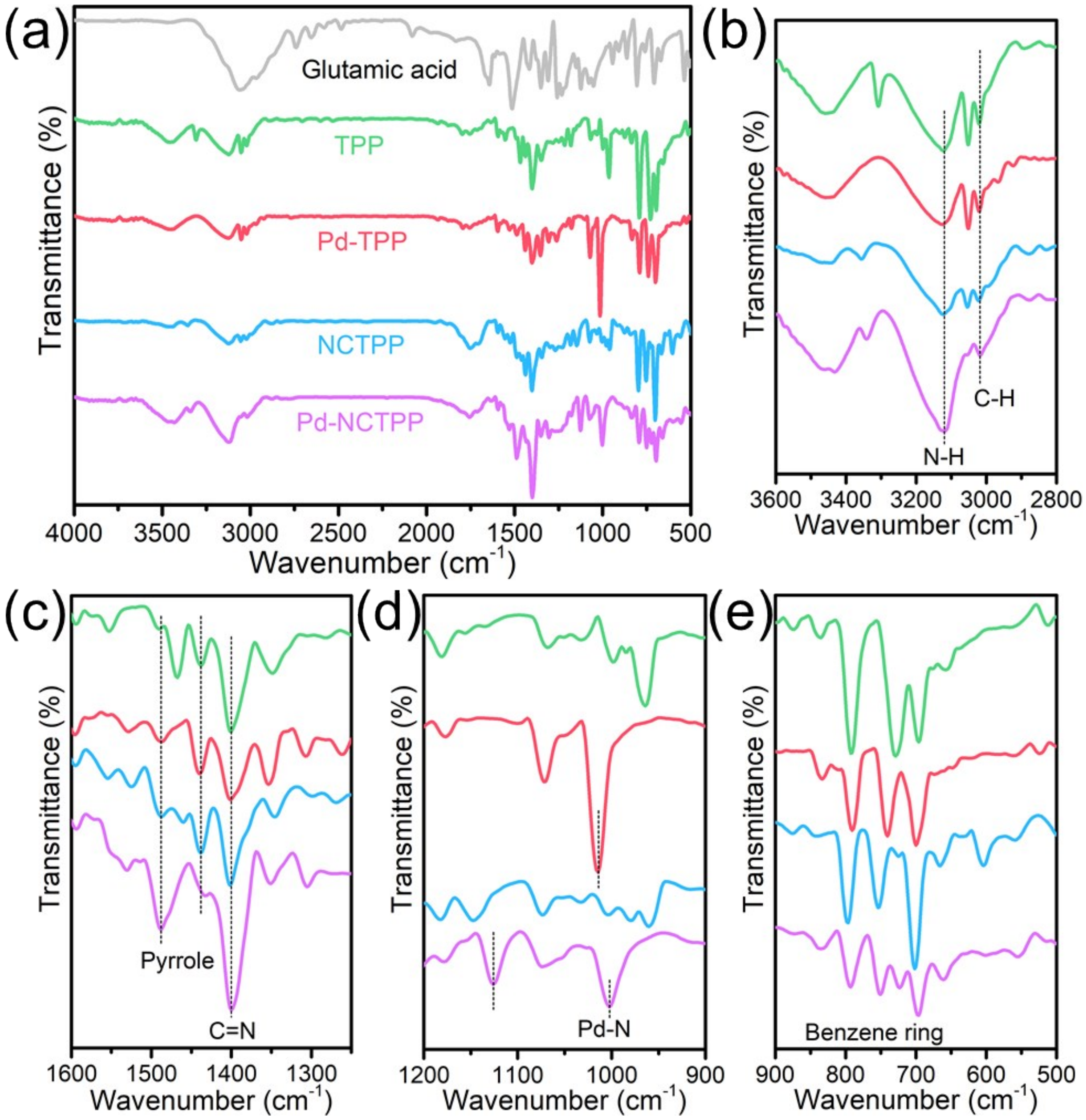


Figure S3. (a) FT-IR spectra of glutamic acid, TPP, NCTPP, Pd-TPP and Pd-NCTPP, and (b-e) the corresponding enlarged figures showing the structural details of each compound.

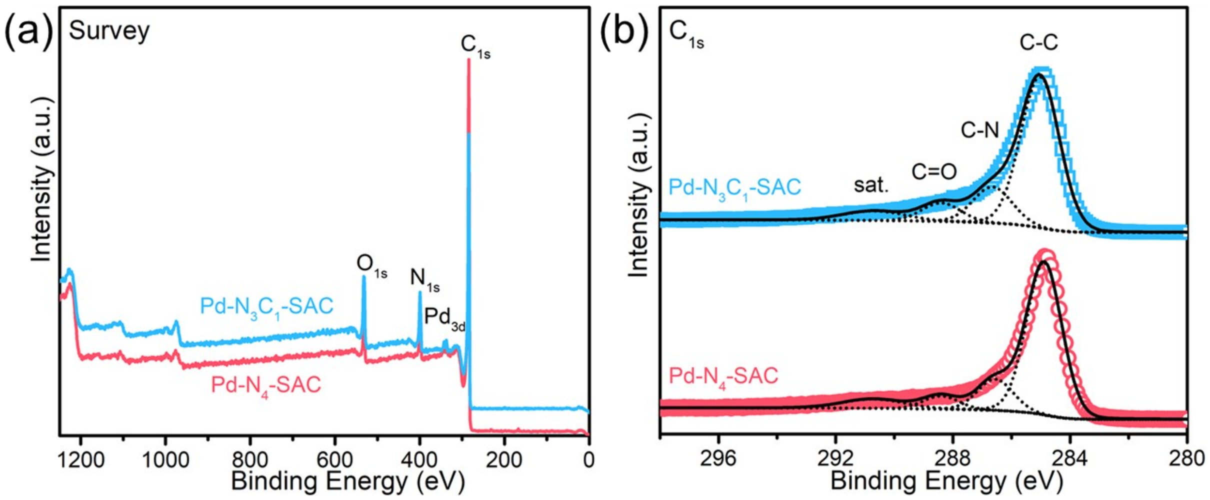


Figure S4. (a) Survey and (b) high resolution XPS C_{1s} spectra of $Pd-N_4$-SAC & $Pd-N_3C_1$-SAC.

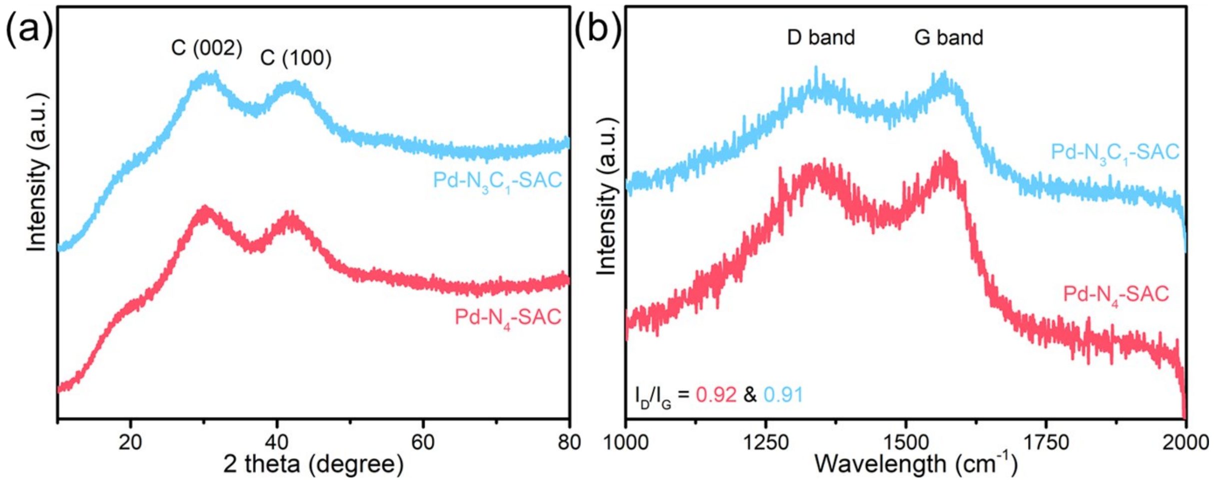


Figure S5. (a) XRD and (b) Raman spectra of Pd-N_4-SAC and Pd-N_3C_1-SAC.

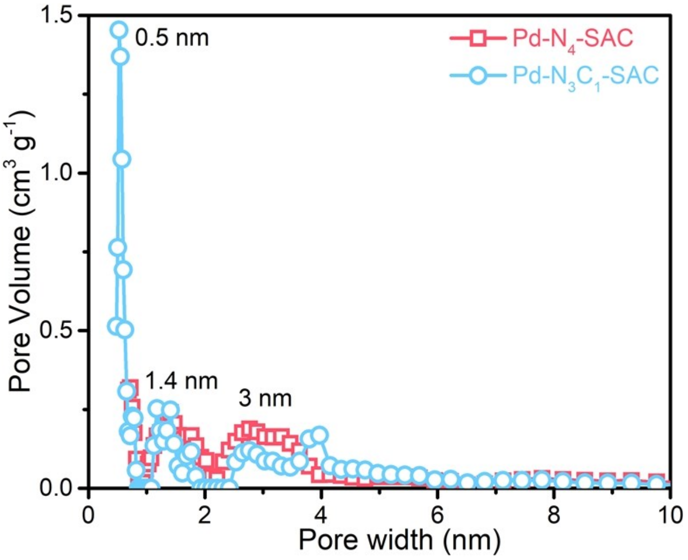


Figure S6. Pore size distributions of Pd SACs with typical pore sizes at 0.5, 1.4 and 3 nm.

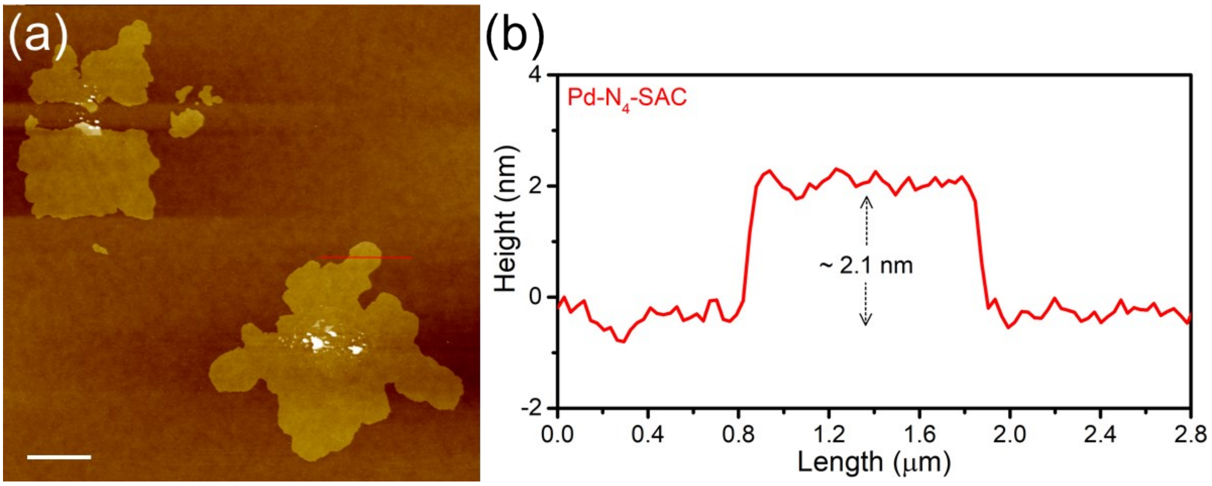


Figure S7. (a) AFM image and (b) the corresponding line profile of Pd-N_4-SAC, showing a molecularly thin morphology of ~ 2 nm. Scale bar: 2 μm.

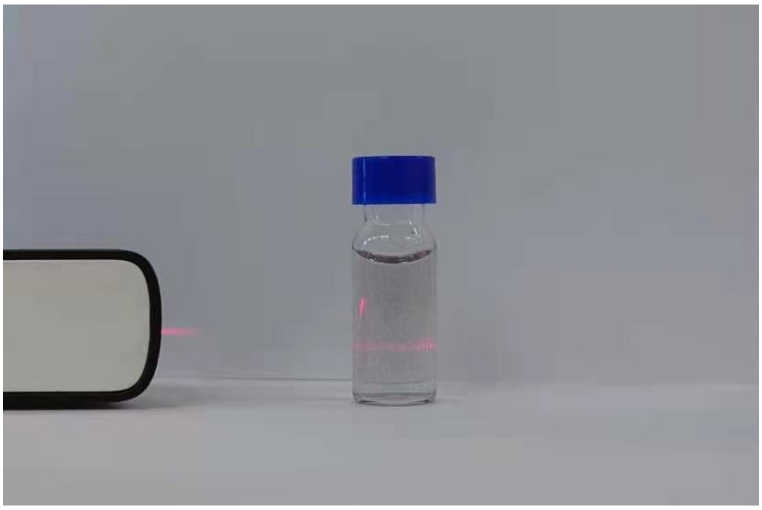
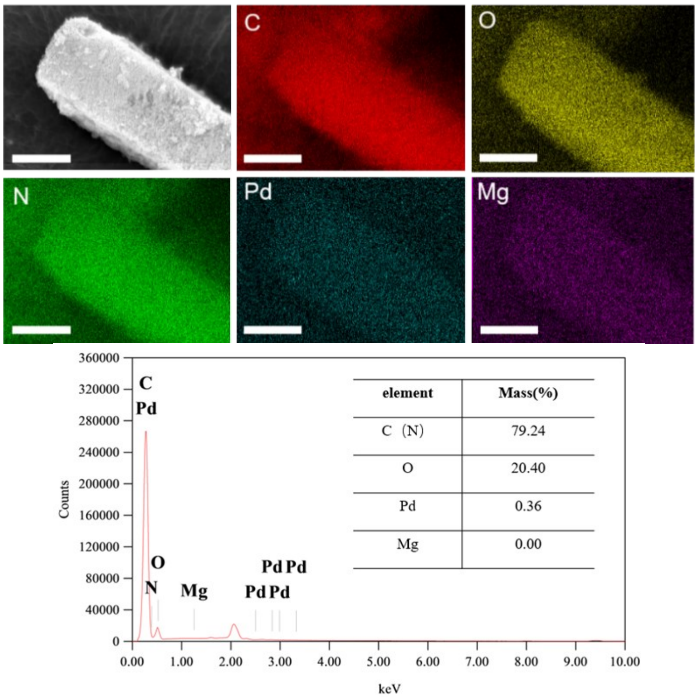


Figure S8. Digital photo showing the Tyndall effect of Pd-N_3C_1-SAC suspension.



element	Mass(%)
C（N）	79.24
O	20.40
Pd	0.36
Mg	0.00

Figure S9. SEM-EDS mapping of the Pd-N_3C_1-SAC. Scale bars: 10 µm.

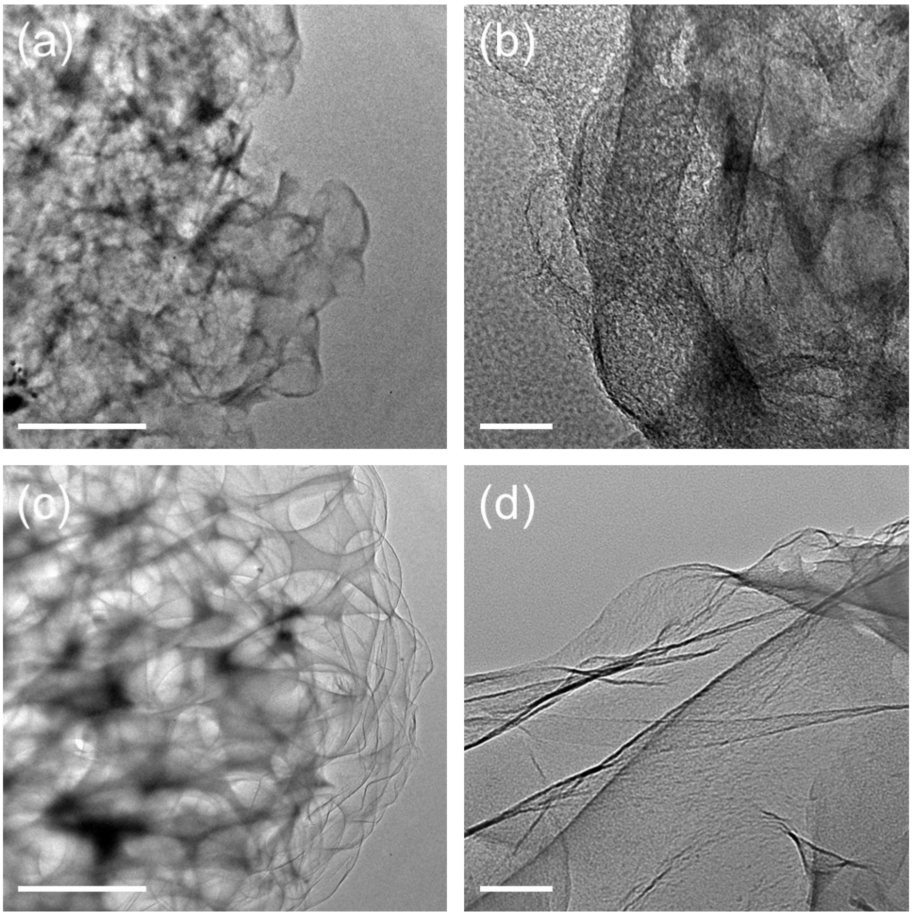


Figure S10. TEM images of (a,b) Pd-N_4-SAC and (c,d) Pd-N_3C_1-SAC at various magnifications. Scale bar: a,c. 500 nm, b,d. 50 nm.

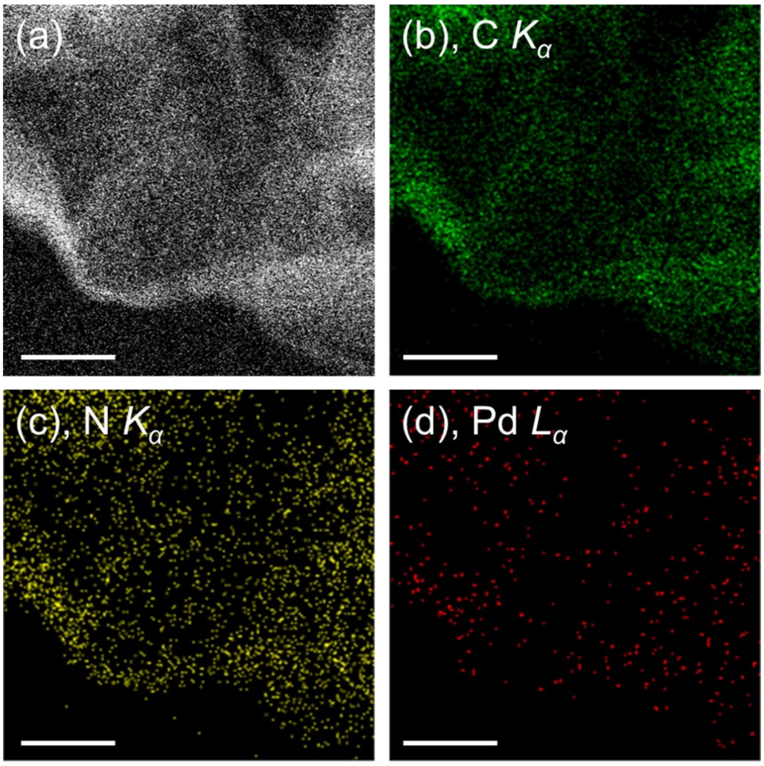


Figure S11. STEM EDS mapping of Pd-N_4-SAC. Scale bars: a-d. 50 nm.

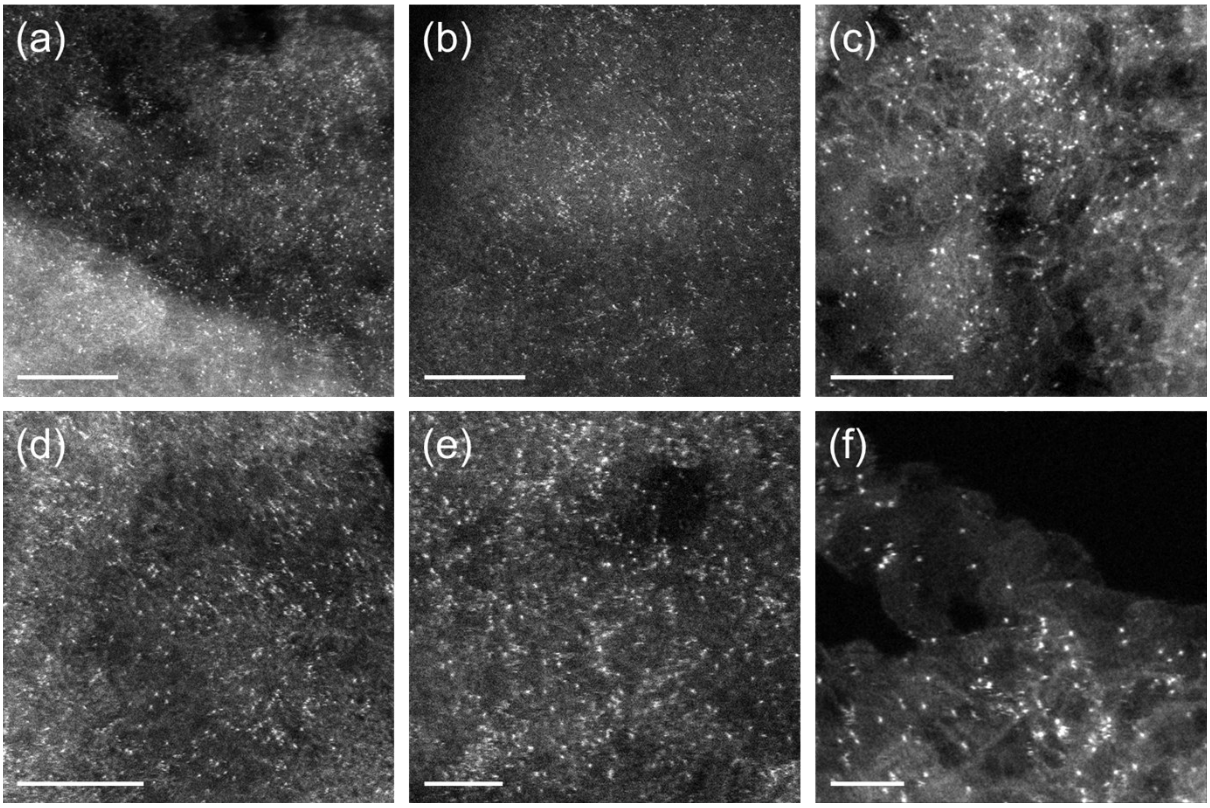


Figure S12. Representative STEM images of Pd-N_4-SAC. Scale bars: a-d. 5 nm, e,f. 2nm.

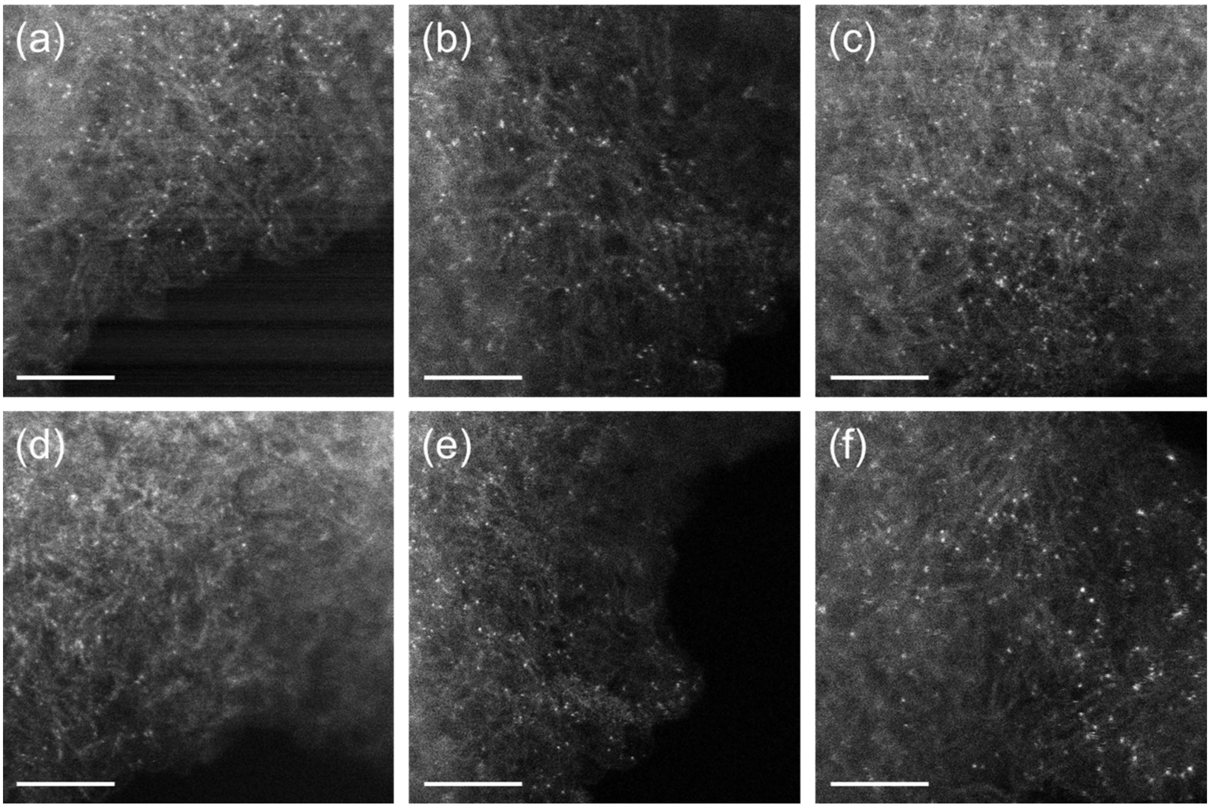


Figure S13. Representative STEM images of Pd-N_3C_1-SAC. Scale bars: 5 nm.

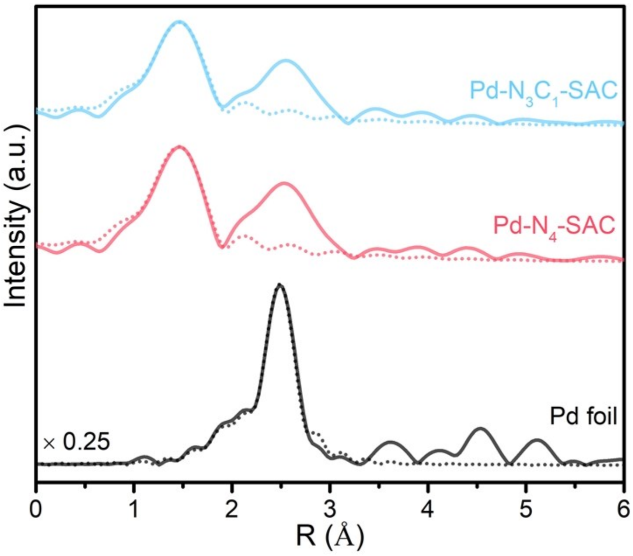


Figure S14. FT-EXAFS spectra of Pd foil, Pd-N_4-SAC and Pd-N_3C_1-SAC. Dotted lines represent the FT- fitting curves;

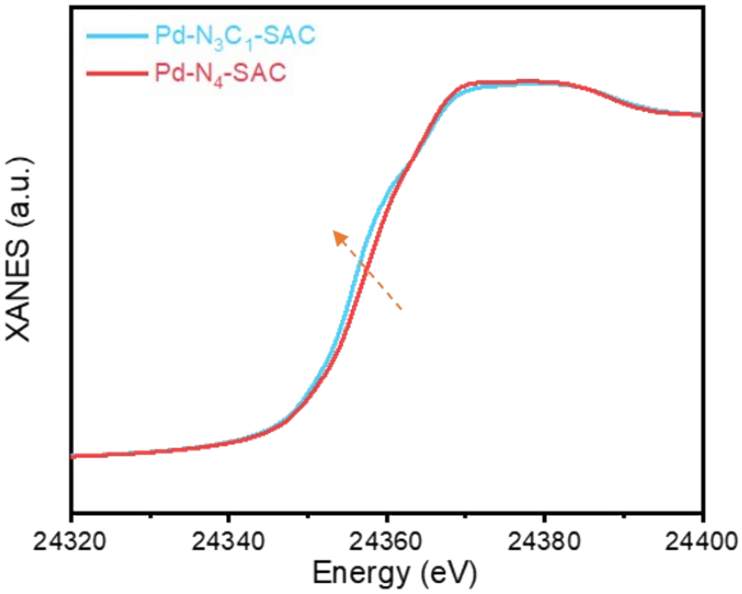


Figure S15. XANES simulation spectra for Pd SACs.

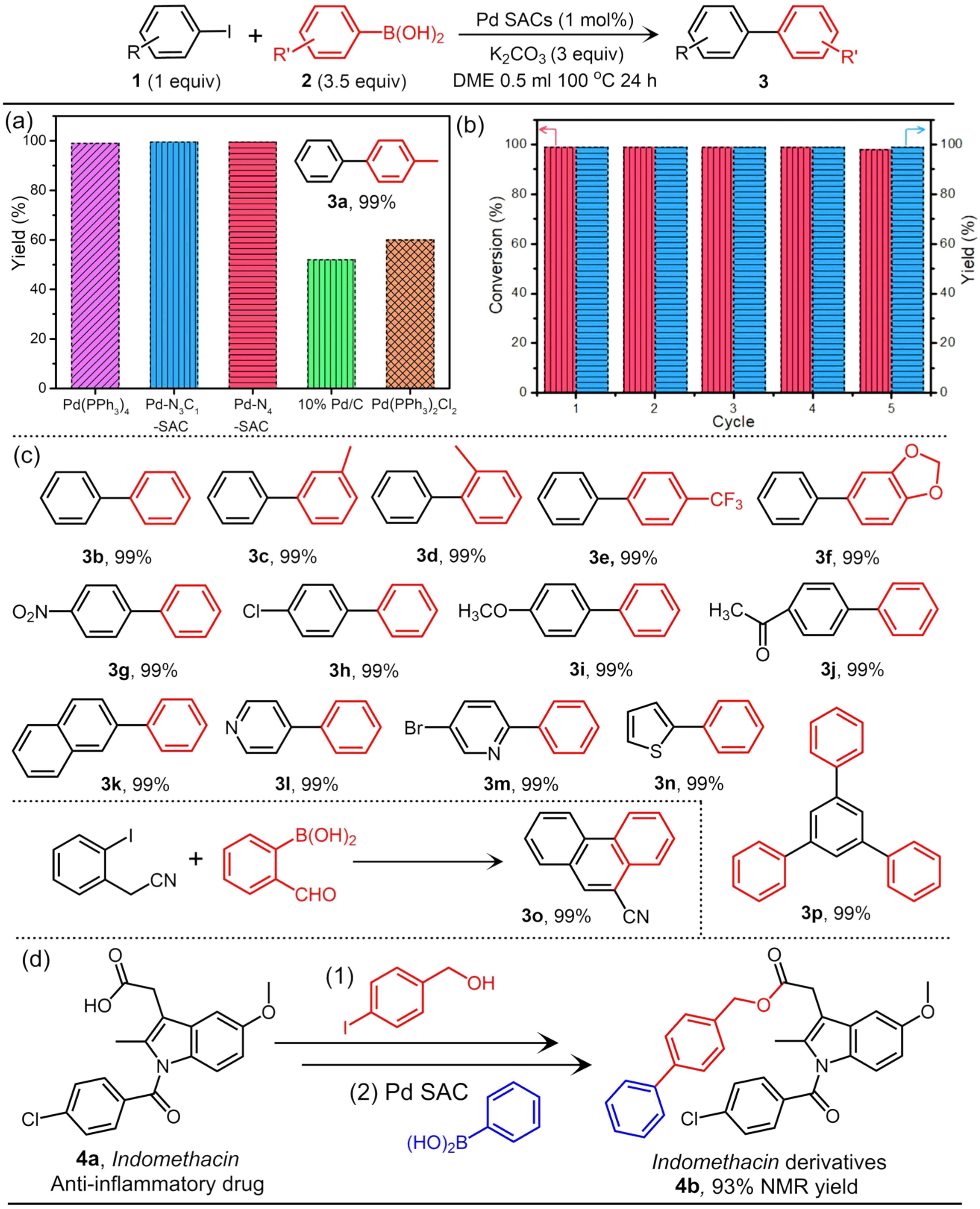


Figure S16. Pd SAC-catalysed Suzuki coupling reaction using iodobenzene. (a) Catalyst screening on the model Suzuki coupling using iodobenzene and 4-methylphenylboronic acid to afford 4-phenyltoluene (3a, inset); (b) Cycling stability of Pd SAC for Suzuki coupling in a batch setup; (c) A wide assortment of functionalized products can be obtained with Pd SACs. GC yields were reported.

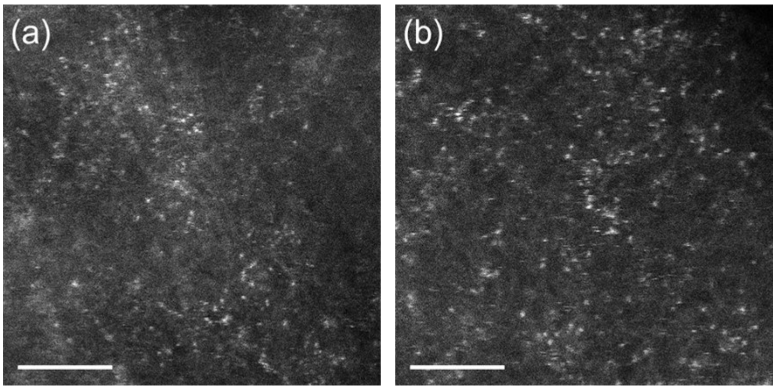


Figure S17. Representative STEM images of the spent Pd-N_3C_1-SAC. Scale bars: 5 nm.

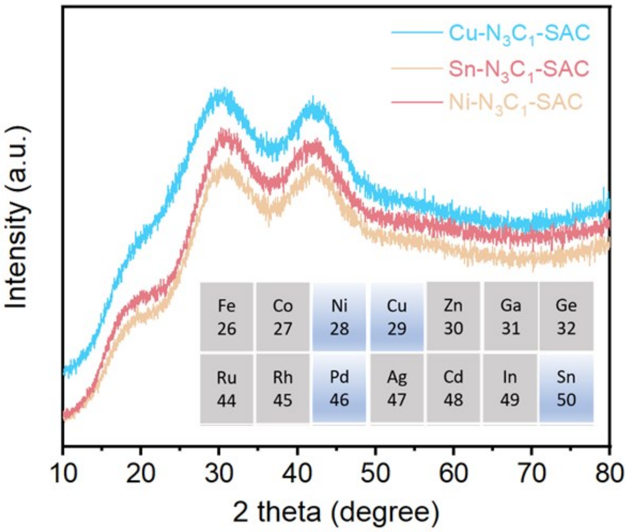


Figure S18. The XRD spectra of Ni-N_3C_1-SAC, Cu-N_3C_1-SAC and Sn-N_3C_1-SAC. Inset shows the applicability of our method toward the highlighted elements (in blue).

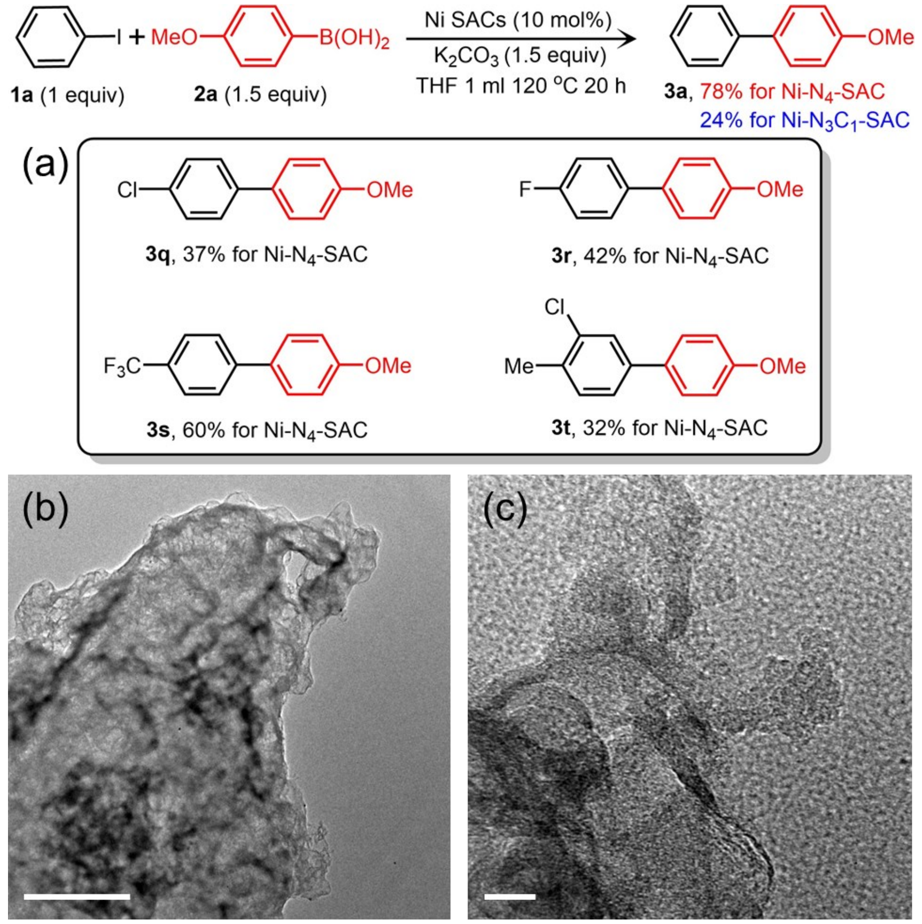


Figure S19. (a) Suzuki cross-coupling using Ni-SACs and the substrate scope; (b, c) TEM images of Ni-N4-SAC. Scale bar: b. 1μm, c, 20 nm.

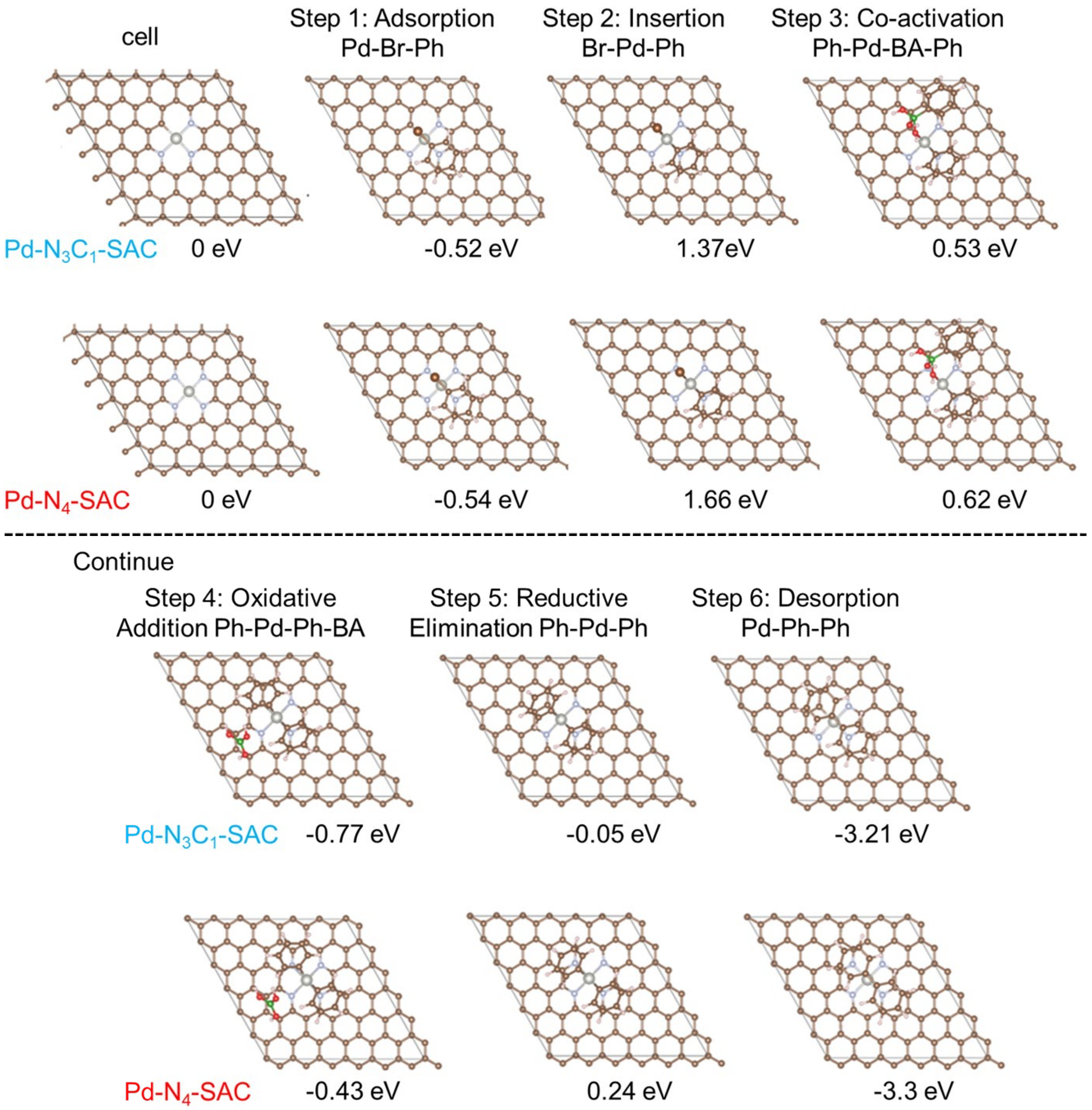


Figure S20. Top-view of the DFT models for the calculation of reaction pathway over Pd-N_4-SAC and Pd-N_3C_1-SAC. The color scheme used: brown for C, light blue for N, grey for Pd, blue for Br, green for B, red for O and light-pink for H. Base is omitted for the sake for clarity.

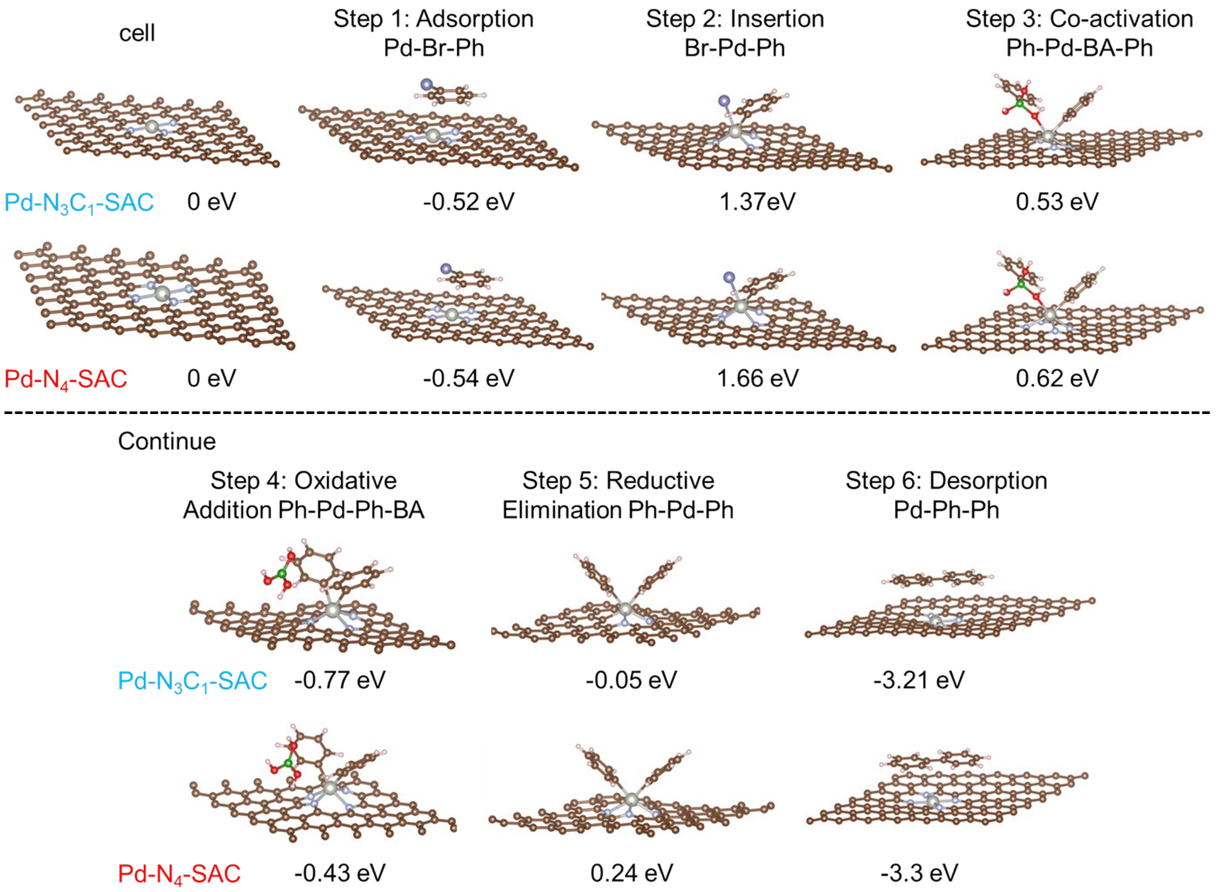
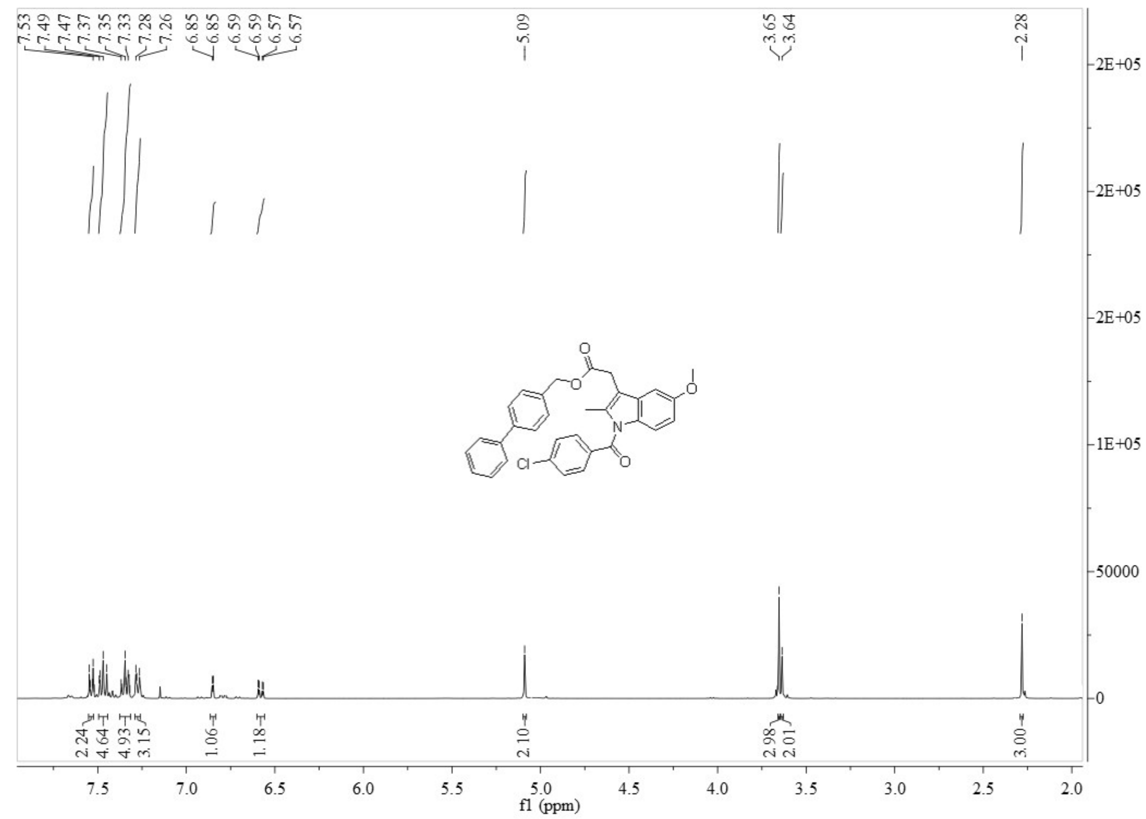
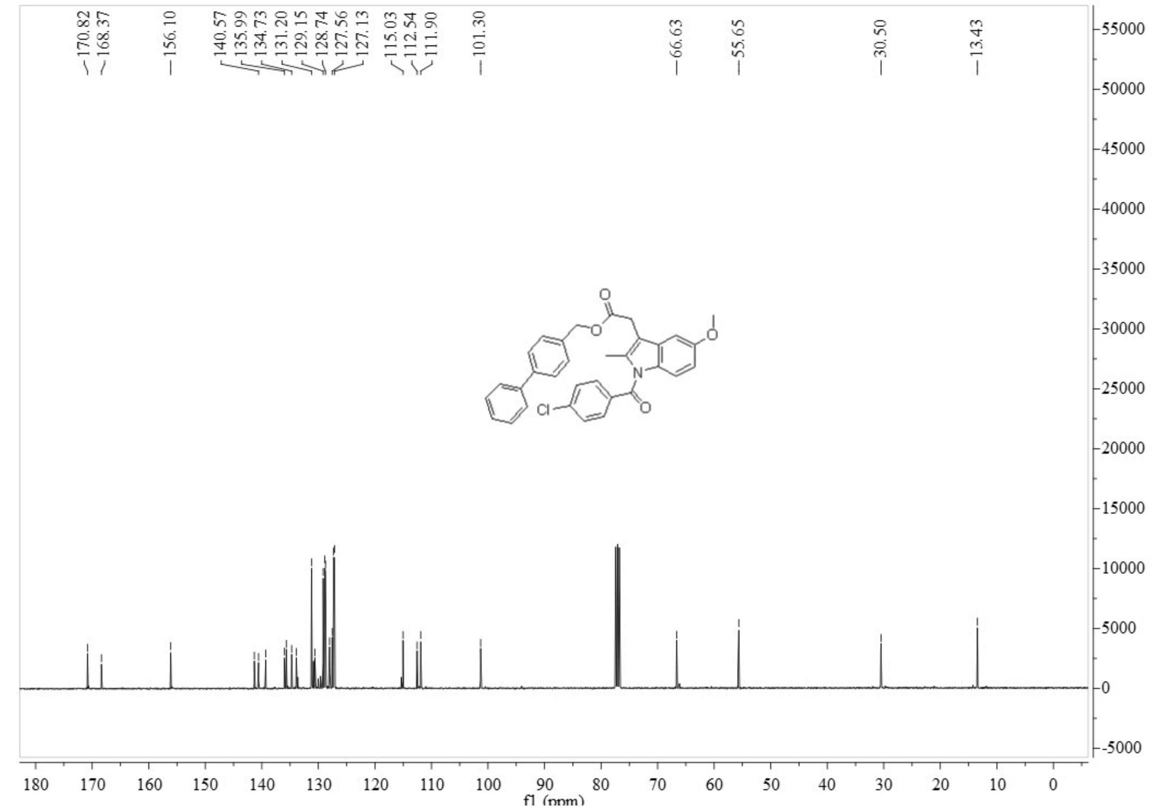


Figure S21. Side-view of the DFT models for the calculation of reaction pathway over Pd-N_4-SAC and Pd-N_3C_1-SAC. The color scheme used: brown for C, light blue for N, grey for Pd, blue for Br, green for B, red for O and light-pink for H. Base is omitted for the sake for clarity.





4b. ^{1}**H NMR** (400 MHz, CDCl$_3$) δ [ppm] 7.55 - 7.52 (m, 2H), 7.47 (dd, J = 12.1, 4.8 Hz, 4H), 7.38 - 7.31 (m, 5H), 7.29 - 7.26 (m, 3H), 6.85 (d, J = 2.5 Hz, 1H), 6.58 (dd, J = 9.0, 2.5 Hz, 1H), 5.09 (s, 2H), 3.65 (s, 3H), 3.64 (s, 2H), 2.28 (s, 3H); ^{13}**C NMR** (400 MHz, CDCl$_3$) δ

[ppm] 170.8, 168.4, 156.1, 141.3, 140.6, 139.3, 136.0, 135.7, 134.7, 133.9, 131.2, 129.2, 128.9, 128.7, 128.0, 127.6, 127.3, 127.1, 115.0, 112.5, 119.0, 101.3, 66.6, 55.6, 30.5, 13.4.

Table S1. Elementary composition from XPS and EA/ICP.[1]

XPS Sample	C/atom%	N/atom%	O/atom%	Pd/atom%	Pd/wt%
Pd-N_4-SAC	89.07	5.02	5.72	0.19	1.62
Pd-N_3C_1-SAC	76.96	12.58	10.19	0.27	2.24
EA Sample	**C/wt%**	**H/wt%**	**N/wt%**	**S/wt%**	**Pd/wt%**
TPP	86.16	4.61	9.64	N.D.	N.D.
NCTPP	85.18	4.63	9.59	N.D.	N.D.
Pd-TPP	70.63	3.70	8.10	N.D.	14.23
Pd-NCTPP	72.50	3.69	8.11	N.D.	14.30
Pd-N_4-SAC	68.42	2.51	7.38	N.D.	2.33
Pd-N_3C_1-SAC	62.76	2.00	3.66	N.D.	3.26

[1] Pd loading in EA is from ICP-OES. Theoretical Pd loadings for Pd-TPP and Pd-NCTPP are 14.8 wt%.

Table S2. Results of the EXAFS fitting for Pd-N_3C_1-SAC and Pd-N_4-SAC.

	Bonding	N	R	Sigma^2	R-factor
Pd Foil	Pd-Pd	12	2.74 (0.01)	0.0054 (0.0003)	0.007
Pd-N_4-SAC	Pd-N	3.2 (0.9)	1.99 (0.02)	0.0043 (0.0012)	0.019
Pd-N_3C_1-SAC	Pd-N/C	3.0 (0.6)	1.99 (0.02)	0.0047 (0.0011)	0.010