Electronic Supplementary Information

Chromophore-Assisted Plasmonic Catalysis: Au-BODIPY-Pd Nanocomposites for Efficient Suzuki Coupling in Water

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Experimental

Materials

Tetrachloroauric (III) acid and palladium(II) chloride were purchased from Sigma Aldrich. L-Tryptophan and BODIPY A ([2-[(methylthio)(2H-pyrrol-2-ylidene)methyl]-1H-pyrrole] (difluoroborane)) were purchased from TCI Chemicals. Milli-Q water (18.2 Mohm.cm) was used for all the synthesis procedures. All the chemicals were used without any further purification.

Synthesis of AuNP

1 mL of 5 mM auric chloride ($HAuCl_4$) was mixed with 1 mL of 25 mM L-tryptophan and 8 mL of distilled water in a clean falcon tube at 25 °C. The mixture was stirred for 15 minutes, during which a purple colour developed, signalling the formation of gold nanoparticles.

The mixture was centrifuged and washed with 10 mL water thrice, and **AuNP** was collected by centrifugation.

Synthesis of Au-BODIPY

1 mL of 5 mM auric chloride (HAuCl4) was mixed with 1 mL of 25 mM L-tryptophan and 8 mL of distilled water in a clean falcon tube at 25 °C. The mixture was stirred for 15 minutes, during which a purple colour developed, signalling the formation of gold nanoparticles. Then, 1 mL of 1 mM A in acetone was added to the solution and the mixture was stirred overnight at 25 °C. The mixture was centrifuged and washed with 10 mL water thrice and **Au-BODIPY** was collected by centrifugation.

Synthesis of Au-BODIPY-Pd

1 mL of 5 mM auric chloride (HAuCl4) was mixed with 1 mL of 25 mM L-tryptophan and 8 mL of distilled water in a clean falcon tube at 25 °C. The mixture was stirred for 15 minutes, during which a purple colour developed, signalling the formation of gold nanoparticles. Then, 1 mL of 1 mM A in acetone was added to the solution and the mixture was stirred overnight. After washing the material with 10 mL water thrice and centrifuging at 7500 rpm for 15 minutes, 1 mL of 5 mM PdCl2 and 1 mL of 5 mM L-tryptophan were added to the mixture. The reaction mixture was stirred at 750 rpm for 2 hours at 25 °C. The reaction mixture was also sonicated for 15 seconds every 30 minutes. Following this, the mixture was centrifuged and washed with 10 mL water thrice and **Au-BODIPY-Pd** was collected by centrifugation.

Synthesis of Au-Pd

1 mL of 5 mM auric chloride (HAuCl4) was mixed with 1 mL of 25 mM L-tryptophan and 8 mL of distilled water in a clean falcon tube at 25 °C. The mixture was stirred for 15 minutes, during which a purple colour developed, signalling the formation of gold nanoparticles. Then, 1 mL of 5 mM PdCl2 was added to the solution containing gold nanoparticles. The mixture was stirred for 2 hours at 25 °C with a sonication of 15 seconds every 30 minutes. Following this, the mixture was centrifuged and washed with 10 mL water thrice and **Au-Pd** was collected by centrifugation.

Characterization

Absorption spectra were recorded on a Shimadzu UV-2700 UV-Vis spectrophotometer in 3 mL quartz cuvettes having a path length of 1 cm at room temperature. TEM images were acquired on a Jeol 2100 HR operating at 200 kV. Samples were prepared by depositing a drop of diluted nanoparticle suspension on a TEM grid (200 mesh carbon film on copper) and dried under vacuum for 2 hours. Compositional analysis of the samples was carried out by X-Ray photoelectron spectroscopy (XPS) using a Thermo Scientific Al K-alpha spectrometer with a monochromatic Al Kα X-ray source (1486.7 eV).

Transient absorption spectroscopy

The transient absorption (TA) measurements were conducted using Helios Fire pump-probe spectrometer. The 800 nm light generated by the Ti:Sapphire amplifier laser system (Astrella, Coherent) has a pulse duration of 35 femtoseconds and 1 kHz repetition rate. The instrument response function (IRF) of our system is approximately 150 fs, providing sufficient temporal resolution to accurately monitor sub-picosecond carrier dynamics. The 800 nm laser output splits into two beams (pump and probe) with the help of a beam splitter. The frequency of the reflected component known as a pump beam can be tuned from the NIR to UV region using an optical parametric amplifier (Opera SOLO) to the desired excitation wavelength. For the measurements, samples were excited at 400 nm pump wavelength. The probe beam travelled through a delay stage and was focused on a CaF_2 window to generate white light pulse in the range of 350-700 nm. All the measurements were carried out on liquid samples dispersed in identical quartz cuvettes. Data analysis was performed using Surface Xplorer software.

Suzuki coupling reactions

A typical Suzuki coupling reaction was performed in a 5 mL glass culture vial under white light illumination in the LZC5 Luzechem (Canada) photoreactor (8W × 8 rods) at 25 °C. For carrying out the reaction, bromobenzene (0.1 mmol) was added to water (2 mL) in the presence of phenylboronic acid (0.1 mmol), K_2CO_3 (0.2 mmol) and **Au-BODIPY-Pd** (1 mg). The mixture was kept under white light illumination for 6 hours. The reaction product was extracted with ethyl acetate and immediately analyzed by gas chromatography-mass spectrometry (GC-FID-MS). The GC-FID-MS analysis was performed on a ThermoScientific Trace 1300 equipped with DB- HeavyWAX/HP-5 column (30 m × 0.320 mm × 0.25 μm), and product yield was quantified based on a series of standards and using with naphthalene as an internal standard. The yield of substituted biphenyl products was calculated by considering 1,1’-biphenyl as the standard. In the case of 1,2- diphenylbenzene as a product, 1,1’-biphenyl was used as the standard and the obtained yield was multiplied with 2/3, as the product contains 18 carbon atoms. All the products were confirmed by GC-MS. After each run during the recyclability studies, the reaction mixture was centrifuged to separate the catalyst from the reaction mixture. The catalyst was then washed three times with water and subsequently dried in a vacuum oven. According to the recovered amount of the catalyst after the first run, the ratio between the substrate, additive, catalyst, and solvent was kept constant in the subsequent runs. The product was extracted from supernatant using ethyl acetate and quantified immediately by GC-MS using naphthalene as the internal standard. The turnover number (TON) and turnover frequency (TOF) were calculated as follows.

$$\text{Turnover number (TON)} = \frac{\text{Number of moles of product formed}}{\text{Number of moles of Pd (from EDX)}}$$

$$\text{Turnover frequency (TOF)} = \frac{\text{Turnover number}}{\text{Time (s)}}$$

Table S1. Relative atomic percentages of catalyst elements determined by EDX and XPS for the fresh catalyst.

Element	Line	Weight %	Atomic %
Au	L series	69	67
Pd	L series	11	14
B	K series	6	3
F	K series	3.5	5
S	K series	8	6
N	K series	2.5	5

Table S2. The optimisation of different compositions of **Au-BODIPY-Pd** on the product yield of 1,1'-biphenyl of a Suzuki coupling reaction.

S. No.	Concentration of Au salt (mM)	Concentration of BODIPY (mM)	Concentration of Pd salt (mM)	% Yield of 1,1'-biphenyl
1	5	5	5	52
2	5	4	5	57
3	5	3	5	72
4	5	2	5	72
5	5	1	5	77
6	5	0.5	5	70
7	5	1	5	77
8	5	1	10	78
9	5	1	15	73
10	5	1	20	71

Reaction conditions: 0.1 mmol phenylboronic acid, 0.1 mmol bromobenzene, 1 mg catalyst, 0.2 mmol K_2CO_3, 2 mL water, 25 °C, white light, 6 hours.

Table S3. Relative atomic percentages of catalyst elements determined by EDX and XPS for the catalyst after three catalytic cycles.

Element	Line	Weight %	Atomic %
Au	L series	68	66
Pd	L series	10.5	13
O	K series	11	9
B	K series	3	2.5
F	K series	2	3
S	K series	3.5	3
N	K series	2	3
K	K series	0.5	0.5

Table S4. Multi-exponential growth and decay components for Au and the composites at the specified probing wavelength upon 400 nm pump excitation.

System	Probe (nm)	τ_g (ps)	$\tau_{e\text{-}ph}$ (ps)	$\tau_{ph\text{-}ph}$(ps)
AuNP	550	0.15±0.03	4.06±0.12	190±5
Au-BODIPY	550	0.15±0.02	6.3±0.15	192±3
Au-Pd	555	0.17±0.03	4±0.15	172±4
Au-BODIPY-Pd	560	0.07±0.005	3.72±0.2	149±3

Fitting model for TA data

The data were fitted to a model consisting of a sum of convoluted exponentials, where the decay functions are convoluted with a Gaussian function to account for the Instrument Response Function (IRF). The experimental signal S(t) is defined by the following equation:

$$S(t) = \frac{1}{t_p\sqrt{\pi}} e^{-\left(\frac{t-t_0}{t_p}\right)^2} * \begin{cases} \sum_i A_i e^{-\frac{t-t_0}{\tau_i}}, & t \geq t_0 \\ 0, & t < t_0 \end{cases} \quad , \quad t_p = \frac{IRF}{2\sqrt{\ln 2}}$$

where t_0 is time zero, A_i and t_i are amplitudes and decay times respectively, * is convolution.

Table S5. Comparison of various catalysts for the C–C coupling reaction.

S. No.	Catalyst	Temperature (°C)	Solvent	Time	Yield (%)	Reference
1	Au-Pd NPs	80	Ethanol:water	24 h	85	*J. Ind. Engg. Chem.*, 2015, **21**, 746-748
2	HUY@S-TOH/AuPd	Room Temperature	Ethanol:water (2:1)	30 min	85	*Catal. Sci. Tech.*, 2019, **9**, 3820-3827
3	Pd NPs@g-C_3N_4	Room temperature	Ethanol:water (2:1)	2 h	90	*ACS Appl. Nano Mater.* 2020, **3**, 2070-2103
4	PdNPs@zeolite	80	Ethanol:water (1:1)	3-4 h	88	*Res. Chem. Inter.*, 2022, **48**, 1111-1128
5	Pd/Au/*PN*-CeO_2	Room temperature	DMF:Water (1:1)	5-6 h	90	*ACS Catal.* 2015, **5**, 6481-6488
6	Au-BODIPY-Pd	Room temperature	Water	6 h	88	This Work

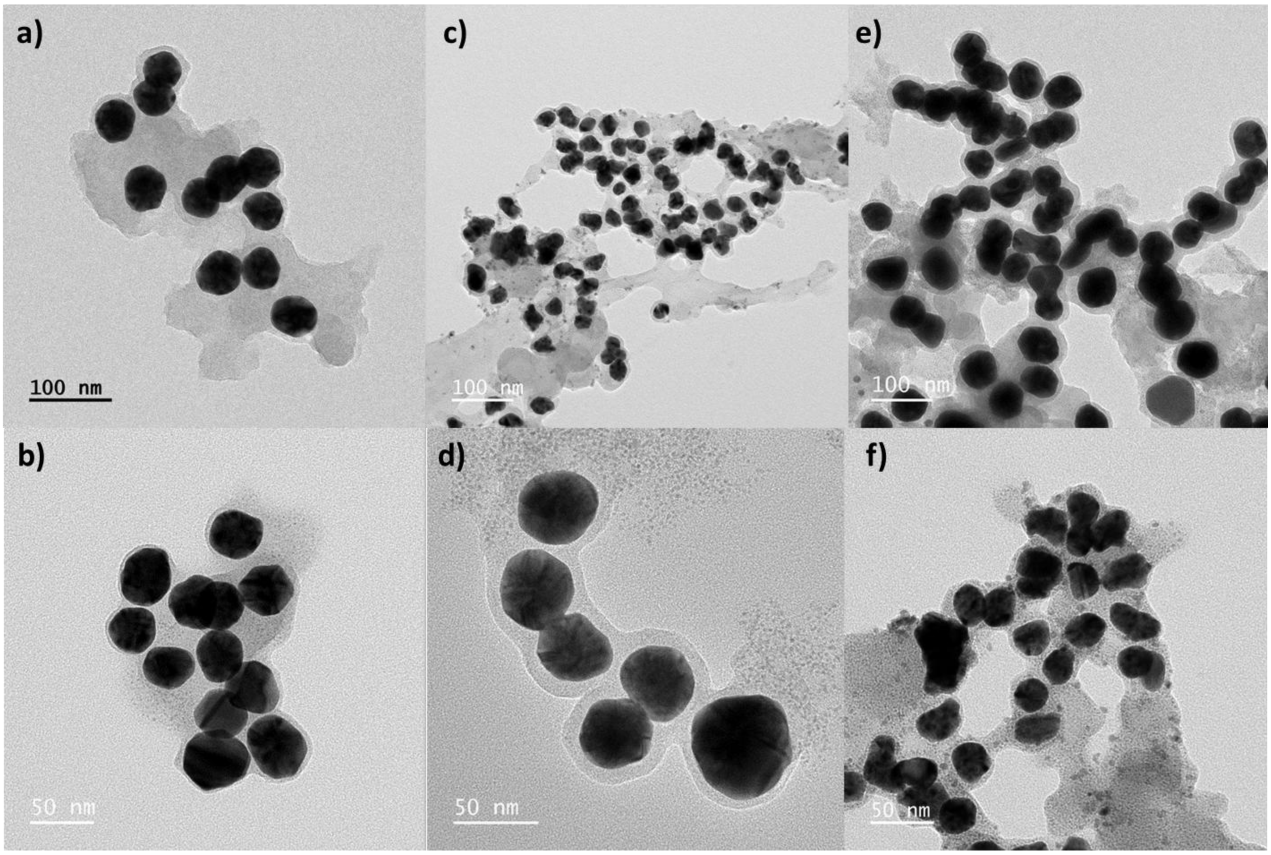

Fig. S1. Transmission electron microscopy (TEM) images of (a, b) **AuNP**, (c, d**) Au-BODIPY** and (e, f) **Au-Pd**.

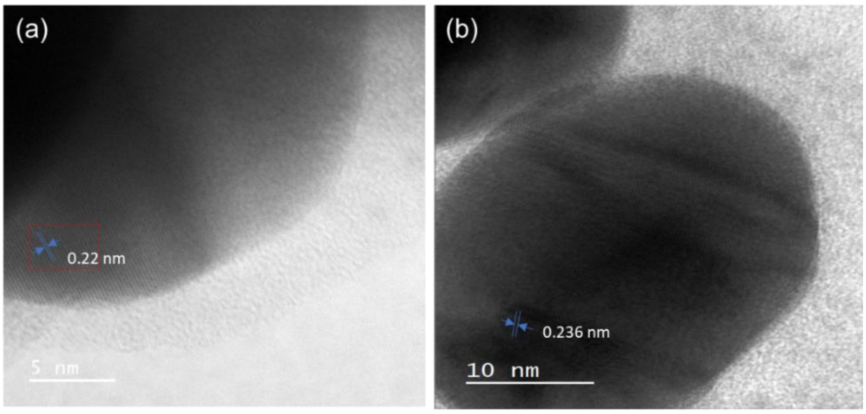

Fig. S2. High-resolution transmission electron microscopy (HR-TEM) images of **Au-BODIPY-Pd** showing the d-spacing of (a) Pd(111) and (b) Au(111).

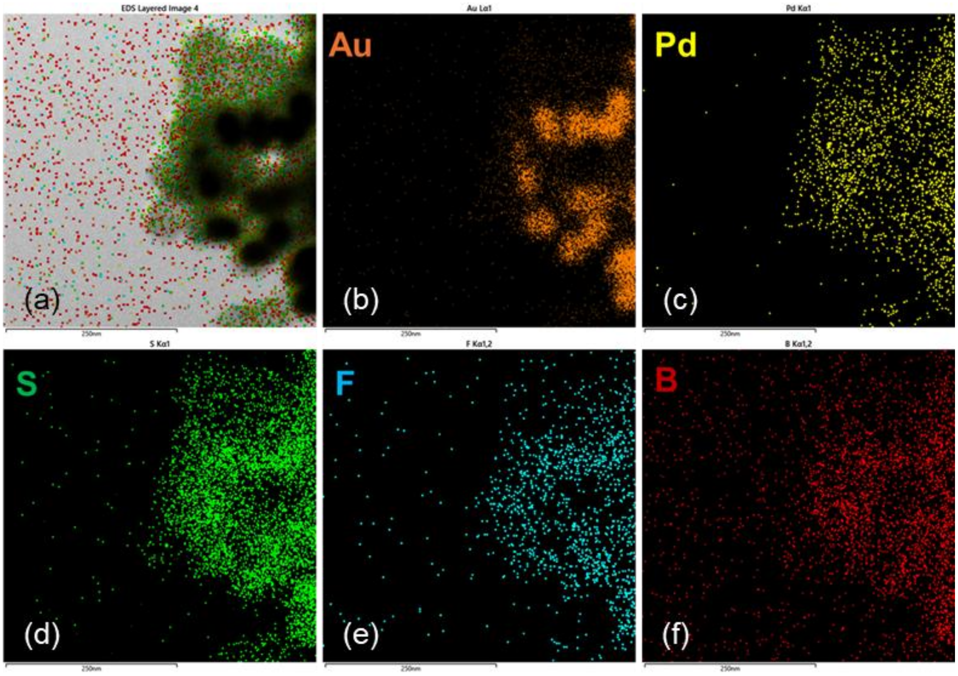

Fig. S3. (a) Overlaid bright-field and (b-f) individual elemental maps of **Au-BODIPY-Pd**. The scale bar is 250 nm.

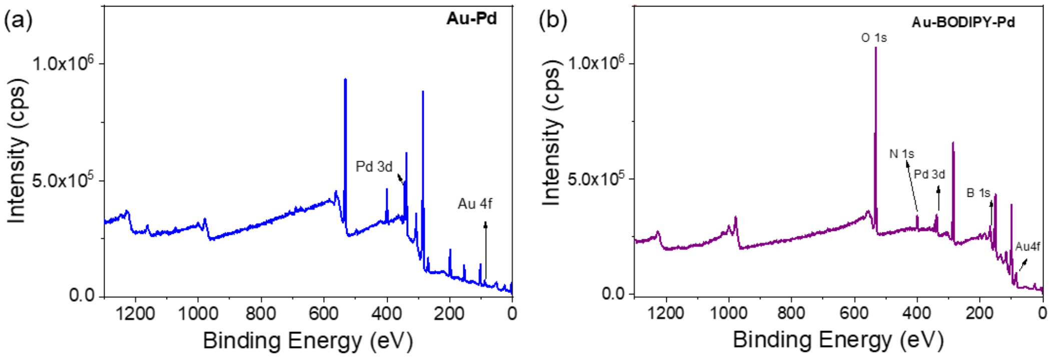

Fig. S4. Full scan XPS of (a) **Au-Pd** and (b) **Au-BODIPY-Pd**.

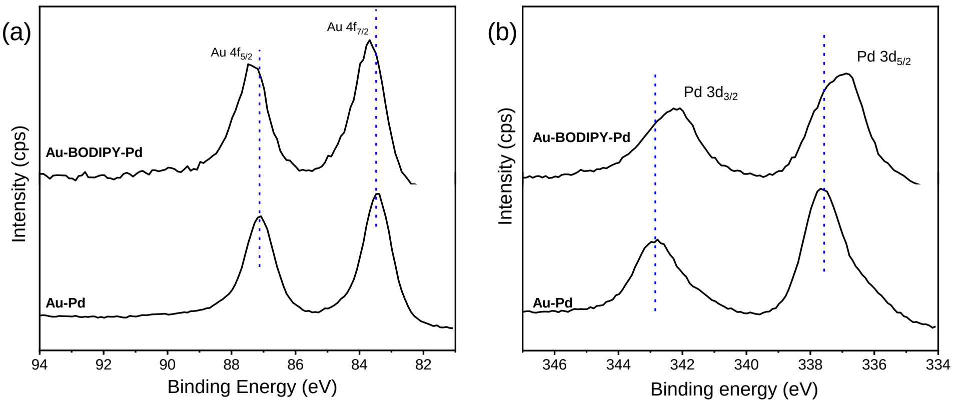

Fig. S5. XPS of (a) Au 4f and (b) Pd 3d of **Au-Pd** and **Au-BODIPY-Pd**.

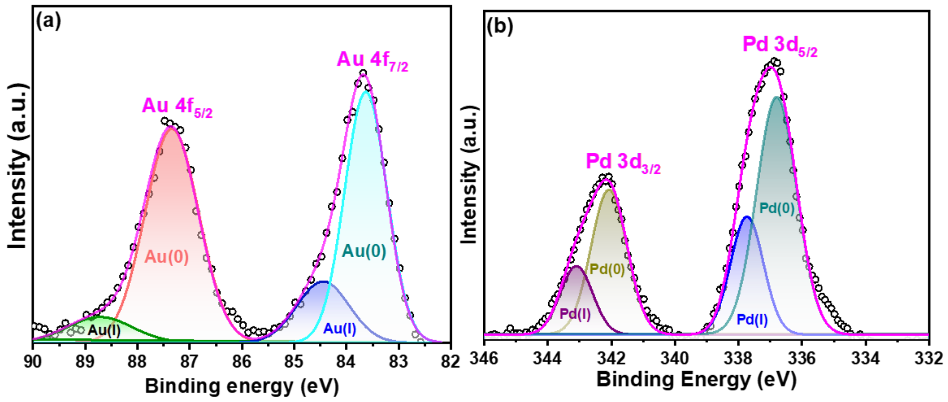

Fig. S6. Deconvoluted XPS data of (a) Au 4f and (b) Pd 3d in **Au-BODIPY-Pd**. Based on XPS data, the percentage of Au(0) and Au(I) were estimated as 82 and 18%, respectively whereas Pd(0) and Pd(II) were estimated as 71 and 29%, respectively.

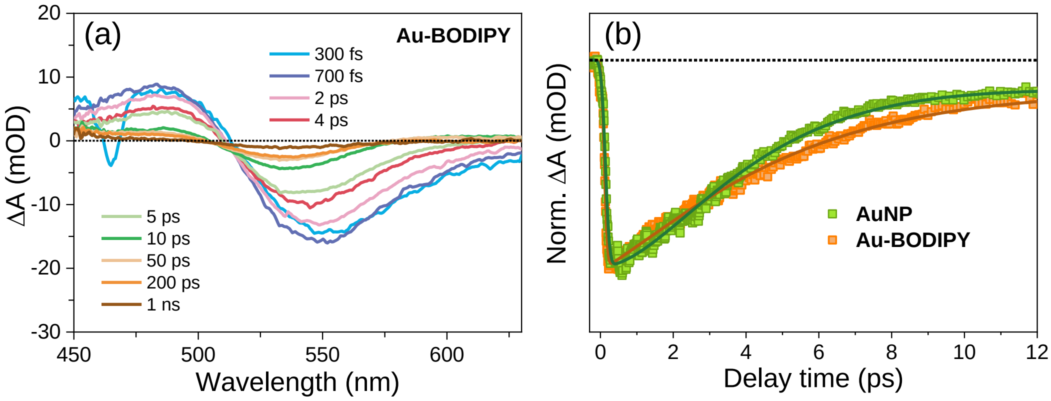

Fig. S7. (a) Transient absorption spectra of **Au-BODIPY** probed in the visible region after 400 nm photoexcitation. (b) Comparative kinetic profiles for **AuNP** and **Au-BODIPY** probed at the respective bleach maxima.

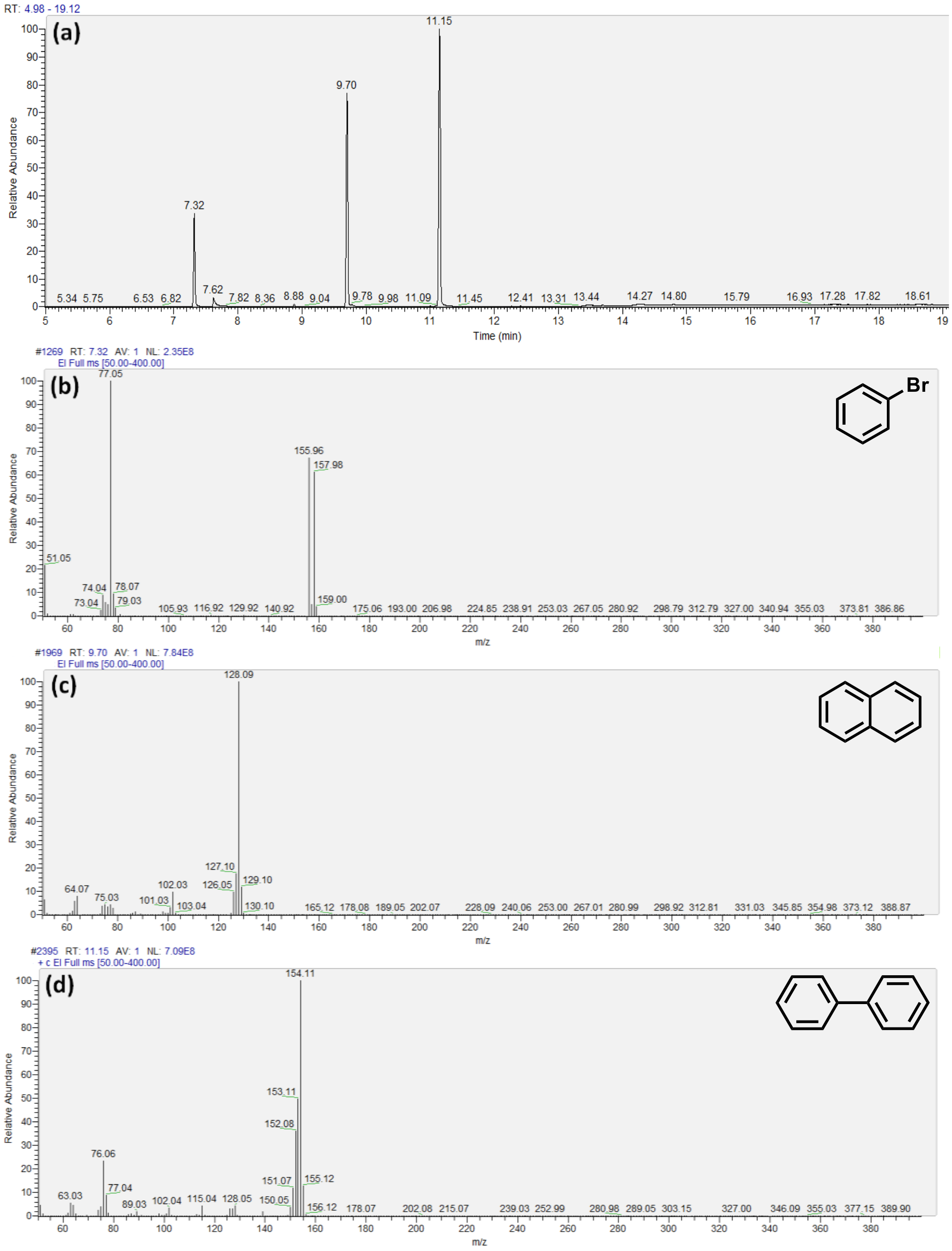

Fig. S8. (a) GC-FID chromatogram for entry 1 in Table 1 in the manuscript. (b-d) GC-MS spectra corresponding to FID chromatogram of (a).

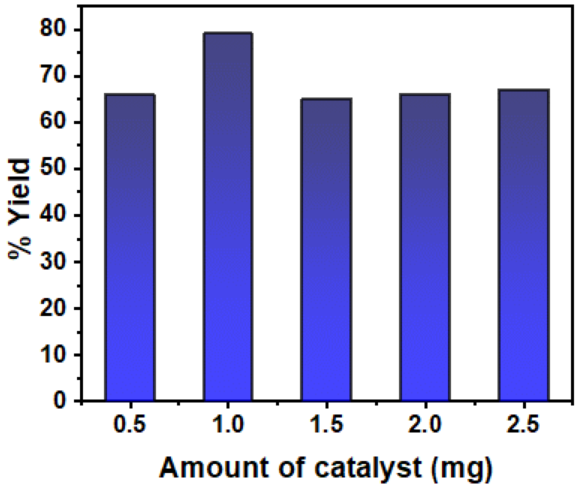

Fig. S9. The influence of catalyst loading on the product (1,1'-biphenyl) yield of a Suzuki coupling reaction with **Au-BODIPY-Pd**. Reaction conditions: 0.1 mmol bromobenzene, 0.1 mmol phenylboronic, 0.2 mmol K_2CO_3, 2 mL water, 25 °C, white light, 6 h.

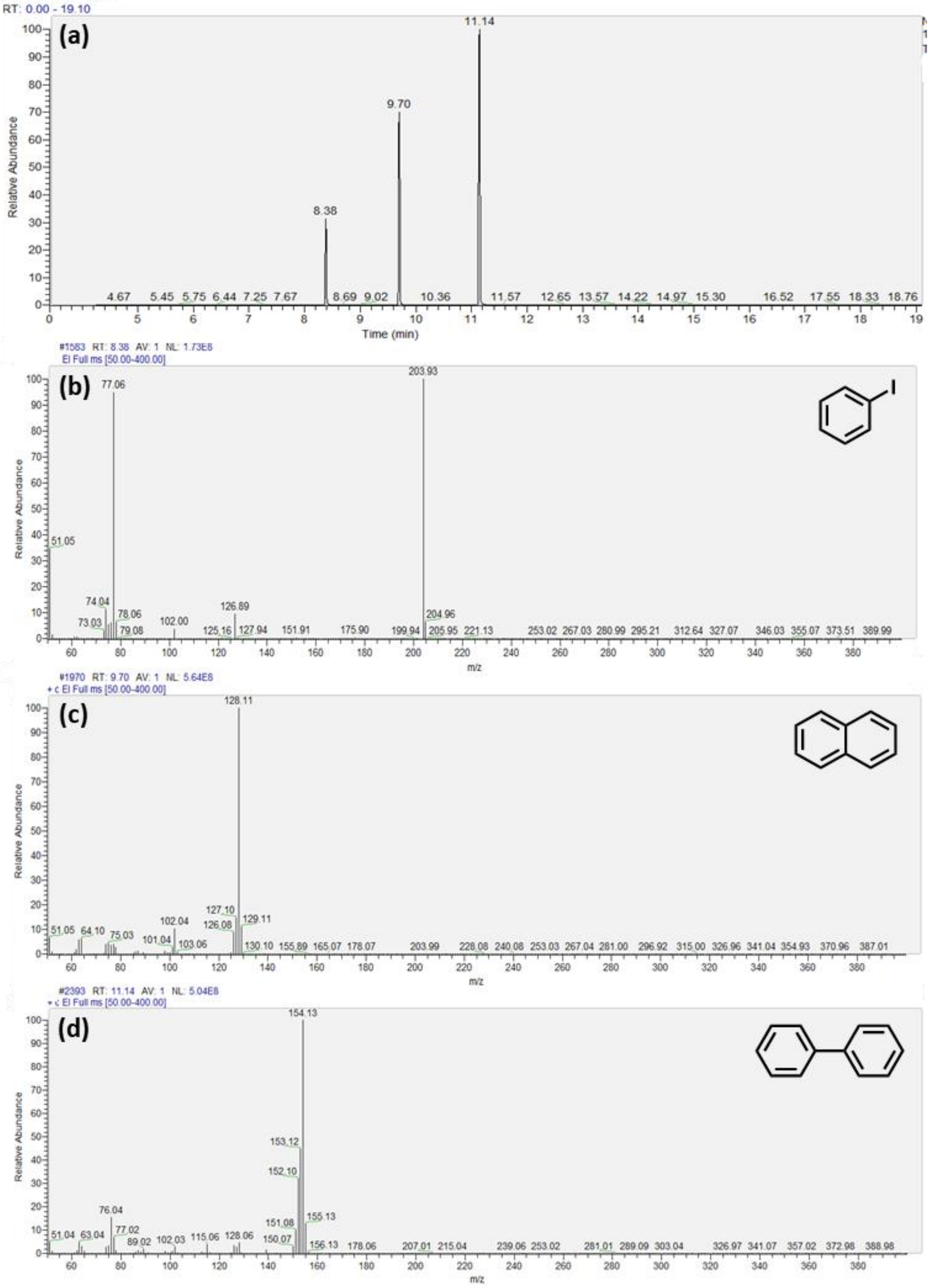

Fig. S10. (a) GC-FID chromatogram for entry 2 in Table 1 in the manuscript. (b-d) GC-MS spectra corresponding to FID chromatogram of (a).

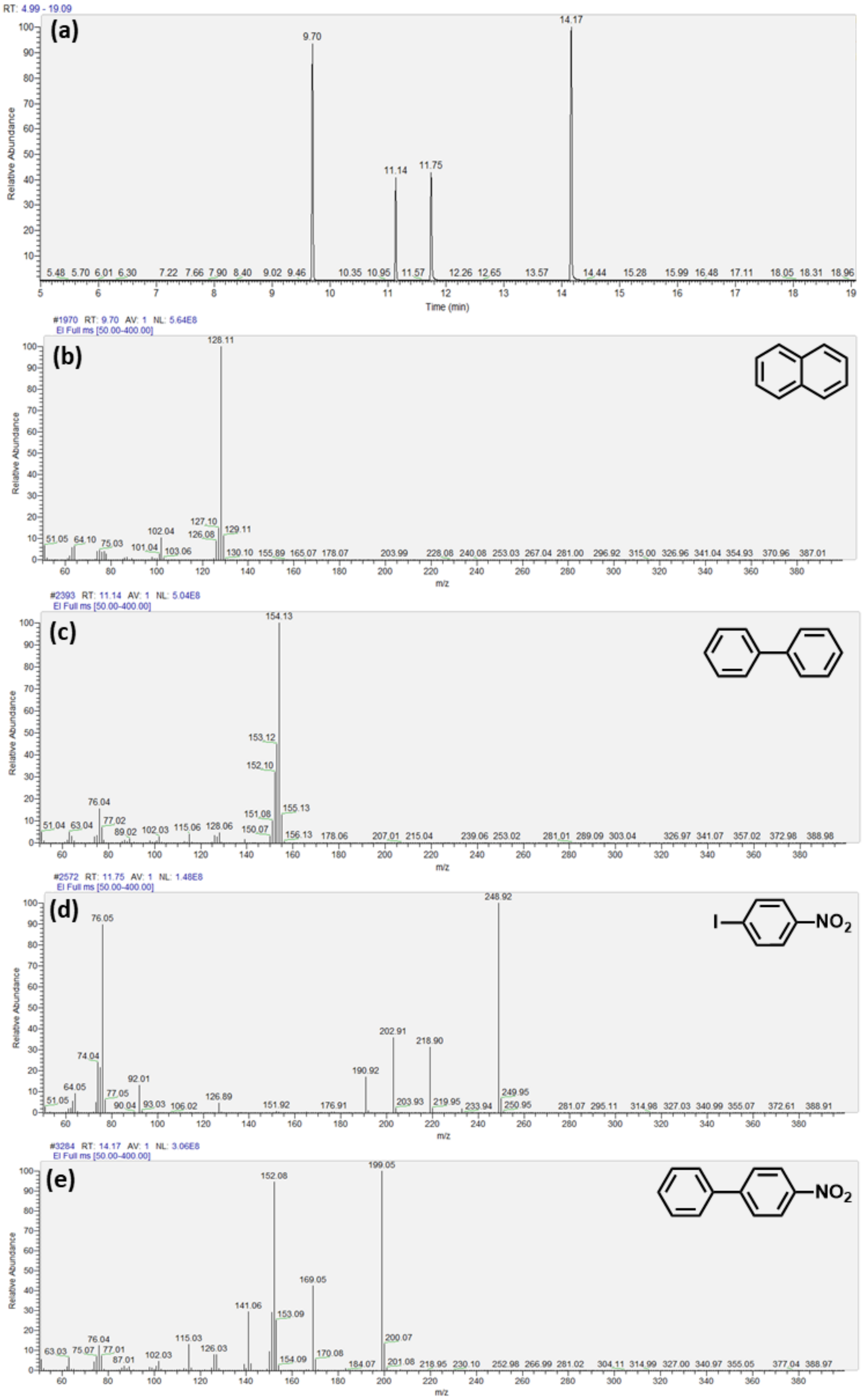

Fig. S11. (a) GC-FID chromatogram for entry 3 in Table 1 in the manuscript. (b-e) GC-MS spectra corresponding to GC-FID chromatogram of (a).

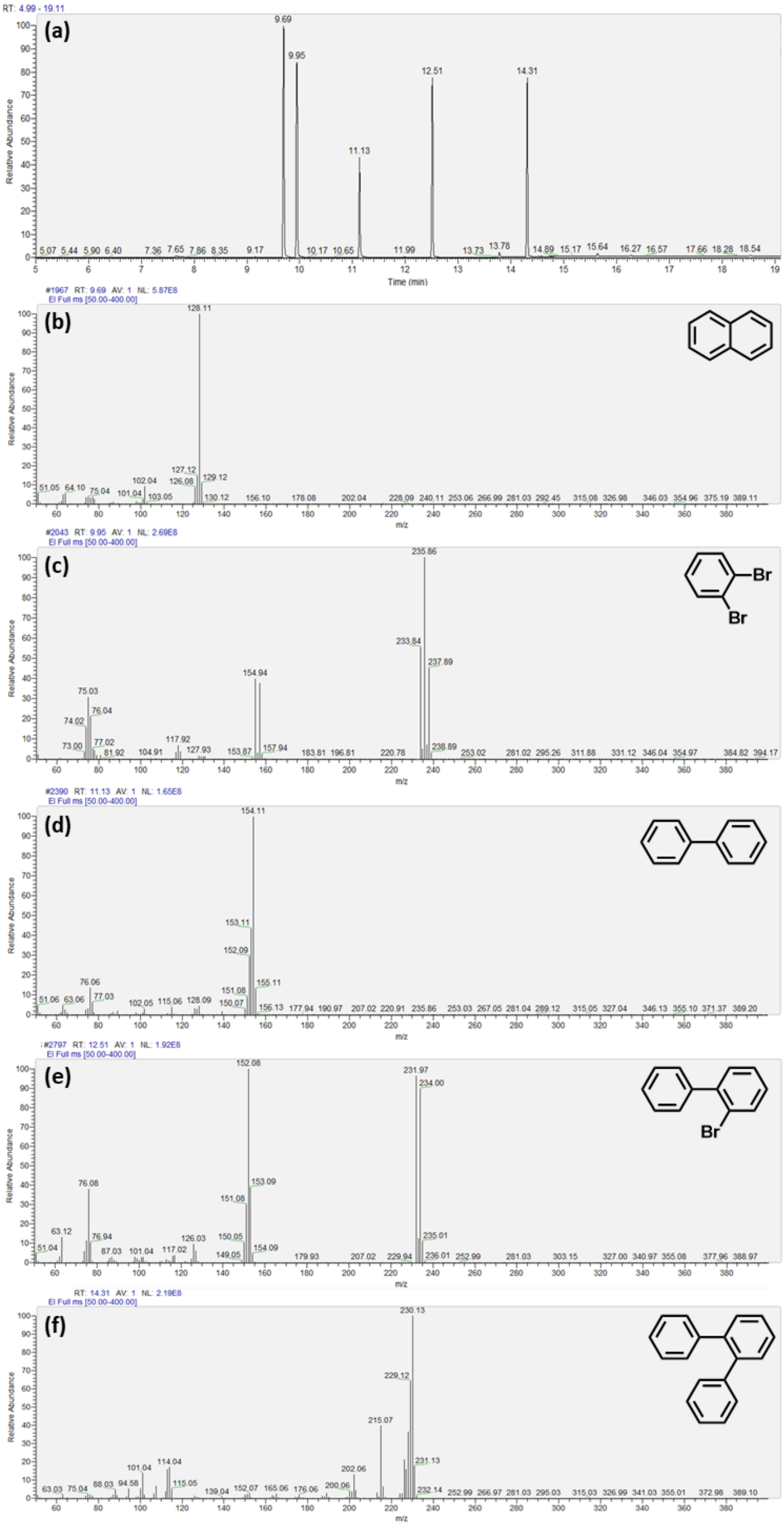

Fig. S12. (a) GC-FID chromatogram for entry 4 in Table 1 in the manuscript. (b-f) GC-MS spectra corresponding to GC-FID chromatogram of (a).

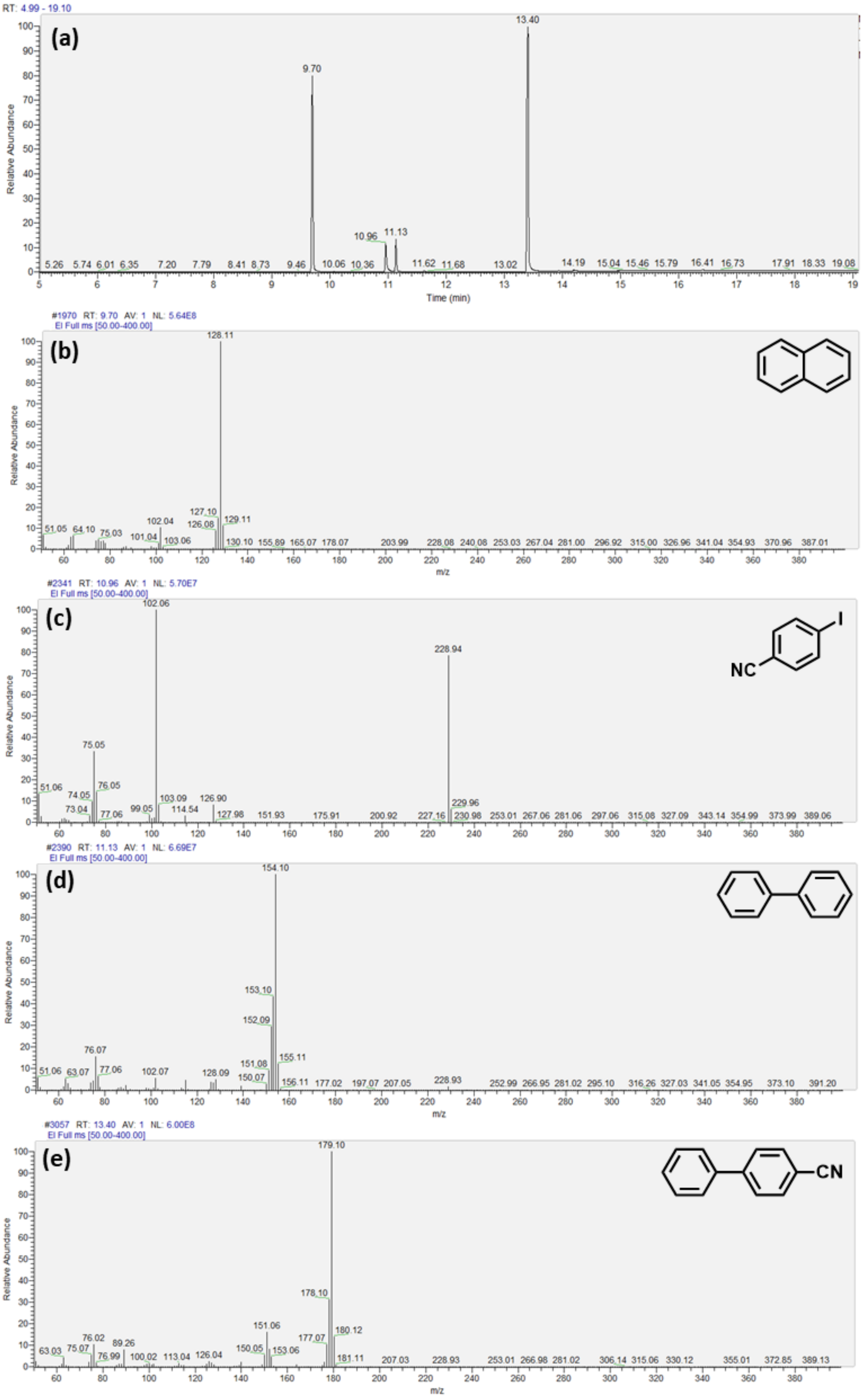

Fig. S13. (a) GC-FID chromatogram for entry 5 in Table 1 in the manuscript. (b-e) GC-MS spectra corresponding to GC-FID chromatogram of (a).

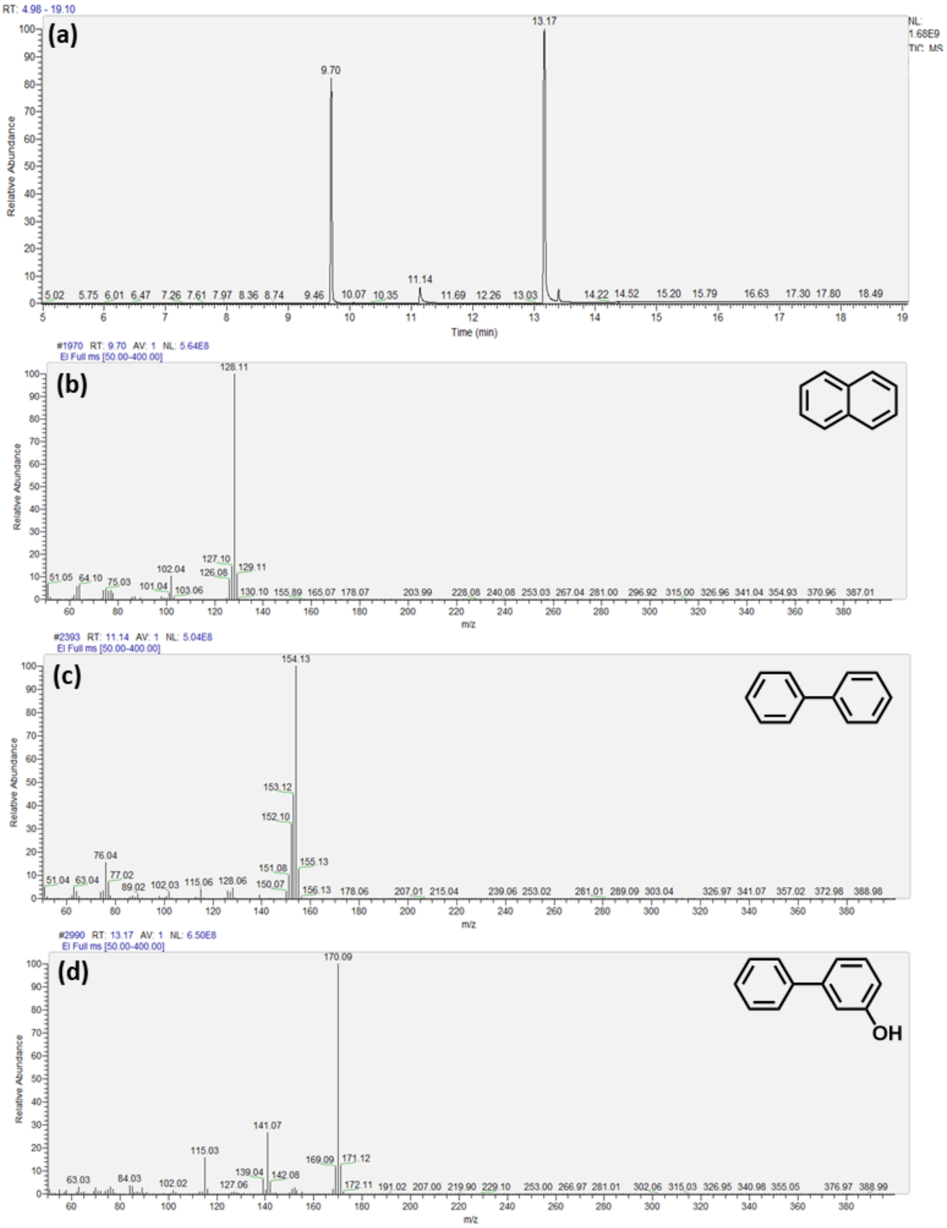

Fig. S14. (a) GC-FID chromatogram for entry 6 in Table 1 in the manuscript. (b-d) GC-MS spectra corresponding to GC-FID chromatogram of (a).

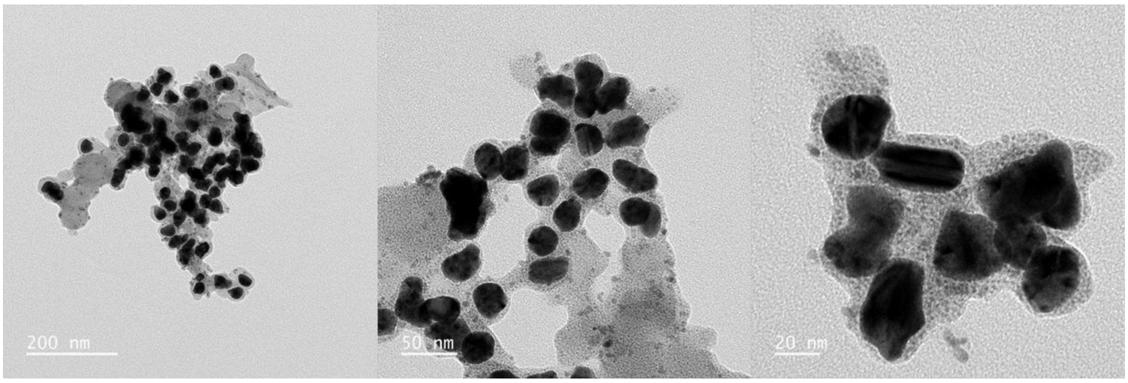

Fig. S15. Transmission electron microscopy (TEM) images of **Au-BODIPY-Pd** after three catalytic cycles.

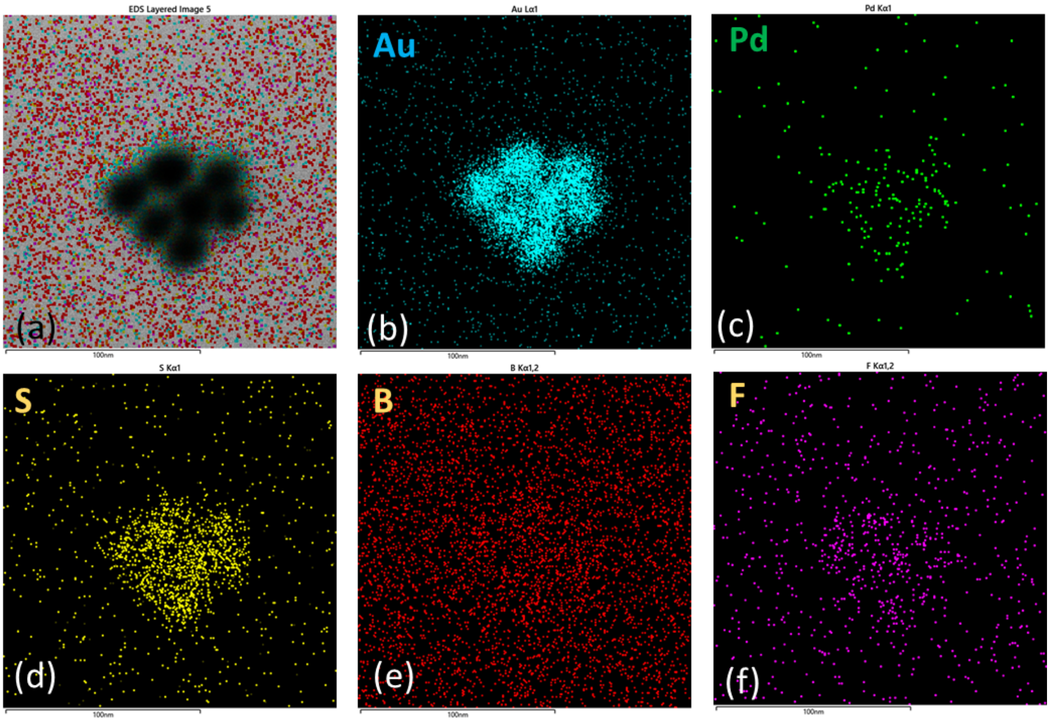

Fig. S16. (a) Overlaid bright-field and (b-f) individual elemental maps of **Au-BODIPY-Pd** after three catalytic cycles. The scale bar is 100 nm.

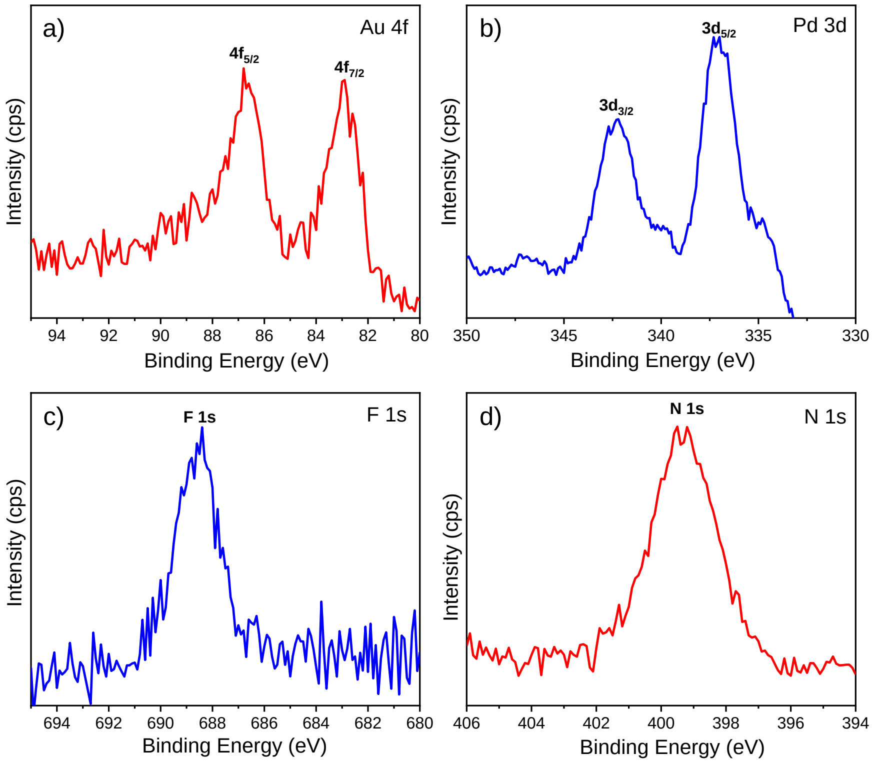

Fig. S17. (a-d) XPS spectra of Au, Pd, F, and N in **Au-BODIPY-Pd** after three catalytic cycles.

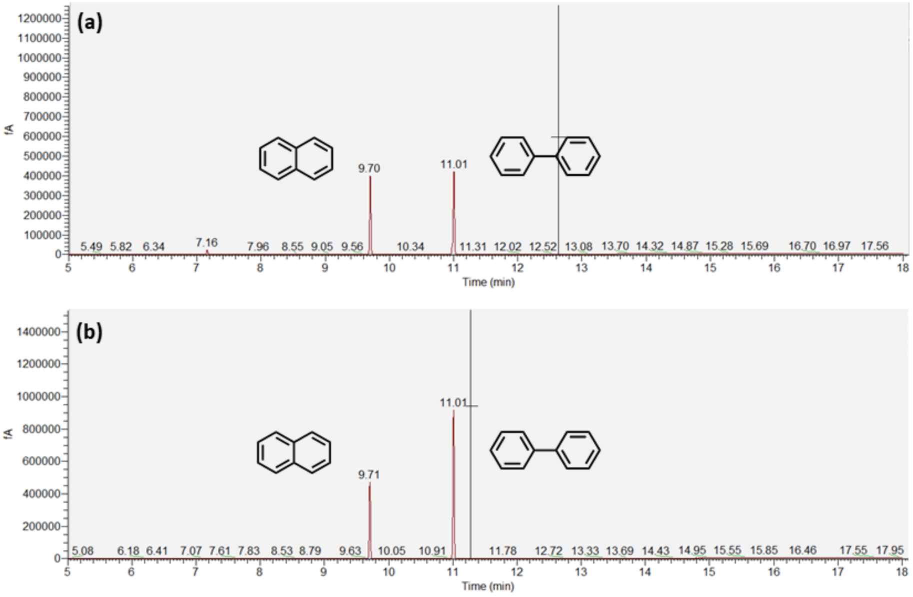

Fig. S18. (a) GC-FID chromatogram for the reaction between phenylboronic acid and bromobenzene catalysed by **Au-Pd**. (b) GC-FID chromatogram of 1,1-biphenyl standard. The peak at 9.70 minutes corresponds to naphthalene (internal standard), and the peak at 11.01 minutes corresponds to the 1,1-biphenyl product. Reaction conditions: 0.1 mmol phenylboronic acid, 0.1 mmol bromobenzene, 1 mg of **Au-Pd**, 0.2 mmol K_2CO_3, 2 mL water, 25 °C, white light, 6 h. Ratio of bromobenzene to **Au-Pd** is 15.7.