Supporting information

Pyridine-Based Hypercrosslinked Polymers as Support for Palladium Photocatalysts and Their Application in Suzuki–Miyaura Coupling Reactions

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Table S1. Details for the synthesis of pyridine-based POFs materials[a]

Entry	2,2'-bipyridine	Co-monomers	$AlCl_3$	Sample
1	0.817 g	Tetraphenylmethane (0.641 g)	4.269	P2
2	0.813 g	Triptycene (0.678 g)	4.261	P3
3	0.819 g	Tetraphenylethylene (0.665 g)	4.271	P4
4	0.811 g	Benzene (0.208 g)	4.265	P5
5	0.812 g	Anthracene (0.357 g)	4.270	P6
6	0.817 g	Pyrene (0.405 g)	4.267	P7
7	0.816 g	Perylene (0.505 g)	4.269	P8

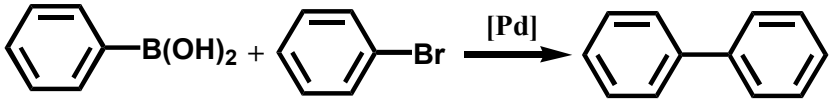
[a] Pyridine-based POFs materials were synthesized by employing the method of P1

Table S2. Textual properties of pyridine-based POFs materials

Entry	Sample	S_{BET}[a] (m^2g^{-1})	Pore Volume[b] (ml g^{-1})
1	P1	846	0.47
2	P2	795	0.98
3	P3	1166	0.57
4	P4	1412	0.75
5	P5	1153	0.58
6	P6	1344	0.79
7	P7	988	0.53
8	P8	1227	1.07

[a] Specific surface area calculated from nitrogen adsorption isotherms at 77.3 K using the BET equation. [b] Pore volume calculated from the nitrogen isotherms at P/P_0=0.995 and 77.3 K.

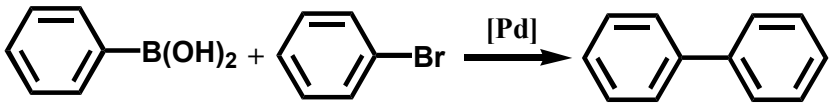
Table S3. Optimization of reaction conditions for S–M reactions over Pd/P6 catalyst. [a]



Entry	Base	Solvent (2mL)	Yield (%)[b]
1	$K_3PO_4·3H_2O$	$V_{Methanol}$:V_{H2O}=3:2	99.2
2	$K_3PO_4·3H_2O$	V_{DMF}:V_{H2O}=3:2	74.7
3	$K_3PO_4·3H_2O$	V_{DCM}:V_{H2O}=3:2	76.9
4	$K_3PO_4·3H_2O$	$V_{1,4\text{-dioxane}}$:V_{H2O}=3:2	87.7
5	$K_3PO_4·3H_2O$	$V_{Acetonitrile}$:V_{H2O}=3:2	75.0
6	$K_3PO_4·3H_2O$	$V_{Ethylene\ acetate}$:V_{H2O}=3:2	70.4
7	$K_3PO_4·3H_2O$	V_{CHCl3}:V_{H2O}=3:2	73.7
8	$K_3PO_4·3H_2O$	V_{EtOH}:V_{H2O}=3:2	96.6
9	KOH	V_{EtOH}:V_{H2O}=3:2	89.4
10	$NaH_2PO_4·2H_2O$	V_{EtOH}:V_{H2O}=3:2	78.7
11	CH_3COONa	V_{EtOH}:V_{H2O}=3:2	90.0
12	CH_3ONa	V_{EtOH}:V_{H2O}=3:2	93.0
13	$NaHCO_3$	V_{EtOH}:V_{H2O}=3:2	63.7
14	K_2CO_3	V_{EtOH}:V_{H2O}=3:2	95.0
15[c]	$K_3PO_4·3H_2O$	V_{EtOH}:V_{H2O}=3:2	-
16[d]	-	V_{EtOH}:V_{H2O}=3:2	-
17[e]	$K_3PO_4·3H_2O$	V_{EtOH}:V_{H2O}=3:2	0.1

[a] Reactions were carried out under blue light irradiation in mixed solvent at room temperature for 3 h with the reaction components in the following ratio: bromobenzene (mol)/phenylboronic acid (mol)/base (mol)/Pd (mol) = 1.0:1.5:3.0:0.00003. [b] Isolated yield of product. [c] P6 as catalyst (i.e., without Pd). [d] No $K_3PO_4·3H_2O$ was used. [e] In darkness.

Table S4. Activity contrast of Suzuki reactions over the prepared Pd catalysts. [a]



Entry	Catalysts	Pd Content	Yield (%)[b]	TOF (h^{-1})
1	Pd/P1	0.34%	97.3	1015
2	Pd/P2	0.85%	97.2	406
3	Pd/P3	0.23%	86.6	1336
4	Pd/P4	0.20%	90.4	1603
5	Pd/P5	0.16%	90.3	2002
6	Pd/P6	0.16%	99.2	2198
7	Pd/P7	0.19%	93.7	1749
8	Pd/P8	1.20%	95.9	284

[a] Reactions were carried out under blue light irradiation in methanol/H_2O mixed solvent at room temperature for 3 h with the reaction components in the following ratio: bromobenzene (mol)/phenylboronic acid (mol)/$K_3PO_4 \cdot 3H_2O$ (mol) /Pd (mol) =1.0:1.5:3.0: 0.00003. [b] Isolated yield of product.

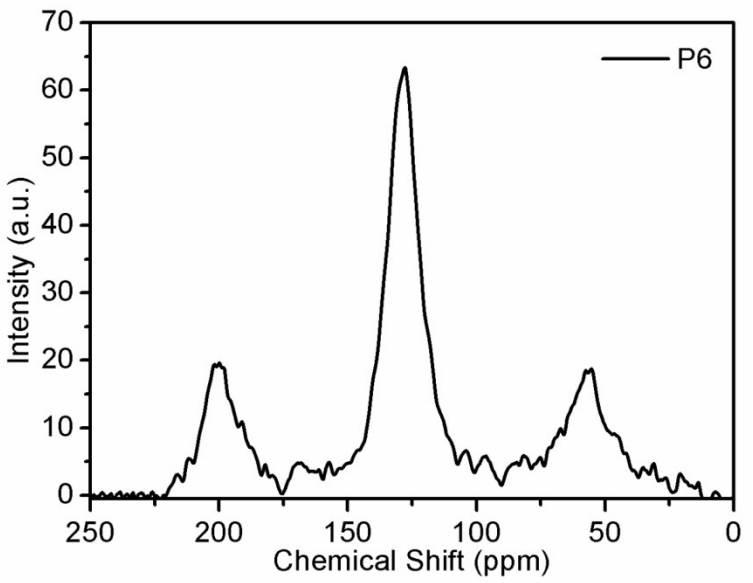


Figure S1. ^{13}C MAS NMR spectrum of polymer P6 in solid state

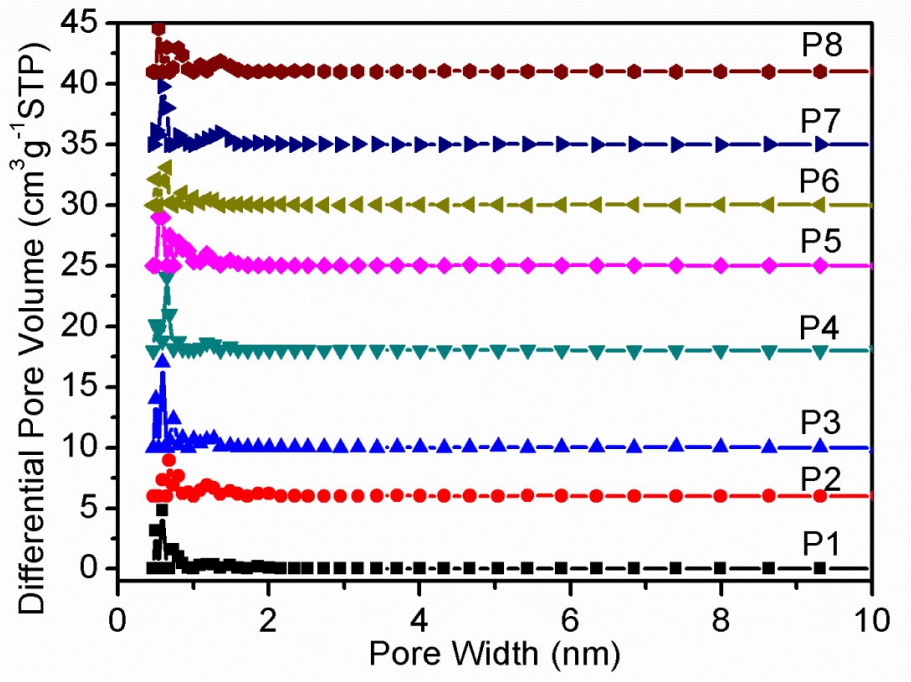


Figure S2. Pore width of the prepared pyridine-based POFs materials

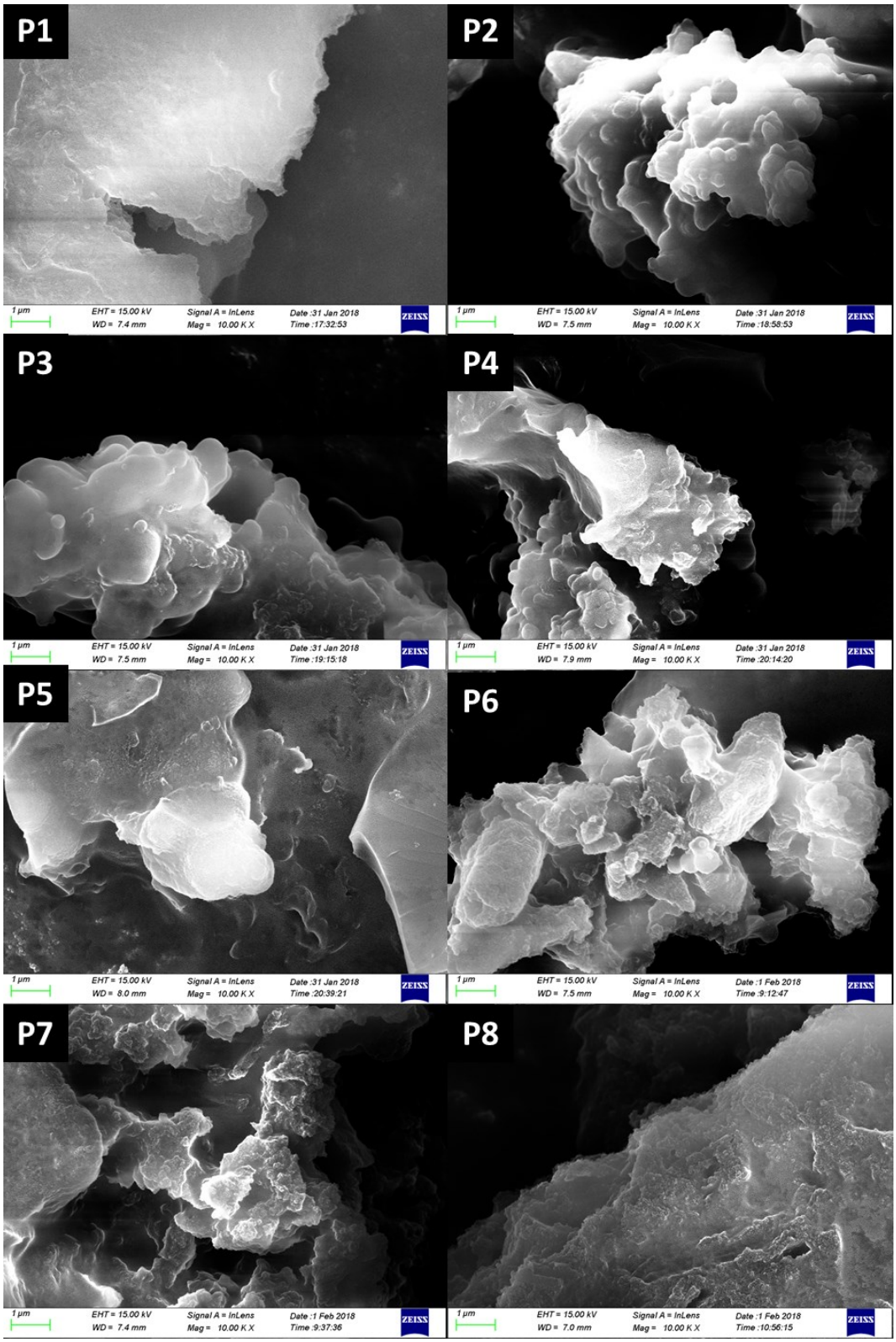


Figure S3. SEM images of the prepared pyridine-based POFs materials

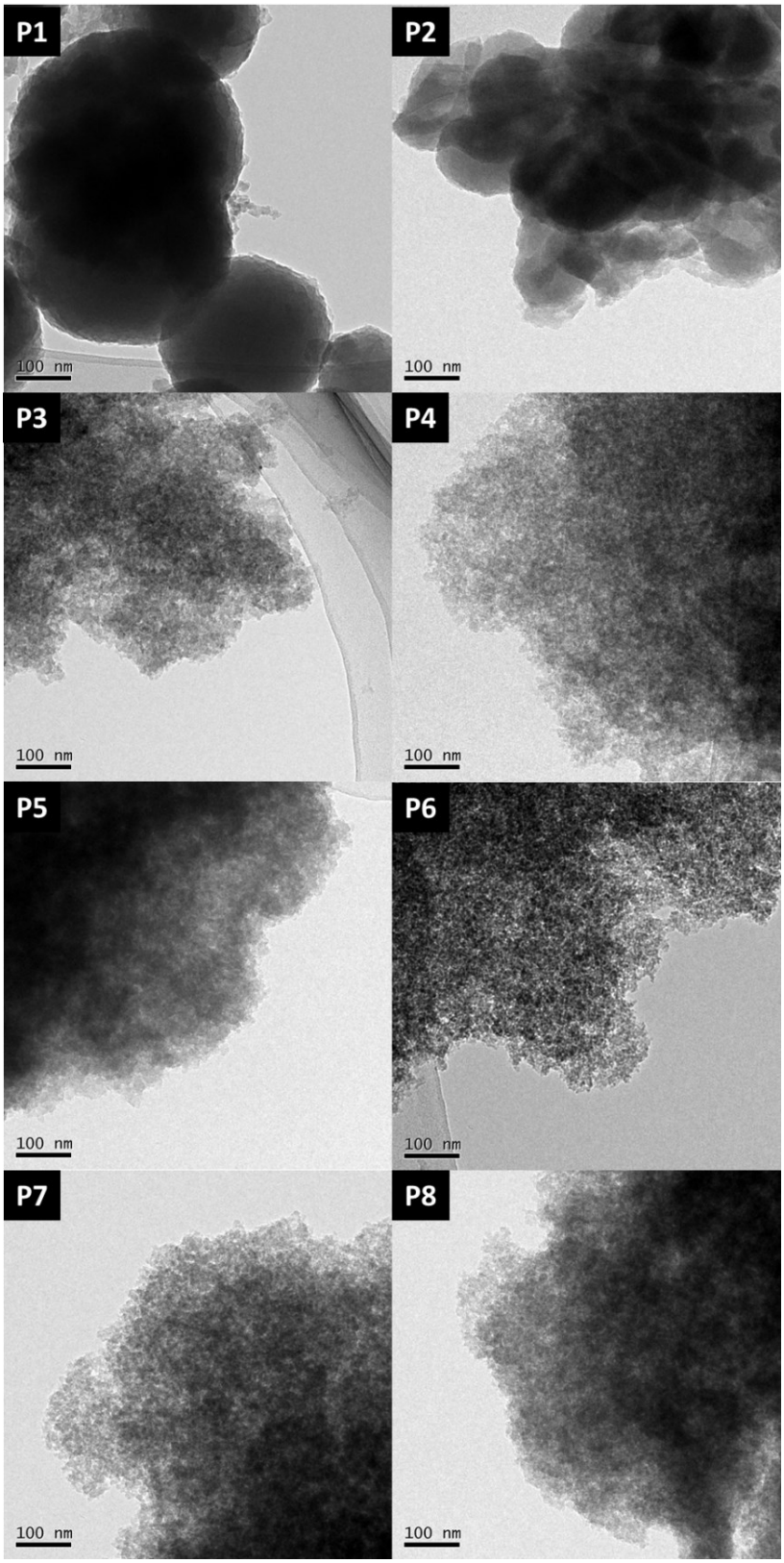


Figure S4. TEM images of the prepared pyridine-based POFs materials

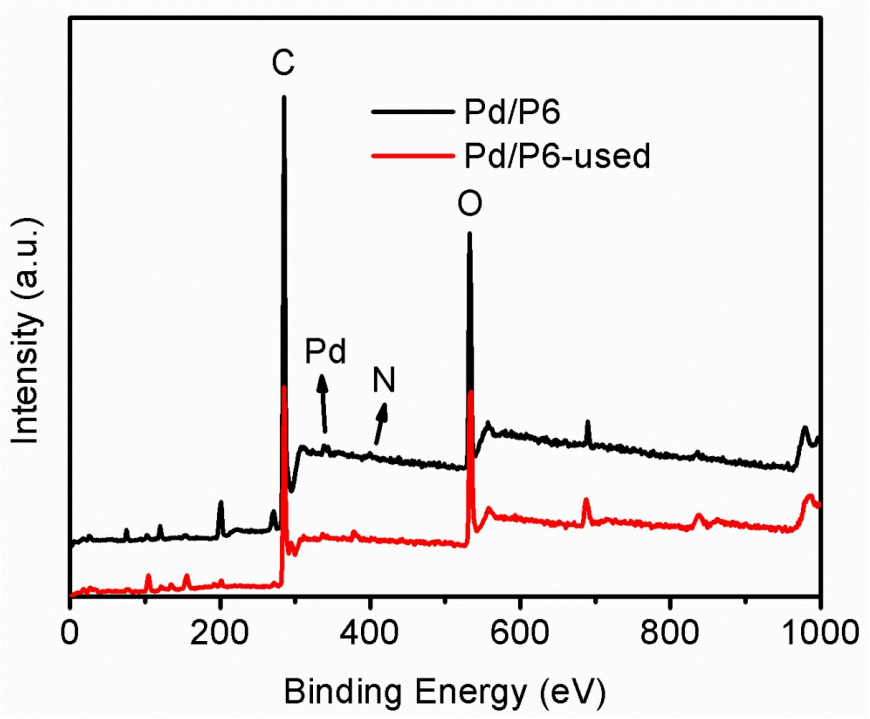
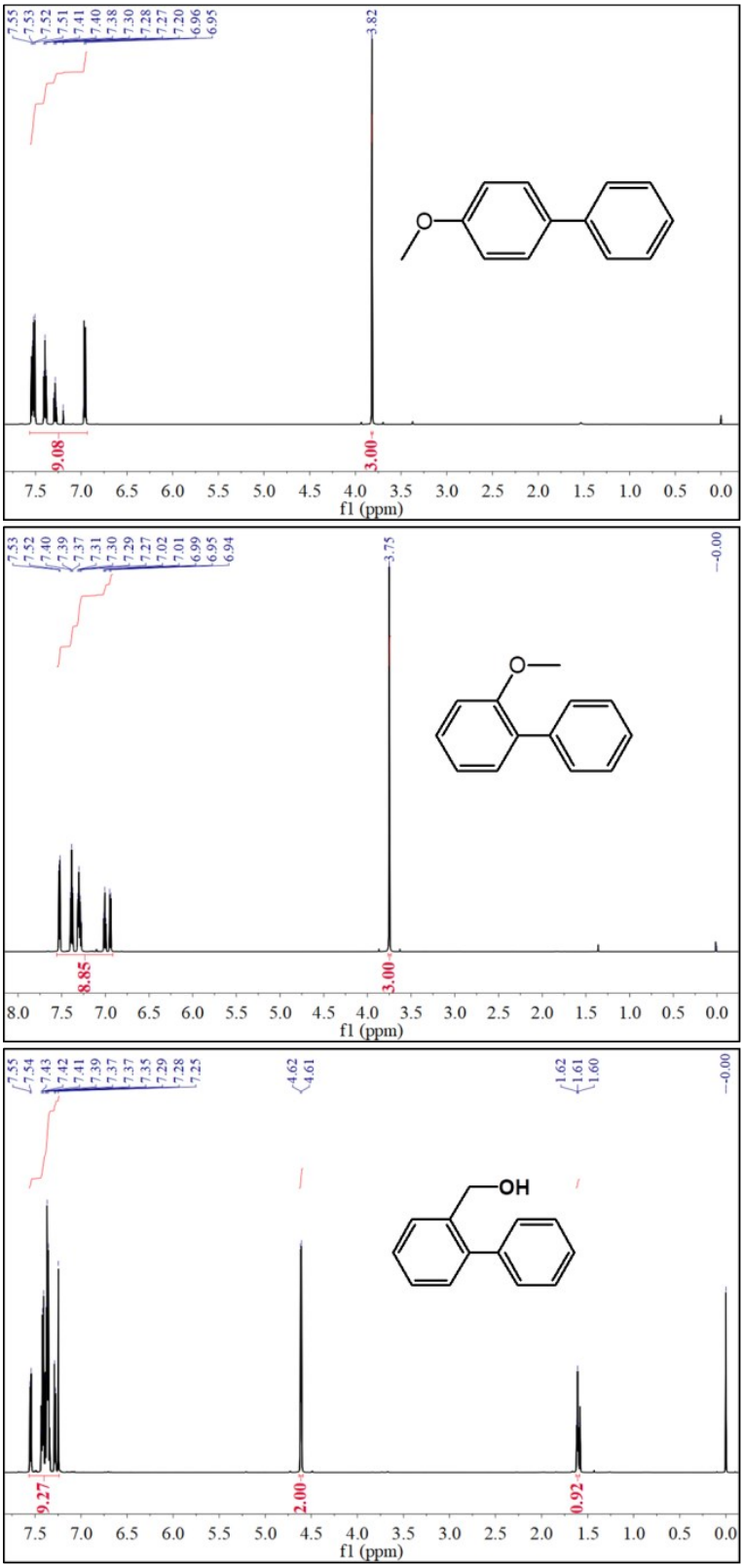
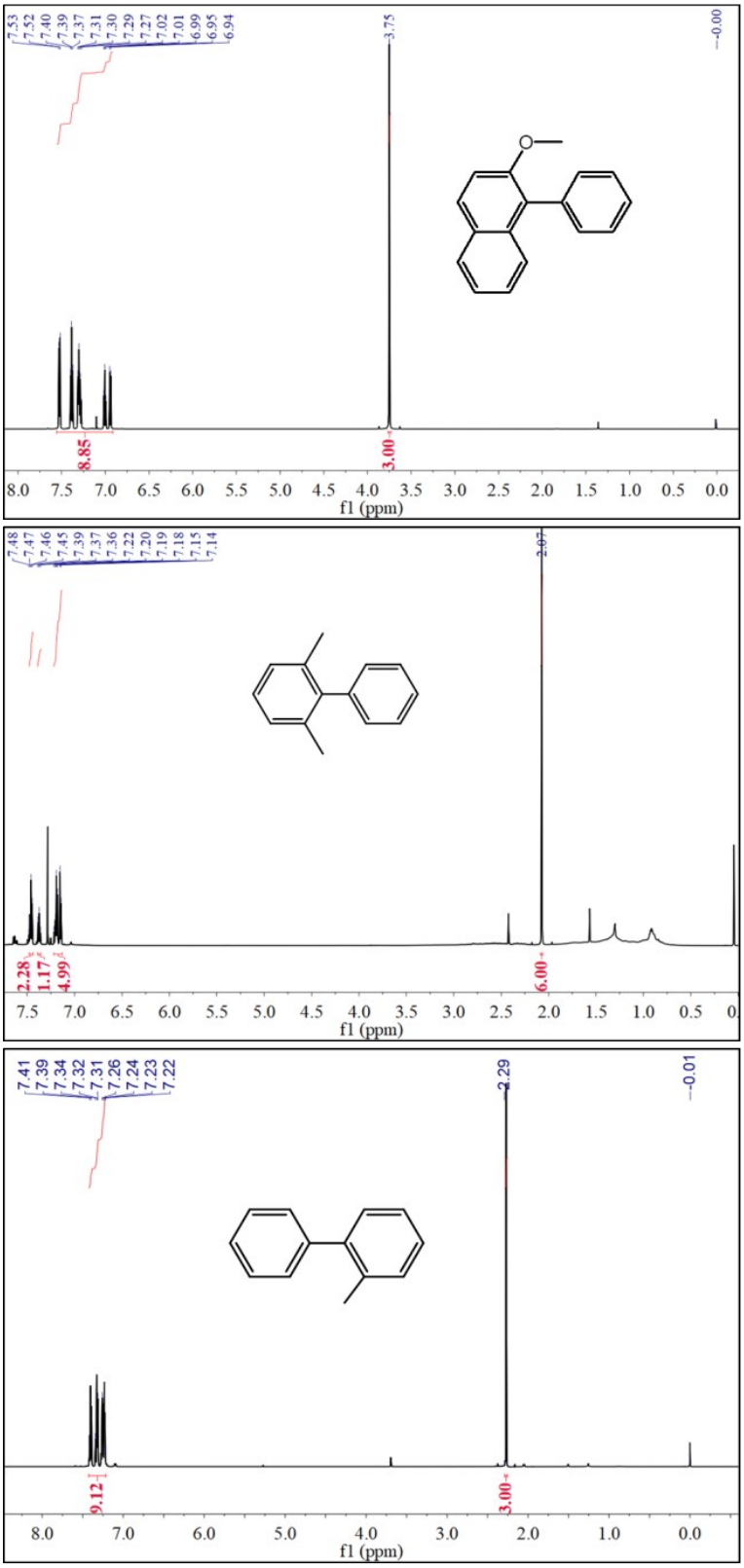
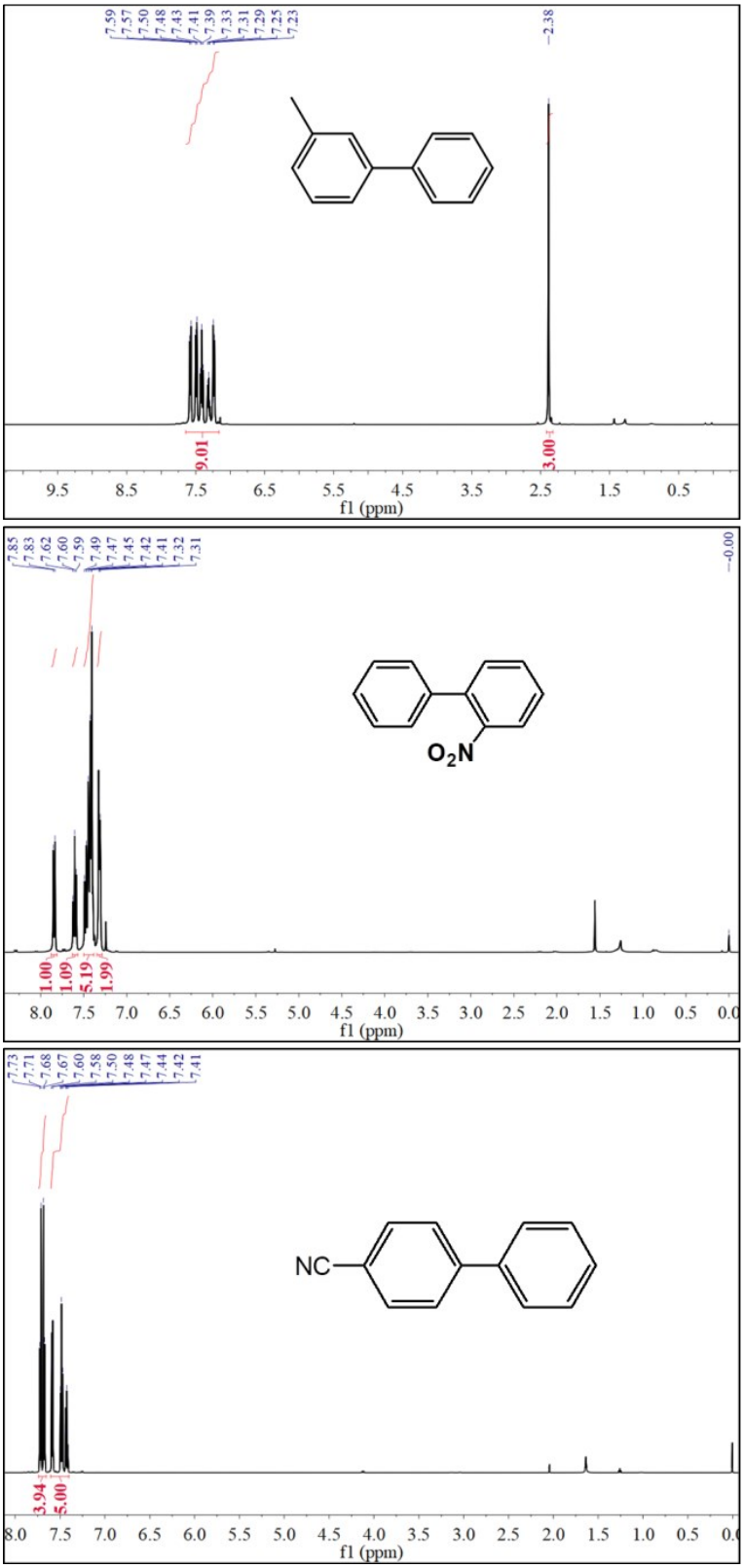


Figure S5. XPS full scan spectra of fresh and used Pd/P6 catalyst


7.55
7.53
7.52
7.51
7.41
7.40
7.38
7.30
7.28
7.27
7.20
6.96
6.95
3.82
9.08
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
7.53
7.52
7.40
7.39
7.37
7.31
7.30
7.29
7.27
7.02
7.01
6.99
6.95
6.94
3.75
-0.00
8.85
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
7.55
7.54
7.43
7.42
7.41
7.39
7.37
7.37
7.35
7.29
7.28
7.25
4.62
4.61
1.62
1.61
1.60
-0.00
OH
9.27
2.00
0.92
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.53
7.52
7.40
7.39
7.37
7.31
7.30
7.29
7.27
7.02
7.01
6.99
6.95
6.94
3.75
-0.00
8.85
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
7.48
7.47
7.46
7.45
7.39
7.37
7.36
7.22
7.20
7.19
7.18
7.15
7.14
2.07
2.28
1.17
4.99
6.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
7.41
7.39
7.34
7.32
7.31
7.26
7.24
7.23
7.22
2.29
-0.01
9.12
3.00
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


7.59
7.57
7.50
7.48
7.43
7.41
7.39
7.33
7.31
7.29
7.25
7.23
2.38
9.01
3.00
f1 (ppm)
7.85
7.83
7.62
7.60
7.59
7.49
7.47
7.45
7.42
7.41
7.32
7.31
0.00
O2N
1.00
1.09
5.19
1.99
f1 (ppm)
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7.71
7.68
7.67
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5.00
f1 (ppm)

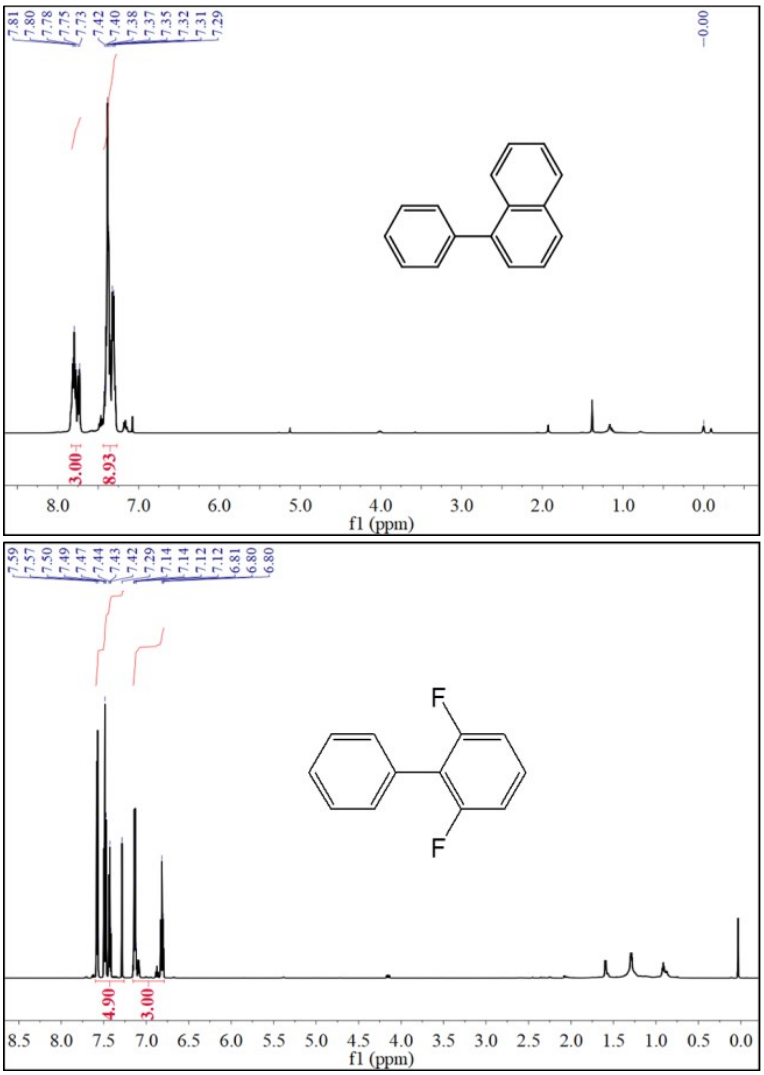

Figure S5. ^{1}H-NMR spectrums of products for S–M coupling reaction.