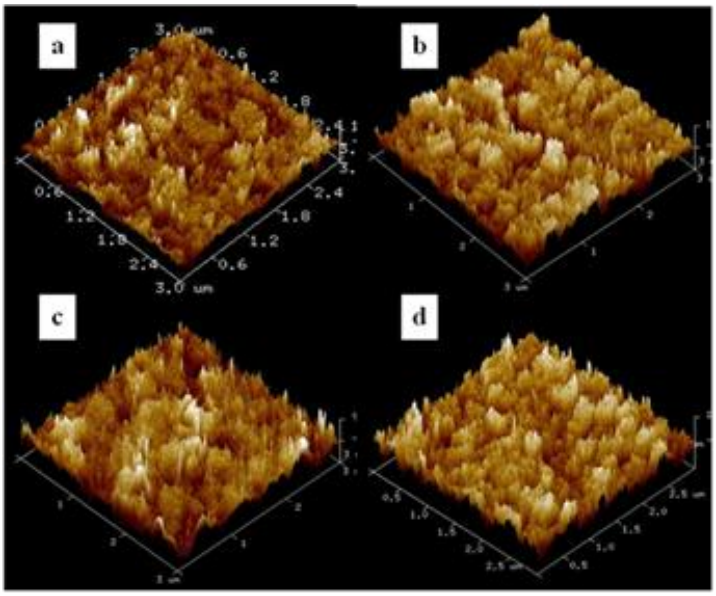


Figure S1 AFM images of surface topographies of prepared palladium catalyst supported on ITO and its precursors. a) **ITO@OH** (hydrophilic treatment), b) **ITO@APTES** (silanization), c) **ITO@Thi** (thienyl Schiff base graft) and d) **ITO@Pd-Thi** (Pd-thienyl Schiff based complex grafted).

Table S1 Data of Rms of **ITO@OH**, **ITO@APTES**, **ITO@Thi** and **ITO@Pd-Thi** monolayers.

Monolayer	**ITO@OH**	**ITO@APTES**	**ITO@Thi**	**ITO@Pd-Thi**
Rms(nm)	48.4	34.4	41.5	29.4

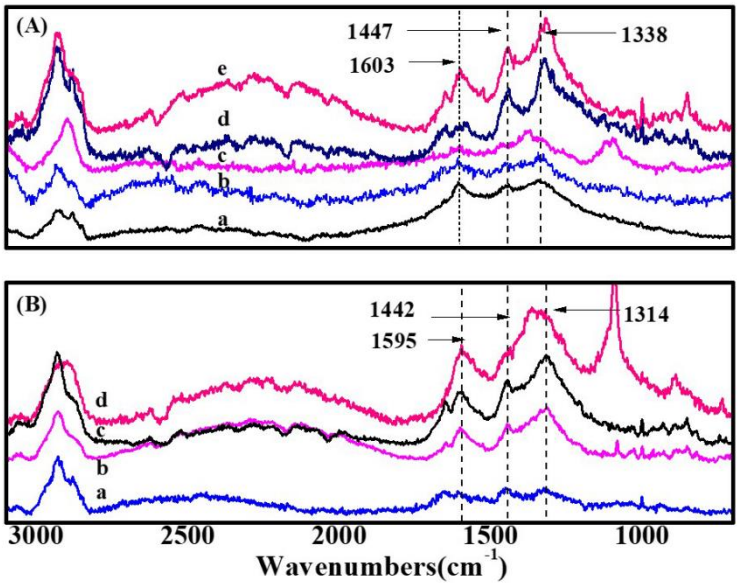


Figure S2 Raman spectra of (A) a, **ITO@Thi**; b, **ITO@PThi**; c, **ITO@PTT**; d, **ITO@PTF**; e, **ITO@PTM**. (B) a, **ITO@Pd-PThi**; b, **ITO@Pd-PTT**; c, **ITO@Pd-PTF**; d, **ITO@Pd-PTE**.

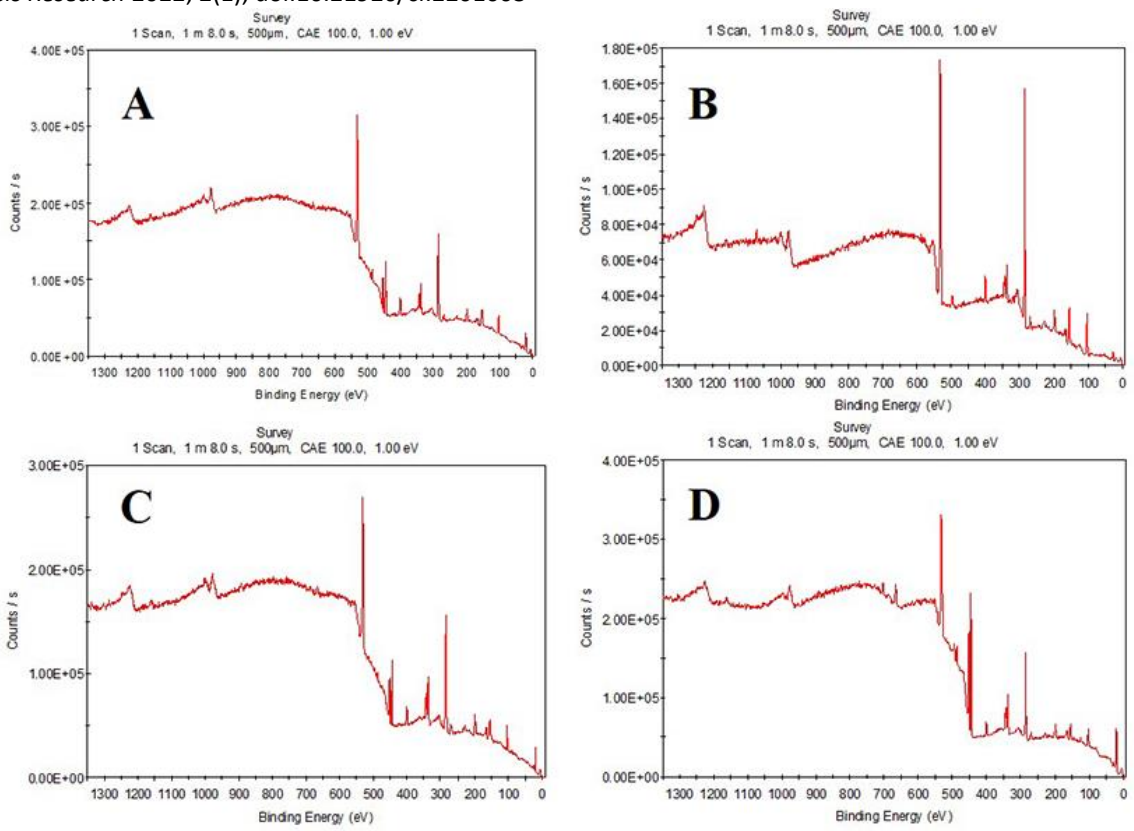


Figure S3 XPS survey spectrum of (A) **ITO@Pd-PThi**, (B) **ITO@Pd-PTT**, (C) **ITO@Pd-PTF** and (D) **ITO@Pd-PTM**.

Table S2 Positions of BE peak in catalyst monolayers.

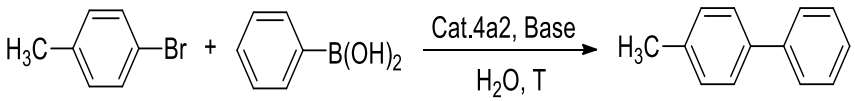
Cat.	Pd 3d5/2	Pd 3d3/2	N1s	S2p	Cl2p	Si2p
ITO@Pd-PThi	343.02	337.67	400.22	164.46	198.31	102.62
ITO@Pd-PTT	343.17	337.87	399.92	164.26	198.16	102.70
ITO@Pd-PTF	343.07	337.82	400.02	164.32	198.17	102.62
ITO@Pd-PTM	343.22	337.97	400.08	164.31	198.33	102.39

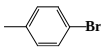
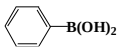
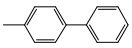
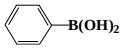
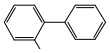
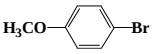
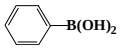
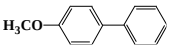
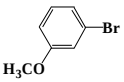
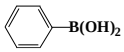
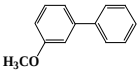
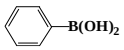
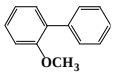
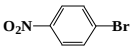
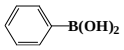
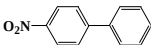
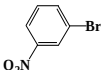
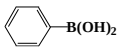
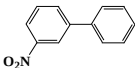
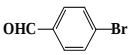
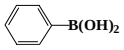
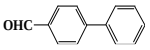
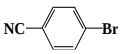
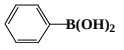
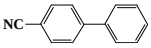
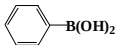
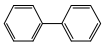
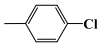
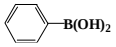
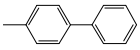
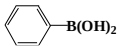
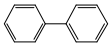
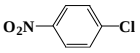
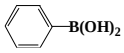
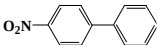
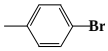
Table S3 Summaries of Pd contents of catalysts prepared[a].

Cat.	**ITO@Pd-Thi**	**ITO@Pd-PThi**	**ITO@Pd-PTT**	**ITO@Pd-PTF**	**ITO@Pd-PTM**
(10^{-9}) mol·cm^{-2}	1.12	1.08	1.10	1.11	1.05

[a]Substrates: 2.5cm*1 cm*0.1 cm.

Table S4 Suzuki coupling reaction of haloarense with phenylboronic acid[a].



Entry	Ar-X	Ar-$B(OH)_2$	Product	Yield (%) [b]
1				99
2				85
3				91
4				88
5				74
6				97
7				92
8				90
9				99
10				99
11				trace
12				trace
13				7
14				41
15				30
16				9
17				10
18				Trace

[a] Reaction condition: 4-Bromotoluene 0.25 mmol, PhB $(OH)_2$ 0.30 mmol, base 0.30 mmol, substrate: 2.5 cm*1 cm*0.1 cm (2.5 cm^2*1.11×10^{-9} mmol/cm^2), solvent 5.0 mL. Reaction time: 24 h.

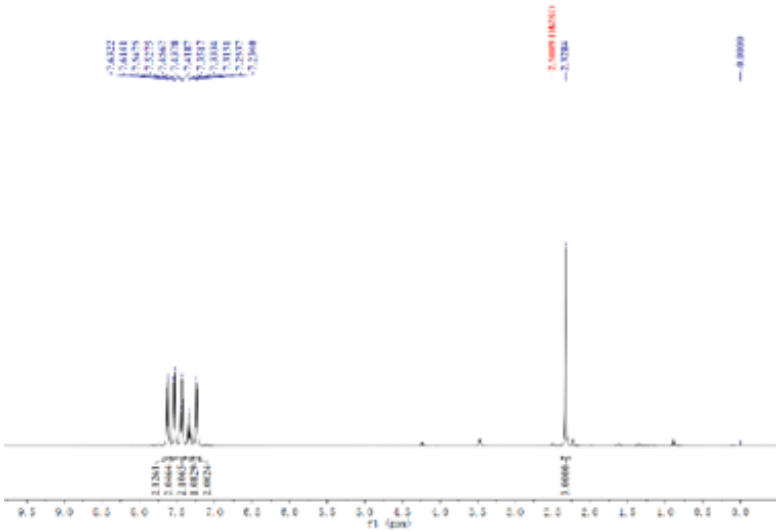
[b]Isolated yield.

Table S5 Comparisons of the results in Suzuki coupling reaction catalyzed by the catalysts supported on different supports.

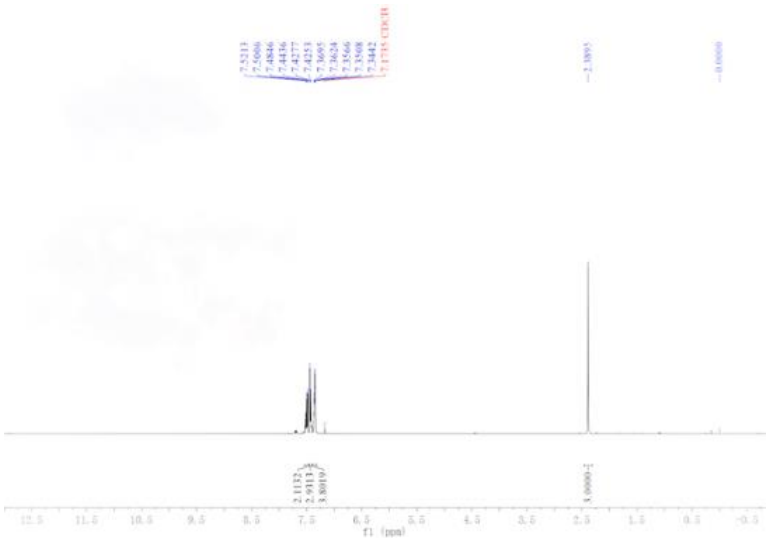
Entry	Catalyst	Reaction conditions	X	Yield (%)	TON (mol/mol$_{Pd}$)	Ref
This work	**ITO@Pd-PTF** (0.0022% mmol) (respect to the *p*-bromotoluene)	K_2CO_3, EtOH: H_2O, 60 °C, 24h.	Br(4-Me)	99[a]	45000	**This work**
1	**Poly-2a film** (0.17mmol%) (content of Pd, 0.5% respect to the iodoarene)	K_2CO_3, Toluene/ EtOH, 80 °C 40 h	I(2-F)	91	182	8
2	**ECP-B3TIE** (0.0051%mmol) (respect to the *p*-bromotoluene)	$K_3PO_4.7H_2O$, H_2O, TBAB, 40°C,48 h. SP=12 mN/m	Br(4-Me)	94	18345	17
3	**Poly-3-ITO** (0.17 mmol%) (content of Pd,0.5% respect to the iodoarene)	K_2CO_3, Toluene/ MOH, 85 °C 16h	Br(*P*-CN)	80	160	9

[a] Isolated yield.

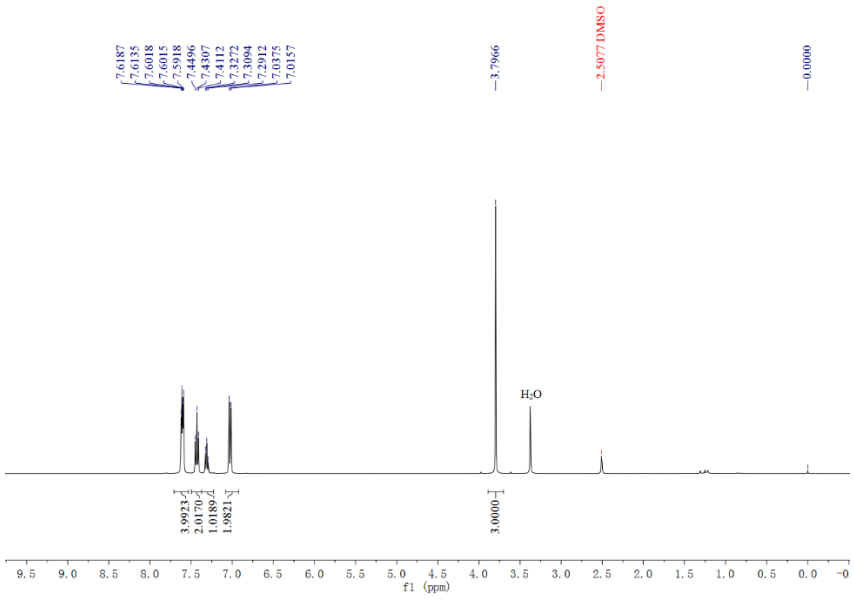
Additive: Characterization of coupling compounds in Suzuki coupling reaction



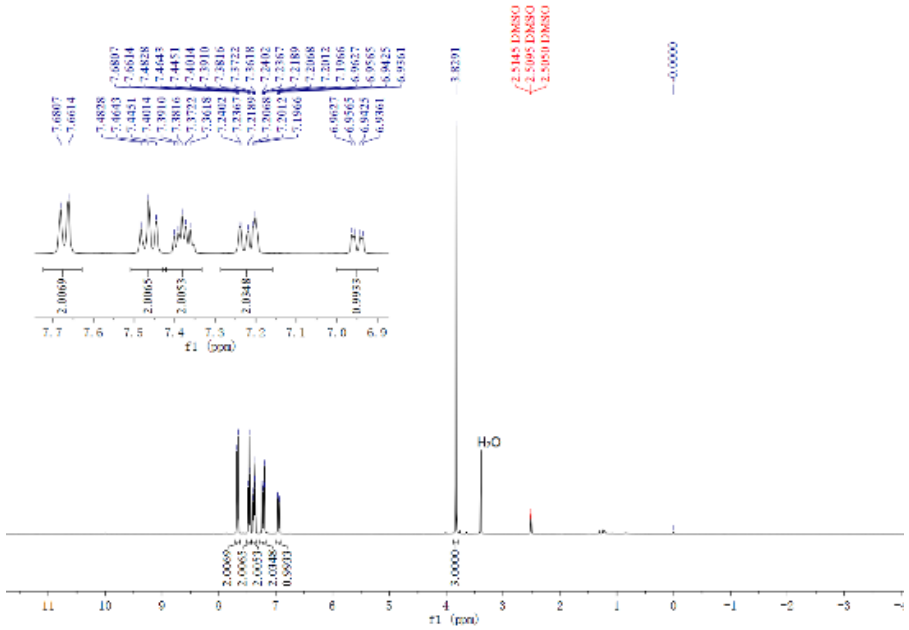
4-Methylbiphenyl (Table S4, Entry 1): ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 2.33(s, 3H), 7.24(d, J=7.88 Hz, 2H), 7.33(t, J=7.08 Hz, J= 7.32 Hz, 1H), 7.43(t, J=7.56 Hz, J= 7.64 Hz, 2H), 7.53(d, 6.40 Hz, 2H), 7.62(d, 7.24 Hz, 2H).



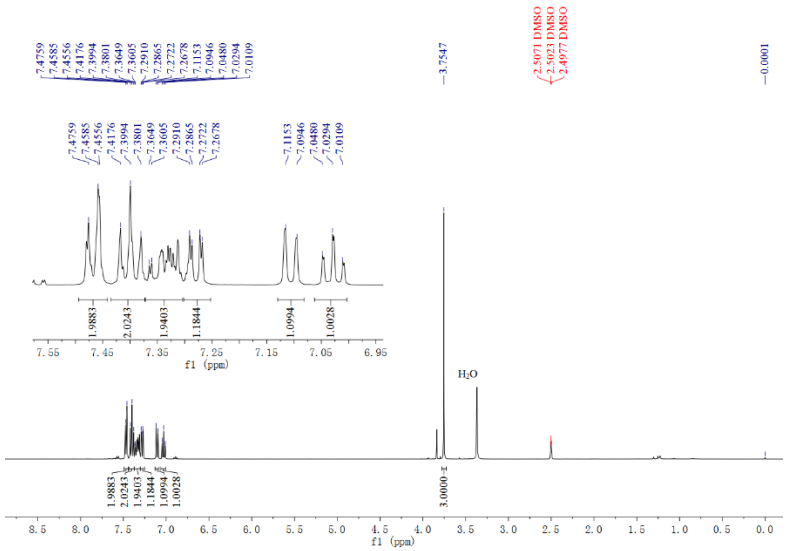
2-Methylbiphenyl(**Table S4, Entry 2):** ^{1}H NMR (400MHz, DMSO, δ ppm): 7.52-7.48(m, 2H), 7.44-7.42 (m, 3H), 7.36-7.34(m, 4H).



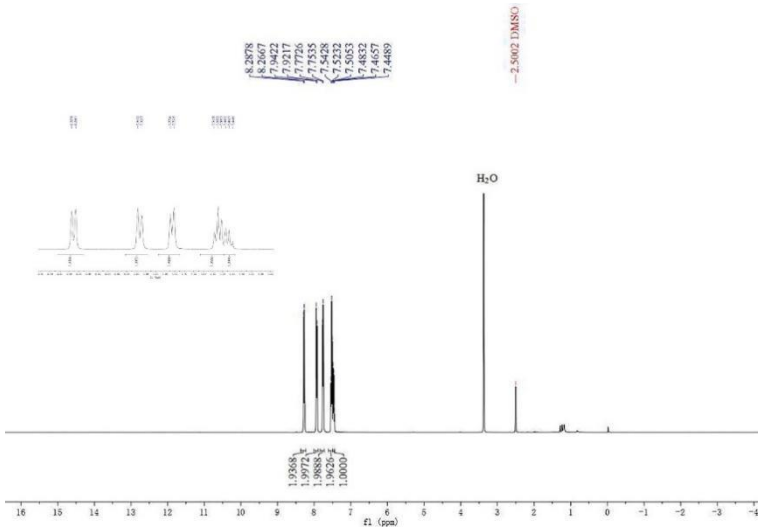
4-Methoxybiphenyl(**Table S4, Entry 3):** ^{1}H NMR (400MHz, DMSO, δ ppm): 7.59-7.61(m, 4H), 7.44-7.41(m, 2H), 7.29-32(m, 1H), 7.02(d, J=8.72, 2H), 3.80(s, 3H).



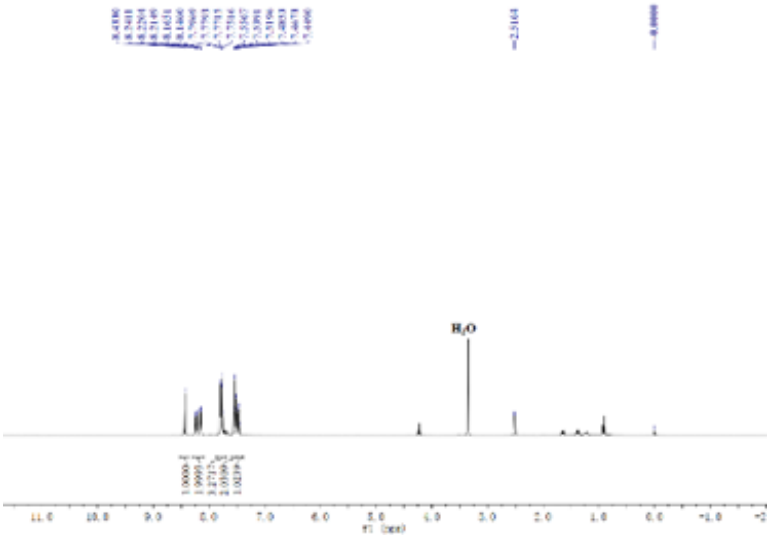
3-Methoxybiphenyl(Table S4, Entry 4): ^{1}H NMR (400MHz, DMSO, δ ppm): 7.68-7.66(d, J=10.23 Hz, 2H), 7.48-744(m, 2H), 7.40-7.36(m, 2H), 7.24-7.7.19(m, 2H), 6.96-6.93(m, 1H), 3.83(S, 3H).



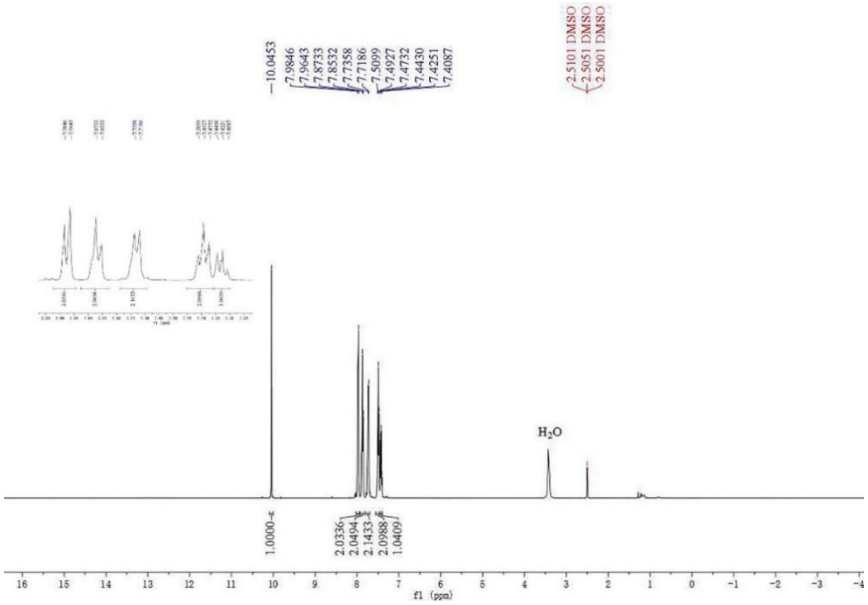
2-Methoxybiphenyl(Table S4, Entry 2): ^{1}H NMR (400MHz, DMSO, δ ppm): 7.47-7.45(m, 2H), 7.41-7.38(m, 2H), 7.30-7.36(m, 2H), 7.26-7.29(dd, J2=1.8 Hz, J1=7.52 Hz,1H), 7.11-7.09(d,J=8.28 Hz, 1H), 7.02(m, 1H), 3.75(s, 3H).



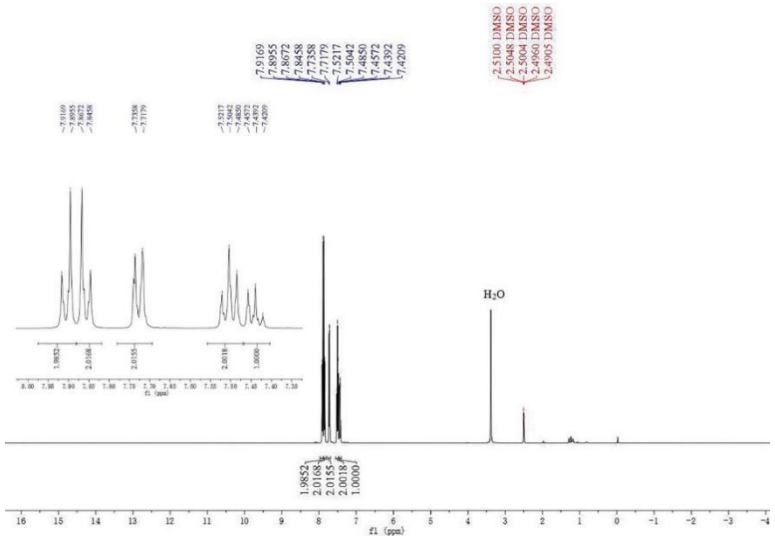
4-nitrobiphyenyl(Table S4, Entry 6): ^{1}H NMR (400MHz DMSO, δ ppm): 8.28-8.26(d, J=8.44 Hz,2H), 7.94-7.92(d, J=8.20Hz,2H), 7.77-7.75(d, J=7.64Hz,2H),7.44-7.54(m, 3H).



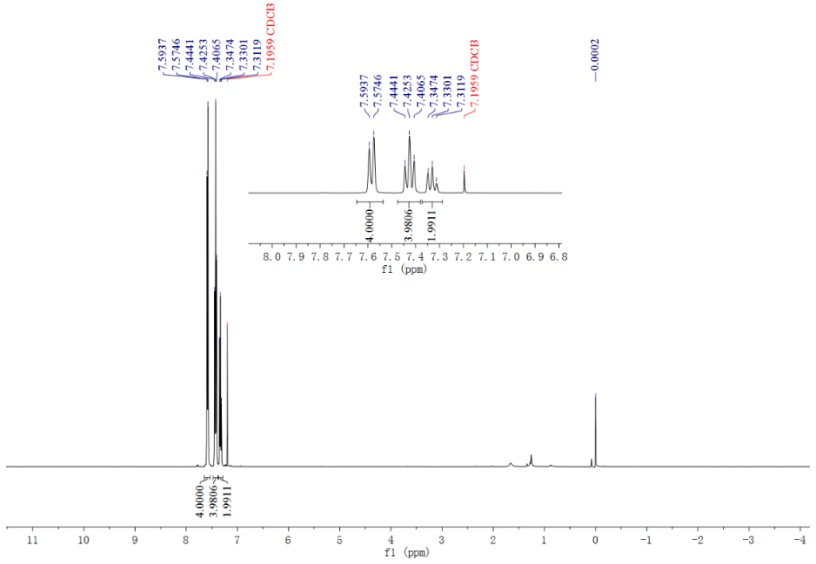
2-nitrobiphyenyl(Table S4, Entry 7): ^{1}H NMR(400MHz, DMSO, δ ppm): 8,43(s, 1H), 8.24-8.23(m, 1H), 8.16-8.14(d, J=7.88Hz, 1H), 7.79-7.85 (m, 3H), 7.54-7.51(m, 2H), 7.48-7.44(m, 1H).



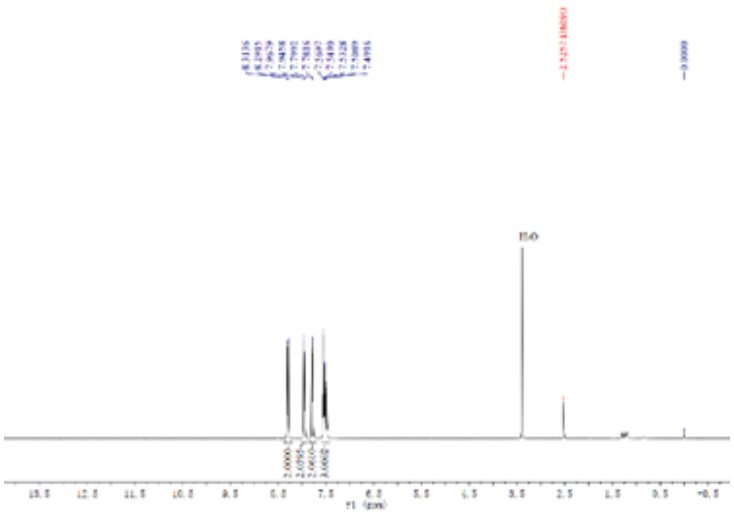
4-Formylbiphenyl(Table S4, Entry 8): ^{1}H NMR (400 MHz, DMSO, δ ppm): 10.04(s, 1H), 7.98-7.96(d, J=8.12 Hz, 2H), 7.87-7.85(d, J=8.04 Hz, 2H), 7.73-7.31(d, J=6.88 Hz, 2H), 7.40-7.50(m, 3H).



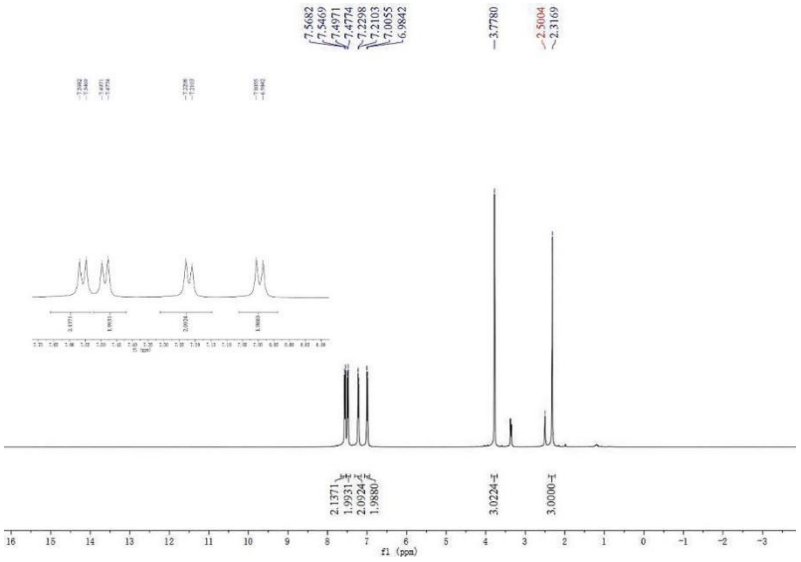
4-Biphenylacetonitrile (Table S4,Entry 9): ^{1}H NMR (400MHz, DMSO, δ ppm): 7.42-7.52(m, 3H), 7.72(d, J=7.16Hz,2H), 7.85(d, J=8.56Hz, 2H), 7.90(d, J=8.56Hz, 2H).



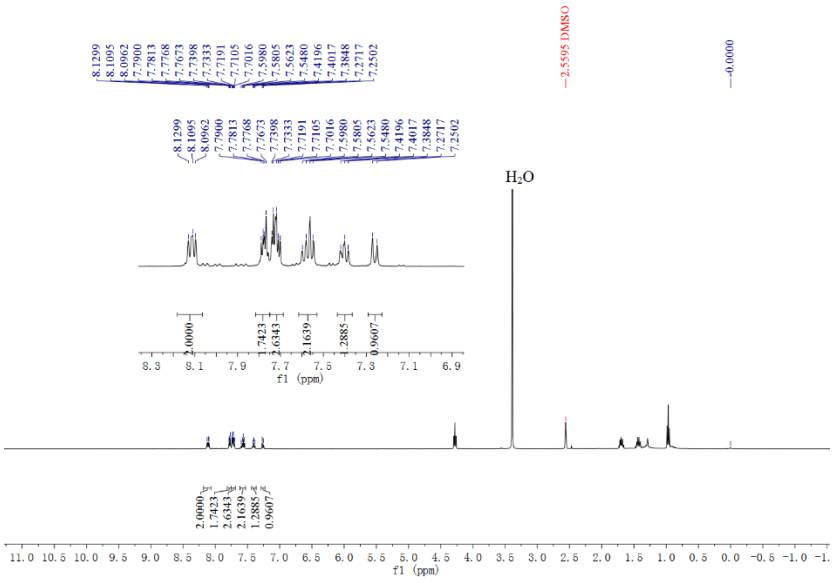
Biphenyl (Table S4, Entry 10): ^{1}H NMR(400MHz, DMSO, δ ppm)**:** 7.59-757(d, J=7.64 Hz, 4H), 7.44-7.40(t, J=7.52, 4H), 7.34-7.31(t, J=6.92 Hz, 2H).



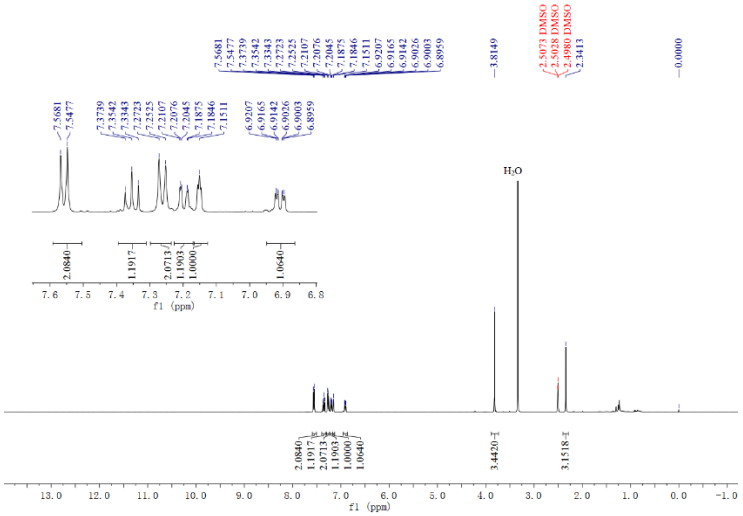
4-nitrobiphenyl(Table S4,**Entry 13)**: ^{1}H NMR (400MHz DMSO, δ ppm): 8.31-8.29(d, 8.83 Hz, 2H),7.97-7.94 (d,J=8.84 Hz, 2H),7.79-78(d, J=7.04 Hz, 2H), 7.56-7.49(m, 3H).



4-methyl,4'-Methoxybiphenyl (Table S4, Entry 14): ^{1}H NMR(400MHz, DMSO, δ ppm): 7.56-7.54(d, J=8.52 Hz, 2H), 7.49-7.47(d, J=7.88 Hz, 2H), 7.23-7.21(d, J=7.80 Hz, 2H), 7.00-6.98(d, J=8.52 Hz, 2H), 3.77(s, 3H),2.31 (s,3H).



1-(*p*-Methylphenyl)naphthalene (Table S4, Entry 15): ^{1}H NMR (400 MHz, DMSO, δ ppm)**:** 8.12-8.09(m, 2H), 7.79-7.70(m, 5H), 7.59-7.54(q, J=7.0 Hz, 2H), 7.41-7.38(t, J=7.16 Hz, 1H), 7.27-7.25(d, 8.60 Hz, 1H).



4-Methyl-3'-methoxybiphenyl (Table S4, Entry 17): ^{1}H NMR (400MHz, DMSO, δ ppm)**:** 7.56-7.54(d, J=8.16 Hz, 2H), 7.37-7.27(t, J=7.88 Hz, 1H), 7.27-7.25(d, J=7.92 Hz, 2H), 7.21-7.18(m, 1H), 7.15(m, 1H), 6.92-6.89(dd, J=1.68, 2.60 Hz, 1H), 3.81(s, 3H), 2.34(s, 3H).

Reference

1. Mino T, Shirae Y, Sakomoto M, Fujita T. Phosphine-free hydrazone-Pd complex as the catalyst precursor for a Suzuki-Miyaura reaction under mild aerobic conditions. J Org Chem. 2005; 70: 2191-2194.
2. Littke AF, Fu GC. A convenient and general method for Pd-catalyzed Suzuki cross-couplings of aryl chlorides and arylboronic acids. Angew Chem Int Ed. 1998; 37: 3387-3388.
3. Rao ML, Jadhav DN, Banerjee D. A new palladium catalyzed protocol for atom-efficient cross-coupling reactions of triarylbismuths with aryl halides and triflates. Tetrahedron. 2008; 64: 5762-5772.
4. Kataoka N, Shelby Q, Stambuli JP, Hartwig JF. Air stable, sterically hindered ferrocenyl dialkylphosphines for palladium-catalyzed C−C, C−N, and C−O bond-forming cross-couplings. J Org Chem. 2002; 67: 5553-5566.
5. Rai RK, Gupta K, Behrens S, Li J, Xu Q, Singh SK. Highly active bimetallic nickel-palladium alloy nanoparticle catalyzed Suzuki-Miyaura reactions. ChemCatChem. 2015; 7: 1806-1812.
6. Bao GY, Bai J, Li CP. Synergistic effect of the Pd-Ni bimetal/carbon nanofiber composite catalyst in Suzuki coupling reaction. Org Chem Front. 2019; 6: 352-361.
7. Simeone JP, Sowa Jr JR. Palladium on carbon as a precatalyst for the Suzuki-Miyuara cross-coupling of aryl chlorides. Tetrahedron. 2007; 63: 12646-12654.
8. Bandini M, Pietrangelo A, Sinisi R, Umani-Ronchi A, Wolf MO. New electrochemically generated polymeric Pd complexes as heterogeneous catalysts for Suzuki cross-coupling reactions. Eur J Org Chem. 2009; 2009: 3554-3561.