Electronic Supplementary Information

Heterogeneous Catalysis by Ultra-small Bimetallic Nanoparticles Surpassing Homogeneous Catalysis for Carbon-Carbon Bond Forming Reactions

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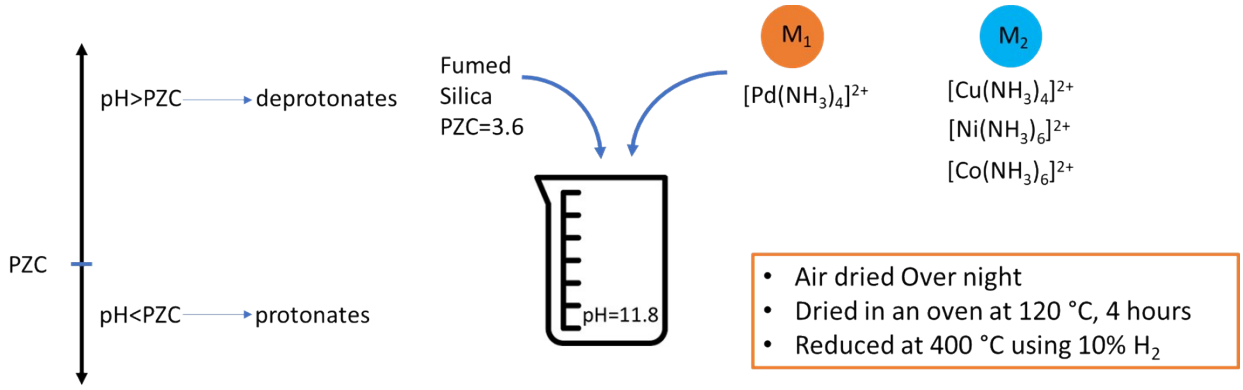


Figure S1. Strong electrostatic adsorption scheme.

Surface loading (SL) in $m^2\ L^{-1}$, surface area (SA) in $m^2\ g^{-1}$, mass of the support in g and total volume of the solution in L.

$$SL = \frac{SA\ \times\ mass\ of\ the\ support}{Volume} \quad \text{(Eq. S1)}$$

Table S1. Bulk composition of various metal loading for the CuPd catalysts as determined by ICP-OES.

Catalyst	Targeted weight loading (wt%)		Adsorbed Metal (%)		Actual weight loading (wt%)		Catalyst Denomination
	Cu	Pd	Cu	Pd	Cu	Pd	
CuPd/SiO_2	1	1	97	97	0.97	0.97	0.97 Cu 0.97 Pd
2Cu1Pd/SiO_2	2	1	89	95	1.78	0.95	1.78 Cu 0.95 Pd
0.5Cu1Pd/SiO_2	0.5	1	98	95	0.49	0.95	0.49 Cu 0.95 Pd
1Cu0.5Pd/SiO_2	1	0.5	97	99	0.97	0.99	0.97 Cu 0.97 Pd

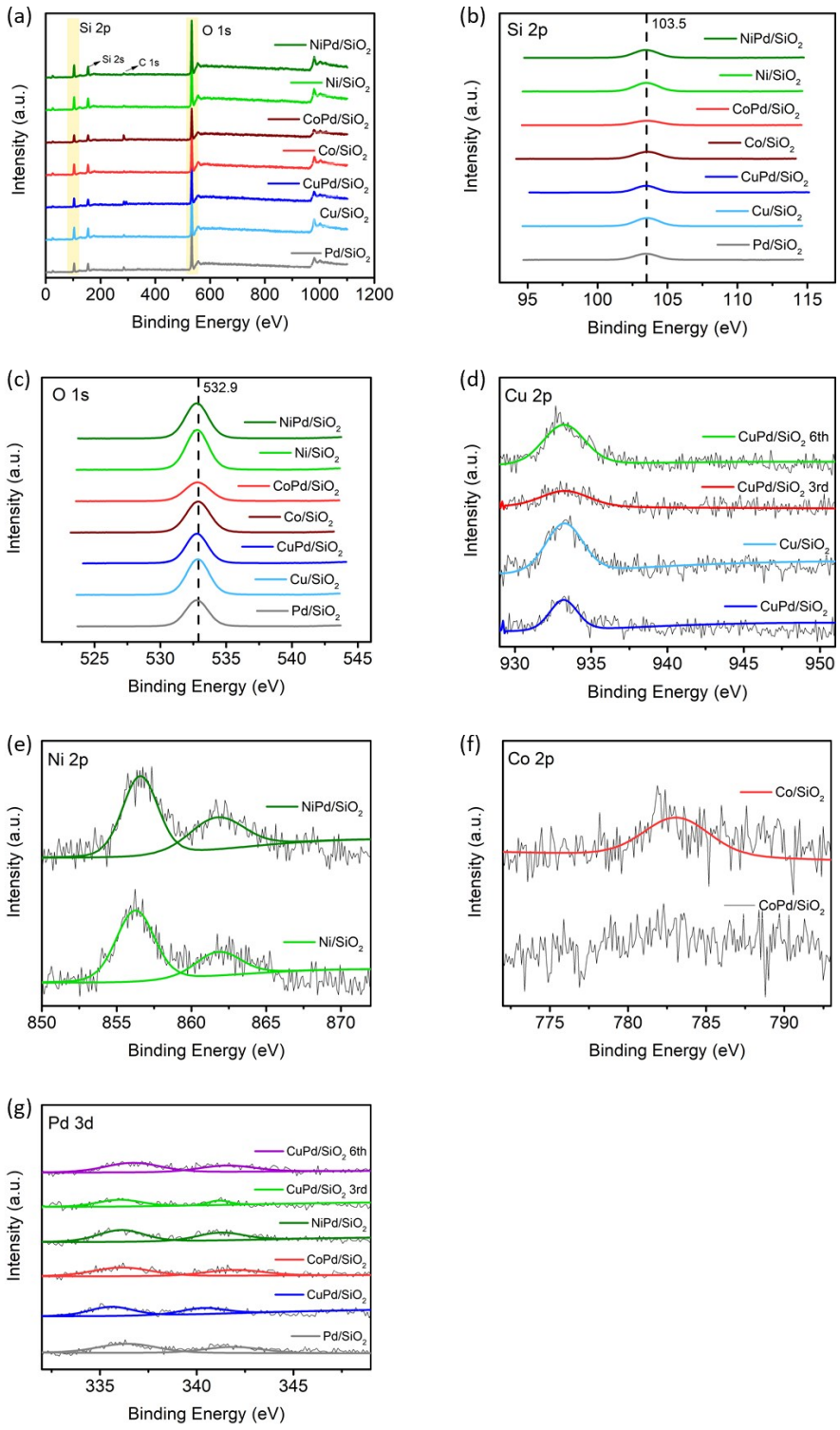


Figure S2. XPS analysis of bimetallic and monometallic catalysts (a) Survey spectra (b) Deconvoluted Si 2p spectra, (c) Deconvoluted O 1s spectra, (d) Deconvoluted Cu 2p spectra, (e) Deconvoluted Ni 2p spectra, (f) Deconvoluted Co 2p spectra, (g) Deconvoluted Pd 3d spectra**.**

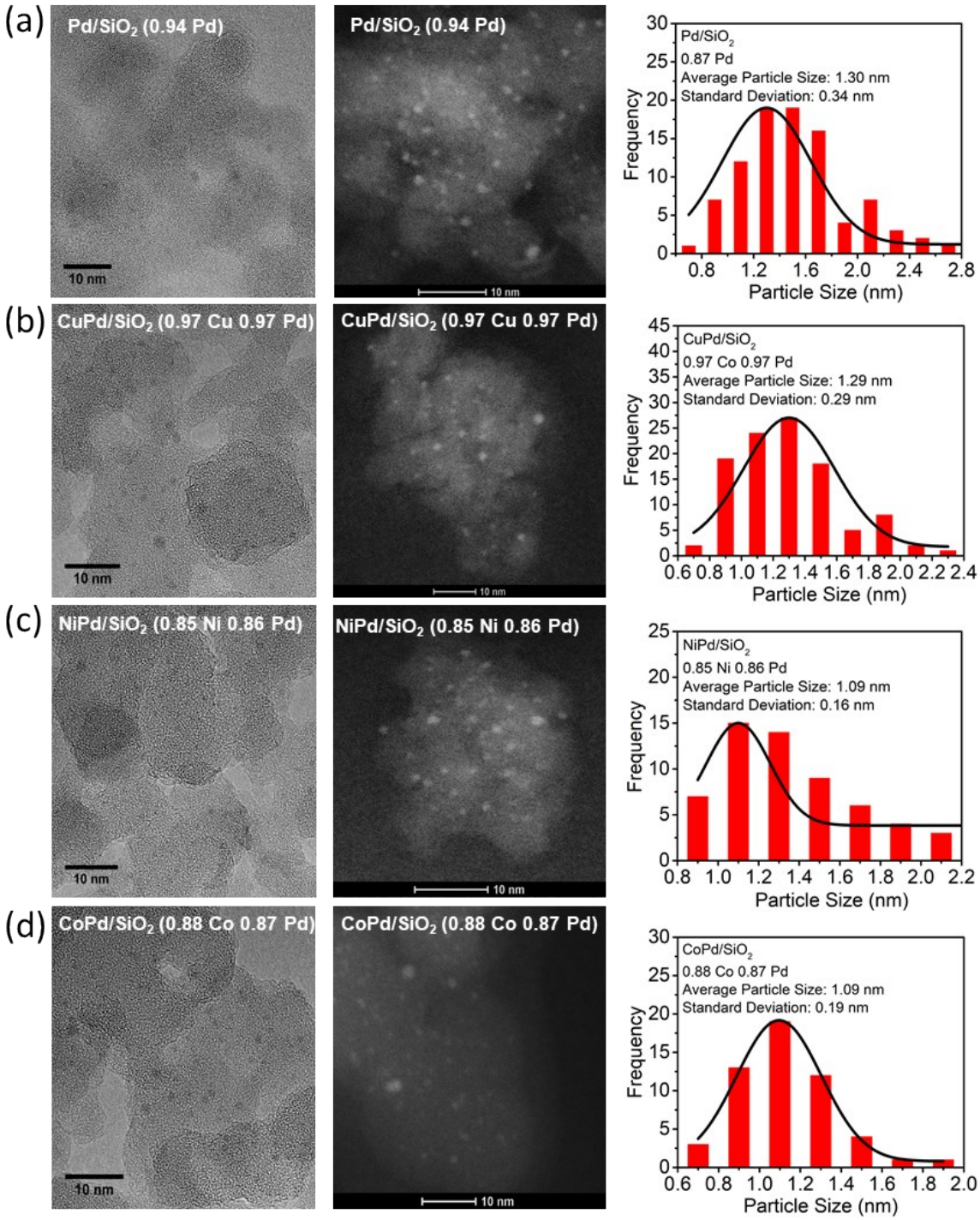


Figure S3. HRTEM, STEM, and the corresponding particle size distribution for (a) Pd/SiO_2, (b) $CuPd/SiO_2$, (c) $NiPd/SiO_2$ and (d) $CoPd/SiO_2$.

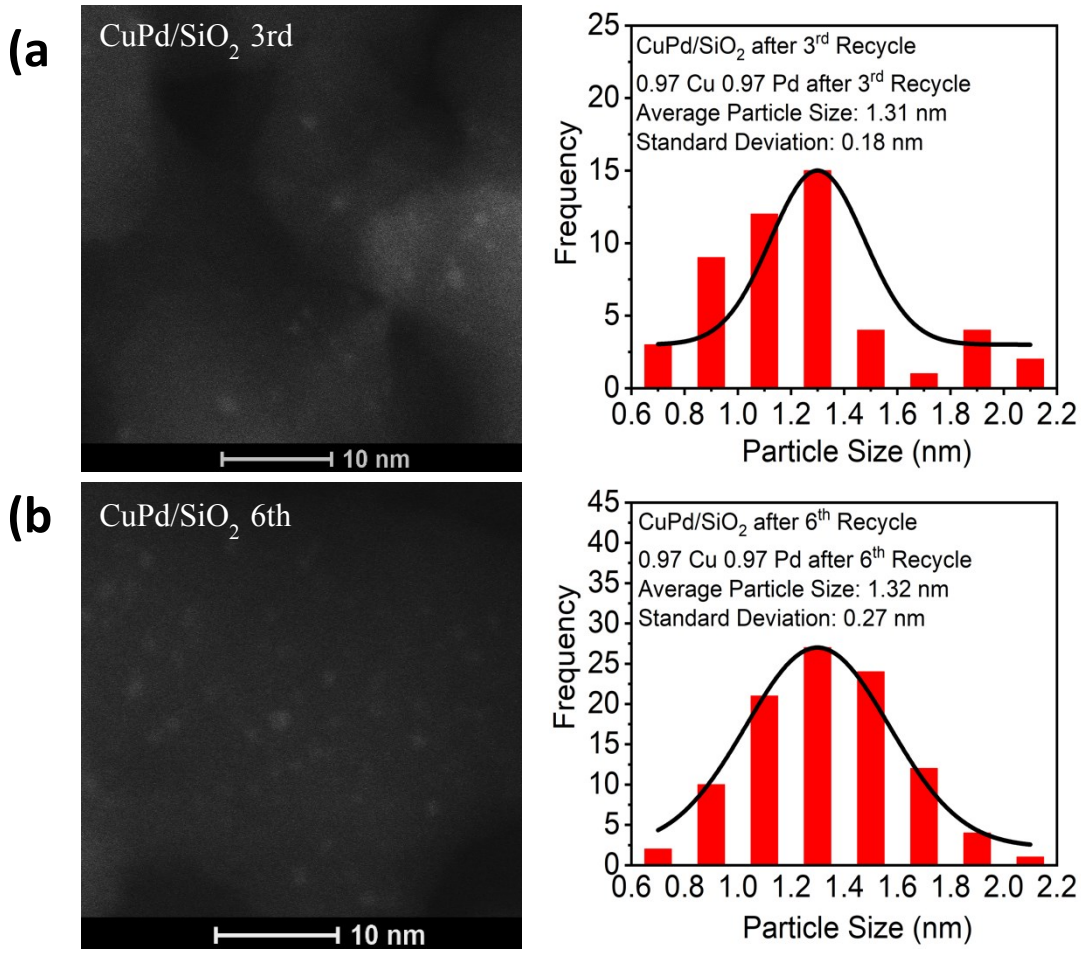


Figure S4. STEM and the corresponding particle size distribution for the $CuPd/SiO_2$ catalyst. **(a)** after the 3rd recycled run and **(b)** after the 6th recycled run.

Table S2. Conversions for recyclability of the Pd/SiO_2 catalyst for the microwave assisted Suzuki cross-coupling reaction (5 min) at 60 °C.

Run	Conversion (%)
1	100
2	97
3	93
4	92
5	91
6	89

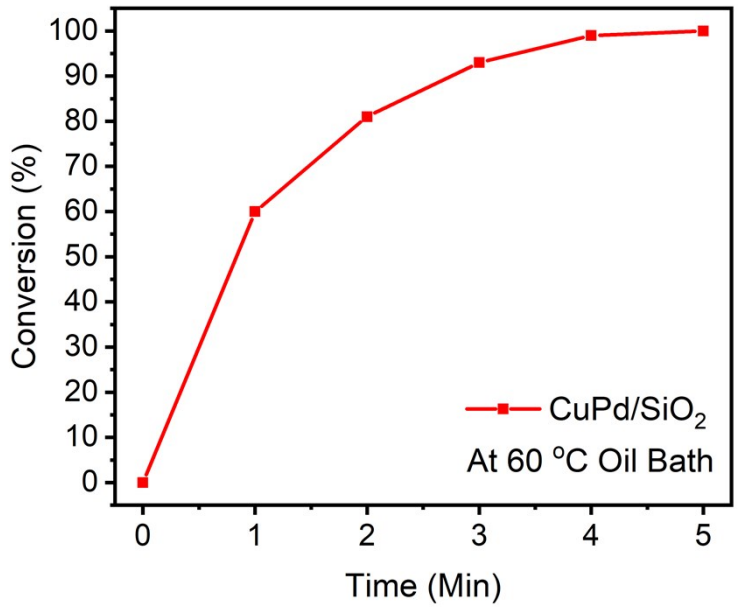


Figure S5. Cross-coupling reaction between bromobenzene with benzeneboronic acid in an oil bath at 60 °C. The $CuPd/SiO_2$ catalyst (Pd: 1.05 μmol, 0.3 mol%) was dispersed in a glass vial with 2 ml of ethanol and 2 ml of deionized (DI) water and the vial was then placed in the 60 °C oil bath. After the solution temperature is reaches 60 °C, bromobenzene (50 mg, 0.32 mmol, 1 equiv) was added to the solution along with benzeneboronic acid (47 mg, 0.38 mmol, 1.2 equiv) and stirred for 30 seconds to ensure a homogeneous mixture. Finally, potassium carbonate (133 mg, 0.96 mmol, 3 equiv) was added to the solution to start the reaction. During the reaction small aliquots were collected every minute and the biphenyl product was extracted using ethyl acetate and centrifugation and analyzed by GC-FID.

Table S3. Surface compositions of the as prepared $CuPd/SiO_2$ catalyst and the 3rd and 6th recycled catalysts as determined by XPS.

Catalyst	Silicon (At%)	Oxygen (At%)
$CuPd/SiO_2$	37.07	62.93
$CuPd/SiO_2$ 3rd	39.76	60.24
$CuPd/SiO_2$ 6th	39.43	60.57

Table S4. Pd content in the Pd/SiO_2 catalyst after each recycling run as determined by ICP-OES.

Run	Metal Concentration (wt%)
	Pd
1	0.96
2	0.95
3	0.93
4	0.93
5	0.93

Table S5. Cu and Pd contents in the $CuPd/SiO_2$ catalyst after each recycling run as determined by ICP-OES**.**

Run	Metal Concentration (wt%)	
	Cu	Pd
1	0.97	0.97
2	0.78	0.95
3	0.77	0.94
4	0.77	0.93
5	0.76	0.86
6	0.76	0.75
7	0.74	0.71

Table S6. Cu and Pd concentrations in solution after removal of the spent catalyst $CuPd/SiO_2$ by hot filtration after each recycling run as determined by ICP-MS**.** The $CuPd/SiO_2$ catalyst was removed by centrifugation (3300 rpm, 10 min) and the supernatant was collected. Catalyst was washed with ethanol (hot, 30 mL) by centrifugation (10 min, 3300 rpm) which was added to the supernatant solution giving a total volume of 50 mL. ICP-MS was run directly on the solution and analyzed for the presence of Pd and Cu.

ICP-MS data shows no leaching of Pd or Cu throughout recyclability trials. Pd and Cu concentrations are below the quantitation limit (BQL).

Recycling Run	**Pd (ppm)**	**Cu (ppm)**
Blank	0.008	0.005
1	<0.008 (BQL)	<0.005 (BQL)
2	<0.008 (BQL)	<0.005 (BQL)
3	<0.008 (BQL)	<0.005 (BQL)
4	<0.008 (BQL)	<0.005 (BQL)
5	<0.008 (BQL)	<0.005 (BQL)
6	<0.008 (BQL)	<0.005 (BQL)
7	<0.008 (BQL)	<0.005 (BQL)

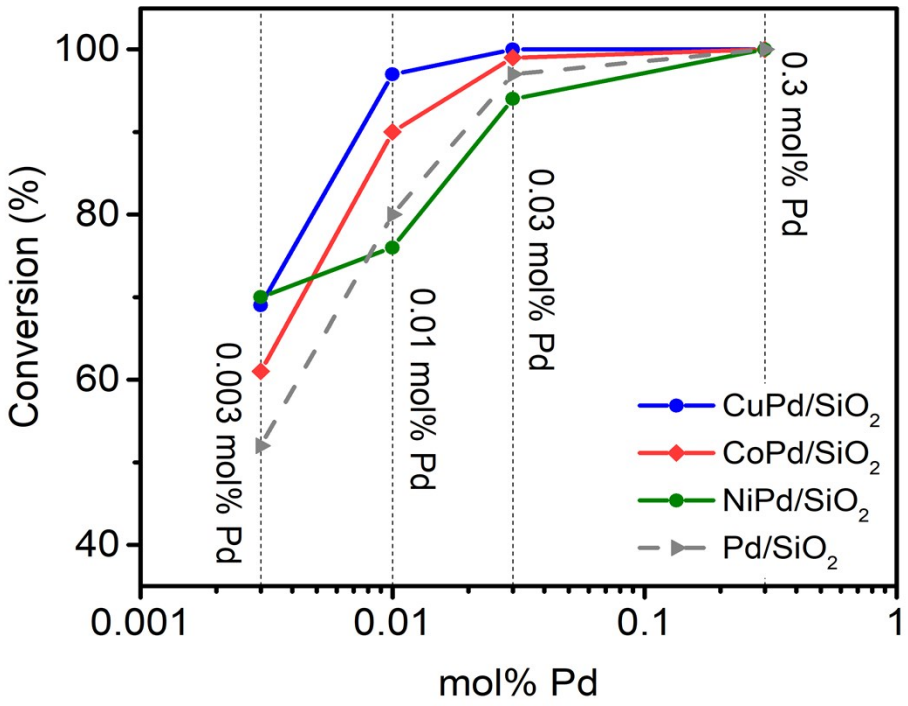


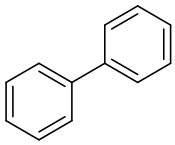
Figure S6. Conversion percentage for the bimetallic catalysts using 0.3 mol%, 0.03 mol% and 0.003 mol% Pd concentrations in the MW assisted reaction at 60 °C.

Table S7. TON and TOF calculations for catalysts using 0.3 mol%, 0.03 mol% and 0.003 mol% Pd concentrations in the MW assisted reaction at 60 °C.

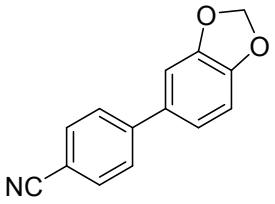
mol% Pd	$CuPd/SiO_2$		$CoPd/SiO_2$		$NiPd/SiO_2$		Pd/SiO_2	
	TON	TOF (h^{-1})	TON	TOF (h^{-1})	TON	TOF (h^{-1})	TON	TOF (h^{-1})
0.3	333	4,000	333	4,000	333	4,000	333	4,000
0.03	3,333	40,000	3,266	39,196	3,233	38,800	3,233	38,800
0.01	9,700	116,400	9,000	108,000	7,600	91,200	8,000	96,000
0.003	23,333	280,000	19,999	239,997	20,667	248,000	17,333	208,000

Table S8. ^{1}H NMR analyses of the reaction products.

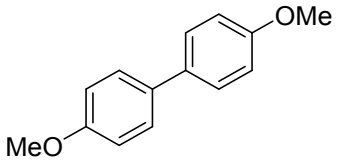
D0. 1,1'-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.43 (m, 2H), 7.34 (t, 2H), 7.29 – 7.20 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.19, 127.70, 126.20, 126.11.



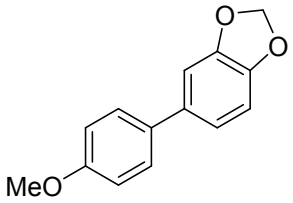
D1. 4-(benzo[d][1,3]dioxol-5-yl)benzonitrile: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.59 (m, 4H), 7.29 (s, 1H), 7.14 – 7.06 (m, 2H), 6.94 (d, 1H), 6.06 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.53, 148.27, 145.33, 133.40, 132.60, 127.36, 121.18, 118.99, 110.47, 108.88, 107.52, 101.51.



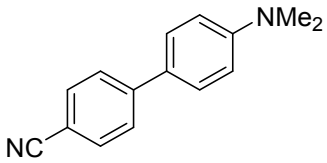
D2. 4,4'-dimethoxy-1,1'-biphenyl: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, 2H), 6.99 (d, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.71, 133.51, 127.75, 114.18, 55.36.



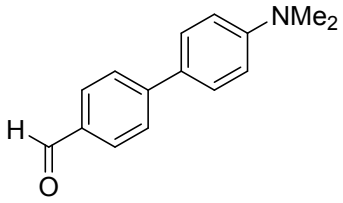
D3. 5-(4-methoxyphenyl)benzo[d][1,3]dioxole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, 2H), 7.05 (d, 2H), 7.02 (s, 1H), 6.98 (d, 2H), 6.89 (d, 1H), 6.01 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.89, 148.07, 146.59, 135.33, 133.60, 127.91, 120.10, 114.18, 108.54, 107.41, 101.07, 55.37.



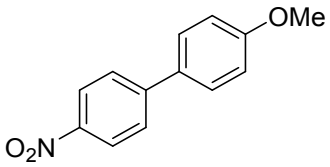
D4. 4'-(dimethylamino)-[1,1'-biphenyl]-4-carbonitrile: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (s, dH), 7.86 – 7.76 (m, 2H), 7.54 (s, 2H), 7.02 (s, 2H), 3.11 (s, 3H).



D5. 4'-(dimethylamino)-[1,1'-biphenyl]-4-carbaldehyde: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.03 (s, 1H), 8.12 (s, 2H), 7.86 – 7.71 (m, 2H), 7.28 (s, 2H), 7.24 – 6.89 (m, 1H), 6.86 – 6.53 (m, 1H), 2.98 – 2.82 (m, 6H).



D6. 4-methoxy-4'-nitro-1,1'-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, 2H), 7.71 (d, 2H), 7.60 (d, 2H), 7.04 (d, 2H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.48, 147.22, 131.08, 128.58, 127.08, 124.16, 114.63, 55.44.



D7. 4'-nitro-[1,1'-biphenyl]-4-carboxamide: ^{1}H NMR (400 MHz, DMSO) δ 8.28 (d, 1H), 8.17 – 7.98 (m, 2H), 7.82 (d, 2H), 7.36 (d, 2H), 7.33 – 7.13 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ 167.96, 142.21, 134.07, 130.08, 128.73, 127.96.