Supporting Information

3D porous polymeric foam supported Pd Nanocrystals as a highly efficient and recyclable catalyst for organic transformations

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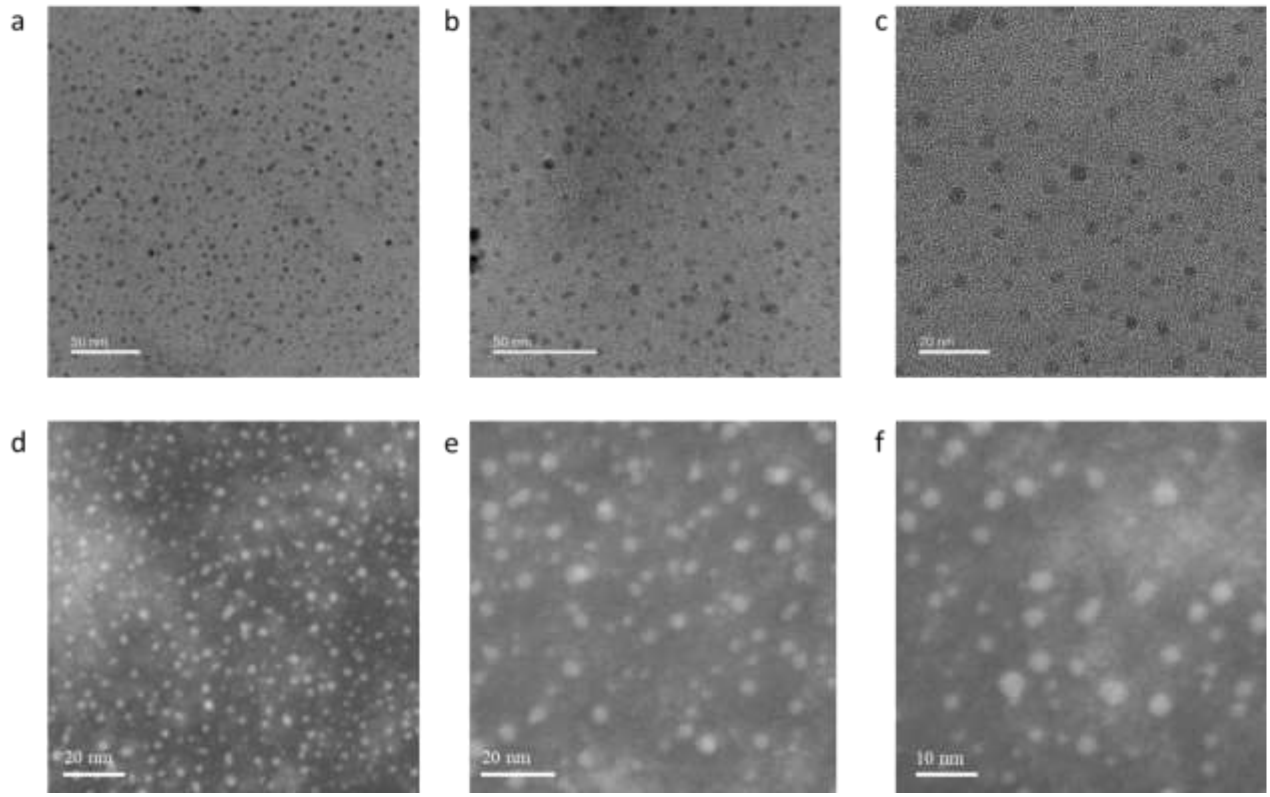

Figure S1. Transmission electron microscopy (TEM) images (a,b,c), high angle annular dark-field scanning TEM (HAADF STEM) images (d,e,f) of Pd NPs.

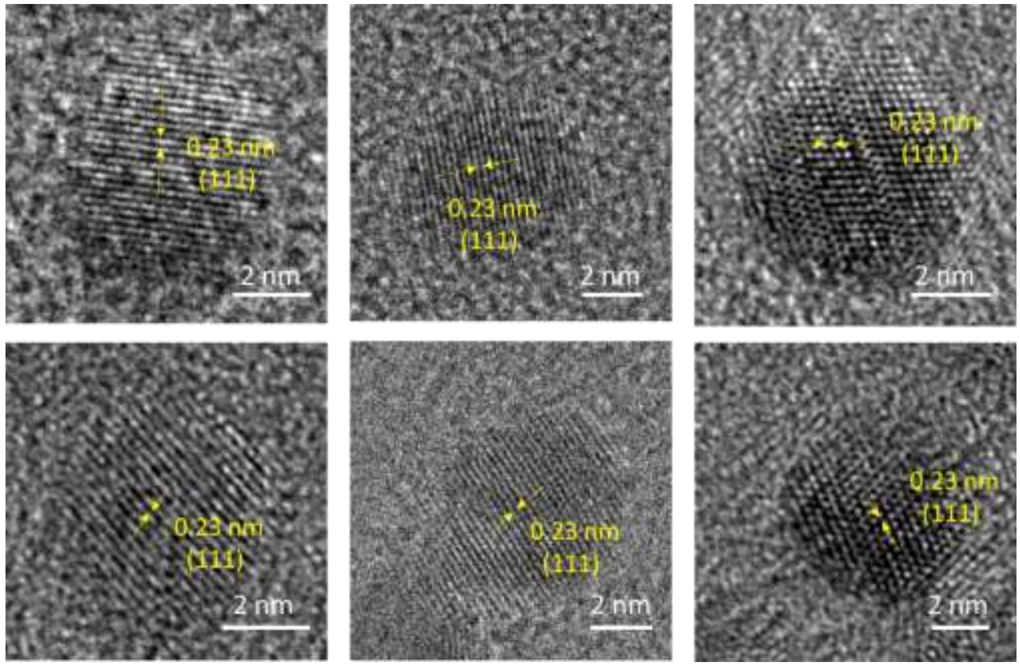

Figure S2. Typical high resolution TEM images of a few Pd NPs.

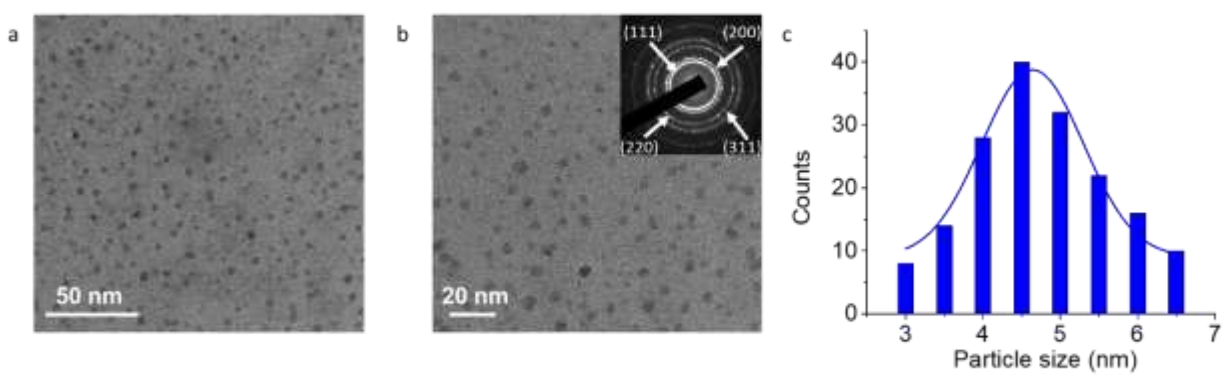

Figure S3. TEM images of recovered Pd NPs obtained after Suzuki-Miyaura cross-coupling reaction (a,b) and corresponding particle-size distribution (c). The inset is the corresponding SAED pattern.

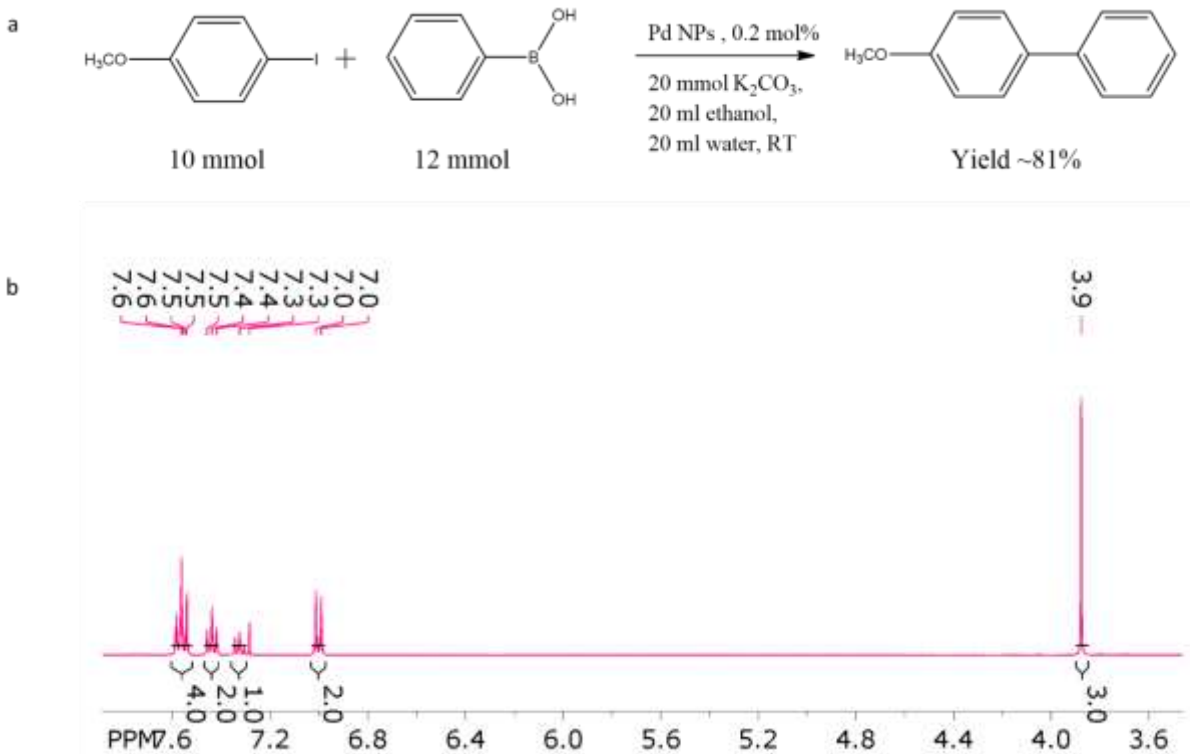

Figure S4. (a) Reaction conditions used for scale-up synthesis of 4-methoxybiphenyl. (b) ^{1}H NMR spectrum of 4-methoxy-1,1'-biphenyl (purified product) in $CDCl_3$.

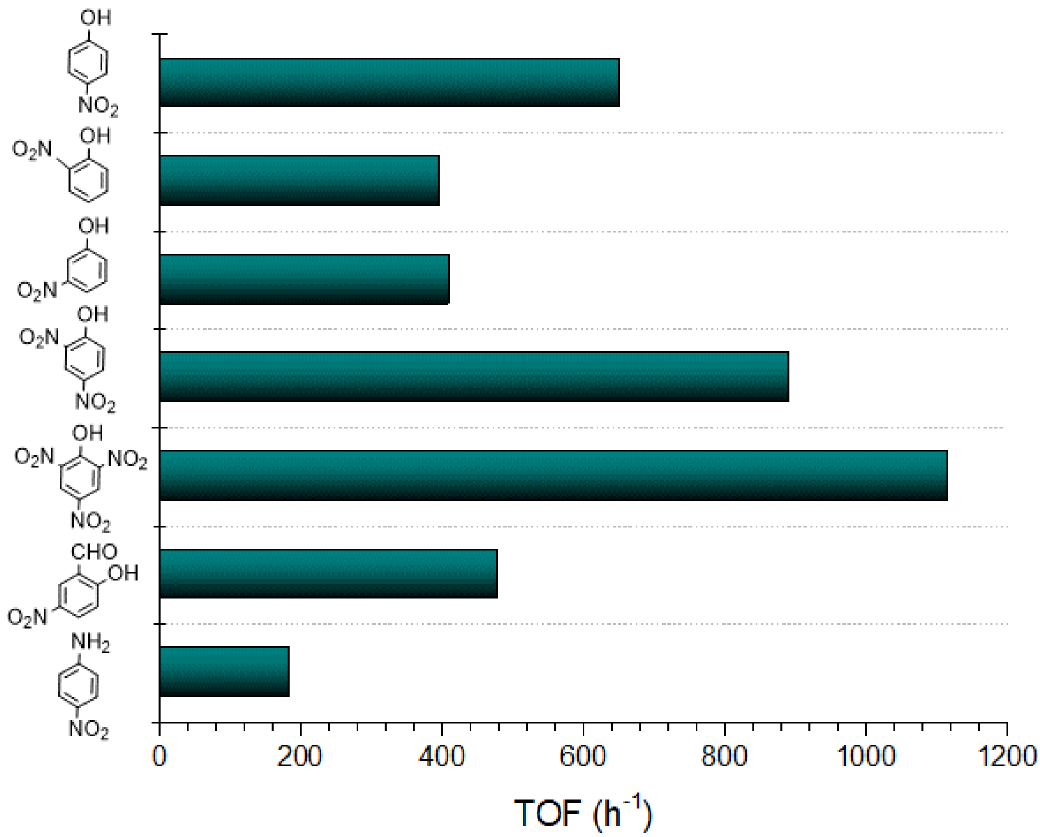

Figure S5. TOF estimated for catalytic reduction of nitroarenes substituted with various electron-withdrawing and donating groups at room temperature using 10 µg of Pd NPs.

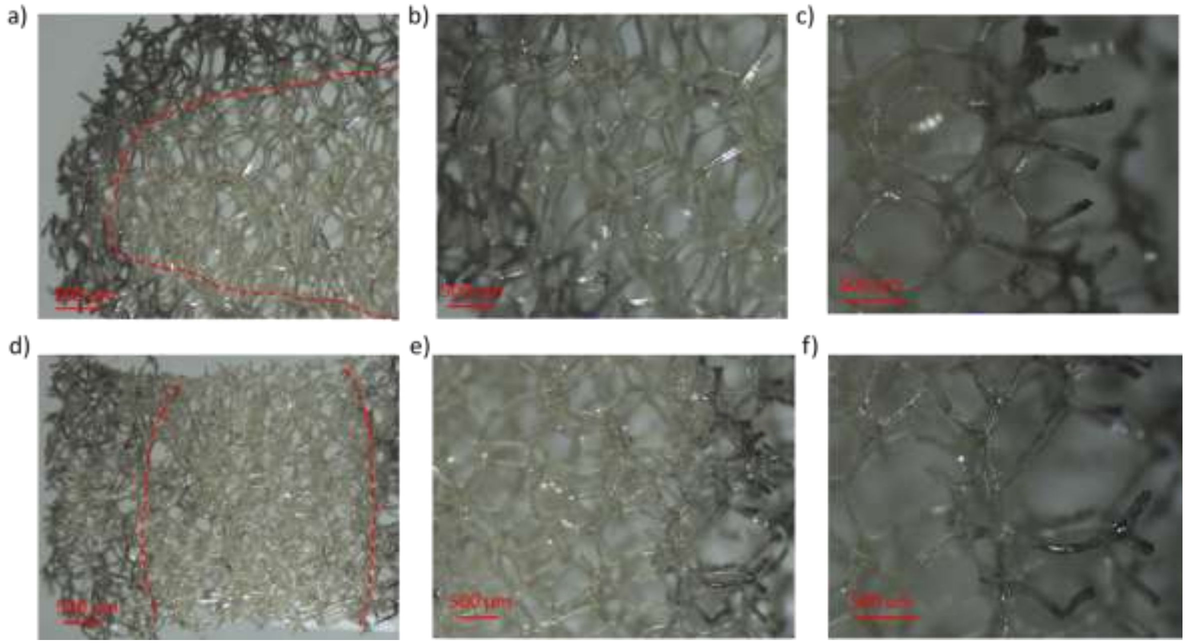

Figure S6. Optical microscope images of a-c) 0.3 cm thick, d-f) 0.5 cm thick Pd loaded PUF. These are the The red doted lines are guide to the eye. Theses images are recorded for small cut piece of the foams after Pd-loading for investigating the Pd loading inside the thick foam. The uneven Pd loading are clearly visible in 0.3 cm and 0.5 cm thick PUF.

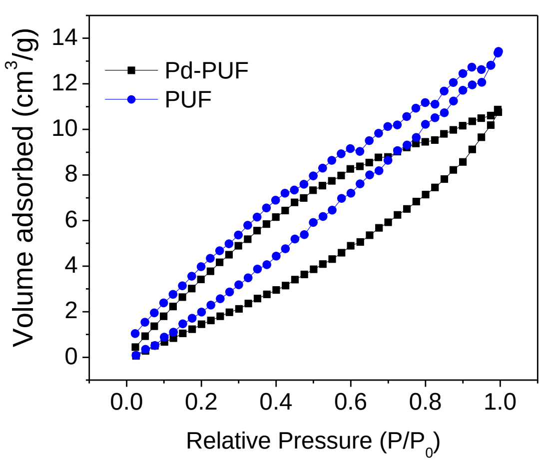

Figure S7. N_2 adsorption−desorption isotherms of PUF and Pd-PUF at 77 K.

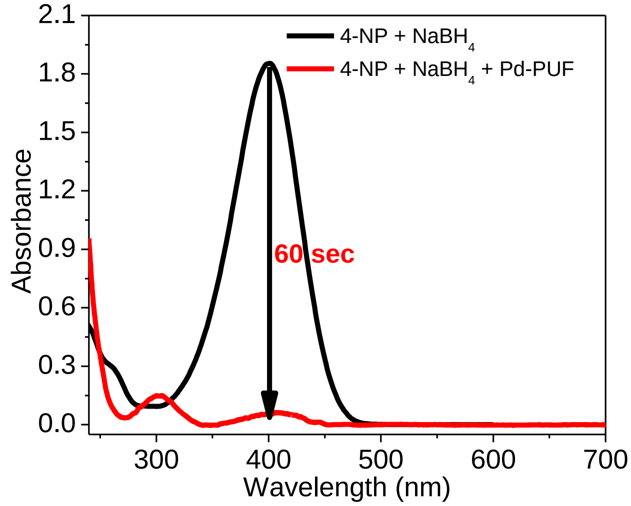

Figure S8. UV-Vis absorption spectra of 4-nitrophenolate ion catalyzed by Pd-PUF.

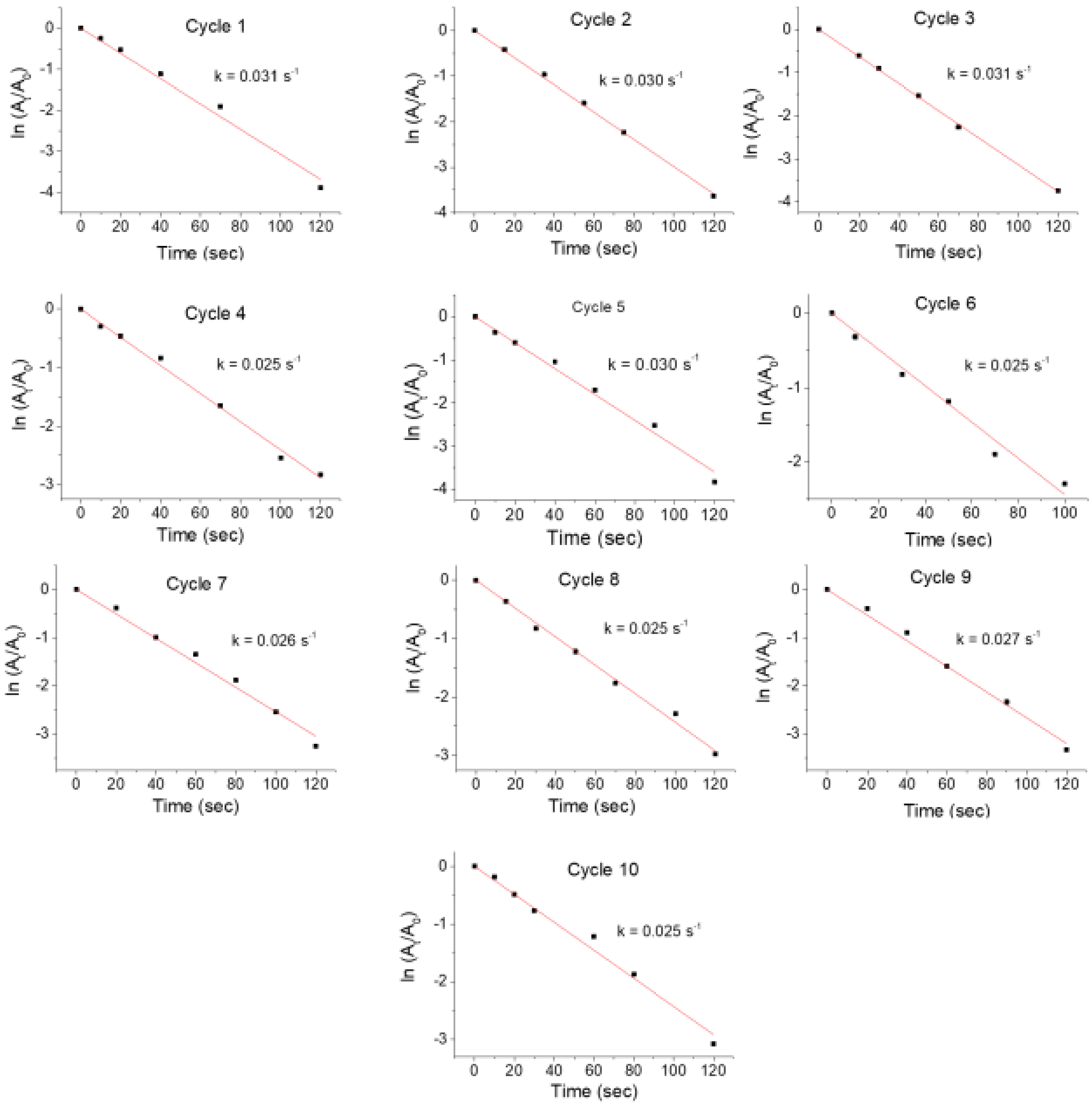

Figure S9. Plot of ln (A_t/A_0) *vs*. time for 4-NP reduction by $NaBH_4$ using Pd loaded PUF for determining rate of the reaction in different catalytic cycles.

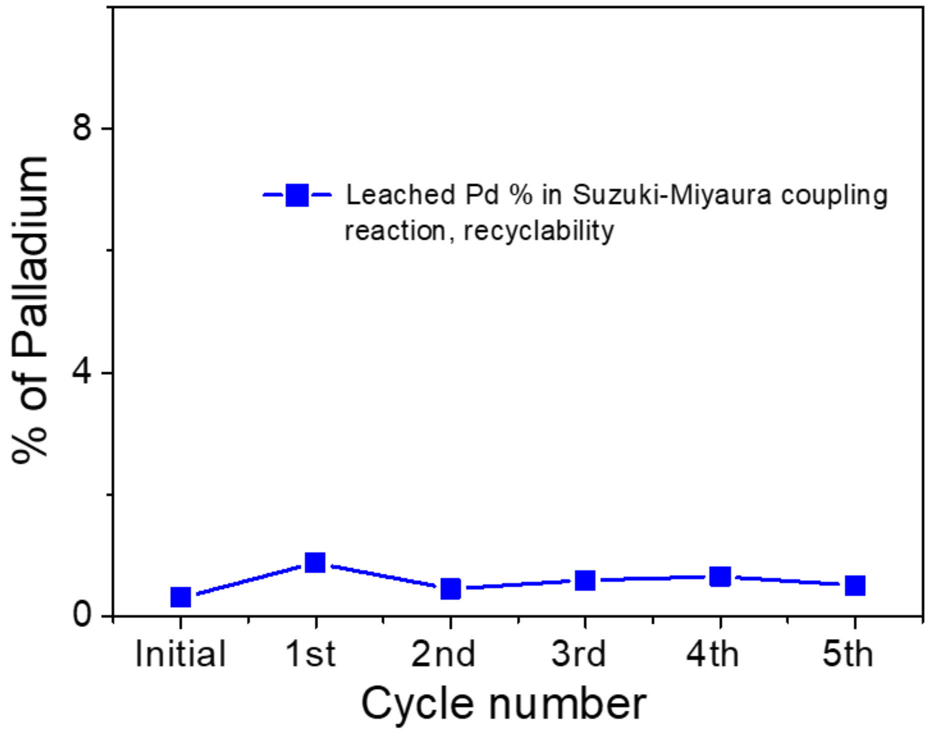

Figure S10. Percentage leaching of Pd during Suzuki-Miyaura coupling reactions using Pd NPs as catalyst after successive cycles.

Table S1. Time taken for completion of Suzuki-Miyaura cross-coupling reactions using different solvents. (Reactant concentrations: 1.2 mmol phenylboronic acid, 1 mmol ododbenzene, 2 mmol K_2CO_3, 0.1 ml Pd NPs (from 10 mg in 1 ml ethanol stock solution), room temperature, stirring rate of 1200 rpm).

Sl No.	Solvent	Time(min)
1	H_2O (4 ml)	120
2	H_2O (3.5ml) + ethanol (0.5ml)	115
3	H_2O (3ml) + ethanol (1ml)	95
4	H_2O (2.5ml) + ethanol (1.5ml)	75
5	H_2O (2ml) + ethanol (2ml)	35
6	H_2O (1.5ml) + ethanol (2.5ml)	45
7	H_2O (1ml) + ethanol (3ml)	80
8	H_2O (0.5ml) + ethanol (3.5ml)	85
9	Ethanol (4 ml)	90

Table S2. Optimization of catalyst amount for Suzuki-Miyaura cross-coupling reaction. (Reaction conditions – 1.2 mmol phenylboronic acid, 1 mmol iododbenzene, 2 mmol K_2CO_3, room temperature, stirring rate of 1200 rpm, solvent-H_2O (2 ml) + ethanol (2 ml).

Sl. No.	Catalyst conc. (µl)	Time	TOF (h^{-1})
1	5	80 min	1516
2	10	65 min	933
3	15	60 min	674
4	20	50 min	638
5	25	35 min	693
6	30	35 min	577
7	40	35 min	456
8	50	35 min	433
9	60	30 min	336
10	80	30 min	253
11	100	30 min	202

Table S3. Comparison of catalytic activity of our Pd NPs for Suzuki-Miyaura cross-coupling reaction using 4-methoxy phenyl boronic acid and 4-iodoanisole in presence K_2CO_3 with other recently developed highly active catalysts.

Catalyst	solvent	tempt	Mol% Pd	time	TOF (h^{-1})	Reference
Pd NPs	**50% ethanol**	**25**	**0.008**	**4 h**	**2927**	**Our work**
Pd NPs	**50% ethanol**	**Reflux**	**0.008**	**18 min**	**37805**	**Our work**
Pd-PUF	**50% ethanol**	**Reflux**	**0.017**	**20 min**	**16784**	**Our work**
Pd NPs on Bacterial cellulose	95% ethanol	80	1.52	1.5 h	261	[1]
Pd NPs on Cellulose sponge	50% ethanol	65	0.001	3 h	~30000	[2]
Pd NPs on Organic molecular cage	90% toluene	100	1	30 min	200	[3]
Pd NPs on Polystyrene/ RGO	50% ethanol	25	0.2	8 h	62	[4]
Pd-Fe NPs on Boron nitride nanosheet	50% ethanol	Reflux	0.02	10 min	30000	[5]
Pd NPs / COF	50% DMF	50	0.1	3h	30444	[6]
Pd NPs on Cellulose filter paper	water	100	0.2	30 min	968	[7]
Fe2O3 on GO	50% ethanol	80	-	24 h	-	[8]
Pd NPs on Fe3O4 tannic acid	50% ethanol	25	0.21	1.5 h	310	[9]
Pd NPs on Organic polymer	ethanol	25	0.47	3 h	70	[10]

Table S4. Comparison of the catalytic activity of our Pd NPs for Suzuki-Miyaura cross-coupling reaction using bromobenzene and 4-methoxy phenylboronic acid in presence K_2CO_3 as base with other recently developed highly active catalysts.

Catalyst	Pd mol%	Solvent	Temperature (ºC)	Time	Yield (%)	TOF (h^{-1})	Reference
Pd NPs	0.008	EtOH: H_2O	Reflux	2 h	94	5802	Our work
Pd NPs	0.2	EtOH: H_2O	26 (RT)	110 min	94	216	Our work
Pd-Fe/BNNS	0.02	EtOH: H_2O	Reflux	1 h	99	4950	[5]
G/MWCNTs/Pd	0.5	EtOH: H_2O	60	1.5 h	92	122.6	[11]
Pd/Al_2O_3	0.1	NMP-H_2O	65	5 h	68	136	[12]
SWCNT-PAMAM3.0-Pd	0.1	EtOH: H_2O	50	5 h	99	198	[13]
Pd-SiO_2 @Fe_3O_4	0.3	EtOH: H_2O	60	24 h	96	13.3	[14]
Pd@C-dots@Fe_3O_4	0.22	EtOH: H_2O	30	12 h	93	35.2	[15]
Pd-BC catalytic sheet	1.52	EtOH	80	3 h	66	261	[1]
PdNP@3a	1.0	toluene / H_2O	140	2.5 h	99	800	[16]

Table S5. Rate constant and TOF for reduction of various nitroarene compounds in the presence of Pd NPs using $NaBH_4$ as reducing agent at room temperature.

Sl. No.	Nitro compound	Time (s)	Conversion (%)	Rate constant (s^{-1})	TOF (h^{-1})
1	4-nitrophenol	10	63	0.106	652
2	2-nitrophenol	20	50	0.051	396
3	3-nitrophenol	9	35	0.059	411
4	2,4 dinitrophenol	11	48	0.072	893
5	Picric acid (2,4,6 trinitrophenol)	19	73	0.090	1118
6	2-hydroxyl-5-nitrobenzaldehyde	14	65	0.095	479
7	4-nitroaniline	34	61	0.045	184

Table S6. Comparison of the catalytic activity of our Pd NPs and Pd-PUF for 4-NP reduction in presence of $NaBH_4$ with that of other efficient catalysts developed recently.

Catalyst	**Time (sec)**	**Rate constant (s^{-1})**	**Catalyst amount**	**TOF**	**Reference**
Pd NPs	**27**	**0.106**	**10 μg**	**652 h^{-1}**	***Our work***
Pd-PUF	**120**	**0.031**	**25 μg**	**379 h^{-1}**	***Our work***
Pd NPs /Polystyrene/ RGO	600	4.77×10^{-3}	-	-	4
Pt NPs/ COF	480	-	0.04 μmol	56 h^{-1}	6
Pd NPs on Cellulose filter paper	900	4.40×10^{-3}	-	-	7
*Cu/*Silica nanosphere	*390*	*0.0093*	50 μl	3 h^{-1}	17
Ag/CMP	*1800*	*0.0014*	*7.4 mg*	198 h^{-1}	18
Pd NPs/Fe3O4	60	*0.051*	5 mg	-	19
PtPd/N-HCS	180	-	2 mg	-	20
AuCu NPs/MgO	1800	*0.0003*	30 mg	4.2 h^{-1}	21
*Au NPs/*peptide	*200*	*0.0109*	0.2 μmol	-	22
Ag NPs/PPA	200	*0.0154*	50 μl	100 mol g^{-1} h^{-1}	23
Pd/TiO2	420	0.012	-	162 h^{-1}	24

Table S7. Optimization of catalyst amount for Suzuki-Miyaura cross-coupling reaction using Pd-PUF. (Reaction conditions – 1.2 mmol phenylboronic acid, 1 mmol iododbenzene, 2 mmol K_2CO_3, room temperature, stirring rate of 1200 rpm, solvent-H_2O (2 ml) + ethanol (2 ml).

Pd in Pd-PUF (μg)	**Time**	**TOF (h^{-1})**
580	25	416
350	35	494
120	80	629
50	150	806
18	300	1120
13	420	1106

Table S8: List of Pd based nanostructures used in Suzuki-Miyaura coupling reactions for demonstrating heterogeneous or homogeneous behavior.

	Catalyst	Pd leaching test	Nature	Reference
1	PVP supported Pd NPs	Negligible leaching	Heterogeneous	[25]
2	polystyrene-divinylbenzene stabilized Pd NPs	Negligible leaching	Heterogeneous	[26]
3	Au−Pd superstructures	Negligible leaching	Heterogeneous	[27]
4	Pd(0)/polyvinyl chloride	Negligible leaching	Heterogeneous	[28]
5	Pd/Al2O3	50% Pd ion leaches out during reaction	Homogeneous	[29]
6	PdCuCeO	Pd particle leaches out	Quasi-heterogeneous	[30]
7	Pd/CeO2	Pd particle leaches out	Homogeneous	[31]
8	Ion exchange resin supported Pd nanoparticle	40% Pd ion leaches out during reaction	Homogeneous	[32]
9	Sillica supported Pd-Au nanocrystal	Pd ion leaches out during reaction	Homogeneous	[33]
10	Pd nanostructures	Pd particle leaches out	Homogeneous	[34]

NOTE: In many articles describing the reaction as homogeneous, it is not clear whether the leached out species is a molecular species or a nanoparticle from the catalyst support. As seen in entries 6 and 7, the authors describe that Pd nanoparticles that had come off the support are responsible for the coupling reaction and in that sense these can still be considered as heterogeneous catalyst.

^{1}H NMR of products obtained from Suzuki-Miyaura cross-coupling reactions.

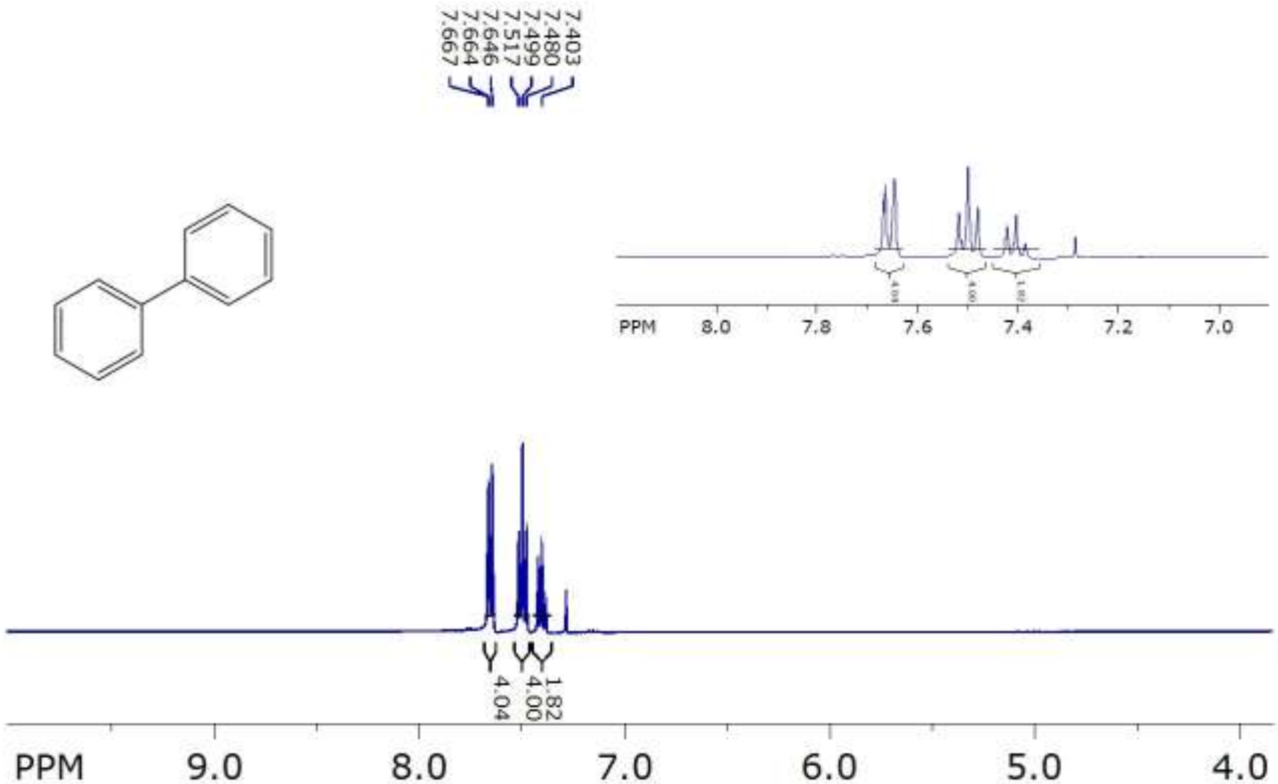

Figure S11. ^{1}H NMR spectrum of 1,1'-biphenyl in $CDCl_3$.

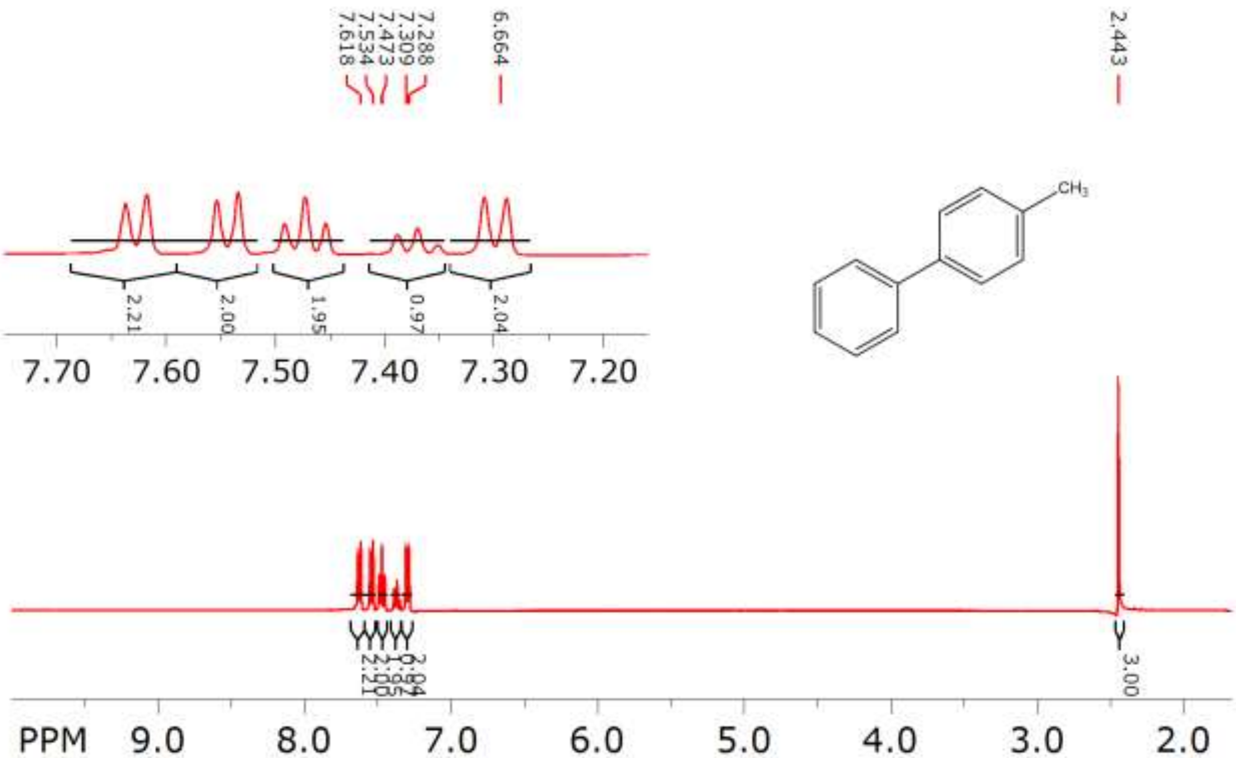

Figure S12. [1]H NMR spectrum of 4-methyl-1,1'-biphenyl in $CDCl_3$.

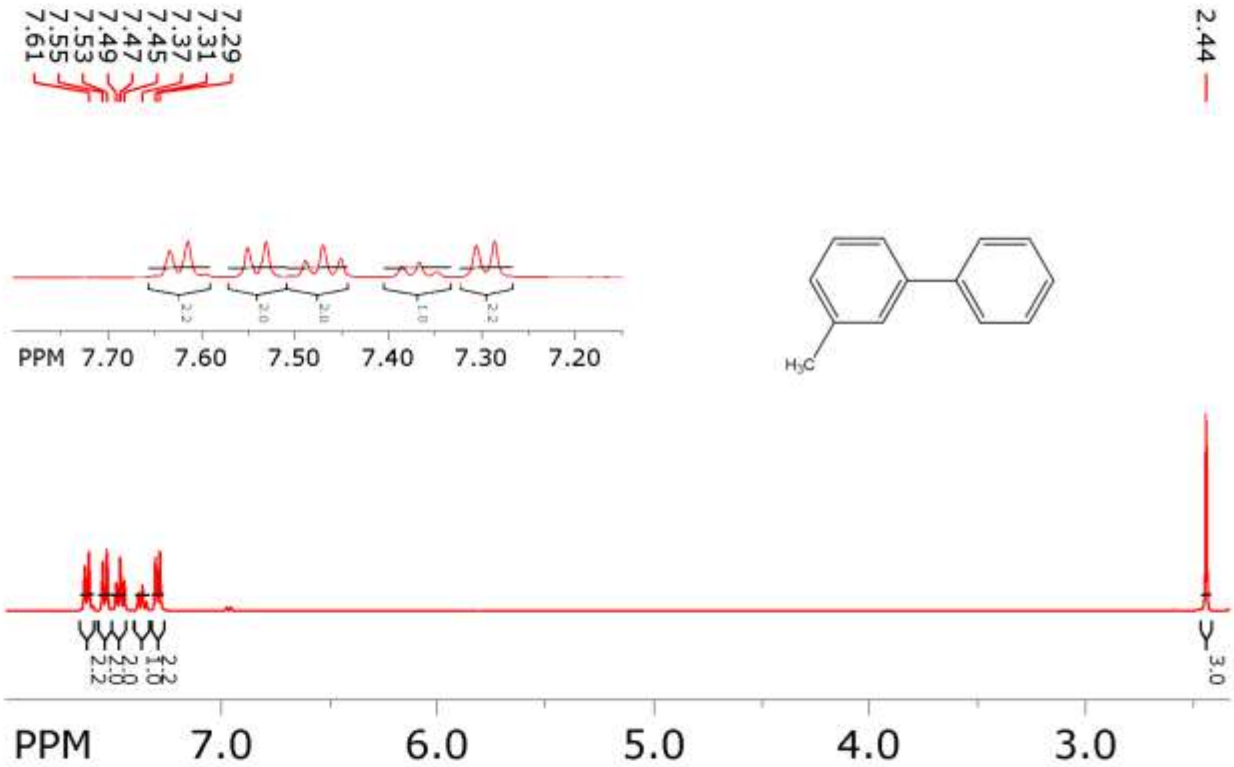

Figure S13. ^{1}H NMR spectrum of 3-methyl-1,1'-biphenyl in $CDCl_3$.

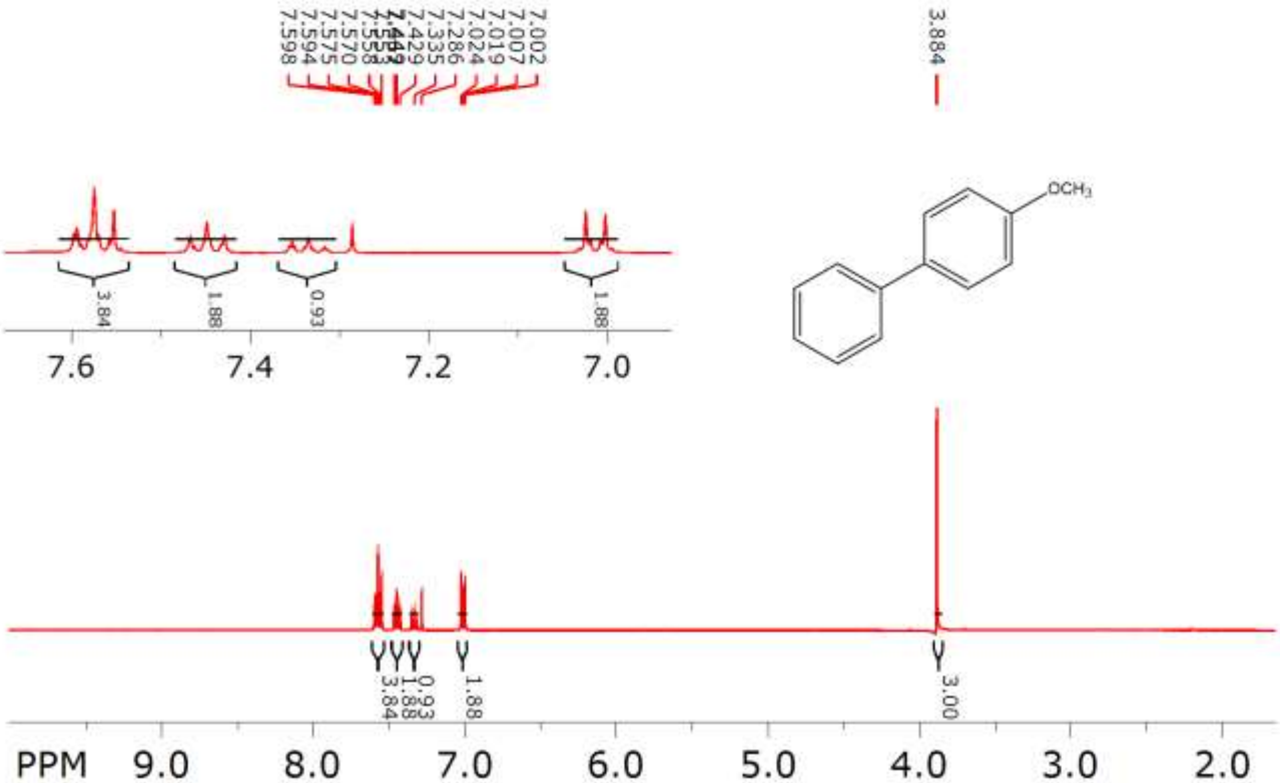

Figure S14. ^{1}H NMR spectrum of 4-methoxy-1,1'-biphenyl in $CDCl_3$.

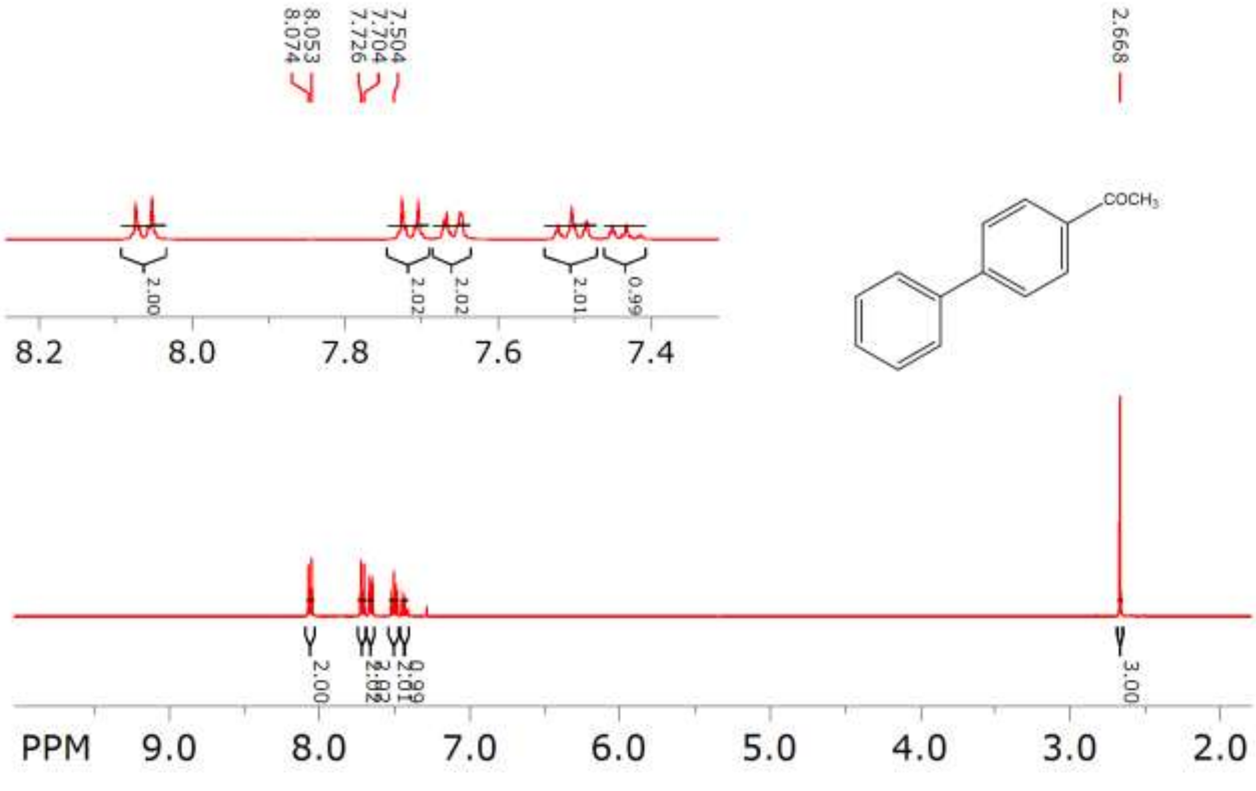

Figure S15. ^{1}H NMR spectrum of 1-([1,1'-biphenyl]-4-yl)ethanone in $CDCl_3$.

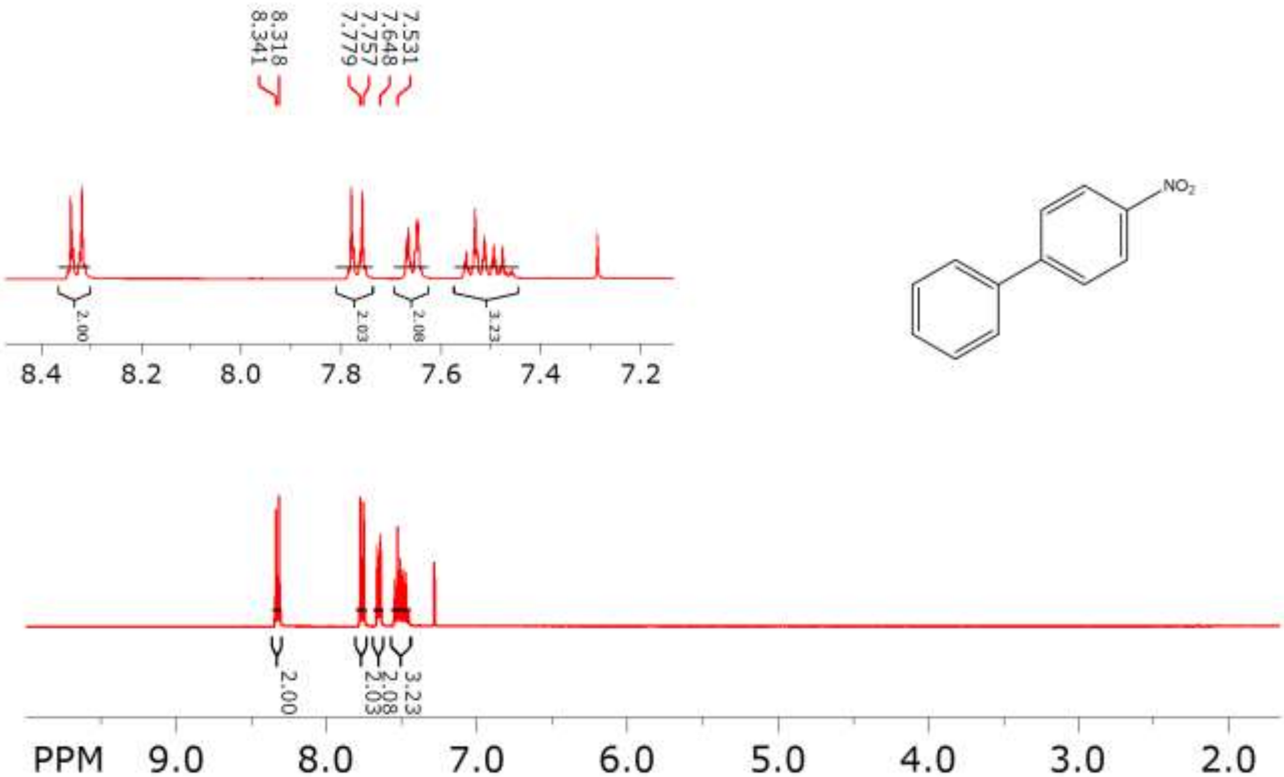

Figure S16. [1]H NMR spectrum of 4-nitro-1,1'-biphenyl in $CDCl_3$.

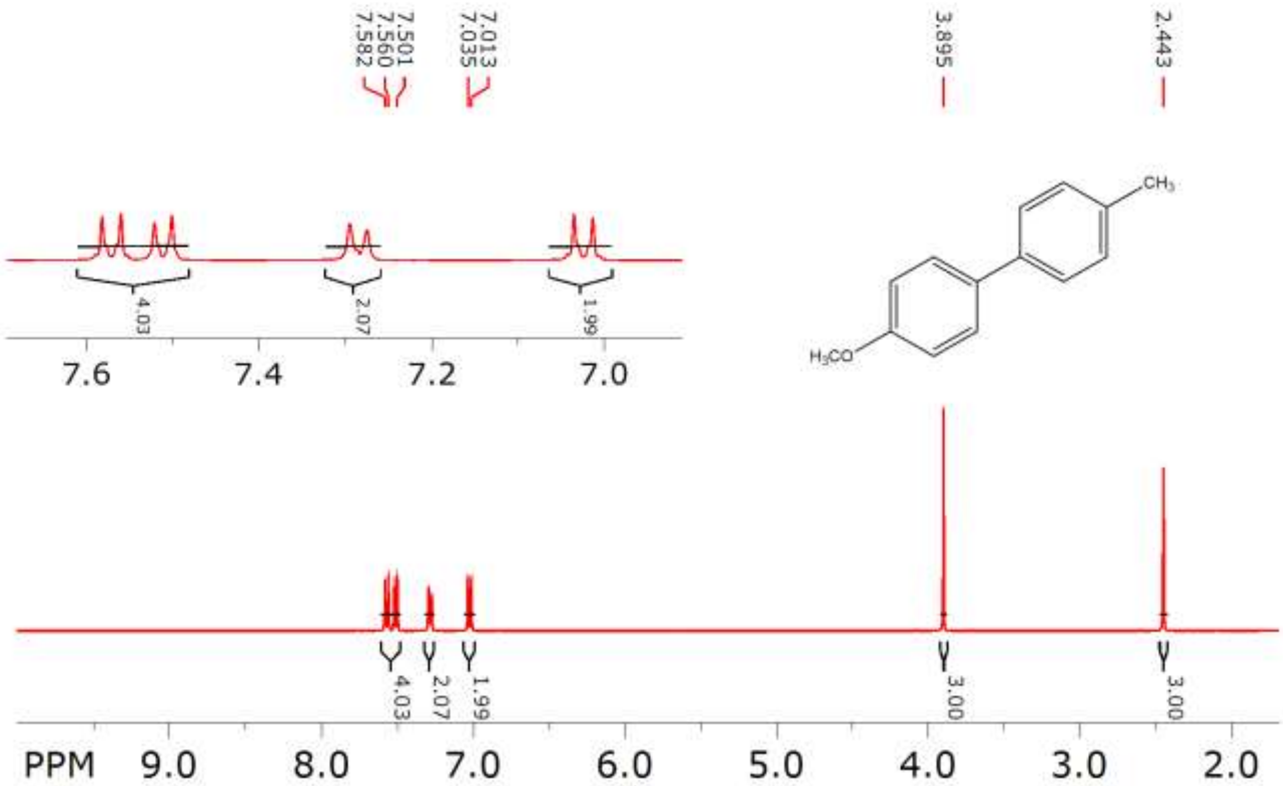

Figure S17. ^{1}H NMR spectrum of 4-methoxy-4'-methyl-1,1'-biphenyl in $CDCl_3$.

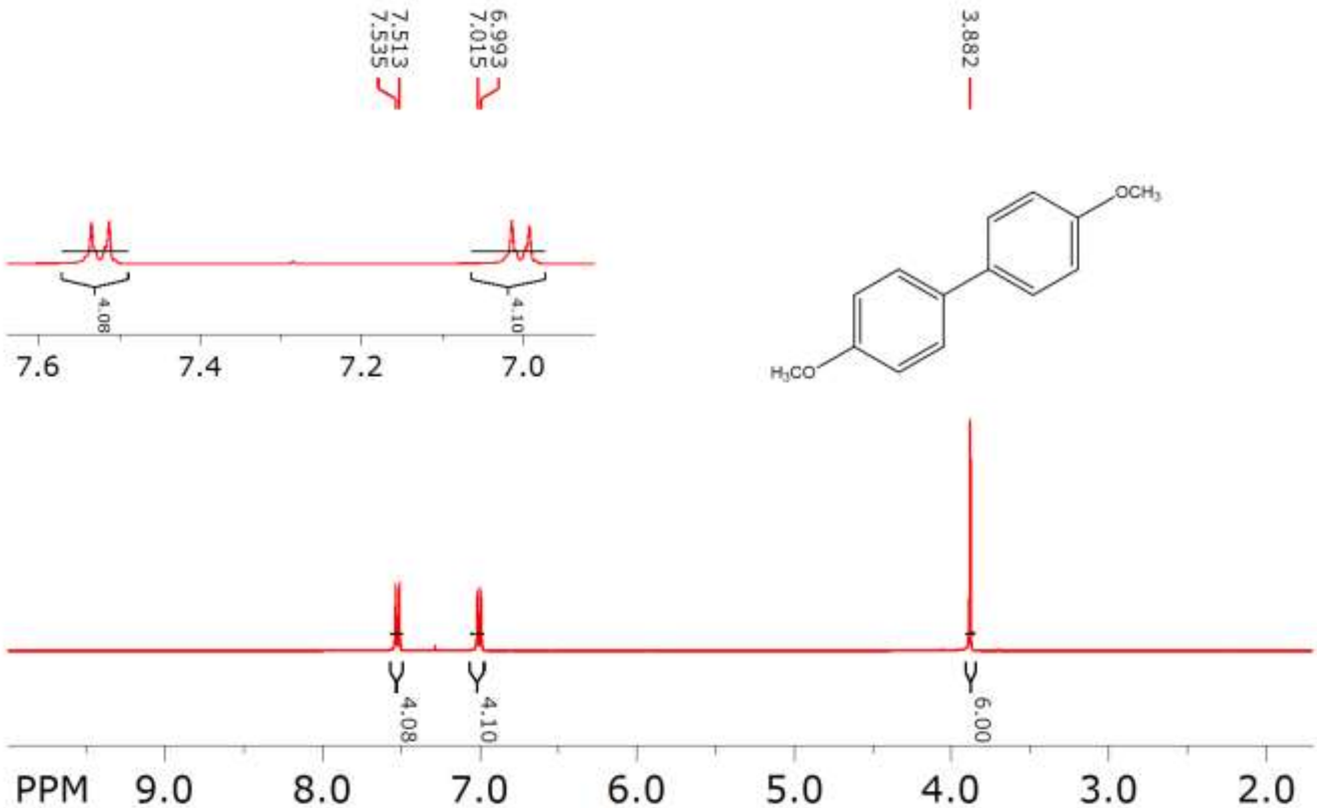

Figure S18. [1]H NMR spectrum of 4,4'-dimethoxy-1,1'-biphenyl in $CDCl_3$.

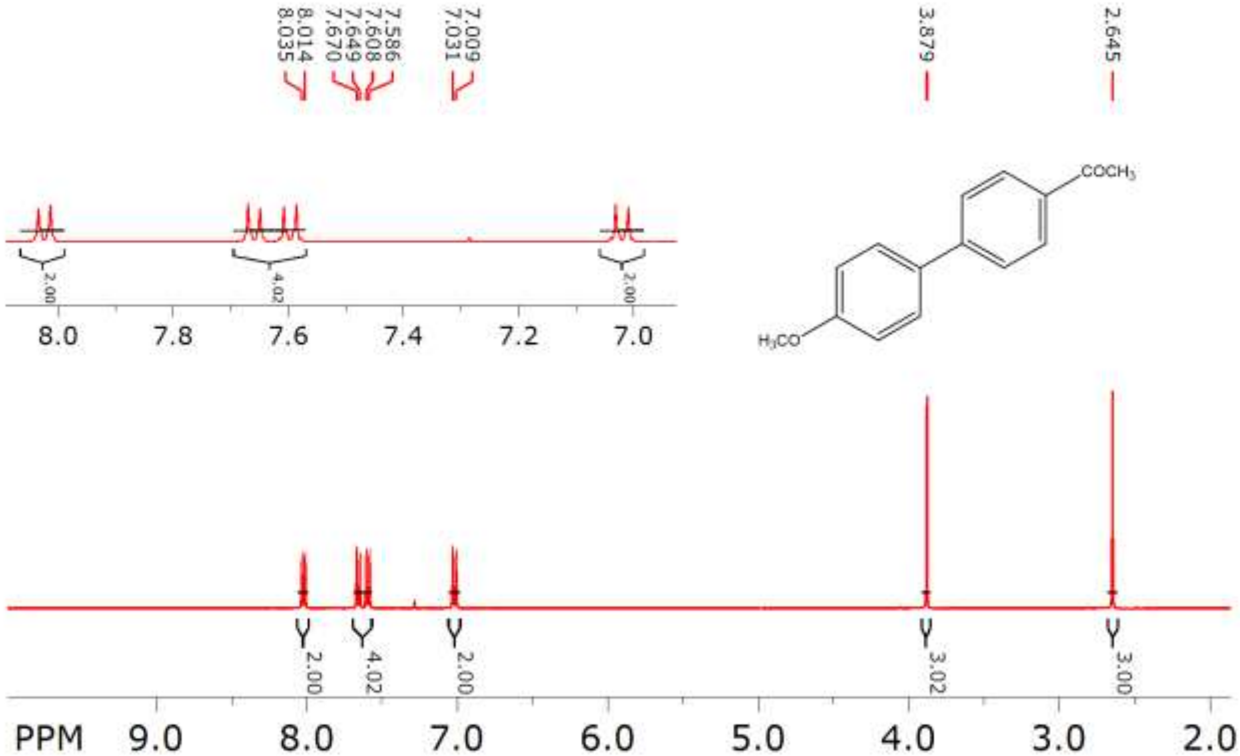

Figure S19. ^{1}H NMR spectrum of 1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethanone in $CDCl_3$.

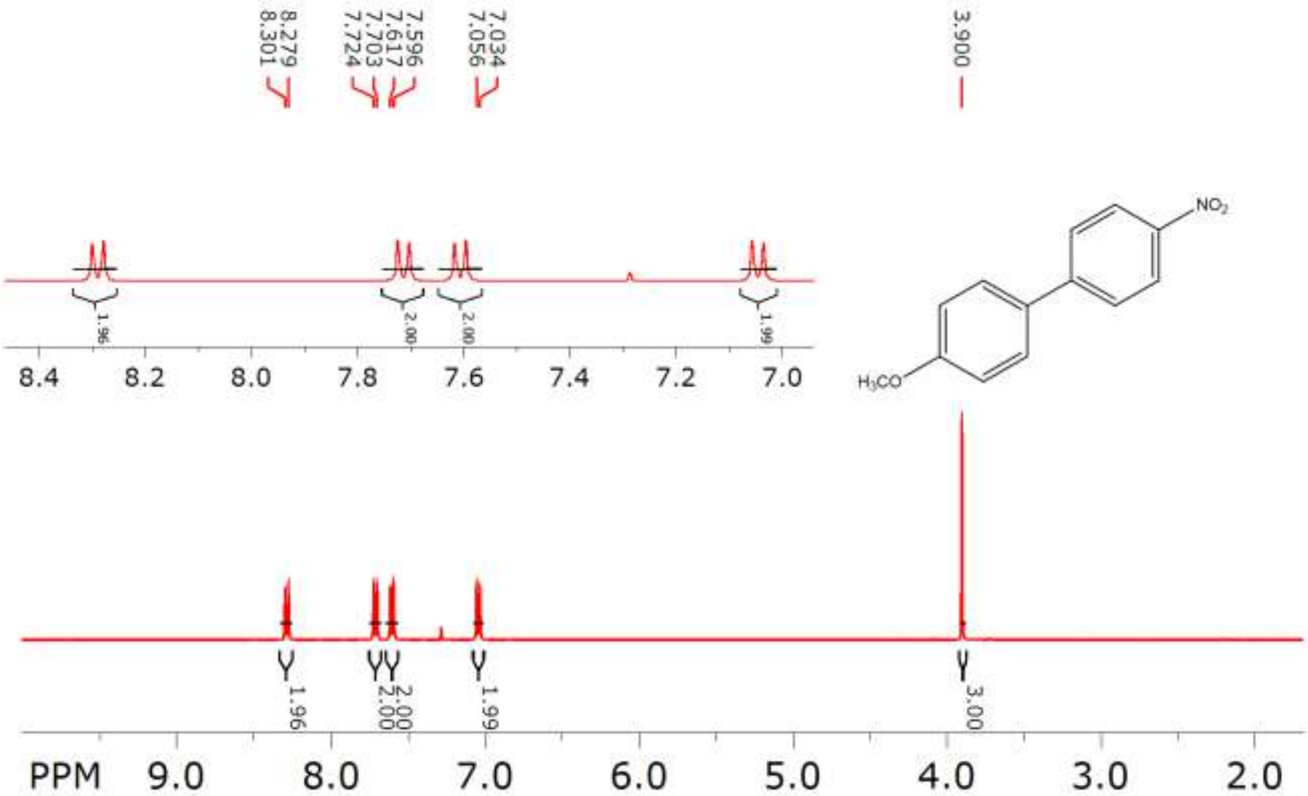

Figure S20. ^{1}H NMR spectrum of 4-methoxy-4'-nitro-1,1'-biphenyl in $CDCl_3$.

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