Supporting Information

A Supramolecular Recyclable Catalyst for Aqueous Suzuki-Miyaura Coupling

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1. Materials

(3,5-Dimethyl-1H-pyrazolyl)methanol, 1-adamantanemethylamine, anhydrous acetonitrile and $PdCl_2$ were purchased from Sigma-Aldrich. Heptakis(2,6-di-O-methyl)-*β*-cyclodextrin-dimethyl (dm*β*-CD) was purchased from Sigma. All substrates for Suzuki-Miyaura coupling reaction were purchased from Sigma-Aldrich. All other reagents and solvents were used as received without further purification.

2. Measurements and Experimental Methods

2.1 General. Proton and carbon nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were recorded at room temperature on a Bruker Avance DRX 300 MHz NMR spectrometer operating at 300.1 and 75.5 MHz, respectively; or on a Bruker Avance DRX 500 MHz NMR spectrometer operating at 500.1 and 125.8 MHz, respectively. Chemical shifts were reported in parts per million (ppm) on the δ scale, and were referenced to residual protonated solvent peaks: $CDCl_3$ spectra were referenced to $CHCl_3$ at δ_H 7.26 and $CDCl_3$ at δ_C 77.36; D_2O spectra were referenced to *H*DO at δ_H 4.70; Acetone-d_6 spectra were referenced to $(CHD_2)(CD_3)CO$ at δ_H 2.09. The two-dimensional nuclear overhauser effect spectroscopy (2D-NOESY) NMR experiments were performed at 500 MHz in D_2O/DMSO-d_6 on a Bruker Avance DRX 500 MHz NMR spectrometer with sodium 3-(trimethylsilyl)propane-1-sulfonate as reference. ESI-MS was performed on a Finnigan LCQ quadrapole ion trap mass spectrometer. Elemental analysis was carried out using a Perkin-Elmer 2400 CHN/CHNS elemental analyzer.

2.2 X-ray Crystal Structure for adamantyl-containing Pd(II) complex (Ad-L-$PdCl_2$)

Crystals suitable for X-ray diffraction were obtained by recrystallization from CH_2Cl_2/diethyl ether. Single crystal X-ray diffraction data was collected on a Bruker-AXS Smart Apex CCD diffractometer. Structure solution and refinement were carried out with the Bruker SHELXTL suite of programmes. Single crystal data and structure refinement parameters for this compound can be found in Table S1.

Table S1. Single crystal data and structure refinement parameters for adamantly-containing Pd(II) complex (Ad-L-$PdCl_2$)

Identification code	Ad-L-$PdCl_2$	
Empirical formula	C23 H35 Cl2 N5 Pd	
Formula weight	558.86	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.8954(5) Å	α= 90°.
	b = 13.9545(6) Å	β= 96.7110(10)°.
	c = 17.7018(8) Å	γ = 90°.
Volume	2427.61(19) $Å^3$	
Z	4	
Density (calculated)	1.529 Mg/m^3	
Absorption coefficient	1.005 mm^{-1}	
F(000)	1152	
Crystal size	0.38 x 0.17 x 0.15 mm^3	
Theta range for data collection	1.86 to 27.50°.	
Index ranges	-12<=h<=12, -18<=k<=15, -21<=l<=22	
Reflections collected	16817	
Independent reflections	5558 [R(int) = 0.0331]	
Completeness to theta = 27.50°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8638 and 0.7013	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5558 / 0 / 284	
Goodness-of-fit on F^2	1.084	
Final R indices [I>2sigma(I)]	R1 = 0.0331, wR2 = 0.0773	
R indices (all data)	R1 = 0.0369, wR2 = 0.0791	
Largest diff. peak and hole	0.656 and -0.449 e.$Å^{-3}$	

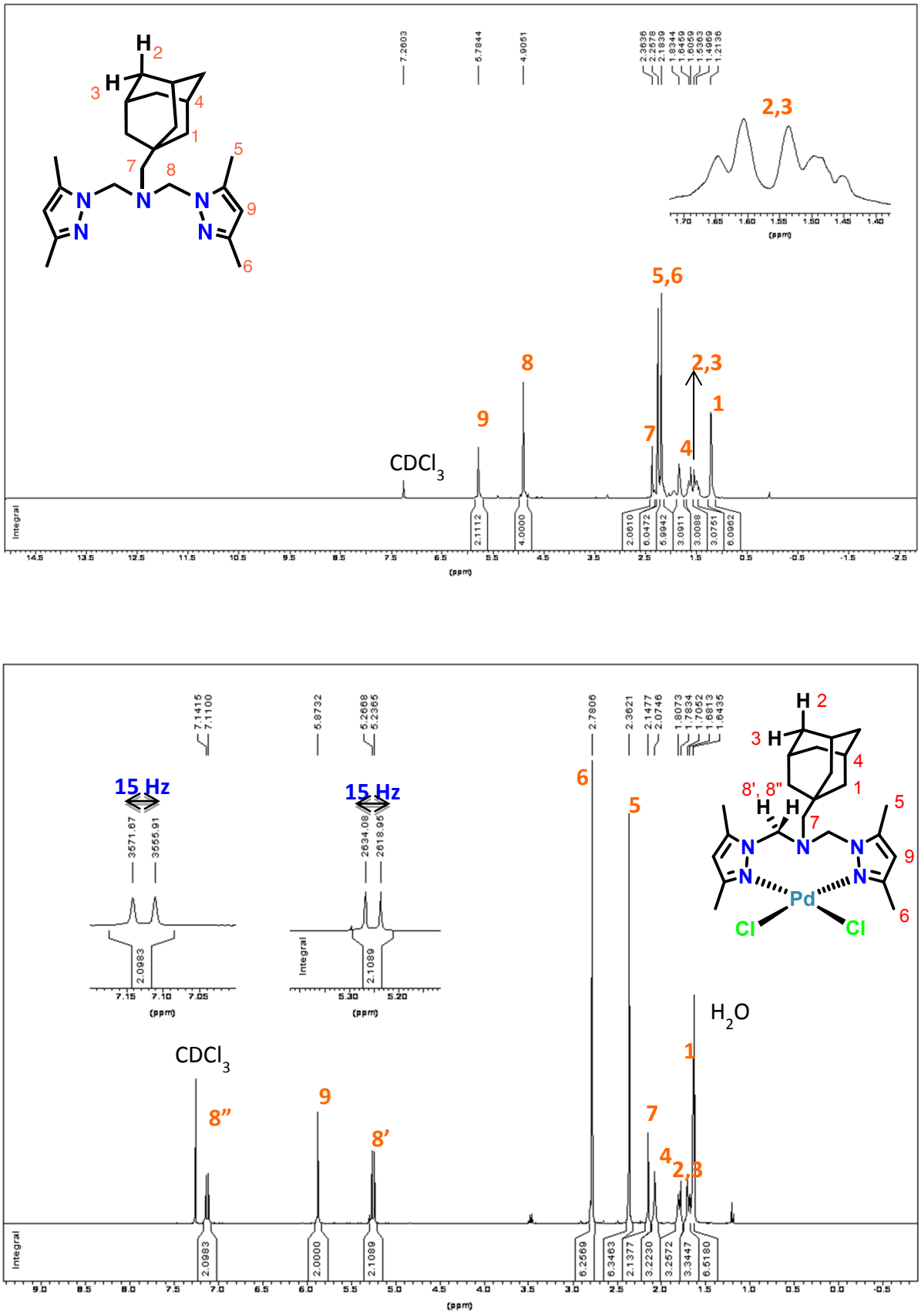

Figure S1. (top) ^{1}H NMR spectrum of the ligand Ad-L in $CDCl_3$ (300 MHz, 25 ^{o}C); (bottom) ^{1}H NMR spectrum of the Pd(II) complex Ad-L-$PdCl_2$ in $CDCl_3$ (500 MHz, 25 ^{o}C).

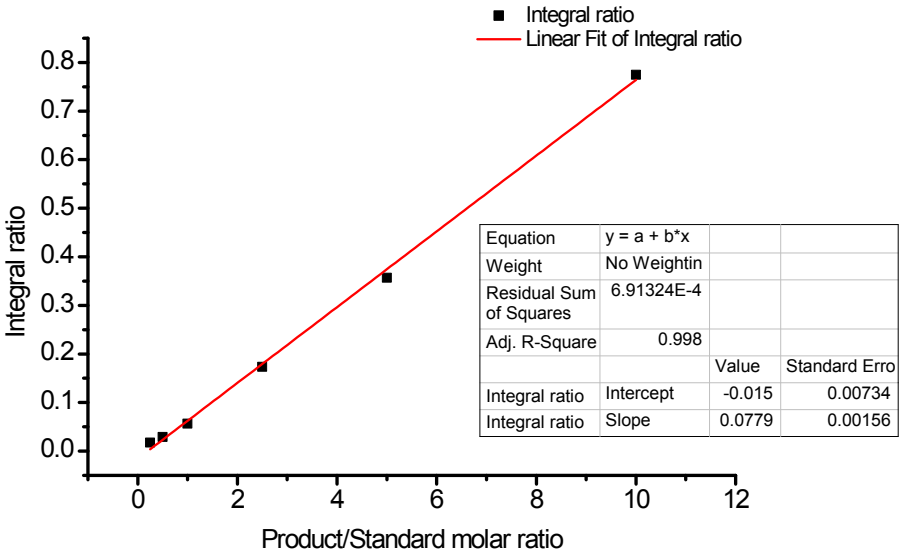

Figure S2. Calibration curve based on ^{1}H NMR analysis (in d_6-acetone) for the yield calculation for Suzuki-Miyaura coupling reaction (product is biphenyl-4-carboxylic acid; standard is hexadecane).