Facile tandem Suzuki coupling/transfer hydrogenation reaction by bis-heteroscorpionate-Pd-Ru complex†

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Experimental

Materials

The precursor complexes $[Ru(p\text{-cym})Cl(\mu\text{-}Cl)]_2$,[1] Li_2PdCl_4,[2] mononuclear complex [(*p*-cym)RuCl(pz_4lut)]Cl[3] dinuclear $[\{(p\text{-cym})RuCl\}_2(\mu\text{-}pz_4lut)]Cl_2$ (**3**)[3] and ligand α,α,α′,α′-tetra(pyrazol-1-yl)-2,6-lutidine (pz_4lut)[4] were prepared by following the reported procedures. All chemicals were purchased from commercial sources and used as received. Solvents were dried by conventional methods and distilled prior to use.

Instrumentation

All inert reactions were carried out under nitrogen using standard Schlenk techniques or inside the MBraun Labstar glove box. UV-Vis spectra were recorded by using a Perkin Elmer Lambda 35 spectrophotometer. FTIR spectra were obtained using Bruker Alpha FTIR spectrophotometer with samples prepared as KBr pellets. Conductivity measurements were done by using OAKton PC2700 conductivity bridge. Electrospray ionisation (ESI) MS spectra of the complexes were acquired on a Flexar SQ 300 MS PerkinElmer mass spectrometer. Elemental analyses were carried out with a Perkin-Elmer 240C elemental analyser. ^{1}H NMR spectra were acquired on a Bruker Avance III 400 spectrometer using $CDCl_3$ and DMSO-d_6 solvent. Electrochemical measurements were conducted in nitrogen atmosphere using a CHI 6205 electrochemical analyser using NEt_4ClO_4 as the supporting electrolyte (0.1 mol dm^{-3}) and the solute concentration was 10^{-3}

mol dm^{-3}. For electrochemical measurements a glassy carbon working electrode, Pt wire counter electrode and aqueous saturated Ag/AgCl reference electrode were used. The half-wave potential E_{298}^{o} was set equal to 0.5 V (E_{pa} + E_{pc}), where E_{pa} and E_{pc} are anodic and cathodic cyclic voltammetric peak potentials, respectively. In this cell, Fc/Fc^{+} couple had an $E_{1/2}$ value of 0.21 V.

Crystallography

Single crystal of **1** was grown by slow diffusion followed by evaporation of methanol/chloroform solution at room temperature. Single crystal X-ray structural studies ware performed on a Bruker D8 venture instrument. Data were collected at 120 (2) K using Mo K_{α} radiation (λ_{α} = 0.71073 Å). The strategy for the data collection was evaluated by using the APEX 10 software. The data were collected by the standard phi-omega scan techniques, and were scaled and reduced using SAINT and XPREP software. The structures were solved by direct methods using XSHELL software and refined by full matrix least-squares with XSHELL software refining on F^2.[5] The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally $1.2U_{eq}$ of their parent atoms.

CCDC reference number for **1** is 1017846.

Synthesis of metal complexes

Synthesis of [{(p-cym)RuCl}(μ-pz$_4$lut)PdCl$_2$]ClO$_4$ (1): Mononuclear [(*p*-cym)RuCl(Pz$_4$lut)]Cl (50 mg, 0.07 mmol) was dissolved in 20 cm^3 methanol and to it 15 cm^3 *in situ* generated Li_2PdCl_4 [$PdCl_2$ (12.3 mg, 0.07 mmol) and LiCl (17.5 mg, 0.4 mmol)] was added dropwise with stirring under aerobic condition. During the course of reaction the yellow colored solution changed to reddish yellow. The stirring was continued for an additional 8 h. Solvent was dried under reduced pressure and redissolved in minimum acetonitrile followed by addition of saturated solution of aqueous $NaClO_4$ resulted light yellow precipitate. The precipitate was filtered, washed with sufficient amount of cold water and dried under vacuum to yield pure **1**. Yield 65.3 mg (97%). Anal. Calc.: C, 43.10; H, 4.59; N, 12.22.Found: C, 42.50; H, 4.77; N, 11.65. Molar conductivity [Λ_M/ (Ω^{-1} cm^2 dm^3 mol^{-1})] in acetonitrile: 68. The positive ion electrospray mass spectrum of **1** in methanol exhibited the signal centred at m/z value of 931.8 corresponding to {**1**-ClO_4}$^+$ (calculated molecular mass 931.69).). ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 298 K: δ (ppm): 0.93 (d, *J* = 4Hz, 6H, $(CH_3)_2$CH-*p*-cym), 1.38 (m, *J* = 4Hz, 8Hz, 8Hz, 4Hz, 1H, CH-*p*-cym), 1.77 (s, 3H, CH_3-*p*-cym), 2.25 (s, 6H, CH_3-pz), 2.36 (s, 6H, CH_3-pz), 2.53 (s, 6H, CH_3-pz), 5.40 (broad, 2H, CH-*p*-cym), 5.75 (broad, 2H, CH-*p*-cym), 6.24 (s, 2H, CH-pz), 6.37 (s, 2H, CH-pz), 6.84 (d, *J* = 8 Hz, 2H, CH-py), 7.32 (s, 1H, CH-$(pz)_2$), 7.38 (d, *J* = 8 Hz, CH-py), 7.74 (s, 1H, CH-$(pz)_2$), 8.18 (t, *J* = 8 Hz, 8Hz, CH-py). λ_{max}/ nm (ε/dm^3 mol^{-1} cm^{-1}) in CH_2Cl_2: 232 (36541), 273 (13263), 330 (1861), 440 (786).

Synthesis of [(PdCl$_2$)$_2$(μ-pz$_4$lut)] (2): To a 5 cm^3 methanolic solution of pz$_4$lut ligand (48.3 mg, 0.1 m mole) a solution of *in situ* generated Li_2PdCl_4 ($PdCl_2$ (60.0 mg, 0.33 mmol) and LiCl (84.0

mg, 1.98 mmol)) was added dropwise with stirring. Immediately the color of the solution changed from brown to yellow with precipitate and stirring was continued for additional 8 h to complete the reaction. It was then filtered and washed thoroughly with cold methanol to get the pure complex **2**. Yield 60 mg (72 %). Anal. Calc.: C, 38.69; H, 3.97; N, 15.04.Found: C, 37.34; H, 3.914; N, 14.62. Molar conductivity [Λ_M/ (Ω^{-1} cm^2 dm^3 mol^{-1})] in CH_2Cl_2: 0.5. The positive ion electrospray mass spectrum of **2** in methanol exhibited the signal centred at m/z value of 803.9 corresponding to {**2**-Cl}$^+$ (calculated molecular mass 802.8). ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 298 K: δ (ppm): 2.36 (s, 12H, (CH_3-pz)), 2.38 (s, 12H, CH_3-pz), 6.16 (s, 4H, CH-pz), 7.50 (d, J- 8Hz, 2H, CH-py),7.81 (s, 2H, CH-$(pz)_2$), 8.21 (t, J = 8Hz, 8 Hz, 1H, CH-py). λ_{max} / nm (ε/dm^3 mol^{-1} cm^{-1}) in CH_2Cl_2: 232 (42414), 271 (12657), 320 (1642), 384 (742).

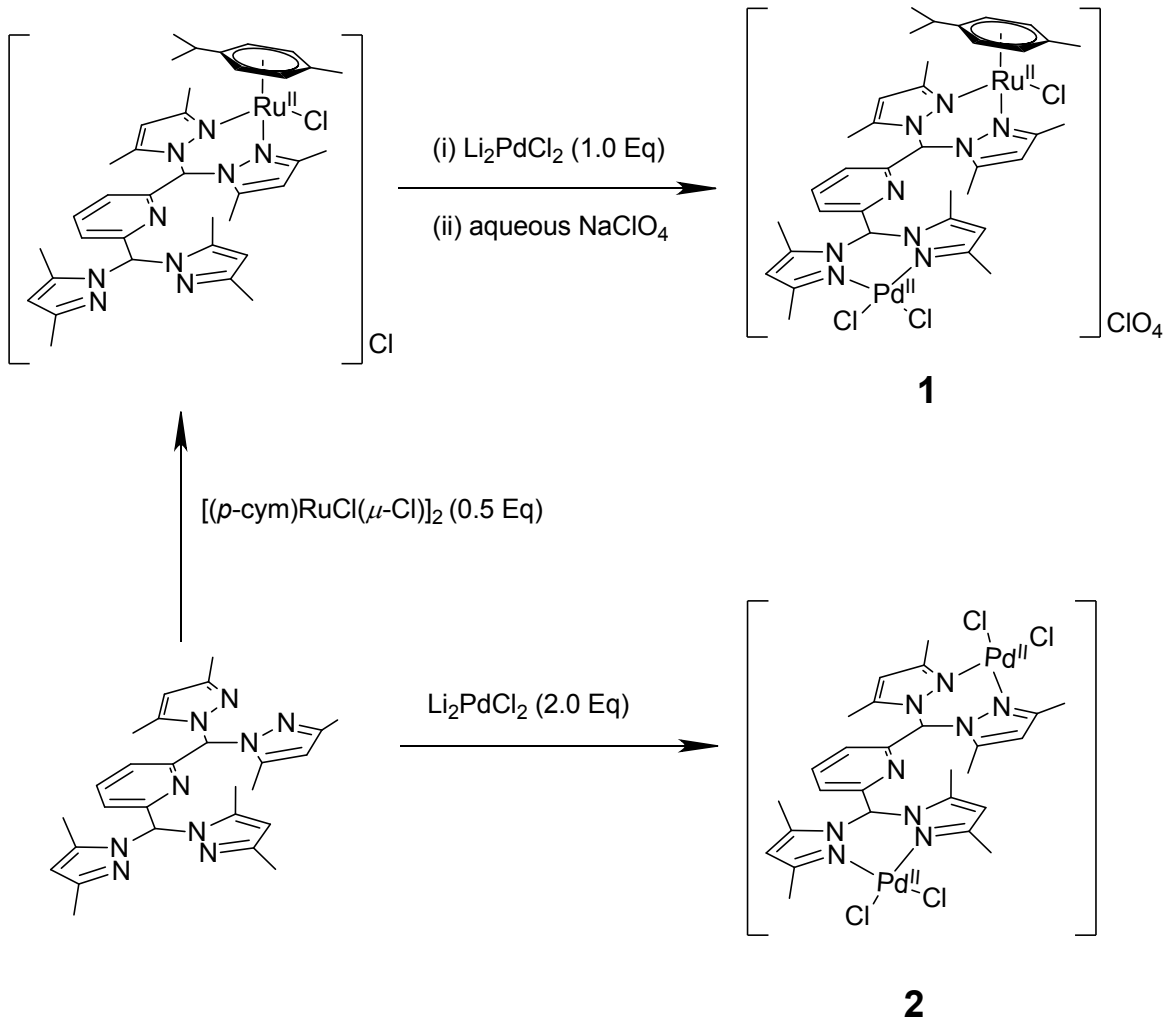
Catalytic Studies

Suzuki Coupling/Transfer Hydrogenation of Ketones.

In general, an oven dried capped vessel containing a stirrer bar was charged with 4-bromoacetophenone (0.5 mmol), phenylboronic acid (0.6 mmol), KO*t*Bu (1.8 mmol), and catalyst **1** (0.12 mol %) in 1 cm^3 of alcohol. The reaction mixture was stirred at room temperature (30 ^{o}C) for the appropriate time inside a glove box. Reaction was quenched by adding excess CH_2Cl_2 and compounds were separated through preparatory thin layered chromatography using *n*-hexanes/ethylacetate (10:1) as eluent. Reactions were also conducted at 80 ^{o}C over preheated oil baths by taking the abovementioned ratios of reactants and catalysts. Isolated products were characterised by ^{1}H NMR spectroscopy.

Hg(0) poisoning experiment.

An oven dried vessel was charged with 4-bromoacetophenone (0.5 mmol), phenylboronic acid (0.6 mmol), KO*t*Bu (1.8 mmol), and catalyst **1** (0.12 mol %) in 1 cm^3 of *i*PrOH. A large excess of Hg (~800 equiv.) was added into the reaction mixture at the middle of the reaction (~ 50% conversion of 4-bromoacetophenone; 0.5 h for the 80 ^oC and 6 h for 30 ^oC), and the reaction was continued until the time (2.5 h for the 80 ^oC and 48 h for 30 ^oC) monitored for normal reaction (without the addition of Hg). Similar reaction condition was followed for a mixture of **2** + **3**. The reactions were quenched and the compounds were purified by following the procedure mentioned for catalytic reactions without the addition of Hg.



Scheme S1 Synthetic route towards the preparation of complexes **1** and **2**.

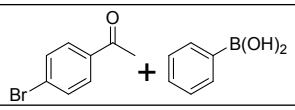
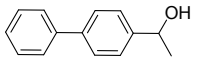
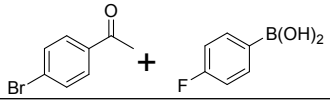
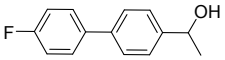
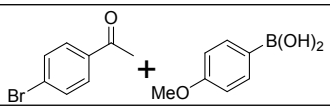
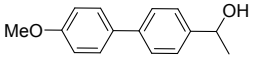
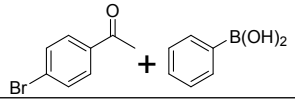
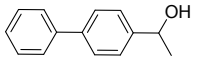
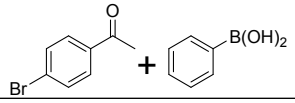
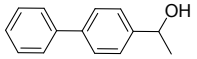
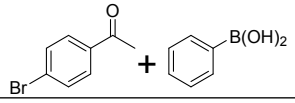
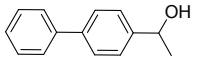
Table T1 Selected crystallographic data for complex **1**.

	1
emperical formula	$C_{37}H_{47}Cl_4N_9O_4PdRu$
Fw	1031.11
radiation	MoK_α
wavelength (Å)	0.71073
temp./ K	120(2)
cryst system	Triclinic
space group	P -1
a/Å	12.3219(15)
b/Å	13.7410(17)
c/Å	14.6240(18)
α(deg)	105.783(3)
β(deg)	110.076(3)
γ(deg)	106.101(3)
V/ Å^3	2041.0(4)
Crystal size (mm)	0.15 x 0.11 x 0.08
Z	2
μ / mm^{-1}	1.127
D_{calcd} / g cm^{-3}	1.678
F(000)	1044
θ range	2.44 - 27.65
Data/restraints/parameters	8228 / 0 / 516
R1,wR2 [I>2σ(I)]	0.0403
R1,wR2 (all data)	0.1094
Largest diff. peak hole (eÅ^{-3})	1.61, -0.55

Table T2 Important bond distances (Å) and bond angles (°) for **1**.

Bond lengths		Bond angles	
Pd(1)-N(7)	2.027(3)	N(7)-Pd(1)-N(9)	86.57(12)
Pd(1)-N(9)	2.038(3)	N(7)-Pd(1)-Cl(2)	91.40(9)
Pd(1)-Cl(2)	2.2801(11)	N(9)-Pd(1)-Cl(3)	92.00(9)
Pd(1)-Cl(3)	2.2805(10)	Cl(2)-Pd(1)-Cl(3)	90.18(4)
Ru(1)-N(5)	2.107(3)	N(5)-Ru(1)-N(3)	86.99(11)
Ru(1)-N(3)	2.125(3)	N(5)-Ru(1)-Cl(1)	81.87(9)
Ru(1)-C(4)	2.249(4)	N(3)-Ru(1)-Cl(1)	84.97(8)
Ru(1)-C(5)	2.194(4)		
Ru(1)-C(6)	2.218(4)		
Ru(1)-C(7)	2.217(4)		
Ru(1)-C(8)	2.190(4)		
Ru(1)-C(9)	2.209(4)		
Ru(1)-Cl(1)	2.4020(10)		
Ru-$C_{centroid}$	1.700		

Table T3 Mercury poisoning test for the tandem Suzuki coupling/transfer hydrogenation reaction on **1** and **2** +**3**.[a]

Sr. No.	Substrates	Cat.	Time (h)	Product	Yield of alcohol (%)[b]	
					No Hg(0)	With Hg(0)
1		**1**	2.5[c]		97	95
2		**1**	3.0[c]		91	91
3		**1**	3.5[c]		82	80
4		**2**+**3**[e]	2.5[c]		97	96
5		**1**	48[d]		67	66
6		**2**+**3**[e]	48[d]		53	53

[a] Reaction conditions: Catalyst/4-bromoacetophenone/$ArB(OH)_2$/KO*t*Bu = 1/800/1000/3000 (molar ratio), Catalyst (0.125 mol%), 4-bromoacetophenone (0.5 mmol), $ArB(OH)_2$ (0.6 mmol), KO*t*Bu (1.8 mmol), *i*PrOH (1 mL); 800 times Hg with respect to catalyst was added during the 50% completion of the reactions.[b] Isolated yields after preparatory thin layered chromatography. [c] 80 °C, [d] 30 °C, [e] **2**:**3** = 1:1 (molar ratio).

Fig. S1. Electrospray (+ve) mass spectra of complexes (a) **1** and (b) **2** in CH_3OH.

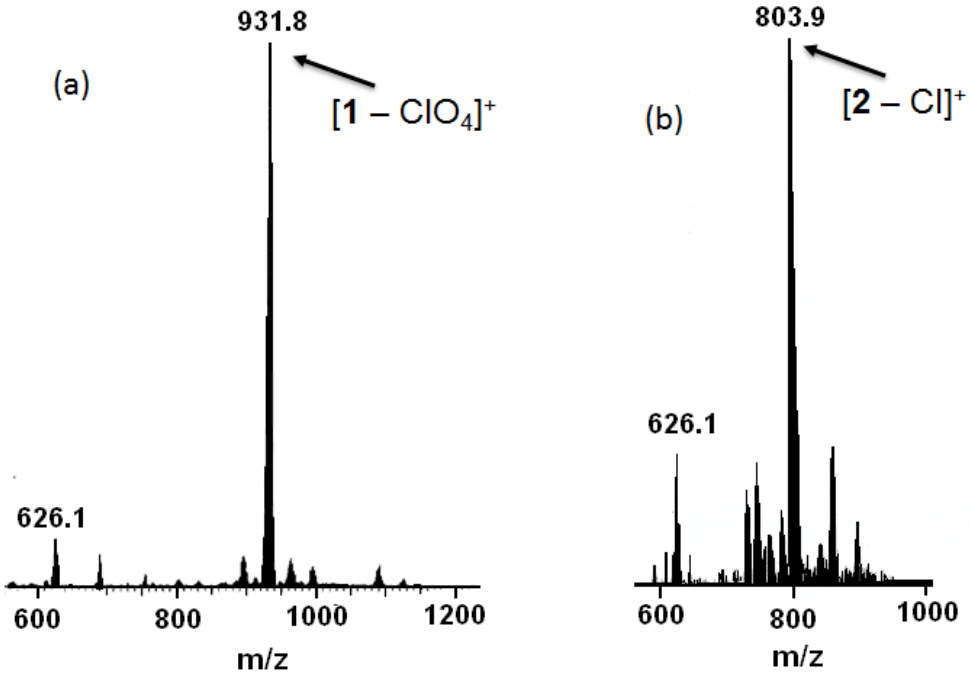


Fig. S2 ^{1}H NMR spectra of complexes **1**and **2** recorded in DMSO d_6.

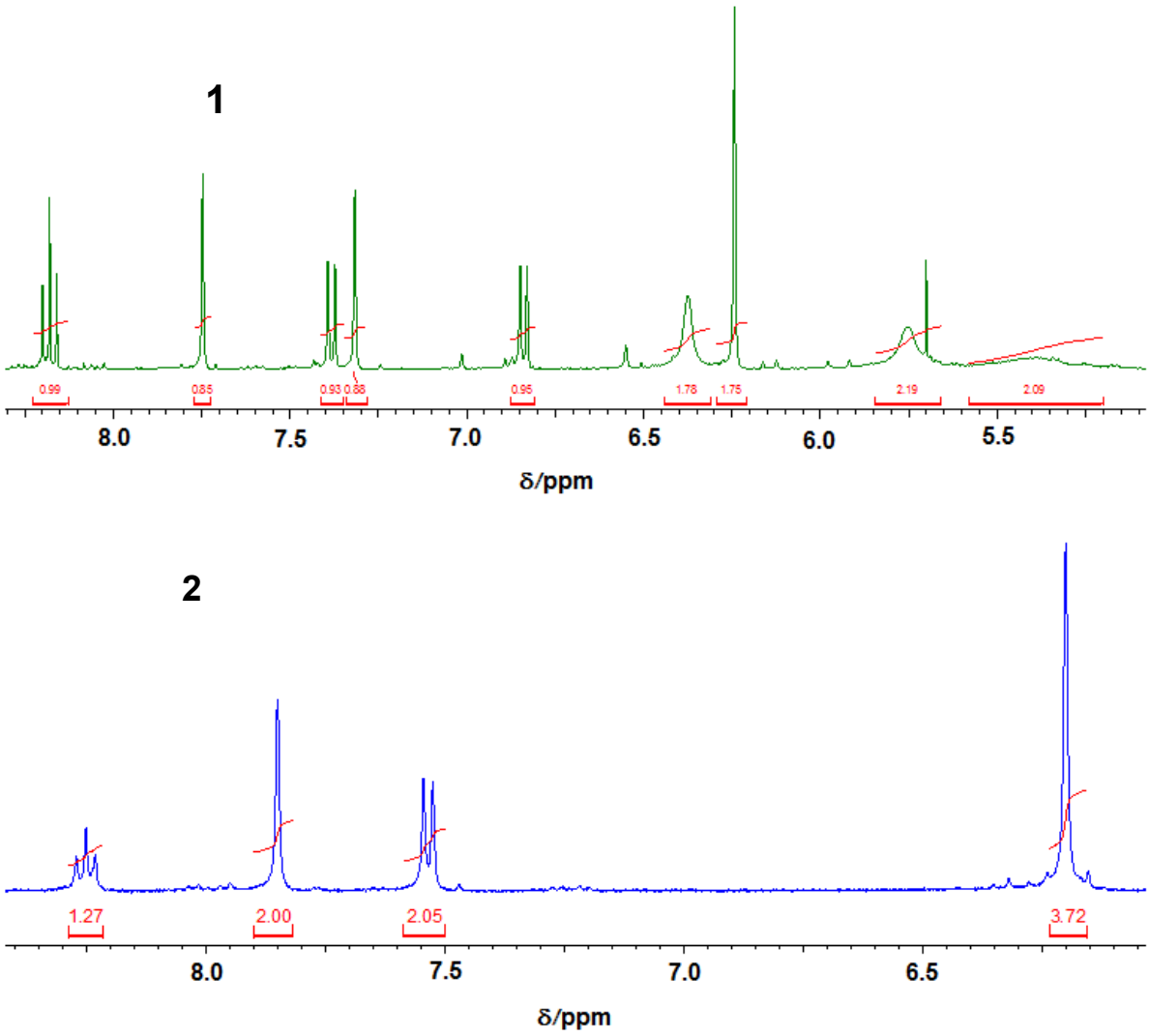


Fig. S3 UV-Vis spectra of **1** and **2** recorded in CH_3CN at room temperature.

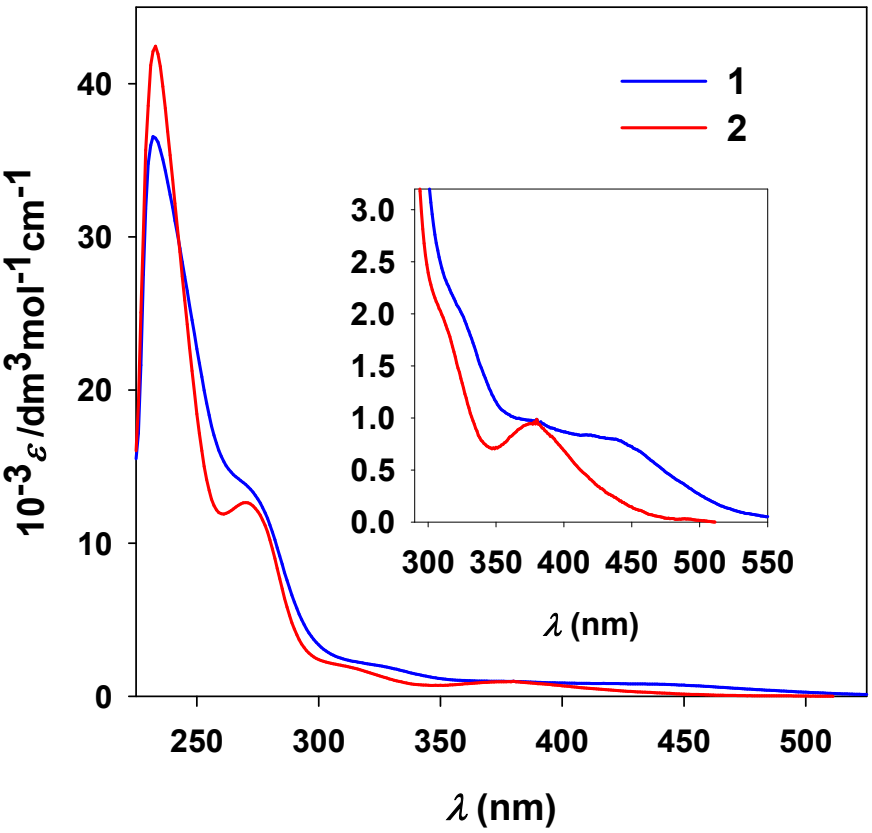


Fig. S4 Cycilc voltammogram of complex **1** recorded in CH_3CN/0.1 mol dm^{-3} Et_4NClO_4 *versus* Ag/AgCl (scan rate 50 mV s^{-1})

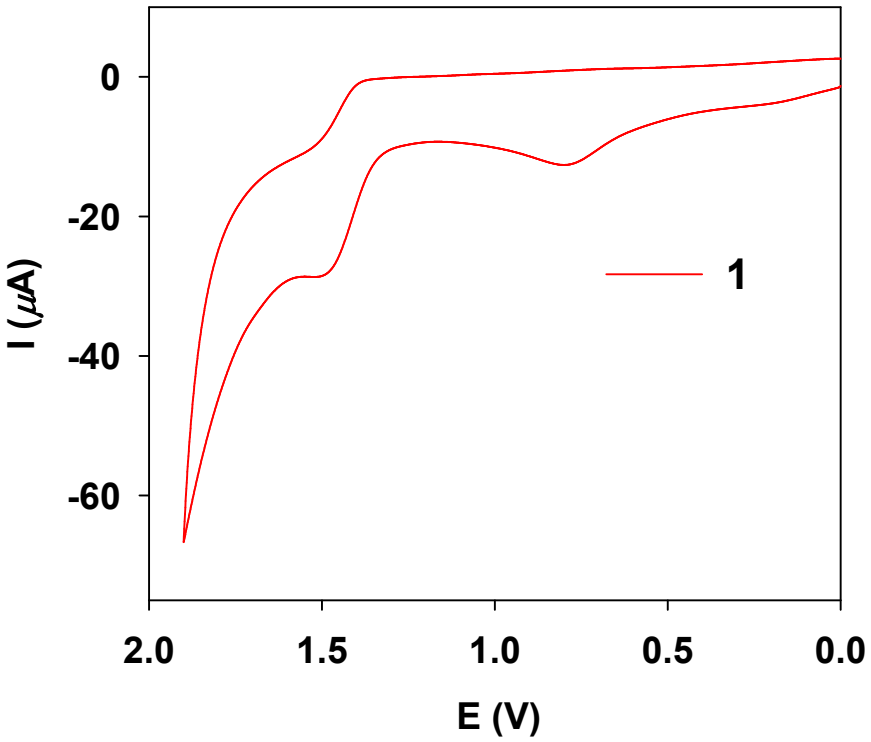
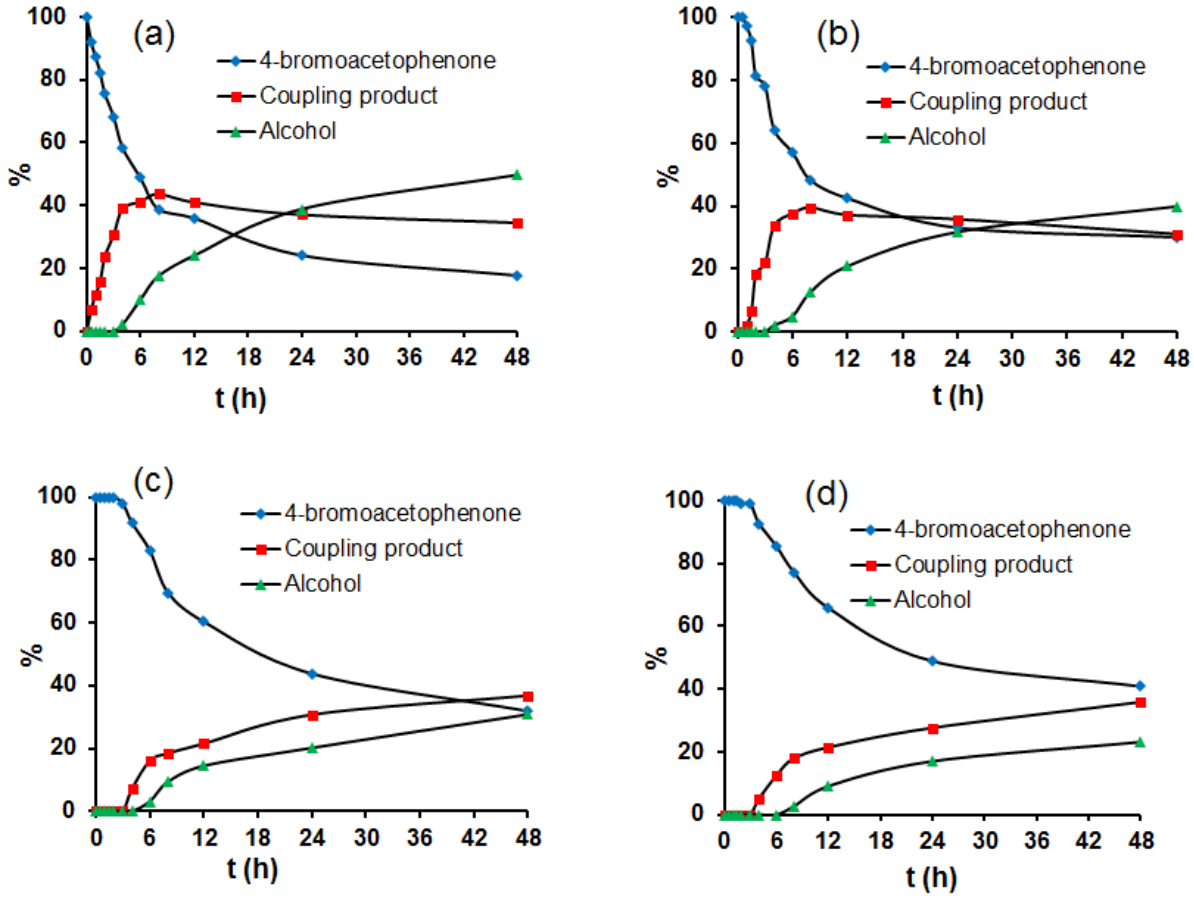
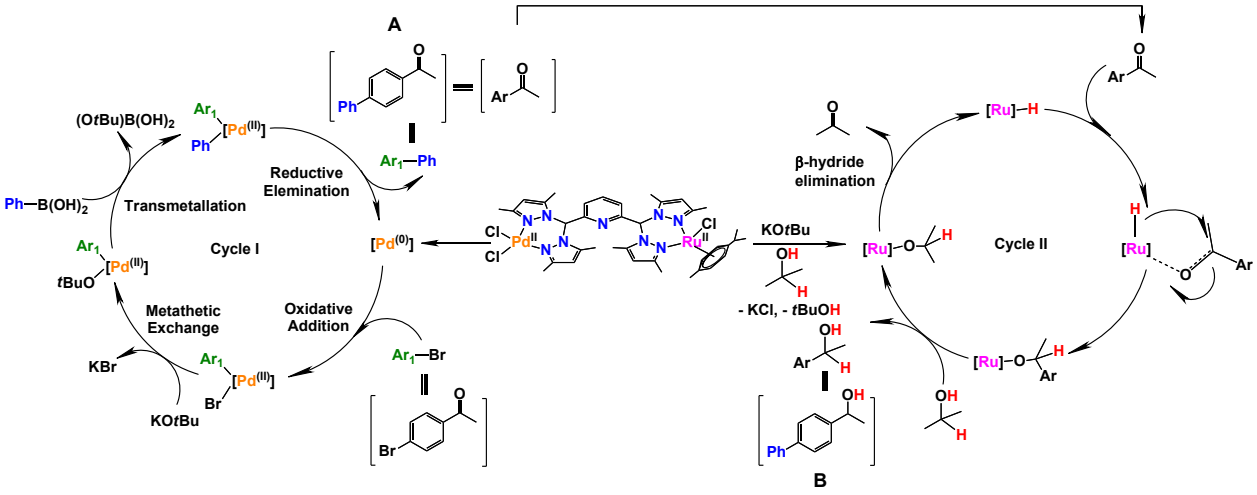


Fig. S5 Time-dependent transformation of 4-bromoacetophenone towards tandem Suzuki coupling/transfer hydrogenation reaction by **1** {(a) and (c)}, and 1:1 mixture of **2** and **3** {(b) and (d)}. Reaction conditions: 4-bromoacetophenone (0.5 mmol), 4-fluorophenylboronic acid {(a) and (b)} and 4-methoxyphenylboronic acid {(c) and (d)} (0.6 mmol), KO*t*Bu (1.8 mmol), *i*PrOH (1 mL), **1** or **2** + **3** (0.125 mol %), at 30 °C.





Scheme S2 Proposed mechanism for tandem Suzuki coupling/transfer hydrogenation reaction catalysed by complex **1**

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