Supporting Information

Four-Electron Oxidation of Phenols to *p*-Benzoquinone Imines by a (Salen)ruthenium(VI) Nitrido Complex

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Materials. $[Ru^{VI}(N)(L)(MeOH)](PF_6)$ (**1**) was prepared by a literature method.[1] Phenol and 2,6-di-*tert*-butylphenol (Sigma-Aldrich) were recrystallized from petroleum ether and ethanol, respectively. Pyridine (Sigma-Aldrich) was dried with KOH and freshly distilled before use under argon atmosphere. Methanol was dried with magnesium turnings and iodine and distilled under argon atmosphere.[2] Other substituted phenols and d_6-phenol (98 atom% D, Sigma-Aldrich) and d_4-methanol (99.8 atom % D, Cambridge Isotope) were used as received.

Instrumentation. Infrared spectra were obtained from KBr plates using a Nicolet 360 FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Bruker (400 MHz) FT NMR spectrometer. The chemical shifts (δ ppm) were reported with reference to tetramethylsilane (TMS). Elemental analyses were done on an Elementar Vario EL analyzer. Electrospray ionization mass spectra (ESI–MS) were obtained on a PE SCIEX API 2000 mass spectrometer. Cyclic voltammetry (CV) was performed with a CH Instruments Electrochemical Workstation CHI660C. A glassy carbon working electrode, a $Ag/AgNO_3$ (0.1 M in CH_3CN) reference electrode, and a Pt wire counter electrode with ferrocene (Cp_2Fe) as the internal standard. The $E_{1/2}$ values were reported with reference to $Cp_2Fe^{+/0}$. Magnetic measurements were performed at room temperature using a Sherwood magnetic balance (Mark II). The kinetics of the reactions were studied by using an Agilent 8453 diode-array spectrophotometer. The temperature of the solutions were maintained with a PolyScience digital temperature controller connected to a circulating water bath.

X-ray crystallography.

Measurements were collected on a Bruker Proteum X8 X-ray single crystal diffractometer with a multilayer mirror-monochromated Cu-K$_\alpha$ radiation ($\lambda = 1.54178$ Å). Details of the intensity data

collection and crystal data are given in Table S1. Absorption corrections were done by the multiscan method. The structures were resolved by the heavy-atom Patterson method or direct methods and refined by full-matrix least-squares using SHELX-97 and expanded using Fourier techniques.[3,4] All non-hydrogen atoms were refined anisotropically. H atoms were generated by the program SHELXL-97. The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times or 1.5 times that of the associated C atoms and 1.2 times that of the associated N atoms, all these were participated in the calculation of final R-indices. All calculations were performed using the teXsan crystallographic software.[5]

Kinetics. The concentrations of phenol were at least in 10-fold excess to that of **1**. The reaction progress was monitored by observing absorbance changes at 616 and 665 nm for the first and second phases, respectively. Pseudo-first-order rate constants, k_{obs}, were obtained by nonlinear least-square fits of A_t vs t according to the equation $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$, where A_0 and A_∞ are the initial and final absorbance, respectively.

Synthesis.

[Ru^{II}(HN-p-C$_6$H$_4$O)(L)(py)]·CH$_3$OH (2a). A solution of **1** (20 mg, 0.033 mmol) in CH_3OH (20 mL) was slowly added into a solution of phenol (940 mg, 10 mmol) and py (1 ml, 12.5 mmol) in CH_3OH (200 mL) with continuously stirring in 10 min. The mixture was stirred at ambient condition for 5 h. The solvent was then evaporated under vacuum and the resulting green oil was loaded onto a silica-gel column (20 × 3 cm). The column was flushed with CH_2Cl_2 (300 mL) and followed by CH_2Cl_2-acetone (v/v, 5:1) to remove the first green band. Elution with CH_2Cl_2-CH_3OH (v/v, 10:1) and recrystallization from CH_2Cl_2 afforded **2a** as a green solid. Yield: 40 %. Single crystals suitable for X-ray analysis were obtained by slow diffusion of Et_2O into a

solution of **2a** in CH_3OH-py (v/v, 1:3) at 5 $^{\circ}C$. IR (KBr, cm^{-1}): ν(N–H) 3173; ν(C=N) 1590. Anal. calcd. (found) for $C_{32}H_{34}N_4O_4Ru$: C, 60.08 (60.37); H, 5.36 (5.41); N, 8.76 (9.00). ^{1}H NMR (400 MHz, d_6-DMSO): δ13.21 (s, 1H, NH), 8.81 (d, J = 11.0 Hz, 1H, CH of benzoquinone imine), 8.62 (s, 1H, N=CH), 8.42 (s, 1H, N=CH), 7.78 (t, J = 7.6 Hz, 1H), 7.49–7.30 (m, 4H), 7.25 (d, J = 5.3 Hz, 2H), 7.12 (dd, J = 16.5, 8.4 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 6.85 (J = 9.4 Hz, 1H, CH of benzoquinone imine), 6.50 (d, J = 10.0 Hz, 1H, CH of benzoquinone imine), 6.43 (dd, J = 11.7, 6.7 Hz, 2H), 6.10 (d, J = 9.5 Hz, 1H, CH of benzoquinone imine), 4.38 (t, J = 9.2 Hz, 1 H, N–CH), 3.27 (t, J = 10.4 Hz, 1 H, N–CH), 3.14 (d, J = 6.0 Hz, 1H), 2.91 (d, J = 9.6 Hz, 1H), 1.98–1.84 (m, 3H), 1.55–1.36 (m, 3H). UV–vis (CH_3OH): λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}]) 201 (43000), 226 (39800), 251sh (31100), 354 (12700), 383 (19400), 428 (13000), 665 (20000).

[Ru^{II}(HN-*p*-$Cl_2C_6H_2O$)(L)(py)]·H_2O (2b). This green solid was prepared by a procedure similar to that for **2a** except 2,6-dichlorophenol was used and the respective green band was eluted by CH_2Cl_2-acetone (v/v, 5:1). Yield: 70%. IR (KBr, cm^{-1}): ν(N–H) 3167; ν(C=N) 1590. Anal. calcd. (found) for $C_{31}H_{30}Cl_2N_4O_4Ru$: C, 53.61 (53.54); H, 4.35 (4.28); N, 8.07 (8.09). ^{1}H NMR (400 MHz, d_6-DMSO): δ13.35 (s, 1H, NH), 9.45 (d, J = 2.0 Hz, 1H, CH of benzoquinone imine), 8.72 (s, 1H, N=CH), 8.50 (s, 1H, N=CH), 7.80 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 8.2 Hz, 2H), 7.35 (t, J = 6.8 Hz, 2H), 7.20 (dd, J = 16.6, 8.6 Hz, 2H), 7.13 (d, J = 2.2 Hz, 1H, CH of benzoquinone imine), 7.03–6.97 (m, 4H), 6.51 (dd, J = 15.4, 7.7 Hz, 2H), 4.48 (t, J = 12.0 Hz, 1 H, N–CH), 3.55 (t, J = 12.0 Hz, 1 H, N–CH), 3.22 (d, J = 11.4 Hz, 1H), 3.01 (d, J = 10.7 Hz, 1H), 2.06–1.90 (m, 3H), 1.67–1.43 (m, 3H). UV–vis (CH_3OH): λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}]) 203 (51300), 232sh (37700), 252sh (28200), 334sh (12800), 380 (17600), 444 (10900), 672 (22300).

[Ru^{III}(HN-*p*-C$_6$H$_4$O)(L)(py)](PF$_6$) (3). A solid [Cp$_2$Fe](PF6) (5 mg, 0.015 mmol) was added into a green solution of **2a** (9 mg, 0.015 mmol) in CH$_3$OH (200 mL) under argon atmosphere and the mixture was stirred for 1 min. The resulting dark purple solution was evaporated under vacuum, re-dissolved in a minimum amount of CH$_2$Cl$_2$ and loaded onto a silica-gel column (20 × 2 cm). The column was flushed with CH$_2$Cl$_2$ (200 mL) and then eluted with CH$_2$Cl$_2$-acetone (v/v, 10:1) to afford **3** as a purple solid. Single crystals suitable for X-ray analysis were obtained by slow diffusion of Et$_2$O into a solution of **3** in CH$_2$Cl$_2$ at 5 ^{o}C. Yield: 70%. IR (KBr, cm^{-1}): ν(N–H) 3268; ν(C=O) 1640; ν(C=N) 1597; ν(P–F) 843. Anal. calcd. (found) for C$_{31}$H$_{30}$F$_6$N$_4$O$_3$PRu: C, 49.47 (49.65); H, 4.02 (4.10); N, 7.44 (7.53). Magnetic moment: μ_{eff} = 1.93 μ_B. UV–vis (CH$_3$OH): λ$_{max}$ [nm] (ε [mol^{-1} dm^3 cm^{-1}]) 236 (43000), 365 (16400).

References

1. Man, W. L.; Tang, T. M.; Wong, T. W.; Lau, T. C.; Peng, S. M.; Wong, W. T. *J. Am. Chem. Soc*. **2004**, *126*, 478–479.
2. Amarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals, 5th ed*.; Butterworth Heinemann: New York, 2003.
3. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.; Polidori G.; Camalli, M. J. *Appl. Crystallogr.* 1994, **27**, 435.
4. DIRDIF 99, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen: The Netherlands, 1999.
5. Crystal Structure, Single Crystal Structure Analysis Software, version 3.5.1 Rigaku/MSC Corporation: The Woodlands, Texas, USA, Rigaku, Akishima, Tokyo, Japan, 2003, D. J. Watkin, C. K. Prout, J. R. Carruthers and P.W. Betteridge, Crystals, Chemical Crystallography. Lab: Oxford, UK, 1996, issue 10.

Table S1. Crystal data and structure refinement details for **2b** and **3**.

	2b•0.75py•0.5CH₃OH	**3•2CH₂Cl₂•0.5CH₃OH**
Formula	$C_{35.25}H_{33.75}Cl_2N_{4.75}O_{3.50}$ Ru	$C_{33.5}H_{36}Cl_4F_6N_4O_{3.5}PRu$
M_r	751.89	938.50
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca*	*P-1*
a/Å	24.8814(6)	12.1017(5)
b/Å	20.0338(5)	12.7507(4)
c/Å	29.5126(7)	14.0794(5)
α (°)	90	71.154(1)
β (°)	90	82.268(1)
γ (°)	90	71.918(1)
V/ Å³	14711.1(6)	1953.10(11)
Z	16	2
ρ_c/Mg m⁻³	1.358	1.596
$F(000)$	6152	948
Collected refl.	114477	31915
Unique refl.	13237	6908
Final R indices, $I > 2\sigma(I)$	R_1(obs) = 0.0477, wR(all) = 0.1361	R_1(obs) = 0.0740, wR(all) = 0.2063
GOF	1.093	1.085
No. of parameters	838	481

Table S2. $E_{1/2}$ values of **2a**, **2b** and $[Ru^{III}(L)(py)_2]^+$ in CH_3CN.

	$E_{1/2}$ (Volts vs $Cp_2Fe^{+/0}$)		
Complex	**Ru$^{IV/III}$**	**Ru$^{III/II}$**	**Benzoquinone imine$^{0/–}$**
2a	+0.72	–0.25	–1.38
2b	+0.76	–0.06	–1.18
$[Ru^{III}(L)(py)_2]^+$	+0.69	–0.58	---

Table S3. Second-order rate constants and KIEs of the reaction of **1** and phenol in the presence of py in methanol at 25 °C.

	1st phase in 0.1 M py / $M^{-1} s^{-1}$	2nd phase in 0.06 M PhOH / $M^{-1} s^{-1}$	KIE (1st phase)	KIE (2nd phase)
C_6H_5OH in CH_3OH	$(1.84 \pm 0.07) \times 10^{-1}$	$(9.32 \pm 0.41) \times 10^{-3}$		
C_6D_5OH in CH_3OH	$(1.78 \pm 0.02) \times 10^{-1}$	$(7.08 \pm 0.17) \times 10^{-3}$	1.03 ± 0.05	1.32 ± 0.07
C_6H_5OD in CD_3OD	$(2.00 \pm 0.05) \times 10^{-1}$	$(9.65 \pm 0.35) \times 10^{-3}$	0.92 ± 0.06	0.97 ± 0.08

Table S4. Second-order rate constants for the first phase of the reaction of **1** with 2,6-disubstituted phenols ($2,6-X_2C_6H_3OH$) in the presence of 0.1 M py in CH_3OH at 25.0 ^0C.

X	$k_2 / M^{-1} s^{-1}$
MeO	8.08 ± 0.81
^tBu	2.38 ± 0.31
Me	1.06 ± 0.08
H	$(1.84 \times 0.07) \times 10^{-1}$
Cl	$(3.89 \pm 0.27) \times 10^{-2}$
Br	$(9.34 \pm 0.70) \times 10^{-2}$
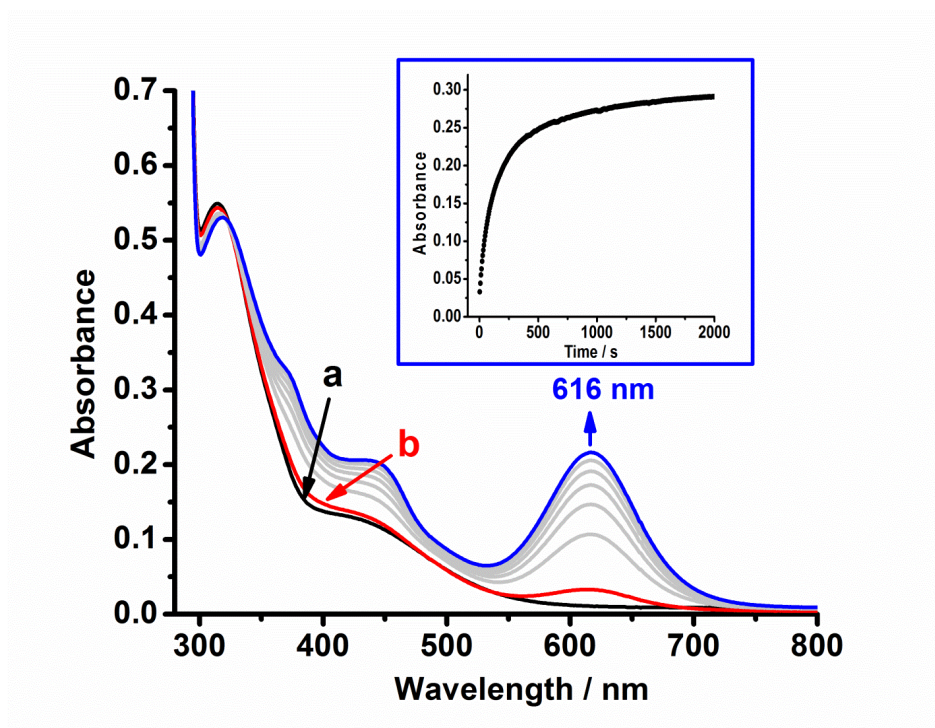
Figure S1. UV–vis spectral changes at 45 s intervals for the reaction of **1** (5.00 × 10^{-5} M) with C$_6$H$_5$OH (0.11 M) in CH$_3$OH at 25.0 ^{0}C. a) before mixing; b) *ca*. 3 s after mixing. Inset shows the time trace at 616 nm.
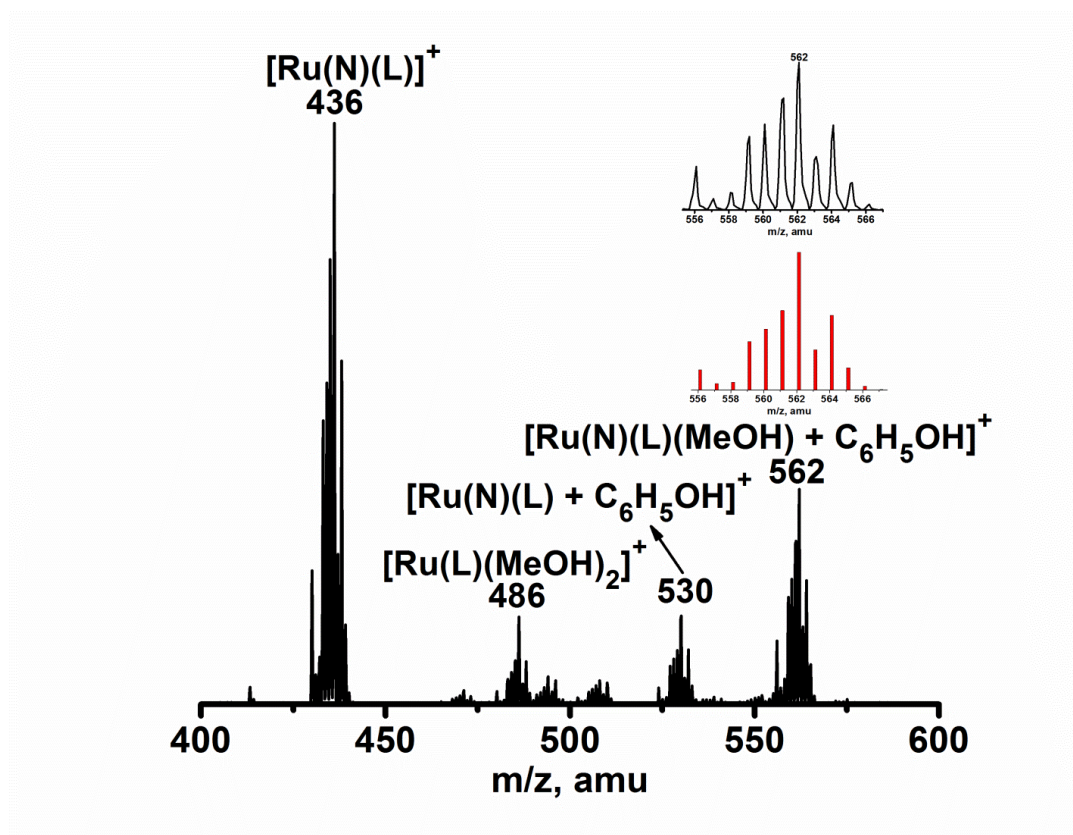
Figure S2. ESI mass spectrum of the green solution for the reaction of **1** with excess phenol in CH$_3$OH. Insets show the expanded (top) and simulated (bottom) patterns of the peak at *m/z* 562.
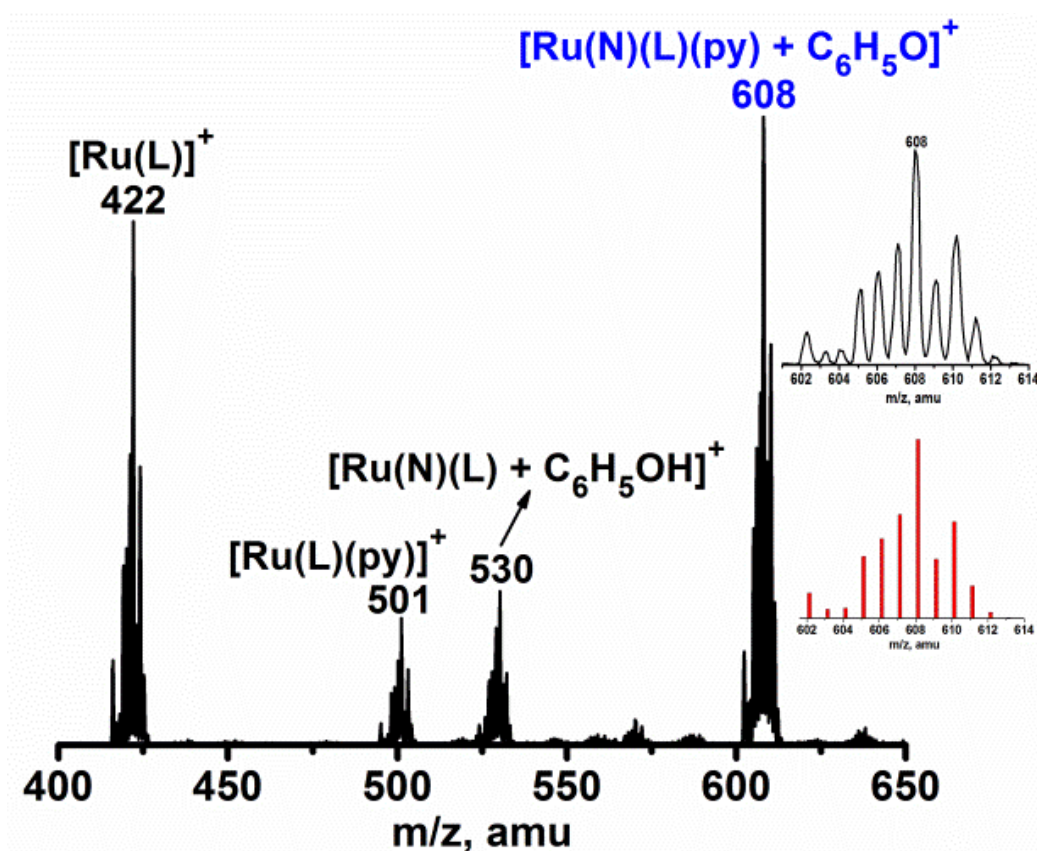
Figure S3. ESI mass spectrum for the reaction of **1** with C_6H_5OH in 0.1 M py in CH_3OH. Insets show the expanded (top) and simulated (bottom) isotopic patterns.
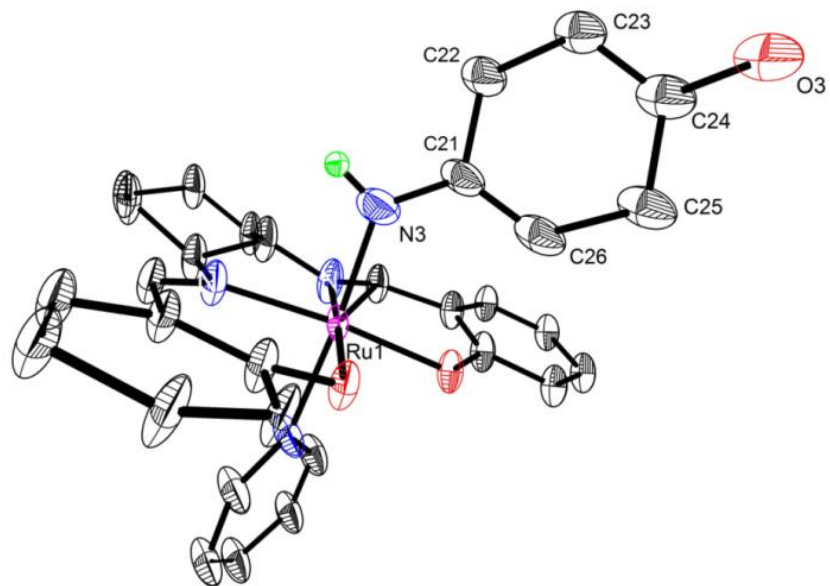
Figure S4. Molecular structure of **2a**.
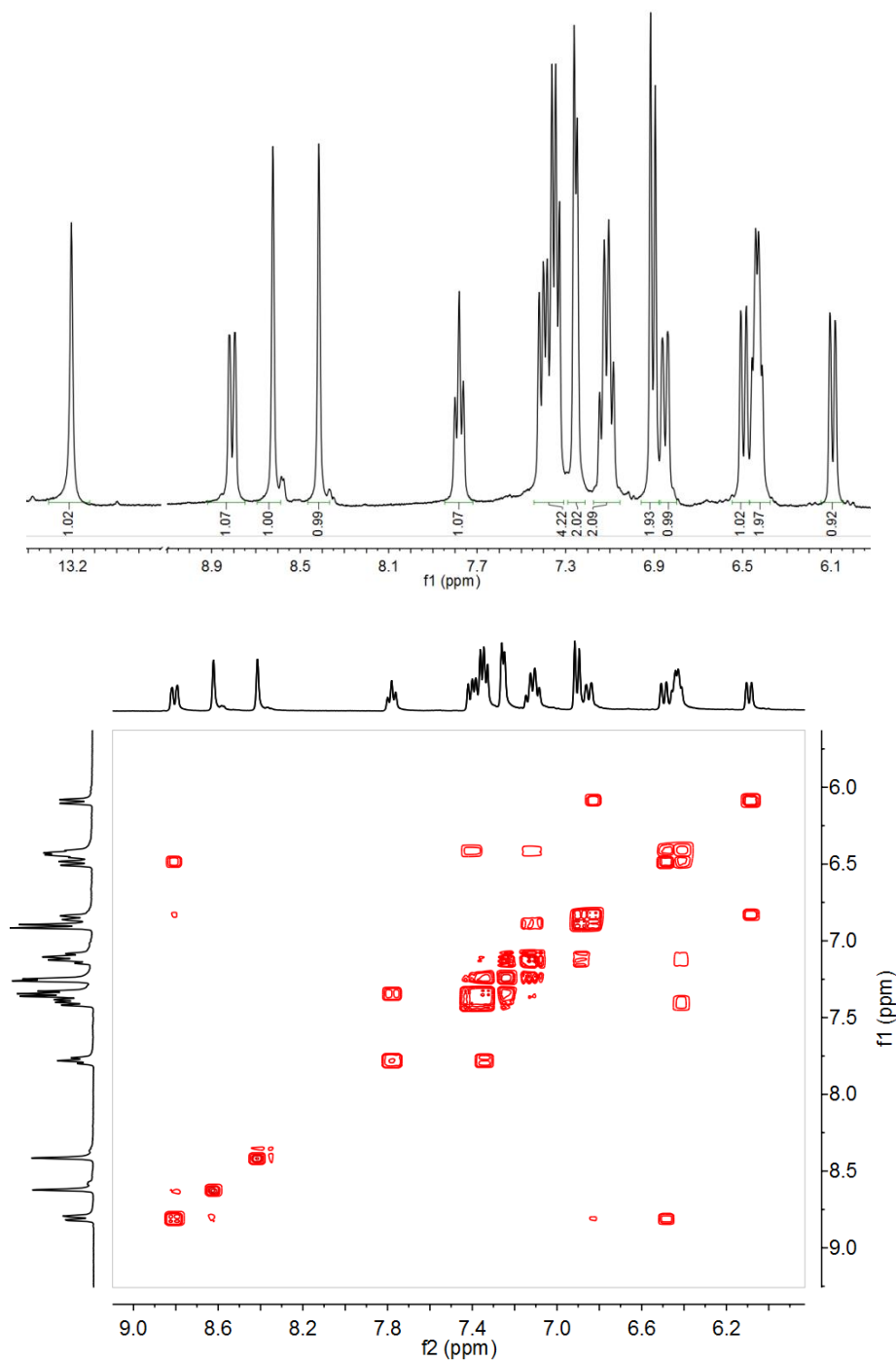
Figure S5. 400 MHz ^{1}H NMR (top) and (*H,H*) COSY (bottom) spectra of **2a** in DMSO-d_6.
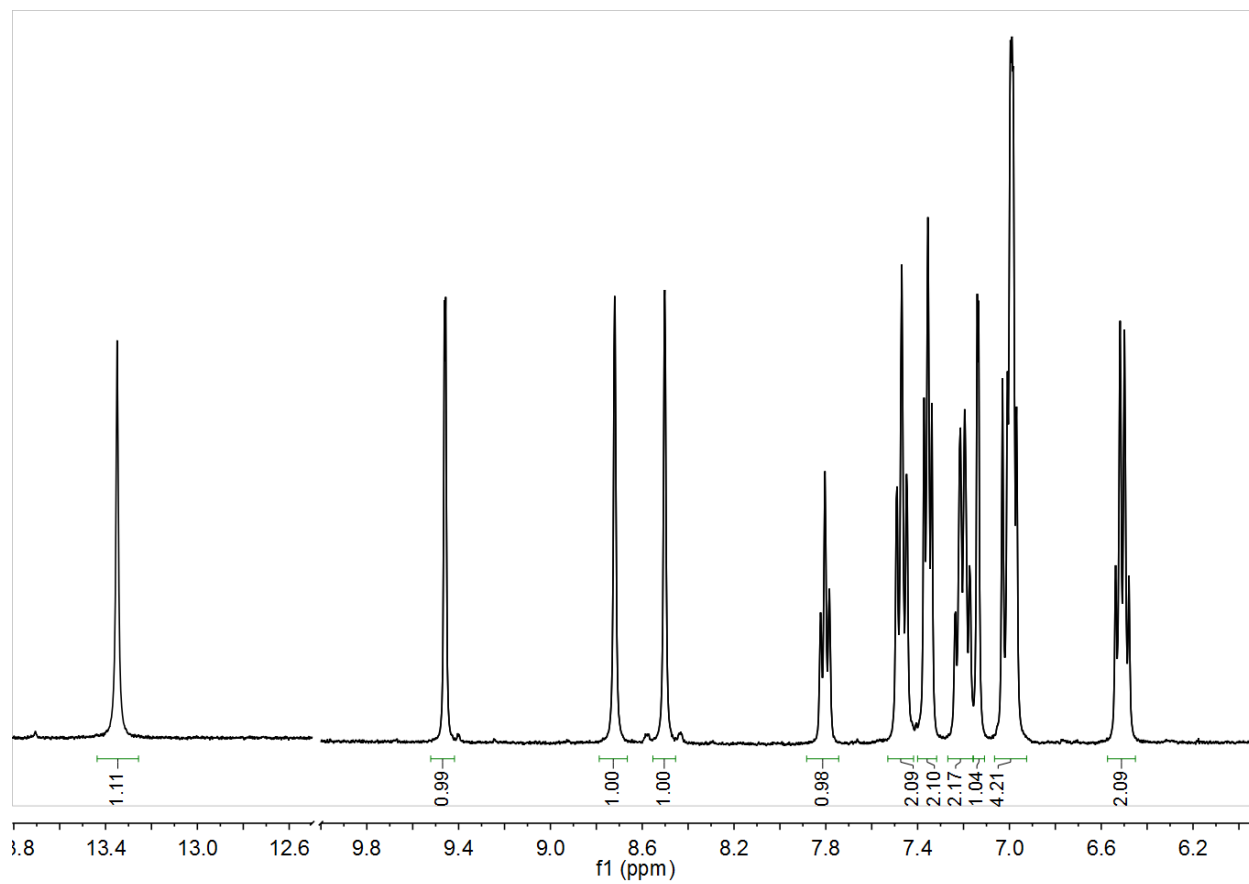
Figure S6. 400 MHz ^{1}H NMR spectrum of **2b** in DMSO-d_6.
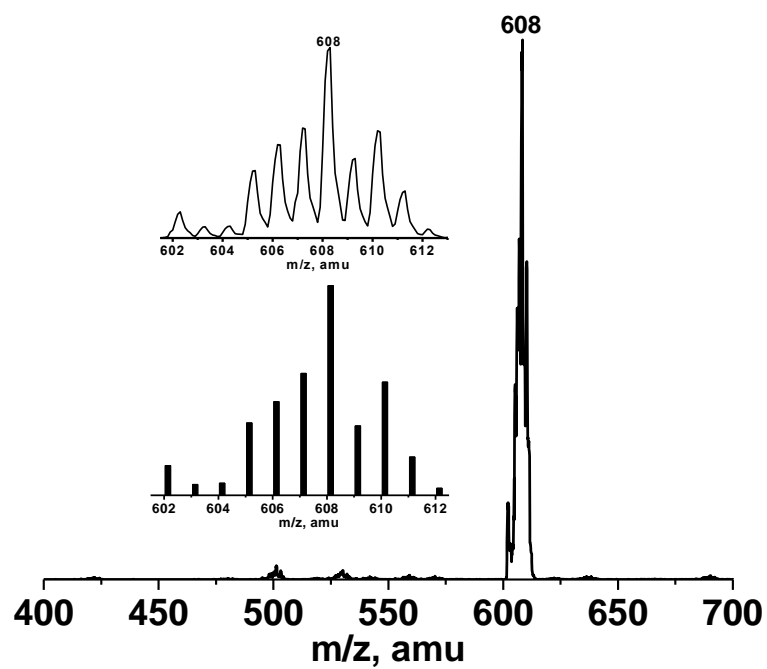
Figure S7. ESI mass spectrum of **2a** in CH$_3$OH. Insets show the expanded (top) and simulated (bottom) patterns of the peak at *m/z* 608.
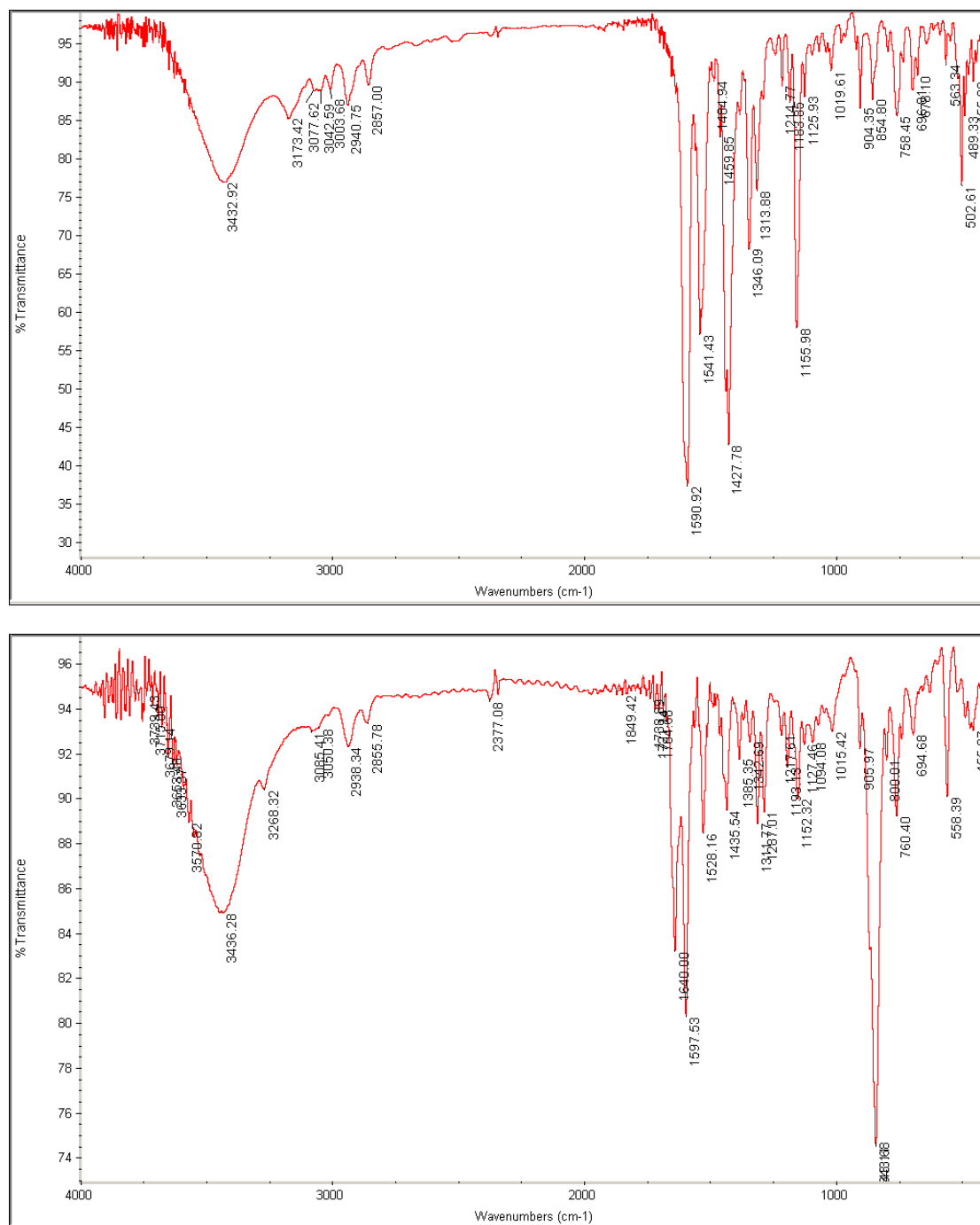
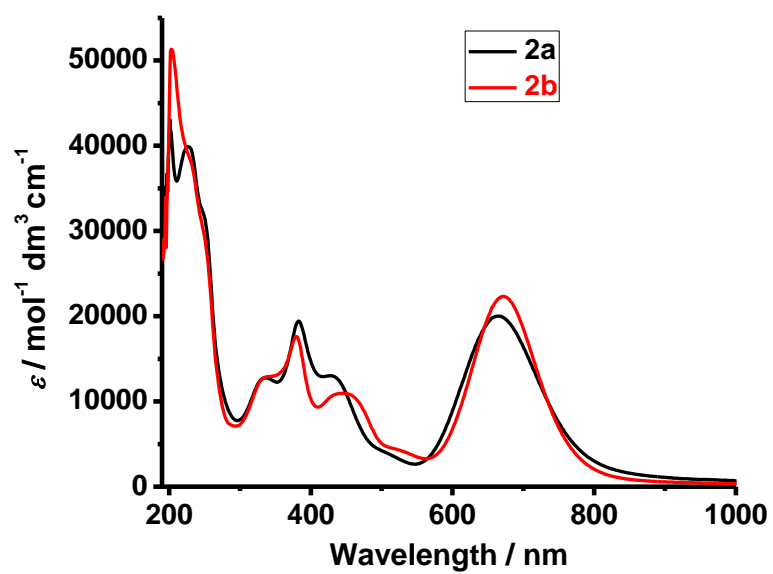**Figure S8**. IR spectra (KBr) of **2a** (top) and **3** (bottom).

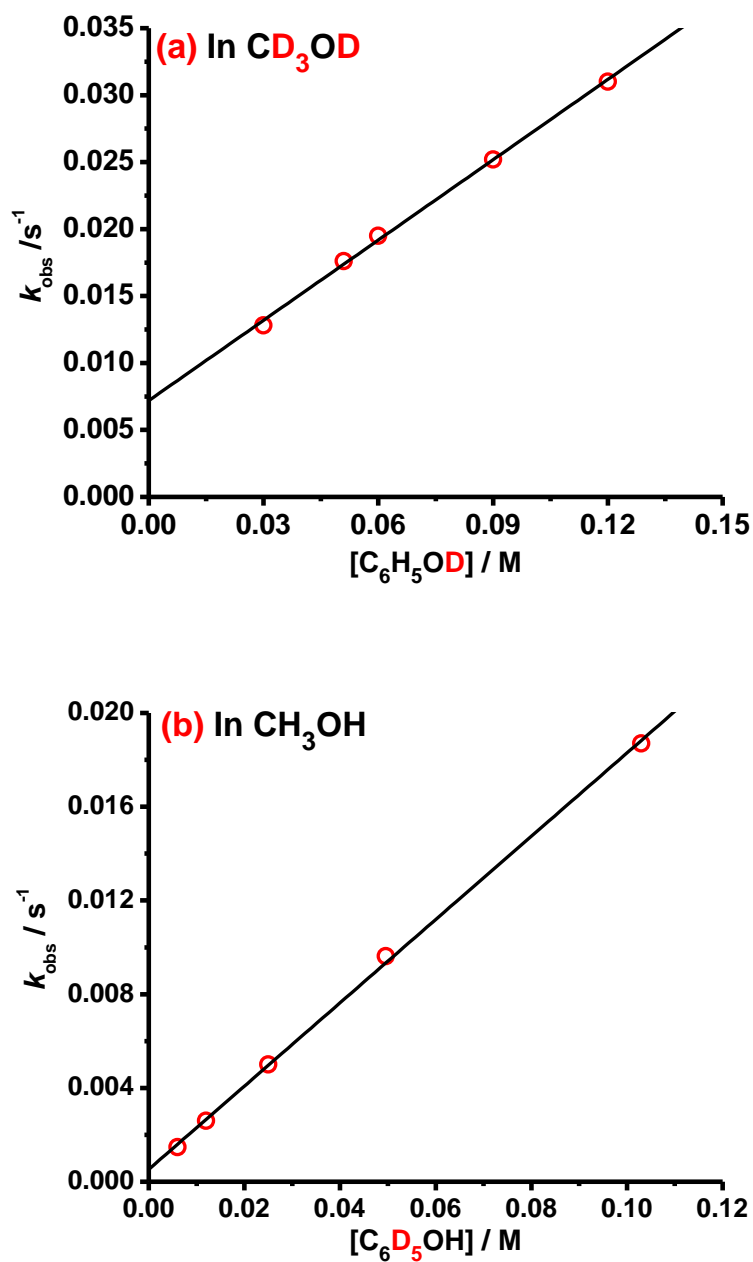**Figure S9**. UV–vis spectra of **2a** (black line) and **2b** (red line) in CH$_3$OH.

Figure S10. Plot of k_{obs} vs [phenol] for the first phase of the reaction of **1** with phenol in the presence of 0.1 M py in methanol at 25.0 ^{0}C. (a) For C_6H_5OD in CD_3OD: [Slope = (2.00 ± 0.05) × 10^{-1}; y-intercept = (7.19 ± 0.36) × 10^{-3}; r^2 = 0.998]. (b) For C_6D_5OH in CH_3OH: [Slope = (1.78 ± 0.02) × 10^{-1}; y-intercept = (5.27 ± 1.30) × 10^{-4}; r^2 = 0.999]
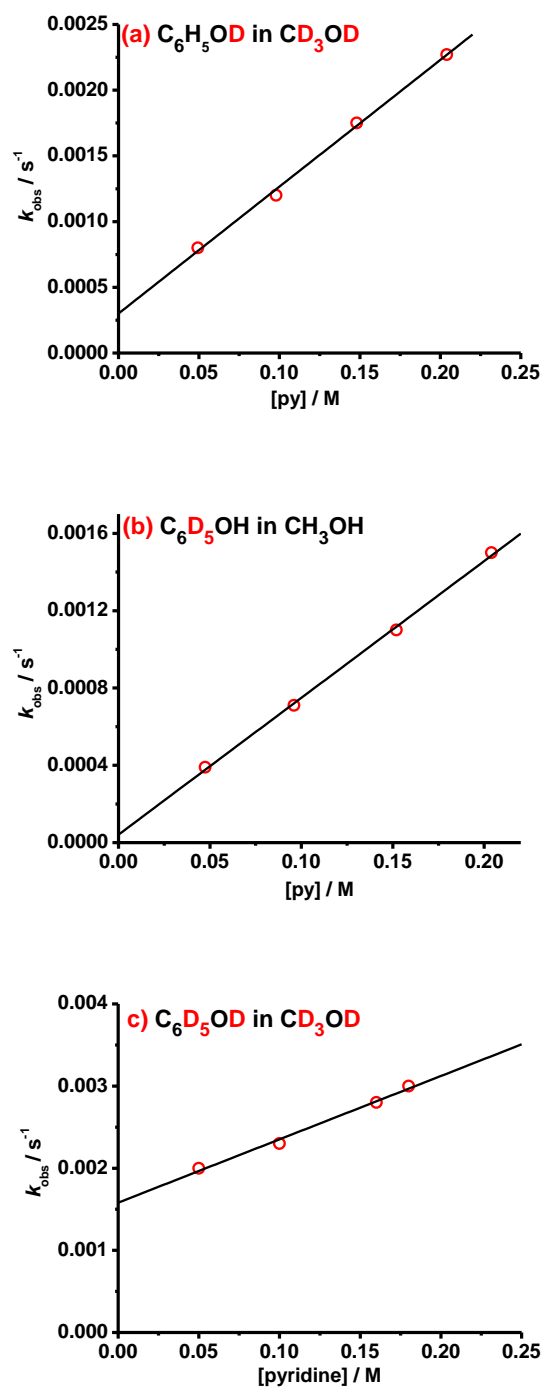
Figure S11. Plot of k_{obs} vs [py] for the second phase of the reaction of **1** (5.00×10^{-5} M) with phenol (0.06 M) in 0.1 M py in methanol at 25.0 ^{0}C. (a) For C_6H_5OD in CD_3OD: [Slope = $(9.65 \pm 0.35) \times 10^{-3}$; y-intercept = $(3.00 \pm 0.47) \times 10^{-4}$; $r^2 = 0.996$]. (b) For C_6D_5OH in CH_3OH: [Slope = $(7.08 \pm 0.17) \times 10^{-3}$; y-intercept = $(4.14 \pm 2.35) \times 10^{-5}$; $r^2 = 0.998$]. (c) For C_6D_5OD in CD_3OD: [Slope = $(7.71 \pm 0.49) \times 10^{-3}$; y-intercept = $(1.58 \pm 0.06) \times 10^{-4}$; $r^2 = 0.99$].
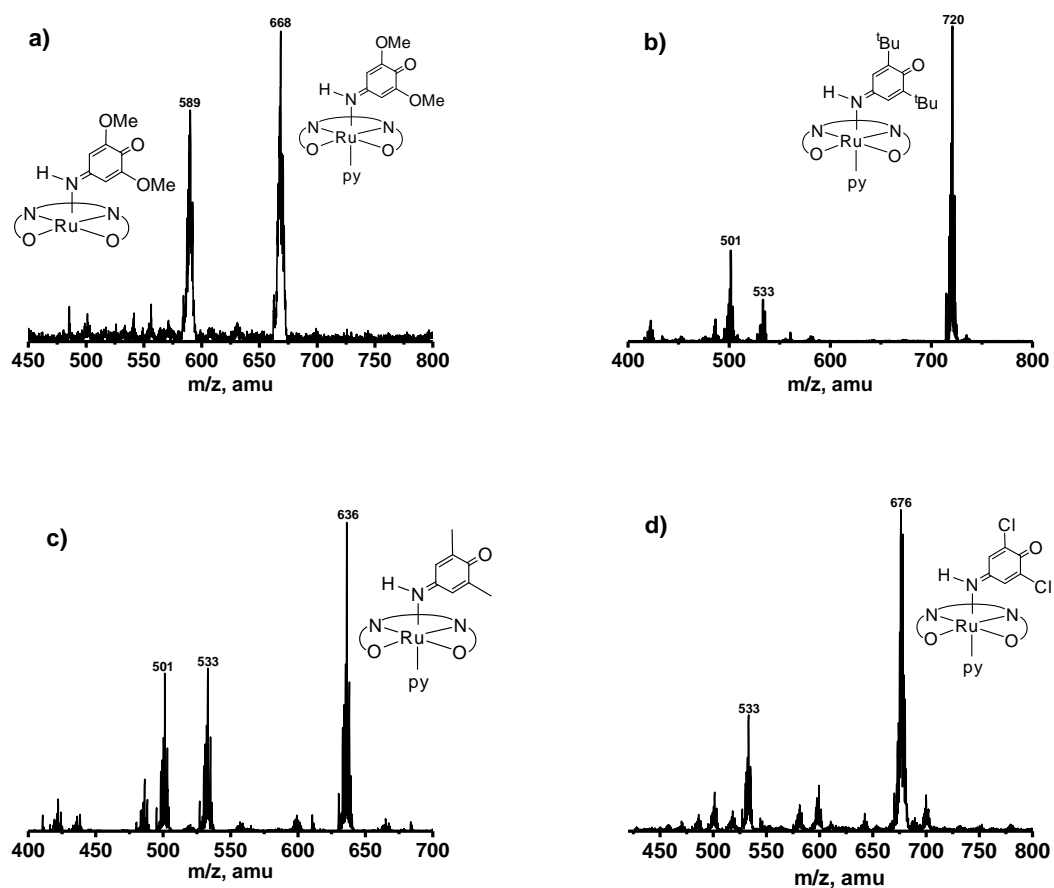
Figure S12. Product analysis by ESI–MS for the reaction of **1** with a) 2,6-(OMe)$_2$-C$_6$H$_3$OH; b) 2,6-(^{t}Bu)$_2$-C$_6$H$_3$OH; c) 2,6-Me$_2$-C$_6$H$_3$OH and d) 2,6-Cl$_2$-C$_6$H$_3$OH in the presence of 0.1 M py in CH$_3$OH.
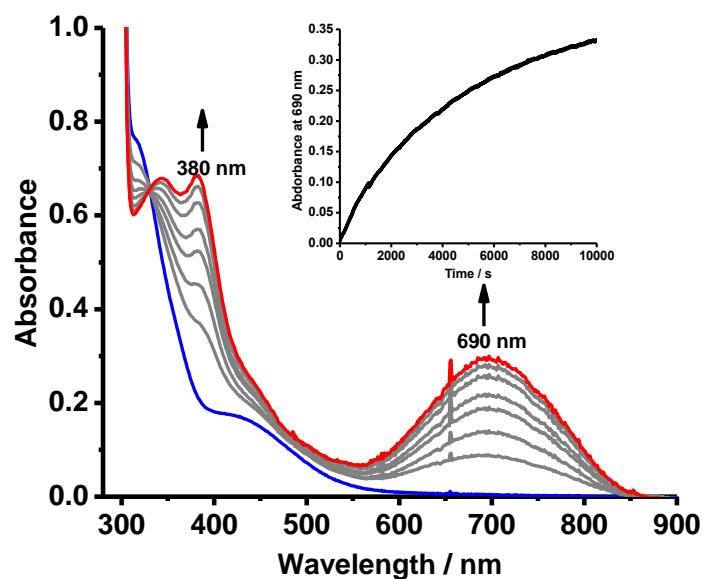
Figure S13. Spectrophotometric changes at 1000 s intervals for the reaction between **1** (5.00 × 10^{-5} M) and *p*-MeO-C$_6$H$_4$OH (0.30 M) in the presence of 0.1 M py in CH$_3$OH at 25.0 ^{0}C. Inset shows the absorbance-time trace at 690 nm.
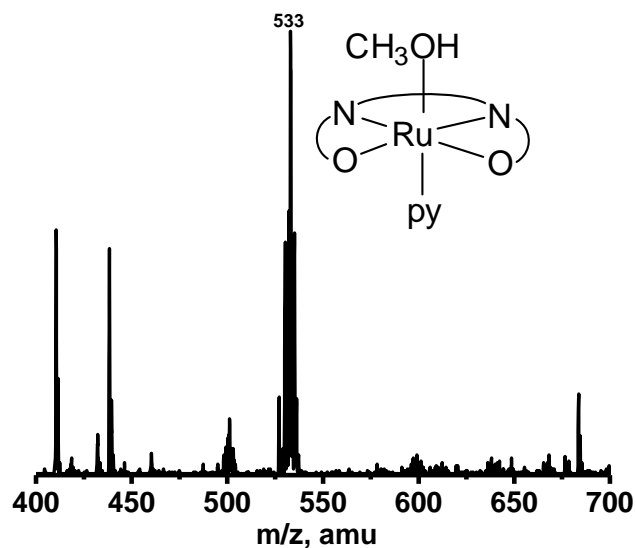

Figure S14. Product analysis for the reaction of **1** with *p*-MeO-C$_6$H$_4$OH in the presence of py in CH$_3$OH.
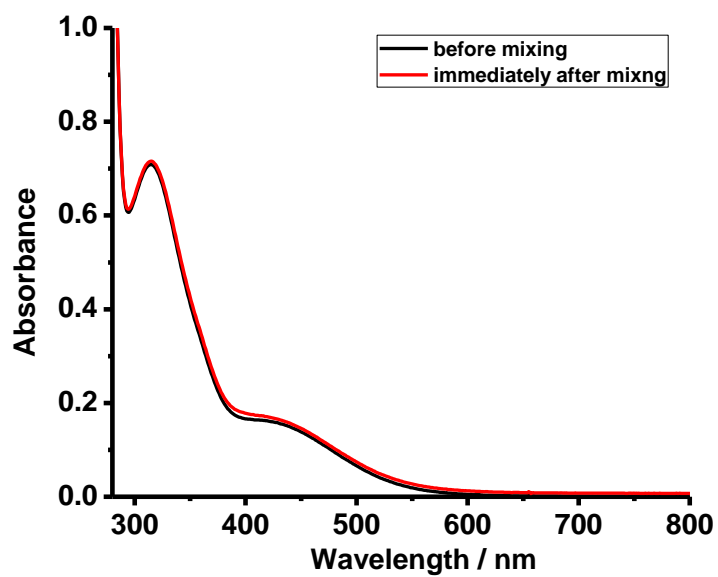
Figure S15. Spectral changes of the reaction of **1** (5×10^{-5} M) with py (0.1 M) in CH_3OH at 25.0 ^{0}C.