Supporting Information

Catalytic Conversion of Alcohols to Carboxylic Acid Salts and Hydrogen with Alkaline Water

Abir Sarbajna, Indranil Dutta, Prosenjit Daw, Shrabani Dinda, S. M. Wahidur Rahaman, Abheek Sarkar and Jitendra K. Bera*

Department of Chemistry and Center for Environmental Science and Engineering,

Indian Institute of Technology Kanpur, Kanpur 208016.

E-mail: jbera@iitk.ac.in

Contents

1. Experimental Section

1.1. General procedures

All reactions with metal complexes were carried out under an atmosphere of purified nitrogen using standard Schlenk–vessel and vacuum line techniques. Glasswares were flame–dried under vacuum prior to use. NMR spectra were obtained on JEOL JNM–LA 400MHz and 500MHz spectrometer. ^{1}H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. The chemical shift is given as dimensionless δ values and is frequency referenced relative to TMS for ^{1}H and ^{13}C NMR and 85% H_3PO_4 in D_2O for ^{31}P NMR spectroscopy. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. The crystallized compounds were powdered, washed several times with dry petroleum ether, and dried in vacuum for at least 48 h prior to elemental analyses. Infrared spectra were recorded in the range 4000−400 cm^{-1} on a Vertex 70 Bruker spectrophotometer on KBr pellets. ESI–MS were recorded on a Waters Micromass Quattro Micro triple–quadrupole mass spectrometer. The GC-MS experiments were performed by using an Agilent 7890 A GC and 5975C MS system.

Materials

Solvents were dried by conventional methods, distilled under nitrogen and deoxygenated prior to use. $RuCl_3$. xH_2O was purchased from Arora Matthey, India. All other chemicals were purchased from Sigma–Aldrich. $RuHCl(CO)(PPh_3)_3$,[1] 2–(2–Pyridyl)–1,8–naphthyridine (py–NP),[2] 2-(2-thiazolyl)-1,8-naphthyridine,[3] 2-(2-pyrazinyl)-1,8-naphthyridine[4] and 2–((2–phenylhydrazono)methyl)–1,8–naphthyridine (phm–NP)[5] were prepared from literature procedures.

1.2. Synthesis and characterization

Synthesis of 1

A suspension of $RuHCl(CO)(PPh_3)_3$ (100 mg, 0.105 mmol) and py–NP (22 mg, 0.105 mmol) in 15 mL of THF was stirred for 4 h. The solvent was then evaporated under reduced pressure and 1 mL dichloromethane was added to redissolve the residue and 15 mL petroleum ether was added to induce precipitation. The solid obtained was washed with 2 X 15 mL of petroleum ether and diethyl ether and dried under vacuum. Crystals suitable for X–ray diffraction were grown by slow diffusion of petroleum ether into a saturated dichloromethane solution of **1** at –20°C. Yield: 83 mg (88%). Anal. Calcd. for $Ru_1P_2C_{53}H_{48}Cl_1N_3O_1$: C, 67.57; H, 5.14; N, 4.46. Found: C, 67.52; H, 5.09; N, 4.41. ESI–MS, *m/z*: 862.169 (z = 1), $[\mathbf{1}–Cl]^+$. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K): δ 9.35–9.34 (d, *J* = 7.6 Hz 1H), 9.30–9.28 (d, *J* = 8.4 Hz, 1H), 8.71–8.70 (m, 2H), 8.47–8.46 (d, *J* = 8.4 Hz, 1H), 8.07–8.04 (t, *J* = 7.2 Hz, 1H), 7.90–7.82 (m, 1H), 7.67–7.63 (m, 1H), 7.51–7.37 (m, 1H), 7.17–6.99 (m, 30H), (−)9.00−9.01 (t, 1H, Ru–H, *J* = 18.7 Hz), ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.5 (C, *C*O), 141.8, 138.7, 138.4, 137.2, 137.0, 133.1, 133.0, 132.9, 132.3, 132.2, 132.0, 129.9, 128.6, 128.1, 128.0, 127.9, 127.9, 127.6, 126.6, 126.3, 126.1, 125.4, 125.2, 125.1, 124.2, 123.5, 123.4, 123.0, 122.6, 122.3, 119.8. ^{31}P NMR (202 MHz, $CDCl_3$, 292 K): δ 46.1 (2P, *P*Ph_3). IR (KBr) data (cm^{-1}): *v*(Ru–H): 2005 (s), *v*(CO): 1915 (s), *v*(NP): 1602 (m), 1480 (m), 1434 (s). Complexes **2** and **3** were prepared similarly to compound **1** in the same millimolar scale and yields obtained were 46% and 84% respectively.

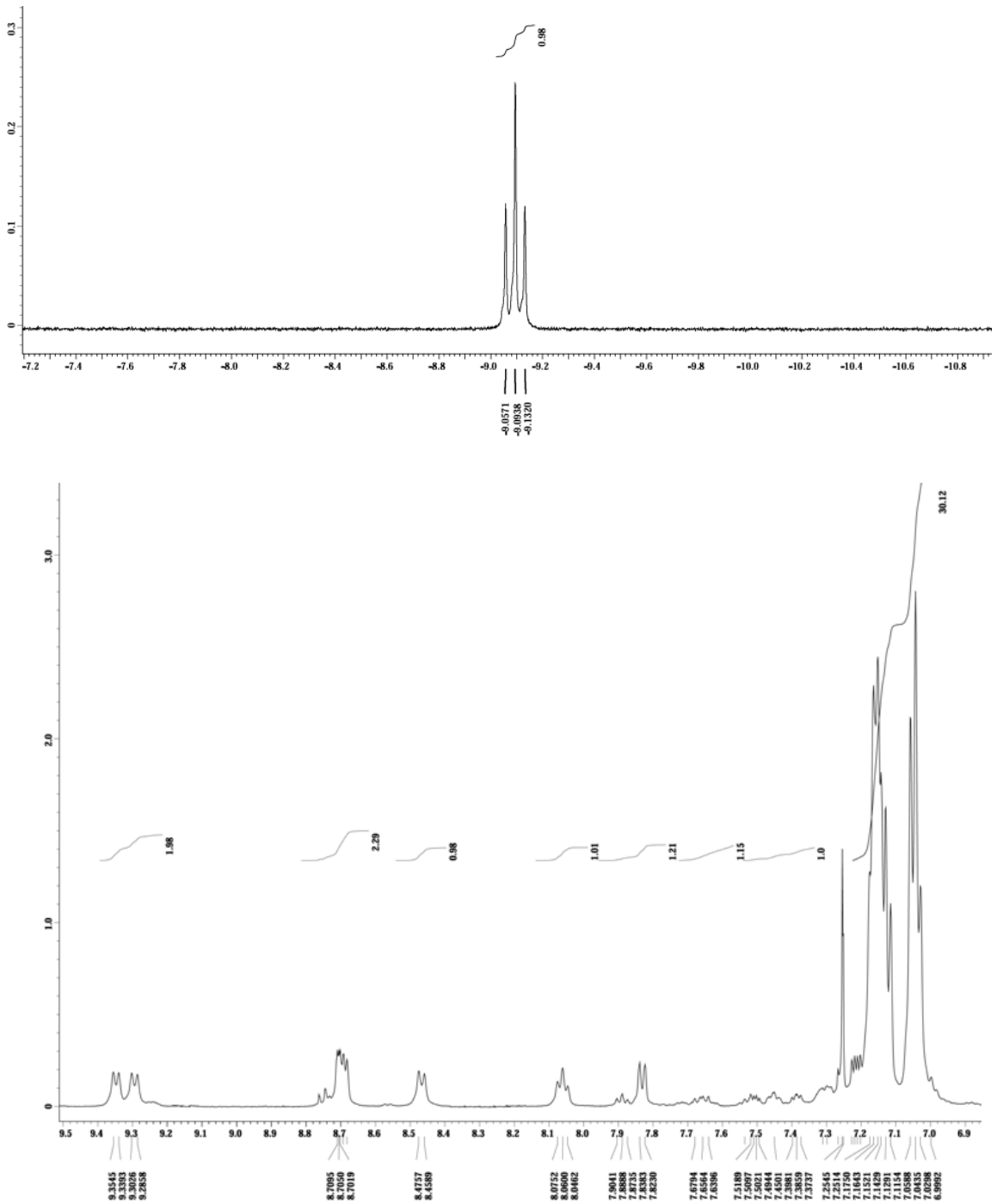


Figure S1. Negative region of ^{1}H NMR spectrum (top) and aromatic region (below) for **1** in $CDCl_3$.

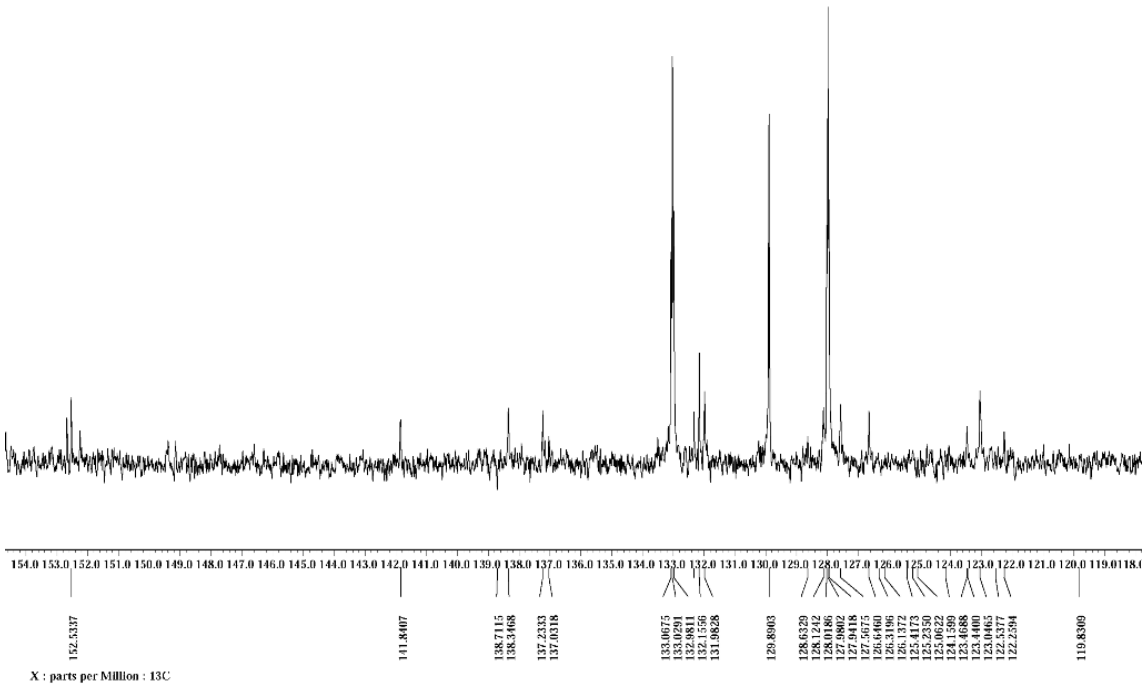


Figure S2. ^{13}C NMR spectrum for **1** in $CDCl_3$.

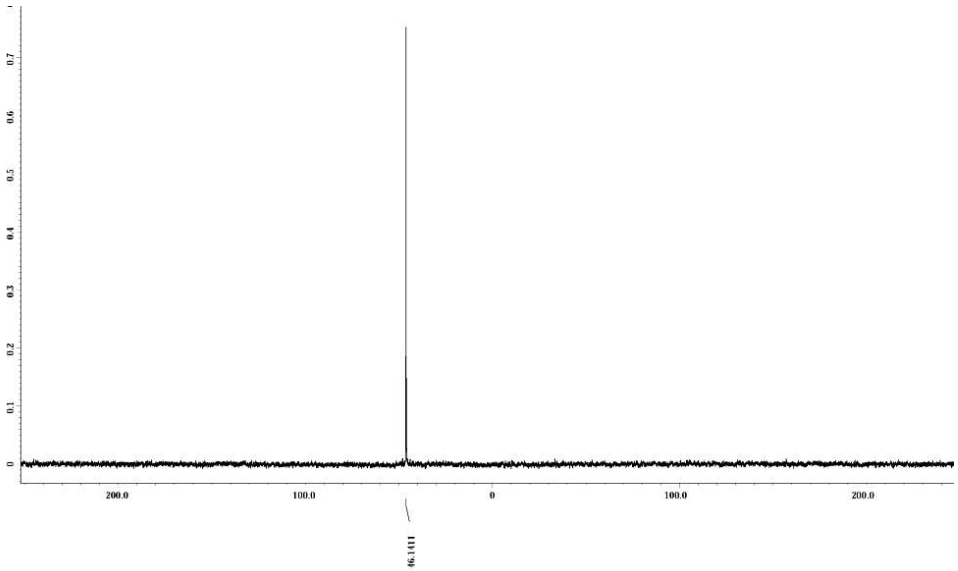


Figure S3. ^{31}P NMR spectrum for **1** in $CDCl_3$.

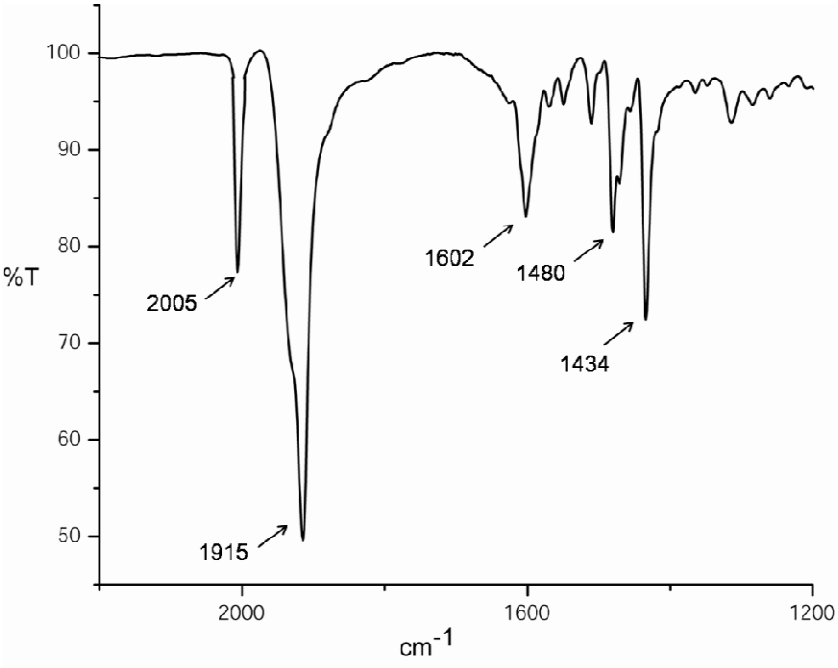


Figure S4. IR spectrum for **1**.

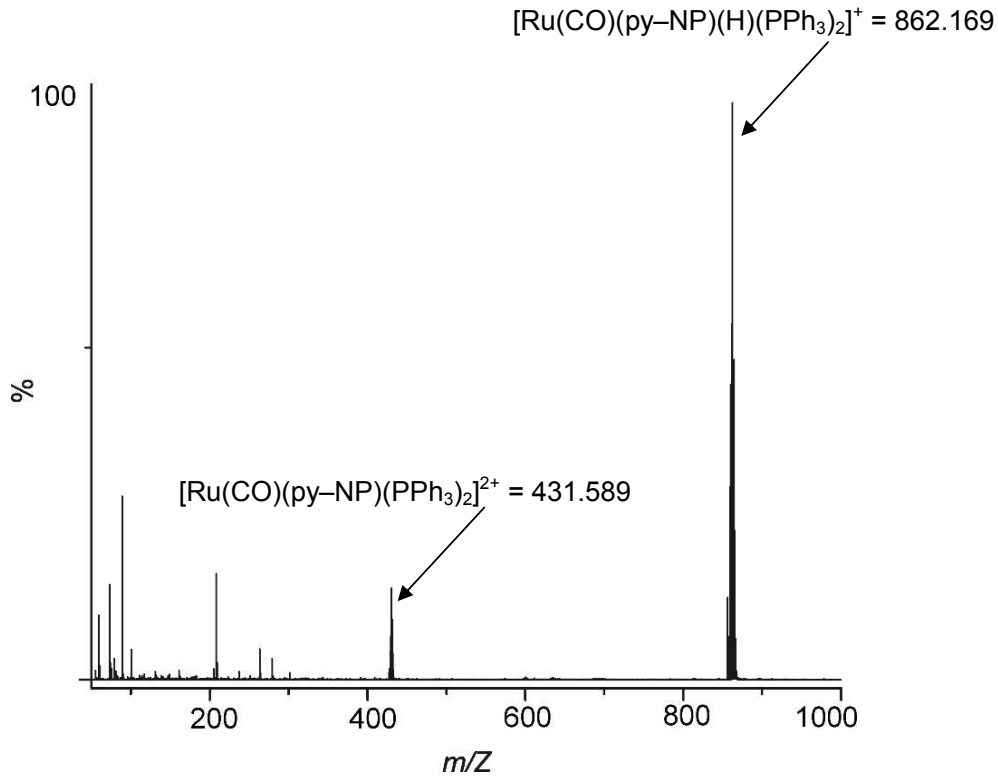


Figure S5. ESI-MS spectrum in the full range for complex **1**.

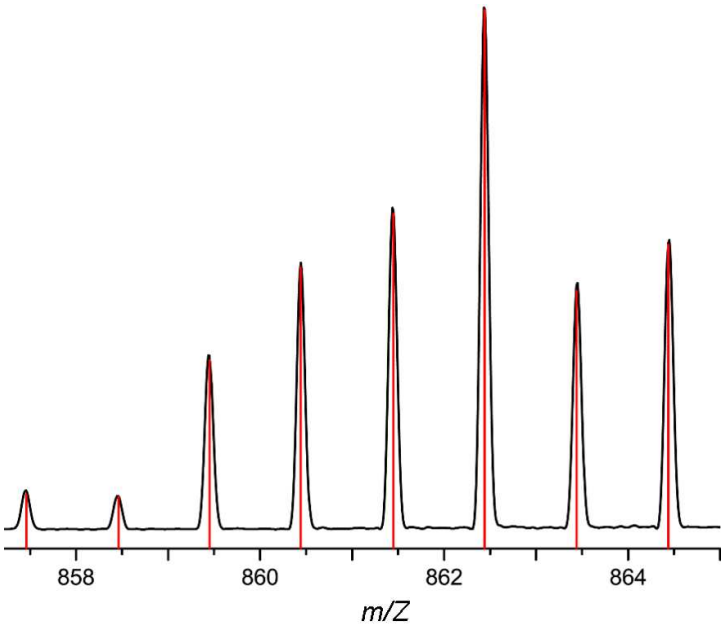


Figure S6. Experimental (black) and simulated (red) ESI-MS for molecular ion at *m/z* = 862.169 (*z*=1) in complex **1**.

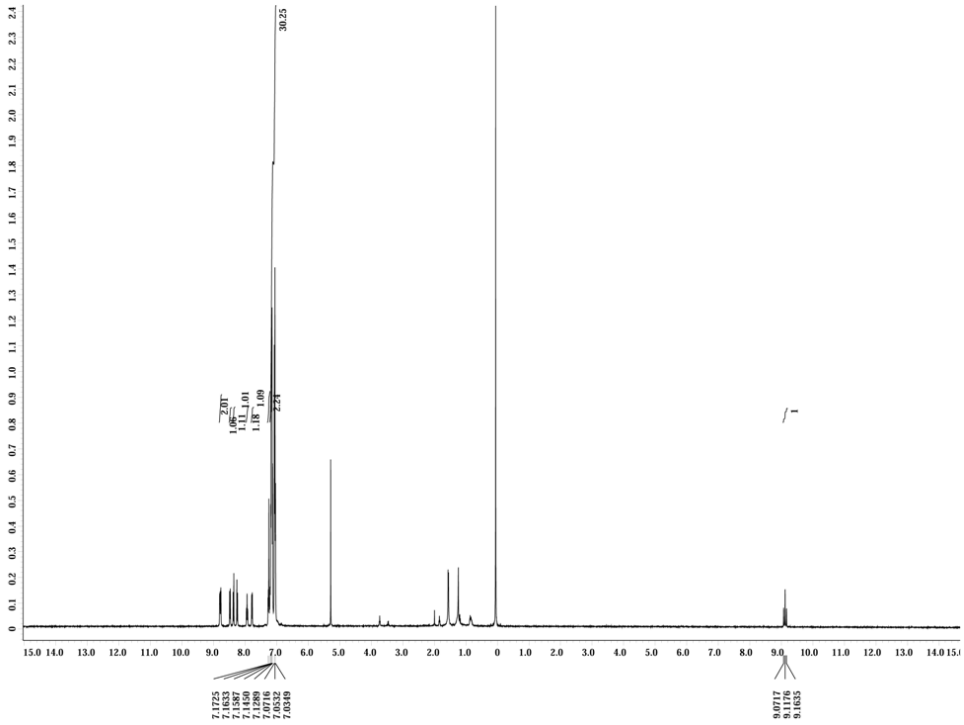


Figure S7. ^{1}H NMR spectrum for **2** in $CDCl_3$.

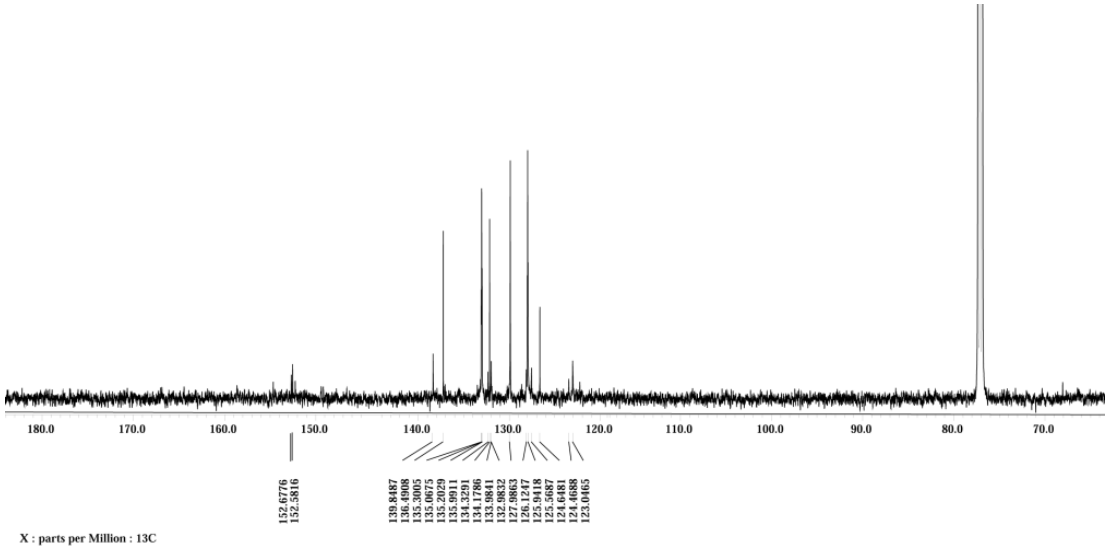


Figure S8. ^{13}C NMR spectrum for **2** in $CDCl_3$.

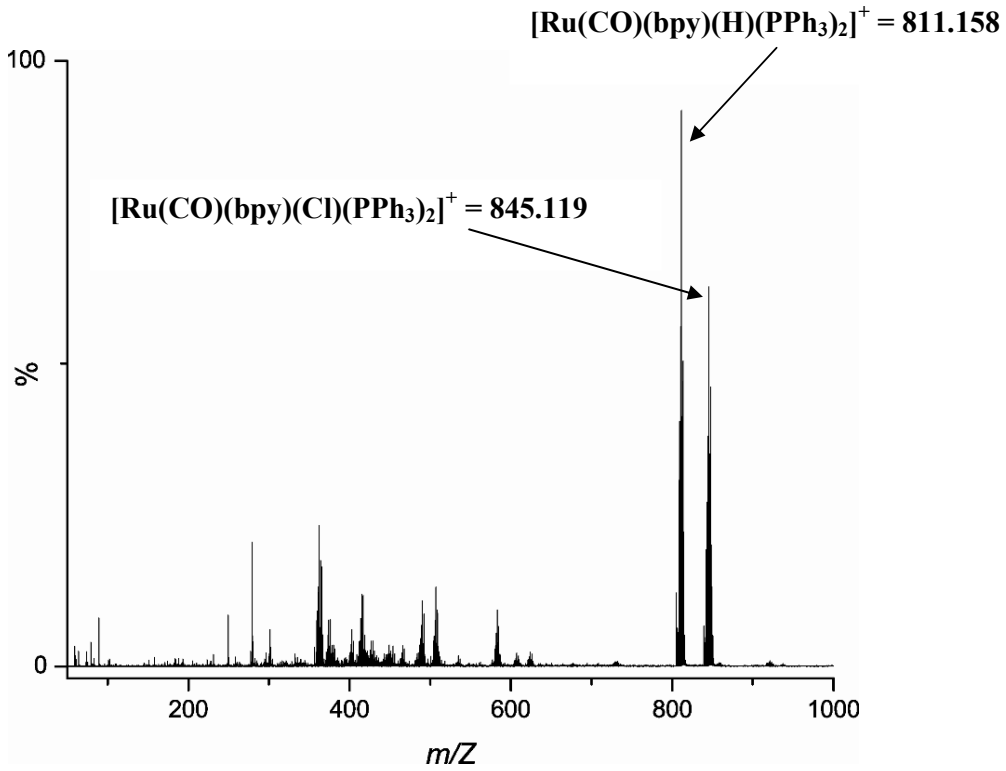


Figure S9. ESI-MS in the full range for complex **2**.

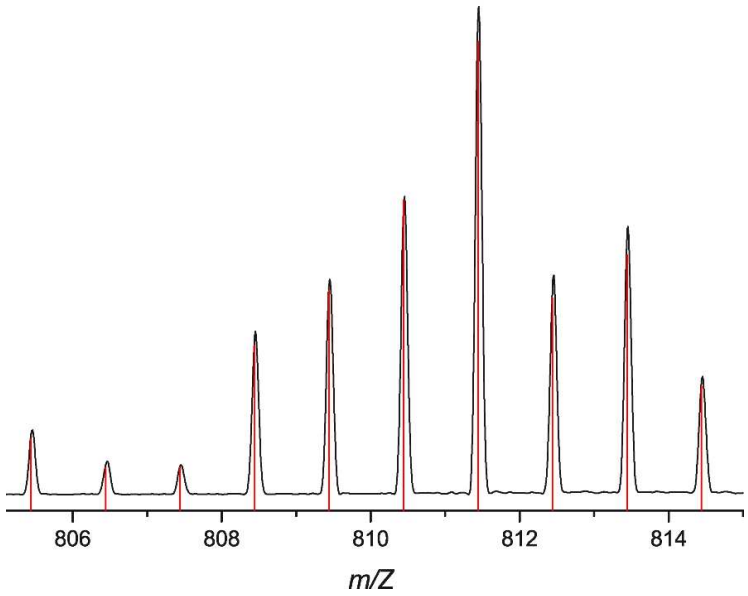


Figure S10. Experimental (black) and simulated (red) ESI-MS Spectrum for molecular ion at *m/z* = 845.119 (*z*=1) in complex **2**.

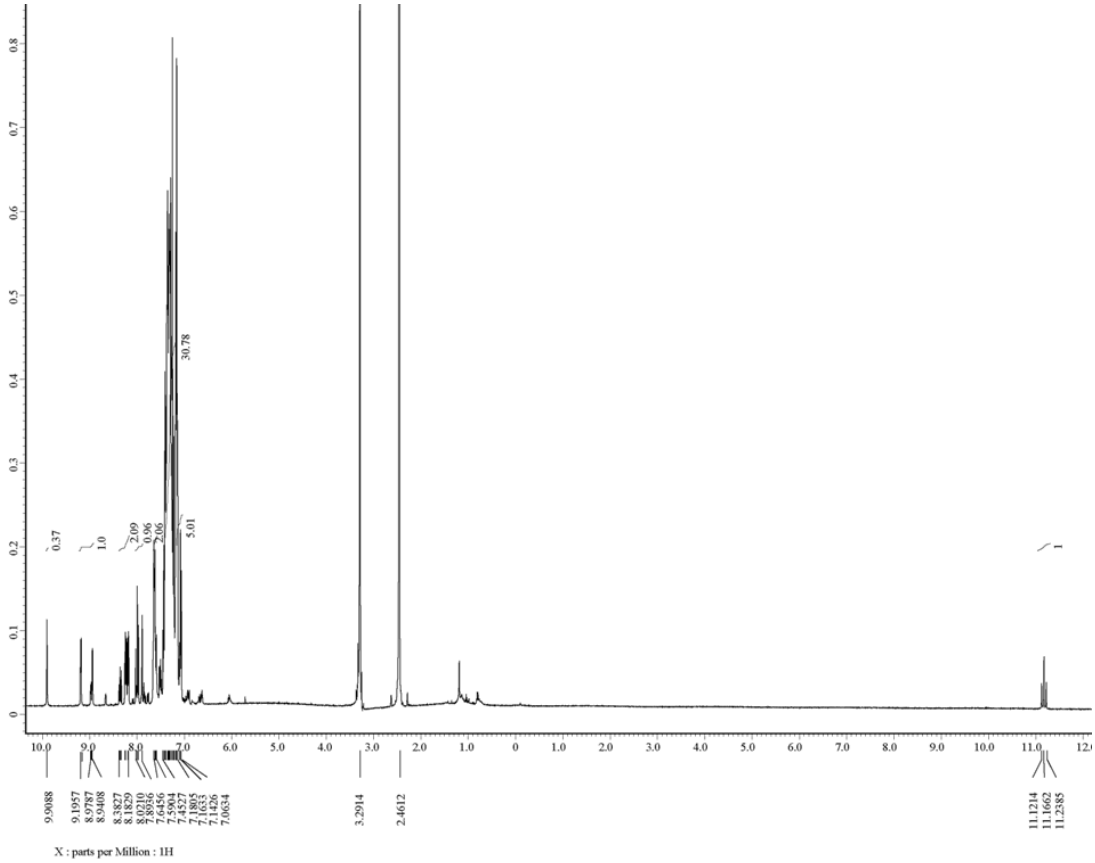


Figure S11. ^{1}H NMR spectrum for **3** in DMSO-d_6.

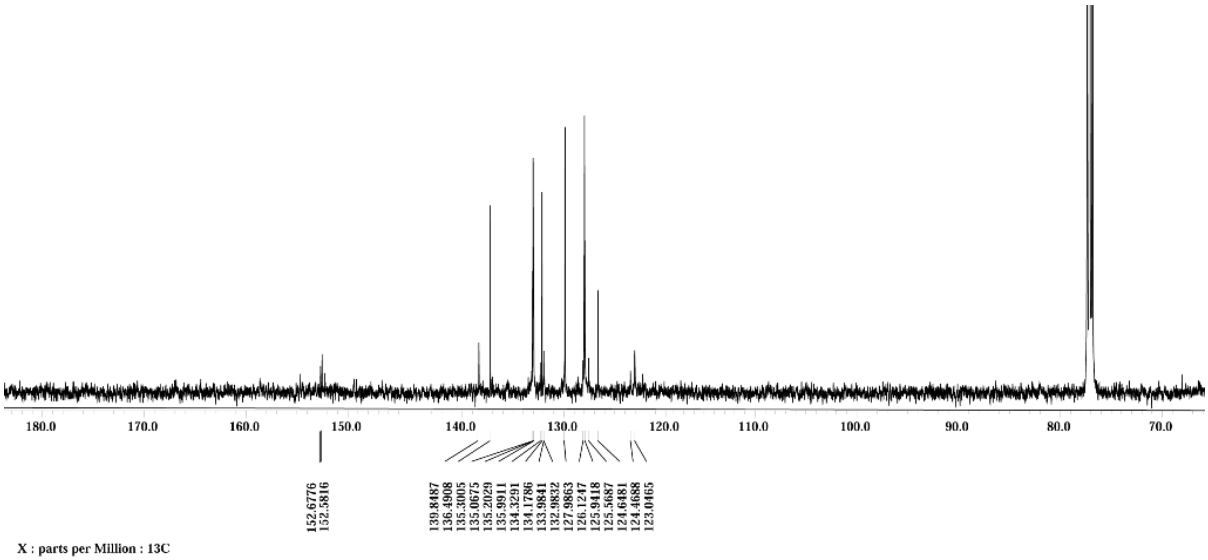


Figure S12. ^{13}C NMR spectrum for **3** in DMSO-d_6.

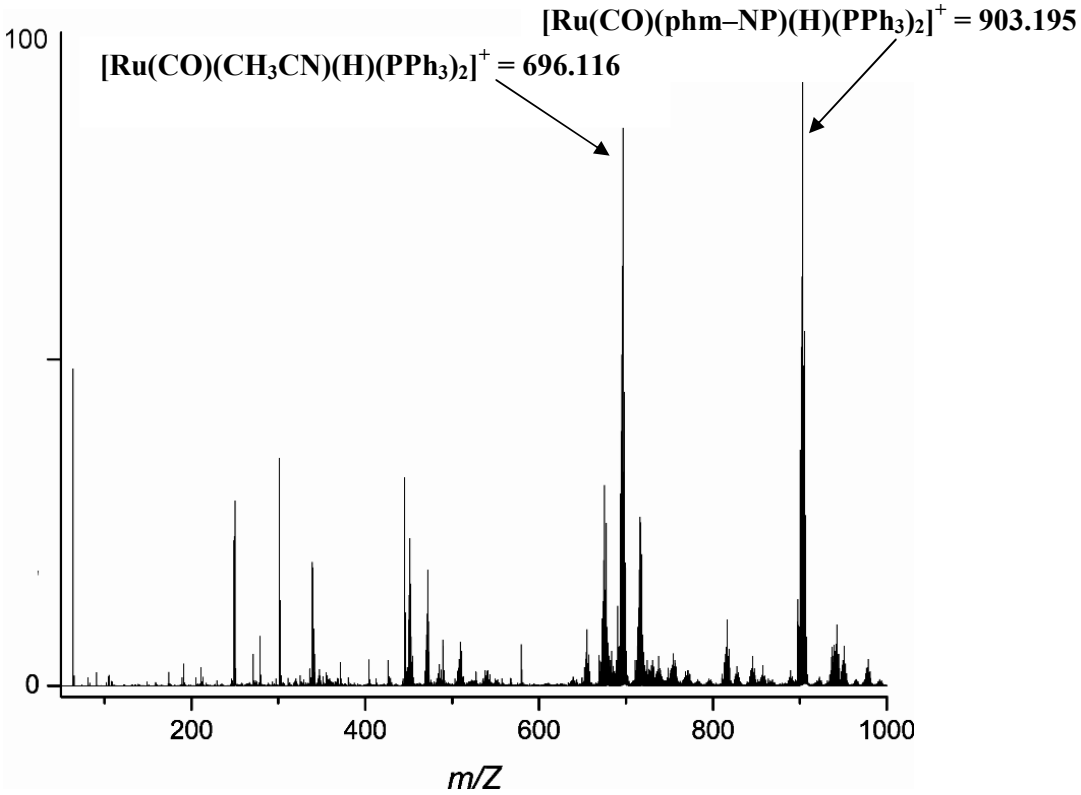


Figure S13. ESI-MS spectrum in the full range for complex **3**.

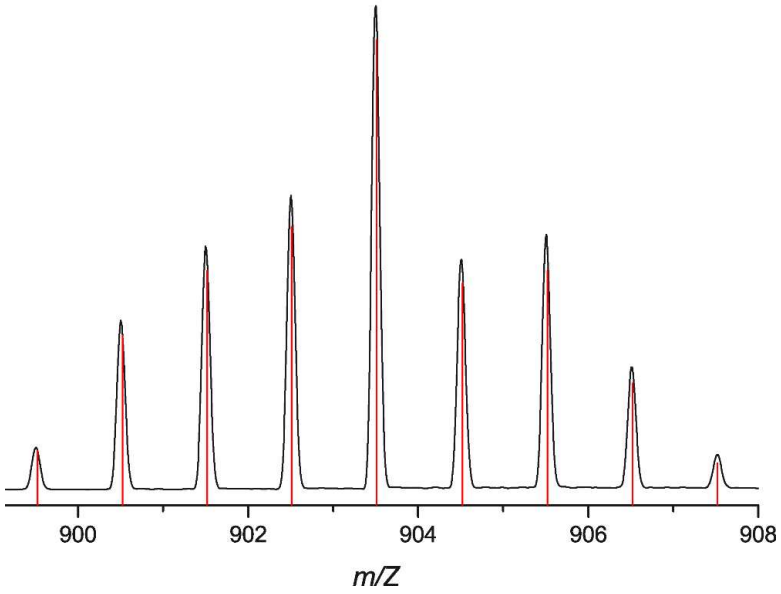


Figure S14. Experimental (black) and simulated (red) ESI-MS Spectrum for molecular ion at *m/z* = 903.195 (*z*=1) in complex **3**.

1.3. X–Ray data collection and refinements

Single–crystal X–ray studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low–temperature attachment. All data were collected at 100(2) K using graphite–monochromated Mo–Kα radiation (λ_α = 0.71073 Å). The frames were indexed, integrated, and scaled using the SMART and SAINT software packages,[6] and the data were corrected for absorption using the SADABS program.[7] The structures were solved and refined with the SHELX suite of programs. All non hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of ligands were included into geometrically calculated positions in the final stages of the refinement and were refined according to 'riding model'. The "SQUEEZE" option in PLATON program was used to remove a disordered solvent molecule from the overall intensity data of all the compounds.[8] Hydride ligands were observed in the difference Fourier maps. Diamond 3.1e software was used to produce the diagrams.[9] CCDC numbers 1506093–1506095 contain the supplementary crystallographic data for compounds **1, 2** and **3**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

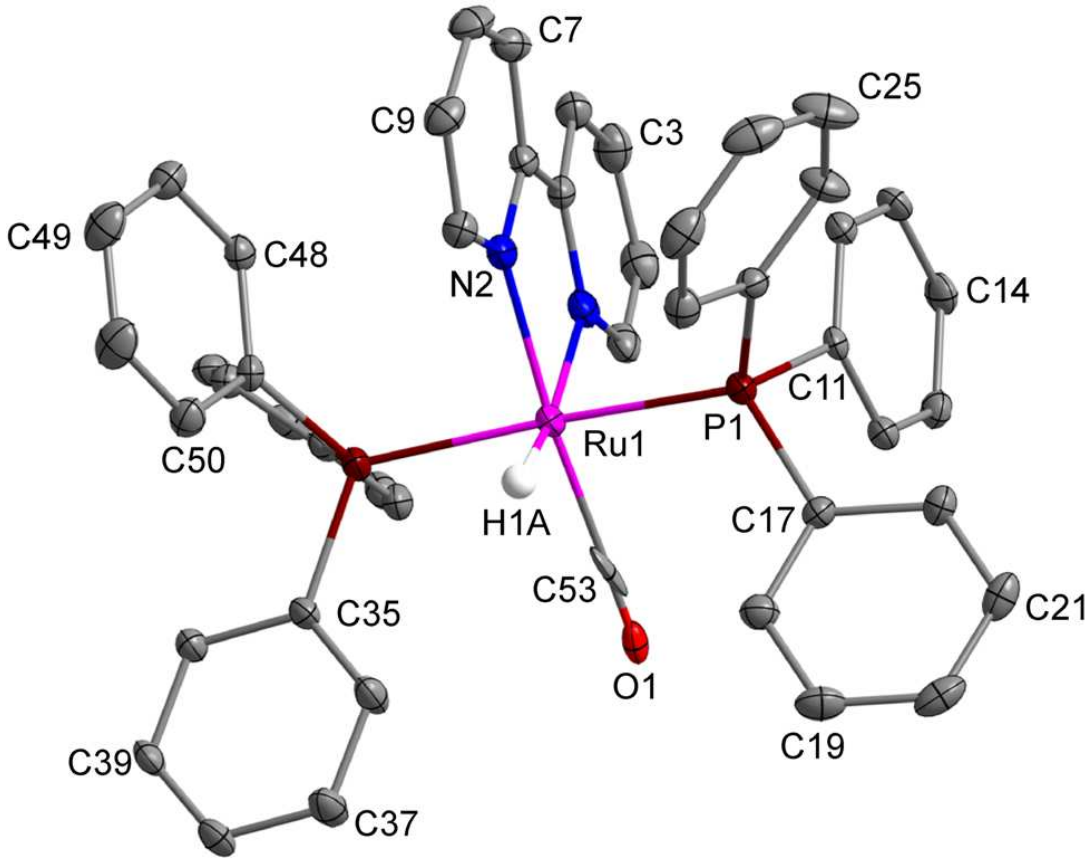


Figure S15. Molecular structure of **2** with important atoms labeled. Except for metal–hydride, all other hydrogens are omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Ru1–C53 1.974(5), Ru1–N2 2.122(3), Ru1–N1 2.150(3), Ru1–P2 2.3644(8), Ru1–P1 2.3689(8), Ru1–H1A 1.545(18), O1–C53 0.932(5). C53–Ru1–N1 98.72(14), N2–Ru1–N1 76.70(11), C53–Ru1–P2 91.52(11), N2–Ru1–P2 91.89(7), N1–Ru1–P2 94.50(7), C53–Ru1–P1 88.26(11), N2–Ru1–P1 88.82(7), N1–Ru1–P1 91.59(7), P2–Ru1–P1 173.87(3).

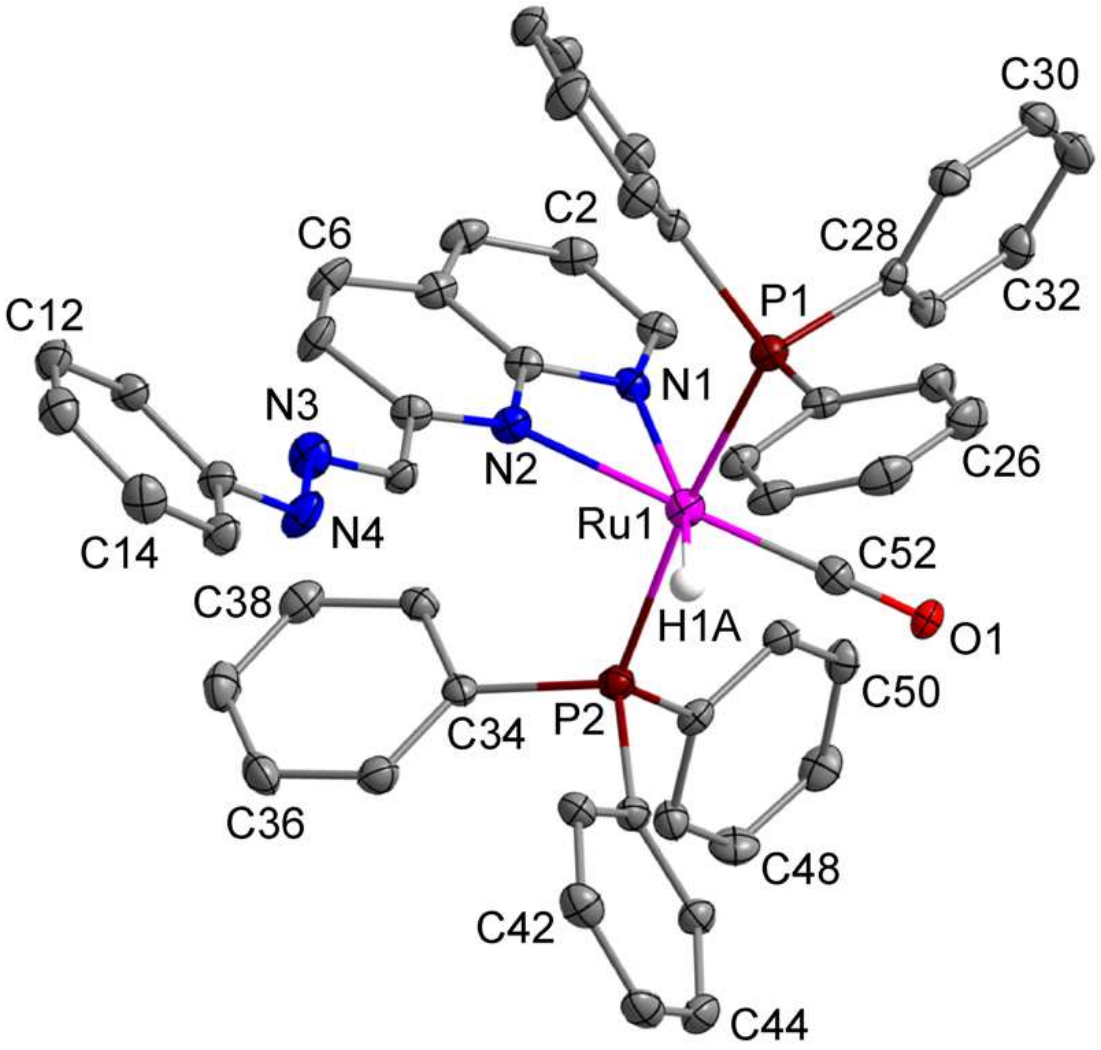


Figure S16. Molecular structure of **3** with important atoms labeled. Except for metal–hydride, all other hydrogens are omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°):Ru1–C52 1.837(6), Ru1–N2 2.161(5), Ru1–N1 2.300(5), Ru1–P1 2.3531(15), Ru1–P2 2.3561(15), Ru1–H1A 1.59(2), O1–C52 1.147(8). C52–Ru1–N2 177.4(2), C52–Ru1–N1 117.0(2), N2–Ru1–N1 60.35(17), C52–Ru1–P1 87.43(19), N2–Ru1–P1 92.57(13), N1–Ru1–P1 93.91(12), C52–Ru1–P2 86.71(19), N2–Ru1–P2 93.56(13), N1–Ru1–P2 94.28(12), P1–Ru1–P2 171.47(5).

Table S1. Crystallographic Data and Pertinent Refinement Parameters for **1, 2** and **3**

	1	**2**	**3**
Empirical formula	$C_{50}H_{40}ClN_3OP_2Ru$	$C_{59}H_{49}Cl_5N_4O_2P_2Ru_2$	$C_{54}H_{47}Cl_5N_4OP_2Ru$
Formula Weight	897.31	1287.35	1108.21
Crystal System	Orthorhombic	Triclinic	Monoclinic
Space Group	*Pnma*	*P-1*	$P2_1/c$
a (Å)	18.5484(9)	11.8324(13)	14.2935(9)
b (Å)	15.0463(7)	14.2246(16)	18.4185(11)
c (Å)	16.1704(8)	18.611(2)	22.7313(13)
α (deg)	90.00	86.239(2)	90.00
β (deg)	90.00	84.443(2)	108.440(4)
γ (deg)	90.00	71.637(2)	90.00
V (Å^3)	4512.9(4)	2956.9(6)	5677.1(6)
Z	4	2	4
ρ_{calcd} (g cm^{-3})	1.321	1.446	1.297
μ (mm^{-1})	0.517	0.835	0.607
F(000)	1840	1300	2264
Reflections			
Collected	40473	34309	52024
Independent	4001	16433	10038
Observed [I >2σ (I)]	3692	13518	8078
No. of variables	295	665	610
GooF	1.109	1.047	1.057
R_{int}	0.0335	0.0322	0.1285
Final R indices	R1 = 0.0317	R1 = 0.0512	R1 = 0.0814
[I > 2σ(I)][a]	wR2 = 0.0799	wR2 = 0.1173	wR2 = 0.2030
R indices (all data)[a]	R1 = 0.0347	R1 = 0.0636	R1 = 0.0965
	wR2 = 0.0814	wR2 = 0.1228	wR2 = 0.2122

[a] $R_1 = \Sigma\, ||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma|F_o^2|^2]^{1/2}$

2. Catalysis Reactions

General procedures

A mixture of an alcohol (1 mmol), **1** (5 mol%) were combined in a flame dried Schlenk–tube under nitrogen. Degassed, deionized alkaline water (18.5 mmol NaOH in 3mL water) and 1,4–Dioxane (0.1 mL, for selected entries) was added to the yellowish mixture and kept it under the heavy flow of nitrogen with occasional shaking for about 10 min under Schlenk line and the reaction mixture was refluxed. After 6–24 h, water was added (3 mL) and the mixture was extracted with diethyl ether (2 X 10 mL). The extracted organic layer was subjected to GC–MS analysis and showed only starting material. The aqueous phase was then acidified with 5N HCl and extracted with ethyl acetate (2 X 5 mL). The combined extracts were washed with brine (25 mL), dried over Na_2SO_4, and subjected to GC–MS analysis using dodecane (1 mmol) as internal standard and the peaks were matched with authentic samples.

For NMR yield, after the end of the reaction and acidification, the aqueous layer extracted with $CDCl_3$ and an NMR obtained from which the yield was calculated. The organic extracts were concentrated and purified by flash column chromatography using ethyl acetate and hexane as solvent. For most cases, spectroscopically pure compounds were obtained and isolated yields were 3-5% less than the GC yields. However for some cases (e.g. entry 13), the sodium salt of the acid was obtained and could not be purified completely. Hence GC yields are reported in the manuscript throughout.

Table S2. Optimization and controlled studies[a]

Entry	Catalyst	Substrate	Base	Solvent	Time (h)	Temp (°C)	Acid[b]
1	**1**	$PhCH_2OH$	NaOH	Water	6	110	100
2	**1**	$PhCH_2OH$	NaOH	Water	6	80	58
3	**1**	$PhCH_2OH$	NaOH	–	24	110	–
4	–	$PhCH_2OH$	NaOH	Water	24	110	–
5	–	PhCHO	NaOH	Water	24	110	<3
6	**1**	n–butanol	–	Water	24	110	–[c]
7	**1**	$PhCH_2OH$	NaOH	Toluene	24	110	–
8	**1**	butyl butyrate	–	Water	24	110	–
9	**1**	$PhCH_2OH$ + 1 eq. pyridine	NaOH	Water	24	110	–
10	**1**	$PhCH_2OH$	NaOH	Water	24	110	62[d]

[a]Reaction conditions: 1 mmol substrate, catalyst (5 mol%), alkaline water (18.5 mmol NaOH in 3mL water). [b]Carboxylic acids were obtained by acid treatment of the salts and determined by GC–MS using dodecane (1 mmol) as internal standard. [c]Ester formation not detected. [d]Reaction performed in closed vessel.

2.1. Volumetric estimation of evolved gas during catalysis

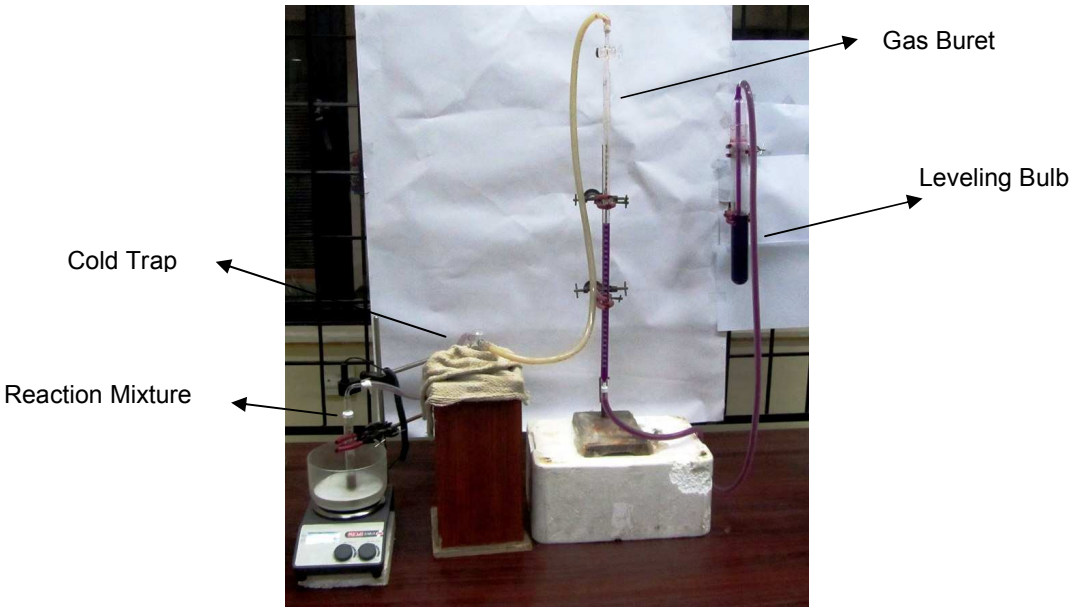


Figure S17. Experimental setup for volumetric estimation of hydrogen.

A mixture of benzyl alcohol (0.5 mmol), **1** (5 mol%) were combined in a flame dried normal Schlenk–tube under nitrogen. Degassed and deionized alkaline water (18.5 mmol NaOH in 3mL water) was added to the yellowish mixture and the reaction mixture was refluxed with the headspace connected to a gas buret via a cold trap to remove any solvent vapors. The reaction was continued till evolution of gas ceased. The experiment was repeated thrice to get consistent readings and the number of moles of hydrogen evolved was calculated taking into account the vapor pressure of water at 298K = 23.7695 Torr. Volume of water displaced = 23.6 mL, Atmopsheric Pressure = 758.3124 Torr, R = 62.3635 L Torr K^{-1} mol^{-1}.

$nH_2 = [(P_{atm} – P_{water}) * V] / RT = 0.00093$ moles

Expected Value = 0.001 mole

2.2. Qualitative estimation of evolved gas by GC-Thermal Detector

A mixture of benzyl alcohol (1 mmol), **1** (5 mol%) were combined in a flame dried normal Schlenk–tube under nitrogen. Degassed and deionized alkaline water (18.5 mmol NaOH in 3mL water) was added to the yellowish mixture and the reaction mixture refluxed with the headspace attached to a eudiometer. After 6 hrs, the gas collected in the eudiometer was subjected to GC analysis and the retention time matched with a sample collected from a hydrogen cylinder of 99.9% purity.

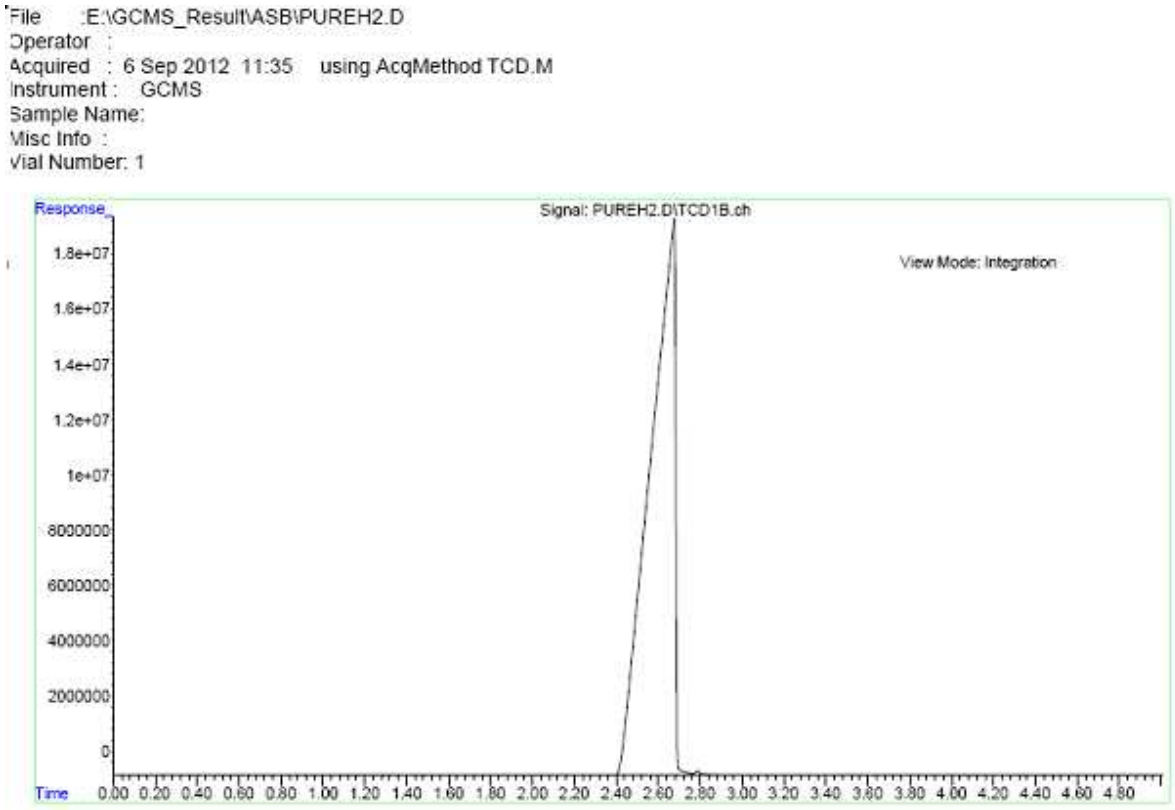


Figure S18. GC Spectrum for pure H_2 (TCD mode).

File :E:\GCMS_Result\ASB\H2liberation.D Operator :
Acquired : 6 Sep 2014 10:43 using AcqMethod TCD.M
Instrument : GCMS
Sample Name:
Misc Info :
Vial Number: 1

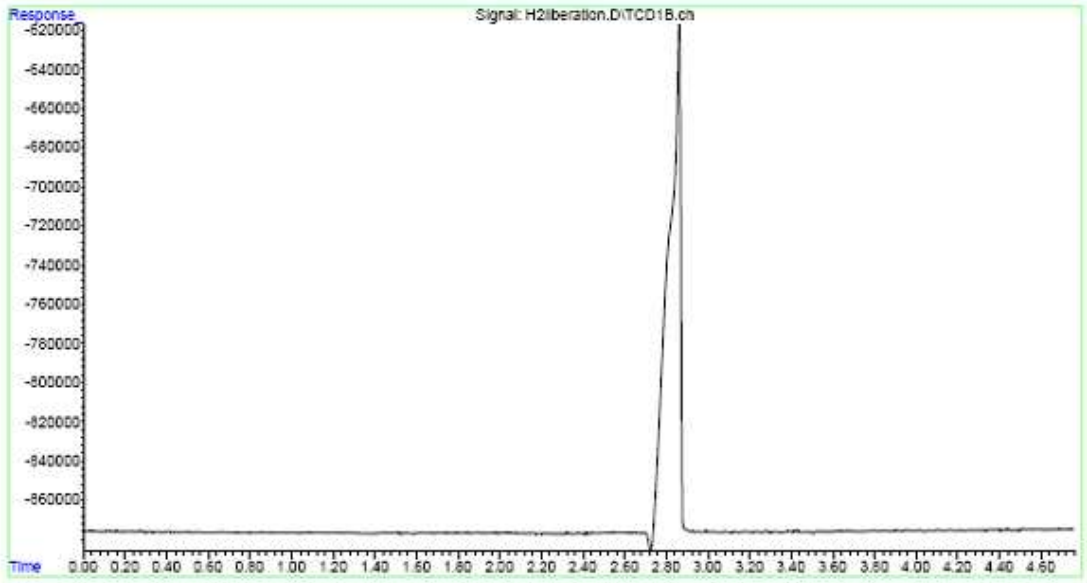
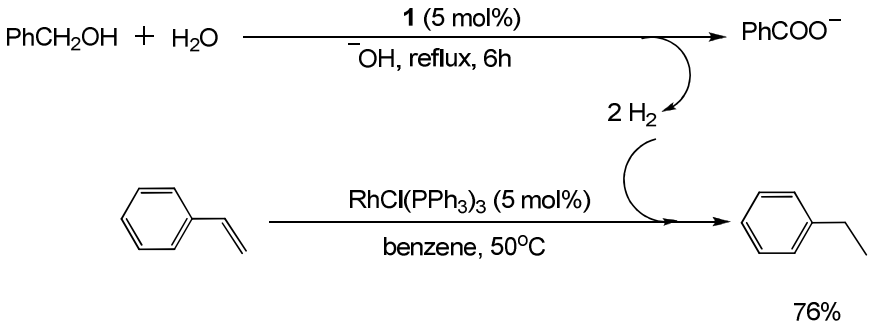


Figure S19. GC Spectrum for evolved gas (TCD Mode).

2.3. Dual reactions involving hydrogenation of styrene

In order to obtain experimental evidence that the evolved gas in the oxidation of alcohols to acids is hydrogen, we carried out the following dual reactions. The catalysis reaction using the catalyst **1** was conducted in a flask that was connected through a rubber tube to another flask in which styrene and a catalytic amount of $RhCl(PPh_3)_3$ in benzene were placed. When the reaction was almost completed, ethylbenzene was produced in 76% yield in the latter flask, demonstrating that the hydrogen gas generated in the former flask was transferred through the tube to reduce styrene in the latter flask.



Scheme S1. Schematic representation of dual reaction.

3. Mechanistic Studies

3.1. Isotope labeling experiments with $^{18}OH_2$

A mixture of an alcohol (0.5 mmol), and alkaline $^{18}OH_2$ (0.3 mL, $^{18}OH_2$:Na^{16}OH = 1.67:1 *m/m*) were combined in a flame dried normal Schlenk–tube under nitrogen and stirred for 10 minutes. Subsequently, 0.025 mmol of **1** was added and the mixture was refluxed for 4 h and subjected to GC–HRMS analysis.

Initial labeling

18 g $^{18}OH_2$ contains 1000 mmol ^{18}O atoms

∴ 18 mL $^{18}OH_2$ contains 1000 mmol ^{18}O atoms (Specific Gravity of water = 1)

∴ 0.3 mL $^{18}OH_2$ contains = 16.67 mmol ^{18}O atoms

Purity of $^{18}OH_2$ = 99%

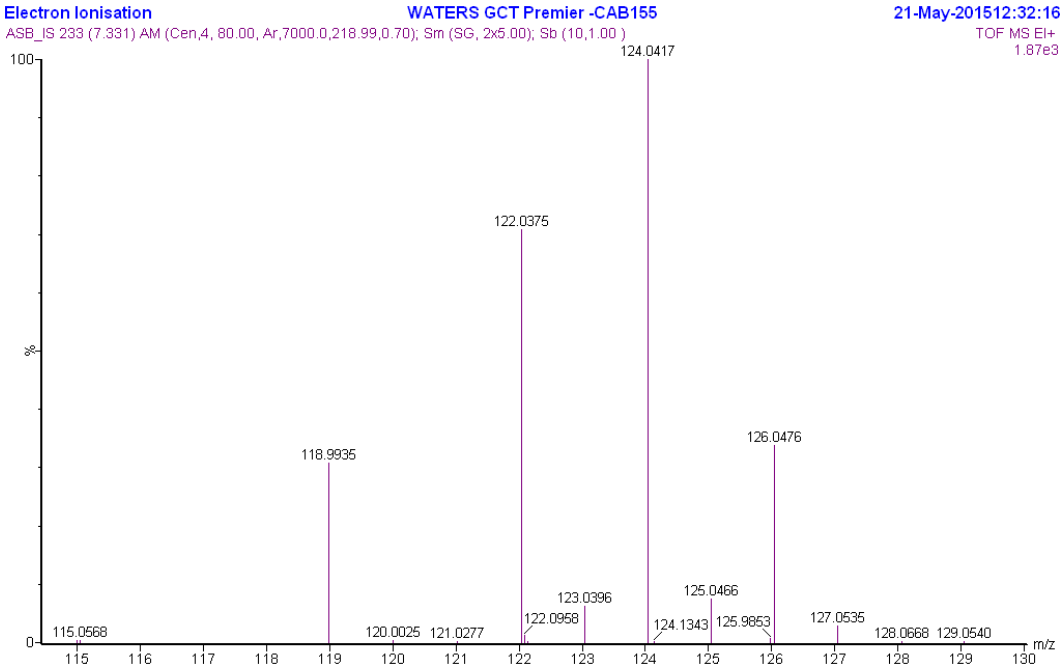
Hence, number of ^{18}O atoms = 16.67 X 0.99 = 16.50 mmol

Total ^{16}O atoms in reaction mixture ($PhCH_2OH$ + NaOH) = 10.5 mmol

Total O atoms in the reaction mixture = 10.5 mmol ^{16}O atoms + 16.67 mmol ^{18}O atoms = 27.17 mmol

Hence, overall labeling (%) = (number of ^{18}O atoms/ Total O atoms in the reaction mixture) X 100 = (16.50/ 27.17) X 100 = 60.73%

N.B. 0.025 mmol catalyst will contribute to scrambling and Specific Gravity of water at 110 °C is not strictly 1.000. Hence, overall labeling will be affected in small margins. For all practical purposes, the labeling was considered as ~60%.



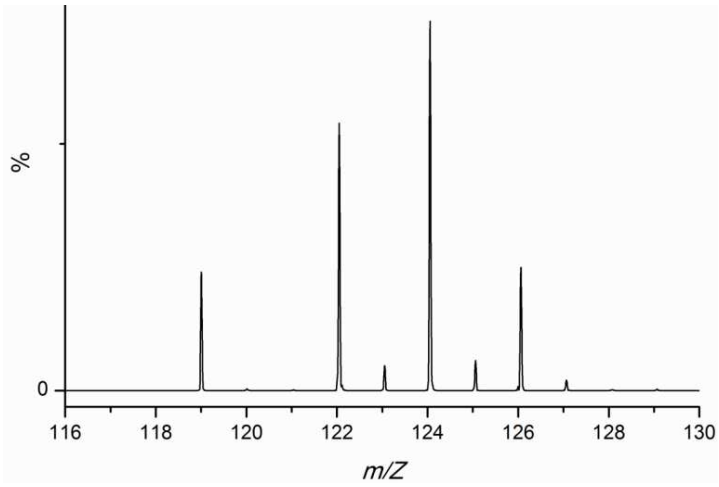


Figure S20. GC-HRMS spectrum of catalysis reaction when $^{18}OH_2$ was used. The spectrum shows the formation of isotopically enriched benzoic acid (M. W. 124). An enlarged Gaussian representation from the data obtained is also represented below. Ratio of peak heights between *m/Z* 124 and 122 is 6: 5.

3.2. Kinetic experiments with H_2O and D_2O

A mixture of benzyl alcohol (1 mmol), **1** (5 mol%) were combined in a flame dried normal Schlenk–tube under nitrogen. Degassed and deionized alkaline H_2O/D_2O (18.5 mmol NaOH in 3mL) was added to the yellowish mixture and kept it under the heavy flow of nitrogen with occasional shaking for about 10 min under Schlenk line and the reaction mixture refluxed. After stipulated time intervals, small aliquots of 0.2 mL were taken out with a hypodermic needle and neutralized by adding 2-3 drops of 5N HCl. The mixture was slowly poured into a vial containing 2 mL ethyl acetate, capped and shaken vigorously. Once the phases separated out, the ethyl acetate layer was subjected to GC–MS analysis.

Table S3. Comparative reaction rates for $PhCH_2OH$ in H_2O and D_2O by **1**[a]

	H_2O		**D_2O**	
Time(h)	Alcohol (%)	Acid (%)	Alcohol (%)	Acid (%)
0	100	0	100	0
0.5	100	0	100	0
1	100	0	100	0
1.5	100	0	100	0
2	98	2	100	0
3	68	32	98	2
4	2	98	42	58
6	1	99	19	81
10	0	100	9	91

[a]Carboxylic acids were obtained by acid treatment and extraction of the aliquots followed by GC–MS using dodecane (1 mmol) as internal standard.

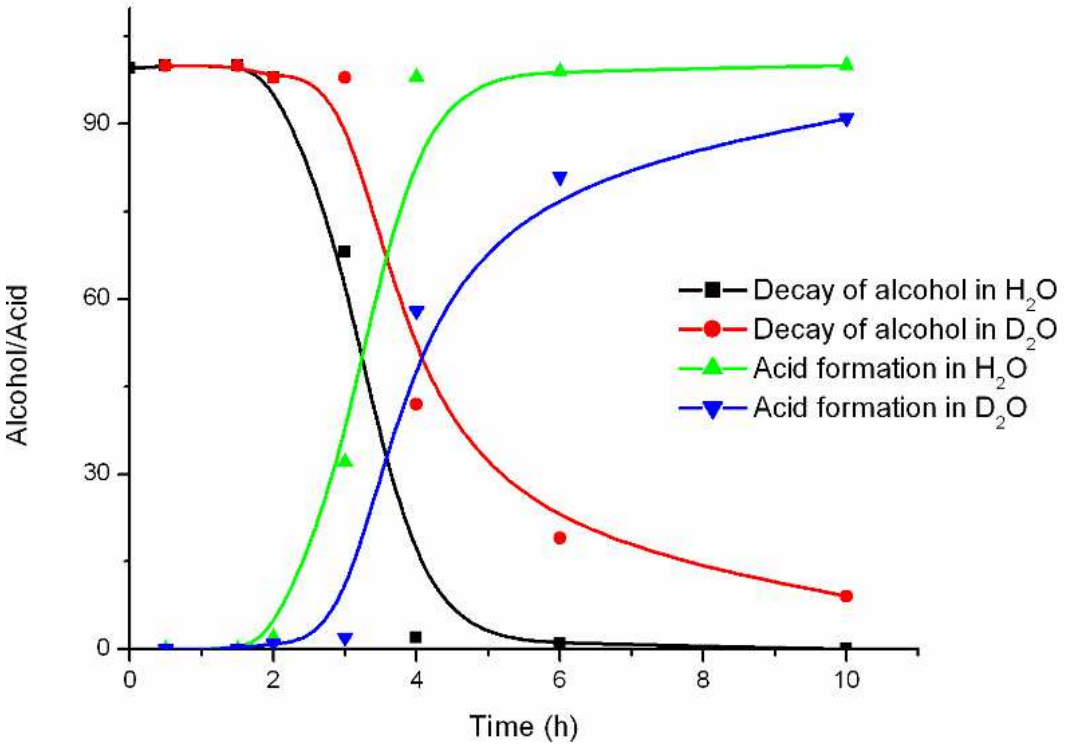


Figure S21. Comparative reaction rates in H_2O and D_2O.

3.3. Experimental procedure for KIE

A mixture of $PhCH_2OH$ (0.5 mmol), $PhCD_2OH$ (0.5 mmol), **1** (5 mol%) were combined in a flame dried normal Schlenk–tube under nitrogen. Degassed and deionized alkaline water was added to the yellowish mixture and kept it under the heavy flow of nitrogen with occasional shaking for about 10 min under Schlenk line and the reaction mixture refluxed. After stipulated time intervals, small aliquots of 0.2 mL were taken out with a hypodermic needle and neutralized by adding 5N HCl. The mixture was slowly poured into a vial containing 2 mL ethyl acetate, capped and shaken vigorously. Once the phases separated out, the ethyl acetate layer was subjected to GC–MS analysis. The ratio of unreacted $PhCH_2OH$ and $PhCD_2OH$ were used to determine the KIE values.

3.4. Phosphine dissociation confirmation studies.

In order to examine the possibility of phosphine dissociation during the conversion of benzyl alcohol under standard reaction conditions, excess PPh_3 (1–8 equiv with respect to catalyst) was added to the reaction mixture, shown in Figure S22. Conversion of benzyl alcohol decreased significantly when excess of PPh_3 was added. This suggests that in the catalytic cycle, elimination of PPh_3 from complex 1 was essential. The decreased yields are more pronounced when more than 5 equivalents of PPh_3 are used and are attributed to the poor solubility of PPh_3 in aqueous media.

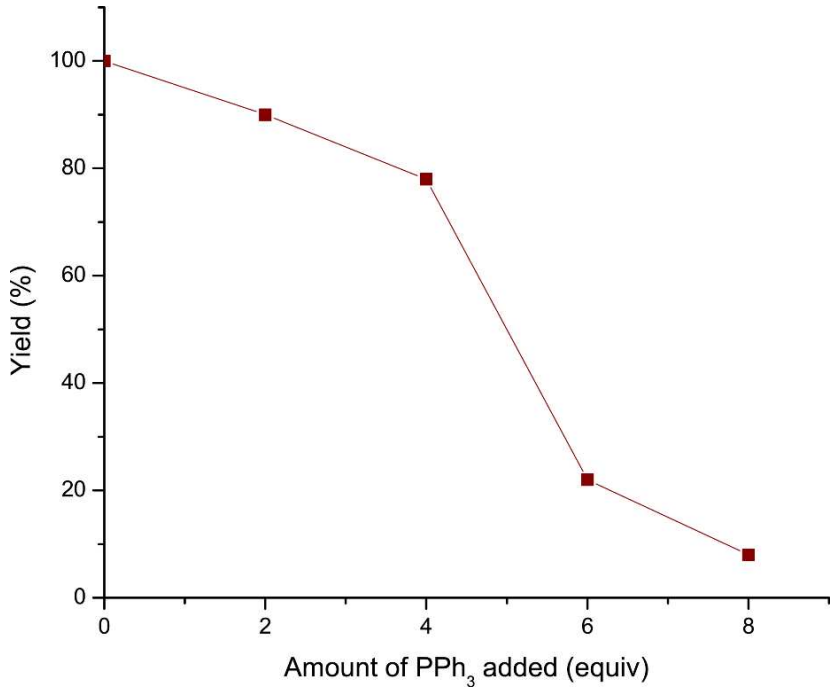


Figure S22. Effect of externally added PPh_3 on yields in conversion of benzyl alcohol to benzoic acid by **1**.

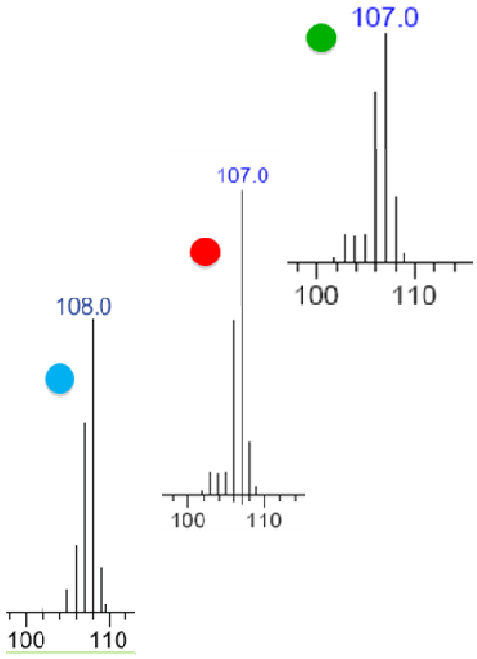
4. Crossover Experiments

Hydrogenation of styrene by 1.

Hydrogenation reaction was performed at constant pressures using a stainless steel 50 mL Parr hydrogenation reactor. The reactor was flushed three times with hydrogen gas at 2−4 bar prior to the addition of catalyst and substrate. In a typical run, catalyst **1** (0.05 mmol), styrene (1 mmol) and dodecane (1 mmol) were dissolved in benzene (10 mL) under a nitrogen atmosphere. The solution was then injected into the reactor against a flow of hydrogen gas. The hydrogen gas was adjusted to 20 bar. The temperature of the system was maintained at 50°C using a thermostat. After 12h, the reaction mixture was diluted with EtOAc and passed through a very short column of silica to remove any impurities and subjected to GC–MS analysis and showed quantitative conversion of styrene.

General procedure for crossover experiments.

A mixture of a $PhCH_2OH/PhCD_2OH$ (1 mmol), styrene (1 mmol), **1** (5 mol%) were combined in a flame dried normal Schlenk–tube under nitrogen. Degassed and deionized alkaline H_2O/D_2O (18.5 mmol NaOH in 3mL) was added to the yellowish mixture and kept it under the heavy flow of nitrogen with occasional shaking for about 10 min under Schlenk line and the reaction mixture refluxed. After 6h, the reaction mixture was extracted with 5 mL ethyl acetate and then subjected to GC–MS analysis.



Experiment 1

$PhCH_2OH + D_2O + PhCH{=}CH_2$ ›
$PhCH_2CH_3$: $PhCHDCH_3$: $PhCHDCH_2D$

H_2: HD: D_2 = 1.5: 2.5: 1

Experiment 2

$PhCD_2OH + H_2O + PhCH{=}CH_2$ ›
$PhCH_2CH_3$: $PhCHDCH_3$: $PhCHDCH_2D$

H_2: HD: D_2 = 3.1: 5.4: 1

Experiment 3

$PhCD_2OH + D_2O + PhCH{=}CH_2$ ›
$PhCH_2CH_3$: $PhCHDCH_3$: $PhCHDCH_2D$

H_2: HD: D_2 = 1: 1.6: 2.5

Scheme S2. Schematic representation of crossover experiments.

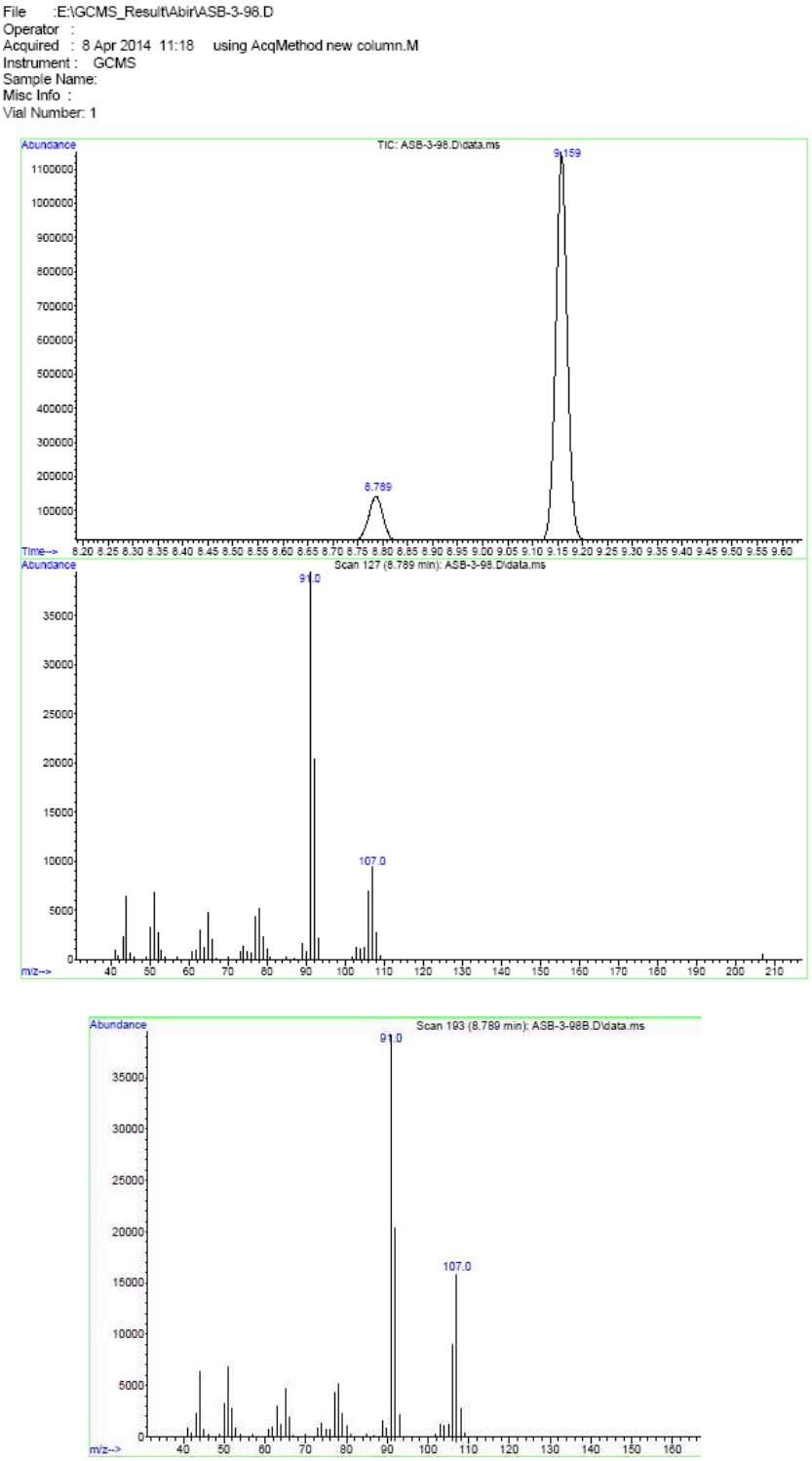


Figure S23. GC-MS spectrum of D-ethylbenzene and styrene and mass distribution for D-ethylbenzene at 107. Abundance of peak at 106:107:108 = 1.5:2.5:1 ($PhCH_2OH–D_2O$, top) and 3.1: 5.4: 1 ($PhCD_2OH–H_2O$, below).

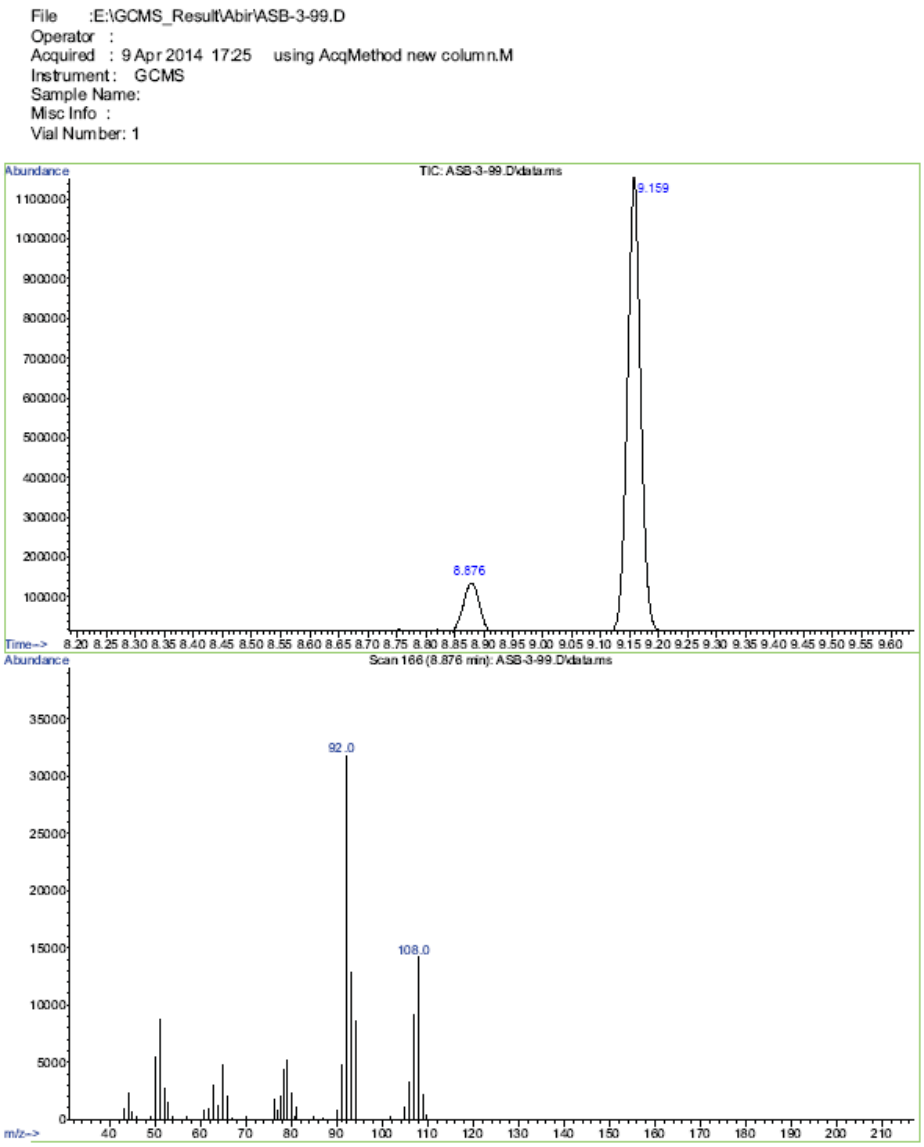
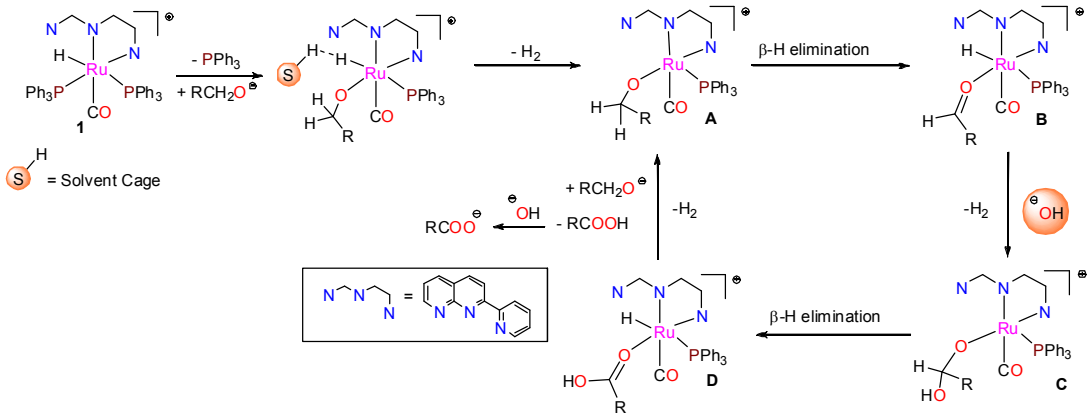
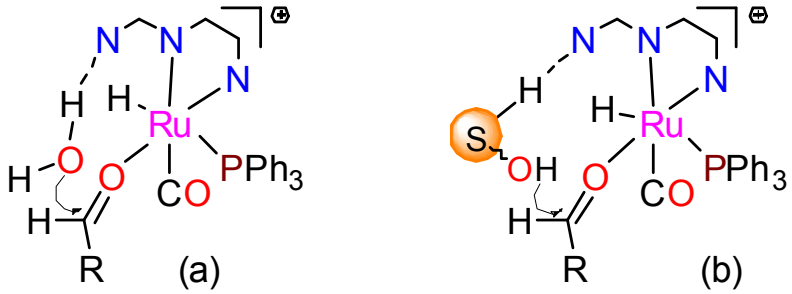


Figure S24. GC-MS spectrum of doubly D_2-ethylbenzene and styrene (top) and mass distribution for D_2-ethylbenzene at 108 (below). Abundance of peak at 106:107:108 = 1:1.6:2.5.

5. Mechanism

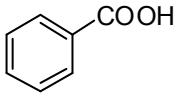


Scheme S3. Mechanism considering an alkoxide attack under basic conditions.

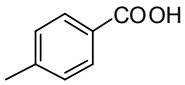


Scheme S4. 2−substituted NP ligands promoting (a) Water attack and (b) solvated hydroxide attack to the metal bound aldehyde.

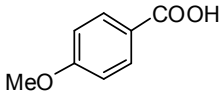
6. Spectroscopic Characterization of Carboxylic acids



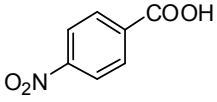
^{1}H NMR ($CDCl_3$, 400 MHz): 12.32 (br, s, 1H), 8.12-8.14 (m, 2H), 7.62 (t, J = 7.6, 1H), 7.48 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 172.9, 134.1, 130.5, 129.6, 128.8.



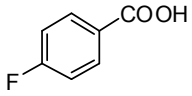
^{1}H NMR ($CDCl_3$, 400 MHz): 12.11 (br, s, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 172.8, 144.9, 130.5, 129.5, 126.9, 22.0.



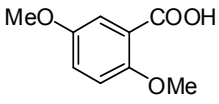
^{1}H NMR ($CDCl_3$, 400 MHz): 8.08 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 9.2 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 171.8, 164.3, 132.7, 121.9, 114.1, 55.8.



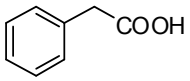
^{1}H NMR (DMSO–d_6, 400 MHz): 13.67 (s, 1H), 8.31 (dt, J_1= 2.4 Hz, J_2 = 2.0 Hz, 2H), 8.15 (dt, J_1= 1.6 Hz, J_2 = 2.0 Hz, 2H); ^{13}C NMR (DMSO–d_6, 100 MHz): 165.5, 149.7, 136.1, 130.4, 123.5.



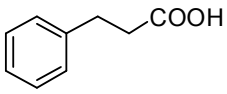
^{1}H NMR ($CDCl_3$, 400 MHz): 8.13-8.16 (m, 2H), 7.15 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 171.5, 166.7, 133.2, 125.8 (d, *J* = 2.6 Hz), 116.1; ^{19}F NMR ($CDCl_3$): -104.1 (s, 1F).



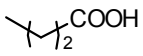
^{1}H NMR ($CDCl_3$, 500 MHz): 11.00 (br, s, 1H), 7.65 (d, *J*= 3.4 Hz), 7.10 (dd, J_1= 9.2 Hz, J_2 = 3.4 Hz, 1H), 6.99 (d, *J*= 9.2 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): 165.4, 154.5, 152.4, 122.1, 118.0, 116.4, 113.3, 57.3, 56.0.



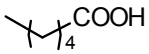
^{1}H NMR (400 MHz, $CDCl_3$): 7.38-7.27 (m, 5H), 3.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 178.0, 133.2, 129.3, 128.6, 127.3, 41.0.



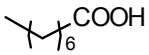
^{1}H NMR (400 MHz, $CDCl_3$): 11.12 (br, s, 1H), 7.35 (m, 2H), 7.27 (m, 3H), 3.01 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 179.4, 140.2, 128.6, 128.3, 126.4, 35.7, 30.6.



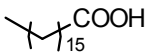
^{1}H NMR (400 MHz, $CDCl_3$): 11.70 (s, 1H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.68 (m, 2H), 1.00 (*t*, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 180.0, 36.0, 18.7, 13.3.



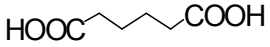
^{1}H NMR (400 MHz, $CDCl_3$): 11.80 (s, 1H), 2.35 (m, 2H), 1.65 (m, 2H), 1.30 (m, 4H), 0.90 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 180.3, 34.0, 31.7, 24.6, 22.0, 14.0.



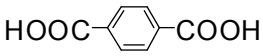
^{1}H NMR (400 MHz, $CDCl_3$): 11.80 (br, s, 1H), 2.34 (t, *J* = 7.7 Hz, 2H), 1.61 (m, 2H), 1.29 (m, 8H), 0.88 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 180.4, 34.3, 31.9, 29.2, 29.1, 24.9, 22.8, 14.3.



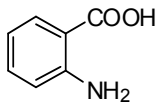
^{1}H NMR (400 MHz, $CDCl_3$): 2.35 (t, *J* = 7.6 Hz, 2H), 1.63 (tt, J_1= 7.6 Hz, J_2 = 6.8 Hz, 1H), 1.27 (bm, 28H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 179.4, 33.9, 31.9, 29.7, 29.6, 29.4, 29.2, 29.0, 24.7, 22.7, 14.1.



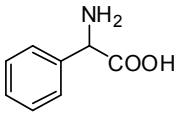
^{1}H NMR (DMSO–d_6, 400 MHz): 11.97 (br, s, 1H), 2.17 (t, *J* = 3.0 Hz, 4H), 1.47 (m, 4H); ^{13}C NMR (DMSO–d_6, 100 MHz): 175.0, 34.0, 24.7.



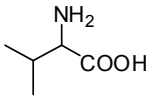
^{1}H NMR (DMSO–d_6, 400 MHz): 8.04 (s, 4H), 13.3 (br, s, 2H); ^{13}C NMR (DMSO–d_6, 100 MHz): 129.9, 134.9, 167.1.



^{1}H NMR (DMSO–d_6, 400 MHz): 8.53 (bs, 2H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 6.49 (t, *J* = 7.4 Hz, 1H), 3.39 (s, 3H); ^{13}C NMR (DMSO–d_6, 100 MHz): 170.1, 152.0, 134.3, 131.7, 116.9, 115.0.



^{1}H NMR (D_2O, 400 MHz): 4.47 (s, CH, 1H), 7.18–7.19 (m, Ar, 5H).^{13}C NMR (D_2O, 100 MHz): 181.5, 140.9, 129.0, 128.2, 127.5, 126.6, 126.4, 65.6.



^{1}H NMR (D_2O, 400 MHz): 3.41 (d, *J* = 4.34 Hz, 1H), 2.05 (m, 1H), 0.83 (d, *J* = 7.0 Hz, 3H), 0.77 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (D_2O, 100 MHz): 174.4, 60.5, 29.2, 18.2, 16.9.

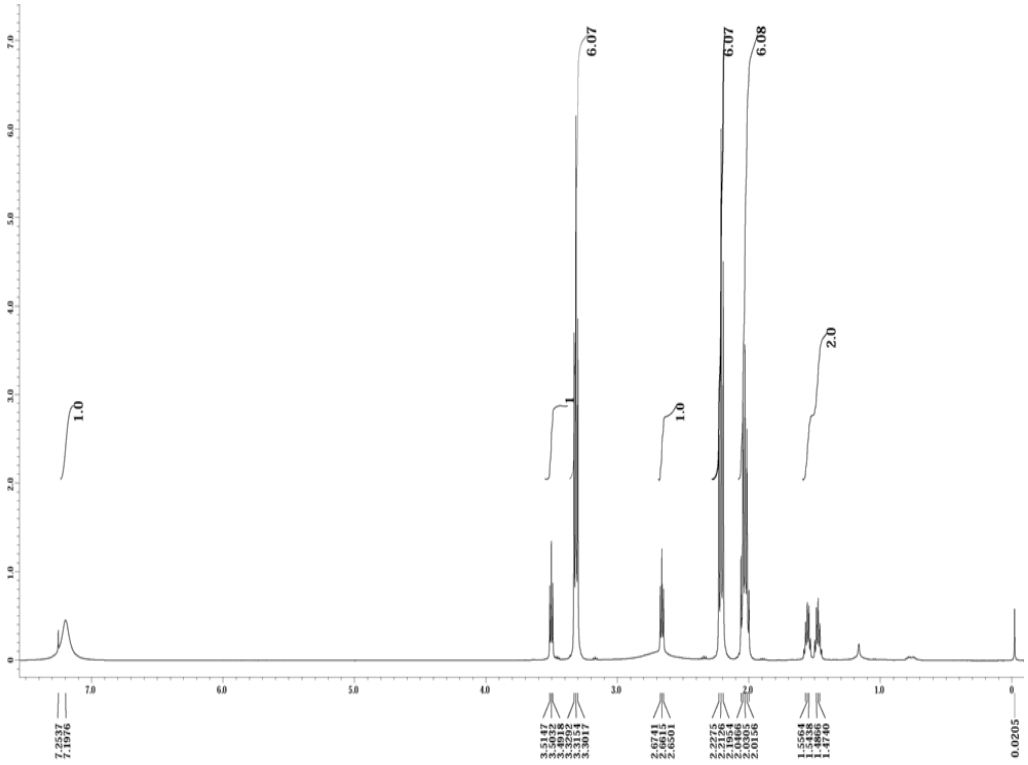


Figure S25. NMR yield for 2-pyrrolidinone. Integration Lactam : Integration Amino alcohol = 6.07 : 1. Yield of Lactam = 6.07 * (100 / 7.07) = 86%

7. References

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