Electronic Supplementary Information

for

Water as a catalytic switch in the oxidation of aryl alcohols by polymer incarcerated rhodium nanoparticles

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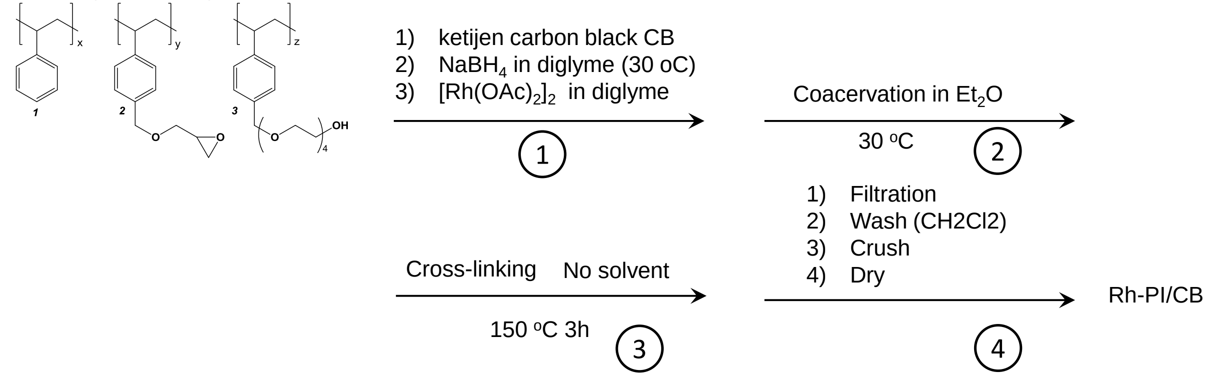
1.1 Preparation of the catalysts and copolymer

Scheme S1. Schematics for the preparation of the Rh-PI catalyst and supported species.[S1,S2] Copolymer, x, y, z: 1:1:1 ratio.



An identical proceudre was used for the preparation of Rh-PI/Al_2O_3 just by substituting CB to Al_2O_3. The Rh complex precursor, $[Rh(OAc)_2]_2$ was purchased from Strem Chemical Inc.

$NaBH_4$ was purchased from Wako Pure Chemical Company and recrystallized from diglyme by heating according to the literature [S1] and stored in a glove box. It is important to manipulate all operations under Ar atmosphere during recrystallization. Activity of catalysts and reproducibility are highly influenced by the purity of $NaBH_4$ in the course of the catalyst preparation.

Activated carbon, Ketjen black EC300J was purchased from Lion Corporation. Ketjen black EC300J was described in [S3].

1.2 Preparation of 2-(2-(2-(2-(4-vinylbenzyloxy)ethoxy)ethoxy)ethoxy)ethanol

To sodium hydride (60% in mineral oil, 5.7 g) suspended in THF (150 mL), tetraethyleneglycol (22.5 g) was added at 0 °C. After the reaction mixture was stirred for 20 min at room temperature, 1-(chloromethyl)-4-vinylbenzene (13.3 g) was added and the mixture was further stirred for 2 h. The mixture was cooled to 0 °C and diluted with diethyl ether. Saturated aqueous ammonium chloride was added to quench the reaction and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over sodium sulfate and the solvent was removed *in vacuo*. The residue was purified by column chromatography to afford 2-(2-(2-(2-(4-vinylbenzyloxy) ethoxy) ethoxy) ethoxy) ethanol ether (21.6 g, 79.7%). ^{1}H NMR ($CDCl_3$) δ = 2.55-2.59 (m, 1H), 3.59-3.73 (m, 16H), 4.55 (s, 2H), 5.25 (d, 1H, J = 6.4 Hz), 5.53 (d, 1H, J = 18 Hz), 6.71 (dd, 1H, J = 11.0, 17.9 Hz), 7.22-7.27 (m, 3H), 7.31-7.39 (m, 2H); ^{13}C NMR δ = 61.8, 69.5, 70.5, 70.69, 70.74, 72.6, 73.0, 113.8, 126.3, 128.0, 136.0, 137.1, 138.0.

1.2 Preparation of 4-Vinylbenzyl glycidyl ether

To sodium hydride (60% in mineral oil, 4.0 g) suspended in DMF (200 mL), glycidol (6.6 mL) was added at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, 1-(chloromethyl)-4-vinylbenzene (7 mL) was added and the mixture was further stirred for 5 h at room temperature. The mixture was cooled to 0 °C and diluted with diethyl ether. Saturated aqueous ammonium chloride was added to quench the reaction and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over sodium sulfate and the solvent was removed *in vacuo*. The residue was purified by column chromatography to afford 4-vinylbenzyl glycidyl ether (7.0 g, 74%). ^{1}H NMR ($CDCl_3$) δ = 2.60 (dd, 1H, J = 2.8, 4.8 Hz), 2.78 (dd, 1H, J = 4.0, 4.8 Hz), 3.17 (m, 1H), 3.42 (dd, 1H, J = 5.6, 11.2 Hz), 3.74 (dd, 1H, J = 2.8, 11.2 Hz), 4.56 (dd, 2H, J = 10.8, 17.6 Hz), 7.30 (d, 2H, J = 8.0 Hz), 7.39 (d, 2H, J = 8.0 Hz); 13C NMR δ = 40.2, 50.7, 70.7, 72.9, 113.8, 126.2, 127.9, 136.4, 137.0, 137.4.

1.3 Preparation of Copolymer

Styrene (2.1 g), 4-vinylbenzyl glycidyl ether (4.1 S-3g), 2-(2-(2-(2-(4-vinylbenzyloxy) ethoxy)ethoxy)ethoxy)ethanol (6.0 g) and 2, 2'-azobis(4 methoxy)-2,4-dimethylvaleronitrile (V-70, 181.2 mg) were combined in chloroform (11.0 mL). The mixture was stirred for 48 h at room temperature. The resulting polymer solution was slowly poured into ether. Solvent was removed by decantation and remaining precipitated polymers were washed with ether several times. Polymers were dissolved in THF, repeated to precipitate for 2 times and dried *in vacuo* to afford the desired copolymer (copolymer, 6.86 g, 56 % yield). The molar ratio of the components was determined by ^{1}H NMR analysis ($x: y: z$ = 1: 1: 1).

1.4 Preparation of PI/CB Rh

Copolymer (100.0 mg), ketjen black EC300J (100.0 mg) and $NaBH_4$ (22.6 mg, 0.6 mmol) were combined in diglyme (8 mL) at room temperature, to this solution was slowly added rhodium(II) acetate dimer (8.8 mg, 0.02 mmol) with 5.0 mL of THF. The mixture was stirred overnight at room temperature and diethyl ether (50 mL) was slowly added to the mixture at room temperature. After the catalysts, which were black powders, were filtered and crashed, they were washed with diethyl ether several times and dried at room temperature. Next, the catalysts were heated at 150 ˚C for 5 h without solvent. The catalysts were transferred to the solution of $NaBH_4$ (22.6 mg, 0.6 mmol) in diglyme (8 mL) and this solution was stirred under air at room temperature for 6 h. The catalysts were filtered and stirred in 1:1 ratio of THF/water co-solvent overnight. The catalysts were filtered, washed with dichloromethane and THF and dried to afford black powder. This powder was heated at 170 ˚C for 5 h without solvent to afford PI/CB Rh. PI/CB Rh (10-20 mg) was heated in mixture of sulfuric acid and nitric acid at 200 ˚C, the mixture was cooled to room temperature and *aqua* *regia* was added. The amount of each metal in the resulting solution was measured by ICP analysis to determine the loading of each metal.

2.1 NMR and GC/MS of reaction mixture

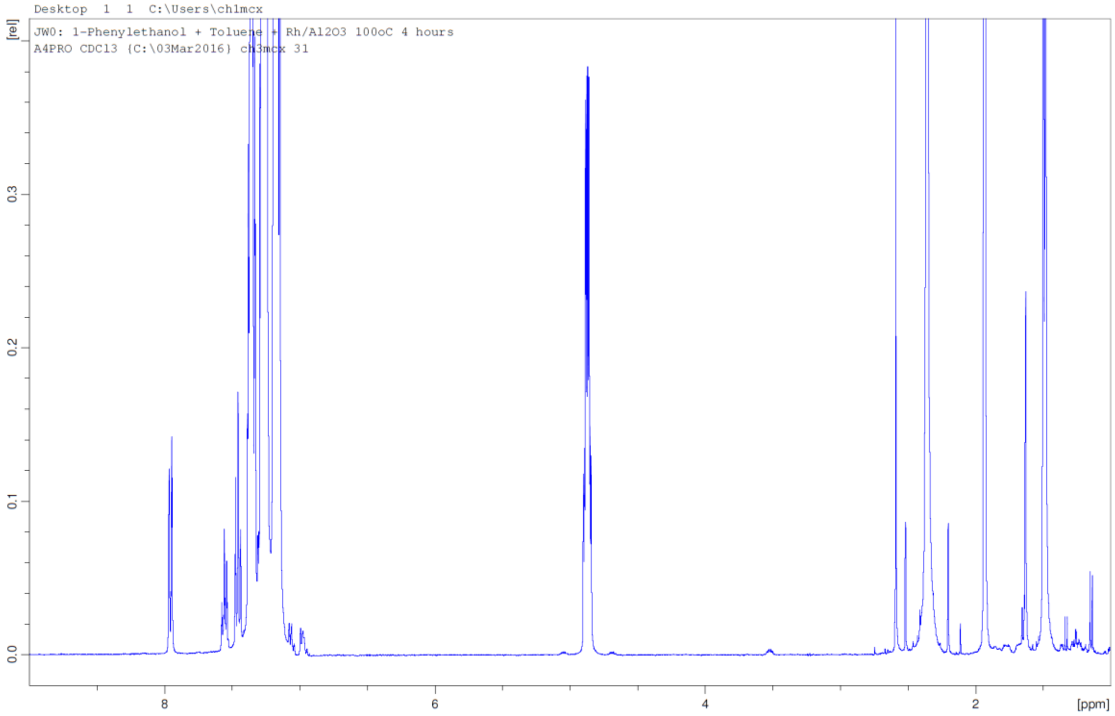


Fig. S1 Representative ^{1}H NMR for a catalytic test of 1-phenylethanol in toluene using Rh/Al_2O_3. M:S 1:100, T = 100 ^oC, P = atmospheric pressure.

^{1}H NMR ($CDCl_3$, 400 MHz), Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (s, 3H); 1-phenylethanol, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 4.87 (CH, q, 1H, J = 3.3 Hz), 1.48 (CH_3, d, 3H, J = 6.3 Hz); Acetophenone, δ: 7.94-7.98 (CH(*o*), m, 2H), 2.59 (CH_3, s, 3H); Ethylbenzene, (from GC/MS); 1-cyclohexyl ethanol, traces (from GC/MS) in the NMR above multiplet at 3.52 ppm (vide infra);

2.1.1 GC/MS characterization

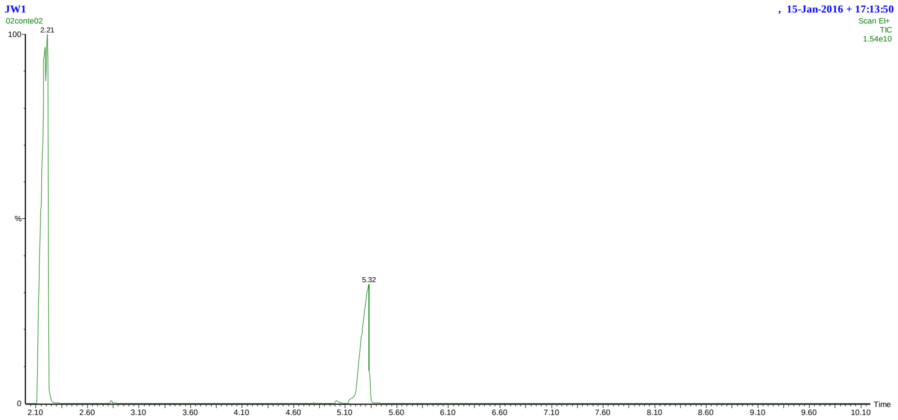


Fig. S2 Gas chromatogram for the reaction mixture of Fig. S1. Peak at 2.21 min toluene, peak at 5.32 min: 1-phenylethanol + acetophenone (shoulder).

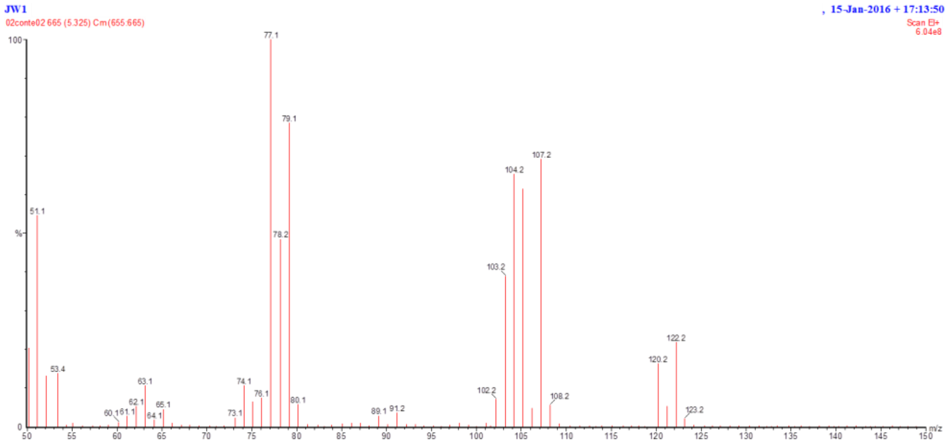


Fig. S3 Mass spectrometry for 1-phenylethanol. Mass of molecular ion 122 Da. Fragmentation pattern m/z: 122 (molecular ion), 120 (loss of 2 H) 107 (loss of methyl CH_3), 104 (loss of water); m/z 79 ($C_6H_7^+$), m/z 77 ($C_6H_5^+$), m/z 51 ($C_4H_3^+$).

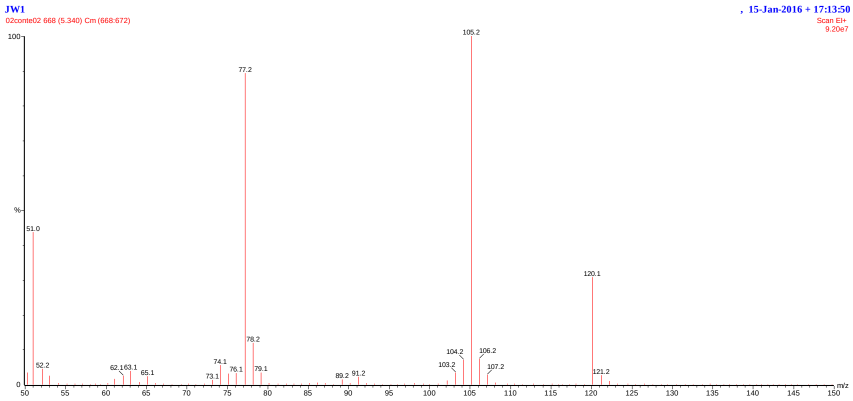
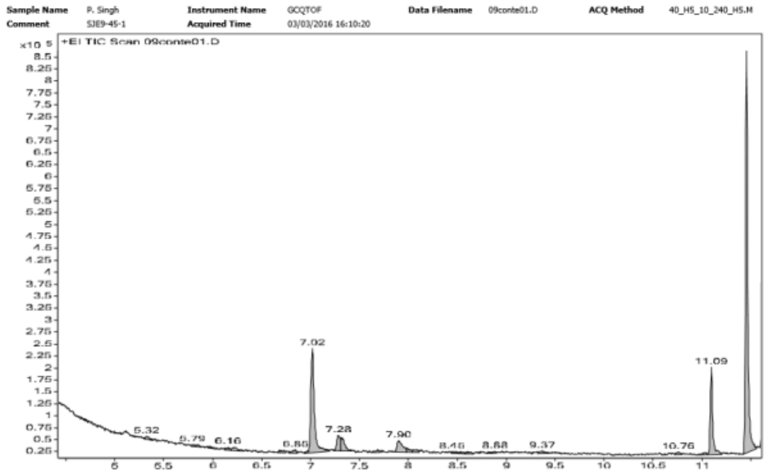


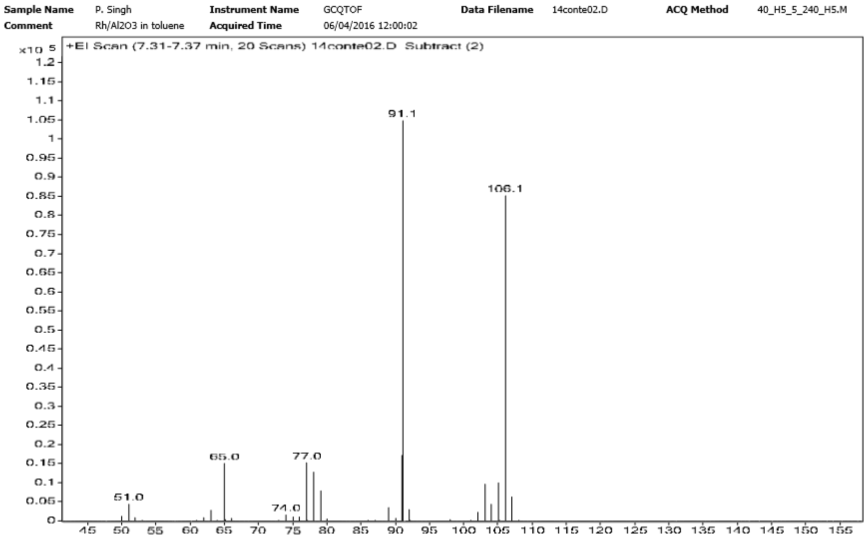
Fig. S4 Mass spectrometry for acetophenone. Mass of molecular ion 120 Da. Fragmentation pattern m/z: 120 (molecular ion), 105 (loss of methyl CH_3), 104 (loss of water); m/z 77 ($C_6H_5^+$), m/z 51 ($C_4H_3^+$).

2.2 GC/MS reaction mixture for impurities in reaction mixtures



Sample Name P. Singh Instrument Name GCQTOF Data Filename 09conte01.D ACQ Method 40_H5_10_240_H5.M
Comment SJE9-45-1 Acquired Time 03/03/2016 16:10:20

Fig. S5 Representative chromatogram's details for the determination of impurities in the reaction mixture of Rh/Al_2O_3 and 1-phenylethanol in toluene. From left to right: Peak at 7.2 min: ethylbenzene Peaks at 7.28 and 7.90; xylenes Peaks at 11.09 and 11.8 min: 1-cyclohexyl ethanol and cyclohexyl methyl ketone.



Sample Name P. Singh Instrument Name GCQTOF Data Filename 14conte02.D ACQ Method 40_H5_5_240_H5.M
Comment Rh/Al2O3 in toluene Acquired Time 06/04/2016 12:00:02

Fig. S6 Mass spectrometry for ethylbenzene, mass of molecular ion 106 Da. Fragmentation pattern m/z: 106 (molecular ion), 91 (loss of 2 H) 107 ($C_7H_7^+$, loss of methyl CH_3), m/z 77 ($C_6H_5^+$), m/z 65 ($C_5H_5^+$), m/z 51 ($C_4H_3^+$).

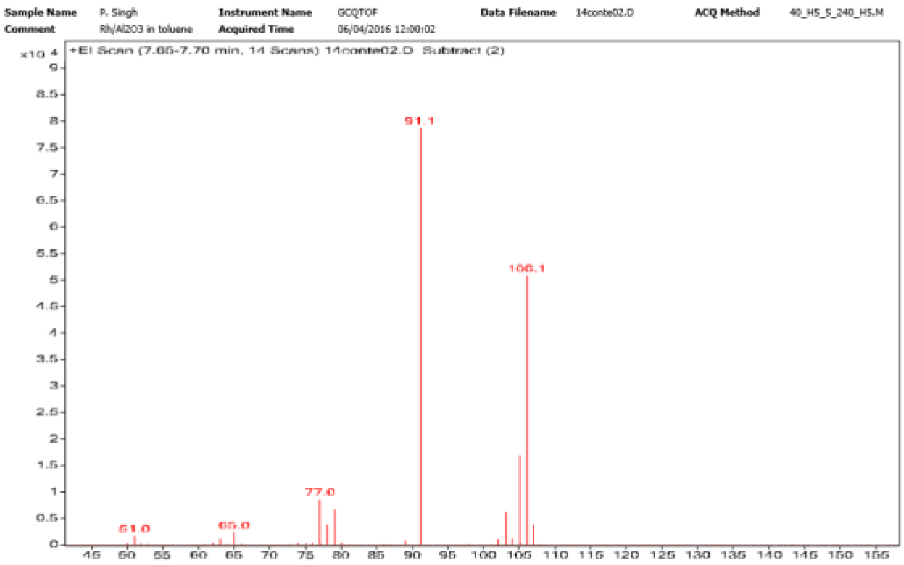


Fig. S7 Mass spectrometry for *o*-xylene, mass of molecular ion 106 Da. Fragmentation pattern: m/z 106 (molecular ion), m/z 91 (loss of 2 H) m/z 107 ($C_7H_7^+$, loss of methyl CH_3), m/z 77 ($C_6H_5^+$), m/z 65 ($C_5H_5^+$), m/z 51 ($C_4H_3^+$).

2.3 Characterization of reagent 1-phenylethanol by GC/MS and NMR

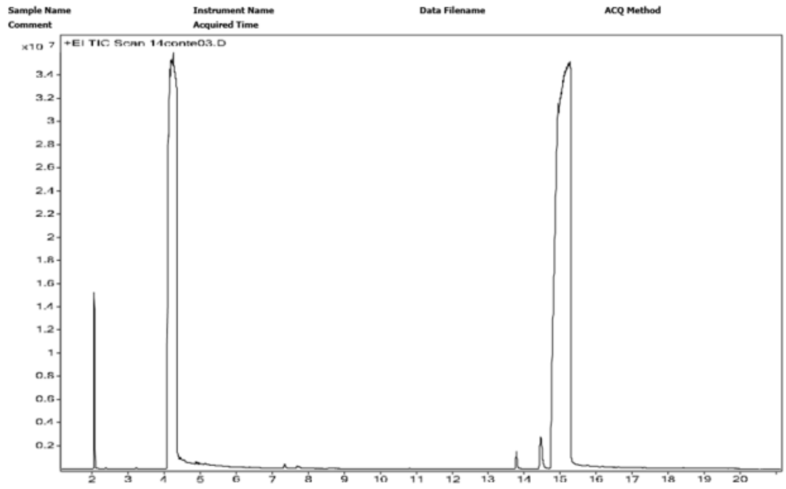


Fig. S8 Representative GC/MS (chromatogram part) of 1-phenylethanol, starting material, in toluene. With enhanced resolution of the species (chromatographic method 2).

Large peak at 4 min: toluene, trace Peak at 7.2 min: ethylbenzene; peaks at 7.28 and 7.90 min xylenes; peak at 13.8 min 1-cyclohexyl ethanol; peak at 14.4 min cyclohexyl methyl ketone. Large peak at 15 min 1-phenylethanol + acetophenone. (peak at 2 min $CHCl_3$ from GC/MS injection procedure).

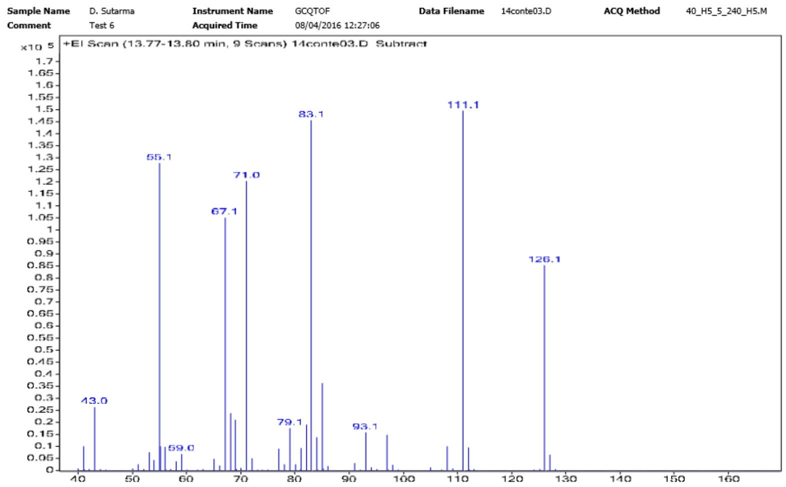


Fig. S9 Mass spectrometry for cyclohexyl methyl ketone. Mass of molecular ion 126 Da. Fragmentation pattern: m/z 128 (molecular ion), m/z 126 (loss of 2 H), m/z 111 (loss of methyl CH_3), m/z 83 (loss of CH_3CO), m/z 71 ($C_5H_{11}^+$ or $C_3H_7CO^+$), m/z 67 ($C_5H_7^+$), m/z 55 ($C_4H_7^+$) m/z 43 ($C_4H_7^+$ or CH_3CO^+).

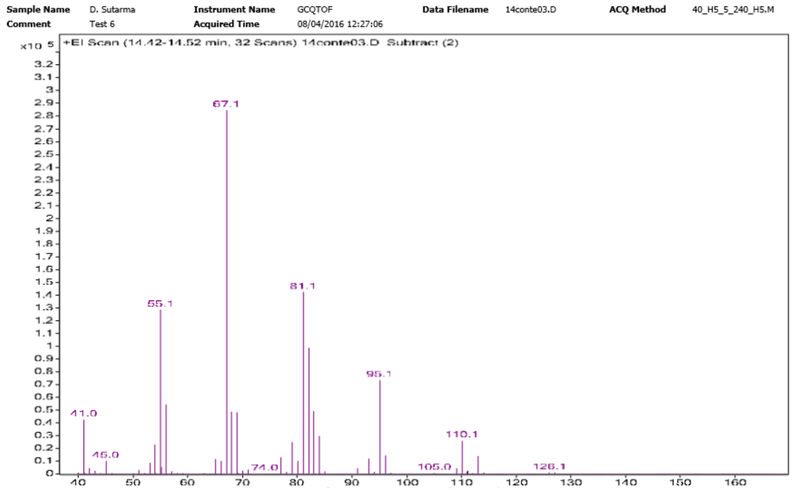


Fig. S10 Mass spectrometry for 1-cyclohexyl ethanol. Mass of molecular ion 128 Da. Fragmentation pattern: m/z 128 (molecular ion), m/z 126 (loss of 2 H), m/z 110 (loss of H_2O from molecular ion), m/z 95 ($C_6H_7O^+$), m/z 81 (loss of CH_2), m/z 67 ($C_5H_7^+$), m/z 55 ($C_4H_7^+$) m/z 43 ($C_4H_7^+$ or CH_3CO^+).

This fragmentation pattern is in principle consisted with 1-cyclohexyl ethanol but also witht 2-cyclohexyl ethanol. In fact, both these species are able to generate diagnostic m/z peaks at 110 and 95. In order to discrimiante between these two compounds determiantion of the coupling constants and multiplicity from NMR was carried out.

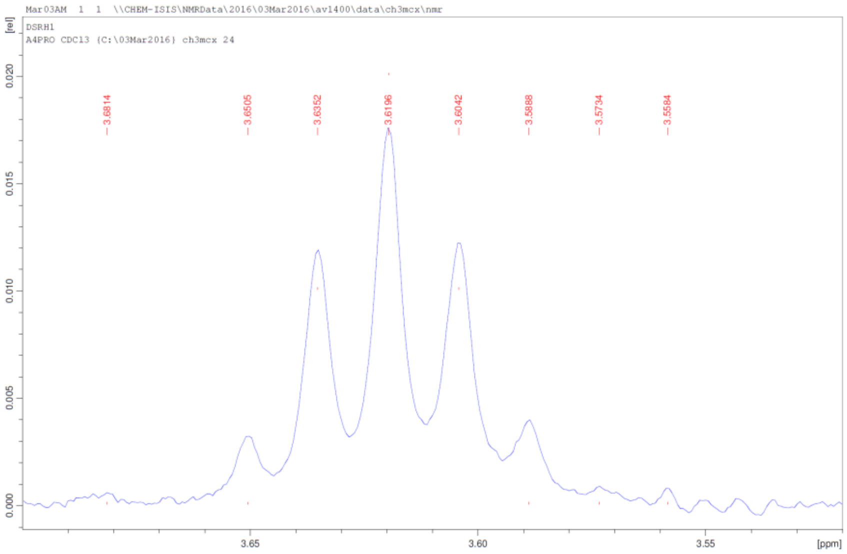


Fig. S11 Apparent quintet for the CH group, with H in alpha to the OH, for 1-cyclohexyl ethanol.

This looks as an apparent quintet/pentet. This signal is generated by the C-H group in beta to the OH and it generates a quarted of doublets with expeced coumpling consntats of 6.1 ad 4.4 Hz. In our case a coupling constant of 6.1 Hz. 2-cyclohexyl ethanol would give a triplet instead.

3. Representative NMR and GC/MS for 1-phenyl ethanol oxidation in water/toluene mixtures

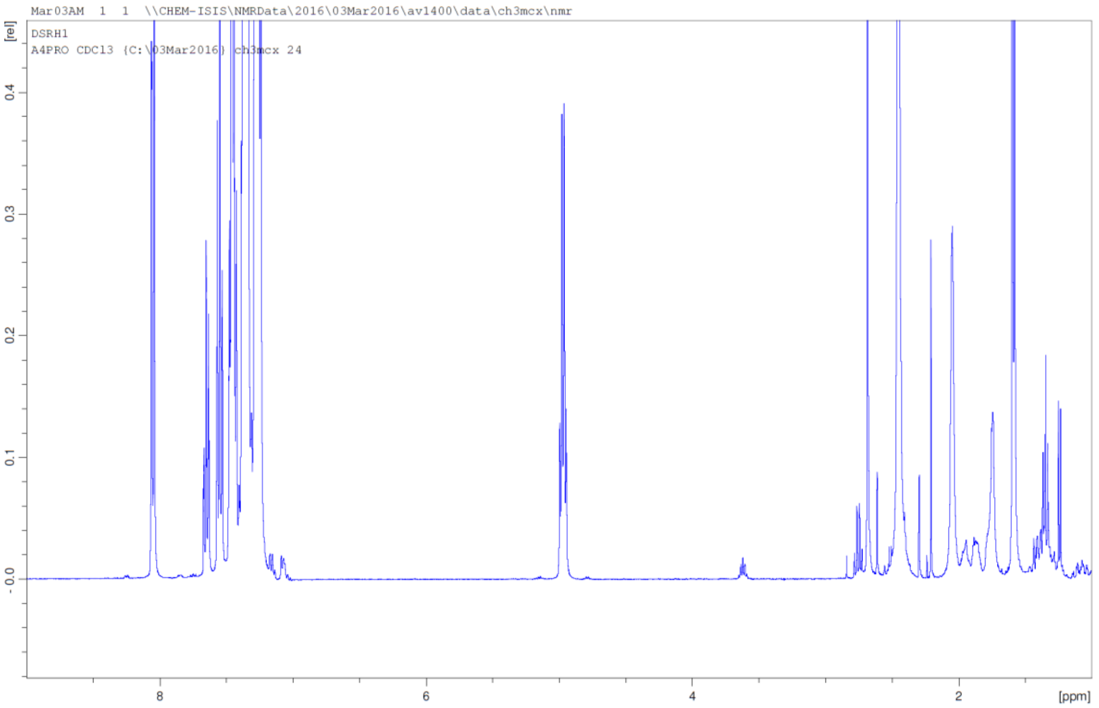


Fig. S12 Representative ^{1}H NMR for the oxidation of 1-phenylethanol using Rh/Al_2O_3 in water/toluene, volume ratio 2:1, M:S = 1:100, T = 100 ^{o}C, P = atmospheric pressure.

Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); 1-phenylethanol, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 4.87 (CH, q, 1H, J = 3.3 Hz), 1.48 (CH_3, d, 3H, J = 6.3 Hz); Acetophenone, δ: 7.94-7.98 (CH(*o*), m, 2H), 2.59 (CH_3, s, 3H); Ethylbenzene, 7-7.7 (C_6H_5, m, 5H), 2.66 (CH_2, q, 2H, J = 7.8 Hz), 1.25 (CH3, t, 3H, J = 7.6 Hz); 1-cyclohexyl ethanol, δ (ppm): 3.53 (CH, q/p, 1H, J = 6.2 Hz), 1.1-1.8 (C_6H_{11}, m, 11H), 1.15 (CH_3, d, J = 6.4 Hz); cyclohexyl methyl ketone δ (ppm): 2.11 (CH_3, s, 3H), 1.3-2 (C_6H_{11}, m, 11H).

Fig. S13 Representative GC/MS (chromatogram part) for the oxidation of 1-phenylethanol using Rh/Al_2O_3 in water/toluene, volume ratio 2:1, M:S = 1:100, T = 100 ^oC, P = atmospheric pressure of air.

Large peak at 4 min: toluene, trace Peak at 7.2 min: ethylbenzene; peaks at 7.28 and 7.90 min xylenes; peak at 13.8 min 1-cyclohexyl ethanol; peak at 14.4 min cyclohexyl methyl ketone. Large peak at 15 min 1-phenylethanol + acetophenone. (peak at 2 min $CHCl_3$ from GC/MS injection procedure).

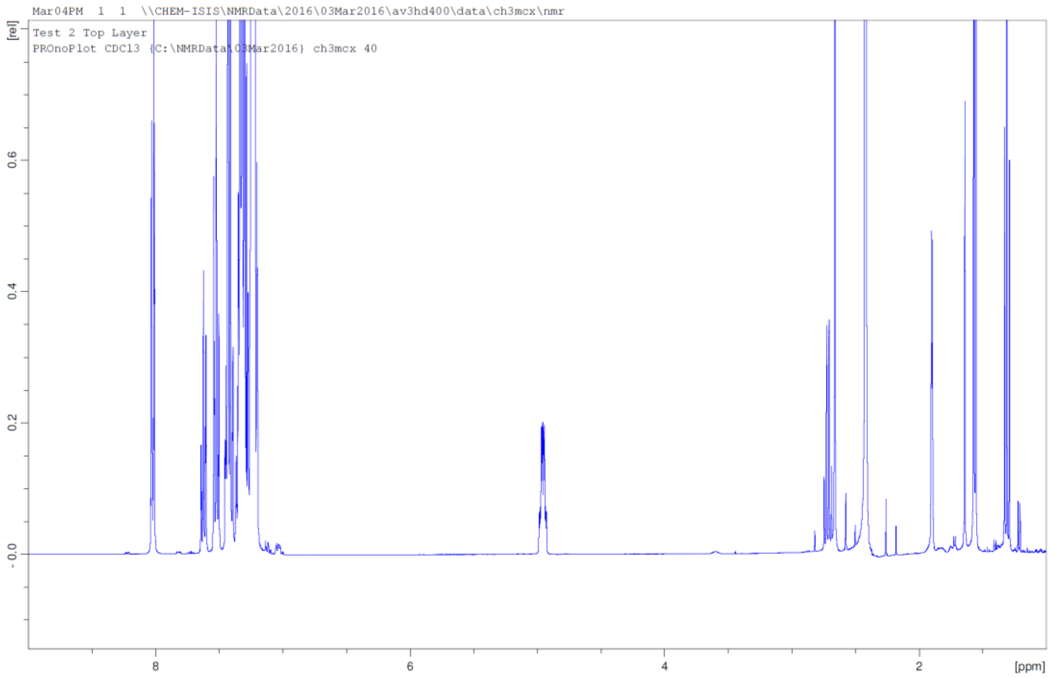


Fig. S14 Representative ^1H NMR for the oxidation of 1-phenylethanol using Rh-PI/CB in water/toluene, volume ratio 2:1, M:S = 1:100, T = 100 °C, P = atmospheric pressure.

Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); 1-phenylethanol, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 4.87 (CH, q, 1H, J = 3.3 Hz), 1.48 (CH_3, d, 3H, J = 6.3 Hz); Acetophenone, δ: 7.94-7.98 (CH(*o*), m, 2H), 2.59 (CH_3, s, 3H); Ethylbenzene, 7-7.7 (C_6H_5, m, 5H), 2.66 (CH_2, q, 2H, J = 7.8 Hz), 1.25 (CH3, t, 3H, J = 7.6 Hz); 1-cyclohexyl ethanol, δ (ppm): 3.53 (CH, q/p, 1H, J = 6.2 Hz), 1.1-1.8 (C_6H_{11}, m, 11H), 1.15 (CH_3, d, J = 6.4 Hz); cyclohexyl methyl ketone δ (ppm): 2.11 (CH_3, s, 3H), 1.3-2 (C_6H_{11}, m, 11H).

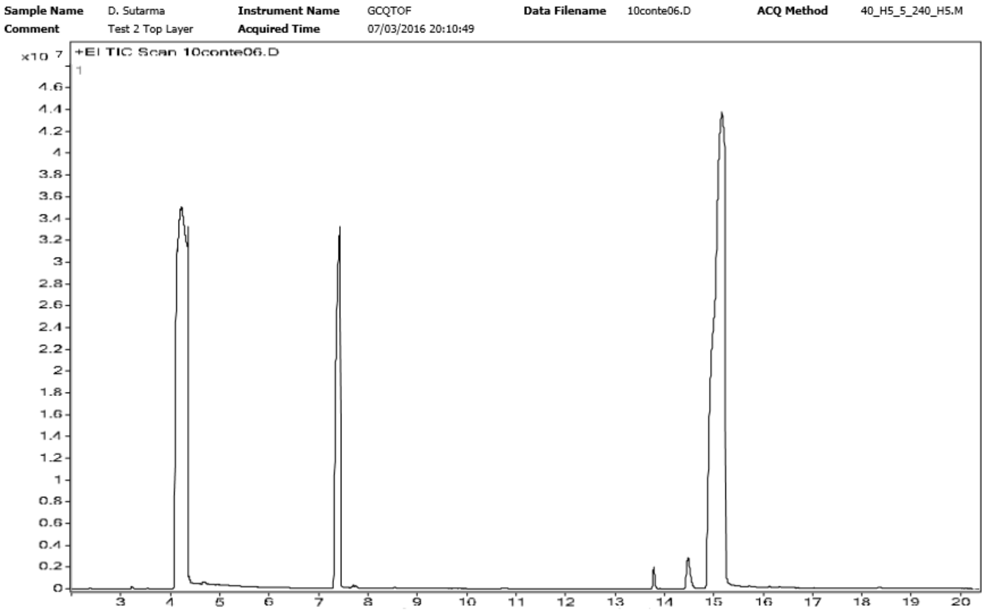


Fig. S15 Representative GC/MS (chromatogram part) for the oxidation of 1-phenylethanol using Rh-PI/CB in water/toluene, volume ratio 2:1, M:S = 1:100, T = 100 °C, P = atmospheric pressure of air.

Large peak at 4 min: toluene, trace Peak at 7.2 min: ethylbenzene; peaks at 7.28 and 7.90 min xylenes; peak at 13.8 min 1-cyclohexyl ethanol; peak at 14.4 min cyclohexyl methyl ketone.

Large peak at 15 min 1-phenylethanol + acetophenone. (peak at 2 min $CHCl_3$ from GC/MS injection procedure)

4. Quantification of oxidation and disproportionation pathways for the oxidation of 1-phenyl ethanol in water/toluene mixtures

The total amount of acetophenone (here denoted in moles as $n_{K,tot}$) is the consequence of two contributions: the direct oxidation route and the disproportionation route, and here denoted as $n_{K,ox}$ and $n_{K,dis}$ respectively. It is possible to calculate the contribution to the formation of the ketone by these two reactions considering that $n_{K,tot} = n_{K,ox} + n_{K,dis}$ and $n_{K,dis} = n_{EB}$ (where n stands for moles, the indices K, and EB stand for: ketone and ethylbenzene, and the indices: *tot*, *ox*, and *dis* stand for: total, oxidation and disproportionation respectively). Using this notation, the molar fraction of ketone x_K, from disproportionation is: $x_{K,dis} = n_{EB}/n_{K,tot}$ and the molar fraction of ketone from direct oxidation is: $x_{K,ox} = 1 - x_{K,dis}$. This data treatment also makes it possible to extract the yield of the ketone from direct oxidation only, $Y_{K,ox}$.

Table S1 Fractions x of ketone K (acetophenone) obtained from direct oxidation route $x_{K,ox}$, and disproportionation $x_{K,dis}$. Total yield of ketone (in %), $Y_{K,tot} = C \cdot S_K$ is the product of the conversion C and the selectivity S_K with their values as reported in table 3 (reaction in presence of toluene and water). The last column, $Y_{K,ox}$, represents the yield of ketone (in %) from the direct oxidation pathway only.

Catalyst	$x_{K,ox}$	$x_{K,dis}$	$Y_{K,tot}$ **(%)**	$Y_{K,ox}$ **(%)**
Rh-PI	0.70	0.30	37	26
Rh-PI/CB	0.49	0.51	36	18
Rh-PI/Al_2O_3	0.84	0.16	19	16
Rh/Al_2O_3	0.85	0.15	31	26

5. Determiantion of partion constants

Standards for the determiantion of the partion constants of 1-phenylethanol and acetophenone in toluene and water were determined by preparing solution containign different toluene/water ratios. *n*-octane was used as internal standard and the amount of each species determined via ^{1}H-NMR.

Table S2 Detemination of $K_{org,aq}$ for acetophenone and 1-phenylethanol in water toluene.

#	$V_{Toluene}$ (mL)	V_{water} (mL)	V_{org} after partion	V_{aq} after partion	$n_{\text{acetophenone, org}}$	$n_{\text{acetophenone, aq}}$	$n_{\text{1phenylethanol, org}}$	$n_{\text{1-phenylethanol, aq}}$	$K_{org,aq}$ acetophenone	$K_{org,aq}$ 1-phenylethanol
1	1	0	0	0	1.68 10^{-2}	-	1.59$10^{-2}$	-		-
2	1	1	0.9	1.1	1.68 10^{-2}	-	1.54$10^{-2}$	5.00$10^{-4}$	-	38
3	1	2	0.9	2.1	1.68 10^{-2}	-	1.51$10^{-2}$	8.00$10^{-4}$	-	44
4	1	4	0.7	4.3	1.68 10^{-2}	-	1.37$10^{-2}$	2.20$10^{-3}$	-	38
5	1	6	0.6	6.4	1.64 10^{-2}	4.00 10^{-4}	1.27$10^{-2}$	3.20$10^{-3}$	437	42
6	1	8	0.5	8.5	1.62 10^{-2}	6.00 10^{-4}	1.17$10^{-2}$	4.20$10^{-3}$	459	47
7	1	10	0.4	10.6	1.60 10^{-2}	8.00 10^{-4}	1.04$10^{-2}$	5.50$10^{-3}$	530	50

Average $K_{org,aq}$ for acetophenone: 475 ± 48

Average $K_{org,aq}$ for 1-phenylethanol: 43 ± 5

Table S3 Corrected conversion values for the reactions in water toluene by considering the partion effect of 1-pehnylethanl in a toluene/water mixture 1:2 volume ratio.

Catalyst	Conversion corrected by partition	Conversion without partition effect
Rh-PI	48	49
Rh-PI/CB	57	58
Rh-PI/Al_2O_3	22	23
Rh/Al_2O_3	38	39

Corrected conversion values by considering the partion constants of 1-phenyl ethanol and acetophenone using a 1:2 volume toluene/water mixture. The diffrence between the two sets is negligible and within the experiemtanl error of the ^{1}H NMR determination.

6. Reaction mixture: extraction of the aqueous phase in 1-phenyl ethanol oxidation

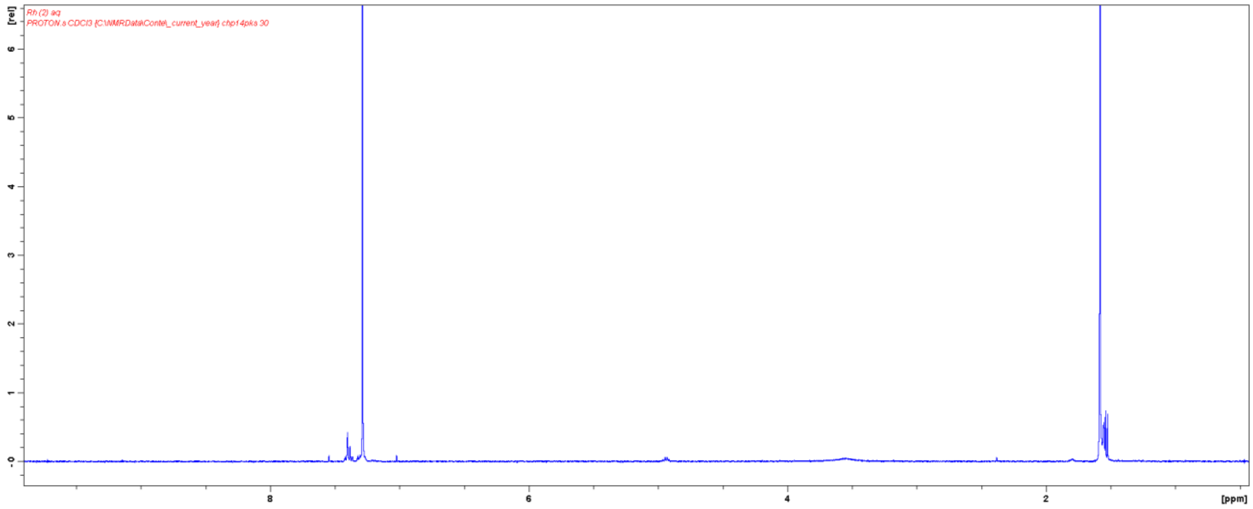


Fig. S16 Representative ^{1}H NMR for the aqueous phase, extracted with chloroform, for the oxidation of 1-phenylethanol using Rh/PI in water/toluene (2:1 volume ratio), M:S = 1:100, T = 100 ^{o}C, P = atmospheric pressure. 1-phenylethanol, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 4.87 (CH, q, 1H, J = 3.3 Hz), 1.48 (CH_3, d, 3H, J = 6.3 Hz); Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); $CHCl_3$: δ: 7.26 (s, 1H); H_2O: δ: 1.59 (s, 2H);

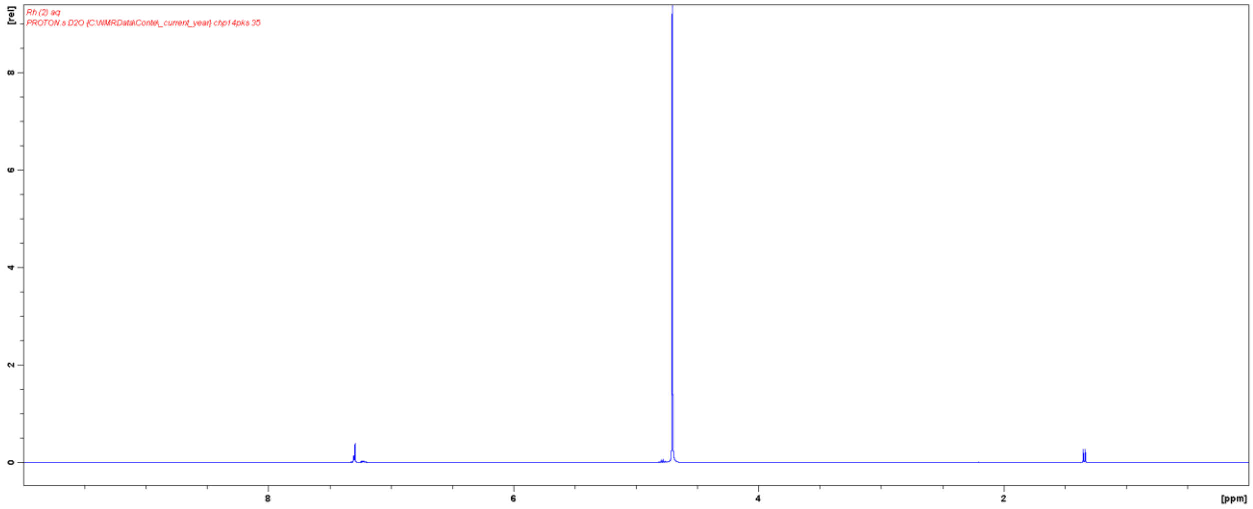


Fig. S17 Representative ^{1}H NMR for the aqueous phase, analysed in D_2O, for the oxidation of 1-phenylethanol using Rh/PI in water/toluene (2:1 volume ratio), M:S = 1:100, T = 100 ^{o}C, P = atmospheric pressure. 1-phenylethanol, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 4.87 (CH, q, 1H, J = 3.3 Hz), 1.48 (CH_3, d, 3H, J = 6.3 Hz); H_2O: δ: 4.79 (s, 2H).

7. Re-usability tests for 1-phenyl ethanol oxidation

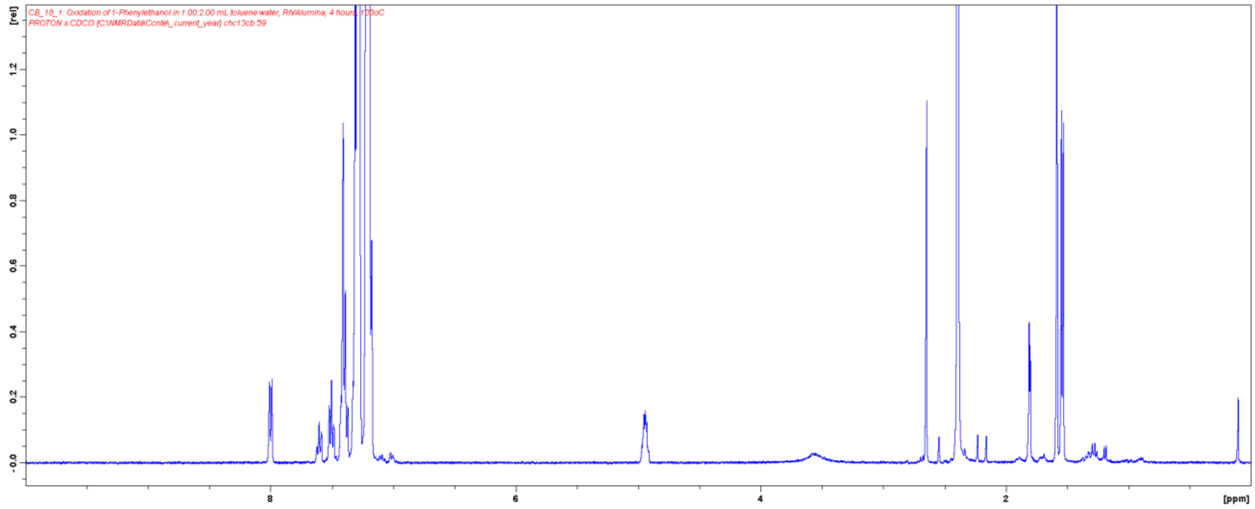


Fig. S18 Representative ^{1}H NMR for the oxidation of 1-phenylethanol for a re-used catalyst using Rh/Al_2O_3 in water/toluene, volume ratio 2:1, M:S = 1:100, T = 100 ^{o}C, P = atmospheric pressure. Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); 1-phenylethanol, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 4.87 (CH, q, 1H, J = 3.3 Hz), 1.48 (CH_3, d, 3H, J = 6.3 Hz); Acetophenone, δ: 7.94-7.98 (CH(*o*), m, 2H), 2.59 (CH_3, s, 3H); Ethylbenzene, 7-7.7 (C_6H_5, m, 5H), 2.66 (CH_2, q, 2H, J = 7.8 Hz), 1.25 (CH3, t, 3H, J = 7.6 Hz); 1-cyclohexyl ethanol, δ (ppm): 3.53 (CH, q/p, 1H, J = 6.2 Hz), 1.1-1.8 (C_6H_{11}, m, 11H), 1.15 (CH_3, d, J = 6.4 Hz).

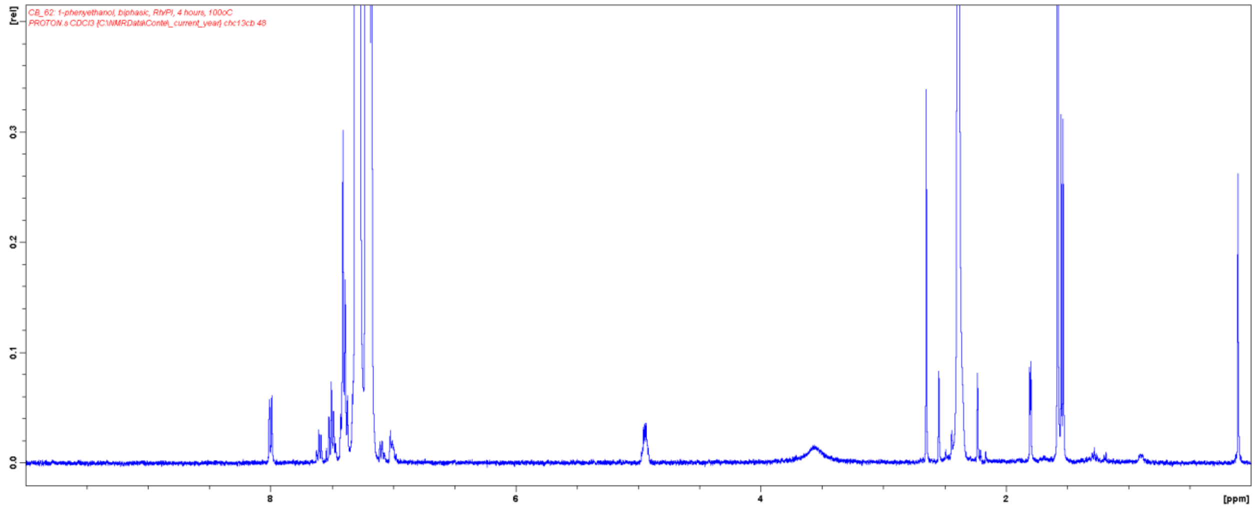
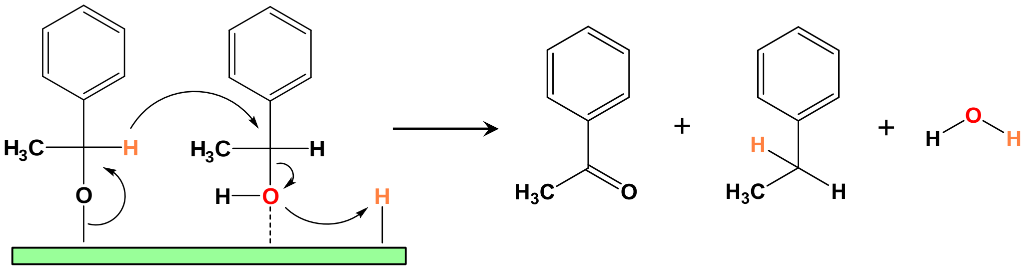


Fig S19 Representative ^{1}H NMR for the oxidation of 1-phenylethanol for a re-used catalyst using Rh/PI in water/toluene, volume ratio 2:1, M:S = 1:100, T = 100 ^{o}C, P = atmospheric pressure. Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); 1-phenylethanol, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 4.87 (CH, q, 1H, J = 3.3 Hz), 1.48 (CH_3, d, 3H, J = 6.3 Hz); Acetophenone, δ: 7.94-7.98 (CH(*o*), m, 2H), 2.59 (CH_3, s, 3H); Ethylbenzene, 7-7.7 (C_6H_5, m, 5H), 2.66 (CH_2, q, 2H, J = 7.8 Hz), 1.25 (CH3, t, 3H, J = 7.6 Hz); 1-cyclohexyl ethanol, δ (ppm): 3.53 (CH, q/p, 1H, J = 6.2 Hz), 1.1-1.8 (C_6H_{11}, m, 11H), 1.15 (CH_3, d, J = 6.4 Hz).

8. Alcohol disproportionation route to acetophenone and ethylbenzene formation



Scheme S2 One of the accepted reaction mechanisms for the disproportionation reaction of an alcohol to a ketone and an alkane. A pre-adsorption of an alcohol molecule is needed to allow hydride transfer over the catalyst surface. A concerted mechanism would then occur, with formation of a ketone, and subsequent further hydride transfer with formation of an alkane and elimination of a water molecule.[S4]

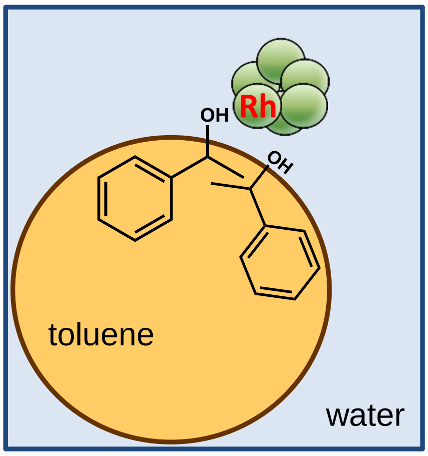


Fig. S20 Possible enhancement of a disproportionation route in agreement with scheme S2. In this case the toluene droplet would promote the formation of a pre-oriented pair of alcohols that could favour the disproportionation pathway and the formation of ethylbenzene (and a ketone) above the catalyst surface.

9. 1-phenylethanol oxidation: control tests in the presence of H_2O, no solvent and D_2O/toluene

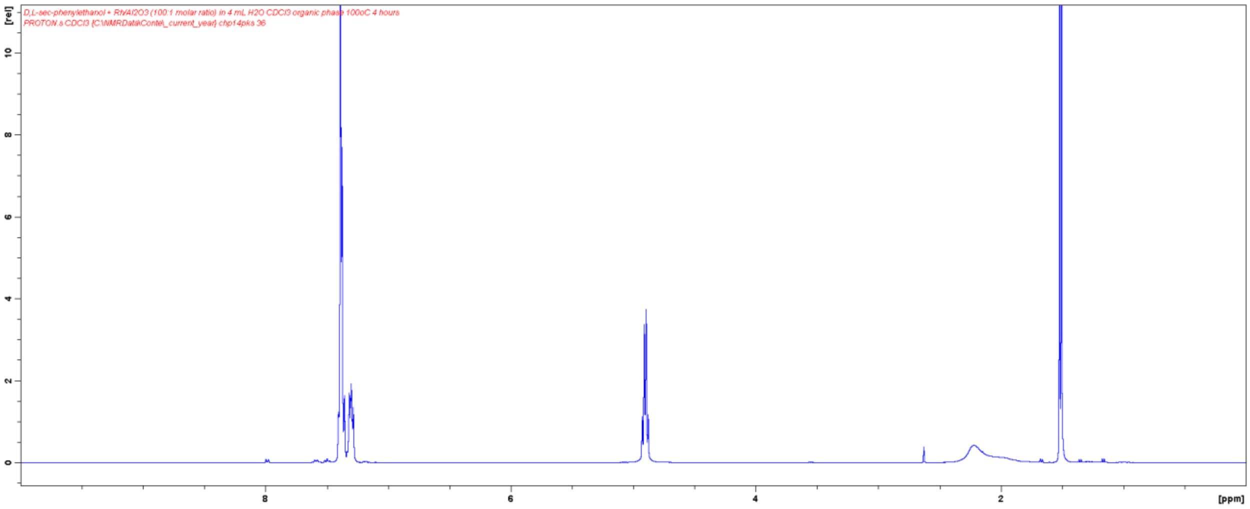


Fig. S21 Representative ^1H NMR for the oxidation of 1-phenylethanol using Rh/Al_2O_3 in water (4mL), M:S = 1:100, T = 100 ^oC, P = atmospheric pressure. Analysis of the organic layer in $CDCl_3$.
1-phenylethanol, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 4.87 (CH, q, 1H, J = 3.3 Hz), 1.48 (CH_3, d, 3H, J = 6.3 Hz); Acetophenone, δ: 7.94-7.98 (CH(*o*), m, 2H), 2.59 (CH_3, s, 3H); Ethylbenzene, 7-7.7 (C_6H_5, m, 5H), 2.66 (CH_2, q, 2H, J = 7.8 Hz), 1.25 (CH3, t, 3H, J = 7.6 Hz); $CHCl_3$: δ: 7.26 (s, 1H); H_2O: δ: 1.59 (s, 2H); broad peak at 2.2 HOD.

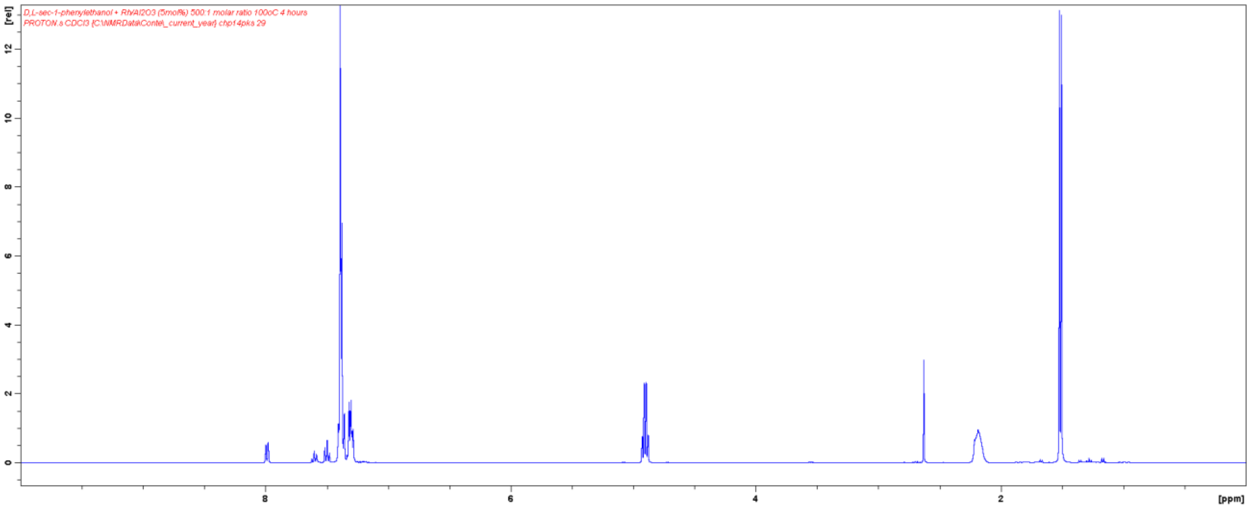


Fig. S22 Representative ^1H NMR for the oxidation of 1-phenylethanol using Rh/Al_2O_3 and no solvent, M:S = 1:500, T = 100 ^oC, P = atmospheric pressure.
1-phenylethanol, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 4.87 (CH, q, 1H, J = 3.3 Hz), 1.48 (CH_3, d, 3H, J = 6.3 Hz); Acetophenone, δ: 7.94-7.98 (CH(*o*), m, 2H), 2.59 (CH_3, s, 3H); Ethylbenzene, 7-7.7 (C_6H_5, m, 5H), 2.66 (CH_2, q, 2H, J = 7.8 Hz), 1.25 (CH3, t, 3H, J = 7.6 Hz); $CHCl_3$: δ: 7.26 (s, 1H); broad peak at 2.2 HOD.

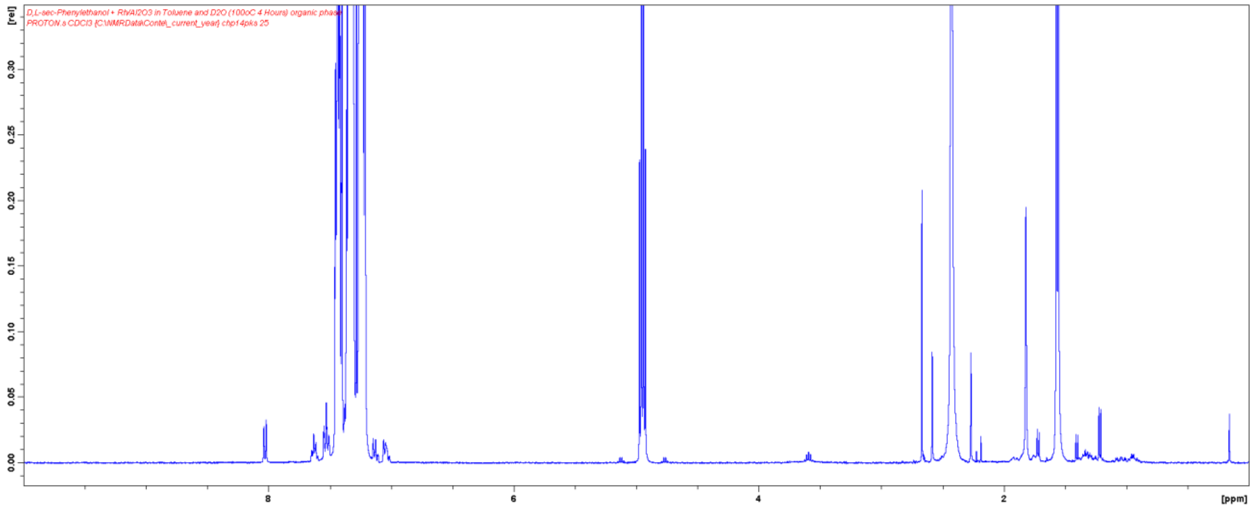


Fig. S23 Representative ^{1}H NMR for the oxidation of 1-phenylethanol using Rh/Al_2O_3 in D_2O/toluene, volume ratio 2:1, M:S = 1:100, T = 100 ^{o}C, P = atmospheric pressure.

Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); 1-phenylethanol, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 4.87 (CH, q, 1H, J = 3.3 Hz), 1.48 (CH_3, d, 3H, J = 6.3 Hz); Acetophenone, δ: 7.94-7.98 (CH(*o*), m, 2H), 2.59 (CH_3, s, 3H); Ethylbenzene, 7-7.7 (C_6H_5, m, 5H), 2.66 (CH_2, q, 2H, J = 7.8 Hz), 1.25 (CH3, t, 3H, J = 7.6 Hz); 1-cyclohexyl ethanol, δ (ppm): 3.53 (CH, q/p, 1H, J = 6.2 Hz), 1.1-1.8 (C_6H_{11}, m, 11H), 1.15 (CH_3, d, J = 6.4 Hz); H_2O (2H, s) 1.59.

10. Representative NMR and GC/MS for 1-phenyl ethanol oxidation in water/toluene mixtures in presence of base

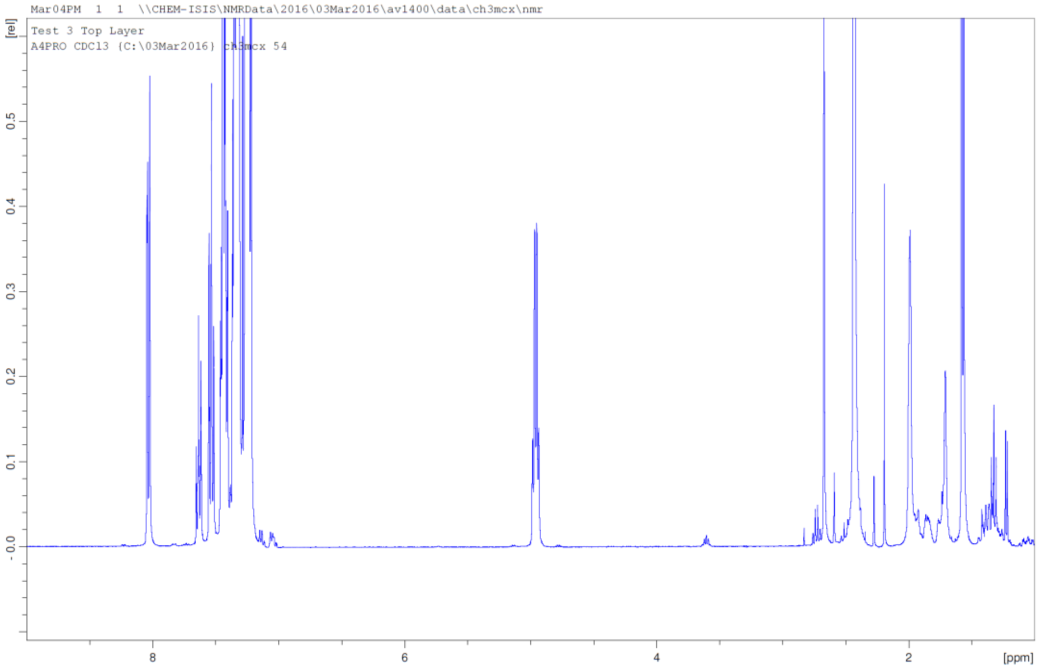


Fig. S24 Representative ^1H NMR for the oxidation of 1-phenylethanol using Rh/Al_2O_3 in water/toluene, volume ratio 2:1, M:S = 1:100, T = 100 ^oC, P = atmospheric pressure and in the presence of base, NaOH (base to alcohol molar ratio 1:10).

Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); 1-phenylethanol, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 4.87 (CH, q, 1H, J = 3.3 Hz), 1.48 (CH_3, d, 3H, J = 6.3 Hz); Acetophenone, δ: 7.94-7.98 (CH(*o*), m, 2H), 2.59 (CH_3, s, 3H); Ethylbenzene, 7-7.7 (C_6H_5, m, 5H), 2.66 (CH_2, q, 2H, J = 7.8 Hz), 1.25 (CH3, t, 3H, J = 7.6 Hz); 1-cyclohexyl ethanol, δ (ppm): 3.53 (CH, q/p, 1H, J = 6.2 Hz), 1.1-1.8 (C_6H_{11}, m, 11H), 1.15 (CH_3, d, J = 6.4 Hz); cyclohexyl methyl ketone δ (ppm): 2.11 (CH_3, s, 3H), 1.3-2 (C_6H_{11}, m, 11H).

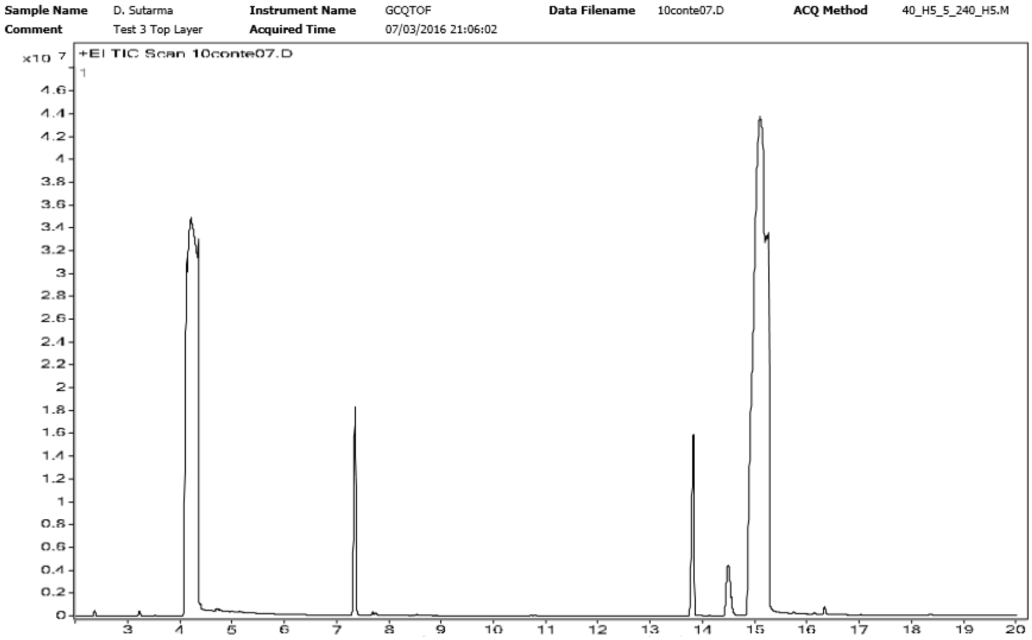


Fig. S25 Representative GC/MS (chromatogram part) for the oxidation of 1-phenylethanol using Rh/Al_2O_3 in water/toluene, volume ratio 2:1, M:S = 1:100, T = 100 ^oC, P = atmospheric pressure and in the presence of base, NaOH (base to alcohol molar ratio 1:10).
Large peak at 4 min: toluene, trace Peak at 7.2 min: ethylbenzene; peaks at 7.28 and 7.90 min xylenes; peak at 13.8 min 1-cyclohexyl ethanol; peak at 14.4 min cyclohexyl methyl ketone. Large peak at 15 min 1-phenylethanol + acetophenone. (peak at 2 min $CHCl_3$ from GC/MS injection procedure)

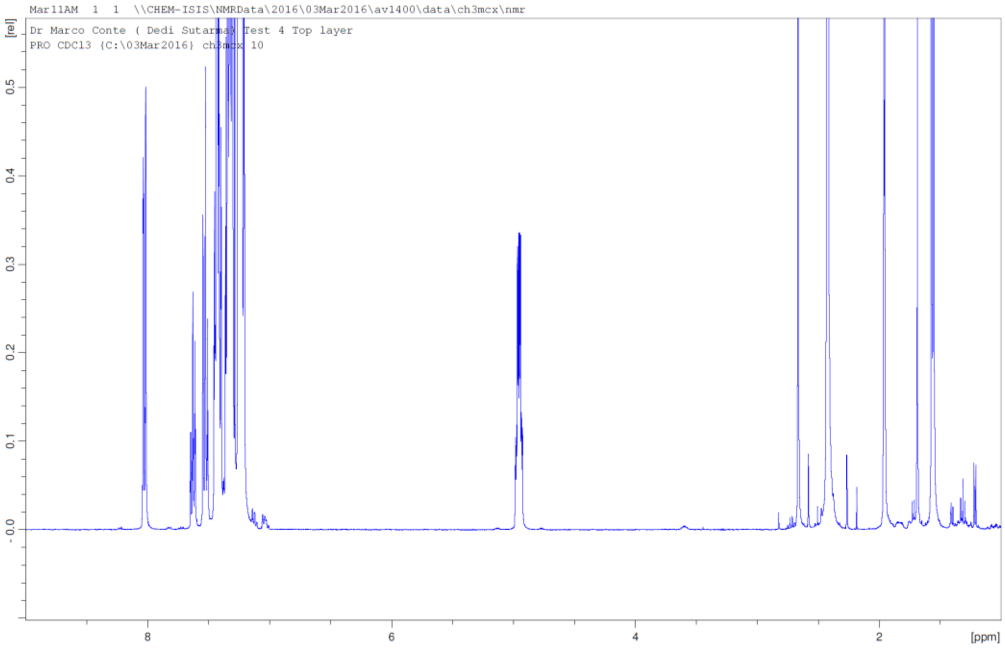
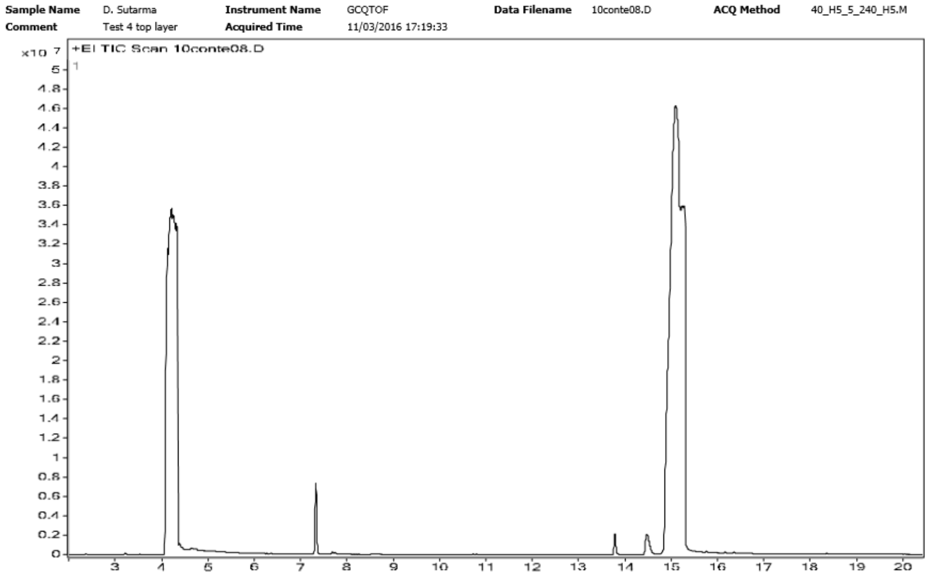


Fig. S26 Representative ^1H NMR for the oxidation of 1-phenylethanol using Rh-PI/CB in water/toluene, volume ratio 2:1, M:S = 1:100, T = 100 ^oC, P = atmospheric pressure and in the presence of base, NaOH (base to alcohol molar ratio 1:10).
Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); 1-phenylethanol, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 4.87 (CH, q, 1H, J = 3.3 Hz), 1.48 (CH_3, d, 3H, J = 6.3 Hz); Acetophenone, δ: 7.94-7.98 (CH(*o*), m, 2H), 2.59 (CH_3, s, 3H); Ethylbenzene, 7-7.7 (C_6H_5, m, 5H), 2.66 (CH_2, q, 2H, J = 7.8 Hz), 1.25 (CH3, t, 3H, J = 7.6 Hz); 1-cyclohexyl ethanol, δ (ppm): 3.53 (CH, q/p, 1H, J = 6.2 Hz),

1.1-1.8 (C_6H_{11}, m, 11H), 1.15 (CH_3, d, J = 6.4 Hz); cyclohexyl methyl ketone δ (ppm): 2.11 (CH_3, s, 3H), 1.3-2 (C_6H_{11}, m, 11H).



Sample Name D. Sutarma **Instrument Name** GCQTOF **Data Filename** 10conte08.D **ACQ Method** 40_H5_5_240_H5.M
Comment Test 4 top layer **Acquired Time** 11/03/2016 17:19:33

Fig. S27 Representative GC/MS (chromatogram part) for the oxidation of 1-phenylethanol using Rh-PI/CB in water/toluene, volume ratio 2:1, M:S = 1:100, T = 100 ^oC, P = atmospheric pressure of air, and in the presence of base, NaOH (base to alcohol molar ratio 1:10).

Large peak at 4 min: toluene, trace Peak at 7.2 min: ethylbenzene; peaks at 7.28 and 7.90 min xylenes; peak at 13.8 min 1-cyclohexyl ethanol; peak at 14.4 min cyclohexyl methyl ketone. Largepeak at 15 min 1-phenylethanol + acetophenone. (peak at 2 min $CHCl_3$ from GC/MS injection procedure).

8. Quantification of oxidation and disproportionation pathways for the oxidation of 1-phenyl ethanol in water/toluene mixtures in the presence of base, NaOH

By using the same approach described in section 4 it was possible to split the contribution for oxidation and disproportionation for the acetophenone and ethylbenzene, and their yields.

Table S4 Fractions x of ketone K (acetophenone) obtained from direct oxidation route $x_{K,ox}$, and disproportionation $x_{K,dis}$. (reaction in presence of toluene, water and NaOH). Total yield of ketone, $Y_{K,tot}$ from conversion C and selectivity S_K reported in table 5 (reaction in presence of toluene, water and base). The last column $Y_{K,ox}$, represents the yield of ketone (in %) from the direct oxidation pathway only $Y_{K,ox}$.

Catalyst	$x_{K,ox}$	$x_{K,dis}$	$Y_{K,tot}$ **(%)**	$Y_{K,ox}$ **(%)**
Rh-PI	1.00	0.0	43	43
Rh-PI/CB	0.96	0.04	28	27
Rh-PI/Al_2O_3	1.00	0.0	7	7
Rh/Al_2O_3	0.88	0.12	29	26

9. Selectivity temporal profiles in the oxidation of: 1-phenyl ethanol in water and water/toluene mixtures by Rh/Al_2O_3 and Rh-PI catalysts

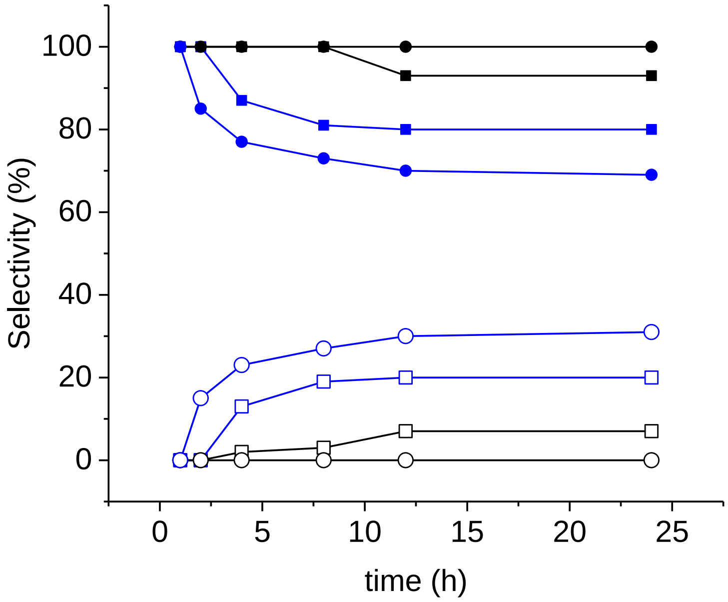


Fig. S28 Temporal profiles for the selectivity to acetophenone (filled symbols) and ethylbenzene (open symbols) in the oxidation of 1-phenyl ethanol, in toluene (black symbols) and water/toluene volume ratio 2:1, (blue symbols). Reaction conditions: T = 100 ^oC, P = atmospheric pressure of air, from 0 to 24h. (•) acetophenone from Rh-PI in toluene, (■) acetophenone from Rh/Al_2O_3 in toluene, (•) acetophenone from Rh-PI in water/toluene, (■) acetophenone from Rh/Al_2O_3 in toluene. (○) ethylbenzene from Rh-PI in toluene, (□) ethylbenzene from Rh/Al_2O_3 in toluene, (○) ethylbenzene from Rh-PI in water/toluene, (□) ethylbenzene from Rh/Al_2O_3 in water/toluene.

13. XPS surface composition for Rh-PI/Al_2O_3 and Rh/Al_2O_3

Table S5 Surface composition (At.%) for the Rh-PI/Al_2O_3 and Rh/Al_2O_3 catalysts as determined by XPS. Last column, total bulk content of Rh in wt% as determined by ICP.

Catalyst	**At%**				**wt%**
	C	O	Al	Rh	Rh $_{\text{total loading}}$
Rh-PI/Al_2O_3	23.1	42.1	32.6	2.2	0.6
Rh/Al_2O_3	23.5	41.8	30.8	3.9	5

14. One-Way ANOVA for the comparison of catalysts particle size

Table S6 Summary of the Statistics for Rh particle size for the catalysts from set comprising 300 particle counts.

Dataset	N	Mean	SD	SE
Rh-PI	300	1.897	0.392	0.023
Rh-PI/CB	300	2.649	1.342	0.078
Rh-PI/Al_2O_3	300	2.978	1.102	0.064
Rh/Al_2O_3	300	3.579	1.495	0.087

Null Hypothesis: The means of all selected datasets are equal

Alternative Hypothesis: The means of one or more selected datasets are different

Table S7 One way ANOVA and F-test from table S3.

source	Degree of freedom	Sum of squares	Mean of squares	F value	P value
Model	3	427.723	142.574	105.435	0
Error	1196	1563.202	1.352		

At the 0.05 level, the population means are significantly different. In this case the particle size of Rh-PI is statistically smaller compared to the others.

15. Selectivity trends in the oxidation of: 1-phenyl ethanol, benzyl alcohol, 1-octanol and 3-octanol by Rh/Al_2O_3 and Rh-PI catalysts for different water:toluene ratios

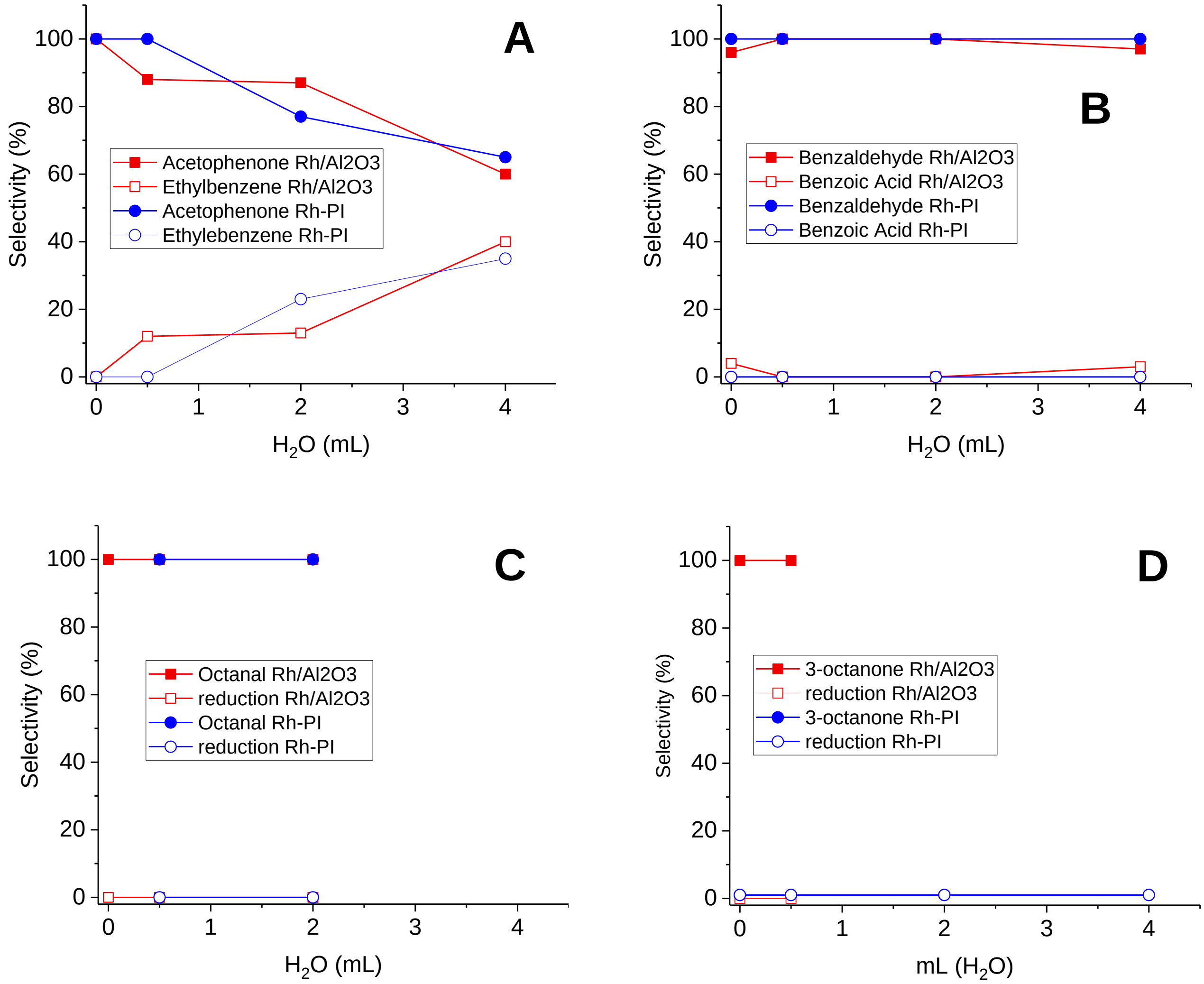


Fig. S29 Selectivity trends for Rh/Al_2O_3 and Rh-PI per different amount of water added to 1 mL of toluene in the oxidation of the alcohols: (A) 1-phenylethanol, (B) benzyl alcohol, (C) 1-octanol and (D) 3-octanol. Reaction conditions: T = 100 ^{o}C, P = atmospheric pressure of air, reaction time 4 h.

16. Representative NMR for benzul alcohol, 1-octanol and 3-octanol oxidation in toluene and water/toluene mixtures

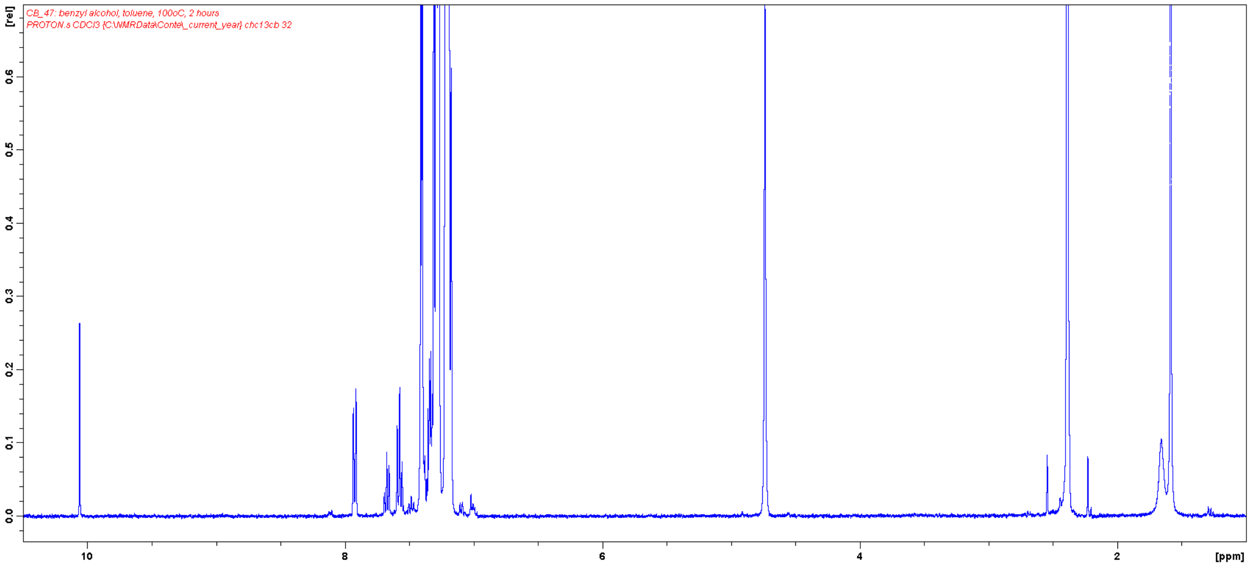


Fig. S30 Representative ^{1}H NMR for the oxidation of benzyl alcohol using Rh/Al_2O_3 in toluene, M:S = 1:100, T = 100 ^oC, P = atmospheric pressure of air, t = 4 h. Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); benzaldehyde, δ (ppm): 10.03 (COH, s, 1H), 7.88-7.91 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m,p*), m, 3H); benzyl alcohol, δ (ppm): 7.14-7.67 (C_6H_5, m, 5H), 4.71 (CH_2, s, 2H); benzoic acid, δ (ppm): 8.08-8.09 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m,p*), m, 3H).

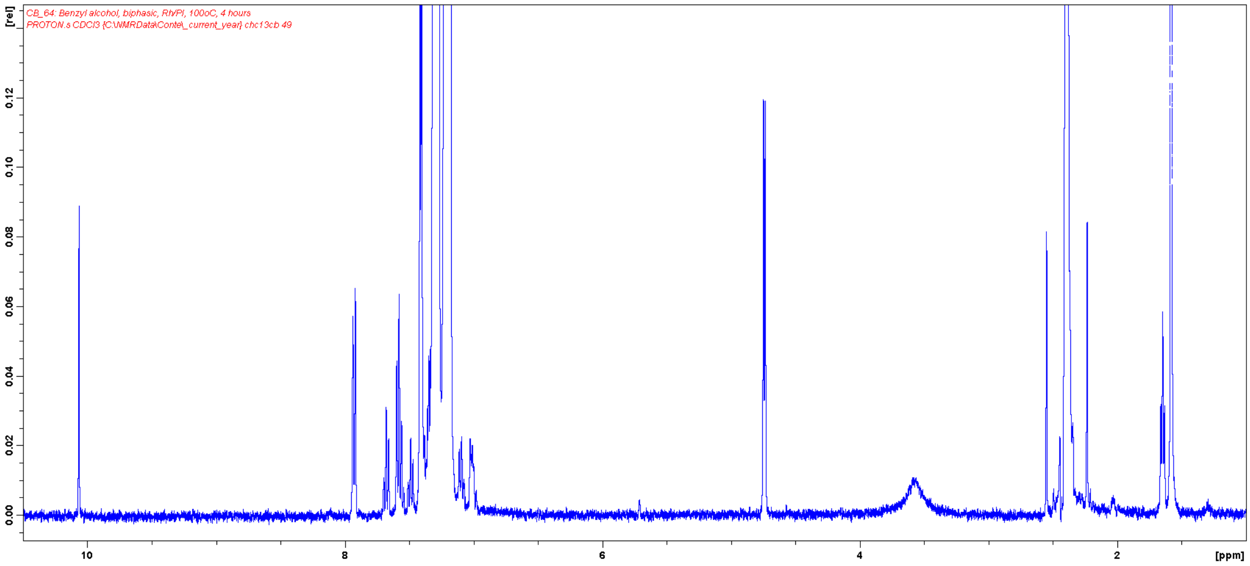


Fig. S31 Representative ^{1}H NMR for the oxidation of benzyl alcohol using Rh-PI in water/toluene, volume ratio 2:1, M:S = 1:100, T = 100 ^oC, P = atmospheric pressure of air, t = 4h. Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); benzaldehyde, δ (ppm): 10.03 (COH, s, 1H), 7.88-7.91 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m,p*), m, 3H); benzyl alcohol, δ (ppm): 7.14-7.67 (C_6H_5, m, 5H), 4.71 (CH_2, s, 2H); benzoic acid, δ (ppm): 8.08-8.09 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m,p*), m, 3H).

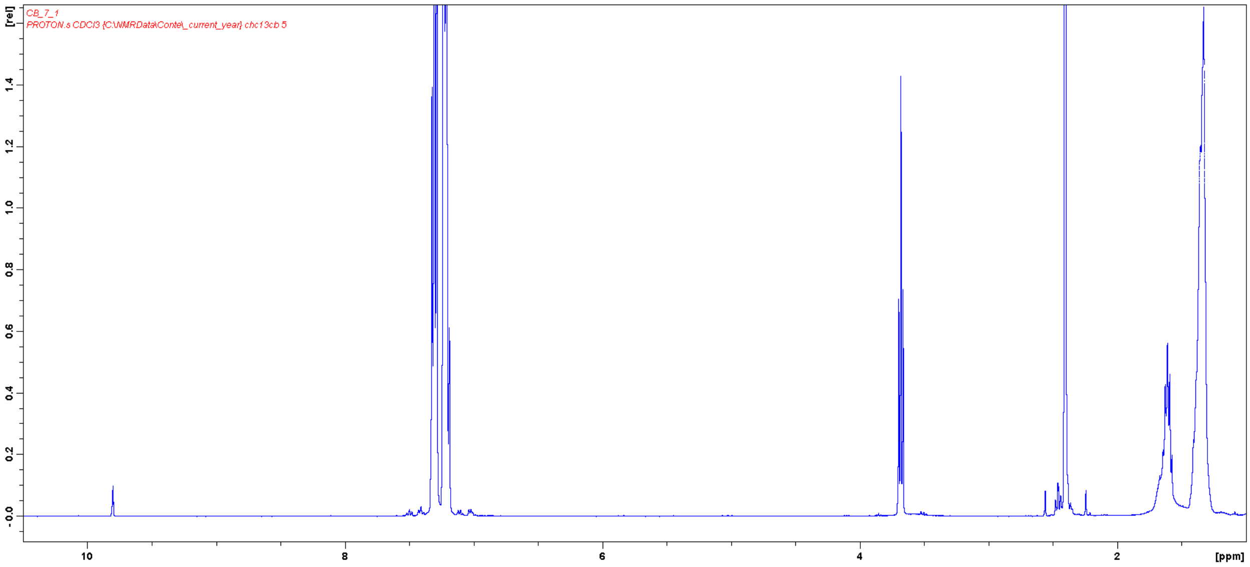


Fig. S32 Representative ^1H NMR for the oxidation of 1-octanol using Rh/Al_2O_3 in toluene, M:S = 1:100, T = 100 ^oC, P = atmospheric pressure of air, t = 4 h.

Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); octanal, δ (ppm): 9.76 (COH, t, 2H, J = 1.8 Hz), 2.40-2.44 ([COH]-C*H*$_2$, td, 2H, *J* = 1.8, 7.4 Hz), 1.53-1.61 ([COH]-CH_2-*CH*$_2$, m, 2H), 1.29-1.32 (CH_2, m, 8H), 0.87-0.91 (CH_3, t, 3H, *J* = 0.9 Hz); 1-octanol, δ (ppm): 3.64 ($HOCH_2$, t, 2H, J = 6.6 Hz), 2.40-2.44 ($HOCH_2$-*CH*$_2$, td, 2H, J = 1.8, 7.4 Hz), 1.53-1.61 (HO-CH_2-CH_2-*CH*$_2$, m, 2H), 1.29-1.32 (CH_2, m, 8H), 0.87-0.91 (CH_3, t, 3H, J = 0.9 Hz).

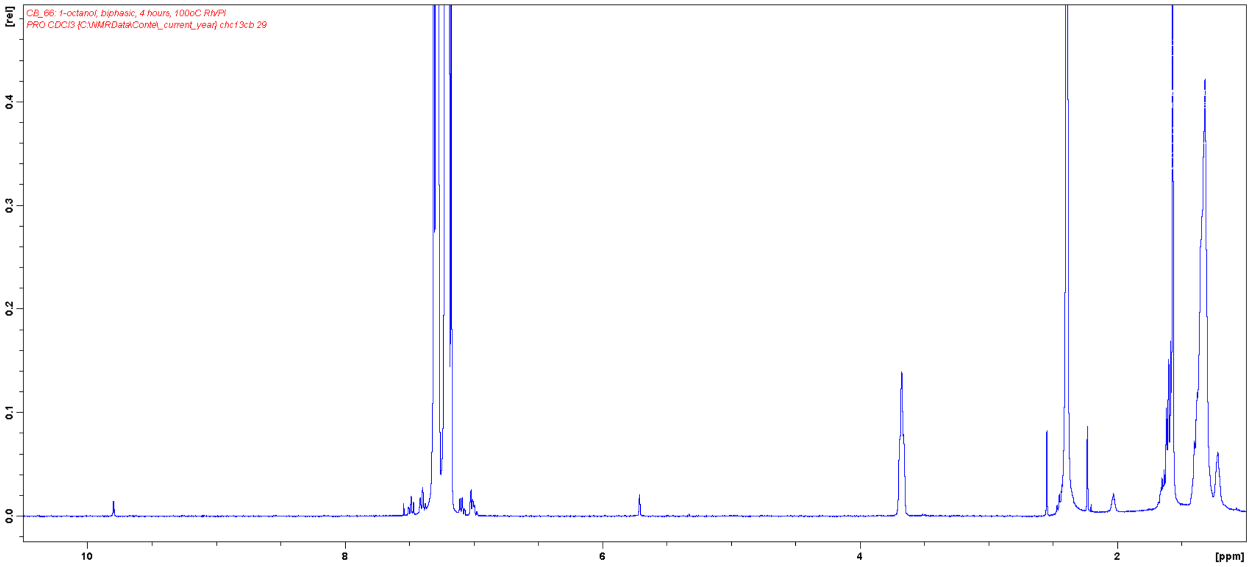


Fig. S33 Representative ^1H NMR for the oxidation of 1-octanol using Rh-PI in water/toluene, volume ratio 2:1, M:S = 1:100, T = 100 ^oC, P = atmospheric pressure of air t = 4 h.

Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); octanal, δ (ppm): 9.76 (COH, t, 2H, J = 1.8 Hz), 2.40-2.44 ([COH]-C*H*$_2$, td, 2H, *J* = 1.8, 7.4 Hz), 1.53-1.61 ([COH]-CH_2-*CH*$_2$, m, 2H), 1.29-1.32 (CH_2, m, 8H), 0.87-0.91 (CH_3, t, 3H, *J* = 0.9 Hz); 1-octanol, δ (ppm): 3.64 ($HOCH_2$, t, 2H, J = 6.6 Hz), 2.40-2.44 ($HOCH_2$-*CH*$_2$, td, 2H, J = 1.8, 7.4 Hz), 1.53-1.61 (HO-CH_2-CH_2-*CH*$_2$, m, 2H), 1.29-1.32 (CH_2, m, 8H), 0.87-0.91 (CH_3, t, 3H, J = 0.9 Hz).

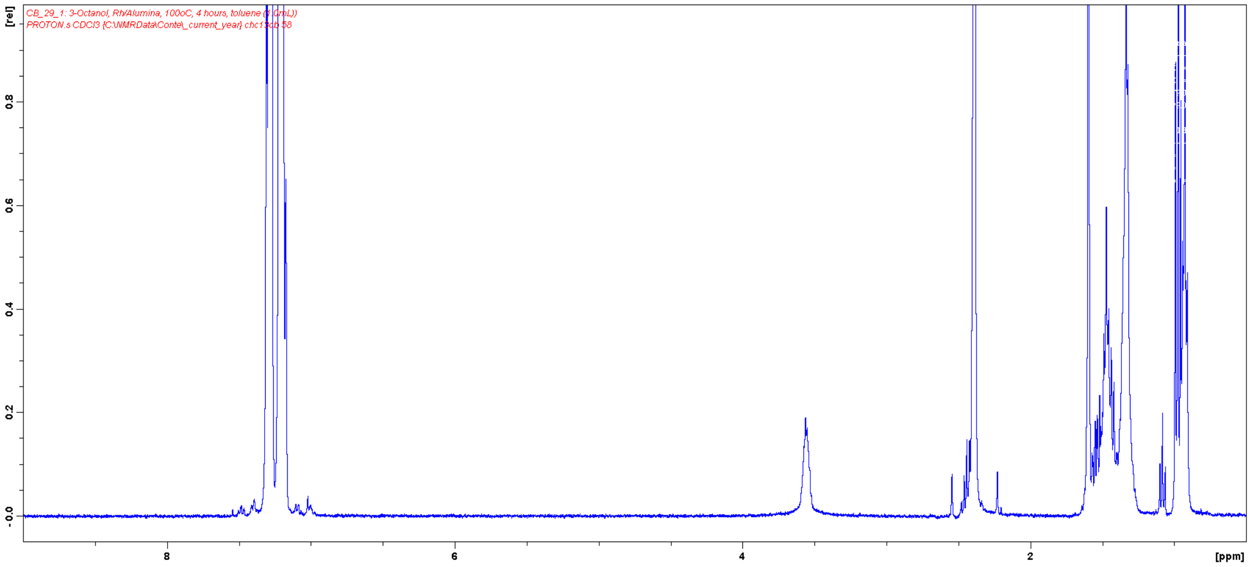


Fig. S34 Representative ^{1}H NMR for the oxidation of 3-octanol using Rh/Al$_2$O$_3$ in toluene, M:S = 1:100, T = 100 ^{o}C, P = atmospheric pressure of air, t = 4h.

Toluene, δ (ppm): 7-7.7 (C$_6$H$_5$, m, 5H), 2.36 (CH$_3$, s, 3H); 3-octanone, δ (ppm): 2.39-2.43 (CH$_2$COCH$_2$, m, 4H), 1.24-1.60 (COCH$_2$CH$_2$, m, 2H), 1.05 (CO-CH$_2$-*CH$_3$*, t, 3H, J = 7.3 Hz); 3-octanol, δ (ppm): 3.52-3.53 ((OH)CH, m, 1H), 0.94 (R-COH-CH$_2$-*CH$_3$*, t, 3H, J = 7.4 Hz), 1.25-1.51 (-*CH$_2$*-HCOH-(*CH$_2$*)$_4$-, m, 10H), 0.88 (CH$_3$-(CH$_2$)$_4$-, t, 3H, J = 6.9 Hz).

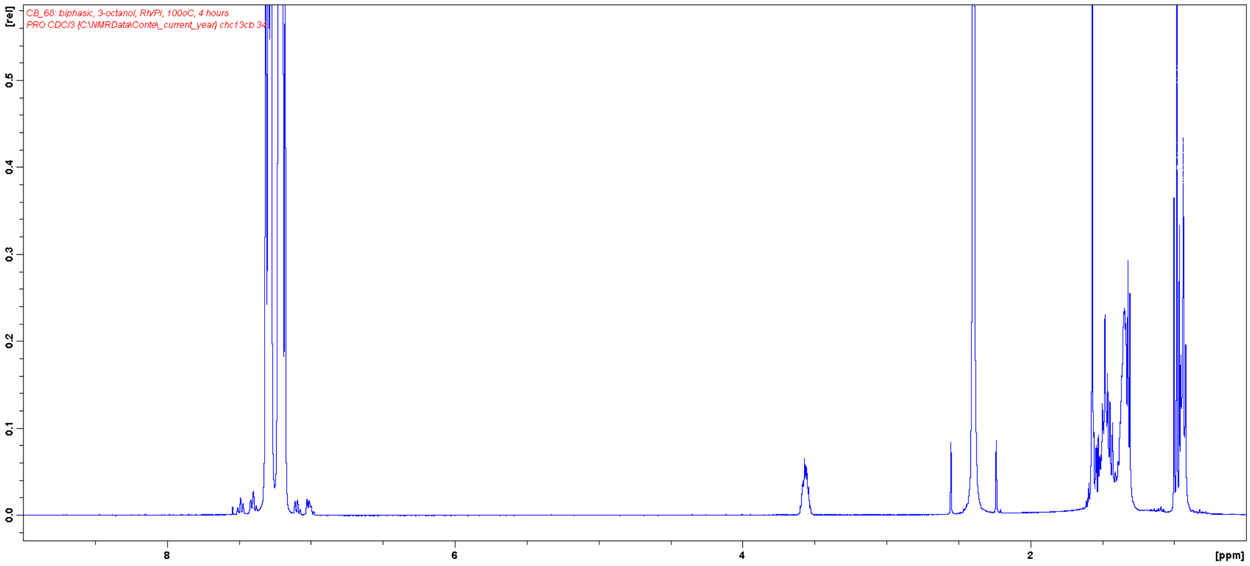


Fig. S35 Representative ^{1}H NMR for the oxidation of 3-octanol using Rh-PI in toluene, M:S = 1:100, T = 100 ^{o}C, P = atmospheric pressure of air, t = 4h.

Toluene, δ (ppm): 7-7.7 (C$_6$H$_5$, m, 5H), 2.36 (CH$_3$, s, 3H); 3-octanone, δ (ppm): 2.39-2.43 (CH$_2$COCH$_2$, m, 4H), 1.24-1.60 (COCH$_2$CH$_2$, m, 2H), 1.05 (CO-CH$_2$-*CH$_3$*, t, 3H, J = 7.3 Hz); 3-octanol, δ (ppm): 3.52-3.53 ((OH)CH, m, 1H), 0.94 (R-COH-CH$_2$-*CH$_3$*, t, 3H, J = 7.4 Hz), 1.25-1.51 (-*CH$_2$*-HCOH-(*CH$_2$*)$_4$-, m, 10H), 0.88 (CH$_3$-(CH$_2$)$_4$-, t, 3H, J = 6.9 Hz).

17. Reaction mixture: extraction of the aqueous phase in benzyl alcohol oxidation

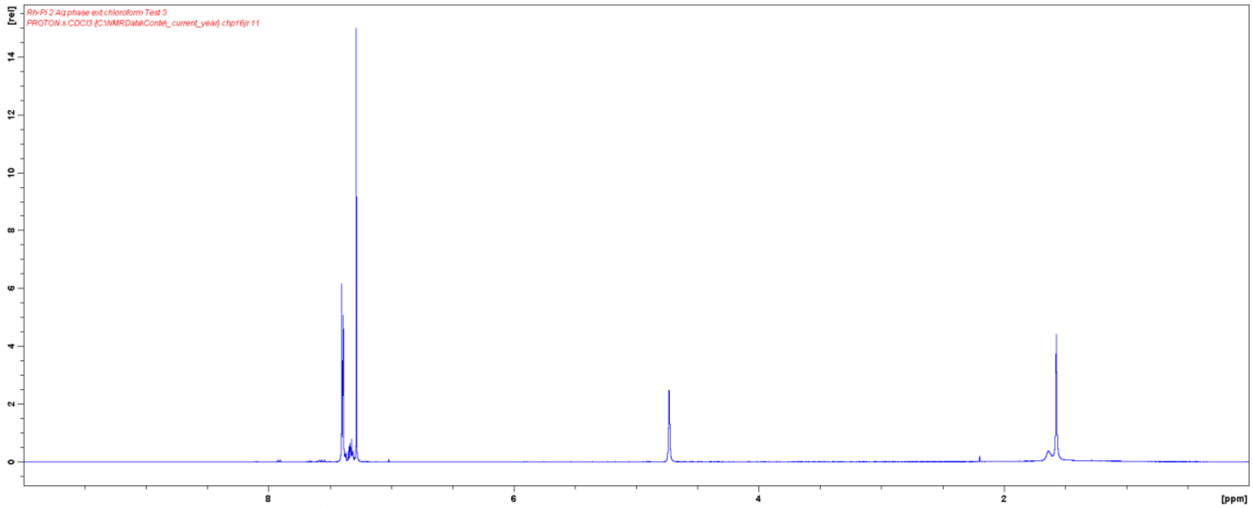


Fig. S36 Representative ^{1}H NMR for aqueous phase for the oxidation of benzyl alcohol using Rh-PI in water/toluene (2:1 volume ratio). M:S = 1:100, T = 100 ^{o}C, P = atmospheric pressure of air, t = 4h. Aqueous layer extracted with chloroform. benzaldehyde, δ (ppm): 10.1 (COH, s, 1H), 7.88-7.91 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m,p*), m, 3H); benzyl alcohol, δ (ppm): 7.14-7.67 (C_6H_5, m, 5H), 4.71 (CH_2, s, 2H); benzoic acid, δ (ppm): 8.08-8.09 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m,p*), m, 3H); $CHCl_3$ δ (ppm): 7.26 (1H, s); H_2O 1.59 (2H, s).

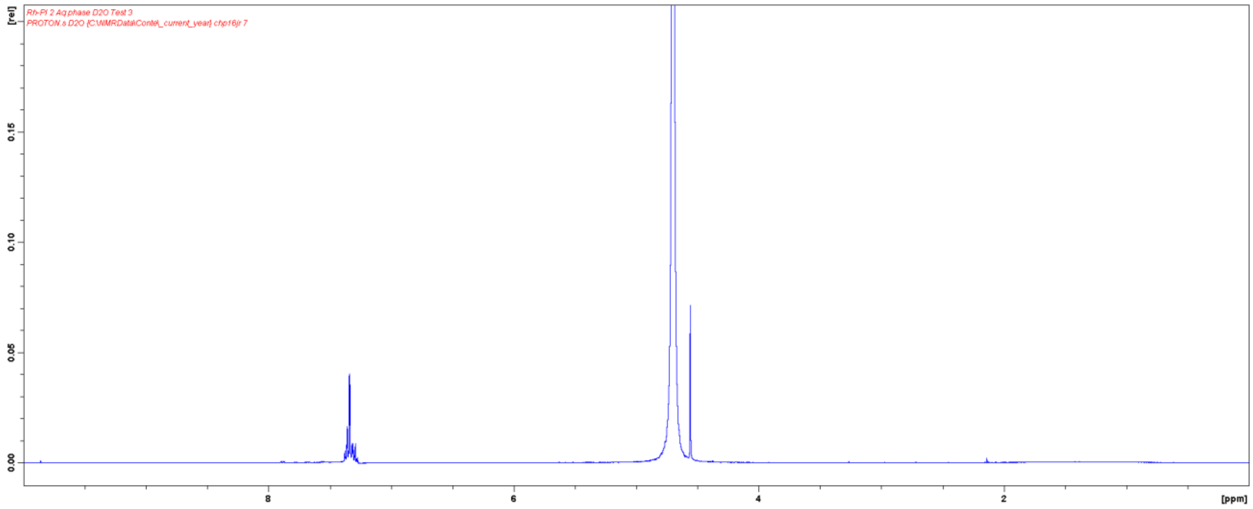


Fig. S37 Representative ^{1}H NMR for aqueous phase for the oxidation of benzyl alcohol using Rh-PI in water/toluene (2:1 volume ratio). M:S = 1:100, T = 100 ^{o}C, P = atmospheric pressure of air, t = 4h. Aqueous layer analysed in D_2O. Benzaldehyde, δ (ppm): 10.1 (COH, s, 1H), 7.88-7.91 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m,p*), m, 3H); benzyl alcohol, δ (ppm): 7.14-7.67 (C_6H_5, m, 5H), 4.71 (CH_2, s, 2H); benzoic acid, δ (ppm): 8.08-8.09 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m,p*), m, 3H); H_2O 4.79 (2H, s).

18. Benzyl alcohol oxidation: control tests in the presence of H_2O, no solvent and D_2O/toluene

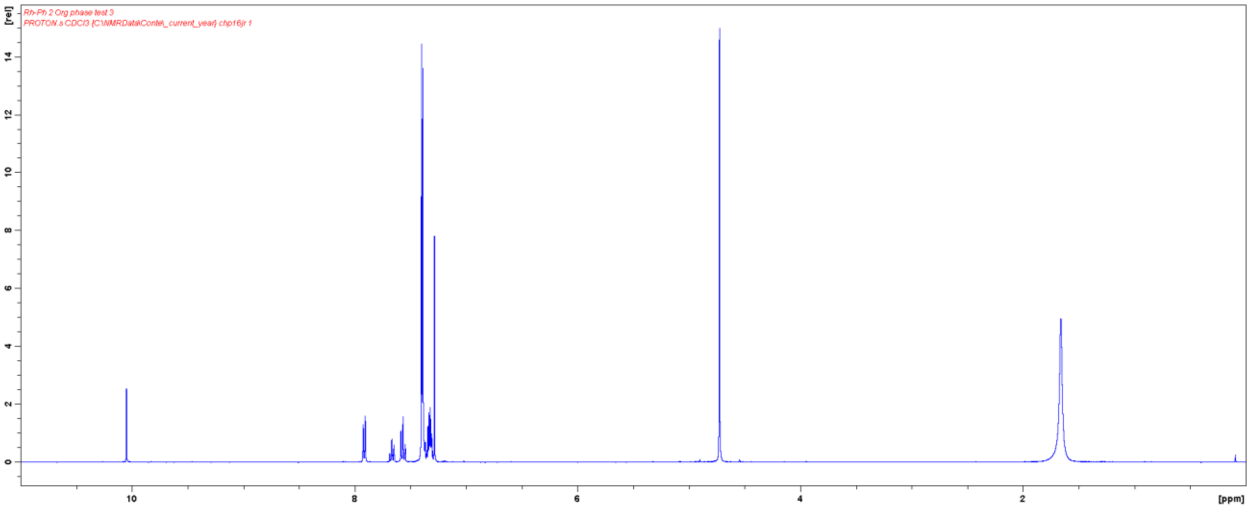


Fig. S38 Representative ^{1}H NMR for the oxidation of benzyl alcohol using Rh-PI in water (4mL), M:S = 1:100, T = 100 ^{o}C, P = atmospheric pressure of air, t = 4h. Spectrum of the organic layer in $CDCl_3$. Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); benzaldehyde, δ (ppm): 10.1 (COH, s, 1H), 7.88-7.91 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m*,*p*), m, 3H); benzyl alcohol, δ (ppm): 7.14-7.67 (C_6H_5, m, 5H), 4.71 (CH_2, s, 2H); benzoic acid, δ (ppm): 8.08-8.09 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m*,*p*), m, 3H); $CHCl_3$ δ (ppm): 7.26 (1H, s); H_2O 1.59 (2H, s).

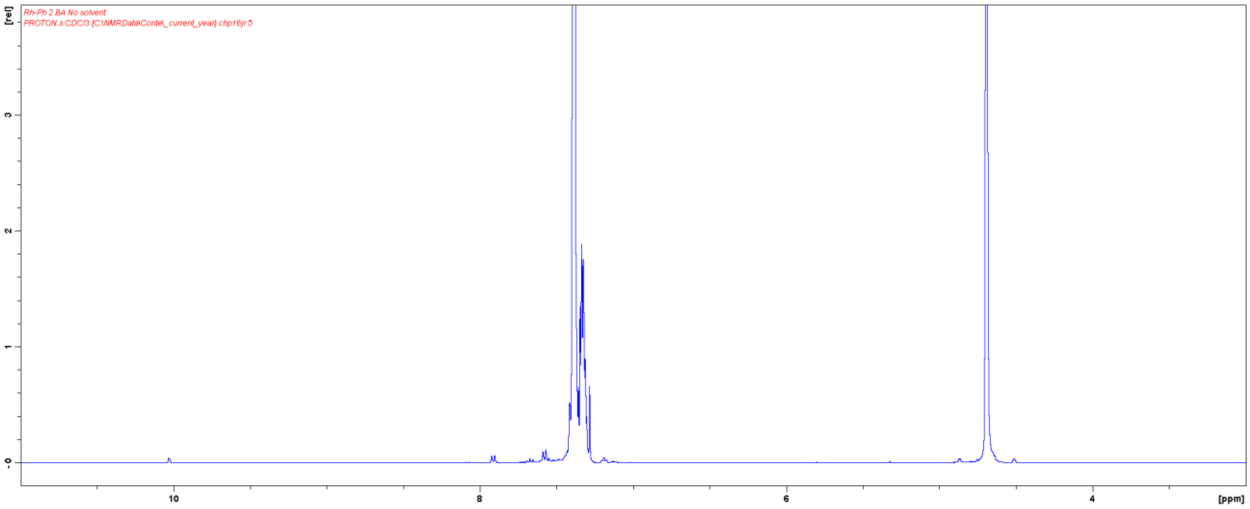


Fig. S39 Representative ^{1}H NMR for the oxidation of benzyl alcohol using Rh-PI and no solvent. M:S = 1:500, T = 100 ^{o}C, P = atmospheric pressure of air, t = 4h. Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); benzaldehyde, δ (ppm): 10.03 (COH, s, 1H), 7.88-7.91 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m*,*p*), m, 3H); benzyl alcohol, δ (ppm): 7.14-7.67 (C_6H_5, m, 5H), 4.71 (CH_2, s, 2H); benzoic acid, δ (ppm): 8.08-8.09 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m*,*p*), m, 3H).

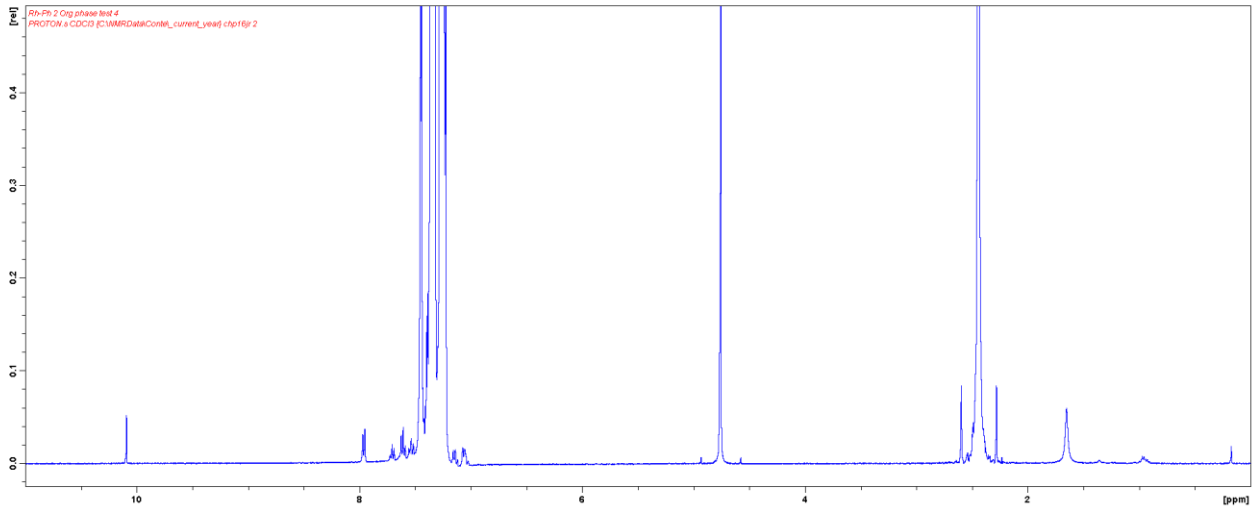


Fig. S40 Representative ^{1}H NMR for the oxidation of benzyl alcohol using Rh-PI and D_2O/Toluene (volume ratio 2:1), M:S = 1:500, T = 100 ^oC, P = atmospheric pressure of air, t = 4h. Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); benzaldehyde, δ (ppm): 10.03 (COH, s, 1H), 7.88-7.91 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m,p*), m, 3H); benzyl alcohol, δ (ppm): 7.14-7.67 (C_6H_5, m, 5H), 4.71 (CH_2, s, 2H); benzoic acid, δ (ppm): 8.08-8.09 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m,p*), m, 3H). H_2O 1.59 (2H, s).

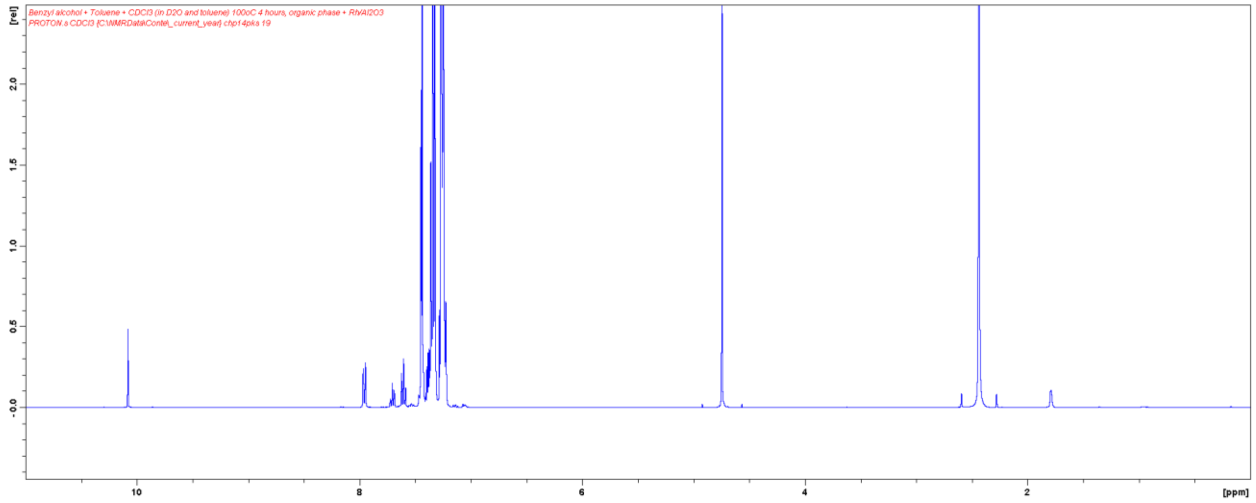


Fig. S41 Representative ^{1}H NMR for the oxidation of benzyl alcohol using Rh/Al_2O_3 and D_2O/Toluene (volume ratio 2:1), M:S = 1:500, T = 100 ^oC, P = atmospheric pressure of air, t = 4h. Toluene, δ (ppm): 7-7.7 (C_6H_5, m, 5H), 2.36 (CH_3, s, 3H); benzaldehyde, δ (ppm): 10.03 (COH, s, 1H), 7.88-7.91 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m,p*), m, 3H); benzyl alcohol, δ (ppm): 7.14-7.67 (C_6H_5, m, 5H), 4.71 (CH_2, s, 2H); benzoic acid, δ (ppm): 8.08-8.09 (CH(*o*), m, 2H), 7.14-7.67 (CH(*m,p*), m, 3H). H_2O 1.59 (2H, s).

19. References

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