Supporting Information

A Switchable Route for Selective Transformation of Ethylene Glycol to Hydrogen and Glycolic Acid by Bifunctional Ruthenium Catalyst

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1. General experimental Information

All experiments were performed in an atmosphere of purified nitrogen in an N_2-filled glovebox or by using the standard Schlenk technique, unless otherwise stated. All the chemicals purchased from commercial suppliers are in the analytical grade and used without further purification. All the solvents were dried according to the literature procedure. Dissolved oxygen in the solvent was removed by degassing nitrogen gas. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on 400 MHz FT-NMR Bruker AVANCE NEO Ascend 400 spectrometer. The chemical shift values of all the spectra were reported with reference to the residual proton of the deuterated solvent (4.79 ppm D_2O, 7.26 ppm $CDCl_3$, and 7.16 ppm C_6D_6). Mass spectra were recorded on Xevo G2-XS QT of Quadrupole Time of Flight Mass spectrometer waters. The evolved hydrogen gas was analyzed on TRACE 1610 gas chromatography (TCD, Porapak Q column, N_2 carrier gas flow, Thermo Scientific). Complex **1** and **2** were synthesized according to previously reported synthetic methods. [1]

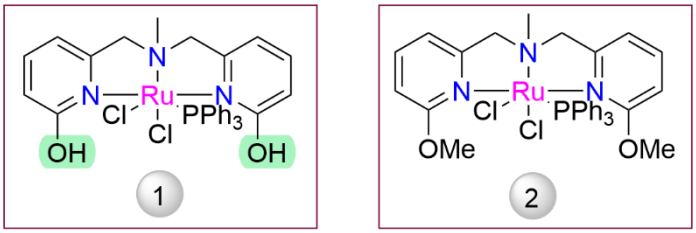


Figure S1 NNN-Ru complexes employed in reforming of ethylene glycol

2. General Procedure for Hydrogen and glycolic acid formation from ethylene glycol

KOH (in equivalent w.r.t. ethylene glycol), catalyst (in mol%), and degassed solvent (1 mL) were added sequentially to a 100 mL sealed tube with a sidearm charged with a magnetic bar in an N_2-filled glove box. The mixture was stirred for 5 minutes at room temperature, followed by the addition of ethylene glycol (2.503 mmol), and the tube was sealed properly. The tube was taken out from the glove box and placed in a preheated oil bath at a specified temperature

for the mentioned time period. The evolved gas volume was measured by a gas collecting system (in an inverted measuring cylinder after passing through a double alkali solution), and for gas chromatography analysis gas sample was taken from the reaction tube. The reaction mixture was dissolved in H_2O (3 mL) and the aliquot was analyzed by ^{1}H and ^{13}C NMR using 2,6-lutidine (1 equiv. w.r.t initial substrate loading) as an internal standard in D_2O. The conversion and yield of products were determined by using following equation.[2]

Conversion of ethylene glycol (conv.$_{EG}$) = (initial mmol of ethylene glycol feed - mmol of ethylene glycol remain)/ initial mmol of ethylene glycol feed· ·**(1)**

%yield of glycolic acid (yield $_{GA}$) = (mmol of glycolic acid obtained from ^{1}H NMR analysis/ mmol of ethylene glycol initially feed) × 100 · **(2)**

% yield of formic acid (yield $_{FA}$) = (mmol of formic acid formed after reaction/ 2 × mmol of ethylene glycol initially feed) × 100· **(3)**

The molar amount of hydrogen gas collected was calculated by using ideal gas law

Mmol of hydrogen gas produced = vol. of hydrogen gas produced (mL) / 22.49 (mol/ L) **(4)**

Turn over number (TON) = mmol of hydrogen gas produced/ mmol of catalyst loading **(5)**

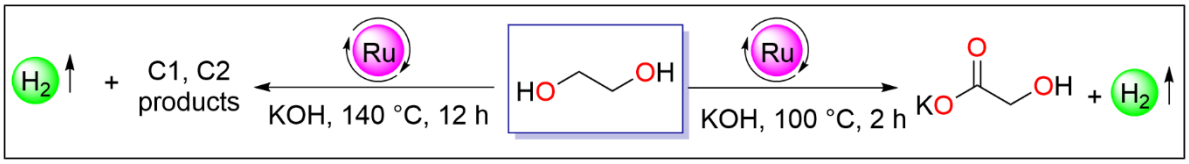
Turn over frequency (TOF) = TON/ t · **(6)**

Where t is time in hour

Equivalent of hydrogen gas produced = mmol of hydrogen produced / mmol of ethylene glycol initially feed· **(7)**

Carbon balance = [100- conv.$_{EG}$ + yield $_{GA}$+ yield $_{FA}$] · **(8)**

3. Table S1 Optimization of reaction conditions



Entry	Catalyst	Solvent	Conv %	Products			CB[i]
				GA%[g]	FA%[g]	H_2 mL (in equiv[h])	
1[j]	**1**	^{t}BuOH	100	94	2	118 (2.1)	96
2[j]	**1**	^{t}AmOH	91	90	1	100 (1.78)	100
3	**1**	THF	-	8		10 (0.18)	-
4[j]	**1**	^{t}BuOH: H_2O (10:1)	81	80	1	90 (1.6)	100
5	-	^{t}BuOH	0	0	0	0	100
6	$RuCl_2(PPh_3)_3$	^{t}BuOH	15	5	0	21 (0.37)	90
7[j]	**2**	^{t}BuOH	40	29	1	50 (0.89)	91
8[a]	**1**	^{t}BuOH	59	49	1	75 (1.33)	91
9[b]	**1**	^{t}BuOH	28	3	1	35 (0.62)	76
10[c, j]	**1**	^{t}BuOH	65	59	0	78 (1.39)	94
11[d, j]	**1**	^{t}BuOH	100	70	4	130 (2.31)	74
12[d]	**1**	diglyme	100	52.7	11.5	146 (2.59)	-
13[d, e, j]	**1**	diglyme	100	0	17	180 (3.2)	-
14[d, e, j]	**1**	Diglyme: H_2O (9: 1)	100	25	2.5	152 (2.7)	-
15[f, j]	**1**	^{t}BuOH	82	81	0	96 (1.71)	99

Reaction conditions: in 100 mL sealed Schlenk tube with a sidearm ethylene glycol (2.503 mmol), KOH (6.25 mmol), catalyst (1 mol%), (solvent (1 mL), at 100 °C for 2 h. [a] KOH (3.75 mmol), [b] KOH (1.25 mmol), [c] 90 °C, [d] 140 °C, [e] 12 h, [f] in presence of Hg (100 mol%), [g] yield was calculated by ^{1}H NMR analysis using 2,6-lutidine as internal standard. In diglyme and THF the conversion of ethylene glycol was not identifiable. [h] Equivalent of hydrogen produced was calculated by using equation 7. [i] carbon balance was calculated

according to equation 8. [j] experiments were repeated 3 times and the average results were reported with an error limit within 5%

4. Monitoring the progress of the reaction by measuring gas volume evolved

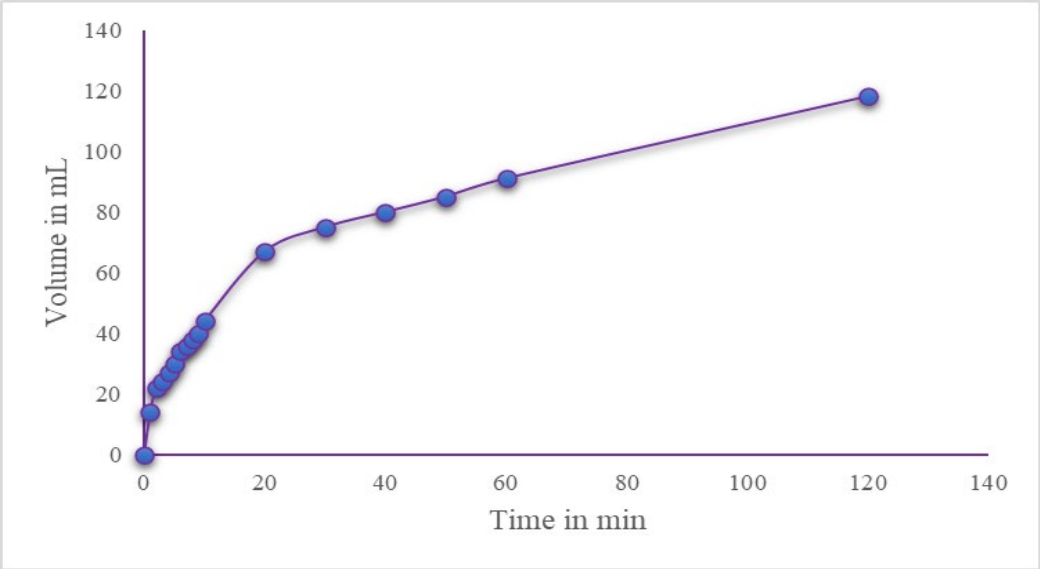


Figure S2 Time course profile of reaction progress monitor by measuring gas volume evolved during dehydrogenation of ethylene glycol to glycolic acid in ^{t}BuOH at 100 °C over 2 h Table 1, entry 1

Initial TOF (in h^{-1}) = mmol of hydrogen gas produced in 10 min / mmol of catalyst feed × t ·

. . . . . **(9)**

t is time in hour

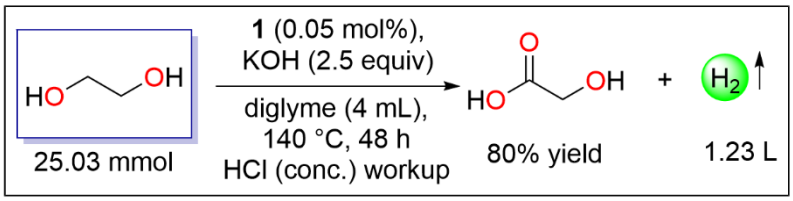
Gas volume evolved in 10 min = 44 mL

mmol of hydrogen gas produced in 10 min = 1.96 mmol

Mmol of catalyst used = 0.02503 mmol

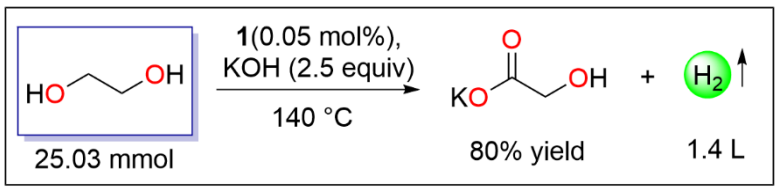
Initial TOF = 469 h^{-1}

5. Reforming of ethylene glycol in gram scale



In a 100 mL sealed Schlenk tube with a sidearm charged with KOH (62.57 mmol), catalyst **1** (0.05 mol%) and diglyme (4 mL) were taken followed by addition of ethylene glycol (25.03 mmol). The reaction tube was sealed properly and heated for 48 h at 140 °C in a preheated oil bath. In each 12 h interval, the evolved gas volume was collected in a inverted measuring cylinder after passing through double alkali solution. A total of 1.23 L of gas volume was collected with the total 86.6% of glycolic acid was observed from NMR analysis of reaction mixture by using 2,6-lutidine as internal standard in D_2O (Fig S33). On acidification of reaction mixture by conc. HCl a white precipitate was formed. The mixture was filtrated and the solvent was evaporated. The free glycolic acid was obtained and quantified (80%) by ^1H NMR analysis by using sodium acetate (2.503 mmol) as internal standard (Fig S34, S35).

6. Reforming of ethylene glycol in neat condition



In an N_2-filled glove box, a 100 ml sealed tube with a sidearm was charged with KOH (62.57 mmol), catalyst **1** (0.05 mol%), and ethylene glycol (25.03 mmol) under an inert atmosphere. The tube was sealed properly and heated for 96 h at 140 °C in a preheated oil bath. In each 12 h interval, the evolved gas volume was collected in a gas colleting system after passing through double alkali solution (Fig S3). A total of 1.4 L of gas volume was collected with the final 80%

yield of glycolic acid (Fig S36, S37). Highly pure gas was collected as no other was detected in GC-TCD analysis (Fig S16d).

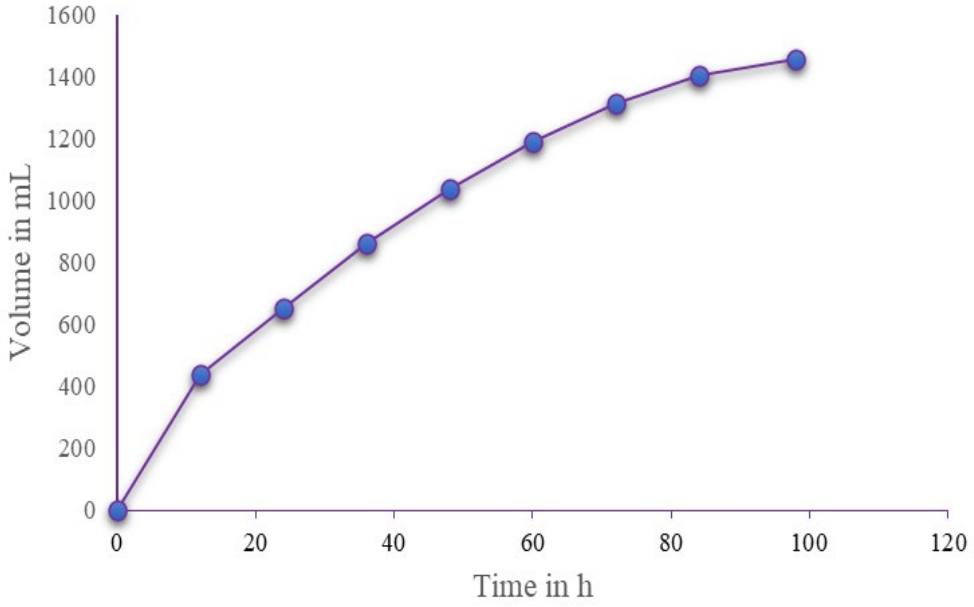
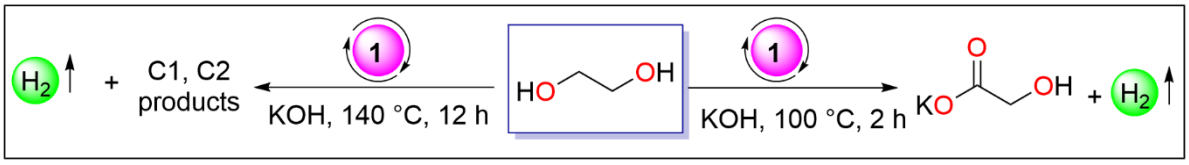


Figure S3 Time course plot of evolved hydrogen gas volume from ethylene glycol by **1** in solvent-free condition at 140 °C over 96 h

7. Table S2 Screening for catalyst loading

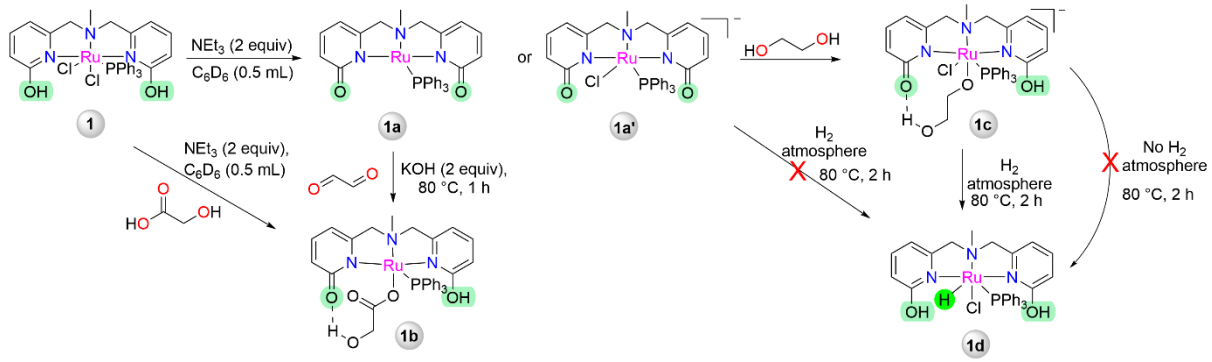


Entry	Catalyst loading	Conv%	GA%	H_2 in mL	TON[e]	TOF (h^{-1})[e]
1[f]	1	100	94	118	210	105
2	0.5	51	23	57	203	102
3[f]	0.1	35	12	41	728	364
4	0.01	33.5	9	36	6395	3197
5[a, f]	0.01	-	62	142	25225	2102
6[b]	0.05	-	86.6 (80)[d]	1230	4370	91
7[c]	0.05	94	82	1400	4974	52

Reaction conditions: In a 100 mL sealed Schlenk tube with a sidearm ethylene glycol (2.503 mmol), KOH (2.5 equivalent w.r.t ethylene glycol), and **1** (x mol%) in ^{t}BuOH at 100 °C for 2 h. [a] in diglyme at 140 °C for 12 h, [b] 25.03 mmol in diglyme at 140 °C for 48 h, [c] 25.03 mmol in solvent-free condition for 96 h, [d] after acid work up free glycolic acid, [e] TON and TOF were calculated on the basis of mmol of hydrogen produced following equation 5 and 6. [f] experiments were repeated 3 times and the average results were reported with an error limit within 5%

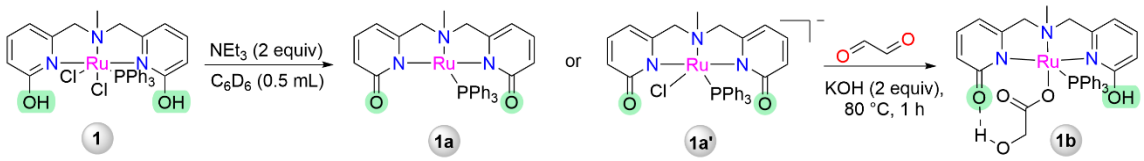
8. Control NMR experiments

NMR experiment for elucidation of catalytic intermediate involved during catalysis by complex **1**, although by the NMR analysis the chloride attachment to the metal center is not confirmatory. The intermediate **1a** may be a neutral specie without the coordinated chloride ion.[3]



Scheme S1 Control NMR experiments to elucidate the catalytic intermediate involved

a) Treatment of glyoxal with complex 1



In an oven-dried J. Young NMR tube, catalyst **1** (0.007 mmol) was dissolved in C_6H_6 (0.5 mL) followed by the addition of NEt_3 (0.014 mmol). To the resulting solution, glyoxal (10 equiv.) was added under the N_2 atmosphere and after 0.5 h treated with KOH (2 equivalent w.r.t glyoxal). The tube was sealed properly and heated for 1 h at 80 °C. The whole experiment was monitored by ^{1}H and ^{31}P NMR analysis. The formation of **1a** and **1b** were characterised separately in our earlier publication[1] and the hydrogen bonding interaction of protic arm with substrate in secondary coordination sphere was well explained. The formation of **1b** was observed separately by the treatment of glycolic acid with **1a** (formed after treatment of **1** with NEt_3). The restricted rotation of coordinated glycolate resulted in splitting of $-CH_2$ proton of glycolate, due to secondary sphere hydrogen bonding interaction with ligand protic arm. The similar result was also observed on treatment of **1a/ 1a'** with glyoxal and KOH resulting formation of **1b**.

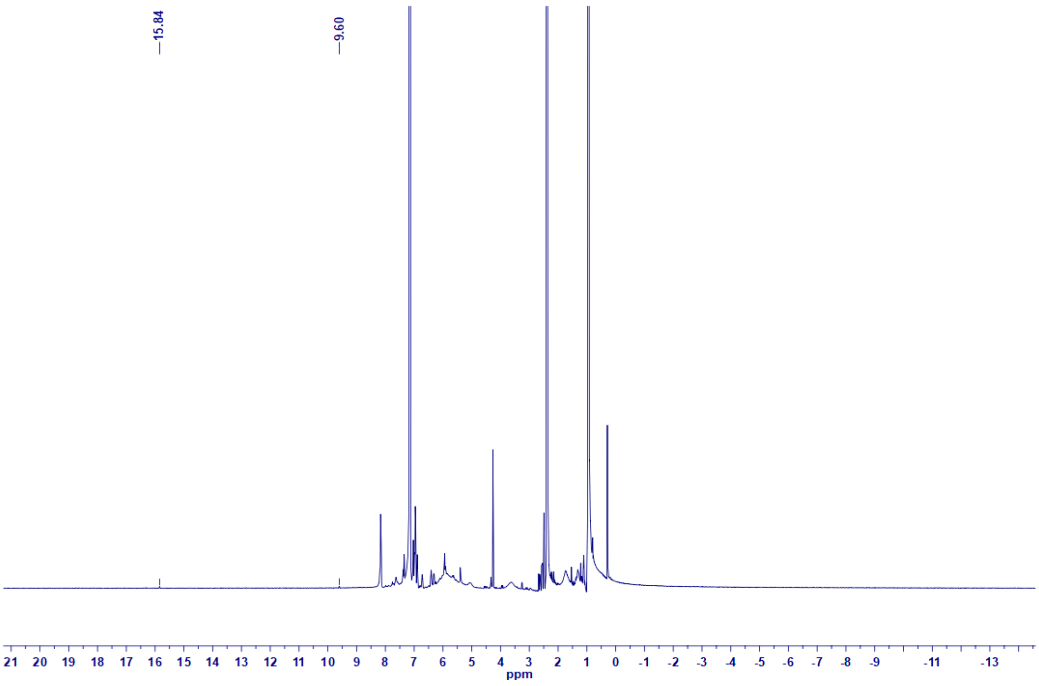


Figure S4 ^{1}H NMR spectrum of treatment of glyoxal with complex **1** in C_6D_6 (formation of **1b**)

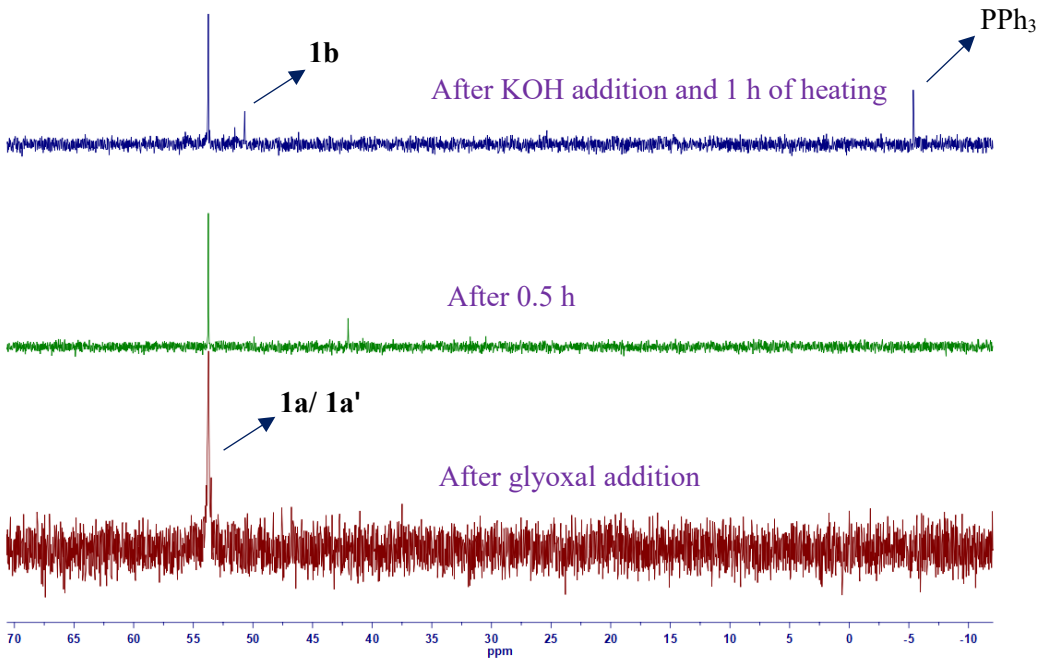
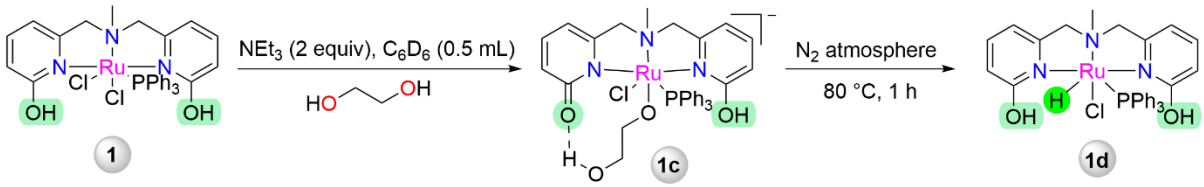


Figure S5 A couple of ^{31}P NMR spectra of treatment of glyoxal with complex **1** in C_6D_6 (formation of **1b**)

b) Reforming of ethylene glycol under N_2 atmosphere



In an oven-dried J. Young NMR tube, to the solution of catalyst **1** (0.007 mmol) in C_6D_6 (0.5 mL), NEt_3 (0.014 mmol) and ethylene glycol (10 equivalent) were added under N_2 atmosphere. The formation of ethylene glycol bound intermediated **1c** was identified after addition of

ethylene glycol. Then the tube was sealed properly and paced in a pre-heated oil-bath at 80 °C for 2 h. The whole experiment was monitored by ^{1}H and ^{31}P NMR analysis.

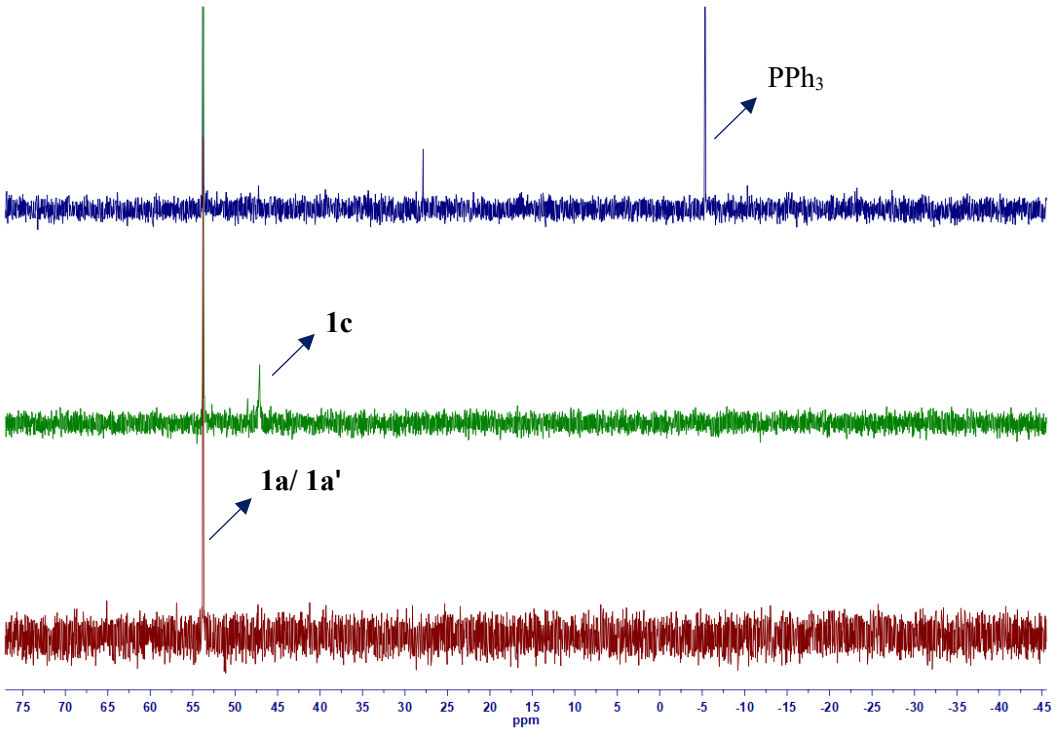
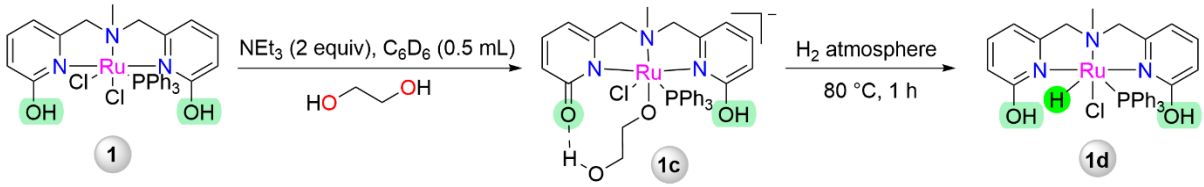


Figure S6 A couple of ^{31}P NMR spectra of monitoring treatment of ethylene glycol with in situ generated **1a/ 1a'** under N_2 atmosphere in C_6D_6

c) Reforming of ethylene glycol under H_2 atmosphere



In an oven-dried J. Young NMR tube, catalyst **1** (0.007 mmol) was dissolved in C_6D_6 (0.5 mL) followed by the addition of NEt_3 (0.014 mmol) affording **1a/ 1a'** in situ. To the resulting

solution, ethylene glycol (10 equiv.) was added under the N_2 atmosphere to generate **1c**. The tube was purged with H_2 gas through the freeze-thaw cycle and heated for 2 h at 80 °C. The whole experiment was monitored by ^1H and ^{31}P NMR analysis. The Hydride intermediate was observed after 2 h of heating.

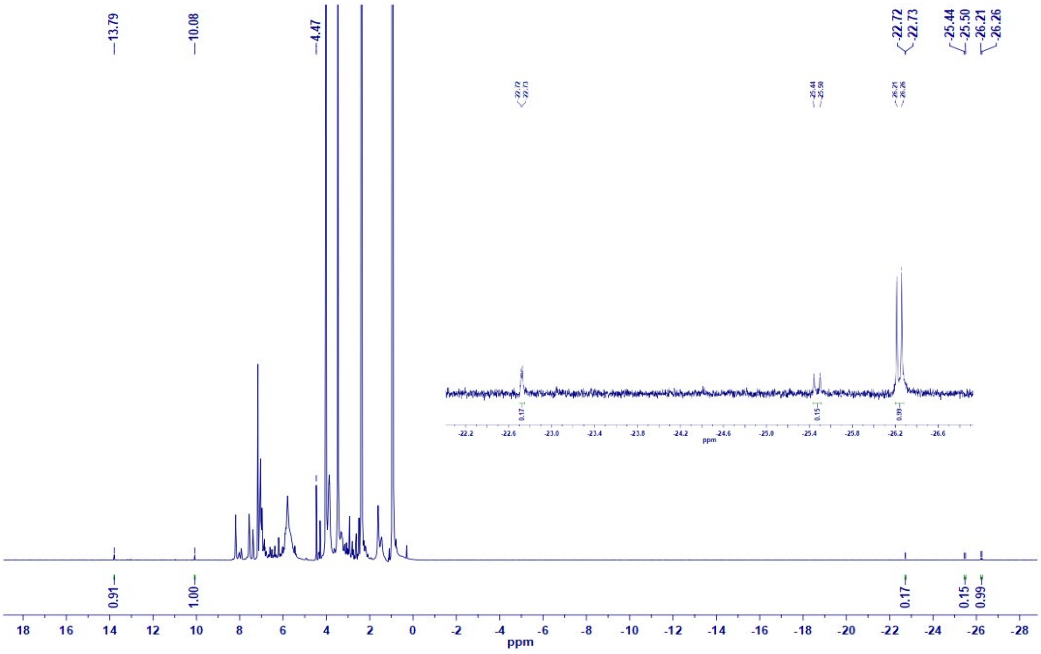


Figure S7 ^1H NMR spectrum of treatment of ethylene glycol with **1** in the presence of NEt_3 under an H_2 atmosphere (formation of **1d**) in C_6D_6

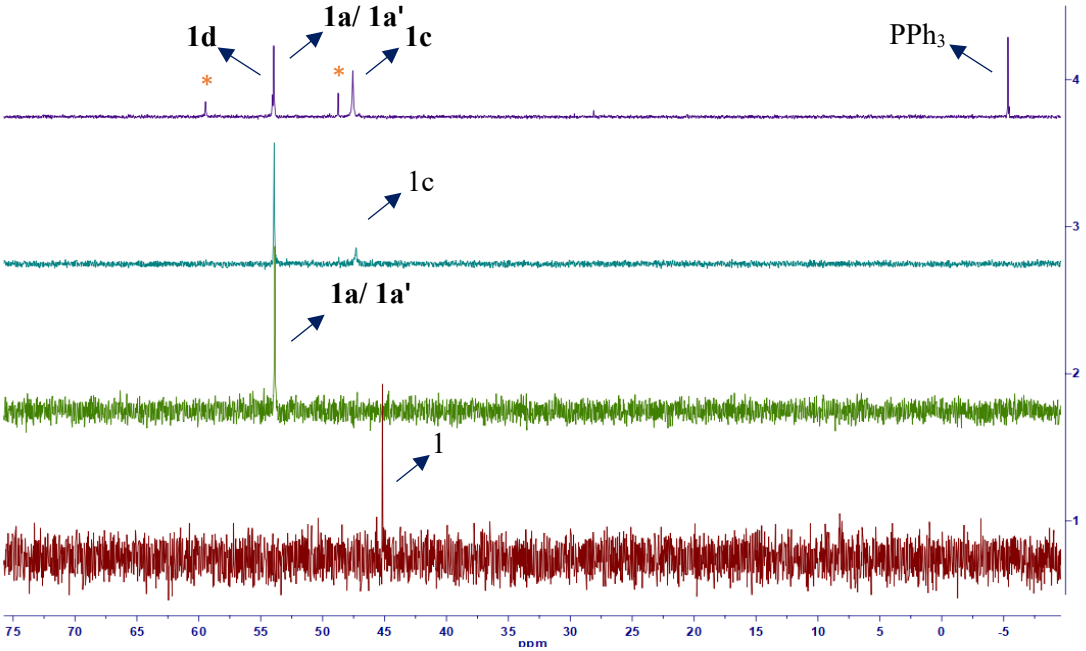
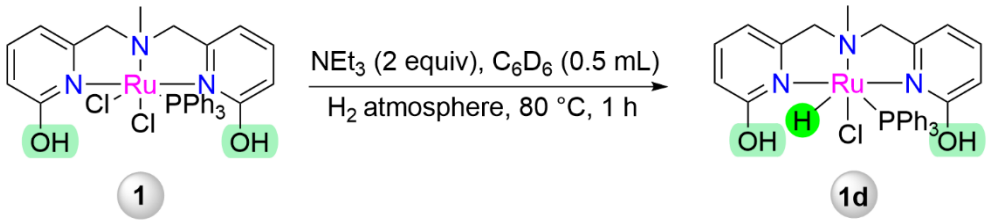


Figure S8 A couple of ^{31}P NMR spectra monitoring treatment of ethylene glycol with **1** in the presence of NEt_3 under an H_2 atmosphere in C_6D_6, *unidentified peak

d) Treatment of in situ generated 1a with H_2 atmosphere



In an oven-dried J. Young NMR tube, catalyst **1** (0.007 mmol) was taken and 0.5 mL of C_6D_6 was added in to the tube followed by addition of NEt_3 (0.014 mmol) in a N_2 filled glove box to produce **1a/ 1a'** in situ. The tube was evacuated by three successive freeze-thaw- cycle and finally purged with hydrogen. The resulting solution was heated for 2 h at 80 °C and the whole experiment was monitored by ^1H and ^{31}P NMR analysis. No hydride peak was observed in ^1H NMR analysis. This observation indicates the hydride intermediate is observed only under high concentration of hydrogen (hydrogen atmosphere).

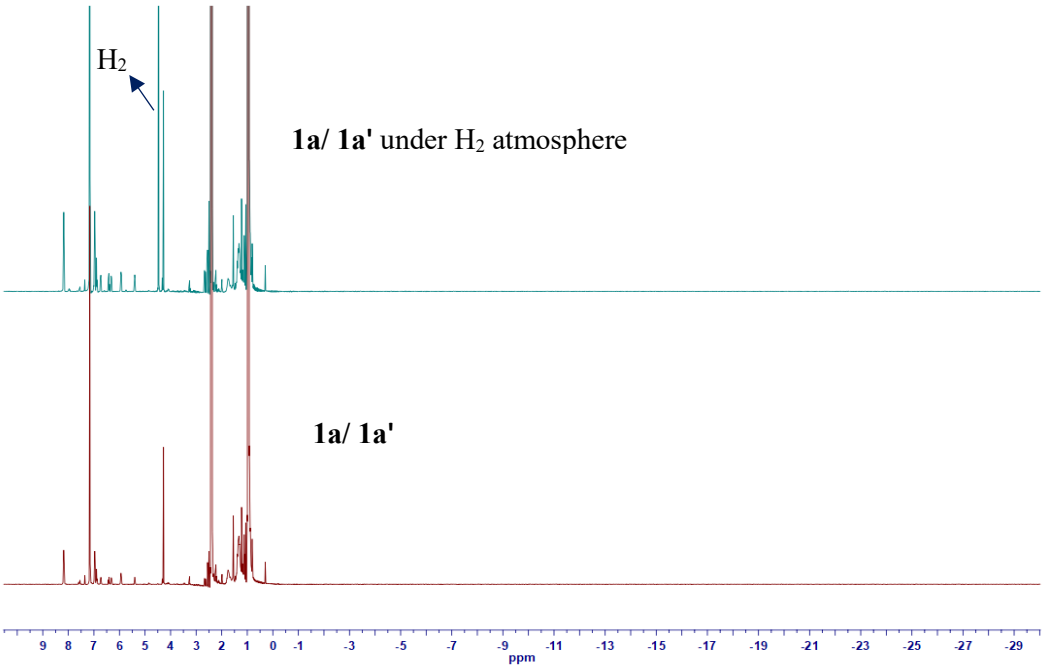


Figure S9 A couple of ^1H NMR spectra monitoring in situ generated **1a/ 1a'** in the presence of NEt_3 and refluxing under an H_2 atmosphere in C_6D_6

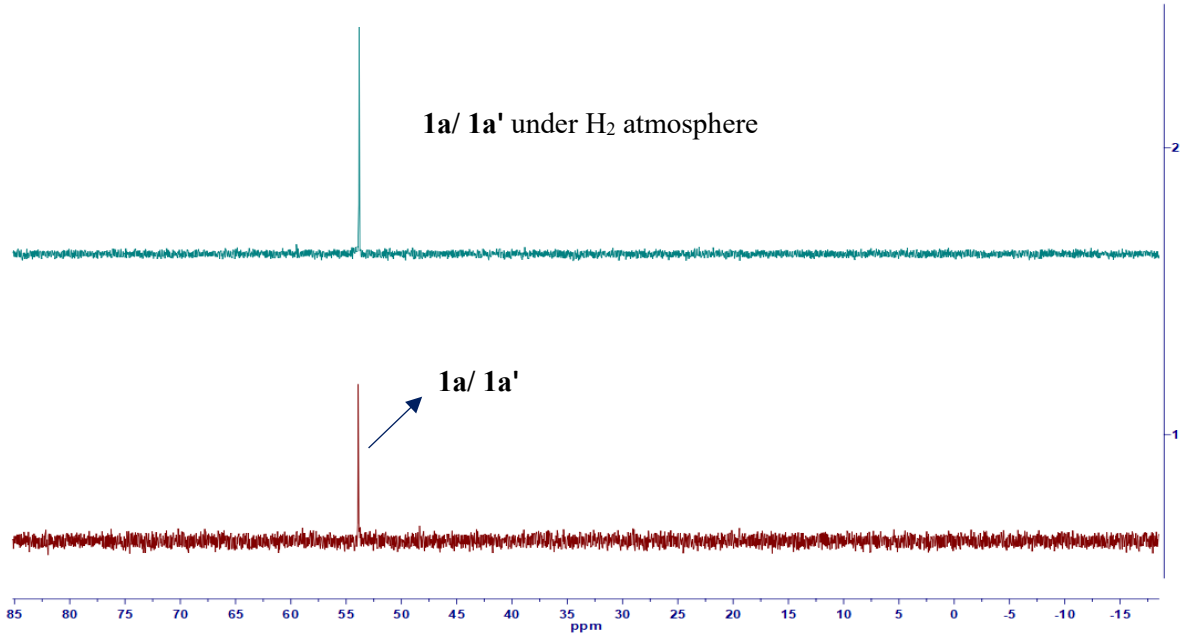


Figure S10 A couple of ^{31}P NMR spectra monitoring in situ generated **1a/ 1a'** in the presence of NEt_3 and refluxing under an H_2 atmosphere in C_6D_6

9. Homogeneity test by mercury drop experiment

In a 100 mL sealed tube with a sidearm, KOH (6.25 mmol), catalyst **1** (1 mol%), and degassed solvent (1 mL) were added sequentially in an N_2-filled glove box. The mixture was stirred for 5 min at room temperature followed by the addition of ethylene glycol (2.503 mmol) and mercury (2.503 mmol) into the tube. The tube was sealed properly, taken out from the glove box, and placed in a preheated oil bath at 100 °C for 2 h. The evolved gas volume was measured by the gas collecting system after cooling to room temperature. The reaction mixture was dissolved in H_2O (3 mL). The aliquot was taken for ^1H NMR analysis (Fig S11) using 2,6-lutidine (2.503 mmol) as the internal standard in D_2O.

Gas volume = 96 mL, EG conv = 82%, GA yield = 80%

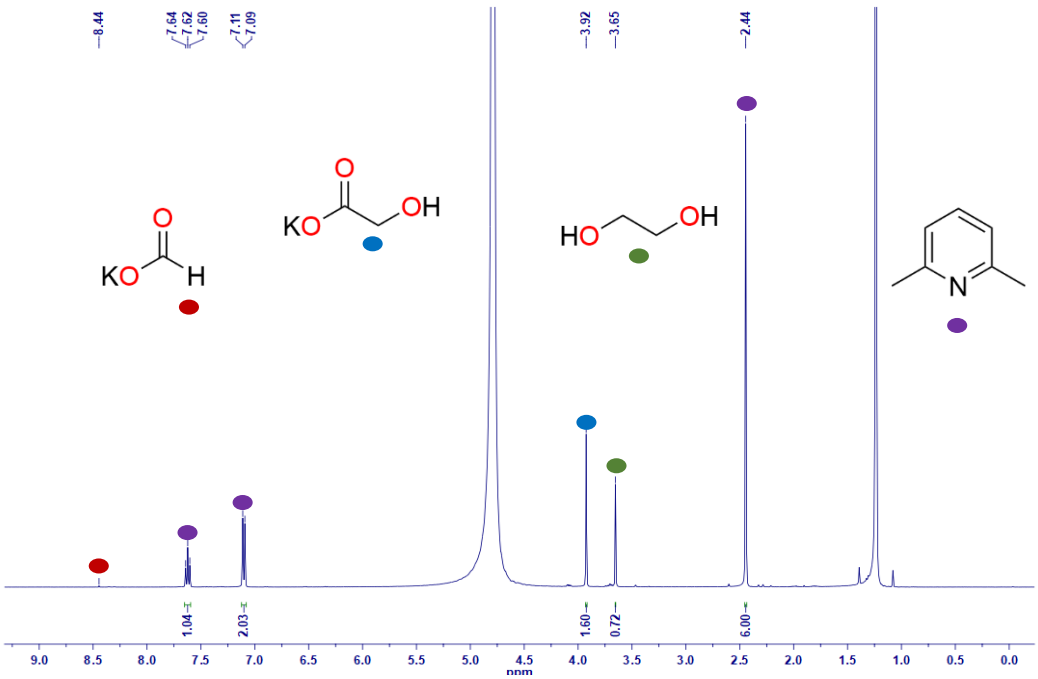
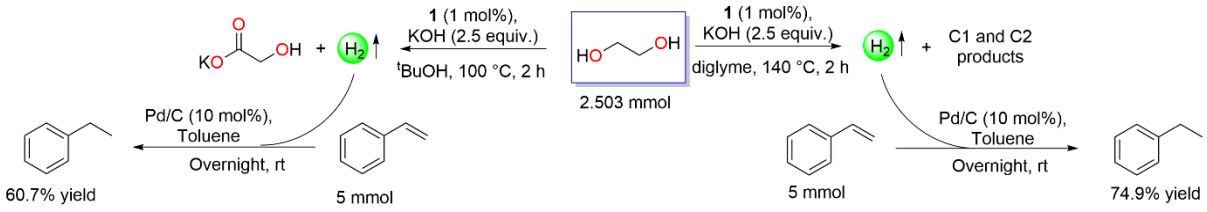


Figure S11 ^{1}H NMR spectrum in D_2O of the reaction mixture of dehydrogenation of ethylene glycol to glycolic acid by **1** in the presence of Hg in Table 1, entry 15

10. Utilization of evolved hydrogen from reforming of ethylene glycol for the hydrogenation of styrene catalyzed by Pd/C



In 50 mL sealed Schlenk tube with sidearm (reaction tube 1) KOH (6.25 mmol), **1** (1 mol%), ethylene glycol (2.503 mmol), solvent (1 mL) was added sequentially in N_2 glove box. The reaction tube 1 was placed in a preheated oil-bath at 100 °C/ 140 °C for 2 h. Another 100 mL sealed Schlenk tube with sidearm (reaction tube 2) was charged with solution of styrene (5 mmol) in toluene (10 mL) followed by addition of Pd/C (10 mol%). The air in reaction tube 2 was evacuated by three successive freeze-thraw-pump cycle and finally kept under vacuum. The reaction tube 2 was warm up to room temperature and connected to reaction tube 1 through a small silicon pipe. The reaction tube 1 was open up to release evolved hydrogen during reforming of ethylene glycol into the reaction tube 2. The reaction tube 2 was stirred overnight. The yield of ethylbenzene (w.r.t initially feed styrene) were determined by ^{1}H NMR analysis of reaction mixture in tube 2 using mesitylene (1 mmol) as an internal standard in $CDCl_3$ (Fig S12, S14). The glycolic acid was determined from ^{1}H NMR analysis of the reaction mixture of tube 1 by using 2,6-lutidine as internal standard in D_2O (Fig S13, S15).

Condition 1: **1** (1 mol%), ethylene glycol (2.503 mmol), ^{t}BuOH (1 mL), KOH (6.25 mmol), 100 °C, 2 h.

$\%Conv._{Styrene}$ = 60.4%; $\%Yield_{Ethyl\ benzene}$ = 60.7%, $\%Conv._{EG}$ = 94.5%; $\%Yield_{GA}$ = 92%

Condition 2: **1** (1 mol%), ethylene glycol (2.503 mmol), diglyme (1 mL), KOH (6.25 mmol), 140 °C, 2 h.

%Conv. $_{Styrene}$ = 79.6%; %Yield $_{Ethyl\ benzene}$ = 74.9%, %Yield $_{GA}$ = 56.5%

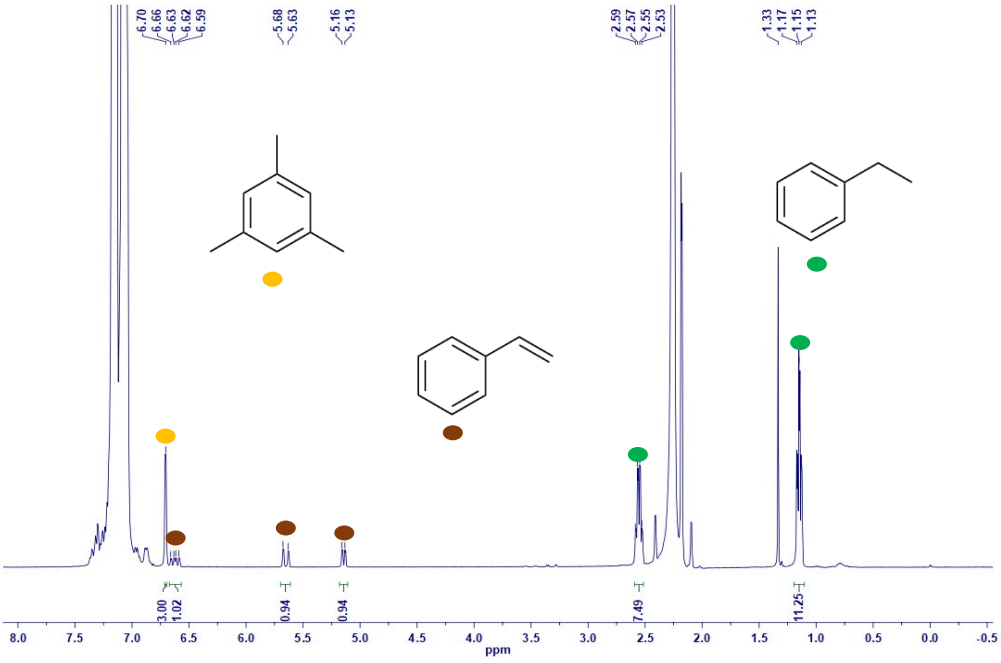


Figure S12 ^{1}H NMR spectrum in $CDCl_3$ of tube 2 reaction mixture Pd/C hydrogenation of styrene using evolved hydrogen produced during reforming of ethylene glycol in ^{t}BuOH at 100 °C for 2 h

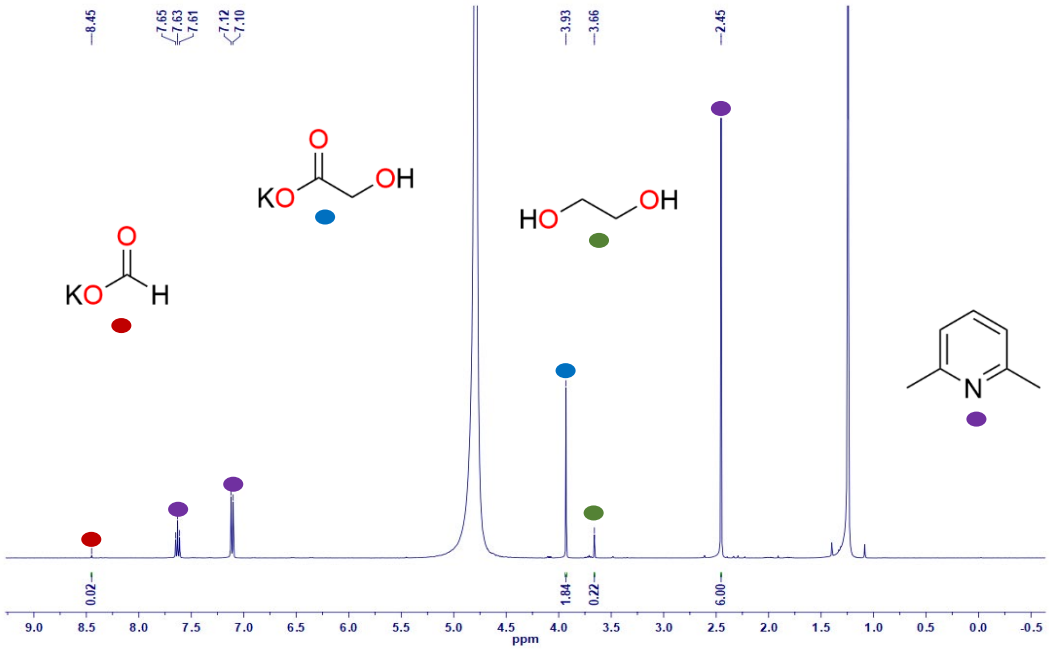


Figure S13 ^{1}H NMR spectrum in D_2O of tube 1 reaction mixture of Pd/C catalyzed hydrogenation of styrene using evolved hydrogen produced during reforming of ethylene glycol in ^{t}BuOH at 100 °C for 2 h

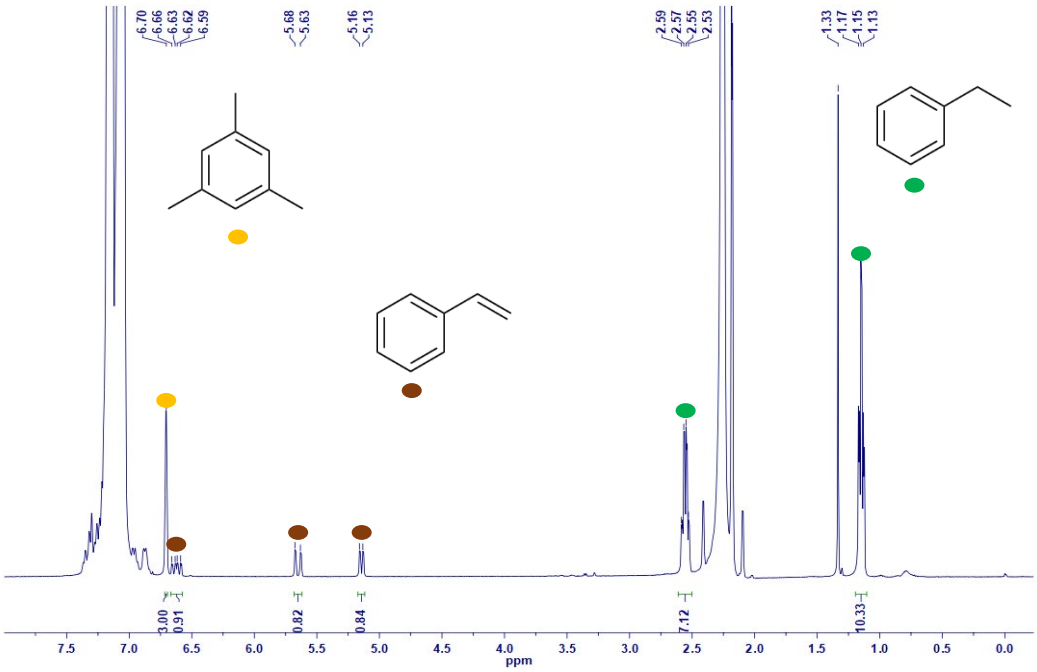


Figure S14 ^{1}H NMR spectrum in $CDCl_3$ of tube 2 reaction mixture of Pd/C catalyzed hydrogenation of styrene using evolved hydrogen produced during reforming of ethylene glycol in diglyme at 140 °C for 2 h

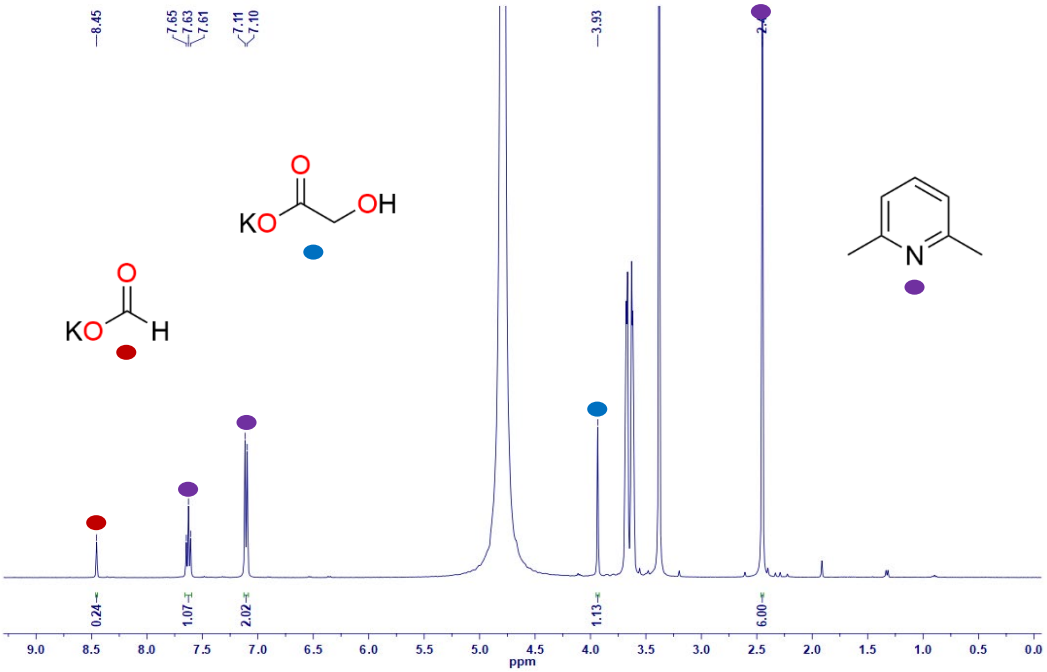


Figure S15 ^{1}H NMR spectrum in D_2O of tube 1 reaction mixture of Pd/C catalyzed hydrogenation of styrene using evolved hydrogen produced during reforming of ethylene glycol in diglyme at 140 °C for 2 h

11. GC analysis of evolved H_2 gas during reforming of ethylene glycol

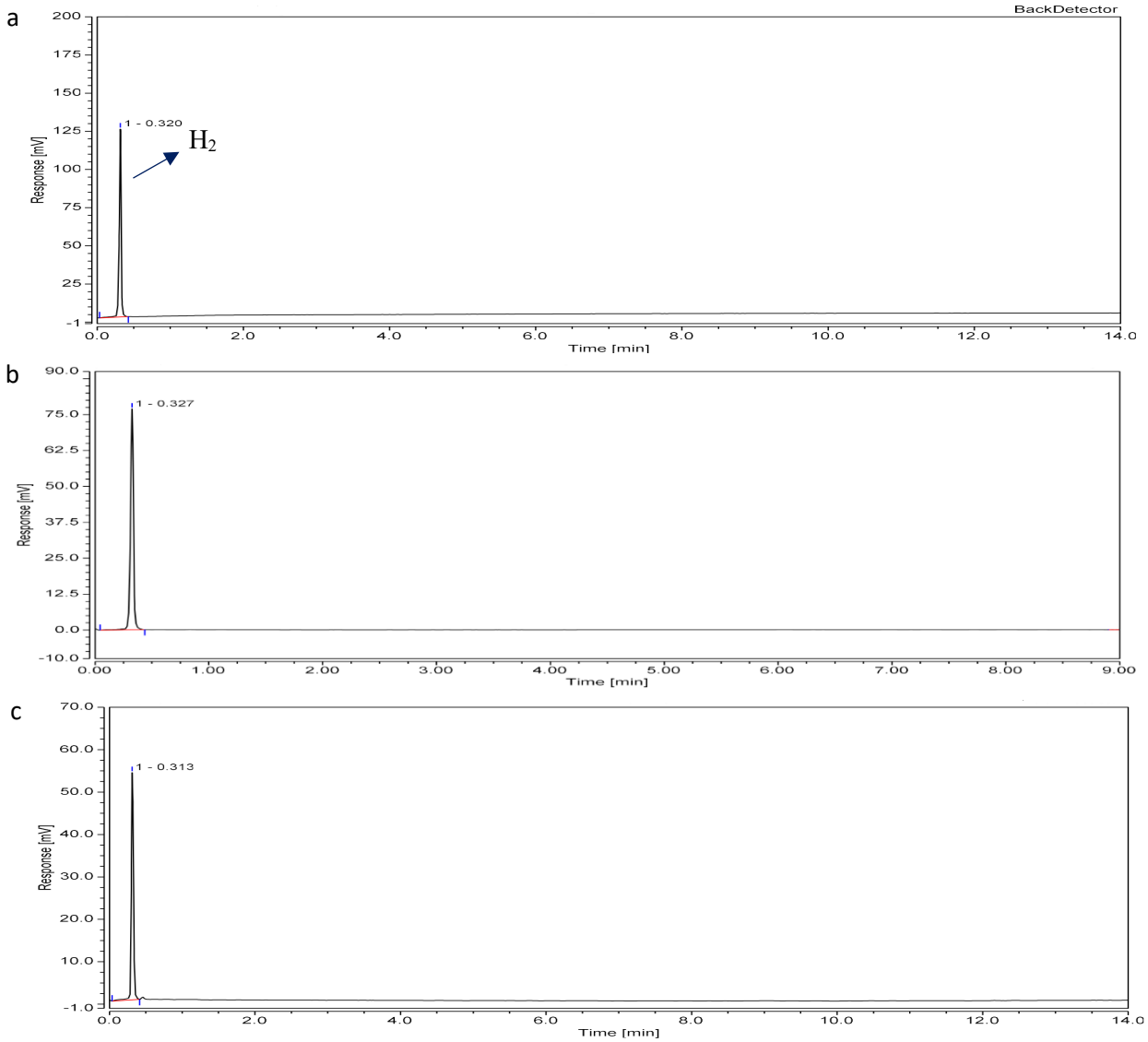


Figure S16A GC TCD analysis for H_2 of 1 mL of gas a) Pure H_2 b) evolved from the dehydrogenation of ethylene glycol in ^{t}BuOH at 100 °C after 2 h catalyzed by **1** c) evolved from reforming of ethylene glycol in diglyme at 140 °C after 12 h catalyzed by **1**.

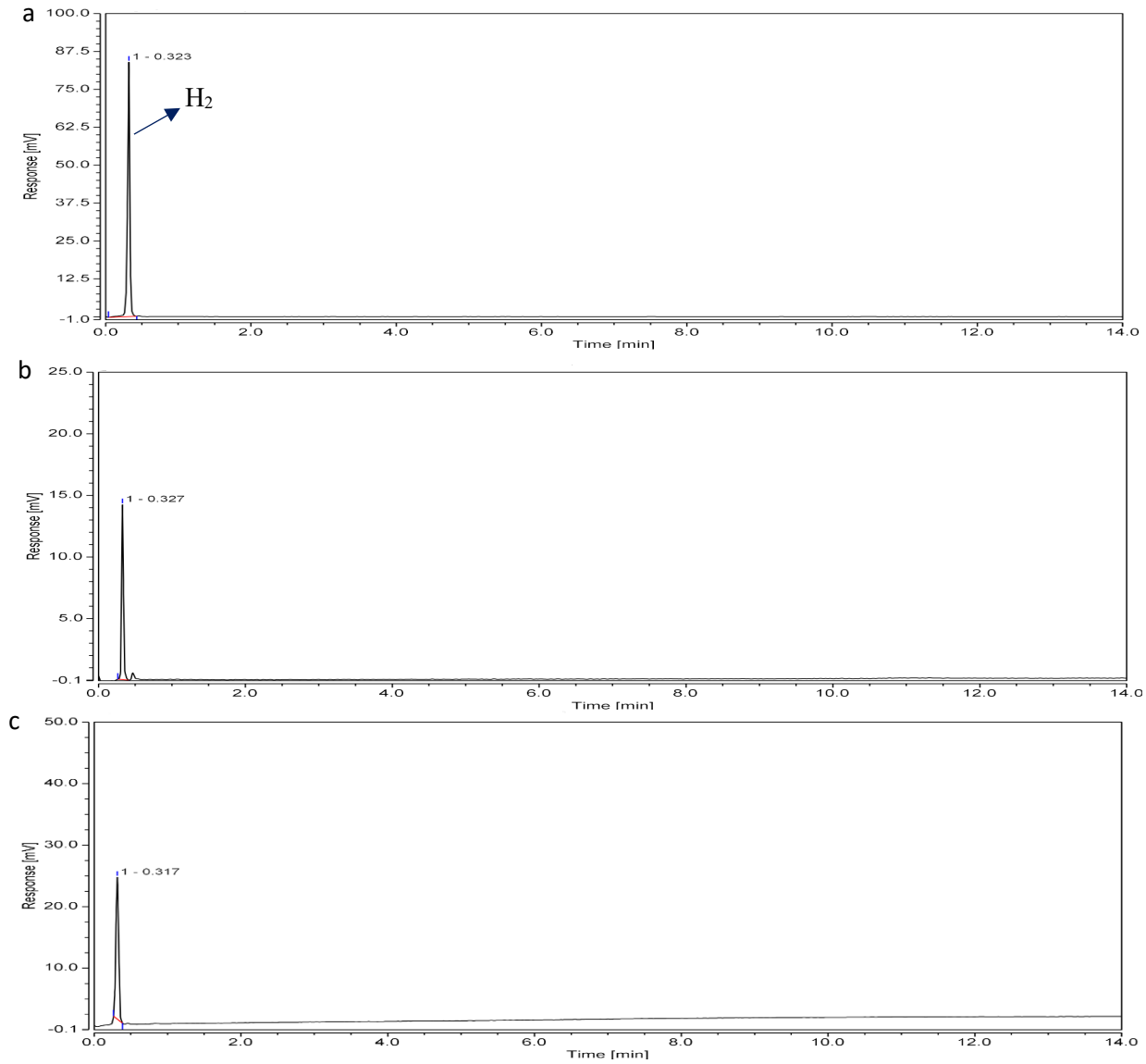


Figure S16B GC TCD analysis for H_2 of 1 mL of gas a) evolved from dehydrogenation of ethylene glycol in solvent-free condition at 140 °C after 96 h catalyzed by **1** b) evolved from the dehydrogenation of ethylene glycol in ^{t}BuOH at 100 °C after 2 h catalyzed by **2** c) evolved from the dehydrogenation of ethylene glycol in ^{t}BuOH at 100 °C after 2 h catalyzed by $RuCl_2(PPh_3)_3$.

12. GC analysis of gas evolved during control experiments

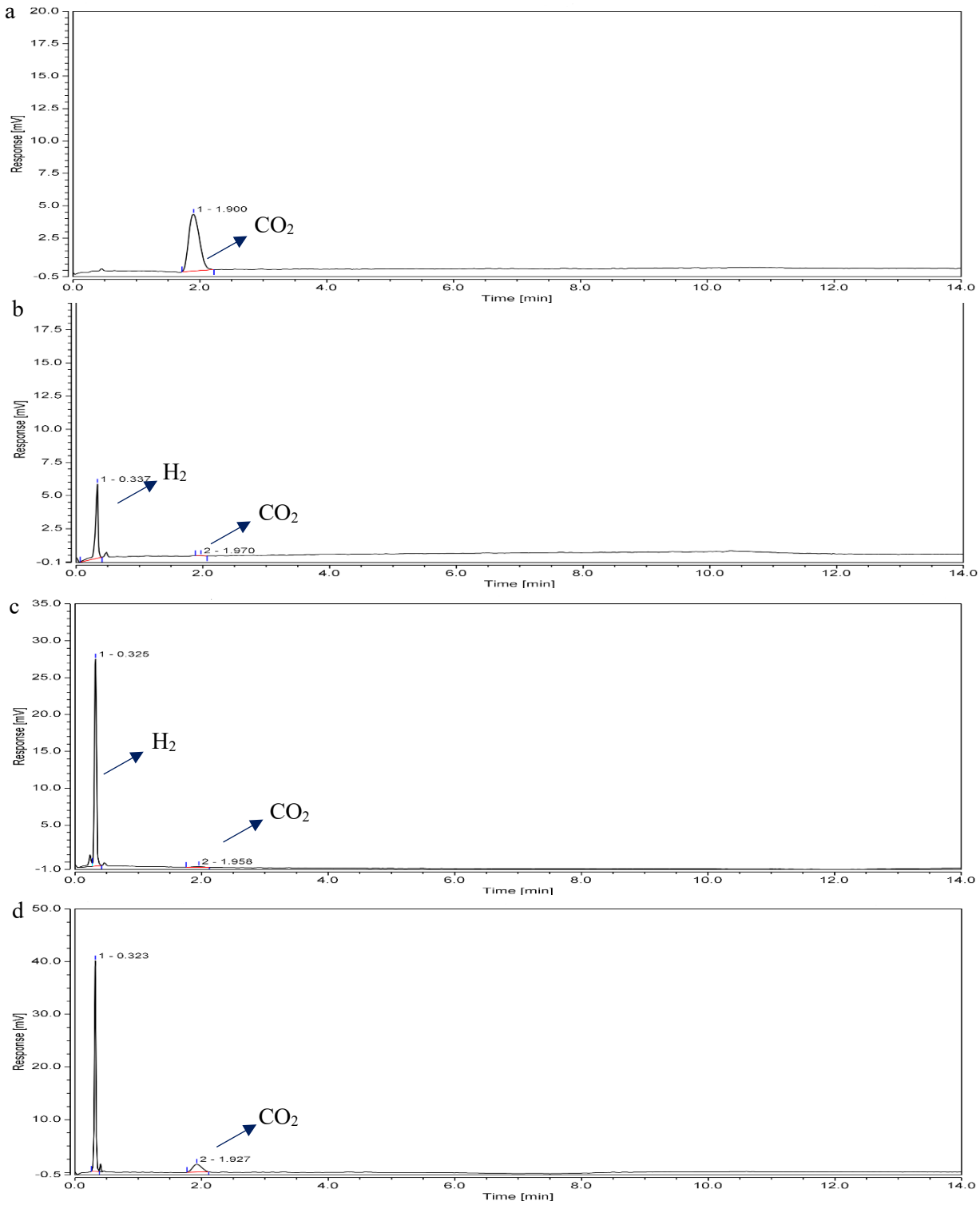


Figure S17 GC TCD analysis for H_2 and CO_2 of 1 mL of gas a) Pure CO_2 b) evolved from the decomposition of glyoxal by **1** c) evolved from the dehydrogenation of glycolic acid in diglyme at 140 °C after 12 h d) evolved from dehydrogenation of formic acid in diglyme at 140 °C after 12 h

13. Possible reaction mechanism of reforming of ethylene glycol catalyzed by 1 to produce hydrogen

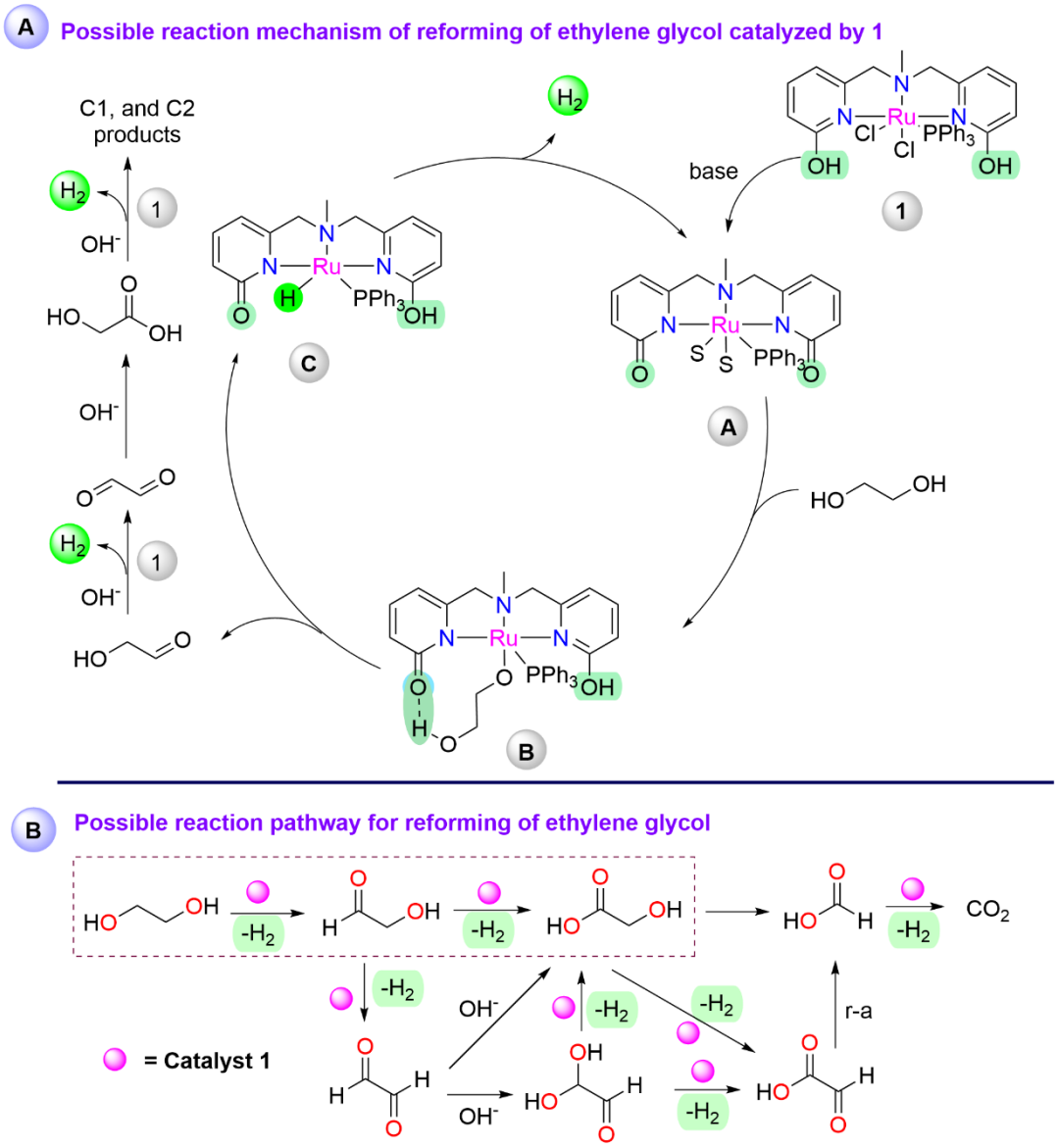


Figure S18 Possible reaction mechanism of reforming of ethylene glycol

14. Spectroscopic data

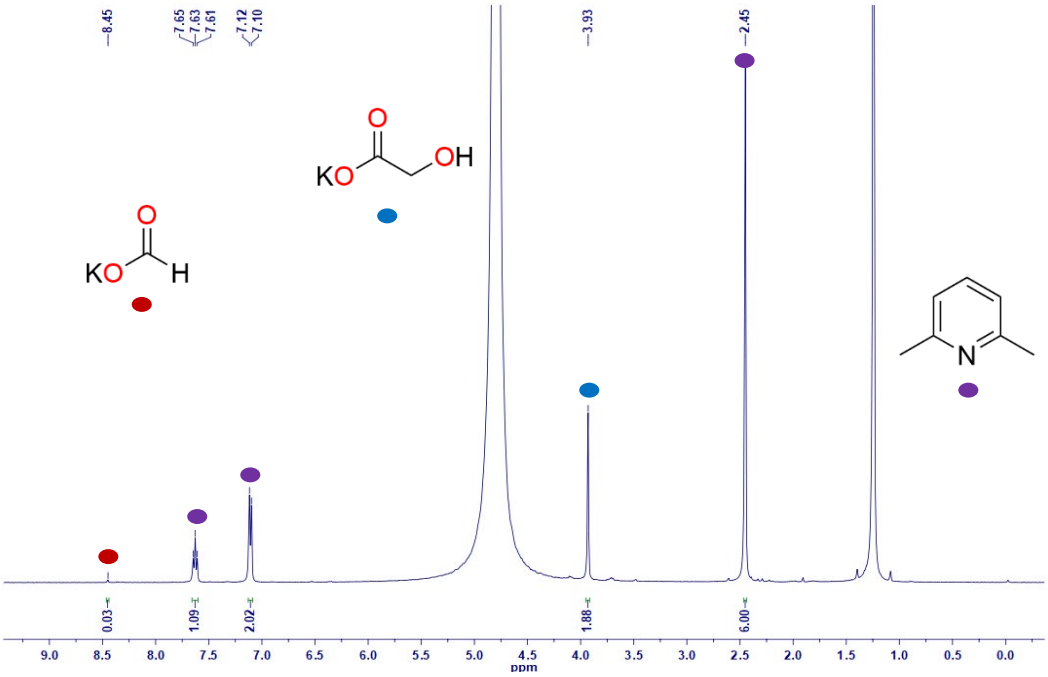


Figure S19 ^{1}H NMR spectrum in D_2O of the reaction mixture of dehydrogenation of ethylene glycol to glycolic acid (Table 1, entry 1)

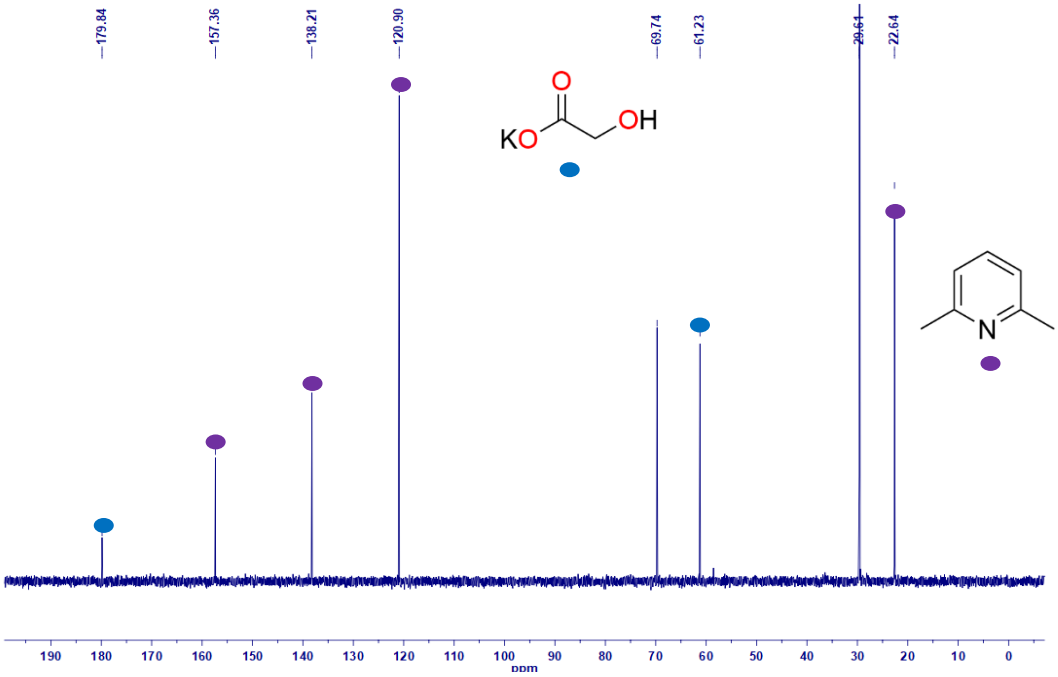


Figure S20 ^{13}C NMR spectrum in D_2O of the reaction mixture of dehydrogenation of ethylene glycol to glycolic acid (Table 1, entry 1)

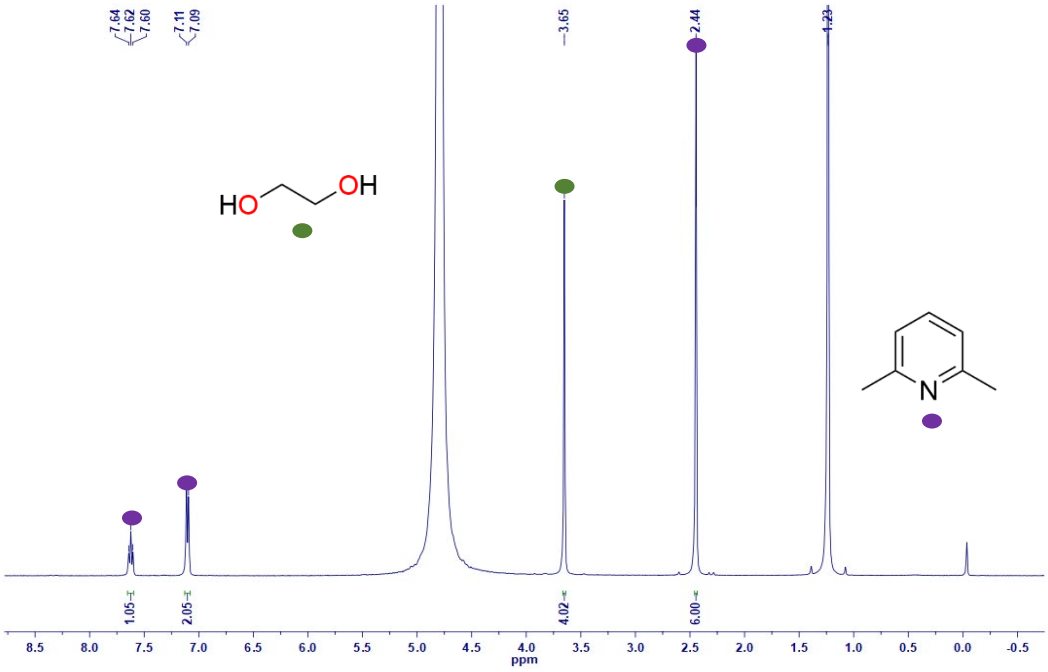


Figure S21 ^{1}H NMR spectrum in D_2O of the reaction mixture of reforming of ethylene glycol in the absence of catalyst **1** (Table 1, entry 5)

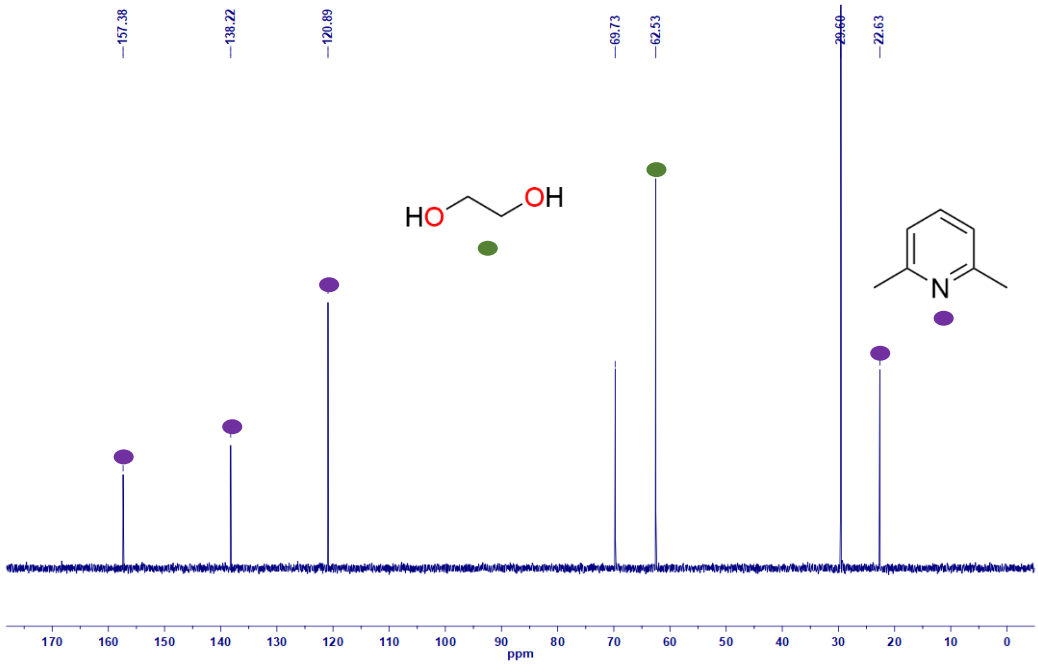


Figure S22 ^{13}C NMR spectrum in D_2O of the reaction mixture of reforming of ethylene glycol in the absence of catalyst **1** (Table 1, entry 5)

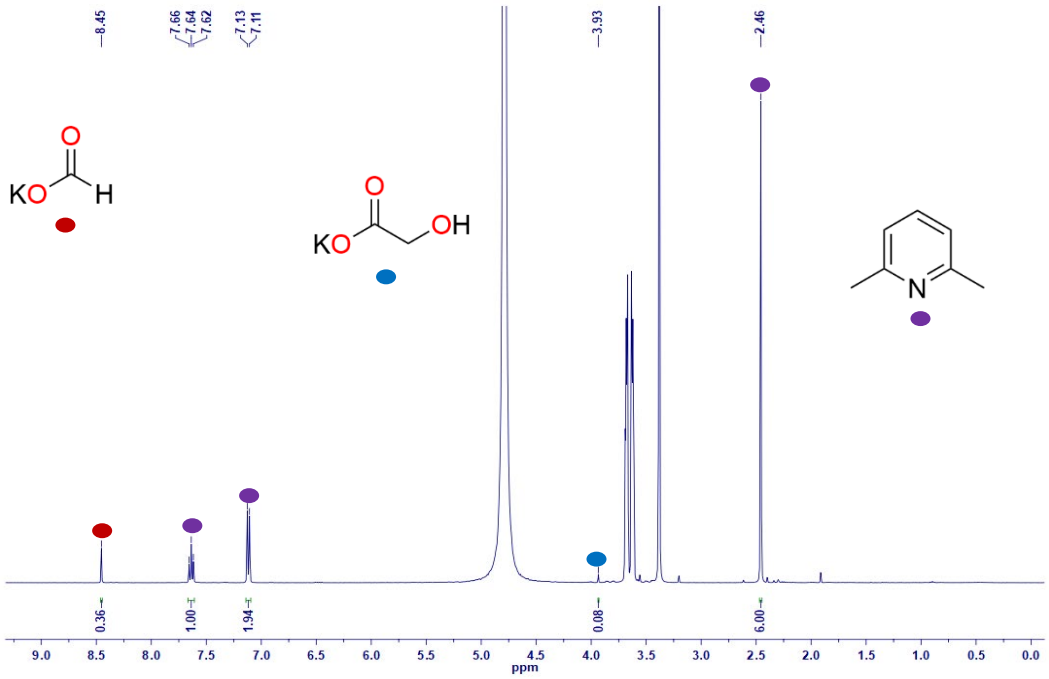


Figure S23 ^{1}H NMR spectrum in D_2O of the reaction mixture of reforming of ethylene glycol for hydrogen production by **1** in diglyme at 140 °C for 12 h (Table 1, entry 13)

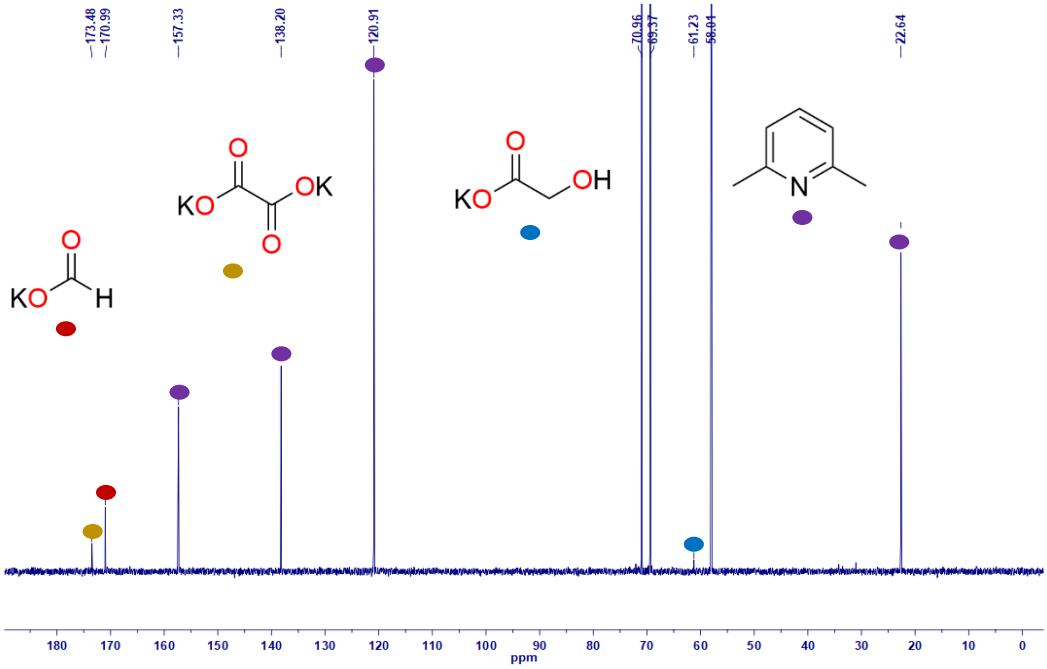


Figure S24 ^{13}C NMR spectrum in D_2O of the reaction mixture of reforming of ethylene glycol for hydrogen production by **1** in diglyme at 140 °C for 12 h (Table 1, entry 13)

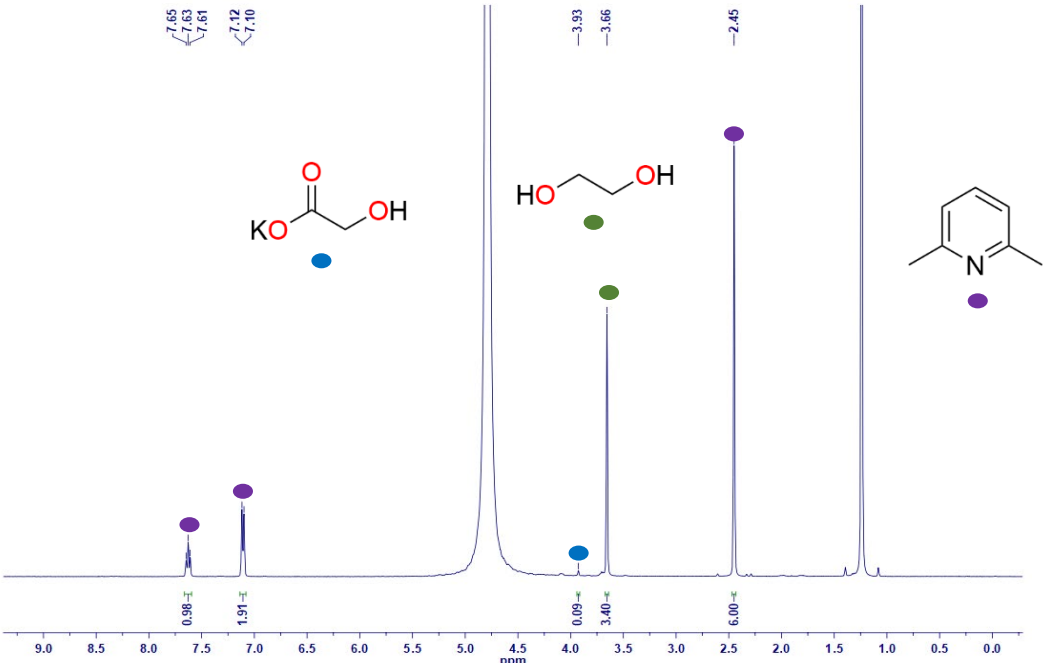


Figure S25 ^{1}H NMR spectrum in D_2O of the reaction mixture of dehydrogenation of ethylene glycol to glycolic acid by $RuCl_2(PPh_3)_3$ (Table 1, entry 6)

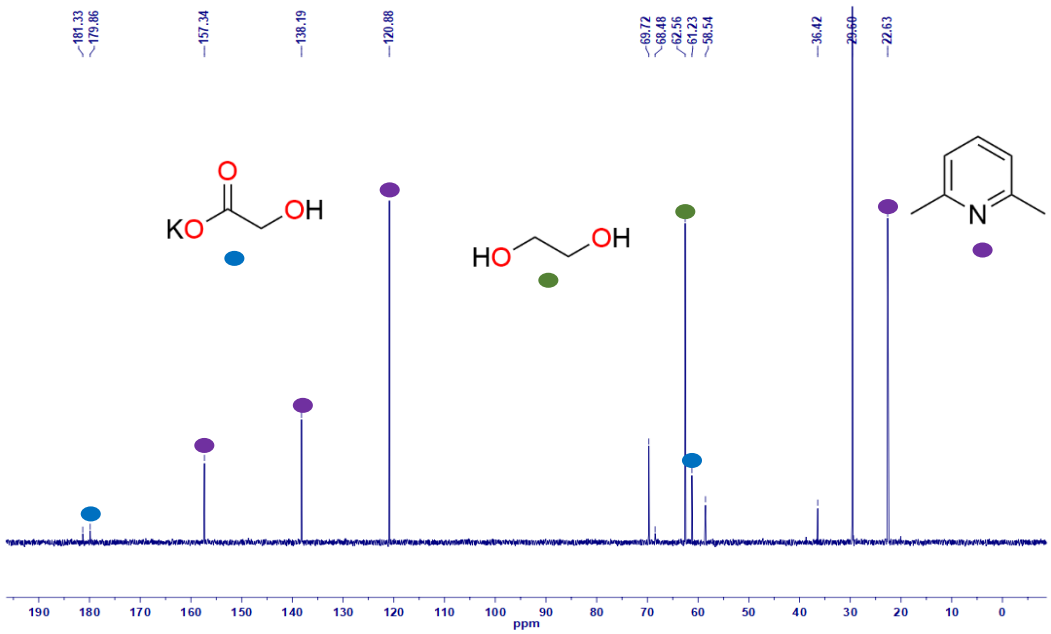


Figure S26 ^{13}C NMR spectrum in D_2O of the reaction mixture of dehydrogenation of ethylene glycol to glycolic acid by $RuCl_2(PPh_3)_3$ (Table 1, entry 6)

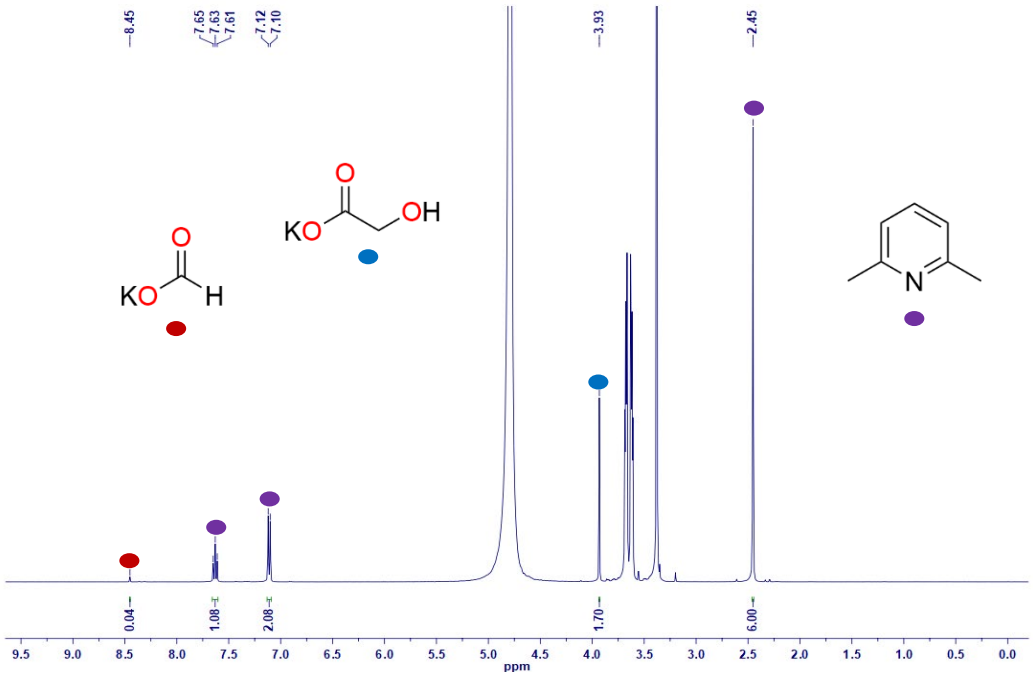


Figure S27 ^{1}H NMR spectrum in D_2O of the reaction mixture of transformation of glyoxal without any catalyst in the presence of KOH

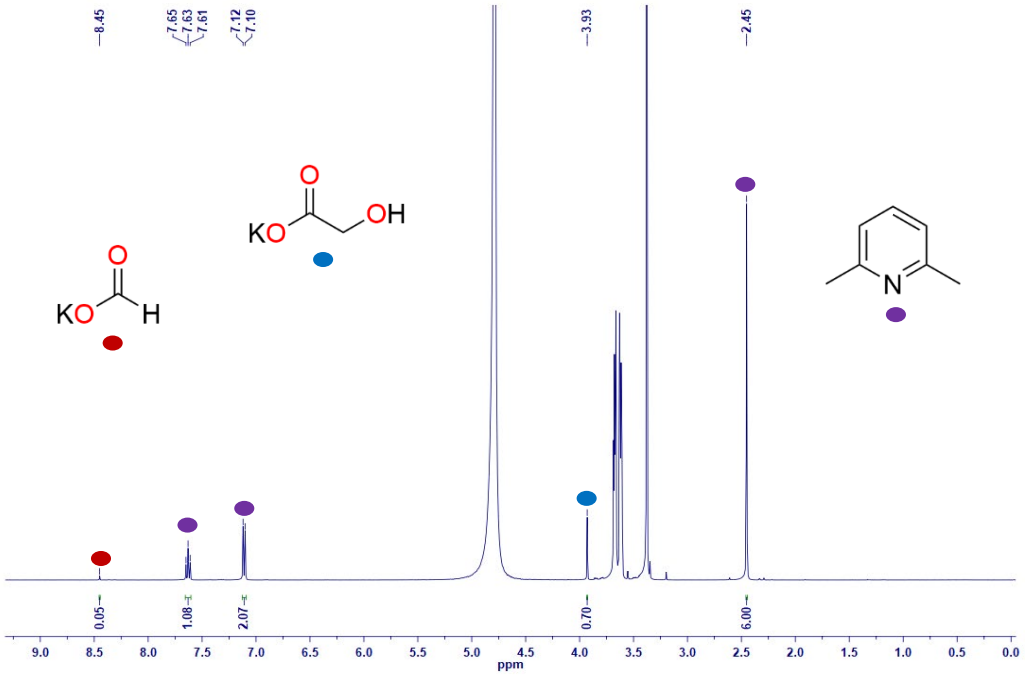


Figure S28 ^{1}H NMR spectrum in D_2O of the reaction mixture of transformation of glyoxal by catalyst **1** in the presence of KOH

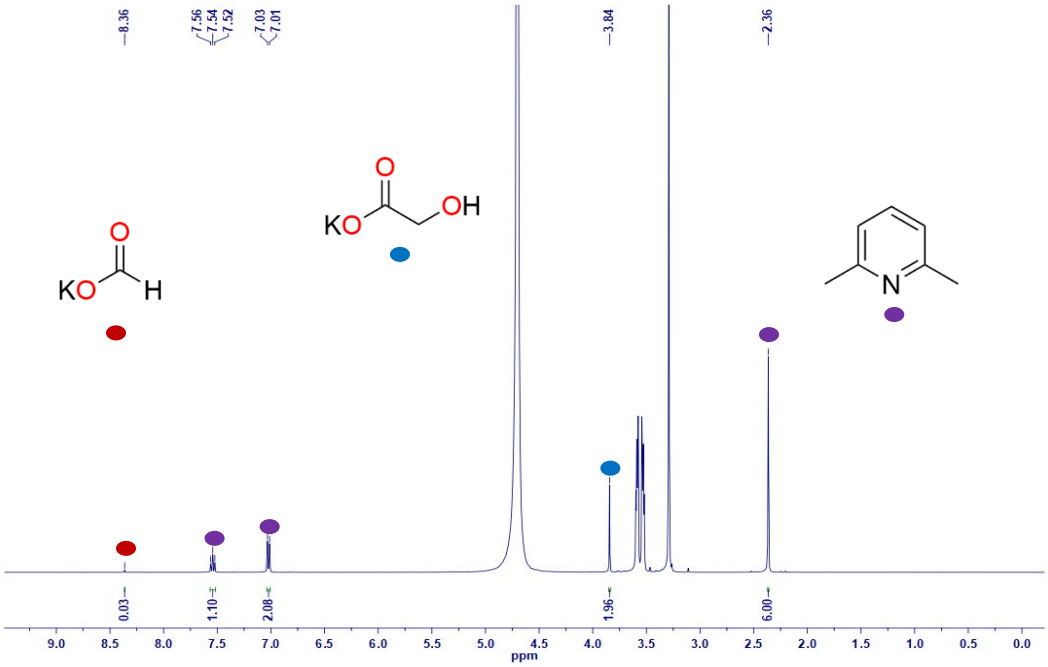


Figure S29 ^{1}H NMR spectrum in D_2O of the reaction mixture of transformation of glycolic acid without any catalyst in the presence of KOH

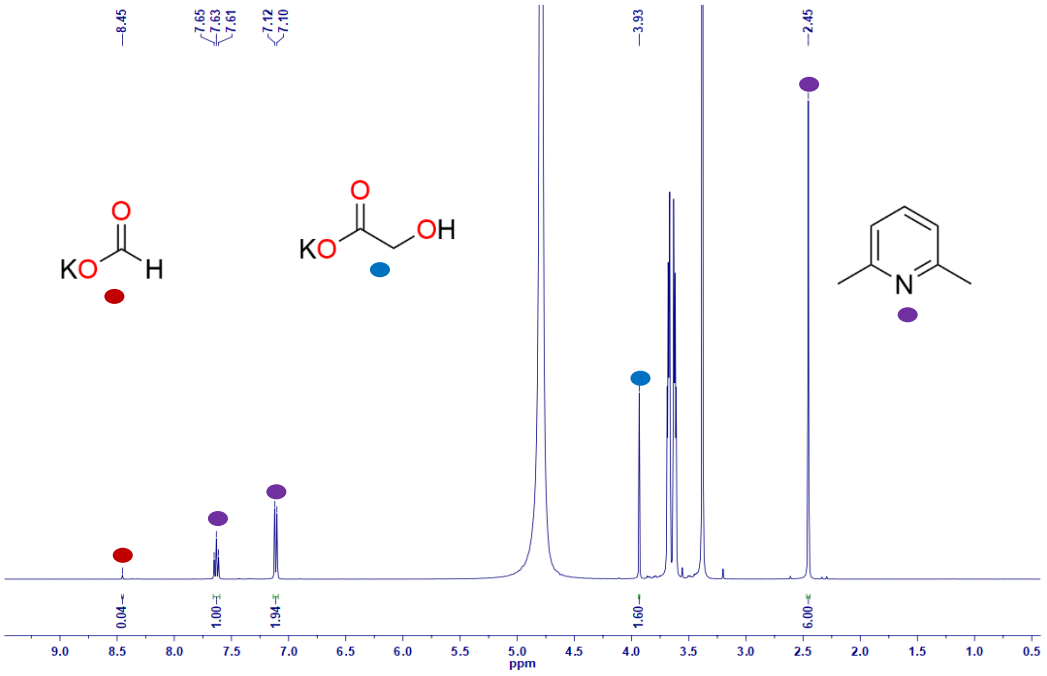


Figure S30 ^{1}H NMR spectrum in D_2O of the reaction mixture of dehydrogenation of glycolic acid by catalyst **1**

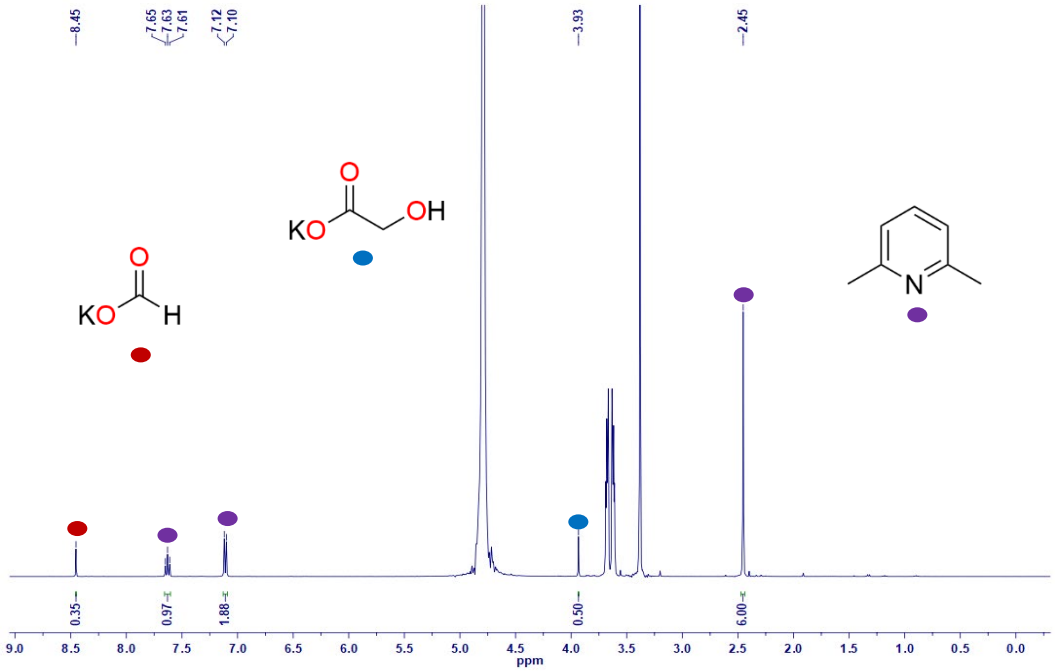


Figure S31 ^{1}H NMR spectrum in D_2O of the reaction mixture of dehydrogenation of 1:1 mixture of glycolic acid and ethylene glycol by catalyst **1**

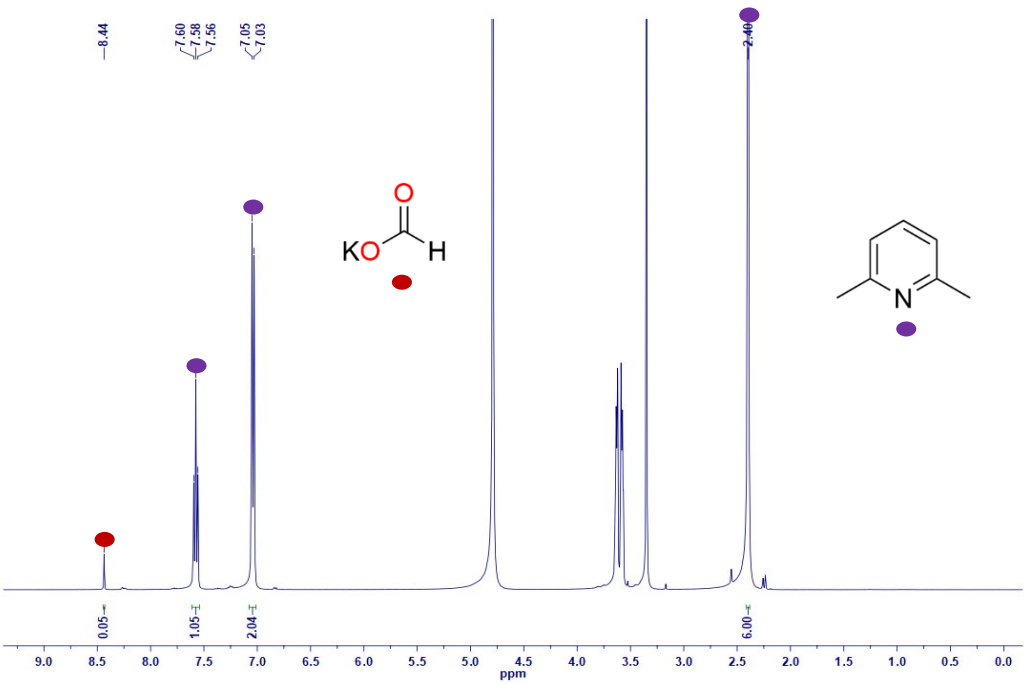


Figure S32 ^{1}H NMR spectrum in D_2O of the reaction mixture of dehydrogenation of formic acid by catalyst **1**

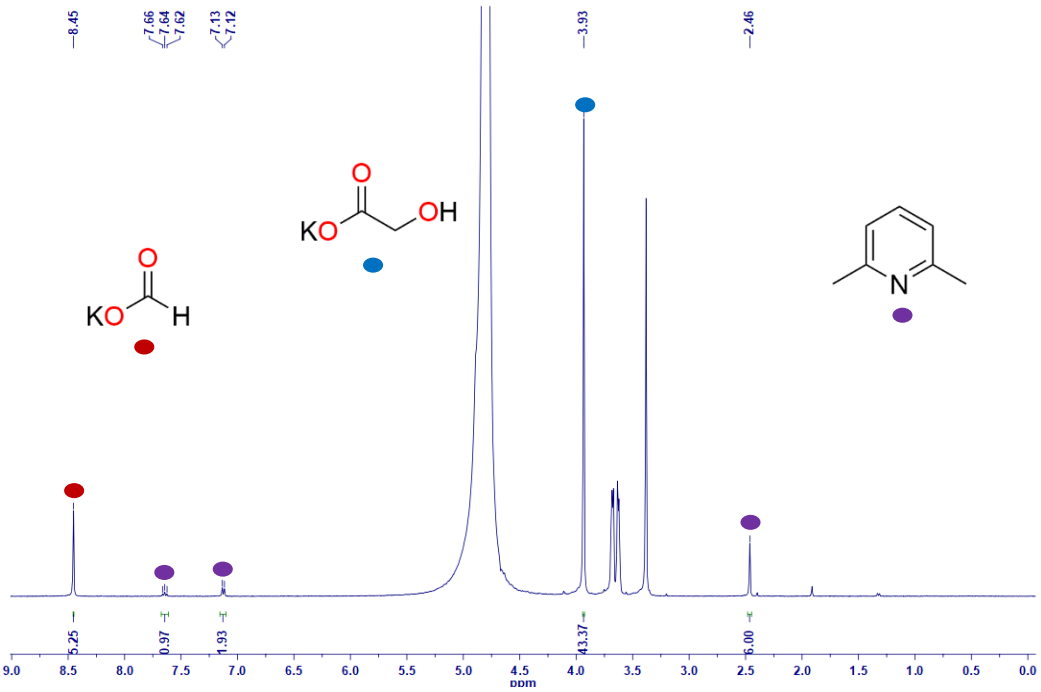


Figure S33 ^{1}H NMR spectrum in D_2O of the scale-up reaction of ethylene glycol by catalyst **1**

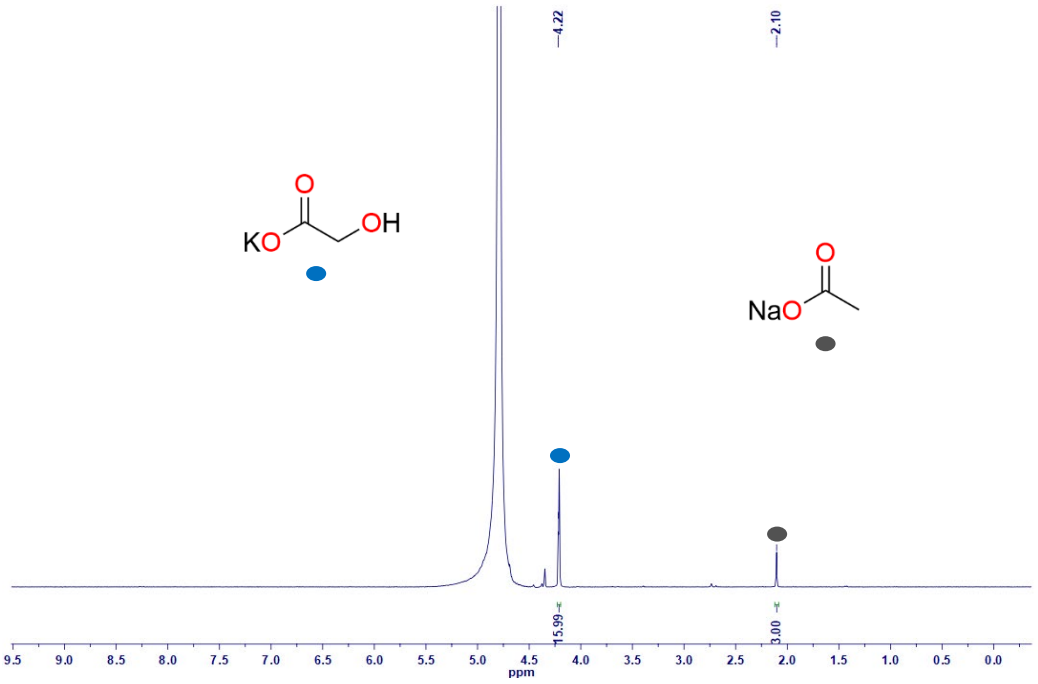


Figure S34 ^{1}H NMR spectrum in D_2O of the free glycolic acid after acid workup during scale-up reaction of ethylene glycol by catalyst **1**

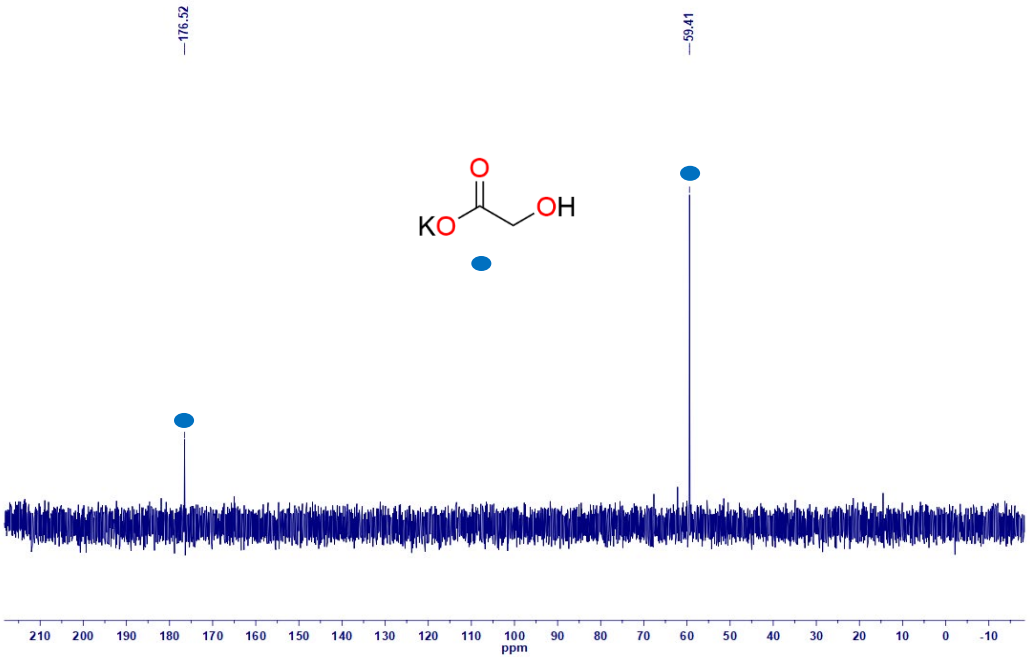


Figure S35 ^{13}C NMR spectrum in D_2O of the free glycolic acid after acid workup during scale-up reaction of ethylene glycol by catalyst **1**

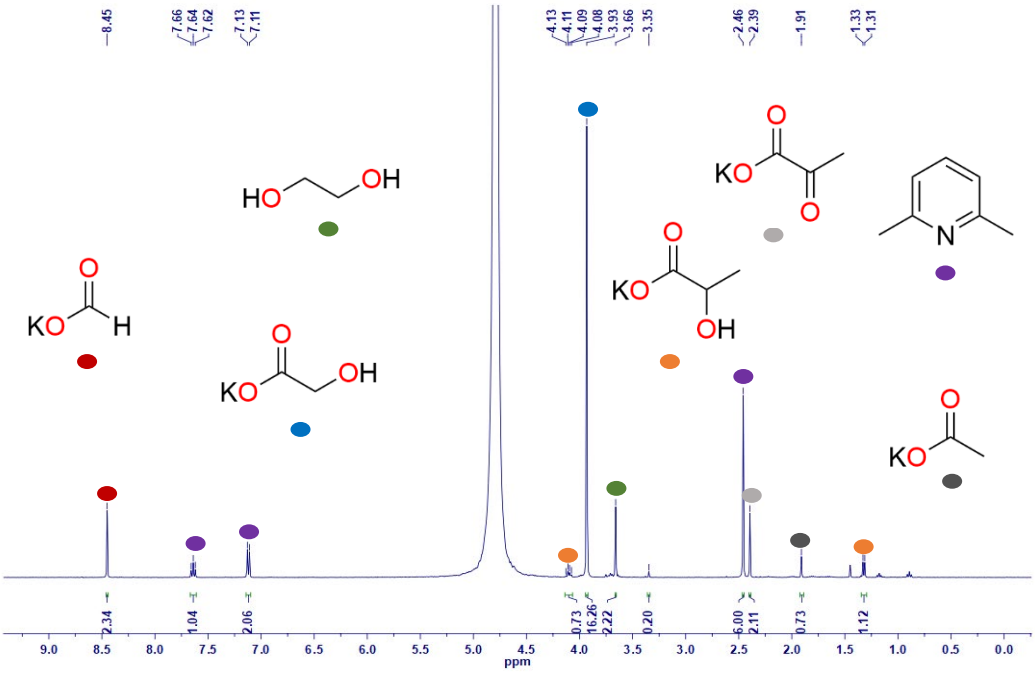


Figure S36 ^{1}H NMR spectrum in D_2O of reforming of ethylene glycol in solvent-free condition catalyzed by **1**

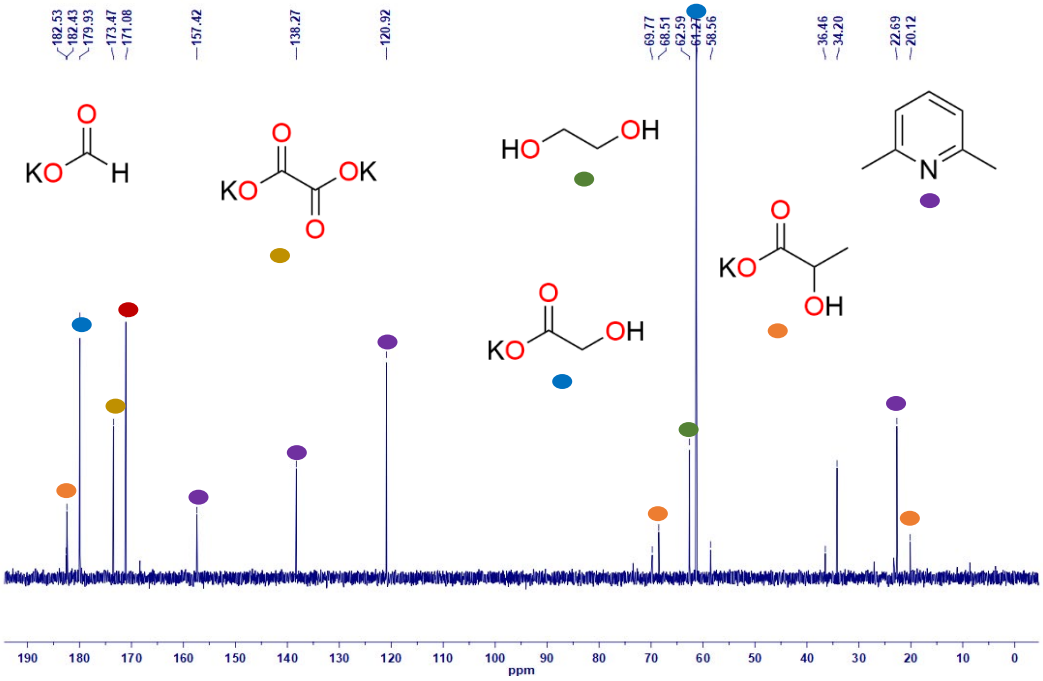


Figure S37 ^{13}C NMR spectrum in D_2O of reforming of ethylene glycol in solvent-free condition catalyzed by **1**

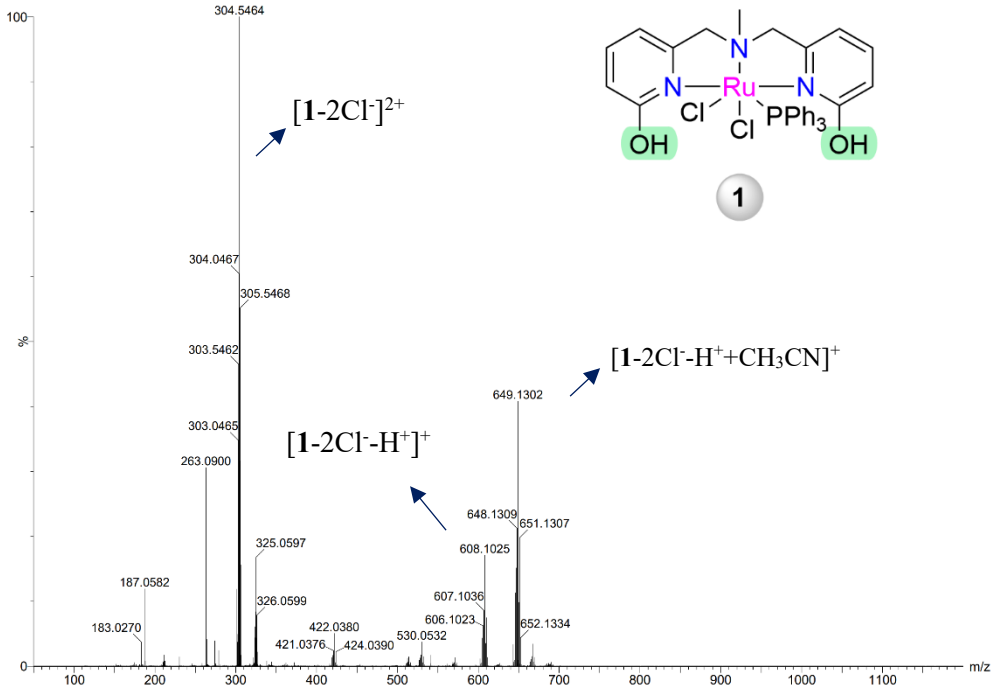


Figure S38 Mass spectrum of analysis of reaction mixture after reforming of ethylene glycol. Reaction conditions: ethylene glycol (2.503 mmol), KOH (6.25 mmol), ^{t}BuOH (1 mL), 100 °C, 2 h.

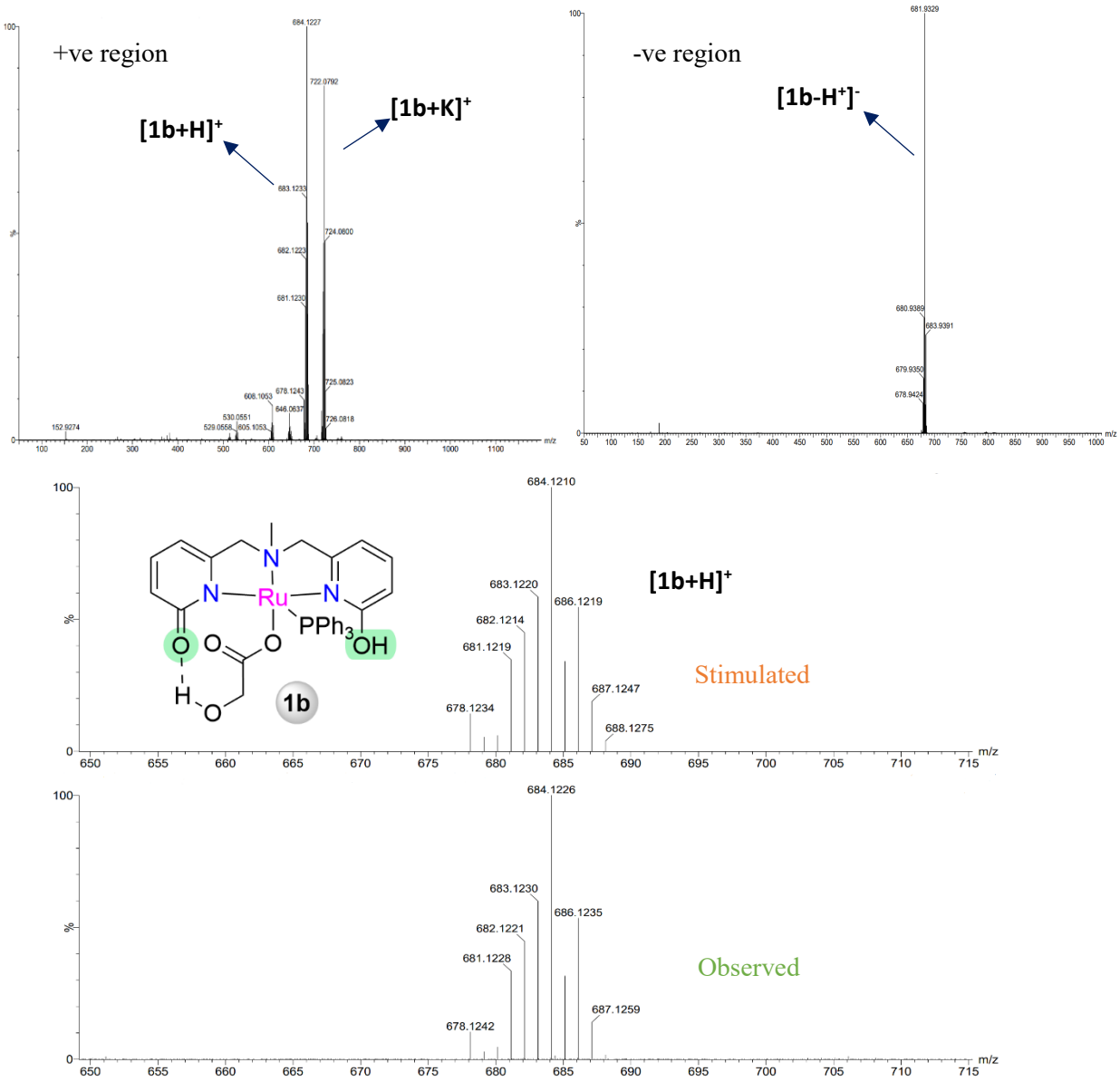


Figure S39 Mass spectrum of analysis of the treatment of glycolic acid with complex **1** in the presence of NEt_3

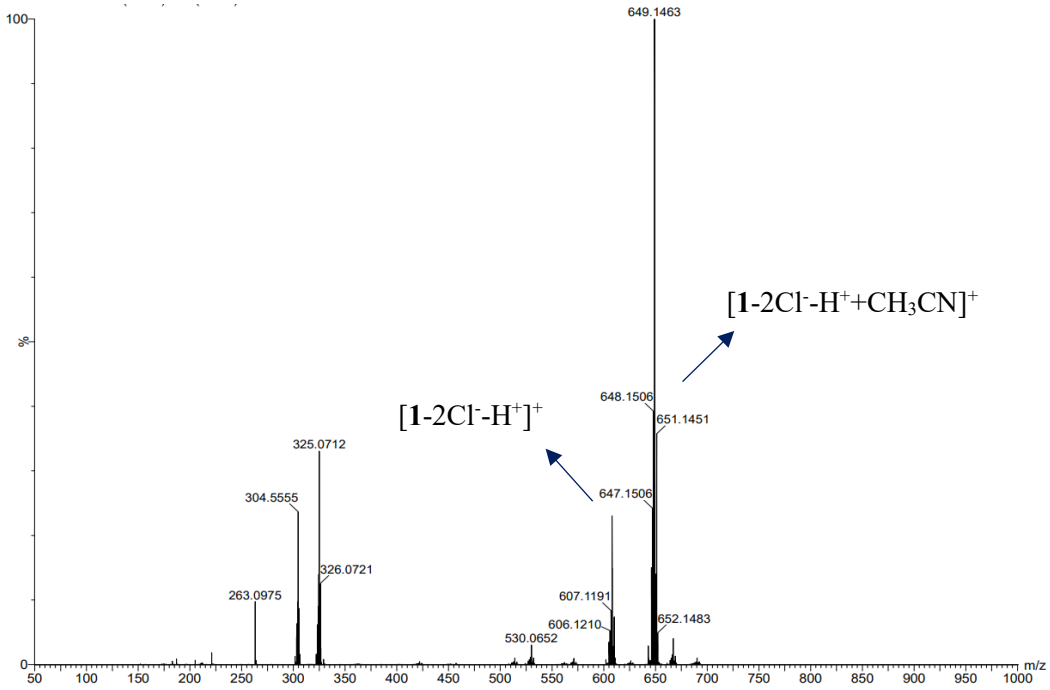


Figure S40 Mass spectrum of analysis of the treatment of complex **1** with NEt_3

15. References

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2 Y. Zhan, W. Hou, G. Li, Y. Shen, Y. Zhang and Y. Tang, *ACS Sustain. Chem. Eng.*, 2019, **7**, 17559–17564.

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