Supplementary Information

Catalytic Hydrogenation of Carbon Dioxide to Methanol by a Homogenous Ruthenium(II) Hydrido Carbonyl Complexes

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Table S1. Crystal data and structure refinement for complex **2**.

Identification code	Complex **2**	
Empirical formula	$C_{41}H_{37}F_6N_2OP_3Ru$	
Formula weight	881.71	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/m	
Unit cell dimensions	a = 9.2610(11) Å	α= 90°.
	b = 22.228(2) Å	β= 110.918(14)°.
	c = 10.4259(13) Å	γ = 90°.
Volume	2004.8(4) Å3	
Z	2	
Density (calculated)	1.461 Mg/m^3	
Absorption coefficient	0.573 mm^{-1}	
F(000)	896	
Crystal size	0.230 x 0.180 x 0.160 mm^3	
Theta range for data collection	2.984 to 27.498°	
Index ranges	-12<=h<=11, -28<=k<=28, -13<=l<=13	
Reflections collected	29409	
Independent reflections	4711 [R(int) = 0.0976]	

Completeness to theta = 25.242°	99.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4711 / 94 / 264
Goodness-of-fit on F^2	1.228
Final R indices [I>2sigma(I)]	R1 = 0.0736, wR2 = 0.1855
R indices (all data)	R1 = 0.0774, wR2 = 0.1882
Largest diff. peak and hole	1.754 and -1.106 e.Å^{-3}

Table S 2. Bond lengths [Å] and angles [°] for complex **2**.

Ru(1)-C(1)	1.847(7)
Ru(1)-N(2)	2.085(6)
Ru(1)-N(1)	2.163(6)
Ru(1)-P(1)	2.3599(12)
Ru(1)-P(1)$^{\#1}$	2.3600(12)
Ru(1)-H(1)	1.6108
N(1)-C(2)	1.116(10)
N(2)-C(4)	1.126(11)
O(1)-C(1)	1.135(9)
P(2)-F(1)	1.429(9)
P(2)-F(4)	1.455(9)
P(2)-F(4)$^{\#2}$	1.455(9)
P(2)-F(3)$^{\#2}$	1.472(8)
P(2)-F(3)	1.472(8)
P(2)-F(2)	1.476(11)
C(1)-Ru(1)-N(2)	169.0(3)
C(1)-Ru(1)-N(1)	100.1(3)
N(2)-Ru(1)-N(1)	90.9(3)
C(1)-Ru(1)-P(1)	88.49(4)
N(2)-Ru(1)-P(1)	90.16(4)
C(5)-Ru(1)-P(1)	91.4(7)
N(2)-Ru(1)-P(1)	91.4(6)
N(1)-Ru(1)-P(1)	97.12(3)
P(1)-Ru(1)-P(1)$^{\#1}$	165.76(6)
N(1)-Ru(1)-H(1)	178.00(3)
N(2)-Ru(1)-H(1)	87.20
P(1)-Ru(1)-H(1)	82.90(6)
C(2)-N(1)-Ru(1)	172.2(7)
C(4)-N(2)-Ru(1)	167.2(9)
O(1)-C(1)-Ru(1)	172.8(8)
N(1)-C(2)-C(3)	177.7(11)

Table S3. Hydrogen bonds in complex **2**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(5)-H(5C)...O(1)$^{\#1}$	0.96	2.60	2.964	103.0
Symmetry transformations used to generate equivalent atoms: $^{\#1}$= x, y, 1+z.				

Entry	Pre-catalyst	Solvent	Additives	$P_{H2/CO2}$ (bar)	T/°C	t/h	TOF/(h mol)$^{-1}$	TON	Ref.
1.	Ru(triphos)(TMM)	THF/MeOH	$HNTf_2$	60/20	140	24	70	221	1
2.	[Co/triphos]	THF/EtOH	$HNTf_2$	70/20	100	96	~1	78	2
3.	Ru(tdppcy)(TMM)	EtOH	$Al(OTf)_3$	90/30	120	20	458	2148	3
4.	$[FeCl_2\{\kappa^3\text{-}HC(pz)_3\}]$	—	PEHA	56/19	80	36	66	2387	4
5.	$Ru[P(CH_2CH_2PPh_2)_3](H)_2$, $Sc(OTf)_3$, Ir-PCP^{tBu}	EtOH	—	80/10	155	40	10.7	428	5
6.	Ru-MACHO ($ZnBr_2$)	THF (—)	KO^{t}Bu (nBu_4NBr)	50/— (—/40)	140 (140)	72 (3)	1200	8700	6
7.	Ru-MACHO (Ru-MACHO)	THF (THF)	KO^{t}Bu (Morpholine)	50/- (35/35)	160 (120)	1 (40)	3600	3600	7
8.	Ru-MACHO-BH	THF	$NHMe_2$, K_3PO_4	50/2.5	95 to 155	18 + 18	6	220	8
9.	Ru-MACHO-BH	Triglyme, THF, or 1,4-dioxane/water	PEHA, K_3PO_4	67.5/7.5	145	200	70	>2000	9
10.	Ru-MACHO-BH (—)	2-MTHF (Water)	K_3PO_4 (PEHA)	70/— (—/0.07)	145 (r.t.)	72 (4)	~70	520	10
11.	Ru-MACHO-BH	THF	Pyrrolizidines, K_3PO_4	65/10	155	134	>1	28	11
12.	Ru-MACHO-BH	THF	Poly(ethyleneimine)	60/20	150	100	6	599	12
13.	Ru-MACHO-BH	Triglyme	PEHA, K_3PO_4	56/19	145	244	41	9900	13
14.	Ru-MACHO-BH	THF	SSA	60/20	145	40	13	520	14
15.	Ru-MACHO-BH (—)	Ethylene glycol (Ethylene glycol)	— (KOH)	70/— (air)	140 (r.t.)	20 (3)	10	200	15
16.	Mn-P^{iPr}NP^{iPr} (Mn-P^{iPr}NP^{iPr})	THF (THF)	— (Amine, KO^{t}Bu)	80/— (30/30)	150 (110)	36 (36)	1	36	16
17.	Fe-P^{iPr}NP^{iPr} (Fe-P^{iPr}NP^{iPr})	THF (THF)	LiOTf, DBU (Morpholine, 3Å molecularcular sieves)	80/— (80/17)	100 (100)	16 (16)	16	590	17
18.	Ru-bisPN	Toluene	^{i}Pr$_2$NH, NaOEt	30/10	100	20	4500	8900	18
19.	Ru-P^{tBu}N^{Py}N^{Py}/Ru-P^{tBu}N^{Py}N^{tBu}Ru-P^{tBu}N^{Py}N^{Py}/Ru–P^{tBu}N^{Py}N^{tBu}	THF (n.r.)	—	10–50/— (n.r.)	110 (n.r.)	14–72 (n.r.)	~1–2500	57-4700	19
20.	Mn-P^{tBu}N^{Py}N^{Py}/Mn-P^{tBu}N^{Py}N^{tBu}	Toluene (n.r.)	— KH/KO^{t}Bu	20–50/— (n.r.)	130–150 (n.r.)	50 (n.r.)	~1	~50	20
21.	Ru-P^{tBu}N^{Py}N$_{Py}$ (Cs_2CO_3)	DMSO (DMSO)	— KO^{t}Bu (—)	60/— (—/3)	135 (150)	72 (24)	<1	30	21
22.	$Ru(PMe_3)_4(OAc)Cl$, $Sc(OTf)_3$,Ru-P^{tBu}N^{Py}N^{Py}	MeOH, 1,4-dioxane	—	30/10	75–135	16	~1	21	22
23.	Ru-P^{tBu}N^{Py}N^{Py}N^{Et}	iPrOH	^{t}BuOK, $NHMe_2$	50/2.5	90 to >170	48 + 72	17.5	2100	23
24.	$[Ru_3(CO)_{12}]$	NMP	KI	20/60	240	3	10	32	24
25.	[Cp*Ir(BPY)(H_2O)](OTf)$_2$	H_2O	–	0/0	80	24	156	6.5	25
26.	[Ru(COD)(methylallyl)$_2$]/triphos	THF	MSA	0/0	150	1	67	67	26
27.	[Cp*Ir(4,4′-DHBP)(H_2O)]SO_4	–	H_2SO_4	0/50	20	72	NA	NA	27
28.	[Ru(acac)$_3$] + Ligand	THF	MSA	60/20	140	20	-	111	28

Table S4. Homogeneous catalysts reported in literature for CO_2 hydrogenation to methanol.

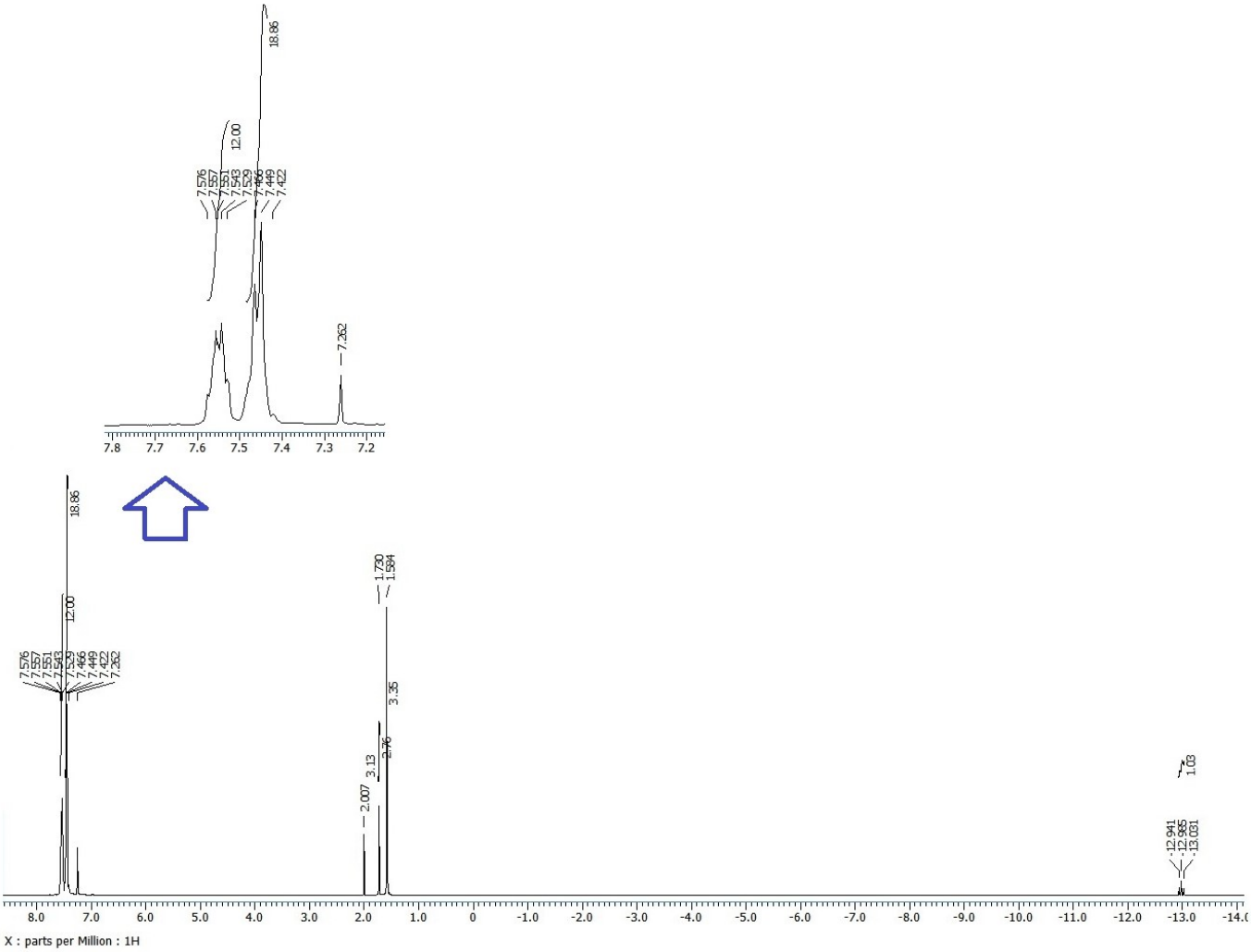

Figure S1. ^{1}H NMR spectrum of $[RuH(CO)(CH_3CN)_2(PPh_3)_2]PF_6$ (**2**) at room temperature (400 MHz, in $CDCl_3$).

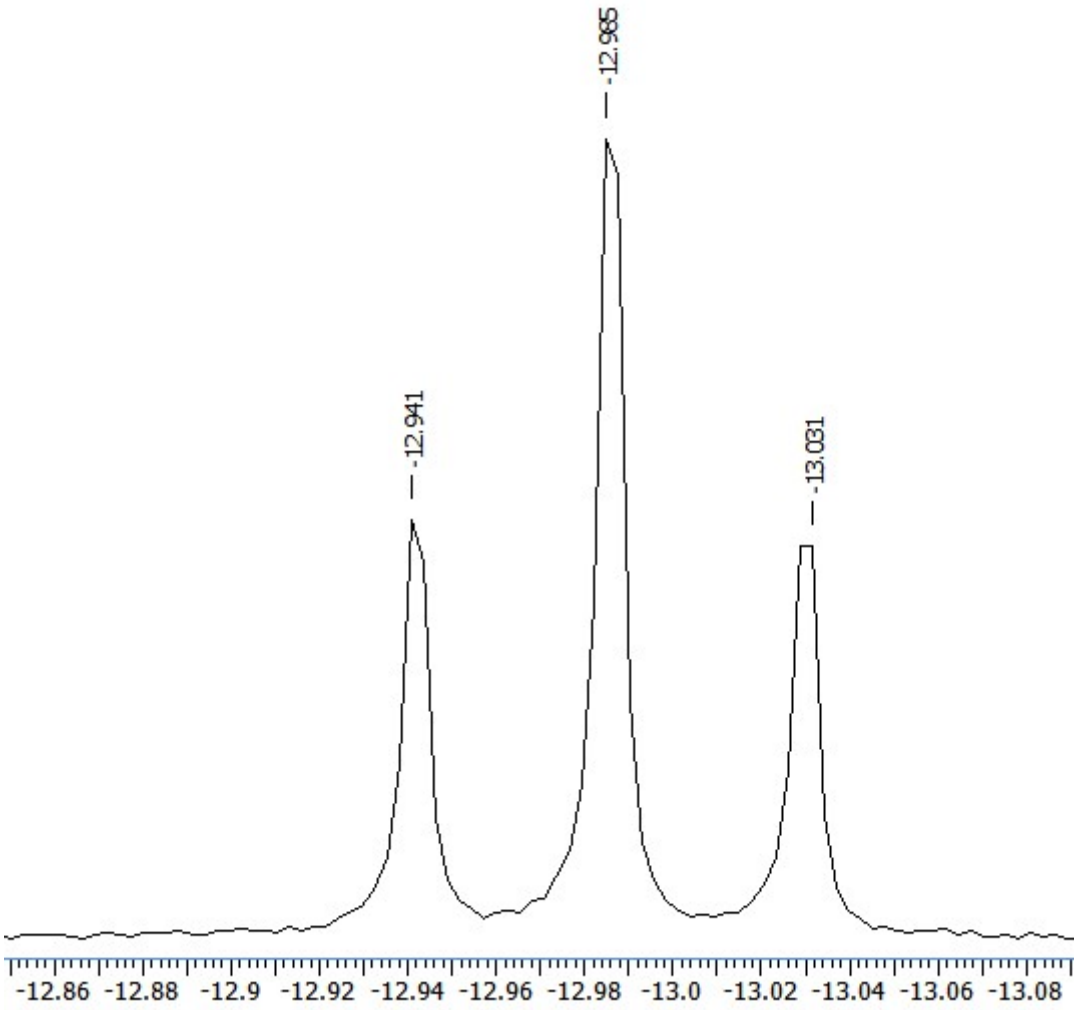
-12.941
-12.985
-13.031
-12.86 -12.88 -12.9 -12.92 -12.94 -12.96 -12.98 -13.0 -13.02 -13.04 -13.06 -13.08

Figure S2. ^{1}H NMR spectrum of $[RuH(CO)(CH_3CN)_2(PPh_3)_2]PF_6$ (**2**) at room temperature (400 MHz, in $CDCl_3$). The region from -13 to -13.3 ppm showing Ru-H signal.

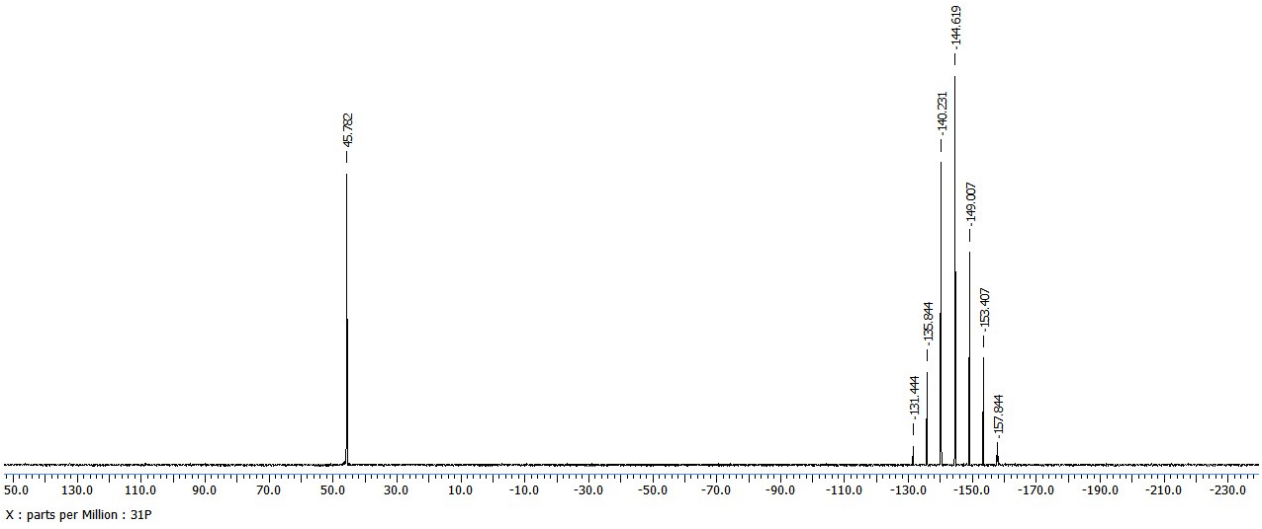

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of $[RuH(CO)(CH_3CN)_2(PPh_3)_2]PF_6$ (**2**) at room temperature (400 MHz, in $CDCl_3$).

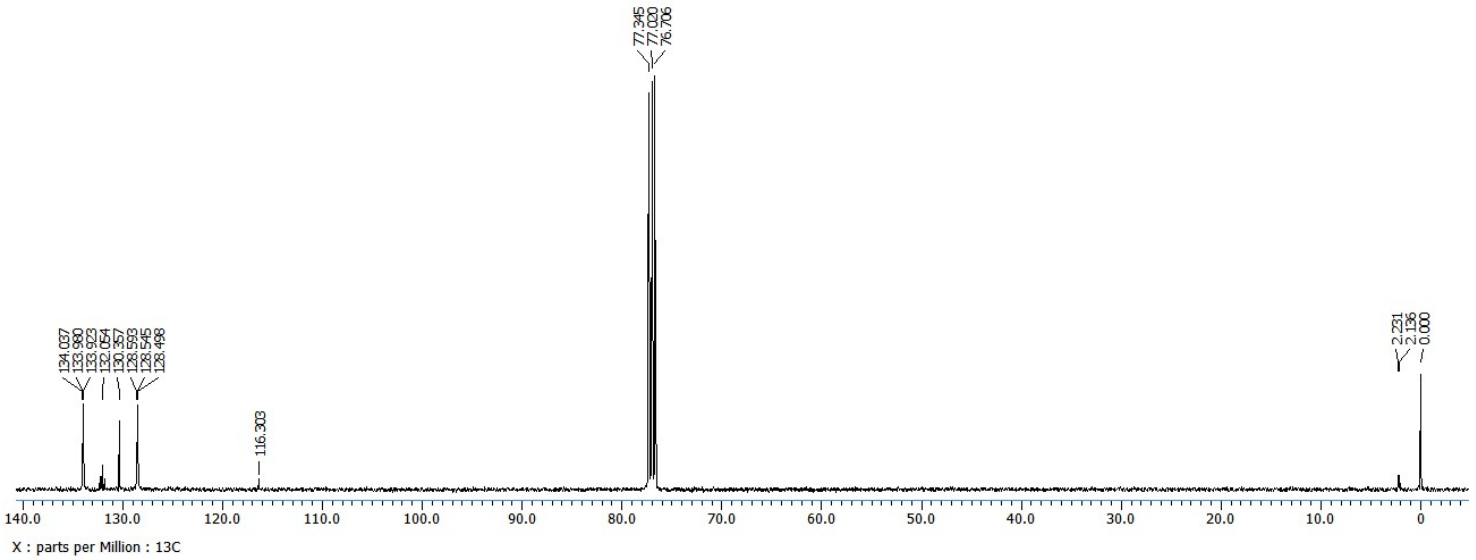

Figure S4. ^{13}C NMR spectrum of $[RuH(CO)(CH_3CN)_2(PPh_3)_2]PF_6$ (**2**) at room temperature (400 MHz, in $CDCl_3$).

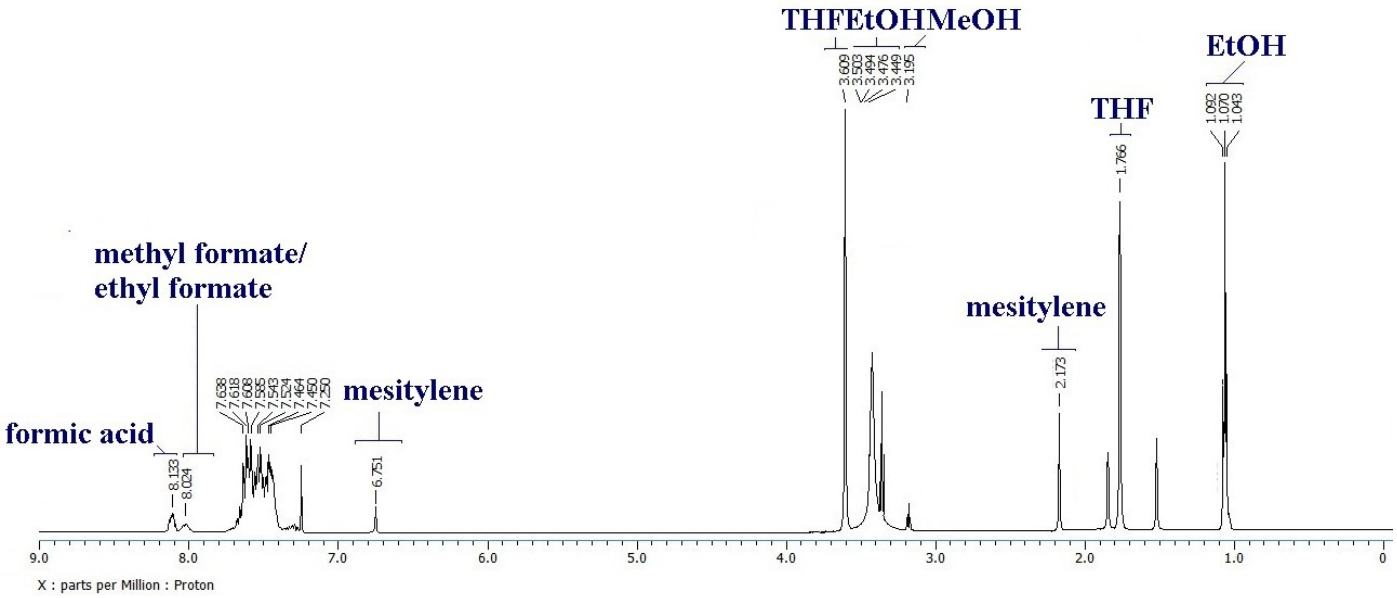

Figure S5. ^{1}H NMR spectrum for reaction solution from ethyl formate hydrogenation in $CDCl_3$ solvent with an internal standard mesitylene. Conditions: $[RuH(CO)(CH_3CN)_2(PPH_3)_2]BF_4$ (0.0025 mmol), 1.0 atm H_2, ethyl formate (2.5 mmol), aluminum tris(trifluoromethanesulfonate) (4.0 mmol), 90°C, 24h, in 5 mL THF.

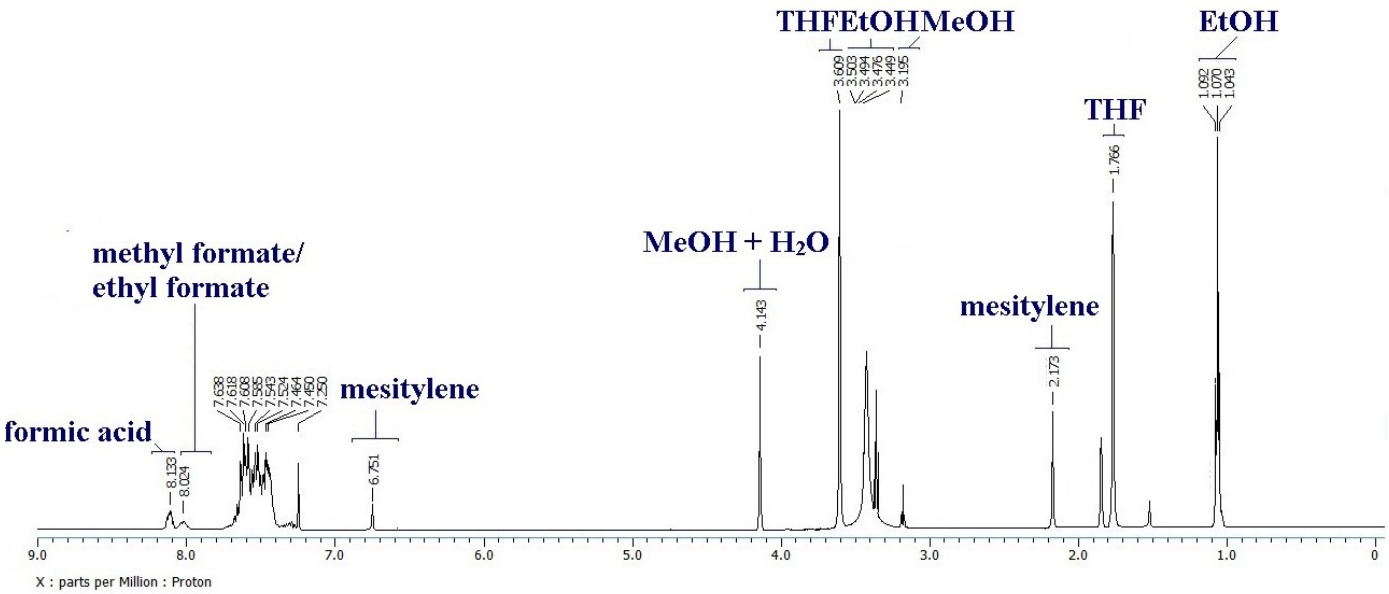

Figure S6. ^{1}H NMR spectrum for reaction solution from CO_2 hydrogenation in $CDCl_3$ solvent with an internal standard mesitylene. Conditions: $[RuH(CO)(CH_3CN)_2(PPH_3)_2]BF_4$ (0.0025 mmol), ethanol(10 mmol), 3.0 atm H_2, 1 atm CO_2, aluminum tris(trifluoromethanesulfonate) (4.0 mmol), 90°C, 24h, in 5 mL THF.

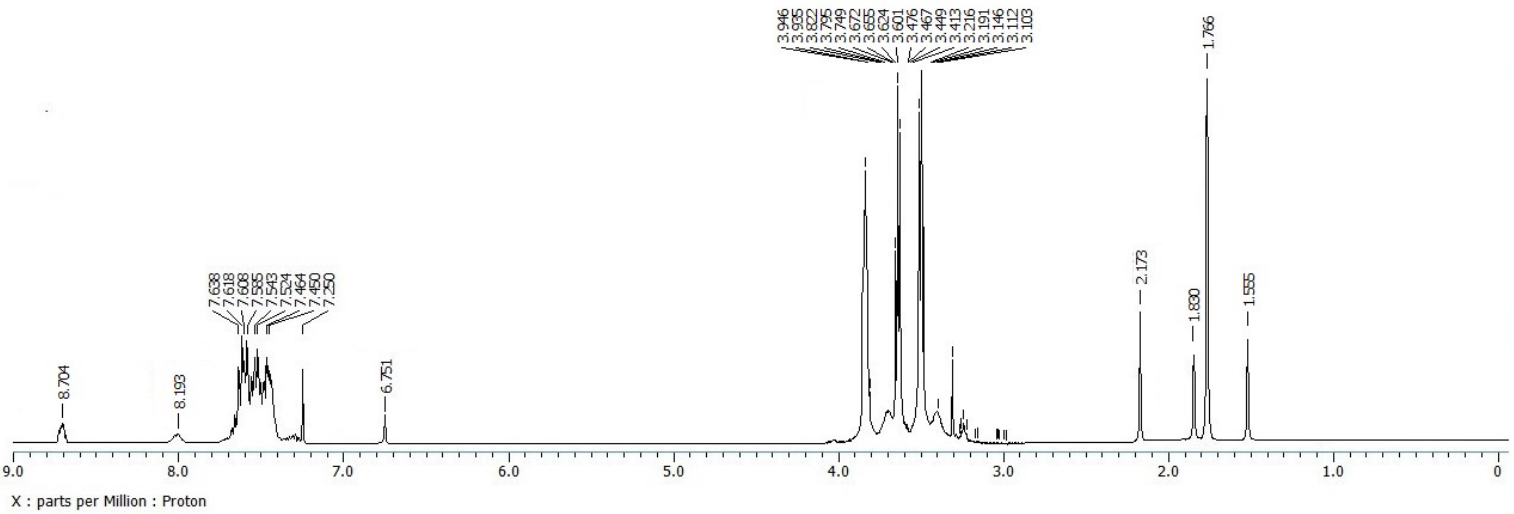

Figure S7. ^{1}H NMR spectrum for reaction solution from CO_2 hydrogenation in $CDCl_3$ solvent with an internal standard mesitylene. Conditions: $[RuH(CO)(CH_3CN)_2(PPH_3)_2]BF_4$ (0.0025 mmol), CD_3OD (10 mmol), 3.0 atm H_2, 1 atm CO_2, aluminum tris(trifluoromethanesulfonate) (4.0 mmol), 90°C, 24h, in 5 mL THF.

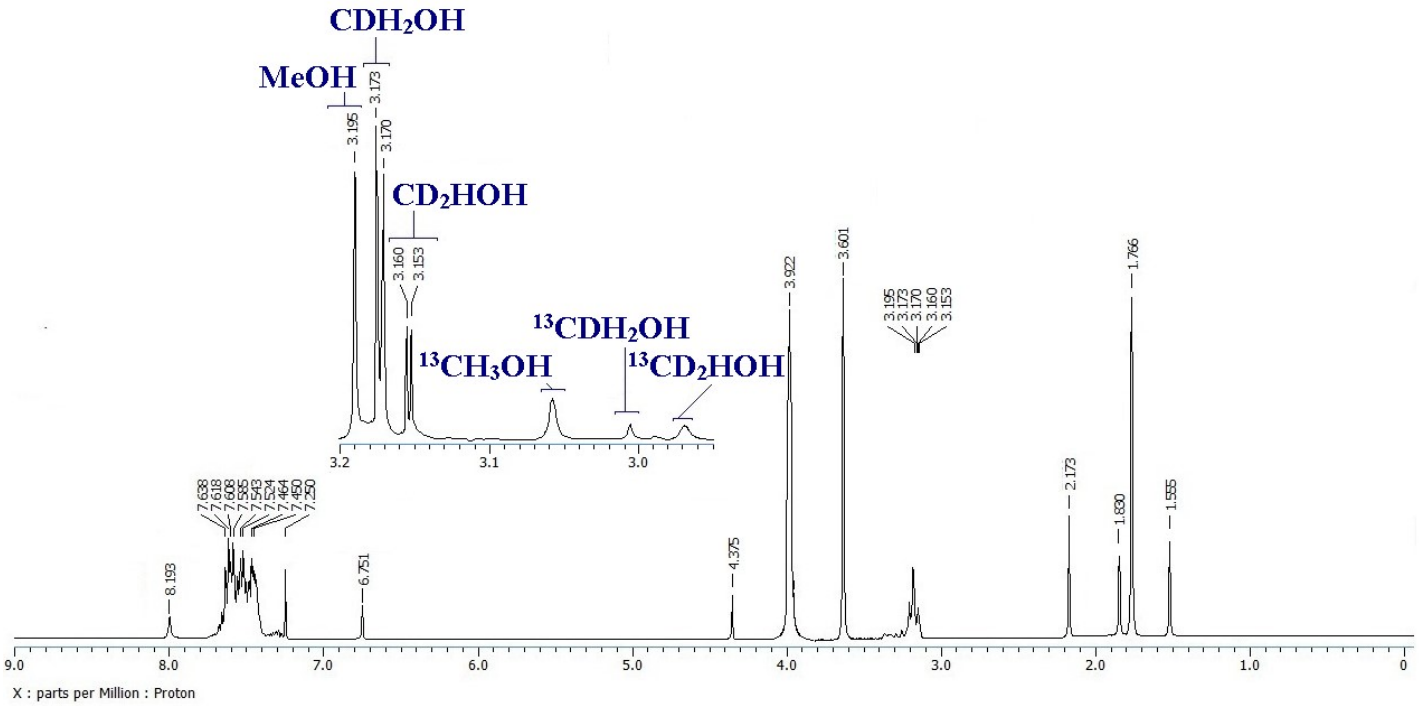

Figure S8. ^{1}H NMR spectrum for reaction solution from CO_2 hydrogenation in $CDCl_3$ solvent with an internal standard mesitylene. Conditions: $[RuH(CO)(CH_3CN)_2(PPH_3)_2]BF_4$ (0.0025 mmol), $^{13}CD_3OD$ (10 mmol), 3.0 atm H_2, 1 atm CO_2, aluminum tris(trifluoromethanesulfonate) (4.0 mmol), 90°C, 24h, in 5 mL THF.

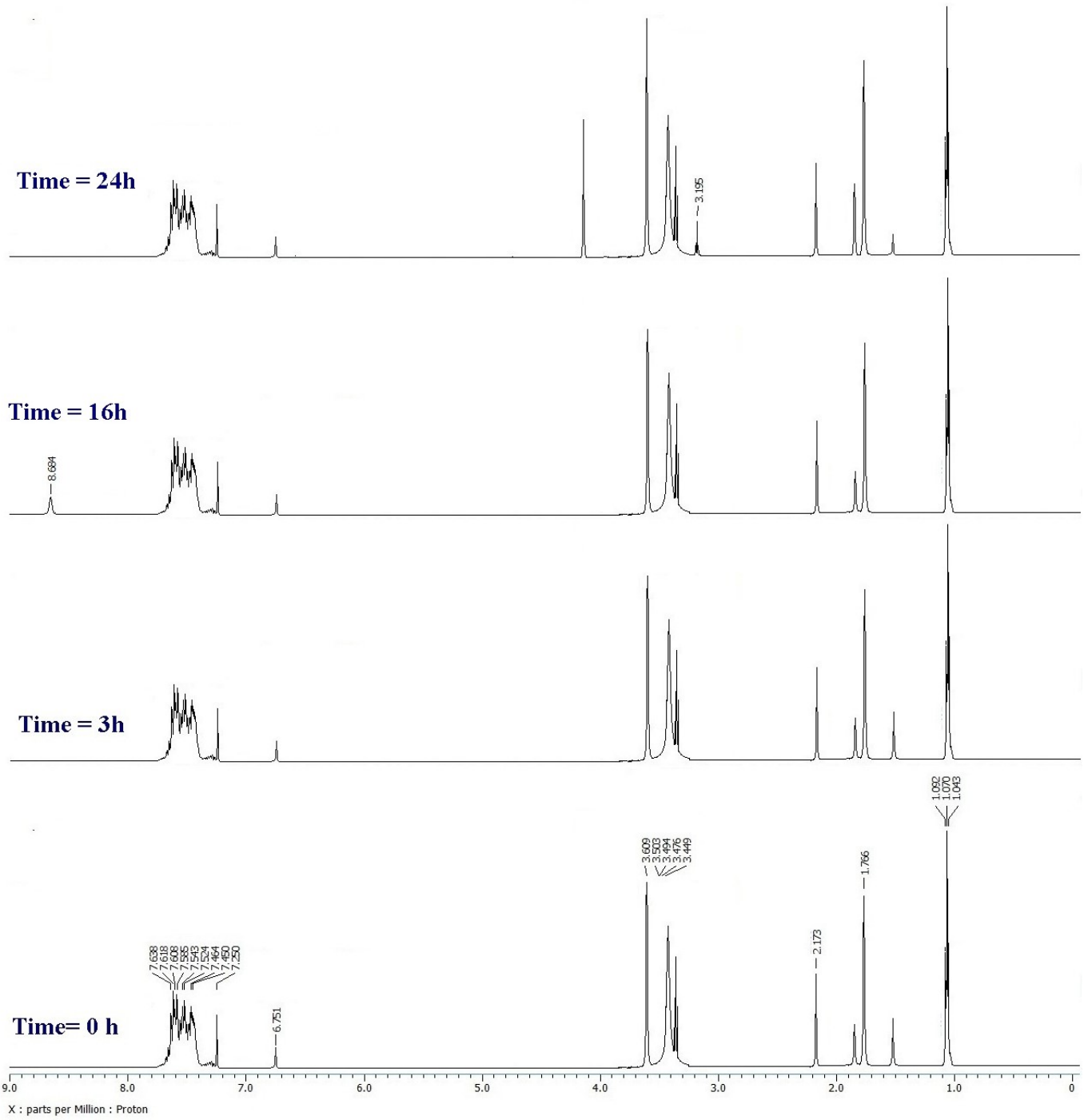

Figure S9. Time-resolved ^{1}H NMR spectra for a representative CO_2 hydrogenation using **1** together with $HNTf_2$. Conditions: 3.0 atm H_2, 1 atm CO_2, 90°C, $[RuH(CO)(CH_3CN)_2(PPH_3)_2]BF_4$ (0.0025 mmol), EtOH (10 mmol), $HNTf_2$ (0.0025 mmol) was run in 5mL THF and 0.25 mL of the reaction mixture was dissolved into 1.0 mL of $CDCl_3$ with internal standard mesitylene for analysis by NMR spectroscopy (Table 6, entry 11). The region from 0 to 9 ppm showing formate and catalyst $[RuH(CO)(CH_3CN)_2(PPH_3)_2]BF_4$ signals are shown. Spectra were acquired at room temperature in $CDCl_3$ solvent with internal standard mesitylene.

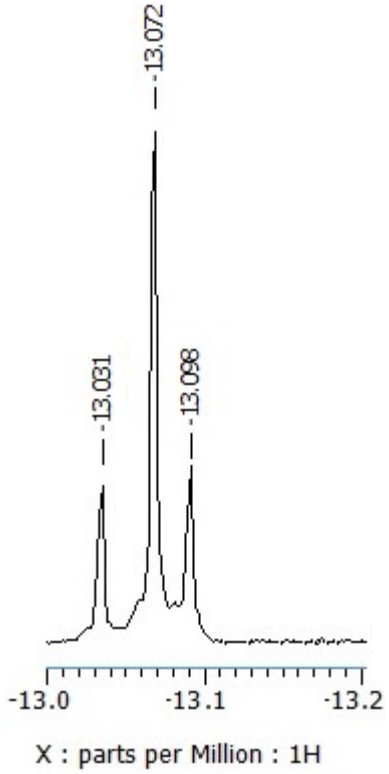

Figure S10. ^{1}H NMR spectrum for a representative CO_2 hydrogenation using **1** together with $HNTf_2$ after 3h. Conditions: 3.0 atm H_2, 1 atm CO_2, 90°C, $[RuH(CO)(CH_3CN)_2(PPH_3)_2]BF_4$ (0.0025 mmol), EtOH (10 mmol), $HNTf_2$ (0.0025 mmol) was run in 5mL THF. The region from -13.0 to -13.2 ppm showing Ru-H signal.

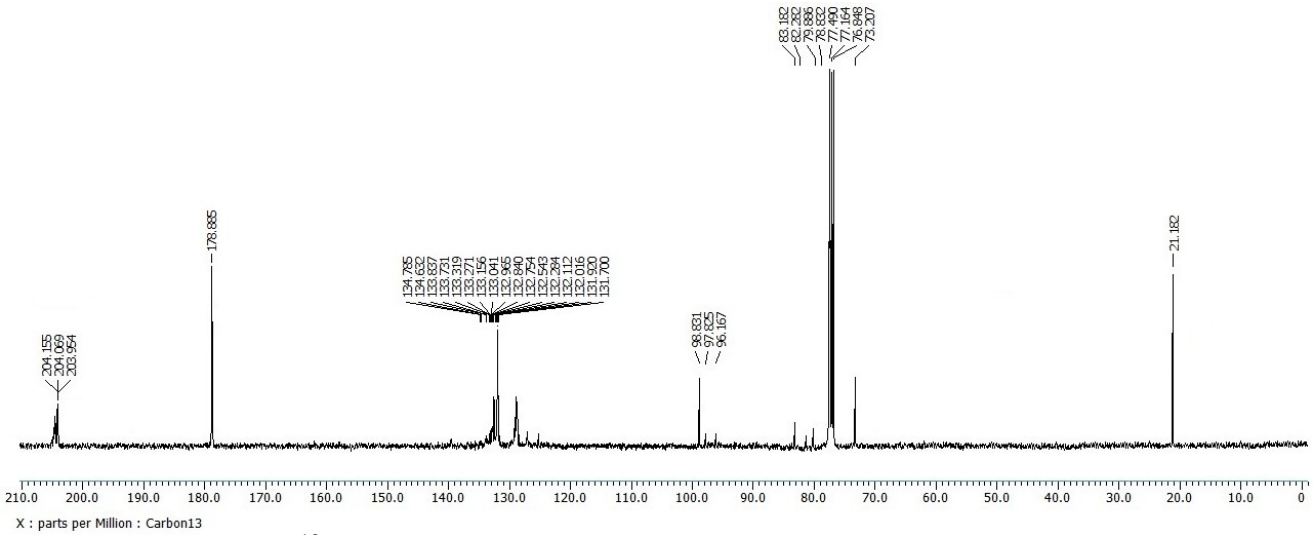

Figure S11. ^{13}C NMR spectrum of reaction mixture for a representative CO_2 hydrogenation using **1** together with $HNTf_2$ after 16h. Conditions: 3.0 atm H_2, 1 atm CO_2, 90°C, $[RuH(CO)(CH_3CN)_2(PPH_3)_2]BF_4$ (0.0025 mmol), EtOH (10 mmol), $HNTf_2$ (0.0025 mmol) was run in 5mL THF.

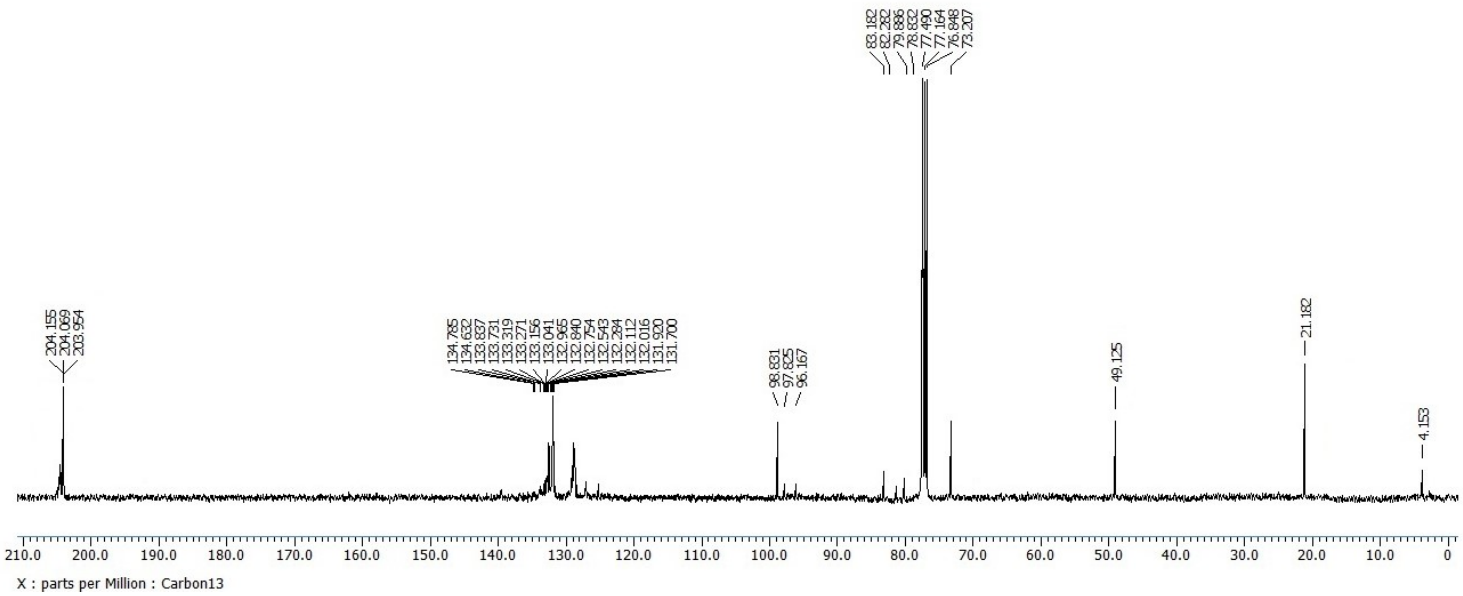

Figure S12. ^{13}C NMR spectrum of reaction mixture for a representative CO_2 hydrogenation using **1** together with $HNTf_2$ after 24h. Conditions: 3.0 atm H_2, 1 atm CO_2, 90°C, $[RuH(CO)(CH_3CN)_2(PPH_3)_2]BF_4$ (0.0025 mmol), EtOH (10 mmol), $HNTf_2$ (0.0025 mmol) was run in 5mL THF.

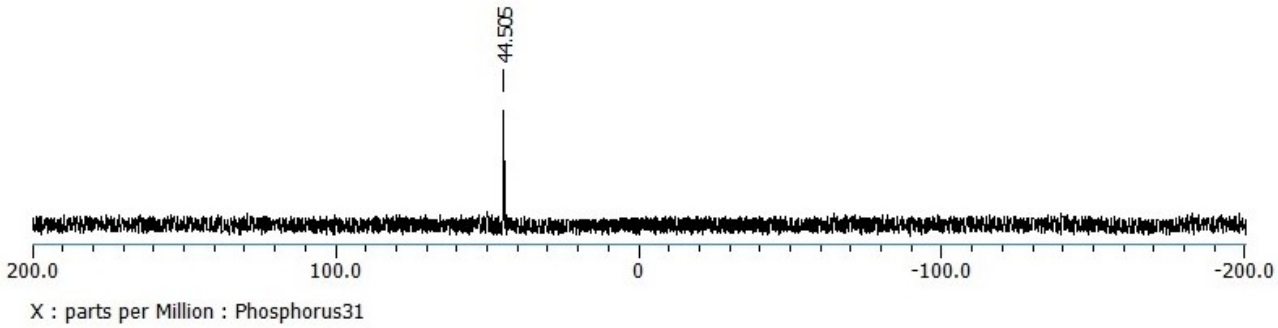

Figure S13. ^{31}P NMR spectrum of the reaction solution from a CO_2 hydrogenation reaction using **1** together with $HNTf_2$ after 24h in $CDCl_3$.

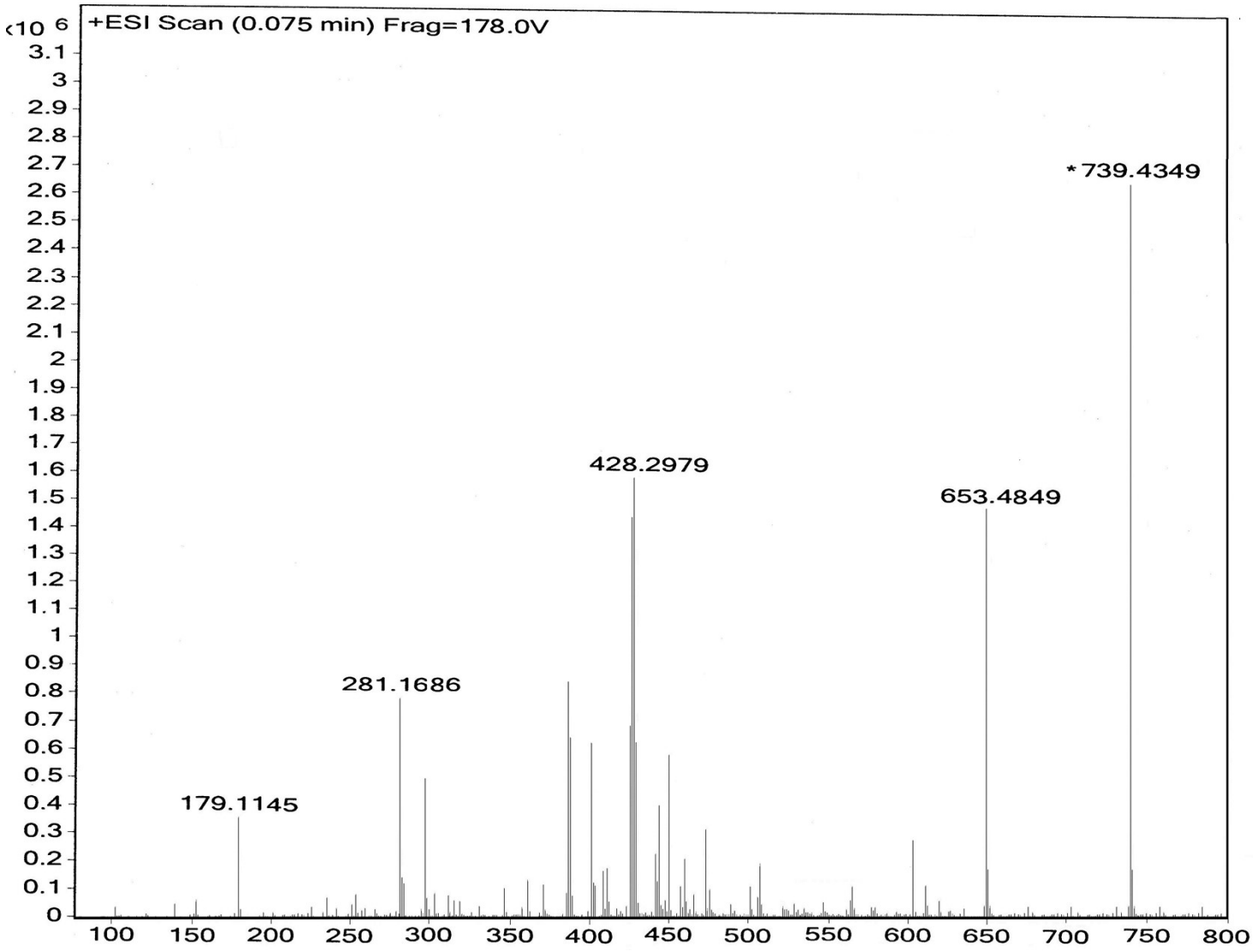

Figure S14. HR-ESI-MS measurement of a post-catalytic reaction mixture for a representative CO_2 hydrogenation using **1** together with $HNTf_2$ after 16h in MeOH.

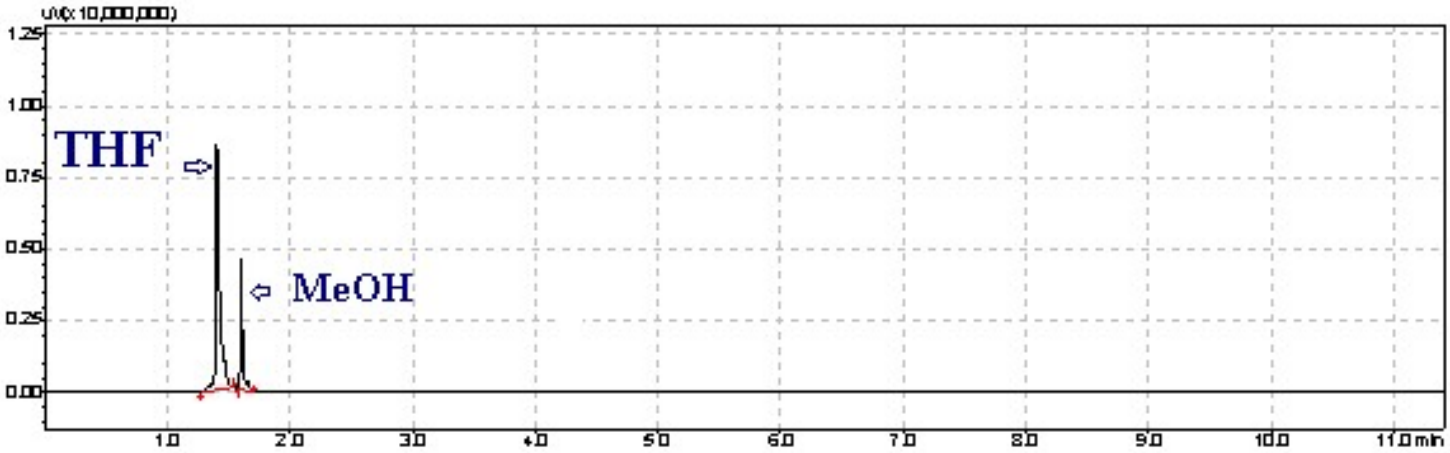

Figure S15. Representative gas chromatogram of the reaction solution from a CO_2 hydrogenation reaction using **1** together with $HNTf_2$ after 24h.

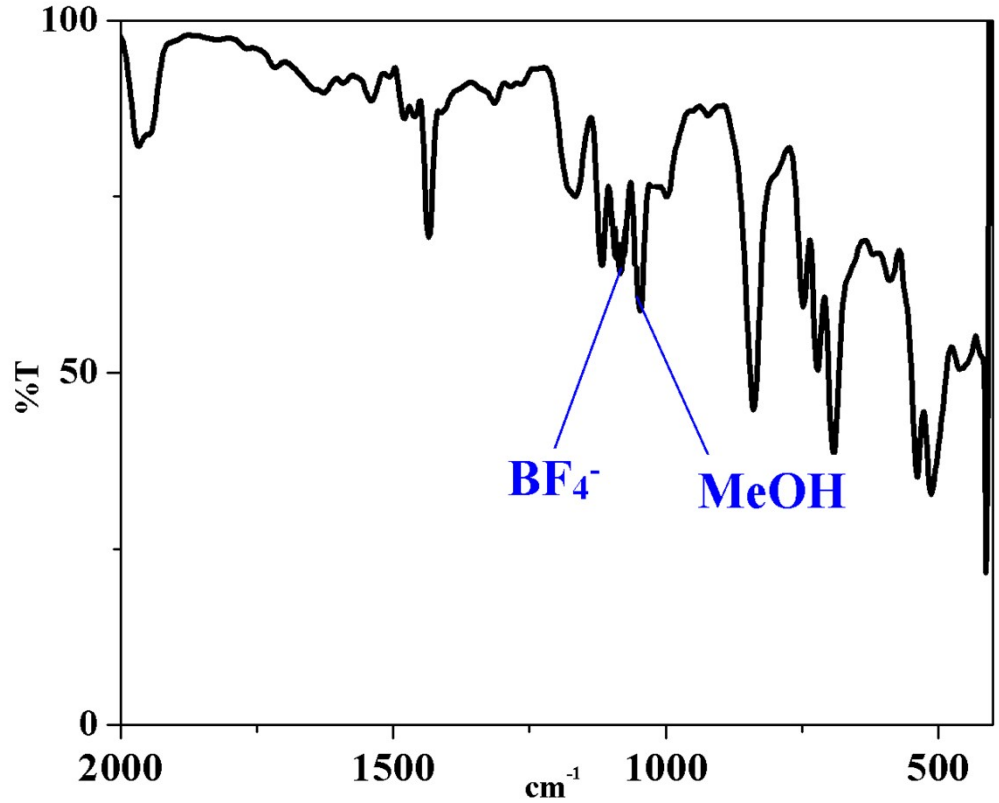

Figure S16. Observation of C-O bands that may belong to methanol in the representative infrared spectrum of the reaction solution in THF from a CO_2 hydrogenation reaction using **1** together with aluminum tris(trifluoromethanesulfonate) after 24h.

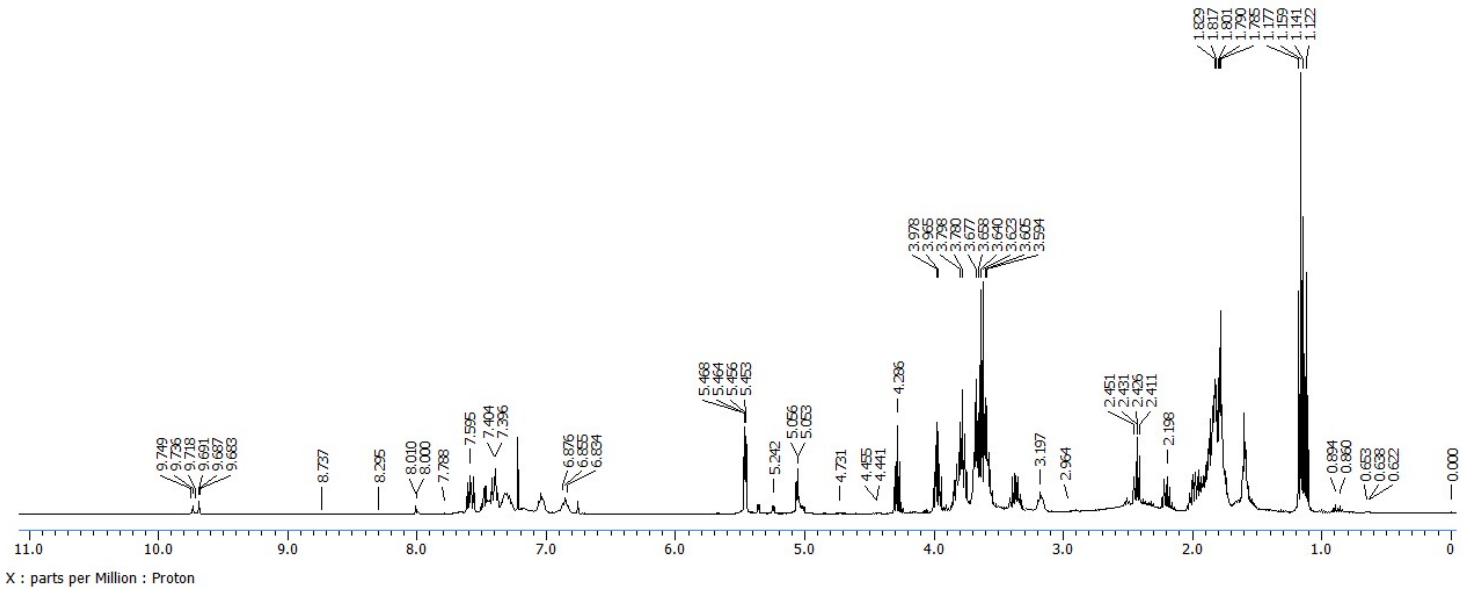

Figure S17. ^{1}H NMR spectrum for a representative CO_2 hydrogenation using **2** together with aluminum tris(trifluoromethanesulfonate) after 24h. Conditions: 3.0 atm H_2, 1 atm CO_2, 90°C, $[RuH(CO)(CH_3CN)_2(PPH_3)_2]PF_6$ (0.0025 mmol), EtOH (10 mmol), $Al(OTf)_3$ (0.0025 mmol) was run in 5mL THF and 0.25 mL of the reaction mixture was dissolved into 1.0 mL of $CDCl_3$ with internal standard mesitylene for analysis by NMR spectroscopy.

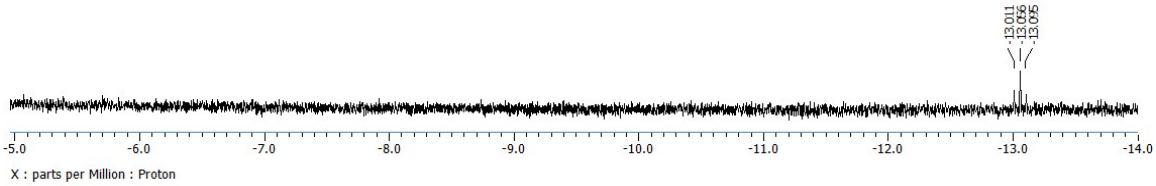

Figure S18. ^{1}H NMR spectrum for a representative CO_2 hydrogenation using **2** together with aluminum tris(trifluoromethanesulfonate) after 24h. Conditions: 3.0 atm H_2, 1 atm CO_2, 90°C, $[RuH(CO)(CH_3CN)_2(PPH_3)_2]PF_6$ (0.0025 mmol), EtOH (10 mmol), $Al(OTf)_3$ (0.0025 mmol) was run in 5mL THF and 0.25 mL of the reaction mixture was dissolved into 1.0 mL of $CDCl_3$ with internal standard mesitylene for analysis by NMR spectroscopy. The region from -5.0 to -14.0 ppm showing Ru-H signal.

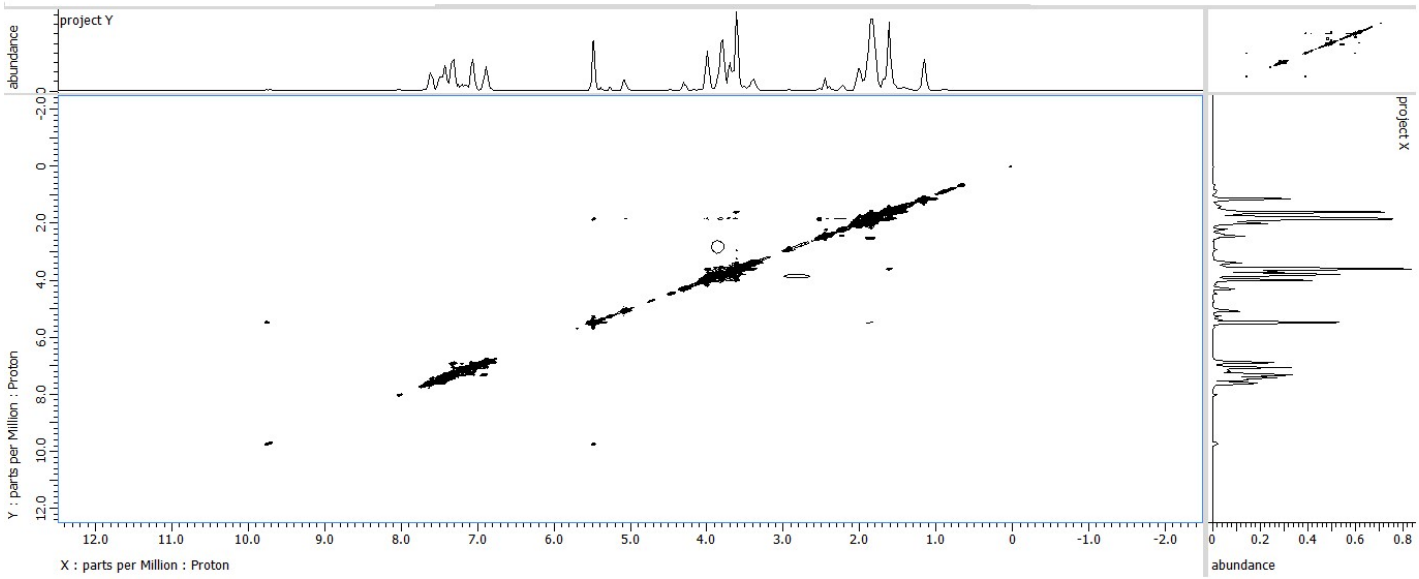

Figure S19. 2D NOESY NMR spectrum for CO_2 hydrogenation using **2** together with aluminum tris(trifluoromethanesulfonate) after 24h. Conditions: 3.0 atm H_2, 1 atm CO_2, 90°C, $[RuH(CO)(CH_3CN)_2(PPH_3)_2]PF_6$ (0.0025 mmol), EtOH (10 mmol), $Al(OTf)_3$ (0.0025 mmol) was run in 5mL THF and 0.25 mL of the reaction mixture was dissolved into 1.0 mL of $CDCl_3$ with internal standard mesitylene.

References

1. (a) S. Wesselbaum, T. Vom Stein, J. Klankermayer and W. Leitner, *Angew. Chem., Int. Ed.,* 2012, **51**, 7499-7502; (b) S. Wesselbaum, V. Moha, M. Meuresch, S. Brosinski, K.M. Thenert, J. Kothe, T.V. Stein, U. Englert, M. Holscher, J. Klankermayer and W. Leitner, *Chem. Sci.*, 2015, **6**, 693-704.
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