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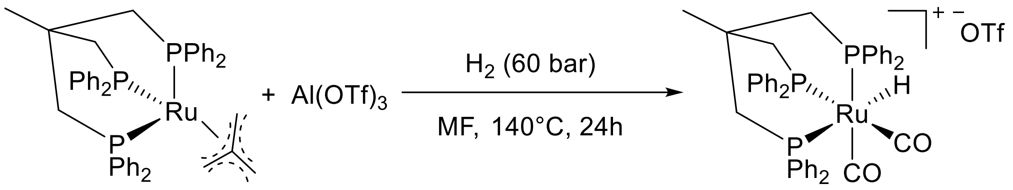
General information

Chemicals were purchased from commercial suppliers and used as received. Ruthenium complexes **1**,[1] **2**,[2] **3**[3] and **8**[4] were synthesized according to literature procedures. The synthesis of $[PPh_3CH_2OCH_3]OTf$ was adapted from a previous report.[5] Dry solvents were purchased from Sigma-Aldrich and stored over 4 Å molecular sieves. Reactions requiring inert conditions were carried out in an MBraun glovebox or in flame-dried glassware under an atmosphere of argon using standard Schlenk-techniques. Reaction gases carbon dioxide (N35) and hydrogen (ALPHAGAZ™ 1) were supplied by Air Liquide and used without further purification. NMR spectra were, if not mentioned otherwise, recorded at room temperature on the following spectrometers: Bruker Avance-III-300. Chemical shifts were given in ppm and coupling constants in Hz. ^{1}H and ^{13}C spectra were calibrated in relation to deuterated solvents. ^{31}P chemical shifts are reported relative to an external standard of phosphoric acid 30% in D_2O (0.0 ppm). The following abbreviations were used for ^{1}H NMR spectra to indicate the signal multiplicity: s (singlet), bs (broad singlet), d (doublet), t (triplet) and m (multiplet) as well as combinations of them. All ^{31}P NMR spectra were measured with ^{1}H-decoupling. All ^{13}C NMR spectra were measured with ^{31}P-decoupling. HR-MS was determined at the chemistry department of the University of Heidelberg under the direction of Dr. J. Gross. For ESI^{+}-spectra a Bruker ApexQe FT-ICR spectrometer was applied.

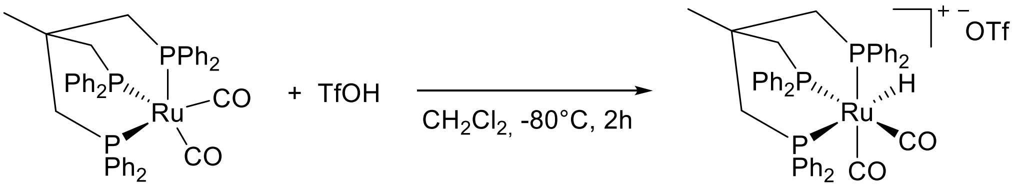
Synthesis of [RuH(CO)$_2$(triphos)]OTf (5)

Method A



[Ru(triphos)(tmm)] (76 mg, 96 μmol) and Al(OTf)$_3$ (46 mg, 96 μmol) were weighed into a teflon insert fitted with a magnetic stirrer bar and placed into a stainless steel 40 mL Premex autoclave. 5 mL of methyl formate (MF) were added and the vessel was tightly closed and purged with H$_2$ (3x10 bar) and finally pressurized with H$_2$ (60 bar). The autoclave was heated in an aluminum block to 140 °C and stirred at 800 rpm for 24 h. The autoclave was cooled to 0°C in an ice bath then carefully vented. All volatiles were removed and the remaining solid was washed with pentane (3x5 mL) and dried *in vacuo* affording a yellow solid.

Method B



[Ru(CO)$_2$(triphos)] (**8**) (154 mg, 0.20 μmol, 1.0 equiv.) was dissolved in 8 mL of dichloromethane and the solution was cooled to -70°C. Triflic acid (17.4 μL, 0.20 mmol, 1.0 equiv.) was added slowly and the solution was kept at -70°C for 30 minutes before being warmed to room temperature and stirred for another 1.5 hours. The volume was reduced to 2 mL and 15 mL of *n*-pentane was added giving a yellow precipitate. The solid was separated, washed with 10 mL of pentane and dried *in vacuo* affording a light yellow solid (162 mg, 88%).

^{1}H NMR (300 MHz, D$_3$COD)	δ = 7.70-7.58 (m, 8H, Ar-C*H*), 7.47-6.90 (m, 22H, Ar-C*H*), 2.83 (d, *J* = 9.4 Hz, 2H, C*H$_2$*), 2.65-2.63 (m, 4H, C*H$_2$*), 1.84-1.81 (m, 3H, C*H$_3$*), -6.70 (dt, $^2J_{HP}$ = 64.4, 15.2 Hz, 1H, Ru*H*) ppm.
^{13}C{^{31}P} NMR (151 MHz, CD$_2$Cl$_2$)	δ = 197.1 (2xCO), 135.5, 133.8, 132.4, 131.4, 131.1, 131.0, 131.0, 129.8, 129.2, 129.1, 38.3, 32.3, 31.8 ppm.
^{19}F NMR (283 MHz, D$_3$COD)	δ = -79.9 ppm.
^{31}P NMR (122 MHz, D$_3$COD)	δ = 18.1 (d, $^2J_{PP}$ = 28.7 Hz, 2P), 6.0 (t, $^2J_{PP}$ = 28.7 Hz, 1P) ppm.

HR-MS (ESI, pos., in CH$_2$Cl$_2$/MeOH) calculated for [$C_{43}H_{40}O_2P_3Ru$]$^+$: m/z = 783.1285; found: m/z = 783.1321.

The analytical data is in line with literature reports.[6, 7]

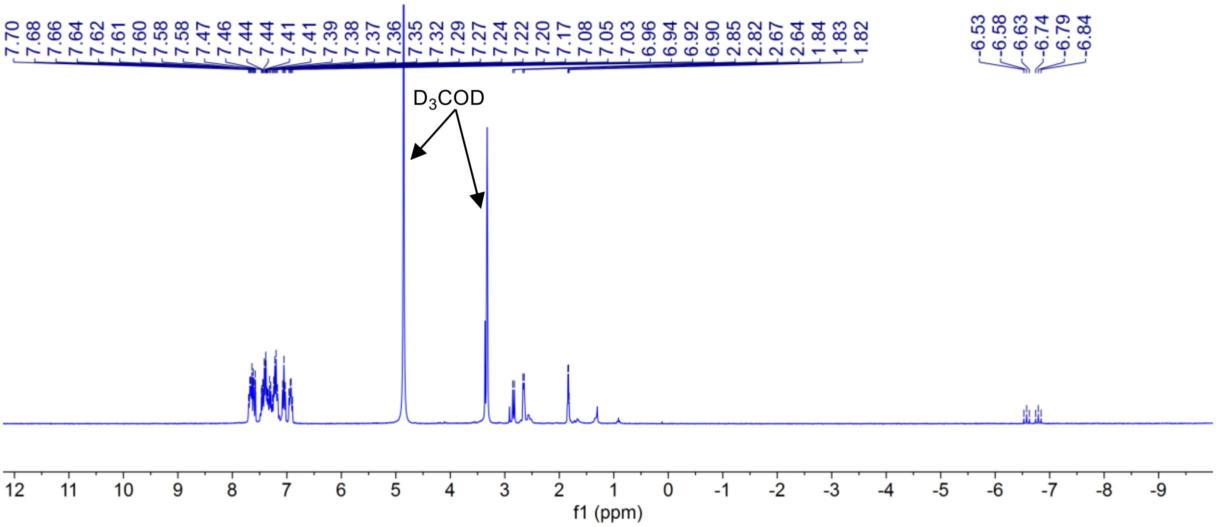


Figure 1 ^{1}H NMR (300 MHz, D_3COD) spectrum of Ru-complex **5**.

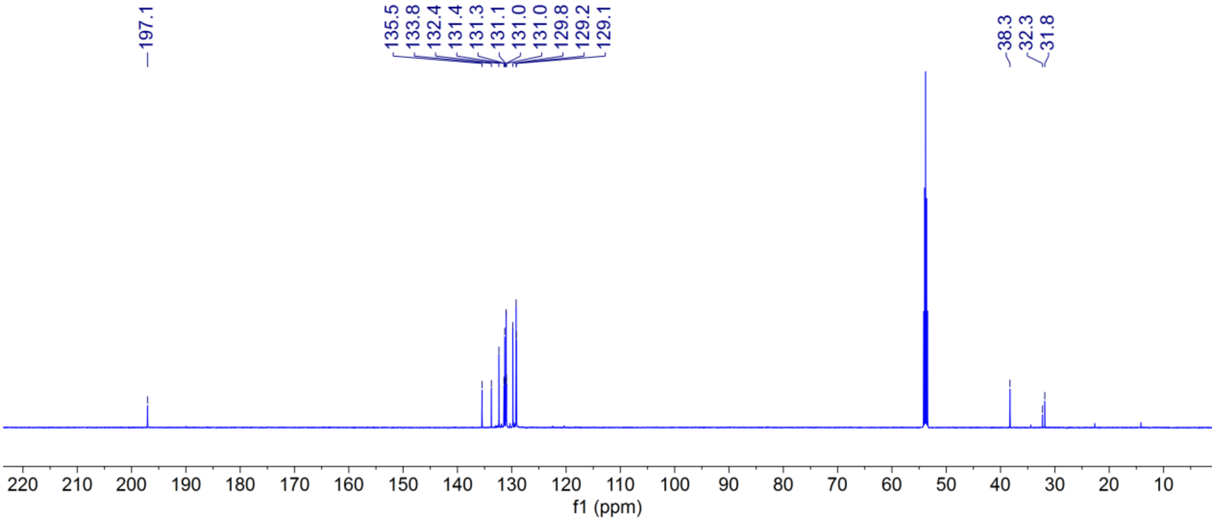


Figure 2 $^{13}C\{^{31}P\}$ NMR (151 MHz, CD_2Cl_2) spectrum of Ru-complex **5**.

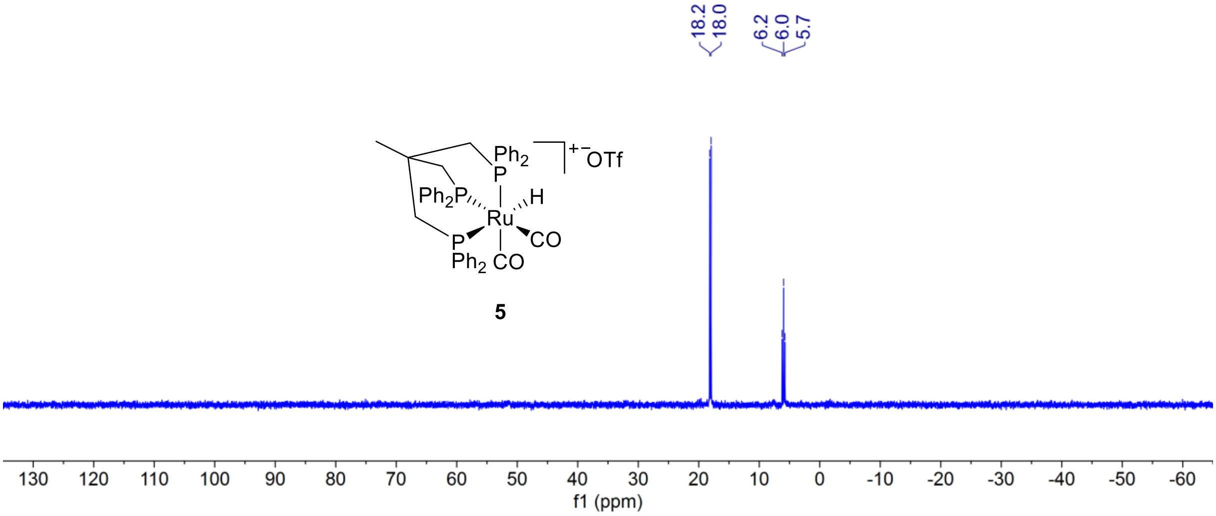
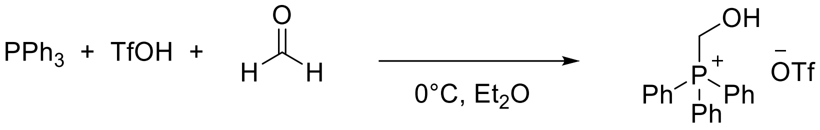


Figure 3 ^{31}P NMR (121 MHz, D_3COD) spectrum of Ru-complex **5**.

Synthesis of [PPh_3CH_2OH]OTf (7)[8]



7

PPh_3 (1.0 g, 3.81 mmol) and formaldehyde (37% solution in water, 0.57 mL, 7.62 mmol) were dissolved in 20 mL of diethyl ether and cooled to 0°C. TfOH (0.68 mL, 7.62 mmol) was added slowly leading to the instant formation of a white precipitate. The mixture was warmed to room temperature and stirred overnight. The precipitate was filtered and washed with diethyl ether (3x10 mL) and dried *in vacuo* affording a white crystalline solid (1.37 g, 81%).

^1H NMR (300 MHz, $CDCl_3$)	δ = 7.85-7.79 (m, 3H, Ar-C*H*), 7.73-7.66 (m, 12H, Ar-C*H*), 5.41 (s, 2H, C*H₂*) ppm.
^{31}P NMR (122 MHz, $CDCl_3$)	δ = 17.2 (s) ppm.

The analytical data is in line with literature reports.[8]

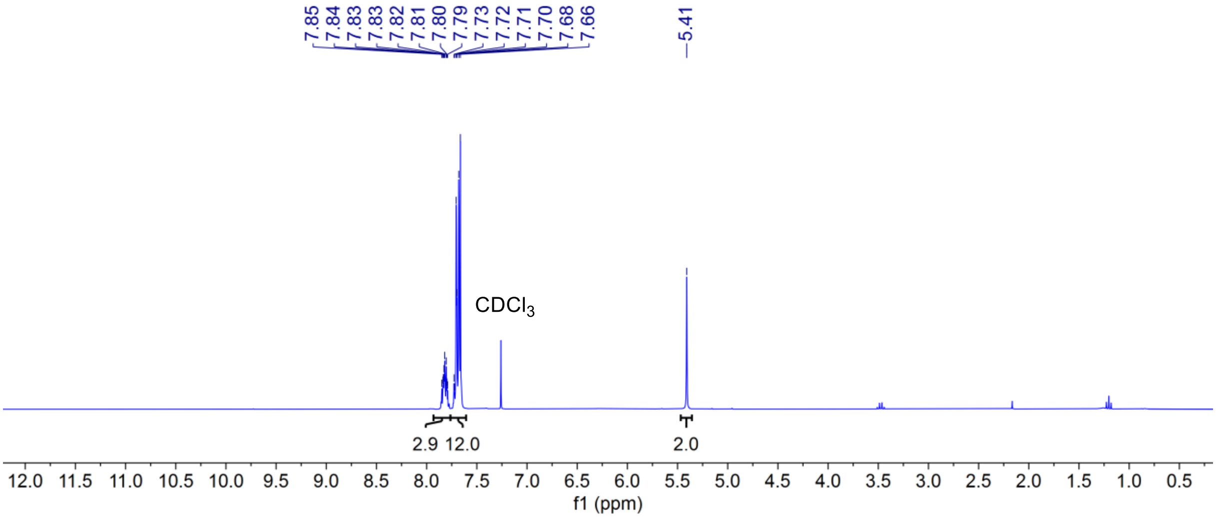


Figure 4 ^1H NMR (300 MHz, $CDCl_3$) spectrum of **7**.

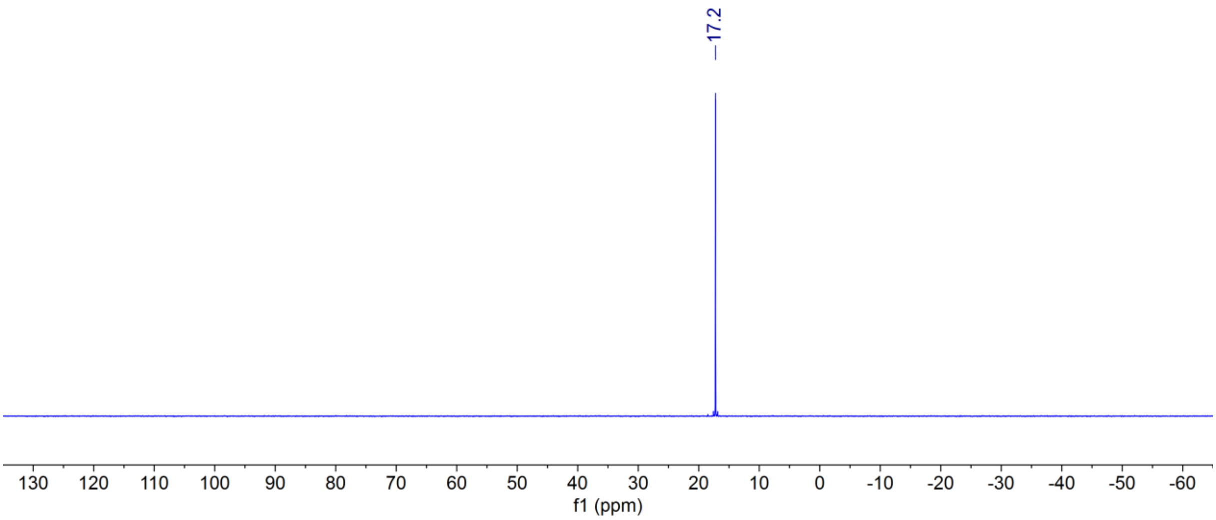


Figure 5 ^{31}P NMR (121 MHz, $CDCl_3$) spectrum of **7**.

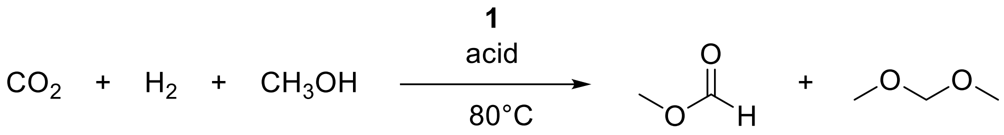
General Procedure for large scale optimization experiments at hte GmbH

Experimental setup and description of experiments in the liquid phase

Screening tests were carried out in 8 parallel steel autoclave reactors (inner volume 300 mL). The general experimental procedure for each screening experiment was as follows: in a first step, a starting reaction mixture was prepared by filling 79.2 g (100 mL) of solvent, **1** (90 mg,125 µmol), acid co-catalyst $Al(OTf)_3$ (237 mg, 500 µmol), and additive $P(OPh)_3$ (155 mg, 500 µmol), into a steel autoclave reactor (inner volume 300 mL). In a second step, the filled steel autoclave reactor was tightly sealed and pressurized with 100 bar H_2 and 20 bar CO_2 (total pressure of 120 bar) and the steel autoclave reactor was heated to a temperature of 100 °C while stirring at 2000 rpm. After the corresponding reaction temperature was reached, the reaction temperature was maintained for given reaction time, while continuing stirring the reaction mixture inside the heated and pressurized steel autoclave reactor. Subsequently, the steel autoclave reactor was allowed to cool down to room temperature (approximately 22 °C), the pressure was released and the steel autoclave reactor was opened. For further analysis, 1 mL of the resulting reaction mixture was subjected to GC/FID/MS analysis to quantify said reaction products.

GC Method: Column: Varian CP7475 CP-Sil 5 CB; 60m*320µm*8µm, Injection volume: 1 µL, Inlet: 250 °C, Split: 20:1, Flow: 5 mL/min constant flow, Oven: start temp. 40 °C hold for 3 minutes, 20 °C/min to 225 °C hold for 8.25 min.

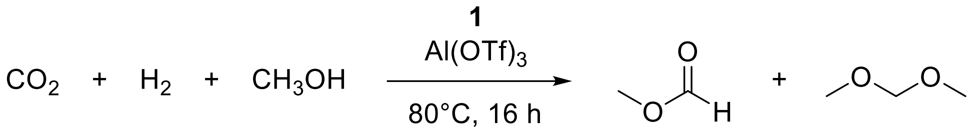
Table 1 Screening of acid co-catalysts.



Entry	Acid	TON[a]		Selectivity$_{DMM}$[a]
		MF	DMM	
1	$HNTf_2$	54	0	0%
2	Fe(OTf)$_3$	200	8	4%
3	Sc(OTf)$_3$	365	76	17%
4	H_2SO_4	71	0	0%
5	Nafion-H	7	1	6%
6	p-TSA	33	0	0%
7	Al(OTf)$_3$	373	94	20%

General conditions: [Ru] = **1** (125 μmol), acid (125 μmol), MeOH (100 mL), CO_2 (20 bar), H_2 (60 bar), 80°C, 16 h; [a] determined by GC analysis.

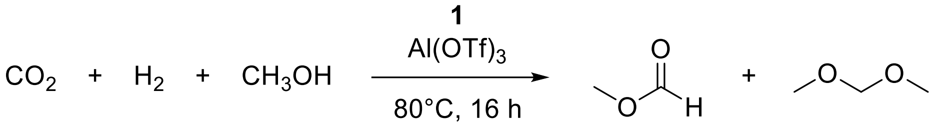
Table 2 Screening of reaction temperature.



Entry	Temperature [°C]	TON[a]		Selectivity$_{DMM}$[a]
		MF	DMM	
1	60	160	3	2%
2	70	313	26	7%
3	80	392	91	18%
4	90	343	207	37%
5	100	229	313	57%
6	110	165	365	68%
7	120	137	303	68%
8	130	135	218	61%
9	140	105	169	61%
10	160	89	54	37%

General conditions: [Ru] = **1** (125 μmol), Al(OTf)$_3$ (125 μmol), MeOH (100 mL), CO_2 (20 bar), H_2 (60 bar), 16 h; [a] determined by GC analysis.

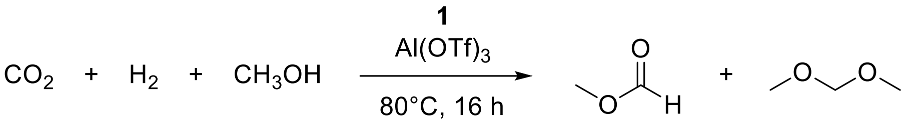
Table 3 Screening of catalyst concentration.



Entry	**1** [μmol]	TON[a]			Selectivity$_{DMM}$[a]
		MF	**DMM**	**HCOOH**	
1	12,5	198	0	98	0%
2	25	332	2	61	1%
3	50	749	179	21	18%
4	75	546	442	9	43%
5	100	313	504	5	60%
6	125	232	467	4	65%
7	150	168	436	3	71%
8	175	134	408	2	74%

General conditions: $Al(OTf)_3$ (125 μmol), MeOH (100 mL), CO_2 (20 bar), H_2 (100 bar), 16 h; [a] determined by GC analysis.

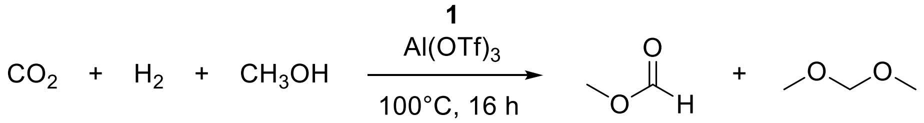
Table 4 Screening of acid co-catalyst concentration.



Entry	**$Al(OTf)_3$** [μmol]	TON[a]		Selectivity$_{DMM}$[a]
		MF	**DMM**	
1	12,5	18	0	0%
2	25	24	0	0%
3	50	1	8	79%
4	75	202	144	40%
5	100	193	359	64%
6	125	181	461	71%
7	150	169	520	74%
8	175	159	564	78%

General conditions: [Ru] = **1** (125 μmol), MeOH (100 mL), CO_2 (20 bar), H_2 (100 bar), 80°C, 16 h; [a] determined by GC analysis.

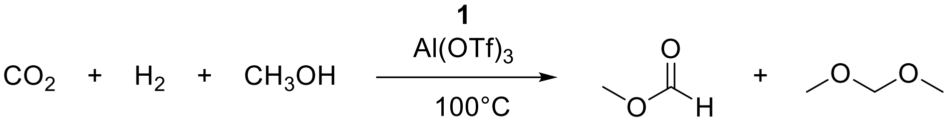
Table 5 Screening of CO_2/H_2 ratios.



Entry	**H_2** [bar]	**TON**[a]		**Selectivity$_{DMM}$**[a]
		MF	**DMM**	
		CO_2 (5 bar)		
1	100	51	323	85%
2	120	39	296	87%
3	140	35	333	89%
		CO_2 (10 bar)		
5	100	81	412	82%
6	120	83	478	84%
7	140	75	493	85%

General conditions: [Ru] = **1** (125 μmol), $Al(OTf)_3$ (500 μmol), MeOH (100 mL), 100°C, 16 h; [a] determined by GC analysis.

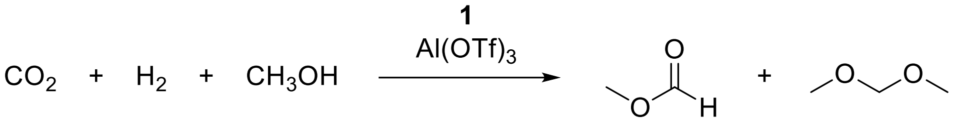
Table 6 Screening of reaction time.



Entry	Time [h]	TON[a]		Selectivity$_{DMM}$[a]
		MF	DMM	
1	1	311	174	35%
2	2	273	359	56%
3	3	255	451	63%
4	4	251	435	62%
5	5	236	519	67%
6	6	207	578	73%
7	7	208	610	74%
8	8	197	631	75%
9	9	202	653	76%
10	10	183	664	78%
11	11	186	680	78%
12	12	184	648	77%
13	13	175	692	79%
14	14	164	639	79%
15	15	165	671	80%
16	16	170	688	80%
17	17	170	706	80%
18	18	164	714	80%
19	36	129	714	84%

General conditions: [Ru] = **1** (125 μmol), $Al(OTf)_3$ (500 μmol), MeOH (100 mL), CO_2 (20 bar), H_2 (120 bar), 100°C; [a] determined by GC analysis.

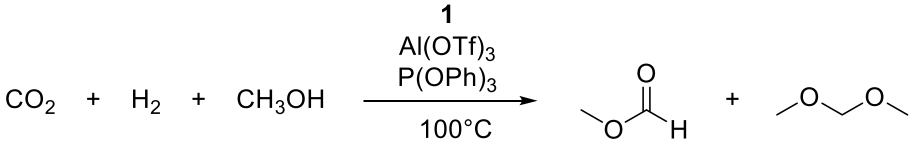
Table 7 Optimization of reaction parameters at a reaction time of 18 h.



Entry	**1** [μmol]	**Al(OTf)$_3$** [μmol]	**Temp.** [°C]	**p(CO$_2$)** [bar]	**p(H$_2$)** [bar]	**TON**[a]		**Selectivity$_{DMM}$**[a]
						MF	**DMM**	
1	125	500	90	20	90	202	903	81%
2	62.5	500	90	20	90	486	1596	77%
3	62.5	250	90	20	100	636	1370	68%
4	31.25	250	90	20	100	1761	1732	49%
5	31.25	250	90	15	100	1254	2025	62%
6	15.63	62.5	90	20	90	4024	651	14%

[a] Determined by GC analysis.

Table 8 Screening of reaction time in presence of P(OPh)$_3$.



Entry	**Time** [h]	**TON**[a]		**Selectivity$_{DMM}$**[a]
		MF	**DMM**	
1	8	191	857	81%
2	10	170	890	84%
3	12	166	930	84%
4	14	171	962	85%
5	16	160	913	85%
6	36	141	780	84%

General conditions: [Ru] = **1** (125 μmol), Al(OTf)$_3$ (500 μmol), P(OPh)$_3$ (500 μmol), MeOH (100 mL), CO$_2$ (20 bar), H$_2$ (120 bar), 100°C; [a] determined by GC analysis.

General procedure for CO_2 hydrogenation experiments at CaRLa (Heidelberg)

In an argon filled glovebox, Ru-catalyst, $Al(OTf)_3$ and additive were weighed into a teflon insert fitted with a magnetic stirrer bar and placed into a stainless steel 40 mL Premex autoclave. MeOH was added and the autoclave was tightly closed before being purged with CO_2 (3x10 bar) and finally pressurized with CO_2 (20 bar) and H_2 (100 bar) to a total pressure of 120 bar at room temperature. The vessel was heated in an aluminum block to 100 °C (150 bar total pressure) and stirred at 800 rpm for 16-24 h (as indicated). The autoclave was cooled to 0°C in an ice bath then carefully vented. To determine the turnover number (TON) of MF and DMM, Mesitylene (30 μL) was added to the mixture as an internal standard. 0.1 mL of the resulting solution were transferred to an NMR tube with 0.5 mL of D_3COD or $CDCl_3$ and analyzed by ^1H NMR.

All high pressure experiments were carried out in Premex reactors with 40 mL nominal volumes equipped with PTFE inserts (see figure below). **Caution:** Reactions must be carried out in a well ventilated fume hood. The used reactors must tolerate up to at least 12 times greater pressure than the working pressure.

Figure 6 Representative picture of a Premex autoclave used in high pressure reaction.

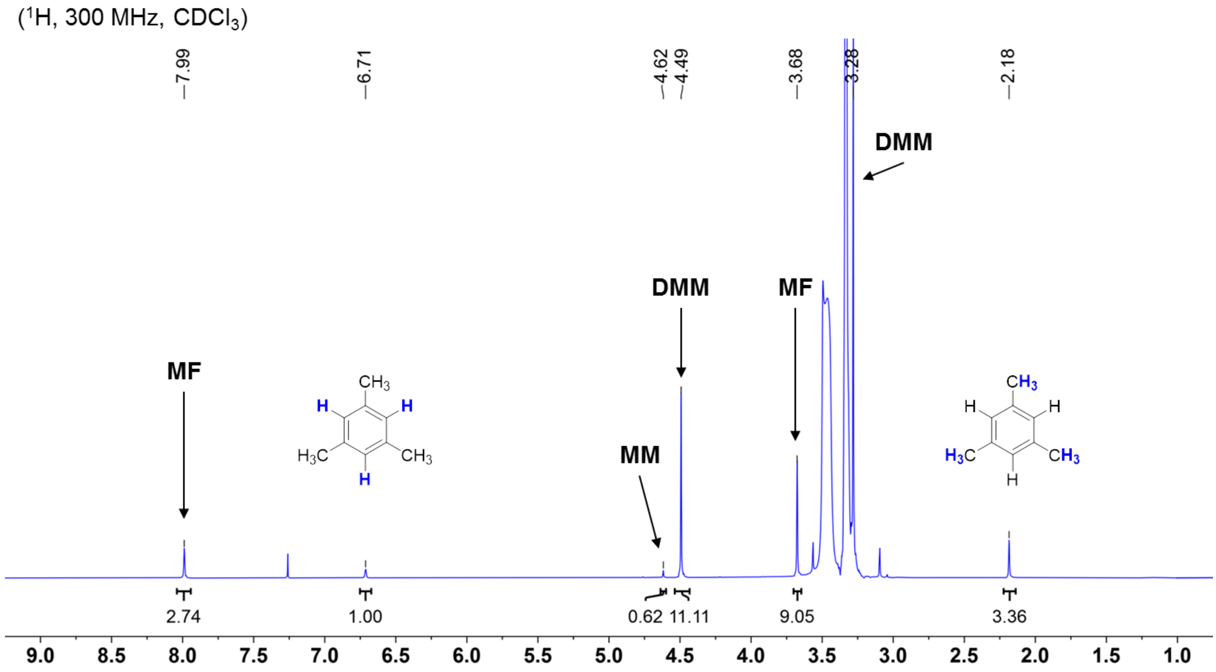


Figure 7 Representative ^1H NMR spectrum in $CDCl_3$ (300 MHz) of a typical CO_2 hydrogenation post-reaction mixture after addition of mesitylene as internal standard. MM = Methoxymethane.

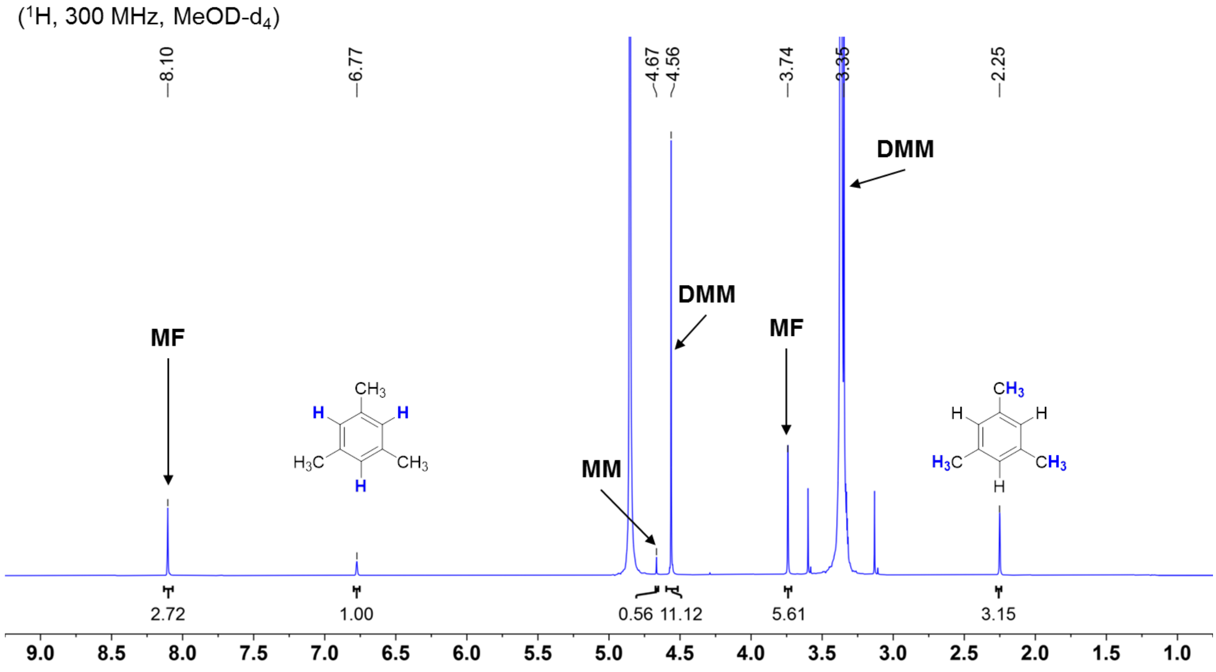
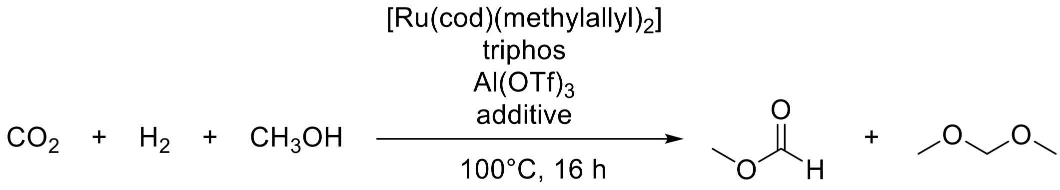


Figure 8 Representative ^1H NMR spectrum in D_3COD (300 MHz) of a typical CO_2 hydrogenation post-reaction mixture after addition of mesitylene as internal standard. MM = Methoxymethane.

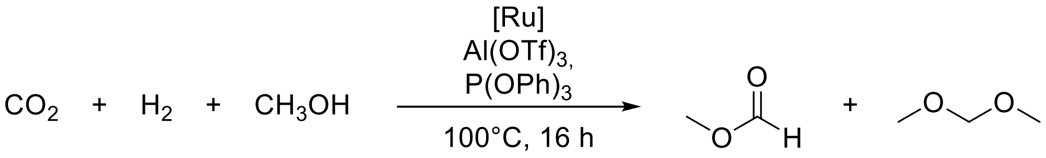
Table 9 Screening of phosphorus ligand additives in CO_2 hydrogenation at low pressure.



Entry	Additive	TON[b]	
		MF	DMM
1	-	18	4
2	PPh_3	21	32
3	P(*p*-Tol)$_3$	21	32
4	$P(4\text{-}MeOC_6H_4)_3$	21	29
5	$P(4\text{-}CF_3OC_6H_4)_3$	28	13
6	P(*o*-Tol)$_3$	17	4
7	PCy_3	9	1
8	P^tBu_3	5	1
9	$P(OPh)_3$	18	46
10[a]	$P(OPh)_3$	24	46

General conditions: [Ru] (12.5 μmol), triphos (12.5 μmol), Al(OTf)$_3$ (25 μmol), additive (25 μmol), MeOH (2 mL), CO_2 (20 bar), H_2 (30 bar), 100°C, 16 h; [a] [Ru] = **1** (12.5 μmol); [b] determined by ^1H NMR using mesitylene as internal standard.

Table 10 Effect of pressure and catalyst loading in CO_2 hydrogenation in presence of $P(OPh)_3$.



Entry	[Ru]	$P(OPh)_3$ [μmol]	TON[b]	
			MF	DMM
1	**1**	0	114	51
2	**1**	25	105	55
3	[Ru(cod)(methylallyl)$_2$]/triphos	25	traces	traces
4[a]	**1**	12	125	68
5[a]	$[RuH_2(PPh_3)_4]$/triphos	0	161	168

General conditions: [Ru] (12.5 μmol), Al(OTf)$_3$ (25 μmol), MeOH (2 mL), CO_2 (20 bar), H_2 (60 bar), 100°C, 16 h; [a] [Ru] (6.0 μmol), Al(OTf)$_3$ (12 μmol); [b] determined by ^1H NMR using mesitylene as internal standard.

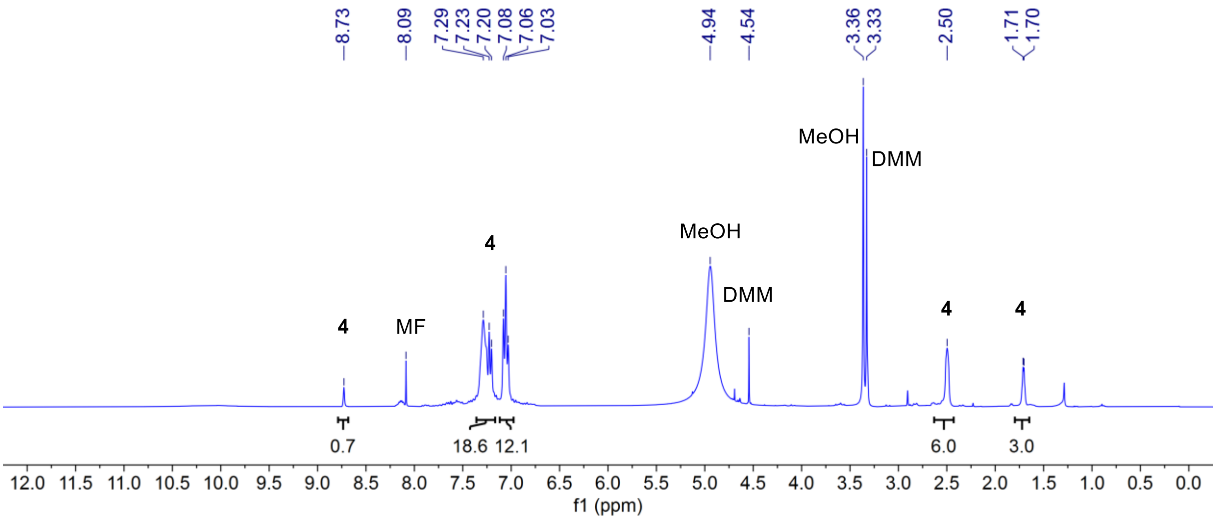


Figure 9 ^{1}H NMR (300 MHz, D_3COD) spectrum of the post-reaction mixture of a CO_2 hydrogenation experiment after evaporation, [Ru] = **1** (50 μmol), $Al(OTf)_3$ (200 μmol), MeOH (10 mL), $p(CO_2)$ = 20 bar, $p(H_2)$ = 100 bar, 100°C, 16 h.

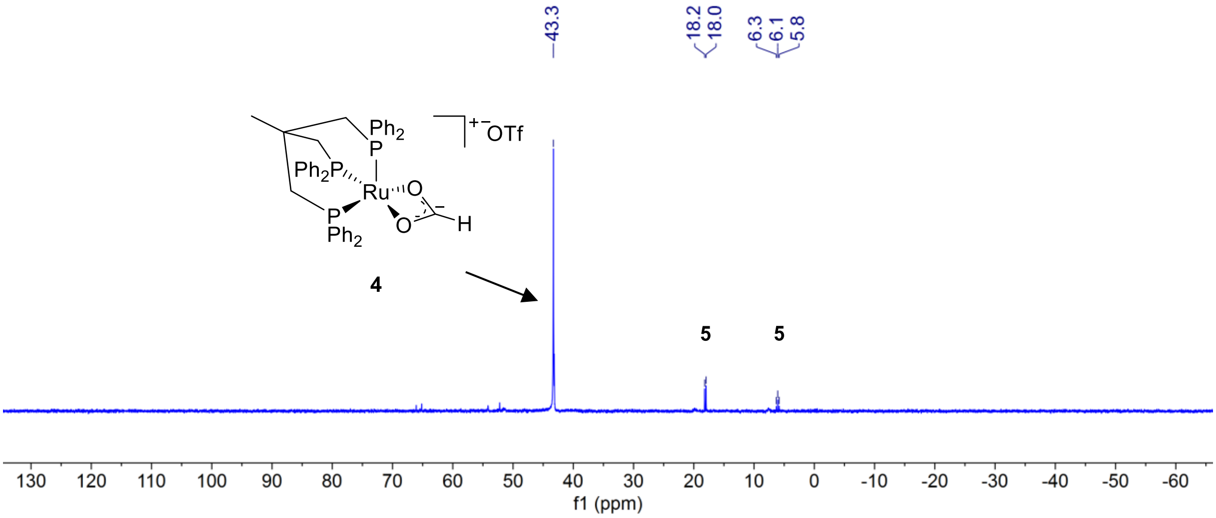


Figure 10 ^{31}P NMR (121 MHz, D_3COD) spectrum of the post-reaction mixture of a CO_2 hydrogenation experiment after evaporation, [Ru] = **1** (50 μmol), $Al(OTf)_3$ (200 μmol), MeOH (10 mL), $p(CO_2)$ = 20 bar, $p(H_2)$ = 100 bar, 100°C, 16 h.

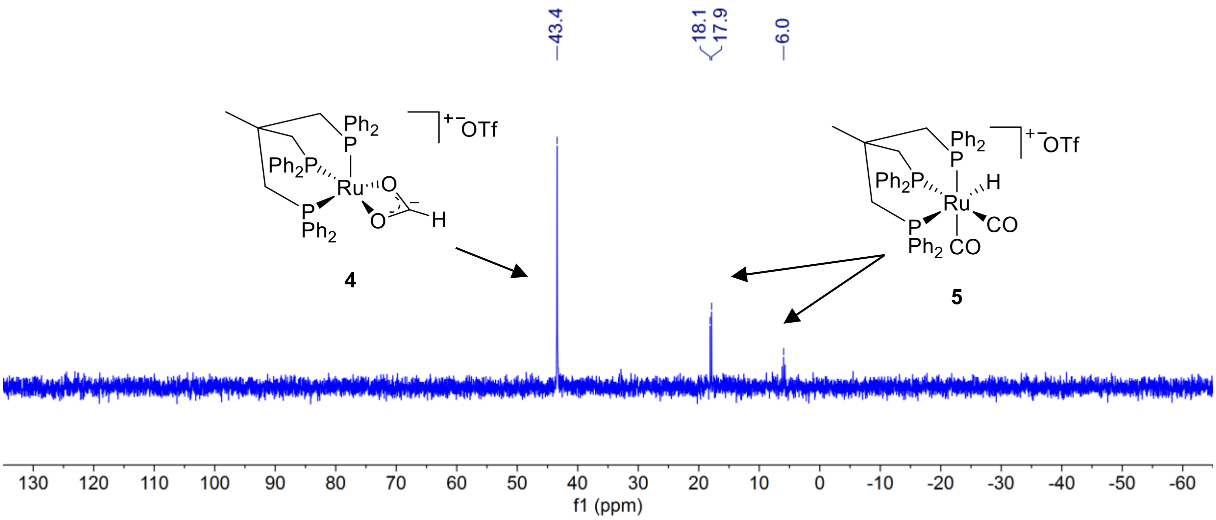


Figure 11 ^{31}P NMR (121 MHz, D_3COD) spectrum of the post-reaction mixture of a CO_2 hydrogenation experiment, [Ru] = [Ru(cod)(2-methylallyl)$_2$] (50 μmol), triphos (50 μmol) $Al(OTf)_3$ (200 μmol), MeOH (10 mL), $p(CO_2)$ = 20 bar, $p(H_2)$ = 100 bar, 100°C, 16 h.

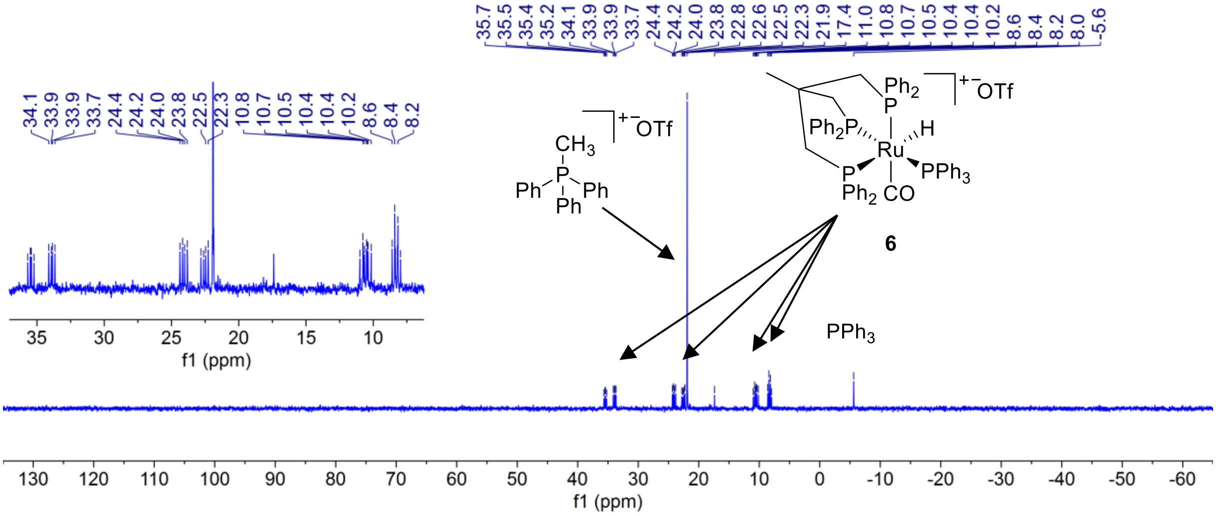


Figure 12 ^{31}P NMR (121 MHz, D_3COD) spectrum of the post-reaction mixture of a CO_2 hydrogenation experiment, [Ru] = **2** (50 μmol), $Al(OTf)_3$ (200 μmol), PPh_3 (200 μmol), MeOH (10 mL), $p(CO_2)$ = 20 bar, $p(H_2)$ = 100 bar, 100°C, 16 h.

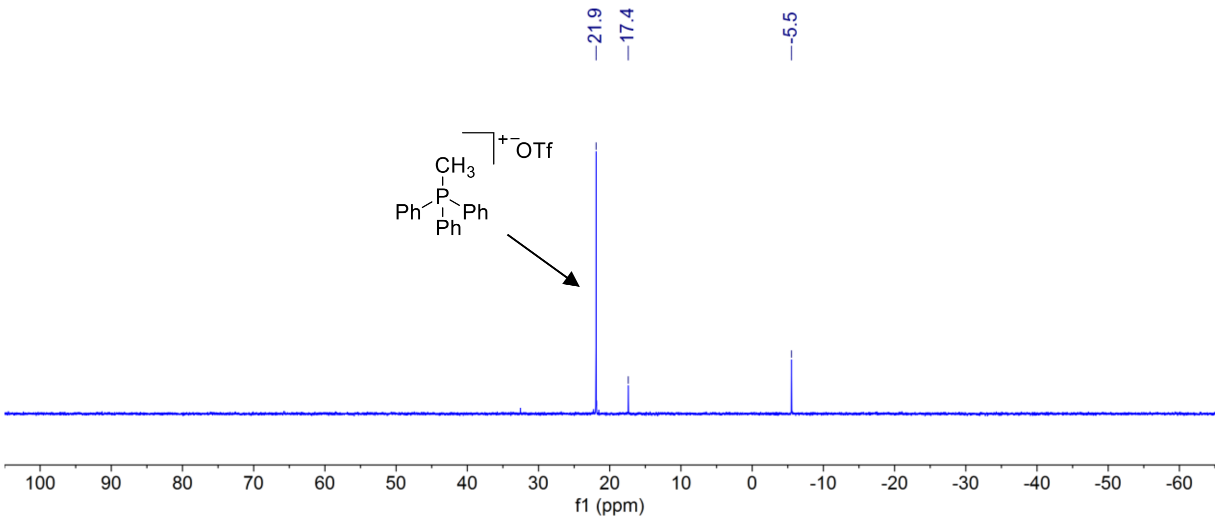


Figure 13 ^{31}P NMR (121 MHz, D_3COD) spectrum of the post-reaction mixture of a CO_2 hydrogenation experiment, $Al(OTf)_3$ (200 μmol), PPh_3 (200 μmol), MeOH (10 mL), $p(CO_2)$ = 20 bar, $p(H_2)$ = 100 bar, 100°C, 16 h.

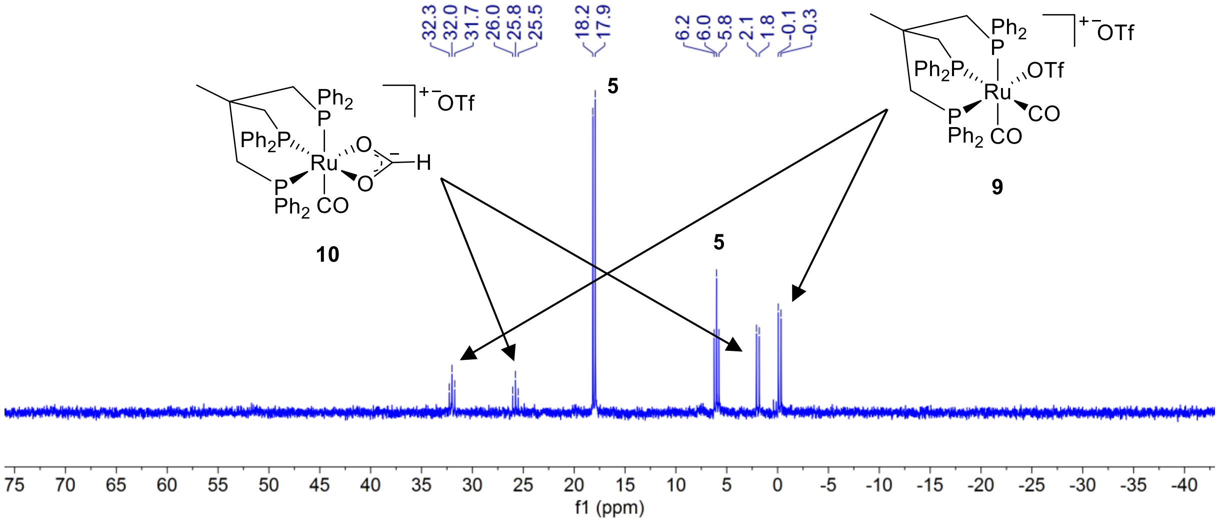


Figure 14 ^{31}P NMR (121 MHz, D_3COD) spectrum of the post-reaction mixture of a CO_2 hydrogenation experiment, [Ru] = **5** (12.5 μmol), $Al(OTf)_3$ (50 μmol), MeOH (5 mL), $p(CO_2)$ = 20 bar, $p(H_2)$ = 100 bar, 100°C, 16 h.

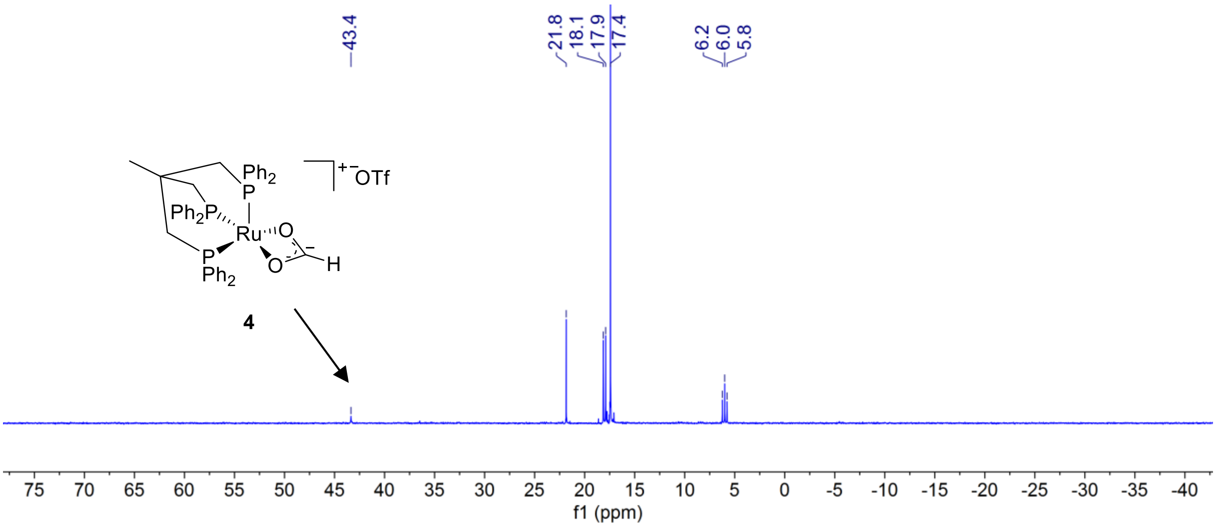


Figure 15 ^{31}P NMR (121 MHz, D_3COD) spectrum of the post-reaction mixture of a CO_2 hydrogenation experiment, [Ru] = **5** (12.5 µmol), $Al(OTf)_3$ (50 µmol), PPh_3 (50 µmol), MeOH (5 mL), $p(CO_2)$ = 20 bar, $p(H_2)$ = 100 bar, 100°C, 16 h.

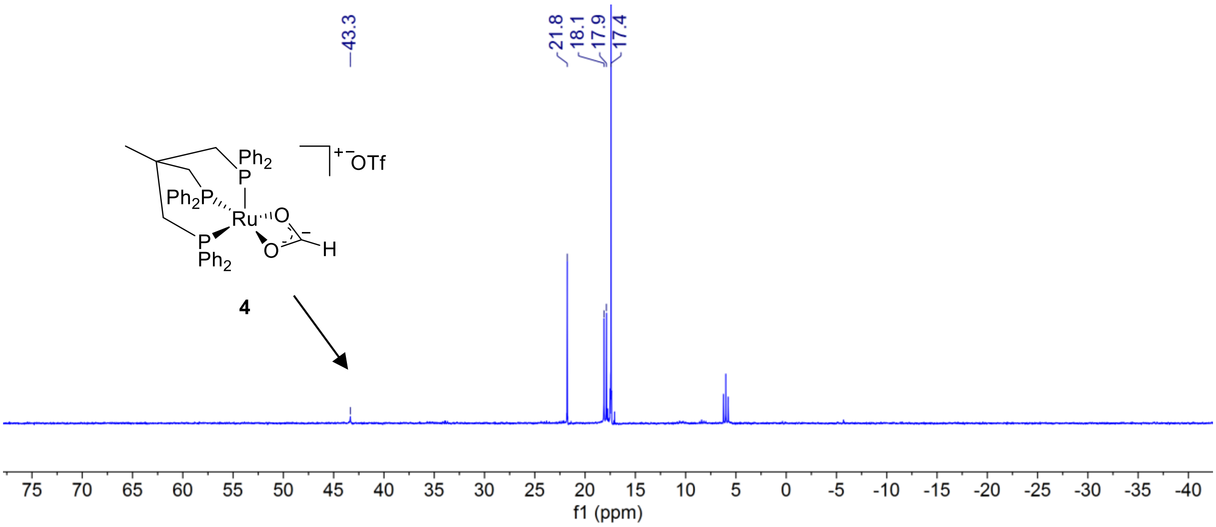


Figure 16 ^{31}P NMR (121 MHz, D_3COD) spectrum of the post-reaction mixture of a CO_2 hydrogenation experiment, [Ru] = **5** (12.5 µmol), $Al(OTf)_3$ (50 µmol), $[PPh_3CH_2OH]OTf$ (50 µmol), MeOH (5 mL), $p(CO_2)$ = 20 bar, $p(H_2)$ = 100 bar, 100°C, 16 h.

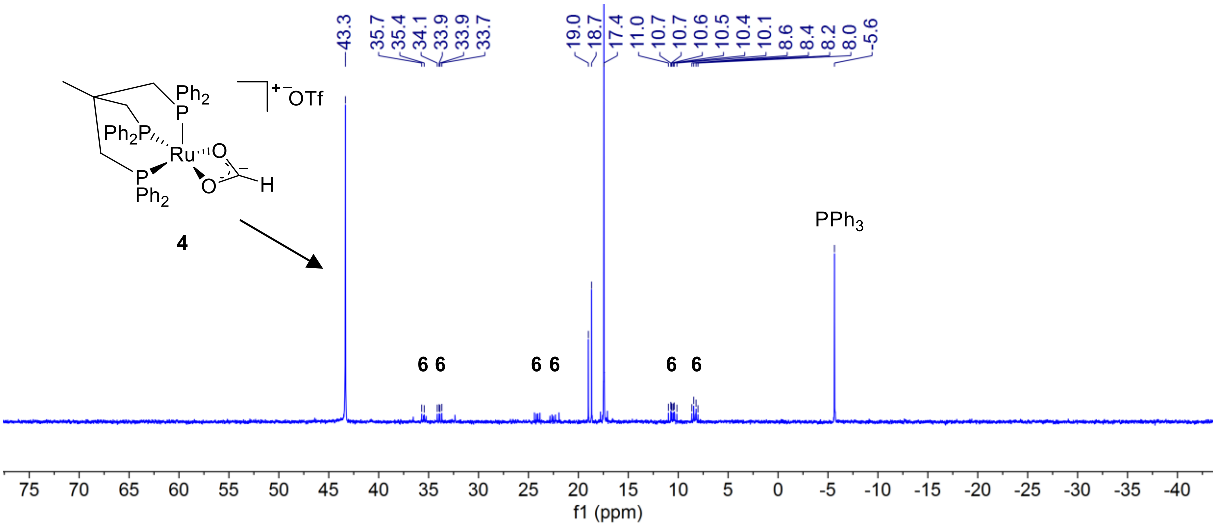


Figure 17 ^{31}P NMR (121 MHz, D_3COD) spectrum of the post-reaction mixture of a CO_2 hydrogenation experiment, [Ru] = **1** (12.5 µmol), [PPh_3CH_2OH]OTf (50 µmol), MeOH (5 mL), $p(CO_2)$ = 20 bar, $p(H_2)$ = 100 bar, 100°C, 16 h.

In-situ NMR study of 5 in the presence of $P(OPh)_3$ and H_2

A high-pressure NMR tube was charged with a 0.6 mL D_3COD solution containing Ru-complex **5** (13.0 mg, 12.5 µmol) and $P(OPh)_3$ (7.8 mg, 25 µmol). After 1 h at 100°C, a ^{31}P NMR spectrum was recorded at 25°C (Figure 15 a). After pressurizing with 10 bar of H_2, the solution was heated to 100°C in an oil bath for 24 h. The mixture was cooled to room temperature and another ^{31}P NMR spectrum was recorded (Figure 15 b).

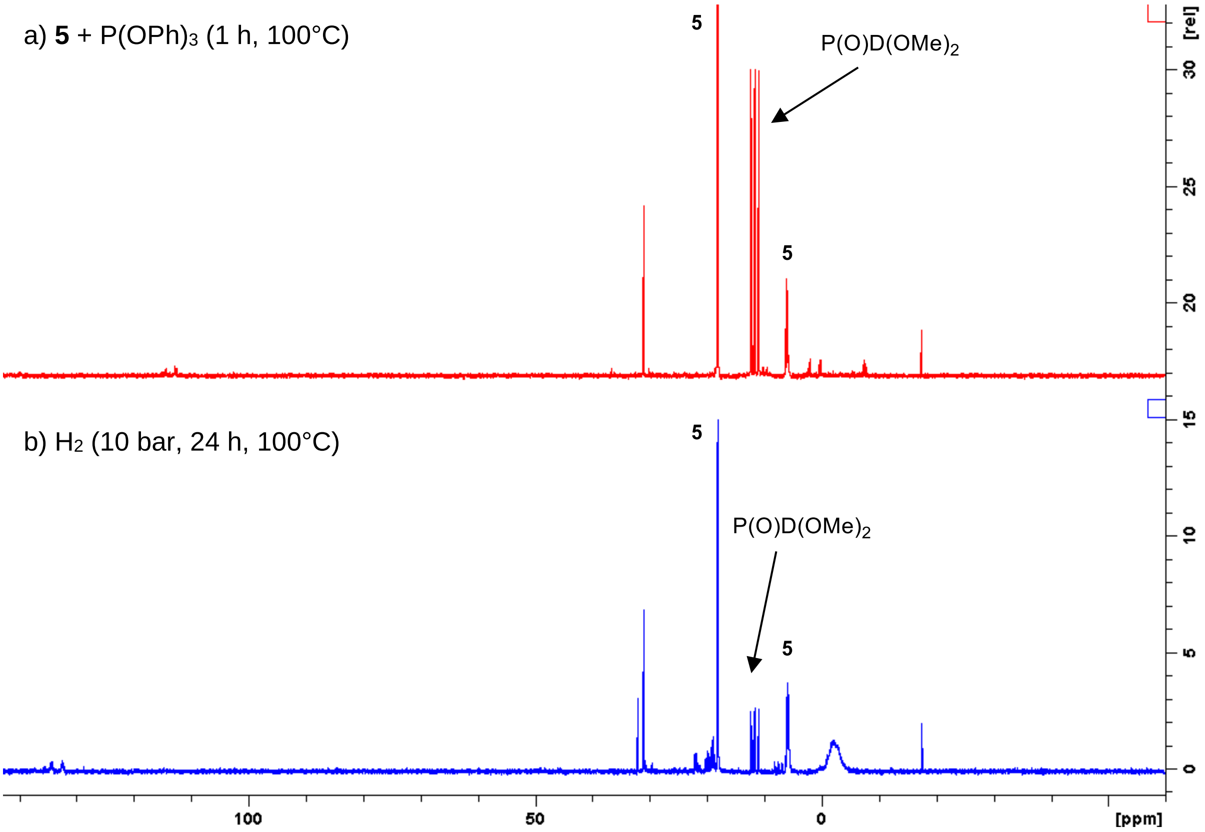


Figure 18 ^{31}P NMR (162 MHz, D_3COD) spectra of a) **5** (12.5 µmol) and $P(OPh)_3$ (25.0 µmol) in 0.6 mL of D_3COD after 1 h at 100°C and b) after 24 h at $p(H_2)$ = 10 bar, 100°C.

General procedure for catalyst recycling experiments

All volatiles of the mixture obtained as in the described general procedure were removed *in vacuo* at 40°C. The remaining solid was transferred into a glovebox and dissolved in MeOH. The mixture was transferred back into a Teflon insert and placed into a stainless steel 40 mL Premex autoclave. The subsequent cycle was performed as described in the general CO_2 hydrogenation procedure.

Recycling of catalyst system 1/Al(OTf)$_3$ without additive

Table 11 Catalyst recycling using **1**/Al(OTf)$_3$.

Entry	Al(OTf)$_3$ [μmol]	TON[a]		Selectivity$_{DMM}$[a]
		MF	DMM	
Run 1	200	52	206	80%
Run 2	-	50	209	81%
Run 3	-	54	207	79%

General conditions: [Ru] = **1** (50 μmol), MeOH (10 mL), CO_2 (20 bar), H_2 (100 bar), 100°C, 16 h; [a] determined by ^1H NMR using mesitylene as internal standard.

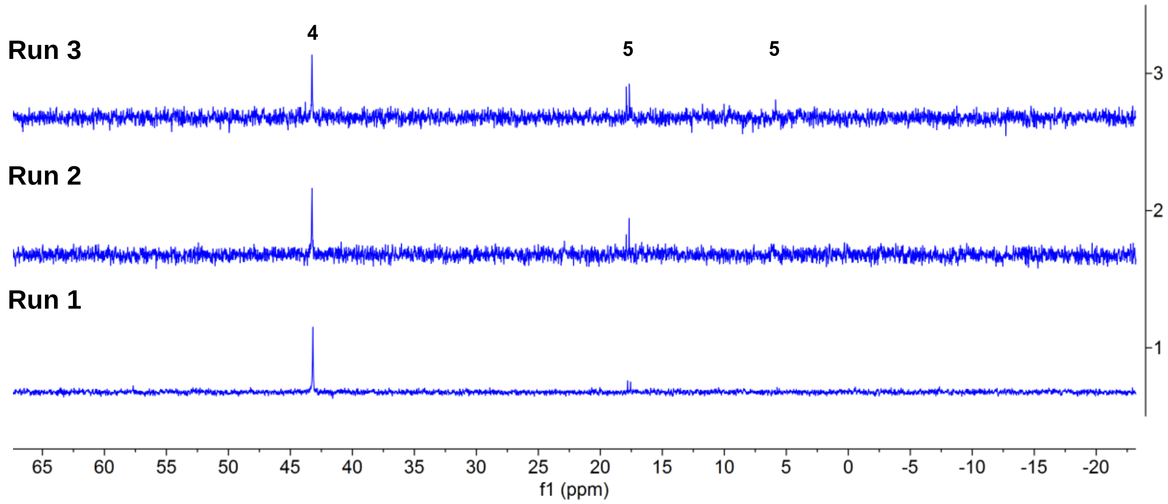


Figure 19 ^{31}P NMR (121 MHz, D_3COD) spectra of post-reaction mixtures in CO_2 hydrogenation recycling experiments, [Ru] = **1** (50 μmol) in run 1, Al(OTf)$_3$ (200 μmol) in run 1, MeOH (10 mL), $p(CO_2)$ = 20 bar, $p(H_2)$ = 100 bar, 100°C, 16 h.

Recycling of catalyst system 3/Al(OTf)$_3$ without additive

Table 12 Catalyst recycling using **3**/Al(OTf)$_3$.

Entry	Al(OTf)$_3$ [μmol]	TON[a]		Selectivity$_{DMM}$[a]
		MF	DMM	
Run 1	200	62	283	82%
Run 2	-	58	261	82%
Run 3	-	50	219	81%

General conditions: [Ru] = **3** (50 μmol), MeOH (10 mL), CO_2 (20 bar), H_2 (100 bar), 100°C, 16 h; [a] determined by ^{1}H NMR using mesitylene as internal standard.

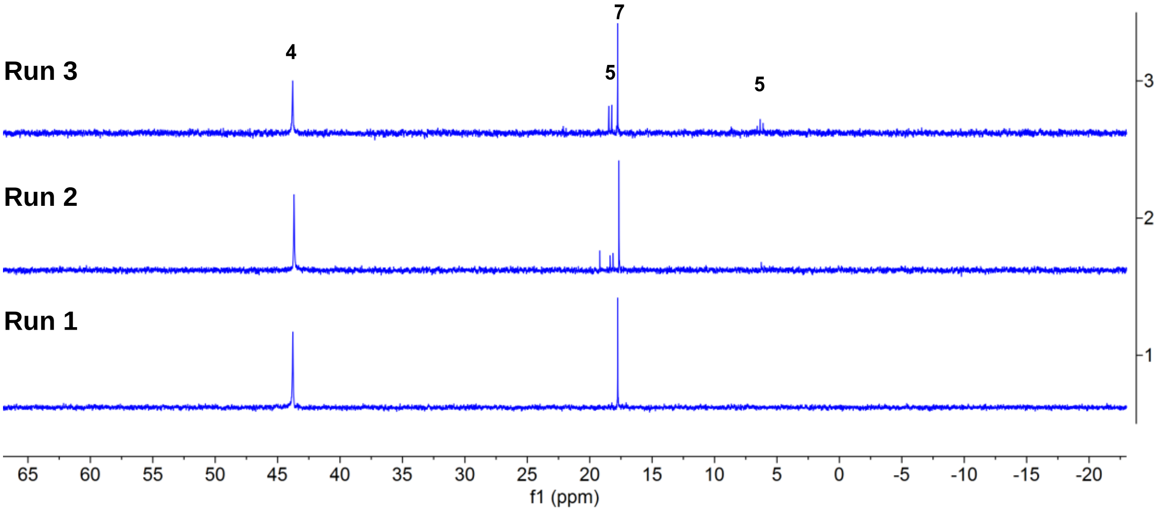


Figure 20 ^{31}P NMR (121 MHz, D_3COD) spectra of post-reaction mixtures in CO_2 hydrogenation recycling experiments, [Ru] = **3** (50 μmol) in run 1, Al(OTf)$_3$ (200 μmol) in run 1, MeOH (10 mL), $p(CO_2)$ = 20 bar, $p(H_2)$ = 100 bar, 100°C, 16 h.

Recycling of catalyst system 3/Al(OTf)$_3$ without additive at low catalyst loading

Table 13 Catalyst recycling using **3**/Al(OTf)$_3$ at low catalyst loading.

Entry	**Al(OTf)$_3$** [μmol]	**TON**[a]		**Selectivity$_{DMM}$**[a]
		MF	**DMM**	
Run 1	25	506	1176	70%
Run 2	-	599	908	60%
Run 3	-	626	577	48%

General conditions: [Ru] = **3** (3.1 μmol), MeOH (5 mL), CO$_2$ (20 bar), H$_2$ (100 bar), 100°C, 24 h; [a] determined by ^{1}H NMR using mesitylene as internal standard.

Recycling of catalyst system 1/Al(OTf)$_3$ with additives PPh$_3$ and HCOOH

Table 14 Catalyst recycling using **1**/Al(OTf)$_3$ in the presence of PPh$_3$ and HCOOH..

Entry	**Al(OTf)$_3$** [μmol]	**PPh$_3$** [μmol]	**HCOOH** [μmol]	**TON**[a]		**Selectivity$_{DMM}$**[a]
				MF	**DMM**	
Run 1	200	200	200	52	220	81%
Run 2	-	-	200	59	241	80%
Run 3	-	-	200	62	239	79%
Run 4	-	-	200	60	216	79%
Run 5	-	-	200	65	211	76%

General conditions: [Ru] = **1** (50 μmol), MeOH (10 mL), CO$_2$ (20 bar), H$_2$ (100 bar), 100°C, 16 h; [a] determined by ^{1}H NMR using mesitylene as internal standard.

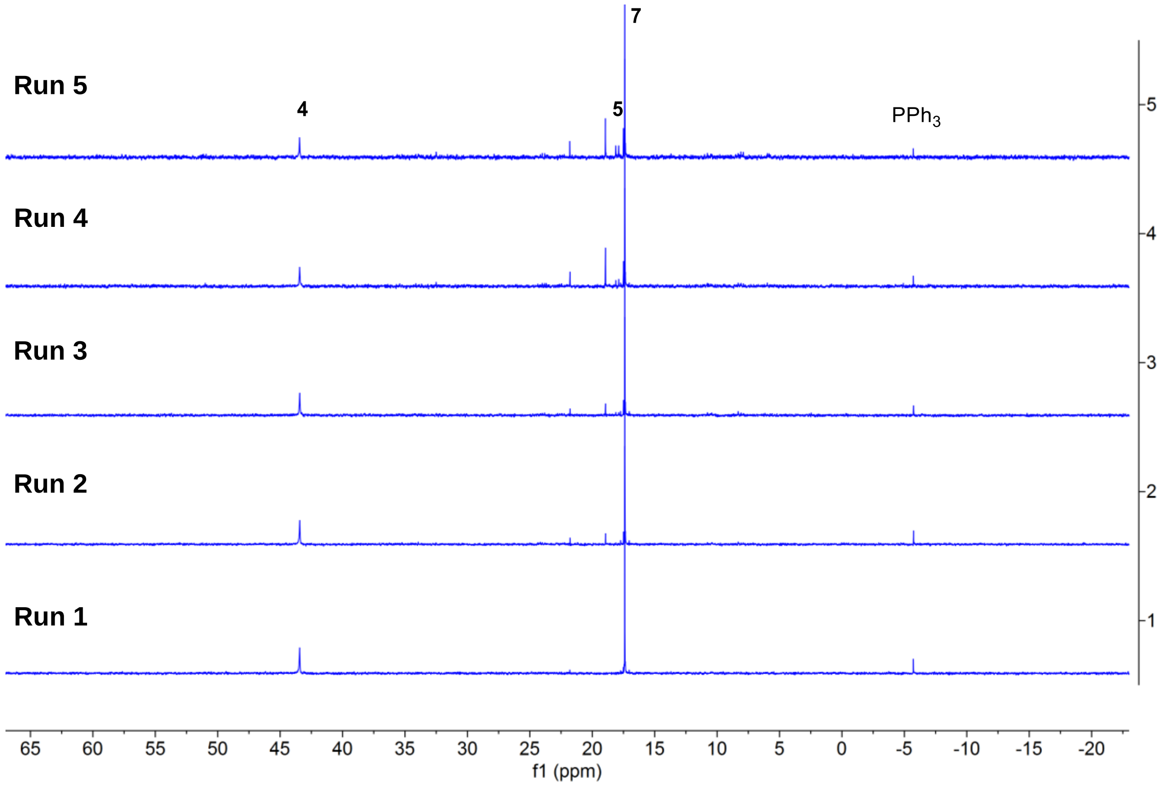


Figure 21 ^{31}P NMR (121 MHz, D_3COD) spectra of post-reaction mixtures in CO_2 hydrogenation recycling experiments, [Ru] = **1** (50 µmol) in run 1, $Al(OTf)_3$ (200 µmol) in run 1, PPh_3 (200 µmol) in run 1, HCOOH (200 µmol), MeOH (10 mL), $p(CO_2)$ = 20 bar, $p(H_2)$ = 100 bar, 100°C, 16 h.

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