Supporting Information

Ni-Catalyzed Reductive Carbonylation of Ethylene with CO_2 and Methanol: Potential for *in situ* CO_2 Capture and Conversion

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1 Material and Methods

General

All operations involving air- or moisture-sensitive compounds were performed were carried out under inert atmosphere using schlenk techniques or in a glovebox. All commercially available reagents were used without further purification (unless otherwise noted). Among these, extra-dry solvents with water ≤ 50 ppm (by K.F.) were bought from Energy Chemical. And all reactions were carried out in a glass-lined stainless-steel reactor of 25 mL capacity equipped with a magnetic stirrer.

Prior to use, all glassware was dried in 80 ^{o}C, evacuated and refilled with argon at least three times.

Instrumentation

Gas chromatography

GC analysis was performed on Shimadzu-2014 with the FID detector and the Stabilwax®-DA column (60 m, 0.53 mm, 0.5 μm) which isothermally at 40 °C for 5 min, then heated to 300 °C at 20 °C min-1 for 13 min, held 1 min, $t_{r\ major}$ = 24 min. The gaseous mixture was collected and analyzed by gas chromatography equipped with thermal conductivity detector (Shimadzu GC-2014C) with Argon as the carrier gas.

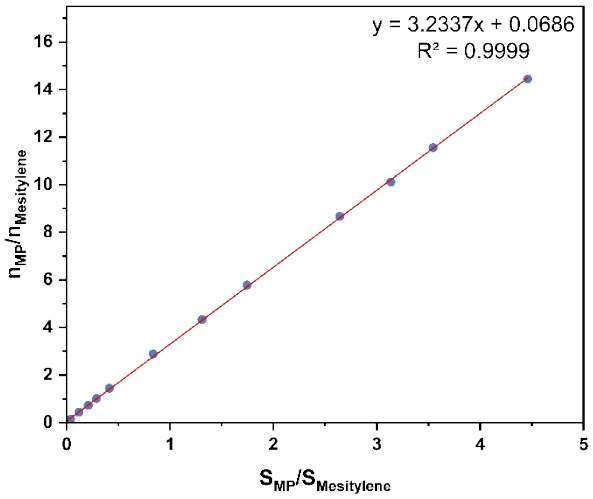
Mass Spectrometry

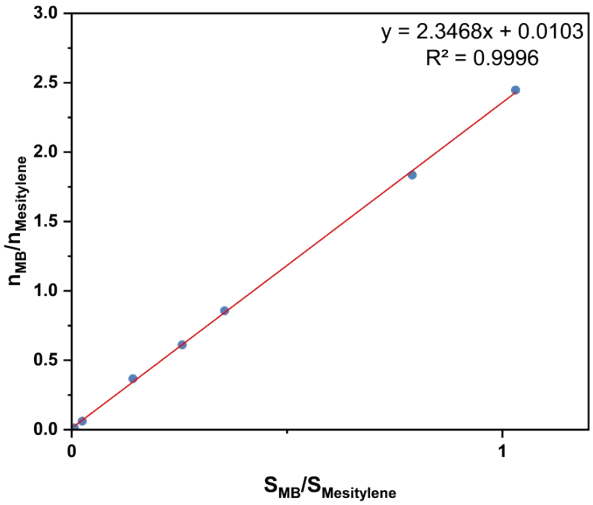
HRMS analysis was performed on Waters Xevo G2-XS QTof High resolution. **GC-MS** analysis was performed on PerkinElmer Clarus 680/SQ8T with the PerkinElmer Elite-5MSII column (30 m 0.25 mm 0.25 μm) which isothermally at 40 °C for 2 min, then heated to 250 °C at 15 °C min^{-1} for 14 min, held 5 min, $t_{r\ major}$ = 21 min. The detected mass is given in m/z units and is associated with the calculated mass of each species.

NMR Spectroscopy NMR spectra were recorded with spectrometers Bruker Avance III 400 MHz spectrometers at ambient temperature at the frequency noted. Chemical shifts (δ values) were reported in ppm relative to internal CD_2Cl_2.

Calculation of the amount of product in the solution product

We quantified the solution from the reactor by the internal standard method (Mesitylene as the internal standard). Measure and plot the internal standard curve of methyl propionate (MP) and methyl butyrate (MB) relative to trimethylbenzene.





Typical procedure for methoxycarbonylation of ethylene with CO_2/MeOH

General procedure.

All reactions were carried out in a glass-lined stainless-steel reactor of 25 mL capacity equipped with a magnetic stirrer. Firstly, in the glove box, $Ni(cod)_2$ (0.1 mmol), ligand (0.15 mmol) and MeOH (5 mL) were loaded into the container. The autoclave was sealed and purged three times with C_2H_4 gas, subsequently charged with C_2H_4 (5 bar), then CO_2 (35 bar) to total pressure of 40 bar. The autoclave was then heated at 140 °C for 12 h. After the reaction, the autoclave was cooled in the water bath and then the gas was vented into the gas collecting bag. The resulting solution was diluted with MeOH (10 mL) and added Mesitylene (100 μl) as internal standard. The sample was filtered through a short cotton plug, then analyzed by GC to determine the yields of the ester. Yields were found to be reproducible within Y = ±5 % in three independent runs for selected experiments.

Preparation of (DCPBz)Ni($C_3H_4O_2$).

We prepared (DCPBz)Ni($C_3H_4O_2$) using literature procedures with slight modifications.[1-5] The entire process was carried out under an argon atmosphere, and a solution was prepared in a glove box. 0.5 mmol of $Ni(cod)_2$ and 0.5 mmol of DCPBz ligands were dissolved in 10 mL of tetrahydrofuran (THF). The high-pressure vessel was pressurized outside the furnace, and 5 bar C_2H_4 and 35 bar CO_2 were introduced. The reaction was then stirred at 60 °C (500 rpm) for 2 h. After cooling to room temperature, the pressure was released, and the orange-yellow solution was transferred to a closed Schlumberger tube filled with argon gas using a long needle under argon protection. A large amount of THF was added for washing, followed by multiple centrifugation steps until the washing solution became colorless. The supernatant was removed using a sleeve, and the nickel compound was placed under dry argon to remove the remaining THF, resulting in the (DCPBz)Ni($C_3H_4O_2$) as a pale yellow solid. ^{1}H NMR (500 MHz, Dichloromethane-d2) δ = 2.70 – 2.78 (m, 1H), 3.10 (tq, J = 10.5, 10.5, 12.5, 22.5, 22.5 Hz, 2H), 3.26 – 3.35 (m, 3H), 3.39 – 3.60 (m, 7H), 9.27 – 9.32 (br, 3H), 9.40 – 9.46 (br, 1H). ^{13}C NMR (126 MHz, Dichloromethane-d2) δ = 26.77 (d, J = 8.2 Hz, Cy), 35.38 (d, J = 15.7 Hz, $NiCH_2CH_2$), 36.99 (d, J = 26.4 Hz,

NiCH2CH2),37.72 (d, J = 4.0 Hz, Cy), 131.10 (dd, J = 4.5, 9.6 Hz, m-Ar), 131.84 (d, J = 14.7 Hz, o-Ar), 132.69 (d, J = 12.4 Hz, ipso-Ar), 191.05 (d, J = 14.9 Hz, COO).

Density functional theory (DFT) calculation

Thermodynamic calculation.

Geometry optimization was performed at MN15/def2-SVP level.[6, 7] Frequencies calculation was carried out at the same level to confirm that we have obtained the minimum (with zero imaginary frequency). All vibrational modes are shown to be positive. When the solvent effect (in methanol) was applicable, it was accounted for using the solvation model based in the Polarizable Continuum Model (PCM).[8] All calculations were done with GAUSSIAN 16.

Kinetic calculation.

Geometry optimization was performed at MN15/def2-SVP level[6, 7]. Frequencies calculation was carried out at the same level to confirm that we have obtained the minimum (with zero imaginary frequency) or the transition state (TS, with a single imaginary frequency). All vibrational modes are shown to be positive for the minimums. Intrinsic reaction coordinate (IRC) analysis was performed to check the connection between the minimum and the corresponding TS. When the solvent effect (in methanol) was applicable, it was accounted for using the solvation model based in the Polarizable Continuum Model (PCM).[8] All calculations were done with GAUSSIAN 16.

2 Result and discussion

Figure

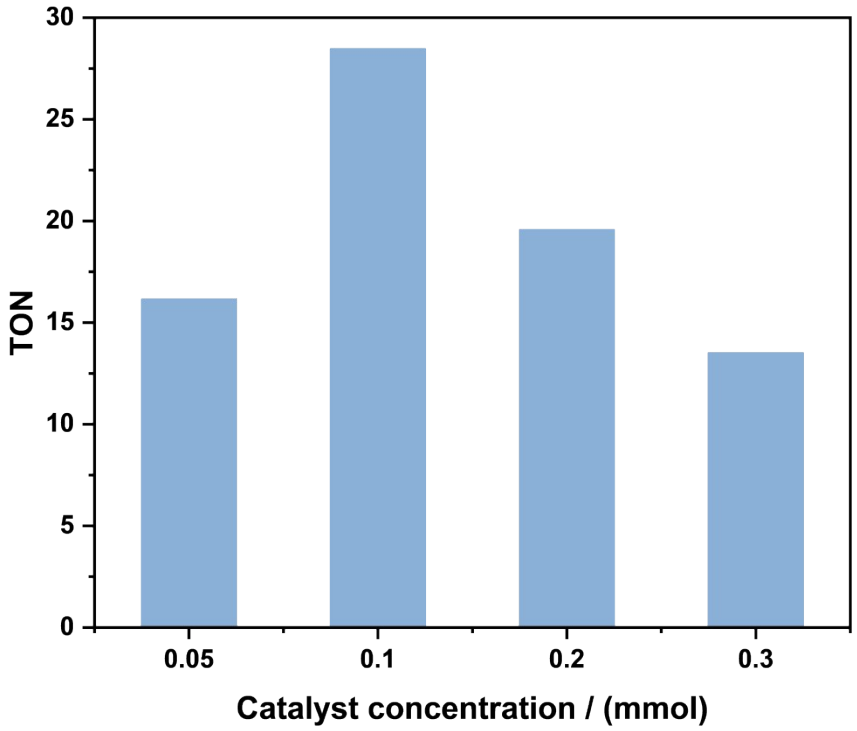
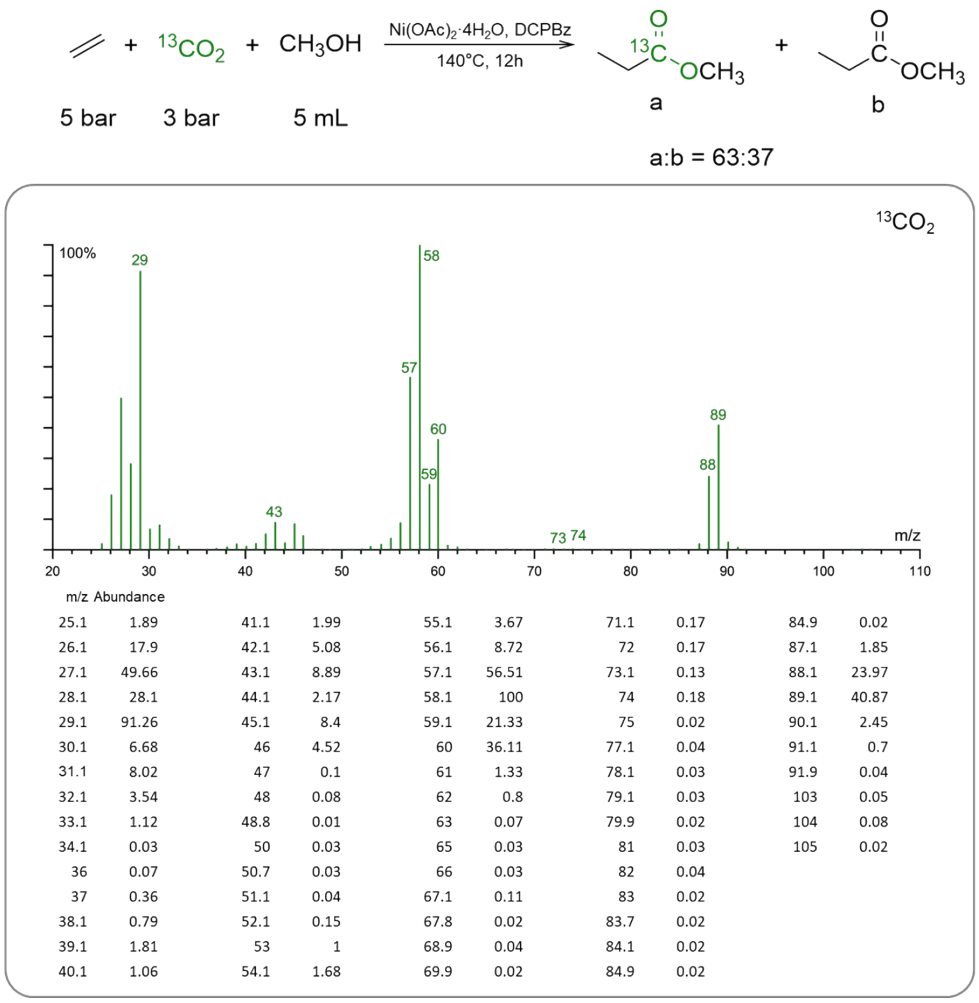


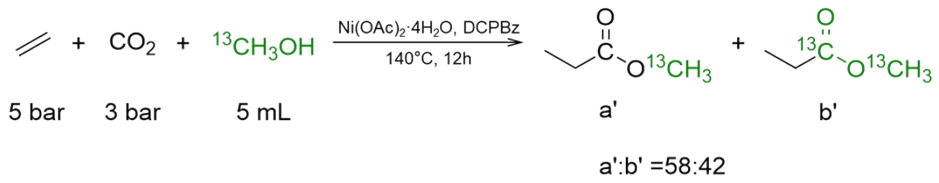
Fig. S1 The effect of catalyst concentration on performance.

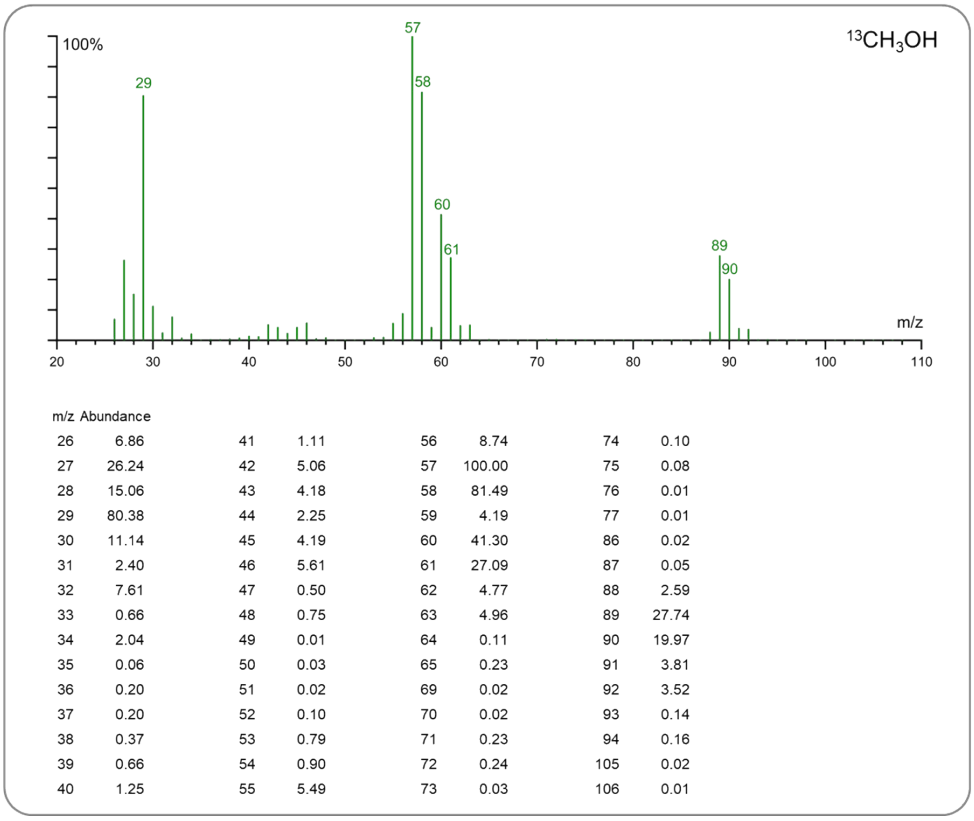


m/z Abundance

25.1	1.89	41.1	1.99	55.1	3.67	71.1	0.17	84.9	0.02
26.1	17.9	42.1	5.08	56.1	8.72	72	0.17	87.1	1.85
27.1	49.66	43.1	8.89	57.1	56.51	73.1	0.13	88.1	23.97
28.1	28.1	44.1	2.17	58.1	100	74	0.18	89.1	40.87
29.1	91.26	45.1	8.4	59.1	21.33	75	0.02	90.1	2.45
30.1	6.68	46	4.52	60	36.11	77.1	0.04	91.1	0.7
31.1	8.02	47	0.1	61	1.33	78.1	0.03	91.9	0.04
32.1	3.54	48	0.08	62	0.8	79.1	0.03	103	0.05
33.1	1.12	48.8	0.01	63	0.07	79.9	0.02	104	0.08
34.1	0.03	50	0.03	65	0.03	81	0.03	105	0.02
36	0.07	50.7	0.03	66	0.03	82	0.04		
37	0.36	51.1	0.04	67.1	0.11	83	0.02		
38.1	0.79	52.1	0.15	67.8	0.02	83.7	0.02		
39.1	1.81	53	1	68.9	0.04	84.1	0.02		
40.1	1.06	54.1	1.68	69.9	0.02	84.9	0.02		

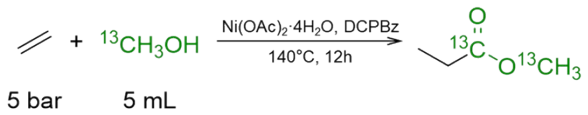
Fig. S2 Isotope-labeling experiment. Liquid MS-data of $^{13}CO_2$.

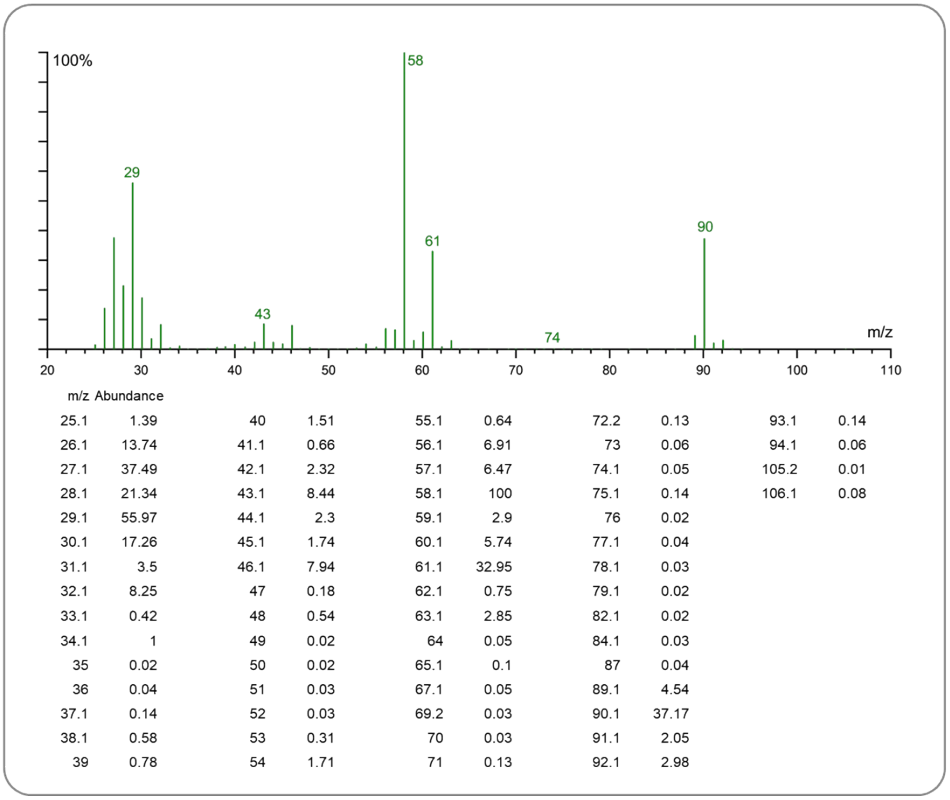




m/z	Abundance						
26	6.86	41	1.11	56	8.74	74	0.10
27	26.24	42	5.06	57	100.00	75	0.08
28	15.06	43	4.18	58	81.49	76	0.01
29	80.38	44	2.25	59	4.19	77	0.01
30	11.14	45	4.19	60	41.30	86	0.02
31	2.40	46	5.61	61	27.09	87	0.05
32	7.61	47	0.50	62	4.77	88	2.59
33	0.66	48	0.75	63	4.96	89	27.74
34	2.04	49	0.01	64	0.11	90	19.97
35	0.06	50	0.03	65	0.23	91	3.81
36	0.20	51	0.02	69	0.02	92	3.52
37	0.20	52	0.10	70	0.02	93	0.14
38	0.37	53	0.79	71	0.23	94	0.16
39	0.66	54	0.90	72	0.24	105	0.02
40	1.25	55	5.49	73	0.03	106	0.01

Fig. S3 Isotope-labeling experiment. Liquid MS-data of $^{13}CH_3OH$.





m/z	Abundance	m/z	Abundance	m/z	Abundance	m/z	Abundance	m/z	Abundance
25.1	1.39	40	1.51	55.1	0.64	72.2	0.13	93.1	0.14
26.1	13.74	41.1	0.66	56.1	6.91	73	0.06	94.1	0.06
27.1	37.49	42.1	2.32	57.1	6.47	74.1	0.05	105.2	0.01
28.1	21.34	43.1	8.44	58.1	100	75.1	0.14	106.1	0.08
29.1	55.97	44.1	2.3	59.1	2.9	76	0.02		
30.1	17.26	45.1	1.74	60.1	5.74	77.1	0.04		
31.1	3.5	46.1	7.94	61.1	32.95	78.1	0.03		
32.1	8.25	47	0.18	62.1	0.75	79.1	0.02		
33.1	0.42	48	0.54	63.1	2.85	82.1	0.02		
34.1	1	49	0.02	64	0.05	84.1	0.03		
35	0.02	50	0.02	65.1	0.1	87	0.04		
36	0.04	51	0.03	67.1	0.05	89.1	4.54		
37.1	0.14	52	0.03	69.2	0.03	90.1	37.17		
38.1	0.58	53	0.31	70	0.03	91.1	2.05		
39	0.78	54	1.71	71	0.13	92.1	2.98		

Fig. S4 Isotope-labeling experiment. Liquid phase MS-data of $^{13}CH_3OH$ without CO_2.

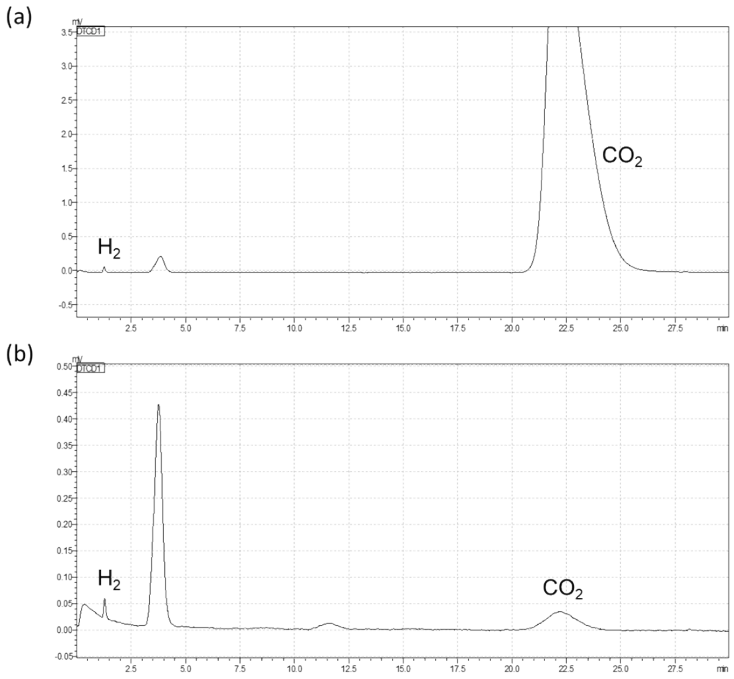


Fig. S5 The TCD data of the gas after the reaction of the system. Type of gas input (a) 5 bar C_2H_4 + 35 bar CO_2; (b) 5 bar C_2H_4 + 35 bar Ar.

s

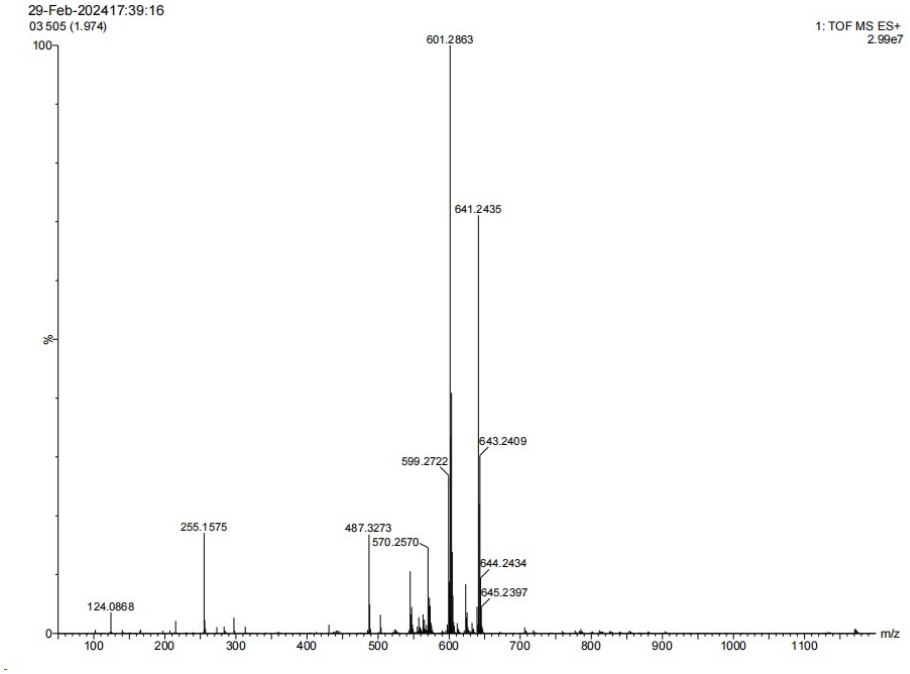


Fig. S6 High-resolution mass spectrometry of nickelalactone.

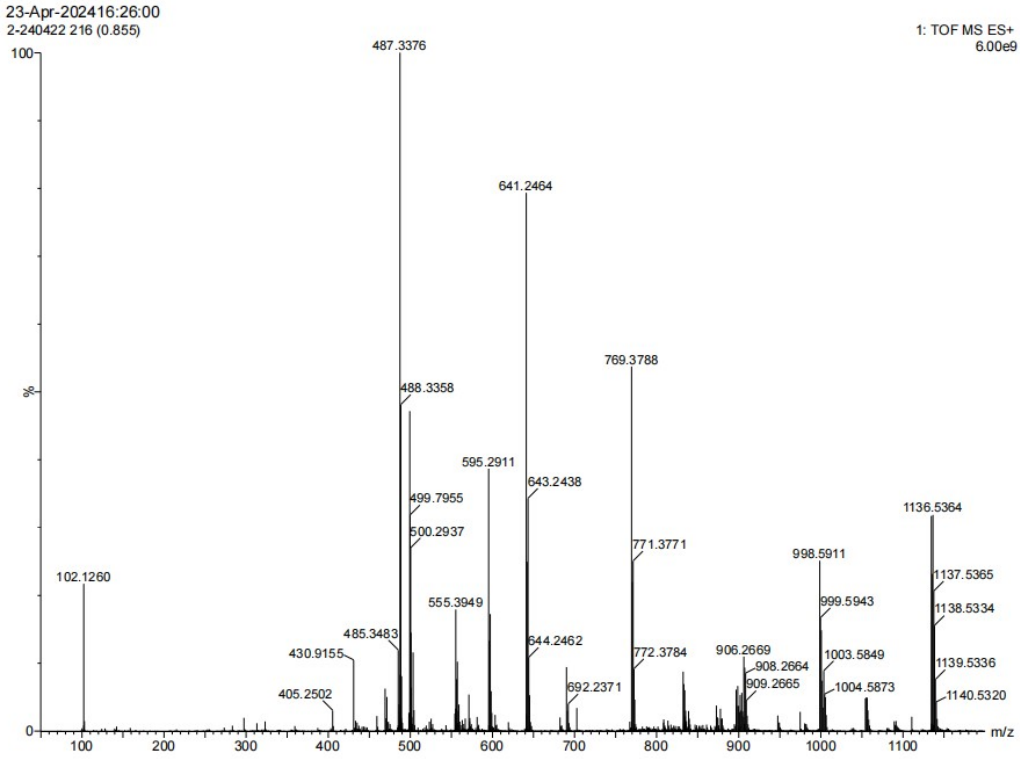


Fig. S7 HRMS of the solution after 2 hours of reaction.

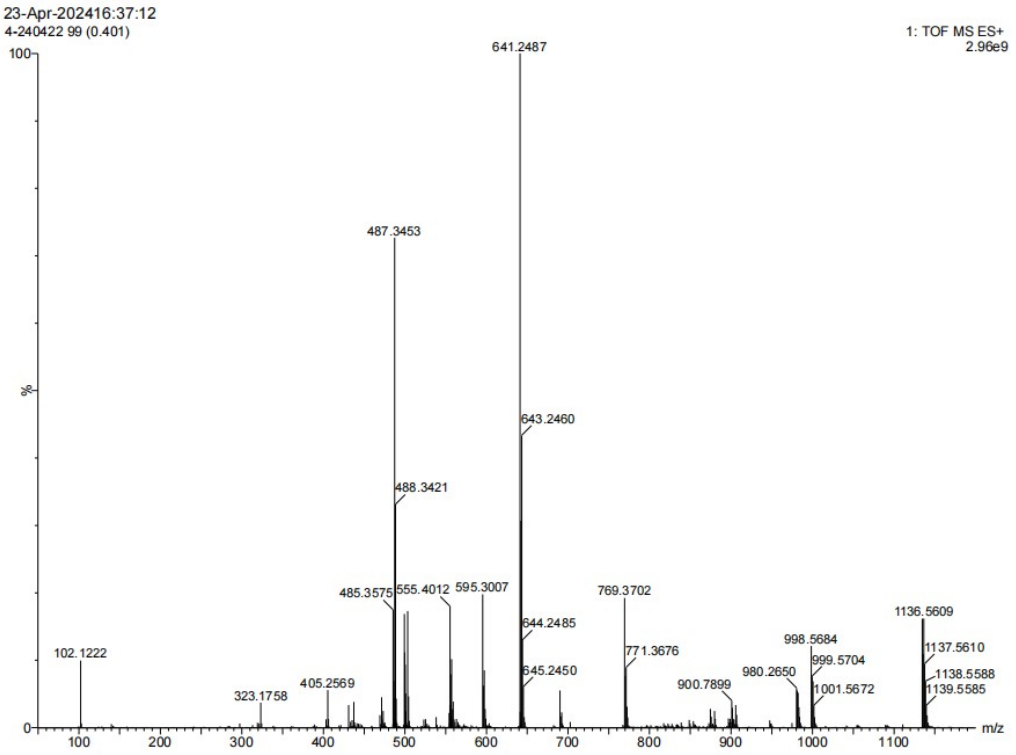


Fig. S8 HRMS of the solution after 4 hours of reaction.

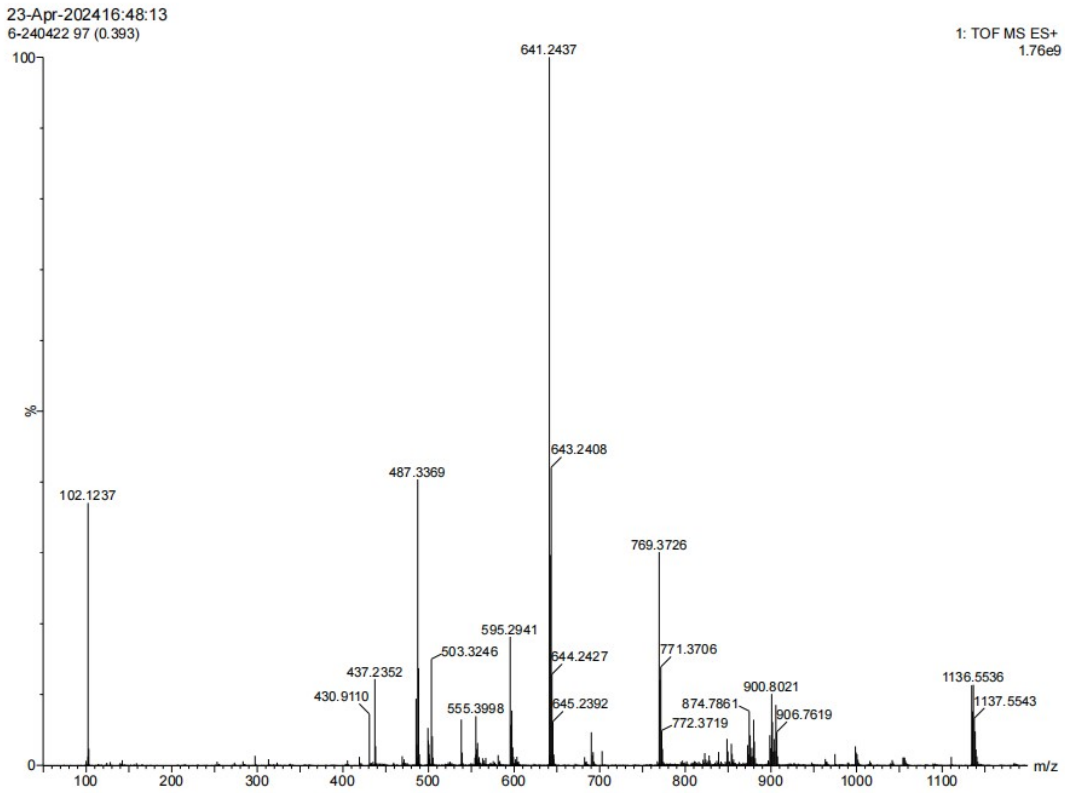


Fig. S9 HRMS of the solution after 6 hours of reactions.

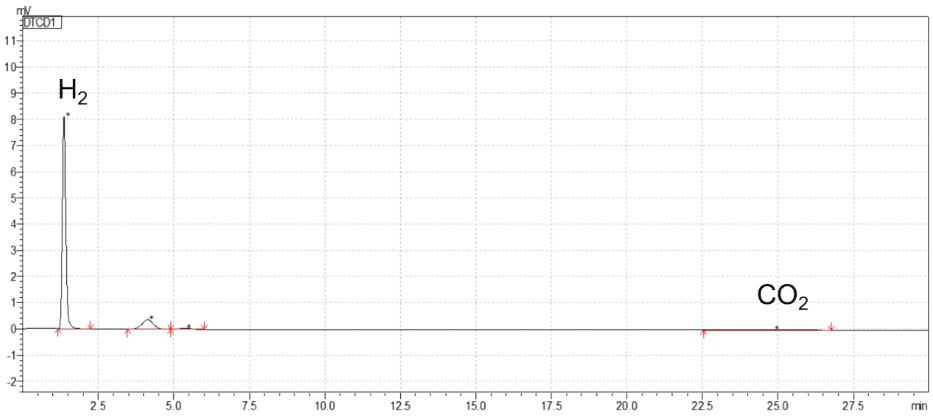


Fig. S10 TCD gas analysis after the ring-opening of nickelalactone.

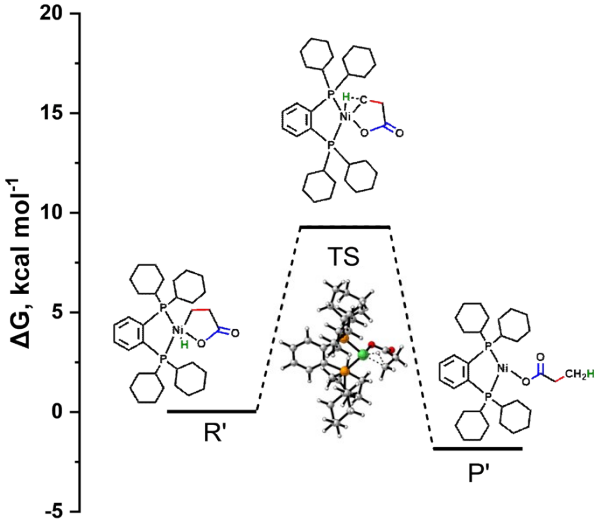


Fig. S11 Kinetic calculation results.

Table

Table S1. Condition optimization.

Entry	Variation	MP TON
1[a]	0.1 mmol Ni, 12h	28
2[a]	0.1 mmol Ni, 36 h	37
3[a]	0.05 mmol Ni, 36 h	67
4[a]	0.025 mmol Ni, 36 h	62
5[a, b]	0.1 mmol Ni 36 h,10 bar C_2H_4,	54
6[a, c]	0.05 mmol Ni, 36 h	83
7[a, c]	0.1 mmol Ni, 36 h	45

[a] $Ni(OAc)_2 \cdot 4H_2O$ and DCPBz (1:1.5) dissolved in 5 mL MeOH; reaction in 25 mL stainless-steel reactor under 5 bar C_2H_4 and 35 bar CO_2. [b] reaction under10 bar C_2H_4. [c] catalyst dissolved in 20 mL MeOH, reaction in 100 mL stainless-steel reactor.

Table S2. Overview of this work and related recent studies.

Entry	Catalyst	Substrate	Promoter	Reaction conditions	Solvent	TON	Ref
1	$Ru_3(CO)_{12}$	ethylene	[Bmim]Cl	160 °C, 40 bar CO_2	MeOH	12	9
2	$[Ru(CO)_3Cl_2]_2$-$Co_2(CO)_8$	cyclohexene	[Bmim]Cl	160 °C, 40 bar CO_2	Alcohol	93	10
3	[Ru]@SILP-A-2	cyclohexene	LiCl	160 °C, 40 bar CO_2	MeOH	94	11
4	$[Rh(CO)_2Cl]_2/Ph_3P$	cyclohexene	p-TsOH	180 °C, 60 bar CO_2	AcOH	19	12
5	IrI_4	THF	LiI	170 °C, 50 bar CO_2	AcOH	86	13
6	Iridium(III) acetate	cyclohexanol	LiI	170 °C, 60 bar CO_2	AcOH	33	14
7	$[Rh(CO)_2Cl]_2$	glycerol	I_2	170 °C, 55 bar CO_2	[bmim]I/H_2O	0.13	15
8	$Rh(acac)(CO)_2$	glucose	I_2	160 °C, 57 bar CO_2	AcOH/H_2O	7.4	16
9	RhI_3	acetone	I_2	170°C, 55 bar CO_2	[EMIm]I/H_2O	80	17
10	$[RhCl(CO)_2]_2/PPh_3$	2-buOH	p-TsOH·H_2O, CHI_3,	160 °C, 20 bar CO_2	AcOH	16	18
11	10Cu@SiO_2-PHM (RWGS) Pd/Ph_2PPy (alkoxycarbonylation)	phenylacetylene	PTSA	400 °C, 25 bar CO_2 25 °C, 60 bar CO (from RWGS)	MeOH	99	19
12	Pt@NaA (RWGS) Pd/DTBPMB (alkoxycarbonylation)	1-Hexene	PTSA	120 °C, 15 bar CO_2	Me-1-butanol	15	20
13	$Ru_3(CO)_{12}$-$Pd(acac)_2$/dtbpx	1-octene	$MeSO_3H$	80 °C, 40 bar CO_2	MeOH	64	21
14	$Ni(OAc)_2$·H_2O/DCPBz	ethylene	-	140 °C, 35 bar CO_2	MeOH	28-110	this work

Table S3. Screening the olefin scope.

Entry[a]	Olefin	Ester TON
1	propylene	0.8
2	butene	-
3	hexene	-
4	cyclohexene	-

[a] 0.1 mmol $Ni(OAc)_2 \cdot 4H_2O$ and 0.15 mmol DCPBz dissolved in 5 mL MeOH; reaction in 25 mL stainless-steel reactor under propylene (5 bar) or butene, hexene, cyclohexene (5 mmol), 35 bar CO_2, 12h.

Table S4. Adaptability of diluted CO_2 gas and flue gas.

Entry[a]	Variation	MP TON
1	99.999% CO_2	28
2	15% CO_2 + 85% N_2	30
3	100 ppm NO + 100 ppm SO_2 + 17.1% CO_2 + 82.7% N_2	29

[a] 0.1 mmol $Ni(OAc)_2 \cdot 4H_2O$ and 0.15 mmol DCPBz dissolved in 5 mL MeOH; reaction in 25 mL stainless-steel reactor under 5 bar C_2H_4 and 35 bar CO_2, 12h.

Table S5 Influence of water on catalytic system performance.

Entry	Addition quantity of H_2O (mmol)	MP TON
1[a]	-	28
2[b]	-	18
3[a]	0.2	20
4[a]	2	12
5[a]	20	3

[a] 0.1 mmol $Ni(OAc)_2 \cdot 4H_2O$ and 0.15 mmol DCPBz dissolved in 5 mL MeOH; reaction in 25 mL stainless-steel reactor under 5 bar C_2H_4 and 35 bar CO_2, 12h. [b] 0.1 mmol $Ni(OAc)_2$.

Table S6. The yield of MP in the reaction of nickelalactone and MeOH under the different conditions.

Entry[a]	Variation	MP Yield %
1	1 bar Ar	5.6
2	40 bar Ar	10.7
3	1 bar H_2	20.4
4	1 bar CO_2	28.4
5	1 bar H_2、35 bar CO_2	74.3

[a] 0.1 mmol nickelalactone dissolved in 5 mL MeOH; reaction in 25 mL stainless-steel reactor under, 12h.

Table S7. Thermodynamic calculation results.

$C_{33}H_{52}NiO_2P_2$			
Gibbs Free energy		-3626.142494	
Ni	0.123129	0.471434	-1.300980
C	-0.668580	-1.792660	3.927356
C	0.716927	-1.962810	3.869972
C	1.430611	-1.478830	2.774649
C	0.775378	-0.823620	1.718837
C	-0.633220	-0.709630	1.744915
C	-1.337010	-1.180750	2.867927
P	-1.464420	-0.046690	0.259261
P	1.695412	-0.049560	0.336301
C	2.982286	-1.286490	-0.120990
C	-2.403880	1.458701	0.726514
C	-2.575570	-1.373920	-0.366570
C	3.727870	-0.834870	-1.385710
C	4.715100	-1.894830	-1.868400
C	4.010775	-3.220540	-2.134800
C	3.269183	-3.687730	-0.886920
C	2.285608	-2.627540	-0.398180
C	-3.241880	1.431494	2.014256
C	-4.200980	2.619946	2.004598
C	-5.269030	2.438997	0.913252
C	-4.722710	1.631704	-0.273590
C	-3.242230	1.928052	-0.489140
C	-3.571990	-2.054610	0.574688
C	-4.435610	-3.051940	-0.197940
C	-3.568080	-4.109820	-0.874130
C	-2.536920	-3.460560	-1.792960
C	-1.692310	-2.433170	-1.043370
O	-0.130420	2.416883	-1.223130
C	-0.708690	2.916990	-2.271730
C	-0.776440	1.962720	-3.465600
C	-0.837980	0.500444	-3.038660
O	-1.135480	4.068913	-2.340950
C	3.596547	1.171369	2.147510
C	4.970119	1.391563	1.519989
C	5.154677	2.862260	1.115074
C	3.820156	3.498571	0.695013
C	2.901956	2.458784	0.060131
C	2.468992	1.432083	1.126500
H	-1.232410	-2.153960	4.789613
H	1.243301	-2.470250	4.680831
H	2.511963	-1.632760	2.736601
H	-2.421710	-1.076410	2.912973
H	3.704325	-1.406420	0.709741
H	-1.581340	2.182438	0.856982
H	-3.143630	-0.855340	-1.165100
H	2.971320	-0.642610	-2.171480
H	4.253418	0.116768	-1.217980
H	5.232766	-1.537170	-2.771720
H	5.490297	-2.041270	-1.094780
H	3.284945	-3.084120	-2.956660
H	4.730469	-3.984000	-2.468370
H	2.735301	-4.631320	-1.078350
H	4.000474	-3.893270	-0.084810
H	1.512134	-2.450830	-1.172830
H	1.755335	-2.984170	0.498388
H	-3.832690	0.503254	2.089683
H	-2.580010	1.455088	2.892707
H	-4.671710	2.752485	2.989973
H	-3.613680	3.534433	1.813795
H	-6.152820	1.930281	1.329876
H	-5.613350	3.426181	0.566612
H	-4.846320	0.550792	-0.084520
H	-5.298510	1.847642	-1.185770
H	-2.872740	1.464616	-1.418810
H	-3.094290	3.010424	-0.631620
H	-3.010690	-2.604430	1.349867
H	-4.206550	-1.319030	1.093351
H	-5.164530	-3.522240	0.479949

H	-5.017210	-2.507250	-0.963750
H	-3.042690	-4.692170	-0.095820
H	-4.191530	-4.822270	-1.436290
H	-1.887630	-4.222260	-2.251670
H	-3.059850	-2.947440	-2.620180
H	-1.085800	-2.935960	-0.264640
H	-0.983660	-1.936740	-1.729860
H	-1.598580	2.295650	-4.122650
H	0.155295	2.151885	-4.029400
H	-0.344320	-0.174590	-3.759760
H	-1.878250	0.146408	-2.926020
H	3.477752	1.870246	2.992449
H	3.522602	0.165547	2.584984
H	5.764590	1.078593	2.213623
H	5.065586	0.738594	0.636181
H	5.587939	3.430095	1.953756
H	5.880316	2.927914	0.288864
H	3.306996	3.921592	1.575952
H	3.992348	4.339151	0.006394
H	2.002091	2.906460	-0.382760
H	3.440186	1.962370	-0.766040
H	1.600916	1.860422	1.659958

$C_{30}H_{48}NiP_2$

Gibbs Free Energy		-3359.465422	
Ni	0.237282	-0.356480	-1.842940
C	-0.560640	0.577804	3.707651
C	0.836077	0.597059	3.715116
C	1.538542	0.476915	2.515567
C	0.859164	0.342169	1.294061
C	-0.553660	0.282133	1.289239
C	-1.247690	0.411018	2.504285
P	-1.350480	-0.042850	-0.334590
P	1.704921	0.258406	-0.336920
C	3.263894	-0.648200	0.007703
C	-2.638500	1.246135	-0.618530
C	-2.115140	-1.716290	-0.159710
C	4.168973	-0.603700	-1.228580
C	5.391375	-1.504780	-1.067060
C	4.983321	-2.940760	-0.752250
C	4.116344	-2.987170	0.502364
C	2.887830	-2.096720	0.344110
C	-3.607810	1.624450	0.513933
C	-4.803750	2.370435	-0.073620
C	-5.654810	1.424892	-0.937100
C	-4.788790	0.334724	-1.586850
C	-3.405160	0.886151	-1.915550
C	-2.978080	-2.049690	1.056897
C	-3.495490	-3.486370	0.976085
C	-2.338300	-4.476610	0.878896
C	-1.458990	-4.159670	-0.327180
C	-0.958180	-2.719940	-0.284420
C	0.962619	2.832939	-1.092370
C	0.498817	3.661266	0.102053
C	1.563145	4.713932	0.458489
C	2.983459	4.211356	0.146782
C	3.067624	2.697540	0.333755
C	2.206304	1.994789	-0.723890
H	-1.116900	0.673916	4.642452
H	1.379460	0.706100	4.656129
H	2.631446	0.489700	2.535811
H	-2.337290	0.363594	2.518553
H	3.802220	-0.193010	0.860029
H	-2.015400	2.134730	-0.828120
H	-2.732510	-1.809880	-1.075670
H	3.568918	-0.933490	-2.100290
H	4.488660	0.430687	-1.435240
H	6.009786	-1.464580	-1.977240
H	6.015926	-1.118120	-0.241540
H	4.407091	-3.347220	-1.603220
H	5.872523	-3.579610	-0.635250
H	3.807875	-4.019980	0.727466
H	4.708819	-2.636110	1.366403
H	2.255128	-2.471700	-0.485450

H	2.263303	-2.125570	1.253100
H	-3.976440	0.728311	1.040044
H	-3.084190	2.237136	1.262844
H	-5.413790	2.821932	0.722812
H	-4.423620	3.206701	-0.685250
H	-6.439580	0.955745	-0.322680
H	-6.175000	2.003712	-1.716790
H	-4.679030	-0.520130	-0.896940
H	-5.276920	-0.061790	-2.489500
H	-2.807290	0.182519	-2.523400
H	-3.520920	1.791304	-2.534600
H	-2.363490	-1.947880	1.968563
H	-3.820620	-1.346890	1.155680
H	-4.126540	-3.709190	1.850506
H	-4.139710	-3.588040	0.083798
H	-1.729820	-4.408270	1.798836
H	-2.714410	-5.510140	0.823157
H	-0.607100	-4.855310	-0.384940
H	-2.048900	-4.301000	-1.250850
H	-0.272240	-2.578980	0.573825
H	-0.375870	-2.479070	-1.199790
H	1.211744	3.515569	-1.922110
H	0.176102	2.158133	-1.478040
H	-0.468670	4.144951	-0.105910
H	0.329448	2.987889	0.960084
H	1.372586	5.644432	-0.099660
H	1.482537	4.970943	1.526670
H	3.250685	4.450553	-0.896650
H	3.720659	4.726670	0.780605
H	4.108004	2.338879	0.274718
H	2.705553	2.451875	1.346849
H	2.802281	1.863252	-1.644260

C_2H_4

Gibbs Free Energy -78.37657

C	0.000000	0.666618	0.000000
H	0.931142	1.240859	0.000000
H	-0.931080	1.240931	0.000000
C	0.000000	-0.666620	0.000000
H	-0.931140	-1.240860	0.000000
H	0.931080	-1.240930	0.000000

CO_2

Gibbs Free Energy -188.249877

O	0.000000	0.000000	1.162108
C	0.000000	0.000000	0.000000
O	0.000000	0.000000	-1.162110

H_2

Gibbs Free Energy -1.16254

H	0.000000	0.000000	0.376930
H	0.000000	0.000000	-0.376930

$C_3H_6O_2$

Gibbs Free Energy -267.81228

C	-1.945840	0.019439	0.000000
H	-1.971940	0.636665	-0.873640
H	-2.792600	-0.634700	-0.000020
H	-1.971960	0.636638	0.873661
C	-0.651980	-0.815740	0.000000
H	-0.625870	-1.432950	0.873652
H	-0.625870	-1.432950	-0.873650
C	0.566722	0.125730	0.000000
O	1.888568	-0.419820	0.000000
H	1.839553	-1.378560	-0.000002
O	0.403342	1.373479	0.000000

CH_4O

Gibbs Free Energy -115.460323

C	0.652742	-0.019870	0.000002
H	1.032902	-0.550270	-0.892180
H	1.100052	0.984718	-0.001030
H	1.033088	-0.548530	0.893150

O	-0.742440	0.123659	0.000004
H	-1.142990	-0.755990	0.000016

H_2O

Gibbs Free Energy -76.275558

O	0.000000	0.000000	0.119920
H	0.000000	0.758804	-0.479680
H	0.000000	-0.758800	-0.479680

$C_4H_8O_2$

Gibbs Free Energy -306.998963

C	2.093308	-0.803710	-0.000014
H	1.813807	-1.389430	0.886560
H	3.185104	-0.681890	-0.000015
H	1.813802	-1.389400	-0.886610
C	1.408313	0.552577	0.000013
H	1.701709	1.154706	0.874575
H	1.701711	1.154746	-0.874520
C	-0.100130	0.534210	0.000012
O	-0.613420	-0.698370	0.000015
O	-0.793940	1.527897	-0.000015
C	-2.030980	-0.788010	-0.000004
H	-2.449430	-0.300820	0.891740
H	-2.449410	-0.300790	-0.891740
H	-2.281500	-1.853820	-0.000025

Cartesian coordinates (in Å) and total energies (in a.u.) of all the stationary points discussed in the text.

Table S8. Kinetic calculation results.

Symbolic Z-matrix:			
Charge=-1	Multiplicity=1		
R’	Gibbs Free Energy		-3626.85
C	0.60889	1.38548	3.94009
C	-0.77062	1.48763	3.92801
C	-1.4716	1.13515	2.78914
C	-0.81047	0.69128	1.64915
C	0.59022	0.61886	1.64726
C	1.27951	0.95634	2.80828
P	1.39385	0.11084	0.06602
P	-1.70189	0.12533	0.13973
C	-2.98576	1.48612	0.00663
C	2.38984	-1.39506	0.53913
C	2.59907	1.51871	-0.27336
C	-3.97432	1.13027	-1.09808
C	-4.90433	2.29673	-1.41984
C	-4.0997	3.5306	-1.81296
C	-3.14813	3.91248	-0.68441
C	-2.21484	2.75051	-0.36446
C	3.15353	-1.46204	1.86222
C	4.05893	-2.69131	1.83536
C	5.1989	-2.49463	0.82837
C	4.76886	-1.57593	-0.32067
C	3.29591	-1.78014	-0.64667
C	3.50766	2.11804	0.79344
C	4.41101	3.18086	0.16512
C	3.57609	4.29484	-0.4583
C	2.62171	3.72043	-1.50141
C	1.74861	2.63667	-0.88075
Ni	-0.25314	-0.33171	-1.36973
O	0.07735	-2.48502	-1.24917
C	0.6714	-2.92488	-2.26305
C	0.60657	-2.04212	-3.55673
C	0.5354	-0.53947	-3.30064
O	1.26847	-4.00253	-2.34076
C	-3.72512	-1.15857	1.85669
C	-4.66618	-2.37151	1.86597
C	-3.87748	-3.65947	1.65673
C	-3.27897	-3.69134	0.24329
C	-3.00484	-2.27972	-0.28153
C	-2.57442	-1.36516	0.86433
H	1.16601	1.6444	4.83137
H	-1.29981	1.83352	4.80669
H	-2.54829	1.21376	2.79415
H	2.3531	0.88224	2.84406
H	-3.52228	1.65007	0.94644
H	1.58371	-2.14133	0.5795
H	3.23486	1.10778	-1.07179
H	-3.40322	0.85257	-1.98953
H	-4.56815	0.26337	-0.80063
H	-5.58177	2.01769	-2.23144
H	-5.51501	2.52971	-0.54169
H	-3.51954	3.3091	-2.71097
H	-4.77188	4.36355	-2.03987
H	-2.5633	4.79151	-0.96854
H	-3.72842	4.17185	0.20657
H	-1.59377	2.52317	-1.23762
H	-1.54511	3.02403	0.45592
H	3.77594	-0.58028	2.02243
H	2.44914	-1.53393	2.69392
H	4.46941	-2.88569	2.83074
H	3.4575	-3.55553	1.54973
H	6.07212	-2.06488	1.32928
H	5.49705	-3.46629	0.42945
H	4.94007	-0.53185	-0.04674
H	5.37769	-1.78277	-1.20431
H	3.02495	-1.191	-1.52649
H	3.12467	-2.82267	-0.91784
H	2.90362	2.59039	1.57072
H	4.13258	1.35208	1.25642

H	5.07824	3.59709	0.92637
H	5.033	2.71917	-0.60668
H	2.99708	4.79103	0.32537
H	4.23064	5.04297	-0.91525
H	1.99619	4.5169	-1.91323
H	3.20055	3.29161	-2.32355
H	1.12069	3.07227	-0.09736
H	1.08064	2.208	-1.63685
H	1.48464	-2.28017	-4.16807
H	-0.28337	-2.3738	-4.10338
H	0.27888	-0.02685	-4.23477
H	1.5207	-0.15795	-3.00082
H	-3.31696	-1.01516	2.85993
H	-4.30821	-0.27123	1.60294
H	-5.20996	-2.40574	2.81495
H	-5.40665	-2.27828	1.06848
H	-3.08187	-3.70615	2.40339
H	-4.52375	-4.52751	1.81316
H	-2.34564	-4.25454	0.25445
H	-3.96329	-4.20203	-0.43877
H	-2.19431	-2.31389	-1.01482
H	-3.89187	-1.87461	-0.77274
H	-1.74381	-1.87825	1.36859
H	-0.90336	-0.10976	-2.58368

TS	Gibbs Free Energy		-3626.83
C	0.60889	1.38548	3.94009
C	-0.77062	1.48763	3.92801
C	-1.4716	1.13515	2.78914
C	-0.81047	0.69128	1.64915
C	0.59022	0.61886	1.64726
C	1.27951	0.95634	2.80828
P	1.39385	0.11084	0.06602
P	-1.70189	0.12533	0.13973
C	-2.98576	1.48612	0.00663
C	2.38984	-1.39506	0.53913
C	2.59907	1.51871	-0.27336
C	-3.97432	1.13027	-1.09808
C	-4.90433	2.29673	-1.41984
C	-4.0997	3.5306	-1.81296
C	-3.14813	3.91248	-0.68441
C	-2.21484	2.75051	-0.36446
C	3.15353	-1.46204	1.86222
C	4.05893	-2.69131	1.83536
C	5.1989	-2.49463	0.82837
C	4.76886	-1.57593	-0.32067
C	3.29591	-1.78014	-0.64667
C	3.50766	2.11804	0.79344
C	4.41101	3.18086	0.16512
C	3.57609	4.29484	-0.4583
C	2.62171	3.72043	-1.50141
C	1.74861	2.63667	-0.88075
Ni	-0.25314	-0.33171	-1.36973
O	0.07735	-2.48502	-1.24917
C	0.6714	-2.92488	-2.26305
C	0.60657	-2.04212	-3.55673
C	0.5354	-0.53947	-3.30064
O	1.26847	-4.00253	-2.34076
C	-3.72512	-1.15857	1.85669
C	-4.66618	-2.37151	1.86597
C	-3.87748	-3.65947	1.65673
C	-3.27897	-3.69134	0.24329
C	-3.00484	-2.27972	-0.28153
C	-2.57442	-1.36516	0.86433
H	1.16601	1.6444	4.83137
H	-1.29981	1.83352	4.80669
H	-2.54829	1.21376	2.79415
H	2.3531	0.88224	2.84406
H	-3.52228	1.65007	0.94644
H	1.58371	-2.14133	0.5795
H	3.23486	1.10778	-1.07179
H	-3.40322	0.85257	-1.98953
H	-4.56815	0.26337	-0.80063
H	-5.58177	2.01769	-2.23144
H	-5.51501	2.52971	-0.54169
H	-3.51954	3.3091	-2.71097

H	-4.77188	4.36355	-2.03987
H	-2.5633	4.79151	-0.96854
H	-3.72842	4.17185	0.20657
H	-1.59377	2.52317	-1.23762
H	-1.54511	3.02403	0.45592
H	3.77594	-0.58028	2.02243
H	2.44914	-1.53393	2.69392
H	4.46941	-2.88569	2.83074
H	3.4575	-3.55553	1.54973
H	6.07212	-2.06488	1.32928
H	5.49705	-3.46629	0.42945
H	4.94007	-0.53185	-0.04674
H	5.37769	-1.78277	-1.20431
H	3.02495	-1.191	-1.52649
H	3.12467	-2.82267	-0.91784
H	2.90362	2.59039	1.57072
H	4.13258	1.35208	1.25642
H	5.07824	3.59709	0.92637
H	5.033	2.71917	-0.60668
H	2.99708	4.79103	0.32537
H	4.23064	5.04297	-0.91525
H	1.99619	4.5169	-1.91323
H	3.20055	3.29161	-2.32355
H	1.12069	3.07227	-0.09736
H	1.08064	2.208	-1.63685
H	1.48464	-2.28017	-4.16807
H	-0.28337	-2.3738	-4.10338
H	0.27888	-0.02685	-4.23477
H	1.5207	-0.15795	-3.00082
H	-3.31696	-1.01516	2.85993
H	-4.30821	-0.27123	1.60294
H	-5.20996	-2.40574	2.81495
H	-5.40665	-2.27828	1.06848
H	-3.08187	-3.70615	2.40339
H	-4.52375	-4.52751	1.81316
H	-2.34564	-4.25454	0.25445
H	-3.96329	-4.20203	-0.43877
H	-2.19431	-2.31389	-1.01482
H	-3.89187	-1.87461	-0.77274
H	-1.74381	-1.87825	1.36859
H	-0.90336	-0.10976	-2.58368
P’	Gibbs Free Energy		-3626.85
C	-0.48674	-1.70761	3.8582
C	0.89137	-1.79191	3.78904
C	1.54577	-1.34481	2.65452
C	0.84169	-0.82929	1.57189
C	-0.55971	-0.77913	1.62443
C	-1.20108	-1.20495	2.78391
P	-1.44908	-0.17167	0.12688
P	1.70644	-0.13414	0.09655
C	2.93457	-1.52885	-0.20324
C	-2.37982	1.32061	0.76534
C	-2.71596	-1.53518	-0.21881
C	3.86411	-1.11507	-1.33941
C	4.75276	-2.27177	-1.78737
C	3.90156	-3.46187	-2.21736
C	2.99566	-3.89928	-1.07091
C	2.10947	-2.7428	-0.62133
C	-3.12364	1.28913	2.10094
C	-4.00676	2.53111	2.19817
C	-5.16051	2.44928	1.19096
C	-4.75816	1.63827	-0.04609
C	-3.28455	1.84662	-0.3649
C	-3.58125	-2.19826	0.84693
C	-4.54107	-3.19302	0.19085
C	-3.76623	-4.27392	-0.55554
C	-2.85555	-3.64127	-1.60343
C	-1.92737	-2.6223	-0.953
Ni	0.13261	0.54011	-1.2047
O	-0.16961	2.57189	-1.28387
C	-0.54736	3.08115	-2.36479
C	-0.3571	2.2199	-3.66944
C	-0.28342	0.72067	-3.39957
O	-1.02185	4.20965	-2.51107
C	3.94449	0.88226	1.76851

C	4.91134	2.0734	1.81666	H	-5.37225	1.93898	-0.89856
C	4.13604	3.38231	1.90861	H	-3.02712	1.34347	-1.30105
C	3.35518	3.62426	0.60971	H	-3.09423	2.90774	-0.52894
C	2.97682	2.30623	-0.07039	H	-2.9484	-2.73996	1.55191
C	2.6803	1.22451	0.96874	H	-4.16424	-1.45912	1.39879
H	-1.0091	-2.03492	4.74812	H	-5.17788	-3.6515	0.95376
H	1.45679	-2.1946	4.61973	H	-5.19094	-2.66319	-0.51099
H	2.62267	-1.40485	2.61613	H	-3.15816	-4.83704	0.15743
H	-2.27251	-1.13918	2.86403	H	-4.46032	-4.9739	-1.03019
H	3.52071	-1.78084	0.68545	H	-2.27069	-4.41652	-2.10599
H	-1.54171	2.02488	0.85999	H	-3.468	-3.14231	-2.35911
H	-3.38421	-1.05414	-0.9487	H	-1.26736	-3.12453	-0.23965
H	3.2498	-0.77691	-2.17952	H	-1.29152	-2.15359	-1.71076
H	4.48578	-0.27301	-1.02667	H	-1.18044	2.45555	-4.34955
H	5.39322	-1.95205	-2.61423	H	0.57221	2.56701	-4.13526
H	5.40269	-2.57339	-0.96011	H	-0.0239	0.17907	-4.31628
H	3.28501	-3.1722	-3.07112	H	-1.26405	0.35138	-3.06957
H	4.54292	-4.29131	-2.53037	H	3.66378	0.61487	2.78968
H	2.37574	-4.74335	-1.38547	H	4.46969	0.03086	1.33318
H	3.612	-4.23332	-0.23076	H	5.58221	1.96453	2.67428
H	1.44789	-2.44261	-1.44019	H	5.53116	2.09246	0.91766
H	1.47638	-3.05808	0.21229	H	3.44837	3.32093	2.75491
H	-3.75882	0.40763	2.19307	H	4.81848	4.21481	2.10062
H	-2.40536	1.27521	2.92298	H	2.44921	4.18995	0.82957
H	-4.40392	2.63903	3.21179	H	3.95588	4.22383	-0.07859
H	-3.39242	3.4079	1.98841	H	2.07974	2.45482	-0.67894
H	-6.03453	1.98644	1.65944	H	3.78053	1.97229	-0.73066
H	-5.44834	3.45919	0.89133	H	1.9235	1.6434	1.64607
H	-4.94354	0.5762	0.1302	H	0.55475	0.49468	-2.66033

Cartesian coordinates (in Å) and total energies (in a.u.) of all the stationary points discussed in the text.

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