Highly efficient ruthenium catalytic system for the direct synthesis of butanol from propylene and CO2: a low temperature reverse water-gas shift route

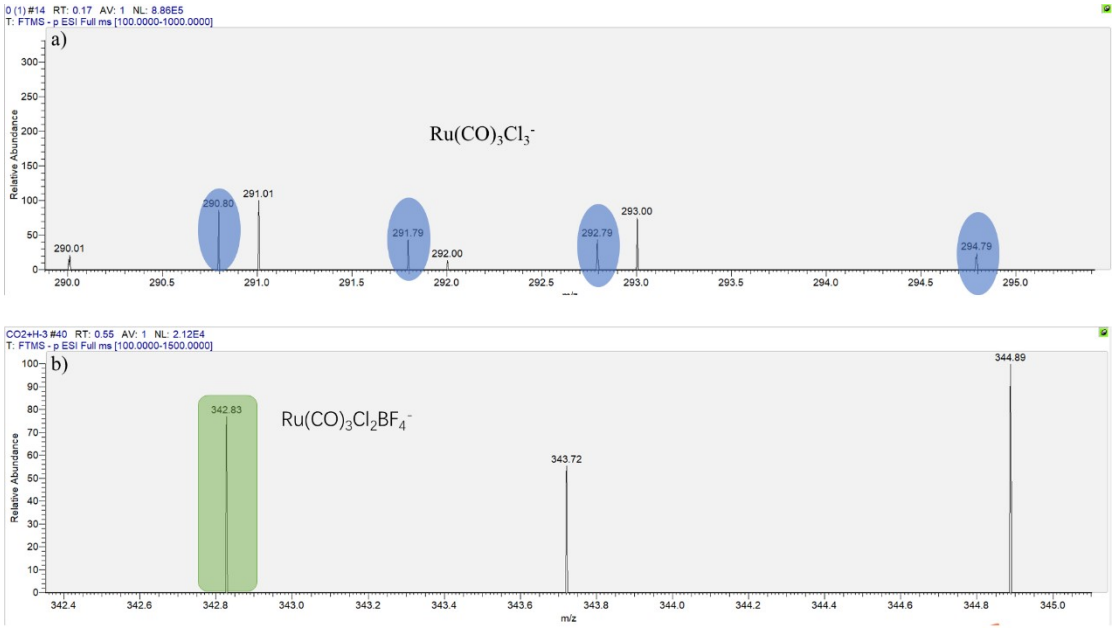


Figure S1 ESI-MS spectrum of $Ru(CO)_3Cl_3^-$ and $Ru(CO)_3Cl_2BF_4^-$

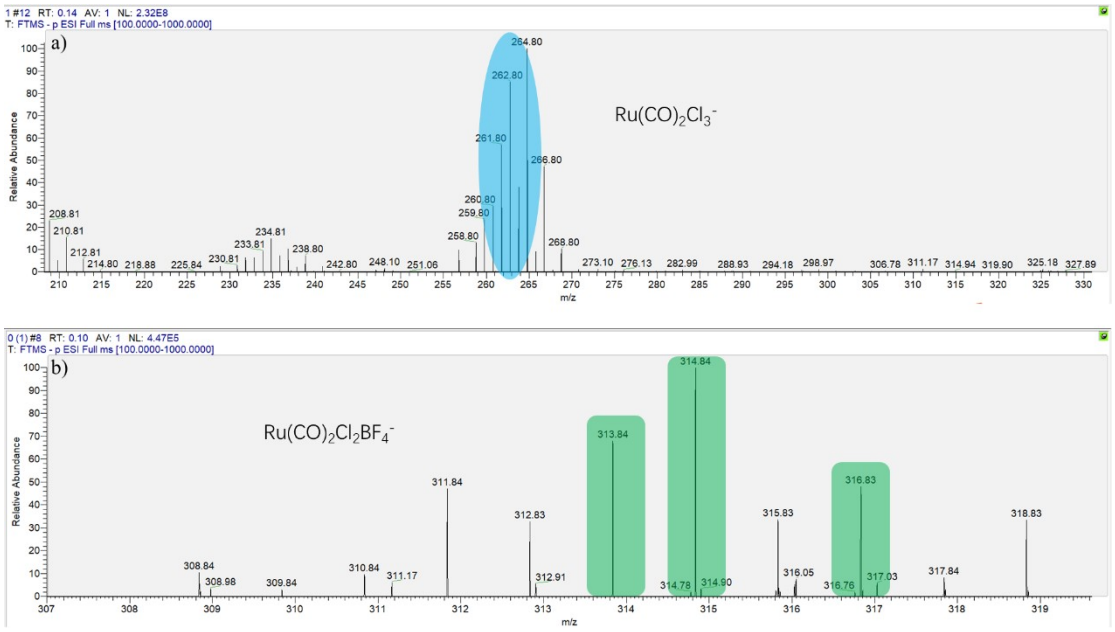


Figure S2 ESI-MS spectrum of $Ru(CO)_2Cl_3^-$ and $Ru(CO)_2Cl_2BF_4^-$

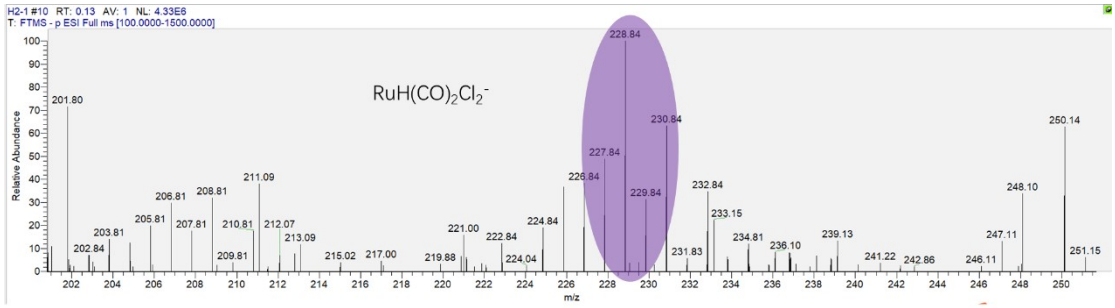
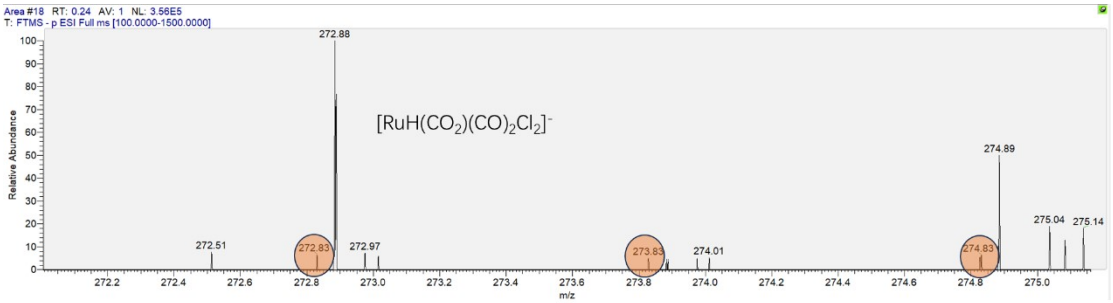
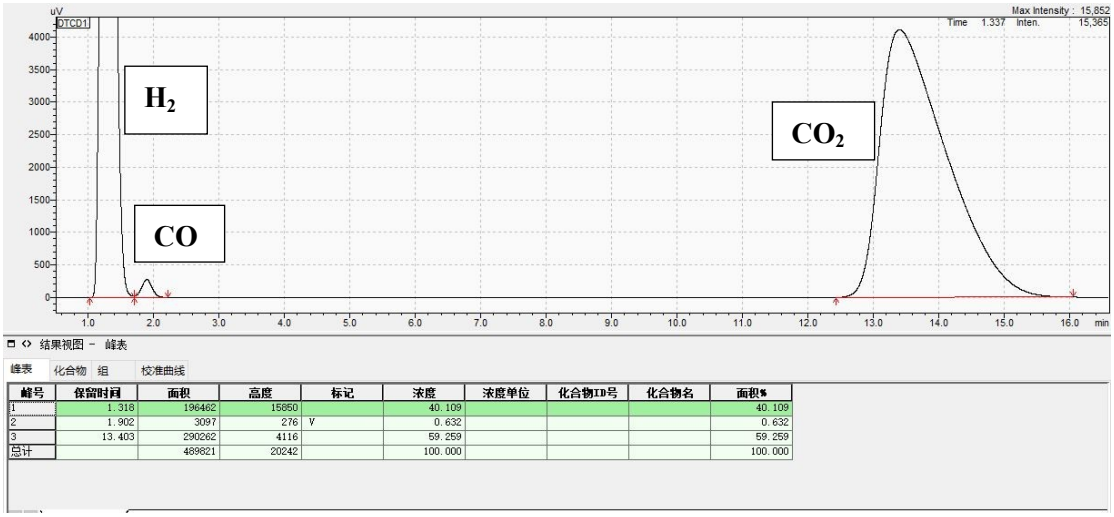


Figure S3 ESI-MS spectrum of $RuH(CO)_2Cl_2^-$

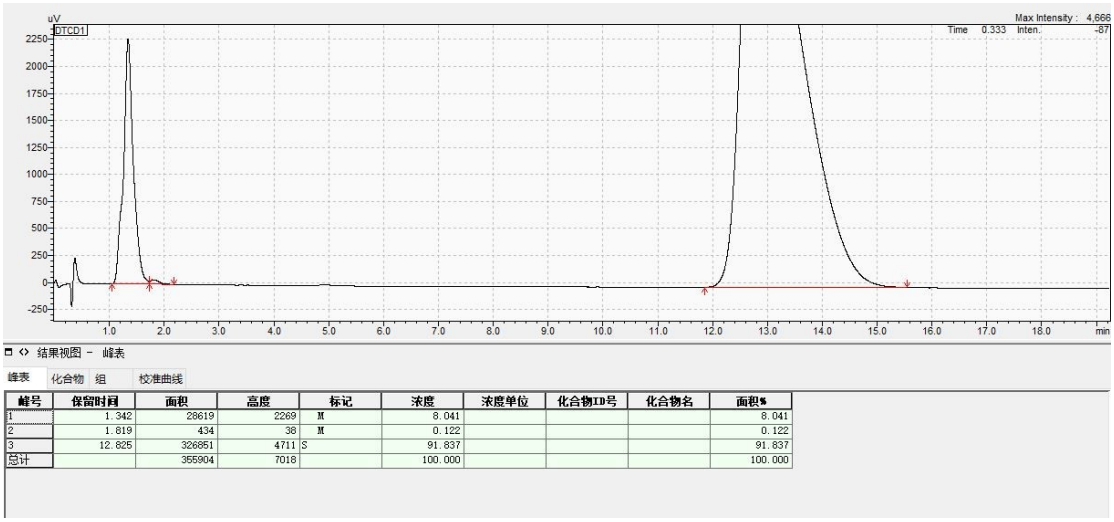


Figrue S4 ESI-MS spectrum of $RuH(CO_2)(CO)_2Cl_2^-$



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	1.318	196462	15650		40.109				40.109
2	1.902	3097	276	V	0.632				0.632
3	13.403	290262	4116		59.259				59.259
总计		489821	20242		100.000				100.000

Figure S5 GC-TCD chromatogram of RWGR at 100 °C in the presence of TEA, IL1, and LiCl



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	1.342	28619	2269	M	8.041				8.041
2	1.819	434	38	M	0.122				0.122
3	12.825	326851	4711	S	91.837				91.837
总计		355904	7018		100.000				100.000

Figure S6 GC-TCD chromatogram of RWGR at 100 °C in the presence of IL1, and LiCl

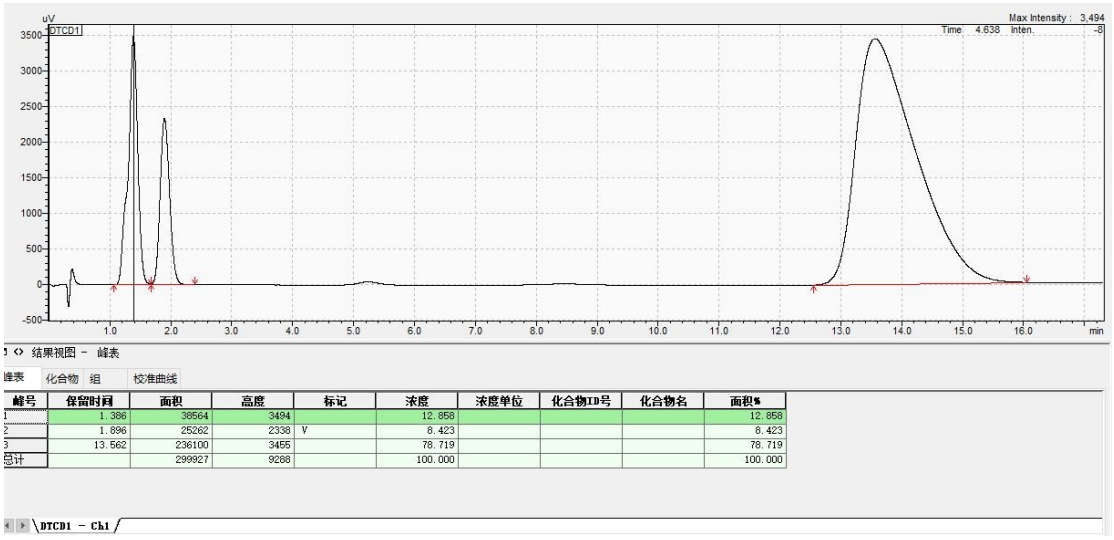


Figure S7 GC-TCD chromatogram of HCOOH decomposition at 120 °C in the presence of TEA, IL1, and LiCl

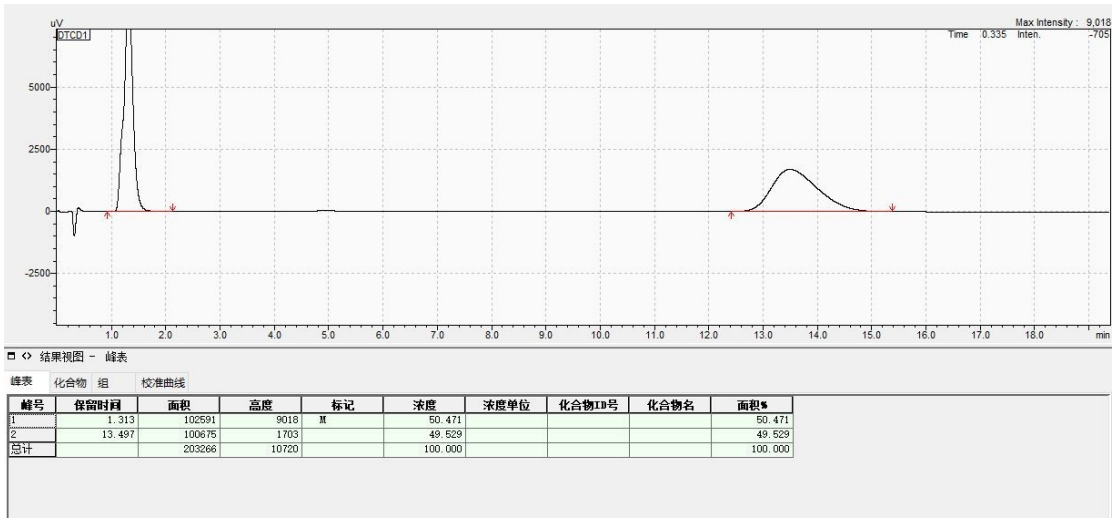
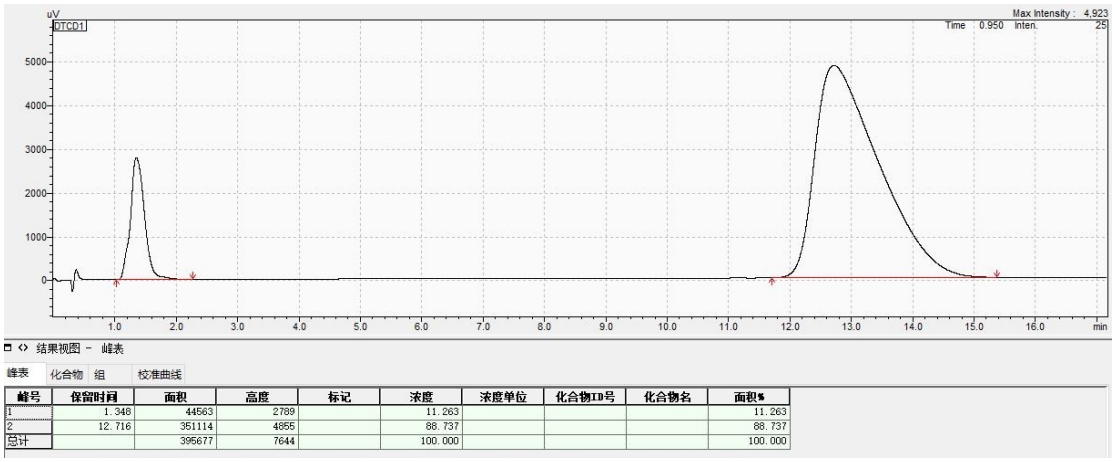


Figure S8 GC-TCD chromatogram of HCOOH decomposition at 120 °C in the presence of only TEA



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	1.348	44563	2789		11.263				11.263
2	12.716	351114	4855		88.737				88.737
总计		395677	7644		100.000				100.000

Figure S9 GC-TCD chromatogram of RWGR at 100 °C in the presence of only TEA

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	1.410	31398	2036	M	8.540				8.540
2	12.562	336275	4762		91.460				91.460
总计		367673	6799		100.000				100.000

Figure S10 GC-TCD chromatogram of RWGR at 100 °C in the presence of TEA and LiCl

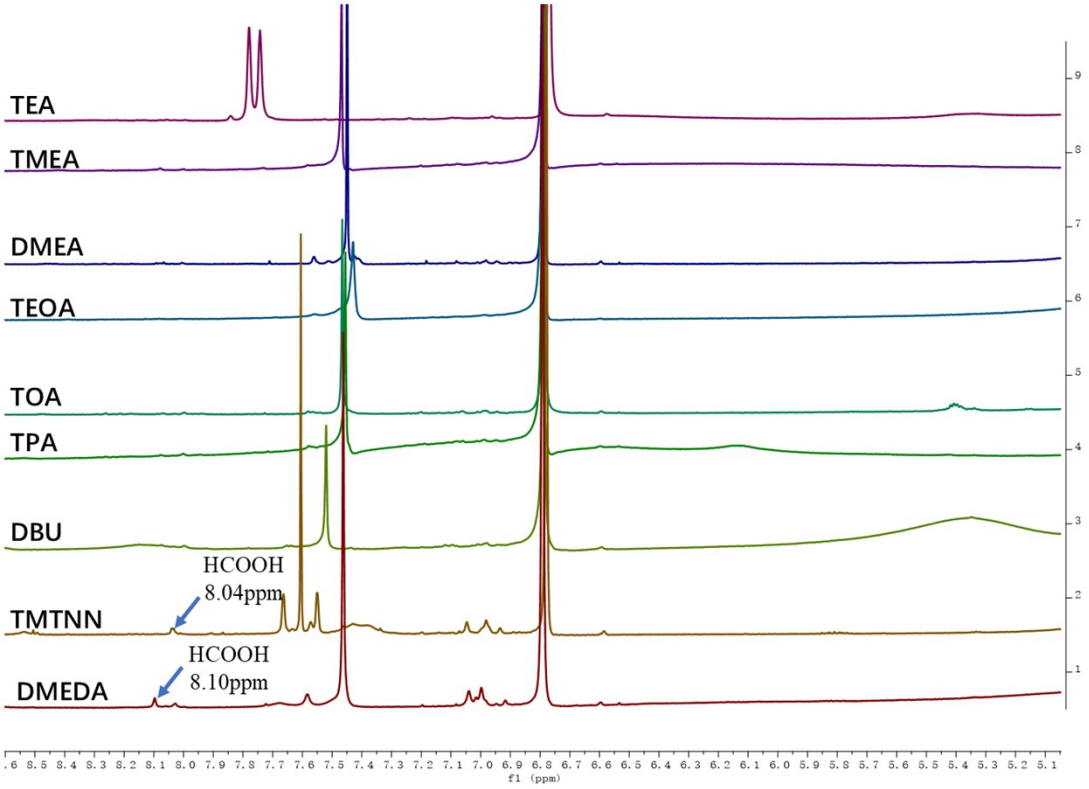


Figure S11 NMR spectra of reaction solutions in the presence of different bases

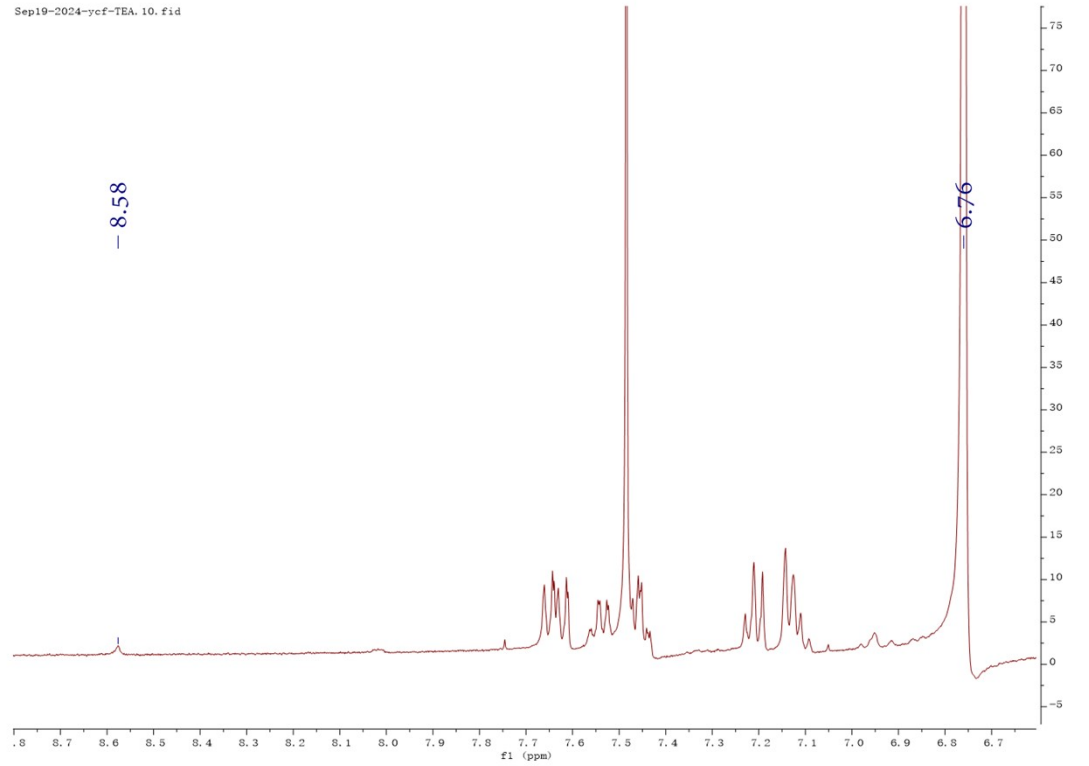


Figure S12 NMR spectrum of reaction solution with only TEA as the additive

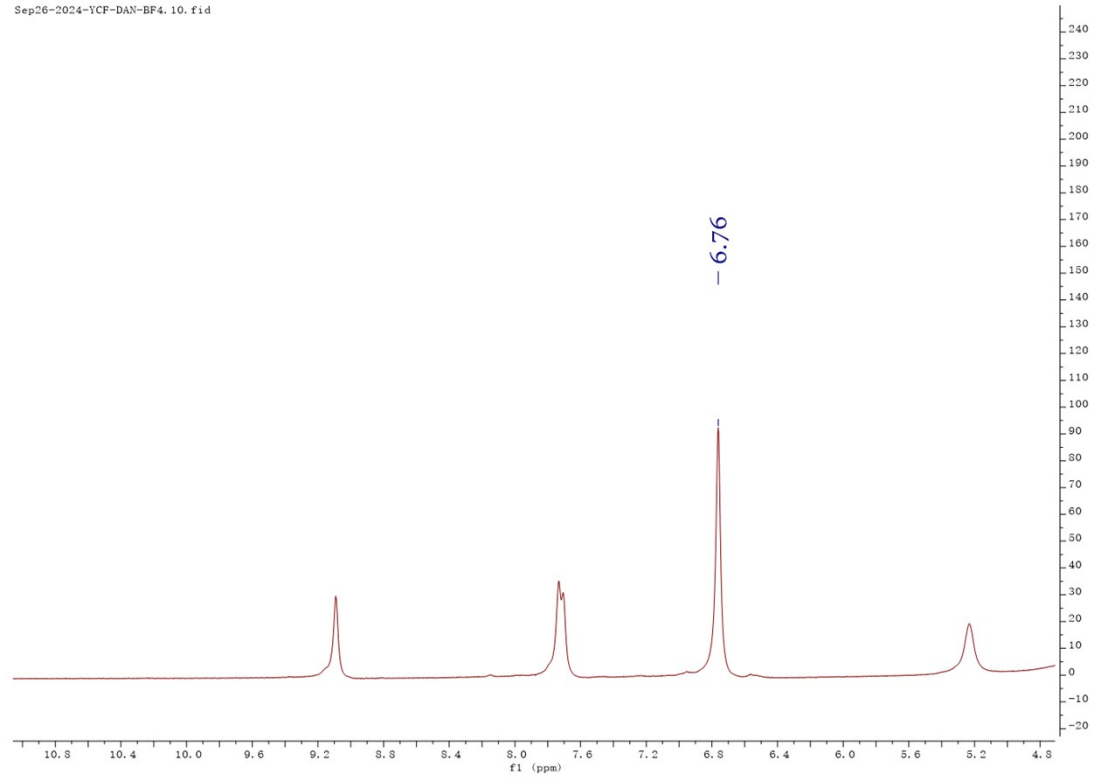


Figure S13 NMR spectrum of reaction solution with only IL1 as the additive

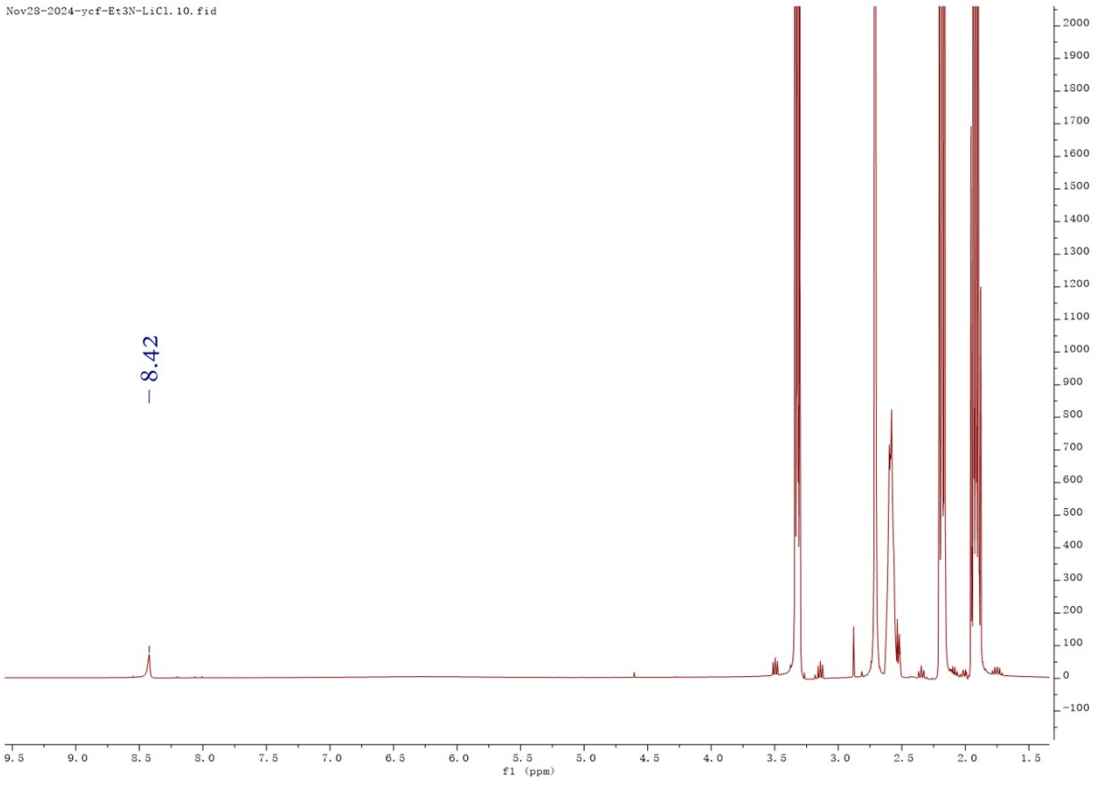


Figure S14 NMR spectrum of RWGR at 100 °C in the presence of TEA and LiCl

Table S1 the catalytic system cycling experiment

Entry	Y %	Sel-al %	Sel-al %	Sel-ke %	al-n/i
1	99	97	0	3	1.3
2	95	97	0	3	1.2
3	99	97	0	3	1.2
4	78	95	0	5	1.4
5	70	94	0	6	1.3
6	48	97	0	3	1.3

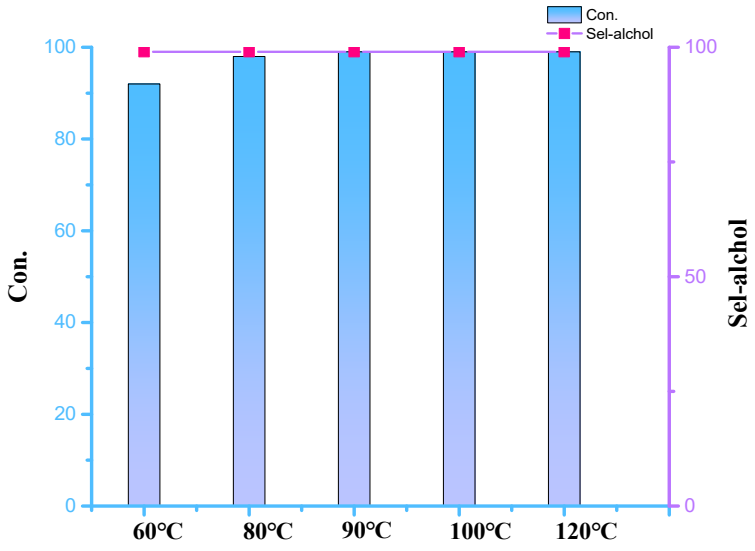


Figure S15 Experimental study on the hydrogenation of butyraldehyde using Ru catalytic system at different temperatures.

Condition: $[Ru(CO)_3Cl_2]_2$, 26mg; LiCl, 0.13g; IL1, 0.2g; TEA 0.32g; NMP, 4mL 10 mmol butyraldehyde, H_2, 3MPa.

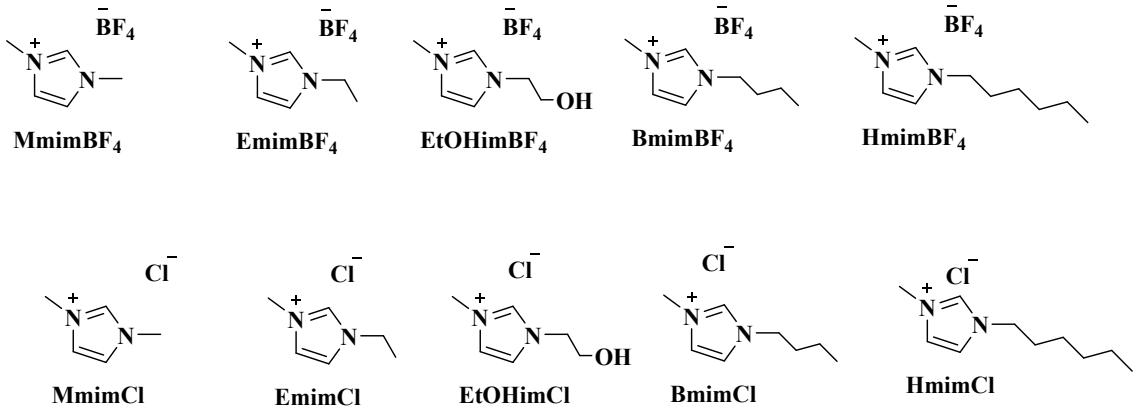


Figure S16 Ionic liquids (ILs) used in the experiment.

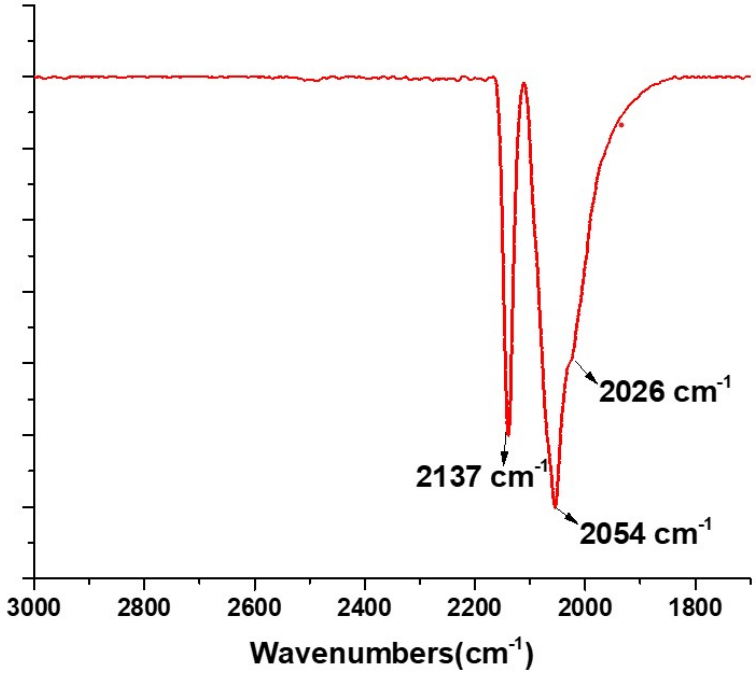
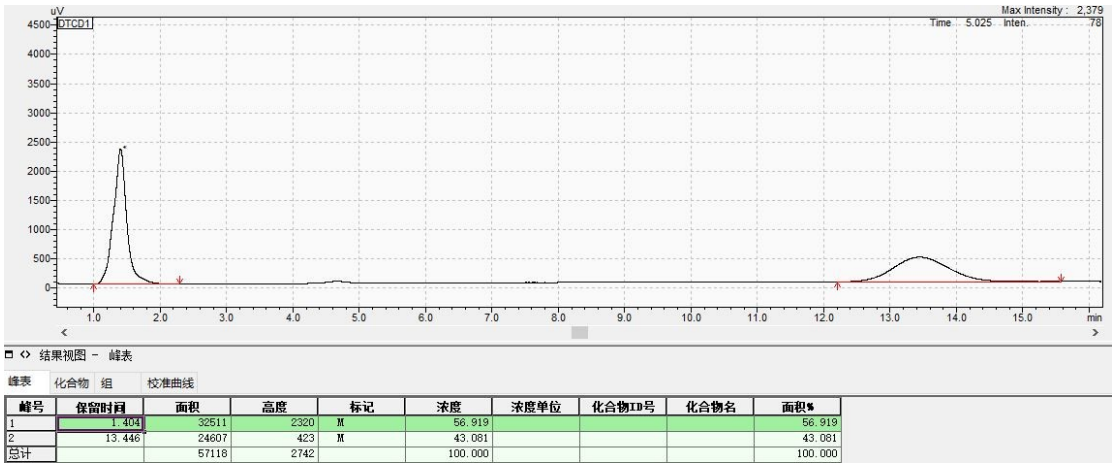


Figure S17 IR spectrum of $(Ru(CO)_3Cl_2)_2$



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	1.404	32511	2320	M	56.919				56.919
2	13.446	24607	423	M	43.081				43.081
总计		57118	2742		100.000				100.000

Figure S18 GC-TCD chromatogram of HCOOH decomposition at 120 °C in the presence of TTCA, IL1, and LiCl

Table S2 Hydroformylation of propylene and carbon dioxide under other conditions.

Entry	Catalytic system		Time	Y (%)	S_{ol} (%)	S_{al} (%)	S_{ke} (%)	$ol_{(n:i)}$
	Catalyst	Additive						
1	$Ru_3(CO)_{12}$	[BMI·Cl]+H_3PO_4	17h	94	89	0	11	1.6
2	$Ru_3(CO)_{12}$	[BMI·Cl]+H_3PO_4	4h	70	87	0	13	1.6

Reaction: propylene, 0.5 MPa; CO_2, 3MPa; H_2, 3MPa; Temperature, 120 ℃. The catalytic system was the same as that reported in *ref. 43*.

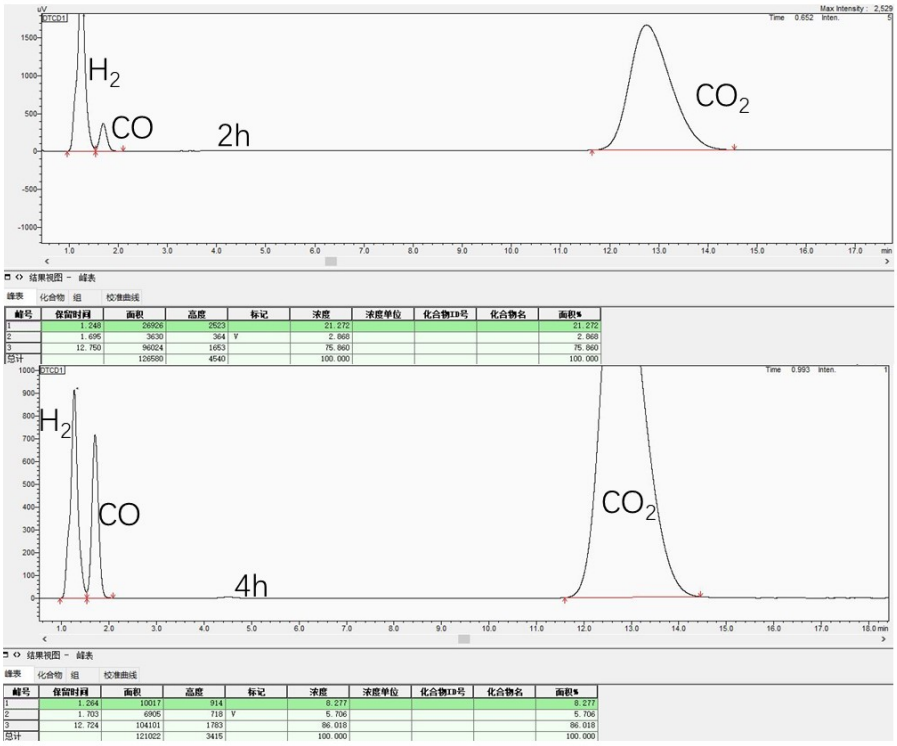


Figure S19 GC-TCD chromatogram of [TEAH][HCOO] decomposition at 120 °C in the presence of $Ru(CO)_3Cl_2$, IL1 and LiCl, 2h and 4h respectively.

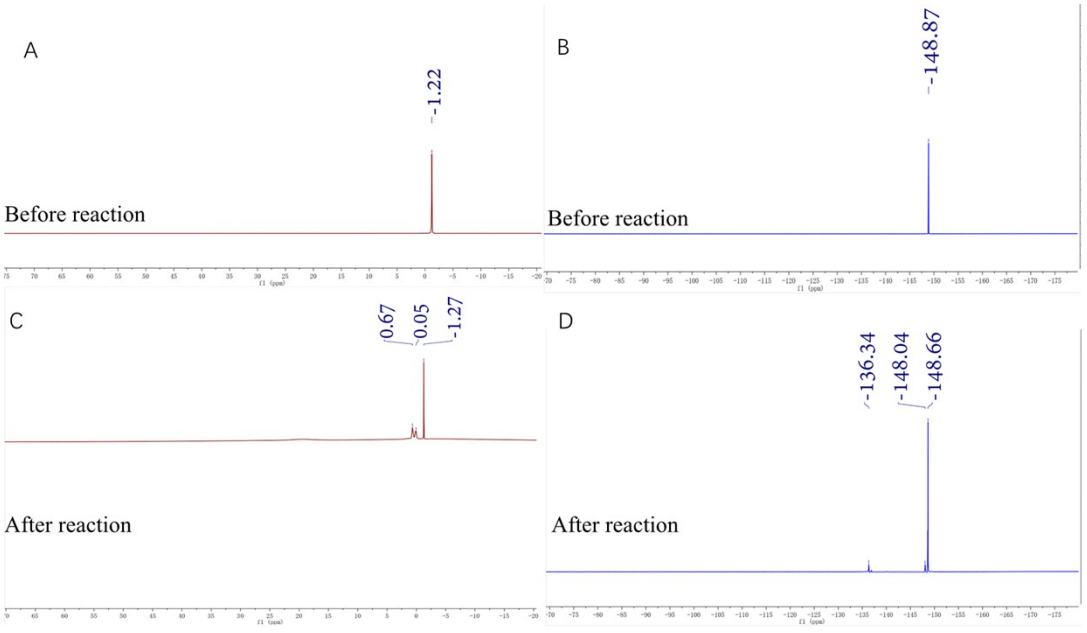


Figure S20 The comparison of NMR ^{19}F and ^{11}B spectrum of reaction solution before and after the [TEAH][HCOO] decomposition experiment. (A: ^{19}F spectrum of the solution before reaction, B: ^{11}B spectrum of the solution before reaction; C: ^{19}F spectrum of the solution after reaction, D: ^{11}B spectrum of the solution after reaction)

Table S3 Reaction performance of different tetrafluoroborates

Entry	Tetrafluoroborate	Y (%)	S_{ol} (%)	S_{al} (%)	S_{ke} (%)	$ol_{(n:i)}$
1	N-ethylpyridine Tetrafluoroborate	50	98	0	2	1.2
2	Tetraethylammonium tetrafluoroborate	42	9	0	2	1.2
3	$LiBF_4$	91	95	0	5	1.2
4	$NaBF_4$	58	96	0	4	1.3
5	KBF_4	80	97	0	3	1.2
6	EtOHimCl+$LiBF_4$	72	98	0	2	1.2

Reaction: $[Ru(CO)_3Cl_2]_2$ 0.05mmol, LiCl, 3mmol, Tetrafluoroborate 1mmol. NMP, 4mL, propylene, 0.5 MPa; CO_2, 3MPa; H_2, 3MPa; Temperature, 120 ℃, Time, 4 h.

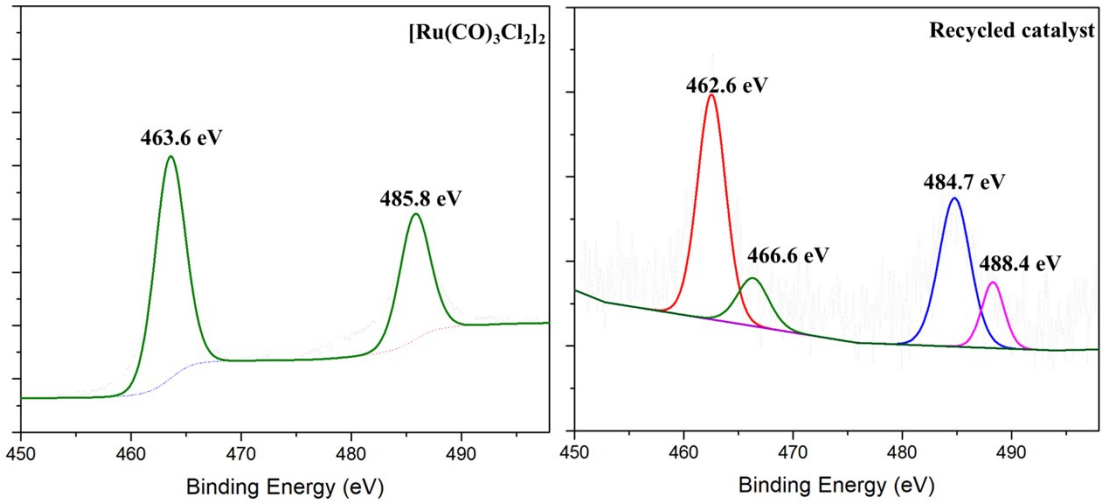


Figure S21 Comparison of XPS spectrum of catalysts before and after cycling.

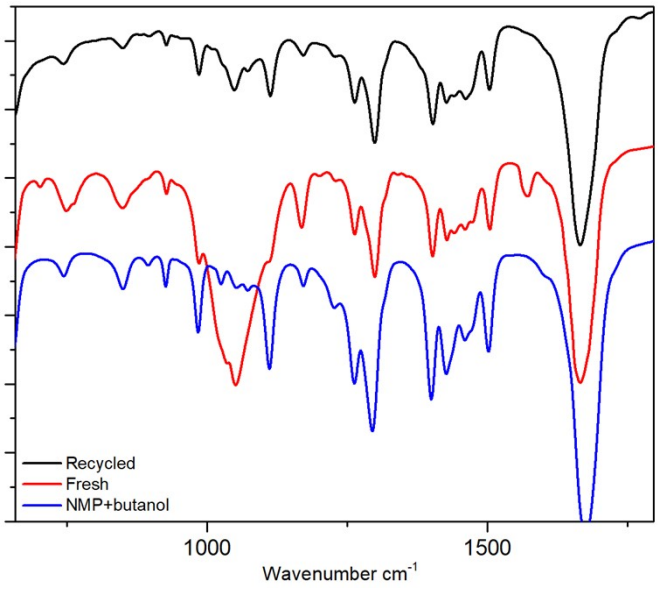


Figure S22 Comparison of FT-IR spectrum of catalysts before and after cycling.

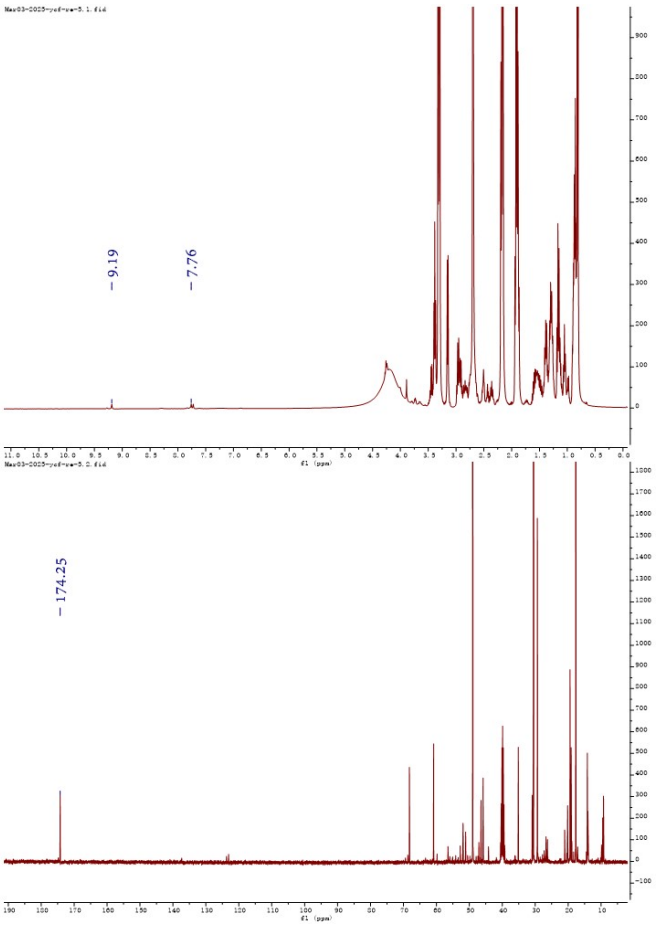


Figure S23 ^{1}H and ^{13}C NMR spectrum of the reaction solution after cycling.

Table S4 Comparison of different catalytic systems for CO_2-to-butanol

Entry	substate	Catalyst	Condition	Additives	Yiled-oxo (%)	Sel-Al (%)	Sel-ol (%)	Ref.
1	propylene	$H_4Ru_4(CO)_{12}$	140 °C,4 MPa CO_2, 4 MP H_2, 30h	LiCl	32	0	33	*Catal. Commun., 2000, 1, 1-3*
2	propylene	$Rh(CO)_2(acac)$ + Bidentate Phosohine ligand	100 °C, 0.5 MPa CO_2, 2 MP H_2, 12h	PMHS (Non-recyclable), KF	59	59	0	*Angew. Chem. Int. Edit., 2017, 56, 310-313*
3	propylene	$Rh(CO)_2(acac)$ +	80 °C, 0.5 MPa	Ac_2O (Non-recyclable)	73	73	0	*Green Chem.,*

		PTA	CO_2, 2 MP H_2, 12h					*2021, 23, 8040-8046*
4	1-hexene	Rh-POL-PPO&PPh_3 (heterogeneous)	60 °C, 1.25 MPa CO_2, 1.25 MP H_2, 2h	$PhSiH_3$ (Non-recyclable), KF	70	70.2	0	*Chem. Eng. J., 2023, 476, 146332*
5	propylene	$Ru(acac)_3$ + PTA	80-120 °C, 4 MPa CO_2, 1 MP H_2, 12h (two-step)	Ac_2O (Non-recyclable)	64	0	64	*ACS Sustain. Chem. Eng., 2021, 9, 16741-16748*
6	propylene	$[Ru(CO)_3Cl_2]_2$	propylene, 0.5 MPa; CO_2, 3MPa; H_2, 3MPa; Temperature, 170 ℃; Time, 2 h	LiCl+TEA+IL1	97	0	97	*This work*

Table S5 Reaction performance of RWGS with different catalysts

Entry	P(CO_2+H_2) (Mpa)	T (°C)	Cat	TOF (h^{-1})	Ref.
1	0.1	400	Cu/CeO_2	85	Int. J. Hydrogen Energ., 2020,45, 11380-11393
2	0.1	500	Ni-SBA-15	180	Crystals 2021, 11, 790, 0
3	0.1	300	Co/β-Mo_2C	495	Angew. Chem. Int. Ed. 2014, 53, 6705−6709
4	0.1	400	Pt-TiO_2	359	Appl. Catal. A-gen, 2012,423,100-107
5	0.1	340	Pd/Al_2O_3	351	Chem. Eng. J. 2024,

					500, 156937
6	6.0	180	[PPN][$RuCl_3(CO)_3$] +[PPN]Cl	19	ACS Catal. 2013, 3, 2865−2868
7	6.0	140	[$RuCl_3(CO)_3$]+Co_2CO_8+BmimCl +AcOH	4.1	ChemCatChem 2019, 11, 1986–1992
8	6.0	160	$Ru_3(CO)_{12}$+$HmimBF_4$	0.2	ChemSusChem 2019, 12, 5149 – 5156
9[a]	6.0	170	[$RuCl_3(CO)_3$]+LiCl+TEA+IL1	40	This work

[a:] The amount of CO produced is calculated based on the amount of CO consumed during the entire hydroformylation process.

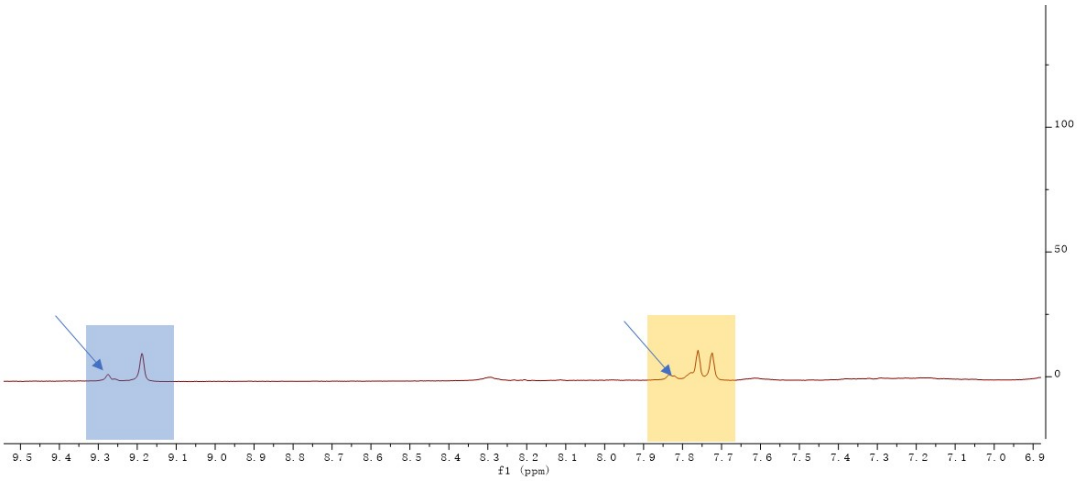


Figure S24 ^1H NMR spectrum of the reaction solution after cycling

Table S6 Catalyst regeneration strategy

Entry	Y %	Sel-al %	Sel-al %	Sel-ke %	al-n/i
1	99	97	0	3	1.3
2	96	97	0	3	1.2
3	98	97	0	3	1.2
4	78	95	0	5	1.4
After treating the reaction solution with 2 MPa CO and 2 MPa H_2 at 170 °C					
5	99	96	0	4	1.2

The coordinates of the optimized structures

CO_2			
C	0	0	0
O	0	0	1.169142
O	0	0	-1.169142

Et_3NHCl			
N	0.167718	-0.137936	-0.049464
C	0.267946	0.763793	-1.235916
H	-0.119767	0.183558	-2.077702
H	1.320787	0.984743	-1.433305
C	-0.559699	2.03338	-1.063905
H	-0.558459	2.588759	-2.006935
H	-1.590739	1.77615	-0.804918
H	-0.15459	2.691967	-0.289603
C	0.62573	0.459793	1.245807
H	-0.180449	1.126593	1.56221
H	0.647462	-0.36336	1.964176
C	1.958574	1.200021	1.21601
H	1.928914	2.072822	0.557518
H	2.176468	1.561047	2.226396
H	2.789402	0.563938	0.902835
C	0.639809	-1.531497	-0.315273
H	0.317399	-2.121399	0.546928
H	0.046135	-1.876975	-1.166219
C	2.129568	-1.707023	-0.58149
H	2.735384	-1.505143	0.305921
H	2.312775	-2.746216	-0.873367
H	2.48366	-1.069296	-1.397571
H	-0.948796	-0.294702	0.111232
Cl	-2.632422	-0.583396	0.389839

Int3			
Ru	-0.000085	0.000019	-0.273181
Cl	-0.000667	-0.000132	2.119967
Cl	-2.421274	-0.053831	-0.630964
Cl	2.421327	0.05378	-0.630366
C	0.04383	-1.954433	-0.16606
C	-0.043302	1.954587	-0.165974
O	0.06952	-3.094033	-0.036603
O	-0.068147	3.0942	-0.036478

Int4			
Ru	-0.780673	0.020768	-0.018282
Cl	-3.215453	-0.039625	-0.390467
Cl	-0.44125	1.411055	-2.084199
Cl	-1.060587	-1.136061	2.186454
C	-0.74936	-1.646232	-1.010986
C	-1.166338	1.676256	0.96191
O	-0.81216	-2.632233	-1.601329
O	-1.480988	2.624677	1.526679
N	1.655528	0.076866	0.247773
C	1.884289	1.490864	0.665487
H	1.362698	2.112962	-0.065448
H	1.370383	1.598522	1.624503
C	3.324368	2.001913	0.824151
H	3.285463	2.975365	1.327908
H	3.950455	1.34132	1.43265
H	3.81619	2.155358	-0.139941
C	2.242904	-0.237111	-1.087145
H	1.721851	-1.118758	-1.462747
H	1.953103	0.579369	-1.748802
C	3.752179	-0.507825	-1.17454
H	3.981967	-0.776925	-2.212589
H	4.366897	0.355539	-0.915328
H	4.066855	-1.344999	-0.543666
C	2.112864	-0.856539	1.308281
H	1.547595	-0.603906	2.207418
H	3.180818	-0.685152	1.509792
C	1.888057	-2.333581	1.003735
H	2.402759	-2.666752	0.097216
H	2.275709	-2.922713	1.843016
H	0.822104	-2.544617	0.918518
H	0.562607	-0.443298	-3.897233
H	0.898828	-0.930458	-4.353804

TS1			
Ru	-1.150308	0.004151	0.084774
Cl	-3.408089	-0.550085	-0.795054
Cl	-1.897095	-0.061673	2.449788
Cl	-0.190055	0.137356	-2.240617
C	-1.661517	1.882674	-0.027422
C	-0.837235	-1.908647	0.177982
O	-1.984225	2.983408	-0.101038
O	-0.696876	-3.050569	0.233101
N	2.418472	0.013874	0.086

C	2.442034	-1.359455	-0.468069
H	1.961454	-2.00372	0.274326
H	1.78078	-1.330763	-1.339114
C	3.815879	-1.918505	-0.839497
H	3.683542	-2.887865	-1.33273
H	4.346771	-1.262301	-1.537473
H	4.452695	-2.077587	0.036976
C	2.988568	0.164403	1.445
H	2.413821	0.952649	1.945473
H	2.760128	-0.761647	1.980935
C	4.481837	0.482478	1.539508
H	4.769702	0.525893	2.596071
H	5.101871	-0.274113	1.051407
H	4.718834	1.453659	1.094056
C	2.814645	1.053369	-0.892614
H	2.323482	0.779343	-1.827826
H	3.903518	1.036884	-1.040071
C	2.34088	2.446466	-0.488004
H	2.765353	2.779022	0.466027
H	2.64359	3.164345	-1.257668
H	1.251344	2.467489	-0.415675
H	1.080165	0.218996	0.348358
H	0.284502	0.485381	0.847067

Int5			
Ru	1.604064	0.067644	-0.029497
Cl	1.578601	-2.237645	-0.864578
Cl	1.023749	2.330848	0.714735
H	1.304648	0.549798	-1.57257
C	3.311292	0.440385	-0.525933
C	2.000776	-0.54252	1.837219
O	2.319822	-0.894353	2.885286
O	4.394229	0.681257	-0.86448
N	-2.4887	0.164719	-0.270586
C	-1.313818	-0.355529	0.49157
H	-1.085475	0.39101	1.251839
H	-0.480479	-0.411369	-0.229034
C	-1.5779	-1.719186	1.112331
H	-0.736091	-1.971498	1.762922
H	-2.502546	-1.694309	1.697119
H	-1.645704	-2.505764	0.356781
C	-2.902972	-0.699438	-1.429991
H	-3.451547	-1.533183	-0.984978
H	-3.634223	-0.108825	-1.988097
C	-1.775478	-1.197486	-2.328185
H	-1.068531	-1.846702	-1.805152
H	-2.223636	-1.77857	-3.142448
H	-1.195979	-0.385047	-2.768883
C	-2.419503	1.637735	-0.572907
H	-3.464216	1.94219	-0.689305
H	-2.03007	2.107543	0.332214
C	-1.575812	2.046728	-1.770654
H	-2.002494	1.692495	-2.714569
H	-1.550465	3.141009	-1.804116
H	-0.542891	1.703573	-1.67907
H	-3.354877	0.090443	0.405775
Cl	-4.936775	-0.062117	1.309631

Int6			
Ru	-0.000331	-0.107187	-0.308395
Cl	-2.400996	0.013161	-0.70164
Cl	2.400266	0.010971	-0.702861
H	-0.001234	-1.504909	-1.164785
C	-0.000413	-1.261596	1.077556
C	0.00143	1.594362	0.764966
O	0.003154	2.49599	1.482768
O	-0.000391	-2.019204	1.961678

Int7			
Ru	-0.256071	-0.013128	-0.13854
Cl	-1.301285	2.198183	-0.329431
Cl	1.254957	-1.964214	0.034017
H	0.37114	0.240832	-1.641168
C	2.656034	0.826281	0.029688
O	1.746984	1.121997	0.715856
O	3.605912	0.621994	-0.613005
C	-1.561349	-0.870948	-1.067002
C	-1.032964	-0.310753	1.682114
O	-1.552935	-0.520149	2.68907
O	-2.385808	-1.412361	-1.680652

TS2			
Ru	0.131093	0.00002	0.033052
Cl	-0.010675	2.458428	0.009852
Cl	-0.014489	-2.458172	0.008632
H	-1.211525	0.000819	1.099085
C	-2.43472	0.001396	-0.095626
O	-1.825076	0.001502	-1.143485

O	-3.437485	0.001554	0.532705
C	1.327091	-0.001476	1.433637
C	1.53805	-0.000571	-1.311293
O	2.372917	-0.000738	-2.104252
O	2.050732	-0.002582	2.336542

Int8			
Ru	-0.212658	0.000006	-0.082487
Cl	-0.060139	2.398676	-0.371403
Cl	-0.063151	-2.398629	-0.373519
H	2.172981	0.000082	-1.380325
C	2.623446	-0.000615	-0.348764
O	1.744836	-0.001885	0.607662
O	3.8383	-0.000234	-0.224722
C	-1.991163	0.001794	-0.797453
C	-0.838046	-0.000824	1.622571
O	-1.216861	-0.001414	2.714596
O	-3.051964	0.00312	-1.245623

Int9			
Ru	2.2111	-0.068171	-0.112245
Cl	0.887943	-1.979013	-0.822611
Cl	3.647252	1.874066	0.0272
H	1.047607	2.697329	0.454559
C	0.327989	2.276924	-0.271632
O	0.626658	1.07844	-0.70973
O	-0.667657	2.902389	-0.611761
C	3.729661	-1.208079	0.154372
C	1.77114	-0.178225	1.64532
O	1.443235	-0.226914	2.753138
O	4.648688	-1.881486	0.307905
N	-3.253136	-0.072181	-0.230507
C	-2.049423	-0.095065	0.664607
H	-1.846757	0.95255	0.89287
H	-1.199022	-0.482541	0.104025
C	-2.302765	-0.873427	1.950437
H	-1.443287	-0.733032	2.614422
H	-3.2066	-0.511309	2.450003
H	-2.40694	-1.948429	1.771999
C	-3.736856	-1.421708	-0.679035
H	-4.304029	-1.818187	0.166787
H	-4.4626	-1.224725	-1.472705
C	-2.667953	-2.406917	-1.135936
H	-1.975128	-2.668928	-0.333926
H	-3.169032	-3.326126	-1.461604
H	-2.066928	-2.031811	-1.964762
C	-3.146256	0.950259	-1.327735
H	-4.173741	1.103336	-1.672161
H	-2.80008	1.867865	-0.850521
C	-2.205378	0.603483	-2.472573
H	-2.573952	-0.23146	-3.077533
H	-2.133097	1.483251	-3.120483
H	-1.19646	0.389064	-2.112583
H	-4.087152	0.278613	0.377881
Cl	-5.667406	0.625325	1.307335

Int10			
Ru	1.456762	-0.053304	0.076596
Cl	0.441228	-1.472184	1.895951
H	0.63305	2.898262	-0.279208
C	-0.348612	2.415861	-0.124375
O	-1.383965	3.097727	-0.223407
O	-0.315799	1.158199	0.14705
C	2.271889	0.968916	1.408319
C	2.900803	-1.24322	-0.066461
O	3.783957	-1.978516	-0.171494
O	2.764765	1.611742	2.233827
N	-3.743819	-0.648361	0.087386
C	-2.411855	-1.273628	0.492908
H	-2.429791	-1.338715	1.581078
H	-1.623033	-0.575631	0.214833
C	-2.252329	-2.646789	-0.126487
H	-1.317063	-3.056688	0.259289
H	-3.084925	-3.314198	0.150679
H	-2.143437	-2.603028	-1.211376
C	-3.820735	-0.235464	-1.37807
H	-3.800879	-1.178097	-1.932007
H	-4.81973	0.201211	-1.490677
C	-2.728404	0.692036	-1.875144
H	-1.748869	0.205404	-1.869566
H	-2.976472	0.936758	-2.915461
H	-2.646102	1.623342	-1.310785
C	-4.234648	0.390749	1.085934
H	-5.068496	0.904714	0.597135
H	-4.643327	-0.202471	1.912156
C	-3.198422	1.372473	1.604867
H	-2.765105	2.018177	0.834487
H	-3.705655	2.001649	2.347047

H	-2.36783	0.863474	2.098595
H	-4.424299	-1.40876	0.158997
Cl	0.331359	-1.387256	-1.735415
Cl	2.473495	1.397656	-1.63959

Int11			
Ru	-1.996671	-0.064947	0.100517
Cl	-2.059564	2.292632	0.729383
H	5.371937	0.499251	1.426023
C	6.00147	-0.074671	0.71054
O	7.180374	-0.265764	0.915219
O	5.335411	-0.504284	-0.348248
C	-2.429855	-0.532982	1.889956
C	-3.734267	-0.146416	-0.432382
O	-4.829186	-0.191015	-0.794123
O	-2.684604	-0.814906	2.97731
N	2.812103	0.248797	-0.239707
C	2.14189	-0.594694	-1.259827
H	2.60781	-0.334156	-2.217515
H	1.077234	-0.356539	-1.353324
C	2.3265	-2.087456	-0.998686
H	1.910232	-2.648997	-1.840362
H	3.386123	-2.344814	-0.889885
H	1.785416	-2.417702	-0.107254
C	2.35311	0.016923	1.143678
H	2.785327	-0.934555	1.475902
H	2.807001	0.799981	1.762454
C	0.839319	-0.02534	1.391288
H	0.385298	-0.858699	0.841928
H	0.648811	-0.200443	2.456407
H	0.3487	0.912487	1.117801
C	2.900256	1.672566	-0.630899
H	3.604885	2.146428	0.066162
H	3.385925	1.680675	-1.614374
C	1.605334	2.487203	-0.692085
H	1.182897	2.671188	0.299324
H	1.819488	3.464937	-1.141095
H	0.831653	2.002027	-1.293481
H	4.335059	-0.212615	-0.289337
Cl	-1.276711	0.537149	-2.127357
Cl	-1.495695	-2.408334	-0.377023

TS3			
Ru	1.603208	-0.016557	-0.017039
Cl	2.332411	1.705467	-1.642478
Cl	0.883397	-1.701226	1.700792
H	-1.368971	2.555948	0.182272
C	0.285089	1.374476	0.778697
O	-1.069891	1.750146	-0.276829
O	0.16865	2.065383	1.728467
C	2.865425	0.619278	1.197935
C	2.820468	-1.318887	-0.813892
O	3.521078	-2.087792	-1.299451
O	3.655437	1.00515	1.948777
N	-2.929445	0.106997	0.051234
C	-3.942001	0.901684	0.782836
H	-3.450861	1.240132	1.701904
H	-4.782125	0.264628	1.082062
C	-4.449673	2.107061	-0.007473
H	-5.075324	2.731219	0.63957
H	-3.620586	2.718883	-0.376076
H	-5.053225	1.808262	-0.869589
C	-3.357268	-0.372268	-1.293625
H	-3.376467	0.508598	-1.943104
H	-2.535206	-0.993078	-1.654537
C	-4.6999	-1.099216	-1.36992
H	-5.535419	-0.480529	-1.022275
H	-4.896614	-1.3561	-2.416896
H	-4.706716	-2.027631	-0.794484
C	-2.264155	-0.918242	0.917025
H	-1.465141	-1.350213	0.314592
H	-1.766407	-0.358419	1.71315
C	-3.138516	-2.008439	1.525255
H	-3.530768	-2.696659	0.771162
H	-2.503329	-2.590202	2.200794
H	-3.980118	-1.615087	2.108368
H	-1.977827	0.90617	-0.159806
Cl	0.000137	-0.996135	-1.716831

Int12			
Ru	1.740647	-0.022332	-0.023851
Cl	3.388471	-1.375746	-1.278176
Cl	0.093757	1.304845	1.291092
H	-1.245261	-0.393947	2.335172
C	3.028507	0.159963	1.455204
O	-1.97323	-1.015502	2.518062
O	3.801695	0.311109	2.282581
C	1.00494	-1.653677	0.612471

C	0.645193	0.059242	-1.651664
O	0.060508	0.145492	-2.631093
O	0.600688	-2.665377	0.980184
N	-3.677561	-0.026866	0.347828
C	-2.686838	-0.367785	-0.67858
H	-1.778609	0.180366	-0.41394
H	-2.985081	-0.022003	-1.683591
C	-2.370862	-1.86278	-0.716674
H	-1.543984	-2.048664	-1.410424
H	-2.076755	-2.201673	0.280317
H	-3.224959	-2.460026	-1.057493
C	-4.978096	-0.682299	0.220972
H	-4.843468	-1.745908	0.45518
H	-5.620372	-0.274978	1.011146
C	-5.702797	-0.578964	-1.132616
H	-5.099439	-1.00584	-1.940779
H	-6.645342	-1.139432	-1.092182
H	-5.934991	0.455491	-1.400353
C	-3.693381	1.39683	0.698349
H	-4.345478	1.509361	1.574123
H	-2.678226	1.647336	1.02415
C	-4.116978	2.398317	-0.388339
H	-5.174835	2.30226	-0.655902
H	-3.954728	3.421421	-0.028434
H	-3.52036	2.272218	-1.297853
H	-2.659767	-0.723858	1.881226
Cl	2.740754	2.069705	-0.876347

Et_3NHBF_4			
N	0.886892	0.034731	-0.06379
C	1.100584	-0.843572	1.140909
H	0.398956	-0.470346	1.885709
H	2.122435	-0.697811	1.496022
C	0.788247	-2.302293	0.832513
H	0.831566	-2.877567	1.76193
H	-0.22006	-2.38309	0.419933
H	1.499597	-2.748337	0.130311
C	1.766019	-0.283271	-1.248186
H	1.312544	-1.154669	-1.72596
H	1.651205	0.557349	-1.937048
C	3.234685	-0.549415	-0.942573
H	3.371044	-1.449053	-0.336706
H	3.755787	-0.711808	-1.891386
H	3.720216	0.285528	-0.434169
C	0.793845	1.502227	0.284343
H	0.380434	1.986795	-0.601434
H	0.01953	1.552423	1.049223
C	2.093895	2.148888	0.734562
H	2.826646	2.223849	-0.073697
H	1.869667	3.167412	1.066483
H	2.553686	1.624683	1.57833
H	-0.075531	-0.223365	-0.399088
F	-2.040981	1.367209	-0.671309
F	-1.761897	0.036169	1.173802
F	-1.442479	-0.829493	-0.919251
F	-3.585665	-0.290987	-0.209556
B	-2.282082	0.098685	-0.142901

Int3’			
Ru	-0.353612	0.000148	-0.000281
Cl	-2.011663	-0.001095	-1.758736
Cl	-2.009706	-0.001157	1.760019
C	-0.490161	1.960098	-0.000088
C	-0.487118	-1.960008	-0.000161
O	-0.655346	3.093149	0.000029
O	-0.650508	-3.093326	0.000021
F	3.255465	-1.152487	0.000173
F	1.611881	0.001585	-1.149306
F	3.257938	1.15238	0.000108
F	1.610991	0.001732	1.14823
B	2.521249	0.000758	-0.000236

Int4’			
Ru	0.320334	0.192647	0.132475
Cl	0.390882	2.055412	-1.53263
Cl	0.266126	-1.538821	1.938977
C	0.183286	1.546157	1.543472
C	0.600283	-1.086919	-1.345429
O	0.173155	2.348773	2.362628
O	0.654294	-1.772374	-2.261902
N	-2.06184	-0.161671	-0.111107
C	-2.201499	-1.640628	-0.316811
H	-1.952189	-1.823914	-1.365155
H	-1.430668	-2.108619	0.295514
C	-3.531985	-2.31957	0.024446
H	-3.433733	-3.380251	-0.236581
H	-3.739212	-2.272948	1.097505
H	-4.392962	-1.92022	-0.516751

C	-2.507696	0.630812	-1.29397
H	-2.50536	1.677844	-0.985406
H	-1.720924	0.550708	-2.043877
C	-3.841999	0.264778	-1.956381
H	-4.002525	0.964154	-2.785558
H	-3.819469	-0.742489	-2.38389
H	-4.703945	0.333915	-1.289271
C	-2.641781	0.325092	1.176254
H	-2.171608	1.288504	1.372914
H	-2.287403	-0.36483	1.94576
C	-4.155366	0.558757	1.282753
H	-4.761916	-0.323493	1.074914
H	-4.367162	0.87502	2.31153
H	-4.483268	1.367828	0.623113
H	-1.354184	3.74932	-0.214325
H	-1.885108	4.120958	0.158799
B	3.580797	-0.340154	-0.137581
F	3.000836	-1.480987	-0.689412
F	2.441842	0.474362	0.434667
F	4.405618	-0.630535	0.923577
F	4.178111	0.448313	-1.093523

TS1’

Ru	-0.672274	0.543222	0.02692
Cl	-1.343846	1.866259	1.994221
Cl	-0.006188	-0.725851	-2.002937
C	-0.770006	2.13255	-1.100101
C	-0.544655	-1.030041	1.22092
O	-0.80647	3.069778	-1.759899
O	-0.341898	-1.866468	1.976081
N	2.799762	-0.094463	0.105913
C	2.619826	-1.556341	0.139687
H	2.383871	-1.819459	1.176231
H	1.73119	-1.774936	-0.460775
C	3.780949	-2.416679	-0.370942
H	3.518471	-3.474406	-0.251643
H	3.957031	-2.245087	-1.437623
H	4.717081	-2.235269	0.166143
C	3.3521	0.526019	1.31509
H	3.43692	1.599992	1.110833
H	2.594051	0.426125	2.104544
C	4.684517	-0.012534	1.849544
H	4.977102	0.560355	2.737736
H	4.594833	-1.061233	2.149797
H	5.489677	0.06322	1.113569
C	3.179334	0.504816	-1.18122
H	2.72053	1.503184	-1.215513
H	2.671381	-0.077347	-1.953429
C	4.676234	0.648354	-1.480744
H	5.198735	-0.311941	-1.458707
H	4.802842	1.080116	-2.480814
H	5.168549	1.32057	-0.769332
H	1.298045	0.481823	0.212096
H	0.796463	1.164879	0.559164
B	-3.556265	-1.036814	-0.16255
F	-2.683454	-1.995832	0.356163
F	-2.71469	0.172931	-0.474948
F	-4.116245	-1.434818	-1.354528
F	-4.488496	-0.636425	0.767747

Int5’

Ru	2.130479	-0.143995	-0.163692
Cl	1.216746	-2.347436	-0.539893
H	2.688789	-0.193134	-1.699606
C	3.779466	-0.827778	0.226209
C	1.421167	-0.141224	1.745926
O	1.100622	-0.230006	2.844587
O	4.832468	-1.261666	0.444609
N	-2.877749	-0.322146	-0.25011
C	-1.811827	-0.216347	0.800271
H	-1.444368	0.809506	0.762051
H	-0.986828	-0.875081	0.521133
C	-2.36197	-0.5265	2.187792
H	-1.590158	-0.296403	2.92798
H	-3.248248	0.082061	2.392222
H	-2.630353	-1.581572	2.303602
C	-3.488111	-1.690129	-0.383281
H	-4.213705	-1.761417	0.430569
H	-4.066375	-1.667226	-1.31049
C	-2.514102	-2.862927	-0.362607
H	-2.00919	-2.959804	0.601571
H	-3.084508	-3.783304	-0.532942
H	-1.738947	-2.791332	-1.126166
C	-2.50771	0.318221	-1.558166
H	-3.464689	0.536538	-2.042167
H	-2.03758	1.267652	-1.301547
C	-1.592968	-0.494159	-2.463987
H	-2.098875	-1.376259	-2.869571

H	-1.298529	0.139051	-3.307326
H	-0.678604	-0.811819	-1.959825
H	-3.727695	0.272585	0.097625
Cl	-5.359197	1.017473	0.562815
F	0.374023	1.211828	-0.882449
F	2.343776	2.092454	-0.1328
F	0.356693	2.62052	0.93184
F	0.792797	3.475406	-1.167544
B	0.928144	2.433339	-0.306299

Int6’			
Ru	-0.47118	-0.253104	-0.141764
Cl	-2.198338	0.846669	-1.423004
H	-0.582967	-1.492148	-1.202359
C	-1.71088	-1.21206	0.786259
C	-0.376132	1.342579	1.118228
O	-0.433246	2.228097	1.847077
O	-2.501868	-1.840484	1.360496
F	1.526068	0.477353	-1.13399
F	1.479303	-1.055953	0.559207
F	2.789995	0.836846	0.762148
F	3.401938	-0.819385	-0.717503
B	2.382778	-0.119681	-0.137047

Int7’			
Ru	-0.801827	0.093797	-0.307442
Cl	-2.869533	1.174753	0.330473
H	-1.038875	0.692962	-1.815051
C	1.528282	2.265149	-0.17103
O	0.438194	2.082635	0.229392
O	2.578352	2.554182	-0.580737
C	-1.677856	-1.359429	-0.966858
C	-0.586329	-0.596757	1.594632
O	-0.592365	-1.00742	2.66508
O	-2.252374	-2.267162	-1.40445
F	2.335306	0.088424	0.961346
F	1.195423	-0.463144	-0.960587
F	1.676589	-2.086721	0.616751
F	3.362248	-1.180407	-0.667406
B	2.203235	-0.953168	0.031761

TS2’			
Ru	0.509046	-0.126316	0.03049
Cl	2.61282	-1.325965	-0.088554
H	1.340744	1.103817	1.032369
C	1.93243	2.113298	-0.075394
O	1.532824	1.684095	-1.14424
O	2.544153	2.923253	0.540323
C	-0.028554	-1.154255	1.473241
C	-0.253954	-1.383067	-1.254421
O	-0.606254	-2.173228	-2.00639
O	-0.294063	-1.792747	2.394729
F	-1.226506	1.182698	0.066843
F	-2.676155	-0.316452	1.061239
F	-2.661612	-0.085317	-1.223944
F	-3.487127	1.614001	0.096581
B	-2.601381	0.57085	-0.002185

Int8’			
Ru	-0.50686	-0.13935	-0.056465
Cl	-2.571343	-1.349765	-0.230172
H	-1.472645	1.493305	-1.212142
C	-1.857985	2.067505	-0.269042
O	-1.521464	1.468064	0.817047
O	-2.482497	3.090339	-0.465336
C	0.348998	-1.512174	-1.097679
C	-0.049047	-1.005675	1.505931
O	0.168533	-1.549957	2.495353
O	0.776239	-2.366565	-1.732568
F	1.158718	1.175309	-0.072277
F	2.694913	-0.076873	-1.256599
F	2.574203	-0.283746	1.027141
F	3.408415	1.651745	0.091602
B	2.556562	0.590646	-0.050098

Int9’			
Ru	-1.694174	-0.633461	0.325766
Cl	-0.189572	-2.488423	0.214411
H	-0.871652	2.235009	0.570454
C	-0.087633	1.724656	1.156556
O	-0.200222	0.411541	1.205263
O	0.819357	2.341746	1.693056
C	-3.155628	-1.770097	-0.240069
C	-1.378858	-0.14696	-1.407929
O	-1.091763	0.122203	-2.489387
O	-4.004049	-2.472525	-0.558137
N	3.709235	0.084539	0.119109
C	2.451482	0.262459	-0.678783

H	2.127146	1.284575	-0.476336
H	1.689034	-0.411403	-0.287409
C	2.68856	0.074	-2.172517
H	1.772566	0.345844	-2.707177
H	3.508537	0.712146	-2.515897
H	2.923171	-0.96402	-2.427713
C	4.352676	-1.266902	-0.008849
H	4.89811	-1.236431	-0.955439
H	5.106769	-1.310492	0.781378
C	3.416701	-2.468169	0.050282
H	2.70917	-2.48206	-0.781423
H	4.024637	-3.378186	-0.012292
H	2.831612	-2.509049	0.969532
C	3.59169	0.590848	1.529845
H	4.623916	0.742573	1.860319
H	3.105938	1.56536	1.460895
C	2.809533	-0.291227	2.492107
H	3.31831	-1.239228	2.694926
H	2.717306	0.25001	3.439618
H	1.796057	-0.479681	2.131233
H	4.46015	0.738684	-0.332856
Cl	5.918856	1.595996	-1.089292
F	-2.988611	0.936526	0.88619
F	-4.589382	2.529491	0.394304
F	-4.425716	0.629364	-0.90286
F	-2.78046	2.227242	-1.010176
B	-3.763957	1.641829	-0.228726

Int10’

Ru	-1.260958	-0.555823	0.001658
Cl	-0.334916	-2.738697	-0.571328
H	-0.45017	0.531583	2.656905
C	0.544453	0.33962	2.228314
O	1.566441	0.590998	2.887558
O	0.552495	-0.149468	1.030477
C	-0.585889	0.059988	-1.643346
C	-2.925707	-0.991533	-0.772378
O	-3.951644	-1.275558	-1.211865
O	-0.189071	0.327492	-2.697342
N	3.875425	0.145969	-0.747301
C	2.514113	-0.263233	-1.276994
H	2.190628	0.555715	-1.922046
H	1.838765	-0.311829	-0.415537
C	2.602337	-1.566901	-2.049453
H	1.609679	-1.799466	-2.43836
H	3.308788	-1.495688	-2.890154
H	2.883206	-2.407567	-1.41029
C	4.449287	-0.815076	0.295154
H	4.871164	-1.637543	-0.290659
H	5.280955	-0.273365	0.75571
C	3.478856	-1.342536	1.337074
H	2.679237	-1.942504	0.895862
H	4.060895	-1.990197	2.004365
H	2.998481	-0.56168	1.936178
C	3.940375	1.625451	-0.383247
H	4.937942	1.771474	0.044377
H	3.908181	2.142205	-1.348914
C	2.846978	2.136699	0.534114
H	2.78265	1.600173	1.483767
H	3.077984	3.187962	0.744098
H	1.857871	2.105195	0.072523
H	4.51363	0.058221	-1.542103
Cl	-2.263826	-1.426355	2.084262
B	-1.581457	2.584001	-0.240344
F	-1.846412	1.423028	0.651079
F	-1.938073	3.712393	0.457164
F	-2.33081	2.382851	-1.388617
F	-0.20964	2.564508	-0.539825

Int11’

Ru	-1.619595	-0.491511	0.139498
Cl	-0.782872	-2.574133	-0.724433
H	5.284808	2.012694	-0.295932
C	6.070788	1.402909	0.200336
O	7.179648	1.840214	0.410508
O	5.666202	0.182193	0.521902
C	-2.082883	-0.014431	-1.666879
C	-3.282024	-1.185338	0.449602
O	-4.315747	-1.64219	0.666858
O	-2.327354	0.175735	-2.770727
N	3.185061	-0.280242	-0.309593
C	2.660583	-1.272208	0.660136
H	3.308245	-2.152387	0.57211
H	1.644125	-1.596565	0.407331
C	2.704371	-0.75427	2.09535
H	2.404112	-1.556267	2.775291
H	3.713303	-0.419159	2.360612
H	1.998524	0.064839	2.257554

C	2.42797	0.985971	-0.355602
H	2.667794	1.551464	0.551599
H	2.822608	1.562809	-1.20022
C	0.900964	0.884082	-0.47509
H	0.513465	0.40916	0.439749
H	0.440064	1.871383	-0.5489
H	0.611733	0.302836	-1.351751
C	3.499929	-0.861148	-1.629845
H	4.095106	-0.114657	-2.172232
H	4.170684	-1.70584	-1.432742
C	2.33734	-1.330575	-2.511802
H	1.777608	-0.48746	-2.928493
H	2.734174	-1.907064	-3.356219
H	1.632696	-1.964368	-1.966138
H	4.685237	0.041806	0.226797
Cl	-0.867213	-1.066469	2.351286
F	-2.051128	1.432045	0.938955
F	-1.755457	2.674911	-0.982201
F	-3.836317	1.855237	-0.461185
F	-2.922942	3.561235	0.798927
B	-2.687537	2.455358	0.03166

TS3’

Ru	1.108193	-0.497349	0.043801
Cl	0.112294	-2.606055	0.815129
H	-1.390111	2.242117	1.216756
C	-0.139314	0.50257	1.339572
O	-1.181081	1.658586	0.464828
O	-0.397869	0.60832	2.482791
C	2.327358	-0.637974	1.472647
C	2.268202	-1.503192	-1.196371
O	2.898507	-2.128749	-1.917598
O	3.039978	-0.805078	2.36083
N	-3.315866	0.412227	0.040706
C	-4.250092	1.041917	1.004335
H	-3.812453	0.879326	1.995293
H	-5.217442	0.527069	0.989235
C	-4.442235	2.538781	0.76473
H	-5.021638	2.968363	1.588815
H	-3.48123	3.059223	0.713939
H	-4.98115	2.742427	-0.164997
C	-3.678522	0.594069	-1.394853
H	-3.43802	1.632123	-1.644931
H	-2.970907	-0.019227	-1.954686
C	-5.126047	0.292629	-1.783254
H	-5.84521	0.927864	-1.254159
H	-5.243816	0.488914	-2.854803
H	-5.402118	-0.748861	-1.60518
C	-2.942101	-0.985062	0.430586
H	-2.12336	-1.275262	-0.228524
H	-2.516682	-0.909962	1.434461
C	-4.044044	-2.038987	0.412592
H	-4.372174	-2.274844	-0.603652
H	-3.627728	-2.95663	0.840511
H	-4.921977	-1.7584	1.006845
H	-2.229515	1.03484	0.200539
Cl	-0.440582	-0.436625	-1.931614
B	3.28562	1.748695	-0.390316
F	1.86042	1.385232	-0.662588
F	3.534763	2.901611	-1.096927
F	4.053685	0.671691	-0.822394
F	3.382619	1.922312	0.983851

Int12’

Ru	-1.189165	-0.511083	-0.0412
Cl	-0.327181	-2.739279	-0.539283
H	0.681495	1.905651	0.547388
C	0.041406	0.148217	-1.480025
O	1.221406	2.051795	-0.248183
O	0.625202	0.297178	-2.451297
C	-2.518175	-0.792086	-1.371522
C	-2.314791	-1.292657	1.380394
O	-2.916431	-1.795382	2.208534
O	-3.299096	-1.053793	-2.17091
N	3.531958	0.346147	-0.104569
C	4.401561	1.002808	-1.080304
H	3.965913	0.80598	-2.067356
H	5.420177	0.573367	-1.098337
C	4.488968	2.516574	-0.872673
H	5.035778	2.975389	-1.704738
H	3.486387	2.951624	-0.822765
H	5.019219	2.772269	0.051414
C	3.900093	0.537064	1.304463
H	3.656549	1.572327	1.574537
H	3.222425	-0.08974	1.889492
C	5.359677	0.262928	1.701371
H	6.058039	0.906859	1.154498
H	5.490133	0.470536	2.770528

H	5.654037	-0.774803	1.522516
C	3.135158	-1.018798	-0.478189
H	2.305628	-1.310024	0.171551
H	2.72613	-0.958158	-1.49227
C	4.215437	-2.110651	-0.453356
H	4.540971	-2.338089	0.566736
H	3.803014	-3.032968	-0.878801
H	5.099227	-1.83263	-1.040577
H	1.960877	1.403329	-0.143389
Cl	0.402491	-0.2466	1.845098
B	-3.274064	1.820788	0.203393
F	-1.830255	1.471767	0.462757
F	-3.483292	3.04819	0.771202
F	-4.016415	0.803828	0.799086
F	-3.419042	1.809652	-1.174997

Int5’’

Ru	-2.276658	-0.174523	-0.155768
Cl	-2.273281	2.230335	0.340013
Cl	-1.613714	-2.440489	-0.772576
H	-1.981401	0.221671	-1.717202
C	-3.970167	-0.263203	-0.794073
C	-2.678434	-0.689833	1.744047
O	-3.006568	-1.003448	2.801736
O	-5.048721	-0.316983	-1.217713
N	1.723835	0.420571	-0.184357
C	0.620718	-0.004514	0.742053
H	0.200964	-0.915419	0.303325
H	-0.133024	0.789991	0.754373
C	1.140144	-0.311815	2.14191
H	0.330669	-0.768295	2.719357
H	1.977975	-1.012267	2.089192
H	1.468451	0.587264	2.671135
C	2.429624	1.694496	0.237339
H	3.142392	1.394966	1.006151
H	3.026997	1.989618	-0.624655
C	1.510529	2.809855	0.718834
H	1.038853	2.573669	1.676241
H	2.121266	3.707594	0.865753
H	0.711556	3.048492	0.016092
C	1.342152	0.377081	-1.65033
H	2.29489	0.229364	-2.16248
H	0.73044	-0.52076	-1.771555
C	0.608109	1.599521	-2.180246
H	1.244568	2.489965	-2.17656
H	0.332267	1.391908	-3.219425
H	-0.316437	1.806802	-1.636533
H	2.449033	-0.324278	-0.090046
F	5.062036	0.141268	1.03154
F	4.448486	0.060463	-1.182173
F	3.576478	-1.45198	0.296731
F	5.807841	-1.587069	-0.304562
B	4.783648	-0.710575	-0.041704

Int9’’

Ru	2.938539	0.046189	0.013061
Cl	1.564038	2.052621	-0.105252
Cl	4.231412	-1.877608	0.69392
H	1.753606	-2.78132	-0.31282
C	0.945269	-2.216724	0.185996
O	1.197543	-0.951326	0.393056
O	-0.106948	-2.764664	0.496661
C	4.529734	1.112708	-0.042606
C	3.030018	-0.23572	-1.779483
O	3.052447	-0.436388	-2.917133
O	5.48951	1.745108	-0.061786
N	-2.54604	0.242788	0.623168
C	-1.703829	0.066609	-0.616005
H	-1.410783	-0.983812	-0.613149
H	-0.796869	0.658998	-0.494279
C	-2.475221	0.407151	-1.884846
H	-1.820226	0.209944	-2.740607
H	-3.376453	-0.203584	-1.982272
H	-2.771193	1.459347	-1.928016
C	-3.039871	1.65403	0.860511
H	-3.914429	1.764204	0.219372
H	-3.396656	1.665563	1.89406
C	-2.018606	2.756772	0.614446
H	-1.739493	2.826741	-0.4395
H	-2.479212	3.7098	0.898653
H	-1.099058	2.633868	1.187088
C	-1.944016	-0.416825	1.844643
H	-2.791926	-0.582315	2.516383
H	-1.558941	-1.381449	1.505562
C	-0.832483	0.363057	2.528961
H	-1.191839	1.286117	2.994818
H	-0.421134	-0.272974	3.320321
H	-0.020027	0.58837	1.836951

H	-3.433215	-0.286727	0.478247
B	-5.782891	-0.459813	-0.43639
F	-4.981912	-0.777398	0.737143
F	-7.106522	-0.728157	-0.162222
F	-5.289269	-1.227153	-1.49507
F	-5.580096	0.909714	-0.708647