Heterogeneous Rh/CPOL-BINAPa&PPh_3 Catalyst for Hydroformylation of Olefins: Chemical and DFT Insights into Active Species and the Roles of BINAPa and PPh_3

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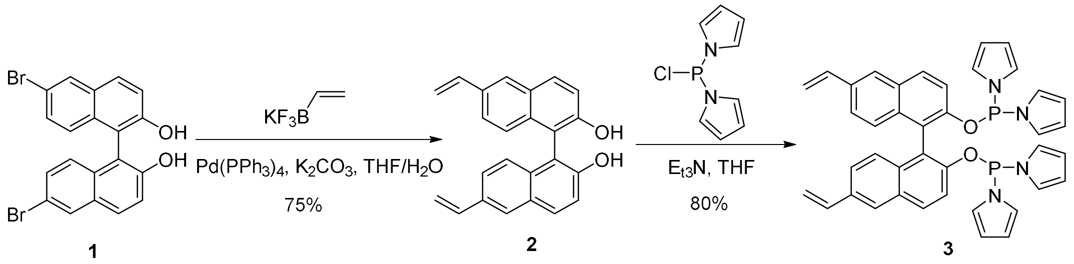
1. General methods

Unless otherwise noted, all manipulations involving air- or moisture-sensitive compounds were performed in a nitrogen-filled glovebox or using standard Schlenk techniques. Solvents were dried according to standard procedures. ^{1}H NMR and ^{31}P NMR spectra were recorded on 500 MHz by using a Bruker Avance 500 spectrometer. Chemical shifts (δ values) were reported in ppm with internal TMS (^{1}HNMR), $CDCl_3$ (^{13}C NMR), or external 85% H_3PO_4 (^{31}P NMR) as the standard, respectively. ICP were determined on ICP-OES: Aglient 5110. The FT-IR spectra were measured on a Thermo (SCIENTIFC) NICOLET iS10 spectrometer. The SEM and TEM spectra were obtained on a Zeiss sigma 500 and JEOL-2100F spectrometers, respectively. N_2 sorption isotherms were obtained on MicroActive for ASAP 2460 Version 2.02. Thermogravimeric analysis was determined onTGA5500. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha+. GC analyses were measured on an Agilent 7820A system using a FID detector. All calculations have been performed using the DFT method implemented in the commercial Gaussian 16 program package. The M062X(D3) functional in combination with SDD pseudopotential basis set for transition metals Rh and 6-311G(d,p) basis set for other elements were employed for all calculations. All of the optimized geometries mentioned were built by Gaussview 6.0. Chiral HPLC analyses were performed on a Chiralpak AS-H liquid chromatography.

2. Synthesis of catalysts

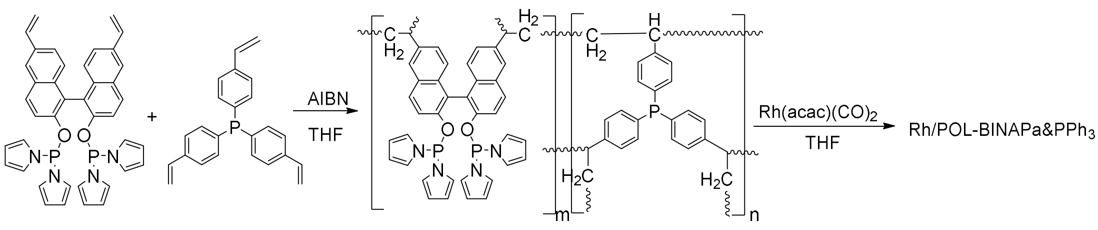
Synthesis of 1,1',1'',1'''-(((6,6'-divinyl-[1,1'-binaphthalene]-2,2'-diyl)bis(oxy)) bis (phosphinetriyl)) tetrakis(1H-pyrrole) (3)



Compound **3** was obtained by following the reported literature procedure.[1] Under nitrogen, the compound **1** (500.0 mg, 1.13 mmol), $C_2H_3BF_3K$ (664.0 mg, 4.95mmol), K_2CO_3 (684.14 mg, 4.95mmol) and $Pd(PPh_3)_4$ (57.78 mg, 0.0495mmol) were dissolved in a mixture solvent (6 mL THF and 1 mL H_2O) in Schlenk tube. The mixture was heated to 90°C for 24 h, then was purified by column chromatography (PE :EA = 2:1). The compound **2** (285.5mg, 75% yield) was obtained as a light yellow solid.

Under nitrogen, THF solution of compound **2** (226.5mg, 0.67 mmol) was added dropwise to a mixture of triethylamine (149.8mg, 1.48 mmol) and chlorodipyrrolylphosphine (293.9 mg, 1.48 mmol) and THF (5.0 mL) in Schlenk tube at 0 °C. After 24 h of stirring at room temperature, the mixture was purified by column chromatography (PE:EA = 20:1). Under reduced pressure to remove the solvent, the compound **3** was evaporated and obtained in 80% yield (356.3 mg). ^1H NMR ($CDCl_3$, 500 MHz):δ 7.93 (d, J = 8.5 Hz, 2H), 7.87 (s, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.25-7.20 (m, 2H), 6.96-6.91 (m, 2H), 6.59 (d, J = 27.0 Hz, 8H), 6.21 (d, J = 27.0 Hz, 8H),5.88 (d, J = 18.0 Hz, 2H), 5.39 (d, J = 10.0 Hz, 2H) ppm; ^{31}P NMR (202 MHz, $CDCl_3$):δ108.9ppm.

Synthesis of Rh/CPOL-BINAPa&PPh₃.

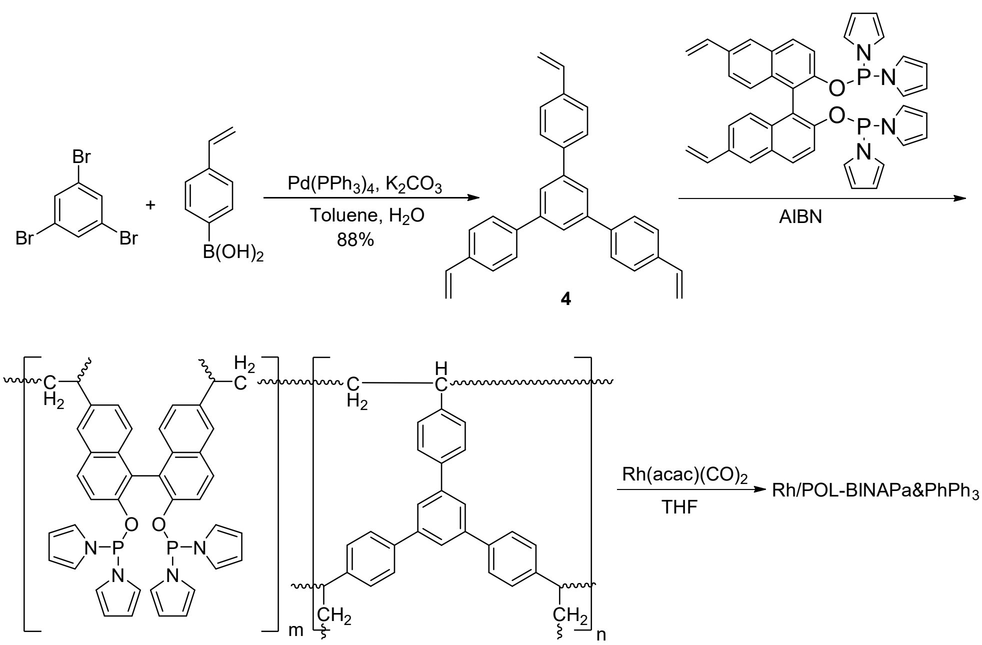


Under N_2 atmosphere, tris(4-vinphenyl) phosphane (137.08 mg, 0.40 mmol), the compound **3** (86.1 mg, 0.13 mmol) and AIBN (5.0 mg，0.03 mmol) were added into

THF (4mL) in Schlenk flask. After stirring for 5 minutes at room temperature, the mixture was heated to 100 ^{o}C for 24 h. The crude product was then washed with toluene and further centrifuged (9000 rpm, 5 min). After removing the residual solvent under reduced pressure, the copolymer of POL-BINAPa&PPh_3 (180.92 mg) was obtained.

Under N_2 atmosphere, CPOL-BINAPa&PPh_3 (180.92 mg) and Rh(acac)$(CO)_2$ (9.25mg) was added to THF (4 mL). After stirring for 24 h under N_2 at room temperature, the crude product was separated by using centrifuge and further washed by toluene. After removing the residual solventunder reduced pressure, the Rh/CPOL-BINAPa&PPh_3 (170.0 mg) was obtained.

Synthesis of Rh/CPOL-BINAPa&PhPh$_3$.



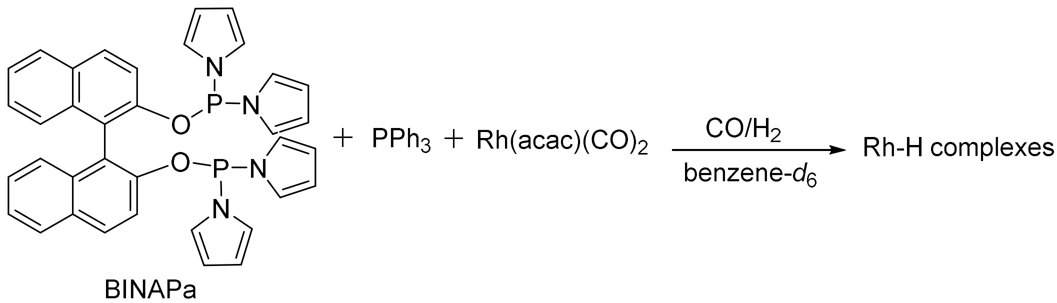
Under N_2 atmosphere, the 1,3,5-tribromobenzene (500 mg,1.59 mmol), 4-vinylbenzeneboronic acid (1.4 g, 9.53 mmol), K_2CO_3 (1317.1 mg, 9.53 mmol) and $Pd(PPh_3)_4$ (110.10 mg, 0.095 mmol) were dissolved in mixture solvent (6 mL toluene and 1 mL H_2O) in Schlenk tube. The mixture was heated to 120 °C for 24 h. The crude product then was purified by column chromatography. The compound **4** (538.3 mg, 88% yield) was obtained as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ7.77 (s, 3H), 7.66 (d, *J*=8.5 Hz,6H), 7.52 (d, *J*=8.5 Hz,6H), 6.78 (dd, *J*=17.5, 11.0 Hz,3H), 5.82 (d, *J*=17.5 Hz,3H), 5.29 (d, *J*=11.0 Hz,3H)ppm[2].

Under N_2 atmosphere, tris(4-vinylphenyl)benzene(234.56 mg, 0.61mmol), compound **3** (134.85 mg, 0.203 mmol) and AIBN (8.0 mg, 0.049 mmol) were dissolved in THF (4 mL) in Schlenk flask. After stirring for 10 minutes at room temperature, the mixture was heated to 100 ^{o}C for 24 h. After the crude product was washed by toluene and separated by using a centrifuge (9000 rpm, 5 min), the copolymer POL-BINPa&PhPh$_3$ (295 mg) was obtained as a light yellow solid.

In glove box, CPOL-BINAPa&PhPh$_3$ (100 mg) and Rh(acac)(CO)$_2$ (4.74mg) was added to THF (4mL). After stirring for 24 h under N_2 at room temperature, the crude product was washed by toluene and was separated by using centrifuge. The light yellow catalyst Rh/CPOL-BINAPa&PhPh$_3$ (84mg) was obtained.

The catalysts of Rh/CPOL-(*S*)-BINAPa&PPh$_3$ and Rh/CPOL-(*S*)-BINAPa&PhPh$_3$ were prepared by using (*S*)-BINOL as starting material according to the procedures of synthesis Rh/CPOL-BINAPa&PPh$_3$ and Rh/CPOL-BINAPa&PhPh$_3$.

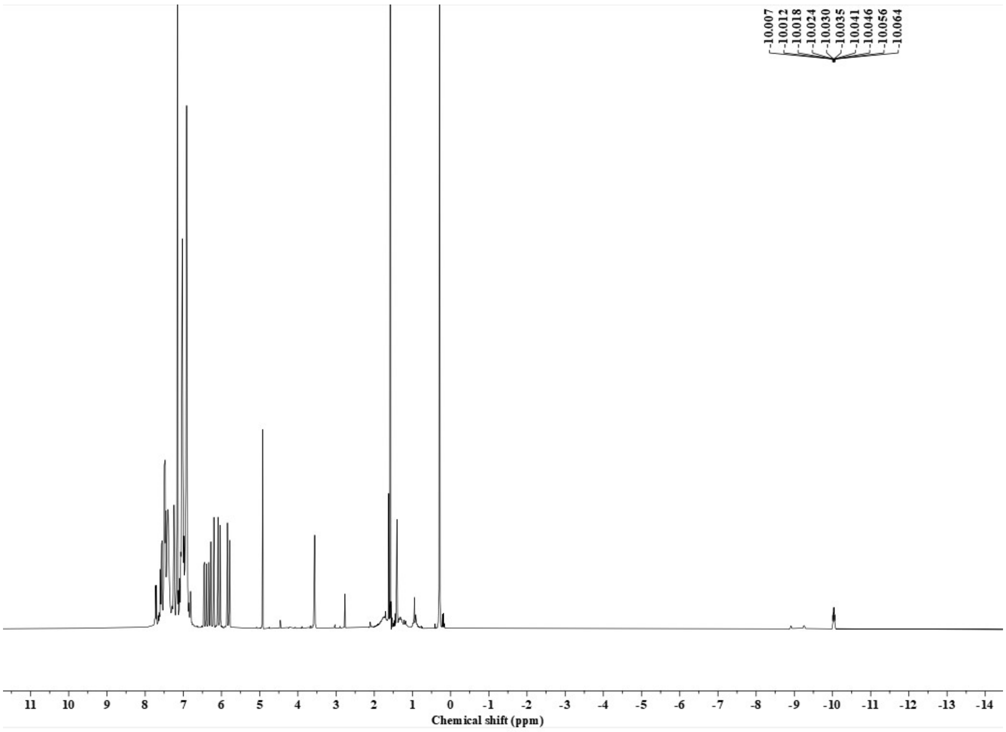
3. Preparation and characterization of Rh-H complexes



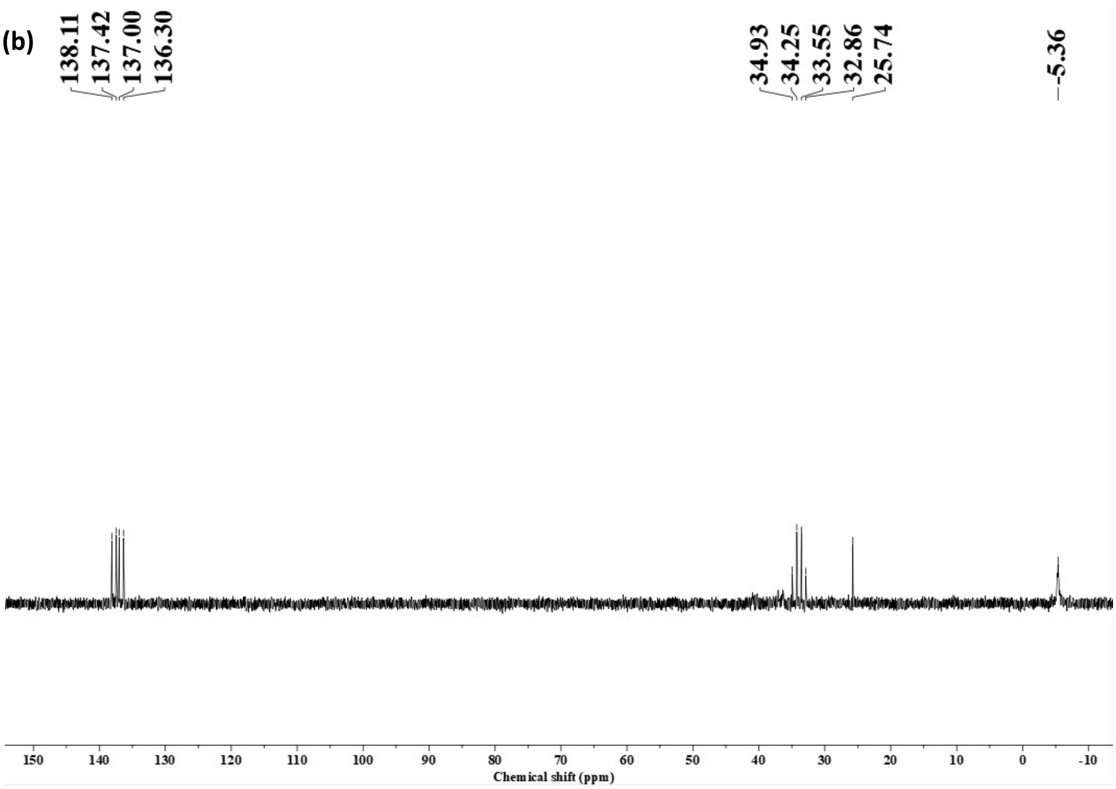
In a glove box, the mixture of Rh(acac)(CO)$_2$ (4.1 mg, 0.016 mmol), PPh$_3$ (12.9 mg, 0.048 mmol) and BINAPa (10 mg, 0.016mmol) in benzene-d_6 (1.5 mL) was stirred for 0.5 hour at room temperature in a 5 mL glass vial, which was then transferred into a stainless steel autoclave and sealed. The autoclave was purged with H_2 three times and subsequently charged with CO (10 bar) and H_2 (10 bar). The autoclave was then heated to 40 ^{o}C (oil bath) and stirred at the temperature for 12 h.

After cooling the autoclave to 0°C, the syngas was carefully released, and the solution was submitted to NMR and IR analysis.

(a)



(b)



(c)

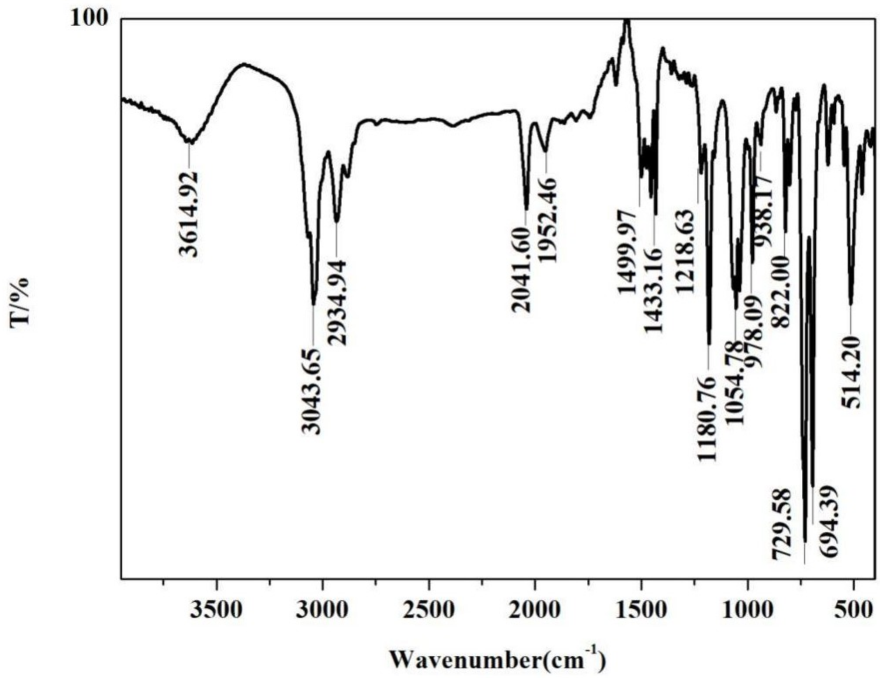
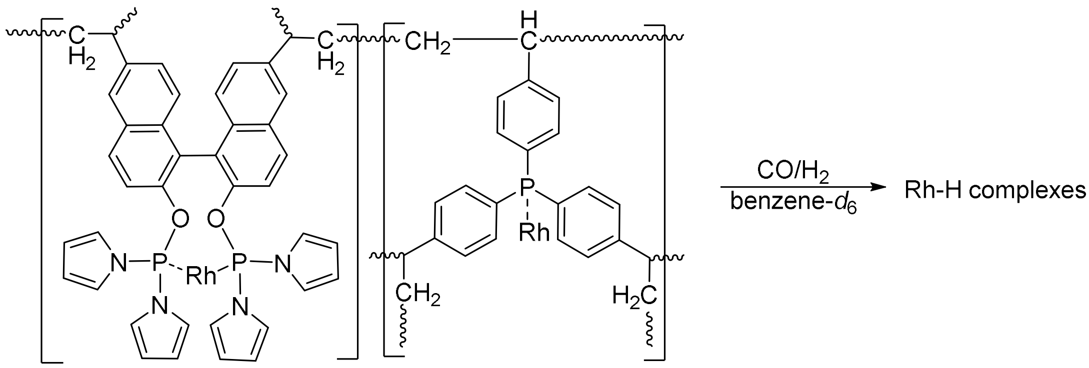


Fig S1. (a) ^{1}H NMR spectra,(b) ^{31}P NMR spectra, (c) FT-IR spectra of [HRh(CO)(BINAPa)(PPh_3)]



In a glove box, Rh/CPOL-BINAPa&PPh_3 (10 mg, Rh loading at 5.3 wt%) and benzene-d_6 (1.5 mL) were added in a glass vial, which was then transferred into a stainless steel autoclave and sealed. The autoclave was purged with H_2 three times and subsequently charged with CO (10 bar) and H_2 (10 bar). The autoclave was then heated to 40 ^{o}C (oil bath) and stirred at the temperature for 12 h. After cooling the autoclave to 0°C, the syngas was carefully released, and the mixture was submitted to IR analysis.

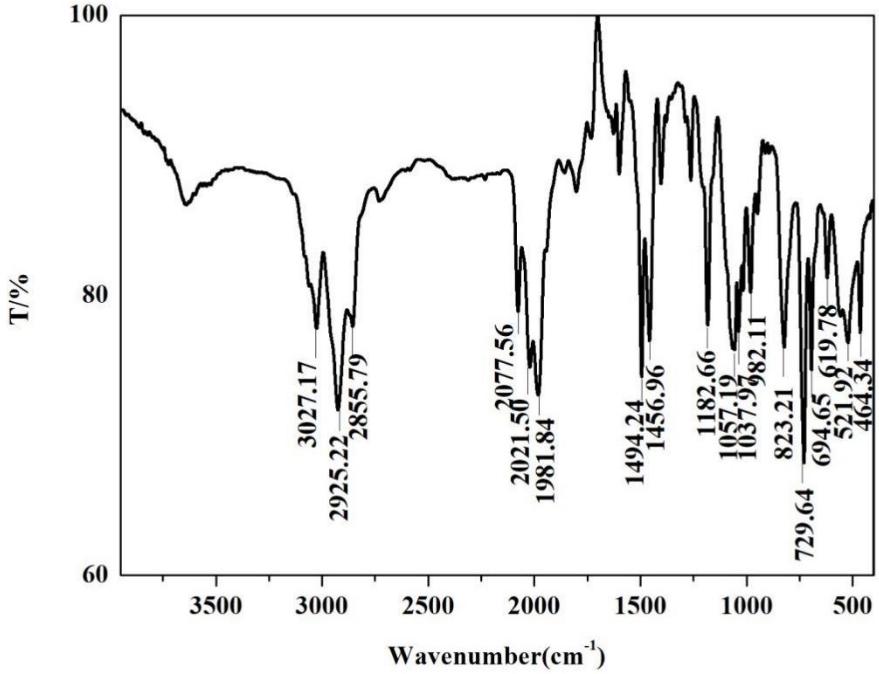
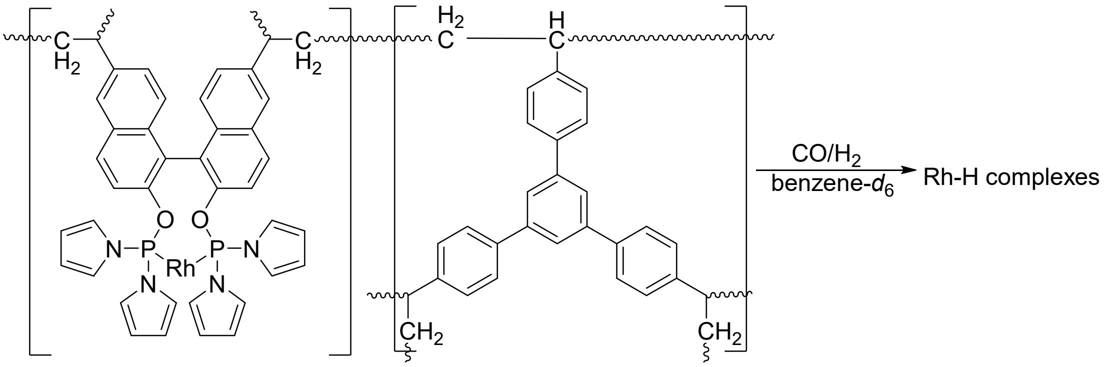


Fig S2. FT-IR spectra of Rh-H complexes



In a glove box, Rh/CPOL-BINAPa&PPh_3 (10 mg, Rh loading at 4.6 wt%) and benzene-d_6 (1.5 mL) were added in a glass vial, which was then transferred into a stainless steel autoclave and sealed. The autoclave was purged with H_2 three times and subsequently charged with CO (10 bar) and H_2 (10 bar). The autoclave was then heated to 40 ^oC (oil bath) and stirred at the temperature for 12 h. After cooling the autoclave to 0°C, the syngas was carefully released, and the mixture was submitted to IR analysis.

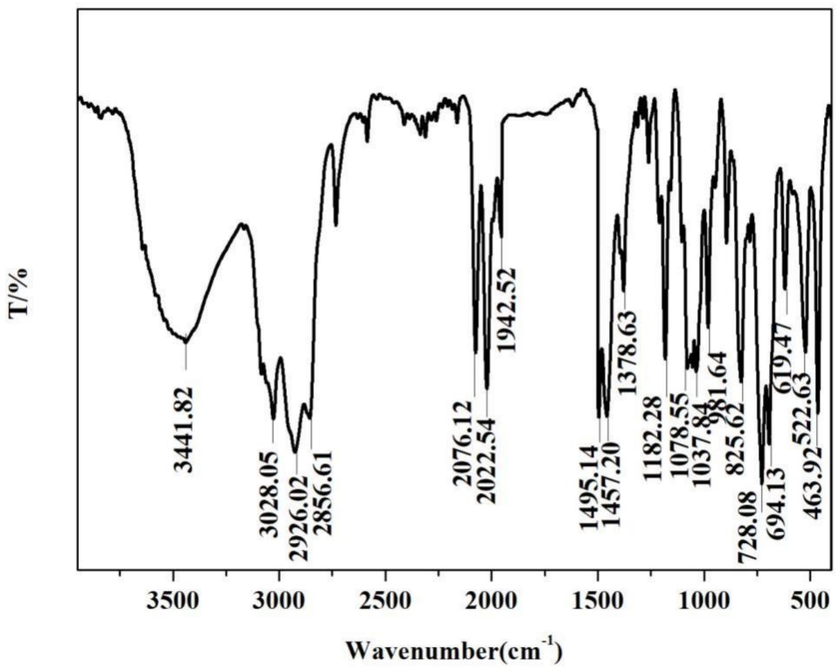


Fig S3. FT-IR spectra of Rh-H complexes

4. XPS spectra of copolymers and catalysts.

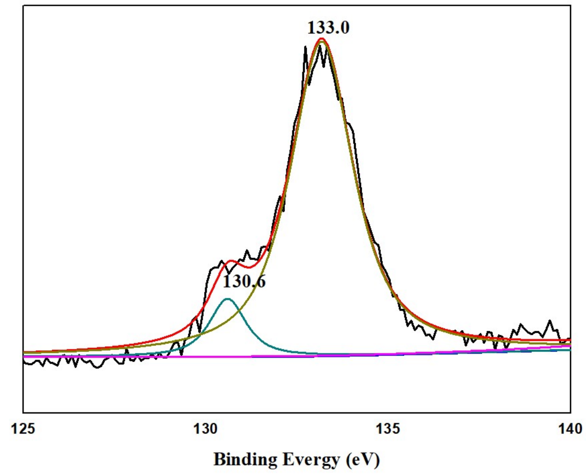


Fig.S4. P2p XPS spectra of CPOL-BINAPa&PPh_3

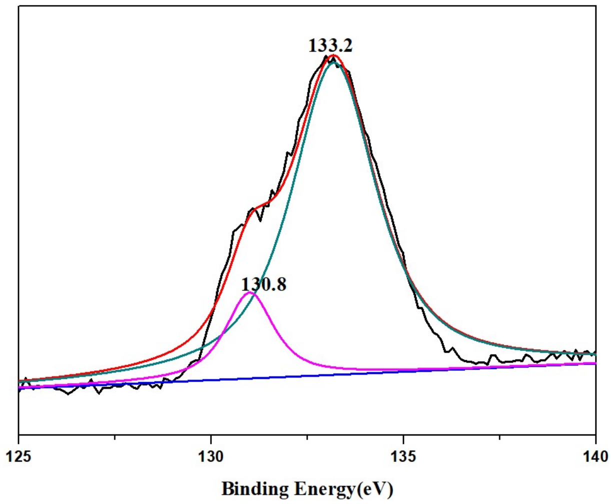


Fig.S5. P2p XPS spectra of Rh/CPOL-BINAPa&PPh_3

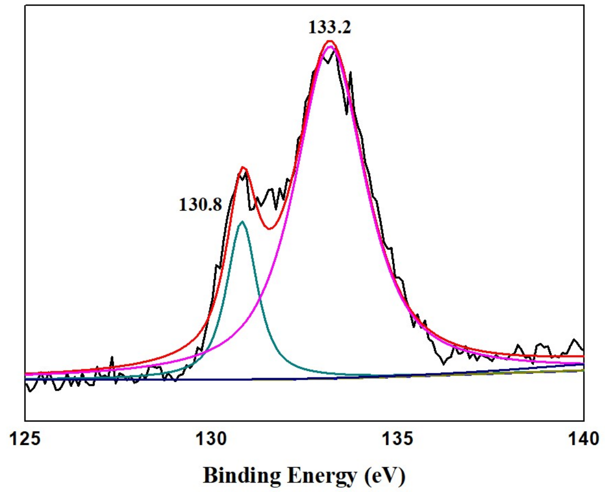


Fig.S6. P2p XPS spectra of the recovered Rh/CPOL-BINAPa&PPh_3

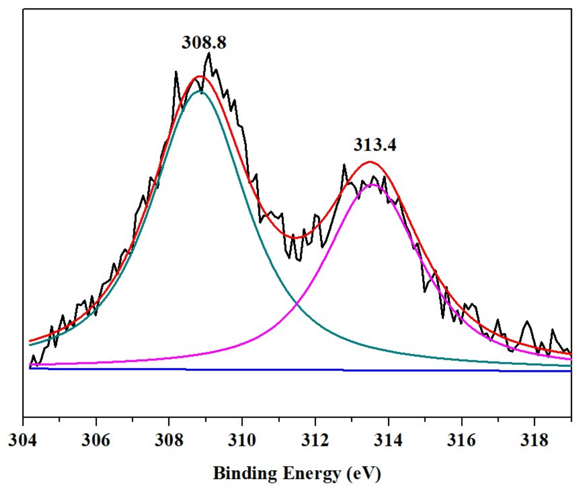


Fig.S7. Rh3$d_{3/2}$ and Rh3$d_{5/2}$ XPS spectra of Rh/CPOL-BINAPa&PPh_3

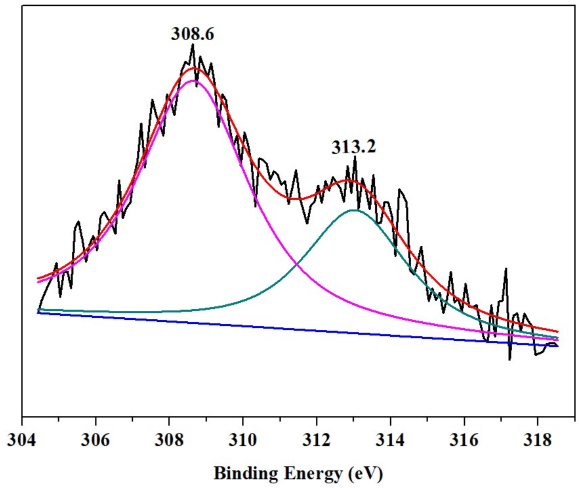


Fig.S8. Rh3d$_{3/2}$ and Rh3d$_{5/2}$ XPS spectra of the recovered Rh/CPOL-BINAPa&PPh$_3$

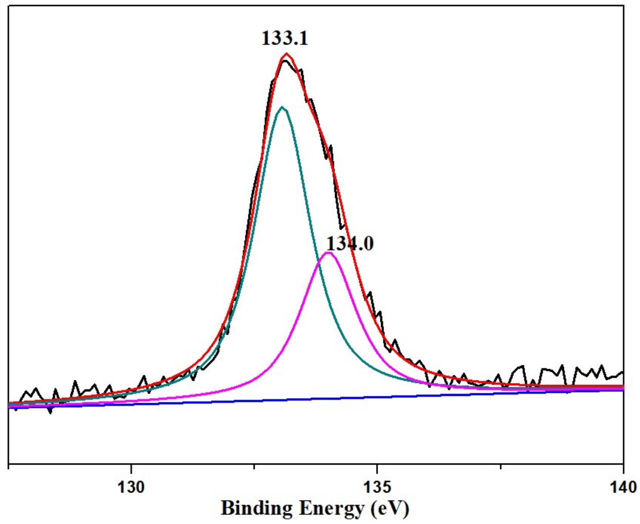


Fig.S9. P2p XPS spectra of CPOL-BINAPa&PhPh$_3$

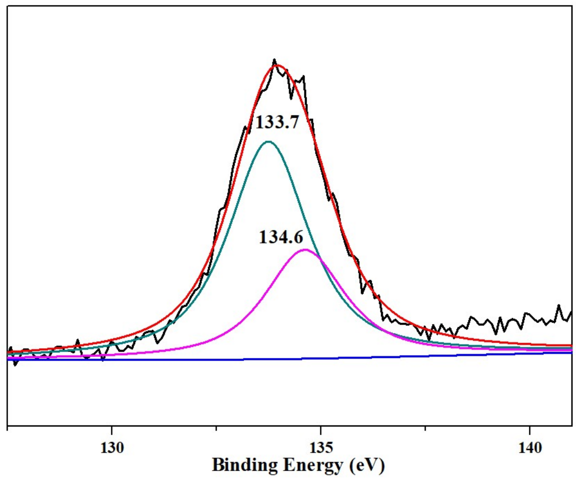


Fig.S10. P2p XPS spectra of Rh/CPOL-BINAPa&PhPh$_3$

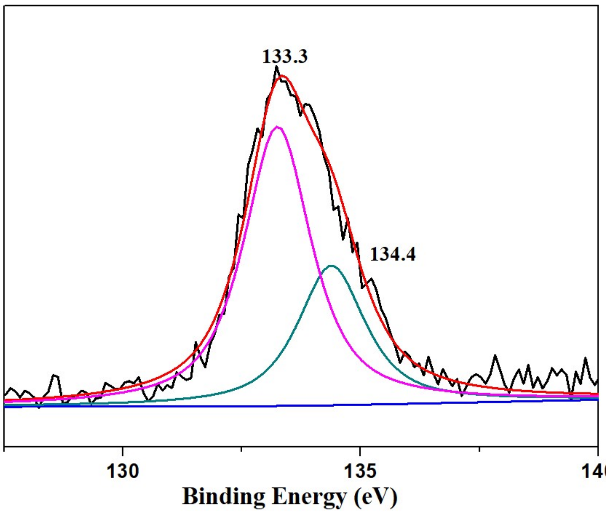


Fig.S11. P2p XPS spectra of the recovered Rh/CPOL-BINAPa&PhPh$_3$

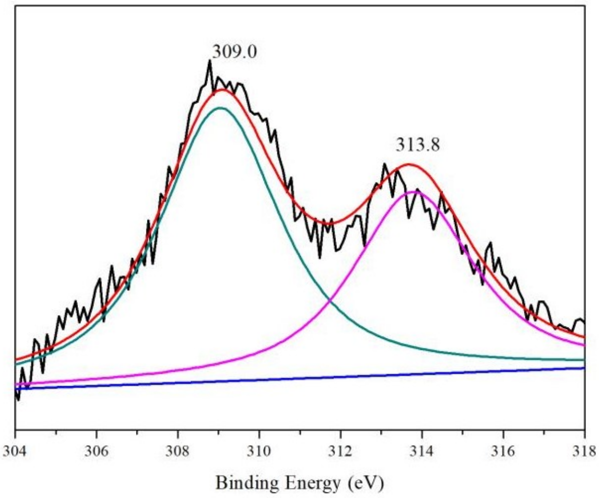


Fig.S12. Rh 3d$_{3/2}$ and Rh 3d$_{5/2}$ XPS spectra of Rh/CPOL-BINAPa&PhPh$_3$

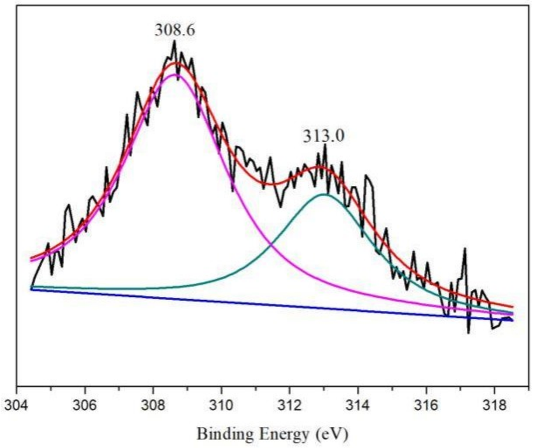


Fig.S13. Rh3d$_{3/2}$ and Rh3d$_{5/2}$ XPS spectra of the recovered Rh/CPOL-BINAPa&PhPh$_3$

5. TGA curves of Rh/CPOL-BINAPa&PPh_3 and Rh/CPOL-BINAPa&$PhPh_3$.

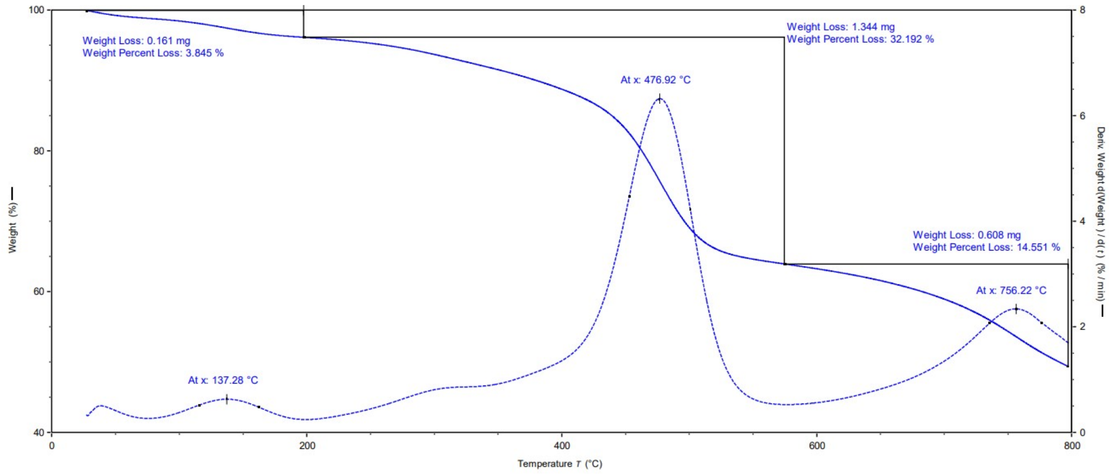


Fig S14. TGA curve of Rh/CPOL-BINAPa&PPh_3

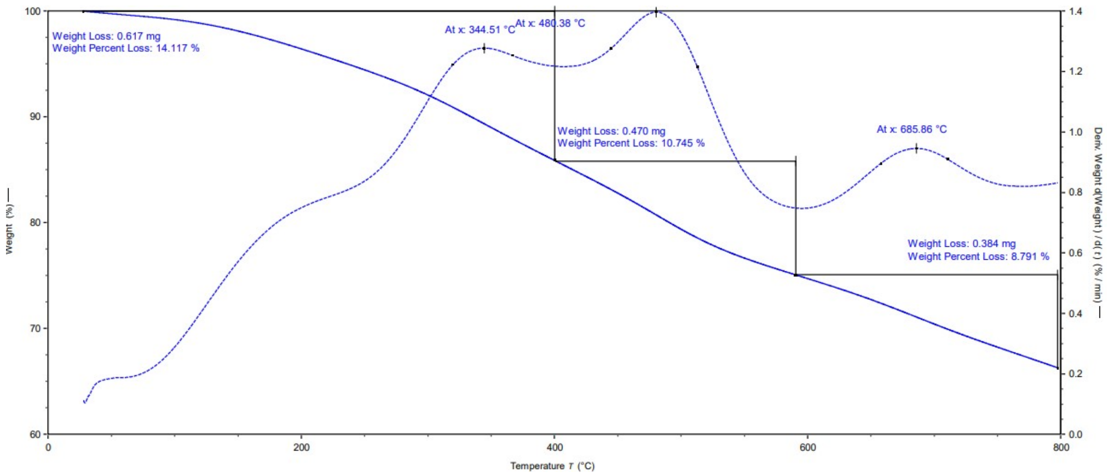


Fig S15. TGA curve of Rh/CPOL-BINAPa&$PhPh_3$

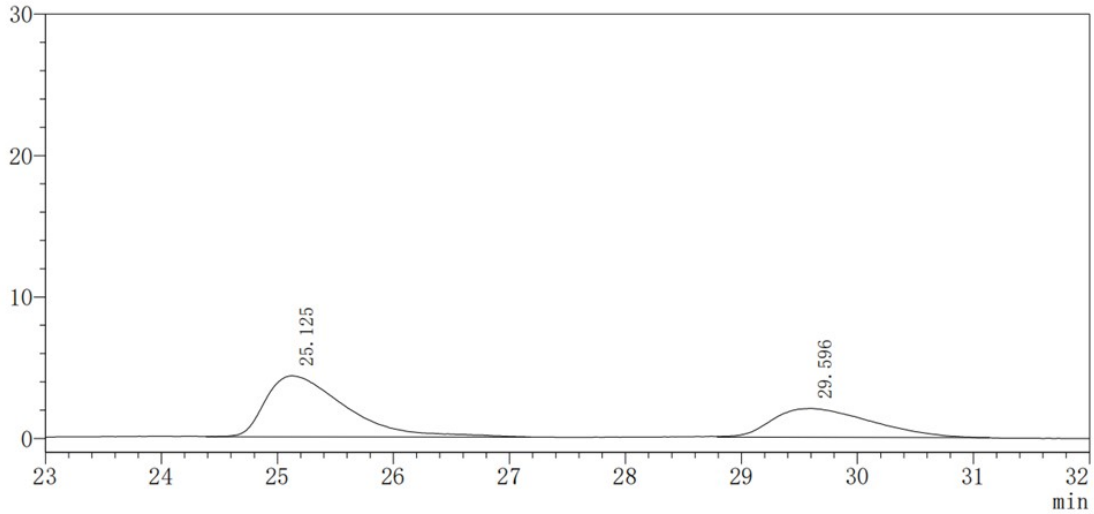
6. General procedure for the hydroformylation of olefins.

In a glove box, an autoclave with a magnetic stirring bar was charged with Rh/POL-BINAPa&PPh_3 (2.1 mg), olefin (3.9 mmol), toluene (1.0 mL) and dodecane (as the internal standard). The mixture was purged with H_2 three times and subsequently charged with CO (10 bar) and H_2 (10 bar). The autoclave was then heated to 100 ^oC (oil bath) for 5 h. The autoclave was cooled in ice water, and the gas was carefully released in a well-ventilated hood. The mixture was subsequently analyzed by gas chromatography (GC).

7. The procedure for the Rh/CPOL-(*S*)-BINAPa&PPh_3-catalyzed hydroformylation of methyl 2-benzylacrylate

In a glove box, a glass vial with a magnetic stirring bar was charged with Rh/CPOL-(*S*)-BINAPa&PPh_3 (14.5 mg), methyl 2-benzylacrylate (0.25 mmol) and toluene (1.0 mL). The vial was then transferred to an autoclave, which was purged with hydrogen for three times and subsequently charged with CO (5 bar) and H_2 (5 bar). The autoclave was then heated to 80 °C (oil bath) and was kept at this temperature for 12 h. The autoclave was cooled in ice water, and the gas was carefully released in a well-ventilated hood. The mixture was purified by chromatography on silicagel to give the chiral aldehyde, which subsequently was analyzed by chiral HPLC on Chiralpak AS-H column for determination of the ee value. Conditions: hexane/isopropanol = 99:1, flow rate = 1.0 mL/min, uv-vis detection at λ = 254 nm, t_R = 25.1 min(*S*), t_R = 29.6 min(*R*).

Methyl 2-benzyl-4-oxobutanoate[3]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.68 (s, 1H), 7.31-7.22 (m, 3H), 7.15-7.12 (m, 2H), 3.66 (s, 3H), 3.20-3.04 (m, 2H), 2.86-2.72 (m, 2H), 2.54-2.48 (m, 1H) ppm.



Index	Time	Area	Area%	Height	Height%
1	25.125	148485	69.799	3493	71.755
2	29.596	64247	30.201	1375	28.245
Totals		212732	100.000	4868	100.000

8. Recycling tests of the Rh/CPOL-BINAPa&PPh_3 and the Rh/CPOL-BINAPa&$PhPh_3$ in hydroformylation of 1-hexene.

In a glove box, an autoclavewith a magnetic stirring bar was charged with Rh/POL-BINAPa&PPh_3 (2.1 mg) or Rh/POL-BINAPa&$PhPh_3$ (2.4 mg), olefin (0.48 mL), toluene (1.0 mL) and dodecaneas the internal standard. The autoclave was purged with hydrogen for three times and subsequently charged with CO (10 bar) and H_2 (10 bar). The autoclave was then heated to 100 °C (oil bath) and was kept at this temperature for 5 h. The autoclave was cooled in ice water, and the gas was carefully released in a well-ventilated hood. The catalyst of reaction mixture was separated in air by using centrifuge and used to test next recycling reaction with the same condition and procedure. The mixture was analyzed by gas chromatography.

Table S1. Rh/CPOL-BINAPa&PPh_3 catalyzed the hydroformylation of 1-hexene

Recycle	Conversion (%)	Aldehydes (%)	Linear (%)[a]	Iso. (%)	[H] (%)
1	99.6	89.7	99.4	9.2	0.7
2	99.6	88.9	99.2	9.8	0.8
3	99.6	89.5	99.1	9.4	0.7
4	98.8	86.2	98.7	11.4	1.0
5	99.4	84.2	99.3	14.3	0.8

[a]Percentage of linear aldehyde in all aldehydes.

Table S2. Rh/CPOL-BINAPa&$PhPh_3$ catalyzed the hydroformylation of 1-hexene

Recycle	Conversion (%)	Aldehydes (%)	Linear (%)[a]	Iso. (%)	[H] (%)
1	99.7	90.5	99	8.5	0.7
2	99.5	84.9	99.2	13.4	1.2
3	99.3	76.7	99.1	21.8	0.7
4	98.8	51.3	98.2	46.7	0.8
5	99.7	45.2	96.3	53.8	0.6

[a]Percentage of linear aldehyde in all aldehydes.

9. GC spectra for olefin hydroformylation mixtures

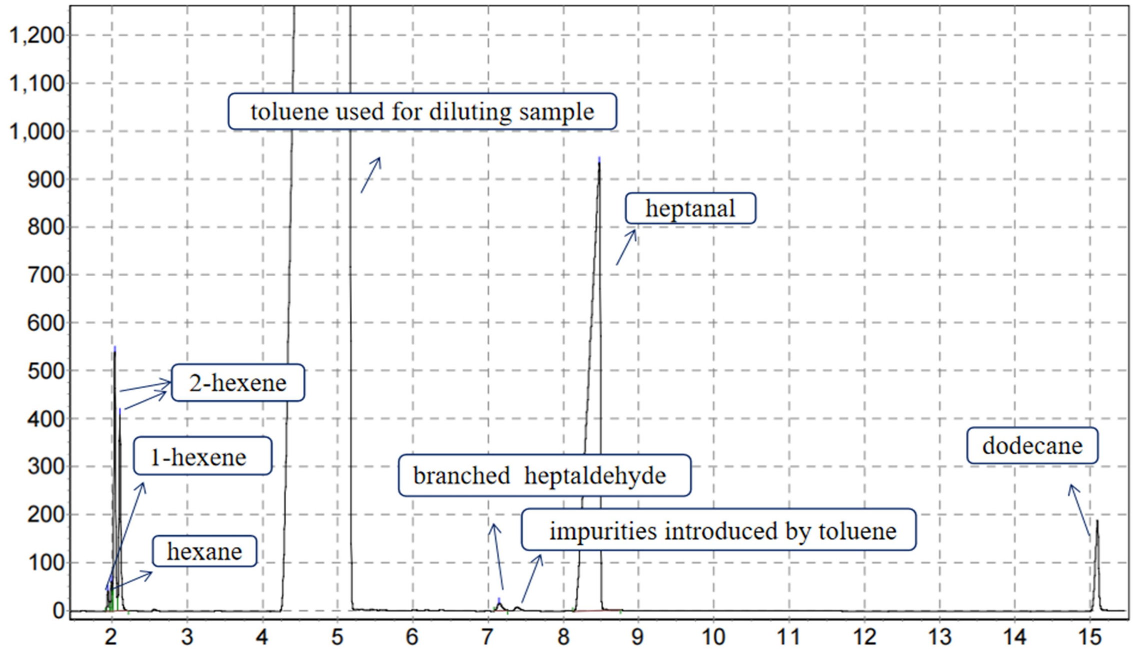


Fig S16. GC spectrum for1-hexenehydroformylation mixture

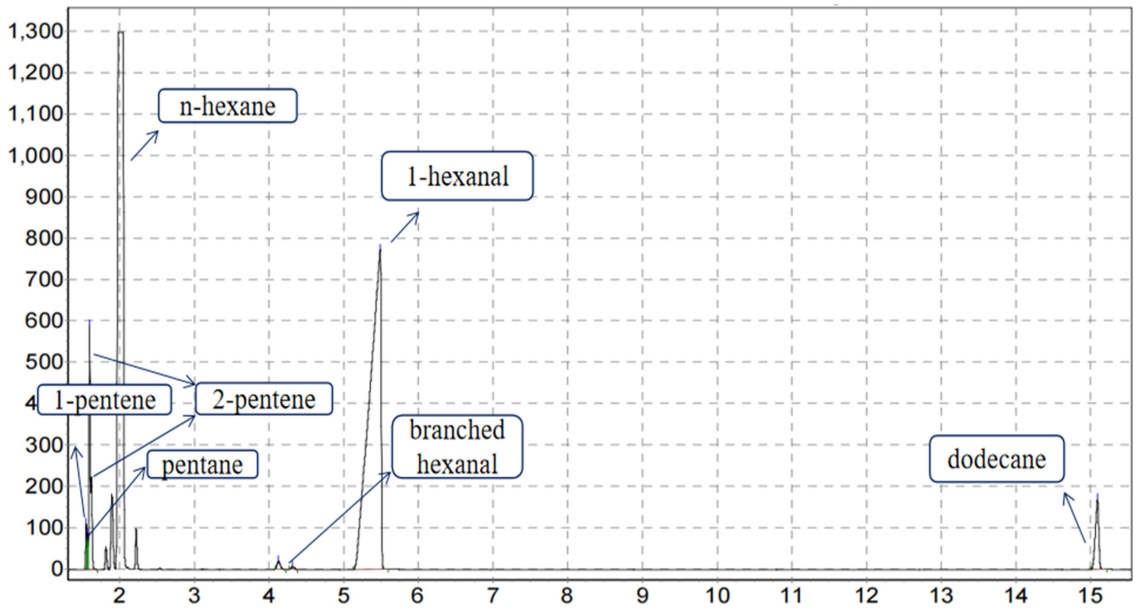


Fig S17. GC spectrum for1-pentenehydroformylation mixture

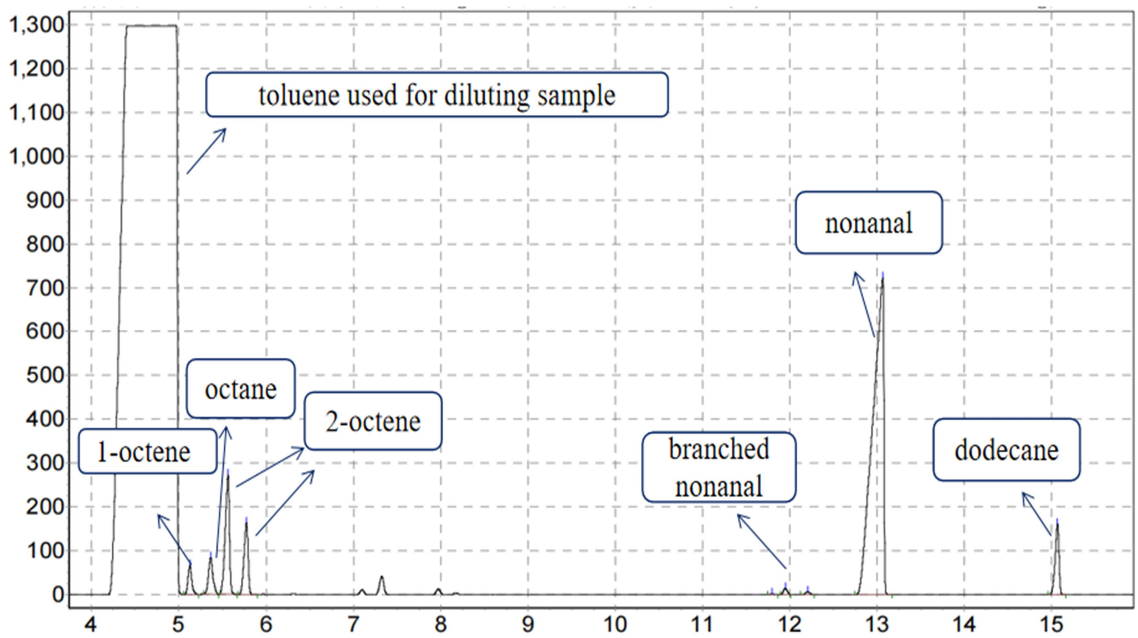


Fig S18. GC spectrum for1-octenehydroformylation mixture

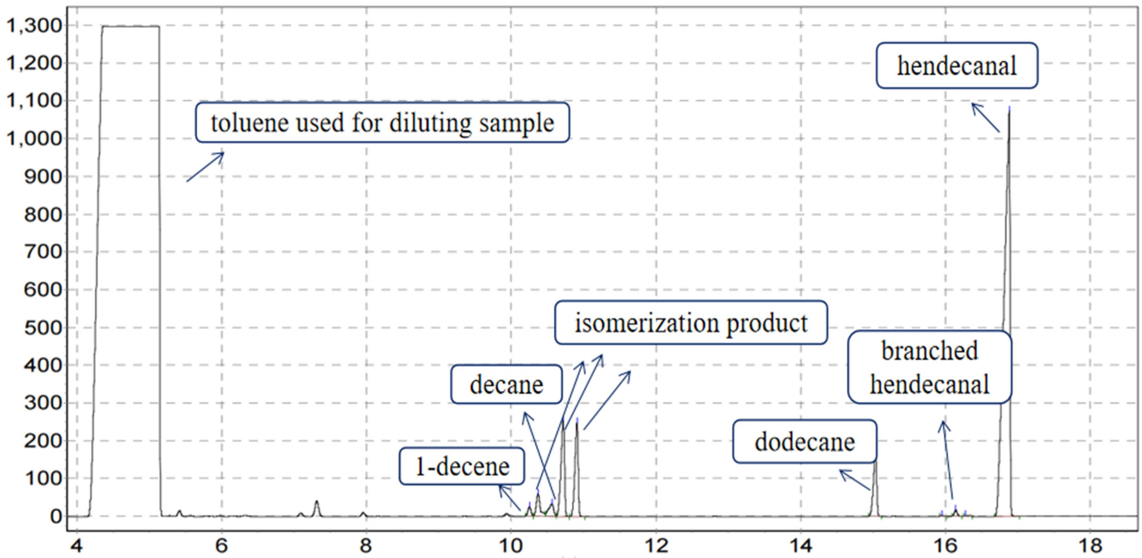


Fig S19. GC spectrum for1-decenehydroformylationmixture

10. Standard orientation, imaginary frequencies of all stationary points

Structure A

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-0.008160	-1.303659	-0.291007

2	1	0	-0.047301	-0.661009	-1.749306
3	6	0	0.021747	-2.092014	1.490320
4	8	0	0.032445	-2.573735	2.529845
5	15	0	-2.066785	-0.083468	-0.033571
6	6	0	-2.501775	0.517380	1.668583
7	6	0	-3.783669	0.400453	2.220031
8	6	0	-1.490196	1.108730	2.436913
9	6	0	-4.046423	0.871172	3.505530
10	1	0	-4.579730	-0.064231	1.652647
11	6	0	-1.758268	1.591003	3.715195
12	1	0	-0.485793	1.185872	2.038553
13	6	0	-3.037740	1.471849	4.254242
14	1	0	-5.042805	0.765233	3.920417
15	1	0	-0.961125	2.047681	4.290673
16	1	0	-3.244767	1.836726	5.254168
17	6	0	-3.574380	-1.069929	-0.497537
18	6	0	-3.573187	-2.449488	-0.263145
19	6	0	-4.722942	-0.481719	-1.043445
20	6	0	-4.694283	-3.222219	-0.555242
21	1	0	-2.682731	-2.919907	0.135656
22	6	0	-5.840399	-1.257553	-1.346434
23	1	0	-4.747022	0.583141	-1.239874
24	6	0	-5.830350	-2.628648	-1.100888
25	1	0	-4.673447	-4.289951	-0.367769
26	1	0	-6.718332	-0.787740	-1.776197
27	1	0	-6.699508	-3.231436	-1.339546
28	6	0	-2.299041	1.435678	-1.075438
29	6	0	-2.158804	1.313048	-2.465882
30	6	0	-2.593599	2.693432	-0.539110
31	6	0	-2.324418	2.416388	-3.296379
32	1	0	-1.916592	0.349528	-2.899437
33	6	0	-2.743594	3.802626	-1.373025
34	1	0	-2.711036	2.814146	0.530285
35	6	0	-2.614440	3.668098	-2.751798
36	1	0	-2.221104	2.299451	-4.369506
37	1	0	-2.968753	4.770544	-0.938848
38	1	0	-2.738131	4.529294	-3.398890
39	15	0	2.072908	-0.079126	-0.091980
40	6	0	2.513411	1.031424	-1.511159
41	6	0	3.801288	1.090254	-2.056243
42	6	0	1.514572	1.849867	-2.053677
43	6	0	4.082003	1.950401	-3.117029
44	1	0	4.588799	0.460730	-1.662723
45	6	0	1.800502	2.718860	-3.102957

46	1	0	0.506732	1.801338	-1.661669
47	6	0	3.085550	2.769749	-3.640159
48	1	0	5.082927	1.976102	-3.533647
49	1	0	1.012706	3.345439	-3.505580
50	1	0	3.306171	3.437946	-4.465222
51	6	0	3.573376	-1.172360	0.035436
52	6	0	3.575350	-2.388677	-0.657092
53	6	0	4.713107	-0.813707	0.767417
54	6	0	4.690162	-3.222612	-0.626884
55	1	0	2.694520	-2.684090	-1.213377
56	6	0	5.823525	-1.655140	0.807439
57	1	0	4.736205	0.121618	1.312636
58	6	0	5.816034	-2.860419	0.109411
59	1	0	4.672622	-4.160562	-1.170629
60	1	0	6.694214	-1.365945	1.385765
61	1	0	6.679868	-3.514993	0.142782
62	6	0	2.316248	1.037272	1.376258
63	6	0	2.214939	0.482569	2.661368
64	6	0	2.552134	2.411497	1.259185
65	6	0	2.361497	1.276712	3.794074
66	1	0	2.026489	-0.577704	2.782025
67	6	0	2.685078	3.209251	2.396480
68	1	0	2.638300	2.865818	0.280420
69	6	0	2.594562	2.646446	3.665693
70	1	0	2.289306	0.825100	4.777294
71	1	0	2.867692	4.272356	2.284110
72	1	0	2.705230	3.266511	4.548226
73	6	0	-0.043351	-2.915602	-1.322355
74	8	0	-0.084149	-3.851001	-1.988726

0 imaginary frequencies

Structure B

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.430821	0.054975	-2.756348
2	6	0	-0.548774	0.376875	-3.754732
3	6	0	0.612438	1.140719	-3.486081
4	6	0	0.869352	1.559978	-2.140441
5	6	0	-0.027402	1.175365	-1.097900
6	6	0	-1.165309	0.455528	-1.425745
7	1	0	1.307588	1.188882	-5.529726
8	1	0	-2.337593	-0.489535	-2.985666
9	1	0	-0.749750	0.063249	-4.773176

10	6	0	1.510865	1.520157	-4.516772
11	6	0	2.009144	2.373677	-1.897509
12	6	0	2.851715	2.733720	-2.922542
13	6	0	2.608517	2.298765	-4.245277
14	1	0	2.206549	2.715582	-0.889557
15	1	0	3.710963	3.361650	-2.714815
16	1	0	3.285034	2.587993	-5.041205
17	6	0	0.926478	0.804617	1.198187
18	6	0	0.188753	1.578130	0.325843
19	6	0	-0.450062	2.755853	0.838339
20	6	0	-0.327288	3.089206	2.223549
21	6	0	0.409173	2.226790	3.072329
22	6	0	1.017619	1.107102	2.575389
23	1	0	-1.312158	3.381955	-1.045430
24	6	0	-1.212130	3.618792	0.006055
25	6	0	-0.961194	4.257815	2.717807
26	1	0	0.476559	2.455867	4.129915
27	1	0	1.539725	0.429249	3.237991
28	6	0	-1.688681	5.071518	1.884768
29	6	0	-1.812194	4.746057	0.515735
30	1	0	-0.861084	4.496622	3.771324
31	1	0	-2.168617	5.962624	2.272749
32	1	0	-2.384584	5.393134	-0.139365
33	8	0	-2.054799	0.203731	-0.404330
34	8	0	1.556683	-0.356888	0.702533
35	15	0	-3.136132	-1.074886	-0.346614
36	15	0	3.081088	-0.918714	1.347673
37	6	0	-4.949184	0.920319	-1.293041
38	6	0	-5.957011	0.975130	-2.218222
39	6	0	-6.085888	-0.324201	-2.798184
40	6	0	-5.150061	-1.128901	-2.207694
41	7	0	-4.440713	-0.372183	-1.275552
42	1	0	-4.543680	1.681162	-0.648473
43	1	0	-6.542967	1.849504	-2.457652
44	1	0	-6.788713	-0.626677	-3.558982
45	1	0	-4.919899	-2.172230	-2.354085
46	6	0	-4.122853	-1.768857	2.093155
47	6	0	-4.506050	-1.215513	3.283155
48	6	0	-4.211697	0.181081	3.219358
49	6	0	-3.664008	0.438580	1.992044
50	7	0	-3.601386	-0.758753	1.286113
51	1	0	-4.158288	-2.788281	1.744136
52	1	0	-4.934618	-1.750327	4.116331
53	1	0	-4.370924	0.910677	3.998654

54	1	0	-3.271152	1.345699	1.567556
55	6	0	3.390404	-1.392793	-1.436575
56	6	0	3.989395	-2.361583	-2.192634
57	6	0	4.523087	-3.346037	-1.304458
58	6	0	4.228174	-2.952499	-0.030428
59	7	0	3.531837	-1.742756	-0.093746
60	1	0	2.840598	-0.513046	-1.722685
61	1	0	4.027181	-2.376917	-3.270926
62	1	0	5.050302	-4.246498	-1.578071
63	1	0	4.435010	-3.415485	0.920744
64	6	0	5.343336	2.270689	0.747508
65	6	0	5.302664	2.159124	2.172770
66	6	0	4.520202	1.083468	2.474522
67	1	0	5.889078	3.004411	0.174008
68	1	0	5.803391	2.794563	2.886474
69	1	0	4.250613	0.651910	3.424620
70	7	0	4.058754	0.515386	1.280054
71	6	0	4.582864	1.262287	0.225472
72	1	0	4.390073	0.988640	-0.795844
73	45	0	0.278386	-2.258467	0.872467
74	1	0	0.198732	-1.970879	2.459111
75	6	0	-0.599407	-3.742274	1.459170
76	8	0	-1.147996	-4.669099	1.853353
77	6	0	0.337463	-2.778718	-1.029810
78	8	0	0.306327	-3.205244	-2.086243

0 imaginary frequencies

Structure C

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.987200	-1.741536	-1.882017
2	6	0	-5.105362	-1.181717	-0.991508
3	6	0	-4.172589	-0.198280	-1.412095
4	6	0	-4.172476	0.189781	-2.781361
5	6	0	-5.089338	-0.412084	-3.678994
6	6	0	-5.981724	-1.357383	-3.241216
7	1	0	-6.687097	-2.497781	-1.540442
8	1	0	-5.102073	-1.504013	0.043886
9	6	0	-3.243389	0.410838	-0.500554
10	6	0	-3.256666	1.182683	-3.222878
11	1	0	-5.071210	-0.105310	-4.721440
12	1	0	-6.683009	-1.811145	-3.934394
13	6	0	-2.375991	1.757869	-2.351929
14	6	0	-2.367446	1.351895	-0.992449

15	1	0	-3.272687	1.486841	-4.265719
16	1	0	-1.682563	2.530941	-2.672295
17	6	0	-3.308929	0.108563	0.957966
18	6	0	-4.476294	0.522449	1.695634
19	6	0	-2.294078	-0.513900	1.657729
20	6	0	-5.534951	1.248638	1.082107
21	6	0	-4.585849	0.241045	3.086268
22	6	0	-2.391071	-0.763902	3.052385
23	6	0	-6.637577	1.636711	1.801104
24	1	0	-5.463147	1.506061	0.031907
25	6	0	-5.742352	0.645308	3.800998
26	6	0	-3.511938	-0.411819	3.744323
27	1	0	-1.531590	-1.204437	3.546407
28	6	0	-6.753904	1.324888	3.174773
29	1	0	-7.428174	2.193323	1.308001
30	1	0	-5.802883	0.410175	4.860303
31	1	0	-3.584377	-0.605744	4.810720
32	1	0	-7.634702	1.633284	3.728480
33	8	0	-1.501187	1.976186	-0.122877
34	8	0	-1.057847	-0.817439	1.149249
35	15	0	-0.370137	-1.471465	-0.194230
36	15	0	0.144868	1.935563	-0.335633
37	7	0	-1.674031	-2.294266	-0.956026
38	6	0	-1.919523	-2.279542	-2.322982
39	6	0	-2.480408	-3.265260	-0.377011
40	6	0	-2.874465	-3.216542	-2.597788
41	1	0	-1.384274	-1.589927	-2.959376
42	6	0	-3.227608	-3.843894	-1.362911
43	1	0	-2.417336	-3.467502	0.683008
44	1	0	-3.292592	-3.421724	-3.572739
45	1	0	-3.960162	-4.625952	-1.220383
46	7	0	0.355836	-2.824646	0.621386
47	6	0	0.105865	-3.326544	1.882709
48	6	0	1.169718	-3.716204	-0.051015
49	6	0	0.763451	-4.521710	2.009781
50	1	0	-0.495674	-2.769588	2.582112
51	6	0	1.438695	-4.771502	0.780257
52	1	0	1.457294	-3.525153	-1.074455
53	1	0	0.781751	-5.136496	2.898718
54	1	0	2.057140	-5.623717	0.537289
55	7	0	0.437411	3.412718	-1.178620
56	6	0	0.003909	4.677081	-0.805222
57	6	0	0.983939	3.495643	-2.452929

58	6	0	0.284545	5.544725	-1.822014
59	1	0	-0.459174	4.826984	0.158945
60	6	0	0.906878	4.794526	-2.869560
61	1	0	1.362264	2.606351	-2.934902
62	1	0	0.075987	6.605201	-1.820914
63	1	0	1.260677	5.174175	-3.817456
64	7	0	0.410800	2.565087	1.264092
65	6	0	1.577519	3.189461	1.673924
66	6	0	-0.360810	2.291282	2.383709
67	6	0	1.537812	3.322655	3.036112
68	1	0	2.319041	3.501512	0.951297
69	6	0	0.307918	2.756434	3.485587
70	1	0	-1.326019	1.820826	2.280254
71	1	0	2.301775	3.789741	3.641159
72	1	0	-0.057836	2.717173	4.502066
73	45	0	0.942643	0.004317	-1.301904
74	1	0	-0.296159	0.214857	-2.235627
75	15	0	2.938527	-0.345243	-0.006975
76	6	0	3.864459	1.222779	0.267306
77	6	0	3.916678	2.139329	-0.789649
78	6	0	4.482765	1.544734	1.478380
79	6	0	4.563204	3.361994	-0.636305
80	1	0	3.425803	1.902981	-1.729435
81	6	0	5.129372	2.769935	1.631767
82	1	0	4.436154	0.852525	2.314093
83	6	0	5.166022	3.681728	0.579799
84	1	0	4.576288	4.069292	-1.459609
85	1	0	5.594563	3.015286	2.581537
86	1	0	5.657825	4.640932	0.707707
87	6	0	2.745890	-1.003371	1.693698
88	6	0	3.351819	-2.177693	2.142374
89	6	0	1.927606	-0.274958	2.566318
90	6	0	3.153855	-2.604958	3.455262
91	1	0	3.964312	-2.770755	1.470772
92	6	0	1.742325	-0.698366	3.877154
93	1	0	1.446854	0.638192	2.231087
94	6	0	2.359683	-1.865611	4.325742
95	1	0	3.619472	-3.526425	3.791120
96	1	0	1.117603	-0.105446	4.539093
97	1	0	2.215555	-2.201410	5.348238
98	6	0	4.234461	-1.417785	-0.746441
99	6	0	5.542934	-1.398809	-0.246498
100	6	0	3.924351	-2.273943	-1.804680

101	6	0	6.516613	-2.228186	-0.790954
102	1	0	5.799366	-0.729110	0.570377
103	6	0	4.901267	-3.104277	-2.351995
104	1	0	2.916889	-2.280875	-2.209354
105	6	0	6.196140	-3.083572	-1.844904
106	1	0	7.527593	-2.203992	-0.396551
107	1	0	4.647813	-3.760699	-3.178356
108	1	0	6.958463	-3.727345	-2.272461
109	6	0	1.816120	-0.052340	-2.989722
110	8	0	2.271668	-0.055645	-4.045594

0 imaginary frequencies

Structure D

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.856304	4.061854	2.388204
2	6	0	-3.794844	2.943886	1.596025
3	6	0	-3.218237	1.738997	2.080744
4	6	0	-2.728045	1.709963	3.418251
5	6	0	-2.809714	2.883395	4.213271
6	6	0	-3.353159	4.037090	3.710793
7	1	0	-4.290945	4.975999	1.996846
8	1	0	-4.176348	2.972500	0.580874
9	6	0	-3.076685	0.577667	1.256351
10	6	0	-2.147078	0.517394	3.924817
11	1	0	-2.424705	2.847762	5.228941
12	1	0	-3.402853	4.931286	4.323692
13	6	0	-2.037985	-0.597588	3.139598
14	6	0	-2.498236	-0.546185	1.801862
15	1	0	-1.783585	0.504046	4.948408
16	1	0	-1.598979	-1.520590	3.509839
17	6	0	-3.479507	0.575166	-0.176019
18	6	0	-4.523937	-0.269162	-0.670332
19	6	0	-2.803942	1.374580	-1.070943
20	6	0	-5.260489	-1.136629	0.180503
21	6	0	-4.817667	-0.274378	-2.064700
22	6	0	-3.106614	1.398403	-2.453270
23	6	0	-6.218989	-1.974137	-0.330058
24	1	0	-5.046713	-1.135242	1.244052
25	6	0	-5.819108	-1.150285	-2.560675
26	6	0	-4.093134	0.581744	-2.935226
27	1	0	-2.545893	2.066852	-3.101393
28	6	0	-6.501489	-1.987104	-1.716800
29	1	0	-6.764968	-2.636048	0.334422

30	1	0	-6.027903	-1.146422	-3.627157
31	1	0	-4.332221	0.576935	-3.994898
32	1	0	-7.259326	-2.658891	-2.106670
33	8	0	-2.353086	-1.671770	1.016672
34	8	0	-1.793150	2.194631	-0.610876
35	15	0	-0.224580	1.719351	-0.897341
36	15	0	-0.841274	-2.003516	0.414384
37	7	0	0.426467	2.996604	0.079613
38	6	0	-0.050610	3.341652	1.333129
39	6	0	1.657553	3.604308	-0.109292
40	6	0	0.857756	4.185550	1.917866
41	1	0	-1.005753	2.972494	1.676039
42	6	0	1.940283	4.351735	1.003615
43	1	0	2.205356	3.466050	-1.031427
44	1	0	0.744138	4.649937	2.887354
45	1	0	2.823976	4.958684	1.140439
46	7	0	0.045224	2.470277	-2.436924
47	6	0	-0.169468	3.807443	-2.739302
48	6	0	0.216230	1.779782	-3.627462
49	6	0	-0.107148	3.959271	-4.096340
50	1	0	-0.341147	4.520267	-1.946563
51	6	0	0.136841	2.668927	-4.662523
52	1	0	0.355672	0.710370	-3.628217
53	1	0	-0.215497	4.891987	-4.631509
54	1	0	0.241445	2.427406	-5.710632
55	7	0	-0.217889	-2.943078	1.723261
56	6	0	-0.877927	-3.988204	2.355816
57	6	0	0.860995	-2.565338	2.510900
58	6	0	-0.208667	-4.280020	3.511707
59	1	0	-1.762259	-4.418779	1.909428
60	6	0	0.895563	-3.375304	3.610601
61	1	0	1.485356	-1.734559	2.218356
62	1	0	-0.470240	-5.062482	4.210176
63	1	0	1.632631	-3.329700	4.399476
64	7	0	-1.391018	-3.310057	-0.571638
65	6	0	-0.626743	-4.418143	-0.904273
66	6	0	-2.394892	-3.168503	-1.515937
67	6	0	-1.168921	-4.992783	-2.022095
68	1	0	0.206590	-4.713129	-0.282643
69	6	0	-2.289907	-4.199477	-2.410209
70	1	0	-3.101657	-2.353708	-1.441627
71	1	0	-0.816264	-5.895659	-2.499696
72	1	0	-2.956695	-4.379805	-3.241088
73	45	0	0.426506	-0.412240	-0.465609

74	1	0	0.290988	0.172339	1.002675
75	15	0	2.766670	-0.300223	-0.064098
76	6	0	3.742109	-1.788042	-0.519850
77	6	0	3.120211	-3.038573	-0.453806
78	6	0	5.087950	-1.713085	-0.895928
79	6	0	3.831487	-4.197771	-0.752296
80	1	0	2.072596	-3.096120	-0.169029
81	6	0	5.795970	-2.872247	-1.200668
82	1	0	5.580363	-0.746064	-0.953472
83	6	0	5.169311	-4.115167	-1.128584
84	1	0	3.336428	-5.162459	-0.699241
85	1	0	6.837887	-2.804393	-1.497746
86	1	0	5.722923	-5.016997	-1.370687
87	6	0	3.646042	1.044038	-0.962489
88	6	0	4.575177	1.895308	-0.358531
89	6	0	3.293191	1.262527	-2.298825
90	6	0	5.120288	2.959521	-1.075781
91	1	0	4.854608	1.746578	0.680265
92	6	0	3.831898	2.326572	-3.014190
93	1	0	2.565902	0.610840	-2.774718
94	6	0	4.743861	3.183419	-2.397898
95	1	0	5.830995	3.623131	-0.592788
96	1	0	3.517770	2.497309	-4.039294
97	1	0	5.154801	4.025626	-2.945694
98	6	0	3.255937	0.012206	1.676465
99	6	0	4.178204	-0.774110	2.370400
100	6	0	2.635591	1.085127	2.329892
101	6	0	4.468619	-0.494172	3.706275
102	1	0	4.662903	-1.611562	1.877135
103	6	0	2.943035	1.372621	3.653965
104	1	0	1.908919	1.699628	1.804313
105	6	0	3.855788	0.577880	4.347804
106	1	0	5.177466	-1.117647	4.242373
107	1	0	2.457712	2.213350	4.140255
108	1	0	4.085546	0.792507	5.386935
109	6	0	0.538076	-1.314170	-2.197653
110	8	0	0.605659	-1.900100	-3.175726

0 imaginary frequencies

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