Supporting Information

The unique phosphine ligand synergy in asymmetric hydroformylation of styrene over Rh@MOF-5 heterogeneous catalysis system

Mengchuan Ma[a] · Chao Zhang[*a] · Weiping Li[a] · Yong Tao[a] · Li Zhou[b] · Lu Li[c,d] · Zhenmei Guo[a] · Zhiguo Lv[*a]

a. State Key Laboratory Base for Eco-chemical Engineering, College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

b. Engineering Research Center of Alternative Energy Materials & Devices, Ministry of Education, Sichuan University, Chengdu 610065, China

c. Key Laboratory of Auxiliary Chemistry and Technology for Chemical Industry, Ministry of Education, Shaanxi University of Science and Technology， Xi'an, 710021, China.

d. Shaanxi Collaborative Innovation Center of Industrial Auxiliary Chemistry and Technology, Shaanxi University of Science and Technology, Xi'an 710021, China.

E-mail: chaozhangchem@qust.edu.cn lvzhiguo@qust.edu.cn

1. Comparison of Performance of Heterogeneous Catalysts of Rh with Previous Reports for Asymmetric Hydroformylation (AHF) of Styrene

Table S1 Comparison of Performance of Heterogeneous Catalysts of Rh with Previous Reports for AHF of Styrene

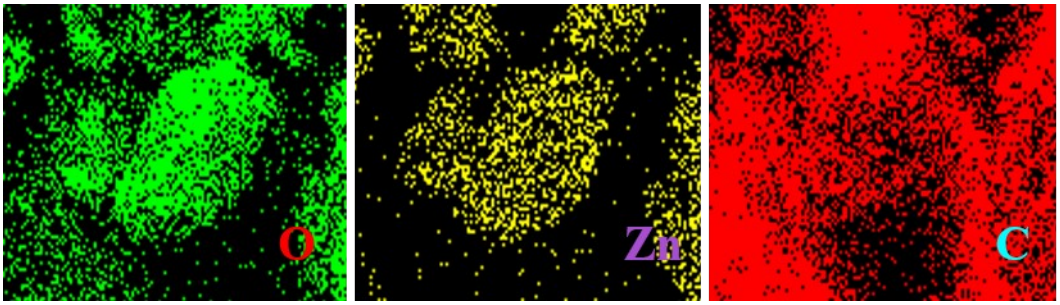
Catalysts	Ligands	Y_{iso} (%)	Iso/n	*Ee* (%)	Ref
Rh@MOF-5	**BINAP**	**87**	**9.3**	**25**	**--**
Rh/DNA	BINAP	86	16.2	29	[1]
Rh/Poly-1	Polymers of BINAP	84	8.5	59	[2]
$[Me(EO)_{16}TMG][Rh(CO)_4]$	BINAP	73	14.2	54	[3]
BINAP-Rh/SiO_2	BINAP	7	＞99.9	59	[4]
Rh-BINAP/SiO_2	BINAP	2	＞99.9	56	[4]
Rh-L/SiO_2 (**L**= BINAP, DIOP, or MEO-BIPHEP)	BINAP	6	11.5	30	[5]
	DIOP	38	1.5	12	[5]
	MEO-BIPHEP	5	11.5	25	[5]

Compared with the catalytic performance of other classical heterogeneous catalysts, the synergistic system of Rh@MOF-5 and (R)-BINAP showed unique advantages in catalytic performance. The synthesized MOF-5 heterogeneous catalytic material by direct mixing of triethylamine not only had the advantages of cheaper synthesis cost and simpler synthesis method than other polymeric materials (DNA, Poly-BINAP, and ployether ionic liquids), but also had a higher yield of iso-aldehyde in the AHF reaction.

2. Characterization Details

The morphological images of the samples were obtained, and the scanning electron microscope (SEM) and transmission electron microscope (TEM) were utilized. Elemental composition and distribution of supplementary analysis were further characterized with Energy Dispersive Spectrometer (EDS). Fourier transform infrared (FT-IR) spectroscopy was utilized to research the chemical structure of the sample. Powder X-ray diffraction (PXRD) patterns were recorded on an X-ray diffractometer with Cu Kα radiation (40 kV and 40 mA) in the 2θ range of 5−50° and a scanning speed of 5°/min. Thermogravimetric analysis (TGA) was employed to analyze the structural stability of the materials, with a sample heated from room temperature (28 ℃) up to 700 ℃ at the rate of 10℃/min, under the air atmosphere. The loading capacity of the active Rh in catalyst was measured with inductively coupled plasma spectrometry optical emission spectrometry (ICP-OES). X-ray photoelectron spectroscopy (XPS) measurements were conducted on the spectrometer, which was equipped with nonmonochromatic Al Kα (hv=1486.6 eV) radiation. The binding energies of Rh 3d, Zn 2p, and O 1s photoelectron peaks were calibrated using the binding energy C 1s (284.5 eV) neutral peak as a reference. N_2 adsorption-desorption of the catalyst was employed to estimate the specific surface area, pore size distribution, and pore volume of the catalyst. Before the testing, the sample of catalyst was subjected to outgassing under the vacuum at 100 ℃ for 12 h to remove H_2O and other impurities. The linear part of the Brunauer-Emmett-Teller (BET) equation was applied to estimate the specific surface area. The pore size distribution

was desorption from the desorption branch of N_2 isotherm, using Barrett–Joyner–Halenda (BJH) method.

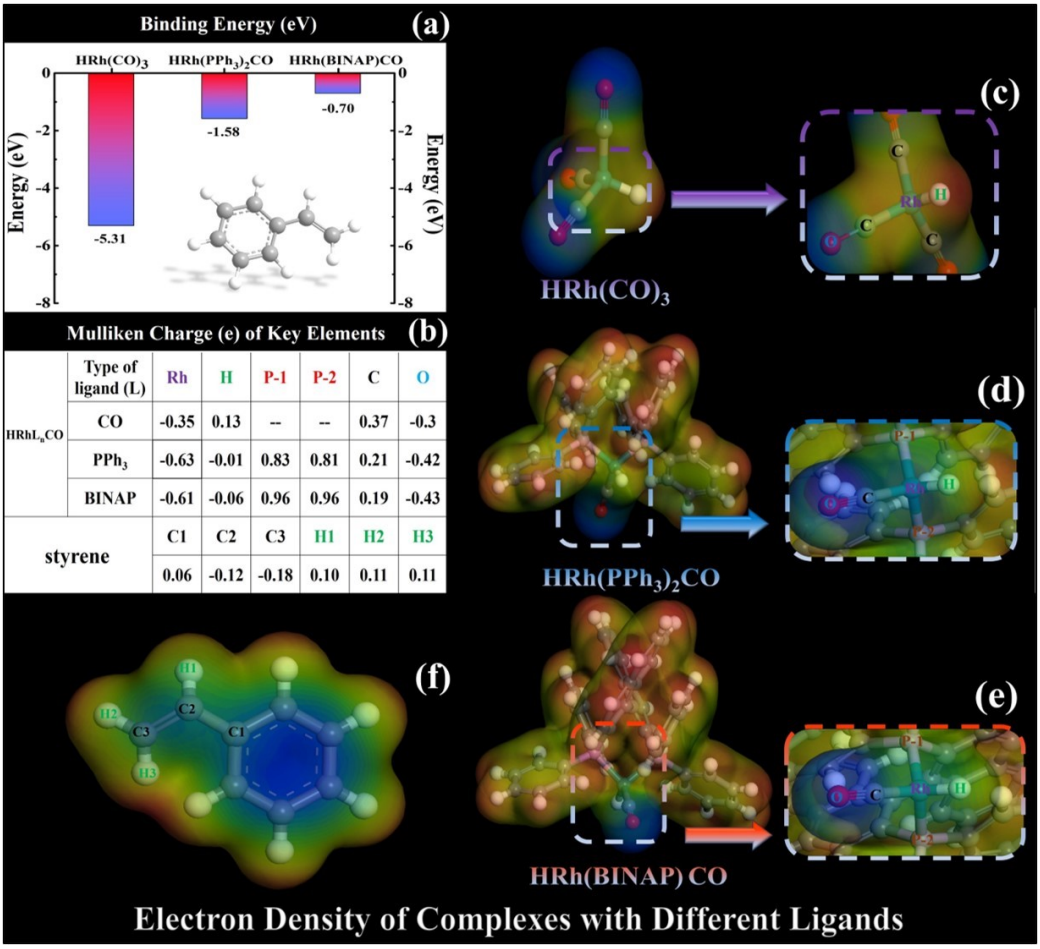


Element distribution in Rh@MOF-5: O, Zn and C.

3. DFT Calculations Detail

The overall research carbonyl rhodium complex with styrene was the binding energy, which was calculated as follows:

$$\triangle E(eV) = 27.212 \times [E_{AB}(Ha) - E_A(Ha) - E_B(Ha)]$$



	Type of ligand (L)	Rh	H	P-1	P-2	C	O
$HRhL_nCO$	CO	-0.35	0.13	--	--	0.37	-0.3
	PPh_3	-0.63	-0.01	0.83	0.81	0.21	-0.42
	BINAP	-0.61	-0.06	0.96	0.96	0.19	-0.43
styrene		C1	C2	C3	H1	H2	H3
		0.06	-0.12	-0.18	0.10	0.11	0.11

Fig. S1 The **a** binding energy of styrene with different carbonyl rhodium complexes ($HRh(CO)_3$, $HRh(PPh_3)_2CO$, and HRh(BINAP)CO). **b** Mulliken charge and **c-e** electron density of three types of carbonyl rhodium complex and styrene, from blue to red indicated an increase in the electron density.

When $HRhL_n(CO)_2$ (L=CO, PPh_3, or BINAP; n=1, 2) complex was involved in catalysis, one molecule of CO was removed, resulting in the formation of the $HRhL_nCO$ complex with an empty coordination site. Fig. S1a revealed that a disparity in the binding energies of various $HRhL_nCO$ complexes and styrene molecules; It was worth noting, the binding energy of $HRh(CO)_3$ (-5.31 eV) was substantially lower than that of $HRh(PPh_3)_2CO$ (-1.58 eV) and HRh(BINAP)CO (-0.70 eV), which

suggested that there was the small kinetic barrier for the hydroformylation of styrene. To quantify this difference, the Mulliken charge and electron density of associated atoms in the $HRhL_nCO$ complex with styrene was calculated and shown in Fig. S1b-f. Compared with 0.35 |e| obtained by $HRh(CO)_3$, 0.63 |e| and 0.61 |e| were obtained by $HRh(PPh_3)_2CO$ and HRh(BINAP)CO modified by phosphine ligand, respectively. The electron density distribution diagram (Fig. S1c-e) also showed that the electronic density of active Rh in these $HRhL_nCO$ was significantly higher than that of $HRh(CO)_3$, which may be caused by the presence of π-backbonding and stronger electron-donating ability of phosphine ligand [6]. The electronic density of active rhodium increased, which increased the binding energy of π bond to alkenes. This was not conducive to the adsorption and binding of styrene, which explained the longer time required for HRh(BINAP)CO to reach equilibrium. Furthermore, the lower charge of the C2 atom (0.12 |e|) than that of the C3 atom (0.18 |e|) observed in styrene was likely attributed to the effect of π-π conjugation [7]. This difference could potentially have an influence on the regioselectivity of the rhodium precursor complexes formed during active Rh inserted to styrene.

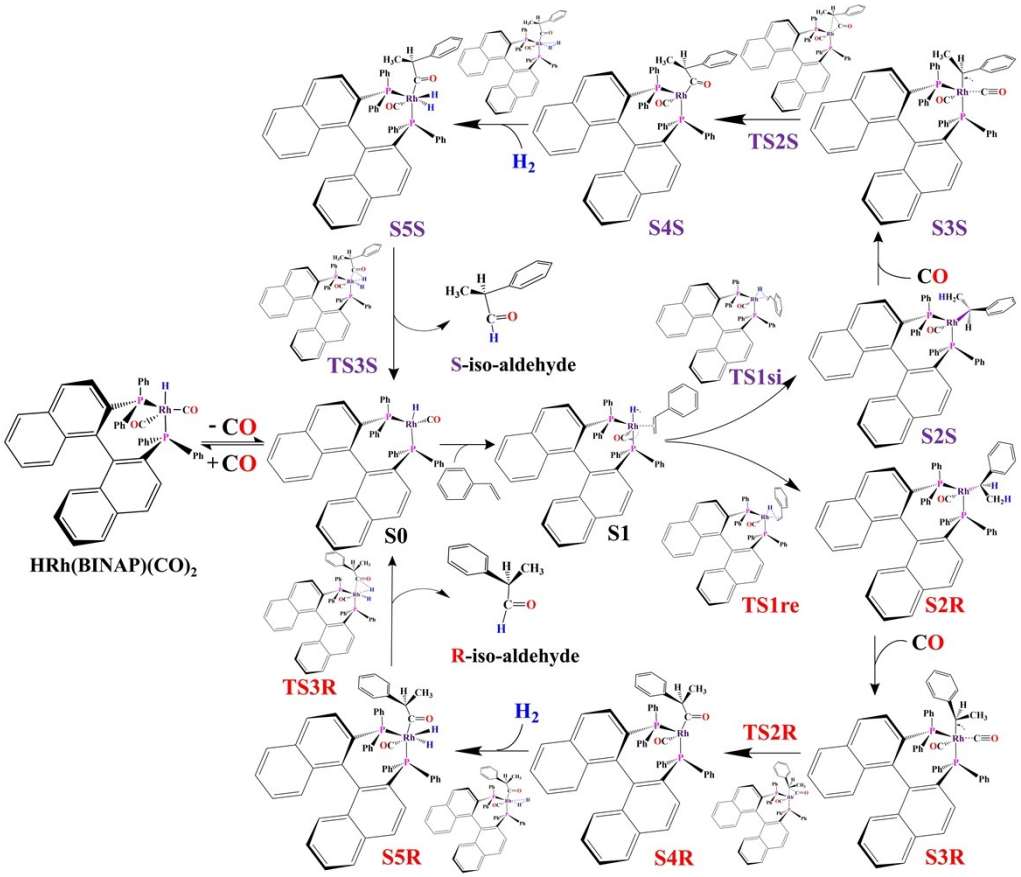


Fig. S2 The mechanism of AHF reaction catalyzed by $HRh(BINAP)(CO)_2$ to prepared optical active iso-aldehydes.

Table S2 Optimized Cartesian coordinates involved in Fig. 6 for S0

Atom	X	Y	Z
C	-2.49	-25.793	13.693
C	-3.713	-26.035	13.192
C	-4.071	-26.961	12.112
C	-5.393	-26.964	11.629
C	-3.152	-27.853	11.527
C	-3.539	-28.705	10.497
C	-5.782	-27.816	10.595
C	-4.857	-28.694	10.027
H	-2.121	-27.877	11.888
H	-2.809	-29.393	10.057
H	-5.158	-29.366	9.218
H	-6.814	-27.797	10.232
H	-6.118	-26.269	12.063
H	-4.558	-25.48	13.615
H	-2.355	-25.065	14.496
H	-1.589	-26.285	13.316
C	-4.667	-25.092	6.247
C	-2.445	-24.935	5.321
C	-2.97	-20.832	13.2
C	-3.724	-25.493	5.295
C	-3.407	-20.787	15.595

C	-2.313	-21.622	15.827
H	-3.954	-24.147	10.054
H	-1.317	-22.105	12.601
H	-0.705	-22.744	14.911
H	-2.052	-21.926	16.845
C	-3.056	-23.555	7.23
C	-5.419	-23.035	11.451
C	-4.331	-24.147	7.216
O	-6.46	-23.315	11.899
C	-2.116	-23.967	6.275
C	-4.948	-18.448	7.109
C	-3.928	-18.326	8.111
C	-3.129	-19.467	8.461
C	-3.392	-20.709	7.862
C	-4.39	-20.797	6.854
C	-5.133	-19.701	6.48
C	-5.73	-17.316	6.765
C	-5.528	-16.1	7.384
C	-4.533	-15.975	8.379
C	-3.753	-17.057	8.73
C	-1.969	-19.232	9.386
C	-0.815	-18.579	8.826
C	0.303	-18.264	9.668

C	0.225	-18.573	11.048
C	-0.887	-19.193	11.568
C	-1.992	-19.548	10.749
C	-0.728	-18.237	7.446
C	0.399	-17.634	6.929
C	1.499	-17.328	7.762
C	1.449	-17.641	9.104
P	-2.697	-22.297	8.543
P	-3.434	-20.497	11.441
C	-0.86	-22.172	8.459
C	-4.735	-19.197	11.571
C	-0.125	-22.815	9.466
C	1.272	-22.813	9.431
C	1.946	-22.163	8.396
C	1.221	-21.521	7.388
C	-0.175	-21.529	7.418
C	-4.497	-17.97	12.214
C	-5.516	-17.027	12.336
C	-6.78	-17.285	11.793
C	-7.015	-18.49	11.13
C	-5.999	-19.443	11.02
C	-3.734	-20.395	14.293
C	-1.891	-21.704	13.442

C	-1.556	-22.078	14.743
H	-4.569	-21.753	6.36
H	-5.885	-19.79	5.689
H	-6.503	-17.428	5.998
H	-6.141	-15.236	7.113
H	-4.388	-15.017	8.884
H	-3	-16.949	9.512
H	1.063	-18.31	11.702
H	-0.921	-19.42	12.635
H	-1.568	-18.464	6.787
H	0.44	-17.381	5.866
H	2.383	-16.842	7.34
H	2.292	-17.408	9.762
H	-0.657	-23.32	10.277
H	1.831	-23.318	10.223
H	3.04	-22.151	8.374
H	1.741	-21.007	6.575
H	-0.733	-21.026	6.624
H	-3.507	-17.752	12.629
H	-5.327	-16.084	12.858
H	-7.58	-16.545	11.887
H	-7.996	-18.693	10.69
H	-6.177	-20.386	10.496

Rh	-3.855	-22.602	10.51
H	-5.052	-23.869	7.99
H	-4.018	-20.438	16.432
H	-4.602	-19.753	14.133
H	-1.691	-25.255	4.597
H	-1.106	-23.553	6.282
H	-3.986	-26.243	4.544
H	-5.668	-25.532	6.249

Table S3 Optimized Cartesian coordinates involved in Fig. 6 for S1 S

Atom	**X**	**Y**	**Z**
C	-0.099	-3.277	2.82
C	0.171	-3.787	1.193
C	-0.934	-4.601	0.49
C	-0.543	-5.524	-0.679
C	-2.404	-4.505	0.931
C	-3.488	-5.298	0.175
C	-1.624	-6.318	-1.433
C	-3.098	-6.202	-1.009
H	-2.693	-3.841	1.811
H	-4.58	-5.213	0.491
H	-3.901	-6.783	-1.573
H	-1.333	-6.987	-2.308

H	0.548	-5.605	-0.999
H	1.224	-4.153	0.954
H	0.834	-3.462	3.448
H	-1.107	-3.663	3.188
C	-2.634	-3.915	-2.734
C	-0.542	-3.727	-4.376
C	-0.167	0.474	3.967
C	-1.894	-4.365	-4.006
C	-0.939	1.33	6.372
C	0.059	0.364	7.038
H	1.461	-1.19	3.988
H	1.668	-1.276	6.659
H	0.144	0.325	8.174
C	-0.673	-2.186	-2.202
C	-2.195	-1.936	1.023
C	-2.024	-2.827	-1.832
O	-3.699	-2.056	0.867
C	0.07	-2.641	-3.471
C	-2.028	3.403	-2.037
C	-0.695	3.366	-1.264
C	-0.1	2.019	-0.815
C	-0.78	0.702	-1.241
C	-2.128	0.74	-1.986

C	-2.76	2.091	-2.37
C	-2.629	4.752	-2.47
C	-1.9	6.065	-2.129
C	-0.573	6.03	-1.349
C	0.029	4.68	-0.916
C	1.19	2.002	0.027
C	2.452	2.696	-0.512
C	3.753	2.683	0.314
C	3.775	2.027	1.706
C	2.507	1.349	2.257
C	1.222	1.315	1.41
C	2.429	3.352	-1.904
C	3.712	3.976	-2.481
C	5.014	3.957	-1.658
C	5.031	3.319	-0.257
P	0.115	-0.93	-1.061
P	-0.32	0.516	2.105
C	1.927	-0.775	-1.493
C	-1.758	1.602	1.597
C	2.994	-1.369	-0.555
C	4.487	-1.24	-0.906
C	4.915	-0.506	-2.19
C	3.849	0.108	-3.117

C	2.355	-0.021	-2.765
C	-1.612	3.133	1.7
C	-2.779	4.05	1.293
C	-4.09	3.438	0.77
C	-4.226	1.909	0.634
C	-3.055	0.992	1.037
C	-1.055	1.382	4.837
C	0.819	-0.503	4.632
C	0.936	-0.554	6.167
H	-2.646	-0.234	-2.274
H	-3.759	2.118	-2.918
H	-3.613	4.779	-3.044
H	-2.343	7.064	-2.456
H	-0.032	7.002	-1.099
H	1.015	4.652	-0.344
H	4.73	2.042	2.328
H	2.52	0.868	3.29
H	1.466	3.358	-2.515
H	3.701	4.446	-3.52
H	5.966	4.417	-2.086
H	5.992	3.315	0.356
H	2.678	-1.913	0.396
H	5.275	-1.692	-0.218

H	6.02	-0.417	-2.454
H	4.166	0.658	-4.064
H	1.567	0.439	-3.448
H	-0.639	3.586	2.085
H	-2.675	5.181	1.389
H	-4.961	4.115	0.482
H	-5.194	1.456	0.238
H	-3.154	-0.136	0.929
Rh	-0.063	-1.777	1.24
H	-2.57	-2.5	-0.889
H	-1.592	2.007	7.016
H	-1.793	2.097	4.344
H	0.005	-4.059	-5.319
H	1.076	-2.176	-3.739
H	-2.346	-5.171	-4.674
H	-3.631	-4.393	-2.454
H	1.669	-1.582	1.423

Table S4 Optimized Cartesian coordinates involved in Fig. 6 for S1 R(or n)

Atom	**X**	**Y**	**Z**
C	0.952	-2.852	1.561
C	-0.251	-3.076	2.29
C	-0.952	-4.38	2.372

C	-1.87	-4.598	3.416
C	-0.705	-5.451	1.492
C	-1.335	-6.683	1.657
C	-2.504	-5.83	3.583
C	-2.24	-6.883	2.705
H	-0.017	-5.315	0.654
H	-1.119	-7.497	0.959
H	-2.733	-7.85	2.836
H	-3.205	-5.969	4.412
H	-2.08	-3.78	4.113
H	-0.422	-2.45	3.17
H	1.699	-2.17	1.975
H	1.388	-3.681	0.997
C	-1.761	-3.502	-4.155
C	0.426	-3.163	-5.109
C	-0.18	0.194	3.419
C	-0.847	-3.728	-5.188
C	-1.189	0.167	5.642
C	-0.016	-0.355	6.191
H	-0.744	-3.202	-0.23
H	1.827	-0.639	3.351
H	1.98	-1.064	5.765
H	0.049	-0.559	7.263

C	-0.132	-2.117	-2.981
C	-2.562	-1.865	0.366
C	-1.402	-2.72	-3.056
O	-3.702	-2.091	0.276
C	0.779	-2.363	-4.02
C	-1.953	2.975	-2.534
C	-0.905	2.994	-1.551
C	-0.143	1.796	-1.286
C	-0.463	0.612	-1.967
C	-1.526	0.619	-2.915
C	-2.237	1.759	-3.199
C	-2.677	4.161	-2.821
C	-2.4	5.337	-2.158
C	-1.39	5.358	-1.169
C	-0.666	4.222	-0.873
C	1.024	1.92	-0.345
C	2.153	2.689	-0.81
C	3.27	2.926	0.06
C	3.219	2.419	1.379
C	2.132	1.698	1.813
C	1.025	1.418	0.967
C	2.216	3.245	-2.121
C	3.303	3.985	-2.538

C	4.398	4.211	-1.673
C	4.378	3.688	-0.399
P	0.276	-1.039	-1.514
P	-0.401	0.367	1.58
C	2.092	-0.792	-1.763
C	-1.758	1.629	1.505
C	2.986	-1.528	-0.972
C	4.365	-1.428	-1.174
C	4.868	-0.583	-2.165
C	3.987	0.154	-2.961
C	2.609	0.047	-2.765
C	-1.639	2.844	2.205
C	-2.659	3.794	2.149
C	-3.804	3.551	1.382
C	-3.919	2.359	0.669
C	-2.903	1.401	0.736
C	-1.271	0.439	4.275
C	0.979	-0.374	3.982
C	1.064	-0.631	5.353
H	-1.772	-0.3	-3.447
H	-3.034	1.736	-3.95
H	-3.46	4.122	-3.584
H	-2.96	6.248	-2.387

H	-1.184	6.284	-0.625
H	0.102	4.261	-0.098
H	4.055	2.616	2.056
H	2.116	1.36	2.848
H	1.38	3.091	-2.806
H	3.314	4.403	-3.549
H	5.251	4.804	-2.015
H	5.215	3.855	0.285
H	2.59	-2.18	-0.193
H	5.044	-2.011	-0.547
H	5.947	-0.494	-2.315
H	4.371	0.826	-3.734
H	1.929	0.626	-3.395
H	-0.745	3.045	2.802
H	-2.557	4.731	2.705
H	-4.599	4.301	1.335
H	-4.801	2.167	0.053
H	-2.992	0.478	0.163
Rh	-0.663	-1.796	0.501
H	-2.115	-2.577	-2.242
H	-2.055	0.367	6.28
H	-2.201	0.842	3.872
H	1.157	-3.343	-5.902

H	1.783	-1.935	-3.988
H	-1.12	-4.352	-6.042
H	-2.759	-3.945	-4.196

Table S5 Optimized Cartesian coordinates involved in Fig. 6 for S2 (S)

Atom	X	Y	Z
C	-0.025	-3.984	2.627
C	-0.067	-3.562	1.151
C	-0.719	-4.589	0.286
C	-0.007	-5.196	-0.766
C	-2.029	-5.051	0.524
C	-2.594	-6.066	-0.247
C	-0.569	-6.21	-1.544
C	-1.868	-6.655	-1.288
H	-2.617	-4.595	1.325
H	-3.614	-6.403	-0.033
H	-2.31	-7.453	-1.892
H	0.014	-6.66	-2.354
H	1.018	-4.869	-0.971
H	0.974	-3.444	0.798
H	0.547	-4.928	2.749
H	-1.032	-4.154	3.039
C	-2.516	-3.498	-2.874
C	-0.554	-3.418	-4.275

C	-0.209	0.617	3.732
C	-1.841	-3.897	-4.029
C	-0.763	1.134	6.043
C	0.16	0.191	6.495
H	1.246	-0.967	3.48
H	1.604	-1.312	5.902
H	0.304	0.032	7.568
C	-0.622	-2.113	-2.225
C	-2.257	-1.821	2.121
C	-1.91	-2.62	-1.976
O	-3.364	-1.938	2.484
C	0.055	-2.535	-3.379
C	-1.83	3.155	-2.217
C	-0.683	3.159	-1.357
C	-0.058	1.912	-0.988
C	-0.566	0.706	-1.492
C	-1.704	0.735	-2.344
C	-2.32	1.915	-2.688
C	-2.44	4.384	-2.589
C	-1.946	5.586	-2.13
C	-0.818	5.598	-1.279
C	-0.208	4.421	-0.898
C	1.142	1.961	-0.087
C	2.379	2.481	-0.604

C	3.53	2.564	0.25
C	3.406	2.157	1.601
C	2.211	1.677	2.087
C	1.063	1.561	1.256
C	2.518	2.938	-1.947
C	3.713	3.45	-2.41
C	4.844	3.515	-1.565
C	4.751	3.074	-0.263
P	0.091	-0.962	-0.957
P	-0.483	0.748	1.904
C	1.881	-0.886	-1.416
C	-1.754	2.074	1.768
C	2.811	-1.418	-0.512
C	4.172	-1.446	-0.824
C	4.62	-0.94	-2.045
C	3.705	-0.391	-2.945
C	2.346	-0.358	-2.63
C	-1.467	3.409	2.096
C	-2.455	4.388	1.989
C	-3.739	4.045	1.557
C	-4.032	2.719	1.234
C	-3.045	1.736	1.34
C	-0.945	1.351	4.673
C	0.697	-0.352	4.2

C	0.89	-0.556	5.565
H	-2.095	-0.201	-2.742
H	-3.195	1.905	-3.346
H	-3.313	4.354	-3.248
H	-2.418	6.527	-2.424
H	-0.429	6.553	-0.913
H	0.658	4.458	-0.235
H	4.272	2.248	2.264
H	2.143	1.395	3.138
H	1.66	2.882	-2.619
H	3.781	3.81	-3.44
H	5.787	3.918	-1.945
H	5.616	3.117	0.405
H	2.462	-1.802	0.45
H	4.886	-1.858	-0.106
H	5.684	-0.969	-2.294
H	4.054	0.025	-3.894
H	1.64	0.093	-3.333
H	-0.463	3.689	2.427
H	-2.217	5.426	2.239
H	-4.51	4.816	1.472
H	-5.034	2.441	0.896
H	-3.271	0.699	1.078
Rh	-0.671	-1.459	1.17

H	-2.419	-2.346	-1.046
H	-1.355	1.712	6.758
H	-1.679	2.087	4.341
H	-0.007	-3.742	-5.166
H	1.073	-2.2	-3.583
H	-2.307	-4.601	-4.724
H	-3.505	-3.903	-2.644
H	0.457	-3.221	3.26

Table S6 Optimized Cartesian coordinates involved in Fig. 6 for S2 (R)

Atom	**X**	**Y**	**Z**
C	1.079	-2.88	1.77
C	-0.435	-2.753	1.836
C	-1.135	-4.058	1.653
C	-2.127	-4.461	2.568
C	-0.787	-4.96	0.627
C	-1.395	-6.209	0.525
C	-2.737	-5.713	2.469
C	-2.371	-6.595	1.45
H	-0.033	-4.671	-0.109
H	-1.096	-6.893	-0.275
H	-2.839	-7.581	1.38
H	-3.494	-6.007	3.202

H	-2.412	-3.779	3.375
H	-0.748	-2.3	2.79
H	1.58	-1.905	1.811
H	1.434	-3.487	2.628
C	-1.473	-4.054	-3.641
C	0.387	-3.324	-4.994
C	-0.251	0.354	3.594
C	-0.756	-4.114	-4.838
C	-1.225	0.269	5.831
C	-0.074	-0.343	6.332
H	1.401	-3.386	0.849
H	1.729	-0.534	3.451
H	1.885	-1.115	5.837
H	-0.003	-0.613	7.39
C	0.07	-2.374	-2.774
C	-2.81	-1.898	0.372
C	-1.057	-3.2	-2.617
O	-3.958	-2.128	0.327
C	0.799	-2.466	-3.971
C	-2.012	2.624	-2.455
C	-0.953	2.749	-1.493
C	-0.14	1.608	-1.15
C	-0.415	0.361	-1.762
C	-1.504	0.263	-2.682

C	-2.263	1.354	-3.027
C	-2.778	3.763	-2.811
C	-2.53	4.992	-2.236
C	-1.502	5.121	-1.275
C	-0.741	4.03	-0.912
C	1.012	1.873	-0.213
C	2.152	2.597	-0.714
C	3.243	2.917	0.167
C	3.137	2.575	1.536
C	2.018	1.938	2.015
C	0.952	1.558	1.155
C	2.247	3.046	-2.062
C	3.353	3.735	-2.515
C	4.439	4.007	-1.653
C	4.38	3.606	-0.336
P	0.495	-1.224	-1.358
P	-0.505	0.602	1.779
C	2.262	-0.84	-1.766
C	-1.816	1.915	1.774
C	3.273	-1.444	-1.005
C	4.619	-1.274	-1.341
C	4.972	-0.499	-2.447
C	3.974	0.117	-3.205
C	2.63	-0.05	-2.866

C	-1.6	3.163	2.382
C	-2.6	4.137	2.374
C	-3.821	3.886	1.739
C	-4.036	2.655	1.118
C	-3.042	1.672	1.144
C	-1.313	0.611	4.481
C	0.896	-0.284	4.109
C	0.983	-0.622	5.462
H	-1.715	-0.701	-3.146
H	-3.071	1.25	-3.758
H	-3.577	3.646	-3.55
H	-3.128	5.864	-2.515
H	-1.31	6.092	-0.809
H	0.043	4.147	-0.162
H	3.945	2.856	2.218
H	1.936	1.739	3.085
H	1.42	2.847	-2.746
H	3.389	4.077	-3.553
H	5.314	4.544	-2.029
H	5.202	3.824	0.354
H	3.006	-2.054	-0.14
H	5.392	-1.753	-0.734
H	6.024	-0.371	-2.717
H	4.238	0.739	-4.065

H	1.859	0.441	-3.465
H	-0.648	3.371	2.878
H	-2.427	5.101	2.863
H	-4.605	4.649	1.732
H	-4.977	2.459	0.597
H	-3.212	0.704	0.668
Rh	-1.03	-1.255	0.447
H	-1.613	-3.151	-1.676
H	-2.065	0.488	6.496
H	-2.225	1.081	4.11
H	0.963	-3.372	-5.923
H	1.7	-1.869	-4.117
H	-1.078	-4.78	-5.644
H	-2.364	-4.673	-3.497

Table S7 Optimized Cartesian coordinates involved in Fig. 6 for S2 (n)

Atom	**X**	**Y**	**Z**
C	0.406	-3.614	0.216
C	0.451	-4.551	1.432
C	-0.879	-5.078	1.927
C	-1.204	-5.049	3.29
C	-1.821	-5.621	1.04
C	-3.046	-6.106	1.499

C	-2.426	-5.536	3.758
C	-3.356	-6.065	2.861
H	-1.599	-5.653	-0.031
H	-3.771	-6.511	0.787
H	-4.321	-6.434	3.22
H	-2.659	-5.489	4.826
H	-0.488	-4.62	3.999
H	1.083	-5.431	1.174
H	1.434	-3.514	-0.181
H	-0.188	-4.056	-0.596
C	-1.611	-3.613	-3.549
C	0.448	-3.333	-4.778
C	-0.219	0.356	3.363
C	-0.806	-3.931	-4.647
C	-0.971	0.627	5.659
C	0.052	-0.207	6.108
H	0.966	-4.056	2.273
H	1.465	-0.98	3.103
H	1.736	-1.438	5.525
H	0.155	-0.427	7.174
C	0.095	-2.082	-2.725
C	-1.777	-2.226	1.561
C	-1.159	-2.705	-2.593
O	-2.866	-2.429	1.928

C	0.897	-2.413	-3.825
C	-1.859	2.946	-2.622
C	-0.829	3.063	-1.63
C	-0.026	1.917	-1.29
C	-0.272	0.687	-1.917
C	-1.291	0.605	-2.906
C	-2.054	1.695	-3.251
C	-2.645	4.079	-2.957
C	-2.438	5.294	-2.339
C	-1.433	5.415	-1.353
C	-0.653	4.331	-1.008
C	1.082	2.116	-0.294
C	2.229	2.886	-0.694
C	3.269	3.164	0.258
C	3.13	2.675	1.578
C	2.028	1.94	1.946
C	0.99	1.644	1.022
C	2.381	3.414	-2.008
C	3.481	4.17	-2.356
C	4.5	4.437	-1.413
C	4.392	3.939	-0.133
P	0.578	-0.888	-1.388
P	-0.414	0.533	1.529
C	2.365	-0.562	-1.724

C	-1.891	1.622	1.366
C	3.311	-1.042	-0.807
C	4.676	-0.833	-1.022
C	5.107	-0.135	-2.153
C	4.172	0.354	-3.068
C	2.809	0.143	-2.855
C	-1.883	2.96	1.793
C	-3.037	3.739	1.698
C	-4.209	3.196	1.165
C	-4.221	1.869	0.73
C	-3.067	1.086	0.825
C	-1.106	0.911	4.297
C	0.794	-0.504	3.826
C	0.941	-0.768	5.186
H	-1.466	-0.342	-3.417
H	-2.825	1.604	-4.022
H	-3.423	3.969	-3.719
H	-3.052	6.159	-2.602
H	-1.28	6.373	-0.848
H	0.11	4.44	-0.236
H	3.907	2.907	2.314
H	1.942	1.593	2.977
H	1.606	3.217	-2.751
H	3.562	4.57	-3.371

H	5.365	5.042	-1.698
H	5.172	4.138	0.609
H	2.971	-1.572	0.087
H	5.404	-1.205	-0.296
H	6.175	0.036	-2.316
H	4.505	0.913	-3.947
H	2.084	0.541	-3.57
H	-0.971	3.396	2.209
H	-3.018	4.781	2.032
H	-5.111	3.809	1.08
H	-5.13	1.439	0.3
H	-3.072	0.052	0.472
Rh	-0.242	-1.617	0.649
H	-1.769	-2.483	-1.712
H	-1.684	1.055	6.37
H	-1.923	1.554	3.962
H	1.091	-3.584	-5.625
H	1.884	-1.961	-3.94
H	-1.151	-4.654	-5.392
H	-2.587	-4.09	-3.426

Table S8 Optimized Cartesian coordinates involved in Fig. 6 for S3

Atom	X	Y	Z
C	0.44	-4.482	2.522
C	0.327	-3.828	1.139
C	-0.577	-4.595	0.224
C	-0.097	-5.042	-1.022
C	-1.867	-5.014	0.604
C	-2.634	-5.841	-0.217
C	-0.859	-5.875	-1.843
C	-2.132	-6.284	-1.444
H	-2.277	-4.695	1.564
H	-3.63	-6.152	0.113
H	-2.731	-6.937	-2.084
H	-0.451	-6.208	-2.802
H	0.902	-4.735	-1.347
H	1.323	-3.825	0.677
H	0.714	-5.551	2.419
H	-0.505	-4.44	3.085
C	-2.87	-3.1	-2.698
C	-1.108	-3.006	-4.344
C	-0.355	0.92	3.894
C	-2.391	-3.409	-3.973
C	-0.964	2.124	5.922
C	-0.264	1.202	6.703

H	0.78	-0.889	4.228
H	0.908	-0.616	6.68
H	-0.229	1.314	7.791
C	-0.792	-1.946	-2.179
C	-1.695	-2.112	2.207
C	-2.073	-2.385	-1.805
O	-2.644	-2.433	2.812
C	-0.314	-2.274	-3.457
C	-1.633	3.306	-2.144
C	-0.513	3.259	-1.248
C	0.059	1.985	-0.876
C	-0.468	0.803	-1.419
C	-1.578	0.89	-2.307
C	-2.144	2.092	-2.654
C	-2.197	4.556	-2.508
C	-1.682	5.738	-2.019
C	-0.579	5.702	-1.138
C	-0.018	4.5	-0.755
C	1.218	2.01	0.077
C	2.482	2.511	-0.394
C	3.6	2.596	0.503
C	3.416	2.227	1.858
C	2.2	1.766	2.304
C	1.091	1.634	1.422

C	2.676	2.956	-1.732
C	3.896	3.432	-2.163
C	5	3.483	-1.281
C	4.849	3.073	0.026
P	0.152	-0.91	-0.964
P	-0.372	0.685	2.046
C	1.852	-0.925	-1.704
C	-1.865	1.651	1.562
C	2.803	-1.809	-1.178
C	4.071	-1.925	-1.752
C	4.41	-1.149	-2.86
C	3.474	-0.259	-3.389
C	2.203	-0.15	-2.821
C	-1.876	3.055	1.622
C	-3.04	3.77	1.341
C	-4.21	3.089	0.995
C	-4.206	1.695	0.921
C	-3.041	0.978	1.203
C	-1.008	1.987	4.534
C	0.316	-0.02	4.694
C	0.373	0.127	6.082
H	-1.993	-0.021	-2.734
H	-2.992	2.117	-3.345
H	-3.052	4.56	-3.19

H	-2.113	6.697	-2.318
H	-0.162	6.638	-0.755
H	0.828	4.503	-0.066
H	4.256	2.317	2.553
H	2.085	1.494	3.355
H	1.838	2.923	-2.429
H	4.009	3.772	-3.196
H	5.966	3.852	-1.635
H	5.689	3.116	0.724
H	2.555	-2.409	-0.303
H	4.796	-2.623	-1.323
H	5.406	-1.227	-3.305
H	3.733	0.363	-4.251
H	1.478	0.548	-3.248
H	-0.957	3.597	1.863
H	-3.023	4.862	1.379
H	-5.122	3.651	0.772
H	-5.118	1.158	0.643
H	-3.041	-0.111	1.13
Rh	-0.066	-1.584	1.389
H	-2.436	-2.17	-0.796
H	-1.486	2.96	6.396
H	-1.581	2.711	3.954
H	-0.718	-3.258	-5.335

H	0.685	-1.963	-3.768
H	-3.01	-3.987	-4.665
H	-3.862	-3.435	-2.385
H	1.207	-3.992	3.141
C	1.733	-1.627	2.04
O	2.819	-1.723	2.456

Table S9 Optimized Cartesian coordinates involved in Fig. 6 for S4

Atom	**X**	**Y**	**Z**
C	-0.41	-5.215	2.588
C	-0.131	-4.515	1.244
C	-0.534	-5.33	0.025
C	0.379	-5.489	-1.029
C	-1.803	-5.915	-0.1
C	-2.138	-6.661	-1.231
C	0.047	-6.234	-2.161
C	-1.211	-6.83	-2.264
H	-2.542	-5.776	0.694
H	-3.132	-7.112	-1.306
H	-1.469	-7.418	-3.149
H	0.773	-6.338	-2.973
H	1.363	-5.014	-0.962

H	0.949	-4.319	1.174
H	0.084	-6.2	2.609
H	-1.488	-5.36	2.745
C	-3.243	-2.855	-2.351
C	-1.464	-3.065	-3.966
C	-0.244	1.29	4.021
C	-2.763	-3.369	-3.558
C	-0.814	2.546	6.027
C	-0.161	1.602	6.823
H	0.843	-0.54	4.375
H	0.955	-0.252	6.829
H	-0.134	1.721	7.91
C	-1.118	-1.735	-1.962
C	-0.836	-3.147	1.25
C	-2.429	-2.047	-1.557
O	-2.057	-3.055	1.333
C	-0.648	-2.254	-3.177
C	-1.44	3.6	-2.225
C	-0.391	3.494	-1.252
C	0.086	2.194	-0.835
C	-0.513	1.038	-1.365
C	-1.558	1.183	-2.32
C	-1.997	2.411	-2.748
C	-1.896	4.878	-2.643

C	-1.357	6.032	-2.117
C	-0.337	5.939	-1.143
C	0.132	4.71	-0.724
C	1.253	2.19	0.113
C	2.53	2.622	-0.395
C	3.649	2.771	0.495
C	3.463	2.504	1.872
C	2.249	2.07	2.346
C	1.13	1.898	1.481
C	2.744	2.924	-1.77
C	3.976	3.33	-2.238
C	5.072	3.466	-1.355
C	4.904	3.195	-0.014
P	-0.069	-0.704	-0.832
P	-0.314	0.982	2.186
C	1.615	-0.911	-1.58
C	-1.841	1.889	1.717
C	2.513	-1.835	-1.03
C	3.765	-2.044	-1.614
C	4.139	-1.323	-2.75
C	3.252	-0.399	-3.305
C	1.997	-0.199	-2.729
C	-1.894	3.286	1.612
C	-3.096	3.929	1.316

C	-4.262	3.182	1.13
C	-4.218	1.789	1.23
C	-3.012	1.143	1.513
C	-0.854	2.395	4.639
C	0.396	0.342	4.834
C	0.449	0.501	6.219
H	-2.013	0.29	-2.748
H	-2.786	2.478	-3.505
H	-2.689	4.926	-3.395
H	-1.709	7.014	-2.447
H	0.086	6.85	-0.712
H	0.916	4.671	0.034
H	4.306	2.633	2.558
H	2.134	1.86	3.412
H	1.912	2.831	-2.468
H	4.109	3.543	-3.303
H	6.047	3.785	-1.734
H	5.742	3.291	0.683
H	2.231	-2.38	-0.128
H	4.456	-2.766	-1.169
H	5.123	-1.478	-3.202
H	3.537	0.178	-4.19
H	1.306	0.52	-3.175
H	-0.985	3.877	1.744

H	-3.117	5.017	1.215
H	-5.204	3.687	0.896
H	-5.125	1.199	1.074
H	-2.975	0.051	1.575
Rh	-0.129	-1.292	1.445
H	-2.807	-1.674	-0.603
H	-1.307	3.406	6.49
H	-1.384	3.14	4.043
H	-1.073	-3.468	-4.904
H	0.365	-2.023	-3.512
H	-3.397	-4.014	-4.172
H	-4.254	-3.102	-2.014
H	-0.022	-4.607	3.421
C	1.379	-1.857	2.389
O	2.44	-2.169	2.782

Table S10 Optimized Cartesian coordinates involved in Fig. 6 for S5

Atom	**X**	**Y**	**Z**
C	-0.793	-4.345	2.871
C	-0.162	-4.611	1.51
C	-1.081	-5.345	0.536
C	-0.527	-6.048	-0.549
C	-2.475	-5.38	0.699
C	-3.284	-6.125	-0.167

C	-1.331	-6.783	-1.418
C	-2.715	-6.834	-1.226
H	-2.944	-4.844	1.528
H	-4.366	-6.155	-0.003
H	-3.345	-7.431	-1.891
H	-0.872	-7.323	-2.252
H	0.553	-6.01	-0.706
H	0.707	-5.276	1.669
H	-1.186	-5.287	3.288
H	-1.614	-3.617	2.821
C	-2.475	-3.208	-2.548
C	-0.74	-3.167	-4.221
C	-0.192	1.129	3.835
C	-1.992	-3.608	-3.796
C	-0.952	2.218	5.877
C	-0.133	1.392	6.647
H	1.192	-0.503	4.151
H	1.283	-0.243	6.604
H	-0.114	1.493	7.735
C	-0.462	-1.893	-2.17
H	-1.299	-1.682	1.063
C	-1.711	-2.369	-1.739
C	0.025	-2.321	-3.413
C	-1.712	3.32	-2.188

C	-0.569	3.367	-1.323
C	0.115	2.146	-0.967
C	-0.324	0.927	-1.506
C	-1.447	0.92	-2.379
C	-2.127	2.07	-2.699
C	-2.409	4.514	-2.51
C	-1.997	5.73	-2.009
C	-0.868	5.789	-1.162
C	-0.173	4.644	-0.829
C	1.274	2.272	-0.02
C	2.503	2.834	-0.515
C	3.605	3.05	0.383
C	3.439	2.728	1.751
C	2.258	2.199	2.214
C	1.162	1.947	1.341
C	2.685	3.197	-1.88
C	3.879	3.721	-2.333
C	4.96	3.92	-1.444
C	4.82	3.59	-0.113
P	0.457	-0.719	-1.065
P	-0.219	0.887	1.988
C	2.109	-0.611	-1.888
C	-1.791	1.733	1.541
C	3.203	-1.292	-1.336

C	4.447	-1.262	-1.971
C	4.61	-0.567	-3.17
C	3.523	0.104	-3.735
C	2.282	0.086	-3.096
C	-1.917	3.132	1.589
C	-3.154	3.738	1.371
C	-4.278	2.957	1.093
C	-4.158	1.567	1.029
C	-2.921	0.958	1.249
C	-0.979	2.093	4.487
C	0.608	0.286	4.625
C	0.647	0.422	6.014
H	-1.784	-0.024	-2.806
H	-2.988	2.028	-3.374
H	-3.279	4.445	-3.17
H	-2.541	6.645	-2.26
H	-0.537	6.755	-0.769
H	0.692	4.72	-0.169
H	4.267	2.909	2.443
H	2.162	1.957	3.274
H	1.864	3.047	-2.583
H	3.99	3.985	-3.389
H	5.903	4.333	-1.813
H	5.648	3.734	0.587

H	3.07	-1.867	-0.421
H	5.291	-1.789	-1.517
H	5.587	-0.542	-3.661
H	3.642	0.653	-4.673
H	1.437	0.616	-3.544
H	-1.039	3.75	1.792
H	-3.235	4.827	1.406
H	-5.246	3.435	0.922
H	-5.032	0.95	0.804
H	-2.819	-0.13	1.199
Rh	0.273	-1.361	1.288
H	-2.076	-2.088	-0.749
H	-1.584	2.97	6.358
H	-1.639	2.742	3.911
H	-0.342	-3.491	-5.187
H	1.01	-2.002	-3.758
H	-2.586	-4.276	-4.426
H	-3.438	-3.574	-2.186
H	-0.047	-3.948	3.576
C	0.516	-3.388	0.778
O	1.271	-3.666	-0.139
C	2.103	-1.323	1.901
H	-0.212	-1.868	2.713
O	3.164	-1.382	2.37

Table S11 Optimized Cartesian coordinates involved in Fig. 6 for S6

Atom	X	Y	Z
C	-0.715	-4.828	2.933
C	-0.112	-5.168	1.584
C	-1.097	-5.766	0.558
C	-0.626	-6.516	-0.538
C	-2.485	-5.66	0.735
C	-3.375	-6.277	-0.146
C	-1.516	-7.126	-1.421
C	-2.897	-7.014	-1.232
H	-2.882	-5.101	1.579
H	-4.447	-6.178	0.012
H	-3.604	-7.502	-1.925
H	-1.137	-7.697	-2.273
H	0.446	-6.625	-0.698
H	0.648	-5.944	1.728
H	-1.264	-5.675	3.376
H	-1.39	-3.955	2.827
C	-2.496	-3.097	-2.207
C	-0.882	-3.156	-4
C	-0.265	1.209	3.826
C	-2.098	-3.572	-3.458
C	-1.078	2.301	5.834

C	-0.267	1.487	6.621
H	1.139	-0.393	4.142
H	1.179	-0.118	6.62
H	-0.282	1.591	7.708
C	-0.469	-1.758	-2.058
H	-1.16	-1.431	1.723
C	-1.68	-2.208	-1.506
C	-0.07	-2.253	-3.311
C	-1.611	3.485	-2.277
C	-0.504	3.521	-1.365
C	0.161	2.292	-0.983
C	-0.264	1.075	-1.535
C	-1.348	1.076	-2.453
C	-2.006	2.231	-2.807
C	-2.29	4.684	-2.628
C	-1.896	5.901	-2.11
C	-0.81	5.954	-1.207
C	-0.136	4.801	-0.844
C	1.284	2.403	0.003
C	2.524	2.998	-0.436
C	3.591	3.222	0.498
C	3.373	2.904	1.862
C	2.195	2.331	2.272
C	1.148	2.039	1.357

C	2.755	3.357	-1.795
C	3.966	3.874	-2.21
C	5.017	4.072	-1.284
C	4.825	3.753	0.044
P	0.511	-0.561	-1.045
P	-0.206	0.937	1.996
C	2.117	-0.495	-1.995
C	-1.811	1.754	1.476
C	3.204	-1.265	-1.553
C	4.402	-1.292	-2.273
C	4.537	-0.548	-3.445
C	3.466	0.22	-3.899
C	2.266	0.251	-3.182
C	-1.962	3.162	1.473
C	-3.208	3.744	1.216
C	-4.323	2.952	0.951
C	-4.19	1.566	0.957
C	-2.948	0.974	1.209
C	-1.078	2.172	4.447
C	0.534	0.381	4.627
C	0.545	0.529	6.012
H	-1.676	0.136	-2.893
H	-2.849	2.196	-3.513
H	-3.13	4.621	-3.328

H	-2.42	6.817	-2.393
H	-0.493	6.919	-0.798
H	0.697	4.875	-0.14
H	4.17	3.1	2.583
H	2.055	2.11	3.33
H	1.961	3.201	-2.525
H	4.118	4.127	-3.263
H	5.975	4.478	-1.623
H	5.632	3.9	0.77
H	3.1	-1.855	-0.64
H	5.234	-1.896	-1.904
H	5.48	-0.564	-3.997
H	3.564	0.804	-4.817
H	1.435	0.855	-3.558
H	-1.113	3.817	1.674
H	-3.296	4.833	1.197
H	-5.284	3.416	0.729
H	-5.054	0.938	0.749
H	-2.845	-0.117	1.216
Rh	0.414	-1.11	1.359
H	-1.957	-1.868	-0.505
H	-1.725	3.047	6.295
H	-1.723	2.82	3.85
H	-0.555	-3.531	-4.973

H	0.884	-1.935	-3.741
H	-2.732	-4.271	-4.005
H	-3.433	-3.439	-1.755
H	0.094	-4.522	3.625
C	0.696	-3.966	1.039
O	1.505	-4.036	0.16
C	2.347	-1.279	1.868
H	0.583	-2.966	1.644
O	3.39	-1.676	2.18

1. W. Alsalahi, A. M. Trzeciak, *ChemistrySelect*, 2018, **3**, 1727-1736.
2. T. Wang, W. Wang, Y. Lyu, K. Xiong, C. Li, H. Zhang, Z. Zhan, Z. Jiang, Y. Ding, *Chinese Journal of Catalysis*, 2017, **38**, 691-698.
3. K. Wang, X. Liu, B. Liu, Z. Guo, C. Zhang, Z. Lv, *Journal of Organometallic Chemistry*, 2021, **948**, 121931.
4. D. Han, X. Li, H. Zhang, Z. Liu, G. Hu, C. Li, *Journal of Molecular Catalysis A: Chemical*, 2008, **283**, 15-22.
5. D. Han, X. Li, H. Zhang, Z. Liu, J. Li, C. Li, *Journal of Catalysis*, 2006, **243**, 318-328.
6. Y. Chen, Y. Qi, H. Gong, *Computational and Theoretical Chemistry*, 2022, **1213**, 113743.

7. J. C. Sancho-García, A. J. Pérez-Jiménez, *Journal of Physics B Atomic Molecular & Optical Physics*, 2002, **35**, 1509-1523.

Reference