Electronic Supplementary Material (ESI) for Dalton Transactions.

Stereoselective coordination: a six-membered P,N-chelate tailored for asymmetric allylic alkylation

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Supporting Information

Contents

1. **Characterization of 2a**

1.1. NMR analysis

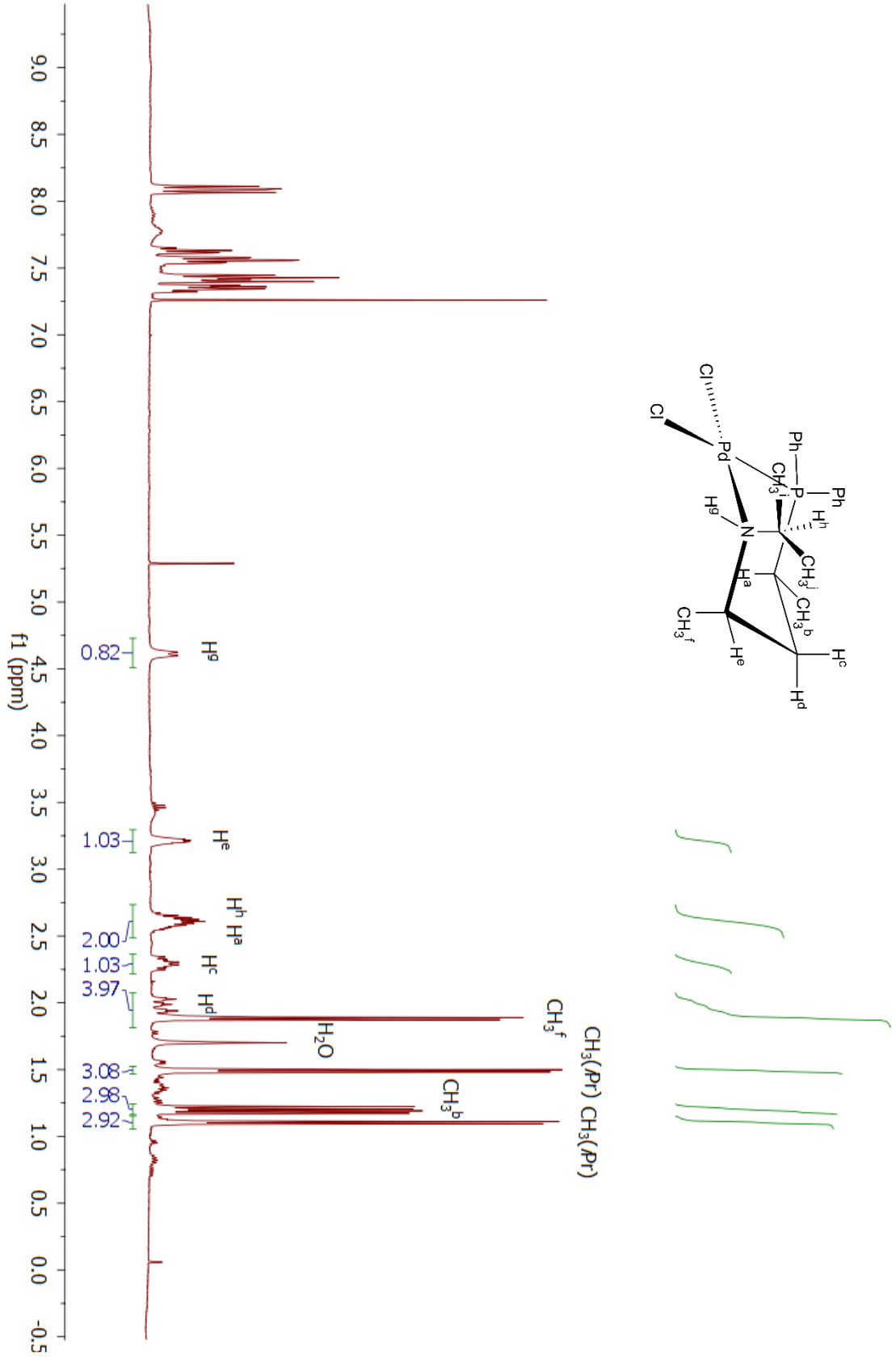


Figure S1 ^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$)

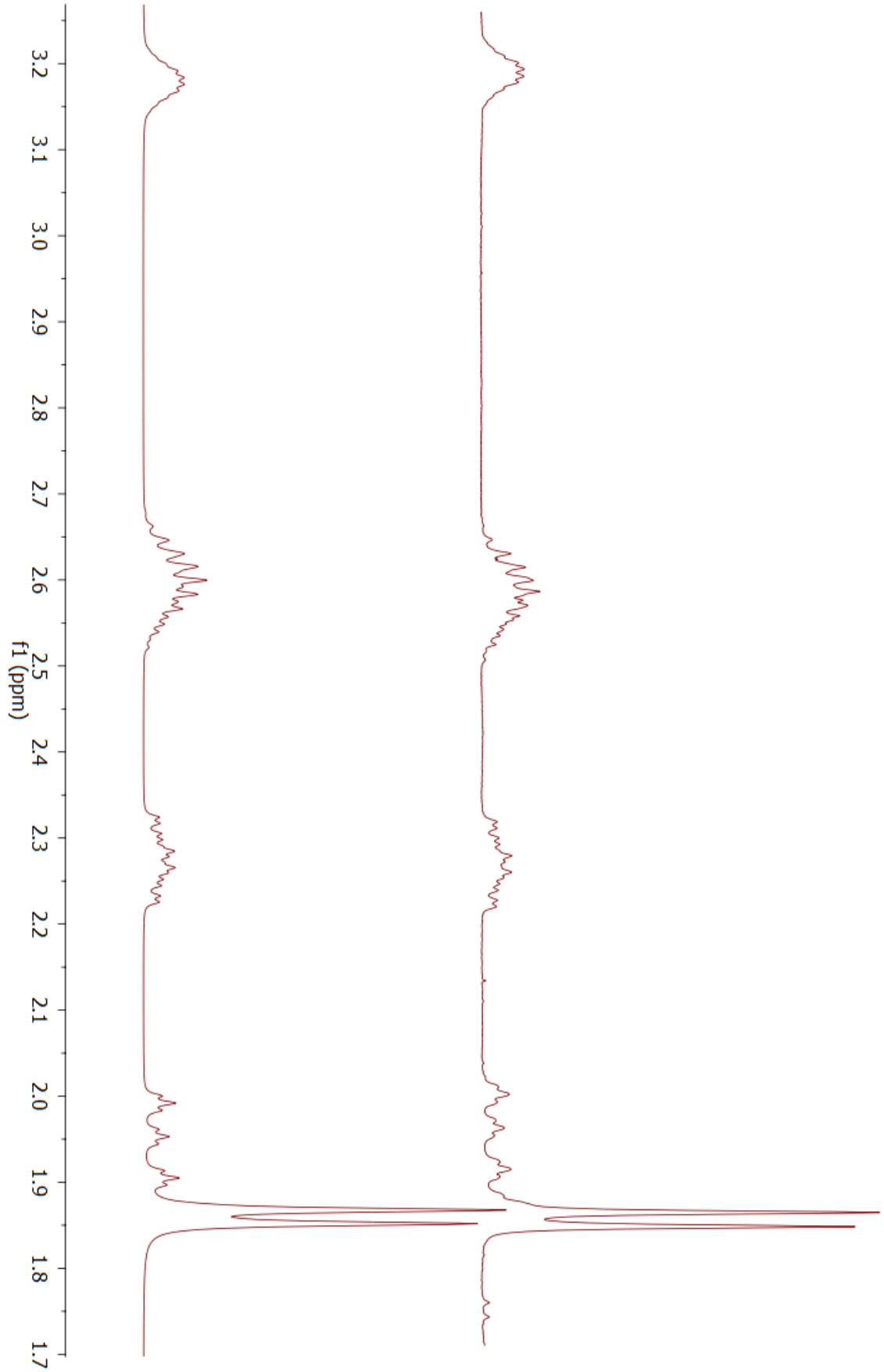


Figure S2 Selected range of ^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$) (experimental ans simulated spectra)

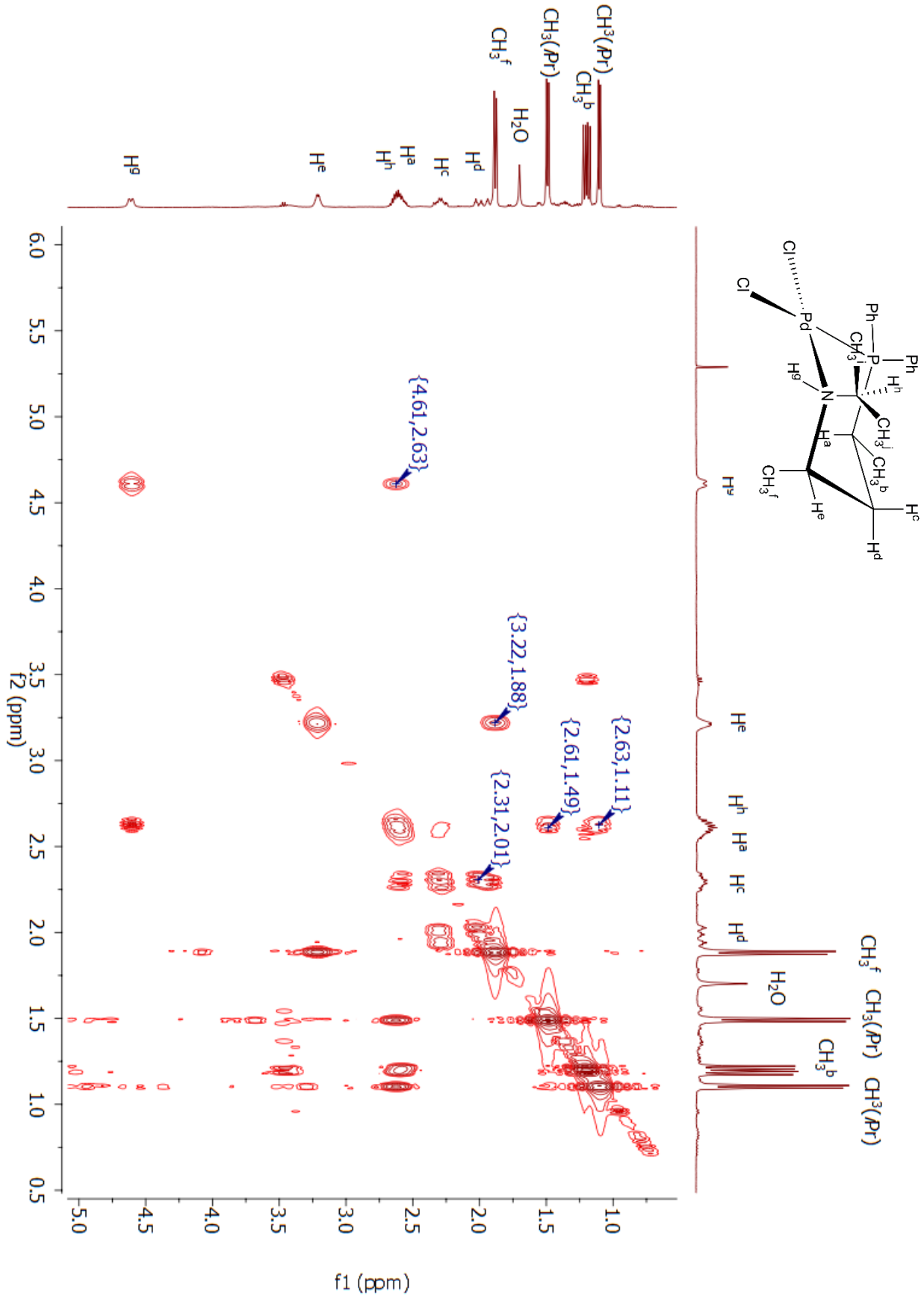


Figure S3 Selected area of ^{1}H-^{1}H COSY spectrum of **2a** (400 MHz, $CDCl_3$)

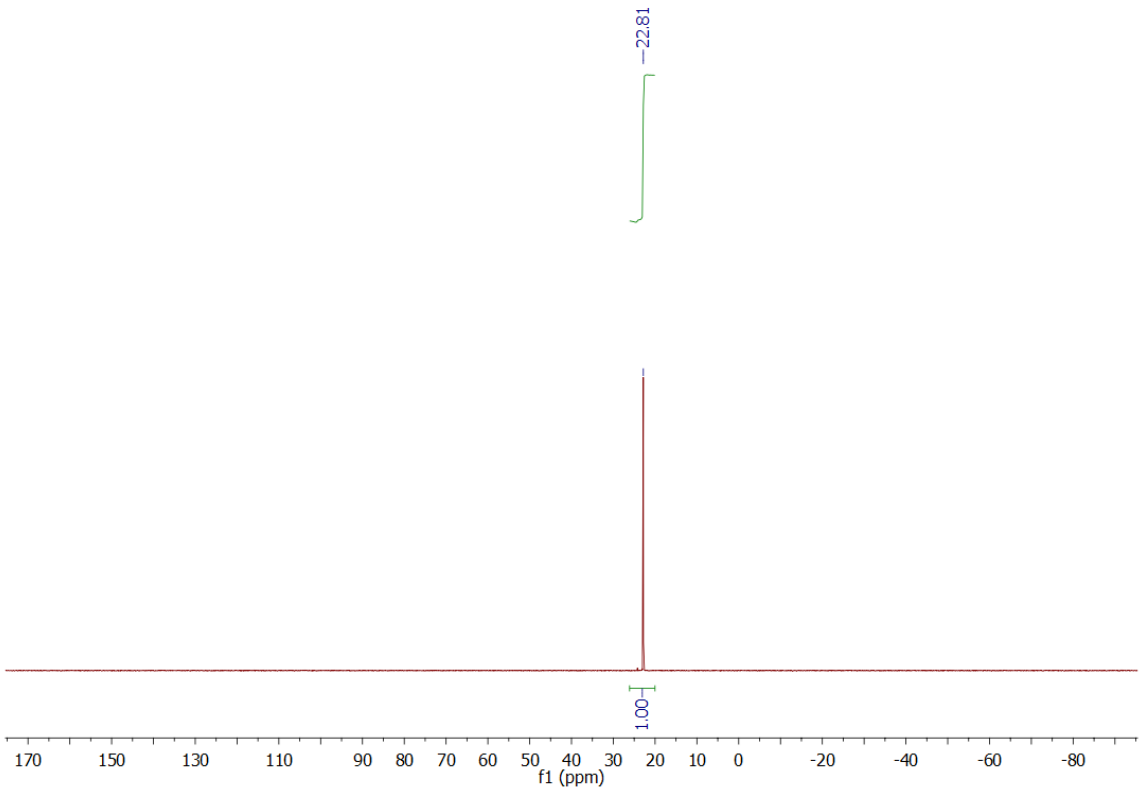


Figure S4 $^{31}P\{^{1}H\}$ NMR spectrum of **2a** (162 MHz, CD_2Cl_2)

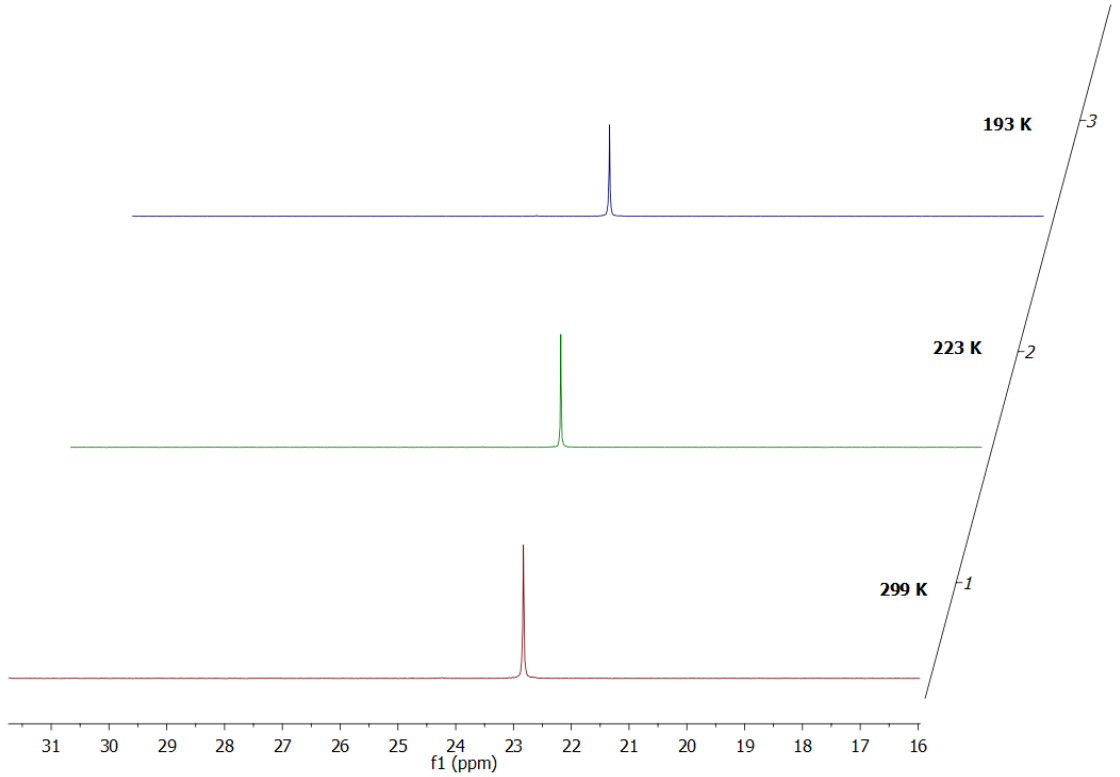


Figure S5 $^{31}P\{^{1}H\}$ NMR spectrum of **2a** at 299 K, 223 K and 193 K (162 MHz, CD_2Cl_2)

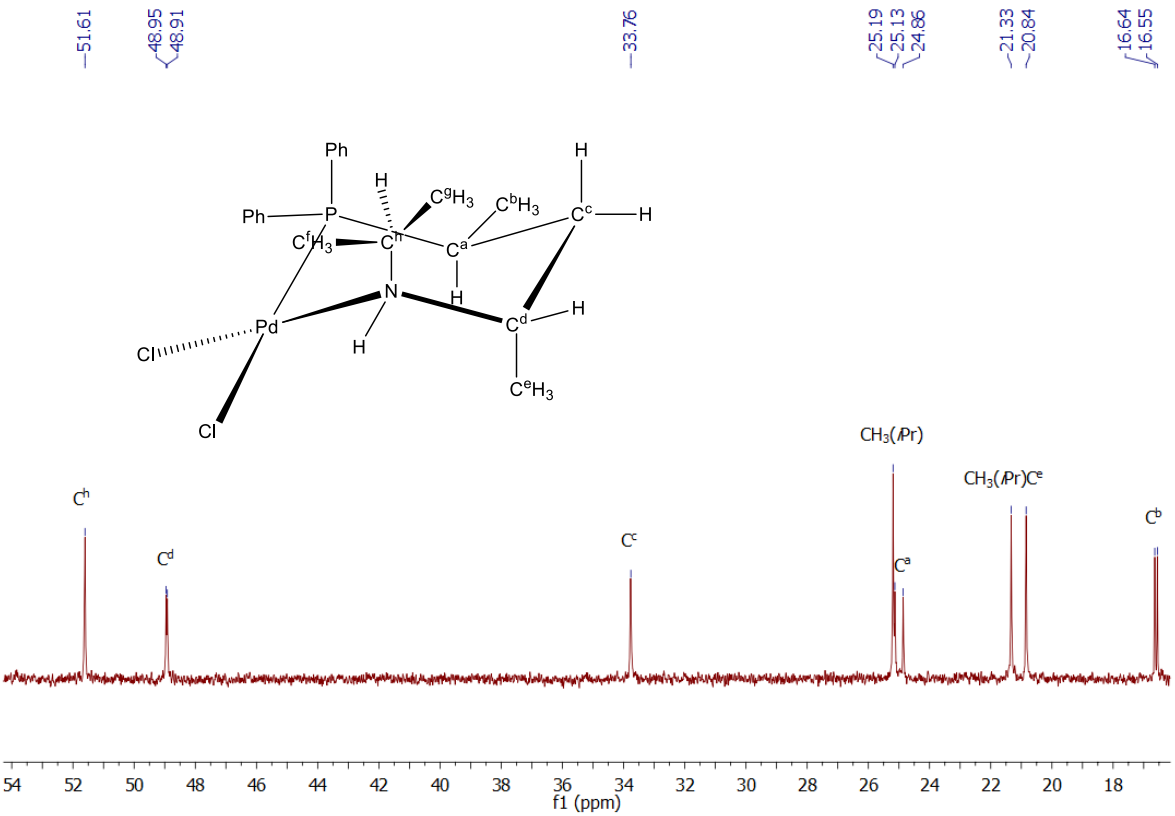


Figure S6 Selected area of $^{13}C\{^1H\}$ NMR spectrum of **2a** (101 MHz, $CDCl_3$)

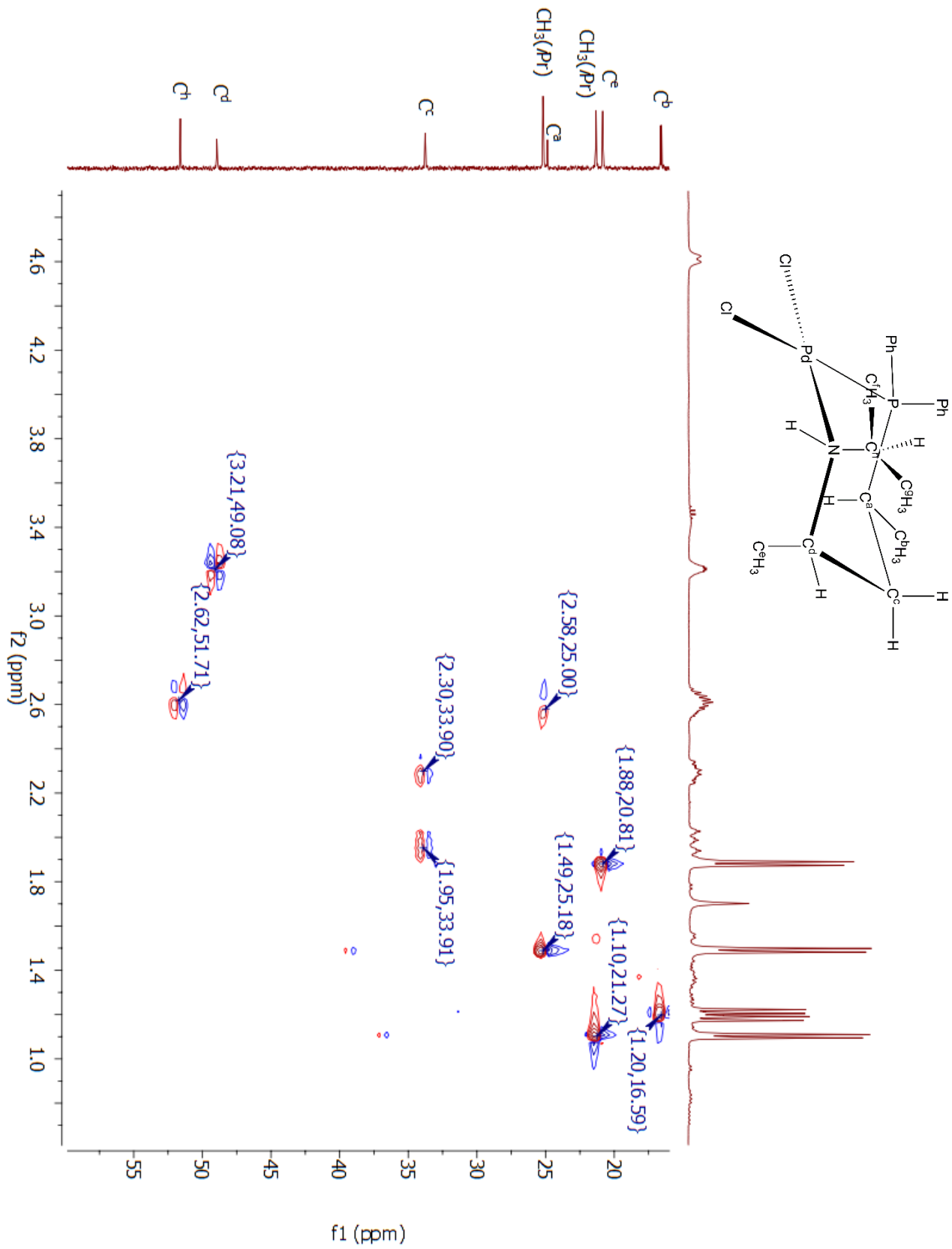


Figure S7 Selected area of HMQC spectrum of **2a** ($CDCl_3$)

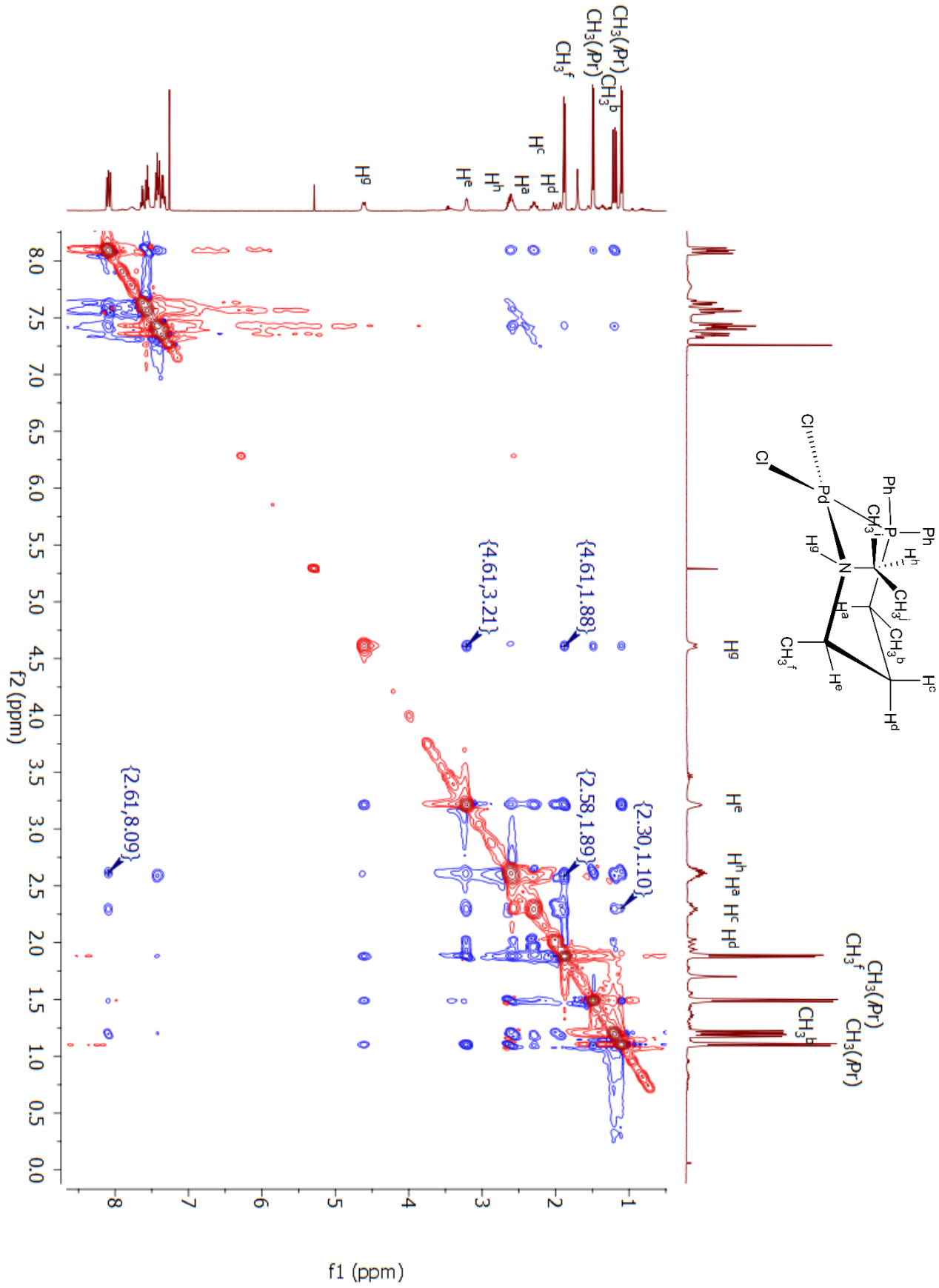
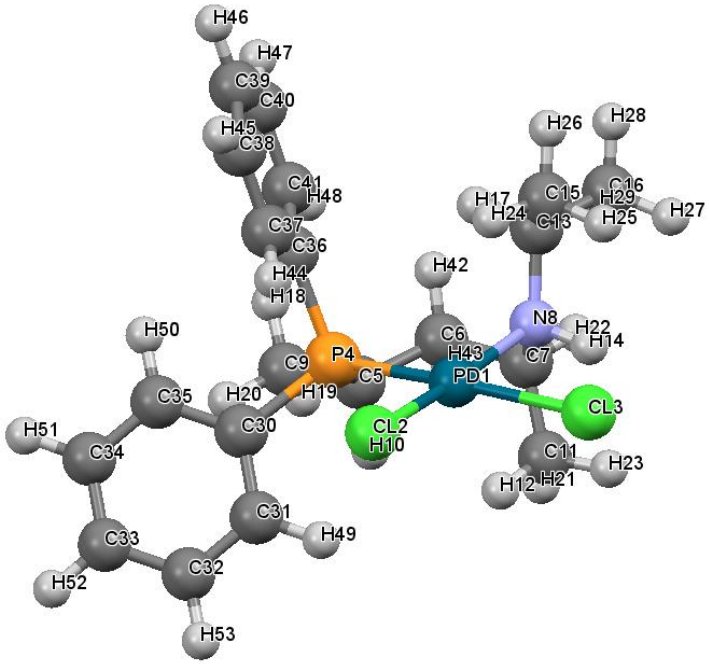


Figure S8 ^{1}H-^{1}H NOESY spectrum of **2a** (400 MHz, $CDCl_3$)

1.2. Theoretical calculations

Cartesian coordinates of *eaa* conformation of complex **2a** (rel. enthalpy: 0 kJ/mol)



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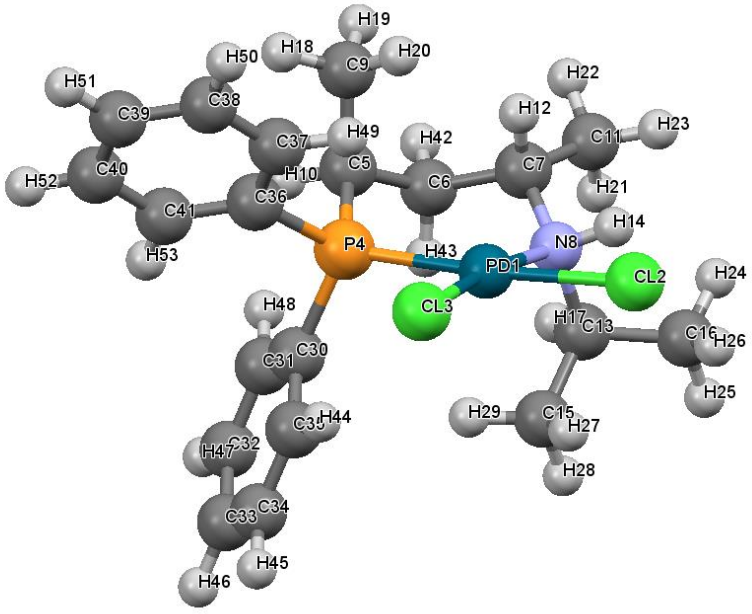
Cartesian coordinates of *aea* conformation of complex **2a** (rel. enthalpy: 8 kJ/mol)



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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14	1	0	3.013754	-0.952668	0.509307
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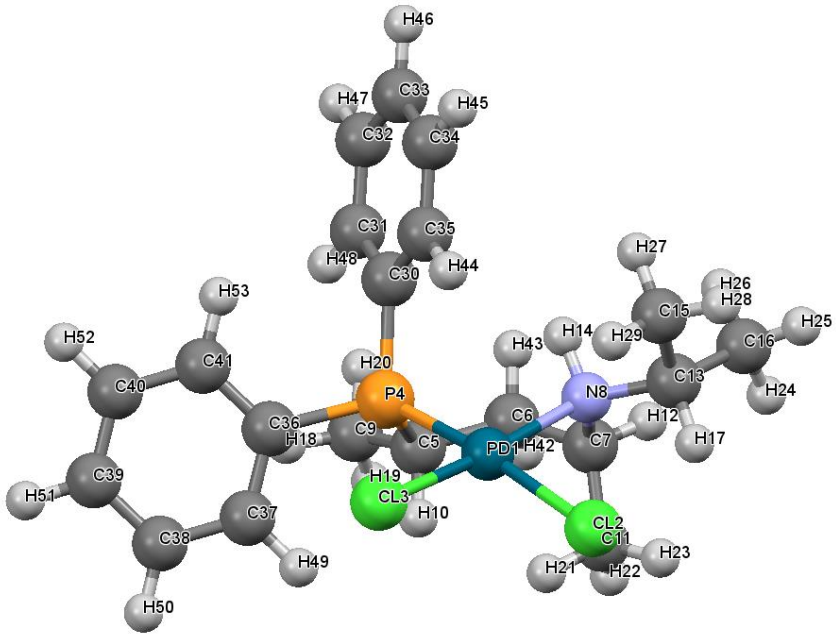
Cartesian coordinates of *eae* conformation of complex **2a** (rel. enthalpy: 28 kJ/mol)



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51	1	0	6.142249	-2.066083	-0.109554
52	1	0	5.706692	0.203083	-1.009428
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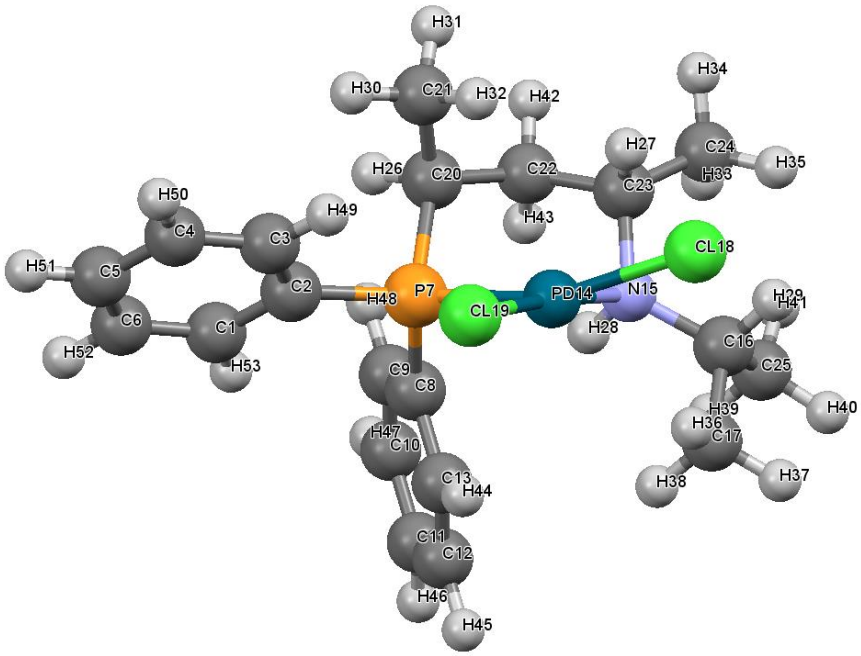
Cartesian coordinates of *aee* conformation of complex **2a** (rel. enthalpy: 47 kJ/mol)



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13	6	0	-0.533023	2.110598	-1.624223
14	46	0	0.793030	-1.135343	-0.478961
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16	6	0	3.345719	0.584935	-0.352188
17	6	0	3.081542	0.541128	-1.856594
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19	17	0	-0.544748	-2.689245	-1.548504
20	6	0	-0.606774	0.172015	2.120737
21	6	0	-0.821033	-1.230634	2.705073
22	6	0	0.791000	0.718646	2.483046
23	6	0	2.042944	0.075850	1.860341
24	6	0	3.270110	0.499691	2.666788
25	6	0	4.005206	1.928196	-0.020590
26	1	0	-1.343194	0.841836	2.582346
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28	1	0	1.555864	1.279195	0.263102
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33	1	0	3.329090	1.582766	2.808961
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35	1	0	4.198524	0.145701	2.215512
36	1	0	2.705818	-0.432245	-2.170899
37	1	0	4.015254	0.733123	-2.393569
38	1	0	2.365033	1.318844	-2.147221
39	1	0	3.329839	2.757299	-0.267028
40	1	0	4.899873	2.047440	-0.638373
41	1	0	4.309747	2.033669	1.018589
42	1	0	0.883266	0.618327	3.570466
43	1	0	0.835925	1.797069	2.282027
44	1	0	-0.359422	1.260358	-2.277886
45	1	0	-0.207760	3.558745	-3.174166
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52	1	0	-5.788333	1.210527	-0.044357
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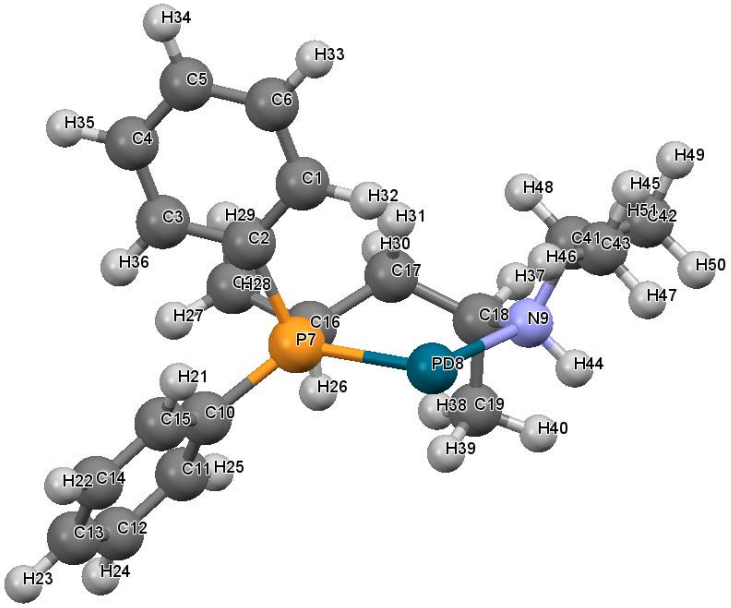
Cartesian coordinates of *eaa* conformation of [Pd(**1a**)] (rel. enthalpy: 0 kJ/mol)



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5	6	0	1.684797	4.406216	0.341060
6	6	0	0.510950	3.961863	-0.255858
7	15	0	0.753216	-0.131288	-0.104055
8	46	0	-1.091865	-0.617615	-1.257521
9	7	0	-2.989048	-0.776182	0.037604
10	6	0	2.419296	-0.921504	-0.198803
11	6	0	2.789955	-2.040952	0.550794
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13	6	0	4.897673	-2.187832	-0.613326
14	6	0	4.540161	-1.077435	-1.373412
15	6	0	3.314557	-0.458534	-1.172112
16	6	0	0.157291	-0.586459	1.633955
17	6	0	-1.316811	-0.169402	1.882651
18	6	0	-2.492192	-1.066158	1.409813
19	6	0	-2.187944	-2.556821	1.511742
20	6	0	1.034583	-0.062613	2.776547
21	1	0	3.045030	0.399697	-1.781123
22	1	0	5.217479	-0.694776	-2.131154
23	1	0	5.854176	-2.676107	-0.772509
24	1	0	4.280421	-3.535548	0.943506
25	1	0	2.122799	-2.442247	1.306106
26	1	0	0.204073	-1.679640	1.646605
27	1	0	2.089040	-0.308485	2.626473
28	1	0	0.722014	-0.501782	3.731265
29	1	0	0.956315	1.024493	2.868330
30	1	0	-1.430377	-0.112798	2.973291
31	1	0	-1.474549	0.854724	1.525011

32	1	0	-0.628177	2.242283	-0.884944
33	1	0	-0.215678	4.677292	-0.629512
34	1	0	1.879127	5.470029	0.440015
35	1	0	3.539469	3.819782	1.260985
36	1	0	3.111204	1.409638	1.028933
37	1	0	-3.308150	-0.859149	2.118031
38	1	0	-1.783523	-2.806108	2.497278
39	1	0	-1.463210	-2.856494	0.748618
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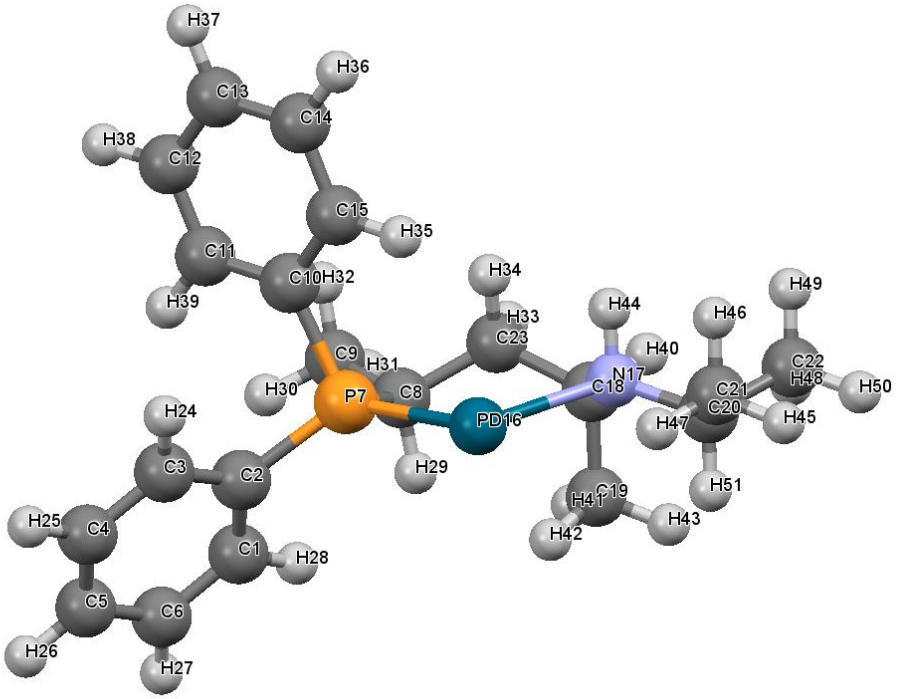
41	6	0	-3.870333	0.407475	-0.079013
42	6	0	-5.240165	0.204437	0.575018
43	6	0	-4.025003	0.772288	-1.551277
44	1	0	-3.529222	-1.586132	-0.264794
45	1	0	-4.641129	1.669459	-1.669556
46	1	0	-3.042234	0.952627	-2.001830
47	1	0	-4.509657	-0.041758	-2.103475
48	1	0	-3.350376	1.227928	0.426106
49	1	0	-5.841258	1.115680	0.499146
50	1	0	-5.791223	-0.598181	0.069682
51	1	0	-5.164775	-0.051532	1.635475

Cartesian coordinates of *eae* conformation of [Pd(**1a**)] (rel. enthalpy: 2 kJ/mol)



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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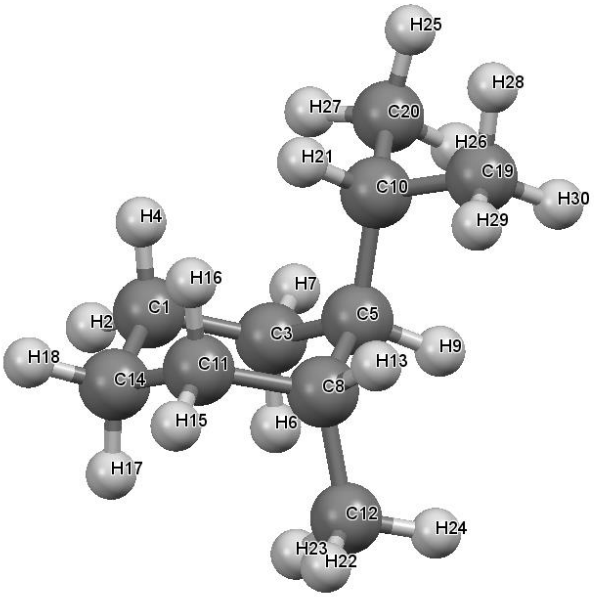
4	6	0	4.387222	-1.689224	-1.328004
5	6	0	4.515321	-2.868000	-0.599076
6	6	0	3.533055	-3.208259	0.321884

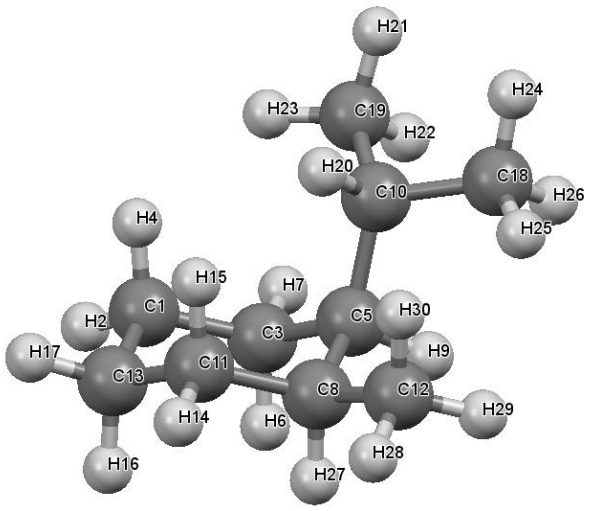
7	15	0	0.789227	-0.121868	-0.102769
8	6	0	0.170023	-0.425704	1.660965
9	6	0	1.167259	-0.073189	2.770469
10	6	0	1.518063	1.572796	0.008022
11	6	0	2.744230	1.864784	0.616510
12	6	0	3.210549	3.172244	0.686978
13	6	0	2.457626	4.214163	0.153746
14	6	0	1.241010	3.939481	-0.459278
15	6	0	0.781199	2.628628	-0.536172
16	46	0	-1.149774	-0.295767	-1.195408
17	7	0	-2.962046	0.049779	0.161867
18	6	0	-2.532466	-0.374758	1.519878
19	6	0	-2.525859	-1.894885	1.637061
20	6	0	-4.315465	-0.368680	-0.264882
21	6	0	-4.558147	0.166543	-1.671835
22	6	0	-5.430671	0.072813	0.687182
23	6	0	-1.186978	0.271197	1.948017
24	1	0	3.201189	0.050077	-1.716146
25	1	0	5.144729	-1.413633	-2.055759
26	1	0	5.371949	-3.517068	-0.752369
27	1	0	3.617628	-4.127066	0.894754
28	1	0	1.682985	-2.671119	1.241956
29	1	0	0.002221	-1.506440	1.691880
30	1	0	2.146476	-0.526948	2.596597
31	1	0	0.801877	-0.430931	3.740278
32	1	0	1.308504	1.008839	2.846918
33	1	0	-1.251825	0.353738	3.040570
34	1	0	-1.154706	1.306954	1.585027
35	1	0	-0.154349	2.399909	-1.040528
36	1	0	0.653468	4.744486	-0.890742
37	1	0	2.824218	5.234897	0.208203
38	1	0	4.166557	3.378174	1.159314
39	1	0	3.348504	1.062559	1.026277
40	1	0	-3.266609	0.005209	2.246861
41	1	0	-2.100539	-2.197921	2.598903
42	1	0	-1.931425	-2.336355	0.831175
43	1	0	-3.536621	-2.308903	1.584449
44	1	0	-2.946586	1.069591	0.151088
45	1	0	-5.521570	-0.178732	-2.058571
46	1	0	-4.569748	1.263360	-1.676865
47	1	0	-3.766340	-0.167147	-2.350632
48	1	0	-5.327284	-0.366529	1.683105
49	1	0	-5.437791	1.164195	0.796468
50	1	0	-6.406946	-0.228167	0.295081
51	1	0	-4.304787	-1.461230	-0.316725

Cartesian coordinates of *aa* conformation of 1-isopropyl-2-methylcyclohexane (rel. enthalpy: 0 kJ/mol)



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.027191	-1.818153	-0.038101
2	1	0	-1.484992	-2.728749	0.362909
3	6	0	-0.288948	-1.068958	1.072295
4	1	0	-0.314652	-2.142765	-0.807137
5	6	0	0.375997	0.229340	0.576016
6	1	0	-1.009158	-0.815509	1.858837
7	1	0	0.449608	-1.717655	1.549357
8	6	0	-0.691401	1.141351	-0.083318
9	1	0	0.759136	0.755850	1.462562
10	6	0	1.603807	-0.005316	-0.343232
11	6	0	-1.480498	0.388966	-1.170855
12	6	0	-1.620955	1.778079	0.954740
13	1	0	-0.174845	1.970562	-0.578058
14	6	0	-2.091202	-0.924474	-0.677045
15	1	0	-2.263891	1.044880	-1.567455
16	1	0	-0.814456	0.169534	-2.013777
17	1	0	-2.876089	-0.717484	0.060776
18	1	0	-2.581104	-1.442695	-1.508292
19	6	0	2.414453	1.282080	-0.529097
20	6	0	2.536244	-1.102858	0.177462
21	1	0	1.247772	-0.320044	-1.332488
22	1	0	-2.328578	2.459604	0.472822
23	1	0	-2.206675	1.038198	1.506131
24	1	0	-1.049237	2.355304	1.687723
25	1	0	3.438099	-1.160741	-0.438864
26	1	0	2.853534	-0.893468	1.205452
27	1	0	2.069698	-2.090188	0.166172
28	1	0	3.261060	1.112400	-1.200667
29	1	0	1.824644	2.099062	-0.949910
30	1	0	2.818279	1.623561	0.430720

Cartesian coordinates of *ae* conformation of 1-isopropyl-2-methylcyclohexane (rel. enthalpy: 7.5 kJ/mol)



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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3	6	0	-0.573885	-1.222412	1.035092
4	1	0	-1.026906	-1.876430	-0.981153
5	6	0	0.325202	-0.012150	0.709206
6	1	0	-1.145307	-0.980030	1.940549
7	1	0	0.032309	-2.095327	1.289563
8	6	0	-0.610513	1.189217	0.397059
9	1	0	0.862655	0.233456	1.636296
10	6	0	1.419568	-0.286054	-0.366139
11	6	0	-1.603693	0.863049	-0.727932
12	6	0	0.083517	2.522659	0.125548
13	6	0	-2.451145	-0.367907	-0.412505
14	1	0	-2.250040	1.731432	-0.899455
15	1	0	-1.057445	0.702197	-1.666838
16	1	0	-3.098577	-0.146971	0.446368
17	1	0	-3.115081	-0.601133	-1.251743
18	6	0	2.674983	0.562789	-0.120304
19	6	0	1.867488	-1.750581	-0.444772
20	1	0	1.016819	-0.016483	-1.351040
21	1	0	2.664768	-1.856361	-1.186388
22	1	0	2.270949	-2.090763	0.515217
23	1	0	1.063542	-2.431418	-0.729403
24	1	0	3.410712	0.403874	-0.914657
25	1	0	2.468842	1.630872	-0.069399
26	1	0	3.145828	0.271950	0.825465
27	1	0	-1.209708	1.327916	1.308982
28	1	0	-0.658846	3.324487	0.065265
29	1	0	0.789285	2.784472	0.919010
30	1	0	0.626638	2.515020	-0.823887

1.3. Crystal structure analysis of **2a**

Diffraction intensity data collection was carried out at 293(2) K on a Bruker-Nonius MACH3 diffractometer equipped with a point detector using graphite-monochromated Mo-*K*α radiation (λ = 0.71073 Å). The structure was solved by SIR-92 program[1] and refined by full-matrix least-squares method on F^2, with all non-hydrogen atoms refined with anisotropic thermal parameters using the SHELXL-97 package.[2] Publication material was prepared with the WINGX- suite.[3] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated with a mixture of independent and constrained refinement. C-H hydrogen atoms were placed into geometric position and methyl protons were refined using a riding model. The hydrogen atom attached to the nitrogen atom was found at the difference electron density map and the N-H distance was constrained during the refinement. Crystallographic experimental and refinement details are summarized in Table S1. There is a hydrogen bond types interaction between the NH proton and one of the coordinated chloride ions. Weak C-H···Cl interactions can also stabilize the structure (Table S2). ORTEP view of the asymmetric unit is shown at Figure S9, while Figure S10 shows the packing. Selected geometric data are shown in Table S3. There is a short H-H distance among H10A and H32 atoms of 1.78 Å (Figure S11).

Table S1 Crystallographic data of **2a**.

Crystal data	
Chemical formula	$C_{20}H_{28}Cl_2NPPd$
M_r	490.7
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	293
a, *b*, *c* (Å)	10.8906 (3), 11.9745 (3), 16.6810 (8)
V (Å^3)	2175.36 (13)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	1.18
Crystal size (mm)	0.35 × 0.3 × 0.2
Data collection	
Diffractometer	Enraf Nonius MACH3 diffractometer
Absorption correction	ψ scan North A.C.T., Phillips D.C. & Mathews F.S. (1968) Acta. Cryst. A24, 351 Number of ψ

	scan sets used was 4 Theta correction was applied. Averaged transmission function was used. Fourier smoothing - Window value 5
T_{min}, T_{max}	0.678, 0.788
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	2344, 2294, 2073
R_{int}	0.008
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.605
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.112, 1.2
No. of reflections	2294
No. of parameters	233
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.50, -0.79
Absolute structure	Classical Flack method preferred over Parsons because only 1 suitable Friedel pairs available.
Absolute structure parameter	0.08 (9)

Table S2. Hydrogen-bond geometry (Å, º) for **2a**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···Cl2^{i}	0.97	2.89	3.834 (10)	165
C13—H13*A*···Cl1	0.96	2.93	3.542 (14)	122
C26—H26···Cl1^{ii}	0.93	2.97	3.655 (13)	131
N1—H1···Cl1	0.85 (2)	2.57 (10)	3.038 (9)	116 (8)

Symmetry codes: (i) -*x*+1/2, -*y*, *z*+1/2; (ii) -*x*, *y*-1/2, -*z*+3/2.

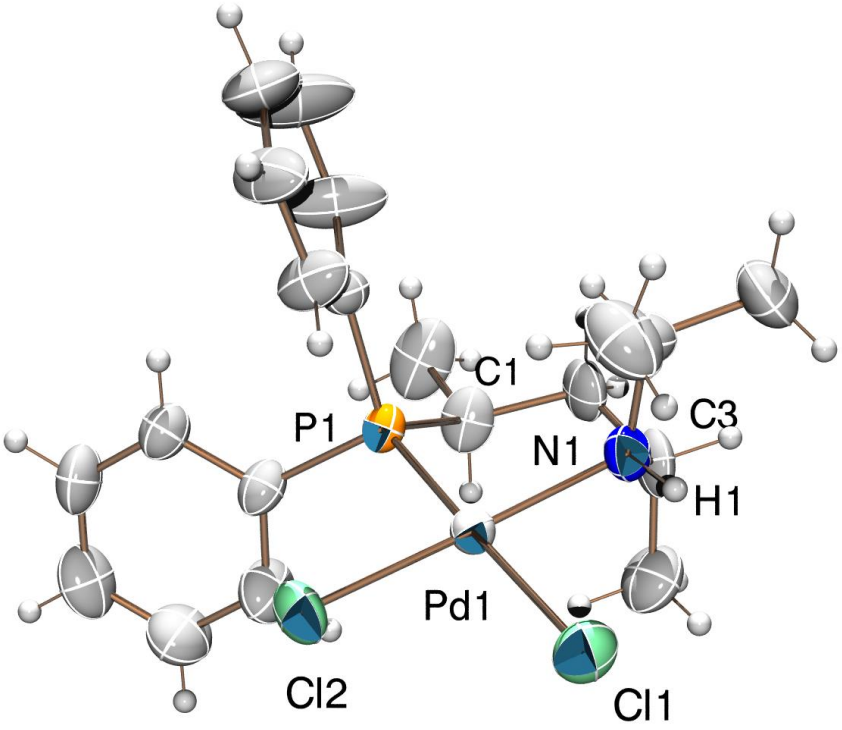


Figure S9 ORTEP view (at 50% probability level) of **2a** with partial numbering scheme

Table S3 Selected bond length (Å), bond angle (°) and torsion angle (°) data for **2a**

C1—P1	1.835 (9)	C3—N1	1.495 (13)
N1—Pd1	2.098 (8)	Cl1—Pd1	2.371 (3)
N1—H1	0.85 (2)	Cl2—Pd1	2.295 (3)
P1—Pd1	2.234 (2)		
N1—C3—C30	110.9 (9)	C3—N1—C11	116.5 (9)
N1—C3—C2	112.0 (9)	C3—N1—Pd1	114.7 (6)
C1—P1—Pd1	109.8 (4)	C11—N1—Pd1	113.9 (6)
N1—Pd1—P1	91.7 (2)	C3—N1—H1	113 (8)
N1—Pd1—Cl2	175.4 (3)	C11—N1—H1	95 (7)
P1—Pd1—Cl2	90.43 (10)	Pd1—N1—H1	101 (7)
N1—Pd1—Cl1	85.4 (2)	C21—P1—C31	106.3 (4)
P1—Pd1—Cl1	175.72 (11)	C21—P1—C1	101.1 (5)
Cl2—Pd1—Cl1	92.65 (11)	C31—P1—C1	112.3 (5)

C10—C1—C2—C3	-166.4 (10)	C2—C3—N1—Pd1	73.5 (10)
P1—C1—C2—C3	58.5 (13)	C13—C11—N1—Pd1	47.7 (11)
C1—C2—C3—N1	-71.8 (13)	C12—C11—N1—Pd1	172.2 (8)
C30—C3—N1—C11	169.4 (9)	C2—C1—P1—C31	77.0 (9)
C2—C3—N1—C11	-63.1 (11)	C10—C1—P1—Pd1	-179.9 (9)
C30—C3—N1—Pd1	-53.9 (10)	C2—C1—P1—Pd1	-47.3 (10)

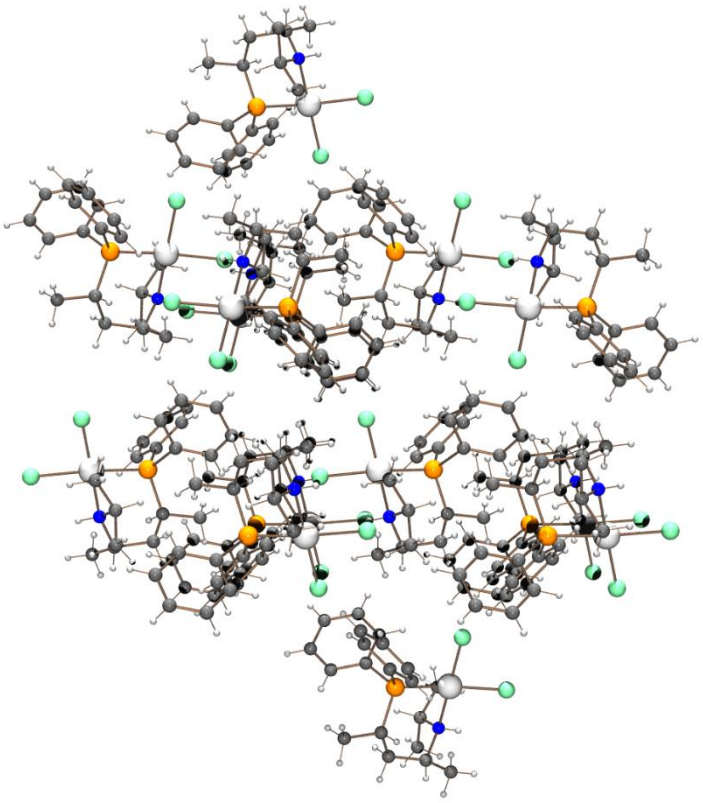


Figure S10 Packing diagram of **2a**, view normal to (010)

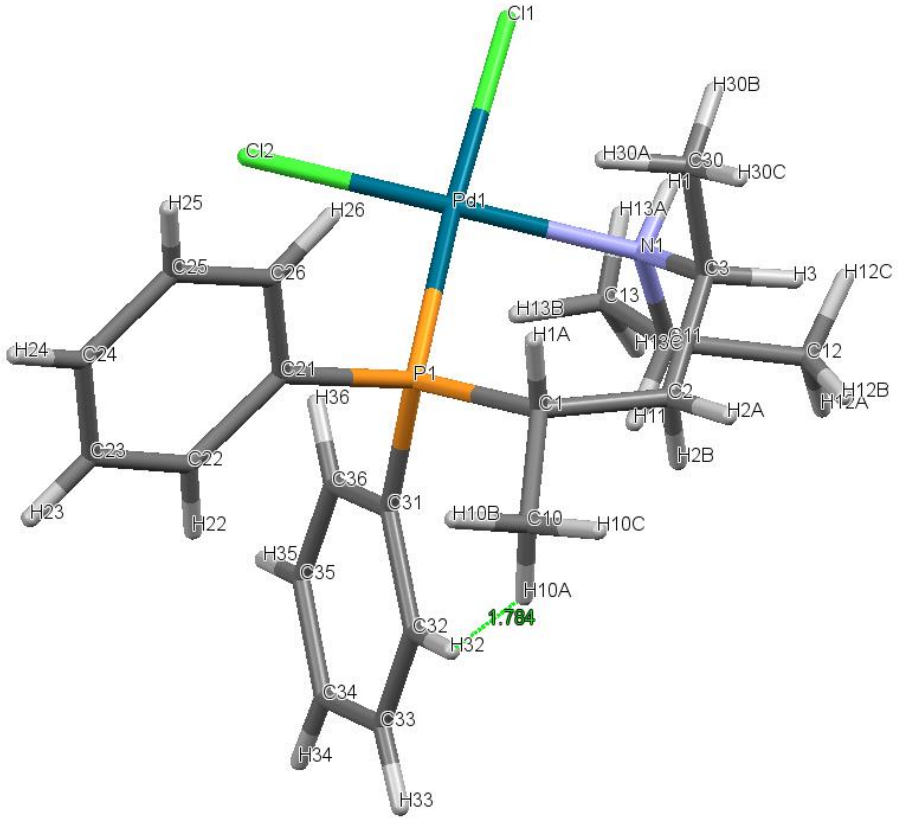


Figure S11 Short H-H distance in the structure between H32 and H10A

2. Characterization of 2b

2.1. NMR analysis

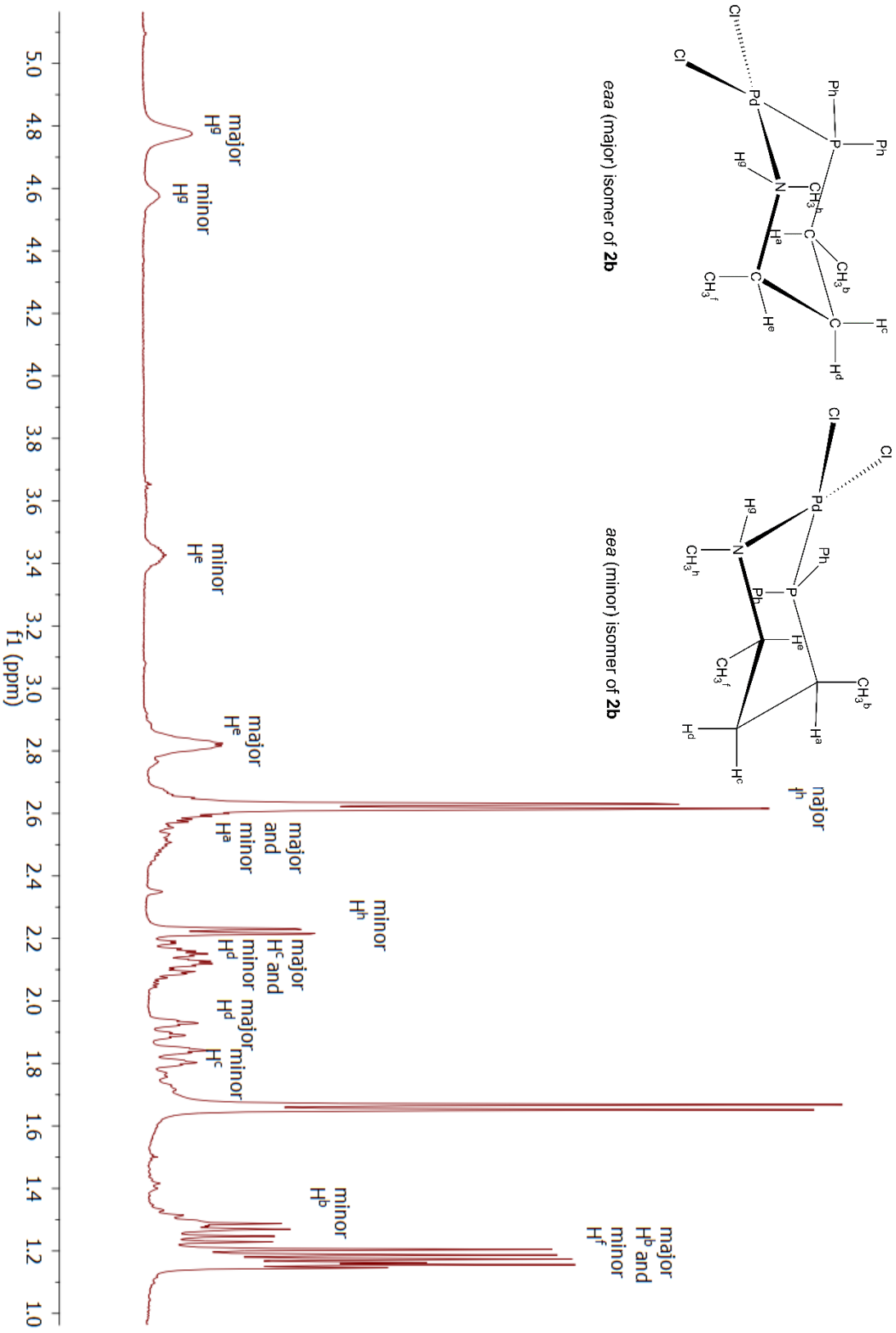


Figure S12. Selected range of ^{1}H NMR spectrum of **2b** (400 MHz, CD_2Cl_2)

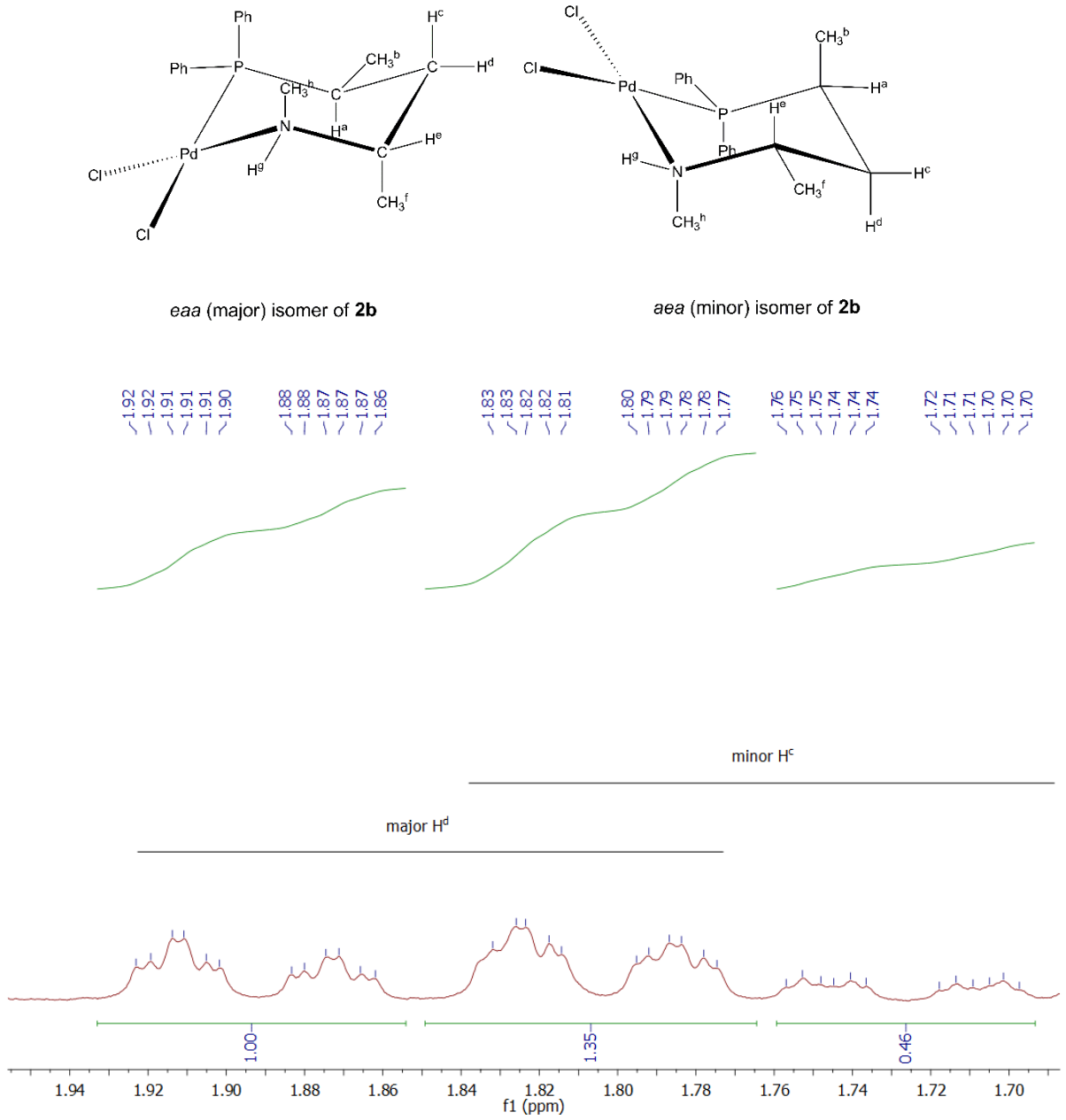


Figure S13 Signals of equatorial methylene protons in the isomers of **2b** (400 MHz, $CDCl_3$); the signals of the equatorial protons of major and minor isomers partly overlap that is indicated by the difference in the corresponding integrals, the coupling constant $^3J(P,H^c)$ is an approximated value.

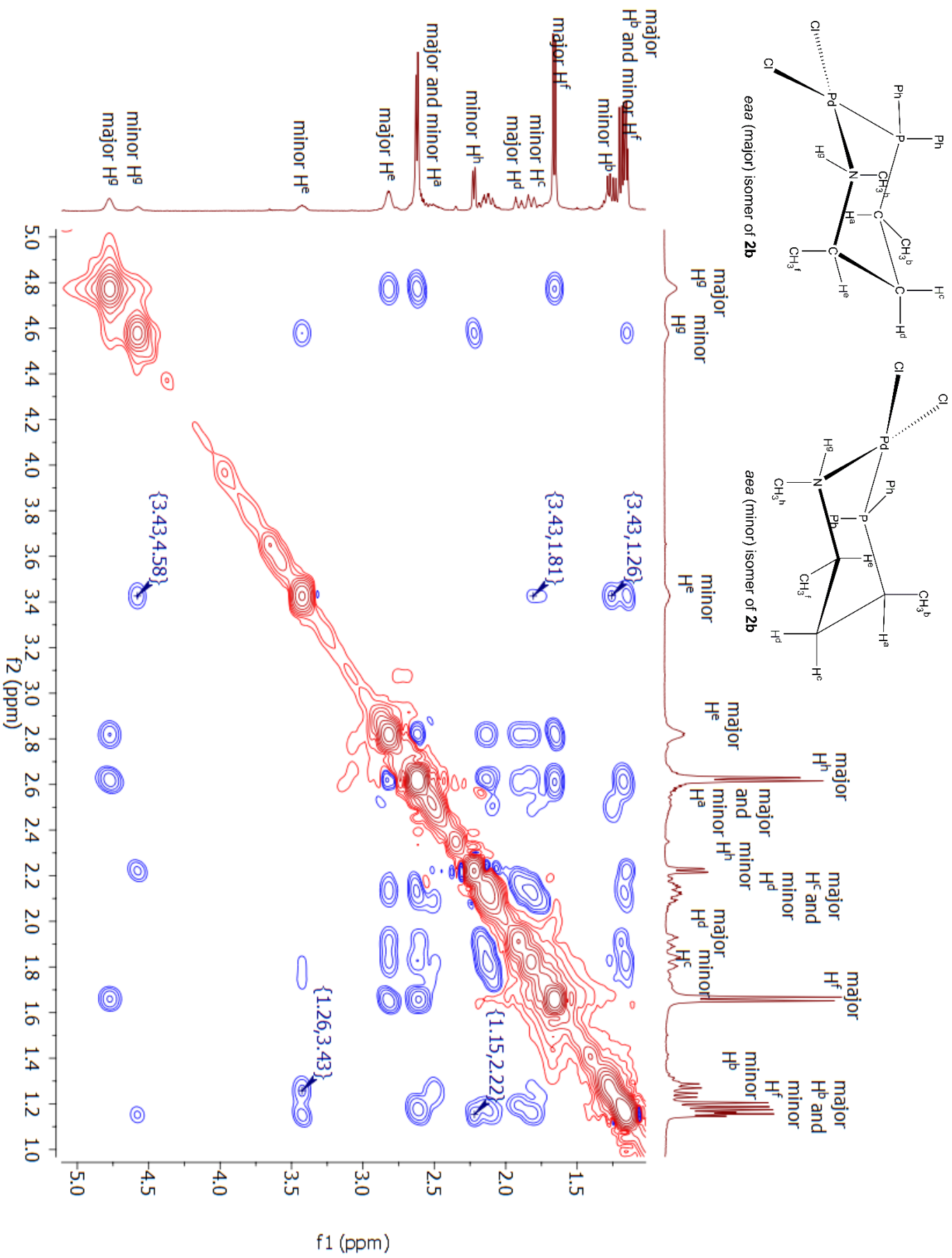
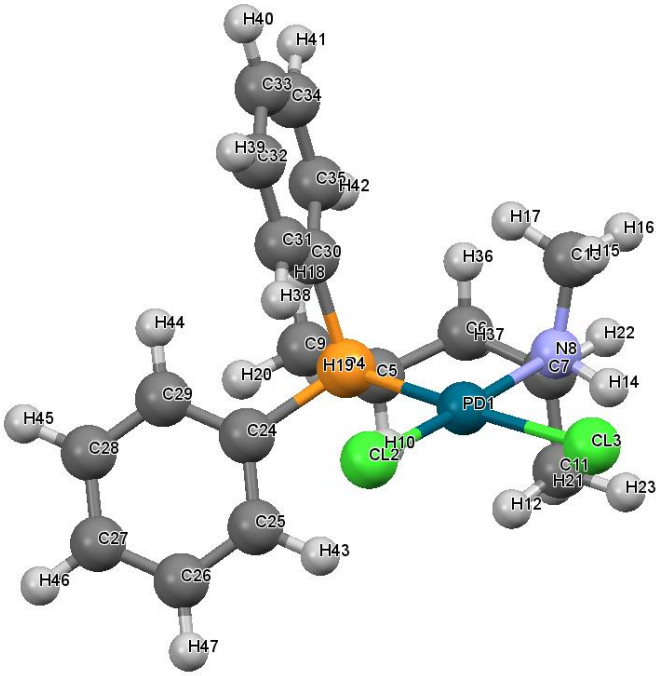


Figure S14 Selected area of ^{1}H-^{1}H NOESY spectrum of **2b** (400 MHz, $CDCl_3$)

2.2. Theoretical Calculations

Cartesian coordinates of *eaa* conformation of complex **2b** (rel. enthalpy: 0 kJ/mol)



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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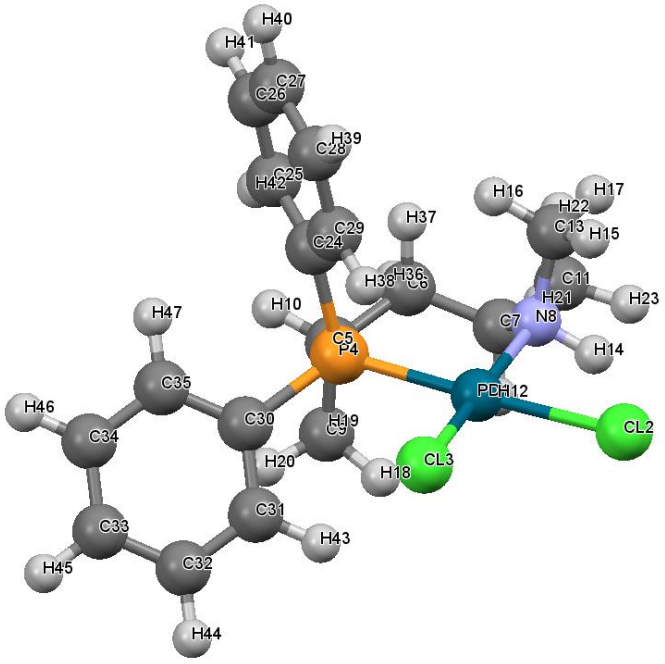
2	17	0	-0.243300	-1.618833	-2.255501
3	17	0	-3.506819	-1.054217	-1.458582
4	15	0	0.590574	0.076224	0.386515
5	6	0	0.363921	0.224130	2.230098
6	6	0	-0.874821	1.033139	2.650806
7	6	0	-2.253691	0.487893	2.256874
8	7	0	-2.526491	0.594194	0.803658
9	6	0	1.605829	0.651281	3.022834
10	1	0	0.176440	-0.825457	2.488626
11	6	0	-2.500341	-0.946456	2.712646
12	1	0	-1.890204	-1.659852	2.152271
13	6	0	-2.693538	1.980404	0.321955
14	1	0	-3.408755	0.111036	0.611083
15	1	0	-3.112065	1.938627	-0.683964
16	1	0	-3.371450	2.539906	0.978854
17	1	0	-1.731087	2.491434	0.277863
18	1	0	1.842357	1.710404	2.899633
19	1	0	1.431539	0.476784	4.089792
20	1	0	2.485562	0.074735	2.729673
21	1	0	-2.277275	-1.051356	3.778605
22	1	0	-2.987722	1.133589	2.761181
23	1	0	-3.547023	-1.225337	2.558383
24	6	0	1.995693	-1.079066	0.270161
25	6	0	1.746124	-2.451789	0.343278
26	6	0	2.801653	-3.354134	0.344769
27	6	0	4.112382	-2.895918	0.258813
28	6	0	4.366740	-1.532000	0.172949

29	6	0	3.312940	-0.624549	0.180464
30	6	0	1.175957	1.649218	-0.336367
31	6	0	1.448027	1.632679	-1.711794
32	6	0	1.852906	2.791709	-2.359329
33	6	0	1.977005	3.984553	-1.652424
34	6	0	1.694214	4.013378	-0.292982
35	6	0	1.296460	2.851947	0.363553
36	1	0	-0.784780	2.071414	2.314788
37	1	0	-0.868075	1.081033	3.746536
38	1	0	1.322062	0.711142	-2.273303
39	1	0	2.061101	2.763717	-3.424007
40	1	0	2.287894	4.890669	-2.162847
41	1	0	1.784066	4.940380	0.264623
42	1	0	1.082608	2.900163	1.423684
43	1	0	0.723979	-2.815063	0.360201
44	1	0	3.519727	0.438193	0.108016
45	1	0	5.387291	-1.170268	0.096630
46	1	0	4.935565	-3.603521	0.248364
47	1	0	2.597306	-4.418858	0.391431

Cartesian coordinates of *aea* conformation of complex **2b** (rel. enthalpy: -2 kJ/mol)



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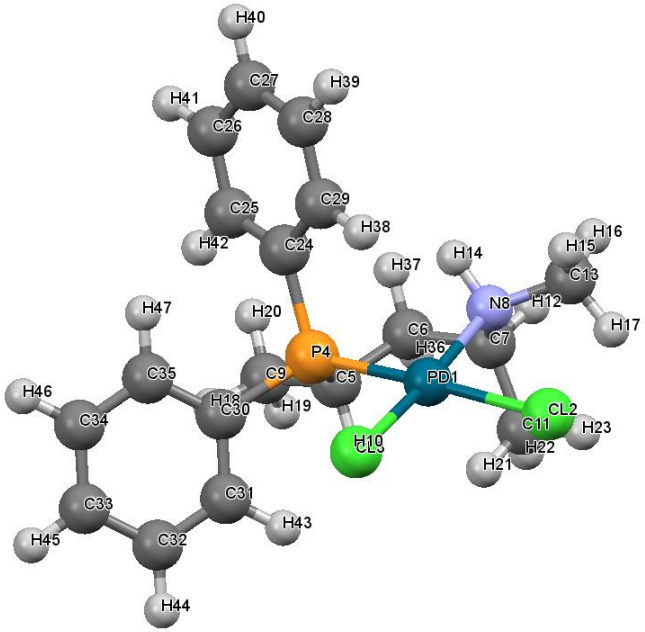
3	17	0	0.144355	-2.004235	-2.043902
4	15	0	0.630636	0.147572	0.372661
5	6	0	0.293192	0.562861	2.152848
6	6	0	-1.049916	1.287897	2.350432
7	6	0	-2.319456	0.487382	2.042588
8	7	0	-2.540447	0.306121	0.582870
9	6	0	0.403197	-0.690056	3.031878

10	1	0	1.085942	1.250606	2.469830
11	6	0	-3.535076	1.112097	2.732447
12	1	0	-2.203543	-0.528615	2.429376
13	6	0	-2.870684	1.533974	-0.173670
14	1	0	-3.333630	-0.330223	0.464110
15	1	0	-3.168827	1.230573	-1.177388
16	1	0	-1.996946	2.182084	-0.250117
17	1	0	-3.693359	2.084906	0.291950
18	1	0	-0.241968	-1.502424	2.683552
19	1	0	0.111804	-0.445579	4.059118
20	1	0	1.425442	-1.071131	3.053000
21	1	0	-3.441502	0.993991	3.815675
22	1	0	-3.626726	2.182093	2.524542
23	1	0	-4.462723	0.619943	2.422949
24	6	0	0.971785	1.730840	-0.477072
25	6	0	1.265090	2.925584	0.186338
26	6	0	1.516081	4.088415	-0.535630
27	6	0	1.483121	4.067254	-1.925002
28	6	0	1.197230	2.880841	-2.593535
29	6	0	0.937315	1.719175	-1.877504
30	6	0	2.237586	-0.713911	0.447679
31	6	0	2.280852	-2.108966	0.510405
32	6	0	3.498400	-2.761759	0.658066
33	6	0	4.679775	-2.031719	0.734110
34	6	0	4.643805	-0.643603	0.662680
35	6	0	3.427655	0.014215	0.520400
36	1	0	-1.101562	1.576277	3.407034
37	1	0	-1.065978	2.226703	1.785976
38	1	0	0.707703	0.795074	-2.400910
39	1	0	1.170506	2.857834	-3.678203
40	1	0	1.679454	4.975113	-2.486760
41	1	0	1.740033	5.010661	-0.008680
42	1	0	1.305022	2.963839	1.269944
43	1	0	1.366588	-2.682499	0.413091
44	1	0	3.522965	-3.845980	0.697020
45	1	0	5.630227	-2.545538	0.840033
46	1	0	5.563803	-0.069632	0.711826
47	1	0	3.410774	1.097312	0.453650

Cartesian coordinates of *eae* conformation of complex **2b** (rel. enthalpy: 30 kJ/mol)



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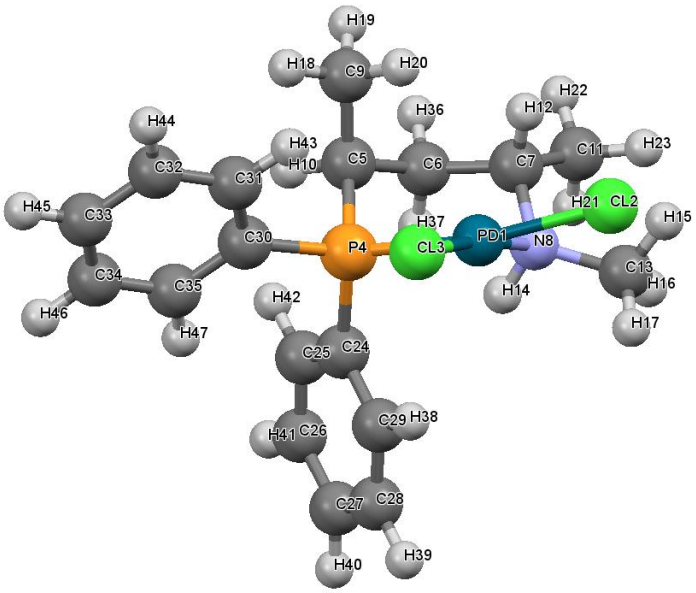
4	15	0	0.674628	0.090007	0.290424
5	6	0	0.464724	0.321200	2.133556
6	6	0	-0.660597	1.311422	2.477180
7	6	0	-2.094573	0.999528	2.030732
8	7	0	-2.221796	1.073059	0.545786
9	6	0	1.726282	0.673591	2.929219
10	1	0	0.149019	-0.681745	2.444684
11	6	0	-2.636804	-0.318316	2.570338
12	1	0	-2.713414	1.811545	2.439017
13	6	0	-3.593052	1.446620	0.129892
14	1	0	-1.627986	1.844722	0.242534
15	1	0	-3.619137	1.556280	-0.953086
16	1	0	-3.882161	2.387024	0.615461
17	1	0	-4.288719	0.653486	0.389042
18	1	0	2.586300	0.073133	2.624238
19	1	0	1.548476	0.487714	3.993685
20	1	0	1.984522	1.731135	2.827317
21	1	0	-2.068691	-1.173385	2.195906
22	1	0	-2.596035	-0.313668	3.664286
23	1	0	-3.675262	-0.472037	2.269746
24	6	0	1.133188	1.703345	-0.444469
25	6	0	2.133655	2.540017	0.068035
26	6	0	2.415602	3.757242	-0.539404
27	6	0	1.711323	4.154907	-1.672218
28	6	0	0.730704	3.326164	-2.202741
29	6	0	0.443755	2.108221	-1.593914
30	6	0	2.133845	-0.991226	0.160350
31	6	0	2.050076	-2.276605	0.706133
32	6	0	3.144447	-3.127628	0.663638
33	6	0	4.328103	-2.713959	0.059002

34	6	0	4.410664	-1.447471	-0.504211
35	6	0	3.318510	-0.586319	-0.453627
36	1	0	-0.687605	1.401579	3.569687
37	1	0	-0.381366	2.308193	2.107780
38	1	0	-0.309291	1.452067	-2.022350
39	1	0	0.190122	3.619966	-3.096719
40	1	0	1.935681	5.105813	-2.145124
41	1	0	3.193012	4.394507	-0.129895
42	1	0	2.713619	2.235556	0.930749
43	1	0	1.117248	-2.627233	1.135693
44	1	0	3.065718	-4.124476	1.085090
45	1	0	5.180252	-3.385050	0.017140
46	1	0	5.325834	-1.124035	-0.989945
47	1	0	3.394840	0.397004	-0.903158

Cartesian coordinates of *aee* conformation of complex **2b** (rel. enthalpy: 35 kJ/mol)



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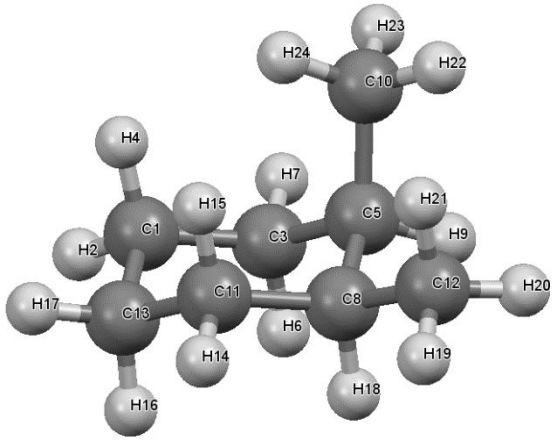
3	17	0	-0.054337	-2.560236	-1.529610
4	15	0	-0.703620	0.137186	0.295619
5	6	0	-0.335026	0.468702	2.091096
6	6	0	0.924733	1.329523	2.295849
7	6	0	2.277977	0.823085	1.773693
8	7	0	2.259543	0.786871	0.273609
9	6	0	-0.247648	-0.847761	2.872918
10	1	0	-1.181280	1.039570	2.493006
11	6	0	3.382967	1.710738	2.351175
12	1	0	2.458246	-0.205119	2.098282
13	6	0	3.584632	0.941416	-0.373596
14	1	0	1.711383	1.590301	-0.034700
15	1	0	4.244722	0.138838	-0.054714
16	1	0	4.017744	1.917843	-0.139057
17	1	0	3.452563	0.844874	-1.450201

18	1	0	-1.195961	-1.388052	2.855632
19	1	0	-0.003415	-0.636478	3.919455
20	1	0	0.523125	-1.511705	2.470040
21	1	0	3.264388	2.756257	2.044351
22	1	0	3.333724	1.676391	3.443028
23	1	0	4.378811	1.374468	2.058722
24	6	0	-0.922524	1.780209	-0.481586
25	6	0	-1.389538	2.906861	0.204518
26	6	0	-1.536258	4.122667	-0.453464
27	6	0	-1.224114	4.226225	-1.805556
28	6	0	-0.764782	3.111923	-2.498873
29	6	0	-0.610754	1.896114	-1.841195
30	6	0	-2.366940	-0.616665	0.315020
31	6	0	-2.504730	-1.982818	0.584641
32	6	0	-3.768419	-2.552369	0.675534
33	6	0	-4.904674	-1.773861	0.484234
34	6	0	-4.774964	-0.419770	0.200057
35	6	0	-3.513185	0.157625	0.115833
36	1	0	1.031281	1.467586	3.377763
37	1	0	0.762628	2.334168	1.884013
38	1	0	-0.247935	1.026251	-2.382029
39	1	0	-0.523038	3.186117	-3.554218
40	1	0	-1.339584	5.176204	-2.317766
41	1	0	-1.897313	4.989687	0.090674
42	1	0	-1.648135	2.841137	1.256867
43	1	0	-1.625667	-2.606493	0.688528
44	1	0	-3.861517	-3.614225	0.878965
45	1	0	-5.890226	-2.224790	0.546570
46	1	0	-5.656758	0.192250	0.038485
47	1	0	-3.429140	1.213579	-0.114459

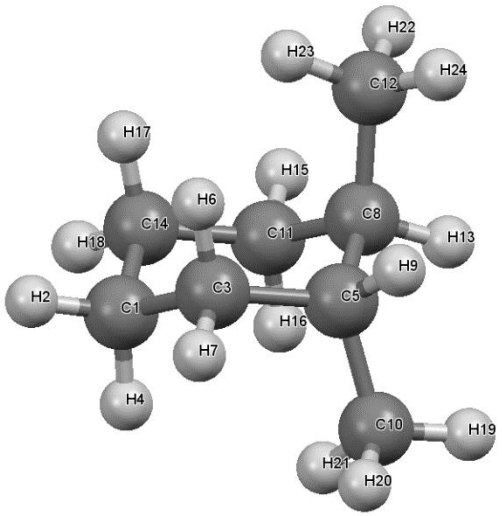
Cartesian coordinates of *ea* conformation of 1,2-dimethylcyclohexane (rel. enthalpy: 0 kJ/mol)



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.962744	0.142938	0.179746
2	1	0	-3.017331	0.194701	-0.110978
3	6	0	-1.122348	1.020748	-0.750637
4	1	0	-1.908628	0.527230	1.205629
5	6	0	0.381255	0.957482	-0.434511
6	1	0	-1.278704	0.684337	-1.783854

7	1	0	-1.467156	2.060071	-0.707274
8	6	0	0.857709	-0.512879	-0.465628
9	1	0	0.909956	1.483169	-1.241050
10	6	0	0.718871	1.690025	0.868234
11	6	0	0.019008	-1.398365	0.465153
12	6	0	2.351609	-0.666069	-0.188661
13	6	0	-1.475614	-1.306444	0.153519
14	1	0	0.358367	-2.437174	0.381274
15	1	0	0.194990	-1.104924	1.508209
16	1	0	-1.659937	-1.727822	-0.843682
17	1	0	-2.049549	-1.916227	0.859386
18	1	0	0.675614	-0.867818	-1.490751
19	1	0	2.676521	-1.695043	-0.369570
20	1	0	2.946575	-0.010082	-0.832172
21	1	0	2.595983	-0.425035	0.850201
22	1	0	1.798112	1.749615	1.028020
23	1	0	0.335791	2.714444	0.837007
24	1	0	0.282917	1.205941	1.746318

Cartesian coordinates of *aa* conformation of 1,2-dimethylcyclohexane (rel. enthalpy: 5 kJ/mol)



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.193312	0.739928	1.668276
2	1	0	-0.792362	0.977663	2.553732
3	6	0	-0.969970	1.106455	0.400927
4	1	0	0.714506	1.351358	1.739600
5	6	0	-0.215010	0.742692	-0.889968
6	1	0	-1.933743	0.583677	0.416444
7	1	0	-1.204479	2.176922	0.396083
8	6	0	0.215010	-0.742692	-0.889968
9	1	0	-0.910260	0.881140	-1.728502
10	6	0	0.969970	1.680639	-1.138211
11	6	0	0.969970	-1.106455	0.400927
12	6	0	-0.969970	-1.680639	-1.138211
13	1	0	0.910260	-0.881140	-1.728502
14	6	0	0.193312	-0.739928	1.668276
15	1	0	1.204479	-2.176922	0.396083
16	1	0	1.933743	-0.583677	0.416444
17	1	0	-0.714506	-1.351358	1.739600

18	1	0	0.792362	-0.977663	2.553732
19	1	0	1.460469	1.446410	-2.087860
20	1	0	0.639260	2.722806	-1.182247
21	1	0	1.728067	1.611986	-0.353393
22	1	0	-0.639260	-2.722806	-1.182247
23	1	0	-1.728067	-1.611986	-0.353393
24	1	0	-1.460469	-1.446410	-2.087860

3. Characterization of complex 3a

3.1. NMR analysis

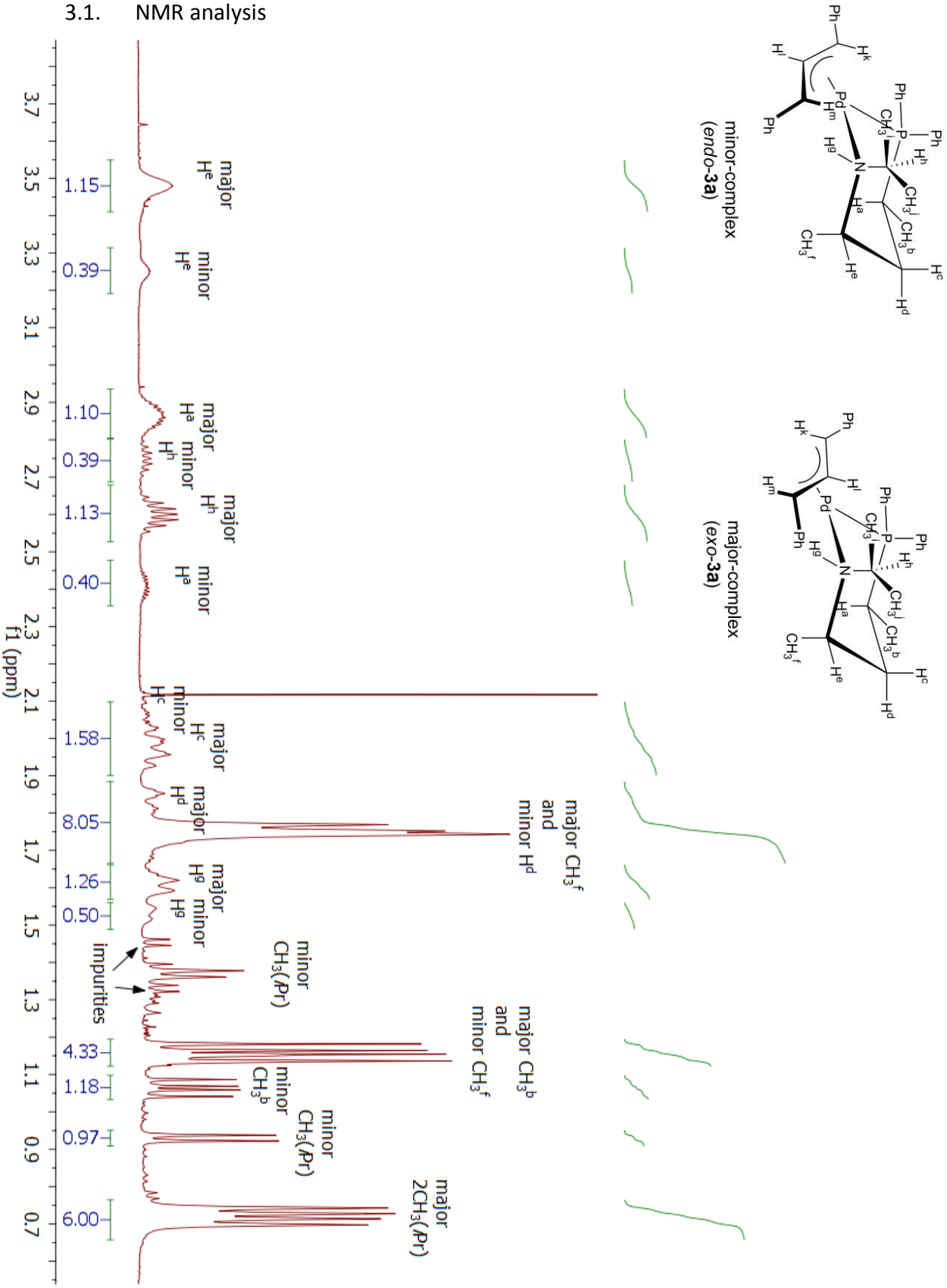


Figure S15 Selected area of ^{1}H NMR spectrum of **3a** (400 MHz, CD_2Cl_2)

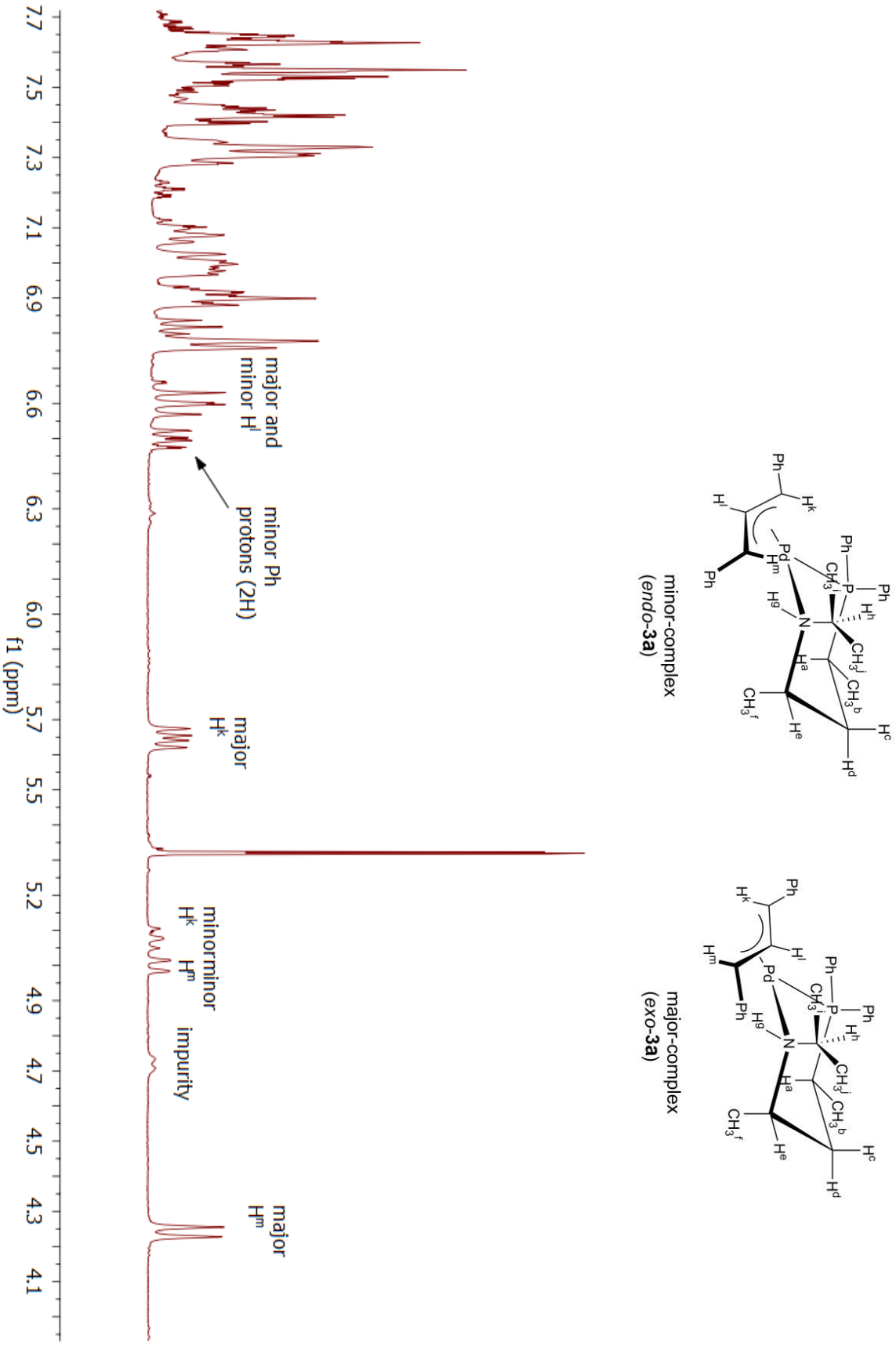


Figure S16 Selected area of ^{1}H NMR spectrum of **3a** (400 MHz, CD_2Cl_2)

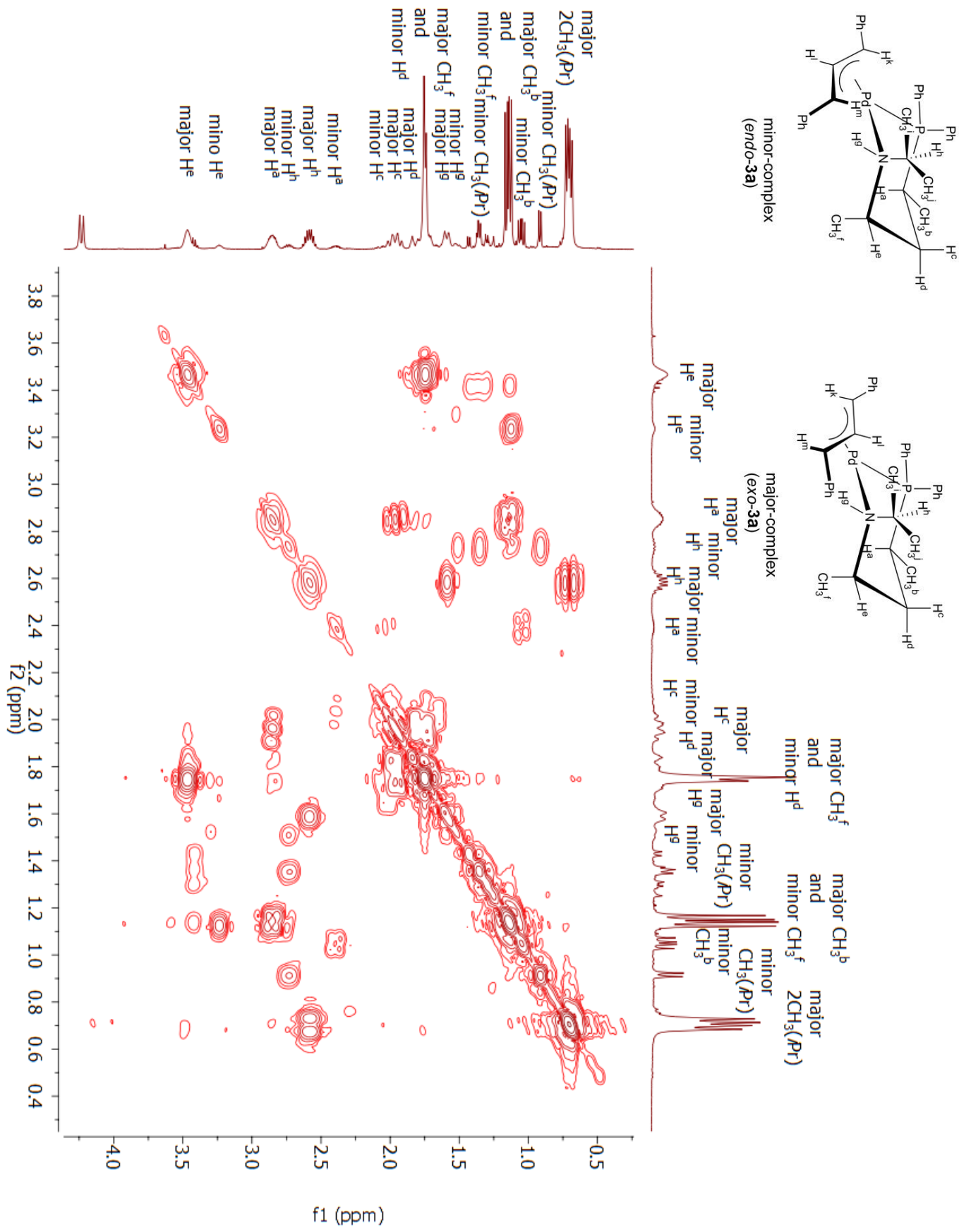


Figure S17 Selected area of ^{1}H-^{1}H COSY NMR spectrum of **3a** (400 MHz, CD_2Cl_2)

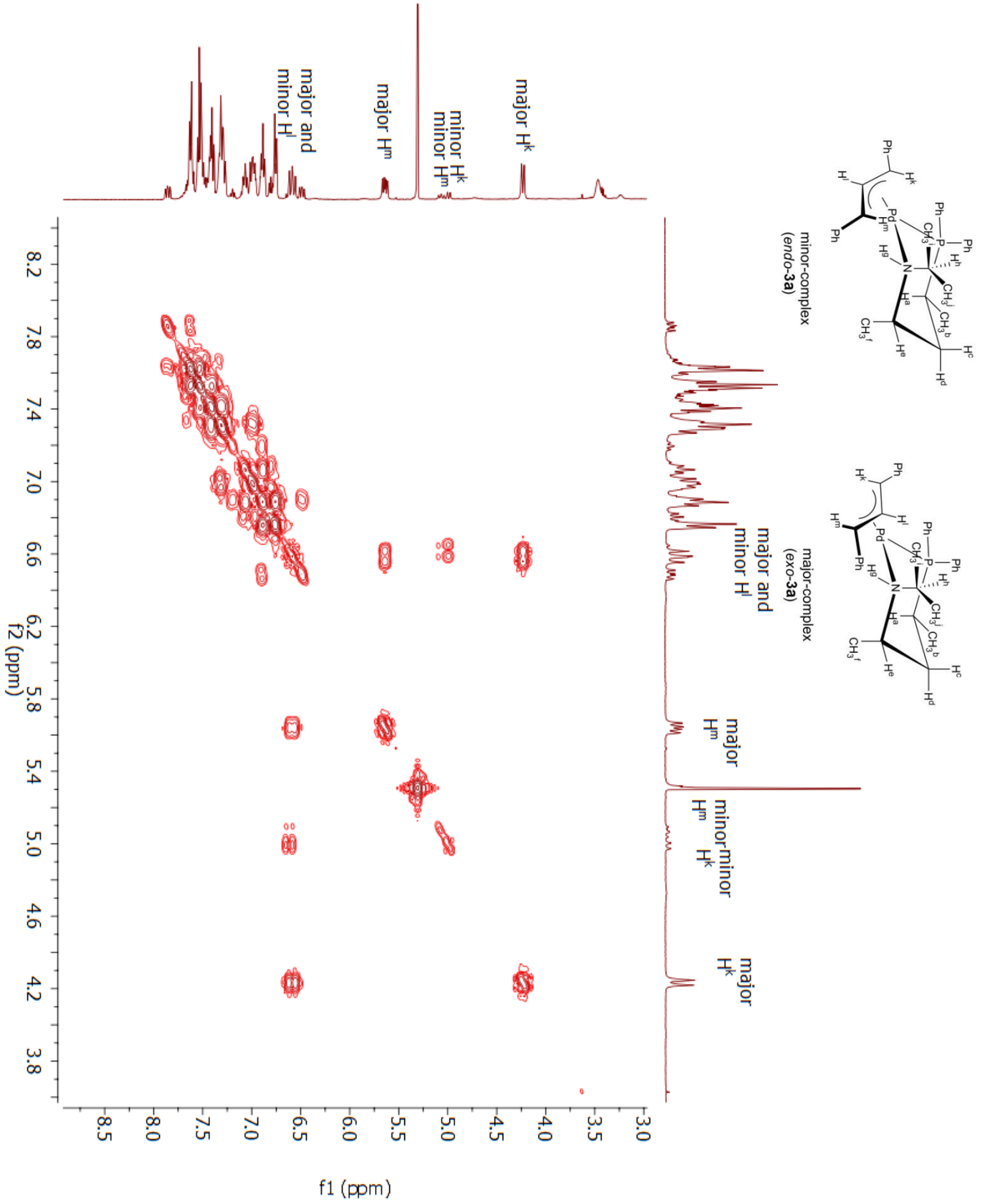


Figure S18 Selected area of ^{1}H-^{1}H COSY NMR spectrum of **3a** (400 MHz, CD_2Cl_2)

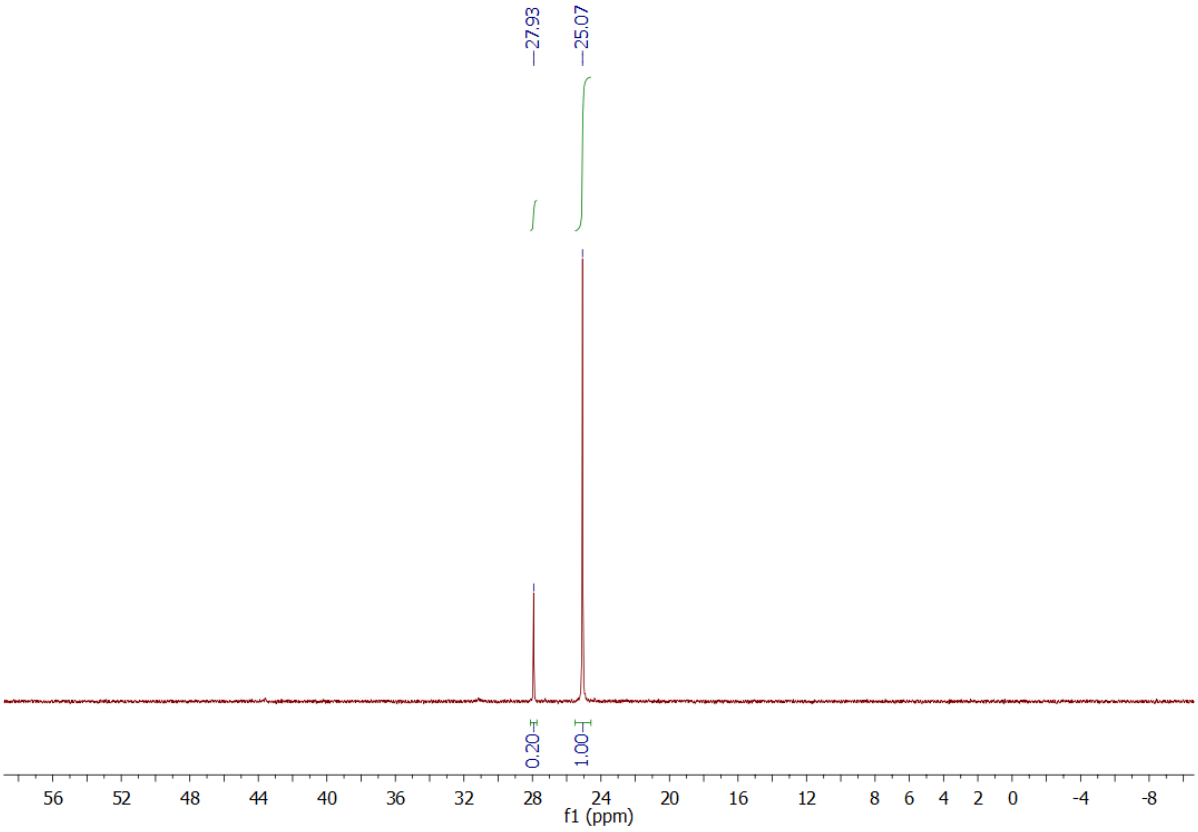


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of **3a** (162 MHz, CD_2Cl_2)

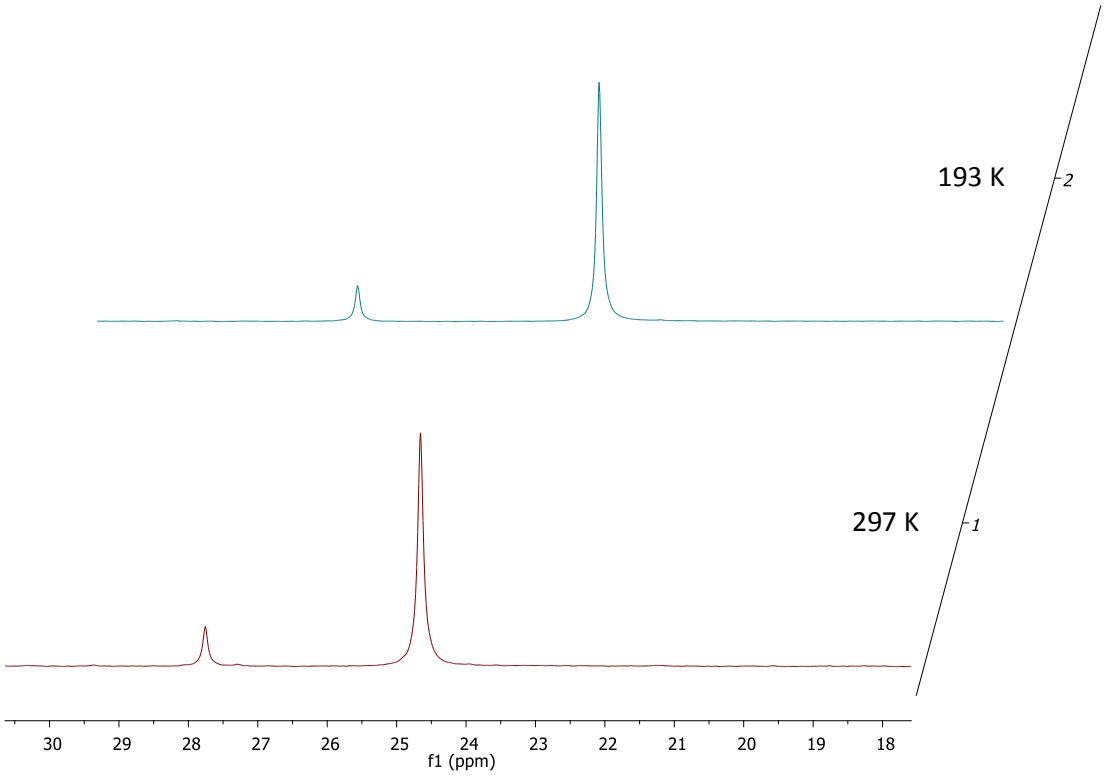


Figure S20. $^{31}P\{^{1}H\}$ NMR spectrum of **3a** (162 MHz, d_6-acetone) at 193 and 297 K. The ratio of the minor and major isomers is approximately 1 to 7 at both temperatures.

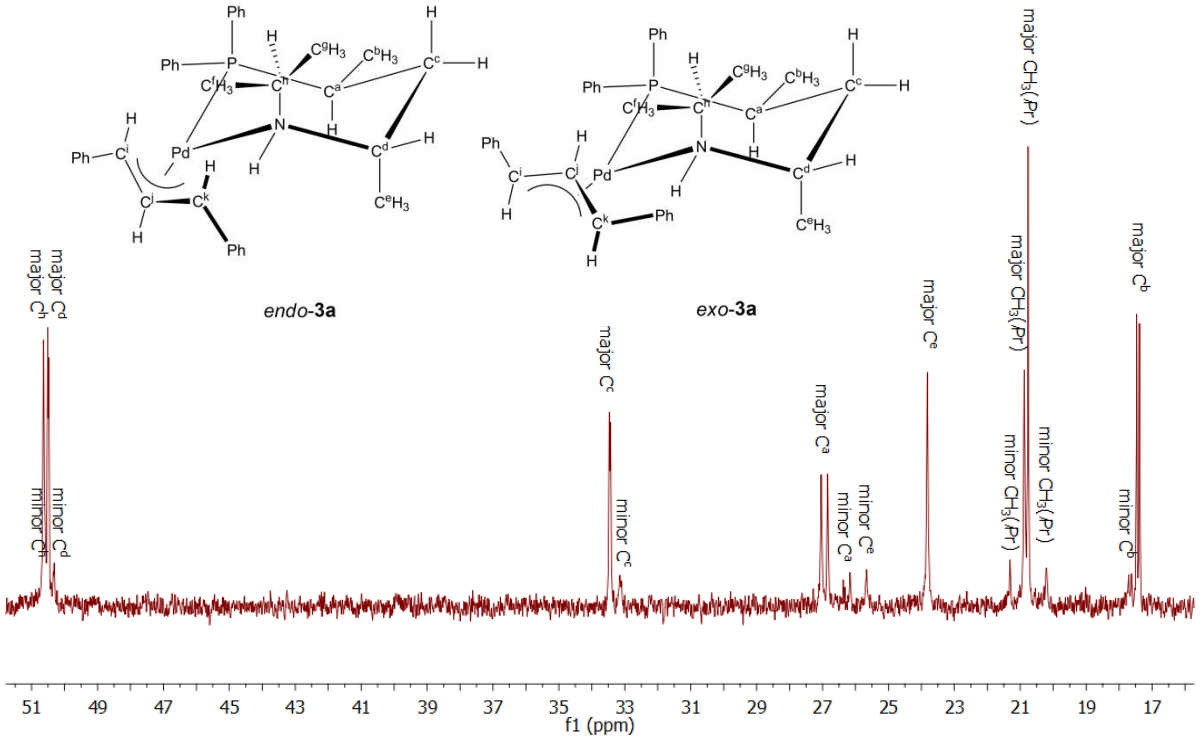


Figure S21 Selected region of $^{13}C\{^{1}H\}$ NMR spectrum of **3a** (101 MHz, CD_2Cl_2)

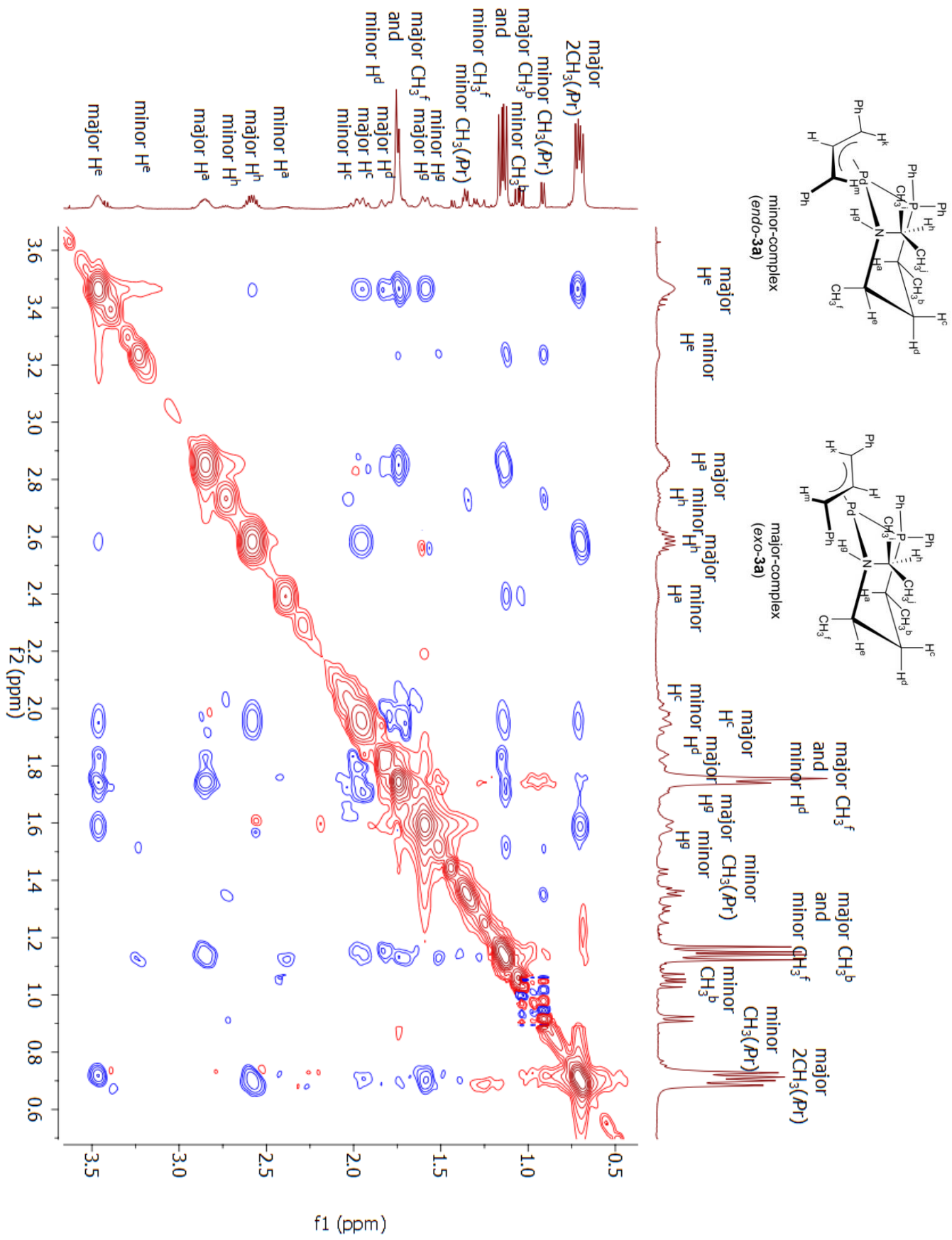


Figure S22 Selected area of ^{1}H-^{1}H NOESY NMR spectrum of **3a** (400 MHz, CD_2Cl_2)

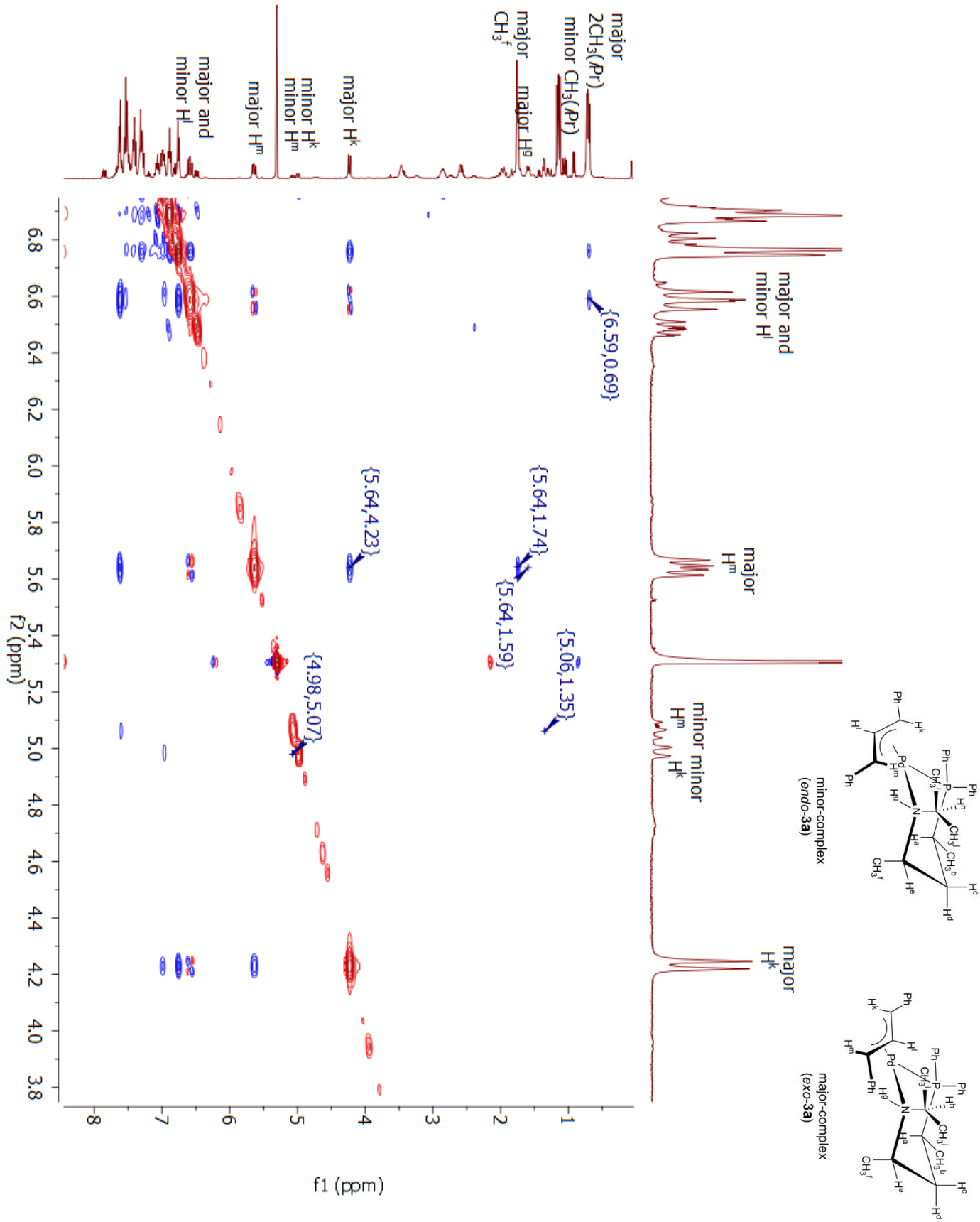
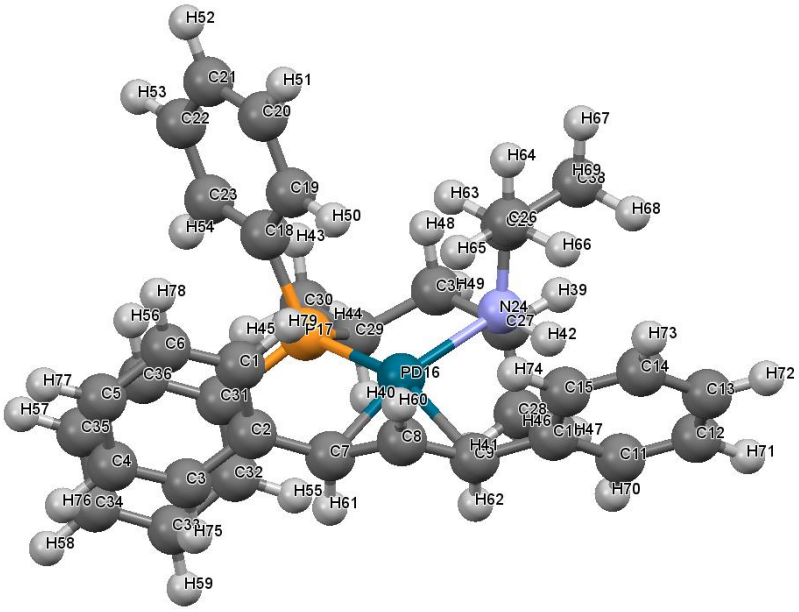


Figure S23 Selected area of ^{1}H-^{1}H NOESY NMR spectrum of **3a** (400 MHz, CD_2Cl_2)

3.2. Theoretical calculations

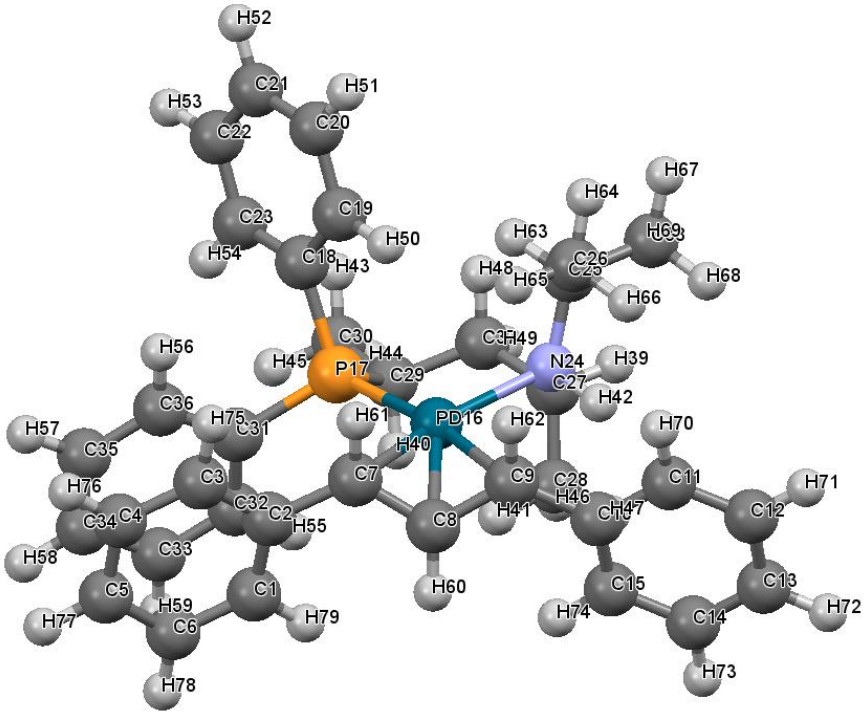
Cartesian coordinates of *exo*-**3a** (rel. enthalpy: 0 kJ/mol)



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.171619	2.660801	1.812398
2	6	0	1.174930	2.761885	0.415696
3	6	0	2.275963	3.352738	-0.208615
4	6	0	3.336044	3.849688	0.540329
5	6	0	3.315345	3.755191	1.926394
6	6	0	2.230196	3.154565	2.560450
7	6	0	0.042915	2.293341	-0.412067
8	6	0	-1.307785	2.389259	0.028316
9	6	0	-2.328680	1.850734	-0.750246
10	6	0	-3.736636	1.678489	-0.360910
11	6	0	-4.617770	1.113357	-1.291721
12	6	0	-5.954911	0.903568	-0.975463
13	6	0	-6.435658	1.264326	0.277842
14	6	0	-5.572649	1.838467	1.209197
15	6	0	-4.236537	2.041192	0.896267
16	46	0	-0.732376	0.274679	-0.315356
17	15	0	1.266242	-0.965061	-0.445126
18	6	0	1.874366	-1.648354	1.134556
19	6	0	1.158872	-1.364512	2.301616
20	6	0	1.567662	-1.873241	3.529764
21	6	0	2.704770	-2.667795	3.607137
22	6	0	3.437683	-2.943418	2.456327
23	6	0	3.029829	-2.436269	1.229369
24	7	0	-2.045977	-1.517620	-0.303581
25	6	0	-2.219436	-2.129290	1.052087
26	6	0	-2.688322	-1.053625	2.024872
27	6	0	-1.728343	-2.475320	-1.400353
28	6	0	-1.897948	-1.773902	-2.743683
29	6	0	0.919406	-2.392139	-1.599100

30	6	0	2.081966	-3.372516	-1.782536
31	6	0	2.683186	-0.120857	-1.234674
32	6	0	2.568624	0.268060	-2.575812
33	6	0	3.606180	0.936966	-3.210743
34	6	0	4.772049	1.238711	-2.511710
35	6	0	4.885924	0.877043	-1.175965
36	6	0	3.847617	0.204597	-0.537781
37	6	0	-0.363125	-3.163681	-1.237788
38	6	0	-3.188681	-3.312528	1.063228
39	1	0	-2.472450	-3.278665	-1.367289
40	1	0	0.758653	-1.892910	-2.560702
41	1	0	-1.245756	-0.899236	-2.833698
42	1	0	-2.948119	-1.097732	-0.540337
43	1	0	2.228059	-3.990763	-0.893090
44	1	0	1.865274	-4.044794	-2.618761
45	1	0	3.019077	-2.856878	-2.008122
46	1	0	-1.667908	-2.460444	-3.563459
47	1	0	-2.931235	-1.437318	-2.877725
48	1	0	-0.269461	-3.578466	-0.227605
49	1	0	-0.392768	-4.036021	-1.901370
50	1	0	0.280437	-0.729753	2.246149
51	1	0	1.001246	-1.642320	4.426148
52	1	0	3.027237	-3.065229	4.564019
53	1	0	4.334192	-3.551910	2.514571
54	1	0	3.627216	-2.640143	0.348917
55	1	0	1.664181	0.050823	-3.137544
56	1	0	3.951066	-0.058716	0.508251
57	1	0	5.786159	1.118648	-0.620359
58	1	0	5.585214	1.757863	-3.008465
59	1	0	3.505949	1.220939	-4.253417
60	1	0	-1.503043	2.680696	1.056422
61	1	0	0.213719	2.362128	-1.486607
62	1	0	-2.142705	1.766117	-1.821557
63	1	0	-1.231969	-2.474731	1.367984
64	1	0	-2.742911	-1.463432	3.036917
65	1	0	-2.004433	-0.199124	2.038300
66	1	0	-3.683978	-0.684169	1.758297
67	1	0	-3.353328	-3.637319	2.094077
68	1	0	-4.162487	-3.029606	0.646955
69	1	0	-2.814893	-4.177271	0.510148
70	1	0	-4.251337	0.854845	-2.282330
71	1	0	-6.623032	0.470715	-1.712842
72	1	0	-7.480329	1.110333	0.526802
73	1	0	-5.946384	2.135169	2.183782
74	1	0	-3.584457	2.494926	1.635495
75	1	0	2.300857	3.425839	-1.291972
76	1	0	4.178799	4.312427	0.037175
77	1	0	4.140891	4.144769	2.513077
78	1	0	2.211181	3.070555	3.642328
79	1	0	0.339103	2.181043	2.319680

Cartesian coordinates of *endo*-**3a** (rel. enthalpy: 5 kJ/mol)



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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2	6	0	1.304236	-2.673182	-1.166111
3	6	0	2.248580	-2.724647	-2.196440
4	6	0	3.406735	-3.479917	-2.063926
5	6	0	3.642927	-4.187260	-0.891212
6	6	0	2.720236	-4.126888	0.150408
7	6	0	0.045817	-1.947174	-1.405544
8	6	0	-1.194348	-2.302880	-0.831850
9	6	0	-2.334822	-1.552939	-1.148292
10	6	0	-3.643772	-1.679861	-0.484822
11	6	0	-4.797196	-1.289260	-1.175622
12	6	0	-6.052625	-1.399978	-0.589469
13	6	0	-6.176168	-1.900249	0.701578
14	6	0	-5.036717	-2.287046	1.403675
15	6	0	-3.782941	-2.173568	0.819827
16	46	0	-0.760644	-0.199816	-0.295531
17	15	0	1.167718	0.926683	0.520062
18	6	0	1.812319	2.205487	-0.617502
19	6	0	1.116184	2.470483	-1.800126
20	6	0	1.557606	3.449538	-2.684440
21	6	0	2.709402	4.171913	-2.398843
22	6	0	3.424136	3.904788	-1.234432
23	6	0	2.983454	2.927555	-0.351735
24	7	0	-2.174987	1.379087	0.386123
25	6	0	-2.371576	2.505676	-0.580919
26	6	0	-2.742819	1.940135	-1.946755
27	6	0	-1.947928	1.793774	1.799451
28	6	0	-2.081796	0.579322	2.711164

29	6	0	0.682468	1.789505	2.105018
30	6	0	1.769608	2.693704	2.694934
31	6	0	2.633107	-0.055965	1.004776
32	6	0	2.701505	-0.672062	2.259666
33	6	0	3.813198	-1.422854	2.620659
34	6	0	4.866293	-1.584870	1.727503
35	6	0	4.796143	-1.001039	0.468343
36	6	0	3.688380	-0.243580	0.107314
37	6	0	-0.638277	2.570521	1.999221
38	6	0	-3.426238	3.516627	-0.125560
39	1	0	-2.752602	2.484075	2.073805
40	1	0	0.520504	0.962981	2.804014
41	1	0	-1.360020	-0.203188	2.455948
42	1	0	-3.046064	0.843826	0.384072
43	1	0	1.912113	3.592285	2.088930
44	1	0	1.474219	3.015313	3.698777
45	1	0	2.729099	2.178444	2.781665
46	1	0	-1.923188	0.870296	3.753704
47	1	0	-3.082989	0.144186	2.635165
48	1	0	-0.543784	3.356221	1.241393
49	1	0	-0.751555	3.105090	2.949671
50	1	0	0.228025	1.893358	-2.037652
51	1	0	1.006228	3.640082	-3.599525
52	1	0	3.058433	4.934633	-3.087304
53	1	0	4.332928	4.455766	-1.015451
54	1	0	3.566987	2.714161	0.536275
55	1	0	1.893165	-0.565857	2.975573
56	1	0	3.656511	0.213423	-0.875613
57	1	0	5.608325	-1.131481	-0.239150
58	1	0	5.737274	-2.166475	2.011562
59	1	0	3.856546	-1.878382	3.604770
60	1	0	-1.222241	-3.022623	-0.018893
61	1	0	0.000895	-1.451291	-2.376257
62	1	0	-2.365446	-1.099190	-2.137898
63	1	0	-1.407431	3.011686	-0.670717
64	1	0	-2.862056	2.752896	-2.667733
65	1	0	-1.973281	1.262028	-2.326090
66	1	0	-3.691307	1.393815	-1.900750
67	1	0	-3.598156	4.245811	-0.921686
68	1	0	-4.382666	3.023357	0.083180
69	1	0	-3.126492	4.076825	0.762757
70	1	0	-4.709621	-0.919269	-2.193583
71	1	0	-6.935228	-1.102657	-1.146224
72	1	0	-7.155166	-1.991159	1.160232
73	1	0	-5.127121	-2.679653	2.411397
74	1	0	-2.903680	-2.466496	1.385595
75	1	0	2.058746	-2.187894	-3.122201
76	1	0	4.119597	-3.522353	-2.881035
77	1	0	4.542978	-4.784294	-0.786133
78	1	0	2.905727	-4.668564	1.072100
79	1	0	0.859561	-3.328393	0.842626

4. Characterization of complex 3b

4.1. NMR analysis

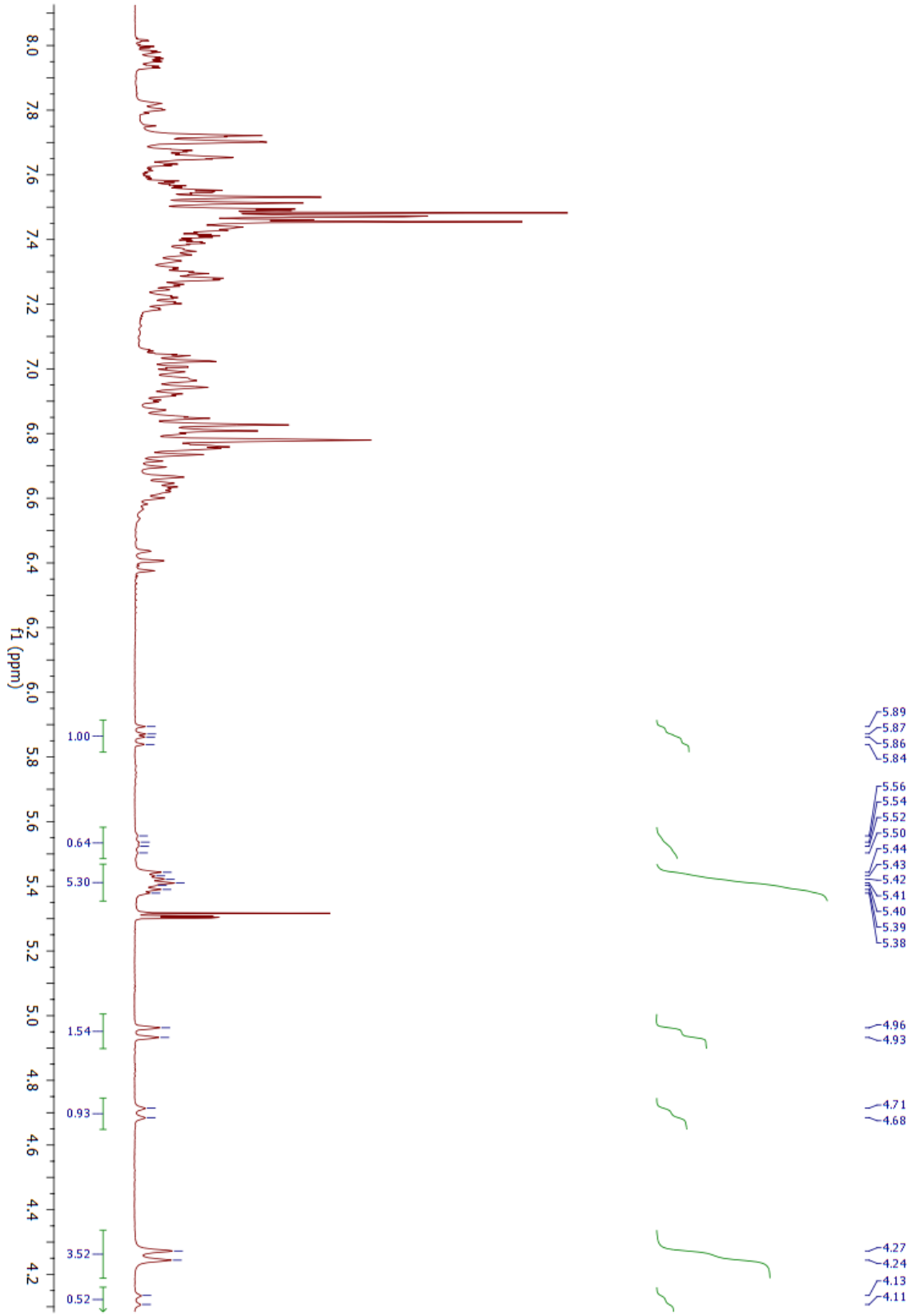

Figure S24 Selected range of ^{1}H NMR spectrum of **3b** (400 MHz, CD_2Cl_2)

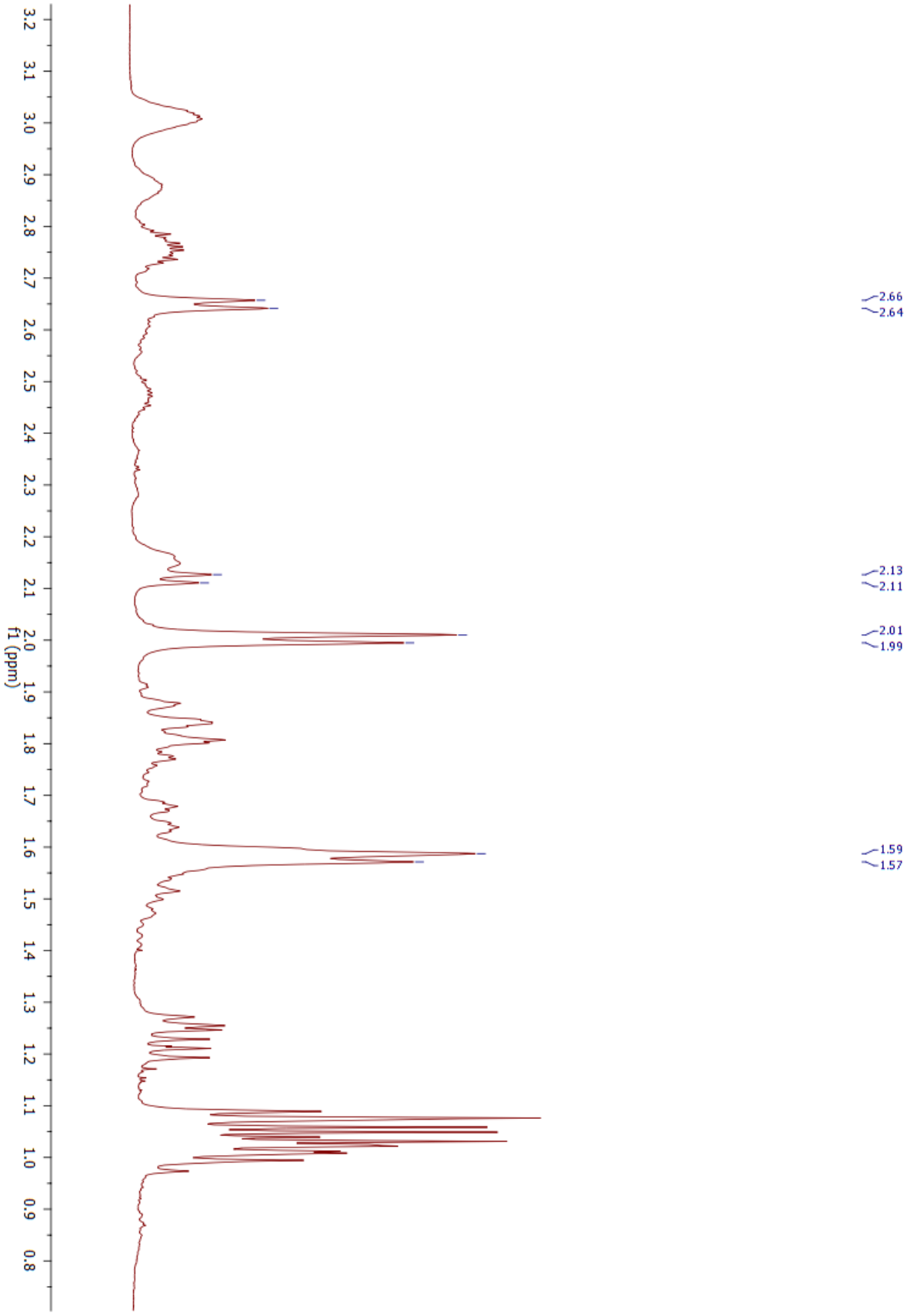

Figure S25 Selected range of ^{1}H NMR spectrum of **3b** (400 MHz, CD_2Cl_2)

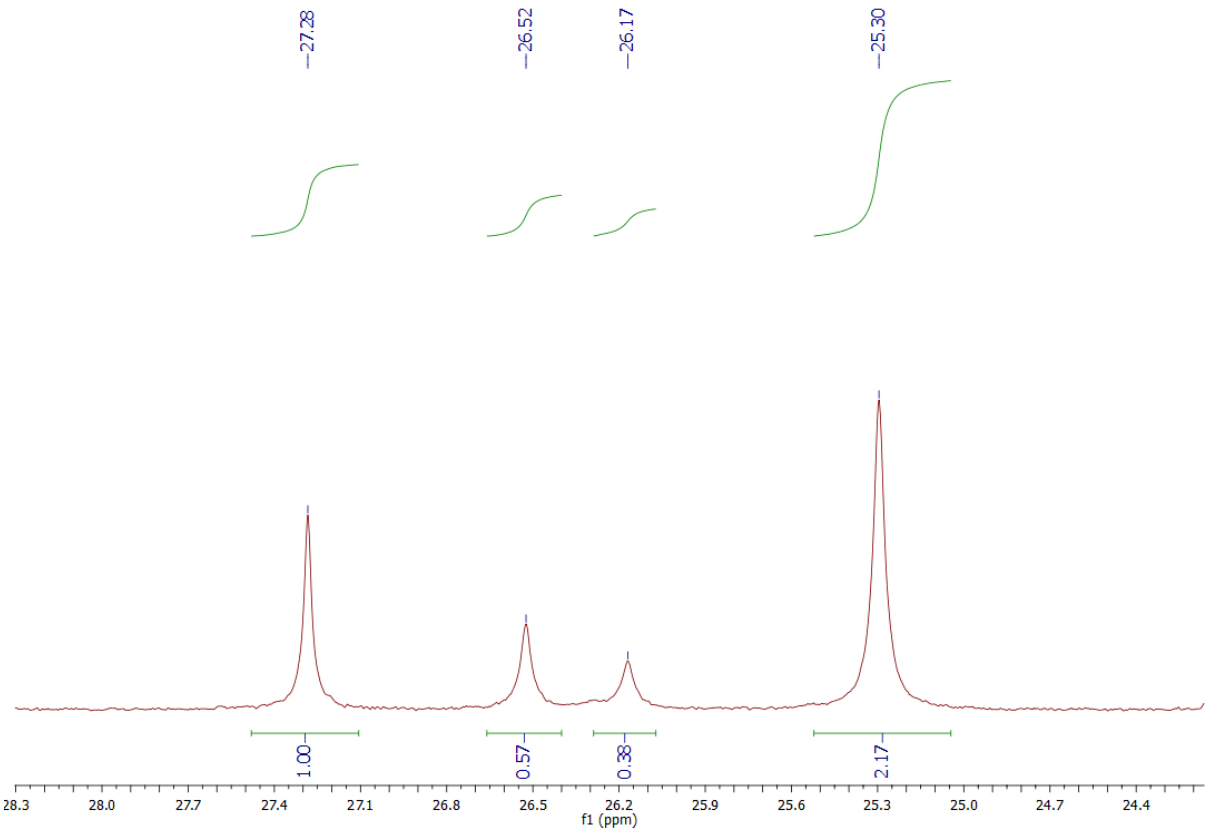

Figure S26 Selected range of $^{31}P\{^{1}H\}$ NMR spectrum of **3b** (162 MHz, CD_2Cl_2)

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