Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supporting Information for: Reversible temperature-induced polymorphic phase transitions of $[Y(OAr)_3]$ and $[Ce(OAr)_3]$ (Ar = 2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$): Interconversions between pyramidal and planar geometries

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NMR spectrum of [Y(O-2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$)$_3$]

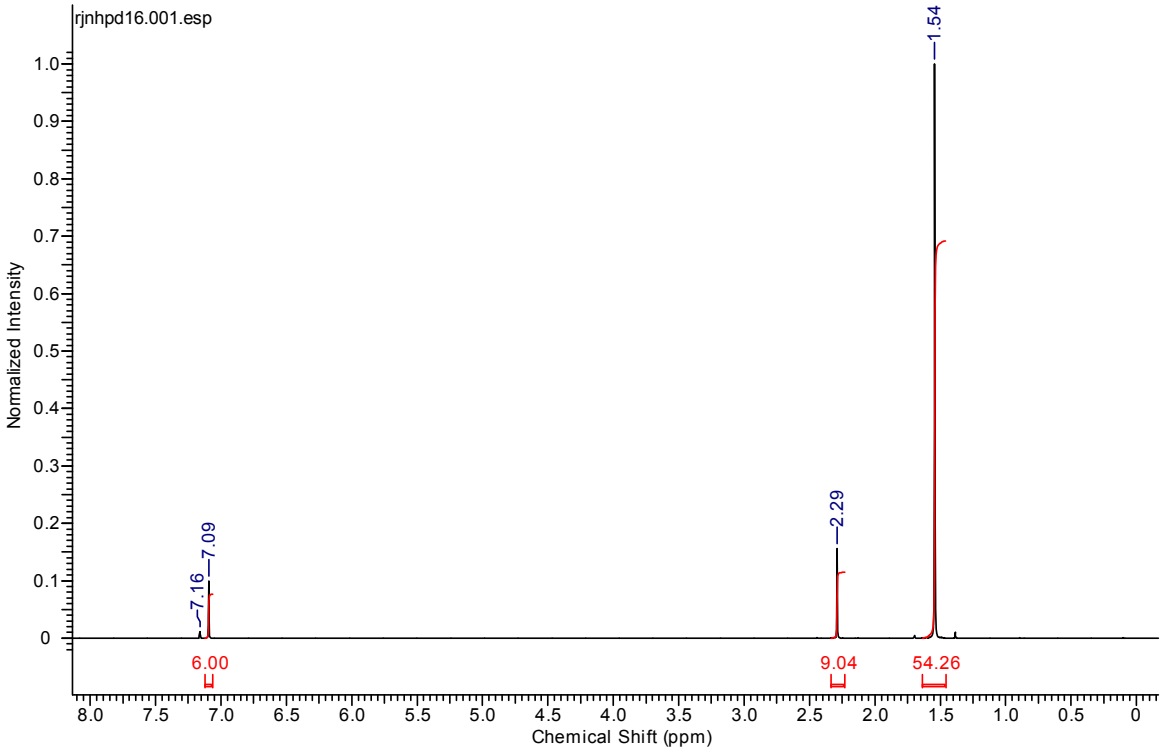

Figure S1. ^{1}H NMR spectrum of **[Y(O-2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$)$_3$]** in C_6D_6 at 25°C.

Crystallographic data

Summary of phases and data for [Y(O-2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$)$_3$] (**1**)

100 K 110 K 120 K 130 K 140 K 160 K 180 K 200 K 250 K

A **B** **B** **B** **C** **D** **D** **D** **D**

Table S1 Crystallographic data for compound **1**.

Phase	A	B	C	D
Empirical formula	$C_{45}H_{69}O_3Y$	$C_{45}H_{69}O_3Y$	$C_{45}H_{69}O_3Y$	$C_{45}H_{69}O_3Y$
Formula weight	746.91	746.91	746.91	746.91
Temperature/K	100(2)	120(2)	140(2)	160(2)
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1	P-1
a/Å	9.6910(6)	9.6914(4)	9.7054(5)	9.7113(3)
b/Å	25.0295(17)	25.0653(10)	25.1144(12)	15.0872(4)
c/Å	45.485(3)	35.4181(14)	17.7491(9)	15.6649(5)
α/°	76.182(4)	92.297(2)	92.271(3)	70.506(2)
β/°	86.604(3)	91.122(2)	91.056(3)	83.665(2)
γ/°	80.933(3)	98.890(2)	98.699(3)	82.160(2)
Volume/Å^3	10577.0(12)	8490.6(6)	4271.8(4)	2138.20(11)
Z	10	8	4	2
ρ_{calc} g/cm^3	1.173	1.169	1.161	1.160
μ/mm^{-1}	1.414	1.409	1.401	1.399
F(000)	4020.0	3216.0	1608.0	804.0
Crystal size/mm^3	0.60 × 0.50 × 0.40	0.60 × 0.50 × 0.40	0.60 × 0.50 × 0.40	0.60 × 0.50 × 0.40
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.694 to 61.342	1.646 to 56.724	3.926 to 60.54	4.594 to 61.124
Index ranges	-10 ≤ h ≤ 13, -31 ≤ k ≤ 35, -64 ≤ l ≤ 65	-12 ≤ h ≤ 12, -33 ≤ k ≤ 33, -47 ≤ l ≤ 47	-13 ≤ h ≤ 13, -29 ≤ k ≤ 35, -24 ≤ l ≤ 25	-13 ≤ h ≤ 13, -21 ≤ k ≤ 21, -22 ≤ l ≤ 22
Reflections collected	279802	163674	90811	50387
Independent reflections	64948 [R_{int} = 0.0870, R_{sigma} = 0.1105]	41905 [R_{int} = 0.0627, R_{sigma} = 0.0748]	24901 [R_{int} = 0.0651, R_{sigma} = 0.0858]	12977 [R_{int} = 0.0353, R_{sigma} = 0.0391]
Data/restraints/parameters	64948/0/2311	41905/0/1849	24901/0/925	12977/15/502
Goodness-of-fit on F^2	1.014	1.056	1.032	1.005
Final R indexes [I>=2σ (I)]	R_1 = 0.0631, wR_2 = 0.1284	R_1 = 0.0572, wR_2 = 0.1175	R_1 = 0.0510, wR_2 = 0.1048	R_1 = 0.0377, wR_2 = 0.0864
Final R indexes [all data]	R_1 = 0.1354, wR_2 = 0.1513	R_1 = 0.1058, wR_2 = 0.1320	R_1 = 0.1123, wR_2 = 0.1221	R_1 = 0.0682, wR_2 = 0.0965
Largest diff. peak/hole / e Å^{-3}	2.90/-1.09	1.81/-0.78	1.16/-0.89	0.29/-0.34

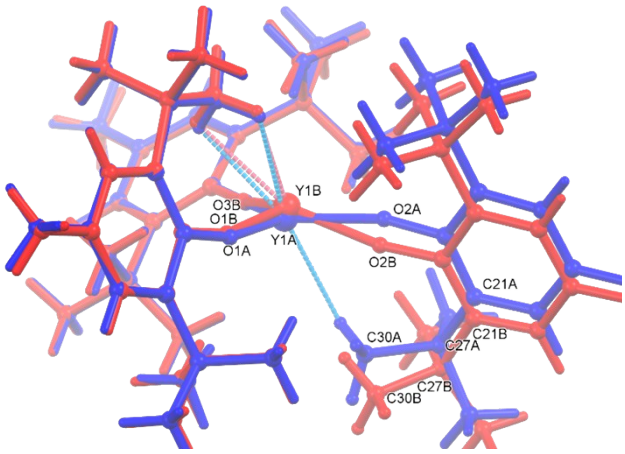

Figure S2. Overlay of planar and pyramidal conformations from the structure at 140 K. The short C-H…Y contacts are shown as dotted lines in matching colours.

Summary of phases and data for [Ce(O-2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$)$_3$] (**2**)

100 K 120 K 140 K 160 K 180 K 190 K 200K

A A A A A A B

Table S2 Crystallographic data for compound for compound **2**.

Phase	A	B
Empirical formula	$C_{45}H_{69}CeO_3$	$C_{45}H_{69}CeO_3$
Formula weight	798.12	798.12
Temperature/K	100.0	200.0
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	9.6480(4)	9.7009(11)
b/Å	17.7941(7)	15.2187(15)
c/Å	25.1982(10)	15.7698(14)
α/°	92.202(2)	70.569(4)
β/°	97.768(2)	84.308(6)
γ/°	91.001(2)	83.265(5)
Volume/Å^3	4282.0(3)	2175.9(4)
Z	4	2
ρ_{calc}g/cm^3	1.238	1.218
μ/mm^{-1}	1.098	1.081
F(000)	1684.0	842.0
Crystal size/mm^3	0.4 × 0.2 × 0.2	0.40 × 0.20 × 0.20
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.632 to 55.224	4.554 to 55.39
Index ranges	-12 ≤ h ≤ 12, -23 ≤ k ≤ 23, -32 ≤ l ≤ 32	-12 ≤ h ≤ 9, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20
Reflections collected	105269	37311
Independent reflections	19495 [R_{int} = 0.0502, R_{sigma} = 0.0385]	9961 [R_{int} = 0.0412, R_{sigma} = 0.0418]
Data/restraints/parameters	19495/0/925	9961/15/472
Goodness-of-fit on F^2	1.057	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0332, wR_2 = 0.0749	R_1 = 0.0399, wR_2 = 0.0943
Final R indexes [all data]	R_1 = 0.0461, wR_2 = 0.0800	R_1 = 0.0687, wR_2 = 0.1071
Largest diff. peak/hole / e Å^{-3}	1.36/-1.21	0.75/-0.63

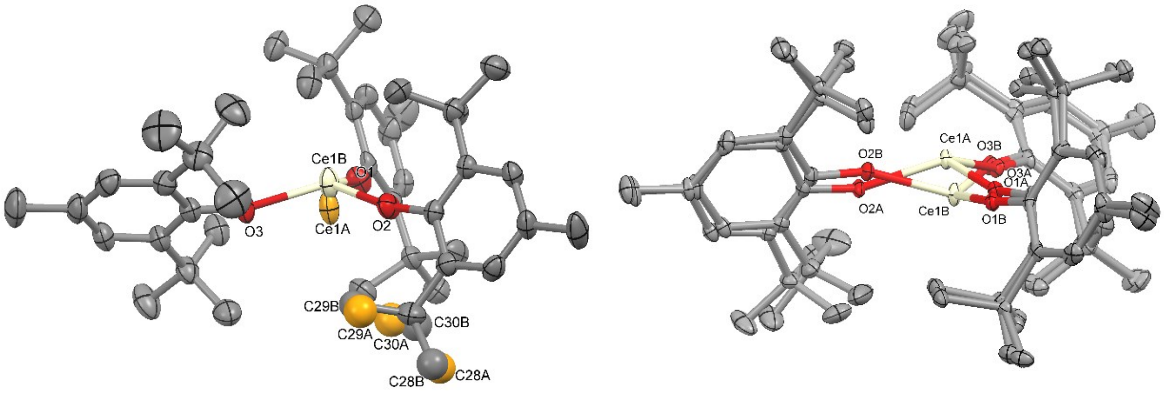

Figure S3. Structure of **2** at 200 K (left, 2nd positions of disorder shown in gold) and overlay of the two independent molecules in the crystal structure of **2** at 100 K (right).

Structural data from the CSD

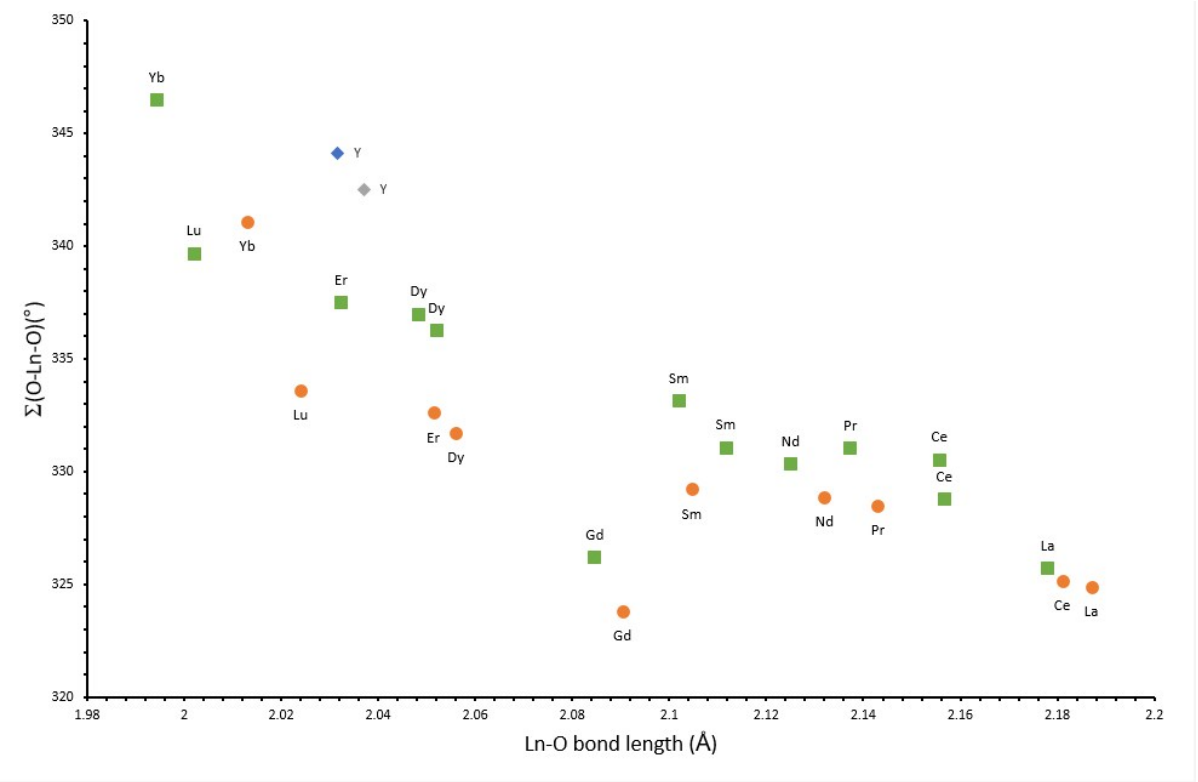

Figure S4. Correlation between bond length and pyramidality in the isomorphous series of structures of $Ln(OAr)_3$ (Ar = 2,6-^{t}Bu$_2$C$_6$H$_3$). All structures show two molecules in the asymmetric unit and are coloured coded by the degree of pyramidality: high (orange) or low (green). Y, as a group 3 element, is shown with blue / grey rhombuses.

Table S3. Proportion of 2,6-^{t}Bu$_2$-4-RC$_6$H$_2$ groups adopting C_s, s-C_{2v} or e-C_{2v}

	Number (percentage of total)		
R	H	Me	^{t}Bu
C_s	61 (**9.6%**)	44 (**9.4%**)	673 (**24.5%**)
C_{2v}-staggered	572 (**89.9%**)	416 (**89.1%**)	1598 (**58.3%**)
C_{2v}-eclipsed	3 (**0.5%**)	7 (**1.5%**)	471 (**17.2%**)
Total	636	467	2742

Conformational analysis of 2,6-^{t}Bu,4-R-Ph moiety (R = H, Me, ^{t}Bu)

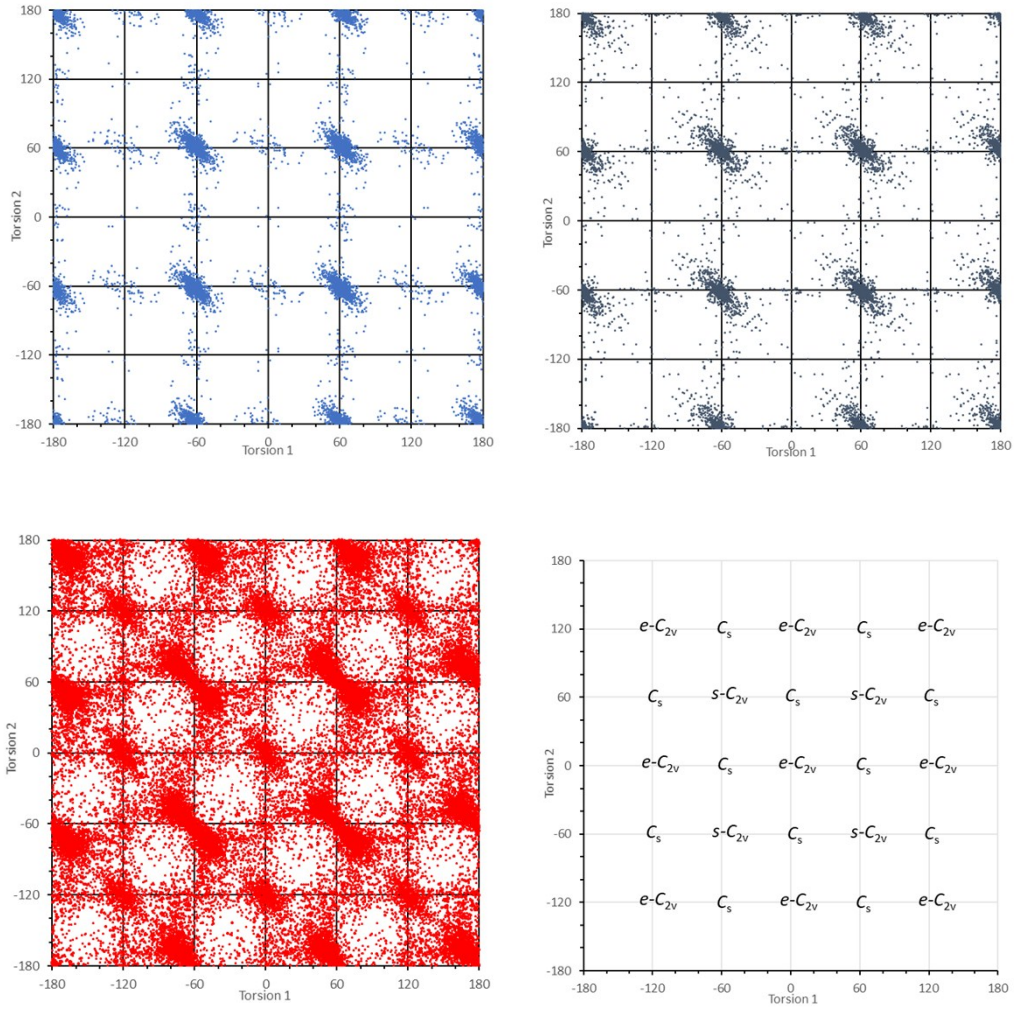

Figure S5. Symmetry-expanded torsion angle (see Figure S6 for definition) correlation for R – H, Me or ^{t}Bu from CSD (V 5.39 (No 2017) + 4 updates) for ^{t}Bu groups in the 2- and 6-position for different substituents in the 4-position. Top left: R = H (blue), top right: R = Me (grey), bottom left, R = ^{t}Bu (red), bottom right: graph superimposed using naming scheme of conformers showing position on graph.

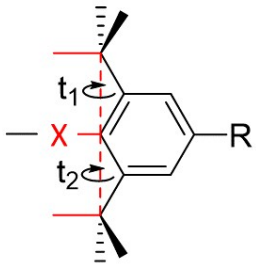

Figure S6. One (of six) torsion angles extracted for ^{t}Bu groups in 2- and 6-positions.

Summary

The graphs in Figure 5 show the correlation of torsion angles of ^{t}Bu groups in the 2-position against those in the 6-position. They show that the distribution of the conformers adopted does not vary much for a Me substituent compared with a H substituent in the 4-position, with the s-C_{2v} conformer the most preferred and with few other conformations observed. However, the distribution varies dramatically when the 4-substiutuent is ^{t}Bu with a more even spread between different conformations as well as the pathways linking conformations being heavily populated.

Conformations of $M(OAr)_3$

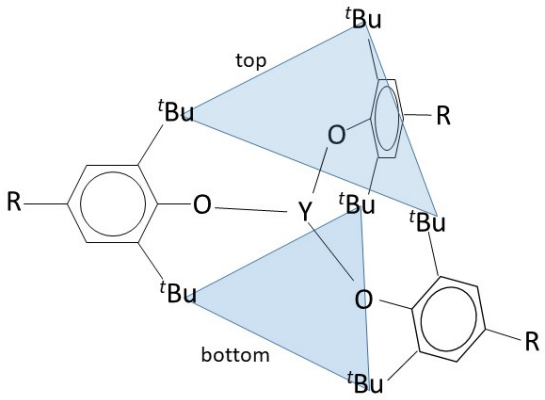

Figure S6: Diagram indicating 'top' and 'bottom' positions of ^{t}Bu groups of $M(OAr)_3$. C_3 symmetry is assumed when considering possible conformations, although the actual structures deviate substantially from this symmetry. Each ^{t}Bu group can be eclipsed (E) or staggered (S) with respect to the Y-O bond. If the structure is planar rather than pyramidal, the top and bottom become equivalent and the number of conformers is halved.

Table S4: All possible conformations of $M(OAr)_3$, where each ^{t}Bu is either E (eclipsed) or S (staggered) with respect to the M-O bond. Highlighted in orange are the two conformers seen in crystal structures.

Top → bottom ↓	EEE	EES			ESS			SSS
EEE	EEE EEE	EES EEE			ESS EEE			SSS EEE
EES	EEE EES	EES EES	EES ESE	EES SEE	ESS EES	ESS ESE	ESS SEE	SSS EES
ESS	EEE ESS	EES ESS	EES SES	EES SSE	ESS ESS	ESS SES	ESS SSE	SSS SSE
SSS	EEE SSS	EES SSS			ESS SSS			SSS SSS

Table of Bond Critical Points (BCPs)

Table S5 BCPs for planar conformer (See Figure S7 for numbering scheme)

BCP	Atoms	ρ	$\nabla^2(\rho)$	Ellipticity	V	G	sum(V+G)
7	C7 - C9	0.306972	-0.803050	0.220677	-0.405813	0.102525	-0.303288
111	C85 - C86	0.304678	-0.793822	0.207093	-0.398367	0.099956	-0.298411
109	C83 - C85	0.304607	-0.793505	0.206555	-0.398133	0.099878	-0.298255
55	C45 - C47	0.304143	-0.790098	0.210138	-0.397494	0.099985	-0.297509
59	C47 - C48	0.303728	-0.788582	0.206544	-0.395973	0.099414	-0.296559
15	C9 - C10	0.302658	-0.785214	0.197373	-0.392462	0.098079	-0.294383
16	C10 - C12	0.302569	-0.773664	0.219291	-0.396378	0.101481	-0.294897
61	C48 - C50	0.300226	-0.762903	0.213786	-0.390016	0.099645	-0.290371
113	C86 - C88	0.300169	-0.762846	0.213772	-0.389793	0.099541	-0.290252
105	C82 - C83	0.300115	-0.762521	0.213352	-0.389640	0.099505	-0.290135
54	C44 - C45	0.299793	-0.761153	0.216792	-0.389252	0.099482	-0.289770
9	C6 - C7	0.297534	-0.751003	0.209107	-0.382623	0.097436	-0.285187
52	C43 - C44	0.290574	-0.722774	0.243264	-0.362668	0.090987	-0.271681
6	C5 - C6	0.290420	-0.717944	0.258455	-0.364182	0.092348	-0.271834
57	C43 - C50	0.289933	-0.721313	0.236291	-0.361338	0.090505	-0.270833
102	C81 - C82	0.288374	-0.712718	0.238716	-0.357280	0.089550	-0.267730
110	C81 - C88	0.288181	-0.711505	0.239345	-0.356844	0.089484	-0.267360
13	C5 - C12	0.286712	-0.707221	0.228828	-0.352587	0.087891	-0.264696
5	O2 - C5	0.285927	-0.317696	0.014666	-0.792934	0.356755	-0.436179
50	O3 - C43	0.284561	-0.325458	0.013888	-0.784451	0.351543	-0.432908
101	O4 - C81	0.283355	-0.314392	0.018241	-0.782308	0.351855	-0.430453
104	C83 - H84	0.276701	-0.946357	0.019341	-0.324107	0.043759	-0.280348
12	C10 - H11	0.276624	-0.946501	0.018560	-0.323700	0.043537	-0.280163
112	C86 - H87	0.276584	-0.945383	0.019440	-0.323918	0.043786	-0.280132
60	C48 - H49	0.276433	-0.944998	0.018956	-0.323362	0.043556	-0.279806
53	C45 - H46	0.276121	-0.941672	0.019565	-0.323198	0.043890	-0.279308
8	C7 - H8	0.274010	-0.923272	0.019618	-0.319375	0.044278	-0.275097
90	C69 - H70	0.272692	-0.916126	0.006091	-0.316335	0.043652	-0.272683
44	C35 - H38	0.271755	-0.906308	0.007044	-0.315109	0.044266	-0.270843
143	C111 - H114	0.271593	-0.903352	0.006576	-0.315377	0.044770	-0.270607
77	C56 - H59	0.271311	-0.905830	0.006586	-0.313262	0.043402	-0.269860
39	C31 - H32	0.271180	-0.898782	0.005948	-0.314743	0.045024	-0.269719
29	C22 - H25	0.270516	-0.896173	0.006319	-0.312668	0.044312	-0.268356
27	C18 - H19	0.270481	-0.895221	0.006291	-0.312839	0.044517	-0.268322
126	C94 - H95	0.270179	-0.889564	0.006284	-0.313864	0.045737	-0.268127
22	C14 - H16	0.270107	-0.896354	0.003793	-0.310679	0.043295	-0.267384
78	C60 - H63	0.269965	-0.890323	0.005376	-0.311587	0.044503	-0.267084
70	C52 - H54	0.269859	-0.895247	0.011397	-0.310574	0.043381	-0.267193
121	C90 - H93	0.269786	-0.885135	0.006857	-0.313131	0.045924	-0.267207
75	C56 - H57	0.269244	-0.887267	0.008269	-0.309770	0.043977	-0.265793
26	C18 - H21	0.268973	-0.884959	0.007143	-0.309041	0.043901	-0.265140
148	C115 - H118	0.268918	-0.882121	0.004758	-0.309953	0.044711	-0.265242
11	C26 - H29	0.268821	-0.882369	0.007734	-0.309469	0.044438	-0.265031
31	C22 - H23	0.268768	-0.883043	0.007290	-0.308762	0.044000	-0.264762
95	C73 - H74	0.268719	-0.882624	0.005575	-0.308866	0.044105	-0.264761
133	C98 - H99	0.268657	-0.879761	0.004685	-0.309517	0.044789	-0.264728
97	C73 - H76	0.268642	-0.875551	0.006130	-0.311473	0.046293	-0.265180
123	C98 - H101	0.268587	-0.878839	0.004861	-0.309478	0.044884	-0.264594
47	C39 - H42	0.268571	-0.878972	0.004718	-0.309385	0.044821	-0.264564
98	C77 - H78	0.268551	-0.879425	0.004550	-0.309248	0.044696	-0.264552
100	C77 - H80	0.268481	-0.877493	0.004842	-0.309375	0.045001	-0.264374
139	C107 - H110	0.268434	-0.880274	0.004465	-0.308508	0.044220	-0.264288
80	C60 - H61	0.268432	-0.879604	0.005514	-0.308503	0.044301	-0.264202
140	C115 - H116	0.268417	-0.877519	0.004908	-0.309151	0.044886	-0.264265
81	C60 - H62	0.268363	-0.876838	0.004966	-0.309460	0.045125	-0.264335
49	C39 - H40	0.268358	-0.876805	0.004803	-0.309131	0.044965	-0.264166

82	C64 - H66	0.268346	-0.878932	0.008085	-0.308801	0.044534	-0.264267
108	C102 - H104	0.268302	-0.878901	0.008055	-0.308709	0.044492	-0.264217
145	C111 - H112	0.268272	-0.877632	0.007722	-0.308711	0.044651	-0.264060
114	C102 - H105	0.268259	-0.878643	0.008084	-0.308643	0.044491	-0.264152
129	C98 - H100	0.268190	-0.875647	0.004101	-0.309253	0.045170	-0.264083
83	C64 - H67	0.268169	-0.878072	0.008228	-0.308496	0.044489	-0.264007
149	C115 - H117	0.268162	-0.875546	0.004250	-0.309162	0.045138	-0.264024
141	C107 - H109	0.268146	-0.877683	0.003916	-0.307961	0.044270	-0.263691
131	C94 - H97	0.268143	-0.876989	0.006424	-0.308345	0.044549	-0.263796
122	C90 - H91	0.268120	-0.876695	0.006521	-0.308395	0.044611	-0.263784
38	C31 - H34	0.268119	-0.875920	0.006700	-0.308421	0.044721	-0.263700
45	C35 - H36	0.268104	-0.876290	0.008077	-0.308401	0.044664	-0.263737
43	C39 - H41	0.268071	-0.874777	0.003867	-0.309117	0.045212	-0.263905
94	C77 - H79	0.268022	-0.874353	0.003984	-0.309031	0.045221	-0.263810
89	C69 - H72	0.267894	-0.874019	0.008370	-0.308228	0.044862	-0.263366
124	C90 - H92	0.267695	-0.873006	0.006000	-0.307482	0.044615	-0.262867
33	C26 - H28	0.267406	-0.872787	0.008583	-0.307270	0.044536	-0.262734
28	C18 - H20	0.267272	-0.869011	0.006880	-0.307000	0.044874	-0.262126
132	C94 - H96	0.267161	-0.867984	0.005497	-0.306934	0.044969	-0.261965
30	C22 - H24	0.267141	-0.867962	0.006700	-0.306764	0.044887	-0.261877
146	C111 - H113	0.267043	-0.867137	0.006645	-0.306701	0.044958	-0.261743
71	C52 - H55	0.266814	-0.869137	0.011723	-0.306557	0.044636	-0.261921
96	C73 - H75	0.266737	-0.865008	0.004895	-0.306212	0.044980	-0.261232
136	C107 - H108	0.266603	-0.855885	0.006047	-0.309636	0.047832	-0.261804
40	C31 - H33	0.266529	-0.862229	0.005918	-0.306221	0.045332	-0.260889
46	C35 - H37	0.266468	-0.861618	0.007263	-0.306200	0.045398	-0.260802
74	C56 - H58	0.266446	-0.862291	0.007427	-0.305578	0.045003	-0.260575
91	C69 - H71	0.266239	-0.859239	0.007378	-0.306022	0.045606	-0.260416
32	C26 - H27	0.265950	-0.861963	0.008367	-0.304852	0.044681	-0.260171
84	C64 - H65	0.265518	-0.858468	0.008142	-0.304116	0.044749	-0.259367
134	C102 - H103	0.265389	-0.857412	0.008032	-0.303974	0.044811	-0.259163
19	C14 - H15	0.264085	-0.840842	0.004329	-0.303803	0.046796	-0.257007
23	C14 - H17	0.262187	-0.825269	0.002452	-0.301521	0.047602	-0.253919
69	C52 - H53	0.257465	-0.783098	0.017112	-0.296224	0.050225	-0.245999
14	C9 - C26	0.247604	-0.558379	0.034384	-0.258316	0.059361	-0.198955
107	C85 - C102	0.247575	-0.558213	0.034133	-0.258234	0.059340	-0.198894
58	C47 - C64	0.247461	-0.557618	0.034877	-0.258056	0.059326	-0.198730
99	C68 - C77	0.236249	-0.506114	0.002462	-0.238308	0.055890	-0.182418
48	C30 - C39	0.236186	-0.505753	0.002533	-0.238194	0.055878	-0.182316
147	C106 - C115	0.235775	-0.504012	0.002333	-0.237649	0.055823	-0.181826
79	C51 - C60	0.235726	-0.504421	0.006606	-0.237170	0.055532	-0.181638
130	C89 - C98	0.235714	-0.503737	0.002040	-0.237500	0.055783	-0.181717
56	C44 - C51	0.235223	-0.496530	0.038571	-0.235489	0.055678	-0.179811
85	C50 - C68	0.235005	-0.496760	0.035990	-0.235720	0.055765	-0.179955
34	C12 - C30	0.234543	-0.494882	0.035883	-0.234982	0.055631	-0.179351
116	C88 - C106	0.234140	-0.492892	0.035876	-0.234042	0.055409	-0.178633
106	C82 - C89	0.234068	-0.492738	0.035377	-0.233953	0.055384	-0.178569
138	C106 - C107	0.233902	-0.497097	0.004797	-0.235342	0.055534	-0.179808
144	C106 - C111	0.233822	-0.496398	0.005586	-0.235229	0.055565	-0.179664
18	C13 - C14	0.233797	-0.497107	0.002151	-0.235871	0.055797	-0.180074
120	C89 - C90	0.233658	-0.495856	0.004449	-0.234837	0.055437	-0.179400
92	C68 - C73	0.233543	-0.495473	0.005055	-0.234880	0.055506	-0.179374
128	C89 - C94	0.233469	-0.495030	0.005521	-0.234517	0.055380	-0.179137
72	C51 - C56	0.233345	-0.494045	0.006079	-0.234499	0.055494	-0.179005
37	C30 - C31	0.233287	-0.494379	0.005246	-0.234239	0.055322	-0.178917
88	C68 - C69	0.233165	-0.493767	0.005605	-0.233918	0.055238	-0.178680
42	C30 - C35	0.232965	-0.492953	0.005386	-0.233676	0.055219	-0.178457
25	C13 - C18	0.232897	-0.492565	0.004536	-0.233319	0.055089	-0.178230
21	C13 - C22	0.232878	-0.492515	0.005238	-0.233320	0.055096	-0.178224
10	C6 - C13	0.230007	-0.475376	0.039568	-0.226923	0.054040	-0.172883

68	C51 - C52	0.225740	-0.465308	0.003258	-0.221745	0.052709	-0.169036
1	Y1 - O2	0.084869	0.456617	0.013216	-0.120890	0.117519	-0.003371
2	Y1 - O3	0.083487	0.430731	0.050667	-0.114900	0.111289	-0.003611
3	Y1 - O4	0.080647	0.449326	0.010828	-0.115255	0.113791	-0.001464
64	Y1 - H53	0.017257	0.071794	0.511995	-0.011687	0.014818	0.003131
4	O2 - C14	0.016533	0.053270	0.454678	-0.011476	0.012397	0.000921
17	Y1 - H15	0.016488	0.071159	2.237740	-0.011175	0.014483	0.003308
87	O3 - H70	0.015364	0.050578	0.148243	-0.011022	0.011833	0.000811
117	H84 - C98	0.015133	0.067565	0.381953	-0.010509	0.013700	0.003191
135	H87 - C115	0.015029	0.067197	0.391990	-0.010417	0.013608	0.003191
36	H11 - C39	0.014871	0.066778	0.496616	-0.010295	0.013495	0.003200
41	O2 - H38	0.014745	0.048728	0.190313	-0.010468	0.011325	0.000857
63	H46 - C60	0.014619	0.064052	1.118556	-0.009455	0.012734	0.003279
51	O3 - C52	0.014611	0.044607	0.328424	-0.009876	0.010514	0.000638
115	O4 - H108	0.014587	0.044815	0.280814	-0.009778	0.010491	0.000713
86	H49 - C77	0.014557	0.065366	0.721684	-0.009969	0.013155	0.003186
125	O4 - H95	0.014478	0.046803	0.189292	-0.010057	0.010879	0.000822
35	O2 - H32	0.014357	0.047239	0.223621	-0.010049	0.010929	0.000880
142	O4 - H114	0.013917	0.045720	0.183633	-0.009675	0.010553	0.000878
62	O3 - H76	0.012782	0.041016	0.297882	-0.008513	0.009383	0.000870
103	O4 - H93	0.012740	0.041744	0.305815	-0.008503	0.009470	0.000967
24	H8 - H19	0.011454	0.048186	2.469864	-0.006444	0.009245	0.002801
73	O3 - H59	0.009696	0.034784	0.385764	-0.006486	0.007591	0.001105
93	H17 - H76	0.007554	0.023903	0.186252	-0.003390	0.004683	0.001293
76	H59 - H114	0.006744	0.023236	0.072654	-0.003071	0.004440	0.001369
118	O2 - H93	0.006323	0.018579	0.968246	-0.003124	0.003884	0.000760
66	H53 - H95	0.006275	0.019756	0.286621	-0.002605	0.003772	0.001167
20	H15 - H108	0.005920	0.018381	1.390021	-0.002579	0.003587	0.001008
67	H38 - H55	0.005725	0.019384	0.207988	-0.002424	0.003635	0.001211
65	H32 - H55	0.003720	0.011499	0.215288	-0.001465	0.002170	0.000705
137	H70 - H109	0.002281	0.007116	0.811340	-0.000879	0.001329	0.000450
119	H21 - H91	0.001988	0.006095	1.154502	-0.000754	0.001139	0.000385
127	H32 - C94	0.001870	0.005697	3.371926	-0.000760	0.001092	0.000332

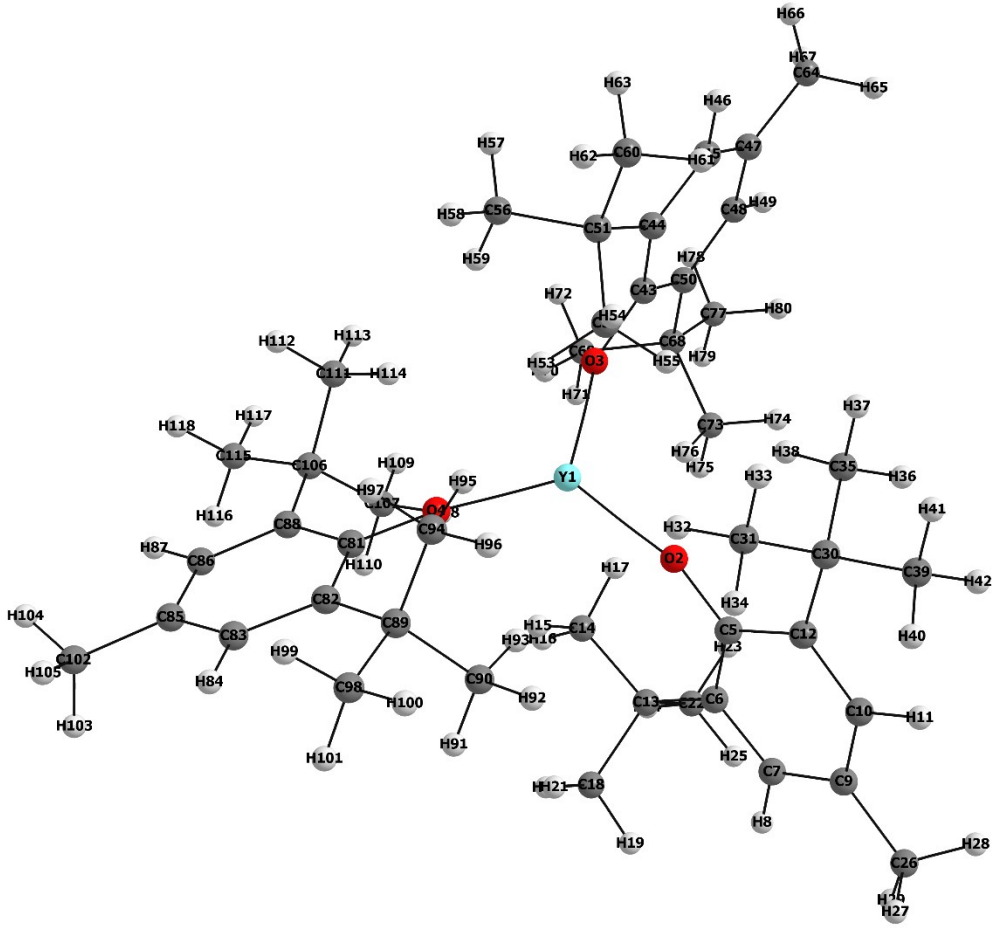

Figure S7. Numbering scheme for planar conformer of Y(O-2,6-^{t}Bu-4-MeC$_6$H$_2$)$_3$

Table S6 BCPs for the pyramidal conformer Y(O-2,6-^{t}Bu-4-MeC$_6$H$_2$)$_3$.(See Figure S8 for numbering scheme)

BCP	Atoms	ρ	$\nabla^2(\rho)$	Ellipticity	V	G	sum(V+G)
7	C7 - C9	0.306916	-0.802669	0.221259	-0.40576	0.102547	-0.303213
106	C85 - C86	0.30449	-0.792781	0.206858	-0.397864	0.099835	-0.298029
58	C47 - C48	0.304487	-0.792036	0.210611	-0.398263	0.100127	-0.298136
105	C83 - C85	0.304481	-0.792668	0.207232	-0.397891	0.099862	-0.298029
57	C45 - C47	0.303676	-0.788588	0.205061	-0.395702	0.099277	-0.296425
17	C10 - C12	0.302544	-0.773534	0.218588	-0.396289	0.101453	-0.294836
15	C9 - C10	0.302481	-0.784302	0.196852	-0.391983	0.097954	-0.294029
52	C44 - C45	0.300477	-0.76425	0.213335	-0.390611	0.099774	-0.290837
110	C86 - C88	0.300225	-0.763221	0.213285	-0.38992	0.099557	-0.290363
99	C82 - C83	0.300078	-0.762392	0.213915	-0.389586	0.099494	-0.290092
61	C48 - C50	0.299805	-0.761224	0.215518	-0.388987	0.09934	-0.289647
9	C6 - C7	0.2975	-0.750716	0.210338	-0.382665	0.097493	-0.285172
6	C5 - C6	0.29033	-0.717346	0.259577	-0.363907	0.092285	-0.271622
51	C43 - C44	0.289897	-0.721973	0.235133	-0.36093	0.090218	-0.270712
59	C43 - C50	0.289489	-0.717386	0.243828	-0.360201	0.090427	-0.269774
107	C81 - C88	0.289199	-0.716993	0.239074	-0.359421	0.090086	-0.269335
98	C81 - C82	0.288952	-0.715663	0.239882	-0.358837	0.08996	-0.268877
14	C5 - C12	0.286902	-0.708629	0.227088	-0.35301	0.087926	-0.265084
4	O2 - C5	0.286611	-0.311329	0.014439	-0.797568	0.359868	-0.4377
50	O3 - C43	0.284583	-0.292573	0.015482	-0.793433	0.360145	-0.433288
97	O4 - C81	0.283183	-0.302654	0.016944	-0.784666	0.354501	-0.430165
16	C10 - H11	0.276752	-0.947799	0.018394	-0.323848	0.043449	-0.280399

53	C45 - H46	0.276591	-0.946251	0.018758	-0.323625	0.043531	-0.280094
109	C86 - H87	0.276575	-0.945661	0.019309	-0.323802	0.043693	-0.280109
101	C83 - H84	0.276573	-0.945365	0.019434	-0.323882	0.04377	-0.280112
60	C48 - H49	0.276127	-0.941758	0.019721	-0.323149	0.043855	-0.279294
8	C7 - H8	0.273812	-0.921518	0.019856	-0.319104	0.044363	-0.274741
39	C31 - H34	0.272193	-0.910328	0.006027	-0.315627	0.044023	-0.271604
45	C35 - H36	0.271523	-0.90186	0.005518	-0.31536	0.044948	-0.270412
67	C52 - H55	0.27123	-0.900369	0.006556	-0.314524	0.044716	-0.269808
27	C18 - H21	0.270804	-0.898947	0.006231	-0.313094	0.044179	-0.268915
77	C56 - H57	0.270774	-0.895971	0.006385	-0.313859	0.044933	-0.268926
33	C22 - H25	0.270572	-0.896632	0.006313	-0.312841	0.044341	-0.2685
118	C90 - H92	0.270462	-0.893393	0.007869	-0.31346	0.045056	-0.268404
25	C14 - H16	0.270231	-0.897915	0.002563	-0.310679	0.0431	-0.267579
139	C111 - H114	0.269919	-0.886896	0.007024	-0.313148	0.045712	-0.267436
96	C77 - H80	0.269158	-0.884712	0.005006	-0.310153	0.044487	-0.265666
92	C73 - H76	0.269001	-0.887272	0.005524	-0.309318	0.04375	-0.265568
93	C77 - H78	0.268971	-0.882797	0.004997	-0.309875	0.044588	-0.265287
34	C22 - H24	0.268921	-0.884601	0.007413	-0.308872	0.043861	-0.265011
87	C69 - H72	0.26888	-0.885756	0.007416	-0.309231	0.043896	-0.265335
127	C98 - H100	0.26884	-0.881395	0.004747	-0.309784	0.044718	-0.265066
13	C26 - H28	0.268802	-0.882101	0.007755	-0.309453	0.044464	-0.264989
120	C94 - H95	0.268782	-0.876455	0.006365	-0.312157	0.046522	-0.265635
136	C115 - H116	0.268666	-0.879754	0.004906	-0.30954	0.044801	-0.264739
144	C115 - H118	0.268649	-0.879639	0.00494	-0.309545	0.044818	-0.264727
117	C90 - H93	0.268606	-0.881279	0.007469	-0.309036	0.044358	-0.264678
125	C98 - H101	0.268576	-0.878886	0.004719	-0.309417	0.044847	-0.26457
134	C107 - H110	0.268557	-0.881045	0.005805	-0.308823	0.044281	-0.264542
62	C64 - H67	0.268482	-0.879916	0.00793	-0.309006	0.044513	-0.264493
80	C60 - H61	0.26844	-0.877618	0.004677	-0.309247	0.044922	-0.264325
81	C60 - H63	0.268428	-0.877576	0.004724	-0.309213	0.044909	-0.264304
47	C39 - H42	0.268427	-0.877671	0.004729	-0.309185	0.044883	-0.264302
28	C18 - H19	0.268406	-0.879725	0.007762	-0.308269	0.044169	-0.2641
129	C102 - H105	0.268307	-0.879032	0.008084	-0.308713	0.044477	-0.264236
104	C102 - H104	0.268306	-0.878963	0.008074	-0.308721	0.04449	-0.264231
43	C39 - H41	0.268262	-0.87645	0.003739	-0.309394	0.045141	-0.264253
49	C39 - H40	0.268258	-0.875775	0.00484	-0.30903	0.045043	-0.263987
123	C94 - H97	0.268244	-0.878475	0.005524	-0.308396	0.044389	-0.264007
141	C115 - H117	0.268197	-0.875918	0.004235	-0.309191	0.045106	-0.264085
76	C56 - H59	0.268193	-0.876869	0.007067	-0.308533	0.044658	-0.263875
142	C111 - H112	0.268161	-0.876921	0.006742	-0.308487	0.044629	-0.263858
75	C60 - H62	0.268157	-0.875488	0.003812	-0.30923	0.045179	-0.264051
69	C52 - H53	0.268131	-0.876384	0.007484	-0.308421	0.044663	-0.263758
88	C69 - H71	0.26813	-0.873742	0.011147	-0.310066	0.045815	-0.264251
137	C107 - H109	0.268098	-0.87665	0.005149	-0.308148	0.044493	-0.263655
122	C98 - H99	0.268036	-0.874265	0.004244	-0.309039	0.045236	-0.263803
56	C64 - H65	0.268016	-0.877039	0.008287	-0.308258	0.044499	-0.263759
143	C111 - H113	0.267835	-0.874167	0.006071	-0.307733	0.044596	-0.263137
40	C31 - H32	0.267817	-0.873234	0.00802	-0.308061	0.044876	-0.263185
44	C35 - H38	0.267816	-0.87313	0.006846	-0.308055	0.044886	-0.263169
91	C77 - H79	0.267807	-0.872485	0.004924	-0.308559	0.045219	-0.26334
12	C26 - H27	0.267357	-0.872506	0.008617	-0.307177	0.044525	-0.262652
135	C107 - H108	0.267351	-0.86538	0.007927	-0.309409	0.046532	-0.262877
32	C22 - H23	0.267185	-0.868365	0.007097	-0.306812	0.04486	-0.261952
29	C18 - H20	0.267132	-0.867808	0.006875	-0.306746	0.044897	-0.261849
46	C35 - H37	0.267039	-0.866904	0.005897	-0.306842	0.045058	-0.261784
41	C31 - H33	0.267037	-0.866478	0.007159	-0.307011	0.045195	-0.261816
124	C94 - H96	0.267022	-0.866907	0.004647	-0.306606	0.04494	-0.261666
94	C73 - H75	0.267016	-0.867444	0.006272	-0.306287	0.044713	-0.261574
70	C52 - H54	0.266939	-0.865839	0.006563	-0.306721	0.045131	-0.26159
78	C56 - H58	0.266882	-0.865319	0.006043	-0.306598	0.045134	-0.261464

116	C90 - H91	0.266852	-0.864994	0.006705	-0.306562	0.045157	-0.261405
86	C69 - H70	0.266285	-0.860549	0.00722	-0.305597	0.04523	-0.260367
35	C26 - H29	0.26603	-0.862666	0.008398	-0.304964	0.044649	-0.260315
82	C64 - H66	0.265505	-0.858279	0.008136	-0.304138	0.044784	-0.259354
128	C102 - H103	0.265392	-0.857404	0.008062	-0.303982	0.044816	-0.259166
89	C73 - H74	0.264162	-0.838527	0.01208	-0.305419	0.047894	-0.257525
23	C14 - H15	0.263555	-0.835805	0.003791	-0.303099	0.047074	-0.256025
26	C14 - H17	0.261392	-0.81892	0.001077	-0.300244	0.047757	-0.252487
11	C9 - C26	0.247605	-0.558359	0.034522	-0.258324	0.059367	-0.198957
103	C85 - C102	0.247538	-0.55807	0.034138	-0.258155	0.059319	-0.198836
55	C47 - C64	0.24746	-0.557645	0.034638	-0.258032	0.05931	-0.198722
79	C51 - C60	0.236111	-0.505469	0.001782	-0.238095	0.055864	-0.182231
48	C30 - C39	0.236107	-0.505408	0.001717	-0.238074	0.055861	-0.182213
126	C89 - C98	0.235827	-0.50427	0.002265	-0.237674	0.055803	-0.181871
95	C68 - C77	0.235775	-0.504169	0.003547	-0.237692	0.055825	-0.181867
145	C106 - C115	0.235718	-0.503767	0.002415	-0.237562	0.05581	-0.181752
111	C88 - C106	0.234601	-0.494975	0.035005	-0.234863	0.05556	-0.179303
54	C44 - C51	0.234507	-0.494822	0.035497	-0.234927	0.055611	-0.179316
64	C50 - C68	0.234374	-0.493401	0.036462	-0.234302	0.055476	-0.178826
19	C12 - C30	0.234339	-0.494164	0.03578	-0.234766	0.055612	-0.179154
102	C82 - C89	0.23419	-0.493181	0.035646	-0.234118	0.055411	-0.178707
42	C30 - C35	0.233624	-0.495786	0.004964	-0.234837	0.055445	-0.179392
115	C89 - C90	0.233559	-0.495368	0.005166	-0.234604	0.055381	-0.179223
121	C89 - C94	0.233488	-0.495202	0.005338	-0.234642	0.055421	-0.179221
133	C106 - C107	0.233389	-0.494773	0.005414	-0.234328	0.055317	-0.179011
74	C51 - C56	0.233381	-0.494726	0.00518	-0.234371	0.055345	-0.179026
68	C51 - C52	0.233366	-0.494652	0.004992	-0.234341	0.055339	-0.179002
140	C106 - C111	0.233315	-0.494384	0.004946	-0.234244	0.055324	-0.17892
20	C13 - C14	0.233222	-0.494765	0.001961	-0.235317	0.055813	-0.179504
85	C68 - C69	0.233114	-0.49329	0.006004	-0.233827	0.055252	-0.178575
90	C68 - C73	0.233057	-0.49332	0.006255	-0.23395	0.05531	-0.17864
38	C30 - C31	0.233009	-0.493148	0.005023	-0.233805	0.055259	-0.178546
31	C13 - C22	0.232951	-0.492788	0.004401	-0.233463	0.055133	-0.17833
24	C13 - C18	0.23282	-0.49228	0.005244	-0.233189	0.05506	-0.178129
10	C6 - C13	0.230045	-0.475351	0.040421	-0.226989	0.054076	-0.172913
1	Y1 - O2	0.085187	0.458533	0.025476	-0.121691	0.118159	-0.003532
2	Y1 - O3	0.084276	0.465931	0.005144	-0.122119	0.119297	-0.002822
3	Y1 - O4	0.082863	0.46513	0.009951	-0.120631	0.118454	-0.002177
21	Y1 - H15	0.017226	0.074509	2.049776	-0.011812	0.01522	0.003408
5	O2 - C14	0.016805	0.054326	0.462178	-0.011741	0.012661	0.00092
63	O3 - H74	0.016448	0.049065	0.167582	-0.011198	0.011732	0.000534
112	H84 - C98	0.014953	0.066941	0.408961	-0.010349	0.013542	0.003193
36	H11 - C39	0.01493	0.066963	0.476507	-0.01034	0.01354	0.0032
130	H87 - C115	0.014874	0.06664	0.445917	-0.010281	0.01347	0.003189
119	O4 - H95	0.014755	0.046853	0.202877	-0.010168	0.010941	0.000773
65	H46 - C60	0.014728	0.066117	0.49775	-0.010151	0.01334	0.003189
108	O4 - H108	0.014626	0.046322	0.207175	-0.009953	0.010767	0.000814
83	H49 - C77	0.014461	0.065203	0.608379	-0.009919	0.01311	0.003191
37	O2 - H34	0.014288	0.047801	0.213041	-0.010098	0.011024	0.000926
84	O3 - H71	0.014179	0.04526	0.191898	-0.009545	0.01043	0.000885
71	O3 - H57	0.0141	0.046502	0.202579	-0.009844	0.010735	0.000891
18	O2 - H36	0.014084	0.046452	0.230287	-0.009822	0.010718	0.000896
138	O4 - H114	0.013668	0.044614	0.225258	-0.009307	0.01023	0.000923
66	O3 - H55	0.013465	0.045006	0.23709	-0.009308	0.01028	0.000972
100	O4 - H92	0.013196	0.043883	0.249556	-0.00897	0.00997	0.001
30	H8 - H25	0.011124	0.0478	7.6354	-0.006296	0.009123	0.002827
22	H15 - H95	0.005494	0.01746	0.952573	-0.002257	0.003311	0.001054
113	H55 - H92	0.004215	0.014108	0.290695	-0.001637	0.002582	0.000945
131	H36 - H109	0.003948	0.012977	0.746932	-0.001603	0.002424	0.000821
114	H74 - H92	0.003656	0.010864	1.320349	-0.001339	0.002028	0.000689

132	H55 - H108	0.002468	0.007047	1.711724	-0.000836	0.001299	0.000463
72	H34 - H57	0.002377	0.007335	0.652959	-0.000885	0.001359	0.000474
73	H36 - H57	0.00173	0.005009	0.404516	-0.000632	0.000942	0.00031

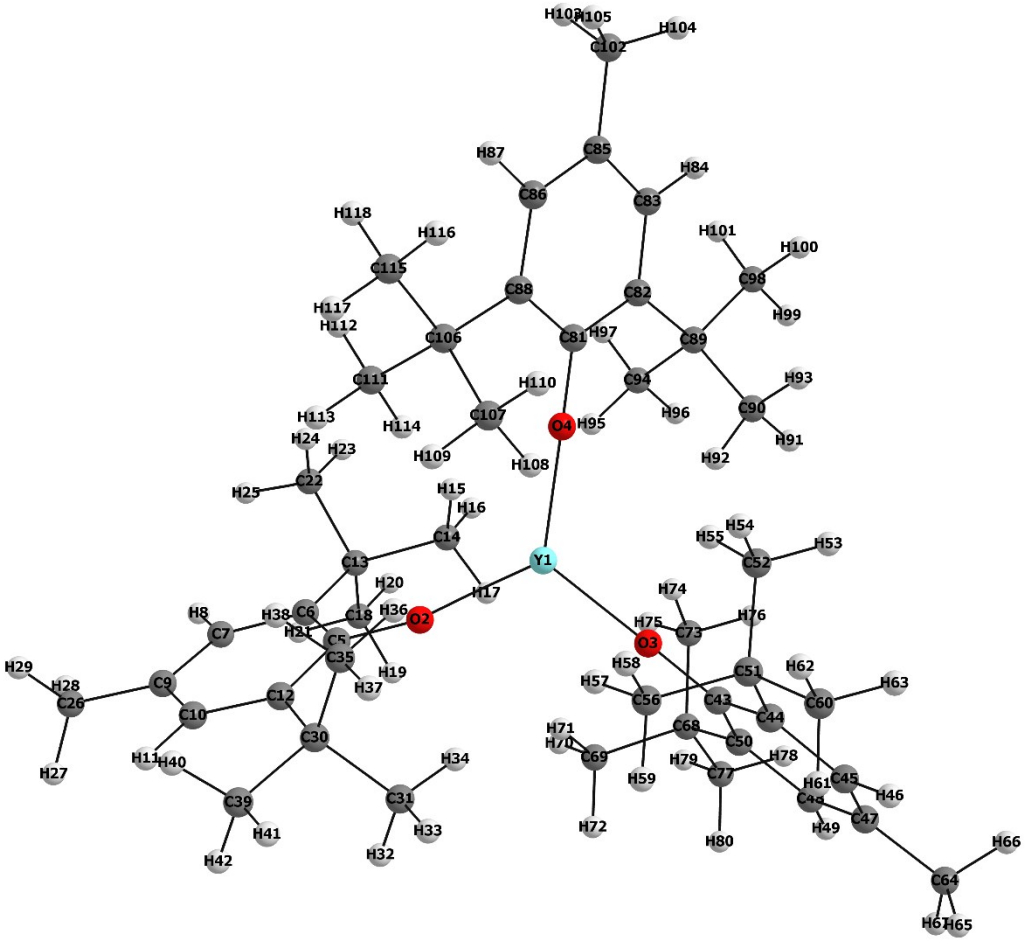

Figure S8. Numbering scheme for the pyramidal conformer of Y(O-2,6-^{t}Bu-4-Me$C_6H_2)_3$.