Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Circular Dichroism Spectroscopy of Catalyst Preequilibrium in Asymmetric Autocatalysis of Pyrimidyl Alkanol

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Contents

Materials

Methylcyclohexane (FUJIFILM Wako Pure Chemical) was dried over freshly activated MS 3A,. THF (FUJIFILM Wako Pure Chemical, super dehydrated grade) was used as purchased. Diisopropylzinc was prepared from the reaction of $ZnCl_2$ with isopropyl magnesium bromide in diethyl ether and purified by vacuum distillation. The solution of diisopropylzinc was prepared by diluting the distilled diisopropylzinc with dry solvents and the concentration was titillated by using iodine with LiCl method[1]. high enantiomeric excess (>99.5% ee) alkanol **2** was obtained by asymmetric autocatalytic reaction of aldehyde **1** with diisopropylzinc.[2]

CD spectrum measurement

The CD spectrum were measured on JASCO-720 spectropolarimeter equipped with a 450 W xenon lamp with 0.1 mm Cylindrical Quartz Cuvette with water jacket. The temperature was controlled by circulation of coolant to cell. All spectra were recorded under following conditions: Band width: 2.0 nm; speed: 200 nm/min; number of scene: 16. The temperature was lowered from 20°C to –20°C, and finally returned to 20°C again to confirm that it returned to the initial spectrum (Fig. S1).

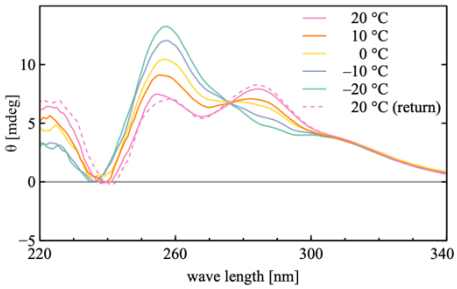


Fig. S1. CD spectra of **(*R*)-2•Zn** in various temperature ([**2•Zn**] = 8.4 ｍM, [*i*Pr$_2$Zn] = 60 mM, cell length = 0.1 mm).

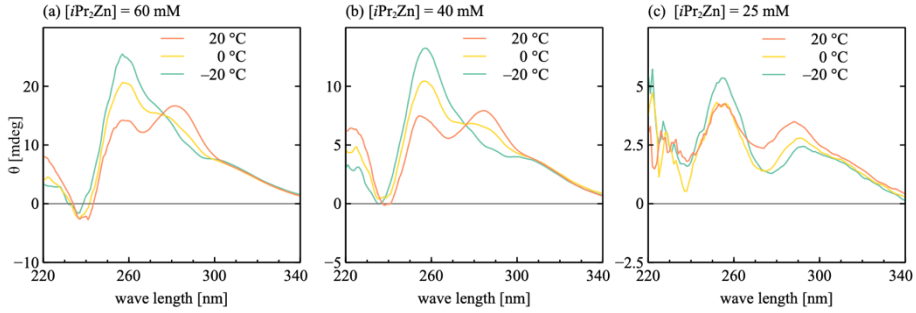


Fig. S2. CD spectra of **(*R*)-2•Zn** different equivalent *i*Pr$_2$Zn.

TD-DFT calculations

The DFT calculations were performed with Gaussian 09 rev. C[3] or Gaussian 16 rev. B[4] with G09Defaults option. The initial coordinates for calculations for the square dimer, macrocycle dimer, tetramer (brandy grass) and square dimer with *i*Pr_2Zn were obtained from reported optimize structure by Gridnev.[5] The initial coordinates for tetramer (crystal) was optimized from crystal structure[6] with B3LYP/6-31G(d) level, and dimer with THF was also optimized with B3LYP/6-31G(d) level from crystal structure of dimer with pyridine by replacing pyridine to THF. TD-DFT caluculation was performed with NState=40 for dimer structure and NState=80 for tetramer structure. solvent effect was accounted by PCM model. Simulation of CD spectra were calculated by Gauss View 6 with Harf-Width = 0.1 eV (for spectra in methyl cyclohexane) or Harf-Width = 0.2 eV (for spectra in THF). Some calculations were performed on *S* conformation. To compare the observed spectrum of *R* isomer, calculated CD was inverted.

To evaluate the basis set effect, TD-DFT calculation with various basis level was performed on square dimer optimized by B3LYP/6-31G(d) level (Fig. S3). As frequently pointed out, including the diffuse function seems indispensable to calculate excited state. Omitting diffuse function on heavy atoms significantly affect excitation energy and shape of calculated spectrum. On the other hand, diffuse function and polar function on hydrogen atom 6-31++G(d), 6-31+G(d,p) or using triple-zeta basis set 6-311+G(d)have little effect on appearance of calculated CD spectrum at least in this zinc alkoxide system. Thus, for the balance of calculation cost we use 6-31+G(d) base function for the CD spectrum calculation. The functional with long-range-correction such as CAM-B3LYP, w97XD afforded more reasonable peak position for this alkoxide system. Thus, we used CAM-B3LYP functional for further calculation of alkoxides (Fig. S4).

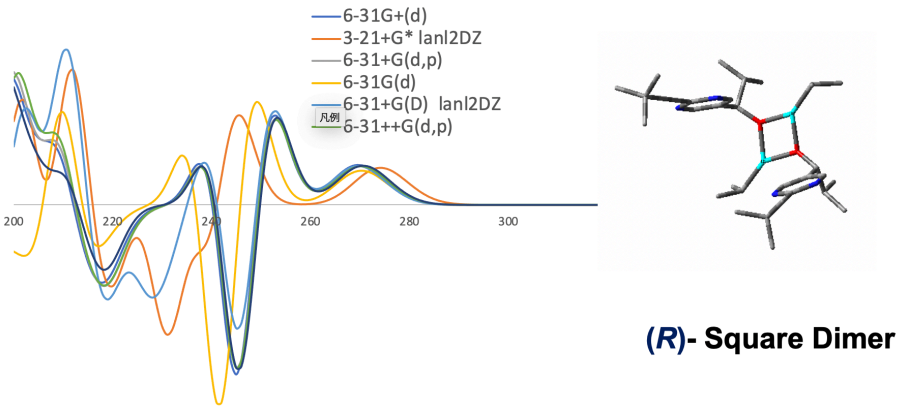


Fig S3. calculated CD spectrum for (*R*)-square dimer with various basis set.

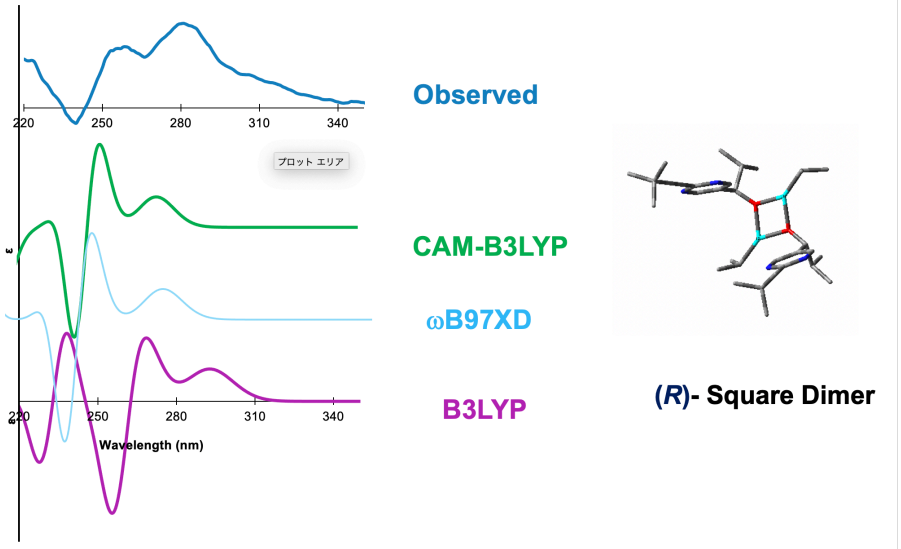


Fig. S4. calculated CD spectrum for (*R*)-square dimer with various functionals.

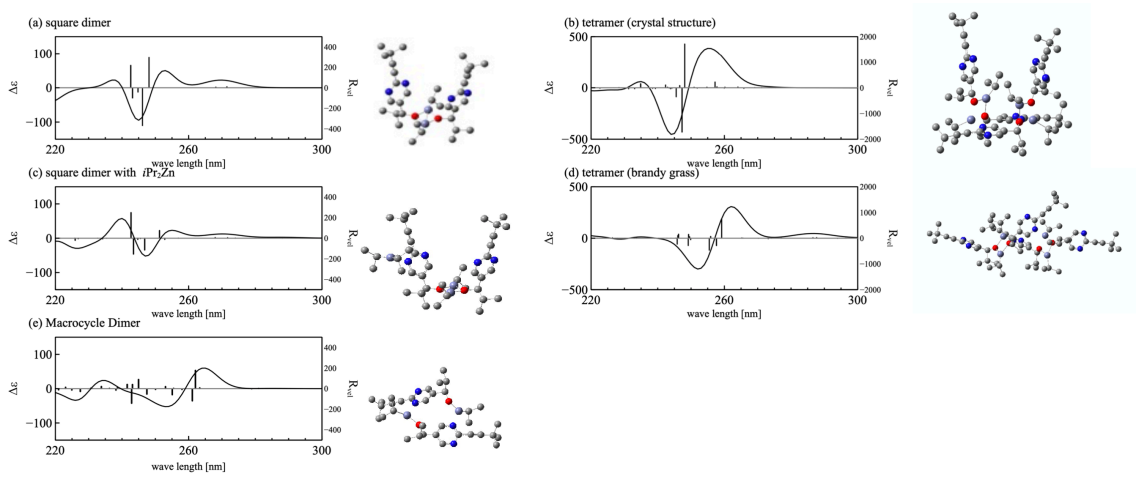
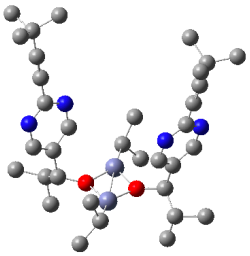


Fig. S5. calculated CD for various conformation of (*R*)-**2•Zn**.

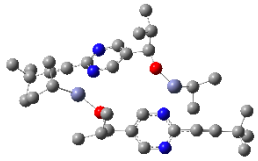
Coordinates for TD-DFT calculations

(*R*)-square dimer (from Gridnev's paper)



No	Symbol	X	Y	Z	32	C	3.5307	0.5457	-4.0917	64	H	2.0235	5.2533	0.7342
1	Zn	2.5115	0.1685	1.4799	33	C	1.0309	0.1593	-3.9652	65	H	2.5745	1.2983	3.7177
2	C	2.4125	0.2485	3.4309	34	C	3.2627	3.4374	0.7052	66	H	3.4865	-0.5042	5.188
3	C	1.032	-0.1669	3.9654	35	C	3.062	4.9537	0.5637	67	H	3.4436	-1.6486	3.846
4	O	2.5967	-1.2636	0.142	36	C	4.7511	3.0805	0.5852	68	H	4.5289	-0.2545	3.7805
5	Zn	2.5086	-0.1909	-1.4807	37	C	3.5276	-0.5806	4.0896	69	H	0.2224	0.4632	3.5762
6	O	2.6134	1.2401	-0.1428	38	C	-6.279	-4.716	1.3662	70	H	0.9944	-0.0972	5.0641
7	C	2.4229	2.6367	-0.3243	39	C	-5.9416	-5.685	-0.9466	71	H	0.7851	-1.2055	3.707
8	C	0.943	2.9718	-0.2708	40	H	0.4725	-1.7949	-1.4862	72	H	-7.3479	-4.9572	1.3241
9	C	0.3089	3.7895	-1.2099	41	H	0.8247	-4.2216	2.0403	73	H	-6.1476	-3.8436	2.0146
10	N	-0.989	4.0954	-1.1646	42	H	2.7583	-2.9343	1.3261	74	H	-5.7514	-5.5605	1.8213
11	C	-1.6912	3.5674	-0.1431	43	H	2.8709	-3.1628	-1.7032	75	H	-5.4087	-6.547	-0.5321
12	N	-1.1961	2.7531	0.8134	44	H	5.293	-3.6572	-1.3511	76	H	-5.5697	-5.5087	-1.9611
13	C	0.1017	2.4706	0.7282	45	H	4.896	-2.055	-0.7044	77	H	-7.0076	-5.9346	-1.0076
14	C	-3.0847	3.8904	-0.0696	46	H	5.1039	-3.4272	0.3945	78	H	-6.1389	-3.0123	-1.681
15	C	-4.2643	4.1624	-0.0093	47	H	1.9636	-5.2716	-0.7294	79	H	-6.3798	-2.3343	-0.061
16	C	-5.6984	4.4846	0.0611	48	H	3.2939	-5.3287	0.44	80	H	-7.5763	-3.4613	-0.7364
17	C	2.391	-2.6579	0.3242	49	H	3.6234	-5.5248	-1.2853	81	H	0.8724	4.2153	-2.0411
18	C	3.2216	-3.4685	-0.705	50	H	2.5576	-1.3225	-3.7178	82	H	0.4963	1.7962	1.4883
19	C	3.0055	-4.9825	-0.5613	51	H	0.9918	0.0894	-5.0639	83	C	-6.1463	4.502	1.5415
20	C	0.9074	-2.9771	0.2712	52	H	0.7955	1.2005	-3.7071	84	C	-6.4932	3.4041	-0.7117
21	C	0.071	-2.4659	-0.7268	53	H	0.2147	-0.4618	-3.5752	85	C	-5.9446	5.8709	-0.5793
22	N	-1.2297	-2.7349	-0.8117	54	H	4.5287	0.2091	-3.7833	86	H	-7.5653	3.6303	-0.6679
23	C	-1.7328	-3.545	0.1441	55	H	3.4878	0.4691	-5.19	87	H	-6.331	2.4123	-0.2774
24	N	-1.0357	-4.0813	1.1648	56	H	3.4584	1.6147	-3.8487	88	H	-6.1899	3.3705	-1.763
25	C	0.2652	-3.789	1.2098	57	H	2.793	2.9096	-1.3261	89	H	-7.0122	6.1174	-0.5374
26	C	-3.1296	-3.854	0.071	58	H	2.9098	3.134	1.7033	90	H	-5.6284	5.88	-1.6273
27	C	-4.3117	-4.1151	0.0128	59	H	5.3366	3.6035	1.3497	91	H	-5.3898	6.652	-0.0492
28	C	-5.7468	-4.4325	-0.0583	60	H	4.9223	2.0066	0.7006	92	H	-7.2158	4.7356	1.6053
29	C	-6.5056	-3.2331	-0.6734	61	H	5.1434	3.3785	-0.3961	93	H	-5.5943	5.258	2.1095
30	C	4.7137	-3.1268	-0.587	62	H	3.6869	5.4888	1.2871	94	H	-5.9756	3.5294	2.0141
31	C	2.4072	-0.2709	-3.4315	63	H	3.3519	5.2982	-0.4378					

(*R*)-Macrocyclic dimer (from Gridnev's paper)



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6	C	-0.928151	2.514699	-0.50244
7	C	-1.307651	1.186599	-0.34054
8	H	-0.561851	0.424799	-0.17194
9	C	0.543749	2.931899	-0.39534
10	O	1.328049	1.796999	-0.26584
11	Zn	2.952549	1.327998	0.49926
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13	H	4.132149	2.568298	2.31546
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15	H	5.910749	0.950398	3.03976
16	H	5.443249	-0.147802	1.73616
17	H	4.308249	0.199998	3.04256
18	C	5.640449	2.529598	0.80296
19	H	5.29075	3.428698	0.27896
20	H	6.469749	2.839298	1.46156
21	H	6.075149	1.864198	0.04446
22	N	2.475749	-0.770302	0.33986
23	C	3.137149	-1.745802	-0.32664
24	N	2.689848	-3.002502	-0.46744
25	C	1.501248	-3.288001	0.07626
26	H	1.146148	-4.307101	-0.07144
27	H	0.752149	-0.291301	1.37316
28	C	1.288849	-1.089201	0.87496
29	C	0.722648	-2.359201	0.77226
30	C	-0.681952	-2.637901	1.30736
31	O	-1.459751	-1.485601	1.17946
32	Zn	-2.747451	-1.335501	-0.17054
33	C	-3.683852	-2.4796	-1.47774
34	H	-2.986252	-3.308701	-1.68004
35	C	-3.927451	-1.761	-2.81294
36	H	-4.596451	-0.8984	-2.69484
37	H	-4.394952	-2.427	-3.55874
38	H	-2.995751	-1.385801	-3.25684
39	C	-4.981252	-3.1059	-0.94734
40	H	-5.453652	-3.7663	-1.69504
41	H	-5.727152	-2.3416	-0.68894
42	H	-4.813452	-3.7076	-0.04454
43	C	4.381649	-1.415902	-0.95014
44	C	5.432149	-1.203502	-1.51994
45	C	-4.910251	1.331	-0.54354
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47	C	-7.546251	0.8244	-0.44384
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49	H	-8.083651	2.8331	-1.14084
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53	H	-8.936151	-0.274799	0.81746
54	H	-7.342251	-1.0464	0.68486
55	H	-7.549851	0.3909	1.70596
56	C	-7.987551	0.1254	-1.75254
57	H	-7.776551	0.7538	-2.62384
58	H	-7.470751	-0.8305	-1.88414
59	H	-9.066051	-0.066799	-1.71874
60	C	6.705049	-0.974402	-2.22324
61	C	6.632149	0.362098	-2.99924
62	H	6.468949	1.205098	-2.32004
63	H	7.574449	0.528298	-3.53374
64	H	5.818849	0.347398	-3.73214
65	C	6.946848	-2.141202	-3.21074
66	H	7.894149	-1.985403	-3.73934
67	H	6.999448	-3.098602	-2.68244
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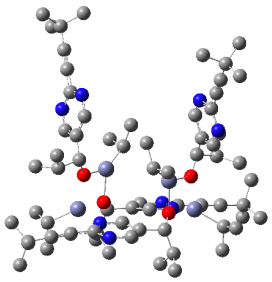
69	C	7.854949	-0.919203	-1.18814
70	H	7.706849	-0.101503	-0.47564
71	H	7.923949	-1.856703	-0.62694
72	H	8.806549	-0.756803	-1.70704
73	C	-0.685352	-3.148401	2.78096
74	H	-1.752352	-3.299401	2.99936
75	C	-0.152151	-2.108601	3.77306
76	H	-0.655851	-1.147501	3.63396
77	H	-0.321452	-2.438701	4.80486
78	H	0.928349	-1.953701	3.65456
79	C	0.026448	-4.498301	2.94306
80	H	1.106948	-4.408701	2.77336
81	H	-0.112152	-4.888301	3.95816
82	H	-0.363052	-5.248801	2.24356
83	H	-1.076352	-3.477801	0.70266
84	C	0.70855	3.998899	0.73756
85	H	-0.08645	4.743099	0.58276
86	C	0.52585	3.398499	2.13706
87	H	0.56955	4.181599	2.90236
88	H	-0.436051	2.882999	2.23836
89	H	1.318449	2.676099	2.35846
90	C	2.04685	4.740399	0.61646
91	H	2.16035	5.195698	-0.37494
92	H	2.11765	5.539099	1.36416
93	H	2.89245	4.063998	0.77646
94	H	0.77655	3.465299	-1.33994

(*R*)-Tetramer (crystal structure)



Row	Symbol	X	Y	Z	49	C	4.2729	4.0791	2.0263	98	H	-0.2872	3.0106	2.8645
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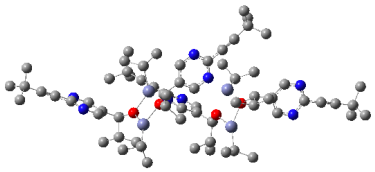
2	C	5.3165	-3.2612	2.084	51	C	3.8408	1.9219	0.4512	100	H	-4.8919	-4.7115	-0.9142
3	C	4.6839	-4.991	0.3562	52	C	3.5923	3.231	0.0255	101	H	-5.3644	-4.2999	0.736
4	C	0.5662	1.002	2.6882	53	C	4.7087	6.1902	3.5597	102	H	-6.5895	-4.4323	-0.5384
5	C	1.2041	1.0529	4.0885	54	C	4.9416	7.3699	4.4083	103	H	-5.8281	-1.226	-2.3201
6	C	0.323	2.4221	2.1591	55	C	3.5936	8.0905	4.6513	104	H	-5.1878	-2.7894	-2.8212
7	C	-5.3981	-2.5864	-0.639	56	C	5.9203	8.3278	3.6875	105	H	-6.8607	-2.6634	-2.2826
8	C	-5.5663	-4.0795	-0.3197	57	C	5.5463	6.9224	5.7594	106	H	0.5329	0.3808	-2.75
9	C	-5.8386	-2.2983	-2.084	58	C	-3.3975	4.7772	-2.0114	107	H	0.578	2.3437	-1.2079
10	C	-0.366	1.0139	-2.6872	59	C	-2.9312	3.7862	-0.0147	108	H	0.8034	2.8538	-2.8891
11	C	0.0873	2.3929	-2.1883	60	C	-3.4171	2.5551	-0.4673	109	H	-0.7503	3.0936	-2.0923
12	C	-0.948	1.123	-4.1084	61	C	-3.8739	2.5599	-1.7916	110	H	-0.2283	1.5897	-4.8001
13	C	1.0392	-2.8119	2.5447	62	C	-3.4044	5.9578	-2.8243	111	H	-1.2104	0.1441	-4.5327
14	C	1.4738	-4.3073	2.5594	63	C	-3.4121	6.956	-3.5117	112	H	-1.8527	1.7443	-4.132
15	C	1.3009	-4.9591	3.9387	64	C	-3.4219	8.1712	-4.3418	113	H	1.4986	-2.3597	3.4416
16	C	0.8101	-5.1525	1.467	65	C	-4.5094	9.1359	-3.8103	114	H	2.548	-4.2635	2.3449
17	C	3.6161	0.7147	-0.4441	66	C	-2.0358	8.8536	-4.2596	115	H	1.7618	-5.9531	3.9463
18	C	4.8942	0.2898	-1.2208	67	C	-3.7336	7.7901	-5.8079	116	H	1.7769	-4.3686	4.7311
19	C	6.0962	-0.011	-0.3173	68	C	4.5113	5.2223	2.8575	117	H	0.244	-5.0917	4.2008
20	C	5.262	1.3167	-2.3022	69	N	2.1501	-2.7431	-1.6845	118	H	0.9406	-4.7078	0.4762
21	C	-1.564	-2.6573	-2.5274	70	N	1.921	-3.0108	-4.0412	119	H	1.2547	-6.1537	1.4399
22	C	-1.7629	-4.962	-1.3707	71	N	-2.6358	-2.2885	1.6955	120	H	-0.2648	-5.2751	1.6462
23	C	-2.2445	-4.0582	-2.5104	72	N	-2.4564	-2.5697	4.0551	121	H	2.88	1.011	-1.2098
24	C	-2.1423	-4.7781	-3.8625	73	N	4.5322	2.8662	2.5575	122	H	4.6125	-0.6407	-1.7332
25	C	-3.4607	1.3175	0.413	74	N	3.8023	4.3081	0.785	123	H	6.9123	-0.4478	-0.9052
26	C	-4.8247	1.1464	1.1419	75	N	-3.8703	3.6432	-2.5694	124	H	6.4842	0.9004	0.1521
27	C	-6.0318	1.1092	0.1966	76	N	-2.9161	4.8942	-0.7589	125	H	5.8402	-0.7225	0.4724
28	C	-5.0158	2.2085	2.2347	77	O	1.5039	-2.1493	1.3849	126	H	5.5759	2.271	-1.8623
29	C	2.6625	-2.9493	-2.9231	78	O	3.0899	-0.3683	0.3123	127	H	6.0947	0.9486	-2.9123
30	C	0.5984	-2.8975	-3.9095	79	O	-1.9089	-1.8964	-1.386	128	H	4.4201	1.5159	-2.9762
31	C	-0.0477	-2.7429	-2.6771	80	O	-3.135	0.16	-0.3459	129	H	-1.9408	-2.1561	-3.4368
32	C	0.815	-2.6487	-1.5883	81	Zn	3.197	-2.4073	0.2006	130	H	-2.3741	-5.87	-1.3225
33	C	4.0733	-3.1121	-3.0808	82	Zn	1.6084	-0.1694	1.5114	131	H	-0.7216	-5.2749	-1.5142
34	C	5.2475	-3.2886	-3.3316	83	Zn	-3.6192	-1.8152	-0.1944	132	H	-1.8381	-4.4625	-0.4006
35	C	6.6588	-3.511	-3.6852	84	Zn	-1.625	0.0618	-1.5245	133	H	-3.3029	-3.8306	-2.3358
36	C	6.7193	-4.546	-4.8355	85	H	5.5848	-3.1029	-0.0232	134	H	-2.4898	-4.1458	-4.6889
37	C	7.4371	-4.0426	-2.4598	86	H	6.257	-3.8048	2.2767	135	H	-1.1143	-5.0913	-4.0825
38	C	7.2744	-2.172	-4.1598	87	H	5.5094	-2.2007	2.2938	136	H	-2.7611	-5.6822	-3.8568
39	C	-3.177	-2.4057	2.9337	88	H	4.6006	-3.6078	2.8429	137	H	-2.707	1.4521	1.2067
40	C	-1.3026	-2.4084	1.6028	89	H	4.4156	-5.1814	-0.6907	138	H	-4.7543	0.17	1.6418
41	C	-0.4688	-2.6368	2.6941	90	H	5.6285	-5.5268	0.5539	139	H	-6.214	2.0884	-0.2608
42	C	-1.1325	-2.6711	3.9264	91	H	3.9197	-5.4781	0.9779	140	H	-5.8966	0.3764	-0.6036
43	C	-4.5969	-2.3628	3.0834	92	H	-0.4205	0.5247	2.7962	141	H	-6.9366	0.8325	0.7493
44	C	-5.7874	-2.3846	3.3177	93	H	1.324	0.0558	4.5341	142	H	-4.1766	2.2209	2.9406
45	C	-7.224	-2.4445	3.6314	94	H	2.1951	1.5242	4.0684	143	H	-5.1137	3.2138	1.8075
46	C	-7.7352	-3.8778	3.3424	95	H	0.5886	1.644	4.7856	144	H	-5.9283	2.0072	2.8076
47	C	-7.4235	-2.1098	5.129	96	H	1.2573	2.9777	2.0166	145	H	0.0287	-2.923	-4.8372
48	C	-7.9966	-1.4292	2.7582	97	H	-0.2013	2.4248	1.1951	146	H	0.4508	-2.4803	-0.5861

147	H	6.1672	-4.1932	-5.7123	161	H	-6.8844	-2.8185	5.7658	175	H	6.502	6.4095	5.6106
148	H	7.763	-4.712	-5.1266	162	H	-7.0632	-1.1018	5.3586	176	H	5.7181	7.7958	6.3998
149	H	6.2921	-5.5047	-4.5247	163	H	-8.4894	-2.1606	5.3799	177	H	4.8711	6.2378	6.283
150	H	8.4838	-4.2158	-2.7359	164	H	-7.6565	-0.4064	2.951	178	H	-2.525	3.8829	0.9922
151	H	7.412	-3.3259	-1.6333	165	H	-7.8612	-1.6422	1.6933	179	H	-4.2532	1.6463	-2.2446
152	H	7.0139	-4.9863	-2.1022	166	H	-9.0665	-1.4839	2.9899	180	H	-4.3092	9.4185	-2.7717
153	H	8.3204	-2.3306	-4.4461	167	H	4.5194	0.8384	2.1971	181	H	-4.5281	10.0472	-4.4199
154	H	6.7355	-1.7749	-5.026	168	H	3.1933	3.4206	-0.9711	182	H	-5.5003	8.672	-3.8532
155	H	7.2468	-1.4209	-3.3639	169	H	2.8822	7.431	5.1591	183	H	-1.7943	9.1271	-3.2274
156	H	-0.9128	-2.3053	0.6013	170	H	3.7532	8.9753	5.2792	184	H	-1.2486	8.1878	-4.6283
157	H	-0.5754	-2.7764	4.8561	171	H	3.145	8.4127	3.7061	185	H	-2.0313	9.7647	-4.8699
158	H	-7.5995	-4.14	2.2887	172	H	6.098	9.2145	4.3077	186	H	-3.7501	8.6905	-6.4336
159	H	-7.2024	-4.6149	3.952	173	H	6.8823	7.839	3.5017	187	H	-2.9752	7.1076	-6.2051
160	H	-8.8033	-3.9406	3.5811	174	H	5.5122	8.6544	2.7256	188	H	-4.7083	7.2974	-5.885

(*S*)-Tetramer (brandy grass, from Gridnev's paper)



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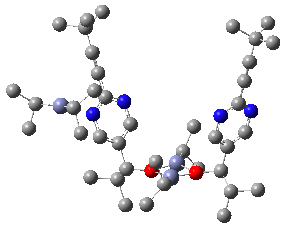
2	N	8.625795	0.293901	1.117504	55	C	-0.528605	0.755196	3.471504	108	H	-2.541707	4.245595	1.890204
3	C	7.418595	0.0487	1.666004	56	N	0.546294	1.521697	3.741304	109	H	-2.349307	3.988895	0.150904
4	C	6.460995	-0.7816	1.068404	57	C	1.589294	1.485597	2.876504	110	H	-1.309507	3.123496	1.288204
5	C	6.831796	-1.3355	-0.165196	58	N	1.592895	0.708797	1.751704	111	H	-5.555506	2.096694	1.189104
6	N	8.030796	-1.1137	-0.738496	59	C	0.519495	-0.083603	1.523504	112	H	-4.997707	3.648994	1.841604
7	C	5.111096	-1.055301	1.710204	60	C	2.716094	2.299098	3.178704	113	H	-4.977607	3.361194	0.098004
8	C	5.067596	-2.416601	2.466304	61	C	3.629394	3.024898	3.530204	114	H	1.422294	1.800297	-4.020396
9	C	3.707896	-2.603702	3.164704	62	C	4.695693	3.930899	4.001404	115	H	-0.575205	-0.486104	-0.957296
10	C	10.176295	-0.066199	-0.660996	63	C	4.434993	4.277199	5.494204	116	H	-0.500004	-2.126204	-3.103296
11	C	11.267195	0.138102	-1.160196	64	C	-1.586404	-2.491204	4.111904	117	H	0.474197	-3.574703	-3.381296
12	C	12.592295	0.385203	-1.762296	65	C	-3.613303	-4.135705	-0.299396	118	H	0.470296	-2.814603	-1.781296
13	C	13.536595	-0.802297	-1.424496	66	C	-5.013603	-4.669506	0.061904	119	H	2.565896	-2.325902	-3.089496
14	O	4.064395	-0.982402	0.715204	67	C	-3.171903	-4.668605	-1.678796	120	H	0.696995	-0.876703	-5.057696
15	Zn	3.036995	0.679998	0.169104	68	C	-5.332504	-1.348606	-2.991896	121	H	1.597296	-2.365703	-5.372296
16	C	3.622194	2.347598	-0.772896	69	C	-6.530604	-1.130307	-3.937196	122	H	2.472095	-0.848102	-5.109796
17	C	2.677793	3.544298	-0.535296	70	C	-4.013804	-1.311306	-3.786596	123	H	2.677495	0.089798	-2.870596
18	Zn	3.293696	-2.299702	-0.510896	71	C	-2.336207	3.477495	1.123004	124	H	4.966798	-5.715801	-1.555596
19	C	3.473797	-4.217302	-0.958896	72	C	0.452096	-2.612503	-2.857096	125	H	5.589997	-4.508201	-0.427496
20	C	2.877497	-5.119202	0.142004	73	C	4.918097	-4.647001	-1.285896	126	H	5.340397	-4.081001	-2.126796
21	O	2.143195	-0.778603	-1.053996	74	C	5.083694	2.750699	-0.493896	127	H	2.945898	-6.185402	-0.133896
22	C	1.827395	-0.455603	-2.430696	75	C	6.211296	-2.552601	3.491204	128	H	3.410597	-5.004002	1.095704
23	C	1.650296	-1.749003	-3.284796	76	C	6.079693	3.241399	3.861404	129	H	1.818497	-4.898903	0.330304
24	C	1.602596	-1.436203	-4.791996	77	C	4.674492	5.234099	3.154004	130	H	2.872597	-4.372902	-1.869496
25	C	0.630695	0.475097	-2.494396	78	C	-4.520408	5.971494	-2.113896	131	H	3.560394	2.094598	-1.847496
26	C	0.586094	1.571497	-3.367496	79	C	-6.012007	4.139693	-3.046096	132	H	5.243094	2.986699	0.567804
27	N	-0.472506	2.401696	-3.449796	80	C	12.445795	0.508502	-3.303696	133	H	5.377493	3.649799	-1.065096
28	C	-1.522506	2.179996	-2.622596	81	C	13.185294	1.700403	-1.187696	134	H	5.790594	1.952999	-0.756396
29	N	-1.545106	1.164396	-1.707696	82	H	-1.357105	0.834596	4.168104	135	H	2.990193	4.434698	-1.110296
30	C	-0.490805	0.316396	-1.674796	83	H	0.586995	-0.696903	0.637204	136	H	2.658993	3.840098	0.522404
31	Zn	-2.967805	0.859395	-0.128596	84	H	-2.656305	-0.505405	2.646304	137	H	1.642593	3.319697	-0.826196
32	C	-3.363206	2.327495	1.171304	85	H	-2.630904	-2.897405	2.280104	138	H	4.927995	-0.266701	2.457904
33	C	-4.798006	2.882494	1.071204	86	H	-1.610803	-3.534804	4.445104	139	H	5.186697	-3.205001	1.706604
34	C	-2.639706	3.052995	-2.733896	87	H	-2.419104	-1.965905	4.595404	140	H	6.126997	-3.505801	4.025204
35	C	-3.552507	3.840595	-2.909296	88	H	-0.649504	-2.050504	4.474304	141	H	6.164696	-1.749501	4.238804
36	C	-4.623607	4.825494	-3.159396	89	H	-0.587103	-3.102304	0.814904	142	H	7.197996	-2.52	3.019104
37	C	-4.445008	5.408794	-4.588996	90	H	0.439496	-2.825803	2.241104	143	H	3.655697	-3.585002	3.650204
38	O	-2.150105	-0.904205	0.663804	91	H	-0.597003	-4.254804	2.161204	144	H	3.565196	-1.837302	3.938404
39	Zn	-3.424004	-2.169905	-0.195496	92	H	-2.908503	-4.537705	0.446704	145	H	2.879396	-2.527802	2.455804
40	O	-4.176105	-0.536006	-0.958796	93	H	-3.227802	-5.769705	-1.718196	146	H	6.861793	3.9168	4.225704
41	C	-5.304305	-0.307106	-1.833696	94	H	-3.814503	-4.289505	-2.485196	147	H	6.118694	2.319199	4.451304
42	C	-6.590105	-0.295207	-1.024496	95	H	-2.139203	-4.386605	-1.922796	148	H	6.293994	2.999399	2.815604
43	C	-7.599705	0.655793	-1.223296	96	H	-5.324603	-4.374606	1.072804	149	H	4.858193	5.018399	2.096904
44	N	-8.749405	0.665592	-0.518096	97	H	-5.043902	-5.771606	0.020604	150	H	3.708992	5.742498	3.243104
45	C	-8.909505	-0.302408	0.422704	98	H	-5.781803	-4.308106	-0.635896	151	H	5.458192	5.911099	3.512304
46	N	-7.979904	-1.257107	0.703004	99	H	-5.181805	0.685694	-2.294296	152	H	3.465393	4.770598	5.617104
47	C	-6.841404	-1.236507	-0.015896	100	H	-5.434904	-2.341106	-2.525296	153	H	4.446093	3.374499	6.113704
48	C	-10.126905	-0.318509	1.165204	101	H	-4.021304	-2.068606	-4.578896	154	H	5.217993	4.954399	5.853304
49	C	-11.167705	-0.335109	1.795604	102	H	-3.152004	-1.498205	-3.140296	155	H	-3.549108	6.472495	-2.178296
50	C	-12.430405	-0.35771	2.560104	103	H	-3.878005	-0.329305	-4.259496	156	H	-5.305908	6.710494	-2.307496
51	C	-1.824105	-0.948104	2.075604	104	H	-6.505304	-1.860707	-4.753596	157	H	-4.647208	5.588294	-1.096596
52	C	-1.685804	-2.418604	2.576704	105	H	-6.495905	-0.129207	-4.387496	158	H	-6.106407	3.325093	-3.772396

159	H	-6.167407	3.734093	-2.041096	169	H	11.784694	1.340602	-3.567696	179	C	-13.557605	0.30049	1.718604
160	H	-6.799807	4.874193	-3.247296	170	H	13.428995	0.690303	-3.752996	180	H	-13.175205	0.41729	4.457804
161	H	-3.473208	5.902495	-4.690896	171	H	12.537394	2.553202	-1.416096	181	H	-11.450305	-0.012709	4.496404
162	H	-4.514407	4.620294	-5.345696	172	H	13.299794	1.635003	-0.100596	182	H	-11.976006	1.476491	3.681804
163	H	-5.232008	6.146194	-4.782796	173	H	14.170794	1.884803	-1.630896	183	H	-14.495705	0.287889	2.285604
164	H	-7.488306	1.440193	-1.966396	174	H	13.658395	-0.908897	-0.341496	184	H	-13.310006	1.33999	1.479604
165	H	-6.103804	-1.991307	0.231004	175	H	13.140196	-1.742097	-1.822996	185	H	-13.712305	-0.24241	0.780204
166	H	7.214695	0.5399	2.613004	176	H	14.522495	-0.624397	-1.869296	186	H	-13.749304	-1.84941	3.451304
167	H	6.147396	-1.969501	-0.716196	177	C	-12.811304	-1.82821	2.884504	187	H	-12.948504	-2.40811	1.965704
168	H	12.032595	-0.410898	-3.731496	178	C	-12.241105	0.43359	3.884504	188	H	-12.031904	-2.310009	3.484004

Square dimer with iPr_2Zn (from Gridnev's paper)



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5	Zn	1.823509	-2.193592	1.36961
6	O	0.713309	-2.692592	-0.18689
7	C	-0.664891	-3.007592	-0.22259
8	C	-1.479391	-1.750192	-0.48739
9	C	-2.623291	-1.416491	0.23441
10	N	-3.343491	-0.313291	-0.00849
11	C	-2.914691	0.492909	-1.00399
12	N	-1.816591	0.274209	-1.74999
13	C	-1.121391	-0.830192	-1.47929
14	C	-3.682391	1.666709	-1.28059
15	C	-4.315091	2.669809	-1.53799
16	C	-5.075891	3.888609	-1.85689
17	C	4.467809	-1.520292	-0.04519
18	C	5.295909	-2.132692	1.11561
19	C	6.728609	-1.580692	1.16031
20	C	4.427609	-0.001892	0.00321
21	C	3.603509	0.690008	0.89641
22	N	3.550409	2.019208	0.97631
23	C	4.348009	2.698408	0.12491
24	N	5.167209	2.147208	-0.79139
25	C	5.192609	0.812208	-0.83559
26	C	4.313709	4.129608	0.19991
27	C	4.283409	5.340108	0.26701
28	C	4.247609	6.809608	0.35221
29	C	2.80741	7.266308	0.68521
30	C	5.315509	-3.664692	1.01691
31	C	1.511909	-1.980092	3.29781
32	C	0.857509	-3.226892	3.91491
33	C	0.699709	-0.718092	3.62861
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35	C	-2.449591	-4.484691	-1.32619
36	C	-0.123491	-5.378592	-0.94349
37	C	3.306109	-3.253292	-4.08159
38	C	4.68981	7.412108	-1.00199
39	C	5.21321	7.272208	1.47031
40	H	2.946009	0.141308	1.56881
41	H	5.854109	0.369708	-1.58069
42	H	4.966009	-1.810292	-0.98459
43	H	4.787509	-1.849892	2.05021
44	H	5.862309	-4.097892	1.86211
45	H	4.305509	-4.083792	1.01331
46	H	5.818009	-3.987492	0.09531
47	H	6.752109	-0.498092	1.31901
48	H	7.263409	-1.796192	0.22591
49	H	7.290509	-2.049392	1.97581
50	H	2.500809	-1.866692	3.76811
51	H	0.559609	-0.605292	4.71611
52	H	-0.304791	-0.748192	3.18481
53	H	1.182609	0.200108	3.27031
54	H	1.457809	-4.132392	3.75871
55	H	0.718709	-3.112792	5.00271
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59	H	-0.290191	-6.152792	-1.70079
60	H	0.946509	-5.155092	-0.91429
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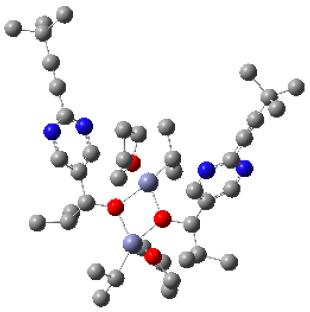
70	H	2.494209	-0.857292	-5.19019
71	H	3.351709	-0.447392	-3.70259
72	H	4.66911	8.506708	-0.94559
73	H	4.02091	7.096108	-1.80929
74	H	5.70731	7.098808	-1.25749
75	H	6.240609	6.959808	1.25671
76	H	4.921409	6.854608	2.43941
77	H	5.19311	8.365708	1.54511
78	H	2.473809	6.848808	1.64081
79	H	2.104709	6.947908	-0.09179
80	H	2.77271	8.359808	0.75461
81	H	-2.981191	-2.051491	1.04221
82	H	-0.224191	-0.990992	-2.07269
83	C	-4.375091	4.632909	-3.01809
84	C	-5.125991	4.797009	-0.60469
85	C	-6.512891	3.495109	-2.27639
86	H	-5.691191	5.707309	-0.83489
87	H	-4.118991	5.087109	-0.28799
88	H	-5.616891	4.288809	0.23171
89	H	-7.084891	4.399209	-2.51429
90	H	-7.028091	2.962909	-1.47019
91	H	-6.502191	2.851009	-3.16159
92	H	-4.933591	5.543709	-3.26239
93	H	-4.327691	4.006509	-3.91479
94	H	-3.354191	4.917609	-2.74359
95	Zn	-5.249291	0.071309	1.16611
96	C	-6.609091	-0.678391	-0.06789
97	H	-6.345291	-0.336291	-1.08199
98	C	-8.032491	-0.177891	0.22071
99	H	-8.773991	-0.591091	-0.48659
100	H	-8.106991	0.916509	0.15961
101	H	-8.370591	-0.463191	1.22741
102	C	-6.582591	-2.214991	-0.09529
103	H	-6.834591	-2.647191	0.88431
104	H	-5.595291	-2.608491	-0.37489
105	H	-7.309191	-2.633591	-0.81419
106	C	-4.576091	0.800209	2.88771
107	H	-5.463291	1.083609	3.47711
108	C	-3.718591	2.064109	2.73061
109	H	-2.826491	1.877409	2.11601
110	H	-3.356491	2.445909	3.70191
111	H	-4.270191	2.883009	2.25001
112	C	-3.816691	-0.254791	3.70811
113	H	-4.428991	-1.141591	3.92251
114	H	-3.473191	0.141309	4.68001
115	H	-2.914191	-0.605191	3.18531

Square dimer with THF (optimized from crystal structure)



Row	Symbol	X	Y	Z
1	Zn	0.022945	-3.184108	-0.615762
2	Zn	0.022481	-0.413541	0.550272
3	C	-0.012959	-4.513416	-2.090594
4	H	-1.059159	-4.855807	-2.158789
5	C	-5.798654	4.201619	0.102597
6	C	3.288816	0.276569	0.643374
7	H	2.873973	-0.249664	1.49924
8	C	-3.308346	-0.534222	0.296699
9	C	6.28668	5.676936	0.615699
10	C	-4.569211	1.859928	0.198361
11	C	-0.187163	0.336213	2.382701
12	H	-1.274041	0.44939	2.522589
13	C	3.165122	-0.260377	-0.644144
14	C	2.49937	-1.595146	-0.926297
15	H	2.208352	-1.582591	-1.992337
16	C	-4.052944	-0.026241	1.365114
17	H	-4.134117	-0.587383	2.296419
18	C	4.379821	2.110666	-0.160984
19	C	-6.485349	5.502498	0.048884
20	C	5.600059	4.406218	0.333031
21	C	5.037396	3.357889	0.101401
22	C	7.028643	5.565728	1.968587
23	H	6.328793	5.351962	2.782901
24	H	7.542452	6.508517	2.191674
25	H	7.774722	4.764748	1.941744
26	C	-2.576582	-1.866077	0.352383
27	H	-2.487405	-2.133461	1.421326
28	C	-5.233909	3.129877	0.146244
29	C	7.299329	5.97498	-0.515047
30	H	8.051701	5.182671	-0.586291
31	H	7.813898	6.922674	-0.315972
32	H	6.794241	6.052296	-1.48338
33	C	-3.37956	-3.025583	-0.310337
34	H	-2.72866	-3.905214	-0.203955
35	C	-3.266365	0.297935	-0.827391
36	H	-2.703401	-0.005452	-1.704525
37	C	3.483389	-2.795562	-0.776091
38	H	2.845483	-3.679828	-0.912545
39	C	-4.685665	-3.32215	0.44048
40	H	-5.400303	-2.495551	0.347397
41	H	-4.510654	-3.491904	1.510579
42	H	-5.167307	-4.219576	0.035534
43	C	3.705794	0.535453	-1.658069
44	H	3.645559	0.214971	-2.698902
45	C	-5.451836	6.609503	-0.269435
46	H	-4.675505	6.654572	0.501518
47	H	-5.951598	7.584706	-0.313106
48	H	-4.966109	6.426823	-1.23353
49	C	5.23763	6.812796	0.689774
50	H	4.698368	6.911476	-0.258045
51	H	5.73638	7.76554	0.904227
52	H	4.506159	6.620365	1.481507
53	C	-3.633503	-2.826224	-1.80917
54	H	-4.340433	-2.008607	-1.99301
55	H	-4.063392	-3.734873	-2.24638
56	H	-2.703401	-2.606413	-2.341597
57	C	-7.153504	5.78827	1.414017
58	H	-7.885452	5.012731	1.661612
59	H	-7.67029	6.75493	1.383199
60	H	-6.408642	5.820085	2.215785
61	C	-7.561466	5.461097	-1.062621
62	H	-7.10969	5.256283	-2.038912
63	H	-8.079173	6.426526	-1.116552
64	H	-8.30416	4.682346	-0.860344
65	C	4.133404	-2.886683	0.609718
66	H	4.876478	-2.094625	0.758823
67	H	4.652137	-3.845779	0.726978
68	H	3.38727	-2.803724	1.405136
69	C	4.545072	-2.816636	-1.884553
70	H	5.228473	-1.962245	-1.805696
71	H	4.089594	-2.794177	-2.882222
72	H	5.151663	-3.727283	-1.818648
73	N	-3.874084	1.483968	-0.896161
74	N	-4.68733	1.14864	1.334824
75	N	3.885794	1.441686	0.900787
76	O	1.353218	-1.781585	-0.118232
77	O	-1.293355	-1.73651	-0.221729
78	C	0.433703	1.709523	2.679182
79	H	0.275474	2.00502	3.730703
80	H	-0.006971	2.50211	2.06131
81	H	1.517631	1.732659	2.506774
82	C	0.32794	-3.884289	-3.451847
83	H	1.364574	-3.519256	-3.48423
84	H	-0.320206	-3.029897	-3.689345
85	H	0.226262	-4.606439	-4.279909
86	C	0.841067	-5.770314	-1.866727
87	H	0.730596	-6.497668	-2.689092
88	H	0.579386	-6.294602	-0.937634
89	H	1.912793	-5.534182	-1.80462
90	C	0.280689	-0.687706	3.431651
91	H	1.359634	-0.889002	3.357858
92	H	-0.23595	-1.651837	3.326038
93	H	0.10184	-0.335581	4.46214
94	N	4.305941	1.709073	-1.444604
95	O	-0.078099	-4.314766	1.294702
96	C	1.026138	-4.383403	2.234814
97	C	-1.024254	-5.383318	1.552816
98	C	0.543395	-5.306925	3.350513
99	H	1.899585	-4.797309	1.717499
100	H	1.249213	-3.365627	2.55743
101	C	-0.351716	-6.292623	2.583093
102	H	-1.945361	-4.935779	1.94535
103	H	-1.246272	-5.879961	0.604387
104	H	-0.043919	-4.744246	4.085322
105	H	1.371167	-5.792879	3.875381
106	H	-1.078804	-6.805362	3.219364
107	H	0.258739	-7.053091	2.082669
108	O	0.070506	0.994184	-1.072865
109	C	-0.065132	2.43562	-0.898237
110	C	-0.026752	0.648564	-2.478518
111	C	-0.035004	3.018384	-2.311481
112	H	-1.020574	2.625792	-0.399249
113	H	0.752217	2.777135	-0.25965
114	C	-0.636302	1.877529	-3.148279
115	H	0.982039	0.444375	-2.857637
116	H	-0.625332	-0.261878	-2.553129
117	H	0.996829	3.220292	-2.620857
118	H	-0.60431	3.94947	-2.382207
119	H	-0.382308	1.939647	-4.210615
120	H	-1.727623	1.872572	-3.049597

X-ray crystallography

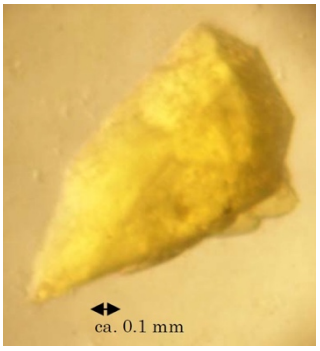
The crystal was covered by Nujol and immediately mounted on X-ray diffractometer and cooled to 100 K by nitrogen gas flow. The X-ray single crystal diffraction was recorded by Bruker Apex2 CCD diffractometer equipped with Mo K□ rotating anode X-ray tube. Data collection, integration, and scaling, were carried out using Bruker APEX II software. The diffraction was recorded at 100 K. Space groups were determined on the basis of systematic absences and intensity statistics, and the structures were solved by direct methods (*SHELXS*[7] or *SIR2011*[8]) and refined by full-matrix least-squares on F^2 using *SHELXL-2018*[1] program. All nonhydrogen atoms were refined using anisotropic displacement parameters otherwise noted. Hydrogen atoms were placed in idealized positions and refined using a riding model.

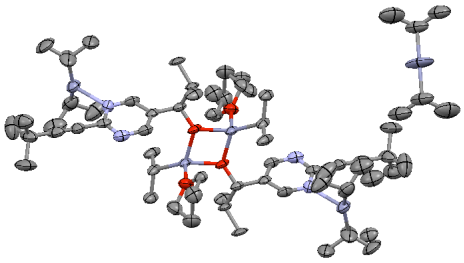
It should be noted that the alkoxide crystal are air and moisture sensitive. In addition, due to a tendency to disorder in the weekly coordinated or free diisopropyl zinc we cannot obtain the high-angle data ideally in some crystals.

Racemic dimer crystal with THF coordination

Single crystal of the racemic zinc alkoxide dimer with THF was made by the reaction with excess neat iPr$_2$Zn (0.1 mL, 0.73 mmol, 8.4 equiv.) with racemic pyrimidylalkanol **2** (20 mg, 0.086 mmol) in THF 0.05 mL at room temperature, The yellow single crystal was obtained after keeping the oil at room temperature for a week.

Table S1: Crystal data for racemic dimer with THF coordination





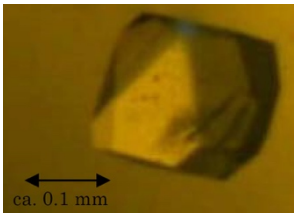
CCDC No	2099174	Formula	$(C_{14}H_{19}N_2OZnC_3H_7)_2$ $(C_4H_8O)_2$ $(C_6H_{14}Zn)_3$
Configuration	racemic (*meso*)	Radiation	Mo Kα
Z	1	Temp. (K)	100
Space group	*P*-1	R_1	0.0964
a (Å)	10.823(5)	wR^2	0.2662
b (Å)	13.099(6)	Flack parameter	–
c (Å)	14.027(7)		
α (deg.)	66.034(5)		
β (deg.)	78.752(6)		
γ (deg.)	67.832(5)		
V	1680.7(14)		

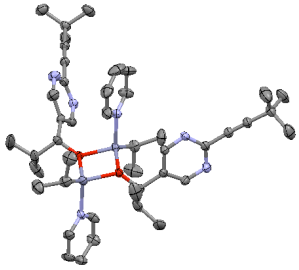
Enantiopure dimer crystal with pyridine coordination

We cannot obtain homochiral THF coordinated dimer crystal in several trials and oligomer or THF coordinated tetramer crystal was obtained as previously reported. Homo chiral dimer crystal was obtained By using more strong coordinated pyridine. We succeeded

Single crystal of the homochiral zinc alkoxide dimer with pyridine was obtained by the addition of *i*Pr_2Zn (0.05 mL, 0.36 mmol, 2.1 equiv.) to the solution of mixture of enantiopure (*R*)-pyrimidylalkanol **2** (40 mg, 0.18 mmol) in pyridine 0.05 mL (0.62 mmol, 3.7 equiv) and triethyl amine (0.5 mL) at room temperature, The colorless single crystal was obtained after few minutes by adding the powder crystal obtained in a previous similar operation as a seed crystal.

Table S2. Crystal data for enantiopure dimer crystal with pyridine





CCDC No	2099173	Formula	$(C_{14}H_{19}N_2OZnC_3H_7)_2$ $(C_5H_5N)_2$
Configuration	*R*	Radiation	Mo Kα
Z	4	Temp. (K)	100
Space group	$P2_12_12_1$	R_1	0.0405
a (Å)	10.0737(12)	wR^2	0.0910
b (Å)	19.301 (8)	Flack parameter	-0.013(9)
c (Å)	23.277 (3)		
α (deg.)	90		
β (deg.)	90		
γ (deg.)	90		
V	4525.8(10)		

Reference

[1] A. Krasovskiy and P. Knochel, *Synthesis*, 2006, 890–891.

[2] I. Sato, H. Urabe, S. Ishiguro, T. Shibata and K. Soai, *Angew. Chem. Int. Ed.*, 2003, **42**, 315–317.

[3] Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[4] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[5] I. D. Gridnev and A. K. Vorobiev, *ACS Catal.*, 2012, **2**, 2137–2149.

[6] (a) A. Matsumoto, T. Abe, A. Hara, T. Tobita, T. Sasagawa, T. Kawasaki and K. Soai, *Angew. Chemie Int. Ed.*, 2015, **54**, 15218–15221. (b) A. Matsumoto, S. Fujiwara, T. Abe, A. Hara, T. Tobita, T. Sasagawa, T. Kawasaki and K. Soai, *Bull. Chem. Soc. Jpn.*, 2016, **89**, 1170–1177.

[7] G. M. Sheldrick, *Acta Crystallogr. A.* 2008, **64**, 112–122.

[8] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* 2012, **45**, 357–361.