Supplementary information file to

On substituent effect in 1,*n*-homodisubstituted polyenes

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Table S1. The total energy differences (kcal/mol) between the *EE*,*EZ*, and *ZZ* 1,*n*–disubstituted *cis* polyalkene isomers where the lowest energy structure was assumed to be the reference point for a given chain length. *EE*, *EZ*, and *ZZ* stand for the substituent position at the chain ends. The apparently deviating values are marked in grey, resulting from intramolecular substituent – substituent interactions.

No. of	BeH			BF_2			BH_2			Br		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	0.00	–	1.66	0.00	–	3.04	0.00	–	1.79	0.10	–	0.00
4	0.00	0.63	1.12	0.00	1.45	2.92	0.00	2.03	4.16	1.37	0.81	0.00
6	0.00	0.82	1.68	0.00	1.52	3.24	0.00	2.28	4.71	0.82	0.34	0.00
8	0.00	0.89	1.75	0.00	1.69	3.33	0.00	2.46	4.90	0.82	0.44	0.00
10	0.00	0.85	1.77	0.00	1.66	3.36	0.00	2.47	4.98	0.82	0.35	0.00
12	0.00	0.88	1.83	0.00	1.71	3.40	0.00	2.53	5.06	0.82	0.41	0.00
14	0.00	0.82	1.80	0.00	1.70	3.42	0.00	2.54	5.09	0.83	0.41	0.00
16	0.00	0.85	1.81	0.00	1.73	3.43	0.00	2.57	5.13	0.82	0.39	0.00
18	0.00	0.90	1.80	0.00	1.71	3.44	0.00	2.57	5.15	0.84	0.41	0.00
20	0.00	0.86	1.81	0.00	1.74	3.46	0.00	2.59	5.18	0.82	0.41	0.00
No. of	CH_3			Cl			CN			F		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	0.00	–	1.34	0.14	–	0.00	0.00	–	1.11	0.02	–	0.00
4	0.00	1.42	3.04	0.47	0.34	0.00	0.00	0.34	5.75	2.05	1.07	0.00
6	0.00	1.59	3.24	0.07	0.00	0.11	0.00	0.03	0.47	1.36	0.61	0.00
8	0.00	1.63	3.30	0.00	0.04	0.02	0.00	0.35	0.45	1.36	0.70	0.00
10	0.00	1.61	3.30	0.01	0.00	0.05	0.00	0.17	0.53	1.34	0.63	0.00
12	0.00	1.67	3.35	0.00	0.03	0.03	0.00	0.32	0.56	1.31	0.61	0.00
14	0.00	1.63	3.32	0.02	0.00	0.04	0.00	0.21	0.58	1.34	0.60	0.00
16	0.00	1.70	3.38	0.03	0.00	0.05	0.00	0.29	0.60	1.34	0.58	0.00
18	0.00	1.64	3.33	0.04	0.00	0.05	0.00	0.23	0.61	1.35	0.63	0.00
20	0.00	1.70	3.38	0.00	0.06	0.06	0.00	0.38	0.66	1.35	0.62	0.00
No. of	NH_2			NO_2			OH transoidal			SiH_3		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	3.35	–	0.00	0.00	–	6.55	3.57	–	0.00	0.00	–	3.01
4	0.00	0.37	0.63	0.00	2.39	3.46	0.00	0.44	0.21	0.00	1.84	3.76
6	0.00	0.69	1.56	0.00	1.81	4.59	0.00	0.34	1.01	0.00	1.92	3.90
8	0.00	0.95	1.96	0.00	2.52	4.65	0.00	0.67	1.33	0.00	1.99	3.97
10	0.00	1.03	2.13	0.00	2.18	4.61	0.00	0.64	1.40	0.00	1.95	3.95
12	0.00	1.12	2.26	0.00	2.40	4.68	0.00	0.71	1.53	0.00	1.97	3.96
14	0.00	1.15	2.33	0.00	2.28	4.64	0.00	0.67	1.52	0.00	1.94	3.96
16	0.00	1.19	2.40	0.00	2.35	4.69	0.00	0.68	1.56	0.00	2.02	4.01
18	0.00	1.21	2.44	0.00	2.27	4.65	0.00	0.73	1.58	0.00	1.94	3.96
20	0.00	1.24	2.48	0.00	2.36	4.72	0.00	0.76	1.63	0.00	2.04	4.03

Table S2. The total energies (Hartree) for the *trans* isomers

No. of	BeH			BF_2		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2						
4						
6	-262.893450	-262.892225	-262.890964	-681.554755	-681.552747	-681.550916
8	-340.304277	-340.302942	-340.301647	-758.966233	-758.964255	-758.962349
10	-417.715102	-417.713777	-417.712436	-836.377541	-836.375546	-836.373585
12	-495.126007	-495.124695	-495.123310	-913.788845	-913.786746	-913.784737
14	-572.537012	-572.535643	-572.534277	-991.199939	-991.197896	-991.195855
16	-649.947908	-649.946601	-649.945174	-1068.611077	-1068.609014	-1068.606949
18	-727.358964	-727.357590	-727.356203	-1146.022188	-1146.020108	-1146.018025
20	-804.769860	-804.768547	-804.767104	-1223.433279	-1223.431184	-1223.429086
No. of	BH_2			Br		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2						
4						
6	-284.303417	-284.300209	-284.297041	-5375.618128	-5375.619111	-5375.620180
8	-361.715381	-361.712090	-361.708808	-5453.028758	-5453.029713	-5453.030779
10	-439.126961	-439.123599	-439.120227	-5530.439478	-5530.440523	-5530.441572
12	-516.538362	-516.534942	-516.531509	-5607.850313	-5607.851348	-5607.852403
14	-593.949659	-593.946193	-593.942713	-5685.261292	-5685.262294	-5685.263358
16	-671.360887	-671.357386	-671.353870	-5762.672144	-5762.673238	-5762.674247
18	-748.772066	-748.768536	-748.764992	-5840.083211	-5840.084224	-5840.085261
20	-826.183211	-826.179657	-826.176090	-5917.494062	-5917.495173	-5917.496171
No. of	CH_3			Cl		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2						
4						
6	-312.056692	-312.054439	-312.052150	-1152.602599	-1152.602875	-1152.603195
8	-389.467114	-389.464857	-389.462585	-1230.013215	-1230.013455	-1230.013788
10	-466.877793	-466.875529	-466.873264	-1307.423904	-1307.424237	-1307.424544
12	-544.288601	-544.286331	-544.284059	-1384.834751	-1384.835094	-1384.835386
14	-621.699492	-621.697206	-621.694928	-1462.245712	-1462.246018	-1462.246344
16	-699.110403	-699.108125	-699.105843	-1539.656657	-1539.656958	-1539.657221
18	-776.521351	-776.519070	-776.516786	-1617.067615	-1617.067912	-1617.068238
20	-853.932316	-853.930033	-853.927746	-1694.478484	-1694.478843	-1694.479139
No. of	CN			F		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2						
4						
6	-417.899550	-417.899408	-417.899827	-431.869372	-431.870681	-431.872010
8	-495.311525	-495.311456	-495.311679	-509.279802	-509.281042	-509.282340
10	-572.723150	-572.723141	-572.723238	-586.690398	-586.691701	-586.692941
12	-650.134626	-650.134620	-650.134615	-664.101164	-664.102474	-664.103681
14	-727.546054	-727.545977	-727.545961	-741.512067	-741.513290	-741.514615
16	-804.957275	-804.957253	-804.957124	-818.922964	-818.924234	-818.925412
18	-882.368585	-882.368462	-882.368380	-896.333897	-896.335112	-896.336453
20	-959.779684	-959.779634	-959.779435	-973.744765	-973.746080	-973.747276
No. of	NH_2			NO_2		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2						
4						

6	-266.719256	-266.718580	-266.718386	-642.410429	-642.407644	-642.405747
8	-344.131881	-344.130847	-344.129738	-719.823402	-719.820822	-719.818735
10	-421.543701	-421.542488	-421.541217	-797.235718	-797.233279	-797.231027
12	-498.955227	-498.953896	-498.952504	-874.647697	-874.645278	-874.642952
14	-576.366607	-576.365189	-576.363716	-952.059509	-952.057064	-952.054665
16	-653.777898	-653.776413	-653.774887	-1029.471024	-1029.468607	-1029.466163
18	-731.189128	-731.187590	-731.186009	-1106.882565	-1106.880085	-1106.877622
20	-808.600312	-808.598732	-808.597113	-1184.293857	-1184.291443	-1184.288910

No. of C–atoms	OH transoidal			SiH_3		
	EE	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2						
4						
6	-383.853013	-383.852248	-383.851435	-814.811036	-814.808236	-814.805450
8	-461.264035	-461.263183	-461.262284	-892.221654	-892.218856	-892.216060
10	-538.674983	-538.674109	-538.673116	-969.632433	-969.629628	-969.626824
12	-616.085892	-616.085027	-616.083954	-1047.043228	-1047.040490	-1047.037682
14	-693.496929	-693.495916	-693.494941	-1124.454218	-1124.451400	-1124.448597
16	-770.907924	-770.906910	-770.905803	-1201.865169	-1201.862349	-1201.859542
18	-848.318925	-848.317858	-848.316849	-1279.276136	-1279.273314	-1279.270506
20	-925.729835	-925.728824	-925.727721	-1356.687115	-1356.684290	-1356.681481

Table S3. The Gibbs free energies (Hartree) for the *trans* isomers

No. of	BeH			BF_2		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2						
4						
6	-262.812002	-262.811323	-262.809488	-681.475505	-681.473151	-681.470897
8	-340.192566	-340.192089	-340.190049	-758.856879	-758.854502	-758.852204
10	-417.573605	-417.572910	-417.570967	-836.238104	-836.235691	-836.233354
12	-494.954510	-494.953539	-494.951792	-913.618775	-913.616815	-913.613845
14	-572.335005	-572.334244	-572.332413	-991.000360	-990.997903	-990.995567
16	-649.717089	-649.715128	-649.713715	-1068.381434	-1068.378970	-1068.376587
18	-727.096742	-727.095796	-727.094125	-1145.762483	-1145.760025	-1145.757597
20	-804.478467	-804.476948	-804.476424	-1223.143518	-1223.141075	-1223.138603
No. of	BH_2			Br		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2						
4						
6	-284.195831	-284.192401	-284.188988	-5375.555170	-5375.556635	-5375.556873
8	-361.577607	-361.574083	-361.570600	-5452.935826	-5452.937335	-5452.937438
10	-438.959061	-438.955468	-438.951913	-5530.316539	-5530.317816	-5530.318081
12	-516.340363	-516.336718	-516.333098	-5607.697488	-5607.698842	-5607.698986
14	-593.721579	-593.717897	-593.714219	-5685.078140	-5685.080095	-5685.079555
16	-671.102744	-671.099027	-671.095303	-5762.460124	-5762.460024	-5762.460840
18	-748.483862	-748.480125	-748.476361	-5839.839752	-5839.841121	-5839.841111
20	-825.864958	-825.861201	-825.857408	-5917.221677	-5917.221896	-5917.222894
No. of	CH_3			Cl		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2						
4						
6	-311.915523	-311.913895	-311.911108	-1152.536262	-1152.536982	-1152.536477
8	-389.296577	-389.294291	-389.291503	-1229.916706	-1229.917554	-1229.917048
10	-466.677186	-466.674899	-466.671961	-1307.297619	-1307.298052	-1307.297828
12	-544.057910	-544.055611	-544.053462	-1384.678321	-1384.678790	-1384.678700
14	-621.437877	-621.436378	-621.434345	-1462.058929	-1462.059475	-1462.059238
16	-698.819519	-698.817175	-698.815232	-1539.440389	-1539.440212	-1539.440650
18	-776.200362	-776.197989	-776.196117	-1616.820583	-1616.821509	-1616.820906
20	-853.580559	-853.578812	-853.576998	-1694.202212	-1694.199952	-1694.203459
No. of	CN			F		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2						
4						
6	-417.817958	-417.818322	-417.817886	-431.798127	-431.799764	-431.800258
8	-495.199690	-495.200142	-495.199694	-509.178430	-509.180234	-509.180644
10	-572.581478	-572.581617	-572.581214	-586.559189	-586.560611	-586.561232
12	-649.962882	-649.962930	-649.962642	-663.939851	-663.941253	-663.941995
14	-727.343849	-727.344091	-727.343563	-741.320398	-741.322288	-741.322309
16	-804.726203	-804.725159	-804.725234	-818.701915	-818.702715	-818.703821
18	-882.106104	-882.106532	-882.105632	-896.082095	-896.084152	-896.083851
20	-959.488089	-959.487689	-959.488338	-973.463496	-973.464734	-973.466516
No. of	NH_2			NO_2		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2						
4						

6	-266.629521	-266.629106	-266.628774	-642.324037	-642.321772	-642.318945
8	-344.012068	-344.011179	-344.010194	-719.706616	-719.704781	-719.701579
10	-421.393180	-421.392766	-421.391645	-797.089014	-797.086878	-797.083749
12	-498.775331	-498.774143	-498.772886	-874.470924	-874.468722	-874.465543
14	-576.156682	-576.155406	-576.154057	-951.852174	-951.849774	-951.846939
16	-653.537943	-653.536603	-653.535196	-1029.234809	-1029.231563	-1029.228626
18	-730.919155	-730.917766	-730.916301	-1106.614948	-1106.612448	-1106.609546
20	-808.300314	-808.298886	-808.297387	-1183.996998	-1183.993684	-1183.991287

	OH transoidal			SiH_3		
No. of C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2						
4						
6	-383.756836	-383.756930	-383.755653	-814.699146	-814.696583	-814.694414
8	-461.137634	-461.137889	-461.136321	-892.079645	-892.077206	-892.075252
10	-538.519139	-538.518371	-538.517974	-969.460328	-969.457976	-969.455515
12	-615.899597	-615.899206	-615.898209	-1046.840994	-1046.838796	-1046.836155
14	-693.280241	-693.280512	-693.278651	-1124.221322	-1124.220015	-1124.216919
16	-770.661776	-770.661131	-770.660117	-1201.602807	-1201.600463	-1201.597746
18	-848.042018	-848.042244	-848.040304	-1278.983679	-1278.981292	-1278.978624
20	-925.423574	-925.423523	-925.422191	-1356.364555	-1356.362117	-1356.359529

Table S4. The total energies (Hartree) for the *cis* isomers

No. of	BeH			BF_2		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	-108.068687		-108.066038	-526.728378		-526.723527
4	-185.482859	-185.481851	-185.481071	-604.142812	-604.140508	-604.138166
6	-262.889945	-262.888634	-262.887266	-681.551309	-681.548893	-681.546142
8	-340.297168	-340.295758	-340.294375	-758.959213	-758.956515	-758.953912
10	-417.704357	-417.702996	-417.701535	-836.366730	-836.364090	-836.361375
12	-495.111650	-495.110256	-495.108742	-913.774235	-913.771503	-913.768823
14	-572.518816	-572.517506	-572.515956	-991.181614	-991.178911	-991.176171
16	-649.926072	-649.924717	-649.923186	-1068.588997	-1068.586242	-1068.583525
18	-727.333286	-727.331850	-727.330411	-1145.996311	-1145.993582	-1145.990822
20	-804.740522	-804.739147	-804.737643	-1223.403636	-1223.400869	-1223.398130
No. of	BH_2			Br		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	-129.471968		-129.469110	-5220.798126		-5220.798277
4	-206.890363	-206.887131	-206.883738	-5298.207764	-5298.208651	-5298.209920
6	-284.299850	-284.296224	-284.292353	-5375.615318	-5375.616078	-5375.616618
8	-361.708080	-361.704168	-361.700272	-5453.022584	-5453.023189	-5453.023883
10	-439.115808	-439.111872	-439.107866	-5530.429715	-5530.430465	-5530.431018
12	-516.523422	-516.519387	-516.515358	-5607.836924	-5607.837576	-5607.838236
14	-593.930883	-593.926841	-593.922765	-5685.244141	-5685.244816	-5685.245469
16	-671.338316	-671.334225	-671.330135	-5762.651393	-5762.652068	-5762.652692
18	-748.745676	-748.741581	-748.737466	-5840.058599	-5840.059290	-5840.059940
20	-826.153026	-826.148903	-826.144780	-5917.465948	-5917.466600	-5917.467250
No. of	CH_3			Cl		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	-157.238527		-157.236400	-997.781468		-997.781687
4	-234.646829	-234.644559	-234.641987	-1075.192301	-1075.192522	-1075.193057
6	-312.053835	-312.051297	-312.048675	-1152.599741	-1152.599853	-1152.599673
8	-389.460966	-389.458370	-389.455703	-1230.006981	-1230.006915	-1230.006944
10	-466.868106	-466.865535	-466.862843	-1307.414102	-1307.414122	-1307.414047
12	-544.275381	-544.272727	-544.270041	-1384.821347	-1384.821303	-1384.821294
14	-621.682546	-621.679950	-621.677258	-1462.228519	-1462.228554	-1462.228495
16	-699.089870	-699.087165	-699.084486	-1539.635769	-1539.635817	-1539.635742
18	-776.497019	-776.494399	-776.491717	-1617.042974	-1617.043041	-1617.042964
20	-853.904328	-853.901624	-853.898950	-1694.450310	-1694.450218	-1694.450222
No. of	CN			F		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	-263.072917		-263.071148	-277.044300		-277.044323
4	-340.487053	-340.486517	-340.487098	-354.459299	-354.460869	-354.462568
6	-417.896028	-417.895988	-417.895275	-431.867063	-431.868259	-431.869236
8	-495.304508	-495.303956	-495.303799	-509.274241	-509.275284	-509.276406
10	-572.712259	-572.711996	-572.711419	-586.681321	-586.682464	-586.683459
12	-650.120082	-650.119572	-650.119194	-664.088552	-664.089667	-664.090646
14	-727.527563	-727.527229	-727.526643	-741.495678	-741.496864	-741.497820
16	-804.935120	-804.934666	-804.934159	-818.902905	-818.904122	-818.905044
18	-882.342491	-882.342130	-882.341520	-896.310106	-896.311248	-896.312248
20	-959.749993	-959.749384	-959.748935	-973.717332	-973.718488	-973.719475
No. of	NH_2			NO_2		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	-189.301648		-189.306982	-487.577412		-487.566982
4	-266.719378	-266.718787	-266.718373	-564.996445	-564.992641	-564.990929

6	-344.129696	-344.128599	-344.127208	-642.406982	-642.404105	-642.399660
8	-421.538411	-421.536904	-421.535282	-719.816815	-719.812793	-719.809401
10	-498.946410	-498.944775	-498.943009	-797.225018	-797.221550	-797.217668
12	-576.354212	-576.352426	-576.350609	-874.633364	-874.629540	-874.625913
14	-653.761821	-653.759988	-653.758101	-952.041072	-952.037434	-952.033679
16	-731.169359	-731.167456	-731.165533	-1029.448886	-1029.445137	-1029.441416
18	-808.576804	-808.574876	-808.572915	-1106.856397	-1106.852781	-1106.848984
20	-885.984218	-885.982250	-885.980267	-1184.264053	-1184.260289	-1184.256526

	OH transoidal			SiH_3		
No. of C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	-229.024391		-229.030073	-659.990485		-659.985690
4	-306.441471	-306.440751	-306.441128	-737.400800	-737.397861	-737.394804
6	-383.850652	-383.850103	-383.849050	-814.807677	-814.804617	-814.801457
8	-461.258686	-461.257615	-461.256561	-892.214825	-892.211648	-892.208493
10	-538.666068	-538.665052	-538.663832	-969.621930	-969.618817	-969.615642
12	-616.073527	-616.072401	-616.071082	-1047.029151	-1047.026018	-1047.022841
14	-693.480764	-693.479691	-693.478341	-1124.436352	-1124.433256	-1124.430045
16	-770.888076	-770.886997	-770.885587	-1201.843672	-1201.840453	-1201.837278
18	-848.295340	-848.294177	-848.292828	-1279.250811	-1279.247713	-1279.244494
20	-925.702664	-925.701458	-925.700069	-1356.658161	-1356.654905	-1356.651732

Table S5. The Gibbs free energies (Hartree) for the *cis* isomers

No. of	BeH			BF_2		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	-108.047754		-108.045226	-526.709724		-526.706187
4	-185.431420	-185.431024	-185.429607	-604.093749	-604.091183	-604.088559
6	-262.808418	-262.807725	-262.805692	-681.471887	-681.469205	-681.466255
8	-340.185420	-340.184800	-340.182803	-758.849640	-758.846679	-758.843910
10	-417.562919	-417.561716	-417.560059	-836.227106	-836.224263	-836.221275
12	-494.939574	-494.938483	-494.937223	-913.604552	-913.601606	-913.598539
14	-572.317600	-572.315528	-572.314684	-990.981960	-990.978890	-990.976009
16	-649.694972	-649.692705	-649.692298	-1068.359147	-1068.356343	-1068.353145
18	-727.072406	-727.071556	-727.069406	-1145.736698	-1145.733399	-1145.730639
20	-804.449827	-804.447478	-804.446799	-1223.113664	-1223.111021	-1223.107738
No. of	BH_2			Br		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	-129.427436		-129.423325	-5220.795284		-5220.795187
4	-206.813152	-206.809735	-206.806191	-5298.174902	-5298.176274	-5298.176732
6	-284.192149	-284.188361	-284.184346	-5375.552264	-5375.553636	-5375.553276
8	-361.570169	-361.566071	-361.562087	-5452.929533	-5452.930605	-5452.930533
10	-438.947809	-438.943681	-438.939592	-5530.306692	-5530.307405	-5530.307602
12	-516.325205	-516.321155	-516.317037	-5607.684113	-5607.685361	-5607.685178
14	-593.702818	-593.698576	-593.694411	-5685.061209	-5685.062861	-5685.062023
16	-671.080022	-671.075951	-671.071764	-5762.438818	-5762.439171	-5762.440051
18	-748.457617	-748.453310	-748.449085	-5839.815750	-5839.816719	-5839.816490
20	-825.834759	-825.830640	-825.826399	-5917.193210	-5917.192959	-5917.193422
No. of	CH_3			Cl		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	-157.157773		-157.155942	-997.775051		-997.775102
4	-234.536316	-234.534022	-234.531044	-1075.155894	-1075.156617	-1075.156402
6	-311.913397	-311.910950	-311.908632	-1152.533356	-1152.533959	-1152.533074
8	-389.290393	-389.287691	-389.285705	-1229.910525	-1229.910980	-1229.910186
10	-466.667888	-466.664844	-466.662998	-1307.287883	-1307.288050	-1307.287542
12	-544.044505	-544.042180	-544.040286	-1384.664725	-1384.665300	-1384.664815
14	-621.422633	-621.419506	-621.417640	-1462.042557	-1462.042431	-1462.042150
16	-698.798882	-698.796992	-698.795000	-1539.420155	-1539.419607	-1539.419550
18	-776.177470	-776.174360	-776.171735	-1616.797306	-1616.796404	-1616.796836
20	-853.553749	-853.551863	-853.549800	-1694.173387	-1694.174853	-1694.174716
No. of	CN			F		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	-263.051498		-263.049736	-277.032926		-277.032852
4	-340.435494	-340.435502	-340.435291	-354.418030	-354.419933	-354.420778
6	-417.814395	-417.814816	-417.813382	-431.795818	-431.797384	-431.797509
8	-495.192687	-495.192705	-495.191651	-509.172872	-509.174438	-509.174670
10	-572.570719	-572.570496	-572.569536	-586.550267	-586.551273	-586.551826
12	-649.948090	-649.948115	-649.947256	-663.926876	-663.927906	-663.928955
14	-727.326238	-727.325354	-727.324894	-741.304935	-741.305106	-741.306398
16	-804.703960	-804.702894	-804.702805	-818.682404	-818.681689	-818.683849
18	-882.081561	-882.080457	-882.080156	-896.059744	-896.060705	-896.061104
20	-959.457550	-959.458917	-959.457222	-973.437131	-973.436671	-973.438477
No. of	NH_2			NO_2		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	-189.242455		-189.247332	-487.552026		-487.542289
4	-266.629521	-266.629106	-266.628774	-564.940245	-564.937286	-564.935473

6	-344.009769	-344.009085	-344.008242	-642.320659	-642.318209	-642.313320
8	-421.388489	-421.387374	-421.386218	-719.699883	-719.696801	-719.692687
10	-498.766516	-498.765248	-498.763946	-797.078593	-797.075157	-797.070849
12	-576.144208	-576.142912	-576.141528	-874.456188	-874.453059	-874.448831
14	-653.521982	-653.520457	-653.519026	-951.834934	-951.829019	-951.826776
16	-730.899326	-730.897973	-730.896463	-1029.212434	-1029.208872	-1029.202561
18	-808.277039	-808.275387	-808.273872	-1106.591096	-1106.585858	-1106.582142
20	-885.654228	-885.652822	-885.651231	-1183.966439	-1183.962671	-1183.959756
	OH transoidal			SiH_3		
No. of C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	-228.988963		-228.994901	-659.938784		-659.934996
4	-306.375408	-306.375894	-306.376036	-737.319015	-737.316379	-737.313791
6	-383.754523	-383.755228	-383.754063	-814.695419	-814.693364	-814.690598
8	-461.132412	-461.132734	-461.131287	-892.072798	-892.070386	-892.067870
10	-538.510052	-538.509627	-538.508608	-969.450541	-969.447421	-969.445005
12	-615.886812	-615.886271	-615.886210	-1046.827465	-1046.824748	-1046.822292
14	-693.265002	-693.263545	-693.263233	-1124.205327	-1124.201653	-1124.199615
16	-770.643464	-770.640172	-770.640571	-1201.580983	-1201.579328	-1201.576916
18	-848.019922	-848.019114	-848.017923	-1278.959639	-1278.956234	-1278.954287
20	-925.396463	-925.395057	-925.395283	-1356.335253	-1356.334064	-1356.331645

Table S6. The total energy differences (kcal/mol) between the *EE*, *EZ*, and *ZZ* 1,*n*–disubstituted *trans* polyalkene isomers obtained from homodesmotic reactions, where for a given chain length, the lowest energy structure was assumed to be the reference point. *EE*, *EZ*, and *ZZ* stand for the substituent position at the chain ends. The *trans* and *cis* isomers appear from the C6 or larger molecules. The deviating values are marked in grey, resulting from intramolecular substituent – substituent interactions.

No. of	BeH			BF_2			BH_2			Br		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
6	0.00	0.77	1.56	0.00	1.26	2.41	0.00	2.01	4.00	1.29	0.67	0.00
8	0.00	0.84	1.65	0.00	1.24	2.44	0.00	2.07	4.13	1.27	0.67	0.00
10	0.00	0.83	1.67	0.00	1.25	2.48	0.00	2.11	4.23	1.31	0.66	0.00
12	0.00	0.82	1.69	0.00	1.32	2.58	0.00	2.15	4.30	1.31	0.66	0.00
14	0.00	0.86	1.72	0.00	1.28	2.56	0.00	2.17	4.36	1.30	0.67	0.00
16	0.00	0.82	1.72	0.00	1.30	2.59	0.00	2.20	4.40	1.32	0.63	0.00
18	0.00	0.86	1.73	0.00	1.31	2.61	0.00	2.22	4.44	1.29	0.65	0.00
20	0.00	0.82	1.73	0.00	1.32	2.63	0.00	2.23	4.47	1.32	0.63	0.00
No. of	CH_3			Cl			CN			F		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
6	0.00	1.41	2.85	0.37	0.20	0.00	0.17	0.26	0.00	1.66	0.83	0.00
8	0.00	1.42	2.84	0.36	0.21	0.00	0.10	0.14	0.00	1.59	0.82	0.00
10	0.00	1.42	2.84	0.40	0.19	0.00	0.06	0.06	0.00	1.60	0.78	0.00
12	0.00	1.42	2.85	0.40	0.18	0.00	0.00	0.00	0.01	1.58	0.76	0.00
14	0.00	1.43	2.86	0.40	0.20	0.00	0.00	0.05	0.06	1.60	0.83	0.00
16	0.00	1.43	2.86	0.35	0.17	0.00	0.00	0.01	0.10	1.54	0.74	0.00
18	0.00	1.43	2.86	0.39	0.20	0.00	0.00	0.08	0.13	1.60	0.84	0.00
20	0.00	1.43	2.87	0.41	0.19	0.00	0.00	0.03	0.16	1.58	0.75	0.00
No. of	NH_2			NO_2			OH			SiH_3		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
6	0.00	0.65	1.35	0.00	1.75	2.94	0.00	0.48	0.99	0.00	1.76	3.51
8	0.00	0.76	1.56	0.00	1.62	2.93	0.00	0.54	1.10	0.00	1.76	3.51
10	0.00	0.84	1.71	0.00	1.53	2.94	0.00	0.55	1.17	0.00	1.76	3.52
12	0.00	0.89	1.81	0.00	1.52	2.98	0.00	0.54	1.22	0.00	1.72	3.48
14	0.00	0.93	1.89	0.00	1.53	3.04	0.00	0.64	1.25	0.00	1.77	3.53
16	0.00	0.97	1.96	0.00	1.52	3.05	0.00	0.64	1.33	0.00	1.77	3.53
18	0.00	0.99	2.01	0.00	1.56	3.10	0.00	0.67	1.30	0.00	1.77	3.53
20	0.00	1.01	2.05	0.00	1.52	3.10	0.00	0.63	1.33	0.00	1.77	3.54

Table S7. The total energy differences (kcal/mol) between the *EE*, *EZ*, and *ZZ* 1,*n*–disubstituted *cis* polyalkene isomers obtained from homodesmotic reactions, where for a given chain length, the lowest energy structure was assumed to be the reference point. *EE*, *EZ*, and *ZZ* stand for the substituent position at the chain ends. The deviating values are marked in grey, resulting from intramolecular substituent – substituent interactions.

No. of	BeH			BF_2			BH_2			Br		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	0.00	–	1.66	0.00	–	3.03	0.00	–	1.79	0.10	–	0.00
4	0.00	0.64	1.13	0.00	1.45	2.92	0.00	2.03	4.16	1.37	0.81	0.00
6	0.00	0.82	1.68	0.00	1.52	3.24	0.00	2.28	4.71	0.82	0.34	0.00
8	0.00	0.89	1.75	0.00	1.69	3.33	0.00	2.46	4.90	0.82	0.44	0.00
10	0.00	0.85	1.77	0.00	1.66	3.36	0.00	2.47	4.98	0.82	0.35	0.00
12	0.00	0.88	1.83	0.00	1.71	3.40	0.00	2.53	5.06	0.82	0.41	0.00
14	0.00	0.82	1.80	0.00	1.70	3.42	0.00	2.54	5.09	0.83	0.41	0.00
16	0.00	0.85	1.81	0.00	1.73	3.43	0.00	2.57	5.13	0.82	0.39	0.00
18	0.00	0.90	1.80	0.00	1.71	3.44	0.00	2.57	5.15	0.84	0.41	0.00
20	0.00	0.86	1.81	0.00	1.74	3.46	0.00	2.59	5.18	0.82	0.41	0.00
No. of	CH_3			Cl			CN			F		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	0.00	–	1.36	0.14	–	0.00	0.00	–	1.11	0.02	–	0.00
4	0.00	1.42	3.04	0.45	0.32	0.00	0.02	0.36	0.00	2.08	1.10	0.00
6	0.00	1.59	3.24	0.07	0.00	0.11	0.00	0.01	0.47	1.36	0.61	0.00
8	0.00	1.63	3.30	0.00	0.04	0.02	0.00	0.35	0.45	1.36	0.70	0.00
10	0.00	1.61	3.30	0.01	0.00	0.05	0.00	0.17	0.53	1.34	0.63	0.00
12	0.00	1.67	3.35	0.00	0.03	0.03	0.00	0.32	0.56	1.31	0.61	0.00
14	0.00	1.63	3.32	0.02	0.00	0.04	0.00	0.21	0.58	1.34	0.60	0.00
16	0.00	1.70	3.38	0.03	0.00	0.05	0.00	0.29	0.60	1.34	0.58	0.00
18	0.00	1.64	3.33	0.04	0.00	0.05	0.00	0.23	0.61	1.35	0.63	0.00
20	0.00	1.70	3.37	0.00	0.06	0.06	0.00	0.38	0.66	1.35	0.62	0.00
No. of	NH_2			NO_2			OH			SiH_3		
C–atoms	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*	*EE*	*EZ*	*ZZ*
2	3.35	–	0.00	0.00	–	6.55	3.57	–	0.00	0.00	–	3.01
4	0.00	0.42	0.55	0.00	2.39	3.46	0.00	0.44	0.22	0.00	1.84	3.76
6	0.00	0.69	1.58	0.00	1.81	4.59	0.09	0.34	1.01	0.00	1.92	3.90
8	0.00	0.97	1.97	0.00	2.52	4.65	0.00	0.67	1.33	0.00	1.99	3.97
10	0.00	1.03	2.13	0.00	2.18	4.61	0.00	0.64	1.40	0.00	1.95	3.95
12	0.00	1.12	2.26	0.00	2.40	4.68	0.00	0.71	1.53	0.00	1.97	3.96
14	0.00	1.15	2.33	0.00	2.28	4.64	0.00	0.67	1.52	0.00	1.94	3.96
16	0.00	1.19	2.40	0.00	2.35	4.69	0.00	0.68	1.56	0.00	2.02	4.01
18	0.00	1.21	2.44	0.00	2.27	4.65	0.00	0.73	1.58	0.00	1.94	3.96
20	0.00	1.24	2.48	0.00	2.36	4.72	0.00	0.76	1.63	0.00	2.04	4.03

Table S8. The distances (Å) between the oxygen atoms from the NO_2 groups and selected hydrogen atoms in 1,*n*–disubstituted *cis* (a) and *trans* (b) polyalkene isomers

a)

NO_2	*EE*		*EZ*				*ZZ*	
cis	**O...HC$_1$**	**O...HC$_2$**	**O...HC$_1$**	**O...HC$_2$**	**O...HC$_n$**	**O...HC$_{n-2}$**	**O...HC$_1$**	**O...HC$_3$**
n	**O...HC$_n$**	**O...HC$_{n-1}$**					**O...HC$_n$**	**O...HC$_{n-2}$**
2	2.490	2.444					2.309	
4	2.407	2.394	2.397	2.441	2.366	2.246	2.359	2.174
6	2.404	2.382	2.406	2.370	2.362	2.211	2.359	2.210
8	2.405	2.372	2.404	2.376	2.362	2.213	2.362	2.212
10	2.404	2.374	2.405	2.372	2.363	2.214	2.362	2.215
12	2.405	2.372	2.405	2.371	2.363	2.221	2.363	2.221
14	2.404	2.373	2.405	2.372	2.363	2.221	2.363	2.220
16	2.405	2.374	2.405	2.373	2.364	2.222	2.363	2.223
18	2.404	2.374	2.405	2.374	2.364	2.224	2.364	2.222
20	2.404	2.376	2.404	2.375	2.364	2.227	2.364	2.224

b)

NO_2	*EE*		*EZ*				*ZZ*	
trans	**O...HC$_1$**	**O...HC$_2$**	**O...HC$_1$**	**O...HC$_2$**	**O...HC$_n$**	**O...HC$_{n-2}$**	**O...HC$_1$**	**O...HC$_3$**
n	**O...HC$_n$**	**O...HC$_{n-1}$**					**O...HC$_n$**	**O...HC$_{n-2}$**
2								
4								
6	2.405	2.389	2.403	2.402	2.368	2.232	2.368	2.231
8	2.405	2.389	2.404	2.392	2.369	2.234	2.369	2.236
10	2.405	2.387	2.404	2.389	2.369	2.239	2.369	2.239
12	2.405	2.387	2.404	2.387	2.370	2.242	2.370	2.241
14	2.404	2.388	2.404	2.389	2.370	2.243	2.370	2.243
16	2.404	2.387	2.404	2.388	2.370	2.243	2.371	2.244
18	2.404	2.389	2.404	2.389	2.371	2.243	2.370	2.245
20	2.404	2.387	2.404	2.389	2.371	2.243	2.371	2.246

Table S9. The distances (Å) between the oxygen atoms from the OH groups and selected hydrogen atoms in 1,*n*–disubstituted *cis* (a) and *trans* (b) polyalkene isomers

a)

OH	**EE**		**EZ**				**ZZ**	
cis	**O...HC$_1$**	**O...HC$_2$**	**O...HC$_1$**	**O...HC$_2$**	**O...HC$_n$**	**O...HC$_{n-2}$**	**O...HC$_1$**	**O...HC$_3$**
n	**O...HC$_n$**	**O...HC$_{n-1}$**					**O...HC$_n$**	**O...HC$_{n-2}$**
2	2.038	2.739					2.713	2.740
4	2.022	2.689	2.021	2.671	2.019	2.820	2.020	2.815
6	2.020	2.682	2.019	2.684	2.014	2.756	2.013	2.756
8	2.019	2.683	2.018	2.682	2.013	2.747	2.012	2.746
10	2.018	2.683	2.018	2.683	2.012	2.743	2.012	2.745
12	2.018	2.683	2.017	2.684	2.012	2.745	2.011	2.743
14	2.018	2.683	2.017	2.684	2.011	2.743	2.011	2.744
16	2.017	2.683	2.017	2.684	2.011	2.744	2.011	2.740
18	2.017	2.683	2.017	2.684	2.011	2.743	2.011	2.744
20	2.017	2.684	2.017	2.684	2.011	2.742	2.011	2.744

b)

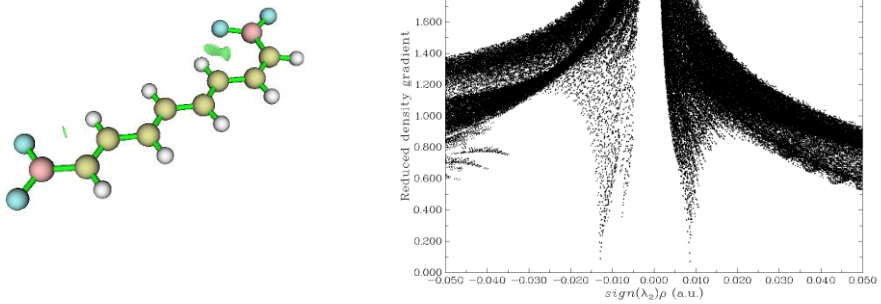
OH	**EE**		**EZ**				**ZZ**	
trans	**O...HC$_1$**	**O...HC$_2$**	**O...HC$_1$**	**O...HC$_2$**	**O...HC$_n$**	**O...HC$_{n-2}$**	**O...HC$_1$**	**O...HC$_3$**
n	**O...HC$_n$**	**O...HC$_{n-1}$**					**O...HC$_n$**	**O...HC$_{n-2}$**
2								
4								
6	2.021	2.690	2.020	2.690	2.016	2.793	2.015	2.792
8	2.020	2.690	2.019	2.691	2.015	2.788	2.014	2.790
10	2.093	2.585	2.019	2.691	2.014	2.789	2.014	2.788
12	2.019	2.690	2.019	2.692	2.014	2.789	2.014	2.788
14	2.019	2.690	2.019	2.690	2.014	2.787	2.013	2.787
16	2.019	2.691	2.018	2.691	2.014	2.789	2.013	2.787
18	2.019	2.691	2.018	2.692	2.014	2.788	2.013	2.788
20	2.018	2.690	2.018	2.691	2.013	2.788	2.013	2.787

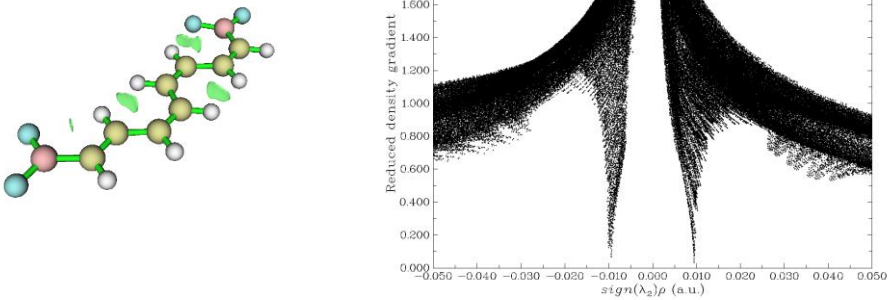
Table S10. The AIM parameters (a.u.) obtained in BCPs of intramolecular contacts in the most stable *trans* isomers: the Rho (Electron Density), Laplacian of Rho (Trace of Hessian of Rho), V (Virial Field = Potential Energy Density), G (Lagrangian Form of Kinetic Energy Density, K (Hamiltonian Form of Kinetic Energy Density), H (H = G + V, Total Energy), L = K − G = Lagrangian Density, ESP (Total Electrostatic Potential), ESPe (Electrostatic Potential from Electrons), and ESPn (Electrostatic Potential from Nuclei) using AIMAll Software [28].

	BCP #	Atoms	Rho	Lap	V	G	K	L	ESP	ESPe	ESPn
BF_2	19	H11 - F20	0.013000	0.051700	-0.010700	0.011800	-0.001130	-0.012900	0.041000	-17.224000	17.265000
BH_2	19	H11 - H19	0.009250	0.035300	-0.004500	0.006670	-0.002170	-0.008830	0.030500	-12.196600	12.227100
CH_3	20	H11 - H19	0.009260	0.037200	-0.004890	0.007100	-0.002210	-0.009310	0.045800	-12.949200	12.995000
NO_2	16	C12 - C13	0.337000	-0.972700	-0.489700	0.123300	0.366500	0.243200	1.007700	-21.139400	22.147100
OH	20	H12 - H18	0.009850	0.045000	-0.006280	0.008760	-0.002480	-0.011200	0.112300	-13.824800	13.937100
SiH_3	21	H11 - H20	0.007700	0.026500	-0.003530	0.005070	-0.001550	-0.006620	0.042400	-14.748100	14.790600

Table S11. The AIM parameters (a.u.) obtained in BCPs of intramolecular contacts in the most stable *cis* isomers: the Rho (Electron Density), Laplacian of Rho (Trace of Hessian of Rho), V (Virial Field = Potential Energy Density), G (Lagrangian Form of Kinetic Energy Density, K (Hamiltonian Form of Kinetic Energy Density), H (H = G + V, Total Energy), L = K − G = Lagrangian Density, ESP (Total Electrostatic Potential), ESPe (Electrostatic Potential from Electrons), and ESPn (Electrostatic Potential from Nuclei) using AIMAll Software [28].

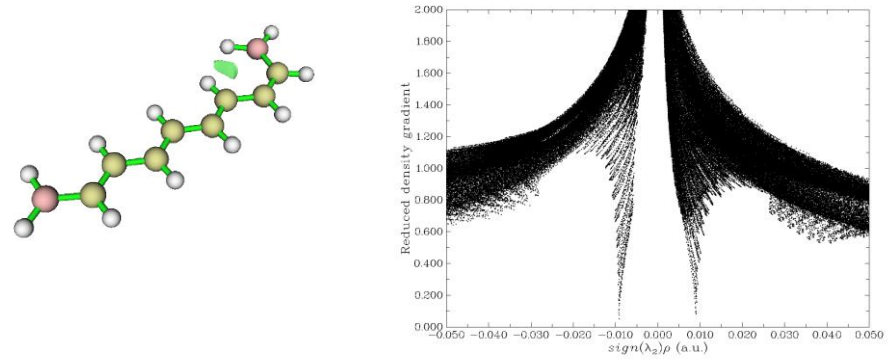
	BCP #	Atoms	Rho	Lap	V	G	K	L	ESP	ESPe	ESPn
BF_2	9	H7 - F21	0.013608	0.052924	-0.011301	0.012266	-0.000965	-0.013231	0.043056	-16.999925	17.042981
BH_2	10	H7 - H21	0.009842	0.037167	-0.004929	0.007111	-0.002181	-0.009292	0.031947	-12.047057	12.079004
Br	9	H7 - Br18	0.010602	0.040949	-0.005909	0.008073	-0.002164	-0.010237	0.051010	-22.756254	22.807264
CH_3	10	H7 - H24	0.010008	0.039612	-0.005456	0.007679	-0.002224	-0.009903	0.048569	-12.798125	12.846694
NH_2	10	H7 - H22	0.008616	0.038511	-0.005151	0.007389	-0.002238	-0.009628	0.069866	-13.306224	13.376090
NO_2	10	H7 - O22	0.018524	0.062999	-0.013944	0.014847	-0.000903	-0.015750	0.039154	-17.400591	17.439745
OH	9	H7 - H20	0.010500	0.045439	-0.006716	0.009038	-0.002322	-0.011360	0.121545	-13.602215	13.723760
SiH_3	9	H7 - H24	0.008169	0.027813	-0.003830	0.005391	-0.001562	-0.006953	0.044467	-14.612285	14.656752

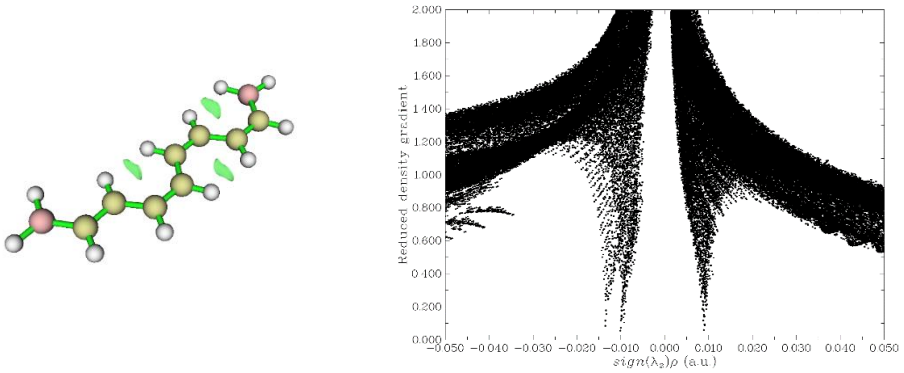




BF_2 (all-*trans*) *EZ*

BF_2 (all-*cis*) *EZ*

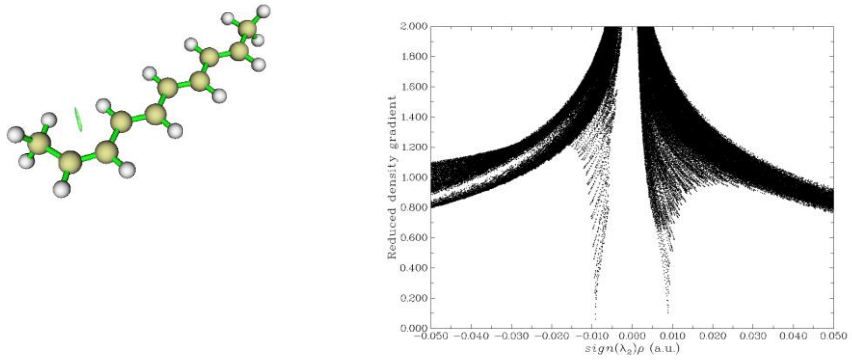




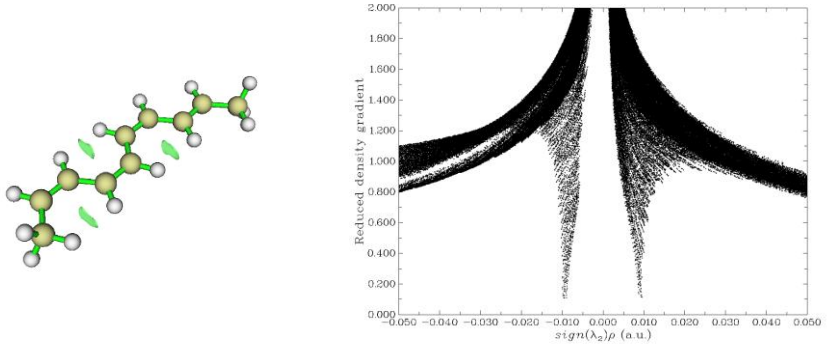
BH_2 (all-*trans*) *EZ*

BH_2 (all-*cis*) *EZ*

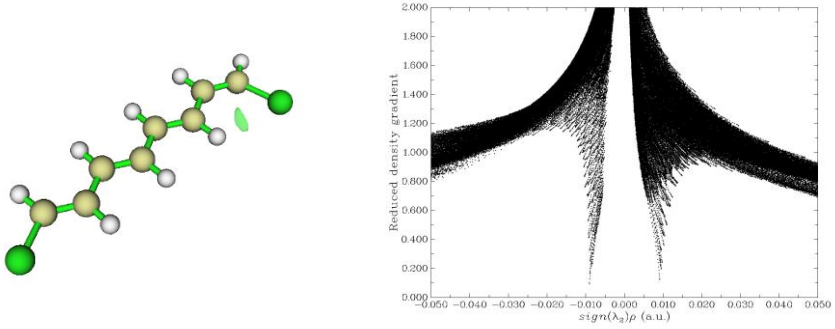
Fig. S1 The non-covalent interactions (NCI) and reduced density gradient (RDG) scatter graphs for the difluoroborano and diborano octatetraenes in all-*trans* and all-*cis* configurations, and the *EZ* arrangement of the end groups. Green NCI surfaces show only intramolecular interactions. RDG peaks appear at $\rho \approx -0.05 - -0.015$ a.u. for hydrogen bonds at $\rho \approx 0.01$a.u. for van der Waals interactions.



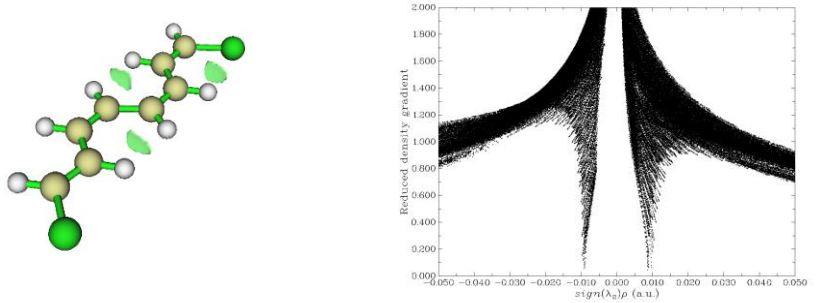
CH_3 (all-*trans*) *EZ*



CH_3 (all-*cis*) *EZ*

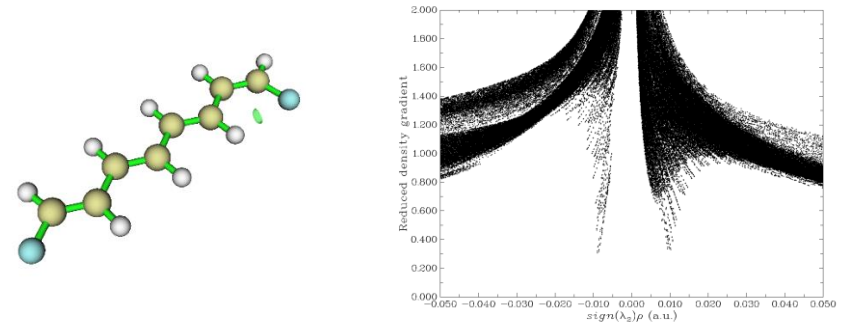


Cl (all-*trans*) *EZ*

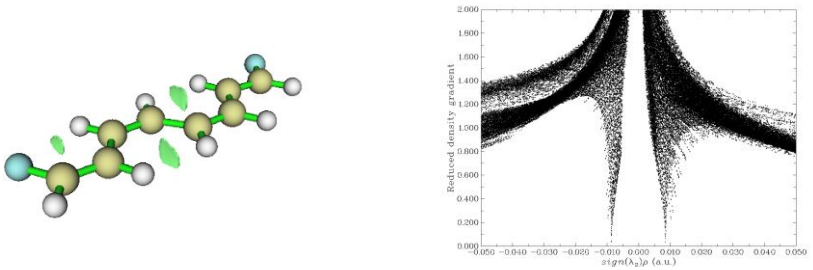


Cl (all-*cis*) *EZ*

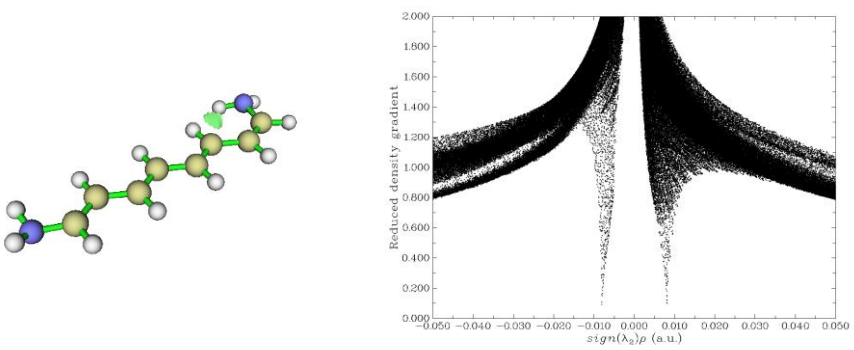
Fig. S2 The non-covalent interactions (NCI) and reduced density gradient (RDG) scatter graphs for the dimethylo and dichloro octatetraenes in all-*trans* and all-*cis* configurations, and the *EZ* arrangement of the end groups. Green NCI surfaces show only intramolecular interactions. RDG peaks appear at $\rho \approx -0.05 - -0.015$ a.u. for hydrogen bonds at $\rho \approx 0.01$a.u. for van der Waals interactions.



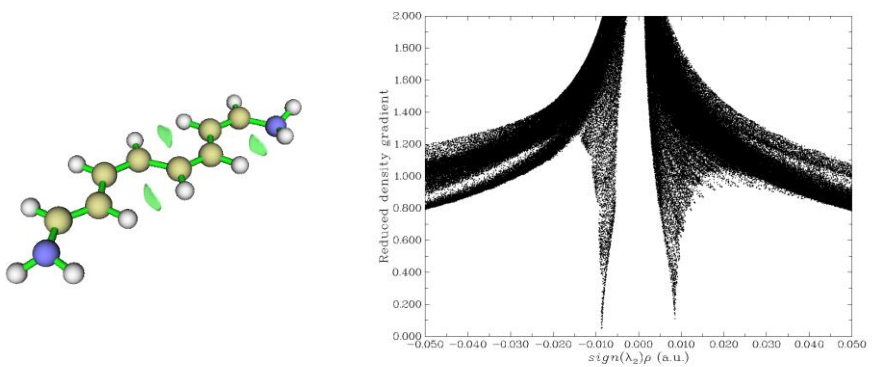
F (all-*trans*) *EZ*



F (all-*cis*) *EZ*

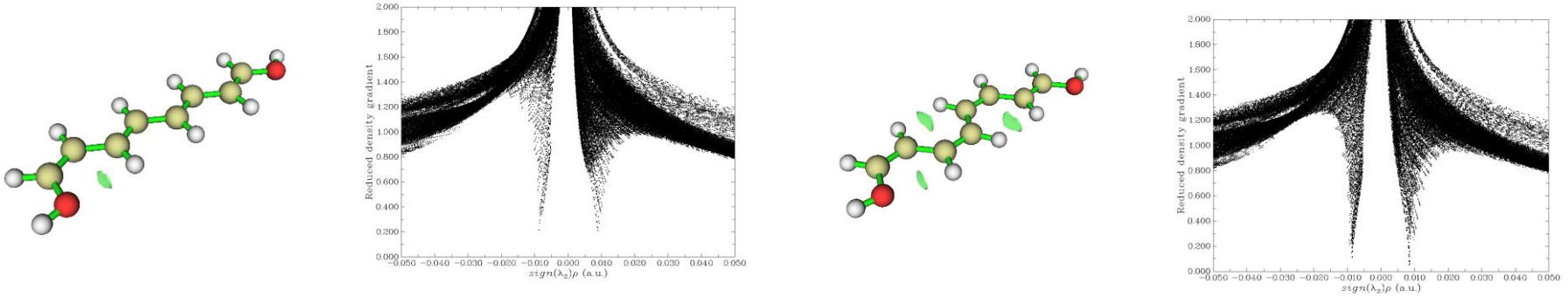


NH_2 (all-*trans*) *EZ*



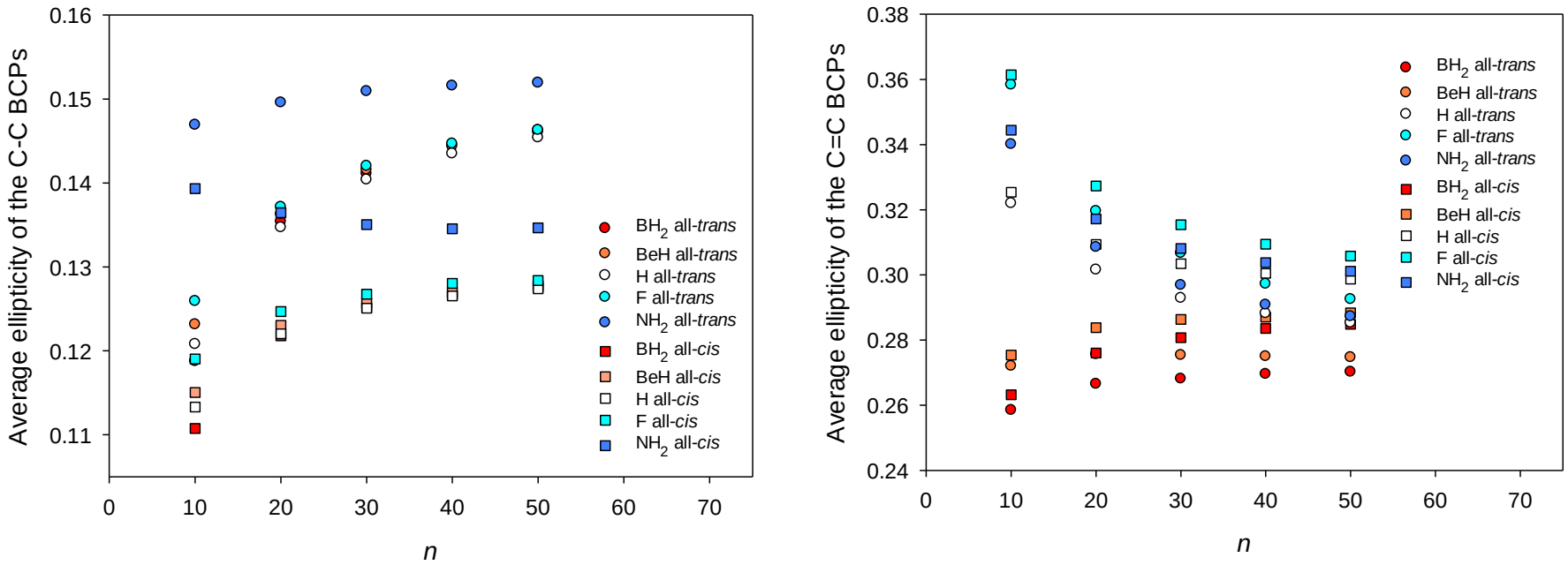
NH_2 (all-*cis*) *EZ*

Fig. S3 The non-covalent interactions (NCI) and reduced density gradient (RDG) scatter graphs for the difluoro diamino octatetraenes in all-*trans* and all-*cis* configurations, and the *EZ* arrangement of the end groups. Green NCI surfaces show only intramolecular interactions. RDG peaks appear at $\rho \approx -0.05 - -0.015$ a.u. for hydrogen bonds at $\rho \approx 0.01$a.u. for van der Waals interactions.



OH (all-*trans*) *EZ* OH (all-*cis*) *EZ*

Fig. S4 The non-covalent interactions (NCI) and reduced density gradient (RDG) scatter graphs for the dihydroxy octatetraenes in all-*trans* and all-*cis* configurations, and the *EZ* arrangement of the end groups. Green NCI surfaces show only intramolecular interactions. RDG peaks appear at $\rho \approx -0.05 - -0.015$ a.u. for hydrogen bonds at $\rho \approx 0.01$a.u. for van der Waals interactions.



(a) (b)

Fig. S5 The asymptotic convergence of the average ellipticity in bond critical points (BCP) of the single C-C (a) and double C=C (b) bonds with the number of carbon atoms in the all-*trans* and all-*cis* isomers disubstituted by differently acting substituents.