SUPPORTING INFORMATION

On The Limits of Tuning Comonomer Affinity of 'Spaleck-Type' *ansa*-Zirconocenes in Ethene/1-Hexene Copolymerization: A High-Throughput Experimentation/QSAR Approach

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1. Polymerization Details

Prior to the execution of a polymerization library, the PPR modules undergo 'bake-and-purge' cycles overnight (8 h at 90-140°C with intermittent dry N_2 flow), to remove any contaminants and left-overs from previous experiments. After cooling to glove-box temperature, the module stir tops are taken off, and the 48 cells are fitted with disposable 10 mL glass inserts (pre-weighed in a Mettler-Toledo Bohdan Balance Automator) and polyether ether ketone (PEEK) stir paddles. The stir tops are then set back in place, and the cells are loaded with the appropriate amounts of toluene solvent, comonomer (see Table S1) and triisobutylaluminum (TIBA, 5 μmol) scavenger, thermostated at 60 °C, and brought to 4.5 bar of pressure with ethene. At this point, the catalyst injection sequence is started; aliquots of (a) a toluene 'chaser', (b) a toluene solution of catalyst (variable amount, see Table S1), (c) a toluene solution of the activator ($HNMe_2Ph^+[B(C_6F_5)_4]^-$ or $[Ph_3C^+]$ $[B(C_6F_5)_4]^-$, the first one was used in 2-fold excess with respect to catalyst, the second one was used in 10-fold excess), (d) a toluene 'buffer', all separated by nitrogen gaps, are uploaded into the slurry needle and subsequently injected into the cell of destination, thus starting the reaction. This is left to proceed under stirring (800 rpm) at constant temperature and pressure with continuous feed of ethene on demand until the desired monomer consumption has been reached (for reaction time, see Table S1), and quenched by over-pressurizing the cell with 50 psi (3.4 bar) of dry air (preferred over other possible catalyst quenchers because in case of cell or quench line leakage oxygen is promptly detected by the dedicated glove-box sensor). Once all cells have been quenched, the modules are cooled down and vented, the stir-tops are removed, and the glass inserts containing the reaction phases are taken out and transferred to a centrifugal evaporator (Genevac EZ-2 Plus or Martin Christ RVC 2-33 CDplus), where all volatiles are distilled out and the polymers are thoroughly dried overnight. Reaction yields are double-checked against on-line monomer conversion measurements by robotically weighing the dry polymers while still in the reaction vials, subtracting the pre-recorded tare. Polymer aliquots are then sent to the characterizations.

GPC curves were recorded with a Freeslate Rapid GPC setup, equipped with a set of two mixed-bed Agilent PLgel 10 μm columns and a Polymer Char IR4 detector. Calibration was performed with the universal method, using 10 monodisperse polystyrene samples (M_n between 1.3 and 3700 kDa).

^{13}C NMR spectra were recorded with a 100 MHz Bruker Avance III 400 spectrometer equipped with a 5 mm high-temperature cryoprobe. Polymer samples (~25 mg) were dissolved at 120 °C in tetrachloroethane-1,2-d_2 (0.5 mL) with 0.40 mg mL^{-1} BHT (2,6-di-*tert*-butyl-4-methylphenol) as

stabilizer. DSC curves were obtained with a differential scanning calorimeter (DSC-822 by Mettler Toledo) in a flowing N_2 atmosphere at a scanning rate of 10 °C/min from 0 to 200 °C.

Table S1. Polymerization Times , Yields and Catalysts Amounts.

Catalyst ID	nmol	t_p (s)	Yield (mg)
M1	20	582	106
	20	878	102
	20	758	109
	20	1146	159
	20	892	147
M2	20	726	72
	10	1201	41
	30	876	94
	30	815	99
M3	20	962	48
	20	1050	70
	40	712	70
	40	600	48
M4	40	539	70
	20	740	42
	60	461	104
	60	481	93
M5	20	1183	84
	20	1055	81
	3[#]	612	59
	3[#]	580	61
	20	2036	104
M6	30	1255	106
	40	6031	42
	20	5346	46
M7	20	1455	31
	20	943	25
	20	3731	32
	20	1264	26
M8	10	2468	67
	10	2409	73
	10	3363	93
M9	40	1191	55
	20	1650	37
	60	891	82
	60	972	84
M10	20	1083	80
	20	1293	71
	20	1411	102
	25	1240	109

Catalyst ID	nmol	t_p (s)	Yield (mg)
M11	20	1139	79
	20	1869	70
	20	1468	82
	20	1225	77
M12	40	4268	58
	20	5402	52
	40	4894	105
	40	5401	91
M13	30	6733	78
	30	4490	74
	30	4512	88
	30	6569	107
	45	4891	110
M14	20	7202	58
	40	3267	71
	40	5232	86
M15	40	5003	62
	40	2890	65
	40	5402	68
	40	2421	92
M16	20	2722	64
	20	5405	60
	30	3555	101
	30	5403	103
M17	20	5402	24
	40	6983	19
	40	5401	32
M18	20	1209	23
	20	6983	35
	20	5401	26
M19	20	1872	55
	20	1765	53
	40	1121	102
	40	995	86
M20	5	399	56
	5	853	55
	5	1659	66
	5	4459	81
M21	40	6118	45
	60	4068	50
	60	3063	51
M22	20	726	63
	20	1233	91
	20	2136	73

Catalyst ID	nmol	t_p (s)	Yield (mg)
M23	20	1035	83
	20	1634	69
M24	30	7200	16
	20	5405	19
	40	5403	31
M25	40	6623	25
	40	5401	42
M26	20	3366	65
	20	5401	68
	40	1920	139
	40	5401	122
M27	20	5426	75
	40	2800	74
	40	3380	117
	60	2564	120
M28	20	1521	64
	10	1062	51
M29	20	5666	58
	20	5880	57
	40	2656	81
M30	45	3722	60
	20	9228	60
	40	5791	66
M31	6	188	121
	5	622	106
	5	1104	53
	8	240	110
	6	325	163
M32	20	1276	76
	20	1440	65
	20	1720	90
	20	1984	87
M33	10[#]	1201	71
	10[#]	2586	47
	40[#]	10015	66
M34	35	1677	64
	35	2387	64
	35	3164	80
	35	2229	84
M35	5[#]	938	61
	35	4523	95
	20	8742	89
	8[#]	354	128

Catalyst ID	nmol	t_p (s)	Yield (mg)
M36	50	5400	51
	40	6706	65
	40	10801	36
	40	7200	47
M37	30	901	94
	35	1343	84
	30	998	110
	20	3064	93
M38	20	4049	65
	20	3541	60
	20	5466	88
	20	6240	128
M39	20	7201	46
	20	4296	67
	40	5640	108
M40	40	8181	75
	60	6036	79
	20	11941	63
	40	6964	78

[#]For these polymerizations, TTB was used as activator ([B]/[Zr] = 10). See experimental details.

Table S2. Full Polymer Characterization.

Catalyst ID	v_H (mL)	M_n [a]	M_w [a]	PDI	$[E]/[H]_{av}$ [b]	[H],conv % [c]	x_H [d]	p_{EE} [e]	p_{HH} [e]	r_E	r_H
M1	3.40	35	75	2.1	0.069	2.8	0.315	0.608	0.126	22.6	0.010
	3.40	30	66	2.2	0.069	2.8	0.355	0.550	0.146	17.8	0.012
	3.40	31	65	2.1	0.069	3.0	0.352	0.544	0.149	17.3	0.012
	4.25	34	72	2.1	0.055	3.7	0.376	0.515	0.180	19.2	0.012
	4.25	30	63	2.1	0.055	3.5	0.405	0.471	0.185	16.1	0.013
M2	0.56	87	182	2.1	0.437	11.8	0.338	0.678	0.332	4.8	0.22
	0.56	92	194	2.1	0.425	6.5	0.316	0.692	0.316	5.3	0.20
	0.85	85	185	2.2	0.287	11.3	0.408	0.595	0.400	5.1	0.19
	0.85	86	178	2.1	0.288	11.9	0.406	0.583	0.394	4.8	0.19
M3	0.56	54	113	2.1	0.423	5.4	0.195	0.814	0.210	10.3	0.11
	0.56	67	139	2.1	0.429	7.9	0.191	0.818	0.213	10.5	0.12
	0.85	52	107	2.1	0.280	6.5	0.266	0.750	0.286	10.7	0.11
	0.85	54	110	2.0	0.277	4.6	0.274	0.743	0.293	10.4	0.12
M4	0.56	74	153	2.1	0.434	10.5	0.293	0.716	0.301	5.8	0.19
	0.56	74	154	2.1	0.425	6.1	0.280	0.740	0.306	6.7	0.19
	0.85	71	147	2.1	0.288	11.7	0.361	0.657	0.391	6.7	0.18
	0.85	70	150	2.1	0.286	10.7	0.373	0.644	0.385	6.3	0.18
M5	0.56	51	103	2.0	0.439	12.2	0.276	0.747	0.314	6.7	0.20
	0.56	47	101	2.1	0.438	11.8	0.280	0.742	0.329	6.6	0.21
	0.85	54	109	2.0	0.291	13.7	0.383	0.655	0.440	6.5	0.23
	0.85	51	108	2.1	0.289	12.2	0.389	0.653	0.452	6.5	0.24
	0.85	52	107	2.1	0.289	12.2	0.380	0.656	0.437	6.6	0.22
M6	0.56	50	106	2.1	0.451	13.5	0.339	0.700	0.409	*4.6*	*0.33*
	0.85	53	119	2.2	0.278	5.2	0.434	0.619	0.497	4.8	0.34
	0.85	52	113	2.2	0.279	5.7	0.439	0.609	0.494	4.6	0.33
M7	0.56	86	185	2.2	0.416	2.3	0.110	0.898	0.161	17.5	0.10
	0.56	85	183	2.2	0.415	1.8	0.109	0.899	0.159	17.8	0.09
	0.85	85	182	2.1	0.274	2.1	0.159	0.858	0.239	18.0	0.11
	0.85	84	180	2.1	0.273	1.7	0.163	0.853	0.235	17.3	0.10

Catalyst ID	v_H (mL)	M_n [a]	M_w [a]	PDI	$[E]/[H]_{av}$ [b]	[H],conv (%) [c]	x_H [d]	p_{EE} [e]	p_{HH} [e]	r_E	r_H
M8	1.00	80	189	2.4	0.236	5.0	0.244	0.811	0.380	18.2	0.14
	1.00	90	195	2.2	0.237	5.4	0.241	0.804	0.353	17.3	0.13
	1.50	98	211	2.2	0.158	5.9	0.357	0.727	0.493	16.8	0.15
M9	0.56	74	167	2.3	0.429	8.2	0.288	0.721	0.301	6.0	0.18
	0.56	77	174	2.3	0.423	5.6	0.300	0.715	0.311	5.9	0.19
	0.85	78	177	2.3	0.285	9.8	0.401	0.611	0.393	5.5	0.18
	0.85	83	181	2.2	0.285	10.0	0.400	0.612	0.396	5.5	0.19
M10	0.56	77	179	2.3	0.440	12.8	0.326	0.680	0.314	4.8	0.20
	0.56	88	185	2.1	0.437	11.5	0.326	0.680	0.314	4.9	0.20
	0.85	88	195	2.2	0.289	12.7	0.429	0.578	0.424	4.7	0.21
	0.85	91	189	2.1	0.291	13.4	0.429	0.570	0.417	4.6	0.21
M11	0.56	98	207	2.1	0.440	13.0	0.341	0.646	0.293	4.1	0.18
	0.56	102	215	2.1	0.437	11.5	0.338	0.647	0.287	4.2	0.18
	0.85	99	211	2.1	0.286	10.3	0.440	0.535	0.395	4.0	0.19
	0.85	102	209	2.0	0.285	9.7	0.439	0.535	0.395	4.0	0.19
M12	0.56	66	170	2.6	0.432	9.4	0.335	0.663	0.305	4.6	0.19
	0.56	67	169	2.5	0.430	8.5	0.334	0.663	0.314	4.6	0.20
	0.85	74	177	2.4	0.290	12.7	0.411	0.579	0.373	4.7	0.17
	0.85	75	173	2.3	0.287	11.2	0.425	0.557	0.398	4.4	0.19
M13	0.56	81	184	2.3	0.440	12.8	0.336	0.630	0.268	3.9	0.161
	0.56	73	182	2.5	0.440	12.6	0.361	0.602	0.296	3.4	0.185
	0.56	79	172	2.2	0.445	14.9	0.361	0.606	0.299	3.5	0.190
	0.85	80	178	2.2	0.287	11.0	0.440	0.511	0.386	3.6	0.180
	0.85	72	171	2.4	0.291	13.7	0.434	0.526	0.382	3.8	0.180
M14	0.56	95	208	2.2	0.433	10.1	0.375	0.586	0.304	3.3	0.19
	0.56	94	198	2.1	0.439	12.4	0.374	0.592	0.307	3.3	0.19
	0.85	89	196	2.2	0.287	11.0	0.455	0.496	0.383	3.4	0.18
M15	0.56	75	155	2.1	0.433	10.0	0.333	0.680	0.340	4.9	0.22
	0.56	73	150	2.1	0.434	10.1	0.308	0.710	0.320	5.6	0.20
	0.85	73	166	2.3	0.283	8.4	0.431	0.573	0.427	4.7	0.21
	0.85	73	158	2.2	0.287	11.3	0.422	0.603	0.442	5.3	0.23

Catalyst ID	v_H (mL)	M_n [a]	M_w [a]	PDI	$[E]/[H]_{av}$ [b]	[H],conv (%) [c]	x_H [d]	p_{EE} [e]	p_{HH} [e]	r_E	r_H
M16	0.56	54	122	2.3	0.434	10.2	0.321	0.695	0.338	5.3	0.22
	0.56	55	130	2.4	0.432	9.6	0.322	0.695	0.340	5.3	0.22
	0.85	67	149	2.2	0.289	12.4	0.418	0.598	0.439	5.1	0.23
	0.85	55	134	2.4	0.289	12.6	0.419	0.597	0.429	5.1	0.22
M17	0.56	46	102	2.2	0.420	3.9	0.336	0.690	0.399	4.5	0.33
	0.85	51	109	2.1	0.274	2.4	0.460	0.587	0.510	4.2	0.35
	0.85	48	109	2.3	0.277	4.1	0.448	0.605	0.508	4.5	0.35
M18	0.56	75	168	2.2	0.415	1.7	0.112	0.898	0.173	17.6	0.10
	0.85	75	173	2.3	0.274	2.4	0.173	0.848	0.258	16.6	0.12
	0.85	76	168	2.2	0.274	1.7	0.168	0.850	0.238	16.9	0.10
M19	0.56	90	199	2.2	0.430	8.8	0.326	0.716	0.386	5.9	0.27
	0.56	89	199	2.2	0.430	8.5	0.322	0.725	0.406	6.1	0.29
	0.85	74	161	2.2	0.290	13.1	0.468	0.582	0.517	4.8	0.31
	0.85	77	171	2.2	0.287	10.9	0.451	0.606	0.518	5.4	0.31
M20	0.56	69	168	2.4	0.431	8.9	0.317	0.715	0.371	5.8	0.25
	0.56	75	180	2.4	0.431	9.0	0.341	0.704	0.409	5.5	0.30
	0.85	72	188	2.6	0.283	8.3	0.444	0.611	0.496	5.6	0.28
	0.85	76	191	2.5	0.286	10.2	0.440	0.608	0.493	5.4	0.28
M21	3.40	145	296	2.0	0.068	0.5	0.111	0.895	0.153	125.4	0.012
	4.25	99	237	2.4	0.054	0.6	0.148	0.865	0.177	117.8	0.012
	4.25	106	229	2.2	0.054	0.6	0.140	0.872	0.197	125.3	0.013
M22	0.56	64	139	2.2	0.428	7.5	0.209	0.803	0.243	9.5	0.14
	0.85	64	130	2.0	0.284	9.1	0.298	0.724	0.332	9.2	0.14
	0.85	225	491	2.2	0.281	7.3	0.293	0.729	0.311	9.6	0.13
M23	0.56	99	215	2.2	0.440	13.0	0.315	0.699	0.317	5.3	0.20
	0.85	107	227	2.1	0.287	11.4	0.401	0.604	0.403	5.3	0.19
M24	0.56	77	179	2.3	0.417	2.4	0.293	0.700	0.263	4.6	0.18
	0.56	77	183	2.4	0.418	3.0	0.314	0.673	0.268	4.1	0.18
	0.85	73	178	2.4	0.276	3.7	0.391	0.585	0.361	4.2	0.19
M25	0.85	70	156	2.2	0.275	3.0	0.417	0.560	0.386	3.8	0.21
	0.85	71	158	2.2	0.278	5.1	0.411	0.561	0.374	3.8	0.20

Catalyst ID	v_H (mL)	M_n [a]	M_w [a]	PDI	$[E]/[H]_{av}$ [b]	[H],conv (%) [c]	x_H [d]	p_{EE} [e]	p_{HH} [e]	r_E	r_H
M26	0.56	79	178	2.3	0.435	10.7	0.335	0.671	0.330	4.7	0.21
	0.56	84	185	2.2	0.435	10.9	0.328	0.683	0.321	4.9	0.21
	0.85	73	160	2.2	0.297	17.4	0.437	0.560	0.427	4.3	0.22
	0.85	78	174	2.2	0.293	15.1	0.433	0.570	0.421	4.5	0.21
M27	0.56	37	79	2.1	0.439	12.5	0.347	0.630	0.314	3.9	0.20
	0.56	36	79	2.2	0.439	12.5	0.360	0.620	0.312	3.7	0.20
	0.85	27	54	2.0	0.293	13.8	0.444	0.515	0.386	3.6	0.18
	0.85	27	55	2.0	0.293	14.0	0.436	0.526	0.380	3.8	0.18
M28	4.25	116	253	2.2	0.054	0.5	0.083	0.913	0.038	193.1	0.002
	4.25	94	207	2.2	0.054	0.4	0.086	0.908	0.041	181.7	0.002
M29	0.56	77	174	2.3	0.433	9.9	0.364	0.615	0.314	3.7	0.20
	0.85	63	139	2.2	0.282	7.5	0.472	0.505	0.431	3.6	0.21
	0.85	52	118	2.3	0.286	10.4	0.461	0.501	0.413	3.5	0.20
M30	0.56	80	177	2.2	0.436	11.1	0.365	0.645	0.364	4.2	0.25
	0.85	73	166	2.3	0.282	7.9	0.489	0.514	0.475	3.7	0.26
	0.85	82	190	2.3	0.283	8.5	0.462	0.535	0.462	4.1	0.24
M31	0.56	41	92	2.2	0.459	10.4	0.353	0.672	0.392	4.5	0.30
	0.85	44	93	2.1	0.290	13.3	0.425	0.604	0.457	5.3	0.24
	0.56	42	81	1.9	0.430	8.5	0.322	0.701	0.362	5.5	0.24
	0.85	41	86	2.1	0.292	14.2	0.460	0.568	0.492	4.5	0.28
	0.85	37	73	2.0	0.302	20.5	0.440	0.587	0.471	4.7	0.27
M32	0.56	66	140	2.1	0.437	11.4	0.290	0.702	0.252	5.4	0.15
	0.56	68	144	2.1	0.433	9.8	0.291	0.705	0.241	5.5	0.14
	0.85	58	126	2.2	0.286	10.6	0.390	0.613	0.360	5.5	0.16
	0.85	68	135	2.0	0.285	10.1	0.378	0.595	0.335	5.1	0.14
M33	0.56	53	115	2.2	0.438	11.8	0.609	0.617	0.250	3.7	0.15
	0.56	51	107	2.1	0.452	12.6	0.356	0.584	0.250	3.1	0.15
	0.85	50	117	2.3	0.281	7.4	0.355	0.528	0.286	4.0	0.11
M34	0.56	74	166	2.2	0.434	10.1	0.316	0.719	0.364	5.9	0.25
	0.56	77	169	2.2	0.434	10.2	0.320	0.714	0.362	5.8	0.25
	0.85	61	140	2.3	0.285	9.8	0.421	0.615	0.457	5.6	0.24
	0.85	63	136	2.2	0.285	10.0	0.401	0.627	0.448	5.9	0.23

Catalyst ID	v_H (mL)	M_n [a]	M_w [a]	PDI	$[E]/[H]_{av}$ [b]	[H],conv (%) [c]	x_H [d]	p_{EE} [e]	p_{HH} [e]	r_E	r_H
M35	0.56	69	175	2.5	0.434	10.4	0.357	0.691	0.433	5.1	0.33
	0.85	88	220	2.5	0.289	12.3	0.467	0.585	0.518	4.9	0.31
	0.85	84	191	2.3	0.288	11.6	0.475	0.579	0.530	4.8	0.32
	0.85	94	239	2.5	0.296	13.7	0.474	0.566	0.507	4.4	0.30
M36	0.56	21	53	2.5	0.431	9.1	0.393	0.575	0.332	3.1	0.21
	0.56	18	40	2.2	0.437	11.6	0.396	0.562	0.336	2.9	0.22
	0.85	16	37	2.3	0.278	4.7	0.483	0.467	0.425	3.2	0.21
	0.85	19	43	2.3	0.280	6.1	0.477	0.459	0.418	3.0	0.20
M37	0.56	118	264	2.2	0.446	14.3	0.332	0.666	0.310	4.5	0.20
	0.56	122	272	2.2	0.442	13.7	0.332	0.664	0.308	4.5	0.20
	0.85	107	233	2.2	0.291	13.8	0.439	0.557	0.419	4.3	0.21
	0.85	122	272	2.2	0.288	11.4	0.423	0.571	0.402	4.6	0.19
M38	0.56	35	75	2.1	0.439	12.5	0.450	0.497	0.373	2.3	0.26
	0.56	37	78	2.1	0.436	11.4	0.437	0.513	0.383	2.4	0.27
	0.85	35	75	2.1	0.289	12.2	0.532	0.388	0.450	2.2	0.24
	0.85	33	70	2.1	0.297	17.6	0.528	0.387	0.469	2.1	0.26
M39	0.56	76	181	2.4	0.428	7.9	0.363	0.604	0.311	3.6	0.19
	0.56	81	185	2.3	0.436	11.2	0.353	0.615	0.283	3.7	0.17
	0.85	72	163	2.3	0.291	13.5	0.435	0.522	0.355	3.8	0.16
M40	0.56	75	187	2.5	0.439	12.3	0.336	0.635	0.274	4.0	0.166
	0.56	75	187	2.5	0.440	12.9	0.333	0.648	0.287	4.2	0.177
	0.85	66	169	2.6	0.282	7.6	0.410	0.557	0.369	4.5	0.165
	0.85	70	173	2.5	0.284	9.3	0.402	0.574	0.364	4.7	0.163

[a] in kDa, [b] average feeding ratio, [c] conversion of 1-hexene in %, [d] mol fraction of 1-hexene in the copolymer, [e] $\mathbf{p_{EE}}$ conditional probability of ethene insertion after ethene insertion; $\mathbf{p_{HH}}$ conditional probability of 1-hexene insertion after 1-hexene insertion

2. QSAR Modeling

Table S3. Procedures for Descriptor Determination.

#	Descriptor	SambVca (D1-D6) or Gaussian (D7) procedure	
D1	$\Delta\%V_{Bur,Zr}$	Coordinate System	center of the Sphere: Zr, z-axis: Si-Zr, xz-plane: Cl
		Deleted Atoms	$ZrCl_2$ + SiR_2 bridge + all atoms in 5-, 6-, and 7-position + additional atoms on the 2-position substituent (for details see *Polymers*, **2020**, *12*, 1005)
		Sphere Size and Position	5.0 Å, Center on Zr
D2	$\%V_{Bur(C2+C3)}$	Coordinate System	center of the Sphere: C3, z-axis: middle of the two opposite C-atoms, xz-plane: C2
		Deleted Atoms	$ZrCl_2$, SiR_2 bridge
		Sphere Size and Position	3.5 Å, Center on C3
D3	$\%V_{Bur(C2+C3),Front}$	Coordinate System	center of the Sphere: Cl, z-axis: Zr-Cl, xz-plane: Si
		Deleted Atoms	$ZrCl_2$
		Sphere Size and Position	3.5 Å, Center on Cl
D4	$\%V_{Bur(C5+C6)}$	Coordinate System	center of the Sphere: Cl, z-axis: Zr-Cl, xz-plane: Si
		Deleted Atoms	$ZrCl_2$, SiR_2 bridge
		Sphere Size and Position	6.5 Å, Center on Cl
D5	$\%V_{Bur,C4}$	Coordinate System	center of the Sphere: Cl, z-axis: Zr-Cl, xz-plane: Si
		Deleted Atoms	$ZrCl_2$
		Sphere Size and Position	3.5 Å, Center +2 Å away from Cl
D6	$\%V_{Bur,open}$	Coordinate System	center of the Sphere: Zr, z-axis: Si-Zr, xz-plane: Cl
		Deleted Atoms	$ZrCl_2$
		Sphere Size and Position	3.0 Å, Center +1.5 Å away from Cl
D7	q_{ZrCl2}	Sum of the NPA charges (NBO 3.0) on Zr and Cl atoms	

QSAR Modeling – Determination of Gibbs Free Energy Differences

Equations

Comonomer affinity after ethene insertion:

$$\Delta\Delta G^{\ddagger}_{EH\text{-}EE} = RT \ln (r_E) \quad \text{(Eq. S1)}$$

Comonomer affinity after 1-hexene insertion:

$$\Delta\Delta G^{\ddagger}_{HE\text{-}HH} = RT \ln (r_H) \quad \text{(Eq. S2)}$$

Table S4. Experimental data used for QSAR modeling.

Catalyst	r_E	r_H	$\Delta\Delta G^{\ddagger}_{EH\text{-}EE}$	$\Delta\Delta G^{\ddagger}_{HE\text{-}HH}$
Training Set				
M21	123	0.012	3.19	-2.93
M7	17.7	0.10	1.90	-1.52
M1	19	0.012	1.95	-2.93
M3	10.5	0.11	1.56	-1.46
M17	4.4	0.34	0.98	-0.71
M5	6.6	0.22	1.25	-1.00
M37	4.5	0.2	1.00	-1.07
M11	4.1	0.18	0.93	-1.14
M15	5.1	0.22	1.08	-1.00
M31	4.9	0.27	1.05	-0.87
M9	5.7	0.19	1.15	-1.10
M23	5.3	0.19	1.10	-1.10
M29	3.6	0.2	0.85	-1.07
M19	5.5	0.3	1.13	-0.80
M27	3.8	0.19	0.88	-1.10
M35	4.8	0.32	1.04	-0.75
M25	3.8	0.21	0.88	-1.03
M33	3.6	0.14	0.85	-1.30
M39	3.7	0.18	0.87	-1.14
M13	3.6	0.18	0.85	-1.14
Validation Set				
M18	17	0.11	1.88	-1.46
M8	17	0.14	1.88	-1.30
M22	9.4	0.14	1.48	-1.30
M6	4.6	0.33	1.01	-0.73
M4	6.4	0.18	1.23	-1.14
M10	4.7	0.21	1.02	-1.03
M12	4.6	0.19	1.01	-1.10
M2	5	0.2	1.07	-1.07
M16	5.2	0.22	1.09	-1.00
M26	4.6	0.21	1.01	-1.03
M14	3.3	0.19	0.79	-1.10
M20	5.6	0.28	1.14	-0.84
M32	5.4	0.15	1.12	-1.26
M24	4.3	0.18	0.97	-1.14
M38	2.2	0.26	0.52	-0.89
M34	5.8	0.24	1.16	-0.94
M30	4	0.25	0.92	-0.92
M36	3.1	0.21	0.75	-1.03
M40	4.5	0.17	1.00	-1.17
M28	187	0.002	3.46	-4.11

QSAR Modeling – r_E model

Table S5. Experimental and predicted $\Delta\Delta G^{\ddagger}_{EH\text{-}EE}$, descriptor values and model deviations.

Catalyst	deleted atoms	r_E	$\Delta\Delta G^{\ddagger}_{EH\text{-}EE}$ kcal/mol	$\%V_{Bur,open}$ (D6)	$\%V_{Bur,C4}$ (D5)	Bondi vdW radius (D8)	$\Delta\Delta G^{\ddagger}_{EH\text{-}EE,QSAR}$ kcal/mol	$\lvert\Delta\rvert_{exp\text{-}pred}$ (kcal/mol)	$\lvert\Delta\rvert^2_{exp\text{-}pred}$
Training Set									
M21	2-Me: far H	123	3.19	39.4	19.5	170	3.21	0.03	0.00
M7	2-Me: far H	17.7	1.90	35.5	7.5	170	1.66	0.24	0.06
M1	2-Me: far H	19.0	1.95	34.6	4.0	120	1.99	0.04	0.00
M3	2-Me: far H	10.5	1.56	34.9	9.5	170	1.34	0.22	0.05
M17	2-Me: far H	4.4	0.98	34.7	7.5	185	1.09	0.11	0.01
M5	2-Me: far H	6.6	1.25	34.6	6.9	175	1.19	0.06	0.00
M37	2-Et: far Me	4.5	1.00	34.8	18.5	170	1.08	0.09	0.01
M11	2-Me: far H	4.1	0.93	34.8	18.1	170	1.09	0.16	0.02
M15	2-Me: far H	5.1	1.08	34.8	19.1	170	1.07	0.01	0.00
M31	2-Me: far H	4.9	1.05	34.7	7.6	185	1.09	0.04	0.00
M9	2-Me: far H	5.7	1.15	34.8	18.4	170	1.08	0.07	0.00
M23	2-Me: far H	5.3	1.10	34.8	18.5	170	1.08	0.02	0.00
M29	2-Me: far H	3.6	0.85	35.4	31.9	170	1.05	0.20	0.04
M19	2-Me: far H	5.5	1.13	34.9	20.2	170	1.09	0.04	0.00
M27	2-Me: far H	3.8	0.88	34.7	18.2	170	1.04	0.16	0.03
M35	2-Me: far H	4.8	1.04	34.8	20.4	170	1.04	0.00	0.00
M25	2-Me: far H	3.8	0.88	34.8	18.7	170	1.08	0.19	0.04
M33	2-Me: far H	3.6	0.85	34.8	33.8	170	0.73	0.12	0.01
M39	2-Me: far H	3.7	0.87	34.8	33.5	170	0.73	0.13	0.02
M13	2-Me: far H	3.6	0.85	35.0	37.1	170	0.74	0.10	0.01
Validation Set									
M18	2-Me: far H	17.0	1.88	35.5	7.5	170	1.66	0.21	0.04
M8	2-Me: far H	17.0	1.88	36.2	16.0	170	1.79	0.08	0.01
M22	2-Me: far H	9.4	1.48	34.9	9.5	170	1.34	0.15	0.02
M6	2-Me: far H	4.6	1.01	34.7	7.5	185	1.09	0.08	0.01
M4	2-Me: far H	6.4	1.23	34.7	18.0	170	1.05	0.18	0.03
M10	2-Me: far H	4.7	1.02	34.7	17.9	170	1.05	0.02	0.00
M12	2-Me: far H	4.6	1.01	34.8	18.7	170	1.08	0.07	0.00
M2	2-Me: far H	5.0	1.07	34.8	18.7	170	1.08	0.01	0.00
M16	2-Me: far H	5.2	1.09	34.7	26.4	170	0.85	0.24	0.06
M26	2-Me: far H	4.6	1.01	34.7	18.5	170	1.04	0.02	0.00
M14	2-Me: far H	3.3	0.79	34.8	33.1	170	0.74	0.05	0.00
M20	2-Me: far H	5.6	1.14	34.9	19.8	170	1.10	0.04	0.00
M32	2-Me: far H	5.4	1.12	34.7	18.3	170	1.04	0.08	0.01
M24	2-Me: far H	4.3	0.97	34.8	18.6	170	1.08	0.11	0.01
M38	2-Me: far H	2.2	0.52	34.4	38.2	155	0.64	0.12	0.01
M34	2-Me: far H	5.8	1.16	35.0	20.5	170	1.13	0.03	0.00
M30	2-Me: far H	4.0	0.92	34.8	22.3	170	0.99	0.08	0.01
M36	2-iPr: far H, far Me, 2 far H on close Me	3.1	0.75	34.3	19.0	170	0.84	0.09	0.01
M40	2-Me: far H	4.5	1.00	35.0	33.7	170	0.82	0.17	0.03
M28	2-Me: far H	187	3.46	40.1	7.8	170	3.81	0.35	0.12

Table S6. Mean average deviation (MAD), mean squared error (MSE) and root mean squared error (RMSE) for $\Delta\Delta G^{\ddagger}_{\text{EH-EE,QSAR}}$.

Test Set		Validation Set	
MAD	0.10 kcal/mol	MAD	0.11 kcal/mol
MSE	0.02 $kcal^2/mol^2$	MSE	0.02 $kcal^2/mol^2$
RMSE	0.12 kcal/mol	RMSE	0.12 kcal/mol

QSAR Modeling – r_E model, Analysis of Variance

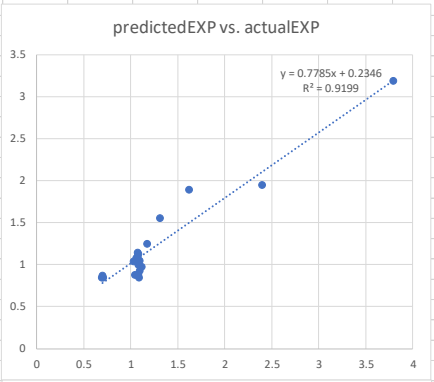
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.974039							
R Square	0.948752							
Adjusted F	0.939143							
Standard E	0.139071							
Observatio	20							
ANOVA								
	df	*SS*	*MS*	*F*	*gnificance F*			
Regressior	3	5.728878	1.909626	98.73569	1.55E-10			
Residual	16	0.309453	0.019341					
Total	19	6.03833						
	Coefficients	*andard Erro*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*ower 95.0%*	*pper 95.0%*
Intercept	-12.5167	1.146111	-10.921	7.95E-09	-14.9463	-10.087	-14.9463	-10.087
X Variable	0.467872	0.030749	15.21595	6.17E-11	0.402688	0.533057	0.402688	0.533057
X Variable	-0.02316	0.003343	-6.92769	3.4E-06	-0.03025	-0.01607	-0.03025	-0.01607
X Variable	-0.01326	0.002584	-5.13336	0.0001	-0.01874	-0.00779	-0.01874	-0.00779

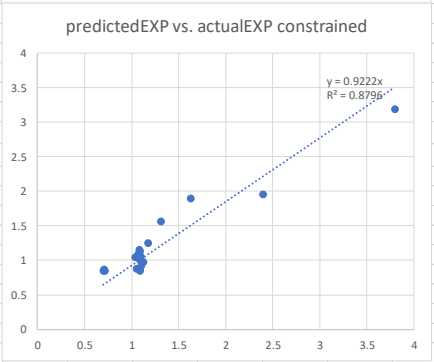
QSAR Modeling – r_E model, Leave-One-Out Analysis

MEAN = mean experimental value; MAD = mean average deviation; MSE = mean squared error; RMSE = root mean squared error; q^2 = cross-validated R^2

Table S7. LOOCV analysis stereoselectivity model.

	Catalyst	Yintercept	slopeA	slopeB	slopeC	redictedEX	actualEXP	R^2	adj. R^2	|Δ|	Δ^2	ualEXP-MEAN)^2
1	M21	-16.9632	0.597009	-0.02379	-0.01351	3.798787	3.19	0.849786	0.819744	0.609	0.371	3.863
2	M7	-12.3092	0.461977	-0.02128	-0.01355	1.62766	1.9	0.9552	0.94624	0.272	0.074	0.456
3	M1	-11.0773	0.463551	-0.0253	-0.0205	2.39981	1.95	0.945997	0.935197	0.450	0.202	0.526
4	M3	-12.5882	0.470058	-0.02179	-0.01352	1.312259	1.56	0.956425	0.94771	0.248	0.061	0.113
5	M17	-12.5857	0.466477	-0.02408	-0.01242	1.122309	0.98	0.950181	0.940218	0.142	0.020	0.060
6	M5	-12.5705	0.470157	-0.02257	-0.0135	1.178166	1.25	0.948846	0.938615	0.072	0.005	0.001
7	M37	-12.5008	0.467562	-0.02305	-0.01328	1.086691	1	0.948857	0.938628	0.087	0.008	0.050
8	M11	-12.4613	0.466434	-0.02308	-0.01325	1.100448	0.93	0.951945	0.942334	0.170	0.029	0.087
9	M15	-12.5488	0.468935	-0.02307	-0.01331	1.067484	1.08	0.947967	0.93756	0.013	0.000	0.021
10	M31	-12.5571	0.467987	-0.0234	-0.01301	1.098048	1.05	0.94815	0.93778	0.048	0.002	0.030
11	M9	-12.5761	0.469715	-0.02306	-0.01332	1.080553	1.15	0.948835	0.938602	0.069	0.005	0.006
12	M23	-12.5519	0.469022	-0.02306	-0.01331	1.080973	1.1	0.948048	0.937657	0.019	0.000	0.016
13	M29	-12.6233	0.471192	-0.02123	-0.01346	1.091668	0.85	0.955189	0.946227	0.242	0.058	0.140
14	M19	-12.5571	0.469168	-0.02311	-0.01331	1.087385	1.13	0.948335	0.938002	0.043	0.002	0.009
15	M27	-12.4313	0.465567	-0.02307	-0.01325	1.051895	0.88	0.951736	0.942083	0.172	0.030	0.119
16	M35	-12.5437	0.468787	-0.02306	-0.0133	1.038075	1.04	0.947823	0.937387	0.002	0.000	0.034
17	M25	-12.4412	0.465862	-0.02302	-0.01325	1.08869	0.88	0.953985	0.944782	0.209	0.044	0.119
18	M33	-12.6483	0.471757	-0.0244	-0.0132	0.700372	0.85	0.949896	0.939875	0.150	0.022	0.140
19	M39	-12.6583	0.47204	-0.02451	-0.01319	0.705258	0.87	0.950698	0.940837	0.165	0.027	0.126
20	M13	-12.6001	0.470358	-0.02455	-0.01317	0.712208	0.85	0.949242	0.93909	0.138	0.019	0.140
							MEAN			MAD	MSE	
							1.22			0.166	0.049	
							MAX					
							3.19					
							MIN					
							0.85					
					q^2=Σ(actualEXP-MEAN)-Σ(Δ^2)/Σ(actualEXP-MEAN)							
							q^2	0.84				





QSAR Modeling – r_H model

Table S8. Experimental and predicted $\Delta\Delta G^{\ddagger}_{HE\text{-}HH}$, descriptor values and model deviations.

Catalyst	deleted atoms	r_H	$\Delta\Delta G^{\ddagger}_{HE\text{-}HH}$ kcal/mol	$\%V_{Bur,open}$ (D6)	$\Delta\%V_{Bur,Zr}$ (D1)	q_{ZrCl2}	Bondi vdW radius (D8)	$\Delta\Delta G^{\ddagger}_{HE\text{-}HH,QSAR}$ kcal/mol	$\lvert\Delta\rvert_{exp\text{-}pred}$ kcal/mol	$\lvert\Delta\rvert^2_{exp\text{-}pred}$
Training Set										
M21	2-Me: far H	0.012	-2.93	39.4	8	0.43973	170	-2.91	0.02	0.00
M7	2-Me: far H	0.10	-1.52	35.5	15.4	0.38406	170	-1.51	0.02	0.00
M1	2-Me: far H	0.012	-2.93	34.6	12.8	0.39032	120	-2.94	0.01	0.00
M3	2-Me: far H	0.11	-1.46	34.9	13.3	0.415	170	-1.46	0.00	0.00
M17	2-Me: far H	0.34	-0.71	34.7	14.8	0.42209	185	-0.77	0.06	0.00
M5	2-Me: far H	0.22	-1.00	34.6	14.9	0.41368	175	-1.06	0.06	0.00
M37	2-Et: far Me	0.2	-1.07	34.8	16.2	0.42189	170	-1.00	0.07	0.00
M11	2-Me: far H	0.18	-1.14	34.8	16.1	0.41192	170	-1.08	0.06	0.00
M15	2-Me: far H	0.22	-1.00	34.8	16.3	0.4139	170	-1.04	0.04	0.00
M31	2-Me: far H	0.27	-0.87	34.7	14.9	0.41091	185	-0.84	0.03	0.00
M9	2-Me: far H	0.19	-1.10	34.8	16.3	0.41178	170	-1.05	0.05	0.00
M23	2-Me: far H	0.19	-1.10	34.8	16.3	0.40469	170	-1.10	0.00	0.00
M29	2-Me: far H	0.2	-1.07	35.4	16.2	0.39728	170	-1.29	0.22	0.05
M19	2-Me: far H	0.3	-0.80	34.9	17.6	0.41418	170	-0.88	0.08	0.01
M27	2-Me: far H	0.19	-1.10	34.7	16	0.40457	170	-1.12	0.02	0.00
M35	2-Me: far H	0.32	-0.75	34.8	17.9	0.418	170	-0.79	0.04	0.00
M25	2-Me: far H	0.21	-1.03	34.8	16.2	0.40338	170	-1.12	0.09	0.01
M33	2-Me: far H	0.14	-1.30	34.8	16.7	0.39839	170	-1.09	0.21	0.04
M39	2-Me: far H	0.18	-1.14	34.8	16.8	0.40132	170	-1.06	0.08	0.01
M13	2-Me: far H	0.18	-1.14	35	16.9	0.40703	170	-1.04	0.09	0.01
Validation Set										
M18	2-Me: far H	0.11	-1.5	35.5	15.3	0.38582	170	-1.51	0.05	0.00
M8	2-Me: far H	0.14	-1.3	36.2	15.0	0.3909	170	-1.66	0.35	0.13
M22	2-Me: far H	0.14	-1.3	34.9	13.1	0.41691	170	-1.47	0.17	0.03
M6	2-Me: far H	0.33	-0.7	34.7	14.8	0.42025	185	-0.78	0.05	0.00
M4	2-Me: far H	0.18	-1.1	34.7	15.3	0.41789	170	-1.13	0.01	0.00
M10	2-Me: far H	0.21	-1.0	34.7	16.1	0.4117	170	-1.06	0.03	0.00
M12	2-Me: far H	0.19	-1.1	34.8	16.3	0.41332	170	-1.04	0.06	0.00
M2	2-Me: far H	0.2	-1.1	34.8	16.2	0.41191	170	-1.07	0.00	0.00
M16	2-Me: far H	0.22	-1.0	34.7	16.8	0.41509	170	-0.94	0.06	0.00
M26	2-Me: far H	0.21	-1.0	34.7	16.3	0.4118	170	-1.03	0.00	0.00
M14	2-Me: far H	0.19	-1.1	34.8	16.8	0.40819	170	-1.01	0.09	0.01
M20	2-Me: far H	0.28	-0.8	34.9	17.65	0.39857	170	-0.98	0.14	0.02
M32	2-Me: far H	0.15	-1.3	34.7	15.2	0.40988	170	-1.19	0.06	0.00
M24	2-Me: far H	0.18	-1.1	34.8	16.2	0.40385	170	-1.12	0.01	0.00
M38	2-Me: far H	0.26	-0.9	34.4	18.2	0.41882	155	-1.06	0.17	0.03
M34	2-Me: far H	0.24	-0.9	35	17.7	0.40482	170	-0.95	0.01	0.00
M30	2-Me: far H	0.25	-0.9	34.8	17.6	0.39993	170	-0.96	0.04	0.00
M36	2-iPr: far H, far Me, 2 far H on close Me	0.21	-1.0	34.3	11.4	0.43049	170	-1.49	0.45	0.20
M40	2-Me: far H	0.17	-1.2	35	16.8	0.40985	170	-1.04	0.13	0.02
M28	2-Me: far H	0.002	-4.1	40.1	5.2	0.41495	170	-3.60	0.51	0.26

Table S9. Mean average deviation (MAD), mean squared error (MSE) and root mean squared error (RMSE) for $\Delta\Delta G^{\ddagger}_{\text{EH-EE,QSAR}}$.

Test Set		Validation Set	
MAD	0.06 kcal/mol	MAD	0.12 kcal/mol
MSE	0.01 $kcal^2/mol^2$	MSE	0.04 $kcal^2/mol^2$
RMSE	0.09 kcal/mol	RMSE	0.19 kcal/mol

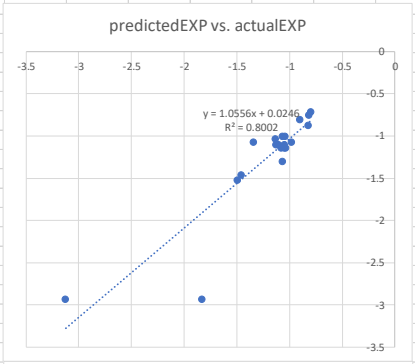
QSAR Modeling – r_H model, Analysis of Variance

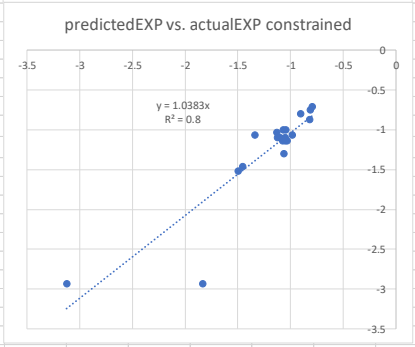
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.989579							
R Square	0.979267							
Adjusted F	0.973738							
Standard E	0.098241							
Observatio	20							
ANOVA								
	df	*SS*	*MS*	*F*	*gnificance F*			
Regressior	4	6.837771	1.709443	177.1213	1.98E-12			
Residual	15	0.144769	0.009651					
Total	19	6.98254						
	Coefficients	*tandard Erro*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*ower 95.0%*	*pper 95.0%*
Intercept	-3.55349	1.562412	-2.27436	0.038062	-6.88369	-0.22328	-6.88369	-0.22328
X Variable	-0.20133	0.036663	-5.49132	6.21E-05	-0.27948	-0.12318	-0.27948	-0.12318
X Variable	0.135321	0.018416	7.348071	2.41E-06	0.096069	0.174574	0.096069	0.174574
X Variable	6.943083	2.433881	2.85268	0.012101	1.755388	12.13078	1.755388	12.13078
X Variable	0.026132	0.002265	11.53582	7.4E-09	0.021304	0.03096	0.021304	0.03096

QSAR Modeling – r_H model, Leave-One-Out Analysis

Table S10. LOOCV analysis stereoselectivity model.

	Catalyst	Yintercept	slopeA	slopeB	slopeC	slopeD	redictedEX	actualEXP	R^2	adj. R^2	|Δ|	Δ^2	ualEXP-MEAN)^2
1	M21	-11.2676	-0.00991	0.123539	10.50907	0.024812	-1.83052	-2.93	0.969281	0.960504	1.099	1.209	2.796
2	M7	-3.44189	-0.2001	0.134457	6.493382	0.026387	-1.49504	-1.52	0.978879	0.972844	0.025	0.001	0.069
3	M1	-4.70298	-0.18583	0.143139	6.896781	0.029048	-3.12291	-2.93	0.964475	0.954324	0.193	0.037	2.796
4	M3	-3.47436	-0.20323	0.134291	6.908543	0.026234	-1.45418	-1.46	0.978927	0.972906	0.006	0.000	0.041
5	M17	-3.78418	-0.1908	0.139835	6.62577	0.025637	-0.79572	-0.71	0.978844	0.972799	0.086	0.007	0.300
6	M5	-3.75829	-0.19463	0.138237	6.822015	0.025955	-1.06841	-1	0.979408	0.973525	0.068	0.005	0.067
7	M37	-3.72252	-0.20445	0.136931	7.690251	0.025846	-0.98077	-1.07	0.979876	0.974126	0.089	0.008	0.035
8	M11	-3.53899	-0.20323	0.135361	7.070655	0.026143	-1.07513	-1.14	0.979572	0.973736	0.065	0.004	0.014
9	M15	-3.44911	-0.20213	0.133972	6.730942	0.026301	-1.04234	-1	0.979078	0.973101	0.042	0.002	0.067
10	M31	-3.26626	-0.20793	0.131388	6.729214	0.026691	-0.82089	-0.87	0.978822	0.972771	0.049	0.002	0.151
11	M9	-3.55491	-0.20252	0.135568	7.039603	0.026142	-1.0499	-1.1	0.979309	0.973397	0.050	0.003	0.025
12	M23	-3.50624	-0.2024	0.13474	6.906196	0.026213	-1.1025	-1.1	0.978975	0.972968	0.002	0.000	0.025
13	M29	-3.19614	-0.22867	0.127714	8.833254	0.025731	-1.3387	-1.07	0.987377	0.98377	0.269	0.072	0.035
14	M19	-2.9824	-0.20997	0.127551	6.325972	0.026717	-0.90347	-0.8	0.979621	0.973799	0.103	0.011	0.210
15	M27	-3.54163	-0.20186	0.134954	6.949021	0.02618	-1.12495	-1.1	0.979058	0.973074	0.025	0.001	0.025
16	M35	-3.12771	-0.20674	0.129715	6.368748	0.026617	-0.8134	-0.75	0.97863	0.972524	0.063	0.004	0.258
17	M25	-3.574	-0.20289	0.134465	7.159081	0.026098	-1.13159	-1.03	0.980277	0.974641	0.102	0.010	0.052
18	M33	-3.44061	-0.19349	0.138204	5.726707	0.026583	-1.06549	-1.3	0.986027	0.982034	0.235	0.055	0.002
19	M39	-3.54713	-0.19891	0.136706	6.622959	0.026263	-1.04988	-1.14	0.980065	0.974369	0.090	0.008	0.014
20	M13	-3.77984	-0.19579	0.139153	6.925023	0.026042	-1.03503	-1.14	0.980426	0.974833	0.105	0.011	0.014
								MEAN			**MAD**	**MSE**	
								-1.26			**0.138**	**0.072**	
								MAX					
								-0.71					
								MIN					
								-2.93					
						q^2=Σ(actualEXP-MEAN)-Σ(Δ^2)/Σ(actualEXP-MEAN)							
								q^2	**0.79**				





3. Lack of Correlation between Performance Indicators in Homo- and Copolymerization

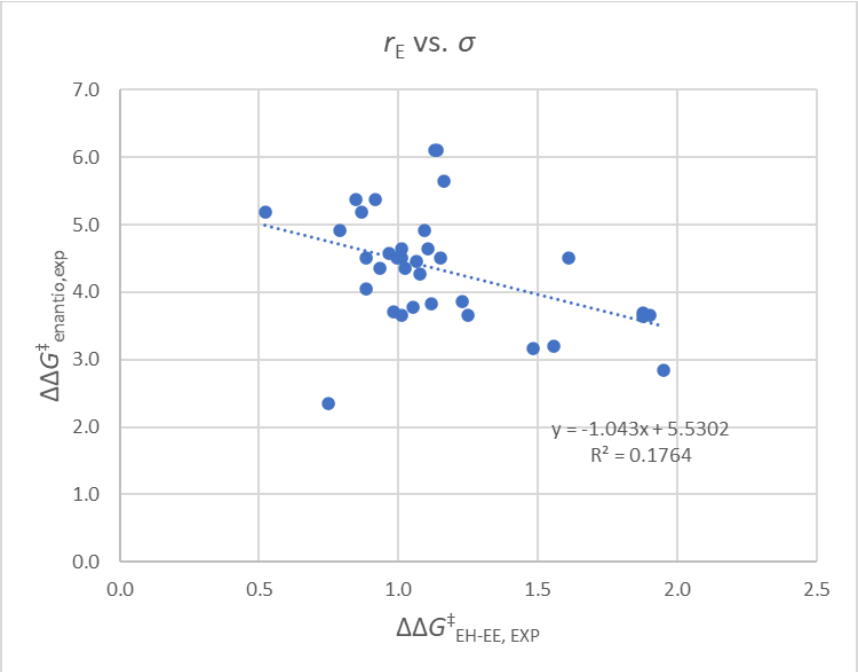


Figure S1. Correlation of enantioselectivity in iPP polymerization and reactivity ratio r_E. In terms of $\Delta\Delta G^{\ddagger}$.

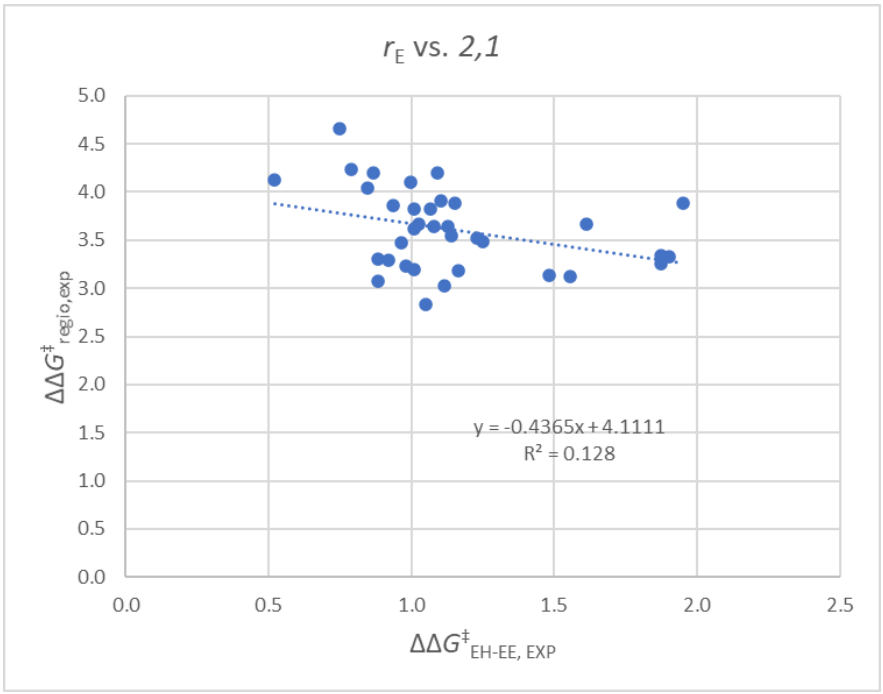


Figure S2. Correlation of regioselectivity in iPP polymerization and reactivity ratio r_E. In terms of $\Delta\Delta G^{\ddagger}$.

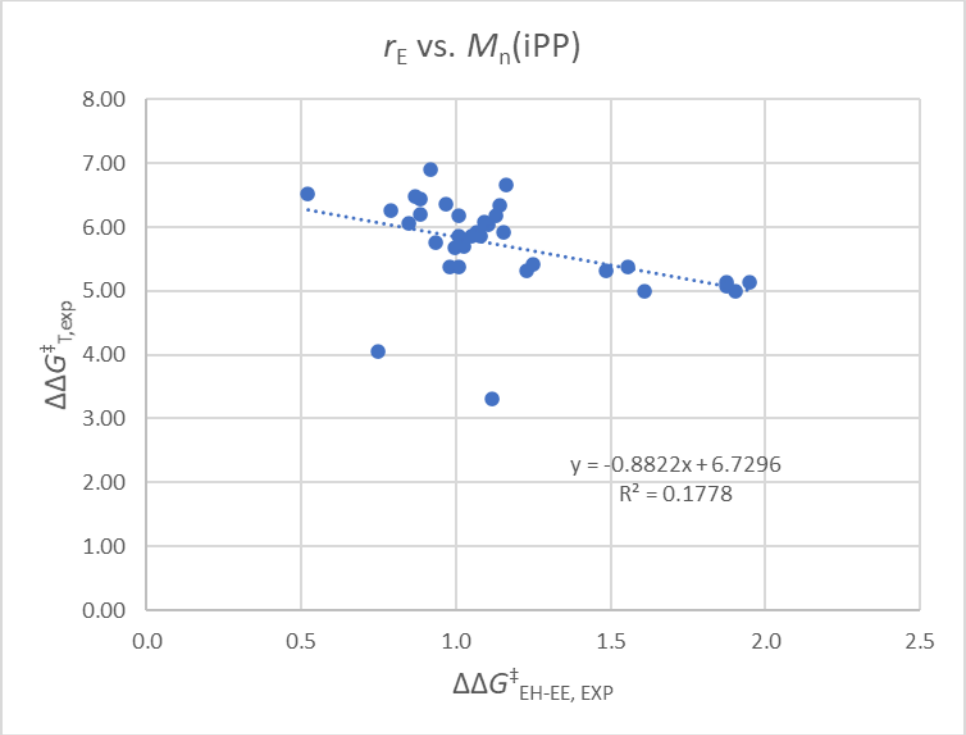


Figure S3. Correlation of molar mass capability in iPP polymerization and reactivity ratio r_E. In terms of $\Delta\Delta G^{\ddagger}$.

4. Full Gaussian Citation

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