Classification: Internal Use

cs-2019-01174y

SUPPORTING INFORMATION

Randomly Functionalized Polyethylenes – In Quest of Avoiding Catalyst Deactivation.

Miloud Bouyahyi,[†] Younes Turki,[†] Akhilesh Tanwar,[‡] Lidia Jasinska-Walc,[†,#] Rob Duchateau[†]*

[†]SABIC Technology & Innovation, STC Geleen, Urmonderbaan 22, Geleen, The Netherlands.

[‡] SABIC Research & Technology Pvt. Ltd. lot No. 81 to 85, Bangalore-562125, India.

[#] Department of Polymer Technology, Chemical Faculty, Gdansk University of Technology, G. Narutowicza Str. 11/12, 80-233 Gdansk, Poland

Corresponding author's email: Rob.Duchateau@sabic.com

cs-2019-01174y

Computational details:

All Calculations were performed with the TURBOMOLE program package [1] by using PBE0 [2] DFT functional and def2-TZVP basis set.[3] Dscf module with Fine grid (gridsize = 6) was used for DFT calculations. All Geometries were fully optimized and analytic hessian was calculated for each optimized structure. Absence of negative eigenvalues ensured true minima for geometry optimization. Thermochemistry of reactions were obtained at 0 K, 298 K and 323 K using uniform frequency scaling factor (λ_{ZPVE}) of 0.9830.[4]

References:

1. TURBOMOLE V6.5 2013, a development of the University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
2. Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: the PBE0 model. *J. Chem. Phys.* **1999**, 110, 6158-6170.
3. Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.*, **2005,** 7, 3297-3305.
4. Kesharwani, M. K.; Brauer, B.; Martin, J. M. L. Frequency and Zero-Point Vibrational Energy Scale Factors for Double-Hybrid Density Functionals (and Other Selected Methods): Can Anharmonic Force Fields Be Avoided?. *J. Phys. Chem. A.* **2015**, 119, 1701-1714.

Complexation enthalpy and free energies were calculated using equation 1-2, respectively.

$$\Delta H_{(complexation)} = \Delta H_{complex} - \Sigma \Delta H_{monomer}$$

(1)

$$\Delta G_{(complexation)} = \Delta G_{complex} - \Sigma \Delta G_{monomer}$$

(2)

Discussions: Optimized geometries of (but-3-en-1-yloxy)diisobutylaluminum, triisobutylaluminum and their complexes are shown in Figure S1. Dimerization of (1) proceeds by sharing of oxygen atoms of (2) with aluminum atoms forming double bridged structure, whereas (2) can form complex with triisobutylaluminum via sharing of CH2 and oxygen with aluminum atoms. Complexation free energy change and enthalpy change for the competing pacification reactions is presented in Table S1. Reaction 1 is thermodynamically more favorable as compared to reaction 2 by ~23 kcal·mol^{-1} implying that only one mole equivalent of TiBA is needed to achieve desired pacification as aluminum alkoxide undergoes self-complexation.

cs-2019-01174y

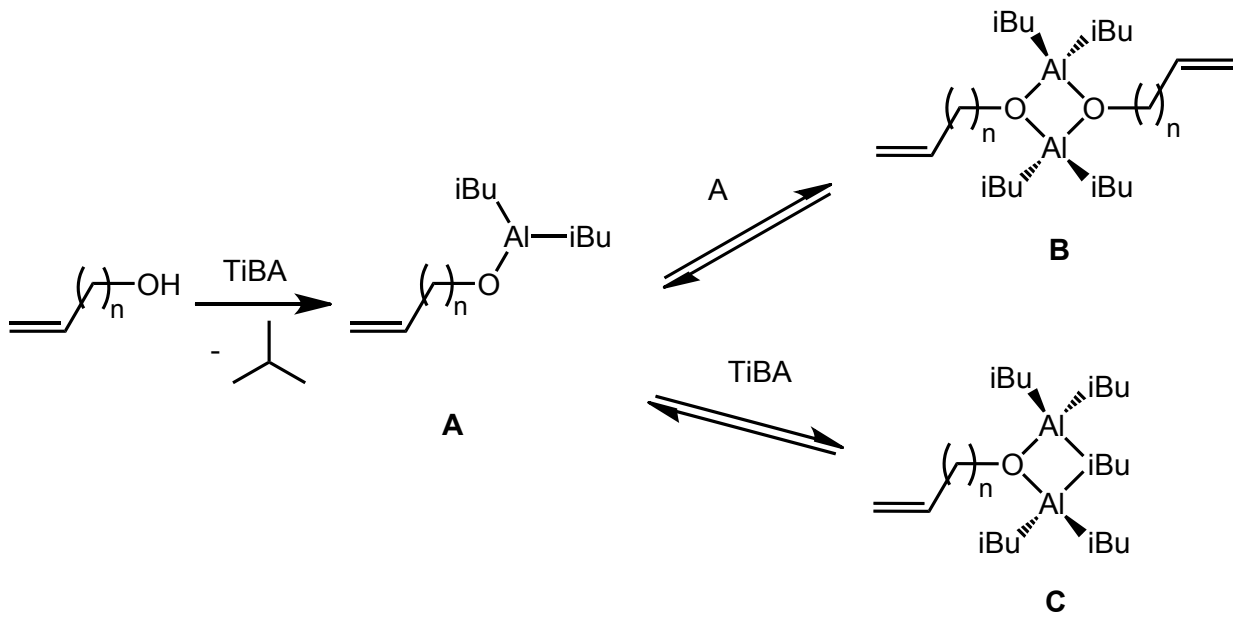

Figure S1: Complexation of 1-butenol with TiBA

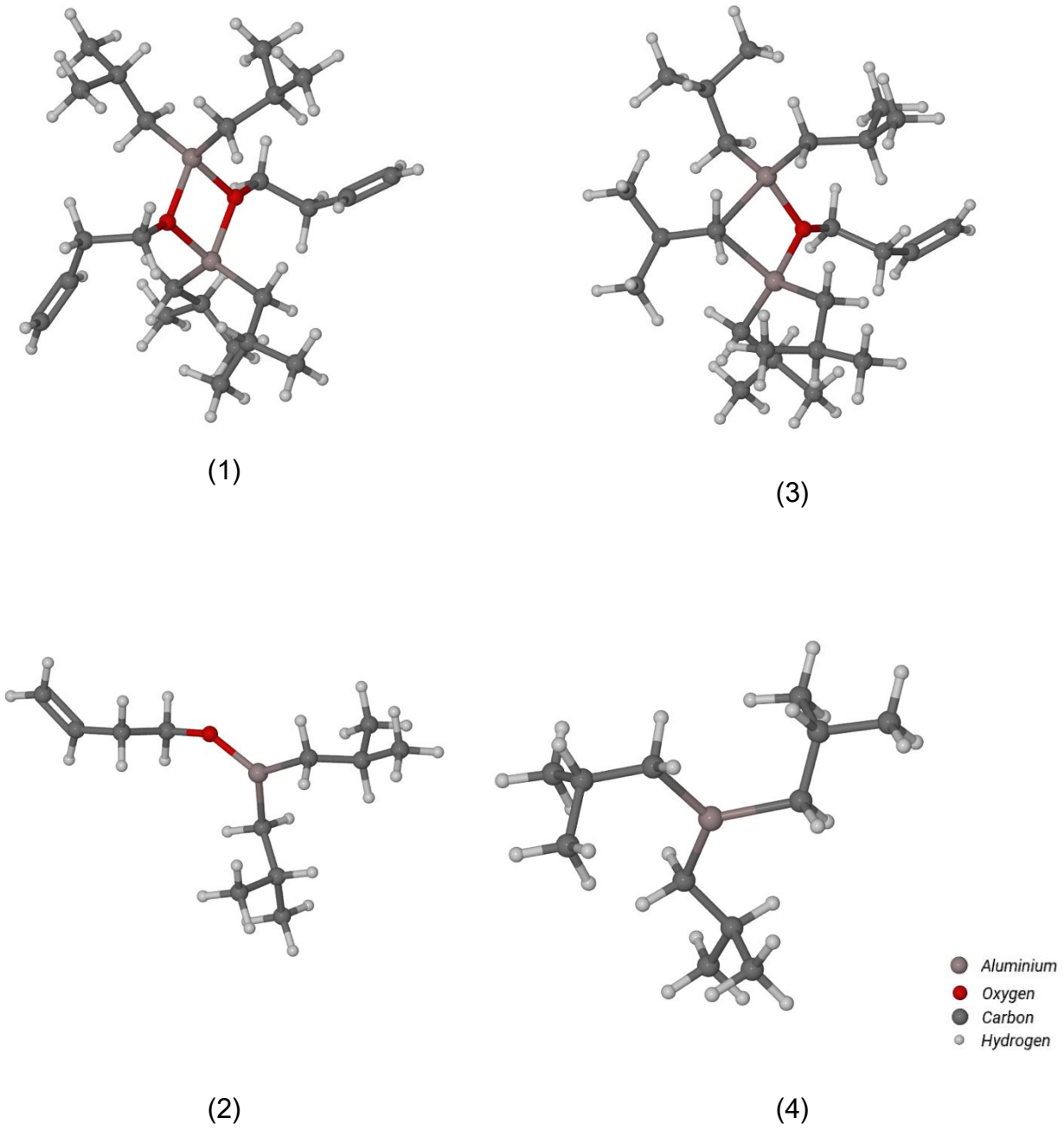

Figure S2: Optimized structures of (1) dimer of (but-3-en-1-yloxy)diisobutylaluminum (2) (but-3-en-1-yloxy)diisobutylaluminum (3) (but-3-en-1-yloxy)pentaisobutyldialuminum and (4) triisobutyl aluminum complex.

cs-2019-01174y

Table S1. Complexation enthalpies and Gibbs free energy change for pacification reactions by triisobutylaluminum in kcal·mol^{-1}

Temp. (K)	ΔG_{Rxn1}	ΔG_{Rxn2}	ΔH_{Rxn1}	ΔH_{Rxn2}
0	-46.95	-24.01		
298	-29.15	-6.36	-47.47	-24.29
323	-27.62	-4.86	-47.40	-24.22

Table S2. XYZ coordinates of dimer of (but-3-en-1-yloxy)diisobutylaluminum at PBE0/def2-TZVP level

H	2.5044764	-0.5962283	-0.8975700
C	2.1247658	-0.2194892	0.0583531
H	2.5917526	0.7534951	0.2417796
O	0.7202156	-0.0350833	-0.0350021
Al	-0.1550305	1.4997626	-0.6162662
Al	-0.6100931	-1.2899530	-0.4114814
C	-0.7345047	2.6546142	0.8812860
H	-1.5330377	2.1240346	1.4199211
H	-1.2111641	3.5660637	0.4895241
C	0.7654047	2.1881238	-2.2256462
H	1.8468333	2.0665927	-2.0607191
H	0.5408272	1.5211930	-3.0721735
C	-0.0601293	-2.3777952	-1.9716959
H	0.2097971	-1.6523903	-2.7543789
H	-0.9491136	-2.8941005	-2.3651677
C	-1.3791270	-1.9632639	1.2833989
H	-0.6711174	-2.7048216	1.6875856
H	-1.3314025	-1.1244710	1.9935530
C	1.0691435	-3.4098381	-1.8538346
H	1.9610579	-2.9126120	-1.4469334
C	-2.7848347	-2.5738173	1.3471948
H	-3.5099825	-1.8022452	1.0543600
C	0.3406503	3.0734985	1.8938326
H	0.8153495	2.1655126	2.2900113
C	0.4964841	3.6351698	-2.6503729
H	0.7209183	4.2910217	-1.7986924
C	1.3923181	4.0653448	-3.8066159
H	2.4487987	3.9569154	-3.5479548
H	1.2194860	5.1089213	-4.0876021
H	1.2030626	3.4454566	-4.6893192
C	-0.9669411	3.8471326	-3.0142571
H	-1.2509980	3.2055808	-3.8554846
H	-1.1633968	4.8818497	-3.3083696
H	-1.6307656	3.6143913	-2.1748624

C	-0.2605530	3.8235104	3.0771809
H	0.5014344	4.0939746	3.8148904
H	-1.0197558	3.2205654	3.5820617
H	-0.7422923	4.7472640	2.7396970
C	1.4320486	3.9136160	1.2429832
H	2.2038497	4.1952764	1.9645243
H	1.0120446	4.8361967	0.8287975
H	1.9243090	3.3837874	0.4210287
C	-3.1417426	-3.0029235	2.7663214
H	-2.4603244	-3.7883466	3.1097167
H	-4.1613870	-3.3958791	2.8262537
H	-3.0600094	-2.1663706	3.4651251
C	-2.9504915	-3.7443106	0.3871464
H	-2.2326712	-4.5374866	0.6189631
H	-2.7862171	-3.4467648	-0.6524096
H	-3.9534274	-4.1749597	0.4548850
C	0.7058940	-4.5451003	-0.9059231
H	1.5187336	-5.2721104	-0.8250114
H	-0.1802484	-5.0764417	-1.2677992
H	0.4781797	-4.1827189	0.1000373
C	1.4559577	-3.9723789	-3.2175580
H	2.2809638	-4.6875599	-3.1416993
H	1.7602912	-3.1765670	-3.9023377
H	0.6045949	-4.4909006	-3.6706302
O	-1.4914291	0.2504976	-0.9765392
C	-2.8877812	0.5008763	-1.0626517
H	-3.1120421	1.4291889	-0.5261533
H	-3.4231167	-0.3071224	-0.5553293
C	2.5013901	-1.1806131	1.1743434
H	3.5799481	-1.3583109	1.1158046
H	2.0144070	-2.1457345	0.9801578
C	2.1387266	-0.6937496	2.5382326
H	1.0819010	-0.5127149	2.7180762
C	3.0093189	-0.4735686	3.5133397
H	2.6923614	-0.1153812	4.4858897
H	4.0725471	-0.6478807	3.3763579
C	-3.3692843	0.6132703	-2.5013555

H	-2.8213632	1.4297748	-2.9852912
H	-4.4248381	0.9034680	-2.4776890
C	-3.2057890	-0.6444223	-3.2880539
H	-2.1856330	-0.9915913	-3.4334157
C	-4.2052592	-1.3479615	-3.8020864
H	-4.0280759	-2.2590548	-4.3618361
H	-5.2389896	-1.0351044	-3.6870713

XYZ coordinates of (but-3-en-1-yloxy)diisobutylaluminum at PBE0/def2-TZVP level

C	-1.6383285	-4.4803355	2.3594575
H	-1.1990901	-5.3824546	2.7934333
H	-2.7158615	-4.5077571	2.5503061
C	-1.3595388	-4.3786881	0.8650987
H	-0.2703177	-4.3200078	0.7344330
C	-1.8392986	-5.6352019	0.1482222
H	-1.6182149	-5.5877256	-0.9209663
H	-2.9227729	-5.7476391	0.2575319
C	-1.9888007	-3.1120194	0.2733031
H	-3.0813976	-3.1676322	0.3680517
H	-1.7925457	-3.0767303	-0.8071594
H	-1.2280250	-3.6252909	2.9108773
Al	-1.3930205	-1.4301627	1.0880416
O	-2.6207866	-0.3164291	1.4622738
C	-2.6752581	0.9683561	2.0018887
H	-1.6716038	1.3476350	2.2494382
H	-3.2443382	0.9443242	2.9401339
C	0.4877326	-0.9940457	1.4719565
H	0.8022556	-1.5431661	2.3703656
H	0.5731246	0.0680518	1.7402147
C	1.4552008	-1.3013718	0.3221125
H	1.3795702	-2.3706478	0.0819294
C	1.0781470	-0.5213646	-0.9310601
H	1.1086902	0.5560921	-0.7389951
H	0.0662509	-0.7661801	-1.2767684
H	1.7596387	-0.7311512	-1.7595777

C	2.9023768	-1.0201780	0.7084988
H	3.1945641	-1.5979769	1.5888220
H	3.0355118	0.0396419	0.9487570
H	3.5929497	-1.2686498	-0.1030106
H	-1.3666876	-6.5359727	0.5512960
C	-3.3532841	1.9379626	1.0404468
H	-2.7947596	1.9212510	0.0961184
H	-4.3626851	1.5770500	0.8243689
C	-3.3987798	3.3292729	1.5760441
H	-2.4358287	3.8022378	1.7660173
C	-4.5052547	4.0086204	1.8446135
H	-4.4716291	5.0173693	2.2399865
H	-5.4877893	3.5795363	1.6722749

XYZ coordinates of (but-3-en-1-yloxy)diisobutylaluminum and triisobutylaluminum complex at PBE0/def2-TZVP level

H	1.8138549	-1.8948928	0.5922420
C	1.7868900	-0.8061547	0.4894347
H	1.8335755	-0.3847750	1.4993738
O	0.5530525	-0.4367790	-0.1081216
C	-2.2486786	0.2871926	-0.4573280
H	-2.7492431	-0.4643518	-1.0958542
H	-2.3631228	1.1329614	-1.1583372
Al	-0.2668127	1.1908039	-0.4194720
Al	-0.9433303	-1.4660732	-0.4210656
C	-0.1430025	2.3726544	1.1672712
H	-0.6707326	1.8853208	1.9983766
H	-0.7161954	3.2906252	0.9693946
C	0.2088175	1.7782569	-2.2515043
H	1.2904476	1.6105238	-2.3636684
H	-0.2478059	1.0749424	-2.9656731
C	-0.9417091	-2.1677051	-2.2790879
H	-1.4629472	-1.4255501	-2.9009820
H	-1.5715123	-3.0681740	-2.3360994
C	-1.3289688	-2.5052174	1.2193713
H	-0.3595894	-2.7918415	1.6571181

H	-1.7517009	-1.7999290	1.9481853
C	0.4102887	-2.4721007	-2.9353954
H	1.0381684	-1.5745115	-2.8528185
C	-2.2089863	-3.7607321	1.1614190
H	-3.1101253	-3.5426424	0.5708208
C	1.2519251	2.7950884	1.6519793
H	1.8560652	1.8933829	1.8239564
C	-0.1115622	3.2074306	-2.7018549
H	0.3780666	3.9042480	-2.0088710
C	0.4334685	3.4938752	-4.0967705
H	1.5126577	3.3256830	-4.1403979
H	0.2400227	4.5264831	-4.4037419
H	-0.0334763	2.8325325	-4.8342603
C	-1.6064414	3.4965918	-2.6542296
H	-2.1577536	2.7949988	-3.2900282
H	-1.8304388	4.5066454	-3.0083673
H	-2.0062644	3.4134785	-1.6386400
C	1.1768322	3.5410053	2.9799428
H	2.1700882	3.8234790	3.3425568
H	0.6965482	2.9316047	3.7497541
H	0.5883245	4.4575432	2.8686132
C	1.9786738	3.6446979	0.6176846
H	2.9757764	3.9301942	0.9640477
H	1.4204333	4.5658872	0.4210830
H	2.0919255	3.1241150	-0.3374829
C	-2.6722042	-4.1839539	2.5509708
H	-1.8105186	-4.4149191	3.1860149
H	-3.3071641	-5.0743993	2.5117253
H	-3.2387754	-3.3870984	3.0402494
C	-1.4886717	-4.9136422	0.4759996
H	-0.5900496	-5.1898509	1.0380811
H	-1.1769820	-4.6513113	-0.5370467
H	-2.1253548	-5.8003910	0.4135142
C	1.1381809	-3.6127178	-2.2367101
H	2.1211489	-3.7928827	-2.6811575
H	0.5656459	-4.5423088	-2.3168582
H	1.2871815	-3.4166057	-1.1701802

C	0.2603749	-2.7827531	-4.4206769
H	1.2285641	-2.9728999	-4.8944963
H	-0.2163806	-1.9541359	-4.9504124
H	-0.3630099	-3.6712948	-4.5652324
C	-3.1459265	0.5419273	0.7796126
H	-2.5519964	0.4066969	1.6909100
C	-3.6879559	1.9657488	0.7943541
H	-2.8863916	2.7068873	0.7881274
H	-4.2957072	2.1442884	1.6854236
H	-4.3200418	2.1437357	-0.0818093
C	-4.3036044	-0.4466624	0.8374355
H	-3.9535535	-1.4809687	0.8557314
H	-4.9527795	-0.3262726	-0.0361849
H	-4.9141247	-0.2865199	1.7301797
C	2.9778293	-0.3423133	-0.3319384
H	2.9101860	0.7448080	-0.4617281
H	2.9313781	-0.7925687	-1.3270223
C	4.2678093	-0.6864662	0.3367603
H	4.4480400	-0.2179407	1.3031339
C	5.1780499	-1.5144497	-0.1555087
H	6.0963119	-1.7301957	0.3780991
H	5.0396095	-2.0021475	-1.1156704

XYZ coordinates of Triisobutyl aluminum at PBE0/def2-TZVP level

Al	-1.9346225	-0.6061163	-0.1921729
C	-2.6018111	-0.0117740	1.5711534
H	-3.5030985	0.6043473	1.4451082
H	-1.8500336	0.6721290	1.9940990
C	-2.6468807	0.2177154	-1.8409933
H	-1.8613412	0.2707662	-2.6077524
H	-3.3788570	-0.4970306	-2.2498148
C	-0.5997921	-2.0661943	-0.1403529
H	-1.1239540	-2.9281354	0.3008957
H	0.1236803	-1.7732912	0.6357031
C	0.1513722	-2.5177533	-1.3945038
C	1.0232029	-1.4023529	-1.9546000

cs-2019-01174y

C	-0.7986559	-3.0538770	-2.4565712
H	0.8232665	-3.3423003	-1.1169266
C	-3.3042270	1.5932786	-1.6981604
C	-2.2971993	2.6315484	-1.2207009
H	-4.0931368	1.5231718	-0.9374383
C	-3.9590619	2.0467109	-2.9980174
C	-2.8918912	-1.1252946	2.5836893
H	-1.9797220	-1.7234080	2.7117731
C	-3.9841203	-2.0556975	2.0709999
C	-3.2709283	-0.5679598	3.9509723
H	-0.2528020	-3.4320754	-3.3254546
H	-1.4772147	-2.2700624	-2.8088161
H	-1.4087596	-3.8725247	-2.0644969
H	1.6004367	-1.7417098	-2.8192087
H	1.7298003	-1.0370976	-1.2041058
H	0.4129583	-0.5529422	-2.2801385
H	-4.1832466	0.0332998	3.8801241
H	-2.4812091	0.0755179	4.3468510
H	-3.4518574	-1.3660428	4.6775717
H	-3.7033954	-2.5310330	1.1237598
H	-4.9129771	-1.5018247	1.8995996
H	-4.2013356	-2.8569464	2.7824248
H	-1.4707728	2.7222814	-1.9335809
H	-1.8713274	2.3634322	-0.2478921
H	-2.7541972	3.6191616	-1.1157129
H	-3.2106491	2.1417187	-3.7915666
H	-4.4514444	3.0173869	-2.8851602
H	-4.7083117	1.3259627	-3.3353402

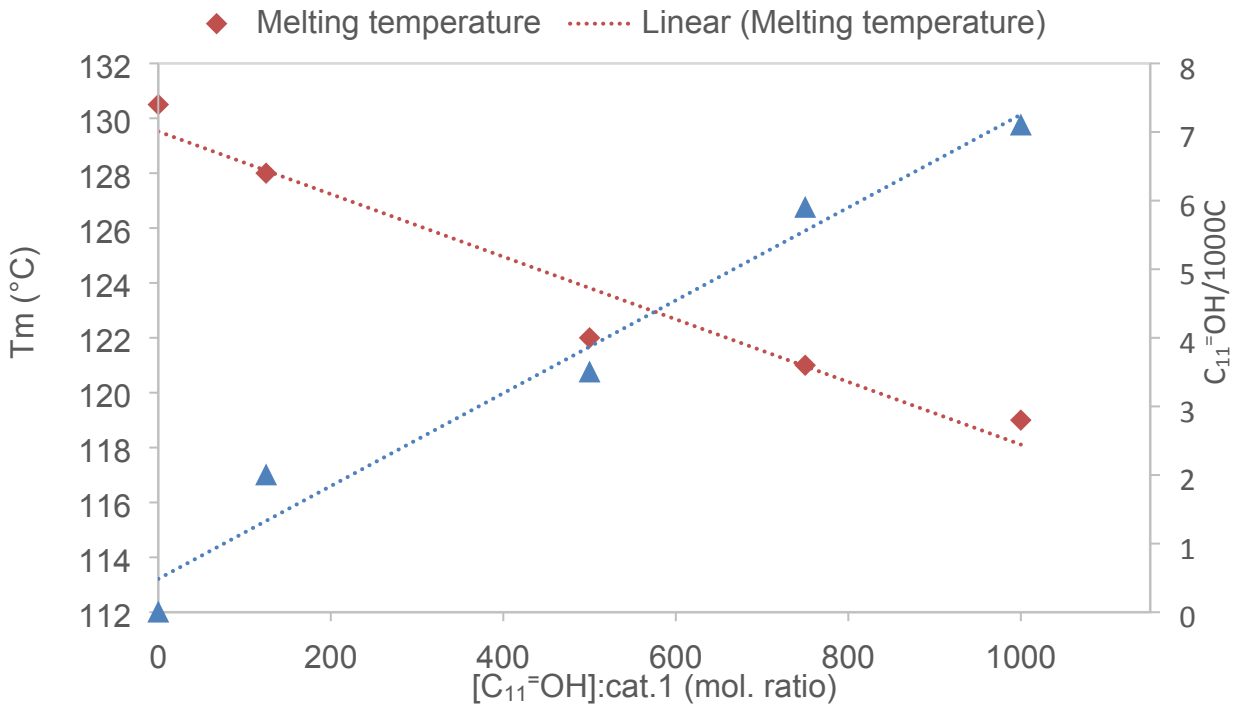

Figure S3. Correlation between copolymer melting temperatures (blue) and comonomer incorporation levels (brown) in $C_2^=$ /$C_{11}^=$OH copolymerization mediated by **1**/MAO (entries 9–12, Table 1). The low molecular weight of the polymers enhances the effect on the melting point of the polymers.

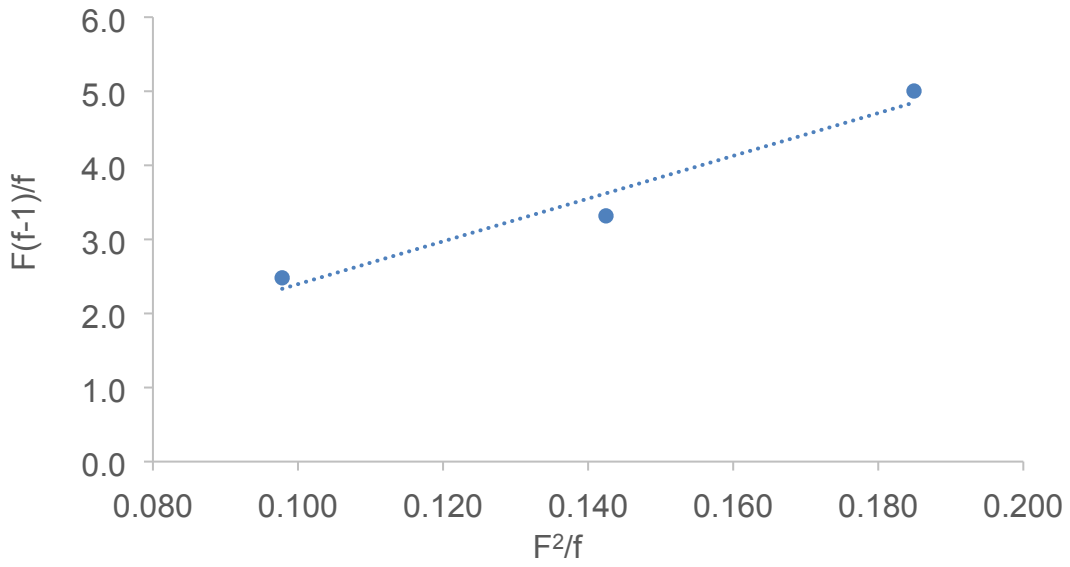

Figure S4. Fineman–Ross plot for copolymerization of ethylene and 10-undecen-1-ol with 1/MAO (F = [ethylene]/[10-undecen-1-ol] in the feed and f = [ethylene]/[10-undecen-1-ol] in the copolymer).[41, 42]

Table S3. Comparative polymerization experiments for catalyst precursor **1** and **2**.

Exp. #	Catalyst	$C_{11}{}^{=}OH$ [b]	BHT:MAO	Activity	M_n[c] (PDI)	T_m[e]
	t	com.:cat	molar ratio	10^6 g/ (mol (cat)·h)	kg/mol	°C

1	**2**	0	n.a.[f]	2.04	18.1 (6.9)	133.2
Comp. 1	**1**	0	n.a.[f]	1.98	7.3 (5.4)	131.1
2[d]	**2**	0	n.a.[f]	2.45	4.9 (4.8)	129.3
3	**2**	500	n.a.[f]	2.18	21.4 (5.8)	131.2
Comp. 3	**1**	500	n.a.[f]	1.86	19.3 (3.4)	130.5
4	**2**	1000	n.a.[f]	1.80	16.9 (3.6)	129.6
Comp.4	**1**	1000	n.a.[f]	2.11	11.1 (4.8)	128.4
5	**2**	2000	n.a.[f]	2.35	13.3 (4.7)	127.9
Comp. 5	**1**	2000	n.a.[f]	2.21	18.6 (7.8)	128.1
7	**2**	2000	0.2	1.60	17.9 (3.8)	128.3

Comp. 7	**1**	2000	0.2	1.73	18.9 (4.5)	127.8
8	**2**	2000	0.4	1.93	76.3 (3.1)	128.1
9	**2**	2000	0.4	1.74	73.6 (3.2)	128.1
10	**2**	2000	0.6	0.93	72.2 (2.8)	126.7
11	**2**	2000	0.8	1.10	83.0 (2.7)	127.1
12	**2**	2000	1	1.03	87.3 (3.9)	125.9
Comp. 12	**1**	2000	1	1.10	96.2 (3.5)	126.1
13	**2**	2000	2	0.84	p.s.[g]	126.5

a) Conditions: reaction performed in 300 mL Büchi reactors, 150 mL PMH, $C_2^=$: 2.5 bar, [MAO]/[Cat]: 1100 eq., T : 40 °C, reaction time: 15 min, cat = 3.1 μmol. b) 10-undecen-1-ol premixed with TiBA (TiBA/com. = 1.0). c) Determined by HT-SEC in o-DCB at 150

°C. d) Extra amount of TiBA was added (1.0 M solution in toluene, 2 mL). e) Determined by DSC. f) Not applicable. g) Poor solubility.

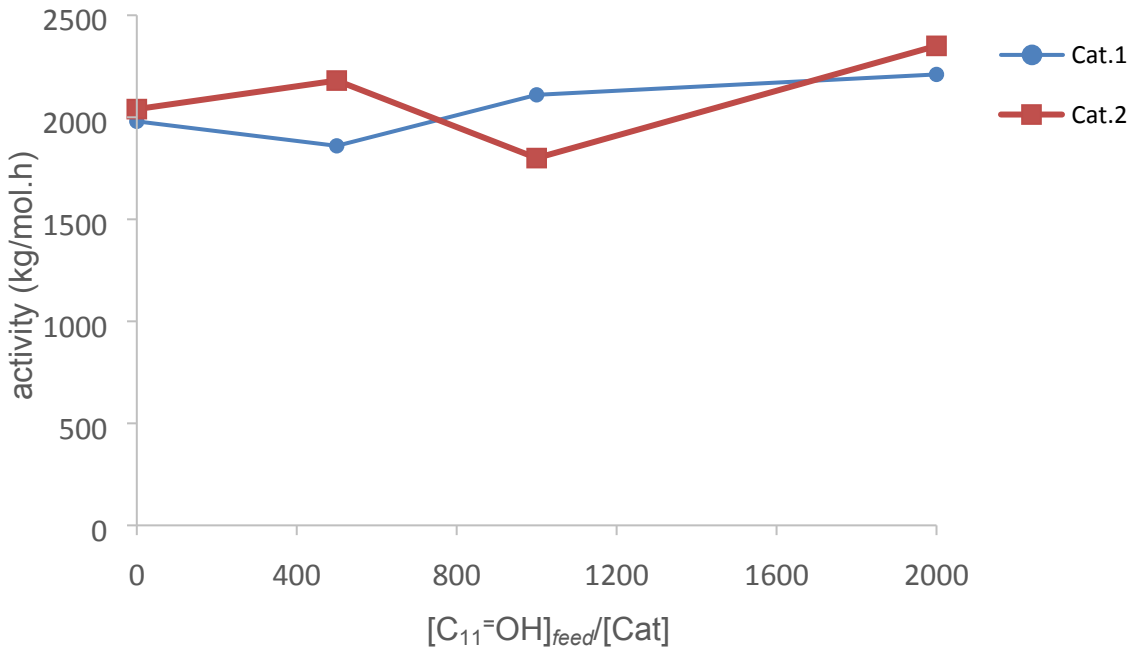

Figure S5. Ethylene/10-undecen-1-ol copolymerization catalyzed by **1** and **2** under identical conditions: catalytic activity versus C_{11}=OH feed/cat ratio. Conditions provided in Table S3.

Figure S6. Toluene solutions of both $[C_5Me_4CH_2CH_2NMe_2]TiCl_2$ (**1**) and $[C_5Me_4CH_2CH_2NMe_2]TiCl_3$ (**2**) activated with MAO.

cs-2019-01174y

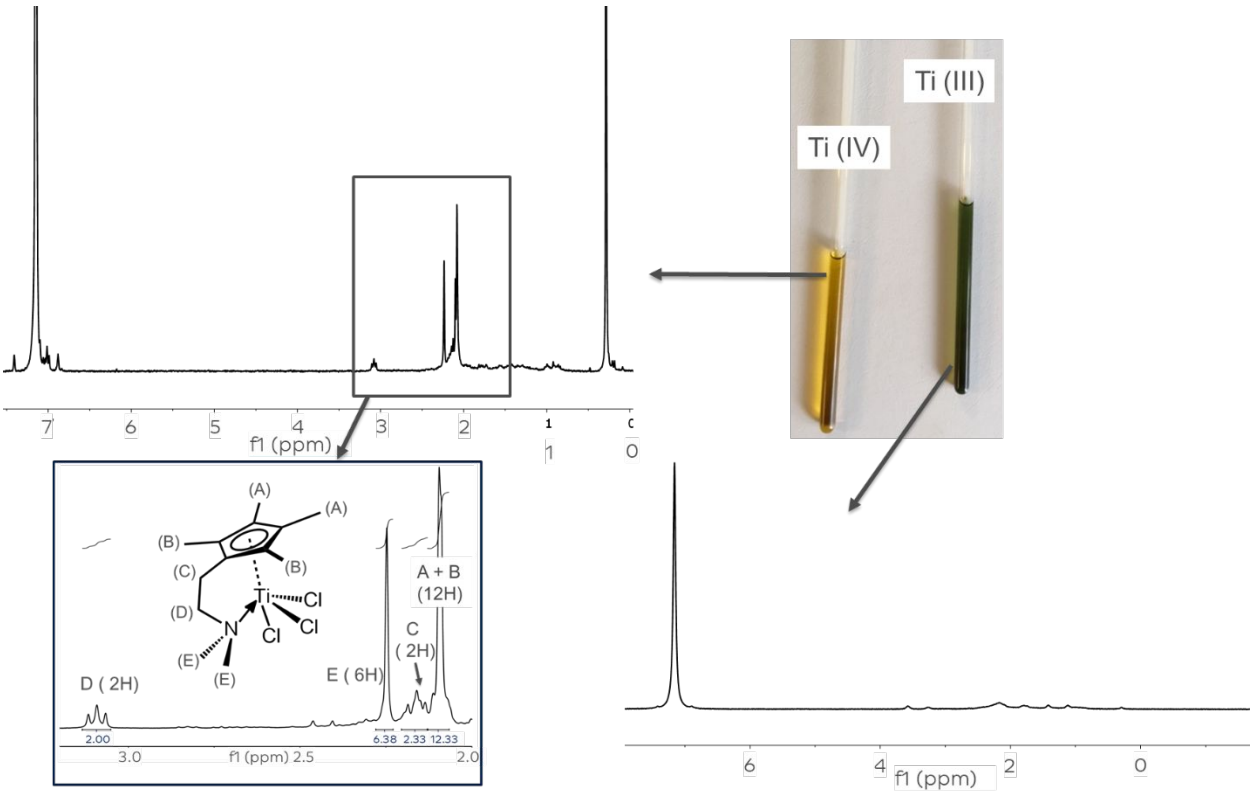

Figure S7. ^{1}H NMR spectra (benzene-d_6) of the yellow $[C_5Me_4CH_2CH_2NMe_2]TiCl_3$ (**2**) and the green $[C_5Me_4CH_2CH_2NMe_2]TiCl_2$ (**1**).

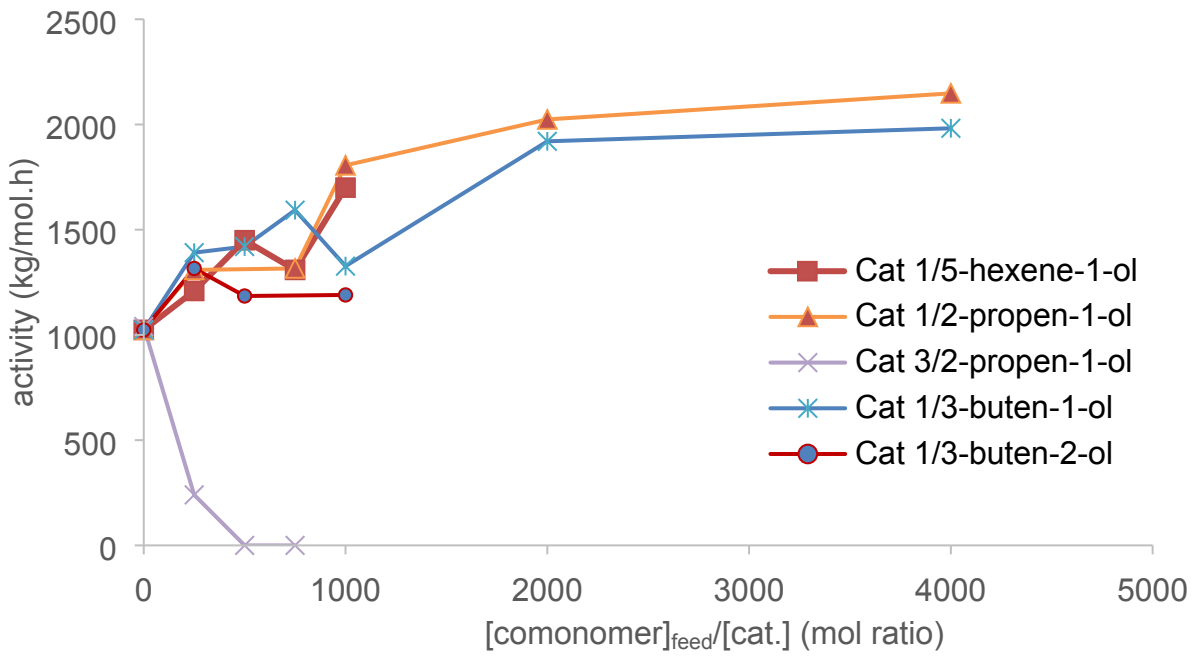

Figure S8. Catalytic activity of 1 and 3 in ethylene copolymerization with various hydroxyl functionalized α-olefins (3-buten-2-ol,5-hexene-1-ol,3-buten-1-ol,2-propen-1-ol). Reaction conditions provided in Table 3.

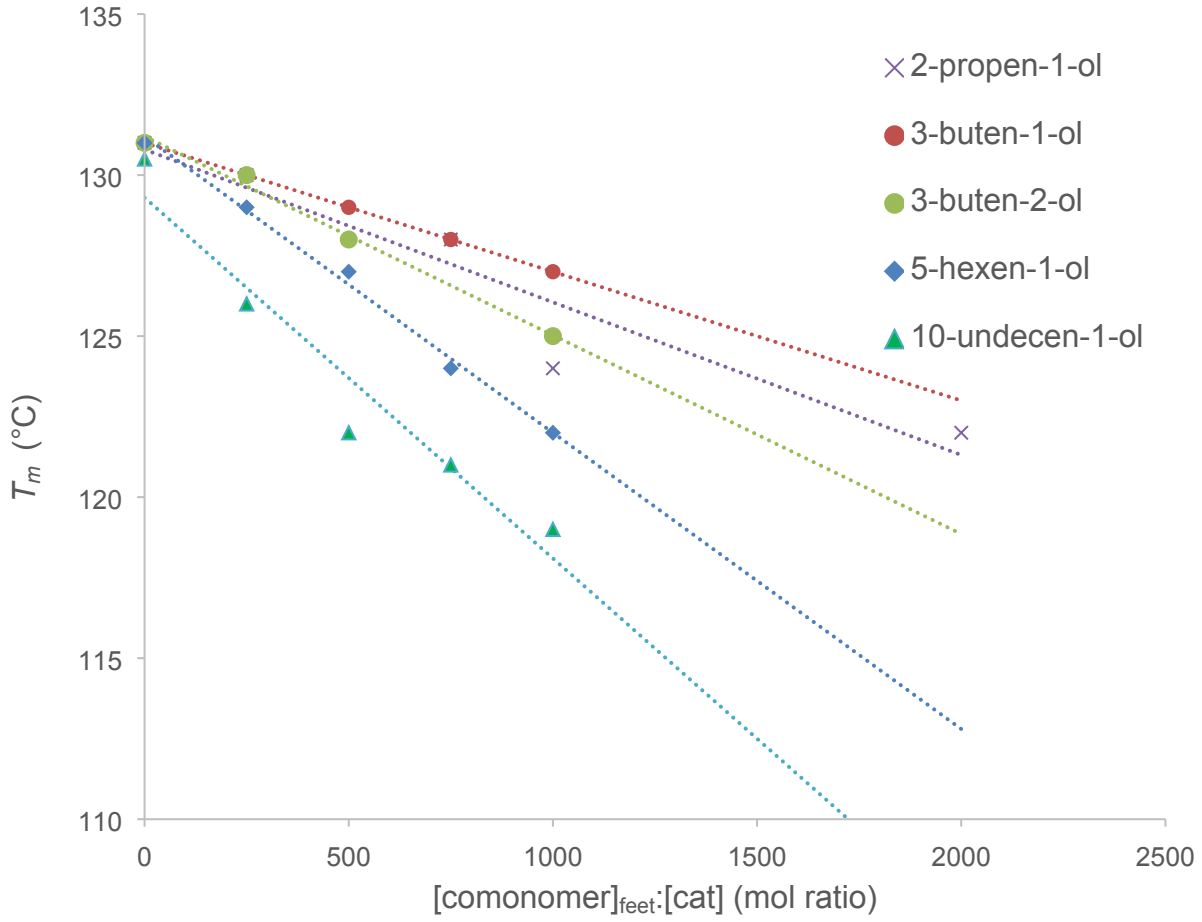

Figure S9. Correlation between melting temperature and comonomer concentration in the feed for ethylene – $C_x^{=}OH$ copolymerization using **1** where $C_x^{=}OH$ = 10-undecen-1-ol, 5-hexen-1-ol, 3-buten-1-ol, 3-buten-2-ol and 2-propen-1-ol. The low molecular weight of the polymers enhances the effect on the melting point of the polymers.

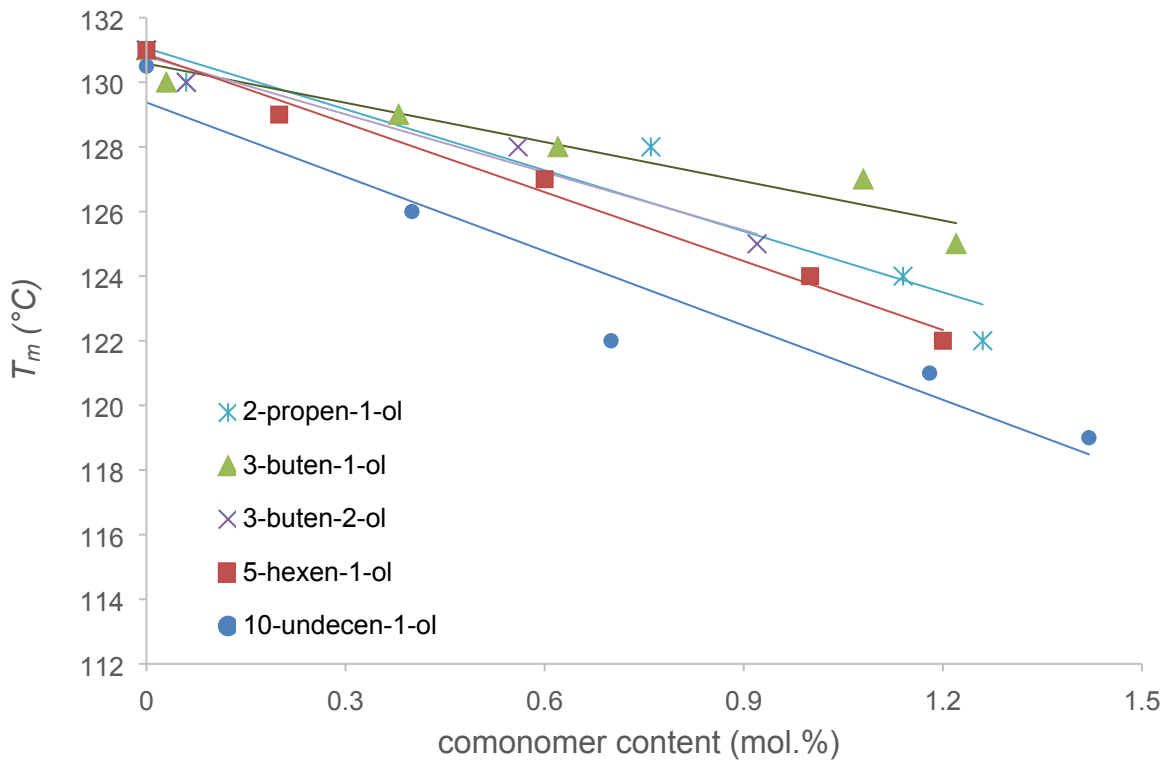

Figure S10. Correlation between copolymer melting temperatures and comonomer incorporation levels in ethylene copolymerization with hydroxyl functionalized alpha-olefins using **1**/MAO. The low molecular weight of the polymers enhances the effect on the melting point of the polymers.

Table S4. Ethylene polymerization in the absence and presence of $BuOAliBu_2$.[a]

Experiment	$BuOAliBu_2$[b]	Activity	M_n ($Đ$)[c]
	[Al]:[cat]	10^6 g/(mol (cat)·h)	kg/mol
1	0	2.12	23.51 (3.9)
2	500	2.15	4.1 (3.3)
3	1000	1.96	3.6 (2.7)

a) Conditions: reaction performed in 300 mL Büchi reactors, 150 mL PMH, $C_2^=$: 2.5 bar, [MAO]/[Cat]: 1100 eq., T : 40 °C, reaction time: 15 min, cat = 3.1 μmol. b) 1-butanol premixed with TiBA (TiBA/com. = 1.1). c) Determined by HT-SEC in o-DCB at 150 °C.

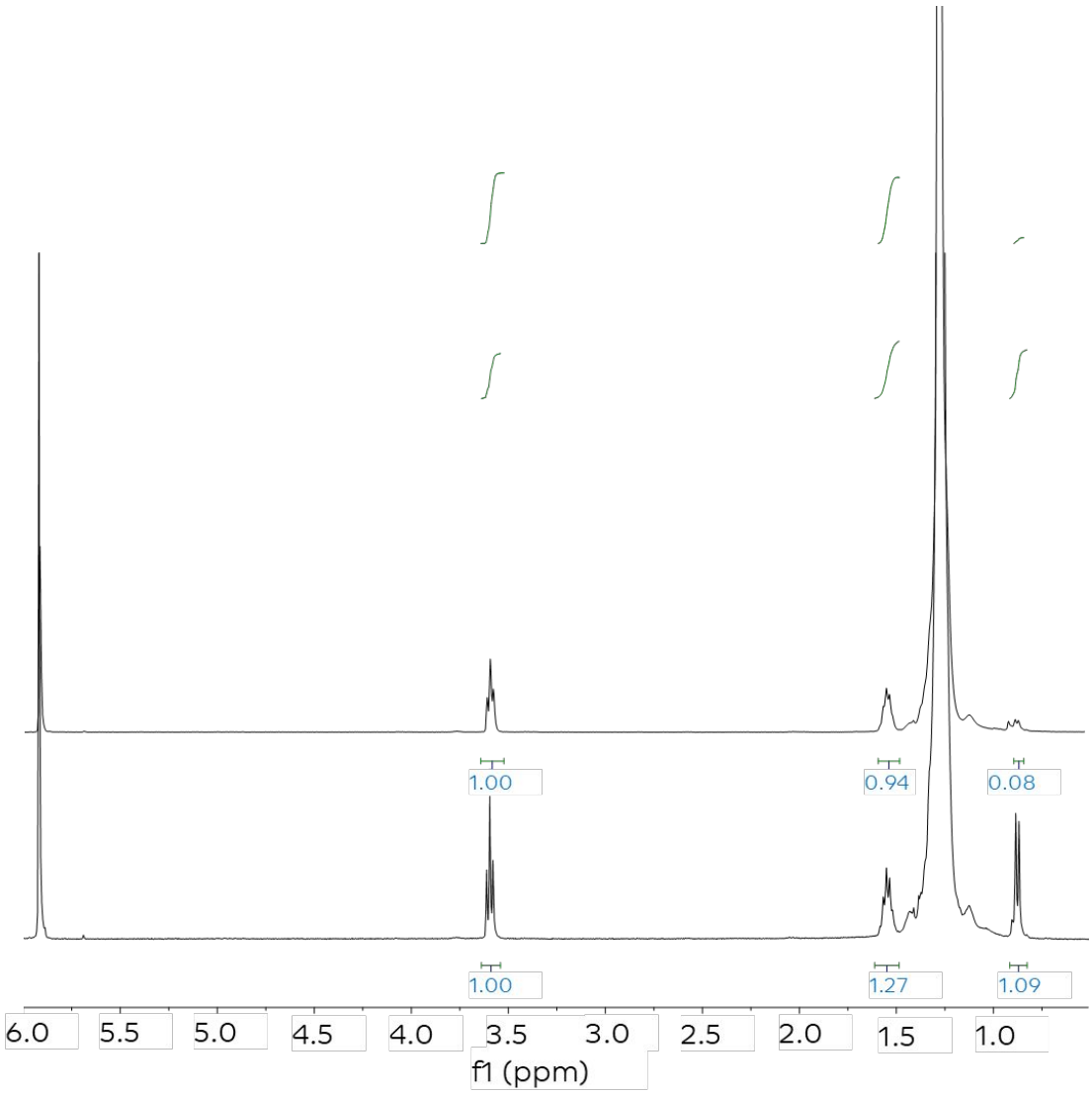

Figure S11. ^{1}H NMR spectrum of poly(ethylene-*co*-10-undecen-1-ol) copolymers prepared using **1**. Bottom: **1**:MAO:TiBA:$C_{11}^{=}$OH = 1:700:1900:500. Top: **1**:MAO:TiBA:$C_{11}^{=}$OH:BHT = 1:700:1900:500:630. Conditions: reactions performed in 300 mL Büchi reactor using PMH, $C_2^{=}$ = 2.5 bar, temperature 40 °C, reaction time 15 min, cat. 8 μmol.

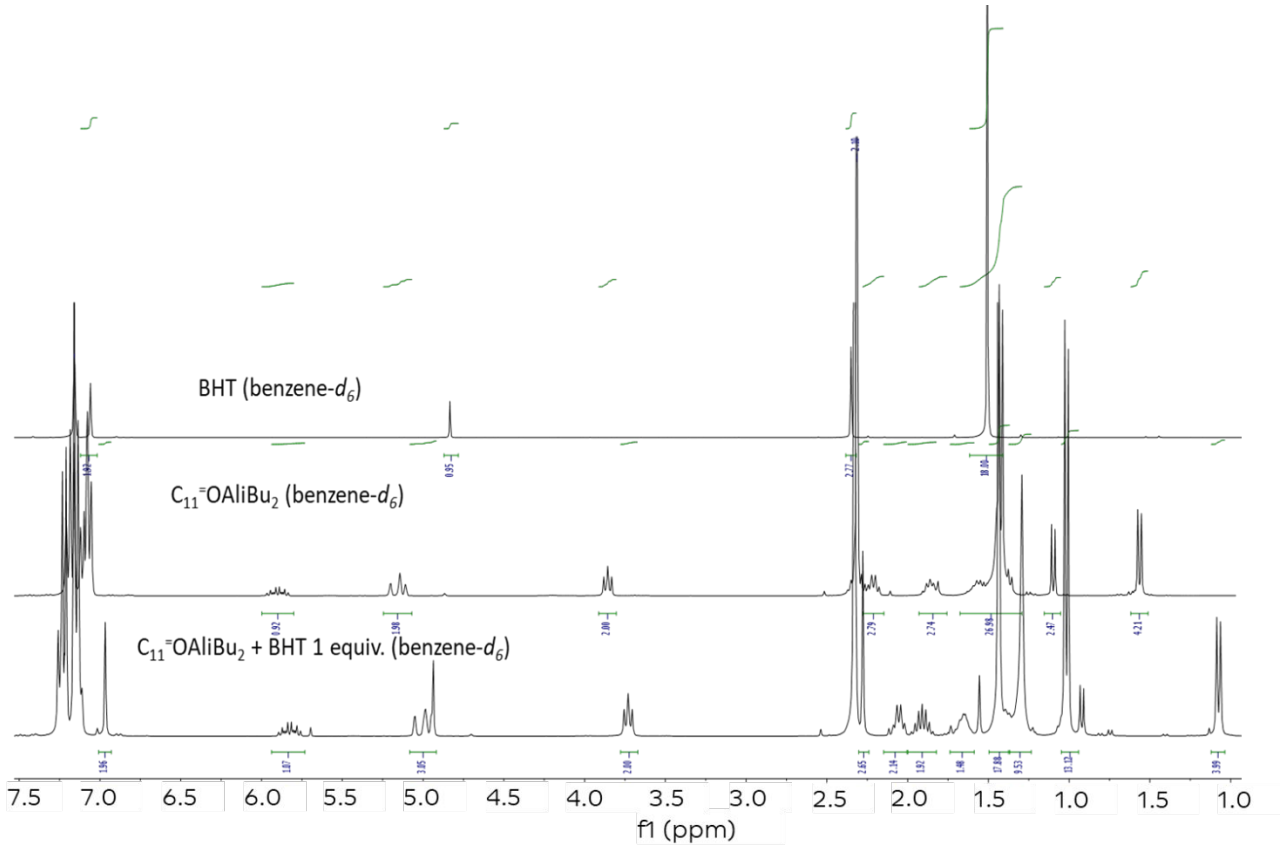

Figure S12. ^{1}H NMR spectrum of BHT in benzene-d_6 (top) and $C_{11}^{=}OH$:TiBA solution in toluene (1:1 molar ratio) + BHT (1 mol equiv.) in benzene-d_6 (bottom).