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DFT probe and visualization of the mechanisms of BF_3-catalyzed cationic oligomerization of olefins

Pavel V. Ivchenko, Dmitry A. Pyatakov, Alexander N. Tavtorkin and Ilya E. Nifant'ev

Supporting Information

S1. Materials and methods

S1.1. Materials

Isobutylene, BF_3 (Voessen, Moscow, Russian Federation) and undec-10-enoic acid (Shanghai Macklin Biochemical Co., Shanghai, China) were used as purchased. Dec-1-ene and Pr^i_2O (Merck, Darmstadt, Germany) were refluxed over sodium (4 h) and distilled. MeOH was purified by distillation over freshly prepared $Mg(OMe)_2$.

Preparation of methyl undec-10-enoate.

A mixture of MeOH (125 mL, 3.0 mol), undec-10-enoic acid (55 g, 0.3 mol) and H_2SO_4 (1 mL) was refluxed for 4 h, cooled and evaporated under reduced pressure. Petroleum ether (100 mL) and water (100 mL) were added, the organic phase was separated, washed with water (20 mL), 5% aq. $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was distilled *in vacuo* (*B. p.* 113 °C, 3.2 Torr). The yield was 51.3 g (86%). ^{1}H NMR ($CDCl_3$, 20 °C, 400 MHz) δ: 5.73–5.83 (m, 1H); 4.96 (d, ^3J = 17.1 Hz, 1H); 4.90 (d, ^3J = 10.1 Hz, 1H); 3.64 (s, 3H); 2.28 (t, ^3J = 7.5 Hz, 2H); 2.01 (q, ^3J = 6.9 Hz, 2H); 1.58–1.62 (m, 2H); 1.27–1.37 (m, 10H). ^{13}C NMR ($CDCl_3$, 20 °C, 101 MHz) δ: 174.34; 139.26; 114.26; 51.43; 34.12; 33.87; 29.31; 29.21; 29.14; 29.06; 28.96; 25.01.

S1.2. Analysis and methods

The ^{1}H and NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400 MHz, Bruker, Billerica, MS, USA) at 20 °C. The chemical shifts are reported relative to the solvent residual peak (δ = 7.26 ppm for $CDCl_3$).

Size exclusion chromatography (SEC) was performed using an Agilent PL-GPC 220 chromatograph (Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with a PLgel column, and THF was used as the eluent (1 mL/min). The measurements were recorded with universal calibration based on a polystyrene standard at 40 °C.

DFT calculations: geometry optimizations, vibrational frequency analysis, transition state (TS) search, and scan along intrinsic reaction coordinates (IRC) were carried out using PRIRODA-06 program (*T* = 298.15 K, gas phase, PBE functional, 3ζ basis set, D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151). The IRC was calculated for each obtained TS to verify the presence of this TS on the potential energy surface (PES).

S2. Oligomerization and oligomer characterization

S2.1. Oligomerization experiments

Preparation of the BF_3/Pr^iOH adducts.

The BF_3/^{i}PrOH adducts were prepared by passing the BF_3 into a cooled (–20 °C) Schlenk vessel containing calculated amount of Pr^iOH with a control of the weight increase to the specified value.

Oligomerization of isobutylene **1**.

Oligomerization experiments were conducted in stainless steel reactor equipped with a pressure sensor. Isobutylene **1** (2.11 g) was dissolved in *n*-hexane (3.4 mL) at –10 °C. The resulting solution ([**1**] = 5.2 M) was cooled with stirring to the given temperature. Calculated amounts of the adduct of $BF_3{\cdot}Pr^iOH$, BF_3 (optionally) and R_2O were dissolved in minimal amount of CH_2Cl_2 and introduced into the reaction mixture. The mixture was stirred within the given time, the reactor was vented, H_2O (20 mL) was added. The organic phase was separated and analyzed by ^1H NMR spectroscopy and SEC.

Oligomerization of dec-1-ene **2**

For dec-1-ene **2** oligomerization, the method of J. Wang (*Chin. J. Chem. Eng.*, 2019, **27**, 2687) was used. Oligomerization experiments were conducted in stainless steel reactor. Dec-1-ene **2** (7.01 g, 50 mmol) was placed into the reactor. Calculated amounts of the adduct of $BF_3{\cdot}Pr^iOH$ and BF_3 (optionally) were dissolved in minimal amount of CH_2Cl_2 and introduced into the reaction mixture. The mixture was stirred within 2 h at 30 °C, the reactor was vented, H_2O (20 mL) was added. The organic phase was separated and analyzed by GC. An attempt of the oligomerization of methyl undec-10-enoate was conducted under the same conditions, using BF_3/Pr^iOH ratio of 1:0.8.

S2.2. ^1H NMR spectrum of HRPIB P1 + P′1

The content of $>C=CH_2$ end-groups was determined by integration of the signals of methylidene $=CH_2$ (δ = 4.85 and 4.64 ppm) and methine =CH (δ = 5.15 ppm) protons. ^1H NMR spectrum of the PIB oligomers (Table 1, entry 6, mail text) is presented in Figure S1, the $>C=CH_2$ end-group content is 91.0%.

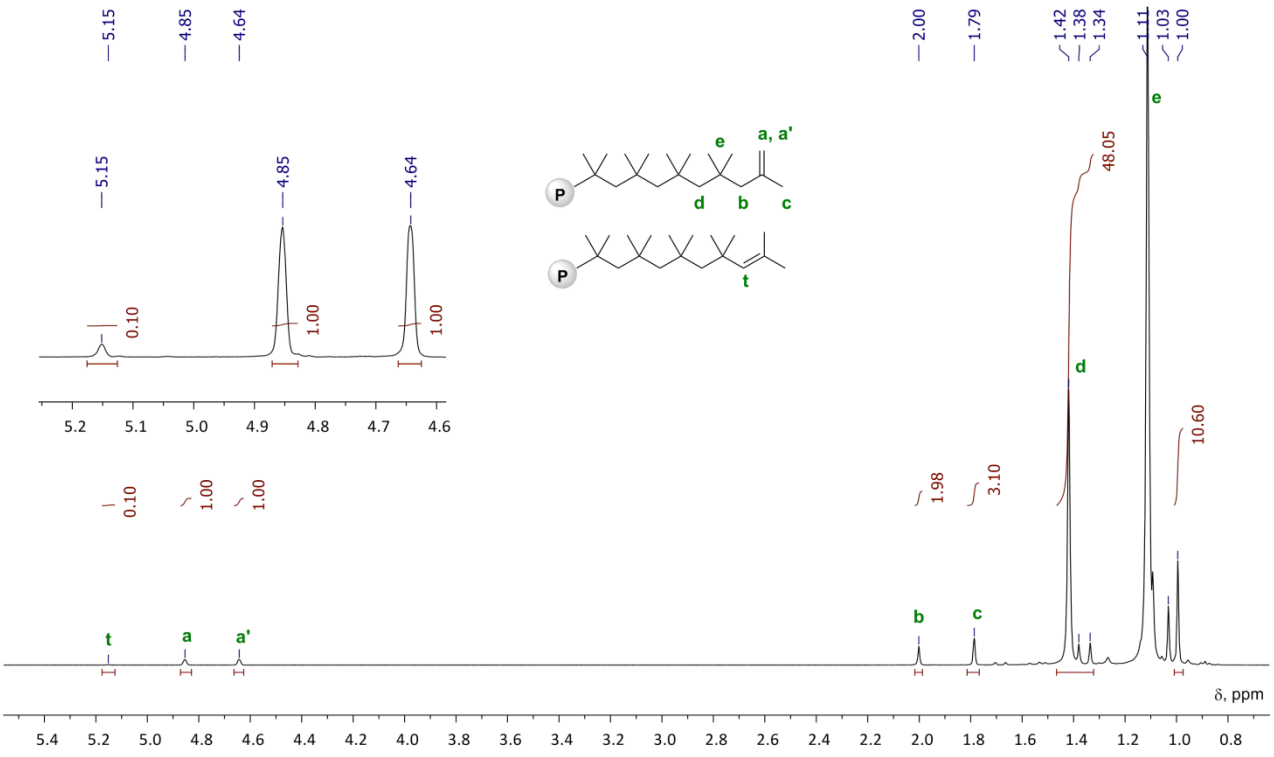


Figure S1. ^1H NMR spectrum ($CDCl_3$, 20 °C, 400 MHz) of the PIB oligomers

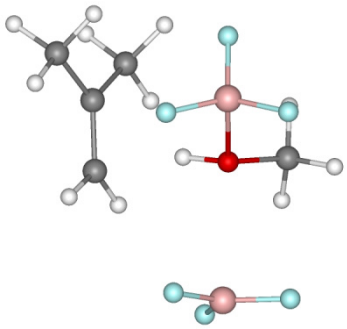
S3. DFT calculations

Geometry optimizations, vibrational frequency analysis, transition state (TS) search, and scan along intrinsic reaction coordinates (IRC) were carried out using PRIRODA-06 program (T = 298.15 K, gas phase, PBE functional, 3ζ basis set, D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151). The IRC was calculated for each obtained TS to verify the presence of this TS on the potential energy surface (PES).

S3.1. Polymerization of IB and C4 mediated by $(BF_3)_2$MeOH

The energy parameters, molecular structures and cartesian coordinates of the complex between IB and (BF_3)MeOH, as well as the TS of protonation and the ion pair formed, are presented below.

1+$(BF_3)_2$MeOH complex



E = –921.481887 E_0 = –921.298997
ZPVE = 0.182890 a.u. = 114.7652 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6964	42.1218	0.8887	1.4812	-11.0774
rotational	14.7933	32.3783	0.8887	0.8887	-8.7649
vibrational	18.0528	67.6282	124.2324	124.2324	104.0691
total	51.5425	142.1283	126.0099	126.6024	84.2268

Cartesian

5	-2.55947065	-0.22082864	-1.41849291	1	0.03816889	0.15559095	0.26745501
5	1.17929888	0.69274217	-1.56203270	6	1.70642304	0.05420263	2.88175178
9	2.38786316	0.51474798	-0.90934849	6	0.82588398	1.09295869	2.24127865
9	0.64477855	1.95007801	-1.43322694	6	1.49660349	2.38605189	1.87105441
9	1.11629736	0.12753803	-2.80732918	6	-0.48784795	0.87607032	2.01410508
8	0.08547240	-0.24101301	-0.66110450	1	2.34014487	2.20197582	1.18918157
9	-2.80619764	-0.72694695	-0.20769066	1	0.80594963	3.08453870	1.38552201
9	-2.66356754	1.08325672	-1.61824787	1	1.91212535	2.86349559	2.77276683
9	-2.29873753	-1.04609454	-2.42418623	1	-1.12059331	1.65220630	1.58045173
6	0.43956834	-1.65768421	-0.55667591	1	-0.97951210	-0.04503106	2.33433700
1	1.44345319	-1.76059961	-0.12886474	1	1.15786529	-0.86445665	3.12525010
1	-0.31447646	-2.15286779	0.06423366	1	2.55168986	-0.19456884	2.22114587
1	0.41565660	-2.05288768	-1.57532513	1	2.14747024	0.45153964	3.80936623

TS 1+$(BF_3)_2$MeOH

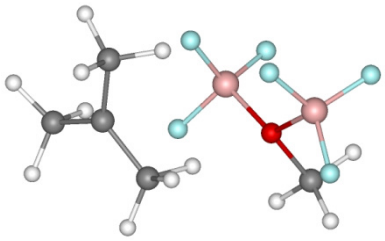
E = –921.466380 E_0 = –921.286440
ZPVE = 0.179939 a.u. = 112.9136 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6964	42.1218	0.8887	1.4812	-11.0774
rotational	14.4953	31.7861	0.8887	0.8887	-8.5883
vibrational	15.1662	60.8742	122.0775	122.0775	103.9278
total	48.3579	134.7822	123.8549	124.4474	84.2621

Cartesian

5	-1.80877244	0.19256420	-1.67401528	1	-0.41124302	-0.42429239	0.27415776
5	1.09876966	-0.45743209	-1.60236549	6	1.85600233	0.46504852	1.95846272
9	1.82644713	-1.33295918	-0.79056251	6	0.45403147	0.81122029	1.62945318
9	1.29458463	0.86117405	-1.22579324	6	0.13273004	2.23507214	1.37377667
9	1.20447648	-0.71437597	-2.93929172	6	-0.52805847	-0.18131749	1.48940194
8	-0.47641847	-0.77919871	-1.17635131	1	0.96547657	2.74852967	0.87625724
9	-2.81506705	-0.27133307	-0.83702916	1	-0.79082632	2.35715199	0.79802835
9	-1.41442394	1.47450840	-1.38063419	1	0.00040577	2.71896696	2.36029339
9	-1.98339546	-0.10061340	-2.99429464	1	-1.57475626	0.14240131	1.48624158
6	-0.79408079	-2.20210552	-1.36049008	1	-0.32606140	-1.15460706	1.94692683
1	-0.00620691	-2.79127240	-0.88339931	1	1.96827483	-0.54086101	2.37474775
1	-1.77012503	-2.38861895	-0.90428698	1	2.42709780	0.51364022	1.01329041
1	-0.82794172	-2.40176463	-2.43638015	1	2.29908037	1.22047448	2.62385345

Bu^t-cat $(BF_3)_2$OMe-anion ion pair



E = –921.467319 E_0 = –921.286131
ZPVE = 0.181189 a.u. = 113.6976 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6964	42.1218	0.8887	1.4812	-11.0774
rotational	14.5028	31.8011	0.8887	0.8887	-8.5928
vibrational	16.2560	64.6818	123.3510	123.3510	104.0661
total	49.4552	138.6047	125.1285	125.7210	84.3960

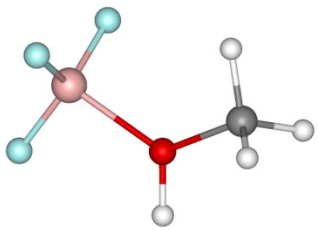
Cartesian

5	-1.48216009	0.34883657	-1.13467979	1	-0.17198928	-0.12222998	1.10145879
5	1.34437788	-0.15355287	-1.00612187	6	2.25220990	0.79536676	2.44975948
9	2.06009722	-0.98588228	-0.10093010	6	0.89298177	1.24230349	2.14851093
9	1.44957936	1.17510295	-0.58023536	6	0.63203889	2.63784671	1.78068924
9	1.72257233	-0.35638207	-2.30962992	6	-0.19724092	0.29257834	2.15872598
8	-0.16660070	-0.58007240	-0.81777018	1	1.53499937	3.18153214	1.48734951
9	-2.51401901	-0.32457250	-0.48270613	1	-0.15485464	2.69646096	1.01416767
9	-1.23016000	1.58294928	-0.54042077	1	0.21513212	3.11530662	2.69270587
9	-1.62186337	0.39708233	-2.49976301	1	-1.19252741	0.74522221	2.23037004
6	-0.38128844	-1.96395671	-1.25414824	1	-0.04533508	-0.56864315	2.81808949
1	0.43024611	-2.57391000	-0.84716892	1	2.28825212	0.00076898	3.20526433
1	-1.34941995	-2.28710198	-0.86386716	1	2.57596850	0.30791044	1.49613023
1	-0.37512493	-1.99303818	-2.34911799	1	2.94843841	1.61408865	2.65871263

S3.2. Dimerization of HBF_3OMe

Geometry optimization for the model complex between BF_3 and MeOH has resulted in a structure with two imaginary vibrational frequencies. We assumed that the complex would undergo spontaneous dimerization due to hydrogen bonding. Indeed, the optimized structure of the dimer $[HBF_3OMe]_2$ has no imaginary frequencies, and its Gibbs free energy is 10.6 kcal·mol^{-1} lower than that of two isolated HBF_3OMe molecules. The dimer is formed by two intermolecular hydrogen bonds OH···F (1.599 Å) and it represents an 8-membered cycle. The energy parameters, molecular structures and cartesian coordinates of HBF_3OMe and its dimer are presented below.

BF_3·MeOH



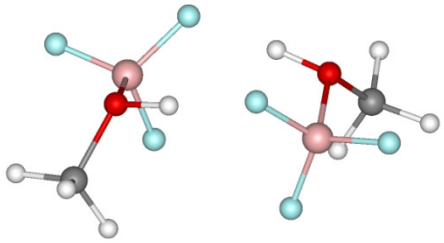
E = –440.024146 E_0 = –439.961027
ZPVE = 0.063119 a.u. = 39.6079 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	17.4865	39.7175	0.8887	1.4812	-10.3605
rotational	12.0048	26.8370	0.8887	0.8887	-7.1127
vibrational	2.7152	12.8118	41.8190	41.8190	37.9992
total	32.2065	79.3662	43.5965	44.1890	20.5259

Cartesian

8	-0.40824643	-0.08594967	-0.38974097	9	1.98735476	0.38345501	-0.46545076
6	-0.95595938	0.76128864	0.64593798	1	-1.02175820	-0.29941556	-1.11097109
5	1.21261346	-0.74017656	-0.45546466	1	-0.14977929	0.90371293	1.37090588
9	1.11427939	-1.42970204	-1.63389492	1	-1.25174427	1.72941995	0.22303438
9	1.28001094	-1.48472905	0.68648177	1	-1.80677104	0.26409632	1.12816226

$(BF_3 \cdot MeOH)_2$



E = –880.088129 E_0 = –879.956484
ZPVE = 0.131645 a.u. = 82.6088 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.5262	41.7836	0.8887	1.4812	-10.9766
rotational	14.1806	31.1607	0.8887	0.8887	-8.4018
vibrational	13.1868	51.8064	90.2418	90.2418	74.7957
total	45.8936	124.7507	92.0193	92.6118	55.4173

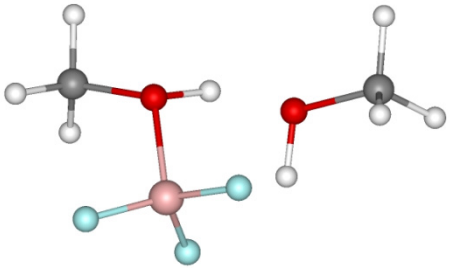
Cartesian

8	-0.99982220	0.48398557	0.09898165	9	-0.64868158	2.84529877	-0.93469757
6	-1.37437141	-0.52949381	-0.89115220	5	0.63860929	3.04186463	-1.52599943
5	0.30937433	0.16163050	0.97936833	9	0.76359332	4.23672724	-2.16800332
9	0.63028520	1.44999528	1.51146674	9	1.01624906	1.93424511	-2.25708055
9	1.29931593	-0.27621588	0.12410852	8	1.58912992	3.12726641	-0.22933532
9	-0.08222827	-0.73396325	1.92806554	1	1.28106606	2.48192883	0.47921282
1	-0.91625488	1.38280475	-0.34639278	6	3.02393198	2.95309520	-0.47190019
1	-1.51107275	-1.46305740	-0.33877251	1	3.30808496	3.71975946	-1.19771767
1	-2.31810403	-0.21021664	-1.34340787	1	3.53778338	3.11734557	0.47996631
1	-0.58206391	-0.62712473	-1.64100850	1	3.21527481	1.94843590	-0.86384946

S3.3. Complexation between HBF_3OMe and the model ethers or alkenes

The energy parameters, molecular structures and cartesian coordinates of the complexes of HBF_3OMe with the model ethers and alkenes are presented below.

$BF_3 \cdot MeOH$-MeOH complex



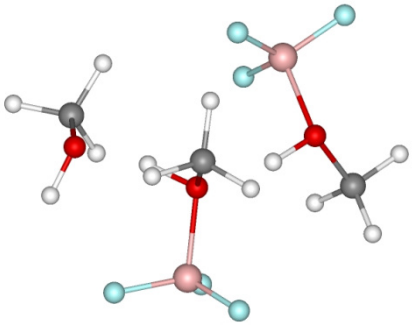
E = –555.685175 E_0 = –555.568087
ZPVE = 0.117087 a.u. = 73.4734 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	17.9031	40.5454	0.8887	1.4812	-10.6074
rotational	13.0583	28.9304	0.8887	0.8887	-7.7369
vibrational	8.4187	33.9597	78.6105	78.6105	68.4855
total	39.3801	103.4355	80.3880	80.9805	50.1412

Cartesian

1	-0.43938750	0.58291173	0.42485565	9	1.46205974	-0.72210431	2.67257071
1	0.17227589	-0.30158260	-1.15068245	9	1.54179907	-0.81198812	0.34913605
8	-0.62830186	0.26048127	-1.08476317	9	-0.24456947	-1.76471400	1.46741712
6	-1.78336978	-0.57103449	-1.36880004	8	-0.09950724	0.59514022	1.40265715
1	-1.74151838	-0.93015563	-2.40588546	6	0.67117029	1.81267607	1.62845778
1	-1.83706713	-1.42005944	-0.67302567	1	1.03959441	1.76761246	2.65616679
1	-2.66448665	0.06713657	-1.24490368	1	-0.00381017	2.66537738	1.49929261
5	0.73941088	-0.79787809	1.51029408	1	1.51271451	1.86890960	0.92572582

$(BF_3 \cdot MeOH)_2$-MeOH complex



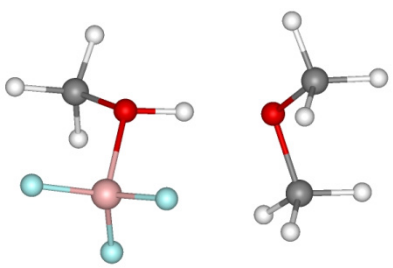
E = –995.731957 E_0 = –995.549388
ZPVE = 0.182569 a.u. = 114.5638 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.7490	42.2263	0.8887	1.4812	-11.1085
rotational	14.7822	32.3563	0.8887	0.8887	-8.7583
vibrational	21.0634	77.5876	125.2168	125.2168	102.0840
total	54.5945	152.1702	126.9942	127.5867	82.2172

Cartesian

1	-0.96227688	0.87699527	1.97807789	1	-2.90378952	-0.10725585	3.89873958
1	0.36413735	0.35323453	-1.83022821	1	-1.17082822	-0.58779454	3.81454015
8	-0.27791777	1.03245068	-1.54499757	1	-2.30534506	-1.06953847	2.49557853
6	-1.62292612	0.59998274	-1.90751719	1	0.00302630	1.15158272	-0.12825505
1	-1.70889580	0.56529486	-3.00068760	5	1.26522231	-0.25829130	0.93415362
1	-1.84991074	-0.37972578	-1.46779835	9	2.03272367	-0.15638949	2.06536126
1	-2.30631685	1.34837139	-1.49793541	9	1.98075044	-0.27511713	-0.25937167
5	-2.97523975	1.62668777	1.67600572	9	0.26319686	-1.21290803	0.98324680
9	-3.87960505	2.07913303	2.59965158	8	0.38378429	1.13710415	0.86974859
9	-3.45144510	0.60907203	0.86164492	6	1.10633922	2.39243793	1.10972512
9	-2.29607534	2.61333346	0.96700561	1	1.55169845	2.32140827	2.10480285
8	-1.76354003	0.96463263	2.56793618	1	0.37265387	3.20288587	1.06188726
6	-2.05575180	-0.30348808	3.23706698	1	1.88663101	2.51243520	0.34919226

$BF_3 \cdot MeOH$-OMe_2 complex



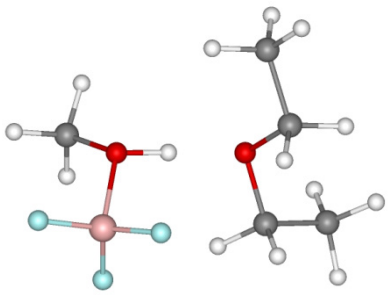
E = –594.941733 E_0 = –594.797790
ZPVE = 0.143942 a.u. = 90.3251 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.0544	40.8461	0.8887	1.4812	-10.6970
rotational	13.4057	29.6208	0.8887	0.8887	-7.9427
vibrational	10.5575	41.4401	96.4253	96.4253	84.0700
total	42.0176	111.9070	98.2028	98.7953	65.4302

Cartesian

1	-0.41637656	-0.43329826	-1.08211195	5	0.66963077	-1.67480361	0.34113362
6	0.20535336	-1.38251305	-3.26870489	9	0.78070718	-1.61186004	1.71033609
1	-0.07576668	-1.45923889	-4.32975721	9	1.88495529	-1.56079686	-0.32825601
1	1.13274205	-0.80903006	-3.16818786	9	-0.12083598	-2.70767021	-0.14498027
1	0.34426090	-2.38359594	-2.83451176	8	-0.18943781	-0.35298350	-0.07681964
8	-0.81821173	-0.65798116	-2.55117130	6	0.44351247	0.92559117	0.20557733
6	-2.07906055	-1.35781538	-2.58391237	1	0.58032632	0.97668159	1.28954232
1	-2.41637945	-1.46457446	-3.62592721	1	-0.23098767	1.72118855	-0.12958103
1	-1.98209786	-2.34725380	-2.11185050	1	1.41470921	0.99227244	-0.3008748
1	-2.79751420	-0.74733084	-2.02544951				

BF_3·MeOH-OEt_2 complex



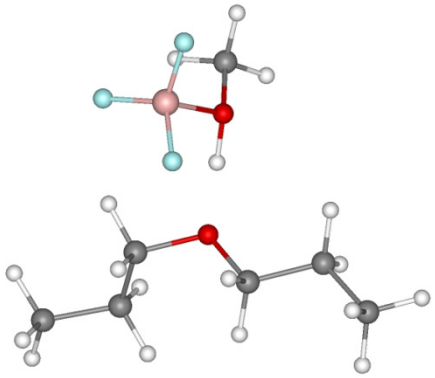
E = –673.492731 E_0 = –673.294066
ZPVE = 0.198665 a.u. = 124.6640 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.3178	41.3694	0.8887	1.4812	-10.8531
rotational	14.0957	30.9920	0.8887	0.8887	-8.3515
vibrational	14.5657	55.1704	132.4830	132.4830	116.0340
total	46.9791	127.5318	134.2605	134.8530	96.8294

Cartesian

6	0.56669736	-1.46135116	-0.72524434	1	-0.40609810	2.25651336	0.50800663
6	1.22622621	-1.04310977	-2.02958846	1	0.55081028	-0.46111557	-2.67073274
1	1.24769139	-2.07265353	-0.11867823	1	2.12933731	-0.44850865	-1.83773541
1	-0.34700647	-2.05283451	-0.89396572	1	1.51977599	-1.94277573	-2.58935857
8	0.23179954	-0.31709000	0.11630330	1	0.15990630	-0.74240690	1.57215083
6	-1.01671660	0.32545775	-0.26656139	5	-0.59758580	-2.53275871	2.58122087
1	-0.94741780	0.61695725	-1.32559013	9	-0.90022451	-2.77634931	3.90171695
1	-1.83288932	-0.40640977	-0.14943323	9	0.37738749	-3.38420510	2.06547952
6	-1.23390865	1.54238665	0.61235487	9	-1.69140446	-2.38748765	1.73890018
1	-2.16283774	2.04584312	0.31107408	8	0.05760770	-1.04447401	2.56275916
1	-1.33281028	1.25913632	1.66869438	6	1.31212509	-0.89424050	3.28016067
1	1.63142347	0.15037400	3.19391322	1	1.11085725	-1.14313591	4.32617998
1	2.07162690	-1.57280898	2.87125039				

BF_3·MeOH-OPr_2 complex



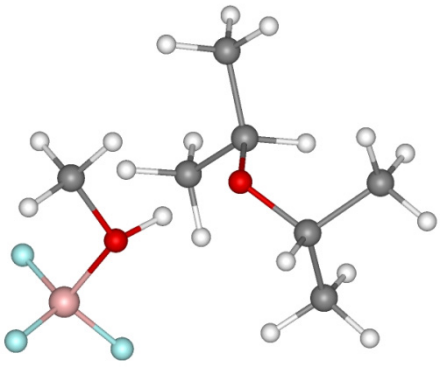
E = –752.034336 E_0 = –751.780235
ZPVE = 0.254101 a.u. = 159.4507 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.5417	41.8144	0.8887	1.4812	-10.9857
rotational	14.7866	32.3649	0.8887	0.8887	-8.7609
vibrational	17.8389	67.4300	168.9857	168.9857	148.8814
total	51.1672	141.6094	170.7631	171.3556	129.1348

Cartesian

6	0.51946789	-1.43994749	-0.09522546	1	2.08121133	-3.27312708	-1.48453736
6	1.12485099	-1.30716813	-1.48756909	1	0.46243727	-3.26176262	-2.21346712
1	1.19312155	-2.00049496	0.56825912	1	-2.33615494	3.59133530	0.88013071
1	-0.44280756	-1.97745645	-0.11666601	1	-2.37073398	2.72916389	-0.67015082
8	0.32172894	-0.14867589	0.55249894	1	-3.17666984	2.03467226	0.75513601
6	-0.92781949	0.49315095	0.17485017	1	0.37818831	-0.30391601	2.05730391
1	-0.96494418	0.56903678	-0.92365575	5	-0.36876929	-1.82019281	3.45302010
1	-1.76292562	-0.14169985	0.51683515	9	-0.54274797	-1.79611242	4.81872749
6	-0.99730766	1.87541103	0.80470812	9	0.49509540	-2.82387781	3.01894689
6	-2.29354000	2.59619093	0.41886035	9	-1.53644013	-1.74871838	2.70556021
1	-0.93877083	1.77901113	1.89974153	8	0.36468619	-0.41568139	3.09303451
1	-0.12418494	2.46238804	0.48018312	6	1.69374573	-0.23216856	3.64997745
1	0.45076162	-0.73292106	-2.14193845	1	1.58933127	-0.26667103	4.73838186
1	2.06279588	-0.73565149	-1.41273415	1	2.06241393	0.75062597	3.33565402
6	1.39182699	-2.68405795	-2.10646391	1	2.36578298	-1.03090405	3.31090307
1	1.84082150	-2.58498693	-3.10334039				

BF_3·MeOH-OPr^i_2 complex



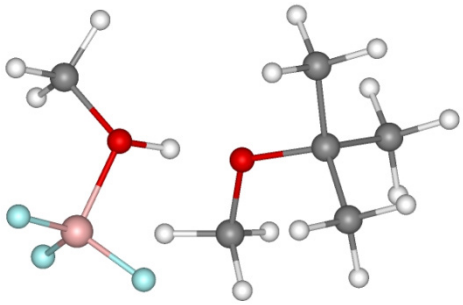
E = –752.038223 E_0 = –751.785605
ZPVE = 0.252619 a.u. = 158.5206 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.5417	41.8144	0.8887	1.4812	-10.9857
rotational	14.5314	31.8578	0.8887	0.8887	-8.6097
vibrational	16.9122	65.5864	168.0549	168.0549	148.5003
total	49.9853	139.2585	169.8323	170.4248	128.9049

Cartesian

6	0.76716125	-1.03996229	-0.66763383	1	2.05258846	3.15756893	1.30786109
6	0.46621552	-1.09688997	-2.16270757	1	-0.96105021	-2.19874954	0.01422978
1	1.85877287	-1.08207726	-0.53120565	1	0.51601267	-3.14182186	-0.24726263
6	0.13276111	-2.18107033	0.12390668	1	-0.61414063	-1.06989849	-2.36485672
8	0.43772089	0.25870180	-0.06703831	1	0.95452875	-0.26847216	-2.69069862
6	-0.95205116	0.72337478	-0.15909065	1	0.85357267	-2.04131985	-2.57049370
1	-1.55909574	-0.12427016	-0.51104450	1	-2.44700432	1.44816220	1.22939491
6	-1.40208161	1.10802639	1.24668610	1	-1.32390571	0.25658241	1.93511963
6	-1.06531894	1.87822843	-1.14891040	1	-0.78652382	1.93156922	1.63618374
1	-2.11496639	2.19699883	-1.22476161	1	1.63279688	1.21001709	-0.14749797
1	-0.46778801	2.74053216	-0.82270139	5	2.71347404	2.68286633	-1.42462575
1	-0.71824950	1.58947051	-2.14808416	9	4.04406929	3.04215288	-1.41552329
1	0.37948641	-2.10166240	1.19078338	9	1.85005796	3.75408959	-1.21376264
6	2.75565052	2.32766676	1.16036272	9	2.33206391	1.86799729	-2.47971582
1	3.78365588	2.70159578	1.16733825	8	2.54167318	1.70639706	-0.13484278
1	2.62492347	1.56052506	1.93168056				

BF_3·MeOH-OBu^{t}Me complex



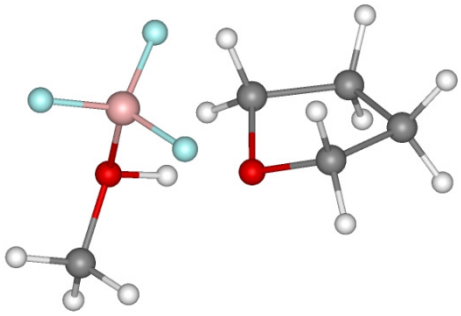
E = –712.764474 E_0 = –712.539386
ZPVE = 0.225088 a.u. = 141.2447 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.4339	41.6002	0.8887	1.4812	-10.9219
rotational	14.2554	31.3093	0.8887	0.8887	-8.4461
vibrational	15.1137	59.1078	149.9130	149.9130	132.2900
total	47.8029	132.0173	151.6905	152.2830	112.9220

Cartesian

6	-1.85228205	-0.63766241	-0.09523312	1	0.42921567	1.72918010	1.06477344
6	-0.63426453	0.28302526	-0.19654785	1	2.48822522	-0.90863150	-0.76744521
8	0.49674788	-0.65567797	-0.41024813	1	1.84386528	0.61441994	-1.42395008
6	-0.77256346	1.24029469	-1.38379407	1	2.11692309	0.43944824	0.35267714
6	-0.42007276	1.03546774	1.11942649	1	0.26601851	-1.72378743	-1.47418749
6	1.80823255	-0.07308866	-0.56827605	5	1.07420301	-2.15649652	-3.47635722
1	-2.75029469	-0.04493325	0.12163432	9	0.70126551	-3.08472228	-4.42299604
1	-1.71801805	-1.36783433	0.71480745	9	2.38525820	-2.31095672	-3.03046274
1	-2.02110600	-1.17559087	-1.03800666	9	0.75492507	-0.84162331	-3.78007364
1	0.06057374	1.95343018	-1.43675411	8	0.12871093	-2.46603918	-2.18853974
1	-1.69670618	1.82435119	-1.27383256	6	0.30304238	-3.77744651	-1.58581769
1	-0.81930906	0.68717945	-2.33099246	1	0.05946189	-4.51489830	-2.35592556
1	-1.31401122	1.63096833	1.34937525	1	-0.39493749	-3.86122465	-0.74536610
1	-0.25208282	0.33202550	1.94638538	1	1.33947062	-3.90997481	-1.25038123

BF_3·MeOH-THF complex



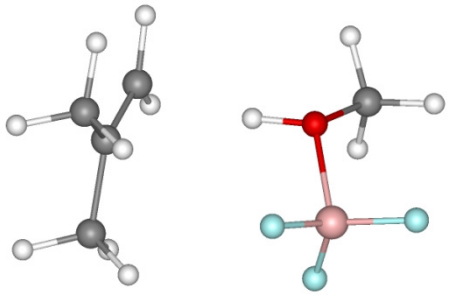
E = –440.024146 E_0 = –439.961027
ZPVE = 0.063119 a.u. = 39.6079 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	17.4865	39.7175	0.8887	1.4812	-10.3605
rotational	12.0048	26.8370	0.8887	0.8887	-7.1127
vibrational	2.7152	12.8118	41.8190	41.8190	37.9992
total	32.2065	79.3662	43.5965	44.1890	20.5259

Cartesian

6	0.28522941	1.65613639	0.50751787	1	-0.17618857	0.24991848	2.16806006
6	-0.06261185	1.38103926	-0.98300731	1	-0.42318267	-2.03612757	0.50653589
6	-0.24503087	-0.13965832	-1.05282319	5	1.31405199	-3.28411007	0.94113761
8	-0.60511911	-0.53223538	0.30511263	9	1.50563300	-4.64517164	0.87514216
6	0.26201782	0.27031523	1.16378236	9	1.50430536	-2.75199246	2.21471834
1	-0.46274230	2.31765223	0.96167350	9	1.95074368	-2.54709530	-0.04974847
1	1.26837397	2.12808657	0.62580001	8	-0.25756785	-3.05660534	0.59473825
1	0.72991806	1.71305001	-1.66502929	6	-1.19899821	-3.64095402	1.53609037
1	-0.98796606	1.89858055	-1.26453865	1	-1.02933431	-4.72142744	1.52354538
1	-1.06015933	-0.46896210	-1.70768762	1	-2.21266031	-3.41187000	1.18925786
1	0.68764466	-0.65515274	-1.33200693	1	-1.02831006	-3.24356437	2.54474497
1	1.26010716	-0.19363797	1.19017613				

BF_3·MeOH-1 complex



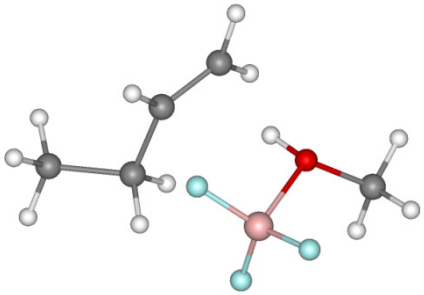
E = –597.099216 E_0 = –596.928675
ZPVE = 0.170541 a.u. = 107.0162 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.1540	41.0439	0.8887	1.4812	-10.7560
rotational	13.7436	30.2922	0.8887	0.8887	-8.1429
vibrational	12.7825	48.9154	114.0269	114.0269	99.4427
total	44.6800	120.2515	115.8043	116.3968	80.5438

Cartesian

5	-0.59111774	-0.47158462	4.27753782	6	-0.47172952	-1.21327400	0.07577350
9	-0.38025439	-1.03597093	5.51108932	6	1.14697015	0.55618376	0.77129364
9	-0.94132984	0.86827087	4.31433296	1	-1.03213060	-1.15796423	-0.87058562
9	-1.34609902	-1.22102511	3.39707613	1	0.42147484	-1.83032703	-0.08136912
8	0.91431874	-0.50590605	3.56830287	1	-1.12775457	-1.71450078	0.80347890
6	1.94323158	0.25847632	4.26531887	1	0.84017932	-0.16996416	2.62264276
1	2.04372168	-0.19607516	5.25413895	1	1.98425627	-0.11059402	0.55521816
1	2.87814116	0.16222908	3.70284033	1	1.38481092	1.57658541	1.07834947
1	1.63951433	1.30856180	4.35676479	1	-0.97188771	2.08200073	1.14075685
6	-1.29169381	1.09532690	0.78542000	1	-1.86214030	1.22255588	-0.14810161
6	-0.12943020	0.17025170	0.55499935	1	-1.98253798	0.66356492	1.52484274

BF_3·MeOH-4 complex



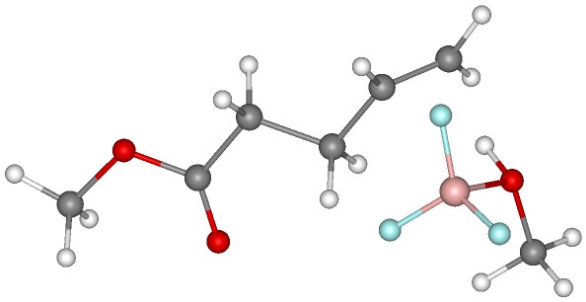
E = –597.091335 E_0 = –596.920053
ZPVE = 0.171282 a.u. = 107.4812 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.1540	41.0439	0.8887	1.4812	-10.7560
rotational	13.8834	30.5701	0.8887	0.8887	-8.2257
vibrational	13.3571	50.1089	114.5072	114.5072	99.5673
total	45.3945	121.7229	116.2847	116.8772	80.5855

Cartesian

5	-0.68791050	-0.83758754	2.01892495	1	-0.68530118	-0.82394105	-1.58670235
9	-0.42471445	-1.36560667	3.25696993	6	1.08289957	0.31530803	-1.55569232
9	-1.33868682	0.38630357	2.04839849	1	0.73928678	-0.21946773	0.45385239
9	-1.18407118	-1.71259379	1.07795930	1	1.73868299	-0.54438066	-1.70277727
8	0.83318478	-0.49969324	1.40965760	1	1.55579221	1.29900801	-1.49901450
6	1.58653021	0.51480329	2.13867617	1	-0.70770764	2.25926828	-1.27033913
1	1.71690822	0.12622510	3.15199661	6	-2.23106885	1.34941530	-2.53843570
1	2.55869794	0.63553077	1.64865911	1	-1.80463743	1.14811075	-0.42737699
1	1.02973497	1.45944095	2.16105342	1	-2.96572423	2.15188289	-2.38849783
6	-1.24005914	1.30003834	-1.36245751	1	-1.71201670	1.53324199	-3.48919749
6	-0.25431165	0.18050800	-1.50941622	1	-2.78186607	0.40262952	-2.62951827

BF_3·MeOH-5 complex (C=C binding)



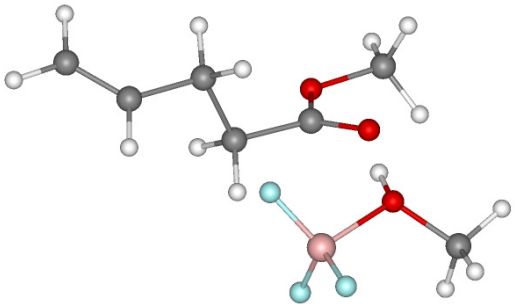
E = –824.810284 E_0 = –824.597334
ZPVE = 0.212950 a.u. = 133.6282 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6279	41.9858	0.8887	1.4812	-11.0368
rotational	15.1130	33.0136	0.8887	0.8887	-8.9543
vibrational	20.7967	74.2709	143.4503	143.4503	121.3064
total	54.5376	149.2703	145.2278	145.8203	101.3153

Cartesian

5	-0.30007359	-1.51473415	2.57355309	1	1.64287627	-1.11817837	-1.10298419
9	-0.00498396	-1.87106359	3.86374044	1	1.70606196	0.74477649	-1.11335039
9	-1.33448935	-0.59930807	2.45440650	1	-0.37385014	2.02115369	-0.72589397
9	-0.35274801	-2.53959227	1.65513003	6	-2.16497016	1.18771040	-1.62608230
8	1.06590915	-0.67966461	2.07635021	1	-1.44542444	1.16965771	0.39892888
6	1.35415375	0.54897147	2.81050301	6	-3.01449347	2.43530750	-1.46123862
1	1.48417604	0.25394040	3.85488129	1	-1.78907037	1.16625500	-2.66096592
1	2.28431749	0.97060889	2.41519332	1	-2.82202864	0.30989093	-1.52663100
1	0.52083671	1.25548112	2.71424985	8	-4.05717993	2.41942501	-2.33675671
6	-1.01256740	1.13360095	-0.61425698	8	-2.80797815	3.33495855	-0.66928542
6	-0.20494010	-0.12173314	-0.75938737	6	-4.92888021	3.57484150	-2.25879669
1	-0.75286466	-1.06471515	-0.65327787	1	-5.70336723	3.40271688	-3.01199675
6	1.11840737	-0.16830441	-0.99082619	1	-5.36963081	3.65396094	-1.25737834
1	0.95324159	-0.46747476	1.10674381	1	-4.36860752	4.49218178	-2.47846532

BF_3·MeOH-5 (C=O binding)



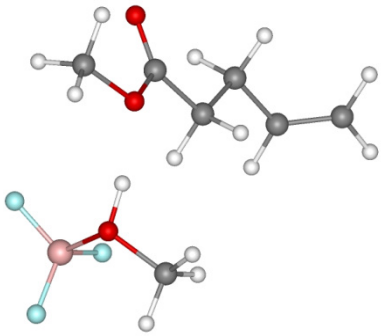
E = –824.822093 E_0 = –824.608388
ZPVE = 0.213705 a.u. = 134.1018 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6279	41.9858	0.8887	1.4812	-11.0368
rotational	14.9292	32.6483	0.8887	0.8887	-8.8454
vibrational	18.1908	67.9634	143.5873	143.5873	123.3240
total	51.7479	142.5976	145.3647	145.9572	103.4418

Cartesian

5	-1.49534869	0.70949638	2.74041152	1	1.80696356	-2.72407675	-1.59018075
9	-1.45226884	0.74292064	4.11526966	1	1.62788665	-1.32191420	-2.79924297
9	-2.59248543	0.01404030	2.22950149	1	0.47224107	0.71819377	-2.10870218
9	-0.30565578	0.35774297	2.12126851	6	-1.40571153	0.31530067	-1.06118619
8	-1.70662117	2.25467134	2.28325367	1	0.52167994	1.00816846	-0.34953883
6	-2.86123896	2.92310548	2.86956692	6	-1.95427454	1.70835662	-1.18520141
1	-2.69710493	2.94532871	3.94988298	1	-1.80710816	-0.30790403	-1.86972582
1	-2.90029097	3.94000006	2.46501088	1	-1.72317624	-0.09634588	-0.09347680
1	-3.77995300	2.37069345	2.63455391	8	-2.31988597	2.01275373	-2.44169664
6	0.14674877	0.32994869	-1.13187766	8	-2.04052401	2.53801942	-0.27257124
6	0.70986241	-1.04355276	-0.90569115	6	-2.80941248	3.36517787	-2.65066481
1	0.51230150	-1.47484243	0.08034825	1	-3.04298115	3.42003274	-3.71735096
6	1.41337705	-1.73179841	-1.80982339	1	-3.70623970	3.53997159	-2.04468465
1	-1.78722572	2.29986715	1.26353979	1	-2.03607512	4.09369469	-2.38028121

BF_3·MeOH-5 complex (OMe binding)



E = –824.812121 E_0 = –824.599464
ZPVE = 0.212657 a.u. = 133.4441 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6279	41.9858	0.8887	1.4812	-11.0368
rotational	14.9417	32.6732	0.8887	0.8887	-8.8528
vibrational	20.4879	73.7549	143.2953	143.2953	121.3052
total	54.0575	148.4138	145.0727	145.6652	101.4156

Cartesian

5	0.23490985	1.30172575	3.04569340	1	1.64972508	-4.71598005	-1.30458343
9	-0.09862149	1.39168036	4.37267399	1	0.97058231	-3.71798611	-2.71998215
9	0.92284280	0.13922714	2.71230531	1	1.00134134	-1.26894879	-2.58985019
9	0.76007044	2.43945217	2.47069263	6	0.45042700	-0.46085793	-0.64865416
8	-1.22610426	1.16990626	2.26984644	1	2.35315824	-0.65398759	-1.63334656
6	-2.01106453	-0.01670496	2.58510542	6	0.25439548	0.97591579	-1.06868279
1	-2.21663737	0.02746497	3.65792012	1	-0.53273290	-0.95530772	-0.60741901
1	-2.94573069	0.03093254	2.01592064	1	0.83258784	-0.44850141	0.38710773
1	-1.44491899	-0.92498249	2.34436846	8	0.86383641	1.58195162	-1.91700327
6	1.41233945	-1.22381783	-1.57106912	8	-0.76658773	1.57634413	-0.33041036
6	1.68734753	-2.60924029	-1.05923367	6	-0.94371629	3.00198197	-0.59086508
1	2.14126205	-2.67074180	-0.06402902	1	-1.80225515	3.30380130	0.01639870
6	1.41985857	-3.73708773	-1.72479558	1	-0.04332256	3.54673100	-0.28638509
1	-1.05485880	1.22673810	1.27968097	1	-1.13954556	3.16103554	-1.65622497

S3.4. Polymerization of butylenes 1 and 4 catalyzed by HBF_3OMe or its dimer

Table S1. Free energies, free enthalpies, and activation barriers ($\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$) of the intermediates and TS of some stages of polymerization catalyzed by HBF_3OMe or its dimer. All energies given in kcal·mol^{-1}. [a]

		$[HBF_3OMe]_2$ catalysis					*HBF_3OMe catalysis*				
		Intermediate/TS	**Free G**	**Free H**	**$\Delta G^{\ddagger}$**	**$\Delta H^{\ddagger}$**	**Intermediate/TS**	**Free G**	**Free H**	**$\Delta G^{\ddagger}$**	**$\Delta H^{\ddagger}$**
Isobutylene 1	Initiation and 1st step of propagation	**$[HBF_3OMe]_2$-IB complex + IB**	−749204.27	−749139.52			**HBF_3OMe-IB complex + IB**	−473104.00	−473053.69		
		TS_dimer_IB2_outside_1	−749191.17	−749133.74	13.10	5.78	**TS_IB2_inside_A**	−473071.15	−473027.91	32.85	25.78
		TS_dimer_IB2_outside_2	−749188.83	−749131.77	15.44	7.75	**TS_IB2_inside_B**	−473070.54	−473027.67	33.46	26.02
		TS_dimer_IB2_inside	−749183.80	−749126.57	20.47	12.95	**TS_IB2_inside_C**	−473070.18	−473027.30	33.82	26.39
	2st step of propagation	**$[HBF_3OMe]_2$-IB2 ion pair + IB**	−847699.01	−847632.20							
		TS_dimer_IB3_outside_1	−847693.90	−847629.97	5.10	2.23					
		TS_dimer_IB3_outside_2	−847688.96	−847624.97	10.05	7.23					
		TS_dimer_IB3_inside	−847690.88	−847625.45	8.13	6.75					
But-1-ene 4	Initiation and 1st step of propagation	**$[HBF_3OMe]_2$-C4 complex + C4**	−749197.44	−749131.99			**HBF_3OMe-C4 complex + C4**	−473095.25	−473044.38		
		TS_dimer_C8_outside	−749179.56	−749119.93	17.88	12.06	**TS_C8_inside_A**	−473060.08	−473016.18	35.17	28.21
		TS_dimer_C8_inside	−749172.75	−749114.45	24.68	17.53	**TS_C8_inside_B**	−473060.05	−473016.43	35.19	27.95
							TS_C8_inside_C	−473059.72	−473015.76	35.52	28.62

2st step of propagation	**TS_dimer_C12_out-side**	−847676.48	−847610.27	
	TS_dimer_C12_in-side	−847679.01	−847611.57	

[a] In the Table S1, isobutylele **1** is denoted as IB, but-1-ene **4** as **C4**

$(BF_3{\cdot}MeOH)_2$-initiated polymerization

The search for TS corresponding to the initiation and 1st step of chain propagation was based on scanning the $C^+\cdots CH_2=$ distance with fixed lengths of C–H bonds in the Bu^t carbocation and $CH_2–H\cdots OMeBF_3$ distance, with using different orientations and angles of attack of alkene. TS for two mechanisms of chain growth, "inside" (also known as "push-pull" mechanism, K. S. Minsker *et al.*, *Theor. Exp. Chem.*, 1985, **20**, 627) and "outside", have been found (Table S1, Fig. S2).

According to our results, the chain growth should be start through "outside" attack of alkene; the corresponding activation barriers for TS of types "outside 1" and "outside 2" are 5.8 and 7.8 kcal·mol^{-1}, respectively. For the "inside" attack of alkene, activation barrier is more than 5.0 kcal·mol^{-1} higher and amounts 13.0 kcal·mol^{-1}, making this mode improbable. One can observe for the "outside" attacks, that the σ-bond C=C is almost coplanar with one of the three C–C bonds in the carbocation, with dihedral angles between the planes including these bonds being 175.0° ("outside 1") and 178.2° ("outside 2") in absolute values. This provides strong overlapping between p-orbitals of the alkene and cation within the transition states. At the same time, in case of the "inside" attack, short contacts between incoming alkene and conteranion seem to cause a distortion of the dihedral angle (146.6° in absolute value) and make corresponding TS to be significantly less stable. Angles of attack ($C{=}CH_2\cdots C^+$) do not demonstrate any differencies and are close to 100°, whereas distancies ${=}CH_2\cdots C^+$ amount 2.606 ("outside 1"), 2.474 ("outside 2"), and 2.820 Å ("inside"). Notably, the TS of type "outside 1" also has the minimum dipole moment (8.87 D) among all the others (10.53 D for "outside 2", 10.25 D for "inside").

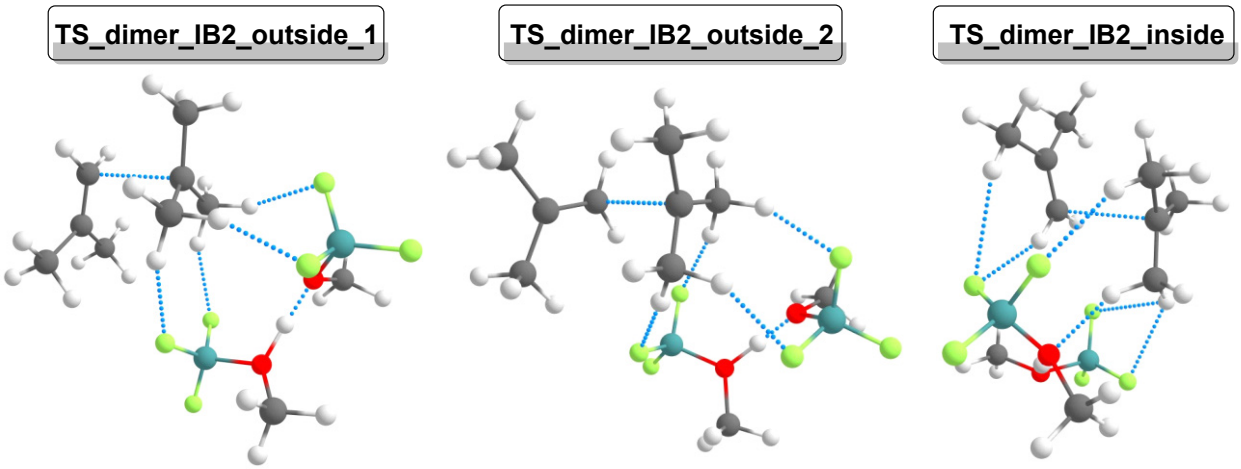


Figure S2. Structures of TS for the 1st step of $[HBF_3OMe]_2$-mediated propagation within polymerization of IB **1**. Colour code of the atoms: dark gray – C, light gray – H, red – O, emerald – B, salad green – F. The short contacts H···O/F and forming C–C bonds are indicated with dashed lines.

Relaxation of the given TS results in ion pairs with only real vibrational frequencies that means they are trully intermediates. In similar fashion, we have obtained TS for the 2nd step of propagation, where the activation barrier for TS of type "outside 1" was estimated to be only 2.2 kcal·mol^{-1}, while for the other two types of addition those are more than 4.5 kcal·mol^{-1} higher (see

Table S1). Therefore, calculations clearly predict that type "outside 1" is the main model for chain propagation.

According to calculations, the polymerization of but-1-ene **4** differs in some ways from that of IB **1**. Firstly, we have found only one TS for "outside" attack, as well as for "inside" attack of alkene at each stage of chain growth. For the initiation and 1st step of propagation, activation barrier for the "outside" attack is estimated at 12.1 kcal·mol^{-1}, while that for the "inside" attack is more than 5 kcal·mol^{-1} higher (see Table S1). In both cases, relaxation is accompanied with proton abstraction and gives complexes of alkene and initiator.

BF_3·MeOH-mediated polymerization

In addition to the polymerization of alkenes initiated by $(BF_3·MeOH)_2$ we have also examined the possibility of BF_3·MeOH to catalyze the process. The starting search for TS for BF_3·MeOH-initiated polymerization (the 1st step of propagation) was based on the structural parameters reported for dimerization of IB catalyzed by sulfated MOF (B. Yang *et al.*, *J. Phys. Chem. C*, 2023, **127**, 8539). It should be noted that the authors of the study have found the TS leading to both *exo*- and *endo*-isomer, but only the former was published. These data allowed us to determine a TS for the system under consideration. Along with that, two alternative TS with different orientation of the carbocation, alkene and anion have been found (Fig. S3).

In contrast to $(BF_3·MeOH)_2$-initiated polymerization, all of the TS belong to "inside" mode of propagation. It is evident that the σ-bond C=C is almost coplanar with one of the three C–C bonds in the carbocation: dihedral angles between the planes including these bonds are −175.0 (TS-A), −178.2 (TS-B) and 172.5° (TS-C). Obtained TS have almost identical values of free enthalpy (see Table S1), with the difference between TS-A (the most stable) and TS-C (the least stable) is only 0.4 kcal ·mol^{-1}. Similarly, the TS corresponding to the 1st step of propagation for but-1-ene were obtained. Most importantly, calculated activation barriers for this stage, 25.8–26.4 kcal·mol^{-1} for IB **1** and 28.2–28.6 kcal·mol^{-1} for but-1-ene **4**, are not passable under conventional reaction conditions (–60 to –20 °C). It allows us to conclude that the mechanism of BF_3·MeOH-ititiated polymerization of alkenes is non-realistic and should be excluded from consideration.

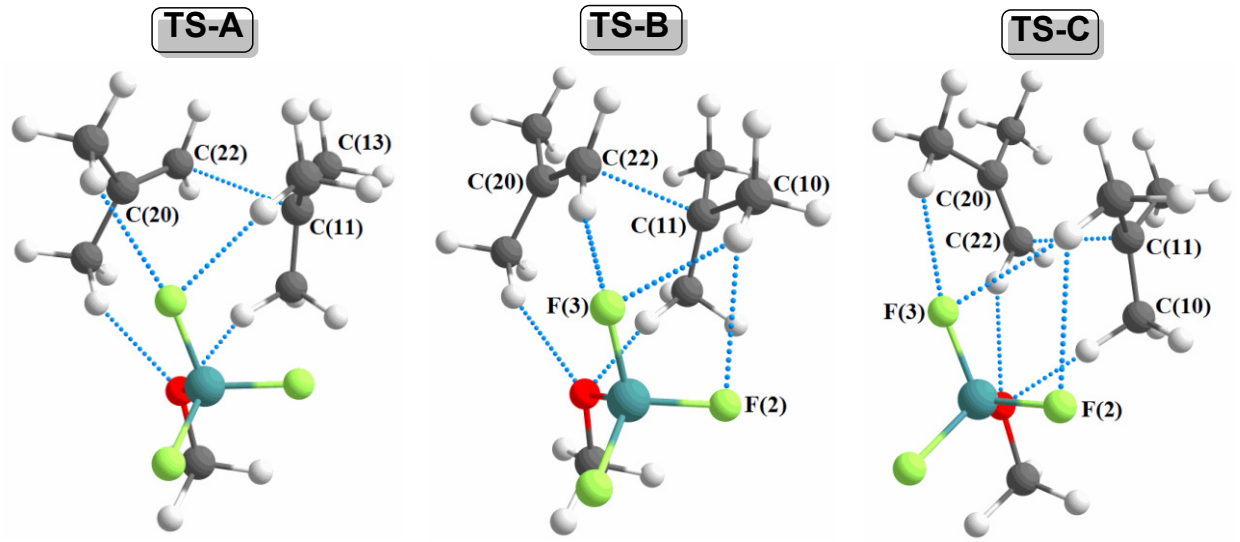
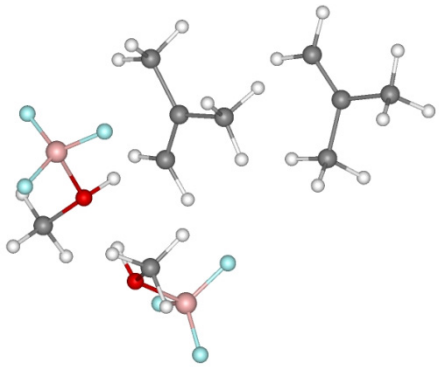


Figure S3. Structures of TS for the 1st step of HBF_3OMe-mediated propagation within polymerization of IB. Colour code of the atoms: dark gray – C, light gray – H, red – O, emerald – B, salad green – F. The short contacts H···O/F and forming C–C bonds are indicated with dashed lines.

The energy parameters, molecular structures and cartesian coordinates of some calculated TS and intermediates in polymerization of IB and but-1-ene catalyzed by $(BF_3{\cdot}MeOH)_2/BF_3{\cdot}MeOH$ are presented below.

$(BF_3{\cdot}MeOH)_2$-1 complex + 1



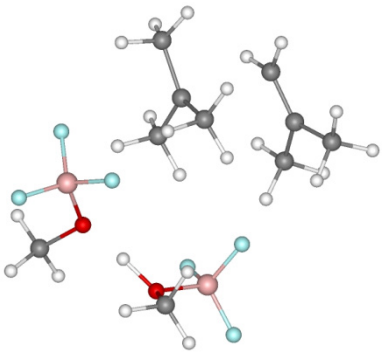
E = –1194.203416 E_0 = –1193.862218
ZPVE = 0.341198 a.u. = 214.1049 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	19.1937	43.1100	0.8887	1.4812	-11.3720
rotational	16.1407	35.0559	0.8887	0.8887	-9.5632
vibrational	40.5823	138.9934	231.5012	231.5012	190.0604
total	75.9167	217.1593	233.2787	233.8712	169.1251

Cartesian

5	-1.47366178	-0.17838590	4.83613205	6	1.13897479	-0.15179119	-2.59877729
9	-1.33709037	-0.88979447	6.00467682	1	-1.65957344	1.86200643	-3.18064833
9	-1.58506894	1.18015134	4.98098993	1	-0.50854188	-1.07565296	-4.69761276
9	-2.31795311	-0.74517733	3.90678120	1	-1.20004511	-1.61982977	-3.16929579
8	0.03768181	-0.42439610	4.09701300	1	-2.01637030	-0.33375895	-4.09968328
6	1.19575667	0.13895153	4.80889750	1	-1.01778340	2.67989540	1.79872978
1	1.17660391	-0.29213604	5.81303692	1	-2.06441712	2.20089459	0.43297282
1	2.09630704	-0.16941372	4.26962185	1	-2.45608282	1.65632677	2.06740069
1	1.09368372	1.22831035	4.85594225	1	-0.07133871	2.28331685	-2.30649185
6	-1.62010348	1.86336243	1.38244629	1	1.68088961	0.64562809	-2.07525468
6	-0.81037933	0.61932075	1.14701498	1	1.05577326	-1.01833165	-1.92314172
6	-1.55391192	-0.55531436	0.57781368	1	1.74979234	-0.48429981	-3.45365095
6	0.51437587	0.56558144	1.41949534	5	1.36858690	-3.37379622	2.66985011
1	-1.95151949	-0.28617790	-0.41355923	9	1.91014218	-4.62114906	2.83205652
1	-0.91621625	-1.44127786	0.47732517	9	0.52427787	-3.25589967	1.57368517
1	-2.41939235	-0.80380350	1.21039379	9	2.25593448	-2.31131935	2.78744555
1	0.03570523	-0.06219826	3.13597465	8	0.41601226	-3.16027570	3.99577284
1	1.10656846	-0.32452393	1.19738472	6	-0.77645063	-4.00274897	4.10054684
1	1.05011153	1.45375073	1.76347160	1	-0.41527319	-5.03382635	4.13719368
6	-0.22080155	0.30182233	-3.06052208	1	-1.29066014	-3.73526859	5.02869511
6	-1.03823352	-0.72790629	-3.79614305	1	-1.42242694	-3.84696651	3.22939277
6	-0.67518431	1.54395473	-2.83441186	1	0.16105054	-2.19789720	4.03738070

TS $(BF_3 \cdot MeOH)_2$ IB2 outside 1



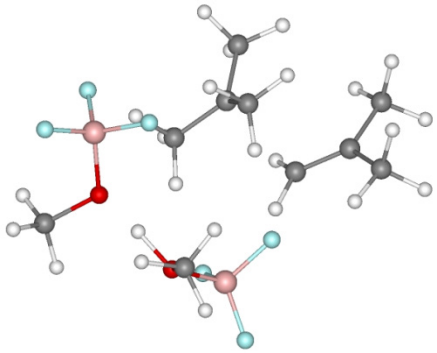
E = –1194.189172 E_0 = –1193.850891
ZPVE = 0.338281 a.u. = 212.2745 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	19.1937	43.1100	0.8887	1.4812	-11.3720
rotational	15.8027	34.3841	0.8887	0.8887	-9.3629
vibrational	30.8064	115.1084	228.3416	228.3416	194.0220
total	65.8028	192.6025	230.1191	230.7116	173.2871

Cartesian

5	-1.49075329	-1.54311728	2.52613544	5	2.23719859	-1.60405827	-0.06117324
9	-1.86668479	-2.31055093	3.61945367	9	3.39061713	-2.26360369	-0.44921815
9	-2.14055467	-0.27089196	2.54670382	9	1.34931839	-1.44631267	-1.16041517
9	-1.77141988	-2.18959785	1.29425681	9	2.48020315	-0.35986423	0.54529572
8	0.00428293	-1.29621315	2.52020645	8	1.54001963	-2.45391655	1.02149570
6	0.63552004	-1.03362906	3.78728080	6	1.07370996	-3.76814890	0.62669992
1	0.53397930	-1.89790428	4.45756245	1	1.93116772	-4.32426262	0.23272710
1	1.69525921	-0.82586867	3.59525633	1	0.67761219	-4.26263142	1.52020633
1	0.16953270	-0.15656455	4.25802088	1	0.28652033	-3.68199039	-0.13251369
6	-2.61766934	2.06298566	-0.04337331	1	0.78953129	-1.92566848	1.68283176
6	-1.40356684	1.23292565	-0.24825110	6	0.49159989	2.02566290	-2.59679198
6	-1.55739093	-0.06193042	-0.91437221	6	-0.64193010	2.69738507	-2.26540565
6	-0.26134342	1.45947254	0.64511025	6	0.48170429	0.89501607	-3.57811737
1	-0.61138189	-0.49876750	-1.25468969	6	1.81616044	2.35605836	-1.98197770
1	-1.89499104	-0.75041980	-0.09740525	1	0.90228349	-0.01496674	-3.11915660
1	-2.33512831	-0.06767216	-1.68611383	1	-0.60469341	3.57136631	-1.61500406
1	-0.56312704	0.91528034	1.57171345	1	-1.58268297	2.49498463	-2.77776098
1	0.67118794	0.98419040	0.32253784	1	1.13610005	1.13464427	-4.43182611
1	-0.12656379	2.51209044	0.91834098	1	2.55044389	2.58971834	-2.76945090
1	-2.39530993	3.10196495	0.22259629	1	1.75930679	3.20726895	-1.29324150
1	-3.32932568	2.00621629	-0.87389570	1	2.21952033	1.48183274	-1.44370365
1	-3.10503983	1.59925330	0.84003049	1	-0.52322257	0.68023473	-3.96060491

TS (BF_3·MeOH)$_2$ IB2 outside 2



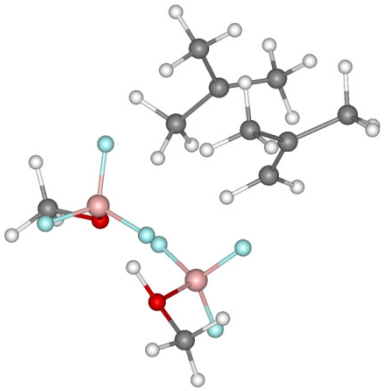
E = –1194.186095 E_0 = –1193.847667
ZPVE = 0.338428 a.u. = 212.3669 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	19.1937	43.1100	0.8887	1.4812	-11.3720
rotational	15.8517	34.4816	0.8887	0.8887	-9.3919
vibrational	30.2277	113.7940	228.3849	228.3849	194.4573
total	65.2731	191.3855	230.1624	230.7549	173.6933

Cartesian

5	-0.89353693	-1.77497065	2.83417392	5	2.31240773	-1.53030980	-0.30882218
9	-1.05849898	-2.64148974	3.90748072	9	3.49511933	-1.99686778	-0.85848749
9	-1.57237935	-0.54122913	3.07229638	9	1.26485407	-1.55749786	-1.27267766
9	-1.32809544	-2.33171964	1.61340654	9	2.43016601	-0.23000818	0.22968321
8	0.57975978	-1.45200121	2.62909222	8	1.92810917	-2.42647028	0.87090635
6	1.37662709	-1.20008814	3.80064273	6	1.57384217	-3.79547811	0.56407160
1	1.38292587	-2.07755303	4.46132755	1	2.40975380	-4.25240469	0.02210583
1	2.39574075	-0.96829820	3.46823692	1	1.41012752	-4.31776762	1.51340199
1	0.96364605	-0.33980128	4.34520435	1	0.65907019	-3.82751656	-0.04121726
6	-2.25065446	2.34183311	-0.11510145	1	1.23283958	-1.97049975	1.69298613
6	-1.18343139	1.31390977	0.02827340	6	-0.18524340	1.95679498	-2.76787376
6	-1.44672465	-0.03926036	-0.48438066	6	0.47967970	2.15869379	-1.59662354
6	-0.22138093	1.47626019	1.13230872	6	-1.07131743	3.00820637	-3.36450744
1	-0.52934742	-0.59585565	-0.72416246	6	-0.05608793	0.67441010	-3.52804852
1	-1.87784946	-0.60965061	0.36922979	1	-2.08789611	2.61680698	-3.53548455
1	-2.16207767	-0.05924819	-1.31366682	1	1.20191526	1.42830765	-1.23110759
1	-0.74062014	1.01159203	2.00585151	1	0.46720892	3.13885045	-1.11880100
1	0.69371867	0.88424259	1.00547290	1	-0.69243520	3.29540062	-4.35881853
1	-0.00531769	2.52318478	1.37149966	1	0.37826666	0.87877065	-4.52105188
1	-1.89592707	3.36122918	0.07456358	1	0.57299924	-0.06081482	-3.01339221
1	-2.78513432	2.28077888	-1.06938052	1	-1.04753780	0.23272716	-3.72268748
1	-2.98548174	2.10364723	0.67936492	1	-1.13180220	3.91115499	-2.74528837

TS (BF_3·MeOH)$_2$ IB2 inside



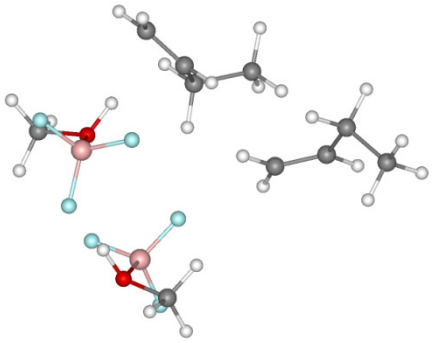
E = –1194.178143 E_0 = –1193.839708
ZPVE = 0.338435 a.u. = 212.3712 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	19.1937	43.1100	0.8887	1.4812	-11.3720
rotational	15.7948	34.3685	0.8887	0.8887	-9.3582
vibrational	30.2270	114.4655	228.5900	228.5900	194.4621
total	65.2155	191.9440	230.3674	230.9599	173.7318

Cartesian

5	-0.38708603	0.62764931	2.63290691	5	2.80222487	-1.96137190	0.50869763
9	-0.50983620	0.93558890	3.98237181	9	3.53372002	-3.13318610	0.51436317
9	-0.82903647	1.71971333	1.82307088	9	1.86247718	-1.92962599	-0.54295528
9	-1.08717251	-0.54483181	2.27888489	9	3.57842755	-0.79879260	0.52383506
8	1.06512392	0.35240006	2.27440214	8	2.00970697	-1.91397345	1.86772227
6	2.04752779	1.23352647	2.84711981	6	1.08582258	-3.00472331	2.12861061
1	2.02794909	1.16361880	3.94312215	1	1.67610550	-3.92478442	2.18076134
1	3.03139496	0.93437648	2.46540236	1	0.59469575	-2.80230498	3.08544040
1	1.83412254	2.27362704	2.55637312	1	0.33857521	-3.07123923	1.32801437
6	-0.78479475	2.41204453	-1.34722924	1	1.55127931	-0.95907944	2.05460882
6	0.28851354	1.43085957	-1.61406040	6	-2.39097762	-0.50268596	-1.37193930
6	0.48371691	0.89596695	-2.97879982	6	-1.15964389	-0.90151191	-0.97042865
6	1.35451353	1.28357661	-0.63560355	6	-3.34302735	0.17020498	-0.42768934
1	1.12679267	1.64525890	-3.48892951	6	-2.88356376	-0.73133433	-2.77270269
1	1.05507052	-0.03986705	-2.97829056	1	-4.25437832	-0.44014436	-0.31476489
1	-0.44161314	0.81148517	-3.55788732	1	-0.49601537	-1.46239650	-1.62788665
1	0.97492629	0.83482558	0.31905884	1	-0.86119127	-0.79891717	0.07210865
1	2.21025586	0.69305509	-0.97299850	1	-3.68185377	1.13985527	-0.83088869
1	1.65572011	2.28528976	-0.27672312	1	-3.17128563	0.21941932	-3.25381804
1	-0.33877361	3.41330075	-1.51540840	1	-2.14019489	-1.23985457	-3.39932370
1	-1.64081872	2.31275511	-2.02213860	1	-3.79853106	-1.34560478	-2.75994134
1	-1.08816695	2.39196539	-0.28948429	1	-2.90070128	0.32586649	0.56301677

$(BF_3 \cdot MeOH)_2$-4 complex + 4



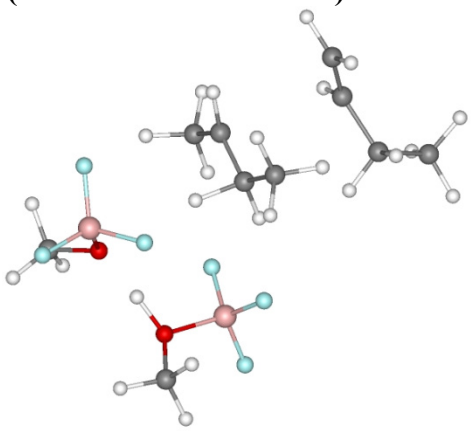
E = –1194.193070 E_0 = –1193.850153
ZPVE = 0.342917 a.u. = 215.1839 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	19.1937	43.1100	0.8887	1.4812	-11.3720
rotational	16.1220	35.0187	0.8887	0.8887	-9.5521
vibrational	41.8567	141.4021	232.5434	232.5434	190.3843
total	77.1723	219.5308	234.3208	234.9133	169.4602

Cartesian

5	1.11315525	1.09470987	2.70941973	6	0.51956809	-3.09058309	2.05635715
9	1.36591160	2.17190385	3.52087116	1	0.68143922	-4.07849550	1.61758089
9	-0.17324416	1.00319302	2.22649145	1	0.24338202	-3.17820501	3.11194324
9	1.56858277	-0.11851745	3.29279661	1	-0.23978667	-2.53498793	1.49356592
8	2.01192832	1.23183930	1.39162505	1	1.72569275	-1.51112723	2.44333458
6	3.41457772	1.61930287	1.54127073	6	-3.14871693	-0.91053122	-1.14997852
1	3.88981390	0.83703876	2.13781261	6	-2.00783277	-0.81734312	-0.45650756
1	3.85710573	1.63607860	0.54090428	6	-4.45911074	-0.29324558	-0.75323594
1	3.48115897	2.59459448	2.03611255	1	-1.08727610	-1.29522276	-0.79437691
6	0.60014570	2.02432013	-1.24108875	1	-1.95351303	-0.25234371	0.47766691
6	1.46285045	1.37258983	-2.27865744	1	-4.77271891	0.41936570	-1.53629756
6	0.86887920	3.18245339	-0.60997277	1	-4.32638454	0.28874755	0.17175873
1	2.36803317	1.97612834	-2.44996548	1	-0.32801658	1.49450481	-0.99595129
1	1.78698754	0.38911223	-1.89733970	6	0.70405853	1.15806067	-3.60014462
1	1.56229949	1.77826691	0.67332822	1	1.34153378	0.63805819	-4.32762432
1	1.76829779	3.75938916	-0.84124428	1	-0.19479932	0.54611135	-3.44071293
1	0.17464682	3.61181259	0.11407116	1	0.39058584	2.11501884	-4.03966331
5	2.46780753	-2.23789191	0.50225806	1	-3.15827250	-1.49169743	-2.07996655
9	2.69071555	-3.52917600	0.08809066	6	-5.57251835	-1.33752739	-0.56649768
9	1.52558970	-1.56160009	-0.27094960	1	-5.72288465	-1.92436004	-1.48447442
9	3.60377765	-1.48773527	0.75184876	1	-5.32092094	-2.03847456	0.24146947
8	1.80503476	-2.39878869	1.99000466	1	-6.52756453	-0.85474634	-0.31593266

TS (BF_3·MeOH)$_2$ C8 outside (C8 is dimer of butene 4)



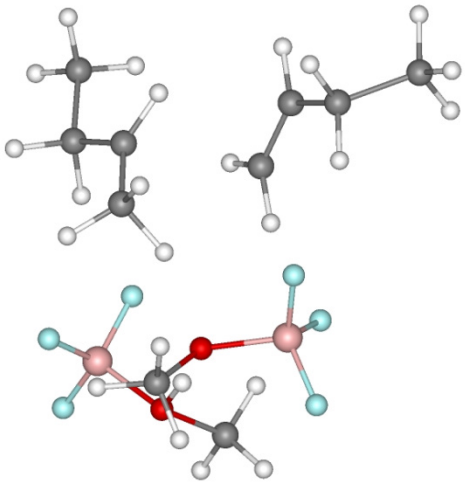
E = –1194.167168 E_0 = –1193.829377
ZPVE = 0.337791 a.u. = 211.9670 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	19.1937	43.1100	0.8887	1.4812	-11.3720
rotational	15.9386	34.6543	0.8887	0.8887	-9.4434
vibrational	33.8609	122.2218	228.3452	228.3452	191.9048
total	68.9932	199.9861	230.1227	230.7152	171.0893

Cartesian

5	-1.51591659	-1.37156677	2.52535748	6	0.77354205	-4.19783020	1.00171161
9	-2.09446883	-2.21682715	3.45515585	1	1.55663335	-4.87168217	0.63971812
9	-1.97822070	-0.04349910	2.64646602	1	0.38483644	-4.54800034	1.96406543
9	-1.84367156	-1.83691442	1.17208934	1	-0.03824659	-4.12215233	0.26777214
8	-0.02864605	-1.39462900	2.57104754	1	0.71823746	-2.24297023	1.77940595
6	0.57303369	-1.15138566	3.85601115	6	0.38012773	2.42922258	-2.74373364
1	0.28137183	-1.92981768	4.57540274	6	-0.86264712	2.93652797	-2.70035315
1	1.66122377	-1.15502977	3.72110486	6	0.82238615	1.25691164	-3.56461215
1	0.25594062	-0.16998641	4.23643494	1	-0.02562857	0.86483544	-4.14681101
6	-1.28524148	-0.18488944	-0.93140405	1	-1.10037076	3.81661510	-2.10157704
6	-1.11928582	1.04526627	-0.27850586	1	-1.67121828	2.51508141	-3.30145788
6	0.03328658	1.41690648	0.55171144	1	1.15203762	0.44906428	-2.88673329
1	-0.29223850	1.26333380	1.60078144	1	-1.99271393	1.70738459	-0.22417819
1	0.92975146	0.81534958	0.36531350	6	-2.45691442	-0.43553564	-1.86300659
1	0.23249976	2.49436331	0.46641675	1	-3.34247780	0.14374883	-1.56980407
1	-1.55026996	-0.72541893	0.11490522	1	-2.18611336	-0.16077797	-2.89213562
1	-0.35700062	-0.73861289	-1.14621449	1	-2.72560954	-1.49857259	-1.86370599
5	2.08383989	-2.23057532	-0.01358158	6	1.99312961	1.60533500	-4.50045347
9	3.17883635	-3.01056719	-0.32861513	1	2.32140756	0.71537369	-5.05325603
9	1.15220141	-2.18798137	-1.07667398	1	1.70260406	2.37593770	-5.22741127
9	2.40540338	-0.94164115	0.42536616	1	2.85419750	1.98196685	-3.93062186
8	1.38188231	-2.89850855	1.21740544	1	1.16458106	2.90766215	-2.14561272

TS (BF_3·MeOH)$_2$ C8 inside



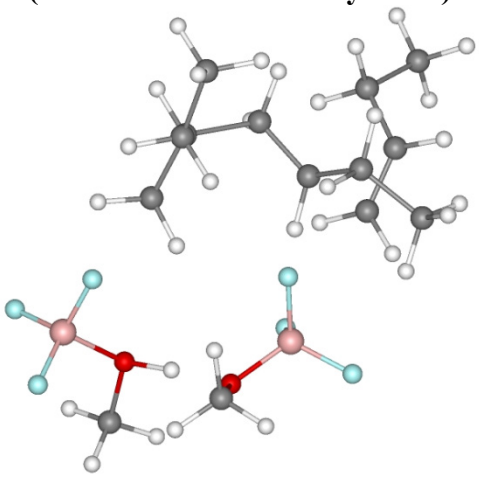
E = –1194.159256 E_0 = –1193.820279
ZPVE = 0.338978 a.u. = 212.7117 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	19.1937	43.1100	0.8887	1.4812	-11.3720
rotational	15.8468	34.4719	0.8887	0.8887	-9.3891
vibrational	32.1100	117.9586	228.8563	228.8563	193.6869
total	67.1505	195.5405	230.6338	231.2262	172.9258

Cartesian

5	-0.27584064	0.28425667	2.78058052	6	1.79681325	-2.86844707	1.94826198
9	-0.05216037	0.17551056	4.14873934	1	2.55035686	-3.65149403	1.81988621
9	-1.03959727	1.41953015	2.45336270	1	1.54701173	-2.74103928	3.00616693
9	-0.83335376	-0.88783258	2.23621392	1	0.89407998	-3.09560823	1.36941803
8	1.08777022	0.42943388	2.05698967	1	1.78091717	-0.77878821	1.74066865
6	1.99086654	1.39581990	2.63333607	6	-2.51645017	-0.14314462	-1.23392928
1	2.21872568	1.11826539	3.67080712	6	-1.42295790	-0.88051325	-0.94878191
1	2.91072226	1.39962327	2.03544331	6	-3.26761985	0.70079124	-0.25154909
1	1.52477419	2.39155483	2.62519646	1	-0.95713001	-1.52351725	-1.69542801
6	0.21244241	1.38123918	-1.64425445	1	-1.02487028	-0.92492604	0.06614021
6	0.98154527	0.64413232	-2.65293884	1	-3.29785752	1.74300611	-0.62005979
6	0.78189594	1.86482501	-0.42190847	1	-2.74778247	0.71101117	0.71661860
1	1.87339652	1.27357924	-2.85788465	1	-0.80305630	1.69196701	-1.89793468
1	1.44559348	-0.23293772	-2.15293169	6	0.26063073	0.27477145	-3.94590092
1	0.66798025	1.10201991	0.43469870	1	0.95657337	-0.20870438	-4.64239645
1	1.87662816	1.94762683	-0.46733931	1	-0.56229293	-0.42641330	-3.75724864
1	0.27590650	2.75423789	-0.02619055	1	-0.15277132	1.16230726	-4.44472075
5	2.87818456	-1.57392406	-0.00218928	1	-2.92405200	-0.17058402	-2.25336003
9	3.89339352	-2.49706483	-0.13163462	6	-4.71857643	0.21314438	-0.07565255
9	1.77527046	-1.87893474	-0.83268571	1	-5.25960445	0.20145798	-1.03314531
9	3.28231859	-0.24376026	-0.19066672	1	-4.73753405	-0.80319589	0.33947620
8	2.39106822	-1.62238860	1.48462212	1	-5.26135778	0.87310690	0.61410451

TS (BF_3·MeOH)$_2$ C12 outside (C12 is trimer of isobutylene 1)



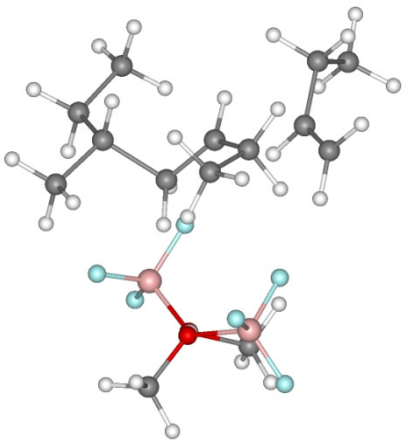
E = –1351.239395 E_0 = –1350.788894
ZPVE = 0.450501 a.u. = 282.6936 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	19.4414	43.6023	0.8887	1.4812	-11.5188
rotational	16.4679	35.7060	0.8887	0.8887	-9.7570
vibrational	38.8394	142.7485	302.2421	302.2421	259.6817
total	74.7487	222.0568	304.0196	304.6121	238.4059

Cartesian

5	-0.76499504	-1.86196482	4.15517092	6	-1.37101889	1.11730123	-1.04926085
9	-0.39596766	-2.87210369	5.04382467	6	0.23522691	-0.43241566	-2.30810571
9	-1.47021806	-0.83325177	4.77877808	1	-0.48208949	-0.38630900	-3.13921618
9	-1.40309930	-2.35349298	3.01596260	1	-1.26330590	2.18258286	-0.79483640
8	0.55833739	-1.20207441	3.60007358	1	-2.00093699	1.02823234	-1.94444299
6	1.48453939	-0.70243520	4.59330082	1	-0.04555508	-1.33013749	-1.67367601
1	1.80720842	-1.51222563	5.26121807	1	-3.08041310	1.06067741	0.19609001
1	2.34345436	-0.27428362	4.06429434	6	-3.32618260	-1.36866558	-1.09011328
1	0.96885115	0.07251757	5.17058182	1	-4.26718187	-0.79684281	-1.08777332
6	-2.44000626	-0.98657215	0.09882597	1	-2.83738160	-1.19833696	-2.06167483
6	-2.12291288	0.50938267	0.21745159	1	-3.58724403	-2.43447709	-1.04625726
6	-1.39537859	0.85089779	1.51908839	6	1.67624080	-0.70013654	-2.74482465
1	-2.00147772	0.53857625	2.37971711	1	1.72528839	-1.64416313	-3.29980516
1	-0.43588263	0.32548967	1.61097336	1	2.03101015	0.10173297	-3.40791011
1	-1.21495032	1.93337131	1.60750139	1	2.34760523	-0.78709126	-1.88258398
1	-2.94812322	-1.27198172	1.03274226	1	0.67514372	0.55825341	-0.43899110
1	-1.50945449	-1.57510602	0.10166529	6	1.60984445	2.50483871	-1.56342757
5	1.92846143	-2.03873658	0.61376929	1	2.45525742	1.81778860	-1.55750930
9	3.06943059	-2.50399494	-0.04801467	1	1.36669838	2.99223423	-0.61711222
9	0.76292700	-2.42234755	-0.13560323	6	0.96147859	2.82815695	-2.70285749
9	1.95473766	-0.61061364	0.71414781	1	1.26778531	2.34255958	-3.63640952
8	1.84519470	-2.55494165	1.99903476	6	-0.13013282	3.84133840	-2.82475448
6	1.67087686	-3.97855878	2.14612317	1	-0.36128622	4.27064037	-1.83847880
1	2.52905631	-4.49827337	1.69921112	1	-1.04628849	3.34096313	-3.18789244
1	1.61856866	-4.20025635	3.21870661	6	0.23590396	4.96244717	-3.81689286
1	0.73944026	-4.30541658	1.66342342	1	0.45564136	4.55369329	-4.81296492
1	1.09400630	-1.82902586	2.87187648	1	-0.59715003	5.67027569	-3.91716528
6	-0.03880625	0.54498696	-1.27049470	1	1.11922395	5.51729345	-3.47450328

TS (BF_3·MeOH)$_2$ C12 inside



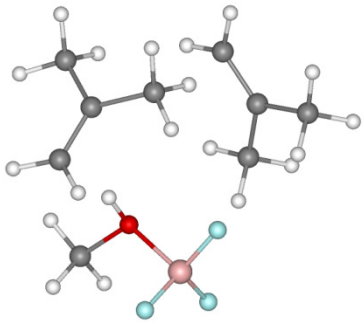
E = –1351.240843 E_0 = –1350.791496
ZPVE = 0.449347 a.u. = 281.9696 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	19.4414	43.6023	0.8887	1.4812	-11.5188
rotational	16.3278	35.4276	0.8887	0.8887	-9.6740
vibrational	40.5003	147.1521	301.8470	301.8470	257.9736
total	76.2694	226.1820	303.6245	304.2170	236.7808

Cartesian

5	0.69178474	1.12835574	3.18451071	6	0.14661309	1.00952363	-0.57555079
9	0.91685885	0.66444254	4.47959423	6	-1.98167908	2.07339668	0.39030355
9	0.41634157	2.50873923	3.15987301	1	0.45298436	-0.04375158	-0.68764877
9	-0.36395392	0.40558794	2.55639720	1	0.68234205	1.47102809	0.25852343
8	1.91180384	0.87316895	2.30952382	1	-1.87169862	1.56648278	1.38085246
6	3.14067531	1.48477340	2.75749421	1	-3.05160141	2.11956835	0.15076514
1	3.41189551	1.12045407	3.75853968	1	-0.30605987	2.36348724	-2.32798314
1	3.92443180	1.22402263	2.03650713	6	-0.29348364	-0.21733741	-3.45565510
1	3.00801945	2.57359004	2.78899193	1	0.00400351	-0.86764622	-4.28904724
6	0.53644568	1.74046886	-1.97529781	1	-0.58027357	-0.87976754	-2.62585855
6	0.85897011	0.70640832	-3.06115580	1	-1.17908514	0.35156405	-3.77989316
6	1.72101259	2.66639781	-1.67501211	1	-1.86765850	0.57351005	-1.21492493
1	1.18774140	1.27271473	-3.94882536	6	-1.35966444	3.47654891	0.57422686
1	1.71842349	0.10840891	-2.72123384	1	-0.34562224	3.41560149	0.98305613
1	2.57563329	2.08150005	-1.31054235	1	-1.35363901	4.02970552	-0.37396115
1	2.01435781	3.18756104	-2.59852839	1	-1.96848190	4.03085518	1.29777408
1	1.47011435	3.42452955	-0.92219174	6	-2.49710298	-1.34807909	0.68523443
5	2.51260567	-1.70963180	0.16363837	1	-3.51794600	-0.97492772	0.80857247
9	3.30877972	-2.82679820	-0.02372362	1	-1.76262629	-1.05515289	1.43621016
9	1.19135547	-1.94725871	-0.32439023	6	-2.18770838	-2.19292402	-0.31523946
9	3.03290629	-0.54044145	-0.41505447	1	-1.15747499	-2.56021881	-0.38796315
8	2.43255186	-1.41146064	1.66816866	6	-3.15342617	-2.71172452	-1.33785653
6	1.81628728	-2.40894222	2.51495051	1	-2.80251598	-2.42799616	-2.34603167
1	2.40049291	-3.33279896	2.43705821	1	-4.14027023	-2.24414754	-1.19537199
1	1.83501077	-2.03157616	3.54365349	6	-3.27989626	-4.24555111	-1.28620756
1	0.77874768	-2.58890367	2.20332813	1	-3.67164469	-4.57332325	-0.31380534
1	2.13277888	-0.33401874	1.96950209	1	-3.95982575	-4.60606194	-2.07023096
6	-1.27548099	1.15437555	-0.50208807	1	-2.30314946	-4.72633171	-1.43597722

BF_3·MeOH-IB complex + IB



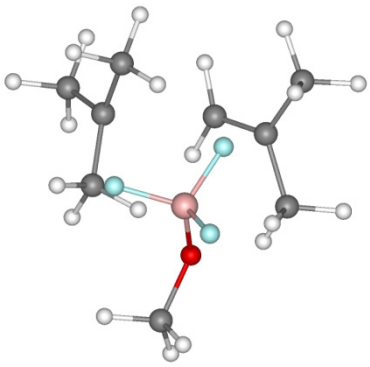
E = –754.157751 E_0 = –753.882461
ZPVE = 0.275290 a.u. = 172.7471 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6143	41.9586	0.8887	1.4812	-11.0287
rotational	14.9199	32.6298	0.8887	0.8887	-8.8399
vibrational	27.1832	94.1579	184.7146	184.7146	156.6414
total	60.7173	168.7463	186.4920	187.0845	136.7728

Cartesian

5	-3.06258726	-1.55202198	0.35016233	1	1.62586308	0.16289262	2.56227708
9	-3.53432417	-2.28855181	1.42119288	1	1.11735106	1.14577043	1.15398383
9	-3.39334631	-0.21302962	0.39726949	6	-0.73281121	1.34622192	-2.27302957
9	-3.23160625	-2.15903473	-0.87418813	6	-0.76291615	-0.00474962	-2.93753624
8	-1.41070390	-1.51470900	0.53682488	6	0.40111151	1.88171756	-1.79290986
6	-0.76266885	-2.82023382	0.59339696	6	-2.05663943	2.05877233	-2.18760777
1	-0.99635834	-3.31886506	-0.35083187	1	1.35536730	1.35812366	-1.87039590
1	0.31725076	-2.66036534	0.68357420	1	-1.47520304	-0.67525291	-2.43180609
1	-1.15242219	-3.40154576	1.43783689	1	-1.11157155	0.08647374	-3.97915912
6	-1.39499438	1.88902318	2.17929268	1	0.22758885	-0.47792032	-2.94629216
6	-0.45422274	0.78775525	2.58251095	1	-1.31588507	2.08832502	1.09980786
6	-0.88240552	-0.32490727	3.21688771	1	-2.43805552	1.64812219	2.41251421
6	0.99530059	1.00078046	2.23914099	1	-1.11912429	2.82392716	2.69298005
1	-1.19184995	-1.00129437	1.37573862	1	0.41273478	2.86919188	-1.32862103
1	-0.17929970	-1.09349597	3.54512143	1	-1.96081722	3.04287291	-1.71084619
1	-1.93089056	-0.45882347	3.48843694	1	-2.48591280	2.19973469	-3.19266224
1	1.36660135	1.92063320	2.71771884	1	-2.78366899	1.45887804	-1.61765528

TS BF_3·MeOH IB2 A



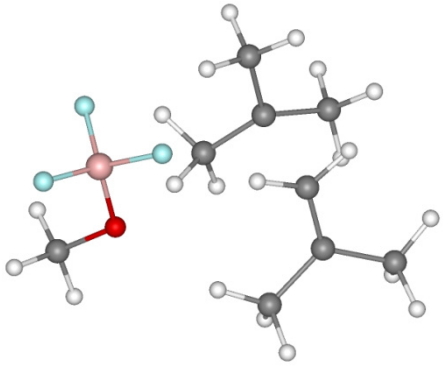
E = –754.112807 E_0 = –753.839185
ZPVE = 0.273622 a.u. = 171.7005 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6143	41.9586	0.8887	1.4812	-11.0287
rotational	14.7120	32.2168	0.8887	0.8887	-8.7167
vibrational	17.7711	70.8296	182.2892	182.2892	161.1713
total	51.0974	145.0050	184.0667	184.6591	141.4259

Cartesian

5	-3.13132668	-1.52202344	0.57581222	1	1.91498327	1.59353340	1.71874428
9	-2.99744892	-1.33721817	1.98758578	1	0.84631246	3.04333544	1.81771708
9	-3.34385014	-0.24264158	-0.03226272	6	-0.59931815	1.21396172	-1.57552707
9	-4.18817759	-2.39123225	0.29506102	6	-0.47335723	-0.14610253	-2.17423940
8	-1.84095705	-2.02346039	0.01435328	6	0.37185338	1.74207687	-0.77438402
6	-1.49899542	-3.34917998	0.40060228	6	-1.86081386	1.96127343	-1.87070060
1	-2.29500985	-4.05625725	0.11877261	1	1.32926261	1.23408580	-0.66022384
1	-0.56767130	-3.63409305	-0.11065812	1	-1.21650922	-0.82677960	-1.71519578
1	-1.34772730	-3.42424417	1.49337935	1	-0.70206374	-0.11222124	-3.25079799
6	-1.56308818	1.74329364	1.69576240	1	0.52603495	-0.57455570	-2.03075862
6	-0.20580278	1.14850426	1.61306608	1	-1.57538044	2.80640578	1.42764771
6	-0.07391512	-0.30385408	1.65228081	1	-2.31284547	1.16783643	1.13579237
6	0.94915920	1.98059881	2.06340957	1	-1.86384630	1.67161286	2.76044941
1	-0.64051026	-0.84001076	0.83799219	1	0.31391761	2.78235388	-0.45686588
1	0.96341062	-0.64936167	1.72327352	1	-1.87985826	2.95452929	-1.40612960
1	-0.66680312	-0.66714627	2.51649714	1	-1.98321211	2.07746339	-2.95943117
1	0.95522255	1.90003157	3.16876125	1	-2.72501445	1.37306929	-1.52103317

TS BF_3·MeOH IB2 B



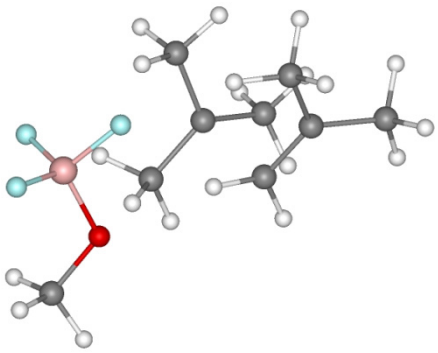
E = –754.112997 E_0 = –753.838671
ZPVE = 0.274326 a.u. = 172.1419 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6143	41.9586	0.8887	1.4812	-11.0287
rotational	14.7379	32.2682	0.8887	0.8887	-8.7320
vibrational	17.2584	69.5602	182.6559	182.6559	161.9166
total	50.6106	143.7870	184.4334	185.0259	142.1558

Cartesian

5	-3.59982967	-0.99171019	0.71872419	1	1.81084645	1.38112366	0.71010607
9	-3.28012919	-0.96055609	2.11252236	1	0.96741086	2.90807509	1.16062796
9	-3.66238618	0.35440126	0.23955052	6	-0.11247602	1.18405831	-1.59304130
9	-4.80786085	-1.65987706	0.50722438	6	-0.27666739	-0.21260951	-2.10013080
8	-2.47918987	-1.63886380	-0.03271160	6	-1.01972592	1.74215245	-0.73544860
6	-2.30915213	-3.02597237	0.23772097	6	1.08714485	1.94157135	-2.07473254
1	-3.22776484	-3.58252573	-0.00602099	1	-1.96701324	1.24121022	-0.51893729
1	-1.48621607	-3.40693021	-0.38564852	1	-0.37323681	-0.19179405	-3.19914269
1	-2.07084441	-3.20738173	1.30145681	1	0.62778115	-0.81025720	-1.89492047
6	-1.37491071	1.77633309	2.08695292	1	-1.15466881	-0.71442455	-1.67367327
6	-0.23256014	1.10887170	1.39334857	1	-1.42498398	2.85299420	1.88710976
6	-0.22522201	-0.35501209	1.36563706	1	-2.33425164	1.28609836	1.87909722
6	1.07248509	1.83852077	1.37833118	1	-1.18320382	1.65228295	3.17069435
1	-1.06383145	-0.78558731	0.73639393	1	-0.93804616	2.80259371	-0.49250165
1	0.73986840	-0.78051776	1.06715584	1	1.15048969	2.94966078	-1.64811361
1	-0.52484852	-0.72740436	2.36193871	1	2.01676512	1.39280570	-1.84955049
1	1.47759235	1.75595105	2.40559840	1	1.05503738	2.03174973	-3.17292261

TS BF_3·MeOH IB2 C



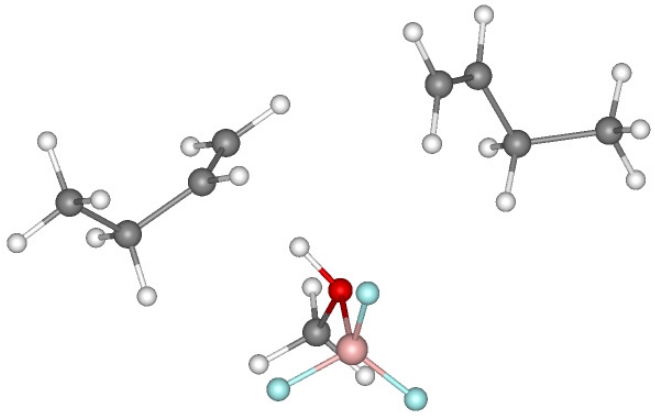
E = –754.112616 E_0 = –753.838078
ZPVE = 0.274538 a.u. = 172.2751 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6143	41.9586	0.8887	1.4812	-11.0287
rotational	14.7547	32.3016	0.8887	0.8887	-8.7420
vibrational	17.2748	69.5705	182.7825	182.7825	162.0400
total	50.6438	143.8307	184.5599	185.1524	142.2693

Cartesian

5	-3.71611047	2.23024082	1.51680589	1	0.78578120	2.31942940	0.71692884
9	-3.04114819	2.53418565	2.73736143	1	-0.89622778	2.49832726	1.36544943
9	-2.89450192	2.67028093	0.42596790	6	-0.39009717	0.64678377	-1.45919800
9	-4.96937943	2.84616756	1.47890520	6	0.72922313	-0.07737767	-2.14192772
8	-3.82915258	0.74791259	1.35795629	6	-1.16690719	0.04636992	-0.50503987
6	-4.74735832	0.11733272	2.24481463	6	-0.63281816	2.06144166	-1.87744081
1	-5.75783253	0.53406012	2.11113119	1	-1.07126844	-1.02688289	-0.33349702
1	-4.77188778	-0.95810646	2.01570225	1	0.53645635	-0.11951093	-3.22670960
1	-4.45610142	0.25572678	3.30204082	1	1.67994130	0.47035024	-2.03189135
6	-1.16255474	-0.04629795	2.34584665	1	0.85700297	-1.10260129	-1.77512503
6	-0.09030032	0.49988598	1.50255930	1	-1.16242325	0.49697170	3.30771136
6	1.14021087	-0.32654044	1.29958808	1	-2.19190526	0.21444926	1.95583868
6	0.06730405	1.98245203	1.47309327	1	-1.07424057	-1.12670231	2.50983596
1	0.91591126	-1.38534462	1.12304258	1	-2.07474113	0.53641897	-0.14970416
1	1.80107963	0.06185870	0.51644933	1	-1.43244112	2.53373694	-1.29644251
1	1.70010281	-0.27625948	2.25334048	1	0.29121742	2.65882850	-1.80168760
1	0.46863949	2.27216935	2.46301770	1	-0.91030067	2.08102822	-2.94537497

BF_3·MeOH 4 complex + 4



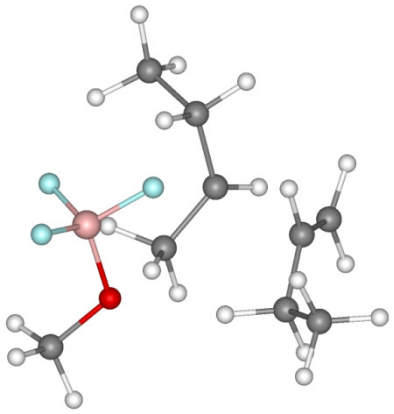
E = –754.144412 E_0 = –753.867501
ZPVE = 0.276910 a.u. = 173.7639 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6143	41.9586	0.8887	1.4812	-11.0287
rotational	15.1161	33.0197	0.8887	0.8887	-8.9561
vibrational	28.0485	95.6086	185.6512	185.6512	157.1455
total	61.7788	170.5870	187.4287	188.0212	137.1607

Cartesian

5	-2.43796682	-0.49787411	0.03192344	6	0.95804489	1.88023591	-1.97075045
9	-2.89243555	-0.66363502	1.33048701	1	-0.09709246	1.84280181	-1.69028139
9	-2.13051319	0.80768526	-0.29075018	1	-0.23349001	-0.30293474	-2.87217283
9	-3.15351200	-1.19520020	-0.90952867	1	0.21633551	-0.36142272	3.87716556
8	-0.93943202	-1.22774935	-0.00068315	1	1.53252459	2.74545860	-1.63759327
6	-0.91492766	-2.62809277	0.40709102	1	2.58333635	0.98946869	-2.96206760
1	-1.56150293	-3.16108346	-0.29481116	1	-0.06809472	1.63054597	1.51769650
1	0.11631267	-2.98781991	0.32509819	6	0.84894955	-0.38767356	-4.75905609
1	-1.29473674	-2.73308849	1.43065989	6	-0.16614221	1.73163998	4.35249090
6	-0.26207566	0.51575613	3.41446996	1	-1.32637203	0.26872778	3.26271272
6	0.35785440	0.78938282	2.07674313	1	-0.66153926	1.52010500	5.30967474
6	1.37421846	0.10144205	1.52691352	1	0.88083768	1.99306715	4.55877924
1	-0.30982018	-0.70494270	0.57751966	1	-0.65430254	2.61068034	3.90863466
1	1.79017735	0.38205400	0.55725163	1	0.35444659	-1.30170798	-5.11664295
1	1.84079754	-0.73477364	2.05424714	1	0.33836570	0.47473732	-5.20906687
6	1.52227759	0.90746981	-2.69674397	1	1.88440537	-0.39659864	-5.13020372
6	0.80866730	-0.30514485	-3.22372246	1	1.28621459	-1.21227860	-2.81195736

TS BF_3·MeOH C8 A



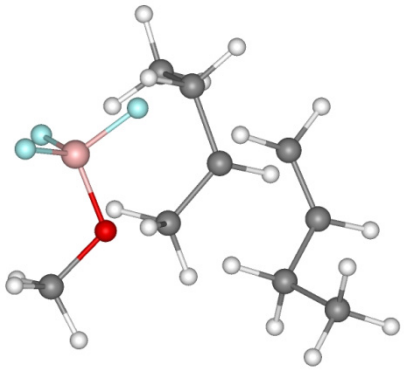
E = –754.095793 E_0 = –753.820323
ZPVE = 0.275470 a.u. = 172.8600 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6143	41.9586	0.8887	1.4812	-11.0287
rotational	14.7650	32.3220	0.8887	0.8887	-8.7481
vibrational	19.0140	72.9625	183.3482	183.3482	161.5945
total	52.3932	147.2432	185.1257	185.7182	141.8176

Cartesian

5	-1.93256629	-1.41929471	0.10561907	6	1.43888938	1.90040433	-0.88275284
9	-2.01307940	-1.18164706	1.51198328	1	2.49300098	1.61565530	-0.86051655
9	-1.96798980	-0.17054333	-0.57726413	1	0.30305102	-0.89118928	-1.81638563
9	-2.96166587	-2.26271272	-0.31333295	6	0.32127038	-0.03443923	-3.79414320
8	-0.58541077	-2.01562953	-0.21116588	1	1.91513705	-0.29882777	-2.30977058
6	-0.37968323	-3.32678056	0.30902129	1	-0.49869946	2.75120592	1.12909830
1	-1.15976357	-4.01120949	-0.05777359	1	-1.27818978	1.13693607	1.18777704
1	0.60391223	-3.68592620	-0.02595254	6	-0.62918502	1.90462589	3.12034011
1	-0.41259107	-3.32977247	1.41331971	1	1.18536282	2.89114022	-0.50783926
6	-0.45901862	1.75155890	1.58286774	1	-1.55813849	2.45722795	3.31113434
6	0.85463238	1.10946774	1.31838083	1	-0.71170056	0.92336375	3.60256004
6	1.03769183	-0.31869543	1.43345761	1	0.20154189	2.46045780	3.57790089
1	0.46961465	-0.91917729	0.63377225	1	1.73420691	1.74811089	1.42966664
1	2.08344722	-0.63678026	1.49182928	1	-0.49280104	1.52653337	-1.66697204
1	0.45185542	-0.68235308	2.29914188	1	0.51413506	-0.99711972	-4.28493404
6	0.54456699	1.18312049	-1.61464894	1	-0.76271695	0.14079468	-3.81342697
6	0.83804470	-0.07386385	-2.34206629	1	0.81283915	0.75535911	-4.37892485

TS BF_3·MeOH C8 B



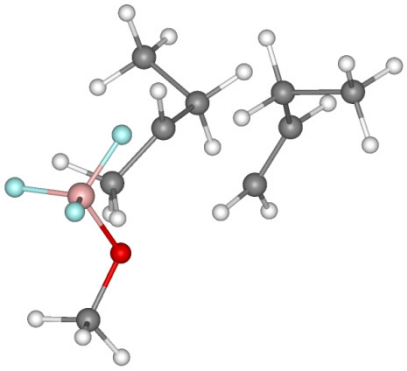
E = –754.096634 E_0 = –753.820587
ZPVE = 0.276047 a.u. = 173.2219 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6143	41.9586	0.8887	1.4812	-11.0287
rotational	14.8344	32.4601	0.8887	0.8887	-8.7892
vibrational	18.6170	71.8861	183.6244	183.6244	162.1915
total	52.0657	146.3048	185.4019	185.9943	142.3736

Cartesian

5	-2.06416154	-0.89491063	1.06984842	6	0.44840038	1.91105473	-0.32053095
9	-1.74475265	-0.86828655	2.46155310	1	-0.52586484	1.43976343	-0.15364307
9	-2.14594126	0.44476554	0.59147120	1	0.33005553	-0.49978495	-1.43531621
9	-3.25241351	-1.59146976	0.84813446	1	-0.75727034	1.34503984	2.47052670
8	-0.92460877	-1.52709711	0.31536663	1	0.56467688	2.95684242	-0.03535977
6	-0.73951417	-2.91592073	0.57788318	1	2.28006339	1.90794671	-1.39272070
1	-1.64971101	-3.47673345	0.31626090	1	2.13976598	1.73563552	1.47651684
1	0.09552683	-3.28059173	-0.03834901	6	1.27301478	0.10310495	-3.31933594
1	-0.51467687	-3.10172987	1.64312565	6	0.72194368	1.89737999	3.97730017
6	0.20340285	1.87526965	2.51504707	1	0.05829291	2.91244245	2.18660808
6	1.22070432	1.17820072	1.66860211	1	0.00799850	2.46474195	4.58869076
6	1.27383149	-0.27130887	1.65173364	1	0.79303378	0.88371372	4.38955402
1	0.42170134	-0.72369379	1.01975238	1	1.70467305	2.38294029	4.06046963
1	2.23536873	-0.68234980	1.32622850	1	1.22670364	-0.90255868	-3.75667500
1	0.97160047	-0.66906494	2.63525844	1	0.41079459	0.67458391	-3.68625736
6	1.36907840	1.34421575	-1.15223885	1	2.18980694	0.59161359	-3.67892265
6	1.24623966	0.00150193	-1.77739584	1	2.10883546	-0.61505449	-1.46264577

TS BF_3·MeOH C8 C



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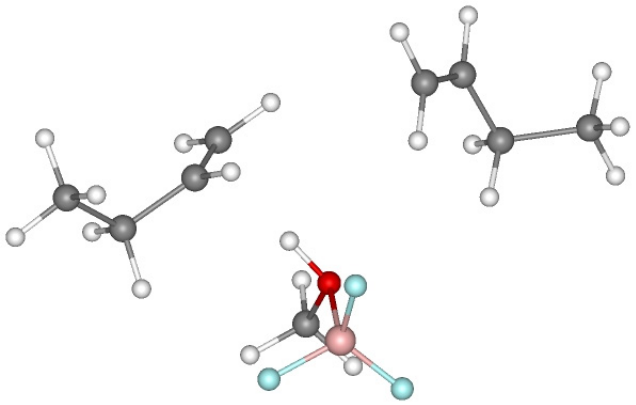
ZPVE = 0.275869 a.u. = 173.1103 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6143	41.9586	0.8887	1.4812	-11.0287
rotational	14.9498	32.6893	0.8887	0.8887	-8.8576
vibrational	19.0137	72.7978	183.5496	183.5496	161.8450
total	52.5777	147.4457	185.3271	185.9196	141.9586

Cartesian

5	-2.19872808	1.46978927	1.13948572	6	0.39629495	1.22833169	-2.36695981
9	-1.96638751	1.55726433	2.53426075	1	0.23542425	-2.00286198	-1.01280987
9	-1.01129067	1.84143794	0.43864518	1	0.00936667	-0.01278432	2.57551956
9	-3.28546619	2.25734639	0.75457013	1	-0.99442244	-0.60542852	1.36579978
8	-2.43910480	0.02561698	0.75874233	1	0.18014535	-1.79695272	2.17931390
6	-3.57671881	-0.57496375	1.37712741	1	-0.97771370	-0.60077113	-0.76541132
1	-4.48916292	-0.02742914	1.09410191	1	-0.49807563	1.57193804	-1.83183229
1	-3.65910578	-1.61335182	1.02579248	1	1.23171329	1.88716173	-2.06605172
1	-3.49069834	-0.56362957	2.47655869	6	0.21912019	1.34963250	-3.89577746
6	0.07094946	-0.78114176	1.78107417	1	1.65452790	-0.57839853	-2.39659452
6	1.07740319	-0.40296119	0.81922877	1	0.02412533	2.39569163	-4.16540337
6	2.35002327	-1.16983724	0.66847873	1	1.11773789	1.01947665	-4.43669701
1	2.15444756	-2.25241280	0.67924458	1	-0.63004875	0.74477243	-4.24006796
1	2.86295199	-0.91770566	-0.26840043	1	4.23149729	-1.33829176	1.74364722
6	3.27465439	-0.81191725	1.86056435	1	3.47930765	0.26650515	1.89624012
6	0.72979736	-0.16698451	-1.97142065	1	2.82795572	-1.11049521	2.81682587
6	-0.00886690	-0.94643342	-1.13380671	1	1.09834731	0.65978742	0.56601131

$(BF_3 \cdot MeOH)_2$-4 complex + 4



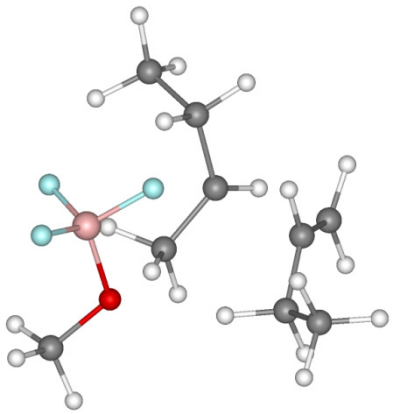
E = –754.144412 E_0 = –753.867501
ZPVE = 0.276910 a.u. = 173.7639 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6143	41.9586	0.8887	1.4812	-11.0287
rotational	15.1161	33.0197	0.8887	0.8887	-8.9561
vibrational	28.0485	95.6086	185.6512	185.6512	157.1455
total	61.7788	170.5870	187.4287	188.0212	137.1607

Cartesian

5	-2.43796682	-0.49787411	0.03192344	6	0.95804489	1.88023591	-1.97075045
9	-2.89243555	-0.66363502	1.33048701	1	-0.09709246	1.84280181	-1.69028139
9	-2.13051319	0.80768526	-0.29075018	1	-0.23349001	-0.30293474	-2.87217283
9	-3.15351200	-1.19520020	-0.90952867	1	0.21633551	-0.36142272	3.87716556
8	-0.93943202	-1.22774935	-0.00068315	1	1.53252459	2.74545860	-1.63759327
6	-0.91492766	-2.62809277	0.40709102	1	2.58333635	0.98946869	-2.96206760
1	-1.56150293	-3.16108346	-0.29481116	1	-0.06809472	1.63054597	1.51769650
1	0.11631267	-2.98781991	0.32509819	6	0.84894955	-0.38767356	-4.75905609
1	-1.29473674	-2.73308849	1.43065989	6	-0.16614221	1.73163998	4.35249090
6	-0.26207566	0.51575613	3.41446996	1	-1.32637203	0.26872778	3.26271272
6	0.35785440	0.78938282	2.07674313	1	-0.66153926	1.52010500	5.30967474
6	1.37421846	0.10144205	1.52691352	1	0.88083768	1.99306715	4.55877924
1	-0.30982018	-0.70494270	0.57751966	1	-0.65430254	2.61068034	3.90863466
1	1.79017735	0.38205400	0.55725163	1	0.35444659	-1.30170798	-5.11664295
1	1.84079754	-0.73477364	2.05424714	1	0.33836570	0.47473732	-5.20906687
6	1.52227759	0.90746981	-2.69674397	1	1.88440537	-0.39659864	-5.13020372
6	0.80866730	-0.30514485	-3.22372246	1	1.28621459	-1.21227860	-2.81195736

TS BF_3·MeOH C8 A



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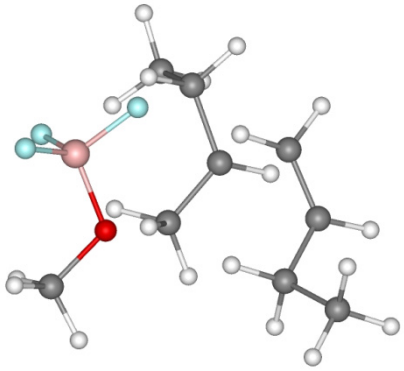
ZPVE = 0.275470 a.u. = 172.8600 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6143	41.9586	0.8887	1.4812	-11.0287
rotational	14.7650	32.3220	0.8887	0.8887	-8.7481
vibrational	19.0140	72.9625	183.3482	183.3482	161.5945
total	52.3932	147.2432	185.1257	185.7182	141.8176

Cartesian

5	-1.93256629	-1.41929471	0.10561907	6	1.43888938	1.90040433	-0.88275284
9	-2.01307940	-1.18164706	1.51198328	1	2.49300098	1.61565530	-0.86051655
9	-1.96798980	-0.17054333	-0.57726413	1	0.30305102	-0.89118928	-1.81638563
9	-2.96166587	-2.26271272	-0.31333295	6	0.32127038	-0.03443923	-3.79414320
8	-0.58541077	-2.01562953	-0.21116588	1	1.91513705	-0.29882777	-2.30977058
6	-0.37968323	-3.32678056	0.30902129	1	-0.49869946	2.75120592	1.12909830
1	-1.15976357	-4.01120949	-0.05777359	1	-1.27818978	1.13693607	1.18777704
1	0.60391223	-3.68592620	-0.02595254	6	-0.62918502	1.90462589	3.12034011
1	-0.41259107	-3.32977247	1.41331971	1	1.18536282	2.89114022	-0.50783926
6	-0.45901862	1.75155890	1.58286774	1	-1.55813849	2.45722795	3.31113434
6	0.85463238	1.10946774	1.31838083	1	-0.71170056	0.92336375	3.60256004
6	1.03769183	-0.31869543	1.43345761	1	0.20154189	2.46045780	3.57790089
1	0.46961465	-0.91917729	0.63377225	1	1.73420691	1.74811089	1.42966664
1	2.08344722	-0.63678026	1.49182928	1	-0.49280104	1.52653337	-1.66697204
1	0.45185542	-0.68235308	2.29914188	1	0.51413506	-0.99711972	-4.28493404
6	0.54456699	1.18312049	-1.61464894	1	-0.76271695	0.14079468	-3.81342697
6	0.83804470	-0.07386385	-2.34206629	1	0.81283915	0.75535911	-4.37892485

TS BF_3·MeOH C8 B



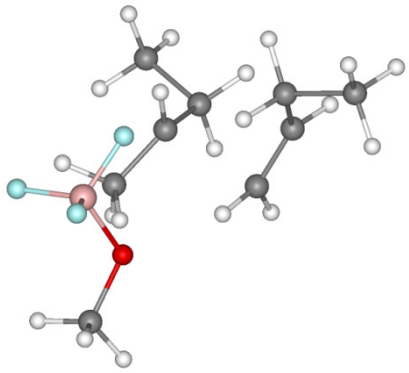
E = –754.096634 E_0 = –753.820587
ZPVE = 0.276047 a.u. = 173.2219 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6143	41.9586	0.8887	1.4812	-11.0287
rotational	14.8344	32.4601	0.8887	0.8887	-8.7892
vibrational	18.6170	71.8861	183.6244	183.6244	162.1915
total	52.0657	146.3048	185.4019	185.9943	142.3736

Cartesian

5	-2.06416154	-0.89491063	1.06984842	6	0.44840038	1.91105473	-0.32053095
9	-1.74475265	-0.86828655	2.46155310	1	-0.52586484	1.43976343	-0.15364307
9	-2.14594126	0.44476554	0.59147120	1	0.33005553	-0.49978495	-1.43531621
9	-3.25241351	-1.59146976	0.84813446	1	-0.75727034	1.34503984	2.47052670
8	-0.92460877	-1.52709711	0.31536663	1	0.56467688	2.95684242	-0.03535977
6	-0.73951417	-2.91592073	0.57788318	1	2.28006339	1.90794671	-1.39272070
1	-1.64971101	-3.47673345	0.31626090	1	2.13976598	1.73563552	1.47651684
1	0.09552683	-3.28059173	-0.03834901	6	1.27301478	0.10310495	-3.31933594
1	-0.51467687	-3.10172987	1.64312565	6	0.72194368	1.89737999	3.97730017
6	0.20340285	1.87526965	2.51504707	1	0.05829291	2.91244245	2.18660808
6	1.22070432	1.17820072	1.66860211	1	0.00799850	2.46474195	4.58869076
6	1.27383149	-0.27130887	1.65173364	1	0.79303378	0.88371372	4.38955402
1	0.42170134	-0.72369379	1.01975238	1	1.70467305	2.38294029	4.06046963
1	2.23536873	-0.68234980	1.32622850	1	1.22670364	-0.90255868	-3.75667500
1	0.97160047	-0.66906494	2.63525844	1	0.41079459	0.67458391	-3.68625736
6	1.36907840	1.34421575	-1.15223885	1	2.18980694	0.59161359	-3.67892265
6	1.24623966	0.00150193	-1.77739584	1	2.10883546	-0.61505449	-1.46264577

TS BF_3·MeOH C8 C



E = –754.095447 E_0 = –753.819578
ZPVE = 0.275869 a.u. = 173.1103 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6143	41.9586	0.8887	1.4812	-11.0287
rotational	14.9498	32.6893	0.8887	0.8887	-8.8576
vibrational	19.0137	72.7978	183.5496	183.5496	161.8450
total	52.5777	147.4457	185.3271	185.9196	141.9586

Cartesian

5	-2.19872808	1.46978927	1.13948572	6	0.39629495	1.22833169	-2.36695981
9	-1.96638751	1.55726433	2.53426075	1	0.23542425	-2.00286198	-1.01280987
9	-1.01129067	1.84143794	0.43864518	1	0.00936667	-0.01278432	2.57551956
9	-3.28546619	2.25734639	0.75457013	1	-0.99442244	-0.60542852	1.36579978
8	-2.43910480	0.02561698	0.75874233	1	0.18014535	-1.79695272	2.17931390
6	-3.57671881	-0.57496375	1.37712741	1	-0.97771370	-0.60077113	-0.76541132
1	-4.48916292	-0.02742914	1.09410191	1	-0.49807563	1.57193804	-1.83183229
1	-3.65910578	-1.61335182	1.02579248	1	1.23171329	1.88716173	-2.06605172
1	-3.49069834	-0.56362957	2.47655869	6	0.21912019	1.34963250	-3.89577746
6	0.07094946	-0.78114176	1.78107417	1	1.65452790	-0.57839853	-2.39659452
6	1.07740319	-0.40296119	0.81922877	1	0.02412533	2.39569163	-4.16540337
6	2.35002327	-1.16983724	0.66847873	1	1.11773789	1.01947665	-4.43669701
1	2.15444756	-2.25241280	0.67924458	1	-0.63004875	0.74477243	-4.24006796
1	2.86295199	-0.91770566	-0.26840043	1	4.23149729	-1.33829176	1.74364722
6	3.27465439	-0.81191725	1.86056435	1	3.47930765	0.26650515	1.89624012
6	0.72979736	-0.16698451	-1.97142065	1	2.82795572	-1.11049521	2.81682587
6	-0.00886690	-0.94643342	-1.13380671	1	1.09834731	0.65978742	0.56601131

S3.5. Chain termination in the presence of an ether

To study the interactions of growing polymer chains with an ether, model reactions of $[Bu^tCH_2CMe_2]^+$ with dimethyl (Me_2O), diethyl (Et_2O), methyl-*tert*-butyl (Bu^tOMe), dipropyl (Pr_2O) and diisopropyl (Pr^i_2O) ethers, as well as tetrahydrofuran (THF), were examined. Along with the chain-controlling reactions of deprotonation of CH_3/CH_2 groups, the formation of C–O complexes that affects on the rate of polymerization has been considered.

As can be seen from the data in Table S2, deprotonation of CH_3 group is a barrierless process for Me_2O, Et_2O, Pr_2O and Pr^i_2O; for Bu^tOMe and THF it is almost barrierless, with activation energies not exceeding ~0.6 kcal·mol^{-1} (*G* scale). In case of the deprotonation of CH_2 group, Gibbs free energy of activation ranges from 1.5 to 6.0 kcal·mol^{-1}, and is 2.1 (^{t}BuOMe) or 1.3 kcal·mol^{-1} (THF) higher than that for the deprotonation of CH_3 group. The most sterically hindered ethers seem to be the least prone to the formation of C–O complexes: ^{t}BuOMe does not form such a complex and ^{i}Pr$_2$O has the highest ΔG value among others; the least sterically hindered ether, THF, exhibits the highest affinity to this process (ΔG < 0). Teking into account the activation barriers for deprotonation and the stability of the corresponding C–O complexes, calculations predict that ^{t}BuOMe and ^{i}Pr$_2$O are the most suitable ethers for the synthesis of HRPIB.

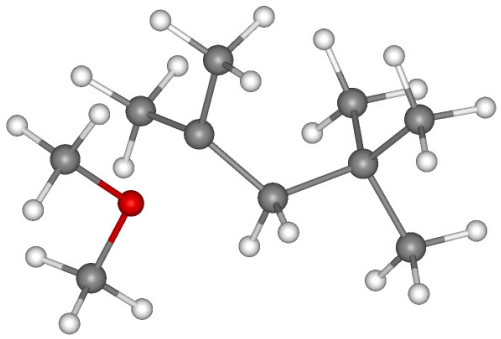
Table S2. Free energies of activation ($\Delta G^{\ddagger}$), free energies (ΔG) and free entalpies (ΔH) for the reactions of **IB2-cat** with ethers (all energies given in kcal·mol^{-1}).

	Me_2O	Et_2O	Bu^tOMe	Pr_2O	Pr^i_2O	THF
			Formation of C–O complexes[a]			
ΔG‡	*barrierless*	*barrierless*	*no*	*barrierless*	*barrierless*	*barrierless*
ΔG	4.83	5.58	*no*	4.56	9.73	−0.61
ΔH	−8.54	−8.88	*no*	−10.11	−5.94	−15.54
			Deprotonation of CH_3 group			
ΔG‡	*barrierless*	*barrierless*	0.57	*barrierless*	*barrierless*	0.21
ΔG	−1.23	−1.34	0.53	−2.27	−4.52	−2.95
ΔH	−10.69	−12.19	−0.31	−13.38	−15.71	−14.24
			Deprotonation of CH_2 group			
ΔG‡	3.05	5.98	2.64	2.93	2.48	1.54
ΔG	4.65	2.34	−2.36	1.26	−1.21	−0.15
ΔH	−6.34	−8.99	−13.57	−10.22	−12.58	−11.99

[a]Instead of a C–O complex, ^{t}BuOMe forms a $CH_3\cdots O$ adduct (ΔG = −2.66 kcal·mol^{-1}, ΔH = −13.22 kcal·mol^{-1}).

The energy parameters, molecular structures and cartesian coordinates of some complexes between [^{t}BuCH$_2$CMe$_2$]$^+$ and ethers, as well as calculated TS of the deprotonation of CH_3 and CH_2 groups are presented below.

[Bu^{t}CH$_2$CMe$_2$]$^+$-OMe$_2$ C-O complex



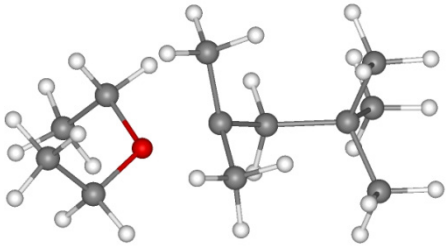
E = –469.381392 E_0 = –469.074275
ZPVE = 0.307117 a.u. = 192.7188 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.1833	41.1022	0.8887	1.4812	-10.7734
rotational	13.9252	30.6532	0.8887	0.8887	-8.2505
vibrational	11.2529	49.7267	200.8776	200.8776	186.0516
total	43.3614	121.4821	202.6551	203.2476	167.0277

Cartesian

6	0.19422533	0.86356962	-0.16190192	1	2.75309300	0.43154544	1.27783537
6	1.16917706	0.50549412	-1.26656055	1	2.10672879	2.08034325	1.52263236
6	1.59315777	-0.93032801	-1.36582816	1	-0.36733341	1.14004409	3.23163843
6	2.25487924	1.50088561	-1.56293428	1	-0.38850722	2.42224336	2.00397015
1	2.22295785	-1.12955558	-2.24012613	1	-1.52330852	1.05210555	1.88783467
1	2.22060180	-1.13020444	-0.48427609	1	0.45170006	-1.08732045	2.77004170
1	0.74802917	-1.62758601	-1.32551873	1	-0.62381691	-1.31408155	1.38047504
1	2.99537325	1.42203367	-0.75149065	1	1.12783611	-1.59671044	1.22676635
1	2.78740025	1.28070354	-2.49717784	6	0.48371509	-0.00756827	-3.93014979
1	1.89734912	2.53705096	-1.56221378	1	1.41207600	0.44350976	-4.30508375
1	0.01688022	1.94756866	-0.19991761	1	0.60855865	-1.07050943	-3.71914315
1	-0.76070487	0.35649368	-0.36690459	1	-0.32536370	0.12919217	-4.65600300
6	0.54613090	0.54190999	1.34643364	8	0.05616033	0.64755052	-2.69085193
6	-0.49718705	1.33925414	2.15952396	6	-0.41395140	2.00609684	-2.98124385
6	0.36844826	-0.94956404	1.68318629	1	-1.28229642	1.90658700	-3.64173722
6	1.95038331	1.01608276	1.75180101	1	-0.72107434	2.45878291	-2.03684974
1	2.07731032	0.89621514	2.83639550	1	0.37790880	2.58996296	-3.46717858

$[Bu^tCH_2CMe_2]^+$-OEt_2 C-O complex



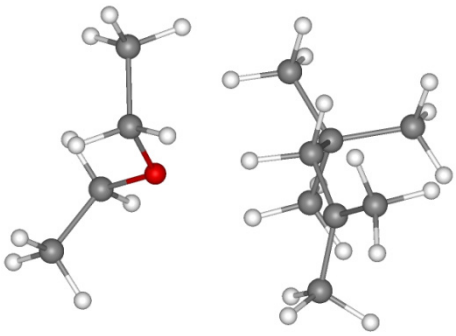
E = –547.932416 E_0 = –547.569799
ZPVE = 0.362617 a.u. = 227.5454 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.4266	41.5857	0.8887	1.4812	-10.9175
rotational	14.4767	31.7491	0.8887	0.8887	-8.5773
vibrational	14.1666	60.6718	237.2412	237.2412	219.1519
total	47.0698	134.0065	239.0186	239.6111	199.6571

Cartesian

6	-0.21710430	-0.04925597	1.22343457	1	-1.11378801	1.26147413	3.44620109
6	0.85472411	-0.21752547	0.14830036	1	-2.08962679	-0.19633628	3.13053346
6	1.42349231	-1.60414362	-0.00044445	1	0.02326152	-2.19939089	4.00996256
6	1.90415573	0.86739188	0.07970875	1	-0.91363329	-2.41456294	2.52196646
1	2.09569240	-1.69905818	-0.86125040	1	0.86472160	-2.50958800	2.49444151
1	2.03953123	-1.78277910	0.89230156	6	0.13726223	-0.81029826	-2.50065327
1	0.65409279	-2.38455939	-0.02135283	6	1.25875068	-0.31283581	-3.38830113
1	2.55498338	0.74854642	0.95768631	1	0.31326377	-1.82403517	-2.13438559
1	2.53790545	0.77991527	-0.81047016	1	-0.82799548	-0.81002522	-3.01930904
1	1.48202145	1.87687480	0.13750057	8	-0.12002926	-0.00580538	-1.26785719
1	-0.50586665	1.01173079	1.24953568	6	-0.56184644	1.39168501	-1.54710424
1	-1.10190856	-0.62111235	0.90629476	6	-1.88293052	1.42345428	-2.28771591
6	0.05577929	-0.45567989	2.72204471	1	-0.66880584	1.84283042	-0.55739689
6	-1.12136972	0.16363429	3.50788069	1	0.24195468	1.90404737	-2.09016490
6	0.00948700	-1.98073983	2.93326187	1	-2.23005629	2.46662259	-2.29470181
6	1.36813509	0.11404584	3.28408003	1	-1.80209351	1.10457718	-3.33351326
1	1.41556966	-0.07594460	4.36513376	1	-2.64425278	0.81995231	-1.77720559
1	2.26036716	-0.35690334	2.84546065	1	1.07467961	0.69213867	-3.78788376
1	1.43854582	1.20226049	3.14160872	1	2.23591208	-0.32801756	-2.89056230
1	-1.05252314	-0.11291632	4.56847715	1	1.31798697	-0.99422920	-4.24961615

TS [Bu^{t}CH$_2$CMe$_2$]$^+$ OEt$_2$ to *endo*



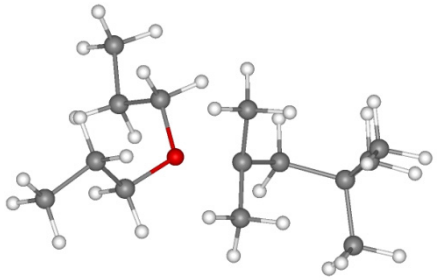
E = –547.923932 E_0 = –547.567736
ZPVE = 0.356196 a.u. = 223.5164 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.4266	41.5857	0.8887	1.4812	-10.9175
rotational	14.6716	32.1365	0.8887	0.8887	-8.6928
vibrational	19.2198	73.1686	233.9441	233.9441	212.1289
total	52.3181	146.8909	235.7216	236.3141	192.5186

Cartesian

6	1.23262823	0.87906402	0.42098114	1	-0.17011109	2.02937555	2.41819978
6	2.23780131	0.53366941	-0.54515362	1	-0.83611512	0.38803080	2.22041154
6	2.67893529	-0.84907633	-0.80015862	1	1.47080708	-1.15545762	3.33517122
6	2.82684493	1.59480643	-1.38788319	1	0.78989226	-1.61872959	1.77059519
1	2.45239282	-1.08165157	-1.85742760	1	2.54826331	-1.34389460	1.95536065
1	3.78165793	-0.90216976	-0.75014609	6	-1.80525875	-1.59359455	-0.37028745
1	2.22691560	-1.60173929	-0.15421376	6	-1.98699403	-2.68334293	-1.41642487
1	3.56997705	2.11741042	-0.74959743	1	-1.23002660	-1.97423041	0.48558825
1	3.34547114	1.22390735	-2.27825856	1	-2.77443695	-1.24052238	0.01430760
1	2.09034443	2.36922240	-1.64615536	8	-1.03934777	-0.46629903	-0.87963253
1	0.99043322	1.94898951	0.36043292	6	-1.83566582	0.50008845	-1.61690116
1	0.31812367	0.29476070	0.03031244	1	-2.49479604	-0.04325429	-2.31200337
6	1.34136569	0.50183398	1.96731389	6	-2.63562322	1.44326174	-0.72966135
6	0.01895964	0.96238387	2.60251284	1	-1.11207473	1.05924118	-2.22748613
6	1.55241370	-0.99022651	2.25184703	1	-2.57402205	-2.33532858	-2.27632999
6	2.51090336	1.31836605	2.54675269	1	-1.01704144	-3.04860973	-1.77858329
1	2.55800366	1.17157376	3.63509703	1	-2.52686834	-3.52999783	-0.96882218
1	3.47716880	1.00135767	2.12714267	1	-3.18997359	2.15170407	-1.36144626
1	2.38619423	2.39550972	2.36529851	1	-3.37154531	0.91045964	-0.11347973
1	0.06451078	0.81676733	3.69044876	1	-1.97912288	2.02298450	-0.06645461

[Bu^{t}CH$_2$CMe$_2$]$^+$-OPr$_2$ C-O complex



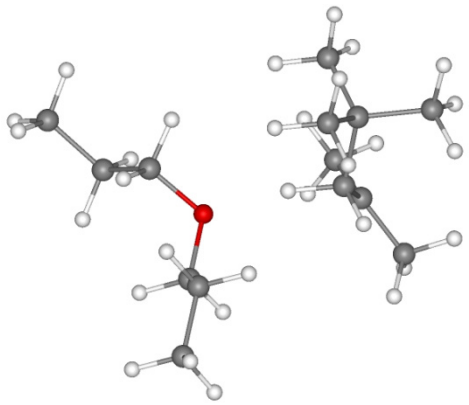
E = –626.476180 E_0 = –626.058059
ZPVE = 0.418122 a.u. = 262.3753 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6359	42.0016	0.8887	1.4812	-11.0416
rotational	15.0687	32.9256	0.8887	0.8887	-8.9280
vibrational	17.9682	74.2217	273.8586	273.8586	251.7294
total	51.6728	149.1489	275.6360	276.2285	231.7598

Cartesian

6	-0.19142036	0.03977639	1.19379878	1	-1.13389301	-2.18223953	2.58605051
6	0.87512600	-0.27955648	0.14518432	1	0.62690759	-2.44882536	2.59794116
6	1.31836438	-1.71885014	0.08159994	6	0.15678976	-0.94053221	-2.47373486
6	2.02510142	0.69794720	0.05150558	6	1.34141123	-0.61769736	-3.36785436
1	1.99202681	-1.91855824	-0.76001108	1	0.22019359	-1.94875920	-2.05637288
1	1.90094757	-1.90508819	0.99460983	1	-0.79269576	-0.86813456	-3.01749134
1	0.48120847	-2.42641068	0.08304008	8	-0.04185069	-0.05120164	-1.28767514
1	2.65066624	0.55738068	0.94408041	6	-0.35154793	1.36545765	-1.64269996
1	2.65789747	0.51232356	-0.82437986	6	-1.65648878	1.49609041	-2.41119576
1	1.69899392	1.74398553	0.05748950	1	-0.43536520	1.87458730	-0.67822617
1	-0.37759843	1.12344587	1.16495001	1	0.50346339	1.77825046	-2.19360876
1	-1.12242508	-0.45878303	0.88502169	6	-2.04096127	2.97974968	-2.51527667
6	0.01745593	-0.31821164	2.71366096	1	-1.56277001	1.07802725	-3.42339277
6	-1.10578191	0.44783404	3.44738770	1	-2.44584680	0.93536001	-1.88839066
6	-0.17947805	-1.81991613	2.99517608	1	1.26451290	0.40576825	-3.76302695
6	1.36989844	0.14922008	3.27536345	1	2.28296924	-0.67977041	-2.80290031
1	1.38229156	0.00704373	4.36473417	6	1.37435937	-1.61251259	-4.53841686
1	2.21907282	-0.42491019	2.87609434	1	-2.97069740	3.08667016	-3.08677936
1	1.54719067	1.21764040	3.08435178	1	-2.20453835	3.42421412	-1.52395332
1	-1.08065963	0.21645097	4.52068710	1	-1.26592577	3.56389880	-3.03069735
1	-0.99050492	1.53572392	3.33593965	1	2.22222972	-1.39280748	-5.19814491
1	-2.09856272	0.16556467	3.06754494	1	1.48432529	-2.64745927	-4.18599749
1	-0.20343696	-1.98680282	4.08094788	1	0.45812857	-1.55341077	-5.14193964

TS [Bu^{t}CH$_2$CMe$_2$]$^+$ OPr$_2$ to *endo*



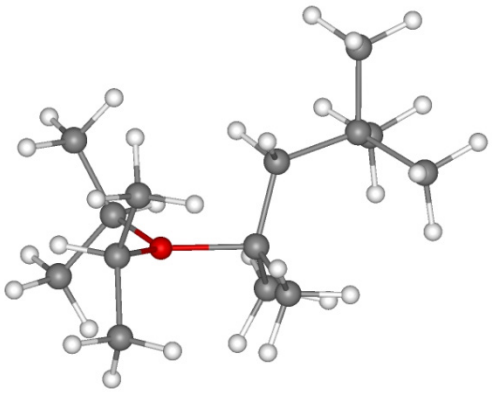
E = –626.466742 E_0 = –626.055313
ZPVE = 0.411430 a.u. = 258.1760 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6359	42.0016	0.8887	1.4812	-11.0416
rotational	15.2218	33.2299	0.8887	0.8887	-9.0188
vibrational	23.4643	87.6420	270.4041	270.4041	244.2736
total	57.3221	162.8735	272.1815	272.7740	224.2133

Cartesian

6	0.86208314	0.81124973	0.20909514	1	0.47801369	-1.71441770	1.52174151
6	1.88027740	0.50572211	-0.75771368	1	2.23403168	-1.41220939	1.68446445
6	2.32476807	-0.86655891	-1.05726147	6	-2.09972048	-1.75037920	-0.63523352
6	2.47912669	1.59834599	-1.55148542	6	-2.14249969	-2.86888623	-1.67254102
1	2.10346723	-1.06092572	-2.12365627	1	-1.56810236	-2.08965087	0.26690415
1	3.42709994	-0.92240369	-1.00359702	1	-3.11641669	-1.45794833	-0.32677099
1	1.86683834	-1.64193726	-0.44286823	8	-1.37616301	-0.58387178	-1.11216223
1	3.18583369	2.12369180	-0.87570643	6	-2.20925784	0.36520815	-1.82794213
1	3.03431582	1.26043272	-2.43275476	1	-2.89093161	-0.19184077	-2.49186087
1	1.73380983	2.36222959	-1.81765270	6	-2.99253511	1.31157827	-0.92161369
1	0.60147560	1.87770939	0.17258558	1	-1.52098060	0.93290836	-2.47275591
1	-0.03972121	0.21245615	-0.17806929	1	-2.63862467	-2.50776458	-2.58665323
6	0.99501085	0.41058919	1.75160158	1	-1.11147594	-3.13444614	-1.95362723
6	-0.33076283	0.83377147	2.40469241	6	-2.87925148	-4.10018635	-1.13331211
6	1.23700452	-1.08227539	2.00366426	6	-3.84778118	2.28511739	-1.74022377
6	2.15374851	1.23853016	2.33458614	1	-3.63738060	0.73269010	-0.24257328
1	2.21141219	1.07623255	3.42027760	1	-2.28560972	1.87100232	-0.28797600
1	3.12271428	0.94538242	1.90400493	1	-2.89404368	-4.90147066	-1.88260925
1	2.00854087	2.31597042	2.17079735	1	-2.39242864	-4.49759674	-0.23096311
1	-0.27442390	0.66583788	3.48901963	1	-3.92205596	-3.86457753	-0.87794250
1	-0.54008603	1.90074897	2.24403834	1	-4.39379025	2.97243357	-1.08208203
1	-1.17795956	0.25248903	2.01569438	1	-3.23027205	2.89229178	-2.41785812
1	1.17538118	-1.26949847	3.08480692	1	-4.58902645	1.75027072	-2.35037994

$[Bu^tCH_2CMe_2]^+$-OPr^i_2 C-O complex



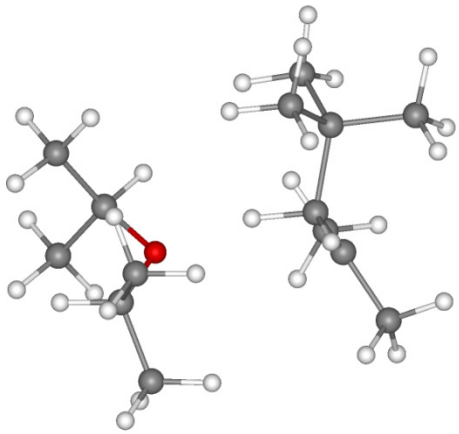
E = –626.474987 E_0 = –626.058166
ZPVE = 0.416821 a.u. = 261.5592 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6359	42.0016	0.8887	1.4812	-11.0416
rotational	14.8095	32.4106	0.8887	0.8887	-8.7745
vibrational	15.9243	69.9751	272.9873	272.9873	252.1242
total	49.3698	144.3873	274.7647	275.3572	232.3082

Cartesian

6	-0.27499878	-0.26324752	1.13052988	1	-0.26686248	-2.93053269	1.94143891
6	0.83929706	0.04106620	0.12704754	1	1.45112717	-2.47690964	2.08480453
6	1.79905713	-1.08473444	-0.21278334	6	-0.65607744	-0.90597546	-1.94983280
6	1.61200440	1.31384647	0.39350611	6	-0.09241052	-1.12402093	-3.34426403
1	2.38386321	-0.84477597	-1.10916972	1	-0.33294839	-1.71954370	-1.29450750
1	2.50883722	-1.16939270	0.62206787	6	-2.17427135	-0.81502819	-1.90488815
1	1.32734644	-2.06587720	-0.32626480	8	0.03775946	0.30239263	-1.32735538
1	2.17314553	1.15112829	1.32269096	6	-0.44466799	1.64874160	-1.88762617
1	2.34265900	1.52139652	-0.39529222	6	-1.36826670	2.39883780	-0.94369531
1	0.97333902	2.18549991	0.56116140	6	0.71785271	2.46498919	-2.42907310
1	-0.84258503	0.66746134	1.27617335	1	-1.03279912	1.29932261	-2.74312210
1	-0.96318358	-0.98855358	0.67268080	1	0.30000556	3.20531654	-3.12691808
6	0.03147080	-0.84440714	2.56091642	1	1.25946259	3.01601458	-1.65426409
6	-1.31975698	-0.75970507	3.30612421	1	1.42110479	1.84140646	-2.99472356
6	0.45248586	-2.32524967	2.51336527	1	-1.80759013	3.23132896	-1.51283455
6	1.06977689	-0.03588786	3.35603118	1	-2.19409943	1.77529478	-0.58336192
1	1.09248495	-0.39356369	4.39479303	1	-0.84579754	2.83745909	-0.08650191
1	2.09073520	-0.15345719	2.96465087	1	-0.38609272	-0.32886362	-4.04266644
1	0.82381928	1.03560889	3.38547182	1	1.00108349	-1.20384252	-3.33253837
1	-1.22415340	-1.19252026	4.31098270	1	-0.49712765	-2.06689382	-3.73799777
1	-1.65234864	0.28227466	3.41924739	1	-2.55470204	-0.61960334	-0.89560026
1	-2.10711741	-1.31665885	2.77674675	1	-2.58341789	-0.06772663	-2.59651184
1	0.48039860	-2.73129082	3.53402305	1	-2.56784177	-1.79112434	-2.22266102

TS [Bu^{t}CH$_2$CMe$_2$]$^+$ OPr$^i_2$ to *endo*



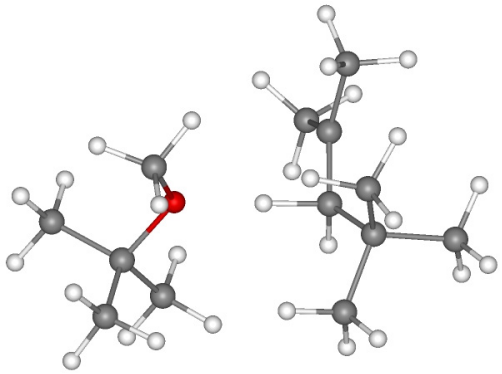
E = –626.472237 E_0 = –626.061972
ZPVE = 0.410265 a.u. = 257.4455 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.6359	42.0016	0.8887	1.4812	-11.0416
rotational	14.9933	32.7758	0.8887	0.8887	-8.8834
vibrational	21.3107	83.0453	269.5791	269.5791	244.8191
total	54.9399	157.8227	271.3566	271.9491	224.8942

Cartesian

6	0.34691194	0.62313086	-0.11680140	1	-0.33413705	-1.68455386	1.44014347
6	1.34585035	0.14803401	-1.03609657	1	1.44626784	-1.58285296	1.60187817
6	1.72008753	-1.27005792	-1.16947305	6	-2.39899945	-2.06365752	-1.12844968
6	1.99576175	1.10739493	-1.95142341	6	-2.65022397	-2.88706326	-2.39142084
1	1.52407885	-1.57230258	-2.21494222	1	-1.51131666	-2.47647572	-0.62163216
1	2.81650519	-1.37119615	-1.06908739	6	-3.57159591	-2.10082293	-0.15131421
1	1.20822942	-1.94674897	-0.48493382	8	-1.96202302	-0.70408756	-1.45810080
1	2.68256521	1.72266972	-1.33493483	6	-2.95281434	0.16655508	-2.09894562
1	2.56924295	0.64122522	-2.75903177	1	-3.82254839	-0.45102972	-2.36892962
1	1.26719820	1.83053505	-2.34983730	6	-3.40519857	1.26242268	-1.13688278
1	0.16790603	1.69646728	-0.26895523	6	-2.33394027	0.73012799	-3.37365484
1	-0.59199768	0.06677551	-0.47393847	1	-3.05988646	1.36414409	-3.90091777
6	0.43687335	0.37378490	1.45696473	1	-1.45848095	1.35426760	-3.13904858
6	-0.82802600	1.01635540	2.04941750	1	-2.02254605	-0.07354393	-4.05275869
6	0.49532264	-1.10294402	1.86674249	1	-3.35549951	-1.52269971	0.75687689
6	1.68562734	1.11570215	1.96584487	1	-4.49633265	-1.71529126	-0.60216099
1	1.72410464	1.06293023	3.06304002	1	-3.76394153	-3.14052963	0.14729194
1	2.61328673	0.66751117	1.57975590	1	-3.54405618	-2.54874253	-2.93320155
1	1.66871715	2.17970276	1.68896544	1	-1.78920472	-2.84071994	-3.07106090
1	-0.79087228	0.95371532	3.14569020	1	-2.81300235	-3.93833089	-2.11657500
1	-0.90927905	2.07874703	1.77972269	1	-4.16977167	1.88900304	-1.61680400
1	-1.73825598	0.50297236	1.71131277	1	-3.83771896	0.84351349	-0.22003073
1	0.40714222	-1.16766512	2.96022248	1	-2.56342053	1.91494167	-0.86307031

$[Bu^tCH_2CMe_2]^+$ OBu^tMe H-O complex



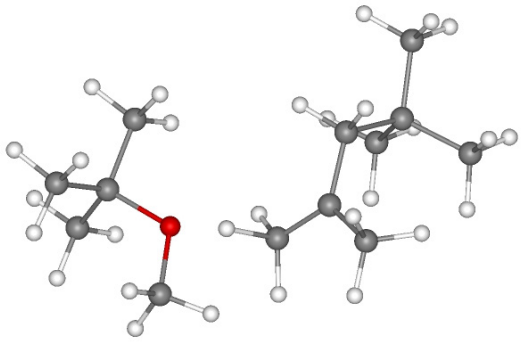
E = –587.205825 E_0 = –586.823016
ZPVE = 0.382809 a.u. = 240.2164 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.5349	41.8009	0.8887	1.4812	-10.9817
rotational	14.9654	32.7203	0.8887	0.8887	-8.8668
vibrational	20.0755	78.0597	251.5954	251.5954	228.3219
total	53.5758	152.5809	253.3729	253.9654	208.4734

Cartesian

6	1.21981359	0.40312693	0.32231465	1	0.62028116	-0.33994418	3.72577500
6	2.05682755	-0.51303941	-0.36897036	1	0.02440993	-1.24370718	2.32999587
6	2.57932687	-1.78085899	0.19828358	1	1.75826740	-1.27372181	2.76393890
6	2.41037750	-0.23827638	-1.78210700	6	-1.62971568	-1.83366704	-0.16137570
1	2.91230273	-2.47737956	-0.57894403	1	-2.22556353	-2.46408963	-0.83441061
1	3.45890999	-1.52974153	0.82100165	1	-2.22811580	-1.56612921	0.72080970
1	1.86973095	-2.26656699	0.87633049	1	-0.75004578	-2.40713406	0.15572348
1	3.51359677	-0.17617629	-1.84329736	8	-1.13821328	-0.66896349	-0.85112727
1	2.14189482	-1.09219670	-2.42375350	6	-2.16974115	0.14889856	-1.57117188
1	1.98366451	0.69031197	-2.17269921	6	-2.62940478	-0.64170939	-2.79920602
1	1.18607450	1.36781776	-0.20857520	1	-3.30750132	-0.01891912	-3.39796138
1	0.19322470	-0.07392203	-0.12869769	1	-3.18181729	-1.55049932	-2.52803969
6	1.08865869	0.62769669	1.85291600	1	-1.77376342	-0.91926426	-3.42866993
6	-0.11215959	1.57156003	2.06178999	1	-3.92045665	-0.39724141	-0.36526987
6	0.86580420	-0.63954902	2.69788170	6	-3.33852315	0.48961678	-0.64690220
6	2.37392259	1.34584582	2.31950116	1	-4.02204990	1.17076528	-1.17096889
1	2.29102921	1.59739327	3.38594413	1	-2.99551225	0.99748284	0.26472566
1	3.26595974	0.71491903	2.19587135	6	-1.42413902	1.41134882	-1.99830639
1	2.53562784	2.28300095	1.76811051	1	-2.08843040	2.04383063	-2.60032487
1	-0.18459362	1.85758829	3.11932373	1	-1.10167587	2.00008607	-1.12909639
1	-0.00774751	2.49587393	1.47492325	1	-0.55228186	1.16180885	-2.61858249
1	-1.05802596	1.08745265	1.78070474				

TS [Bu^{t}CH$_2$CMe$_2$]$^+$ OBu^{t}Me to *exo*



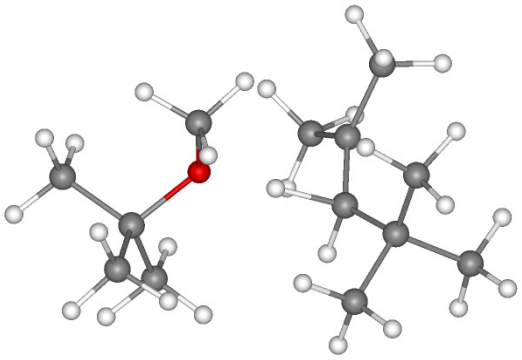
E = –587.205797 E_0 = –586.823862
ZPVE = 0.381935 a.u. = 239.6677 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.5349	41.8009	0.8887	1.4812	-10.9817
rotational	14.9510	32.6917	0.8887	0.8887	-8.8583
vibrational	18.6227	73.6639	250.5969	250.5969	228.6340
total	52.1086	148.1565	252.3743	252.9668	208.7940

Cartesian

6	0.94962043	0.48002416	0.47319219	1	2.40470767	-1.18164325	3.22948718
6	2.07646942	0.79021072	-0.43924651	1	1.77382195	-1.88417971	1.73213565
6	2.78515744	-0.22620650	-1.09676838	1	3.22979760	-0.84912419	1.70300722
6	2.37886786	2.21743202	-0.72180510	6	2.50540519	0.25949010	-4.42152214
1	2.13298345	-0.28612712	-2.20421100	1	1.98134041	0.56336170	-5.33427334
1	3.78318810	0.02361979	-1.47494161	1	3.32539368	-0.42977047	-4.66209316
1	2.67360616	-1.24549818	-0.71497244	1	2.90703773	1.15307975	-3.93002224
1	3.28566313	2.36277318	-1.31856287	8	1.56292105	-0.32675159	-3.49028444
1	1.51798534	2.67127347	-1.24275804	6	0.92746061	-1.64064527	-3.89453602
1	2.46250248	2.77787876	0.22236913	6	0.19168359	-1.42204773	-5.21565294
1	0.21614955	1.29888904	0.45433530	1	-0.40111962	-2.31832790	-5.44138002
1	0.45646223	-0.44834912	0.14879932	1	0.87875909	-1.26881683	-6.05731297
6	1.34240615	0.25010005	2.00304484	1	-0.49618730	-0.56890368	-5.14872456
6	0.00587316	0.01063839	2.72898412	1	2.70179987	-2.54247260	-4.81849766
6	2.24027371	-0.98479527	2.16098905	6	1.99298894	-2.72965312	-4.00185680
6	2.03295612	1.48576748	2.59796429	1	1.50287831	-3.68865919	-4.21668577
1	2.16204619	1.34670460	3.68025041	1	2.55108571	-2.84402966	-3.06267858
1	3.03465152	1.65126097	2.17598534	6	-0.05948250	-1.92409503	-2.76475501
1	1.43355191	2.39750719	2.45781875	1	-0.63218969	-2.82987952	-3.00023341
1	0.19235452	-0.17066158	3.79652834	1	0.45661134	-2.10132885	-1.81123865
1	-0.65954041	0.88159782	2.64747167	1	-0.76810992	-1.09401059	-2.64571810
1	-0.52093035	-0.86611199	2.32625556				

TS [Bu^{t}CH$_2$CMe$_2$]$^+$ OBu^{t}Me to *endo*



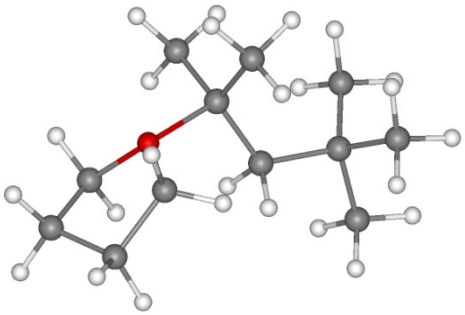
E = –587.198129 E_0 = –586.817136
ZPVE = 0.380993 a.u. = 239.0766 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.5349	41.8009	0.8887	1.4812	-10.9817
rotational	14.7223	32.2372	0.8887	0.8887	-8.7228
vibrational	17.6066	72.2051	250.1729	250.1729	228.6449
total	50.8638	146.2432	251.9503	252.5428	208.9404

Cartesian

6	0.43783334	0.49858245	-0.22551568	1	-0.11323425	-0.24042597	3.19044065
6	1.22131789	-0.42941213	-0.92628407	1	-0.66039413	-1.21284473	1.82214200
6	1.71450877	-1.73025048	-0.39104396	1	1.07638061	-1.11382389	2.23272991
6	1.57621145	-0.15512756	-2.34809494	6	-2.33093071	-1.68144560	-0.66036618
1	1.85032213	-2.46954775	-1.19007170	1	-2.94336128	-2.30059648	-1.32642794
1	2.71469235	-1.55082369	0.04539484	1	-2.91219568	-1.39082003	0.22442789
1	1.09528756	-2.14098096	0.40982056	1	-1.45456767	-2.26385760	-0.35342118
1	2.67654824	-0.18137564	-2.43808341	8	-1.83179736	-0.52710319	-1.37356985
1	1.21269965	-0.96158510	-3.00369930	6	-2.86260080	0.30931845	-2.10848665
1	1.22046971	0.81540227	-2.70800686	6	-3.30661798	-0.49409324	-3.33100915
1	0.37786272	1.46008849	-0.75800586	1	-3.98211265	0.12282285	-3.93875480
1	-0.64625102	-0.01280501	-0.75874919	1	-3.85937071	-1.40181971	-3.05749297
6	0.27361548	0.71892506	1.29657197	1	-2.44591975	-0.77245009	-3.95284534
6	-0.97769034	1.59423959	1.50945079	1	-4.61078978	-0.24069053	-0.90287942
6	0.14149153	-0.54420048	2.16591406	6	-4.03289270	0.64733148	-1.18866932
6	1.51757777	1.51891339	1.75005257	1	-4.71804428	1.31817687	-1.72400796
1	1.42614472	1.77250969	2.81549764	1	-3.69872618	1.16829050	-0.28180441
1	2.44166422	0.93802518	1.61982572	6	-2.10947871	1.56633759	-2.53247380
1	1.62000191	2.45950031	1.19047749	1	-2.77181363	2.19229364	-3.14350295
1	-1.04833126	1.89728749	2.56237292	1	-1.79684234	2.16320014	-1.66580153
1	-0.93857139	2.51146650	0.90370089	1	-1.23351812	1.31642747	-3.14600706
1	-1.89982557	1.05100691	1.25922573				

$[Bu^tCH_2CMe_2]^+$ THF C-O complex



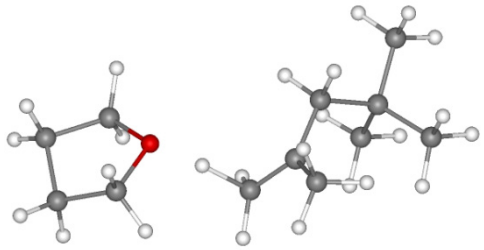
E = –546.744098 E_0 = –546.400282
ZPVE = 0.343816 a.u. = 215.7477 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.4104	41.5534	0.8887	1.4812	-10.9079
rotational	14.3761	31.5492	0.8887	0.8887	-8.5177
vibrational	11.5895	51.1341	224.1267	224.1267	208.8811
total	44.3759	124.2366	225.9041	226.4966	189.4555

Cartesian

6	-0.08646881	-0.06013330	0.74611592	1	-1.70231175	-0.13836046	3.79266000
6	1.20849478	-0.23886520	-0.04684120	1	-1.53207648	1.22857070	2.67284679
6	1.83441424	-1.61853004	-0.07828108	1	-2.36744642	-0.25757733	2.15236735
6	2.24768019	0.84661525	0.15486409	1	-0.46193579	-2.20694304	3.51596498
1	2.60644507	-1.67864466	-0.85614175	1	-1.02219546	-2.44311404	1.85344946
1	2.33217216	-1.78602457	0.88594335	1	0.71810144	-2.48305011	2.23601890
1	1.10677159	-2.42607617	-0.21329042	6	-0.08244979	-1.05934870	-2.30866838
1	2.71095395	0.69374597	1.13771629	1	-0.56526047	-1.65579903	-1.52932560
1	3.04385376	0.78344315	-0.59795076	1	0.61612993	-1.67593575	-2.88437128
1	1.81380308	1.85349953	0.15906389	6	-1.04460657	-0.25686783	-3.16940188
1	-0.36415741	1.00348103	0.68616468	1	-1.29484737	-0.79899079	-4.08903790
1	-0.88744640	-0.62955099	0.24819650	1	-1.97670066	-0.05373403	-2.62476206
6	-0.17926140	-0.45756924	2.26533747	6	-0.28155777	1.04872262	-3.44223166
6	-1.52467895	0.13119395	2.74302983	1	0.48042777	0.90995282	-4.22097206
6	-0.23141505	-1.98366094	2.46521211	1	-0.94310582	1.86896384	-3.74647474
6	0.94619811	0.14409055	3.12285638	6	0.36764267	1.34181905	-2.10562086
1	0.73185980	-0.03662195	4.18509054	1	-0.33858591	1.75516880	-1.37440956
1	1.92556429	-0.31230909	2.91904163	1	1.28001976	1.94152546	-2.15521574
1	1.02980113	1.23221624	2.98760223	8	0.78642416	-0.02099659	-1.63360667

TS $[Bu^tCH_2CMe_2]^+$ THF to *exo*



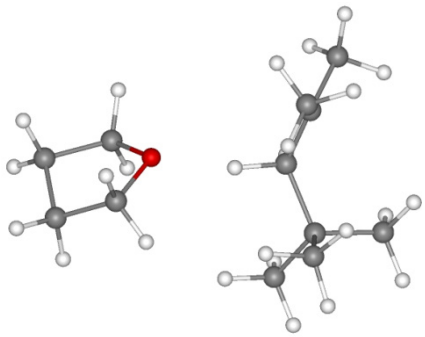
E = –546.737625 E_0 = –546.401079
ZPVE = 0.336546 a.u. = 211.1857 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.4104	41.5534	0.8887	1.4812	-10.9079
rotational	14.7483	32.2888	0.8887	0.8887	-8.7382
vibrational	15.4650	59.9717	219.9034	219.9034	202.0229
total	48.6236	133.8139	221.6809	222.2734	182.3768

Cartesian

6	0.84770882	1.39418221	1.46710694	1	0.26650262	2.86817336	4.55307150
6	1.13841641	0.09076517	0.81576777	1	1.29541266	3.44108772	3.22395682
6	0.11007187	-0.73022616	0.34503728	1	-0.45854810	3.24453592	2.97617960
6	2.55953598	-0.27774969	0.58020025	1	-0.75636423	0.58724546	4.50607443
1	0.03480350	-0.26375860	-0.88140577	1	-1.49070501	0.88261634	2.92258620
1	0.34689391	-1.78175414	0.14914834	1	-0.45808905	-0.55091894	3.18805599
1	-0.90547305	-0.53149021	0.70240903	6	0.26190335	-0.91320270	-3.13500357
1	2.68654513	-1.28629375	0.17253727	1	0.74361104	-1.72284293	-2.57196689
1	3.01458097	0.45701385	-0.10599806	1	0.99490803	-0.44179833	-3.80224109
1	3.13232327	-0.18186989	1.51570153	6	-1.01916885	-1.31191170	-3.85314035
1	1.66651773	2.10059762	1.26837349	1	-0.81845236	-1.66865182	-4.87035894
1	-0.08522455	1.80989742	1.05782008	1	-1.54413712	-2.10818076	-3.30684686
6	0.64956874	1.34992766	3.04704690	6	-1.83113837	-0.00701420	-3.82976317
6	0.42590982	2.81432366	3.46729016	1	-1.47179496	0.68975043	-4.59932375
6	-0.58265299	0.51516265	3.42346072	1	-2.90428042	-0.16984260	-3.98586392
6	1.89610660	0.80042017	3.75607991	6	-1.54172802	0.53725058	-2.43936372
1	1.77919257	0.91391647	4.84270144	1	-2.18410778	0.07939588	-1.67231035
1	2.05146360	-0.27068099	3.56240082	1	-1.57610726	1.62907243	-2.35520077
1	2.80560875	1.34852374	3.46875668	8	-0.13989057	0.13401519	-2.15841699

TS [Bu^{t}CH$_2$CMe$_2$]$^+$ THF to *endo*



E = –546.729219 E_0 = –546.391968
ZPVE = 0.337251 a.u. = 211.6285 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.4104	41.5534	0.8887	1.4812	-10.9079
rotational	14.6542	32.1019	0.8887	0.8887	-8.6824
vibrational	17.3843	65.4640	220.8466	220.8466	201.3285
total	50.4488	139.1193	222.6241	223.2165	181.7381

Cartesian

6	1.04623485	0.80232006	0.41525155	1	0.01010162	0.76631868	3.73301649
6	2.07484293	0.50764042	-0.54584754	1	-0.35441521	1.92117190	2.43671370
6	2.54885340	-0.85979348	-0.81488872	1	-0.90020937	0.22910213	2.30445933
6	2.65027523	1.59898579	-1.35641718	1	1.57418418	-1.10041463	3.38378453
1	2.29974771	-1.08565176	-1.87007892	1	0.84917337	-1.66083944	1.87064695
1	3.65270138	-0.89141005	-0.79482305	1	2.58945227	-1.25524998	1.95259047
1	2.12117696	-1.62914848	-0.17124461	6	-2.24688888	0.12895119	-1.23065245
1	3.30177927	2.18741369	-0.67743051	1	-1.88495898	0.56379354	-2.17167115
1	3.25079179	1.25923622	-2.20652223	1	-2.41586161	0.93602502	-0.49805990
1	1.87581766	2.31267023	-1.67591012	6	-3.48461843	-0.74605274	-1.38593519
1	0.72939122	1.85069764	0.33473057	1	-4.41251659	-0.16255444	-1.34966254
1	0.17603973	0.13047193	0.10331146	1	-3.45397520	-1.29068708	-2.34009552
6	1.25238717	0.49720460	1.97831666	6	-3.33473158	-1.71396434	-0.20277502
6	-0.08038555	0.87724847	2.64362860	1	-3.66067791	-1.23410761	0.73118097
6	1.58718646	-0.96469492	2.29320526	1	-3.90782118	-2.64020658	-0.32973203
6	2.37363458	1.42025137	2.48342633	6	-1.82950258	-1.96913493	-0.18461967
1	2.46361160	1.32460964	3.57487154	1	-1.54516065	-2.80764437	-0.83899766
1	3.34907150	1.15721571	2.04810071	1	-1.42790842	-2.15178919	0.82218683
1	2.16375923	2.47673965	2.26316690	8	-1.19955862	-0.75951749	-0.72431237