Electronic Supplementary Material (ESI) for Polymer Chemistry

Electronic Supporting Information

for

Scope and Limitations of the Nitroxide-Mediated Radical Ring Opening Polymerization of Cyclic Ketene Acetals

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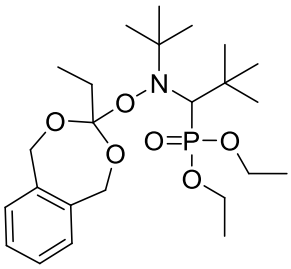
1. DFT Calculations

Enthalpies of compounds at various levels of theory and Cartesian coordinates of UBMK/6-31G(d) geometries of compounds involved in BDE calculations.

Notation	Complete Level of theory
UB3LYP	UB3LYP/6-31G(d)// UB3LYP/6-31G(d)
B3P86	B3P86/6-311++G(d,p) // UB3LYP/6-31G(d)
UBMK	UBMK/6-31G(d)// UBMK/6-31G(d)
UBMK 2	UBMK/6-311+Gg(3df,3pd)// UBMK/6-31G(d)



H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-1786,62521	-1791,687473	-1785,64651	-1786,168685

P	1.7116960	1.2402000	-0.4219840
O	-0.1703470	-0.8235740	0.4189420
N	1.1323490	-1.3994280	0.5912810
O	3.1164650	1.8081290	0.1344760
O	0.7122860	1.8143350	0.6886100
O	1.3554680	1.6792330	-1.7956070
H	3.0050090	-0.5301550	0.4214680
C	2.0937340	-0.5744160	-0.1825220
C	1.4309980	-1.5143640	2.0638000

H	1.3097120	-0.2341010	-3.0222020
H	0.5311590	-1.6496730	-2.3245770
H	1.8523680	-1.8672520	-3.4914290
C	2.5620170	-1.2440930	-1.5391950
C	1.4916980	-1.2483180	-2.6573230
H	3.5539950	0.5325970	-2.3861230
H	4.2084240	-1.0197580	-2.9399860
H	4.6004100	-0.4323780	-1.3088590
H	0.4939880	0.3342640	2.7755860
H	2.2131590	0.5200090	2.3864590
H	1.7336290	-0.3412600	3.8629020
C	3.8074300	-0.4845470	-2.0684020
H	-1.0235550	1.5325680	-0.4251160
H	-1.2094680	2.1126640	1.2455030
C	1.4689200	-0.1630470	2.8120200
H	2.1870130	-3.2955670	-0.8265370
H	3.8330440	-2.7082350	-0.5066000
H	3.3645210	-3.1693480	-2.1561410
C	-0.6183640	2.2168760	0.3281640
H	-0.6468360	-2.0653380	2.5481070
H	0.5497360	-2.4450060	3.8057860
H	0.4508980	-3.4517410	2.3501850
C	3.0074280	-2.6943370	-1.2324080
H	3.2617720	3.5229050	-1.0117000
H	2.5877690	3.7436820	0.6246990
C	0.3713660	-2.4233040	2.7232030
H	4.9652300	4.5744680	0.5269750
H	5.5054360	2.9628730	-0.0089930
H	4.8302910	3.1771710	1.6253190
C	3.3531490	3.2165190	0.0384260
H	-1.6646050	3.9791230	-0.3616170
H	-0.0518840	3.7446740	-1.0910400
H	-0.2019950	4.3309730	0.5940460

C	4.7521280	3.4991980	0.5800260
H	3.6480210	-1.6107410	1.9433690
H	2.8154290	-3.1556400	1.6291020
H	2.9190700	-2.5043110	3.2810970
C	-0.6317220	3.6638040	-0.1648190
C	2.7918440	-2.2355480	2.2247550
C	-1.2147820	-1.6256670	-0.0995250
O	-2.2552270	-1.7088330	0.8289230
O	-1.6178720	-0.8986450	-1.2326260
C	-0.8247500	-3.0768920	-0.4335010
C	-2.6661140	-0.5230530	1.4782840
C	-2.9990620	-0.8147800	-1.5235130
C	-1.9450450	-3.8763830	-1.1216080
H	0.0624000	-3.0543880	-1.0671330
H	-0.5440120	-3.5685060	0.5013400
H	-1.7838670	0.0479480	1.7993020
H	-3.1910850	-0.8603410	2.3809690
C	-3.5984750	0.3694900	0.6655670
H	-3.0511450	-0.5758400	-2.5919090
C	-3.7288140	0.2640970	-0.7315420
H	-3.4927470	-1.7813490	-1.3659380
H	-2.1783860	-3.4692610	-2.1128210
H	-1.6173070	-4.9145370	-1.2587170
H	-2.8584300	-3.8857950	-0.5148500
C	-4.3281780	1.3507920	1.3535280
C	-4.5875400	1.1464340	-1.4055430
C	-5.1835260	2.2238020	0.6740070
H	-4.2306030	1.4247720	2.4373850
C	-5.3154710	2.1203360	-0.7149680
H	-4.6799310	1.0697060	-2.4887220
H	-5.7432000	2.9766810	1.2259290
H	-5.9747300	2.7956810	-1.2569220

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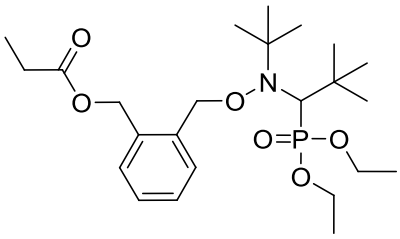
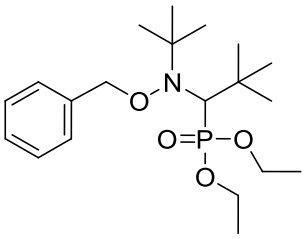


H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-1786,66063	-1791,720121	-1785,67411	-1786,200493

P	-2.2859540	-0.7546490	0.4032410
O	0.0342140	0.3830390	-0.5115660
N	-0.8964620	1.4806700	-0.5988670
O	-3.6908450	-0.5907190	1.1717140
O	-1.3057830	-0.8003580	1.6659340
O	-2.1903780	-1.9448340	-0.4850820
H	-2.7892180	1.5495990	0.3178070
C	-2.2542350	0.9164710	-0.4016130
C	-0.4635320	2.5324660	0.3809200
H	-2.1781340	-0.8361220	-2.6003320
H	-1.5709110	0.7169810	-3.2579460
H	-3.1636890	0.1171250	-3.7345400
C	-3.1160700	0.9526900	-1.7321710
C	-2.4555480	0.1816490	-2.8965240
H	-4.4947110	-0.7155850	-1.3212410
H	-5.1476120	0.5538100	-2.3771590
H	-5.0188360	0.8329540	-0.6231710
H	0.1899320	1.2000410	1.9883930
H	-1.4648680	1.7979850	2.2048550
H	-0.0926860	2.8877460	2.4884420
C	-4.5300870	0.3670660	-1.4884300
H	-0.2407620	-2.4687340	1.0638340
H	0.7132060	-0.9950280	1.3276190

C	-0.4617110	2.0697100	1.8553870
H	-2.3053430	2.8792300	-2.3747510
H	-3.7969090	3.0234670	-1.4057860
H	-3.8786860	2.4676730	-3.0916370
C	-0.1164940	-1.5962830	1.7149080
H	1.6899800	2.1671010	0.1250780
H	1.2660410	3.8153440	0.6355130
H	0.9922780	3.3157500	-1.0486560
C	-3.2813650	2.4256910	-2.1704720
H	-4.2723070	-2.5753920	1.1654820
H	-3.5484190	-1.9861890	2.6859230
C	0.9639160	2.9765220	-0.0047890
H	-6.0438170	-2.1974070	2.9299850
H	-6.2742550	-1.0981690	1.5454670
H	-5.5451130	-0.4900560	3.0529660
C	-4.2238550	-1.7256010	1.8590840
H	1.0298810	-2.6030570	3.2454500
H	-0.7283370	-2.6117590	3.5354130
H	0.2104580	-1.1240350	3.8094080
C	-5.6096720	-1.3530940	2.3795790
H	-1.3890650	4.1328280	-0.7992460
H	-2.4187670	3.5626020	0.5372080
H	-1.0029290	4.5622520	0.8818440
C	0.1107340	-2.0082240	3.1676930
C	-1.3851410	3.7643150	0.2325680
C	0.8241760	0.2633400	-1.6922160
C	1.6484560	-1.0105580	-1.5763830
H	0.1653770	0.1947770	-2.5634190
H	1.4560930	1.1497810	-1.8029040
C	3.0597770	-1.0139530	-1.5594250
C	0.9578510	-2.2333250	-1.5131130
C	3.8787630	0.2618090	-1.6685040
C	3.7457880	-2.2359570	-1.4559140

C	1.6519840	-3.4431310	-1.4193150
H	-0.1323860	-2.2274500	-1.5148930
H	4.9232750	0.0170700	-1.8835880
H	3.4988180	0.9279640	-2.4483220
O	3.8252480	1.0434790	-0.4664310
C	3.0513820	-3.4460770	-1.3873120
H	4.8334340	-2.2239640	-1.4154020
H	1.0983050	-4.3794140	-1.3731340
C	4.6823190	0.7048390	0.5102380
H	3.6003100	-4.3830390	-1.3106880
O	5.4974490	-0.1774520	0.4099910
C	4.4885750	1.5897900	1.7350620
C	5.4728840	1.2451140	2.8600700
H	3.4453300	1.4775230	2.0630160
H	4.5925320	2.6347350	1.4108560
H	5.3035560	1.8949790	3.7268580
H	5.3531160	0.2019910	3.1735590
H	6.5077720	1.3722880	2.5228370

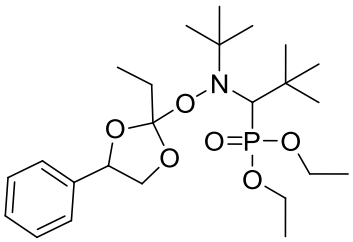


H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-1480,26006	-1484,407344	-1479,43878	-1479,865593

O	0.8253990	0.7947470	0.0754890
N	-0.3242240	1.6527450	0.2005500
C	-0.2128720	2.2767060	1.5593270
C	-0.1944630	1.2549390	2.7198700
C	1.1051110	3.0835580	1.5713410
C	-1.3736100	3.2695690	1.7796590
H	-1.1108080	0.6536940	2.7529340
H	0.6588050	0.5761690	2.6258910
H	-0.1058920	1.7937400	3.6727140
H	1.1154820	3.8077810	0.7461500
H	1.1939620	3.6335300	2.5169360
H	1.9708630	2.4191510	1.4749210
H	-1.2278410	3.7569690	2.7520010
H	-1.3875590	4.0458000	1.0072890
H	-2.3541190	2.7801830	1.8035160
C	-1.5222650	0.8196820	-0.0855070
H	-2.2367470	0.9020210	0.7466520
C	-2.2881720	1.3208320	-1.3850640
C	-3.5403780	0.4559820	-1.6756440
C	-2.7695480	2.7713710	-1.1518290
C	-1.3909710	1.3220820	-2.6422280
H	-4.1662560	0.3295380	-0.7833180
H	-3.2740120	-0.5381860	-2.0500740

H	-4.1390540	0.9567530	-2.4485830
H	-1.9207740	3.4408470	-0.9789780
H	-3.3020920	3.1227420	-2.0461270
H	-3.4606670	2.8426340	-0.3007110
H	-1.9936690	1.6224600	-3.5108060
H	-0.5770130	2.0477220	-2.5341980
H	-0.9718380	0.3278900	-2.8351430
P	-1.0988700	-0.9843600	-0.1380560
O	-0.4475590	-1.5036140	-1.3719960
C	-2.7533780	-2.9878010	0.1007100
H	-2.4276480	-3.3539520	-0.8818280
H	-2.1282800	-3.4560470	0.8742450
C	0.9577290	-1.8930220	1.3117820
H	1.2214010	-2.3954210	0.3742130
H	1.6229680	-1.0319970	1.4347930
O	-0.3893850	-1.4193680	1.2312350
O	-2.5690450	-1.5718850	0.1535340
C	-4.2326160	-3.2789880	0.3404760
H	-4.4134240	-4.3609870	0.3081390
H	-4.5424640	-2.9000450	1.3217010
H	-4.8453930	-2.7970590	-0.4307230
C	1.0464500	-2.8446180	2.5031030
H	0.3890760	-3.7111090	2.3591790
H	2.0781170	-3.2017800	2.6161390
H	0.7495750	-2.3326130	3.4267680
C	1.6190170	1.1185220	-1.0611840
C	2.9024120	0.3204040	-0.9526970
C	4.0534930	0.8786010	-0.3780610
C	2.9356900	-1.0051700	-1.4166800
C	5.2280200	0.1240540	-0.2668600
H	4.0314050	1.9098900	-0.0253860
C	4.1083900	-1.7600370	-1.3056540
H	2.0290220	-1.4343350	-1.8446830

C	5.2558940	-1.1962750	-0.7311990
H	6.1186480	0.5668620	0.1759880
H	4.1290030	-2.7859830	-1.6695840
H	6.1688820	-1.7837180	-0.6485560
H	1.8184820	2.1986630	-1.0667440
H	1.0835870	0.8430090	-1.9757760

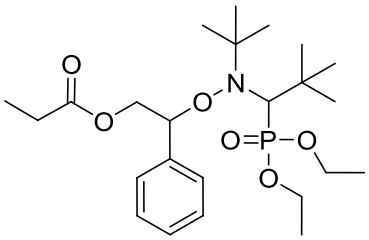


H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-1786,63631	-1791,69796	-1785,65861	-1786,182189

P	1.3138910	1.3533230	-0.3787760
O	-0.0364730	-0.9763210	0.4185830
N	1.3278570	-1.2298400	0.7950410
O	2.5311010	2.3740840	-0.1141170
O	0.3025980	1.8703310	0.7496090
O	0.7460330	1.3872900	-1.7523950
H	2.8675280	0.1850230	0.9395110
C	2.1882750	-0.1938540	0.1654090
C	1.3652830	-1.2664190	2.3033860
H	1.7033220	-0.6171000	-2.6197830
H	1.7681940	-2.2324920	-1.8971020
H	3.1021530	-1.6846690	-2.9284850
C	3.1335590	-0.7863760	-0.9634650
C	2.3694820	-1.3616090	-2.1748140
H	3.5945020	1.0656550	-2.0709740
H	4.8585560	-0.1778780	-2.1248060
H	4.6372840	0.8015470	-0.6553530
H	-0.0609500	0.3431130	2.7161730
H	1.6247460	0.8896650	2.7009530
H	1.0197670	-0.0623120	4.0723490
C	4.1106950	0.3014950	-1.4787420
H	-1.3927490	2.1222770	-0.4095270
H	-1.4648370	0.8130550	0.7992100

C	0.9634180	0.0627800	2.9828840
H	3.3454970	-2.7172310	0.0528080
H	4.6267660	-1.5488580	0.4670810
H	4.6325980	-2.3508390	-1.1179850
C	-1.1219510	1.8357630	0.6141940
H	-0.6181850	-2.1862280	2.4705490
H	0.4248330	-2.3897490	3.8942360
H	0.7338000	-3.3565890	2.4385610
C	3.9839560	-1.9195070	-0.3434910
H	2.0619950	3.7364070	-1.5964510
H	1.6135130	4.2141650	0.0629310
C	0.4098710	-2.3728890	2.7971690
H	3.6642490	5.4698570	-0.6985940
H	4.4991180	3.9216570	-0.9889130
H	4.0539200	4.3950390	0.6694950
C	2.3871980	3.7288010	-0.5478160
H	-2.8169210	2.7672020	1.5554750
H	-1.3875040	3.8324280	1.4335230
H	-1.4252880	2.5294230	2.6475050
C	3.7368410	4.4222400	-0.3798980
H	3.5404630	-0.8955970	2.5379890
H	3.1023480	-2.6038880	2.2935760
H	2.7757190	-1.8023140	3.8467480
C	-1.7218550	2.8058850	1.6277620
C	2.7888390	-1.6625600	2.7583760
C	-0.6924640	-1.9312370	-0.4219690
C	-0.2250430	-3.3833100	-0.2616870
O	-0.6193460	-1.5541760	-1.7528850
O	-2.0409840	-1.8071400	-0.0473190
H	-0.5295800	-3.7079220	0.7370410
H	0.8678300	-3.4139270	-0.3020380
C	-0.8519720	-4.3035320	-1.3217860
C	-1.6720290	-0.6523320	-2.0184550

C	-2.7831870	-1.1823340	-1.0831980
H	-0.5158390	-4.0314850	-2.3276440
H	-0.5685730	-5.3454630	-1.1271040
H	-1.9476410	-4.2389760	-1.2924580
H	-1.9237650	-0.7284270	-3.0809260
H	-1.3713180	0.3739920	-1.7821280
H	-3.3642570	-1.9633930	-1.6014410
C	-3.7352470	-0.1309900	-0.5362730
C	-4.2227210	0.8806920	-1.3794380
C	-4.1668150	-0.1763560	0.7978870
C	-5.1233800	1.8360550	-0.8942170
H	-3.8961510	0.9281830	-2.4182090
C	-5.0687650	0.7781660	1.2824030
H	-3.7815340	-0.9549080	1.4511370
C	-5.5497610	1.7872650	0.4386910
H	-5.4884320	2.6194820	-1.5560940
H	-5.3952400	0.7333760	2.3200200
H	-6.2500890	2.5301680	0.8162180

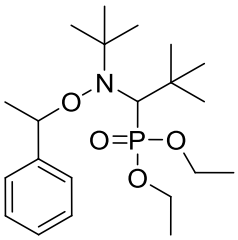


H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-1786,65506	-1791,715365	-1785,67049	-1786,196807

P	-1.9793770	-0.3547200	-0.1209750
O	0.7484590	-0.1518370	-0.7403140
N	0.6647440	-1.3197160	0.1025910
O	-3.2301880	-1.3233790	0.1768530
O	-1.8956560	-0.5347970	-1.7062590
O	-2.1506410	1.0558370	0.3200360
H	-1.0558510	-2.3739160	0.6591260
C	-0.6756210	-1.3483980	0.7449390
C	0.9921060	-2.5292810	-0.7335050
H	1.3172840	-2.0061550	2.5552000
H	-0.0452670	-3.1185560	2.8465830
H	0.3618520	-1.8799710	4.0529060
C	-0.6436070	-1.0656590	2.3091400
C	0.3076100	-2.0860900	2.9751320
H	0.9218300	0.4471180	2.6134340
H	-0.4084630	0.5214470	3.7639110
H	-0.6512100	1.1337130	2.1134480
H	-0.0795510	-1.9996820	-2.5669700
H	-1.0379920	-3.0139020	-1.4733310
H	0.2956140	-3.7304450	-2.3972440
C	-0.1652200	0.3512620	2.7058330
H	-1.3772550	1.4399290	-2.0488690
H	-0.5090270	0.2159580	-3.0050690

C	-0.0275650	-2.8308680	-1.8568020
H	-2.4904530	-2.2393120	2.6032800
H	-2.7478520	-0.4798910	2.6044330
H	-1.9853270	-1.2633870	4.0028730
C	-1.4884340	0.5032200	-2.6021420
H	2.3808660	-1.4978480	-2.0754810
H	2.6269430	-3.2529740	-1.9433840
H	3.1520050	-2.1759190	-0.6249120
C	-2.0591130	-1.2769050	2.9072110
H	-4.7342850	0.0960850	0.1316040
H	-4.5333990	-0.8682060	-1.3566930
C	2.3783270	-2.3431560	-1.3820260
H	-6.5538570	-1.6449100	-0.0729170
H	-5.5315500	-1.9520110	1.3547420
H	-5.3136410	-2.9251820	-0.1212440
C	-4.5280210	-0.9094170	-0.2586150
H	-2.2230170	1.3821310	-4.4384710
H	-3.5039190	0.9176030	-3.2926260
H	-2.6552030	-0.3349010	-4.2348960
C	-5.5454560	-1.9231010	0.2587650
H	0.1404030	-4.0187990	0.6738860
H	1.8347490	-3.5759510	0.9955370
H	1.4220030	-4.6173940	-0.3851830
C	-2.5335670	0.6209950	-3.7106190
C	1.0956470	-3.7528600	0.2063930
C	1.5961050	0.8646980	-0.1863140
C	1.4168130	2.1083970	-1.0750460
C	3.0680710	0.4680730	-0.0994130
H	2.2102580	2.8238230	-0.8334300
H	1.4742460	1.8298650	-2.1329680
O	0.1534640	2.7377830	-0.9279910
C	3.5782790	-0.0352370	1.1065220
C	3.9330130	0.5814160	-1.2007260

C	-0.0333520	3.4795400	0.1804850
C	4.9166320	-0.4334460	1.2098800
H	2.9184260	-0.1262140	1.9674180
C	5.2712490	0.1870470	-1.1030680
H	3.5633090	0.9642620	-2.1508030
C	-1.4044230	4.1317390	0.1815520
O	0.8054180	3.5949160	1.0404800
C	5.7660020	-0.3259330	0.1026570
H	5.2936180	-0.8238060	2.1535520
H	5.9263090	0.2791570	-1.9676310
H	-2.1306750	3.3079340	0.1875000
H	-1.5269390	4.6624150	-0.7731640
C	-1.5946070	5.0698920	1.3808020
H	6.8069400	-0.6351770	0.1784670
H	-1.4597660	4.5221360	2.3200300
H	-0.8646370	5.8878850	1.3641580
H	-2.6033080	5.5002270	1.3683840
H	1.2411820	1.1178830	0.8126460

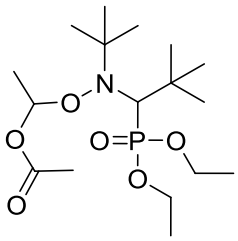


H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-1519,54009	-1523,844942	-1518,6912	-1519,129914

O	-0.8742950	-0.6882620	0.0595920
N	0.2402570	-1.5777360	0.2527420
C	0.0663910	-2.1801980	1.6183300
C	0.0247070	-1.1395490	2.7629970
C	-1.2635480	-2.9660680	1.6267930
C	1.2029490	-3.1927670	1.8765000
H	0.9549720	-0.5666980	2.8499410
H	-0.8005560	-0.4375220	2.6045490
H	-0.1428280	-1.6608370	3.7148610
H	-1.2888810	-3.6880870	0.8005700
H	-1.3529260	-3.5192340	2.5705970
H	-2.1239090	-2.2923870	1.5445620
H	1.0828300	-3.6010710	2.8880360
H	1.1555620	-4.0243740	1.1646070
H	2.1997970	-2.7386020	1.8217170
C	1.4888760	-0.7926410	0.0574520
H	2.0571690	-0.8250930	0.9972890
C	2.4815920	-1.3703460	-1.0626150
C	3.9259640	-1.3036490	-0.5032400
C	2.1756170	-2.8538520	-1.3773730
C	2.4514870	-0.5864940	-2.4017960
H	4.0272490	-1.9238160	0.3995700
H	4.2092550	-0.2757890	-0.2524760

H	4.6329990	-1.6882330	-1.2512940
H	1.1489260	-3.0009190	-1.7246850
H	2.8641920	-3.1925710	-2.1634840
H	2.3308700	-3.4930140	-0.5023830
H	3.1190360	-1.0858190	-3.1170820
H	1.4483510	-0.5466400	-2.8359880
H	2.8034660	0.4431090	-2.2756960
P	1.1561400	1.0203180	-0.1162790
O	0.4552520	1.5664920	-1.3083580
C	2.9619330	2.9096410	-0.1533380
H	2.5828760	3.2235600	-1.1342500
H	2.4384140	3.4822200	0.6251090
C	-0.7621270	2.0577600	1.4129220
H	-0.9450000	2.7503130	0.5825040
H	-1.4848460	1.2382840	1.3393690
O	0.5580200	1.5150610	1.2854390
O	2.6823400	1.5188770	0.0285430
C	4.4729090	3.1003520	-0.0489970
H	4.7305200	4.1586600	-0.1831290
H	4.8324570	2.7734440	0.9340620
H	4.9848110	2.5146090	-0.8222560
C	-0.8431020	2.7617430	2.7646510
H	-0.1248940	3.5890050	2.8190510
H	-1.8539800	3.1624290	2.9133270
H	-0.6237280	2.0571360	3.5766200
C	-1.7777680	-1.1284720	-0.9636710
C	-3.0046470	-0.2353930	-0.8258160
C	-1.1729950	-1.0686910	-2.3714560
C	-4.2329550	-0.7762100	-0.4219530
C	-2.9210900	1.1386810	-1.1149610
H	-1.9404410	-1.3402800	-3.1078160
H	-0.8023210	-0.0601410	-2.5843730
H	-0.3444220	-1.7791140	-2.4574510

C	-5.3688870	0.0367320	-0.3095920
H	-4.3027730	-1.8407830	-0.1979850
C	-4.0537060	1.9505050	-0.9983590
H	-1.9619990	1.5606650	-1.4157110
C	-5.2806150	1.4022600	-0.5976730
H	-6.3179660	-0.3970610	0.0008760
H	-3.9822710	3.0128430	-1.2268540
H	-6.1610820	2.0368270	-0.5118510
H	-2.0692790	-2.1630650	-0.7420240

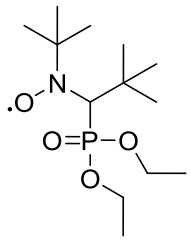


H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-1516,41078	-1520,539661	-1515,61449	-1516,057845

P	1.2839310	-0.2139800	0.2188500
N	-1.1698360	0.9634250	-0.4249020
O	2.5624280	0.6130220	0.7347610
O	1.6213400	-0.3646440	-1.3424370
O	1.0668940	-1.5168870	0.8965820
H	0.6104920	1.9872880	-0.0171760
C	0.0520930	1.1430760	0.4061310
C	-1.3079220	1.9454450	-1.5538710
H	1.2340720	0.2202000	2.9401230
H	-0.4119890	-0.4502050	2.8467840
H	-0.0495010	0.8630290	3.9818130
C	-0.2269890	1.5480520	1.9395870
C	0.1678950	0.4667750	2.9805570
H	1.6830300	2.6213970	2.0731710
H	0.4804790	3.1138390	3.2889270
H	0.3106690	3.6610930	1.6109470
H	-0.0147860	0.8968370	-2.9681750
H	0.8169550	2.2161570	-2.1211820
H	-0.3568380	2.5898510	-3.3965140
C	0.6154880	2.8135920	2.2411110
H	0.7119440	-2.2268080	-1.4222220
H	0.6231780	-1.2307560	-2.8961750
C	-0.1370440	1.9071130	-2.5648870

H	-2.3378200	0.9747070	1.9927000
H	-2.0797790	2.6762160	1.5339830
H	-1.8504550	2.1716830	3.2177130
C	1.2738570	-1.5470710	-2.0715300
H	-2.5014440	0.7493570	-2.9464610
H	-2.8837250	2.4786850	-2.9487400
H	-3.4395510	1.4587410	-1.5999240
C	-1.7219940	1.8617620	2.1713140
H	4.2586600	0.2637070	1.7957780
H	3.6826060	-1.1334520	0.8662730
C	-2.6173170	1.6289710	-2.3074540
H	5.7208940	-0.1082810	-0.2272180
H	4.8668430	1.4524350	-0.3423870
H	4.2871150	0.0546390	-1.2812020
C	3.8320440	-0.0462180	0.8350130
H	2.3087640	-3.0818370	-3.2003800
H	3.1804160	-2.5281060	-1.7491140
H	3.1260220	-1.4982550	-3.2053880
C	4.7347190	0.3637350	-0.3294450
H	-0.5985140	3.6593080	-0.3417390
H	-2.3666210	3.4592900	-0.3770020
H	-1.5051800	4.0804480	-1.8009180
C	2.5534570	-2.2029570	-2.5892720
C	-1.4486230	3.3678590	-0.9682590
O	-1.1561780	-0.3463330	-1.0314810
C	-2.2220150	-1.1777050	-0.6408290
O	-1.6984240	-2.2667970	0.1047050
C	-2.8611390	-1.8103070	-1.8769730
H	-2.9197510	-0.6063910	-0.0233920
C	-1.8291060	-2.2703960	1.4436100
H	-3.5752740	-2.5804650	-1.5649990
H	-3.3854000	-1.0614440	-2.4762580
H	-2.0809000	-2.2807190	-2.4881840

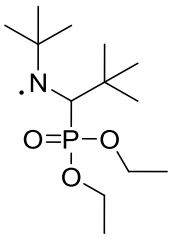
C	-1.1013980	-3.4457550	2.0548600
O	-2.4477680	-1.4347370	2.0561020
H	-0.0303030	-3.2117000	2.0087630
H	-1.4232150	-3.5730430	3.0914490
H	-1.2835740	-4.3565410	1.4740560



H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-1209,40635	-1212,60375	-1208,78874	-1209,132848

P	1.1621050	-0.0374710	-0.4430830
O	-1.6135550	0.6456130	-1.3257530
N	-1.5251020	0.1719820	-0.1301380
O	2.0611330	-0.4903340	0.8078500
O	1.0388490	1.5398200	-0.1839410
O	1.6948410	-0.3981080	-1.7789860
H	-0.3273680	-0.8935940	1.1952550
C	-0.4389930	-0.7781170	0.1124360
C	-2.3545330	0.8570500	0.9071430
H	-0.1836920	-1.7406310	-2.5431680
H	-1.9242130	-1.6084490	-2.2143840
H	-1.1664860	-3.2165530	-2.3417710
C	-0.7314880	-2.2118120	-0.4751610
C	-1.0199110	-2.1845270	-1.9925790
H	1.3571780	-2.8143360	-0.7915230
H	0.2368780	-4.1553150	-0.4775930
H	0.7675390	-3.1139410	0.8646560
H	-2.0276730	2.7981700	-0.0230600
H	-0.8754910	2.4224980	1.2842090
H	-2.5557540	2.8827820	1.6806080
C	0.4887530	-3.1234920	-0.1981810
H	1.5325390	2.1457300	-2.1011440
H	-0.1555280	2.4282510	-1.6110510

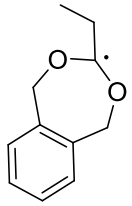
C	-1.9220860	2.3404070	0.9671780
H	-2.8401460	-2.1513440	0.1344240
H	-1.7608600	-2.9068970	1.3409860
H	-2.2011040	-3.7840760	-0.1389510
C	0.8867300	2.4660070	-1.2755110
H	-3.9269510	1.1448430	-0.5687050
H	-4.4675940	1.3320420	1.1248510
H	-4.1643600	-0.2910670	0.4588150
C	-1.9580290	-2.7922140	0.2651300
H	3.8944710	-0.5891560	-0.1451670
H	3.5863740	0.9021270	0.7848090
C	-3.8258360	0.7534450	0.4484350
H	5.1781110	-0.5903650	2.0333810
H	3.9758830	-1.9054460	2.0031980
H	3.6463940	-0.4193030	2.9290850
C	3.4627280	-0.1894510	0.7812070
H	1.1547670	4.5860040	-1.5761040
H	2.3070030	3.8698750	-0.4200860
H	0.6162100	4.1521150	0.0654490
C	4.1045090	-0.8167550	2.0154320
H	-1.1734740	0.3364040	2.6885550
H	-2.4421930	-0.8564420	2.2797040
H	-2.8776830	0.7099740	2.9880050
C	1.2665050	3.8533690	-0.7664100
C	-2.1898110	0.2108170	2.2943090



H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-1134,21813	-1137,249789	-1133,61228	-1133,931022

P	-1.0037590	0.3371720	-0.2073490
N	1.5339750	-0.4974980	-0.2541870
O	-1.6819490	0.1229310	1.2249480
O	-1.0879320	-1.1470000	-0.8201020
O	-1.6325370	1.3678130	-1.0721640
H	0.7500710	0.6178490	1.3937960
C	0.7763240	0.5999970	0.2905060
C	1.8609540	-1.6377730	0.5999740
H	0.3815190	2.1199910	-2.1337720
H	1.9377010	1.2357140	-2.1532940
H	1.9166140	3.0116270	-2.0197900
C	1.3696500	1.9799810	-0.1846430
C	1.3974560	2.0890760	-1.7246890
H	-0.4666760	3.1662130	0.0419780
H	1.0403770	4.0972920	0.1796800
H	0.5227630	3.0631900	1.5259780
H	-0.1273680	-2.1431390	1.3738640
H	0.8281930	-1.1432740	2.4949240
H	1.2292360	-2.8532880	2.2791990
C	0.5571210	3.1424790	0.4291250
H	-0.1150770	-0.6274580	-2.5874740
H	-0.4562250	-2.3466560	-2.3214530
C	0.8813970	-1.9524340	1.7566770

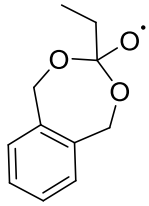
H	3.4411000	1.2641390	-0.0748760
H	2.8453730	1.9824220	1.4456310
H	3.2622170	3.0285360	0.0712420
C	-0.8722260	-1.3371930	-2.2295730
H	0.9520550	-3.1146910	-0.7169000
H	2.3419220	-3.7372130	0.2071870
H	2.6076030	-2.6469230	-1.1847010
C	2.8193170	2.0622940	0.3486870
H	-3.5730180	0.7591440	0.6730670
H	-3.3817800	-1.0022670	0.8905650
C	1.9504220	-2.8658600	-0.3344790
H	-4.6152320	0.0070280	2.8431170
H	-3.2412620	1.1020640	3.1431130
H	-3.0450820	-0.6548790	3.3671520
C	-3.1102350	-0.0179840	1.2939760
H	-2.0076560	-1.4289970	-4.0685230
H	-2.5639380	-0.1777810	-2.9200540
H	-2.9287690	-1.9010270	-2.6183310
C	-3.5268770	0.1170800	2.7556470
H	3.2427240	-0.4681650	1.8521650
H	3.9898350	-1.1493940	0.3841560
H	3.6117930	-2.2092430	1.7700040
C	-2.1801830	-1.2000320	-3.0083600
C	3.2700300	-1.3422730	1.1888910



H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-577,155953	-579,0186144	-576,792469	-576,9777125

C	1.9374380	0.4184560	-0.5711720
O	1.2466440	1.1731650	0.3290350
O	1.2675450	-0.6728980	-1.0500800
C	3.3928250	0.2274910	-0.2163300
C	0.0126350	1.6865480	-0.1427470
C	0.3709290	-1.3215710	-0.1531890
C	3.6152300	-0.6915930	1.0124610
H	3.9016850	-0.1990220	-1.0904330
H	3.8272080	1.2163750	-0.0238280
H	0.1301770	1.9848250	-1.1963150
H	-0.1820740	2.5898530	0.4476580
C	-1.1621220	0.7269480	-0.0008080
H	0.2655240	-2.3451550	-0.5304290
C	-1.0029140	-0.6704800	-0.0623200
H	0.8234850	-1.3695580	0.8480750
H	3.2416970	-1.7037740	0.8105350
H	4.6842730	-0.7662550	1.2503910
H	3.0932930	-0.2935850	1.8917260
C	-2.4488880	1.2657520	0.1466650
C	-2.1364850	-1.4923670	0.0227570
C	-3.5737990	0.4394350	0.2299310
H	-2.5685740	2.3482910	0.1984590
C	-3.4167330	-0.9489810	0.1699940
H	-2.0119960	-2.5741410	-0.0275770

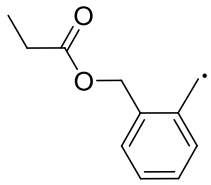
H	-4.5638910	0.8767730	0.3443700
H	-4.2830110	-1.6045860	0.2342720



H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-652,361504	-654,3873419	-651,974788	-652,1838231

O	2.0716520	-1.2502560	1.3831260
C	1.8083140	-0.3537040	0.4149400
O	1.1293730	-0.8772600	-0.6820570
O	1.1101260	0.7205680	0.9899960
C	3.2464080	0.0512180	-0.0677960
C	-0.0624210	-1.5722220	-0.3639680
C	0.1708120	1.3997760	0.1791140
C	3.2064840	1.0961300	-1.1971290
H	3.7765980	0.4427660	0.8064110
H	3.7474510	-0.8617800	-0.4073060
H	0.0925280	-2.1631960	0.5525600
H	-0.2245850	-2.2781510	-1.1873870
C	-1.2854610	-0.6739640	-0.2164450
H	0.0333110	2.3739500	0.6630800
C	-1.1797280	0.6994010	0.0732160
H	0.5736980	1.5751570	-0.8265310
H	2.7898980	2.0457010	-0.8425410
H	4.2303760	1.2853990	-1.5442120
H	2.6127010	0.7337450	-2.0435490
C	-2.5554630	-1.2541000	-0.3494090
C	-2.3514010	1.4562900	0.2229220
C	-3.7178250	-0.4919180	-0.1971880
H	-2.6324900	-2.3172320	-0.5799800
C	-3.6154080	0.8733930	0.0883860

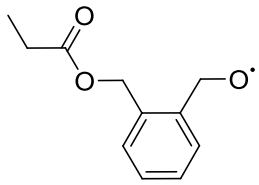
H	-2.2699410	2.5185070	0.4535680
H	-4.6941190	-0.9611390	-0.3036720
H	-4.5105060	1.4800540	0.2111760



H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-577,200553	-579,0614881	-576,834167	-577,0222035

C	-0.1052320	0.4985670	1.4683010
C	-2.0367240	-0.0620900	0.2342470
C	1.4959420	2.3370170	-0.2308350
H	-0.4279150	-0.2979900	2.1455530
H	0.1599970	1.3881370	2.0493770
H	2.1129940	3.0171470	-0.8138360
O	-1.2246140	0.9130330	0.6702080
C	1.8256060	0.9644320	-0.1559120
C	1.0616460	0.0272520	0.6240780
C	1.4075840	-1.3227570	0.6226430
C	2.5122470	-1.7925470	-0.1062040
C	3.2857660	-0.8878380	-0.8538980
C	2.9505240	0.4597140	-0.8806020
H	4.1457610	-1.2433150	-1.4188750
H	2.7646100	-2.8507030	-0.0912790
H	0.7938450	-2.0200560	1.1906460
H	3.5437430	1.1604930	-1.4670660
O	-1.8922450	-1.2273100	0.5087430
H	0.6129710	2.7461080	0.2503770
C	-4.1270760	-0.5815810	-1.1053270
H	-4.9187620	-0.1419210	-1.7236820
H	-3.6001110	-1.3402840	-1.6947100
H	-4.5892560	-1.0886440	-0.2507120
C	-3.1550890	0.5060770	-0.6306120

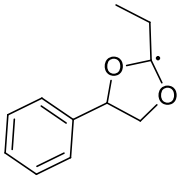
H	-2.6856250	1.0262210	-1.4776330
H	-3.6685460	1.2815460	-0.0450400



H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-652,387155	-654,4120981	-651,994999	-652,2074514

O	2.5422050	2.6963530	-0.5135510
C	1.6637500	1.9530920	0.2012260
C	1.7708730	0.4363710	0.0434800
H	1.7589190	2.2569320	1.2674840
H	0.6414860	2.3006890	-0.0634520
C	0.8483840	-0.4201650	0.6802880
C	2.7887570	-0.1082830	-0.7465540
C	-0.2707800	0.1401580	1.5403930
C	0.9563710	-1.8060620	0.5012740
C	2.8964150	-1.4947270	-0.9094340
H	3.4891110	0.5678230	-1.2312300
H	-0.7360010	-0.6553400	2.1297850
H	0.0869450	0.9267240	2.2139000
O	-1.2786590	0.7843670	0.7448070
C	1.9785250	-2.3467650	-0.2870270
H	0.2207410	-2.4563410	0.9714600
H	3.6942010	-1.9060430	-1.5255910
C	-2.2307960	-0.0132170	0.2291230
H	2.0506670	-3.4247690	-0.4175620
O	-2.2940860	-1.1979150	0.4395090
C	-3.2023570	0.7824040	-0.6328610
C	-4.3440640	-0.0888780	-1.1721580
H	-2.6222910	1.2345630	-1.4499940
H	-3.5798510	1.6188310	-0.0284610

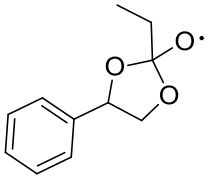
H	-5.0202100	0.5108910	-1.7930600
H	-3.9492410	-0.9131040	-1.7764110
H	-4.9206300	-0.5268680	-0.3494920



H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-577,160468	-579,0232728	-576,798109	-576,9848622

C	-2.1105880	0.5778600	0.3761630
C	-3.4539190	0.8820390	-0.2378500
O	-2.0942260	-0.4796530	1.2500170
O	-1.0606640	0.4518010	-0.5111410
H	-3.3534170	1.7971720	-0.8349060
H	-4.1588970	1.0922210	0.5764820
C	-3.9796090	-0.2766930	-1.1193640
C	-0.7468710	-0.8907180	1.3365630
C	-0.2197430	-0.6157670	-0.0956220
H	-4.0936700	-1.1883360	-0.5207680
H	-4.9535560	-0.0231290	-1.5568590
H	-3.2757420	-0.4805200	-1.9358200
H	-0.7107300	-1.9444530	1.6270950
H	-0.2025430	-0.2770040	2.0703090
H	-0.4092940	-1.4849800	-0.7441090
C	1.2458620	-0.2355780	-0.1514190
C	2.2093610	-1.1931740	-0.4950500
C	1.6548150	1.0625250	0.1908010
C	3.5701510	-0.8630060	-0.4874750
H	1.8950150	-2.1984070	-0.7763070
C	3.0127160	1.3942820	0.1925390
H	0.9003180	1.8075200	0.4362700
C	3.9741680	0.4315090	-0.1435510
H	4.3105370	-1.6139230	-0.7575830

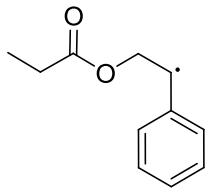
H	3.3221470	2.4047240	0.4539290
H	5.0308890	0.6922460	-0.1431600



H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-652,371685	-654,397359	-651,982199	-652,1919832

O	-1.4989410	1.7307760	0.4782320
C	-1.9725640	0.4935810	0.1382890
C	-3.3385590	0.5469130	-0.5421270
O	-1.9839080	-0.3885180	1.2113850
O	-0.9498160	0.0440960	-0.7351370
H	-3.2265160	1.2106310	-1.4076270
H	-4.0350550	1.0279380	0.1576870
C	-3.8482830	-0.8402320	-0.9633660
C	-0.6312590	-0.7128430	1.4390960
C	-0.0610480	-0.7964630	-0.0044610
H	-4.0047070	-1.4792520	-0.0876450
H	-4.7977680	-0.7479210	-1.5046810
H	-3.1226560	-1.3284580	-1.6254190
H	-0.5792940	-1.6571840	1.9879890
H	-0.1254440	0.0837000	2.0020240
H	-0.1834880	-1.8158880	-0.3983170
C	1.3872150	-0.3649120	-0.1239190
C	2.3972290	-1.3351260	-0.1819570
C	1.7344530	0.9950380	-0.1188600
C	3.7440000	-0.9545130	-0.2225920
H	2.1299630	-2.3919140	-0.1988930
C	3.0790620	1.3744170	-0.1675010
H	0.9464430	1.7454470	-0.0898390
C	4.0872250	0.4018250	-0.2159650

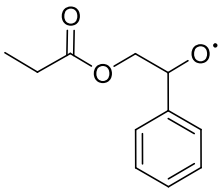
H	4.5206220	-1.7159700	-0.2676890
H	3.3414130	2.4308300	-0.1694420
H	5.1329750	0.7010990	-0.2537970



H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-577,201364	-579,0627012	-576,834359	-577,0230431

C	0.4077170	-1.4640640	0.0387050
C	-0.6344890	-1.3966030	1.1203780
C	1.5303280	-0.5911270	-0.0271870
H	-1.3040700	-2.2594860	1.0576940
H	-0.1821700	-1.3550740	2.1181770
O	-1.4269380	-0.1914530	1.0555300
C	2.4944970	-0.7461530	-1.0679310
C	1.7422530	0.4561630	0.9195280
C	-2.3421390	-0.1466210	0.0771270
C	3.6053210	0.0859620	-1.1480590
H	2.3477480	-1.5370320	-1.8027150
C	2.8582350	1.2828050	0.8297060
H	1.0099130	0.6195760	1.7073590
C	-3.0771780	1.1886360	0.0742510
O	-2.5415750	-1.0529850	-0.6927570
C	3.7981110	1.1056930	-0.1996360
H	4.3269740	-0.0539310	-1.9511350
H	2.9990860	2.0778270	1.5601700
H	-2.3339370	1.9681700	-0.1477360
H	-3.4286280	1.3857010	1.0960980
C	-4.2283880	1.2107900	-0.9397480
H	4.6677990	1.7563920	-0.2654010
H	-3.8573220	1.0036350	-1.9495460
H	-4.9738760	0.4444430	-0.6978130

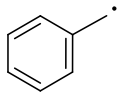
H	-4.7199270	2.1910070	-0.9376120
H	0.2709100	-2.1986100	-0.7525230



H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-652,388721	-654,4138206	-651,997658	-652,210486

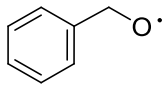
O	-0.0773190	-1.8330660	-0.7707890
C	-0.2749970	-0.5698760	-0.3383420
C	0.4872540	-0.3354590	1.0109810
C	-1.7338420	-0.1331530	-0.2089200
H	0.3646770	0.7119330	1.3071280
H	0.0718560	-0.9966280	1.7768070
O	1.8579970	-0.6643460	0.9118660
C	-2.0577290	1.2281400	-0.0990140
C	-2.7551600	-1.0915700	-0.1789130
C	2.6371950	0.1914210	0.2329540
C	-3.3912970	1.6265200	0.0422950
H	-1.2651820	1.9767110	-0.1368050
C	-4.0889440	-0.6929670	-0.0368670
H	-2.4936650	-2.1425680	-0.2827720
C	4.0814230	-0.2844820	0.2059020
O	2.2196060	1.2027190	-0.2780850
C	-4.4097380	0.6653440	0.0753490
H	-3.6359770	2.6844430	0.1195880
H	-4.8784310	-1.4424250	-0.0168760
H	4.0838520	-1.3065030	-0.1976150
H	4.4195940	-0.3699250	1.2484800
C	4.9870100	0.6505720	-0.6057820
H	-5.4477500	0.9748290	0.1831560
H	4.6516430	0.7078730	-1.6475310

H	4.9677110	1.6659300	-0.1942520
H	6.0204390	0.2846870	-0.5908550
H	0.2519180	0.0822500	-1.0702480



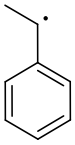
H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-270,797924	-271,7463721	-270,595876	-270,6842648

C	-1.8445000	0.0000120	0.0000020
C	-1.1368760	1.2156200	0.0000040
C	0.2530550	1.2216910	-0.0000010
C	0.9954380	-0.0000250	-0.0000130
C	0.2530320	-1.2217050	-0.0000010
C	-1.1369150	-1.2155980	-0.0000010
H	-2.9326300	0.0000350	0.0000110
H	-1.6807770	2.1589320	0.0000040
H	0.7978430	2.1652700	-0.0000020
H	0.7977780	-2.1653090	-0.0000060
H	-1.6808190	-2.1589060	-0.0000060
C	2.4094060	-0.0000050	0.0000040
H	2.9714110	-0.9312740	0.0000500
H	2.9713460	0.9313050	-0.0000150



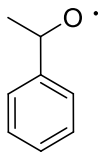
H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-345,984385	-347,0971181	-345,757151	-345,8702711

C	2.2695730	0.2813220	-0.0214410
C	1.3546330	1.3403740	0.0176420
C	-0.0210730	1.0830600	0.0455970
C	-0.4885500	-0.2364150	0.0320270
C	0.4287190	-1.2960300	-0.0117250
C	1.8039770	-1.0393530	-0.0361260
H	3.3390240	0.4831680	-0.0430800
H	1.7117220	2.3688220	0.0245680
H	-0.7411670	1.8979590	0.0688340
H	0.0683660	-2.3255080	-0.0293980
H	2.5088250	-1.8683340	-0.0713950
C	-1.9856530	-0.5309700	0.0840740
O	-2.8175730	0.5136810	-0.1421520
H	-2.2529900	-1.3831460	-0.5746340
H	-2.2629400	-0.8943420	1.1020390



H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-310,087199	-311,1923795	-309,855243	-309,9557899

C	2.3028940	0.3598490	-0.0000010
C	1.3299390	1.3732860	0.0000030
C	-0.0252530	1.0540290	0.0000020
C	-0.4602330	-0.3054060	-0.0000020
C	0.5480710	-1.3171080	-0.0000030
C	1.8984820	-0.9871910	-0.0000050
H	3.3606170	0.6152720	0.0000010
H	1.6364730	2.4181260	0.0000110
H	-0.7667750	1.8507960	0.0000150
H	0.2399450	-2.3623570	-0.0000040
H	2.6462110	-1.7788780	-0.0000070
C	-1.8380850	-0.6600810	0.0000060
C	-2.9632400	0.3400920	-0.0000100
H	-2.9235700	0.9976730	-0.8838240
H	-3.9368580	-0.1620250	-0.0002130
H	-2.9238210	0.9974250	0.8840060
H	-2.0876670	-1.7208520	0.0000690



H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-385,270954	-386,5395687	-385,016859	-385,1417956

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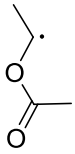
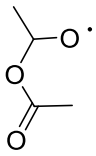
C	-2.6005270	-0.1272980	0.1556520
C	-1.7795760	-1.2563270	0.2717280
C	-0.3963940	-1.1437270	0.0908360
C	0.1747420	0.1008120	-0.2059300
C	-0.6494550	1.2277390	-0.3292120
C	-2.0328840	1.1164910	-0.1469660
H	-3.6765250	-0.2161530	0.2941500
H	-2.2166540	-2.2270100	0.5001500
H	0.2482790	-2.0171600	0.1635760
H	-0.2093440	2.1954620	-0.5738300
H	-2.6656690	1.9965470	-0.2476760
C	1.6902470	0.2424900	-0.3619560
C	2.3518190	0.5641460	1.0278030
H	2.1402780	-0.2528050	1.7259030
H	3.4339630	0.6837380	0.9113340
H	1.9088620	1.4913570	1.4085680
O	2.3198840	-0.8869150	-0.7709910
H	1.9299060	1.0953920	-1.0259840



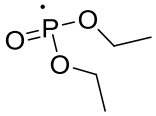
H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-306,93535	-307,8680135	-306,757837	-306,8640281

C	-1.3162800	0.3958750	-0.1385650
O	-0.2099950	-0.4106890	-0.0735850
C	-2.6098210	-0.3226110	0.0679400
H	-1.1490330	1.4406460	0.1075750
C	1.0148080	0.1633130	-0.0020820
H	-2.7263100	-0.6761810	1.1080340
H	-3.4488390	0.3461900	-0.1560410
H	-2.6787100	-1.2026990	-0.5861410
C	2.0979060	-0.8969970	0.0259390
O	1.1874700	1.3526400	0.0368130
H	2.0151620	-1.5388940	-0.8593770
H	3.0750540	-0.4092510	0.0495660
H	1.9731980	-1.5328980	0.9111670



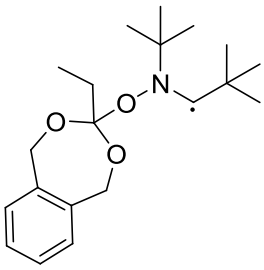
H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-382,147264	-383,2431366	-381,944063	-382,0747367

O	-2.0327610	-1.1157230	-0.3795440
C	-1.1695280	-0.1219370	-0.2720010
O	0.1023800	-0.6055820	0.2018520
C	-1.7026960	0.9737320	0.6888660
H	-1.0124990	0.3329450	-1.2707020
C	1.1829370	0.1226950	-0.1060710
H	-0.9818820	1.7974810	0.6981350
H	-2.6754600	1.3268030	0.3337910
H	-1.8052530	0.5490600	1.6929760
C	2.4545310	-0.5446400	0.3830070
O	1.1317210	1.1671710	-0.7106920
H	2.6191180	-1.4673200	-0.1879930
H	3.2976650	0.1349930	0.2388870
H	2.3561270	-0.8199870	1.4391710



H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-725,325853	-	-725,006938	-

P	-0.0036460	-0.6771690	0.4478470
O	-1.2142830	-0.7053890	-0.6179650
O	1.2158990	-0.7045350	-0.6080390
O	-0.0089970	0.4474580	1.4325290
H	2.6620760	-0.5666360	0.8910330
H	3.2272020	-0.8601220	-0.7697400
C	2.5169520	-0.2897360	-0.1620100
H	-3.2233020	-0.8390820	-0.8132870
H	-2.6814820	-0.5898940	0.8622200
H	-3.6969520	1.5231320	-0.0559780
H	-2.5030240	1.5179480	-1.3805870
H	-1.9628460	1.7415540	0.3082950
C	-2.5181950	-0.2888280	-0.1815790
H	3.7095250	1.5146470	-0.0635980
H	1.9736850	1.7579100	0.2716830
H	2.5333310	1.4882400	-1.4036590
C	-2.6793450	1.2233520	-0.3391470
C	2.6931760	1.2168070	-0.3533110

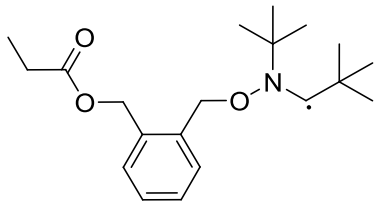


H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-1061,20299	-	-1060,52238	-

O	0.6282840	0.2455540	-0.2694790
N	2.0225020	0.5653600	-0.0411050
H	3.5695820	0.4079070	-1.4453790
C	2.8006130	-0.1694310	-0.9396840
C	2.2186920	2.0530380	-0.1219450
H	1.1480060	-2.3085880	-1.6737420
H	1.2125800	-2.4088880	0.0821220
H	2.0982370	-3.6020840	-0.8909860
C	3.0720720	-1.6631390	-0.8499700
C	1.8032990	-2.5445690	-0.8268050
H	3.3124230	-1.8705130	-3.0196550
H	4.1854390	-3.0972260	-2.0698930
H	4.8175150	-1.4391670	-2.1713630
H	0.6389890	2.4952850	-1.5682420
H	2.2012680	2.0930200	-2.3135530
H	1.9643850	3.6837430	-1.5464210
C	3.8977400	-2.0378640	-2.1056860
C	1.7243760	2.6148000	-1.4744120
H	3.4046800	-1.6425700	1.3240180
H	4.8832270	-1.4005880	0.3704560
H	4.1599490	-3.0243320	0.4873680
H	0.4158950	2.4889340	1.0685940
H	1.5678570	3.8355860	0.9141430

H	1.9294120	2.4815220	2.0019890
C	3.9327130	-1.9505640	0.4129640
C	1.4766800	2.7486650	1.0381320
H	4.3235990	2.1632900	-0.8285760
H	4.1331580	1.7548490	0.8953040
H	3.8432710	3.4145110	0.3231870
C	3.7267570	2.3531890	0.0699190
C	-0.1865660	-0.1238690	0.8250360
O	-1.1133070	0.8836650	1.1154830
O	-0.8537610	-1.2511320	0.3199280
C	0.6020140	-0.4139170	2.1149910
C	-1.8412510	1.3968140	0.0114350
C	-2.1766310	-1.5000920	0.7542700
C	-0.2434390	-0.9138420	3.2998060
H	1.3667410	-1.1553480	1.8634290
H	1.1256030	0.5027850	2.3987540
H	-1.1880920	1.4279880	-0.8705940
H	-2.0998490	2.4286800	0.2806220
C	-3.1126620	0.6251320	-0.3134300
H	-2.3249800	-2.5781470	0.6184230
C	-3.2458840	-0.7441200	-0.0240180
H	-2.2905050	-1.2764070	1.8205470
H	-0.6592680	-1.9098080	3.1071900
H	0.3923660	-0.9890860	4.1910060
H	-1.0640190	-0.2219200	3.5239510
C	-4.1552620	1.2953990	-0.9688010
C	-4.4209540	-1.4113330	-0.3998160
C	-5.3238380	0.6233440	-1.3414490
H	-4.0507920	2.3584300	-1.1887300
C	-5.4584320	-0.7386750	-1.0536600
H	-4.5208490	-2.4737270	-0.1766650
H	-6.1221730	1.1614210	-1.8491720
H	-6.3611430	-1.2755520	-1.3390950

Electronic Supplementary Material (ESI) for Polymer Chemistry

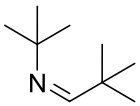


H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-1061,23681	-	-1060,54818	-

O	-1.4611880	-0.5424070	0.4891250
N	-2.2652450	0.6609930	0.3479850
H	-4.3683100	0.7862530	0.4688770
C	-3.5427620	0.3558580	-0.0918540
C	-2.1556130	1.4381470	1.6173520
H	-4.0303140	-2.3300750	-0.6878770
H	-2.4200030	-1.9638390	-1.3245530
H	-3.7796270	-2.2181740	-2.4487500
C	-3.8401130	-0.2789540	-1.4400000
C	-3.4899460	-1.7916240	-1.4774340
H	-5.9364600	-0.6414550	-0.9020660
H	-5.6370650	-0.5741460	-2.6534490
H	-5.6575220	0.9266440	-1.6981550
H	-2.1766380	-0.2917140	2.9412420
H	-3.7895810	0.4076680	2.6633800
H	-2.6367770	1.2356850	3.7365580
C	-5.3610000	-0.1313410	-1.6871170
C	-2.7293700	0.6465850	2.8147590
H	-1.9953550	0.4238570	-2.4156330
H	-3.3761190	1.5179600	-2.6081730
H	-3.3071790	0.0036550	-3.5450830
H	-0.0784210	0.8449320	2.0179370
H	-0.5858040	2.3582360	2.7945490
H	-0.2446930	2.3388640	1.0501050

C	-3.0797410	0.4612360	-2.5716610
C	-0.6684000	1.7580590	1.8794740
H	-2.5748440	3.2702280	0.5053930
H	-3.9933030	2.6478610	1.3827830
H	-2.6833810	3.4341020	2.2763580
C	-2.9060530	2.7754450	1.4271970
C	-0.3085160	-0.4996300	-0.3203020
C	0.7616350	-1.4180860	0.2593700
H	-0.5592170	-0.8270850	-1.3447300
H	0.0722480	0.5274630	-0.3911140
C	2.0294940	-1.4930440	-0.3606900
C	0.5090540	-2.2016750	1.3931550
C	2.3509630	-0.6550600	-1.5857740
C	3.0147020	-2.3354540	0.1711070
C	1.4999060	-3.0449530	1.9132300
H	-0.4691920	-2.1553190	1.8619510
H	3.2080320	-1.0732700	-2.1218290
H	1.4965510	-0.5831370	-2.2660890
O	2.6428520	0.7081250	-1.2342870
C	2.7555820	-3.1135510	1.3052200
H	3.9944490	-2.3581430	-0.3022200
H	1.2845890	-3.6477340	2.7939500
C	3.9077940	0.9756090	-0.8750570
H	3.5303960	-3.7622680	1.7093180
O	4.7940410	0.1576860	-0.8772910
C	4.0640460	2.4372220	-0.4747970
C	5.5249770	2.8057700	-0.1856950
H	3.4282650	2.6032480	0.4064800
H	3.6387630	3.0543970	-1.2779010
H	5.5987870	3.8564420	0.1192610
H	5.9306320	2.1770210	0.6146220
H	6.1483220	2.6542890	-1.0743240

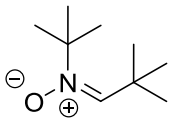
Electronic Supplementary Material (ESI) for Polymer Chemistry



H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-408,882896	-	-408,583758	-

N	-0.4965610	-0.4229270	0.0000230
H	0.3101150	1.4982820	0.0000410
C	0.4600770	0.4050630	0.0000610
C	-1.9009430	0.0058670	0.0000040
H	1.5860820	-1.9857220	-0.8840630
H	1.5861560	-1.9857720	0.8839880
H	3.1301500	-1.8300590	-0.0000980
C	1.9249960	-0.0194580	0.0000030
C	2.0674160	-1.5509050	-0.0000450
H	2.1428700	0.1716530	-2.1762880
H	3.6655160	0.3521640	-1.2700420
H	2.4803540	1.6770560	-1.2863520
H	-1.7165040	2.0092880	-0.8912090
H	-1.7166080	2.0092430	0.8913520
H	-3.2248100	1.7279330	-0.0000220
C	2.5913590	0.5833600	-1.2621610
C	-2.1451620	1.5307290	0.0000350
H	2.1429840	0.1715390	2.1762920
H	2.4804340	1.6769860	1.2864140
H	3.6655840	0.3520850	1.2699740
H	-2.0925230	-0.1915310	-2.1699590
H	-3.6190410	-0.4340770	-1.2809240
H	-2.3621400	-1.7036940	-1.2721750
C	2.5914290	0.5832900	1.2621630
C	-2.5369580	-0.6210520	-1.2620670
H	-2.0926260	-0.1916320	2.1699480

H	-2.3621850	-1.7037570	1.2720820
H	-3.6190970	-0.4341530	1.2808250
C	-2.5370120	-0.6211170	1.2620150



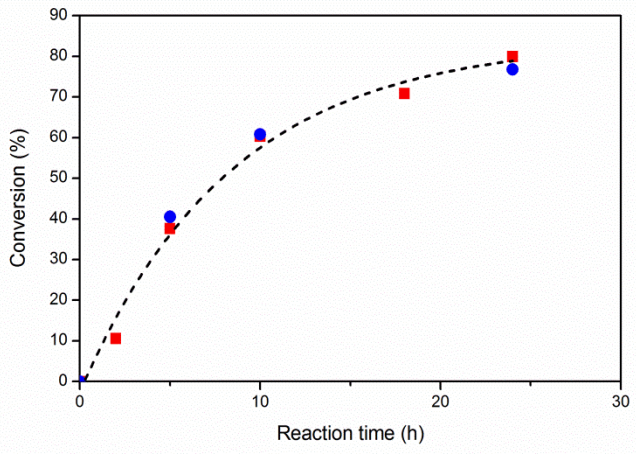
H_{298K} (a.u.)			
UB3LYP	B3P86	UBMK	UBMK 2
-484,046256	-	-483,714869	-

O	-0.3373270	-1.5548150	-0.0001510
N	-0.4718540	-0.2708970	-0.0002360
H	0.2882260	1.6149950	-0.0001160
C	0.5281590	0.5590140	-0.0001270
C	-1.9179990	0.1820380	0.0000050
H	2.1346860	-0.1133390	-2.1753090
H	1.6252180	-1.5912150	-1.3112650
H	3.3302600	-1.0524930	-1.2508640
C	1.9819480	0.1181000	-0.0000040
C	2.2836920	-0.7179220	-1.2702060
H	2.6680490	2.0053690	-0.8912200
H	3.9204770	1.1135790	0.0003790
H	2.6675970	2.0056040	0.8911110
H	-2.4167980	-1.4998890	-1.2803960
H	-2.0979360	0.0116840	-2.1700180
H	-3.6300390	-0.1843980	-1.2814660
C	2.8582260	1.3906510	0.0000770
C	-2.5577110	-0.4158410	-1.2689780
H	1.6249710	-1.5912790	1.3110680
H	2.1342230	-0.1134580	2.1753430
H	3.3300290	-1.0525850	1.2511820
H	-2.4160640	-1.4994130	1.2812070
H	-3.6294440	-0.1839920	1.2825780
H	-2.0968370	0.0124760	2.1702030
C	2.2834550	-0.7179790	1.2702380

C	-2.5571200	-0.4153740	1.2695680
H	-1.6332690	2.1699300	-0.8953880
H	-1.6326940	2.1703730	0.8942640
H	-3.1453390	1.9444330	-0.0000430
C	-2.0732710	1.7120500	-0.0003020

2. BMDO Polymerization initiated by BlocBuilder MA with and without temperature ramp

a)



b)

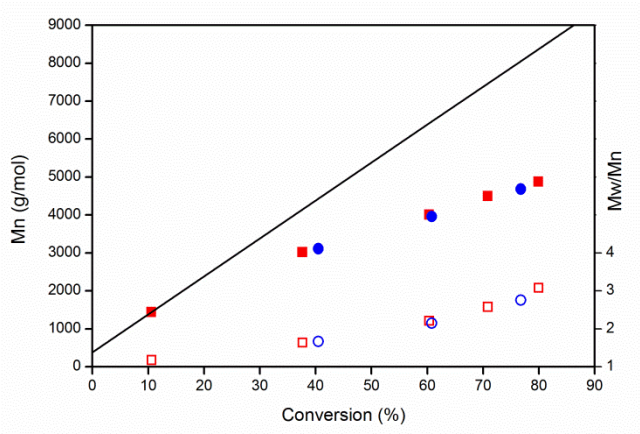


Figure S1. a) Kinetics of the bulk BMDO polymerization initiated by BlocBuilder MA ($[BMDO]_0$: $[Alkoxyamine]_0$ = 62:1) at 140 °C, (■) without temperature ramp, (●) with temperature ramp. b) Evolution of number-average molar mass (M_n full symbols) and polydispersity index (PDI empty symbols) vs conversion for the bulk BMDO polymerization initiated by BlocBuilder MA at 140°C, (■) without temperature ramp, (●) with temperature ramp.

3. MDPL Polymerization without pyridine

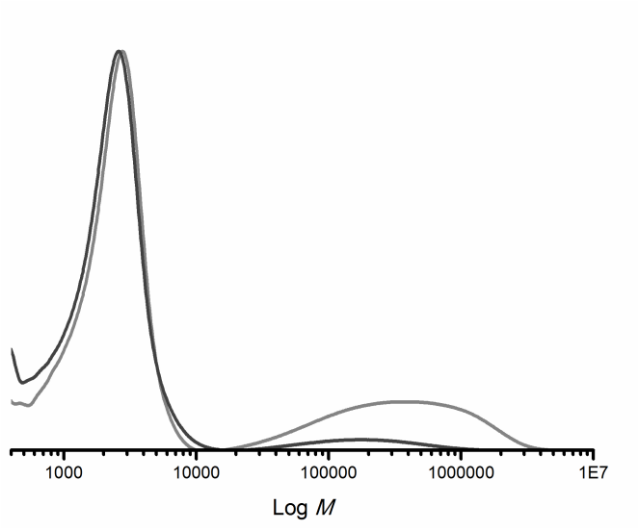


Figure S2. Molar mass distribution obtained from the bulk MDPL polymerization at 120 °C initiated by BlocBuilder MA. (solid black line) with 3 wt% of pyrine/monomer. (solid gray line) without pyridine.

4. ^{31}P NMR analyses of PMDPL

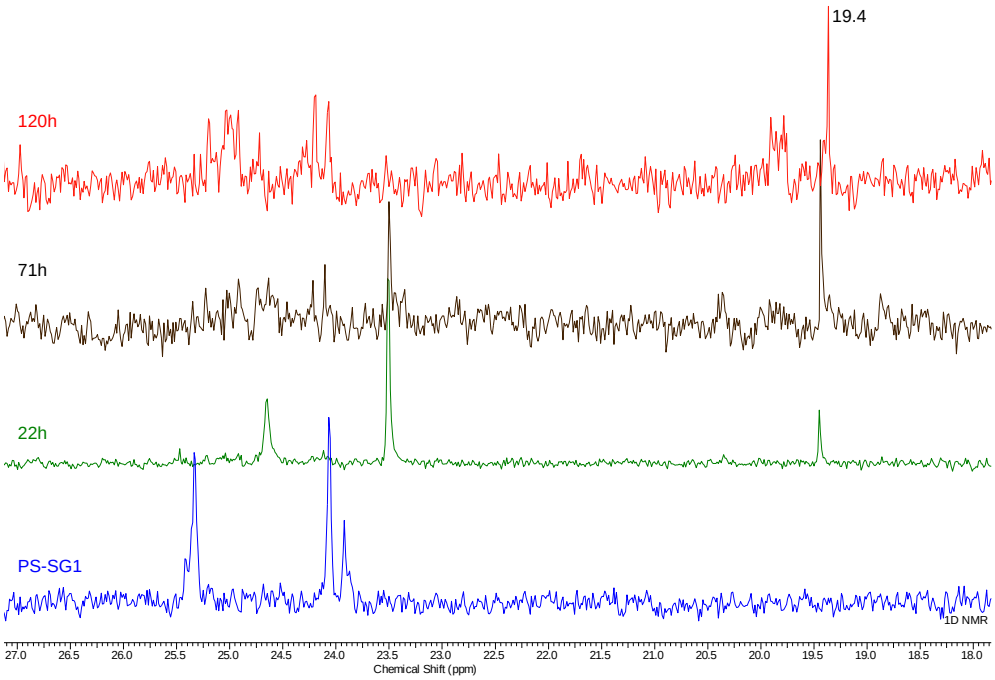
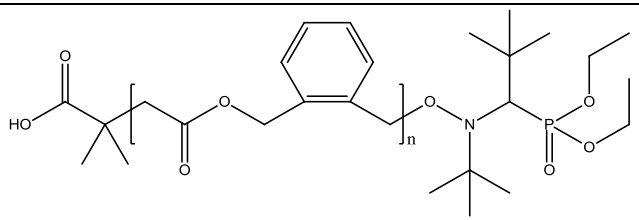
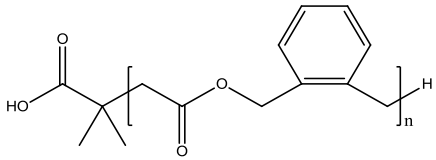
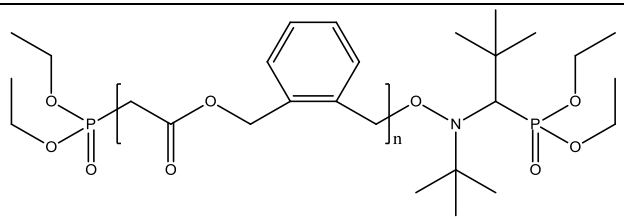
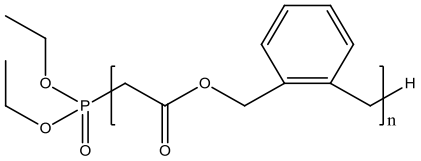


Figure S3. ^{31}P NMR ($CDCl_3$) spectra of the MDPL polymerization.

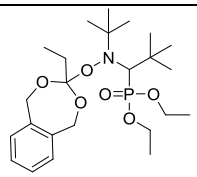
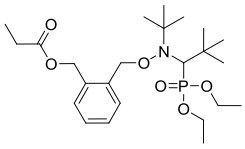
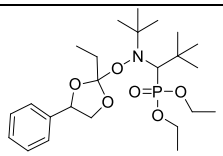
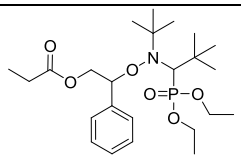
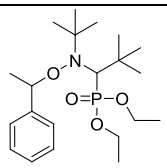
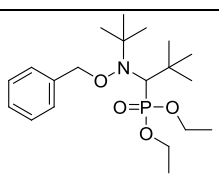
5. Accurate mass measurements of PBMDO oligomers

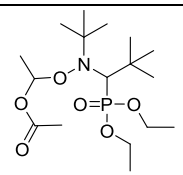
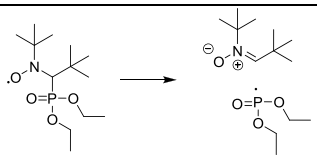
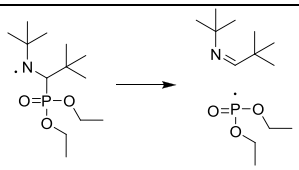
Table S1

Structure	n	elemental composition	m/z_{theo}	m/z_{exp}	Abs. error (mDa)	Rel. error (ppm)
 $m_\alpha+m_\omega$ = 381 Da (▼)	3 4	$C_{47}H_{66}NO_{12}PNa^+$ $C_{57}H_{76}NO_{14}PNa^+$	890.4215 1052.4896	890.4204 1052.4905	- 1.1 + 0.9	- 1.2 + 0.9
 $m_\alpha+m_\omega$ = 88 Da (■)	3 4	$C_{34}H_{38}O_8Na^+$ $C_{44}H_{48}O_{10}Na^+$	597.2459 759.3140	597.2419 759.3115	- 4.0 - 2.5	- 6.7 - 3.3
 $m_\alpha+m_\omega$ = 431 Da (●)	3 4	$C_{47}H_{69}NO_{13}P_2Na^+$ $C_{57}H_{79}NO_{15}P_2Na^+$	940.4136 1102.4817	940.4143 1102.4819	+ 0.7 + 0.2	+ 0.7 + 0.2
 $m_\alpha+m_\omega$ = 138 Da (↓)	4 5	$C_{44}H_{51}O_{11}PNa^+$ $C_{54}H_{61}O_{13}PNa^+$	809.3061 971.3742	809.3130 971.3835	+ 6.9 + 9.3	+ 8.5 + 9.6

6. Theoretical BDE obtained by DFT calculations

Table S2.

Compounds	BDE	BDE (kJ/mol)			
		UB3LYP/6-31G(d)// UB3LYP/6-31G(d)	B3P86/6-311++G(d,p) // UB3LYP/6-31G(d)	UBMK/6-31G(d)// UBMK/6-31G(d)	UBMK/6-311+Gg(3df,3pd) // UBMK/6-31G(d)
	C-ON	165.17	170.94	171.44	152.61
	N-O	119.67	132.17	156.06	141.36
	C-P	253.01	-	307.66	-
	C-ON	141.08	144.09	134.44	119.31
	N-O	145.33	152.89	175.48	162.83
	C-P	257.23	-	312.42	-
	C-ON	182.47	186.24	188.40	169.29
	N-O	122.09	133.41	168.37	155.39
	C-ON	124.31	128.42	124.43	107.42
	N-O	126.58	135.88	158.99	145.19
	C-ON	122.19	128.16	123.98	108.37
	N-O	133.92	145.94	162.96	149.91
	C-ON	146.47	150.24	142.22	127.29
	N-O	151.09	158.68	182.09	168.82

	C-ON N-O	181.37 119.17	178.27 122.70	178.31 152.67	160.07 136.75
	C-P	89.89	-	175.73	-
	C-P	24.62	-	56.66	-

7. PREDICI modelings: mechanism with the sole SG1 degradation

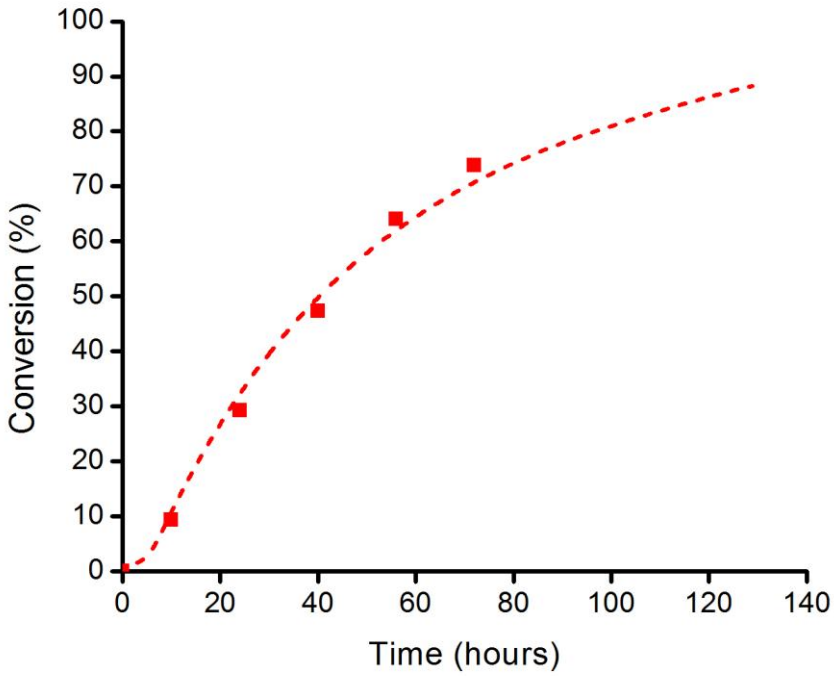


Figure S4. Kinetics of the BMDO polymerization at 120 °C in bulk initiated by the BlocBuilder MA ($[CKA]_0$: $[Alkoxyamine]_0$ = 62:1) (■).The dashed line corresponds to the PREDICI modeling using the SG1 degradation as the sole side reaction.

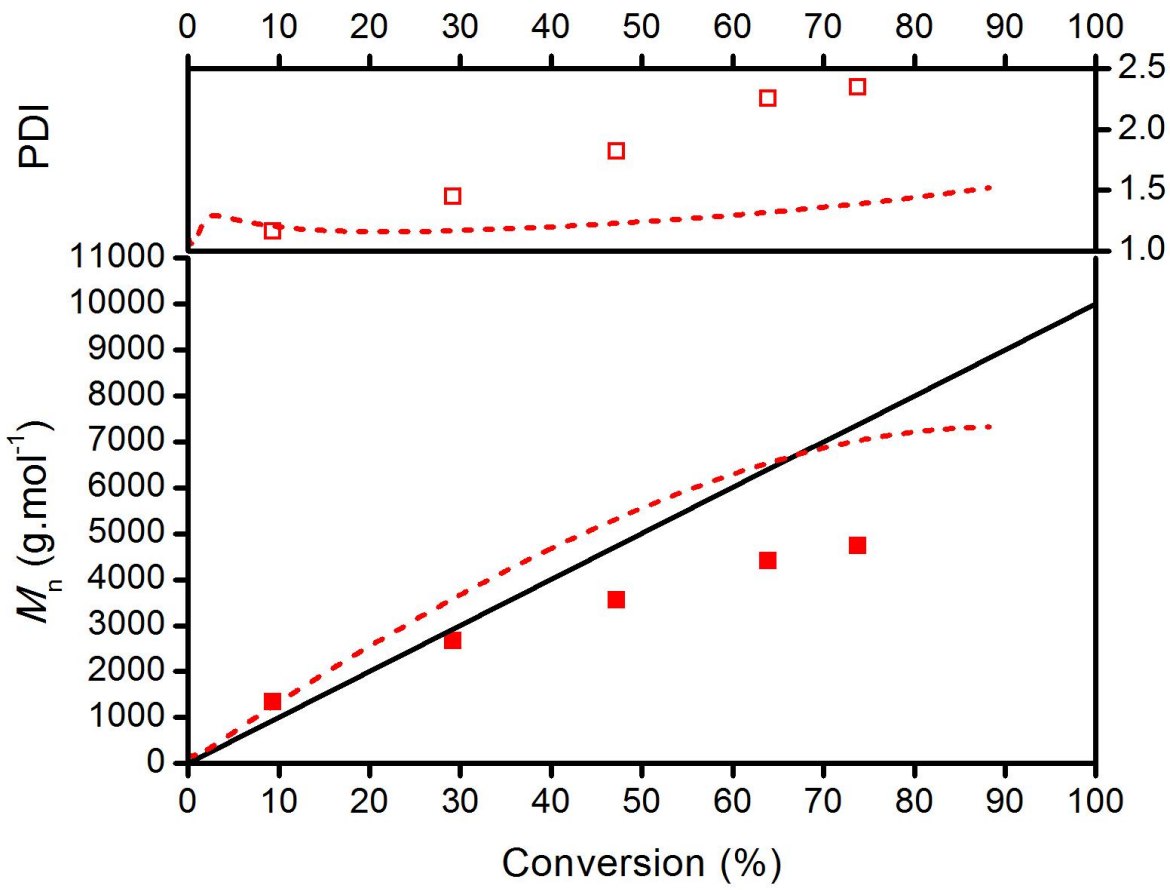
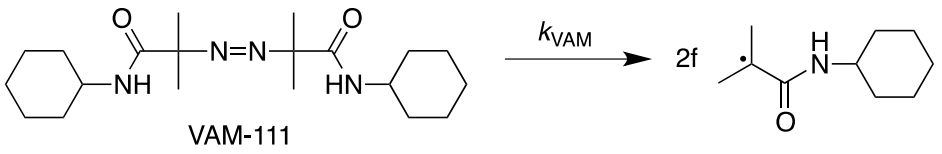


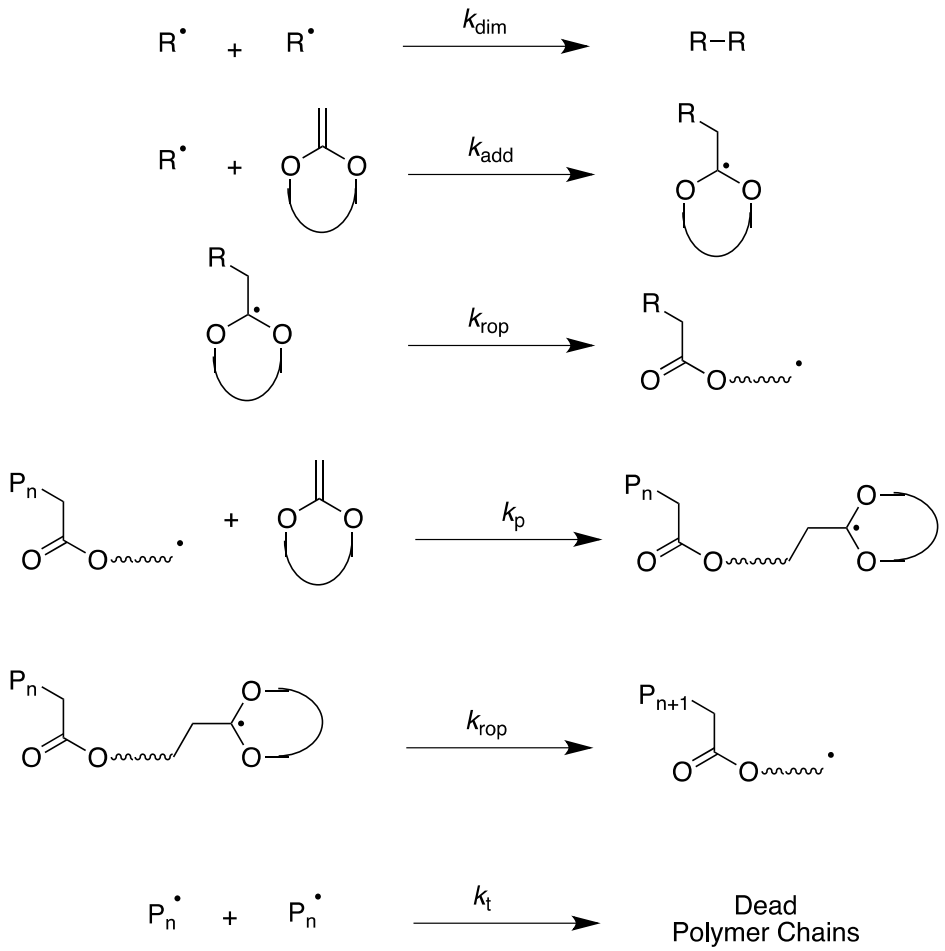
Figure S5. Evolution of number-average molar mass (M_n full symbols) and polydispersity index (PDI empty symbols) vs conversion for the bulk BMDO polymerization initiated by the BlocBuilder MA ($[BMDO]_0$: $[BlocBuilder]_0$ = 62:1). The solid line corresponds to the theoretical M_n. The dashed lines correspond to the PREDICI modeling using the SG1 degradation as the sole side reaction.

8. PREDICI modelings: discussion about the kinetic rate constants

To perform the PREDICI modelings, many kinetic rate constants are necessary and very few data are available for CKA monomers. We decided to investigate first the conventional bulk BMDO polymerization initiated by VAM-111, an oil-soluble azo-initiator that enables polymerizing at 120 °C.

The kinetic scheme that is used for such polymerization is described below:





The first part of this study consists in determining the initial concentration of BMDO. The weight of a pre-determined volume leads to 7.5 mol.L^{-1}.

The dissociation of VAM-111 is not well described; *i.e.* only the temperature that lead to 10 hours of half-life is described (111 °C) as well as an indication of the activation energy (132 kJ.mol^{-1}).[1] Besides these values are determined in ethyl-benzene. This leads to k_{dVAM} = 5 10^{-5} s^{-1}, that seems a too low value to describe the kinetics. A value of 1.45 10^{-4} s^{-1} give a better description of the kinetics. This 3-fold increase is in the error of the data given by the supplier and the difference of solvent (bulk BMDO compared to literature data given in ethylbenzene).

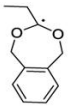
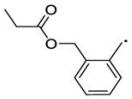
The k_{dim} value is classical for such kind of radicals.[2] An average efficiency of 75 % was used to take the cage effect into account ($[VAM\text{-}111]_0$= 1.7 10^{-1} mol.L^{-1}). The termination rate constant k_t is in a narrow range of value (5 10^7 – 5 10^8 L.mol^{-1}.s^{-1}) and a k_t value of 2.8 10^8 L.mol^{-1}.s^{-1} was used.

Two main constants are unknown, *i.e.* the ring opening rate constant k_{rop} and the propagation rate constant k_p of the macromolecular species.

According to Endo and coworkers,[3] the activation energy for the ring-opening of CKA monomers is close to 40 kJ.mol^{-1}. The pre-exponential factor of this kind of unimolecular dissociation reaction[4] is usually in a range 10^{12}-10^{14} s^{-1} and an experimental value was obtained by Ingold et al.[5] at 10^{13} s^{-1}. This led us to use a k_{rop} value of 4.8 × 10^7 s^{-1}. This rather good approximation of k_{rop} allowed us to fit the experimental conversion to estimate the k_p value. The k_p value at 120 °C was thus estimated to 1.6 10^2 L.mol^{-1}.s^{-1}. Only one publication was performed on the determination of k_p value for CKA monomers. Coote and Davis[6] estimated the k_p of 2-methylene 1,3-dioxepane (MDO) to 40-50 L.mol^{-1}.s^{-1} at 40 °C, an extrapolation at 120 °C will lead to 1.0 × 10^3 L.mol^{-1}.s^{-1}. In that case the propagating radical is a methylene radical compared to the PBMDO whose propagating radical is benzylic. The six-fold lower value for the PBMDO seems thus coherent with the work of Coote and Davis.[6]

The k_{add} value is also important since it is known that the copolymerization of CKA with other vinyl monomers is not straightforward. Using the work of Coote and Davis[6] we could use the reactivity ratio between MDO and MMA to estimate the k_{add} value. Indeed the r_2 (r_{MMA} = 34.1) value is equals to k_{p22}/k_{p21} and thus k_{p12} could be extracted knowing the k_p of MMA at such temperature. The k_{p21} is then around to 10 L.mol^{-1}.s^{-1}, i. e. a 4-fold decrease compared to the k_p value. This led us to use a k_{add} value of 40. L.mol^{-1}.s^{-1} for the addition of methacrylate type radicals onto the BMDO.

The modelling and the experimental data were finally presented in Figure 13a. Since the conventional free radical polymerization of BMDO is well described with our modeling, we could make the mechanism more complex by adding the NMP equilibrium. The dissociation of the BlocBuilder and MONAMS alkoxyamine is now well described and the k_{d1} and k_{c1} were taken from reference [2] and therein. The dissociation rate constant of the macroalkoxyamine is not known. The macroradical is benzylic and the dissociation rate constant of the model benzyl-SG1 alkoxyamine has been determined to 3.14×10^{-4} s^{-1} (E_a of 134.6 $kJ.mol^{-1}$). Nevertheless the presence of an alkyl moiety in the ortho position should lead to an increase of the k_d value. This increase could be related to the increase of the activation energy determined by the DFT calculations (see table 1: 134.5 instead of 142.2 $kJ.mol^{-1}$). The DFT calculations cannot afford a realistic E_a value. To have a better estimation of the k_d value, we consequently used the approach developed by Marque and Coote[7] that use linear free-energy relationships.

G3(MP2)-RAD		Energy	Enthalpy H	BDE-H kJ/mol	RSE kJ/mol	1 Ha = 27,2107 eV vIP eV	Tolman Angle Theta rad?
	Hydrogen		-0.501427				
					0	*9.88*	*1.85*
Methyl°	AT_KG-CH3,log	-39.785198	-39.751884	429.78	0.0	9.82	1.85
	_____H		-40.417007				
	_____+						
		-39.42429352					
	AT_KG-0fer.log	-576.65271	-576.42572	395.75	34.0	6.71	2.80
	_____H		-577.077881				
	_____+						
		-576.4059448					
	AT_KG-0ouv2.log	-576.696594	-576.471558	368.99	60.8	7.30	2.27
	_____H	-576.352173	-577.113525				
	_____1+						
		-576.4282227					
					59.0	*7.39*	*2.06*
Benzyl°	AT_KG-BZ.log	-270.537415	-270.417969	368.51	61.3	7.32	2.06
	_____H	-271.192841	-271.059753				
	_____+						
		-270.2682495					
					68.0	*7.03*	*2.37*
Styryl°	AT_KG-STY.log	-309.802307	-309.653351	360.02	69.8	6.98	2.39
	_____H	-310.453613	-310.291901				
	_____+						
		-309.5456848					

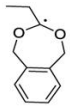
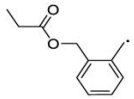
	SG1		
	RSE kJ/mol		
	5.8	log kc, eq	log kd, eq	log K
Methyl°		9.4	-8.9	26.7
		7.8	-3.0	24.1
		7.3	-3.2	18.8
		7	*-3.5*	
Benzyl°		7.5	-4.4	18.6
		5.41	*-2.12*	
		6.5	*-2.3*	
Styryl°		7.0	-2.0	17.5

Table S3

The experimental and theoretical values obtained for the styryl, benzyl and open-BMDO - based SG1 alkoxyamines are summarized in the table above. We then used 9.5×10^{-4} s^{-1} as k_d value for the open-BMDO SG1 based alkoxyamine. Concerning the k_c value, the effect affecting the k_d value are usually opposite, we could therefore expect a decrease of the k_c value compared to the one of the model benzyl-SG1 system[8] ($k_c = 1.1 \times 10^7$ $M^{-1}s^{-1}$). Using the same linear free-energy relationships, only a very small decrease is expected (i.e. k_c around 1.0×10^7 $M^{-1}s^{-1}$). Since the k_c value that has to be used is a value for macromolecular species, an order of magnitude lower value is expected as explained in reference 9. We then used 1.0×10^6 $M^{-1}s^{-1}$ as k_c value for the recombination of open-BMDO radicals and SG1.

Concerning the addition of the MONAMS alkyl radical onto CKA, we expected an increase of one order of magnitude compared to the 1-carboxy-1-methylethyl radical issed from the BlocBuilder since the alkyl radical is secondary instead of tertiary. We hen used 5.0×10^2 $M^{-1}s^{-1}$ as k_{add} for the alkyl radical issued from the MONAMS alkoxyamine.

The SG1 degradation rate constant has been determined using the paper of Fischer et al.[10] that measured the half-life of this nitroxide to 15 hours at 120 °C and moreover showed that the decomposition followed a first order decay. We then used a k_{deg} value of 1.3×10^{-5} s^{-1}.

The recombination of the SG1 and the ketal-based macroradical has never been studied. Moreover the recombination of nitroxide with alkyl radical that bears a heteroatom in alpha-position was never investigated as well. We only know that usually the k_d and k_c values are anti-correlated[11] and that the k_d value of the corresponding alkoxyamine is very low due to the anomeric effect.[12] This could envision a rather high k_c value. As this kind of alkyl radicals was not studied before, the correlation determined for other alkyl radicals cannot be used.[7] Nevertheless it has been demonstrated that the log k_c is related to the strength of the BDE_{C-H} of the corresponding alkane.[13, 14] The BDE of the opened and closed BMDO macroradical are

respectively 369 and 395 kJ.mol^{-1} (Table S3) that is 25 kJ.mol^{-1} higher value for the closed macroradical, that could lead to an increase of k_c value by one or two order of magnitude. Secondly the k_c value is dependent of the hybridization of the radical center, i.e. the closer the s-type, the better the reactivity.[11, 14] This is due to the fact that the overlapping between the two SOMOs is required to induce the recombination. The presence of three oxygen atoms in alpha position on the alkyl radical leads to a nearly s-type hybridization and thus could enhance drastically the recombination rate constant. This contributes as well to an increase of the k_c value by at least two order of magnitude. We used then a k_{ctrap} value of 4.0×10^8 M^{-1}s^{-1}.

Once the ketal-based macroradical has been trapped, the corresponding alkoxyamine cannot dissociate by a C-ON bond dissociation since the DFT calculations gave a BDE (C-ON) above 170 kJ.mol^{-1}. When high BDE (C-ON) are observed, the undesired CO-N dissociation has to be investigated. The DFT calculations (Table S2) showed indeed lower BDE (CO-N) than BDE (C-ON) and thus the dissociation of the macroalkoxyamine should occur by a CO-N dissociation. We do not have any information of such dissociation but we could expect a dissociation that could be similar to the C-ON one. Because of these results and the determined BDE value, we used a k_{dec} value close to 10^{-3} s^{-1}. The last unknown kinetic rate constant is the k_{addP}, the addition of the diethyl phosphonyl radical onto the CKA. It has been shown that the addition of such radical onto electron-rich alkene is very fast. We tested different values and whatever the value above 5.0×10^2 M^{-1}s^{-1}, similar conversion and M_n profiles were obtained. We thus decided to use 1.0×10^4 M^{-1}s^{-1}.

When investigated the MPDL polymerization, only few kinetic rate constants were changed. The k_d value for the macromolecular species was estimated at 3.0×10^{-3} s^{-1}, a value close to the corresponding polystyryl radical (7.5×10^{-3} s^{-1}), but the ester located onto the backbone

should decrease the steric hindrance due to the polymer chain and thus a lower value was used. The same analysis has been performed for the k_c value. Instead of 2-5 × 10^5 $M^{-1}s^{-1}$ that corresponds to the k_c value for the polystyryl radical and the SG1 nitroxide, a k_c value of 7.0 × 10^5 $M^{-1}s^{-1}$ was used.

Once opened, the propagating radical of the CKA monomers are different and the addition of the open-radical onto another monomer could differ due to the steric hindrance. To take into account the more stabilized MDPL-based styryl radical compared to the benzylic BMDO-based radical, the propagation rate constant was decreased from 1.6 × 10^2 $M^{-1}s^{-1}$ to 6.0 × 10^1 $M^{-1}s^{-1}$.

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