SUPPORTING INFORMATION

Polymerization of Cyclic Esters Using *N*-Heterocyclic Carbene Carboxylate Catalysts

Emilie Brulé, Vincent Guérineau, Philippe Vermaut, Frédéric Prima, Janos Balogh, L. Maron, Alexandra M. Z. Slawin, Steven P. Nolan, Christophe M. Thomas

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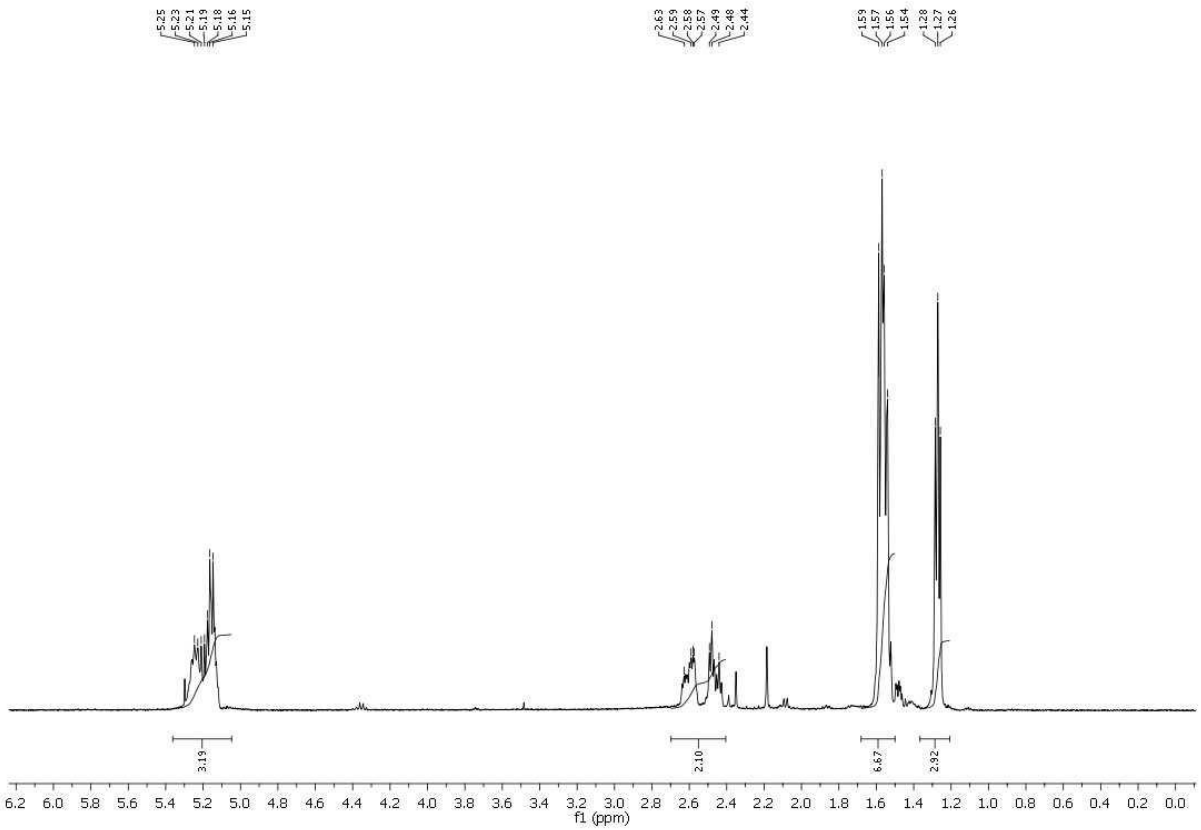
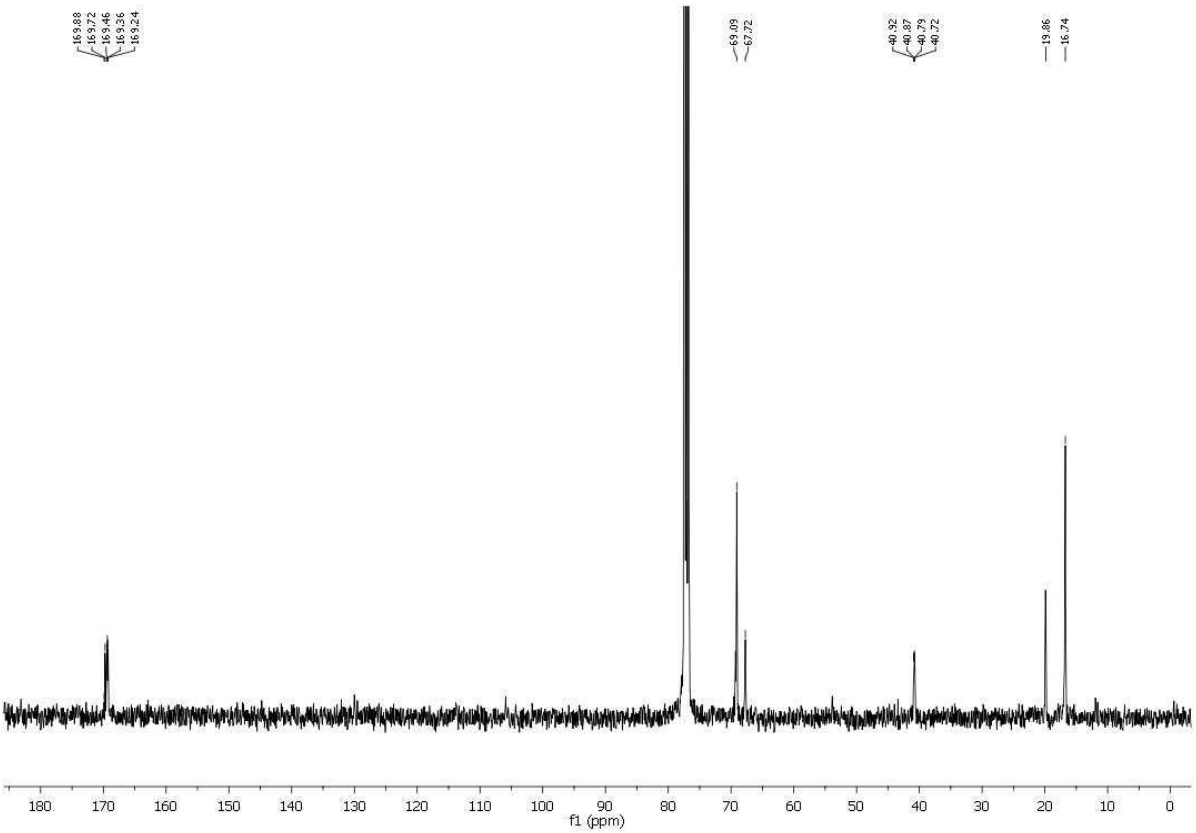
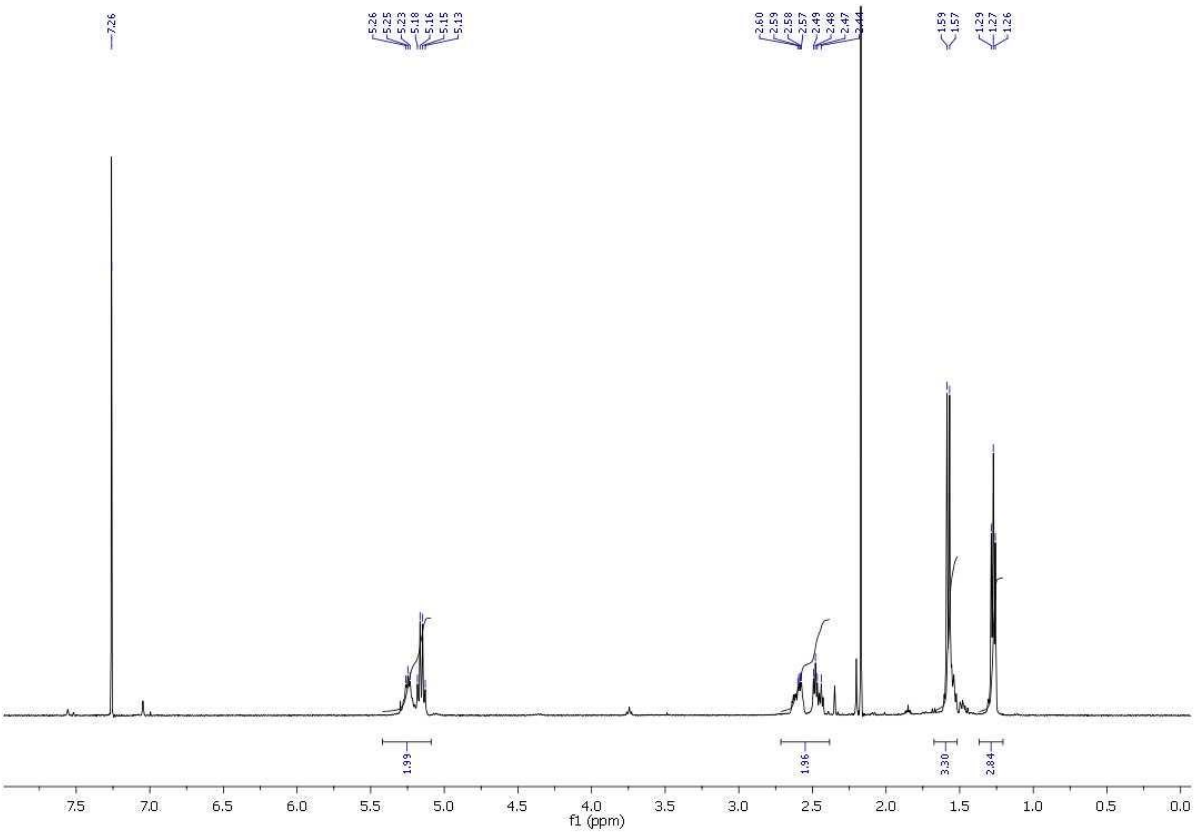
^{1}H NMR spectrum of copolymer from *rac*-BBL + *rac*-PLA



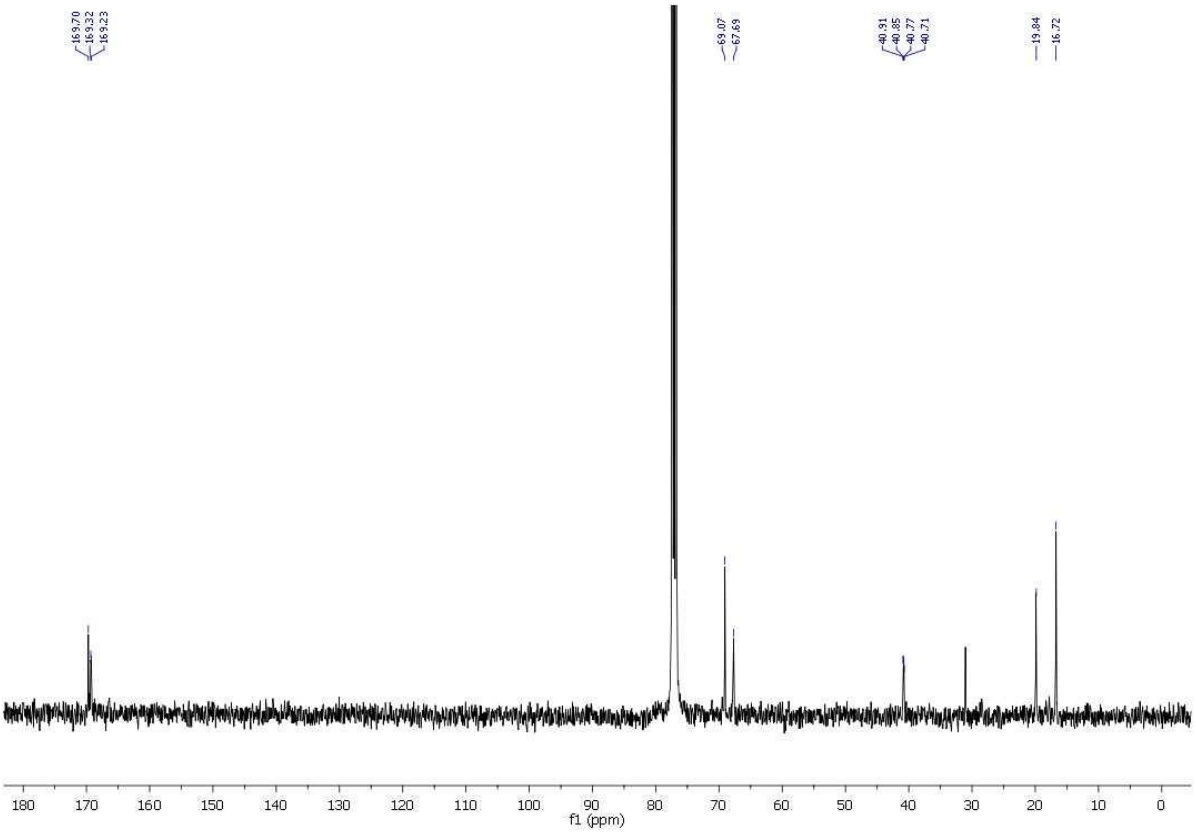
^{13}C NMR spectrum of copolymer from *rac*-BBL + *rac*-PLA



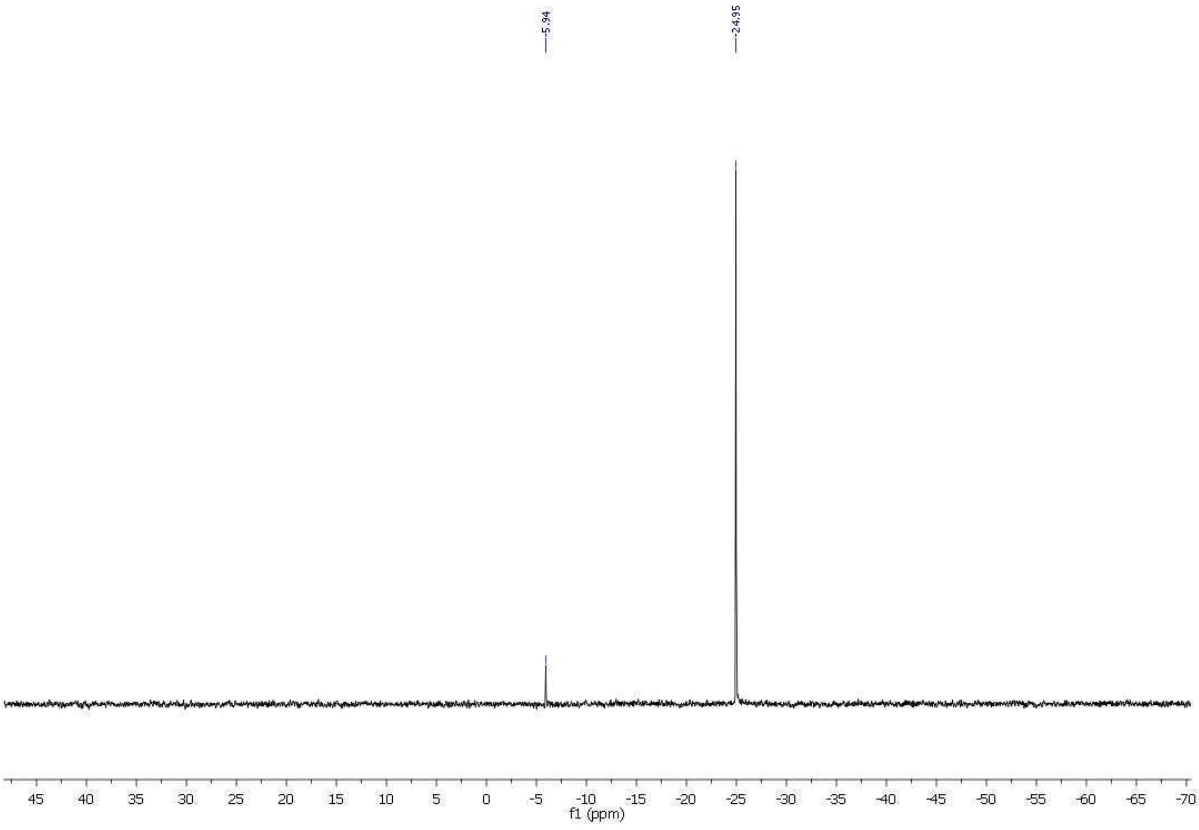
^{1}H NMR spectrum of copolymer from *rac*-BBL + *L*-PLA



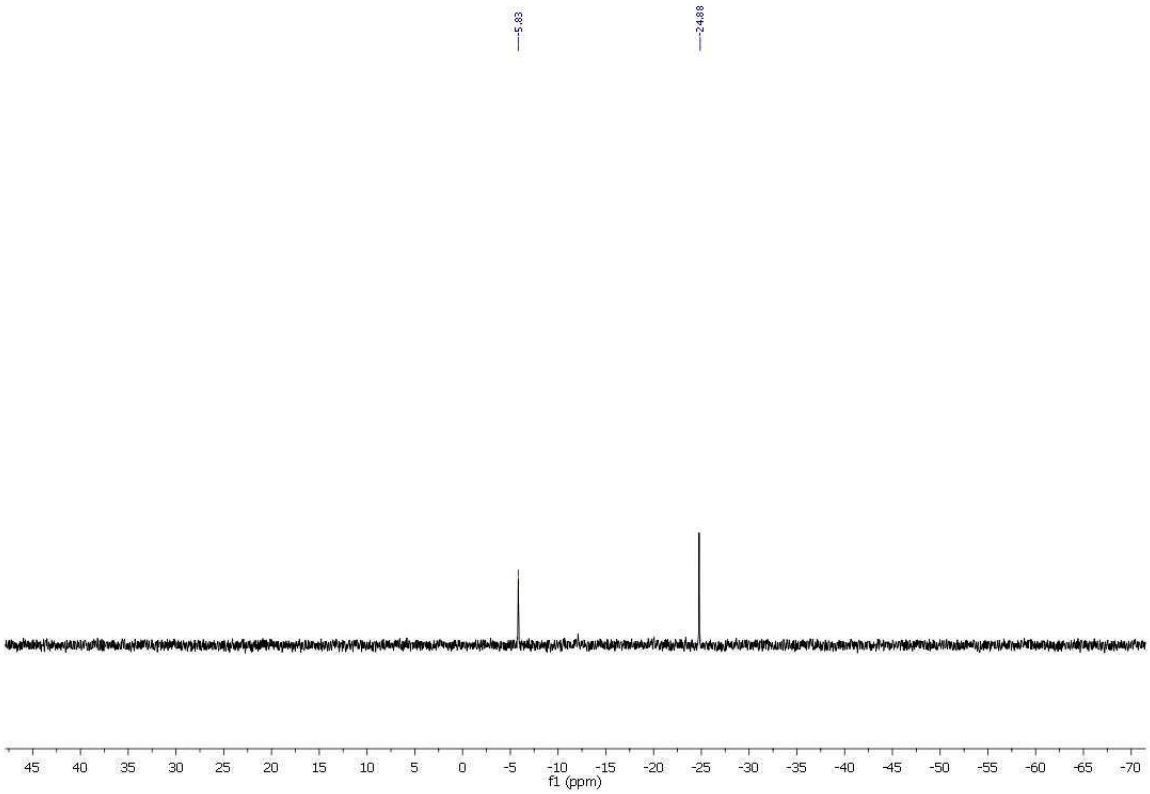
^{13}C NMR spectrum of copolymer from *rac*-BBL + *L*-PLA



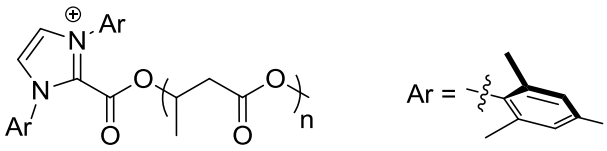
^{31}P NMR spectrum in C_6D_6 obtained from the addition of excess of $(PhO)_2POCl$ (δ= -5.94) on the polymerization reaction mixture of BBL in C_6D_6

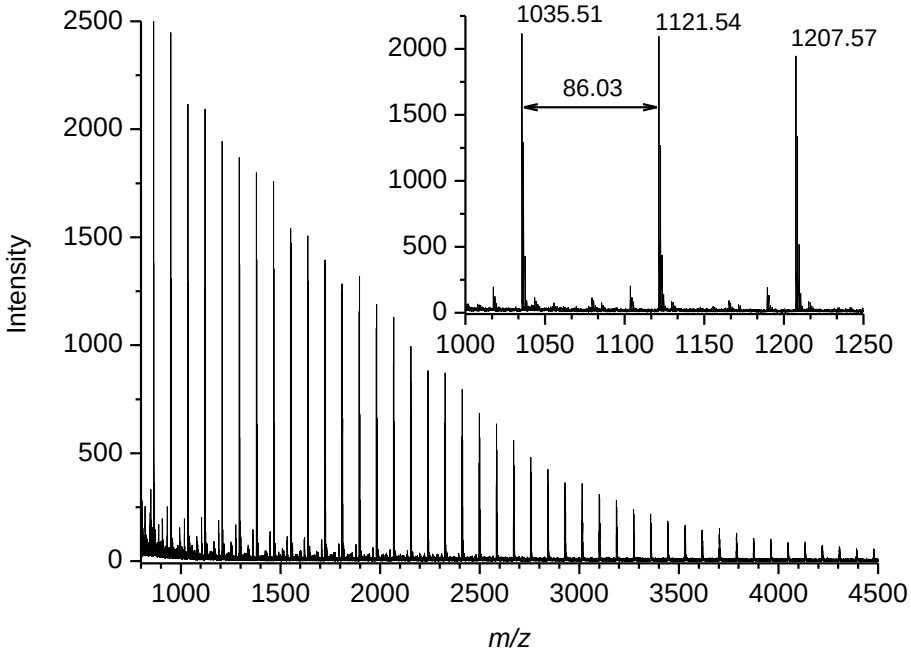


^{31}P NMR spectrum in C_6D_6 obtained from the addition of excess of $(PhO)_2POCl$ (δ= -5.84) on the bulk polymerization reaction mixture of BBL

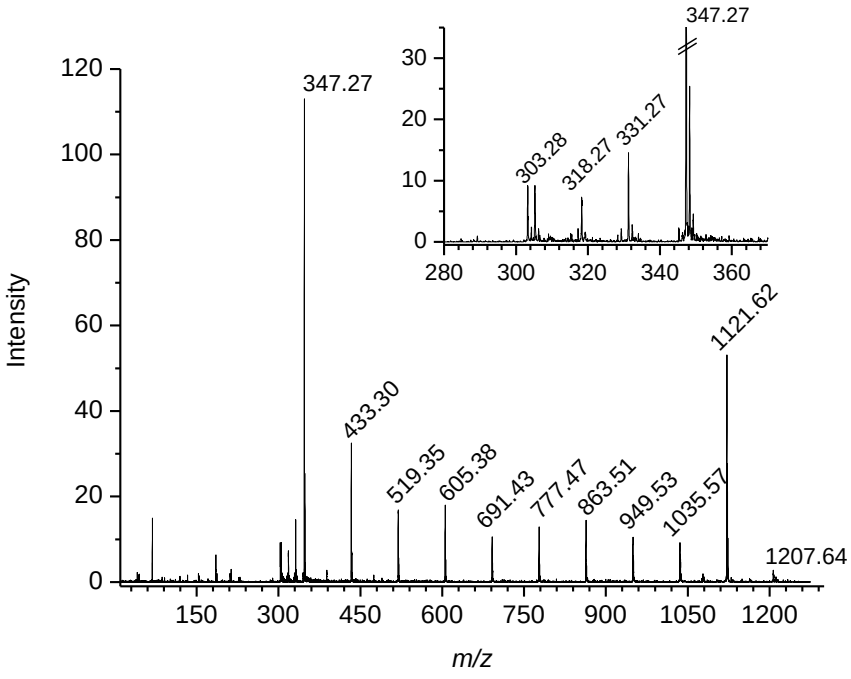


MALDI-TOF spectrum of oligomer after ROP of BBL with IMes.CO_2 without solvent

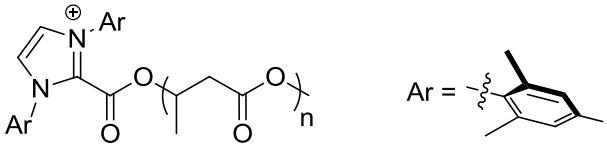


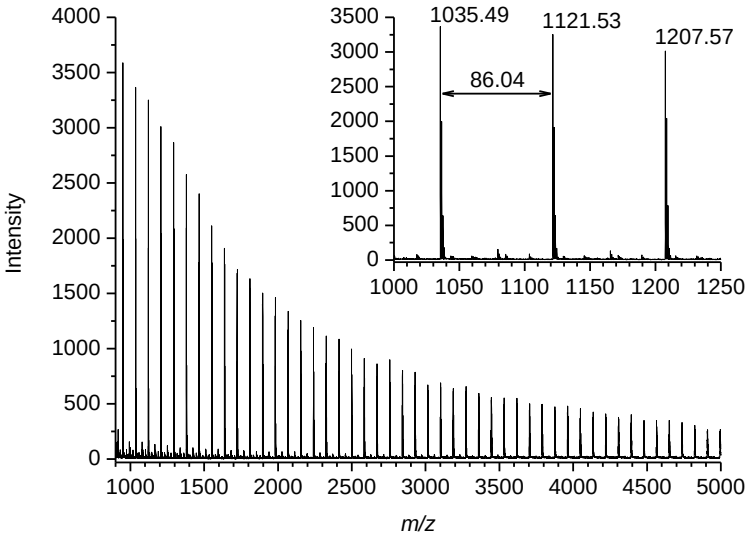


MS-MS spectrum of the ion at *m/z* 1207

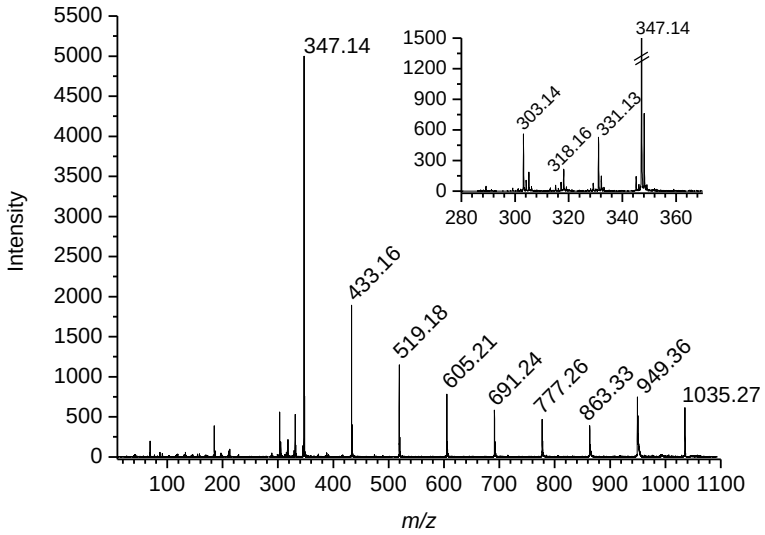


MALDI-TOF spectrum of oligomer after ROP of BBL with IMes.CO_2 in CH_3CN

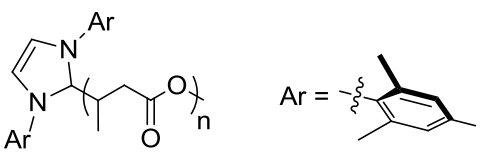


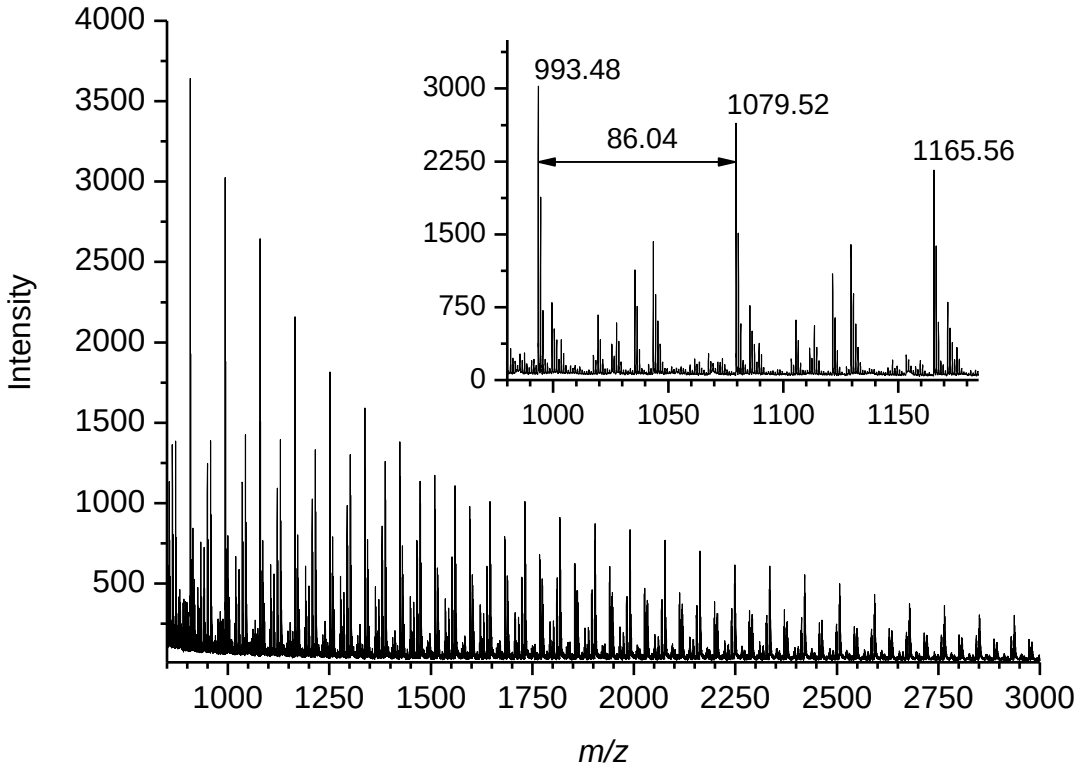


MS-MS spectrum of the ion at *m/z* 1035



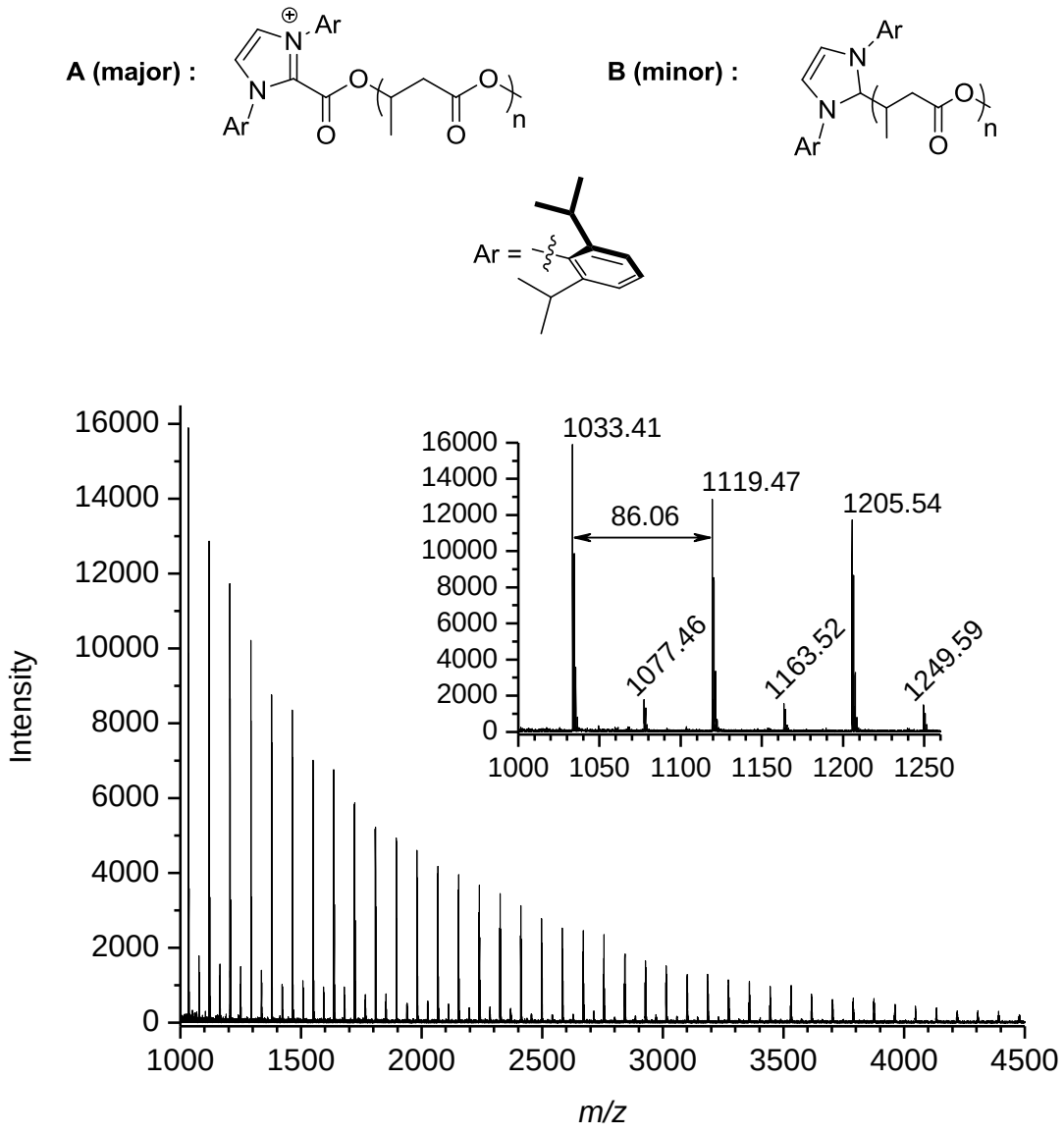
MALDI-TOF spectrum of oligomer after ROP of BBL with IMes.CO_2 in THF



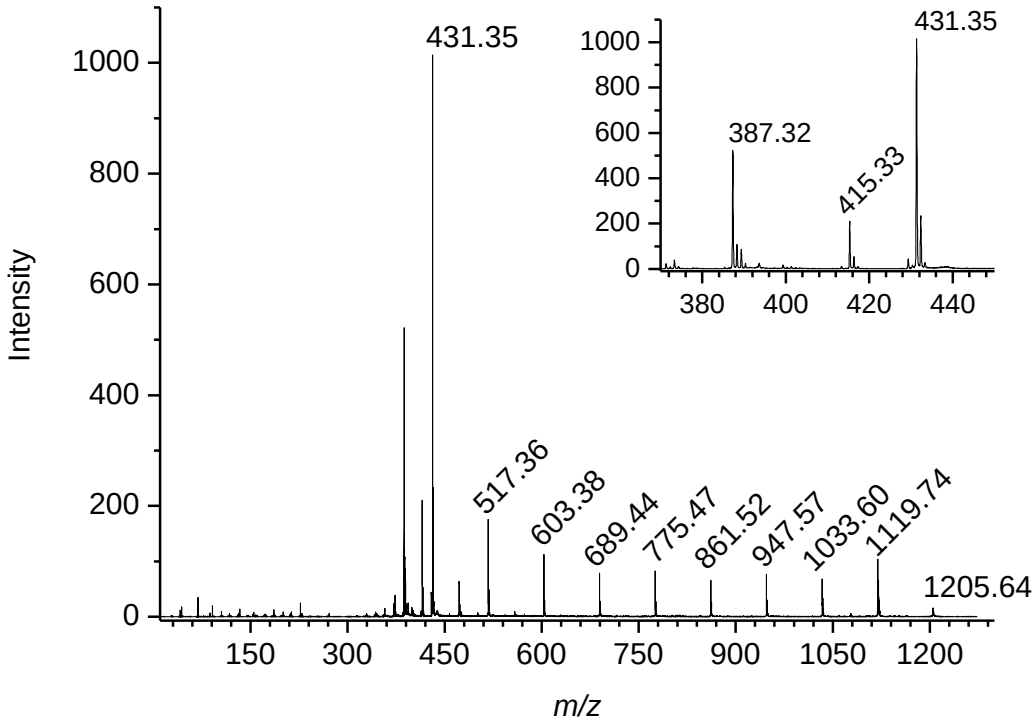


MALDI-TOF spectrum of oligomer after ROP of BBL with IPr.CO_2

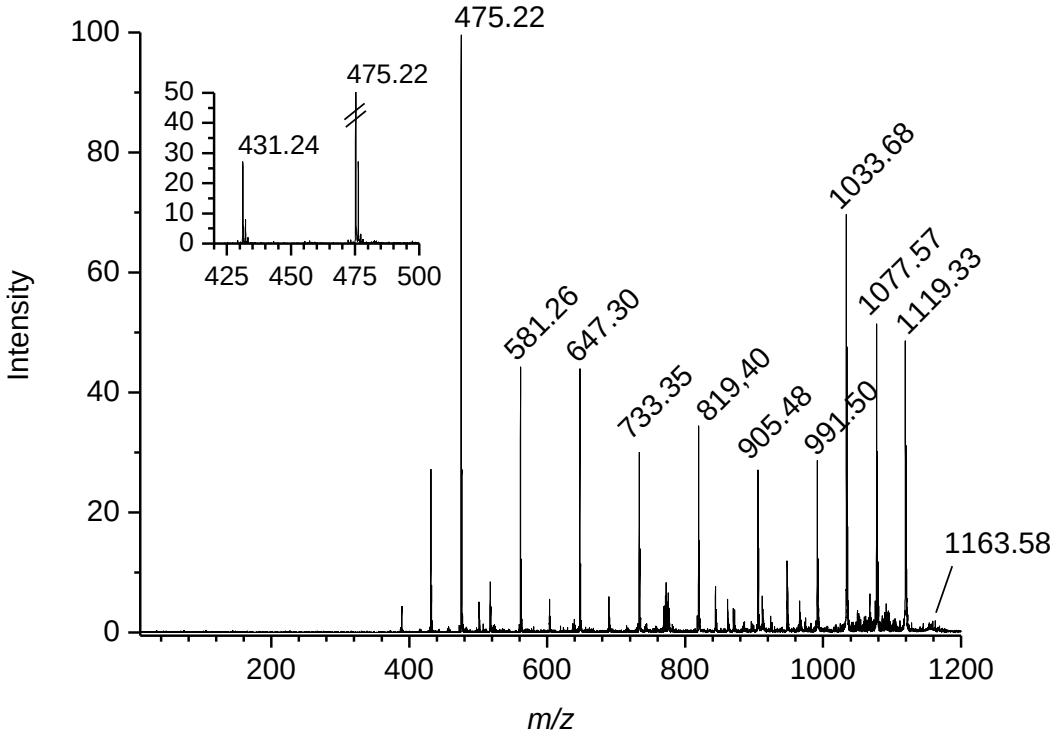
in neat monomer at 80°C



MSMS spectrum of the ion at *m/z* 1205 from distribution A

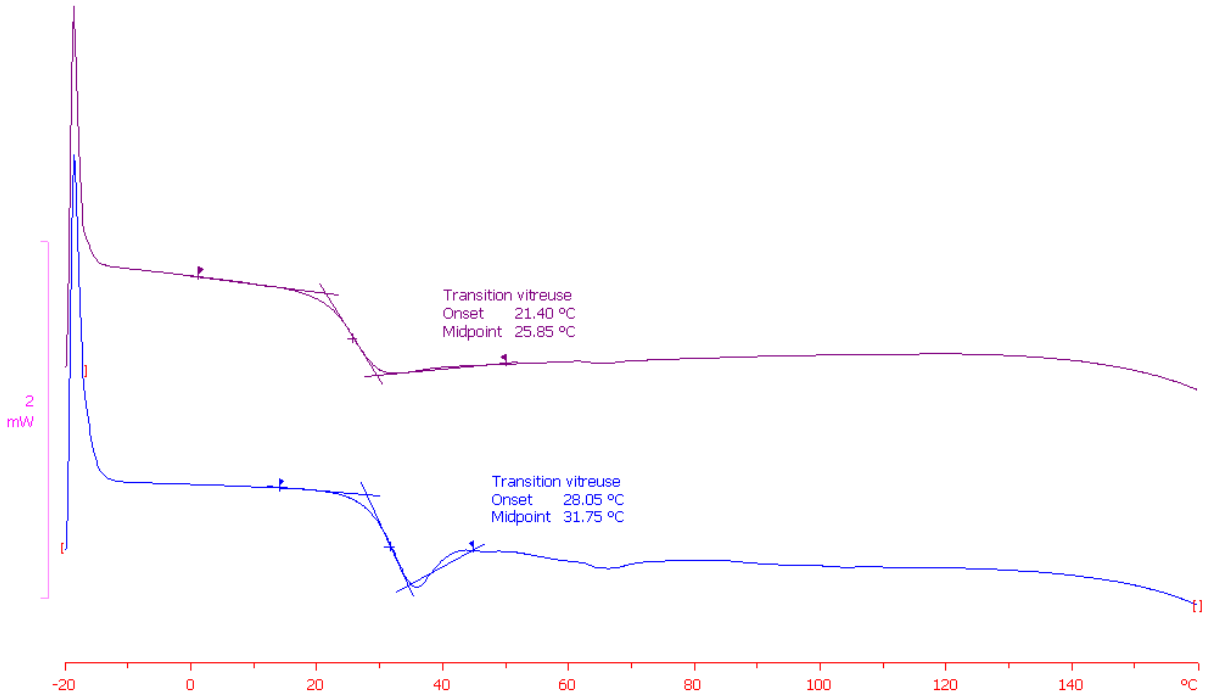


MSMS spectrum of the ion at *m/z* 1163 from distribution B

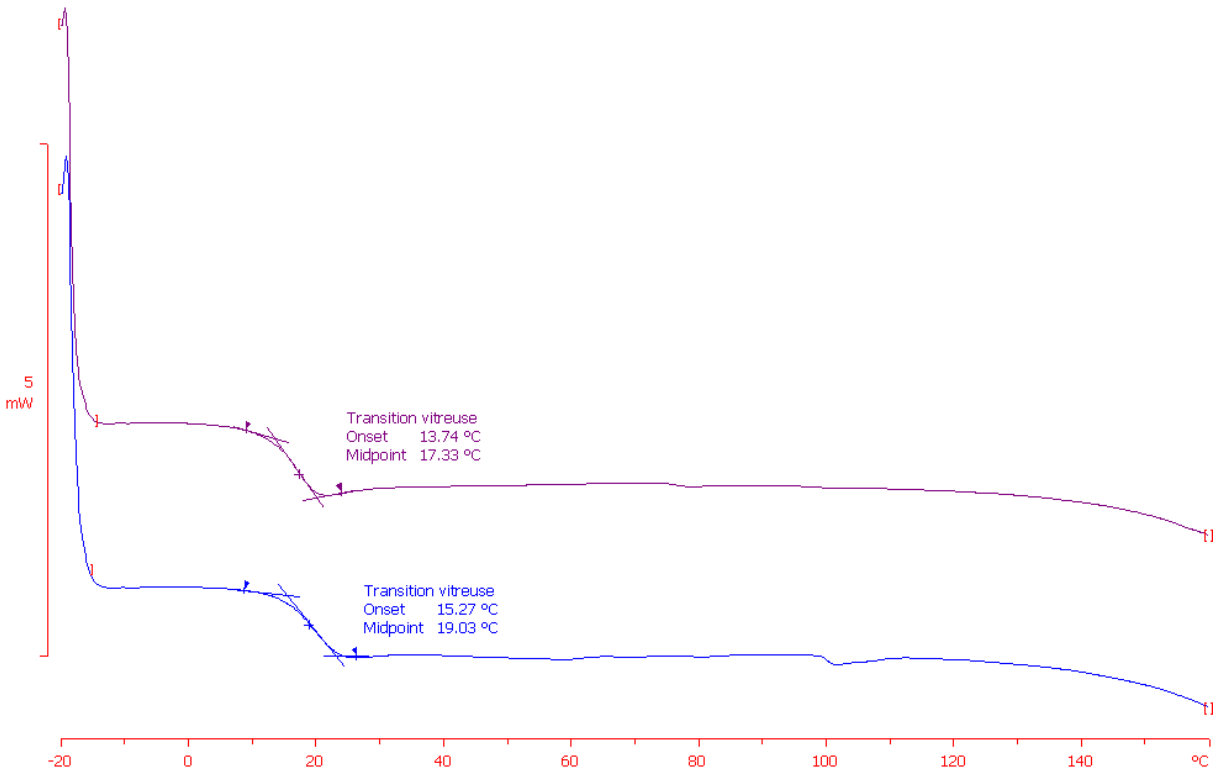


Differential Scanning Calorimetry

DSC thermogram of Copolymer obtained from *rac*-BBL + *rac*-LA



DSC thermogram of Copolymer obtained from *rac*-BBL + L-LA



DFT

Cartesian coordinates of all optimized structures

IMes.CO_2

50

E=-1112.4123083

C	0.890239	0.251603	1.820997
C	0.313438	0.986344	2.864669
C	0.750586	0.894917	4.192134
C	1.846318	0.069696	4.450166
C	2.481687	-0.652722	3.436935
C	1.982707	-0.558319	2.135201
N	-0.788770	1.862357	2.561987
C	-2.087318	1.512830	2.582899
N	-2.796927	2.604420	2.245611
C	-1.931795	3.664957	2.006647
C	-0.673799	3.200082	2.204980
C	-2.657261	0.119364	2.928647
C	-4.232194	2.664133	2.144546
C	-4.829392	2.360667	0.914175
C	-6.218677	2.463899	0.833623
C	-6.996296	2.839400	1.932398
C	-6.356552	3.094816	3.147590
C	-4.969912	3.006785	3.284329
C	-4.009261	1.875187	-0.248467
C	-8.490777	2.970218	1.805324
C	-4.297864	3.201586	4.614818
C	0.022253	1.603006	5.300359
C	3.681712	-1.509585	3.740588
C	0.307851	0.283621	0.435464
H	-2.297089	4.638447	1.721178
H	0.286973	3.683491	2.128828
H	-6.951309	3.354495	4.020316
H	-6.705397	2.227899	-0.109970
H	2.444365	-1.142198	1.342183
H	2.200924	-0.021332	5.474301
H	-3.819432	2.264014	4.923203
H	-3.523309	3.975681	4.576095
H	-5.024636	3.489521	5.377910
H	-3.216381	2.582063	-0.517251
H	-3.533834	0.921793	0.012575
H	-4.637442	1.721785	-1.128971
H	-8.767547	3.966154	1.438002
H	-8.896994	2.239165	1.100180
H	-8.988628	2.826432	2.768271
H	0.901250	-0.327007	-0.248915
H	-0.715003	-0.111593	0.459927
H	0.263818	1.300752	0.030257
H	-1.003351	1.219951	5.366875
H	0.519106	1.436728	6.258931
H	-0.034242	2.684218	5.131627

H	3.650650	-1.892756	4.764493
H	3.746626	-2.363324	3.059989
H	4.610311	-0.935256	3.634174
O	-2.767306	-0.612398	1.931963
O	-2.899703	-0.010565	4.139106

CO_2

3

E=-188.4955728

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.220000
O	0.021292	0.000000	-1.219814

BBL adduct

62

E=-1418.7928682

C	-5.540856	4.537158	4.837562
O	-6.277088	3.904016	3.881848
O	-4.469271	5.061584	4.698329
O	-5.792187	1.587721	7.765479
C	-6.030640	0.659176	6.973000
C	-5.053774	-0.521248	7.113171
O	-6.875738	0.488903	6.076890
C	-6.540957	4.301478	5.953764
C	-7.352829	3.601217	4.855835
C	-8.664459	4.210886	4.428956
N	-5.208299	-1.618700	7.872918
C	-4.102235	-2.444812	7.716071
C	-3.268546	-1.826938	6.842152
N	-3.875065	-0.633472	6.478345
C	-6.341995	-1.894390	8.717507
C	-6.316935	-1.437307	10.041457
C	-7.409342	-1.756191	10.849548
C	-8.497989	-2.486436	10.365639
C	-8.488073	-2.894711	9.029535
C	-7.422053	-2.603326	8.176745
C	-3.344736	0.352184	5.569160
C	-3.684823	0.264567	4.213867
C	-3.185061	1.252839	3.364124
C	-2.394695	2.303245	3.835426
C	-2.081119	2.343223	5.197251
C	-2.552516	1.383471	6.091597
C	-5.183495	-0.591521	10.551969
C	-9.676459	-2.787331	11.252981
C	-7.453762	-2.982227	6.722237
C	-4.608286	-0.808151	3.705974
C	-1.956451	3.412617	2.921130
C	-2.286811	1.494113	7.567479
H	-6.187250	3.641284	6.752199
H	-2.308784	-2.115713	6.444654
H	-4.020803	-3.383472	8.240266

H	-1.483910	3.166551	5.580938
H	-3.449576	1.217090	2.310106
H	-9.337631	-3.445973	8.633047
H	-7.412014	-1.414004	11.881923
H	-3.227129	1.692728	8.095066
H	-1.855935	0.575933	7.982107
H	-1.596062	2.314590	7.774497
H	-4.257890	-1.813487	3.965294
H	-5.604443	-0.676432	4.144494
H	-4.701231	-0.753691	2.618963
H	-2.641049	4.260699	3.038900
H	-0.948145	3.761349	3.164689
H	-1.970884	3.102673	1.872530
H	-8.355362	-3.553547	6.490069
H	-7.447452	-2.075714	6.105484
H	-6.586724	-3.586963	6.434345
H	-5.136355	0.346410	9.986093
H	-5.324959	-0.351353	11.608141
H	-4.215092	-1.092963	10.446356
H	-10.190485	-3.700875	10.941045
H	-9.372583	-2.906169	12.297034
H	-10.408217	-1.971262	11.216913
H	-7.413813	2.518762	4.996011
H	-6.972709	5.215858	6.369931
H	-9.006997	3.775952	3.485052
H	-9.428443	4.016164	5.188930
H	-8.572739	5.294152	4.296732

TS O-acyl

62

E=-1418.7244506

C	-6.754456	2.469872	7.656960
O	-5.800829	2.333883	6.211493
O	-6.184661	2.665739	8.712389
O	-7.350568	1.072046	7.432778
C	-6.661123	0.506042	6.430368
C	-5.353225	-0.138749	6.878249
O	-7.160635	0.079820	5.398602
C	-7.597821	3.449908	6.836557
C	-6.805172	3.124912	5.562559
C	-6.199387	4.294541	4.811316
N	-5.297715	-1.048291	7.873398
C	-4.021635	-1.574395	7.944275
C	-3.293332	-0.973730	6.971974
N	-4.130953	-0.090745	6.312034
C	-6.385723	-1.499907	8.711441
C	-6.488095	-0.982784	10.009762
C	-7.519942	-1.477760	10.809721
C	-8.418536	-2.443580	10.351618
C	-8.260916	-2.938784	9.055401
C	-7.247085	-2.485291	8.209921

C	-3.655653	0.700843	5.198651
C	-3.857637	0.215840	3.901670
C	-3.303578	0.950914	2.850181
C	-2.563530	2.113400	3.070003
C	-2.371158	2.540928	4.387005
C	-2.906846	1.853632	5.476150
C	-5.557307	0.081208	10.514228
C	-9.545848	-2.922308	11.226821
C	-7.100500	-3.039462	6.818422
C	-4.635022	-1.043914	3.638516
C	-1.999784	2.900566	1.916855
C	-2.711764	2.353397	6.879132
H	-8.665133	3.216516	6.826237
H	-2.260748	-1.081453	6.681599
H	-3.762894	-2.322176	8.676363
H	-1.791737	3.441859	4.576076
H	-3.451603	0.595180	1.833082
H	-8.944267	-3.700270	8.686616
H	-7.624554	-1.086688	11.819087
H	-3.679633	2.621605	7.315301
H	-2.248037	1.601269	7.527259
H	-2.069404	3.237250	6.885084
H	-4.196312	-1.904316	4.157912
H	-5.667462	-0.934256	3.987125
H	-4.646886	-1.271637	2.570036
H	-2.674000	3.718508	1.635495
H	-1.034958	3.349432	2.171649
H	-1.860600	2.272901	1.032085
H	-7.783471	-3.878787	6.668273
H	-7.325516	-2.277730	6.064344
H	-6.082460	-3.398687	6.629660
H	-5.704609	1.015236	9.952768
H	-5.742828	0.279799	11.572551
H	-4.505892	-0.209272	10.408687
H	-9.841852	-3.945468	10.977699
H	-9.271924	-2.893875	12.285451
H	-10.430310	-2.286067	11.101515
H	-7.384481	2.492278	4.872040
H	-7.441656	4.469121	7.203379
H	-5.521473	3.937079	4.030258
H	-6.981918	4.899648	4.338676
H	-5.630146	4.935110	5.492978

TS O-acyl product

62

E=-1418.777575

C	-7.435959	2.468492	8.045487
O	-5.926779	1.972957	5.862810
O	-7.747654	2.806762	9.171914
O	-7.044199	1.220795	7.801489
C	-6.465206	0.780198	6.420983

C	-5.246755	-0.036359	6.892981
O	-7.264347	0.091615	5.738828
C	-7.463438	3.460608	6.892061
C	-6.990899	2.878711	5.562513
C	-6.468992	3.922656	4.595663
N	-5.272586	-1.012162	7.824868
C	-4.057382	-1.675693	7.825827
C	-3.283357	-1.100245	6.875628
N	-4.034633	-0.085484	6.301738
C	-6.364148	-1.438891	8.675702
C	-6.471377	-0.917112	9.969674
C	-7.474476	-1.441536	10.789013
C	-8.349020	-2.435087	10.349575
C	-8.202302	-2.921244	9.047939
C	-7.215563	-2.441364	8.187034
C	-3.524793	0.708545	5.208529
C	-3.814604	0.305501	3.900093
C	-3.231645	1.037325	2.863323
C	-2.397276	2.131279	3.105617
C	-2.151082	2.500683	4.430570
C	-2.710378	1.806937	5.504501
C	-5.613979	0.209723	10.470162
C	-9.446728	-2.947876	11.243242
C	-7.096186	-2.954854	6.780138
C	-4.741351	-0.845325	3.623735
C	-1.805507	2.916024	1.964804
C	-2.492454	2.255992	6.922584
H	-8.480043	3.863021	6.826883
H	-2.277959	-1.306903	6.546090
H	-3.869394	-2.490144	8.506552
H	-1.513438	3.357541	4.636940
H	-3.440065	0.741835	1.837411
H	-8.876095	-3.694752	8.686243
H	-7.578595	-1.045293	11.796622
H	-3.447577	2.548597	7.372024
H	-2.064209	1.466486	7.549766
H	-1.819522	3.115778	6.959308
H	-4.373601	-1.777461	4.068504
H	-5.734035	-0.647303	4.048529
H	-4.844972	-1.006910	2.548170
H	-2.477799	3.726314	1.657479
H	-0.851571	3.372703	2.244041
H	-1.636695	2.283779	1.088272
H	-7.839241	-3.733032	6.590069
H	-7.256976	-2.124813	6.081239
H	-6.105750	-3.381641	6.581418
H	-6.120065	1.158914	10.256348
H	-5.469174	0.134524	11.551572
H	-4.629506	0.236242	9.995527
H	-9.671682	-3.999345	11.040770
H	-9.181624	-2.852595	12.300141

H	-10.371727	-2.380062	11.085872
H	-7.797589	2.301043	5.094565
H	-6.819176	4.294138	7.197793
H	-6.140355	3.452517	3.665114
H	-7.252703	4.650682	4.361582
H	-5.618917	4.459156	5.030139

TS O-alkyl

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E= -1418.7579223

C	-2.805465	1.460198	5.774651
C	-3.649249	0.410366	5.387863
C	-4.212621	0.316230	4.107367
C	-3.945035	1.356685	3.216478
C	-3.159145	2.457618	3.572093
C	-2.562050	2.462958	4.837073
N	-4.011133	-0.580770	6.374840
C	-5.148064	-0.556919	7.090588
N	-5.154762	-1.636440	7.888700
C	-3.990365	-2.359054	7.679880
C	-3.279119	-1.701354	6.727530
C	-6.270895	0.467345	6.936679
O	-7.276198	0.070645	6.353221
C	-6.186417	-1.974769	8.838991
C	-6.107934	-1.430674	10.127643
C	-7.102086	-1.796061	11.036779
C	-8.140714	-2.662860	10.687423
C	-8.184480	-3.160945	9.382325
C	-7.219020	-2.829408	8.431065
C	-5.023253	-0.459738	10.508497
C	-9.182424	-3.063953	11.696763
C	-7.315734	-3.321262	7.014048
C	-5.115127	-0.823674	3.717640
C	-3.067535	3.657213	2.675683
C	-2.265165	1.561002	7.174695
O	-5.962773	1.599613	7.422932
C	-6.895531	3.110400	6.637092
C	-5.771231	3.577619	5.774216
C	-6.513262	4.578897	4.858606
O	-7.727910	4.643440	5.244220
C	-7.236977	3.797537	7.920318
H	-4.972921	4.055114	6.350563
H	-2.330926	-1.922827	6.264278
H	-3.784379	-3.263953	8.228800
H	-1.941780	3.307740	5.126343
H	-4.404672	1.329669	2.231755
H	-9.000354	-3.816976	9.088485
H	-7.066402	-1.383491	12.042228
H	-3.087216	1.717013	7.882396
H	-1.725204	0.659621	7.484217
H	-1.580419	2.407235	7.262276

H	-4.667336	-1.797190	3.946179
H	-6.071958	-0.764250	4.248419
H	-5.324570	-0.794114	2.646282
H	-2.131322	4.203902	2.820678
H	-3.154581	3.385018	1.620056
H	-3.903251	4.329747	2.925903
H	-8.156321	-4.008927	6.899972
H	-7.469037	-2.471898	6.338954
H	-6.407609	-3.844356	6.694890
H	-5.110250	0.466537	9.929332
H	-5.091984	-0.201716	11.567413
H	-4.023065	-0.867989	10.326663
H	-10.156708	-3.219425	11.224867
H	-8.905110	-4.003266	12.190447
H	-9.298604	-2.306084	12.476191
H	-5.336881	2.765041	5.190805
H	-7.954701	3.218450	8.505493
H	-6.336375	3.965214	8.518196
H	-7.678998	4.763065	7.667575
O	-5.943532	5.154538	3.929469
H	-7.648478	2.487146	6.174915

TS O-alkyl product

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E=-1418.7858407

C	-2.795412	1.489463	5.769833
C	-3.626357	0.422496	5.401854
C	-4.195979	0.301092	4.126031
C	-3.965000	1.341805	3.226630
C	-3.217117	2.473036	3.572074
C	-2.592782	2.492417	4.824572
N	-3.984377	-0.552760	6.408836
C	-5.140646	-0.542744	7.093392
N	-5.164928	-1.622059	7.892880
C	-3.987485	-2.327046	7.720586
C	-3.254625	-1.662448	6.786595
C	-6.268180	0.442789	6.898395
O	-7.323329	0.049790	6.440268
C	-6.211608	-1.962801	8.828222
C	-6.158754	-1.407514	10.113809
C	-7.168125	-1.771254	11.006668
C	-8.193952	-2.648681	10.646229
C	-8.206178	-3.163798	9.346991
C	-7.225513	-2.835092	8.410633
C	-5.082180	-0.434966	10.514629
C	-9.253536	-3.044984	11.638260
C	-7.287723	-3.354950	7.001565
C	-5.070028	-0.865308	3.746337
C	-3.214648	3.687885	2.698429
C	-2.224121	1.607561	7.156491
O	-5.893520	1.640147	7.251258

C	-6.697731	2.847530	6.769781
C	-5.842818	3.501009	5.714315
C	-6.575939	4.644034	4.903438
O	-7.703784	4.977854	5.320442
C	-6.987190	3.695529	7.981060
H	-4.936947	3.921980	6.166523
H	-2.292474	-1.876896	6.349430
H	-3.786227	-3.227003	8.279415
H	-1.992430	3.355285	5.101654
H	-4.434423	1.297028	2.247227
H	-9.008874	-3.832453	9.045789
H	-7.153849	-1.349954	12.008898
H	-3.024625	1.771190	7.886862
H	-1.671125	0.713072	7.463405
H	-1.541438	2.457670	7.216991
H	-4.631543	-1.824318	4.043359
H	-6.058694	-0.792606	4.213623
H	-5.221073	-0.888171	2.665042
H	-2.303536	4.280364	2.821649
H	-3.333308	3.434640	1.641185
H	-4.081147	4.303863	3.009993
H	-8.104592	-4.070851	6.890190
H	-7.460986	-2.526497	6.306319
H	-6.360329	-3.855518	6.702868
H	-5.161201	0.499654	9.948007
H	-5.164870	-0.186718	11.574700
H	-4.078145	-0.837841	10.342828
H	-10.218659	-3.203915	11.149199
H	-8.984125	-3.981389	12.141584
H	-9.384597	-2.283001	12.411091
H	-5.523116	2.751338	4.986559
H	-7.611351	3.173005	8.712643
H	-6.060987	4.025303	8.463812
H	-7.521229	4.567132	7.590228
O	-5.906087	5.062379	3.933271
H	-7.616525	2.444703	6.342418