Supporting information

Chemically Triggered C—ON Bond in Alkoxyamines: Part 9. Selective Activation.

Gérard Audran, Paul Brémond*, Matisse Bim batsiandzy, Sylvain R. A. Marque*, Valérie Roubaud, and Didier Siri*

Aix-Marseille Université, CNRS, ICR UMR 7273, case 551, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20 FRANCE. Fax: 33-(0)4-91-28-87-58. E-mail: sylvain.marque@univ-amu.fr; g.audran@univ-amu.fr; paul.bremond@univ-amu.fr

1.1. Optimization of structures and NBO charges by DFT **2**

1.2. Radical Stabilization Energies **14**

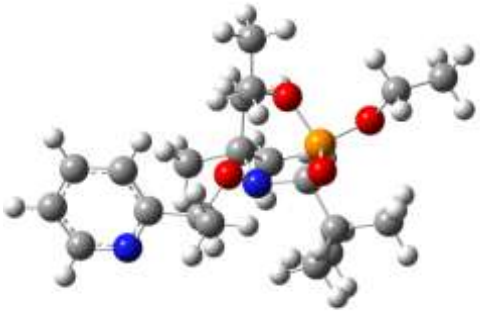
2. Synthesis of 2a-g,4 **22**

1.1. Optimization of structures and NBO charges by DFT

All calculations were performed using Gaussian package 09, revision A02.[1]

The geometry of the species were optimized at the B3LYP/6-31G(d,p) level of theory. Vibrational frequencies were calculated at B3LYP/6-31G(d,p) level to insure that the obtained geometries are minima (no imaginary frequency). The vibrational frequencies were scaled by a usual factor of 0.9608. The corresponding thermal corrections were included to obtain the enthalpy and Gibbs free energy values under the standard conditions (p = 1 atm and T = 298.15 K). Values are given in a.u. Calculations for **3a-c and 3g** were previously reported.[ii]

1a



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H = -1535.647887
G = -1535.745712

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H	-1.752159	-1.221789	1.117489
C	-1.530292	-2.296621	-0.736074
C	-1.047432	-3.586980	-0.044166
H	-1.266308	-4.446354	-0.686856
H	-1.554617	-3.753169	0.912041
H	0.029670	-3.561074	0.133079
C	-0.877048	-2.227596	-2.128433
H	0.212545	-2.251817	-2.062468
H	-1.184191	-1.332872	-2.671625
H	-1.182604	-3.104564	-2.710278
C	-3.060014	-2.410513	-0.923710
H	-3.460773	-1.604046	-1.541466
H	-3.591723	-2.401555	0.032984
H	-3.287462	-3.356600	-1.426298
C	-4.420838	1.346953	-0.063538
H	-4.507297	1.469392	-1.148500
H	-4.111315	2.305087	0.369359
C	-5.723961	0.865865	0.546787
H	-6.028391	-0.088976	0.109409
H	-6.516133	1.598778	0.362791
H	-5.620083	0.733734	1.627563
C	-0.583136	2.847109	-0.162049

H	-0.676625	2.811519	-1.250582
H	0.453357	2.625378	0.107007
C	-1.026993	4.188823	0.393600
H	-2.056987	4.413624	0.101442
H	-0.380228	4.983728	0.006973
H	-0.968512	4.199102	1.485927
C	0.575428	-0.874351	2.035749
C	0.014472	-2.111859	2.764633
H	-1.077441	-2.161889	2.757352
H	0.323295	-2.061946	3.812982
H	0.406956	-3.037637	2.339463
C	0.034039	0.400056	2.709273
H	0.427223	1.295371	2.226239
H	0.343803	0.413359	3.759848
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C	2.104755	-0.916828	2.187264
H	2.530511	-1.754998	1.628991
H	2.362076	-1.038818	3.244113
H	2.570403	0.003511	1.836713
C	1.845751	-0.242627	-1.117181
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C	3.259842	0.101549	-0.671573
C	4.926353	1.654941	0.105904
H	5.219516	2.643416	0.448177
C	5.432232	-0.615715	-0.447450
H	6.134934	-1.441307	-0.546195
C	1.516886	0.471919	-2.430496
H	0.492924	0.265394	-2.742488
H	2.212739	0.146276	-3.210223
H	1.624905	1.555566	-2.318994
N	0.254928	-0.988002	0.561979
O	-1.907156	0.774563	-1.919000
O	-1.412191	1.814917	0.417414
O	-3.401880	0.360757	0.220265
O	0.845547	0.142738	-0.133977
P	-1.927464	0.541403	-0.445601
C	5.867449	0.629792	0.000592
H	6.909884	0.789937	0.256368
N	4.161470	-0.886217	-0.775540
C	3.604976	1.389953	-0.239496
H	2.845667	2.162181	-0.173367

1b

ZPE = 0.549804
E = -1536.036777
H = -1536.035833

G = -1536.131993

C	0.653969	0.943142	0.453181
H	1.211573	1.161407	1.367797
C	0.322585	2.353976	-0.208485
C	-0.637297	3.154528	0.699994
H	-0.868370	4.108263	0.216568
H	-0.189318	3.380693	1.670937
H	-1.590468	2.649423	0.880336
C	-0.306548	2.250514	-1.613667
H	-1.314012	1.822662	-1.591257
H	0.306578	1.657537	-2.294922
H	-0.408603	3.255505	-2.034733
C	1.604132	3.214432	-0.324047
H	2.274350	2.863558	-1.106700
H	2.167183	3.235285	0.613800
H	1.314816	4.242250	-0.562878
C	4.432471	0.362559	-0.964151
H	4.283820	0.161360	-2.029435
H	4.722031	-0.566988	-0.464001
C	5.457149	1.455115	-0.737127
H	5.164797	2.380201	-1.240814
H	6.424175	1.137579	-1.138715
H	5.578713	1.660175	0.329781
C	2.134744	-2.763681	-0.083730
H	2.170149	-2.792115	-1.175960
H	1.154728	-3.123550	0.243278
C	3.256272	-3.575298	0.535460
H	4.233202	-3.223776	0.192612
H	3.150878	-4.625915	0.247291
H	3.229644	-3.514128	1.626683
C	-0.664557	-0.240321	2.345299
C	-0.664247	1.021606	3.224054
H	0.273353	1.578820	3.174911
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H	-1.485404	1.697973	2.976851
C	0.486985	-1.163053	2.774600
H	0.475839	-2.099540	2.216939
H	0.363189	-1.399799	3.835295
H	1.467806	-0.702575	2.650153
C	-1.998181	-0.977361	2.571356
H	-2.863207	-0.327345	2.409207
H	-2.042434	-1.309245	3.611613
H	-2.087419	-1.858692	1.935391
C	-1.399833	-1.060157	-1.122686
H	-0.901870	-0.358829	-1.801814
C	-2.844035	-0.615765	-0.958926
C	-5.206929	-0.566479	-1.433131
H	-6.069215	-0.973676	-1.951294
C	-4.241814	1.012498	0.077176
H	-4.264510	1.846511	0.768603
C	-1.252514	-2.459731	-1.704778
H	-0.191113	-2.666594	-1.828361
H	-1.709421	-2.511594	-2.696193
H	-1.704476	-3.216737	-1.058003
N	-0.589737	0.179748	0.864302
O	1.425243	-0.453617	-1.936688

O	2.270881	-1.385297	0.357292
O	3.163212	0.806637	-0.394963
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P	1.854456	-0.115729	-0.547740
C	-5.360500	0.528235	-0.575853
H	-6.326115	0.991951	-0.414735
C	-3.950871	-1.141666	-1.624440
H	-3.830921	-1.990824	-2.283945
N	-3.042114	0.440819	-0.138933
H	-2.150683	0.709466	0.384533

1c

ZPE = 0.540984
E = -1610.806239
H = -1610.805294
G = -1610.904384

C	1.290096	-1.049233	-0.220402
H	1.851070	-1.221388	-1.143636
C	1.598352	-2.305674	0.702501
C	1.082183	-3.574942	-0.004062
H	1.279203	-4.446325	0.629404
H	1.585041	-3.744075	-0.962023
H	0.005919	-3.519808	-0.178964
C	0.934993	-2.230635	2.089122
H	-0.153828	-2.210277	2.009727
H	1.273382	-1.357404	2.648584
H	1.198196	-3.127575	2.661004
C	3.122766	-2.463858	0.898306
H	3.542769	-1.672973	1.523528
H	3.659949	-2.463929	-0.055437
H	3.320434	-3.419186	1.395927
C	4.595555	1.264817	0.066882
H	4.676188	1.385319	1.152505
H	4.314803	2.230412	-0.368927
C	5.890311	0.748447	-0.532203
H	6.164723	-0.214080	-0.091910
H	6.700398	1.459744	-0.341488
H	5.792215	0.618706	-1.613798
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H	1.270346	4.238071	-1.442380
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C	0.013110	-2.068389	-2.776352
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C	0.138473	0.441315	-2.728696
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H	-2.402288	0.206294	-1.860160
C	-1.721121	-0.142691	1.095160
H	-1.759396	-1.227793	1.165588
C	-3.090714	0.324608	0.641094
C	-5.330105	-0.258640	0.092270
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C	-4.685013	2.055003	0.018839
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C	-3.411174	1.658815	0.415927
H	-2.625277	2.393095	0.556356
C	-1.360082	0.495530	2.438213
H	-0.350137	0.217348	2.737456
H	-2.071816	0.171054	3.204280
H	-1.402457	1.587763	2.382904
N	-0.145375	-0.930231	-0.578104
O	2.061573	0.745717	1.912015
O	1.604965	1.817018	-0.417944
O	3.552702	0.306074	-0.225026
O	-0.699262	0.216014	0.125289
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C	-5.654774	1.063155	-0.136792
H	-6.669425	1.303111	-0.436277
N	-4.066459	-0.640921	0.469163
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1g

ZPE = 0.569139
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H = -1562.279137
G = -1562.379344

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C	-1.566075	-2.363768	-0.693303
C	-0.985261	-3.593346	0.033406
H	-1.117211	-4.480847	-0.594305
H	-1.492685	-3.784986	0.984338
H	0.082252	-3.471134	0.228056
C	-0.906916	-2.273703	-2.081847
H	0.181616	-2.221344	-2.008939
H	-1.271072	-1.414528	-2.646362
H	-1.142486	-3.181619	-2.648005
C	-3.078856	-2.609065	-0.893042
H	-3.540135	-1.849373	-1.527568
H	-3.618472	-2.629355	0.059040
H	-3.220412	-3.579042	-1.381078
C	-4.749771	1.064681	-0.169793
H	-4.817120	1.164651	-1.258244
H	-4.524170	2.048755	0.256168
C	-6.026162	0.491572	0.416216
H	-6.242925	-0.490742	-0.012307
H	-6.867943	1.156961	0.199506
H	-5.941005	0.384893	1.501371
C	-1.046615	2.858753	-0.235318
H	-1.117856	2.792754	-1.324139
H	0.000319	2.729717	0.054957
C	-1.608155	4.170923	0.282656
H	-2.648276	4.302452	-0.029409
H	-1.023544	5.007852	-0.113926
H	-1.568095	4.210607	1.375044
C	0.328888	-0.707558	2.106243
C	-0.126830	-1.983942	2.840923
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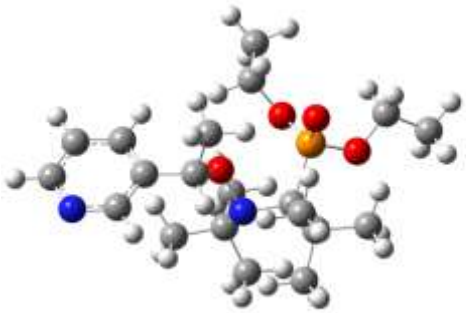
H	0.381430	-2.869844	2.455216
C	-0.369795	0.515427	2.728121
H	-0.055428	1.438481	2.240063
H	-0.105461	0.581065	3.788798
H	-1.458864	0.453647	2.661440
C	1.845345	-0.581798	2.318243
H	2.381381	-1.397779	1.825281
H	2.066757	-0.629500	3.388540
H	2.228459	0.366124	1.942446
C	1.620939	-0.063906	-1.058223
H	1.612138	-1.148429	-1.177704
C	3.009177	0.359700	-0.605713
C	4.596862	2.006517	0.155344
H	4.851049	3.007971	0.484409
C	1.262479	0.625989	-2.377714
H	0.248029	0.370428	-2.684629

H	1.970644	0.329506	-3.157814
H	1.321249	1.713910	-2.272126
N	0.076896	-0.887608	0.623867
O	-2.149889	0.638274	-1.960091
O	-1.797265	1.774124	0.355427
O	-3.664022	0.163049	0.153763
O	0.602722	0.272508	-0.082432
P	-2.194489	0.442551	-0.481620
C	5.595556	1.040563	0.070553
H	6.630199	1.239517	0.319540
C	3.294031	1.668044	-0.190059
H	2.499053	2.404783	-0.133060
N	5.332094	-0.213324	-0.331966
C	4.065111	-0.541251	-0.660060
H	3.928284	-1.570060	-0.974564
B	6.492927	-1.338879	-0.419690
H	6.178384	-2.190978	0.384713
H	6.456882	-1.755674	-1.557813
H	7.529045	-0.779219	-0.143214

2a



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H = -1535.645172
G = -1535.742953

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H	-1.756153	-1.222785	1.110405
C	-1.521720	-2.297762	-0.739785
C	-1.031970	-3.585679	-0.048047
H	-1.244155	-4.446084	-0.691561
H	-1.539878	-3.755512	0.906968
H	0.044534	-3.553368	0.132469
C	-0.873343	-2.227087	-2.134597
H	0.216782	-2.255980	-2.074610
H	-1.178902	-1.330212	-2.674950
H	-1.183782	-3.101835	-2.717087
C	-3.051273	-2.419817	-0.925345
H	-3.457053	-1.616534	-1.543865
H	-3.581622	-2.411643	0.032022
H	-3.274620	-3.368005	-1.425729

C	-4.426313	1.338747	-0.078103
H	-4.508911	1.465772	-1.162807
H	-4.119724	2.295158	0.360383
C	-5.730484	0.852139	0.525329
H	-6.031687	-0.101113	0.082332
H	-6.523243	1.584509	0.341908
H	-5.630245	0.715276	1.605843
C	-0.596495	2.852897	-0.161540
H	-0.698401	2.829609	-1.249654
H	0.441519	2.626021	0.097198
C	-1.033729	4.188685	0.412866
H	-2.065649	4.418496	0.131674
H	-0.388699	4.986678	0.029879
H	-0.966206	4.186602	1.504672
C	0.557003	-0.865584	2.049251
C	-0.015986	-2.098458	2.776825
H	-1.108111	-2.142181	2.763406
H	0.286797	-2.047804	3.826824
H	0.373641	-3.027951	2.357138
C	0.010496	0.412931	2.710461
H	0.414475	1.305428	2.231175
H	0.304570	0.427798	3.765378
H	-1.079867	0.470826	2.668316
C	2.083325	-0.910676	2.221598
H	2.509996	-1.771799	1.699619
H	2.326788	-1.000501	3.284765
H	2.560876	-0.007396	1.845100
C	1.840527	-0.223662	-1.113379
H	1.763095	-1.303659	-1.252329
C	3.255782	0.105955	-0.673936
C	4.956932	1.631275	0.088330
H	5.278003	2.611350	0.427385
C	1.499218	0.511255	-2.413020
H	0.468191	0.321953	-2.712496
H	2.179965	0.191821	-3.208463
H	1.623485	1.591406	-2.286899
N	0.254294	-0.983433	0.570366
O	-1.900114	0.771218	-1.925896
O	-1.424140	1.815798	0.412393
O	-3.405984	0.352856	0.204852
O	0.848083	0.151821	-0.116764
P	-1.929337	0.540246	-0.452185
C	5.878203	0.587442	-0.023490
H	6.925097	0.747263	0.228211
C	3.629003	1.385866	-0.248339
H	2.886332	2.175193	-0.174496
N	5.549810	-0.642122	-0.434474
C	4.265888	-0.859720	-0.744956
H	4.021242	-1.869766	-1.073909

2b

ZPE = 0.550437
E = -1536.019923
H = -1536.018979
G = -1536.117055

C	-0.776588	-0.953548	0.438892
H	-1.286265	-1.093178	1.396675
C	-0.674945	-2.409870	-0.207192
C	0.375497	-3.251051	0.548715
H	0.495422	-4.213283	0.040804
H	0.067944	-3.462422	1.575854
H	1.349166	-2.756574	0.586087
C	-0.302140	-2.414471	-1.705130
H	0.731034	-2.092892	-1.878588
H	-0.952032	-1.773089	-2.302694
H	-0.375863	-3.436400	-2.090326
C	-2.020628	-3.158382	-0.053305
H	-2.794424	-2.765926	-0.710663
H	-2.397099	-3.106553	0.973502
H	-1.870031	-4.214731	-0.297610
C	-4.573222	0.041055	-0.660813
H	-4.474665	0.290744	-1.721896
H	-4.738336	0.962878	-0.093779
C	-5.686177	-0.959894	-0.424450
H	-5.522368	-1.873625	-1.001874
H	-6.641606	-0.525519	-0.734139
H	-5.755015	-1.222741	0.634515
C	-1.851012	2.873283	-0.065489
H	-2.016520	2.897878	-1.145649
H	-0.797363	3.095885	0.127898
C	-2.764594	3.839008	0.664851
H	-3.815558	3.619126	0.458104
H	-2.557926	4.862097	0.334974
H	-2.607752	3.788118	1.745736
C	0.819173	0.068040	2.173205
C	0.743141	-1.179541	3.071511
H	-0.252502	-1.627215	3.102180
H	0.986626	-0.878620	4.094050
H	1.459549	-1.945363	2.768206
C	-0.154210	1.134973	2.707861
H	-0.090135	2.055970	2.127609
H	0.107960	1.368056	3.744392
H	-1.192025	0.798065	2.695664
C	2.252484	0.617756	2.268171

H	2.983936	-0.123640	1.930725
H	2.479539	0.855820	3.310748
H	2.370158	1.531124	1.683293
C	1.421678	0.738842	-1.272765
H	0.989142	-0.092311	-1.832223
C	2.890706	0.429961	-0.998926
C	5.204352	1.082702	-0.576553
H	5.967411	1.845358	-0.476311
C	1.204871	2.017748	-2.072498
H	0.152721	2.064511	-2.351828
H	1.808522	2.006475	-2.985140
H	1.459787	2.908227	-1.489629
N	0.565221	-0.331514	0.724750
O	-1.612288	0.483932	-1.917639
O	-2.121091	1.533803	0.423862
O	-3.323637	-0.553267	-0.202358
O	0.697204	0.906190	-0.041380
P	-1.931435	0.210493	-0.485207
C	5.545688	-0.246145	-0.415179
H	6.544657	-0.596425	-0.187637
C	3.877288	1.416359	-0.866622
H	3.609695	2.459944	-0.991192
N	4.581825	-1.184445	-0.553714
C	3.292404	-0.891810	-0.836320
H	2.614915	-1.729674	-0.926385
H	4.837398	-2.161131	-0.440270

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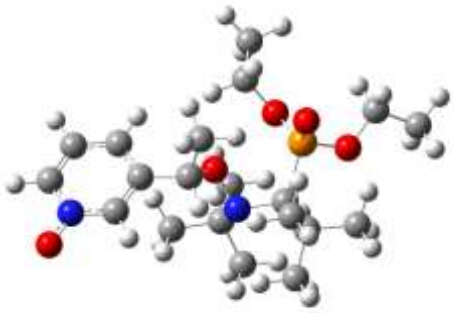
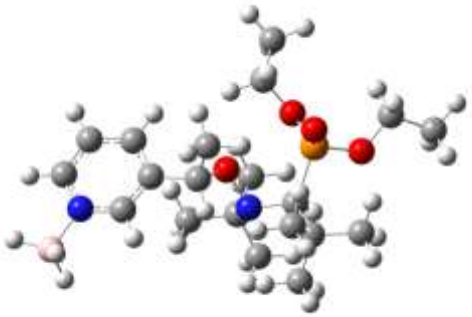


ZPE = 0.540981
E = -1610.803577
H = -1610.802633
G = -1610.901729

C	-1.346204	-1.075897	0.213162
H	-1.925638	-1.260537	1.121647
C	-1.591156	-2.352067	-0.702862
C	-1.027895	-3.592518	0.019039
H	-1.174111	-4.476147	-0.611137
H	-1.536568	-3.779137	0.970380
H	0.041540	-3.486150	0.212587
C	-0.930844	-2.265887	-2.091103

H	0.158109	-2.226222	-2.017411
H	-1.284203	-1.400058	-2.652330
H	-1.177832	-3.168938	-2.660422
C	-3.107415	-2.574424	-0.902859
H	-3.557153	-1.805704	-1.534796
H	-3.647069	-2.589431	0.049320
H	-3.263963	-3.540647	-1.393925
C	-4.722724	1.122885	-0.148245
H	-4.795630	1.229302	-1.235807
H	-4.477549	2.101087	0.280445
C	-6.005394	0.569560	0.443385
H	-6.242402	-0.406590	0.011449
H	-6.836812	1.250807	0.235941
H	-5.914735	0.455633	1.527390
C	-0.990109	2.856367	-0.233466
H	-1.067552	2.795813	-1.322167
H	0.054418	2.702809	0.052062
C	-1.521551	4.178232	0.291590
H	-2.559933	4.333529	-0.015507
H	-0.920386	5.003742	-0.104188
H	-1.475968	4.212927	1.383969
C	0.331108	-0.730591	2.098348
C	-0.140659	-2.002044	2.831426
H	-1.221871	-2.154333	2.782939
H	0.120431	-1.906017	3.889439
H	0.353092	-2.894221	2.441075
C	-0.350337	0.500366	2.723796
H	-0.022888	1.419825	2.237763
H	-0.084501	0.559644	3.784532
H	-1.440289	0.454024	2.657714
C	1.849410	-0.624774	2.307196
H	2.371970	-1.450739	1.816657
H	2.071534	-0.669998	3.377671
H	2.245280	0.314610	1.923246
C	1.632771	-0.093791	-1.061709
H	1.609429	-1.177545	-1.185420
C	3.026352	0.313474	-0.604627
C	4.635360	1.926611	0.156409
H	4.907415	2.923230	0.488530
C	1.283986	0.605630	-2.378504
H	0.268914	0.359527	-2.691413
H	1.993451	0.306885	-3.156545
H	1.352867	1.691908	-2.266829
N	0.074324	-0.903908	0.616000
O	-2.143954	0.656943	-1.958565
O	-1.763249	1.786344	0.356175
O	-3.651311	0.201363	0.164094
O	0.612477	0.249889	-0.088654
P	-2.180565	0.460897	-0.479875
C	5.630455	0.968153	0.078697
H	6.671215	1.128043	0.323634
C	3.320832	1.619316	-0.187838
H	2.540149	2.368740	-0.129458
N	5.347952	-0.308844	-0.335540
C	4.049687	-0.618040	-0.667893
H	3.922061	-1.646921	-0.978201
O	6.263996	-1.192079	-0.408248

2g



ZPE = 0.568435
E = -1562.280715
H = -1562.279771
G = -1562.382874

C	-1.340744	-1.080239	0.218038
H	-1.918987	-1.269324	1.126317
C	-1.566075	-2.363768	-0.693303
C	-0.985261	-3.593346	0.033406
H	-1.117211	-4.480847	-0.594305
H	-1.492685	-3.784986	0.984338
H	0.082252	-3.471134	0.228056
C	-0.906916	-2.273703	-2.081847
H	0.181616	-2.221344	-2.008939
H	-1.271072	-1.414528	-2.646362
H	-1.142486	-3.181619	-2.648005
C	-3.078856	-2.609065	-0.893042
H	-3.540135	-1.849373	-1.527568
H	-3.618472	-2.629355	0.059040
H	-3.220412	-3.579042	-1.381078
C	-4.749771	1.064681	-0.169793
H	-4.817120	1.164651	-1.258244
H	-4.524170	2.048755	0.256168
C	-6.026162	0.491572	0.416216
H	-6.242925	-0.490742	-0.012307
H	-6.867943	1.156961	0.199506
H	-5.941005	0.384893	1.501371
C	-1.046615	2.858753	-0.235318
H	-1.117856	2.792754	-1.324139
H	0.000319	2.729717	0.054957
C	-1.608155	4.170923	0.282656
H	-2.648276	4.302452	-0.029409
H	-1.023544	5.007852	-0.113926
H	-1.568095	4.210607	1.375044
C	0.328888	-0.707558	2.106243
C	-0.126830	-1.983942	2.840923
H	-1.205397	-2.151820	2.788426
H	0.128536	-1.881030	3.899608
H	0.381430	-2.869844	2.455216
C	-0.369795	0.515427	2.728121
H	-0.055428	1.438481	2.240063
H	-0.105461	0.581065	3.788798

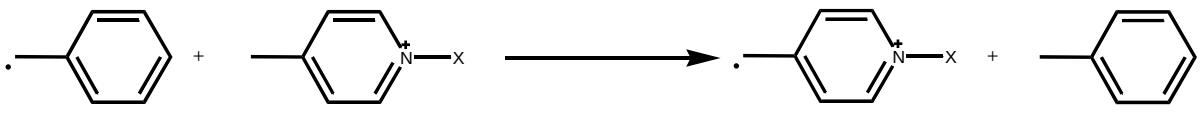
H	-1.458864	0.453647	2.661440
C	1.845345	-0.581798	2.318243
H	2.381381	-1.397779	1.825281
H	2.066757	-0.629500	3.388540
H	2.228459	0.366124	1.942446
C	1.620939	-0.063906	-1.058223
H	1.612138	-1.148429	-1.177704
C	3.009177	0.359700	-0.605713
C	4.596862	2.006517	0.155344
H	4.851049	3.007971	0.484409
C	1.262479	0.625989	-2.377714
H	0.248029	0.370428	-2.684629
H	1.970644	0.329506	-3.157814
H	1.321249	1.713910	-2.272126
N	0.076896	-0.887608	0.623867
O	-2.149889	0.638274	-1.960091
O	-1.797265	1.774124	0.355427
O	-3.664022	0.163049	0.153763
O	0.602722	0.272508	-0.082432
P	-2.194489	0.442551	-0.481620
C	5.595556	1.040563	0.070553
H	6.630199	1.239517	0.319540
C	3.294031	1.668044	-0.190059
H	2.499053	2.404783	-0.133060
N	5.332094	-0.213324	-0.331966
C	4.065111	-0.541251	-0.660060
H	3.928284	-1.570060	-0.974564
B	6.492927	-1.338879	-0.419690
H	6.178384	-2.190978	0.384713
H	6.456882	-1.755674	-1.557813
H	7.529045	-0.779219	-0.143214

3.2-Radical Stabilization Energies

RSE is given by the isodesmic reaction as displayed in Scheme 1SI and by eq. 1.

For RSE calculations, the geometry optimizations were performed using R(O)B3LYP/6-31G(d). Vibrational frequencies were calculated at R(O)B3LYP/6-31G(d) level using the scale factor of 0.9806 to provide zero point vibrational energy. The UBMK/6-311+G(3df,2p) method was used for calculating energies on the R(O)B3LYP/6-31G(d) geometries.[iii] Values are given in a.u.

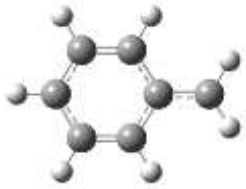
For the sake of the simplicity, calculations were performed with the benzylic model of $\mathbf{a_n}\bullet\text{-}\mathbf{c_n}\bullet$ and $\mathbf{g_n}\bullet$ alkyl radicals (Figures 7 and 1SI). Calculations for $\mathbf{a_p}\bullet\text{-}\mathbf{c_p}\bullet$ and $\mathbf{g_p}\bullet$ were previously reported[ii] and for $\mathbf{a_o}\bullet\text{-}\mathbf{c_o}\bullet$ has been submitted[iv]



Scheme 1SI. Isodesmic reaction applied to determine RSE values

$$RSE = D_r H = H_f(\text{toluene}) + H_f(\text{heteroarylalkyl radical}) - H_f(\text{benzylic radical}) - H_f(\text{charged/non charged methylpyridine}) \quad (1)$$

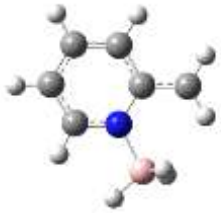
Benzyl radical



E = -270.7986032
$<S^2>$= 0.786259
ZPE = 0.112721

C	-0.003119	0.041570	0.017227
C	-0.009328	0.042358	1.403071
C	1.207959	0.000130	2.146517
C	2.425315	-0.042689	1.403210
C	2.419229	-0.043006	0.017369
C	1.208084	-0.000998	-0.688709
H	-0.944419	0.074225	-0.525585
H	-0.951477	0.075473	1.944912
H	3.367414	-0.075370	1.945164
H	3.360574	-0.076091	-0.525339
H	1.208135	-0.001429	-1.775003
C	1.207902	0.000694	3.553070
H	0.280441	0.033051	4.115546
H	2.135319	-0.031183	4.115645

g_o'

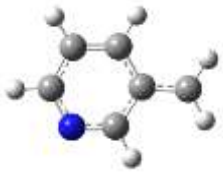


E = -313.4888422
$<S^2>$= 0.782107
ZPE = 0.134201

C	-0.053993	-0.030655	0.001602
C	-0.042233	-0.029304	1.384454
C	1.181271	-0.008775	2.103263
C	2.346328	0.008393	0.066605

H	-0.993301	-0.046397	-0.543031
H	-0.967487	-0.043908	1.951311
H	3.319873	0.023721	-0.407494
C	1.188577	-0.007048	3.507781
H	2.114060	0.008678	4.063925
H	0.245787	-0.021843	4.042570
N	2.377801	0.009988	1.406845
C	1.168743	-0.011292	-0.675978
H	1.221822	-0.011298	-1.758965
H	3.820593	1.040485	2.843692
H	3.852312	-0.969970	2.846874
H	4.641829	0.045600	1.289315
B	3.805214	0.033659	2.163845

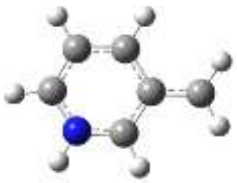
a_m'



E = -286.842156
<S^2>= 0.784199
ZPE = 0.101211

C	0.026520	0.043819	-0.017292
C	0.056197	-0.005057	2.413243
H	0.582437	-0.028357	3.360927
C	0.747075	0.014556	1.209050
H	1.831629	0.004894	1.191070
C	-1.345094	0.008017	2.382886
H	-1.918175	-0.002595	3.310234
C	-1.393616	0.048514	0.099117
H	-1.994215	0.065724	-0.811958
N	-2.064823	0.031964	1.246785
C	0.663977	0.058199	-1.284162
H	1.746003	0.079437	-1.365910
H	0.085886	0.116108	-2.200736

b_m'

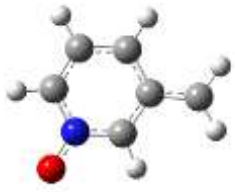


E = -287.2120156

$<S^2>$= 0.77751
ZPE = 0.115318

C	0.016844	0.046624	-0.028903
C	0.060626	-0.005173	2.422524
H	0.604182	-0.028156	3.360194
C	0.729045	0.014485	1.206737
H	1.814801	0.006069	1.186895
C	-1.329427	0.004888	2.443235
H	-1.929594	-0.007220	3.344182
C	-1.392175	0.051805	0.061049
H	-2.039196	0.072322	-0.807994
N	-1.994185	0.031554	1.262990
C	0.662932	0.074356	-1.284216
H	1.744574	0.074160	-1.349682
H	0.097499	0.099330	-2.208824
H	-3.011926	0.036956	1.285812

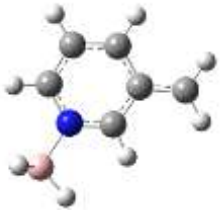
c_m'



E = -361.999399
$<S^2>$= 0.810947
ZPE = 0.105333

C	0.018828	0.046403	-0.011461
C	0.063789	-0.003463	2.410280
H	0.591254	-0.027188	3.358068
C	0.755254	0.017741	1.205627
H	1.839204	0.007082	1.182430
C	-1.325660	0.008193	2.428447
H	-1.940363	-0.004337	3.319187
C	-1.390228	0.051018	0.072450
H	-2.047619	0.066031	-0.787467
N	-2.057012	0.032707	1.263521
C	0.661858	0.053244	-1.282889
H	1.744164	0.066244	-1.354107
H	0.091201	0.126619	-2.202325
O	-3.330425	0.035599	1.305589

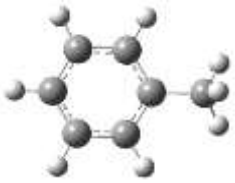
g_m'



E = -313.4872389
$<S^2>$= 0.785807
ZPE = 0.133551

C	0.031893	0.014994	-0.010083
C	0.075475	0.088910	2.413854
H	0.608727	0.120542	3.358225
C	0.758935	0.055965	1.206820
H	1.844977	0.061221	1.183455
C	-1.314705	0.081369	2.416291
H	-1.904696	0.105732	3.324081
C	-1.383488	0.010535	0.098174
H	-2.017799	-0.019623	-0.780099
N	-2.027588	0.042501	1.265880
C	0.655065	-0.020054	-1.275177
H	1.735354	-0.016897	-1.365816
H	0.069326	-0.050977	-2.186818
B	-3.647162	0.035908	1.343262
H	-3.933211	-0.953614	1.985486
H	-3.944252	1.058368	1.926127
H	-4.039938	-0.000045	0.198400

Toluene

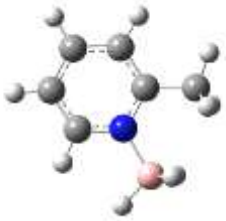


E = -271.4505291
ZPE = 0.125841

C	0.002638	-0.002514	-0.009320
C	0.005564	0.011946	1.386223
C	1.207757	0.015302	2.105966
C	2.410231	0.010516	1.386430
C	2.413418	-0.003945	-0.008982
C	1.208048	-0.011178	-0.713000
H	-0.942263	-0.002551	-0.546864
H	-0.938918	0.022671	1.926307

H	3.354619	0.020135	1.926729
H	3.358396	-0.005101	-0.546393
H	1.208205	-0.019189	-1.799737
C	1.207907	-0.001995	3.617648
H	2.087873	0.507588	4.025242
H	0.315819	0.486030	4.025075
H	1.220602	-1.030092	4.004467

g_o'-H



E = -314.1442586
ZPE = 0.147454

C	-0.046670	-0.017374	-0.024074
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C	1.171544	0.026463	2.069594
C	2.341038	-0.067526	0.046720
H	-0.986099	-0.014759	-0.568967
H	-0.963873	0.074262	1.926550
H	3.321240	-0.103802	-0.411424
C	1.205617	0.081703	3.566324
H	1.773384	0.953995	3.906409
H	0.191341	0.124736	3.971356
N	2.351598	-0.021792	1.395388
C	1.171951	-0.068624	-0.698458
H	1.225661	-0.107694	-1.781060
H	3.771915	-1.003102	2.890293
H	4.621178	-0.078205	1.308532
H	3.820096	1.001195	2.815565
B	3.776574	-0.026095	2.170839
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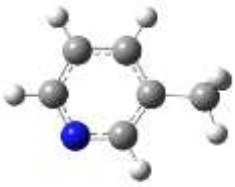
a_m'-H



E = -287.4947147
ZPE = 0.114378

C	0.009286	0.042032	0.015418

C	0.040853	0.005352	2.426866
H	0.573922	-0.010082	3.374415
C	0.727864	0.025407	1.216391
H	1.817072	0.026414	1.200822
C	-1.354594	0.001709	2.401814
H	-1.924929	-0.013355	3.328895
C	-1.388148	0.031126	0.118591
H	-1.993491	0.035637	-0.788040
N	-2.067629	0.012569	1.270464
C	0.696005	0.082396	-1.327676
H	1.132970	1.070133	-1.523016
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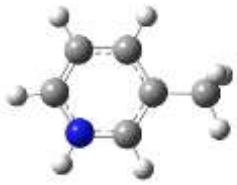
H	-0.006131	-0.132327	-2.139457

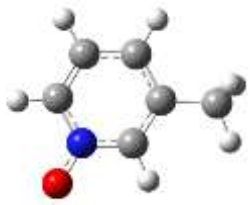
b*m*'-H



E = -287.8685936
ZPE = 0.128299

C	0.000783	0.027914	-0.002975
C	0.046885	-0.002057	2.442884
H	0.594276	-0.018674	3.377892
C	0.709391	0.007365	1.212602
H	1.794845	-0.000144	1.191518
C	-1.338590	0.007704	2.462152
H	-1.939083	0.000483	3.364465
C	-1.386663	0.039827	0.080402
H	-2.033990	0.058258	-0.789267
N	-2.002003	0.028766	1.286474
H	-3.019792	0.034154	1.306245
C	0.698582	0.080495	-1.336007
H	1.069098	1.094217	-1.536604
H	1.560906	-0.593352	-1.352415
H	0.029404	-0.198553	-2.154426

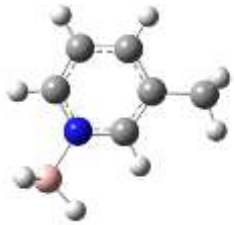
c*m*'-H



E = -362.653428
ZPE = 0.118514

C	0.006644	0.042995	0.020086
C	0.047149	0.027398	2.424263
H	0.579158	0.026536	3.371733
C	0.739828	0.045617	1.215161
H	1.825764	0.060301	1.196602
C	-1.334191	0.005679	2.449463
H	-1.944685	-0.011597	3.341506
C	-1.379035	0.018283	0.088785
H	-2.033007	0.009355	-0.773384
N	-2.059066	0.002258	1.282477
O	-3.333372	-0.019243	1.303308
C	0.689436	0.080347	-1.326645
H	1.139328	1.063811	-1.508586
H	1.493521	-0.661314	-1.379174
H	-0.013189	-0.121062	-2.139999

g*m*'-H



E = -314.1409714

ZPE = 0.146687

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C	0.062206	0.053366	2.432836
H	0.598903	0.060329	3.375672
C	0.740505	0.067541	1.215089
H	1.827300	0.085916	1.193299
C	-1.324685	0.030097	2.433976
H	-1.913176	0.018291	3.343761
C	-1.376304	0.034484	0.115194
H	-2.012564	0.025867	-0.762116
N	-2.033291	0.020692	1.289122
B	-3.651999	-0.007819	1.351255
H	-3.935564	-1.025339	1.950045
H	-3.970494	0.987238	1.969785
H	-4.035269	-0.003455	0.202442
C	0.694756	0.072796	-1.328140
H	1.317677	0.967090	-1.447180
H	1.348410	-0.798755	-1.451005
H	-0.035230	0.061876	-2.142425

General information

All corresponding glassware was oven-dried (80 °C). All solvents were used as received. Routine monitoring of reactions was performed using Merck Silica gel 60 F_{254}, aluminum supported TLC plates; spots were visualized using UV light and ethanolic acidic *para*-anisaldehyde solution or ethanolic phosphomolybdic solution, followed by heating. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ solutions on 300 or 400 MHz spectrometers. Chemical shifts (δ) in ppm are reported using residual non-deuterated solvents as internal reference. High resolution mass spectra (HRMS) have been performed using a mass spectrometer equipped with a pneumatically assisted atmospheric pressure ionization. The sample was ionized in positive mode electrospray in the following conditions: electrospray voltage (ISV): 5500 V; orifice voltage (OR): 80 V; nebulizing gas flow pressure (air): 20 psi.The measure was realized in triplicate, with double internal standardization. The sample was dissolved in CH_2Cl_2 (400 µL) then diluted (dilution factor $1/10^4$) in a methanolic solution of ammonium acetate (3 mM). The sample solution was infused in the ionization source at a 10 µL/min flow rate. Compound **2a** was synthesized as 2:1 mixture of diastereomers according to the literature.

Preparation and caracterization of compounds 2a-g, 4

3-(1-bromo-ethyl)pyridine (4): A solution of *N*- bromosuccinimide (5.6g, 31.22 mmol), AIBN (459.7 mg, 2.8 mmol) and 3-ethylpyridine (3g, 28 mmol) in carbon tetrachloride (80 ml) was stirred at 90°C for 1 hour. After cooling, the reaction mixture was subjected to filtration. The filtrate was washed with satured aqueous solution of sodium bicarbonate and satured aqueous solution of sodium chloride, dried over magnesium sulfate and the filtrate concentrated *in vacuo* to give crude **4** (4.8 mg, 92%).which was used without further

purication. ^{1}H NMR (400 MHz,$CDCl_3$) : δ = 8.60 (d, *J* = 2.2 Hz, 1H), 8.47 (dd, *J* = 4.77 Hz, *J* = 3.26, 1H), 7.72 (dt, *J*= 2 Hz, *J* = 7.7 Hz, 1H) 7.31 (m, 1H), 5.13 (q, j=6.77 Hz, 1H), 2.00 (d, *J* = *7*.0 Hz, 3H). ^{13}C NMR (75 MHz , $CDCl_3$): δ = 149.2, 147.9,138.71 134.2, 45.4, 26.4. HRMS (ESI) *m*/*z* calcd for C_7H_8NBr $(M+H)^+$ 185.9913, found 185.9911.

(1-(*tert*-butyl-(1-(pyridin-3-yl-ethoxy)-amino)-2,2-dimethyl-propyl)phosphonic acid diethyl ester (2a)

To stirred suspension of CuBr (1.1g, 7 mmol) and Cu (1.01g, 16 mmol) in degassed benzene (16 ml) was added *N,N,N',N",N"*- pentamethyldiethylenetriamine (1.60 ml, 7 mmol). The resulting mixture was stirred under argon at room temperature for 30 min then a solution of **4** (3g, 16 mmol) and SG1 (4.3g,14 mmol) in degassed benzene (16 ml) was slowly added. The mixture was stirred overnight under argon. It was then diluted with ethyl acetate, filtered and washed several times with satured aqueous ammonia solution, water and brine. After drying with $MgSO_4$, filtration and concentration, column chromatographie on silica gel (eluent: gradient of ethyl acetate/pentane) gave **2a** (3.8 g, 67%) as a 2:1 mixture of diastereomers . Separation of diastereomers on silica gel chromatography (eluent: gradient ethyl acetate/ pentane). **Major** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (br s, 1H) 8.49 (d, *J* = 3.7 Hz, 1H) 7.64 (dt, *J* = 2.0.Hz, *J* = 8.0 Hz, 1H), 7.25-7.20 (m, 1H) 5.05 (q, *J* = 6.7 Hz, 1H,) 4.37-4.30 (m, 1H)4.37-4.06 (m, 2H), 4.01-3.95 (m, 1H),), 3.39 (d, *J* = 24.6 Hz, 1H), 1.62 (d, *J* = 6.7 Hz, 3H) 1.31 (br, q, *J* = 7.0 Hz, 6H), 1.24 (br, s, 9H), 0.82 (br, s, 9H) ^{13}*C* NMR (75 MHz, $CDCl_3$): δ =149.43, 148.92, 140.43, 135.14, 123.45, 82.45, 70.74 (d, *J* = 139.3 Hz), 61.90 (d, *J* = 6.6 Hz), 61.62, 59.38 (d, *J* = 6.7 Hz), 35.90 (d, *J* = 5.1 Hz), 30.66 (d, *J* = 5.8 Hz), 28.84, 23.58, 17.03 (d, *J* = 6.7 Hz), 16.61 (d, *J* = 7.2 Hz), ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.55, **minor**, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (br, s, 1H), 8.48 (br, d, *J* = 3.4 Hz, 1H), 7.64, (dt *J* = 1.7, *J* = 7.7 Hz, 1H), 7.20-7.25 (m, 1H), 5.02 (q, *J* = 6.7 Hz, 1H), 4.35-4.31 (m, 1H) 4.16-4.07 (m, 2H), 4.01-3.94 (m, 1H), 3.37 (d, *J* = 26.3 Hz, 1H), 1.62 (d, *J* = 6.3Hz ,

3H), 1;32 (q, J = 7.1 Hz, 6H), 1.23 (br, s, 9H), 0.81 (br, s, 9H), ^{13}X NMR (75 MHz, $CDCl_3$): δ = 148.95, 148.47, 140.00, 134.73, 123.04, 82.00, 70.55 (d, J = 139.7 Hz), 61.49 (d, J = 6.4 Hz), 61.19, 58.97 (d, J = 7.6 Hz), 35.47 (d, J = 5.1 Hz) 30.25 (d, J = 5.6 Hz), 28.42, 23.44, 16.66 (d, J = 6.2 Hz), 16.19 (d, J = 5.8 Hz), ^{31}P NMR (162 MHz, $CDCl_3$): δ = 25.44, HRMS (ESI) *m*/*z* calcd for $C_{20}H_{38}N_2O_4P^+$ $(M+H)^+$ 401.2564 found 401.2561.

Trifluoro-acetate 3-(1((*N*-*tert*-butyl-*N*-(1-(diethoxyphosphoryl)-2,2-dimethyl-propyl) amino)oxy)ethyl)pyridinium (2b): Compound **2b** was prepared by adding 1.1 eq; of trifluoroacetic acid to a $CDCl_3$ solution of compound **2a** in a NMR tube. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.89 (br,s, 1H, maj), 8.83 (br, s, 1H, min), 8.79 (br, d, J = 5.5 Hz, 1H min), 8.77 (br, d, J = 5.7 Hz, 1H, maj), 8.49 (br, d, J = 8.0 Hz , 1H, maj), 8.42 (br, d, J = 8.0 Hz, 1H, min), 7.90-7.83 5 (m, 1H, min and maj) 5.35 (q, J = 6.5 Hz, 1H, maj) 5.24-5.21 (m, 1H, min), 4.31-4.59 (m, 4H, min and Maj), 3.52 (d, J = 27.6 Hz, 1H, maj), 3.48 (d, J = 24.3 Hz, 1H min), 1.65 (d, J = 6.7 Hz, 3H, min), 1.62 (d, J = 6.7 Hz, 3H, Maj), 1.34-1.21 (m, 3H Maj and 6H min),1.23 (s, 9H, min), 1.20 (s, 9H, Maj), 1.12 (s, 9H, min), 1.08 (t, J = 7.0 Hz, 3H, Maj), 0.84 (s, 9H, min). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.3 (q, J = 39.1 Hz, min and Maj), 144.51 (min), 144.15 (Maj), 143.52 (min), 143.43 (Maj), 141.08 (min and Maj), 140.74 (min and Maj), 126.45 (mino), 126.31 (Maj), 121.33 (d, J = 289.94 Hz),77.20 (min), 75.90 (maj), 70.22 (d, J = 140.2, min and Maj), 62.60 (br, d, J = 7.1 Hz min), 62.24 (br, d, J = 7.7 Hz, Maj), 61.97 (d, J =3.8 Hz, min and Maj), 60.75 (d, J = 8.2 Hz, min and Maj), 35.63 (d, J = 4.4 Hz, min), 35.40 (d, J = 4.4 Hz, Maj), 30.55 (d, J = 6.0 Hz, min), 30.36 (d, J = 6.0 Hz, min), 28.43(min), 27.99 (Maj), 22.90 (min), 21.26 (Maj) 16.33 (d, J = 6.0 Hz, min), 16.03-15.82 (Min and Maj), ^{31} P NMR (162 MHz, $CDCl_3$): δ = 24.61 (min), 24.43 (maj). HRMS (ESI) *m*/*z* calcd for $C_{20}H_{38}N_2O_4P^+$ $(M+H)^+$ 401.2564 found 401.2563.

(1-((*tert*–butyl(1-(1-oxy-pyridin-3-yl)-ethoxy)amino)-2,2-dimethyl-propyl)phosphonic acid diethyl ester (2c): To stirred solution of **2a** (500 mg, 1.25 mmol) in CH_2Cl_2 (14 ml) was

added *m*- CPBA (70% in water, 616 mg, 2.50 mmol). The resulting mixture was stirred at room temperature under argon for 2h. It was then poured into aqueous Na_2SO_3 solution, extracted three times with CH_2Cl_2, washed with aqueous $NaHCO_3$ solution, washed with brine, dried and concentrated *in vacuo*. After purification by column chromatography on silica gel (gradients of MeOH/CH_2Cl_2). Compound **2c** (497 mg, 95% yield) was obtained as an oil ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (br, s, 1H, Maj), 8.09 (br,s, 1H, min), 8.01 (br, d, *J* = 6.0 Hz, 1H, Maj and min), 7.32 (br, *J* = 7.7 Hz, 1H, Maj) 7.16 (m, 2H min and 1H Maj), 5.09 (q, *J* = 6.2 Hz, 1H, Maj), 4.87 (m, 1H, min), 4.21-3.41 (m, 4H, min and Maj), 3.33 (d, *J* = 26.61 Hz, 1H, min), 3.29 (br,s 1H), 1.49 (d, *J* = 6.2 Hz, 3H, min), 1.44 (d, *J* = 6.5 Hz, 3H, Maj) 1.23-1.17 (m, 6H, min), 1.15 (t, *J* = 7.0 Hz, 3H, Maj), 1.09 (s, 9H, min), 1.06 (s, 9H, Maj), 1.04 (s, 9H, Maj), 0.95 (t, *J* = 7.0 Hz, 3H, Maj), 0.77 (s, 3H, min), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.01 (min), 142.48 (Maj), 138.14 (Maj), 138.00 (min), 137.67 (Maj), 137.55 (min), 126.23 (Maj and min), 125.29 (min), 125.14 (Maj), 81.04 (min),79.44 (Maj), 69.93 (d, *J* = 138.6 Hz, min), 69.83 (d, *J* = 139.3 Hz, Maj), 61.37 (d, *J* = 5.8 Hz, min), 61.25(br,s, Maj and min), 61.24 (d, *J* = 7.3 Hz, Maj), 35.25 (d, *J* = 5.1 Hz, min), 34.99 (d, *J* = 4.4 Hz, Maj), 30.43 (d, *J* = 5.8 Hz, Maj), 30.04 (d, *J* = 5.8 Hz, min), 28.28 (min), 27.81 (Maj), 22.74 (min), 20.56 (Maj), 16.39 (d, *J* = 5.1 Hz, min), 16.10 (d, *J* = 5.8 Hz, Maj), 15.89 (br,d , *J* = 7.34 Hz, Maj and min) : ^{31} P NMR (162 MHz, $CDCl_3$): δ = 24.37 (mino), 23.70 (Maj), HRMS (ESI) *m*/*z* calcd for $C_{20}H_{38}N_2O_5P_1$ $(M+H)^+$ 417.2513 found 417.2510

1-Acetyl-3-(1-((*N*-*tert*-butyl-*N*-(1-(diethoxyphosphoryl)-2,2-dimethylpropyl)amino)oxy) ethylpyridinium chloride (2d) : compound **2d** was prepared *in situ* and was not purified. For NMR analyses, Compound **2d** was prepared by adding 1.05 equiv. of acetyl chloride to a C_6D_6 solution of compound **2a** in a NMR tube. ^{1}H NMR (400 MHz, C_6D_6): δ = 8.99 (br, s, 1H, Maj), 8.78 (br, s, 1H, min), 8.66 (br, s, 1H, Maj and min), 7.80 (br,d, *J* = 7.8 Hz, Maj),

7.55 (br, d, *J* = 7.7 Hz, 1H, min), 7.02 (m, 1H, Maj and min), 5.35 (q, *J* = 6.2 Hz, 1H, maj), 5.06 (m, 1H, min), 3.40 (d, *J* = 26.3 Hz, 1H, Maj), 3.38 (d, *J* = 26.1 Hz, 1H, min), 1.64 (d, *J* = 6.7 Hz, 3H, min), 1.39 (d, *J* = 6.7 Hz, 3H, Maj) 1.34 (s, 9H, min), 1.23 (s, 9H, Maj), 120-1.08 (m, 3H, Maj and 6H min), 1.05 (s, 9H, Maj), 0.80 (t, *J* = 7.0 Hz, 3H, m), 0.74 (s, 9H, min), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.10 ,166.65, 147.04 (m), 146.37, 147.79, 140.39, 139.21, 137.68, 124.71, 78.74, 71.31 (d, *J* = 139.2 Hz), 71.12 (d, *J* = *139.2* Hz), 62.09-61.77 (m), .59.53 (br, d, *J* = 6.1 Hz) 36.20 (d, *J* = 5.5 Hz), 35.8 (d, *J*= 5.5 Hz), 31.41 (d, *J* = 6.0), 31.04 (*J* = 5.6 Hz), 29.01, 28.58, 21.96, 20.87, 17.24 (d, *J* = 5.6 Hz), 16.84-16.59 (m) ^{31} P NMR (162 MHz, $CDCl_3$): δ = 24.49 (mino), 24.26 (Maj)

Toluene-4-sulfonate-3-(1-((*N*-tert-butyl-*N*-(1-(diethoxyphosphoryl)-2,2-dimethylpropyl) amino)oxy)ethyl)-1-methyl-pyridinium (2e): To stirred solution of **2a** (500 mg, 1.25 mmol), in THF (15 ml), was added methyl sulfonate (931.15 mg, 5 mmol).The resulting mixture was stirred at room temperature under argon for 24h. It was then concentrated *in vacuo* and triturated with an ether/pentane mixture (1/1 v/v) to give a powder white **2e** (572 mg, 78%), **Major** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.19 (br, s, 1H), 9.00 (br, s, 1H,), 8.38 (br, d, *J* = 8.03 Hz,1H,), 7.96 (m, 1H,), 7.66 (d, *J* = 8.03 Hz, 2H,), 7.07 (d, *J* = 8.0 Hz, 2H,).5.21 (q, *J* = 7.02 Hz, 1H),4.48 (s, 3H), 3.91-3.57 (m, 4H,), 3.36 (d, *J* = 27.1 Hz, 1H), 2.27 (s, 3H), 1.52 (d, *J* = 6.7 Hz), 1.30-1.17 (m, 6H), 1.13 (s, 9H, Maj), 0.98 (s, 9H, Maj), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.02, 144.36, 143.77, 142.91, 139.25 , 128.41, 127.60, 125.65, 76.42, 69.73 (d, *J* = 139.3 Hz), 61.83, 61.40 (d, *J* = 6.6 Hz), 59.63 (d, *J* = 7.7 Hz), 48.49,34.47 (d, *J* =5.1), 32.02 (d, *J* = 4.4 Hz), 30.33 (d, *J* = 6.05 Hz), 27.91, 21.00 , 20.89, 16.10 (d, *J* = 6.05 Hz) 15.92 (d, *J* = 6.1 Hz) ^{31} P NMR (162 MHz, $CDCl_3$): δ = 24.86,

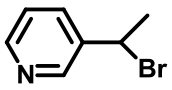
minor ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.26 (br, s, 1H, min), 9.02 (br, s, 1H,), 8.34 (br, d, *J* = 7.5 Hz, 1H), 7.99 (m, 1H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 7.3 Hz, 2H), 5.16 (m, 1H), 4.56 (s, 3H), 4.58 (s, 3H), 4.14-3.85 (m, 4H), 3.35 (d, *J* = 26.8 Hz, 1H), 2.29 (s, 3H), 1.62 (d, *J* = 6.1 Hz, 3H), 1.29 (br, s, 6H), 1.17 (s, 9H), 0.85 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.44, 145.01, 143.42, 143.03, 139.26, 128.54, 127.93 , 125.74, 80.01, 70.12 (d, *J* = 138.4 Hz), 61.71 , 61.48 (d, *J* = 6.6 Hz,), 59.63 (d, *J* = 7.7 Hz), 48.78 , 37.45 (d, *J* = 4.8 Hz), 30.31 (d, *J* = 5.7 Hz), 28.39, 22.71, 21.15, 20.89,16.15 (d, *J* = 6.5 Hz), 16.18 (d, *J* = 6.7 Hz) ^{31}P NMR (162 MHz, $CDCl_3$): δ = 25.40, HRMS (ESI) *m/z* calcd for $C_{21}H_{40}N_2O_4P_1$ $(M+H)^+$ 415.2721 found 415.2713.

1-benzyl-3-(1-((*N*-tert-butyl-*N*-(1-(diethoxyphosphoryl)-2,2-dimethylpropyl)amino)oxy) ethyl)pyridinium, bromide (2f):To stirred solution of **2**a (500 mg, 1.25 mmol) in THF (14 ml), was added benzyl bromide (297 µL, 2.5 mmol). The resulting mixture was stirred at room temperature under argon for 12h. It was then concentrated *in vacuo* and triturated with an ether/pentane mixture to give compound **2f** (550 mg, 77 %, yield) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ = 10.02 (d, *J* = 5.4 Hz, 1H, mino) 9.89 (d, *J* = 5.3 Hz, Maj), 9.35 (br,s, 1H, Maj), 9.19 (br, s, 1H, min), 8.43 (d, *J* = 7.9 Hz, Maj), 8.37 (d, *J* = 7.4 Hz, min), 8.10-8.01 (m, 1H, mino and Majo) 7.74 (br, s, 2H, Maj), 7.66 (br, s, 2H, min), 7.37 (br, s, 3H, min and Maj), 6.57-6.18 (m, 2H, min and maj), 5.29 (br, 1H, Majo), 5.25 (br, 1H, mino), 4.22-3.46 (m, 4H, mino and majo), 3.49 (d, *J* = 26.7 Hz, 1H, Maj), 3.46 (d, *J* = 27.1 Hz, 1H, mino), 1.72 (d, *J* = 6.51 Hz, 3H, mino), 1.64 (d, *J* = 1.64 Hz, 3H, Majo), 1.33-1.24 (m, 3H, Majo and 6H mino), 1.22 (s, 9H, mino), 1.17 (s, 9H, Majo), 1.03 (s, 9H, mino), 0.99 (m, 3H, Majo), 0.74 (s, 9H, mino), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.10, 144.35, 144.05, 144.00, 143.82, 143.68, 143.54, 143.48, 133.15, 132.95, 129.80, 129.55, 129.51, 129.42, 129.29, 129.17, 128.75, 128.52, 128.23, 128.15, 127.86, 127.66, 77.22, 76.41, 69.56 (d, *J* =

138.65), 65.55, 63.93, 63.76, 61.84, 61.80, 61.01 (d, *J* = 7.3 Hz), 59.53 (br,d, *J* = 8.07 Hz), 35.23 (d, *J* = 4.4 Hz), 35.05 (d, *J* = 4.4 Hz), 30.34 (d, *J* = 5.87 Hz), 28.15, 27.92, 22.22, 20.90, 16.40-15.85 (m) ^{31} P NMR (162 MHz, $CDCl_3$): δ = 23.90 (mino), 23.76 (Maj) HRMS (ESI) *m/z* calcd for $C_{21}H_{40}N_2O_4P_1$ $(M)^+$ 491.3035 found 491.3040.

Borane 3-(1-((*tert*–butyl(1-(diethoxyphosphoryl)-2,2-dimethylpropyl)amino)oxy)ehyl) pyridine complex (2g) : To stirred solution of **2a** (500 mg, 1.25 mmol) in THF (14 ml), was added Borane –THF complex (1.0 M solution in THF, 2 ml, 2 mmol); The resulting mixture was stirred at room temperature under argon for 12h. It was then concentrated *in vacuo* to give compound **2g** (492 mg, 95 % yield) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (br,s, 1H, Maj), 8.52 (br,s, 1H, min), 8.45 (d, *J* = 5.5 Hz, 1H, min), 8.42 (d, *J* = 5.5 Hz, 1H, Maj), 7.45-7.37 (m, 1H, min and Maj), 5.24 (q, t = 5.2 Hz, 1H, Maj), 5.05 (m,1H, min), 4.28-3.82 (m, 4H, mino and majo), 3.41 (d, *J* = 26.6 Hz, 1H, Majo), 3.44 (d, *J* = 26.9 Hz, 1H, min), 1.59 (d, *J* = 6.5 Hz, 3H, min), 1.53 (d, *J* = 6.7 Hz, 3H,Maj), 1.47-1.27 (m, 3H, Maj and 6H min), 1.18 (s, 9H, min), 1.15 (s, 9H, Maj), 1.11(s, 9H, Maj), 1.01 (t, *J* = 7.03 Hz 0.78 (s, 9H, min), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.57 (min), 146.25 (Maj), 145.97 (min), 145.86 (Maj), 142.32 (min), 141.25 (Maj), 138.63 (Maj), 137.80 (min), 124.68 (Maj), 80.46 (min), 75.67 (Maj), 70.03 (d, *J* = 138.6 Hz, min), 68.65 (d, *J* = 139.3 Hz, Maj), 61.54 (d, *J* = 6.6 Hz, 1H, min), 61.40 (br, s, Maj and min) 61.38 (d, *J* = 6.6 Hz; Maj), 59.44 (d, *J* = 8.0 Hz, min and Maj), 35.34 (d, *J* = 5.1 Hz, min), 35.11 (d, *J* = 4.4 Hz, Min), 30.55 (d, *J* = 5.8 Hz, Maj), 30.28 (d, *J* = 5.1 Hz, min), 28.29 (min), 27.97 (Maj), 22.50 (min), 20.79 (Maj), 16.42 (d, *J* = 5.14 Hz, min), 16.11 (d, *J* = 5.8 Hz), 15.99-15.91 (m, mino and Majo), ^{31} P NMR (162 MHz, $CDCl_3$): δ = 24.90 (mino), 24.37 (Maj) HRMS (ESI) *m/z* calcd for $C_{20}H_{40}N_2O_4P_1B_1$ $(M+Na)^+$ 437.2715 found 437.2716

^{1}H and ^{13}C NMR spectra of **2a-4**



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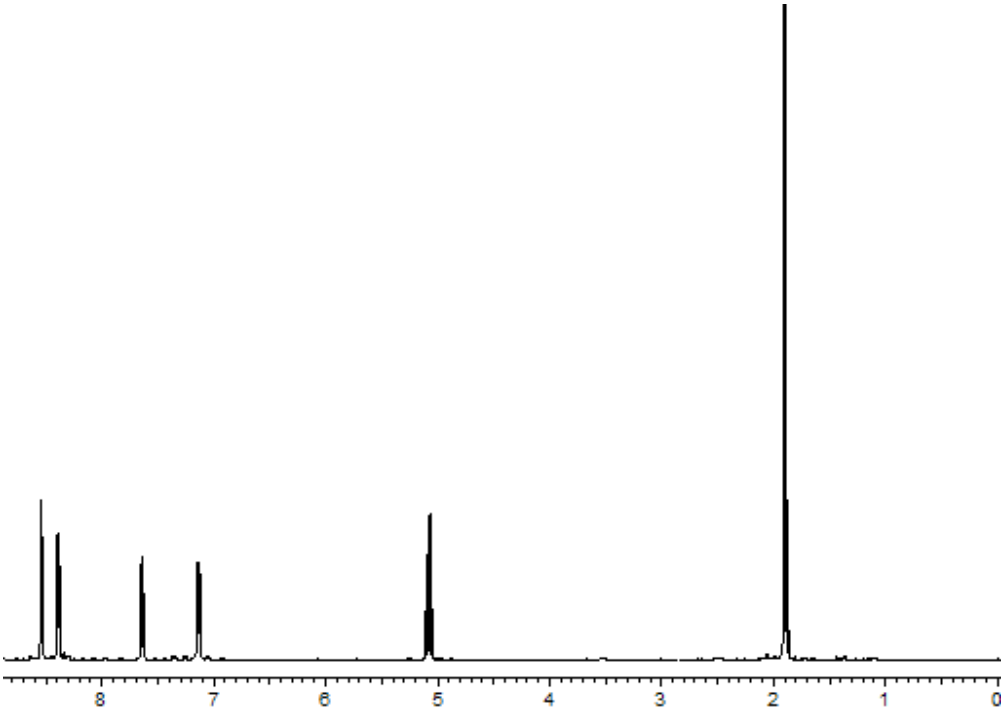
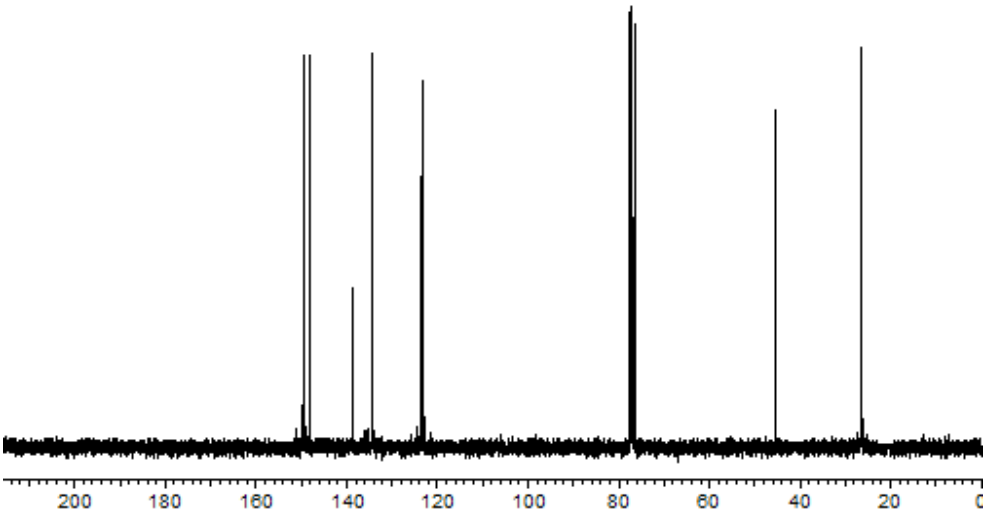
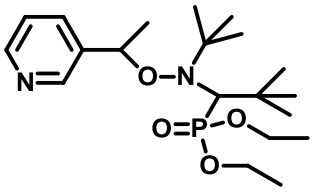
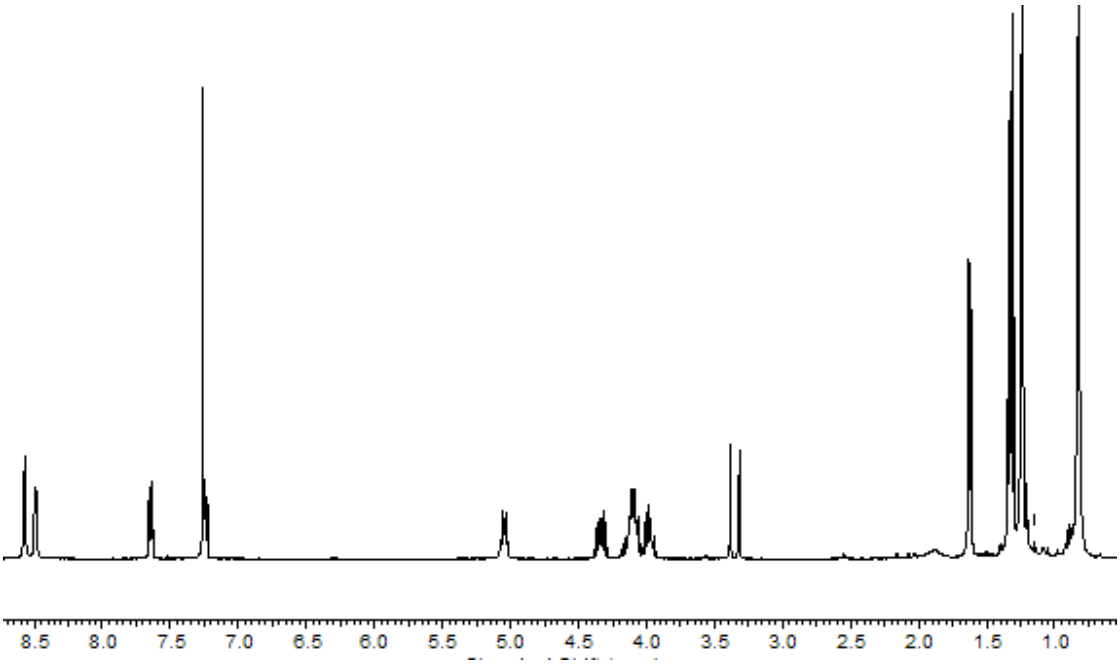
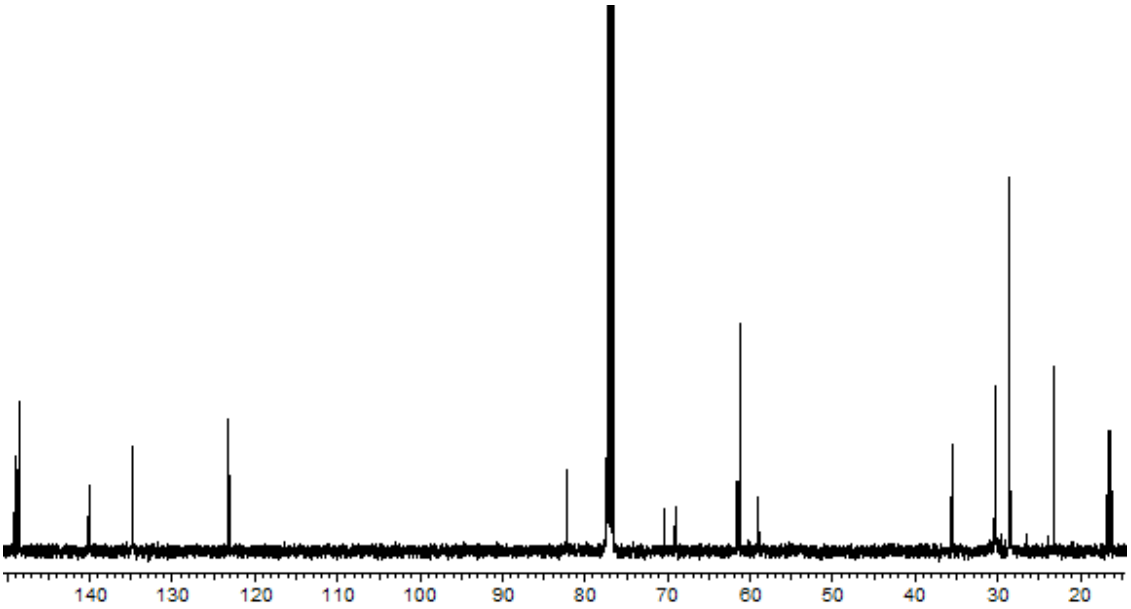


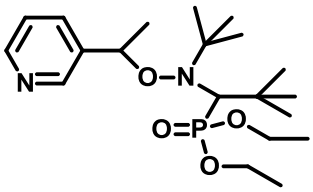




2a (majo)



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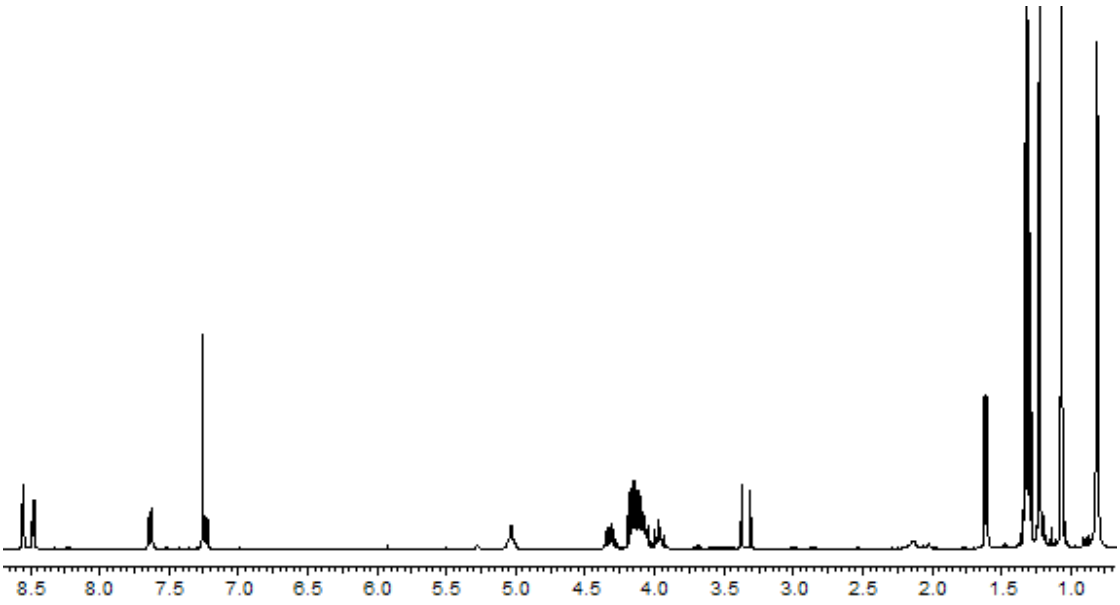
O
O

2a (mino)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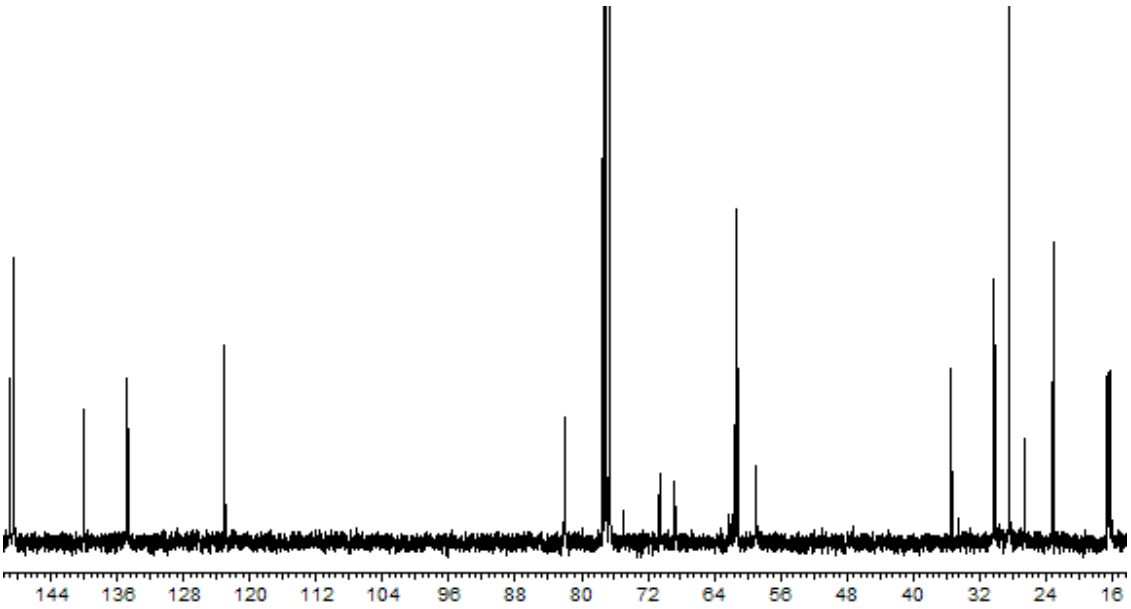
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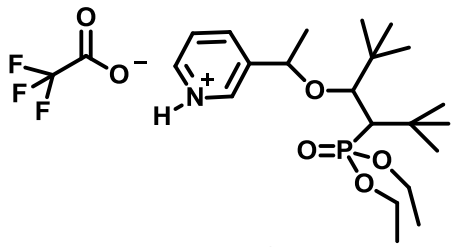

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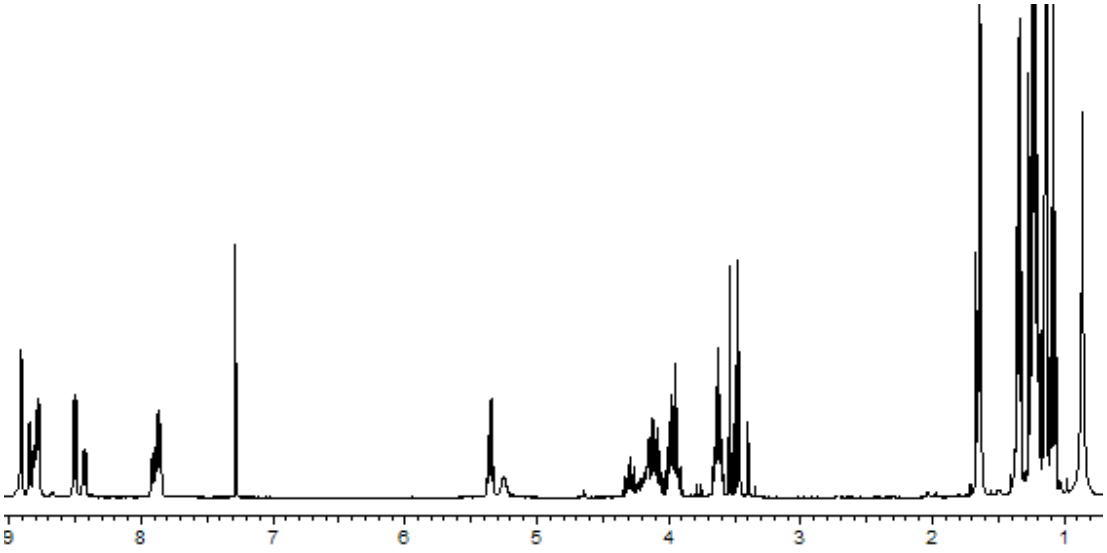
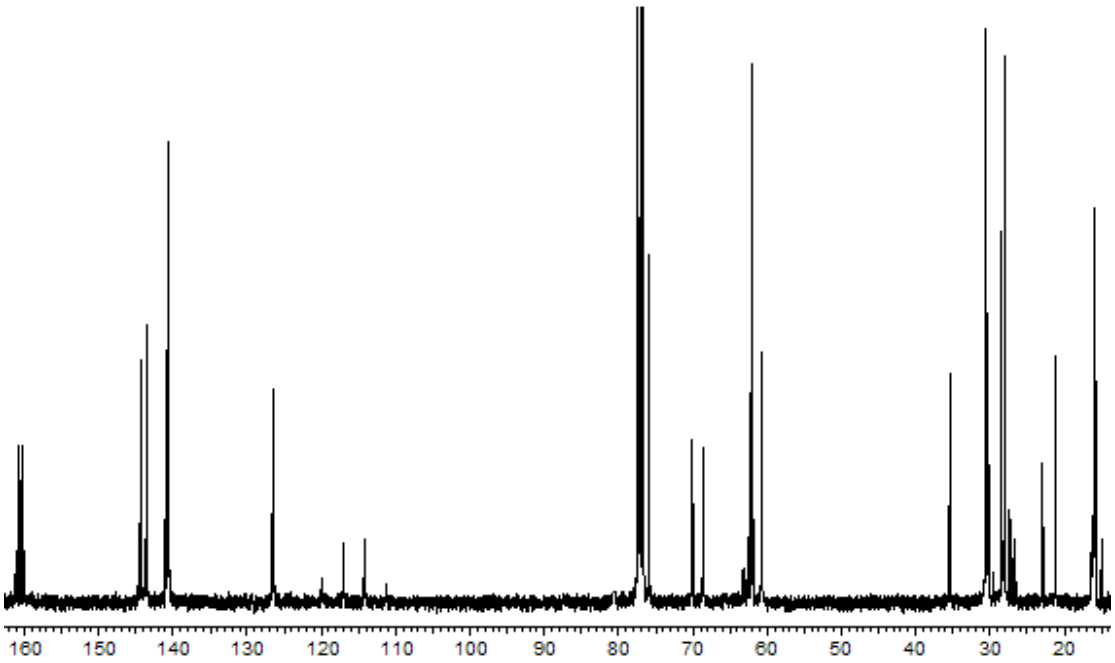
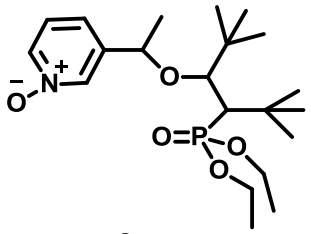
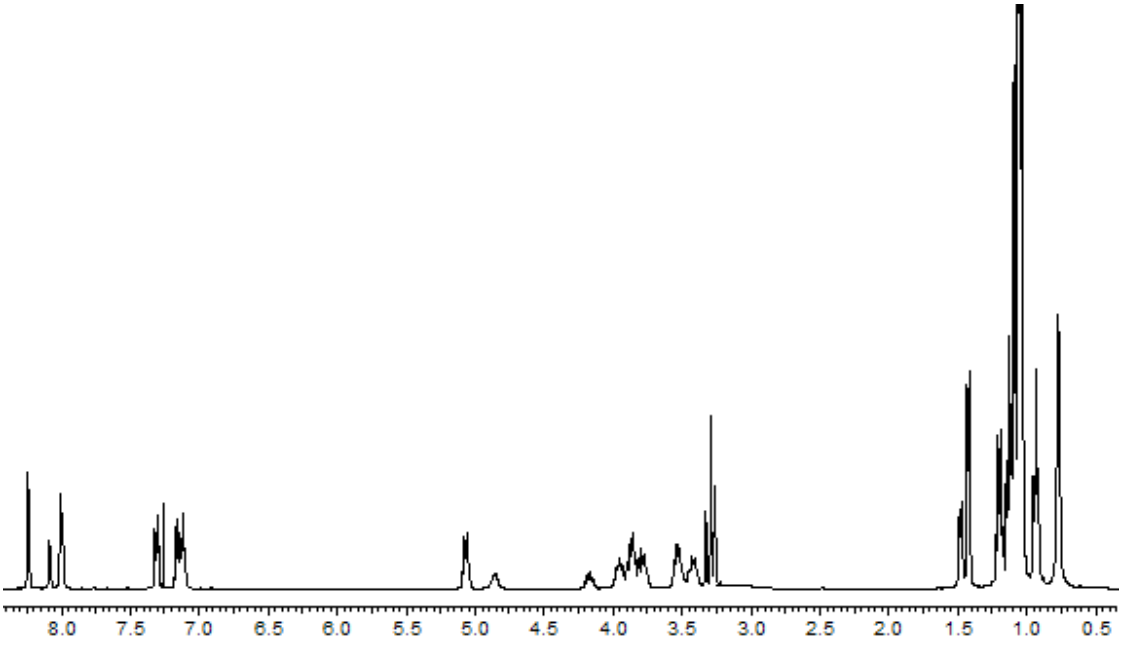
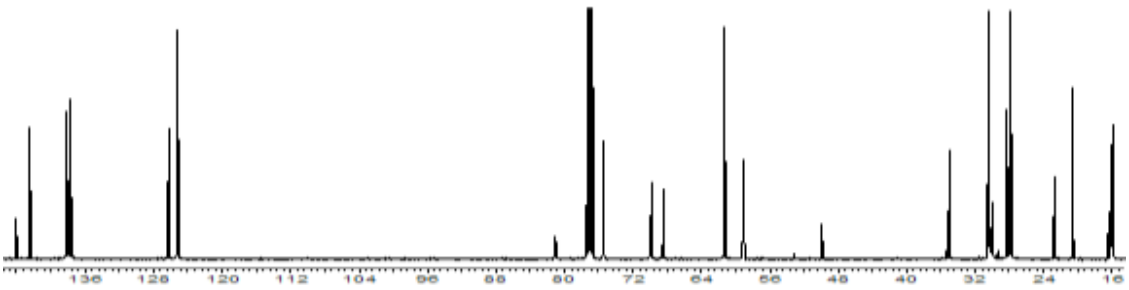


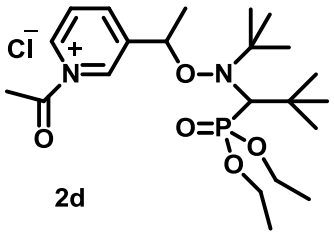




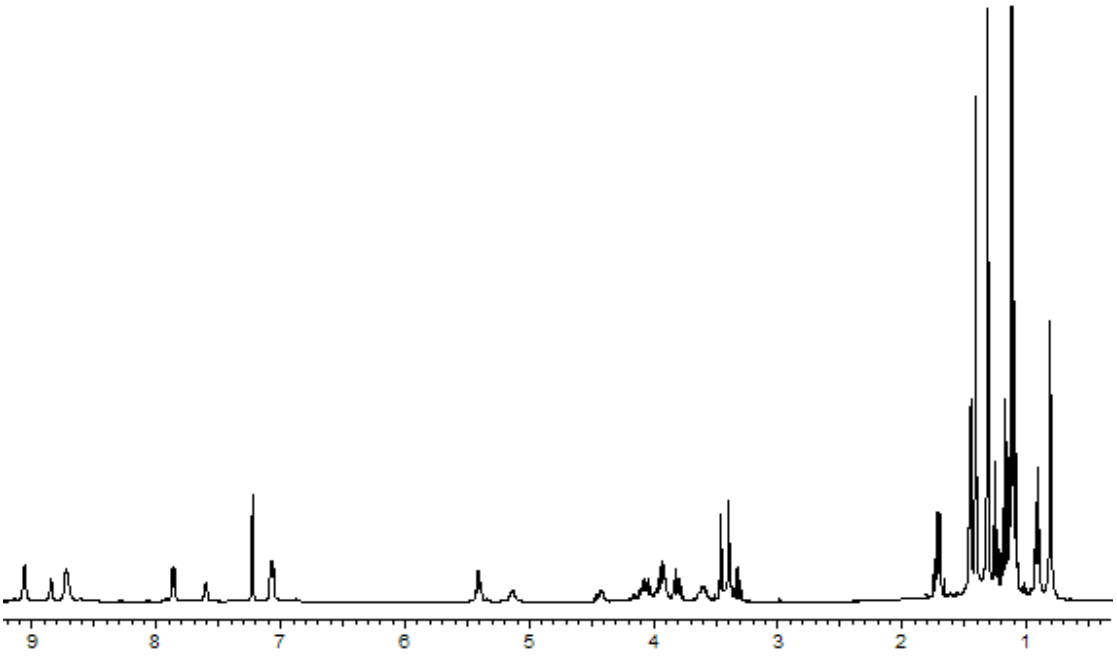
2c

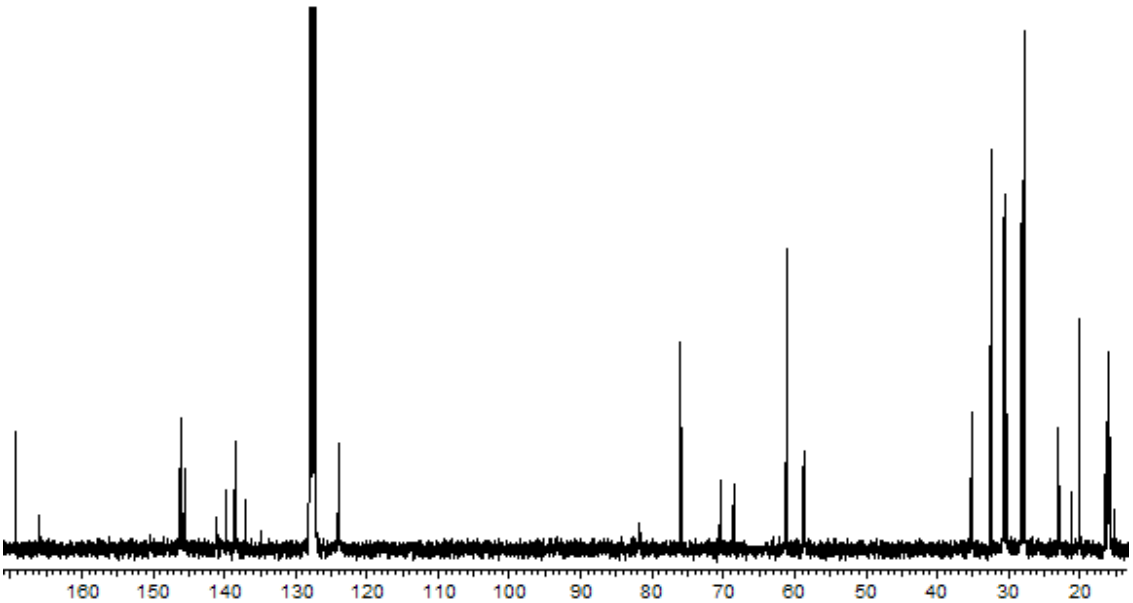


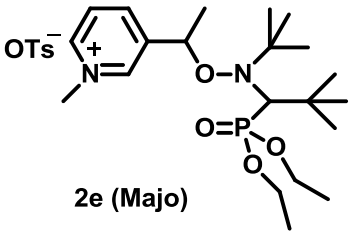




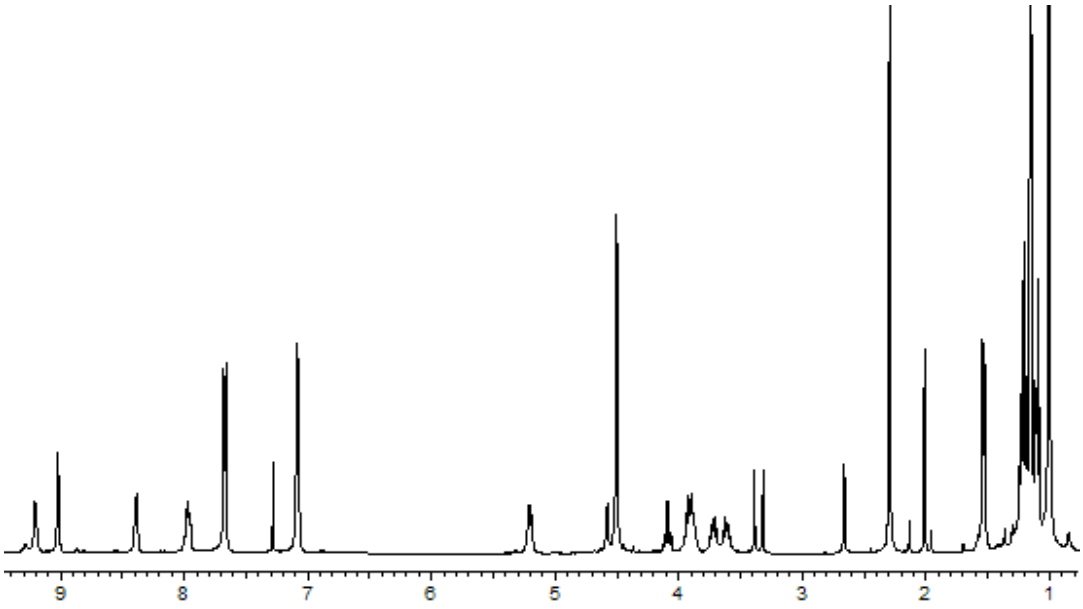
2d

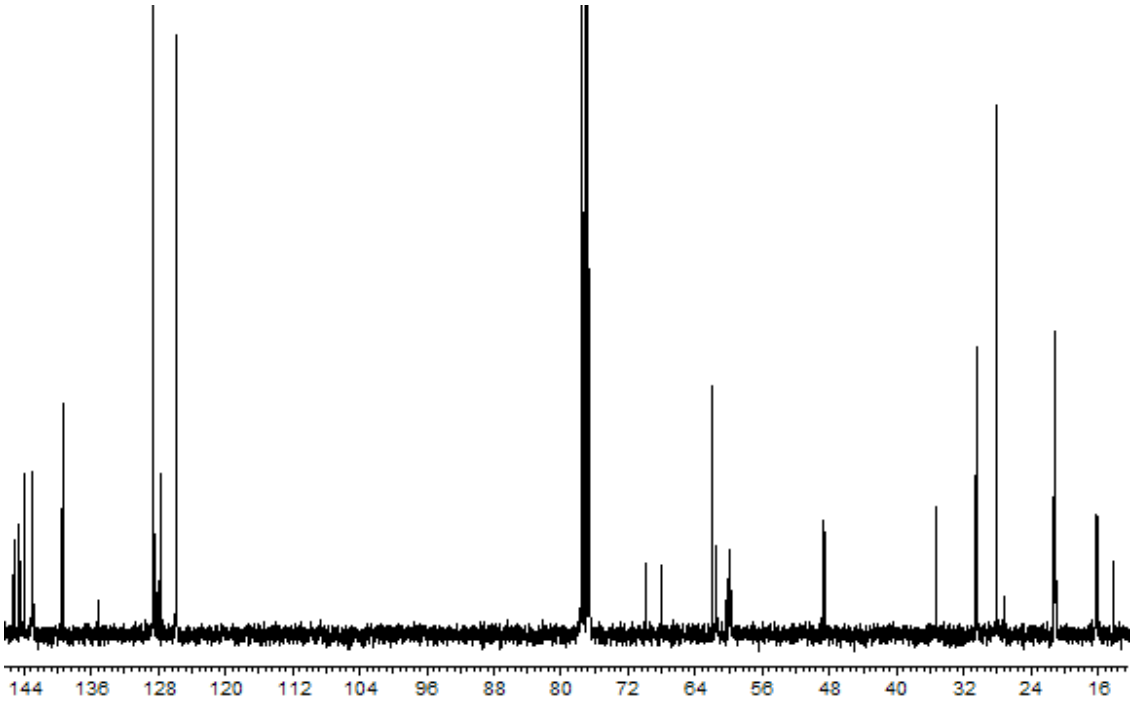


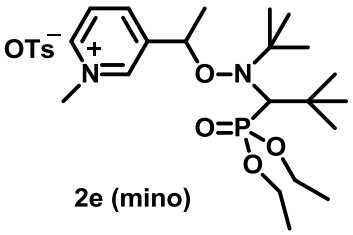




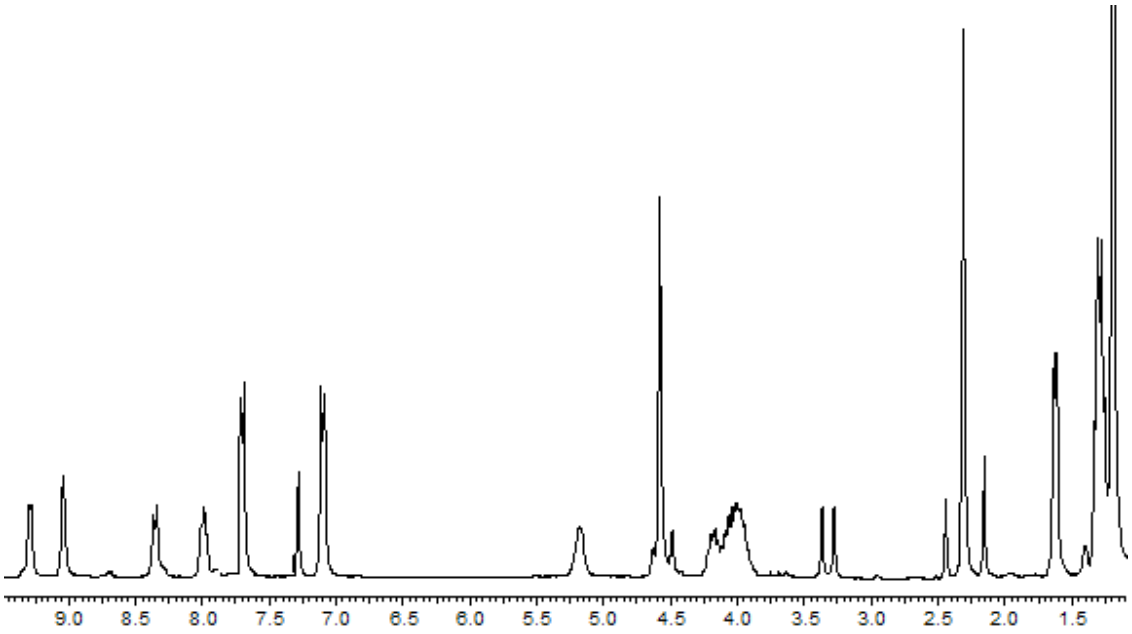
2e (Majo)

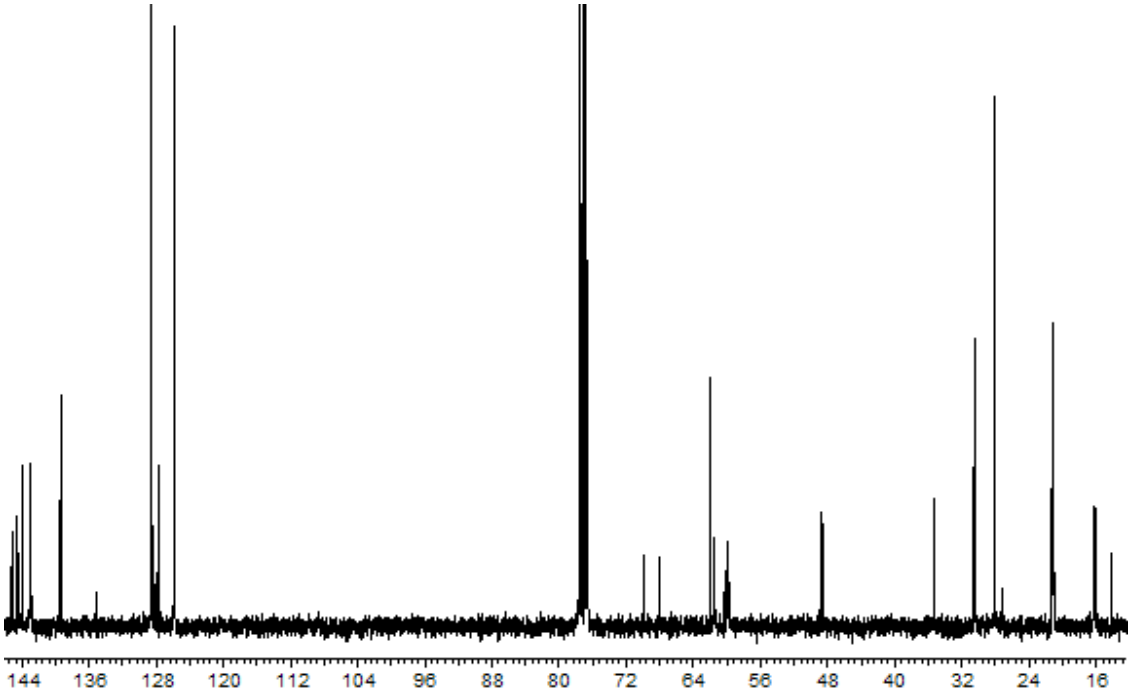


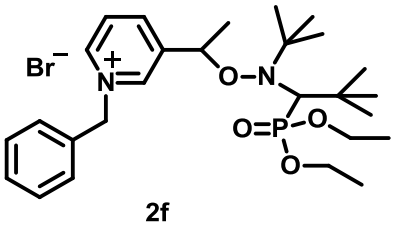




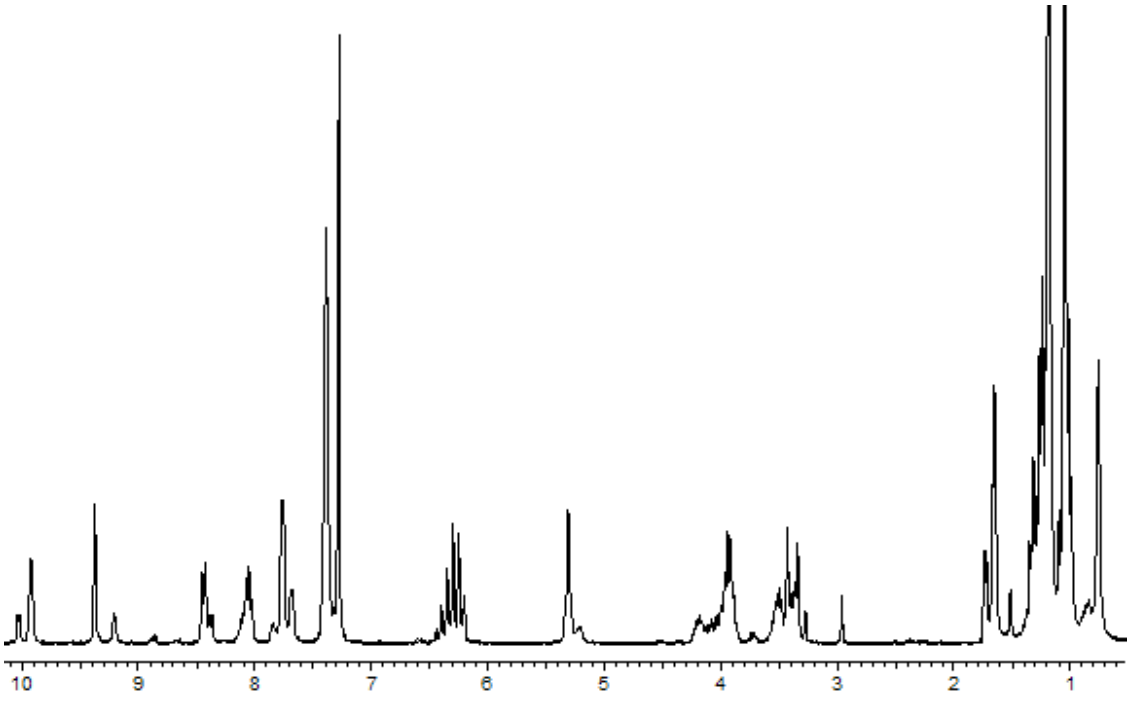
2e (mino)

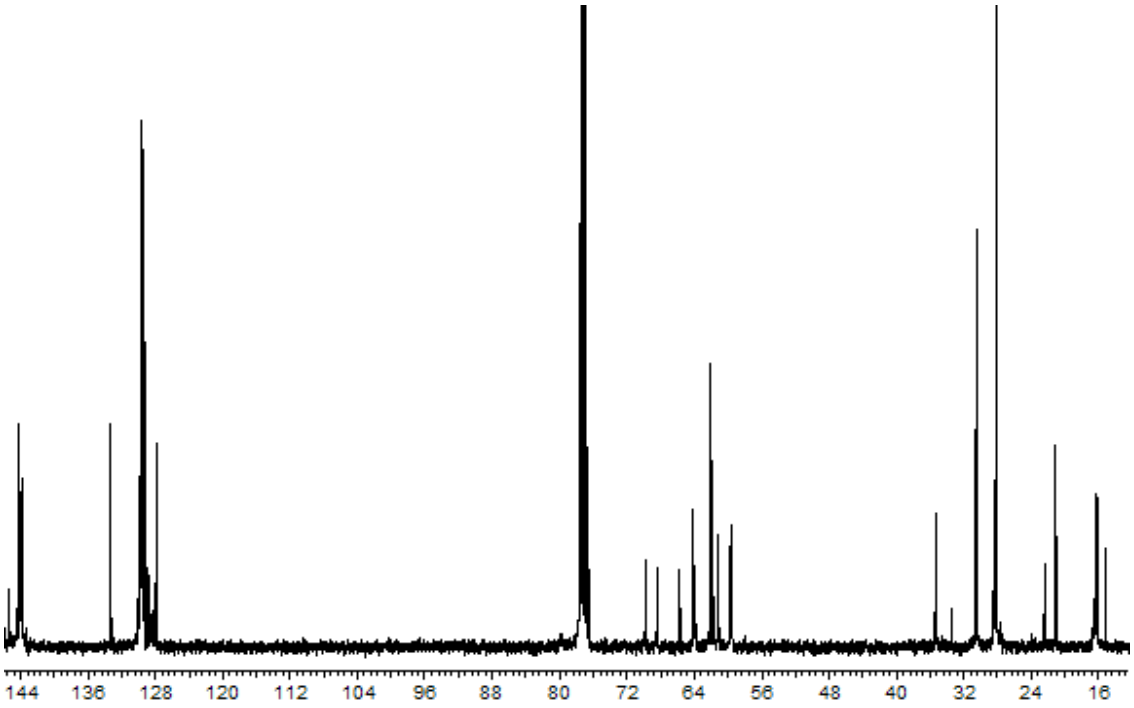


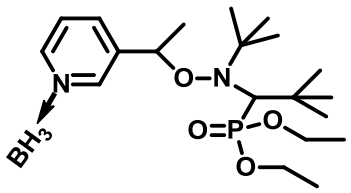




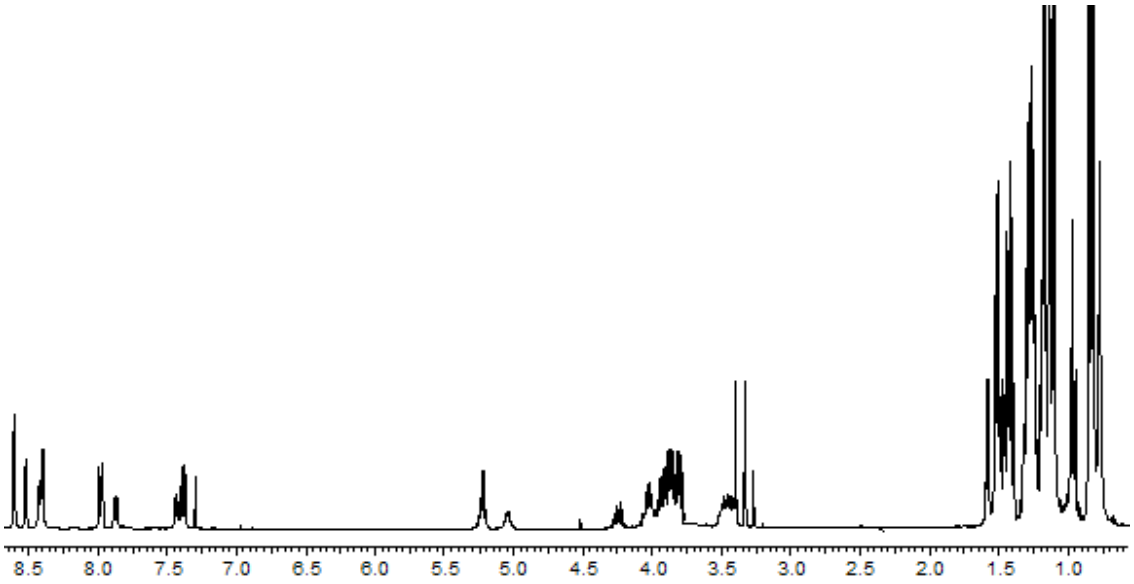
2f

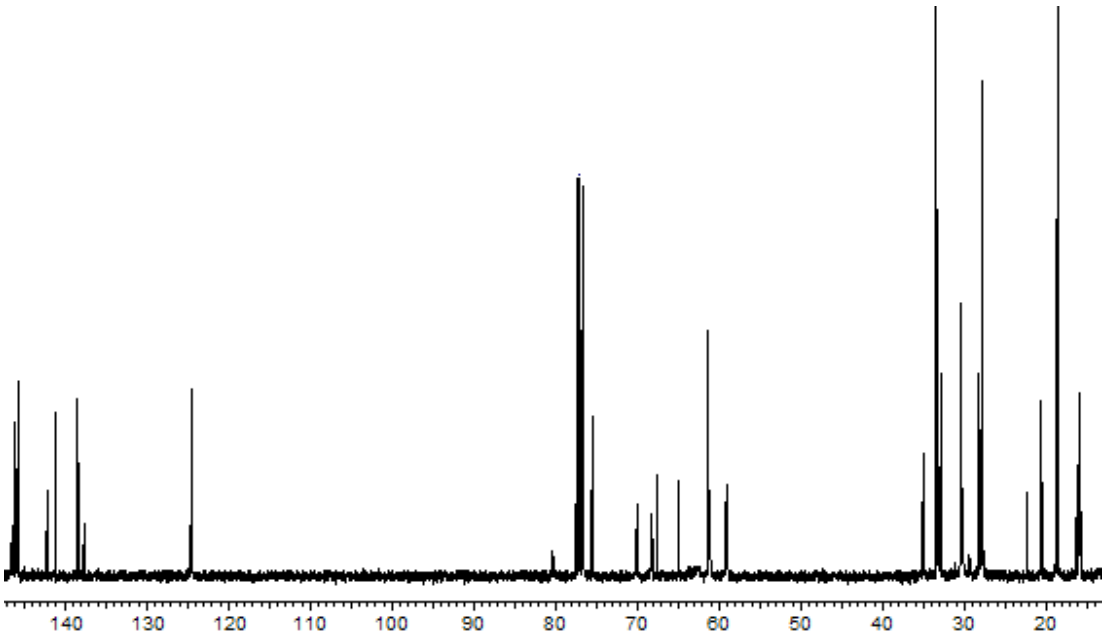






2g





[1] Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E;. Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A., Burant, J. C.; Iyengar, S. S., Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

[ii] Bremond, P.; Koıta, A.; Marque, S. R. A.; Pesce, V. Roubaud, V. ; Siri, D. *Organic Letters*, **2012**, 14(1), 358-361.

[iii] Menon, A. S.; Wood, G. P. F.; Moran, D.; Radom, L. *J. Phys. Chem*. **2007**, *111*, 13638-13644.

[iv] "Chemically Triggered C—ON Bond Homolysis of Alkoxyamines. Part 6. Quaternization and Steric effects." Bremond, P.; Marque, S. R. A.; Roubaud, V.; Siri, D. Submitted