Experimental and DFT study on the indium-mediated synthesis of benzophenones via arylstannanes

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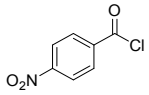
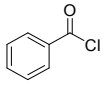
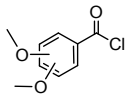
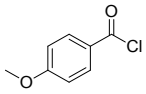
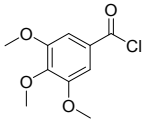
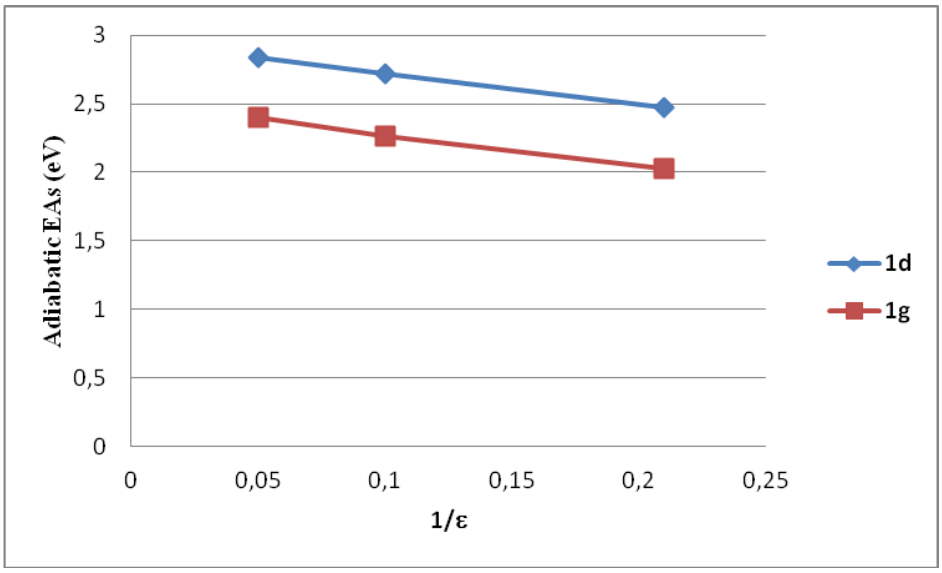
Computational Section

Spectra Section

Adiabatic electron affinities energy (B3LYP/6-31+G*) for benzoyl chlorides

Benzoyl chlorides	Adiabatic EAs energy (eV)	
	Gas Phase	Condensed Phase [SCRF(PCM)]
 **1c**	2.37	
 **1a**	0.98	
 **1d (3,5)**	0.89	2.47 (ε=4.7); 2.72 (ε=9.9); 2.84 (ε=20.7)
1g (2,6)	0.58	2.03 (ε=4.7); 2.26 (ε=9.9); 2.39 (ε=20.7)
1e (3,4)	0.80	
 **1b**	0.88	
 **1f**	0.94	

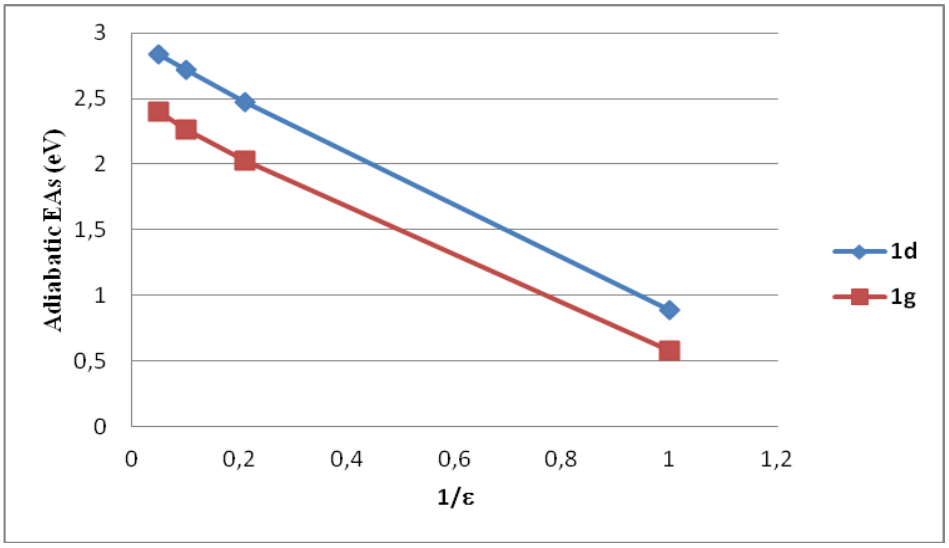
Adiabatic electron affinities vs 1/ε for 1d and 1g [Condensed Phase, SCRF(PCM)]



	AEAs	
1/ε	**1d**	**1g**
0,21	2,47	2,03
0,10	2,72	2,26
0,05	2,84	2,39

ε=4.7; ε=9.9; ε=20.7

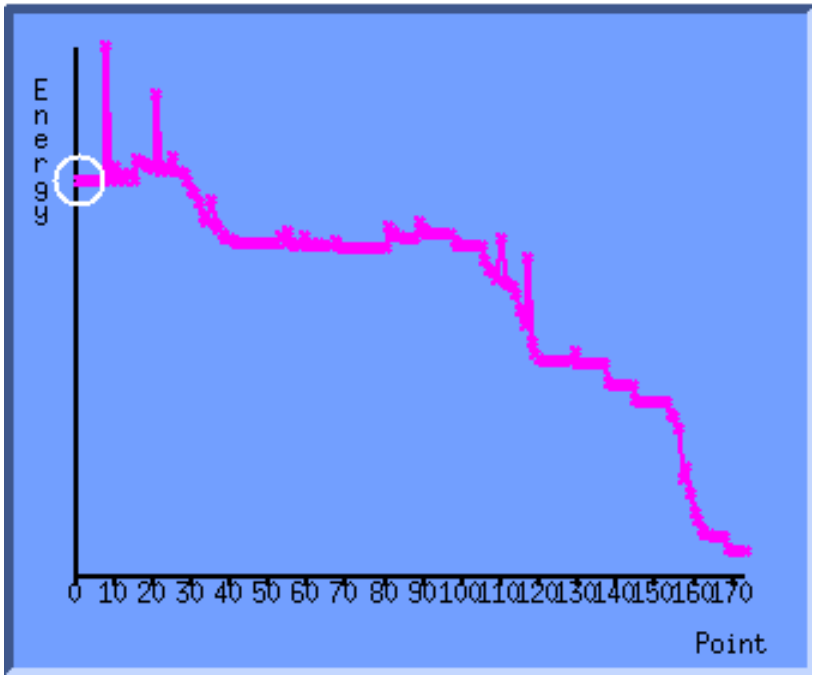
Adiabatic electron affinities vs 1/ε for 1d and 1g [Condensed Phase, SCRF(PCM) and Gas Phase]



	AEAs	
1/ε	**1d**	**1g**
1	0,89	0,58
0,21	2,47	2,03
0,10	2,72	2,26
0,05	2,84	2,39

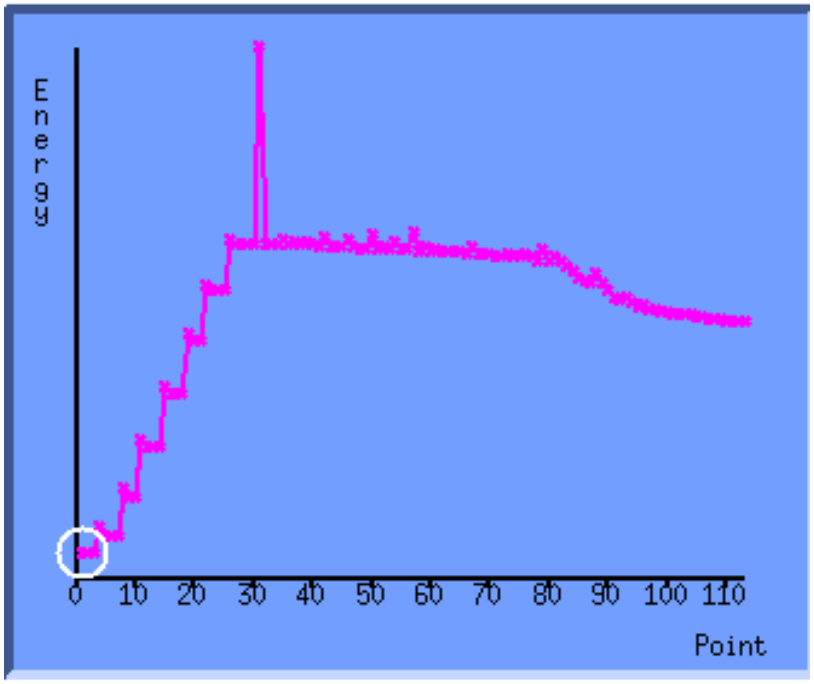
ε=1; ε=4.7; ε=9.9; ε=20.7

Graph of elongation of C(O)-Cl bond for $1g^{-}$ (B3LYP/6-31+G*)



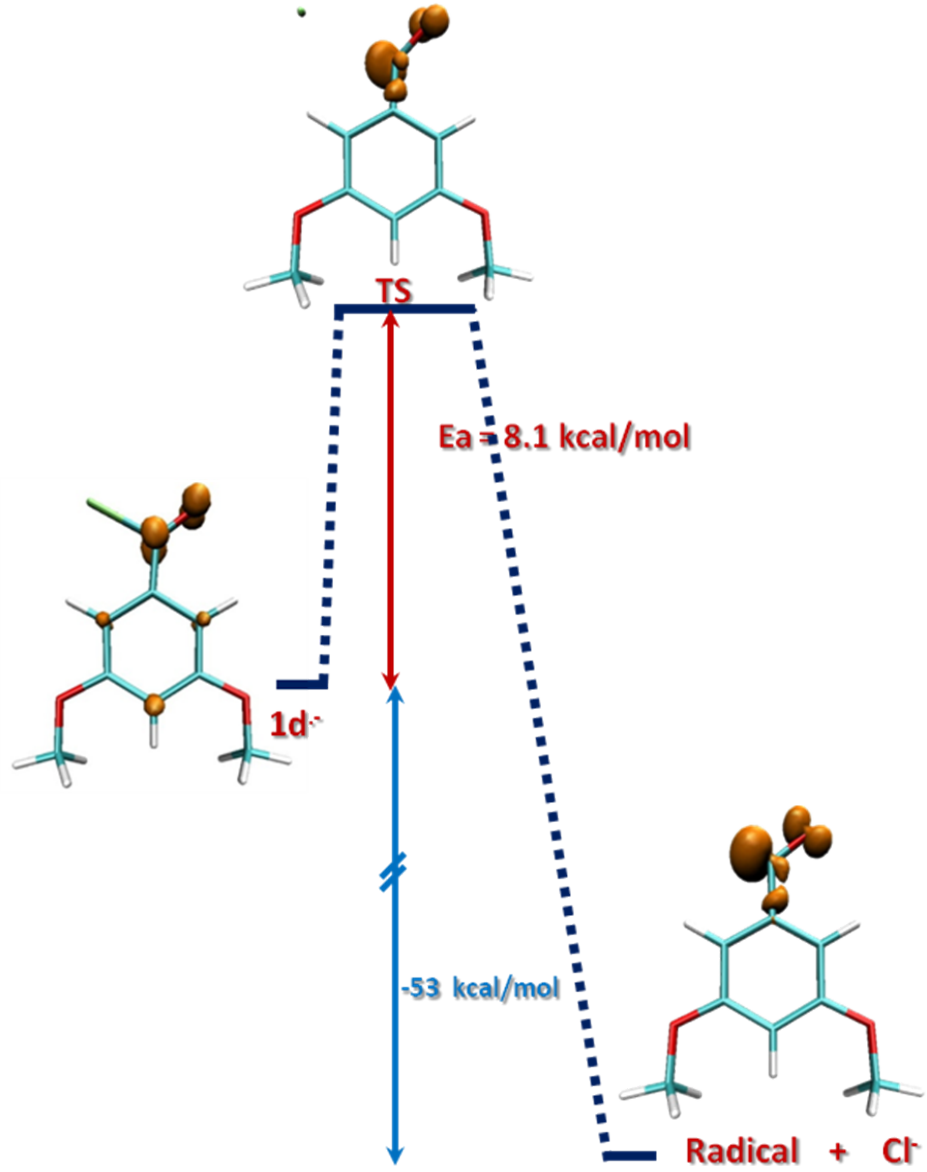
C(O)-Cl distance (Å)	Energy (Hartree)
2.00	-1034.251800
2.10	-1034.254660
2.20	-1034.254233
2.30	-1034.254036
2.40	-1034.254548
2.50	-1034.259592
2.60	-1034.260489
2.70	-1034.261197
2.80	-1034.266826
2.90	-1034.267465

Graph of elongation of C(O)-Cl bond for $1d^{-}$ (B3LYP/6-31+G*)



C(O)-Cl distance (Å)	Energy (Hartree)
1.97	-1034.280338
2.07	-1034.279640
2.17	-1034.278005
2.27	-1034.275938
2.37	-1034.273717
2.47	-1034.271523
2.57	-1034.269459
2.67	-1034.270718
2.77	-1034.270103

PES for Cl-C(O) bond fragmentation of 1d$^{\bullet-}$ (B3LYP/6-31+G*)



Activation Energy for Cl-C(O) bond fragmentation of 1d$^{\bullet-}$ [B3LYP/6-31+G*, SCRF(PCM)]

AE (Kcal/mol)	ε
8.1	1
9.2	4.7
10.8	9.9
11.5	20.7

Cartesians coordinates

1d$^{\cdot-}$

```
 22
ZPE: -1034.121015 a.u., thermal energy: -1034.107268 a.u.(B3LYP/6-31+G* - scaled
factor 0.986)
ZPE: -1034.185922 a.u., thermal energy: -1034.196858 a.u.(B3LYP/6-31+G* - scaled
factor 0.986 – SCRF(PCM,solvent=chloroform) - ε=4.7)
ZPE: -1034.196858 a.u., thermal energy: -1034.183168 a.u.(B3LYP/6-31+G* - scaled
factor 0.986 – SCRF(PCM,solvent=o-dichlorobenzene) - ε=9.9)
ZPE: -1034.202094 a.u., thermal energy: -1034.188398 a.u.(B3LYP/6-31+G* - scaled
factor 0.986 – SCRF(PCM,solvent=acetone) - ε=20.7)
-1 2
 C    -0.000272    -0.000005    -0.005893
 C     0.023071    -0.000033     1.408940
 C     1.198137    -0.000070     2.136197
 C     2.463670    -0.000089     1.464589
 C     2.448922    -0.000058     0.024372
 C     1.252138    -0.000018    -0.664050
 O    -1.147497    -0.000025     2.165625
 C    -2.385151     0.000007     1.493941
 C     3.736049    -0.000091     2.087247
 O     4.872630     0.000066     1.630016
 O     1.356225     0.000002    -2.053851
 C     0.173077     0.000027    -2.818440
Cl     3.651945     0.000269     4.054551
 H     3.384534    -0.000066    -0.523246
 H     1.149955    -0.000088     3.217549
 H     0.489924     0.000036    -3.866010
 H    -0.439844    -0.894755    -2.630020
 H    -0.439820     0.894821    -2.629997
 H    -0.929154     0.000025    -0.557245
 H    -3.152724     0.000006     2.274090
 H    -2.513935     0.894826     0.865622
 H    -2.513964    -0.894786     0.865591
```

Cartesians coordinates

TS$^{\cdot-}$

```
 22
ZPE: -1034.107654 a.u., thermal energy: -1034.094315 a.u.(B3LYP/6-31+G* - scaled
factor 0.986)
ZPE: -1034.170955 a.u., thermal energy: -1034.157643 a.u.(B3LYP/6-31+G* - scaled
factor 0.986 – SCRF(PCM,solvent=chloroform) - ε=4.7)
ZPE: -1034.179222 a.u., thermal energy: -1034.165875 a.u.(B3LYP/6-31+G* - scaled
factor 0.986 – SCRF(PCM,solvent=o-dichlorobenzene) - ε=9.9)
ZPE: -1034.182099 a.u., thermal energy: -1034.170046 a.u.(B3LYP/6-31+G* - scaled
factor 0.986 – SCRF(PCM,solvent=acetone) - ε=20.7)
-1 2
 C     0.000000     0.000000     0.000000
 C     0.000000     0.000000     1.407214
 C     1.219230     0.000000     2.078600
 C     2.429685    -0.019827     1.367135
 C     2.395779    -0.031457    -0.038282
 C     1.186230    -0.002644    -0.739040
 O     1.151919     0.013015     3.457955
 C     2.357918    -0.044110     4.195646
 O     3.531487    -0.055300    -0.807562
 C     4.791676    -0.098799    -0.171295
 C    -1.305487     0.104303    -0.703286
```

```
Cl     0.123062    -0.474672    -3.961188
 O    -2.374468    -0.288471    -0.334938
 H    -0.929661    -0.001031     1.965457
 H     1.142640    -0.025387    -1.833151
 H     2.066507    -0.047921     5.248192
 H     2.926374    -0.958430     3.975745
 H     2.996113     0.829806     4.003474
 H     3.373748    -0.021586     1.893642
 H     5.530506    -0.127058    -0.974576
 H     4.969084     0.792319     0.448567
 H     4.904040    -0.997557     0.452218
```

Cartesians coordinates

Radical·

```
 21
ZPE: -573.828112 a.u., thermal energy: -573.816401 a.u.(B3LYP/6-31+G* - scaled factor
0.986)
0 2
 C    -0.014717     0.000000    -0.024579
 C     0.010941     0.000000     1.382087
 C     1.243375     0.000000     2.052894
 C     2.442430     0.000000     1.331942
 C     2.393797     0.000000    -0.064817
 C     1.173850     0.000000    -0.757035
 O     1.367577     0.000000     3.411997
 C     0.193667     0.000000     4.214341
 C     3.675041     0.000000    -0.813467
 O    -1.166279     0.000000    -0.757530
 C    -2.418831     0.000000    -0.084452
 O     3.851857     0.000000    -1.994102
 H     1.145509     0.000000    -1.841190
 H     3.391485     0.000000     1.857122
 H    -3.175351     0.000000    -0.870820
 H    -2.539259    -0.897921     0.535838
 H    -2.539259     0.897921     0.535838
 H    -0.913850     0.000000     1.942886
 H     0.543297     0.000000     5.247981
 H    -0.412310     0.897859     4.034970
 H    -0.412310    -0.897859     4.034971
```

Cartesians coordinates

1d

```
 22
ZPE: -1034.087112 a.u., thermal energy: -1034.074320 a.u.(B3LYP/6-31+G* - scaled
factor 0.986)
ZPE: -1034.094404 a.u., thermal energy: -1034.081519 a.u.(B3LYP/6-31+G* - scaled
factor 0.986 – SCRF(PCM,solvent=chloroform) - ε=4.7)
ZPE: -1034.096070 a.u., thermal energy: -1034.083155 a.u.(B3LYP/6-31+G* - scaled
factor 0.986 – SCRF(PCM,solvent=o-dichlorobenzene) - ε=9.9)
ZPE: -1034.096926 a.u., thermal energy: -1034.083994 a.u.(B3LYP/6-31+G* - scaled
factor 0.986 – SCRF(PCM,solvent=acetone) - ε=20.7)
0 1
 C     0.001855     0.000000    -0.013573
 C     0.014093     0.000000     1.391244
 C     1.243740     0.000000     2.066749
 C     2.449686     0.000000     1.358233
 C     2.415883     0.000000    -0.039846
 C     1.197528     0.000000    -0.734398
```

O	1.360077	0.000000	3.425168
C	0.182481	0.000000	4.221631
C	3.643749	0.000000	-0.882314
Cl	5.226293	0.000000	0.024458
O	-1.139423	0.000000	-0.758982
C	-2.399072	0.000000	-0.100029
O	3.674140	0.000000	-2.077301
H	1.175192	0.000000	-1.817642
H	3.382157	0.000000	1.907219
H	-3.146805	0.000000	-0.894705
H	-2.526157	-0.897954	0.518951
H	-2.526157	0.897954	0.518951
H	-0.914258	0.000000	1.946295
H	0.527310	0.000000	5.256857
H	-0.422595	0.897935	4.039430
H	-0.422595	-0.897935	4.039430

Cartesians coordinates

1c

16

ZPE: -1009.602810 a.u., thermal energy: -1009.592746 a.u.(B3LYP/6-31+G* - scaled factor 0.986)

0 1

C	0.009134	0.000012	-0.132221
C	-0.053311	0.000003	1.268897
C	1.132456	0.000011	2.026271
C	2.370079	0.000029	1.391834
C	2.403405	0.000040	-0.002972
C	1.244649	0.000030	-0.776760
C	-1.331956	-0.000017	2.037379
O	-1.417479	-0.000031	3.229867
N	3.716999	0.000062	-0.685030
O	4.724041	-0.000093	0.021456
O	3.719307	-0.000091	-1.915184
H	1.070393	0.000003	3.109076
H	3.295253	0.000035	1.955518
H	1.316024	0.000038	-1.857703
H	-0.901301	0.000006	-0.719179
Cl	-2.848073	-0.000037	1.044703

Cartesians coordinates

1c^{-}

16

ZPE: -1009.690394 a.u., thermal energy: -1009.680191 a.u.(B3LYP/6-31+G* - scaled factor 0.986)

-1 2

C	0.014938	0.000034	-0.132007
C	-0.073572	0.000040	1.290374
C	1.151836	0.000030	2.030743
C	2.373976	0.000020	1.397298
C	2.440136	0.000017	-0.021352
C	1.235758	0.000025	-0.772583
C	-1.290310	0.000054	2.048795
O	-1.463389	-0.000069	3.245884
N	3.683870	0.000006	-0.672565
O	4.742992	-0.000079	0.026592

```
 O     3.713032    -0.000070    -1.941023
 H     1.100179     0.000033     3.115235
 H     3.299909     0.000014     1.960179
 H     1.300032     0.000024    -1.854120
 H    -0.896522     0.000040    -0.718584
Cl    -2.883246    -0.000120     0.993087
```

Cartesians coordinates

1a

```
 14
ZPE: -805.099795 a.u., thermal energy: -805.092340 a.u.(B3LYP/6-31+G* - scaled factor
0.986)
0 1
 C     0.004891     0.000001    -0.005191
 C     0.007667     0.000002     1.398162
 C     1.231314     0.000001     2.094522
 C     2.433287     0.000000     1.391733
 C     2.426175    -0.000001    -0.007771
 C     1.213164     0.000000    -0.702319
 C    -1.224159     0.000003     2.225921
Cl    -2.798737    -0.000005     1.299846
 O    -1.268688    -0.000002     3.421181
 H     1.221258     0.000001     3.179570
 H     3.375230    -0.000001     1.933304
 H     3.365091    -0.000002    -0.555448
 H     1.206161     0.000000    -1.788726
 H    -0.934264     0.000002    -0.545910
```

Cartesians coordinates

1a$^{\cdot-}$

```
 14
ZPE: -805.136543 a.u., thermal energy: -805.128530 a.u.(B3LYP/6-31+G* - scaled factor
0.986)
-1 2
 C     0.00627500   -0.00000700   -0.00510000
 C    -0.02241900   -0.00000800    1.43115900
 C     1.25716200   -0.00000200    2.10235300
 C     2.44250700    0.00000300    1.38746300
 C     2.45162200    0.00000300   -0.02524100
 C     1.20701900   -0.00000200   -0.69567000
 C    -1.17505000   -0.00001000    2.24967600
 Cl   -2.87290700    0.00002200    1.22220800
 O    -1.32857100    0.00000300    3.46338700
 H     1.26670400   -0.00000200    3.18847200
 H     3.38720400    0.00000600    1.93252500
 H     3.38730300    0.00000600   -0.58002700
 H     1.18442400   -0.00000200   -1.78583300
 H    -0.93288200   -0.00001000   -0.54649800
```

Cartesians coordinates

1g

```
 22
ZPE: -1034.078108 a.u., thermal energy: -1034.065056 a.u.(B3LYP/6-31+G* - scaled
factor 0.986)
ZPE: -1034.086146 a.u., thermal energy: -1034.073113 a.u.(B3LYP/6-31+G* - scaled
factor 0.986 – SCRF(PCM,solvent=chloroform) - ε=4.7)
```

ZPE: -1034.088004 a.u., thermal energy: -1034.074976 a.u.(B3LYP/6-31+G* - scaled factor 0.986 – SCRF(PCM,solvent=o-dichlorobenzene) - ε=9.9)
ZPE: -1034.088952 a.u., thermal energy: -1034.075931 a.u.(B3LYP/6-31+G* - scaled factor 0.986 – SCRF(PCM,solvent=acetone) - ε=20.7)
0 1

C	-0.054036	-0.856477	0.509020
C	-0.014606	-0.568209	1.880433
C	1.221712	-0.462168	2.539517
C	2.418764	-0.646510	1.828687
C	2.383728	-0.937039	0.458052
C	1.146329	-1.036029	-0.179333
O	-1.109434	-0.357940	2.658344
C	-2.403038	-0.442424	2.069053
C	1.252501	-0.174153	4.003326
O	1.048796	-0.934920	4.895188
O	3.554244	-0.535851	2.568263
C	4.816783	-0.667326	1.922459
Cl	1.624863	1.575247	4.374062
H	3.297304	-1.087336	-0.104128
H	1.116560	-1.261051	-1.242165
H	-0.997551	-0.938328	-0.016754
H	-3.105499	-0.242121	2.879091
H	-2.527967	0.309087	1.279566
H	-2.587290	-1.444621	1.662663
H	5.561257	-0.517936	2.705520
H	4.936365	-1.667639	1.488037
H	4.943356	0.095086	1.143918

Cartesians coordinates

1g$^{\cdot-}$

22
ZPE: -1034.099715 a.u., thermal energy: -1034.086248 a.u.(B3LYP/6-31+G* - scaled factor 0.986)
ZPE: -1034.161368 a.u., thermal energy: -1034.147810 a.u.(B3LYP/6-31+G* - scaled factor 0.986 – SCRF(PCM,solvent=chloroform) - ε=4.7)
ZPE: -1034.171471 a.u., thermal energy: -1034.157980 a.u.(B3LYP/6-31+G* - scaled factor 0.986 – SCRF(PCM,solvent=o-dichlorobenzene) - ε=9.9)
ZPE: -1034.177586 a.u., thermal energy: -1034.163749 a.u.(B3LYP/6-31+G* - scaled factor 0.986 – SCRF(PCM,solvent=acetone) - ε=20.7)
-1 2

C	-0.017637	0.046227	0.009216
C	0.003901	-0.003198	1.468336
C	1.183355	0.009679	2.192177
C	2.440087	0.008574	1.554870
C	2.461909	-0.097245	0.152862
C	1.296451	-0.110734	-0.596659
O	-1.169377	0.056955	2.207315
C	-1.890820	-1.167925	2.299353
O	1.465053	-0.309319	-1.960085
C	0.948725	-1.536546	-2.458029
C	-1.252191	0.305610	-0.646468
O	-2.416858	0.150166	-0.306567
Cl	-1.100663	1.080195	-2.450782
H	1.102422	0.035335	3.276963
H	3.361648	0.037085	2.130474
H	3.400497	-0.204139	-0.387508
H	1.126207	-1.530108	-3.537821
H	1.474177	-2.391344	-2.001006

```
 H    -0.127858    -1.630517    -2.275283
 H    -2.772119    -0.959430     2.915370
 H    -2.218692    -1.510257     1.312605
 H    -1.276540    -1.941187     2.788914
```

Cartesians coordinates

1e

```
 22
ZPE: -1034.084160 a.u., thermal energy: -1034.071254 a.u.(B3LYP/6-31+G* - scaled
factor 0.986)
0 1
 C     0.003369    -0.035099     0.025682
 C     0.004950    -0.022599     1.410805
 C     1.241868    -0.025511     2.109287
 C     2.441233    -0.021218     1.383977
 C     2.426728    -0.029420    -0.009892
 C     1.211348    -0.040491    -0.704227
 O    -1.188448    -0.095954     2.081043
 C    -1.593170     1.084809     2.788629
 O     1.162701    -0.043040     3.461390
 C     2.367385    -0.102762     4.223540
 C     1.094508    -0.052975    -2.173785
 O     0.080846    -0.053901    -2.809995
Cl     2.687843    -0.066923    -3.089790
 H    -0.947769    -0.051193    -0.496057
 H     3.394405    -0.021295     1.900604
 H     3.365315    -0.030748    -0.551304
 H     2.050661    -0.135315     5.267006
 H     2.939563    -1.007490     3.984574
 H     2.987116     0.786521     4.053800
 H    -2.563063     0.847642     3.230946
 H    -0.878594     1.339116     3.578100
 H    -1.702488     1.927833     2.093677
```

Cartesians coordinates

1e$^{\cdot-}$

```
  22
ZPE: -1034.114465 a.u., thermal energy: -1034.100806 a.u.(B3LYP/6-31+G* - scaled
factor 0.986)
-1 2
 C    -0.039872    -0.000683     0.002696
 C     0.003867    -0.024571     1.447008
 C     1.199054    -0.034845     2.135103
 C     2.439794    -0.021387     1.449416
 C     2.420292     0.013004     0.041963
 C     1.225880     0.022794    -0.667876
 O     1.173054    -0.107973     3.528054
 C     1.521795     1.104939     4.182655
 O     3.593555    -0.045302     2.233794
 C     4.827988    -0.129915     1.563023
 C    -1.317621     0.000967    -0.600918
Cl    -1.244563     0.049649    -2.581788
 O    -2.452059    -0.008855    -0.139666
 H    -0.924969    -0.046304     2.007652
 H     3.351518     0.027623    -0.517817
 H     1.248999     0.046279    -1.750835
 H     5.596653    -0.177545     2.340798
 H     4.891561    -1.033307     0.936395
```

```
 H     5.014309     0.750770     0.927772
 H     1.421331     0.918459     5.257611
 H     2.555530     1.399315     3.959354
 H     0.839030     1.917058     3.890303
```

Cartesians coordinates

1b

```
 18
ZPE: -919.592316 a.u., thermal energy: -919.582938 a.u.(B3LYP/6-31+G* - scaled factor
0.986)
0 1
 C    -0.000232     0.001426    -0.006103
 C     0.007701     0.000708     1.400712
 C     1.208012     0.000077     2.092429
 C     2.433120     0.000157     1.397732
 C     2.415400     0.000847    -0.008190
 C     1.215240     0.001484    -0.711895
 C     3.756979    -0.000472     2.046033
 O     4.821051    -0.001050     1.494940
 O    -1.224831     0.001958    -0.587444
 C    -1.318353     0.003398    -2.010875
Cl     3.735111    -0.002200     3.878798
 H     1.234327     0.001977    -1.796088
 H    -0.942464     0.000668     1.926421
 H     3.358329     0.000881    -0.546550
 H     1.200403    -0.000457     3.176521
 H    -2.387026     0.004202    -2.232784
 H    -0.853434     0.901811    -2.436362
 H    -0.854434    -0.894708    -2.438110
```

Cartesians coordinates

1b^{-}

```
  18
ZPE: -919.626095 a.u., thermal energy: -919.615265 a.u.(B3LYP/6-31+G* - scaled factor
0.986)
-1 2
 C     0.000000     0.000000     0.000000  0.568164
 C     0.000000     0.000000     1.404644 -0.031780
 C     1.234914     0.000000     2.089929 -0.818614
 C     2.433962     0.000000     1.403589 -0.928478
 C     2.476216     0.000000    -0.032758  1.110651
 C     1.199915     0.000000    -0.705447 -0.438817
 O    -1.145076    -0.000044     2.207686 -0.399954
 C    -2.391389     0.000347     1.555853 -0.308688
 C     3.634922     0.000000    -0.840482 -0.285033
Cl     5.324805    -0.000032     0.207862 -0.216969
 O     3.799607    -0.000016    -2.054366 -0.460583
 H    -0.931978    -0.000016    -0.559701  0.140951
 H     1.224695     0.000000     3.178154  0.154767
 H     1.188679     0.000000    -1.791037  0.179043
 H     3.367504     0.000016     1.954365  0.187651
 H    -3.151883     0.000428     2.343230  0.175415
 H    -2.525802     0.894380     0.925707  0.186174
 H    -2.526263    -0.893455     0.925477  0.186156
```

Cartesians coordinates

1f

```
 26
ZPE:  -1148.569662  a.u.,  thermal  energy:  -1148.553858  a.u.(B3LYP/6-31+G*  -  scaled
factor 0.986)
0 1
 C     0.000771    -0.000110    -0.000580
 C     0.000454    -0.000286     1.399338
 C     1.205676    -0.000410     2.100822
 C     2.431894    -0.005694     1.406514
 C     2.438656    -0.024111     0.016404
 C     1.217836    -0.011052    -0.709833
 C     1.296785     0.009333     3.577369
Cl    -0.296087    -0.003885     4.469786
 O     3.572333    -0.093478    -0.739643
 C     4.828787    -0.188349    -0.072449
 O     1.183082    -0.130762    -2.068593
 C     1.837095     0.870420    -2.866763
 O    -1.227584    -0.059883    -0.592356
 C    -1.512516     0.732122    -1.751779
 O     2.307017     0.023437     4.221277
 H     3.351390    -0.017534     1.976837
 H    -0.954400     0.005446     1.909267
 H    -1.059214     1.727375    -1.664538
 H    -1.163508     0.242523    -2.663322
 H    -2.600251     0.831786    -1.772846
 H     5.575507    -0.261879    -0.864509
 H     5.023728     0.703648     0.535623
 H     4.872705    -1.083917     0.559126
 H     1.558302     0.645830    -3.898283
 H     1.473271     1.869984    -2.596528
 H     2.921341     0.824196    -2.750984
```

Cartesians coordinates

1f$^{\cdot-}$

```
  26
ZPE:  -1148.604928  a.u.,  thermal  energy:  -1148.588566  a.u.(B3LYP/6-31+G*  -  scaled
factor 0.986)
-1 2
 C     0.001489    -0.001302    -0.004391
 C    -0.000499     0.000006     1.378666
 C     1.228424     0.000659     2.111306
 C     2.451170    -0.032205     1.344215
 C     2.425241    -0.047331    -0.038239
 C     1.200897     0.001522    -0.758412
 C     1.369952     0.022923     3.518601
Cl    -0.334385     0.072447     4.481270
 O     3.564795    -0.118103    -0.825787
 C     4.812307    -0.218148    -0.168546
 O     1.151230    -0.106965    -2.142704
 C     1.692771     0.991379    -2.870164
 O    -1.226335    -0.075488    -0.659786
 C    -1.663609     1.135219    -1.255118
 O     2.364222     0.019574     4.237307
 H     3.383806    -0.050869     1.893490
 H    -0.950449    -0.011528     1.898410
 H    -1.702438     1.947138    -0.513119
 H    -1.015869     1.437376    -2.088661
```

```
 H    -2.672756     0.947491    -1.637964
 H     5.564138    -0.290224    -0.960090
 H     5.016425     0.666980     0.451009
 H     4.861951    -1.113015     0.467421
 H     1.473423     0.799231    -3.926940
 H     1.220889     1.939024    -2.567038
 H     2.776347     1.070318    -2.727881
```

Cartesians coordinates

1d$^{\cdot-}$

```
 22
ZPE: -1034.134281 a.u., thermal energy: -1034.120565 a.u.(B3LYP/6-31+G** - scaled
factor 0.986)
-1 2
 C     0.001010     0.000048     0.000101
 C     0.001037     0.000021     1.414961
 C     1.264706     0.000079     2.051714
 C     2.455003     0.000158     1.349982
 C     2.448367     0.000197    -0.082596
 C     1.166598     0.000133    -0.739582
 O     1.388783     0.000059     3.439838
 C     0.216238    -0.000019     4.221220
 C     3.591238     0.000194    -0.919156
Cl     5.293326    -0.000111     0.070867
 O    -1.180914     0.000009    -0.737941
 C    -2.408070    -0.000059    -0.044671
 O     3.714965     0.000046    -2.137953
 H     1.117067     0.000154    -1.821761
 H     3.389720     0.000194     1.894333
 H    -3.189461    -0.000080    -0.809865
 H    -2.526840    -0.893752     0.585821
 H    -2.526923     0.893602     0.585852
 H    -0.917917    -0.000041     1.981037
 H     0.545789    -0.000021     5.264061
 H    -0.400223     0.893630     4.042610
 H    -0.400126    -0.893728     4.042575
```

TS$^{\cdot-}$

```
 22
ZPE: -1034.120998 a.u., thermal energy: -1034.107643 a.u.(B3LYP/6-31+G** - scaled
factor 0.986)
-1 2
 C     0.000843    -0.002129    -0.000711
 C     0.000139    -0.005177     1.406485
 C     1.219285    -0.005329     2.078273
 C     2.430160    -0.023157     1.367582
 C     2.396813    -0.032401    -0.037892
 C     1.187555    -0.002331    -0.738868
 O     1.151280     0.005489     3.457739
 C     2.357525    -0.038739     4.195714
 O     3.532631    -0.055173    -0.807200
 C     4.792710    -0.101880    -0.171041
 C    -1.304009     0.105307    -0.704495
Cl     0.111475    -0.455773    -3.953694
 O    -2.372442    -0.294678    -0.342576
 H    -0.929508    -0.007539     1.964778
 H     1.143577    -0.021736    -1.833007
 H     2.066173    -0.038662     5.248287
 H     2.932864    -0.950163     3.981477
```

```
 H     2.989031     0.838743     3.998001
 H     3.373867    -0.025414     1.894795
 H     5.531539    -0.130525    -0.974322
 H     4.971791     0.788131     0.449904
 H     4.903085    -1.001670     0.451299
```

Cartesians coordinates

1c

```
16
ZPE: -1009.609391 a.u., thermal energy: -1009.599330 a.u.(B3LYP/6-31+G** - scaled
factor 0.986)
0 1
 C    -0.000015    -0.000037     0.000103
 C    -0.000318    -0.000015     1.393320
 C     1.213166    -0.000005     2.096604
 C     2.433232    -0.000016     1.396101
 C     2.443366    -0.000037     0.005544
 C     1.222175    -0.000048    -0.668615
 C     1.303656     0.000017     3.585492
Cl    -0.277701     0.000052     4.470369
 N     1.224746    -0.000070    -2.148728
 O     0.134983    -0.000069    -2.719546
 O     2.321598     0.000040     4.212643
 O     2.316771    -0.000050    -2.715116
 H     3.363174    -0.000007     1.953017
 H     3.369552    -0.000045    -0.555342
 H    -0.923561    -0.000045    -0.564948
 H    -0.940941    -0.000006     1.929409
```

Cartesians coordinates

1c^{-}

```
 16
ZPE: -1009.697050 a.u., thermal energy: -1009.686848 a.u.(B3LYP/6-31+G** - scaled
factor 0.986)
-1 2
 C     0.000000     0.000000     0.000000 -0.021197
 C     0.000000     0.000000     1.378673 -1.305567
 C     1.218401     0.000000     2.117930  1.331601
 C     2.443364     0.000000     1.376825  0.181773
 C     2.450283     0.000000     0.000296  0.217280
 C     1.224797     0.000000    -0.717428 -0.571458
 C     1.324654     0.000000     3.547742 -0.224752
Cl    -0.350299    -0.000182     4.467794 -0.061309
 N     1.226022     0.000000    -2.121333 -0.413722
 O     0.116343    -0.000078    -2.736514 -0.150803
 O     2.304268    -0.000129     4.257203 -0.384611
 O     2.337226    -0.000078    -2.734346 -0.153255
 H     3.379690     0.000000     1.926450  0.132597
 H     3.378934     0.000000    -0.558090  0.145128
 H    -0.927845     0.000000    -0.559425  0.144696
 H    -0.942910     0.000000     1.913232  0.133410
```

Cartesians coordinates

1g$^{\cdot-}$

```
  22
ZPE: -1034.110681 a.u., thermal energy: -1034.097423 a.u.(B3LYP/6-31+G** - scaled
factor 0.986)
-1 2
 C     0.003120    -0.001554    -0.001394
 C     0.001697    -0.000659     1.453919
 C     1.340281     0.001112     2.037227
 C     2.479148     0.196475     1.276065
 C     2.414955     0.342063    -0.123969
 C     1.159599     0.192358    -0.739347
 C    -1.121371     0.069534     2.322852
Cl    -2.762905     0.802573     1.519934
 O     1.526212    -0.072863     3.410593
 C     1.414876    -1.380619     3.966844
 O    -1.148768    -0.220115    -0.744260
 C    -1.716003    -1.517863    -0.610999
 O    -1.275897    -0.230874     3.498490
 H     3.427485     0.247303     1.805086
 H     3.311546     0.512888    -0.712063
 H     1.060468     0.192094    -1.822107
 H    -2.621483    -1.523947    -1.223965
 H    -1.016708    -2.286263    -0.977411
 H    -1.990079    -1.739474     0.425945
 H     1.603208    -1.276102     5.039920
 H     0.410189    -1.788996     3.821387
 H     2.169428    -2.052204     3.527908
```

Cartesians coordinates

1d$^{\cdot-}$

```
 22
ZPE: -1034.134380 a.u., thermal energy: -1034.120710 a.u.(B3LYP/6-31++G** - scaled
factor 0.986)
-1 2
 C     0.000000     0.000000     0.000000 -0.011406
 C     0.000000     0.000000     1.414815  0.881602
 C     1.263287     0.000000     2.052311 -0.443943
 C     2.453690     0.000000     1.350438 -1.476352
 C     2.447889     0.000000    -0.082251  1.651026
 C     1.166135     0.000000    -0.739174 -0.543002
 O     1.388573     0.000000     3.440513 -0.353140
 C     0.218241     0.000000     4.223627 -0.199646
 C     3.590970     0.000040    -0.918921 -0.434526
Cl     5.293332     0.000446     0.070685 -0.188933
 O    -1.181841     0.000000    -0.738669 -0.354357
 C    -2.409060     0.000000    -0.047025 -0.191941
 O     3.714944     0.000219    -2.137735 -0.448316
 H     1.116617     0.000000    -1.822135  0.128626
 H     3.388499     0.000000     1.896128  0.105933
 H    -3.188972     0.000000    -0.814835  0.128085
 H    -2.527379    -0.894782     0.583192  0.145444
 H    -2.527386     0.894791     0.583179  0.145440
 H    -0.920165     0.000000     1.980595  0.041207
 H     0.551770     0.000000     5.266009  0.127872
 H    -0.397884     0.894807     4.045351  0.145153
 H    -0.397884    -0.894807     4.045351  0.145157
```

Cartesians Cordinates

TS^{-}

```
 22
ZPE: -1034.121231 a.u., thermal energy: -1034.107872 a.u.(B3LYP/6-31++G** - scaled
factor 0.986)
-1 2
 C     0.000000     0.000000     0.000000
 C     0.000000     0.000000     1.397515
 C     1.194553     0.000000     2.141290
 C     2.408911     0.003448     1.460914
 C     2.445046    -0.013731     0.057331
 C     1.233993    -0.025876    -0.656616
 C    -1.287172     0.103173     2.133837
 O    -1.542274    -0.297177     3.232566
 O     3.544221     0.017012     2.247397
 C     4.808156    -0.023334     1.613216
 O     1.180510    -0.048276    -2.027434
 C     2.385963    -0.096228    -2.761588
Cl    -3.297023    -0.456620    -0.781610
 H     1.177466    -0.002823     3.225519
 H    -0.952374    -0.022078    -0.540355
 H     5.547763    -0.021260     2.416850
 H     4.933199    -0.934193     1.011275
 H     4.971601     0.854777     0.972829
 H     3.391149    -0.012810    -0.465581
 H     2.093627    -0.126392    -3.813089
 H     3.008164     0.793938    -2.587549
 H     2.972746    -0.995727    -2.525568
```

Cartesians coordinates

1c

```
16
ZPE: -1009.609495 a.u., thermal energy: -1009.599434 a.u.(B3LYP/6-31++G** - scaled
factor 0.986)
0 1
 C     0.000000     0.000000     0.000000 -0.331187
 C     0.000000     0.000000     1.393531 -0.987044
 C     1.213358     0.000000     2.096947  1.201750
 C     2.433292     0.000000     1.395935  0.648189
 C     2.443220     0.000000     0.005207 -0.113316
 C     1.221992     0.000000    -0.669475 -0.582177
 C     1.303287     0.000000     3.586044 -0.123294
Cl    -0.278069     0.000000     4.471102  0.137744
 N     1.224860     0.000000    -2.149584 -0.235678
 O     0.135269    -0.000171    -2.720614 -0.019239
 O     2.320990     0.000000     4.213437 -0.270723
 O     2.317021    -0.000171    -2.715659 -0.023260
 H     3.364614     0.000000     1.951775  0.175704
 H     3.370902     0.000000    -0.554340  0.200762
 H    -0.925358     0.000000    -0.563246  0.202054
 H    -0.941499     0.000000     1.929247  0.119833
```

Cartesians coordinates

1c^{-}

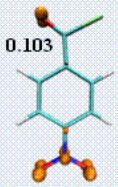
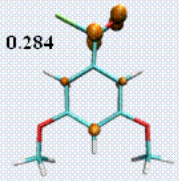
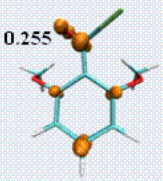
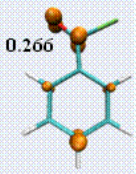
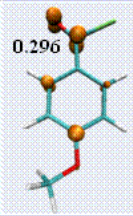
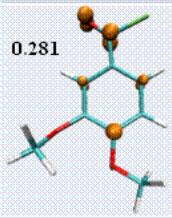
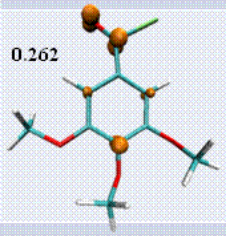
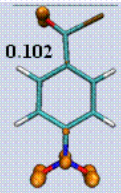
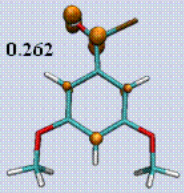
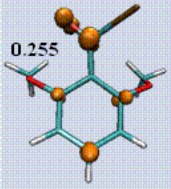
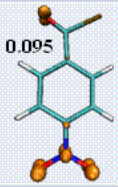
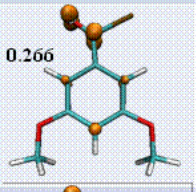
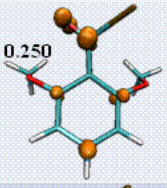
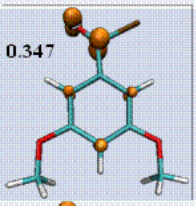
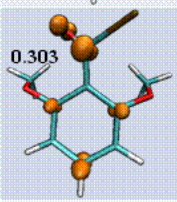
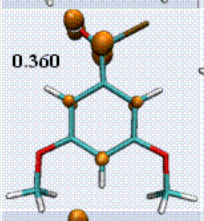
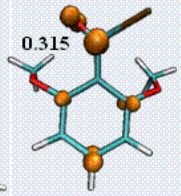
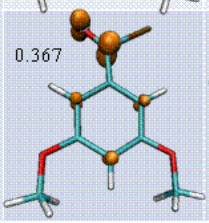
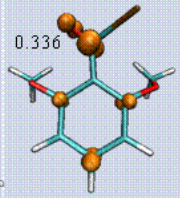
```
16
ZPE: -1009.6697134 a.u., thermal energy: -1009.686935 a.u.(B3LYP/6-31++G** - scaled
factor 0.986)
```

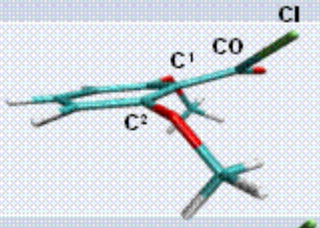
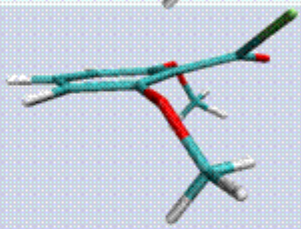
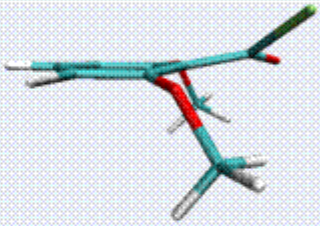
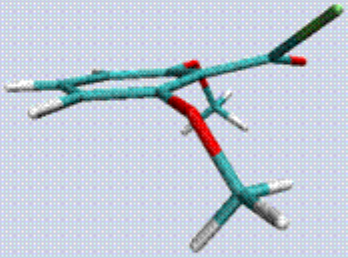
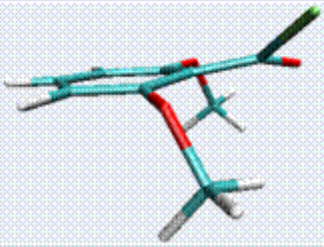
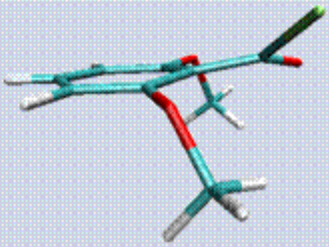
```
-1 2
 C    -0.000112    -0.000072     0.000263
 C    -0.000220     0.000002     1.378642
 C     1.218585     0.000045     2.117621
 C     2.443808    -0.000010     1.376869
 C     2.450621    -0.000084     0.000616
 C     1.224927    -0.000124    -0.716311
 C     1.324718     0.000111     3.547222
Cl    -0.350613    -0.000216     4.466814
 N     1.225820    -0.000188    -2.120470
 O     0.116129     0.000162    -2.735214
 O     2.304338    -0.000070     4.257038
 O     2.336704     0.000150    -2.733633
 H     3.378763     0.000013     1.927265
 H     3.377183    -0.000118    -0.559944
 H    -0.925752    -0.000099    -0.561472
 H    -0.941972     0.000032     1.913702
```

Cartesians coordinates

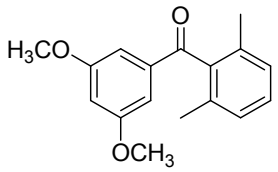
1g$^{\cdot-}$

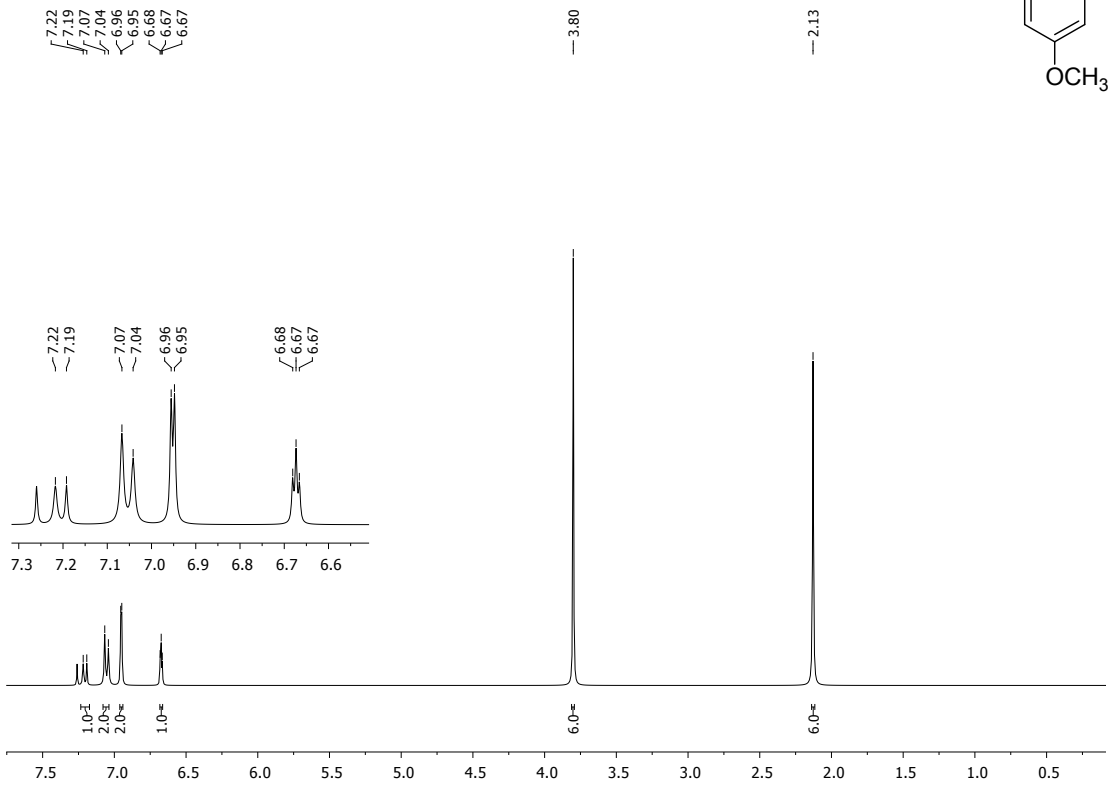
```
  22
ZPE: -1034.110971 a.u., thermal energy: -1034.097717 a.u.(B3LYP/6-31++G** - scaled
factor 0.986)
-1 2
 C     0.002920    -0.001215    -0.001243
 C     0.001559     0.000350     1.453956
 C     1.339934     0.001380     2.037390
 C     2.478937     0.196528     1.276176
 C     2.414750     0.341442    -0.123815
 C     1.159463     0.192276    -0.739311
 C    -1.121687     0.070503     2.322863
Cl    -2.763195     0.802832     1.519731
 O     1.525840    -0.072768     3.410625
 C     1.414907    -1.380812     3.966447
 O    -1.149081    -0.219806    -0.743696
 C    -1.715499    -1.517945    -0.610670
 O    -1.276177    -0.230741     3.498186
 H     3.427317     0.247204     1.805087
 H     3.311408     0.511802    -0.711940
 H     1.060357     0.192047    -1.822065
 H    -2.621058    -1.524293    -1.223507
 H    -1.015587    -2.285711    -0.977260
 H    -1.989279    -1.740205     0.426258
 H     1.603445    -1.276627     5.039534
 H     0.410267    -1.789314     3.820883
 H     2.169460    -2.052062     3.527024
```

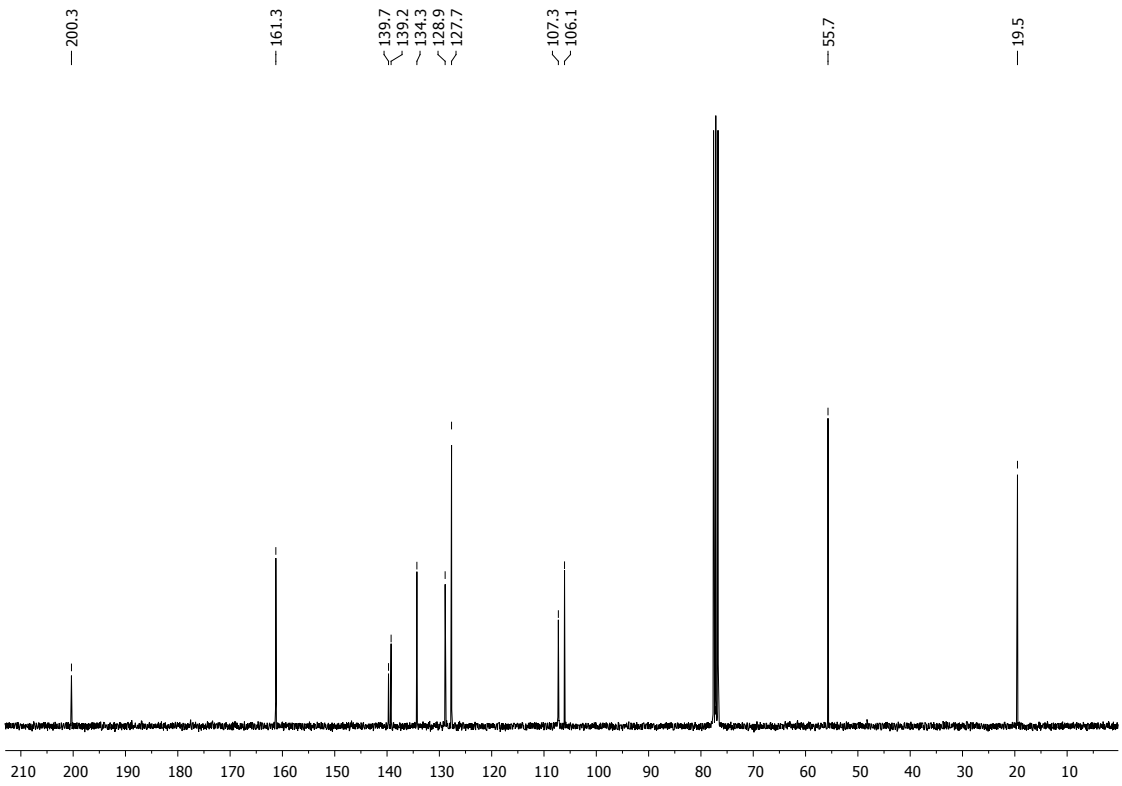
Spin density distribution (orange) and value on *C*(O)-Cl								
Phase	**Basis set**	**1c$^{\cdot-}$**	**1d$^{\cdot-}$**	**1g$^{\cdot-}$**	**1a$^{\cdot-}$**	**1b$^{\cdot-}$**	**1e$^{\cdot-}$**	**1f$^{\cdot-}$**
Gas	6-31+G*	 0.103	 0.284	 0.255	 0.266	 0.296	 0.281	 0.262
	6-31+G**	 0.102	 0.262	 0.255				
	6-31++G**	 0.095	 0.266	 0.250				
Condensed (PCM)	6-31+G* ε=4.7		 0.347	 0.303				
	6-31+G* ε=9.9		 0.360	 0.315				
	6-31+G* ε=20.7		 0.367	 0.336				

1g⁻ Geometry		
Phase	**Basis set**	**Dihedral angle Cl-C(O)-C^1-C^2**
Gas	6-31+G*	-20.5° 
	6-31+G**	-20.7° 
	6-31++G**	-20.8° 
Condensed (PCM)	6-31+G* ε=4.7	-23.2° 
	6-31+G* ε=9.9	-23.8° 
	6-31+G* ε=20.7	-24.5° 

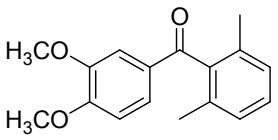
^{1}H and ^{13}C NMR of **3dd**

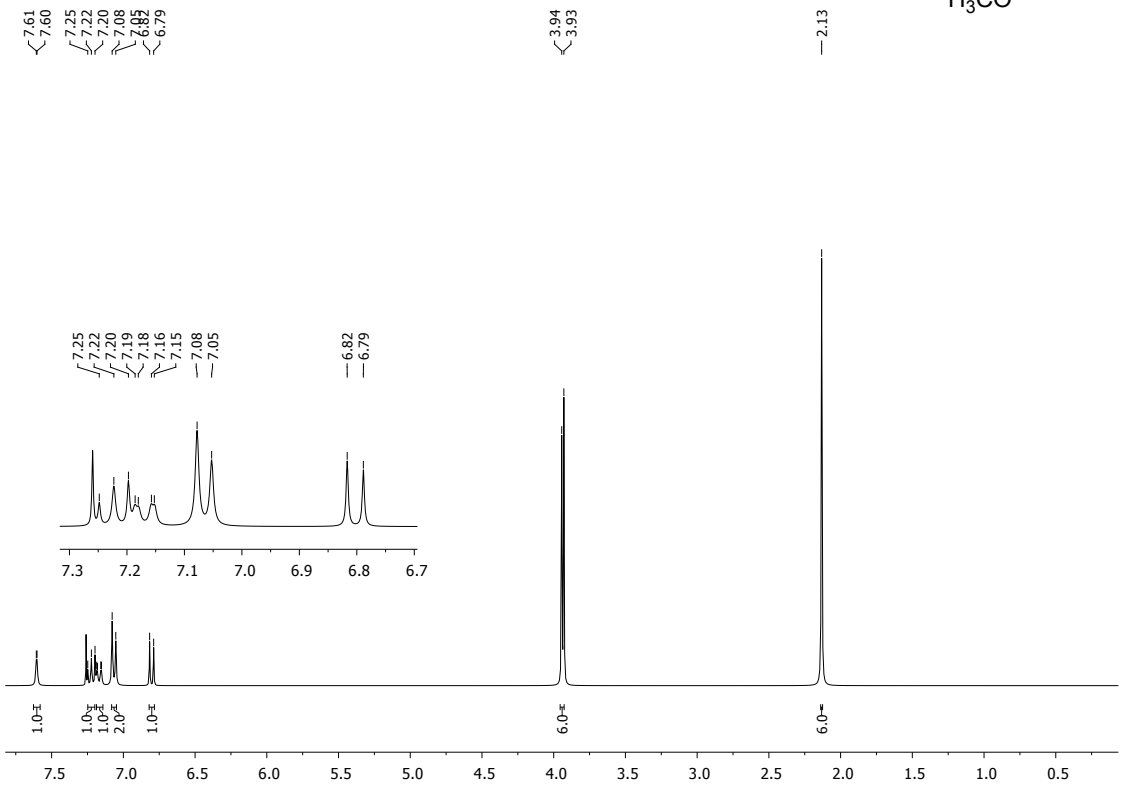


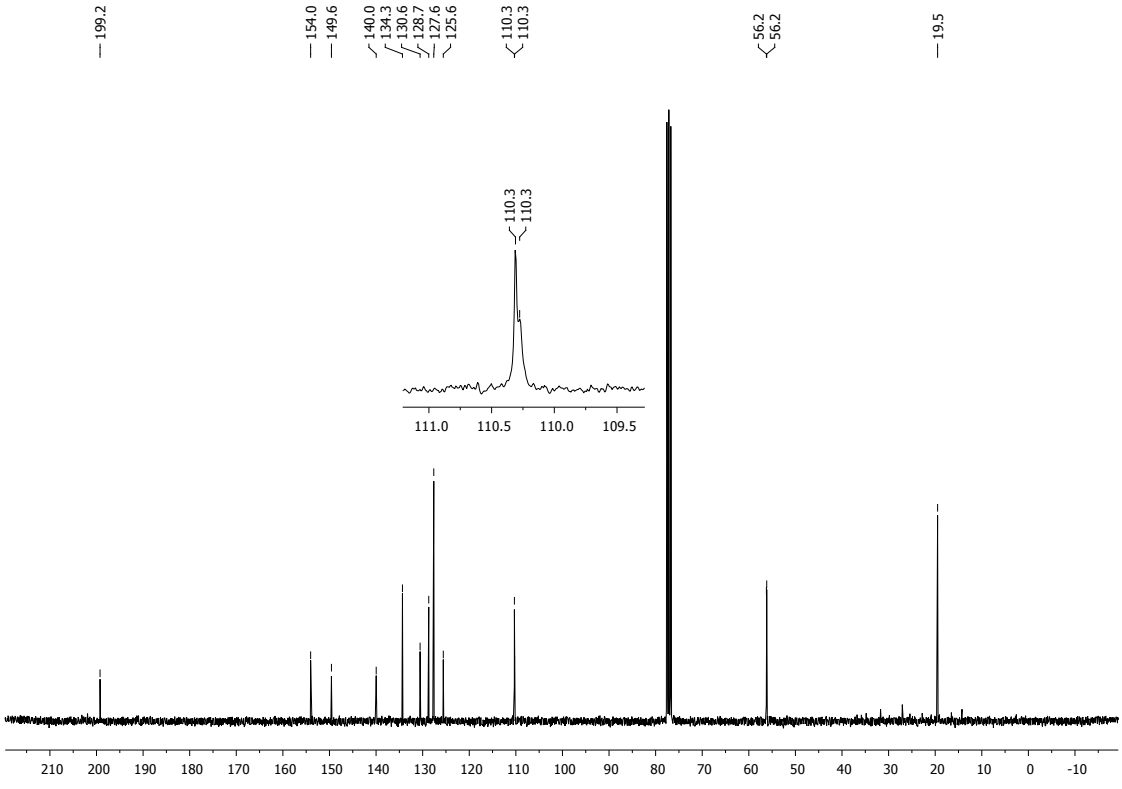




^{1}H and ^{13}C NMR of **3ed**







^{1}H and ^{13}C NMR of **3fd**