Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Search for a photoinduced (site-selective) cleavage of the Ar-Cl bond in dichloroanisoles

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Supporting Information

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1 Experimental Section

1.1 Photophysical parameters measured for 1-5

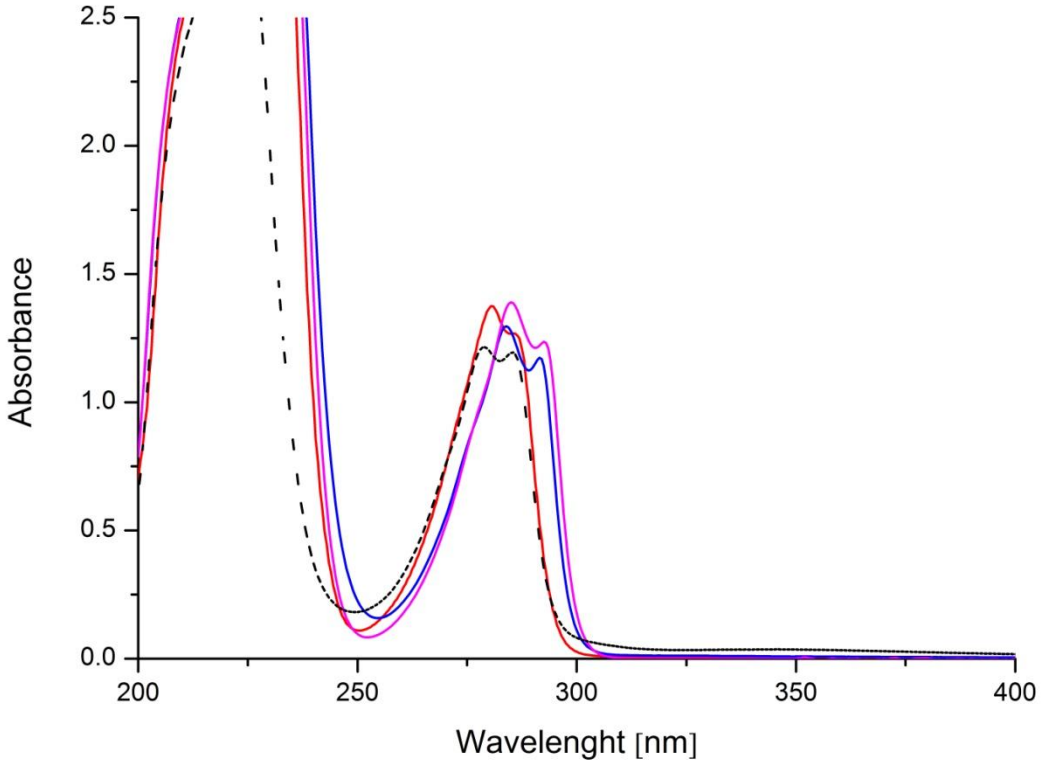
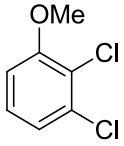
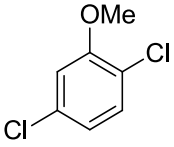
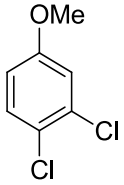
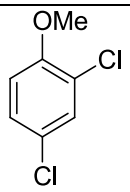
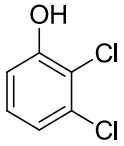


Fig. S1 UV-Vis Absorption spectra of 5×10^{-4} M solutions of: **1** (black line), **2** (red line) and **3** (blue line), **4** (magenta line), **5** (black dashed line) in MeOH.

Table S1 Photophysical parameters measured for compounds **1-5** in MeOH[a]

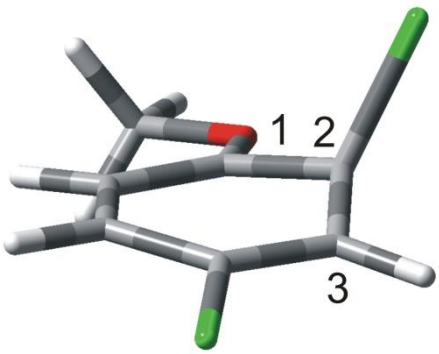
Compound	**λ_{MAX} [nm], ε (M^{-1} cm^{-1})**	**λ_{EM} [nm], Φ_F ($\cdot 10^3$)** [a]
 **1**	284, 2557 277, 2557 225, 5859	/
 **2**	287, 2493 281, 2747 227, 5973	/
 **3**	292, 2337 284, 2593 228, 6160	/
 **4**	293, 2464 285, 2780 229, 6069	317 (0.8) 322 (15)[b]
 **5**	286, 2372 280, 2404 223, 5602	/

[a] Calculated by using 4-chloroanisole as reference, see ref S1; [b] Fluorescence quantum yield (Φ_F) measured in cyclohexane.

2. Computational Details

All the calculations were carried out using the Gaussian 09 program package.[S2] In our investigation, the level of theory chosen for the optimization of all of the stationary points was DFT (Density Functional Theory) adopting the M06-2X functional and the standard def2TZVP basis set. An unrestricted approach was adopted when triplet states were considered. Frequency calculations were performed in vacuo at the same level of theory to check that minima had no imaginary frequencies. Solvation was carried out by using SMD model with the RADII=UAHF option.[S3]

The equilibrium geometries of ^{3}**1**-^{3}**5** were optimized in solvent (MeOH and C_6H_{12} bulk) at M06-2X/ def2TZVP level of theory. To analyzed the detachment of chlorine atom the C-Cl bond was stretched up to 3.00 Å. These geometries were optimized in solvent (MeOH and C_6H_{12} bulk) at M06-2X/ def2TZVP level of theory constraining via OPT=MODREDUNDANT keyword the C-Cl at 3.00 Å. Moreover the angles among C_1-C_2-Cl and C_3-C_2-Cl (see the figure below as an example) were fixed in order to maintain the same trajectory when removing the halogen atom. The energies labeled "$E_{STRETCH}$" refer to calculations upon stretching the C-Cl atom bond up to 3.00 Å.



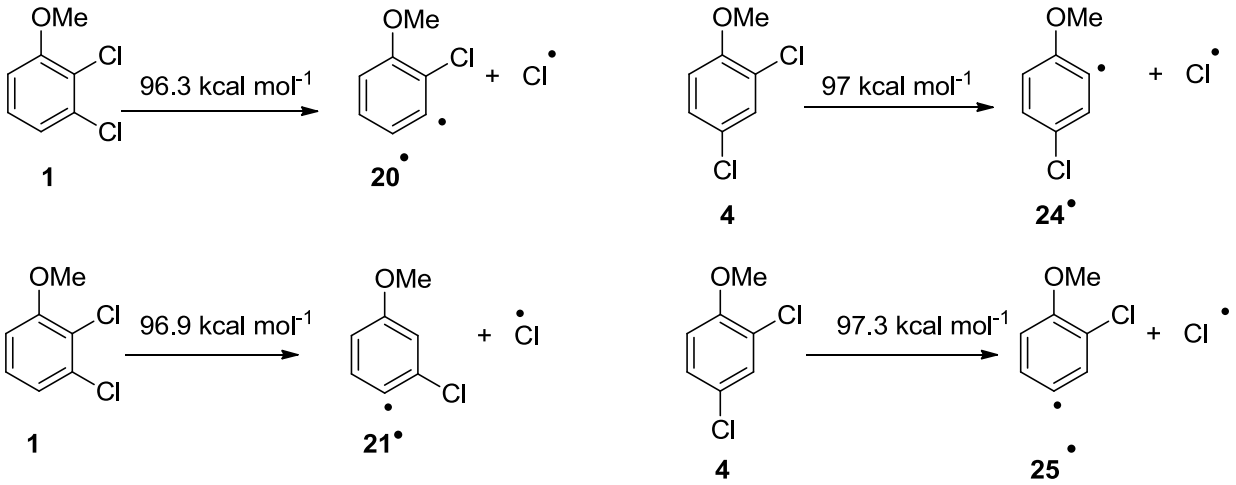
Several conformations, differing for the orientation of the substituents attached to the aromatic ring were analyzed, when required. Nevertheless, for the sake of simplicity, only the most stable structures for each electronic state have been reported in the following.

Optimized geometry listed in cartesian format (coordinates are given in Å), minimum energies and thermochemical data (in Hartree; the default options were adopted in the latter case, *viz.* temperature: 298.150 K and pressure: 1.00000 atm) for ^{1}**14**$^{+}$-^{1}**17**$^{+}$, ^{1}**19**$^{+}$,^{3}**14**$^{+}$-^{3}**17**$^{+}$, ^{3}**19**$^{+}$, ^{1}**Ph**$^{+}$, ^{3}**Ph**$^{+}$,

20$^{\bullet}$**, 21**$^{\bullet}$, **23**$^{\bullet}$, **24**$^{\bullet}$, **25**$^{\bullet}$, **26**$^{\bullet}$, the triplet state of **1-6**, **7**, **9**, the singlet state of **1**, **4**, **6**, **8**, **9**, **PhH** are reported below.

The conversion of energy values between Hartree and kcal mol^{-1} has been carried out according to the following relationship: 1 Hartree = 627.5095 kcal mol^{-1}.

2.1 Calculated Bond Dissociation Energies (BDEs)



Bond dissociation energies (BDEs) have been evaluated according to eq. S1

$$E_{BDE} = \Delta H_f^{298}{}_{\mathbf{20}^{\bullet}, \mathbf{21}^{\bullet}, \mathbf{24}^{\bullet}, \mathbf{25}^{\bullet}} - \Delta H_f^{298}{}_{\mathbf{1, 4}} - \Delta H_f^{298}{}_{\mathbf{Cl}^{\bullet}} \quad \text{(S1)}$$

ΔH^{298} have been determined according to eq. S2.

$$\Delta H^{298} = E_0(\text{M06-2X,vacuo}) + \Delta H_{CORR}(\text{M06-2X,vacuo}) \quad \text{(S2)}$$

where: - E_0(M06-2X,vacuo) is the total electronic energy calculated at the M06-2X/def2TZVP ;

- ΔH_{CORR}(M06-2X,vacuo) is the thermal correction to enthalpy as from the output of the frequency calculation at the M06-2X/def2TZVP level (in vacuo).

2.2 Figures of triplet states, cations, radicals

a) b)

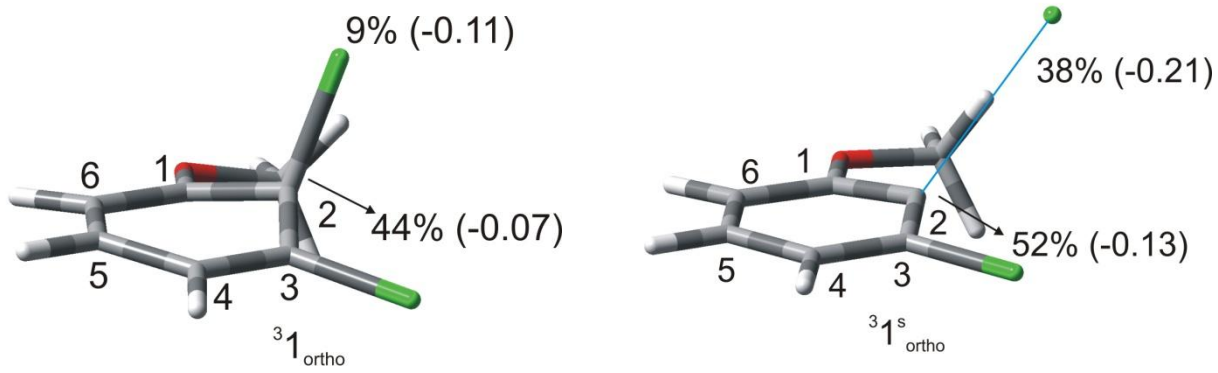


Fig. S2. Geometries, spin densities and ESP charge (in parentheses) calculated in C_6H_{12} at the SMD- M06-2X/def2TZVP level for (a) $^{3}\mathbf{1}_{\mathbf{ortho}}$ (Ar-Cl_{ortho} bond length: 1.80 Å); (b) $^{3}\mathbf{1}^{\mathbf{s}}_{\mathbf{ortho}}$ upon stretching the Ar-Cl_{ortho} up to 3 Å.

a) b)

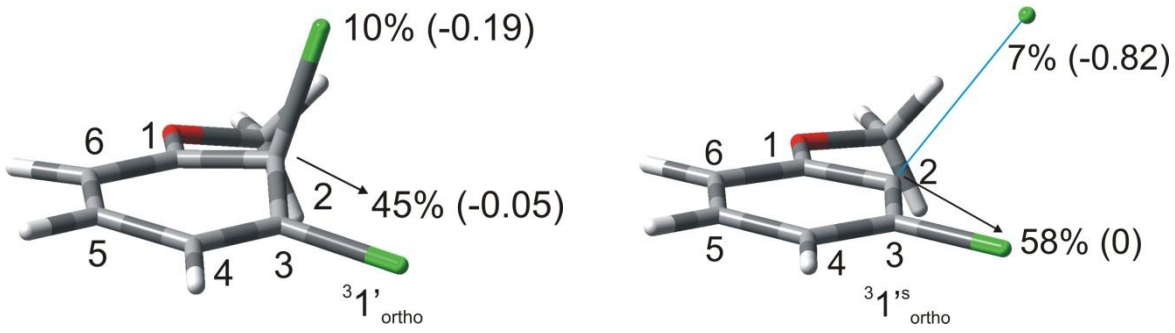


Fig. S3. Geometries, spin densities and ESP charge (in parentheses) calculated in MeOH at the SMD- M06-2X/def2TZVP level for (a) $^{3}\mathbf{1'}_{\mathbf{ortho}}$ (Ar-Cl_{ortho} bond length: 1.85 Å); (b) $^{3}\mathbf{1'}^{\mathbf{s}}_{\mathbf{ortho}}$ upon stretching the Ar-Cl_{ortho} up to 3 Å.

a) b)

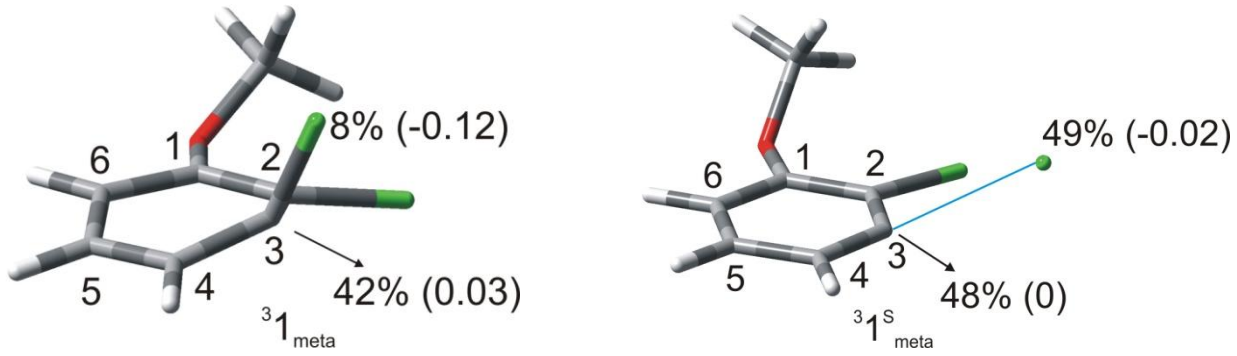


Fig. S4. Geometries, spin densities and ESP charge (in parentheses) calculated in C_6H_{12} at the SMD- M06-2X/def2TZVP level for (a) ^{3}**1**$_{meta}$ (Ar-Cl$_{meta}$ bond length: 1.77 Å); (b) ^{3}**1**$^s_{meta}$ upon stretching the Ar-Cl$_{meta}$ up to 3 Å.

a) b)

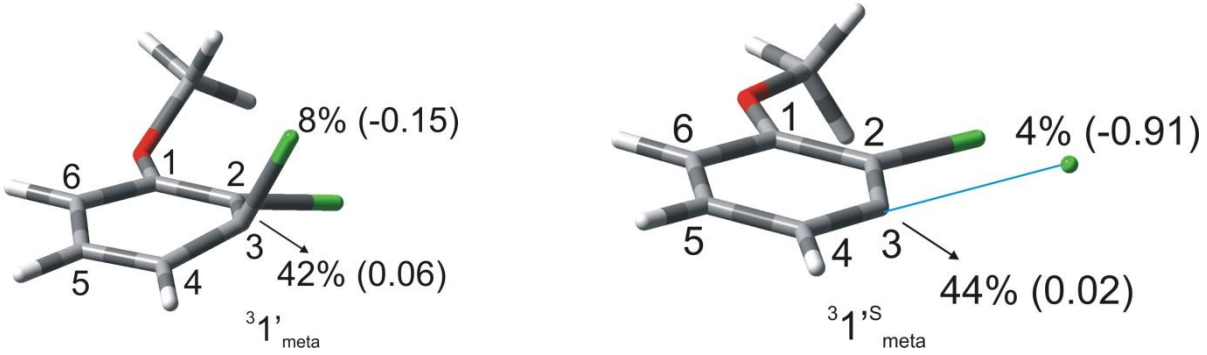


Fig. S5. Geometries, spin densities and ESP charge (in parentheses) calculated in MeOH at the SMD- M06-2X/def2TZVP level for (a) ^{3}**1'**$_{meta}$ (Ar-Cl$_{meta}$ bond length: 1.78 Å); (b) ^{3}**1'**$^s_{meta}$ upon stretching the Ar-Cl$_{meta}$ up to 3 Å.

a) b)

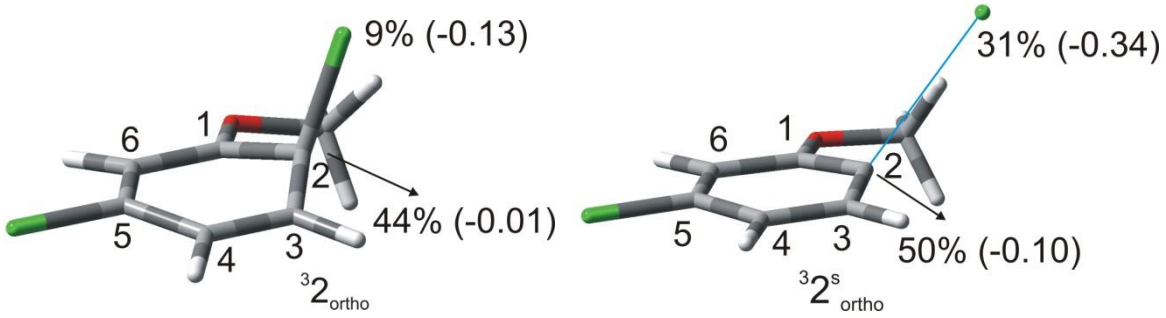


Fig. S6. Geometries, spin densities and ESP charge (in parentheses) calculated in C_6H_{12} at the SMD- M06-2X/def2TZVP level for (a) ^{3}**2$_{ortho}$** (Ar-Cl$_{ortho}$ bond length: 1.81 Å); (b) ^{3}**2$^{s}_{ortho}$** upon stretching the Ar-Cl$_{ortho}$ up to 3 Å.

a) b)

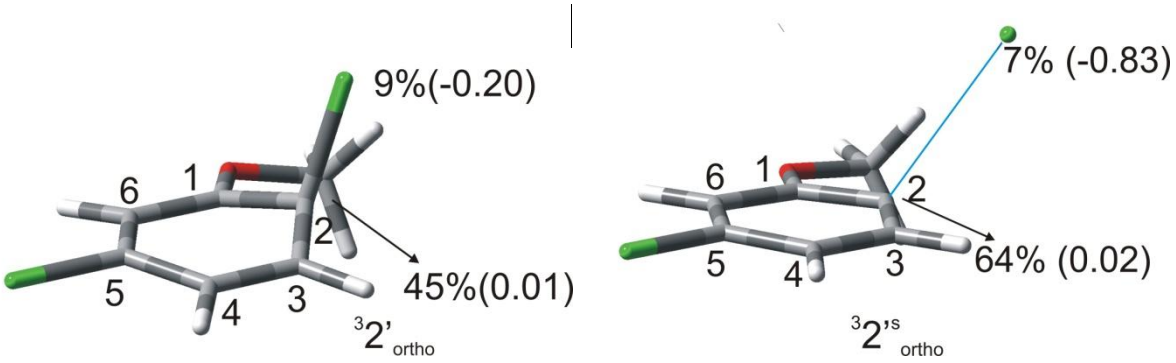


Fig. S7. Geometries, spin densities and ESP charge (in parentheses) calculated in MeOH at the SMD- M06-2X/def2TZVP level for (a) ^{3}**2'$_{ortho}$** (Ar-Cl$_{ortho}$ bond length: 1.84 Å); (b) ^{3}**2'$^{s}_{ortho}$** upon stretching the Ar-Cl$_{ortho}$ up to 3 Å.

a) b)

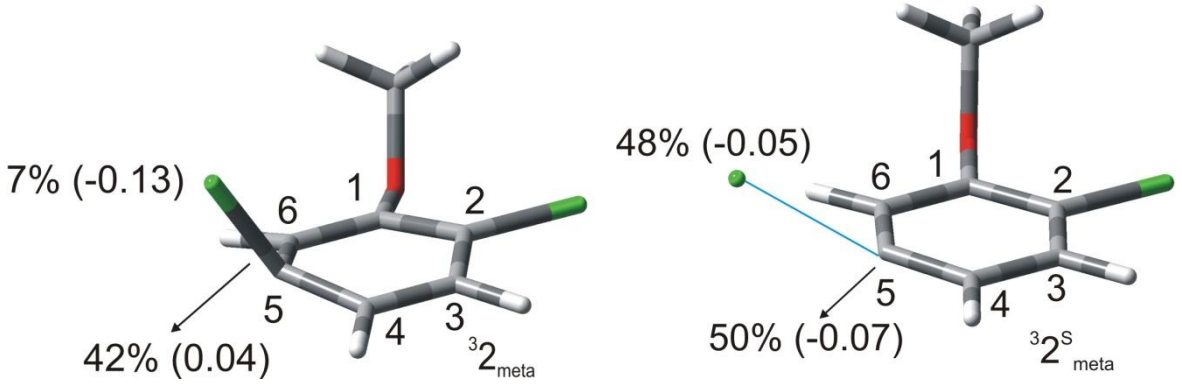


Fig. S8. Geometries, spin densities and ESP charge (in parentheses) calculated in C_6H_{12} at the SMD- M06-2X/def2TZVP level for (a) ^{3}**2$_{meta}$** (Ar-Cl$_{meta}$ bond length: 1.77 Å); (b) ^{3}**2$^s_{meta}$** upon stretching the Ar-Cl$_{meta}$ up to 3 Å.

a) b)

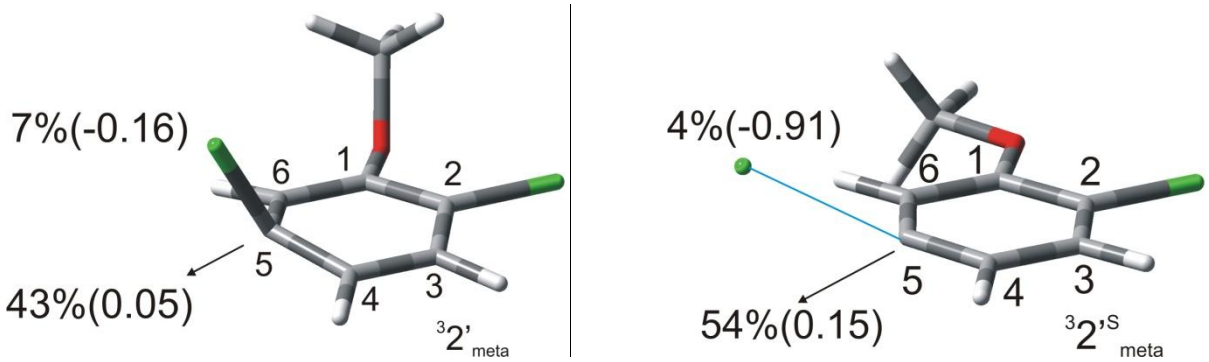


Fig. S9. Geometries, spin densities and ESP charge (in parentheses) calculated in MeOH at the SMD- M06-2X/def2TZVP level for (a) ^{3}**2'$_{meta}$** (Ar-Cl$_{meta}$ bond length: 1.77 Å); (b) ^{3}**2'$^s_{meta}$** upon stretching the Ar-Cl$_{meta}$ up to 3 Å.

a) b)

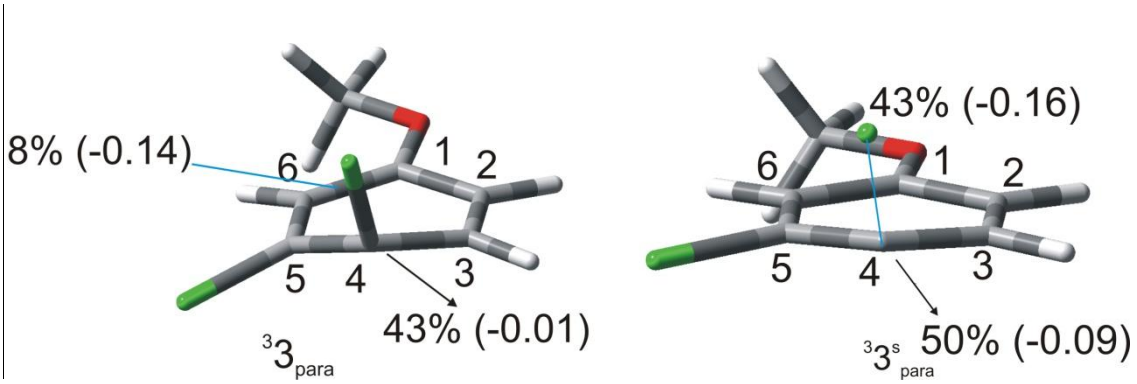


Fig. S10. Geometries, spin densities and ESP charge (in parentheses) calculated in C_6H_{12} at the SMD- M06-2X/def2TZVP level for (a) $^{3}\mathbf{3}_{\mathbf{para}}$ (Ar-Cl_{para} bond length: 1.79 Å); (b) $^{3}\mathbf{3}^{\mathbf{S}}_{\mathbf{para}}$ upon stretching the Ar-Cl_{para} up to 3 Å.

a) b)

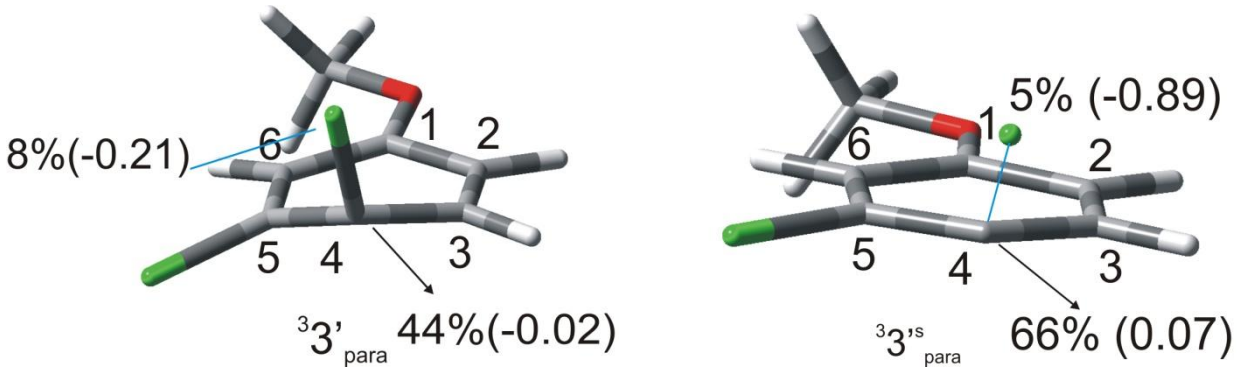


Fig. S11. Geometries, spin densities and ESP charge (in parentheses) calculated in MeOH at the SMD- M06-2X/def2TZVP level for (a) $^{3}\mathbf{3'}_{\mathbf{para}}$ (Ar-Cl_{para} bond length: 1.83 Å); (b) $^{3}\mathbf{3'}^{\mathbf{S}}_{\mathbf{para}}$ upon stretching the Ar-Cl_{para} up to 3 Å.

a) b)

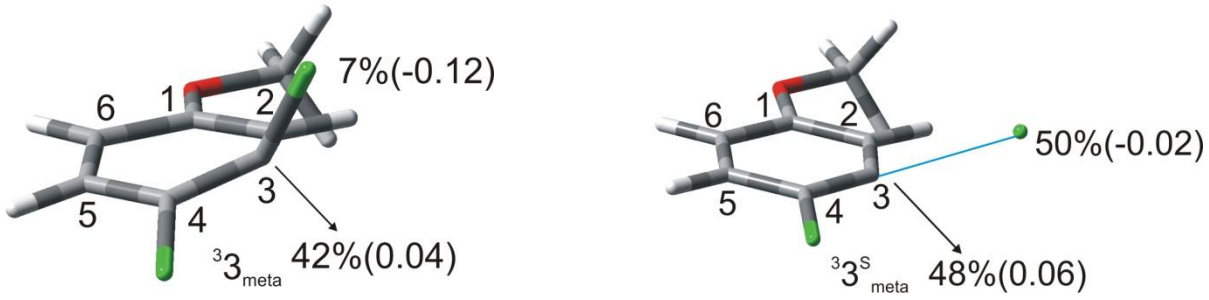


Fig. S12. Geometries, spin densities and ESP charge (in parentheses) calculated in C_6H_{12} at the SMD- M06-2X/def2TZVP level for (a) ^{3}**3$_{meta}$** (Ar-Cl$_{meta}$ bond length: 1.77 Å); (b) ^{3}**3$^S_{meta}$** upon stretching the Ar-Cl$_{meta}$ up to 3 Å.

a) b)

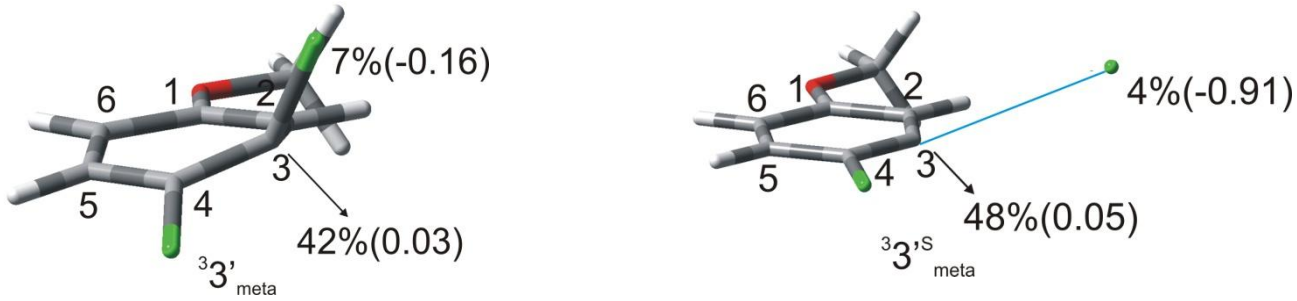


Fig. S13. Geometries, spin densities and ESP charge (in parentheses) calculated in MeOH at the SMD- M06-2X/def2TZVP level for (a) ^{3}**3'$_{meta}$** (Ar-Cl$_{meta}$ bond length: 1.79 Å); (b) ^{3}**3'$^S_{meta}$** upon stretching the Ar-Cl$_{meta}$ up to 3 Å.

a) b)

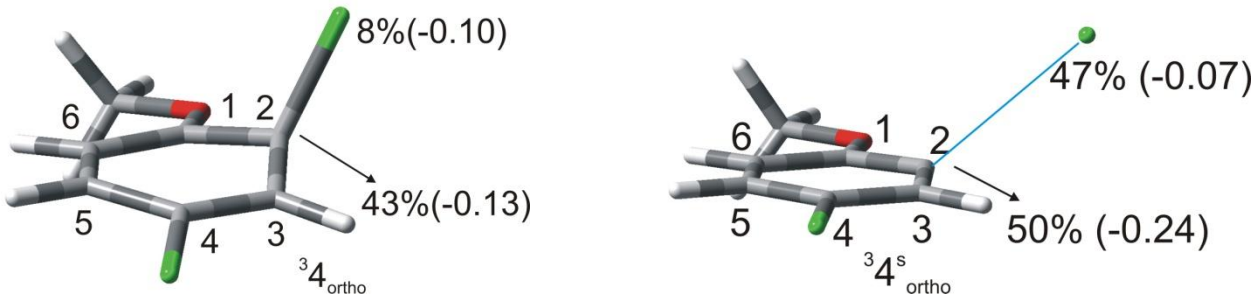


Fig. S14. Geometries, spin densities and ESP charge (in parentheses) calculated in C_6H_{12} at the SMD- M06-2X/def2TZVP level for (a) **^{3}4$_{ortho}$** (Ar-Cl_{ortho} bond length: 1.77 Å); (b) **^{3}4$^S_{ortho}$** upon stretching the Ar-Cl_{ortho} up to 3 Å.

a) b)

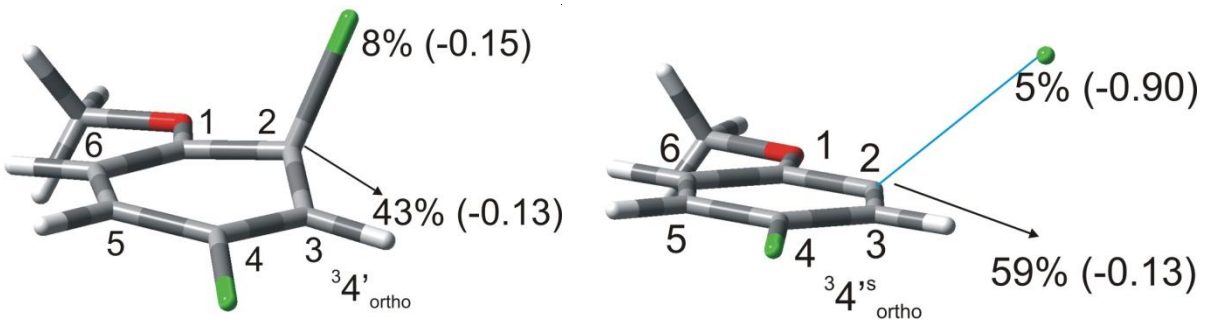


Fig. S15. Geometries, spin densities and ESP charge (in parentheses) calculated in MeOH at the SMD- M06-2X/def2TZVP level for (a) **^{3}4'$_{ortho}$** (Ar-Cl_{ortho} bond length: 1.79 Å); (b) **^{3}4'$^S_{ortho}$** upon stretching the Ar-Cl_{ortho} up to 3 Å.

a) b)

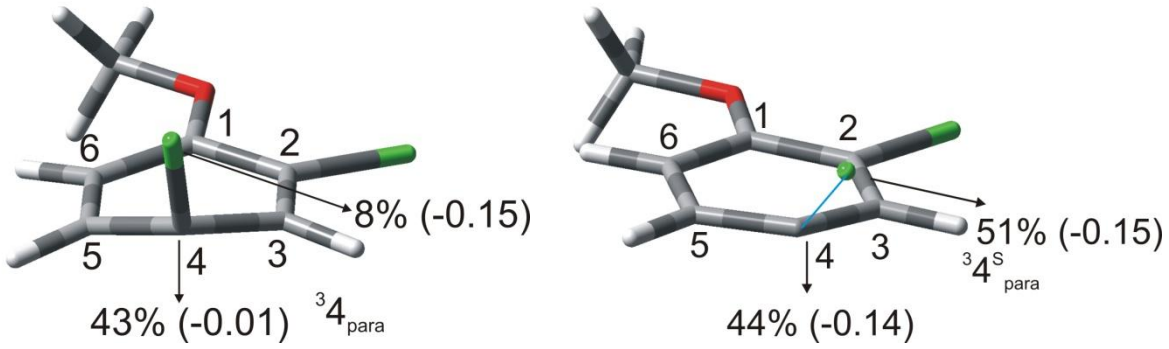


Fig. S16. Geometries, spin densities and ESP charge (in parentheses) calculated in C_6H_{12} at the SMD- M06-2X/def2TZVP level for (a) **^{3}4$_{para}$** (Ar-Cl_{para} bond length: 1.85 Å); (b) **^{3}4$^S_{para}$** upon stretching the Ar-Cl_{para} up to 3 Å.

a) b)

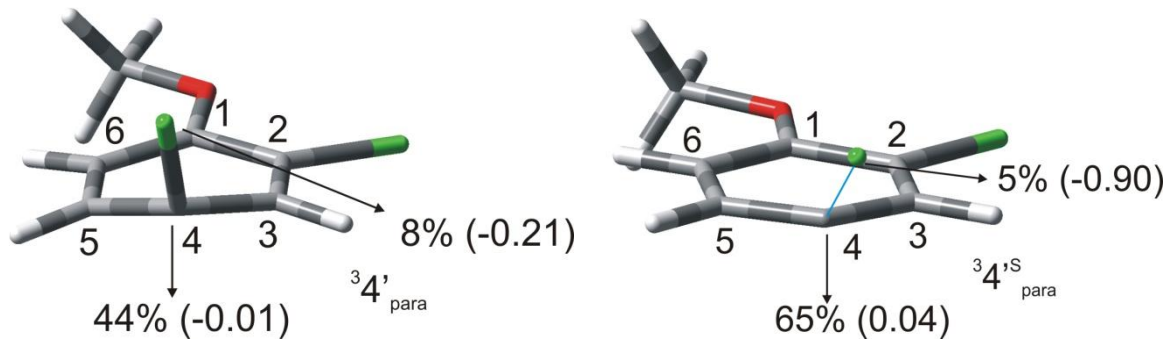


Fig. S17 . Geometries, spin densities and ESP charge (in parentheses) calculated in MeOH at the SMD- M06-2X/def2TZVP level for (a) **^{3}4'$_{para}$** (Ar-Cl_{para} bond length: 1.85 Å); (b) **^{3}4'$^S_{para}$** upon stretching the Ar-Cl_{para} up to 3 Å.

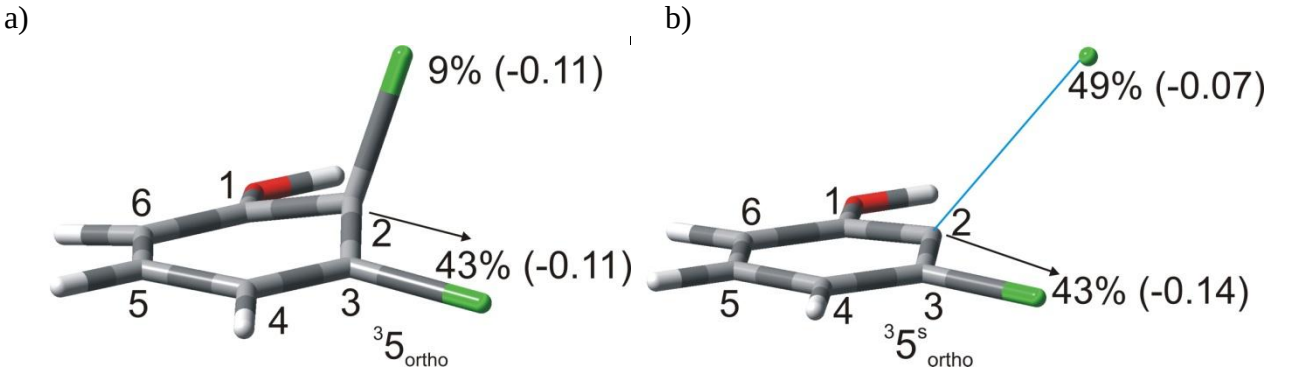


Fig. S18. Geometries, spin densities and ESP charge (in parentheses) calculated in C_6H_{12} at the SMD- M06-2X/def2TZVP level for (a) $^{3}\mathbf{5}_{\mathbf{ortho}}$ (Ar-Cl_{ortho} bond length: 1.79 Å); (b) $^{3}\mathbf{5}^{\mathbf{S}}_{\mathbf{ortho}}$ upon stretching the Ar-Cl_{ortho} up to 3 Å.

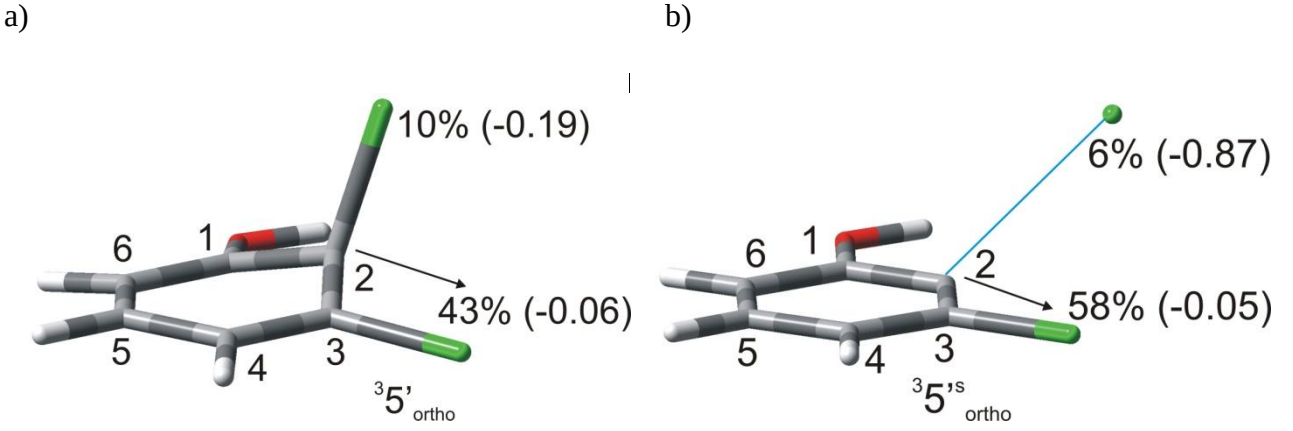


Fig. S19. Geometries, spin densities and ESP charge (in parentheses) calculated in MeOH at the SMD- M06-2X/def2TZVP level for (a) $^{3}\mathbf{5'}_{\mathbf{ortho}}$ (Ar-Cl_{ortho} bond length: 1.84 Å); (b) $^{3}\mathbf{5'}^{\mathbf{S}}_{\mathbf{ortho}}$ upon stretching the Ar-Cl_{ortho} up to 3 Å.

a) b)

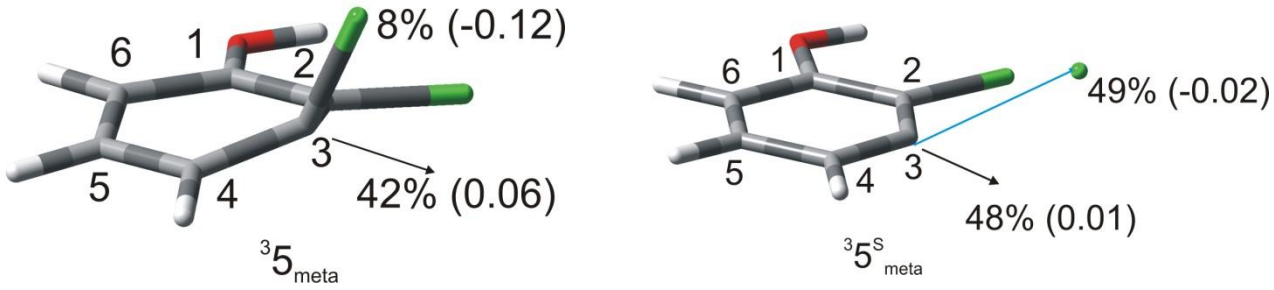


Fig. S20. Geometries, spin densities and ESP charge (in parentheses) calculated in C_6H_{12} at the SMD- M06-2X/def2TZVP level for (a) ^{3}**5$_{meta}$** (Ar-Cl$_{meta}$ bond length: 1.77 Å); (b) ^{3}**5$^S_{meta}$** upon stretching the Ar-Cl$_{meta}$ up to 3 Å.

a) b)

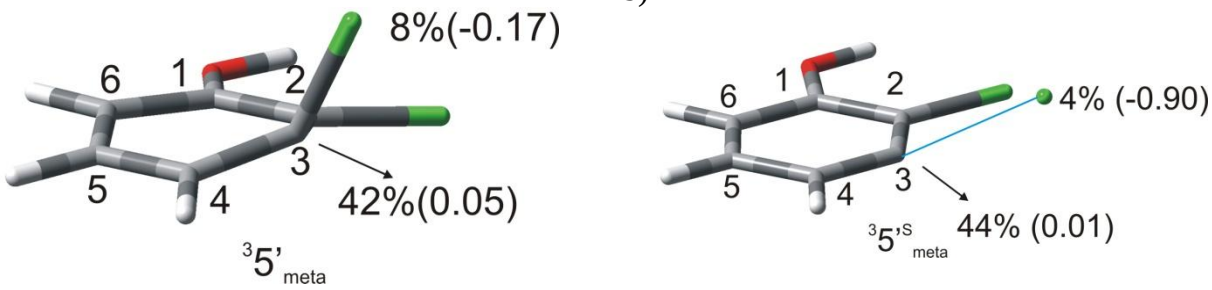


Fig. S21. Geometries, spin densities and ESP charge (in parentheses) calculated in MeOH at the SMD- M06-2X/def2TZVP level for (a) ^{3}**5'$_{meta}$** (Ar-Cl$_{meta}$ bond length: 1.79 Å); (b) ^{3}**5'$^S_{meta}$** upon stretching the Ar-Cl$_{meta}$ up to 3 Å.

a) b)

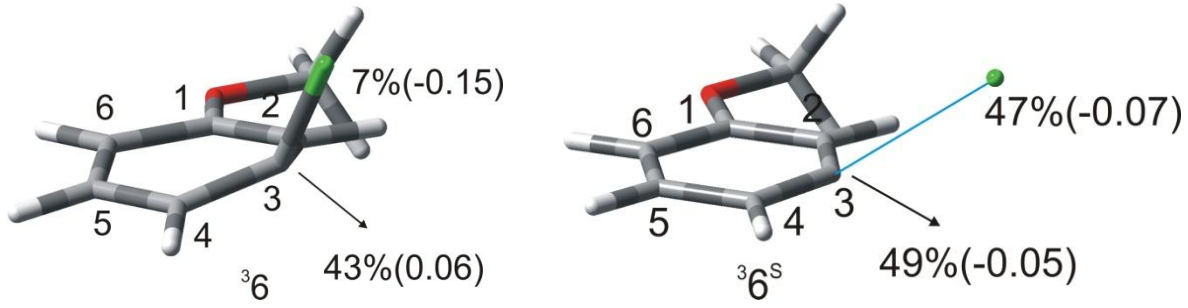


Fig. S22. Geometries, spin densities and ESP charge (in parentheses) calculated in C_6H_{12} at the SMD- M06-2X/def2TZVP level for (a) ^{3}**6** (Ar-Cl bond length: 1.78 Å); (b) ^{3}**6**^{S} upon stretching the Ar-Cl up to 3 Å.

a) b)

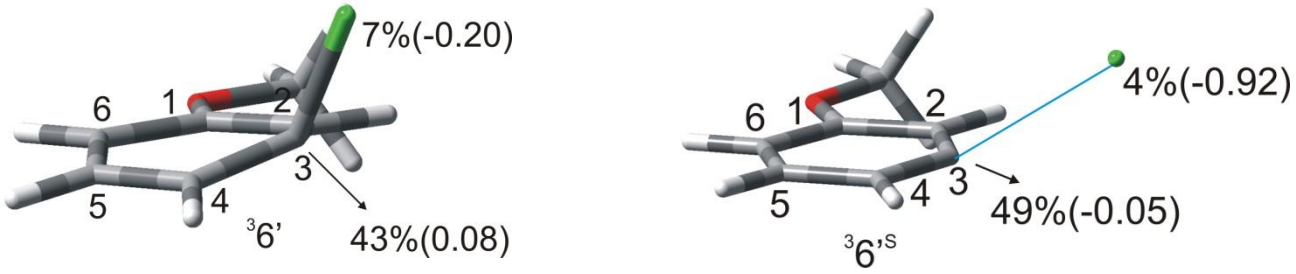


Fig. S23. Geometries, spin densities and ESP charge (in parentheses) calculated in MeOH at the SMD- M06-2X/def2TZVP level for (a) ^{3}**6'** (Ar-Cl bond length: 1.81 Å); (b) ^{3}**6'**^{S} upon stretching the Ar-Cl up to 3 Å.

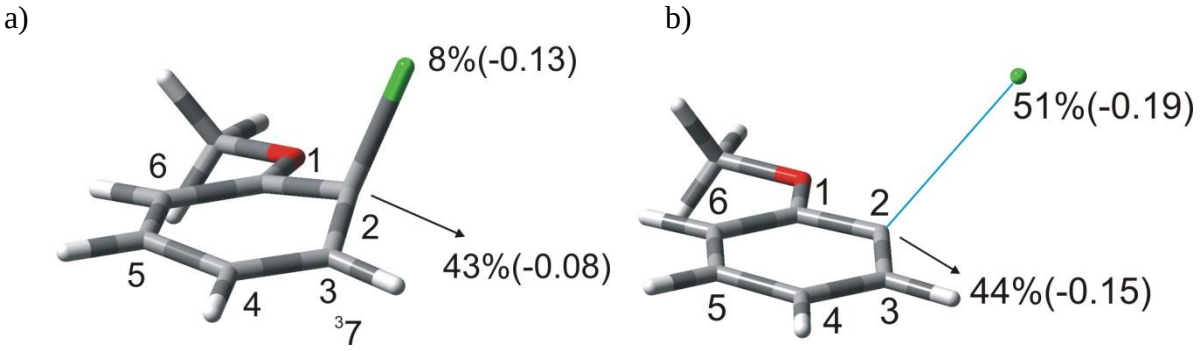


Fig. S24. Geometries, spin densities and ESP charge (in parentheses) calculated in C_6H_{12} at the SMD- M06-2X/def2TZVP level for (a) ^{3}**7** (Ar-Cl bond length: 1.78 Å); (b) ^{3}**7**^{S} upon stretching the Ar-Cl up to 3 Å.

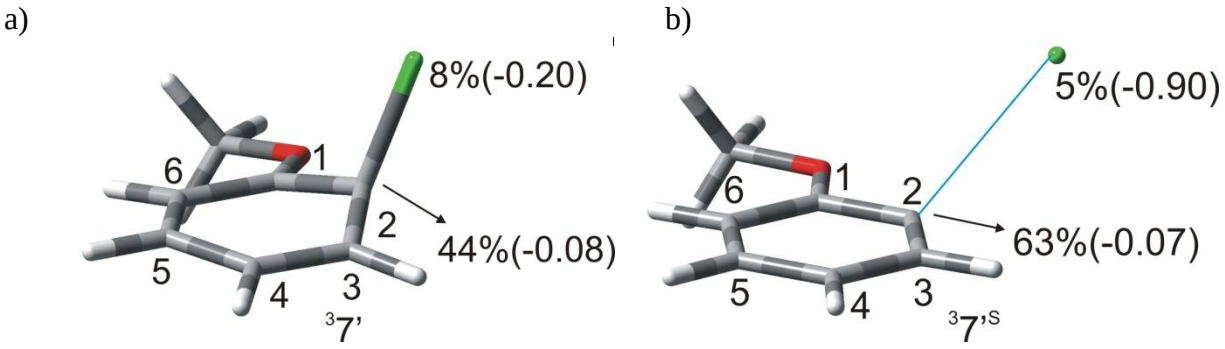


Fig. S25. Geometries, spin densities and ESP charge (in parentheses) calculated in MeOH at the SMD- M06-2X/def2TZVP level for (a) ^{3}**7'** (Ar-Cl bond length: 1.82 Å); (b) ^{3}**7'**^{S} upon stretching the Ar-Cl up to 3 Å.

a) b)

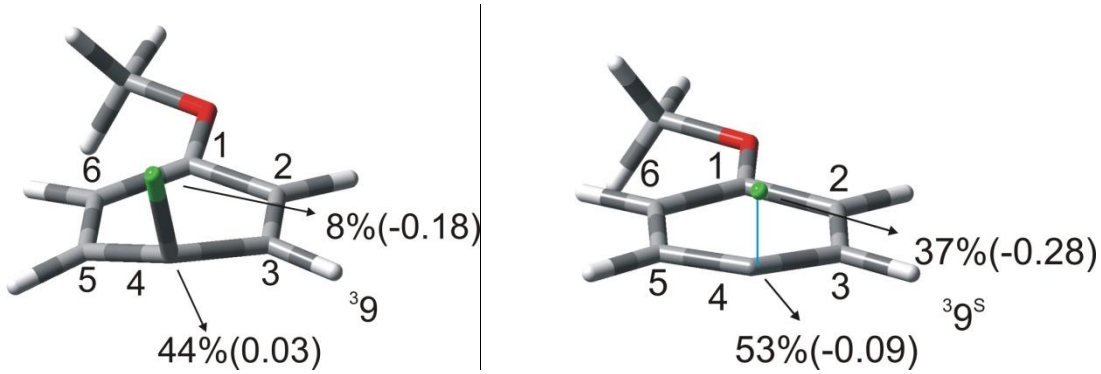


Fig. S26. Geometries, spin densities and ESP charge (in parentheses) calculated in C_6H_{12} at the SMD- M06-2X/def2TZVP level for (a) ^{3}**9** (Ar-Cl bond length: 1.80 Å); (b) ^{3}**9**^{S} upon stretching the Ar-Cl up to 3 Å.

a) b)

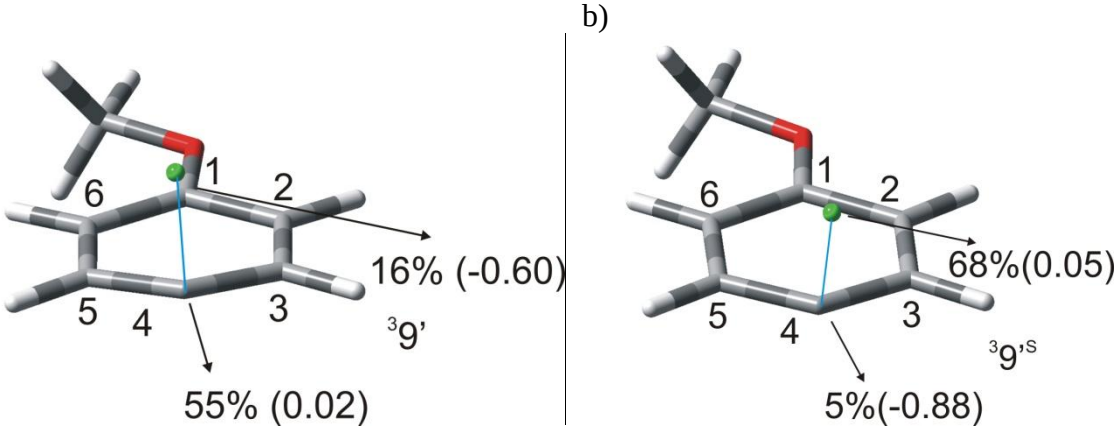


Fig. S27. Geometries, spin densities and ESP charge (in parentheses) calculated in MeOH at the SMD- M06-2X/def2TZVP level for (a) ^{3}**9'** (Ar-Cl bond length: 2.37 Å); (b) ^{3}**9'**^{S} upon stretching the Ar-Cl up to 3 Å.

a) b)

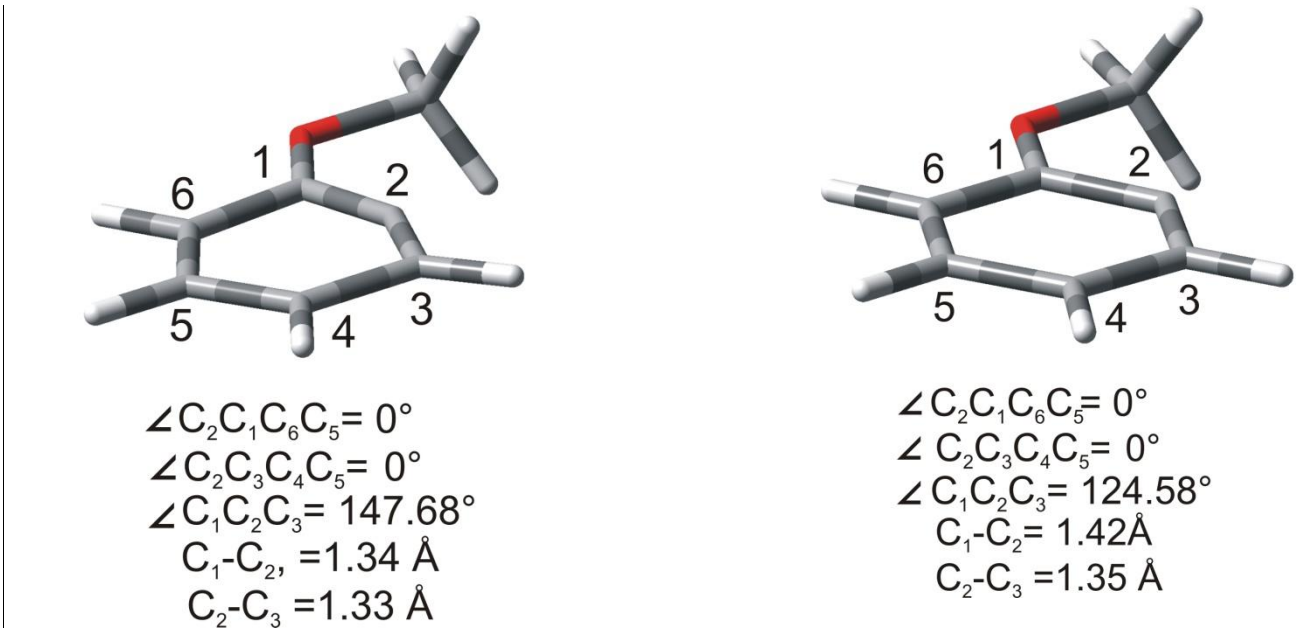


Fig. S28. Bond lengths (Å), angles (∠, in degrees) for ^{1}**19**$^{+}$ (a) and ^{3}**19**$^{+}$ (b).

a) b)

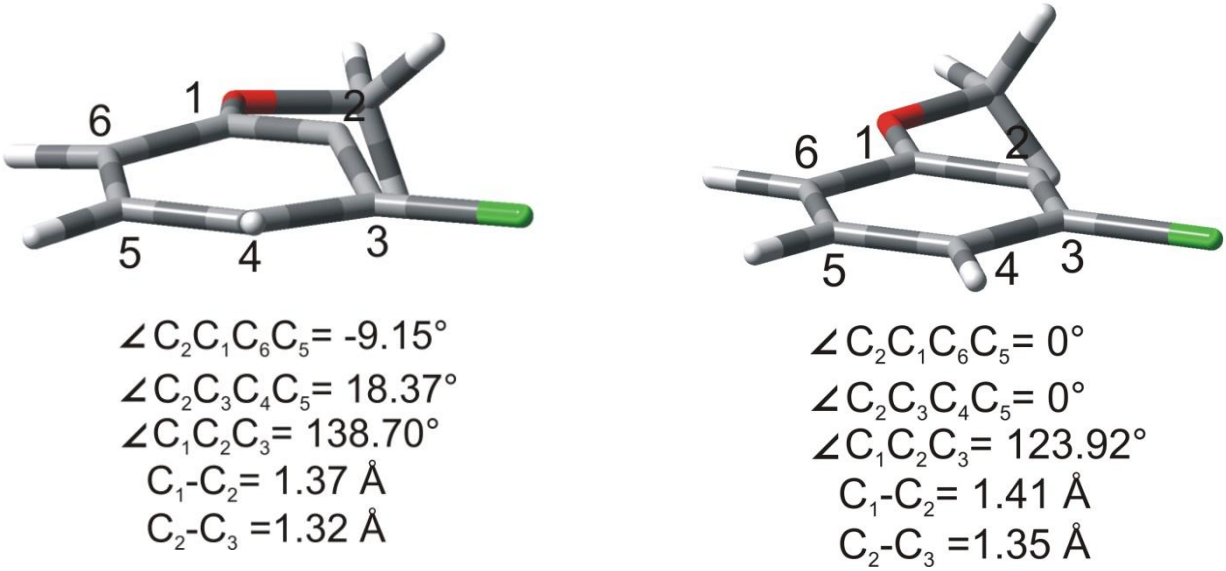


Fig. S29. Bond lengths (Å), angles (∠, in degrees) for ^{1}**14**$^{+}$ (a) and ^{3}**14**$^{+}$ (b).

a) b)

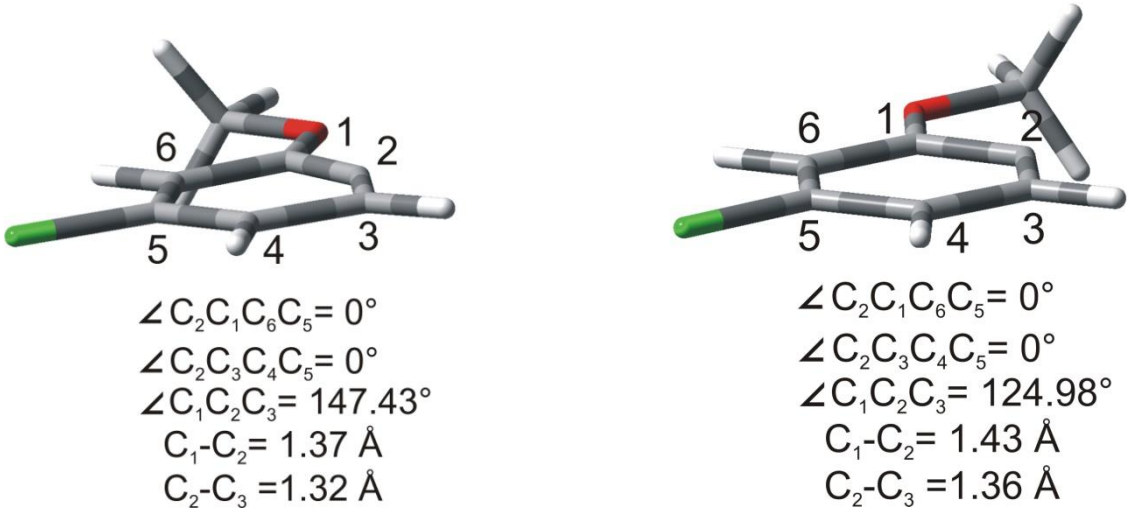


Fig. S30. Bond lengths (Å), angles (∠, in degrees) for ^{1}**15**$^{+}$ (a) and ^{3}**15**$^{+}$ (b).

a) b)

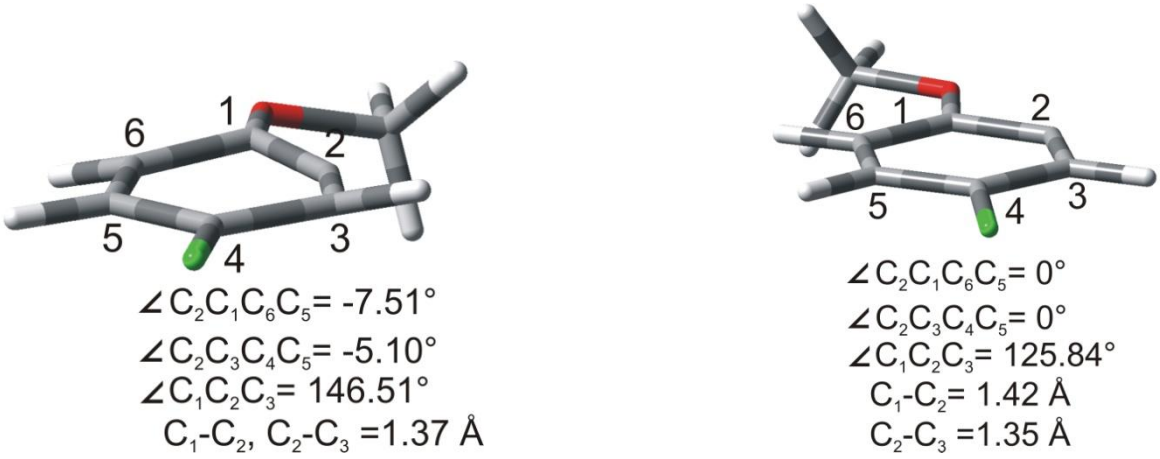
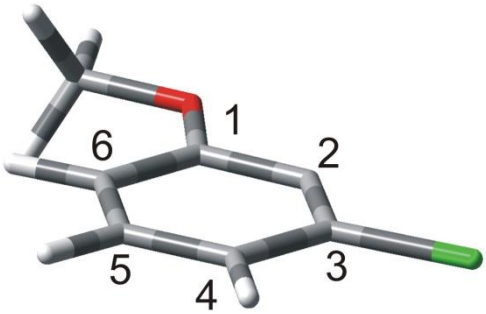


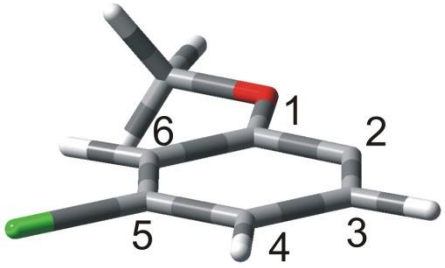
Fig. S31. Bond lengths (Å), angles (∠, in degrees) for ^{1}**17**$^{+}$ (a) and ^{3}**17**$^{+}$ (b).

a)



∠$C_2C_1C_6C_5$= 0°
∠$C_2C_3C_4C_5$= 0°
∠$C_1C_2C_3$= 124.73°
C_1-C_2= 1.38 Å
C_2-C_3 =1.36 Å

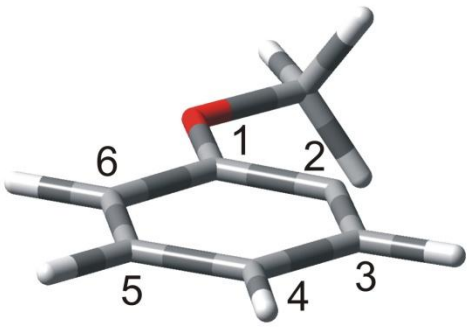
b)



∠$C_2C_1C_6C_5$= 0°
∠$C_2C_3C_4C_5$= 0°
∠$C_2C_2C_3$= 125.17°
C_1-C_2= 1.38 Å
C_2-C_3 =1.36 Å

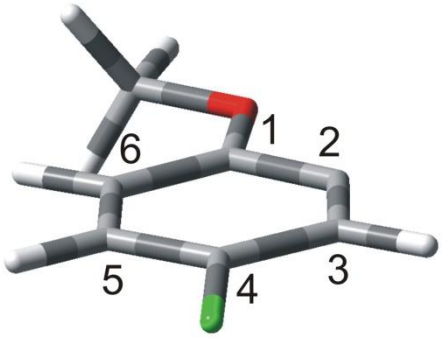
Fig. S32. Bond lengths (Å), angles (∠, in degrees) for **21**$^{\bullet}$ (a) and **23**$^{\bullet}$ (b).

a)



∠$C_2C_1C_6C_5$= 0°
∠$C_2C_3C_4C_5$= 0°
∠$C_2C_2C_3$= 125.04°
C_1-C_2= 1.38 Å
C_2-C_3 =1.37 Å

b)

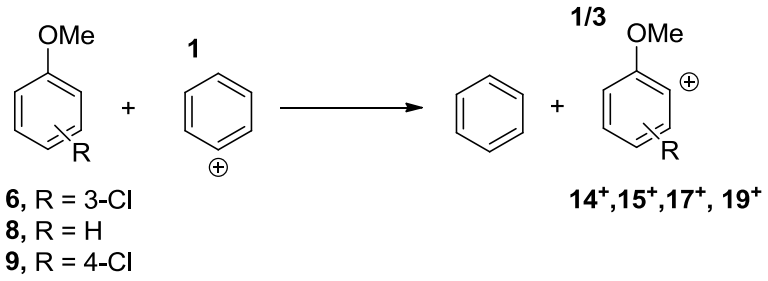


∠$C_2C_1C_6C_5$= 0°
∠$C_2C_3C_4C_5$= 0°
∠$C_1C_2C_3$= 126.01°
C_1-C_2= 1.38 Å
C_2-C_3 =1.36 Å

Fig. S33. Bond lengths (Å), angles (∠, in degrees) for **24**$^{\bullet}$ (a) and **26**$^{\bullet}$ (b).

2.3 Isodesmic equation for cations

Relative energy of singlet and triplet cations ***14*** $^{+}$ *-* ***17*** $^{+}$ *,* ***19*** $^{+}$. For all the structures reported in the isodesmic reaction in eq. S3, G(M06-2X) values have been adopted, according to the definition given in eq. S4.



6, R = 3-Cl
8, R = H
9, R = 4-Cl

14^{+}**,15**$^{+}$**,17**$^{+}$**, 19**$^{+}$

(S3)

$$G(M06\text{-}2X) = E_0(M06\text{-}2X,SMD) + \Delta G_{CORR}(M06\text{-}2X,vacuo) \quad (S4)$$

where: - E_0(M06-2X,SMD) is the total electronic energy calculated at the SMD- M06-2X/def2TZVP (MeOHbulk);

- ΔG_{CORR}(M06-2X,vacuo) is the unscaled thermal correction to Gibbs free energy as from the output of the frequency calculation at the M06-2X/def2TZVP level (in vacuo), also including the zero-point vibrational energy (ZPVE).

Table S2 G(M06-2X) values for the isodesmic reaction

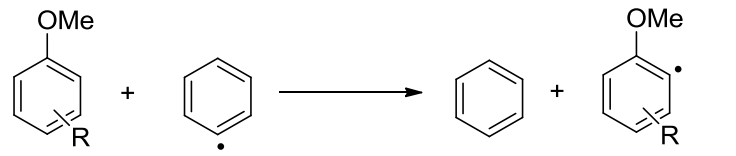
STRUCTURE	G(M06-2X) [HARTREE]
^{1}**19**$^{+}$	-345.759388
^{3}**19**$^{+}$	-345.761665
^{1}**14**$^{+}$	-805.350428
^{3}**14**$^{+}$	-805.366301
^{1}**15**$^{+}$	-805.364946500
^{3}**15**$^{+}$	-805.370291100
^{1}**17**$^{+}$	-805.365496
^{3}**17**$^{+}$	-805.372725
^{1}**Ph**$^{+}$	-231.276748
^{3}**Ph**$^{+}$	-231.224197
PhH	-232.1591207
6	-806.2753223
8	-346.6577001
9	-806.2759892

Table S3 Relative stability of phenyl cations according to the isodesmic reaction in eq. S3

STRUCTURE	ΔG [kcal mol^{-1}]
^{1}**19**$^{+}$	10
^{3}**19**$^{+}$	8.57
^{1}**14**$^{+}$	26.68
^{3}**14**$^{+}$	16.72
^{1}**15**$^{+}$	17.57
^{3}**15**$^{+}$	14.22
^{1}**17**$^{+}$	17.65
^{3}**17**$^{+}$	13.11
^{3}**Ph**$^{+}$	33

2.4 Isodesmic equation for radicals

Relative energy of phenyl radicals **21**$^{\bullet}$, **23**$^{\bullet}$, **24**$^{\bullet}$, **26**$^{\bullet}$. For all the structures reported in the isodesmic reaction in eq. S5, G(M06-2X) values have been adopted, according to the definition given in eq. S6.



6, R = 3-Cl
8, R = H
9, R = 4-Cl

21$^{\bullet}$, **23**$^{\bullet}$, **24**$^{\bullet}$, **26**$^{\bullet}$

(S5)

$$G(M06\text{-}2X) = E_0(M06\text{-}2X,SMD) + \Delta G_{CORR}(M06\text{-}2X,vacuo) \quad (S6)$$

where: - E_0(M06-2X,SMD) is the total electronic energy calculated at the SMD- M06-2X/def2TZVP (C_6H_{12} bulk);

- ΔG_{CORR}(M06-2X,vacuo) is the unscaled thermal correction to Gibbs free energy as from the output of the frequency calculation at the M06-2X/def2TZVP level (in vacuo), also including the zero-point vibrational energy (ZPVE).

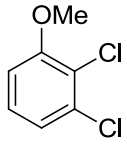
Table S4 G(M06-2X) values for the isodesmic reaction

STRUCTURE	G(M06-2X) [HARTREE]
21$^{\bullet}$	-805.594334
23$^{\bullet}$	-805.596532
24$^{\bullet}$	-805.596717
26$^{\bullet}$	-345.985137
Ph$^{\bullet}$	-231.487272
PhH	-232.1586304
6	-806.2730167
8	-346.6560636
9	-806.2731634

Table S5 Relative stability of phenyl radicals according to the isodesmic reaction in eq. S5

STRUCTURE	ΔG [kcal mol^{-1}]
21$^{\bullet}$	4.60
23$^{\bullet}$	3.22
24$^{\bullet}$	3.19
26$^{\bullet}$	-0.27

3. Cartesian coordinates

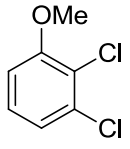


1

E (Vacuo) = -1265.9524149

Zero-point correction=	0.115330
Thermal correction to Energy=	0.124427
Thermal correction to Enthalpy=	0.125371
Thermal correction to Gibbs Free Energy=	0.080233

C -0.0011969638 0.0000450614 -0.0018193296
C 0.0107970574 0.0000084561 1.3871297066
C 1.200436689 -0.0000239433 2.0867142557
C 2.4002038922 -0.0000192125 1.3841737847
C 2.4128635343 0.0000174571 -0.0029898596
C 1.1969452358 0.0000496851 -0.7054119567
H -0.9428011788 0.0000670093 -0.5297676062
H -0.9270932074 0.0000042668 1.9261810495
C 0.0904109882 0.0001890409 -2.79533334
H 0.3899669857 0.000243797 -3.8394487513
H -0.5046228699 -0.892570407 -2.5863883951
H -0.5045308941 0.8929810241 -2.586265099
O 1.2880126649 0.0000776797 -2.0489166686
Cl 3.882065725 0.0000246438 -0.8901116496
H 1.2219417549 -0.0000530278 3.1667946187
Cl 3.8791885115 -0.0000572091 2.2715996996



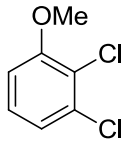
$^{3}\mathbf{1}_{\mathbf{ortho}}$

E (Vacuo) = -1265.8281735

Zero-point correction=	0.111300
Thermal correction to Energy=	0.121255
Thermal correction to Enthalpy=	0.122199
Thermal correction to Gibbs Free Energy=	0.074157

E (MeOH) = -1265.8403013
E (MeOH, stretched) = -1265.8273906
E (Cyclohexane) = -1265.8380453
E (Cyclohexane, stretched) = -1265.8145075

C 0.0117353178 0.0977539834 -0.0639950982
C 0.0521190387 0.0703711926 1.3328801249
C 1.2863796986 -0.0256467727 2.0354246641
C 2.4523306651 0.0534702024 1.3521563447
C 2.4242869119 0.4745065848 -0.0445369786
C 1.1850563127 0.1539322194 -0.7765507894
H -0.9228874149 -0.0122562933 -0.5982611021
H -0.8711373338 0.0203467597 1.8921286323
C 2.4189565537 -0.2310737421 -2.7569643568
H 2.1784155068 -0.3578504767 -3.8084683589
H 3.1041385853 0.606961768 -2.6302583551
H 2.8751685989 -1.143029809 -2.3687344701
O 1.1780392555 0.0224541922 -2.1052468305
Cl 2.9583421951 2.1645891337 -0.2985639937
H 1.2923745502 -0.2162767114 3.1007870049
Cl 3.9888493516 -0.2073744436 2.0832523099



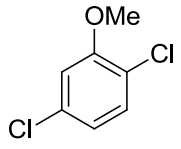
$^{3}\mathbf{1}_{\mathbf{meta}}$

E (Vacuo) = -1265.8192445

Zero-point correction=	0.111145
Thermal correction to Energy=	0.121124
Thermal correction to Enthalpy=	0.122068
Thermal correction to Gibbs Free Energy=	0.073798

E (MeOH) = -1265.8308773
E (MeOH, stretched) = -1265.8140646
E (Cyclohexane) = -1265.8289643
E (Cyclohexane, stretched) = -1265.80414

C 0.1674923513 -0.0221881891 -0.05163024
C 0.0628810862 0.0427079074 1.371248097
C 1.1713340981 0.1001184637 2.1375147202
C 2.4637626539 0.2441932192 1.4514898046
C 2.5488758586 -0.2351680913 0.0693402523
C 1.4153337548 -0.230834097 -0.6936208635
H -0.7148764438 -0.0162261124 -0.6755758382
H -0.9201072211 0.0143383973 1.8244729205
C 2.2925229243 0.0747591205 -2.8936989452
H 1.7582245091 0.2808829165 -3.8191342734
H 2.6718119271 1.007097641 -2.4722104048
H 3.1250778508 -0.5978440515 -3.0928293066
O 1.3502551118 -0.5288721928 -2.0126310225
Cl 4.0670361916 -0.8230290465 -0.479804224
H 1.1372791765 0.1150011961 3.2186794827
Cl 3.2562968989 1.7847806204 1.7416781846



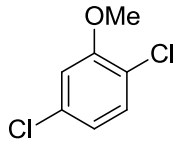
$^{3}\mathbf{2}_{\mathbf{ortho}}$

E (Vacuo) = -1265.8293793

Zero-point correction=	0.111559
Thermal correction to Energy=	0.121461
Thermal correction to Enthalpy=	0.122405
Thermal correction to Gibbs Free Energy=	0.074346

E (MeOH) = -1265.8417656
E (MeOH, stretched) = -1265.8311916
E (Cyclohexane) = -1265.8393745
E (Cyclohexane, stretched) = -1265.8176007

C 0.035404835 0.1527562267 -0.0536173285
C 0.0719137836 0.0704488458 1.3420774582
C 1.2933941043 -0.1368001707 2.0530196805
C 2.471745097 -0.1020296609 1.3922819291
C 2.4700664754 0.3690613423 0.0085118195
C 1.2182170959 0.1739544415 -0.745837681
H -0.9056542008 0.1137050736 -0.5858546307
C 2.426981342 -0.2218599144 -2.7382786946
H 2.1957840845 -0.229444751 -3.7993970838
H 3.1999599027 0.5177200522 -2.5302985043
H 2.7678278236 -1.2108105148 -2.4269545636
O 1.2092355224 0.1136747912 -2.0806771447
Cl 3.1301494879 2.0265894161 -0.1880295006
H 1.2448387486 -0.368359868 3.1092118074
H 3.4118743826 -0.3090372031 1.8855812444
Cl -1.402179042 0.0536210432 2.2220573017



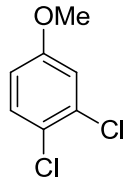
$^{3}\mathbf{2}_{\mathbf{meta}}$

E (Vacuo) = -1265.8201224

Zero-point correction=	0.111130
Thermal correction to Energy=	0.121080
Thermal correction to Enthalpy=	0.122025
Thermal correction to Gibbs Free Energy=	0.073546

E (MeOH) = -1265.832763
E (MeOH, stretched) = -1265.8266242
E (Cyclohexane) = -1265.8301207
E (Cyclohexane, stretched) = -1265.8070004

C 0.3226538373 -0.305497691 -0.2235437386
C 0.0670096373 0.2039851232 1.1284723171
C 1.1535414368 0.091881394 2.1168252816
C 2.4222980057 -0.0179628604 1.6743308354
C 2.6794916169 -0.1840931522 0.2808041246
C 1.5990595166 -0.4041947107 -0.6489416492
H -0.4955664413 -0.5509683958 -0.8883868357
C 2.089508458 0.2558098476 -2.8292074875
H 1.1685315189 0.8345708303 -2.9330202853
H 2.8980565181 0.9131125002 -2.4999885938
H 2.3535432091 -0.1967390857 -3.7815915845
O 1.8983147848 -0.8141494014 -1.91119405
Cl 4.2881029637 -0.3175925896 -0.2628229054
H 0.9209560156 0.1529116911 3.1718521469
H 3.2616303168 -0.0389685118 2.3577251399
Cl -0.7485447123 1.7638774242 1.1689735136



$^{3}3_{para}$

```
E (Vacuo) = -1265.8295136

Zero-point correction=                           0.111459
Thermal correction to Energy=                    0.121354
Thermal correction to Enthalpy=                  0.122298
Thermal correction to Gibbs Free Energy=         0.074043

E (MeOH) = -1265.8441167
E (MeOH, stretched) = -1265.8322079
E (Cyclohexane) = -1265.8403346
E (Cyclohexane, stretched) = -1265.8121705

C -0.0049612545 -0.0002254951 0.0053650826
C -0.003210312 0.0059569804 1.3504468324
C 1.2881701482 -0.027243274 2.0416999614
C 2.4205518482 0.5202065787 1.2935053046
C 2.4205056574 0.4750341315 -0.0718552257
C 1.2245257602 0.1355605363 -0.7304075642
H -0.9216271604 -0.0629137036 -0.5678677869
H -0.9183160786 -0.0461941531 1.9257878365
Cl 1.6284647895 -1.5512187529 2.8803306975
C 2.253050324 0.1867900017 -2.8623842995
H 1.9451368576 -0.0189682172 -3.883317259
H 2.6205945264 1.2128968247 -2.7906259666
H 3.0425315516 -0.5080001975 -2.5670149219
O 1.1018759448 0.0065769346 -2.059667584
H 3.3029116818 0.7726056793 -0.6214725097
Cl 3.7321619348 1.1935952956 2.1752111762
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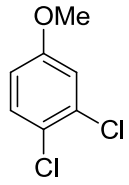


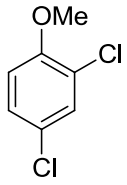
$^{3}3_{meta}$

E (Vacuo) = -1265.8291094

Zero-point correction=	0.111507
Thermal correction to Energy=	0.121286
Thermal correction to Enthalpy=	0.122231
Thermal correction to Gibbs Free Energy=	0.074301

E (MeOH) = -1265.8423234
E (MeOH, stretched) = -1265.8306142
E (Cyclohexane) = -1265.8394556
E (Cyclohexane, stretched) = -1265.8114431

C 0.0111752552 0.0168101648 0.0005236183
C 0.0118299774 -0.0136761028 1.3883246963
C 1.2133790851 -0.0200127197 2.0515677703
C 2.4662978135 0.2218856745 1.3126887645
C 2.4587326521 -0.0647152009 -0.1119671133
C 1.2607866553 -0.0933847583 -0.7384895762
H -0.907428715 0.0302288601 -0.5675182507
H -0.9150948188 -0.1046887352 1.9398304574
Cl 1.318534984 -0.343411311 3.7265287707
C 2.2130353275 -0.4072992221 -2.868524388
H 1.8555548232 -0.5187206007 -3.8881124082
H 2.8549228941 0.474092368 -2.7950651702
H 2.7787943003 -1.2947508404 -2.5743563992
O 1.0647033025 -0.2566525005 -2.0588692901
H 3.3998770721 -0.1432375946 -0.6363023035
Cl 3.2973327953 1.6957619529 1.7972828825

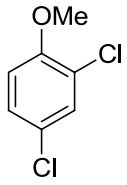


4

E (Vacuo) = -1265.9545007

Zero-point correction=	0.115502
Thermal correction to Energy=	0.124561
Thermal correction to Enthalpy=	0.125506
Thermal correction to Gibbs Free Energy=	0.080441

C 0.0012413745 0.0000484033 -0.0001586209
C -0.0003009395 0.0000134084 1.3888055819
C 1.1979985381 -0.0000214317 2.0745145016
C 2.404193 -0.000021199 1.388533044
C 2.3992582837 0.0000153137 0.0079170365
C 1.1969273851 0.000050847 -0.7105711674
H -0.9435342067 0.0000714525 -0.5233774916
H -0.9344118518 0.0000120011 1.9330154447
H 3.3436919421 -0.0000478297 1.9226455744
Cl 1.2068385681 -0.0000659819 3.8070570109
C 0.0882322655 0.0001892194 -2.7969390613
H 0.3828792313 0.0002474157 -3.8423958659
H -0.5063612535 -0.8923690499 -2.5855325045
H -0.5062726559 0.8927762993 -2.5854058843
O 1.2881489008 0.0000764964 -2.0547195426
Cl 3.8946520019 0.0000149634 -0.8482113713



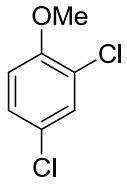
$^{3}4_{ortho}$

E (Vacuo) = -1265.8295226

Zero-point correction=	0.111747
Thermal correction to Energy=	0.121516
Thermal correction to Enthalpy=	0.122460
Thermal correction to Gibbs Free Energy=	0.074557

E (MeOH) = -1265.8437045
E (MeOH, stretched) = -1265.8321891
E (Cyclohexane) = -1265.8402009
E (Cyclohexane, stretched) = -1265.8104341

C 0.0069720706 0.0055663601 -0.0147655153
C 0.0063111161 0.022023207 1.3882172845
C 1.2484920971 0.0048774273 2.1040972163
C 2.4410383313 0.1118766571 1.4875475166
C 2.4235776464 0.4555946806 0.0669966153
C 1.1961976054 0.1239621127 -0.688082819
H -0.922305443 -0.1670223413 -0.5400262105
H -0.9179941109 -0.0437394467 1.941434356
H 3.3772191719 0.0380760274 2.022983945
Cl 1.1626105496 -0.2491204908 3.8170326492
C 0.2545986619 -0.2699710631 -2.806606236
H 0.6199718452 -0.3446743831 -3.826231119
H -0.2194125947 -1.2084169073 -2.5103388543
H -0.4657435246 0.5471593722 -2.7281215352
O 1.3882206721 -0.0081650608 -1.9988012907
Cl 3.0720914904 2.0393925629 -0.3348087043



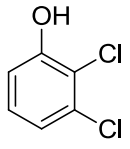
$^{3}4_{para}$

E (Vacuo) = -1265.8252001

Zero-point correction=	0.111972
Thermal correction to Energy=	0.121695
Thermal correction to Enthalpy=	0.122639
Thermal correction to Gibbs Free Energy=	0.074906

E (MeOH) = -1265.8403773
E (MeOH, stretched) = -1265.8324743
E (Cyclohexane) = -1265.8361779
E (Cyclohexane, stretched) = -1265.811368

C -0.0010757557 -0.0102112184 -0.0035622168
C -0.0060459888 -0.0060841978 1.3529203974
C 1.2828926051 0.0451159055 2.0547851889
C 2.4393199355 -0.5198349431 1.3585651631
C 2.4137501464 -0.5316133739 0.0133877344
C 1.2169464996 -0.1780680689 -0.7142358366
H -0.9329251883 0.0509029417 -0.5498586337
H -0.9283111712 0.0200065348 1.9177952835
H 3.3112878968 -0.8499002864 1.9071780765
Cl 1.6014644396 1.5994688301 2.8513908059
C 0.1758131162 0.1691059257 -2.8117097209
H 0.5139820576 0.2310608653 -3.841728587
H -0.5685977766 -0.624221032 -2.7185336166
H -0.259276166 1.1229313979 -2.5064724159
O 1.3269432005 -0.1271512946 -2.0430920495
Cl 3.7845721258 -1.0550238602 -0.8982132268



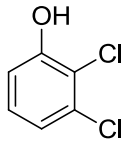
$^{3}5_{ortho}$

E (Vacuo) = -1226.5361169

Zero-point correction=	0.082998
Thermal correction to Energy=	0.091457
Thermal correction to Enthalpy=	0.092401
Thermal correction to Gibbs Free Energy=	0.047782

E (MeOH) = -1226.5597447
E (MeOH, stretched) = -1226.5458238
E (Cyclohexane) = -1226.5502728
E (Cyclohexane, stretched) = -1226.5230395

C 0.0272765947 0.0470987795 -0.0662240525
C 0.0841575503 0.2056046029 1.3286060423
C 1.2934998972 0.000472107 2.0474236863
C 2.4449158671 -0.2434157822 1.3769645555
C 2.4752629665 -0.0609580567 -0.0720177819
C 1.1788111559 -0.1886082518 -0.759481399
H -0.9190812879 0.0412782107 -0.5903567724
H -0.8221961106 0.4093729287 1.8801860954
O 1.1681237984 -0.483003937 -2.0682541299
Cl 3.4201213006 1.3365861873 -0.6404696691
H 1.283404952 -0.0205572676 3.1295157453
Cl 3.9102877421 -0.6841587163 2.1624283938
H 2.0743478666 -0.5421790314 -2.3948397863



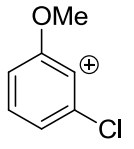
$^{3}5_{meta}$

E (Vacuo) = -1226.5339741

Zero-point correction=	0.082905
Thermal correction to Energy=	0.091285
Thermal correction to Enthalpy=	0.092230
Thermal correction to Gibbs Free Energy=	0.047810

E (MeOH) = -1226.5539759
E (MeOH, stretched) = -1226.5399336
E (Cyclohexane) = -1226.546654
E (Cyclohexane, stretched) = -1226.5229793

C 0.0269710734 0.1140407526 -0.0109353167
C 0.0528790903 0.0061429173 1.4028568963
C 1.2304867601 -0.0557479171 2.0680064766
C 2.4759216477 0.1883618655 1.3140686921
C 2.4279233937 -0.0454641316 -0.1245240069
C 1.2379910302 0.0078070529 -0.7694911391
H -0.9024500253 0.1821482079 -0.5572864974
H -0.8840779798 -0.0809242569 1.937974104
O 1.087063853 -0.09794496 -2.1044167028
Cl 3.8950554993 -0.3016209331 -0.9967992686
H 1.2861534798 -0.2128486934 3.1369080344
Cl 3.3040432217 1.6580328446 1.8060681816
H 1.9575891943 -0.1685112084 -2.5183855258



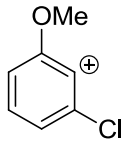
^{1}14^{+}

E (Vacuo) = -805.3392961

Zero-point correction=	0.109924
Thermal correction to Energy=	0.118495
Thermal correction to Enthalpy=	0.119439
Thermal correction to Gibbs Free Energy=	0.075917

E (MeOH) = -805.4263448

C	0.0417866681	-0.0402731121	0.0403780947
C	0.0042532265	-0.0063569209	1.4160383338
C	1.3139000563	-0.0032486156	1.9748139095
C	2.3326957385	-0.2293508547	1.0903754254
C	2.0878170763	-0.3877795849	-0.2865935773
C	0.8173770892	-0.5194725863	-0.9248289505
H	1.4204631656	-0.0057361453	3.0526129051
H	3.361474352	-0.2598574259	1.4258397505
C	-2.2913327072	-0.3910075168	1.4765252952
H	-3.0921392263	-0.1345984532	2.1609359196
H	-2.3509586709	0.2203095719	0.5666450465
H	-2.3195790636	-1.4511740929	1.2309509782
O	-1.0605310764	-0.0853506622	2.155454437
H	2.8843901251	-0.1595589048	-0.9936972244
Cl	0.6097836852	-0.6368451934	-2.5886055103



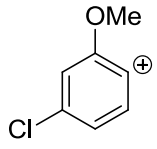
$^{3}\mathbf{14}^{+}$

E (Vacuo) = -805.3554574

Zero-point correction=	0.111064
Thermal correction to Energy=	0.119455
Thermal correction to Enthalpy=	0.120400
Thermal correction to Gibbs Free Energy=	0.075893

E (MeOH) = -805.4421938

C	0.0959720513	0.6332327705 0.294212206
C	0.2112627167	0.3930162608 1.6775413787
C	1.4640319649	-0.1089658124 2.1807278743
C	2.4819594677	-0.3311058436 1.3042915321
C	2.3200019423	-0.076146579 -0.0764176145
C	1.0900657167	0.4202090503 -0.5923273534
H	1.5475637588	-0.2913976372 3.2442960354
H	3.432585305	-0.7077575779 1.6564054194
C	-2.0136040757	1.1017518486 2.0705714898
H	-2.6341178235	1.1473667879 2.9577623355
H	-1.8646936995	2.0921955973 1.642990699
H	-2.4268760653	0.4126912475 1.3353690913
O	-0.7340167502	0.59328687 2.5250099126
H	3.1339708641	-0.2553039228 -0.768475653
Cl	0.9191017013	0.7190559168 -2.256305742



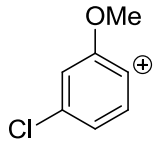
^{1}15^{+}

E (Vacuo) = -805.3464097

Zero-point correction=	0.108681
Thermal correction to Energy=	0.117441
Thermal correction to Enthalpy=	0.118385
Thermal correction to Gibbs Free Energy=	0.074731

E (MeOH) = -805.4396775

C 0.0218486738 0.2237864054 0.0377667376
C -0.0836971851 0.1356066769 1.3774054635
C 1.2896139038 0.1249828406 1.757129175
C 2.3494646297 0.1945728234 0.8567283667
C 2.1407949429 0.2817939151 -0.5156681389
C 0.8163136285 0.3003741233 -1.0115791816
H 1.4745490691 0.0572264309 2.8244004998
C -0.9843857893 -0.0136144808 3.5516367177
H -1.9934388359 -0.0490849633 3.9465152679
H -0.4471597073 -0.9271362037 3.8053621527
H -0.4653989013 0.8708810684 3.9201876058
O -1.152584472 0.0759164805 2.1228944387
H 2.9533503082 0.3366617448 -1.228037505
H 0.5562390163 0.3660931015 -2.0601953408
Cl 3.9465341631 0.1717762405 1.4603954771



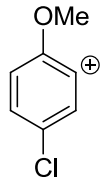
^{3}**15**$^{+}$

E (Vacuo) = -805.3589839

Zero-point correction=	0.110921
Thermal correction to Energy=	0.119209
Thermal correction to Enthalpy=	0.120153
Thermal correction to Gibbs Free Energy=	0.076209

E (MeOH) = -805.4465001

C	-0.0146247564	-0.0007719854	0.0163862522
C	0.0009341056	0.0004143663	1.4430933204
C	1.2582735062	0.0008072389	2.0958565578
C	2.3822135919	0.0001129975	1.3229814043
C	2.317261629	-0.0010264189	-0.1156716443
C	1.0902098585	-0.0014882276	-0.7746345976
H	1.2962656104	0.0016493997	3.1768737117
C	-2.3696369254	0.0004013381	1.5151700878
H	-3.0871414638	0.0034252698	2.3272181913
H	-2.4663088232	0.8978942627	0.9059305979
H	-2.4678908257	-0.9005431246	0.9112928813
O	-1.0701768621	0.000955142	2.1567750739
H	3.2454695723	-0.0015562599	-0.6728540631
H	1.0328759787	-0.00238286	-1.8554613795
Cl	3.9224590422	0.0005853513	2.0284847902



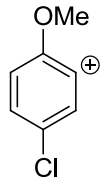
^{1}17^{+}

E (Vacuo) = -805.3483081

Zero-point correction=	0.108924
Thermal correction to Energy=	0.117739
Thermal correction to Enthalpy=	0.118683
Thermal correction to Gibbs Free Energy=	0.074450

E (MeOH) = -805.4399459

C 0.304375407 -0.5346089737 0.4285723107
C 0.0502613226 -0.1926831343 1.6887885778
C 1.3963260616 0.1993504672 2.0397872022
C 2.5025785816 0.3249142925 1.220808323
C 2.4271728541 -0.0374628418 -0.1215737793
C 1.1579377687 -0.4675640921 -0.586675808
H 1.5142304021 0.1762763247 3.123740132
H 3.4414642286 0.6530741362 1.645616472
H 0.8894793021 -0.4855079409 -1.6364807089
Cl 3.6952971149 0.2083488773 -1.2151009475
C -2.0102601548 -1.1725334101 2.1561775141
H -2.7293429069 -1.1105295213 2.9648395092
H -2.430816672 -0.7555816315 1.2388750136
H -1.6828099848 -2.2010500416 2.0100461246
O -0.8854188984 -0.3654315942 2.5713176047



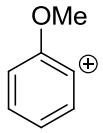
$^{3}\mathbf{17}^{+}$

(Vacuo) = -805.362785

Zero-point correction=	0.111677
Thermal correction to Energy=	0.119828
Thermal correction to Enthalpy=	0.120772
Thermal correction to Gibbs Free Energy=	0.077114

E (MeOH) = -805.4498385

C 0.0548409957 -0.0000087335 0.0115414542
C 0.0146415154 0.0000025752 1.430002152
C 1.2657387628 0.0000076517 2.1182235256
C 2.415777713 -0.0000063314 1.3907212953
C 2.3891994372 -0.0000245687 -0.0372687016
C 1.1674188291 -0.0000235232 -0.7451578819
H 1.3002015776 0.000027094 3.1988574753
H 3.3791483946 -0.0000023953 1.8838295104
H 1.1510850528 -0.0000347784 -1.8277716822
Cl 3.8440280419 -0.0000452975 -0.8716290195
C -1.2932299204 -0.0000049615 3.422460691
H -2.3628540403 -0.0000962156 3.5971679637
H -0.837247834 -0.9002169191 3.8320780508
H -0.8374026871 0.9002892848 3.8320705507
O -1.1489588349 0.0000088519 1.9863459203



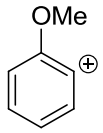
$^{1}19^{+}$

E (Vacuo) = -345.7533287

Zero-point correction=	0.117349
Thermal correction to Energy=	0.124579
Thermal correction to Enthalpy=	0.125523
Thermal correction to Gibbs Free Energy=	0.085525

E (MeOH) = -345.8449128

C 0.0100489989 -0.00021465 -0.0203313924
C -0.0100924841 -0.0000263736 1.3568231984
C 1.1536768661 0.0002866571 2.2009330647
C 2.1153633343 0.0003912417 1.2713421626
C 2.428346601 0.0002610458 -0.0173325423
C 1.2090438841 -0.0000340882 -0.7275953872
H -0.9298977871 -0.0004171705 -0.5549386568
H -0.9270957978 0.0004161459 1.9430467495
H 3.4087288691 -0.0001679503 -0.474926981
H 1.262835099 -0.0004829566 -1.8084845959
C 2.3590418334 0.002125586 4.192986616
H 2.1190810802 0.0019474873 5.2502470212
H 2.9139562257 -0.8998213521 3.9303859804
H 2.9121072714 0.9051577686 3.9302605151
O 1.0919673252 0.0007651302 3.5006743917



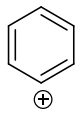
^{3}19^{+}

E (Vacuo) = -345.761722

Zero-point correction=	0.120428
Thermal correction to Energy=	0.127729
Thermal correction to Enthalpy=	0.128674
Thermal correction to Gibbs Free Energy=	0.086930

E (MeOH) = -345.8485947

C -0.0237154998 -0.00038612 0.0244054677
C -0.0678028368 0.0000366247 1.3824424687
C 1.168281148 0.0007649587 2.1099325145
C 2.3773817574 0.0010197946 1.365326376
C 2.447099076 0.000619306 0.0171501376
C 1.2177347316 -0.0001041867 -0.670916398
H -0.9420287733 -0.0009491664 -0.5477108867
H -0.9924193961 -0.0001536157 1.9453981618
H 3.3877882568 0.0008264233 -0.5186618947
H 1.2171201728 -0.0004525812 -1.7536380629
C 2.3474176873 0.0018439994 4.1661647926
H 2.0306615437 0.0035123364 5.202403322
H 2.9140259288 -0.8975316509 3.9298096586
H 2.9149631188 0.8999290477 3.9271541513
O 1.1206044043 0.0012113512 3.3938303357



$^1Ph^+$

E (Vacuo) = -231.2341511

Zero-point correction=	0.085570
Thermal correction to Energy=	0.090320
Thermal correction to Enthalpy=	0.091264
Thermal correction to Gibbs Free Energy=	0.058038

E (MeOH) = -231.3347856

C 0.015091158 0. 0.0043958702
C 0.001907652 0. 1.3208922123
C 1.3866279714 0. 1.660762146
C 2.378858845 0. 0.6928427106
C 2.0615228458 0. -0.6564848127
C 0.7108595206 0. -1.1132975208
H -0.8104725282 0. 2.0331153462
H 1.6082202069 0. 2.7220570785
H 3.4169954163 0. 0.9951976974
H 2.8183227273 0. -1.4328251148
H 0.4079599114 0. -2.1503485488

$^3Ph^+$

E (Vacuo) = -231.1879799

Zero-point correction=	0.091157
Thermal correction to Energy=	0.095941
Thermal correction to Enthalpy=	0.096885
Thermal correction to Gibbs Free Energy=	0.062372

E (MeOH) = -231.2865686

C	-0.2639426648	0. -0.076871371
C	0.0153326596	0. 1.2560112986
C	1.4151422398	0. 1.6539957325
C	2.4206434432	0. 0.7050116104
C	2.0819475777	0. -0.6354688615
C	0.6873505355	0. -1.051352411
H	-0.758423361	0. 2.0158693897
H	1.6492600127	0. 2.7119664816
H	3.4584460937	0. 1.0072706195
H	2.8475310866	0. -1.4022773734
H	0.4426061034	0. -2.1078480514

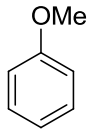
PhH

E (Vacuo) = -232.2246238

Zero-point correction=	0.101155
Thermal correction to Energy=	0.105518
Thermal correction to Enthalpy=	0.106462
Thermal correction to Gibbs Free Energy=	0.073716

E (MeOH) = -232.2328367
E (Cyclohexane) = -232.2323464

C	0.003133918	-0.0000029511	0.0018815605
C	0.0028994971	-0.0000140332	1.390188208
C	1.2051042649	-0.0000079814	2.0846117242
C	2.4077230875	0.0000129506	1.3905633042
C	2.4079572991	0.0000256134	0.0022853334
C	1.2057275472	0.0000167252	-0.6921523511
H	-0.9344872328	-0.0000106732	-0.539205464
H	-0.9348401807	-0.0000335304	1.9311407517
H	1.2051960327	-0.0000220428	3.167142919
H	3.3453238575	0.0000171507	1.9316857355
H	3.3456769704	0.0000418309	-0.5387017915
H	1.2056756839	0.0000269663	-1.774683549



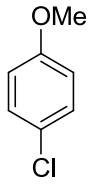
8

E (Vacuo) = -346.7507325

Zero-point correction=	0.134139
Thermal correction to Energy=	0.140901
Thermal correction to Enthalpy=	0.141845
Thermal correction to Gibbs Free Energy=	0.103206

E (MeOH) = -346.7609061
E (Cyclohexane) = -346.7592696

C	0.0086960279	-0.0002535487	0.0038543417
C	-0.0074212955	0.0002444505	1.3848612294
C	1.1924140305	0.0007144408	2.0965260959
C	2.4036432701	0.000657556	1.4137295231
C	2.4020786765	0.0001888026	0.0214564241
C	1.215895405	-0.0002636309	-0.6898111717
H	-0.928392875	-0.0005607147	-0.5383764951
H	-0.9351007204	0.0003090259	1.9417953854
H	3.3441573671	0.0009723318	1.9452110019
H	3.3486991969	0.0001930049	-0.5042084478
H	1.2250379001	-0.0005825098	-1.7713851296
C	2.2659407348	0.0037472531	4.206891452
H	1.961367461	0.0052513191	5.2503311066
H	2.8679523531	-0.887485233	4.0070964211
H	2.8659626026	0.8956013105	4.0039210252
O	1.0795698529	0.0010801458	3.4490112298



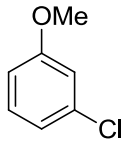
9

E (Vacuo) = -806.354249

Zero-point correction=	0.124474
Thermal correction to Energy=	0.132523
Thermal correction to Enthalpy=	0.133467
Thermal correction to Gibbs Free Energy=	0.091028

E (MeOH) = -806.3670172
E (Cyclohexane) = -806.3641914

C 0.0101726196 0.0540420186 0.0358839897
C -0.0085656174 -0.0195653109 1.4289304574
C 1.1851480041 0.0553842218 2.1377288949
C 2.3870054767 0.202909888 1.4533587445
C 2.3935844325 0.2746599266 0.0746436232
C 1.2041920903 0.2004250355 -0.6400727815
H -0.9288739748 -0.0061721548 -0.4977213898
H 1.2010387203 0.0012961169 3.2163551083
H 3.3185639309 0.2617622025 1.9995027941
H 1.221442618 0.2577493894 -1.7198879506
Cl 3.8959861433 0.4587749663 -0.7742488872
C -1.2941600172 -0.2415546507 3.4044745072
H -2.3456839249 -0.3528973572 3.6549875946
H -0.7380075362 -1.1061255527 3.7777132767
H -0.9040316407 0.668317514 3.8692498389
O -1.2299406266 -0.1629907189 1.998389707



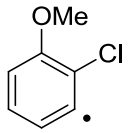
6

E (Vacuo) = -806.3549303

Zero-point correction=	0.124694
Thermal correction to Energy=	0.132625
Thermal correction to Enthalpy=	0.133569
Thermal correction to Gibbs Free Energy=	0.091496

E (MeOH) = -806.3668183
E (Cyclohexane) = -806.3645127

C -0.0110809197 -0.0458577597 -0.0046602949
C -0.018933031 -0.1377248056 1.387195069
C 1.1499758826 0.0810233254 2.1085750151
C 2.3208175527 0.3912157703 1.4246430126
C 2.3480574917 0.4866811746 0.0455854674
C 1.1667510968 0.2634603935 -0.6510661745
H -0.9259426481 -0.2180314086 -0.5536131301
H 1.1625139461 0.014178035 3.186019325
H 3.2297803672 0.5612781348 1.9870469249
C -1.2799560865 -0.550977962 3.3481226607
H -2.3106929782 -0.8004280047 3.584465646
H -0.6209056234 -1.341929063 3.7163458124
H -1.0154436153 0.3948612341 3.8287204408
O -1.2141447133 -0.4450994986 1.9432944487
H 3.2562747765 0.7274398577 -0.4876421583
Cl 1.1715203399 0.3766778834 -2.3826464573

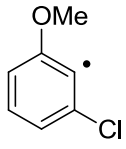


20$^{\bullet}$

(Vacuo) = -805.6643714

Zero-point correction=	0.112116
Thermal correction to Energy=	0.119974
Thermal correction to Enthalpy=	0.120918
Thermal correction to Gibbs Free Energy=	0.078462

C 0.0051058083 0.0000555571 -0.0008110707
C 0.0076566769 0.0000084431 1.3899869106
C 1.1996951759 -0.0000428515 2.1056349955
C 2.345220833 -0.0000427461 1.353069361
C 2.410881777 0.0000025414 -0.0066588506
C 1.1998214647 0.0000535201 -0.71928422
H -0.9388272085 0.0000935554 -0.5251889802
H -0.9370955394 0.000011259 1.9188140229
C 0.0826987949 0.0001894268 -2.8024711723
H 0.3748002343 0.0002435762 -3.8487054228
H -0.5110564608 -0.8922965524 -2.5890531038
H -0.510984171 0.8926960714 -2.5889380651
O 1.2850618258 0.0000945602 -2.0626264498
Cl 3.9223164423 -0.0000023182 -0.8375921982
H 1.2165098969 -0.000079721 3.18656599



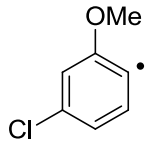
21$^{\bullet}$

E (Vacuo) = -805.6632097

Zero-point correction=	0.111914
Thermal correction to Energy=	0.119860
Thermal correction to Enthalpy=	0.120804
Thermal correction to Gibbs Free Energy=	0.077977

E (Cyclohexane) = -805.6723108

C	-0.0107179671	0.0000360098	-0.000350064
C	0.0153767453	0.000004664	1.3925741547
C	1.2021839142	-0.0000198117	2.1030079407
C	2.3998539126	-0.0000120001	1.3875127067
C	2.3504320808	0.0000194613	0.0287590204
C	1.1874644899	0.000044302	-0.7162329765
H	-0.9605286593	0.0000508318	-0.5159197595
H	-0.9227106494	-0.0000019324	1.9318609458
C	0.0973950839	0.0001944267	-2.809223642
H	0.3952073538	0.0002639379	-3.8539005329
H	-0.4983156701	-0.8924239129	-2.6001805307
H	-0.4982157835	0.8928441671	-2.6000300264
O	1.2949036602	0.0000677136	-2.0618561324
H	1.2191672471	-0.0000448106	3.1840424201
Cl	3.9222882209	-0.000038725	2.2145218628



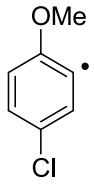
23

E (Vacuo) = -805.6649599

Zero-point correction=	0.111773
Thermal correction to Energy=	0.119720
Thermal correction to Enthalpy=	0.120664
Thermal correction to Gibbs Free Energy=	0.077880

E (Cyclohexane) = -805.6744115

C 0.0010427919 0.0000208118 -0.0086552931
C 0.0088208236 0.0000044448 1.3835855188
C 1.1753695384 -0.0000102713 2.1231732445
C 2.3944431606 -0.0000087865 1.4371210061
C 2.3633308526 0.0000078795 0.0763938122
C 1.2152248308 0.000023179 -0.6939767014
H -0.9451751222 0.0000305795 -0.529388988
C 0.1541792123 0.0000869949 -2.8018533381
H 0.4647982503 0.0001185233 -3.842754998
H -0.4438232254 -0.8924998539 -2.599527404
H -0.443788734 0.8926821312 -2.5994625081
O 1.3415720785 0.0000367122 -2.0375087025
H 1.1389023349 -0.0000224754 3.2032121653
H 3.3302369236 -0.0000199659 1.9819033697
Cl -1.5182183782 0.0000023441 2.2104607402.



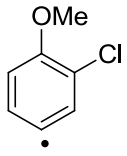
24$^{\bullet}$

E (Vacuo) = -805.664861

Zero-point correction=	0.111720
Thermal correction to Energy=	0.119736
Thermal correction to Enthalpy=	0.120680
Thermal correction to Gibbs Free Energy=	0.077640

E (Cyclohexane) = -805.6743567

C	-0.00769144	0.0000290023	-0.000619077
C	0.0081075756	0.0000100608	1.3921448168
C	1.2051250681	-0.0000111613	2.0818532304
C	2.4195758943	-0.0000168145	1.3913744899
C	2.3468476274	0.0000034439	0.032492028
C	1.1876235339	0.0000293685	-0.7187934009
H	-0.9605801907	0.0000424205	-0.5117038683
H	-0.9232942933	0.0000114857	1.9409776435
H	3.36140335	-0.0000340572	1.9245664944
Cl	1.2073534859	-0.0000290467	3.8160506412
C	0.0936127641	0.0001966538	-2.8090299691
H	0.3861798495	0.000300595	-3.8553627298
H	-0.5015953983	-0.8924033298	-2.5972319284
H	-0.5014978445	0.8928121726	-2.5970254335
O	1.2932069661	0.0000495342	-2.0660717086

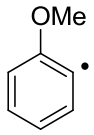


25$^{\bullet}$

E (Vacuo) = -805.6644743

Zero-point correction=	0.111864
Thermal correction to Energy=	0.119754
Thermal correction to Enthalpy=	0.120698
Thermal correction to Gibbs Free Energy=	0.078152

C -0.0067231333 0.0000389669 0.0006622144
C -0.012408723 -0.0000017153 1.3971379345
C 1.1975622984 -0.00003539 2.0295170163
C 2.4146812615 -0.0000331077 1.3971836286
C 2.4039385908 0.0000082768 0.0101426684
C 1.1951713081 0.0000457359 -0.7014834892
H -0.9477232658 0.000063396 -0.5304707439
H -0.948880794 -0.0000061948 1.9392539669
H 3.3569486586 -0.0000608035 1.9287595727
C 0.0908990474 0.0001961564 -2.7932071276
H 0.3874347715 0.0002650589 -3.8383530689
H -0.5046807292 -0.8924476275 -2.5833584388
H -0.504596473 0.8928620718 -2.5832149534
O 1.2882109599 0.000081038 -2.0485166303
Cl 3.8947793874 0.000014466 -0.8601001765



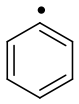
26$^{\bullet}$

E (Vacuo) = -346.0654719

Zero-point correction=	0.120752
Thermal correction to Energy=	0.127749
Thermal correction to Enthalpy=	0.128693
Thermal correction to Gibbs Free Energy=	0.088671

E (Cyclohexane) = -346.0738081

C -0.0169431518 0.0816168199 -0.0695704303
C 0.007808002 0.1432889773 1.2983501541
C 1.1473627647 0.1119821205 2.070656935
C 2.3636165545 0.0091715199 1.3916734013
C 2.3818487682 -0.0557264191 0.0081666194
C 1.2039963151 -0.0206465003 -0.7316948175
H -0.9499638949 0.1110999149 -0.6188805686
H 3.2769207315 -0.0176670964 1.9729403963
H 3.3330197486 -0.1351506813 -0.5020382298
H 1.2323589567 -0.0721496981 -1.8120510348
C -0.1053791865 0.2761615038 4.0395969011
H 0.0766711926 0.3153632827 5.1102741505
H -0.6224475932 1.1836977387 3.7163654709
H -0.725931687 -0.5912822874 3.7989427518
O 1.1620720807 0.1734297514 3.4200723517



Ph$^{\bullet}$

E (Vacuo) = -231.538926

Zero-point correction=	0.088107
Thermal correction to Energy=	0.092435
Thermal correction to Enthalpy=	0.093379
Thermal correction to Gibbs Free Energy=	0.060097

E (Cyclohexane) = -231.5473688

C	-0.0045613081	-0.0000007573	0.0007977278
C	-0.0160470098	-0.0000014114	1.3956149004
C	1.2024360057	-0.0000010574	2.0224583402
C	2.4208822508	-0.0000002843	1.3955423113
C	2.4093141937	0.000000219	0.0007266993
C	1.202355606	0.0000000177	-0.6873752621
H	-0.9405314739	-0.0000008796	-0.5440981895
H	-0.9473698303	-0.0000019375	1.9473828476
H	3.3522377335	-0.0000000626	1.9472555476
H	3.3452513909	0.0000008676	-0.5442257841
H	1.2023243053	0.0000004978	-1.7694068339

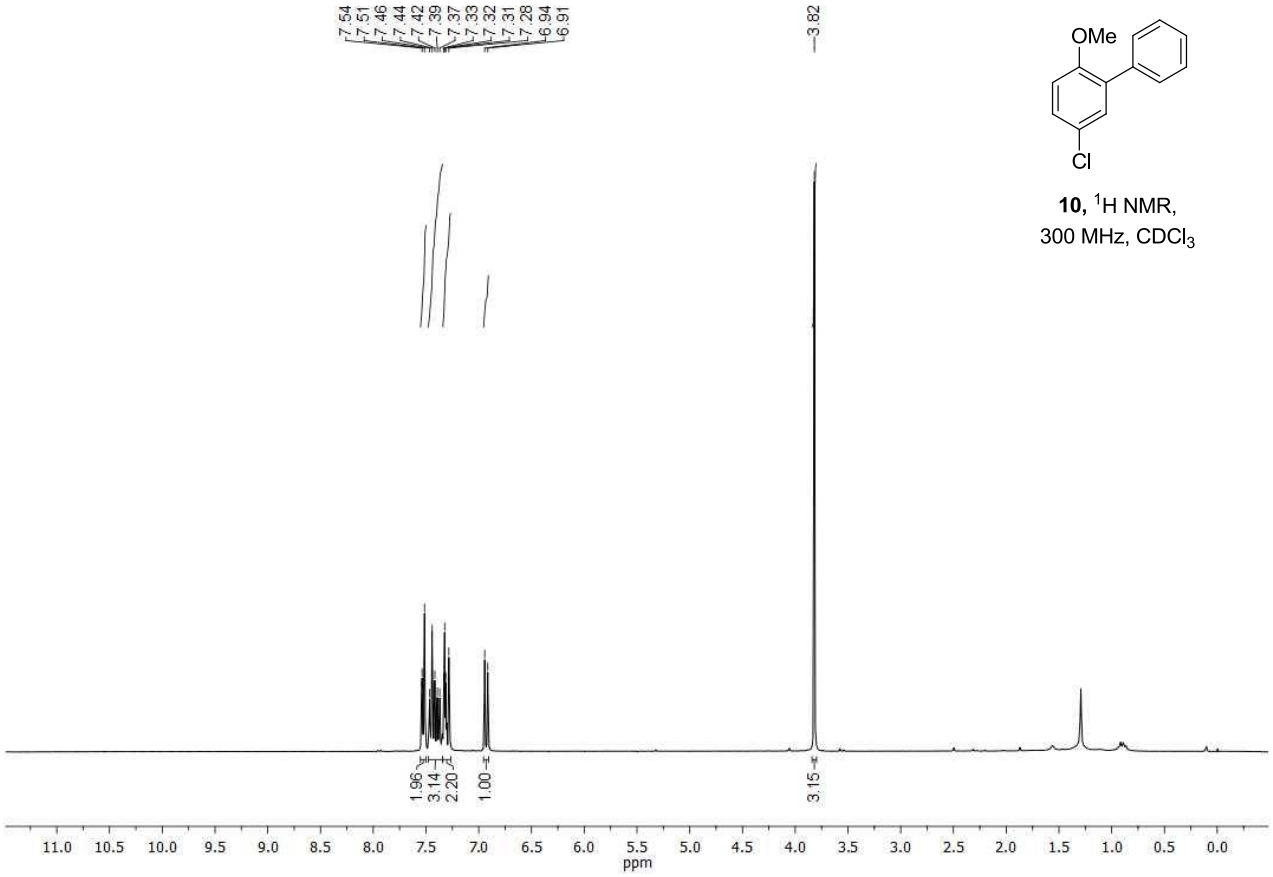
4. References

S1 V. Dichiarante, D. Dondi, S. Protti, M. Fagnoni and A. Albini, Phenyl Radical, Cation, and Anion. The Triplet−Singlet Gap and Higher Excited States of the Phenyl Cation, *J. Am. Chem. Soc.*, 2007, **129**, 5605–5611. Correction: 11662.

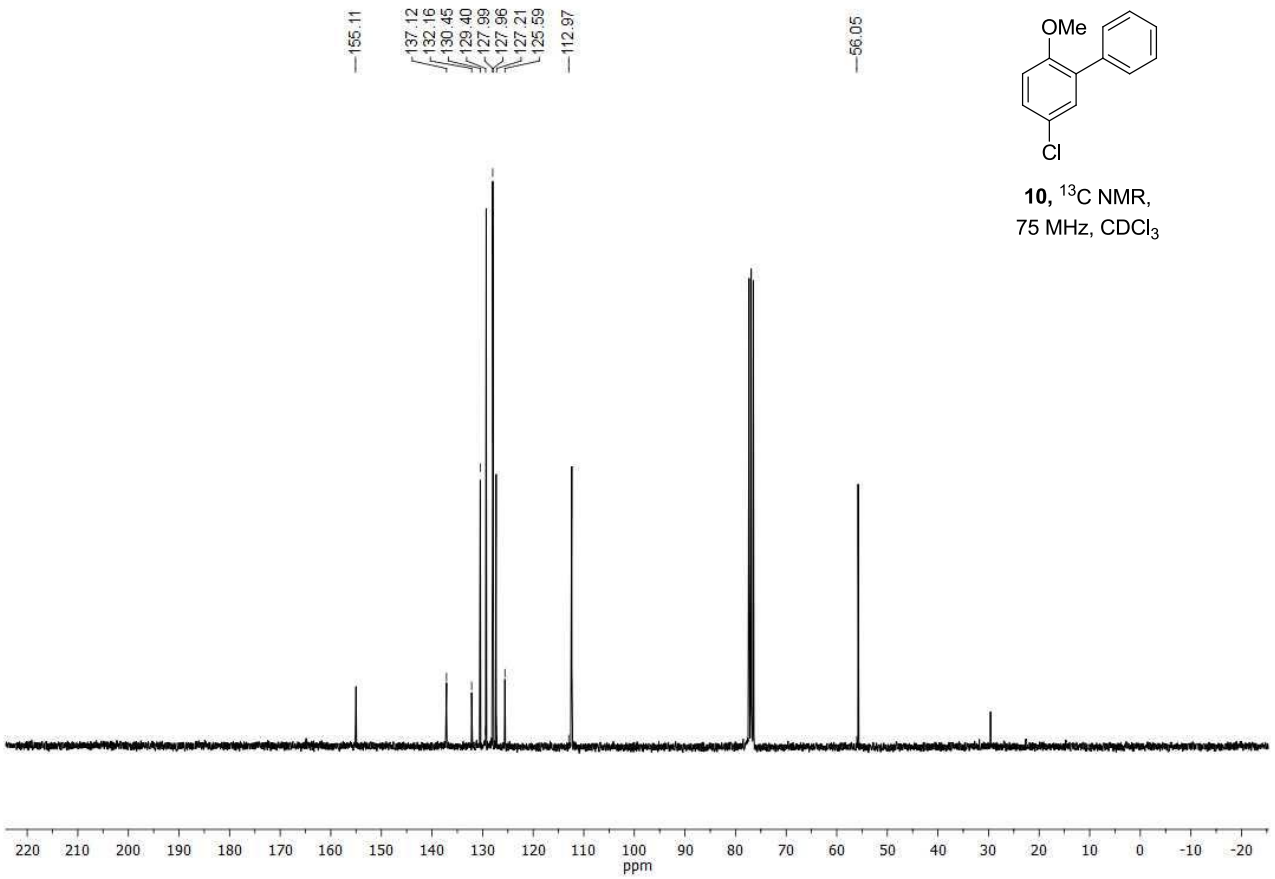
S2 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford CT, 2010.

S3 A. V. Marenich, C. J. Cramer and D.G. Truhlar, Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.

5. NMR Spectra of compound 10



10, ^{1}H NMR,
300 MHz, $CDCl_3$



10, ^{13}C NMR,
75 MHz, $CDCl_3$