Supporting Information
**Computational Data**

# Inexpensive and Bench Stable Diarylmethylium Tetrafluoroborates as Organocatalysts in the Light Mediated Hydrosulfonylation of Unactivated Alkenes.

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**Computational method.**

The structures of the reactants, intermediates and transition states have been optimized by using the density functional method (DFT)[1] with the functional M0-2X[2,3] and the basis sets def2-SVP.[4] The electronic energy values where refined by re-optimization with the basis set def2-TZVP.[5] The nature of the critical points was characterized by using vibrational analysis[6] which also furnished the Zero Point Energies (ZPE) and entropies for the calculations of the Free Energies. These have been converted from the gas phase to the 1 M standard state at 1 atm and 298.15 K.[7] The solvent effects (dichloromethane and water for some cases) were introduced in all calculations using the universal solvation model (SMD) by Truhalr *et al*.[8] The singlet excited states have been optimized with the Time-Dependet DFT.[9] The calculations were performed by the quantum package Gaussian 16-A.03[10] The figures were obtained using the graphical program Molden.[11]


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[11] G. Schaftenaar, J.H. Noordik, Molden: A pre- and post-processing program for molecular and electronic structures, J. Comput. Aided. Mol. Des. 14 (2000) 123–134, DOI: 10.1023/A:1008193805436.

**The molecular and electronic structure of the catalyst I and the role of the solvent.**

The catalyst **I** is the 1,2-Dimethyl-3-(2-methoxynaphth-1-yl-methenyl)-indolynium (hereafter, indolynium $\mathbf{I}^+$) tetrafluoroborate. Here we report the result of the analisys of its possible configurations and conformation.

Considering the rotation of the 2-methoxynaphth-1-yl moiety with respects to the indole plane, the indolynium $\mathbf{I}^+$ exists in two conformations, *anti* and *syn* (each one with its enantiomer) with the same energies (Table S-1a in the SI). The group charges and the shape of the LUMO are coherent with the delocalization of the positive charge on the π system of the indol and methenyl ($C^{10}$) moieties and a small contribution of the aromatic ring of the naphthyl bound through the $C^{10}$ to the indol moiety (see Figure S-1 in the SI). The addition of the counter-ion tetrafluoborate generates at least eight ion-couples $\mathbf{C}^+$ $BF_4^-$ whose free energies span by only 2.3 kcal $mol^{-1}$ (Table S-1b in the SI). The electrostatic interaction in not specific therefore $BF_4^-$ can assume different positions with almost the same energy. Interestingly, the most stable ion-couple is isoergic with the dissociated carbocation and $BF_4^-$. However, we must take in account that the real environment is not that of the pure dichloromethane as used for in the calculations, but possibly a more polar environment because of the presence of large amounts of water and acetic acid. As a matter of fact, the dissociation of the ion-couple when calculated in water (Table S-1c in the SI) is thermodynamically favored ($\Delta G$ = -5.6 kcal $mol^{-1}$ vs -0.03 in $CH_2Cl_2$). We assumed that the correct value should be somewhere in the middle.

The charges on the catalyzer are quite delocalized so the interaction with the solvent are expected to be non too strong and the SMD solvation model is expected to be reliable. By contrast, in the case of the sodium phenylsulphinate **2a**, the charges are mole localized. This is, of course, particularly true for the sodium cation. Therefore, the interaction with the solvent are expected to be stronger and more specific, so, the SMD solvation model could be not reliable. Moreover, as observed above, the presence of water and acetic acid makes the modeling of the solvent even more difficult. As a consequence, the energy differences that imply different levels of solvation of the components and derivatives of **2a** cannot be taken as very accurate. For a recent discussion on the solvation of iocic specis see, for example, M. Bensberg, P. L. Türtscher, J. P. Unsleber, M. Reiher, J Neugebauer "Solvation Free Energies in Subsystem Density Functional Theory." *J. Chem. Theory Comput.* **2022**, *18*, 723−740

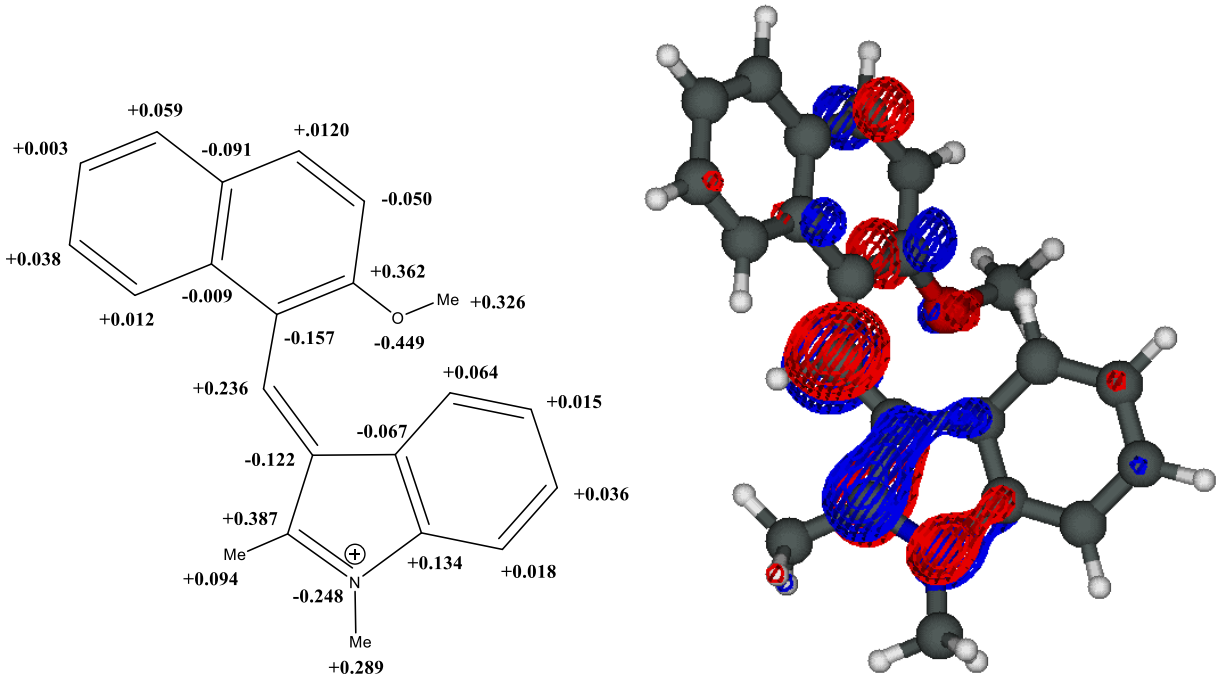



**Figure S-1.** Natural Atomic Group charges (left) and LUMO (right) of the *anti*-Indolynium $\mathbf{I}^{+}$.

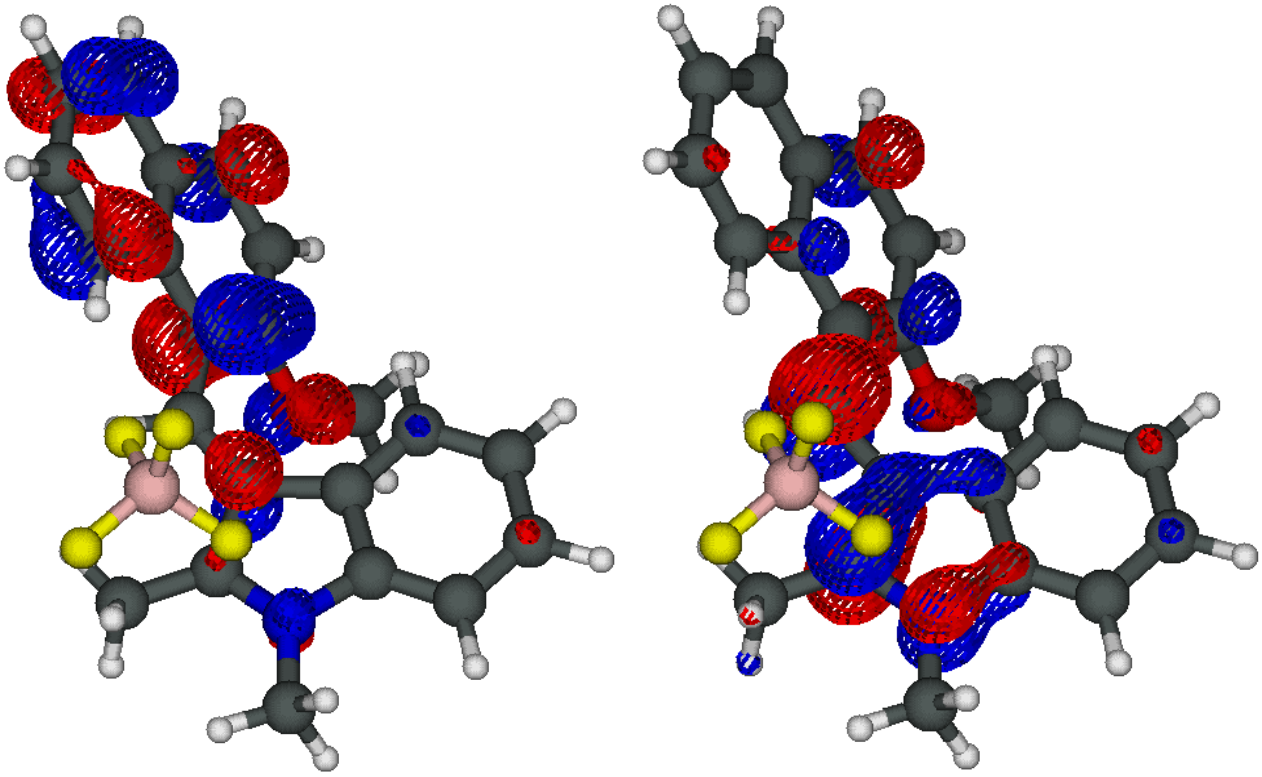


**Figure S-2.** HOMO (left) and LUMO (right) of the ion-couple *anti*-Indolynium $\mathbf{I}^{+}$ $BF_4^-$.

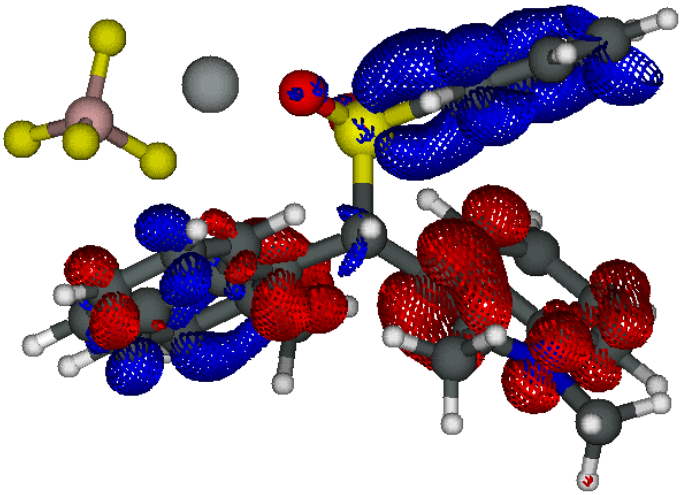


**Figure S-3.** Differential density map for the first excited state of the S–C adduct **AD**. Right, the red areas correspond to a reduction in the electronic density when going from $S_0$ to $S_1$, and the blue areas correspond to an increase in the electronic density.

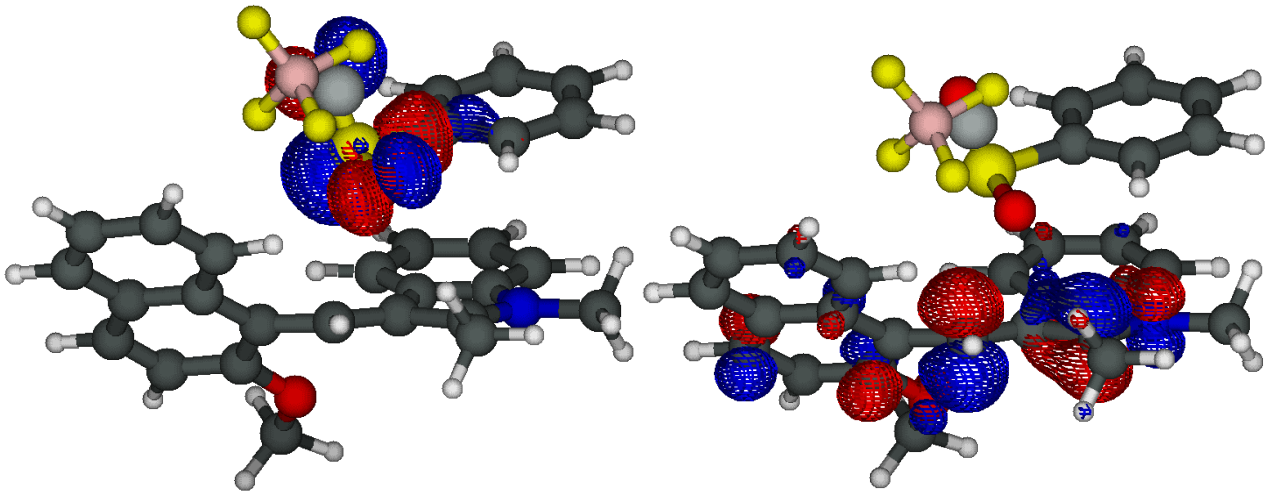


**Figure S-4a.** HOMO (left) and LUMO (right) of the complex **A** between **I** and the phenylsuphinate **2a**.

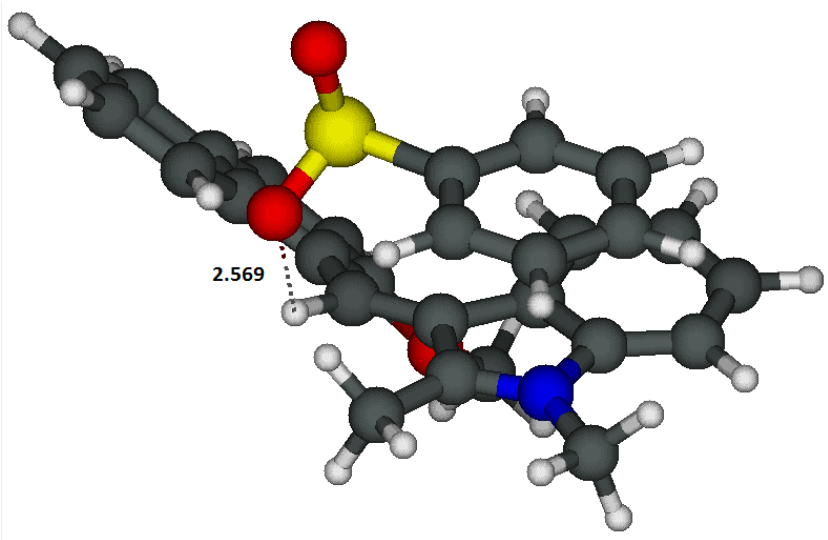



**Figure S-4b.** Complex **A'** between $\mathbf{I}^+$ and the phenylsuphinate $\mathbf{2a}^-$.

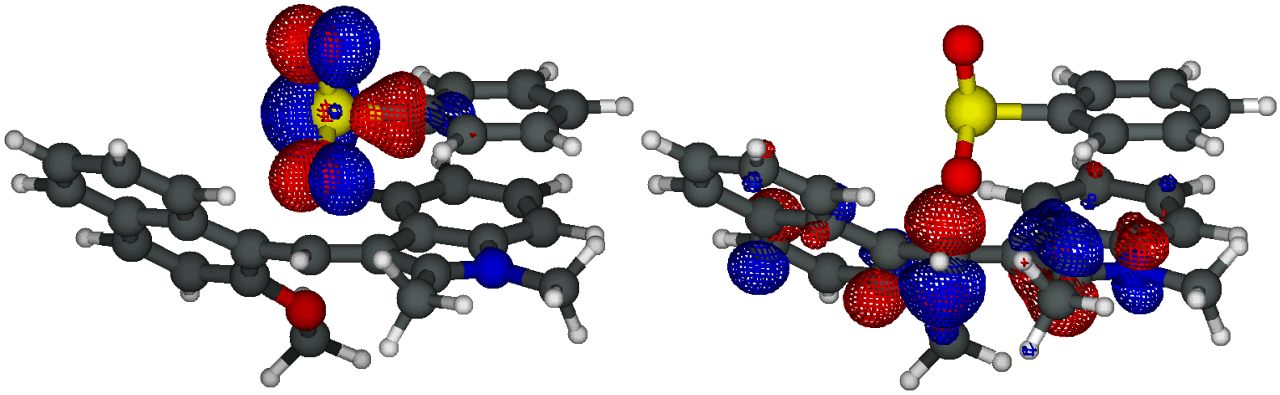


**Figure S-4c.** HOMO (left) and LUMO (right) of the complex **A'** between $\mathbf{I}^+$ and the phenylsuphinate $\mathbf{2a}^-$.

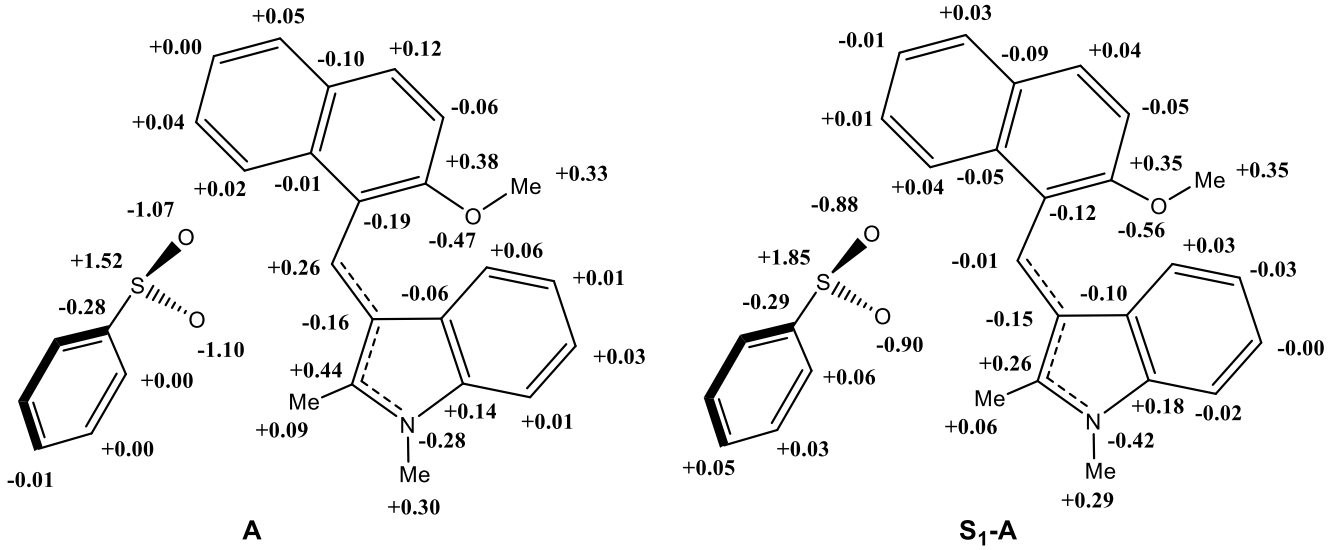



**Figure S-5.** Natural Atomic Group charges in the complex **A'** between the phenylsulphinate $\mathbf{2a}^-$ and the *anti*-indolynium $\mathbf{I}^+$ (left) and in its first excited state $\mathbf{S_1}$**-A'*** (right). The phenylsulphinate has been reoriented for clarity.

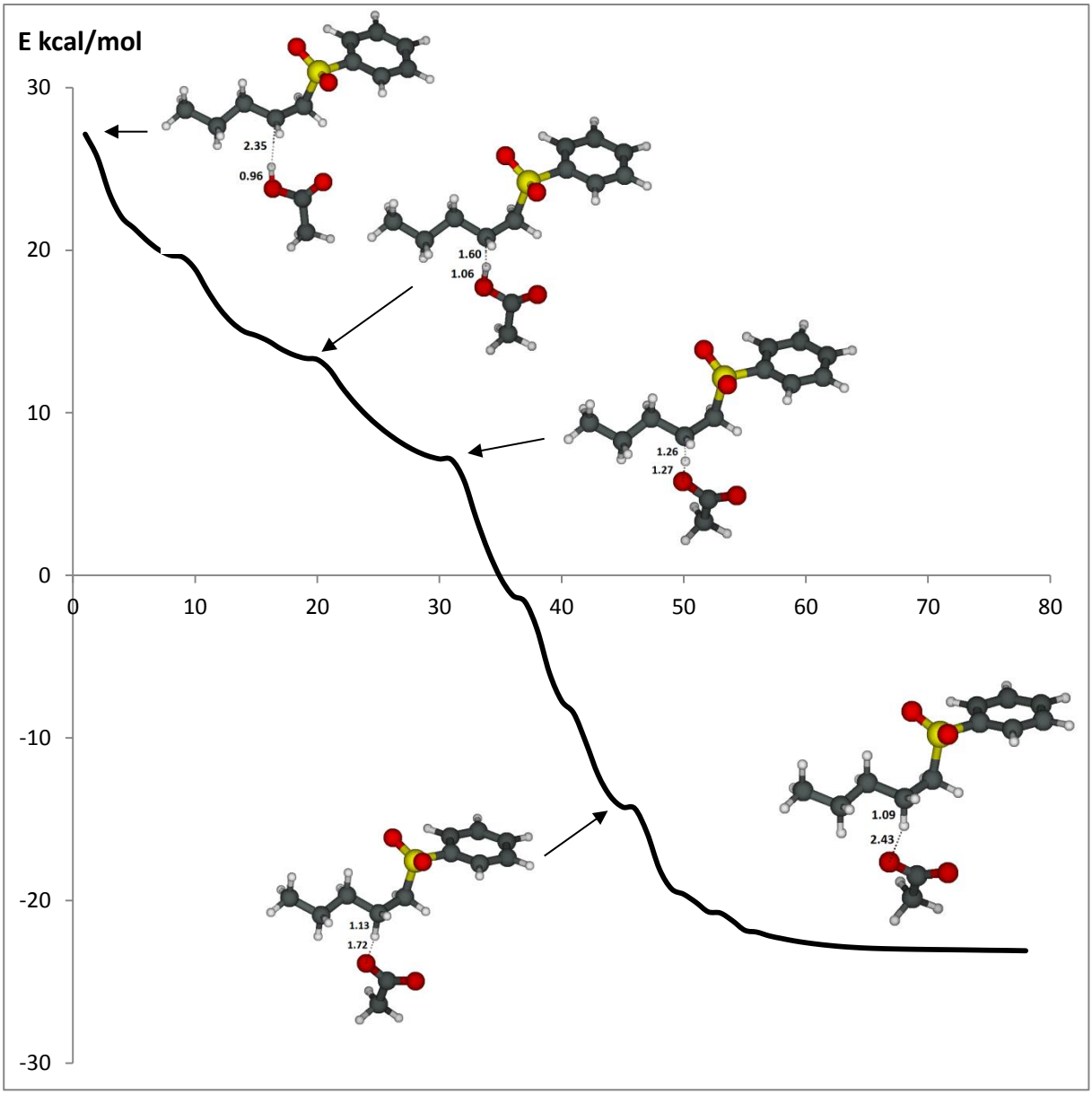



**Figure S-6.** Energy profile of the PCET in the reduced complex **CA** between the radical **3d**$^{\bullet}$ and the acetic acid.

**Table S-1a.** Calculated absolute and relative (in kcal $mol^{-1}$) energies of the configurations of the Indolynium $I^+$ in $CH_2Cl_2$.

| Table S-1a | $I^+(x)$ | E /au[a] | $\Delta E^a$ | ZPE /au[a] | $\delta G^{298K}$ /au[a] | E TZ(D)/ au[b] | $\Delta E^b$ | $E^{0K}$ TZ(D)/ au[c] | $\Delta E^{0K}$ | G TZ(D) / au[c] | $\Delta G^{298K}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *anti*-MeO Cation | *a* | -979.101504 | **0.00** | 0.367875 | 0.319918 | -980.173815 | **0.00** | -979.805940 | **0.00** | -979.853897 | **0.00** |
| *syn*-MeO Cation | *s* | -979.100085 | **0.89** | 0.367260 | 0.318828 | -980.172734 | **0.68** | -979.805474 | **0.29** | -979.853906 | **-0.01** |

[a] M06-2X/def2-SVP; [b] M06-2X/def2-TZVP; [c] M06-2X/def2-TZVP enegies combined with thermal corrections M06-2X/def2-SVP.

**Table S-1b.** Calculated absolute and relative (in kcal $mol^{-1}$) energies of the configurations of the ion-couple AS14, $I^+$ $BF_4^-$ in $CH_2Cl_2$.

| Table S-1b | $I^+(x,y)$ | E /au[a] | $\Delta E^a$ | ZPE /au[a] | $\delta G^{298K}$ /au[a] | E TZ(D)/ au[b] | $\Delta E^b$ | $E^{0K}$ TZ(D)/ au[c] | $\Delta E^{0K}$ | G TZ(D) / au[c] | $\Delta n$ | $\Delta G^{298K}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *anti*-MeO, *anti*(MeO)-$BF_4$ | *a,a* | -1403.278588 | **0.00** | 0.383544 | 0.325757 | -1404.872015 | **0.00** | -1404.488471 | **0.00** | -1404.546258 | **0** | **0.00** |
| *anti*-MeO, *syn*(MeO)-$BF_4$ | *a,s* | -1403.279124 | **-0.34** | 0.382939 | 0.325881 | -1404.871706 | **0.19** | -1404.488767 | **-0.19** | -1404.545825 | | **0.27** |
| *syn*-MeO, *anti*(MeO)-$BF_4$ | *s,a* | -1403.281360 | **-1.74** | 0.383330 | 0.326713 | -1404.872874 | **-0.54** | -1404.489545 | **-0.67** | -1404.546162 | | **0.06** |
| *syn*-MeO, *syn*(MeO)-$BF_4$ | *s,s* | -1403.277236 | **0.85** | 0.383272 | 0.325631 | -1404.871137 | **0.55** | -1404.487864 | **0.38** | -1404.545505 | | **0.47** |
| *anti*-MeO, *perp*-$BF_4$ | *a,p* | -1403.279686 | **-0.69** | 0.383670 | 0.326196 | -1404.871895 | **0.07** | -1404.488226 | **0.15** | -1404.545700 | | **0.35** |
| *anti*-MeO, *on-plane*-$BF_4$ | *a,pl* | -1403.276463 | **1.33** | 0.383468 | 0.325338 | -1404.869201 | **1.77** | -1404.485733 | **1.72** | -1404.543863 | | **1.50** |
| *syn*-MeO, *perp*-$BF_4$ | *s,p* | -1403.274166 | **2.77** | 0.383321 | 0.325152 | -1404.869179 | **1.78** | -1404.485858 | **1.64** | -1404.544027 | | **1.40** |
| *syn*-MeO, *on-plane*-$BF_4$ | *s,pl* | -1403.273119 | **3.43** | 0.383137 | 0.324370 | -1404.866930 | **3.19** | -1404.483793 | **2.94** | -1404.542560 | | **2.32** |
| $BF_4$ Anion | | -424.153019 | | 0.014756 | -0.012802 | -424.682628 | | -424.667873 | | -424.695431 | | |
| **Separated Ions** | | -1403.254523 | **15.10** | 0.382631 | 0.307116 | -1404.856443 | **9.77** | -1404.473813 | **9.20** | -1404.549328 | **1** | **-0.03** |

[a] M06-2X/def2-SVP; [b] M06-2X/def2-TZVP; [c] M06-2X/def2-TZVP enegies combined with thermal corrections M06-2X/def2-SVP.

**Table S-1c.** Calculated absolute and relative (in kcal $mol^{-1}$) energies of the ion-couple AS14 $I^+$ $BF_4^-$ and separated ions in water.

| Table S-1c | $I^+(x)$ | E /au[a] | $\Delta E^a$ | ZPE /au[a] | $\delta G^{298K}$ /au[a] | E TZ(D)/ au[b] | $\Delta E^b$ | $E^{0K}$ TZ(D)/ au[c] | $\Delta E^{0K}$ | G TZ(D) / au[c] | $\Delta n$ | $\Delta G^{298K}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *anti*-MeO, *anti*(MeO)-$BF_4$ | ***a,a*** | *-1403.264082* | **0.00** | 0.383613 | 0.326721 | -1404.856978 | **0.00** | -1404.473365 | **0.00** | -1404.530257 | **0** | **0.00** |
| *anti*-MeO Cation | ***a*** | -979.086402 | | 0.367090 | 0.318423 | -980.159142 | | -979.792052 | | -979.840719 | | |
| $BF_4$ Anion | | -424.158941 | | 0.014718 | -0.012839 | -424.688569 | | -424.673851 | | -424.701408 | | |
| **Separated Ions** | | -1403.245343 | **11.76** | 0.381808 | 0.305584 | -1404.847711 | **5.82** | -1404.465903 | **4.68** | -1404.542127 | **1** | **-5.55** |

[a] M06-2X/def2-SVP; [b] M06-2X/def2-TZVP; [c] M06-2X/def2-TZVP enegies combined with thermal corrections M06-2X/def2-SVP.

**Table S-2a.** Calculated absolute and relative (in kcal $mol^{-1}$) energies of the generation of the photo-active complex **A˙** from **2a** and **I** in $CH_2Cl_2$.

| Table S-2a | | E /au[a] | $\Delta E^a$ | ZPE /au[a] | $\delta G^{298K}$ /au[a] | E TZ(D)/ au[b] | $\Delta E^b$ | $E^{0K}$ TZ(D)/ au[c] | $\Delta E^{0K}$ | G TZ(D) / au[c] | $\Delta n$ | $\Delta G^{298K}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *anti*-MeO, *anti*(MeO)-$BF_4$ | I | -1403.282845 | | 0.383563 | 0.325957 | -1404.876211 | | -1404.492648 | | -1404.550254 | | |
| $C_6H_5SO_2Na$ | 2a | -941.962390 | | 0.100536 | 0.064633 | -942.621206 | | -942.520670 | | -942.556573 | | |
| Rgts 2a + I | | -2345.245235 | 0.00 | 0.484099 | 0.390590 | -2347.497417 | 0.00 | -2347.013318 | 0.00 | -2347.106827 | 0 | 0.00 |
| C–S Adduct X | AD | -2345.292562 | -29.70 | 0.487121 | 0.415494 | -2347.534990 | -23.58 | -2347.047869 | -21.68 | -2347.119496 | -1 | -9.84 |
| Complex A | A | -2345.288174 | -26.94 | 0.485026 | 0.411854 | -2347.527419 | -18.83 | -2347.042393 | -18.24 | -2347.115565 | -1 | -7.38 |

[a] M06-2X/def2-SVP; [b] M06-2X/def2-TZVP; [c] M06-2X/def2-TZVP enegies combined with thermal corrections M06-2X/def2-SVP.

**Table S-2b.** Calculated absolute and relative (in kcal mol$^{-1}$) energies of the generation of the radical **2a$^{\bullet}$** from **2a$^{-}$** and **I$^{+}$** in $CH_2Cl_2$.

| Table S-2b | | E /au[a] | $\Delta E^a$ | ZPE /au[a] | $\delta G^{298K}$ /au[a] | E TZ(D)/ au[b] | $\Delta E^b$ | $E^{0K}$ TZ(D)/ au[c] | $\Delta E^{0K}$ | G TZ(D) / au[c] | $\Delta n$ | $\Delta G^{298K}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *anti*-MeO Cation | **I$^{+}$** | -979.104519 | | 0.367382 | 0.318597 | -980.176921 | | -979.809539 | | -979.858324 | | |
| $C_6H_5SO_2$ Anion | **2a$^{-}$** | -779.767525 | | 0.098720 | 0.065631 | -780.395586 | | -780.296866 | | -780.329955 | | |
| Ox. $C_6H_5SO_2$ Anion | | | | | | *-780.214409* | *4.93* | *eV* | | | | |
| **Ions 2a$^{-}$ + I$^{+}$** | | -1758.872045 | **0.00** | 0.466103 | 0.384229 | -1760.572507 | **0.00** | -1760.106404 | **0.00** | -1760.188278 | **0** | **0.00** |
| **Complex A'** | **A** | -1758.909163 | **-23.29** | 0.467745 | 0.407375 | -1760.597724 | **-15.82** | -1760.129979 | **-14.79** | -1760.190349 | **-1** | **-3.19** |
| **Complex $S_1$-A'*** | | -1758.866587 | **3.42** | | | -1760.545659 | **16.85** | | | | | |
| **Complex $T_1$ A'** | | -1758.879100 | **-4.43** | 0.465134 | 0.402151 | -1760.561815 | **6.71** | -1760.096681 | **6.10** | -1760.159664 | **-1** | **16.06** |
| *anti*-MeO Radical | **I$^{\bullet}$** | -979.243199 | | 0.364413 | 0.314966 | -980.314750 | | -979.950336 | | -979.999783 | | |
| $C_6H_5SO_2$ Radical | **2a$^{\bullet}$** | -779.613116 | | 0.099784 | 0.066233 | -780.230838 | | -780.131054 | | -780.164605 | | |
| **Radicals 2a$^{\bullet}$ + I$^{\bullet}$** | | -1758.856315 | **9.87** | 0.464197 | 0.381199 | -1760.545587 | **16.89** | -1760.081390 | **15.70** | -1760.164388 | **0** | **14.99** |

[a] M06-2X/def2-SVP; [b] M06-2X/def2-TZVP; [c] M06-2X/def2-TZVP enegies combined with thermal corrections M06-2X/def2-SVP.

**Table S-2c.** Calculated absolute and relative (in kcal $mol^{-1}$) energies of the reactions from the radical **R-2a** to the products in $CH_2Cl_2$.

| Table S-2c | | E /au[a] | $\Delta E^a$ | ZPE /au[a] | $\delta G^{298K}$ /au[a] | E TZ(D)/ au[b] | $\Delta E^b$ | $E^{0K}$ TZ(D)/ au[c] | $\Delta E^{0K}$ | G TZ(D) / au[c] | $\Delta n$ | $\Delta G^{298K}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-Penthene | **1x** | -196.279205 | | 0.136924 | 0.106958 | -196.504400 | | -196.367475 | | -196.397441 | | |
| $C_6H_5SO_2$ Radical | **2a**$^\bullet$ | -779.613116 | | 0.099784 | 0.066233 | -780.230838 | | -780.131054 | | -780.164605 | | |
| **Reactants 1x + 2a**$^\bullet$ | | -975.892321 | **0.00** | 0.236708 | 0.173191 | -976.735237 | **0.00** | -976.498529 | **0.00** | -976.562046 | **0** | **0.00** |
| $TS_{Add}$ | | -975.892052 | **0.17** | 0.237484 | 0.191843 | -976.733624 | **1.01** | -976.496140 | **1.50** | -976.541781 | **-1** | **10.82** |
| **Radical Adduct 3d** | **3d**$^\bullet$ | -975.907468 | **-9.51** | 0.239243 | 0.194960 | -976.751851 | **-10.43** | -976.512608 | **-8.83** | -976.556891 | **-1** | **1.34** |
| AcOH | | -228.823833 | | 0.062241 | 0.035207 | -229.097734 | | -229.035493 | | -229.062527 | | |
| ***anti*-MeO Radical** | **I**$^\bullet$ | -979.243199 | | 0.364413 | 0.314966 | -980.314750 | | -979.950336 | | -979.999783 | | |
| **3d**$^\bullet$ **+ AcOH + I**$^\bullet$ | | -2183.974501 | **0.00** | 0.665898 | 0.545134 | -2186.164335 | **0.00** | -2185.498437 | **0.00** | -2185.619201 | **0** | **0.00** |
| Product | **3d** | -976.569322 | | 0.253716 | 0.210769 | -977.414128 | | -977.160412 | | -977.203359 | | |
| $AcO^-$ | | -228.319884 | | 0.048910 | 0.021839 | -228.609806 | | -228.560896 | | -228.587967 | | |
| ***anti*-MeO Cation** | **I**$^+$ | -979.104519 | | 0.367382 | 0.318597 | -980.176921 | | -979.809539 | | -979.858324 | | |
| **3d + AcO**$^-$ **+ I**$^+$ | | -2183.993725 | **-12.06** | 0.670008 | 0.551205 | -2186.200855 | **-22.92** | -2185.530847 | **-20.34** | -2185.649650 | **0** | **-19.11** |
| **3d**$^\bullet$ **+ I**$^\bullet$ | | -1955.150668 | **0.00** | 0.603657 | 0.509927 | -1957.066601 | **0.00** | -1956.462944 | **0.00** | -1956.556674 | **0** | **0.00** |
| Reduced 3d$^\bullet$ | **Not stable: breacks in 1-pentene and 2a'** | | | | | ***-976.837591*** | | | | | | |
| **Reduced 3d**$^\bullet$ **+ I**$^+$ | | | | | | -1957.014512 | **32.69** | | | | | |
| Cpl AcOH * 3d$^\bullet$ | **CA** | -1204.739497 | **-5.14** | 0.302570 | 0.246552 | -1205.854626 | **-5.14** | -1205.552055 | **-5.14** | -1205.608073 | **-1** | **7.13** |
| **CA + I**$^\bullet$ | | -2183.982697 | **0.00** | 0.666984 | 0.561519 | -2186.169363 | **0.00** | -2185.502379 | **0.00** | -2185.607844 | **0** | **0.00** |
| Cpl $AcO^-$ * 3d | **CB** | -1204.909312 | | 0.304204 | 0.251221 | -1206.033950 | | -1205.729746 | | -1205.782729 | | |
| **CB + I**$^+$ | | -2184.013831 | **-19.54** | 0.671586 | 0.569818 | -2186.210871 | **-26.05** | -2185.539284 | **-23.16** | -2185.641052 | **0** | **-20.84** |
| $NaBF_4$ | | -586.311112 | | 0.015738 | 0.014928 | -586.880016 | | -586.864278 | | -586.894944 | | |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **CB + $I^+$ + $NaBF_4$** | | -2770.324943 | **0.00** | 0.687324 | 0.554890 | -2773.090887 | **0.00** | -2772.403562 | **0.00** | -2772.535996 | **0** | **0.00** |
| *anti*-MeO, *anti*(MeO)-$BF_4$ | **C(*a,a*)** | -1403.282845 | | 0.383563 | 0.325957 | -1404.876211 | | -1404.492648 | | -1404.550254 | | |
| AcONa | | -390.512843 | | 0.050765 | 0.019824 | -390.838719 | | -390.787953 | | -390.818894 | | |
| **3d + AcONa + C(*a,a*)** | | -2770.365010 | **-25.14** | 0.688044 | 0.556550 | -2773.129058 | **-23.95** | -2772.441013 | **-23.50** | -2772.572507 | **1** | **-21.02** |

[a] M06-2X/def2-SVP; [b] M06-2X/def2-TZVP; [c] M06-2X/def2-TZVP enegies combined with thermal corrections M06-2X/def2-SVP.

**Table S-1d'.** Calculated absolute and relative (in kcal $mol^{-1}$) energies of whole reaction in $CH_2Cl_2$.

| Table S-2d' | | E /au[a] | $\Delta E^a$ | ZPE /au[a] | $\delta G^{298K}$ /au[a] | E TZ(D)/ au[b] | $\Delta E^b$ | $E^{0K}$ TZ(D)/ au[c] | $\Delta E^{0K}$ | G TZ(D) / au[c] | $\Delta n$ | $\Delta G^{298K}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-Penthene | **1x** | -196.279205 | | 0.136924 | 0.106958 | -196.504400 | | -196.367475 | | -196.397441 | | |
| $C_6H_5SO_2Na$ | **2a** | -941.962390 | | 0.100536 | 0.064634 | -942.621206 | | -942.520671 | | -942.556573 | | |
| AcOH | | -228.823833 | | 0.062241 | 0.035207 | -229.097734 | | -229.035493 | | -229.062527 | | |
| **1x + 2a + AcOH** | | -1367.065428 | **0.00** | 0.299701 | 0.206799 | -1368.223340 | **0.00** | -1367.923639 | **0.00** | -1368.016541 | **0** | **0.00** |
| Product | **3d** | -976.569322 | | 0.253716 | 0.210769 | -977.414128 | | -977.160412 | | -977.203359 | | |
| AcONa | | -390.512843 | | 0.050765 | 0.019824 | -390.838719 | | -390.787953 | | -390.818894 | | |
| **3d + AcONa** | | -1367.082165 | **-10.50** | 0.304481 | 0.230593 | -1368.252847 | **-18.52** | -1367.948366 | **-15.52** | -1368.022254 | **1** | **-1.69** |

[a] M06-2X/def2-SVP; [b] M06-2X/def2-TZVP; [c] M06-2X/def2-TZVP enegies combined with thermal corrections M06-2X/def2-SVP.

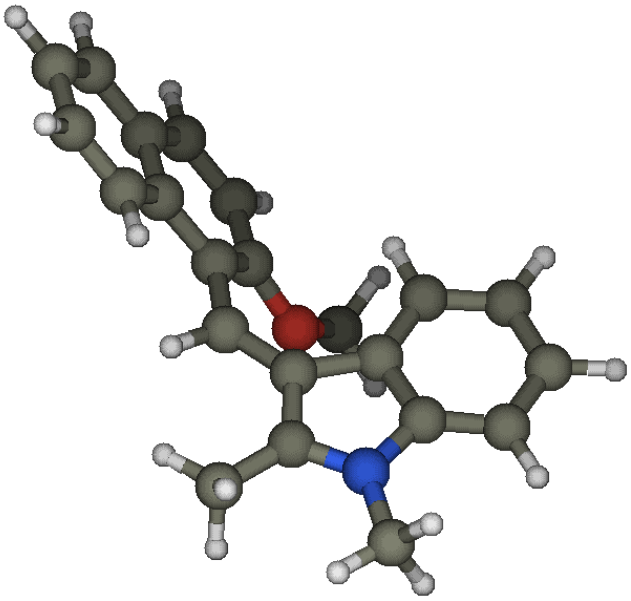
**Table S-2d".** Calculated absolute and relative (in kcal $mol^{-1}$) energies of whole reaction in in water.

| Table S-2d" | | E /au[a] | $\Delta E^a$ | ZPE /au[a] | $\delta G^{298K}$ /au[a] | E TZ(D)/ au[b] | $\Delta E^b$ | $E^{0K}$ TZ(D)/ au[c] | $\Delta E^{0K}$ | G TZ(D) / au[c] | $\Delta n$ | $\Delta G^{298K}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-Penthene | **1x** | -196.270649 | | 0.136923 | 0.106936 | -196.496021 | | -196.359098 | | -196.389085 | | |
| $C_6H_5SO_2Na$ | **2a** | -941.968281 | | 0.100548 | 0.064822 | -942.625426 | | -942.524878 | | -942.560604 | | |
| AcOH | | -228.825051 | | 0.061963 | 0.034903 | -229.098744 | | -229.036781 | | -229.063841 | | |
| **1x + 2a + AcOH** | | -1367.063981 | **0.00** | 0.299434 | 0.206661 | -1368.220191 | **0.00** | -1367.920757 | **0.00** | -1368.013530 | **0** | **0.00** |
| Product | **3d** | -976.564264 | | 0.253612 | 0.210521 | -977.407710 | | -977.154098 | | -977.197189 | | |
| AcONa | | -390.523303 | | 0.050543 | 0.019468 | -390.848380 | | -390.797837 | | -390.828912 | | |
| **3d + AcONa** | | -1367.087567 | **-14.80** | 0.304155 | 0.229989 | -1368.256090 | **-22.53** | -1367.951935 | **-19.56** | -1368.026101 | **1** | **-5.99** |

[a] M06-2X/def2-SVP; [b] M06-2X/def2-TZVP; [c] M06-2X/def2-TZVP enegies combined with thermal corrections M06-2X/def2-SVP.

**Pictures** and **Cartesian coordinates** of optimized structures M06-2X/def2-TZVP.

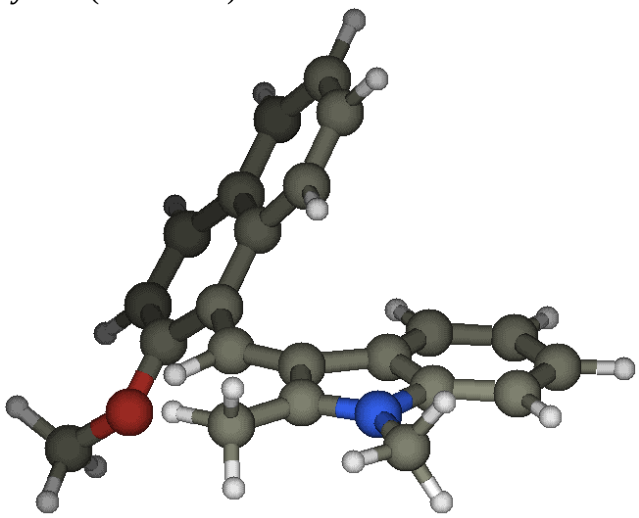
***anti*-$\mathbf{I}^+$** (Table S-1a)



| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 0.006505 | -0.007916 | 0.019078 |
| 2 | 6 | 0 | -0.003622 | 0.022015 | 1.332708 |
| 3 | 6 | 0 | 1.367010 | 0.022168 | 1.815601 |
| 4 | 6 | 0 | 2.204071 | -0.043221 | 0.618947 |
| 5 | 6 | 0 | 1.330629 | -0.065602 | -0.469578 |
| 6 | 6 | 0 | 1.741571 | -0.160042 | -1.784220 |
| 7 | 6 | 0 | 3.111230 | -0.251286 | -2.001260 |
| 8 | 6 | 0 | 4.006910 | -0.262852 | -0.933118 |
| 9 | 6 | 0 | 3.568160 | -0.160344 | 0.381709 |
| 10 | 6 | 0 | -1.259506 | 0.082841 | 2.113164 |
| 11 | 1 | 0 | -1.809918 | 0.991047 | 1.858008 |
| 12 | 1 | 0 | -1.892819 | -0.772193 | 1.869673 |
| 13 | 1 | 0 | -1.066383 | 0.089192 | 3.180778 |
| 14 | 6 | 0 | -1.142555 | 0.007204 | -0.869116 |
| 15 | 1 | 0 | 1.036483 | -0.171088 | -2.604769 |
| 16 | 1 | 0 | 3.484730 | -0.326118 | -3.014053 |
| 17 | 1 | 0 | 5.066927 | -0.354002 | -1.131736 |
| 18 | 1 | 0 | 4.280697 | -0.186580 | 1.194186 |
| 19 | 6 | 0 | 1.662227 | -0.007294 | 3.142278 |
| 20 | 6 | 0 | 2.939769 | 0.126696 | 3.799903 |
| 21 | 1 | 0 | 0.826027 | -0.170472 | 3.814421 |
| 22 | 6 | 0 | 3.856622 | 1.105902 | 3.410983 |
| 23 | 6 | 0 | 5.057292 | 1.298846 | 4.135374 |
| 24 | 6 | 0 | 5.318278 | 0.539719 | 5.236838 |
| 25 | 6 | 0 | 4.412654 | -0.450403 | 5.689975 |
| 26 | 6 | 0 | 3.210417 | -0.660541 | 4.971332 |
| 27 | 8 | 0 | 3.519106 | 1.888049 | 2.380194 |
| 28 | 1 | 0 | 5.757740 | 2.060475 | 3.826326 |
| 29 | 6 | 0 | 4.697371 | -1.228526 | 6.835012 |
| 30 | 6 | 0 | 2.339125 | -1.681935 | 5.418600 |
| 31 | 1 | 0 | 6.236447 | 0.695169 | 5.791282 |
| 32 | 6 | 0 | 3.822142 | -2.189852 | 7.260433 |
| 33 | 1 | 0 | 5.625152 | -1.046853 | 7.364642 |
| 34 | 1 | 0 | 4.042051 | -2.783488 | 8.138107 |
| 35 | 6 | 0 | 2.633825 | -2.415429 | 6.538808 |
| 36 | 1 | 0 | 1.437971 | -1.908142 | 4.863869 |

| | | | | | |
|---|---|---|---|---|---|
| 37 | 1 | 0 | 1.949399 | -3.187948 | 6.866220 |
| 38 | 1 | 0 | -1.138335 | -0.901293 | -1.470107 |
| 39 | 1 | 0 | -2.055752 | 0.057515 | -0.286534 |
| 40 | 1 | 0 | -1.072783 | 0.875459 | -1.523136 |
| 41 | 6 | 0 | 4.467995 | 2.811917 | 1.859539 |
| 42 | 1 | 0 | 4.000451 | 3.246159 | 0.979642 |
| 43 | 1 | 0 | 4.686069 | 3.598591 | 2.583547 |
| 44 | 1 | 0 | 5.389991 | 2.303763 | 1.570957 |

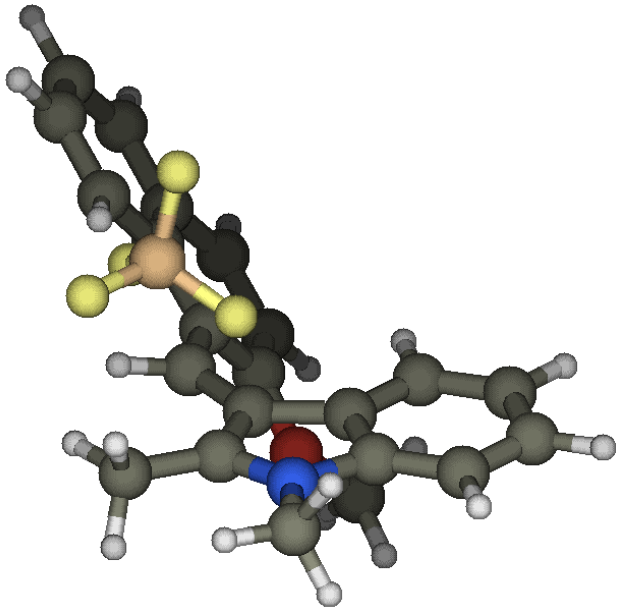
***syn*-I**$^{+}$ (Table S-1a)



| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 0.007964 | -0.002135 | 0.013316 |
| 2 | 6 | 0 | -0.000183 | -0.033502 | 1.326476 |
| 3 | 6 | 0 | 1.371480 | -0.017823 | 1.807298 |
| 4 | 6 | 0 | 2.206865 | 0.062037 | 0.608252 |
| 5 | 6 | 0 | 1.329876 | 0.073484 | -0.478334 |
| 6 | 6 | 0 | 1.735874 | 0.179968 | -1.793090 |
| 7 | 6 | 0 | 3.103898 | 0.291561 | -2.013039 |
| 8 | 6 | 0 | 4.002003 | 0.310306 | -0.947919 |
| 9 | 6 | 0 | 3.568802 | 0.199113 | 0.368604 |
| 10 | 6 | 0 | -1.252704 | -0.110519 | 2.110358 |
| 11 | 1 | 0 | -1.904476 | 0.727330 | 1.856578 |
| 12 | 1 | 0 | -1.784204 | -1.033770 | 1.869106 |
| 13 | 1 | 0 | -1.056415 | -0.096930 | 3.177315 |
| 14 | 6 | 0 | -1.142470 | -0.028439 | -0.873148 |
| 15 | 1 | 0 | 1.028610 | 0.186311 | -2.611770 |
| 16 | 1 | 0 | 3.473523 | 0.376484 | -3.026445 |
| 17 | 1 | 0 | 5.060298 | 0.414841 | -1.148434 |
| 18 | 1 | 0 | 4.283394 | 0.228013 | 1.178370 |
| 19 | 6 | 0 | 1.670716 | 0.005613 | 3.132632 |
| 20 | 6 | 0 | 2.958593 | -0.101878 | 3.779441 |
| 21 | 1 | 0 | 0.841115 | 0.172699 | 3.811486 |
| 22 | 6 | 0 | 3.184322 | 0.763072 | 4.853577 |
| 23 | 6 | 0 | 4.410604 | 0.752423 | 5.552706 |
| 24 | 6 | 0 | 5.382008 | -0.134435 | 5.189534 |
| 25 | 6 | 0 | 5.182592 | -1.076000 | 4.152525 |
| 26 | 6 | 0 | 3.952363 | -1.080704 | 3.445299 |
| 27 | 8 | 0 | 2.199486 | 1.629100 | 5.136381 |
| 28 | 1 | 0 | 4.587107 | 1.449985 | 6.358052 |
| 29 | 6 | 0 | 6.180535 | -2.030338 | 3.842777 |
| 30 | 6 | 0 | 3.743170 | -2.106616 | 2.492322 |
| 31 | 1 | 0 | 6.330102 | -0.136902 | 5.714487 |

| | | | | | |
|---|---|---|---|---|---|
| 32 | 6 | 0 | 5.963207 | -2.983169 | 2.887466 |
| 33 | 1 | 0 | 7.113993 | -1.995861 | 4.392128 |
| 34 | 1 | 0 | 6.726883 | -3.713754 | 2.655035 |
| 35 | 6 | 0 | 4.721813 | -3.025898 | 2.221187 |
| 36 | 1 | 0 | 2.795277 | -2.178213 | 1.978440 |
| 37 | 1 | 0 | 4.535282 | -3.802023 | 1.489507 |
| 38 | 1 | 0 | -1.056402 | -0.887327 | -1.537410 |
| 39 | 1 | 0 | -2.053393 | -0.103851 | -0.289759 |
| 40 | 1 | 0 | -1.156009 | 0.887109 | -1.463282 |
| 41 | 6 | 0 | 2.344915 | 2.503771 | 6.250502 |
| 42 | 1 | 0 | 1.413699 | 3.060120 | 6.310990 |
| 43 | 1 | 0 | 2.496763 | 1.940976 | 7.172823 |
| 44 | 1 | 0 | 3.173669 | 3.195293 | 6.092359 |

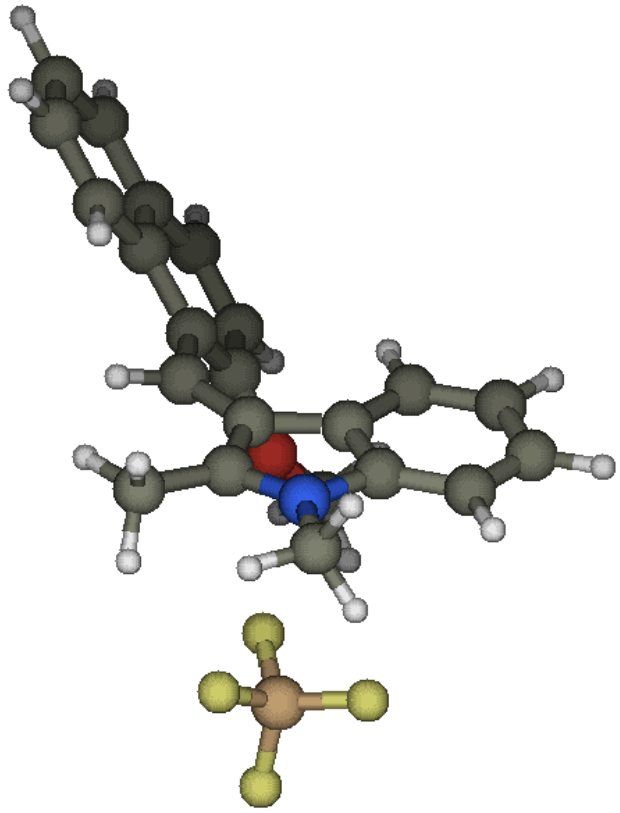
**Ion couple $I^+$ $BF_4^-$ (*a,a*)** (Table S-1b)



| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 0.033023 | -0.029907 | 0.006067 |
| 2 | 6 | 0 | 0.012790 | -0.013926 | 1.317735 |
| 3 | 6 | 0 | 1.382009 | -0.011238 | 1.810513 |
| 4 | 6 | 0 | 2.228003 | -0.050758 | 0.618552 |
| 5 | 6 | 0 | 1.360131 | -0.073066 | -0.474776 |
| 6 | 6 | 0 | 1.780095 | -0.153103 | -1.787133 |
| 7 | 6 | 0 | 3.152308 | -0.224935 | -1.998068 |
| 8 | 6 | 0 | 4.042134 | -0.232027 | -0.925773 |
| 9 | 6 | 0 | 3.594146 | -0.147287 | 0.387768 |
| 10 | 6 | 0 | -1.246216 | 0.045706 | 2.091076 |
| 11 | 1 | 0 | -1.774585 | 0.972496 | 1.854303 |
| 12 | 1 | 0 | -1.890465 | -0.792296 | 1.822567 |
| 13 | 1 | 0 | -1.059797 | 0.016288 | 3.159153 |
| 14 | 6 | 0 | -1.110362 | -0.068768 | -0.886325 |
| 15 | 1 | 0 | 1.079363 | -0.170592 | -2.611274 |
| 16 | 1 | 0 | 3.531468 | -0.289495 | -3.009542 |
| 17 | 1 | 0 | 5.104354 | -0.308878 | -1.118848 |
| 18 | 1 | 0 | 4.302038 | -0.174178 | 1.203892 |
| 19 | 6 | 0 | 1.664622 | -0.093247 | 3.133689 |
| 20 | 6 | 0 | 2.944004 | -0.006727 | 3.804202 |
| 21 | 1 | 0 | 0.820933 | -0.276652 | 3.790513 |
| 22 | 6 | 0 | 3.867756 | 0.985756 | 3.480506 |
| 23 | 6 | 0 | 5.067566 | 1.122620 | 4.218851 |

| | | | | | |
|---|---|---|---|---|---|
| 24 | 6 | 0 | 5.319469 | 0.293778 | 5.271853 |
| 25 | 6 | 0 | 4.405095 | -0.715784 | 5.656988 |
| 26 | 6 | 0 | 3.205159 | -0.870628 | 4.920071 |
| 27 | 8 | 0 | 3.541527 | 1.833897 | 2.494770 |
| 28 | 1 | 0 | 5.775979 | 1.895312 | 3.959980 |
| 29 | 6 | 0 | 4.676541 | -1.569881 | 6.750865 |
| 30 | 6 | 0 | 2.322631 | -1.914157 | 5.291173 |
| 31 | 1 | 0 | 6.237095 | 0.406550 | 5.837475 |
| 32 | 6 | 0 | 3.792289 | -2.551388 | 7.104545 |
| 33 | 1 | 0 | 5.601955 | -1.430769 | 7.297547 |
| 34 | 1 | 0 | 4.002525 | -3.204176 | 7.941834 |
| 35 | 6 | 0 | 2.607176 | -2.722200 | 6.360937 |
| 36 | 1 | 0 | 1.426154 | -2.098770 | 4.713278 |
| 37 | 1 | 0 | 1.917717 | -3.512961 | 6.628837 |
| 38 | 1 | 0 | -1.068303 | -0.987292 | -1.470366 |
| 39 | 1 | 0 | -2.027595 | -0.047183 | -0.308350 |
| 40 | 1 | 0 | -1.072236 | 0.791792 | -1.553416 |
| 41 | 6 | 0 | 4.504536 | 2.773205 | 2.035421 |
| 42 | 1 | 0 | 4.047895 | 3.267778 | 1.181881 |
| 43 | 1 | 0 | 4.731512 | 3.511709 | 2.806332 |
| 44 | 1 | 0 | 5.421365 | 2.271784 | 1.718820 |
| 45 | 9 | 0 | -0.195438 | -2.673820 | 2.963114 |
| 46 | 5 | 0 | -0.888453 | -3.373287 | 1.963906 |
| 47 | 9 | 0 | -0.492853 | -4.710030 | 1.965529 |
| 48 | 9 | 0 | -2.263996 | -3.283381 | 2.206454 |
| 49 | 9 | 0 | -0.602895 | -2.797551 | 0.716454 |

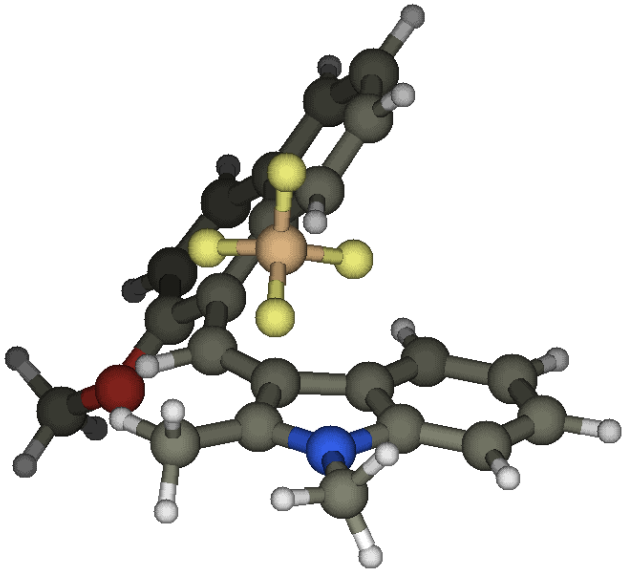
**Ion couple $I^+$ $BF_4^-$ (*a,s*)** (Table S-1b)



| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 0.021390 | -0.028410 | 0.046739 |
| 2 | 6 | 0 | 0.013417 | 0.041897 | 1.355447 |
| 3 | 6 | 0 | 1.389377 | 0.083943 | 1.837034 |

| | | | | | |
|---|---|---|---|---|---|
| 4 | 6 | 0 | 2.223772 | 0.025875 | 0.637011 |
| 5 | 6 | 0 | 1.346624 | -0.047200 | -0.445679 |
| 6 | 6 | 0 | 1.754623 | -0.145234 | -1.759858 |
| 7 | 6 | 0 | 3.125976 | -0.185888 | -1.983887 |
| 8 | 6 | 0 | 4.026428 | -0.144998 | -0.921630 |
| 9 | 6 | 0 | 3.589683 | -0.038969 | 0.394283 |
| 10 | 6 | 0 | -1.238752 | 0.090303 | 2.140231 |
| 11 | 1 | 0 | -1.790220 | 0.993445 | 1.868908 |
| 12 | 1 | 0 | -1.864002 | -0.773399 | 1.907543 |
| 13 | 1 | 0 | -1.042352 | 0.111330 | 3.207089 |
| 14 | 6 | 0 | -1.128566 | -0.124754 | -0.836908 |
| 15 | 1 | 0 | 1.046135 | -0.185773 | -2.576394 |
| 16 | 1 | 0 | 3.496441 | -0.256323 | -2.998164 |
| 17 | 1 | 0 | 5.088505 | -0.193096 | -1.124516 |
| 18 | 1 | 0 | 4.307609 | -0.019984 | 1.201656 |
| 19 | 6 | 0 | 1.689455 | 0.058952 | 3.157485 |
| 20 | 6 | 0 | 2.984382 | 0.168699 | 3.801002 |
| 21 | 1 | 0 | 0.858028 | -0.085597 | 3.839432 |
| 22 | 6 | 0 | 3.886558 | 1.167660 | 3.440078 |
| 23 | 6 | 0 | 5.110531 | 1.320760 | 4.135762 |
| 24 | 6 | 0 | 5.405245 | 0.502910 | 5.185716 |
| 25 | 6 | 0 | 4.510368 | -0.507969 | 5.612178 |
| 26 | 6 | 0 | 3.285821 | -0.676917 | 4.919010 |
| 27 | 8 | 0 | 3.517922 | 1.997232 | 2.458259 |
| 28 | 1 | 0 | 5.803164 | 2.096056 | 3.843143 |
| 29 | 6 | 0 | 4.823658 | -1.347382 | 6.706222 |
| 30 | 6 | 0 | 2.419915 | -1.715217 | 5.341851 |
| 31 | 1 | 0 | 6.341129 | 0.626181 | 5.718166 |
| 32 | 6 | 0 | 3.956504 | -2.326152 | 7.106591 |
| 33 | 1 | 0 | 5.767328 | -1.197273 | 7.217681 |
| 34 | 1 | 0 | 4.198892 | -2.965694 | 7.945317 |
| 35 | 6 | 0 | 2.743802 | -2.507695 | 6.411660 |
| 36 | 1 | 0 | 1.497458 | -1.901753 | 4.807583 |
| 37 | 1 | 0 | 2.063843 | -3.291595 | 6.721018 |
| 38 | 1 | 0 | -1.123326 | -1.106361 | -1.311237 |
| 39 | 1 | 0 | -2.040465 | 0.010932 | -0.266837 |
| 40 | 1 | 0 | -1.054202 | 0.654917 | -1.591490 |
| 41 | 6 | 0 | 4.427391 | 2.982743 | 1.988233 |
| 42 | 1 | 0 | 3.923599 | 3.471476 | 1.158694 |
| 43 | 1 | 0 | 4.645900 | 3.715763 | 2.766854 |
| 44 | 1 | 0 | 5.354049 | 2.525338 | 1.635709 |
| 45 | 9 | 0 | 0.626485 | 2.942727 | 0.696028 |
| 46 | 5 | 0 | -0.377951 | 3.275659 | -0.217799 |
| 47 | 9 | 0 | -0.558432 | 4.659466 | -0.238453 |
| 48 | 9 | 0 | -0.015027 | 2.827859 | -1.494771 |
| 49 | 9 | 0 | -1.576821 | 2.652935 | 0.165585 |

**Ion couple $I^+$ $BF_4^-$ (*s,a*)** (Table S-1b)

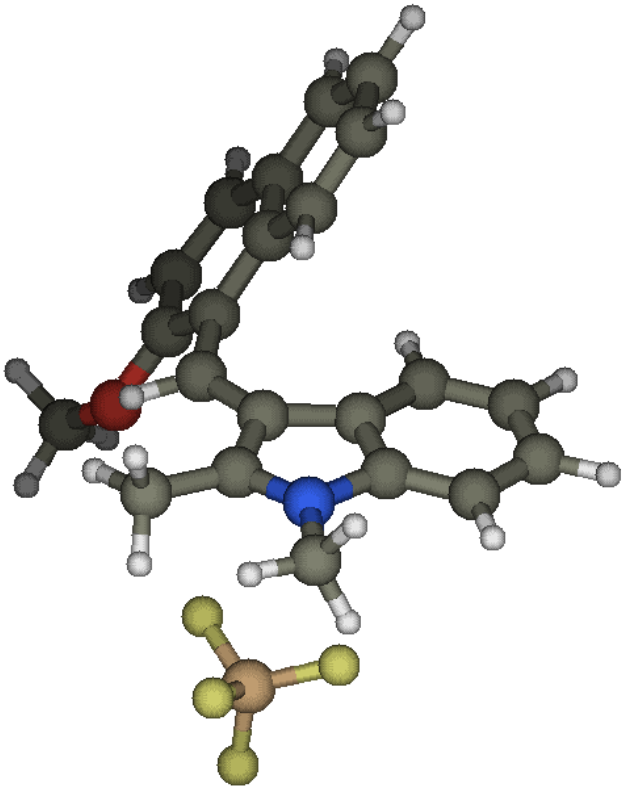


---

| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 0.002578 | 0.025703 | 0.017178 |
| 2 | 6 | 0 | 0.011487 | -0.000095 | 1.327645 |
| 3 | 6 | 0 | 1.394018 | -0.034312 | 1.787344 |
| 4 | 6 | 0 | 2.212482 | 0.019897 | 0.574842 |
| 5 | 6 | 0 | 1.318796 | 0.056851 | -0.496101 |
| 6 | 6 | 0 | 1.706759 | 0.129898 | -1.817245 |
| 7 | 6 | 0 | 3.075259 | 0.182804 | -2.061055 |
| 8 | 6 | 0 | 3.990710 | 0.172587 | -1.011900 |
| 9 | 6 | 0 | 3.573810 | 0.091476 | 0.313067 |
| 10 | 6 | 0 | -1.230432 | -0.003035 | 2.130513 |
| 11 | 1 | 0 | -1.824660 | 0.881019 | 1.890100 |
| 12 | 1 | 0 | -1.818065 | -0.889700 | 1.888185 |
| 13 | 1 | 0 | -1.017535 | -0.009510 | 3.194259 |
| 14 | 6 | 0 | -1.159286 | 0.016145 | -0.852959 |
| 15 | 1 | 0 | 0.987166 | 0.147614 | -2.624853 |
| 16 | 1 | 0 | 3.430823 | 0.238283 | -3.081588 |
| 17 | 1 | 0 | 5.049340 | 0.225350 | -1.230454 |
| 18 | 1 | 0 | 4.301769 | 0.087462 | 1.111677 |
| 19 | 6 | 0 | 1.717916 | -0.074714 | 3.100570 |
| 20 | 6 | 0 | 3.027719 | -0.262503 | 3.698100 |
| 21 | 1 | 0 | 0.912273 | 0.076840 | 3.811153 |
| 22 | 6 | 0 | 3.362015 | 0.581593 | 4.753904 |
| 23 | 6 | 0 | 4.613784 | 0.479553 | 5.398523 |
| 24 | 6 | 0 | 5.500446 | -0.478294 | 4.997548 |
| 25 | 6 | 0 | 5.185962 | -1.399368 | 3.971719 |
| 26 | 6 | 0 | 3.928146 | -1.309143 | 3.320429 |
| 27 | 8 | 0 | 2.452153 | 1.518336 | 5.078740 |
| 28 | 1 | 0 | 4.875180 | 1.160815 | 6.194611 |
| 29 | 6 | 0 | 6.093647 | -2.425103 | 3.611621 |
| 30 | 6 | 0 | 3.596878 | -2.305407 | 2.368718 |
| 31 | 1 | 0 | 6.466876 | -0.552485 | 5.482361 |
| 32 | 6 | 0 | 5.760960 | -3.349021 | 2.661676 |
| 33 | 1 | 0 | 7.051160 | -2.466457 | 4.117685 |
| 34 | 1 | 0 | 6.455310 | -4.134108 | 2.391520 |
| 35 | 6 | 0 | 4.490877 | -3.291515 | 2.049049 |
| 36 | 1 | 0 | 2.623432 | -2.301932 | 1.897513 |
| 37 | 1 | 0 | 4.212079 | -4.043396 | 1.321141 |
| 38 | 1 | 0 | -1.076798 | -0.830095 | -1.532933 |
| 39 | 1 | 0 | -2.061206 | -0.081564 | -0.259391 |

| | | | | | |
|---|---|---|---|---|---|
| 40 | 1 | 0 | -1.184047 | 0.945297 | -1.422098 |
| 41 | 6 | 0 | 2.694940 | 2.350295 | 6.206314 |
| 42 | 1 | 0 | 1.808288 | 2.969590 | 6.312187 |
| 43 | 1 | 0 | 2.834987 | 1.754802 | 7.110240 |
| 44 | 1 | 0 | 3.565423 | 2.987237 | 6.040502 |
| 45 | 9 | 0 | 0.943632 | -2.850911 | 0.307736 |
| 46 | 5 | 0 | -0.176668 | -3.303301 | 1.017625 |
| 47 | 9 | 0 | -0.239386 | -4.695122 | 0.962939 |
| 48 | 9 | 0 | -0.081003 | -2.885052 | 2.351189 |
| 49 | 9 | 0 | -1.334428 | -2.755673 | 0.444316 |

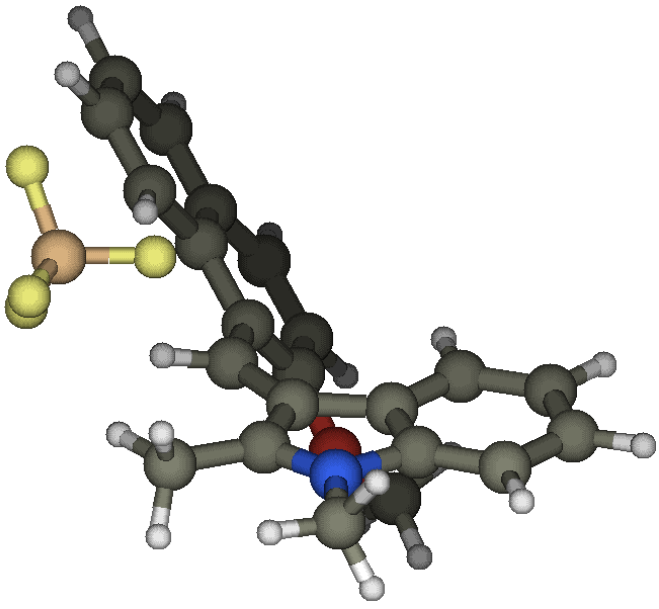
**Ion couple $I^+$ $BF_4^-$ (*s,s*)** (Table S-1b)



| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 0.041033 | -0.004689 | -0.039753 |
| 2 | 6 | 0 | 0.028206 | -0.019207 | 1.270337 |
| 3 | 6 | 0 | 1.404054 | -0.021488 | 1.756109 |
| 4 | 6 | 0 | 2.242338 | 0.036205 | 0.556933 |
| 5 | 6 | 0 | 1.366462 | 0.049787 | -0.529300 |
| 6 | 6 | 0 | 1.774495 | 0.143427 | -1.843225 |
| 7 | 6 | 0 | 3.144432 | 0.235357 | -2.063571 |
| 8 | 6 | 0 | 4.042225 | 0.247524 | -0.998895 |
| 9 | 6 | 0 | 3.605698 | 0.151983 | 0.318227 |
| 10 | 6 | 0 | -1.221571 | -0.076526 | 2.057756 |
| 11 | 1 | 0 | -1.920441 | 0.677891 | 1.698050 |
| 12 | 1 | 0 | -1.681617 | -1.061345 | 1.942046 |
| 13 | 1 | 0 | -1.032134 | 0.094462 | 3.112476 |
| 14 | 6 | 0 | -1.100799 | -0.030863 | -0.937034 |
| 15 | 1 | 0 | 1.067182 | 0.162464 | -2.661541 |
| 16 | 1 | 0 | 3.514761 | 0.313322 | -3.077367 |
| 17 | 1 | 0 | 5.101889 | 0.338631 | -1.199001 |
| 18 | 1 | 0 | 4.319136 | 0.179998 | 1.129027 |
| 19 | 6 | 0 | 1.700075 | 0.010347 | 3.075996 |
| 20 | 6 | 0 | 2.998442 | -0.075904 | 3.719552 |

| | | | | | |
|---|---|---|---|---|---|
| 21 | 1 | 0 | 0.871084 | 0.172851 | 3.756566 |
| 22 | 6 | 0 | 3.239980 | 0.837500 | 4.744831 |
| 23 | 6 | 0 | 4.472706 | 0.850645 | 5.433664 |
| 24 | 6 | 0 | 5.434295 | -0.061189 | 5.107706 |
| 25 | 6 | 0 | 5.218633 | -1.046557 | 4.116297 |
| 26 | 6 | 0 | 3.981598 | -1.071984 | 3.420121 |
| 27 | 8 | 0 | 2.260023 | 1.720512 | 4.995633 |
| 28 | 1 | 0 | 4.659974 | 1.584441 | 6.203694 |
| 29 | 6 | 0 | 6.208074 | -2.019047 | 3.833674 |
| 30 | 6 | 0 | 3.761217 | -2.128292 | 2.501286 |
| 31 | 1 | 0 | 6.386526 | -0.046770 | 5.624928 |
| 32 | 6 | 0 | 5.978171 | -3.003798 | 2.914940 |
| 33 | 1 | 0 | 7.147051 | -1.969284 | 4.372630 |
| 34 | 1 | 0 | 6.736239 | -3.746546 | 2.703119 |
| 35 | 6 | 0 | 4.732236 | -3.061492 | 2.255810 |
| 36 | 1 | 0 | 2.810704 | -2.205675 | 1.992368 |
| 37 | 1 | 0 | 4.538491 | -3.859369 | 1.549761 |
| 38 | 1 | 0 | -1.013165 | -0.902794 | -1.584670 |
| 39 | 1 | 0 | -2.018571 | -0.086377 | -0.362934 |
| 40 | 1 | 0 | -1.096234 | 0.878855 | -1.534819 |
| 41 | 6 | 0 | 2.426488 | 2.658668 | 6.051517 |
| 42 | 1 | 0 | 1.501487 | 3.227477 | 6.087904 |
| 43 | 1 | 0 | 2.584002 | 2.151706 | 7.005193 |
| 44 | 1 | 0 | 3.259624 | 3.331797 | 5.843393 |
| 45 | 9 | 0 | -0.144372 | 2.796842 | 1.756438 |
| 46 | 5 | 0 | -0.696654 | 3.245200 | 0.549014 |
| 47 | 9 | 0 | -0.883685 | 4.626257 | 0.601337 |
| 48 | 9 | 0 | 0.164271 | 2.922618 | -0.506298 |
| 49 | 9 | 0 | -1.932081 | 2.610355 | 0.346891 |

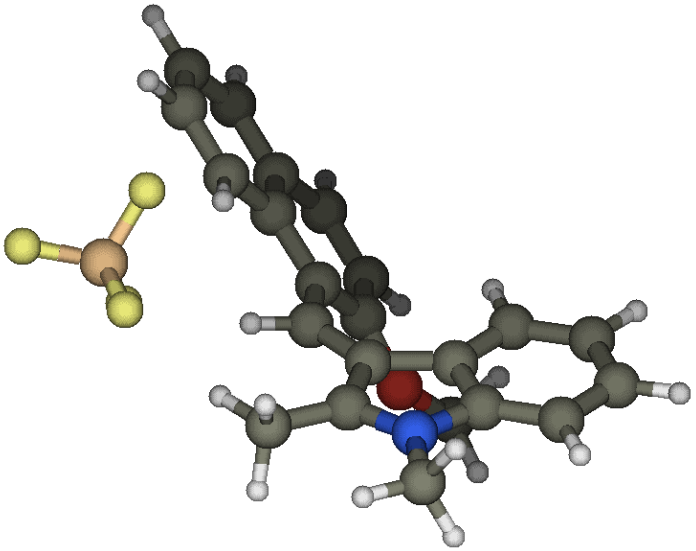
**Ion couple $I^+$ $BF_4^-$ (*a,p*)** (Table S-1b)



| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 0.011711 | 0.013182 | 0.045601 |
| 2 | 6 | 0 | -0.003226 | 0.045747 | 1.360200 |
| 3 | 6 | 0 | 1.365691 | 0.034610 | 1.846923 |
| 4 | 6 | 0 | 2.206995 | -0.025747 | 0.652534 |
| 5 | 6 | 0 | 1.336483 | -0.048398 | -0.438652 |
| 6 | 6 | 0 | 1.751535 | -0.142517 | -1.752127 |
| 7 | 6 | 0 | 3.121835 | -0.231208 | -1.966352 |

| | | | | | |
|---|---|---|---|---|---|
| 8 | 6 | 0 | 4.014598 | -0.240265 | -0.895844 |
| 9 | 6 | 0 | 3.571742 | -0.139479 | 0.417895 |
| 10 | 6 | 0 | -1.259135 | 0.140506 | 2.134955 |
| 11 | 1 | 0 | -1.781211 | 1.063121 | 1.869666 |
| 12 | 1 | 0 | -1.912498 | -0.699497 | 1.894626 |
| 13 | 1 | 0 | -1.069728 | 0.140629 | 3.202692 |
| 14 | 6 | 0 | -1.134035 | 0.035525 | -0.846110 |
| 15 | 1 | 0 | 1.048117 | -0.156017 | -2.574093 |
| 16 | 1 | 0 | 3.497800 | -0.306080 | -2.978296 |
| 17 | 1 | 0 | 5.075447 | -0.329098 | -1.091355 |
| 18 | 1 | 0 | 4.282240 | -0.164628 | 1.232126 |
| 19 | 6 | 0 | 1.657998 | -0.026810 | 3.172427 |
| 20 | 6 | 0 | 2.945824 | 0.086087 | 3.821109 |
| 21 | 1 | 0 | 0.821013 | -0.209292 | 3.840559 |
| 22 | 6 | 0 | 3.855531 | 1.079648 | 3.457823 |
| 23 | 6 | 0 | 5.064155 | 1.248735 | 4.174737 |
| 24 | 6 | 0 | 5.341629 | 0.449344 | 5.243984 |
| 25 | 6 | 0 | 4.445211 | -0.560493 | 5.668319 |
| 26 | 6 | 0 | 3.235376 | -0.745989 | 4.955233 |
| 27 | 8 | 0 | 3.507574 | 1.898427 | 2.455837 |
| 28 | 1 | 0 | 5.758961 | 2.023566 | 3.886454 |
| 29 | 6 | 0 | 4.743055 | -1.383943 | 6.778698 |
| 30 | 6 | 0 | 2.370929 | -1.787906 | 5.367046 |
| 31 | 1 | 0 | 6.266156 | 0.587319 | 5.792602 |
| 32 | 6 | 0 | 3.873857 | -2.363874 | 7.172408 |
| 33 | 1 | 0 | 5.675493 | -1.221382 | 7.306679 |
| 34 | 1 | 0 | 4.103066 | -2.991233 | 8.024073 |
| 35 | 6 | 0 | 2.678635 | -2.564846 | 6.453190 |
| 36 | 1 | 0 | 1.465899 | -1.991845 | 4.811068 |
| 37 | 1 | 0 | 1.996792 | -3.350484 | 6.753916 |
| 38 | 1 | 0 | -1.126940 | -0.867693 | -1.454994 |
| 39 | 1 | 0 | -2.049226 | 0.077567 | -0.266066 |
| 40 | 1 | 0 | -1.064525 | 0.910097 | -1.492015 |
| 41 | 6 | 0 | 4.453008 | 2.836694 | 1.959619 |
| 42 | 1 | 0 | 3.980047 | 3.301647 | 1.098300 |
| 43 | 1 | 0 | 4.678918 | 3.599298 | 2.707003 |
| 44 | 1 | 0 | 5.372447 | 2.338264 | 1.646033 |
| 45 | 9 | 0 | -2.545481 | -2.431178 | 4.030304 |
| 46 | 5 | 0 | -1.217162 | -2.415329 | 4.459692 |
| 47 | 9 | 0 | -0.979671 | -3.486632 | 5.321574 |
| 48 | 9 | 0 | -0.364775 | -2.511610 | 3.348316 |
| 49 | 9 | 0 | -0.957544 | -1.209390 | 5.131660 |

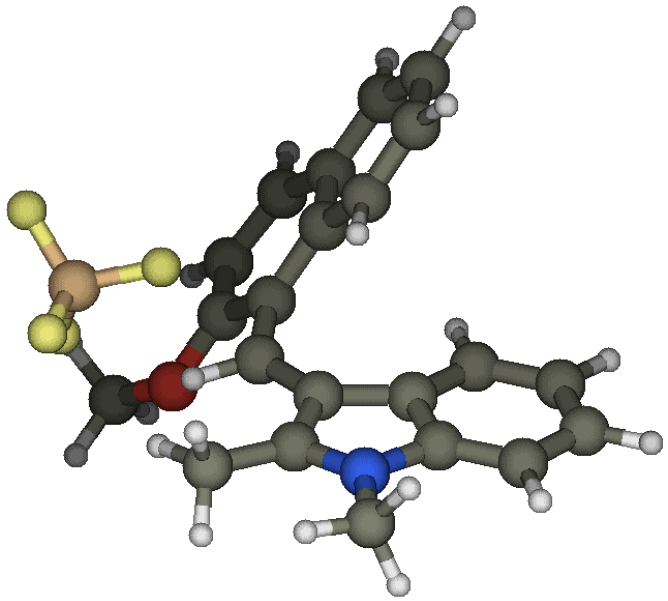
**Ion couple $I^+$ $BF_4^-$ (*a,pl*)** (Table S-1b)



| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 0.000000 | 0.000000 | 0.000000 |
| 2 | 6 | 0 | 0.000000 | 0.000000 | 1.314924 |
| 3 | 6 | 0 | 1.374207 | 0.000000 | 1.786540 |
| 4 | 6 | 0 | 2.202404 | -0.033266 | 0.581886 |
| 5 | 6 | 0 | 1.319973 | -0.037197 | -0.500039 |
| 6 | 6 | 0 | 1.721033 | -0.098377 | -1.819852 |
| 7 | 6 | 0 | 3.089399 | -0.174240 | -2.050877 |
| 8 | 6 | 0 | 3.993972 | -0.203524 | -0.990697 |
| 9 | 6 | 0 | 3.565112 | -0.134529 | 0.329681 |
| 10 | 6 | 0 | -1.247009 | 0.030399 | 2.108510 |
| 11 | 1 | 0 | -1.794773 | 0.952023 | 1.897589 |
| 12 | 1 | 0 | -1.885719 | -0.810245 | 1.832989 |
| 13 | 1 | 0 | -1.046957 | -0.019017 | 3.173525 |
| 14 | 6 | 0 | -1.156800 | 0.021681 | -0.877473 |
| 15 | 1 | 0 | 1.008843 | -0.097041 | -2.634390 |
| 16 | 1 | 0 | 3.454659 | -0.223512 | -3.068324 |
| 17 | 1 | 0 | 5.053028 | -0.282888 | -1.199669 |
| 18 | 1 | 0 | 4.284739 | -0.175197 | 1.135230 |
| 19 | 6 | 0 | 1.676773 | -0.055121 | 3.110896 |
| 20 | 6 | 0 | 2.965844 | 0.061681 | 3.753830 |
| 21 | 1 | 0 | 0.844882 | -0.233098 | 3.786705 |
| 22 | 6 | 0 | 3.880770 | 1.045636 | 3.376529 |
| 23 | 6 | 0 | 5.102740 | 1.200555 | 4.073069 |
| 24 | 6 | 0 | 5.387554 | 0.397559 | 5.137876 |
| 25 | 6 | 0 | 4.482575 | -0.595811 | 5.582381 |
| 26 | 6 | 0 | 3.256346 | -0.763954 | 4.893092 |
| 27 | 8 | 0 | 3.524770 | 1.868261 | 2.381102 |
| 28 | 1 | 0 | 5.802853 | 1.965815 | 3.772149 |
| 29 | 6 | 0 | 4.786599 | -1.416724 | 6.693097 |
| 30 | 6 | 0 | 2.376102 | -1.779224 | 5.336161 |
| 31 | 1 | 0 | 6.323684 | 0.522419 | 5.669777 |
| 32 | 6 | 0 | 3.905303 | -2.374369 | 7.113540 |
| 33 | 1 | 0 | 5.732410 | -1.268456 | 7.201094 |
| 34 | 1 | 0 | 4.138438 | -2.999018 | 7.966166 |
| 35 | 6 | 0 | 2.688928 | -2.551558 | 6.423987 |
| 36 | 1 | 0 | 1.443716 | -1.960530 | 4.819801 |
| 37 | 1 | 0 | 1.991778 | -3.313035 | 6.750996 |
| 38 | 1 | 0 | -1.166325 | -0.888063 | -1.476837 |
| 39 | 1 | 0 | -2.063963 | 0.080981 | -0.286293 |
| 40 | 1 | 0 | -1.087038 | 0.888513 | -1.533448 |

| | | | | | |
|---|---|---|---|---|---|
| 41 | 6 | 0 | 4.470097 | 2.799634 | 1.871518 |
| 42 | 1 | 0 | 3.987547 | 3.269943 | 1.018454 |
| 43 | 1 | 0 | 4.713590 | 3.558830 | 2.616890 |
| 44 | 1 | 0 | 5.380666 | 2.294506 | 1.543056 |
| 45 | 9 | 0 | -0.795819 | -0.893921 | 5.321347 |
| 46 | 5 | 0 | -1.526862 | -2.095146 | 5.333516 |
| 47 | 9 | 0 | -2.149429 | -2.246275 | 6.572038 |
| 48 | 9 | 0 | -2.489971 | -2.057846 | 4.319626 |
| 49 | 9 | 0 | -0.654002 | -3.165498 | 5.105230 |

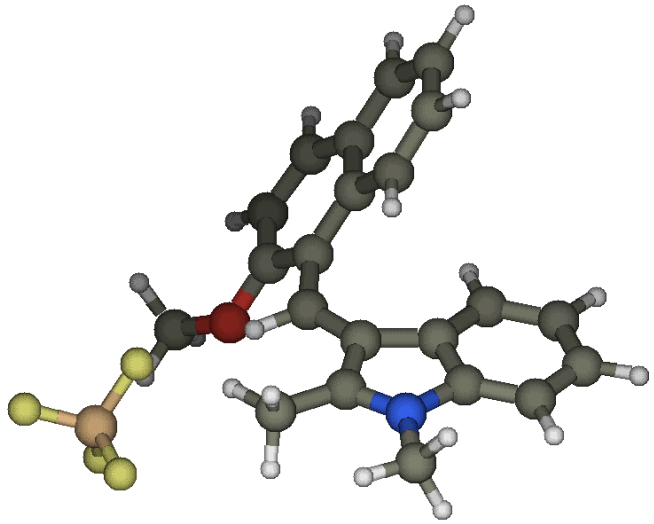
**Ion couple $I^+$ $BF_4^-$ (*s,p*)** (Table S-1b)



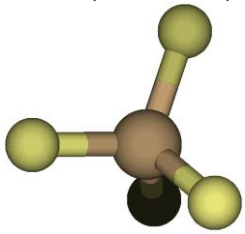
| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 0.000739 | -0.026075 | 0.025580 |
| 2 | 6 | 0 | 0.015609 | -0.026440 | 1.341452 |
| 3 | 6 | 0 | 1.392888 | -0.050567 | 1.795922 |
| 4 | 6 | 0 | 2.209518 | -0.015434 | 0.583106 |
| 5 | 6 | 0 | 1.314397 | -0.000027 | -0.489126 |
| 6 | 6 | 0 | 1.702979 | 0.064730 | -1.812456 |
| 7 | 6 | 0 | 3.069697 | 0.129107 | -2.056811 |
| 8 | 6 | 0 | 3.985980 | 0.141646 | -1.006659 |
| 9 | 6 | 0 | 3.571065 | 0.071756 | 0.318317 |
| 10 | 6 | 0 | -1.221590 | -0.038689 | 2.151218 |
| 11 | 1 | 0 | -1.892400 | 0.756692 | 1.822567 |
| 12 | 1 | 0 | -1.736457 | -0.993504 | 2.022246 |
| 13 | 1 | 0 | -1.007602 | 0.086834 | 3.207568 |
| 14 | 6 | 0 | -1.166009 | -0.045644 | -0.838729 |
| 15 | 1 | 0 | 0.982925 | 0.073384 | -2.619973 |
| 16 | 1 | 0 | 3.424827 | 0.180223 | -3.077706 |
| 17 | 1 | 0 | 5.043636 | 0.207576 | -1.226429 |
| 18 | 1 | 0 | 4.298534 | 0.092667 | 1.117134 |
| 19 | 6 | 0 | 1.707048 | -0.057678 | 3.118314 |
| 20 | 6 | 0 | 2.996699 | -0.226297 | 3.748674 |
| 21 | 1 | 0 | 0.892998 | 0.115572 | 3.812863 |
| 22 | 6 | 0 | 3.264709 | 0.609769 | 4.834381 |
| 23 | 6 | 0 | 4.496852 | 0.540495 | 5.520339 |
| 24 | 6 | 0 | 5.433100 | -0.371509 | 5.128719 |
| 25 | 6 | 0 | 5.187824 | -1.286395 | 4.077673 |
| 26 | 6 | 0 | 3.947872 | -1.236568 | 3.389822 |
| 27 | 8 | 0 | 2.320332 | 1.512863 | 5.139127 |

| | | | | | |
|---|---|---|---|---|---|
| 28 | 1 | 0 | 4.704773 | 1.214832 | 6.337839 |
| 29 | 6 | 0 | 6.146006 | -2.270767 | 3.737066 |
| 30 | 6 | 0 | 3.681660 | -2.245331 | 2.432682 |
| 31 | 1 | 0 | 6.386472 | -0.417109 | 5.642113 |
| 32 | 6 | 0 | 5.877613 | -3.201947 | 2.773406 |
| 33 | 1 | 0 | 7.088894 | -2.278097 | 4.271224 |
| 34 | 1 | 0 | 6.610031 | -3.956805 | 2.518447 |
| 35 | 6 | 0 | 4.621766 | -3.194867 | 2.132343 |
| 36 | 1 | 0 | 2.716806 | -2.281769 | 1.947077 |
| 37 | 1 | 0 | 4.391699 | -3.958932 | 1.400391 |
| 38 | 1 | 0 | -1.083115 | -0.890173 | -1.521336 |
| 39 | 1 | 0 | -2.063766 | -0.149401 | -0.239383 |
| 40 | 1 | 0 | -1.205316 | 0.881377 | -1.410073 |
| 41 | 6 | 0 | 2.464580 | 2.289758 | 6.322697 |
| 42 | 1 | 0 | 1.545110 | 2.861712 | 6.412475 |
| 43 | 1 | 0 | 2.583455 | 1.648442 | 7.197415 |
| 44 | 1 | 0 | 3.312035 | 2.972243 | 6.239296 |
| 45 | 9 | 0 | -2.121593 | -2.132417 | 4.568344 |
| 46 | 5 | 0 | -0.777066 | -2.131844 | 4.954829 |
| 47 | 9 | 0 | -0.575226 | -3.072692 | 5.964849 |
| 48 | 9 | 0 | 0.026110 | -2.445371 | 3.849559 |
| 49 | 9 | 0 | -0.432717 | -0.854861 | 5.427595 |

**Ion couple $I^+$ $BF_4^-$ (*s,pl*)** (Table S-1b)

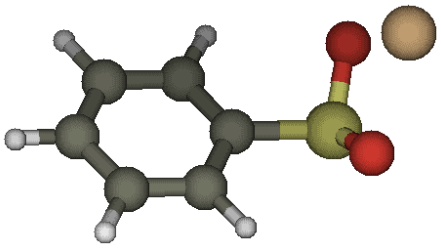


**$BF_4^-$** (Table S-1b)



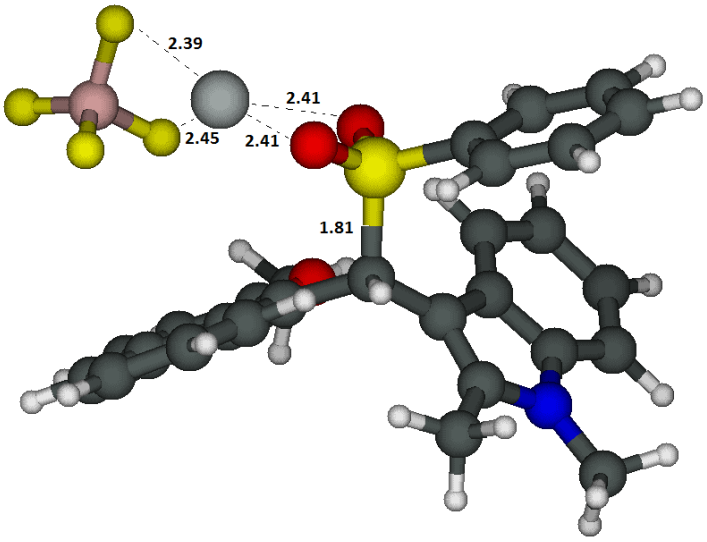
| | | | | | |
|---|---|---|---|---|---|
| 1 | 5 | 0 | 0.000000 | 0.000000 | 0.000000 |
| 2 | 9 | 0 | 0.000000 | -0.000000 | 1.399936 |
| 3 | 9 | 0 | 1.319872 | -0.000000 | -0.466645 |
| 4 | 9 | 0 | -0.659936 | -1.143043 | -0.466645 |
| 5 | 9 | 0 | -0.659936 | 1.143043 | -0.466645 |

**$C_6H_5SO_2Na$ 2a** (Table S-1d)



| | | | | | |
|---|---|---|---|---|---|
| 1 | 16 | 0 | 0.060999 | 0.017678 | 0.014193 |
| 2 | 6 | 0 | 0.027292 | 0.018210 | 1.823057 |
| 3 | 6 | 0 | 1.226571 | -0.020853 | 2.524115 |
| 4 | 8 | 0 | -1.238407 | 0.717837 | -0.327167 |
| 5 | 8 | 0 | 1.191409 | 0.984068 | -0.278821 |
| 6 | 11 | 0 | -0.203617 | 2.619706 | -0.915974 |
| 7 | 6 | 0 | 1.208029 | -0.071390 | 3.911520 |
| 8 | 1 | 0 | 2.165781 | 0.005045 | 1.984772 |
| 9 | 1 | 0 | 2.139450 | -0.093684 | 4.463531 |
| 10 | 6 | 0 | -0.004994 | -0.089311 | 4.591347 |
| 11 | 6 | 0 | -1.200507 | -0.055514 | 3.884294 |
| 12 | 1 | 0 | -0.017465 | -0.128003 | 5.673474 |
| 13 | 6 | 0 | -1.186967 | -0.006657 | 2.495236 |
| 14 | 1 | 0 | -2.144725 | -0.065312 | 4.414600 |
| 15 | 1 | 0 | -2.110326 | 0.028833 | 1.930602 |

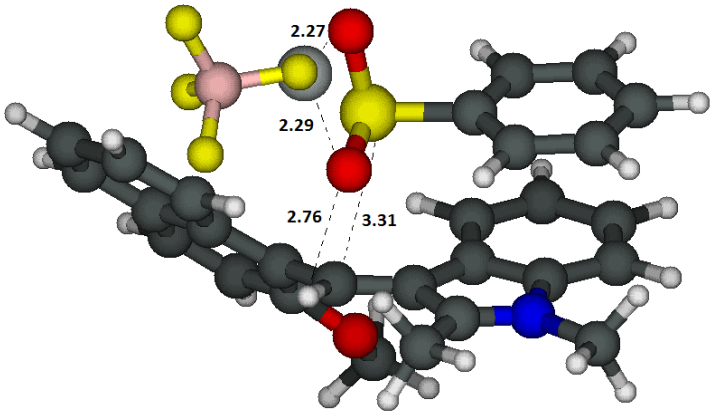
**C–S Adduct 2a + $I^+$ $BF_4^-$** (Table S-2a)




| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 0.004291 | -0.022757 | 0.028487 |
| 2 | 6 | 0 | 0.015781 | -0.003459 | 1.397915 |
| 3 | 6 | 0 | 1.318125 | -0.028699 | 1.853841 |
| 4 | 6 | 0 | 2.165616 | -0.058722 | 0.686830 |
| 5 | 6 | 0 | 1.296906 | -0.057949 | -0.428844 |
| 6 | 6 | 0 | 1.753090 | -0.084951 | -1.746876 |
| 7 | 6 | 0 | 3.118214 | -0.127257 | -1.949809 |
| 8 | 6 | 0 | 4.004667 | -0.134464 | -0.861003 |
| 9 | 6 | 0 | 3.547303 | -0.096576 | 0.442590 |
| 10 | 6 | 0 | -1.260391 | 0.060269 | 2.164406 |
| 11 | 1 | 0 | -1.884542 | 0.879966 | 1.803947 |
| 12 | 1 | 0 | -1.832749 | -0.864963 | 2.060608 |

| | | | | | |
|---|---|---|---|---|---|
| 13 | 1 | 0 | -1.075389 | 0.234807 | 3.222537 |
| 14 | 6 | 0 | -1.159807 | 0.035151 | -0.829121 |
| 15 | 1 | 0 | 1.060403 | -0.069840 | -2.578863 |
| 16 | 1 | 0 | 3.509026 | -0.149649 | -2.959239 |
| 17 | 1 | 0 | 5.071265 | -0.160638 | -1.047359 |
| 18 | 1 | 0 | 4.246527 | -0.085417 | 1.265261 |
| 19 | 6 | 0 | 1.597373 | -0.110654 | 3.331079 |
| 20 | 6 | 0 | 1.818790 | 1.148607 | 4.149585 |
| 21 | 1 | 0 | 0.733770 | -0.620550 | 3.754522 |
| 22 | 6 | 0 | 2.696161 | 2.127293 | 3.710397 |
| 23 | 6 | 0 | 2.845863 | 3.346516 | 4.415224 |
| 24 | 6 | 0 | 2.126032 | 3.566864 | 5.549437 |
| 25 | 6 | 0 | 1.235726 | 2.593118 | 6.055146 |
| 26 | 6 | 0 | 1.083499 | 1.360754 | 5.360509 |
| 27 | 8 | 0 | 3.383438 | 1.867304 | 2.587116 |
| 28 | 1 | 0 | 3.536366 | 4.095738 | 4.057482 |
| 29 | 6 | 0 | 0.511026 | 2.836338 | 7.246899 |
| 30 | 6 | 0 | 0.193558 | 0.406891 | 5.927154 |
| 31 | 1 | 0 | 2.241657 | 4.497688 | 6.091967 |
| 32 | 6 | 0 | -0.342298 | 1.899391 | 7.754621 |
| 33 | 1 | 0 | 0.656011 | 3.786475 | 7.747841 |
| 34 | 1 | 0 | -0.892290 | 2.089162 | 8.667173 |
| 35 | 6 | 0 | -0.494551 | 0.670426 | 7.080178 |
| 36 | 1 | 0 | 0.055072 | -0.561877 | 5.469422 |
| 37 | 1 | 0 | -1.160482 | -0.082006 | 7.484075 |
| 38 | 1 | 0 | -1.047668 | -0.680970 | -1.642676 |
| 39 | 1 | 0 | -2.047308 | -0.228391 | -0.260597 |
| 40 | 1 | 0 | -1.286779 | 1.034718 | -1.249482 |
| 41 | 6 | 0 | 4.229965 | 2.865569 | 2.039683 |
| 42 | 1 | 0 | 4.633054 | 2.439417 | 1.124062 |
| 43 | 1 | 0 | 3.665512 | 3.769131 | 1.799466 |
| 44 | 1 | 0 | 5.047372 | 3.105789 | 2.721287 |
| 45 | 16 | 0 | 2.862842 | -1.318037 | 3.796577 |
| 46 | 6 | 0 | 2.434637 | -2.798901 | 2.952933 |
| 47 | 6 | 0 | 1.307397 | -3.495308 | 3.374994 |
| 48 | 6 | 0 | 0.947312 | -4.646600 | 2.694089 |
| 49 | 6 | 0 | 1.709609 | -5.083410 | 1.615363 |
| 50 | 6 | 0 | 2.835795 | -4.378122 | 1.212304 |
| 51 | 6 | 0 | 3.207556 | -3.220166 | 1.881381 |
| 52 | 1 | 0 | 0.731354 | -3.150562 | 4.225318 |
| 53 | 1 | 0 | 0.075663 | -5.205691 | 3.007449 |
| 54 | 1 | 0 | 1.423825 | -5.984340 | 1.087531 |
| 55 | 1 | 0 | 3.427172 | -4.725692 | 0.375596 |
| 56 | 1 | 0 | 4.080022 | -2.655149 | 1.581843 |
| 57 | 8 | 0 | 4.195360 | -0.893730 | 3.407304 |
| 58 | 8 | 0 | 2.721005 | -1.512888 | 5.233586 |
| 59 | 11 | 0 | 4.673590 | -0.153953 | 5.648017 |
| 60 | 5 | 0 | 5.994238 | 1.888339 | 6.410705 |
| 61 | 9 | 0 | 6.685075 | 2.976742 | 6.868628 |
| 62 | 9 | 0 | 4.725292 | 1.768392 | 7.016746 |
| 63 | 9 | 0 | 5.778587 | 1.936895 | 5.021170 |
| 64 | 9 | 0 | 6.670685 | 0.676890 | 6.671020 |

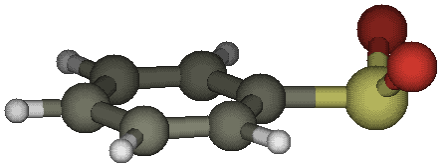
**Complex A 2a + $I^+ BF_4^-$** (Table S-2a)




| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 0.034687 | -0.078960 | 0.040624 |
| 2 | 6 | 0 | 0.057456 | -0.118504 | 1.356525 |
| 3 | 6 | 0 | 1.437050 | -0.091870 | 1.806976 |
| 4 | 6 | 0 | 2.248163 | -0.116532 | 0.595957 |
| 5 | 6 | 0 | 1.351626 | -0.103407 | -0.474540 |
| 6 | 6 | 0 | 1.740080 | -0.153333 | -1.798977 |
| 7 | 6 | 0 | 3.104353 | -0.253326 | -2.044782 |
| 8 | 6 | 0 | 4.019497 | -0.315331 | -0.994584 |
| 9 | 6 | 0 | 3.605818 | -0.245733 | 0.330472 |
| 10 | 6 | 0 | -1.131958 | -0.180548 | 2.231994 |
| 11 | 1 | 0 | -1.205605 | 0.732924 | 2.824740 |
| 12 | 1 | 0 | -2.055495 | -0.315384 | 1.678831 |
| 13 | 1 | 0 | -0.999876 | -1.023414 | 2.915527 |
| 14 | 6 | 0 | -1.111207 | -0.016065 | -0.849831 |
| 15 | 1 | 0 | 1.021516 | -0.135668 | -2.607754 |
| 16 | 1 | 0 | 3.457703 | -0.301017 | -3.066527 |
| 17 | 1 | 0 | 5.073984 | -0.419684 | -1.215704 |
| 18 | 1 | 0 | 4.329466 | -0.312224 | 1.131284 |
| 19 | 6 | 0 | 1.735484 | -0.122966 | 3.134871 |
| 20 | 6 | 0 | 2.997610 | 0.051783 | 3.808145 |
| 21 | 1 | 0 | 0.892281 | -0.323873 | 3.788669 |
| 22 | 6 | 0 | 3.927347 | 1.005905 | 3.383380 |
| 23 | 6 | 0 | 5.137015 | 1.203463 | 4.089504 |
| 24 | 6 | 0 | 5.393168 | 0.480718 | 5.216540 |
| 25 | 6 | 0 | 4.467799 | -0.464451 | 5.720437 |
| 26 | 6 | 0 | 3.253792 | -0.678562 | 5.022100 |
| 27 | 8 | 0 | 3.594150 | 1.762004 | 2.331909 |
| 28 | 1 | 0 | 5.850690 | 1.936985 | 3.745095 |
| 29 | 6 | 0 | 4.745382 | -1.191649 | 6.900978 |
| 30 | 6 | 0 | 2.354142 | -1.642503 | 5.537713 |
| 31 | 1 | 0 | 6.321247 | 0.635496 | 5.754576 |
| 32 | 6 | 0 | 3.849035 | -2.103933 | 7.384807 |
| 33 | 1 | 0 | 5.684423 | -1.009046 | 7.410179 |
| 34 | 1 | 0 | 4.062784 | -2.659779 | 8.288463 |
| 35 | 6 | 0 | 2.642664 | -2.324660 | 6.691847 |
| 36 | 1 | 0 | 1.433883 | -1.866764 | 5.014534 |
| 37 | 1 | 0 | 1.935145 | -3.052763 | 7.069523 |
| 38 | 1 | 0 | -1.041302 | -0.830398 | -1.569375 |
| 39 | 1 | 0 | -2.033528 | -0.104510 | -0.288676 |
| 40 | 1 | 0 | -1.092762 | 0.936800 | -1.378451 |
| 41 | 6 | 0 | 4.546422 | 2.664846 | 1.784317 |
| 42 | 1 | 0 | 4.075982 | 3.084459 | 0.898728 |
| 43 | 1 | 0 | 4.777124 | 3.465071 | 2.489672 |
| 44 | 1 | 0 | 5.462228 | 2.143480 | 1.499280 |

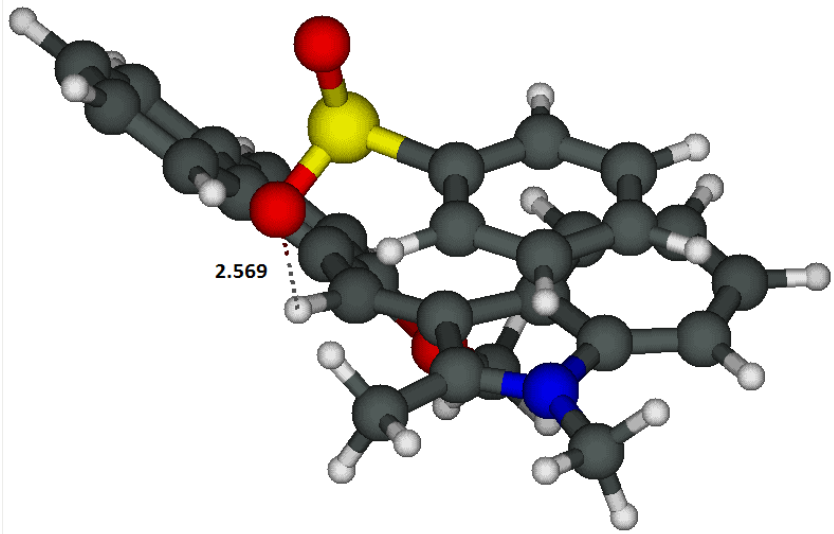
| | | | | | |
|---|---|---|---|---|---|
| 45 | 16 | 0 | 1.596227 | -3.390351 | 2.644800 |
| 46 | 6 | 0 | 1.186826 | -3.435108 | 0.880196 |
| 47 | 6 | 0 | -0.126221 | -3.356143 | 0.444201 |
| 48 | 6 | 0 | -0.401912 | -3.459442 | -0.915685 |
| 49 | 6 | 0 | 0.635031 | -3.622311 | -1.826247 |
| 50 | 6 | 0 | 1.952584 | -3.681003 | -1.381964 |
| 51 | 6 | 0 | 2.230010 | -3.586003 | -0.025789 |
| 52 | 1 | 0 | -0.920126 | -3.221022 | 1.170186 |
| 53 | 1 | 0 | -1.426898 | -3.415027 | -1.263724 |
| 54 | 1 | 0 | 0.418136 | -3.700434 | -2.884538 |
| 55 | 1 | 0 | 2.760824 | -3.799860 | -2.092903 |
| 56 | 1 | 0 | 3.254185 | -3.634196 | 0.329687 |
| 57 | 8 | 0 | 1.789582 | -4.854769 | 2.964625 |
| 58 | 8 | 0 | 0.280875 | -2.964902 | 3.267645 |
| 59 | 11 | 0 | -0.120189 | -5.022419 | 4.185257 |
| 60 | 9 | 0 | -2.084726 | -6.016780 | 4.729595 |
| 61 | 5 | 0 | -2.005272 | -5.829565 | 6.134464 |
| 62 | 9 | 0 | -0.774981 | -5.160933 | 6.360793 |
| 63 | 9 | 0 | -3.055367 | -5.039858 | 6.562158 |
| 64 | 9 | 0 | -2.000143 | -7.054695 | 6.772313 |

**$C_6H_5SO_2$ anion 2a$^-$** (Table S-2b)



| | | | | | |
|---|---|---|---|---|---|
| 1 | 16 | 0 | 0.018749 | 0.005871 | 0.021004 |
| 2 | 6 | 0 | 0.006003 | 0.003172 | 1.849908 |
| 3 | 6 | 0 | 1.208186 | -0.016460 | 2.547395 |
| 4 | 8 | 0 | -1.301806 | 0.646621 | -0.283773 |
| 5 | 8 | 0 | 1.176284 | 0.916667 | -0.261461 |
| 6 | 6 | 0 | 1.207962 | -0.075267 | 3.935670 |
| 7 | 1 | 0 | 2.139076 | 0.038289 | 1.994752 |
| 8 | 1 | 0 | 2.145947 | -0.080742 | 4.478308 |
| 9 | 6 | 0 | 0.003266 | -0.119186 | 4.629926 |
| 10 | 6 | 0 | -1.198940 | -0.101022 | 3.932290 |
| 11 | 1 | 0 | 0.002240 | -0.162838 | 5.712319 |
| 12 | 6 | 0 | -1.196506 | -0.045000 | 2.542756 |
| 13 | 1 | 0 | -2.138321 | -0.126257 | 4.472041 |
| 14 | 1 | 0 | -2.123716 | -0.012968 | 1.982746 |

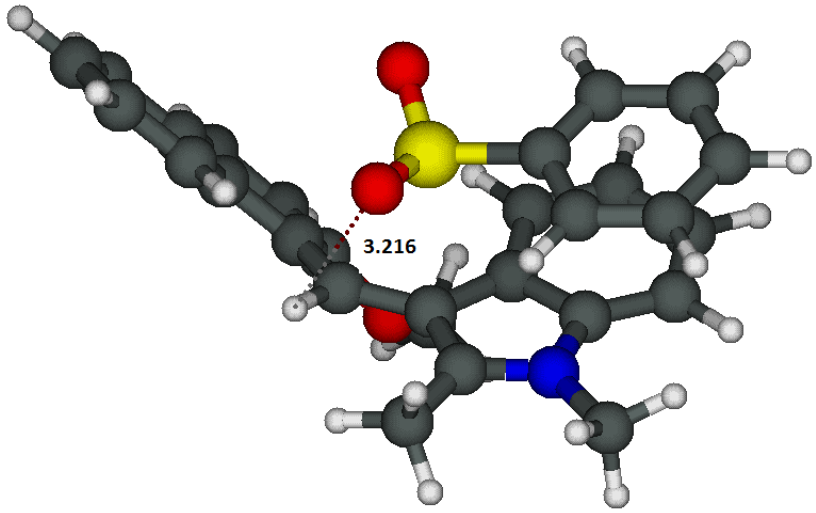
**Complex A' 2a$^{-}$ + I$^{+}$** (Table S-2b)




| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 0.002990 | -0.022531 | 0.024006 |
| 2 | 6 | 0 | -0.007105 | -0.023757 | 1.342127 |
| 3 | 6 | 0 | 1.362571 | -0.019051 | 1.826414 |
| 4 | 6 | 0 | 2.199868 | -0.089244 | 0.634156 |
| 5 | 6 | 0 | 1.331173 | -0.077395 | -0.457905 |
| 6 | 6 | 0 | 1.752703 | -0.154157 | -1.771282 |
| 7 | 6 | 0 | 3.120273 | -0.283887 | -1.981550 |
| 8 | 6 | 0 | 4.007778 | -0.347638 | -0.907726 |
| 9 | 6 | 0 | 3.561058 | -0.248959 | 0.404244 |
| 10 | 6 | 0 | -1.220015 | 0.023319 | 2.183681 |
| 11 | 1 | 0 | -1.296205 | 1.004129 | 2.658723 |
| 12 | 1 | 0 | -2.127749 | -0.164275 | 1.618744 |
| 13 | 1 | 0 | -1.122702 | -0.735760 | 2.966839 |
| 14 | 6 | 0 | -1.122054 | 0.104118 | -0.887879 |
| 15 | 1 | 0 | 1.056186 | -0.133143 | -2.598884 |
| 16 | 1 | 0 | 3.497761 | -0.352149 | -2.993446 |
| 17 | 1 | 0 | 5.065328 | -0.474789 | -1.100051 |
| 18 | 1 | 0 | 4.263478 | -0.311446 | 1.224261 |
| 19 | 6 | 0 | 1.632945 | 0.021674 | 3.161464 |
| 20 | 6 | 0 | 2.882477 | 0.255615 | 3.844568 |
| 21 | 1 | 0 | 0.777855 | -0.151824 | 3.807474 |
| 22 | 6 | 0 | 3.817679 | 1.177616 | 3.362292 |
| 23 | 6 | 0 | 5.025458 | 1.419364 | 4.057318 |
| 24 | 6 | 0 | 5.273331 | 0.779356 | 5.234778 |
| 25 | 6 | 0 | 4.334803 | -0.111804 | 5.806529 |
| 26 | 6 | 0 | 3.120761 | -0.368408 | 5.121212 |
| 27 | 8 | 0 | 3.494235 | 1.863792 | 2.260562 |
| 28 | 1 | 0 | 5.745728 | 2.120222 | 3.662551 |
| 29 | 6 | 0 | 4.597574 | -0.738401 | 7.046798 |
| 30 | 6 | 0 | 2.197960 | -1.259718 | 5.720041 |
| 31 | 1 | 0 | 6.201276 | 0.964969 | 5.763252 |
| 32 | 6 | 0 | 3.683648 | -1.588424 | 7.604856 |
| 33 | 1 | 0 | 5.538196 | -0.527500 | 7.542049 |
| 34 | 1 | 0 | 3.885402 | -2.067450 | 8.554258 |
| 35 | 6 | 0 | 2.472853 | -1.841769 | 6.930986 |
| 36 | 1 | 0 | 1.266318 | -1.503107 | 5.225458 |
| 37 | 1 | 0 | 1.747793 | -2.516732 | 7.369013 |
| 38 | 1 | 0 | -1.029834 | -0.647354 | -1.668711 |
| 39 | 1 | 0 | -2.056074 | -0.044559 | -0.359554 |
| 40 | 1 | 0 | -1.104174 | 1.099079 | -1.333645 |

| | | | | | |
|---|---|---|---|---|---|
| 41 | 6 | 0 | 4.446974 | 2.734886 | 1.665924 |
| 42 | 1 | 0 | 3.981789 | 3.096877 | 0.752466 |
| 43 | 1 | 0 | 4.668507 | 3.578448 | 2.322381 |
| 44 | 1 | 0 | 5.367632 | 2.202103 | 1.420144 |
| 45 | 16 | 0 | 0.686145 | -3.328847 | 3.333070 |
| 46 | 6 | 0 | 0.144410 | -3.282185 | 1.592079 |
| 47 | 6 | 0 | -1.207807 | -3.214956 | 1.278600 |
| 48 | 6 | 0 | -1.610002 | -3.251488 | -0.048840 |
| 49 | 6 | 0 | -0.659040 | -3.350743 | -1.062814 |
| 50 | 6 | 0 | 0.691768 | -3.408544 | -0.746325 |
| 51 | 6 | 0 | 1.093577 | -3.372569 | 0.586034 |
| 52 | 1 | 0 | -1.929833 | -3.135031 | 2.083796 |
| 53 | 1 | 0 | -2.663588 | -3.204970 | -0.298957 |
| 54 | 1 | 0 | -0.974547 | -3.381211 | -2.098841 |
| 55 | 1 | 0 | 1.432542 | -3.481195 | -1.533597 |
| 56 | 1 | 0 | 2.147575 | -3.416896 | 0.842880 |
| 57 | 8 | 0 | 0.462333 | -4.766305 | 3.674997 |
| 58 | 8 | 0 | -0.347407 | -2.453417 | 3.992672 |

**Complex $S_1$-A' $2a^-$ + $I^+$** (Table S-2b)

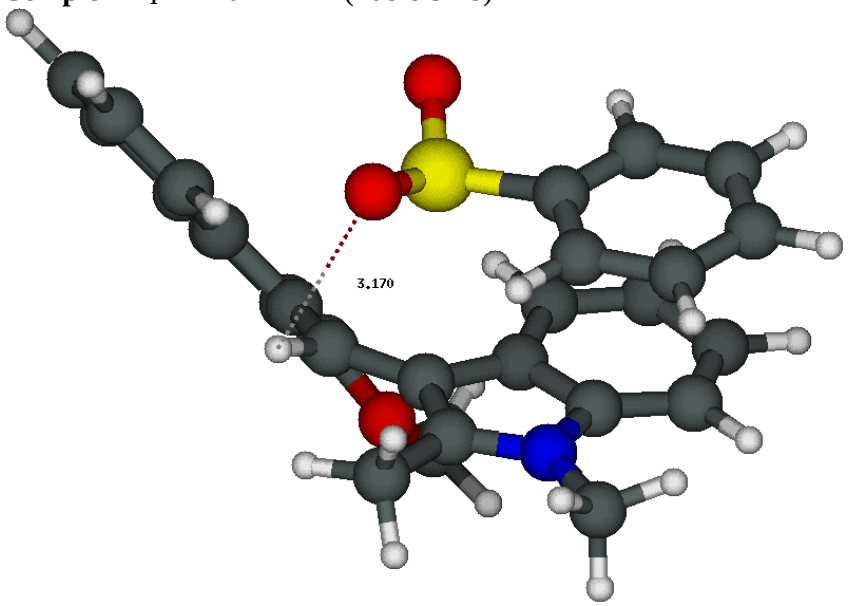



| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | -0.013952 | -0.020189 | 0.021708 |
| 2 | 6 | 0 | -0.011240 | -0.033391 | 1.383768 |
| 3 | 6 | 0 | 1.315321 | -0.004032 | 1.864404 |
| 4 | 6 | 0 | 2.150572 | -0.028734 | 0.671964 |
| 5 | 6 | 0 | 1.285607 | -0.018389 | -0.441754 |
| 6 | 6 | 0 | 1.749005 | -0.057192 | -1.753911 |
| 7 | 6 | 0 | 3.116273 | -0.157011 | -1.943087 |
| 8 | 6 | 0 | 3.993470 | -0.228226 | -0.852021 |
| 9 | 6 | 0 | 3.522833 | -0.162754 | 0.449079 |
| 10 | 6 | 0 | -1.281764 | -0.058659 | 2.151067 |
| 11 | 1 | 0 | -1.971790 | 0.709416 | 1.795139 |
| 12 | 1 | 0 | -1.782686 | -1.026512 | 2.051453 |
| 13 | 1 | 0 | -1.094274 | 0.117696 | 3.207291 |
| 14 | 6 | 0 | -1.191666 | 0.024839 | -0.816954 |
| 15 | 1 | 0 | 1.070057 | -0.023170 | -2.596066 |
| 16 | 1 | 0 | 3.512074 | -0.195567 | -2.950247 |
| 17 | 1 | 0 | 5.056425 | -0.331371 | -1.030513 |
| 18 | 1 | 0 | 4.214488 | -0.227302 | 1.279182 |
| 19 | 6 | 0 | 1.656181 | -0.124243 | 3.224622 |
| 20 | 6 | 0 | 2.937936 | 0.064454 | 3.857247 |
| 21 | 1 | 0 | 0.843751 | -0.397744 | 3.886005 |

| | | | | | |
|---|---|---|---|---|---|
| 22 | 6 | 0 | 3.829263 | 1.067561 | 3.462716 |
| 23 | 6 | 0 | 5.069234 | 1.249726 | 4.106396 |
| 24 | 6 | 0 | 5.418238 | 0.470867 | 5.175826 |
| 25 | 6 | 0 | 4.543720 | -0.529158 | 5.654474 |
| 26 | 6 | 0 | 3.303969 | -0.741641 | 4.993724 |
| 27 | 8 | 0 | 3.412238 | 1.898052 | 2.479134 |
| 28 | 1 | 0 | 5.738720 | 2.029581 | 3.772225 |
| 29 | 6 | 0 | 4.892177 | -1.327123 | 6.772892 |
| 30 | 6 | 0 | 2.474166 | -1.787281 | 5.474763 |
| 31 | 1 | 0 | 6.367823 | 0.623228 | 5.674460 |
| 32 | 6 | 0 | 4.056310 | -2.308350 | 7.225254 |
| 33 | 1 | 0 | 5.842404 | -1.140499 | 7.260441 |
| 34 | 1 | 0 | 4.330291 | -2.913139 | 8.080411 |
| 35 | 6 | 0 | 2.834374 | -2.541744 | 6.558884 |
| 36 | 1 | 0 | 1.544919 | -2.009874 | 4.968081 |
| 37 | 1 | 0 | 2.180580 | -3.334621 | 6.900504 |
| 38 | 1 | 0 | -0.961016 | -0.422015 | -1.781733 |
| 39 | 1 | 0 | -1.995469 | -0.545868 | -0.355510 |
| 40 | 1 | 0 | -1.524691 | 1.053622 | -0.969480 |
| 41 | 6 | 0 | 4.349277 | 2.767954 | 1.874121 |
| 42 | 1 | 0 | 3.837028 | 3.216263 | 1.025342 |
| 43 | 1 | 0 | 4.664791 | 3.556896 | 2.561428 |
| 44 | 1 | 0 | 5.226704 | 2.221844 | 1.518120 |
| 45 | 16 | 0 | 1.400502 | -2.971909 | 1.975337 |
| 46 | 6 | 0 | 1.140812 | -3.274851 | 0.236301 |
| 47 | 6 | 0 | -0.146578 | -3.183541 | -0.268146 |
| 48 | 6 | 0 | -0.334529 | -3.354807 | -1.632850 |
| 49 | 6 | 0 | 0.755735 | -3.599739 | -2.459051 |
| 50 | 6 | 0 | 2.039920 | -3.675027 | -1.932937 |
| 51 | 6 | 0 | 2.244801 | -3.500591 | -0.571877 |
| 52 | 1 | 0 | -0.980998 | -2.992938 | 0.394791 |
| 53 | 1 | 0 | -1.332190 | -3.297632 | -2.048418 |
| 54 | 1 | 0 | 0.603164 | -3.732385 | -3.522582 |
| 55 | 1 | 0 | 2.884985 | -3.863082 | -2.582035 |
| 56 | 1 | 0 | 3.236507 | -3.549038 | -0.142407 |
| 57 | 8 | 0 | 2.664502 | -3.568780 | 2.364831 |
| 58 | 8 | 0 | 0.186857 | -3.313321 | 2.697769 |

---

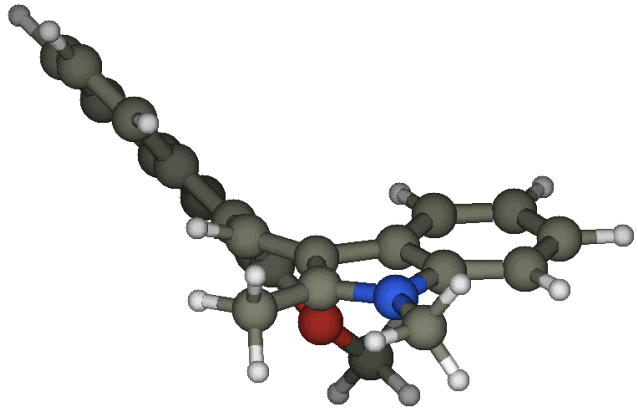
**Complex $T_1$-A' $2a^-$ + $I^+$** (Table S-2b)



| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 0.030145 | -0.015095 | 0.006607 |
| 2 | 6 | 0 | 0.015850 | -0.034694 | 1.371508 |
| 3 | 6 | 0 | 1.329235 | -0.045731 | 1.864275 |
| 4 | 6 | 0 | 2.182601 | -0.067455 | 0.688876 |
| 5 | 6 | 0 | 1.335275 | -0.032329 | -0.437880 |
| 6 | 6 | 0 | 1.821411 | -0.055092 | -1.742675 |
| 7 | 6 | 0 | 3.191072 | -0.159993 | -1.910864 |
| 8 | 6 | 0 | 4.049831 | -0.252450 | -0.806644 |
| 9 | 6 | 0 | 3.558054 | -0.205623 | 0.487227 |
| 10 | 6 | 0 | -1.266687 | -0.035229 | 2.120878 |
| 11 | 1 | 0 | -1.919474 | 0.772182 | 1.781307 |
| 12 | 1 | 0 | -1.807215 | -0.976449 | 1.983068 |
| 13 | 1 | 0 | -1.086738 | 0.100019 | 3.184596 |
| 14 | 6 | 0 | -1.135748 | 0.048500 | -0.846357 |
| 15 | 1 | 0 | 1.156853 | -0.003233 | -2.595554 |
| 16 | 1 | 0 | 3.603386 | -0.184748 | -2.911862 |
| 17 | 1 | 0 | 5.115239 | -0.357103 | -0.969486 |
| 18 | 1 | 0 | 4.235329 | -0.283452 | 1.328349 |
| 19 | 6 | 0 | 1.657097 | -0.154846 | 3.240204 |
| 20 | 6 | 0 | 2.922007 | 0.052256 | 3.883748 |
| 21 | 1 | 0 | 0.854527 | -0.502292 | 3.879040 |
| 22 | 6 | 0 | 3.803327 | 1.071269 | 3.493151 |
| 23 | 6 | 0 | 5.028855 | 1.282140 | 4.153245 |
| 24 | 6 | 0 | 5.377256 | 0.517315 | 5.233220 |
| 25 | 6 | 0 | 4.518101 | -0.502360 | 5.703664 |
| 26 | 6 | 0 | 3.292757 | -0.746478 | 5.027853 |
| 27 | 8 | 0 | 3.382353 | 1.885297 | 2.499823 |
| 28 | 1 | 0 | 5.687373 | 2.073355 | 3.823848 |
| 29 | 6 | 0 | 4.873189 | -1.290509 | 6.825607 |
| 30 | 6 | 0 | 2.489225 | -1.818505 | 5.492796 |
| 31 | 1 | 0 | 6.316026 | 0.691868 | 5.745006 |
| 32 | 6 | 0 | 4.059294 | -2.296588 | 7.265967 |
| 33 | 1 | 0 | 5.811402 | -1.078358 | 7.325791 |
| 34 | 1 | 0 | 4.338928 | -2.894314 | 8.124236 |
| 35 | 6 | 0 | 2.856398 | -2.565060 | 6.581583 |
| 36 | 1 | 0 | 1.575014 | -2.071706 | 4.972748 |
| 37 | 1 | 0 | 2.221856 | -3.378634 | 6.910640 |
| 38 | 1 | 0 | -0.898486 | -0.397276 | -1.810267 |
| 39 | 1 | 0 | -1.952461 | -0.514620 | -0.398010 |
| 40 | 1 | 0 | -1.455402 | 1.081565 | -0.999766 |
| 41 | 6 | 0 | 4.308539 | 2.770739 | 1.899555 |
| 42 | 1 | 0 | 3.798092 | 3.200089 | 1.039987 |
| 43 | 1 | 0 | 4.596951 | 3.571908 | 2.584545 |
| 44 | 1 | 0 | 5.202017 | 2.240072 | 1.560678 |
| 45 | 16 | 0 | 1.603832 | -3.136939 | 2.033209 |
| 46 | 6 | 0 | 1.264971 | -3.338998 | 0.299332 |
| 47 | 6 | 0 | -0.041689 | -3.193319 | -0.144996 |
| 48 | 6 | 0 | -0.289862 | -3.298201 | -1.506135 |
| 49 | 6 | 0 | 0.758025 | -3.528486 | -2.390426 |
| 50 | 6 | 0 | 2.061678 | -3.656418 | -1.923967 |
| 51 | 6 | 0 | 2.328963 | -3.552593 | -0.567406 |
| 52 | 1 | 0 | -0.843023 | -3.016578 | 0.561101 |
| 53 | 1 | 0 | -1.303174 | -3.203161 | -1.874846 |
| 54 | 1 | 0 | 0.557231 | -3.607733 | -3.451387 |
| 55 | 1 | 0 | 2.873924 | -3.832663 | -2.617157 |
| 56 | 1 | 0 | 3.336678 | -3.647475 | -0.185196 |
| 57 | 8 | 0 | 2.846478 | -3.823380 | 2.345912 |
| 58 | 8 | 0 | 0.396088 | -3.447748 | 2.781326 |

---

**Radical *anti*-I$^{\bullet}$** (Table S-2a)



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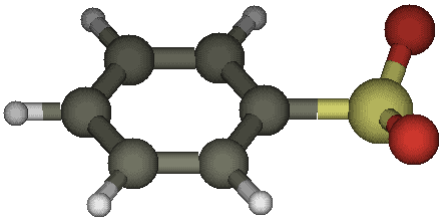
| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 0.007571 | -0.007524 | 0.012296 |
| 2 | 6 | 0 | 0.002451 | 0.006147 | 1.379935 |
| 3 | 6 | 0 | 1.317652 | 0.013740 | 1.861026 |
| 4 | 6 | 0 | 2.164337 | -0.018693 | 0.681938 |
| 5 | 6 | 0 | 1.308748 | -0.028657 | -0.437180 |
| 6 | 6 | 0 | 1.778622 | -0.076083 | -1.747181 |
| 7 | 6 | 0 | 3.149346 | -0.136673 | -1.929219 |
| 8 | 6 | 0 | 4.021834 | -0.159795 | -0.831452 |
| 9 | 6 | 0 | 3.542096 | -0.102307 | 0.466345 |
| 10 | 6 | 0 | -1.271605 | 0.028588 | 2.144353 |
| 11 | 1 | 0 | -1.872639 | 0.902754 | 1.882305 |
| 12 | 1 | 0 | -1.873583 | -0.860437 | 1.940775 |
| 13 | 1 | 0 | -1.071550 | 0.070261 | 3.212070 |
| 14 | 6 | 0 | -1.140546 | -0.003221 | -0.866299 |
| 15 | 1 | 0 | 1.098230 | -0.073215 | -2.589611 |
| 16 | 1 | 0 | 3.552753 | -0.175550 | -2.933258 |
| 17 | 1 | 0 | 5.088994 | -0.223400 | -1.003715 |
| 18 | 1 | 0 | 4.231752 | -0.127187 | 1.300564 |
| 19 | 6 | 0 | 1.663851 | -0.060055 | 3.235392 |
| 20 | 6 | 0 | 2.914030 | 0.236264 | 3.868110 |
| 21 | 1 | 0 | 0.883581 | -0.426616 | 3.890361 |
| 22 | 6 | 0 | 3.745857 | 1.283457 | 3.437010 |
| 23 | 6 | 0 | 4.954267 | 1.586244 | 4.091263 |
| 24 | 6 | 0 | 5.335547 | 0.892379 | 5.208323 |
| 25 | 6 | 0 | 4.525488 | -0.145990 | 5.722647 |
| 26 | 6 | 0 | 3.320328 | -0.486397 | 5.051740 |
| 27 | 8 | 0 | 3.287344 | 2.035733 | 2.412013 |
| 28 | 1 | 0 | 5.572754 | 2.395200 | 3.728968 |
| 29 | 6 | 0 | 4.909354 | -0.857131 | 6.885967 |
| 30 | 6 | 0 | 2.570406 | -1.574559 | 5.564785 |
| 31 | 1 | 0 | 6.259889 | 1.140094 | 5.715912 |
| 32 | 6 | 0 | 4.143974 | -1.880235 | 7.372251 |
| 33 | 1 | 0 | 5.830176 | -0.571462 | 7.381905 |
| 34 | 1 | 0 | 4.445332 | -2.417635 | 8.262470 |
| 35 | 6 | 0 | 2.963657 | -2.245372 | 6.693387 |
| 36 | 1 | 0 | 1.678140 | -1.900782 | 5.048654 |
| 37 | 1 | 0 | 2.368364 | -3.072628 | 7.059647 |
| 38 | 1 | 0 | -1.131331 | -0.889025 | -1.503565 |
| 39 | 1 | 0 | -2.052155 | -0.006235 | -0.276113 |
| 40 | 1 | 0 | -1.131784 | 0.886767 | -1.497811 |
| 41 | 6 | 0 | 4.165229 | 2.950319 | 1.784673 |

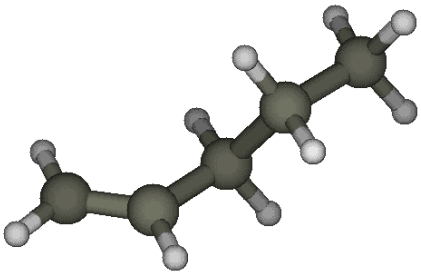
| | | | | | |
|---|---|---|---|---|---|
| 42 | 1 | 0 | 3.635722 | 3.320737 | 0.909374 |
| 43 | 1 | 0 | 4.405248 | 3.789527 | 2.442495 |
| 44 | 1 | 0 | 5.088728 | 2.459615 | 1.466507 |

**$C_6H_5SO_2$ radical 2a$^{\bullet}$** (Table S-2a)



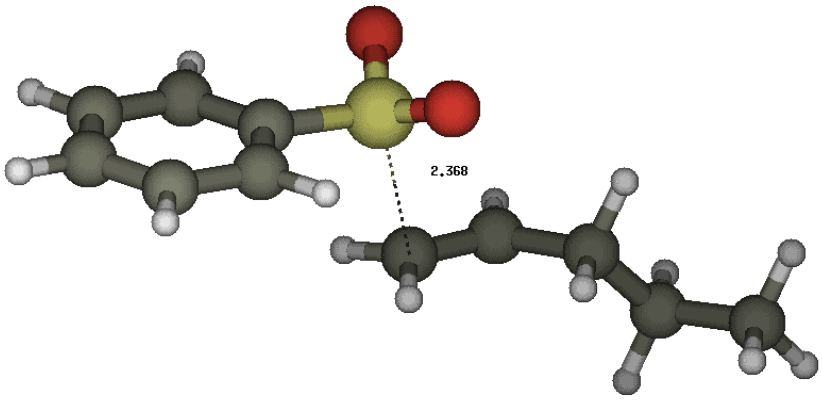
| | | | | | |
|---|---|---|---|---|---|
| 1 | 16 | 0 | -0.000325 | 0.009313 | 0.016485 |
| 2 | 6 | 0 | -0.000221 | 0.005036 | 1.796366 |
| 3 | 6 | 0 | 1.218592 | 0.000395 | 2.460427 |
| 4 | 8 | 0 | -1.273278 | 0.527832 | -0.449613 |
| 5 | 8 | 0 | 1.246432 | 0.587965 | -0.449393 |
| 6 | 6 | 0 | 1.208857 | -0.039683 | 3.846488 |
| 7 | 1 | 0 | 2.146818 | 0.042619 | 1.906670 |
| 8 | 1 | 0 | 2.145277 | -0.030557 | 4.388499 |
| 9 | 6 | 0 | 0.001963 | -0.090023 | 4.534381 |
| 10 | 6 | 0 | -1.205841 | -0.099481 | 3.846352 |
| 11 | 1 | 0 | 0.002745 | -0.123502 | 5.616411 |
| 12 | 6 | 0 | -1.217396 | -0.060090 | 2.460291 |
| 13 | 1 | 0 | -2.141650 | -0.136576 | 4.388251 |
| 14 | 1 | 0 | -2.146442 | -0.064025 | 1.906345 |

**1-pentene 1x** (Table S-2c)



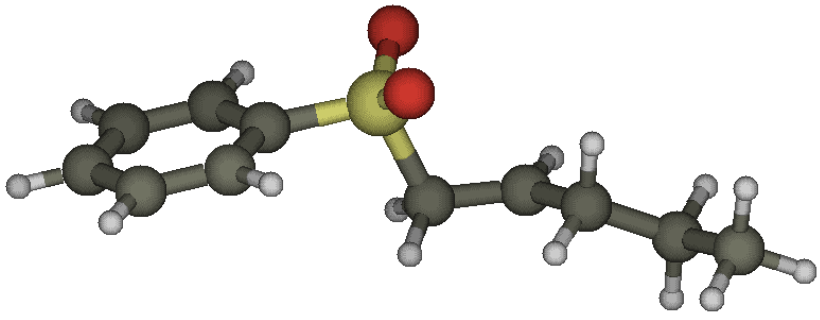
| | | | | | |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.004005 | 0.000583 | -0.003659 |
| 2 | 6 | 0 | -0.002636 | 0.001136 | 1.322639 |
| 3 | 1 | 0 | 0.946621 | -0.000919 | -0.533692 |
| 4 | 1 | 0 | 0.920376 | -0.005114 | 1.890238 |
| 5 | 1 | 0 | -0.930018 | 0.005676 | 1.886858 |
| 6 | 6 | 0 | -1.230007 | 0.026463 | -0.861959 |
| 7 | 6 | 0 | -1.289948 | 1.266912 | -1.755928 |
| 8 | 1 | 0 | -1.241473 | -0.862398 | -1.502683 |
| 9 | 1 | 0 | -2.122536 | -0.018558 | -0.231679 |
| 10 | 6 | 0 | -2.512871 | 1.264540 | -2.662256 |
| 11 | 1 | 0 | -1.294880 | 2.159904 | -1.124963 |
| 12 | 1 | 0 | -0.380062 | 1.316684 | -2.360930 |
| 13 | 1 | 0 | -2.545999 | 2.156965 | -3.289195 |
| 14 | 1 | 0 | -2.508459 | 0.392275 | -3.319887 |
| 15 | 1 | 0 | -3.433190 | 1.233498 | -2.074624 |

**$TS_{Add}$ $2a^{\bullet}$ + 1x** (Table S-2c) **Imaginary Frequancy 332.5 $cm^{-1}$.**



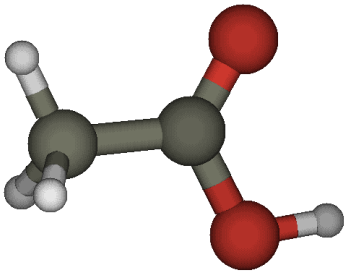

| | | | | | |
|---|---|---|---|---|---|
| 1 | 16 | 0 | -0.413500 | 0.252747 | 0.070899 |
| 2 | 6 | 0 | -0.132051 | 0.062814 | 1.813616 |
| 3 | 6 | 0 | 1.174986 | 0.034677 | 2.283760 |
| 4 | 8 | 0 | -1.752288 | 0.777293 | -0.127175 |
| 5 | 8 | 0 | 0.713197 | 0.967041 | -0.503084 |
| 6 | 6 | 0 | 1.390490 | -0.184137 | 3.636506 |
| 7 | 1 | 0 | 2.001595 | 0.197107 | 1.604356 |
| 8 | 1 | 0 | 2.401140 | -0.196904 | 4.023461 |
| 9 | 6 | 0 | 0.312200 | -0.382657 | 4.491131 |
| 10 | 6 | 0 | -0.988792 | -0.362395 | 4.001574 |
| 11 | 1 | 0 | 0.486906 | -0.554013 | 5.545701 |
| 12 | 6 | 0 | -1.220729 | -0.144974 | 2.651374 |
| 13 | 1 | 0 | -1.824796 | -0.513459 | 4.672094 |
| 14 | 1 | 0 | -2.226811 | -0.120258 | 2.253389 |
| 15 | 6 | 0 | -0.371939 | -1.916352 | -0.878428 |
| 16 | 6 | 0 | -0.675974 | -1.684791 | -2.185406 |
| 17 | 1 | 0 | 0.663343 | -2.056507 | -0.580048 |
| 18 | 1 | 0 | -1.129337 | -2.292586 | -0.198904 |
| 19 | 6 | 0 | 0.322767 | -1.320498 | -3.225914 |
| 20 | 1 | 0 | -1.719152 | -1.696409 | -2.488757 |
| 21 | 6 | 0 | 0.229040 | -2.210347 | -4.469565 |
| 22 | 1 | 0 | 0.146871 | -0.281024 | -3.532724 |
| 23 | 1 | 0 | 1.331313 | -1.363234 | -2.806588 |
| 24 | 6 | 0 | 1.222091 | -1.792013 | -5.544141 |
| 25 | 1 | 0 | 0.407702 | -3.249023 | -4.179657 |
| 26 | 1 | 0 | -0.789503 | -2.164169 | -4.864280 |
| 27 | 1 | 0 | 1.149190 | -2.434415 | -6.422918 |
| 28 | 1 | 0 | 1.039814 | -0.763324 | -5.862613 |
| 29 | 1 | 0 | 2.246974 | -1.848815 | -5.170899 |

**Radical adduct 4** (Table S-2c)



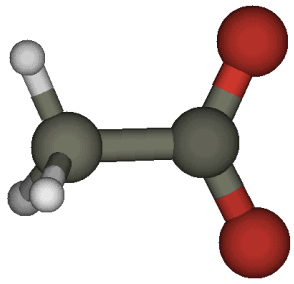
| | | | | | |
|---|---|---|---|---|---|
| 1 | 16 | 0 | -0.221265 | 0.152678 | 0.020270 |
| 2 | 6 | 0 | -0.085164 | 0.040475 | 1.780280 |
| 3 | 6 | 0 | 1.176221 | 0.057441 | 2.361494 |
| 4 | 8 | 0 | -1.531552 | 0.665136 | -0.305673 |
| 5 | 8 | 0 | 0.938916 | 0.850376 | -0.483800 |
| 6 | 6 | 0 | 1.280093 | -0.061987 | 3.739741 |
| 7 | 1 | 0 | 2.057230 | 0.175182 | 1.743753 |
| 8 | 1 | 0 | 2.255222 | -0.043985 | 4.208685 |
| 9 | 6 | 0 | 0.134177 | -0.198353 | 4.514290 |
| 10 | 6 | 0 | -1.121605 | -0.214178 | 3.918996 |
| 11 | 1 | 0 | 0.220306 | -0.289136 | 5.589680 |
| 12 | 6 | 0 | -1.238704 | -0.096125 | 2.541581 |
| 13 | 1 | 0 | -2.011205 | -0.313814 | 4.527129 |
| 14 | 1 | 0 | -2.209079 | -0.096277 | 2.062052 |
| 15 | 6 | 0 | -0.132487 | -1.566484 | -0.538785 |
| 16 | 6 | 0 | -0.245310 | -1.636861 | -2.007806 |
| 17 | 1 | 0 | 0.828286 | -1.931675 | -0.167359 |
| 18 | 1 | 0 | -0.950161 | -2.070932 | -0.020678 |
| 19 | 6 | 0 | 0.921059 | -1.425317 | -2.903224 |
| 20 | 1 | 0 | -1.239180 | -1.662296 | -2.437555 |
| 21 | 6 | 0 | 0.807672 | -2.193221 | -4.220134 |
| 22 | 1 | 0 | 1.025429 | -0.353956 | -3.131306 |
| 23 | 1 | 0 | 1.841789 | -1.706416 | -2.380880 |
| 24 | 6 | 0 | 1.993360 | -1.935866 | -5.138773 |
| 25 | 1 | 0 | 0.726726 | -3.262314 | -4.005706 |
| 26 | 1 | 0 | -0.120285 | -1.902759 | -4.720569 |
| 27 | 1 | 0 | 1.899772 | -2.489445 | -6.074245 |
| 28 | 1 | 0 | 2.072682 | -0.874161 | -5.382930 |
| 29 | 1 | 0 | 2.928624 | -2.238370 | -4.662253 |

**AcOH** (Table S-2c)



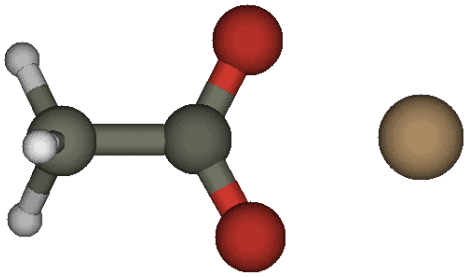
| | | | | | |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.003251 | -0.000000 | -0.003226 |
| 2 | 8 | 0 | -0.000593 | -0.000000 | 1.338688 |
| 3 | 8 | 0 | 1.014892 | 0.000000 | -0.645053 |
| 4 | 6 | 0 | -1.390059 | -0.000000 | -0.561156 |
| 5 | 1 | 0 | -1.351281 | 0.000000 | -1.646278 |
| 6 | 1 | 0 | -1.924115 | -0.881009 | -0.202917 |
| 7 | 1 | 0 | -1.924115 | 0.881009 | -0.202917 |
| 8 | 1 | 0 | 0.923540 | 0.000000 | 1.640476 |

**$AcO^-$ anion** (Table S-2c)



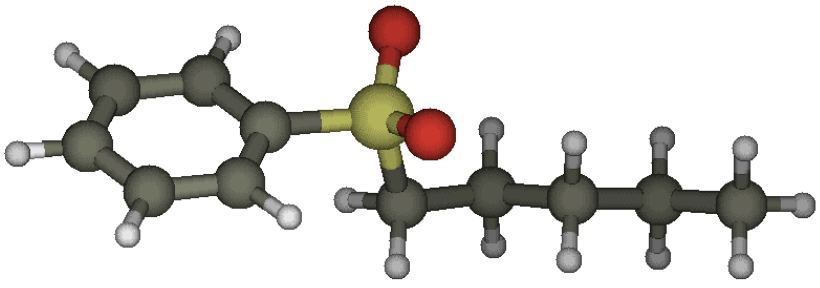
| | | | | | |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.020397 | -0.007537 | 0.007678 |
| 2 | 8 | 0 | -0.010415 | -0.191252 | 1.245715 |
| 3 | 8 | 0 | 1.030975 | 0.206103 | -0.697358 |
| 4 | 6 | 0 | -1.340582 | -0.044746 | -0.706146 |
| 5 | 1 | 0 | -1.238340 | 0.067079 | -1.784640 |
| 6 | 1 | 0 | -1.847407 | -0.985902 | -0.484412 |
| 7 | 1 | 0 | -1.971468 | 0.759017 | -0.319970 |

**AcONA** (Table S-2c)



| | | | | | |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.012163 | 0.002630 | 0.008184 |
| 2 | 8 | 0 | 0.013380 | 0.252375 | 1.242386 |
| 3 | 8 | 0 | 1.018580 | -0.251807 | -0.670549 |
| 4 | 6 | 0 | -1.352821 | -0.026070 | -0.697057 |
| 5 | 1 | 0 | -1.259396 | 0.363378 | -1.709589 |
| 6 | 1 | 0 | -1.678451 | -1.066587 | -0.768150 |
| 7 | 1 | 0 | -2.101674 | 0.533684 | -0.140898 |
| 8 | 11 | 0 | 2.223504 | -0.006768 | 1.181311 |

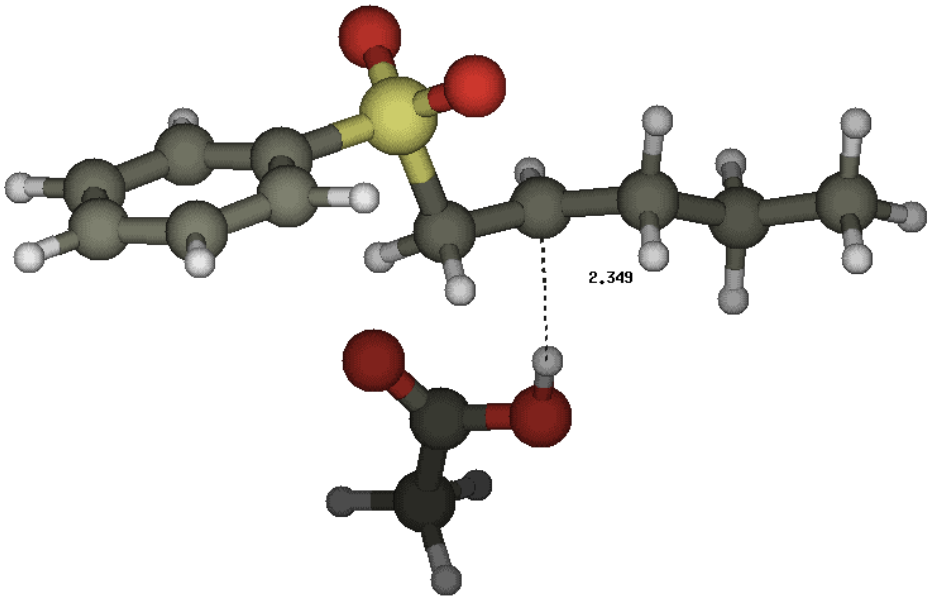
**Product $C_6H_5SO_2CH_2CH_2CH_2CH_2CH_3$ 3** (Table S-2c)



| | | | | | |
|---|---|---|---|---|---|
| 1 | 16 | 0 | -0.105847 | 0.087823 | 0.018511 |
| 2 | 6 | 0 | -0.040301 | 0.030459 | 1.787607 |
| 3 | 6 | 0 | 1.196840 | 0.027843 | 2.417504 |
| 4 | 8 | 0 | -1.377872 | 0.654054 | -0.368316 |
| 5 | 8 | 0 | 1.104045 | 0.725070 | -0.447914 |
| 6 | 6 | 0 | 1.243259 | -0.034461 | 3.803178 |

| | | | | | |
|---|---|---|---|---|---|
| 7 | 1 | 0 | 2.104593 | 0.085644 | 1.830885 |
| 8 | 1 | 0 | 2.199638 | -0.032123 | 4.309555 |
| 9 | 6 | 0 | 0.064396 | -0.092836 | 4.536246 |
| 10 | 6 | 0 | -1.167473 | -0.087648 | 3.892103 |
| 11 | 1 | 0 | 0.105247 | -0.138277 | 5.617181 |
| 12 | 6 | 0 | -1.226374 | -0.027202 | 2.507611 |
| 13 | 1 | 0 | -2.082873 | -0.125915 | 4.468071 |
| 14 | 1 | 0 | -2.176748 | -0.012247 | 1.989701 |
| 15 | 6 | 0 | -0.094670 | -1.630082 | -0.457593 |
| 16 | 6 | 0 | -0.496245 | -1.839089 | -1.913417 |
| 17 | 1 | 0 | 0.912124 | -1.993905 | -0.243295 |
| 18 | 1 | 0 | -0.799354 | -2.121038 | 0.216050 |
| 19 | 6 | 0 | 0.449201 | -1.227197 | -2.940716 |
| 20 | 1 | 0 | -1.508167 | -1.454990 | -2.061195 |
| 21 | 6 | 0 | 0.080825 | -1.626649 | -4.364481 |
| 22 | 1 | 0 | 0.436501 | -0.137128 | -2.857899 |
| 23 | 1 | 0 | 1.476043 | -1.541774 | -2.725541 |
| 24 | 6 | 0 | 1.007230 | -1.005184 | -5.400541 |
| 25 | 1 | 0 | 0.108178 | -2.717132 | -4.451044 |
| 26 | 1 | 0 | -0.951616 | -1.324742 | -4.565015 |
| 27 | 1 | 0 | 0.731384 | -1.302180 | -6.413668 |
| 28 | 1 | 0 | 0.971866 | 0.085318 | -5.349425 |
| 29 | 1 | 0 | 2.042017 | -1.311860 | -5.231356 |
| 30 | 1 | 0 | -0.544697 | -2.920871 | -2.064797 |

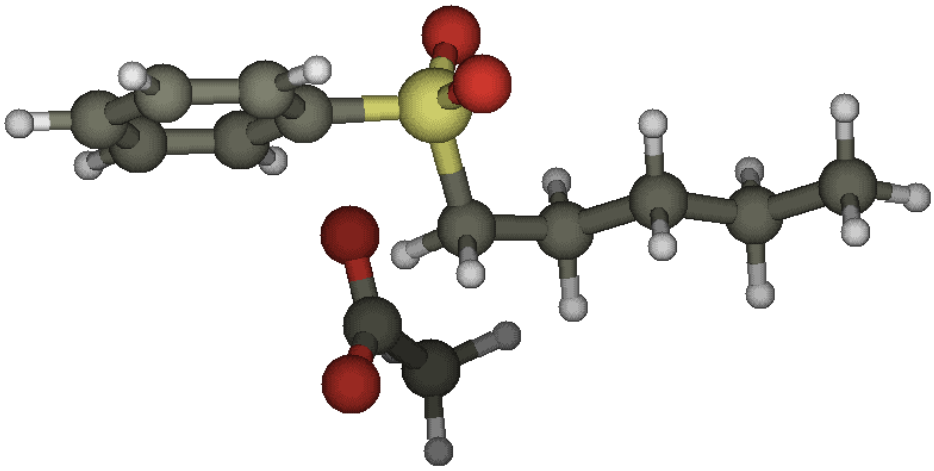
**Complex CA AcOH + 4** (Table S-2c)




| | | | | | |
|---|---|---|---|---|---|
| 1 | 16 | 0 | 0.046795 | 0.020412 | -0.002279 |
| 2 | 6 | 0 | 0.018437 | 0.007065 | 1.765849 |
| 3 | 6 | 0 | 1.213268 | -0.130183 | 2.459788 |
| 4 | 8 | 0 | -1.098238 | 0.762475 | -0.474375 |
| 5 | 8 | 0 | 1.362486 | 0.430825 | -0.434999 |
| 6 | 6 | 0 | 1.181180 | -0.165698 | 3.846469 |
| 7 | 1 | 0 | 2.149605 | -0.194836 | 1.920837 |
| 8 | 1 | 0 | 2.104144 | -0.264883 | 4.402790 |
| 9 | 6 | 0 | -0.032277 | -0.068633 | 4.516637 |
| 10 | 6 | 0 | -1.220698 | 0.066675 | 3.808291 |
| 11 | 1 | 0 | -0.051998 | -0.095086 | 5.598820 |
| 12 | 6 | 0 | -1.202081 | 0.104404 | 2.421924 |

| | | | | | |
|---|---|---|---|---|---|
| 13 | 1 | 0 | -2.162439 | 0.147352 | 4.335308 |
| 14 | 1 | 0 | -2.116889 | 0.218764 | 1.854650 |
| 15 | 6 | 0 | -0.183912 | -1.713971 | -0.451982 |
| 16 | 6 | 0 | -0.247050 | -1.861665 | -1.921899 |
| 17 | 1 | 0 | 0.667284 | -2.235455 | -0.007263 |
| 18 | 1 | 0 | -1.110615 | -2.017979 | 0.037386 |
| 19 | 6 | 0 | 0.977872 | -1.866904 | -2.764281 |
| 20 | 1 | 0 | -1.204276 | -1.677520 | -2.397946 |
| 21 | 6 | 0 | 0.785160 | -2.565429 | -4.109137 |
| 22 | 1 | 0 | 1.289411 | -0.827922 | -2.950882 |
| 23 | 1 | 0 | 1.804889 | -2.326108 | -2.212426 |
| 24 | 6 | 0 | 2.029059 | -2.482207 | -4.981760 |
| 25 | 1 | 0 | 0.523456 | -3.613665 | -3.938245 |
| 26 | 1 | 0 | -0.064057 | -2.110518 | -4.626549 |
| 27 | 1 | 0 | 1.880560 | -2.991930 | -5.934742 |
| 28 | 1 | 0 | 2.286537 | -1.442010 | -5.192795 |
| 29 | 1 | 0 | 2.885467 | -2.943236 | -4.484544 |
| 30 | 1 | 0 | -1.082026 | -4.054294 | -2.025334 |
| 31 | 8 | 0 | -1.604021 | -4.877433 | -2.070695 |
| 32 | 6 | 0 | -2.632391 | -4.772432 | -1.218295 |
| 33 | 8 | 0 | -2.804354 | -3.793653 | -0.536548 |
| 34 | 6 | 0 | -3.500992 | -5.988607 | -1.230755 |
| 35 | 1 | 0 | -4.314781 | -5.868891 | -0.522309 |
| 36 | 1 | 0 | -3.895479 | -6.139086 | -2.236292 |
| 37 | 1 | 0 | -2.902607 | -6.863542 | -0.974601 |

**Complex CB $AcO^-$ + 3** (Table S-2c)



| | | | | | |
|---|---|---|---|---|---|
| 1 | 16 | 0 | -0.073271 | 0.190660 | 0.010898 |
| 2 | 6 | 0 | -0.014020 | 0.057753 | 1.780020 |
| 3 | 6 | 0 | 1.217551 | -0.010697 | 2.412376 |
| 4 | 8 | 0 | -0.797119 | 1.397466 | -0.324851 |
| 5 | 8 | 0 | 1.281858 | 0.065907 | -0.486015 |
| 6 | 6 | 0 | 1.256952 | -0.070493 | 3.799950 |
| 7 | 1 | 0 | 2.125810 | -0.015162 | 1.824346 |
| 8 | 1 | 0 | 2.210832 | -0.120716 | 4.309117 |
| 9 | 6 | 0 | 0.074688 | -0.070810 | 4.527722 |
| 10 | 6 | 0 | -1.153524 | -0.011616 | 3.876491 |
| 11 | 1 | 0 | 0.108353 | -0.122320 | 5.608883 |
| 12 | 6 | 0 | -1.209055 | 0.056679 | 2.492535 |
| 13 | 1 | 0 | -2.072775 | -0.021376 | 4.448075 |
| 14 | 1 | 0 | -2.164539 | 0.085330 | 1.971908 |
| 15 | 6 | 0 | -1.035521 | -1.219894 | -0.484329 |

| | | | | | |
|---|---|---|---|---|---|
| 16 | 6 | 0 | -1.659121 | -1.052384 | -1.862688 |
| 17 | 1 | 0 | -0.352798 | -2.070411 | -0.430022 |
| 18 | 1 | 0 | -1.818885 | -1.340020 | 0.266500 |
| 19 | 6 | 0 | -0.666108 | -0.956563 | -3.014446 |
| 20 | 1 | 0 | -2.309400 | -0.174670 | -1.848019 |
| 21 | 6 | 0 | -1.357664 | -0.935364 | -4.372133 |
| 22 | 1 | 0 | -0.056529 | -0.054122 | -2.906178 |
| 23 | 1 | 0 | 0.025999 | -1.804686 | -2.970478 |
| 24 | 6 | 0 | -0.371887 | -0.837896 | -5.528447 |
| 25 | 1 | 0 | -1.964272 | -1.839870 | -4.479168 |
| 26 | 1 | 0 | -2.051977 | -0.090381 | -4.406471 |
| 27 | 1 | 0 | -0.883725 | -0.825439 | -6.492273 |
| 28 | 1 | 0 | 0.225528 | 0.073667 | -5.454349 |
| 29 | 1 | 0 | 0.316271 | -1.686527 | -5.525666 |
| 30 | 1 | 0 | -2.307778 | -1.921432 | -2.008462 |
| 31 | 8 | 0 | -3.634606 | -2.586074 | 0.834614 |
| 32 | 6 | 0 | -4.268748 | -1.573099 | 0.462520 |
| 33 | 8 | 0 | -3.994386 | -0.382024 | 0.743790 |
| 34 | 6 | 0 | -5.483514 | -1.790172 | -0.447173 |
| 35 | 1 | 0 | -6.341632 | -1.236363 | -0.063594 |
| 36 | 1 | 0 | -5.259368 | -1.392157 | -1.439879 |
| 37 | 1 | 0 | -5.737313 | -2.845288 | -0.537566 |