A New Tool to Guide Halofunctionalization Reactions: the Halenium Affinity (HalA) Scale

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I. General remarks:

All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen or argon. Molecular sieves (4Å) were dried at 160 °C under 0.25 mtorr pressure prior to use. Unless otherwise mentioned, solvents were purified as follows. THF was distilled from sodium benzophenone ketyl. NMR spectra were obtained using a 500 MHz Varian NMR spectrometer and referenced using the residual $^1$H peak from the deuterated solvent. Infrared spectra were measured on a Nicolet IR/42 spectrometer FT-IR (thin film, NaCl cells). For HRMS (ESI) analysis, a Waters 2795 (Alliance HT) instrument was used and referenced against Polyethylene Glycol (PEG-400-600).

Column chromatography was performed using Silicycle 60Å, 35-75 µm silica gel. Pre-coated 0.25 mm thick silica gel 60 F254 plates were used for analytical TLC and visualized using UV light, iodine, potassium permanganate stain, $p$-anisaldehyde stain or phosphomolybdic acid in EtOH stain.

Halenium sources used in this study: $N$-chlorosuccinimide (NCS), $N$-bromosuccinimide (NBS), $N$-iodosuccinimide (NIS), 1,3-dichloro-5,5-dimethylhydantoin (DCDMH), 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) and $N$-chlorophthalimide (NCP) were re-crystallized prior to use. Chlorodiethylsulfonium hexachloroantimonate (CDSC), bromodiethylsulfonium bromopentachloroantimonate (BDSB), iododiethylsulfonium iodopentachloroantimonate (IDSI) were synthesized as reported previously.$^1$ Substituted pyridines were distilled and stored over KOH prior to use (except 4-bromopyridine which was distilled immediately after basification of its commercially available HCl salt and used right away). All other commercially available reagents and solvents were used as received unless otherwise mentioned.
II. Guide to halenium affinity (HalA) calculations:

Since we have derived parallels between protonation and halogenation chemistry, the evaluation of gas phase Halenium Affinity (HalA) is essentially similar to the reported methods used for derivation of Proton Affinity (PA). We define the computationally evaluated HalA as the molar enthalpy change for a given Lewis base (:LB) upon its attachment to a halenium ion (X⁺), as shown below:

$$\text{HalA} = -\Delta E(\text{elec}) - \Delta ZPE - \Delta E'(\text{vib}) + \frac{5}{2}RT;$$

$$E'(\text{vib})(T) = \sum_{i=1}^{3n-6} \frac{Nh\nu_i}{e^{Nh\nu_i/RT} - 1}$$

where; $\Delta E_{(elec)} = E_{(\text{electronic})(X\text{-LB adduct})} - [E_{(\text{electronic})(:LB)} + E_{(\text{electronic})(X^+)}]$; zero point energy change $\Delta ZPE = ZPE(X\text{-LB adduct}) - ZPE(:LB)$; $\Delta E'(\text{vib}) = E'(\text{vib})(X\text{-LB adduct}) - E'(\text{vib})(:LB)$ i.e. difference in temperature dependence of vibrational energy; $N$ is Avogadro’s number, $h$ is Planck’s constant, and $n_i$ is the $i^{\text{th}}$ vibrational frequency. Finally, the $5/2$ RT quantity accounts for translational degrees of freedom and the ideal gas value for the change from two particles to one.

The acceptor fragment (Lewis base) may be neutral or anionic (i.e. the X-LB complex is cationic or neutral), leading to two distinct cases:

$$\Delta H_{\text{rxn}}(X^+ + :LB \rightarrow X\text{-LB}^+) \text{ or } \Delta H_{\text{rxn}}(X^+ + :LB^- \rightarrow X\text{-LB})$$
The $\text{HalA}$ values (gas phase) in kcal/mol are derived at $T = 298.15$ K (unless noted otherwise) assuming ideal gas behavior.

$\textit{Ab initio}$ assessments may provide accurate $\text{HalA}$ values, but their computational expense quickly becomes impractical with increasing molecular size. A Density Functional Theory (DFT) approach is affordable and widely available to most organic chemists who wish to evaluate $\text{HalA}$ values and apply them in the planning of halofunctionalization reactions. Our combined theoretical-experimental optimizations for the best compromise between computational expense and reliability of $\text{HalA}$ values, have led us to the application of the following basis sets based on the halenium ion under consideration: a.) for fluorenium, chlorenium and bromenium ions - B3LYP/6-31G*. b.) for iodenum ion – B3LYP/6-31G*/LANL2DZ. To calculate $\text{HalA}$ values from theory for gas phase reactions (appropriate solvent models can be applied if necessary) the following steps were followed:

1. An appropriate basis set must be chosen based on the halenium ion under consideration.

2. The Lewis base is initially subjected to a conformational search at the level of theory decided from step 1. To confirm that each structure was a true minimum, vibrational analyses were performed. If necessary, the lowest energy conformer can be re-subjected to a full geometry optimization to verify convergence.

3. The halenium ion (in its triplet state) is also subjected to the same level of theory for a geometry optimization.
4. The Lewis base-halenium ion adduct is then subjected to step 2 as described above.

If there are multiple nucleophilic sites within the same molecule (Lewis base), then separate calculations must be initiated with appropriate attachment of the halenium ion to each nucleophilic site.

5. The following three values are extracted from each of the output files for geometry minimized Lewis base (lowest energy conformer) and the Lewis base-halenium ion adduct/complex: a.) electronic energy \( E \), b.) zero point energy \( ZPE \) and, c.) temperature dependence of vibrational energy \( E'_{(vib)} \).

The electronic energy of the halenium ion is also obtained from its corresponding output file.

6.) Finally, these values (converted to kcal/mol) are then substituted in the following equation to obtain the \( HalA \) (X) for the Lewis base.

\[
HalA = -\Delta E_{(elec)} - \Delta ZPE - \Delta E'_{(vib)} + \frac{5}{2}RT
\]

Alternatively, the excel file template provided as a separate section of supporting information can be used to obtain the \( HalA \) value by simply entering the six values obtained from the output files for geometry minimized Lewis base (lowest energy conformer) and the Lewis base-halenium ion adduct/complex.
III. Interpreting the halenium affinity table:

The Halenium affinity table (attached as a separate section of supporting information) provides over 500 $\text{HalA (Cl)}$ values for various halenium acceptors that are categorized based on functional groups. Each category includes an organized trend of $\text{HalA}$ values for acceptors based on their ring size, substitution pattern, nucleophilicity etc. For searching a category of acceptors or even a particular acceptor, the table also provides labels and molecular formulas. The labels are based on the functionalities and/or the acceptor atom. For instance, the $\text{HalA (Cl)}$ of morpholine can be found by searching the document for molecular formula- $\text{C}_4\text{H}_9\text{NO}$. Since, morpholine incorporates nitrogen and oxygen atoms serving as halenium ion acceptors, searching the document under the label ‘NO’ will lead to a quick recognition of compounds incorporating Nitrogen and Oxygen atoms that have been evaluated for halenium affinity (e.g. N-methyl morpholine, 4-hydroxypyridine, methoxypyridines, amides etc.). Apart from simply being a listing of $\text{HalA (Cl)}$ values, the table also provides the reader with useful and handy trends that can be interpreted based on their ring size, steric strain etc. The following four examples illustrate a few of several trends.
Example 1

The relationship of sterics incorporated in substituted phosphines to their electron donating ability can be best described by the Tolman’s concept of cone angles. To represent the trend of halenium affinity in phosphines, we have employed the cone angle where the metal center is replaced by a chlorine atom. As shown above, the increasing steric demand of the substituents on phosphine leads to an increased internal angle ($\theta_1$) for R-P-R ($\text{P1}-93.4^\circ < \text{P2}-93.0^\circ < \text{P6}-102.6^\circ < \text{P8}-103.0^\circ < \text{P5}-107.4^\circ$) eventually shifting the trigonal pyramidal geometry of the phosphine towards trigonal planar. Thus in sterically bulky phosphines, the R-P bond gains more ‘s’ character leading to higher ‘p’ character in the lone pair. A lone pair with more ‘p’ character is less bound to the nucleus and displays enhanced nucleophilicity for the free phosphine. Meanwhile, as substituent bulk increases, the strain in the larger cone angle ($\theta_2$) cases of the halo-phosphonium ion opposes this effect, leading to a leveling off of the rate of increase in the $\text{HalA (Cl)}$ values.
Example 2

As described for example 1 above, a similar trend of HalA (Cl) is observed for compounds S13 to S16 and N58 to N61. With increasing ring size, the angle strain for C-N-C or C-S-C (θ) is relieved. The increase in ‘p’ character of the lone pair with increasing ring size enhances the nucleophilicity of the heteroatoms and hence their halenium affinity. In contrast, as we go from left to right the increasing ‘p’ character of the lone pair results in a longer bond to the chlorine atom (intrinsic effect due to the geometry). This can be seen from increasing N-Cl distance in the chlorinated analogs. Among the compounds shown above, the lone pair electrons in S13 and N58 are tightly
bound to the nucleus as they have the highest ‘s’ character and hence the resulting S-Cl or N-Cl bond is the strongest.

**Example 3**

The ascending trend of HalA (Cl) values in this example (as anticipated) displays the increasing reluctance of chlorenium ion to form a three membered cyclic intermediate (chloriranium ion) with the increasing inductive and hyperconjugative donating effects of the substituent on the terminal olefin. Ethylene (A44) by itself forms a symmetrically bridged chloriranium ion A44-Cl. The increasing donating effect of the substituents (A45-A48) distorts this symmetry as indicated by the C-Cl distances and the bond angles $\theta_1$ and $\theta_2$. The phenyl ring in styrene (A49) stabilizes the chlorenium ion via resonance electron donation. The delocalization of this positive charge results in the corresponding chloromethyl carbenium ion A49-Cl.$^4$
Example 4

Forming a chlorenium ion adduct of the above cycloalkenes leads to re-hybridization of the olefinic carbons from sp\(^2\) (\(\angle C-C=C = 120^\circ\)) to hybridization between sp\(^2\) and sp\(^3\) (similar to oxirane carbons). The initial strain introduced due to presence of olefinic carbons (in the parent cycloalkene) can be relieved to a certain extent if the concomitant re-hybridization in its chlorenium adduct leads to a bond angle (\(\theta_2\)) that is close to the corresponding bond angle (\(\theta\)) in the parent cycloalkane. As shown above, the \(HalA\) (Cl) value of the cycloalkenes increase with the ring size, except for A88 and A89. Cyclopropene (A86) incorporates a higher ring strain and angular strain \(\theta_1 = 64.6^\circ\) (55.4° deviation from the normal bond angle of 120° for an sp\(^2\) carbon). Formation of the chlorenium ion adduct A86-Cl, alleviates this strain to a certain extent as \(\theta_2 (61.7^\circ)\)
approaches the natural bond angle in cyclopropane ($\theta = 60.0^\circ$) via partial hybridization of the sp$^2$ carbons. Though cyclobutene undergoes similar changes in its bond angles upon formation of A$^{87}$-Cl, it has a relatively higher $HalA$ (Cl). A switch in the trend of $HalA$ (Cl) values is observed for cyclopentene (A$^{88}$) and cyclohexene (A$^{89}$). Their orbital energies being similar, the only difference arises due to the change in angle strain upon formation of A$^{88}$-Cl and A$^{89}$-Cl. The resulting hybridization in A$^{88}$-Cl brings $\theta_2$ ($109.2^\circ$) closer to the bond angle in the parent cyclopentane ($\theta = 103.3^\circ$, $\theta_2 - \theta = 5.9^\circ$) in comparison to formation of A$^{89}$-Cl, which results in elevated angle strain as $\theta_2$ ($120.8^\circ$) deviates further from cyclohexane ($\theta = 111.5^\circ$, $\theta_2 - \theta = 9.3^\circ$). Finally, as $\theta_1$ increases with increasing ring size ($\theta_1$-A$^{91}$), the corresponding change in the geometry of the olefin escalates its nucleophilicity.
IV. Equilibrium and titration studies on halopyridinium salts:

a. Screening of chlorenium sources for the formation of chloropyridinium complexes of 1a:

To test the validity of theoretically evaluated halenium affinity values, we studied the possibility for the formation of chloropyridinium complexes via $^1$H NMR. In this respect, 2,4,6-trimethylpyridine 1a was initially chosen as a model substrate and acetone-$d_6$ was identified as the optimum solvent of choice. The corresponding halopyridinium salts of 1a displayed low solubility in other commercially available deuterated solvents. Halo-pyridinium salts of 1a were found to be soluble in tetrahydrofuran-$d_8$ (THF), but this solvent was prohibitively expensive for the large number of planned experiments. Furthermore, the possibility of chlorination of acetone under reaction conditions was ruled out based on three control experiments (see section III-h for further discussion), thus assuring that acetone is not a reactive solvent.

The formation of halo-pyridinium complex (1a-X) was monitored by observing the

![Figure S1](image)

**Figure S1.** Plot for titration of 1a with various halenium ion sources representing the chemical shift change of C3-H (ppm, 1a) as a function of added halenium ion source.
chemical shift (ppm) change of the C3-H aromatic hydrogens of 1a upon treatment with various amounts of halenium sources (X⁺). As seen in Figure S1, halenium ion sources such as NCS, NCP, dichloramine-T and TCCA with HalA values lower than 1a did not fully transfer halenium ion to 1a, whereas XtalFluor-E®, CDSC, BDSB, and IDSI did form the halo-pyridinium salts. A significant downfield shift of C3-H (approximately 0.9 ppm) is evident when 1.0 equivalent of the latter halenium sources are added to 1a (since the extent of positive charge localized on the pyridine nucleus is the same in the halo-pyridinium salts 1a-F, 1a-Cl, 1a-Br and 1a-I, the extent of downfield chemical shift observed for C3-H was also the same upon addition of 1.0 equiv of halenium sources). After addition of 1.0 equivalent of halenium ion source to 1a, there no further observable change in the chemical shift of C3-H (of 1a-Cl) as the titration is extended beyond 1.0 equiv of the halenium source (indication for the formation of 1:1 complex). Based on the HalA values, TCCA and DAST do not have the ability to completely transfer X⁺ ion, resulting only in stronger halogen bonding that leads to a 0.16 and 0.34 ppm downfield shift of C3-H, respectively. No chemical shift changes were observed when NCS, DCDMH, dichloramine-T, and N-chlorophthalimide sources were used. Addition of up to 5.0 equiv of TCCA (i.e. 15.0 equiv of active chlorenium ion) did not shift C3-H further downfield. However, with this excess of halogenating reagent, new peaks appeared in the aromatic region of the ¹H-NMR spectrum, suggesting side reactions such as benzylic chlorination. EI-MS studies on the crude mixture displayed masses for mono, di- and tri-chlorinated 1a). Radical chlorination of the aromatic ring can be ruled out since the same product was obtained when the experiment was repeated in the dark.
Table S1. Absolute and relative $HalA$ values (gas phase) of 1a in comparison to different halenium sources. Since SM8 is not compatible for elements $>$Kr, the gas phase $HalA$ values are depicted for comparison of the halenium (F, Cl, Br and I) sources.

| Entry | Halenium source | Halenium Ion (X) | $HalA$ (X) of 1a (kcal/mol) | $HalA$ (X) of halenium ion source (kcal/mol) | $\Delta HalA$ (kcal/mol) |
|-------|-----------------|------------------|-----------------------------|---------------------------------------------|------------------------|
| 1     | DAST            | F$^+$            | 288.8                       | 432.2                                       | 143.4                 |
| 2     | XfF             | F$^+$            | 288.8                       | 294.7                                       | 5.9                   |
| 3     | NCS             | Cl$^+$           | 168.2                       | 290.1                                       | 121.9                 |
| 4     | DCDMH           | Cl$^+$           | 168.2                       | 275.7                                       | 107.5                 |
| 5     | NCP             | Cl$^+$           | 168.2                       | 286.7                                       | 118.5                 |
| 6     | Dichloramine-T  | Cl$^+$           | 168.2                       | 273.3                                       | 105.1                 |
| 7     | TCCA            | Cl$^+$           | 168.2                       | 253.0                                       | 84.8                  |
| 8     | CDSC            | Cl$^+$           | 168.2                       | 161.3                                       | -6.9                  |
| 9     | BDSB            | Br$^+$           | 179.4                       | 133.2                                       | -46.2                 |
| 10    | IDSI            | I$^+$            | 141.1                       | 96.7                                        | -44.4                 |

NCS, DCDMH, NCP and Dichloramine-T, and have 121.9, 107.5, 118.5, and 105.1 (kcal/mol) higher gas phase chlorenium affinities than trimethyl pyridine, respectively (Table S1, entries 3-6). These large differences are corroborated by the experimental data and explain why the corresponding halo-pyridinium complexes are not formed. In organic solvents, conversion of neutral species into charged products is typically uphill in energy, so the conjugate anion of the halenium ion donor will always be more potent acceptor than 1a. Thus, it is no surprise that chlorenium ion transfer from neutral donors to substituted pyridines to yield halo-pyridiniums is unlikely. Therefore, for all subsequent experiments, CDSC was employed as the chlorenium donor, BDSB as the Br$^+$ donor and IDSI as the I$^+$ donor; the corresponding gas phase $HalA$ values (gas phase) are 161.3, 133.2, and 96.7 kcal/mol, respectively (Table S1, entries 8-10).
b. Titration studies of pyridine derivatives with CDSC:

Substituted pyridines 4-phenylpyridine (1h), 4-cyanopyridine (1f), pyridine 4-carbaldehyde (1i), 4-trifluoromethylpyridine (1e), and 4-dimethylaminopyridine (1j) were titrated with CDSC (0.0-2.0 equiv) in acetone-$d_6$ at room temperature (Figure S2). The range of $\text{HalA (Cl)}$ values (gas phase) for these pyridines spans from 145.2 to 176.0 kcal/mol. B3LYP/6-31G*/SM8 is not compatible for the antimony (VI) chloride counterion associated with CDSC, hence we resorted comparing gas phase $\text{HalA (Cl)}$ values of diethyl sulfide and substituted pyridines. The gas phase $\text{HalA (Cl)}$ values are 161.3 for diethyl sulfide and 168.2 for 1a. Figure S2 depicts the downfield shifts of the pyridines’ C3-H resonances as they are titrated with CDSC (0.0-2.0 equiv), forming chloropyridinium complexes. In all cases the formation of a 1:1 complex of Lewis base:halonium ion was confirmed on the basis of the unchanged chemical shifts of C3-H beyond addition of a stoichiometric equivalent of CDSC.

Figure S2. Plot for titration of pyridines 1a-i with various CDSC representing the chemical shift change of C3-H (ppm) as a function of added CDSC. The biphasic nature of the data for the titration of 1a is illustrated by two straight lines.
As Table S2 shows, halenium ion transfer to substituted pyridines can be easily monitored from the downfield chemical shift change of the aromatic proton (meta proton, C3-H). The most electron rich pyridine 1j (DMAP) shows an attenuated shift as a result of the electron donating C4-N,N-dimethylamine, which prior to chlorenium transfer alters the chemical shift of the C3-H significantly in comparison to other substituted pyridines. The observed chemical shift change between the free pyridine derivatives and their protonated analogs (~1 ppm downfield), closely matches those observed upon treatment of pyridine derivatives 1a-j with 1.0 equiv of CDSC. This clearly suggests complete chlorenium atom transfer to the nitrogen in all these pyridines to form the corresponding chloropyridinium salts. However, the exact chemistry of Cl+ delivery by CDSC is not completely understood. The range of $\text{HalA} \ (\text{Cl})$ values (SM8-acetone) for the pyridines in Table S2 spans from 137.2 to 154.3 kcal/mol, while that simply calculated for diethyl sulfide is 151.6, yet as noted above, complete chlorenium transfer is clearly indicated by the NMR results. Exploratory studies of possible explanations

Table S2. Absolute and relative $\text{HalA}$ values in kcal/mol obtained from gas phase and (SM8-acetone) calculation of pyridine derivatives 1a-j in comparison to diethyl sulfide–mimicking CDSC. aThe $\Delta \text{HalA}$ values displayed below represent the difference in $\text{HalA} \ (\text{Cl})$ values between the pyridine derivatives and diethyl sulfide. The $\text{HalA}$ value of diethyl sulfide is 161.3 kcal/mol (gas phase) and 151.6 kcal/mol (SM8-acetone).

| Entry | Pyridine derivatives | $\text{HalA}$ gas phase | $\text{HalA}$ | $\Delta \text{HalA}$ | $\Delta \text{HalA}$ SM8-acetone | $\Delta ppm$ (C3-H) |
|-------|----------------------|-------------------------|--------------|---------------------|-------------------------------|------------------|
| 1     | 1j (4-NMe2)          | 176.0                   | 154.3        | 14.7                | 2.7                           | 0.576            |
| 2     | 1a (2,4,6-trimethyl) | 168.2                   | 148.2        | 6.9                 | -3.4                          | 0.868            |
| 3     | 1h (4-Ph)            | 165.7                   | 145.7        | 4.4                 | -5.9                          | 0.936            |
| 4     | 1i (4-CHO)           | 150.8                   | 140.8        | -10.5               | -10.8                         | 0.921            |
| 5     | 1f (4-CN)            | 145.2                   | 138.0        | -16.1               | -13.6                         | 1.048            |
| 6     | 1e (4-CF3)           | 149.3                   | 137.2        | -12.0               | -14.4                         | 1.050            |
involving differential ion pairing of the $\text{SbCl}_6^-$ counterion with $\text{Et}_2\text{SCl}^+$ vs the chloropyridinium cations are not accessible to the present method as the SM8 solvent model included in the Spartan code does not extend to antimony. Hence, we focus our analysis on comparisons of the $\text{HalA}$ values within the same class (i.e. the pyridine derivatives in this case) of Lewis bases.

c. Qualitative analysis of competition experiments between pyridine derivatives:

To validate the $\text{HalA}$ scale on a more conclusive manner, the equilibrium of various substituted chloropyridiniums were investigated. In a typical experiment, a stock solution of CDSC (1.0 equiv) was added at room temperature to an acetone-$d_6$ solution of pyridine A (1.0 equiv), which has a lower calculated $\text{HalA}$ than diethyl sulfide. Complete formation of the chloro-pyridinium complex (A-Cl) was then confirmed by $^1\text{H}$ NMR analysis. To this complex (A-Cl), pyridine B (1.0 equiv), chose to have a higher calculated $\text{HalA}$ value than A was added to generate B-Cl via abstraction of chlorenium.

| Entry | Pyridine derivatives (A) | $\text{HalA}$ (kcal/mol) of pyridines (A) | (A$_C$/A) | Pyridine derivatives (B) | $\text{HalA}$ (kcal/mol) | (B$_C$/B) |
|-------|-------------------------|------------------------------------------|----------|-------------------------|--------------------------|----------|
| 1     | 1e (4-CF$_3$)           | 137.2                                    | 0.35     | 1a (2,4,6-trimethyl)    | 148.2                    | 0.80     |
| 2     | 1f (4-CN)               | 138.0                                    | 0.37     | 1a (2,4,6-trimethyl)    | 148.2                    | 0.80     |
| 3     | 1f (4-CN)               | 138.0                                    | 0.52     | 1e (4-CF$_3$)           | 137.2                    | 0.56     |
| 4     | 1e (4-CF$_3$)           | 137.2                                    | 0.04     | 1j (4-NMe$_2$)          | 154.3                    | 0.75     |
| 5     | 1a (2,4,6-trimethyl)    | 148.2                                    | 0.29     | 1j (4-NMe$_2$)          | 154.3                    | 0.79     |
| 6     | 1i (4-CHO)              | 150.8                                    | 0.29     | 1h (4-Ph)               | 165.7                    | 1.0      |
| 7     | 1h                      | 165.7                                    | 0.28     | 1a                      | 168.2                    | 0.70     |

Table S3. Absolute and relative $\text{HalA}$ values in kcal/mol (SM8-acetone) of pyridine derivatives 1a-j.
ion from A-Cl. The established equilibrium was then analyzed via $^1$H-NMR analysis. The amount of each chlorinated pyridine derivative was determined by examining the chemical shift change of C3-H and correlating it with the titration data of each substituted pyridine with CDSC (Figure S2). For example, in the competition between 1e and 1a, C3-H for 1e-Cl under the equilibrium mixture resonates at 8.27 ppm. Using linear interpolation based on the biphasic behavior seen between the limiting shifts observed for unchlorinated and chlorinated pyridines in titrations with CDSC, this shift indicates that 0.35 mol fraction of 1e is chlorinated. Similarly, C3-H of 1a, resonating at 7.67 ppm correlates to a 0.80 mol fraction of 1a. (Note: the sum of the individual mole fractions is over 100% (0.35 + 0.80 = 1.15) and this can be attributed to the fact that the actual chemical shift observed for C3-H under sub-stoichiometric amounts of halenium source is influenced by dimerization). Table S3 shows the fraction of chlorinated pyridine A and B, extracted from the titration curves in Figure S2 based on the changes in the chemical shifts of C3-H aromatic proton of the substituted pyridines. This shows a correlation between the calculated chlorenium affinities and experimental results. As anticipated, pyridine B with higher HalA value yields a greater ratio of BCl:B. This is a fair qualitative comparison to display the transfer of chlorenium ion from pyridine A (with a relatively lower HalA) to pyridine B exhibiting a relatively higher HalA value. Pyridine derivative 1a has 18.9 and 23.0 kcal/mol higher HalA than 1e and 1f, respectively, and thus the chlorenium ion is mostly transferred to 1a (with 0.80 equivalents chlorinated, Table S3, entry 1 and 2). The smallest difference in the fraction of chlorinated complex is observed between 1f and 1e (0.56 versus 0.52, Table S3, entry 3). This is in
complete agreement with the HalA values of the two pyridines. HalA (Cl) of 1f is 138.0 kcal/mol and HalA (Cl) of 1e is 137.2 kcal/mol.

These experiments qualitatively display the correlation between theoretically calculated HalA values and the fraction of chlorinated pyridine observed by $^1$H NMR. However, these experimental results cannot be used for quantitative analysis. As shown in Figures S1 and S2, the titration curves are nonlinear prior to addition of full stoichiometric equivalent amounts of halenium ion sources (CDSC, BDSB and IDSI), clearly suggesting the possibility of dimerization. This dimerization was confirmed when treatment of 1a with 0.5 equivalents of BDSB (or IDSI) in CDCl$_3$ displayed a downfield shift of the C3-H to 7.2 ppm. The extent of this shift is in accordance to the reported halogenated dimers of 1a.$^5$ The tendency of halo-pyridinium to undergo dimerization with the free base when subjected to sub-stoichiometric amounts of halenium source limits the quantitative analysis.$^6$ Moreover, the rapid exchange of chlorenium ion between the chlorinated and non-chlorinated acceptors leads to an averaged NMR signal, which does not allow for a direct measure of each species via integration.

Seeking reliable means for qualitative and quantitative analysis, we attempted to block pyridine-halogen-pyridine dimerization and the fast exchange of halenium ion in order to observe the chlorinated and non-chlorinated species under NMR timescale. Our rigorous optimizations identified pyridines 1b and 1c as model candidates for this study. Chlorinated 1b-Cl and 1c-Cl and their non-chlorinated counterparts 1b and 1c could be observed by $^1$H NMR at -90 °C in acetone-$d_6$. This enables the integration of each
individual species (free base and its chlorinated analog) such that the ratios of chlorinated and non-chlorinated counterparts could be obtained.
d. $^1$H-NMR analysis of chlorination of 4-methyl-2,6-di-tert-butyl pyridine (1c):

To rigorously confirm $\text{HalA}$ assessments on a quantitative scale, we resorted to equilibrium studies of chloropyridinium salts. Addition of 0.5 equiv of CDSC to 1c in acetone-$d_6$ at room temperature led to the observation of two species (broad peaks) by $^1$H NMR (Figure S3). Lowering the temperature to -30 °C, resulted in two sharp peaks corresponding to 1c and chlorinated 1c-Cl in a 1:1 ratio. This demonstrates that 1c has a slow exchange with its chlorinated form (1c-Cl) under the NMR timescale; thus enabling the observation of the chlorinated pyridine and its free base by $^1$H-NMR analysis at -30 °C. The bulky t-butyl substituents on the ortho positions efficiently inhibited the dimerization and the rapid intermolecular transfer of halenium ions. 1c was

![Chemical reaction diagram](image)

**Figure S3.** $^1$H NMR spectra of 1c at different temperatures under sub-stoichiometric amounts (0.5 equiv) of CDSC.
then titrated with CDSC to observe the ratios of 1c and 1c-Cl at -30 °C. Figure S4 shows the overlay of $^1$H NMR spectra (C3-H) with different amounts of CDSC. The resonance at 7.06 ppm corresponds to the free base, while the downfield peak at 8.06 ppm corresponds to 1c-Cl. Upon addition of 1.0 equiv of CDSC, the resonance at 7.06 ppm disappears, and only 1c-Cl is observed (8.06 ppm, Figure S4, entry 6).

e. Formation of halopyridinium salts of 1c with different halenium donors:

![Diagram showing the formation of halopyridinium salts](image)

| Entry | CDSC (equiv) | 1c (%) | 1c-Cl (%) |
|-------|-------------|--------|----------|
| 1     | 0.0         | 100    | 0.0      |
| 2     | 0.3         | 69.0   | 30.0     |
| 3     | 0.5         | 53.0   | 50.0     |
| 4     | 0.7         | 31.0   | 70.0     |
| 5     | 0.9         | 3.0    | 90.0     |
| 6     | 1.0         | 0.0    | 100      |
| 7     | 1.5         | 0.0    | 100      |
| 8     | 2.0         | 0.0    | 100      |

**Figure S4.** Titration data for chlorination of 1c with CDSC.
Since 1c and 1c-Cl can be observed as separate entities under the NMR timescale at -30 °C, we initiated similar studies with different halenium sources to observe the formation of 1c-X and validate the theoretical HalA estimates. The counter anions of DAST and TCCA have a higher HalA than 1c (Table S4, entries 1 and 3) therefore, as anticipated, ¹H NMR showed no evidence of their transferring halenium ion. Similarly, as expected from the HalA values, only CDSC, BDSCB and IDSI led to a complete transfer of halenium ion to 1c forming the corresponding halo-pyridinium salts (Table S4, entries 4-6).

Table S4. Absolute HalA values and experimentally observed ratios of 1c and 1c-X using different halenium ion sources. Since SM8 is not compatible for elements >Kr, the gas phase HalA values are depicted for comparison of the halenium (F, Cl, Br and I) sources.

| Entry | Halenium source | Halenium ion (X) | HalA (X) of 1c gas phase (kcal/mol) | HalA of Halenium source gas phase (kcal/mol) | (1c-Cl)% |
|-------|----------------|-----------------|----------------------------------|--------------------------------|---------|
| 1     | DAST           | F⁺              | 287.9                            | 432.2                         | 0.0     |
| 2     | XIF            | F⁺              | 287.9                            | 294.7                         | 47.0    |
| 3     | TCCA           | Cl⁺             | 153.1                            | 253.0                         | 0.0     |
| 4     | CDSC           | Cl⁺             | 153.1                            | 161.3                         | 100     |
| 5     | BDSB           | Br⁺             | 160.4                            | 133.2                         | 100     |
| 6     | IDSI           | I⁺              | 118.4                            | 96.7                          | 100     |
f. Quantitative analysis via competition experiments:

The optimized conditions mentioned above were employed to study the competition for chlorenium ion capture between 1a and 1c. Since, 1a has a 15.0 kcal/mol higher chlorenium affinity than 1c, halenium ions should preferentially bind to 1a over 1c with an equilibrium constant $> 10^{10}$. As shown by the $^1$H-NMR spectra overlay (Figure S5), titration of the pre-formed 1c-Cl complex with 1a leads to a corresponding decrease in the concentration of 1c-Cl as the chlorenium ion is now transferred onto the stronger Lewis base 1a (intensity of the peak at 8.06 ppm for 1c-Cl decreases while the intensity of the peak at 7.06 ppm which corresponds to free 1c, increases). Moreover, a careful inspection of Figure S5 indicates a downfield shift of the

Figure S5. Quantification of HalA assessment via competitive chlorination between 1c and 1a.
chlorinated species \(1\text{a}-\text{Cl}\) and \(1\text{c}-\text{Cl}\) until the mixture is titrated with 1.0 equiv of \(1\text{a}\), a Lewis base capable of undergoing dimerization (as discussed earlier). The fraction of \(1\text{c}-\text{Cl}\) listed in Table S5 is derived from the integration of these two peaks corresponding to \(1\text{c}\) and \(1\text{c}-\text{Cl}\). Formation of \(1\text{a}-\text{Cl}\) is also revealed by the downfield shift of C3-H of \(1\text{a}\). The fraction of \(1\text{a}-\text{Cl}\) (Table S5) is derived by correlating its observed chemical shift to its titration data (Figure S2). Similarly, as shown below (Figure S6), the fraction of \(1\text{c}-\text{Cl}\) and \(1\text{a}\) was plotted against the number of equivalents of \(1\text{a}\) added.

![Plot](image.png)

**Figure S6.** Plot for mol fraction (%) of \(1\text{a}-\text{Cl}\) and \(1\text{c}-\text{Cl}\) vs equiv of \(1\text{a}\) added.
Table S5. Data for titration of 1c-Cl with 1a. \( \text{HalA (Cl)}_{1c} = 127.2 \text{ kcal/mol (SM8-acetone)} \). \( \text{HalA (Cl)}_{1a} = 148.2 \text{ kcal/mol (SM8-acetone)} \).

| Entry | 1a (equiv) | (1c-Cl)% | (1a-Cl)% |
|-------|------------|----------|----------|
| 1     | 0.0        | 100      | 0.0      |
| 2     | 0.5        | 67.0     | 37.0     |
| 3     | 0.7        | 44.0     | 58.0     |
| 4     | 1.0        | 16.0     | 85.0     |
| 5     | 1.5        | 0.0      | 100      |

Note: Although our NMR analysis conditions were chosen to minimize exchange and dimerization of 1c and 1c-Cl, the formation of hetero-dimers of 1c-Cl with free 1a is possible, and dimerization of 1a with 1a-Cl certainly occurs even under low temperature.

Figure S7. Overlay of \(^1\text{H} \) NMR spectra displaying the titration of 1b-Cl with 1c.
condition in the presence of sub-stoichiometric amounts of halenium ion source.

To thwart the competing dimerization, we resorted on competition studies using 2,6-di-tert-butylpyridine (1b) and 1c. At -90 °C in acetone-$d_6$ the free bases 1b and 1c were distinctly observed from the corresponding chloropyridiniums 1b-Cl and 1c-Cl by $^1$H-NMR. The fraction of free bases 1b and 1c was derived simply by integration of the corresponding peaks at 7.06 (1c) and 8.06 (1c-Cl) ppm (see Figure S7). Furthermore, the C3-H resonances of 1b and 1b-Cl were distinctly observable at 7.24 and 8.16 ppm, respectively, whereas the corresponding C4-H could be observed at 7.69 and 8.73 ppm. The overlay of $^1$H-NMR spectra at different equivalents of 1c is shown in Figure S7. As the spectra show, addition of the stronger Lewis base 1c depletes 1b-Cl, confirming the equilibrium shift anticipated by HalA calculations. When an equimolar mixture of 1b and 1c was treated with 1.0 equiv of CDSC, an equilibrium mixture of 1b-Cl and 1c-Cl (in a 1:7 ratio, Table S6, entry 8) was observed by $^1$H-NMR. The experimental result is in complete accord with the theoretical HalA predictions at the B3LYP/6-31G*/SM8 (acetone) level of theory ($\Delta$HalA at -90 °C = 1.1 kcal/mol; predicting a 1:7 ratio).

Table S6. Data for titration of 1c-Cl with 1b. HalA (Cl)$_{1c}$ = 127.2 kcal/mol. HalA (Cl)$_{1b}$ = 126.1 kcal/mol (B3LYP/6-31G*/SM8-acetone).

| Entry | 1c (equiv) | (1b-Cl)% | (1c-Cl)% |
|-------|------------|----------|----------|
| 1     | 0.0        | 100      | 0.0      |
| 2     | 0.2        | 82.0     | 100.0    |
| 3     | 0.3        | 69.0     | 97.0     |
| 4     | 0.5        | 58.0     | 98.0     |
| 5     | 0.6        | 37.0     | 93.0     |
| 6     | 0.7        | 36.7     | 95.0     |
| 7     | 0.9        | 19.8     | 86.2     |
| 8     | 1.0        | 12.0     | 88.0     |
| 9     | 1.5        | 0.0      | 56.0     |
fraction of chlorinated 1b and 1c were plotted against the equivalents of added 1c (Figure S8). This study not only validates quantification via HalA but also highlights its value in predicting the outcome of reactions involving subtle steric and electronic changes.

The competition reaction between 1b and 1c was repeated at different temperatures (ranging from -90 °C to -30 °C) to probe the effect on chlorenium ion

Table S7. Effect of temperature on equilibrium ratios of 1b-Cl and 1c-Cl in presence of their free bases 1b and 1c.

| Entry | Temperature (°C) | ΔHalA (kcal/mol) at T °C | (1b-Cl)% | (1c-Cl)% |
|-------|-----------------|--------------------------|----------|----------|
| 1     | -30             | 1.104                    | 17.0     | 88.0     |
| 2     | -50             | 1.094                    | 20.0     | 87.0     |
| 3     | -70             | 1.091                    | 22.0     | 85.0     |
| 4     | -90             | 1.081                    | 21.0     | 83.0     |
transfer. Table S7 displays the fraction of chlorinated 1b and 1c at different temperatures (listed HalA values were calculated using the SM8 model to simulate acetone). The calculated $\Delta$HalA values decrease upon lowering the temperature, which is in agreement with the experimental results (fraction of 1c that is chlorinated drops from 88.0 to 83.0 %). Note that a slight excess of chlorenium donor is reflected in the >100% sum of these percentages.

g. **Competition study for chlorenium ion transfer from 1c-Cl to pyridines derivatives (a quantitative trend):**

Having qualitatively and quantitatively validated the chlorenium ion transfers, 1c was subjected to similar competition studies with a series of pyridines exhibiting different electronic and steric profiles. Pyridine derivative (A) with a lower inherent HalA than 1c was chlorinated by its reaction with CDSC. To this chloropyridinium complex A-

| Entry | Pyridine Derivatives (A) | $\text{HalA}_1$ (A) (kcal/mol) | $\text{HalA}_1$ (1c) (kcal/mol) | $\Delta$HalA (kcal/mol) | (1c-Cl)% |
|-------|--------------------------|-------------------------------|-------------------------------|-------------------------|----------|
| 1     | 1f (4-CN)                | 138.0                         | 127.2                         | +10.8                   | 100      |
| 2     | 1e (4-CF$_3$)            | 137.2                         | 127.2                         | +10.0                   | 97       |
| 3     | 1b (2,6-di-t-Bu)         | 126.1                         | 127.2                         | -1.1                    | 88       |
| 4     | 1g (4-Br)                | 138.8                         | 127.2                         | +11.6                   | 53       |
| 5     | 1d (4-t-Bu)              | 146.3                         | 127.2                         | +19.1                   | 4        |
| 6     | 1a (2,4,6-trimethyl)     | 148.2                         | 127.2                         | +21.0                   | 0        |
| 7     | 1h (4-Ph)                | 145.7                         | 127.2                         | +18.5                   | 32       |
| 8     | 1j (4-NMe$_2$)           | 154.3                         | 127.2                         | +27.1                   | 30       |
Cl, 1.0 equiv of 1c was added and the corresponding ratio at equilibrium was evaluated by $^1$H NMR. As shown in Table S8 (entry 1-3), the difference in $HalA$ between 1c and the corresponding pyridine derivative 1f, 1e, and 1b correlates to the observed equilibrium ratio of 1c-Cl by $^1$H NMR. Thus, the fraction of 1c-Cl calculated from experimental results compliments the theoretical $HalA$ estimates. On the other hand, 4-bromopyridine (1g), 4-tert-butylpyridine (1d), and 2,4,6-trimethylpyridine (1a), which have higher $HalA$ values than 1c also demonstrate experimental results that comply with the theoretical estimations (entry 4-6). The calculated $\Delta HalA$ values decrease upon

**Figure S9.** Overlay of $^1$H NMR spectra displaying equilibrium ratios when chloropyridinium derivatives 1(a-f)-Cl were treated with 1.0 equiv of 1c.
lowering the temperature, which is in agreement with the experimental results (fraction of 1c that is chlorinated drops from 88.0 to 83.0 %). The identity of this precipitated could not established due to instability of the chlorinated complexes, hence reliable experimental results were not obtained upon chlorination of 1h and 1j.

The overlay of $^1$H-NMR spectra of 1c-Cl in competition with other pyridines is shown in Figure S9. These examples clearly demonstrate the validity of HalA as an efficient tool that allows quantitative ranking of halenium ion affinities for Lewis bases.

**Figure S10.** Overlay of $^1$H NMR spectra of 1c-Cl, 1c-HCl and 1c displaying their relative chemical shifts.
h. Control experiments:

The halo-pyridinium salts with antimony (VI) halide as the counter anion were insoluble in most of the commercially available deuterated solvents. Although THF-\(d_6\) was efficient in dissolving these salts, it was not economically viable for the entire set of planned experiments. Furthermore, use of acetonitrile-\(d_3\) led to Ritter-type reactions causing decomposition of the halo-pyridinium salts. Hence, for all the above experiments involving analyses of halo-pyridinium salts, acetone-\(d_6\) was identified as the optimum solvent. We were aware of the possibility that treatment of pyridines with halenium sources in acetone might lead to protonation (rather than chlorination) of the pyridinium nitrogen atom yielding \(\alpha\)-chloroacetone as the end product. The protonated pyridines would exhibit a similar downfield shift of the C3-H and thus lead to an erroneous result. This possibility was ruled out based on our control experiments - 1.) by observing no change in chemical shift of the chloropyridiniums upon addition of K\(_2\)CO\(_3\),

![Figure S11. Overlay of \(^1\)H NMR spectra displaying the protonated salt (1c-HSbCl\(_6\)) and the analogous chlorinated salt (1c-Cl) in presence of the free base (1c) in acetone-\(d_6\) at room temperature.](image)
2.) by employing THF as a solvent and observing identical behavior as seen with acetone-\textit{d}_6, and, 3.) by successfully initiating a chlorolactonization of alkenoic acid using the \textit{in situ} generated chloro-pyridinium 1a-Cl.

1.) To verify whether the species under consideration were chloro-pyridinium salts, we deliberately synthesized their protonated analogs by bubbling HCl gas in the ethereal solution of 1c at 0 °C followed by filtration of the precipitated salt (1c-HCl). The salt was dried and suspended in 1,2-dichloroethane and treated with 1.5 equiv of SbCl$_5$ at -40 °C. This yielded the protonated pyridinium-SbCl$_6$ salt. Having the same counter anion - SbCl$_6^-$, $^1$H NMR spectra of 1c-H (protonated salt) and 1c-Cl (chlorinated salt) were compared in acetone-\textit{d}_6 at room temperature (Figure S11). The equilibrium mixture of 1c and 1c-Cl at room temperature shows a set of poorly resolved peaks between 7.0-7.6 ppm. In contrast, the equilibrium mixture of 1c and 1c-HSbCl$_6$ displays a set of two sharp peaks at 7.06 and 8.06 ppm corresponding to the protonated salt and the free base, respectively. The difference in their chemical shifts (ppm) and broadness of the peak clearly confirms the identity of two different species (protonated and chlorinated) and the relative rate of exchange (compared to NMR timescale) under similar conditions. Furthermore, the protonated and chlorinated species shown above were subjected to 1.0 equiv of K$_2$CO$_3$ and the resulting mixtures were analyzed by $^1$HNMR. Upon addition of K$_2$CO$_3$ at room temperature, the peak corresponding to 1c-HSbCl$_6$ disappeared instantaneously with increased intensity for the peak due to free 1c. However, addition of K$_2$CO$_3$ to the equilibrium mixture of 1c and 1c-Cl did not lead to any immediate observable change in the intensity or ratio of the free base and its
chlorinated counterpart. When this solution was left at room temperature for over 30 min, some evidence of decomposition of 1c-Cl was observed by $^1$H NMR. This clearly shows that under the standard optimized conditions, the addition of halenium source leads to the formation of halo-pyridinium salts rather than simple protonation.

2.) Chlorination of 1c with CDSC was performed using non-deuterated THF as a solvent ($^1$H NMR spectrum at -90 °C was obtained using suppression of THF resonances). A similar behavior (when acetone-$d_6$ was employed) of 1c and 1c-Cl was observed leading to two distinct peaks in $^1$H NMR at 7.06 ppm for 1c and 8.06 ppm for

![Chemical Structures](image)

**Figure S12.** Competition for chloremium ion capture between 1b and 1c at -90 °C in THF as a solvent. The chemical shifts (ppm) for the free bases (1b and 1c) and the corresponding chloremium salts (1b-Cl and 1c-Cl) are identical to those observed in acetone-$d_6$ at -90 °C.
1c-Cl (Figure S12). Since there are no enolizable protons available in THF, the appearance of the downfield peak at 8.06 ppm clearly demonstrates formation of 1c-Cl.

3.) Finally, the *in-situ* generated complex – 1a-Cl (using 1.0 equiv each, 1a and CDSC) in CDCl₃ was treated with 1.0 equiv of alkenoic acid (17) at room temperature (Figure S13). The chlorenium ion from 1a-Cl was transferred to the alkenoic acid (17), successfully initiating a chlorolactonization reaction yielding the chlorolactone (17a).

![Figure S13. Chlorolactonization of 17 using 1c-Cl as an active chlorenium source.](image-url)
V. Synthesis of substrates and intramolecular chlorocyclization of alkenes:

a. Synthesis of substrates 2, 4 and 9:

\[ \text{NH}_2 \quad \xrightarrow{(i) \text{Ph} \quad \text{CHO}} \quad \text{Ph} \quad \xrightarrow{(ii) \text{NaBH}_4, \quad \text{H}_3\text{BO}_3} \quad \text{MeO} \quad \xrightarrow{\text{TsCl, NEt}_3, \quad \text{DMAP} \quad (10 \text{ mol\%})} \quad \text{MeO} \]

\(2\)

\(N\)-cinnamyl-\(N\)-(4-methoxyphenyl)-4-methylbenzenesulfonamide (2):

Intermediate \(A\) was synthesized as reported previously.\(^7\) \(p\)-Anisidine (1.0 g, 8.12 mmol) was placed in a porcelain mortar along with freshly distilled \textit{trans}-cinnamaldehyde (1.02 mL, 1.0 equiv, 8.12 mmol). This mixture was grinded using a pestle for about 10 min until a bright yellow solid was obtained. Part of this mixture was analyzed by \(^1\text{H}\) NMR to verify completion of the reaction (imine formation is quantitative). To this crude imine, a 1:1 mixture (pre-mixed) of \text{NaBH}_4 (768 mg, 2.5 equiv, 20.3 mmol) and \text{H}_3\text{BO}_3 (1.26 g, 2.5 equiv, 20.3 mmol) were added at once. Mixing was continued using mortar and pestle for another 20 min until a dry yellow solid was obtained. The reaction mixture was then transferred to a separatory funnel. The motor was washed with \text{CH}_2\text{Cl}_2 (15 mL) and the washings were transferred to the same separatory funnel. This solution was then washed with 50% aqueous \text{NaHCO}_3 solution following by 5 mL of brine. The organics were separated, dried over anhydrous \text{Na}_2\text{SO}_4, filtered, concentrated and then subjected to the next step without further purification. The crude amine \(A\) was transferred to a 100 mL round bottom flask and dissolved in dry \text{CH}_2\text{Cl}_2 (10 mL). To this mixture were added \text{NEt}_3 (2.3 mL, 2.0 equiv, 16.24 mmol) and...
4-(N,N-dimethylamino)pyridine (91 mg, 0.1 equiv, 0.81 mmol) followed by tosyl chloride (1.86 g, added in 3 portions). This mixture was allowed to stir for 5 h at room temperature and the progress of the reaction was monitored by thin layer chromatography (TLC). Upon completion of the reaction, the organics were poured in a separatory funnel and washed with satd. aqueous NaHCO₃ solution. The organics were separated, dried over anhydrous Na₂SO₄, filtered, concentrated and subjected to purification using silica gel column chromatography employing 20% ethyl acetate in hexanes as eluent. Pure product 2 was obtained as a white solid (2.14 g, 67% overall yield).

Analytical data for 2: White solid, mp 79 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.54-7.51 (2H, m.), 7.26-7.20 (7H, m.), 6.98-6.94 (2H, m.), 6.79-6.76 (2H, m.), 6.35 (1H, dd, J = 16.0, 5.0 Hz), 6.13-6.06 (1H, m.), 4.29 (2H, ddd, J = 1.5, 5.0, 11.0 Hz), 3.76 (3H, s.), 2.42 (3H, s.) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 159.0, 143.3, 136.4, 135.7, 133.7, 131.7, 129.4, 129.4, 128.5, 127.8, 126.4, 124.2, 114.1, 55.3, 53.6, 21.6 ppm; IR (film) 3019, 2932, 2837, 1595, 1507 (s), 1447, 1346 (s), 1249, 1162 (s), 684 cm⁻¹. HRMS (ESI) Calculated Mass for C₂₃H₂₄NO₃S: ([M+H]⁺) = 394.1477, Found ([M+H]⁺) = 394.1478.
**N-cinnamyl-4-methyl-N-(3,4,5-trimethoxyphenyl)benzenesulfonamide (4):**

The same procedure used for the synthesis of 2 (as described above) was employed for the synthesis of 4. Using 1.0 g (5.5 mmol) of 3,4,5-trimethoxyaniline, pure product (4) was isolated (2.14 g, 74% overall yield).

Analytical data for 4: White solid, mp 121 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.58 (2H, dd, \(J = 8.0\) Hz.), 7.27-7.19 (7H, m.), 6.38 (1H, d, \(J = 16.0\) Hz.), 6.23 (2H, s.), 6.10 (1H, ddd, \(J = 6.5, 13.5, 16.0\) Hz), 4.27 (2H, dd, \(J = 1.0\) Hz, 7.0 Hz), 3.80 (3H, s.), 3.66 (6H, s.), 2.41 (3H, s.) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 153.0, 143.6, 137.7, 136.3, 135.7, 134.8, 133.9, 129.4, 128.6, 127.9, 127.8, 126.4, 124.1, 106.5, 60.9, 56.1, 53.7, 21.5 ppm; IR (film) 3000, 2938, 2837, 1595 (s), 1503, 1454, 1416, 1347, 1232, 1163 (s), 1128 (s), 661 cm\(^{-1}\). HRMS (ESI) Calculated Mass for C\(_{25}\)H\(_{28}\)NO\(_5\)S: ([M+H\(^+\)]) = 454.1688, Found ([M+H\(^+\)]) = 454.1685.
**N-cinnamyl-4-methyl-N-(2-phenylallyl)benzenesulfonamide (9):**

![Chemical structure image]

Substrate 9 was synthesized as reported previously.8

Analytical data for 9: Crystalline white solid, mp 130 °C; 1H NMR (500 MHz, CDCl3) δ 7.66 (2H, d, J = 8.0 Hz.), 7.39-7.37 (2H, m.), 7.31-7.19 (8H, m.), 7.13 (2H, d, J = 6.5 Hz.), 6.30 (1H, d, J = 15.5 Hz.), 5.78 (1H, ddd, J = 7.0, 14.0 and 16.0 Hz.), 5.45 (1H, apparent singlet.), 5.24 (1H, d, J = 1.0 Hz.), 4.26 (2H, s.), 3.86 (2H, d, J = 7.0 Hz.), 2.41 (3H, s.) ppm; 13C NMR (125 MHz, CDCl3) δ 143.3, 142.8, 138.5, 137.0, 136.2, 134.1, 129.6, 128.5, 128.4, 128.0, 127.8, 127.4, 126.6, 126.3, 123.4, 116.3, 50.6, 48.9, 21.5 ppm; IR (film) 3056, 3031, 2922, 1599, 1495, 1447, 1340 (s), 1159 (s), 1093, 910, 738, 659 cm⁻¹. HRMS (ESI) Calculated Mass for C25H26NO2S: ([M+H]+) = 404.1684, Found ([M+H]+) = 404.1687.

b. Chlorocyclization of alkenes 2, 4 and 9:

![Chemical reaction image]

**trans-3-chloro-6-methoxy-4-phenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (3):**

A 5 mL round bottom flask containing a stir bar was charged with 2 (100 mg, 0.25 mmol) and dissolved in a 9:1 mixture of 1,2-dichloroethane:hexafluoroisopropanol (2.5
mL). To this solution 1,4-diazabicyclo[2.2.2]octane (1.5 mg, 0.05 equiv, ~0.01 mmol) was added and the reaction mixture was placed in an ice bath for about 5 min. Subsequently, 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) (60 mg, 1.2 equiv, 0.31 mmol) was added and stirring was continued for another 3.5 h. The progress of the reaction was monitored by TLC and upon complete consumption of substrate 2, the reaction was quenched with 10% aqueous sodium sulfite (1 mL). The organics were then separated, dried over anhydrous Na₂SO₄, filtered, concentrated and subjected to purification using silica gel column chromatography employing 10% ethyl acetate in hexanes as eluent. After purification, pure product 3 was obtained as a white solid (101 mg, 93%).

Analytical data for 3: White solid, mp 118 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.82 (1H, d, J = 9.0 Hz.), 7.55 (2H, d, J = 8.5 Hz.), 7.27 (2H, d, J = 8.0 Hz.), 7.19 (1H, t, J = 8.0 Hz.), 7.11 (2H, t, J = 7.0 Hz.), 6.70 (1H, dd, J = 3.0 and 9.5 Hz.), 6.47 (2H, d, J = 7.5 Hz.), 6.13 (1H, d, J = 2.0 Hz.), 4.65 (1H, dd, J = 4.0 and 13.5 Hz.), 3.89 (1H, d, J = 9.5 Hz.), 3.76-3.70 (1H, m.), 3.60-3.56 (4H, m.), 2.44 (3H, s.) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 157.4, 144.2, 141.1, 136.3, 133.5, 130.0, 128.8, 128.6, 128.3, 127.5, 127.4, 126.5, 114.9, 113.1, 57.0, 55.2, 54.2, 52.3, 21.5 ppm; IR (film) 3030, 2928, 2838, 1610 (s), 1493 (s), 1356 (s), 1248, 1163 (s), 1037, 910, 801, 736 cm⁻¹. HRMS (ESI) Calculated Mass for C₂₃H₂₃NO₃ClS: ([M+H]+) = 428.1087, Found ([M+H]+) = 428.1087.
Attempted chlorocyclization of substrate 4:

Compound 4 (100 mg, 0.22 mmol) was subjected to the same chlorocyclization conditions (as described above for substrate 2) and 79 mg (73% yield) of the ring-chlorinated product 5 was obtained as pale yellow oil.

Analytical data for 5: Pale yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) two rotamers (~2.5:1 ratio) along N-Ts were observed at room temperature. Heating the sample to 50 °C did not lead to complete convergence of the spectral lines corresponding to the rotamers.

Major rotamer: $\delta$ 7.68 (1H, d, $J = 8.0$ Hz.), 7.27-7.19 (10H, m.), 6.54 (1H, s.), 6.30 (1H, d, $J = 16.0$ Hz.), 6.18 (1H, ddd, $J = 7.0$, 13.5 and 16.0 Hz.), 4.41-4.38 (1H, m.), 4.20-4.14 (1H, m.), 3.86 (3H, s.), 3.80 (3H, s.), 3.68 (3H, s.), 2.41 (3H, s.) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.5, 150.4, 143.6, 136.3, 134.2, 131.5, 129.6, 129.5, 128.5, 127.9, 127.3, 126.4, 123.9, 111.7, 61.1, 56.1, 53.1, 21.6 ppm; IR (film) 3023, 2940, 1596, 1576, 1485 (s), 1444, 1396, 1351, 1240, 1163 (s), 1112 (s), 1016, 870, 661 cm$^{-1}$.

HRMS (ESI) Calculated Mass for C$_{25}$H$_{27}$NO$_5$ClS: ([M+H]$^+$) = 487.1220, Found ([M+H]$^+$) = 487.1221.
Chlorocyclization of substrate 9:

In a 5 mL round bottom flask containing a stir bar, 9 (100 mg, 0.25 mmol) was dissolved in a 9:1 mixture of 1,2-dichloroethane:hexafluoroisopropanol (2.5 mL). Then, 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) (54 mg, 1.1 equiv, 0.27 mmol) was added and the reaction mixture was stirred for 24 h. The progress of the reaction was monitored by TLC and upon complete consumption of substrate 9, the reaction was quenched with 10% aqueous sodium sulfite (1 mL). The organics were then separated, dried over anhydrous Na₂SO₄, filtered, concentrated and subjected to purification using silica gel column chromatography employing 20% ethyl acetate in hexanes as eluent. After purification, product 10 was obtained as a white solid (60 mg, 55% yield). Crude ¹H NMR analysis indicated a 5:1 dr for 10. Although complete conversion of 9 was attained (as judged by TLC and ¹H NMR), the mass balance was accounted by a complex mixture of products, which were inseparable by chromatography (identity of these products could not be assigned due to overlapping peaks in NMR). An analytically pure sample of 10 was obtained via preparative TLC. The relative stereochemistry of the major diastereomer could not be assigned with the aid of NOESY experiments owing to the nature of cis-(5,5) fusion in the tricyclic framework of 10.
Analytical data for 10: White waxy solid; $^1$H NMR (500 MHz, CDCl$_3$) 5:1 $dr$, major diastereomer: $\delta$ 7.67 (2H, d, $J = 8.0$ Hz.), 7.32-7.20 (8H, m.), 7.07 (2H, d, $J = 7.5$ Hz.), 6.89 (1H, d, $J = 8.0$ Hz.), 4.15 (1H, d, $J = 5.5$ Hz.), 3.67 (2H, s.), 3.47 (2H, dd, $J = 3.5$ and 9.5 Hz.), 3.34 (1H, d, $J = 9.5$ Hz.), 3.28 (1H, dd, $J = 6.5$ and 9.5 Hz.), 2.88 (1H, ddd, $J = 2.5$, 6.5 and 8.5 Hz.), 2.42 (3H, s.) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 145.4, 144.1, 144.0, 143.9, 132.0, 129.7, 128.8, 128.8, 128.1, 127.9, 127.0, 125.7, 123.3, 60.0, 57.5, 56.7, 53.9, 49.9, 21.6 ppm; IR (film) 3928, 2961, 2867, 1598, 1453, 1349 (s), 1260, 1165 (s), 1099, 1026, 911, 807, 702, 665 cm$^{-1}$. HRMS (ESI) Calculated Mass for C$_{25}$H$_{25}$NO$_2$ClS: ([M+H]$^+$) = 438.1295, Found ([M+H]$^+$) = 438.1297.
VI. Quantum mechanical modeling studies:

Based on the nature of halenium ion (F, Cl, Br or I), full optimizations for all conformations of the ‘halenium ion’ acceptors and the corresponding ‘Lewis base-halenium ion’ complexes were performed using density functional calculations at the B3LYP/6-31G* level (with the LANL2DZ(d) pseudopotential and basis used for iodine) as implemented in the Spartan-10 software running on Macintosh and Linux platforms. To confirm that each structure was a true minimum, vibrational analyses were performed. For structures presented in Figure 2, Figure 5b and Figure 6 in the manuscript, the \( \text{HalA (Cl)} \) values were calculated using the energies obtained from a full geometry optimization of the structures in simulated acetone at B3LYP/6-31G*/SM8 level of theory. Alternatively, when the \textit{gas phase} energies of the same structures were corrected for solvation in simulated acetone using the SM8 model available in the Spartan code to run single point (i.e. B3LYP/6-31G*/SM8) calculations, the resulting data led to the same conclusion. To verify convergence and consistency of the optimizations, a number of examples were re-optimized from multiple starting points; energetic variations of 0.02 kcal/mol or less were found among these calculated structures. Relative enthalpies \( \Delta H^\circ_{\text{rel}} \) were calculated for the \textit{gas phase} structures by including zero-point and thermal corrections to 298.15 K. Importantly, neither the vibration nor the solvation corrections introduced differences between relative \( E^\circ \) and relative \( H^\circ \) values that were large enough to reorder the relative energy structures; thus, either set of data led to the same conclusions.
Cartesian coordinates for geometry minimized styrene:

Atom	X	 Y	 Z
1 H H1	3.8906963	-0.1039465	0.0006791
2 C C1	2.8698467	0.2657609	0.0010817
3 C C2	1.8324097	-0.5808014	-0.0009399
4 H H2	2.7517904	1.3461327	0.0033224
5 H H3	2.0454119	-1.6501016	-0.0027489
6 C C3	0.3985202	-0.2467405	-0.0006402
7 C C4	-2.3724006	0.2865908	0.0003848
8 C C5	-0.0834339	1.0750850	-0.0010208
9 C C6	-0.5422606	-1.2906386	0.000292
10 C C7	-1.9121771	-1.0300166	0.0005909
11 C C8	-1.4498423	1.3375891	-0.0004488
12 H H6	0.6174931	1.9048299	0.0018638
13 H H7	-0.1890770	-2.3197190	0.0002462
14 H H8	-2.6188624	-1.8558522	0.0012169
15 H H9	-1.7991778	2.3669659	-0.0007321
16 H H10	-3.4389364	0.4948622	0.0008431

Cartesian coordinates for geometry minimized styrene + F cation:

Atom	X	 Y	 Z
1 H H2	2.8006008	0.8488801	0.6519632
2 C C1	2.7085660	0.2902544	-0.2938554
3 C C2	1.5334306	-0.6181780	-0.2430910
4 H H3	2.5850185	1.0299477	-1.1015570
5 H H4	1.7830570	-1.6715264	-0.3782480
6 C C3	0.2035457	-0.2816827	-0.0507188
### Cartesian coordinates for geometry minimized styrene + Cl cation:

| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| Cl 1 | 3.2758162 | 0.0329725 | -1.8063251 |
| H 2  | 3.5289469 | -0.0248172 | 0.5680118 |
| C 1  | 2.7218866 | 0.2924718 | -0.0971674 |
| C 2  | 1.5507764 | -0.6129596 | 0.1816959 |
| C 3  | 0.2067354 | -0.2710434 | 0.0403656 |
| C 4  | -2.5261721 | 0.2862665 | 0.1816959 |
| C 5  | -0.2565230 | 1.0888791 | 0.0506730 |
| C 6  | -0.7568595 | -1.3372371 | 0.0969362 |
| C 7  | -2.1046711 | -1.0552540 | 0.1714872 |
| C 8  | -1.6064943 | 1.3533468 | 0.1197515 |
| C 9  | 0.4526671 | 1.9073041 | -0.0037532 |
| C 10 | -0.4056968 | -2.3653040 | 0.0845860 |
| C 11 | -2.8352386 | -1.8558000 | 0.2181726 |
| C 12 | -1.9665647 | 2.3766974 | 0.1247055 |
| C 13 | -3.5887611 | 0.5076062 | 0.2363835 |
**Cartesian coordinates for geometry minimized styrene + Br cation:**

![Image]

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 1    | H H2      | 3.5697360 | -0.0504926| 0.5475900 |
| 2    | C C1      | 2.7137838 | 0.2913182 | -0.0319186|
| 3    | C C2      | 1.5582490 | -0.6125257| 0.0299976 |
| 4    | H H3      | 2.5259948 | 1.3517069 | 0.1031904 |
| 5    | H H4      | 1.8038016 | -1.6736580| 0.0441067 |
| 6    | C C3      | 0.2050238 | -0.2699339| 0.0549767 |
| 7    | C C4      | -2.5422655| 0.2870390 | 0.1691956 |
| 8    | C C5      | -0.2622947| 1.0902243 | 0.0582713 |
| 9    | C C6      | -0.7607195| -1.3372320| 0.1043399 |
| 10   | C C7      | -2.1141792| -1.0555682| 0.1637094 |
| 11   | C C8      | -1.6177899| 1.3545758 | 0.1150925 |
| 12   | H H6      | 0.4442188 | 1.9103845 | 0.0134268 |
| 13   | H H7      | -0.4108292| -2.3647834| 0.0969540 |
| 14   | H H8      | -2.8416681| -1.8570948| 0.2036541 |
| 15   | H H9      | -1.9764367| 2.3767833 | 0.1182231 |
| 16   | H H10     | -3.6039676| 0.5069392 | 0.2149216 |
| 17   | Br Br1    | 3.3093428 | 0.0523175 | -2.0057309|

**Cartesian coordinates for geometry minimized styrene + I cation at the B3LYP/6-31G*/LANL2DZ level:**

![Image]
### Cartesian coordinates for geometry minimized $\alpha$-methylstyrene:

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 1 H  | 0.0543720 | 2.2503769 | -0.1497244 |
| 2 C  | -0.4286364| 1.3767145 | 0.3754165 |
| 3 C  | -1.4766033| -0.8504688| 1.6715387 |
| 4 C  | 0.0410623 | 1.002697  | 0.0136178 |
| 5 C  | -1.3892479| 1.5375872 | 1.3704535 |
| 6 C  | -1.9175001| 0.423843  | 2.0275127 |
| 7 C  | -0.5145509| -1.009413 | 0.6737549 |
| 8 C  | -1.7367171| 2.5357278 | 1.6248454 |
| 9 C  | -2.6712871| 0.5487679 | 2.8002426 |
| 10 H | -0.1837947| -2.0110102| 0.4172445 |
| 11 H | -1.8819748| -1.7273009| 2.1701069 |
| 12 C | 1.0786076 | -0.071543 | -1.0405486 |
| 13 C | 1.9807647 | 0.8846413 | -1.3109147 |
| 14 H | 2.0297302 | 1.8131783 | -0.7504886 |
| 15 C | 1.0973650 | -1.3792354| -1.8012150 |
| 16 H | 1.3966913 | -2.2169699| -1.1577300 |
| 17 H | 0.1063311 | -1.6244976| -2.2022647 |
| 18 H | 2.7179693 | 0.7566693 | -2.0985613 |
### Cartesian coordinates for geometry minimized α-methylstyrene + F cation:

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| 1 H  | 0.8268993 | 1.9386516 | 0.7763814 |
| 2 C  | -0.0748199 | 1.3466181 | 0.7544581 |
| 3 C  | -2.4366449 | -0.1956646 | 0.6883418 |
| 4 C  | -0.0841211 | 0.0831349 | 0.0673998 |
| 5 C  | -1.2177010 | 1.8098166 | 1.3786756 |
| 6 C  | -2.3929706 | 1.0458066 | 1.3506329 |
| 7 C  | -1.3092163 | -0.6698768 | 0.0553704 |
| 8 H  | -1.2039172 | 2.7654028 | 1.8921011 |
| 9 H  | -3.2856129 | 1.4171075 | 1.8467243 |
| 10 H | -1.3499687 | -1.6261442 | -0.4517926 |
| 11 H | -3.3548840 | -0.7733159 | 0.6769108 |
| 12 C | 1.0490968 | -0.4357215 | -0.5833723 |
| 13 C | 2.4079159 | 0.1818604 | -0.6473422 |
| 14 H | 2.6411853 | 0.3464377 | -1.7126624 |
| 15 C | 1.0223894 | -1.7419414 | -1.3223742 |
| 16 H | 0.8367010 | -2.5681402 | -0.6235004 |
| 17 H | 0.2232622 | -1.7632673 | -2.0709981 |
| 18 H | 3.1285884 | -0.5680494 | -0.2826502 |
| 19 H | 1.9694056 | -1.9432586 | -1.8291552 |
| 20 F | 2.6044127 | 1.3505437 | 0.0368513 |
**Cartesian coordinates for geometry minimized α-methylstyrene + Cl cation:**

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 1 H  | 0.8524194 | 1.8777405 | 0.7165050 |
| 2 C  | -0.0810083| 1.3318856 | 0.6510305 |
| 3 C  | -2.5061903| -0.0938857| 0.5581270 |
| 4 C  | -0.1230751| 0.0425115 | 0.0205688 |
| 5 C  | -1.2133218| 1.8736161 | 1.2232405 |
| 6 C  | -2.4269518| 1.1669125 | 1.1725448 |
| 7 C  | -1.3752485| -0.6575056| 0.0027165 |
| 8 H  | -1.1682477| 2.8411187 | 1.7119204 |
| 9 H  | -3.3174398| 1.6013467 | 1.6185220 |
| 10 H | -1.4492442| -1.6287982| -0.4703050|
| 11 H | -3.4520204| -0.6242397| 0.5260742 |
| 12 C | 1.0279102 | -0.5162342| -0.5687384|
| 13 C | 2.3205086 | 0.2521563 | -0.6608431|
| 14 H | 2.1970268 | 1.3308190 | -0.7283068|
| 15 C | 1.0981013 | -1.8830376| -1.1487562|
| 16 H | 2.0446183 | -2.3540930| -0.8564681|
| 17 H | 0.2761186 | -2.5452394| -0.8848084|
| 18 H | 2.9264954 | -0.0974754| -1.4974917|
| 19 H | 1.1388190 | -1.7911799| -2.2469288|
| 20 Cl| 3.2307301 | -0.1264182| 0.8613968 |

**Cartesian coordinates for geometry minimized α-methylstyrene + Br cation:**

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 1 H  | 0.8327779 | 1.9119966 | 0.7084753 |
Cartesian coordinates for geometry minimized α-methylstyrene + I cation at the B3LYP/6-31G*/LANL2DZ level:

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| 1 H  | 0.8216134 | 1.9349950 | 0.6952996 |
| 2 C  | -0.0974624 | 1.3649121 | 0.6285659 |
| 3 C  | -2.4905437 | -0.1062810 | 0.5325283 |
| 4 C  | -0.1048925 | 0.0669882 | 0.0276392 |
| 5 C  | -1.2518304 | 1.8998675 | 1.1662200 |
| 6 C  | -2.4499482 | 1.1694591 | 1.1156606 |
| 7 C  | -1.3372975 | -0.6571308 | 0.0060733 |
| 8 H  | -1.2329263 | 2.8812592 | 1.6283797 |
| 9 H  | -3.3559224 | 1.5960944 | 1.5368294 |
| 10 H | -1.3795844 | -1.6426269 | -0.4422513 |
| 11 H | -3.4228396 | -0.6601748 | 0.4999604 |
| 12 C | 1.0635820 | -0.4921789 | -0.5559665 |
| 13 C | 2.3305740 | 0.2606205 | -0.6583741 |
| 14 H | 2.2610386 | 1.3417721 | -0.5902834 |
| 15 C | 1.0721913 | -1.8617905 | -1.1622284 |
Cartesian coordinates for geometry minimized *trans*-β-methylstyrene:

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| 1 H  | 0.3032617 | 1.4434338 | -1.2951095 |
| 2 C  | -0.2150847 | 1.3742470 | -0.2145948 |
| 3 C  | -0.0084324 | 1.2430075 | 2.5620160 |
| 4 C  | 0.0119607 | 0.1209177 | 0.3934372 |
| 5 C  | -0.3097799 | 2.5340009 | 0.5486210 |
| 6 C  | -0.2062783 | 2.4766153 | 1.9417906 |
| 7 C  | 0.0862075 | 0.0823323 | 1.7954828 |
| 8 H  | -0.4670086 | 3.4895036 | 0.0544467 |
| 9 H  | -0.2816820 | 3.3841314 | 2.5347258 |
| 10 H | 0.2416392 | -0.8755999 | 2.2871534 |
| 11 H | 0.0722434 | 1.1821635 | 3.6443459 |
| 12 C | 0.1021490 | -1.1377356 | -0.3598294 |
| 13 H | 0.2068386 | -2.0296220 | 0.2601989 |
| 14 C | 0.0986798 | -1.3016486 | -1.6911815 |
| 15 H | 0.0036050 | -0.4336465 | -2.3438352 |
| 16 C | 0.2234347 | -2.6262418 | -2.3843957 |
| 17 H | 0.3212531 | -3.4486447 | -1.6676358 |
| 18 H | -0.6515615 | -2.8292254 | -3.0174953 |
| 19 H | 1.0989995 | -2.6479705 | -3.0481412 |

Cartesian coordinates for geometry minimized *trans*-β-methylstyrene + F cation:
### Cartesian coordinates for geometry minimized trans-β-methylstyrene + Cl cation:

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| 1 H  | 1.27197 | 0.76397 | -1.9816 |
| 2 C  | 1.4255  | 0.8629  | 0.3293  |
| 3 C  | 0.3502  | 0.4903  | 1.3908  |
| 4 C  | 0.1727  | 0.1512  | 0.7149  |
| 5 C  | 0.2195  | 0.0283  | 0.1235  |
| 6 C  | 0.1316  | 0.5607  | -0.0567 |
| 7 C  | 0.8351  | 0.5375  | -1.1506 |
| 8 C  | 1.0636  | 0.7922  | -0.4044 |
| 9 C  | 0.4535  | 0.7105  | 0.4822  |
| 10 H | 1.0832  | 0.3957  | 0.5044  |
| 11 H | 0.7733  | 0.1064  | 0.0823  |
| 12 H | 0.9756  | 0.2255  | -0.0835 |
| 13 H | 0.5850  | 0.9035  | 0.3793  |
| 14 H | 0.2185  | 0.3601  | 0.7852  |
| 15 H | 0.1486  | 0.6192  | 0.1937  |
| 16 H | 0.2576  | 0.1093  | 0.3126  |
| 17 H | 0.1096  | 0.0086  | 0.6989  |
| 18 H | 0.3786  | 0.0086  | 0.4872  |
| 19 H | 0.9323  | -0.0086 | 0.9872  |
| 20 F | -0.2586 | -0.0086 | 1.3582  |

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Cartesian coordinates for geometry minimized *trans*-β-methylstyrene + Br cation:

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| 1 H  | 1.8574729 | 0.3830576 | -0.5330532 |
| 2 C  | 1.2617372 | 0.6444875 | 0.3333469  |
| 3 C  | -0.2904247 | 1.3409636 | 2.5990273  |
| 4 C  | -0.1292304 | 0.2929226 | 0.3901490  |
| 5 C  | 1.8468260 | 1.3248348 | 1.3859169  |
| 6 C  | 1.0756437 | 1.6724980 | 2.5167296  |
| 7 C  | -0.8910606 | 0.6634599 | 1.5511735  |
| 8 H  | 2.8957440 | 1.5930012 | 1.3471919  |
| 9 H  | 1.5456894 | 2.2057584 | 3.3365620  |
| 10 H | -1.9439914 | 0.4038623 | 1.590776   |
| 11 H | -0.8644809 | 1.6179014 | 3.4748436  |
| 12 C | -0.7866125 | -0.4129093 | -0.6258795 |
| 13 H | -1.8380584 | -0.6510893 | -0.4669806 |
| 14 C | -0.2356687 | -0.9020513 | -1.9008857 |
| 15 H | 0.8341550 | -0.7594681 | -2.0334701 |
| 16 C | -0.7310299 | -2.2520803 | -2.3839682 |
| 17 H | -0.2724791 | -3.0425599 | -1.7753894 |
| 18 H | -1.8184063 | -2.3407703 | -2.3106930 |
| 19 H | -0.4376409 | -2.4160850 | -3.4232182 |
| 20 Br| -1.0781843 | 0.6342663  | -3.0774805 |
Cartesian coordinates for geometry minimized \textit{trans}-\(\beta\)-methylstyrene + I cation:

![Image of trans-\(\beta\)-methylstyrene + I cation]

| Atom | X             | Y             | Z             |
|------|---------------|---------------|---------------|
| 1 H  | H1            | 1.8494486     | 0.4237718     | -0.5496064 |
| 2 C  | C1            | 1.2515656     | 0.6678248     | 0.3201486 |
| 3 C  | C4            | -0.2852244    | 1.3201876     | 2.5871639 |
| 4 C  | C2            | -0.1321358    | 0.3299062     | 0.3668280 |
| 5 C  | C6            | 1.8402660     | 1.3137967     | 1.3850405 |
| 6 C  | C5            | 1.0759639     | 1.6379051     | 2.5175545 |
| 7 C  | C3            | -0.8879579    | 0.6788587     | 1.5236835 |
| 8 H  | H6            | 2.8924886     | 1.5702541     | 1.3530702 |
| 9 H  | H5            | 1.5503198     | 2.1431802     | 3.3521744 |
| 10 H | H3            | -1.9428120    | 0.4287196     | 1.5638640 |
| 11 H | H4            | -0.8598802    | 1.5772193     | 3.4689331 |
| 12 C | C7            | -0.7883929    | -0.3803678    | -0.6546760 |
| 13 H | H7            | -1.8324835    | -0.6314673    | -0.4804312 |
| 14 C | C8            | -0.2316178    | -0.9099972    | -1.894633 |
| 15 H | H8            | 0.8369943     | -0.7660635    | -2.0198083 |
| 16 C | C9            | -0.7154934    | -2.2725801    | -2.3491641 |
| 17 H | H2            | -0.2478077    | -3.0362309    | -1.7185189 |
| 18 H | H10           | -1.7985210    | -2.3752239    | -2.2697020 |
| 19 H | H14           | -0.4223518    | -2.4638129    | -3.3810689 |
| 20 I | I1            | -1.1523684    | 0.7441194     | -3.1205218 |

Cartesian coordinates for geometry minimized \textit{cis}-\(\beta\)-methylstyrene:

![Image of cis-\(\beta\)-methylstyrene]

| Atom | X             | Y             | Z             |
|------|---------------|---------------|---------------|

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### Cartesian coordinates for geometry minimized cis-β-methylstyrene + F cation:

| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| H1   | 1.1119258 | 1.1495487 | -0.8902513 |
| C1   | 0.6798624 | 1.0649594 | 0.1012788 |
| C4   | -0.4077372 | 0.8127077 | 2.7050387 |
| C2   | 0.1023642 | -0.1792678 | 0.5297595 |
| C6   | 0.6954936 | 2.1448640 | 0.9555887 |
| C5   | 0.1540619 | 2.0187079 | 2.2521613 |
| C3   | -0.4347183 | -0.2773156 | 1.8595014 |
| H6   | 1.1295815 | 3.0884175 | 0.6421690 |
| H5   | 0.1787208 | 2.8758949 | 2.9197088 |
| H3   | -0.8642102 | -1.2203051 | 2.1858766 |
| H4   | -0.8128270 | 0.7434694 | 3.7089588 |
| C7   | 0.0403306 | -1.2998401 | -0.2845878 |
| H7   | -0.3913257 | -2.2105820 | 0.1331818 |
| C8   | 0.4378418 | -1.4373396 | -1.7109923 |
| H8   | 1.3519814 | -0.8768709 | -1.9421268 |
| C9   | -0.7141760 | -0.9792857 | -2.6296449 |
| H2   | -1.6356511 | -1.5198861 | -2.3977861 |
Cartesian coordinates for geometry minimized cis-β-methylstyrene + Cl cation:

| Atom | X             | Y             | Z             |
|------|---------------|---------------|---------------|
| 1 H  | -0.0963462    | 1.2459008     | -1.0864510    |
| 2 C  | -0.0647157    | 1.1065062     | -0.0152871    |
| 3 C  | 0.0356081     | 0.7524627     | 2.7927693     |
| 4 C  | 0.0453575     | -0.2127516    | 0.5403547     |
| 5 C  | -0.1271382    | 2.2019182     | 0.8192681     |
| 6 C  | -0.0778132    | 2.0280931     | 2.2163611     |
| 7 C  | 0.0943225     | -0.3541759    | 1.9711455     |
| 8 H  | -0.2119710    | 3.2004379     | 0.4035825     |
| 9 H  | -0.1272708    | 2.9013878     | 2.8611325     |
| 10 H | 0.1757665     | -1.3497128    | 2.3980117     |
| 11 H | 0.0731585     | 0.6416445     | 3.8712205     |
| 12 C | 0.1210474     | -1.3932821    | -0.1967684    |
| 13 H | 0.2200235     | -2.3019809    | 0.3954807     |
| 14 C | 0.0444923     | -1.6943180    | -1.6568612    |
| 15 H | 0.7119536     | -2.5366193    | -1.8602527    |
| 16 C | 0.1760078     | -0.6378408    | -2.7380225    |
| 17 H | -0.6311985    | 0.0971960     | -2.7078397    |
| 18 H | 1.1451344     | -0.1327757    | -2.6531436    |
| 19 H | 0.1401085     | -1.1278607    | -3.7143236    |
| 20 Cl| -1.6465270    | -2.4342294    | -1.6403767    |
Cartesian coordinates for geometry minimized cis-β-methylstyrene + Br cation:

| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| 1 H  | -0.1242977 | 1.2525088 | -1.0822717 |
| 2 C  | -0.0805535 | 1.1087581 | -0.0132837 |
| 3 C  | 0.0438337  | 0.7574816 | 2.7966616 |
| 4 C  | 0.0456347  | -0.2117892 | 0.5387691 |
| 5 C  | -0.1436356 | 2.2077448 | 0.8251486 |
| 6 C  | -0.0823670 | 2.0375338 | 2.2248518 |
| 7 C  | 0.1049413  | -0.3519290 | 1.9714021 |
| 8 H  | -0.2385979 | 3.2035717 | 0.4091723 |
| 9 H  | -0.1326469 | 2.9086491 | 2.8698093 |
| 10 H | 0.1967266  | -1.3455523 | 2.3983420 |
| 11 H | 0.0897453  | 0.6443622 | 3.8729635 |
| 12 C | 0.1359628  | -1.3976990 | -0.2044704 |
| 13 H | 0.2593054  | -2.3034865 | 0.3879168 |
| 14 C | 0.0964777  | -1.6778479 | -1.6551731 |
| 15 H | 0.6841846  | -2.5711030 | -1.8747749 |
| 16 C | 0.2170468  | -0.6317856 | -2.7410982 |
| 17 H | -0.5843437 | 0.1094068 | -2.7182471 |
| 18 H | 1.1862720  | -0.1222955 | -2.6580732 |
| 19 H | 0.1860556  | -1.1185417 | -3.7187228 |
| 20 Br| -1.8597441 | -2.4979874 | -1.6289216 |
Cartesian coordinates for geometry minimized cis-β-methylstyrene + I cation at the B3LYP/6-31G*/LANL2DZ level:

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 1    | 1.2570456 | -0.8310066| -0.7161051|
| 2    | -0.9804834| -0.4643835| 0.2609092 |
| 3    | -0.3075297| 0.4980664 | 2.8219562 |
| 4    | 0.2425273 | 0.2419302 | 0.4558242 |
| 5    | 1.8346219 | -0.6719027| 1.3230695 |
| 6    | 1.5009766 | -0.1977252| 2.6008649 |
| 7    | -0.5528466| 0.7174189 | 1.7662658 |
| 8    | -2.7678775| -1.2016890| 1.1725929 |
| 9    | 2.1809933 | -0.3714524| 3.4279800 |
| 10   | 1.4820386 | 1.2538936 | 1.9274982 |
| 11   | -0.0619948| 0.8601786 | 3.8130887 |
| 12   | 1.1749812 | 0.5523158 | -0.5538332|
| 13   | 1.9956325 | 1.1862742 | -0.2286387|
| 14   | 1.2384836 | 0.2443922 | -1.9843568|
| 15   | 1.7953812 | 1.0219839 | -2.5039000|
| 16   | 0.1006584 | -0.2994382| -2.8159743 |
| 17   | 0.2671061 | 1.2667538 | -2.4774542 |
| 18   | -0.7254075| 0.4203349 | -2.8108847 |
| 19   | 0.4280237 | -0.4139104| -3.8490132 |
| 20   | 2.8734633 | -1.2785270| -1.6298892 |

Cartesian coordinates for geometry minimized 2,4,6-trimethyl pyridine (1a):
### Cartesian coordinates for geometry minimized 2,4,6-trimethyl pyridine (1a) at the B3LYP/6-31G*//SM8 (acetone) level:

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| 1 C  | -1.4232569 | -0.0123923 | -0.0000003 |
| 2 N  | 1.3924566  | 0.0055747  | 0.0000006 |
| 3 C  | -0.6932652  | -0.0105984 | 1.1928980 |
| 4 C  | -0.6932644  | -0.0105946 | 1.1928982 |
| 5 C  | 0.7035880   | -0.0000109 | 1.1576148 |
| 6 C  | 0.7035875   | -0.0000113 | 1.1576158 |
| 7 H  | -1.2090640  | -0.0188997 | -2.1492029 |
| 8 H  | -1.209681   | -0.0189057 | 2.1492009 |
| 9 C  | 1.5214692   | 0.0026874  | 2.4232737 |
| 10 H | 2.1790071   | -0.8736897 | 2.4638131 |
| 11 H | 0.8876639   | -0.0014102 | 3.3143907 |
| 12 H | 2.1697001   | 0.8859043  | 2.4653907 |
| 13 C | 1.5214683   | 0.0026782  | 2.4232731 |
| 14 H | 2.1789699   | -0.8737259 | 2.4638298 |
| 15 H | 2.1697355   | 0.8858690  | 2.4653754 |
| 16 H | 0.8876623   | -0.0013784 | 3.3143898 |
| 17 C | -2.9293029  | 0.0102676  | -0.0000001 |
| 18 H | -3.3390691  | -0.4830526 | 0.8870475 |
| 19 H | -3.3390684  | -0.4830271 | -0.8870619 |
| 20 H | -3.3012808  | 1.0438393  | 0.0000153 |
Cartesian coordinates for geometry minimized 2,4,6-trimethyl pyridine + F cation

(1a-F):

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| 1 C  | -0.4605306 | -0.0037852 | -1.3936822 |
| 2 N  | 0.3959968 | -0.0043049 | 1.1699148 |
| 3 C  | -0.2329322 | -1.2069616 | -0.7084838 |
| 4 C  | -0.2268752 | 1.2011880 | -0.7085148 |
| 5 C  | 0.2111258 | 1.2174310 | 0.6072769 |
| 6 C  | 0.2061741 | -1.2237407 | 0.6092894 |
| 7 H  | -0.3969880 | -2.1606090 | -1.1982709 |
| 8 H  | -0.3866077 | 2.1554514 | -1.1992386 |
| 9 C  | 0.4775200 | -2.4441823 | 1.4309164 |
| 10 C | 0.4873300 | 2.4365565 | 1.4296020 |
| 11 C | -0.9531236 | 0.0049386 | -2.8123576 |
| 12 H | -0.3643753 | 0.6938957 | -3.4271886 |
| 13 H | -1.9943060 | 0.3504879 | -2.8471818 |
| 14 H | -0.9121060 | -0.9891229 | -3.2627882 |
| 15 H | 0.2625566 | -3.3362828 | 0.8412759 |
| 16 H | 1.5244478 | -2.4751041 | 1.7519449 |
| 17 H | -0.1455202 | -2.4548581 | 2.3316222 |
| 18 H | 1.5339301 | 2.4630265 | 1.7519018 |
| 19 H | -0.1370456 | 2.4505478 | 2.3293070 |
| 20 H | 0.2771937 | 3.3295574 | 0.8395081 |
| 21 F | 0.8341353 | -0.0041291 | 2.4651471 |
Cartesian coordinates for geometry minimized 2,4,6-trimethyl pyridine + Cl cation

(1a-Cl):

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 1 C  | -0.4587553| -0.0039247| -1.3860869|
| 2 N  | 0.4160348 | -0.0044046| 1.2281940 |
| 3 C  | -0.2278196| -1.1992827| -0.6959907|
| 4 C  | -0.2214938| 1.1932565 | -0.6962449|
| 5 C  | 0.2166656 | 1.2116364 | 0.6184780 |
| 6 C  | 0.2118328 | -1.2180391| 0.6205759 |
| 7 H  | -0.3910220| -2.1538065| -1.1843174|
| 8 H  | -0.3799483| 2.1481905 | -1.1855733|
| 9 Cl | 0.9620075 | -0.0043125| 2.8758940 |
| 10 C | 0.4605612 | -2.4885560| 1.3717030 |
| 11 C | 0.4704970 | 2.4810328 | 1.3702715 |
| 12 C | -0.9549018| 0.0046660 | -2.8024847|
| 13 H | -0.3678287| 0.6934960 | -3.4192827|
| 14 H | -1.9957340| 0.3518944 | -2.8340770|
| 15 H | -0.9166225| -0.9895156| -3.2503273|
| 16 H | 0.2497825 | -3.3405299| 0.7235766 |
| 17 H | 1.5014445 | -2.5568983| 1.7067503 |
| 18 H | -0.1795422| -2.5589923| 2.2580331 |
| 19 H | 1.5119483 | 2.5464022 | 1.7039618 |
| 20 H | -0.1685648| 2.5536607 | 2.2571103 |
| 21 H | 0.2614589 | 3.3337983 | 0.7225462 |
**Cartesian coordinates for geometry minimized 2,4,6-trimethyl pyridine + Cl cation**

(1a-Cl) at the B3LYP/6-31G*/SM8 (acetone) level:

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| C1   | -0.4559613 | -0.0048480 | -1.3816389 |
| N1   | 0.4159178   | -0.0046638 | 1.2261837  |
| C2   | -0.2255991  | -1.2002788 | -0.6946727 |
| C6   | -0.2207756  | 1.1927408  | -0.6948392 |
| C5   | 0.2164722   | 1.2125342  | 0.6191172  |
| C3   | 0.2128388   | -1.2195999 | 0.6214042  |
| H2   | -0.3878407  | -2.1548634 | -1.1818630 |
| H6   | -0.3803688  | 2.1472686  | -1.1837641 |
| Cl1  | 0.9646636   | -0.0041663 | 2.8807573  |
| C4   | 0.4601370   | -2.4886766 | 1.3693577  |
| C10  | 0.4678066   | 2.4808341  | 1.3675074  |
| C14  | -0.9523920  | 0.0057120  | -2.7959546 |
| H7   | -0.3598737  | 0.6865478  | -3.4158629 |
| H22  | -1.9890795  | 0.3634138  | -2.8301598 |
| H23  | -0.9251701  | -0.9887968 | -3.2463149 |
| H24  | 0.2438912   | -3.3368015 | 0.7188772  |
| H25  | 1.5015671   | -2.5660677 | 1.6991569  |
| H26  | -0.1787264  | -2.5644022 | 2.2555277  |
| H27  | 1.5095090   | 2.5557429  | 1.6968617  |
| H28  | -0.1708472  | 2.5589875  | 2.2535668  |
| H29  | 0.2538312   | 3.3293832  | 0.7167522  |

**Cartesian coordinates for geometry minimized 2,4,6-trimethyl pyridine + Br cation**

(1a-Br):

![3D structure of the molecule](image)

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| C1   | -0.5085398 | -0.0016614 | -1.3774365 |
| N1   | 0.4439891   | -0.0027266 | 1.2220452  |
### Cartesian coordinates for geometry minimized 2,4,6-trimethyl pyridine + I cation

(1a-I) at the B3LYP/6-31G*/LANL2DZ level:

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| 1 C  | -0.4641932 0.0083029 -1.3901767 |
| 2 N  | 0.4078970  | 0.0024977 | 1.2422231 |
| 3 C  | -0.2246739  | -1.1848352  | -0.7031872 |
| 4 C  | -0.2124777  | 1.1958822  | -0.7038429 |
| 5 C  | 0.2216503  | 1.2058075  | 0.6138388 |
| 6 C  | 0.2081600  | 1.2155932  | 0.6154715 |
| 7 H  | -0.4290950  | -2.1534307  | -1.1806020 |
| 8 H  | -0.4376370  | 2.1513820  | -1.1749086 |
| 9 C  | 0.4950209  | -2.5000639  | 1.3417112 |
| 10 C | 0.4859306  | 2.4951871  | 1.3478531 |
| 11 Br | 1.0961805  | -0.0033691  | 3.0796683 |
| 12 C | -1.0170364  | 0.0034186  | -2.7910386 |
| 13 H | -0.1929687  | 0.1941550  | -3.4918370 |
| 14 H | -1.7590922  | 0.7930121  | -2.9439227 |
| 15 H | -1.4667739  | -0.9543223  | -3.0624677 |
| 16 H | 1.5341897  | 2.5731946  | 1.6573596 |
| 17 H | -0.1330370  | 2.5792812  | 2.2481237 |
| 18 H | 0.2594518  | 3.3428033  | 0.6997847 |
| 19 H | 0.2716547  | -3.3466338  | 0.6912466 |
| 20 H | 1.5434864  | -2.5752096  | 1.6513179 |
| 21 H | -0.1236955  | -2.5885957  | 2.2417710 |
Cartesian coordinates for geometry minimized 2,6-di-tert-butyl pyridine (1b):

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -0.7108567 | 0.0218167 | -2.5990573 |
| N    | 0.0215260 | -0.0006476 | 0.0675877  |
| C    | -0.5264361 | -1.1870869 | -1.9336875 |
| C    | -0.5270256 | 1.2193147  | -1.9131182 |
| C    | -0.1565644 | 1.1709519  | -0.5626801 |
| C    | -0.1561866 | -1.1613723 | -0.5824331 |
| H    | -0.6699041 | -2.1246244 | -2.4577590 |
| C    | 0.0749097  | -2.4292451 | 0.2564900  |
| C    | 1.5395838  | -2.4319098 | 0.7507208  |
| H    | 1.7605028  | -1.5156513 | 1.3050322  |
| H    | 2.2402534  | -2.4997350 | -0.0904048 |
| H    | 1.7171826  | -3.2910537 | 1.4092421  |
| C    | -0.1854748 | -3.7185630 | -0.5422495 |
| H    | 0.4887314  | -3.8089299 | -1.4020010 |
| H    | -1.2179519 | -3.772915 | -0.9073025 |
| H    | -0.0171941 | -4.5901615 | 0.1002301  |
| C    | -0.8725708 | -2.3946492 | 1.4767446  |
| H    | -0.7137117 | -1.4859947 | 2.0633833  |
| H    | -0.6929792 | -3.2637641 | 2.1212907  |
| H    | -1.9231185 | -2.4174559 | 1.1624936  |
| C    | 0.0748656  | 2.4241997  | 0.2977723  |
| C    | -0.8684097 | 2.3669328  | 1.5203620  |
| H    | -0.7060186 | 1.4492478  | 2.0917641  |
| H    | -1.9200240 | 2.3928464  | 1.2099448  |
| H    | -0.6881079 | 3.2260124  | 2.1778977  |
### Cartesian coordinates for geometry minimized 2,6-di-tert-butyl pyridine (1b) at the B3LYP/6-31G*/SM8 (acetone) level:

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 1 C  | -0.6976228| 0.0218416| -2.5978550|
| 2 N  | 0.0232949 | -0.0007424| 0.0730001 |
| 3 C  | -0.5164122| -1.1870101| -1.9316710|
| 4 C  | -0.5170915| 1.2192235 | -1.9109971|
| 5 C  | -0.1528030| 1.1733293 | -0.5596962|
| 6 C  | -0.1523930| -1.1638580| -0.5795889|
| 7 H  | -0.6584949| -2.1235922| -2.4568693|
| 8 H  | -0.6600756| 2.1644802 | -2.4202576|
| 9 H  | -0.9805322| 0.0308844 | -3.6467636|
| 10 C | 0.0732644 | -2.4368880| 0.2555882 |
| 11 C | 1.5379310 | -2.4567669| 0.7473401 |
| 12 H | 1.7757813 | -1.5506580| 1.3131499 |
| 13 H | 2.2408825 | -2.5243401| -0.0920335|
| 14 H | 1.7115489 | -3.3232595| 1.3968737 |
| 15 C | -0.1972043| -3.7203930| -0.5478623|
| 16 H | 0.4752553 | -3.8167970| -1.4078288|
| 17 H | -1.2298864| -3.7689506| -0.9120559|
| 18 H | -0.0353894| -4.5969813| 0.0895222 |
| 19 C | -0.8692403| -2.4075368| 1.4789386 |
| 20 H | -0.7077716| -1.5079568| 2.0802919 |
| 21 H | -0.6952668| -3.2830763| 2.1158943 |
| 22 H | -1.9227674| -2.4225039| 1.1736151 |
| 23 C | 0.0731915 | 2.4317642 | 0.2971174 |
| 24 C | -0.8652168| 2.3799751 | 1.5227846 |
| 25 H | -0.6998838| 1.4716424 | 2.1097797 |
| 26 H | -1.9197355| 2.3972385 | 1.2210483 |
| 27 H | -0.6910147| 3.2460906 | 2.1722965 |
| 28 C | 1.5393723 | 2.4456210 | 0.7843487 |
| 29 H | 1.7804060 | 1.5304629 | 1.3340306 |
| 30 H | 1.7137353 | 3.3012601 | 1.4479078 |
| 31 H | 2.2395967 | 2.5283922 | -0.0559094|
| 32 C | -0.2029202| 3.7290858 | -0.4818121|
| 33 H | 0.4671020 | 3.8450745 | -1.3413420|
| 34 H | -0.0430390| 4.5940425 | 0.1717877 |
| 35 H | -1.2247959| 3.7841369 | -0.8380848|
Cartesian coordinates for geometry minimized 2,6-di-tert-butyl pyridine + F cation

(1b-F):

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| 1 C  | -0.8153856 | 0.0018584 | -2.5292359 |
| 2 N  | -0.0076080 | 0.0000015 | 0.0069609  |
| 3 C  | -0.6056235 | -1.2059500 | -1.8717847 |
| 4 C  | -0.6050219 | 1.2086951  | -1.8701861 |
| 5 C  | -0.1824163 | 1.2349054  | -0.5444135 |
| 6 C  | -0.1830476 | -1.2340843 | -0.5460274 |
| 7 H  | -0.7666090 | 2.1466724  | -2.3821219 |
| 8 H  | -0.7666090 | 2.1466724  | -2.3821219 |
| 9 H  | -1.1439983 | 0.0026314  | -3.5627262 |
| 10 C | 0.0811380  | -2.5143276 | 0.2620033  |
| 11 C | 1.5672427  | -2.5733125 | 0.6994424  |
| 12 H | 1.8412775  | -1.7831052 | 1.4008763  |
| 13 H | 2.2362648  | -2.5138774 | -0.1655373 |
| 14 H | 1.7544688  | -3.5326748 | 1.1925066  |
| 15 C | -0.8663260 | -2.5817913 | 1.4866062  |
| 16 H | -0.6904016 | -1.7811859 | 2.2072537  |
| 17 H | -0.7120474 | -3.5333416 | 2.0061081  |
| 18 H | -1.9167325 | -2.5431799 | 1.1788333  |
| 19 C | -0.1962408 | -3.7474929 | -0.6229126 |
| 20 H | 0.4620842  | -3.7847549 | -1.4961540 |
| 21 H | -1.2370333 | -3.7954905 | -0.9578081 |
| 22 H | -0.0034497 | -4.6496875 | -0.0348991 |
| 23 C | 0.0824153  | 2.5139597  | 0.2652872  |
| 24 C | 1.5686052  | 2.5716721  | 0.7026211  |
| 25 H | 2.2374939  | 2.5128958  | -0.1625067 |
| 26 H | 1.8423233  | 1.7805161  | 1.4031180  |
| 27 H | 1.7563872  | 3.5303618  | 1.1967832  |
| 28 C | -0.8648432 | 2.5802038  | 1.4901203  |
| 29 H | -0.6893206 | 1.7784212  | 2.2095554  |
| 30 H | -1.9153143 | 2.5427052  | 1.1824361  |
| 31 H | -0.7098988 | 3.5308809  | 2.0110284  |
| 32 C | -0.1945323 | 3.7484215  | -0.6179541 |
| 33 H | 0.4637766  | 3.7865983  | -1.4911685 |
Cartesian coordinates for geometry minimized 2,6-di-tert-butyl pyridine + Cl cation (1b-Cl):

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| 1 C  | -0.8375940 | 0.0018043 | -2.4068683 |
| 2 N  | 0.0065405   | -0.0001172 | 0.1780200 |
| 3 C  | -0.6109334  | -1.1967978 | -1.7493376 |
| 4 C  | -0.6104954  | 1.1994141  | -1.7476744 |
| 5 C  | -0.1742322  | 1.2384747  | -0.4241244 |
| 6 C  | -0.1746757  | -1.2378117 | -0.4258099 |
| 7 H  | -0.7744358  | -2.125625  | -2.2710596 |
| 8 H  | -0.7737061  | 2.129383   | -2.2681431 |
| 9 Cl | 0.4827766   | -0.0013802 | 1.8545350 |
| 10 H | -1.1840302  | 0.0025913  | -3.4357701 |
| 11 C | 0.0865667   | -2.603961  | 0.2679741 |
| 12 C | 1.5771690   | -2.7495031 | 0.6844715 |
| 13 H | 1.8947323   | -2.0798011 | 1.4816704 |
| 14 H | 2.2364015   | -2.6001653 | -0.175470 |
| 15 H | 1.7299133   | -3.7726734 | 1.0409613 |
| 16 C | -0.8934461  | -2.8460161 | 1.4491616 |
| 17 H | -0.7509982  | -2.1821728 | 2.2999487 |
| 18 H | -0.7463517  | -3.8694111 | 1.8076945 |
| 19 H | -1.9325252  | -2.7596699 | 1.1137842 |
| 20 C | -0.1779716  | -3.7546293 | -0.7376907 |
| 21 H | 0.4798385   | -3.7112225 | -1.6117440 |
| 22 H | -1.2203331  | -3.7947152 | -1.0696885 |
| 23 H | 0.0314141   | -4.6984392 | -0.2280347 |
| 24 C | 0.0878939   | 2.6027141  | 0.2714171 |
| 25 C | 1.5786859   | 2.7477473  | 0.6876000 |
| 26 H | 2.2375553   | 2.5995897  | -0.1748268 |
| 27 H | 1.8961614   | 2.0764722  | 1.4835755 |
Cartesian coordinates for geometry minimized 2,6-di-tert-butyl pyridine + Cl
cation (1b-Cl) at the B3LYP/6-31G*/SM8 (acetone) level:

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 1 C  | -0.8403860| 0.0018033| -2.4067225|
| 2 N  | 0.0051419 | -0.0001151| 0.1761942 |
| 3 C  | -0.6130383| -1.1961978| -1.7497632|
| 4 C  | -0.6125882| 1.1988138 | -1.7481071|
| 5 C  | -0.1763412| 1.2371096 | -0.4265391|
| 6 C  | -0.1768860| -1.2364431| -0.4282175|
| 7 H  | -0.7767653| -2.1251510| -2.2730114|
| 8 H  | -0.7760135| 2.1285285 | -2.2701066|
| 9 Cl | 0.4804495 | -0.0013820| 1.8588655 |
| 10 H | -1.1875700| 0.0025877 | -3.4343923|
| 11 C | 0.0863240 | -2.6006941| 0.2668197 |
| 12 C | 1.5742177 | -2.7469990| 0.6854239 |
| 13 H | 1.8900100 | -2.0834877| 1.4890025 |
| 14 H | 2.2381001 | -2.5867091| -0.1709681|
| 15 H | 1.7355224 | -3.7719481| 1.0342031|
| 16 C | -0.8905225| -2.8463750| 1.4473577 |
| 17 H | -0.7457491| -2.1877271| 2.3022757 |
| 18 H | -0.7518997| -3.8717997| 1.8047519 |
| 19 H | -1.9309392| -2.7530957| 1.1182573 |
| 20 C | -0.1760444| -3.7517532| -0.7380087|
| 21 H | 0.4805046 | -3.7073350| -1.6121810|
| 22 H | -1.2173957| -3.7937083| -1.0710380|
| 23 H | 0.0337907 | -4.6981544| -0.2321012|
| 24 C | 0.0876613 | 2.6003121 | 0.2702526 |
| 25 C | 1.5757425 | 2.7452555 | 0.686125 |
| 26 H | 2.2392535 | 2.5862554 | -0.1683051|
| 27 H | 1.8914924 | 2.0800840 | 1.4908294 |
| 28 H | 1.7376023 | 3.7694927 | 1.0392180|
| 29 C | -0.8869294| 2.8449803 | 1.4514113|
| 30 H | -0.7434706| 2.1856836 | 2.3057492 |
| 31 H | -1.9292613| 2.7519179 | 1.1227279 |
| 32 H | -0.7499614| 3.8701294 | 1.8095427 |
| 33 C | -0.1744052| 3.7528130 | -0.7330044|
| 34 H | 0.4818500 | 3.7093111 | -1.6074280|
| 35 H | 0.0361081 | 4.6984469 | -0.2259483|
| 36 H | -1.2158415| 3.7957301 | -1.0656523|
Cartesian coordinates for geometry minimized 2,6-di-tert-butyl pyridine + Br cation (1b-Br):

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| 1    | C1      | -0.9251432 | 0.0017925 | -2.3610830 |
| 2    | N1      | -0.0335458 | -0.0001516 | 0.2259457  |
| 3    | C2      | -0.6738107 | -1.1981399 | -1.7100091 |
| 4    | C6      | -0.6732567 | 1.2007286  | -1.7083771 |
| 5    | C5      | -0.2084019 | 1.2402906  | -0.3879434 |
| 6    | C3      | -0.2090079 | -1.2396769 | -0.3896139 |
| 7    | H2      | -0.8387886 | -2.1263680 | -2.2295835 |
| 8    | H6      | -0.8378412 | 2.1297126  | -2.2267366 |
| 9    | H7      | -1.3016699 | 0.0025765  | -3.3776333 |
| 10   | C4      | 0.0923253  | -2.6258999 | 0.2613572  |
| 11   | C7      | 1.5894350  | -2.7330317 | 0.6870791  |
| 12   | H1      | 1.8860423  | -2.0475144 | 1.4778788  |
| 13   | H8      | 2.2446075  | -2.5730100 | -0.1761527 |
| 14   | H9      | 1.7655337  | -3.7493022 | 1.0531535  |
| 15   | C8      | -0.8976335 | -2.9522238 | 1.4228763  |
| 16   | H4      | -0.7985797 | -2.3104939 | 2.2950903  |
| 17   | H10     | -0.7110853 | -3.9802206 | 1.7493049  |
| 18   | H11     | -1.9327860 | -2.8982012 | 1.0688652  |
| 19   | C9      | -0.1185754 | -3.7601258 | -0.7864801 |
| 20   | H3      | 0.5322622  | -3.6527297 | -1.6602535 |
| 21   | H12     | -1.1599691 | -3.8426683 | -1.1137469 |
| 22   | H13     | 0.1407849  | -4.7065565 | -0.3054912 |
| 23   | C10     | 0.0936889  | 2.6255039  | 0.2648601  |
| 24   | C11     | 1.5909260  | 2.7313168  | 0.6904570  |
| 25   | H5      | 2.2458728  | 2.5719686  | -0.1730705 |
| 26   | H16     | 1.8872672  | 2.0446865  | 1.4803920  |
| 27   | H17     | 1.7676420  | 3.7470566  | 1.0577039  |
| 28   | C12     | -0.8958848 | 2.9508331  | 1.4269801  |
| 29   | H14     | -0.7966978 | 2.3082028  | 2.2985140  |
| 30   | H18     | -1.9311508 | 2.8973885  | 1.0732164  |
| 31   | H19     | -0.7090312 | 3.9784555  | 1.7544062  |
| 32   | C13     | -0.1168537 | 3.7611966  | -0.7814617 |
Cartesian coordinates for geometry minimized 2,6-di-tert-butyl pyridine + I cation (1b-I) at the B3LYP/6-31G*/LANL2DZ level:

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 1 C  | -0.4391450| -0.0006867| -2.5328415|
| 2 N  | 0.4356437 | -0.0009252| 0.0503267 |
| 3 C  | -0.3167948| -1.1938785| -1.8414288|
| 4 C  | -0.3101791| 1.1930383 | -1.8432877|
| 5 C  | 0.1067361 | 1.2193629 | 0.5165189 |
| 6 C  | 0.0999141 | -1.2201592| 0.5145197 |
| 7 H  | -0.5408065| -2.1246544| -2.3341821|
| 8 H  | -0.5365337| 2.1240960 | -2.3378114|
| 9 H  | -0.6993825| 0.0007661 | 3.5855831 |
| 10 C | 0.0672006 | -2.5630347| 0.2659293 |
| 11 C | 1.4316376 | -3.2959964| 0.2569615 |
| 12 H | 2.1949738 | 2.8039015 | 0.8539289 |
| 13 H | 1.8141320 | -3.4082796| -0.7603967|
| 14 H | 1.2932110 | -4.2979368| 0.6686024 |
| 15 C | -0.4671951| -2.3587095| 1.7037328 |
| 16 H | 0.1887293 | -1.7835733| 2.3524893 |
| 17 H | -0.5844486| -3.3376336| 2.1717722 |
| 18 H | -1.4487696| -1.8786890| 1.6942843 |
| 19 C | -0.9437548| -3.5149194| -0.4289093|
| 20 H | -0.5860813| -3.8934831| -1.3882338|
| 21 H | -1.9231480| -3.0533890| -0.5736734|
| 22 H | -1.0859853| -4.3874804| 0.2098904 |
| 23 C | 0.0806072 | 2.5630108 | 0.2628786 |
| 24 C | 1.4506084 | 3.2859680 | 0.2630515 |
| 25 H | 1.8443961 | 3.3884109 | -0.7510301|
### Cartesian coordinates for geometry minimized 4-methyl-2,6-di-tert-butyl pyridine (1c):

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| 1 C  | -0.6284016 | 0.0187703 | -2.2477325 |
| 2 N  | 0.1242676  | -0.0038483 | 0.4408914  |
| 3 C  | -0.4366253  | -1.1830914 | -1.5616066 |
| 4 C  | -0.4373023  | 1.2089264  | -1.5411106 |
| 5 C  | -0.0592428  | 1.1640502  | 0.0084256  |
| 6 C  | -0.0588919  | -1.1607703 | 0.2141019  |
| 7 H  | -0.5858641  | -2.1236251 | -2.0807194 |
| 8 H  | -0.5874527  | 2.1580282  | -2.0442575 |
| 9 C  | 0.1727253   | -2.4328237 | 0.6190273  |
| 10 C | 1.6388383   | -2.4385614 | 1.1088571  |
| 11 H | 1.8622217   | -1.5244278 | 1.6656124  |
| 12 H | 2.3366234   | -2.5036738 | 0.2650820  |
| 13 H | 1.8180384   | -3.3004130 | 1.7634867  |
| 14 C | -0.0907855  | -3.7203686 | -0.1815422 |
| 15 H | 0.5796658   | -3.8086575 | -1.0444375 |
| 16 H | -1.1247757  | -3.7735015 | -0.5423196 |
| 17 H | 0.0804665   | -4.5932806 | 0.4584769  |
| 18 C | -0.7708848  | -2.4013599 | 1.8423063  |
| 19 H | -0.6099456  | -1.4942609 | 2.4307592  |
| 20 H | -0.5901002  | -3.2723577 | 2.4841196  |
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| 1 C  | -0.6212014 | 0.0187613 | -2.2470346 |
| 2 N  | 0.1241599  | -0.0039484 | 0.4471678  |
| 3 C  | -0.4309204 | -1.1827829 | -1.5582805 |
| 4 C  | -0.4316626 | 1.2085313  | -1.5377253 |
| 5 C  | -0.0581096 | 1.1662310  | -0.1909117 |
| 6 C  | -0.0577181 | -1.1630742 | -0.2106811 |
| 7 H  | -0.5782762 | -2.1229461 | -2.0775189 |
| 8 H  | -0.5800082 | 2.1572810  | -2.0409609 |
| 9 C  | 0.1702272  | -2.4405863 | 0.6178154  |
| 10 C | 1.6373152  | -2.4636483 | 1.1022307  |
| 11 H | 1.8791879  | -1.5592625 | 1.6690420  |
| 12 H | 2.3357535  | -2.5297244 | 0.2589213  |
| 13 H | 1.8134056  | -3.3321755 | 1.7483926  |
| 14 C | -0.1049135 | -3.7221002 | -0.1872315 |
| 15 H | 0.5617607  | -3.8159295 | -1.0519857 |
| 16 H | -1.1399494 | -3.7703071 | -0.5447142 |
| 17 H | 0.0616943  | -4.6001431 | 0.4469714  |
| 18 C | -0.7659766 | -2.4148220 | 1.0461063  |
| 19 H | -0.6012597 | -1.5170582 | 2.4492828  |
| 20 H | -0.5896234 | -3.2924115 | 2.4796697  |
| 21 H | -1.8210542 | -2.4282420 | 1.5459234  |
| 22 C | 0.1701966  | 2.4292858  | 0.6592582  |
| 23 C | -0.7623323 | 2.3813374  | 1.8895945  |
| 24 H | -0.5941020 | 1.4748336  | 2.4785829  |
| 25 H | -1.8182743 | 2.3971480  | 1.5926132  |
| 26 H | -0.5857981 | 3.2496116  | 2.5356762  |
| 27 C | 1.6386002  | 2.4461427  | 1.1397547  |

**Cartesian coordinates for geometry minimized 4-methyl-2,6-di-tert-buty pyridine**

(1c) at the B3LYP/6-31G*SM8 (acetone) level:
| Atom | X    | Y    | Z    |
|------|------|------|------|
| 28   | H H5 | 1.8832117 | 1.5326777 | 1.6906227 |
| 29   | H H18| 1.8153437 | 3.3038783 | 1.7999909 |
| 30   | H H19| 2.3346826 | 2.5272480 | 0.2958409 |
| 31   | C C13| -0.1100037 | 3.7246628 | -0.1214590 |
| 32   | H H15| 0.5544337 | 3.8378720 | -0.9856993 |
| 33   | H H20| 0.0548059 | 4.5911320 | 0.5289689 |
| 34   | H H21| 1.1459397 | 3.7763282 | -0.0124983 |
| 35   | C C14| 0.0103782 | 0.0314527 | 3.7072396 |
| 36   | H H4 | 0.3959265 | 0.0408316 | -0.9856993 |
| 37   | H H22| -1.5788784 | 0.9191163 | -3.8625977 |
| 38   | H H23| -1.5725123 | -0.8552012 | -3.9825581 |

**Cartesian coordinates for geometry minimized 4-methyl-2,6-di-tert-butyl pyridine**

+ F cation (1c-F):

![Diagram of the molecule]
### Cartesian coordinates for geometry minimized 4-methyl-2,6-di-tert-butyl pyridine

+ Cl cation (1c-Cl):

![Molecular Structure](image)

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| 1 C  | -0.7323920 | -0.0026391 | -2.0920847 |
| 2 N  | 0.1203104 | -0.0029836 | 0.5231432  |
| 3 C  | -0.4948810 | -1.1928246 | -1.4085605 |
| 4 C  | -0.4890660 | 1.1893390 | -1.4086707 |
| 5 C  | -0.0569179 | 1.2324233 | -0.0892231 |
| 6 C  | -0.0604620 | -1.2358068 | -0.0872536 |
| 7 H  | -0.6544210 | -2.1266098 | -1.9252725 |
| 8 H  | -0.6437656 | 2.1236661 | -1.9266022 |
| 9 C1 | 0.5782652  | -0.0022435 | 2.2039077  |
| 10 C | 0.2025356  | -2.6029612 | 0.6030984  |
| 11 C | 1.6903658  | -2.7426481 | 1.0307164  |
| 12 H | 1.9988597  | -2.0701274 | 1.8290800  |
### Cartesian coordinates for geometry minimized 4-methyl-2,6-di-tert-butyl pyridine

+ Cl cation (1c-Cl) at the B3LYP/6-31G*SM8 (acetone) level:

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| 1 C  | -0.7321229 | -0.0032640 | -2.0917719 |
| 2 N  | 0.1211046  | -0.0033231  | 0.5206143  |
| 3 C  | -0.4943470  | -1.1937572  | -1.4096610 |
| 4 C  | -0.4903184  | 1.1891562   | 1.4092914  |
| 5 C  | -0.0579421  | 1.2312254   | -0.0916995 |
| 6 C  | -0.0606379  | -1.2352426  | -0.0897907 |
| 7 H  | -0.6537221  | -2.1269697  | -1.9275283 |
| 8 H  | -0.6476660  | 2.1223756   | -1.9286416 |
| 9 C  | 0.5797063   | 0.0032829   | 2.2062999  |
| 10 C | 0.2025965   | -2.6016394  | 0.6019078  |
| 11 C | 1.6878499   | -2.7428057  | 1.0310239  |
| 12 H | 1.9958122   | -2.0767939  | 1.8355615  |
| 13 H | 2.3571422   | -2.5813527  | 0.1790149  |
| 14 H | 1.8503839   | -3.7665878  | 1.3820914  |
| 15 C | -0.7814430  | -2.8524004  | 1.7753399  |
| 16 H | -0.649283   | -2.1919951  | 2.6306486  |
| 17 H | -0.6403048  | -3.8768399  | 2.1346810  |
| 18 H | -1.8197373  | -2.7645944  | 1.4380504  |

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Cartesian coordinates for geometry minimized 4-methyl-2,6-di-tert-butyl pyridine

+ Br cation (1c-Br):

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 1 C  | -0.8268129| -0.0005627| -2.0434049|
| 2 N  | 0.0901652 | -0.0019158| 0.5662924 |
| 3 C  | -0.5545282| 1.1937201 | -1.3711676|
| 4 C  | 1.1930933 | 1.930933  | -1.3666207|
| 5 C  | 1.2354396 | -1.2354396| -0.0538007|
| 6 C  | 1.2371064 | -1.2371064| -0.0567113|
| 7 H  | 2.1252105 | -2.1252105| 0.871348  |
| 8 H  | 2.1254017 | 2.1254017 | 0.871348  |
| 9 C  | 0.5662924 | -0.0019158| 0.5662924 |
| 10 C | -0.0005627| -0.0005627| -0.0005627|
| 11 H | 1.871348  | 0.871348  | 0.871348  |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| 1 H  | 2.3799112 | -2.5566088 | 0.1597923 |
| 12 H | -2.5566088 | 2.3799112 | 0.1597923 |
| 13 H | 1.9047864  | -3.7337231 | 1.3903955 |
| 14 C | -0.7644797 | -2.9636272 | 1.7451397 |
| 15 H | -0.6700909 | -2.3267630 | 2.6215076 |
| 16 H | -0.5747408 | -3.9929265 | 2.0657710 |
| 17 H | -1.7989347 | -2.9118488 | 1.3888042 |
| 18 C | 0.0301437  | -3.7574104 | -0.4634727 |
| 19 H | -0.0096640 | 3.8498960  | -0.7929522 |
| 20 H | 0.2986435  | -4.7027179 | 0.0148659 |
| 21 C | 0.2171316  | -3.6220345 | 0.1546524 |
| 23 C | 1.7122773  | 2.7206109  | 1.0277159 |
| 24 H | 2.3707914  | 3.5565880  | 0.0676984 |
| 25 H | 2.0007676  | 3.0322439  | 1.1820545 |
| 26 H | 1.8934405  | 3.7353850  | 1.3955073 |
| 27 C | -0.7753186 | 2.9565145  | 1.7513660 |
| 28 C | -0.6830437 | 2.3148271  | 2.6244472 |
| 29 C | -1.8093279 | 2.9068986  | 1.3932001 |
| 30 H | -0.5850571 | 3.9838745  | 2.0780045 |
| 31 C | 0.0185905  | 3.7564639  | -0.4552144 |
| 32 H | 0.6884338  | 3.6396024  | -1.3284809 |
| 33 H | 0.2870295  | 4.7013736  | 0.0239501 |
| 34 H | -1.0216900 | 3.8487668  | -0.7836160 |
| 35 Br| 0.5184882  | -0.0029731 | 2.5054794 |
| 36 C | 0.3481808  | 0.0047148  | -3.4531967 |
| 37 H | -0.5308437 | 0.1915462  | -4.1626623 |
| 38 H | -2.0898648 | 0.7960051  | -3.5998015 |
| 39 H | -1.8044302 | -0.9518875 | -3.7190667 |

**Cartesian coordinates for geometry minimized 4-methyl-2,6-di-tert-butyl pyridine**

+ I cation (1c-I) at the B3LYP/6-31G*/LANL2DZ level:
|   |   |   |   |
|---|---|---|---|
| C | C2 | -0.2514858 | -1.1868603 | -1.4884587 |
| C6 | -0.2436710 | 1.1868304 | -1.4899658 |
| C5 | 0.1702778 | 1.2151586 | -0.1668479 |
| C3 | 0.1626493 | -0.1668479 | 1.2162254 |
| H2 | 0.4941952 | -2.1204654 | -1.9719039 |
| H6 | -0.4801908 | 2.1214325 | -1.9745711 |
| C4 | 0.1241351 | -2.5581825 | -0.1668479 |
| C7 | 1.4792944 | -3.3066383 | 0.5820558 |
| H1 | 2.2622653 | -2.8149741 | 1.1538343 |
| H8 | 1.8349824 | -3.4329114 | -0.4434773 |
| H9 | 1.3418492 | -4.3029015 | 1.0078142 |
| C8 | -0.3761179 | -2.3471726 | 2.0651387 |
| H4 | 0.3046516 | -1.7844696 | 2.6992220 |
| H10 | -0.5005094 | -3.3243176 | 2.5351804 |
| H11 | -1.3485646 | -1.8490435 | 2.0779785 |
| C9 | -0.9127685 | -3.4971948 | -0.0568739 |
| H3 | -0.5788561 | -3.8812114 | -1.0225426 |
| H12 | -1.8876794 | -3.0211431 | -0.1836318 |
| H13 | -1.0551328 | -4.3673756 | 0.5853273 |
| C10 | 0.1390957 | 2.5580220 | 0.6138149 |
| C11 | 1.4988105 | 3.2984513 | 0.5812490 |
| H5 | 1.8509179 | 3.4189626 | -0.4434310 |
| H16 | 2.2768526 | 2.8044417 | 1.1577008 |
| H17 | 1.3656545 | 4.2970321 | 1.0028629 |
| C12 | -0.3647605 | 2.3508979 | 2.0617100 |
| H14 | 0.3107190 | 1.7828233 | 2.6966899 |
| H18 | -1.3411058 | 1.8604126 | 2.0731828 |
| H19 | -0.4821969 | 3.3289701 | 2.5316498 |
| C13 | -0.8908952 | 3.5029135 | -0.0618815 |
| H15 | -0.5530784 | 3.8845282 | -1.0271680 |
| H20 | -1.0290923 | 4.3741829 | 0.5797348 |
| H21 | -1.8684414 | 3.0327026 | -0.1901052 |
| I1 | 2.1988780 | -0.0053861 | 1.7551371 |
| C14 | -0.6589015 | -0.000189 | 3.6793782 |
| H7 | 0.2832533 | -0.0015435 | 4.2397791 |
| H22 | -1.2142006 | 0.8878465 | -3.9847444 |
| H23 | -1.2169808 | -0.8862339 | -3.9844013 |
**Cartesian coordinates for geometry minimized 4-tert-butyl pyridine (1d) at the B3LYP/6-31G*/SM8 (acetone) level:**

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| 1 C  | -0.0162441 | -0.0280881 | 0.5708035 |
| 2 N  | 0.0243695  | -0.0018726  | 3.4198254  |
| 3 C  | -0.5088386  | -1.0960941  | 1.3311343  |
| 4 C  | 0.4993514  | 1.0556825  | 1.3013208  |
| 5 C  | 0.4975842  | 1.0242972  | 2.6915516  |
| 6 C  | -0.4668378  | -1.0371726  | 2.7243038  |
| 7 H  | -0.9283441  | -1.9776933  | 0.8610756  |
| 8 H  | 0.9028770  | 1.9285990  | 0.7981336  |
| 9 H  | 0.8961523  | 1.8643753  | 3.2572091  |
| 10 H | -0.8503401  | -1.8678842  | 3.3141297  |
| 11 C | -0.0144542  | -0.0110348  | -0.9661056 |
| 12 C | -0.7888372  | 1.2299156  | -1.4673411 |
| 13 H | -0.3446463  | 2.1649996  | -1.1113799 |
| 14 H | -1.8337108  | 1.2107073  | -1.1370778 |
| 15 H | -0.7839552  | 1.2609468  | -2.5633546 |
| 16 C | -0.6719191  | -1.2680469  | -1.5631408 |
| 17 H | -0.1363641  | -2.1846107  | -1.2911561 |
| 18 H | -0.6661800  | -1.2022387  | -2.6567102 |
| 19 H | -1.7163327  | -1.3756291  | -1.2487450 |
| 20 C | 1.4474883  | 0.0643320  | -1.4656700 |
| 21 H | 2.0287576  | -0.8023252  | -1.1306587 |
| 22 H | 1.9561794  | 0.9648568  | -1.1064045 |
| 23 H | 1.4742446  | 0.0839779  | -2.5617435 |
Cartesian coordinates for geometry minimized 4-tert-butyl pyridine + Cl cation

(1d-Cl) at the B3LYP/6-31G*/SM8 (acetone) level:

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| 1 C  | -0.0168800 | 0.0238236 | 0.3580877 |
| 2 N  | 0.0199414  | -0.0655038 | 3.1236867 |
| 3 C  | 0.4582897  | -1.1034779 | 1.0558977 |
| 4 C  | -0.4696841 | 1.1018311  | 1.1355522 |
| 5 C  | -0.4476572 | 1.0494411  | 2.5159949 |
| 6 C  | 0.4731570  | -1.1421331 | 2.4330715 |
| 7 H  | 0.8264225  | -1.9786320 | 0.5342313 |
| 8 H  | -0.8519122 | 2.0086900  | 0.6850832 |
| 9 H  | -0.7871592 | 1.8573793  | 3.1512649 |
| 10 H | 0.8276820  | -1.9877491 | 3.0080262 |
| 11 Cl| 0.0414484  | -0.1229053 | 4.8591048 |
| 12 C | -0.0173859 | 0.0407103  | -1.1713867 |
| 13 C | 1.4469948  | -0.0881652 | -1.6607719 |
| 14 H | 1.9117556  | -1.0226243 | -1.3314806 |
| 15 H | 2.0656503  | 0.7418628  | -1.3027446 |
| 16 H | 1.4747249  | -0.0774781 | -2.7560186 |
| 17 C | -0.8430916 | -1.1638530 | -1.6861646 |
| 18 H | -0.4247953 | -2.1235718 | -1.3678808 |
| 19 H | -0.8534684 | -1.1630856 | -2.7815281 |
| 20 H | -1.8825476 | -1.1179576 | -1.3433862 |
| 21 C | -0.6223383 | 1.3366583  | -1.7401576 |
| 22 H | -0.0491923 | 2.2254824  | -1.4535975 |
| 23 H | -1.6639914 | 1.4785291  | -1.4309968 |
| 24 H | -0.6159630 | 1.2927287  | -2.8338872 |
Cartesian coordinates for geometry minimized 4-trifluoromethyl pyridine (1e) at the B3LYP/6-31G*/SM8 (acetone) level:

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C1   | -0.0222821 | -0.0106755 | -0.4744081 |
| N1   | 0.0267116    | 0.0033123    | 2.3239245   |
| C2   | -0.5036816   | -1.015115   | 0.2453358   |
| C6   | 0.4847055    | 1.0895113    | 0.2199553   |
| C5   | 0.4861782    | 1.0448612    | 1.6120285   |
| C3   | -0.4564999   | -1.0422108   | 1.6391966   |
| H2   | -0.9062120   | -1.9736740   | 0.2564578   |
| H6   | 0.8676625    | 1.9591618    | 0.3035633   |
| H5   | 0.8741630    | 1.8832196    | 2.1853080   |
| H3   | -0.8256281   | -1.8753595   | 2.2324071   |
| C4   | -0.0139667   | -0.0025448   | -1.9816058  |
| F1   | -0.6038592   | 1.1107440    | -2.4726993  |
| F2   | -0.6570396   | -1.0663946   | -2.5049903  |
| F3   | 1.2497487    | -0.0184396   | -2.4644314  |

Cartesian coordinates for geometry minimized 4-trifluoromethyl pyridine + Cl cation (1e-Cl) at the B3LYP/6-31G*/SM8 (acetone) level:

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C1   | -0.0261847 | 0.0278727 | -0.7328823 |
| N1   | 0.0206052  | -0.0475513 | 1.9879863  |
### Cartesian coordinates for geometry minimized 4-cyanopyridine (1f) at the B3LYP/6-31G*/SM8 (acetone) level:

| Atom | X     | Y     | Z      |
|------|-------|-------|--------|
| 1    | N N1  | 0.0000000 | 0.0000000 | 2.1997659 |
| 2    | C C4  | 0.0000000 | 0.0000000 | -0.5971539 |
| 3    | C C2  | 1.1474557 | 0.0000000 | 1.5039004 |
| 4    | C C6  | -1.1474557 | 0.0000000 | 1.5039004 |
| 5    | C C5  | -1.2094198 | 0.0000000 | 0.1121569 |
| 6    | C C3  | 1.2094198 | 0.0000000 | 0.1121569 |
| 7    | H H2  | 2.0636346 | 0.0000000 | 2.0887390 |
| 8    | H H6  | -2.0636346 | 0.0000000 | 2.0887390 |
| 9    | H H5  | -2.1624575 | 0.0000000 | -0.4040951 |
| 10   | H H3  | 2.1624575 | 0.0000000 | -0.4040951 |
| 11   | C C1  | 0.0000000 | 0.0000000 | -2.0309621 |
| 12   | N N2  | 0.0000000 | 0.0000000 | -3.1988059 |
**Cartesian coordinates for geometry minimized 4-cyanopyridine + Cl cation (1f-Cl)**

at the B3LYP/6-31G*/SM8 (acetone) level:

```
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 1 N  | 0.000000  | 0.000000  | 1.2123809 |
| 2 C  | 0.000000  | 0.000000  | -1.5124756|
| 3 C  | 1.1942669 | 0.000000  | 0.5726390 |
| 4 C  | -1.1942669| 0.000000  | 0.5726390 |
| 5 C  | -1.2129175| 0.000000  | -0.8096542|
| 6 C  | 1.2129175 | 0.000000  | -0.8096542|
| 7 H  | 2.0911625 | 0.000000  | 1.1785270 |
| 8 H  | -2.0911625| 0.000000  | 1.1785270 |
| 9 H  | 2.1683554 | 0.000000  | -1.3199379|
| 10 H | 2.1683554 | 0.000000  | -1.3199379|
| 11 C | 0.000000  | 0.000000  | -2.9430404 |
| 12 N | 0.000000  | 0.000000  | -4.1101481 |
| 13 Cl| 0.000000  | 0.000000  | 2.9496747  |
```

**Cartesian coordinates for geometry minimized 4-bromopyridine (1g) at the B3LYP/6-31G*/SM8 (acetone) level:**

```
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 1 N  | 0.000000  | 0.000000  | 2.9013478 |
| 2 C  | 0.000000  | 0.000000  | 0.1105270 |
| 3 C  | 1.1431628 | 0.000000  | 2.2001341 |
| 4 C  | -1.1431628| 0.000000  | 2.2001341 |
| 5 C  | -1.2058464| 0.000000  | 0.8057399 |
```
Cartesian coordinates for geometry minimized 4-bromopyridine (1g) at the B3LYP/6-31G*/SM8 (acetone) level:

| Atom | X     | Y     | Z       |
|------|-------|-------|---------|
| 1 N  | 0.000000 | 0.000000 | 2.9013478 |
| 2 C  | 0.000000 | 0.000000 | 0.1105270 |
| 3 C  | 1.1431628 | 0.000000 | 2.2001341 |
| 4 C  | -1.1431628 | 0.000000 | 2.2001341 |
| 5 C  | -1.2058464 | 0.000000 | 0.8057399 |
| 6 C  | 1.2058464 | 0.000000 | 0.8057399 |
| 7 H  | 2.0633399 | 0.000000 | 2.7801079 |
| 8 H  | -2.0633399 | 0.000000 | 2.7801079 |
| 9 H  | -2.1618483 | 0.000000 | 0.2948206 |
| 10 H | 2.1618483 | 0.000000 | 0.2948206 |
| 11 Br| 0.000000 | 0.000000 | -1.8055126 |

Cartesian coordinates for geometry minimized 4-bromopyridine + Cl (1g-Cl) at the B3LYP/6-31G*/SM8 (acetone) level:

| Atom | X     | Y     | Z       |
|------|-------|-------|---------|
| 1 N  | 0.000000 | 0.000000 | 1.9983709 |
Cartesian coordinates for geometry minimized succinimide anion at the B3LYP/6-31G*/SM8 (acetone) level:

| Atom  | X       | Y       | Z       |
|-------|---------|---------|---------|
| N1    | 0.0000000 | -0.0000001 | -1.6430693 |
| C2    | 1.1154878 | 0.0000020 | -0.8517536 |
| C3    | 0.7624587 | -0.0000015 | 0.6543592 |
| C4    | -0.7624590 | 0.0000015 | 0.6543592 |
| C6    | -1.1154881 | -0.0000019 | -0.8517539 |
| H2    | 1.2117654 | -0.8791951 | 1.1310469 |
| H5    | 1.2117711 | 0.8791874 | 1.1310524 |
| H7    | -1.2117663 | 0.8791950 | 1.1310476 |
| H8    | -1.2117695 | -0.8791875 | 1.1310528 |
| O1    | -2.2901120 | -0.0000053 | -1.2431711 |
| O2    | 2.2901119 | 0.0000051 | -1.2431703 |
 Cartesian coordinates for geometry minimized \textit{N}-chlorosuccinimide (NCS) at the B3LYP/6-31G*/SM8 (acetone) level:

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 1 N  | 0.0000000 | 0.0000000 | 0.3164687 |
| 2 C  | 1.1937515 | 0.0000000 | -0.434312 |
| 3 C  | 0.7701646 | 0.0000000 | -1.8896497|
| 4 C  | -0.7701646| 0.0000000 | -1.8896497|
| 5 C  | -1.1937515| 0.0000000 | -0.434312 |
| 6 H  | 1.2017538 | 0.8800770 | -2.3749307|
| 7 H  | 1.2017538 | -0.8800770| -2.3749307|
| 8 H  | -1.2017538| -0.8800770| -2.3749307|
| 9 H  | -1.2017538| 0.8800770 | -2.3749307|
| 10 O | -2.3092282 | 0.0000000 | 0.0392154 |
| 11 O | 2.3092282  | 0.0000000 | 0.0392154 |
| 12 Cl| 0.0000000  | 0.0000000 | 2.0320450 |

 Cartesian coordinates for geometry minimized phthalimide anion at the B3LYP/6-31G*/SM8 (acetone) level:
### Cartesian coordinates for geometry minimized N-chlorophthalimide (NCP) at the B3LYP/6-31G*/SM8 (acetone) level:

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 1 H  H1 | -2.5094267 | 0.0000000 | -1.9981670 |
| 2 C  C1 | -1.4246386 | 0.0000000 | -2.0071608 |
| 3 C  C4 | 1.4246386  | 0.0000000 | -2.0071608 |
| 4 C  C2 | -0.7003910 | 0.0000000 | -0.8246524 |
| 5 C  C6 | -0.6994171 | 0.0000000 | -3.2067501 |
| 6 C  C5 | 0.6994171  | 0.0000000 | -3.2067501 |
| 7 C  C3 | 0.7003910  | 0.0000000 | -0.8246524 |
| 8 H  H6 | -1.2337089 | 0.0000000 | -4.1513571 |
| 9 H  H5 | 1.2337089  | 0.0000000 | -4.1513571 |
| 10 H H4 | 2.5094267  | 0.0000000 | -1.9981670 |
| 11 C  C7 | -1.1885780 | 0.0000000 | 0.5794528  |
| 12 C  C8 | 1.1885780  | 0.0000000 | 0.5794528  |
| 13 N  N1 | 0.0000000  | 0.0000000 | 1.3548439  |
| 14 O  O1 | -2.3178198 | 0.0000000 | 1.0194892  |
| 15 O  O2 | 2.3178198  | 0.0000000 | 1.0194892  |
| 16 C1 C11 | 0.0000000  | 0.0000000 | 3.0595670  |
Cartesian coordinates for geometry minimized 1-chloro-5,5-dimethylhydantoin anion at the B3LYP/6-31G*/SM8 (acetone) level:

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| 1 N  | 0.6348933 | 0.0196044 | 0.3935199 |
| 2 C  | -0.6531504 | 0.6392987 | 0.0309234 |
| 3 C  | -1.5052790 | -0.6642301 | -0.0227940 |
| 4 N  | -0.7208693 | -1.7740805 | -0.0182634 |
| 5 C  | 0.5910462 | -1.3817227 | 0.0862221 |
| 6 O  | 1.6019229 | -2.0704046 | 0.0071321 |
| 7 C  | 2.1122480 | 0.8730693 | -0.0155140 |
| 8 O  | -2.7385370 | -0.6168048 | -0.0837156 |
| 9 C  | -1.1419147 | 1.5967263 | 1.1165117 |
| 10 H | -2.1772458 | 1.8873707 | 0.9139982 |
| 11 H | -0.5224837 | 2.5002971 | 1.1491672 |
| 12 H | -1.1044665 | 1.1195958 | 2.1019300 |
| 13 C | -0.6779273 | 1.3096456 | -1.3495440 |
| 14 H | -1.7126081 | 1.5648848 | -1.5992339 |
| 15 H | -0.2943829 | 0.6407735 | -2.1284128 |
| 16 H | -0.0789338 | 2.2256011 | -1.3557543 |
Cartesian coordinates for geometry minimized 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) at the B3LYP/6-31G*/SM8 (acetone) level:

| Atom | X          | Y              | Z          |
|------|------------|----------------|------------|
| 1 N  | 0.9282227  | -0.4666650     | 0.1325938  |
| 2 C  | 0.8021885  | 1.0067936      | 0.0069192  |
| 3 C  | -0.7369431 | 1.1495839      | -0.0022491 |
| 4 N  | -1.2394160 | -0.1435735     | -0.0110006 |
| 5 C  | -0.2432908 | -1.1677794     | 0.0380491  |
| 6 O  | -0.4438673 | -2.3600104     | 0.0133999  |
| 7 C1 | -2.9051737 | -0.5190372     | -0.0053392 |
| 8 C1 | 2.4338512  | -1.2747265     | -0.0064335 |
| 9 O  | -1.3715844 | 2.1802447      | -0.0088350 |
| 10 C | 1.3958776  | 1.7246436      | 1.2215635  |
| 11 H | 1.1803832  | 2.7940166      | 1.1572922  |
| 12 H | 2.4811459  | 1.5890967      | 1.2404434  |
| 13 H | 0.9801868  | 1.3368335      | 2.1559728  |
| 14 C | 1.3704076  | 1.5323056      | -1.3174170 |
| 15 H | 1.1316766  | 2.5941448      | -1.4168392 |
| 16 H | 0.9534980  | 0.9969963      | -2.1756197 |
| 17 H | 2.4581197  | 1.4194055      | -1.3299791 |
Cartesian coordinates for geometry minimized dichloroisocyanuric acid anion at the B3LYP/6-31G*/SM8 (acetone) level:

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| 1 N  | 1.1975822 | -0.2247672 | 0.000000 |
| 2 N  | -0.7933257 | 0.9247690 | 0.000000 |
| 3 N  | -0.8359088 | -1.4478491 | 0.000000 |
| 4 C  | -1.5565342 | -0.3094036 | 0.000000 |
| 5 C  | 0.5102035 | -1.5032357 | 0.000000 |
| 6 C  | 0.5986729 | 1.0367859 | 0.000000 |
| 7 O  | 1.1895880 | -2.5203278 | 0.000000 |
| 8 O  | -2.7770002 | -0.2295546 | 0.000000 |
| 9 O  | 1.2055501 | 2.0885643 | 0.000000 |
| 10 Cl| -1.6594540 | 2.4145250 | 0.000000 |
| 11 Cl| 2.9206261 | -0.2295063 | 0.000000 |

Cartesian coordinates for geometry minimized trichloroisocyanuric acid (TCCA) at the B3LYP/6-31G*/SM8 (acetone) level:
| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| N1   | 1.3469650  | 0.0000000  | 0.0000000  |
| N2   | -0.6734825 | 1.1665059  | 0.0000000  |
| N4   | -0.6734825 | -1.1665059 | 0.0000000  |
| C10  | -1.4589410 | 0.0000000  | 0.0000000  |
| C8   | 0.7294705  | -1.2634800 | 0.0000000  |
| C7   | -2.6624057 | 1.26348    | 0.0000000  |
| O1   | 1.3312028  | 2.3057110  | 0.0000000  |
| O3   | 1.3312028  | -2.3057110 | 0.0000000  |
| Cl1  | 3.0624432  | 0.0000000  | 0.0000000  |
| Cl2  | -1.5312216 | -2.6521536 | 0.0000000  |
| Cl3  | -1.5312216 | 2.6521536  | 0.0000000  |

**Cartesian coordinates for geometry minimized N-cinnamyl-N-methylmethanesulfonamide (6):**

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| H1   | -1.0305135 | 2.8665909  | 0.2373861  |
| C1   | -0.8216126 | 2.8025379  | 1.3014642  |
| C4   | -0.3076293 | 2.6799012  | 4.0400905  |
| C2   | -0.5060062 | 1.5598968  | 1.8819111  |
| C6   | -0.8759614 | 3.9582720  | 2.0742966  |
| C5   | -0.6187115 | 3.9037641  | 3.4477347  |
| C3   | -0.2538330 | 1.5229252  | 3.2643776  |
| H6   | -1.1218425 | 4.9072444  | 1.6048414  |
| H5   | -0.6626065 | 4.8082310  | 4.0483011  |
| H3   | -0.0090709 | 0.5717361  | 3.7314987  |
| H4   | -0.1065007 | 2.6241747  | 5.1065983  |
| C7   | -0.4305058 | 0.3056322  | 1.1187739  |
| H7   | -0.2254035 | -0.5807294 | 1.7203402  |
| C8   | -0.5762908 | 0.1369422  | -0.2039278 |
| H8   | -0.7743776 | 0.9896481  | -0.8511283 |
| C9   | -0.4950434 | -1.2136049 | -0.8658559 |
| H2   | -0.5170834 | -1.9941192 | -0.1038638 |
Cartesian coordinates for geometry minimized N-cinnamyl-N-methylmethanesulfonamide + Cl cation (6-Cl):

| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| 1 H  | 1.696809 | 0.089600 | 2.023526 |
| 2 C  | 2.332408 | 0.307593 | 1.169557 |
| 3 C  | 3.992070 | 0.892344 | -1.004801|
| 4 C  | 1.830245 | 0.221613 | -0.138968 |
| 5 C  | 3.655330 | 0.682201 | 1.384550 |
| 6 C  | 4.486524 | 0.971503 | 0.298089 |
| 7 C  | 2.665650 | 0.525013 | -1.223308 |
| 8 H  | 4.040476 | 0.745197 | 2.395753 |
| 9 H  | 5.519885 | 1.258081 | 0.469166 |
| 10 H | 2.281007 | 0.464077 | -2.238175 |
| 11 H | 4.636648 | 1.116080 | -1.849071 |
| 12 C | 0.421433 | -0.175635 | -0.410150 |
| 13 H | 0.231330 | -0.268935 | -1.481678 |
| 14 C | -0.162246 | -1.365370 | 0.353177 |
| 15 C | -1.658009 | -1.566799 | 0.082392 |
| 16 H | -1.830369 | -1.801693 | -0.976270 |
| 17 H | -2.021154 | -2.406688 | 0.678479 |
| 18 N | -2.475689 | -0.389740 | 0.515604 |
| 19 C | -3.939658 | -0.642526 | 0.438464 |
| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| 1 H  | -0.8280239 | 0.7464126 | -1.6579833 |
| 2 C  | -0.5385586 | 0.8203226 | -0.6141097 |
| 3 C  | 0.2194106  | 0.9770287 | 2.0610019  |
| 4 C  | -0.1258567 | -0.3300109 | 0.0536762 |
| 5 C  | -0.5839693 | 2.0532117 | 0.0407250  |
| 6 C  | -0.2037210 | 2.1333012 | 1.3857781  |
| 7 C  | 0.2561821  | -0.2422025 | 1.4006387 |
| 8 H  | 0.5951375  | -1.1321139 | 1.9236242  |
| 9 H  | 0.5187042  | 1.0646910 | 3.1005799  |
| 10 N | -0.1399570 | -1.5884436 | -0.6547433 |
| 11 S | 1.4026110  | -2.2684655 | -0.9778075 |
| 12 C | -1.1403989 | -2.5640997 | -0.1868703 |
| 13 H | -0.9272789 | -2.9506061 | 0.8170278  |
| 14 H | -1.1874974 | -3.4098397 | -0.8787659 |
| 15 H | -2.1119680 | -2.0640287 | -0.1865897 |
| 16 O | 1.6165569  | -3.4481067 | -0.1276428 |
| 17 O | 2.3706445  | -1.1724327 | -0.9986819 |
| 18 C | 1.1818779  | -2.8512269 | -2.6716374 |
| 19 H | 0.3468644  | -3.5529778 | -2.7153607 |
| 20 H | 2.1084281  | -3.3572086 | -2.9529498 |
| 21 H | 1.0026214  | -1.9882426 | -3.3137483 |
| 22 H | -0.9097852 | 2.9325063 | -0.5026876 |

Cartesian coordinates for geometry minimized N-(4-methoxyphenyl)-N-methylethanesulfonamide (7):
Cartesian coordinates for geometry minimized $N$-(4-methoxyphenyl)-$N$-methylmethanesulfonamide + Cl cation (7-Cl-1):

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| 1 H  | -1.1679408 | 0.5393404 | -1.6202229 |
| 2 C  | -0.7071932 | 0.6233359 | -0.6415009 |
| 3 C  | 0.5938769  | 0.9454410 | 1.8844954 |
| 4 C  | -0.1605279 | -0.4538131 | -0.0349923 |
| 5 C  | -0.6757176 | 1.9887666 | -0.0350380 |
| 6 C  | 0.0082726  | 2.0832961 | 1.3096646 |
| 7 C  | 0.4923162  | -0.2733502 | 1.2515724 |
| 8 H  | 0.9038626  | -1.1467847 | 1.7464521 |
| 9 H  | 1.0860336  | 1.0455490 | 2.8458153 |
| 10 N | -0.2327809 | -1.7339681 | -0.6523380 |
| 11 S | 1.2837435  | -2.5734204 | -0.7285060 |
| 12 C | -1.4212535 | -2.5671320 | -0.3583811 |
| 13 H | -1.4486017 | -2.9059666 | 0.6821118 |
| 14 H | -1.4129427 | -3.4419995 | -1.0160684 |
| 15 H | 2.3161982  | -1.9823760 | -0.5824029 |
| 16 O | 1.1695434  | -3.8118467 | 0.0372507 |
| 17 O | 2.2815977  | -1.5497212 | -0.3886037 |
| 18 C | 1.4185300  | -2.9705831 | -2.4755154 |
| 19 H | 0.5695161  | -3.5913106 | -2.7678497 |
| 20 H | 2.3499476  | -3.5302390 | -2.5933903 |
| 21 H | 1.4500789  | -2.0411476 | -3.0452141 |
| 22 H | 1.6969950  | 2.3825780  | 0.0524142 |
| 23 O | 0.0497280  | 3.1756452  | 2.0069334 |
| 24 C | -0.5504572 | 4.4498204  | 1.6323065 |
| 25 H | 0.1334203  | 4.9750858  | 0.9663904 |
| 26 H | -0.6623669 | 4.9808296  | 2.5756889 |
| 27 H | 1.5216109  | 4.2987124  | 1.1561738 |
| 28 Cl| 0.1841190  | 3.0888881  | -1.2126455 |
Cartesian coordinates for geometry minimized $N$-(4-methoxyphenyl)-$N$-methylmethanesulfonamide + Cl cation (7-Cl-2):

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| 1 H  | 0.7545233 | 0.5200014 | -1.4597529 |
| 2 C  | -0.0171488 | 0.6432198 | -0.7030059 |
| 3 C  | -0.2950814 | 1.2157281 | 2.0530766 |
| 4 C  | 0.0577609 | -0.4652841 | 0.3395080 |
| 5 C  | -0.0488950 | 2.0403395 | -0.2017802 |
| 6 C  | -0.1979156 | 2.3151498 | 1.1178931 |
| 7 C  | -0.1857158 | -0.0996765 | 1.6977841 |
| 8 H  | -0.2395970 | -0.8544463 | 2.4698079 |
| 9 H  | -0.4455950 | 1.4789221 | 3.0969806 |
| 10 N | 0.2818921 | -1.7366073 | 0.0086877 |
| 11 S | 1.0417889 | -2.3347658 | -1.5918841 |
| 12 C | 0.1865904 | -2.8096704 | 1.0275572 |
| 13 H | 0.9900449 | -2.7123523 | 1.7627925 |
| 14 H | 0.2946411 | -3.7766796 | 0.5418474 |
| 15 H | -0.7893717 | -2.7567642 | 1.5143265 |
| 16 O | 1.9001411 | -3.4131185 | -1.1385160 |
| 17 O | 1.5596151 | -1.1591264 | -2.2712309 |
| 18 C | -0.3869241 | -2.9984357 | -2.4562879 |
| 19 H | -0.8553384 | -3.7604173 | -1.8312377 |
| 20 H | 0.0140180 | -3.4519453 | -3.3680495 |
| 21 H | -1.0684675 | -2.1809029 | -2.6904622 |
| 22 H | 0.0142887 | 2.8116955 | -0.9591045 |
| 23 O | -0.2622823 | 3.5162128 | 1.7088567 |
| 24 C | -0.1872241 | 4.6844471 | 0.8791927 |
| 25 H | 0.7691045 | 4.7145086 | 0.3449722 |
| 26 H | -0.2587461 | 5.5313609 | 1.5600164 |
| 27 H | -1.0198338 | 4.7053353 | 0.1672088 |
| 28 Cl| -1.6062723 | 0.3332715 | -1.6191967 |
Cartesian coordinates for geometry minimized \(N\)-methyl-\(N\)-(3,4,5-trimethoxyphenyl) methanesulfonamide:

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| 1 C  | -1.0309926 | -0.1353219 | 1.3399131 |
| 2 C  | 1.2672646  | -0.2438739 | -0.2635019 |
| 3 C  | 0.2375798  | -0.1321330 | 1.9427107  |
| 4 C  | -1.1547915 | -0.1516611 | -0.0556783 |
| 5 C  | -0.0017465 | -0.2103991 | -0.8502877 |
| 6 C  | 1.3836172  | -0.1881716 | 1.1293493  |
| 7 H  | -2.1333625 | -0.1301962 | -0.5156833 |
| 8 O  | -2.0863011 | -0.1074981 | 2.2031059  |
| 9 C  | -3.3959952 | -0.0835119 | 1.6622379  |
| 10 H | -3.5647534 | 0.8124029  | 1.0494296  |
| 11 H | -4.0714074 | -0.0639328 | 2.5194953  |
| 12 H | -3.6033941 | -0.9772719 | 1.0579932  |
| 13 O | 0.3476819  | -0.0293952 | 3.3049787  |
| 14 C | 0.5303604  | -1.2732688 | 3.9835550  |
| 15 H | -0.3256224 | -1.9401431 | 3.8189956  |
| 16 H | 0.6017975  | -1.0324363 | 5.0469483  |
| 17 H | 1.4531692  | -1.7686339 | 3.6598364  |
| 18 H | 2.1360535  | -0.3046660 | -0.9015499 |
| 19 O | 2.5705937  | -0.2044372 | 1.7957345  |
| 20 C | 3.7687652  | -0.2124201 | 1.0303176  |
| 21 H | 3.8605057  | -1.1293497 | 0.4338031  |
| 22 H | 4.5825460  | -0.1705282 | 1.7563869  |
| 23 H | 3.8254452  | 0.6572571  | 0.3645174  |
| 24 N | -0.1141312 | -0.2770905 | -2.2810391 |
| 25 C | -1.2980093 | -0.9250009 | -2.8606351 |
| 26 H | -1.1011638 | -1.1416912 | -3.903918  |
| 27 H | -2.2127137 | -0.3170400 | -2.7910372 |
| 28 H | -1.4578432 | -1.8614691 | -2.3210899 |
| 29 S | 0.5770077  | 0.9726944  | -3.2100336 |
| 30 O | 0.2609094  | 0.6636564  | 4.6058365  |
| 31 O | 1.9615227  | 1.1592723  | -2.7768471 |
| 32 C | -0.3295774 | 2.4691429  | -2.7488351 |
| 33 H | 0.1200532  | 3.2962346  | 3.3025786  |
| 34 H | -0.2250918 | 2.6290482  | 1.6742912  |
| 35 H | -1.3779757 | 2.3518328  | -3.0309924 |

S97
Cartesian coordinates for geometry minimized \(N\)-methyl-\(N\)-(3,4,5-trimethoxyphenyl) methanesulfonamide + Cl cation:

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| 1    | -0.138405  | 1.082979   | 1.305737   |
| 2    | -0.340888  | -1.137890  | -0.432317  |
| 3    | -0.233881  | -0.220594  | 1.906811   |
| 4    | -0.003333  | 1.300556   | -0.086200  |
| 5    | -0.006754  | 0.239999   | -0.971432  |
| 6    | -0.312871  | -1.304612  | 1.067177   |
| 7    | 0.169988   | 2.306836   | -0.435328  |
| 8    | -0.136328  | 2.066960   | 2.181463   |
| 9    | -0.076789  | 3.451629   | 1.775274   |
| 10   | 0.877992   | 3.664001   | 1.286200   |
| 11   | -0.154226  | 4.017311   | 2.702239   |
| 12   | -0.916787  | 3.690375   | 1.117889   |
| 13   | -0.326434  | -0.333941  | 3.261283   |
| 14   | 0.888728   | -0.121459  | 4.010964   |
| 15   | 1.648936   | -0.859964  | 3.730307   |
| 16   | 0.612188   | -0.253388  | 5.057248   |
| 17   | 1.275079   | 0.889413   | 3.858424   |
| 18   | -0.406258  | -2.584299  | 1.370218   |
| 19   | -0.616412  | -3.090793  | 2.713036   |
| 20   | 0.274392   | -2.928774  | 3.322122   |
| 21   | -0.786580  | -4.156939  | 2.569003   |
| 22   | -1.485142  | -2.615119  | 3.166789   |
| 23   | 0.156790   | 0.426542   | -2.312556  |
| 24   | 0.165627   | 1.799552   | -2.854713  |
| 25   | 0.130623   | 1.759667   | -3.941817  |
| 26   | 1.074295   | 2.338836   | -2.567688  |
| 27   | -0.721019  | 2.323165   | -2.489781  |
| 28   | 0.883255   | -0.790652  | -3.424970  |
| 29   | 1.363667   | -1.889502  | -2.595545  |
| 30   | 1.780538   | -0.009760  | -4.260439  |
| 31   | -0.530337  | -1.326943  | -4.396542  |
| 32   | -0.133603  | -2.033737  | -5.130623  |
| 33   | -0.961701  | -0.461553  | -4.902453  |
| 34   | -1.252046  | -1.809942  | -3.737307  |
| 35   | -2.048707  | -1.519402  | -0.986314  |
| 36   | 0.286395   | -1.908558  | -0.876161  |
Cartesian coordinates for geometry minimized *N*-cinnamyl-*N*-(2-phenylallyl)methanesulfonamide (9):

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| 1    | -3.566164  | -1.288921  | 0.001150   |
| 2    | -3.086618  | -1.326162  | -0.972973  |
| 3    | -1.823591  | -1.353055  | -3.451814  |
| 4    | -1.937901  | -2.118310  | -1.141664  |
| 5    | -3.602261  | -0.570975  | -2.025066  |
| 6    | -2.974204  | -0.583002  | -3.271561  |
| 7    | -1.306663  | -2.107323  | -2.398482  |
| 8    | -4.490656  | 0.035172   | -1.867224  |
| 9    | -3.372990  | 0.007050   | -4.092311  |
| 10   | -0.411133  | -2.699010  | -2.563266  |
| 11   | -1.326074  | -1.371414  | -4.418072  |
| 12   | -1.415929  | -2.944957  | -0.020240  |
| 13   | -2.227222  | -3.513929  | 0.885049   |
| 14   | -1.830236  | -4.094874  | 1.713473   |
| 15   | -3.308773  | -3.446626  | 0.815148   |
| 16   | 0.082527   | -3.161655  | 0.076511   |
| 17   | 0.304048   | -3.798152  | 0.944391   |
| 18   | 0.459573   | -3.686248  | -0.803156  |
| 19   | 0.809548   | -1.879215  | 0.170155   |
| 20   | 2.285718   | -1.758489  | -0.665970  |
| 21   | 2.104954   | -0.236950  | -1.614194  |
| 22   | 1.969792   | 0.596333   | -0.924302  |
| 23   | 1.245919   | -0.342398  | -2.277913  |
| 24   | 3.028173   | -0.118284  | -2.186659  |
| 25   | 3.384012   | -1.560137  | 0.288852   |
| 26   | 2.326176   | -2.868048  | -1.628568  |
| 27   | 0.747034   | -1.189784  | 1.481361   |
| 28   | 1.641703   | -1.405607  | 2.077861   |

S99
Cartesian coordinates for geometry minimized $N$-cinnamyl-$N$-(2-phenylallyl)methanesulfonamide $+\text{Cl cation (11):}$

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| 1    | H H1    | 0.4549913 | 2.0183789 | 1.7077815 |
| 2    | C C1    | 0.5066882 | 1.0313050 | 2.1604949 |
| 3    | C C4    | 0.6975914 | -1.4359402 | 3.4106276 |
| 4    | C C2    | 1.1993595 | -0.0113499 | 1.5084218 |
| 5    | C C6    | -0.0786043 | 0.8433627 | 3.4143703 |
| 6    | C C5    | 0.0158508 | -0.3955723 | 4.0451046 |
| 7    | C C3    | 1.2847970 | -1.2487676 | 2.1561092 |
| 8    | H H6    | -0.5923547 | 1.6691832 | 3.8978753 |
| 9    | H H5    | -0.4308388 | -0.5502060 | 5.0225903 |
| 10   | H H3    | 1.7824480 | -2.0921076 | 1.6947347 |
| 11   | H H4    | 0.7759200 | -2.4067240 | 3.8910208 |
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| 12 | C | C7 | 1.7851769 | 0.2794130 | 0.1099132 |
| 13 | C | C8 | 2.8139646 | 1.4281692 | 0.1885687 |
| 14 | C | C9 | 2.4345817 | -0.9373404 | -0.6425019 |
| 15 | H | H2 | 3.3671011 | -0.6085093 | -1.1123530 |
| 16 | H | H10 | 2.6765158 | -1.7876940 | -0.0128273 |
| 17 | N | N1 | 1.5130468 | -1.3435279 | -1.7137435 |
| 18 | C | C10 | 0.8269234 | -0.1459696 | -2.1619329 |
| 19 | H | H12 | -0.0960951 | -0.3784577 | -2.6949177 |
| 20 | H | H13 | 1.4837303 | 0.4176882 | -2.8350368 |
| 21 | S | S1 | 0.5769296 | -2.7702302 | -1.4858746 |
| 22 | O | O1 | 1.1976880 | -3.5179864 | -0.3930321 |
| 23 | O | O2 | -0.8447235 | -2.3823087 | -1.4216509 |
| 24 | C | C11 | 0.8465008 | -3.6522302 | -3.0259219 |
| 25 | H | H9 | 1.9115313 | -3.8709640 | -3.1142946 |
| 26 | H | H16 | 0.4989974 | -3.0365016 | -3.8574062 |
| 27 | H | H17 | 0.2646101 | -4.5753398 | -2.9670175 |
| 28 | C1 | C11 | 4.2727823 | 0.9555377 | 1.1415987 |
| 29 | H | H7 | 3.1647131 | 1.7030058 | -0.8104295 |
| 30 | H | H8 | 2.3999105 | 2.3137482 | 0.6722100 |
| 31 | C | C12 | 0.6120050 | 0.7374592 | -0.8630435 |
| 32 | C | C13 | -0.7222052 | 0.4169234 | -0.3143275 |
| 33 | C | C14 | -1.8931821 | 1.1946979 | -0.3583255 |
| 34 | C | C15 | -4.3173697 | 2.5869618 | -0.4463631 |
| 35 | C | C16 | -3.1171917 | 0.5640554 | 0.0392914 |
| 36 | C | C17 | -1.9296688 | 2.5524898 | -0.7973009 |
| 37 | C | C18 | -3.1308509 | 3.2333717 | -0.8384861 |
| 38 | C | C19 | -4.3094075 | 1.2550129 | -0.0094144 |
| 39 | H | H11 | -3.0830762 | -0.4712906 | 0.3664428 |
| 40 | H | H18 | -1.0151519 | 3.0569078 | -1.0910547 |
| 41 | H | H19 | -3.1635573 | 4.2663023 | -1.1693814 |
| 42 | H | H20 | -5.2349387 | 0.7720893 | 0.2859926 |
| 43 | H | H21 | -5.2563291 | 3.1322903 | -0.4824387 |
| 44 | H | H14 | 0.6980765 | 1.7942684 | -1.1269414 |
| 45 | H | H15 | -0.8522859 | -0.6035739 | 0.0328690 |
Cartesian coordinates for geometry minimized \( N \)-cinnamyl-\( N \)-(2-phenylallyl)methanesulfonamide + Cl cation (11'):

| Atom | X       | Y        | Z        |
|------|---------|----------|----------|
| 1 H  | -3.2829057 | -1.2992582 | 1.4088336 |
| 2 C  | -3.1287234 | -0.3289719 | 1.8773291 |
| 3 C  | -2.7785524 | 2.1528531  | 3.1025715 |
| 4 C  | -1.8923738 | 0.3259241  | 1.7693848 |
| 5 C  | -4.1749707 | 0.2482735  | 2.5937201 |
| 6 C  | -4.0023543 | 1.4919498  | 3.2084540 |
| 7 C  | -1.7317067 | 1.5755984  | 2.3822455 |
| 8 H  | -5.1239514 | -0.2734148 | 2.6760318 |
| 9 H  | -4.8178121 | 1.9395918  | 3.7686355 |
| 10 H | -0.7748707 | 2.0877958  | 2.3175731 |
| 11 H | -2.6333389 | 3.1150808  | 3.5848418 |
| 12 C | -0.7417111 | -0.2802080 | 0.9891320 |
| 13 C | -0.2601987 | -1.6293813 | 1.5575898 |
| 14 C | 0.6602368  | -2.4782880 | 0.6392513 |
| 15 H | 1.3005567  | -3.0881135 | 1.2791047 |
| 16 H | 0.0261732  | -3.1684705 | 0.0640496 |
| 17 N | 1.4870992  | -1.7366961 | -0.3134464 |
| 18 C | 0.9089934  | -1.3860597 | -1.6110930 |
| 19 H | 0.2885380  | -2.2112378 | -1.9902566 |
| 20 H | 1.7032570  | -1.2086742 | -2.3301670 |
| 21 S | 3.1875234  | -1.6542560 | -0.1189567 |
| 22 O | 3.6323624  | -0.7031560 | -1.1422493 |
| 23 O | 3.4375913  | -1.4547759 | 1.2995091  |
| 24 C | 3.8006000  | -3.2879854 | -0.5819418 |
| 25 H | 3.5274466  | -3.4943721 | -1.6184087 |
| 26 H | 3.3884834  | -4.0361355 | 0.0976473  |
| 27 H | 4.8879798  | -3.2509778 | -0.4779862 |
| 28 Cl| 0.5478180  | -1.3038265 | 3.1501563  |
| 29 H | -1.1241145 | -2.2515945 | 1.8055946  |
|   |   |   |   |   |
|---|---|---|---|---|
| 30 | C | C12 | 0.0226030 | -0.1709775 | -1.4061625 |
| 31 | C | C13 | -1.1648650 | -0.4211315 | -0.5586246 |
| 32 | C | C14 | 0.3592331 | 1.1164985 | -1.8903380 |
| 33 | C | C15 | 1.0165054 | 3.6771755 | -2.8664472 |
| 34 | C | C16 | -0.5651384 | 2.2097330 | -1.7909891 |
| 35 | C | C17 | 1.6359519 | 1.3764363 | -2.4898543 |
| 36 | C | C18 | 1.9509414 | 2.6376679 | -2.9623704 |
| 37 | C | C19 | -0.2398920 | 3.4598021 | -2.2768567 |
| 38 | H | H14 | -1.5440470 | 2.0644575 | -1.3516639 |
| 39 | H | H18 | 2.3983170 | 0.6083968 | -2.5087901 |
| 40 | H | H19 | 2.9283056 | 2.8222721 | -3.3957091 |
| 41 | H | H20 | -0.9554010 | 4.2725332 | -2.2072737 |
| 42 | H | H21 | 1.2676636 | 4.6637969 | -3.2456570 |
| 43 | H | H15 | -1.5636142 | -1.4257587 | -0.7305025 |
| 44 | H | H11 | -1.9684687 | 0.2874998 | -0.7407650 |
| 45 | H | H7  | 0.1048300 | 0.4103848 | 1.0348538 |
VI. NMR spectra
VIII. References:

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