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Supplementary material: On the regioselective molecular sieves-promoted oxidative three-component synthesis of fused-benzimidazoles from β-ketoesters

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General informations

NMR spectra were recorded on a Bruker AC 400 (400 MHz) spectrometer in DMSO in general. Chemical shifts are given in ppm, using as internal standards the residual DMSO signal for ^{1}H NMR (δ = 2.50) and the deuterated solvent signal for ^{13}C NMR (δ = 39.51). Data for ^{13}C NMR are reported as follows: chemical shift. Data for ^{1}H NMR are reported as follows: chemical shift (multiplicity [s = singulet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad], coupling constants J in Hertz (Hz), integration). The solvents were used in their commercial form without further purification excepted for toluene, which was freshly distilled before use. Thin-Layer Chromatography (TLC) were developed on silica Merck 60F254 and revealed under UV lamp (λ = 254 nm) and with universal stain: p-Anisaldehyde (prepared with 30 g of ice, 60 ml of EtOH, 5 ml of H_2SO4, 5 ml of p-anisaldehyde and 0.5 ml of AcOH). Flash Chromatography was performed following the method of Still on 40–63 μm silica gel eluted-with the specified eluent or using an automated combiflash system. High resolution mass spectra (HRMS) were recorded on a Waters Synapt G2 HDMS apparatus using a positive electrospray (ESI) ionization source.

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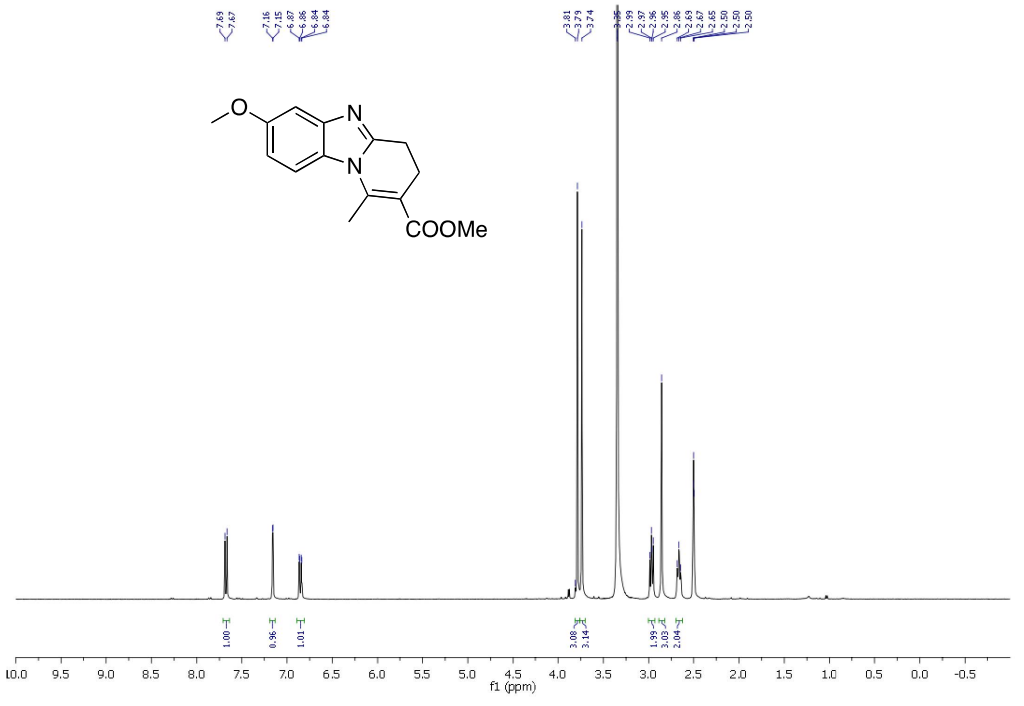
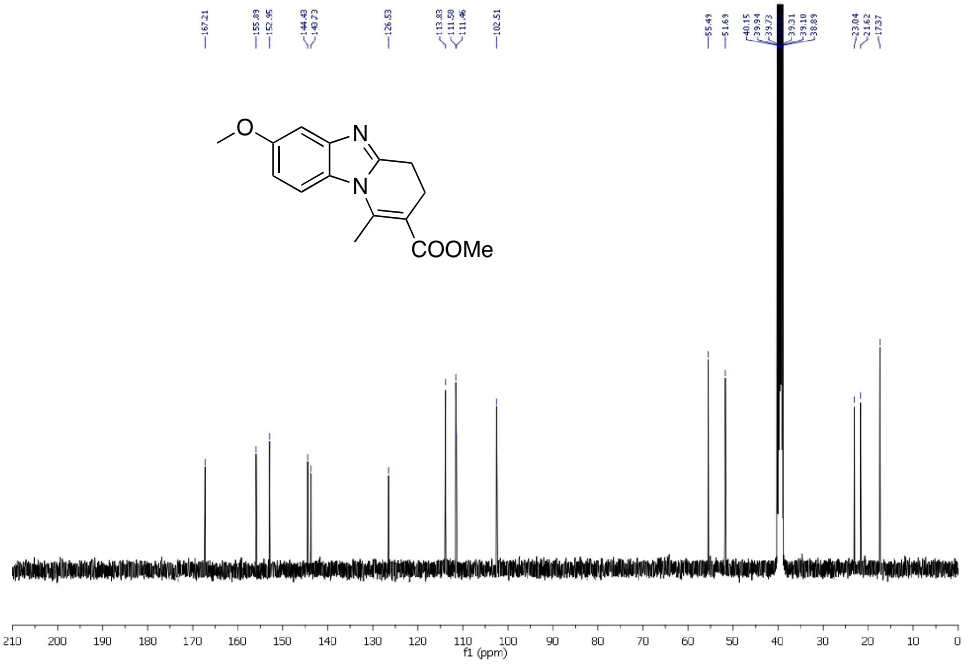
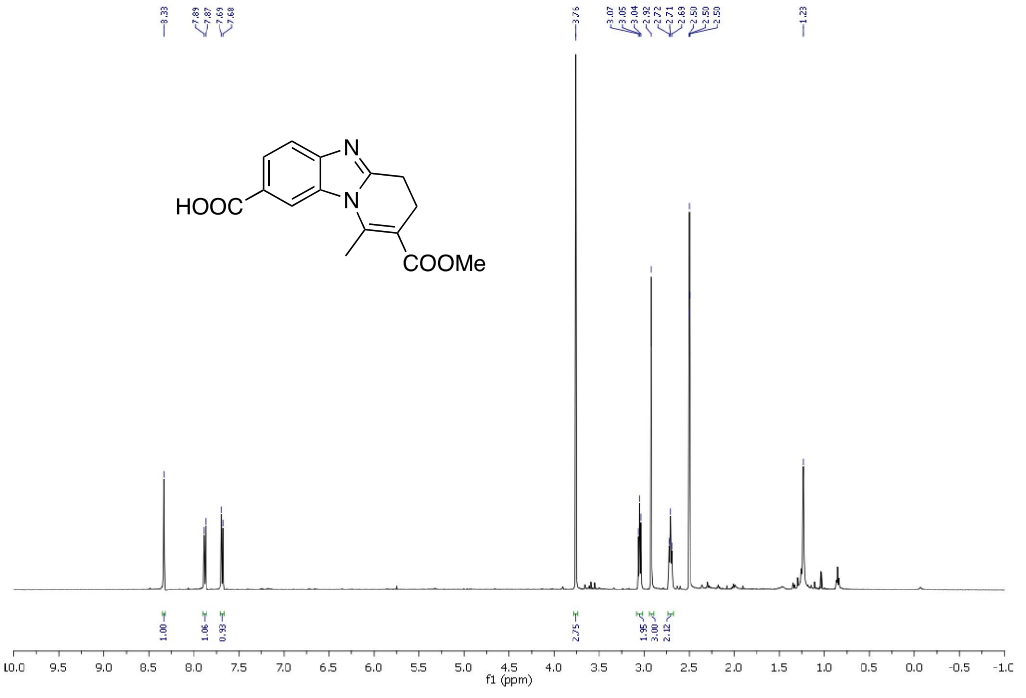
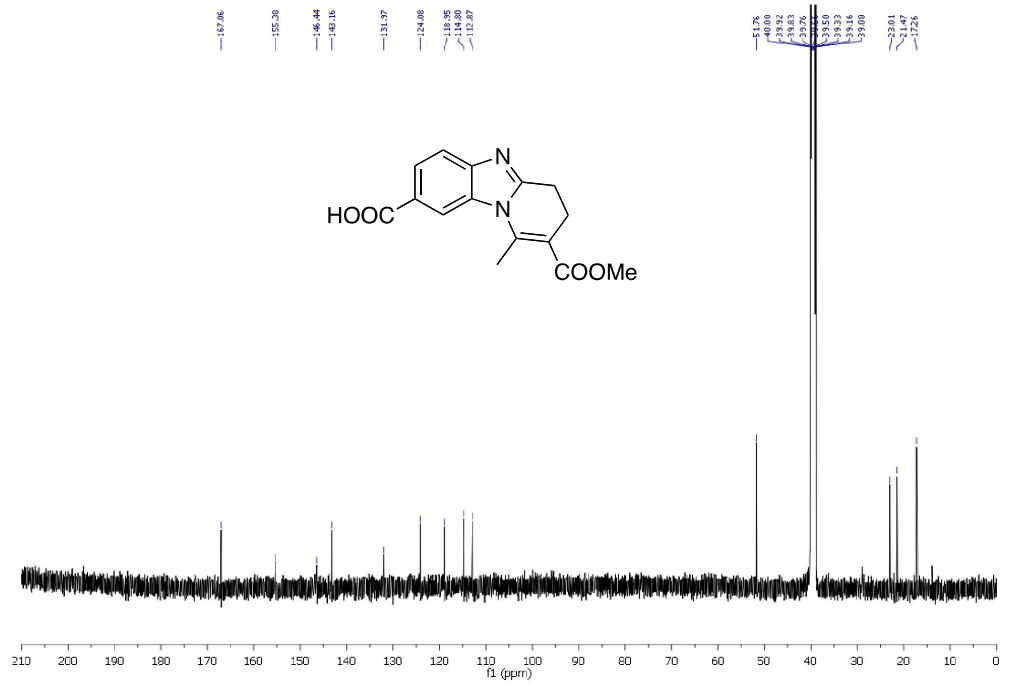
methyl 7-methoxy-1-methyl-3,4-dihydrobenzo[4,5]imidazo[1,2-a]pyridine-2-carboxylate (**5b**)



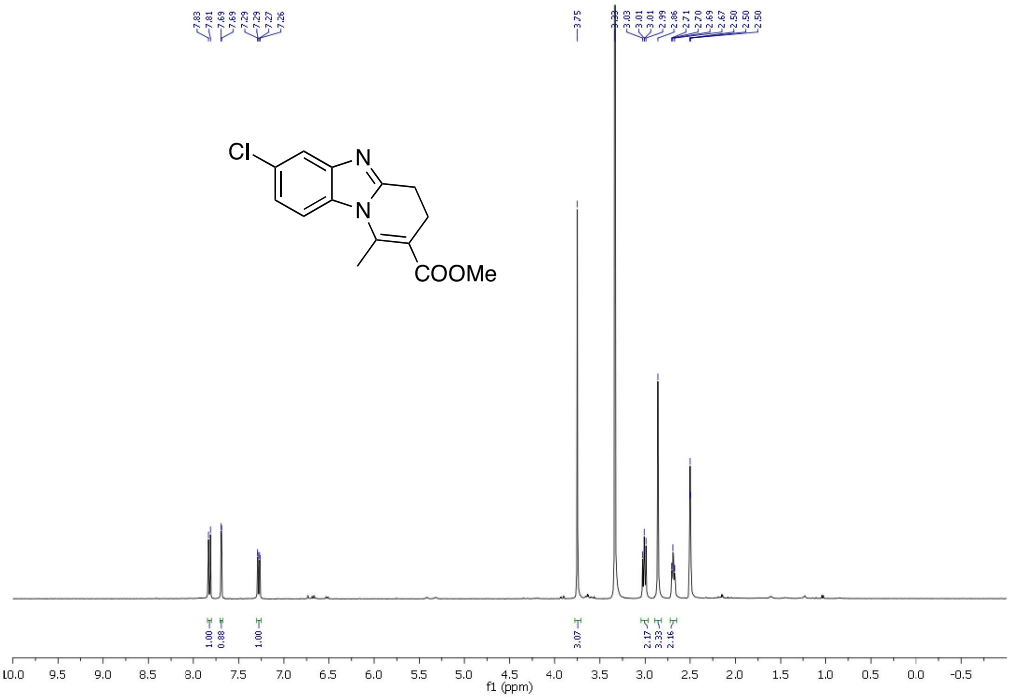


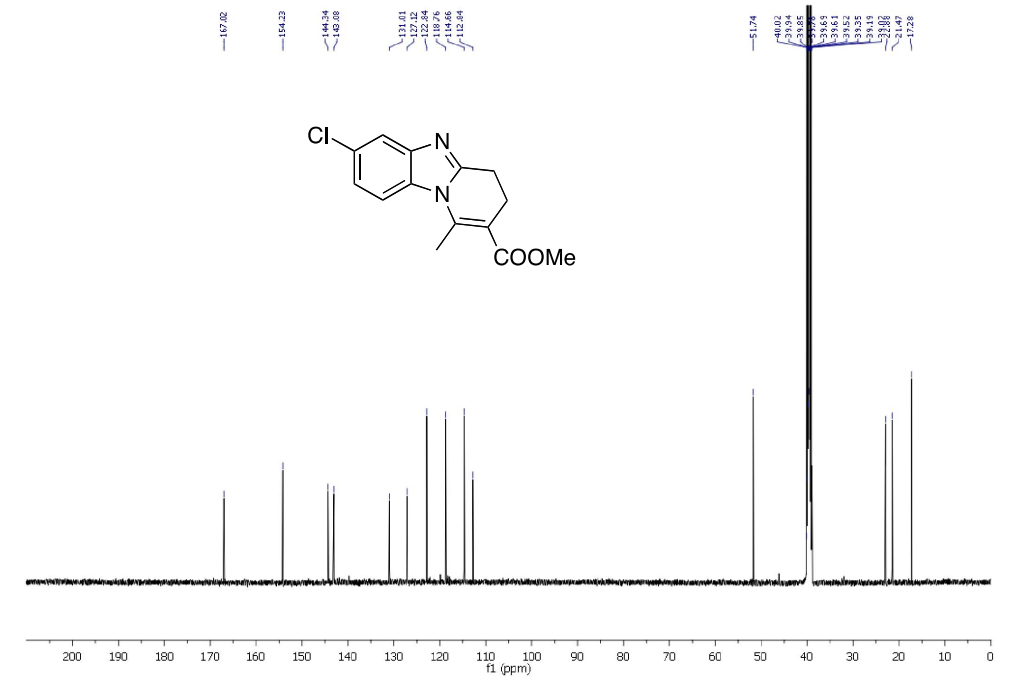
2-(methoxycarbonyl)-1-methyl-3,4-dihydrobenzo[4,5]imidazo[1,2-a]pyridine-8-carboxylic acid (**5c'**)



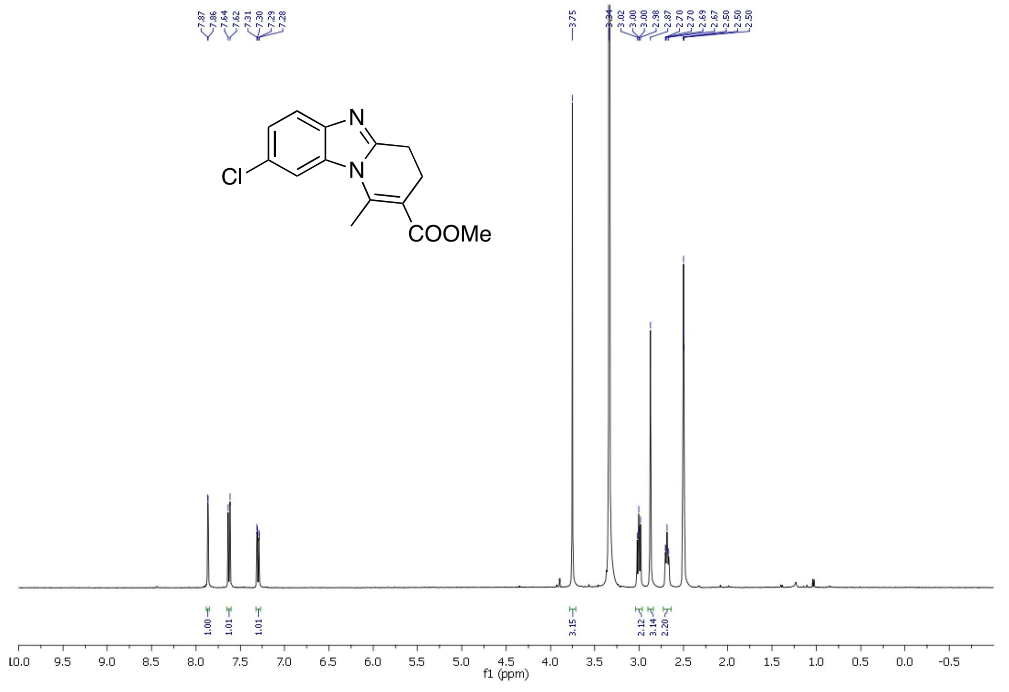


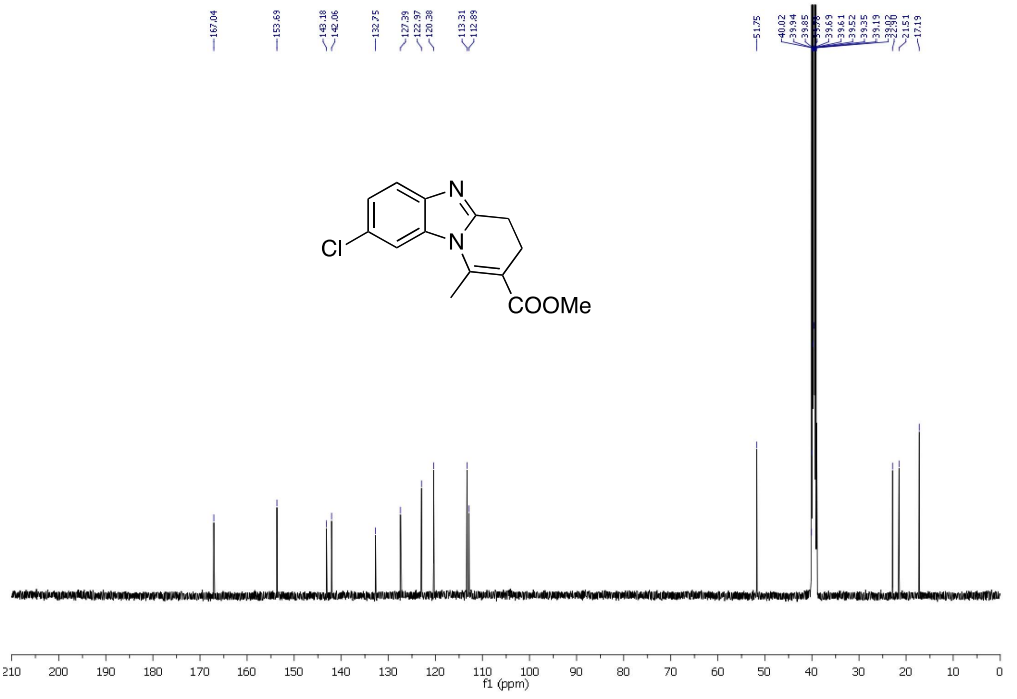
methyl 7-chloro-1-methyl-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-2-carboxylate (**5d**)



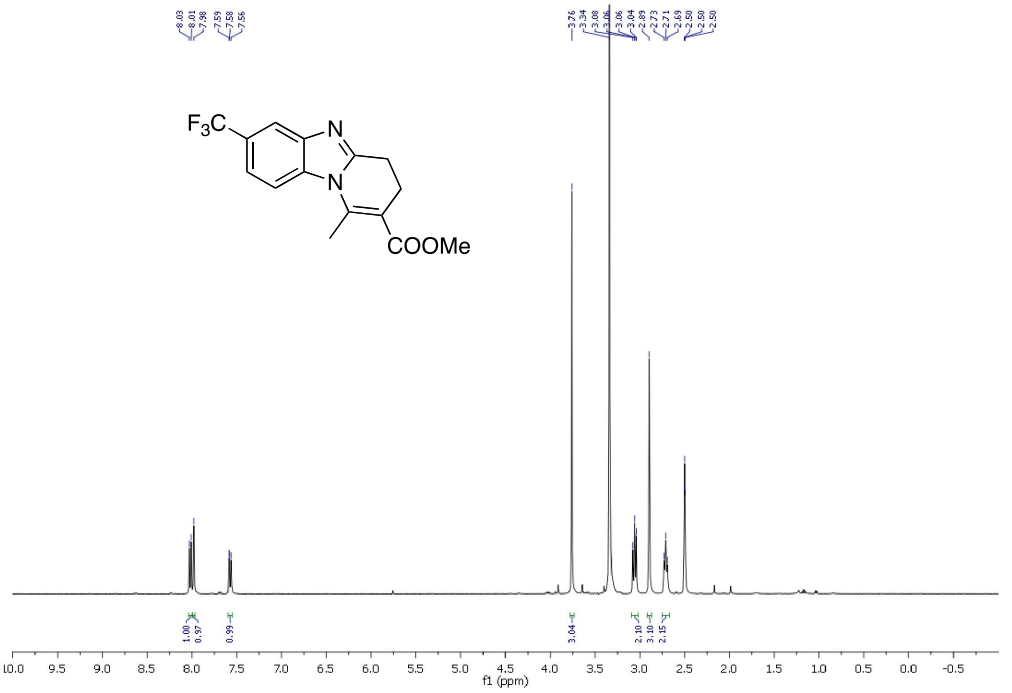


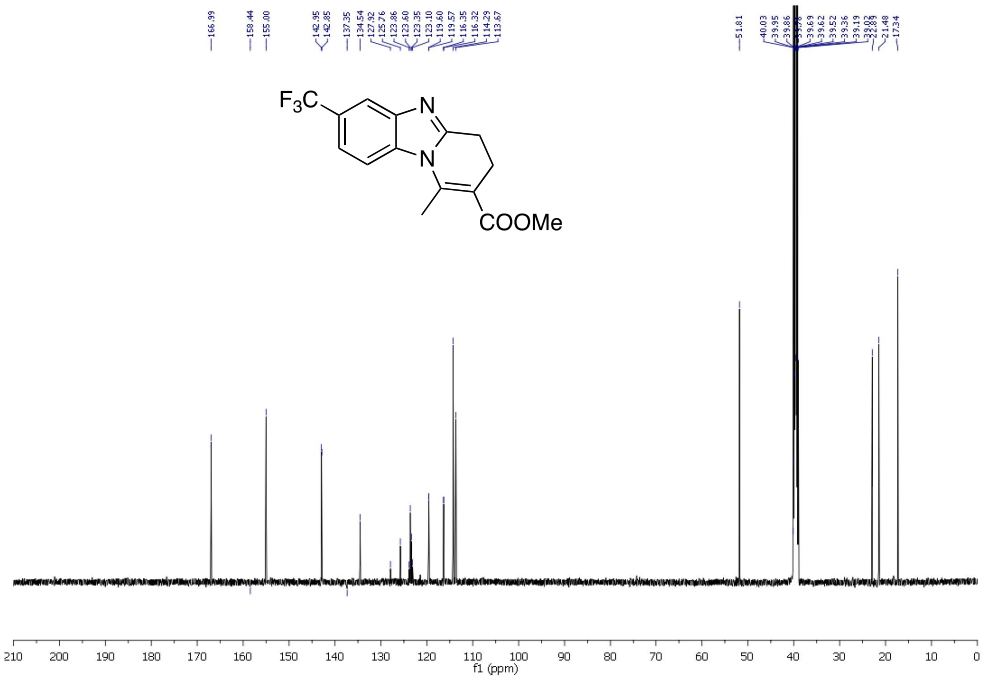
methyl 8-chloro-1-methyl-3,4-dihydrobenzo[4,5]imidazo[1,2-a]pyridine-2-carboxylate (**5d'**)



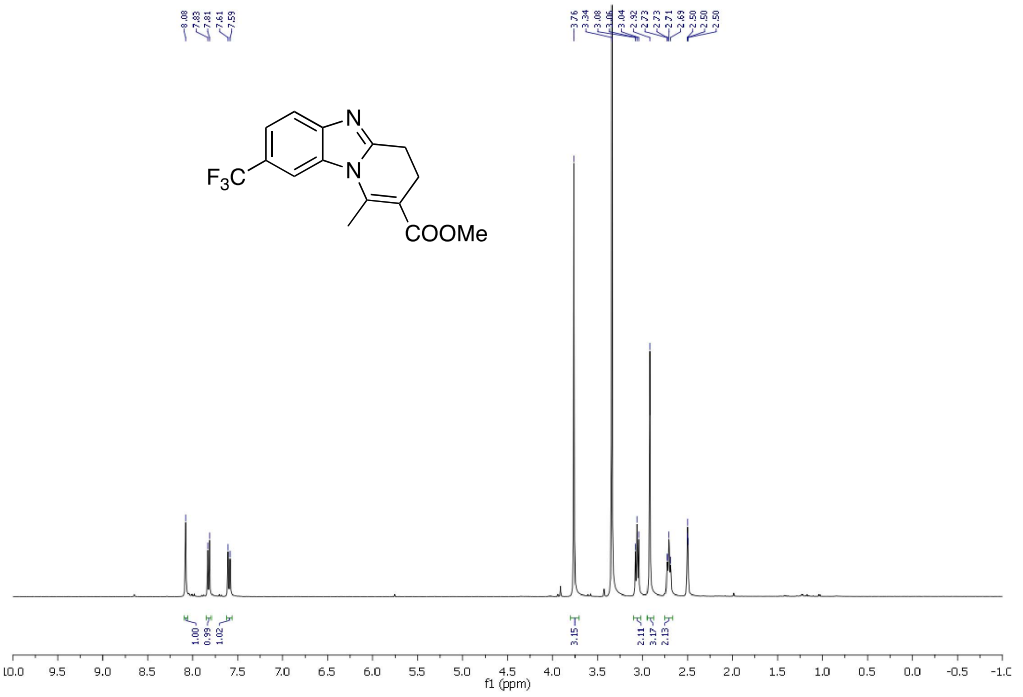


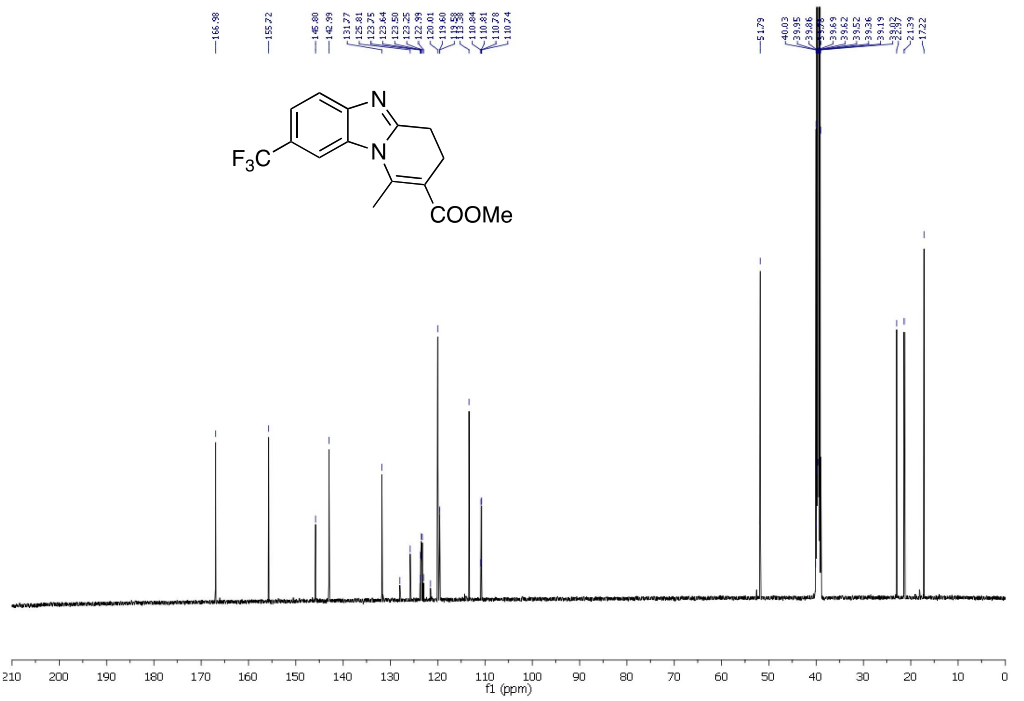
methyl 1-methyl-7-(trifluoromethyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-a]pyridine-2-carboxylate (**5e**)



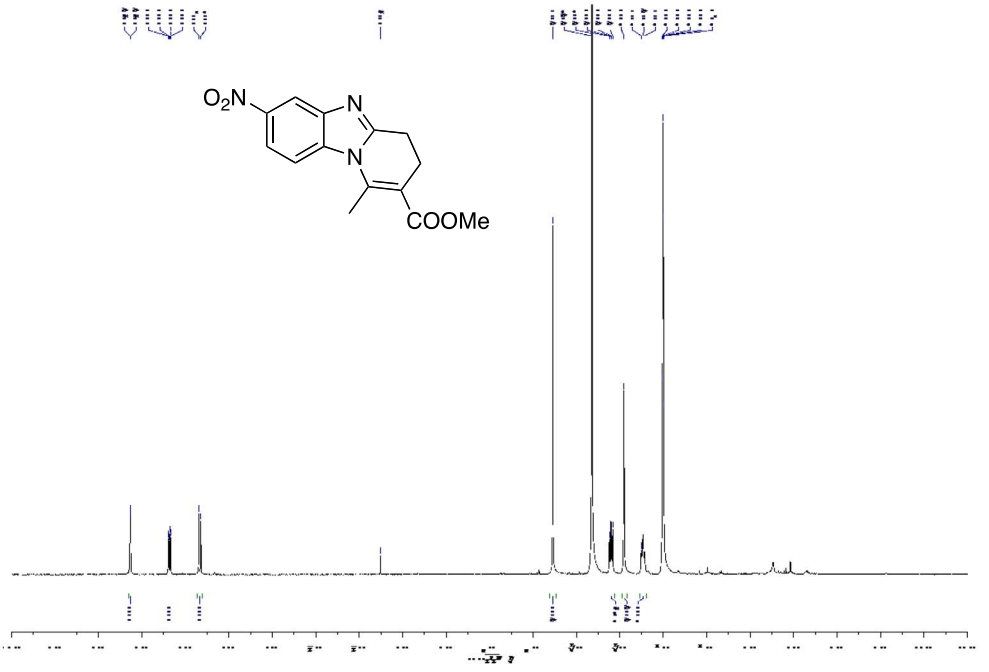


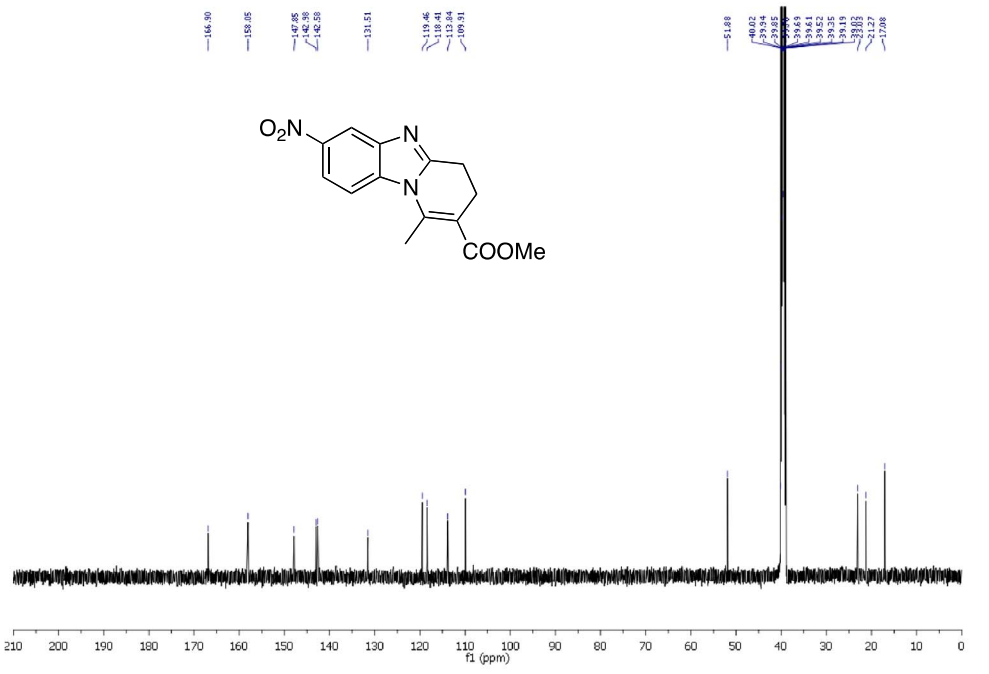
methyl 1-methyl-8-(trifluoromethyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-a]pyridine-2-carboxylate (**5e'**)



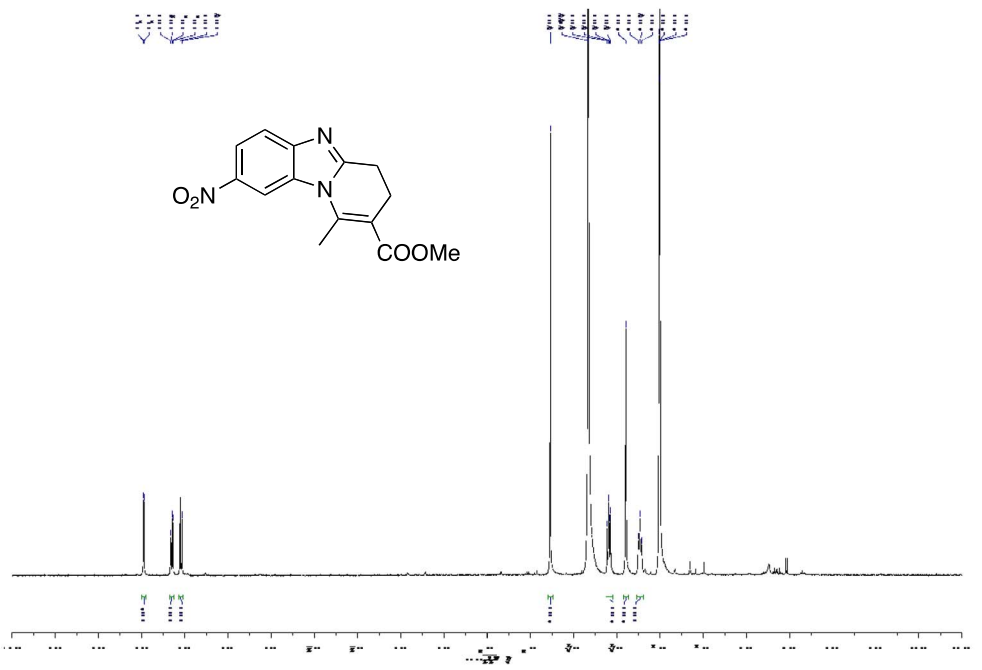


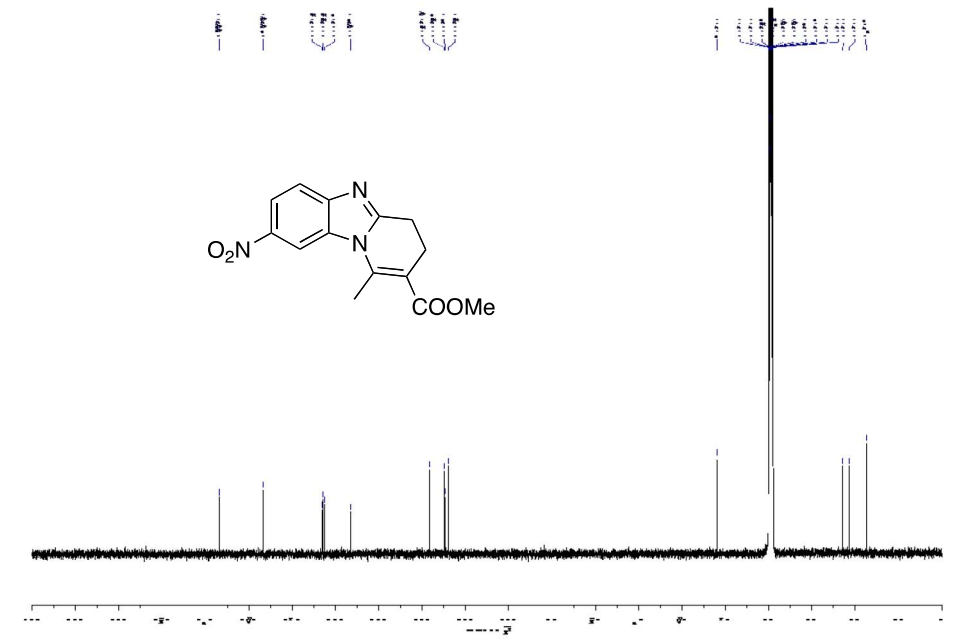
methyl 1-methyl-7-nitro-3,4-dihydrobenzo[4,5]imidazo[1,2-a]pyridine-2-carboxylate (**5f**)



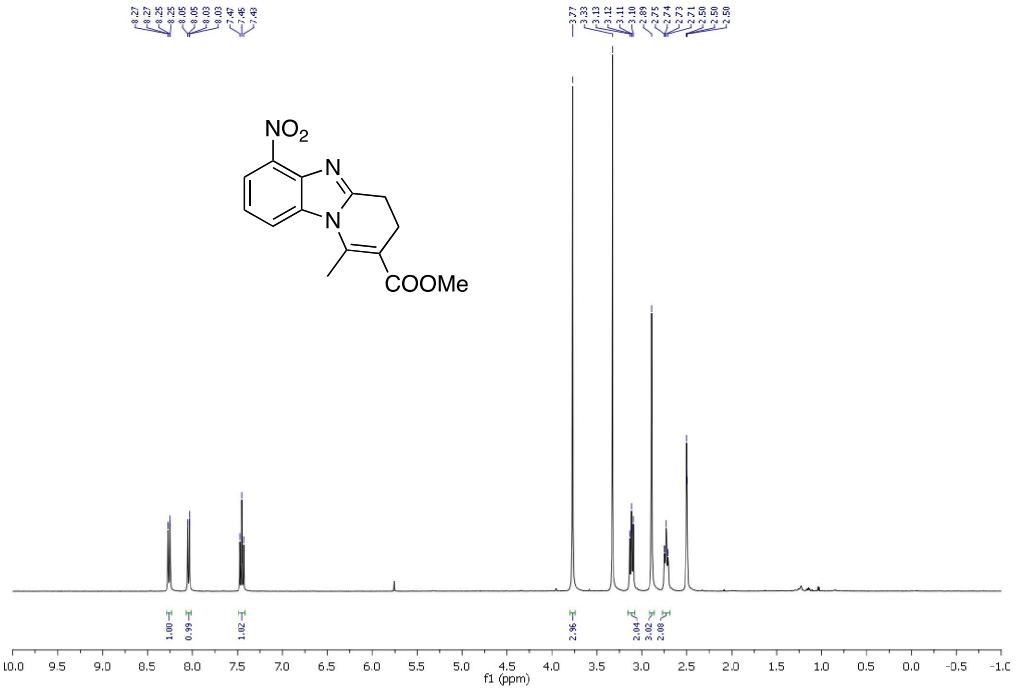


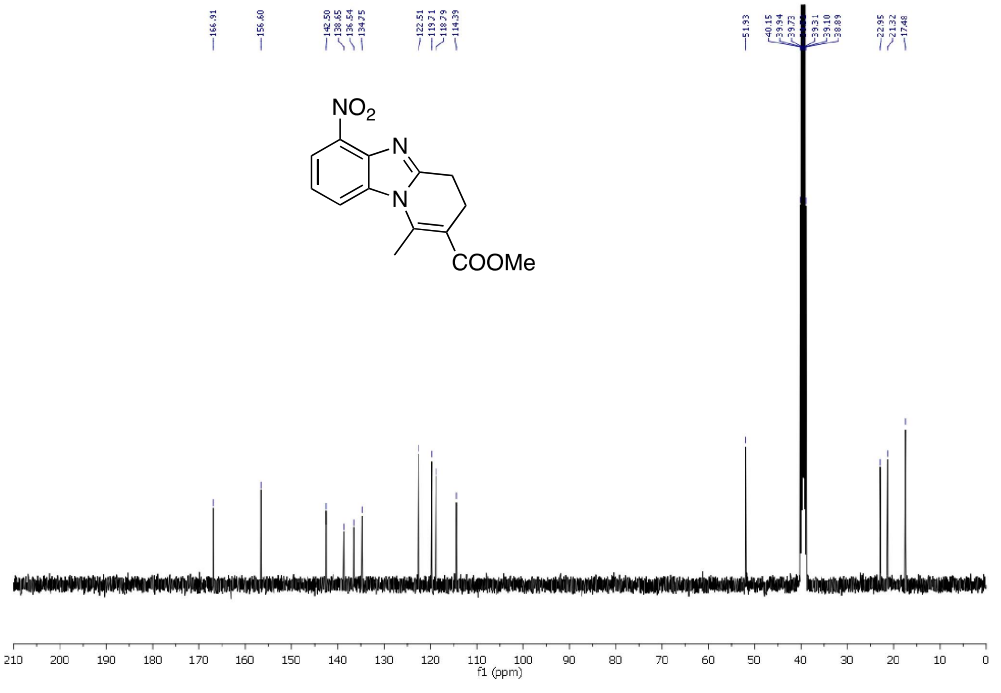
methyl 1-methyl-8-nitro-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridine-2-carboxylate (**5f'**)



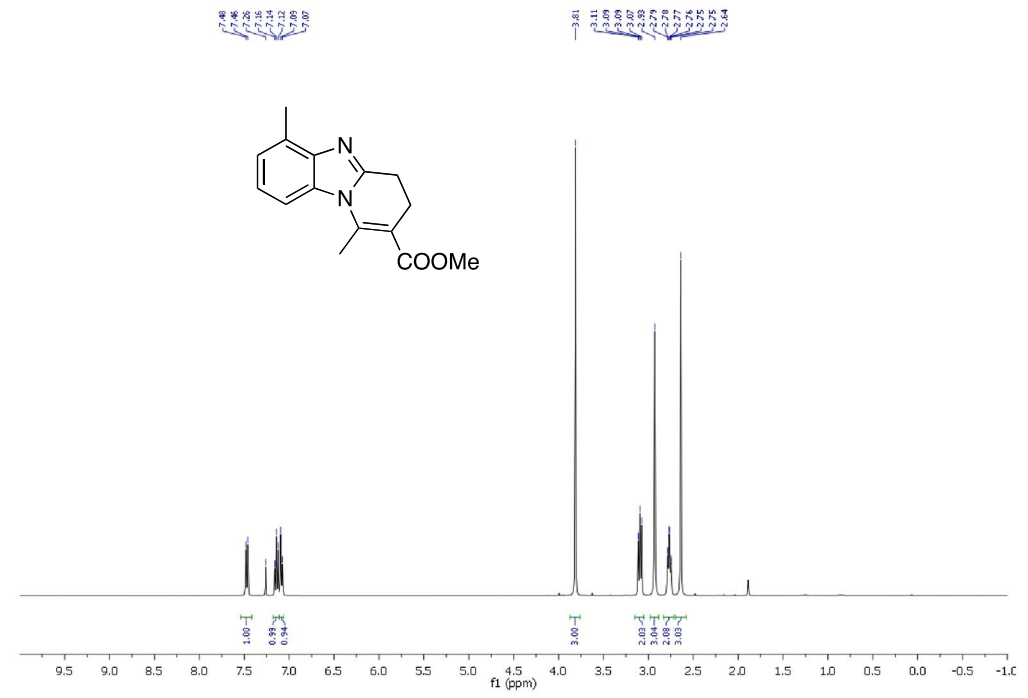


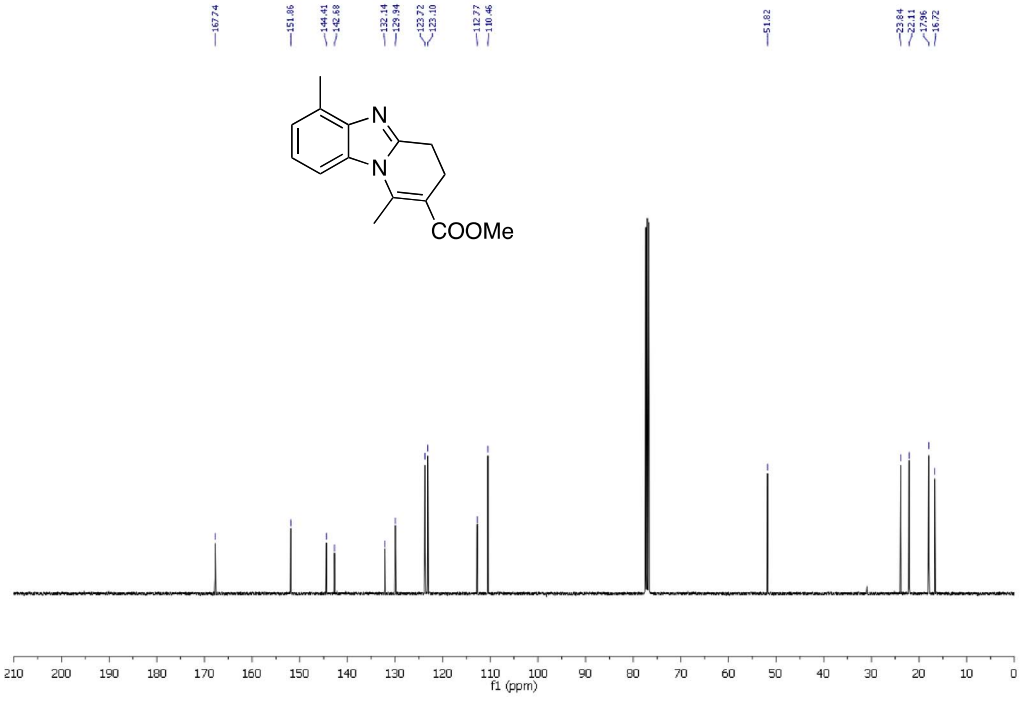
methyl 1-methyl-6-nitro-3,4-dihydrobenzo[4,5]imidazo[1,2-a]pyridine-2-carboxylate (**5g**)





methyl 1,6-dimethyl-3,4-dihydrobenzo[4,5]imidazo[1,2-a]pyridine-2-carboxylate (**5h**)





Tunneling effect

In intramolecular transfer of a light atom (typically a proton), the tunneling effect might play a significant role. It can be readily illustrated by the transmission coefficient $\kappa(T)$ determined by the Skodje–Truhlar method [1], which is more accurate than the Wigner method [2]. The Skodje–Truhlar method depends on the imaginary frequency $\nu^{\neq}$ (Hz) at the transition state and the endothermicity of the reaction, as given in (1) (h and k_B are the Planck and Boltzmann constants, respectively).

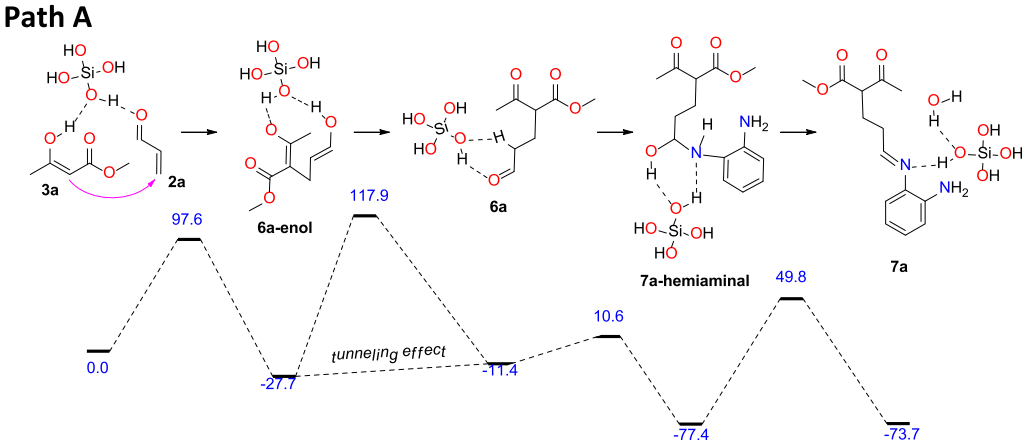
$$\kappa(T) = \frac{\beta\pi/\alpha}{\sin(\beta\pi/\alpha)} - \frac{\beta}{\alpha-\beta}[(\beta-\alpha)(G^{\neq}-G)] \qquad (1)$$

where $\alpha = 2\pi/(h\nu^{\neq})$, $\beta = 1/(k_B T)$, G is the reaction free energy and $G^{\neq}$ the activation free energy.

Using the Skodje–Truhlar method, the $\kappa(T)$ value was calculated for $\mathbf{TS_{B\text{-}C}}$ at 383 K and was estimated close to 1.3×10^6.

Optimized structures and thermodynamic data at 298.15 K

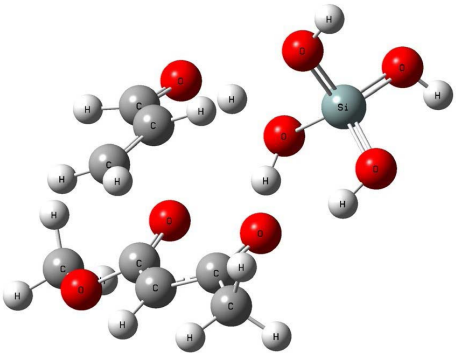
E(M06-2X) corresponds to the electronic energy at the IEFPCM(toluene)M06-2X/6-311++G(d,p)//M06-2X/6-31G(d,p) level. Values are given in Hartree.



2a + 3a

E(M06-2X) = -1205.888068
ZPE = 0.243063
H_{corr} = 0.267413
G_{corr} = 0.187792

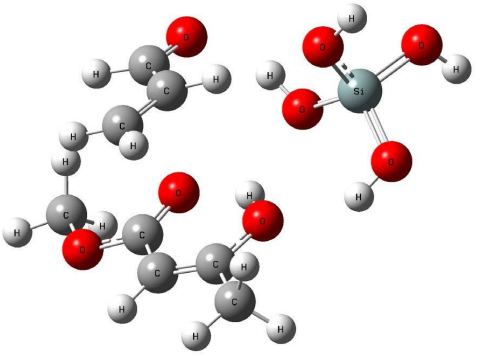
C	2.295000	0.551000	-0.541000
O	1.492000	-0.024000	-1.263000
C	2.034000	1.777000	0.195000
H	2.829000	2.211000	0.785000
C	0.821000	2.376000	0.141000
C	0.492000	3.640000	0.867000
H	0.178000	4.401000	0.147000
H	-0.348000	3.462000	1.545000
H	1.346000	4.008000	1.434000
O	-0.218000	1.913000	-0.556000
H	-0.014000	1.052000	-0.995000
O	3.535000	0.079000	-0.336000
C	3.835000	-1.134000	-1.021000
H	4.877000	-1.353000	-0.796000
H	3.189000	-1.941000	-0.665000
H	3.685000	-1.017000	-2.096000
C	1.834000	-1.328000	2.106000
C	0.818000	-1.433000	1.249000
H	2.542000	-2.144000	2.239000
H	2.002000	-0.430000	2.690000
H	0.089000	-0.645000	1.085000
C	0.676000	-2.660000	0.449000
H	1.380000	-3.477000	0.711000
O	-0.126000	-2.818000	-0.448000
Si	-2.720000	-0.157000	-0.125000
O	-4.123000	-0.937000	-0.472000
H	-4.654000	-0.522000	-1.158000
O	-3.024000	1.448000	-0.237000
H	-2.221000	1.967000	-0.384000
O	-1.452000	-0.461000	-1.111000
H	-1.009000	-1.325000	-1.010000
O	-2.283000	-0.686000	1.373000
H	-3.022000	-0.889000	1.955000



$TS_{2a + 3a/6a\text{-enol}}$

E(M06-2X) = -1205.853406 $\nu^{\neq} = i165\ cm^{-1}$
ZPE = 0.240492
H_{corr} = 0.262879
G_{corr} = 0.190322

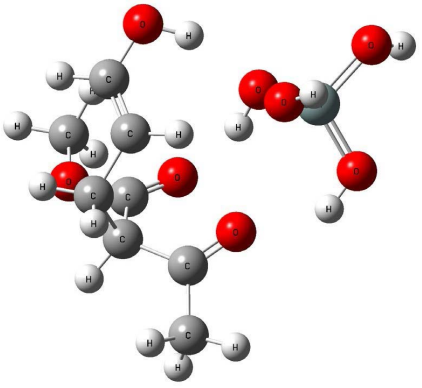
C	2.402000	0.091000	-0.592000
O	1.552000	-0.742000	-0.904000
C	2.184000	1.412000	-0.093000
H	3.057000	2.004000	0.147000
C	0.921000	2.016000	-0.086000
C	0.817000	3.458000	0.365000
H	0.418000	4.060000	-0.457000
H	0.099000	3.523000	1.188000
H	1.773000	3.875000	0.682000
O	-0.165000	1.452000	-0.407000
H	-0.608000	-0.103000	-0.812000
O	3.726000	-0.229000	-0.640000
C	4.012000	-1.518000	-1.163000
H	5.098000	-1.602000	-1.175000
H	3.582000	-2.305000	-0.537000
H	3.609000	-1.629000	-2.172000
C	1.473000	0.098000	2.230000
C	0.423000	-0.605000	1.757000
H	2.481000	-0.308000	2.214000
H	1.347000	1.071000	2.691000
H	-0.587000	-0.209000	1.749000
C	0.668000	-1.878000	1.151000
H	1.614000	-2.386000	1.365000
O	-0.155000	-2.516000	0.445000
Si	-2.808000	-0.122000	-0.299000
O	-4.070000	-0.859000	-1.029000
H	-4.295000	-0.523000	-1.902000
O	-2.805000	1.456000	-0.677000
H	-1.908000	1.842000	-0.597000
O	-1.342000	-0.796000	-0.744000
H	-0.835000	-1.801000	-0.063000
O	-2.889000	-0.496000	1.299000
H	-3.753000	-0.420000	1.713000



6a-enol

E(M06-2X) = -1205.904911
ZPE = 0.246021
H_{corr} = 0.269134
G_{corr} = 0.19409

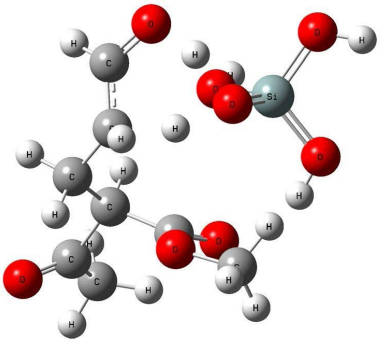
C	2.105000	0.009000	-0.769000
O	1.256000	-0.203000	-1.602000
C	2.090000	1.098000	0.288000
H	3.062000	1.601000	0.289000
C	0.978000	2.107000	0.069000
C	1.327000	3.553000	0.311000
H	2.047000	3.885000	-0.444000
H	0.429000	4.168000	0.264000
H	1.810000	3.664000	1.287000
O	-0.145000	1.757000	-0.231000
H	-0.606000	-0.503000	-0.962000
O	3.196000	-0.749000	-0.629000
C	3.224000	-1.915000	-1.463000
H	4.138000	-2.443000	-1.199000
H	2.344000	-2.531000	-1.265000
H	3.231000	-1.627000	-2.515000
C	1.881000	0.392000	1.676000
C	0.715000	-0.544000	1.614000
H	2.805000	-0.150000	1.897000
H	1.758000	1.166000	2.442000
H	-0.288000	-0.128000	1.591000
C	0.893000	-1.854000	1.409000
H	1.881000	-2.312000	1.474000
O	-0.067000	-2.746000	1.104000
Si	-2.710000	-0.093000	-0.250000
O	-4.094000	-0.904000	-0.588000
H	-4.357000	-0.904000	-1.512000
O	-2.772000	1.330000	-1.056000
H	-1.984000	1.877000	-0.943000
O	-1.394000	-0.987000	-0.660000
H	-0.798000	-2.259000	0.678000
O	-2.645000	0.058000	1.386000
H	-3.479000	0.273000	1.814000



$TS_{6a\text{-}enol/6a}$

E(M06-2X) = -1205.846365 $\nu^{\neq}$ = *i*1707 cm^{-1}
ZPE = 0.240504
H_{corr} = 0.262034
G_{corr} = 0.190997

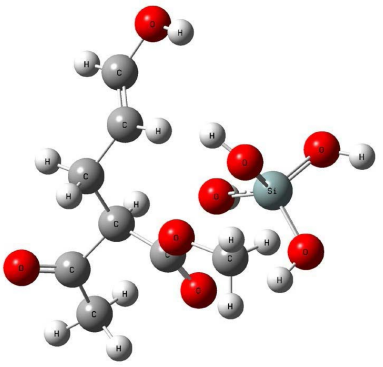
C	-1.161000	0.827000	-0.392000
O	-0.787000	1.851000	0.146000
C	-1.769000	-0.345000	0.361000
H	-1.211000	-0.348000	1.306000
C	-3.243000	-0.034000	0.678000
C	-3.505000	1.080000	1.661000
H	-3.223000	0.735000	2.662000
H	-2.886000	1.952000	1.437000
H	-4.564000	1.334000	1.654000
O	-4.126000	-0.687000	0.175000
H	4.420000	1.178000	0.576000
O	-1.070000	0.615000	-1.701000
C	-0.342000	1.605000	-2.442000
H	-0.406000	1.295000	-3.482000
H	-0.791000	2.589000	-2.300000
H	0.698000	1.611000	-2.106000
C	-1.604000	-1.683000	-0.368000
C	-0.161000	-1.930000	-0.758000
H	-1.981000	-2.471000	0.296000
H	-2.254000	-1.687000	-1.244000
H	0.053000	-2.014000	-1.825000
C	0.690000	-2.705000	0.051000
H	0.322000	-3.251000	0.929000
O	1.956000	-2.695000	-0.111000
Si	2.289000	0.565000	0.418000
O	1.918000	-0.413000	-0.840000
H	0.705000	-0.914000	-0.739000
O	2.021000	2.150000	0.087000
H	1.087000	2.406000	0.077000
O	3.860000	0.456000	0.877000
H	2.169000	-1.685000	-0.584000
O	1.332000	-0.008000	1.644000
H	1.547000	0.326000	2.520000



6a

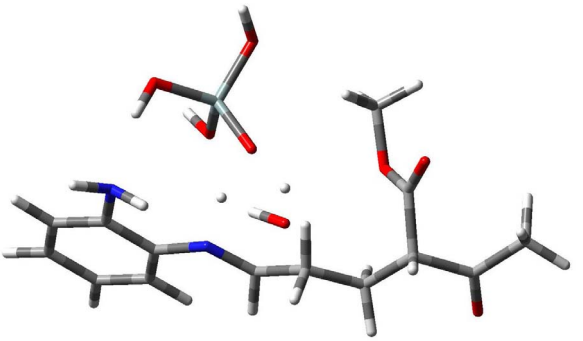
E(M06-2X) = -1205.899771
ZPE = 0.246619
H_{corr} = 0.269538
G_{corr} = 0.195139

C	-0.782000	-0.842000	0.875000
O	-0.146000	-1.876000	0.801000
C	-1.516000	-0.226000	-0.300000
H	-0.729000	-0.125000	-1.062000
C	-2.524000	-1.234000	-0.883000
C	-1.982000	-2.551000	-1.383000
H	-1.024000	-2.407000	-1.889000
H	-1.788000	-3.210000	-0.533000
H	-2.719000	-3.007000	-2.044000
O	-3.694000	-0.940000	-0.962000
H	4.546000	-0.045000	-0.373000
O	-0.887000	-0.139000	1.998000
C	-0.030000	-0.574000	3.059000
H	-0.208000	0.115000	3.882000
H	-0.273000	-1.597000	3.349000
H	1.008000	-0.518000	2.721000
C	-2.166000	1.135000	-0.030000
C	-1.184000	2.225000	0.301000
H	-2.734000	1.403000	-0.926000
H	-2.901000	1.026000	0.773000
H	-0.733000	2.214000	1.292000
C	-0.855000	3.190000	-0.562000
H	-1.280000	3.250000	-1.561000
O	0.019000	4.205000	-0.344000
Si	2.344000	-0.366000	-0.447000
O	1.493000	0.730000	0.437000
H	0.971000	1.373000	-0.063000
O	2.618000	-1.665000	0.504000
H	1.801000	-2.068000	0.833000
O	3.812000	0.154000	-0.962000
H	0.353000	4.149000	0.560000
O	1.435000	-0.623000	-1.798000
H	1.925000	-0.945000	-2.561000



$TS_{6a/7a\text{-hemiaminal}}$

E(M06-2X) = -1205.899771 $\nu^{\neq}$ = *i*177 cm^{-1}
ZPE = 0.246619
H_{corr} = 0.269538
G_{corr} = 0.195139

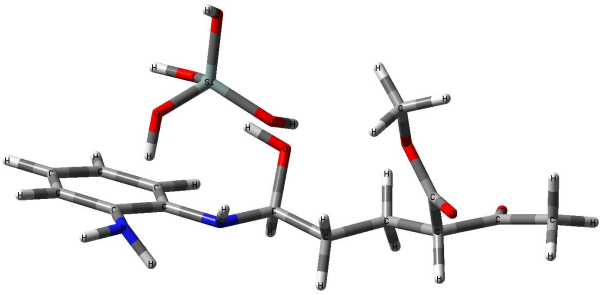


C	2.332000	0.160000	1.453000
C	0.981000	-0.505000	1.753000
C	-0.202000	0.470000	1.693000
O	-1.348000	0.050000	2.128000
Si	-3.273000	-2.185000	0.027000
O	-3.981000	-2.784000	1.385000
H	-4.940000	-2.845000	1.334000
O	-4.360000	-1.129000	-0.644000
H	-4.385000	-1.180000	-1.605000
O	-3.061000	-3.319000	-1.162000
H	-2.261000	-3.842000	-1.053000
O	-1.841000	-1.550000	0.411000
H	-1.705000	-0.924000	1.321000
H	0.094000	1.480000	2.051000
N	-0.357000	0.759000	0.047000
H	-0.824000	-0.116000	-0.252000
H	0.548000	0.828000	-0.434000
C	-1.186000	1.898000	-0.241000
C	-0.565000	3.143000	-0.385000
C	-2.562000	1.749000	-0.338000
C	-1.359000	4.243000	-0.700000
C	-3.342000	2.863000	-0.640000
H	-3.006000	0.768000	-0.202000
C	-2.738000	4.101000	-0.836000
H	-0.892000	5.216000	-0.829000
H	-4.417000	2.754000	-0.727000
H	-3.341000	4.969000	-1.082000
N	0.848000	3.211000	-0.257000
H	1.200000	4.121000	-0.530000
H	1.142000	3.033000	0.700000
H	0.761000	-1.331000	1.067000
H	2.187000	1.056000	0.833000
H	0.975000	-0.927000	2.761000
H	2.803000	0.496000	2.381000
C	3.322000	-0.752000	0.719000
H	3.502000	-1.672000	1.284000
C	4.674000	-0.025000	0.612000
C	2.804000	-1.105000	-0.657000
C	4.905000	0.825000	-0.616000
H	5.094000	0.168000	-1.472000
H	4.017000	1.420000	-0.854000
H	5.771000	1.466000	-0.457000
O	1.924000	-0.513000	-1.245000
O	3.475000	-2.128000	-1.190000
C	3.081000	-2.491000	-2.518000
H	3.254000	-1.658000	-3.203000
H	3.697000	-3.346000	-2.786000
H	2.022000	-2.752000	-2.538000
O	5.469000	-0.104000	1.516000

7a-hemiaminal

E(M06-2X) = -1548.860361
ZPE = 0.381617
H_{corr} = 0.411322
G_{corr} = 0.321741

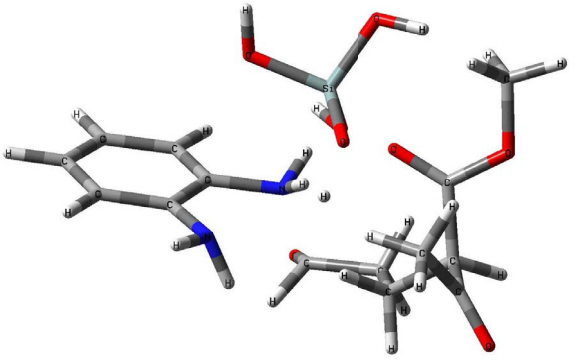
C	2.431000	-1.573000	-0.145000
C	1.194000	-1.339000	0.719000
C	-0.109000	-1.579000	-0.031000
O	-0.041000	-0.831000	-1.239000
Si	-1.671000	2.139000	-0.502000
O	-2.162000	0.944000	-1.541000
H	-3.106000	0.887000	-1.720000
O	-1.637000	3.556000	-1.326000
H	-1.789000	4.338000	-0.787000
O	-0.189000	1.648000	0.012000
H	0.217000	0.953000	-0.541000
O	-2.671000	2.357000	0.764000
H	-0.937000	-0.593000	-1.536000
H	-0.222000	-2.646000	-0.269000
N	-1.211000	-1.197000	0.820000
H	-2.747000	1.624000	1.410000
H	-1.066000	-0.253000	1.174000
C	-2.529000	-1.400000	0.382000
C	-3.560000	-0.805000	1.136000
C	-2.872000	-2.160000	-0.738000
C	-4.884000	-0.941000	0.742000
C	-4.206000	-2.305000	-1.117000
H	-2.095000	-2.623000	-1.337000
C	-5.214000	-1.687000	-0.389000
H	-5.662000	-0.460000	1.329000
H	-4.448000	-2.896000	-1.994000
H	-6.252000	-1.788000	-0.686000
N	-3.183000	-0.006000	2.251000
H	-3.979000	0.208000	2.842000
H	-2.473000	-0.473000	2.811000
H	1.206000	-1.974000	1.611000
H	2.606000	-2.642000	-0.299000
H	1.172000	-0.295000	1.062000
H	2.281000	-1.132000	-1.133000
C	3.682000	-0.961000	0.476000
H	3.874000	-1.371000	1.478000
C	4.941000	-1.280000	-0.352000
C	3.589000	0.542000	0.696000
O	4.156000	1.133000	1.582000
O	4.892000	-2.083000	-1.252000
C	6.219000	-0.568000	0.028000
H	6.175000	0.465000	-0.331000
H	6.337000	-0.517000	1.113000
H	7.063000	-1.075000	-0.438000
O	2.840000	1.145000	-0.237000
C	2.723000	2.566000	-0.095000
H	2.082000	2.892000	-0.911000
H	2.260000	2.807000	0.862000
H	3.711000	3.027000	-0.154000



TS$_{7a\text{-}hemiaminal/7a}$

E(M06-2X) = -1548.80503 $\nu^{\neq}$ = *i*336 cm^{-1}
ZPE = 0.375341
H_{corr} = 0.404926
G_{corr} = 0.314889

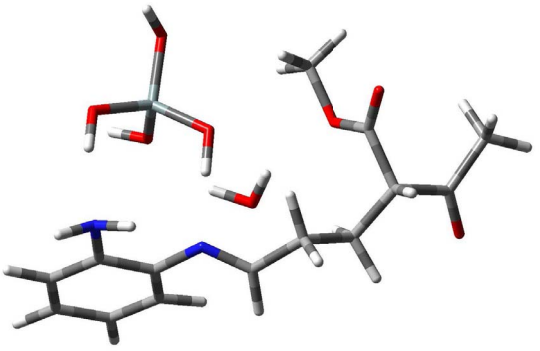
C	2.418000	-1.742000	0.079000
C	1.164000	-1.446000	0.908000
C	-0.149000	-1.665000	0.201000
O	0.150000	-0.618000	-1.269000
Si	-1.461000	2.125000	-0.322000
O	-1.854000	1.239000	-1.688000
H	-2.516000	1.636000	-2.262000
O	-0.836000	3.551000	-0.870000
H	-1.003000	4.292000	-0.281000
O	-0.409000	1.179000	0.455000
H	0.204000	0.241000	-0.715000
O	-2.783000	2.514000	0.567000
H	-0.707000	-0.468000	-1.717000
H	-0.261000	-2.611000	-0.330000
N	-1.220000	-1.125000	0.799000
H	-3.022000	1.817000	1.209000
H	-0.945000	0.029000	0.867000
C	-2.524000	-1.370000	0.307000
C	-3.579000	-0.755000	1.009000
C	-2.822000	-2.144000	-0.816000
C	-4.892000	-0.936000	0.582000
C	-4.139000	-2.328000	-1.230000
H	-2.023000	-2.607000	-1.387000
C	-5.175000	-1.722000	-0.530000
H	-5.695000	-0.448000	1.128000
H	-4.347000	-2.934000	-2.105000
H	-6.203000	-1.854000	-0.847000
N	-3.276000	0.097000	2.094000
H	-4.037000	0.163000	2.759000
H	-2.418000	-0.175000	2.565000
H	1.132000	-2.083000	1.800000
H	2.676000	-2.803000	0.113000
H	1.152000	-0.410000	1.266000
H	2.250000	-1.487000	-0.968000
C	3.612000	-0.933000	0.579000
H	3.841000	-1.162000	1.630000
C	4.890000	-1.268000	-0.209000
C	3.373000	0.572000	0.563000
O	3.872000	1.342000	1.348000
O	4.911000	-2.211000	-0.964000
C	6.094000	-0.387000	0.023000
H	5.961000	0.551000	-0.527000
H	6.195000	-0.120000	1.077000
H	6.986000	-0.893000	-0.346000
O	2.575000	0.939000	-0.443000
C	2.259000	2.338000	-0.500000
H	1.632000	2.467000	-1.381000
H	1.696000	2.622000	0.389000
H	3.178000	2.922000	-0.577000



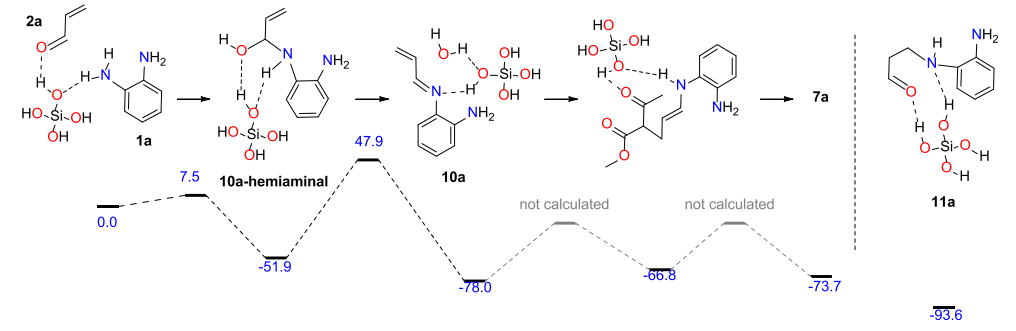
7a

E(M06-2X) = -1548.850885
ZPE = 0.376458
H_{corr} = 0.408119
G_{corr} = 0.313685

C	2.331000	-1.752000	0.398000
C	1.217000	-1.493000	1.428000
C	-0.117000	-1.934000	0.914000
O	0.176000	-0.584000	-1.720000
Si	-1.545000	2.249000	-0.191000
O	-1.859000	1.416000	-1.589000
H	-2.622000	1.719000	-2.089000
O	-0.980000	3.735000	-0.602000
H	-1.170000	4.420000	0.045000
O	-0.374000	1.411000	0.580000
H	0.641000	0.025000	-1.131000
O	-2.893000	2.460000	0.708000
H	-0.643000	-0.106000	-1.920000
H	-0.186000	-2.926000	0.449000
N	-1.125000	-1.159000	0.974000
H	-3.167000	1.679000	1.230000
H	-0.659000	0.514000	0.884000
C	-2.337000	-1.474000	0.322000
C	-3.509000	-0.915000	0.861000
C	-2.398000	-2.203000	-0.868000
C	-4.730000	-1.150000	0.231000
C	-3.620000	-2.430000	-1.490000
H	-1.469000	-2.527000	-1.326000
C	-4.786000	-1.911000	-0.931000
H	-5.636000	-0.721000	0.651000
H	-3.659000	-2.992000	-2.416000
H	-5.744000	-2.081000	-1.411000
N	-3.422000	-0.066000	1.986000
H	-4.258000	-0.080000	2.558000
H	-2.598000	-0.254000	2.547000
H	1.449000	-2.027000	2.359000
H	2.654000	-2.795000	0.430000
H	1.144000	-0.427000	1.674000
H	1.965000	-1.570000	-0.616000
C	3.543000	-0.862000	0.655000
H	3.924000	-0.994000	1.677000
C	4.712000	-1.225000	-0.281000
C	3.245000	0.626000	0.543000
O	3.699000	1.469000	1.276000
O	4.726000	-2.284000	-0.859000
C	5.825000	-0.213000	-0.410000
H	5.476000	0.619000	-1.034000
H	6.090000	0.209000	0.562000
H	6.686000	-0.680000	-0.886000
O	2.466000	0.895000	-0.512000
C	2.173000	2.285000	-0.730000
H	1.517000	2.310000	-1.599000
H	1.659000	2.698000	0.137000
H	3.100000	2.828000	-0.922000



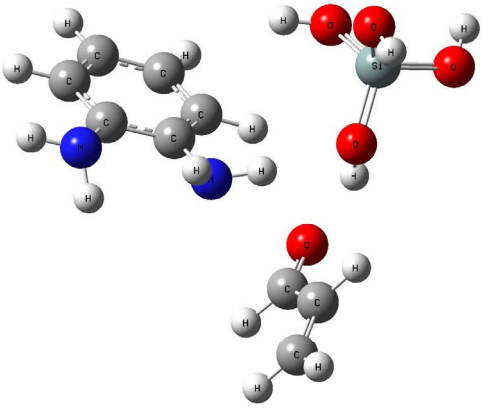
Path B



1a+2a

E(M06-2X) = -1127.792754
ZPE = 0.261442
H_{corr} = 0.283405
G_{corr} = 0.209103

C	-0.587000	4.574000	0.341000
C	-1.023000	3.387000	-0.078000
C	-0.433000	2.768000	-1.277000
O	-0.842000	1.742000	-1.784000
Si	-2.379000	-1.314000	0.343000
O	-3.869000	-1.420000	-0.333000
H	-4.097000	-2.292000	-0.671000
O	-1.443000	-2.390000	-0.457000
H	-0.516000	-2.450000	-0.195000
O	-2.333000	-1.684000	1.942000
H	-2.659000	-0.999000	2.533000
O	-1.897000	0.256000	0.244000
H	-1.831000	0.668000	-0.637000
H	0.418000	3.312000	-1.729000
N	1.006000	1.032000	0.827000
H	0.002000	0.885000	0.758000
H	1.277000	1.109000	1.803000
C	1.717000	-0.001000	0.196000
C	3.042000	-0.257000	0.601000
C	1.170000	-0.745000	-0.849000
C	3.755000	-1.290000	0.001000
C	1.895000	-1.778000	-1.445000
H	0.167000	-0.512000	-1.188000
C	3.184000	-2.063000	-1.009000
H	4.773000	-1.487000	0.331000
H	1.444000	-2.349000	-2.250000
H	3.754000	-2.867000	-1.462000
N	3.559000	0.529000	1.654000
H	4.536000	0.337000	1.833000
H	3.436000	1.521000	1.471000
H	-1.819000	2.839000	0.420000
H	-1.008000	5.070000	1.209000
H	0.216000	5.089000	-0.181000



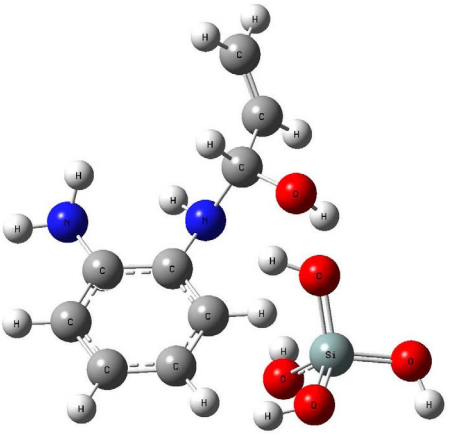
$TS_{1a+2a/10a\text{-hemiaminal}}$

E(M06-2X) = -1127.7926802 $\nu^{\neq}$ = *i*658 cm^{-1}

ZPE = 0.247025

H_{corr} = 0.267827

G_{corr} = 0.19787

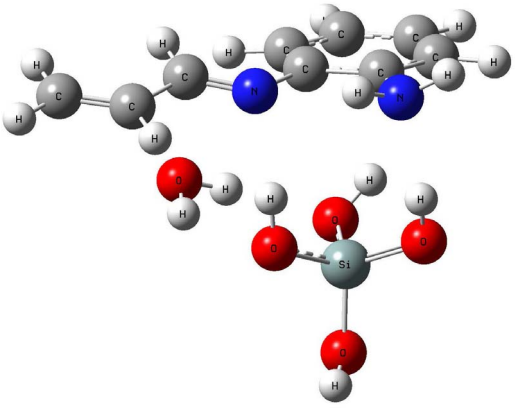


C	1.073000	4.122000	0.029000
C	0.257000	3.083000	-0.115000
C	0.693000	1.789000	-0.752000
O	-0.166000	1.177000	-1.517000
Si	-2.927000	-0.441000	0.166000
O	-3.885000	-0.123000	-1.134000
H	-4.388000	-0.882000	-1.445000
O	-2.467000	-2.030000	0.037000
H	-2.491000	-2.490000	0.882000
O	-3.747000	-0.411000	1.605000
H	-3.878000	0.473000	1.961000
O	-1.715000	0.619000	0.199000
H	-1.112000	0.899000	-0.764000
H	1.716000	1.865000	-1.165000
N	0.957000	0.802000	0.584000
H	-0.025000	0.631000	0.882000
H	1.492000	1.298000	1.302000
C	1.614000	-0.432000	0.243000
C	3.007000	-0.478000	0.361000
C	0.875000	-1.516000	-0.210000
C	3.653000	-1.677000	0.066000
C	1.540000	-2.700000	-0.514000
H	-0.204000	-1.435000	-0.293000
C	2.922000	-2.782000	-0.363000
H	4.733000	-1.737000	0.165000
H	0.973000	-3.557000	-0.861000
H	3.440000	-3.707000	-0.591000
N	3.676000	0.673000	0.847000
H	4.652000	0.487000	1.044000
H	3.621000	1.454000	0.200000
H	-0.784000	3.109000	0.202000
H	0.744000	5.055000	0.474000
H	2.103000	4.082000	-0.319000

10a-hemiaminal

E(M06-2X) = -1127.817584
ZPE = 0.250904
H_{corr} = 0.272228
G_{corr} = 0.200155

C	1.924000	4.120000	0.142000
C	0.973000	3.208000	-0.019000
C	1.199000	1.881000	-0.693000
O	0.350000	1.683000	-1.780000
Si	-2.761000	-0.207000	0.300000
O	-4.202000	0.409000	-0.172000
H	-4.842000	-0.250000	-0.456000
O	-2.494000	-1.557000	-0.595000
H	-1.825000	-2.158000	-0.248000
O	-2.715000	-0.712000	1.870000
H	-2.752000	-0.015000	2.531000
O	-1.691000	1.012000	0.077000
H	-0.566000	1.684000	-1.451000
H	2.219000	1.830000	-1.101000
N	0.988000	0.825000	0.329000
H	-0.764000	0.863000	0.407000
H	1.435000	1.088000	1.205000
C	1.356000	-0.507000	-0.023000
C	2.452000	-1.116000	0.614000
C	0.601000	-1.227000	-0.948000
C	2.727000	-2.459000	0.353000
C	0.901000	-2.560000	-1.218000
H	-0.230000	-0.736000	-1.439000
C	1.954000	-3.180000	-0.551000
H	3.565000	-2.934000	0.856000
H	0.308000	-3.107000	-1.942000
H	2.187000	-4.222000	-0.743000
N	3.194000	-0.364000	1.551000
H	3.946000	-0.902000	1.964000
H	3.578000	0.487000	1.152000
H	-0.043000	3.376000	0.338000
H	1.731000	5.068000	0.631000
H	2.933000	3.952000	-0.226000



$TS_{10a\text{-}hemiaminal/10a}$

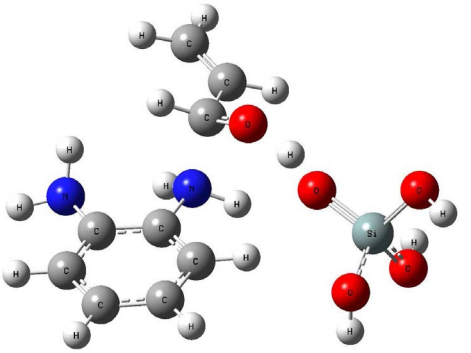
E(M06-2X) = -1127.778739 $\nu^{\neq}$ = *i*866 cm^{-1}

ZPE = 0.246337

H_{corr} = 0.266512

G_{corr} = 0.199316

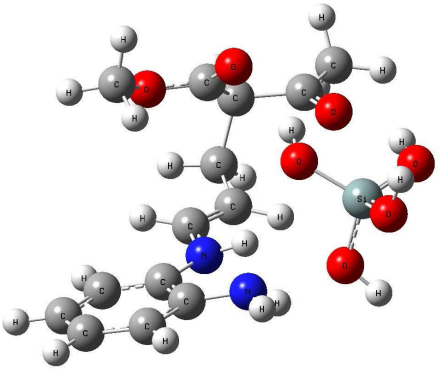
C	3.434000	-3.008000	0.494000
C	2.663000	-1.937000	0.651000
C	1.355000	-1.810000	-0.027000
O	1.871000	-0.671000	-1.349000
Si	0.638000	2.146000	-0.143000
O	0.073000	1.451000	-1.555000
H	-0.534000	1.991000	-2.069000
O	1.407000	3.526000	-0.604000
H	1.502000	4.173000	0.100000
O	1.579000	0.985000	0.487000
H	1.982000	0.132000	-0.679000
O	-0.569000	2.599000	0.868000
H	1.076000	-0.361000	-1.828000
H	1.075000	-2.656000	-0.654000
N	0.398000	-1.162000	0.658000
H	-0.884000	1.881000	1.450000
H	0.871000	-0.075000	0.832000
C	-0.929000	-1.135000	0.172000
C	-1.872000	-0.475000	0.983000
C	-1.352000	-1.689000	-1.038000
C	-3.201000	-0.394000	0.576000
C	-2.684000	-1.613000	-1.433000
H	-0.637000	-2.176000	-1.694000
C	-3.610000	-0.963000	-0.626000
H	-3.915000	0.126000	1.208000
H	-2.990000	-2.050000	-2.377000
H	-4.649000	-0.892000	-0.928000
N	-1.428000	0.158000	2.165000
H	-2.167000	0.268000	2.849000
H	-0.632000	-0.322000	2.575000
H	2.940000	-1.107000	1.297000
H	4.379000	-3.107000	1.015000
H	3.141000	-3.825000	-0.159000



10a

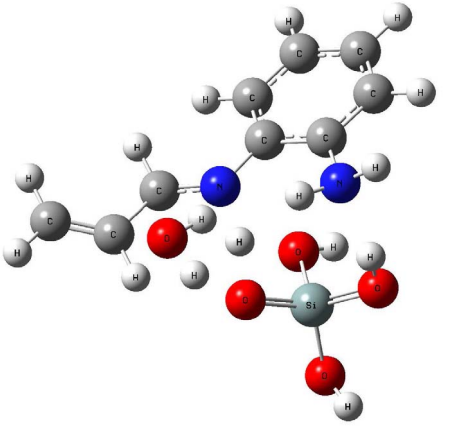
E(M06-2X) = -1127. 8289998
ZPE = 0.249667
H_{corr} = 0.271399
G_{corr} = 0.201602

C	4.775000	0.530000	0.163000
C	3.587000	0.393000	0.756000
C	2.580000	-0.527000	0.244000
O	1.409000	0.875000	-1.995000
Si	-1.388000	1.731000	-0.030000
O	-1.437000	0.762000	-1.365000
H	-1.827000	-0.109000	-1.220000
O	-1.958000	3.182000	-0.518000
H	-1.769000	3.914000	0.075000
O	0.169000	1.965000	0.466000
H	1.401000	1.562000	-1.315000
O	-2.299000	1.096000	1.171000
H	0.461000	0.727000	-2.132000
H	2.866000	-1.140000	-0.616000
N	1.420000	-0.588000	0.781000
H	-1.828000	0.500000	1.782000
H	0.616000	1.195000	0.860000
C	0.401000	-1.379000	0.212000
C	-0.722000	-1.604000	1.032000
C	0.391000	-1.844000	-1.108000
C	-1.826000	-2.289000	0.520000
C	-0.705000	-2.537000	-1.606000
H	1.215000	-1.590000	-1.765000
C	-1.814000	-2.759000	-0.788000
H	-2.700000	-2.431000	1.149000
H	-0.707000	-2.878000	-2.635000
H	-2.681000	-3.286000	-1.175000
N	-0.763000	-1.041000	2.320000
H	-1.292000	-1.590000	2.986000
H	0.162000	-0.813000	2.666000
H	3.311000	0.979000	1.629000
H	5.517000	1.230000	0.530000
H	5.031000	-0.049000	-0.719000



11a

E(M06-2X) = -1472.401686
ZPE = 0,350761
H_{corr} = 0.380605
G_{corr} = 0.289483

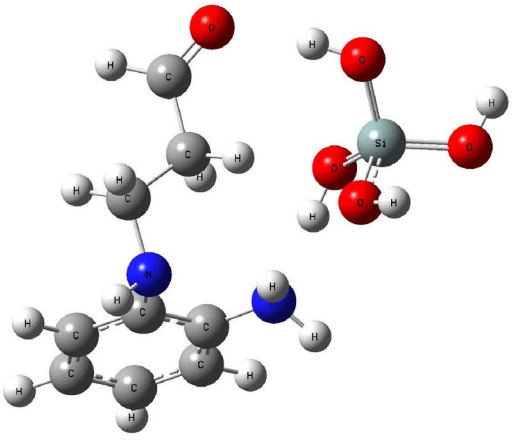


C	-1.961000	-1.880000	0.950000
O	-1.873000	-1.038000	1.811000
C	-2.850000	-1.817000	-0.279000
H	-3.525000	-2.680000	-0.269000
C	-3.649000	-0.529000	-0.347000
C	-5.076000	-0.642000	-0.816000
H	-5.498000	0.349000	-0.978000
H	-5.125000	-1.231000	-1.737000
H	-5.662000	-1.176000	-0.060000
O	-3.136000	0.544000	-0.101000
H	-1.209000	0.721000	1.099000
O	-1.251000	-3.011000	0.955000
C	-0.242000	-3.077000	1.972000
H	0.264000	-4.029000	1.823000
H	0.454000	-2.243000	1.853000
H	-0.697000	-3.028000	2.962000
C	-1.934000	-1.899000	-1.549000
C	-0.826000	-0.897000	-1.480000
H	-1.531000	-2.915000	-1.584000
H	-2.563000	-1.763000	-2.436000
H	-1.061000	0.154000	-1.623000
C	0.420000	-1.233000	-1.107000
H	0.700000	-2.280000	-0.992000
Si	-0.637000	2.738000	0.242000
O	0.188000	3.965000	0.948000
H	-0.112000	4.214000	1.827000
O	-2.203000	3.195000	0.098000
H	-2.828000	2.470000	-0.037000
O	-0.455000	1.326000	1.030000
H	1.013000	0.571000	-0.454000
O	0.098000	2.515000	-1.228000
H	0.064000	3.268000	-1.826000
N	1.386000	-0.300000	-0.813000
C	2.724000	-0.553000	-0.532000
C	3.337000	-1.793000	-0.712000
C	3.491000	0.539000	-0.057000
C	4.676000	-1.981000	-0.371000
H	2.771000	-2.619000	-1.129000
C	4.824000	0.330000	0.280000
C	5.418000	-0.925000	0.139000
H	5.131000	-2.955000	-0.513000
H	5.405000	1.170000	0.653000
H	6.460000	-1.061000	0.407000
N	2.853000	1.772000	0.126000
H	3.473000	2.516000	0.415000
H	2.254000	2.077000	-0.636000

12a

E(M06-2X) = -1127.8363606
ZPE = 0.265893
H_{corr} = 0.285568
G_{corr} = 0.218767

C	-1.025000	2.122000	0.819000
H	-0.688000	2.810000	1.601000
C	0.171000	1.639000	0.009000
H	-0.157000	0.875000	-0.712000
C	0.826000	2.715000	-0.805000
O	2.004000	2.742000	-1.083000
H	0.161000	3.517000	-1.189000
H	-1.721000	2.676000	0.167000
N	-1.680000	0.986000	1.480000
H	-2.265000	1.335000	2.232000
C	-2.484000	0.183000	0.602000
C	-3.756000	0.587000	0.198000
C	-1.983000	-1.056000	0.168000
C	-4.545000	-0.217000	-0.616000
H	-4.129000	1.548000	0.547000
C	-2.775000	-1.857000	-0.661000
C	-4.044000	-1.444000	-1.044000
H	-5.536000	0.109000	-0.913000
H	-2.382000	-2.810000	-1.003000
H	-4.644000	-2.085000	-1.683000
H	0.910000	1.169000	0.664000
N	-0.683000	-1.458000	0.523000
H	-0.307000	-0.922000	1.304000
H	-0.609000	-2.451000	0.708000
Si	2.793000	-0.809000	-0.014000
O	2.038000	-0.826000	1.467000
H	2.636000	-0.984000	2.204000
O	3.879000	-2.041000	0.034000
H	4.651000	-1.908000	-0.523000
O	3.656000	0.543000	-0.308000
H	3.163000	1.318000	-0.628000
O	1.587000	-0.966000	-1.100000
H	0.731000	-1.222000	-0.693000



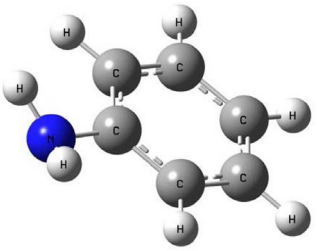
Substituent effect : Optimized structures and NPA charges

E(MP2) corresponds to the electronic energy at the MP2/6-311++G(d,p)//MP2/6-31+G(d,p) level. Values are given in Hartree. Charges resulting from natural population analysis (NPA) were calculated using NBO 6.0 [3] at the same level of calculation.

Aniline

E(MP2) = -286.8161601

C	1.882000	-0.000000	0.005000
C	1.173000	-1.206000	0.008000
C	1.173000	1.206000	0.008000
H	2.964000	-0.000000	0.019000
C	-0.223000	-1.208000	-0.012000
H	1.706000	-2.149000	0.004000
C	-0.223000	1.208000	-0.012000
C	-0.936000	0.000000	0.004000
H	-0.764000	2.149000	-0.018000
N	-2.340000	0.000000	-0.083000
H	-2.774000	-0.831000	0.296000
H	-2.774000	0.830000	0.297000
H	1.706000	2.149000	0.004000
H	-0.764000	-2.148000	-0.017000



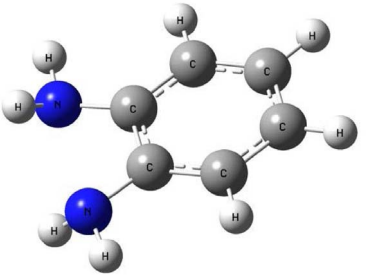
Natural Population

Atom No	Natural Charge	Core	Valence	Rydberg	Total
C 1	-0.25616	1.99920	4.23173	0.02523	6.25616
C 2	-0.14531	1.99922	4.12216	0.02393	6.14531
C 3	-0.14530	1.99922	4.12215	0.02393	6.14530
H 4	0.19460	0.00000	0.80343	0.00197	0.80540
C 5	-0.26874	1.99910	4.24566	0.02398	6.26874
H 6	0.19210	0.00000	0.80608	0.00182	0.80790
C 7	-0.26877	1.99910	4.24570	0.02398	6.26877
C 8	0.22545	1.99903	3.75187	0.02365	5.77455
H 9	0.19052	0.00000	0.80754	0.00195	0.80948
N 10	**-0.82780**	1.99951	5.80563	0.02266	7.82780
H 11	**0.36341**	0.00000	0.63434	0.00225	0.63659
H 12	**0.36342**	0.00000	0.63432	0.00225	0.63658
H 13	0.19210	0.00000	0.80608	0.00182	0.80790
H 14	0.19050	0.00000	0.80756	0.00195	0.80950
[t!] * Total *	-0.00000	13.99437	35.82425	0.18138	50.00000

1a

E(MP2)=-342.0505454

C	-1.926000	-0.698000	-0.015000
C	-0.712000	-1.393000	-0.043000
C	-1.926000	0.698000	0.015000
H	-2.859000	-1.246000	-0.047000
C	0.504000	-0.705000	0.019000
H	-0.706000	-2.478000	-0.042000
C	-0.712000	1.393000	0.043000
C	0.504000	0.705000	-0.019000
H	-0.706000	2.478000	0.042000
N	1.753000	-1.361000	-0.037000
H	2.419000	-0.966000	0.621000
H	1.676000	-2.359000	0.112000
N	1.753000	1.361000	0.037000
H	2.419000	0.966000	-0.620000
H	1.676000	2.359000	-0.112000
H	-2.859000	1.246000	0.047000



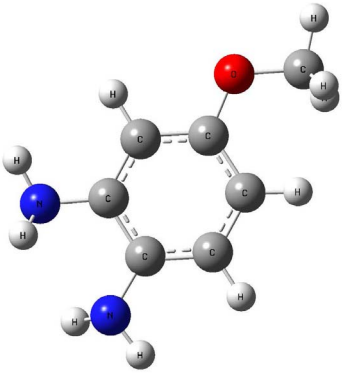
Natural Population

Atom No	Natural Charge	Core	Valence	Rydberg	Total
C 1	-0.20374	1.99922	4.17985	0.02468	6.20374
C 2	-0.22759	1.99911	4.20506	0.02341	6.22759
C 3	-0.20372	1.99922	4.17983	0.02468	6.20372
H 4	0.19293	0.00000	0.80518	0.00189	0.80707
C 5	0.16239	1.99894	3.81492	0.02376	5.83761
H 6	0.18813	0.00000	0.80976	0.00211	0.81187
C 7	-0.22761	1.99911	4.20508	0.02341	6.22761
C 8	0.16241	1.99894	3.81489	0.02376	5.83759
H 9	0.18813	0.00000	0.80976	0.00211	0.81187
N 10	**-0.84253**	1.99953	5.81990	0.02310	7.84253
H 11	**0.36940**	0.00000	0.62776	0.00284	0.63060
H 12	**0.36099**	0.00000	0.63680	0.00221	0.63901
N 13	**-0.84253**	1.99953	5.81990	0.02310	7.84253
H 14	**0.36941**	0.00000	0.62775	0.00284	0.63059
H 15	**0.36099**	0.00000	0.63680	0.00221	0.63901
H 16	0.19293	0.00000	0.80518	0.00189	0.80707
* Total *	-0.00000	15.99360	41.79841	0.20799	58.00000

1b

E(MP2)= -456.3075221

C	-0.879000	-1.152000	-0.018000
C	0.464000	-1.559000	-0.038000
C	-1.170000	0.215000	0.000000
H	-1.657000	-1.900000	-0.057000
C	1.506000	-0.636000	0.023000
H	0.695000	-2.619000	-0.030000
C	-0.131000	1.154000	0.038000
C	1.199000	0.742000	-0.018000
H	-0.385000	2.208000	0.027000
N	2.873000	-1.004000	-0.039000
H	3.421000	-0.531000	0.674000
H	3.003000	-2.005000	0.050000
N	2.273000	1.654000	0.040000
H	3.031000	1.382000	-0.579000
H	1.991000	2.607000	-0.153000
O	-2.441000	0.750000	0.019000
C	-3.520000	-0.180000	0.001000
H	-3.493000	-0.830000	0.878000
H	-4.423000	0.423000	0.019000
H	-3.502000	-0.788000	-0.907000



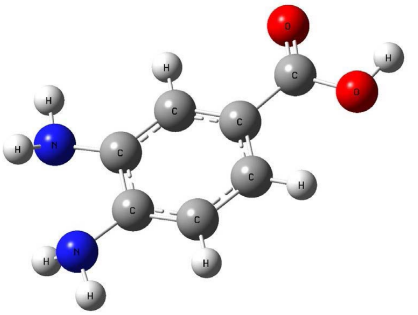
Natural Population

Atom No	Natural Charge	Core	Valence	Rydberg	Total
C 1	-0.32120	1.99911	4.29939	0.02271	6.32120
C 2	-0.18595	1.99914	4.16394	0.02287	6.18595
C 3	0.37969	1.99881	3.59379	0.02771	5.62031
H 4	0.20058	0.00000	0.79755	0.00187	0.79942
C 5	0.11609	1.99892	3.86152	0.02347	5.88391
H 6	0.18704	0.00000	0.81075	0.00220	0.81296
C 7	-0.28285	1.99887	4.25904	0.02493	6.28285
C 8	0.20468	1.99896	3.77288	0.02348	5.79532
H 9	0.20257	0.00000	0.79479	0.00263	0.79743
N 10	**-0.84375**	1.99954	5.82134	0.02287	7.84375
H 11	**0.36407**	0.00000	0.63302	0.00290	0.63593
H 12	**0.35874**	0.00000	0.63904	0.00222	0.64126
N 13	**-0.83937**	1.99952	5.81692	0.02293	7.83937
H 14	**0.37336**	0.00000	0.62385	0.00280	0.62664
H 15	**0.36258**	0.00000	0.63520	0.00222	0.63742
O 16	-0.63013	1.99975	6.61028	0.02010	8.63013
C 17	-0.09637	1.99932	4.07545	0.02160	6.09637
H 18	0.14319	0.00000	0.85473	0.00208	0.85681
H 19	0.16426	0.00000	0.83443	0.00131	0.83574
H 20	0.14276	0.00000	0.85516	0.00208	0.85724
* Total *	-0.00000	19.99194	53.75309	0.25497	74.00000

1c

E(MP2)= -530.2506935

C	0.450000	-1.404000	0.045000
C	-0.926000	-1.628000	0.055000
C	0.932000	-0.088000	0.025000
H	1.140000	-2.235000	0.083000
C	-1.830000	-0.562000	-0.024000
H	-1.307000	-2.644000	0.046000
C	0.033000	0.988000	-0.015000
C	-1.341000	0.764000	0.029000
H	0.425000	1.999000	-0.007000
N	-3.221000	-0.748000	0.003000
H	-3.711000	-0.105000	-0.612000
H	-3.502000	-1.702000	-0.185000
N	-2.284000	1.808000	-0.039000
H	-3.043000	1.685000	0.624000
H	-1.865000	2.722000	0.085000
C	2.376000	0.224000	-0.010000
O	2.857000	1.352000	-0.021000
O	3.162000	-0.894000	-0.025000
H	4.078000	-0.568000	-0.037000

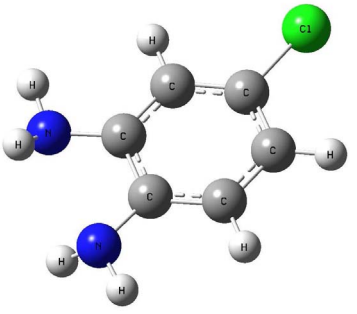


Natural Population

Atom No	Natural Charge	Core	Valence	Rydberg	Total
C 1	-0.12514	1.99917	4.10345	0.02252	6.12514
C 2	-0.25525	1.99912	4.23255	0.02359	6.25525
C 3	-0.24103	1.99896	4.21735	0.02472	6.24103
H 4	0.21718	0.00000	0.78102	0.00179	0.78282
C 5	0.21857	1.99896	3.75865	0.02382	5.78143
H 6	0.19353	0.00000	0.80435	0.00212	0.80647
C 7	-0.14219	1.99893	4.12074	0.02252	6.14219
C 8	0.13600	1.99895	3.84110	0.02394	5.86400
H 9	0.21879	0.00000	0.77907	0.00214	0.78121
N 10	**-0.83724**	1.99951	5.81480	0.02292	7.83724
H 11	**0.37773**	0.00000	0.61952	0.00274	0.62227
H 12	**0.36684**	0.00000	0.63102	0.00213	0.63316
N 13	**-0.84282**	1.99953	5.82002	0.02328	7.84282
H 14	**0.36829**	0.00000	0.62890	0.00281	0.63171
H 15	**0.36657**	0.00000	0.63132	0.00211	0.63343
C 16	0.96561	1.99932	2.98419	0.05088	5.03439
O 17	-0.71871	1.99976	6.70561	0.01334	8.71871
O 18	-0.76045	1.99978	6.74874	0.01193	8.76045
H 19	0.49371	0.00000	0.50236	0.00393	0.50629
* Total *	-0.00000	21.99198	57.72477	0.28325	80.00000

1d

E(MP2)= -801.1108686



C	-0.742000	-1.395000	-0.030000
C	0.639000	-1.613000	-0.047000
C	-1.216000	-0.084000	-0.017000
H	-1.433000	-2.226000	-0.067000
C	1.539000	-0.547000	0.024000
H	1.018000	-2.629000	-0.036000
C	-0.334000	0.998000	0.027000
C	1.045000	0.774000	-0.024000
H	-0.720000	2.010000	0.016000
N	2.939000	-0.722000	-0.021000
H	3.418000	-0.136000	0.656000
H	3.216000	-1.688000	0.107000
N	1.979000	1.826000	0.038000
H	2.763000	1.676000	-0.590000
H	1.566000	2.734000	-0.132000
Cl	-2.932000	0.220000	0.020000

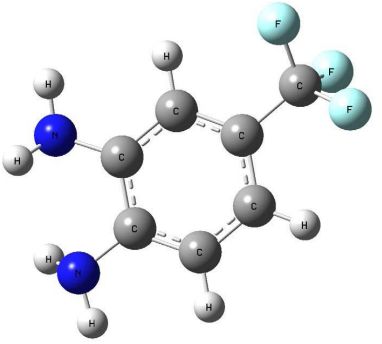
Natural Population

Atom No	Natural Charge	Core	Valence	Rydberg	Total
C 1	-0.22663	1.99904	4.20116	0.02644	6.22663
C 2	-0.20771	1.99912	4.18599	0.02260	6.20771
C 3	-0.03846	1.99863	4.01175	0.02808	6.03846
H 4	0.21005	0.00000	0.78811	0.00184	0.78995
C 5	0.15715	1.99894	3.82049	0.02342	5.84285
H 6	0.19310	0.00000	0.80480	0.00210	0.80690
C 7	-0.24239	1.99880	4.21765	0.02593	6.24239
C 8	0.18178	1.99896	3.79571	0.02356	5.81822
H 9	0.20478	0.00000	0.79290	0.00232	0.79522
N 10	**-0.84153**	1.99953	5.81901	0.02299	7.84153
H 11	**0.37002**	0.00000	0.62714	0.00284	0.62998
H 12	**0.36293**	0.00000	0.63490	0.00217	0.63707
N 13	**-0.83944**	1.99952	5.81685	0.02307	7.83944
H 14	**0.37351**	0.00000	0.62368	0.00281	0.62649
H 15	**0.36454**	0.00000	0.63330	0.00216	0.63546
Cl 16	-0.02171	9.99963	7.00045	0.02163	17.02171
* Total *	0.00000	25.99216	47.77389	0.23396	74.00000

1e

E(MP2)= -678.5118635

C	-0.119000	-1.449000	-0.070000
C	1.265000	-1.635000	-0.056000
C	-0.631000	-0.149000	-0.058000
H	-0.784000	-2.301000	-0.112000
C	2.136000	-0.544000	0.024000
H	1.673000	-2.640000	-0.046000
C	0.228000	0.955000	-0.015000
C	1.611000	0.767000	-0.032000
H	-0.178000	1.960000	-0.034000
N	3.534000	-0.687000	0.007000
H	3.997000	-0.048000	0.644000
H	3.840000	-1.637000	0.178000
N	2.521000	1.838000	0.037000
H	3.302000	1.722000	-0.602000
H	2.085000	2.739000	-0.110000
C	-2.106000	0.071000	0.007000
F	-2.558000	0.159000	1.294000
F	-2.483000	1.227000	-0.607000
F	-2.806000	-0.936000	-0.578000



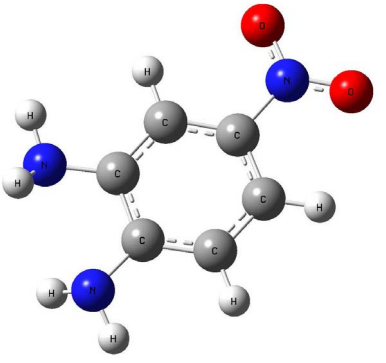
Natural Population

Atom No	Natural Charge	Core	Valence	Rydberg	Total
C 1	-0.15562	1.99916	4.13418	0.02229	6.15562
C 2	-0.23351	1.99912	4.21128	0.02311	6.23351
C 3	-0.19965	1.99896	4.17760	0.02310	6.19965
H 4	0.21414	0.00000	0.78404	0.00182	0.78586
C 5	0.19636	1.99895	3.78092	0.02376	5.80364
H 6	0.19522	0.00000	0.80271	0.00208	0.80478
C 7	-0.17816	1.99893	4.15732	0.02191	6.17816
C 8	0.15739	1.99896	3.81968	0.02397	5.84261
H 9	0.20876	0.00000	0.78905	0.00219	0.79124
N 10	**-0.83871**	1.99952	5.81634	0.02285	7.83871
H 11	**0.37575**	0.00000	0.62149	0.00276	0.62425
H 12	**0.36665**	0.00000	0.63123	0.00213	0.63335
N 13	**-0.84067**	1.99952	5.81801	0.02314	7.84067
H 14	**0.37181**	0.00000	0.62537	0.00282	0.62819
H 15	**0.36631**	0.00000	0.63157	0.00212	0.63369
C 16	1.21506	1.99904	2.72716	0.05874	4.78494
F 17	-0.40791	1.99992	7.40325	0.00474	9.40791
F 18	-0.40812	1.99992	7.40329	0.00490	9.40812
F 19	-0.40509	1.99992	7.40039	0.00478	9.40509
* Total *	0.00000	23.99194	65.73487	0.27319	90.00000

1f

E(MP2)= -546.1598027

C	0.480000	-1.427000	0.019000
C	-0.900000	-1.631000	0.029000
C	0.948000	-0.115000	0.020000
H	1.175000	-2.254000	0.040000
C	-1.792000	-0.555000	-0.030000
H	-1.289000	-2.643000	0.005000
C	0.088000	0.984000	-0.005000
C	-1.290000	0.766000	0.037000
H	0.495000	1.986000	0.017000
N	-3.185000	-0.725000	0.000000
H	-3.672000	-0.080000	-0.613000
H	-3.480000	-1.676000	-0.178000
N	-2.219000	1.819000	-0.008000
H	-2.993000	1.683000	0.635000
H	-1.799000	2.728000	0.138000
N	2.392000	0.127000	-0.012000
O	3.148000	-0.861000	0.055000
O	2.782000	1.308000	-0.096000



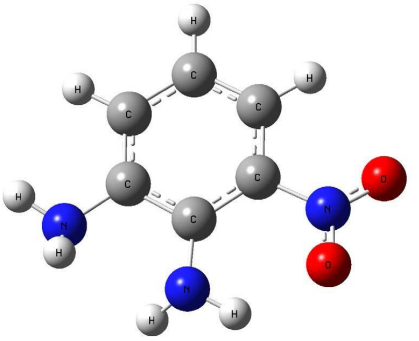
Natural Population

Atom No	Natural Charge	Core	Valence	Rydberg	Total
C 1	-0.14525	1.99913	4.12311	0.02301	6.14525
C 2	-0.24608	1.99912	4.22389	0.02307	6.24608
C 3	0.03426	1.99881	3.94038	0.02656	5.96574
H 4	0.23743	0.00000	0.76070	0.00187	0.76257
C 5	0.22293	1.99896	3.75454	0.02357	5.77707
H 6	0.19976	0.00000	0.79826	0.00198	0.80024
C 7	-0.17512	1.99889	4.15311	0.02311	6.17512
C 8	0.14805	1.99897	3.82879	0.02418	5.85195
H 9	0.23393	0.00000	0.76383	0.00224	0.76607
N 10	**-0.83515**	1.99951	5.81281	0.02282	7.83515
H 11	**0.37986**	0.00000	0.61743	0.00271	0.62014
H 12	**0.37016**	0.00000	0.62774	0.00210	0.62984
N 13	**-0.84030**	1.99952	5.81758	0.02319	7.84030
H 14	**0.37250**	0.00000	0.62470	0.00280	0.62750
H 15	**0.36984**	0.00000	0.62808	0.00209	0.63016
N 16	0.60102	1.99946	4.34206	0.05746	6.39898
O 17	-0.46115	1.99981	6.44615	0.01519	8.46115
O 18	-0.46668	1.99981	6.45129	0.01559	8.46668
* Total *	0.00000	21.99200	57.71446	0.29354	80.00000

1g

E(MP2)= -546.1589323

C	0.921000	2.147000	-0.058000
C	1.985000	1.239000	0.006000
C	-0.387000	1.684000	-0.073000
H	1.117000	3.211000	-0.075000
C	1.747000	-0.135000	-0.004000
H	3.009000	1.596000	-0.010000
C	-0.623000	0.301000	-0.064000
C	0.420000	-0.642000	0.038000
N	2.786000	-1.077000	0.093000
H	2.661000	-1.861000	-0.540000
H	3.703000	-0.668000	-0.031000
N	0.287000	-2.026000	0.049000
H	0.940000	-2.478000	0.679000
H	-0.664000	-2.358000	0.128000
H	-1.230000	2.356000	-0.128000
N	-2.017000	-0.124000	-0.013000
O	-2.283000	-1.319000	-0.281000
O	-2.881000	0.722000	0.281000



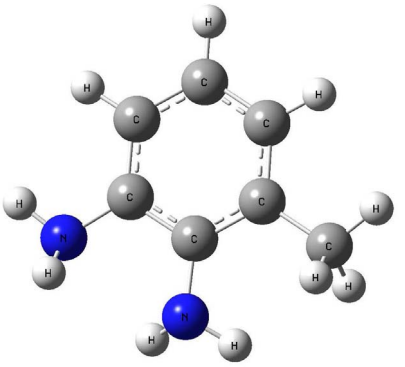
Natural Population

Atom No	Natural Charge	Core	Valence	Rydberg	Total
C 1	-0.21839	1.99922	4.19534	0.02384	6.21839
C 2	-0.18466	1.99915	4.16173	0.02379	6.18466
C 3	-0.15833	1.99915	4.13570	0.02348	6.15833
H 4	0.20406	0.00000	0.79399	0.00195	0.79594
C 5	0.16418	1.99877	3.81221	0.02484	5.83582
H 6	0.19641	0.00000	0.80161	0.00199	0.80359
C 7	0.00913	1.99874	3.96587	0.02627	5.99087
C 8	0.22859	1.99895	3.74689	0.02557	5.77141
N 9	**-0.84336**	1.99953	5.82022	0.02361	7.84336
H 10	**0.37476**	0.00000	0.62239	0.00285	0.62524
H 11	**0.36717**	0.00000	0.63073	0.00209	0.63283
N 12	**-0.84200**	1.99949	5.81898	0.02354	7.84200
H 13	**0.38167**	0.00000	0.61570	0.00263	0.61833
H 14	**0.41988**	0.00000	0.57781	0.00231	0.58012
H 15	0.23563	0.00000	0.76249	0.00188	0.76437
N 16	0.60313	1.99945	4.34018	0.05723	6.39687
O 17	-0.49260	1.99981	6.47695	0.01584	8.49260
O 18	-0.44528	1.99981	6.43031	0.01516	8.44528
* Total *	0.00000	21.99205	57.70907	0.29887	80.00000

1h

E(MP2)= -381.251393

C	-0.103000	2.127000	-0.023000
C	-1.282000	1.378000	-0.034000
C	1.132000	1.475000	-0.003000
H	-0.149000	3.209000	-0.056000
C	-1.229000	-0.017000	0.025000
H	-2.247000	1.874000	-0.018000
C	1.210000	0.076000	0.029000
C	0.020000	-0.669000	-0.032000
N	-2.389000	-0.828000	-0.019000
H	-2.372000	-1.554000	0.691000
H	-3.239000	-0.285000	0.078000
N	0.017000	-2.079000	0.009000
H	-0.731000	-2.469000	-0.556000
H	0.901000	-2.493000	-0.256000
C	2.539000	-0.630000	0.042000
H	2.690000	-1.224000	-0.864000
H	3.353000	0.092000	0.099000
H	2.628000	-1.301000	0.900000
H	2.049000	2.054000	0.025000



Natural Population

Atom No	Natural Charge	Core	Valence	Rydberg	Total
C 1	-0.19611	1.99922	4.17238	0.02452	6.19611
C 2	-0.24071	1.99914	4.21698	0.02459	6.24071
C 3	-0.20573	1.99912	4.18230	0.02430	6.20573
H 4	0.19185	0.00000	0.80599	0.00216	0.80815
C 5	0.17752	1.99872	3.79940	0.02436	5.82248
H 6	0.18744	0.00000	0.81053	0.00203	0.81256
C 7	-0.06532	1.99902	4.04594	0.02035	6.06532
C 8	0.15840	1.99887	3.81850	0.02423	5.84160
N 9	**-0.84586**	1.99954	5.82292	0.02339	7.84586
H 10	**0.36574**	0.00000	0.63143	0.00283	0.63426
H 11	**0.36063**	0.00000	0.63720	0.00217	0.63937
N 12	**-0.84705**	1.99953	5.82342	0.02411	7.84705
H 13	**0.37350**	0.00000	0.62379	0.00271	0.62650
H 14	**0.36537**	0.00000	0.63260	0.00203	0.63463
C 15	-0.52047	1.99940	4.50477	0.01630	6.52047
H 16	0.17805	0.00000	0.81983	0.00211	0.82195
H 17	0.18873	0.00000	0.80984	0.00142	0.81127
H 18	0.18550	0.00000	0.81253	0.00198	0.81450
H 19	0.18851	0.00000	0.80971	0.00178	0.81149
* Total *	-0.00000	17.99255	47.78006	0.22738	66.00000

References

[1] R. T. Skodje, D. G. Truhlar, "Parabolic tunneling calculations", *J. Phys. Chem.*, 1981, **85**, 624-628.

[2] E. Wigner, "Über das Überschreiten von Potentialschwellen bei chemischen Reaktionen", *Z. Phys. Chem.*, 1932, **19B**, 203-216.

[3] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold, "NBO 6.0", 2013, published by the Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, http://nbo6.chem.wisc.edu/.