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SUPPLEMENTARY INFORMATION

Hydrogen Tunneling Above Room Temperature Evidenced by Infrared Ion Spectroscopy

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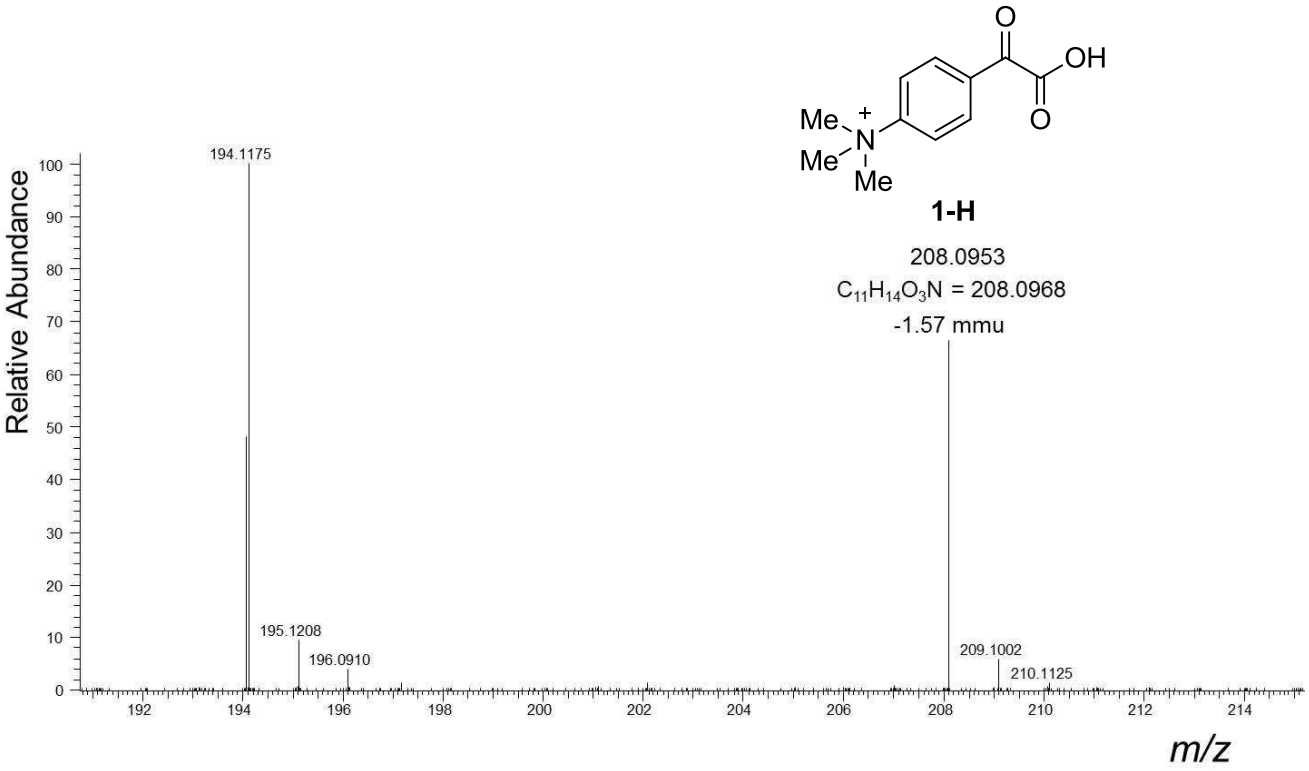
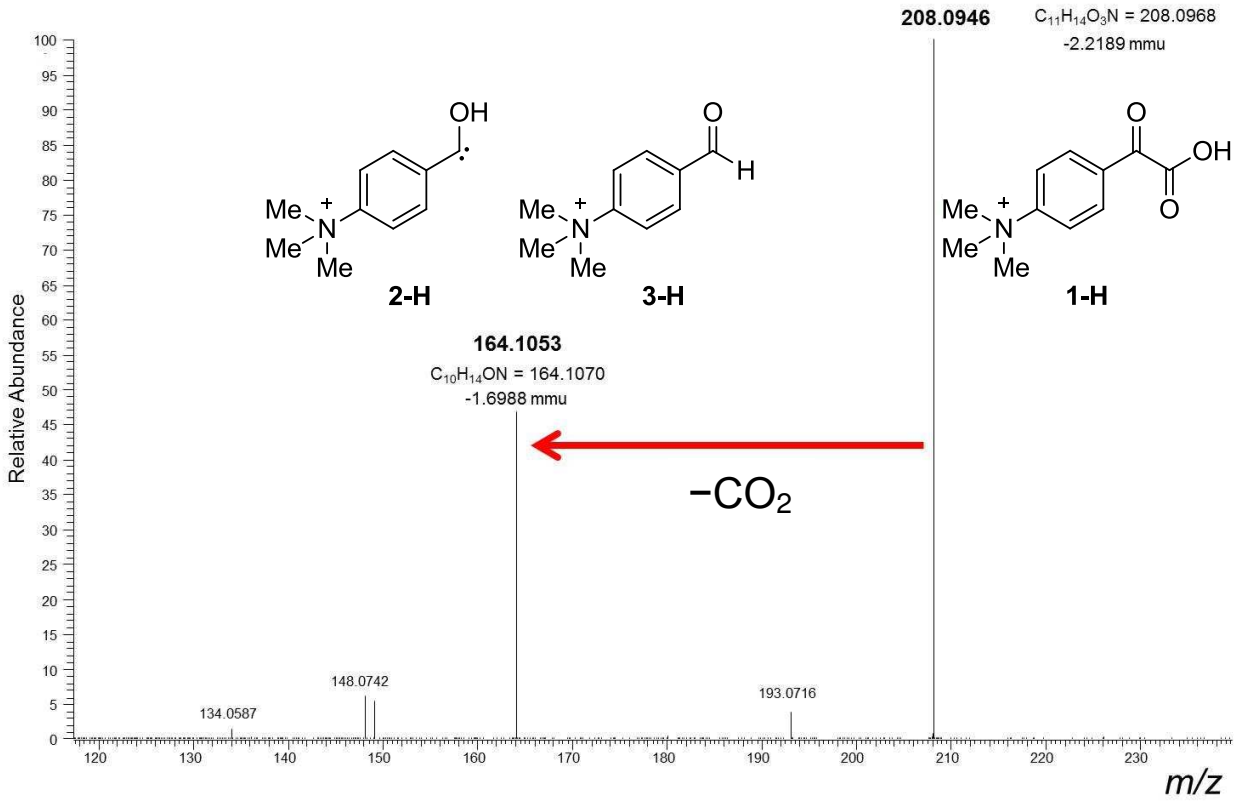
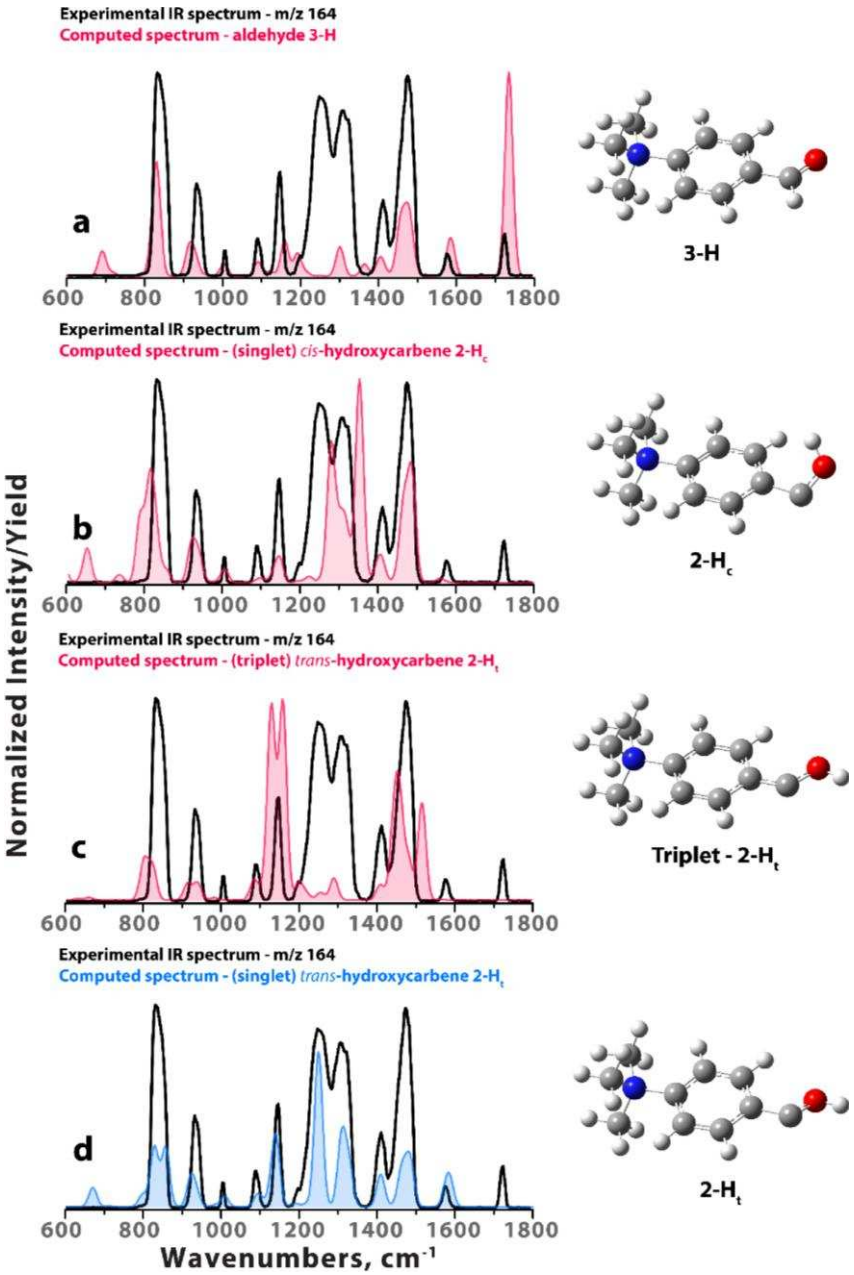


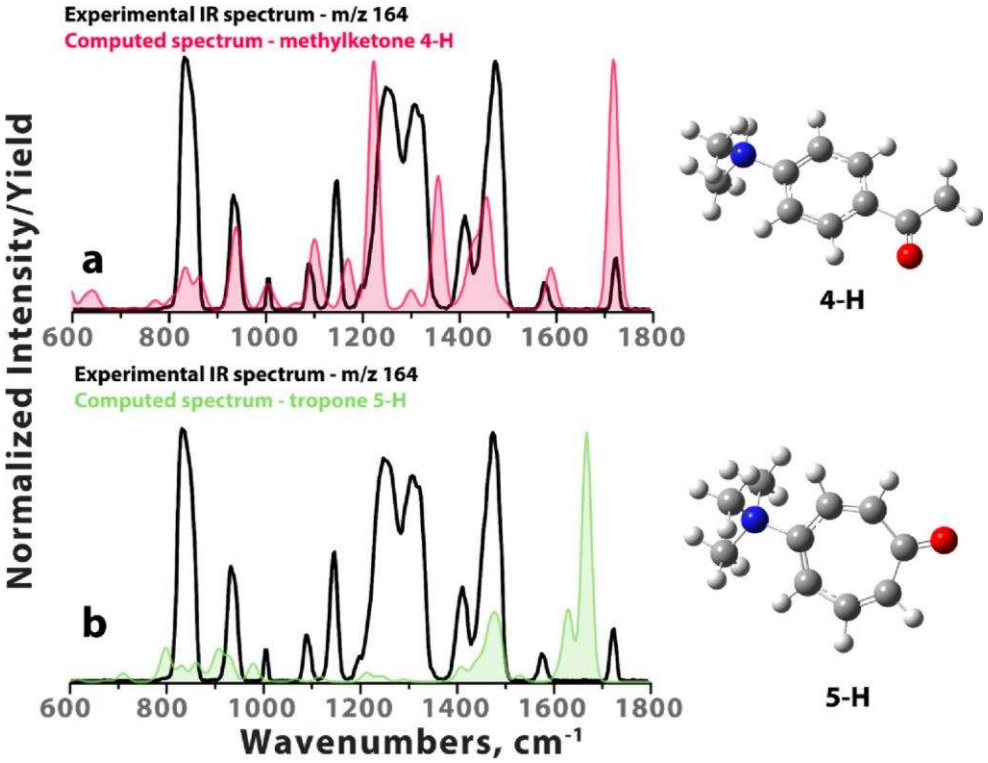
Supplementary Figure 1 | (+)ESI-MS of **1-H** acquired from a CH_3OH solution (c ~ 10^{-5} M). The ESI-MS experiment was conducted on a LTQ-Orbitrap XL instrument and the accurate ion mass was determined in the orbitrap analyzer with a resolution R: 30000 FWHM with external calibration (experimental error Δm < 3 ppm).



Supplementary Figure 2 | (+)ESI-MS^2 of **1-H**. The ESI-MS^2 CID experiment was conducted in the linear quadrupole ion trap LTQ-part of a LTQ-Orbitrap XL instrument (Thermo Fisher, Bremen, Germany) and the accurate ion mass was determined in the orbitrap analyzer with a resolution R: 30000 FWHM with external calibration (Δm < 3 ppm).



Supplementary Figure 3 | Experimental and calculated infrared spectra of alternative *m*/*z* 164 hydroxycarbene ions. The experimental IR spectrum of the ion population at *m*/*z* 164 generated by CO_2 loss from **1-H** is presented in black in all panels. (**a**) The calculated spectrum of the aldehyde model compound **3-H**. (**b**) The calculated spectrum of (singlet) *cis*-hydroxycarbene **2-H$_c$**. (**c**) The calculated spectrum of (triplet) *trans*-hydroxycarbene **2-H$_t$**. (**d**) The calculated spectrum of (singlet) *trans*-hydroxycarbene **2-H$_t$**. Calculated IR spectra were obtained at the dispersion-corrected B3LYP-GD3BJ/cc-pVTZ level of theory. Calculated frequencies are scaled by 0.97 and broadened using a Gaussian function with a FWHM of 25 cm^{-1} to facilitate comparison with experiment.[1–3]



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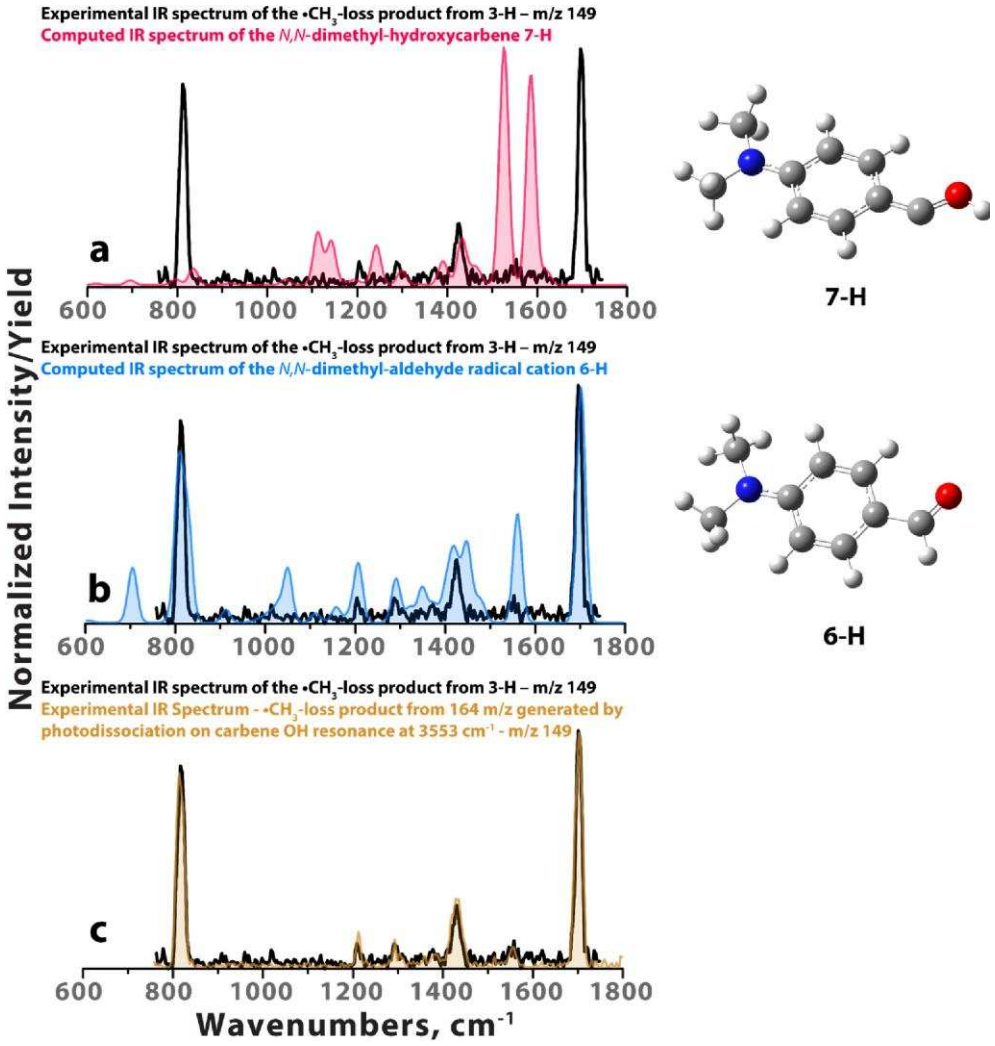
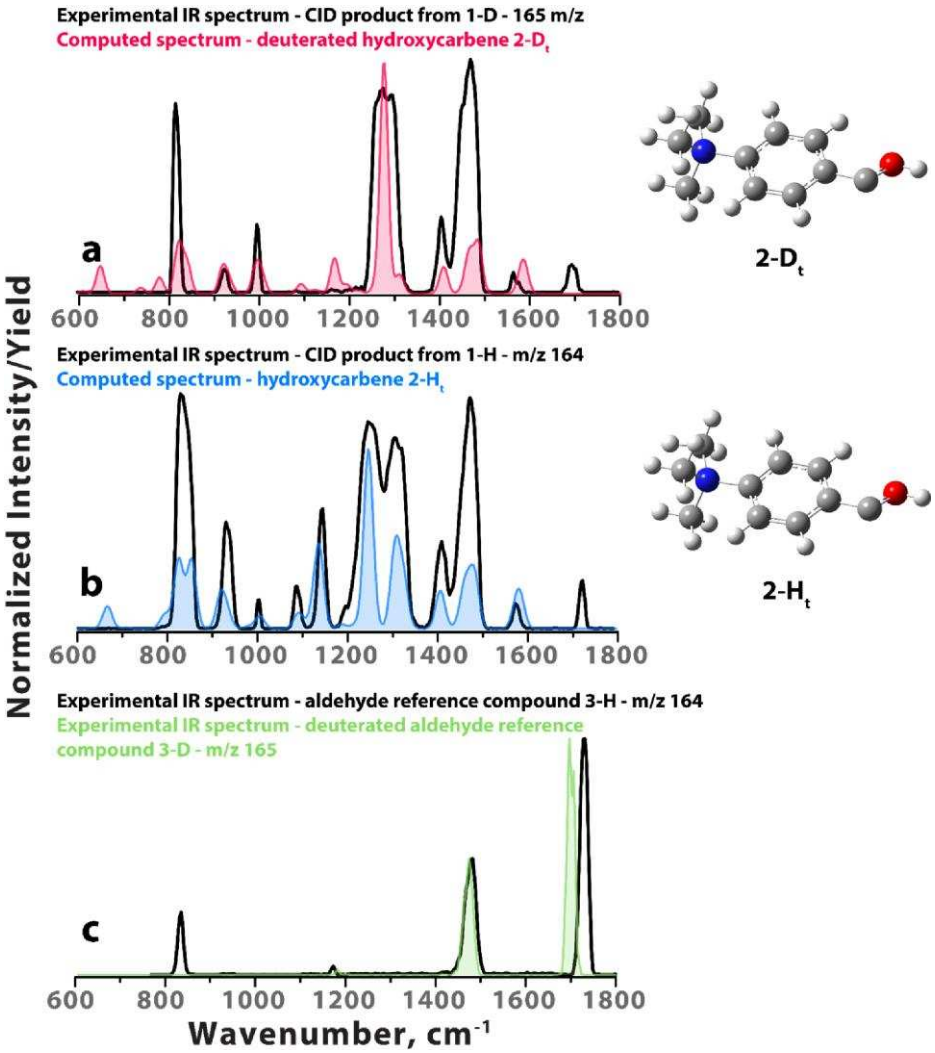
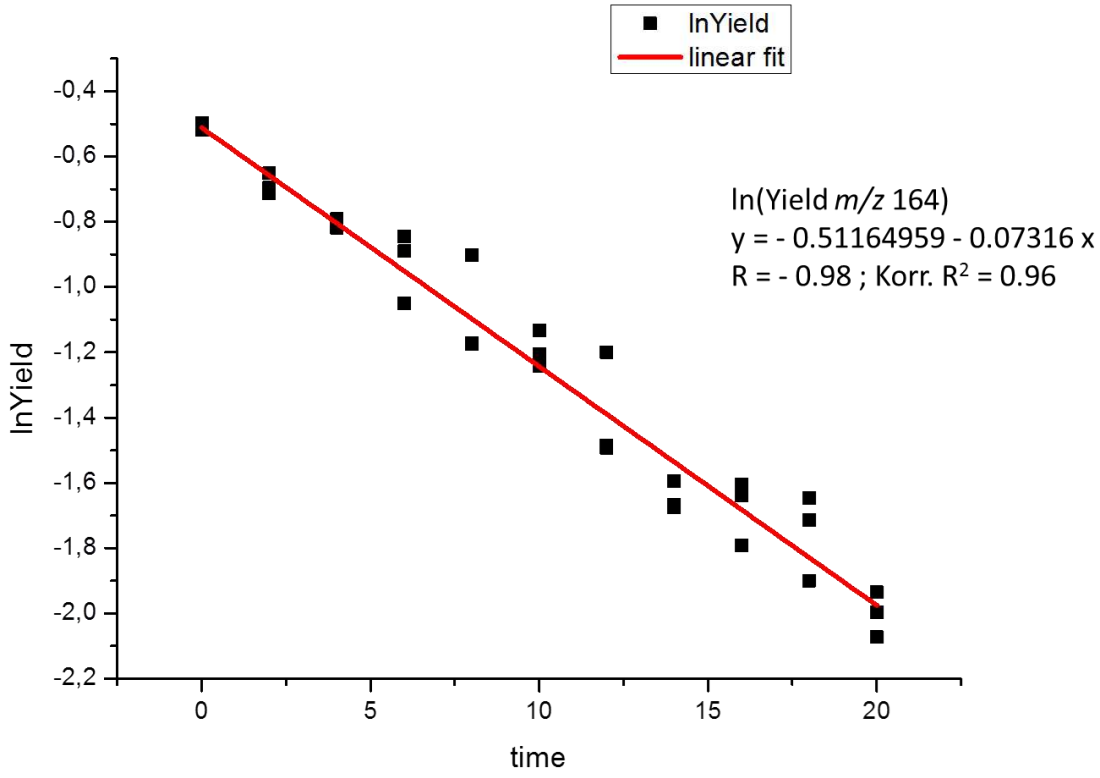


Supplementary Figure 5 | Experimental and calculated infrared spectra of the $^{\bullet}CH_3$-loss product from ions at *m*/*z* 164. The experimental IR spectrum of the CID-generated $^{\bullet}CH_3$-loss product (*m*/*z* 149) from the aldehyde model compound **3-H** is presented in black in all panels. (**a**) The computed IR spectrum of the *N,N*-dimethyl-hydroxycarbene **7-H**. (**b**) The computed spectrum of the *N,N*-dimethyl-aldehyde **6-H**. (**c**) The experimental IR spectrum of photofragment ions (*m*/*z* 149) exclusively generated from the hydroxycarbene **2-H$_t$** by IR photodissociation at 3553 cm^{-1}. The prominent mode at 800 cm^{-1} in the experimental spectra of *m*/*z* 149 relates to a combination of vibrations, *i.e.* H-C=C-H out of plane, NCCC-stretching and C-CO stretching modes. Calculated IR spectra were obtained at the dispersion-corrected B3LYP-GD3BJ/cc-pVTZ level of theory. Calculated frequencies are scaled by 0.97 and broadened using a Gaussian function with a FWHM of 25 cm^{-1} to facilitate comparison with experiment.[1–3]

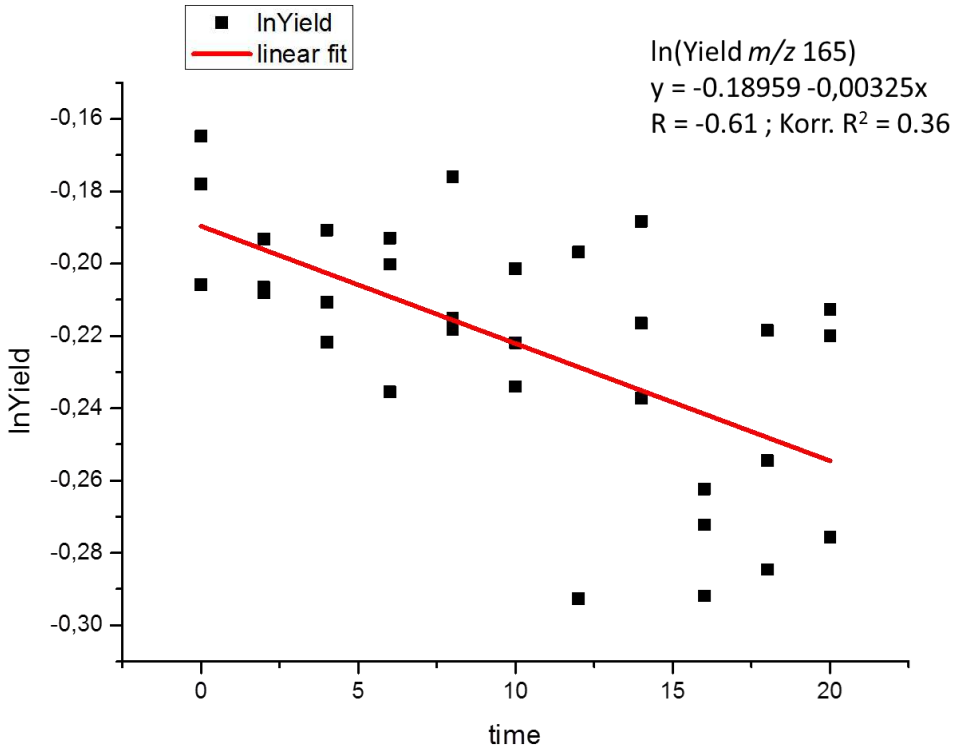


Supplementary Figure 6 | Comparison of experimental and calculated IR spectra for the deuterated analogues of the hydroxycarbene and aldehyde model compounds. (**a**) The calculated spectrum of the deuterated hydroxycarbene **2-D** (red) is compared to the experimental IR spectrum of product ions at *m*/*z* 165 generated by CO_2 loss from **1-D** (black; see Supplementary Table 3). (**b**) The calculated spectrum of (singlet) *trans*-hydroxycarbene **2-H$_t$** (blue) is compared to the experimental IR spectrum of the ion population at *m*/*z* 164 generated by CO_2 loss from **1-H** (black). (**c**) The experimental IR spectrum of the 4-(trimethylammonio)benzaldehyde model compound **3-H** is compared with the experimental IR spectrum of the deuterated 4-(trimethylammonio)benzaldehyde model compound **3-D** (see Supplementary Table 3). Calculated IR spectra were obtained at the dispersion-corrected B3LYP-GD3BJ/cc-pVTZ level of theory. Calculated frequencies are scaled by 0.97 and broadened using a Gaussian function with a FWHM of 25 cm^{-1} to facilitate comparison with experiment.[1–3]



Supplementary Figure 7 | Data analysis of the time-dependent measurement of the hydroxycarbene ion population **2-H$_t$** at *m*/*z* 164. The isomer-selective experiment is accomplished due to the exclusive resonance of **2-H$_t$** near 1300 cm^{-1} as Supplementary Figure 6b illustrates. The isomerization reaction from **2-H** to **3-H** obeys first order kinetics with k_H = 0.07316 ± 0.00258 s^{-1}. Accordingly, a half-life of **2-H$_t$** can be deduced $\mathbf{t_{1/2} = \ln 2 / k_H = 9.5 \pm 0.3\ s}$.

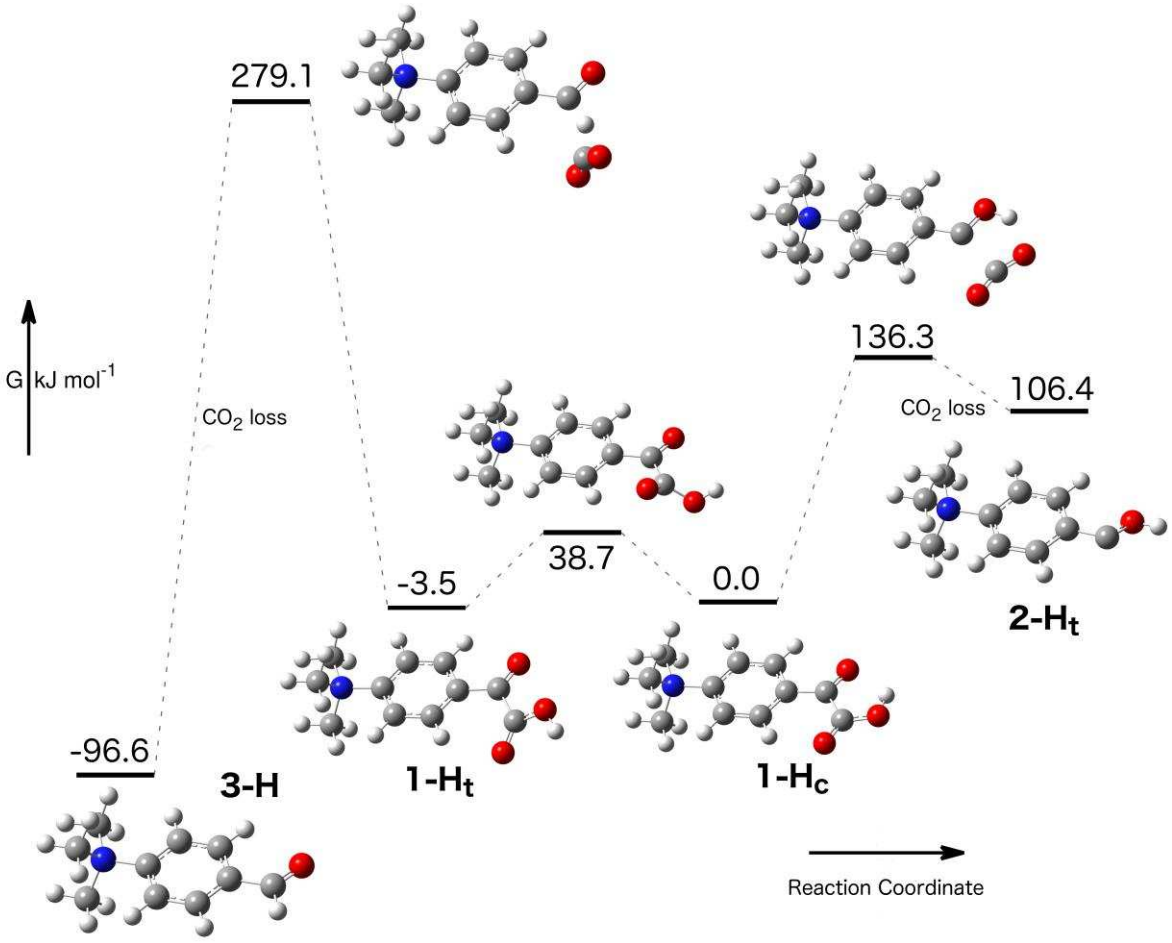
Linear fit: $y(x) = -0.51164 - 0.07316x$
Uncertainty of x: $\Delta x = \pm 0.00258$
$k_H = 0.07316 \pm 0.00258$



Supplementary Figure 8 | Data analysis of the time-dependent measurement of the deuterated hydroxycarbene ion population **2-D$_t$** at *m/z* 165. The isomer-selective experiment is accomplished due to the exclusive resonance of **2-D$_t$** near 1300 cm^{-1} as Supplementary Figure 6a illustrates. The isomerization reaction **2-D$_t$** → **3-D** is very slow **(2-D $t_{1/2}$ = 213 ± 50 s)** and substantially retarded compared to **2-H$_t$** → **3-H** (Supplementary Figure 7). From the time-dependent measurements a primary kinetic effect KIE can be approximated:

KIE = k_H / k_D = 0.07316 / 0.00325 = 22.51

Linear fit: $y(x) = -0.18959 - 0.00325x$
Uncertainty of x: $\Delta x = \pm 0.00075$
$k_D = 0.00325 \pm 0.00075$



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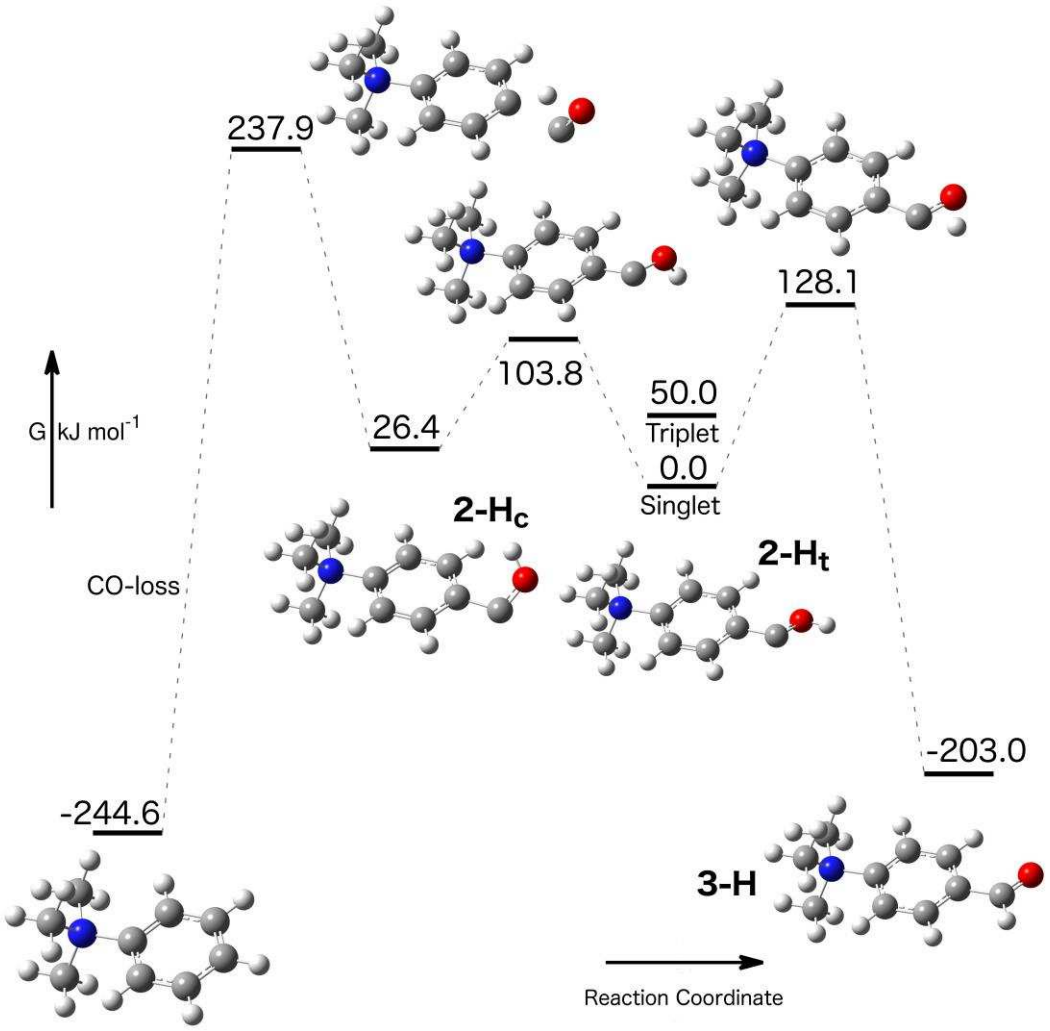
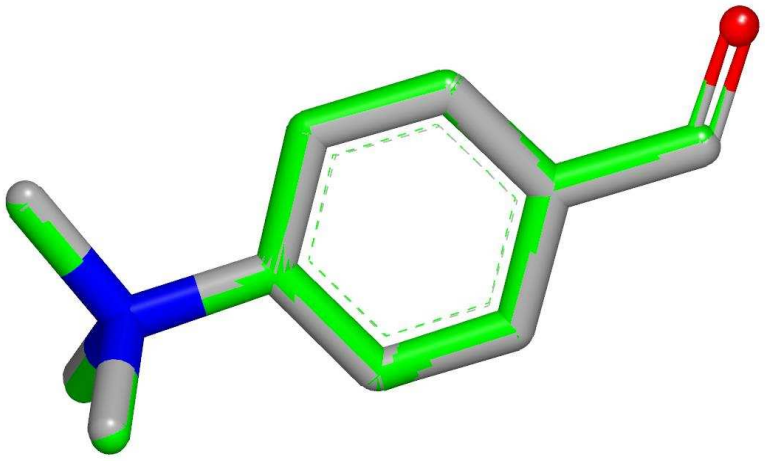
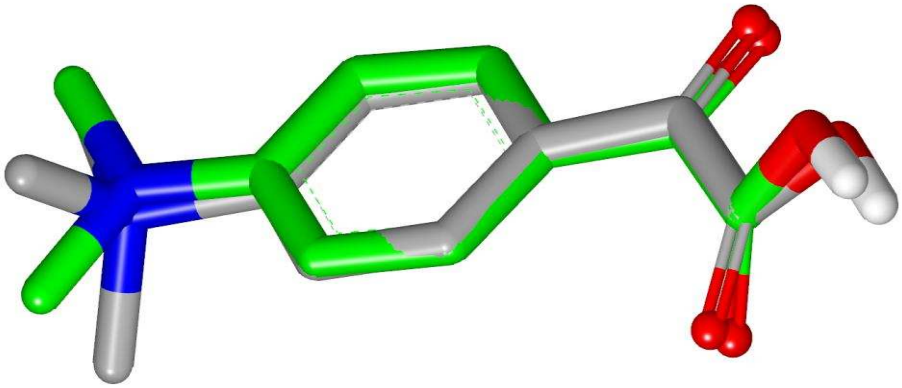


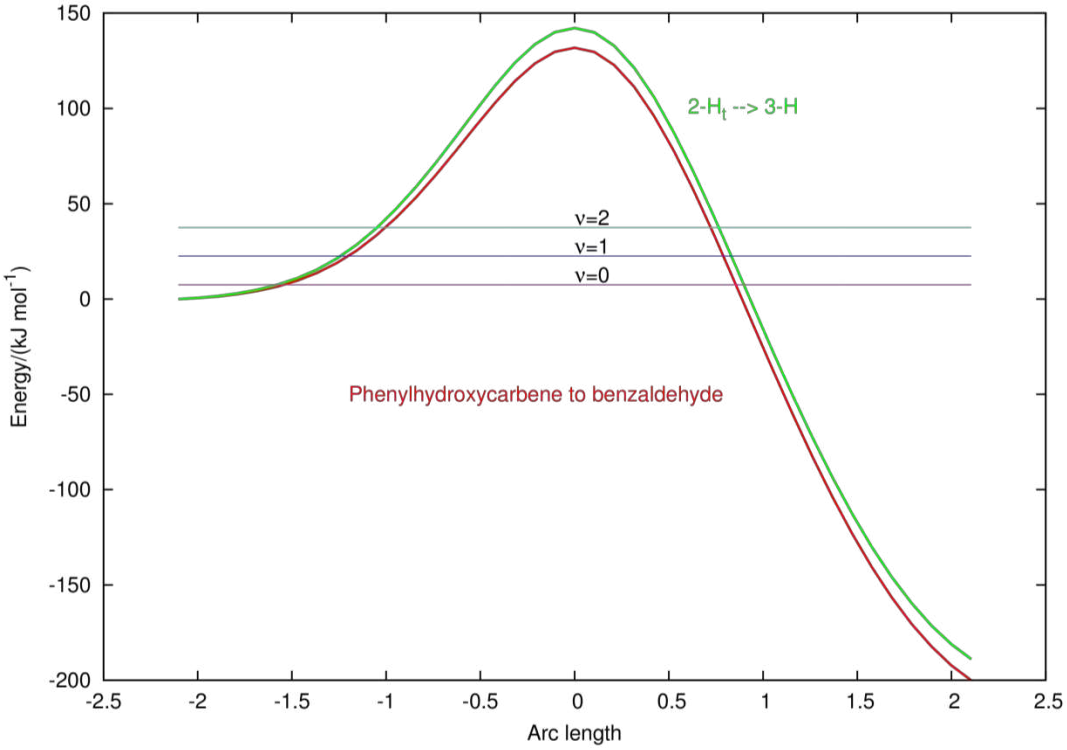
Supplementary Figure 10 | Gibbs energy profile for the conversion of **2-H$_t$** into **3-H**. All structures have been computed using dispersion-corrected DFT using the B3LYP-GD3BJ functional and the cc-pVTZ basis set.



Supplementary Figure 11 | Overlay between experimental crystal structure of 4-(trimethylammonio)benzaldehyde (**3-H**) (green) and its calculated structure (gray). Overlay generated using ROCS, part of the OpenEye Toolkit.[4,5]



Supplementary Figure 12 | Overlay between experimental crystal structure of [4-(Dimethylamino)phenyl]oxo(*O*-^{2}H)acetic acid (**S-2-D**) (green) and the calculated structure of oxo[4-(trimethylammonio)phenyl]acetic acid (**1-H**) (gray). Overlay generated using ROCS, part of the OpenEye Toolkit.[4,5]



Supplementary Figure 13 | Intrinsic reaction coordinate (IRC) profile for the conversion of **2-H$_t$** into **3-H** and the conversion of phenylhydroxycarbene into benzaldehyde.[6] The horizontal lines indicate the approximate positions of the vibrational energy levels associated with the conversion. Everything has been computed using dispersion-corrected DFT using the B3LYP-GD3BJ functional and the cc-pVTZ basis set with frequencies calculated at every step of the IRC process.

S2 Additional Tables

Supplementary Table 1 | The experimental and calculated IR band positions for **2-H_t/2-D_t** and **3-H/3-D**. Line positions are found to closely correspond to those found under cryogenic conditions for the analogous phenylhydroxycarbene/benzaldehyde systems.[6] All modes are listed in wavenumbers (cm^{-1}). A scaling factor of 0.97 is applied for the 800 – 2000 cm^{-1} spectral region. *A scaling factor of 0.95 is applied for the 2800 – 3700 cm^{-1} spectral region.[7] **R = $N(CH_3)_3$, R' = C-OH/D. [$]The pulse energy in this spectral region of the pulsed OPO used in this experiment was not sufficient for photodissociation of this ion.

	Theory		**Experiment**		**Theory**		**Experiment**	
Vibrational Mode	Aldehyde **3-H**	Carbene **2-H_t**	Aldehyde **3-H**	Carbene **2-H_t**	Aldehyde **3-D**	Carbene **2-D_t**	Aldehyde **3-D**	Carbene **2-D_t**
O-H/D stretch*	–	3555	–	3553	–	2589	–	–[$]
C=O stretch	1744	–	1722	–	1725	–	1700	–
H-C_{Ar}=C_{Ar}-H in-plane	1594	1588	–	1574	1594	1588	–	1573
H-C=C-R/R'**	1585	1578	–	1574	1585	1578	–	1573
N-CH_3 bend	1485	1462	1473	1476	1485	1485	1475	1472
HCC in-plane bend	1304	1310	–	1307	1310	1312	–	1310
C-OH/D stretch	–	1248	–	1247	–	1276	–	1276
C-OD bend	–	–	–	–	–	993	–	1001
H-C_{Ar} deformation	1196	–	1169	–	1169	–	1181	–
H/DOCC bend	–	1138	–	1146	–	1166	–	–
C-$N(CH_3)_3$ torsion	916	918	–	932	916	918	–	926
H/DOCC torsion	–	853	–	–	–	529	–	–
N-C_{Ar} stretch	834	825	834	831	823	820	–	818

Supplementary Table 2 | Summary of the most important energies and free energies calculated for this paper. All energies are in kJ mol^{-1}.

	2-H_t → 3-H	Phenylhydroxycarbene → Benzaldehyde	**2-D_t → 3-D**
$\Delta E^{‡}$ (B3LYP)+ ZPE (B3LYP)	127.67	117.23	131.82
$\Delta_r E$ (B3LYP)+ ZPE (B3LYP)	−205.09	−217.24	−203.06
$\Delta E^{‡}$ (CCSD(T)-F12b) + ZPE (B3LYP)	128.94	119.94	
$\Delta_r E$ (CCSD(T)-F12b) + ZPE (B3LYP)	−199.68	−211.31	
$\Delta G^{‡}$ (B3LYP)	128.09	117.64	128.55
$\Delta_r G$ (B3LYP)	−202.96	−216.29	−205.40

Supplementary Table 3 | Precursor ion species selected for the acquisition of the IR spectra presented. Major IRMPD product ions are presented in bold characters. *IR spectrum presented in Figure 1a; §IR spectrum presented in Supplementary Figure 6a; †IR spectrum presented in Figure 1c; ‡IR spectrum presented in Supplementary Figure 6c.

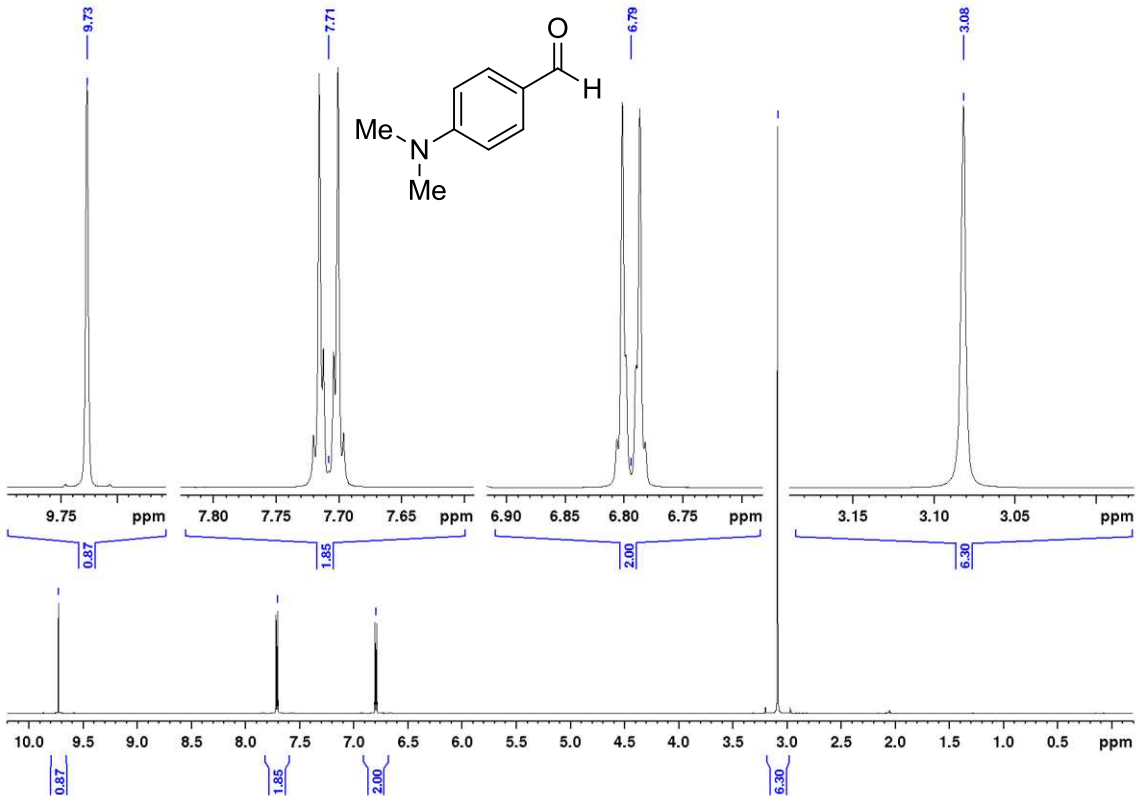
Precursor ion species	**IRMPD Product ions**	**Neutral loss**
2H & 3H (*m/z* 208 → ***m/z* 164**) *	**149.1** 136.2 121.3	15 Da (•CH_3) 28 Da (C_2H_4) 43 Da (C_2H_4 & •CH_3)
2D & 3D (*m/z* 209 → ***m/z* 165**) §	**150.1** 137.2 122.3	15 Da (•CH_3) 28 Da (C_2H_4) 43 Da (C_2H_4 & •CH_3)
3H (***m/z* 164**) †	**149.1** 148.1	15 Da (•CH_3) 16 Da (CH_4)
3D (***m/z* 165**) ‡	**150.1** 149.1 122.3	15 Da (•CH_3) 16 Da (CH_4) 43 Da (C_2H_4 & •CH_3)

S3 Synthesis of the Carbene Precursors and Reference Aldehydes

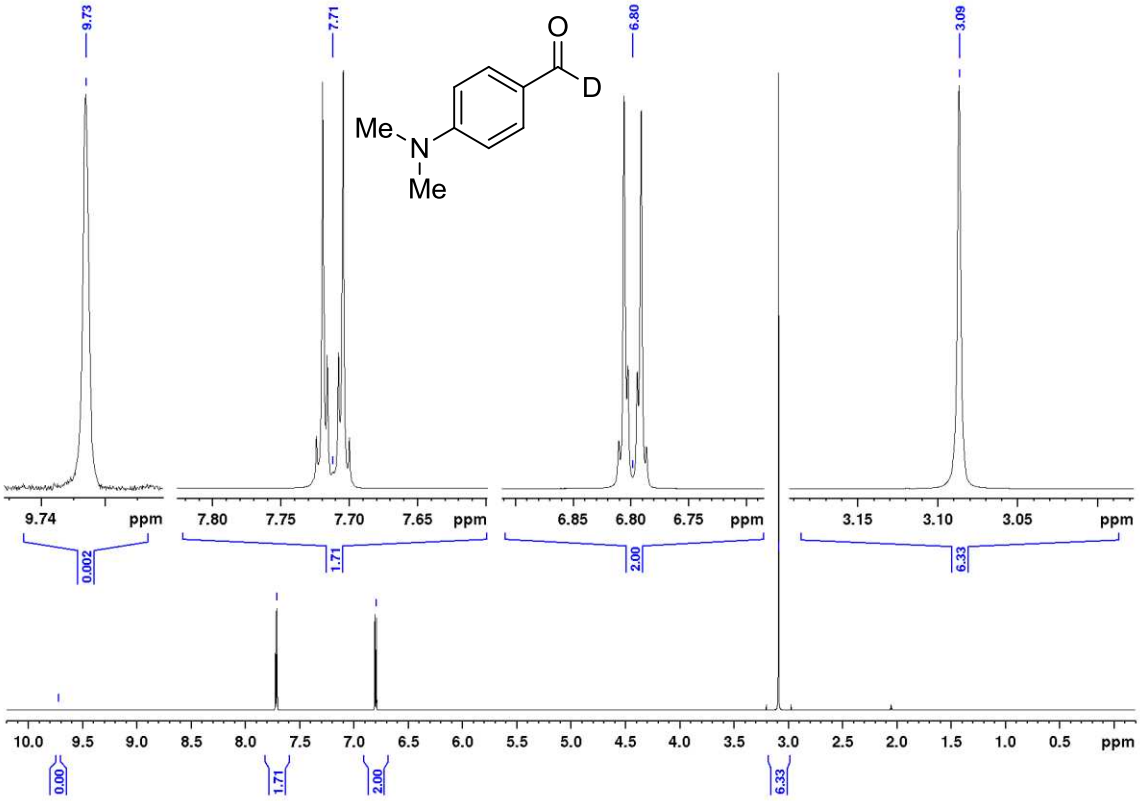
S3.1 General

The ester **S-1** was synthesized according to a literature known procedure.[8] The quaternization of the oxoacetic acid **S-2-H** and of its deuterated form **S-2-D** to give the ammonio oxoacetic acid **1-H-MeSO$_4$/SO$_4$** and the deuterated **1-D-MeSO$_4$/SO$_4$** was performed under argon atmosphere in a glovebox. Acetone-d_6, from glass ampules, was used as purchased. 4-(Dimethylamino)benzaldehyde (**S-3-H**) was purchased from Sigma-Aldrich, the deuterated form **S-3-D** was synthesized according to a literature known procedure.[9] For comparison of the ^{1}H and ^{13}C spectra see Supplementary Figure 14 to Supplementary Figure 17.

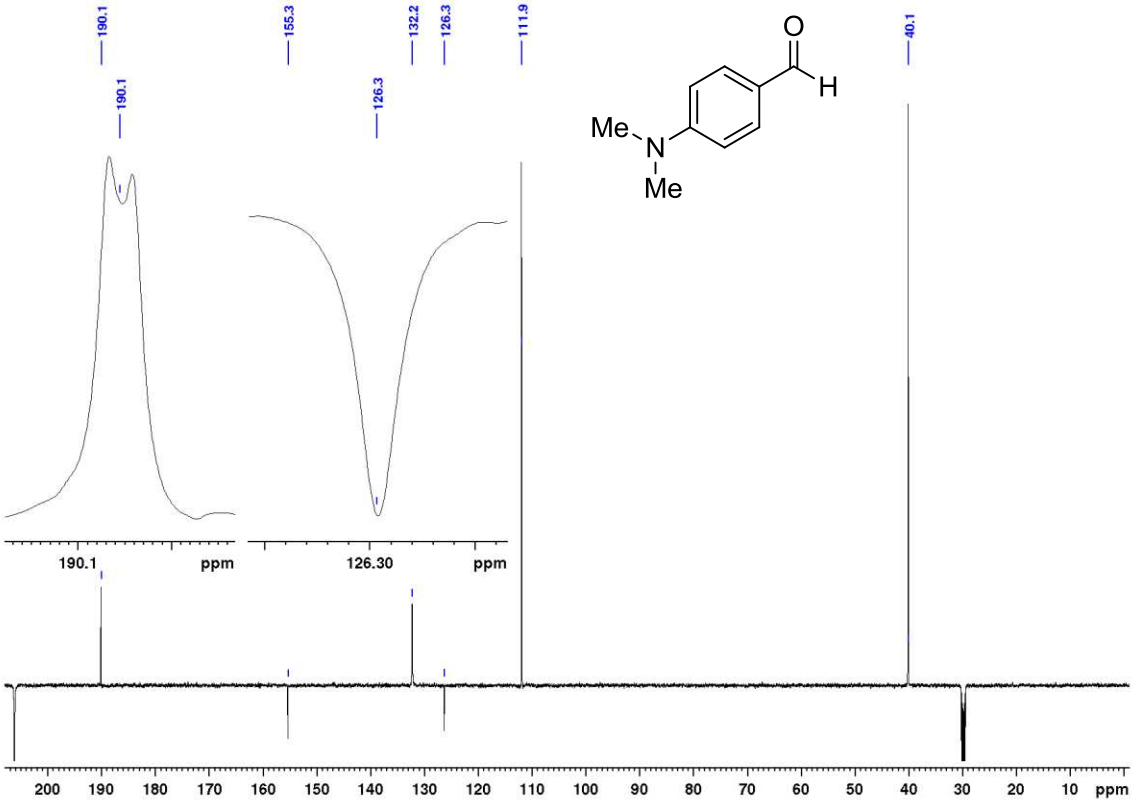
Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance II 600 instrument (^{1}H: 600.20 MHz, ^{13}C: 150.92 MHz) and on a Bruker AV 300 instrument (^{1}H: 300.13 MHz, ^{13}C: 75.46 MHz). Spectra were recorded at room temperature. Chemical shifts (δ) are reported in parts per million relative to tetramethylsilane (TMS) or solvent residual signals. The following abbreviations were used for chemical shift multiplicities in ^{1}H NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, mc = centered multiplet, br = broad.
HR-MS was performed on a ThermoFisher LTQ-Orbitrap XL instrument. Melting points were determined on a Büchi apparatus and are uncorrected.



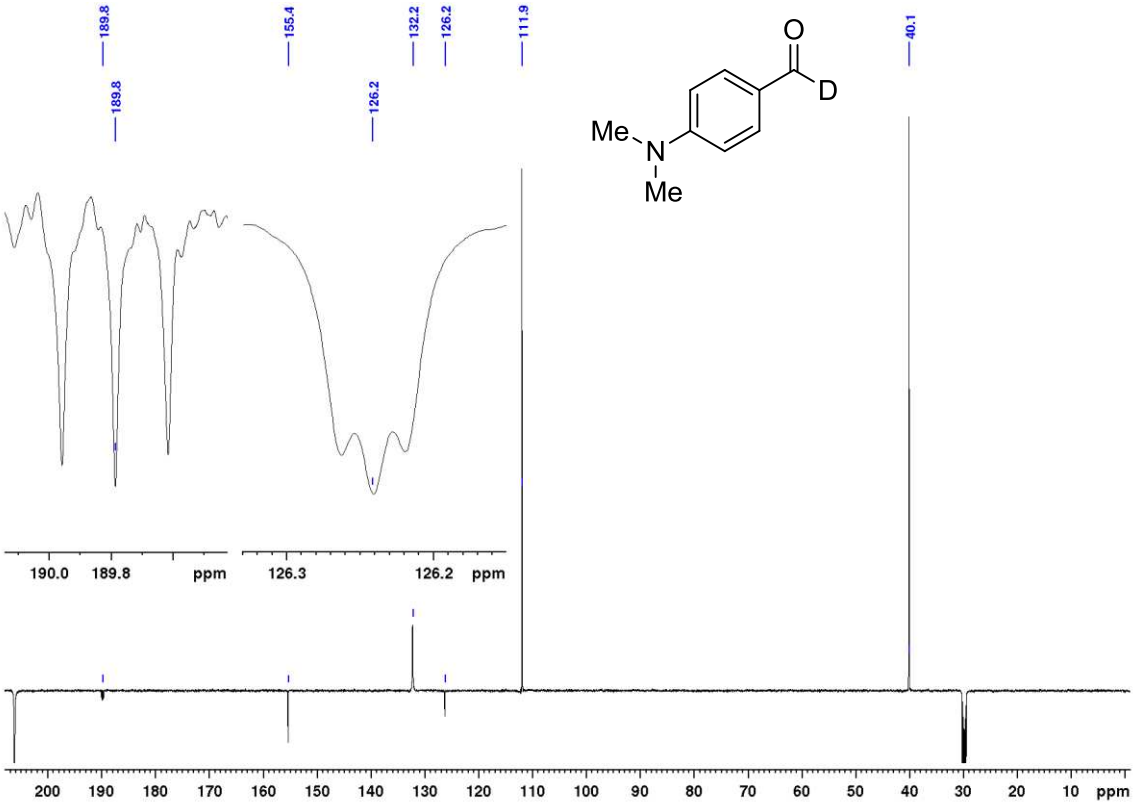
Supplementary Figure 14 | ^{1}H NMR spectrum of commercial **S-3-H** (600 MHz, acetone-d_6, 298 K).



Supplementary Figure 15 | ^{1}H NMR spectrum of **S-3-D** (600 MHz, acetone-d_6, 298 K).

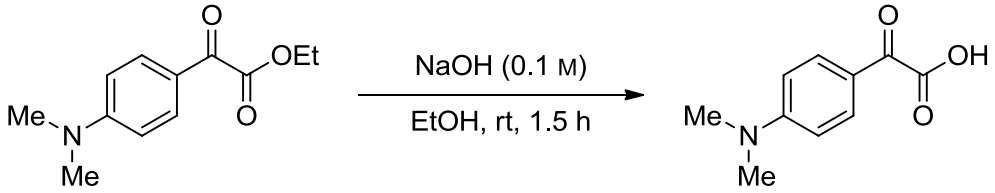


Supplementary Figure 16 | ^{13}C NMR spectrum of commercial **S-3-H** (151 MHz, acetone-d_6, 298 K).



Supplementary Figure 17 | ^{13}C NMR spectrum of **S-3-D** (151 MHz, acetone-d_6, 298 K).

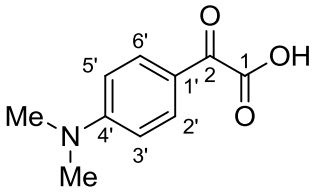
S3.2 [4-(Dimethylamino)phenyl]oxoacetic acid (S-2-H)



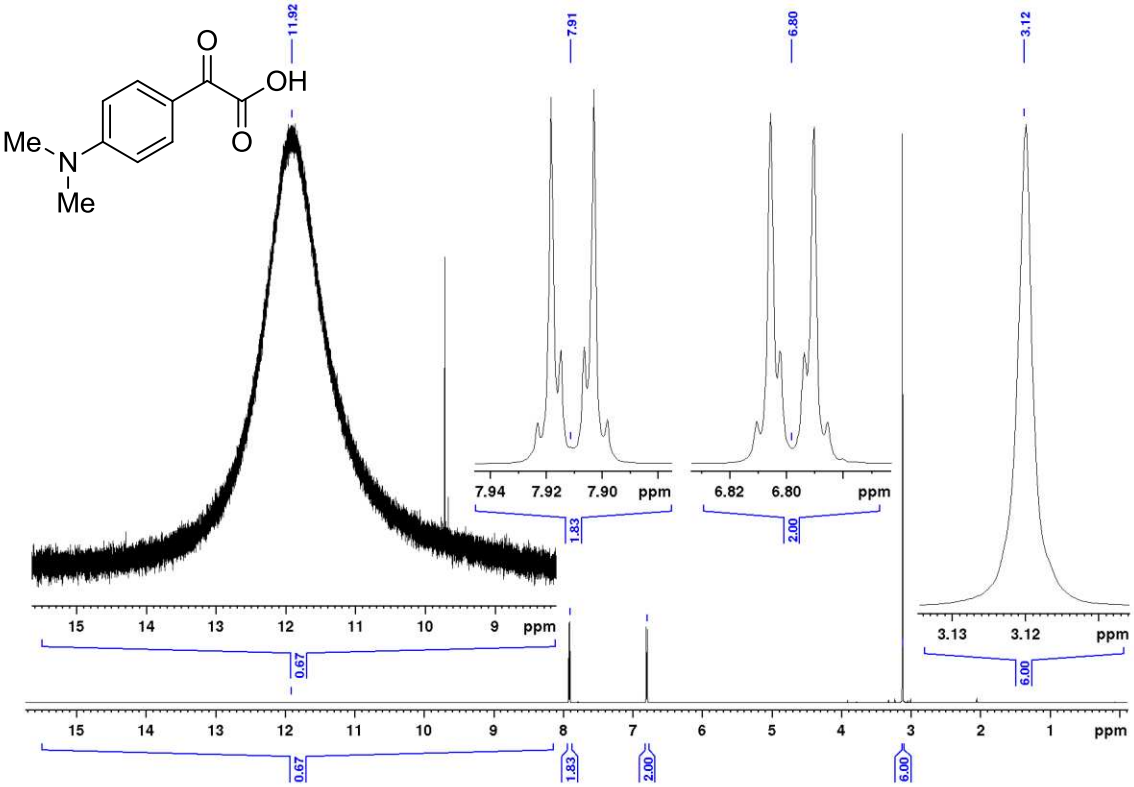
S-1 **S-2-H**, 91%

In a 250-mL-round bottom flask equipped with a magnetic stir bar, ethyl [4-(dimethylamino)phenyl]oxoacetate (**S-1**) (2.5 g, 11.31 mmol, 1.0 eq) was dissolved in ethanol (80 mL). Aqueous NaOH (80 mL, 0.1 M) was added, and the mixture was stirred for 1.5 h at room temperature. The mixture was then extracted with Et_2O (5 × 40 mL), and the ether extracts were discarded. The aqueous phase was acidified with sulfuric acid to pH 4, and then extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, and concentrated under reduced pressure. A green solid (0.920 g, 4.76 mmol, 42%) was obtained. Analytically pure material was obtained by recrystallization from methanol in 91% yield in the form of yellow plates.

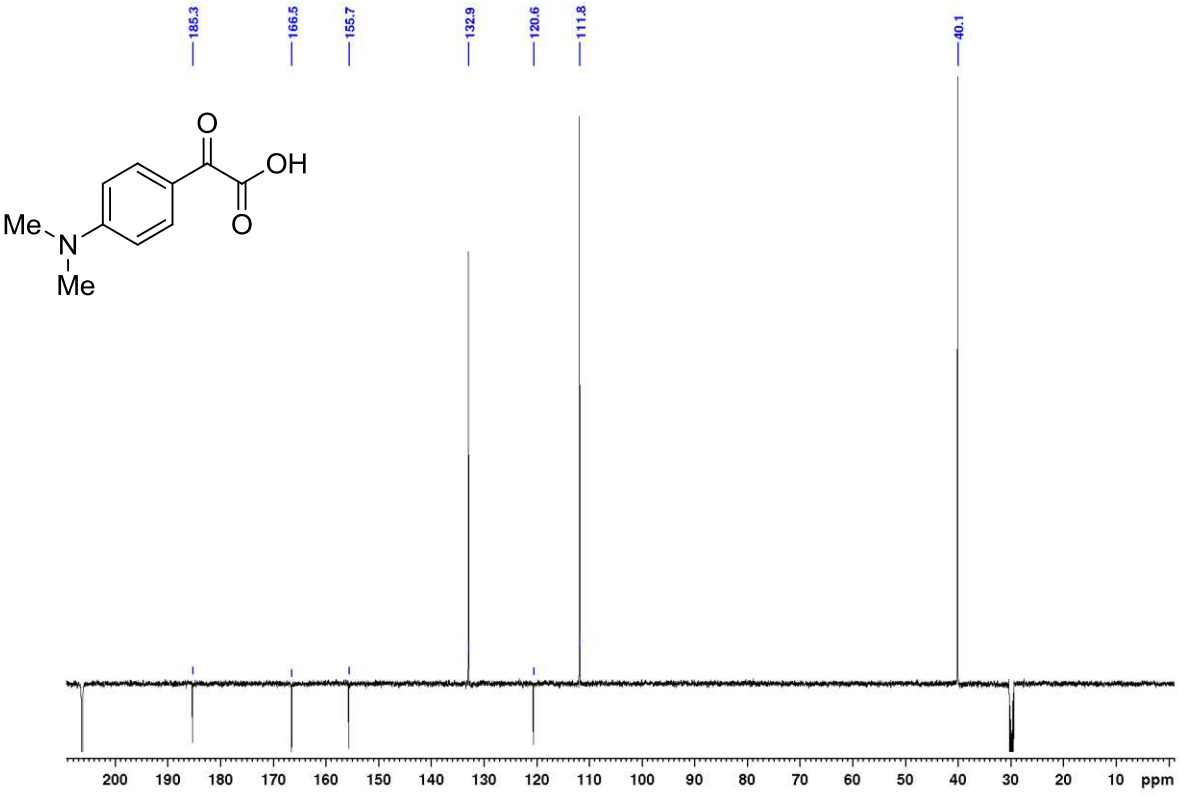
S-2-H: $C_{10}H_{11}NO_3$, M = 193.20 g mol^{-1}.
Yield: 0.920 g, 4.76 mmol, 42%.
m.p.: 186 °C, decomposition (lit.:[10] 186 – 187 °C, decomposition)
HR-ESI-MS: [$^m/_z$] of $[M]^+$:
calculated: 194.08117 amu
measured: 194.08129 amu
difference: −0.11597 ppm
FT-IR: (ATR): $\tilde{\nu}$ [cm^{-1}] = 2361 (m), 1719 (m), 1622 (m), 1560 (s), 1524 (s), 1460 (m), 1437 (m), 1387 (m), 1308 (m), 1231 (s), 1157 (s), 1063 (m), 939 (m), 833 (s), 800 (s), 773 (s), 739 (m), 691 (m), 662 (m).
EA: calc. (found) [%]: C: 62.17 (62.17), H: 5.74 (5.79), N: 7.25 (7.21).



^{1}H NMR (600 MHz, acetone-d_6, 298 K) δ [ppm] = 11.92 (brs, 1H, OH), 7.91 (mc, 4H, H-2',6'), 6.80 (mc, 4H, H-3',5'), 3.12 (s, 6H, NMe_2).
^{13}C NMR (151 MHz, acetone-d_6, 298 K) δ [ppm] = 185.3 (1C, C-2), 166.5 (1C, C-1), 155.7 (1C, C-1'), 132.9 (2C, C-2',6'), 120.6 (1C, C-4'), 111.8 (2C, C-3',5'), 40.1 (2C, NMe_2).

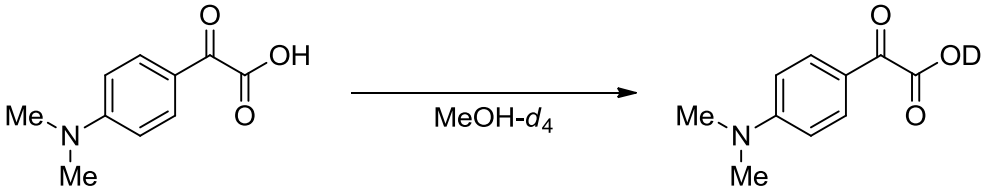


Supplementary Figure 18 | ^{1}H NMR spectrum of **S-2-H** (600 MHz, acetone-d_6, 298 K).



Supplementary Figure 19 | Multiplicity-edited ^{13}C DEPTQ NMR spectrum of **S-2-H** (151 MHz, acetone-d_6, 298 K).

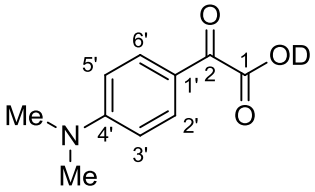
S3.3 [4-(Dimethylamino)phenyl]oxo(*O*-^{2}H)acetic acid (S-2-D)



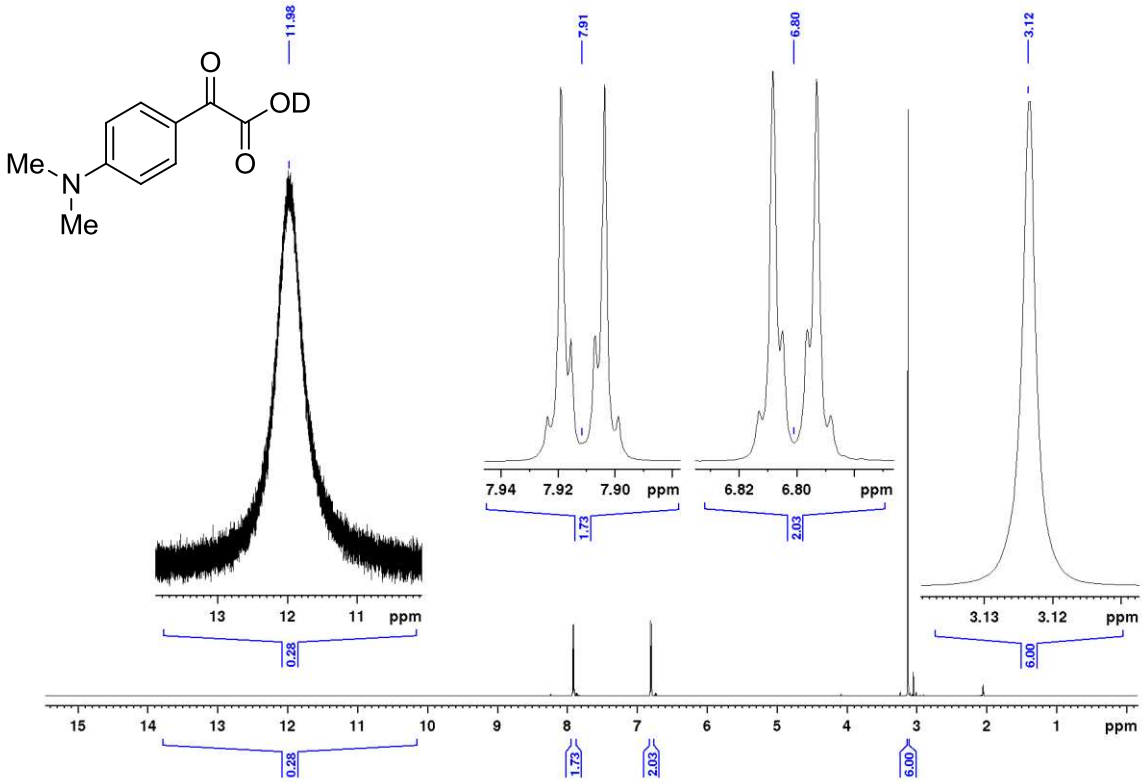
S-2-H **S-2-D**, 98%

[4-(Dimethylamino)phenyl]oxoacetic acid (**S-2-H**) (51.5 mg, 0.267 mmol) was dissolved in methanol-d_4 (1.0 mL) with heating. After cooling to room temperature, crystals (suitable for X-ray crystallography) separated and the solvent was evaporated under reduced pressure. This procedure was repeated four times to afford the deuterated acid **S-2-D** (50.5 mg, 0.260 mmol, 98% yield).

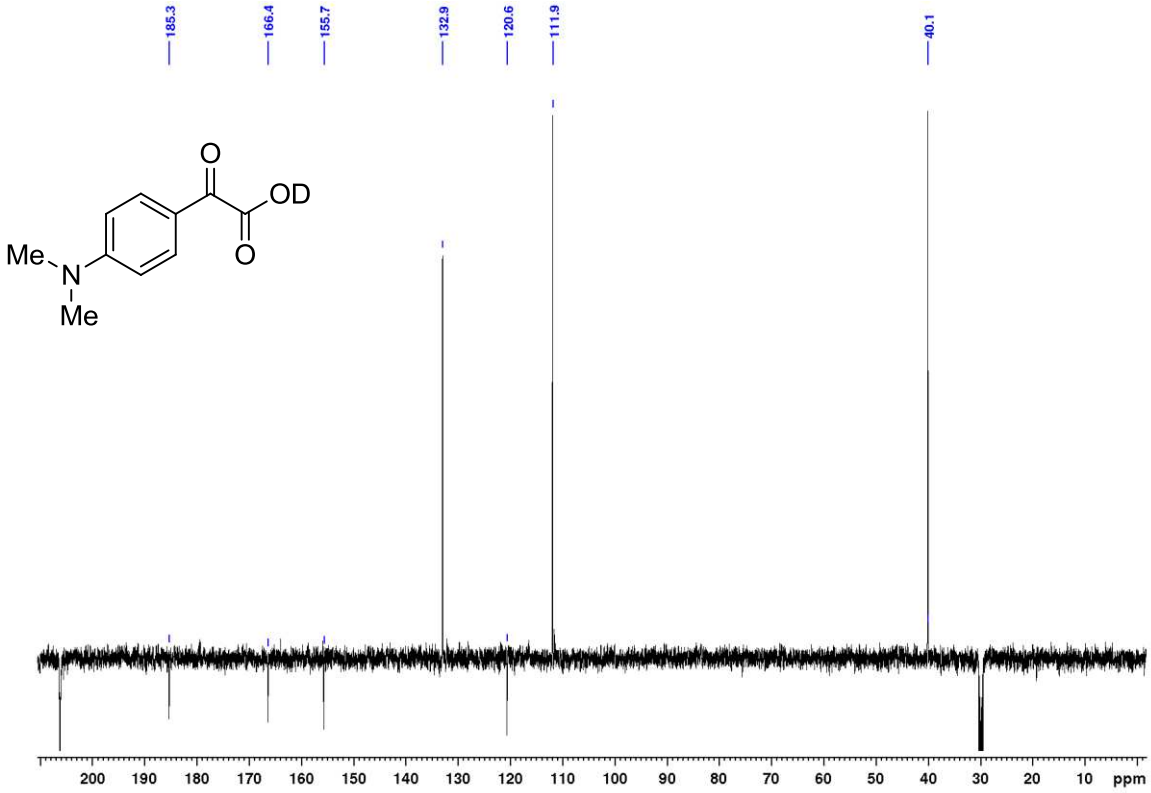
S-2-D: $C_{10}H_{10}DNO$, M = 194.21 g mol^{-1}.
Yield: 50.5 mg, 0.260 mmol, 98%.



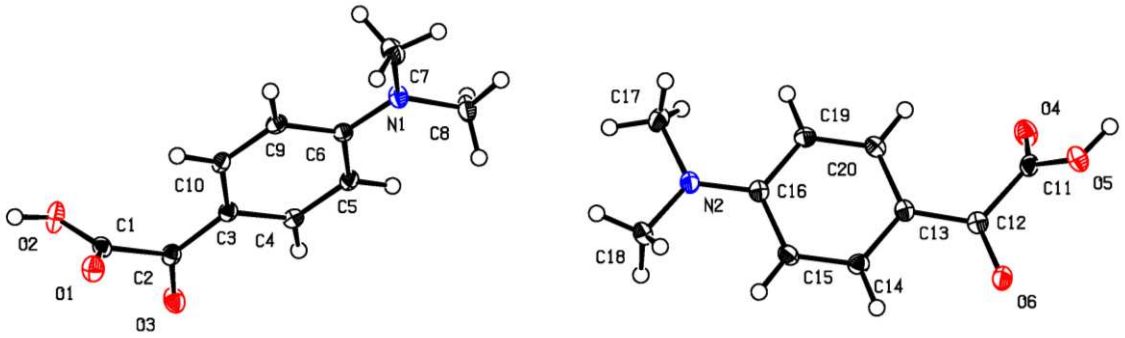
^{1}H NMR (600 MHz, acetone-d_6, 298 K) δ [ppm] = 11.98 (brs, residual OH), 7.91 (mc, 4H, H-2',6'), 6.80 (mc, 4H, H-3',5'), 3.12 (s, 6H, NMe_2).
^{13}C NMR (151 MHz, acetone-d_6, 298 K) δ [ppm] = 185.3 (1C, C-2), 166.4 (1C, C-1), 155.7 (1C, C-1'), 132.9 (2C, C-2',6'), 120.6 (1C, C-4'), 111.9 (2C, C-3',5'), 40.1 (2C, NMe_2).



Supplementary Figure 20 | ^{1}H NMR spectrum of **S-2-D** (600 MHz, acetone-d_6, 298 K).



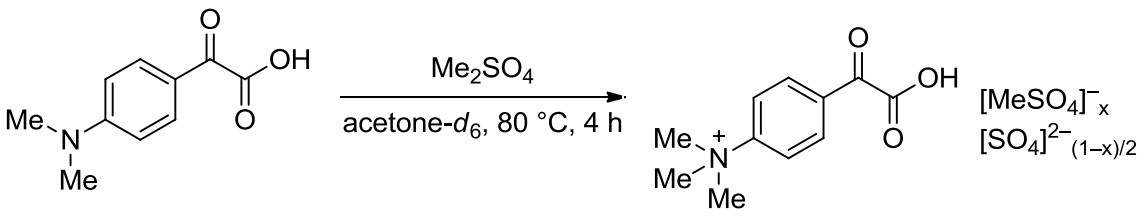
Supplementary Figure 21 | Multiplicity-edited ^{13}C DEPTQ NMR spectrum of **S-2-D** (151 MHz, acetone-d_6, 298 K).



Supplementary Figure 22 | ORTEP of the X-ray crystal structure of **S-2-D**. Thermal ellipsoids are drawn at 50% probability level. CCDC 1469242.

Formula	$C_{10}H_{10}DNO_3$
Formula weight	193.20
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 20.0813(6) Å α = 90°
	b = 7.5198(2) Å β = 91.5650(10)°
	c = 12.1237(3) Å γ = 90°
Volume	1830.09(9) $Å^3$
Z	8
Density (calculated)	1.402 g cm^{-3}
Absorption coefficient	0.870 mm^{-1}
F(000)	816
Crystal size	0.300 × 0.200 × 0.070 mm^{-3}
Θ range for data collection	4.405 to 72.191°
Index ranges	−24 ≤ h ≤ 24, −9 ≤ k ≤ 9, −13 ≤ l ≤ 14
Reflections collected	49049
Independent reflections	3606 [R(int) = 0.0311]
Completeness to Θ = 67.679°	99.8%
Absorption correction	Multiscan
Max. and min. transmission	0.7536 and 0.6085
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3606 / 0 / 266
Goodness-of-fit on F^2	1.148
Final R indices [I > 2σ(I)]	R1 = 0.0354, wR2 = 0.0949
R indices (all data)	R1 = 0.0388, wR2 = 0.1038
Extinction coefficient	0.0141(7)
Largest diff. peak and hole	0.426 and −0.473 e $Å^{-3}$

S3.4 Oxo[4-(trimethylammonio)phenyl]acetic acid methyl sulfate / sulfate (1:x:y) (1-H-$MeSO_4/SO_4$)



S-2-H **1-H-$MeSO_4/SO_4$**

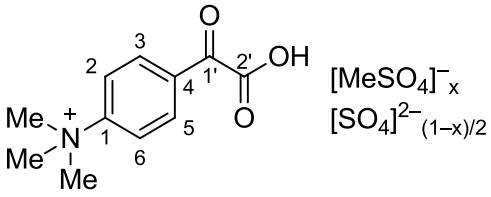
In a glovebox, a NMR tube was charged with [4-(dimethylamino)phenyl]oxoacetic acid (**S-2-H**) (20 mg, 0.103 mmol, 1 eq), and acetone-d_6 (0.4 mL) was added. The tube was sealed with a septum, and dimethyl sulfate (19.54 µL, 0.206 mmol, 2.0 eq) was added with a syringe. The tube was placed in an oil bath and heated to 80 °C for 4 h. The reaction was monitored by ^{1}H and ^{13}C NMR. After 4 h, the optimal ratio of *N*-methylation product **1-H** *vs.* remaining starting material / decomposition was reached (see Supplementary Figure 23 to Supplementary Figure 28 for NMR spectra). After cooling to room temperature, the reaction mixture was filtered and diluted with methanol for MS analysis as described in section S1.1.
Methylating agents other than dimethyl sulfate gave inferior results: Methyl iodide did not react with **S-2-H**. The Meerwein salt Me_3OBF_4 and methyl triflate afforded mixtures containing additionally the ammonio methyl ester.

1-H-$MeSO_4/SO_4$: $C_{12}H_{17}NO_7S$, M = 319.33 g mol^{-1},
$C_{22}H_{28}N_2O_{10}S$, M = 512.53 g mol^{-1}.

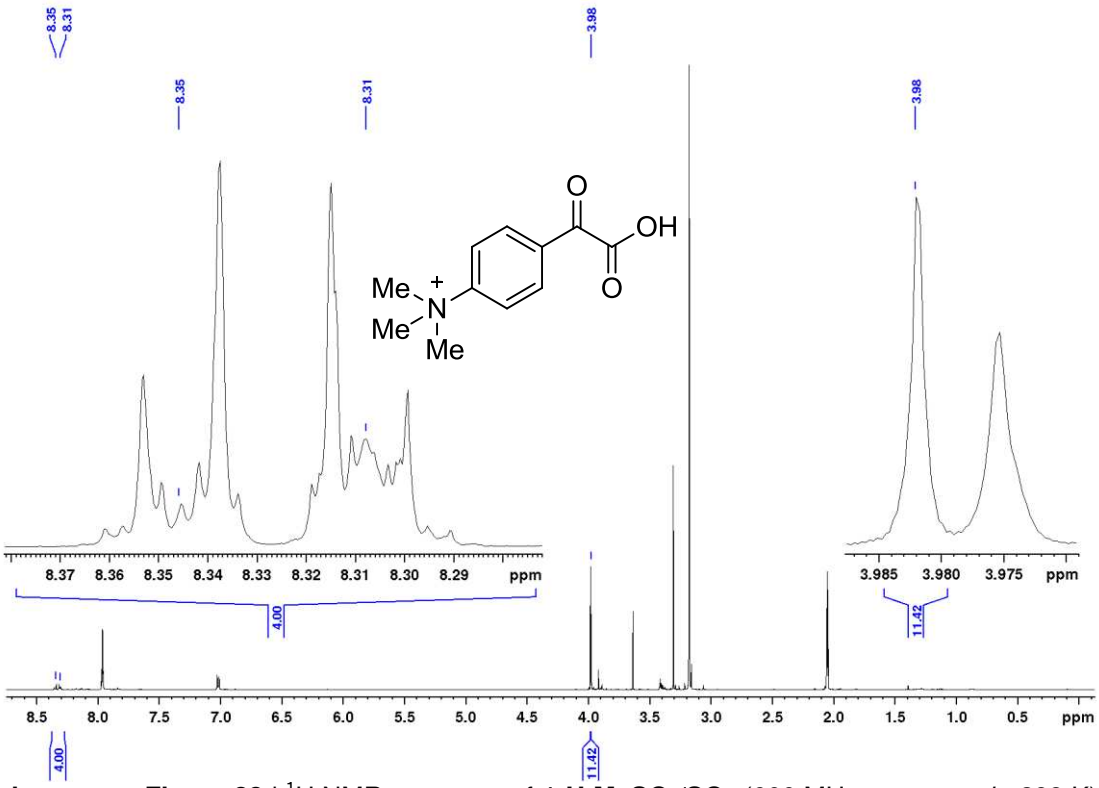
Yield: n.a.

HR-ESI-MS:

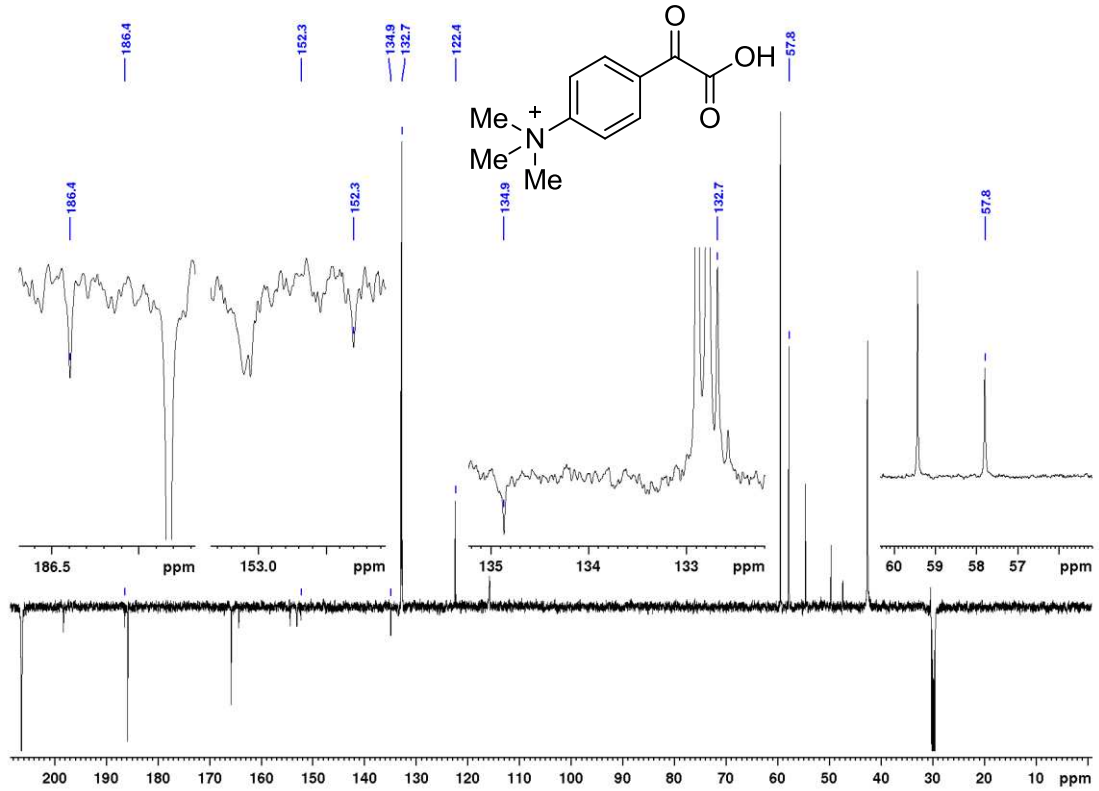
$[^m/_z]$ of $[M]^+$:	$[^m/_z]$ of $[Carbene]^+$:
calculated: 208.0968 amu	calculated: 164.1070 amu
measured: 208.0953 amu	measured: 164.1053 amu
difference: +1.57 ppm	difference: +1.69 ppm



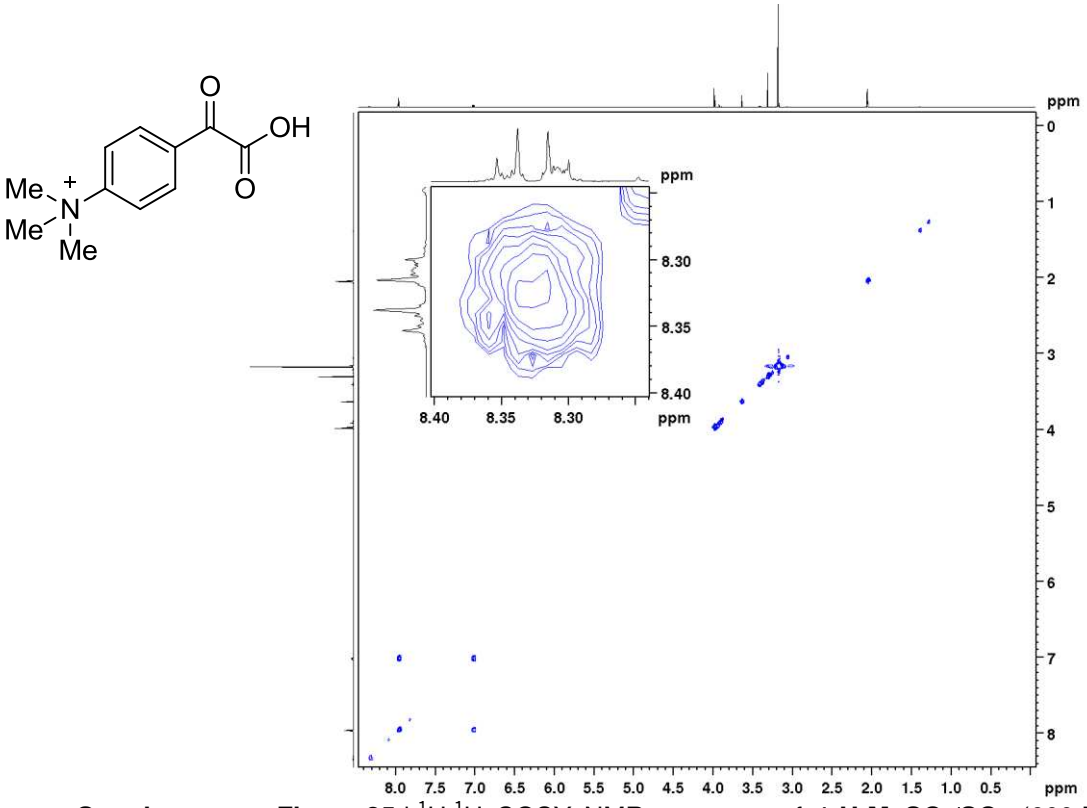
^{1}H NMR (600 MHz, acetone-d_6, 298 K) δ [ppm] = 8.35 (mc, 2H, H-2,6), 8.31 (mc, 2H, H-3,5), 3.98 (s, 9H, NMe_3).
^{13}C NMR (151 MHz, acetone-d_6, 298 K) δ [ppm] =186.4 (1C, C-1'), 152.3 (1C, C-1), 134.9(1C, C-4), 132.7 (2C, C-3,5), 122.4 (2C, C-2,6), 57.8 (3C, NMe_3).



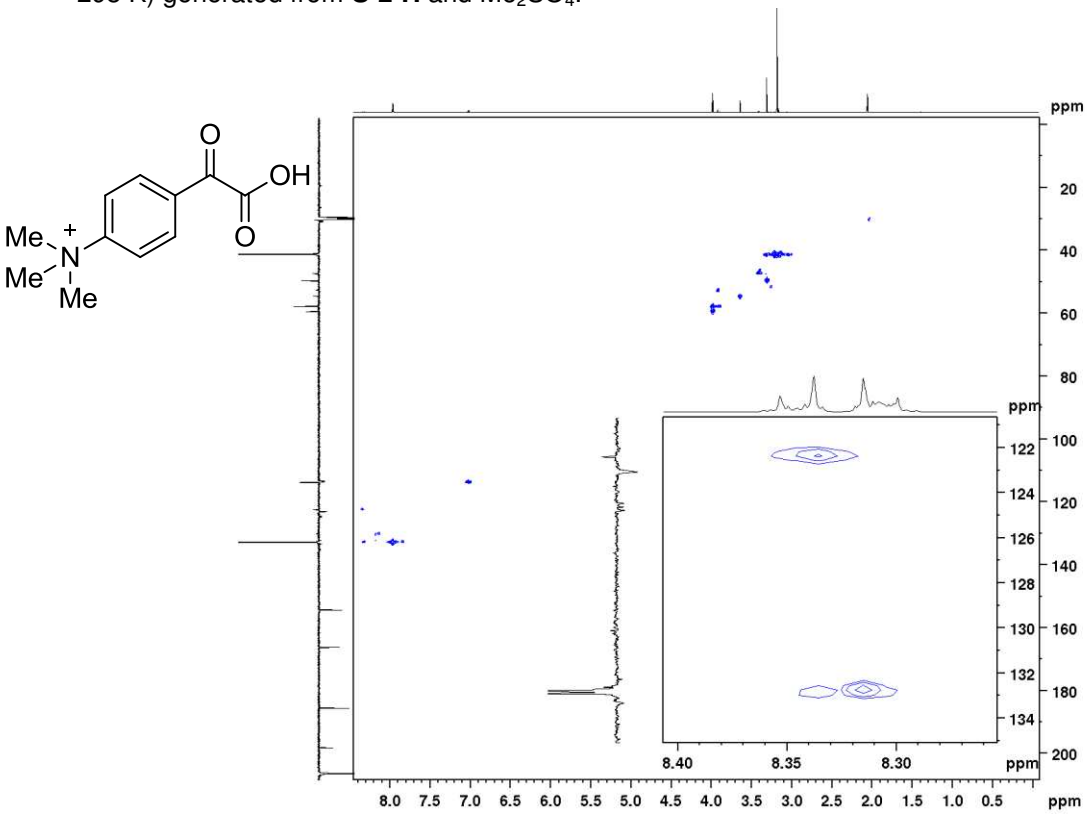
Supplementary Figure 23 | ^{1}H NMR spectrum of **1-H-MeSO$_4$/SO$_4$** (600 MHz, acetone-d_6, 298 K) generated from **S-2-H** and Me_2SO_4. The **1-H-MeSO$_4$/SO$_4$** to **S-2-H** ratio in this spectrum is 1:4.



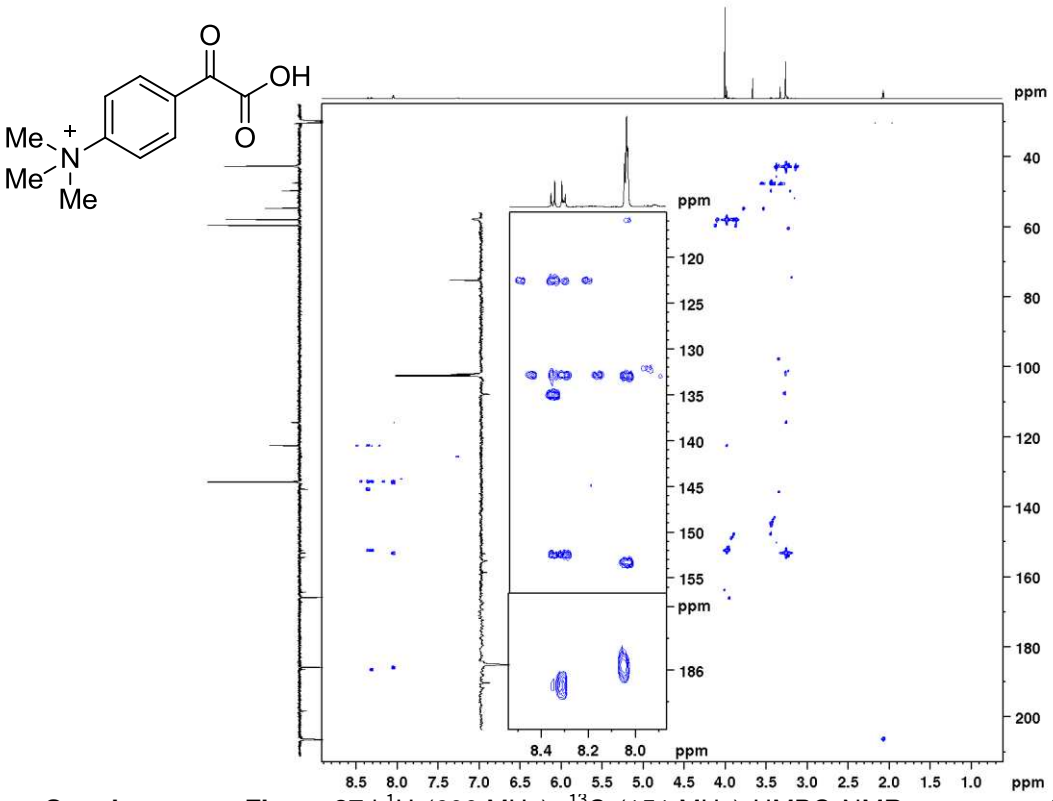
Supplementary Figure 24 | Multiplicity-edited ^{13}C DEPTQ NMR spectrum of **1-H-MeSO$_4$/SO$_4$** (151 MHz, acetone-d_6, 298 K) generated from **S-2-H** and Me_2SO_4.



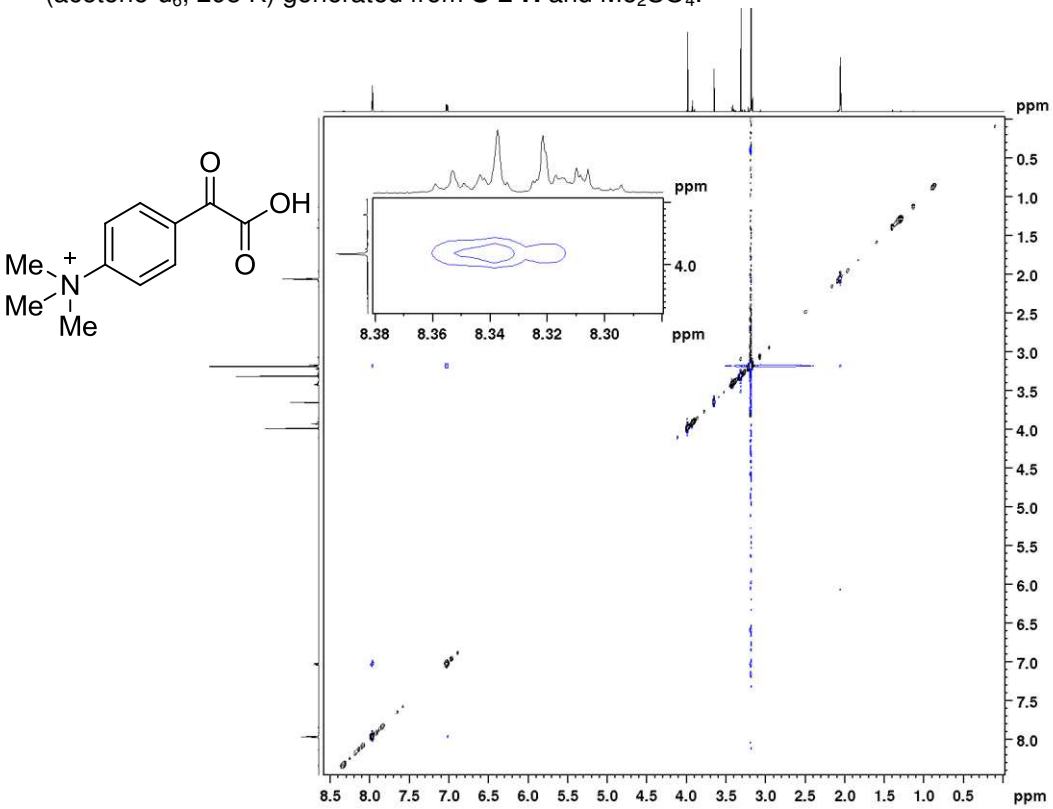
Supplementary Figure 25 | ^{1}H,^{1}H COSY NMR spectrum of **1-H-MeSO$_4$/SO$_4$** (600 MHz, acetone-d_6, 298 K) generated from **S-2-H** and Me_2SO_4.



Supplementary Figure 26 | ^{1}H (600 MHz), ^{13}C (151 MHz) HMQC NMR spectrum of **1-H-MeSO$_4$/SO$_4$** (acetone-d_6, 298 K) generated from **S-2-H** and Me_2SO_4.

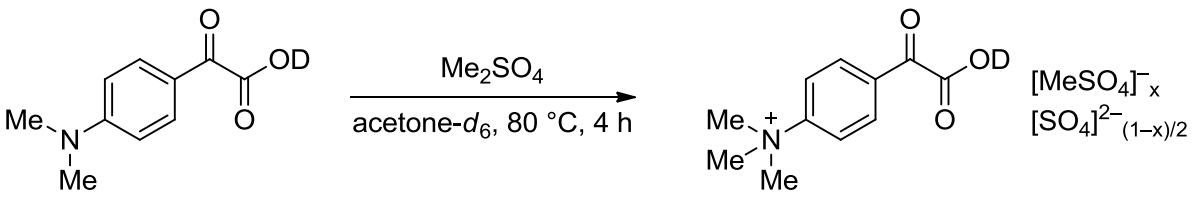


Supplementary Figure 27 | ^{1}H (600 MHz), ^{13}C (151 MHz) HMBC NMR spectrum of **1-H-MeSO$_4$/SO$_4$** (acetone-d_6, 298 K) generated from **S-2-H** and Me_2SO_4.



Supplementary Figure 28 | ^{1}H,^{1}H NOESY NMR spectrum of **1-H-MeSO$_4$/SO$_4$** (600 MHz, acetone-d_6, 298 K, mixing time = 600 ms) generated from **S-2-H** and Me_2SO_4.

S3.5 Oxo[4-(trimethylammonio)phenyl](*O*-^{2}H)acetic acid methyl sulfate / sulfate (1:x:y) (1-D-MeSO$_4$/SO$_4$)



S-2-D **1-D-MeSO$_4$/SO$_4$**

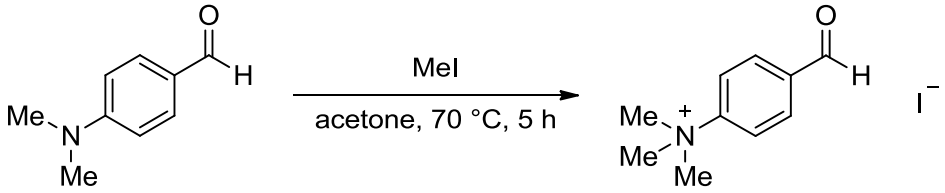
Using the same procedure as in section S4.4 [4-(dimethylamino)phenyl]oxo(*O*-^{2}H)acetic acid (**S-2-D**) (20 mg, 0 103 mmol, 1 eq) and dimethyl sulfate (9.77 µL, 0.103 mmol, 1.0 eq) were reacted in acetone-d_6 (0.4 mL) in an oil bath at 80 °C for 4 h. The reaction was monitored by NMR, and the solution was used for the IRMPD measurements as described for **1-H-MeSO$_4$/SO$_4$**.

1-D-MeSO$_4$/SO$_4$: $C_{12}H_{16}DNO_7S$, M = 320.37 g mol^{-1},
$C_{22}H_{26}D_2N_2O_{10}S$, M = 514.54 g mol^{-1}.

Yield: n.a.

HR-ESI-MS: [$^m/_z$] of $[M]^+$ ($C_{11}H_{13}DNO_3$):
calculated: 209.10310 amu
measured: 209.10355 amu
difference: +0.45319 ppm

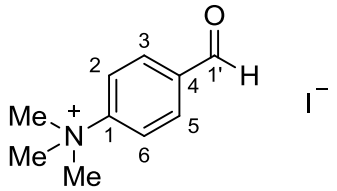
S3.6 4-(Trimethylammonio)benzaldehyde iodide (3-H-I)



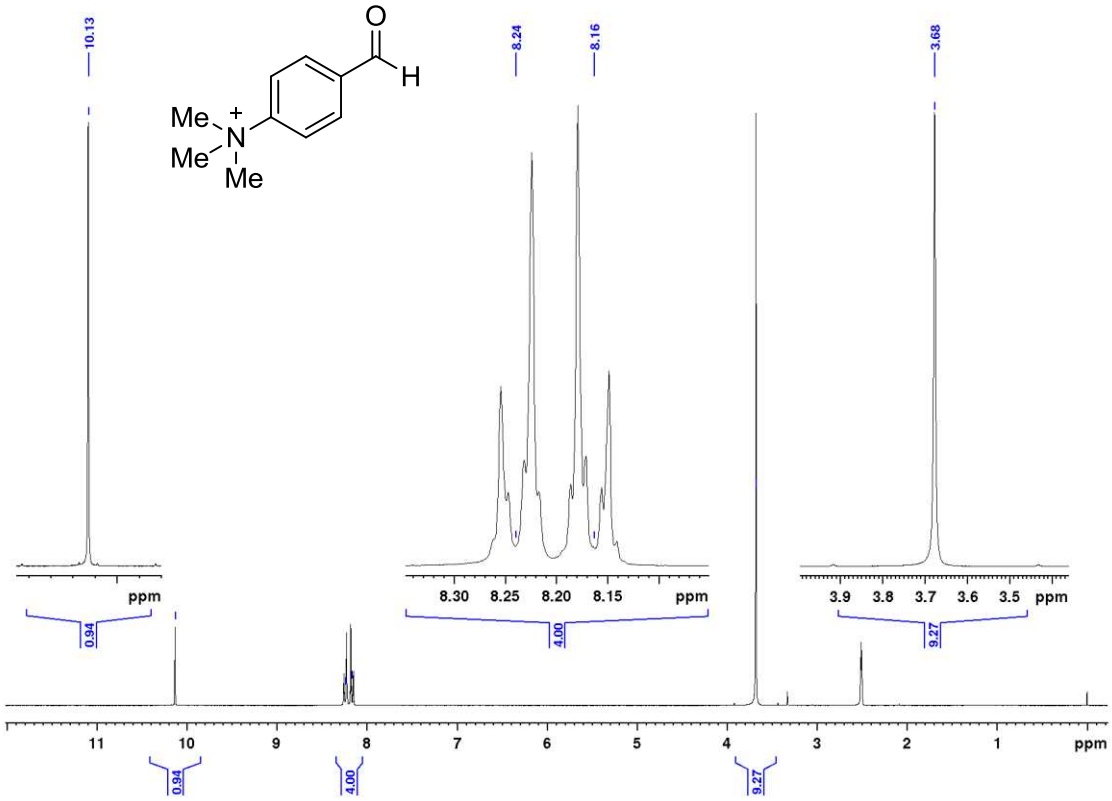
S-3-H **3-H-I**, 18%

In a screw-capped vial equipped with a magnetic stir bar, 4-(dimethylamino)benzaldehyde (**S-3-H**) (2.5711 g, 17.23 mmol, 1 eq) was dissolved in acetone (9.0 mL), and iodomethane (3.27 mL, 51.7 mmol, 3 eq) was added. The vial was closed tightly and the mixture was heated to 70 °C in an oil bath for 5 h. After cooling to room temperature, the yellow suspension was filtered through a glass frit. The colorless crystalline solid was washed with diethyl ether, and dried *in vacuo* to give crystalline 4-(trimethylammonio)benzaldehyde iodide (**3-H-I**) (0.917 g, 3.15 mmol, 18%), suitable for x-ray crystal structure determination.

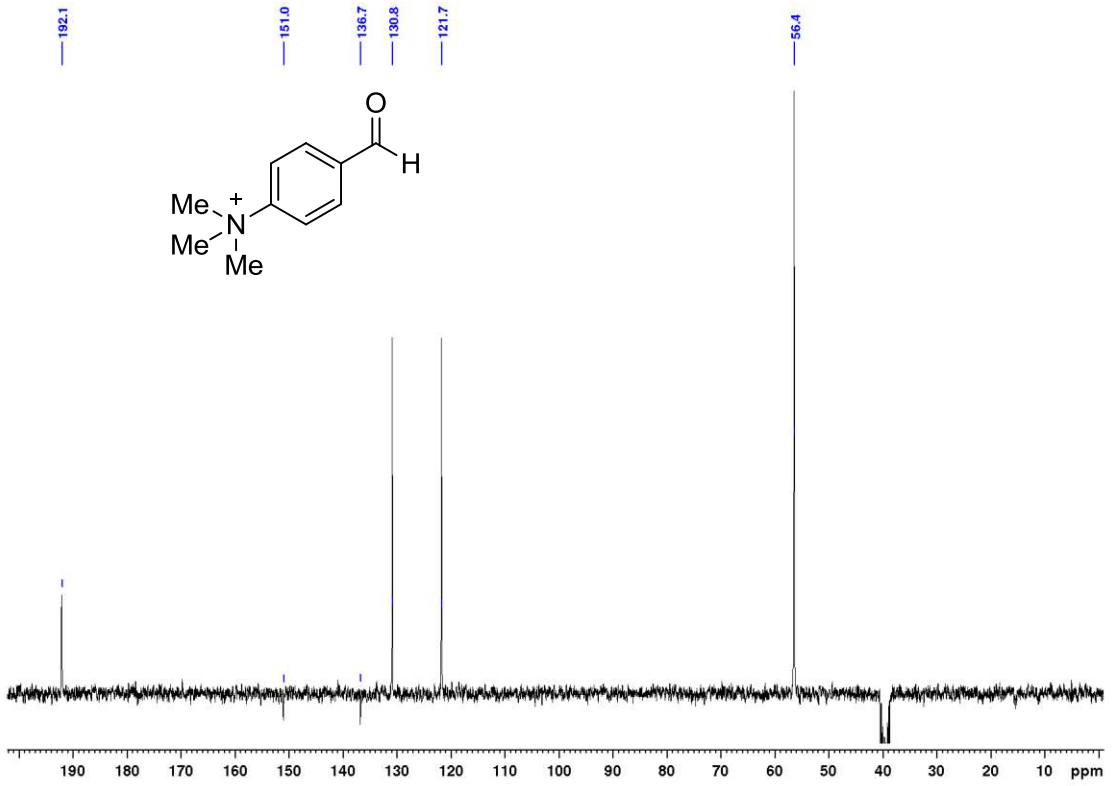
3-H-I: $C_{10}H_{14}INO$, M = 291.13 g mol^{-1}.
Yield: 0.917 g, 3.15 mmol, 18% (lit.:[11] 94%).
m.p.: 161 – 163 °C (lit.:[11] 168 – 169 °C)
HR-ESI-MS: [$^{m}/_{z}$] of $[M]^+$ ($C_{10}H_{14}NO$):
calculated: 164.10699 amu
measured: 164.10698 amu
difference: –0.00681 ppm
FT-IR: (ATR): $\tilde{\nu}$ [cm^{-1}] = 3134 (w), 3113 (w), 3046 (w), 3016 (m), 3003 (m), 1701 (s), 1600 (m), 1493 (m), 1476 (m), 1452 (w), 1400 (w), 1321 (m), 1308 (m), 1225 (m), 1178 (s), 1117 (m), 1015 (w), 961 (s), 939 (s), 856 (s), 827 (s), 704 (s), 631 (m).
EA: calc. (found) [%]: C: 41.26 (41.57), H: 4.85 (4.95), N: 4.81 (4.68).



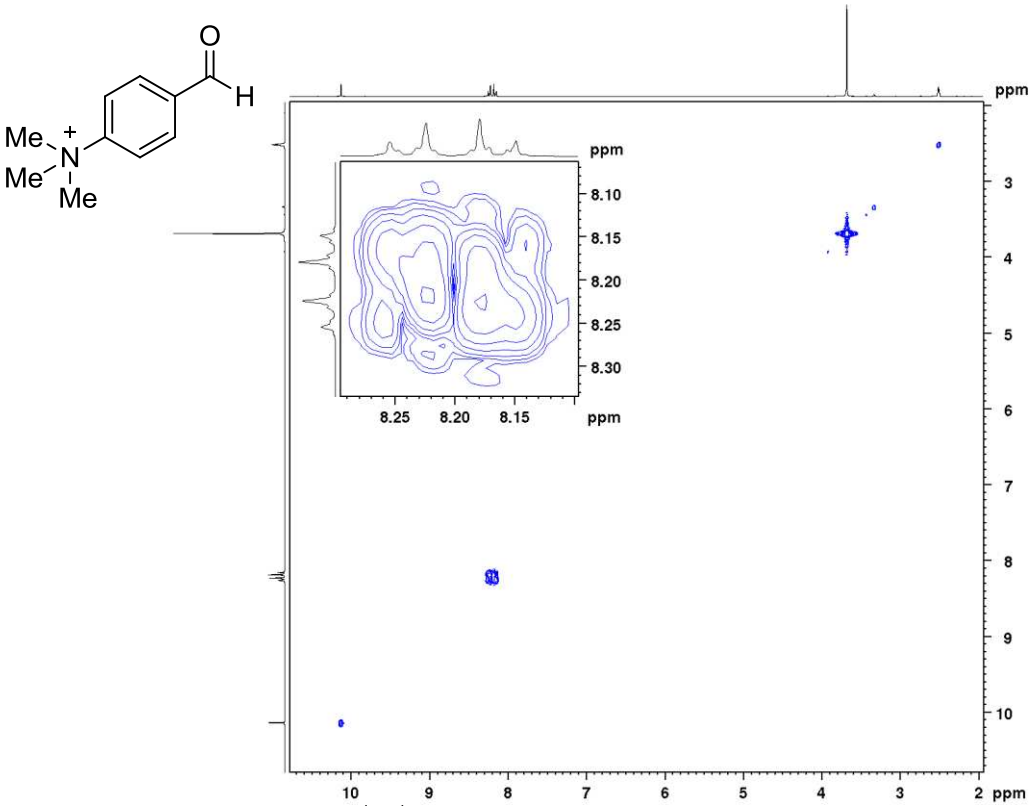
^{1}H NMR (300 MHz, dmso-d_6, 298 K) δ [ppm] = 10.13 (s, 1H, H-1'), 8.24 (mc, 2H, H-2,6), 8.16 (mc, 2H, H-3,5), 3.68 (s, 9H, NMe_3).
^{13}C NMR (75 MHz, dmso-d_6, 298 K) δ [ppm] = 192.1 (1C, C-1'), 151.0 (1C, C-1), 136.7 (1C, C-4), 130.8 (2C, C-3,5), 121.7 (2C, C-2,6), 56.4 (3C, NMe_3).



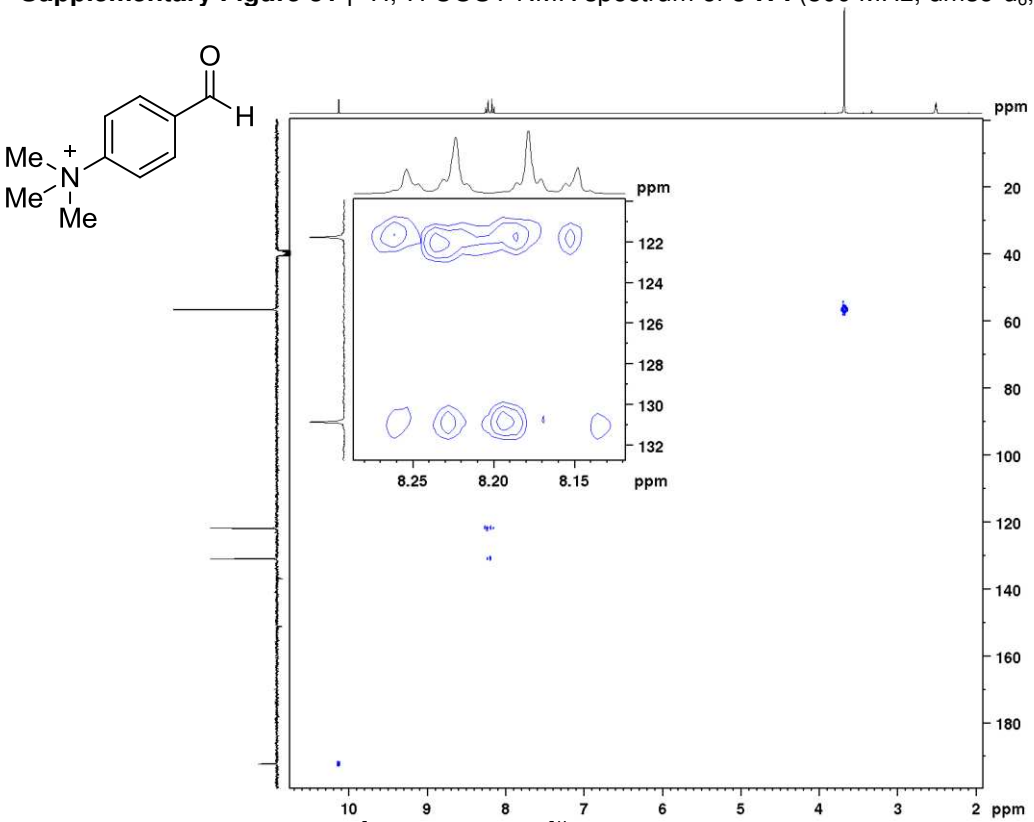
Supplementary Figure 29 | ^{1}H NMR spectrum of **3-H-I** (300 MHz, dmso-d_6, 298 K).



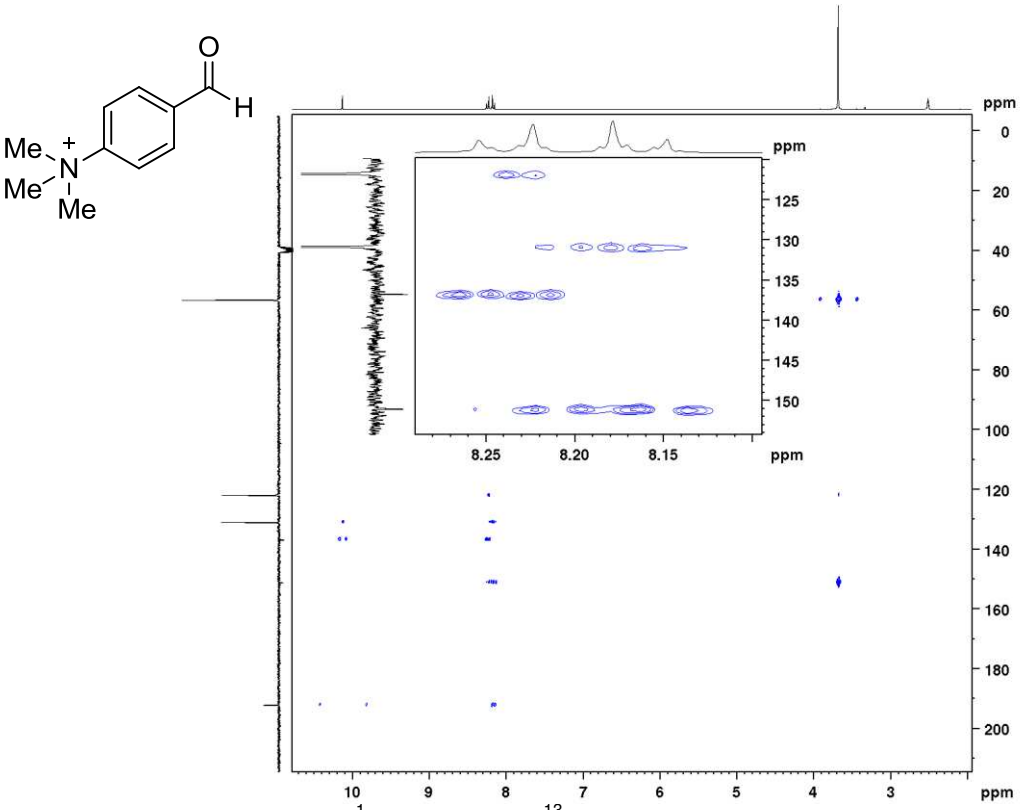
Supplementary Figure 30 | Multiplicity-edited ^{13}C DEPTQ NMR spectrum of **3-H-I** (75 MHz, dmso-d_6, 298 K).



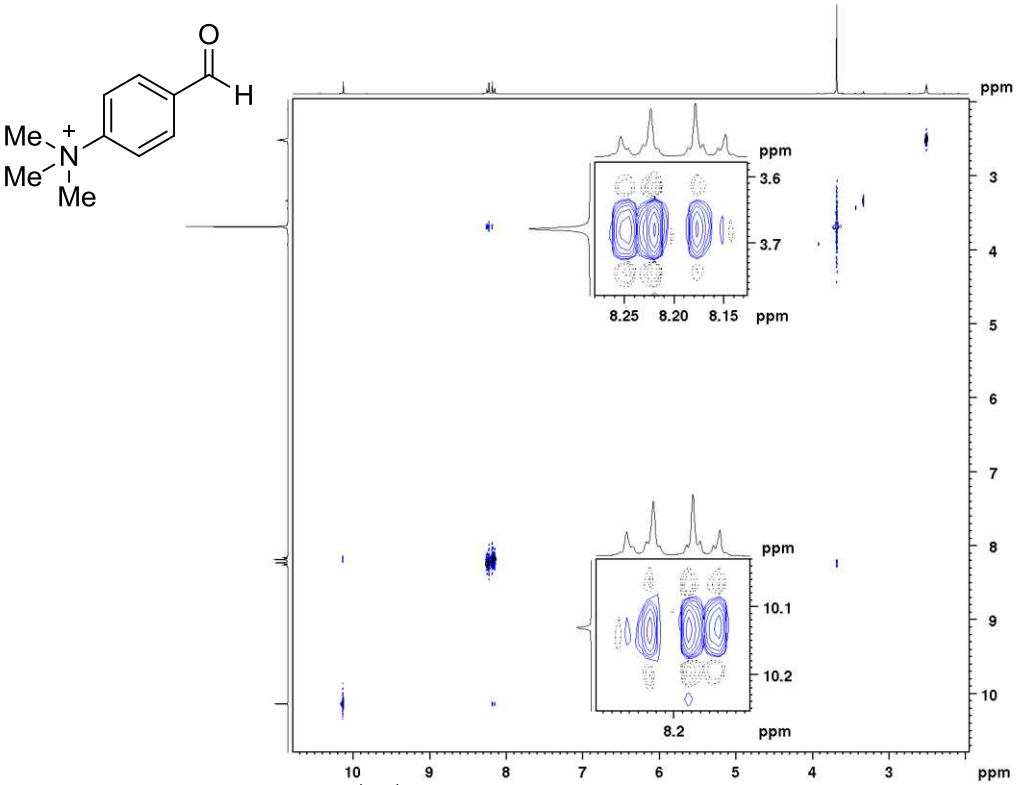
Supplementary Figure 31 | ^{1}H,^{1}H COSY NMR spectrum of **3-H-I** (300 MHz, dmso-d_6, 298 K).



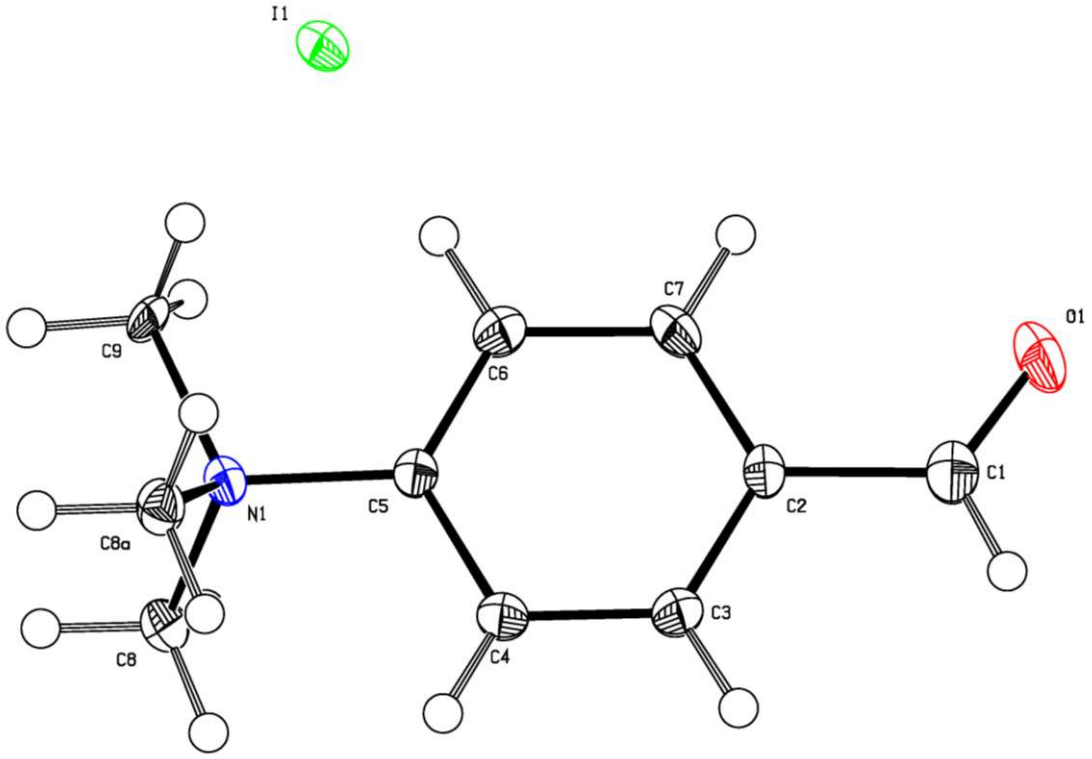
Supplementary Figure 32 | ^{1}H (300 MHz), ^{13}C (75 MHz) HMQC NMR spectrum of **3-H-I** (dmso-d_6, 298 K).



Supplementary Figure 33 | ^{1}H (300 MHz), ^{13}C (75 MHz) HMBC NMR spectrum of **3-H-I** (dmso-d_6, 298 K).



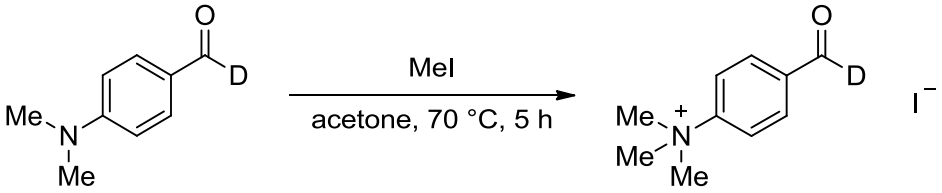
Supplementary Figure 34 | ^{1}H,^{1}H NOESY NMR spectrum of **3-H-I** (300 MHz, dmso-d_6, 298 K, mixing time = 700 ms).



Supplementary Figure 35 | ORTEP of the X-ray crystal structure of **3-H-I**. Thermal ellipsoids are drawn at 50% probability level. CCDC 1469243.

Formula	$C_{10}H_{13}INO$
Formula weight	290.11
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pnma
Unit cell dimensions	a = 12.2358(5) Å α = 90°
	b = 7.3081(5) Å β = 90°
	c = 13.0259(9) Å γ = 90°
Volume	1164.78(12) $Å^3$
Z	4
Density (calculated)	1.654 g cm^{-3}
Absorption coefficient	2.715 mm^{-1}
F(000)	564
Crystal size	0.200 × 0.100 × 0.100 mm^3
Θ range for data collection	2.284 to 26.996°
Index ranges	−15 ≤ h ≤ 13, −9 ≤ k ≤ 7, −15 ≤ l ≤ 16
Reflections collected	5624
Independent reflections	1375 [R(int) = 0.0352]
Completeness to Θ = 25.242°	99.9%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1375 / 0 / 77
Goodness-of-fit on F^2	1.035
Final R indices [I > 2σ(I)]	R1 = 0.0230, wR2 = 0.0527
R indices (all data)	R1 = 0.0328, wR2 = 0.0547
Extinction coefficient	n/a
Largest diff. peak and hole	0.548 and −0.624 e $Å^{-3}$

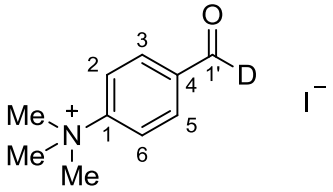
S3.7 4-(Trimethylammonio)benz(^{2}H)aldehyde iodide (3-D-I)



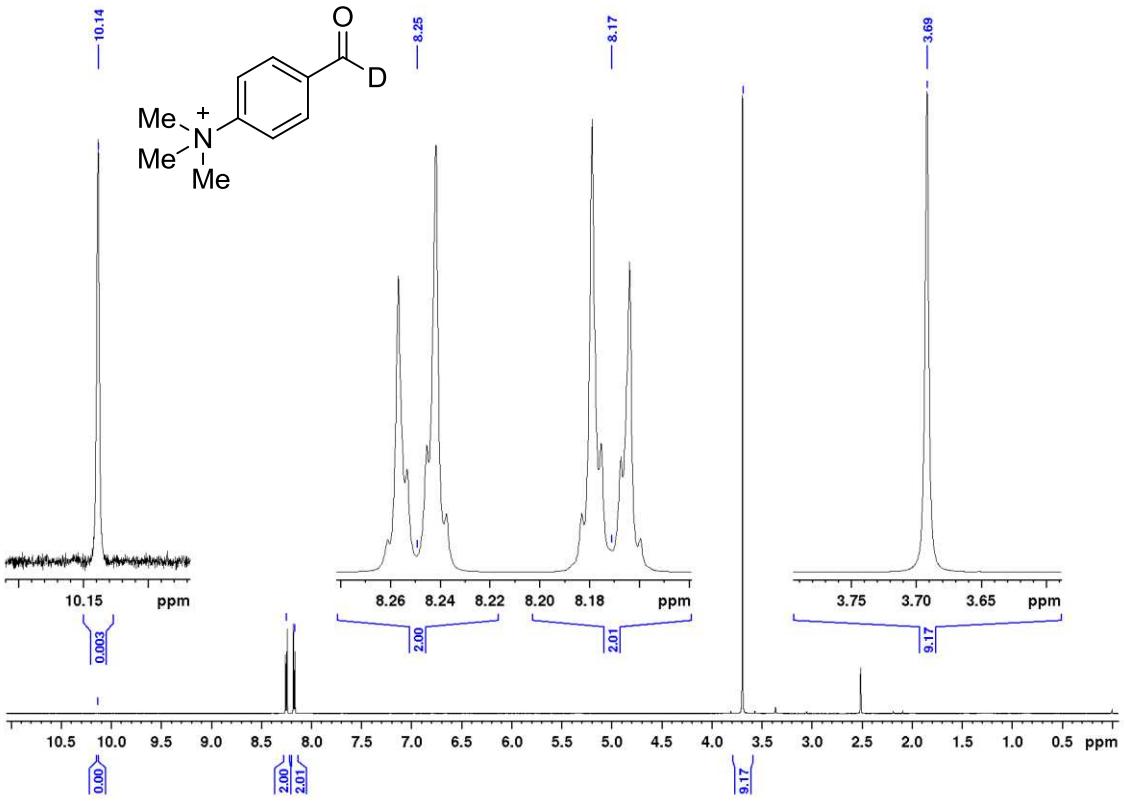
S-3-D **3-D-I**, 37%

Using the same procedure as in section S4.6, 4-(dimethylamino)benz(^{2}H)aldehyde (**S-3-D**) (200 mg, 1.332 mmol, 1 eq) afforded 4-(trimethylammonio)benz(^{2}H)aldehyde iodide (**3-D-I**) (142.3 mg, 0.487 mmol, 37%).

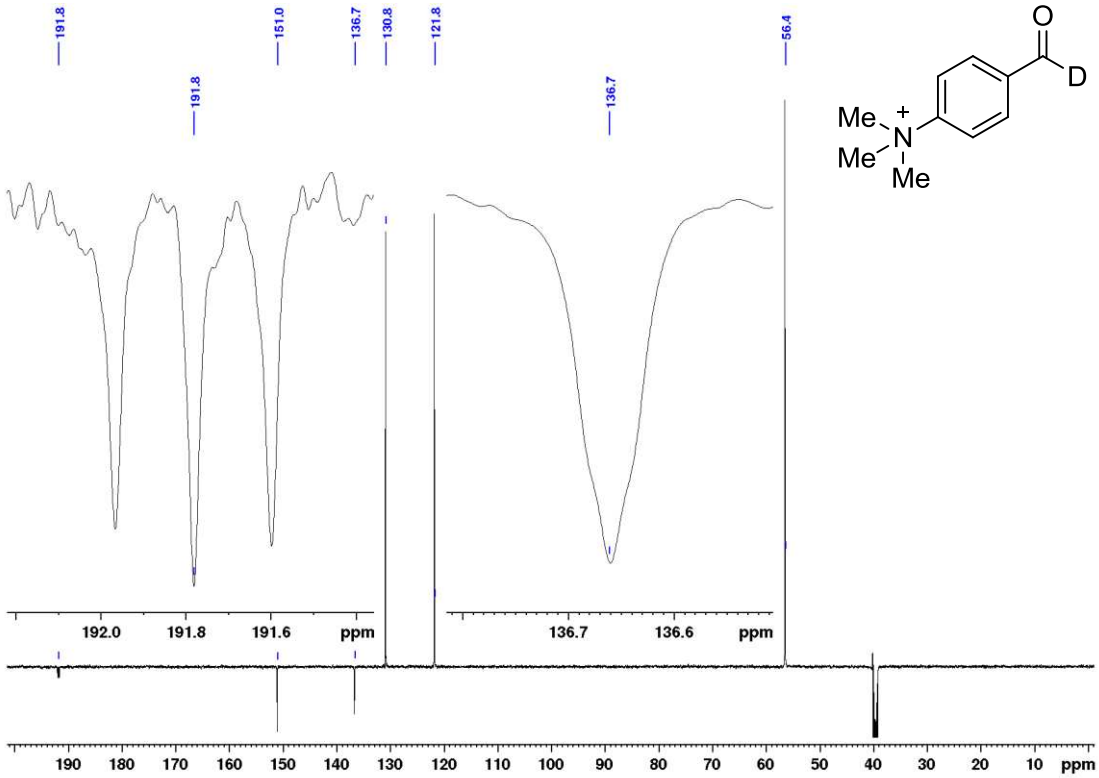
3-D-I: $C_{10}H_{13}DINO$, M = 292.13 g mol^{-1}.
Yield: 142.3 mg, 0.487 mmol, 37%.
m.p.: 162 – 163 °C.
HR-ESI-MS: [$^m/_z$] of $[M]^+$ ($C_{10}H_{13}DNO$):
calculated: 165.11327 amu
measured: 164.11324 amu
difference: –0.187 ppm
FT-IR: (ATR): $\tilde{\nu}$ [cm^{-1}] = 3051 (w), 3017 (w), 2998 (w), 2127 (w), 1680 (s), 1605 (w), 1493 (w), 1476 (w), 1458 (w), 1452 (w), 1418 (w), 1327 (w), 1310 (w), 1234 (w), 1186 (m), 1117 (w), 1051 (w), 1013 (w), 961 (w), 943 (m), 893 (w), 849 (m), 812 (s), 710 (w), 694 (m), 631 (w).
EA: calc. (found) [%]: C: 41.11 (41.04), H: 5.17 (5.040), N: 4.79 (4.58).



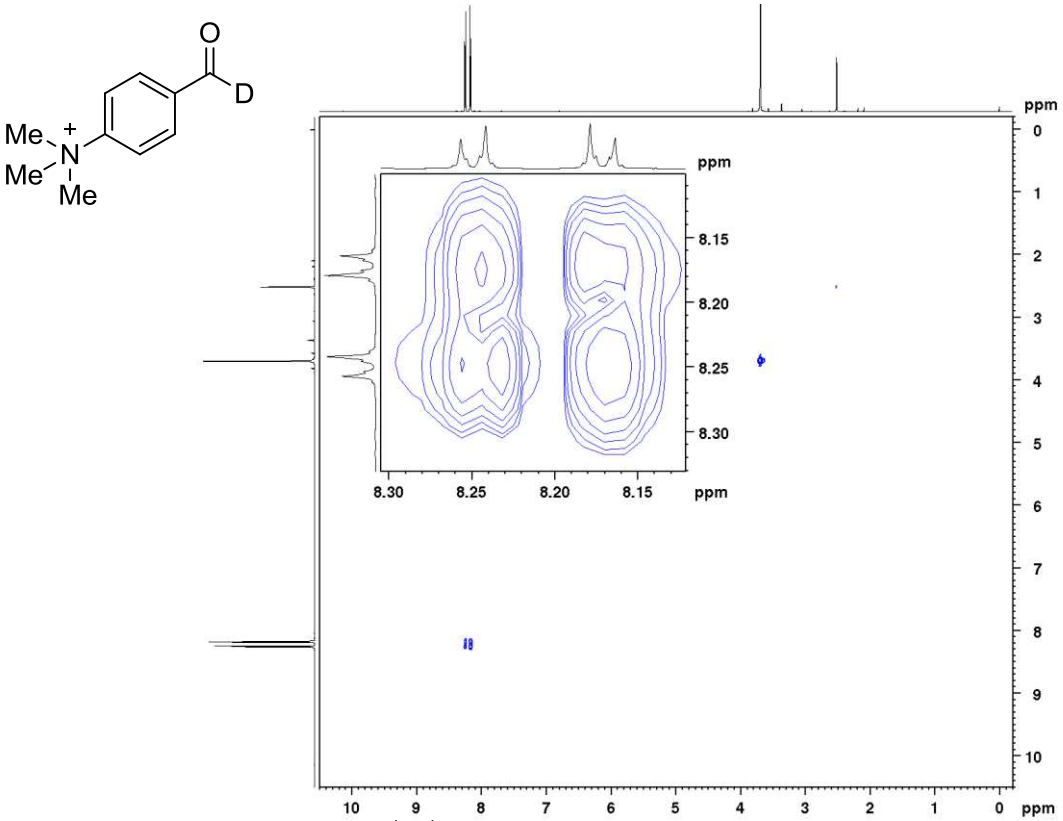
^{1}H NMR (600 MHz, dmso-d_6, 298 K) δ [ppm] = 10.14 (s, residual H, H-1'), 8.25 (mc, 2H, H-2,6), 8.17 (mc, 2H, H-3,5), 3.69 (s, 9H, NMe_3).
^{13}C NMR (151 MHz, dmso-d_6, 298 K) δ [ppm] = 191.8 (t, $^1J_{CD}$ = 27.8 Hz, 1C, C-1'), 151.0 (1C, C-1), 136.7 (brt, $^2J_{CD}$ = 3.5 Hz, 1C, C-4), 130.8 (2C, C-3,5), 121.8 (2C, C-2,6), 56.4 (3C, NMe_3).



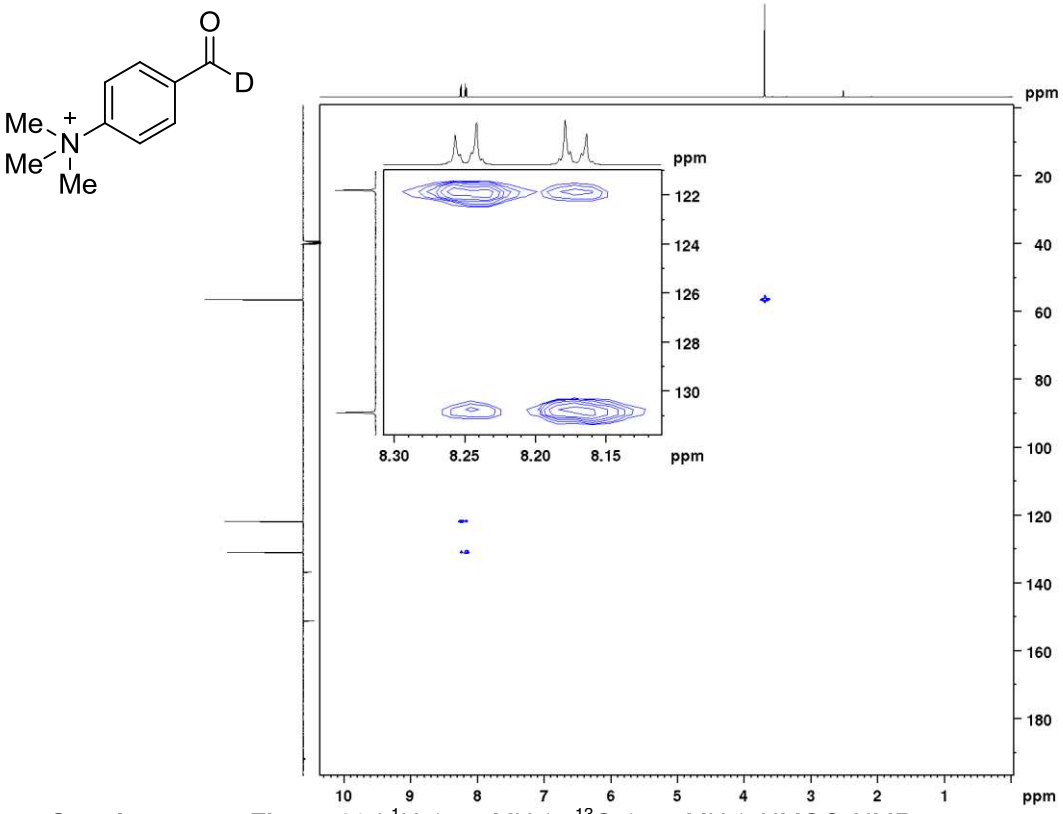
Supplementary Figure 36 | ^{1}H NMR spectrum of **3-D-I** (600 MHz, dmso-d_6, 298 K).



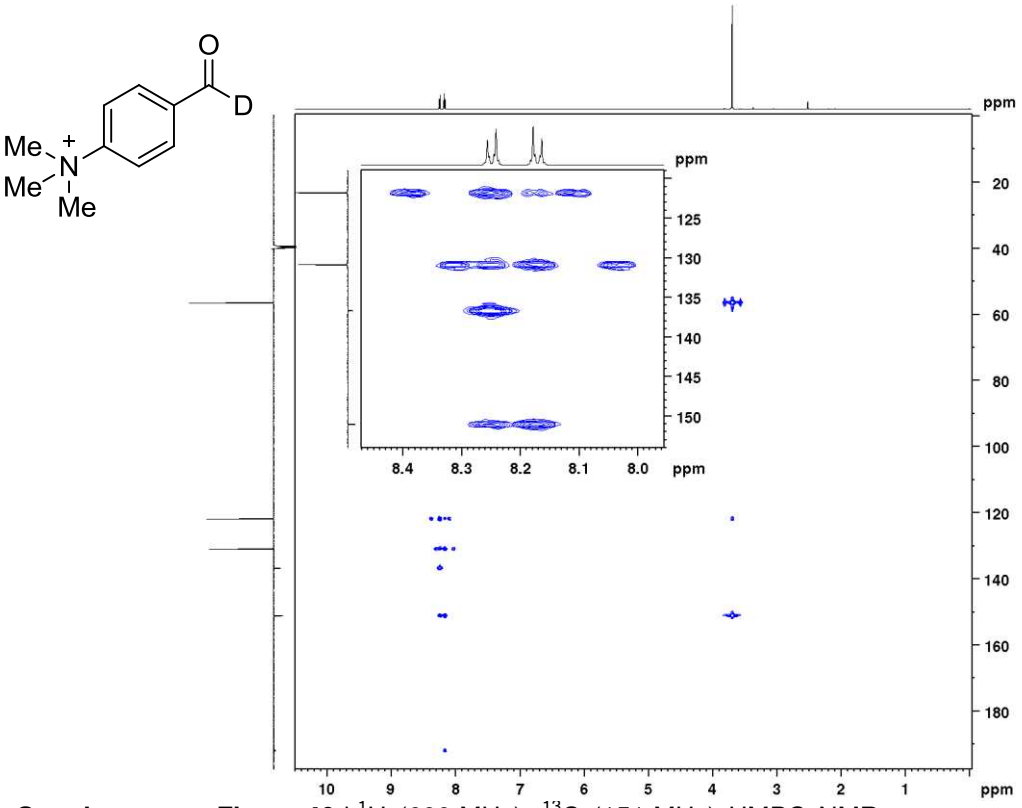
Supplementary Figure 37 | Multiplicity-edited ^{13}C DEPTQ NMR spectrum of **3-D-I** (151 MHz, dmso-d_6, 298 K).



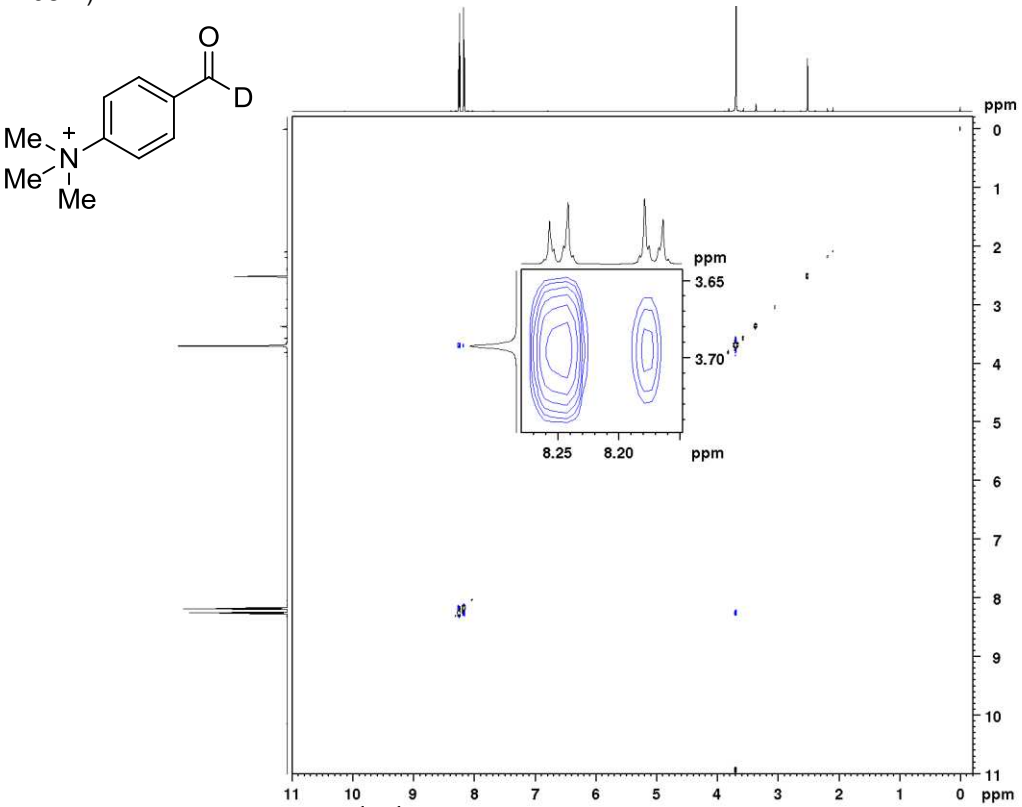
Supplementary Figure 38 | ^{1}H,^{1}H COSY NMR spectrum of **3-D-I** (600 MHz, dmso-d_6, 298 K).



Supplementary Figure 39 | ^{1}H (600 MHz), ^{13}C (151 MHz) HMQC NMR spectrum of **3-D-I** (dmso-d_6, 298 K).



Supplementary Figure 40 | ^{1}H (600 MHz), ^{13}C (151 MHz) HMBC NMR spectrum of **3-D-I** (dmso-d_6, 298 K).



Supplementary Figure 41 | ^{1}H,^{1}H NOESY NMR spectrum of **3-D-I** (600 MHz, dmso-d_6, 298 K, mixing time = 700 ms).

S4 Additional references

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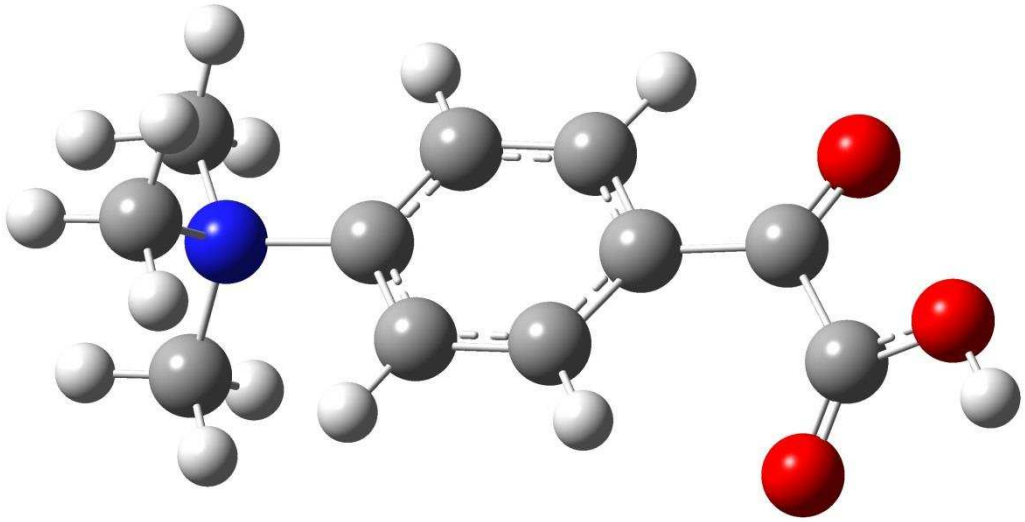
S5 Coordinates and properties of molecules studied computationally

S5.1 *cis*-Oxo[4-(trimethylammonio)phenyl]acetic acid (1-H_c)



Route	:	# opt freq b3lyp/cc-pvtz geom = connectivity empiricaldispersion = gd3bj int =ultrafine
SMILES	:	C[N](C)(C)c1ccc(cc1)C(=O)C(=O)O
Formula	:	$C_{11}H_{14}NO_3^+$
Charge	:	1
Multiplicity	:	1
Energy	:	−708.08892889 a.u.
Gibbs Energy	:	−707.89168500 a.u.

Cartesian Coordinates (XYZ format)

29

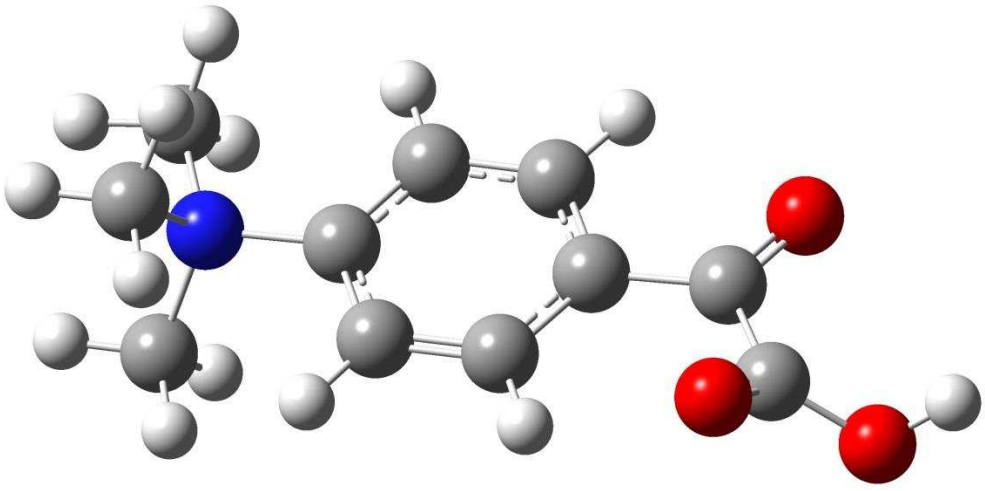
C	−0.10077800	−1.30344200	0.01412800
C	1.27917898	−1.43195796	−0.00180700
C	2.09014392	−0.29639101	−0.00763700
C	1.49427605	0.96246499	0.00853200
C	0.11444800	1.10073400	0.01811200
C	−0.67536300	−0.03940100	0.01975400
H	−0.70169902	−2.20006490	0.01591000
H	1.71887195	−2.41512203	−0.02798600
H	2.12757897	1.83740306	0.01289100
H	−0.30317900	2.09295702	0.02461300
N	−2.17756009	0.05491900	0.02413700
C	−2.67282009	1.47381198	0.02966700
H	−3.75743103	1.44281006	0.03237000
H	−2.31730795	1.97586596	0.92269403
H	−2.32197595	1.98113203	−0.86220402
C	−2.72858596	−0.61645103	−1.21157598
H	−2.44332194	−1.66115797	−1.20975196
H	−3.81065607	−0.52442598	−1.19813299
H	−2.31295490	−0.12021400	−2.08262706
C	−2.72379398	−0.62434900	1.25726902
H	−2.30567908	−0.13322400	2.13003111
H	−3.80595589	−0.53293598	1.24820304
H	−2.43831396	−1.66893303	1.24773800
C	3.58974695	−0.33361799	0.00552700
O	4.24169207	0.67155600	0.12165200
C	4.29848099	−1.68583500	−0.20413101
O	3.81592393	−2.58814502	−0.83967400
O	5.50198221	−1.69048500	0.35621199
H	5.93053007	−2.53763890	0.15483800

Frequencies

Mode	IR frequency	IR intensity
1	15.84240000	1.77110000
2	34.09140000	3.73260000
3	51.97750000	0.30840000
4	67.11390000	0.13630000
5	128.32480000	1.03880000
6	181.58550000	0.94600000
7	223.43140000	5.73150000
8	231.37420000	1.95240000
9	256.68990000	1.97100000
10	277.03400000	2.09750000
11	298.17660000	3.97790000
12	351.09630000	0.63570000
13	354.62290000	0.11860000
14	360.85230000	4.26210000
15	393.66610000	0.84430000
16	400.53930000	0.58950000
17	419.91570000	0.13580000
18	437.82130000	0.04790000
19	472.01160000	2.13040000
20	481.51110000	4.48720000
21	558.30010000	15.43700000
22	590.91380000	9.22550000
23	617.11010000	25.70920000
24	652.04100000	25.67200000
25	663.26580000	126.49340000
26	687.05870000	101.08330000
27	745.78850000	3.54530000
28	767.91590000	6.36850000
29	817.55670000	4.57030000
30	842.66950000	8.24040000
31	844.95990000	31.31380000
32	882.16580000	14.47060000
33	946.07140000	27.61730000
34	960.53140000	14.39840000
35	990.32890000	134.49580000
36	1004.37830000	0.26320000
37	1019.09990000	2.52550000
38	1040.51670000	1.72490000
39	1076.86550000	0.02510000
40	1130.82290000	21.95240000
41	1133.45290000	1.01340000
42	1140.02320000	0.48790000

43	1167.29210000	47.51110000
44	1173.75090000	272.59510000
45	1227.47250000	5.97880000
46	1254.67640000	30.23990000
47	1257.56700000	1.66910000
48	1258.57140000	13.63260000
49	1296.02060000	0.12390000
50	1346.81250000	12.45180000
51	1354.59600000	4.40200000
52	1399.31770000	24.25150000
53	1447.26470000	2.57910000
54	1451.87690000	4.69410000
55	1452.80560000	17.42770000
56	1479.60860000	0.00140000
57	1489.06100000	0.34740000
58	1493.44370000	1.56080000
59	1495.30130000	0.64570000
60	1507.08280000	27.40790000
61	1513.36030000	24.40440000
62	1530.49890000	50.67790000
63	1541.25230000	17.36080000
64	1629.58010000	7.53740000
65	1642.54430000	32.98580000
66	1780.45600000	164.59560000
67	1799.23230000	232.35690000
68	3080.76890000	0.25560000
69	3081.53130000	0.89680000
70	3088.29110000	0.81320000
71	3168.49110000	0.02520000
72	3168.92960000	0.46380000
73	3176.03900000	4.44490000
74	3183.18600000	0.10590000
75	3189.42520000	0.01310000
76	3189.96750000	2.20040000
77	3203.63290000	0.87230000
78	3208.12640000	5.75400000
79	3237.62270000	6.55410000
80	3238.84610000	6.68060000
81	3724.12430000	134.53130000

S5.2 Transition State between 1-H_c and 1-H_t



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Formula	:	$C_{11}H_{14}NO_3^+$
Charge	:	1
Multiplicity	:	1
Energy	:	−708.07134712 a.u.
Gibbs Energy	:	−707.87562500 a.u.

Cartesian Coordinates (XYZ format)

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C	1.12597203	0.35023099	−0.03945900
C	0.30270499	1.47298503	−0.02589200
C	−1.07825398	1.34442103	−0.01385700
C	−1.63556194	0.07409000	−0.02059900
H	−1.24971497	−2.05226302	−0.04580400
H	1.16689396	−1.80177796	−0.04721500
H	0.75805300	2.45252609	−0.02438000
H	−1.67849100	2.23801804	−0.00045200
N	−3.12789297	−0.12060000	−0.00296300
C	−3.88546896	1.17725801	0.01664600
H	−4.94398212	0.93905902	0.02794800
H	−3.62450504	1.73311305	0.91042697
H	−3.64658809	1.74719000	−0.87445498
C	−3.55388808	−0.87950599	−1.23734403
H	−3.07427096	−1.85041106	−1.24530697
H	−4.63329697	−0.99664998	−1.21214294
H	−3.25125909	−0.30883101	−2.10941195
C	−3.52055812	−0.89748597	1.23154199
H	−3.19361591	−0.33973399	2.10318804
H	−4.60033703	−1.01398802	1.23411500
H	−3.04112697	−1.86836696	1.21223104
C	2.60417008	0.58163100	−0.07593000
O	3.07535601	1.69228804	−0.09622200
C	3.56079197	−0.62022197	0.00096800
O	3.34327102	−1.54242599	0.73120302
O	4.62567616	−0.51861399	−0.82257402
H	5.39549780	−0.09959300	−0.41783100

Frequencies

Mode	IR frequency	IR intensity
1	−630.29590000	122.49040000
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5	71.46640000	1.06860000
6	123.19110000	3.38680000
7	182.98410000	1.81170000
8	216.54440000	12.60110000
9	228.35450000	0.57540000
10	255.45900000	0.59930000
11	275.94220000	3.70590000
12	290.69440000	4.70400000
13	344.87880000	9.68380000
14	354.21090000	0.01900000
15	358.26160000	5.19110000
16	386.37520000	1.62130000
17	389.53530000	0.79600000
18	419.20560000	0.04520000
19	434.17040000	0.25270000
20	474.84340000	0.61740000
21	483.33230000	5.21720000
22	559.35330000	19.07750000
23	601.54460000	1.05260000
24	641.30880000	25.46380000
25	664.12470000	34.59190000
26	713.84640000	44.53460000
27	734.65330000	13.51960000
28	779.60080000	2.90910000
29	791.08740000	42.31910000
30	842.81100000	5.08230000
31	844.92200000	29.85000000
32	874.64370000	15.01510000
33	945.43860000	24.14930000
34	960.25450000	13.58300000
35	980.18790000	176.80920000
36	1001.90480000	2.92500000
37	1018.19790000	0.06680000
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40	1076.92250000	0.03600000
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42	1133.16130000	0.06450000

43	1140.16230000	0.53160000
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46	1233.77140000	16.43710000
47	1257.41960000	1.53850000
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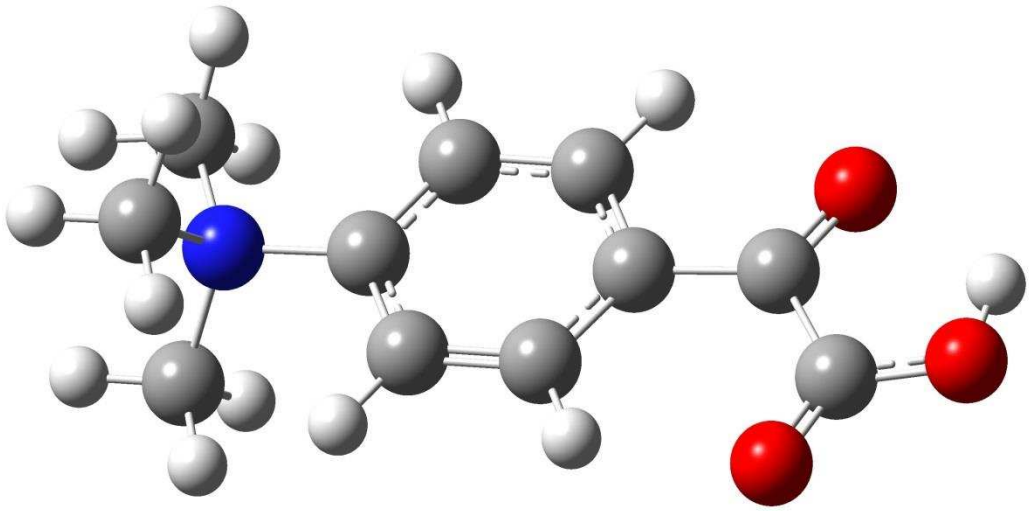
57	1488.91000000	0.34300000
58	1493.54640000	1.60230000
59	1495.20750000	0.79550000
60	1507.32840000	27.55860000
61	1513.50420000	24.42100000
62	1530.47540000	50.55770000
63	1542.16590000	15.03950000
64	1630.26030000	8.43390000
65	1643.15910000	34.51220000
66	1768.69080000	135.10530000
67	1817.77490000	210.26250000
68	3080.75390000	0.23560000
69	3081.51010000	0.85930000
70	3088.28870000	0.70640000
71	3168.58140000	0.01620000
72	3169.01030000	0.46060000
73	3176.17070000	4.28880000
74	3183.19740000	0.10180000
75	3189.05480000	0.25860000
76	3189.90370000	1.81370000
77	3204.25640000	0.51220000
78	3207.26530000	5.77780000
79	3231.84770000	7.38470000
80	3238.16100000	2.08220000
81	3796.10760000	227.19400000

S5.3 *trans*-Oxo[4-(trimethylammonio)phenyl]acetic acid (1-H_t)



Route	:	# opt freq b3lyp/cc-pvtz geom = connectivity empiricaldispersion = gd3bj int = ultrafine
SMILES	:	C[N](C)(C)c1ccc(cc1)C(=O)C(=O)O
Formula	:	$C_{11}H_{14}NO_3^+$
Charge	:	1
Multiplicity	:	1
Energy	:	−708.09087119 a.u.
Gibbs Energy	:	−707.89036500 a.u.

Cartesian Coordinates (XYZ format)

29

C	−0.12288800	−1.30898499	−0.00040600
C	1.25448298	−1.46316695	−0.00119300
C	2.08490610	−0.33955899	−0.00192900
C	1.50948703	0.93094301	−0.00184800
C	0.13239899	1.09158003	−0.00109800
C	−0.67608601	−0.03587200	−0.00037600
H	−0.73842800	−2.19557309	0.00015900
H	1.68878806	−2.44908190	−0.00128800
H	2.15395093	1.79743004	−0.00238400
H	−0.26922899	2.09038496	−0.00109800
N	−2.17628503	0.08336500	0.00044700
C	−2.64859700	1.51017702	0.00045500
H	−3.73352408	1.49654698	0.00107500
H	−2.28710699	2.00924492	0.89278698
H	−2.28812599	2.00891900	−0.89247203
C	−2.73623705	−0.58386201	−1.23391294
H	−2.46813393	−1.63309205	−1.22783101
H	−3.81665301	−0.47433501	−1.22182405
H	−2.31212091	−0.09723200	−2.10632491
C	−2.73485708	−0.58341098	1.23567402
H	−2.30976510	−0.09646700	2.10743594
H	−3.81528401	−0.47388399	1.22475195
H	−2.46676993	−1.63264501	1.22967398
C	3.57517600	−0.40511900	−0.00270000
O	4.24942684	0.60214800	−0.00232900
C	4.32846880	−1.76230705	−0.00400800
O	3.78636289	−2.83336592	−0.00475300
O	5.64260578	−1.60043097	−0.00440400
H	5.83478117	−0.64506501	−0.00374200

Frequencies

Mode	IR frequency	IR intensity
1	−12.13090000	0.95720000
2	45.88380000	1.63940000
3	52.51620000	0.89150000
4	82.71720000	1.27580000
5	127.60660000	2.55850000
6	188.87570000	1.75540000
7	231.47400000	0.39500000
8	233.97830000	13.30860000
9	253.52500000	1.17420000
10	278.26310000	4.16810000
11	315.25880000	23.02310000
12	351.76650000	2.67020000
13	355.49400000	3.06100000
14	360.68690000	5.18950000
15	405.67820000	15.66850000
16	412.25420000	0.82910000
17	420.28880000	0.29470000
18	458.29850000	3.34070000
19	479.29990000	2.91130000
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21	571.68690000	47.85350000
22	580.79770000	2.02760000
23	615.51730000	9.81370000
24	655.96810000	0.87290000
25	699.91770000	69.42950000
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27	742.56600000	9.55010000
28	772.82790000	2.82560000
29	820.18960000	15.16360000
30	844.21960000	36.38880000
31	847.05020000	0.05410000
32	882.55340000	10.01890000
33	945.72230000	29.26220000
34	960.53890000	15.25380000
35	995.75220000	109.64940000
36	1012.70480000	0.48870000
37	1026.15210000	0.00240000
38	1040.64880000	4.09200000
39	1077.13830000	0.02160000
40	1130.03150000	10.72820000
41	1133.62290000	2.96280000
42	1140.19790000	0.52830000

43	1165.22480000	3.93170000
44	1193.19050000	37.97490000
45	1225.77060000	61.67220000
46	1257.14010000	13.21250000
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48	1265.00290000	335.67890000
49	1296.45350000	5.70930000
50	1344.60660000	28.99440000
51	1350.79350000	8.79140000
52	1383.18410000	306.06860000
53	1446.91580000	3.01580000
54	1452.05430000	4.82580000
55	1452.44180000	18.13890000
56	1479.89290000	0.00220000
57	1488.86390000	0.37370000
58	1493.31770000	1.26240000
59	1494.97830000	0.83940000
60	1507.44600000	27.52470000
61	1513.39200000	24.57870000
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63	1538.78930000	20.75120000
64	1625.39660000	9.05360000
65	1641.99390000	46.35030000
66	1750.21040000	146.45660000
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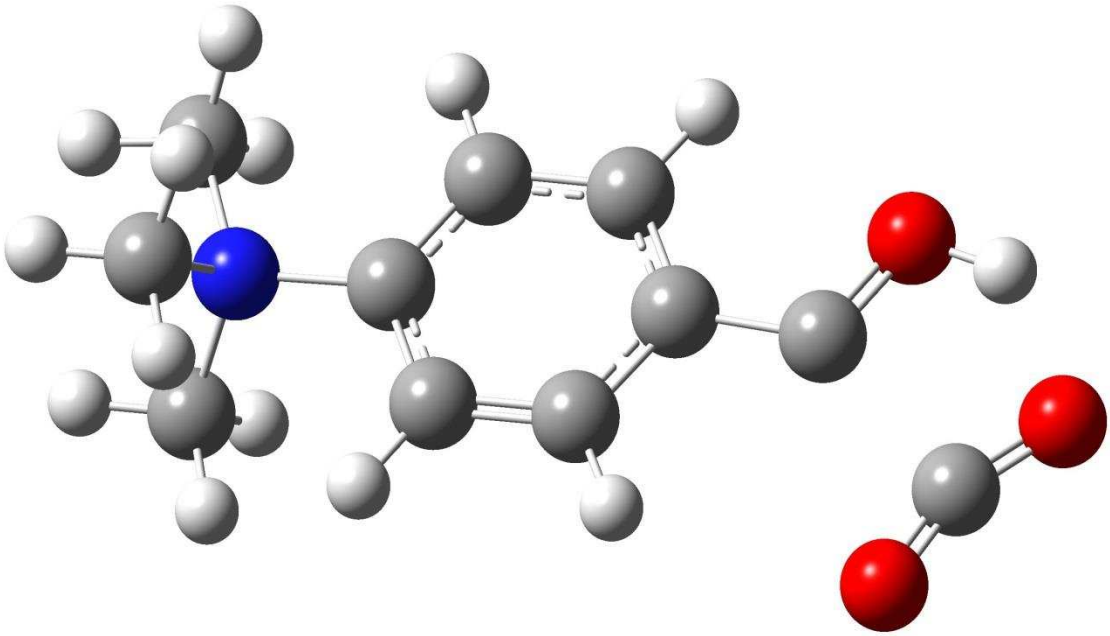
68	3080.80490000	0.20370000
69	3081.47060000	0.76670000
70	3088.18780000	0.56660000
71	3168.84020000	0.00760000
72	3169.19490000	0.40990000
73	3176.35410000	3.99900000
74	3182.96940000	0.10030000
75	3188.81930000	0.01280000
76	3189.47160000	1.61840000
77	3204.71480000	0.59160000
78	3210.13510000	4.72370000
79	3236.95830000	31.26740000
80	3238.72610000	9.23530000
81	3640.79030000	108.81200000

S5.4 Transition state between 1-H_c and 2-H_t



Route	:	# opt=(calcall,qst3) freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj int=ultrafine	
SMILES	:	C[N](C)(C)c1ccc(cc1)[C]O.C(=O)=O	
Formula	:	$C_{11}H_{14}NO_3^+$	
Charge	:	1	
Multiplicity	:	1	
Energy	:	−708.03302970	a.u.
Gibbs Energy	:	−707.83843200	a.u.

Cartesian Coordinates (XYZ format)

29

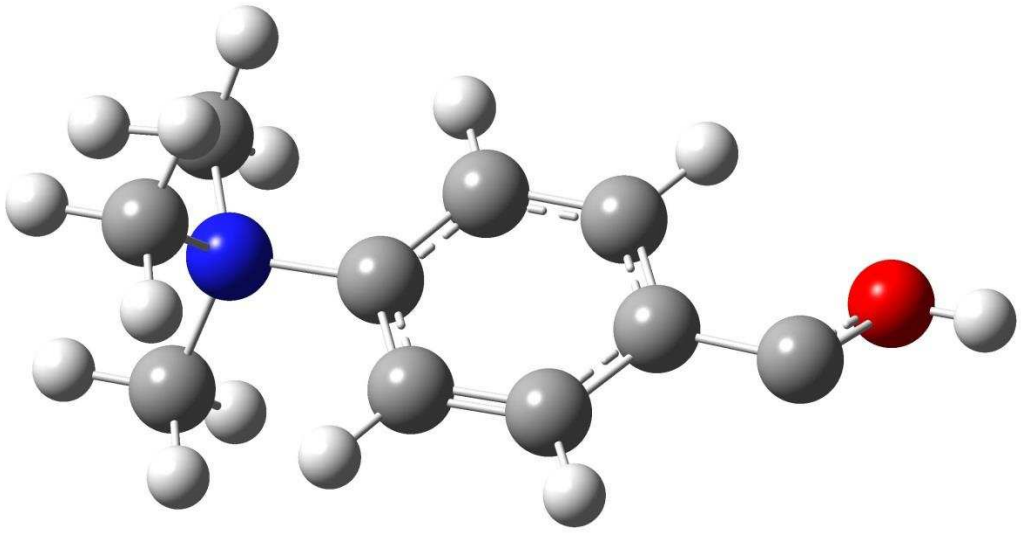
C	−0.86308599	−1.22713399	0.00223400
C	0.51803398	−1.12019598	0.00183200
C	1.13037503	0.13524801	0.00311700
C	0.33972499	1.28600204	0.00469000
C	−1.04395497	1.18898904	0.00491800
C	−1.63217497	−0.07001600	0.00369200
H	−1.31186199	−2.20856094	0.00129400
H	1.14160097	−2.00326300	0.00046900
H	0.80962801	2.25879002	0.00565100
H	−1.62656701	2.09442210	0.00604700
N	−3.13010406	−0.22314200	0.00389900
C	−3.85461807	1.09401500	0.00497200
H	−4.91874981	0.88220400	0.00493300
H	−3.59118795	1.64971006	0.89815599
H	−3.59136796	1.65104604	−0.88743597
C	−3.55989289	−0.97945601	−1.23170602
H	−3.10773301	−1.96346796	−1.22642899
H	−4.64235497	−1.06600904	−1.22000802
H	−3.23003292	−0.42358199	−2.10350204
C	−3.55929995	−0.98120898	1.23863196
H	−3.22914910	−0.42649499	2.11105704
H	−4.64175701	−1.06788898	1.22726798
H	−3.10698605	−1.96514595	1.23179805
C	2.59880996	0.13176900	0.00225400
O	3.13065004	1.29763806	0.00502700
C	4.33177805	−1.22545099	−0.00300900
O	3.95340800	−2.33532310	−0.00581000
O	5.12708902	−0.33852699	−0.00121100
H	4.11256409	1.12586296	0.00377500

Frequencies

Mode	IR frequency	IR intensity
1	−161.54010000	113.50720000
2	17.23780000	0.28820000
3	44.39290000	0.57910000
4	59.55570000	0.09670000
5	70.49770000	7.27110000
6	102.31610000	0.19280000
7	155.24890000	0.04260000
8	200.52440000	5.69940000
9	222.04870000	0.00040000
10	253.77210000	6.83250000
11	273.88310000	0.66850000
12	290.33660000	0.91430000
13	305.92710000	3.95790000
14	353.54300000	0.38710000
15	354.62550000	0.02140000
16	387.30500000	0.00210000
17	393.42620000	11.18440000
18	423.07000000	0.02200000
19	441.71590000	1.30490000
20	475.04770000	3.02210000
21	495.65100000	24.42920000
22	567.93780000	34.00800000
23	591.65120000	76.20740000
24	603.33550000	385.98730000
25	648.38490000	0.99220000
26	682.59570000	11.31420000
27	713.21830000	12.86020000
28	749.54810000	0.85790000
29	837.84690000	20.21890000
30	843.10480000	2.66100000
31	862.09360000	13.38510000
32	874.36720000	46.66890000
33	944.48020000	22.89320000
34	960.27840000	15.00310000
35	998.76510000	25.85210000
36	1016.41980000	26.53990000
37	1024.00670000	17.05480000
38	1037.68190000	14.24850000
39	1077.18750000	0.02040000
40	1125.84560000	13.46480000
41	1132.11580000	0.77820000
42	1140.20930000	0.56970000

43	1161.27490000	4.59320000
44	1205.09510000	65.77040000
45	1235.87700000	21.72790000
46	1256.75520000	1.57130000
47	1256.86370000	1.80710000
48	1273.64000000	64.44660000
49	1295.33800000	1.21520000
50	1335.85280000	70.66040000
51	1349.73280000	1.94970000
52	1412.25930000	90.04310000
53	1450.64790000	0.19760000
54	1452.31830000	4.88120000
55	1461.75610000	219.08780000
56	1474.01770000	233.36560000
57	1480.14640000	0.00110000
58	1488.91370000	0.36650000
59	1493.54930000	2.97070000
60	1495.21130000	5.53210000
61	1507.67340000	24.06180000
62	1513.55510000	24.67240000
63	1530.20510000	48.65560000
64	1539.06060000	5.82250000
65	1627.19720000	24.90980000
66	1640.25100000	44.80990000
67	2210.92890000	435.50640000
68	3081.19900000	0.16210000
69	3081.64870000	0.68350000
70	3088.33660000	0.44880000
71	3169.15750000	0.00990000
72	3169.33280000	0.28100000
73	3176.48230000	4.40400000
74	3183.16820000	0.08770000
75	3189.45420000	0.01430000
76	3189.94110000	1.24410000
77	3198.97580000	2.65040000
78	3204.96560000	1.08930000
79	3210.71580000	7.12260000
80	3236.24750000	2.23040000
81	3252.81210000	474.85650000

S5.5 *trans*-Hydroxy[4-(trimethylazaniumyl)phenyl]methylidene (2-H_t)



Route	:	# opt freq b3lyp/cc-pvtz geom = connectivity empiricaldis-persion = gd3bj int = ultrafine
SMILES	:	C[N](C)(C)c1ccc(cc1)[C]O
Formula	:	$C_{10}H_{14}NO^{+}$
Charge	:	1
Multiplicity	:	1
Energy	:	−519.36506012 a.u.
Gibbs Energy	:	−519.17798100 a.u.
CCSD(T)-F12b//cc-pVDZ-F12	:	−518.35132703 a.u.

Cartesian Coordinates (XYZ format)

26

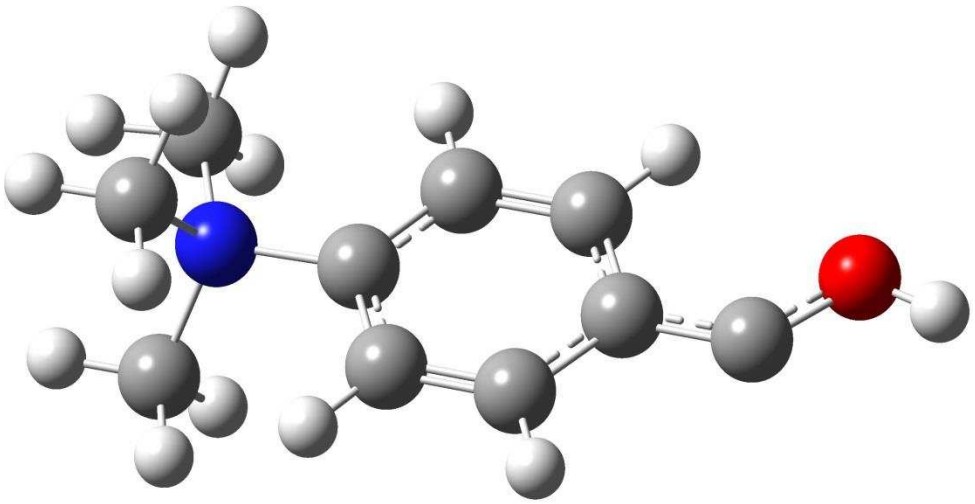
C	−0.08855000	−1.23780203	−0.40435201
C	1.28946197	−1.37142801	−0.38032201
C	2.10875106	−0.28015801	−0.08748100
C	1.51652598	0.94714099	0.21553899
C	0.13561299	1.08809102	0.22474200
C	−0.65564001	−0.00703500	−0.09445300
H	−0.69448698	−2.09745097	−0.64738899
H	1.75303400	−2.32536507	−0.58785200
H	2.14069605	1.79645097	0.45194501
H	−0.28542301	2.04763007	0.47336501
N	−2.15824294	0.09738300	−0.10264600
C	−2.65061307	1.47481799	0.24002600
H	−3.73491812	1.45432401	0.20389500
H	−2.32137108	1.73692799	1.23934603
H	−2.27162695	2.18375397	−0.48776099
C	−2.68059611	−0.24391501	−1.47768104
H	−2.39759707	−1.25883603	−1.72757900
H	−3.76254511	−0.14981399	−1.46697402
H	−2.24309611	0.44869399	−2.18942690
C	−2.73666811	−0.85995698	0.91187400
H	−2.33831692	−0.60270298	1.88800395
H	−3.81815696	−0.76012802	0.90089101
H	−2.45291710	−1.87224197	0.65200400
C	3.57230401	−0.54209101	−0.05213100
O	4.19887400	0.60490000	−0.15078500
H	5.15165377	0.44451401	−0.09943500

Frequencies

Mode	IR frequency	IR intensity
1	40.95200000	3.57660000
2	59.78770000	2.67540000
3	92.22370000	3.62950000
4	174.74570000	1.10180000
5	206.24540000	1.30830000
6	239.37760000	1.32270000
7	263.50070000	1.35320000
8	274.57700000	0.08630000
9	339.50780000	0.93000000
10	353.30140000	0.13800000
11	355.57180000	0.21230000
12	372.45290000	0.97020000
13	419.93210000	1.52900000
14	429.37490000	1.61310000
15	476.40790000	0.57510000
16	488.58440000	0.94740000
17	554.14290000	31.57330000
18	592.54880000	6.63240000
19	648.43430000	0.38940000
20	679.87540000	12.74960000
21	735.47050000	6.03070000
22	814.45000000	5.48110000
23	825.53520000	10.92010000
24	842.43450000	1.77350000
25	850.33090000	63.44470000
26	879.34700000	79.44770000
27	946.15600000	35.27300000
28	961.85400000	15.31070000
29	1002.49560000	5.24910000
30	1017.95680000	1.06710000
31	1036.39060000	9.98910000
32	1076.97430000	0.02070000
33	1124.85310000	12.34530000
34	1131.36380000	1.94040000
35	1140.10140000	0.55590000
36	1158.66400000	13.79340000
37	1177.07790000	39.58250000
38	1226.40150000	4.52110000
39	1257.30600000	2.55440000
40	1257.89410000	1.60220000
41	1289.30960000	215.55360000
42	1294.97780000	1.44520000

43	1346.82800000	16.24590000
44	1349.73200000	55.13030000
45	1369.17860000	57.03040000
46	1446.06810000	10.68530000
47	1451.75660000	4.66000000
48	1452.09680000	21.65170000
49	1479.64320000	0.00190000
50	1489.17410000	0.38450000
51	1493.36720000	1.66680000
52	1495.40650000	0.79580000
53	1506.95220000	26.44050000
54	1513.17350000	24.16400000
55	1530.61380000	50.96930000
56	1534.93780000	9.90200000
57	1622.42370000	10.96350000
58	1636.82000000	18.68560000
59	3080.36330000	0.37430000
60	3081.34040000	1.01510000
61	3088.24290000	1.04560000
62	3167.96210000	0.06400000
63	3168.41620000	0.39970000
64	3175.58390000	5.13360000
65	3183.46180000	0.14050000
66	3188.68830000	1.75040000
67	3189.35230000	0.02230000
68	3197.33020000	0.63220000
69	3203.61910000	0.68380000
70	3207.92490000	4.38980000
71	3232.43070000	2.08000000
72	3735.53220000	259.96000000

S5.6 *trans*-Hydroxy[4-(trimethylazaniumyl)phenyl]methylidene (2-H_t) (^{3}A)



Route	:	# opt freq b3lyp/cc-pvtz geom = connectivity empiricaldispersion = gd3bj int = ultrafine
SMILES	:	C[N](C)(C)c1ccc(cc1)[C]O
Formula	:	$C_{10}H_{14}NO^+$
Charge	:	1
Multiplicity	:	3
Energy	:	−519.34259425 a.u.
Gibbs Energy	:	−519.15893300 a.u.

Cartesian Coordinates (XYZ format)

26

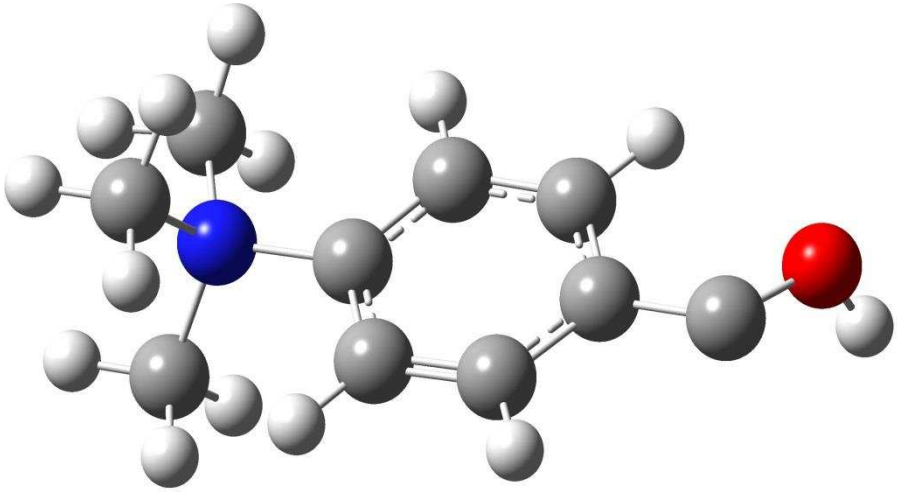
C	−1.36374903	−0.33521399	0.00143000
C	0.00756800	−0.36896500	0.00262500
C	0.76505297	0.83341002	0.00166800
C	0.05414400	2.06694102	−0.00055200
C	−1.32446694	2.08659601	−0.00172100
C	−2.04084301	0.89159697	−0.00078100
H	−1.89918101	−1.27305496	0.00224400
H	0.52122498	−1.31874096	0.00431200
H	0.60255998	2.99631596	−0.00132800
H	−1.81422698	3.04628491	−0.00341500
N	−3.54146504	0.87223601	−0.00181300
C	−4.13798809	2.24953389	−0.00511700
H	−5.21788216	2.14239311	−0.00571400
H	−3.82101202	2.78012609	0.88584298
H	−3.81958199	2.77643394	−0.89776897
C	−4.04273319	0.15658000	−1.23271406
H	−3.67201900	−0.86102998	−1.22946203
H	−5.12910986	0.15837599	−1.21814096
H	−3.66957092	0.68235898	−2.10544109
C	−4.04442787	0.16164100	1.23130500
H	−3.67400503	0.69207501	2.10238600
H	−5.13078022	0.16173001	1.21433997
H	−3.67208004	−0.85537601	1.23365903
C	2.15078902	0.80013901	0.00289100
O	2.97069001	1.82899499	0.00230200
H	3.89934897	1.56228101	0.00286900

Frequencies

Mode	IR frequency	IR intensity
1	43.47490000	0.30810000
2	66.01590000	7.92030000
3	99.63920000	120.05700000
4	146.62040000	3.55680000
5	172.19020000	14.15860000
6	227.58770000	2.09620000
7	247.03600000	1.04580000
8	277.50490000	0.10170000
9	303.76880000	2.65260000
10	330.93610000	2.39800000
11	352.84250000	1.80500000
12	353.21740000	0.47760000
13	390.76310000	1.13780000
14	424.82130000	2.52700000
15	455.94810000	0.05450000
16	470.41060000	1.85910000
17	484.72960000	3.16500000
18	533.81060000	28.61920000
19	571.64570000	5.15480000
20	643.62000000	1.44070000
21	673.58620000	2.62810000
22	713.58170000	0.04220000
23	805.45850000	1.86460000
24	820.80050000	34.90750000
25	825.72880000	6.88340000
26	844.12460000	34.21140000
27	937.45670000	17.41960000
28	963.47650000	17.25190000
29	964.17340000	0.85220000
30	980.49520000	0.17080000
31	1009.18760000	2.60980000
32	1076.42640000	0.02010000
33	1114.61040000	19.17460000
34	1129.69090000	5.80310000
35	1138.12070000	0.46740000
36	1155.26020000	44.45000000
37	1163.06240000	167.12380000
38	1192.49550000	206.35140000
39	1236.24060000	18.69230000
40	1256.41630000	5.19170000
41	1257.47880000	1.00440000
42	1293.42240000	7.83240000

43	1329.17990000	22.98050000
44	1347.77530000	0.12250000
45	1445.52650000	0.15270000
46	1449.59960000	4.49280000
47	1455.08390000	11.89440000
48	1478.88420000	0.00780000
49	1488.23990000	52.39790000
50	1489.15490000	0.40640000
51	1493.45820000	11.64570000
52	1500.08010000	57.15020000
53	1506.49830000	32.99770000
54	1512.34340000	23.31230000
55	1530.18130000	37.53460000
56	1553.58380000	1.03240000
57	1565.16130000	101.37530000
58	1614.05530000	1.08130000
59	3077.57940000	0.79440000
60	3079.70080000	2.83580000
61	3087.19400000	2.41790000
62	3165.21950000	0.00110000
63	3166.51200000	1.88290000
64	3173.90990000	8.08920000
65	3182.43540000	0.26900000
66	3185.22000000	2.85530000
67	3187.45220000	0.07720000
68	3195.27170000	1.05450000
69	3208.19540000	1.29520000
70	3209.41940000	0.09890000
71	3228.35390000	0.76680000
72	3777.86120000	431.67090000

S5.7 Transition state between 2-H_t and 2-H_c



Route	:	# opt=(calcfc,qst2) freq b3lyp/cc-pvtz geom = connectivity empiricaldis-persion = gd3bj int=ultrafine
SMILES	:	C[N](C)(C)c1ccc(cc1)[C]O
Formula	:	$C_{10}H_{14}NO^{+}$
Charge	:	1
Multiplicity	:	1
Energy	:	−519.32258175 a.u.
Gibbs Energy	:	−519.13842600 a.u.

Cartesian Coordinates (XYZ format)

26

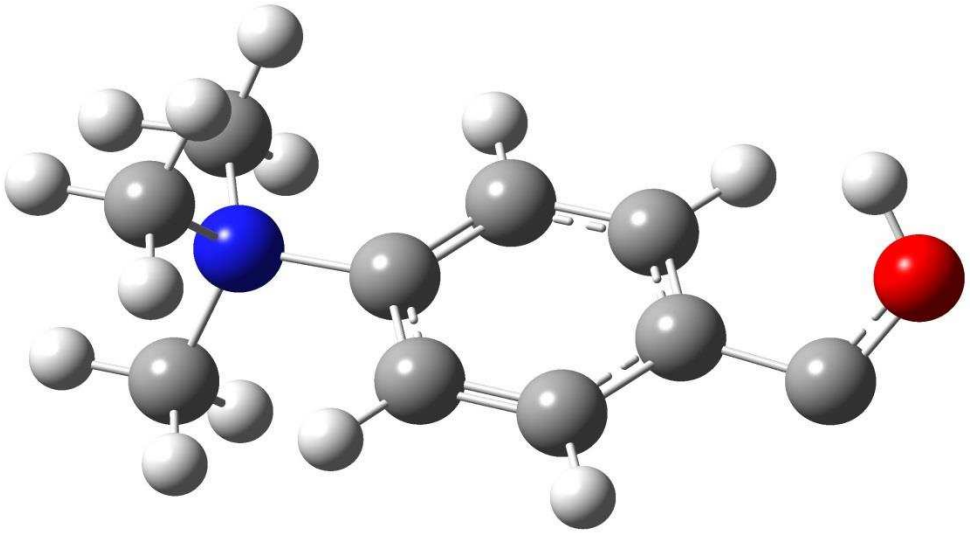
C	0.08338000	−1.26734102	−0.06751100
C	−1.29391503	−1.36306095	−0.14763100
C	−2.08958697	−0.21267200	−0.16050699
C	−1.47243798	1.04087496	−0.13828200
C	−0.08899900	1.15011895	−0.10615200
C	0.67614001	−0.00747200	−0.06007600
H	0.67253399	−2.17137599	−0.03923400
H	−1.77932203	−2.32750201	−0.20426500
H	−2.08505797	1.93031502	−0.16950300
H	0.35508499	2.13131309	−0.11217500
N	2.18016791	0.05924600	−0.02664700
C	2.70406294	1.46768796	−0.01162600
H	3.78733611	1.41419804	0.02062000
H	2.38880897	1.97941899	−0.91409701
H	2.33464408	1.97968495	0.87005699
C	2.68952394	−0.62906998	1.21743202
H	2.38478088	−1.66805601	1.20412004
H	3.77318311	−0.55843800	1.22857702
H	2.26476502	−0.12859000	2.08163404
C	2.74218893	−0.62416601	−1.25123703
H	2.35219502	−0.12152800	−2.13044691
H	3.82536006	−0.55186701	−1.21740496
H	2.43748093	−1.66337895	−1.25359094
C	−3.54854608	−0.41714600	−0.32417399
O	−4.22587681	0.69816798	0.00886600
H	−4.52334499	0.79768699	0.92078799

Frequencies

Mode	IR frequency	IR intensity
1	−1134.06790000	57.65630000
2	45.52880000	2.02840000
3	73.44940000	0.48820000
4	124.24510000	25.60080000
5	172.40660000	1.40730000
6	204.32120000	20.08850000
7	235.70360000	12.89080000
8	261.38080000	2.56330000
9	273.59390000	0.02950000
10	337.81200000	0.99470000
11	352.09780000	1.72960000
12	355.88250000	0.10260000
13	368.00760000	8.42180000
14	420.91610000	5.22430000
15	427.38360000	2.67090000
16	476.41110000	1.65610000
17	484.73040000	1.06780000
18	555.74790000	18.34380000
19	593.08280000	3.82300000
20	645.50110000	2.89050000
21	682.79110000	7.97790000
22	745.96980000	46.86660000
23	778.96550000	381.14360000
24	822.74160000	5.38960000
25	842.70870000	2.76850000
26	848.47930000	37.56120000
27	865.89800000	59.23460000
28	944.79260000	29.06650000
29	960.82360000	16.15180000
30	1000.62200000	7.70050000
31	1015.98090000	1.89480000
32	1033.71920000	9.16100000
33	1076.87160000	0.02210000
34	1121.28620000	15.49060000
35	1129.96820000	1.73280000
36	1139.80000000	0.55550000
37	1155.91140000	13.96090000
38	1160.78440000	7.16050000
39	1210.47360000	148.68270000
40	1231.32030000	129.20080000
41	1257.22070000	1.18020000
42	1257.26750000	1.49680000

43	1294.75430000	0.09680000
44	1338.25480000	1.28170000
45	1346.75970000	12.44630000
46	1438.95070000	11.60790000
47	1451.20070000	10.47190000
48	1451.82080000	4.97250000
49	1479.68630000	0.00240000
50	1488.98850000	0.38080000
51	1493.11310000	1.69980000
52	1495.06420000	0.70340000
53	1506.81430000	27.22600000
54	1513.26130000	24.34380000
55	1526.88380000	13.23470000
56	1530.53480000	45.99340000
57	1610.89720000	6.60410000
58	1629.94340000	27.85800000
59	3080.58770000	0.37850000
60	3081.58270000	0.77800000
61	3088.35480000	0.82010000
62	3168.34950000	0.07160000
63	3168.73890000	0.32300000
64	3175.91180000	4.79520000
65	3183.57150000	0.12210000
66	3188.30200000	0.89020000
67	3189.54280000	0.01460000
68	3194.86220000	2.00310000
69	3201.04770000	0.69900000
70	3206.60620000	4.77830000
71	3231.14330000	2.32520000
72	3809.65420000	326.83860000

S5.8 *cis*-Hydroxy[4-(trimethylazaniumyl)phenyl]methylidene (2-H_c)



Route	:	# opt freq b3lyp/cc-pvtz geom = connectivity empiricaldispersion = gd3bj int = ultrafine
SMILES	:	C[N](C)(C)c1ccc(cc1)[C]O
Formula	:	$C_{10}H_{14}NO^{+}$
Charge	:	1
Multiplicity	:	1
Energy	:	−519.35456936 a.u.
Gibbs Energy	:	−519.16790700 a.u.

Cartesian Coordinates (XYZ format)

26

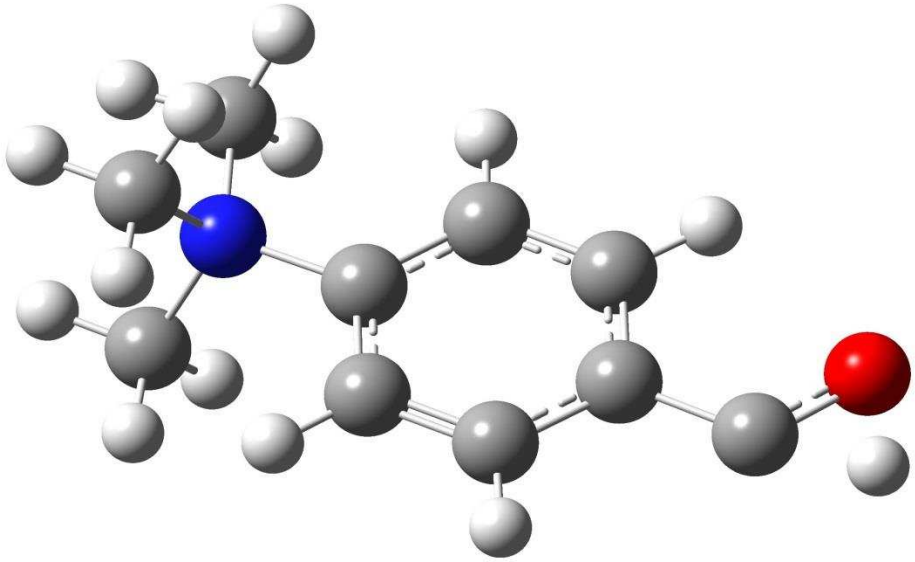
C	2.25937200	−2.52678800	−2.84601688
C	2.71635604	−2.12867689	−1.60591102
C	3.46070910	−0.95114601	−1.46558297
C	3.77635694	−0.21143900	−2.60822296
C	3.36207891	−0.63421100	−3.86709809
C	2.59554005	−1.78226697	−3.97617292
H	1.66912401	−3.42786503	−2.91743898
H	2.50585508	−2.72521591	−0.72980100
H	4.38780403	0.67779797	−2.53310299
H	3.64882493	−0.05009400	−4.72527981
N	2.12484694	−2.28235507	−5.31468582
C	2.54251289	−1.39127100	−6.44978523
H	2.15383601	−1.82244205	−7.36649609
H	2.12417603	−0.40161300	−6.30265617
H	3.62508392	−1.34865999	−6.49492121
C	2.70261598	−3.65377688	−5.57415581
H	2.36439800	−4.33640385	−4.80435514
H	2.36251903	−3.99150205	−6.54883623
H	3.78480291	−3.57662106	−5.55130577
C	0.61673802	−2.35826302	−5.32663584
H	0.22444400	−1.36526203	−5.13260508
H	0.29819399	−2.71197391	−6.30282402
H	0.28547800	−3.04418993	−4.55690479
C	3.99432111	−0.60911399	−0.13762800
O	3.87970996	0.64030600	0.18214101
H	3.39650297	1.20202601	−0.46748900

Frequencies

Mode	IR frequency	IR intensity
1	47.70470000	1.67620000
2	73.51170000	0.51720000
3	115.90480000	15.80280000
4	175.34430000	4.95570000
5	212.62470000	20.35810000
6	230.87990000	8.12430000
7	271.94200000	11.38010000
8	275.28330000	0.20410000
9	335.82930000	6.13240000
10	347.60650000	6.09540000
11	354.02240000	0.17700000
12	370.76850000	14.93420000
13	414.66580000	4.16770000
14	422.77130000	3.07720000
15	478.41230000	3.66650000
16	488.44900000	0.05900000
17	542.77400000	12.00570000
18	598.19100000	19.58000000
19	647.56270000	1.54720000
20	665.12250000	21.64300000
21	750.73100000	5.25300000
22	805.95590000	41.60070000
23	830.18870000	51.35460000
24	839.87840000	15.15800000
25	848.57480000	26.90680000
26	875.60240000	8.14500000
27	943.02860000	24.01270000
28	961.67970000	17.47610000
29	977.41860000	0.96300000
30	1006.06440000	0.51110000
31	1031.55200000	8.81680000
32	1076.61860000	0.02190000
33	1123.67040000	2.45120000
34	1132.12630000	0.62160000
35	1139.95270000	0.48570000
36	1162.66960000	4.50580000
37	1178.11020000	15.36710000
38	1228.86700000	1.17430000
39	1257.47830000	2.15150000
40	1257.61960000	1.83060000
41	1294.88540000	3.53950000
42	1316.55500000	86.96960000

43	1339.80630000	32.34260000
44	1357.14900000	31.60540000
45	1392.11020000	130.26610000
46	1438.02360000	7.68930000
47	1450.94450000	8.92310000
48	1451.51620000	4.86560000
49	1479.72260000	0.00540000
50	1489.04180000	0.36570000
51	1493.31930000	2.03260000
52	1494.97450000	0.32940000
53	1506.93320000	27.19830000
54	1513.25620000	24.16430000
55	1530.42660000	42.38360000
56	1534.07110000	27.12130000
57	1607.40900000	2.88390000
58	1635.43370000	0.37870000
59	3080.41000000	0.41860000
60	3081.40020000	0.97680000
61	3088.16090000	0.90000000
62	3168.29560000	0.01910000
63	3168.70790000	0.48640000
64	3175.83560000	5.13810000
65	3180.80370000	0.18410000
66	3182.75340000	0.15820000
67	3188.15180000	1.55710000
68	3188.99220000	0.02670000
69	3196.71450000	0.70610000
70	3207.32120000	3.36750000
71	3232.67490000	1.04950000
72	3384.10130000	52.18220000

S5.9 Transition state between 2-H_t and 3-H



Route	:	# opt=qst2 freq b3lyp/cc-pvtz geom = connectivity empiri-caldispersion = gd3bj int = ultrafine
SMILES	:	C[N](C)(C)c1ccc(cc1)[C]O
Formula	:	$C_{10}H_{14}NO^{+}$
Charge	:	1
Multiplicity	:	1
Energy	:	−519.31063961 a.u.
Gibbs Energy	:	−519.12919400 a.u.
CCSD(T)-F12b//cc-pVDZ-F12	:	−518.29642578 a.u.

Cartesian Coordinates (XYZ format)

26

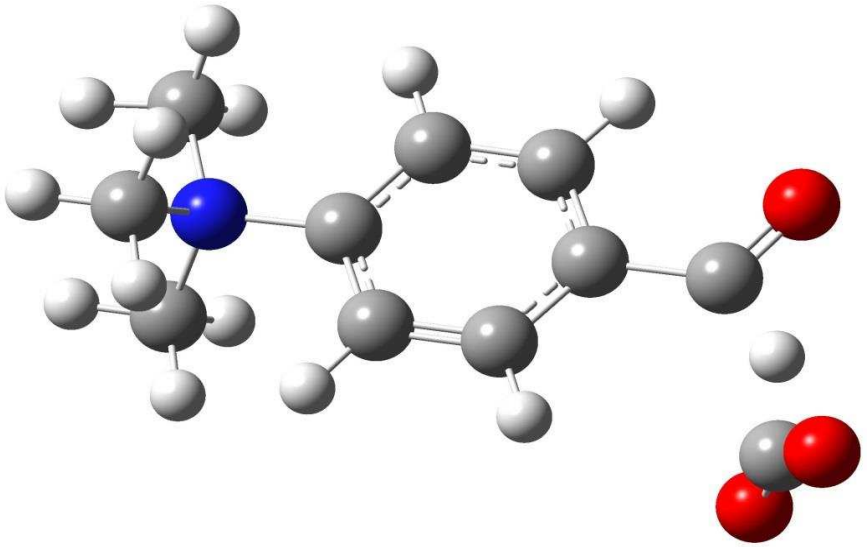
C	−0.14458500	−1.32966495	0.01837800
C	1.23252296	−1.48310995	0.01819100
C	2.06185389	−0.36515599	−0.00015700
C	1.50532901	0.91040099	−0.01831700
C	0.12836701	1.07732999	−0.01839900
C	−0.68488997	−0.04885000	−0.00002400
H	−0.77004099	−2.20918703	0.03280300
H	1.67543304	−2.46894097	0.03227200
H	2.16194105	1.76981103	−0.03226100
H	−0.27383599	2.07612395	−0.03264400
N	−2.18547702	0.08060900	0.00094900
C	−2.64966607	1.51001406	−0.02107500
H	−3.73469901	1.50215197	−0.01935400
H	−2.28468990	2.02109790	0.86291999
H	−2.28727698	1.99272299	−0.92192602
C	−2.75231910	−0.60142797	−1.22173095
H	−2.49224591	−1.65243304	−1.19985795
H	−3.83190894	−0.48370701	−1.21026301
H	−2.32561207	−0.13176900	−2.10213089
C	−2.74712396	−0.56181198	1.24724400
H	−2.31658101	−0.06436800	2.11035204
H	−3.82674098	−0.44421500	1.23665500
H	−2.48720098	−1.61304402	1.25783205
C	3.53185701	−0.55054402	−0.00005800
O	4.26049614	0.52738899	−0.01699800
H	4.78924322	−0.52827799	−0.00212600

Frequencies

Mode	IR frequency	IR intensity
1	−2042.60160000	477.02920000
2	43.12200000	0.00500000
3	66.09640000	0.00010000
4	107.46250000	1.40390000
5	162.34110000	0.77150000
6	209.58580000	0.31850000
7	246.21200000	1.43420000
8	256.66440000	1.51490000
9	273.83360000	0.02270000
10	335.70020000	0.02550000
11	353.64430000	1.08020000
12	356.26960000	0.02860000
13	370.96910000	0.45460000
14	419.68010000	0.73720000
15	428.73780000	2.61640000
16	474.15210000	0.99120000
17	483.72550000	1.15370000
18	543.22540000	44.45190000
19	594.89320000	1.56410000
20	599.76720000	0.81730000
21	645.82690000	0.03240000
22	705.58360000	20.83280000
23	751.79370000	6.27720000
24	835.58160000	1.45850000
25	846.41710000	0.53240000
26	861.47180000	89.04680000
27	862.44610000	34.14130000
28	945.66080000	30.15600000
29	960.60040000	16.33320000
30	1009.02420000	0.81590000
31	1020.27890000	0.11170000
32	1036.10610000	12.93230000
33	1077.11090000	0.02270000
34	1124.74640000	14.83650000
35	1130.88870000	0.27190000
36	1140.13960000	0.52470000
37	1157.85360000	3.00200000
38	1184.82050000	87.40600000
39	1230.62730000	25.24540000
40	1257.16450000	1.21460000
41	1257.36790000	1.71070000
42	1295.24740000	0.21060000

43	1339.32040000	85.15660000
44	1347.04980000	16.09510000
45	1397.40610000	190.07580000
46	1450.15680000	3.08730000
47	1452.09040000	4.82060000
48	1460.41260000	61.91680000
49	1479.88300000	0.00090000
50	1488.97680000	0.40100000
51	1493.45430000	1.67780000
52	1495.50810000	1.52960000
53	1507.30040000	26.19640000
54	1513.43000000	24.42570000
55	1530.57930000	51.85340000
56	1537.25220000	14.16940000
57	1632.98410000	12.12650000
58	1639.63880000	21.90840000
59	2600.56880000	168.62390000
60	3080.66620000	0.23700000
61	3081.48310000	0.86260000
62	3088.35390000	0.70160000
63	3168.40080000	0.01000000
64	3168.77560000	0.39420000
65	3176.02910000	4.25030000
66	3183.62360000	0.09690000
67	3188.92810000	0.62230000
68	3189.25550000	0.01690000
69	3190.65250000	6.05250000
70	3197.35200000	0.44530000
71	3208.62300000	3.92640000
72	3233.72250000	2.14910000

S5.10 Transition state between 1-H_t and 3-H



Route	:	# opt = (calcall,qst3) freq b3lyp/cc-pvtz geom = connectivity empiricaldispersion = gd3bj int = ultrafine
SMILES	:	C[N](C)(C)c1ccc(cc1)[C]=O.[C](=O)O
Formula	:	$C_{11}H_{14}NO_3^+$
Charge	:	1
Multiplicity	:	1
Energy	:	−707.97350053 a.u.
Gibbs Energy	:	−707.78540200 a.u.

Cartesian Coordinates (XYZ format)

29

C	0.10832600	−0.38801500	2.72786903
C	1.29711103	−0.39889601	2.01583099
C	1.58266997	0.60955203	1.10172999
C	0.66297901	1.63524902	0.90755200
C	−0.53386801	1.65649700	1.60866404
C	−0.80179602	0.64028198	2.51569009
H	−0.08680000	−1.18305194	3.43131304
H	2.00216794	−1.20223403	2.17995811
H	0.89657301	2.41676211	0.19827101
H	−1.22381604	2.46335292	1.42847800
N	−2.08870792	0.61580402	3.29663110
C	−2.98522997	1.78012002	2.98067904
H	−3.87969708	1.67899799	3.58652091
H	−2.47575688	2.70464993	3.22886300
H	−3.24919200	1.75658906	1.92919195
C	−2.85113311	−0.64756203	2.97424293
H	−2.25590801	−1.50751996	3.25537801
H	−3.78197408	−0.63875097	3.53369403
H	−3.04623795	−0.66449499	1.90683198
C	−1.78538299	0.66235602	4.77526808
H	−1.22896802	1.57124805	4.98032379
H	−2.72570205	0.65836000	5.31868410
H	−1.19461906	−0.20327701	5.04818010
C	2.86772799	0.61067301	0.32277101
O	3.16517401	1.53653204	−0.39112601
C	3.60163403	−1.34803104	−0.09927900
O	2.79703212	−2.00227404	−0.61871600
O	4.75294018	−1.18889499	0.35938099
H	4.16830778	−0.16773000	0.64260697

Frequencies

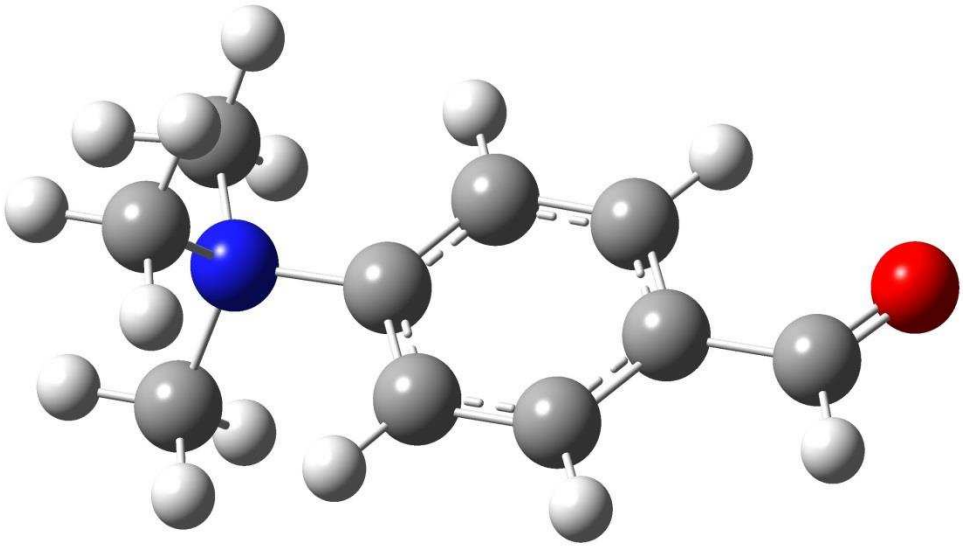
Mode	IR frequency	IR intensity
1	−2207.73280000	436.03840000
2	17.83010000	0.47520000
3	39.78210000	1.12070000
4	52.25380000	0.16600000
5	69.38160000	0.19900000
6	78.43310000	0.25090000
7	128.06860000	10.15770000
8	185.72200000	2.98040000
9	198.92040000	13.98920000
10	230.92530000	3.35040000
11	259.48410000	3.19400000
12	274.58230000	3.16740000
13	297.92990000	32.30000000
14	352.26920000	10.42020000
15	354.43260000	2.18100000
16	356.46390000	0.90870000
17	372.68530000	4.01890000
18	415.96680000	2.81650000
19	426.47670000	1.07720000
20	473.89900000	4.47230000
21	483.96640000	0.01070000
22	527.69380000	50.66180000
23	576.68940000	18.72360000
24	588.03210000	80.52490000
25	601.80470000	4.53820000
26	646.24720000	78.11620000
27	663.64490000	493.82120000
28	742.79860000	21.00160000
29	751.52590000	1.71670000
30	841.78990000	7.11570000
31	842.13740000	13.33720000
32	859.68350000	25.35420000
33	878.78060000	71.49720000
34	944.83520000	26.36520000
35	960.54840000	15.51420000
36	987.83430000	8.95360000
37	998.76080000	13.10220000
38	1016.85120000	1.04930000
39	1037.75080000	11.10420000
40	1077.00360000	0.02850000
41	1127.66660000	27.80490000
42	1132.13400000	1.59380000

43	1140.25790000	0.47220000
44	1162.73080000	23.92310000
45	1184.07460000	255.22700000
46	1226.97500000	67.81320000
47	1248.48720000	279.62870000
48	1257.50660000	3.93290000
49	1257.69040000	2.79100000
50	1295.38870000	0.28830000
51	1348.74010000	14.62720000
52	1350.94940000	0.65560000
53	1446.72050000	2.61910000
54	1452.03140000	5.52470000
55	1452.35970000	12.77920000
56	1479.92290000	0.00290000
57	1489.00130000	0.28400000
58	1493.37360000	2.00610000
59	1495.25590000	0.60670000
60	1507.48940000	27.64940000
61	1513.40310000	24.28850000
62	1530.46870000	51.38010000
63	1538.89740000	9.60970000
64	1631.42830000	21.64320000
65	1640.62420000	21.29320000
66	1713.76750000	76.07900000
67	1795.33750000	131.41650000
68	2166.05420000	382.28160000
69	3080.57620000	0.24150000
70	3081.47500000	0.89260000
71	3088.26990000	0.69960000
72	3168.45260000	0.01760000
73	3168.94320000	0.47530000
74	3176.11660000	4.57210000
75	3183.38380000	0.75870000
76	3183.46410000	0.99990000
77	3188.63960000	0.03390000
78	3190.66540000	1.44600000
79	3199.06650000	4.76040000
80	3206.27250000	3.20910000
81	3235.35850000	2.09230000
82	−2207.73230000	436.03830000
83	17.82910000	0.47520000
84	39.78080000	1.12070000
85	52.25300000	0.16600000
86	69.38130000	0.19900000
87	78.43320000	0.25090000
88	128.06870000	10.15780000

89	185.72200000	2.98040000
90	198.92050000	13.98900000
91	230.92520000	3.35040000
92	259.48410000	3.19400000
93	274.58230000	3.16730000
94	297.93000000	32.30010000
95	352.26930000	10.41980000
96	354.43260000	2.18130000
97	356.46390000	0.90880000
98	372.68530000	4.01890000
99	415.96690000	2.81650000
100	426.47690000	1.07720000
101	473.89890000	4.47220000
102	483.96630000	0.01070000
103	527.69410000	50.66140000
104	576.68910000	18.72310000
105	588.03200000	80.52560000
106	601.80470000	4.53820000
107	646.24740000	78.11800000
108	663.64480000	493.81920000
109	742.79860000	21.00150000
110	751.52690000	1.71670000
111	841.78980000	7.11260000
112	842.13740000	13.34020000
113	859.68360000	25.35440000
114	878.78070000	71.49720000
115	944.83510000	26.36520000
116	960.54840000	15.51410000
117	987.83440000	8.95380000
118	998.76080000	13.10190000
119	1016.85150000	1.04930000
120	1037.75090000	11.10430000
121	1077.00370000	0.02850000
122	1127.66660000	27.80500000
123	1132.13410000	1.59380000
124	1140.25800000	0.47220000
125	1162.73080000	23.92330000
126	1184.07470000	255.22630000
127	1226.97510000	67.81380000
128	1248.48710000	279.62860000
129	1257.50670000	3.93290000
130	1257.69050000	2.79070000
131	1295.38880000	0.28830000
132	1348.73970000	14.62720000
133	1350.94960000	0.65570000
134	1446.72070000	2.61900000

135	1452.03150000	5.52480000
136	1452.35990000	12.77910000
137	1479.92310000	0.00290000
138	1489.00160000	0.28400000
139	1493.37380000	2.00610000
140	1495.25620000	0.60660000
141	1507.48960000	27.64940000
142	1513.40330000	24.28860000
143	1530.46900000	51.38020000
144	1538.89760000	9.60960000
145	1631.42840000	21.64310000
146	1640.62420000	21.29340000
147	1713.76790000	76.07920000
148	1795.33780000	131.41690000
149	2166.05420000	382.28150000
150	3080.57620000	0.24150000
151	3081.47500000	0.89260000
152	3088.26990000	0.69960000
153	3168.45260000	0.01760000
154	3168.94320000	0.47530000
155	3176.11650000	4.57210000
156	3183.38380000	0.75710000
157	3183.46410000	1.00160000
158	3188.63950000	0.03390000
159	3190.66530000	1.44600000
160	3199.06650000	4.76040000
161	3206.27250000	3.20920000
162	3235.35860000	2.09230000

S5.11 4-(Trimethylammonio)benzaldehyde (3-H)



Route	:	# opt freq b3lyp/cc-pvtz geom = connectivity empiricaldis-persion = gd3bj int=ultrafine
SMILES	:	C[N](C)(C)c1ccc(cc1)C=O
Formula	:	$C_{10}H_{14}NO^{+}$
Charge	:	1
Multiplicity	:	1
Energy	:	−519.44317494 a.u.
Gibbs Energy	:	−519.25528500 a.u.
CCSD(T)-F12b//cc-pVDZ-F12	:	−518.42767991 a.u.

Cartesian Coordinates (XYZ format)

26

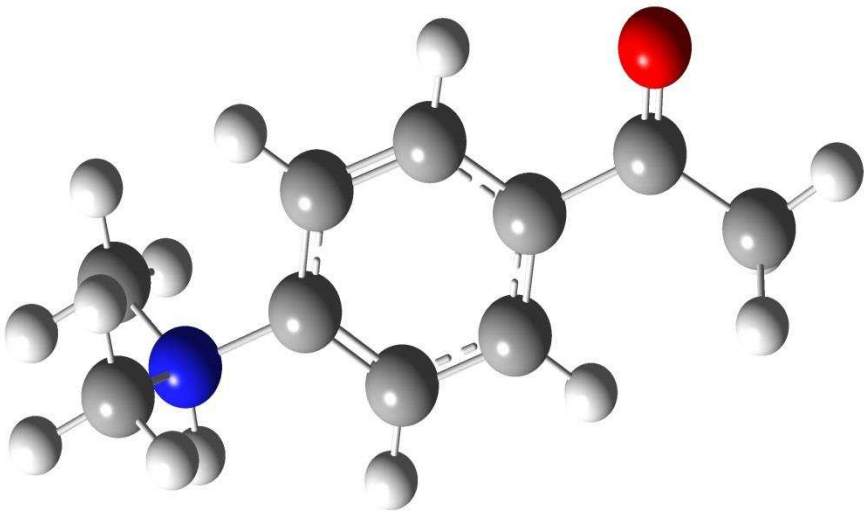
C	−1.37152398	−0.33982199	0.00145600
C	0.01441100	−0.36185101	0.00259900
C	0.73788297	0.82664102	0.00150100
C	0.06232600	2.04243803	−0.00070200
C	−1.32407904	2.07856703	−0.00183900
C	−2.03106904	0.88320702	−0.00079900
H	−1.90991402	−1.27530503	0.00240200
H	0.53327698	−1.31117904	0.00434500
H	0.63639498	2.95812702	−0.00151100
H	−1.81521499	3.03665209	−0.00354400
N	−3.53673410	0.87267399	−0.00181500
C	−4.13018322	2.25370097	−0.00494000
H	−5.20992804	2.14640689	−0.00560400
H	−3.81429696	2.78365588	0.88683897
H	−3.81279397	2.78023005	−0.89822298
C	−4.03709507	0.15902400	−1.23523402
H	−3.68177390	−0.86398101	−1.22727203
H	−5.12296820	0.17686400	−1.22509003
H	−3.65414810	0.67815900	−2.10794497
C	−4.03865623	0.16381800	1.23371994
H	−3.65803695	0.68721497	2.10490394
H	−5.12453508	0.18028100	1.22140598
H	−3.68198204	−0.85874897	1.23089004
C	2.22971392	0.80528700	0.00269600
O	2.89823008	1.80445004	0.00209700
H	2.68725204	−0.20112400	0.00419100

Frequencies

Mode	IR frequency	IR intensity
1	43.84490000	0.50830000
2	71.61620000	0.15240000
3	133.40510000	8.68670000
4	165.54090000	5.21260000
5	215.40800000	0.91830000
6	257.74250000	3.07260000
7	259.05140000	4.10710000
8	274.66280000	0.01180000
9	333.86190000	0.86560000
10	354.36120000	2.15100000
11	356.65510000	0.01640000
12	378.85470000	0.00010000
13	424.68990000	0.01090000
14	435.71790000	1.01170000
15	474.70230000	1.67880000
16	483.55120000	1.81450000
17	561.47150000	26.60460000
18	599.04300000	1.64420000
19	647.93280000	0.93460000
20	712.77620000	22.81050000
21	741.00270000	3.31730000
22	835.43030000	1.08860000
23	843.40450000	6.83720000
24	851.22610000	19.54630000
25	858.80210000	85.96800000
26	944.27960000	24.73310000
27	960.55030000	16.63200000
28	987.33500000	0.93230000
29	1013.32440000	0.02480000
30	1036.59280000	8.51070000
31	1040.76960000	2.57520000
32	1077.07160000	0.02480000
33	1127.24160000	11.97580000
34	1131.48020000	0.88440000
35	1140.25720000	0.49870000
36	1161.03870000	4.03860000
37	1199.65020000	32.25610000
38	1233.85560000	20.84110000
39	1257.49620000	1.58410000
40	1257.50190000	1.56850000
41	1295.32350000	0.30660000
42	1345.69610000	18.85110000

43	1350.02070000	8.28070000
44	1412.93140000	11.20470000
45	1450.27910000	3.40510000
46	1452.08720000	4.80190000
47	1459.11360000	10.82000000
48	1479.98850000	0.00130000
49	1488.99750000	0.39080000
50	1493.54480000	1.98960000
51	1495.57150000	0.47970000
52	1507.49050000	27.93070000
53	1513.48450000	24.47940000
54	1530.66650000	50.58260000
55	1541.89940000	9.35790000
56	1635.74390000	9.02420000
57	1644.53600000	28.08810000
58	1798.13510000	185.80510000
59	2926.02250000	77.54350000
60	3080.48820000	0.23360000
61	3081.37050000	0.86830000
62	3088.24030000	0.67110000
63	3168.25770000	0.01020000
64	3168.73770000	0.49550000
65	3176.03670000	3.95150000
66	3182.00150000	0.84530000
67	3183.40980000	0.08940000
68	3188.79570000	0.00980000
69	3190.52230000	1.62150000
70	3202.43780000	3.45810000
71	3206.35320000	3.33860000
72	3237.62100000	1.48560000

S5.12 Phenyl-methyl-ketone 4-H



Route	:	# opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj int=ultrafine
SMILES	:	CC(=O)c1ccc(cc1)[NH](C)C
Formula	:	$C_{10}H_{14}NO^{+}$
Charge	:	1
Multiplicity	:	1
Energy	:	−519.46225650 a.u.
Gibbs Energy	:	−519.27628600 a.u.

Cartesian Coordinates (XYZ format)

26

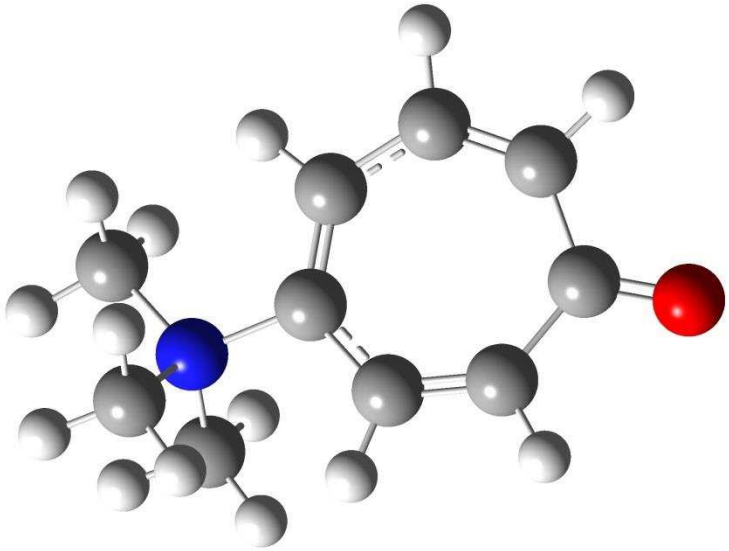
C	−0.10975000	−1.27524602	0.30050200
C	1.27624595	−1.38385296	0.32427701
C	2.07125807	−0.34867200	−0.15904500
C	1.46511197	0.80179799	−0.66887301
C	0.08744600	0.92437601	−0.69909197
C	−0.67829102	−0.12378600	−0.21045400
H	−0.72431201	−2.08348107	0.67770398
H	1.72352695	−2.28166199	0.72268099
H	2.10064101	1.59303796	−1.03887498
H	−0.36537099	1.82140398	−1.09691000
N	−2.15978789	−0.02604900	−0.22758301
C	−2.67870688	1.08293700	0.64899600
H	−3.76376510	1.03237104	0.66608697
H	−2.26945496	0.95117903	1.64544201
H	−2.35343003	2.03069901	0.23427600
C	−2.72033501	0.05310900	−1.62301302
H	−2.33964109	−0.78849101	−2.19267893
H	−3.80460906	0.02173700	−1.56331003
H	−2.39574790	0.98524499	−2.07225800
C	3.58350706	−0.40474099	−0.16151300
O	4.20071220	0.53719503	−0.60030198
C	4.26323891	−1.63182104	0.38273799
H	3.99243903	−1.79408205	1.42790103
H	3.96369195	−2.52107096	−0.17542601
H	5.33811283	−1.50302303	0.30500799
H	−2.49837589	−0.89977002	0.17466000

Frequencies

Mode	IR frequency	IR intensity
1	33.96590000	1.86870000
2	53.88350000	1.43770000
3	73.45260000	0.99140000
4	154.03270000	2.40170000
5	161.24510000	0.22410000
6	185.16660000	0.07910000
7	217.81770000	0.00740000
8	233.27510000	0.21390000
9	257.08770000	0.01490000
10	299.19070000	8.14380000
11	361.47520000	1.06390000
12	381.85860000	1.36480000
13	416.96270000	0.00410000
14	444.97390000	1.41020000
15	522.22370000	1.17310000
16	529.05290000	10.96080000
17	580.47220000	16.77540000
18	604.49300000	25.04120000
19	646.64780000	6.46580000
20	666.28370000	9.15020000
21	750.55460000	0.85480000
22	796.84600000	5.09550000
23	833.79470000	6.58320000
24	861.24820000	23.46280000
25	891.78000000	18.04680000
26	967.44930000	29.72280000
27	973.83730000	17.00310000
28	982.82270000	4.50060000
29	1022.51950000	0.23350000
30	1036.44160000	12.57430000
31	1049.57720000	3.22170000
32	1054.99030000	0.21950000
33	1097.89630000	3.49810000
34	1135.67980000	29.42980000
35	1145.42260000	14.05550000
36	1162.17480000	1.92570000
37	1201.05520000	1.00670000
38	1210.03720000	27.99520000
39	1254.65200000	16.45620000
40	1266.33190000	132.99280000
41	1334.02910000	1.19150000
42	1346.03820000	10.28640000

43	1393.59860000	12.25290000
44	1404.33720000	62.13360000
45	1409.46840000	7.03940000
46	1451.47240000	4.70570000
47	1468.24800000	10.36390000
48	1477.49950000	8.28670000
49	1478.51740000	13.09600000
50	1478.97290000	0.68960000
51	1488.53820000	1.08600000
52	1490.22230000	14.07900000
53	1504.51920000	28.79260000
54	1511.53440000	34.33150000
55	1539.99480000	6.04310000
56	1641.82340000	11.65610000
57	1647.74100000	12.89700000
58	1779.44250000	142.48270000
59	3035.34040000	4.19370000
60	3077.57950000	0.05440000
61	3080.53770000	0.86070000
62	3089.31810000	3.32010000
63	3155.16630000	2.53970000
64	3163.59410000	4.33200000
65	3168.71950000	0.12940000
66	3171.50690000	2.29640000
67	3181.14570000	0.79120000
68	3181.21350000	0.03410000
69	3190.47360000	0.82640000
70	3210.69260000	9.50100000
71	3213.64830000	0.14540000
72	3446.86000000	40.17550000

S5.13 Tropone 5-H



Route	:	# opt freq b3lyp/cc-pvtz geom = connectivity empiricaldispersion = gd3bj int = ultrafine
SMILES	:	C[N](C)(C)c1cccc(=O)cc1
Formula	:	$C_{10}H_{14}NO^{+}$
Charge	:	1
Multiplicity	:	1
Energy	:	−519.39986704 a.u.
Gibbs Energy	:	−519.21212800 a.u.

Cartesian Coordinates (XYZ format)

26

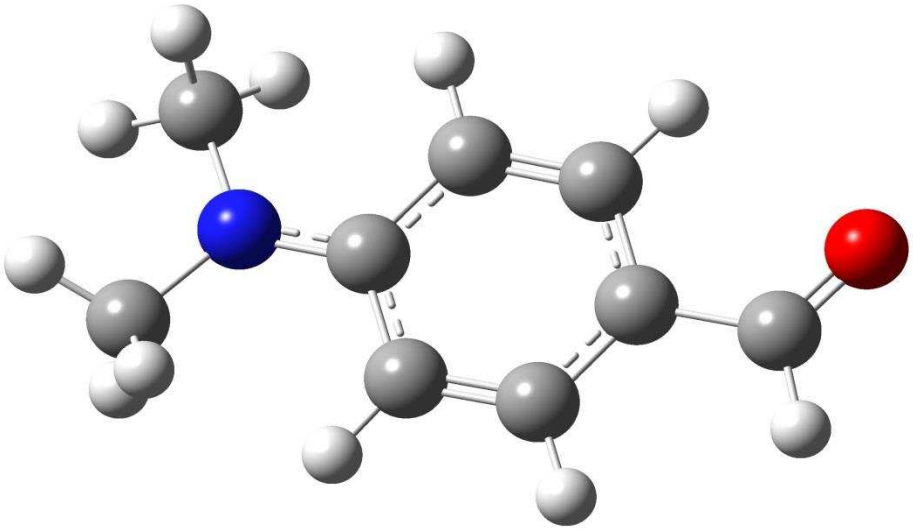
C	−0.01890300	−1.30077195	−0.28656599
C	1.26953197	−1.69552600	−0.32576099
C	2.54212403	0.51656997	−0.15646100
C	1.52183402	1.39622104	−0.08954400
C	0.11116900	1.17422295	0.03075800
C	−0.56093800	0.00469600	−0.04805500
H	−0.73236299	−2.09449911	−0.45423999
H	1.45884800	−2.74419999	−0.51743001
H	1.79462194	2.44392705	−0.10167300
H	−0.44720301	2.08262491	0.18071200
N	−2.07463098	0.02034200	0.09095300
C	−2.64380503	1.37938297	0.39122701
H	−3.71723795	1.26359403	0.49762100
H	−2.22314596	1.75256598	1.31845701
H	−2.43301105	2.05412793	−0.43086100
C	−2.71279311	−0.44922501	−1.19685602
H	−2.40187812	−1.46297300	−1.41420996
H	−3.79125690	−0.41376200	−1.07542896
H	−2.39619207	0.21565101	−1.99404204
C	−2.48451209	−0.88611698	1.23022902
H	−2.01734400	−0.52028298	2.13903499
H	−3.56632710	−0.85532099	1.31744003
H	−2.15950608	−1.89885795	1.02974606
C	2.51536608	−0.94967800	−0.07980900
O	3.54140496	−1.56713104	0.14118600
H	3.54866695	0.91008502	−0.22301400

Frequencies

Mode	IR frequency	IR intensity
1	22.10620000	3.77330000
2	72.93620000	0.31370000
3	134.98600000	4.10270000
4	202.55540000	0.17710000
5	228.62420000	0.40900000
6	257.75690000	0.12040000
7	259.75940000	0.90140000
8	295.94180000	3.22220000
9	334.24610000	2.09260000
10	350.99530000	1.36440000
11	378.58980000	0.92880000
12	401.62640000	4.69850000
13	410.77700000	3.47620000
14	446.23530000	3.45670000
15	471.79850000	2.66240000
16	484.17810000	4.41850000
17	527.04950000	3.83060000
18	580.88730000	12.97580000
19	628.92970000	2.13040000
20	691.49270000	1.18840000
21	727.90150000	7.69190000
22	804.26150000	4.56030000
23	820.55530000	29.65560000
24	853.31430000	14.39430000
25	885.08320000	17.17190000
26	912.91070000	6.21330000
27	932.51650000	27.39040000
28	955.98810000	16.00670000
29	957.79380000	5.35850000
30	1006.95570000	16.55800000
31	1033.46480000	0.65100000
32	1053.62400000	0.37490000
33	1075.49490000	0.03950000
34	1098.94040000	2.23340000
35	1138.80440000	0.47080000
36	1150.60830000	4.30440000
37	1246.82100000	5.04850000
38	1253.89240000	1.67430000
39	1255.89240000	2.10810000
40	1277.91730000	3.11280000
41	1287.52370000	2.63560000
42	1329.37560000	2.04650000

43	1415.35130000	0.55580000
44	1449.78020000	4.62190000
45	1451.78780000	5.51590000
46	1458.95310000	3.83270000
47	1480.61470000	2.57550000
48	1482.70260000	9.08070000
49	1490.34100000	0.28580000
50	1492.78900000	5.45160000
51	1499.51940000	8.38990000
52	1515.02400000	19.21200000
53	1516.07510000	23.33930000
54	1532.83550000	46.40630000
55	1578.28870000	5.87050000
56	1662.66010000	9.41170000
57	1683.00020000	64.00630000
58	1722.15970000	225.32570000
59	3082.57620000	0.44650000
60	3083.29800000	0.14320000
61	3089.75830000	0.28580000
62	3164.09060000	2.49140000
63	3168.48250000	0.68420000
64	3169.58320000	0.00210000
65	3171.14360000	2.44380000
66	3176.41840000	3.08850000
67	3183.69850000	0.11810000
68	3184.18690000	0.02470000
69	3185.65400000	2.97460000
70	3193.29510000	0.07680000
71	3200.66300000	0.79670000
72	3232.04630000	1.13340000

S5.14 *N,N*-Dimethyl-aldehyde radical cation 6-H



Route	:	# opt freq b3lyp/cc-pvtz geom = connectivity empiricaldispersion = gd3bj int = ultrafine
SMILES	:	CN(C)c1ccc(cc1)C=O
Formula	:	$C_9H_{11}NO^{\cdot+}$
Charge	:	1
Multiplicity	:	2
Energy	:	−479.48602076 a.u.
Gibbs Energy	:	−479.34149600 a.u.

Cartesian Coordinates (XYZ format)

22

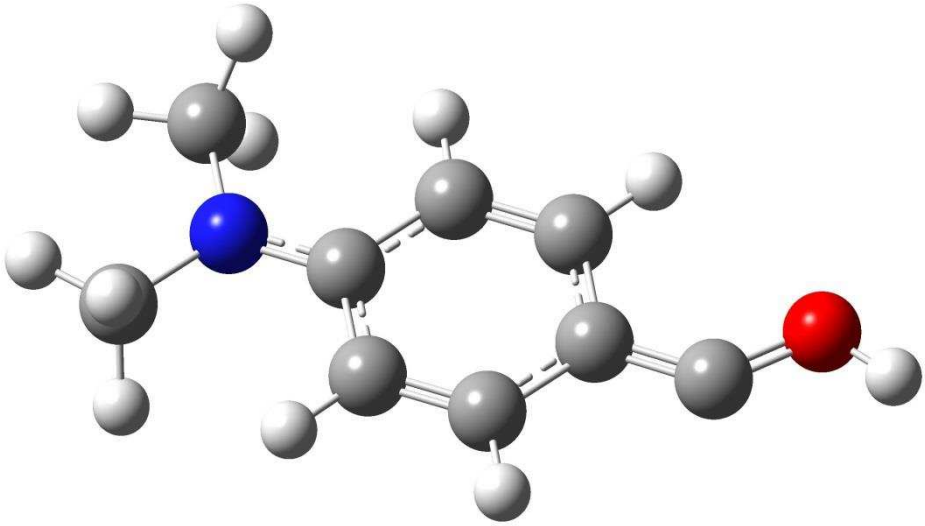
C	−0.00751100	−1.13930595	−0.56096399
C	1.34729803	−1.28524804	−0.41264501
C	2.14198089	−0.20578501	0.00121100
C	1.54772997	1.04360795	0.26191401
C	0.20138800	1.21760798	0.10919700
C	−0.62155998	0.12475300	−0.30584601
H	−0.59748602	−1.97334301	−0.90297598
H	1.81044197	−2.24009490	−0.62255901
H	2.18145895	1.85497403	0.59058100
H	−0.23911500	2.17440701	0.33589399
N	−1.95170295	0.28474599	−0.45507500
C	−2.59111595	1.60162795	−0.39691100
H	−3.52127504	1.55408502	−0.95454103
H	−2.81641603	1.86210406	0.63931799
H	−1.95390499	2.36047411	−0.83722800
C	−2.85792804	−0.84231800	−0.68671602
H	−2.51639390	−1.72862899	−0.16435499
H	−3.84102988	−0.57102299	−0.31408900
H	−2.93351698	−1.04683805	−1.75670803
C	3.61253095	−0.36828700	0.16814700
O	4.32088709	0.53851098	0.52311701
H	4.01313019	−1.37220597	−0.05408300

Frequencies

Mode	IR frequency	IR intensity
1	61.36310000	0.89030000
2	71.23440000	0.14810000
3	82.04760000	0.39030000
4	123.65540000	5.32600000
5	139.72510000	5.77890000
6	177.05600000	7.72250000
7	247.57910000	0.33480000
8	288.83740000	5.98030000
9	349.46430000	1.26930000
10	373.09740000	6.46400000
11	403.25230000	0.67230000
12	474.79780000	2.33110000
13	490.84190000	2.52190000
14	526.15250000	10.29510000
15	594.48670000	2.34680000
16	624.10320000	0.75640000
17	716.84610000	3.45320000
18	724.96000000	22.22870000
19	810.89100000	1.67640000
20	831.14110000	70.32080000
21	852.06200000	45.41990000
22	939.79260000	5.86420000
23	996.28860000	0.40290000
24	1009.75340000	0.33430000
25	1019.90560000	1.49960000
26	1038.48420000	3.77620000
27	1059.59870000	7.51870000
28	1082.84680000	24.23900000
29	1144.03330000	2.83970000
30	1146.82800000	0.74330000
31	1157.59000000	1.10510000
32	1194.69230000	7.01200000
33	1225.61860000	3.69630000
34	1245.75720000	26.47340000
35	1332.96170000	19.99290000
36	1365.13130000	6.87500000
37	1393.36400000	15.86930000
38	1419.07520000	8.26490000
39	1446.25220000	12.14910000
40	1460.60160000	15.52960000
41	1470.85050000	20.54990000
42	1488.65990000	6.90700000

43	1493.94770000	11.88680000
44	1499.54720000	19.40280000
45	1515.12970000	2.78440000
46	1525.01170000	5.34500000
47	1532.89530000	4.56310000
48	1613.64580000	49.43220000
49	1760.39290000	106.60830000
50	2951.93370000	69.55160000
51	3040.11390000	0.14640000
52	3043.88440000	3.19060000
53	3129.07440000	0.72140000
54	3133.30000000	1.80610000
55	3168.63680000	0.52280000
56	3172.10500000	0.28040000
57	3187.05470000	0.04420000
58	3205.14970000	6.14180000
59	3232.85700000	1.71390000
60	3233.53460000	0.65420000

S5.15 {4-[Dimethyl(ylo)azaniumyl]phenyl}hydroxymethyli-dene (7-H_t)



Route	:	# opt freq b3lyp/cc-pvtz geom = connectivity empiricaldispersion = gd3bj int = ultrafine
SMILES	:	CN(C)c1ccc(cc1)[C]O
Formula	:	$C_9H_{11}NO^{\cdot +}$
Charge	:	1
Multiplicity	:	2
Energy	:	−479.44469992 a.u.
Gibbs Energy	:	−479.30026800 a.u.

Cartesian Coordinates (XYZ format)

22

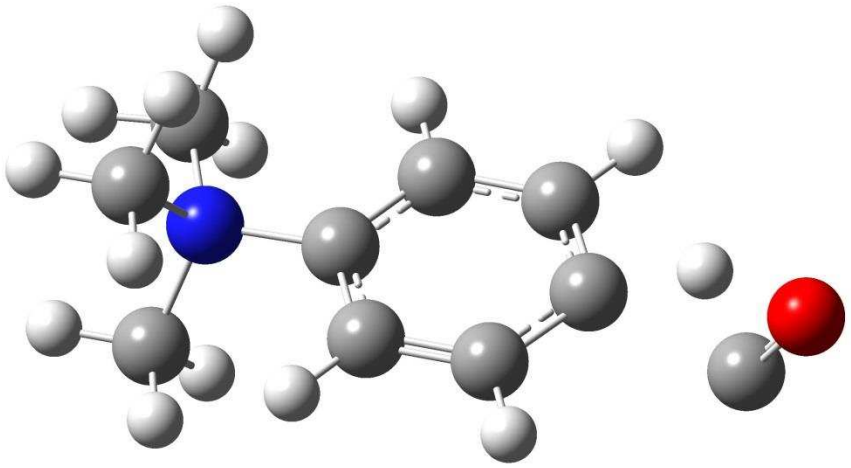
C	0.02831200	−1.12765098	0.56750000
C	−1.31337094	−1.28137505	0.44019201
C	−2.14577699	−0.18626800	0.05684000
C	−1.53007603	1.08523905	−0.19201700
C	−0.19012401	1.23857903	−0.06490600
C	0.64936697	0.13951799	0.32058400
H	0.62769300	−1.97358000	0.85794300
H	−1.76908004	−2.24251103	0.62920803
H	−2.14798594	1.92226005	−0.48280501
H	0.24503000	2.20481992	−0.25790301
N	1.96662402	0.29604501	0.44426101
C	2.60182095	1.59322596	0.19003300
H	3.66956496	1.49594498	0.34398600
H	2.42941999	1.91530097	−0.83651400
H	2.22237492	2.35206795	0.87379301
C	2.82444191	−0.82552898	0.83979499
H	2.76102710	−1.63661802	0.11483400
H	3.85111308	−0.48305899	0.88323098
H	2.54335189	−1.20033300	1.82358003
C	−3.49087596	−0.36008599	−0.06549400
O	−4.41395807	0.47071201	−0.39168501
H	−5.30577707	0.08753400	−0.40548199

Frequencies

Mode	IR frequency	IR intensity
1	38.74530000	0.00220000
2	58.73300000	0.15460000
3	116.26590000	1.13840000
4	126.29010000	44.26430000
5	148.91610000	2.58560000
6	160.04530000	4.09060000
7	210.55340000	35.76950000
8	262.73420000	0.52380000
9	319.40320000	30.59420000
10	348.58590000	0.22870000
11	406.61480000	4.98250000
12	474.31100000	0.60300000
13	481.25030000	28.99260000
14	501.42750000	1.62250000
15	538.16970000	0.11420000
16	576.89500000	24.68350000
17	634.81280000	5.01420000
18	712.69870000	17.37030000
19	755.32220000	1.12810000
20	804.48570000	0.14760000
21	818.05330000	21.94960000
22	859.12550000	61.68280000
23	944.45410000	6.30750000
24	998.87100000	0.13250000
25	1008.35370000	0.00210000
26	1010.90110000	0.26610000
27	1072.50690000	21.18020000
28	1119.10280000	0.00580000
29	1146.75430000	197.16510000
30	1151.25310000	0.10370000
31	1177.90530000	164.25700000
32	1203.77320000	5.77660000
33	1228.75690000	17.64920000
34	1246.28280000	5.86200000
35	1282.19960000	149.05970000
36	1340.65830000	53.11400000
37	1379.89830000	3.19070000
38	1435.95220000	89.61770000
39	1455.54120000	0.63880000
40	1479.88770000	174.28180000
41	1490.43000000	0.02870000
42	1501.08080000	0.02540000

43	1505.07190000	24.25300000
44	1508.00650000	26.82570000
45	1519.64290000	30.55240000
46	1561.25780000	2.76280000
47	1577.24550000	894.12600000
48	1639.34610000	794.56250000
49	1675.15470000	52.28370000
50	3042.82190000	14.08610000
51	3046.80440000	14.09810000
52	3103.36790000	0.46110000
53	3104.46810000	10.77940000
54	3163.11190000	0.27460000
55	3176.77260000	5.64810000
56	3201.91100000	0.36600000
57	3203.43100000	0.45240000
58	3233.88960000	0.25860000
59	3238.94740000	0.19910000
60	3713.64190000	672.71440000

S5.16 Transition state between 2-H_c and (*N*,*N*,*N*)-trimethylammoniobenzene



Route	:	# opt = (calcall,qst3) freq b3lyp/cc-pvtz geom = connectivity empiricaldispersion = gd3bj int = ultrafine
SMILES	:	C[N](C)(C)c1cc[c]cc1.[C]O
Formula	:	$C_{10}H_{14}NO^{+}$
Charge	:	1
Multiplicity	:	1
Energy	:	−519.26579635 a.u.
Gibbs Energy	:	−519.08735700 a.u.

Cartesian Coordinates (XYZ format)

26

C	0.07931000	−0.21010800	0.29181901
C	1.43264604	−0.40966901	0.50482303
C	2.38932204	0.34947801	−0.17815700
C	1.94912899	1.29923105	−1.10024095
C	0.59378201	1.51232600	−1.32728100
C	−0.33117601	0.75186598	−0.62720400
H	−0.63264197	−0.80755401	0.84194398
H	1.74295700	−1.17105603	1.20920300
H	2.66505003	1.88680196	−1.66109705
H	0.29917601	2.26186395	−2.04245591
N	−1.81008601	0.93329799	−0.84362203
C	−2.12597704	2.00029707	−1.85327494
H	−3.20588207	2.06051612	−1.94034600
H	−1.73143101	2.94988108	−1.50900197
H	−1.69486201	1.72925794	−2.81060910
C	−2.40948105	−0.35966599	−1.34375405
H	−2.25589299	−1.13570595	−0.60417902
H	−3.47190309	−0.20483600	−1.50790501
H	−1.91372800	−0.62818599	−2.27101898
C	−2.46815896	1.32739902	0.45706001
H	−2.01612401	2.25220609	0.80069900
H	−3.53040195	1.46423995	0.27688700
H	−2.31295490	0.54493201	1.18942499
C	4.06432009	−0.43873501	−0.47264299
O	4.78425407	0.16073801	0.35202199
H	3.70550799	0.61251402	0.49544501

Frequencies

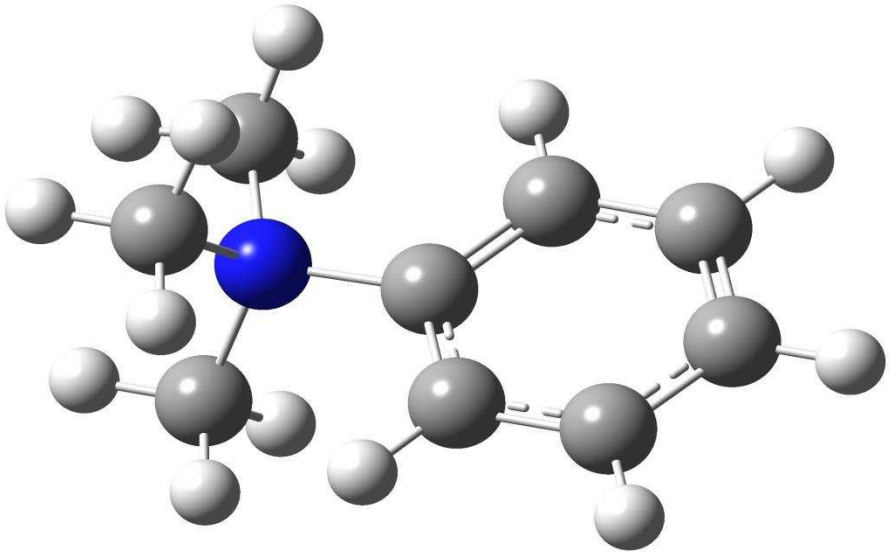
Mode	IR frequency	IR intensity
1	−2409.12730000	430.88300000
2	48.43410000	0.38530000
3	63.79740000	1.28500000
4	71.71350000	0.24620000
5	160.55860000	3.26480000
6	174.53290000	2.12280000
7	228.73680000	0.06420000
8	242.08150000	33.99940000
9	265.41810000	3.29410000
10	287.16570000	8.33260000
11	346.55860000	5.62090000
12	351.42770000	0.56140000
13	354.35790000	4.57840000
14	394.67050000	0.66390000
15	400.51030000	64.12020000
16	423.66200000	7.64130000
17	477.12500000	2.45580000
18	526.44550000	16.73290000
19	567.42870000	44.80070000
20	609.36900000	15.03300000
21	640.31860000	0.11120000
22	738.74940000	24.79410000
23	749.34190000	0.05040000
24	837.49750000	30.35270000
25	842.08460000	18.63770000
26	842.11370000	36.33080000
27	943.62280000	23.46910000
28	960.16010000	9.92210000
29	985.49020000	27.12640000
30	987.24370000	3.58720000
31	1000.80460000	0.43700000
32	1030.45720000	0.36490000
33	1058.57130000	68.41030000
34	1076.73690000	0.02250000
35	1128.22840000	3.35810000
36	1132.30020000	0.48370000
37	1139.75990000	0.49510000
38	1163.60310000	0.94550000
39	1228.08780000	2.70960000
40	1257.04270000	1.12490000
41	1257.50790000	1.56050000
42	1294.48810000	1.21150000

43	1330.10670000	2.29360000
44	1353.09490000	2.88090000
45	1430.41390000	10.30310000
46	1450.86340000	8.12290000
47	1451.48140000	4.80930000
48	1479.56900000	0.00130000
49	1489.24620000	0.31360000
50	1492.87230000	5.06190000
51	1494.48220000	3.49010000
52	1506.16100000	73.58240000
53	1508.13710000	384.30470000
54	1513.14060000	26.35550000
55	1522.00460000	2.54510000
56	1530.42920000	36.97010000
57	1607.55870000	62.18120000
58	1614.79900000	11.71610000
59	1989.17530000	282.12910000
60	3080.48770000	0.33990000
61	3081.42520000	1.01940000
62	3088.20430000	0.91750000
63	3168.18550000	0.00570000
64	3168.50470000	0.72060000
65	3169.26340000	0.02610000
66	3170.30360000	1.55090000
67	3175.75060000	5.25870000
68	3183.18830000	0.13740000
69	3188.31440000	4.70570000
70	3189.20040000	0.07560000
71	3199.45730000	3.30600000
72	3231.09050000	1.40770000
73	−2409.13310000	430.88280000
74	48.43560000	0.38540000
75	63.79700000	1.28500000
76	71.70810000	0.24620000
77	160.55570000	3.26480000
78	174.53320000	2.12270000
79	228.73720000	0.06420000
80	242.08140000	33.99960000
81	265.41820000	3.29410000
82	287.16590000	8.33260000
83	346.55830000	5.62090000
84	351.42790000	0.56150000
85	354.35780000	4.57850000
86	394.67050000	0.66410000
87	400.51000000	64.12020000
88	423.66220000	7.64130000

89	477.12490000	2.45580000
90	526.44540000	16.73270000
91	567.42910000	44.79990000
92	609.36910000	15.03300000
93	640.31820000	0.11120000
94	738.74890000	24.79410000
95	749.34140000	0.05040000
96	837.49740000	30.35430000
97	842.08470000	18.74740000
98	842.11380000	36.21920000
99	943.62300000	23.46920000
100	960.16020000	9.92190000
101	985.48910000	27.12780000
102	987.24350000	3.58620000
103	1000.80340000	0.43700000
104	1030.45630000	0.36490000
105	1058.57110000	68.40970000
106	1076.73660000	0.02250000
107	1128.22850000	3.35800000
108	1132.29990000	0.48360000
109	1139.75940000	0.49510000
110	1163.60270000	0.94550000
111	1228.08750000	2.70970000
112	1257.04210000	1.12490000
113	1257.50740000	1.56050000
114	1294.48750000	1.21160000
115	1330.10730000	2.29350000
116	1353.09460000	2.88090000
117	1430.41340000	10.30320000
118	1450.86310000	8.12290000
119	1451.48100000	4.80940000
120	1479.56840000	0.00130000
121	1489.24540000	0.31360000
122	1492.87190000	5.06130000
123	1494.48150000	3.49080000
124	1506.16040000	73.57680000
125	1508.13660000	384.31290000
126	1513.14000000	26.35530000
127	1522.00400000	2.54520000
128	1530.42850000	36.96970000
129	1607.55860000	62.17960000
130	1614.79870000	11.71570000
131	1989.17580000	282.12740000
132	3080.48790000	0.33990000
133	3081.42550000	1.01940000
134	3088.20450000	0.91740000

135	3168.18590000	0.00570000
136	3168.50500000	0.72070000
137	3169.26320000	0.02610000
138	3170.30340000	1.55080000
139	3175.75100000	5.25860000
140	3183.18870000	0.13740000
141	3188.31470000	4.70570000
142	3189.20090000	0.07560000
143	3199.45770000	3.30590000
144	3231.09070000	1.40770000

S5.17 (*N*,*N*,*N*)-Trimethylammoniobenzene



Route	:	# opt freq b3lyp/cc-pvtz geom = connectivity empiricaldispersion = gd3bj int = ultrafine
SMILES	:	C[N](C)(C)c1ccccc1
Formula	:	$C_9H_{14}N^+$
Charge	:	1
Multiplicity	:	1
Energy	:	−406.08126022 a.u.
Gibbs Energy	:	−405.89907000 a.u.

Cartesian Coordinates (XYZ format)

24

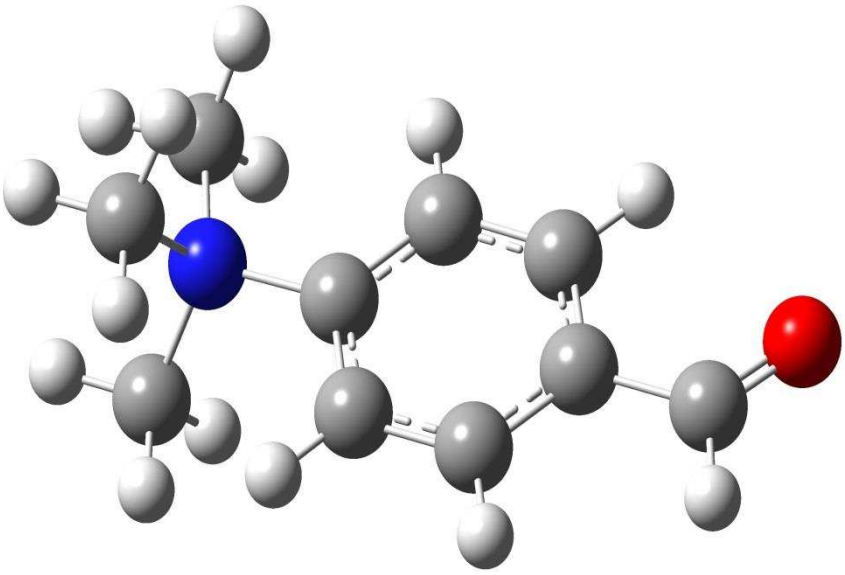
C	−0.08475400	−1.27939701	0.00099200
C	1.29624200	−1.40300202	0.00068700
C	2.10142493	−0.27004600	−0.00081300
C	1.51856506	0.98719102	−0.00199600
C	0.13341300	1.12547803	−0.00170000
C	−0.65680897	−0.01258500	−0.00021500
H	−0.68844998	−2.17439103	0.00218100
H	1.73956096	−2.38804007	0.00162700
H	2.13442707	1.87463105	−0.00316100
H	−0.28508100	2.11746502	−0.00264600
N	−2.16052604	0.08331200	0.00019400
C	−2.65337396	1.50214303	−0.00087600
H	−3.73811507	1.47373605	−0.00057900
H	−2.29870796	2.00700402	0.89084399
H	−2.29914999	2.00550103	−0.89362103
C	−2.71131110	−0.59154803	−1.23249400
H	−2.42552996	−1.63608503	−1.22725797
H	−3.79357910	−0.50054300	−1.22062397
H	−2.29508495	−0.09837700	−2.10492897
C	−2.71047211	−0.58941400	1.23442197
H	−2.29373407	−0.09466600	2.10571909
H	−3.79275489	−0.49853101	1.22308004
H	−2.42458797	−1.63393199	1.23084199
H	3.17699599	−0.36977899	−0.00105000

Frequencies

Mode	IR frequency	IR intensity
1	51.00730000	0.04520000
2	132.57460000	1.16010000
3	226.21770000	0.00450000
4	254.01710000	0.11240000
5	280.93930000	0.04540000
6	337.02850000	0.84090000
7	341.08830000	1.43720000
8	353.55490000	0.01500000
9	375.72460000	1.47080000
10	417.20650000	0.00310000
11	423.69880000	0.15420000
12	476.47610000	1.78500000
13	557.61020000	20.23680000
14	562.19970000	0.18860000
15	632.08580000	0.00420000
16	712.39990000	34.05340000
17	721.29880000	0.23100000
18	782.28010000	28.69210000
19	841.53770000	0.02150000
20	843.89750000	30.50380000
21	933.01670000	6.89250000
22	956.16400000	14.52420000
23	962.16270000	15.90470000
24	1003.23740000	0.03010000
25	1026.61040000	6.66720000
26	1038.55180000	0.01480000
27	1056.60390000	3.02280000
28	1076.81540000	0.02430000
29	1116.83400000	1.54460000
30	1129.75600000	4.79610000
31	1140.35530000	0.49730000
32	1149.00980000	3.18990000
33	1201.26740000	0.02170000
34	1224.70360000	0.29050000
35	1258.60960000	1.55840000
36	1259.12590000	1.61740000
37	1294.47630000	0.59020000
38	1347.77720000	2.30980000
39	1372.53070000	0.31630000
40	1450.37270000	4.88030000
41	1451.55280000	4.67350000
42	1479.66240000	0.00310000

43	1489.49260000	0.33350000
44	1490.28970000	6.80740000
45	1493.81030000	0.84010000
46	1502.70340000	15.30130000
47	1507.65970000	16.02360000
48	1513.15850000	24.15310000
49	1530.64150000	48.88310000
50	1535.28940000	30.70040000
51	1634.73310000	3.26380000
52	1646.09010000	6.89270000
53	3080.27490000	0.40440000
54	3081.28290000	1.12980000
55	3088.14610000	1.17040000
56	3167.78640000	0.00340000
57	3168.27570000	0.47700000
58	3175.34520000	4.35490000
59	3182.99430000	0.16850000
60	3187.89090000	2.56150000
61	3188.98580000	0.02420000
62	3193.53760000	0.15240000
63	3199.43630000	0.35190000
64	3205.97830000	1.71180000
65	3213.49880000	0.05310000
66	3237.16660000	0.28580000

S5.18 4-(Trimethylammonio)benz(^{2}H)aldehyde (3-D)



Route	:	# opt freq b3lyp/cc-pvtz geom = connectivity empiricaldispersion = gd3bj int = ultrafine
SMILES	:	C[N](C)(C)c1ccc(cc1)C=O
Formula	:	$C_{10}H_{13}DNO^{+}$
Charge	:	1
Multiplicity	:	1
Energy	:	−519.44317494 a.u.
Gibbs Energy	:	−519.25853900 a.u.

Cartesian Coordinates (XYZ format)

26

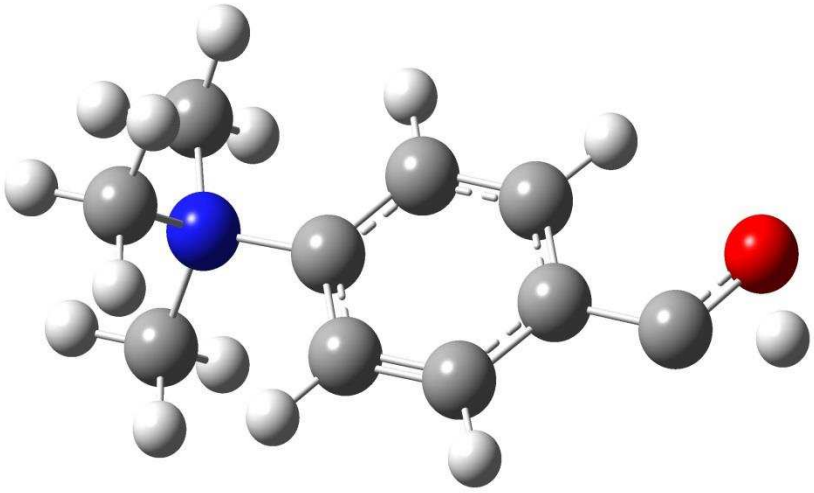
C	−0.06695500	−1.26533997	−0.00004600
C	1.31547701	−1.36626101	−0.00001800
C	2.10545802	−0.22089900	−0.00007100
C	1.50023401	1.03139901	−0.00009900
C	0.11813700	1.14642406	−0.00010300
C	−0.65578002	−0.00673500	−0.00012900
H	−0.65774500	−2.16864491	0.00005300
H	1.77943802	−2.34359908	0.00003700
H	2.12551904	1.91291106	−0.00011600
H	−0.31764200	2.13092494	−0.00012600
N	−2.15960193	0.06849600	0.00001900
C	−2.67344189	1.48108006	−0.00077200
H	−3.75754404	1.43545103	−0.00073700
H	−2.32726002	1.99093997	0.89147699
H	−2.32721090	1.98992801	−0.89358902
C	−2.70065999	−0.61377698	−1.23397505
H	−2.40417004	−1.65536702	−1.22767603
H	−3.78374696	−0.53414297	−1.22295702
H	−2.28938508	−0.11607500	−2.10628104
C	−2.70020795	−0.61235201	1.23498404
H	−2.28978610	−0.11269700	2.10657811
H	−3.78339601	−0.53406000	1.22354198
H	−2.40234900	−1.65356600	1.23048997
C	3.59365201	−0.32717600	−0.00007200
O	4.31798410	0.63229400	0.00016000
D	3.99313402	−1.35801101	−0.00029800

Frequencies

Mode	IR frequency	IR intensity
1	43.69130000	0.52530000
2	71.54750000	0.13600000
3	123.57280000	7.93400000
4	163.68300000	5.02280000
5	210.08380000	0.58440000
6	246.81530000	1.09610000
7	259.04670000	4.11620000
8	274.36510000	0.00990000
9	329.70210000	0.77470000
10	354.32080000	2.19840000
11	356.63450000	0.02350000
12	374.08000000	0.09340000
13	423.97290000	0.02010000
14	432.08330000	0.55350000
15	474.34090000	1.35300000
16	481.03620000	2.17600000
17	559.34300000	23.60220000
18	597.88520000	2.05910000
19	647.43330000	1.35450000
20	699.20700000	25.65570000
21	732.59610000	7.22550000
22	816.57340000	9.52690000
23	826.16200000	22.07410000
24	845.68770000	0.31070000
25	847.94960000	55.27190000
26	907.88630000	2.41110000
27	946.80850000	29.16250000
28	960.52950000	16.36670000
29	999.40020000	0.09400000
30	1018.23400000	0.41000000
31	1033.94970000	13.74920000
32	1061.45920000	1.66550000
33	1077.07190000	0.02470000
34	1127.23170000	11.64730000
35	1131.88910000	0.98660000
36	1140.25610000	0.49450000
37	1162.14420000	3.89940000
38	1206.63850000	26.59820000
39	1240.73690000	38.97660000
40	1257.45980000	1.47700000
41	1257.49890000	1.66040000
42	1295.46320000	0.12430000

43	1349.96170000	7.23190000
44	1351.61990000	9.78380000
45	1447.98390000	2.34950000
46	1452.08690000	4.80260000
47	1453.02130000	17.33840000
48	1479.98800000	0.00130000
49	1488.99720000	0.39080000
50	1493.53920000	1.97930000
51	1495.47680000	0.45880000
52	1507.45570000	27.91050000
53	1513.48380000	24.47830000
54	1530.66460000	50.75060000
55	1541.77490000	10.05460000
56	1634.74290000	8.12710000
57	1644.46970000	28.58710000
58	1778.20260000	194.09150000
59	2165.11960000	62.34350000
60	3080.48910000	0.23360000
61	3081.37110000	0.86870000
62	3088.24050000	0.67060000
63	3168.25900000	0.01030000
64	3168.73980000	0.49640000
65	3176.03910000	3.96270000
66	3181.98390000	0.76820000
67	3183.40630000	0.08940000
68	3188.79520000	0.00980000
69	3190.51950000	1.66480000
70	3202.43090000	3.47840000
71	3206.35090000	3.36110000
72	3237.61980000	1.49210000

S5.19 Transition state between 2-D_t and 3-D



Route	:	# opt = (ts,calcfc) freq b3lyp/cc-pvtz geom = connectivity empiricaldispersion = gd3bj int = ultrafine
SMILES	:	C[N](C)(C)c1ccc(cc1)[C]O
Formula	:	$C_{10}H_{13}DNO^{+}$
Charge	:	1
Multiplicity	:	1
Energy	:	−519.31063966 a.u.
Gibbs Energy	:	−519.13134400 a.u.

Cartesian Coordinates (XYZ format)

26

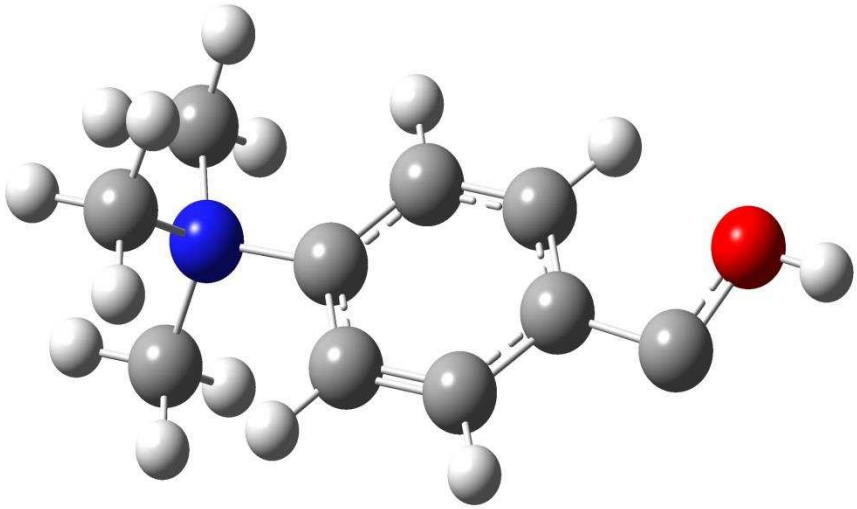
C	−0.09213100	−1.28599405	0.00106900
C	1.28784001	−1.41127706	0.00105500
C	2.09413791	−0.27646101	0.00007100
C	1.51164699	0.98757797	−0.00089400
C	0.13158700	1.12634301	−0.00087800
C	−0.65849298	−0.01635500	0.00011200
H	−0.69951397	−2.17820597	0.00181700
H	1.75075901	−2.38797498	0.00179800
H	2.15058088	1.86031997	−0.00165900
H	−0.29091501	2.11682105	−0.00163300
N	−2.16140103	0.08249300	0.00010200
C	−2.65460300	1.50231600	−0.00066800
H	−3.73924708	1.47231698	−0.00054300
H	−2.30102611	2.00709391	0.89154601
H	−2.30121708	2.00607300	−0.89353198
C	−2.71206594	−0.59187400	−1.23415399
H	−2.43077803	−1.63762200	−1.22787595
H	−3.79383802	−0.49615899	−1.22319496
H	−2.29331708	−0.10019300	−2.10631204
C	−2.71204996	−0.59048897	1.23512101
H	−2.29324698	−0.09786900	2.10672212
H	−3.79381609	−0.49472699	1.22408903
H	−2.43083811	−1.63626003	1.22999001
C	3.56770897	−0.43126801	0.00005400
O	4.27351093	0.66190797	−0.00092000
D	4.82429314	−0.38252100	−0.00011500

Frequencies

Mode	IR frequency	IR intensity
1	−1510.23160000	235.28540000
2	43.12670000	0.00570000
3	65.94210000	0.00110000
4	103.98890000	1.55370000
5	159.84110000	0.73800000
6	203.90250000	0.72830000
7	237.62880000	1.48640000
8	256.22180000	1.46850000
9	273.66480000	0.02060000
10	333.64350000	0.02820000
11	353.46730000	1.03740000
12	355.82180000	0.54510000
13	357.04840000	1.51700000
14	412.14770000	4.37380000
15	424.43770000	1.44360000
16	473.77470000	0.73350000
17	482.11960000	1.52730000
18	484.98630000	15.41840000
19	570.99850000	13.28660000
20	594.89990000	1.53690000
21	645.62030000	0.06760000
22	703.34870000	23.38820000
23	749.72870000	4.51020000
24	833.24690000	0.09010000
25	846.41240000	0.52530000
26	856.81330000	94.06150000
27	861.78980000	31.62910000
28	945.65630000	29.66650000
29	960.60290000	16.34190000
30	1008.93060000	0.67810000
31	1020.28940000	0.11530000
32	1036.09930000	12.84160000
33	1077.10820000	0.02280000
34	1124.66140000	16.41880000
35	1130.88190000	0.29500000
36	1140.14960000	0.52020000
37	1157.80920000	2.92960000
38	1179.11900000	106.00840000
39	1228.49350000	24.05690000
40	1257.11740000	1.17660000
41	1257.37340000	1.70620000
42	1295.21900000	0.10750000

43	1334.38160000	117.23400000
44	1347.03220000	14.83260000
45	1381.38410000	130.19450000
46	1449.82190000	1.75200000
47	1452.09200000	4.82240000
48	1457.39400000	38.13600000
49	1479.87940000	0.00090000
50	1488.98110000	0.39960000
51	1493.44310000	1.71160000
52	1495.46690000	1.02850000
53	1507.29040000	26.86310000
54	1513.43170000	24.42320000
55	1530.58340000	52.36220000
56	1537.21850000	14.01660000
57	1632.56550000	11.51600000
58	1639.59310000	21.19580000
59	1909.64740000	36.71530000
60	3080.67180000	0.23610000
61	3081.49160000	0.86690000
62	3088.36460000	0.70030000
63	3168.41830000	0.00900000
64	3168.79420000	0.39750000
65	3176.05170000	4.26830000
66	3183.63120000	0.09670000
67	3188.93080000	0.62980000
68	3189.23980000	0.01050000
69	3190.65900000	6.16060000
70	3197.34470000	0.45130000
71	3208.62900000	3.96280000
72	3233.74660000	2.18500000

S5.20 *trans*-(^{2}H)Hydroxy[4-(trimethylazaniumyl)-phenyl]-methylidene (2-D_t)



Route	:	# opt freq b3lyp/cc-pvtz geom = connectivity empiricaldispersion = gd3bj int = ultrafine
SMILES	:	C[N](C)(C)c1ccc(cc1)[C]O
Formula	:	$C_{10}H_{13}DNO^+$
Charge	:	1
Multiplicity	:	1
Energy	:	−519.36506012 a.u.
Gibbs Energy	:	−519.18168100 a.u.

Cartesian Coordinates (XYZ format)

26

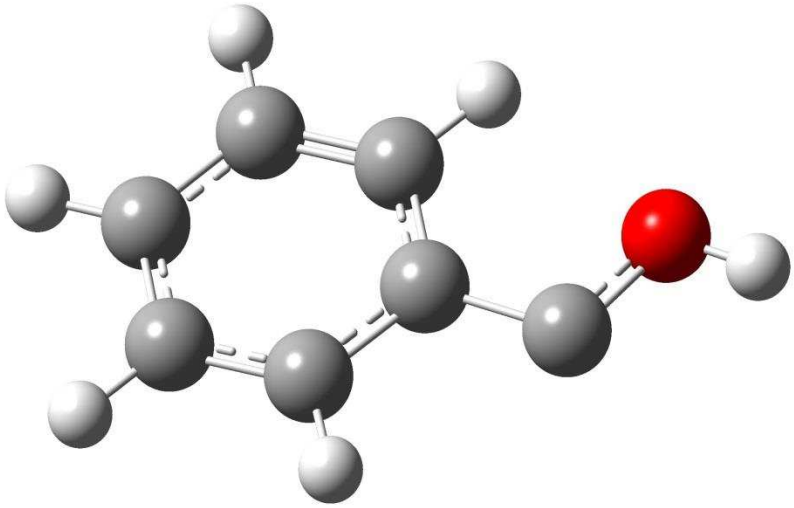
C	−0.09072500	−1.17903805	0.62328702
C	1.28644300	−1.32247305	0.60876399
C	2.10869098	−0.28615400	0.16402100
C	1.52007103	0.89146203	−0.30025601
C	0.13981600	1.03760505	−0.31964701
C	−0.65425599	0.00093000	0.15158901
H	−0.69891101	−1.99392104	0.98563099
H	1.74703503	−2.24164200	0.94184899
H	2.14651299	1.69688797	−0.65474802
H	−0.27850601	1.95646405	−0.69447798
N	−2.15626693	0.11395300	0.15520000
C	−2.64470506	1.43427896	−0.36954999
H	−3.72880101	1.42499399	−0.32381099
H	−2.25712705	2.23400402	0.25183100
H	−2.32155299	1.55531096	−1.39749098
C	−2.74645710	−0.96994901	−0.71495003
H	−2.46548009	−1.93872094	−0.32086399
H	−3.82736802	−0.86355603	−0.71063203
H	−2.35402489	−0.85087198	−1.71969295
C	−2.67029405	−0.03305700	1.56737196
H	−2.22449088	0.74799299	2.17475510
H	−3.75184488	0.06470600	1.55090594
H	−2.39020395	−1.00579202	1.95199800
C	3.57070088	−0.55874801	0.15542100
O	4.20333290	0.58744502	0.09248200
D	5.15495205	0.41614401	0.05739800

Frequencies

Mode	IR frequency	IR intensity
1	40.60490000	3.56630000
2	59.59090000	2.50520000
3	91.81840000	3.76910000
4	170.32430000	1.07510000
5	204.23560000	1.48680000
6	237.20360000	1.23400000
7	261.09760000	1.37610000
8	274.45250000	0.09140000
9	336.86100000	0.83830000
10	352.42090000	0.15760000
11	355.49450000	0.19800000
12	368.05680000	1.10650000
13	418.64620000	2.03880000
14	426.95940000	1.96610000
15	475.47300000	0.39620000
16	486.92690000	0.93940000
17	542.60060000	39.32340000
18	585.99180000	11.03910000
19	628.03010000	5.09800000
20	648.34850000	0.29370000
21	665.23340000	23.99150000
22	758.73200000	6.73610000
23	801.99120000	13.30900000
24	840.79320000	8.23230000
25	845.99500000	49.62320000
26	863.19600000	42.43650000
27	945.79970000	30.64620000
28	961.78270000	14.60070000
29	999.77030000	6.86030000
30	1017.65060000	1.17020000
31	1026.85960000	22.20150000
32	1037.97140000	20.01430000
33	1076.97330000	0.02010000
34	1125.09250000	9.17970000
35	1131.92750000	0.26750000
36	1140.10130000	0.54020000
37	1159.48050000	4.81340000
38	1198.30100000	14.62090000
39	1230.66160000	4.74170000
40	1257.85140000	1.39100000
41	1257.89200000	1.58370000
42	1294.71400000	6.31110000

43	1323.03780000	245.43560000
44	1347.10770000	7.73090000
45	1350.11820000	29.37040000
46	1444.76430000	9.81480000
47	1451.71800000	9.66570000
48	1451.80250000	11.38470000
49	1479.64110000	0.00200000
50	1489.17380000	0.38220000
51	1493.35800000	1.77900000
52	1495.38620000	0.68090000
53	1506.94440000	26.86710000
54	1513.16940000	24.17200000
55	1530.60970000	50.96710000
56	1534.89080000	9.65550000
57	1622.10520000	9.78160000
58	1636.65630000	18.69970000
59	2720.48020000	147.04360000
60	3080.36380000	0.37530000
61	3081.34700000	1.01040000
62	3088.25000000	1.04260000
63	3167.96420000	0.06480000
64	3168.42360000	0.39570000
65	3175.59190000	5.07520000
66	3183.47670000	0.14050000
67	3188.69530000	1.71770000
68	3189.35590000	0.02430000
69	3197.33780000	0.63840000
70	3203.61060000	0.68240000
71	3207.93770000	4.32330000
72	3232.45480000	2.03150000

S5.21 Phenylhydroxycarbene



Route	:	# opt freq b3lyp/cc-pvtz geom = connectivity empiricaldis-persion = gd3bj int =ultrafine
SMILES	:	c1ccc(cc1)[C]O
Formula	:	C_7H_6O
Charge	:	0
Multiplicity	:	1
Dipole	:	3.6861 Debye
Energy	:	−345.64055244 a.u.
Gibbs Energy	:	−345.56181400 a.u.
CCSD(T)-F12b//cc-pVDZ-F12	:	−344.96931662 a.u.

Cartesian Coordinates (XYZ format)

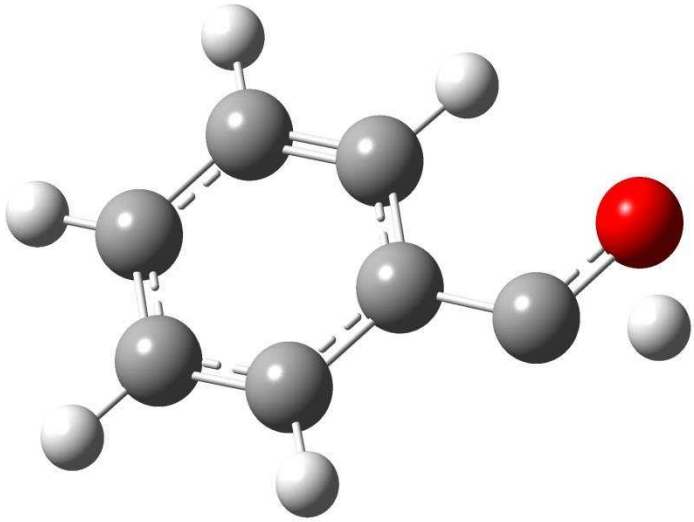
14

C	−0.08816100	1.03020096	0.14619900
C	1.26272202	1.31811202	0.21106000
C	−0.52157801	−0.27630299	−0.13261800
C	0.43234199	−1.27724302	−0.34266499
C	1.78832304	−0.98957300	−0.27765700
C	2.20136404	0.30789101	−0.00092800
H	−0.82322800	1.80521798	0.30899301
H	0.07813600	−2.27626705	−0.55588800
H	2.52005196	−1.76864505	−0.44093901
H	3.25733805	0.53784800	0.05090900
H	1.59541905	2.32478595	0.42572701
C	−1.92624497	−0.70043200	−0.22682600
O	−2.71132302	0.34748200	−0.00581900
H	−3.62387490	0.04557700	−0.07272000

Frequencies

Mode	IR frequency	IR intensity
1	74.71750000	3.42310000
2	213.11680000	0.00320000
3	242.69610000	1.32650000
4	417.28820000	0.11830000
5	452.63450000	0.28150000
6	458.05420000	9.59080000
7	625.50010000	24.63050000
8	633.64020000	0.91170000
9	703.03100000	46.88420000
10	745.48840000	0.59320000
11	823.39670000	89.97900000
12	826.72150000	18.61510000
13	873.84790000	0.00720000
14	978.70310000	6.79550000
15	1013.92310000	0.01330000
16	1025.17570000	2.26700000
17	1028.97900000	0.31480000
18	1048.37650000	6.08070000
19	1100.93110000	19.11840000
20	1179.48650000	117.94590000
21	1185.80550000	5.02730000
22	1211.71110000	9.32160000
23	1241.93650000	272.06830000
24	1330.77270000	59.52950000
25	1354.41300000	4.65390000
26	1372.48190000	48.71560000
27	1488.22940000	26.23210000
28	1521.58020000	0.74700000
29	1619.64270000	2.48960000
30	1639.02320000	32.23570000
31	3164.49930000	0.70800000
32	3176.27140000	9.04490000
33	3184.91610000	11.75260000
34	3195.57140000	15.06510000
35	3198.47110000	8.91010000
36	3782.87710000	177.12820000

S5.22 Transition state between phenylhydroxycarbene and benzaldehyde



Route	:	# opt = (calcfc,ts) freq b3lyp/cc-pvtz geom = connectivity empiricaldispersion = gd3bj int = ultrafine
SMILES	:	c1ccc(cc1)[C]O
Formula	:	C_7H_6O
Charge	:	0
Multiplicity	:	1
Dipole	:	5.8746 Debye
Energy	:	−345.59013696 a.u.
Gibbs Energy	:	−345.51700700 a.u.
CCSD(T)-F12b//cc-pVDZ-F12	:	−344.91787008 a.u.

Cartesian Coordinates (XYZ format)

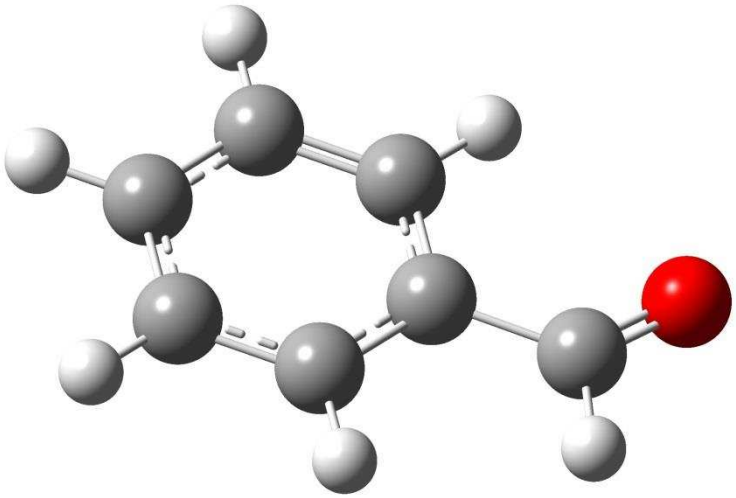
14

C	−0.08561500	−1.28542101	−0.00009400
C	1.29574800	−1.41192901	0.00000100
C	2.10165596	−0.27194101	−0.00000900
C	1.51675701	0.99973702	−0.00011300
C	0.13932700	1.12372196	−0.00020600
C	−0.66048801	−0.01907700	−0.00019600
H	−0.71382201	−2.16525006	−0.00008900
H	1.77095604	−2.38327408	0.00008200
H	2.16156197	1.86792803	−0.00012100
H	−0.32027099	2.10268402	−0.00028700
C	3.55337310	−0.43123001	0.00009000
O	4.29695082	0.65585202	0.00005200
H	4.80889797	−0.39692900	0.00015300
H	−1.73758602	0.08142600	−0.00026800

Frequencies

Mode	IR frequency	IR intensity
1	−2013.48940000	461.73480000
2	101.67220000	0.08960000
3	216.44300000	0.98190000
4	224.44240000	2.41500000
5	415.96000000	0.11590000
6	445.30570000	13.24140000
7	445.54100000	0.03850000
8	590.45540000	13.05090000
9	631.48140000	0.11280000
10	649.04550000	23.74690000
11	707.90550000	28.77250000
12	787.23900000	50.65340000
13	852.24200000	23.62040000
14	874.96320000	0.00400000
15	974.73570000	3.84780000
16	1012.98070000	0.02060000
17	1024.80580000	1.70160000
18	1029.20640000	0.18420000
19	1045.94460000	6.04760000
20	1101.30060000	7.72040000
21	1184.25410000	61.53440000
22	1186.95180000	1.64990000
23	1234.17240000	68.05830000
24	1318.20180000	248.50550000
25	1356.43620000	8.80010000
26	1366.03620000	149.82980000
27	1490.96240000	23.71730000
28	1522.71120000	0.01080000
29	1623.38500000	0.91020000
30	1639.92050000	24.99610000
31	2630.24980000	91.85570000
32	3167.40330000	0.56780000
33	3178.02790000	4.34880000
34	3184.22570000	5.25510000
35	3192.26230000	14.56240000
36	3196.62610000	14.50990000

S5.23 Benzaldehyde



Route	:	# opt freq b3lyp/cc-pvtz geom = connectivity empiricaldis-persion = gd3bj int = ultrafine
SMILES	:	c1ccc(cc1)C=O
Formula	:	C_7H_6O
Charge	:	0
Multiplicity	:	1
Dipole	:	8.5812 Debye
Energy	:	−345.72339693 a.u.
Gibbs Energy	:	−345.64419400 a.u.
CCSD(T)-F12b//cc-pVDZ-F12	:	−345.04990087 a.u.

Cartesian Coordinates (XYZ format)

14

C	−0.05633700	−1.26378906	−0.00007000
C	1.32826996	−1.36069798	−0.00005600
C	2.11207104	−0.20790701	−0.00006800
C	1.50222600	1.04886401	−0.00009400
C	0.12162500	1.14491701	−0.00010800
C	−0.65782201	−0.01085900	−0.00009500
H	−0.66447300	−2.15760803	−0.00006000
H	1.80916595	−2.33105707	−0.00003700
H	2.13000393	1.92874706	−0.00010400
H	−0.35423499	2.11583710	−0.00012800
C	3.58309507	−0.32917899	−0.00005500
O	4.35455513	0.60089302	−0.00004700
H	3.95664406	−1.37358296	−0.00001400
H	−1.73650706	0.06801200	−0.00010600

Frequencies

Mode	IR frequency	IR intensity
1	117.39360000	4.28600000
2	221.39860000	7.68460000
3	236.37550000	7.26610000
4	418.71990000	0.07860000
5	445.30500000	0.25680000
6	467.48010000	6.37380000
7	634.17040000	0.38890000
8	665.50250000	23.79620000
9	709.58020000	30.46090000
10	767.62220000	41.84610000
11	844.00890000	32.79400000
12	869.60300000	0.02150000
13	948.92470000	1.29990000
14	1002.54070000	0.02400000
15	1020.82960000	0.03520000
16	1025.30460000	0.65790000
17	1039.72100000	0.86550000
18	1048.36360000	2.71980000
19	1104.72230000	4.61410000
20	1187.00920000	2.75260000
21	1191.55300000	23.62030000
22	1230.39240000	57.01220000
23	1340.51720000	17.36150000
24	1357.50790000	5.32690000
25	1423.71500000	5.54440000
26	1493.21870000	13.60070000
27	1528.89750000	0.47560000
28	1627.81390000	12.19730000
29	1645.00660000	30.64310000
30	1777.93700000	253.09550000
31	2877.91150000	122.09730000
32	3161.44010000	4.15150000
33	3171.66300000	1.22150000
34	3183.13790000	13.06540000
35	3193.12760000	12.82870000
36	3199.83150000	8.39610000