



This is a repository copy of *Hydrogen bonding shuts down tunneling in hydroxycarbenes: a gas-phase study by tandem-mass spectrometry, infrared ion spectroscopy, and theory.*

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/208085/>

Version: Supplemental Material

Article:

Paul, M., Thomulka, T., Harnying, W. et al. (8 more authors) (2023) Hydrogen bonding shuts down tunneling in hydroxycarbenes: a gas-phase study by tandem-mass spectrometry, infrared ion spectroscopy, and theory. *Journal of the American Chemical Society*, 145 (22). pp. 12124-12135. ISSN 0002-7863

<https://doi.org/10.1021/jacs.3c01698>

© 2023 The Authors. Except as otherwise noted, this author-accepted version of a journal article published in *Journal of the American Chemical Society* is made available via the University of Sheffield Research Publications and Copyright Policy under the terms of the Creative Commons Attribution 4.0 International License (CC-BY 4.0), which permits unrestricted use, distribution and reproduction in any medium, provided the original work is properly cited. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>

Reuse

This article is distributed under the terms of the Creative Commons Attribution (CC BY) licence. This licence allows you to distribute, remix, tweak, and build upon the work, even commercially, as long as you credit the authors for the original work. More information and the full terms of the licence here: <https://creativecommons.org/licenses/>

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

SUPPLEMENTARY INFORMATION

Hydrogen Bonding Shuts Down Tunneling in Hydroxycarbenes: A Gas-Phase Study by Tandem-Mass Spectrometry, Infrared Ion Spectroscopy, and Theory

Mathias Paul,[†] Thomas Thomulka,[†] Wacharee Harnying,[†] Jörg-Martin Neudörfl,[†]
Charlie R. Adams,[‡] Jonathan Martens,[§] Giel Berden,[§] Jos Oomens,^{*,§,#}
Anthony J. H. M. Meijer,^{*,‡} Albrecht Berkessel,^{*,†} and Mathias Schäfer^{*,†}

[†]Department of Chemistry, Organic Chemistry, University of Cologne, Greinstraße 4, 50939 Cologne, Germany

[‡]Department of Chemistry, University of Sheffield, Sheffield S3 7HF, U.K.

[§]Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7, 6525 ED Nijmegen, The Netherlands

[#]Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

**Correspondence to:*

*j.oomens@science.ru.nl; a.meijer@sheffield.ac.uk;
berkessel@uni-koeln.de; mathias.schaefer@uni-koeln.de*

Table of Contents:

General.....	S4
1. Synthesis	
1.1 5-(Trimethylammonio)-2-oxopentanoate (6).....	S5
1.2 (N-Methyl-4-quinuclidinio)glyoxylate (10)	
1.2.1 Ethyl (4-quinuclidinyl)glyoxylate (18).....	S6
1.2.2 Ethyl (N-methyl-4-quinuclidinio)glyoxylate iodide (19).....	S8
1.2.3 (N-Methyl-4-quinuclidinio)glyoxylate (10).....	S9
1.3 (N-Benzyl-4-quinuclidinio)glyoxylate (13)	
1.3.1 Ethyl (N-benzyl-4-quinuclidinio)glyoxylate bromide (20).....	S10
1.3.2 (N-Benzyl-4-quinuclidinio)glyoxylate (13).....	S11
1.4 (N-Methyl-4-quinuclidinio)carbaldehyde iodide (12).....	S12
2. NMR Spectra	
2.1 5-(Trimethylammonio)-2-oxopentanoate (6).....	S14
2.2 (N-Methyl-4-quinuclidinio)glyoxylate (10)	
Ethyl (4-quinuclidinyl)glyoxylate (18).....	S15
Ethyl (N-methyl-4-quinuclidinio)glyoxylate iodide (19).....	S16
(N-Methyl-4-quinuclidinio)glyoxylate (10).....	S17
2.3 (N-Benzyl-4-quinuclidinio)glyoxylate (13)	
Ethyl (N-benzyl-4-quinuclidinio)glyoxylate bromide (20).....	S18
(N-Benzyl-4-quinuclidinio)glyoxylate (13).....	S19
2.4 (N-Methyl-4-quinuclidinio)carbaldehyde (12).....	S20
3. X-Ray Crystal Structures	
3.1 5-(Trimethylammonio)-2-oxopentanoate (6).....	S22
3.2 (N-Methyl-4-quinuclidinio)glyoxylate (10).....	S24

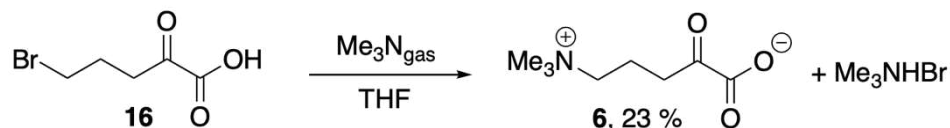
3.3	(N-Methyl-4-quinuclidinio)carbaldehyde (12).....	S26
3.4	References.....	S28
4.	Mass Spectrometry	S29
	Table S1, Figures S19-S24	
5.	IR Ion Spectroscopy	S33
	Tables S3+S4, Figures S25-S45	
6.	Computations	S57
	Figures S46-S50	
7.	Kinetics	S63
	Figures S51-S59	
8.	Coordinates of all computed Structures	S72

General:

Commercially available starting materials were used without further purification. Absolute solvents were prepared according to literature procedures.¹ ¹H NMR (500 MHz, 300 MHz) and ¹³C NMR (125 MHz) spectra were recorded on *Bruker Avance* (500, 300) instruments at 298 K. Chemical shifts were referenced to TMS as internal standard or to residual solvent signals. If necessary, 2D NMR techniques (¹H-¹H COSY, ¹H-¹³C-HSQC, ¹H-¹³C-HMBC) were applied for resonance assignments IR-spectra were recorded from neat material on a *Shimadzu IRaffinity-1* ATR spectrometer. The position of the absorption maxima is given in wavenumbers in cm⁻¹. The letters in brackets refer to the intensity of the absorption bands (w = weak, m = medium, s = strong, vs = very strong). ESI-MS measurements were done with an *Agilent 1100 Series* instrument. HR-MS measurements were performed on a *THERMO Scientific LRQ Orbitrap XL* spectrometer with a FTMS analyzer. C,H,N-Analyses were carried out on an *Elementar Vario Micro Cube* from *Elementar Analysensysteme GmbH*. Melting points were measured in open glass capillaries on a *Mettler Toledo MP 50* digital melting point system.

1. Synthesis

5-(Trimethylammonio)-2-oxopentanoate (**6**)

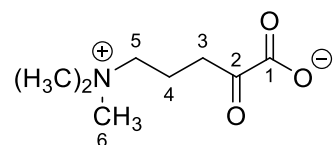


5-Bromo-2-oxopentanoic acid (**16**) was prepared from γ -butyrolactone according to *Öhler* and *Schmidt*.² In a 50 mL Schlenk flask, 2.01 g (10.3 mmol, 1 eq.) of 5-bromo-2-oxopentanoic acid (**16**) were dissolved in 30 mL dry THF. In a second flask, gaseous trimethylamine was liberated from trimethylammonium chloride (3.37 g, 51.3 mmol, 5.0 eq.) by treatment with solid potassium hydroxide (4.90 g, 51.3 mmol, 5.0 eq.). The trimethylamine generated was bubbled into the stirred solution of 5-bromo-2-oxopentanoic acid (**16**) by means of a Teflon tube. Towards the end of the addition, the clear solution became turbid. When the precipitation was complete, the solid was filtered off and washed with ether and DCM. After drying in vacuo, 402 mg (2.32 mmol, 23 %) of the pure zwitterion **6** were obtained as a colorless powder. Crystals suitable for X-ray structural analysis were obtained by gas-phase diffusion of diethyl ether into a methanol solution of the zwitterion **6**.

$\text{C}_8\text{H}_{15}\text{NO}_3$, 173.21 g mol⁻¹

Appearance: colorless crystals

Yield: 402 mg (2.32 mmol, 23%)



¹H-NMR: (500 MHz, DMSO-*d*₆) δ [ppm]: 3.26–3.23 (m, 2H, H-5), 3.04 (s, 9H, H-6), 2.53 (t, ³*J* = 7.0 Hz, 2H, H-3), 1.89–1.83 (m, 2H, H-4)

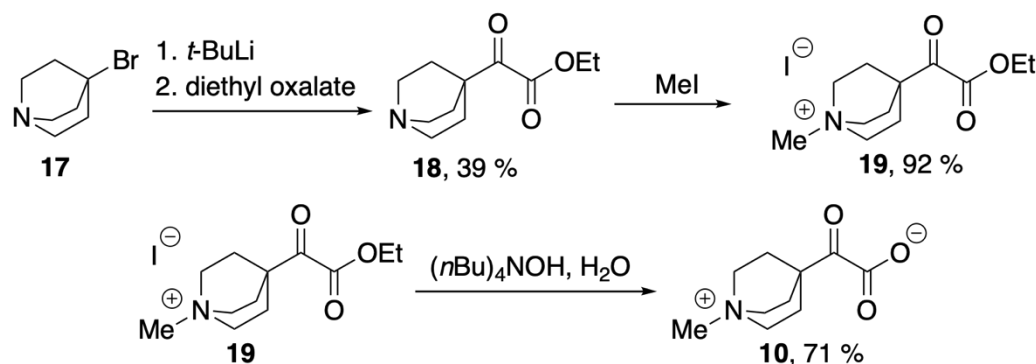
¹³C-NMR: (125.76 MHz, DMSO-*d*₆) δ [ppm]: 205.3 (1C, C-2), 168.7 (1C, C-1), 64.9 (1C, C-5), 52.2 (3C, C-6), 35.1 (1C, C-3), 16.6 (1C, C-4)

FT-IR:(ATR) $\tilde{\nu}$ [cm^{-1}]: 3025.7 (w), 2942.6 (w), 2907.9 (w), 1699.6 (s), 1662.9 (w), 1615.8 (vs), 1493.6 (s), 1445.9 (w), 1409.9 (w), 1399.6 (m), 1369.1 (s), 1348.8 (m), 1335.9 (s), 1290.0 (w), 1273.7 (w), 1251.0 (w), 1219.3 (w), 1145.3 (m), 1098.1 (m), 1040.4 (s), 1001.2 (m), 971.1 (m), 952.2 (m), 933.0 (s), 886.1 (m), 842.7 (m), 795.0 (s), 760.5 (m), 719.4 (m), 687.2 (s), 556.4 (m), 522.7 (m)

HR-ESI-MS:	m/z of $[\text{M}+\text{H}]^+$	m/z of $[\text{M}+\text{Na}]^+$:
	calculated: 174.1125 u	calculated: 196.0944 u
	found: 174.1126 u	found: 196.0947 u
	difference: +0.56 ppm	difference: +1.21 ppm

M.p.: 276–277 °C (dec.)

(N-Methyl-4-quinuclidinio)glyoxylate (10)



Ethyl (4-quinuclidinyl)glyoxylate (18)

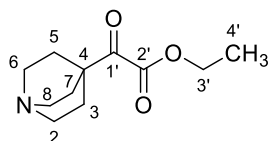
4-Bromoquinuclidine (**17**) was prepared according to *Grob and Brenneisen*.³ In a 50 mL Schlenk flask, 1.00 g (5.26 mmol, 1 eq.) of 4-bromoquinoline (**17**) was dissolved in 30 mL abs. THF under Ar-atmosphere. In a second Schlenk flask, 0.79 mL of freshly distilled diethyl oxalate were dissolved in 8 mL abs. THF under Ar-atmosphere. Both flasks were placed in a dry ice/2-propanol bath and stirred. *Tert*-butyllithium (4.75 mL of a 1.66 M solution in pentane, 7.89 mmol, 1.5 eq.) was added to the solution of 4-bromoquinoline (**17**), and stirring was continued for 30 min. This solution was then added to the one of diethyl oxalate, by means of a Teflon tube, and in a dropwise

manner. After an additional 30 min of stirring at dry ice temperature, the reaction was quenched with brine and the reaction mixture was allowed to warm to room temperature and extracted with DCM (6 x 5 mL). After drying of the organic extract over magnesium sulfate, filtration and removal of the solvent in vacuo, 1.02 g of a resinous yellow material were obtained. The latter was subjected to Kugelrohr distillation (90-110 °C, 0.8 mbar), affording 438 mg (2.07 mmol, 39 %) of ethyl (4-quinuclidinyl)glyoxylate (**18**) as a colorless oil. For elemental analysis, this material was additionally dried at room temperature under high vacuum (10^{-5} – 10^{-4} mbar) for 6 h.

211.26 g mol⁻¹, C₁₁H₁₇NO₃

Appearance: colorless oil

Yield: 438 mg (2.07 mmol, 39%)



¹H-NMR: (500.13 MHz, CDCl₃) δ [ppm]: 4.31 (q, ³J = 7.1 Hz, 2H, H-3'), 2.95–2.92 (m, 6H, H-2,6,8), 1.79–1.76 (m, 6H, H-3,5,7), 1.36 (t, ³J = 7.1 Hz, 3H, H-4')

¹³C-NMR: (125.76 MHz, CDCl₃) δ [ppm]: 199.5 (1C, C-1'), 163.5 (1C, C-2'), 62.0 (1C, C-3'), 47.2 (3C, C-2,6,8), 41.0 (1C, C-4), 26.9 (3C, C-3,5,7), 14.2 (1C, C-4')

FT-IR: (ATR) $\tilde{\nu}$ [cm⁻¹]: 2943.4 (w), 2920.2 (w), 2872.0 (w), 1732.1 (s), 1708.9 (vs), 1456.3 (m), 1388.8 (w), 1367.5 (w), 1317.4 (w), 1290.4 (m), 1259.5 (m), 1182.4 (m), 1134.1 (vs), 1095.6 (w), 1051.2 (m), 1012.6 (s), 989.5 (s), 964.4 (w), 931.6 (w), 877.6 (w), 854.5 (w), 827.5 (w), 781.2 (m), 742.6 (w), 717.5 (w), 638.4 (vs)

C,H,N-Analysis: calcd. (found) [%]: C: 62.54 (62.35); H: 8.11 (8.10); N: 6.65 (6.64)

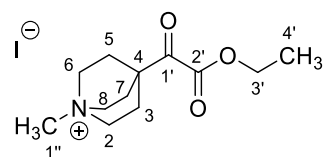
Ethyl (N-methyl-4-quinuclidinio)glyoxylate iodide (**19**)

Iodomethane (320 μL , 5.14 mmol, 5.14 eq.) was added at room temperature to a stirred solution of 202 mg (0.96 mmol, 1.0 eq.) ethyl (4-quinuclidinyl)glyoxylate (**18**) in 10 mL diethyl ether. A colorless precipitate appeared instantaneously. The solvent and excess iodomethane were removed under reduced pressure, affording 310 mg (0.88 mmol, 92 %) of ethyl (N-methyl-4-quinuclidinio)glyoxylate iodide (**19**) as a colorless solid. For elemental analysis, part of this material was recrystallized, by gas-phase diffusion of diethyl ether into a solution of **19** in acetonitrile, followed by drying in high vacuum (10^{-5} – 10^{-4} mbar) for 6 h at 80 $^{\circ}\text{C}$.

353.05 g mol^{-1} , $\text{C}_{12}\text{H}_{20}\text{INO}_3$

Appearance: colorless solid

Yield: 310 mg (0.88 mmol, 92%)



$^1\text{H-NMR}$: (500.13 MHz, CD_3CN) δ [ppm]: 4.32 (q, $^3J = 7.1$ Hz, 2H, H-3'), 3.60–3.57 (m, 6H, H-2,6,8), 3.04 (s, 3H, H-1''), 2.26–2.23 (m, 6H, H-3,5,7), 1.32 (t, $^3J = 7.1$ Hz, 3H, H-3')

$^{13}\text{C-NMR}$: (125.76 MHz, CD_3CN) δ [ppm]: 196.6 (1C, C-1'), 162.3 (1C, C-2'), 63.6 (1C, C-3'), 57.1 (3C, C-2,6,8), 52.7 (1C, C-1''), 40.2 (1C, C-4), 25.8 (3C, C-3,5,7), 14.2 (1C, C-4')

FT-IR:(ATR) $\tilde{\nu}$ [cm^{-1}]: 3001.2 (w), 2974.2 (w), 1735.9 (vs), 1716.7 (vs), 1471.7 (m), 1450.5 (m), 1292.3 (s), 1275.0 (m), 1199.7 (s), 1159.2 (vs), 1118.7 (m), 1093.6 (m), 1033.9 (s), 1008.8 (s), 945.1 (s), 858.4 (m), 841.0 (m), 819.8 (w), 742.6 (w), 715.6 (w), 694.4 (m)

M.p.: 125.0–127.5 $^{\circ}\text{C}$

HR-ESI-MS: m/z of $[M-I]^{+}$:
calculated: 226.1438 u
measured: 226.1439 u
difference: +0.66 ppm

C,H,N-Analysis: calcd. (found) [%]: C: 40.81 (40.89); H: 5.71 (5.67); N: 3.97 (3.88)

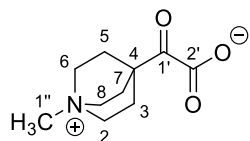
(N-Methyl-4-quinuclidinio)glyoxylate (10)

In a 25 mL flask, 230 mg (0.65 mmol, 1.0 eq.) of ethyl (N-methyl-4-quinuclidinio)-glyoxylate iodide (**19**) were dissolved in 3 mL of DCM. Tetra-*n*-butylammonium hydroxide triacontahydrate (540 mg, 0.68 mmol, 1.05 eq.) was added to this solution, resulting in the formation of two layers. This mixture was stirred overnight. The DCM solvent was then stripped off with argon, followed by the removal of residual water and DCM under reduced pressure. The colorless residue was suspended in DCM, and the solid crude product was filtered off with a sintered-glass funnel. This material was washed with DCM (3 x 1 mL) and dried under reduced pressure to afford 90 mg (0.46 mmol, 71 %) of the zwitterion **10**. A sample for elemental analysis was obtained by recrystallization from an acetonitrile/ethanol mixture (3/1), followed by drying of the resulting crystals in high vacuum (10^{-5} – 10^{-4} mbar) at 80 °C.

197.23 g mol⁻¹, C₁₀H₁₅NO₃

Appearance: colorless solid

Yield: 90 mg (0.46 mmol, 71%)



¹H-NMR: (500.13 MHz, DMSO-*d*₆) δ [ppm]: 3.43 (m, 6H, H-2,6,8), 2.91 (s, 3H, H-1''), 2.01 (m, 6H, H-3,5,7)

¹³C-NMR: (125.76 MHz, DMSO-*d*₆) δ [ppm]: 206.6 (1C, C-1'), 167.9 (1C, C-2'), 55.7 (3C, C-2,6,8), 50.9 (1C, C-1''), 36.2 (1C, C-4), 25.8 (3C, C-3,5,7)

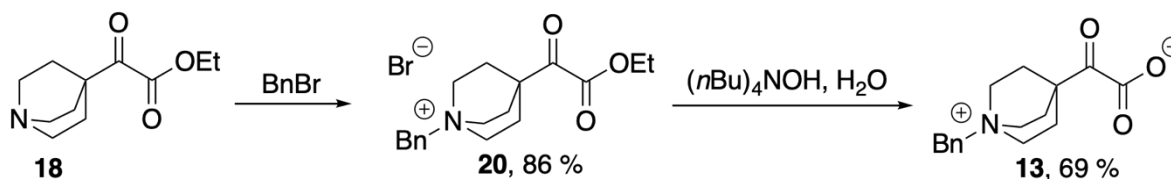
FT-IR:(ATR) $\tilde{\nu}$ [cm⁻¹]: 3364.0 (br, w), 3009.7 (w), 2963.8 (w), 2887.3 (w), 1688.1 (s), 1667.5 (m), 1591.9 (s), 1477.0 (m), 1438.2 (w), 1403.3 (s), 1368.9 (w), 1333.1 (w), 1276.6.0 (w), 1202.8 (m), 1172.5 (s), 1133.7 (w), 1052.7 (w), 1041.0 (m), 1003.0 (w), 946.5 (m), 932.6 (m), 839.6 (m), 826.7 (m), 772.7 (w), 726.2 (s), 694.7 (s), 662.3 (m), 576.3 (m), 534.8 (m)

HR-ESI-MS:	m/z of [M+H-I] ⁺ :	m/z of [M+H-CO ₂] ⁺ :
	calculated: 198.1125 u	calculated: 154.1226 u
	measured: 198.1125 u	measured: 154.1223 u
	difference: -0.10 ppm.	difference: -1.94 ppm.

M.p.: >360 °C (dec.)

C,H,N-Analysis: calcd. for 10•H₂O: (found): C: 55.80 (55.96); H: 7.96 (7.77); N: 6.51 (6.37).

(N-Benzyl-4-quinuclidinio)glyoxylate (13)



Ethyl (N-benzyl-4-quinuclidinio)glyoxylate bromide (20)

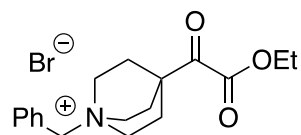
Under argon atmosphere, benzyl bromide (120 μ L, 1.0 mmol, 2.0 eq.) was added at room temperature to a stirred solution of 110 mg (0.52 mmol, 1.0 eq.) ethyl (4-quinuclidinyl)glyoxylate (18) in 5 mL dry diethyl ether. A colorless precipitate appeared instantaneously. After stirring at room temperature for 3h, the solvent and excess benzyl bromide were removed under reduced pressure, affording 190 mg (0.50 mmol, 96 %) of

ethyl (N-benzyl-4-quinuclidinio)glyoxylate bromide (**20**) as a colorless solid. This material was used in the next step without further purification.

382.30 g mol⁻¹, C₁₈H₂₄BrNO₃

Appearance: colorless solid

Yield: 190 mg (0.50 mmol, 96%)



¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.70 (d, *J* = 6.2 Hz, 2H, ArH), 7.50 – 7.36 (m, 3H, ArH), 5.11 (s, 2H, CH₂Ph), 4.30 (q, *J* = 7.1 Hz, 2H, CH₂CH₃), 4.12 – 3.88 (m, 6H, 3xCH₂), 2.43 – 2.16 (m, 6H, 3xCH₂), 1.34 (t, *J* = 7.1 Hz, 3H, CH₂CH₃)

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 194.8 (C=O), 161.2 (C=O), 133.3 (2xArCH), 130.6 (ArCH), 129.23 (2xArCH), 126.9 (ArC), 66.5 (CH₂), 62.8 (OCH₂), 53.2 (CH₂), 40.3 (C_q), 25.3 (CH₂), 14.0 (CH₂)

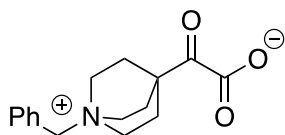
(N-Benzyl-4-quinuclidinio)glyoxylate (**13**)

The ester **20** (150 mg, 0.39 mmol, 1.0 eq.) was dissolved in 1.0 mL of ethanol, and tetra-*n*-butylammonium hydroxide triacontayhydrate (320 mg, 0.40 mmol, 1.0 eq.) was added. The resulting homogeneous solution was stirred at room temperature for 1h, and the solvent was removed under reduced pressure. Cyclohexane (2 mL) was added, and volatiles were removed on a rotary evaporator, this operation was repeated twice. The remaining viscous oil was then triturated successively with DM and diethyl ether with vigorous stirring. Upon drying in high vacuum (10⁻⁵–10⁻⁴ mbar), the remaining viscous oil was converted to a colorless, highly hygroscopic amorphous solid (74 mg, 0.27 mmol, 69 %).

197.23 mol⁻¹, C₁₀H₁₅NO₃

Appearance: colorless, highly hygroscopic solid

Yield: 74 mg (0.27 mmol, 69%)



¹H NMR (500.13 MHz, DMSO-*d*₆): δ (ppm) = 7.51 (app. s, 5H, ArH), 4.43 (s, 2H, CH₂Ph), 3.44 (m, 6H, 3xCH₂), 2.01 (m, 6H, 3xCH₂)

¹³C NMR (125.76 MHz, DMSO-*d*₆): δ (ppm) = 207.0 (C=O), 168.5 (C=O), 133.5 (2xArCH), 130.6 (ArCH), 129.4 (2xArCH), 128.2 (ArC), 66.5 (CH₂), 54.0 (CH₂), 37.5 (C_q), 26.1 (CH₂); IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3383 (br), 2967 (w), 2886 (w), 1688 (m), 1597 (s), 1497 (w), 1462 (m), 1377 (m), 1192 (m), 1153 (m), 926 (m), 845 (m), 824 (m), 768 (m), 706 (s), 691 (m)

ESI-MS (positive): *m/z* = 306 (M⁺+MeOH, 100%), 274 (M⁺+H⁺), 242, 230, 201, 190, 160, 142, 122, 114, 105, 91, 85, 67

M.p.: 58-62 °C

C,H,N-Analysis: calcd. for **13**•H₂O: (found): C: 65.96 (66.04); H: 7.27 (7.52); N: 4.81 (4.34)

(N-Methyl-4 quinuclidinio)carbaldehyde iodide (12)



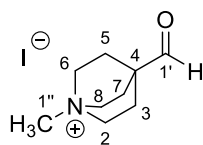
Quinuclidine-4-carbaldehyde (**21**) was prepared according to *Diederich et al.*⁴ In a 2 mL vial, 50 mg (0.36 mmol, 1.0 eq.) of the aldehyde **21** were dissolved in 1 mL of diethyl ether. Iodomethane (40.3 μL, 0.65 mmol, 1.8 eq.) was added at room temperature with stirring, resulting in the instantaneous formation of a precipitate, and stirring was continued overnight. After removal of all volatiles under reduced pressure, 80 mg (0.29

mmol, 79 %) of the product **12** were obtained as a slightly yellow solid. A sample for elemental analysis was obtained by additional drying of this material in high vacuum (10^{-5} – 10^{-4} mbar) at 80 °C for 8 h.

281.14 g mol⁻¹, C₉H₁₆NO

Appearance: slightly yellow solid

Yield: 80 mg (0.29 mmol, 79%)



¹H-NMR: (500 MHz, DMSO-*d*₆) δ [ppm]: 9.53 (s, 1H, H-1'), 3.52–3.48 (m, 6H, H-2,6,8), 2.97 (s, 3H, H-1''), 2.00–1.95 (m, 6H, H-3,5,7)

¹³C-NMR:(125.76 MHz, DMSO-*d*₆) δ [ppm]: 202.9 (1C, C-1'), 55.3 (3C, C-2,6,8), 51.0 (1C, C-1''), 38.8 (1C, C-4) 23.5 (3C, C-3,5,7)

Note: The chemical shift of the C-4 resonance was assigned from the ¹H,¹³C-HSQC spectrum.

FT-IR:(ATR) $\tilde{\nu}$ [cm⁻¹]: 3402.4 (w), 3232.7 (w), 1722.4 (m), 1465.9 (w), 1421.5 (w), 1190.1 (w), 1159.2 (w), 1066.6 (s), 1035.8 (s), 991.4 (s), 977.9 (s), 866.0 (w), 837.1 (m), 736.8 (m), 698.2 (w), 667.4 (w)

HR-ESI-MS: m/z of [M-I]⁺:
calculated: 154.1226 u
measured: 154.1225 u
difference: -0.78 ppm

M.p.: 240 – 247 °C

C,H,N-Analysis: calc. (found) [%]: C: 38.45 (38.29); H: 5.74 (5.47); N: 4.98 (4.60).

2. NMR Spectra

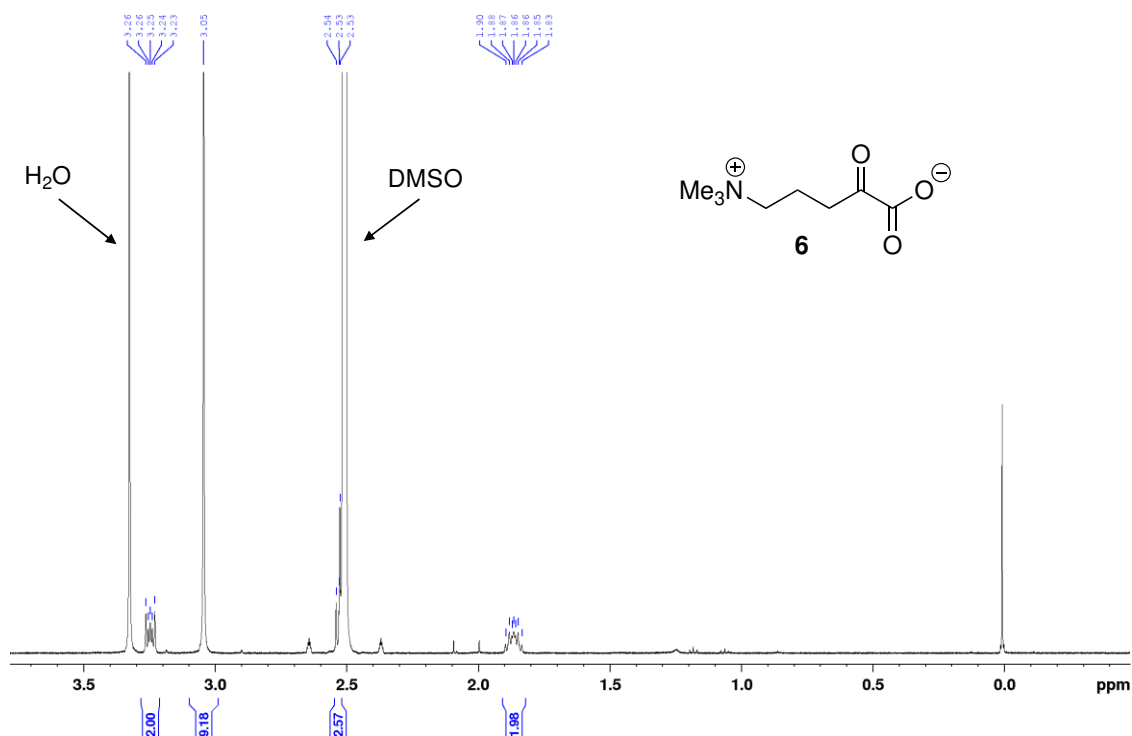


Figure S1: ^1H NMR spectrum (500 MHz, $\text{DMSO}-d_6$, 298 K) of the zwitterion **6**.

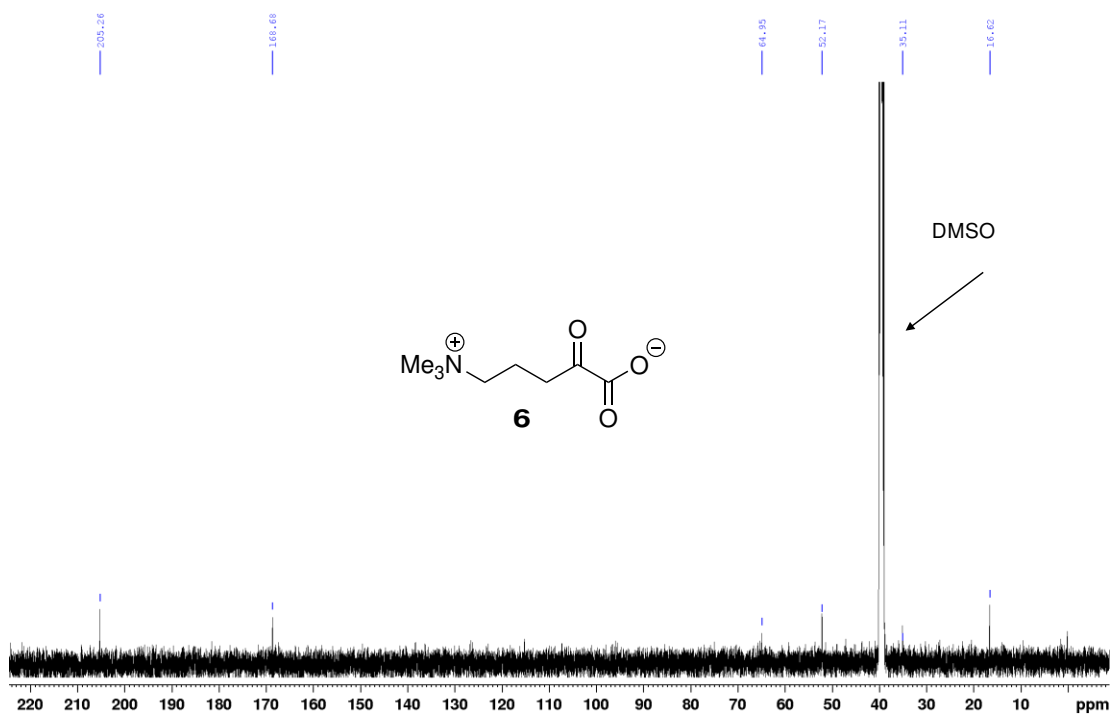


Figure S2: ^{13}C NMR spectrum (126 MHz, $\text{DMSO}-d_6$, 298 K) of the zwitterion **6**.

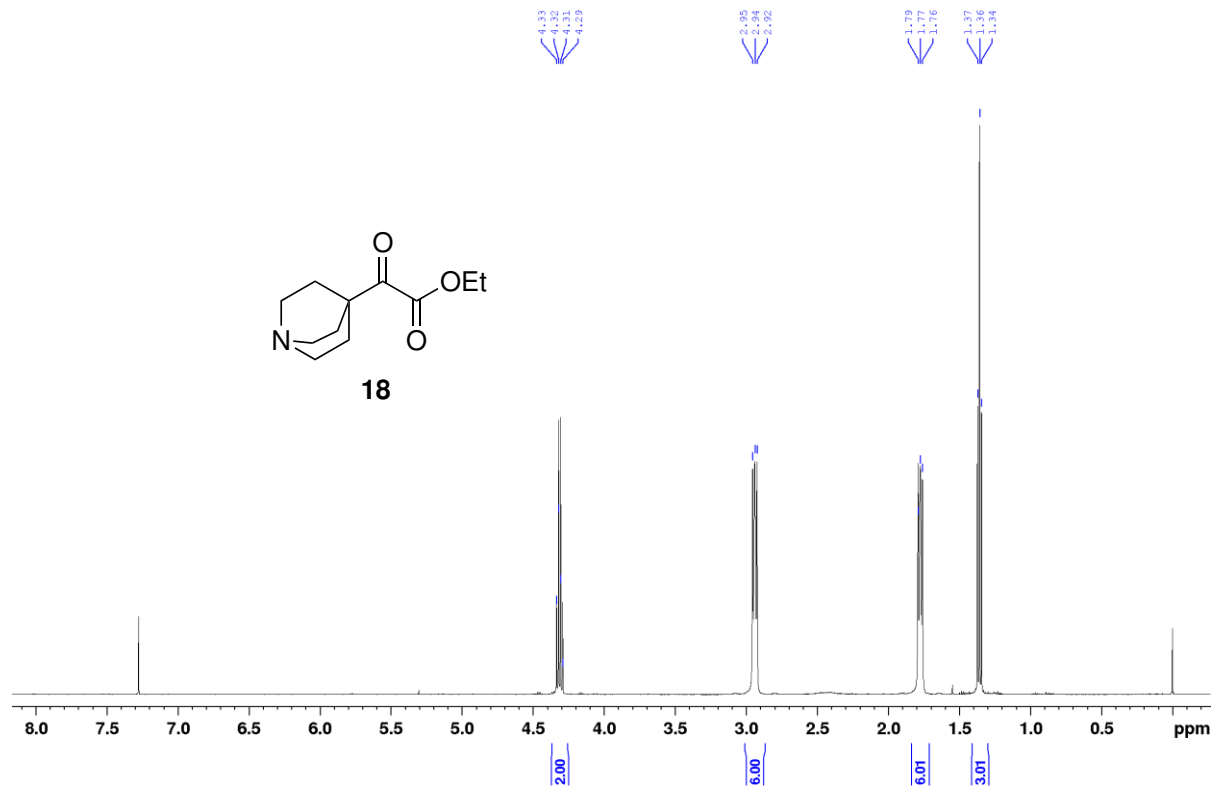


Figure S3: ¹H NMR spectrum (500 MHz, CDCl₃, 298 K) of the ethyl ester **18**.

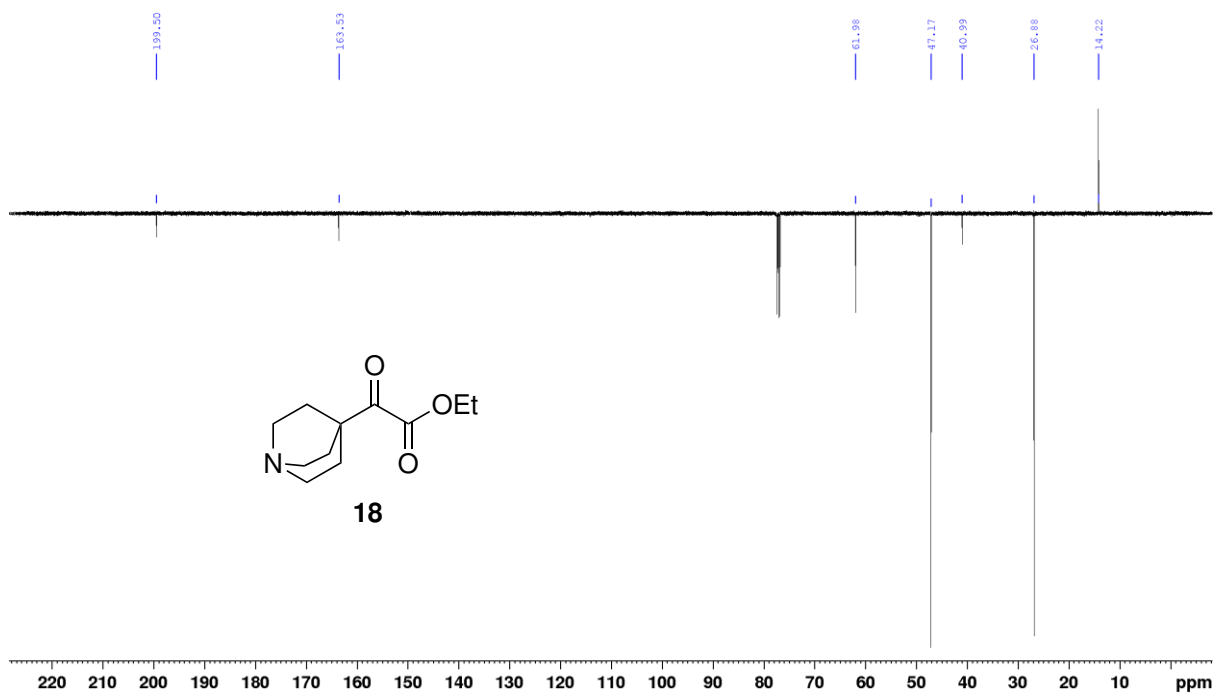


Figure S4: ¹³C-APT NMR spectrum (126 MHz, CDCl₃, 298 K) of the ethyl ester **18**.

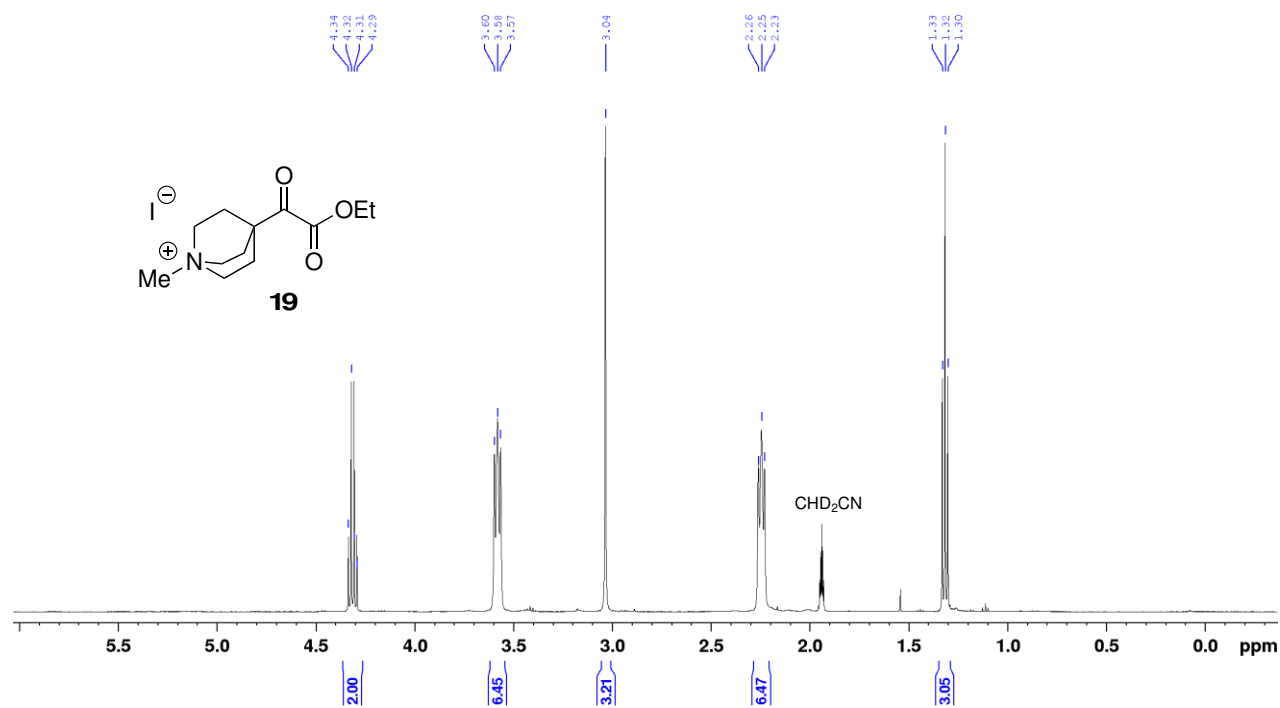


Figure S5: ^1H NMR spectrum (500 MHz, CD_3CN , 298 K) of the quinuclidinium salt **19**.

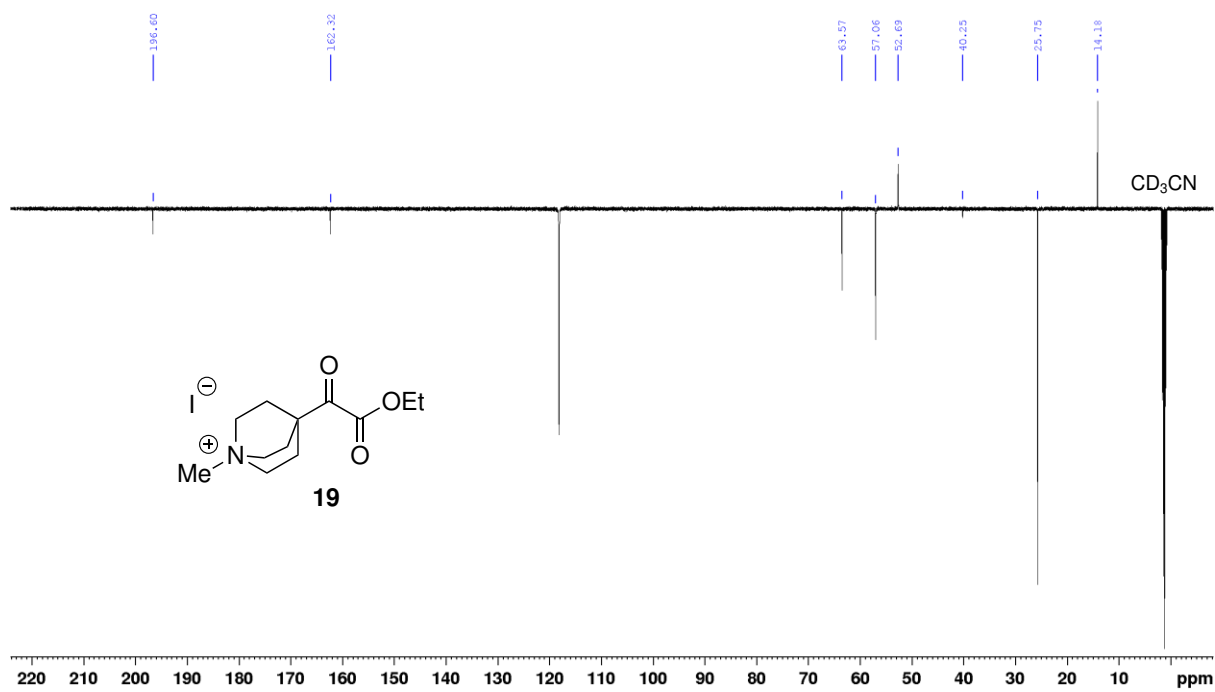


Figure S6: ^{13}C -APT NMR spectrum (126 MHz, CD_3CN , 298 K) of the quinuclidinium salt **19**.

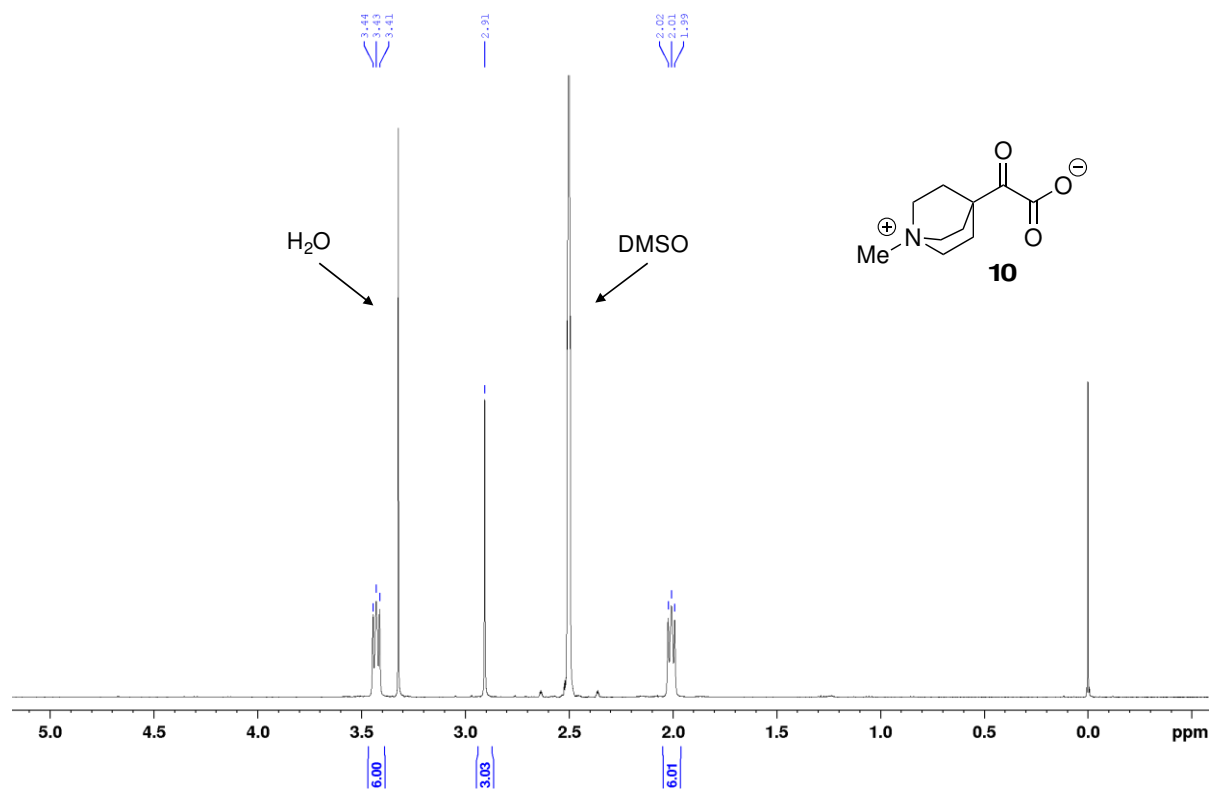


Figure S7: ¹H NMR spectrum (500 MHz, DMSO-*d*₆, 298 K) of the zwitterion **10**.

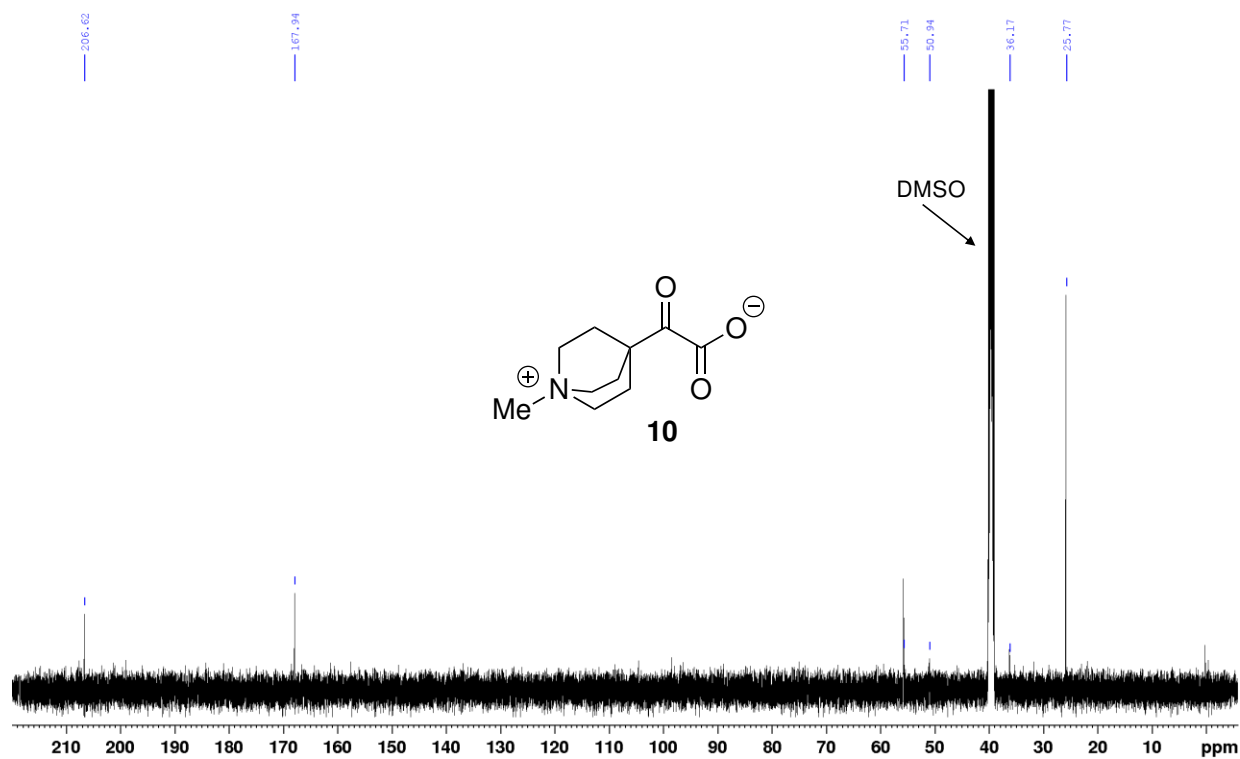


Figure S8: ¹³C NMR spectrum (126 MHz, DMSO-*d*₆, 298 K) of the zwitterion **10**.

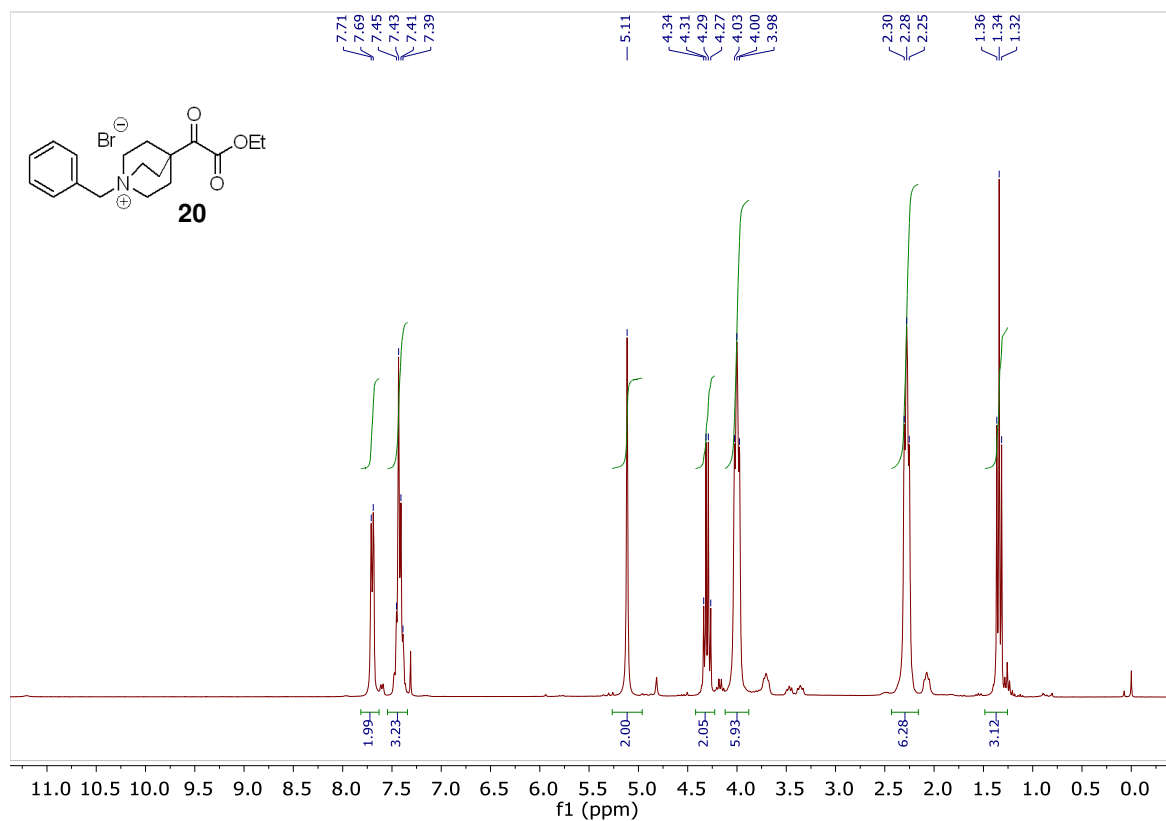


Figure S9: ^1H NMR spectrum (300 MHz, CDCl_3 , 298 K) of the quinuclidinium salt **20**.

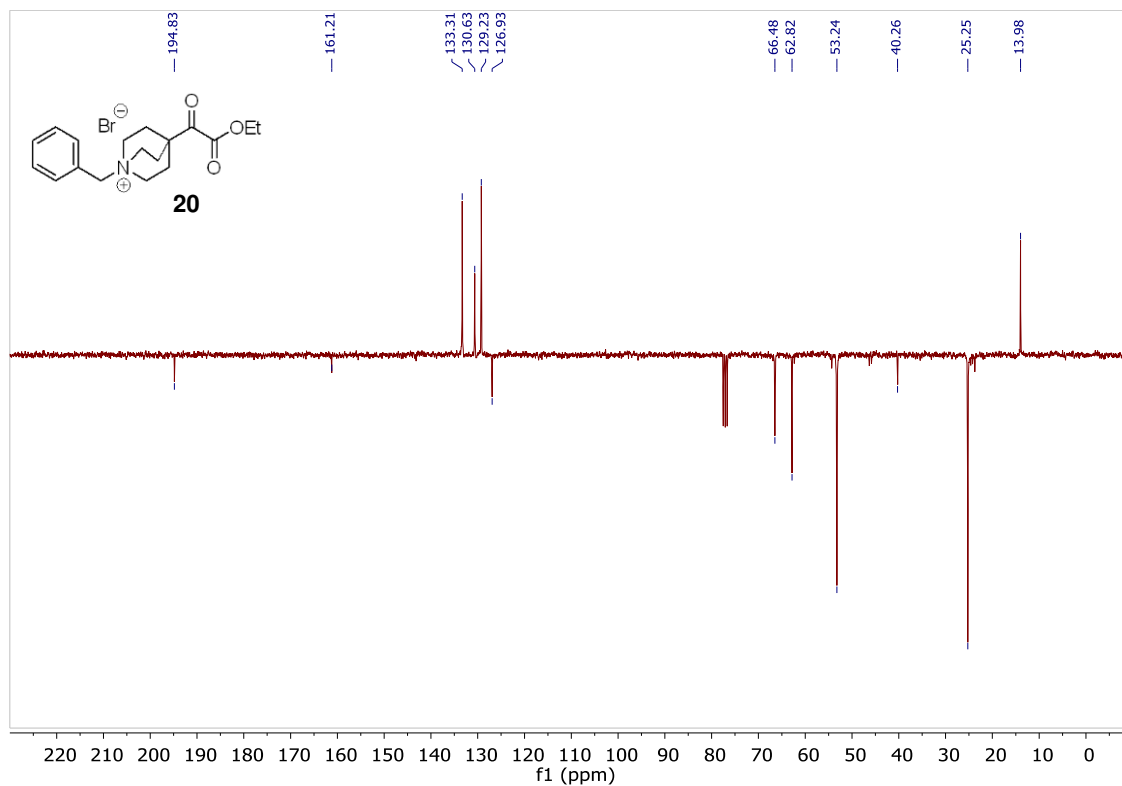


Figure S10: ^{13}C -APT NMR spectrum (75 MHz, CDCl_3 , 298 K) of the quinuclidinium salt **20**.

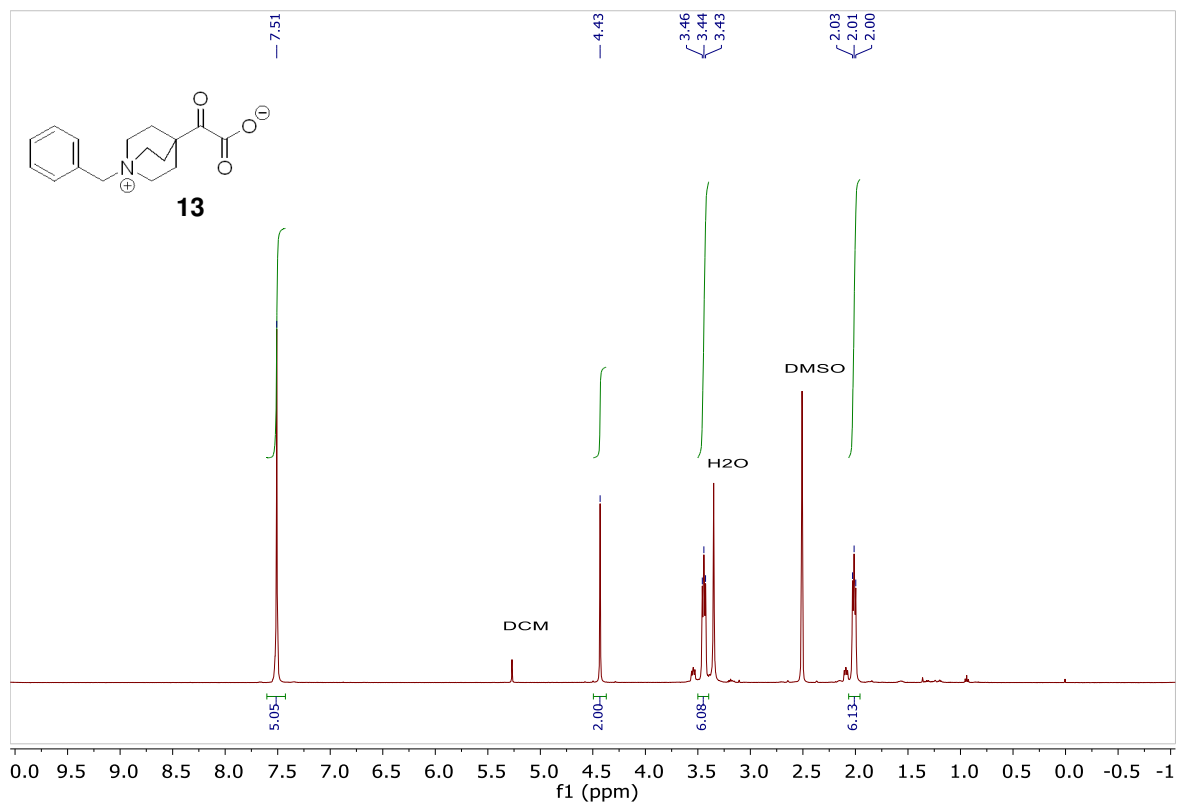


Figure S11: ^1H NMR spectrum (500 MHz, $\text{DMSO-}d_6$, 298 K) of the zwitterion **13**.

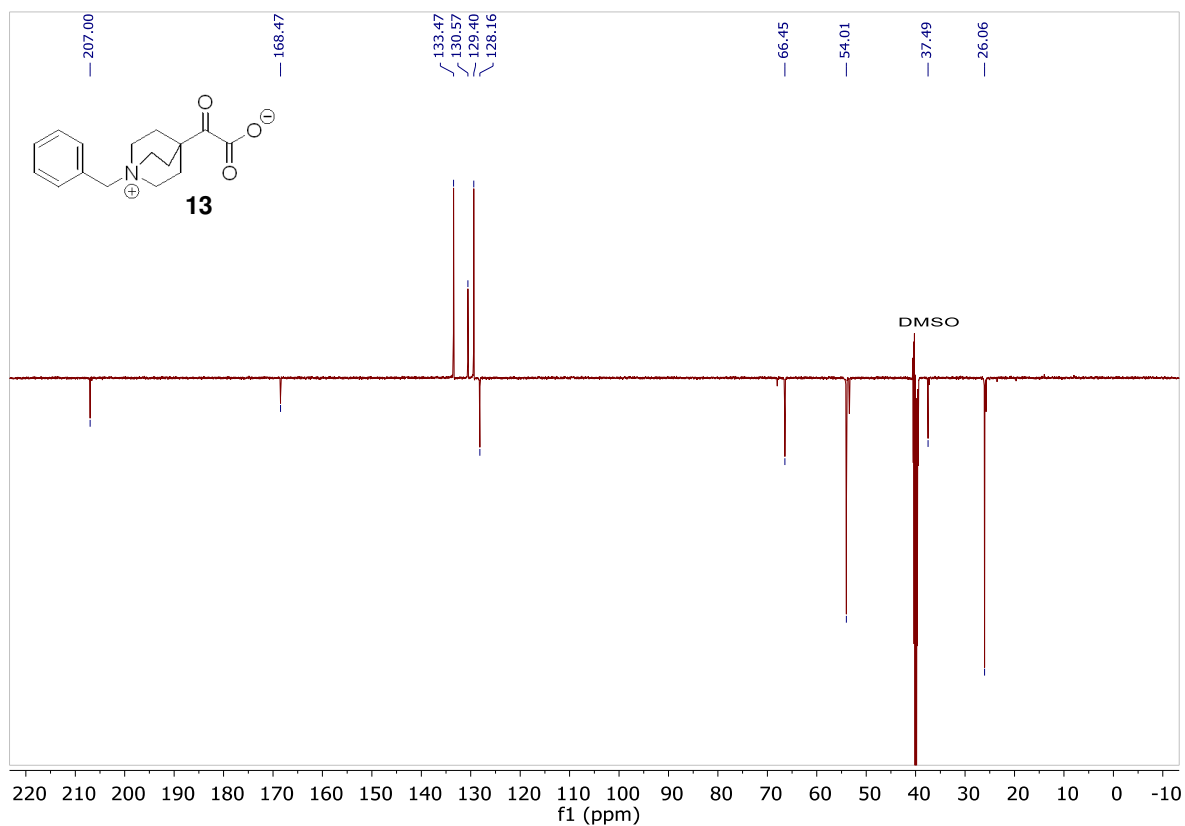


Figure S12: ^{13}C -APT NMR spectrum (126 MHz, $\text{DMSO-}d_6$, 298 K) of the zwitterion **13**.

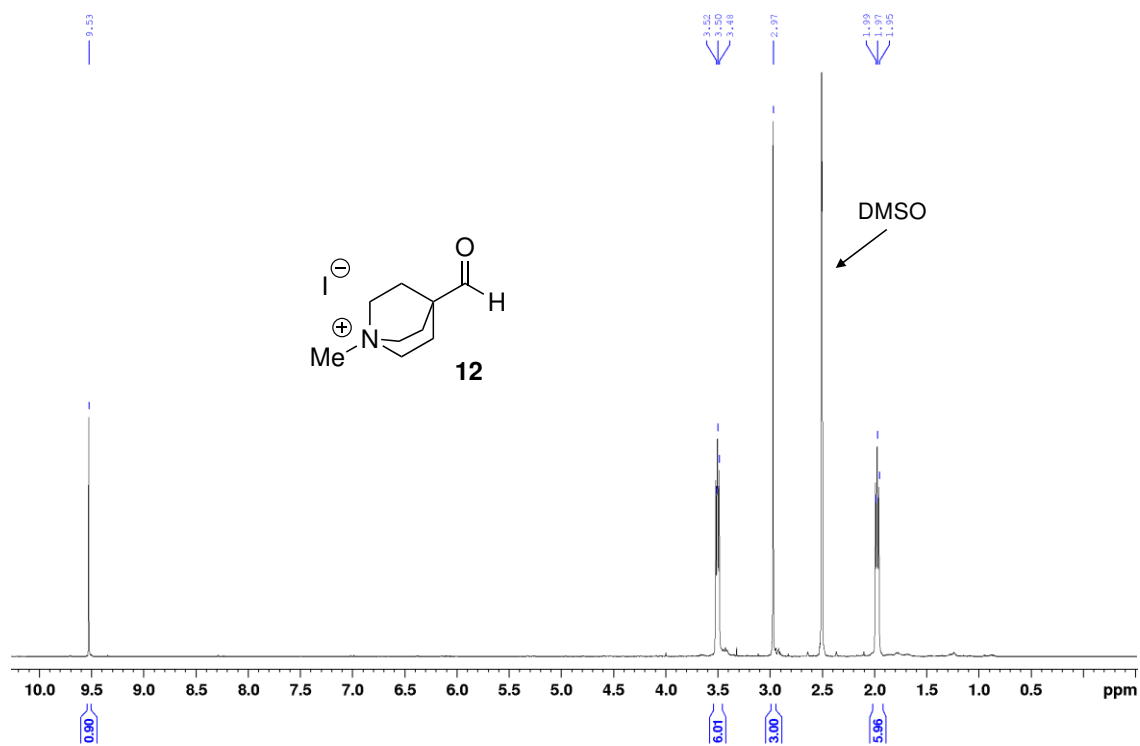


Figure S13: ^1H NMR spectrum (500 MHz, $\text{DMSO}-d_6$, 298 K) of the aldehyde **12**.

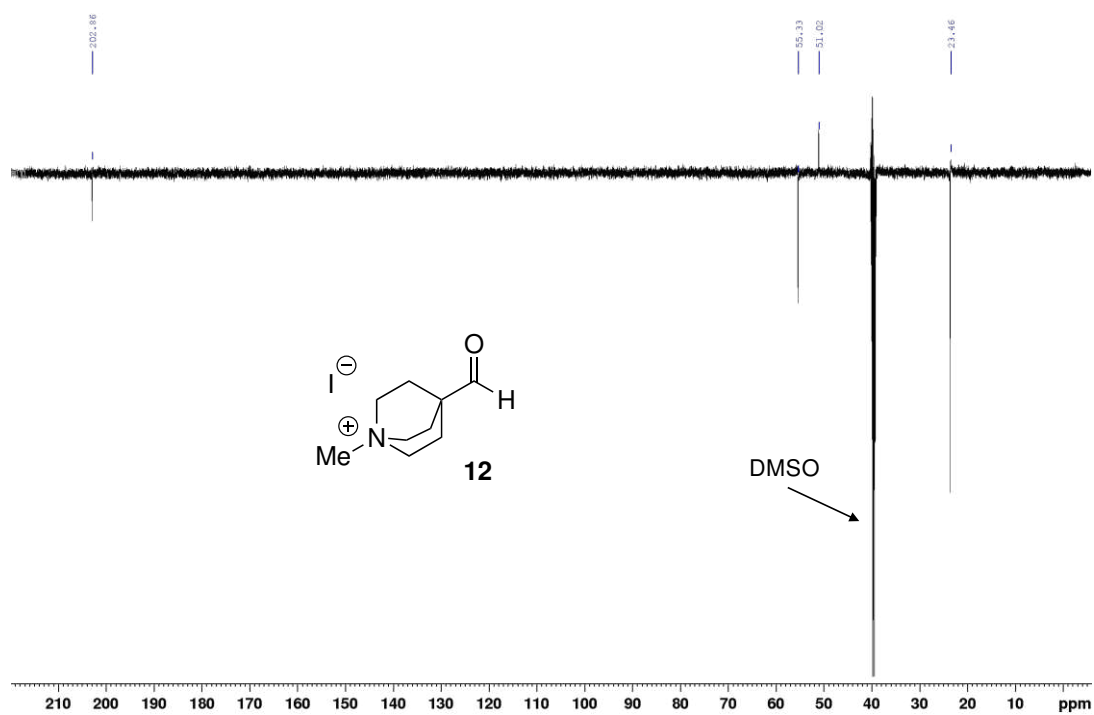


Figure S14: ^{13}C -APT NMR spectrum (126 MHz, $\text{DMSO}-d_6$, 298 K) of the aldehyde **12**.

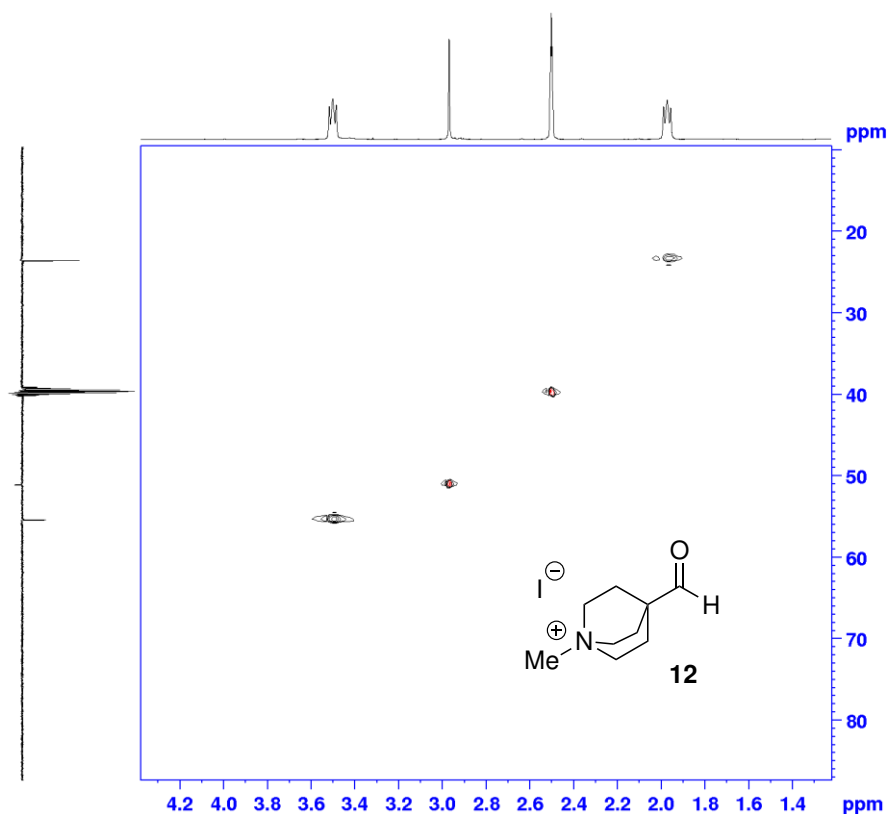


Figure S15: Partial ^1H , ^{13}C -HSQC NMR spectrum (500 MHz/126 MHz, $\text{DMSO-}d_6$, 298 K) of the aldehyde 12.

3. X-Ray Crystal Structures

X-Ray crystal structures were determined on a *Bruker D8 Venture* instrument (kappa geometry), equipped with a copper micro source and a *PhotonIII M14* detector. *Apex3* software (Bruker) was used for the measurements and data analysis. Structure solution was done using SHELXT, and structure refinement using SHELXL. SHELXLe was employed as the graphical interface.

5-(Trimethylammonio)-2-oxopentanoate (6)

CCDC	2220666
Empirical formula	C ₈ H ₁₅ NO ₃
Moiety formula	C ₈ H ₁₅ NO ₃
Formula weight	173.21
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 10.4578(4) Å α = 90°. b = 8.5771(3) Å β = 117.157(2)° c = 10.6606(4) Å γ = 90°.
Volume	850.81(6) Å ³
Z	4
Density (calculated)	1.352 Mg m ⁻³
Absorption coefficient	0.853 mm ⁻¹
F(000)	376
Crystal size	0.080 × 0.060 × 0.020 mm
Θ range for data collection	4.752 to 72.039°
Index ranges	-12 ≤ h ≤ 12, -10 ≤ k ≤ 10, -10 ≤ l ≤ 13
Reflections collected	7754
Independent reflections	1664 [R(int) = 0.0557]
Completeness to Θ = 67.679°	99.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7536 and 0.5948
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1664 / 0 / 112
Goodness-of-fit on F ²	1.076
Final R indices [I > 2σ(I)]	R1 = 0.0411, wR2 = 0.1075
R indices (all data)	R1 = 0.0499, wR2 = 0.1137
Extinction coefficient	n/a
Largest diff. peak and hole	0.311 and -0.189 e Å ⁻³

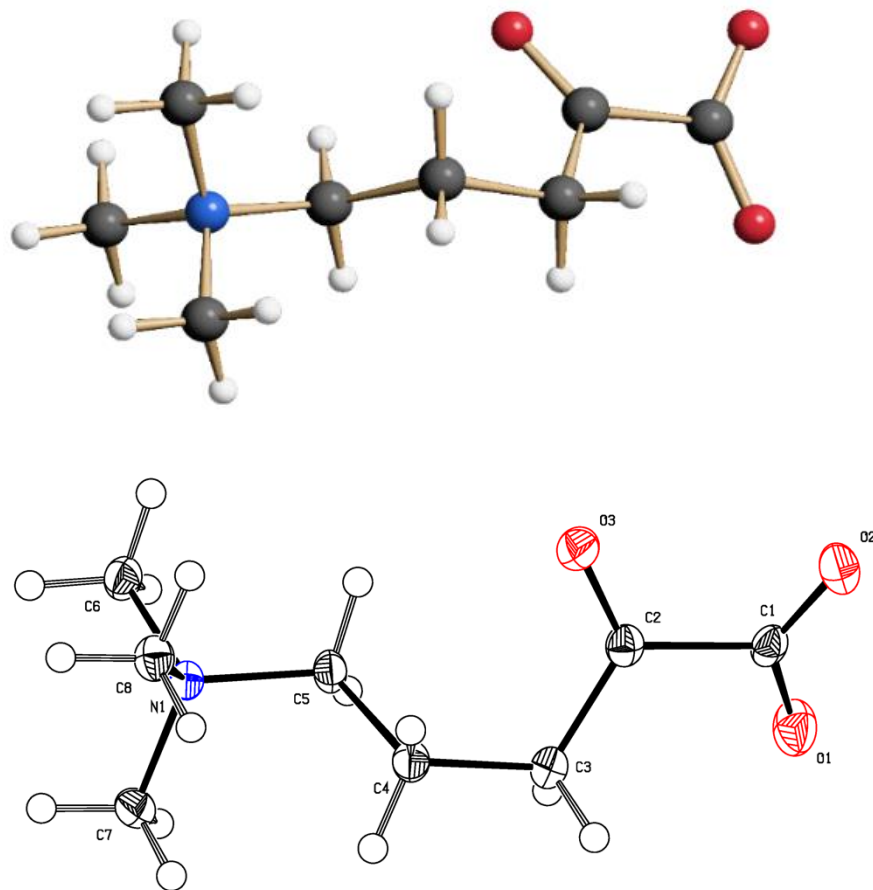


Figure S16: Molecular structure (top) and ORTEP (bottom) of 5-(trimethylammonio)-2-oxopentanoate (**6**). Thermal ellipsoids are drawn at 50 % probability level.

(N-Methyl-4-quinuclidinio)glyoxylate hydrate (10•H₂O)

CCDC	2220667
Empirical formula	C ₁₀ H ₁₇ NO ₄
Moiety formula	C ₁₀ H ₁₇ NO ₄
Formula weight	215.24
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	Pna2 ₁
Unit cell dimensions	a = 15.6501(5) Å α = 90° b = 6.7135(2) Å β = 90° c = 10.1988(3) Å γ = 90°
Volume	1071.56(6) Å ³
Z	4
Density (calculated)	1.334 Mg/m ³
Absorption coefficient	0.858 mm ⁻¹
F(000)	464
Crystal size	0.100 × 0.070 × 0.020 mm
Θ range for data collection	5.654 to 72.100°.
Index ranges	-19 ≤ h ≤ 19, -8 ≤ k ≤ 8, -12 ≤ l ≤ 9
Reflections collected	18529
Independent reflections	1901 [R(int) = 0.1192]
Completeness to Θ = 67.679°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7536 and 0.4661
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1901 / 1 / 145
Goodness-of-fit on F ²	1.105
Final R indices [I > 2σ(I)]	R1 = 0.0475, wR2 = 0.1175
R indices (all data)	R1 = 0.0532, wR2 = 0.1203
Absolute structure parameter	0.2(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.263 and -0.166 e Å ⁻³

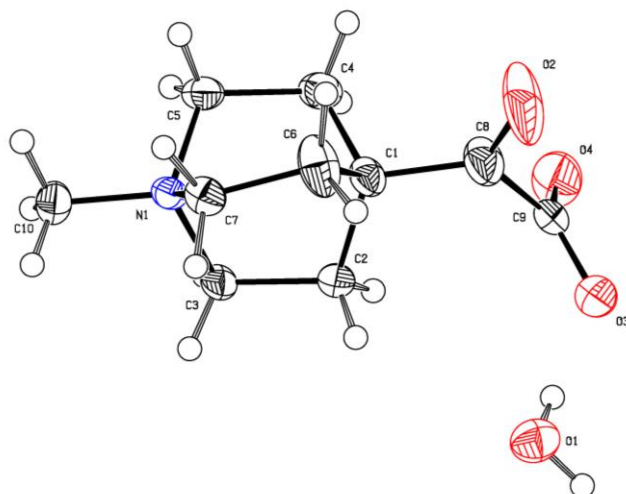
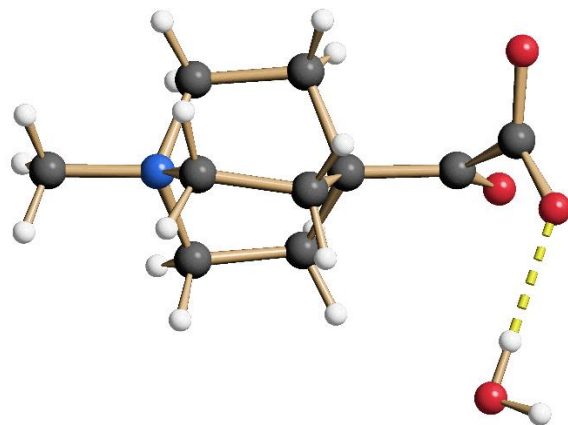


Figure S17: Molecular structure (top) and ORTEP (bottom) of (N-methyl-4-quinuclidinio)glyoxylate hydrate ($10 \cdot \text{H}_2\text{O}$). Thermal ellipsoids are drawn at 50 % probability level.

(N-Methyl-4-quinuclidinio)carbaldehyde (12)

CCDC	2220665
Empirical formula	C ₉ H ₁₆ INO
Moiety formula	C ₉ H ₁₆ NO; I
Formula weight	281.13
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions	a = 6.8811(4) Å α = 90° b = 12.7389(7) Å β = 102.434(2)° c = 12.6694(7) Å γ = 90°
Volume	1084.52(11) Å ³
Z	4
Density (calculated)	1.722 Mg/m ³
Absorption coefficient	22.866 mm ⁻¹
F(000)	552
Crystal size	0.100 x 0.030 x 0.030 mm ³
Θ range for data collection	6.952 to 72.342°
Index ranges	-8 ≤ h ≤ 8, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	8788
Independent reflections	2034 [R(int) = 0.0411]
Completeness to Θ = 67.679°	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7536 and 0.2871
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2034 / 2 / 110
Goodness-of-fit on F ²	1.073
Final R indices [I > 2σ(I)]	R1 = 0.0178, wR2 = 0.0429
R indices (all data)	R1 = 0.0180, wR2 = 0.0430
Absolute structure parameter	0.072(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.584 and -0.297 e Å ⁻³

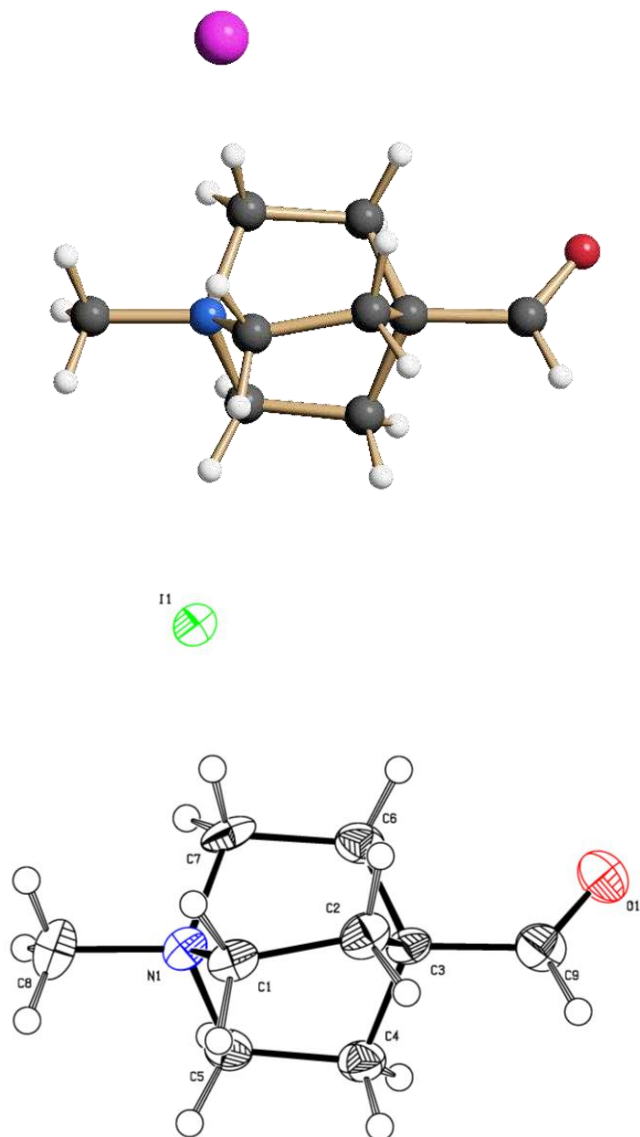


Figure S18: Molecular structure (top) and ORTEP (bottom) of (N-methyl-4-quinuclidinio)carbaldehyde (**12**). Thermal ellipsoids are drawn at 50 % probability level.

3.4 References

1. Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed., Butterworth-Heinemann: Amsterdam, Boston, 2003.
2. Öhler, E., Schmidt, U. *Chem. Ber.* **1975**, *108*, 2907-2916.
3. Grob, C. A.; Brenneisen, P. *Helv. Chim. Acta* **1958**, *41*, 1184-1190.
4. Dumele, O.; Schreib, B.; Warzok, U.; Trapp, N.; Schalley, C. A.; Diederich, F. *Angew. Chem. Int. Ed.* **2017**, *56*, 1152-1157.

4. Mass Spectrometry

Analyte Ion	Composition	Calculated Molecular Ion Mass [u]	Observed Ion Mass [u]	Experimental Error Δ [ppm]
6-H	[C ₈ H ₁₆ O ₃ N] ⁺	174.1130	174.1126	2.4
7-H	[C ₇ H ₁₆ ON] ⁺	130.1232	130.1227	3.7
10-H	[C ₁₀ H ₁₆ O ₃ N] ⁺	198.1128	198.1125	0.1
10-D	[C ₁₀ ¹ H ₁₅ ² H ₁ O ₃ N] ⁺	199.1187	199.1196	0.9
11-D	[C ₉ ¹ H ₁₅ ² H ₁ ON] ⁺	155.1289	155.1295	0.6
11-H	[C ₉ H ₁₆ ON] ⁺	154.1226	154.1223	1.9
12-H	[C ₉ H ₁₆ ON] ⁺	154.1226	154.1225	0.8
13-H	[C ₁₆ H ₂₀ O ₃ N] ⁺	274.1437	274.1436	0.5
14-H	[C ₁₅ H ₂₀ ON] ⁺	230.1545	230.1539	2.6
13-D	[C ₁₆ ¹ H ₁₉ ² H ₁ O ₃ N] ⁺	275.1506	275.1501	0.1
14-D	[C ₁₅ ¹ H ₁₉ ² H ₁ ON] ⁺	231.1602	231.1603	0.1

Table S1: Accurate ion mass determinations of the analytes measured on an ESI-MS Orbitrap XL instrument at R = 30000 (FWHM) with internal standard mass calibration.

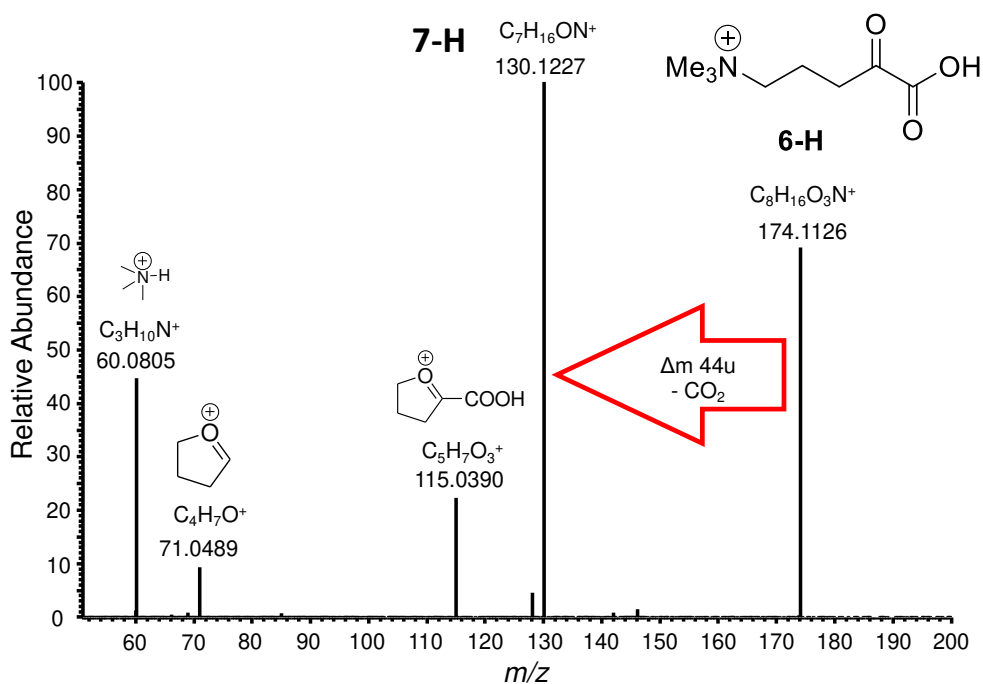


Figure S19: (+)ESI-MS²-Product ion spectrum of the molecular ion at m/z 174 of the precursor ion **6-H**.

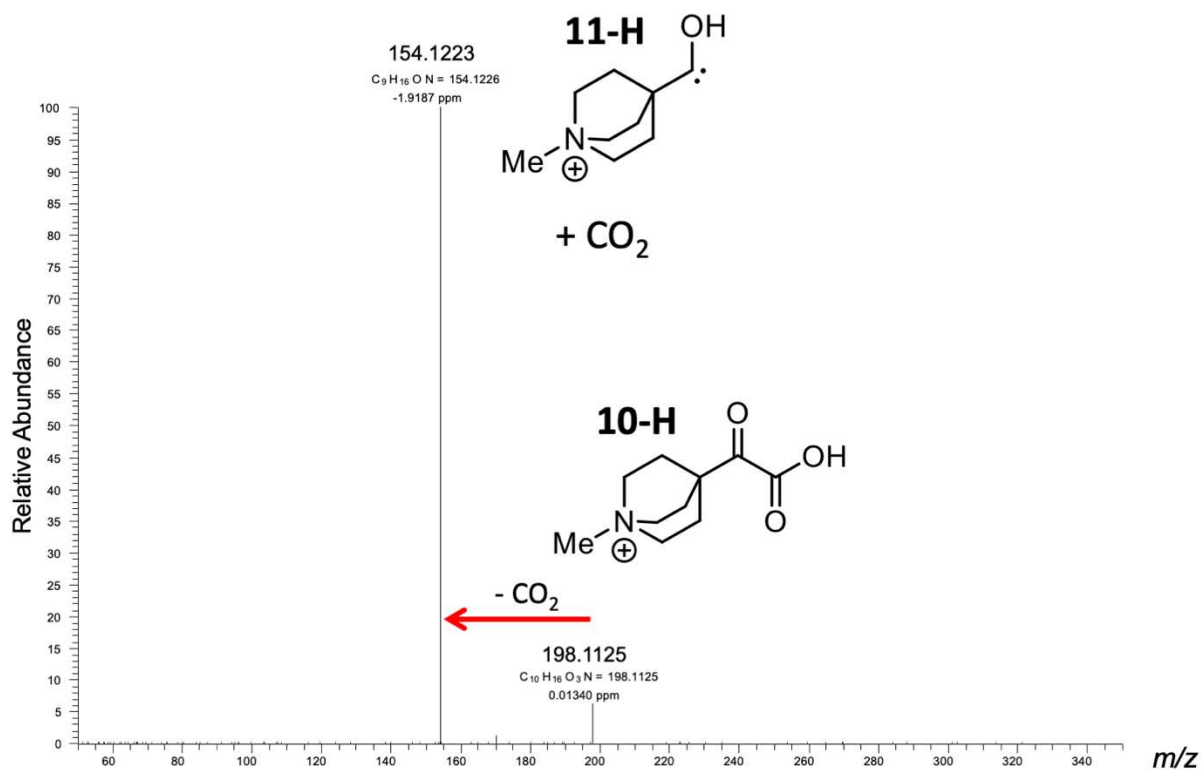


Figure S20: (+)ESI-MS²-Product ion spectrum of the molecular ion at m/z 198 of the precursor ion **10-H**.

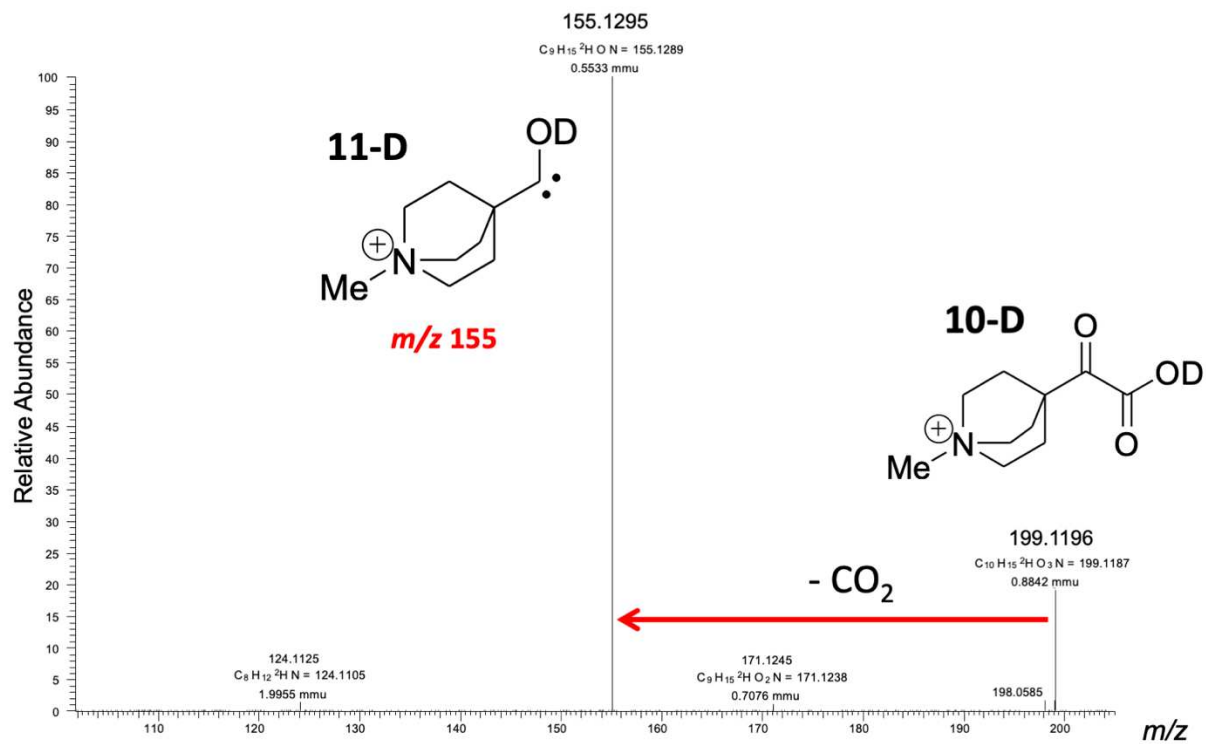


Figure S21: (+)ESI-MS² CID product ion at m/z 155 formed by CO₂ loss from the precursor ion **10-D** at m/z 199.

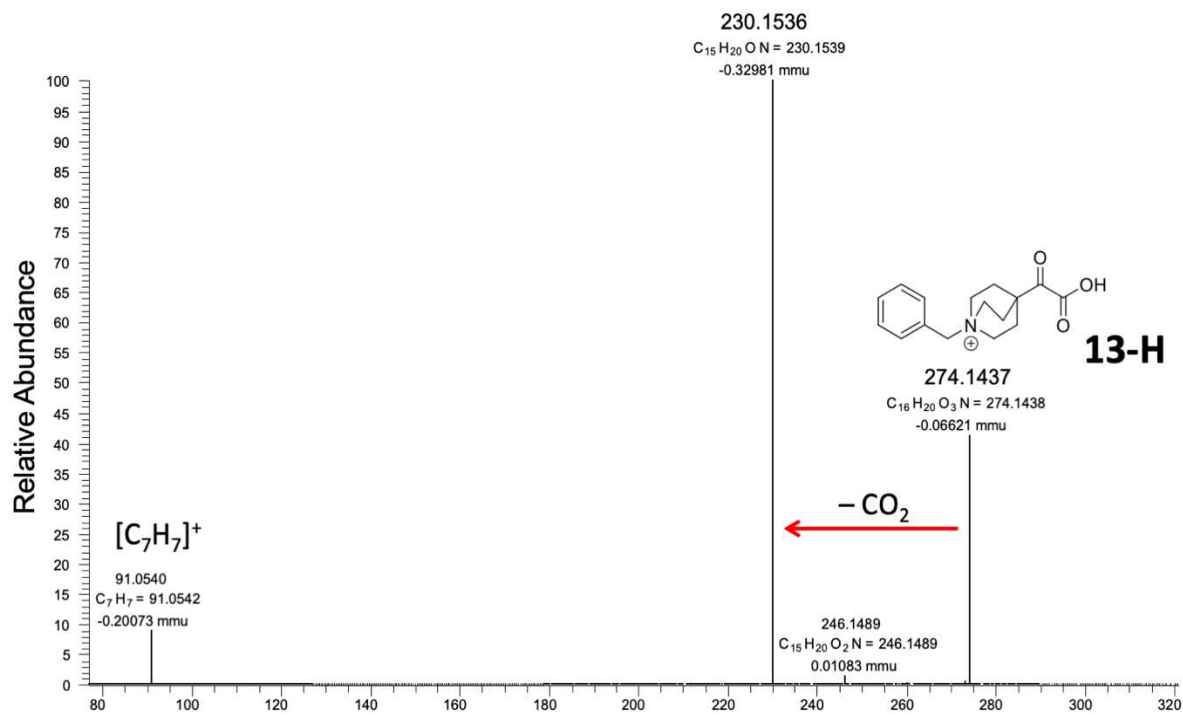


Figure S22: (+)ESI-MS² of the molecular ion of the benzyl quinuclidine analyte **13-H** at m/z 274. The CO₂ loss delivers the product ion at m/z 230.

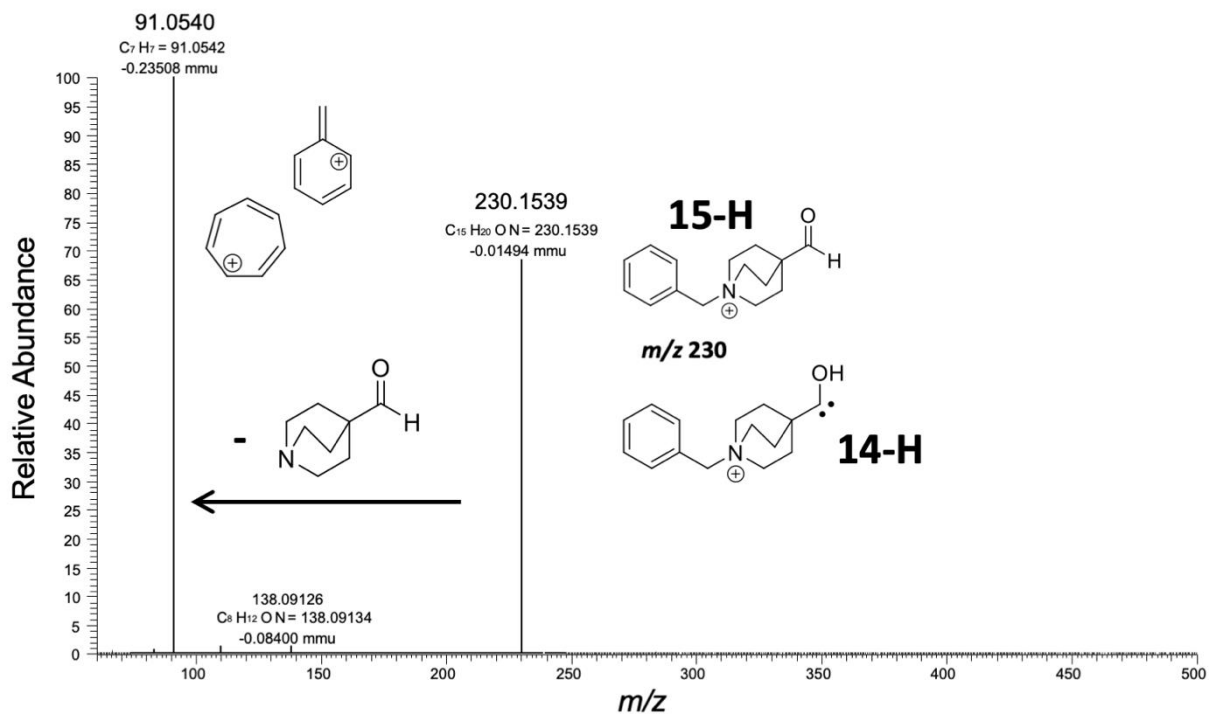


Figure S23: (+)ESI-MS³ of the product ion experiment of the ion at m/z 230 (presumably **14-H** or **15-H**) generated upon CID, *i.e.* CO₂-loss from the precursor ion **13-H** (see Supplementary Figure S22). The exclusive formation of the benzylic ion [C₇H₇]⁺ at m/z 91 is the basis for the kinetic measurement of **14-H** and **15-H** presented in Figure 4.

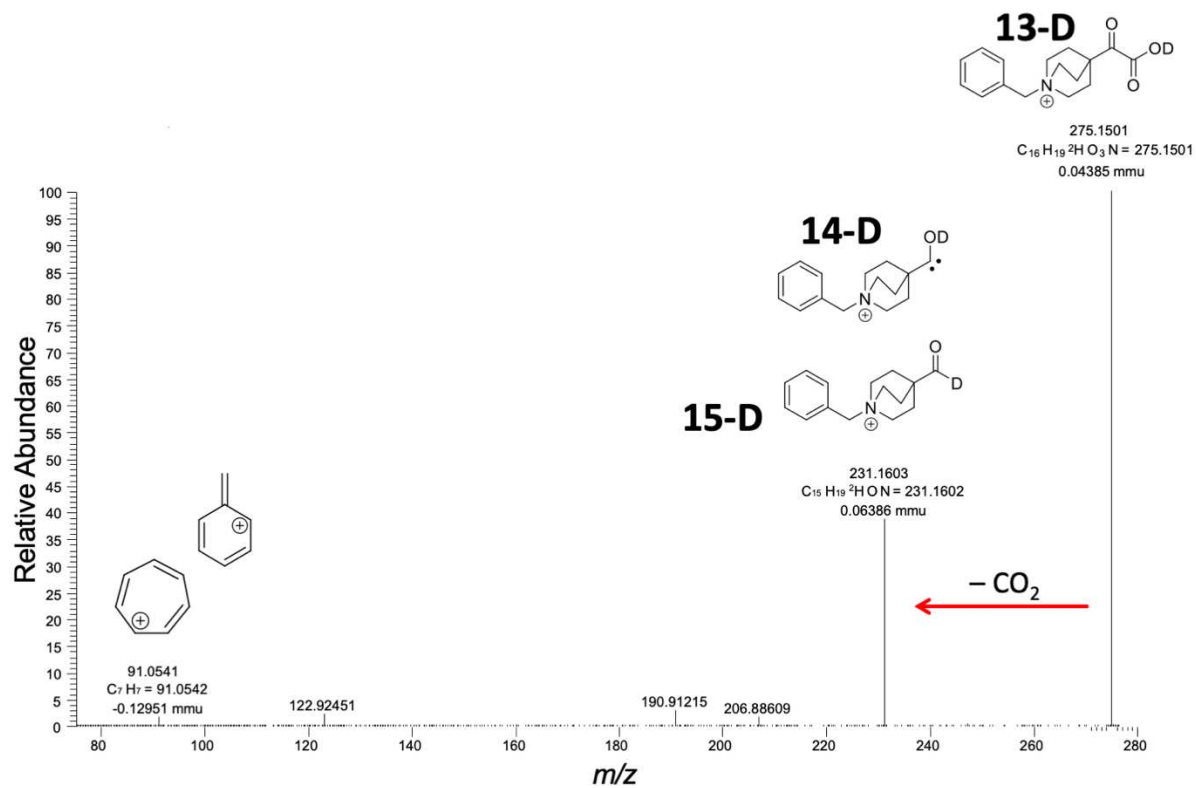


Figure S24: (+)ESI-MS² of the molecular ion of the D₁-benzyl quinuclidine analyte **13-D** at m/z 275. The CO₂ loss delivers the respective product ions **14-D** and/or **15-D** at m/z 231.

5. Ion Spectroscopy

Table S2. Bands found in the IR-ion spectrum of the CO₂-loss product ion at m/z 130 (black trace in Figure 1) of **6-H** upon CID, compared with the calculated, scaled IR bands predicted for the 5-membered ring hydroxycarbene **7-H_{5r}** with intramolecular **C[⋯]H-C** H-bonding (**7-H_{5r}**; +208 kJ mol⁻¹, green trace in Figure 1). *Scaling: 0.97; **Scaling: 0.95

Band found [cm ⁻¹]	7-H _{5r} computed absorption bands * [cm ⁻¹]	7-H _{5r} modes
	763	δ CH ₂ bending
860	852	δ O-H wagging / bending ν _{N-CH2}
888	882	δ O-H wagging / bending ν _{N-CH2}
960	928	δ N-CH ₃ wagging / bending
1005-1013	999	δ CH ₂ bending
1054	1042	δ N-CH ₃ wagging / bending
1116	1116	δ CH ₃ bending
1193	1191	δ CH ₂ bending
1260	1252	ν _{N-CH2}
1310	1304	δ O-H wagging / bending
1349, 1361, 1370	1365	ν _{C-OH}
1418		
1480	1476	δ CH ₃ wagging / bending
3560	3535**	ν _{O-H}

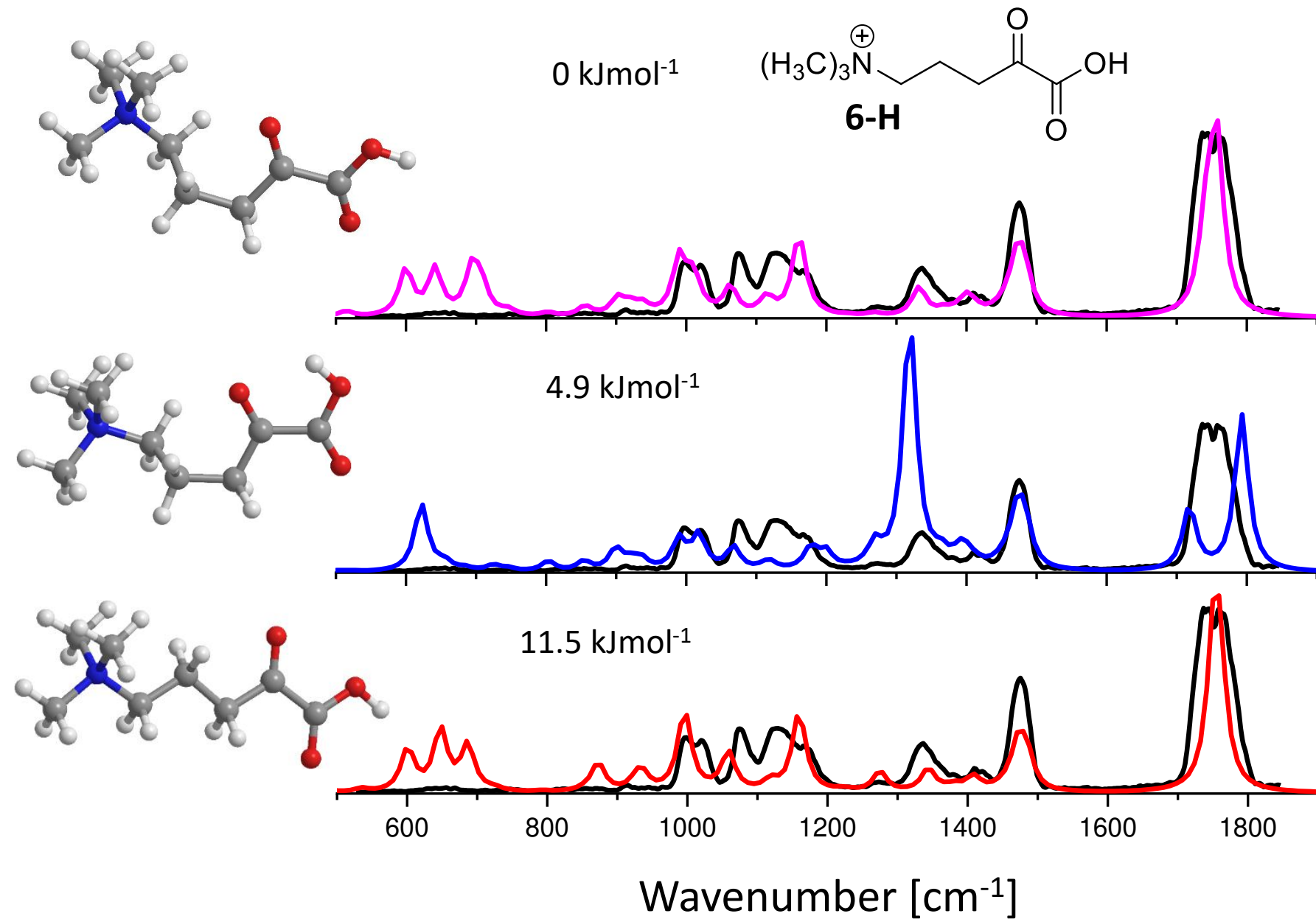


Figure S25. IR ion spectrum acquired of the precursor ion of **6-H** at m/z 174 compared to ion structures identified by theory. Scaling: 0.97.

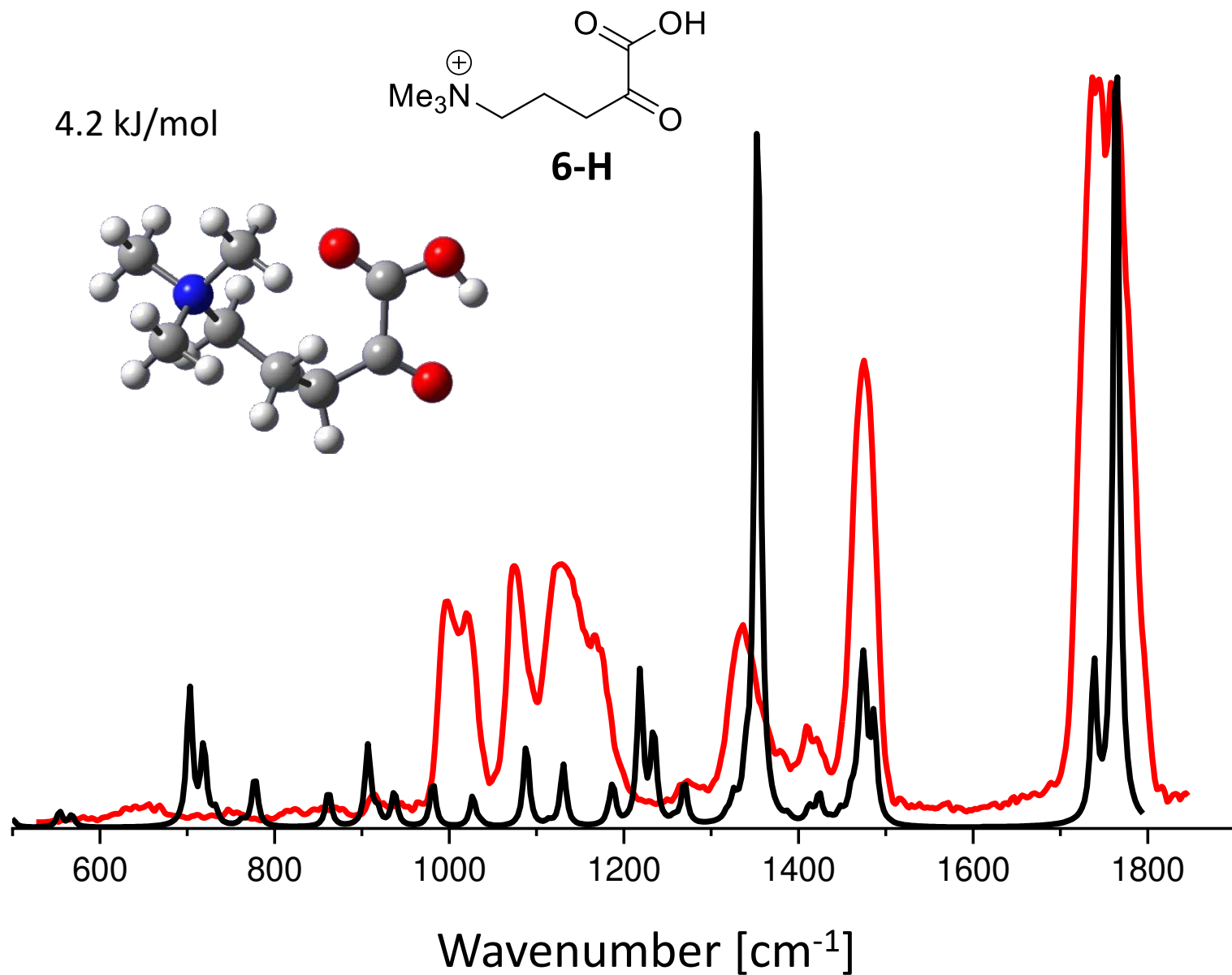


Figure S26. IR ion spectrum acquired of the precursor ion of **6-H** at m/z 174 compared to an alternative ion structure identified by theory. Scaling: 0.97.

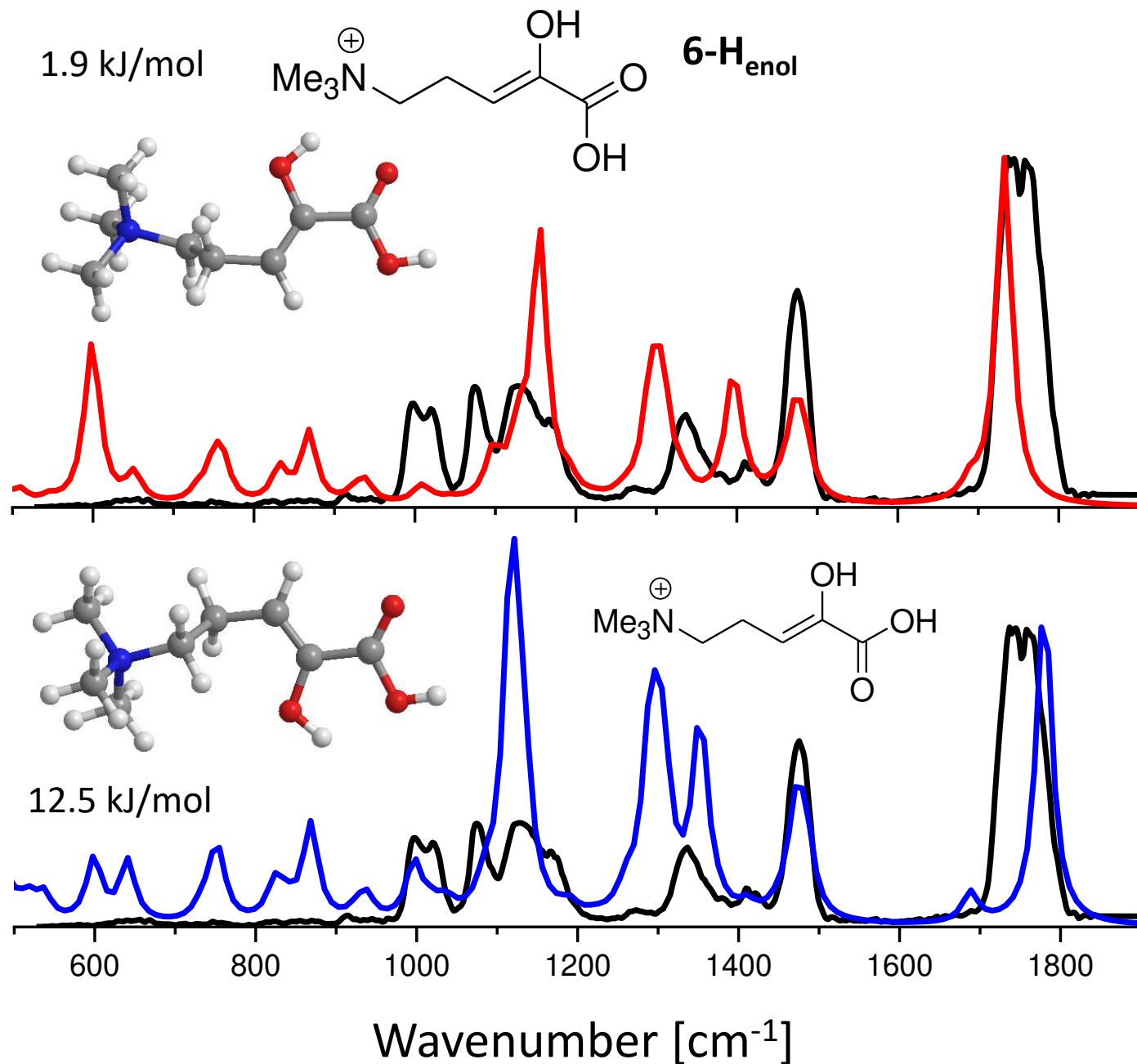


Figure S27. IR ion spectrum acquired of the precursor ion of **6-H** at m/z 174 compared to tautomeric enol ion structures identified by theory. Scaling: 0.97.

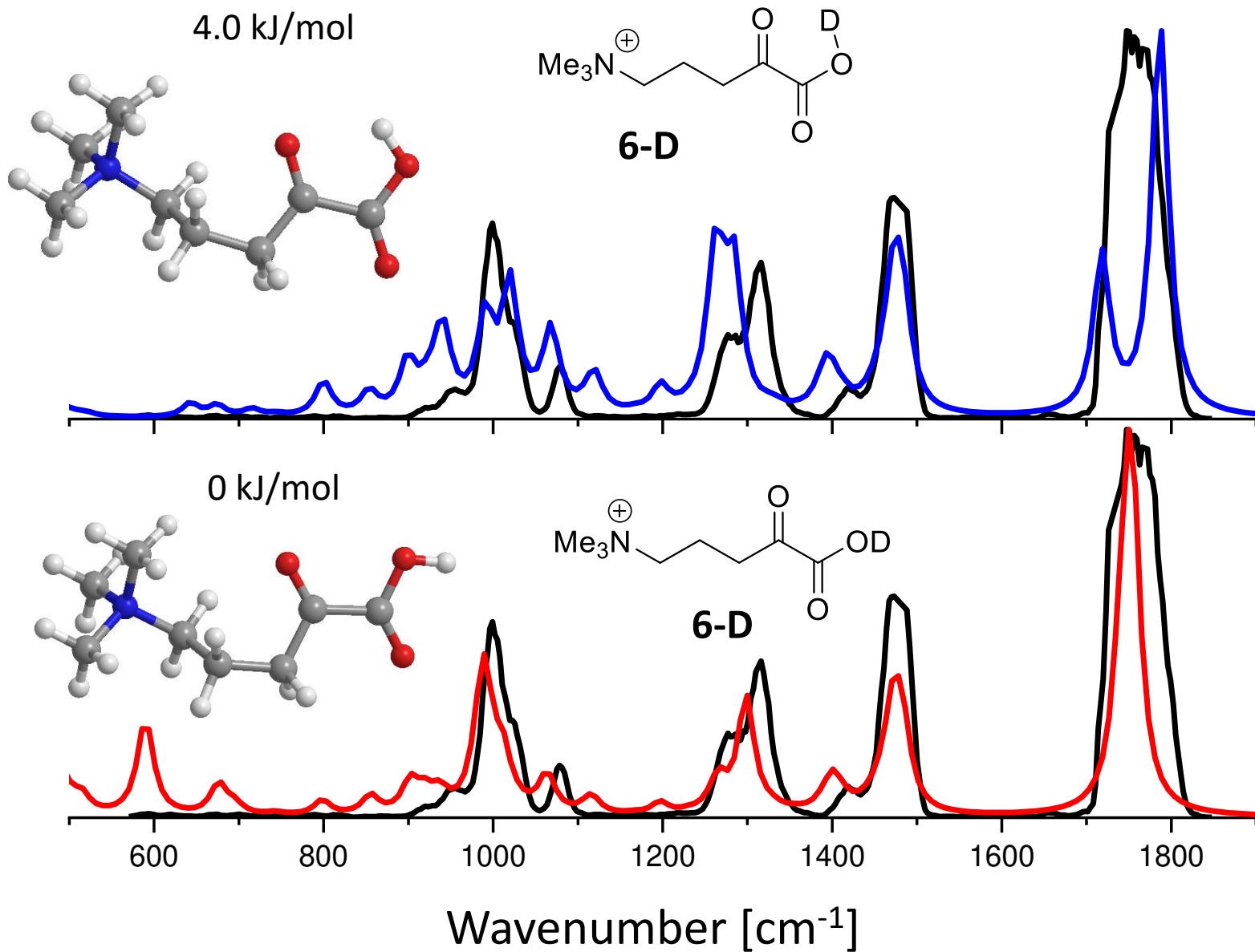


Figure S28. IR ion spectrum acquired of the precursor ion of 6-D at m/z 175 compared to ion structures identified by theory. Scaling: 0.97.

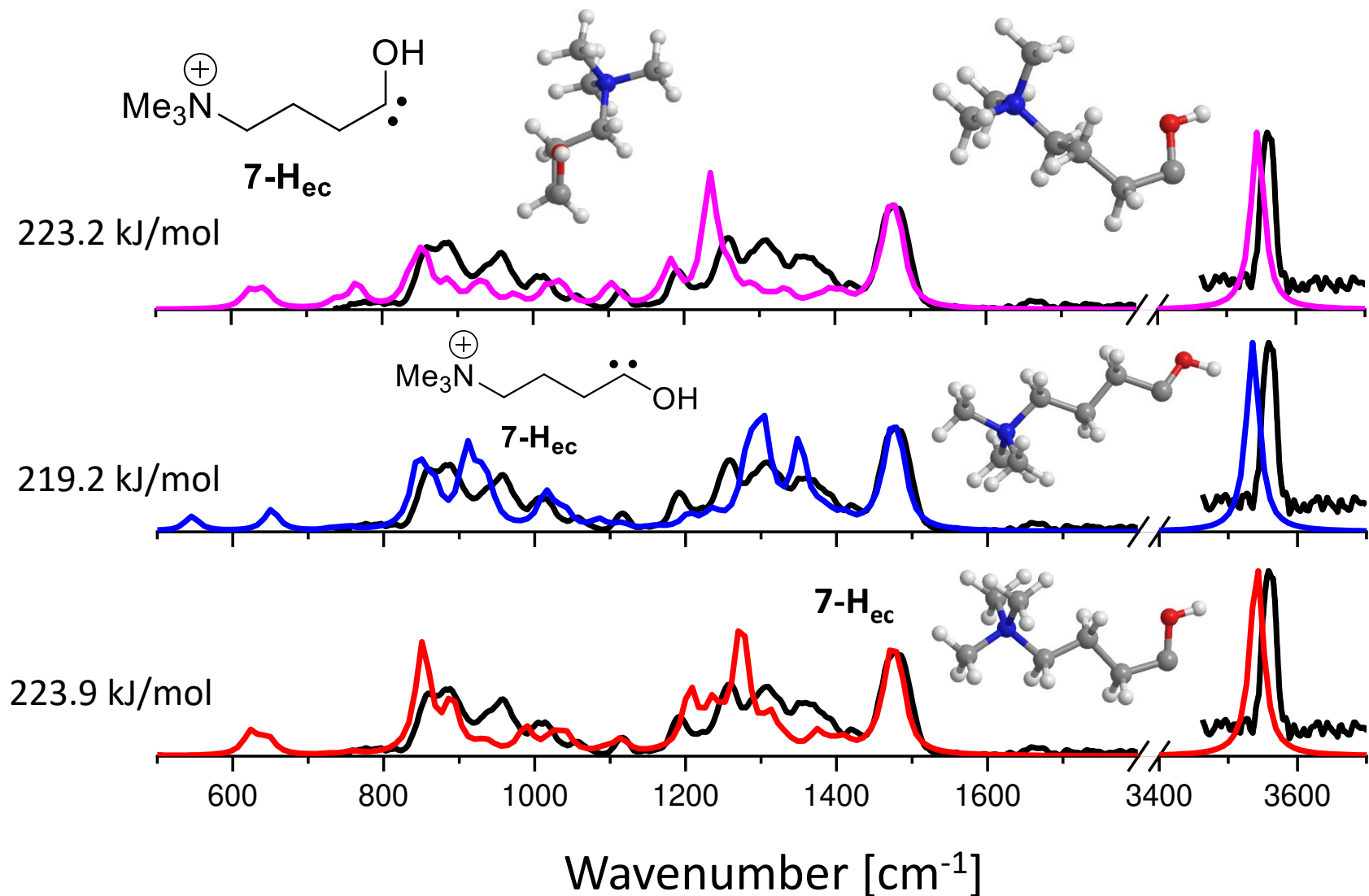


Figure S29. IR-ion spectrum of the CO₂-loss product ion at m/z 130 (black trace) produced from **6-H** upon CID compared with the calculated, linear IR spectra of three structural alternatives for the hydroxycarbene ion **7-H_{ec}**, together with relative energy values vs aldehyde **8-H**. Scaling: 0.97/0.95; scaled intensity of the wavenumber range 3500-3700 cm⁻¹ covered by the OPO-Laser.

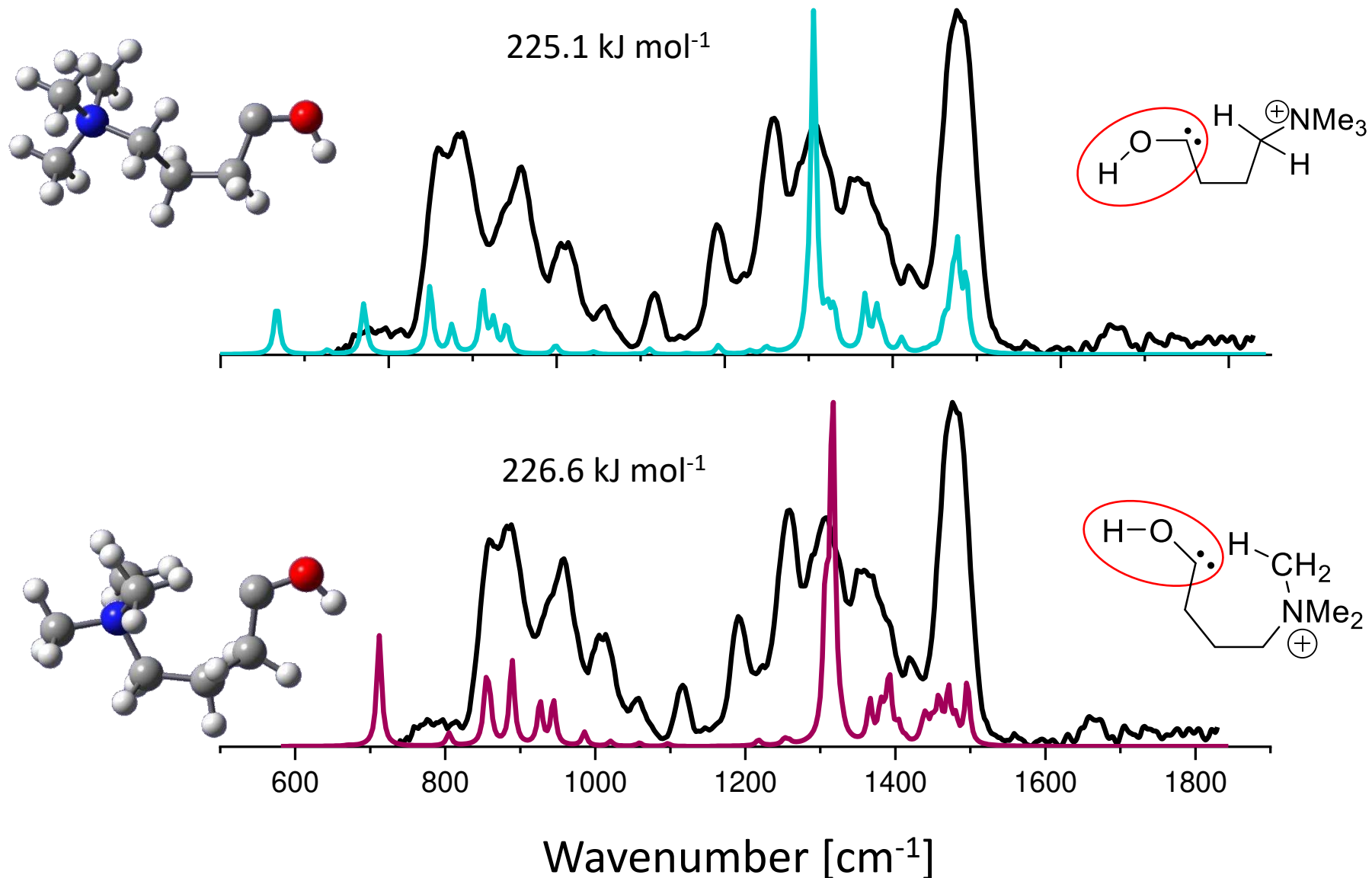


Figure S30. IR-ion spectrum of the CO_2 -loss product ion at m/z 130 (black trace) produced from **6-H** upon CID compared with the calculated, linear IR spectra of two structural alternatives of the hydroxycarbene ion **7-H_{5r}** and **7-H_{7r}**, with single bond cis conformation together with relative energy values vs aldehyde **8-H**. Scaling: 0.97.

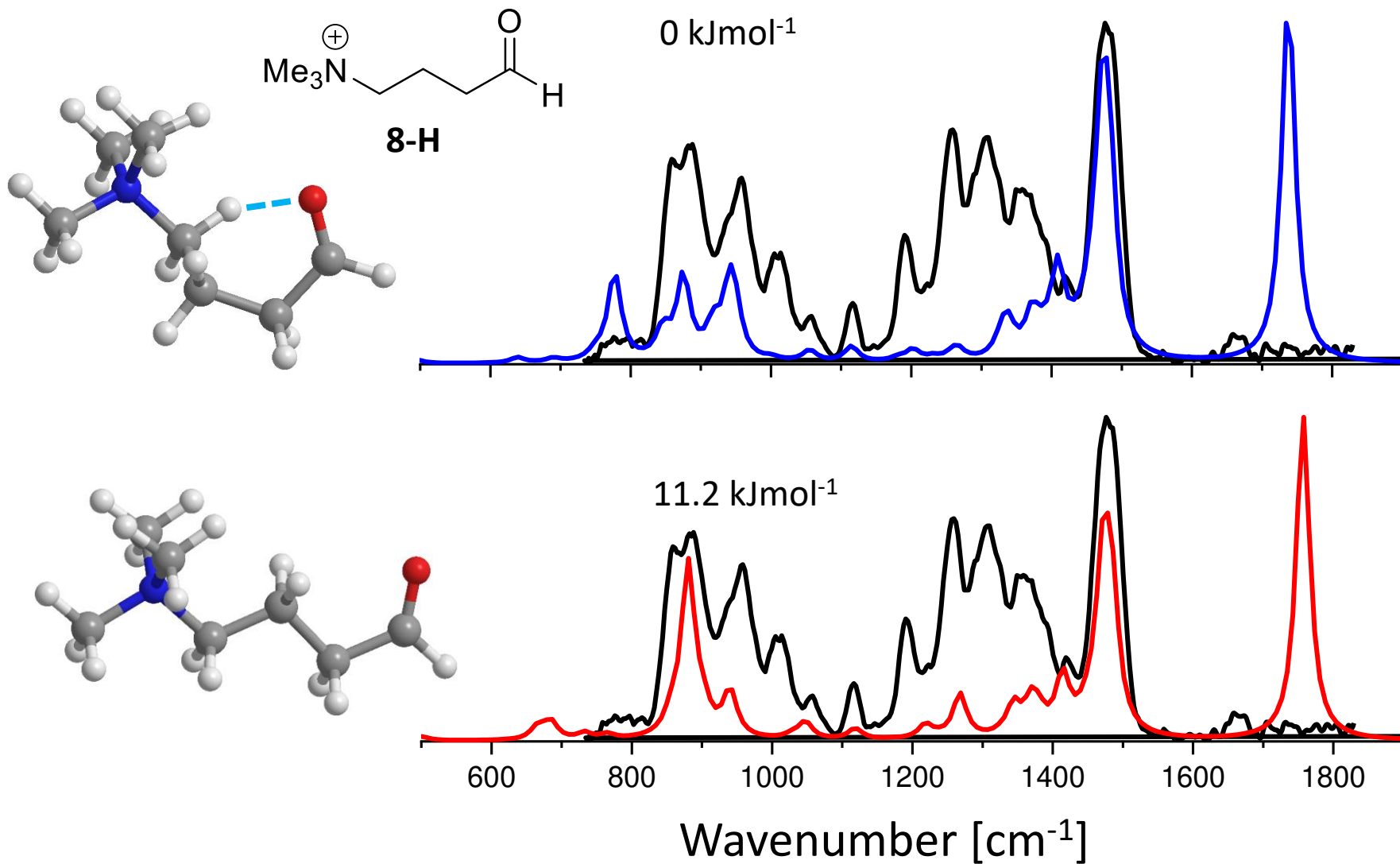


Figure S31. IR-ion spectrum of the CO₂-loss product ion at m/z 130 (black trace) produced from **6-H** upon CID compared with the calculated, linear IR spectra of two structural alternatives of the aldehyde ion **8-H**, together with relative energy values. The ion structure of **8-H** with the intramolecular C=O \cdots H-C interaction (dotted blue line) is the global ground structure to which all hydroxycarbene and enol ion structures refer to. Scaling: 0.97.

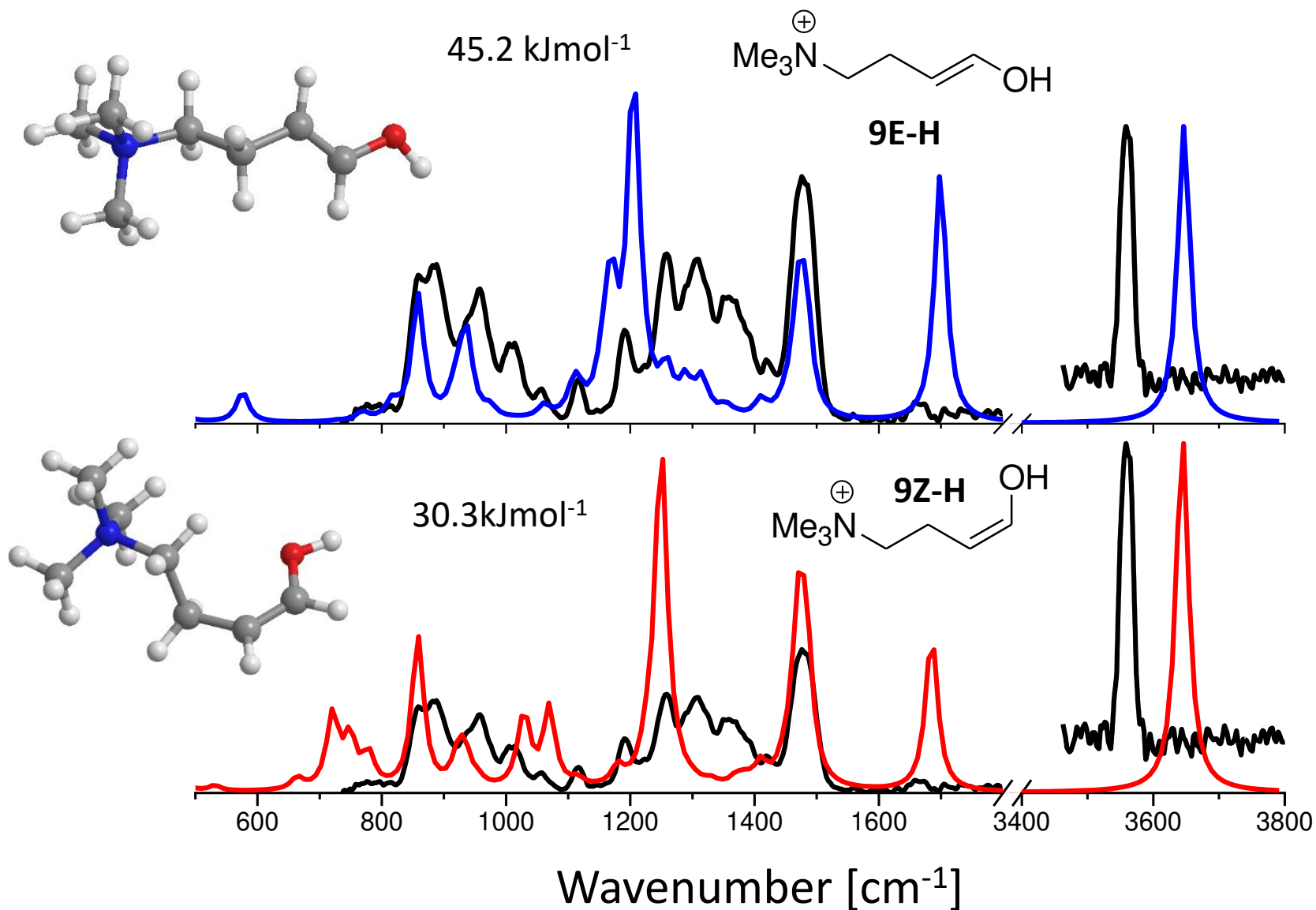


Figure S32. IR-ion spectrum of the CO_2 -loss product ion at m/z 130 (black trace) produced from **6-H** upon CID compared with the calculated, linear IR spectra of two structural alternatives of the enol ion **9E-H** and **9Z-H**, together with relative energy values vs aldehyde **8-H**. The small band at 1660 cm^{-1} is assumed to originate from the $\nu_{\text{C=COH}}$ mode of **9Z-H**. The $\nu_{\text{O-H}}$ mode detected around 3560 cm^{-1} is attributed to the presence of hydroxycarbenes **7-H_{5r}** and **7-H_{7r}** ions (compare Figure 1). Scaling: 0.97/0.95; scaled intensity of the wavenumber range $3500\text{-}3700 \text{ cm}^{-1}$ covered by the OPO-Laser.

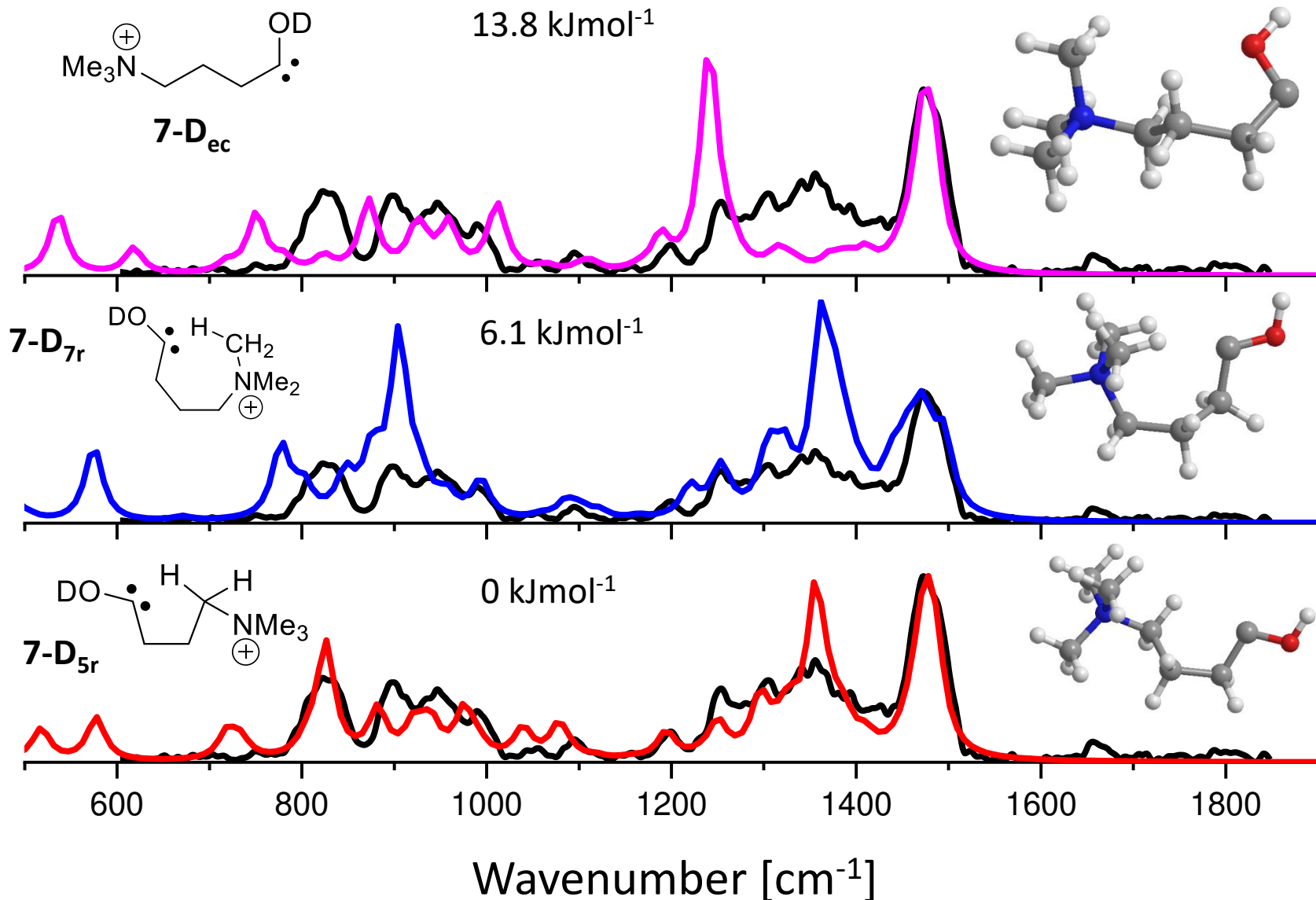


Figure S33. IR-ion spectrum of the CO_2 -loss product ion at m/z 131 (black trace) generated upon CO_2 -loss from **6-D** compared with the calculated, linear IR spectra of three structural alternatives for the D_1 -hydroxycarbene ion **7-D**, together with relative energy values relative to the most stable hydroxycarbene tautomer **7-D_{5r}**. Note, that the global minimum is the aldehyde **8-D** (compare Figure 2). (a) Hydroxycarbene conformer with an extended propyl chain (**7-D_{ec}**), pink trace; (b) hydroxycarbene with intramolecular $\text{C}\cdots\text{H}-\text{C}$ H-bonding, resulting in a 5-membered ring (**7-D_{5r}**), blue trace; (c) ditto with intramolecular H-bonding, resulting in a 7-membered ring (**7-D_{7r}**), red trace.

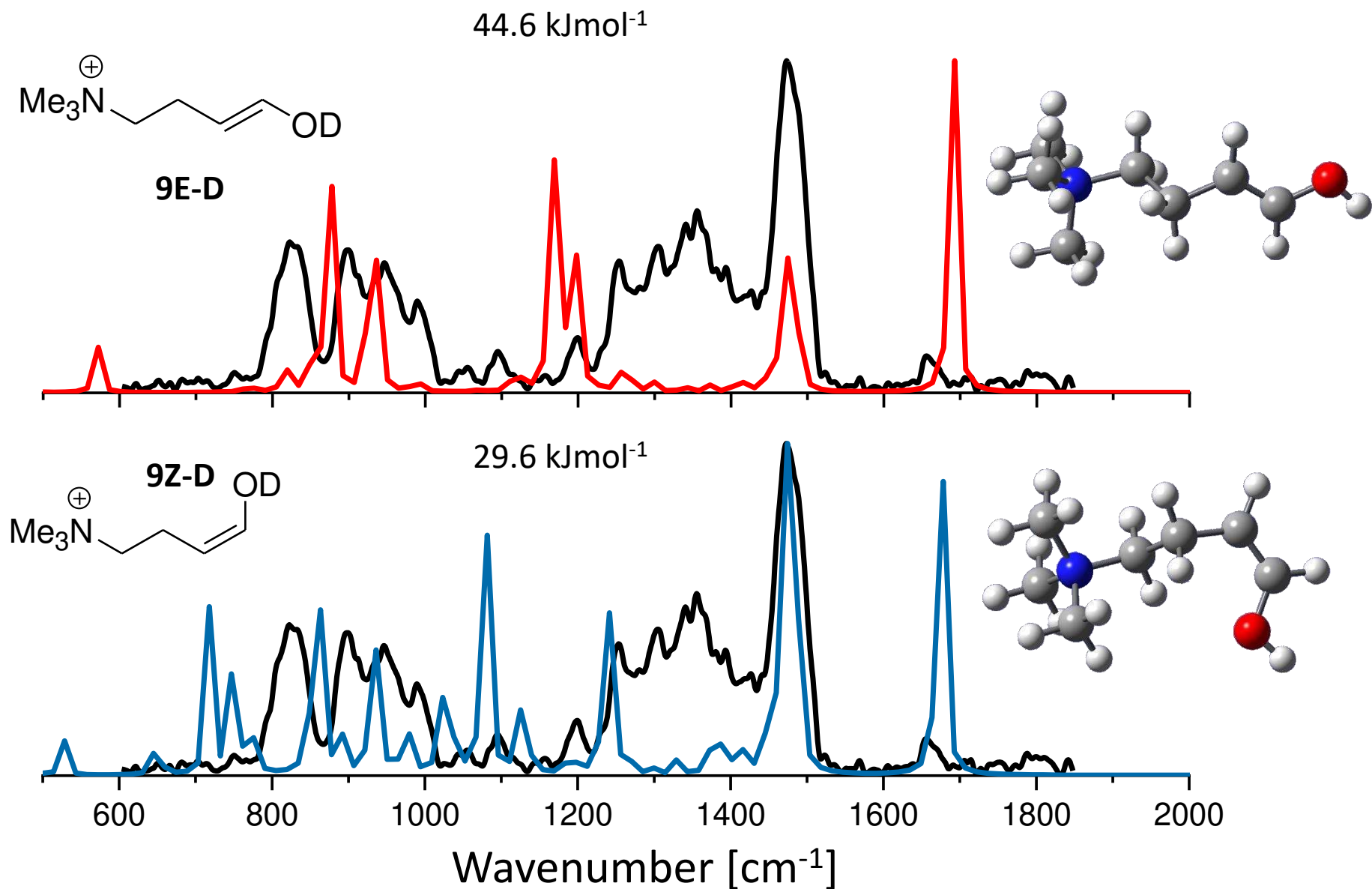


Figure S34. IR-ion spectrum of the CO₂-loss product ion at m/z 131 (black trace) produced from **6-D** upon CID compared with the calculated, linear IR spectra of two structural alternatives of the enol ion **9E-D** and **9Z-D**, together with relative energy values vs aldehyde **8-D** (compare Figure 2). The small band at 1660 cm⁻¹ is assumed to originate from the $\nu_{\text{C=COH}}$ mode of **9Z-H**. Scaling: 0.97.

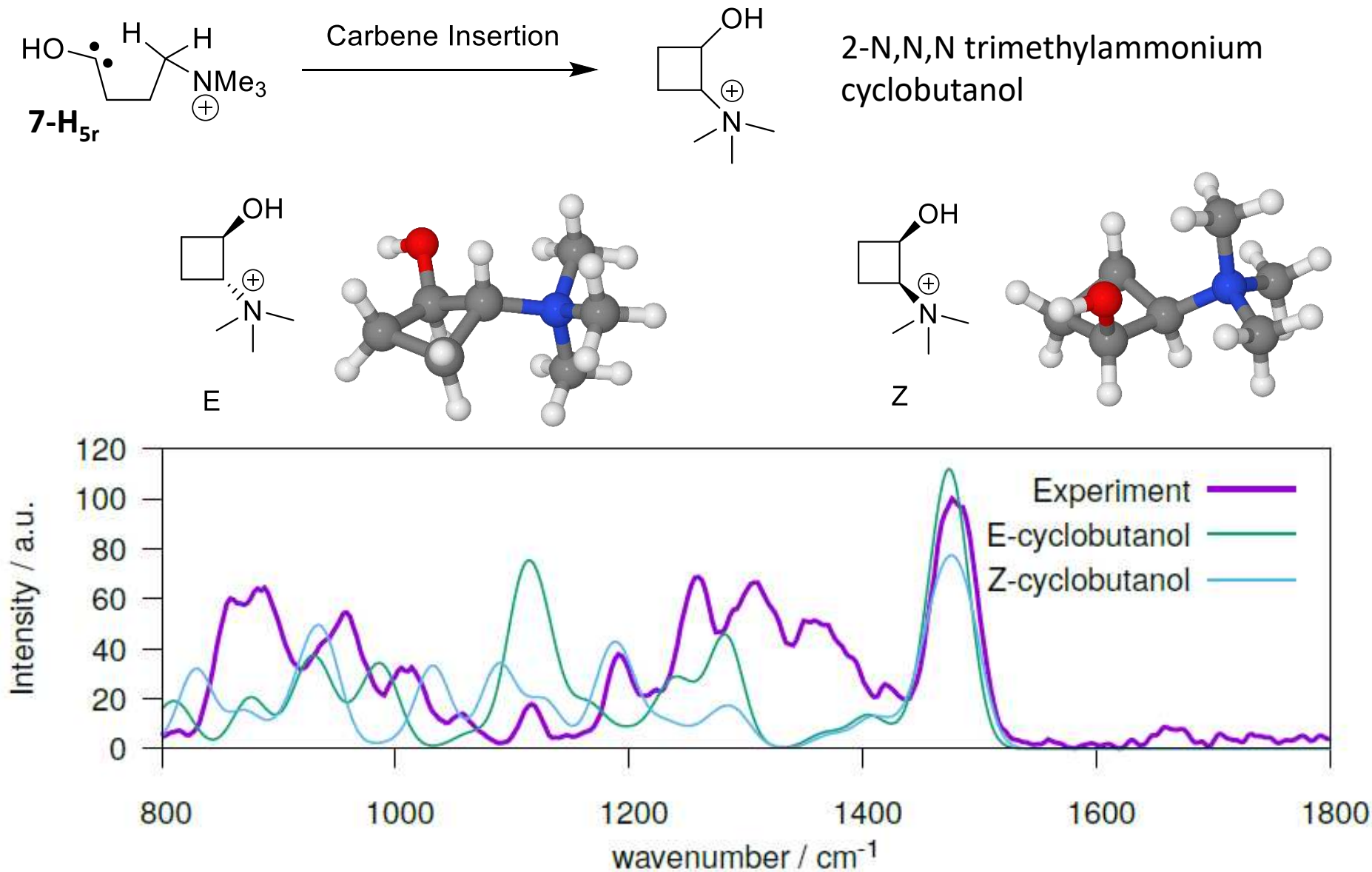


Figure S35. IR-ion spectrum of the CO₂-loss product ion at *m/z* 130 (violet trace) produced from **6-H** upon CID compared with the calculated, linear IR spectra of two cyclic, diastereomeric carbene C-H insertion products of **7-H_{5r}**, namely E/Z-2-N,N,N-trimethylammonium cyclobutanol. Scaling: 0.97.

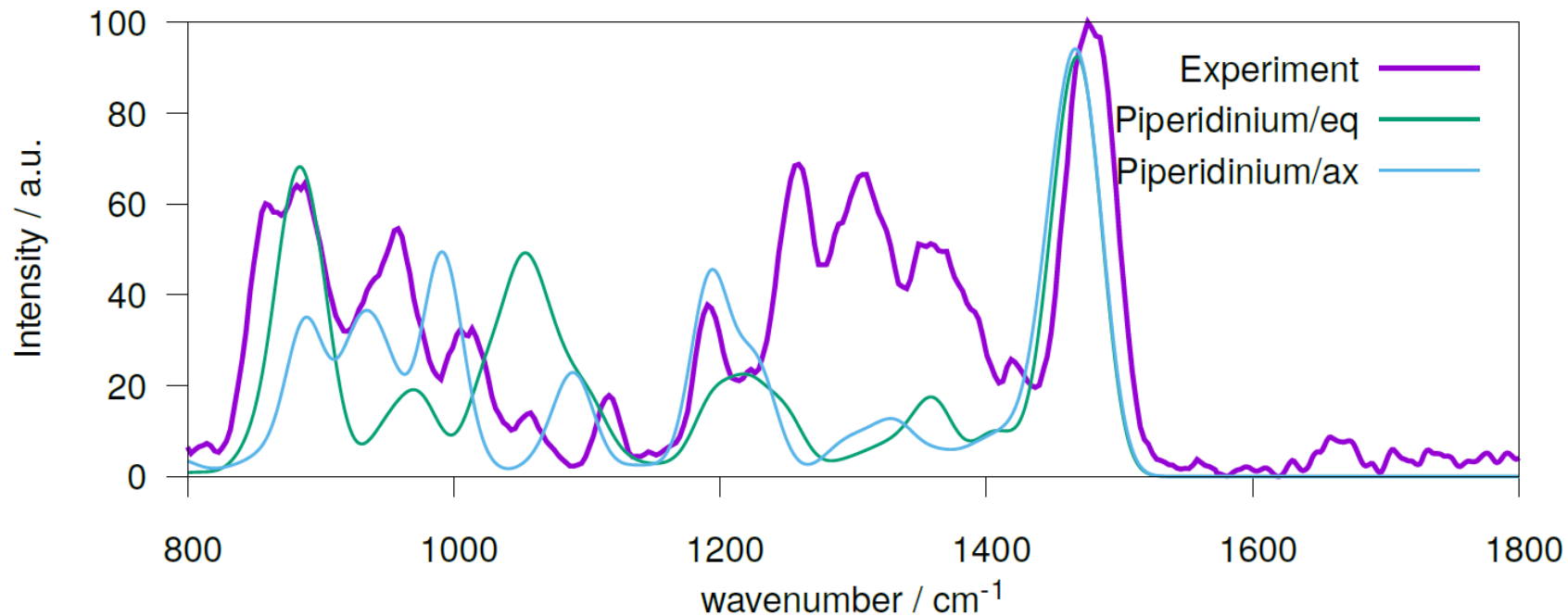
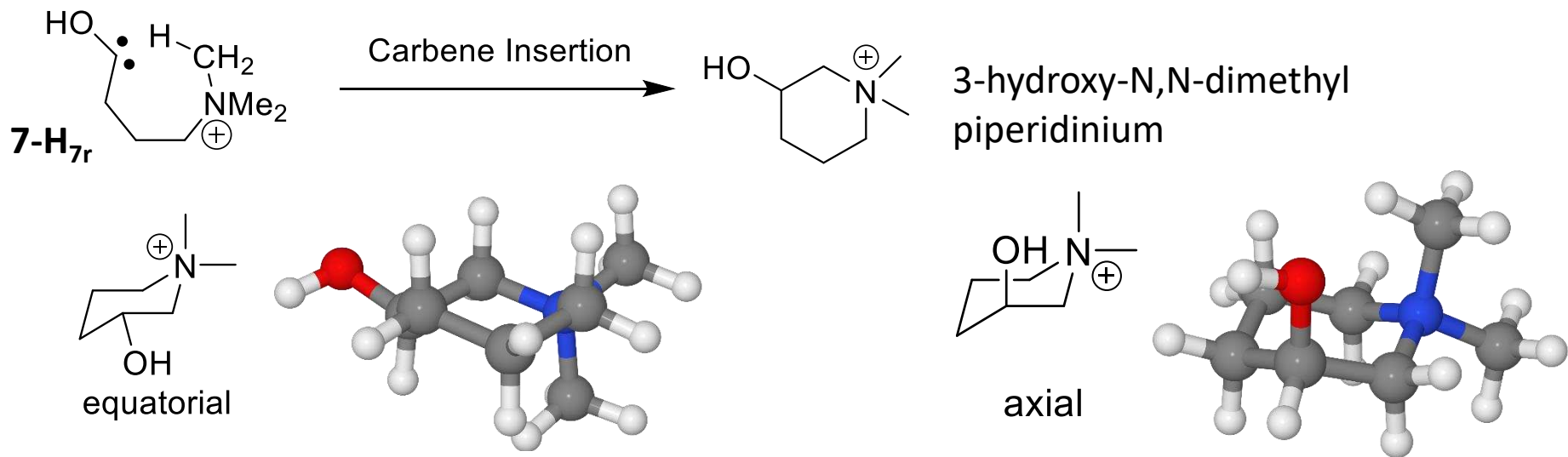


Figure S36. IR-ion spectrum of the CO₂-loss product ion at m/z 130 (violet trace) produced from **6-H** upon CID compared with the calculated, linear IR spectra of two cyclic carbene C-H insertion products of **7-H_{7r}**, namely eq/ax-3-hydroxy-*N,N*-dimethyl-piperidinium. Scaling: 0.97.

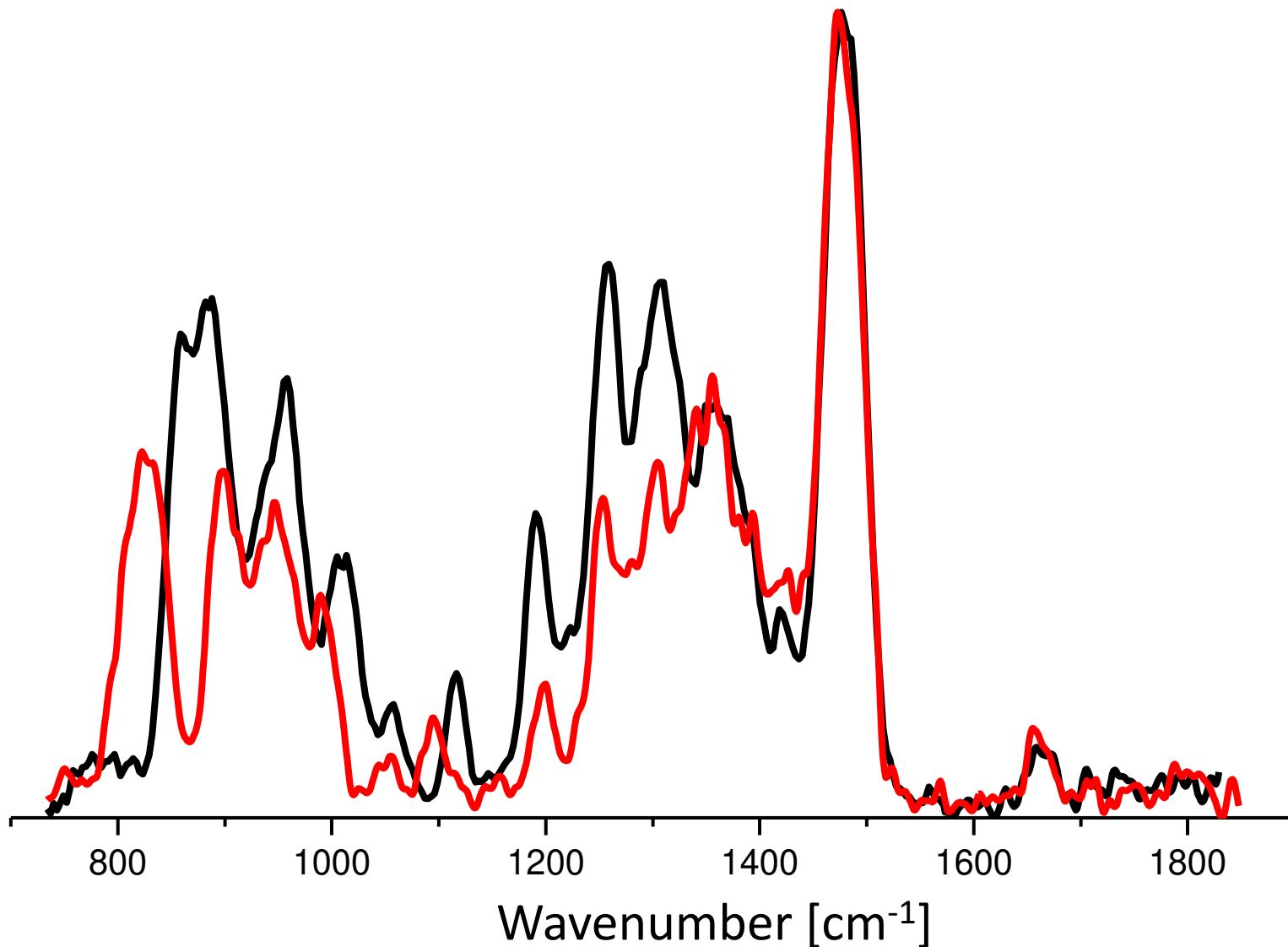


Figure S37. IR ion spectra of the CO₂-loss product ions at *m/z* 130 (black trace) and *m/z* 131 (red trace) produced from **6-H**, respectively **6-D** upon CID. The abundance of the band at 1660 cm⁻¹ is not time dependent or influenced by the presence or absence of 1H /2H, indicating no kinetic isotopic effect. We attribute the band to the enol $\nu_{\text{C}=\text{COH}}$ stretching vibration of a small percentage of enols generated via a classic pathway from hydroxycarbene intermediates.

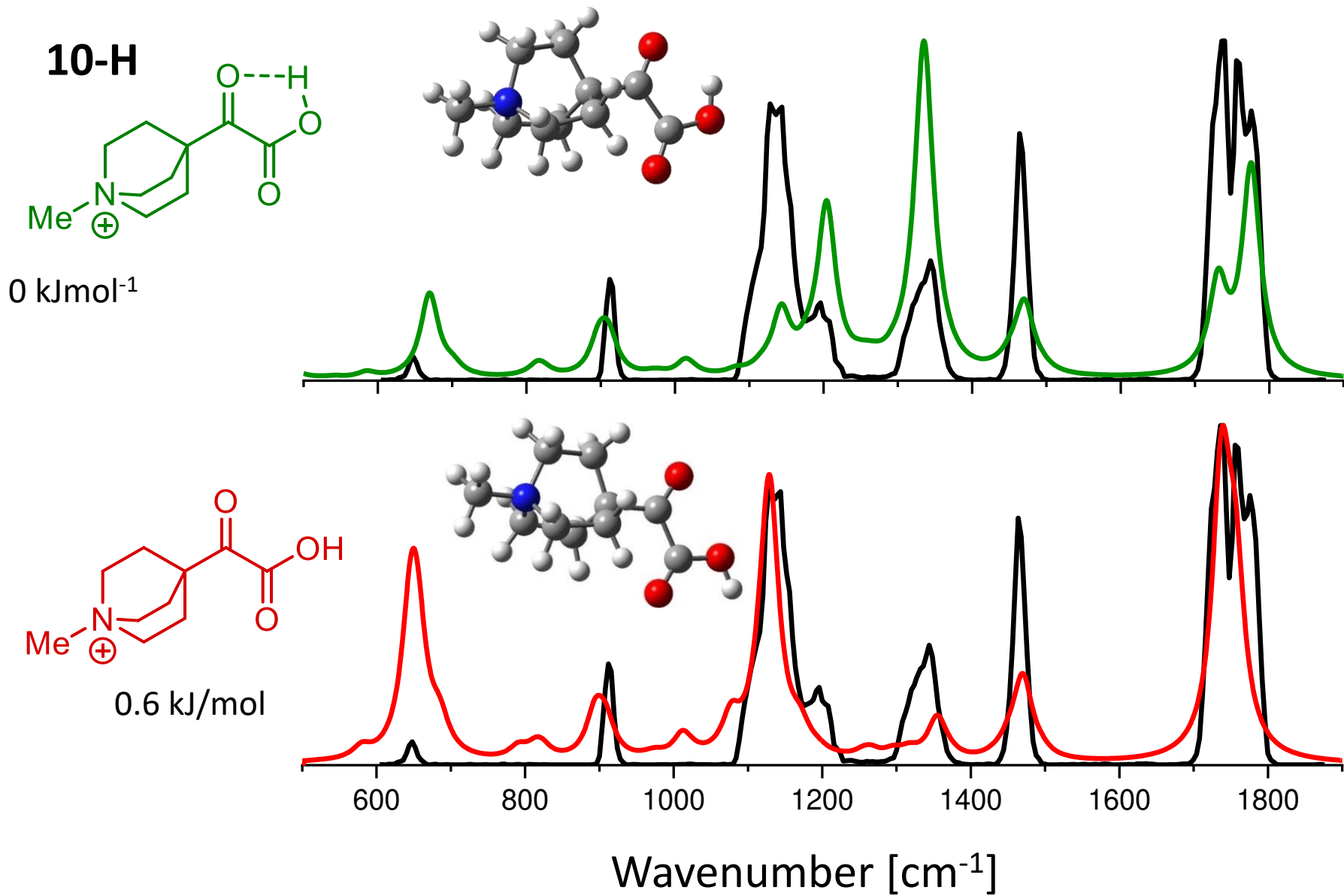


Figure S38. IR ion spectrum acquired of the precursor ion of **10-H** at m/z 198 compared to ion structures identified by theory. Scaling: 0.97.

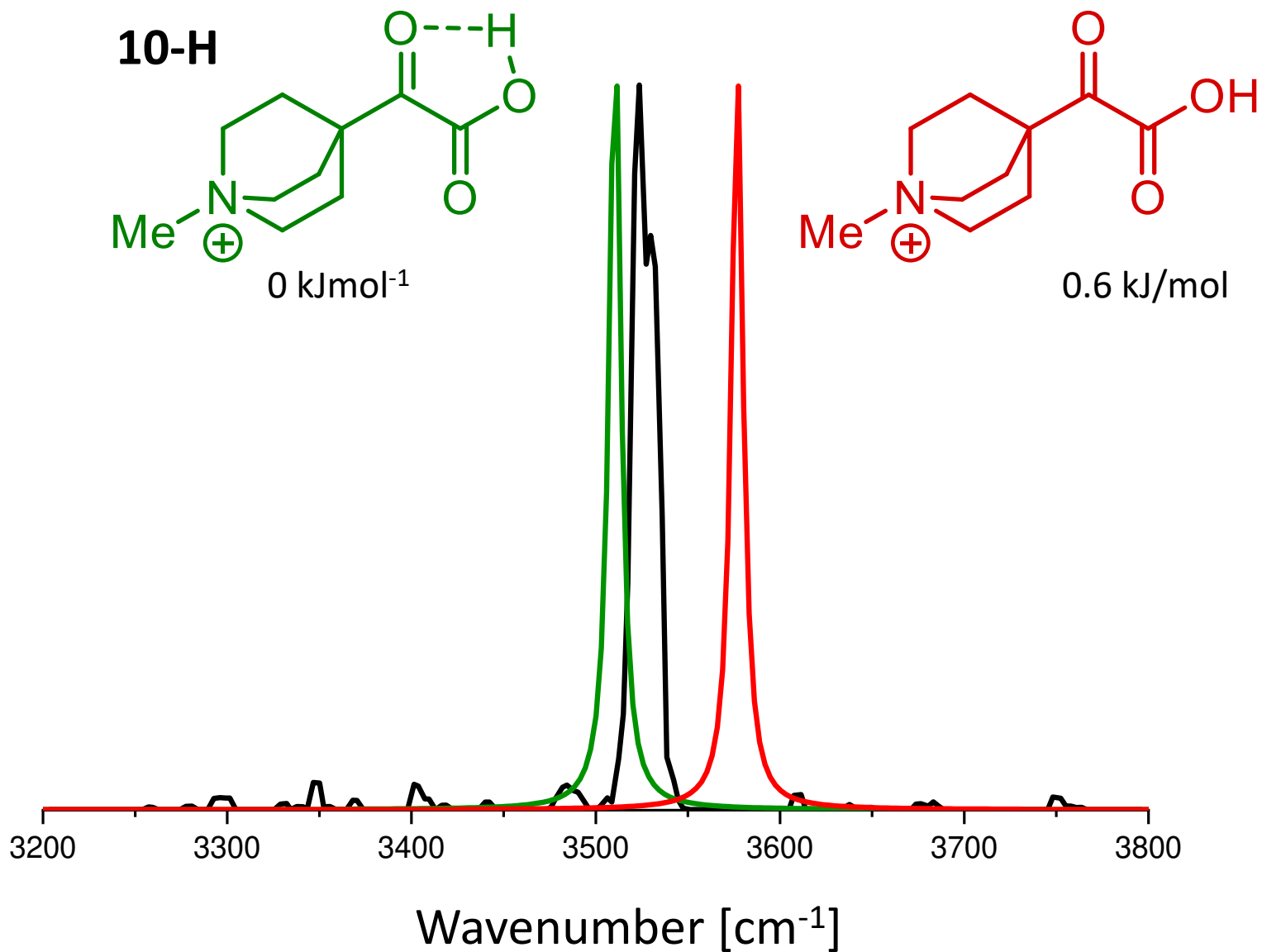


Figure S39. IR ion spectrum acquired of the precursor ion of **10-H** at m/z 198 compared to ion structures identified by theory. Scaling: 0.97.

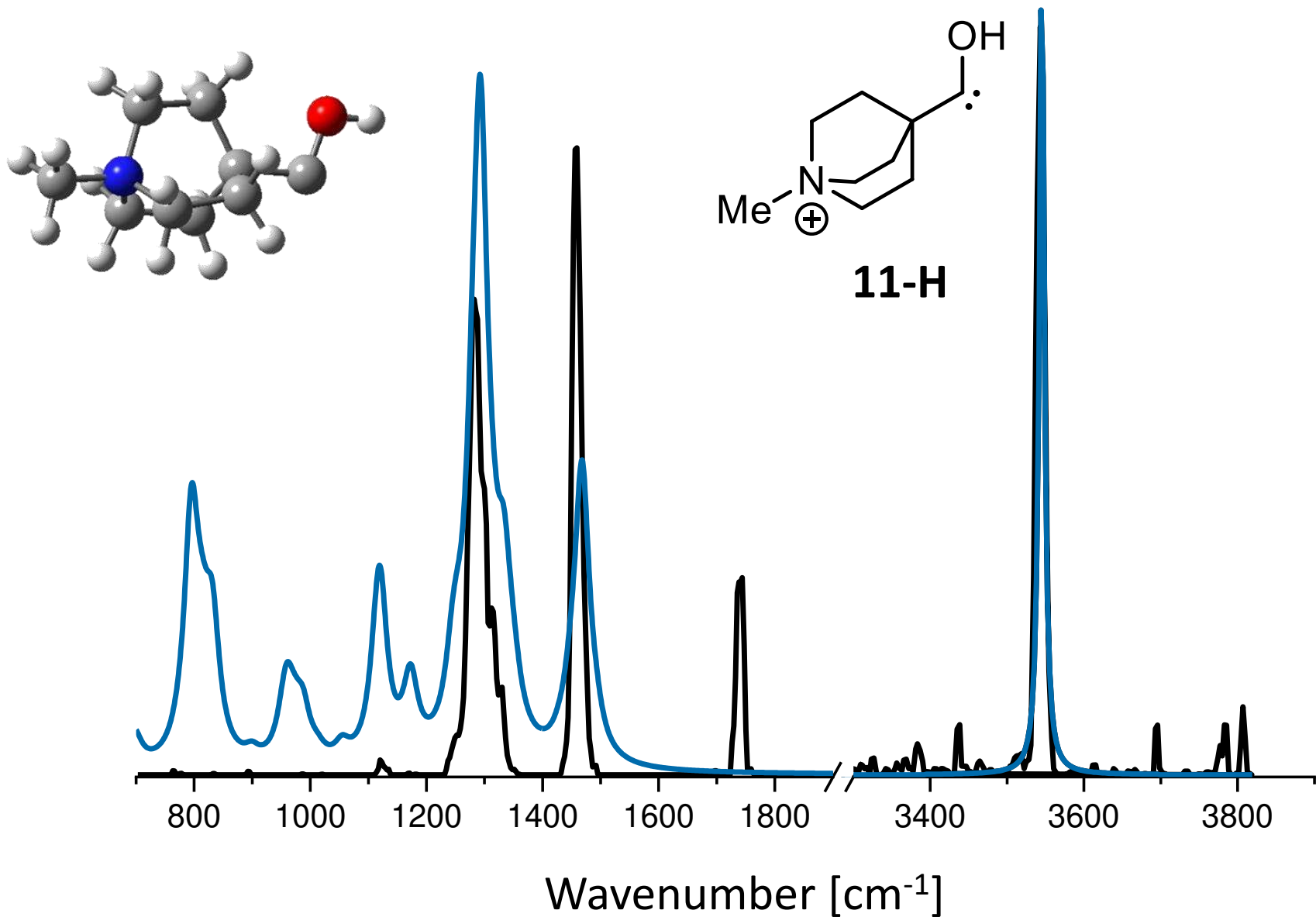
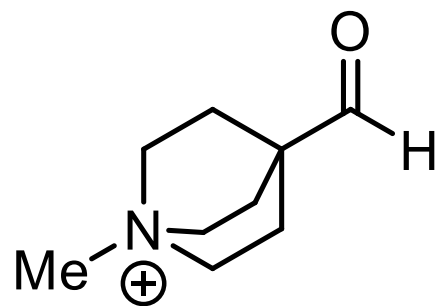
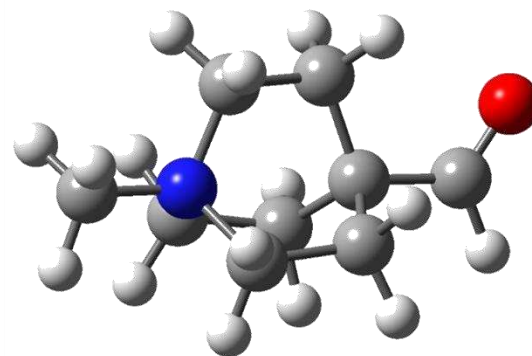


Figure S40. IR ion spectrum acquired of the CO₂-loss product ion at m/z 154 generated upon CID of precursor ion **10-H** at m/z 198 compared to the IR spectrum of the hydroxycarbene **11-H** (+ 195.3 kJmol⁻¹) of identified by theory. Scaling: 0.97.



12-H



0 kJmol⁻¹

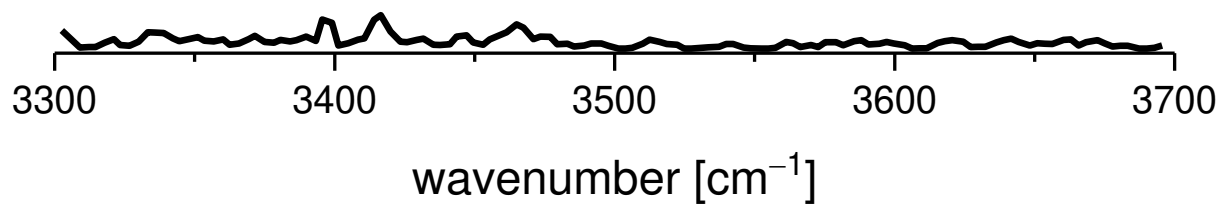


Figure S41. IR ion spectrum acquired of the synthesized aldehyde **12-H** with its molecular ion at m/z 154.

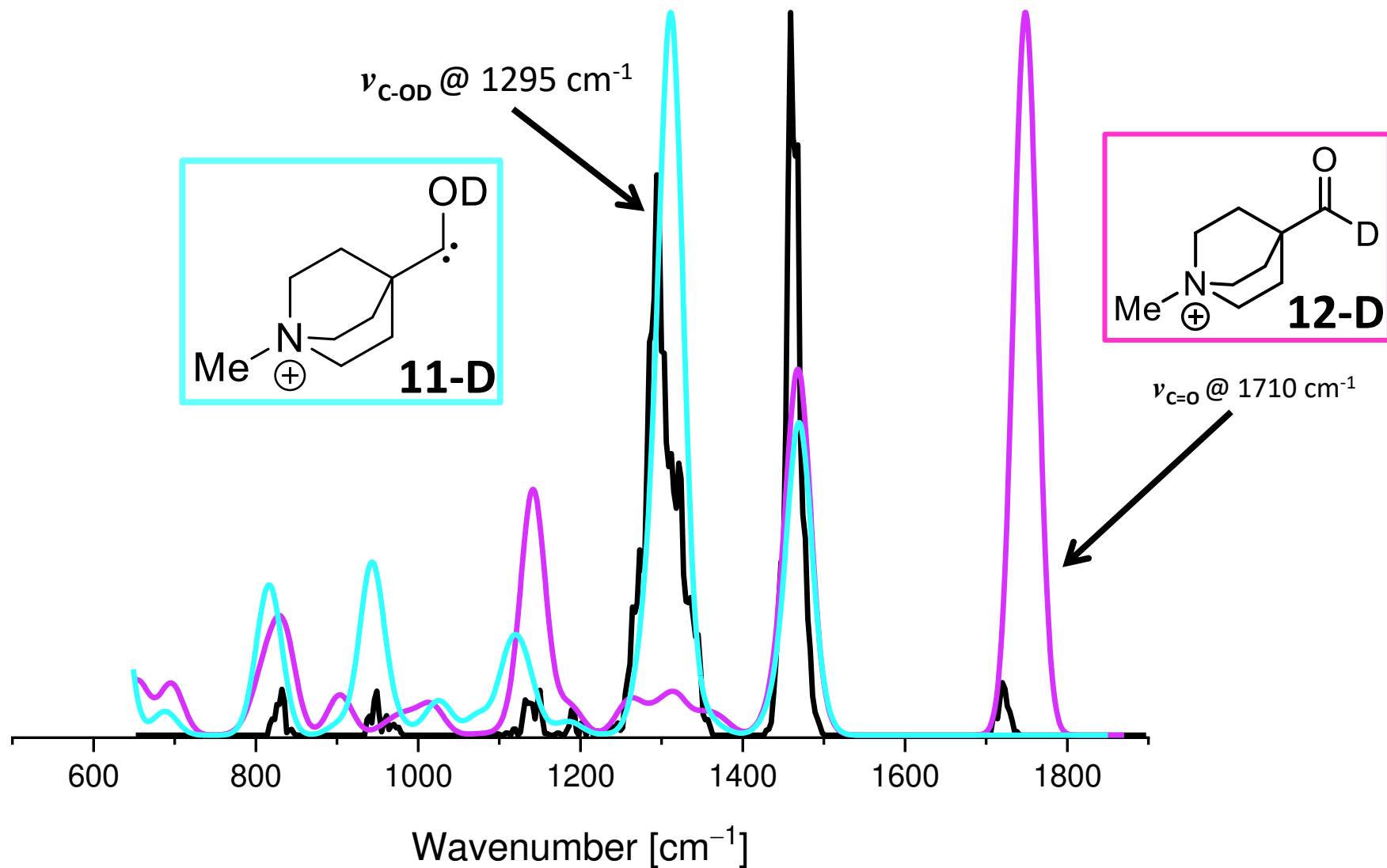


Figure S42. IR ion spectrum of the deuterated CO₂-loss product ion at *m/z* 155 (black trace) formed from the quinuclidine precursor **10-D** upon CID vs. computed IR spectrum of the hydroxycarbene **11-D** (light blue trace), and the computed IR ion spectrum of the aldehyde **12-D** (pink trace). Spectra scaled by 0.97.

Table S3. Bands found in the IR-ion spectrum of the CO₂-loss product ion at *m/z* 154 (black trace) produced from **10-H** upon CID compared with the calculated, linear IR spectrum of the hydroxycarbene ion **11-H** (+195 kJmol⁻¹; blue trace in Figure 3). *The strong band at 1741 cm⁻¹ is absent in the IR spectrum of hydroxycarbene **11-H** and is attributed to the carbonyl stretching mode $\nu_{\text{C=O}}$ of the respective aldehyde **12-H** indicative of its increasing formation. Computed IR bands are scaled by 0.97.

Band found [cm ⁻¹]	11-H computed absorption bands [cm ⁻¹]	11-H modes
	648	$\nu_{\text{N-CH}_2}$ δ O-H wagging / bending
	696	$\nu_{\text{CH}_2\text{-CH}_2}$
	798	δ O-H wagging / bending
	831	$\nu_{\text{CH}_2\text{-CH}_2}$ δ CH ₂ -CH ₂ wagging / bending
	962	δ CH ₂ bending
	982	$\nu_{\text{CH}_2\text{-CH}_2}$ $\nu_{\text{N-CH}_2}$
	1053	$\nu_{\text{N-CCOH}}$ δ CH ₂ wagging / bending
1123	1122	$\nu_{\text{N-CH}_3}$
1171	1178	δ O-H wagging / bending δ CH ₂ -CH ₂ wagging / bending
1282	1292	$\nu_{\text{C-OH}}$ δ O-H wagging / bending
1315	1332	δ O-H wagging / bending
1330		
1459	1471	δ CH ₂ wagging / bending
1741*		

Table S4. Bands found in the IR ion spectrum of the CO₂-loss product ion at *m/z* 230 (black trace) produced from **13-H** upon CID compared with the calculated, linear IR spectrum of the hydroxycarbene ion **14-H** (+197 kJmol⁻¹; blue trace in Figure 3). *The strong band at 1744 cm⁻¹ is absent in the IR spectrum of hydroxycarbene **14-H** and is attributed to the carbonyl stretching mode $\nu_{\text{C=O}}$ of the respective aldehyde **15-H** indicative of its increasing formation. Computed absorption bands are scaled by 0.97.

Band found [cm ⁻¹]	14-H computed absorption bands [cm ⁻¹]	14-H modes
649	659	$\nu_{\text{N-CH}_2}$ δ O-H wagging / bending δ C _{Ar} -H in plane bending
700	699	$\nu_{\text{CH}_2\text{-CH}_2}$ δ C _{Ar} -H bending
727		
755	764	δ C _{Ar} -H bending
795	809	$\nu_{\text{CAr-CAr}}$ δ CH ₂ -CH ₂ wagging / bending
835		
985	970	δ C _{Ar} -H out of plane bending
1000	1030	δ C _{Ar} -H in plane bending
1045		$\nu_{\text{CH}_2\text{-CH}_2}$ $\nu_{\text{N-CH}_2}$
1114	1095	$\nu_{\text{C-COH}}$ δ CH ₂ wagging / bending
1165	1157	δ CH ₂ wagging / bending
1210	1206	$\nu_{\text{CAr-CH}_2}$
1255	1289	δ O-H wagging / bending δ CH ₂ wagging / bending
1289, 1310, 1319		
1355, 1365	1357	δ benzyl CH ₂ wagging / bending
1390	1396	δ NCH ₂ wagging / bending
1460	1462	δ CH ₂ wagging / bending
1585	1589	$\nu_{\text{CAr-CAr}}$
1744*		

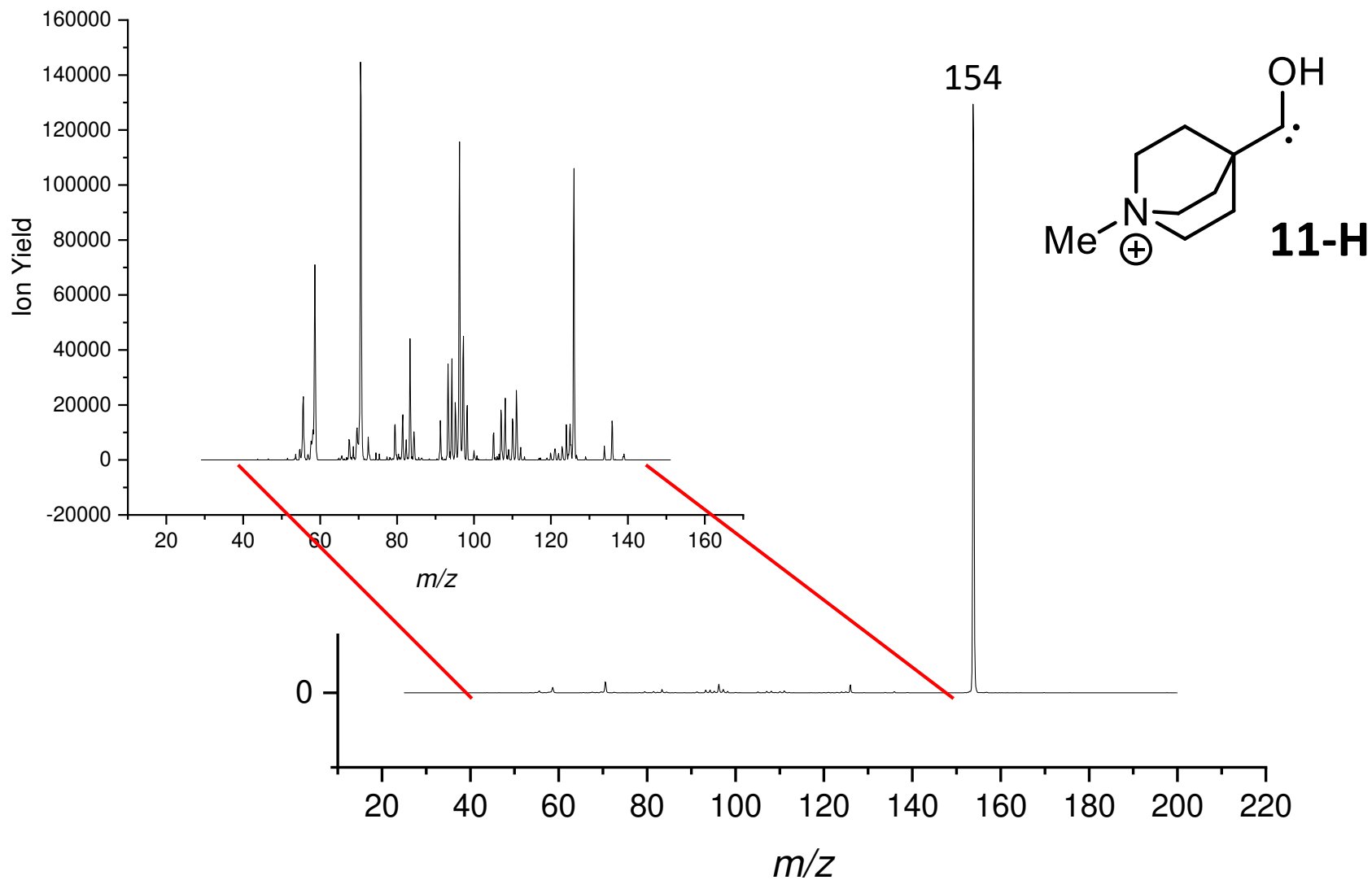


Figure S43. Photodissociation spectrum of the molecular ion **11-H** at m/z 154 excited at $\nu_{\text{C-OH}}$ 1285 cm^{-1} exhibiting many very low abundant photo fragment ions, which fluctuate in intensity and hamper a proper measurement of the isomerization kinetics (see Figures S50 and S51).

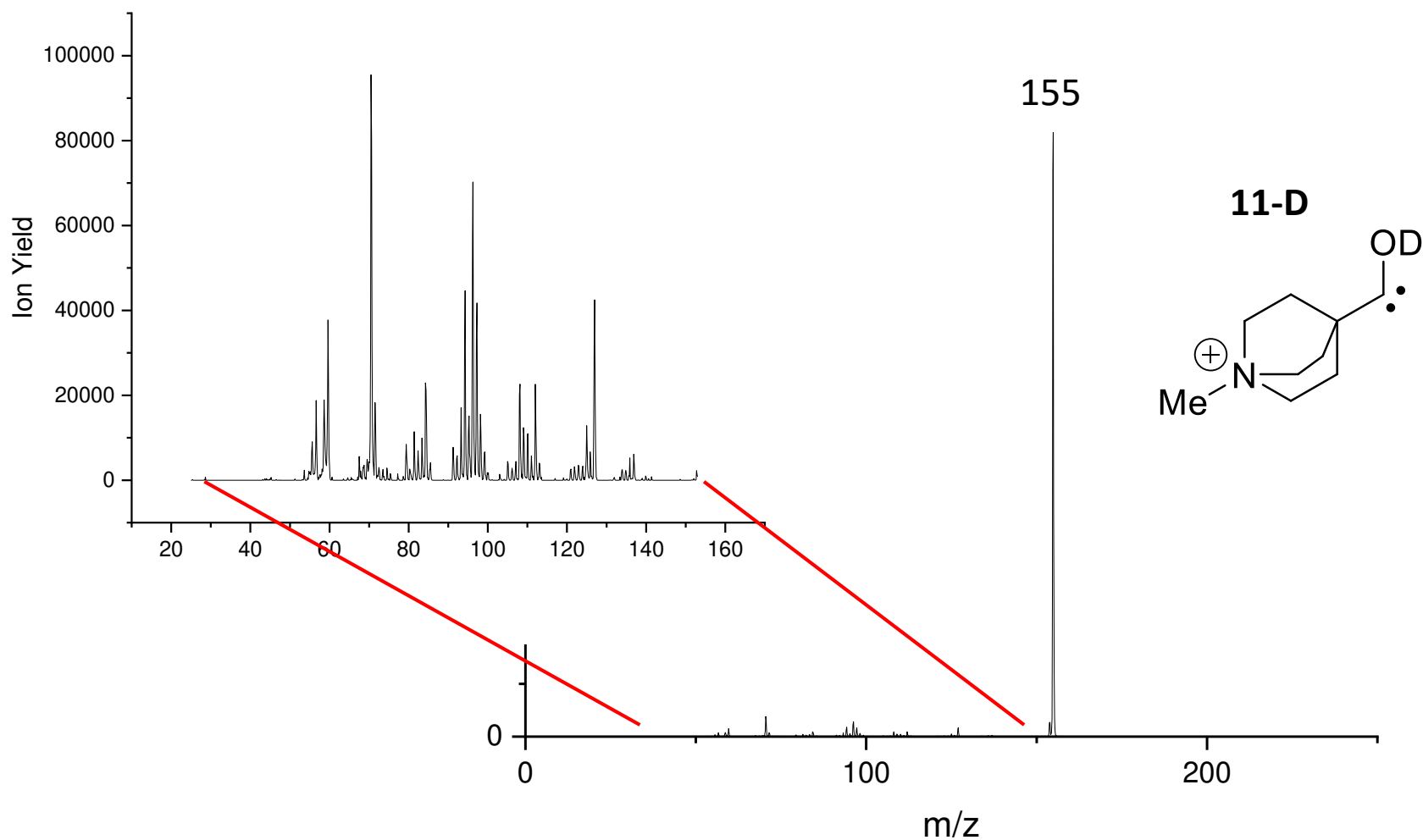


Figure S44. Photodissociation spectra of the molecular ion **11-D** at m/z 155 excited at $\nu_{\text{C-OD}}$ 1295 cm^{-1} exhibiting many very low abundant photo fragment ions, which fluctuate in intensity and hamper a proper measurement of the isomerization kinetics (see Figure S52 and S53).

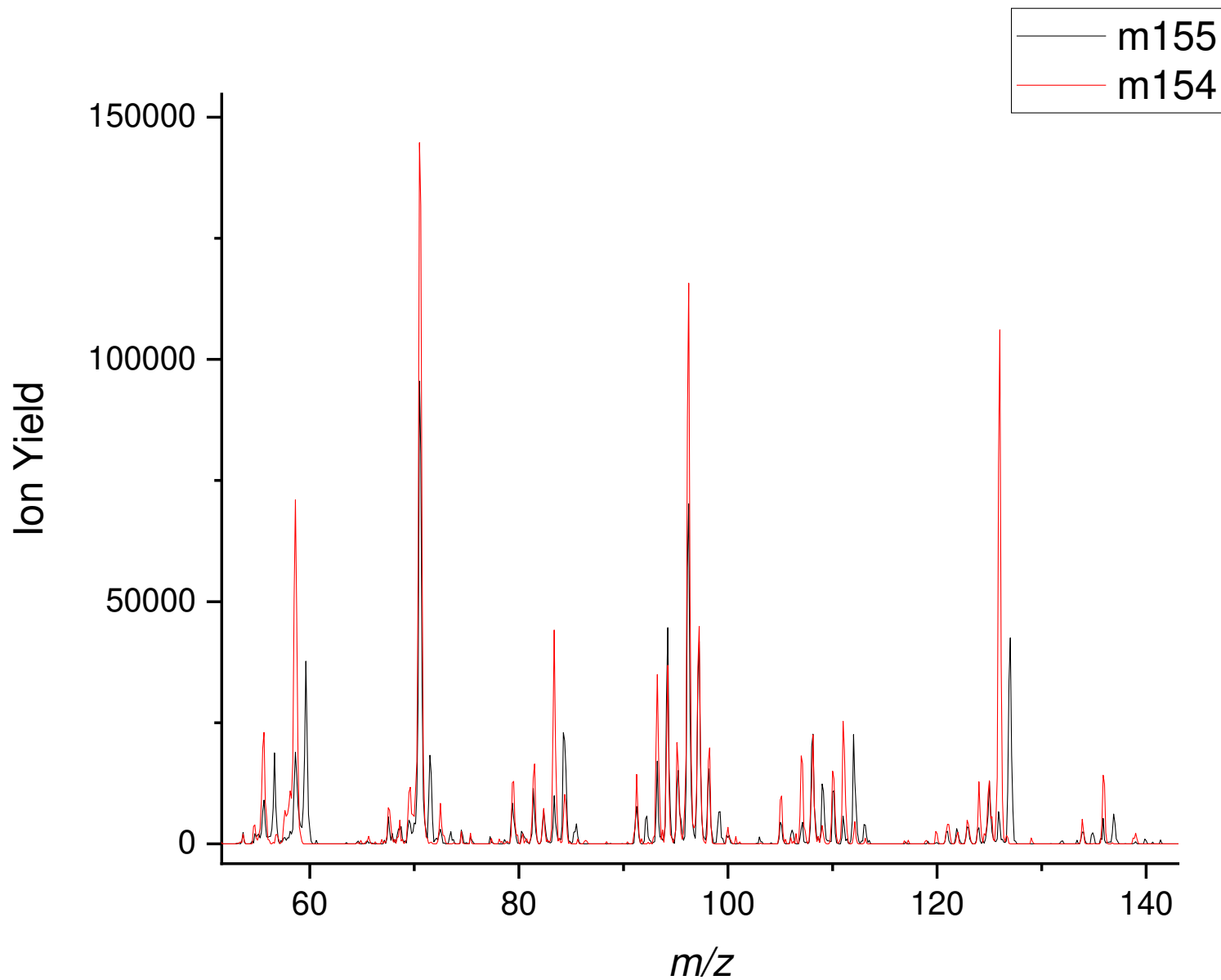


Figure S45. Photodissociation fragments of **11-D** at m/z 155 compared those of **11-H** at m/z 154.

6. Computations

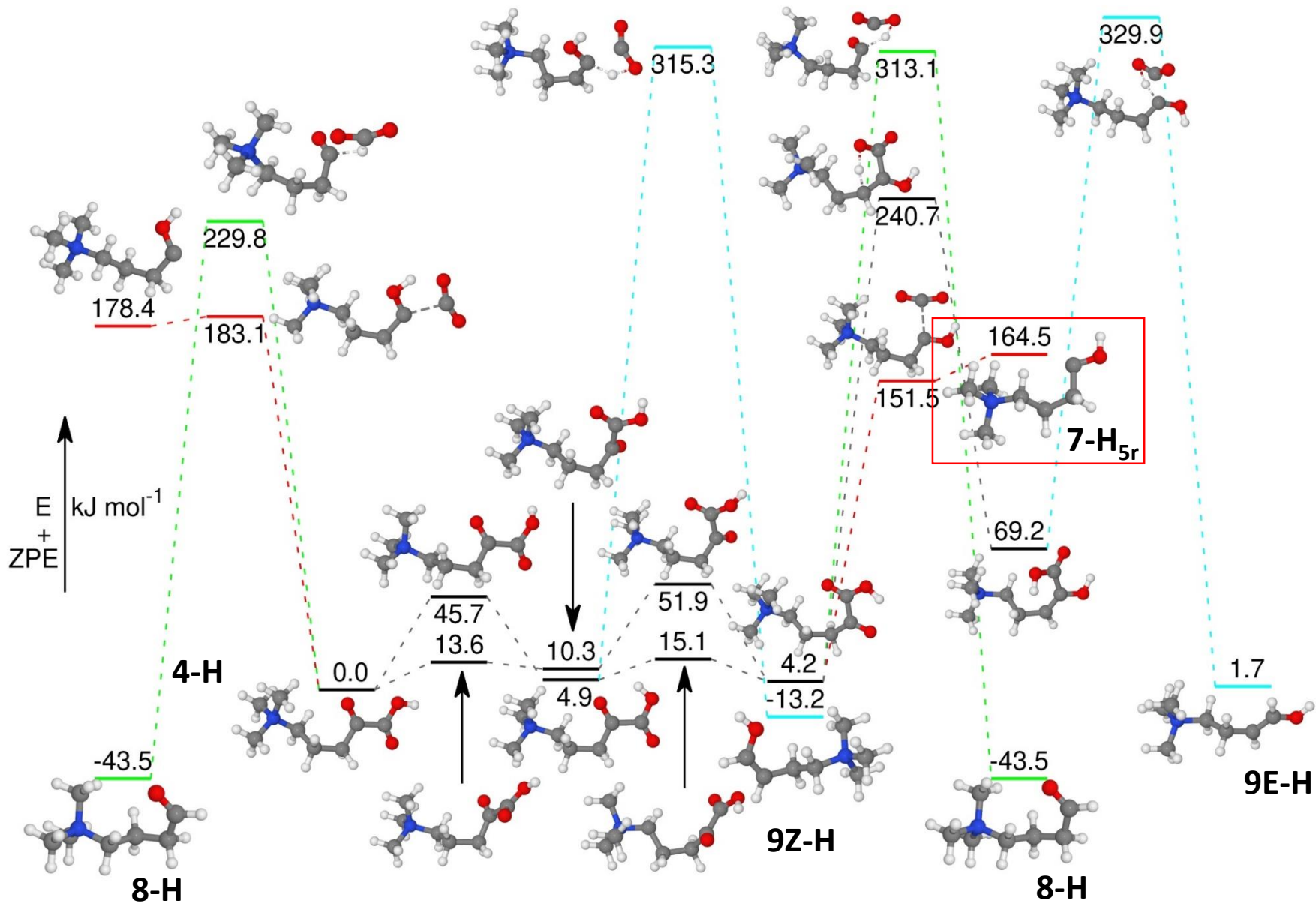


Figure S46. Energy profile computed for the CO_2 -loss reaction of the keto acid **4-H**, to the hydroxycarbene **7-H_{5r}** (red box), and the tautomeric ions, *i.e.* the enols **9E-H** and **9Z-H**, and the most stable isomer aldehyde **8-H**.

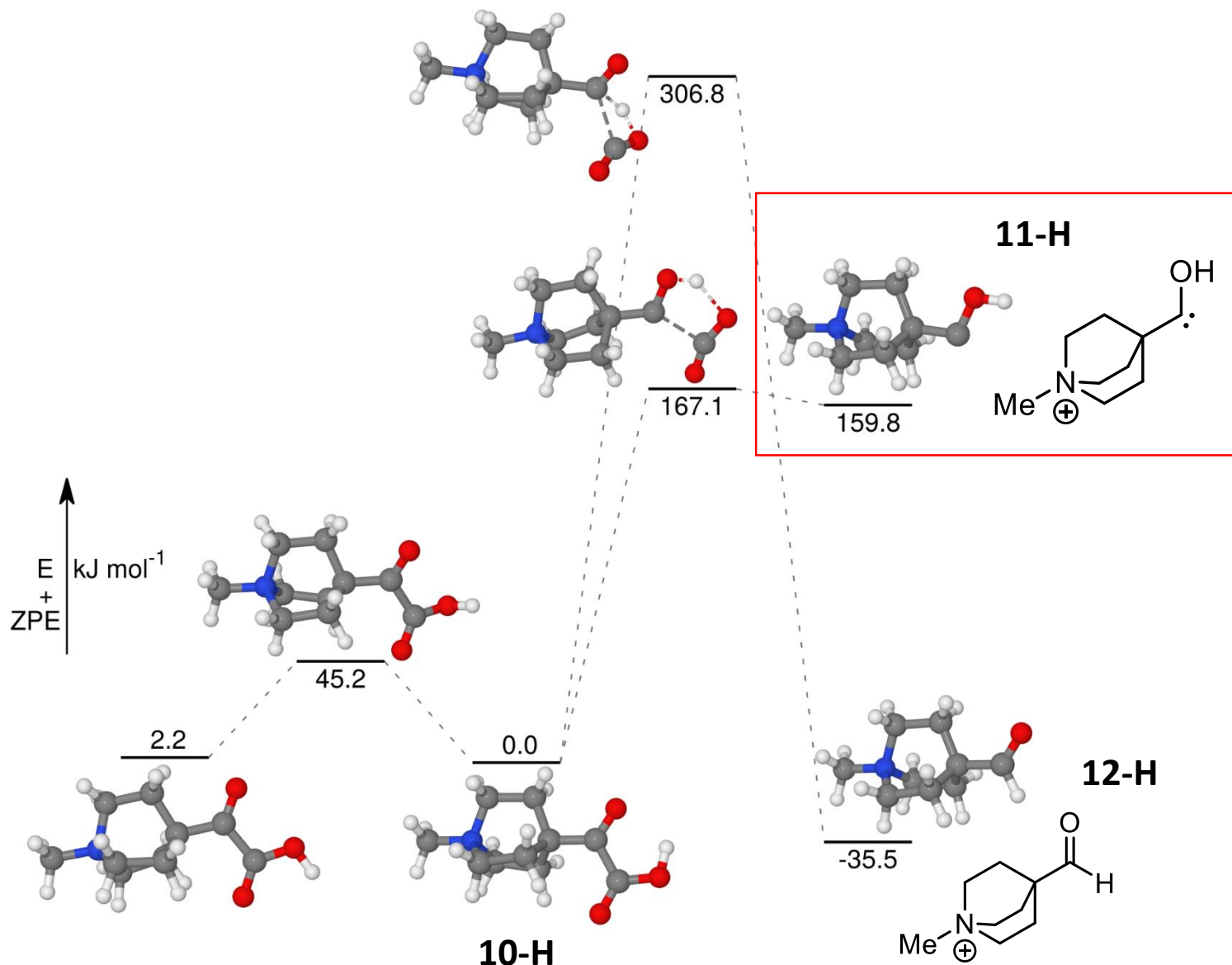


Figure S47. Energy profile computed for the CO_2 -loss reaction of the *N*-methylquinuclidinio keto acid **10-H** to the hydroxycarbene **11-H** (red box), and the tautomeric aldehyde **12-H**.

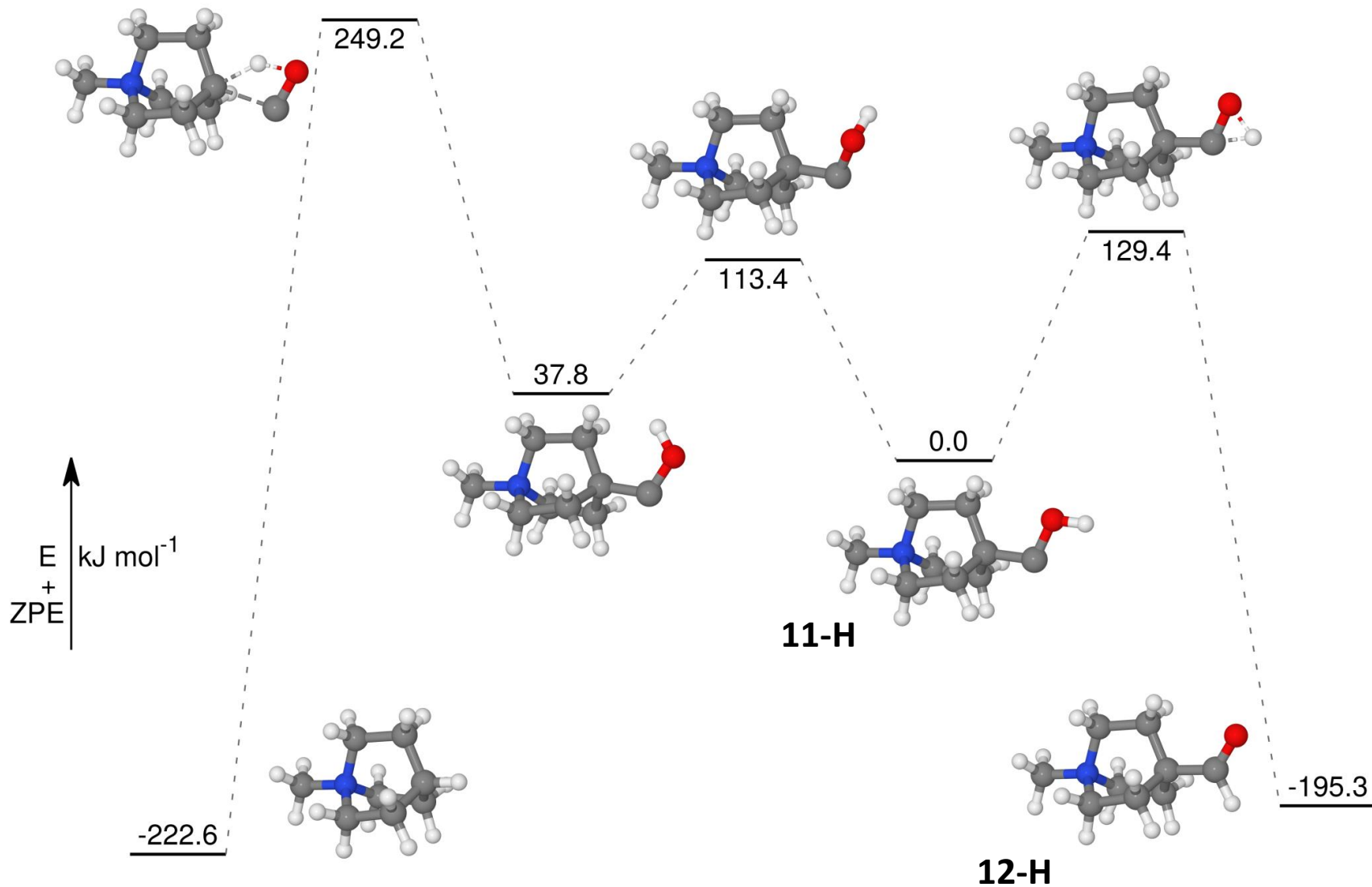


Figure S48. Energy profile computed for [1,2]H-shift reaction of the quinuclidine hydroxycarbene **11-H** to the respective aldehyde **12-H**. Alternatively, the CO-loss reaction of the quinuclidine hydroxycarbene **11-H** is included on the left hand side, delivering the methylquinuclidinium core structure.

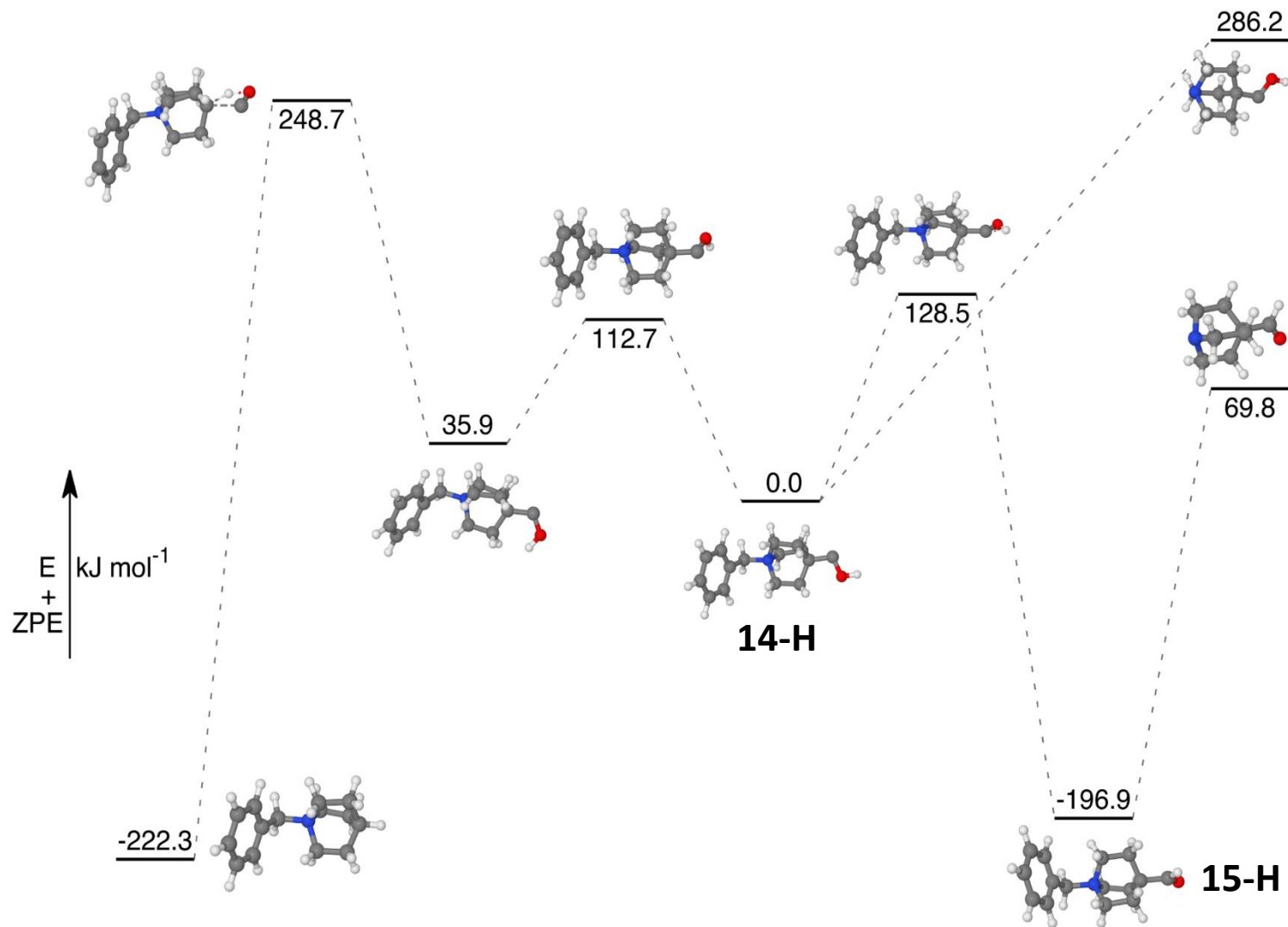


Figure S49. Energy profile computed for [1,2]H-shift reaction of the *N*-benzylquinuclidinio hydroxycarbene **14-H** to the respective aldehyde **15-H**. The important fragmentation reaction of the hydroxycarbene **14-H** delivering the very abundant $[\text{C}_7\text{H}_7]^+$ ion is included. Additionally, the CO-loss reaction is also shown on the left hand side, leading to the respective *N*-benzylquinuclidinio core structure (experimentally not observed).

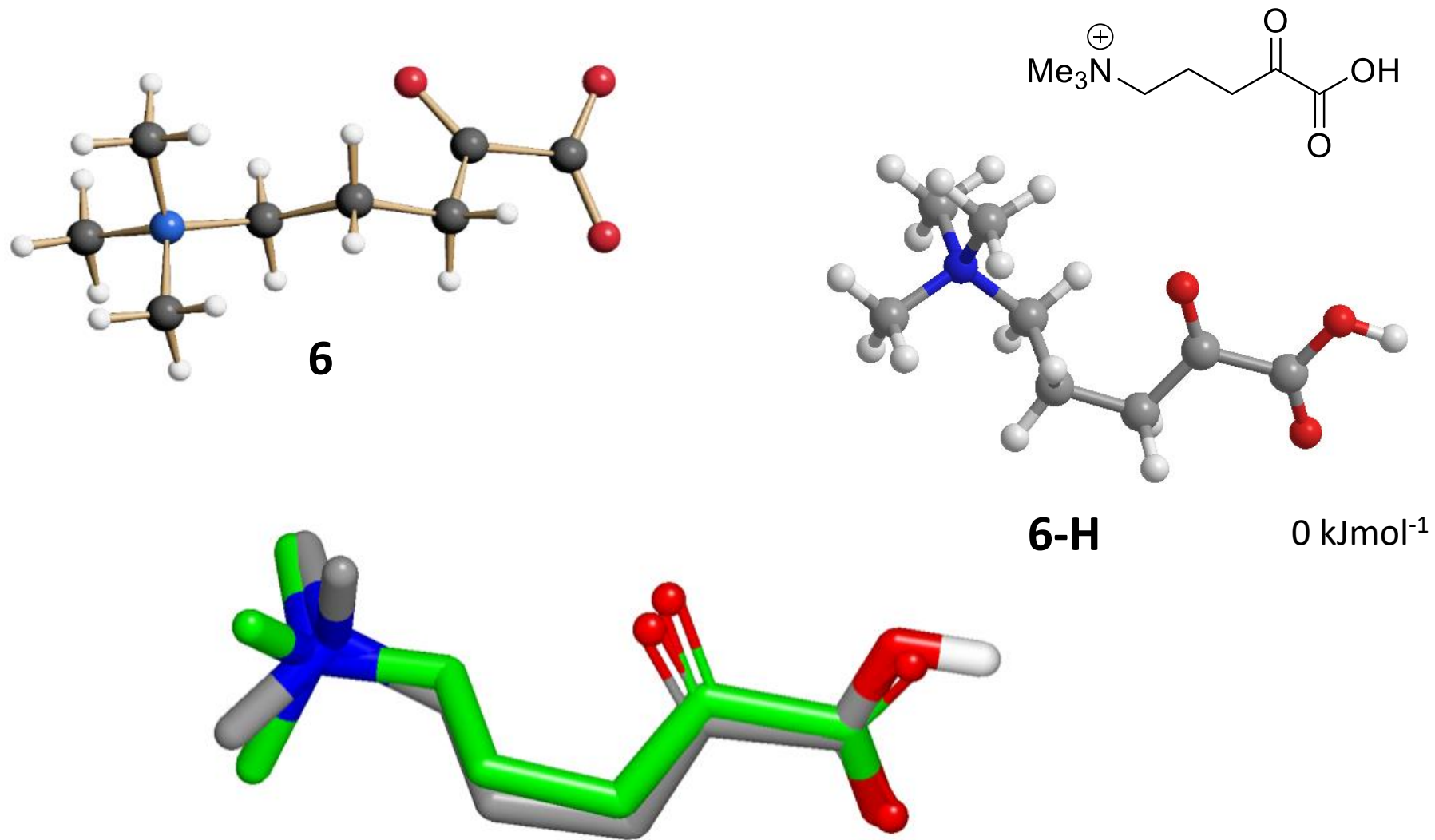


Figure S50. Overlay of the X-ray crystal structure of 5-(Trimethylammonio)-2-oxopentanoate **6** (see Figure S16) and of the most stable ion structure computed for **6-H** identified by theory as depicted in Figure S25.

7. Kinetics

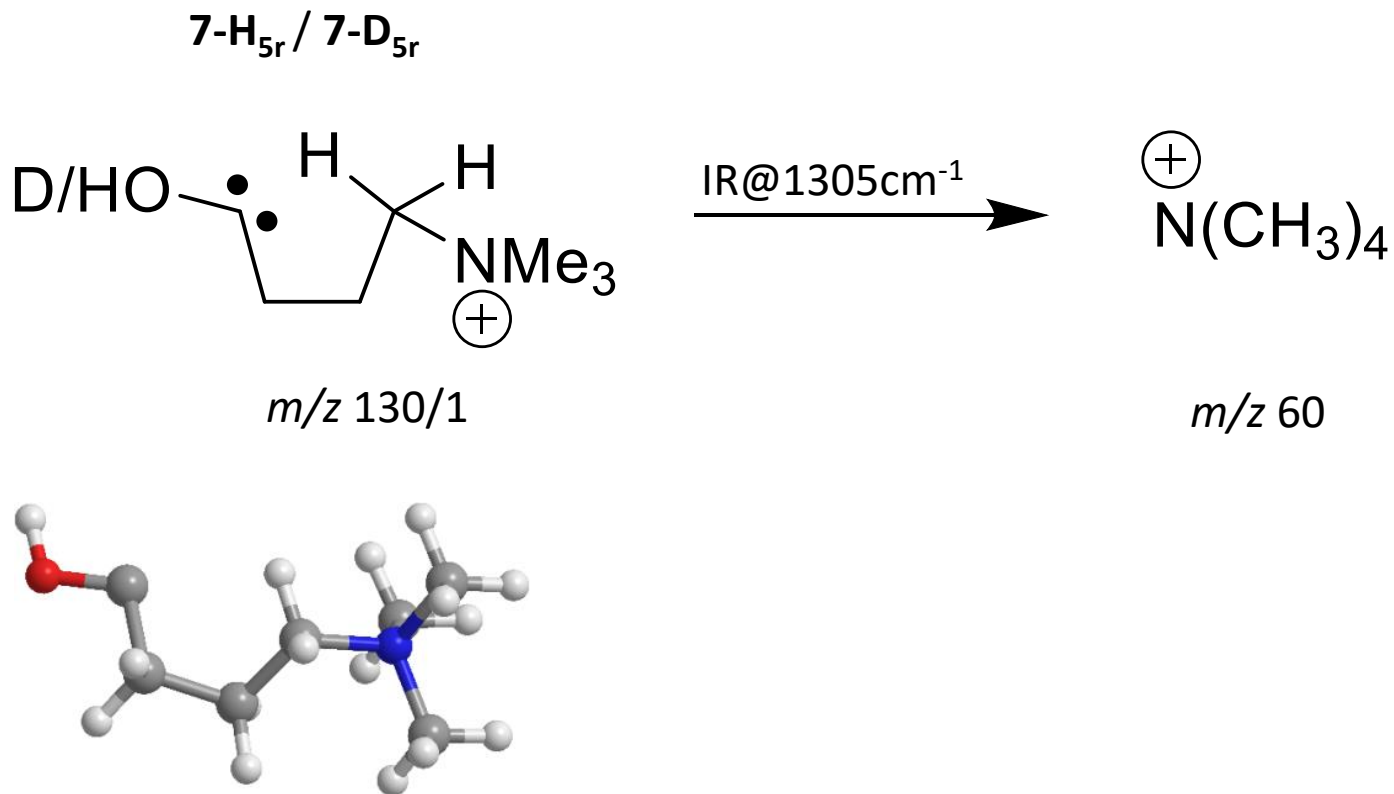


Figure S51. Photodissociation reaction of **7-H** and **7-D** to NH_4^+ at $m/z\ 60$ used for the tautomer selective kinetic measurements at 1305 cm^{-1} .

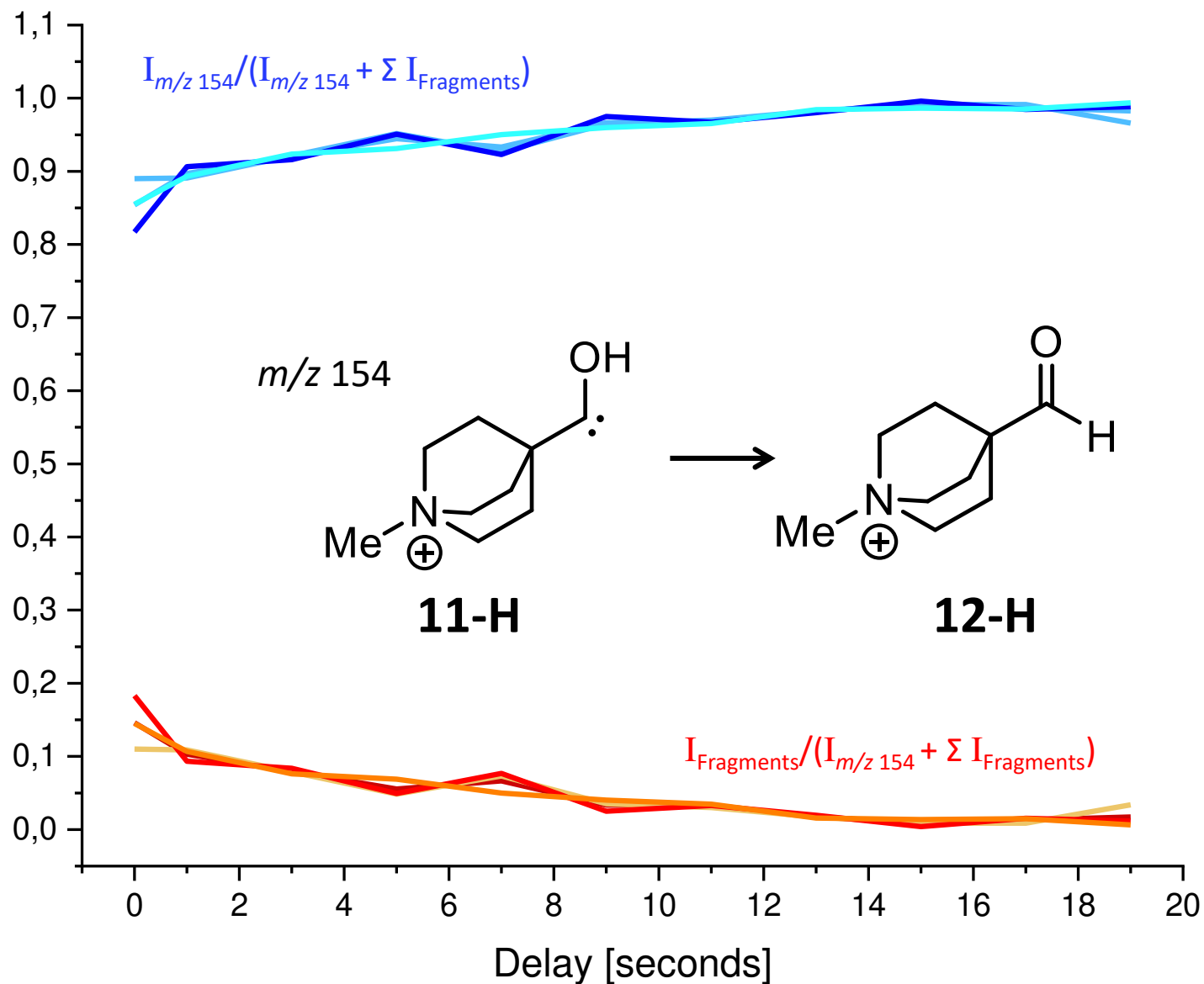
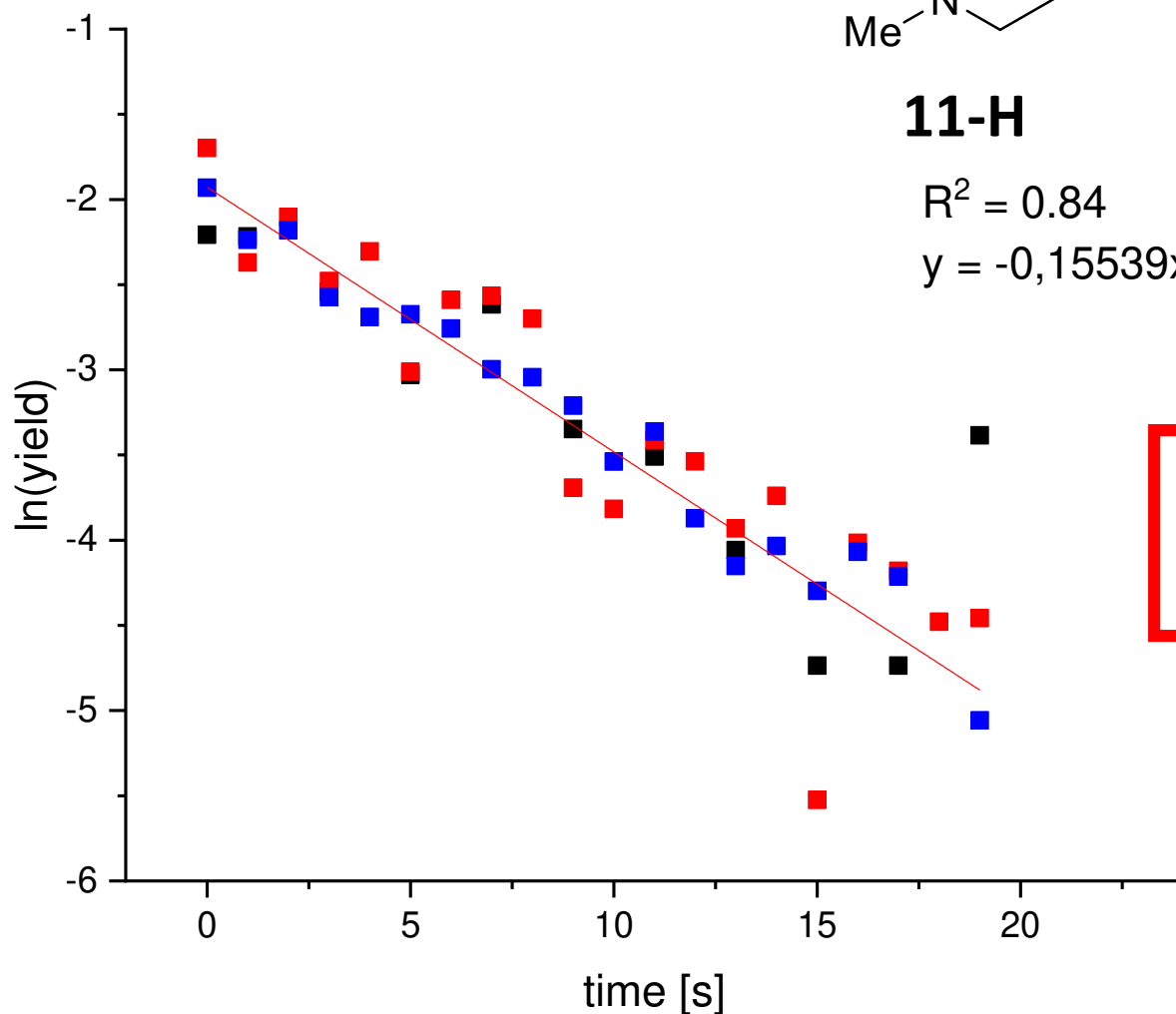
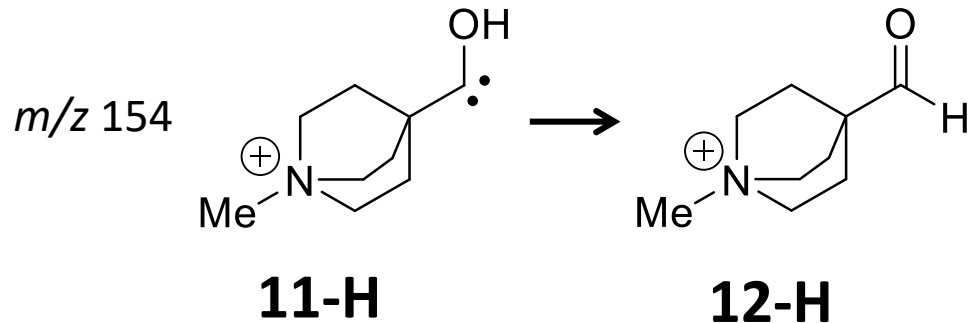


Figure S52. Tautomer-selective IR kinetics of the quinuclidine hydroxycarbene **11-H**. The kinetics were measured at the C-OH stretching mode ν_{C-OH} of carbene **11-H** at 1285 cm^{-1} .



$$R^2 = 0.84$$

$$y = -0,15539x - 1,92736$$

$$t_{\frac{1}{2}} = \frac{\ln 2}{0.155} = 4.47 \text{ s}$$

Figure S53. Data analysis of the time-dependent measurement of the hydroxycarbene ion population **11-H** at m/z 154. The isomer-selective experiment is accomplished due to the exclusive resonance of **11-H** near 1285 cm^{-1} as Figure 3a illustrates. The isomerization reaction from **11-H** to **12-H** obeys first order kinetics with $k_H = 0.155 \pm 0.010 \text{ s}^{-1}$. Accordingly, a half-life of **11-H** can be deduced to be around $t_{1/2} = \ln 2 / k_H = 4.7 \pm 0.3 \text{ s}$.

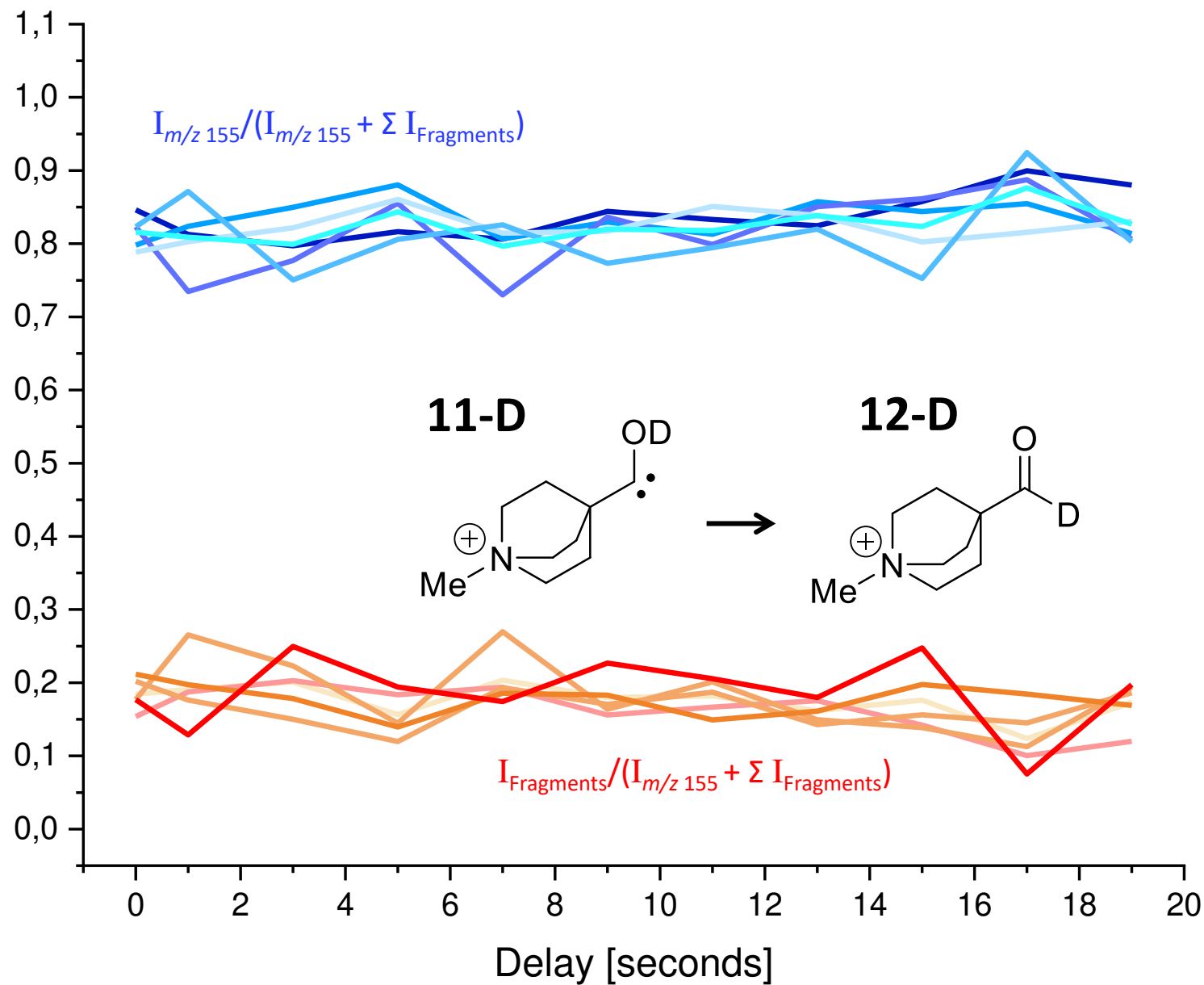
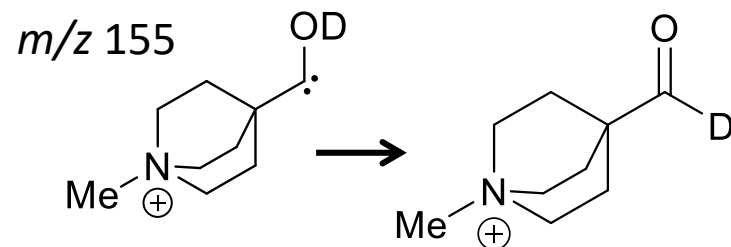
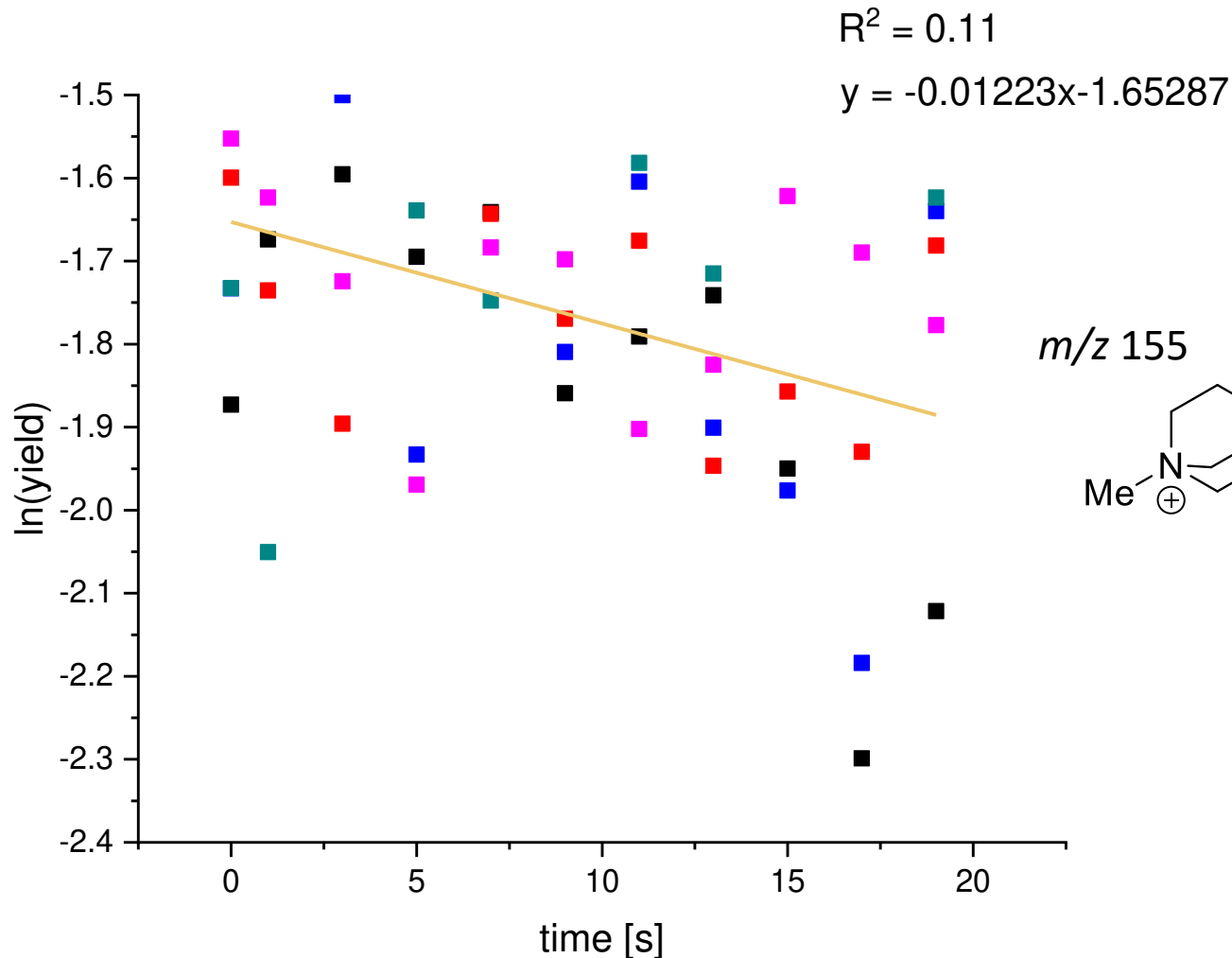


Figure S54. Tautomer-selective IR kinetics of the ^2H -quinuclidine hydroxycarbene **11-D** at m/z 155. The kinetics were measured at the C-OD stretching mode $\nu_{\text{C-OD}}$ of carbene **11-D** at 1293-1297 cm^{-1} .



$$\frac{k_H}{k_D} = \frac{0.155}{0.012} = 12.9$$

Figure S55. Data analysis of the time-dependent measurement of the hydroxycarbene ion population **11-D** at m/z 155. The isomer-selective experiment is accomplished due to the exclusive resonance of the C-OD stretching mode $\nu_{\text{C-OD}}$ of carbene **11-D** at 1293-1297 cm^{-1} as Figure S40 illustrates. The isomerization reaction from **11-D** to **12-D** obeys first order kinetics. However, the measurements are impeded by the production of many low abundant photo-fragments as Figure S42 and S43 document. Accordingly, the linear fit is quite bad leading to a rough estimate of $k_D = 0.012 \text{ s}^{-1}$. A half-life of **11-D** can roughly be deduced $t_{1/2} = \ln 2 / k_D = 57.8 \text{ s}$. On the basis of this experiment we find a rough estimate of the KIE = $k_H / k_D = 12.9$.

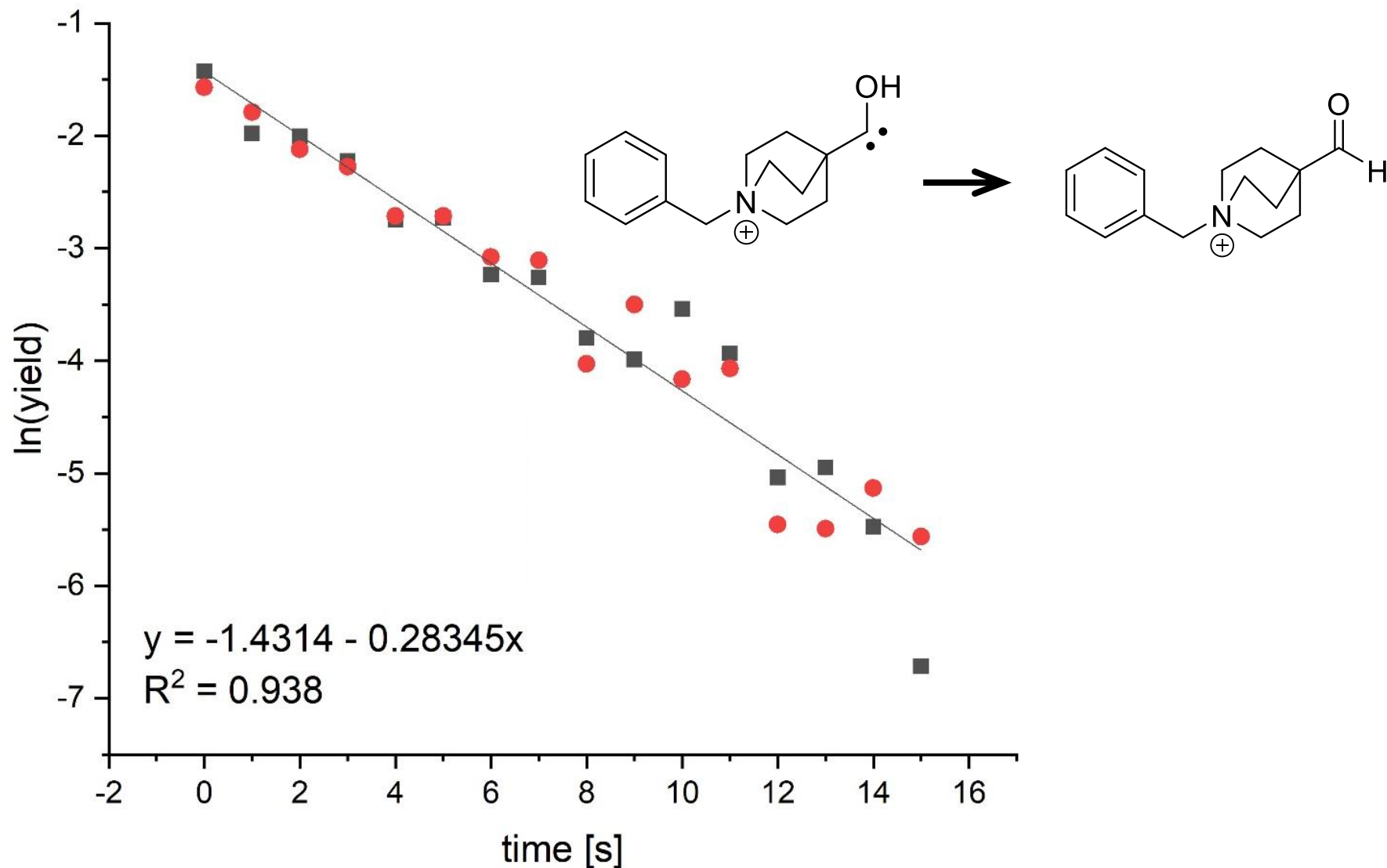


Figure S56. Data analysis of the time-dependent measurements of the depletion the hydroxycarbene ion population **14-H** at m/z 230 to the respective aldehyde **15-H**. The isomer-selective experiment is accomplished due to the exclusive resonance of **14-H** near 1300 cm^{-1} (see Figure 3b). The isomerization reaction from **14-H** to **15-H** obeys first order kinetics with a rate constant of about $k_H = 0.28\text{ s}^{-1}$. A half-life of **14-H** can be deduced to be around $t_{1/2} = \ln 2/k_H = 2.5\text{ s}$.

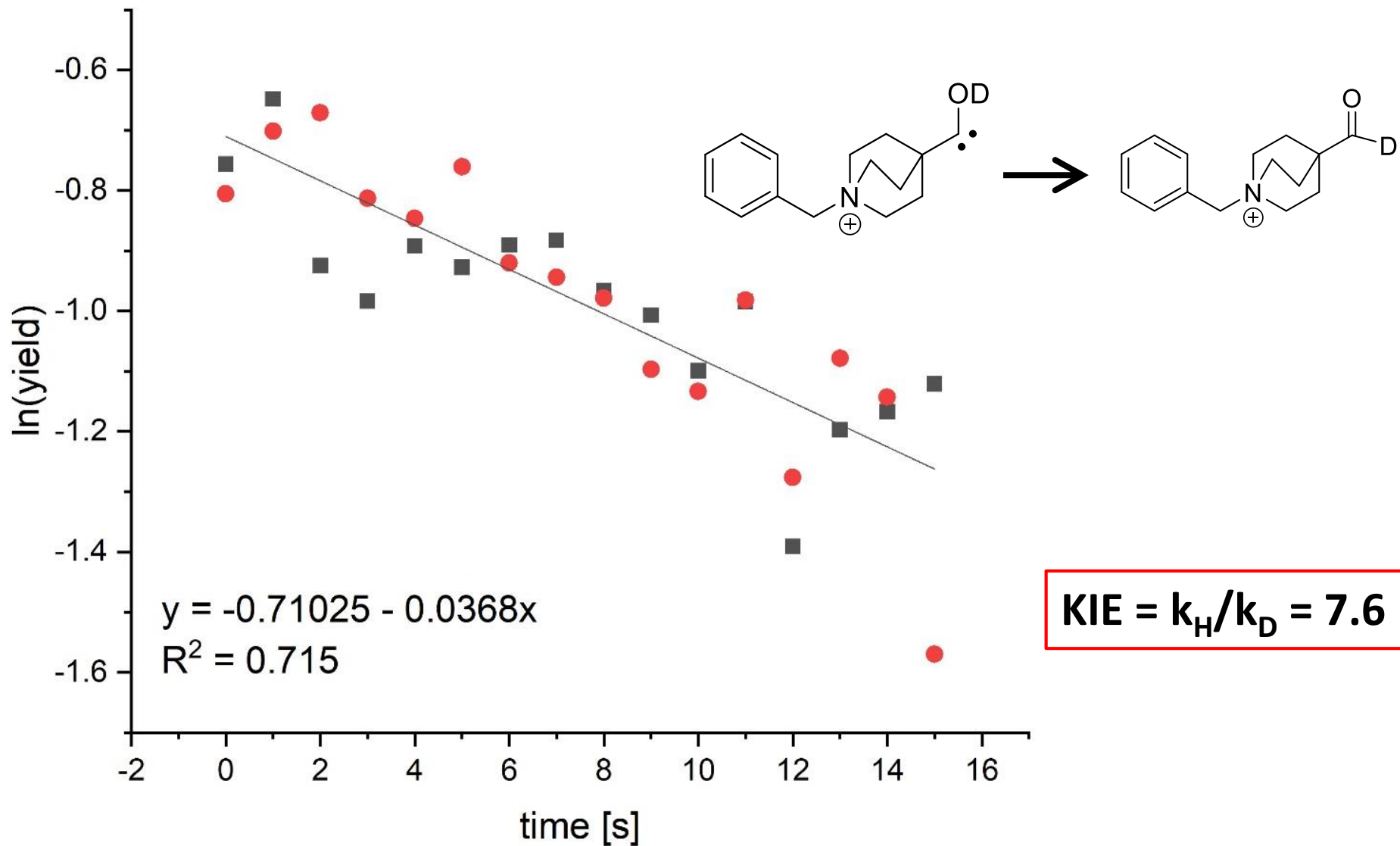


Figure S57. Data analysis of the time-dependent measurements of the depletion of the hydroxycarbene ion population **14-D** at m/z 231 to the respective aldehyde **15-D**. The isomer-selective experiment is accomplished due to the exclusive resonance of **14-D** near 1303 cm^{-1} . The reaction from **14-D** to **15-D** obeys first order kinetics with $k_D = 0.037\text{ s}^{-1}$. A half-life of **14-D** can be estimated to be around $t_{1/2} = \ln 2/k_D = 19\text{ s}$.

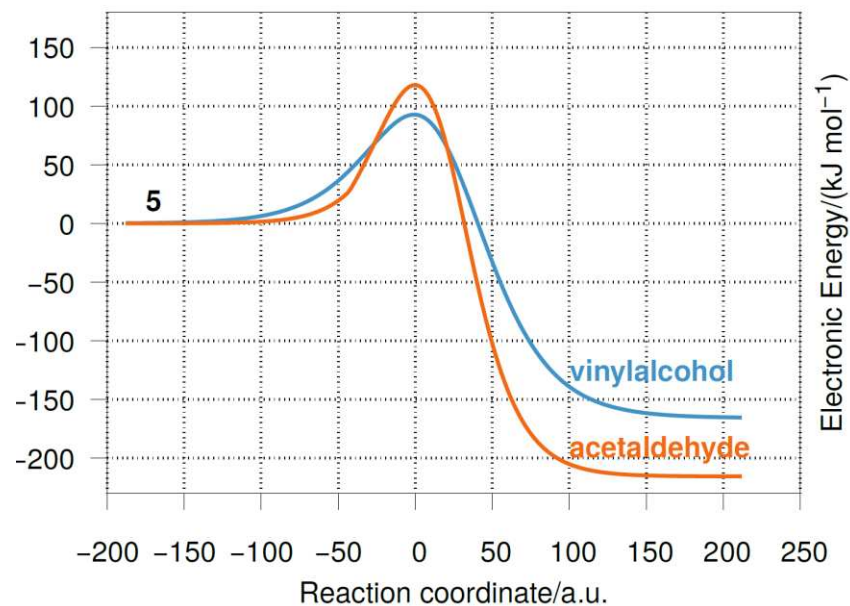
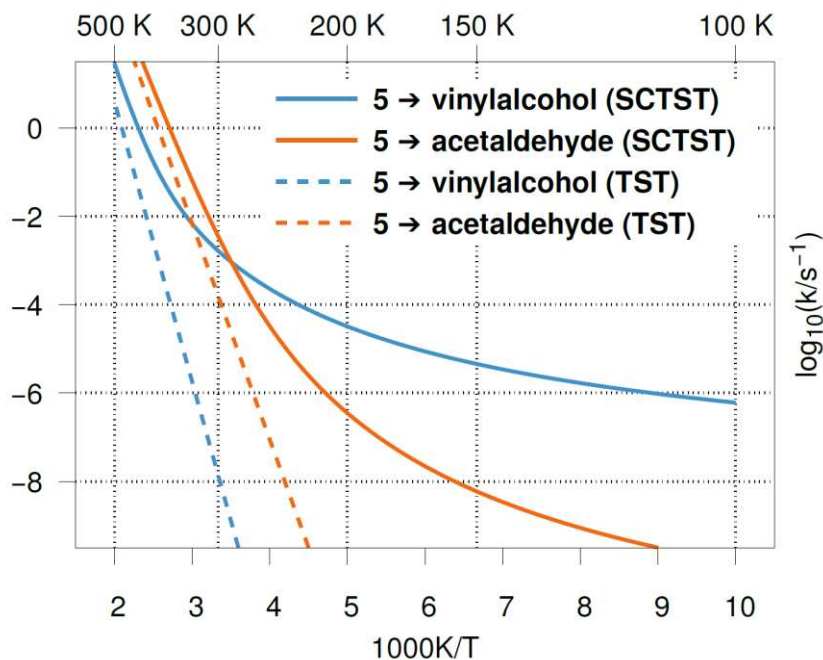
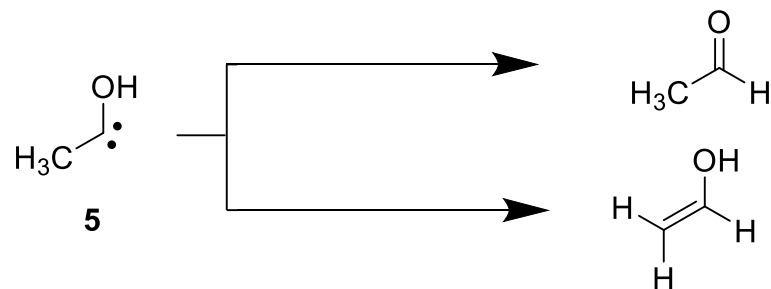


Figure S58. Left panel: Tunnelling rates for Methylhydroxycarbene **5** towards the formation of acetaldehyde and vinylalcohol, respectively. The right panel shows the barrier towards formation of the aldehyde and enol. According to previous results and in line with tunneling control, acetaldehyde should be obtained at low T. At T higher than the inversion point at about 285 K the products invert and the kinetic product vinylalcohol is formed.

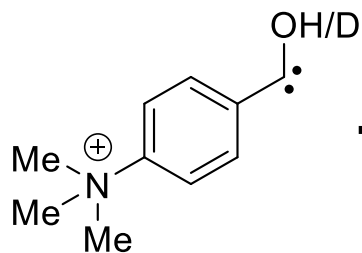
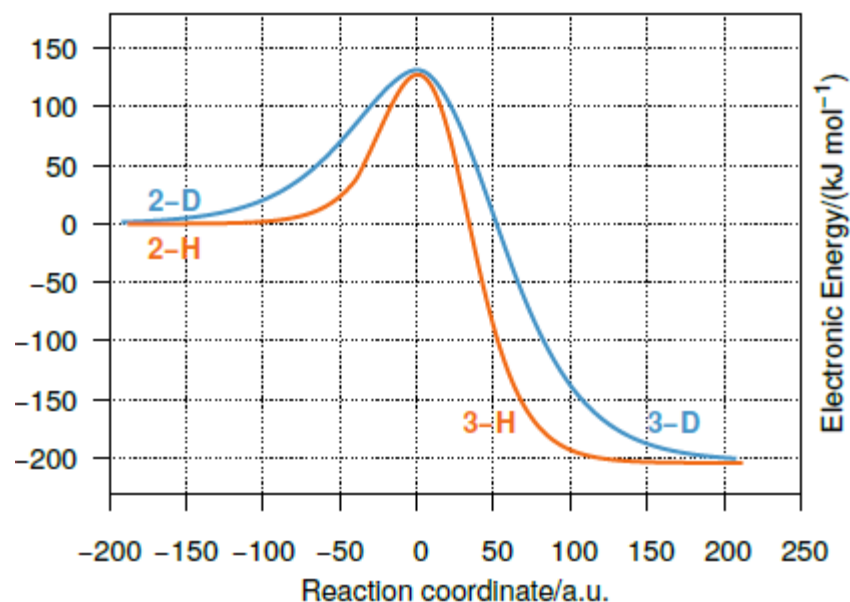
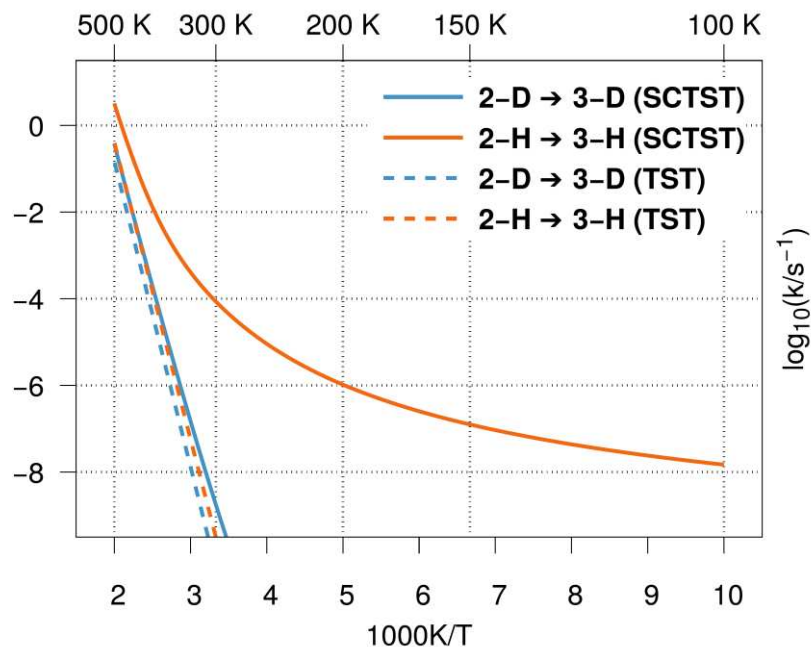
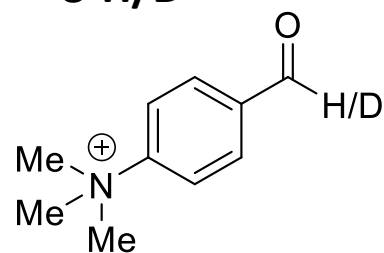
2-H/D**3-H/D**

Figure S59. Left panel: Tunneling rate for aromatic phenylhydroxycarbene **2-H** towards the formation of the respective aldehyde **3-H** compared with the respective data for the isotopologue **2-D** to **3-D**. The right panel shows the barriers towards formation of the aldehyde **3-H/D**. The barrier for the 1,2-D shift is substantially broader compared to the ¹H case, consistent with a substantially lower tunneling rate of **2-D** and prolonged half-life; consistent with results discussed in reference 8.

8. Coordinates of all computed Structures

Hydrogen Bonding Shuts Down Tunneling in Hydroxycarbenes: A Gas-Phase Study by Tandem-Mass Spectrometry, Infrared Ion Spectroscopy, and Theory

Supplementary information calculations

Mathias Paul,¹ Thomas Thomulka,¹ Wacharee Harnying,¹ Jörg-Martin Neudörfl,¹ Charlie R. Adams,² Jonathan Martens,³ Giel Berden,³ Jos Oomens,^{3,4} Anthony J. H. M. Meijer,^{2,*} Albrecht Berkessel,^{1,†} and Mathias Schäfer^{1,‡}

¹*Department of Chemistry, Organic Chemistry, University of Cologne, Greinstraße 4, 50939 Cologne, Germany*

²*Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK*

³*Institute for Molecules and Materials, Radboud University, Nijmegen, FELIX Facility, Toernooiveld 7, 6525 ED Nijmegen, The Netherlands*

⁴*van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands*

(Dated: May 5, 2023)

CONTENTS

S1. Calculations on 4 – H	S79
S1.1. Cartesian Co-ordinates (XYZ format)	S79
S1.2. Frequencies	S81
S2. Calculations on 4 – H \longrightarrow 7 – H_{ec}	S83
S2.1. Cartesian Co-ordinates (XYZ format)	S83
S2.2. Frequencies	S85
S3. Calculations on 4 – H \longrightarrow 8 – H	S87
S3.1. Cartesian Co-ordinates (XYZ format)	S87
S3.2. Frequencies	S89
S4. Calculations on 4 – H \longrightarrow 4 – H (E+ZPE=4.9 kJ mol ⁻¹) (TS)	S91
S4.1. Cartesian Co-ordinates (XYZ format)	S91
S4.2. Frequencies	S93
S5. Calculations on 4 – H (E+ZPE=4.9 kJ mol ⁻¹)	S95
S5.1. Cartesian Co-ordinates (XYZ format)	S95
S5.2. Frequencies	S97
S6. Calculations on 4 – H (E+ZPE=4.9 kJ mol ⁻¹) \longrightarrow 4 – H (E+ZPE=4.2 kJ mol ⁻¹) (TS)	S99
S6.1. Cartesian Co-ordinates (XYZ format)	S99
S6.2. Frequencies	S101
S7. Calculations on 4 – H (E+ZPE=4.2 kJ mol ⁻¹)	S103
S7.1. Cartesian Co-ordinates (XYZ format)	S103
S7.2. Frequencies	S105
S8. Calculations on 4 – H \longrightarrow 4 – H (E+ZPE=10.3 kJ mol ⁻¹) (TS)	S107

* a.meijer@sheffield.ac.uk

† berkessel@uni-koeln.de

‡ mathias.schaefer@uni-koeln.de

	S74
S8.1. Cartesian Co-ordinates (XYZ format)	S107
S8.2. Frequencies	S109
S9. Calculations on 4 – H (E+ZPE=10.3 kJ mol ⁻¹) (TS)	S111
S9.1. Cartesian Co-ordinates (XYZ format)	S111
S9.2. Frequencies	S113
S10. Calculations on 4 – H (E+ZPE=10.3 kJ mol ⁻¹) → 4 – H (E+ZPE=4.2 kJ mol ⁻¹) (TS)	S115
S10.1. Cartesian Co-ordinates (XYZ format)	S115
S10.2. Frequencies	S117
S11. Calculations on 4 – H (E+ZPE=4.9 kJ mol ⁻¹) → 9Z – H (TS)	S119
S11.1. Cartesian Co-ordinates (XYZ format)	S119
S11.2. Frequencies	S121
S12. Calculations on 4 – H (E+ZPE=4.2 kJ mol ⁻¹) → 7 – H _{5r} (TS)	S123
S12.1. Cartesian Co-ordinates (XYZ format)	S123
S12.2. Frequencies	S125
S13. Calculations on 4 – H (E+ZPE=4.2 kJ mol ⁻¹) → 4 – H (E+ZPE=69.2 kJ mol ⁻¹) (TS)	S127
S13.1. Cartesian Co-ordinates (XYZ format)	S127
S13.2. Frequencies	S129
S14. Calculations on 4 – H (E+ZPE=69.2 kJ mol ⁻¹) (TS)	S131
S14.1. Cartesian Co-ordinates (XYZ format)	S131
S14.2. Frequencies	S133
S15. Calculations on 4 – H (E+ZPE=69.2 kJ mol ⁻¹) → 9E – H (TS)	S135
S15.1. Cartesian Co-ordinates (XYZ format)	S135
S15.2. Frequencies	S137
S16. Calculations on 4 – H (E+ZPE=4.2 kJ mol ⁻¹) → 8 – H (TS)	S139
S16.1. Cartesian Co-ordinates (XYZ format)	S139
S16.2. Frequencies	S141
S17. Calculations on 7 – H _{5r}	S143
S17.1. Cartesian Co-ordinates (XYZ format)	S143
S17.2. Frequencies	S145
S18. Calculations on 7 – H _{5r} → 7 – H _{7r} (TS)	S147
S18.1. Cartesian Co-ordinates (XYZ format)	S147
S18.2. Frequencies	S149
S19. Calculations on 7 – H _{7r}	S151
S19.1. Cartesian Co-ordinates (XYZ format)	S151
S19.2. Frequencies	S153
S20. Calculations on 7 – H _{7r} → 9E – H (TS)	S155
S20.1. Cartesian Co-ordinates (XYZ format)	S155
S20.2. Frequencies	S157

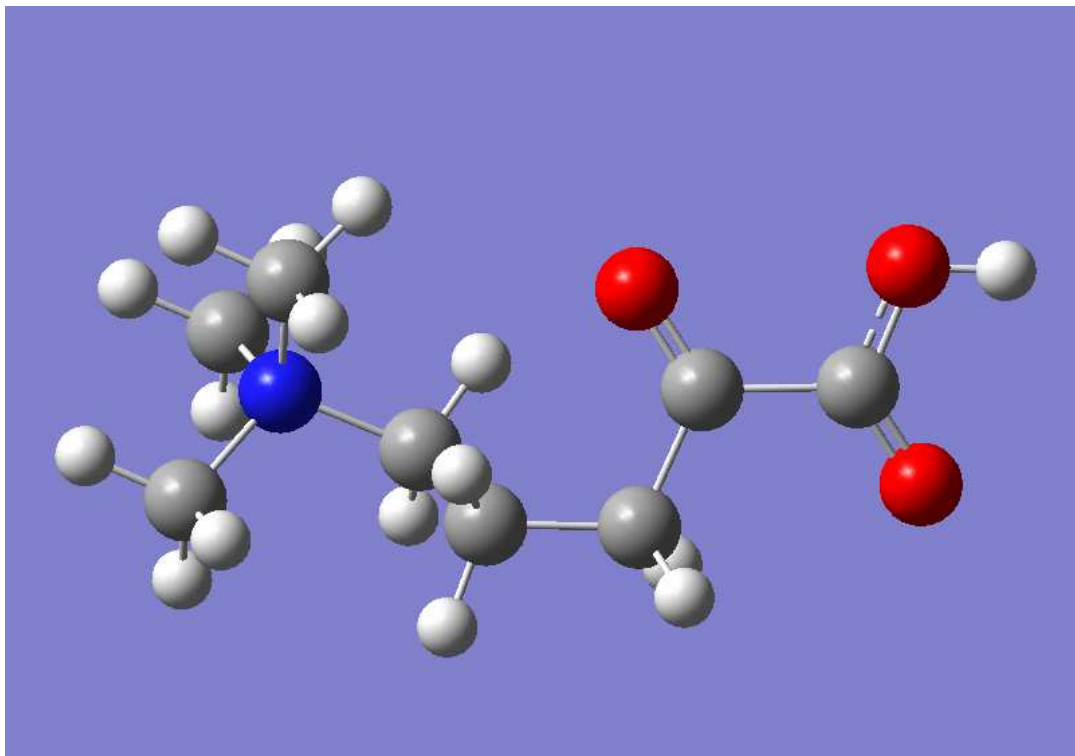
	S75
S21. Calculations on 9E – H (TS)	S159
S21.1. Cartesian Co-ordinates (XYZ format)	S159
S21.2. Frequencies	S161
S22. Calculations on 7 – H_{7r} → 8 – H (TS)	S163
S22.1. Cartesian Co-ordinates (XYZ format)	S163
S22.2. Frequencies	S165
S23. Calculations on 8 – H	S167
S23.1. Cartesian Co-ordinates (XYZ format)	S167
S23.2. Frequencies	S169
S24. Calculations on 7 – H_{5r} → 7 – H_{ec} (TS)	S171
S24.1. Cartesian Co-ordinates (XYZ format)	S171
S24.2. Frequencies	S173
S25. Calculations on 7 – H_{ec}	S175
S25.1. Cartesian Co-ordinates (XYZ format)	S175
S25.2. Frequencies	S177
S26. Calculations on 7 – H_{ec} → 9Z – H (TS)	S179
S26.1. Cartesian Co-ordinates (XYZ format)	S179
S26.2. Frequencies	S181
S27. Calculations on 9Z – H	S183
S27.1. Cartesian Co-ordinates (XYZ format)	S183
S27.2. Frequencies	S185
S28. Calculations on 7 – H_{ec} → 8 – H (TS)	S187
S28.1. Cartesian Co-ordinates (XYZ format)	S187
S28.2. Frequencies	S189
S29. Calculations on 8 – H	S191
S29.1. Cartesian Co-ordinates (XYZ format)	S191
S29.2. Frequencies	S193
S30. Calculations on 7 – H_{5r} → 9E – H (TS)	S195
S30.1. Cartesian Co-ordinates (XYZ format)	S195
S30.2. Frequencies	S197
S31. Calculations on 7 – H_{5r} → 8 – H (TS)	S199
S31.1. Cartesian Co-ordinates (XYZ format)	S199
S31.2. Frequencies	S201
S32. Calculations on 7 – H_{5r} (³A)	S203
S32.1. Cartesian Co-ordinates (XYZ format)	S203
S32.2. Frequencies	S205
S33. Calculations on 7 – H_{7r} (³A)	S207
S33.1. Cartesian Co-ordinates (XYZ format)	S207

	S76
S33.2. Frequencies	S209
S34. Calculations on 7 – H_{ec} (³ A)	S211
S34.1. Cartesian Co-ordinates (XYZ format)	S211
S34.2. Frequencies	S213
S35. Calculations on 5	S215
S35.1. Cartesian Co-ordinates (XYZ format)	S215
S35.2. Frequencies	S216
S36. Calculations on 5 → acetaldehyde (TS)	S217
S36.1. Cartesian Co-ordinates (XYZ format)	S217
S36.2. Frequencies	S218
S37. Calculations on acetaldehyde	S219
S37.1. Cartesian Co-ordinates (XYZ format)	S219
S37.2. Frequencies	S220
S38. Calculations on 5 → vinylalcohol (TS)	S221
S38.1. Cartesian Co-ordinates (XYZ format)	S221
S38.2. Frequencies	S222
S39. Calculations on vinylalcohol	S223
S39.1. Cartesian Co-ordinates (XYZ format)	S223
S39.2. Frequencies	S224
S40. Calculations on 10 – H Z-isomer	S225
S40.1. Cartesian Co-ordinates (XYZ format)	S225
S40.2. Frequencies	S227
S41. Calculations on 10 – H (Z-isomer) → 10 – H (TS)	S229
S41.1. Cartesian Co-ordinates (XYZ format)	S229
S41.2. Frequencies	S231
S42. Calculations on 10 – H	S233
S42.1. Cartesian Co-ordinates (XYZ format)	S233
S42.2. Frequencies	S235
S43. Calculations on 10 – H → 12 – H (TS)	S237
S43.1. Cartesian Co-ordinates (XYZ format)	S237
S43.2. Frequencies	S239
S44. Calculations on 10 – H → 11 – H (TS)	S241
S44.1. Cartesian Co-ordinates (XYZ format)	S241
S44.2. Frequencies	S243
S45. Calculations on 11 – H	S245
S45.1. Cartesian Co-ordinates (XYZ format)	S245
S45.2. Frequencies	S247
S46. Calculations on 11 – H (³ A)	S249

	S77
S46.1. Cartesian Co-ordinates (XYZ format)	S249
S46.2. Frequencies	S251
S47. Calculations on 11 – H → 12 – H (TS)	S253
S47.1. Cartesian Co-ordinates (XYZ format)	S253
S47.2. Frequencies	S255
S48. Calculations on 12 – H	S257
S48.1. Cartesian Co-ordinates (XYZ format)	S257
S48.2. Frequencies	S259
S49. Calculations on 11 – H → 11 – H (cis-isomer) (TS)	S261
S49.1. Cartesian Co-ordinates (XYZ format)	S261
S49.2. Frequencies	S263
S50. Calculations on 11 – H (cis-isomer)	S265
S50.1. Cartesian Co-ordinates (XYZ format)	S265
S50.2. Frequencies	S267
S51. Calculations on 11 – H (cis-isomer) → 1 – methyl – 1λ ⁴ – azabicyclo[2.2.2]octane (TS)	S269
S51.1. Cartesian Co-ordinates (XYZ format)	S269
S51.2. Frequencies	S271
S52. Calculations on 13 – H	S273
S52.1. Cartesian Co-ordinates (XYZ format)	S273
S52.2. Frequencies	S275
S53. Calculations on 11 – H → 11 – H (cis-isomer) (TS)	S277
S53.1. Cartesian Co-ordinates (XYZ format)	S277
S53.2. Frequencies	S279
S54. Calculations on 13 – H (cis-isomer)	S281
S54.1. Cartesian Co-ordinates (XYZ format)	S281
S54.2. Frequencies	S283
S55. Calculations on 13 – H → 15 – H (TS)	S285
S55.1. Cartesian Co-ordinates (XYZ format)	S285
S55.2. Frequencies	S287
S56. Calculations on 13 – H → 14 – H (TS)	S289
S56.1. Cartesian Co-ordinates (XYZ format)	S289
S56.2. Frequencies	S291
S57. Calculations on 14 – H	S293
S57.1. Cartesian Co-ordinates (XYZ format)	S293
S57.2. Frequencies	S295
S58. Calculations on 14 – H (³ A)	S297
S58.1. Cartesian Co-ordinates (XYZ format)	S297
S58.2. Frequencies	S299

S59. Calculations on 14 – H → 15 – H (TS)	S301
S59.1. Cartesian Co-ordinates (XYZ format)	S301
S59.2. Frequencies	S303
S60. Calculations on 15 – H	S305
S60.1. Cartesian Co-ordinates (XYZ format)	S305
S60.2. Frequencies	S307
S61. Calculations on 14 – H → 14 – H (cis-isomer) (TS)	S309
S61.1. Cartesian Co-ordinates (XYZ format)	S309
S61.2. Frequencies	S311
S62. Calculations on 14 – H (cis-isomer) (TS)	S313
S62.1. Cartesian Co-ordinates (XYZ format)	S313
S62.2. Frequencies	S315
S63. Calculations on 14 – H (cis-isomer) → 1 – benzyl – 1 λ^4 – azabicyclo[2.2.2]octane	S317
S63.1. Cartesian Co-ordinates (XYZ format)	S317
S63.2. Frequencies	S319
S64. Calculations on 1 – benzyl – 1 λ^4 – azabicyclo[2.2.2]octane	S321
S64.1. Cartesian Co-ordinates (XYZ format)	S321
S64.2. Frequencies	S323
S65. Calculations on E-2-N,N,N trimethylammonium cyclobutanol	S325
S65.1. Cartesian Co-ordinates (XYZ format)	S325
S65.2. Frequencies	S327
S66. Calculations on Z-2-N,N,N trimethylammonium cyclobutanol	S329
S66.1. Cartesian Co-ordinates (XYZ format)	S329
S66.2. Frequencies	S331
S67. Calculations on 3-hydroxy-N,N-dimethyl-piperidinium (Axial geometry)	S333
S67.1. Cartesian Co-ordinates (XYZ format)	S333
S67.2. Frequencies	S335
S68. Calculations on 3-hydroxy-N,N-dimethyl-piperidinium (Equatorial geometry)	S337
S68.1. Cartesian Co-ordinates (XYZ format)	S337
S68.2. Frequencies	S339

S1. CALCULATIONS ON 4 – H



```

Route : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
       : nt=ultrafine pop=regular
SMILES : C[NH3+](C)CCCC(=O)C(=O)O
Formula : C8H16NO3+
Charge : 1
Multiplicity : 1
Energy : -594.94747382 a.u.
Gibbs Energy : -594.74399100 a.u.
Number of imaginary frequencies : 0

```

S1.1. Cartesian Co-ordinates (XYZ format)

28

```

C -1.23979497 0.48412099 0.56695002
H -0.67156601 -0.32702300 1.01080799
H -1.50599802 1.19187105 1.34974301
C -0.43965301 1.17113304 -0.53483802
H -0.82937503 2.17056394 -0.71898901
H -0.50999701 0.61331397 -1.46679401
C 1.03692198 1.26531196 -0.15650900
H 1.19448304 1.71098697 0.82924199
H 1.56988001 1.92999005 -0.83934599
N -2.54711509 -0.15373200 0.11757600
C -3.24726105 -0.67745203 1.33793902
H -4.17740393 -1.14838600 1.03450799
H -2.60426497 -1.40438199 1.82490897
H -3.45115805 0.15042900 2.01023889

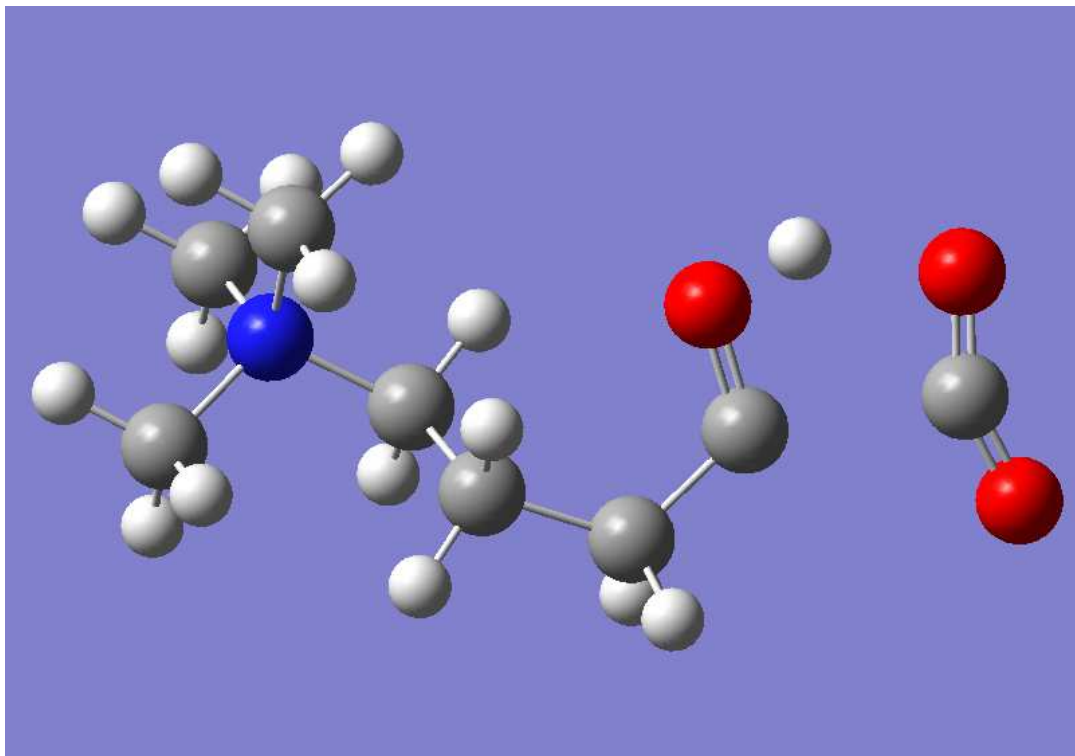
```


C -3.42849302 0.85239297 -0.55846697
H -3.59868002 1.68286097 0.12074000
H -2.94401503 1.20236897 -1.46300697
H -4.37234402 0.37642801 -0.80719203
C -2.28299189 -1.30604005 -0.81203300
H -1.59343100 -1.99232805 -0.33175299
H -3.22866607 -1.79542100 -1.02465999
H -1.84414601 -0.93763900 -1.73099196
C 1.71863103 -0.08261700 -0.19137500
O 1.14450097 -1.11177599 -0.44658700
C 3.22232509 -0.05079800 0.14411700
O 3.75995898 0.95841497 0.51463199
O 3.79790497 -1.23780894 -0.01813900
H 4.73817587 -1.15522206 0.20772500

S1.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	25.99320000	1.31040000	0.00000000
2	32.02220000	1.24560000	0.00000000
3	46.03560000	2.24550000	0.00000000
4	61.45980000	5.49150000	0.00000000
5	146.04410000	3.54850000	0.00000000
6	168.10560000	5.42170000	0.00000000
7	206.80430000	2.49490000	0.00000000
8	220.49920000	5.21130000	0.00000000
9	266.44970000	0.05690000	0.00000000
10	277.20440000	0.42450000	0.00000000
11	294.21550000	0.37920000	0.00000000
12	336.83360000	8.59110000	0.00000000
13	364.32200000	0.56040000	0.00000000
14	370.01870000	1.81650000	0.00000000
15	384.68560000	0.17180000	0.00000000
16	418.20140000	5.79910000	0.00000000
17	447.68580000	0.64410000	0.00000000
18	454.97890000	0.28820000	0.00000000
19	513.92700000	0.86890000	0.00000000
20	530.96150000	7.65280000	0.00000000
21	618.82720000	64.89950000	0.00000000
22	661.61930000	64.49120000	0.00000000
23	715.97540000	62.34640000	0.00000000
24	730.03190000	36.96070000	0.00000000
25	768.83250000	7.63620000	0.00000000
26	828.13510000	5.01350000	0.00000000
27	882.23540000	13.94510000	0.00000000
28	930.31980000	23.51710000	0.00000000
29	948.31720000	13.16640000	0.00000000
30	966.83110000	13.82840000	0.00000000
31	1021.13590000	79.34960000	0.00000000
32	1042.21440000	49.96060000	0.00000000
33	1059.27230000	1.89160000	0.00000000
34	1078.00110000	0.25920000	0.00000000
35	1096.10090000	38.95790000	0.00000000
36	1142.65330000	2.61210000	0.00000000
37	1150.50640000	22.56810000	0.00000000
38	1196.84970000	107.40510000	0.00000000
39	1203.24980000	5.15660000	0.00000000
40	1235.39400000	1.26630000	0.00000000
41	1268.00110000	1.60390000	0.00000000
42	1295.49200000	0.59770000	0.00000000
43	1308.47260000	4.17720000	0.00000000
44	1367.35700000	2.16880000	0.00000000
45	1372.89710000	31.14040000	0.00000000
46	1378.40200000	7.87170000	0.00000000
47	1409.89280000	7.82820000	0.00000000
48	1430.08490000	4.22920000	0.00000000
49	1443.61050000	24.18490000	0.00000000
50	1455.67370000	5.12350000	0.00000000
51	1457.58060000	2.47990000	0.00000000
52	1478.64540000	0.95120000	0.00000000
53	1480.40520000	0.73040000	0.00000000
54	1486.38830000	2.10710000	0.00000000
55	1493.54420000	1.11950000	0.00000000
56	1499.99920000	6.61520000	0.00000000
57	1507.00780000	6.86500000	0.00000000
58	1516.43860000	33.00680000	0.00000000
59	1520.24790000	41.93490000	0.00000000
60	1529.93320000	47.70690000	0.00000000

61	1795.56270000	106.91070000	0.00000000
62	1811.19510000	243.50150000	0.00000000
63	3046.86350000	2.89550000	0.00000000
64	3067.07150000	8.79720000	0.00000000
65	3073.52040000	0.13460000	0.00000000
66	3077.00660000	0.19880000	0.00000000
67	3078.45180000	1.13690000	0.00000000
68	3082.66690000	6.34590000	0.00000000
69	3088.47280000	1.94370000	0.00000000
70	3110.27440000	5.21030000	0.00000000
71	3146.65250000	1.68450000	0.00000000
72	3161.72430000	0.14980000	0.00000000
73	3166.12680000	0.67930000	0.00000000
74	3167.77030000	1.35870000	0.00000000
75	3174.58620000	1.20290000	0.00000000
76	3178.80780000	0.68780000	0.00000000
77	3190.68380000	1.39850000	0.00000000
78	3724.24550000	127.36340000	0.00000000

S2. CALCULATIONS ON 4 - H \rightarrow 7 - H_{ec}

```

Route                : # opt=(calcf,ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper
                    : sion=gd3bj int=ultrafine pop=regular
SMILES               : C[N](C)(C)CCC[C]O.[C](=O)[O]
Formula              : C8H16NO3+
Charge               : 1
Multiplicity         : 1
Energy               : -594.88116226 a.u.
Gibbs Energy        : -594.68084300 a.u.
Number of imaginary frequencies : 1

```

S2.1. Cartesian Co-ordinates (XYZ format)

28

```

C -1.30717301 0.33143699 0.50511402
H -0.73181498 -0.55004501 0.77437502
H -1.44383895 0.93925703 1.39787805
C -0.60058200 1.12774706 -0.58107001
H -1.11454999 2.07091999 -0.76021302
H -0.58090502 0.57522100 -1.51892996
C 0.84868801 1.42753398 -0.16657200
H 0.91517103 1.89965296 0.81945199
H 1.28566098 2.18085003 -0.83186698
N -2.69324899 -0.19046800 0.14438900
C -3.24804211 -0.89118201 1.35196400
H -4.23272610 -1.28006804 1.11079502
H -2.58210397 -1.70525801 1.62186599
H -3.31863499 -0.18044600 2.16977596

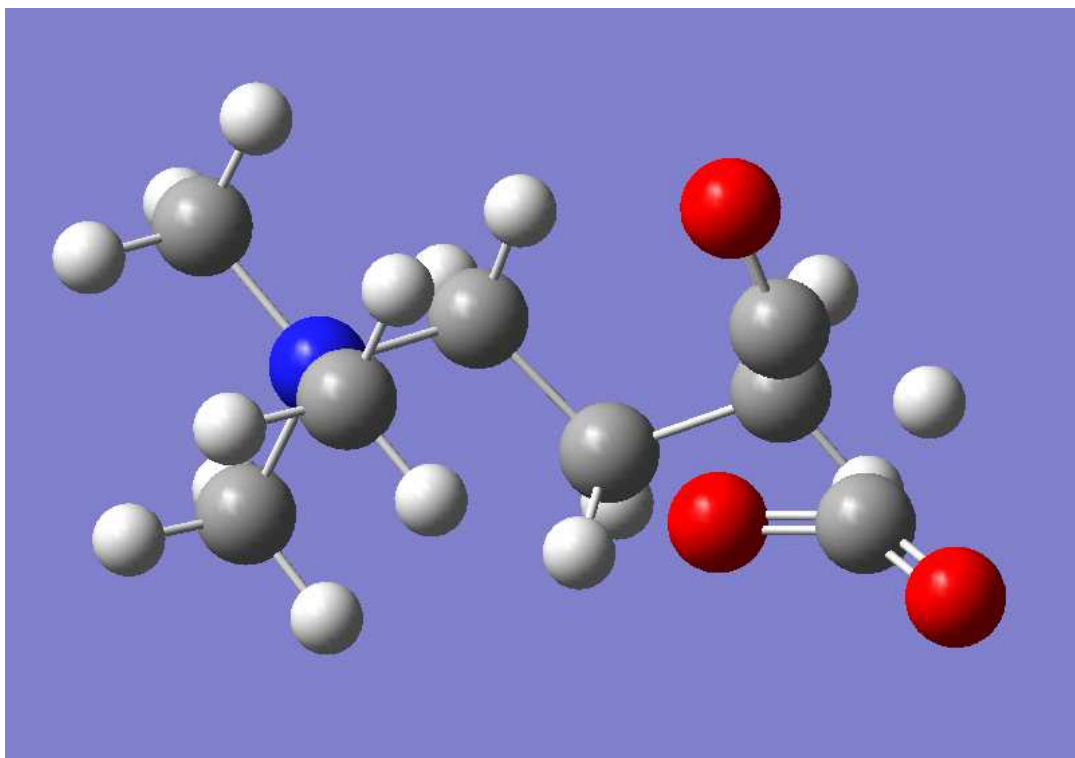
```

C -3.61273694 0.93380201 -0.23056100
H -3.63897395 1.65241301 0.58348101
H -3.25187492 1.40675998 -1.13672304
H -4.60549688 0.52725899 -0.39895901
C -2.61222291 -1.17453897 -0.98724598
H -1.90801203 -1.95679498 -0.72084200
H -3.59955001 -1.59696198 -1.14777696
H -2.28161407 -0.66627502 -1.88529396
C 1.82911396 0.31221399 -0.17172900
O 1.37233102 -0.81320101 -0.57339501
C 3.88024712 -0.20437700 0.24742100
O 4.48229313 0.71464002 0.64968598
O 3.74543190 -1.35279202 -0.08298600
H 2.18957591 -1.41753101 -0.52086198

S2.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-195.66230000	100.46100000	0.00000000
2	25.07440000	0.73210000	0.00000000
3	29.39320000	1.03810000	0.00000000
4	51.97580000	2.41900000	0.00000000
5	111.95370000	0.26160000	0.00000000
6	135.90090000	0.94490000	0.00000000
7	160.01360000	5.08820000	0.00000000
8	193.56260000	0.91060000	0.00000000
9	226.11790000	6.59230000	0.00000000
10	237.46190000	2.44600000	0.00000000
11	262.99970000	2.65130000	0.00000000
12	278.76410000	0.40510000	0.00000000
13	292.48100000	0.71370000	0.00000000
14	335.22690000	3.03660000	0.00000000
15	361.65390000	0.18940000	0.00000000
16	366.62280000	0.40770000	0.00000000
17	409.77760000	2.91330000	0.00000000
18	448.40790000	0.07180000	0.00000000
19	450.59390000	1.29480000	0.00000000
20	517.15750000	3.94970000	0.00000000
21	630.34210000	327.01980000	0.00000000
22	662.83150000	83.73860000	0.00000000
23	673.89880000	43.61510000	0.00000000
24	738.35550000	0.12230000	0.00000000
25	794.07640000	10.67650000	0.00000000
26	807.28100000	6.32910000	0.00000000
27	902.49510000	44.01900000	0.00000000
28	925.23030000	5.06970000	0.00000000
29	952.16890000	15.29160000	0.00000000
30	970.83390000	13.30810000	0.00000000
31	1018.50130000	3.37620000	0.00000000
32	1042.89770000	7.21400000	0.00000000
33	1077.25040000	5.50850000	0.00000000
34	1079.84430000	9.69120000	0.00000000
35	1114.35510000	23.79850000	0.00000000
36	1145.02450000	14.54390000	0.00000000
37	1147.91770000	13.76960000	0.00000000
38	1207.59900000	5.08430000	0.00000000
39	1228.67960000	19.31450000	0.00000000
40	1247.42800000	40.64720000	0.00000000
41	1268.18460000	1.01400000	0.00000000
42	1294.20540000	2.58490000	0.00000000
43	1300.44920000	14.83510000	0.00000000
44	1357.60690000	4.41140000	0.00000000
45	1362.71090000	54.52100000	0.00000000
46	1377.39280000	9.73930000	0.00000000
47	1399.55960000	93.01190000	0.00000000
48	1426.13850000	4.95200000	0.00000000
49	1454.55690000	6.98350000	0.00000000
50	1456.16920000	4.56530000	0.00000000
51	1470.94810000	289.33530000	0.00000000
52	1479.62840000	9.99220000	0.00000000
53	1481.55820000	0.54940000	0.00000000
54	1485.99480000	32.30290000	0.00000000
55	1491.20390000	4.92990000	0.00000000
56	1493.47980000	2.12980000	0.00000000
57	1501.53660000	5.97010000	0.00000000
58	1509.24380000	3.81800000	0.00000000
59	1516.45510000	33.01350000	0.00000000
60	1520.33140000	39.29220000	0.00000000

61	1531.18340000	50.42030000	0.00000000
62	2185.92390000	513.60280000	0.00000000
63	2916.44750000	530.77570000	0.00000000
64	3025.81800000	3.55800000	0.00000000
65	3041.31940000	1.75270000	0.00000000
66	3064.16470000	8.48050000	0.00000000
67	3073.43380000	0.12830000	0.00000000
68	3078.09530000	1.01460000	0.00000000
69	3079.60000000	5.54330000	0.00000000
70	3085.35420000	0.51780000	0.00000000
71	3105.85640000	4.22420000	0.00000000
72	3138.66170000	2.49900000	0.00000000
73	3162.80060000	0.10490000	0.00000000
74	3165.05570000	0.04010000	0.00000000
75	3168.19720000	0.92040000	0.00000000
76	3170.46140000	1.73140000	0.00000000
77	3179.13110000	0.20510000	0.00000000
78	3184.86230000	1.18310000	0.00000000

S3. CALCULATIONS ON 4 - H \rightarrow 8 - H

```

Route                : # opt=(calcf,ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper
                     : sion=gd3bj int=ultrafine pop=regular
SMILES               : C[N](C)(C)CCC[C]=O.C(=O)[O]
Formula              : C8H16NO3+
Charge               : 1
Multiplicity         : 1
Energy               : -594.86582224 a.u.
Gibbs Energy        : -594.66531500 a.u.
Number of imaginary frequencies : 1

```

S3.1. Cartesian Co-ordinates (XYZ format)

28

```

C -1.41083896 -1.00020397 0.11203000
H -1.04554904 -1.22407496 -0.88630700
H -2.14988804 -1.75262201 0.37553301
C -0.27085099 -0.96460903 1.13757205
H -0.56319302 -1.50475502 2.03592491
H -0.04156000 0.05214200 1.44414604
C 1.03975701 -1.58578098 0.62705302
H 0.90410203 -2.61991405 0.30507299
H 1.78313696 -1.56815898 1.41707206
N -2.18391705 0.30258799 -0.03365900
C -3.30910301 0.06081800 -0.99945700
H -3.86051011 0.98668402 -1.13150895
H -2.89222789 -0.26145101 -1.94882298
H -3.96247792 -0.70734698 -0.59681499

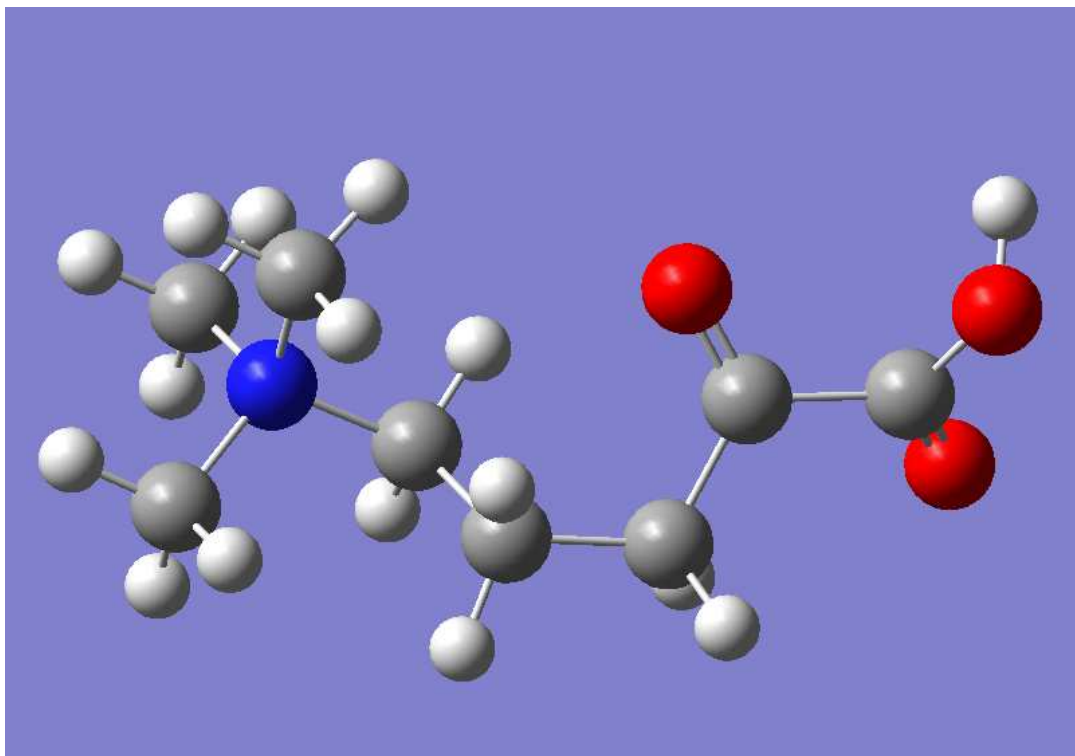
```


C	-2.75923109	0.73266000	1.28306198
H	-3.37868500	-0.06944200	1.67415905
H	-1.95445299	0.95648599	1.97404397
H	-3.36036611	1.62263095	1.12346399
C	-1.30411601	1.39084804	-0.58865798
H	-1.90788603	2.28495002	-0.71017301
H	-0.47991601	1.58553100	0.08714900
H	-0.91437900	1.06506801	-1.54795802
C	1.53367603	-0.83545297	-0.57488602
O	1.20220900	-0.79918098	-1.69418597
C	3.02768302	0.59943002	0.10481300
O	4.09369707	1.06845903	0.28944999
O	1.80433202	0.89153397	0.20016800
H	3.02409506	-0.60718602	-0.34039301

S3.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-905.63380000	631.99260000	0.00000000
2	38.71220000	1.08190000	0.00000000
3	54.44470000	1.12440000	0.00000000
4	61.11640000	5.81520000	0.00000000
5	100.75770000	1.38760000	0.00000000
6	164.83110000	10.22210000	0.00000000
7	177.16660000	2.97950000	0.00000000
8	221.19210000	1.65920000	0.00000000
9	268.91300000	7.48900000	0.00000000
10	281.12610000	0.50440000	0.00000000
11	284.86130000	1.18080000	0.00000000
12	294.41660000	3.84240000	0.00000000
13	314.48340000	1.87100000	0.00000000
14	347.76600000	78.36380000	0.00000000
15	369.90170000	1.64280000	0.00000000
16	385.20300000	11.39700000	0.00000000
17	429.62410000	42.19660000	0.00000000
18	443.90620000	0.96140000	0.00000000
19	466.23120000	0.67900000	0.00000000
20	493.35040000	119.67850000	0.00000000
21	520.42760000	101.40820000	0.00000000
22	562.13560000	14.71870000	0.00000000
23	717.04630000	83.14770000	0.00000000
24	752.39240000	52.21570000	0.00000000
25	801.32920000	49.96980000	0.00000000
26	872.87530000	15.18200000	0.00000000
27	894.15100000	77.03410000	0.00000000
28	908.32530000	22.93110000	0.00000000
29	952.62300000	72.00460000	0.00000000
30	964.53940000	10.23980000	0.00000000
31	1000.96930000	52.05690000	0.00000000
32	1043.93380000	2.58660000	0.00000000
33	1059.87100000	21.57110000	0.00000000
34	1078.10770000	0.90380000	0.00000000
35	1086.17930000	15.46090000	0.00000000
36	1100.67000000	3.24960000	0.00000000
37	1144.19620000	5.30640000	0.00000000
38	1147.60590000	1.98730000	0.00000000
39	1213.87690000	11.51100000	0.00000000
40	1235.93360000	5.56040000	0.00000000
41	1266.82400000	5.29890000	0.00000000
42	1292.93160000	6.58240000	0.00000000
43	1301.02410000	3.75240000	0.00000000
44	1359.88420000	16.26940000	0.00000000
45	1364.97510000	127.86400000	0.00000000
46	1370.67350000	1.21790000	0.00000000
47	1378.89980000	0.18300000	0.00000000
48	1434.79840000	3.21550000	0.00000000
49	1457.20420000	2.41660000	0.00000000
50	1458.15600000	5.82650000	0.00000000
51	1479.96510000	11.52860000	0.00000000
52	1481.74960000	1.03590000	0.00000000
53	1486.65570000	2.06410000	0.00000000
54	1490.87200000	1.69290000	0.00000000
55	1495.89970000	1.91660000	0.00000000
56	1501.33970000	1.75910000	0.00000000
57	1511.70290000	5.22320000	0.00000000
58	1518.93280000	43.97570000	0.00000000
59	1524.02600000	49.28410000	0.00000000
60	1531.02360000	53.39830000	0.00000000

61	1777.37900000	147.38200000	0.00000000
62	1948.45750000	640.72990000	0.00000000
63	1988.31190000	188.84500000	0.00000000
64	3063.36920000	0.58000000	0.00000000
65	3074.11830000	0.11550000	0.00000000
66	3078.69670000	0.44220000	0.00000000
67	3081.27760000	2.19620000	0.00000000
68	3084.72720000	2.03460000	0.00000000
69	3090.15170000	7.01320000	0.00000000
70	3124.29720000	3.18620000	0.00000000
71	3139.64480000	0.86340000	0.00000000
72	3147.41450000	0.25880000	0.00000000
73	3162.91380000	0.05450000	0.00000000
74	3166.66360000	0.09410000	0.00000000
75	3168.13570000	0.91640000	0.00000000
76	3172.57450000	0.85990000	0.00000000
77	3179.54080000	1.10570000	0.00000000
78	3191.11410000	2.24660000	0.00000000

S4. CALCULATIONS ON 4 - H \rightarrow 4 - H ($E+ZPE=4.9$ KJ MOL $^{-1}$) (TS)

```

Route : # opt=(calcfc.ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper
       : sion=gd3bj int=ultrafine pop=regular
SMILES : C[N](C)(C)CCCC(=O)C(=O)O
Formula : C8H16NO3+
Charge : 1
Multiplicity : 1
Energy : -594.92783014 a.u.
Gibbs Energy : -594.72648200 a.u.
Number of imaginary frequencies : 1

```

S4.1. Cartesian Co-ordinates (XYZ format)

28

```

C -1.23441994 0.54108000 0.46906999
H -0.66588002 -0.20102000 1.02073002
H -1.48262000 1.36038005 1.14115000
C -0.44356000 1.04686999 -0.73158997
H -0.84763998 1.99506998 -1.08144999
H -0.49947000 0.33859000 -1.55631006
C 1.02884996 1.22758996 -0.36833999
H 1.17567003 1.82464004 0.53492999
H 1.55000997 1.78232002 -1.15288997
N -2.55352998 -0.14201000 0.13619000
C -3.23772001 -0.47665000 1.43004000
H -4.17658997 -0.97667003 1.21204996
H -2.59264994 -1.13208997 2.00735998
H -3.42356992 0.44182000 1.97851002

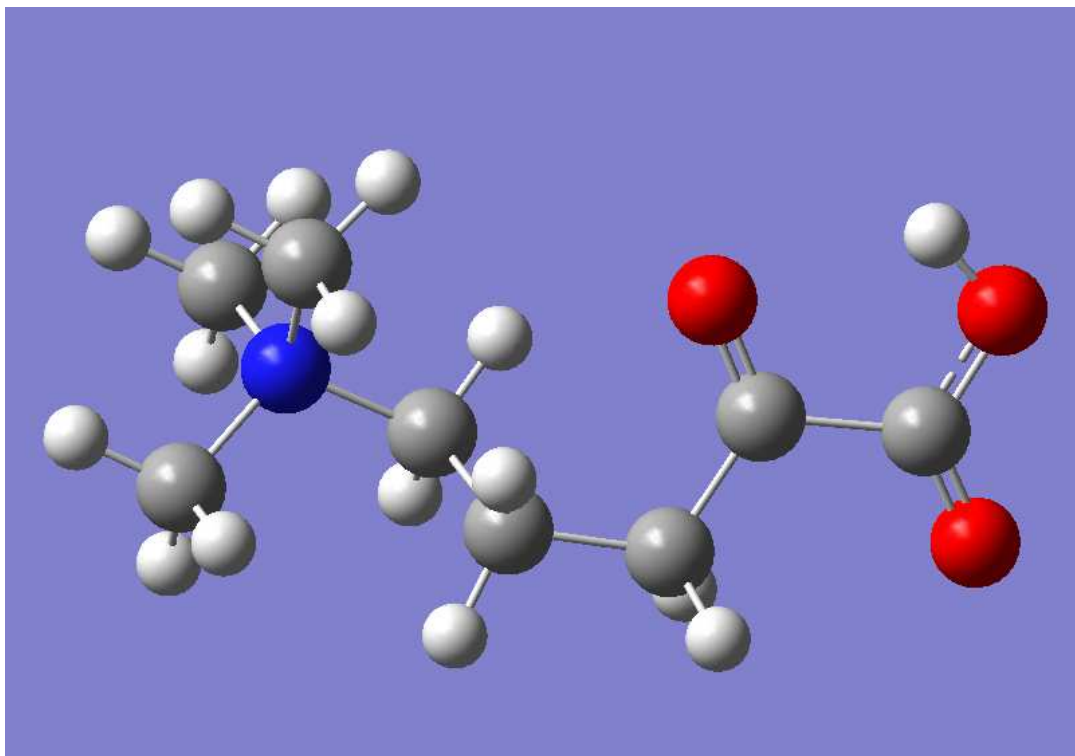
```

C -3.43879008 0.76379001 -0.66544998
H -3.59094000 1.68605995 -0.11208000
H -2.96752000 0.97315001 -1.61910999
H -4.39039993 0.26613000 -0.82687998
C -2.31236005 -1.41867006 -0.62072998
H -1.61521995 -2.03175998 -0.05899000
H -3.26324010 -1.92897999 -0.74071002
H -1.89252996 -1.19029999 -1.59261000
C 1.74312997 -0.09062000 -0.18817000
O 1.19691002 -1.16534996 -0.27875999
C 3.22630000 -0.00540000 0.21162000
O 3.60516000 0.88328999 0.91446000
O 4.00816011 -0.96548003 -0.32800001
H 4.08690023 -1.76086998 0.21266000

S4.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-631.20290000	131.51960000	0.00000000
2	26.10380000	1.56960000	0.00000000
3	27.70320000	1.77770000	0.00000000
4	47.11970000	1.50050000	0.00000000
5	63.48980000	6.83920000	0.00000000
6	142.45800000	3.00550000	0.00000000
7	163.37800000	6.82220000	0.00000000
8	206.21750000	5.22170000	0.00000000
9	217.67230000	4.88220000	0.00000000
10	262.05870000	0.26220000	0.00000000
11	273.01340000	0.45180000	0.00000000
12	292.58720000	0.07860000	0.00000000
13	306.61570000	6.77000000	0.00000000
14	347.62130000	13.56440000	0.00000000
15	366.97000000	3.70550000	0.00000000
16	369.91150000	0.49340000	0.00000000
17	413.12680000	1.43920000	0.00000000
18	448.16930000	0.59330000	0.00000000
19	453.82200000	0.50990000	0.00000000
20	522.26660000	3.72910000	0.00000000
21	564.65030000	0.55940000	0.00000000
22	663.48000000	41.11340000	0.00000000
23	689.34710000	5.28890000	0.00000000
24	749.94300000	9.36100000	0.00000000
25	768.26230000	17.73570000	0.00000000
26	828.94520000	20.44960000	0.00000000
27	876.27680000	14.79220000	0.00000000
28	924.87630000	46.16260000	0.00000000
29	948.69800000	12.33360000	0.00000000
30	965.70170000	18.71720000	0.00000000
31	1007.21420000	174.53480000	0.00000000
32	1038.93200000	26.21120000	0.00000000
33	1050.26670000	30.12190000	0.00000000
34	1078.29610000	8.04430000	0.00000000
35	1079.98440000	115.81090000	0.00000000
36	1097.18750000	8.44130000	0.00000000
37	1143.71000000	10.09330000	0.00000000
38	1151.03920000	6.47370000	0.00000000
39	1205.45410000	7.29750000	0.00000000
40	1235.15050000	6.28810000	0.00000000
41	1268.06020000	2.07130000	0.00000000
42	1280.15280000	64.28390000	0.00000000
43	1296.19810000	2.16610000	0.00000000
44	1313.77730000	4.59480000	0.00000000
45	1367.19060000	2.74050000	0.00000000
46	1376.25390000	2.79740000	0.00000000
47	1391.81170000	7.05750000	0.00000000
48	1430.20500000	3.49710000	0.00000000
49	1448.81580000	25.00150000	0.00000000
50	1455.84050000	5.97700000	0.00000000
51	1457.14880000	2.13700000	0.00000000
52	1478.90830000	0.66420000	0.00000000
53	1480.56830000	0.86730000	0.00000000
54	1486.73830000	1.79540000	0.00000000
55	1493.30890000	0.98160000	0.00000000
56	1499.21570000	6.38310000	0.00000000
57	1507.08870000	7.02160000	0.00000000
58	1516.10650000	31.57990000	0.00000000
59	1520.07830000	43.01330000	0.00000000
60	1529.81090000	46.74440000	0.00000000

61	1779.11530000	83.95780000	0.00000000
62	1825.07530000	214.25820000	0.00000000
63	3044.61020000	4.54680000	0.00000000
64	3064.61730000	5.64590000	0.00000000
65	3073.46460000	0.42860000	0.00000000
66	3073.86700000	1.60070000	0.00000000
67	3078.17370000	1.08930000	0.00000000
68	3082.56760000	6.17770000	0.00000000
69	3087.78860000	1.74390000	0.00000000
70	3109.73490000	4.60780000	0.00000000
71	3145.55460000	1.74870000	0.00000000
72	3161.80660000	0.13800000	0.00000000
73	3165.94950000	0.60060000	0.00000000
74	3167.78760000	1.24870000	0.00000000
75	3173.72540000	1.28310000	0.00000000
76	3178.64270000	0.58510000	0.00000000
77	3188.95430000	1.36210000	0.00000000
78	3801.56320000	174.40070000	0.00000000

S5. CALCULATIONS ON 4 - H (E+ZPE=4.9 KJ MOL⁻¹)

```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N](C)(C)CCCC(=O)C(=O)O
Formula              : C8H16NO3+
Charge               : 1
Multiplicity         : 1
Energy               : -594.94597910
Gibbs Energy         : -594.74210900
Number of imaginary frequencies : 0

```

a.u.
a.u.

S5.1. Cartesian Co-ordinates (XYZ format)

28

```

C  1.21643996 -0.39651999  0.53434998
H  0.67585999  0.46799001  0.90785003
H  1.40032995 -1.07758999  1.36328995
C  0.42829001 -1.09171999 -0.56800002
H  0.83871001 -2.08036995 -0.76490998
H  0.47488999 -0.52161002 -1.49426997
C -1.04048002 -1.23263001 -0.17222001
H -1.17490005 -1.68867004  0.81251001
H -1.56177998 -1.91244996 -0.84982997
N  2.58082008  0.13857000  0.12169000
C  3.24582005  0.69599003  1.34753001
H  4.21670008  1.09502995  1.06976998
H  2.62204003  1.48545003  1.75582004
H  3.36513996 -0.09998000  2.07629991

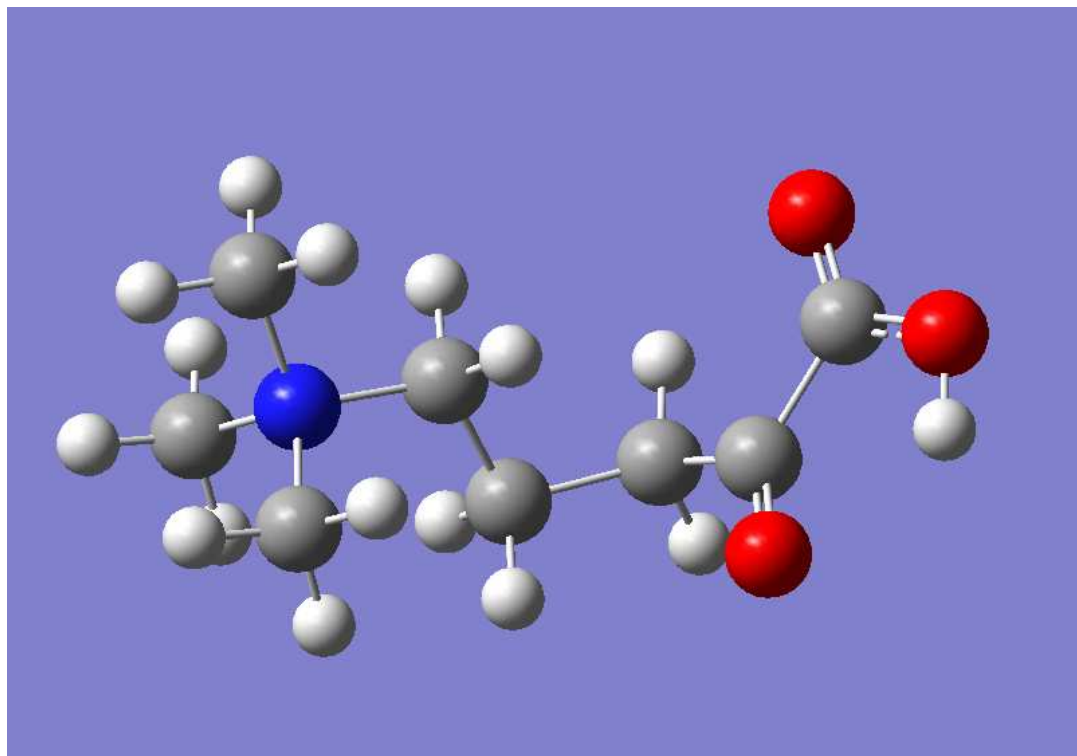
```


C	3.43815994	-0.95305002	-0.44541001
H	3.51801991	-1.75256002	0.28556001
H	2.98843002	-1.32458997	-1.35920000
H	4.42187977	-0.54584998	-0.65924001
C	2.43261003	1.24331999	-0.88664001
H	1.75907004	1.99418998	-0.48583999
H	3.41303992	1.67118001	-1.07269001
H	2.02768993	0.84135997	-1.80750000
C	-1.78076005	0.07551000	-0.19192000
O	-1.27031004	1.14111996	-0.46427000
C	-3.27987003	0.01359000	0.16491000
O	-3.79806995	-1.01480997	0.49346000
O	-3.90059996	1.18507004	0.08024000
H	-3.26032996	1.86040998	-0.20051999

S5.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	22.58580000	0.76650000	0.00000000
2	36.72000000	1.58500000	0.00000000
3	50.03370000	0.97390000	0.00000000
4	87.71110000	4.74020000	0.00000000
5	141.06170000	2.81860000	0.00000000
6	167.45940000	11.14060000	0.00000000
7	204.69540000	5.74080000	0.00000000
8	222.29690000	2.86320000	0.00000000
9	256.76620000	0.40410000	0.00000000
10	276.06130000	0.47710000	0.00000000
11	293.34820000	0.16270000	0.00000000
12	338.95570000	37.46870000	0.00000000
13	361.90340000	1.51370000	0.00000000
14	366.40280000	0.88100000	0.00000000
15	391.73480000	12.01720000	0.00000000
16	415.52530000	0.55320000	0.00000000
17	448.69440000	0.45820000	0.00000000
18	453.47150000	1.77080000	0.00000000
19	518.48020000	1.39830000	0.00000000
20	540.26600000	1.08940000	0.00000000
21	641.54970000	89.38810000	0.00000000
22	675.69770000	11.21930000	0.00000000
23	706.15040000	4.00060000	0.00000000
24	747.85530000	7.77270000	0.00000000
25	769.52520000	4.05430000	0.00000000
26	828.32040000	13.49300000	0.00000000
27	880.62890000	12.95380000	0.00000000
28	927.59810000	28.69280000	0.00000000
29	949.41210000	11.26610000	0.00000000
30	965.16600000	13.88230000	0.00000000
31	1020.83960000	41.33700000	0.00000000
32	1049.67940000	45.08930000	0.00000000
33	1062.29860000	0.79730000	0.00000000
34	1078.45440000	0.18990000	0.00000000
35	1100.76030000	30.70550000	0.00000000
36	1142.88070000	1.76180000	0.00000000
37	1153.36550000	11.44430000	0.00000000
38	1203.43070000	0.26940000	0.00000000
39	1214.45400000	29.21020000	0.00000000
40	1236.97920000	22.21690000	0.00000000
41	1267.96070000	1.44810000	0.00000000
42	1295.50770000	1.74600000	0.00000000
43	1309.57110000	30.60200000	0.00000000
44	1359.71590000	326.85580000	0.00000000
45	1366.89000000	1.83640000	0.00000000
46	1377.96150000	3.74980000	0.00000000
47	1406.18650000	16.76140000	0.00000000
48	1428.36700000	6.56390000	0.00000000
49	1439.18680000	26.26420000	0.00000000
50	1455.46120000	5.34350000	0.00000000
51	1457.04430000	2.43820000	0.00000000
52	1479.81340000	0.46460000	0.00000000
53	1481.19910000	0.75920000	0.00000000
54	1488.55630000	1.45570000	0.00000000
55	1493.34180000	1.21940000	0.00000000
56	1499.46490000	6.83380000	0.00000000
57	1507.83760000	5.97110000	0.00000000
58	1516.43200000	27.62750000	0.00000000
59	1520.52160000	45.46300000	0.00000000
60	1530.72020000	46.65890000	0.00000000

61	1771.35830000	84.14670000	0.00000000
62	1848.26400000	207.57850000	0.00000000
63	3046.06510000	3.47560000	0.00000000
64	3064.97030000	8.49160000	0.00000000
65	3073.46030000	0.04690000	0.00000000
66	3074.30250000	0.85020000	0.00000000
67	3078.11900000	0.75230000	0.00000000
68	3082.00270000	6.06990000	0.00000000
69	3086.91720000	0.99670000	0.00000000
70	3109.31250000	4.17020000	0.00000000
71	3143.45780000	1.86490000	0.00000000
72	3162.27410000	0.12660000	0.00000000
73	3165.92680000	0.28910000	0.00000000
74	3168.07990000	1.09560000	0.00000000
75	3172.25200000	1.39130000	0.00000000
76	3178.31240000	0.44010000	0.00000000
77	3187.74740000	1.31160000	0.00000000
78	3683.34880000	92.63480000	0.00000000

S6. CALCULATIONS ON 4 - H ($E+ZPE=4.9$ KJ MOL⁻¹) \rightarrow 4 - H ($E+ZPE=4.2$ KJ MOL⁻¹) (TS)

```

Route                : # opt=(calcfc.ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper
                    : sion=gd3bj int=ultrafine pop=regular
SMILES               : C[N](C)(C)CCCC(=O)C(=O)O
Formula              : C8H16NO3+
Charge               : 1
Multiplicity         : 1
Energy               : -594.94234695 a.u.
Gibbs Energy        : -594.73701500 a.u.
Number of imaginary frequencies : 1

```

S6.1. Cartesian Co-ordinates (XYZ format)

28

```

C -0.97135699 0.20096099 -0.37721801
H -0.37418699 0.70859802 0.37789801
H -0.94646299 0.80471802 -1.28234506
C -0.43279201 -1.19558096 -0.64880198
H -0.99297100 -1.67956603 -1.44658005
H -0.49234700 -1.82309902 0.23908500
C 1.04018795 -1.09901202 -1.07128406
H 1.17699301 -0.42311001 -1.91162205
H 1.38362002 -2.08952689 -1.37607205
N -2.40380406 0.27103400 0.13451400
C -2.75593805 1.72105503 0.31310701
H -3.77434993 1.79159606 0.68304801
H -2.06845307 2.16388893 1.02745903
H -2.67122507 2.22402596 -0.64541298

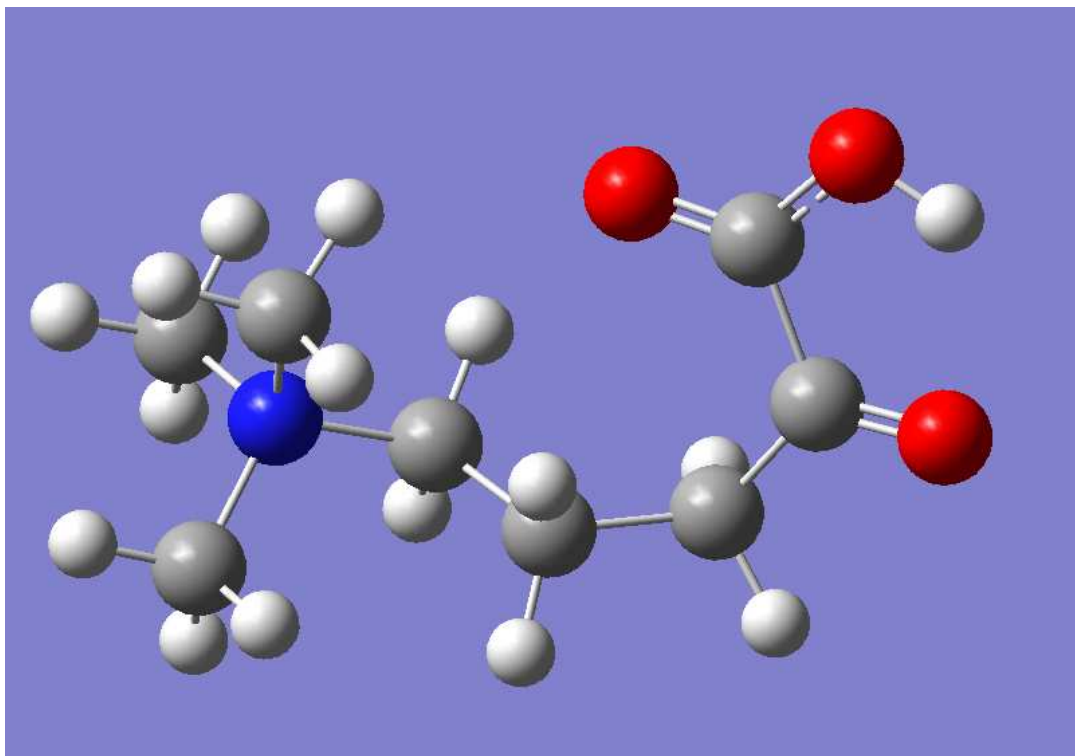
```

C -3.35642910 -0.34152499 -0.84955400
H -3.22902608 0.14632601 -1.81154096
H -3.15175700 -1.40240097 -0.93655300
H -4.36957121 -0.19204900 -0.48850799
C -2.53171301 -0.42403901 1.45925403
H -1.80999804 0.00214200 2.14978600
H -3.54007101 -0.27217600 1.83233500
H -2.34375596 -1.48357296 1.33099604
C 1.91873896 -0.67218202 0.08018100
O 1.90097296 -1.20436895 1.16593003
C 2.81349111 0.56603599 -0.13193800
O 2.62795591 1.31523097 -1.05175197
O 3.71985197 0.75068003 0.81851500
H 3.62565708 0.04754900 1.48383403

S6.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-38.45260000	3.21490000	0.00000000
2	18.33380000	0.44760000	0.00000000
3	49.12150000	1.13880000	0.00000000
4	77.06760000	11.63900000	0.00000000
5	114.08090000	2.97070000	0.00000000
6	162.29640000	2.20130000	0.00000000
7	216.04400000	1.49490000	0.00000000
8	234.36230000	0.53850000	0.00000000
9	271.31300000	28.34140000	0.00000000
10	278.02210000	2.33400000	0.00000000
11	290.15210000	0.45600000	0.00000000
12	317.27070000	13.36390000	0.00000000
13	359.57010000	0.47350000	0.00000000
14	361.84610000	1.70210000	0.00000000
15	386.84560000	4.22720000	0.00000000
16	435.42140000	11.50230000	0.00000000
17	448.88710000	0.52950000	0.00000000
18	452.96900000	0.66200000	0.00000000
19	526.84670000	2.59850000	0.00000000
20	550.41280000	5.11960000	0.00000000
21	639.21590000	38.51150000	0.00000000
22	661.26110000	63.46580000	0.00000000
23	746.97840000	6.57120000	0.00000000
24	756.00350000	1.57360000	0.00000000
25	765.30910000	1.63740000	0.00000000
26	843.58690000	9.99000000	0.00000000
27	882.37740000	17.96270000	0.00000000
28	930.74100000	31.31750000	0.00000000
29	952.30900000	8.01190000	0.00000000
30	961.76430000	11.11800000	0.00000000
31	996.18570000	35.47390000	0.00000000
32	1061.58480000	4.60750000	0.00000000
33	1067.32410000	6.18700000	0.00000000
34	1078.22910000	0.22730000	0.00000000
35	1102.36360000	53.14200000	0.00000000
36	1144.91310000	0.62760000	0.00000000
37	1155.07560000	27.99370000	0.00000000
38	1210.05210000	1.17760000	0.00000000
39	1226.09160000	5.76380000	0.00000000
40	1227.80210000	58.69180000	0.00000000
41	1268.95930000	2.38030000	0.00000000
42	1295.41440000	0.58970000	0.00000000
43	1300.68580000	24.05060000	0.00000000
44	1361.59620000	126.86690000	0.00000000
45	1362.35140000	199.27660000	0.00000000
46	1378.57690000	3.78600000	0.00000000
47	1402.28590000	30.29320000	0.00000000
48	1429.59910000	4.11990000	0.00000000
49	1454.66080000	5.35280000	0.00000000
50	1456.50080000	2.78090000	0.00000000
51	1477.80950000	13.46970000	0.00000000
52	1480.39240000	1.26930000	0.00000000
53	1482.18030000	0.10840000	0.00000000
54	1491.67710000	1.20750000	0.00000000
55	1493.06410000	1.85920000	0.00000000
56	1500.86670000	5.26060000	0.00000000
57	1509.87330000	2.93290000	0.00000000
58	1515.84890000	24.23150000	0.00000000
59	1518.50890000	37.98640000	0.00000000
60	1530.11440000	53.25070000	0.00000000

61	1781.50290000	65.80610000	0.00000000
62	1833.86930000	208.34010000	0.00000000
63	3056.88250000	2.60520000	0.00000000
64	3065.12850000	4.48500000	0.00000000
65	3073.21820000	1.21700000	0.00000000
66	3077.82740000	4.01210000	0.00000000
67	3078.42350000	4.98280000	0.00000000
68	3084.44770000	0.25170000	0.00000000
69	3105.34670000	0.79550000	0.00000000
70	3124.56080000	0.13830000	0.00000000
71	3132.02100000	6.99990000	0.00000000
72	3163.21530000	0.08010000	0.00000000
73	3164.08990000	0.01400000	0.00000000
74	3168.29860000	0.70960000	0.00000000
75	3169.93480000	1.97410000	0.00000000
76	3179.57380000	0.12120000	0.00000000
77	3184.09670000	0.97710000	0.00000000
78	3677.53600000	96.90220000	0.00000000

S7. CALCULATIONS ON 4 - H (E+ZPE=4.2 KJ MOL⁻¹)

```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N](C)(C)CCCC(=O)C(=O)O
Formula              : C8H16NO3+
Charge               : 1
Multiplicity         : 1
Energy               : -594.94722832
Gibbs Energy        : -594.74162800
Number of imaginary frequencies : 0

```

a.u.
a.u.

S7.1. Cartesian Co-ordinates (XYZ format)

28

```

C -1.15230298  0.55184799  0.63946301
H -0.64927500 -0.23627900  1.18812001
H -1.57844305  1.26761901  1.34036803
C -0.16598700  1.24152398 -0.29392901
H -0.58218598  2.17634511 -0.66432101
H  0.04131100  0.62179601 -1.16369498
C  1.15917802  1.55533004  0.44430000
H  1.02155304  1.47090697  1.52660406
H  1.48087096  2.57461691  0.24734700
N -2.33779407 -0.12247200 -0.03683500
C -3.20292592 -0.70387602  1.04440796
H -4.06032181 -1.18714905  0.58583999
H -2.62056303 -1.42982399  1.60357594
H -3.53305006  0.09610600  1.70021498

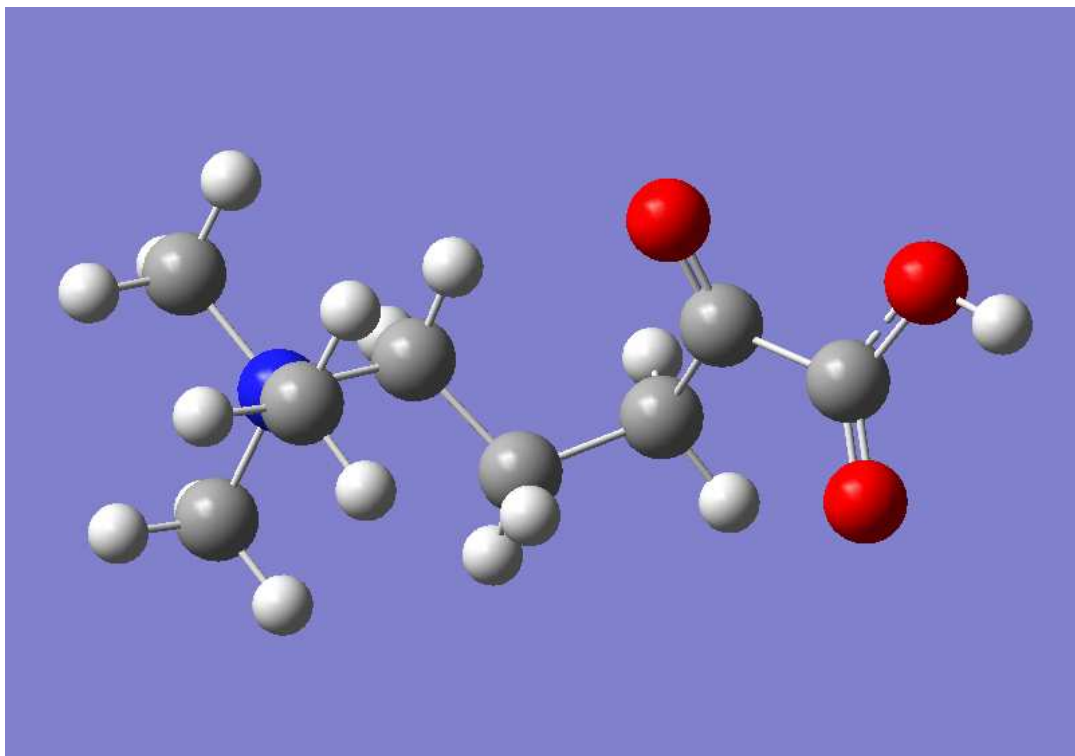
```


C -3.13979793 0.86450499 -0.82868600
H -3.46143198 1.66620004 -0.17002501
H -2.52808189 1.26224101 -1.63085902
H -4.00477886 0.35669199 -1.24509501
C -1.88101804 -1.24189901 -0.93216002
H -1.21575499 -1.89043701 -0.37206399
H -2.75838804 -1.78355300 -1.27242303
H -1.35660505 -0.82887000 -1.78578699
C 2.32229805 0.66672599 0.07306500
O 3.40852094 1.08883405 -0.23532701
C 2.13500404 -0.87250000 0.09756700
O 1.08932900 -1.40150797 0.38599199
O 3.22519803 -1.53351796 -0.23420000
H 3.93126106 -0.88340300 -0.41526800

S7.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	37.64770000	0.21270000	0.00000000
2	44.22820000	0.94430000	0.00000000
3	68.40430000	4.40700000	0.00000000
4	92.31350000	7.56540000	0.00000000
5	147.53240000	1.25750000	0.00000000
6	193.14800000	10.57290000	0.00000000
7	199.56900000	3.48070000	0.00000000
8	226.81580000	3.67220000	0.00000000
9	249.92520000	2.53760000	0.00000000
10	282.01900000	2.08110000	0.00000000
11	294.82080000	0.43870000	0.00000000
12	317.03490000	16.56050000	0.00000000
13	367.44940000	4.94250000	0.00000000
14	368.89670000	2.01510000	0.00000000
15	383.38780000	12.62620000	0.00000000
16	447.93750000	3.75700000	0.00000000
17	454.45400000	5.01570000	0.00000000
18	455.50170000	0.13600000	0.00000000
19	515.96050000	3.72400000	0.00000000
20	571.28090000	6.71960000	0.00000000
21	585.56370000	5.21380000	0.00000000
22	725.04390000	59.54380000	0.00000000
23	741.57750000	33.31810000	0.00000000
24	755.14270000	6.25500000	0.00000000
25	786.69670000	2.14000000	0.00000000
26	802.32680000	22.25160000	0.00000000
27	888.79430000	15.54100000	0.00000000
28	935.30240000	34.69460000	0.00000000
29	946.64670000	6.17370000	0.00000000
30	966.50600000	15.04000000	0.00000000
31	1011.97070000	19.40610000	0.00000000
32	1059.25720000	13.39440000	0.00000000
33	1068.63600000	1.58660000	0.00000000
34	1079.42460000	0.13530000	0.00000000
35	1122.44040000	35.96220000	0.00000000
36	1148.76300000	1.84410000	0.00000000
37	1166.05530000	26.46390000	0.00000000
38	1219.88200000	3.31500000	0.00000000
39	1224.51680000	16.76670000	0.00000000
40	1256.70580000	65.61990000	0.00000000
41	1272.78340000	39.30590000	0.00000000
42	1296.66280000	2.27400000	0.00000000
43	1309.01320000	18.55220000	0.00000000
44	1358.85750000	2.38930000	0.00000000
45	1367.44340000	8.82450000	0.00000000
46	1381.64960000	17.01140000	0.00000000
47	1395.29660000	321.08560000	0.00000000
48	1431.24590000	2.44130000	0.00000000
49	1455.57330000	4.37380000	0.00000000
50	1458.48920000	3.13560000	0.00000000
51	1468.30040000	12.79260000	0.00000000
52	1478.56870000	0.47970000	0.00000000
53	1481.67590000	1.33560000	0.00000000
54	1492.12830000	1.98780000	0.00000000
55	1494.08940000	3.02900000	0.00000000
56	1505.69500000	9.51920000	0.00000000
57	1510.50600000	5.39170000	0.00000000
58	1517.13230000	30.93130000	0.00000000
59	1521.64440000	55.97660000	0.00000000
60	1533.16900000	42.05260000	0.00000000

61	1792.21490000	66.16670000	0.00000000
62	1818.61490000	361.25510000	0.00000000
63	3030.68700000	1.95350000	0.00000000
64	3069.61950000	7.56740000	0.00000000
65	3073.39410000	0.21840000	0.00000000
66	3077.12610000	1.06930000	0.00000000
67	3080.35370000	6.98180000	0.00000000
68	3087.04130000	5.17000000	0.00000000
69	3107.39270000	8.98010000	0.00000000
70	3122.32270000	1.70870000	0.00000000
71	3158.30880000	3.01850000	0.00000000
72	3161.22370000	0.51400000	0.00000000
73	3166.63660000	1.60150000	0.00000000
74	3168.66150000	0.53330000	0.00000000
75	3173.21650000	0.39920000	0.00000000
76	3176.67710000	1.41900000	0.00000000
77	3186.93730000	4.58760000	0.00000000
78	3610.84130000	129.91890000	0.00000000

S8. CALCULATIONS ON 4-H \rightarrow 4-H (E+ZPE=10.3 KJ MOL⁻¹) (TS)

```

Route                : # opt=(calcf,ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper
                    : sion=gd3bj int=ultrafine pop=regular
SMILES               : C[N](C)(C)CCCC(=O)C(=O)O
Formula              : C8H16NO3+
Charge               : 1
Multiplicity         : 1
Energy               : -594.94298558 a.u.
Gibbs Energy        : -594.73782800 a.u.
Number of imaginary frequencies : 1

```

S8.1. Cartesian Co-ordinates (XYZ format)

28

```

C -1.29288006 0.01322000 0.71806002
H -0.80620998 -0.95784998 0.69720000
H -1.66709995 0.18824001 1.72529995
C -0.31490999 1.11080003 0.32071000
H -0.71279001 2.09186006 0.57545000
H -0.12426000 1.11040998 -0.75238001
C 1.03175998 0.92786998 1.05036998
H 0.86646003 0.75274003 2.11547995
H 1.62085998 1.83264995 0.93842000
N -2.52517009 -0.11938000 -0.16764000
C -3.41856003 -1.15867996 0.44674999
H -4.29274988 -1.28846002 -0.18425000
H -2.86881995 -2.09208989 0.52108002
H -3.71875000 -0.82393998 1.43499005

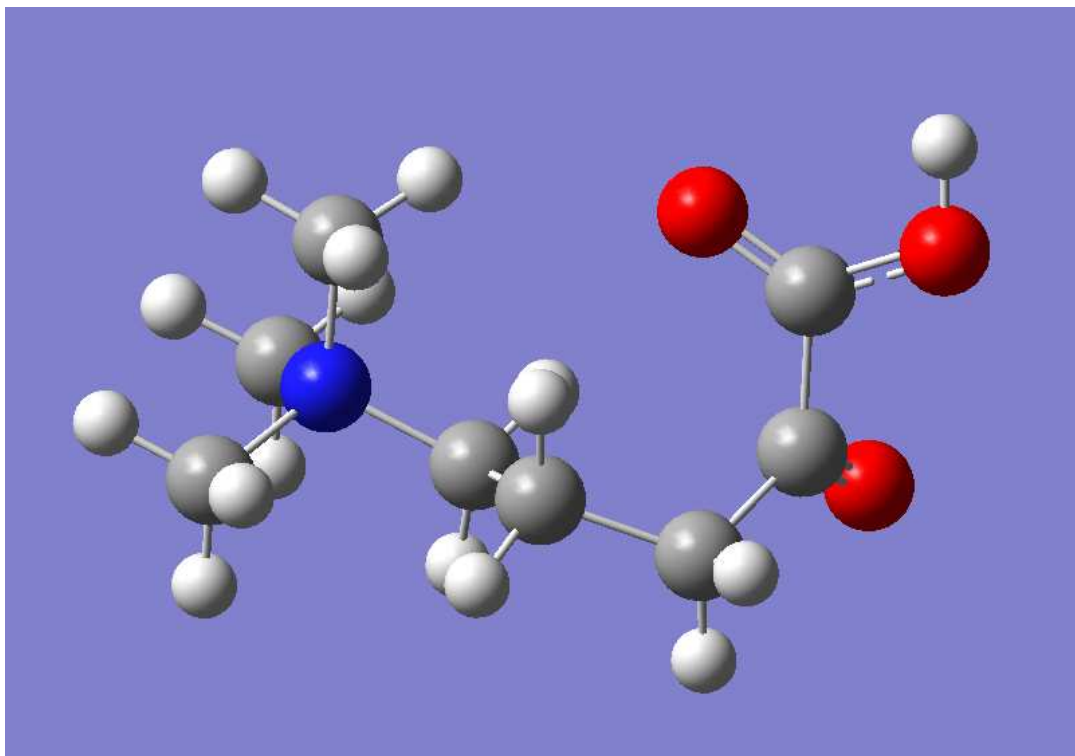
```

C -3.27152991 1.17743003 -0.25674999
H -3.51997995 1.50860000 0.74743003
H -2.65049005 1.91612995 -0.75095999
H -4.17970991 1.01768005 -0.83039999
C -2.13761997 -0.57683003 -1.54419005
H -1.57025003 -1.49862003 -1.45780003
H -3.04278994 -0.74527001 -2.11989999
H -1.53719997 0.18700001 -2.02431011
C 1.79418004 -0.26086000 0.50108999
O 1.38113999 -1.39347005 0.54847997
C 3.08266997 0.07321000 -0.26993999
O 3.19935989 1.12505996 -0.84355998
O 3.95852995 -0.92357999 -0.26299000
H 4.72897005 -0.66439003 -0.79385000

S8.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-25.78720000	1.85940000	0.00000000
2	24.78120000	0.70920000	0.00000000
3	38.75650000	6.61530000	0.00000000
4	58.20340000	2.85270000	0.00000000
5	134.34580000	0.69940000	0.00000000
6	164.14700000	7.10760000	0.00000000
7	217.17720000	2.97300000	0.00000000
8	242.48410000	2.70890000	0.00000000
9	251.16130000	4.51220000	0.00000000
10	279.63350000	1.07900000	0.00000000
11	293.44480000	2.14610000	0.00000000
12	296.43520000	3.84720000	0.00000000
13	361.26550000	0.13280000	0.00000000
14	365.15330000	0.23050000	0.00000000
15	382.65080000	0.48300000	0.00000000
16	407.10810000	3.48400000	0.00000000
17	450.04210000	0.24580000	0.00000000
18	452.43660000	0.55620000	0.00000000
19	524.47400000	2.79420000	0.00000000
20	559.44570000	23.55700000	0.00000000
21	605.11590000	63.89760000	0.00000000
22	686.74290000	85.93330000	0.00000000
23	720.24870000	52.59090000	0.00000000
24	752.11150000	6.21970000	0.00000000
25	796.86590000	11.61100000	0.00000000
26	842.47390000	7.06510000	0.00000000
27	876.00820000	18.69920000	0.00000000
28	920.66010000	21.03760000	0.00000000
29	950.97190000	7.11550000	0.00000000
30	965.22140000	17.29920000	0.00000000
31	1013.51000000	52.94630000	0.00000000
32	1039.77400000	40.49560000	0.00000000
33	1072.27570000	6.80340000	0.00000000
34	1078.82870000	0.20090000	0.00000000
35	1105.91400000	98.77440000	0.00000000
36	1143.13300000	3.78890000	0.00000000
37	1150.80820000	29.10380000	0.00000000
38	1196.38960000	103.65240000	0.00000000
39	1208.06410000	5.83580000	0.00000000
40	1244.24910000	4.72040000	0.00000000
41	1271.12190000	2.63050000	0.00000000
42	1295.10110000	0.89190000	0.00000000
43	1304.11650000	6.60830000	0.00000000
44	1350.27090000	1.76100000	0.00000000
45	1371.98780000	30.11920000	0.00000000
46	1378.71360000	13.17560000	0.00000000
47	1409.99640000	11.42600000	0.00000000
48	1429.75840000	2.64310000	0.00000000
49	1454.29870000	5.75970000	0.00000000
50	1456.11660000	2.81950000	0.00000000
51	1478.25670000	14.72360000	0.00000000
52	1482.04210000	0.24710000	0.00000000
53	1486.29150000	0.85220000	0.00000000
54	1491.98820000	0.35710000	0.00000000
55	1494.70360000	1.44440000	0.00000000
56	1506.46800000	8.72640000	0.00000000
57	1510.22560000	9.74590000	0.00000000
58	1517.35980000	22.02580000	0.00000000
59	1523.84220000	45.34770000	0.00000000
60	1534.48290000	40.37090000	0.00000000

61	1788.95180000	71.22820000	0.00000000
62	1801.98870000	281.46280000	0.00000000
63	3050.37490000	0.49820000	0.00000000
64	3058.31860000	12.52350000	0.00000000
65	3072.96280000	0.31930000	0.00000000
66	3076.84720000	1.22080000	0.00000000
67	3077.78790000	5.12420000	0.00000000
68	3084.16960000	1.67430000	0.00000000
69	3097.38000000	10.62070000	0.00000000
70	3138.62310000	6.98200000	0.00000000
71	3141.07050000	0.49640000	0.00000000
72	3162.01340000	0.18600000	0.00000000
73	3164.15180000	0.08040000	0.00000000
74	3168.22070000	1.40470000	0.00000000
75	3169.57180000	1.21580000	0.00000000
76	3176.66430000	0.33520000	0.00000000
77	3182.95950000	1.56550000	0.00000000
78	3718.58340000	123.94530000	0.00000000

S9. CALCULATIONS ON 4 - H (E+ZPE=10.3 KJ MOL⁻¹) (TS)

```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N](C)(C)CCCC(=O)C(=O)O
Formula              : C8H16NO3+
Charge               : 1
Multiplicity         : 1
Energy               : -594.94445421 a.u.
Gibbs Energy         : -594.74040800 a.u.
Number of imaginary frequencies : 0

```

S9.1. Cartesian Co-ordinates (XYZ format)

28

```

C  0.97430003 -0.65806001  0.27702001
H  0.36719000 -0.09973000  0.98422003
H  1.27302003 -1.59508002  0.74369001
C  0.19983000 -0.90998000 -1.00755000
H  0.74251997 -1.58942997 -1.66336000
H  0.04099000  0.02073000 -1.54472995
C -1.16518998 -1.54718006 -0.69111001
H -1.05078995 -2.53655005 -0.24945000
H -1.71413004 -1.66462004 -1.62898004
N  2.24804997  0.16017000  0.12352000
C  2.85597992  0.31312999  1.48835003
H  3.77571988  0.88345999  1.40065002
H  2.15193009  0.83741999  2.12733006
H  3.06544995 -0.67223001  1.89365005

```

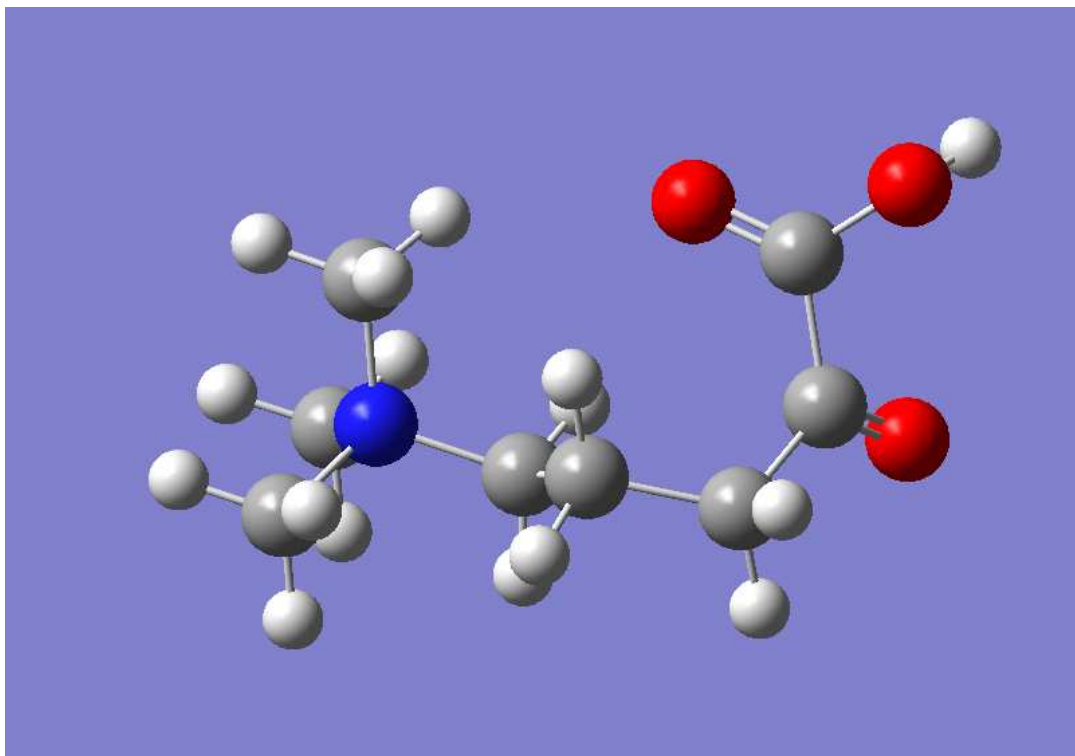

C 3.22885990 -0.53381997 -0.77221000
H 3.43586993 -1.52126002 -0.36969000
H 2.80944991 -0.61563998 -1.76856995
H 4.14247990 0.05227000 -0.80659002
C 1.94332004 1.52888000 -0.42131001
H 1.14418006 1.97044003 0.16473000
H 2.84742999 2.12705994 -0.36133000
H 1.62955999 1.44256997 -1.45472002
C -2.03120995 -0.74835002 0.26236001
O -2.45198011 -1.18658996 1.29969001
C -2.28297997 0.72965997 -0.06995000
O -1.36749995 1.51991999 -0.12489000
O -3.56416988 1.01898003 -0.22018000
H -3.66540003 1.97528994 -0.36205000

S9.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	30.11460000	0.83380000	0.00000000
2	38.01860000	1.83340000	0.00000000
3	53.51850000	4.71740000	0.00000000
4	72.71500000	6.63960000	0.00000000
5	126.09270000	2.88140000	0.00000000
6	175.61840000	0.10730000	0.00000000
7	209.71690000	4.50820000	0.00000000
8	231.62780000	3.15460000	0.00000000
9	247.90070000	0.42350000	0.00000000
10	272.20710000	0.48670000	0.00000000
11	275.61180000	1.25530000	0.00000000
12	291.69450000	0.32890000	0.00000000
13	345.65600000	0.92600000	0.00000000
14	362.25720000	0.36040000	0.00000000
15	368.76110000	0.02440000	0.00000000
16	398.79520000	2.29940000	0.00000000
17	447.64510000	0.23360000	0.00000000
18	457.47760000	0.36890000	0.00000000
19	522.27970000	6.06130000	0.00000000
20	560.64240000	45.95130000	0.00000000
21	623.46360000	81.90260000	0.00000000
22	710.02040000	10.54070000	0.00000000
23	721.91450000	50.60000000	0.00000000
24	754.00540000	7.09800000	0.00000000
25	777.78330000	33.35380000	0.00000000
26	808.25240000	14.91370000	0.00000000
27	885.69630000	15.10930000	0.00000000
28	933.72160000	28.52820000	0.00000000
29	946.06940000	3.22950000	0.00000000
30	963.85220000	16.65750000	0.00000000
31	1001.34400000	37.11010000	0.00000000
32	1042.05350000	17.21820000	0.00000000
33	1072.96740000	4.56990000	0.00000000
34	1079.32880000	0.24910000	0.00000000
35	1116.03940000	40.43320000	0.00000000
36	1146.29150000	8.33430000	0.00000000
37	1166.43550000	109.16340000	0.00000000
38	1190.36470000	80.60820000	0.00000000
39	1229.70430000	0.49260000	0.00000000
40	1238.83970000	13.50010000	0.00000000
41	1269.81150000	2.64190000	0.00000000
42	1296.76970000	0.62250000	0.00000000
43	1298.26240000	0.92430000	0.00000000
44	1367.26100000	0.38430000	0.00000000
45	1369.41390000	2.95020000	0.00000000
46	1386.24300000	8.67910000	0.00000000
47	1414.89340000	51.63910000	0.00000000
48	1438.38470000	3.83430000	0.00000000
49	1456.65600000	3.72960000	0.00000000
50	1459.34220000	2.74660000	0.00000000
51	1472.24380000	12.46140000	0.00000000
52	1477.59900000	1.65670000	0.00000000
53	1480.77520000	2.06250000	0.00000000
54	1490.18690000	3.28460000	0.00000000
55	1493.56260000	1.46520000	0.00000000
56	1499.43500000	7.14010000	0.00000000
57	1509.54830000	2.50480000	0.00000000
58	1515.85500000	39.07240000	0.00000000
59	1518.12880000	36.55540000	0.00000000
60	1530.40020000	52.54630000	0.00000000

61	1773.05900000	385.84030000	0.00000000
62	1803.60800000	114.92490000	0.00000000
63	3040.64410000	2.76320000	0.00000000
64	3069.20930000	7.66990000	0.00000000
65	3073.46180000	0.09000000	0.00000000
66	3077.99400000	2.49950000	0.00000000
67	3080.32710000	5.15220000	0.00000000
68	3087.10210000	3.23510000	0.00000000
69	3096.82840000	0.71660000	0.00000000
70	3123.47350000	2.87900000	0.00000000
71	3140.45650000	3.78770000	0.00000000
72	3161.64770000	0.18510000	0.00000000
73	3166.93570000	1.22900000	0.00000000
74	3167.89990000	0.93130000	0.00000000
75	3174.57680000	0.55880000	0.00000000
76	3178.39760000	0.78620000	0.00000000
77	3186.91570000	2.92220000	0.00000000
78	3698.70830000	112.23790000	0.00000000

S10. CALCULATIONS ON 4 - H ($E+ZPE=10.3$ KJ MOL⁻¹) \rightarrow 4 - H ($E+ZPE=4.2$ KJ MOL⁻¹) (TS)



```

Route                : # opt=(calcfc.ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper
                    : sion=gd3bj int=ultrafine pop=regular
SMILES               : C[N](C)(C)CCCC(=O)C(=O)O
Formula              : C8H16NO3+
Charge               : 1
Multiplicity         : 1
Energy               : -594.92642229 a.u.
Gibbs Energy        : -594.72415600 a.u.
Number of imaginary frequencies : 1
  
```

S10.1. Cartesian Co-ordinates (XYZ format)

28

```

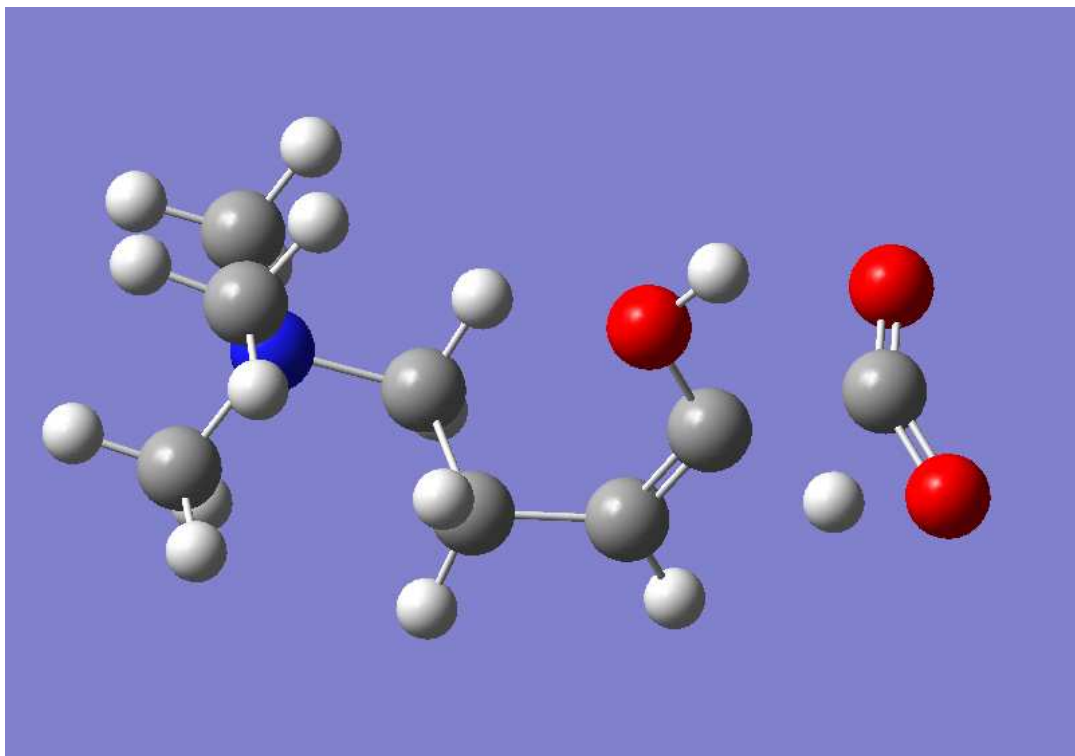
C -0.98923701 0.65206802 0.31440300
H -0.39228001 0.06377200 1.00546300
H -1.29008996 1.57304394 0.81073999
C -0.19761799 0.94983798 -0.94976097
H -0.73421699 1.65037799 -1.58813202
H -0.03296000 0.04022500 -1.52147806
C 1.15979195 1.57735598 -0.59553599
H 1.04329598 2.52954888 -0.07795700
H 1.69582295 1.78080702 -1.52716994
N -2.26633692 -0.15160400 0.11392800
C -2.89295411 -0.35137701 1.46415997
H -3.81493902 -0.91195500 1.34343004
H -2.20062995 -0.90410203 2.09187007
H -3.10179806 0.61953598 1.90327501
  
```

C	-3.23091888	0.58291298	-0.76721501
H	-3.43478703	1.55681002	-0.33147100
H	-2.79935098	0.69714499	-1.75514805
H	-4.14870214	0.00615700	-0.83336699
C	-1.96590602	-1.50146198	-0.47850800
H	-1.18534696	-1.97642303	0.10619400
H	-2.87803602	-2.09014297	-0.46080899
H	-1.63050199	-1.37863696	-1.50150096
C	2.07406092	0.72468400	0.25926101
O	2.65005398	1.13887095	1.23288202
C	2.24237204	-0.76284897	-0.07654500
O	1.30665100	-1.51449001	-0.01387500
O	3.48877192	-1.12322903	-0.43856001
H	4.05083704	-1.40285397	0.29613400

S10.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-632.03090000	113.80470000	0.00000000
2	33.42370000	0.15830000	0.00000000
3	34.25540000	1.27600000	0.00000000
4	58.44410000	9.25510000	0.00000000
5	74.79380000	5.93080000	0.00000000
6	133.97220000	3.37540000	0.00000000
7	178.56310000	1.67790000	0.00000000
8	203.97890000	11.45290000	0.00000000
9	230.93100000	2.55450000	0.00000000
10	248.55480000	1.68390000	0.00000000
11	273.06990000	2.12040000	0.00000000
12	278.44440000	3.27010000	0.00000000
13	292.92240000	0.46600000	0.00000000
14	332.64190000	7.65370000	0.00000000
15	363.10640000	0.38320000	0.00000000
16	368.50120000	0.15860000	0.00000000
17	408.53130000	1.42820000	0.00000000
18	447.91430000	0.30540000	0.00000000
19	456.99380000	0.87040000	0.00000000
20	521.57970000	5.04050000	0.00000000
21	570.42410000	26.69590000	0.00000000
22	677.71250000	22.22150000	0.00000000
23	709.38740000	30.24640000	0.00000000
24	755.17300000	2.99700000	0.00000000
25	769.86720000	7.14490000	0.00000000
26	803.63450000	12.70030000	0.00000000
27	878.68210000	6.12270000	0.00000000
28	926.19690000	63.10580000	0.00000000
29	943.77900000	3.31260000	0.00000000
30	963.87130000	17.70110000	0.00000000
31	998.15290000	34.65750000	0.00000000
32	1029.23600000	44.87570000	0.00000000
33	1068.66180000	219.06860000	0.00000000
34	1076.35360000	52.67150000	0.00000000
35	1079.17380000	4.61470000	0.00000000
36	1112.19100000	22.87530000	0.00000000
37	1146.97930000	2.57320000	0.00000000
38	1167.07110000	22.47580000	0.00000000
39	1215.45280000	18.89310000	0.00000000
40	1231.45910000	2.68320000	0.00000000
41	1267.78010000	3.97020000	0.00000000
42	1296.63040000	1.14800000	0.00000000
43	1297.91810000	2.29760000	0.00000000
44	1325.05190000	46.81600000	0.00000000
45	1367.69840000	0.75630000	0.00000000
46	1372.19510000	2.06840000	0.00000000
47	1385.59110000	1.58590000	0.00000000
48	1436.48750000	3.57960000	0.00000000
49	1456.06290000	3.56070000	0.00000000
50	1458.56450000	3.74630000	0.00000000
51	1466.36710000	13.25180000	0.00000000
52	1476.85810000	0.71760000	0.00000000
53	1480.81440000	1.97490000	0.00000000
54	1491.24430000	2.86330000	0.00000000
55	1493.44080000	1.73690000	0.00000000
56	1500.57100000	7.28690000	0.00000000
57	1509.88360000	2.50030000	0.00000000
58	1516.12920000	37.44710000	0.00000000
59	1518.30680000	39.26290000	0.00000000
60	1530.75100000	51.74000000	0.00000000

61	1789.43810000	71.10920000	0.00000000
62	1793.64890000	349.25120000	0.00000000
63	3034.54080000	2.95610000	0.00000000
64	3068.82760000	6.85810000	0.00000000
65	3073.48810000	0.11300000	0.00000000
66	3077.92040000	2.41410000	0.00000000
67	3080.25520000	5.17550000	0.00000000
68	3087.53000000	3.31650000	0.00000000
69	3090.46460000	0.76280000	0.00000000
70	3118.62940000	4.86650000	0.00000000
71	3140.40190000	2.68670000	0.00000000
72	3161.72870000	0.17830000	0.00000000
73	3167.03870000	1.23190000	0.00000000
74	3167.98440000	0.91210000	0.00000000
75	3174.64310000	0.58760000	0.00000000
76	3178.61070000	0.89430000	0.00000000
77	3187.77600000	2.88410000	0.00000000
78	3784.59850000	224.77720000	0.00000000

S11. CALCULATIONS ON 4 - H ($E+ZPE=4.9$ KJ MOL⁻¹) \rightarrow 9Z - H (TS)

```

Route : # opt=(calcf,ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper
       : sion=gd3bj int=ultrafine pop=regular
SMILES : C[N](C)(C)CCC=[C]O.[C](=O)O
Formula : C8H16NO3+
Charge : 1
Multiplicity : 1
Energy : -594.82740802 a.u.
Gibbs Energy : -594.63151800 a.u.
Number of imaginary frequencies : 1

```

S11.1. Cartesian Co-ordinates (XYZ format)

28

```

C 1.10143602 -0.02722200 -0.50868601
H 0.58857298 -0.87939799 -0.07189800
H 1.07610202 -0.12079800 -1.59197700
C 0.42885301 1.27116096 -0.06295300
H 0.82151598 2.12591100 -0.60910898
H 0.59636801 1.43605399 1.00177896
C -1.05119300 1.13306797 -0.29596499
H -1.50698602 1.66440904 -1.11896801
N 2.56532311 -0.18309399 -0.10849700
C 3.05904007 -1.47979701 -0.68294299
H 4.09834290 -1.61696899 -0.39952600
H 2.45427704 -2.29040194 -0.28776100
H 2.96954393 -1.44210994 -1.76433897
C 3.39457989 0.94045198 -0.65284300

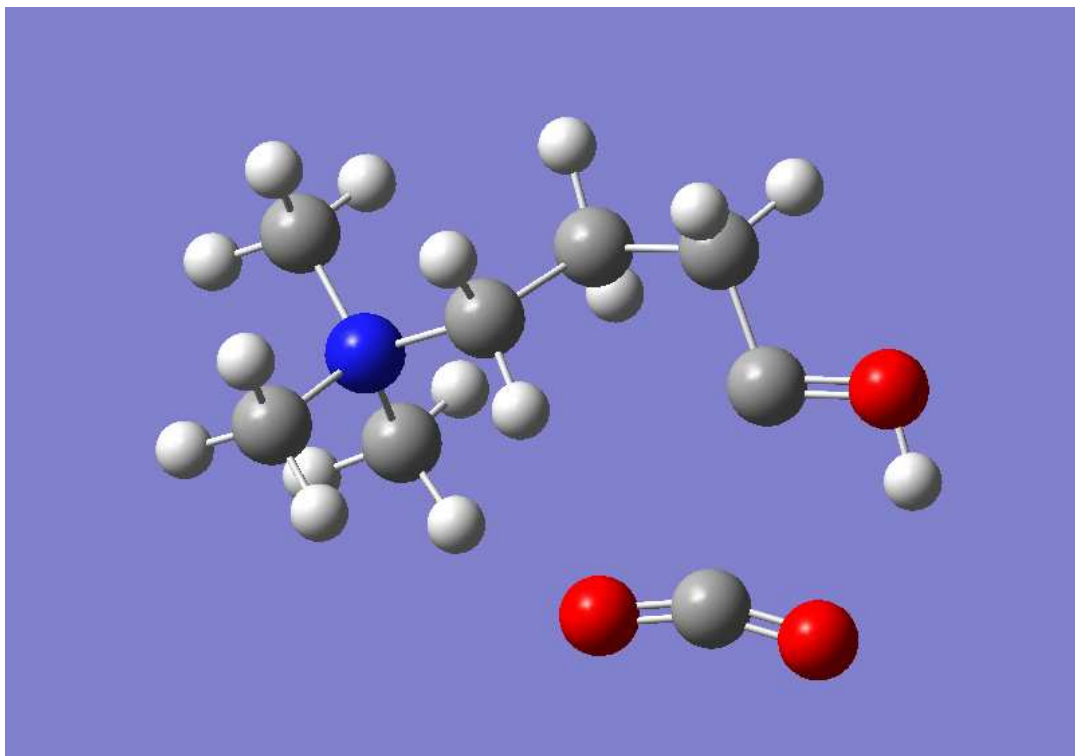
```


H	3.26547003	0.98175800	-1.73051703
H	3.07540703	1.87317598	-0.20170900
H	4.43650198	0.75284398	-0.41064101
C	2.70150900	-0.23599900	1.38557601
H	2.04505610	-1.01139402	1.76821697
H	3.73529410	-0.46114501	1.63004994
H	2.42656708	0.72333997	1.80771804
C	-1.83757997	0.36420199	0.48023000
O	-1.25287998	-0.33870500	1.49862099
C	-3.38849497	-0.39517200	-0.35247400
O	-4.13474989	0.60857099	-0.29170799
O	-3.29519892	-1.52289796	-0.64703101
H	-1.92004895	-0.81124902	2.00647807
H	-3.11819005	0.95501602	0.41041499

S11.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2036.23720000	698.15440000	0.00000000
2	25.05870000	0.24620000	0.00000000
3	40.49460000	2.63100000	0.00000000
4	47.34900000	1.04360000	0.00000000
5	83.03370000	0.87420000	0.00000000
6	117.71520000	1.21170000	0.00000000
7	128.16340000	0.51570000	0.00000000
8	173.82390000	9.42170000	0.00000000
9	224.32850000	2.77850000	0.00000000
10	243.79860000	1.33600000	0.00000000
11	273.03230000	5.94340000	0.00000000
12	288.30320000	33.00710000	0.00000000
13	294.70420000	18.69950000	0.00000000
14	308.87340000	10.58660000	0.00000000
15	363.16470000	0.26200000	0.00000000
16	376.65560000	39.43530000	0.00000000
17	384.67930000	38.95190000	0.00000000
18	442.56890000	32.61500000	0.00000000
19	450.48620000	1.83890000	0.00000000
20	473.35580000	19.77020000	0.00000000
21	525.20950000	13.12100000	0.00000000
22	603.45780000	53.98710000	0.00000000
23	648.03360000	33.89600000	0.00000000
24	693.69210000	589.67350000	0.00000000
25	713.91190000	30.32730000	0.00000000
26	762.38200000	11.90200000	0.00000000
27	809.02600000	26.12250000	0.00000000
28	838.94390000	14.67640000	0.00000000
29	895.60580000	66.26330000	0.00000000
30	950.17960000	16.52260000	0.00000000
31	961.48060000	22.87150000	0.00000000
32	988.60900000	2.37330000	0.00000000
33	1044.65170000	10.48500000	0.00000000
34	1065.14260000	18.83320000	0.00000000
35	1078.56600000	0.29620000	0.00000000
36	1102.71020000	118.78080000	0.00000000
37	1132.58930000	24.14270000	0.00000000
38	1147.68190000	2.53670000	0.00000000
39	1156.30690000	9.04960000	0.00000000
40	1222.37650000	30.71440000	0.00000000
41	1258.34170000	129.75950000	0.00000000
42	1263.09540000	503.92110000	0.00000000
43	1281.85000000	225.35800000	0.00000000
44	1292.21640000	6.50400000	0.00000000
45	1302.76780000	19.93660000	0.00000000
46	1336.58080000	12.81150000	0.00000000
47	1360.89250000	5.63080000	0.00000000
48	1376.18860000	2.60570000	0.00000000
49	1421.42440000	3.52090000	0.00000000
50	1454.60980000	5.42460000	0.00000000
51	1455.65180000	3.53670000	0.00000000
52	1478.31520000	0.40330000	0.00000000
53	1481.57550000	0.17540000	0.00000000
54	1489.71780000	1.87110000	0.00000000
55	1493.18780000	1.85800000	0.00000000
56	1496.55280000	2.32000000	0.00000000
57	1506.95780000	4.59760000	0.00000000
58	1515.89110000	26.25640000	0.00000000
59	1518.77130000	40.52350000	0.00000000
60	1530.00530000	48.80330000	0.00000000

61	1599.81820000	39.60740000	0.00000000
62	1728.73400000	68.78920000	0.00000000
63	2091.26850000	366.02590000	0.00000000
64	3054.53340000	11.02490000	0.00000000
65	3073.61410000	0.26210000	0.00000000
66	3077.57010000	0.28630000	0.00000000
67	3083.39890000	2.30560000	0.00000000
68	3088.55030000	3.76220000	0.00000000
69	3107.04170000	6.45110000	0.00000000
70	3145.35220000	1.39310000	0.00000000
71	3161.83610000	0.16410000	0.00000000
72	3164.60390000	0.18400000	0.00000000
73	3168.34980000	1.14250000	0.00000000
74	3170.01310000	2.16500000	0.00000000
75	3178.00770000	0.30190000	0.00000000
76	3184.26820000	1.36490000	0.00000000
77	3198.64140000	1.39470000	0.00000000
78	3817.63000000	128.67900000	0.00000000

S12. CALCULATIONS ON 4 - H ($E+ZPE=4.2 \text{ KJ MOL}^{-1}$) \rightarrow 7 - H_{5r} (TS)

```

Route                : # opt=(calcf,ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper
                    : sion=gd3bj int=ultrafine pop=regular
SMILES               : C[N](C)(C)CCC[C]O.C(=O)=O
Formula              : C8H16NO3+
Charge               : 1
Multiplicity         : 1
Energy               : -594.89355954 a.u.
Gibbs Energy         : -594.69146800 a.u.
Number of imaginary frequencies : 1

```

S12.1. Cartesian Co-ordinates (XYZ format)

28

```

C  0.97487998 -0.54194999  0.56317002
H  0.23702000  0.23412000  0.73961997
H  1.27831995 -0.96398002  1.51997006
C  0.39067000 -1.61907995 -0.33822000
H  1.02020001 -2.50748992 -0.35464999
H  0.30265000 -1.26260996 -1.36366999
C -1.01328003 -2.00025010  0.15413000
H -0.98550999 -2.28327990  1.21544003
H -1.39800000 -2.87315989 -0.37970001
N  2.19856000  0.18652000  0.02611000
C  2.59184003  1.21499002  1.04816997
H  3.47324991  1.74152005  0.69463003
H  1.76613998  1.90846002  1.17550004
H  2.80942011  0.71315998  1.98623002

```

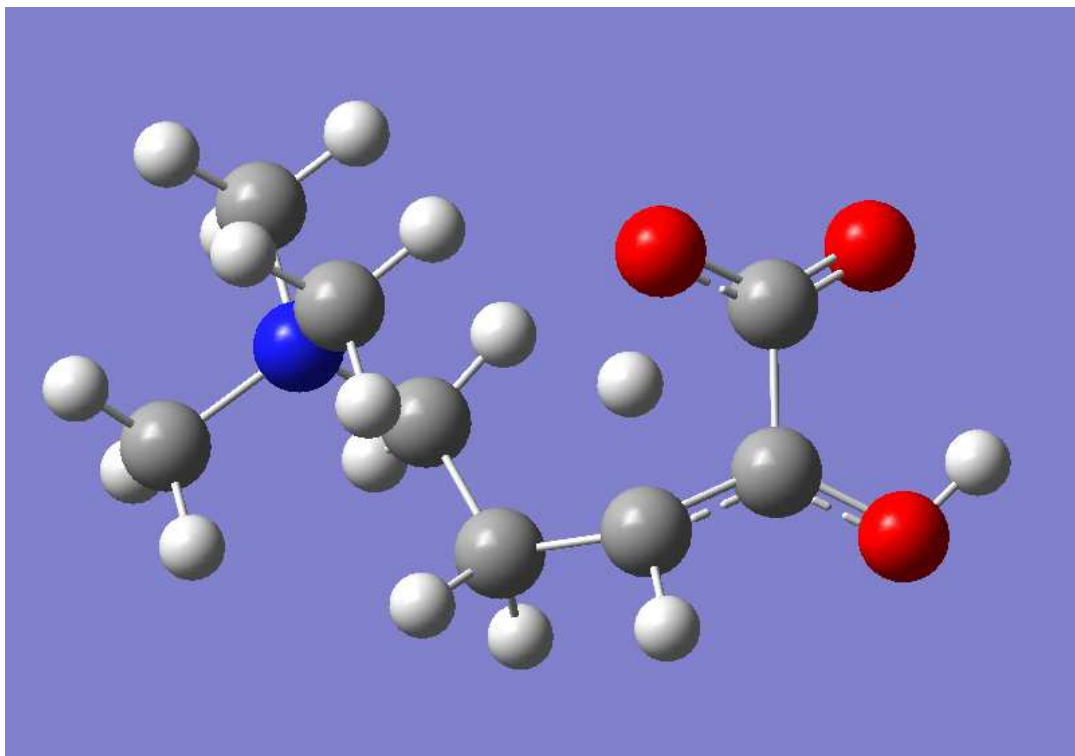
C 3.33772993 -0.76168001 -0.18641999
H 3.55852008 -1.26248002 0.75186002
H 3.06169009 -1.48890996 -0.94212002
H 4.20436001 -0.19791999 -0.51903999
C 1.88190997 0.89793003 -1.26003003
H 0.99940002 1.51091003 -1.10827994
H 2.73540998 1.51442003 -1.52579999
H 1.70615995 0.16790999 -2.04137993
C -1.95815003 -0.84709001 0.07400000
O -3.18192005 -1.22502005 0.05306000
C -2.15896010 1.48857999 -0.02953000
O -1.07185996 1.93578005 -0.00424000
O -3.33342004 1.43542004 -0.07351000
H -3.74128008 -0.41442001 0.01462000

S12.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-141.31050000	70.55440000	0.00000000
2	40.58060000	0.65240000	0.00000000
3	46.85140000	2.12840000	0.00000000
4	81.45230000	6.64440000	0.00000000
5	101.95730000	0.17910000	0.00000000
6	141.09040000	9.10730000	0.00000000
7	148.33390000	2.15860000	0.00000000
8	184.23200000	0.82570000	0.00000000
9	215.18710000	0.50430000	0.00000000
10	240.40910000	0.51620000	0.00000000
11	266.35530000	0.52670000	0.00000000
12	286.30450000	0.12700000	0.00000000
13	299.14000000	0.37800000	0.00000000
14	313.65320000	1.05710000	0.00000000
15	361.59360000	0.54100000	0.00000000
16	369.21310000	4.80570000	0.00000000
17	400.88770000	23.72800000	0.00000000
18	449.21120000	0.31770000	0.00000000
19	461.55880000	1.72670000	0.00000000
20	493.68620000	3.75280000	0.00000000
21	554.87800000	137.08880000	0.00000000
22	576.46940000	171.24140000	0.00000000
23	666.11880000	20.99030000	0.00000000
24	719.75190000	5.97980000	0.00000000
25	767.52990000	6.13420000	0.00000000
26	812.36180000	9.31370000	0.00000000
27	900.68390000	45.66140000	0.00000000
28	938.08500000	16.09530000	0.00000000
29	953.03260000	17.21210000	0.00000000
30	963.05470000	6.11950000	0.00000000
31	975.97860000	42.03620000	0.00000000
32	1044.36830000	9.33820000	0.00000000
33	1056.37630000	36.36050000	0.00000000
34	1080.09520000	5.94120000	0.00000000
35	1083.21540000	3.76770000	0.00000000
36	1131.68190000	6.62400000	0.00000000
37	1148.05790000	7.59260000	0.00000000
38	1195.45950000	5.14880000	0.00000000
39	1234.01860000	20.74120000	0.00000000
40	1269.23860000	1.84380000	0.00000000
41	1293.59650000	42.51410000	0.00000000
42	1296.05960000	23.05180000	0.00000000
43	1298.96820000	11.60170000	0.00000000
44	1347.21110000	2.84770000	0.00000000
45	1360.96620000	4.67700000	0.00000000
46	1379.68470000	8.90590000	0.00000000
47	1407.84610000	200.89530000	0.00000000
48	1422.08200000	15.21440000	0.00000000
49	1434.65530000	8.49520000	0.00000000
50	1456.12860000	5.14550000	0.00000000
51	1456.93340000	3.53730000	0.00000000
52	1482.46660000	64.92030000	0.00000000
53	1483.52280000	8.02540000	0.00000000
54	1485.88540000	4.16210000	0.00000000
55	1494.93080000	0.57750000	0.00000000
56	1497.13860000	3.00700000	0.00000000
57	1505.06450000	6.98300000	0.00000000
58	1511.75280000	4.71690000	0.00000000
59	1517.45260000	24.19860000	0.00000000
60	1524.72130000	42.40770000	0.00000000

61	1535.53890000	33.16140000	0.00000000
62	2256.45950000	629.28700000	0.00000000
63	2990.78750000	4.75910000	0.00000000
64	3051.05540000	4.33070000	0.00000000
65	3063.81880000	9.16750000	0.00000000
66	3072.52540000	0.25870000	0.00000000
67	3076.19670000	1.21220000	0.00000000
68	3078.53420000	7.46010000	0.00000000
69	3085.30970000	9.24140000	0.00000000
70	3103.01940000	10.85950000	0.00000000
71	3149.70310000	4.29210000	0.00000000
72	3160.74840000	0.19010000	0.00000000
73	3165.45050000	2.41780000	0.00000000
74	3168.57680000	0.45620000	0.00000000
75	3171.13830000	0.70110000	0.00000000
76	3175.39020000	1.38150000	0.00000000
77	3185.94260000	6.07610000	0.00000000
78	3438.18730000	168.89250000	0.00000000

S13. CALCULATIONS ON 4 - H (E+ZPE=4.2 KJ MOL⁻¹) → 4 - H (E+ZPE=69.2 KJ MOL⁻¹) (TS)



```

Route : # opt=(calcfc.ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper
       : sion=gd3bj int=ultrafine pop=regular
SMILES : C[N](C)(C)CC[CH][C](C(=O)O)O
Formula : C8H16NO3+
Charge : 1
Multiplicity : 1
Energy : -594.85857681 a.u.
Gibbs Energy : -594.65675200 a.u.
Number of imaginary frequencies : 1

```

S13.1. Cartesian Co-ordinates (XYZ format)

28

```

C -0.97816002 0.30653000 0.88477999
H -0.35964999 -0.57669997 0.97408998
H -1.39627004 0.53368998 1.86199999
C -0.19268000 1.51337004 0.36772001
H 0.07151000 2.11016989 1.24162996
H -0.83903003 2.15894008 -0.22449000
C 1.10035002 1.31436002 -0.46132001
H 1.37819004 2.25332999 -0.93103999
N -2.18570995 -0.12119000 0.04714000
C -2.65522003 -1.44408000 0.58504999
H -3.54909992 -1.74344003 0.04595000
H -1.86567998 -2.17470002 0.43860000
H -2.87752008 -1.33539999 1.64256001
C -3.29008007 0.88314998 0.19132000

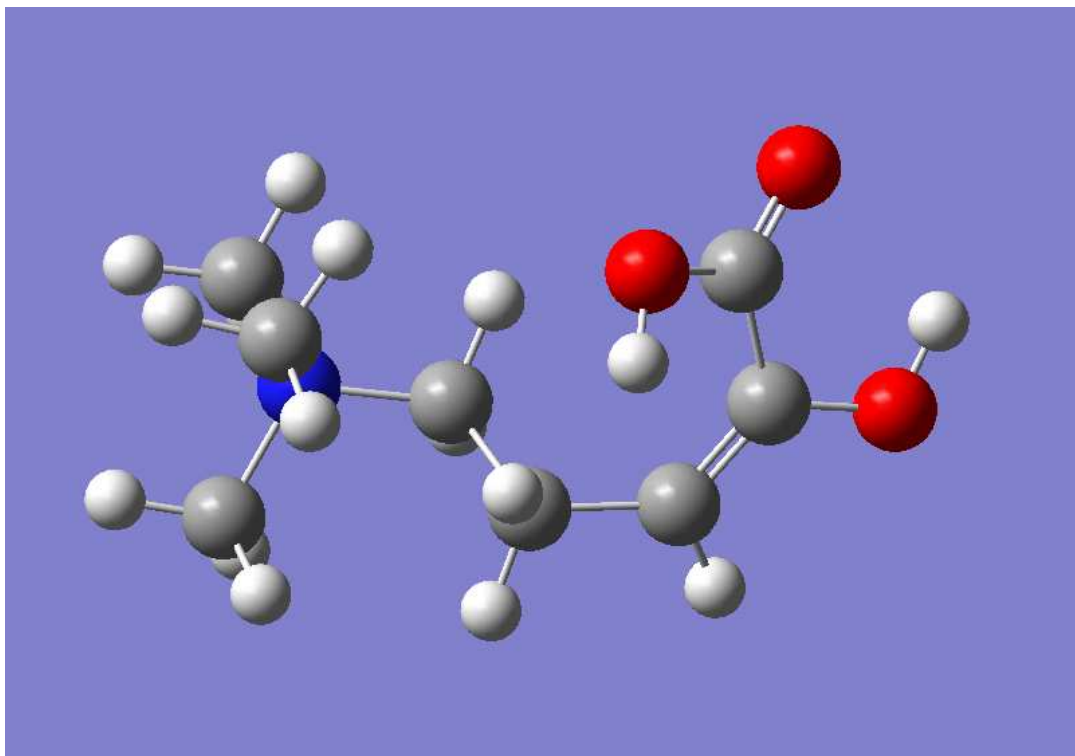
```


H	-3.55527997	0.96780002	1.24088001
H	-2.95789003	1.84375000	-0.18769000
H	-4.14675999	0.54277998	-0.38233000
C	-1.86148000	-0.29146001	-1.41046000
H	-1.10047996	-1.05515003	-1.51420999
H	-2.77212000	-0.58731002	-1.92260003
H	-1.51038003	0.65301001	-1.81225002
C	2.21191001	0.58113003	-0.02157000
O	3.41388988	1.02595997	0.10728000
C	2.02487993	-0.94220001	-0.01769000
O	2.84118009	-1.65190005	0.52494001
O	0.96929997	-1.20084000	-0.72103000
H	0.81844002	0.08832000	-1.05276000
H	4.00980997	0.25874999	0.25516000

S13.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-1664.77970000	1258.47020000	0.00000000
2	35.65870000	2.13000000	0.00000000
3	53.66370000	4.25040000	0.00000000
4	101.05340000	1.61890000	0.00000000
5	104.65370000	5.18990000	0.00000000
6	175.40280000	4.44810000	0.00000000
7	208.67550000	5.95360000	0.00000000
8	232.64660000	1.94530000	0.00000000
9	260.03290000	2.57030000	0.00000000
10	271.31460000	5.86700000	0.00000000
11	280.06990000	27.71350000	0.00000000
12	311.71170000	0.16930000	0.00000000
13	322.87820000	1.06280000	0.00000000
14	374.27320000	0.48460000	0.00000000
15	401.75180000	1.90170000	0.00000000
16	441.23030000	0.71540000	0.00000000
17	462.11350000	2.52370000	0.00000000
18	475.70740000	10.12740000	0.00000000
19	505.41250000	2.96450000	0.00000000
20	557.74310000	1.56630000	0.00000000
21	642.35800000	21.29260000	0.00000000
22	659.85170000	8.55050000	0.00000000
23	702.55270000	3.14680000	0.00000000
24	790.38130000	83.79120000	0.00000000
25	807.30220000	41.27970000	0.00000000
26	837.48110000	17.94290000	0.00000000
27	849.71690000	18.29360000	0.00000000
28	877.29790000	19.06050000	0.00000000
29	920.41510000	31.85460000	0.00000000
30	939.22580000	15.63760000	0.00000000
31	958.86090000	21.89520000	0.00000000
32	1001.74410000	1.73840000	0.00000000
33	1021.90780000	5.05800000	0.00000000
34	1079.13950000	10.41650000	0.00000000
35	1081.16010000	0.56610000	0.00000000
36	1141.04810000	0.31020000	0.00000000
37	1148.58350000	1.63430000	0.00000000
38	1205.20650000	85.92180000	0.00000000
39	1235.67720000	27.21010000	0.00000000
40	1248.80700000	15.20920000	0.00000000
41	1277.20850000	60.79490000	0.00000000
42	1290.68740000	50.66860000	0.00000000
43	1293.89640000	81.72700000	0.00000000
44	1307.31600000	16.98030000	0.00000000
45	1315.73270000	57.67490000	0.00000000
46	1379.30310000	20.79680000	0.00000000
47	1385.52950000	49.00810000	0.00000000
48	1436.88000000	174.62490000	0.00000000
49	1441.62200000	17.52030000	0.00000000
50	1455.84780000	4.56390000	0.00000000
51	1457.21930000	5.92910000	0.00000000
52	1480.15190000	7.24920000	0.00000000
53	1485.01500000	1.27330000	0.00000000
54	1488.27240000	4.22460000	0.00000000
55	1494.96340000	2.95560000	0.00000000
56	1499.46610000	3.51490000	0.00000000
57	1507.52200000	11.64480000	0.00000000
58	1516.48190000	26.43930000	0.00000000
59	1522.89470000	32.65050000	0.00000000
60	1533.72110000	64.62630000	0.00000000

61	1614.94840000	222.64340000	0.00000000
62	1733.60600000	135.40860000	0.00000000
63	1857.44750000	223.29410000	0.00000000
64	3052.40920000	5.58420000	0.00000000
65	3072.90110000	0.64920000	0.00000000
66	3077.99010000	0.65580000	0.00000000
67	3084.82490000	0.90200000	0.00000000
68	3090.90750000	15.95280000	0.00000000
69	3101.50880000	5.37370000	0.00000000
70	3122.41750000	0.19100000	0.00000000
71	3162.67620000	0.05580000	0.00000000
72	3165.44110000	0.65350000	0.00000000
73	3168.21110000	0.65430000	0.00000000
74	3169.57610000	1.88950000	0.00000000
75	3173.80190000	2.56240000	0.00000000
76	3177.27620000	1.22390000	0.00000000
77	3195.06340000	9.06140000	0.00000000
78	3526.95760000	201.08290000	0.00000000

S14. CALCULATIONS ON 4 - H (E+ZPE=69.2 KJ MOL⁻¹) (TS)

```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N](C)(C)CCC=C(C(=O)O)O
Formula              : C8H16NO3+
Charge               : 1
Multiplicity         : 1
Energy               : -594.92298110 a.u.
Gibbs Energy        : -594.71836800 a.u.
Number of imaginary frequencies : 0

```

S14.1. Cartesian Co-ordinates (XYZ format)

28

```

C -0.98919398 -0.21485101 -0.55980098
H -0.41402599 0.69764698 -0.43654999
H -1.07491004 -0.42393601 -1.62370205
C -0.30290699 -1.38261104 0.15056700
H -0.83415800 -2.31058002 -0.05105100
H -0.33813700 -1.24693704 1.23076105
C 1.10172105 -1.52947700 -0.38406301
H 1.27663600 -2.36702895 -1.04584503
N -2.39619493 0.13404700 -0.08184600
C -2.88624811 1.28313100 -0.91710299
H -3.88930702 1.54756200 -0.59594899
H -2.21637607 2.12668610 -0.77989799
H -2.89608192 0.98074800 -1.95987797
C -3.32802296 -1.02730298 -0.25495300

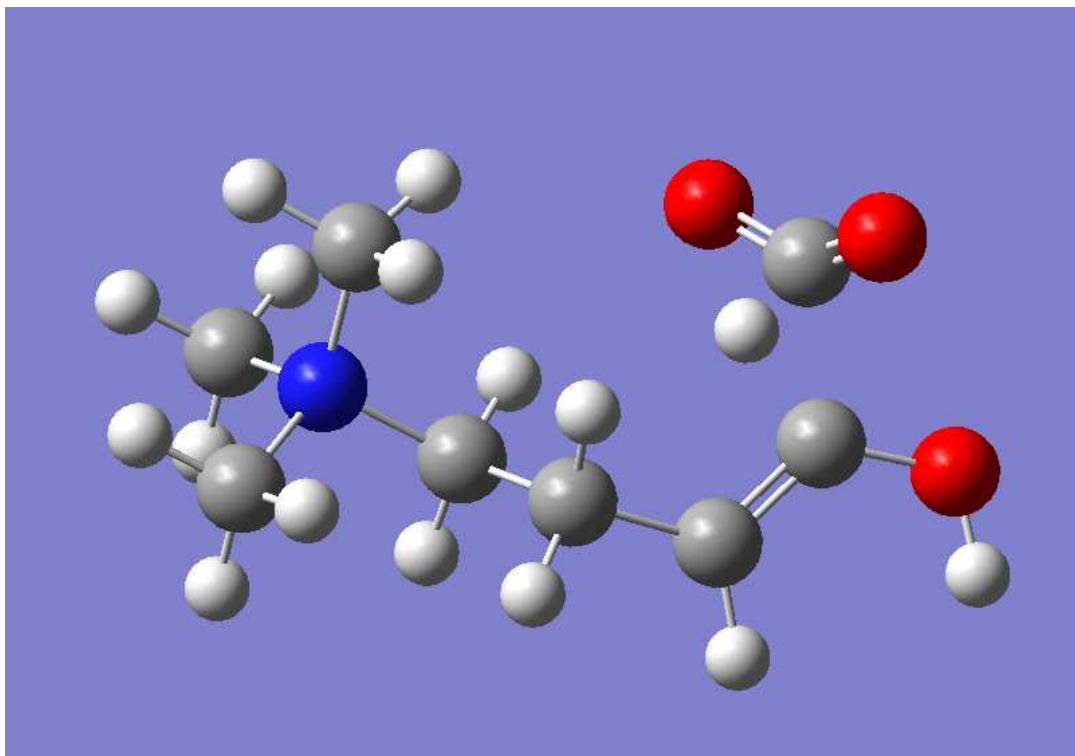
```

H -3.31513190 -1.33546805 -1.29637694
H -3.00735998 -1.84450305 0.38125500
H -4.32906580 -0.71467900 0.02725800
C -2.37654209 0.56099600 1.35751402
H -1.63017905 1.33996797 1.48259401
H -3.36113310 0.93614697 1.62014198
H -2.13562799 -0.29127100 1.98244905
C 2.13084698 -0.68149602 -0.23810300
O 3.28591704 -0.90149099 -0.89196002
C 2.12125492 0.61274701 0.52478403
O 2.78635406 1.54282606 0.16819200
O 1.31064999 0.70335197 1.60855496
H 1.13091302 -0.17997099 1.95255005
H 3.83884811 -0.10828800 -0.82150102

S14.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	34.95470000	5.21510000	0.00000000
2	41.21650000	5.14220000	0.00000000
3	54.09810000	0.20230000	0.00000000
4	98.01530000	0.40110000	0.00000000
5	120.23800000	0.52570000	0.00000000
6	216.79060000	2.41250000	0.00000000
7	225.74810000	1.05480000	0.00000000
8	251.51590000	4.82620000	0.00000000
9	277.19820000	0.91900000	0.00000000
10	283.71170000	5.05460000	0.00000000
11	293.62400000	1.73120000	0.00000000
12	316.28500000	14.69590000	0.00000000
13	359.12760000	5.49440000	0.00000000
14	371.50070000	16.92470000	0.00000000
15	376.03200000	1.07330000	0.00000000
16	443.27270000	0.62450000	0.00000000
17	454.63450000	2.04760000	0.00000000
18	465.73210000	4.50170000	0.00000000
19	489.76230000	44.38050000	0.00000000
20	506.15390000	174.87110000	0.00000000
21	519.54950000	25.99620000	0.00000000
22	613.28930000	7.67250000	0.00000000
23	637.24820000	4.52640000	0.00000000
24	758.42060000	2.09770000	0.00000000
25	767.73230000	7.24200000	0.00000000
26	794.74350000	10.11540000	0.00000000
27	802.15910000	17.82380000	0.00000000
28	861.27890000	20.49990000	0.00000000
29	894.19780000	64.00940000	0.00000000
30	951.05730000	19.49240000	0.00000000
31	964.51570000	18.38240000	0.00000000
32	1019.55960000	1.42480000	0.00000000
33	1048.09010000	2.60900000	0.00000000
34	1078.91520000	0.66280000	0.00000000
35	1083.95840000	13.10150000	0.00000000
36	1143.64840000	19.84880000	0.00000000
37	1147.96060000	0.44860000	0.00000000
38	1164.34070000	54.83560000	0.00000000
39	1212.10830000	57.28900000	0.00000000
40	1250.86660000	109.21540000	0.00000000
41	1259.51140000	8.10530000	0.00000000
42	1269.38900000	242.55180000	0.00000000
43	1287.59340000	89.13840000	0.00000000
44	1293.54990000	23.34280000	0.00000000
45	1320.92500000	33.01740000	0.00000000
46	1342.94650000	2.15410000	0.00000000
47	1373.70060000	1.50200000	0.00000000
48	1422.34100000	4.70630000	0.00000000
49	1428.49370000	59.28080000	0.00000000
50	1455.44730000	5.10160000	0.00000000
51	1456.17350000	4.03970000	0.00000000
52	1477.04580000	0.15620000	0.00000000
53	1482.95240000	0.35630000	0.00000000
54	1492.65070000	0.66380000	0.00000000
55	1493.90390000	1.91090000	0.00000000
56	1503.62540000	4.77680000	0.00000000
57	1515.27800000	31.24100000	0.00000000
58	1517.35330000	33.94610000	0.00000000
59	1519.92910000	6.94260000	0.00000000
60	1530.47590000	52.55720000	0.00000000

61	1709.63320000	52.63640000	0.00000000
62	1831.80660000	301.72910000	0.00000000
63	3055.69320000	18.61560000	0.00000000
64	3073.34090000	0.31780000	0.00000000
65	3076.89880000	0.15220000	0.00000000
66	3082.11760000	2.41910000	0.00000000
67	3091.57930000	2.91390000	0.00000000
68	3096.72840000	7.68140000	0.00000000
69	3148.45360000	1.57230000	0.00000000
70	3162.32100000	0.09030000	0.00000000
71	3163.95640000	0.05890000	0.00000000
72	3168.39620000	0.73240000	0.00000000
73	3169.18820000	1.92300000	0.00000000
74	3176.65870000	0.07740000	0.00000000
75	3179.95170000	3.13210000	0.00000000
76	3180.70070000	2.19850000	0.00000000
77	3716.64430000	163.15570000	0.00000000
78	3788.41130000	38.87280000	0.00000000

S15. CALCULATIONS ON 4 - H ($E+ZPE=69.2 \text{ KJ MOL}^{-1}$) \rightarrow 9E - H (TS)

```

Route : # opt=(calcf,ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper
       : sion=gd3bj int=ultrafine pop=regular
SMILES : C[N](C)(C)CCC=[C]O.[C](=O)O
Formula : C8H16NO3+
Charge : 1
Multiplicity : 1
Energy : -594.82129426 a.u.
Gibbs Energy : -594.62491400 a.u.
Number of imaginary frequencies : 1

```

S15.1. Cartesian Co-ordinates (XYZ format)

28

```

C 1.06860006 -0.77538002 0.36566001
H 0.60851002 -0.26962000 1.20827997
H 1.41038001 -1.75558996 0.69165999
C 0.07111000 -0.89577001 -0.78794998
H 0.46445000 -1.55227005 -1.56241000
H -0.08989000 0.07744000 -1.24507999
C -1.24764001 -1.45790005 -0.31373999
H -1.39994001 -2.52632999 -0.43990001
N 2.32347012 0.03186000 0.05607000
C 3.16878009 0.04623000 1.29807997
H 4.07765007 0.60495001 1.09639001
H 2.60855007 0.52353001 2.09641004
H 3.41268992 -0.97610998 1.57091999
C 3.10472989 -0.59261000 -1.06020999

```

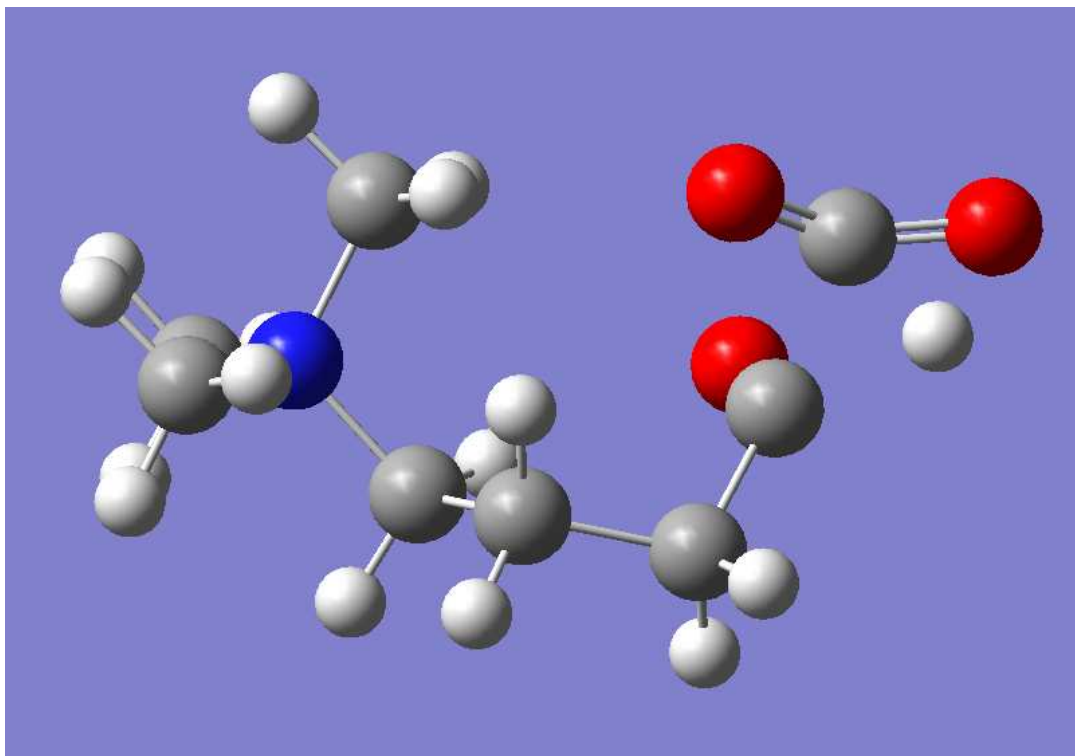

H 3.34818006 -1.61629999 -0.79035002
H 2.51200008 -0.57415003 -1.96793997
H 4.01630020 -0.02112000 -1.20790005
C 1.97340000 1.45219004 -0.30015999
H 1.29705000 1.84932005 0.45045000
H 2.89246011 2.02907991 -0.33603001
H 1.49398005 1.47335994 -1.27171004
C -2.22353005 -0.69766003 0.23264000
O -3.44613004 -1.11280000 0.60681999
C -2.14280009 1.11514997 -0.07399000
O -2.83323002 1.55761003 -0.91020000
O -1.26424003 1.45436001 0.77802998
H -1.57897997 0.17294000 1.02885997
H -3.62480998 -2.02093005 0.32672000

S15.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-1947.48510000	416.93450000	0.00000000
2	36.95510000	3.14140000	0.00000000
3	43.56640000	5.28380000	0.00000000
4	78.68980000	3.24380000	0.00000000
5	98.65860000	3.72000000	0.00000000
6	124.95580000	1.75790000	0.00000000
7	157.49530000	12.78350000	0.00000000
8	193.82170000	11.89220000	0.00000000
9	225.40590000	0.56240000	0.00000000
10	246.89100000	0.11190000	0.00000000
11	274.49440000	0.91820000	0.00000000
12	289.18650000	0.17370000	0.00000000
13	299.16080000	16.65670000	0.00000000
14	313.76410000	28.69280000	0.00000000
15	361.08920000	47.18930000	0.00000000
16	377.05350000	68.56900000	0.00000000
17	381.38450000	45.79950000	0.00000000
18	400.98670000	73.02610000	0.00000000
19	448.26560000	2.88310000	0.00000000
20	466.08060000	4.09090000	0.00000000
21	494.54890000	13.18120000	0.00000000
22	545.80870000	2.83480000	0.00000000
23	613.96520000	36.00150000	0.00000000
24	672.02500000	27.48440000	0.00000000
25	679.22770000	211.75300000	0.00000000
26	754.77520000	0.82760000	0.00000000
27	784.63110000	8.58730000	0.00000000
28	865.09390000	25.12350000	0.00000000
29	901.57290000	80.94020000	0.00000000
30	941.16000000	23.07620000	0.00000000
31	960.81510000	27.40160000	0.00000000
32	995.16280000	14.81930000	0.00000000
33	1045.21090000	4.17480000	0.00000000
34	1066.31780000	108.41700000	0.00000000
35	1078.87930000	0.78130000	0.00000000
36	1101.88980000	81.38050000	0.00000000
37	1139.82060000	54.23130000	0.00000000
38	1150.60310000	10.98940000	0.00000000
39	1168.85100000	21.87620000	0.00000000
40	1219.09330000	29.34110000	0.00000000
41	1239.49410000	379.99050000	0.00000000
42	1258.03830000	3.75800000	0.00000000
43	1281.05070000	39.39630000	0.00000000
44	1294.72710000	0.20750000	0.00000000
45	1322.43760000	10.36740000	0.00000000
46	1327.55870000	29.05480000	0.00000000
47	1350.80530000	14.03220000	0.00000000
48	1375.27390000	2.22950000	0.00000000
49	1424.62440000	3.42940000	0.00000000
50	1455.56620000	4.44150000	0.00000000
51	1458.88910000	3.24010000	0.00000000
52	1478.01620000	0.82250000	0.00000000
53	1482.08520000	1.14320000	0.00000000
54	1491.36920000	2.83490000	0.00000000
55	1493.66300000	2.66810000	0.00000000
56	1503.69030000	3.74300000	0.00000000
57	1512.21430000	5.78480000	0.00000000
58	1516.59020000	32.89140000	0.00000000
59	1517.92600000	36.05310000	0.00000000
60	1530.34550000	55.98600000	0.00000000

61	1581.13680000	43.92240000	0.00000000
62	1681.25020000	136.05280000	0.00000000
63	2036.19380000	392.46330000	0.00000000
64	3070.15110000	5.60100000	0.00000000
65	3073.53790000	0.27250000	0.00000000
66	3077.51050000	0.38590000	0.00000000
67	3083.55390000	4.55430000	0.00000000
68	3088.10620000	3.49060000	0.00000000
69	3110.78480000	1.83910000	0.00000000
70	3126.78580000	11.08510000	0.00000000
71	3151.04710000	1.05290000	0.00000000
72	3161.65980000	0.13500000	0.00000000
73	3166.43280000	0.89160000	0.00000000
74	3168.06510000	0.92880000	0.00000000
75	3172.62470000	0.47000000	0.00000000
76	3177.18960000	0.39680000	0.00000000
77	3184.18810000	3.10930000	0.00000000
78	3741.83470000	59.60740000	0.00000000

S16. CALCULATIONS ON 4 - H (E+ZPE=4.2 KJ MOL⁻¹) → 8 - H (TS)



```

Route : # opt=(calcf,ts) freq b3lyp/cc-pvtz geom=connectivity empiricdispers
       : sion=gd3bj int=ultrafine pop=regular
SMILES : C[N](C)(C)CCC[C]=O.[C](=O)O
Formula : C8H16NO3+
Charge : 1
Multiplicity : 1
Energy : -594.82759030 a.u.
Gibbs Energy : -594.63195100 a.u.
Number of imaginary frequencies : 1

```

S16.1. Cartesian Co-ordinates (XYZ format)

28

```

C  1.33783996 -0.99996001 -0.13720000
H  0.89731002 -1.24150002  0.82560003
H  2.04281998 -1.78471994 -0.40145999
C  0.25551000 -0.84990001 -1.20983005
H  0.60425001 -1.26531994 -2.15352988
H  0.02530000  0.19608000 -1.39950001
C -1.05631995 -1.55931997 -0.80862999
H -0.86071002 -2.60022998 -0.54159999
H -1.73850000 -1.55129004 -1.65671003
N  2.17676997  0.24586000  0.11107000
C  3.23779988 -0.10878000  1.11287999
H  3.83422995  0.77464998  1.32003999
H  2.75695992 -0.45592001  2.02238989
H  3.86488008 -0.89280999  0.69941998

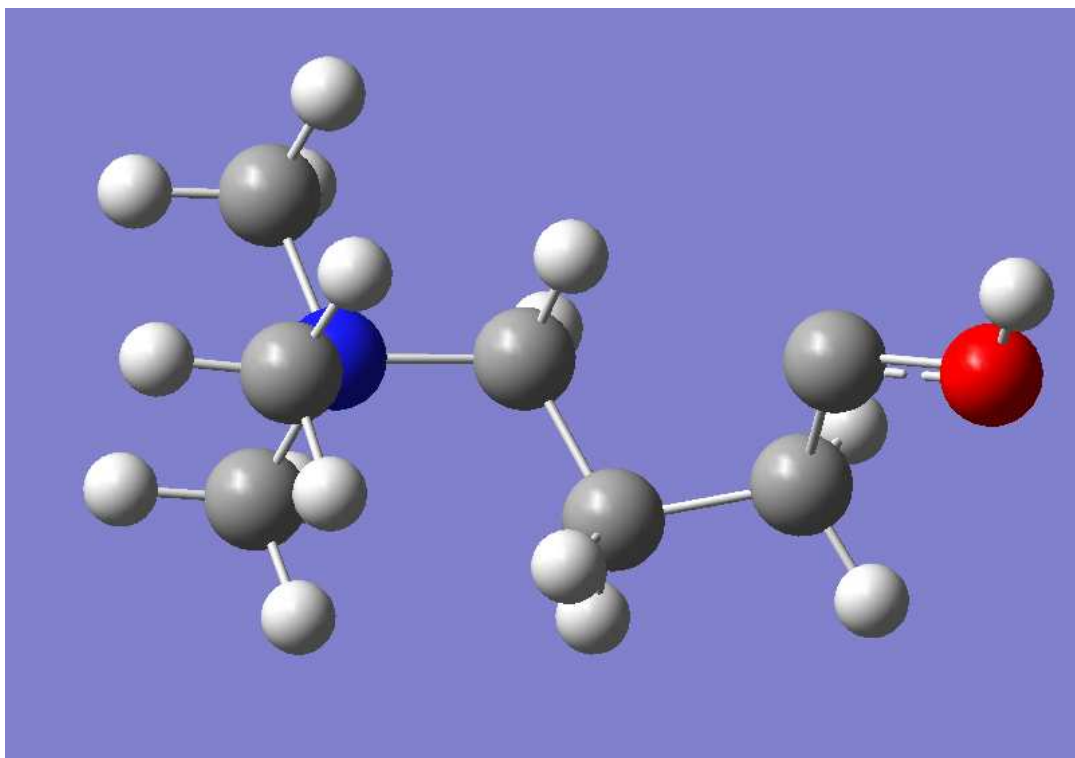
```

C	2.83385992	0.71145999	-1.15298998
H	3.43407011	-0.09993000	-1.55457997
H	2.07282996	1.00251997	-1.86830997
H	3.46649003	1.56370997	-0.92337000
C	1.32896996	1.34701002	0.68472999
H	0.85427999	0.98170000	1.59013999
H	1.97212994	2.19273996	0.90837997
H	0.57242000	1.64117002	-0.03336000
C	-1.69314003	-0.87597001	0.38777000
O	-1.22546995	-0.93889999	1.49972999
C	-2.73712993	0.80984998	-0.11449000
O	-2.00067997	1.56585002	-0.62123001
O	-3.88708997	0.55128002	0.29080999
H	-3.17456007	-0.45401999	0.46103001

S16.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2232.53310000	392.69060000	0.00000000
2	29.19200000	3.63600000	0.00000000
3	39.04590000	2.00720000	0.00000000
4	55.13560000	0.33590000	0.00000000
5	68.03410000	1.99680000	0.00000000
6	127.14890000	0.80890000	0.00000000
7	150.45270000	10.56550000	0.00000000
8	179.29680000	10.35060000	0.00000000
9	189.32630000	4.23740000	0.00000000
10	216.15410000	3.03470000	0.00000000
11	277.38190000	0.41520000	0.00000000
12	281.18750000	0.65600000	0.00000000
13	287.70730000	18.75790000	0.00000000
14	295.30790000	3.52370000	0.00000000
15	359.02460000	1.39380000	0.00000000
16	373.05680000	4.60430000	0.00000000
17	380.36820000	0.17000000	0.00000000
18	445.62360000	1.15290000	0.00000000
19	456.04370000	0.75010000	0.00000000
20	506.99960000	0.98780000	0.00000000
21	514.11530000	6.69400000	0.00000000
22	601.64170000	14.42020000	0.00000000
23	609.41890000	266.18750000	0.00000000
24	692.79090000	213.42370000	0.00000000
25	741.50750000	3.05160000	0.00000000
26	811.14130000	13.77590000	0.00000000
27	855.36420000	7.24770000	0.00000000
28	893.15240000	37.96740000	0.00000000
29	936.81680000	2.13220000	0.00000000
30	948.94670000	21.08880000	0.00000000
31	966.45250000	18.47060000	0.00000000
32	1006.87540000	53.79170000	0.00000000
33	1037.47430000	3.46140000	0.00000000
34	1058.90240000	8.13520000	0.00000000
35	1077.47240000	26.29180000	0.00000000
36	1079.54250000	4.89030000	0.00000000
37	1135.89230000	0.46740000	0.00000000
38	1146.41630000	3.70650000	0.00000000
39	1197.67400000	10.65460000	0.00000000
40	1231.07820000	52.17050000	0.00000000
41	1260.37940000	368.65850000	0.00000000
42	1268.29230000	4.21430000	0.00000000
43	1289.12380000	29.12780000	0.00000000
44	1298.11910000	1.75340000	0.00000000
45	1344.55790000	1.79790000	0.00000000
46	1373.34410000	3.79750000	0.00000000
47	1377.23100000	0.40700000	0.00000000
48	1436.02200000	3.25610000	0.00000000
49	1456.15620000	5.59360000	0.00000000
50	1457.01210000	2.08290000	0.00000000
51	1481.25310000	0.58970000	0.00000000
52	1485.84390000	4.74810000	0.00000000
53	1486.41970000	5.26540000	0.00000000
54	1492.42680000	0.49330000	0.00000000
55	1495.48870000	1.98700000	0.00000000
56	1505.40320000	4.64730000	0.00000000
57	1511.37290000	12.18300000	0.00000000
58	1518.85470000	34.98640000	0.00000000
59	1525.33060000	45.87150000	0.00000000
60	1534.72970000	46.77460000	0.00000000

61	1697.86360000	49.42760000	0.00000000
62	1788.12850000	126.52970000	0.00000000
63	2109.81030000	437.82160000	0.00000000
64	3044.67430000	2.77090000	0.00000000
65	3071.97590000	7.64130000	0.00000000
66	3073.67160000	1.48030000	0.00000000
67	3077.68100000	0.53490000	0.00000000
68	3081.59620000	2.85920000	0.00000000
69	3086.85060000	8.55950000	0.00000000
70	3105.97600000	4.77420000	0.00000000
71	3112.90930000	2.67500000	0.00000000
72	3139.99940000	3.07470000	0.00000000
73	3161.79860000	0.10730000	0.00000000
74	3165.32460000	0.25140000	0.00000000
75	3168.09970000	1.05600000	0.00000000
76	3170.95430000	0.78080000	0.00000000
77	3177.21590000	0.87390000	0.00000000
78	3185.15560000	0.21780000	0.00000000

S17. CALCULATIONS ON 7 – H_{5r}

```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N](C)(C)CCC[O]
Formula              : C7H16NO+
Charge               : 1
Multiplicity         : 1
Energy               : -406.21926201
Gibbs Energy        : -406.02683200
Number of imaginary frequencies : 0

```

a.u.
a.u.

S17.1. Cartesian Co-ordinates (XYZ format)

25

```

C  0.00000000  0.00000000  0.00000000
H  0.00000000 -0.00000000  1.08832002
H  1.03018403  0.00000000 -0.35250801
C -0.74105197 -1.22861803 -0.50181699
H -0.55768299 -1.39537704 -1.56223798
H -1.81670499 -1.11501098 -0.36790401
C -0.29190600 -2.45419693  0.30559301
H  0.80124301 -2.55866599  0.26934299
H -0.69661999 -3.37649012 -0.12082400
N -0.58267498  1.34423006 -0.41672400
C  0.33589801  2.41883397  0.08761800
H -0.07270500  3.38792491 -0.18295901
H  0.41254801  2.33384895  1.16733599
H  1.31342399  2.28704405 -0.36610699

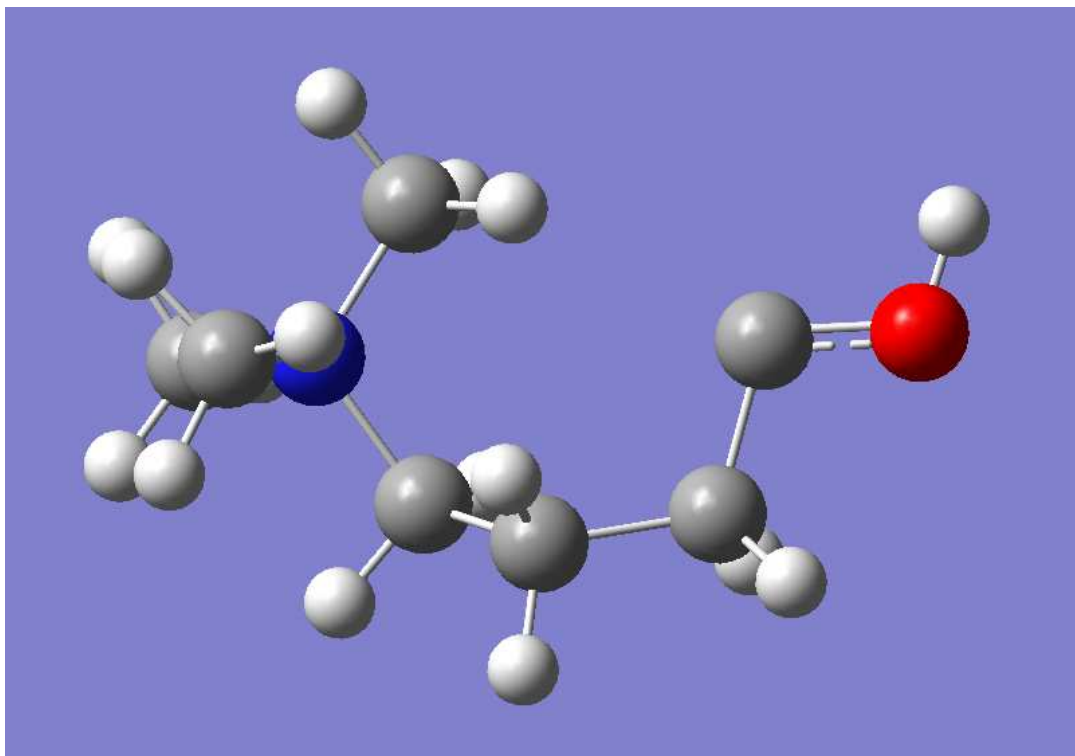
```


C	-0.68560702	1.44742799	-1.90810800
H	0.29676601	1.27894497	-2.33970809
H	-1.38488495	0.70244902	-2.27064610
H	-1.03927600	2.44153094	-2.16549492
C	-1.93694794	1.54555595	0.19947700
H	-1.85345101	1.41457903	1.27397096
H	-2.27642703	2.55018497	-0.03445200
H	-2.63099909	0.82033801	-0.20822100
C	-0.64007300	-2.30297995	1.75863004
O	-0.62176198	-3.48621607	2.30444193
H	-0.82337600	-3.41252995	3.24862003

S17.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	32.59490000	0.44470000	0.00000000
2	67.05060000	1.37670000	0.00000000
3	100.17220000	3.14960000	0.00000000
4	155.97200000	3.24570000	0.00000000
5	188.78110000	0.19260000	0.00000000
6	230.85970000	1.22800000	0.00000000
7	259.46870000	0.99740000	0.00000000
8	280.20020000	0.35230000	0.00000000
9	295.35240000	0.42910000	0.00000000
10	340.66770000	3.24630000	0.00000000
11	361.50070000	0.18210000	0.00000000
12	373.60160000	0.21080000	0.00000000
13	449.51050000	0.19540000	0.00000000
14	456.54460000	0.75780000	0.00000000
15	491.45830000	3.30920000	0.00000000
16	558.96370000	8.45520000	0.00000000
17	671.64370000	18.11510000	0.00000000
18	757.84590000	4.45960000	0.00000000
19	789.52860000	18.44690000	0.00000000
20	875.83930000	35.90680000	0.00000000
21	901.82580000	52.21290000	0.00000000
22	933.32090000	8.82840000	0.00000000
23	953.95880000	18.28700000	0.00000000
24	969.56150000	20.85160000	0.00000000
25	1029.59000000	18.43420000	0.00000000
26	1031.64030000	20.16970000	0.00000000
27	1077.13280000	6.91980000	0.00000000
28	1079.48740000	6.07380000	0.00000000
29	1125.30430000	4.65070000	0.00000000
30	1144.20260000	14.20310000	0.00000000
31	1192.03110000	4.93740000	0.00000000
32	1224.46100000	37.73200000	0.00000000
33	1268.47710000	1.58270000	0.00000000
34	1287.42800000	28.79100000	0.00000000
35	1295.54350000	2.17830000	0.00000000
36	1336.61400000	16.94690000	0.00000000
37	1341.08600000	75.57460000	0.00000000
38	1356.69400000	42.74560000	0.00000000
39	1369.93750000	5.25870000	0.00000000
40	1404.50650000	43.67270000	0.00000000
41	1414.21050000	17.28080000	0.00000000
42	1430.79200000	12.33300000	0.00000000
43	1454.03380000	5.13950000	0.00000000
44	1455.07370000	2.64290000	0.00000000
45	1481.19620000	0.19530000	0.00000000
46	1482.47640000	0.72230000	0.00000000
47	1491.00730000	0.78000000	0.00000000
48	1493.64920000	1.28050000	0.00000000
49	1503.67100000	5.71210000	0.00000000
50	1508.43340000	7.79380000	0.00000000
51	1516.22710000	25.45590000	0.00000000
52	1522.99230000	44.73500000	0.00000000
53	1533.03520000	38.68010000	0.00000000
54	2987.72570000	5.63830000	0.00000000
55	3043.74250000	7.43150000	0.00000000
56	3057.36770000	10.22970000	0.00000000
57	3067.11010000	8.87950000	0.00000000
58	3074.22090000	2.80660000	0.00000000
59	3077.49990000	0.72630000	0.00000000
60	3084.47170000	1.87440000	0.00000000

61	3095.39520000	6.89850000	0.00000000
62	3123.19810000	5.45130000	0.00000000
63	3161.21340000	0.19410000	0.00000000
64	3164.31580000	0.31400000	0.00000000
65	3167.78790000	1.49590000	0.00000000
66	3169.76320000	1.91560000	0.00000000
67	3177.96810000	0.37970000	0.00000000
68	3184.88240000	1.48320000	0.00000000
69	3721.49260000	149.55970000	0.00000000

S18. CALCULATIONS ON 7 - H_{5r} → 7 - H_{7r} (TS)

```

Route : # opt=(calcfc,qst3) freq b3lyp/cc-pvtz geom=connectivity empiricaldisp
       : ersion=gd3bj int=ultrafine pop=regular
SMILES : C[N](C)(C)CCC[C]O
Formula : C7H16NO+
Charge : 1
Multiplicity : 1
Energy : -406.21568990 a.u.
Gibbs Energy : -406.02169600 a.u.
Number of imaginary frequencies : 1

```

S18.1. Cartesian Co-ordinates (XYZ format)

25

```

C  0.79475898  1.29568398 -0.16992900
H  0.72796202  0.79510498 -1.13363004
H  1.32979703  2.23048210 -0.31804201
C -0.59981698  1.57483804  0.41137901
H -0.76328701  2.64839697  0.32764599
H -0.63318402  1.36268604  1.47827101
C -1.76810396  0.85760099 -0.27384499
H -1.66729903  0.91354197 -1.36609006
H -2.70972490  1.36725295 -0.04425900
N  1.75431705  0.44027999  0.65775299
C  3.10375190  0.51970702  0.00354900
H  3.78580189 -0.14174300  0.52914399
H  3.01028490  0.20730799 -1.03204095
H  3.46444607  1.54279995  0.05377700

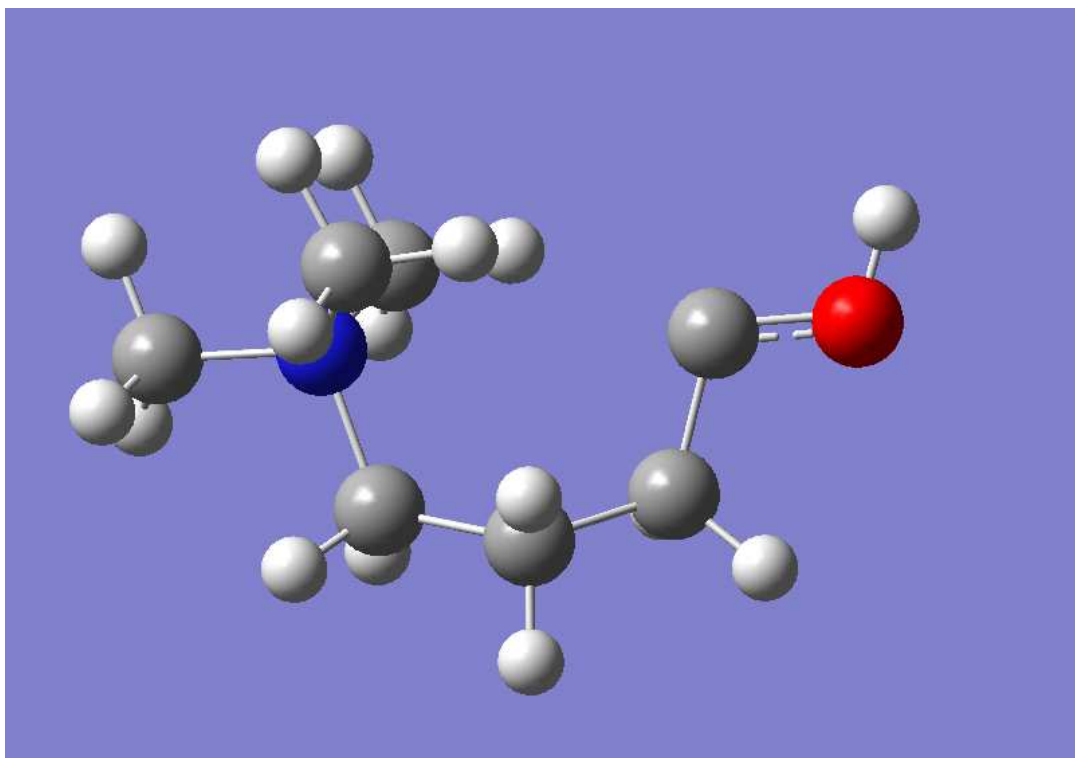
```

C	1.87788296	0.95993602	2.05874801
H	2.08399010	2.02594995	2.02511001
H	0.95847303	0.77124602	2.59941006
H	2.69641399	0.43791401	2.54507995
C	1.32011795	-0.99787903	0.69060600
H	1.40795398	-1.40268397	-0.31366000
H	1.97560596	-1.53701699	1.36856103
H	0.27731001	-1.05719995	0.99308503
C	-1.86428905	-0.59859198	0.06240100
O	-3.05886698	-1.00788403	-0.26024401
H	-3.14700389	-1.95279396	-0.06894200

S18.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-60.76670000	0.71600000	0.00000000
2	68.97980000	1.74520000	0.00000000
3	93.19780000	2.27150000	0.00000000
4	129.84940000	2.00990000	0.00000000
5	223.86150000	2.06340000	0.00000000
6	235.02910000	2.53530000	0.00000000
7	270.64270000	0.65320000	0.00000000
8	274.38530000	2.12350000	0.00000000
9	296.47900000	0.85340000	0.00000000
10	331.32200000	1.96190000	0.00000000
11	354.11110000	1.01960000	0.00000000
12	394.53650000	0.18560000	0.00000000
13	440.51830000	0.03780000	0.00000000
14	453.73280000	0.95480000	0.00000000
15	485.76790000	3.02430000	0.00000000
16	538.77110000	8.52680000	0.00000000
17	666.31240000	18.90300000	0.00000000
18	699.02090000	2.00030000	0.00000000
19	809.84560000	19.43170000	0.00000000
20	873.17620000	43.81120000	0.00000000
21	910.97090000	18.09570000	0.00000000
22	920.57530000	8.54970000	0.00000000
23	958.00080000	19.57360000	0.00000000
24	978.97780000	38.97890000	0.00000000
25	1006.87510000	27.47720000	0.00000000
26	1036.85830000	26.55240000	0.00000000
27	1082.19030000	0.28530000	0.00000000
28	1086.22810000	1.79020000	0.00000000
29	1133.54190000	6.66060000	0.00000000
30	1151.12160000	3.92370000	0.00000000
31	1183.11650000	3.14350000	0.00000000
32	1238.21910000	4.24940000	0.00000000
33	1259.60550000	3.78890000	0.00000000
34	1275.60130000	50.84090000	0.00000000
35	1296.33690000	8.00870000	0.00000000
36	1339.28550000	24.77330000	0.00000000
37	1344.64960000	79.11470000	0.00000000
38	1366.30260000	21.72340000	0.00000000
39	1386.13240000	27.06250000	0.00000000
40	1406.50610000	37.44130000	0.00000000
41	1415.66310000	13.02990000	0.00000000
42	1434.65520000	8.58120000	0.00000000
43	1453.57780000	2.58960000	0.00000000
44	1465.24110000	3.07880000	0.00000000
45	1480.39150000	1.97820000	0.00000000
46	1483.89830000	2.37400000	0.00000000
47	1487.17800000	5.21030000	0.00000000
48	1491.34610000	4.86230000	0.00000000
49	1495.40950000	1.71980000	0.00000000
50	1511.69090000	10.45570000	0.00000000
51	1513.65500000	31.51270000	0.00000000
52	1521.58340000	43.85090000	0.00000000
53	1528.12910000	46.18780000	0.00000000
54	2989.47430000	5.30510000	0.00000000
55	3033.23070000	6.17880000	0.00000000
56	3049.77530000	38.46180000	0.00000000
57	3070.14480000	4.65640000	0.00000000
58	3073.05630000	1.30970000	0.00000000
59	3076.22630000	4.55910000	0.00000000
60	3082.77750000	4.71170000	0.00000000

61	3104.22070000	7.13360000	0.00000000
62	3125.31620000	3.87470000	0.00000000
63	3141.69650000	29.98970000	0.00000000
64	3158.23840000	0.55970000	0.00000000
65	3161.57010000	0.11040000	0.00000000
66	3165.87460000	2.12190000	0.00000000
67	3167.95610000	2.26960000	0.00000000
68	3185.38250000	0.81140000	0.00000000
69	3724.64280000	143.86720000	0.00000000

S19. CALCULATIONS ON 7 – H_{7r}

```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N](C)(C)CCC[C]O
Formula              : C7H16NO+
Charge               : 1
Multiplicity         : 1
Energy               : -406.21939976 a.u.
Gibbs Energy        : -406.02508700 a.u.
Number of imaginary frequencies : 0

```

S19.1. Cartesian Co-ordinates (XYZ format)

25

```

C  0.00000000 -0.00000000  0.00000000
H  0.00000000 -0.00000000  1.08867097
H  1.03532302 -0.00000000 -0.33378899
C -0.66762602 -1.25614798 -0.54786098
H  0.02323200 -2.05049706 -0.25871599
H -0.65056300 -1.25007105 -1.63758004
C -2.06281805 -1.65592802 -0.04790000
H -2.17529297 -1.39929402  1.01451695
H -2.18585110 -2.74132991 -0.11024100
N -0.53345799  1.37728906 -0.40383700
C  0.54399198  2.37626505 -0.09656800
H  0.17000601  3.37172699 -0.31488299
H  0.80428499  2.30136108  0.95541799
H  1.41274703  2.16279507 -0.71203500

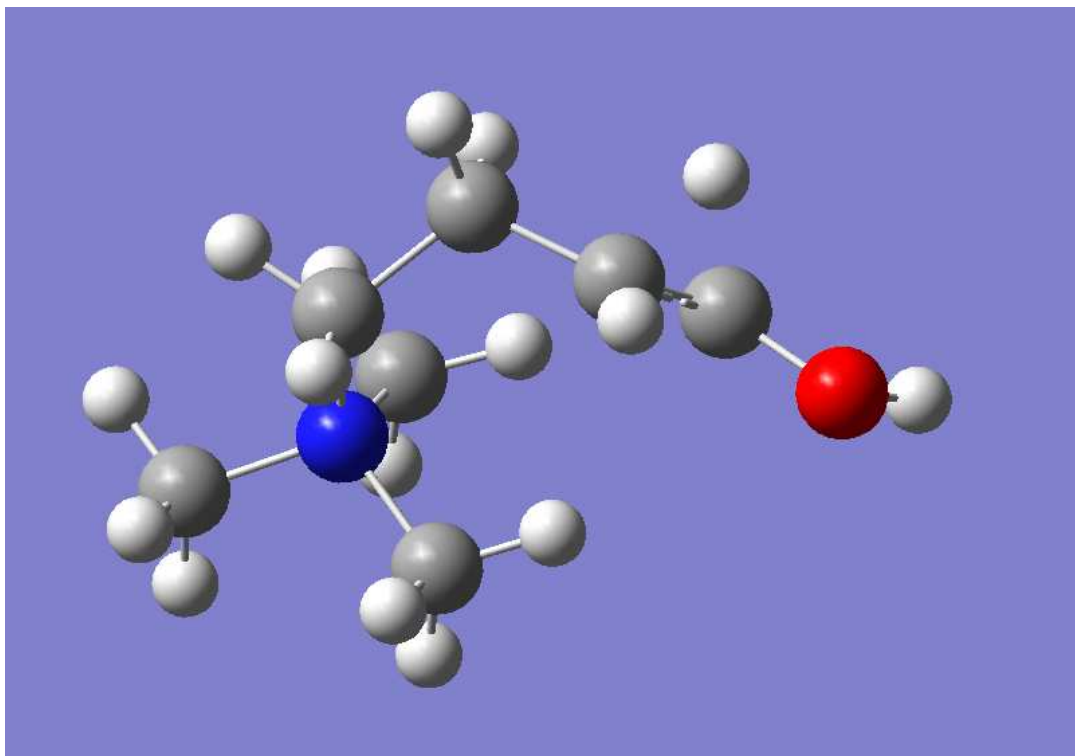
```


C	-0.85467601	1.43331897	-1.86837494
H	0.01045100	1.09756601	-2.43305707
H	-1.71633506	0.79942501	-2.05415297
H	-1.08619702	2.46308494	-2.12483501
C	-1.76196897	1.74828506	0.37902400
H	-1.53641701	1.67180896	1.43863595
H	-2.02546811	2.77238011	0.13030800
H	-2.56554890	1.07600904	0.08894300
C	-3.17387295	-0.93492901	-0.74752301
O	-4.19588804	-1.73613799	-0.83058798
H	-4.93943691	-1.28478003	-1.25733304

S19.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	62.39830000	0.51550000	0.00000000
2	87.77870000	2.34490000	0.00000000
3	118.31330000	2.10640000	0.00000000
4	162.83470000	6.53670000	0.00000000
5	243.19380000	1.52600000	0.00000000
6	256.91130000	0.27180000	0.00000000
7	270.60930000	0.69190000	0.00000000
8	313.59710000	0.98350000	0.00000000
9	328.97180000	0.00840000	0.00000000
10	349.63540000	2.04590000	0.00000000
11	365.96620000	1.45460000	0.00000000
12	403.61120000	0.25450000	0.00000000
13	445.10940000	0.32320000	0.00000000
14	449.21220000	0.04200000	0.00000000
15	509.94300000	6.72080000	0.00000000
16	520.35630000	2.40090000	0.00000000
17	692.51560000	2.09380000	0.00000000
18	718.26550000	21.19210000	0.00000000
19	828.03800000	7.73600000	0.00000000
20	879.30210000	58.49480000	0.00000000
21	888.53070000	19.33200000	0.00000000
22	914.22260000	14.58150000	0.00000000
23	955.90460000	6.35030000	0.00000000
24	974.94990000	48.17970000	0.00000000
25	1011.75890000	20.75590000	0.00000000
26	1045.56790000	35.60880000	0.00000000
27	1086.50700000	0.05100000	0.00000000
28	1095.02110000	2.65990000	0.00000000
29	1131.09240000	7.11920000	0.00000000
30	1150.43760000	2.03960000	0.00000000
31	1197.15230000	5.93400000	0.00000000
32	1249.05020000	44.76930000	0.00000000
33	1256.25190000	0.04140000	0.00000000
34	1288.05210000	24.75890000	0.00000000
35	1297.79200000	4.79840000	0.00000000
36	1344.18940000	1.93800000	0.00000000
37	1351.22890000	73.18370000	0.00000000
38	1364.07500000	46.24270000	0.00000000
39	1404.71080000	48.33930000	0.00000000
40	1421.96800000	26.04190000	0.00000000
41	1424.33030000	2.97720000	0.00000000
42	1433.57320000	17.41710000	0.00000000
43	1449.84810000	6.96830000	0.00000000
44	1457.54060000	1.38890000	0.00000000
45	1477.68180000	0.50760000	0.00000000
46	1480.87500000	7.06930000	0.00000000
47	1484.81800000	8.86400000	0.00000000
48	1495.32180000	6.90130000	0.00000000
49	1502.53660000	15.68420000	0.00000000
50	1507.45860000	2.54630000	0.00000000
51	1517.19210000	28.90000000	0.00000000
52	1526.62540000	9.83460000	0.00000000
53	1541.94300000	27.92220000	0.00000000
54	2987.12580000	3.84000000	0.00000000
55	3036.05630000	14.60390000	0.00000000
56	3044.19680000	33.93340000	0.00000000
57	3053.75150000	5.22990000	0.00000000
58	3064.24360000	8.16170000	0.00000000
59	3068.80630000	3.00020000	0.00000000
60	3075.45070000	9.47340000	0.00000000

61	3086.68690000	6.98260000	0.00000000
62	3121.52730000	4.72290000	0.00000000
63	3137.88460000	15.46300000	0.00000000
64	3157.30930000	3.16200000	0.00000000
65	3158.20360000	0.77350000	0.00000000
66	3160.74680000	7.60340000	0.00000000
67	3163.51410000	1.73640000	0.00000000
68	3167.54070000	3.25200000	0.00000000
69	3715.78310000	147.34520000	0.00000000

S20. CALCULATIONS ON 7 - H_{7r} → 9E - H (TS)

```

Route : # opt=(calcall,qst3) freq b3lyp/cc-pvtz geom=connectivity empiricaldis
       : persion=gd3bj int=ultrafine pop=regular
SMILES : C[N](C)(C)CC[CH][CH]O
Formula : C7H16NO+
Charge : 1
Multiplicity : 1
Energy : -406.18042195 a.u.
Gibbs Energy : -405.98952000 a.u.
Number of imaginary frequencies : 1

```

S20.1. Cartesian Co-ordinates (XYZ format)

25

```

C  0.87195402  1.21638405 -0.23122600
H  0.90118498  1.37861001 -1.30676603
H  1.58339095  1.89634204  0.23151200
C -0.51285398  1.51241505  0.34372401
H -0.66551697  2.57572699  0.14612900
H -0.50322902  1.39076805  1.42625105
C -1.64001203  0.70674801 -0.24500000
H -1.92729998  0.92070502 -1.27946603
H -2.53188896  0.77438003  0.79241103
N  1.44599700 -0.18400900 -0.01035600
C  2.92796493 -0.10159300 -0.24387600
H  3.35088992 -1.09762096 -0.15548199
H  3.10688305  0.29026300 -1.24108601
H  3.36715889  0.55563200  0.50024700

```

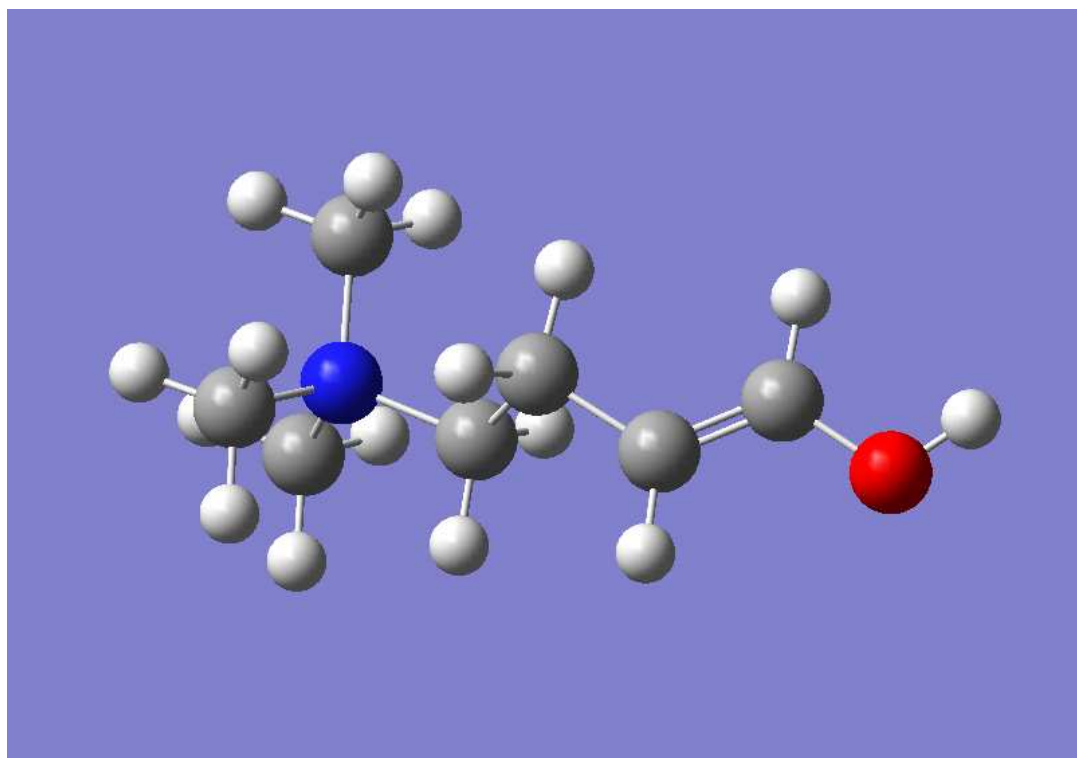
C 1.19608200 -0.66668701 1.39106798
H 1.57828104 0.07320200 2.08870792
H 0.12786600 -0.81226200 1.52989602
H 1.72597897 -1.60552096 1.52300704
C 0.87694901 -1.17559695 -0.98857599
H 1.06739604 -0.81871098 -1.99638700
H 1.37550700 -2.12790704 -0.83348501
H -0.18538199 -1.28576803 -0.81875300
C -2.14473295 -0.39639899 0.43854901
O -3.03354001 -1.09774804 -0.29611200
H -3.43927789 -1.76580000 0.26613799

S20.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-1419.48800000	70.85570000	0.00000000
2	74.28100000	1.44680000	0.00000000
3	100.33120000	3.63310000	0.00000000
4	135.86790000	2.05180000	0.00000000
5	221.44240000	2.27170000	0.00000000
6	237.33310000	1.83450000	0.00000000
7	249.67990000	2.00020000	0.00000000
8	289.76510000	0.71020000	0.00000000
9	323.78300000	0.49620000	0.00000000
10	335.87990000	1.71740000	0.00000000
11	362.17060000	0.64030000	0.00000000
12	370.35330000	0.73250000	0.00000000
13	415.91040000	0.23760000	0.00000000
14	448.96050000	0.15770000	0.00000000
15	457.39870000	0.41800000	0.00000000
16	536.78920000	6.92800000	0.00000000
17	559.15520000	1.09070000	0.00000000
18	648.73860000	113.49160000	0.00000000
19	704.06730000	0.12200000	0.00000000
20	848.60300000	7.84430000	0.00000000
21	886.98350000	27.43720000	0.00000000
22	915.75870000	31.85900000	0.00000000
23	956.41920000	11.72210000	0.00000000
24	959.33920000	9.52670000	0.00000000
25	991.94560000	6.90550000	0.00000000
26	1048.75550000	0.52610000	0.00000000
27	1082.05890000	0.15840000	0.00000000
28	1092.47800000	7.67360000	0.00000000
29	1138.66620000	22.93750000	0.00000000
30	1150.37020000	17.10140000	0.00000000
31	1166.22730000	56.01200000	0.00000000
32	1179.91930000	153.27300000	0.00000000
33	1221.84600000	7.54120000	0.00000000
34	1241.50660000	32.94740000	0.00000000
35	1258.32010000	10.10710000	0.00000000
36	1292.60970000	10.95320000	0.00000000
37	1302.53300000	10.77760000	0.00000000
38	1346.28400000	24.91450000	0.00000000
39	1360.84380000	11.81310000	0.00000000
40	1406.71140000	1.90980000	0.00000000
41	1423.39060000	3.77860000	0.00000000
42	1452.71660000	4.03460000	0.00000000
43	1457.91500000	3.57420000	0.00000000
44	1478.93230000	1.82050000	0.00000000
45	1480.59710000	12.03310000	0.00000000
46	1484.12840000	0.30010000	0.00000000
47	1494.29840000	8.31830000	0.00000000
48	1499.61180000	1.35850000	0.00000000
49	1504.55850000	26.73470000	0.00000000
50	1511.31030000	9.22810000	0.00000000
51	1516.99950000	30.92770000	0.00000000
52	1522.17220000	16.58310000	0.00000000
53	1537.87260000	28.04070000	0.00000000
54	2073.58910000	19.69030000	0.00000000
55	3029.99180000	16.45920000	0.00000000
56	3045.63200000	4.17510000	0.00000000
57	3056.23790000	15.63320000	0.00000000
58	3072.29760000	0.13870000	0.00000000
59	3077.37290000	3.75510000	0.00000000
60	3084.76230000	6.53510000	0.00000000

61	3095.24640000	3.70220000	0.00000000
62	3129.07450000	2.71270000	0.00000000
63	3148.72400000	10.18320000	0.00000000
64	3158.76000000	0.69930000	0.00000000
65	3160.33210000	0.23640000	0.00000000
66	3165.61370000	1.37200000	0.00000000
67	3168.70990000	1.82090000	0.00000000
68	3206.41440000	4.02900000	0.00000000
69	3806.26200000	163.22200000	0.00000000

S21. CALCULATIONS ON 9E – H (TS)



```

Route : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
       : nt=ultrafine pop=regular
SMILES : C[N](C)(C)CCC=CO
Formula : C7H16NO+
Charge : 1
Multiplicity : 1
Energy : -406.28394605 a.u.
Gibbs Energy : -406.09056900 a.u.
Number of imaginary frequencies : 0

```

S21.1. Cartesian Co-ordinates (XYZ format)

25

```

C  0.35747999 -0.10287000 -0.48980999
H  0.12974000 -1.14566004 -0.69949001
H  0.32407001  0.44652000 -1.42862999
C -0.65445000  0.46735001  0.50053000
H -0.35986000  1.47298002  0.80944002
H -0.69876999 -0.14914000  1.39850998
C -2.00323009  0.51020998 -0.15203001
H -2.14662004  1.18827999 -0.98442000
N  1.82305002 -0.07372000 -0.05300000
C  2.63654995 -0.74237001 -1.12256002
H  3.68375993 -0.71983999 -0.83532000
H  2.30121994 -1.76953995 -1.22860003
H  2.49524999 -0.20753001 -2.05690002
C  2.30468011  1.33771002  0.10727000

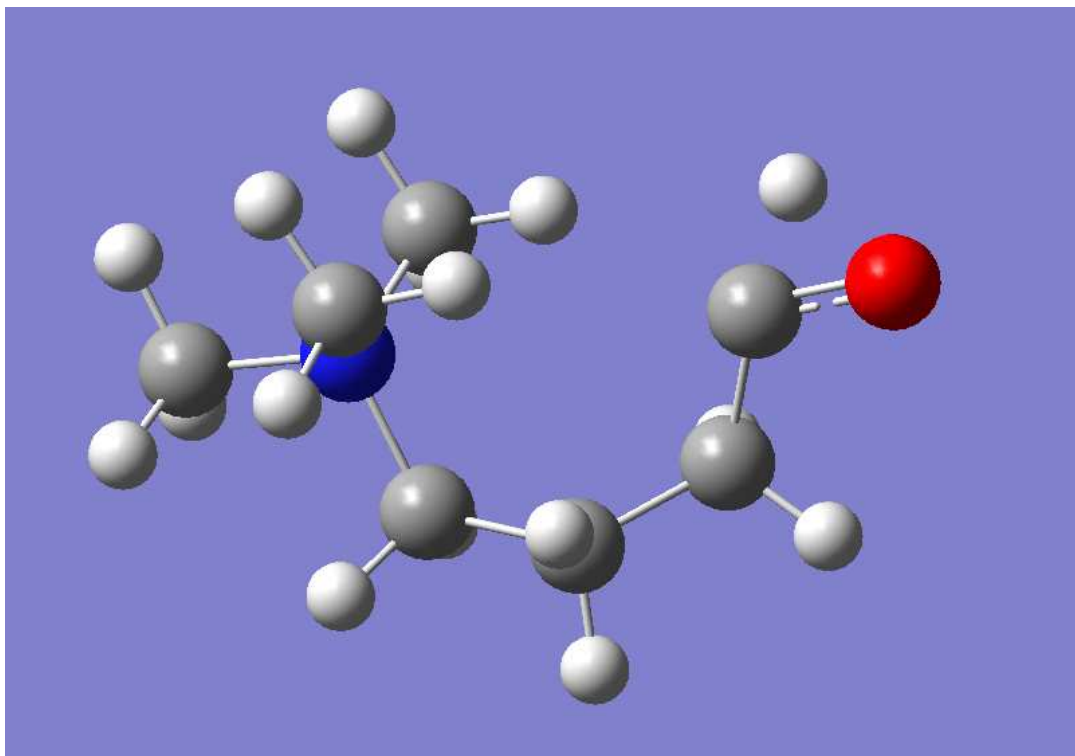
```


H	2.14321995	1.87067997	-0.82501000
H	1.75741005	1.81686997	0.91052002
H	3.36420989	1.31763005	0.34523001
C	2.00805998	-0.81674999	1.23556995
H	1.62041998	-1.82442999	1.11765003
H	3.06842995	-0.85139000	1.46789002
H	1.47519004	-0.30153000	2.02648997
C	-3.02686000	-0.23713000	0.25386000
O	-4.23101997	-0.18234000	-0.35398999
H	-4.86686993	-0.74835998	0.09285000
H	-2.93740010	-0.91760999	1.09570003

S21.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	45.28420000	2.41020000	0.00000000
2	64.82570000	2.51770000	0.00000000
3	101.90490000	0.98250000	0.00000000
4	165.07630000	10.76170000	0.00000000
5	228.44450000	4.09080000	0.00000000
6	232.57640000	3.54850000	0.00000000
7	277.61620000	0.51660000	0.00000000
8	287.77520000	2.46380000	0.00000000
9	304.09550000	4.26070000	0.00000000
10	306.86890000	10.22160000	0.00000000
11	353.95490000	61.94200000	0.00000000
12	360.73560000	2.16430000	0.00000000
13	388.56040000	25.70600000	0.00000000
14	449.71690000	0.24910000	0.00000000
15	466.32740000	3.36510000	0.00000000
16	499.69460000	2.98360000	0.00000000
17	594.14530000	17.51780000	0.00000000
18	750.36920000	0.57590000	0.00000000
19	793.47020000	4.86010000	0.00000000
20	842.58470000	9.82310000	0.00000000
21	885.05750000	71.33180000	0.00000000
22	947.18550000	15.90040000	0.00000000
23	963.65610000	34.60800000	0.00000000
24	967.33970000	16.41550000	0.00000000
25	1004.78540000	5.75120000	0.00000000
26	1050.09840000	0.20900000	0.00000000
27	1077.98410000	0.02900000	0.00000000
28	1094.15930000	6.90580000	0.00000000
29	1142.76470000	12.17400000	0.00000000
30	1150.48660000	11.08450000	0.00000000
31	1191.71020000	20.36460000	0.00000000
32	1205.84450000	70.66160000	0.00000000
33	1242.34400000	189.61510000	0.00000000
34	1259.69390000	12.10670000	0.00000000
35	1291.15010000	0.30920000	0.00000000
36	1297.48050000	23.31570000	0.00000000
37	1328.82910000	18.12250000	0.00000000
38	1354.25860000	18.76750000	0.00000000
39	1366.32220000	3.33290000	0.00000000
40	1394.99370000	5.78700000	0.00000000
41	1412.95190000	1.45630000	0.00000000
42	1453.39700000	5.85130000	0.00000000
43	1454.88900000	3.71220000	0.00000000
44	1478.11520000	0.18920000	0.00000000
45	1482.01420000	0.29350000	0.00000000
46	1490.84510000	1.61020000	0.00000000
47	1493.30710000	1.54600000	0.00000000
48	1495.93390000	1.05040000	0.00000000
49	1505.42280000	3.90410000	0.00000000
50	1515.42670000	25.31700000	0.00000000
51	1517.73330000	37.22220000	0.00000000
52	1529.43510000	52.96440000	0.00000000
53	1751.95070000	142.89240000	0.00000000
54	3028.26730000	23.54830000	0.00000000
55	3072.30300000	0.34220000	0.00000000
56	3074.30100000	1.74410000	0.00000000
57	3077.22500000	4.18670000	0.00000000
58	3080.08600000	7.80840000	0.00000000
59	3083.79100000	1.32020000	0.00000000
60	3131.02560000	3.29980000	0.00000000

61	3131.55360000	14.96570000	0.00000000
62	3161.27130000	0.05420000	0.00000000
63	3161.55530000	0.13490000	0.00000000
64	3165.22570000	4.94070000	0.00000000
65	3167.18790000	4.01950000	0.00000000
66	3167.84940000	1.23940000	0.00000000
67	3178.77910000	0.12610000	0.00000000
68	3183.28610000	1.32350000	0.00000000
69	3838.56370000	168.84300000	0.00000000

S22. CALCULATIONS ON 7 - H_{7r} → 8 - H (TS)

```

Route : # opt=(noeigen,calcall,ts) freq b3lyp/cc-pvtz geom=connectivity empiri
       : calcdispersion=gd3bj int=ultrafine pop=regular
SMILES : C[N](C)(C)CCC[C]O
Formula : C7H16NO+
Charge : 1
Multiplicity : 1
Energy : -406.15906304 a.u.
Gibbs Energy : -405.97098900 a.u.
Number of imaginary frequencies : 1

```

S22.1. Cartesian Co-ordinates (XYZ format)

25

```

C  0.39273399  0.32315999 -0.34305900
H  0.45355701  0.71357203 -1.35741699
H  1.31051505  0.59250301  0.17515700
C -0.77632397  0.94426900  0.41161501
H -0.47757900  1.98845994  0.51825899
H -0.82283801  0.56007499  1.43055999
C -2.17480302  0.93409199 -0.22462200
H -2.10648203  0.99402601 -1.31675994
H -2.75031495  1.80528605  0.10371200
N  0.46583501 -1.19807005 -0.49010000
C  1.86320102 -1.53475201 -0.92713100
H  1.92905498 -2.60574007 -1.09207201
H  2.08083606 -1.00374603 -1.84931803
H  2.55992508 -1.23466802 -0.15032500

```

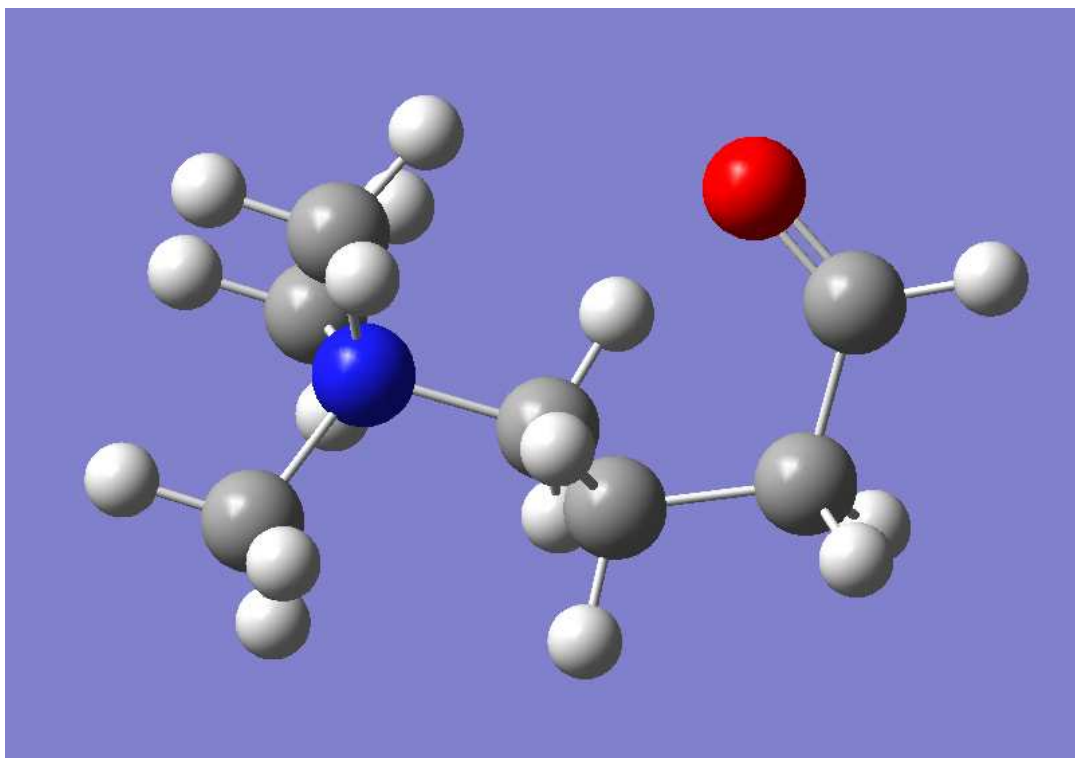
C	0.18127599	-1.88603199	0.81203902
H	0.83017099	-1.47352600	1.57927895
H	-0.86239302	-1.73537600	1.06644905
H	0.38190499	-2.94623995	0.68848002
C	-0.49066299	-1.70163500	-1.53386796
H	-0.30142301	-1.17490602	-2.46443605
H	-0.31683701	-2.76515889	-1.66997004
H	-1.50519502	-1.53638303	-1.18600094
C	-2.98910499	-0.27948201	0.09847200
O	-4.23067617	-0.10194600	0.40077400
H	-3.78413200	-1.20694196	0.36431700

S22.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2058.67980000	898.49270000	0.00000000
2	56.17480000	1.08440000	0.00000000
3	81.27030000	1.42230000	0.00000000
4	119.11930000	0.04460000	0.00000000
5	141.41850000	3.79860000	0.00000000
6	239.82180000	0.26620000	0.00000000
7	247.87690000	0.28360000	0.00000000
8	268.45720000	0.51870000	0.00000000
9	305.23220000	0.18920000	0.00000000
10	318.91170000	0.08430000	0.00000000
11	338.28460000	0.70130000	0.00000000
12	365.76620000	0.97970000	0.00000000
13	403.14340000	1.02610000	0.00000000
14	442.00910000	0.23420000	0.00000000
15	449.99070000	0.04230000	0.00000000
16	497.29520000	5.38900000	0.00000000
17	520.66430000	0.51710000	0.00000000
18	566.57710000	27.00630000	0.00000000
19	691.78880000	0.63290000	0.00000000
20	818.49610000	8.78890000	0.00000000
21	837.76270000	5.98710000	0.00000000
22	884.90760000	23.86650000	0.00000000
23	914.06270000	31.11850000	0.00000000
24	953.84630000	7.74010000	0.00000000
25	974.17690000	30.23620000	0.00000000
26	1022.65560000	3.52430000	0.00000000
27	1062.96830000	14.69290000	0.00000000
28	1084.03560000	0.01800000	0.00000000
29	1090.89390000	3.92650000	0.00000000
30	1129.43550000	4.50160000	0.00000000
31	1150.68000000	0.91340000	0.00000000
32	1199.25140000	2.60490000	0.00000000
33	1253.67040000	8.73420000	0.00000000
34	1256.56840000	5.11640000	0.00000000
35	1289.85110000	9.08690000	0.00000000
36	1296.45010000	4.63870000	0.00000000
37	1349.37870000	2.04550000	0.00000000
38	1365.39200000	6.69510000	0.00000000
39	1409.74880000	15.19880000	0.00000000
40	1425.39540000	0.48630000	0.00000000
41	1443.06280000	22.77900000	0.00000000
42	1452.95850000	5.11860000	0.00000000
43	1456.99980000	2.32430000	0.00000000
44	1473.33270000	187.05070000	0.00000000
45	1478.77000000	1.10920000	0.00000000
46	1481.37550000	12.74950000	0.00000000
47	1484.05120000	5.43360000	0.00000000
48	1495.03790000	13.33640000	0.00000000
49	1500.50080000	15.73180000	0.00000000
50	1508.91890000	0.49760000	0.00000000
51	1517.56730000	34.45060000	0.00000000
52	1523.45840000	13.28560000	0.00000000
53	1537.46860000	29.21200000	0.00000000
54	2586.98120000	88.49820000	0.00000000
55	3004.69820000	2.90750000	0.00000000
56	3045.99410000	3.09590000	0.00000000
57	3058.20930000	3.47950000	0.00000000
58	3063.29770000	15.54120000	0.00000000
59	3069.21600000	1.47960000	0.00000000
60	3071.13930000	1.91180000	0.00000000

61	3077.87360000	9.18240000	0.00000000
62	3088.32990000	5.55300000	0.00000000
63	3123.08090000	4.03980000	0.00000000
64	3154.85060000	10.98400000	0.00000000
65	3160.34410000	0.54590000	0.00000000
66	3161.72190000	4.85100000	0.00000000
67	3165.58150000	2.26220000	0.00000000
68	3168.36400000	1.69690000	0.00000000
69	3170.45310000	4.89220000	0.00000000

S23. CALCULATIONS ON 8 – H



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N](C)(C)CCCC=O
Formula              : C7H16NO+
Charge               : 1
Multiplicity         : 1
Energy               : -406.30039923
Gibbs Energy         : -406.10647000
Number of imaginary frequencies : 0

```

a.u.
a.u.

S23.1. Cartesian Co-ordinates (XYZ format)

25

```

C  0.14841400  0.43915701 -0.65180898
H -0.29697701 -0.43386301 -1.11722195
H  0.44472399  1.13803399 -1.43176496
C -0.82651901  1.09334397  0.32336199
H -0.56672102  2.13939095  0.47501799
H -0.78734702  0.60149598  1.29335201
C -2.26350403  0.98765898 -0.18677300
H -2.37347007  1.36479294 -1.20950103
H -2.93016696  1.61183298  0.41448799
N  1.44340503 -0.06601400 -0.03107100
C  2.31569505 -0.57827699 -1.14024103
H  3.24140310 -0.95347202 -0.71445799
H  1.79247200 -1.37840104 -1.65504706
H  2.52524090  0.23481099 -1.82869005

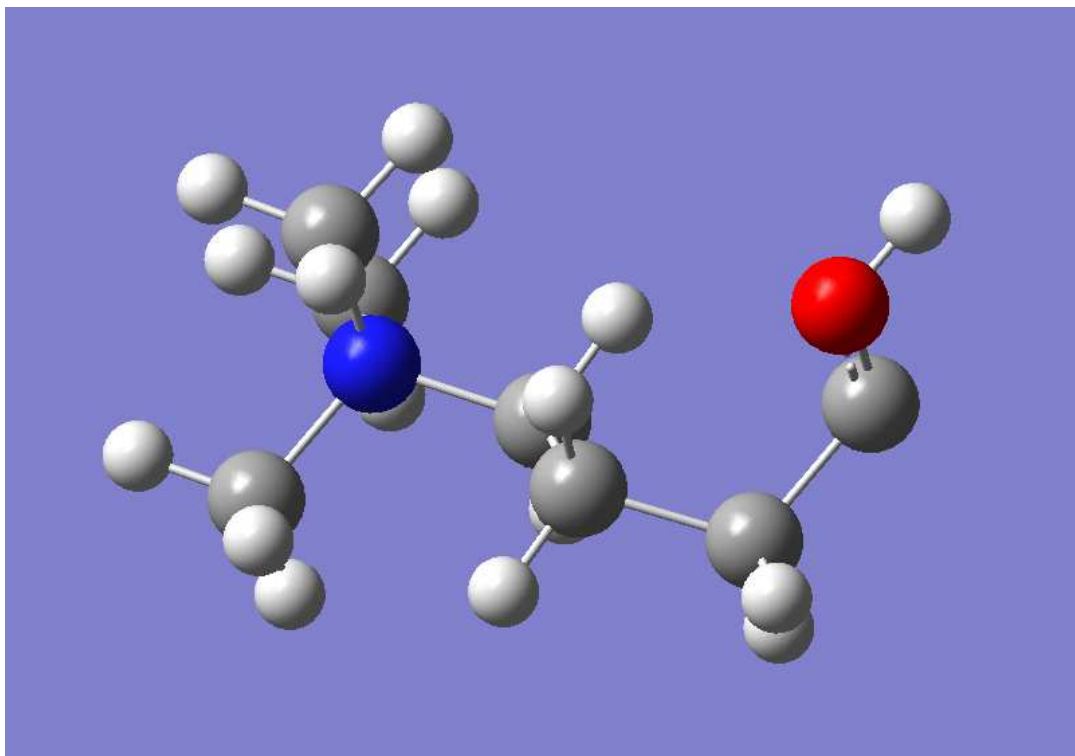
```


C	2.15948391	1.03888202	0.68447202
H	2.34204412	1.84990597	-0.01475800
H	1.54766202	1.38687503	1.50914204
H	3.10235405	0.65499800	1.06249106
C	1.17064905	-1.19808602	0.92140102
H	0.59118700	-1.95690095	0.40647700
H	2.12355304	-1.59754801	1.25524497
H	0.60723299	-0.83077103	1.77011395
C	-2.79652405	-0.42392001	-0.14410000
O	-2.13386202	-1.37174797	0.20225000
H	-3.84860992	-0.55002803	-0.45269799

S23.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	39.95450000	2.80940000	0.00000000
2	63.77770000	5.43150000	0.00000000
3	133.99440000	7.86160000	0.00000000
4	171.81550000	3.37390000	0.00000000
5	218.00190000	1.66050000	0.00000000
6	226.18720000	5.08460000	0.00000000
7	266.96770000	0.06750000	0.00000000
8	281.06370000	1.43920000	0.00000000
9	293.93660000	1.71740000	0.00000000
10	325.25740000	4.62560000	0.00000000
11	366.51850000	0.62060000	0.00000000
12	374.75790000	0.19130000	0.00000000
13	446.82130000	0.26670000	0.00000000
14	453.38580000	0.53060000	0.00000000
15	510.79390000	1.17210000	0.00000000
16	658.95040000	1.85760000	0.00000000
17	711.56080000	1.32500000	0.00000000
18	773.47010000	2.65200000	0.00000000
19	801.73120000	30.17810000	0.00000000
20	872.26820000	9.76780000	0.00000000
21	902.39100000	28.30600000	0.00000000
22	945.99930000	10.51350000	0.00000000
23	969.28830000	18.24690000	0.00000000
24	977.53230000	15.84510000	0.00000000
25	1032.17350000	1.03100000	0.00000000
26	1077.87600000	0.04120000	0.00000000
27	1087.58060000	3.48730000	0.00000000
28	1094.07190000	0.38610000	0.00000000
29	1148.23050000	3.38330000	0.00000000
30	1151.99750000	1.91590000	0.00000000
31	1217.95460000	1.28190000	0.00000000
32	1239.79400000	3.98530000	0.00000000
33	1269.37050000	1.39340000	0.00000000
34	1295.51930000	1.41230000	0.00000000
35	1305.35970000	4.00590000	0.00000000
36	1366.65500000	2.03010000	0.00000000
37	1374.31380000	7.54850000	0.00000000
38	1381.06080000	7.07570000	0.00000000
39	1414.64130000	13.93950000	0.00000000
40	1431.18370000	4.24450000	0.00000000
41	1451.38940000	20.91200000	0.00000000
42	1455.79000000	6.72120000	0.00000000
43	1457.43350000	2.15500000	0.00000000
44	1477.72100000	1.77690000	0.00000000
45	1480.07270000	0.50520000	0.00000000
46	1485.44210000	2.37490000	0.00000000
47	1493.28500000	1.09890000	0.00000000
48	1499.62990000	5.38450000	0.00000000
49	1506.78290000	7.37430000	0.00000000
50	1516.26140000	33.97740000	0.00000000
51	1519.94280000	41.19220000	0.00000000
52	1529.60950000	45.89420000	0.00000000
53	1791.24710000	123.26580000	0.00000000
54	2949.33460000	71.06030000	0.00000000
55	3022.56580000	8.71620000	0.00000000
56	3055.58140000	3.50080000	0.00000000
57	3071.69500000	5.53330000	0.00000000
58	3073.49780000	0.17070000	0.00000000
59	3077.93660000	1.28440000	0.00000000
60	3082.30410000	6.60980000	0.00000000

61	3088.58930000	2.37240000	0.00000000
62	3110.96150000	6.22850000	0.00000000
63	3148.58460000	1.43950000	0.00000000
64	3161.45470000	0.16650000	0.00000000
65	3166.23330000	0.86000000	0.00000000
66	3167.73390000	1.38410000	0.00000000
67	3175.37130000	0.76760000	0.00000000
68	3178.28430000	0.89680000	0.00000000
69	3190.56080000	1.42240000	0.00000000

S24. CALCULATIONS ON 7 - H_{5r} → 7 - H_{6c} (TS)

```

Route : # opt=(calcf,ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper
       : sion=gd3bj int=ultrafine pop=regular
SMILES : C[N](C)(C)CCC[C]O
Formula : C7H16NO+
Charge : 1
Multiplicity : 1
Energy : -406.21046150 a.u.
Gibbs Energy : -406.01727400 a.u.
Number of imaginary frequencies : 1

```

S24.1. Cartesian Co-ordinates (XYZ format)

25

```

C  0.00000000  0.00000000 -0.00000000
H  0.00000000 -0.00000000  1.08815098
H  1.03601801 -0.00000000 -0.33380899
C -0.73792702 -1.21424603 -0.54288602
H -0.73614001 -1.21453404 -1.63191903
H -1.77286005 -1.22947001 -0.20642000
C -0.03859900 -2.49459291 -0.04385500
H  1.00467598 -2.50505996 -0.35532799
H -0.52807099 -3.36076188 -0.50238699
N -0.56341702  1.35811305 -0.40909600
C  0.29056701  2.41850090  0.22453099
H -0.09559400  3.39448810 -0.05397100
H  0.25710699  2.29798603  1.30308104
H  1.31067002  2.30628800 -0.13004200

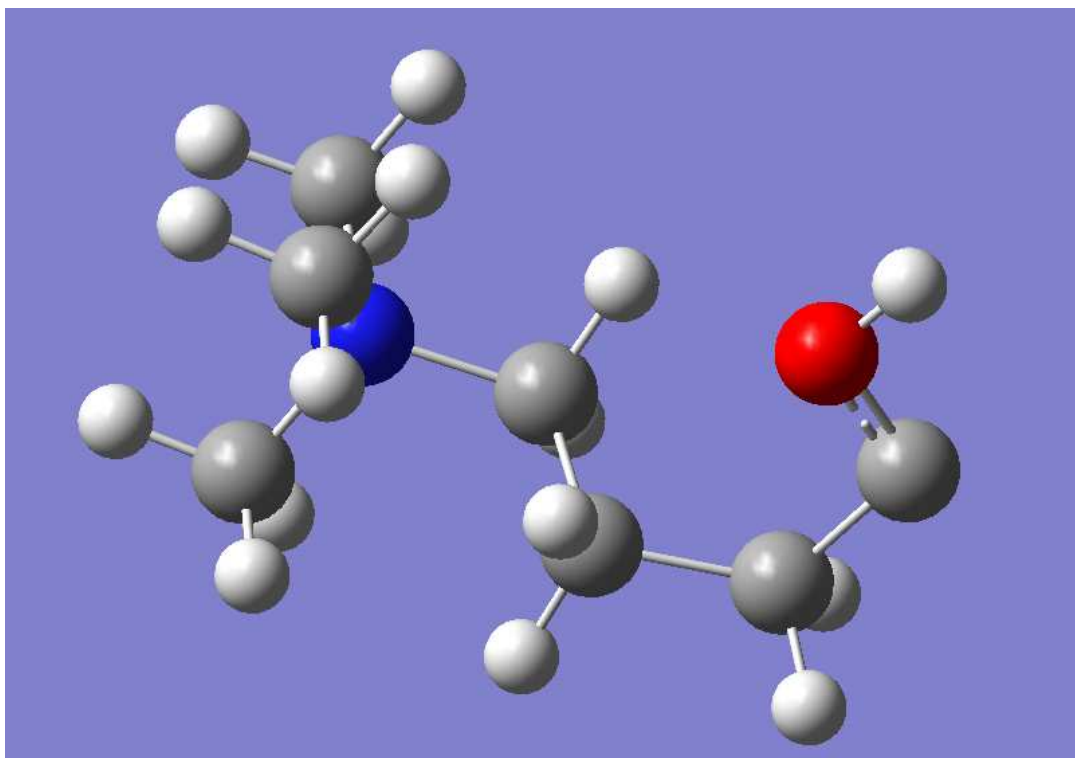
```

C	-0.52307600	1.53021705	-1.89859295
H	0.49673900	1.38139403	-2.24112391
H	-1.18318200	0.80687398	-2.36296391
H	-0.85312301	2.53630304	-2.13970304
C	-1.97364795	1.51757503	0.07693400
H	-1.99415696	1.35470605	1.15044403
H	-2.30765200	2.52485108	-0.15350100
H	-2.61001396	0.79616499	-0.42218801
C	-0.10659000	-2.67723107	1.45837998
O	-1.38130701	-2.71743894	1.77480304
H	-1.46019101	-2.86399198	2.72792912

S24.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-156.86400000	4.03400000	0.00000000
2	29.50940000	0.38940000	0.00000000
3	69.80970000	0.92470000	0.00000000
4	120.20870000	0.77800000	0.00000000
5	186.28320000	0.88950000	0.00000000
6	227.52900000	0.59110000	0.00000000
7	245.86110000	1.62950000	0.00000000
8	280.28040000	0.20370000	0.00000000
9	291.31270000	0.04280000	0.00000000
10	344.65870000	0.99970000	0.00000000
11	360.93070000	0.17920000	0.00000000
12	373.44090000	0.07420000	0.00000000
13	448.96740000	0.25690000	0.00000000
14	450.79630000	1.07130000	0.00000000
15	518.26570000	0.30880000	0.00000000
16	562.71350000	7.58790000	0.00000000
17	749.89200000	0.65830000	0.00000000
18	764.44660000	12.94670000	0.00000000
19	818.24140000	43.42200000	0.00000000
20	877.76000000	42.20870000	0.00000000
21	885.21610000	41.63860000	0.00000000
22	921.29640000	2.36290000	0.00000000
23	955.69540000	18.92760000	0.00000000
24	964.21110000	14.25810000	0.00000000
25	1000.71110000	24.29190000	0.00000000
26	1046.19780000	13.96530000	0.00000000
27	1068.47080000	19.36070000	0.00000000
28	1078.47020000	0.13590000	0.00000000
29	1130.46530000	10.16120000	0.00000000
30	1137.64150000	13.69350000	0.00000000
31	1182.19620000	4.20560000	0.00000000
32	1211.28310000	12.31480000	0.00000000
33	1265.42150000	0.58260000	0.00000000
34	1283.51170000	28.34700000	0.00000000
35	1293.57570000	0.83470000	0.00000000
36	1320.80590000	80.42600000	0.00000000
37	1330.60270000	6.16000000	0.00000000
38	1364.27630000	16.93810000	0.00000000
39	1372.03420000	4.31010000	0.00000000
40	1375.85420000	30.59180000	0.00000000
41	1419.15630000	5.13980000	0.00000000
42	1454.01870000	5.73360000	0.00000000
43	1455.40430000	3.29960000	0.00000000
44	1481.03780000	1.17640000	0.00000000
45	1482.26900000	0.30130000	0.00000000
46	1483.55610000	7.50100000	0.00000000
47	1492.72000000	0.68360000	0.00000000
48	1493.34820000	2.78210000	0.00000000
49	1501.46090000	4.28100000	0.00000000
50	1510.80400000	2.67660000	0.00000000
51	1515.69130000	25.05240000	0.00000000
52	1518.79420000	38.75750000	0.00000000
53	1530.80110000	52.85490000	0.00000000
54	3018.20040000	2.78580000	0.00000000
55	3061.36300000	9.57420000	0.00000000
56	3072.86100000	0.92410000	0.00000000
57	3077.30780000	5.68360000	0.00000000
58	3077.79500000	1.30060000	0.00000000
59	3084.11240000	0.58730000	0.00000000
60	3090.06320000	4.43920000	0.00000000

61	3105.96130000	5.73090000	0.00000000
62	3129.32980000	7.64530000	0.00000000
63	3162.63930000	0.09490000	0.00000000
64	3163.06880000	0.06850000	0.00000000
65	3168.04450000	0.97510000	0.00000000
66	3168.87760000	2.47510000	0.00000000
67	3179.66160000	0.00410000	0.00000000
68	3183.45450000	1.16660000	0.00000000
69	3731.36550000	155.10940000	0.00000000

S25. CALCULATIONS ON 7 – H_{ec}

```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N](C)(C)CCC[C]O
Formula              : C7H16NO+
Charge               : 1
Multiplicity         : 1
Energy               : -406.21399256 a.u.
Gibbs Energy        : -406.02146600 a.u.
Number of imaginary frequencies : 0

```

S25.1. Cartesian Co-ordinates (XYZ format)

25

```

C  0.00000000  0.00000000 -0.00000000
H  0.00000000  0.00000000  1.08656204
H  1.03267395  0.00000000 -0.34483701
C -0.74444801 -1.21015406 -0.53622299
H -0.68748897 -1.24456000 -1.62348497
H -1.79584599 -1.17399299 -0.25613901
C -0.13048100 -2.50213099  0.03301700
H  0.95216298 -2.54794693 -0.12425500
H -0.49970499 -3.36798000 -0.52929401
N -0.56549102  1.35997295 -0.40270299
C  0.31481701  2.41901207  0.19474600
H -0.07549800  3.39569712 -0.07540000
H  0.31757700  2.30454612  1.27447402
H  1.32154405  2.30004501 -0.19422700

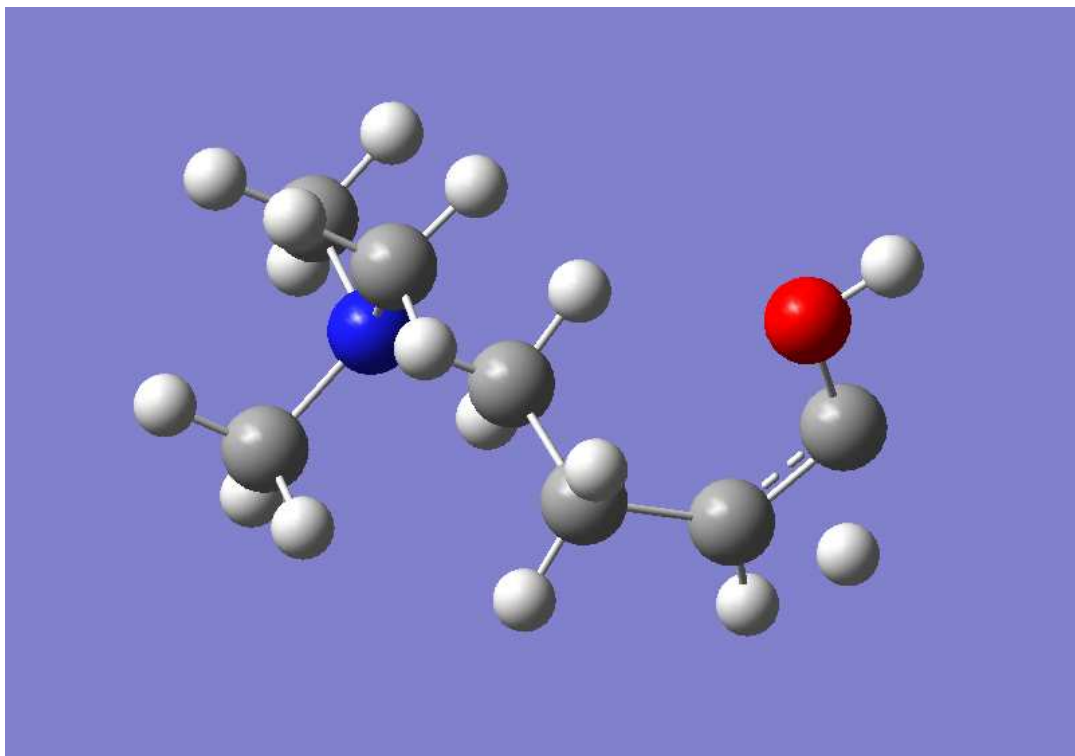
```


C	-0.57357699	1.51973796	-1.89362502
H	0.43362901	1.36298800	-2.26862502
H	-1.25156796	0.79490900	-2.32909203
H	-0.90669799	2.52536511	-2.13261509
C	-1.95789897	1.53295195	0.12922800
H	-1.94486904	1.36799896	1.20229304
H	-2.28930807	2.54334092	-0.09105700
H	-2.61703300	0.81782198	-0.34849900
C	-0.36517099	-2.89241695	1.46131897
O	-1.18622899	-2.02023697	2.01609898
H	-1.35696101	-2.30465889	2.92507410

S25.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	27.50280000	0.14770000	0.00000000
2	69.88330000	0.67720000	0.00000000
3	118.63870000	3.47390000	0.00000000
4	144.04130000	4.47350000	0.00000000
5	206.27190000	1.30200000	0.00000000
6	227.03520000	0.12500000	0.00000000
7	254.77200000	0.39230000	0.00000000
8	275.88530000	0.06050000	0.00000000
9	290.82870000	0.07690000	0.00000000
10	331.34230000	1.72940000	0.00000000
11	361.47070000	0.16980000	0.00000000
12	367.12550000	0.21670000	0.00000000
13	447.67170000	0.29530000	0.00000000
14	449.18510000	1.04900000	0.00000000
15	512.18600000	0.19540000	0.00000000
16	643.82520000	14.58530000	0.00000000
17	664.31360000	15.51800000	0.00000000
18	761.44320000	6.57240000	0.00000000
19	791.05580000	21.46940000	0.00000000
20	863.70770000	23.13880000	0.00000000
21	881.38960000	46.81120000	0.00000000
22	915.57710000	18.96590000	0.00000000
23	952.61050000	13.05040000	0.00000000
24	965.81190000	15.10680000	0.00000000
25	1005.79520000	9.69990000	0.00000000
26	1050.34840000	15.27000000	0.00000000
27	1069.46530000	18.83860000	0.00000000
28	1077.88600000	0.45210000	0.00000000
29	1135.16100000	13.01850000	0.00000000
30	1142.13630000	9.33010000	0.00000000
31	1203.20460000	3.47780000	0.00000000
32	1219.69620000	37.01920000	0.00000000
33	1268.00050000	1.07210000	0.00000000
34	1272.80330000	112.74140000	0.00000000
35	1292.65520000	2.01880000	0.00000000
36	1299.24710000	19.76090000	0.00000000
37	1330.95860000	14.00750000	0.00000000
38	1355.53270000	4.73560000	0.00000000
39	1374.56170000	7.76000000	0.00000000
40	1378.47730000	5.97160000	0.00000000
41	1414.84960000	5.21410000	0.00000000
42	1435.34030000	11.08570000	0.00000000
43	1453.32610000	5.94360000	0.00000000
44	1455.07670000	3.05140000	0.00000000
45	1480.65780000	0.31240000	0.00000000
46	1481.58110000	0.44070000	0.00000000
47	1491.47320000	2.75820000	0.00000000
48	1493.04640000	1.62930000	0.00000000
49	1498.71440000	3.49570000	0.00000000
50	1508.11750000	4.97300000	0.00000000
51	1515.43970000	26.00290000	0.00000000
52	1519.51220000	40.83310000	0.00000000
53	1531.08430000	48.94280000	0.00000000
54	3021.13200000	7.32540000	0.00000000
55	3040.30190000	1.01960000	0.00000000
56	3060.66550000	9.97690000	0.00000000
57	3073.01860000	0.19280000	0.00000000
58	3077.78780000	2.15140000	0.00000000
59	3078.20510000	5.18730000	0.00000000
60	3084.78520000	1.00590000	0.00000000

61	3103.16180000	6.44440000	0.00000000
62	3138.02830000	3.45690000	0.00000000
63	3161.87860000	0.11580000	0.00000000
64	3163.74550000	0.06630000	0.00000000
65	3167.71880000	1.29280000	0.00000000
66	3169.11130000	2.39910000	0.00000000
67	3179.79280000	0.10890000	0.00000000
68	3184.73880000	1.17550000	0.00000000
69	3730.86430000	157.81360000	0.00000000

S26. CALCULATIONS ON 7 - H_{ec} → 9Z - H (TS)

```

Route : # opt=(calcf,ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper
       : sion=gd3bj int=ultrafine pop=regular
SMILES : C[N](C)(C)CC[CH][CH]O
Formula : C7H16NO+
Charge : 1
Multiplicity : 1
Energy : -406.18083828 a.u.
Gibbs Energy : -405.99141600 a.u.
Number of imaginary frequencies : 1

```

S26.1. Cartesian Co-ordinates (XYZ format)

25

```

C  0.14195000 -0.28332999  0.57467997
H -0.28806999  0.65148002  0.92237997
H  0.31985000 -0.92790002  1.43298995
C -0.80018002 -0.94730997 -0.42247999
H -0.45969999 -1.94439006 -0.69362003
H -0.87830001 -0.34272999 -1.32529998
C -2.18128991 -1.00884998  0.20652001
H -2.48009992 -1.92033005  0.70968997
N  1.52276003  0.07961000  0.03455000
C  2.30631995  0.68934000  1.16131997
H  2.39327002 -0.03763000  1.96314001
H  3.29237008  0.96166998  0.79698998
H  1.78210998  1.57216001  1.51451004
C  2.24505997 -1.13692999 -0.46053001

```

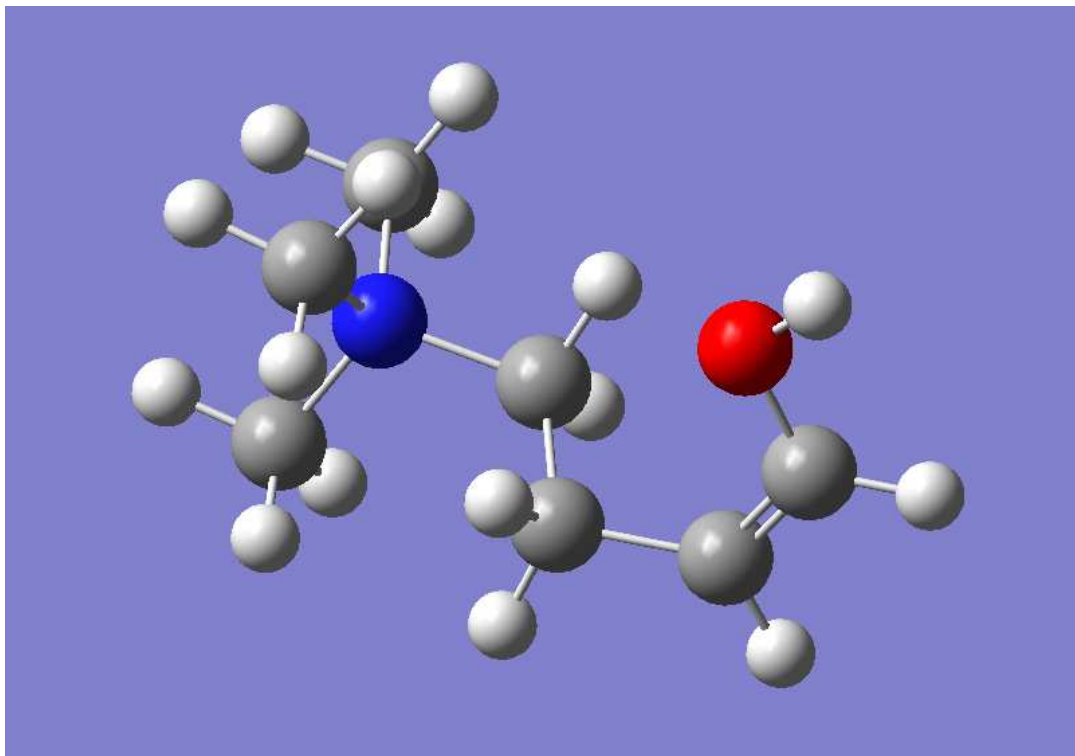
H 3.24536991 -0.84614003 -0.76747000
H 1.70886004 -1.55365002 -1.30561996
H 2.30029988 -1.86438000 0.34415001
C 1.40890002 1.08659995 -1.07328999
H 2.40821004 1.40899003 -1.35011005
H 0.82367998 1.92997003 -0.71990001
H 0.92246997 0.63034999 -1.92730999
C -3.01503992 0.09476000 0.38341999
O -2.48606992 1.21466005 -0.18467000
H -3.15282989 1.90704000 -0.13628000
H -3.34252000 -0.86475998 -0.44051999

S26.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-1384.45190000	81.74440000	0.00000000
2	29.70960000	0.50570000	0.00000000
3	60.21640000	1.25800000	0.00000000
4	118.28350000	0.76290000	0.00000000
5	165.57060000	2.16800000	0.00000000
6	226.09230000	0.49490000	0.00000000
7	245.73080000	0.27750000	0.00000000
8	275.34920000	0.05280000	0.00000000
9	291.31120000	0.16610000	0.00000000
10	305.38280000	1.45340000	0.00000000
11	360.79150000	0.10580000	0.00000000
12	366.90120000	0.43070000	0.00000000
13	431.99700000	1.65270000	0.00000000
14	448.62080000	0.22070000	0.00000000
15	504.19960000	1.04010000	0.00000000
16	538.17060000	6.79540000	0.00000000
17	668.24920000	64.09500000	0.00000000
18	683.22210000	39.66450000	0.00000000
19	755.49860000	2.98630000	0.00000000
20	794.27830000	12.18810000	0.00000000
21	811.53610000	37.24240000	0.00000000
22	893.97060000	39.77800000	0.00000000
23	934.93160000	11.51120000	0.00000000
24	955.36910000	9.39890000	0.00000000
25	975.52350000	12.88740000	0.00000000
26	1047.59060000	41.61530000	0.00000000
27	1062.24640000	29.07470000	0.00000000
28	1078.20350000	0.32580000	0.00000000
29	1092.72200000	19.91580000	0.00000000
30	1146.27610000	9.11350000	0.00000000
31	1151.77800000	2.74680000	0.00000000
32	1219.13510000	20.19240000	0.00000000
33	1240.24790000	93.19860000	0.00000000
34	1260.90350000	9.56920000	0.00000000
35	1284.52420000	20.12440000	0.00000000
36	1293.16360000	0.34450000	0.00000000
37	1325.84650000	17.72200000	0.00000000
38	1333.17630000	20.67320000	0.00000000
39	1369.69050000	6.94230000	0.00000000
40	1377.40900000	4.22060000	0.00000000
41	1418.03750000	6.25010000	0.00000000
42	1453.96740000	5.46410000	0.00000000
43	1455.68530000	3.88850000	0.00000000
44	1479.05350000	0.73990000	0.00000000
45	1481.63500000	0.42740000	0.00000000
46	1488.91090000	3.80870000	0.00000000
47	1491.95920000	2.49480000	0.00000000
48	1494.42310000	1.54850000	0.00000000
49	1503.15480000	12.77170000	0.00000000
50	1507.69840000	5.02610000	0.00000000
51	1516.24000000	26.15690000	0.00000000
52	1519.50410000	39.89880000	0.00000000
53	1530.73510000	47.84880000	0.00000000
54	2080.58600000	8.62480000	0.00000000
55	3062.58470000	9.52010000	0.00000000
56	3073.53410000	0.20140000	0.00000000
57	3077.66340000	0.43540000	0.00000000
58	3083.20130000	3.59630000	0.00000000
59	3086.94840000	2.89770000	0.00000000
60	3109.89850000	4.52680000	0.00000000

61	3145.26270000	1.34470000	0.00000000
62	3162.00610000	0.11290000	0.00000000
63	3164.95700000	0.17330000	0.00000000
64	3168.09500000	1.11070000	0.00000000
65	3170.28740000	1.85100000	0.00000000
66	3171.38540000	0.13660000	0.00000000
67	3177.77400000	0.37080000	0.00000000
68	3184.84100000	1.22060000	0.00000000
69	3810.13580000	166.27820000	0.00000000

S27. CALCULATIONS ON 9Z – H



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N](C)(C)CCC=CO
Formula              : C7H16NO+
Charge               : 1
Multiplicity         : 1
Energy               : -406.28968784
Gibbs Energy         : -406.09579100
Number of imaginary frequencies : 0

```

a.u.

a.u.

S27.1. Cartesian Co-ordinates (XYZ format)

25

```

C -0.14291000  0.25062999  0.55432999
H  0.29411000 -0.69755000  0.85549998
H -0.29297000  0.86400998  1.44006002
C  0.77689999  0.95275998 -0.43961000
H  0.40171999  1.94457996 -0.68419999
H  0.83923000  0.37854001 -1.36444998
C  2.15287995  1.06296003  0.16294000
H  2.49394011  2.01603007  0.53513002
N -1.54252994 -0.09085000  0.04148000
C -2.30069995 -0.73019999  1.16705000
H -3.29629993 -0.99049997  0.81967998
H -1.77076006 -1.62366998  1.48298001
H -2.36609006 -0.02649000  1.99131000
C -2.26881003  1.14423001 -0.39667001

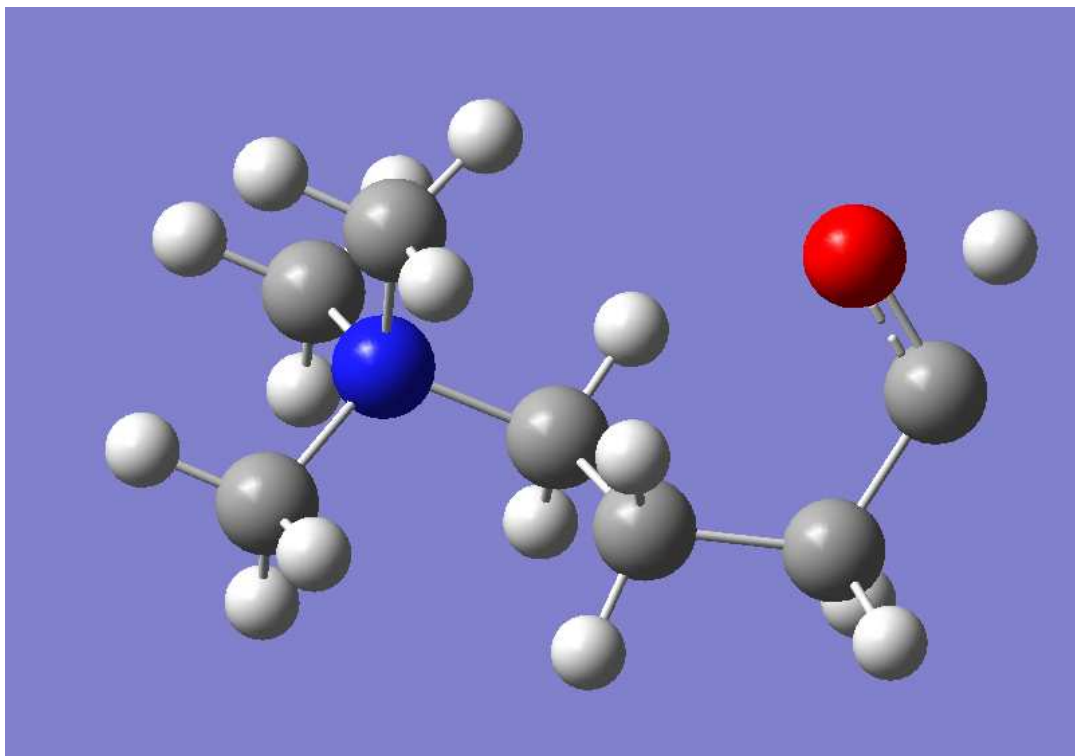
```


H	-2.29110003	1.84937000	0.42914999
H	-1.75523996	1.58034003	-1.24574995
H	-3.28130007	0.87124002	-0.67956001
C	-1.46290004	-1.06175995	-1.09944999
H	-0.88375002	-1.92409003	-0.78351003
H	-2.47086000	-1.36316001	-1.36905003
H	-0.98338997	-0.58451003	-1.94579995
C	2.96776009	0.01698000	0.24952000
O	2.57030010	-1.21511996	-0.18593000
H	3.30111003	-1.83835006	-0.13978000
H	3.96363997	0.08740000	0.66671997

S27.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	33.54340000	0.39660000	0.00000000
2	53.62470000	1.12340000	0.00000000
3	110.48610000	0.55760000	0.00000000
4	166.75720000	2.31820000	0.00000000
5	223.24190000	1.06190000	0.00000000
6	236.48150000	0.50090000	0.00000000
7	274.59420000	0.55130000	0.00000000
8	291.45310000	0.11500000	0.00000000
9	298.55290000	22.59780000	0.00000000
10	353.71580000	66.58230000	0.00000000
11	361.58070000	5.50570000	0.00000000
12	369.57540000	20.79250000	0.00000000
13	435.58010000	0.59850000	0.00000000
14	450.34600000	0.13010000	0.00000000
15	504.17540000	1.59290000	0.00000000
16	548.19910000	2.26940000	0.00000000
17	684.82810000	4.91260000	0.00000000
18	743.47250000	31.47370000	0.00000000
19	772.52540000	20.66170000	0.00000000
20	803.61210000	13.69730000	0.00000000
21	884.83070000	64.79240000	0.00000000
22	950.43870000	10.55630000	0.00000000
23	956.60290000	1.06150000	0.00000000
24	962.27460000	13.93590000	0.00000000
25	984.11110000	3.25110000	0.00000000
26	1051.69880000	2.39740000	0.00000000
27	1061.66560000	29.89880000	0.00000000
28	1078.06780000	0.20450000	0.00000000
29	1102.93940000	33.76200000	0.00000000
30	1148.38100000	0.91380000	0.00000000
31	1150.18950000	2.35200000	0.00000000
32	1216.80490000	7.68750000	0.00000000
33	1259.82560000	2.94080000	0.00000000
34	1266.21270000	9.17170000	0.00000000
35	1288.35100000	140.35840000	0.00000000
36	1291.80350000	3.55140000	0.00000000
37	1313.03950000	4.65050000	0.00000000
38	1339.69910000	1.55550000	0.00000000
39	1371.74300000	2.03980000	0.00000000
40	1413.05820000	3.60900000	0.00000000
41	1428.62680000	3.21420000	0.00000000
42	1453.67720000	5.69440000	0.00000000
43	1454.77890000	3.61290000	0.00000000
44	1477.97450000	0.16760000	0.00000000
45	1481.56370000	0.16280000	0.00000000
46	1491.20870000	2.67570000	0.00000000
47	1493.19040000	1.55790000	0.00000000
48	1496.90000000	1.98950000	0.00000000
49	1506.71570000	3.89090000	0.00000000
50	1515.39680000	25.20630000	0.00000000
51	1517.77370000	40.69790000	0.00000000
52	1530.01890000	51.02160000	0.00000000
53	1737.18260000	66.07210000	0.00000000
54	3051.74310000	13.77850000	0.00000000
55	3072.74170000	0.37350000	0.00000000
56	3077.08350000	0.41280000	0.00000000
57	3081.87980000	4.19470000	0.00000000
58	3086.48420000	3.88440000	0.00000000
59	3100.13840000	6.83140000	0.00000000
60	3142.26910000	2.53600000	0.00000000

61	3160.50220000	0.10640000	0.00000000
62	3162.73490000	0.30400000	0.00000000
63	3167.25430000	2.27880000	0.00000000
64	3168.16860000	2.21960000	0.00000000
65	3178.91380000	0.25610000	0.00000000
66	3180.79080000	2.38410000	0.00000000
67	3184.55380000	1.29950000	0.00000000
68	3218.56890000	3.86130000	0.00000000
69	3835.71760000	151.29780000	0.00000000

S28. CALCULATIONS ON 7 – H_{ec} → 8 – H (TS)

```

Route : # opt=(calcf,ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper
       : sion=gd3bj int=ultrafine pop=regular
SMILES : C[N](C)(C)CCC[C]O
Formula : C7H16NO+
Charge : 1
Multiplicity : 1
Energy : -406.16422981 a.u.
Gibbs Energy : -405.97713400 a.u.
Number of imaginary frequencies : 1

```

S28.1. Cartesian Co-ordinates (XYZ format)

25

```

C -0.14586499 0.38449499 0.61213899
H 0.28061199 -0.50026602 1.07539499
H -0.39223301 1.09985495 1.39481199
C 0.82500499 0.99374002 -0.38957199
H 0.50962001 1.99669099 -0.67045701
H 0.87051898 0.39154500 -1.29576302
C 2.23899794 1.05405605 0.20346799
H 2.26335812 1.48180997 1.21066403
H 2.87930393 1.71623194 -0.38701800
N -1.47868502 -0.07521400 0.03331700
C -2.33017707 -0.56298798 1.16954195
H -3.28128910 -0.90657097 0.77402598
H -1.81656301 -1.38082397 1.66593206
H -2.49024510 0.25440001 1.86612105

```

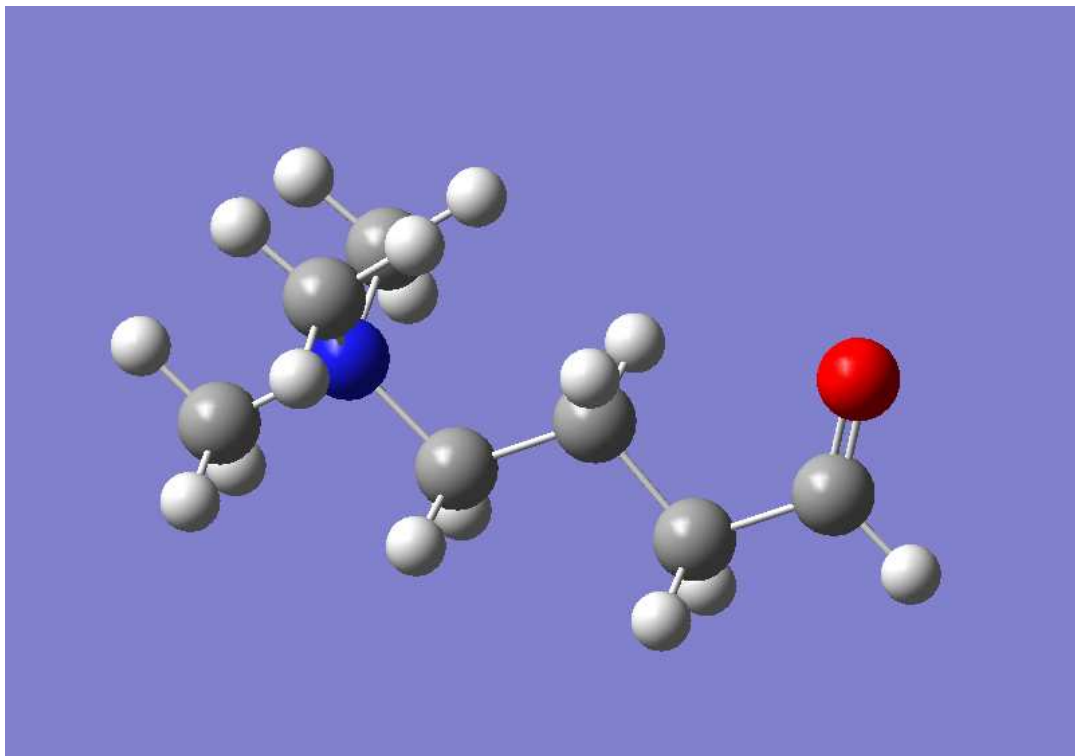
C	-2.18302011	1.05473197	-0.65530699
H	-2.30628800	1.87286603	0.04851400
H	-1.59417796	1.37856197	-1.50596201
H	-3.15442491	0.70476103	-0.99172097
C	-1.27367103	-1.20829594	-0.93260902
H	-0.70739299	-1.99117601	-0.43826500
H	-2.24775600	-1.57764006	-1.23894501
H	-0.72736400	-0.85200500	-1.79738998
C	2.94697499	-0.26306200	0.25475201
O	2.30215192	-1.30238199	-0.21364400
H	3.38365889	-1.45617104	0.19955100

S28.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2028.18990000	479.62900000	0.00000000
2	29.46010000	1.07960000	0.00000000
3	62.66530000	2.59420000	0.00000000
4	124.05760000	0.90030000	0.00000000
5	165.55080000	1.00720000	0.00000000
6	215.52970000	0.29150000	0.00000000
7	227.53170000	0.97890000	0.00000000
8	265.52670000	0.73370000	0.00000000
9	276.21250000	0.62780000	0.00000000
10	294.53700000	0.45620000	0.00000000
11	324.32190000	1.01680000	0.00000000
12	363.21310000	0.18920000	0.00000000
13	370.81440000	0.40080000	0.00000000
14	447.88760000	0.11340000	0.00000000
15	450.13620000	1.37030000	0.00000000
16	511.83700000	0.35830000	0.00000000
17	550.51090000	34.35700000	0.00000000
18	659.59050000	1.06460000	0.00000000
19	745.06710000	1.80300000	0.00000000
20	795.11770000	20.12370000	0.00000000
21	813.70210000	6.94230000	0.00000000
22	886.87760000	15.42580000	0.00000000
23	912.29620000	30.55150000	0.00000000
24	948.10890000	11.66340000	0.00000000
25	966.55590000	16.01630000	0.00000000
26	1009.44720000	4.28390000	0.00000000
27	1039.87680000	10.19950000	0.00000000
28	1075.90350000	7.43470000	0.00000000
29	1078.50510000	2.01550000	0.00000000
30	1136.16610000	4.20550000	0.00000000
31	1144.88250000	9.08250000	0.00000000
32	1195.24020000	1.01740000	0.00000000
33	1224.63340000	17.18810000	0.00000000
34	1266.66560000	1.30500000	0.00000000
35	1292.38770000	17.44270000	0.00000000
36	1296.77180000	8.97200000	0.00000000
37	1347.99920000	87.15950000	0.00000000
38	1356.07600000	5.37170000	0.00000000
39	1373.00700000	17.85880000	0.00000000
40	1385.88730000	61.44280000	0.00000000
41	1424.29590000	7.24360000	0.00000000
42	1441.69530000	1.10560000	0.00000000
43	1454.83400000	4.75500000	0.00000000
44	1456.60070000	3.73510000	0.00000000
45	1480.10800000	0.89810000	0.00000000
46	1481.51740000	1.30900000	0.00000000
47	1487.51860000	1.52340000	0.00000000
48	1493.62580000	1.41520000	0.00000000
49	1497.66200000	2.26480000	0.00000000
50	1507.25760000	6.17220000	0.00000000
51	1516.23110000	29.95620000	0.00000000
52	1520.05190000	43.41950000	0.00000000
53	1530.51710000	48.29710000	0.00000000
54	2582.58530000	166.33210000	0.00000000
55	3032.10220000	4.00520000	0.00000000
56	3054.62770000	2.68770000	0.00000000
57	3067.73280000	5.64620000	0.00000000
58	3073.29390000	0.13230000	0.00000000
59	3077.93110000	1.30040000	0.00000000
60	3081.21450000	6.59400000	0.00000000

61	3086.9630000	1.1810000	0.0000000
62	3107.4637000	3.7277000	0.0000000
63	3142.0459000	1.8476000	0.0000000
64	3161.7635000	0.1172000	0.0000000
65	3165.4409000	0.3813000	0.0000000
66	3167.6674000	1.2462000	0.0000000
67	3172.0113000	1.5486000	0.0000000
68	3178.7442000	0.4543000	0.0000000
69	3189.0701000	1.0924000	0.0000000

S29. CALCULATIONS ON 8 – H



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N](C)(C)CCCC=O
Formula              : C7H16NO+
Charge                : 1
Multiplicity         : 1
Energy                : -406.29481828
Gibbs Energy         : -406.10217600
Number of imaginary frequencies : 0

```

a.u.
a.u.

S29.1. Cartesian Co-ordinates (XYZ format)

25

```

C  0.44732001 -0.79768002 -0.00041000
H  0.52095997 -1.43338001  0.88059998
H  0.52109998 -1.43272996 -0.88186997
C -0.84922999 -0.01244000 -0.00027000
H -0.92142999  0.63382000 -0.87351000
H -0.92114002  0.63401997  0.87283999
C -2.05079007 -0.95499003  0.00003000
H -2.05211997 -1.61646998  0.87252998
H -2.05230999 -1.61688995 -0.87215000
N  1.72068000  0.04553000  0.00003000
C  2.89414001 -0.89128000 -0.00052000
H  3.80994010 -0.30785000 -0.00043000
H  2.84893990 -1.51227999  0.88907999
H  2.84867001 -1.51160002 -0.89058000

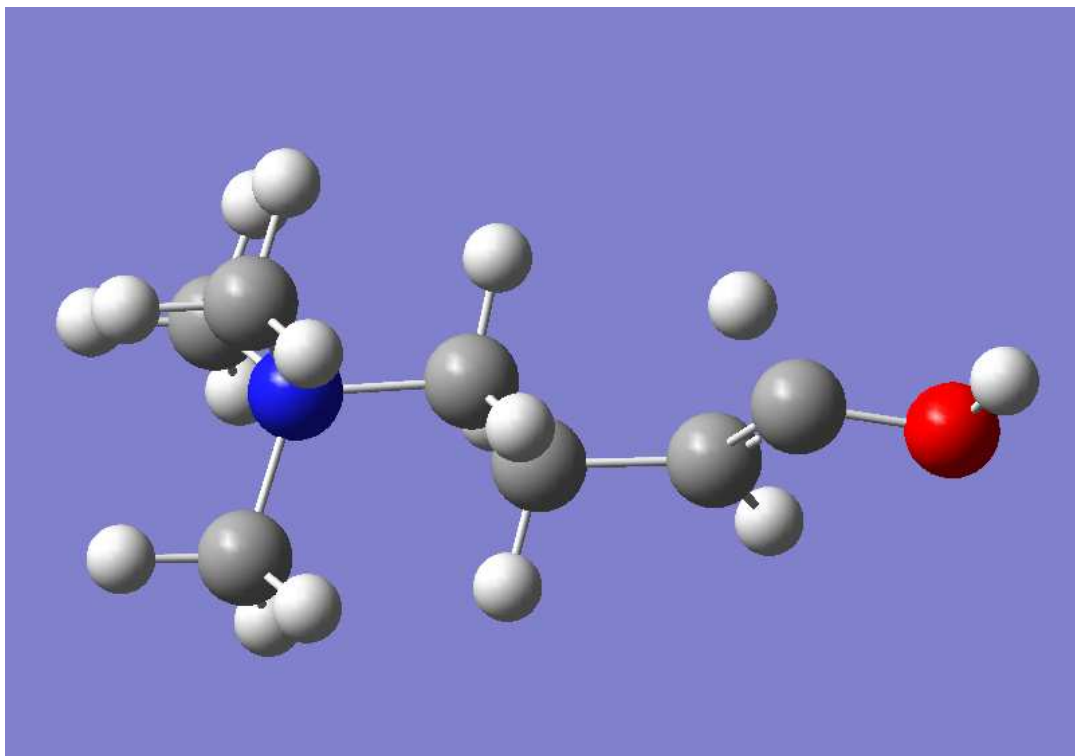
```


C	1.79119003	0.91027999	-1.22485995
H	1.70380998	0.27974999	-2.10484004
H	0.98580998	1.63502002	-1.20155001
H	2.74790001	1.42394996	-1.22941005
C	1.79132998	0.90894997	1.22581995
H	1.70379996	0.27750000	2.10512996
H	2.74815989	1.42238998	1.23095000
H	0.98615003	1.63391995	1.20327997
C	-3.35531998	-0.18609001	0.00007000
O	-3.40805006	1.01458001	0.00005000
H	-4.27035999	-0.80492002	0.00014000

S29.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	32.13950000	4.66860000	0.00000000
2	67.68390000	0.71760000	0.00000000
3	106.81840000	6.99430000	0.00000000
4	111.98270000	1.07380000	0.00000000
5	195.21560000	3.04520000	0.00000000
6	235.96730000	0.16590000	0.00000000
7	239.40160000	7.04140000	0.00000000
8	278.74140000	1.09030000	0.00000000
9	292.32040000	0.00010000	0.00000000
10	307.77340000	0.21060000	0.00000000
11	361.68120000	0.22210000	0.00000000
12	382.87080000	2.89200000	0.00000000
13	448.14590000	0.28700000	0.00000000
14	458.77810000	2.99570000	0.00000000
15	517.12670000	1.56550000	0.00000000
16	687.26820000	5.30850000	0.00000000
17	706.02570000	7.48280000	0.00000000
18	755.78700000	2.76090000	0.00000000
19	789.57790000	2.15510000	0.00000000
20	883.86930000	7.75040000	0.00000000
21	907.92690000	71.86430000	0.00000000
22	930.16720000	9.46000000	0.00000000
23	967.95900000	12.21690000	0.00000000
24	971.57740000	7.11610000	0.00000000
25	1061.08680000	1.64680000	0.00000000
26	1078.58810000	0.01880000	0.00000000
27	1080.21240000	7.14820000	0.00000000
28	1099.11460000	0.01950000	0.00000000
29	1152.70650000	4.19440000	0.00000000
30	1161.54080000	0.44650000	0.00000000
31	1209.52250000	0.22010000	0.00000000
32	1256.48590000	5.74610000	0.00000000
33	1275.57970000	0.86340000	0.00000000
34	1292.29810000	0.09550000	0.00000000
35	1307.15660000	18.63010000	0.00000000
36	1336.66740000	0.09030000	0.00000000
37	1368.42720000	1.00770000	0.00000000
38	1386.42300000	12.61230000	0.00000000
39	1411.51870000	12.96650000	0.00000000
40	1423.49130000	7.28770000	0.00000000
41	1454.68070000	5.59830000	0.00000000
42	1455.80150000	0.18570000	0.00000000
43	1459.21070000	18.61920000	0.00000000
44	1482.21260000	0.91980000	0.00000000
45	1482.63330000	0.18270000	0.00000000
46	1493.09210000	0.70870000	0.00000000
47	1493.89770000	3.24120000	0.00000000
48	1498.87970000	2.25260000	0.00000000
49	1510.18550000	3.25010000	0.00000000
50	1516.23530000	25.22260000	0.00000000
51	1519.15250000	42.47780000	0.00000000
52	1530.93440000	49.66710000	0.00000000
53	1811.17260000	135.66530000	0.00000000
54	2935.81540000	79.55580000	0.00000000
55	3018.21570000	11.08840000	0.00000000
56	3045.01860000	3.30240000	0.00000000
57	3062.76680000	2.84600000	0.00000000
58	3072.34430000	3.42830000	0.00000000
59	3076.08760000	7.18710000	0.00000000
60	3077.93250000	0.39160000	0.00000000

61	3084.09080000	0.78860000	0.00000000
62	3101.89720000	0.82260000	0.00000000
63	3124.64720000	9.26380000	0.00000000
64	3162.65350000	0.11970000	0.00000000
65	3162.86130000	0.03490000	0.00000000
66	3167.32770000	1.18110000	0.00000000
67	3168.97230000	2.15810000	0.00000000
68	3181.21980000	0.00830000	0.00000000
69	3185.09030000	0.66210000	0.00000000

S30. CALCULATIONS ON 7 - H_{5r} → 9E - H (TS)

```

Route : # opt=(calcf,ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper
       : sion=gd3bj int=ultrafine pop=regular
SMILES : C[N](C)(C)CC[CH][CH]O
Formula : C7H16NO+
Charge : 1
Multiplicity : 1
Energy : -406.17734066 a.u.
Gibbs Energy : -405.98841300 a.u.
Number of imaginary frequencies : 1
  
```

S30.1. Cartesian Co-ordinates (XYZ format)

25

```

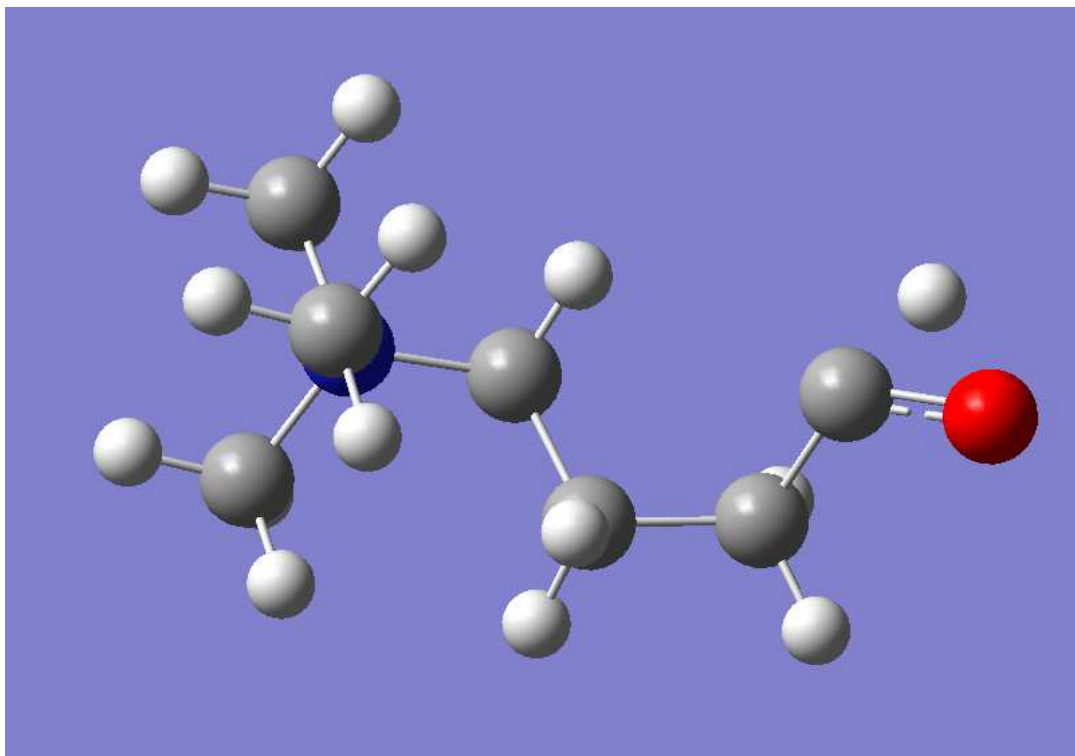
C  0.18752000 -0.27610999 -0.14738999
H -0.13293000 -1.01028001  0.58578998
H  0.03230000 -0.71390003 -1.13042998
C -0.59878999  1.01602006  0.01419000
H -0.31301001  1.75896001 -0.73171002
H -0.39842001  1.46456003  0.98992002
C -2.09133005  0.78741002 -0.03501000
H -2.20718002 -0.03543000 -1.13941002
H -2.70734000  1.67973006  0.10693000
N  1.69918001 -0.13405000  0.00651000
C  2.29841995 -1.49695003 -0.19728000
H  3.37636995 -1.42702997 -0.08646000
H  1.88873005 -2.17418003  0.54576999
H  2.04734993 -1.84496999 -1.19456005
  
```

C	2.26759005	0.80070001	-1.01944995
H	1.96638000	0.46235999	-2.00654006
H	1.89877999	1.80375004	-0.83841002
H	3.35050011	0.78930002	-0.93785000
C	2.06026006	0.34674999	1.38094997
H	1.60832000	-0.31568000	2.11322999
H	3.14153004	0.32997999	1.48048997
H	1.69833004	1.35915995	1.51791000
C	-2.63220000	-0.49395001	-0.02070000
O	-3.97463989	-0.48767000	0.10254000
H	-4.29577017	-1.38972998	0.00764000

S30.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-1418.93320000	87.05850000	0.00000000
2	27.50010000	0.22650000	0.00000000
3	99.23650000	0.76200000	0.00000000
4	126.96990000	2.57770000	0.00000000
5	174.28980000	1.44570000	0.00000000
6	232.46520000	1.02230000	0.00000000
7	237.97190000	3.14030000	0.00000000
8	281.64240000	0.62520000	0.00000000
9	286.32030000	0.66960000	0.00000000
10	303.44580000	1.80630000	0.00000000
11	334.12670000	2.75330000	0.00000000
12	360.39550000	0.19050000	0.00000000
13	383.28830000	0.61860000	0.00000000
14	449.36220000	0.17310000	0.00000000
15	467.35210000	0.88630000	0.00000000
16	498.53930000	1.99200000	0.00000000
17	625.33200000	86.85880000	0.00000000
18	636.87110000	35.94950000	0.00000000
19	777.10560000	1.29110000	0.00000000
20	778.15810000	6.26650000	0.00000000
21	893.93210000	41.64550000	0.00000000
22	921.47060000	4.31210000	0.00000000
23	954.10860000	15.26940000	0.00000000
24	962.95110000	14.08350000	0.00000000
25	977.39530000	12.02630000	0.00000000
26	1058.72680000	14.62070000	0.00000000
27	1077.49840000	26.22700000	0.00000000
28	1077.92830000	6.66900000	0.00000000
29	1133.83090000	46.33480000	0.00000000
30	1143.62180000	13.09560000	0.00000000
31	1178.07120000	10.59130000	0.00000000
32	1191.37280000	222.88330000	0.00000000
33	1218.53120000	26.47790000	0.00000000
34	1243.09790000	18.96430000	0.00000000
35	1264.48700000	5.48170000	0.00000000
36	1292.17740000	0.22640000	0.00000000
37	1302.92810000	0.18230000	0.00000000
38	1338.90930000	1.91930000	0.00000000
39	1358.88880000	31.40560000	0.00000000
40	1361.01770000	0.98750000	0.00000000
41	1417.81680000	2.84470000	0.00000000
42	1453.78240000	5.17320000	0.00000000
43	1454.60080000	5.26220000	0.00000000
44	1481.00340000	0.75130000	0.00000000
45	1482.74040000	0.19620000	0.00000000
46	1490.45000000	3.16950000	0.00000000
47	1492.31900000	1.05150000	0.00000000
48	1496.45580000	1.06320000	0.00000000
49	1500.21770000	8.52110000	0.00000000
50	1514.33360000	34.16910000	0.00000000
51	1515.67010000	18.00460000	0.00000000
52	1517.75380000	18.52610000	0.00000000
53	1529.74000000	56.84120000	0.00000000
54	2060.71100000	10.24770000	0.00000000
55	3036.28830000	8.19410000	0.00000000
56	3047.42790000	16.30840000	0.00000000
57	3070.08170000	4.59720000	0.00000000
58	3074.54640000	0.56510000	0.00000000
59	3078.72980000	2.71710000	0.00000000
60	3082.61770000	0.81370000	0.00000000

61	3095.06000000	1.95580000	0.00000000
62	3146.41240000	1.16680000	0.00000000
63	3161.99030000	0.23390000	0.00000000
64	3163.39660000	0.07200000	0.00000000
65	3169.03010000	2.12270000	0.00000000
66	3169.95400000	0.97890000	0.00000000
67	3178.16950000	0.04450000	0.00000000
68	3182.06230000	1.73870000	0.00000000
69	3813.60250000	154.65420000	0.00000000

S31. CALCULATIONS ON 7 - H_{5r} → 8 - H (TS)

```

Route : # opt=(calcf,ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper
       : sion=gd3bj int=ultrafine pop=regular
SMILES : C[N](C)(C)CCC[C]O
Formula : C7H16NO+
Charge : 1
Multiplicity : 1
Energy : -406.16061270 a.u.
Gibbs Energy : -405.97449600 a.u.
Number of imaginary frequencies : 1

```

S31.1. Cartesian Co-ordinates (XYZ format)

25

```

C  0.26133999  0.02764000 -0.53131002
H -0.16500001 -0.97320998 -0.54728001
H  0.35997000  0.37593001 -1.55823004
C -0.63723999  0.96070999  0.26442000
H -0.30404001  1.99389994  0.18065999
H -0.63282001  0.69783002  1.32224000
C -2.07623005  0.85184002 -0.25507000
H -2.11155009  1.02842999 -1.33713996
H -2.72744989  1.59993005  0.20615999
N  1.68434000 -0.13105001 -0.01039000
C  2.42355990 -1.02587998 -0.96360999
H  3.43783998 -1.16444004 -0.60140997
H  1.91146004 -1.98196006 -1.01453996
H  2.43870997 -0.55914003 -1.94379997

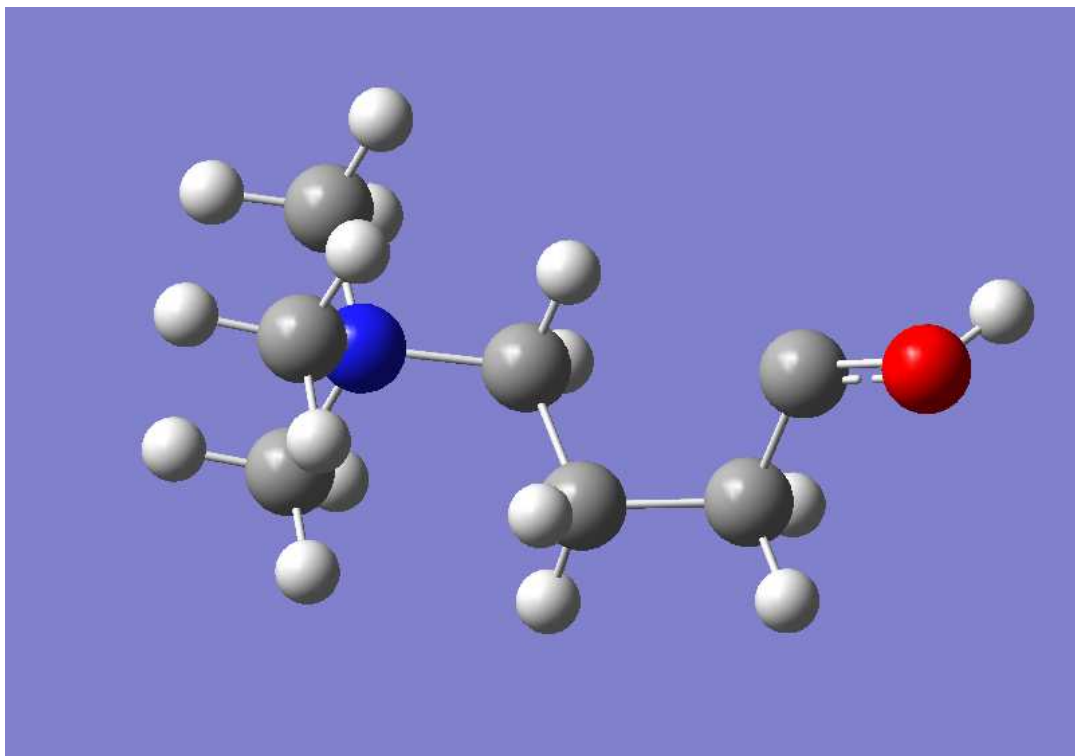
```


C	2.38442993	1.19343996	0.05691000
H	2.34865999	1.65928996	-0.92359000
H	1.89164996	1.82343996	0.78862000
H	3.41630006	1.02623999	0.35123000
C	1.68624997	-0.77140999	1.34733999
H	1.14326000	-1.71008003	1.29165995
H	2.71564007	-0.95117998	1.64270997
H	1.21194994	-0.10791000	2.06081009
C	-2.67162991	-0.50625998	-0.03687000
O	-3.95531988	-0.58064997	0.09420000
H	-3.30525994	-1.57495999	0.11030000

S31.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2062.91140000	848.00480000	0.00000000
2	29.13210000	0.45850000	0.00000000
3	69.30250000	1.72220000	0.00000000
4	82.47580000	0.67670000	0.00000000
5	134.75510000	1.42950000	0.00000000
6	190.28670000	0.12320000	0.00000000
7	229.20370000	0.58950000	0.00000000
8	250.67550000	1.42180000	0.00000000
9	280.23160000	0.16940000	0.00000000
10	292.63560000	0.25810000	0.00000000
11	331.95170000	0.65180000	0.00000000
12	360.22990000	0.22520000	0.00000000
13	369.02310000	0.46430000	0.00000000
14	449.28330000	0.26980000	0.00000000
15	454.57420000	1.60200000	0.00000000
16	489.61580000	3.00600000	0.00000000
17	528.45180000	19.36380000	0.00000000
18	580.59710000	15.81310000	0.00000000
19	740.82860000	6.29940000	0.00000000
20	766.02520000	6.31660000	0.00000000
21	835.17420000	2.37430000	0.00000000
22	897.75630000	43.64170000	0.00000000
23	940.89410000	8.03760000	0.00000000
24	956.33820000	19.29550000	0.00000000
25	968.07490000	24.99550000	0.00000000
26	1027.29520000	7.34140000	0.00000000
27	1047.95840000	12.04870000	0.00000000
28	1077.80450000	1.02400000	0.00000000
29	1080.59370000	7.76950000	0.00000000
30	1123.49080000	1.54860000	0.00000000
31	1148.15590000	5.93350000	0.00000000
32	1194.13630000	2.32180000	0.00000000
33	1230.54490000	16.91050000	0.00000000
34	1267.41520000	1.93970000	0.00000000
35	1290.31000000	8.58290000	0.00000000
36	1295.29870000	0.41850000	0.00000000
37	1344.65180000	4.03800000	0.00000000
38	1356.20290000	0.27690000	0.00000000
39	1369.49410000	9.10100000	0.00000000
40	1416.76980000	2.81270000	0.00000000
41	1438.31760000	15.98560000	0.00000000
42	1453.86440000	7.31630000	0.00000000
43	1455.21330000	10.09010000	0.00000000
44	1466.32500000	199.63660000	0.00000000
45	1482.03590000	0.11660000	0.00000000
46	1483.12050000	1.19410000	0.00000000
47	1491.68600000	0.92470000	0.00000000
48	1493.56260000	1.74510000	0.00000000
49	1503.05140000	5.13510000	0.00000000
50	1510.47900000	6.08680000	0.00000000
51	1516.05180000	24.13050000	0.00000000
52	1521.49640000	39.85160000	0.00000000
53	1531.82160000	44.17590000	0.00000000
54	2600.17000000	108.19050000	0.00000000
55	3001.39010000	3.92240000	0.00000000
56	3049.56910000	4.84160000	0.00000000
57	3059.21370000	7.13380000	0.00000000
58	3071.05240000	4.16250000	0.00000000
59	3075.24330000	4.34430000	0.00000000
60	3077.58690000	0.71450000	0.00000000

61	3084.10080000	0.82400000	0.00000000
62	3097.00260000	5.41940000	0.00000000
63	3127.02600000	4.43490000	0.00000000
64	3162.21020000	0.13230000	0.00000000
65	3163.96460000	0.03940000	0.00000000
66	3168.12880000	1.09900000	0.00000000
67	3169.44250000	1.99980000	0.00000000
68	3178.49250000	0.17100000	0.00000000
69	3183.67410000	1.33820000	0.00000000

S32. CALCULATIONS ON 7 – H_{5r} (³A)

```

Route : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
       : nt=ultrafine pop=regular
SMILES : C[N](C)(C)CCC[C]O
Formula : C7H16NO+,3
Charge : 1
Multiplicity : 3
Energy : -406.17153436 a.u.
Gibbs Energy : -405.98251000 a.u.
Number of imaginary frequencies : 0

```

S32.1. Cartesian Co-ordinates (XYZ format)

25

```

C -0.00000000 0.00000000 0.00000000
H -0.00000000 0.00000000 1.08830798
H 1.03381395 0.00000000 -0.34235999
C -0.73851502 -1.22031999 -0.52037299
H -0.67580301 -1.28277600 -1.60632706
H -1.79055297 -1.18451798 -0.24085100
C -0.12384200 -2.49025393 0.08571600
H 0.90709400 -2.60734296 -0.28000101
H -0.68028200 -3.36056495 -0.27684301
N -0.57238001 1.35168302 -0.41436601
C 0.31304801 2.41991496 0.15894100
H -0.08454700 3.39234209 -0.11599300
H 0.33169699 2.31663799 1.23962700
H 1.31431496 2.29973197 -0.24344100

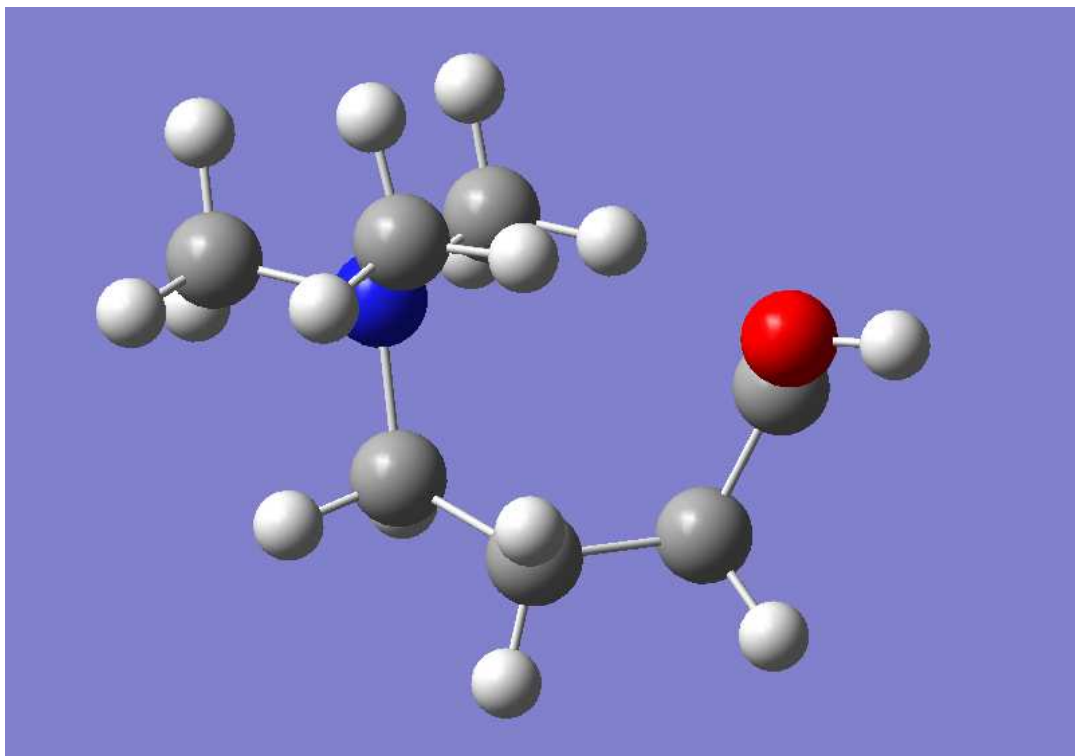
```

C	-0.59817803	1.49087596	-1.90705097
H	0.40395299	1.32610202	-2.29202008
H	-1.28318298	0.76169199	-2.32403994
H	-0.93193799	2.49380898	-2.15638804
C	-1.95873106	1.53208697	0.13153000
H	-1.93221402	1.38809001	1.20749903
H	-2.29438496	2.53774405	-0.10361800
H	-2.62307096	0.80757898	-0.32438201
C	-0.17829700	-2.48587108	1.57521904
O	-0.26562601	-3.56215906	2.34598398
H	0.56119800	-3.76992607	2.80892706

S32.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	27.66810000	1.25840000	0.00000000
2	71.45760000	3.19220000	0.00000000
3	76.46380000	13.06330000	0.00000000
4	129.44210000	3.30850000	0.00000000
5	194.11890000	2.92800000	0.00000000
6	229.77690000	0.81890000	0.00000000
7	255.41920000	5.62660000	0.00000000
8	279.90920000	1.75730000	0.00000000
9	291.95830000	0.27560000	0.00000000
10	316.11650000	21.56570000	0.00000000
11	346.20020000	84.54620000	0.00000000
12	360.08370000	0.26820000	0.00000000
13	369.38240000	0.69810000	0.00000000
14	447.92780000	0.26490000	0.00000000
15	453.12440000	1.76030000	0.00000000
16	474.74780000	0.97650000	0.00000000
17	550.43920000	1.84820000	0.00000000
18	751.87940000	0.07600000	0.00000000
19	773.21150000	1.06740000	0.00000000
20	868.88920000	23.83420000	0.00000000
21	892.71350000	15.34080000	0.00000000
22	927.64160000	18.81930000	0.00000000
23	955.60550000	11.53740000	0.00000000
24	967.43680000	15.25060000	0.00000000
25	1035.80610000	1.43170000	0.00000000
26	1055.90360000	31.56360000	0.00000000
27	1075.55860000	2.35080000	0.00000000
28	1078.50940000	0.26580000	0.00000000
29	1126.47300000	51.84840000	0.00000000
30	1144.88450000	25.69860000	0.00000000
31	1155.46000000	69.23870000	0.00000000
32	1204.29430000	9.29930000	0.00000000
33	1232.32030000	2.99400000	0.00000000
34	1268.15490000	2.09930000	0.00000000
35	1290.90330000	5.72960000	0.00000000
36	1294.65970000	0.89490000	0.00000000
37	1334.19100000	19.97670000	0.00000000
38	1353.48990000	2.41220000	0.00000000
39	1365.17690000	11.17530000	0.00000000
40	1401.58510000	22.30920000	0.00000000
41	1420.85070000	17.47990000	0.00000000
42	1453.80510000	5.67490000	0.00000000
43	1454.94470000	3.18160000	0.00000000
44	1466.70950000	4.72700000	0.00000000
45	1480.18640000	0.35260000	0.00000000
46	1481.74110000	0.15030000	0.00000000
47	1492.02010000	1.47890000	0.00000000
48	1493.27060000	1.86290000	0.00000000
49	1498.33320000	3.85920000	0.00000000
50	1507.51820000	3.74120000	0.00000000
51	1515.50930000	25.05000000	0.00000000
52	1518.48400000	38.91730000	0.00000000
53	1530.41380000	51.04750000	0.00000000
54	2935.74460000	31.30800000	0.00000000
55	3019.87680000	4.92180000	0.00000000
56	3055.71270000	9.88430000	0.00000000
57	3068.54330000	6.21670000	0.00000000
58	3074.50770000	3.09380000	0.00000000
59	3077.42960000	0.27370000	0.00000000
60	3083.85770000	1.05980000	0.00000000

61	3097.05150000	6.28680000	0.00000000
62	3123.98660000	7.25730000	0.00000000
63	3161.71640000	0.11990000	0.00000000
64	3163.27740000	0.05790000	0.00000000
65	3167.79550000	1.42830000	0.00000000
66	3168.80180000	2.38750000	0.00000000
67	3179.34940000	0.14960000	0.00000000
68	3184.23580000	1.20710000	0.00000000
69	3654.07300000	66.40010000	0.00000000

S33. CALCULATIONS ON 7 – H_{7r} (³A)

```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N](C)(C)CCC[C]O
Formula              : C7H16NO+,3
Charge                : 1
Multiplicity         : 3
Energy                : -406.17350453
Gibbs Energy         : -405.98183900
Number of imaginary frequencies : 0

```

a.u.
a.u.

S33.1. Cartesian Co-ordinates (XYZ format)

25

```

C  0.78295100  1.20003605 -0.21071400
H  0.94805801  1.43508899 -1.26083004
H  1.42034805  1.85274601  0.38198000
C -0.66384500  1.46106803  0.18956000
H -0.75145799  2.54823089  0.12684900
H -0.82604700  1.21821797  1.23902404
C -1.80000603  0.85908002 -0.66650403
H -1.56505704  0.93710798 -1.72896504
H -2.69170904  1.47959399 -0.50693899
N  1.37336302 -0.19885500 -0.01277500
C  2.86816001 -0.06610000 -0.07879500
H  3.31033492 -1.05546498 -0.01226400
H  3.13881302  0.39762300 -1.02285099
H  3.20662498  0.54883403  0.74954402

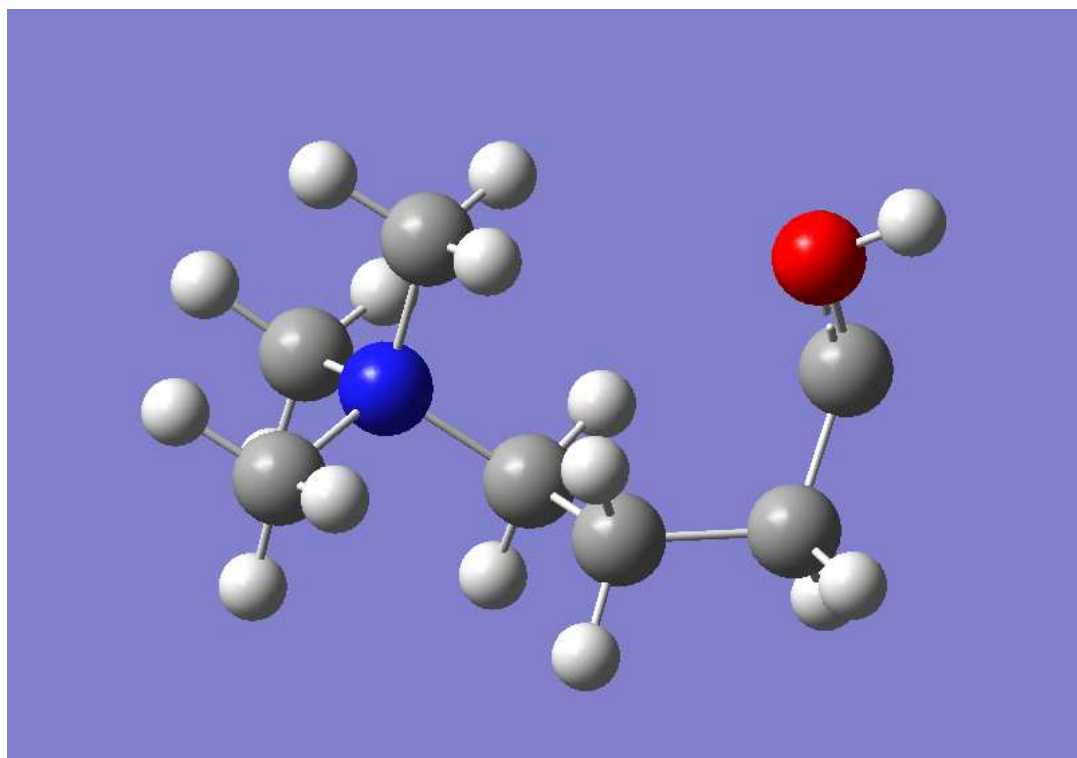
```


C 0.99763799 -0.76880401 1.32342505
H 1.27023494 -0.05650900 2.09691000
H -0.06720200 -0.96791703 1.34925306
H 1.54901397 -1.69386697 1.46414495
C 0.93846601 -1.13733101 -1.10221195
H 1.24743295 -0.72580099 -2.05849004
H 1.41796601 -2.09804511 -0.93854302
H -0.14325200 -1.24530602 -1.05981302
C -2.12564802 -0.55440700 -0.34696001
O -2.37880397 -1.01151705 0.88468200
H -3.30998206 -1.24893200 1.01712000

S33.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	67.34740000	2.08570000	0.00000000
2	96.44300000	1.68580000	0.00000000
3	117.51290000	3.17960000	0.00000000
4	167.65530000	4.39640000	0.00000000
5	237.09460000	18.28980000	0.00000000
6	247.42910000	1.08930000	0.00000000
7	277.74490000	3.02240000	0.00000000
8	303.61230000	53.16890000	0.00000000
9	312.87880000	2.84400000	0.00000000
10	326.21130000	17.78120000	0.00000000
11	357.56430000	27.51590000	0.00000000
12	364.75310000	1.33140000	0.00000000
13	409.24430000	1.68240000	0.00000000
14	437.74280000	0.66850000	0.00000000
15	449.71240000	0.06320000	0.00000000
16	515.96880000	3.11920000	0.00000000
17	542.41290000	3.16610000	0.00000000
18	693.67040000	0.61660000	0.00000000
19	810.31060000	1.58890000	0.00000000
20	855.64790000	3.16400000	0.00000000
21	887.50790000	19.19350000	0.00000000
22	891.65120000	17.24070000	0.00000000
23	946.02080000	16.40380000	0.00000000
24	962.74310000	6.77950000	0.00000000
25	990.26360000	36.38270000	0.00000000
26	1066.31290000	5.51640000	0.00000000
27	1077.22800000	11.66920000	0.00000000
28	1082.71890000	0.19150000	0.00000000
29	1134.47820000	55.45050000	0.00000000
30	1148.49430000	1.00930000	0.00000000
31	1156.70410000	66.99530000	0.00000000
32	1213.62800000	0.40940000	0.00000000
33	1250.23270000	1.61470000	0.00000000
34	1263.59170000	1.54320000	0.00000000
35	1287.84610000	3.96860000	0.00000000
36	1296.56490000	4.88460000	0.00000000
37	1340.98630000	26.77270000	0.00000000
38	1351.30330000	6.05550000	0.00000000
39	1372.34020000	8.67340000	0.00000000
40	1406.93100000	2.95930000	0.00000000
41	1424.21920000	1.43220000	0.00000000
42	1454.13220000	3.76180000	0.00000000
43	1457.31210000	3.82520000	0.00000000
44	1460.92550000	8.58910000	0.00000000
45	1478.48870000	1.55990000	0.00000000
46	1481.55160000	10.83280000	0.00000000
47	1483.13230000	3.61130000	0.00000000
48	1495.08810000	6.05700000	0.00000000
49	1500.64370000	10.42800000	0.00000000
50	1508.30070000	2.08590000	0.00000000
51	1516.04270000	29.05110000	0.00000000
52	1521.61840000	16.70600000	0.00000000
53	1534.41670000	33.49290000	0.00000000
54	2966.82570000	15.15270000	0.00000000
55	3035.15060000	29.92840000	0.00000000
56	3044.39630000	3.94640000	0.00000000
57	3067.30750000	4.22310000	0.00000000
58	3070.45960000	1.37800000	0.00000000
59	3074.04370000	0.82440000	0.00000000
60	3079.97790000	8.40040000	0.00000000

61	3093.58580000	7.40770000	0.00000000
62	3121.39670000	4.78220000	0.00000000
63	3131.13760000	7.17930000	0.00000000
64	3159.07920000	0.36390000	0.00000000
65	3160.54920000	0.59150000	0.00000000
66	3165.72680000	1.77010000	0.00000000
67	3167.76670000	2.53790000	0.00000000
68	3187.42260000	4.92830000	0.00000000
69	3665.51250000	103.22410000	0.00000000

S34. CALCULATIONS ON 7 – H_{ec} (³A)

```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N](C)(C)CCC[C]O
Formula              : C7H16NO+,3
Charge               : 1
Multiplicity         : 3
Energy               : -406.17396628 a.u.
Gibbs Energy        : -405.98449500 a.u.
Number of imaginary frequencies : 0

```

S34.1. Cartesian Co-ordinates (XYZ format)

25

```

C -0.24186900  0.45904499  0.78788298
H  0.20873301 -0.41771099  1.24996603
H -0.58779901  1.12694204  1.57347095
C  0.76831800  1.14932001 -0.12383500
H  0.62304097  2.22877407 -0.10920200
H  0.65571898  0.82764399 -1.15794301
C  2.21494699  0.80814499  0.30627200
H  2.38437700  1.09007597  1.34585905
H  2.90490794  1.40873396 -0.29887399
N -1.49788702 -0.05915500  0.09834400
C -2.42708707 -0.58227098  1.15441597
H -3.31260896 -0.98847401  0.67465699
H -1.91727805 -1.36024594  1.71456802
H -2.70307589  0.23316200  1.81604898

```

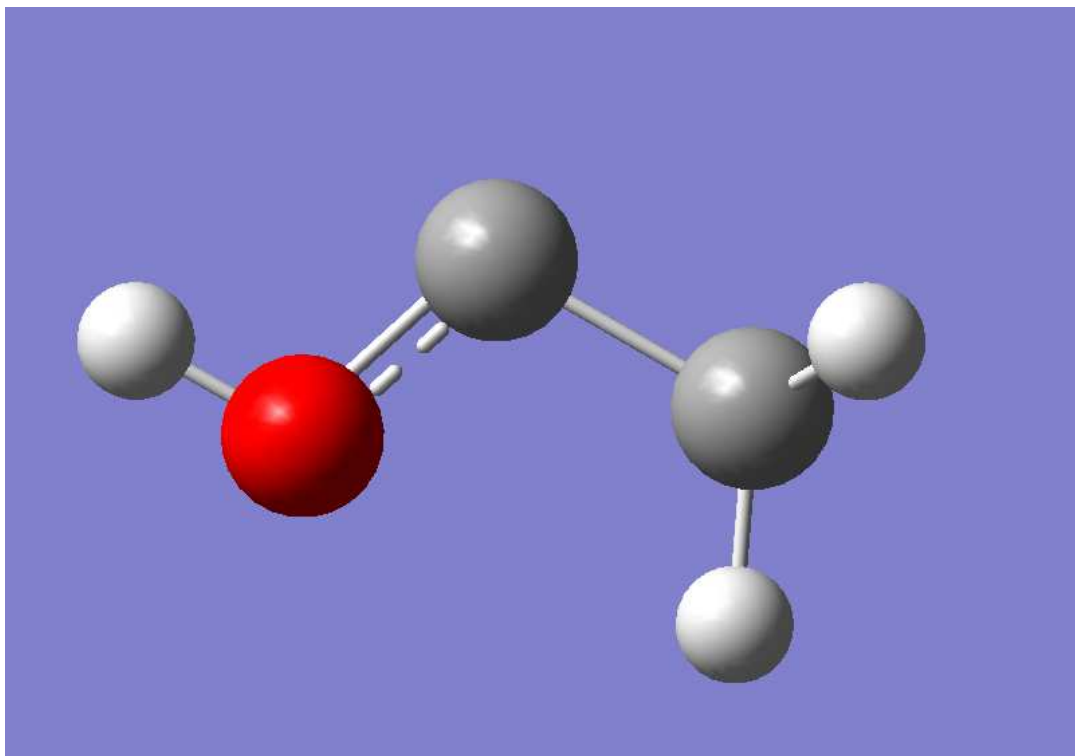
C -2.18396592 1.03985095 -0.65502399
H -2.40475106 1.85045898 0.03336700
H -1.53358197 1.39166296 -1.44773495
H -3.10479689 0.64985400 -1.07860303
C -1.15270305 -1.18452203 -0.83537197
H -0.67755300 -1.97569704 -0.26412201
H -2.06888795 -1.54490995 -1.29340601
H -0.46861601 -0.83088702 -1.59717095
C 2.49856710 -0.64080298 0.14732100
O 2.32502198 -1.30962896 -1.00152302
H 3.16352797 -1.60629499 -1.38745499

S34.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	19.40570000	1.59250000	0.00000000
2	54.93150000	1.25910000	0.00000000
3	98.64350000	2.90810000	0.00000000
4	163.17530000	1.06790000	0.00000000
5	201.67330000	2.78940000	0.00000000
6	242.47730000	22.11470000	0.00000000
7	268.84640000	1.52490000	0.00000000
8	276.49770000	1.56070000	0.00000000
9	290.44440000	11.56720000	0.00000000
10	307.90400000	84.79870000	0.00000000
11	364.41330000	0.68840000	0.00000000
12	370.24590000	9.25790000	0.00000000
13	378.96050000	0.30860000	0.00000000
14	444.95830000	0.10860000	0.00000000
15	447.93810000	1.07820000	0.00000000
16	502.79920000	0.47990000	0.00000000
17	573.59300000	7.21770000	0.00000000
18	741.74580000	2.82410000	0.00000000
19	775.33360000	5.87560000	0.00000000
20	865.17110000	12.49800000	0.00000000
21	894.52730000	8.41290000	0.00000000
22	915.16140000	23.23790000	0.00000000
23	948.69040000	5.22710000	0.00000000
24	966.76220000	17.36240000	0.00000000
25	1013.54500000	12.28210000	0.00000000
26	1057.52300000	13.33480000	0.00000000
27	1060.64210000	18.53390000	0.00000000
28	1076.88050000	0.09240000	0.00000000
29	1130.14230000	37.82430000	0.00000000
30	1143.74170000	4.77630000	0.00000000
31	1160.46660000	78.33800000	0.00000000
32	1207.48880000	2.05680000	0.00000000
33	1227.07740000	2.84170000	0.00000000
34	1267.26980000	0.77050000	0.00000000
35	1279.35910000	1.25260000	0.00000000
36	1296.57600000	0.81990000	0.00000000
37	1331.36680000	24.61890000	0.00000000
38	1341.02010000	1.41620000	0.00000000
39	1363.28520000	11.70400000	0.00000000
40	1375.16950000	4.65750000	0.00000000
41	1422.64590000	1.37150000	0.00000000
42	1453.94680000	5.71470000	0.00000000
43	1454.76710000	3.37140000	0.00000000
44	1466.68940000	6.80740000	0.00000000
45	1479.78060000	0.29330000	0.00000000
46	1481.18300000	0.04150000	0.00000000
47	1487.08660000	2.04430000	0.00000000
48	1492.20870000	1.47330000	0.00000000
49	1502.56310000	3.45740000	0.00000000
50	1507.86130000	7.92070000	0.00000000
51	1515.81320000	34.63270000	0.00000000
52	1522.74950000	39.87460000	0.00000000
53	1528.68050000	46.95630000	0.00000000
54	2983.48220000	17.51070000	0.00000000
55	3060.65390000	8.77200000	0.00000000
56	3066.45740000	5.94100000	0.00000000
57	3073.97530000	1.77510000	0.00000000
58	3077.17380000	4.72500000	0.00000000
59	3078.46240000	1.03430000	0.00000000
60	3085.82850000	1.29600000	0.00000000

61	3099.64280000	8.21810000	0.00000000
62	3123.53350000	4.58520000	0.00000000
63	3161.35780000	0.12200000	0.00000000
64	3164.70690000	0.35330000	0.00000000
65	3167.40990000	1.36990000	0.00000000
66	3171.22980000	1.77480000	0.00000000
67	3178.98850000	0.62860000	0.00000000
68	3188.11720000	0.67130000	0.00000000
69	3673.45580000	95.68800000	0.00000000

S35. CALCULATIONS ON 5



```
Route : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
       : nt=ultrafine pop=regular
SMILES : C[C]O
Formula : C2H4O
Charge : 0
Multiplicity : 1
Dipole : 2.6437 Debye
Energy : -153.81646378 a.u.
Gibbs Energy : -153.78684900 a.u.
Number of imaginary frequencies : 0
```

S35.1. Cartesian Co-ordinates (XYZ format)

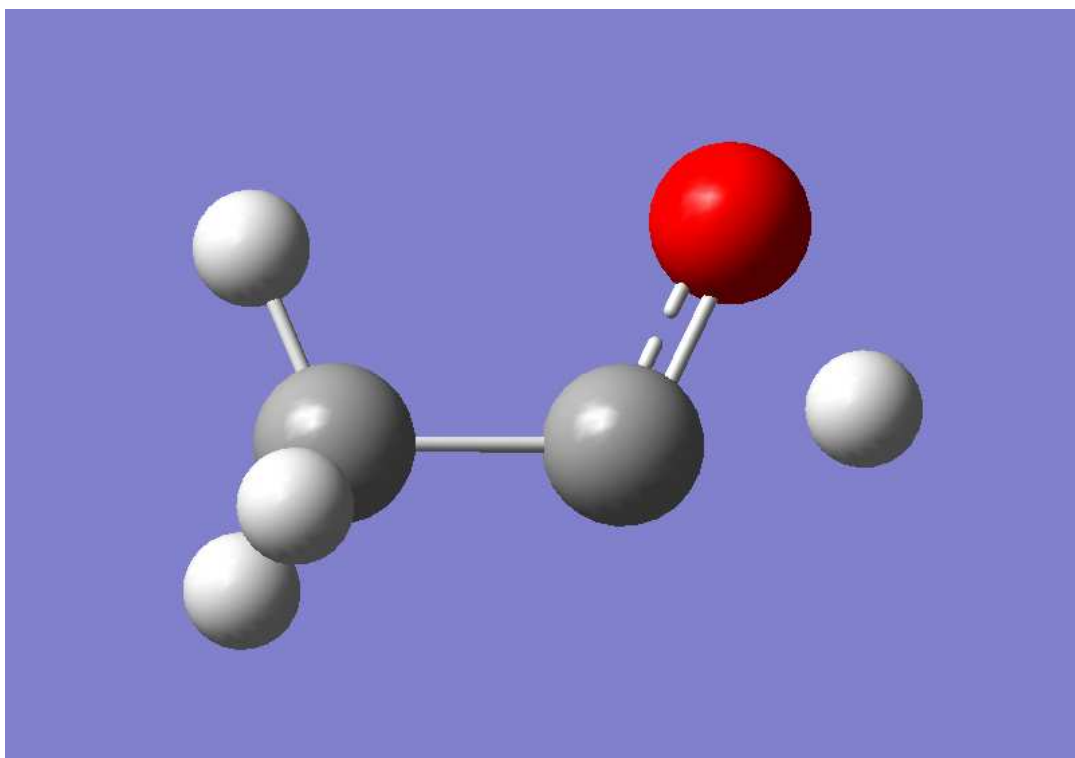
7

```
C -2.92655110 0.18839300 0.17453200
H -3.36808991 -0.22705200 1.08506703
H -3.62113404 0.09201500 -0.66620600
C -2.48691511 1.57868195 0.48435700
O -3.07614589 2.38759494 -0.37549499
H -2.79418612 3.29038000 -0.17854799
H -2.02726698 -0.40897301 -0.00173200
```


S35.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	101.02190000	7.95990000	0.00000000
2	511.16800000	8.67090000	0.00000000
3	733.65180000	45.49830000	0.00000000
4	915.03390000	5.97010000	0.00000000
5	974.85150000	40.38390000	0.00000000
6	1053.89620000	81.20380000	0.00000000
7	1289.52690000	180.71670000	0.00000000
8	1343.31360000	25.51190000	0.00000000
9	1373.57940000	28.32720000	0.00000000
10	1445.27440000	12.87530000	0.00000000
11	1466.71300000	2.51630000	0.00000000
12	2988.21470000	19.90390000	0.00000000
13	3066.52700000	1.82920000	0.00000000
14	3073.88960000	29.64980000	0.00000000
15	3743.10270000	95.49880000	0.00000000

S36. CALCULATIONS ON 5 → ACETALDEHYDE (TS)



```

Route                : # opt=(calcf,ts,noeigen) freq b3lyp/cc-pvtz geom=connectivity empiric
                    : aldispersion=gd3bj int=ultrafine pop=regular
SMILES               : C[C]O
Formula              : C2H4O
Charge               : 0
Multiplicity         : 1
Dipole               : 3.0777
Energy               : -153.76579670
Gibbs Energy         : -153.74171500
Number of imaginary frequencies : 1

```

Debye
a.u.
a.u.

S36.1. Cartesian Co-ordinates (XYZ format)

7

```

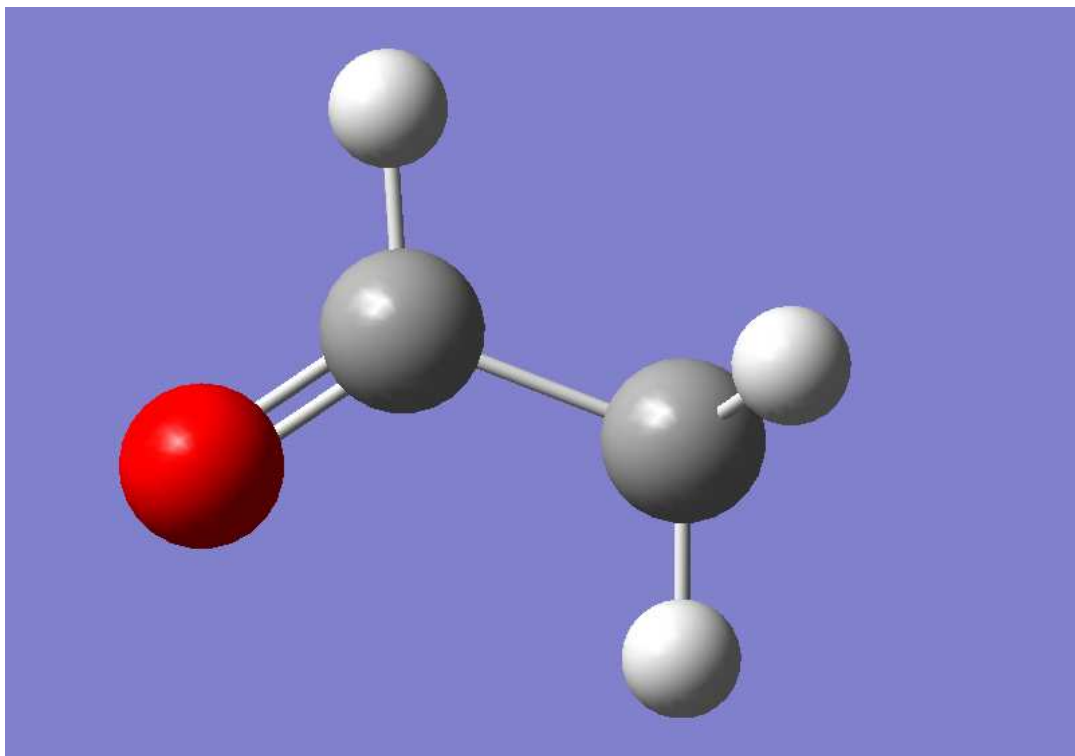
C -2.09933591  0.85060197 -0.27721301
H -1.89157295  1.07034504 -1.32727003
H -2.76861596  1.60330796  0.15114100
C -2.69515896 -0.50407499 -0.17411400
O -3.87208104 -0.59376198  0.38591000
H -3.35155296 -1.56697202 -0.00127300
H -1.13376701  0.85556602  0.23440100

```

S36.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2020.19540000	560.71090000	0.00000000
2	138.36070000	1.21970000	0.00000000
3	488.20910000	3.47510000	0.00000000
4	557.11250000	34.76070000	0.00000000
5	903.81960000	3.26350000	0.00000000
6	925.53080000	4.36440000	0.00000000
7	1123.82380000	46.17390000	0.00000000
8	1359.48870000	77.52300000	0.00000000
9	1380.85120000	159.22150000	0.00000000
10	1443.66420000	11.27180000	0.00000000
11	1474.13210000	22.29480000	0.00000000
12	2617.71520000	93.98810000	0.00000000
13	2996.53170000	7.06630000	0.00000000
14	3081.25360000	1.62110000	0.00000000
15	3085.54030000	13.93320000	0.00000000

S37. CALCULATIONS ON ACETALDEHYDE



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : CC=O
Formula              : C2H4O
Charge               : 0
Multiplicity         : 1
Dipole               : 6.9534
Energy               : -153.89891670
Gibbs Energy        : -153.86858900
Number of imaginary frequencies : 0

```

Debye
a.u.
a.u.

S37.1. Cartesian Co-ordinates (XYZ format)

7

```

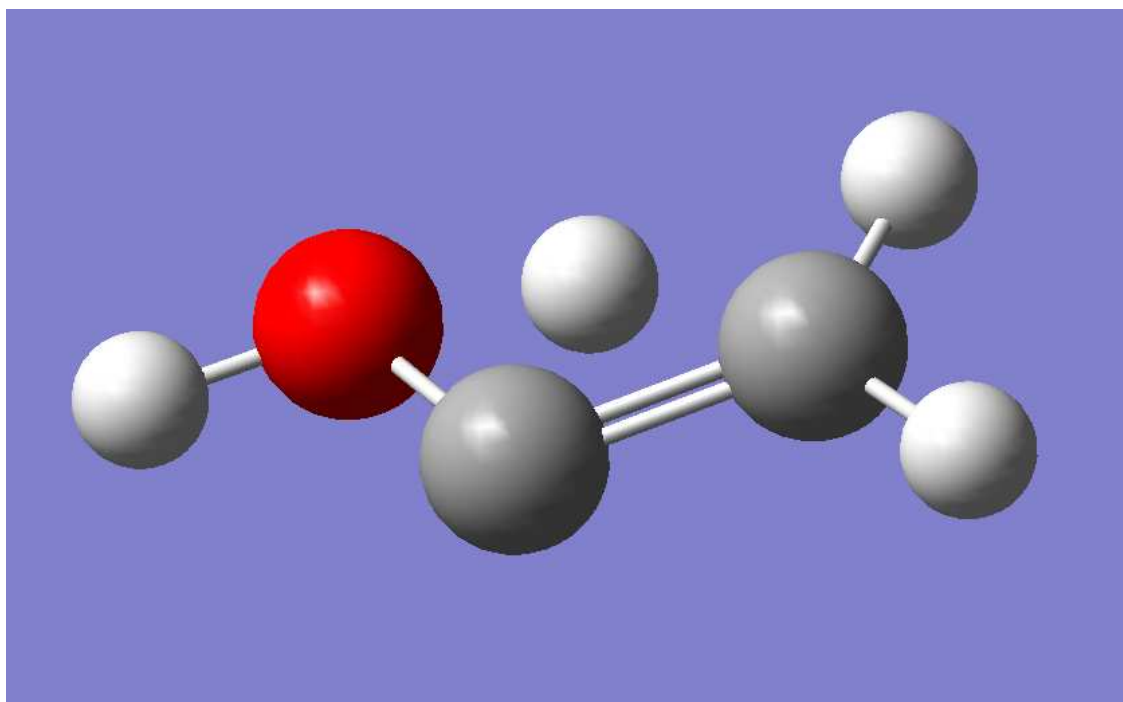
C -2.88403702  0.18223800  0.14061899
H -3.21099997 -0.12135200  1.13855505
H -3.71217608  0.11705500 -0.56096298
C -2.34006000  1.57992995  0.19455500
O -2.76038003  2.50472999 -0.45034900
H -2.08828902 -0.50828600 -0.15086900
H -1.48913395  1.72435606  0.89348102

```

S37.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	160.3010000	0.73270000	0.00000000
2	510.10930000	13.63340000	0.00000000
3	776.20600000	0.83940000	0.00000000
4	886.96200000	10.09760000	0.00000000
5	1130.44370000	25.08980000	0.00000000
6	1137.70380000	0.27790000	0.00000000
7	1379.39880000	25.69670000	0.00000000
8	1426.12740000	9.40690000	0.00000000
9	1460.95940000	20.62480000	0.00000000
10	1470.46770000	9.47000000	0.00000000
11	1817.91570000	178.59080000	0.00000000
12	2863.06560000	131.30300000	0.00000000
13	3022.72280000	2.32000000	0.00000000
14	3074.55450000	7.63020000	0.00000000
15	3135.71700000	9.97440000	0.00000000

S38. CALCULATIONS ON 5 → VINYLALCOHOL (TS)



```

Route : # opt=(calcall,ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldispe
       : rsion=gd3bj int=ultrafine pop=regular
SMILES : [CH2][CH]O
Formula : C2H4O
Charge : 0
Multiplicity : 1
Dipole : 2.3380 Debye
Energy : -153.77774711 a.u.
Gibbs Energy : -153.75058000 a.u.
Number of imaginary frequencies : 1

```

S38.1. Cartesian Co-ordinates (XYZ format)

7

```

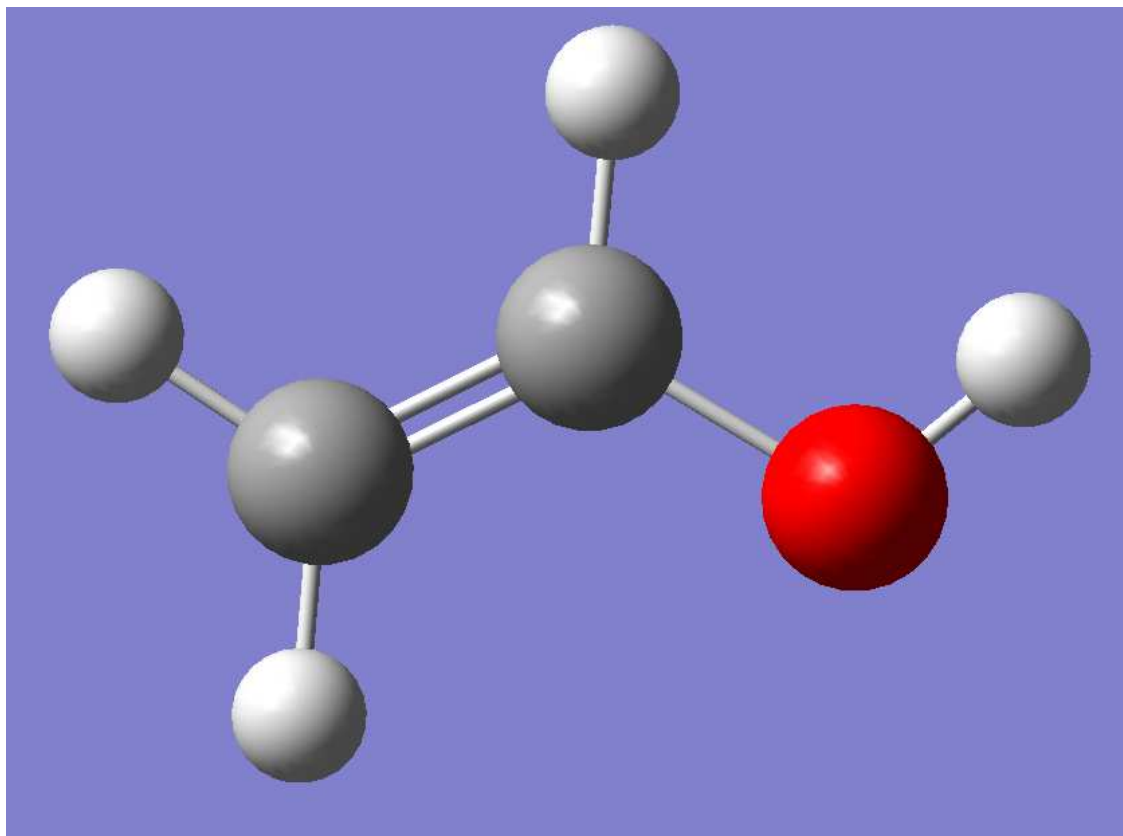
C 2.54211593 -0.50430202 0.42426500
H 1.93972802 -1.39248204 0.63389802
C 3.84273195 -0.54873502 -0.05257200
O 4.31580210 -1.82106102 -0.13921501
H 3.62935495 -0.09968300 1.13468695
H 5.24055481 -1.76506102 -0.39305800
H 2.05208802 0.45946100 0.46387699

```

S38.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-1421.92280000	88.27910000	0.00000000
2	485.67650000	5.81650000	0.00000000
3	620.05770000	103.69750000	0.00000000
4	703.84360000	19.62430000	0.00000000
5	965.87340000	96.13660000	0.00000000
6	1024.04710000	35.29010000	0.00000000
7	1145.62590000	12.69330000	0.00000000
8	1252.25310000	197.05420000	0.00000000
9	1319.69500000	26.85740000	0.00000000
10	1408.84170000	4.30890000	0.00000000
11	1525.62250000	25.84890000	0.00000000
12	2099.03040000	6.27160000	0.00000000
13	3028.64120000	34.62520000	0.00000000
14	3199.87570000	2.87620000	0.00000000
15	3828.51550000	103.91960000	0.00000000

S39. CALCULATIONS ON VINYLALCOHOL



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C=CO
Formula              : C2H4O
Charge               : 0
Multiplicity         : 1
Dipole               : 4.7826
Energy               : -153.88085077
Gibbs Energy         : -153.84930300
Number of imaginary frequencies : 0

```

Debye
a.u.
a.u.

S39.1. Cartesian Co-ordinates (XYZ format)

7

```

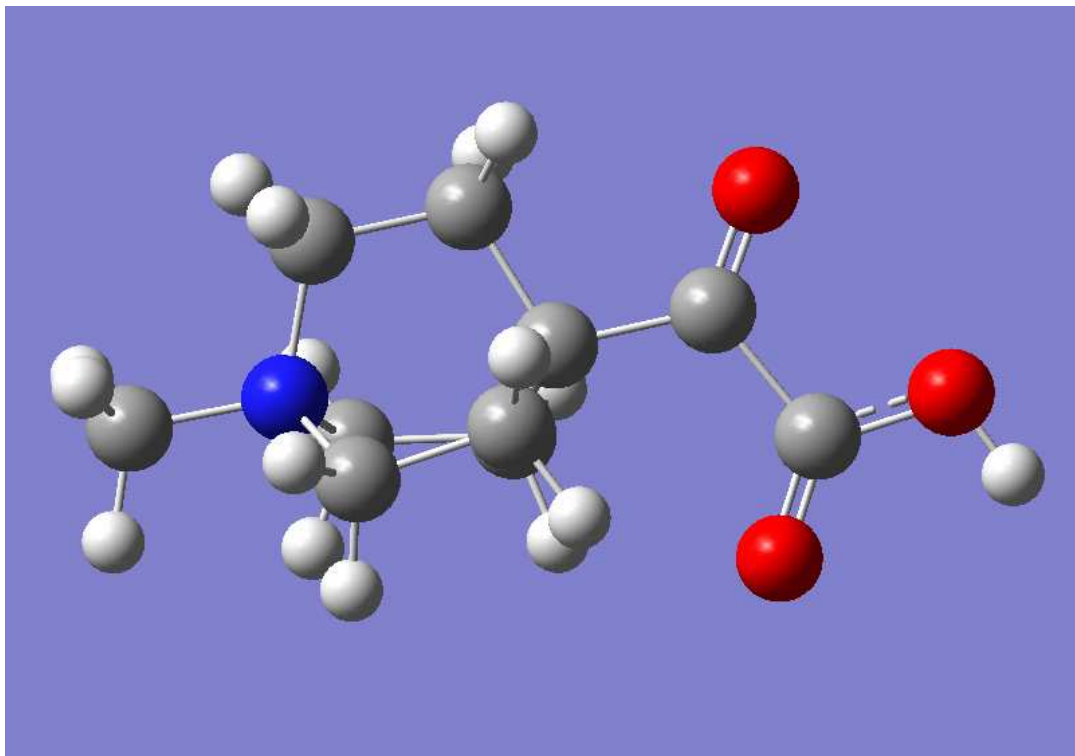
C -2.69569802  0.21358199 -0.09440400
H -3.63489199 -0.06075000 -0.55299997
C -2.37335706  1.48169994  0.11245300
O -3.19769192  2.51384711 -0.23659600
H -2.78521299  3.34875488 -0.00411100
H -2.01249194 -0.56783098  0.19783600
H -1.43265104  1.76572096  0.57211697

```


S39.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	277.46350000	97.32870000	0.00000000
2	484.89580000	3.29780000	0.00000000
3	717.56030000	19.23180000	0.00000000
4	858.11680000	57.39980000	0.00000000
5	959.53400000	53.15840000	0.00000000
6	976.64530000	19.69030000	0.00000000
7	1145.70720000	15.41460000	0.00000000
8	1287.78130000	214.74150000	0.00000000
9	1352.09510000	3.59270000	0.00000000
10	1442.74680000	0.30700000	0.00000000
11	1731.19680000	104.13850000	0.00000000
12	3140.13220000	19.01330000	0.00000000
13	3163.74230000	0.25690000	0.00000000
14	3254.48550000	5.74820000	0.00000000
15	3854.35910000	83.07430000	0.00000000

S40. CALCULATIONS ON 10 – H Z-ISOMER



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N]12CCC(CC1)(CC2)C(=O)C(=O)O
Formula              : C10H16NO3+
Charge               : 1
Multiplicity         : 1
Energy               : -671.19181923
Gibbs Energy        : -670.96910800
Number of imaginary frequencies : 0

```

a.u.
a.u.

S40.1. Cartesian Co-ordinates (XYZ format)

30

```

C -1.99590600 -0.29457599 -0.00929800
C -0.46496600 -0.17728800 -0.00902700
C -2.60825801 1.09470403 -0.22250700
H -2.32446790 -0.96794599 -0.79626000
H -2.33390999 -0.72648799 0.93065000
H -2.94473791 1.25093198 -1.24472904
H -3.44307399 1.28797805 0.44574299
C -0.05136600 0.65362197 -1.24314904
H 1.02584803 0.64237100 -1.37291002
H -0.50356603 0.22651200 -2.13712192
C -0.51938301 2.10180211 -1.04409099
H 0.28814700 2.75617599 -0.72459298
H -0.96662599 2.51907396 -1.94223201
C -0.90516901 1.86580598 1.37338603

```

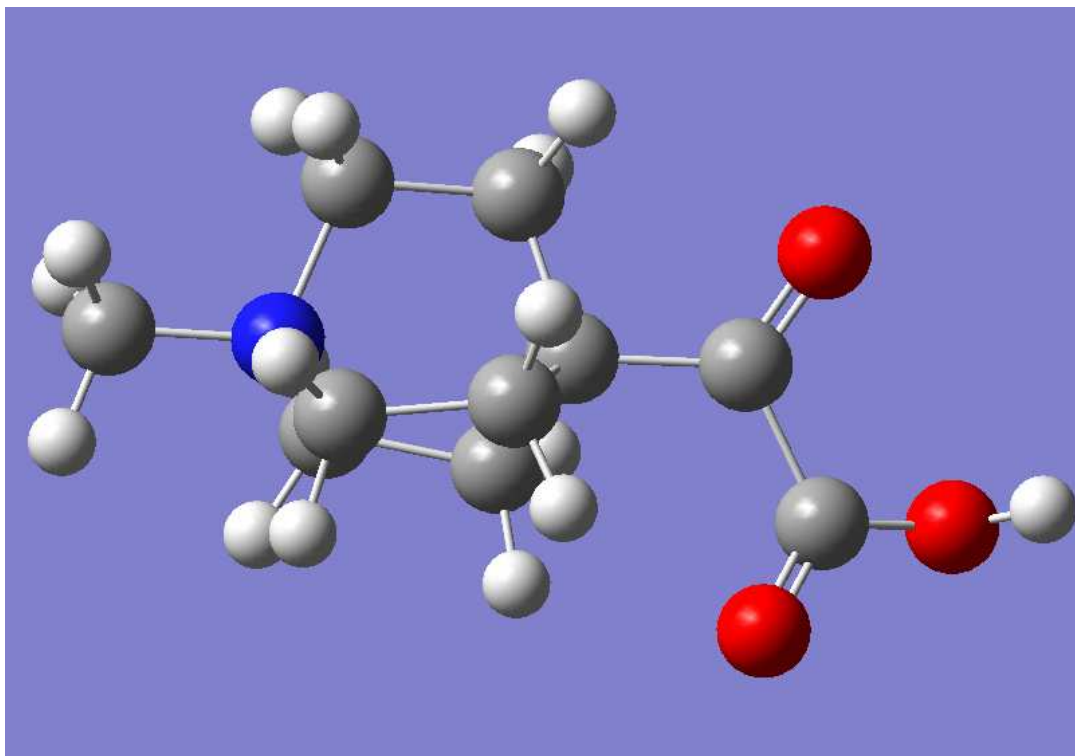
H	-0.31506899	2.73922706	1.63779402
H	-1.70992601	1.76157105	2.09708095
C	-0.04364700	0.59963500	1.25803697
H	1.01041102	0.85180598	1.20295000
H	-0.19084001	-0.01125300	2.14720011
N	-1.56926596	2.16457009	0.04585100
C	-2.20511389	3.51213193	0.07626700
H	-2.88758898	3.56169295	0.91998500
H	-1.43073702	4.26670980	0.18096200
H	-2.75008702	3.66626000	-0.85072798
C	0.14977901	-1.57605898	-0.03927600
O	-0.51878703	-2.56938410	-0.09836200
C	1.69472396	-1.66859996	0.01086200
O	2.40871191	-0.69649202	0.03272500
O	2.10327101	-2.92820501	0.02246600
H	3.07358503	-2.93995690	0.04950300

S40.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	28.84000000	5.10570000	0.00000000
2	70.43000000	0.04250000	0.00000000
3	120.66380000	1.18590000	0.00000000
4	133.55680000	0.40350000	0.00000000
5	151.47740000	1.34510000	0.00000000
6	244.70080000	11.16770000	0.00000000
7	262.81560000	0.00210000	0.00000000
8	267.94180000	0.45460000	0.00000000
9	271.73780000	1.30170000	0.00000000
10	302.48570000	3.63330000	0.00000000
11	341.92000000	0.08850000	0.00000000
12	359.42160000	3.98890000	0.00000000
13	408.22350000	0.46970000	0.00000000
14	424.61460000	0.09790000	0.00000000
15	425.18440000	0.00340000	0.00000000
16	468.45920000	3.53920000	0.00000000
17	538.59350000	0.26400000	0.00000000
18	541.46980000	0.04900000	0.00000000
19	554.52780000	0.09880000	0.00000000
20	598.21890000	9.80330000	0.00000000
21	666.09720000	113.68660000	0.00000000
22	675.36580000	91.43460000	0.00000000
23	706.52200000	27.02630000	0.00000000
24	798.33230000	0.16580000	0.00000000
25	815.51060000	10.49950000	0.00000000
26	839.37350000	6.63150000	0.00000000
27	841.47440000	4.09650000	0.00000000
28	849.28520000	7.97080000	0.00000000
29	922.36480000	39.15740000	0.00000000
30	931.81880000	3.54260000	0.00000000
31	937.01980000	27.03110000	0.00000000
32	990.83500000	0.80950000	0.00000000
33	1002.43160000	2.92870000	0.00000000
34	1008.51940000	2.06440000	0.00000000
35	1043.07820000	18.15790000	0.00000000
36	1048.72380000	2.79250000	0.00000000
37	1056.80750000	1.77810000	0.00000000
38	1110.87170000	31.26270000	0.00000000
39	1148.45180000	2.26440000	0.00000000
40	1152.48230000	24.22990000	0.00000000
41	1164.19750000	236.08150000	0.00000000
42	1205.49080000	14.05690000	0.00000000
43	1208.79160000	3.81280000	0.00000000
44	1210.66030000	3.00520000	0.00000000
45	1231.41090000	3.42410000	0.00000000
46	1285.61610000	0.41110000	0.00000000
47	1296.55460000	5.60690000	0.00000000
48	1307.10180000	5.25610000	0.00000000
49	1334.38920000	3.22800000	0.00000000
50	1336.83800000	3.28680000	0.00000000
51	1356.82170000	4.87490000	0.00000000
52	1361.21200000	2.96920000	0.00000000
53	1391.78620000	2.38760000	0.00000000
54	1393.02120000	6.75010000	0.00000000
55	1396.48010000	4.08790000	0.00000000
56	1398.48610000	25.64690000	0.00000000
57	1416.03420000	2.32620000	0.00000000
58	1475.04340000	1.90520000	0.00000000
59	1494.47480000	4.86140000	0.00000000
60	1495.23170000	4.60530000	0.00000000

61	1505.33340000	3.00500000	0.00000000
62	1511.29890000	5.70280000	0.00000000
63	1514.22000000	24.06000000	0.00000000
64	1516.43830000	21.87530000	0.00000000
65	1518.93790000	21.98080000	0.00000000
66	1541.16520000	4.72860000	0.00000000
67	1791.31890000	243.15220000	0.00000000
68	1810.53010000	142.27970000	0.00000000
69	3069.76210000	0.07740000	0.00000000
70	3071.17380000	6.64110000	0.00000000
71	3075.99780000	1.91820000	0.00000000
72	3079.98930000	3.69460000	0.00000000
73	3083.23390000	3.36300000	0.00000000
74	3083.62850000	5.05400000	0.00000000
75	3087.65380000	11.24200000	0.00000000
76	3121.71140000	1.04160000	0.00000000
77	3127.08780000	0.35340000	0.00000000
78	3131.21000000	2.24350000	0.00000000
79	3138.65360000	2.90740000	0.00000000
80	3144.40900000	1.42030000	0.00000000
81	3147.17640000	2.73030000	0.00000000
82	3160.61210000	1.11260000	0.00000000
83	3160.85160000	1.01110000	0.00000000
84	3722.32390000	141.05300000	0.00000000

S41. CALCULATIONS ON 10 – H (Z-ISOMER) → 10 – H (TS)



```

Route : # opt=(qst3,calcfc) freq b3lyp/cc-pvtz geom=connectivity empiricaldisp
       : ersion=gd3bj int=ultrafine pop=regular
SMILES : C[N]12CCC(CC1)(CC2)C(=O)C(=O)O
Formula : C10H16NO3+
Charge : 1
Multiplicity : 1
Energy : -671.17320299 a.u.
Gibbs Energy : -670.95237300 a.u.
Number of imaginary frequencies : 1

```

S41.1. Cartesian Co-ordinates (XYZ format)

30

```

C  0.53770500  1.61700904  0.06785200
C -0.24150500  0.30456299 -0.09761400
C  2.03530407  1.33908606 -0.10686400
H  0.20595001  2.34527612 -0.66670501
H  0.33758101  2.04437709  1.04921496
H  2.40202904  1.62616205 -1.08952403
H  2.64133906  1.83848000  0.64419299
C  0.25531501 -0.38524699 -1.38879299
H -0.36769000 -1.24127495 -1.62845004
H  0.19668300  0.31686199 -2.21885991
C  1.70202804 -0.85183102 -1.17463696
H  1.76608098 -1.91667295 -0.96404701
H  2.33817005 -0.63021302 -2.02734804
C  1.61763096 -0.65243602  1.27598703

```

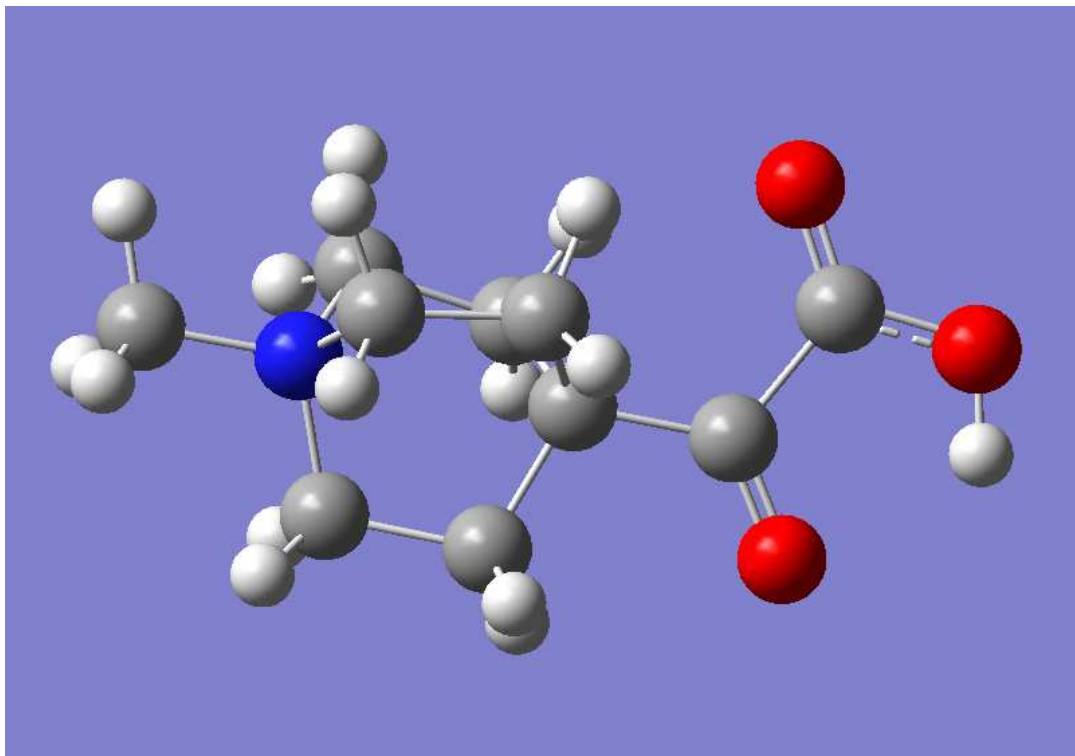
H	1.98494399	-1.65915596	1.45603895
H	1.95775294	-0.01190900	2.08603811
C	0.09339100	-0.61512703	1.09310400
H	-0.29513100	-1.61367798	0.91430598
H	-0.36478400	-0.24389300	2.00869012
N	2.30351210	-0.14718001	0.02353600
C	3.76948810	-0.40680501	0.09568000
H	4.16163683	0.03326700	1.00818205
H	3.93926406	-1.47972596	0.09866300
H	4.25036097	0.04222100	-0.76870501
C	-1.73582900	0.59937298	-0.19792899
O	-2.16526008	1.68949199	-0.46522999
C	-2.71874809	-0.58127099	-0.03908700
O	-2.41625404	-1.68690395	-0.38688299
O	-3.88389707	-0.24725600	0.54573500
H	-4.58579779	0.00553400	-0.06726600

S41.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-642.11190000	122.41750000	0.00000000
2	45.28150000	6.61640000	0.00000000
3	55.68680000	0.87700000	0.00000000
4	121.77440000	2.65530000	0.00000000
5	129.59040000	1.38550000	0.00000000
6	142.63310000	2.64680000	0.00000000
7	235.49160000	16.28790000	0.00000000
8	263.19470000	0.00060000	0.00000000
9	267.64020000	0.75540000	0.00000000
10	271.06550000	1.20110000	0.00000000
11	284.41970000	0.82700000	0.00000000
12	341.05050000	0.83960000	0.00000000
13	352.95910000	8.66960000	0.00000000
14	393.69560000	1.15290000	0.00000000
15	423.02400000	0.71930000	0.00000000
16	424.41610000	0.04180000	0.00000000
17	439.09520000	3.40420000	0.00000000
18	538.42540000	0.17620000	0.00000000
19	541.29320000	0.06180000	0.00000000
20	574.25420000	0.91720000	0.00000000
21	638.15640000	38.91760000	0.00000000
22	694.64300000	3.47360000	0.00000000
23	736.47580000	32.94650000	0.00000000
24	778.23320000	29.71950000	0.00000000
25	799.72820000	0.37770000	0.00000000
26	838.98480000	10.10100000	0.00000000
27	840.89340000	10.05290000	0.00000000
28	849.88230000	6.24890000	0.00000000
29	920.32040000	54.79060000	0.00000000
30	930.46410000	7.94390000	0.00000000
31	936.15240000	23.59340000	0.00000000
32	990.20850000	1.19480000	0.00000000
33	994.89520000	22.84180000	0.00000000
34	1009.53620000	3.67440000	0.00000000
35	1038.39920000	51.22570000	0.00000000
36	1047.52240000	19.76340000	0.00000000
37	1057.25510000	2.37230000	0.00000000
38	1066.10290000	207.50490000	0.00000000
39	1110.82440000	4.96060000	0.00000000
40	1149.05590000	1.07190000	0.00000000
41	1153.14610000	7.41720000	0.00000000
42	1171.45780000	114.19040000	0.00000000
43	1206.57450000	1.41790000	0.00000000
44	1210.71290000	3.05410000	0.00000000
45	1222.03800000	17.58370000	0.00000000
46	1284.86000000	1.18810000	0.00000000
47	1293.38660000	15.20390000	0.00000000
48	1305.61370000	3.19580000	0.00000000
49	1305.86890000	27.73420000	0.00000000
50	1335.55930000	2.53750000	0.00000000
51	1337.17000000	3.78970000	0.00000000
52	1357.56370000	3.09550000	0.00000000
53	1360.41310000	4.25050000	0.00000000
54	1391.90900000	2.19750000	0.00000000
55	1393.41540000	2.11030000	0.00000000
56	1397.28220000	1.39460000	0.00000000
57	1415.98810000	2.26390000	0.00000000
58	1475.35300000	2.01280000	0.00000000
59	1494.69510000	4.51820000	0.00000000
60	1495.14950000	4.44240000	0.00000000

61	1508.02380000	2.28740000	0.00000000
62	1511.40040000	6.63120000	0.00000000
63	1514.80840000	25.96260000	0.00000000
64	1517.34900000	22.29100000	0.00000000
65	1517.85730000	22.22100000	0.00000000
66	1541.39370000	3.79700000	0.00000000
67	1794.67460000	32.63800000	0.00000000
68	1812.23370000	292.66060000	0.00000000
69	3069.91190000	0.05260000	0.00000000
70	3072.31390000	2.50870000	0.00000000
71	3074.27560000	7.19380000	0.00000000
72	3074.76350000	3.26190000	0.00000000
73	3083.05690000	2.63210000	0.00000000
74	3083.92660000	4.29280000	0.00000000
75	3087.81200000	11.24890000	0.00000000
76	3121.21790000	0.12280000	0.00000000
77	3123.95380000	1.48920000	0.00000000
78	3129.56880000	1.68180000	0.00000000
79	3138.08870000	0.95180000	0.00000000
80	3141.67780000	3.70760000	0.00000000
81	3144.68670000	2.15650000	0.00000000
82	3160.74980000	1.05070000	0.00000000
83	3161.13750000	0.93630000	0.00000000
84	3794.01670000	225.69310000	0.00000000

S42. CALCULATIONS ON 10 – H



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N]12CCC(CC1)(CC2)C(=O)C(=O)O
Formula              : C10H16NO3+
Charge               : 1
Multiplicity         : 1
Energy               : -671.19318885
Gibbs Energy         : -670.96938100
Number of imaginary frequencies : 0

```

a.u.

a.u.

S42.1. Cartesian Co-ordinates (XYZ format)

30

```

C -2.23890591 -0.24079700 -0.17616700
C -0.69564301 -0.33737299 -0.18043500
C -2.64116693  1.23433399 -0.31671101
H -2.66015792 -0.80420899 -1.00704205
H -2.62998605 -0.66715598  0.74200499
H -2.95015502  1.49085701 -1.32712102
H -3.44052792  1.50576305  0.36754599
C -0.16524000  0.48516199 -1.36274505
H  0.90055400  0.31853199 -1.49546003
H -0.64887100  0.16518299 -2.28367090
C -0.42944199  1.97255599 -1.09685397
H  0.45805800  2.49937391 -0.75451201
H -0.81720501  2.48776603 -1.97142601
C -0.84777099  1.66818500  1.30931604

```

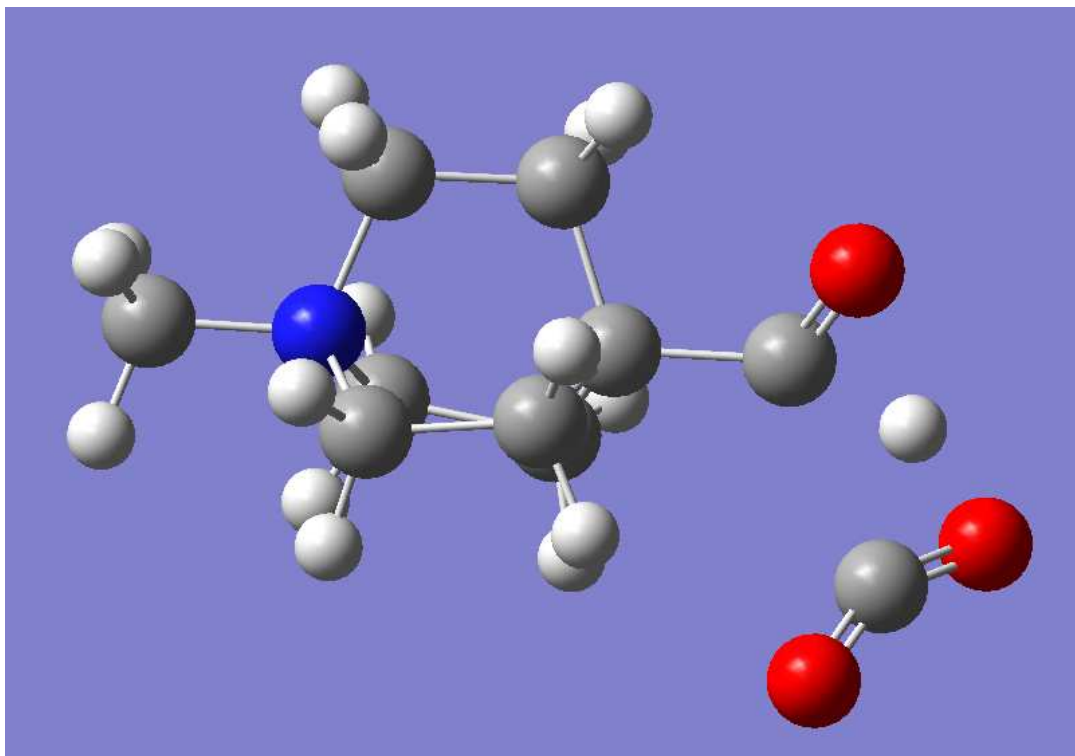
H	-0.14632000	2.43732190	1.62084794
H	-1.66161096	1.63075197	2.02937198
C	-0.17162600	0.30287001	1.12470996
H	0.90969199	0.41796401	1.06529903
H	-0.39750099	-0.32689399	1.97905302
N	-1.46072400	2.12734008	0.00243300
C	-1.89990997	3.54817510	0.10729200
H	-2.57031703	3.64925194	0.95599300
H	-1.02621901	4.17824221	0.24776000
H	-2.41506195	3.82704496	-0.80754101
C	-0.24491000	-1.78160906	-0.30305400
O	0.45061901	-2.17765093	-1.20555699
C	-0.70451999	-2.79586196	0.77526700
O	-1.39507306	-2.48050904	1.70687795
O	-0.25905699	-4.02187395	0.55844498
H	0.27707800	-4.02339220	-0.25475100

S42.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	67.27750000	0.02840000	0.00000000
2	72.61210000	3.34730000	0.00000000
3	120.09630000	3.45070000	0.00000000
4	133.77430000	0.58300000	0.00000000
5	158.42120000	5.13900000	0.00000000
6	244.39260000	22.23110000	0.00000000
7	263.00870000	0.00360000	0.00000000
8	268.21190000	1.34650000	0.00000000
9	271.39180000	2.06650000	0.00000000
10	300.77010000	4.41440000	0.00000000
11	342.64280000	3.58580000	0.00000000
12	360.43320000	15.34890000	0.00000000
13	411.81670000	4.58410000	0.00000000
14	424.61050000	0.12400000	0.00000000
15	424.94820000	1.81490000	0.00000000
16	491.38120000	17.89350000	0.00000000
17	538.71340000	0.10600000	0.00000000
18	541.22700000	0.27020000	0.00000000
19	559.38950000	1.55560000	0.00000000
20	603.21920000	5.90280000	0.00000000
21	690.36200000	85.86580000	0.00000000
22	691.85040000	3.68860000	0.00000000
23	722.76700000	9.58090000	0.00000000
24	799.13790000	0.24730000	0.00000000
25	817.76570000	0.77550000	0.00000000
26	839.88670000	6.95420000	0.00000000
27	842.29870000	6.98070000	0.00000000
28	851.13690000	3.66200000	0.00000000
29	925.39640000	34.22860000	0.00000000
30	932.20350000	3.98990000	0.00000000
31	938.89150000	36.57280000	0.00000000
32	991.33510000	0.60910000	0.00000000
33	1000.46640000	2.39760000	0.00000000
34	1009.54320000	2.23930000	0.00000000
35	1045.53330000	13.41150000	0.00000000
36	1049.37130000	3.01550000	0.00000000
37	1057.05230000	1.83790000	0.00000000
38	1115.91050000	4.30810000	0.00000000
39	1148.01520000	0.79560000	0.00000000
40	1152.68620000	5.01350000	0.00000000
41	1178.56480000	63.29870000	0.00000000
42	1207.35730000	0.59110000	0.00000000
43	1209.50240000	0.23780000	0.00000000
44	1215.97980000	13.77280000	0.00000000
45	1241.46010000	176.15450000	0.00000000
46	1286.62660000	4.63430000	0.00000000
47	1297.36130000	6.37760000	0.00000000
48	1308.84740000	5.03810000	0.00000000
49	1334.75120000	3.16140000	0.00000000
50	1337.46160000	3.15810000	0.00000000
51	1356.94080000	4.84990000	0.00000000
52	1361.61880000	2.84460000	0.00000000
53	1376.33250000	346.12600000	0.00000000
54	1392.19380000	2.48100000	0.00000000
55	1393.81010000	3.10420000	0.00000000
56	1399.81500000	5.57940000	0.00000000
57	1416.51620000	0.94130000	0.00000000
58	1475.45760000	1.82230000	0.00000000
59	1494.50200000	4.90410000	0.00000000
60	1495.26180000	4.57370000	0.00000000

61	1505.76570000	2.51390000	0.00000000
62	1511.38020000	6.01140000	0.00000000
63	1514.45030000	24.44660000	0.00000000
64	1516.65760000	22.41090000	0.00000000
65	1518.94990000	22.21510000	0.00000000
66	1541.34900000	4.11380000	0.00000000
67	1784.82560000	94.83930000	0.00000000
68	1830.65150000	220.61610000	0.00000000
69	3070.05350000	0.09170000	0.00000000
70	3071.45240000	6.36730000	0.00000000
71	3077.04140000	0.96010000	0.00000000
72	3079.14070000	4.45720000	0.00000000
73	3084.22540000	2.74070000	0.00000000
74	3084.54960000	4.22850000	0.00000000
75	3088.47220000	10.48820000	0.00000000
76	3120.10590000	1.15240000	0.00000000
77	3128.17900000	0.53210000	0.00000000
78	3132.24170000	2.56460000	0.00000000
79	3139.07300000	2.48500000	0.00000000
80	3145.03160000	1.41430000	0.00000000
81	3147.91090000	2.52150000	0.00000000
82	3161.00850000	0.99380000	0.00000000
83	3161.42320000	0.78720000	0.00000000
84	3653.26800000	105.76900000	0.00000000

S43. CALCULATIONS ON 10 – H → 12 – H (TS)



```

Route : # opt=(calcfc,qst3) freq b3lyp/cc-pvtz geom=connectivity empiricaldisp
       : ersion=gd3bj int=ultrafine pop=regular
SMILES : C[N]12CCC(CC1)(CC2)[C]=O.[C](=O)O
Formula : C10H16NO3+
Charge : 1
Multiplicity : 1
Energy : -671.07397347 a.u.
Gibbs Energy : -670.86122600 a.u.
Number of imaginary frequencies : 1

```

S43.1. Cartesian Co-ordinates (XYZ format)

30

```

C -0.04199200 1.15048504 0.46509901
C -0.53431797 -0.13754600 -0.20428599
C 1.48897302 1.21872795 0.35158199
H -0.47508201 2.02565289 -0.01731100
H -0.34217399 1.17273200 1.51121795
H 1.81834996 1.90268302 -0.42674401
H 1.96288800 1.50839996 1.28553796
C 0.10885200 -0.24402100 -1.59614003
H -0.33931801 -1.06872499 -2.14406800
H -0.08400400 0.66551101 -2.16374803
C 1.61792803 -0.46932799 -1.43996501
H 1.90590596 -1.50434995 -1.60837305
H 2.20546198 0.16236299 -2.10084200
C 1.45436597 -1.17927802 0.91046798

```

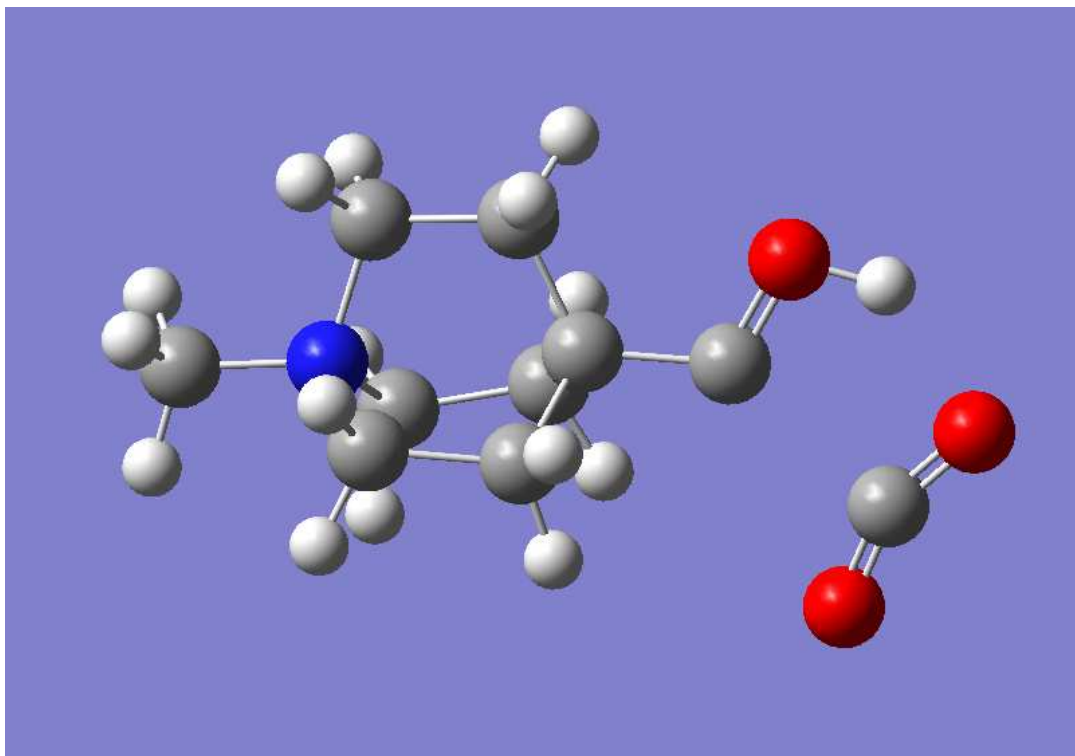
H	2.00459099	-2.10211706	0.74674499
H	1.65910304	-0.83127397	1.92015100
C	-0.04831200	-1.33698297	0.63646603
H	-0.25078800	-2.25889897	0.09511100
H	-0.58234203	-1.38889897	1.58193600
N	2.04457903	-0.14139301	-0.02166800
C	3.53157496	-0.13754299	0.08407400
H	3.81251502	0.01454700	1.12232697
H	3.91275406	-1.09225702	-0.26682299
H	3.92745209	0.66710299	-0.52902400
C	-2.06615305	-0.20628500	-0.31553000
O	-2.59031296	-0.96490502	-1.08888996
C	-3.09667397	0.44098201	1.47711098
O	-2.65875196	-0.05157100	2.43268490
O	-3.90568399	1.19749105	0.90645099
H	-3.16011906	0.84134197	0.02531400

S43.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2202.75890000	372.31640000	0.00000000
2	37.66440000	0.78980000	0.00000000
3	48.64620000	1.40050000	0.00000000
4	79.02340000	0.27690000	0.00000000
5	117.24910000	3.15050000	0.00000000
6	124.76220000	2.31060000	0.00000000
7	143.26610000	8.11920000	0.00000000
8	209.16950000	13.48340000	0.00000000
9	261.23410000	0.00630000	0.00000000
10	267.83270000	2.40480000	0.00000000
11	270.36080000	0.16930000	0.00000000
12	298.98840000	24.38670000	0.00000000
13	338.19920000	7.88230000	0.00000000
14	352.83640000	1.13190000	0.00000000
15	420.79240000	0.09720000	0.00000000
16	423.67300000	0.05060000	0.00000000
17	431.96830000	3.41170000	0.00000000
18	535.22200000	20.33390000	0.00000000
19	536.44420000	7.87290000	0.00000000
20	546.55480000	43.88410000	0.00000000
21	575.08190000	3.36290000	0.00000000
22	576.91750000	50.24200000	0.00000000
23	654.19790000	517.92690000	0.00000000
24	699.27330000	47.03220000	0.00000000
25	786.91130000	11.11180000	0.00000000
26	803.24160000	0.37410000	0.00000000
27	837.47650000	7.48850000	0.00000000
28	840.50160000	6.71300000	0.00000000
29	869.98500000	34.61320000	0.00000000
30	927.69600000	4.81180000	0.00000000
31	931.29570000	3.17510000	0.00000000
32	960.56020000	16.94890000	0.00000000
33	984.32040000	2.90360000	0.00000000
34	993.20750000	5.71430000	0.00000000
35	1011.37240000	9.92710000	0.00000000
36	1026.00950000	9.60810000	0.00000000
37	1045.02680000	2.09920000	0.00000000
38	1055.02040000	3.88070000	0.00000000
39	1091.06760000	24.62700000	0.00000000
40	1147.08830000	29.65950000	0.00000000
41	1153.41130000	14.96830000	0.00000000
42	1154.52690000	68.71020000	0.00000000
43	1204.69960000	1.30530000	0.00000000
44	1208.40910000	0.87920000	0.00000000
45	1215.40380000	87.66280000	0.00000000
46	1240.19830000	363.86930000	0.00000000
47	1284.54910000	0.54870000	0.00000000
48	1295.37330000	1.12960000	0.00000000
49	1307.33790000	14.76390000	0.00000000
50	1334.01550000	0.95010000	0.00000000
51	1335.29600000	3.09540000	0.00000000
52	1355.61010000	3.99810000	0.00000000
53	1360.11160000	6.64670000	0.00000000
54	1389.13020000	1.43750000	0.00000000
55	1390.81790000	1.89680000	0.00000000
56	1393.73920000	0.90490000	0.00000000
57	1415.23590000	2.27160000	0.00000000
58	1474.88700000	2.21970000	0.00000000
59	1494.08990000	4.02620000	0.00000000
60	1494.38380000	4.25930000	0.00000000

61	1508.53240000	0.87440000	0.00000000
62	1509.28960000	3.56460000	0.00000000
63	1515.27080000	25.09160000	0.00000000
64	1515.53990000	23.37630000	0.00000000
65	1515.81940000	24.84140000	0.00000000
66	1539.72800000	5.34420000	0.00000000
67	1719.47660000	44.94690000	0.00000000
68	1798.98510000	141.18750000	0.00000000
69	2168.32230000	362.80940000	0.00000000
70	3063.49100000	5.64780000	0.00000000
71	3067.38530000	6.57850000	0.00000000
72	3070.13550000	0.16260000	0.00000000
73	3078.36480000	2.59000000	0.00000000
74	3082.02380000	2.97040000	0.00000000
75	3083.32970000	4.34840000	0.00000000
76	3087.39710000	11.94600000	0.00000000
77	3103.23050000	3.18890000	0.00000000
78	3119.28210000	2.74130000	0.00000000
79	3120.28190000	0.32530000	0.00000000
80	3134.81620000	0.05810000	0.00000000
81	3139.14500000	4.33630000	0.00000000
82	3139.96770000	3.33150000	0.00000000
83	3160.75780000	1.07890000	0.00000000
84	3161.22280000	0.93510000	0.00000000

S44. CALCULATIONS ON 10 – H → 11 – H (TS)



```

Route : # opt=(calcfc,qst3) freq b3lyp/cc-pvtz geom=connectivity empiricaldisp
       : ersion=gd3bj int=ultrafine pop=regular
SMILES : C[N]12CCC(CC1)(CC2)[C]O.C(=O)=O
Formula : C10H16NO3+
Charge : 1
Multiplicity : 1
Energy : -671.13212323 a.u.
Gibbs Energy : -670.91338500 a.u.
Number of imaginary frequencies : 1

```

S44.1. Cartesian Co-ordinates (XYZ format)

30

```

C  0.27092099  1.56912601 -0.10462500
C -0.47582299  0.23157001 -0.00676200
C  1.76959705  1.31990695  0.12144800
H  0.09978900  2.02078295 -1.08007896
H -0.09942200  2.27015090  0.63978601
H  2.39239311  1.83292997 -0.60640800
H  2.09493494  1.61177897  1.11707795
C -0.06000200 -0.66481698 -1.19738495
H -0.45918399 -1.66629303 -1.05409598
H -0.47248599 -0.28147799 -2.12854004
C  1.47213304 -0.67876202 -1.29006898
H  1.86499596 -1.67984104 -1.44643998
H  1.84636497 -0.03425700 -2.08161592
C  1.43870401 -0.89202499  1.16004395

```

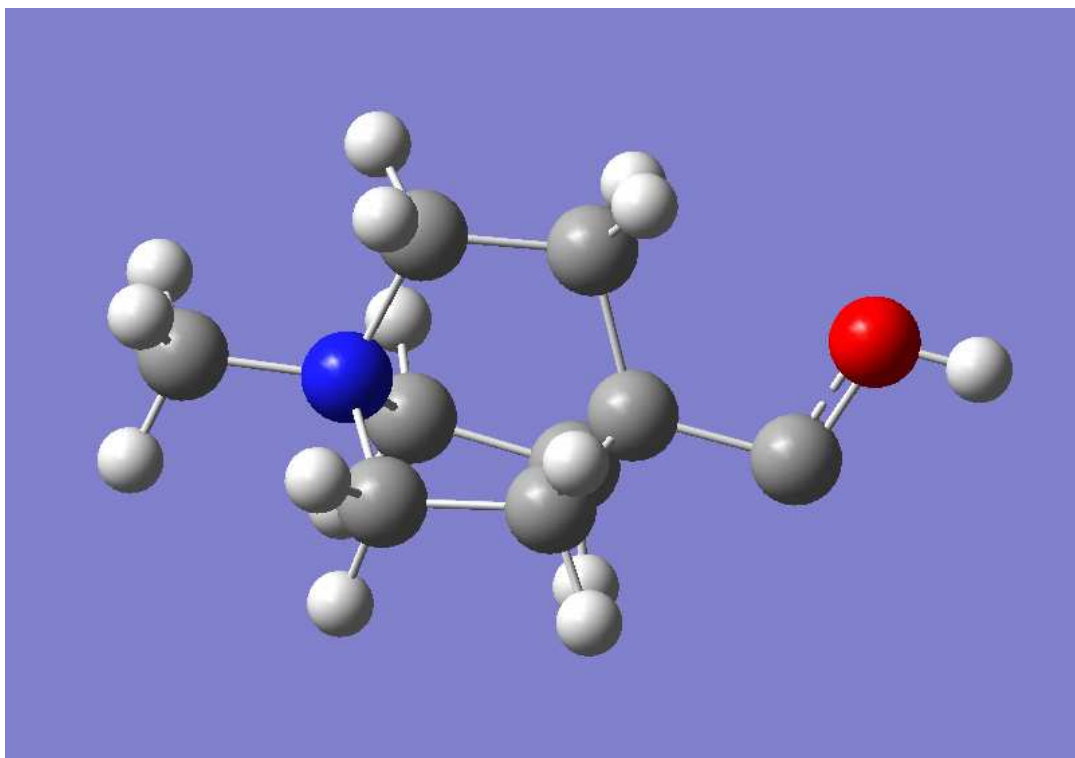
H 1.56688797 -1.95272100 0.95840400
H 2.01148009 -0.63875902 2.04794407
C -0.03854300 -0.49502000 1.28633702
H -0.65047097 -1.38072205 1.44039905
H -0.18636200 0.16041601 2.14287400
N 2.07792902 -0.16064399 -0.00232500
C 3.55284691 -0.38192001 -0.00138500
H 3.97678709 0.06764400 0.89200801
H 3.74989295 -1.45010900 -0.00819000
H 3.97995400 0.07963700 -0.88712502
C -1.96659100 0.27793401 -0.00770100
O -2.48173189 1.43898702 -0.07868000
C -3.66592002 -1.04354596 0.07854500
O -3.29841805 -2.15665102 0.15430900
O -4.47233009 -0.16448300 0.01944700
H -3.47144198 1.27230501 -0.07006000

S44.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-176.5100000	103.26870000	0.0000000
2	27.46400000	1.25110000	0.0000000
3	60.12910000	0.00690000	0.0000000
4	75.65580000	7.79300000	0.0000000
5	112.45120000	0.00670000	0.0000000
6	117.59960000	0.22860000	0.0000000
7	209.81340000	6.43350000	0.0000000
8	260.63540000	0.00280000	0.0000000
9	263.40120000	0.12760000	0.0000000
10	267.51580000	0.14640000	0.0000000
11	307.46560000	0.27280000	0.0000000
12	310.57520000	8.11530000	0.0000000
13	348.94990000	1.57130000	0.0000000
14	420.75170000	0.01710000	0.0000000
15	422.10050000	0.20650000	0.0000000
16	454.57200000	6.38990000	0.0000000
17	459.76040000	24.17260000	0.0000000
18	534.23360000	7.17950000	0.0000000
19	538.50980000	0.31000000	0.0000000
20	569.03000000	2.35730000	0.0000000
21	609.58170000	410.59640000	0.0000000
22	687.80630000	3.43270000	0.0000000
23	690.60110000	15.72860000	0.0000000
24	755.14770000	14.53510000	0.0000000
25	801.22640000	0.30830000	0.0000000
26	832.69260000	8.53300000	0.0000000
27	837.88980000	6.32320000	0.0000000
28	867.98610000	26.54180000	0.0000000
29	925.49370000	6.35060000	0.0000000
30	929.90050000	2.42010000	0.0000000
31	961.37020000	0.40520000	0.0000000
32	988.49590000	0.18260000	0.0000000
33	1005.73200000	5.92590000	0.0000000
34	1025.08150000	9.80250000	0.0000000
35	1044.47190000	13.25860000	0.0000000
36	1052.27100000	0.18830000	0.0000000
37	1063.22540000	39.76710000	0.0000000
38	1103.37930000	6.91290000	0.0000000
39	1148.34630000	3.37640000	0.0000000
40	1148.79400000	4.07910000	0.0000000
41	1170.42590000	37.34990000	0.0000000
42	1204.52150000	1.04280000	0.0000000
43	1206.94250000	2.42590000	0.0000000
44	1214.66010000	20.15240000	0.0000000
45	1264.45710000	78.45440000	0.0000000
46	1283.78780000	1.64030000	0.0000000
47	1296.38800000	3.15560000	0.0000000
48	1304.37300000	20.26550000	0.0000000
49	1330.54880000	0.50380000	0.0000000
50	1334.37720000	4.76190000	0.0000000
51	1355.29420000	5.38240000	0.0000000
52	1357.90090000	11.69880000	0.0000000
53	1390.50830000	0.65270000	0.0000000
54	1391.35670000	1.75540000	0.0000000
55	1394.07280000	15.41490000	0.0000000
56	1415.05510000	9.46460000	0.0000000
57	1433.45830000	215.94970000	0.0000000
58	1475.17020000	8.57280000	0.0000000
59	1493.35250000	6.27540000	0.0000000
60	1494.02770000	4.49170000	0.0000000

61	1504.35230000	81.06140000	0.00000000
62	1505.77710000	62.23930000	0.00000000
63	1508.68020000	0.80210000	0.00000000
64	1514.02880000	26.70150000	0.00000000
65	1515.30750000	29.73840000	0.00000000
66	1515.95980000	19.89460000	0.00000000
67	1539.06650000	4.19680000	0.00000000
68	2188.48990000	438.00700000	0.00000000
69	3070.32700000	0.11200000	0.00000000
70	3071.79370000	4.34220000	0.00000000
71	3074.49790000	3.33730000	0.00000000
72	3076.34150000	2.85440000	0.00000000
73	3083.66710000	2.90860000	0.00000000
74	3084.60740000	2.79810000	0.00000000
75	3088.63090000	11.15450000	0.00000000
76	3114.45150000	1.16100000	0.00000000
77	3115.63910000	1.02040000	0.00000000
78	3116.74170000	0.83900000	0.00000000
79	3135.92850000	0.46720000	0.00000000
80	3140.40420000	4.18500000	0.00000000
81	3141.54740000	2.28020000	0.00000000
82	3155.45720000	365.84940000	0.00000000
83	3161.51380000	0.90010000	0.00000000
84	3161.74500000	0.77330000	0.00000000

S45. CALCULATIONS ON 11 – H



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N]12CCC(CC1)(CC2)[C]O
Formula              : C9H16NO+
Charge               : 1
Multiplicity         : 1
Energy               : -482.46579543
Gibbs Energy        : -482.25492900
Number of imaginary frequencies : 0

```

a.u.

a.u.

S45.1. Cartesian Co-ordinates (XYZ format)

27

```

C -2.03976107 -0.30266500 0.17854200
C -0.49844199 -0.28552499 0.10429300
C -2.57180405 1.10529304 -0.12113500
H -2.44965601 -1.00393200 -0.54579997
H -2.35162306 -0.64150000 1.16378498
H -2.95523190 1.19929004 -1.13427305
H -3.35270000 1.40931702 0.57114202
C -0.07893700 0.41002801 -1.20081103
H 0.99385202 0.32258099 -1.35406601
H -0.56032002 -0.07064400 -2.05072498
C -0.46775600 1.89330697 -1.12984896
H 0.38203499 2.53837490 -0.91892302
H -0.94735199 2.24583697 -2.03929996
C -0.74229199 1.89679897 1.31919706

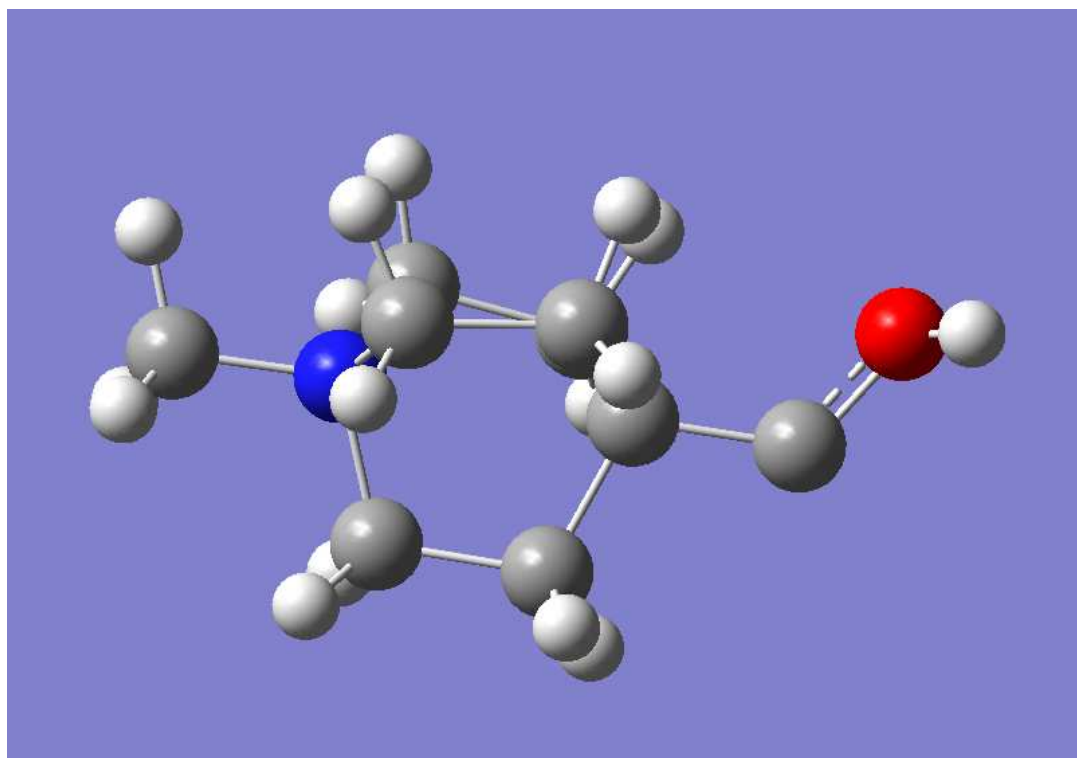
```

H	-0.07813200	2.74399495	1.46812201
H	-1.51261401	1.92486799	2.08625293
C	0.01083200	0.56014597	1.29133403
H	1.08185506	0.72798097	1.18906701
H	-0.14658900	0.02377500	2.22428608
N	-1.45409799	2.12028503	0.00069400
C	-2.00324607	3.50405693	-0.06172100
H	-2.64064693	3.67127490	0.80185997
H	-1.17936802	4.21207619	-0.05667600
H	-2.58069110	3.61456609	-0.97518897
C	-0.03314700	-1.70781600	0.34049600
O	0.75608701	-2.06087494	-0.63621700
H	1.05817497	-2.96979094	-0.48805800

S45.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	33.59660000	4.82230000	0.00000000
2	117.28550000	0.02770000	0.00000000
3	189.92690000	1.02440000	0.00000000
4	257.00730000	0.33090000	0.00000000
5	260.45530000	0.00100000	0.00000000
6	268.77110000	0.11410000	0.00000000
7	287.38210000	1.38380000	0.00000000
8	338.67620000	1.06210000	0.00000000
9	405.06300000	0.29600000	0.00000000
10	410.67010000	1.74520000	0.00000000
11	422.16810000	0.00140000	0.00000000
12	422.85020000	0.03170000	0.00000000
13	531.90660000	0.41340000	0.00000000
14	538.06860000	0.14830000	0.00000000
15	569.13620000	2.33230000	0.00000000
16	668.51720000	11.43300000	0.00000000
17	718.40800000	8.36640000	0.00000000
18	798.35220000	1.56220000	0.00000000
19	820.24800000	61.00130000	0.00000000
20	835.94540000	7.18900000	0.00000000
21	841.44160000	11.34180000	0.00000000
22	857.56080000	31.29640000	0.00000000
23	927.58240000	2.55930000	0.00000000
24	931.14060000	0.07590000	0.00000000
25	982.76140000	4.18150000	0.00000000
26	989.93810000	16.46690000	0.00000000
27	1003.42860000	6.17240000	0.00000000
28	1018.25920000	11.66980000	0.00000000
29	1043.88150000	2.13090000	0.00000000
30	1047.52820000	0.27780000	0.00000000
31	1087.90300000	4.08860000	0.00000000
32	1146.92690000	3.71030000	0.00000000
33	1148.59790000	7.24620000	0.00000000
34	1155.18550000	39.90740000	0.00000000
35	1200.38040000	0.62760000	0.00000000
36	1205.12590000	2.18780000	0.00000000
37	1209.85280000	17.10950000	0.00000000
38	1280.96040000	2.57130000	0.00000000
39	1285.34310000	13.95860000	0.00000000
40	1293.87850000	7.89930000	0.00000000
41	1319.39640000	43.09910000	0.00000000
42	1330.81160000	7.31740000	0.00000000
43	1333.58910000	133.26150000	0.00000000
44	1352.60370000	5.04690000	0.00000000
45	1354.81830000	11.17190000	0.00000000
46	1374.57770000	33.09570000	0.00000000
47	1384.13160000	4.24450000	0.00000000
48	1390.41990000	2.19510000	0.00000000
49	1395.00660000	5.85560000	0.00000000
50	1415.51890000	0.26740000	0.00000000
51	1474.22780000	1.75550000	0.00000000
52	1493.09110000	4.66980000	0.00000000
53	1494.05780000	4.51700000	0.00000000
54	1504.56980000	1.29890000	0.00000000
55	1506.50130000	1.19020000	0.00000000
56	1512.94470000	19.35490000	0.00000000
57	1514.12060000	26.42210000	0.00000000
58	1514.86630000	25.64050000	0.00000000
59	1537.77320000	5.47490000	0.00000000
60	3068.45570000	5.34660000	0.00000000

61	3069.58630000	0.88540000	0.00000000
62	3072.99780000	4.02700000	0.00000000
63	3074.69660000	4.98220000	0.00000000
64	3080.54370000	4.99620000	0.00000000
65	3082.08370000	4.36060000	0.00000000
66	3086.17050000	11.75000000	0.00000000
67	3111.94930000	1.07590000	0.00000000
68	3112.87080000	1.99160000	0.00000000
69	3114.06960000	2.28770000	0.00000000
70	3132.71000000	0.38870000	0.00000000
71	3137.23360000	6.32750000	0.00000000
72	3138.32380000	4.92240000	0.00000000
73	3160.15660000	1.31580000	0.00000000
74	3160.30770000	1.27200000	0.00000000
75	3711.95160000	196.03490000	0.00000000

S46. CALCULATIONS ON 11 – H (³A)

```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N]12CCC(CC1)(CC2)[C]O
Formula              : C9H16NO+,3
Charge               : 1
Multiplicity         : 3
Energy               : -482.42249796
Gibbs Energy        : -482.21423800
Number of imaginary frequencies : 0

```

a.u.
a.u.

S46.1. Cartesian Co-ordinates (XYZ format)

27

```

C -0.35255799  0.92625701 -1.30036497
C -1.05420196  0.14497700 -0.17914100
C  1.14639199  0.59457701 -1.29393196
H -0.78112698  0.66139197 -2.26424408
H -0.51103699  1.99373603 -1.15820003
H  1.42306602 -0.09736100 -2.08585310
H  1.76910198  1.48089302 -1.38145399
C -0.61281502 -1.33718097 -0.28112301
H -1.19050896 -1.94401705  0.41185501
H -0.81760800 -1.70346999 -1.28496897
C  0.88155800 -1.45430303  0.04853300
H  1.06127703 -1.84109604  1.04885304
H  1.41719198 -2.07866311 -0.66186702
C  0.99603498  0.73694199  1.16216898

```

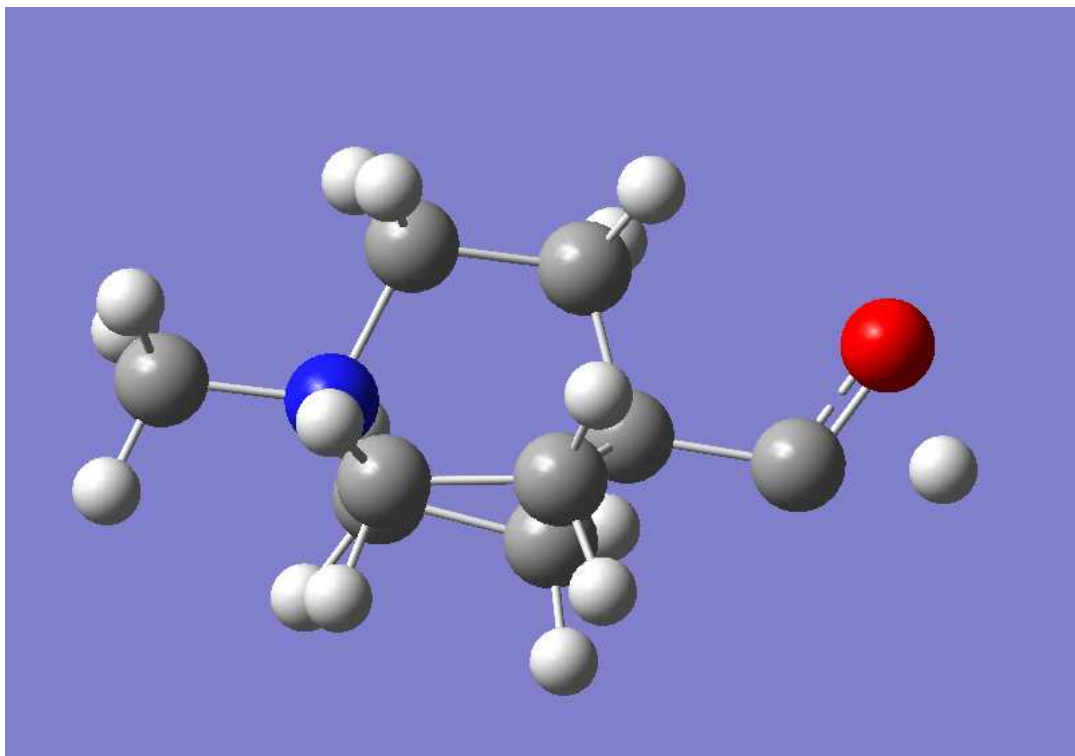
H	1.43547106	0.32696900	2.06792212
H	1.38185203	1.74352098	1.01927495
C	-0.53878701	0.69300097	1.17474496
H	-0.90068400	0.06081300	1.98333001
H	-0.92749900	1.69508398	1.34131801
N	1.52882302	-0.08455100	0.00603700
C	3.01036906	-0.21125600	0.10395900
H	3.44807100	0.78163600	0.15512900
H	3.25891495	-0.77238703	1.00029898
H	3.37926102	-0.73380297	-0.77403498
C	-2.52897406	0.25944999	-0.31055301
O	-3.39256811	-0.34680101	0.50383401
H	-3.98394299	0.27231601	0.95644599

S46.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	79.97820000	4.01670000	0.00000000
2	110.87000000	0.11540000	0.00000000
3	148.08640000	0.33000000	0.00000000
4	247.38400000	78.36780000	0.00000000
5	262.03940000	0.00660000	0.00000000
6	265.27610000	3.47140000	0.00000000
7	270.17540000	26.35420000	0.00000000
8	305.93110000	27.27810000	0.00000000
9	317.78970000	1.55640000	0.00000000
10	415.21230000	3.47370000	0.00000000
11	421.24690000	0.41390000	0.00000000
12	423.23240000	0.12640000	0.00000000
13	447.86760000	8.43280000	0.00000000
14	531.91090000	0.32870000	0.00000000
15	535.72720000	0.63010000	0.00000000
16	548.07050000	1.36240000	0.00000000
17	665.91250000	2.98910000	0.00000000
18	713.53390000	1.76620000	0.00000000
19	801.48310000	0.09410000	0.00000000
20	830.26300000	5.93150000	0.00000000
21	835.72200000	6.97100000	0.00000000
22	864.54710000	9.95230000	0.00000000
23	925.17690000	1.76530000	0.00000000
24	928.97640000	2.00080000	0.00000000
25	981.55100000	1.99800000	0.00000000
26	983.79220000	6.68400000	0.00000000
27	998.49500000	16.92480000	0.00000000
28	1017.33600000	3.00960000	0.00000000
29	1034.50150000	2.14510000	0.00000000
30	1044.81170000	2.29680000	0.00000000
31	1080.95760000	12.85630000	0.00000000
32	1139.95280000	110.74170000	0.00000000
33	1142.56500000	4.86410000	0.00000000
34	1143.69790000	9.48430000	0.00000000
35	1155.46470000	47.45690000	0.00000000
36	1200.99530000	0.41810000	0.00000000
37	1204.65760000	1.65300000	0.00000000
38	1215.38160000	1.64200000	0.00000000
39	1279.08790000	4.55120000	0.00000000
40	1289.56250000	6.02210000	0.00000000
41	1295.30340000	6.35380000	0.00000000
42	1324.99130000	2.86430000	0.00000000
43	1327.32390000	3.04800000	0.00000000
44	1351.84630000	4.75690000	0.00000000
45	1353.70780000	4.17980000	0.00000000
46	1369.92820000	49.15060000	0.00000000
47	1390.55150000	3.61950000	0.00000000
48	1390.83110000	7.17960000	0.00000000
49	1394.30330000	8.85140000	0.00000000
50	1415.21220000	0.94980000	0.00000000
51	1474.81470000	2.02390000	0.00000000
52	1493.20820000	4.15460000	0.00000000
53	1493.89390000	4.75210000	0.00000000
54	1506.07150000	1.33600000	0.00000000
55	1506.85130000	0.82040000	0.00000000
56	1513.53540000	19.91820000	0.00000000
57	1514.33530000	23.85770000	0.00000000
58	1515.07020000	27.25430000	0.00000000
59	1538.34020000	6.85840000	0.00000000
60	3069.59730000	0.30840000	0.00000000

61	3071.32720000	5.90250000	0.00000000
62	3072.42690000	6.69020000	0.00000000
63	3076.13680000	4.49710000	0.00000000
64	3080.71680000	5.50180000	0.00000000
65	3081.80970000	4.06830000	0.00000000
66	3086.33050000	11.03140000	0.00000000
67	3111.22230000	1.37430000	0.00000000
68	3112.29130000	2.74880000	0.00000000
69	3116.99760000	1.14280000	0.00000000
70	3132.65710000	0.37430000	0.00000000
71	3137.42940000	6.09210000	0.00000000
72	3138.49130000	5.68000000	0.00000000
73	3160.39590000	1.31490000	0.00000000
74	3160.44220000	1.25980000	0.00000000
75	3697.95630000	107.95940000	0.00000000

S47. CALCULATIONS ON 11 – H → 12 – H (TS)



```

Route : # opt=(calcall,ts,noeigen) freq b3lyp/cc-pvtz geom=connectivity empiri
       : calcdispersion=gd3bj int=ultrafine pop=regular
SMILES : C[N]12CCC(CC1)(CC2)[C]O
Formula : C9H16NO+
Charge : 1
Multiplicity : 1
Energy : -482.41096490 a.u.
Gibbs Energy : -482.20574200 a.u.
Number of imaginary frequencies : 1

```

S47.1. Cartesian Co-ordinates (XYZ format)

27

```

C  0.34571299 -1.33944798 -0.81861001
C  1.02868295 -0.22743300 -0.00467000
C -1.13934898 -0.98413402 -0.98498601
H  0.80604202 -1.43447101 -1.80004704
H  0.46641901 -2.29510403 -0.31249800
H -1.36241198 -0.58077902 -1.96969402
H -1.79273105 -1.83386195 -0.80557299
C  0.65762401  1.13234794 -0.61108601
H  1.24890494  1.92607105 -0.16008399
H  0.88314497  1.13723695 -1.67607498
C -0.83559197  1.38714302 -0.37354100
H -1.01818895  2.07736206  0.44675401
H -1.34038401  1.76529300 -1.25850904
C -1.05218899 -0.32656601  1.38350201

```

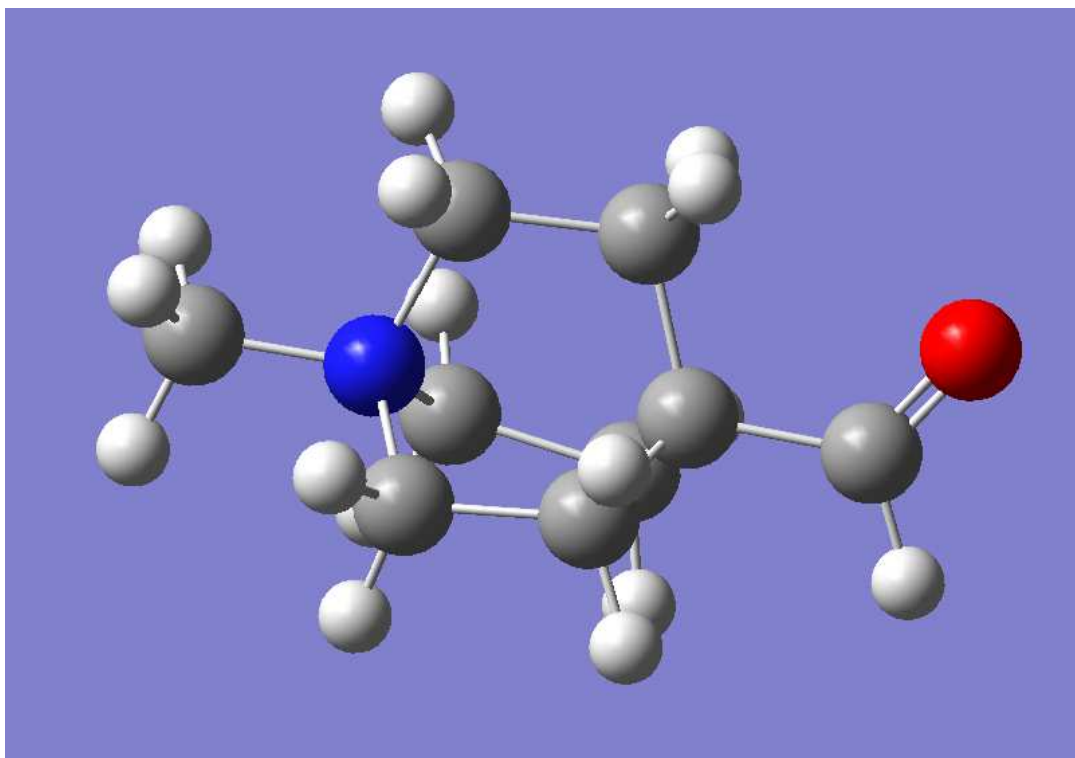
H	-1.50575304	0.35391900	2.09911489
H	-1.45303202	-1.32288206	1.55384004
C	0.48153400	-0.29230300	1.43699396
H	0.82716697	0.57309598	1.99978304
H	0.85352600	-1.18053496	1.94329000
N	-1.53084195	0.09167400	0.00876700
C	-3.00954103	0.27977100	0.01114400
H	-3.48195291	-0.63013101	0.37018099
H	-3.25904393	1.11002898	0.66574401
H	-3.33999705	0.49419701	-1.00119603
C	2.51744604	-0.47105700	0.05136600
O	3.29431510	0.53465199	-0.19054100
H	3.77742290	-0.50955600	0.08116000

S47.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2046.40450000	561.47480000	0.00000000
2	47.52560000	0.05350000	0.00000000
3	121.62420000	0.06580000	0.00000000
4	178.06720000	0.68140000	0.00000000
5	254.46880000	0.33000000	0.00000000
6	262.01970000	0.00060000	0.00000000
7	268.73430000	0.07520000	0.00000000
8	279.88340000	0.08130000	0.00000000
9	336.66660000	1.73280000	0.00000000
10	387.30800000	1.49450000	0.00000000
11	406.61130000	0.71940000	0.00000000
12	421.53580000	0.08860000	0.00000000
13	422.17430000	0.03660000	0.00000000
14	532.72070000	0.01710000	0.00000000
15	537.72020000	0.14100000	0.00000000
16	571.23800000	0.20140000	0.00000000
17	605.92810000	38.38310000	0.00000000
18	681.49480000	3.37120000	0.00000000
19	733.60740000	10.55800000	0.00000000
20	797.96070000	0.45680000	0.00000000
21	833.14510000	7.25840000	0.00000000
22	837.26900000	7.43390000	0.00000000
23	859.89890000	34.76140000	0.00000000
24	925.65530000	2.74100000	0.00000000
25	928.73570000	3.29230000	0.00000000
26	980.60320000	5.84730000	0.00000000
27	985.47660000	0.17770000	0.00000000
28	1003.47700000	2.86610000	0.00000000
29	1026.59160000	6.10480000	0.00000000
30	1042.74320000	2.68610000	0.00000000
31	1051.78480000	0.70680000	0.00000000
32	1089.20550000	2.00590000	0.00000000
33	1145.60640000	5.89070000	0.00000000
34	1150.16540000	8.76140000	0.00000000
35	1159.54760000	35.81020000	0.00000000
36	1201.54650000	0.24870000	0.00000000
37	1203.76380000	1.54330000	0.00000000
38	1218.73710000	9.19230000	0.00000000
39	1281.61940000	2.80880000	0.00000000
40	1289.15510000	7.35640000	0.00000000
41	1297.81970000	4.39880000	0.00000000
42	1328.49610000	2.73680000	0.00000000
43	1332.90310000	1.81670000	0.00000000
44	1353.90950000	4.13370000	0.00000000
45	1358.19670000	4.40050000	0.00000000
46	1385.39150000	4.91800000	0.00000000
47	1390.48250000	1.77550000	0.00000000
48	1392.59410000	4.11110000	0.00000000
49	1412.53010000	35.29610000	0.00000000
50	1437.64440000	217.37970000	0.00000000
51	1474.98670000	0.60250000	0.00000000
52	1493.59870000	4.29570000	0.00000000
53	1493.83530000	4.46250000	0.00000000
54	1505.44270000	1.42100000	0.00000000
55	1506.82390000	0.86670000	0.00000000
56	1513.29200000	18.82300000	0.00000000
57	1514.28800000	27.48520000	0.00000000
58	1514.62130000	27.16160000	0.00000000
59	1537.68730000	4.93510000	0.00000000
60	2580.05460000	158.42680000	0.00000000

61	3069.7370000	1.43630000	0.00000000
62	3070.34940000	3.56850000	0.00000000
63	3072.86400000	3.63360000	0.00000000
64	3073.86760000	3.51140000	0.00000000
65	3082.22940000	3.68760000	0.00000000
66	3083.20380000	3.16160000	0.00000000
67	3087.24000000	11.33720000	0.00000000
68	3110.77520000	1.12070000	0.00000000
69	3111.54330000	2.62650000	0.00000000
70	3114.04030000	2.02880000	0.00000000
71	3134.30440000	0.11860000	0.00000000
72	3138.74660000	4.69820000	0.00000000
73	3139.53250000	4.15390000	0.00000000
74	3160.71650000	1.07390000	0.00000000
75	3161.00660000	1.07800000	0.00000000

S48. CALCULATIONS ON 12 – H



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N]12CCC(CC1)(CC2)C=O
Formula              : C9H16NO+
Charge               : 1
Multiplicity         : 1
Energy               : -482.54206689
Gibbs Energy         : -482.33072500
Number of imaginary frequencies : 0

```

a.u.
a.u.

S48.1. Cartesian Co-ordinates (XYZ format)

27

```

C -2.09041309 -0.30418801 0.06763300
C -0.55221498 -0.29604501 -0.01628400
C -2.60628510 1.12748003 -0.14525899
H -2.51183796 -0.95413798 -0.69705802
H -2.41357708 -0.68793702 1.03447700
H -3.01134992 1.27617395 -1.14305997
H -3.36580205 1.40853798 0.57943797
C -0.13378300 0.44066900 -1.29031205
H 0.93536800 0.33236200 -1.45383501
H -0.62736499 -0.00333800 -2.15260291
C -0.50159001 1.92402196 -1.15415597
H 0.35902199 2.55011606 -0.93069202
H -0.98924702 2.31714797 -2.04209399
C -0.74210298 1.83028197 1.29722595

```

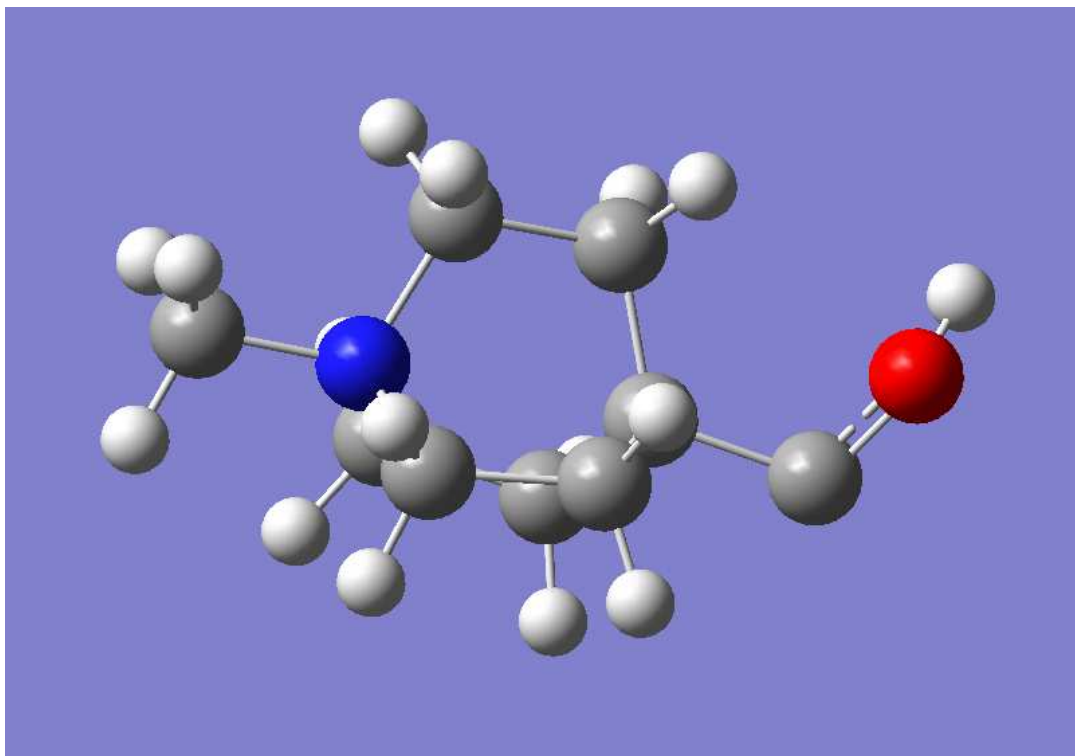
H	-0.05687700	2.65633702	1.46685898
H	-1.49835205	1.84537601	2.07840610
C	-0.01696100	0.47938401	1.20297301
H	1.05659699	0.62801403	1.09973598
H	-0.17949700	-0.08314500	2.12127495
N	-1.46921301	2.11747408	0.00008900
C	-1.99706805	3.51199889	0.00274300
H	-2.62162089	3.65331888	0.88023502
H	-1.16125202	4.20539188	0.02688500
H	-2.58269811	3.66951609	-0.89845800
C	-0.02081200	-1.71972895	0.01111800
O	0.70160699	-2.17411995	-0.82979500
H	-0.34954801	-2.32166696	0.88151598

S48.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	60.31850000	5.43980000	0.00000000
2	110.90750000	0.07180000	0.00000000
3	179.76370000	5.85930000	0.00000000
4	245.07530000	1.59660000	0.00000000
5	259.95300000	0.00040000	0.00000000
6	266.94890000	0.28710000	0.00000000
7	275.61000000	0.30570000	0.00000000
8	340.33400000	5.21660000	0.00000000
9	387.96410000	0.17410000	0.00000000
10	401.77090000	0.32400000	0.00000000
11	421.94760000	0.05590000	0.00000000
12	422.96830000	0.05960000	0.00000000
13	536.97200000	0.04130000	0.00000000
14	538.05460000	0.10250000	0.00000000
15	574.24310000	0.09170000	0.00000000
16	685.65810000	6.03820000	0.00000000
17	736.27790000	21.61910000	0.00000000
18	801.52570000	0.14360000	0.00000000
19	832.98690000	7.53570000	0.00000000
20	838.33280000	9.24920000	0.00000000
21	865.30100000	27.56280000	0.00000000
22	914.82790000	1.10180000	0.00000000
23	930.45970000	4.94510000	0.00000000
24	947.64910000	4.01180000	0.00000000
25	986.08520000	0.05670000	0.00000000
26	1004.24850000	1.89290000	0.00000000
27	1027.13340000	2.31730000	0.00000000
28	1041.81200000	3.70780000	0.00000000
29	1051.42000000	0.48870000	0.00000000
30	1057.99080000	1.85710000	0.00000000
31	1098.88910000	0.02190000	0.00000000
32	1149.90600000	10.17050000	0.00000000
33	1151.33920000	2.70390000	0.00000000
34	1167.97710000	34.18100000	0.00000000
35	1204.18000000	0.30210000	0.00000000
36	1211.85080000	1.53230000	0.00000000
37	1226.70760000	10.43770000	0.00000000
38	1282.73390000	1.33040000	0.00000000
39	1297.00040000	5.99070000	0.00000000
40	1306.02880000	4.21200000	0.00000000
41	1331.85190000	4.22860000	0.00000000
42	1335.65400000	1.81000000	0.00000000
43	1356.77460000	4.12120000	0.00000000
44	1359.35290000	4.06910000	0.00000000
45	1390.78360000	3.67240000	0.00000000
46	1392.09480000	2.00730000	0.00000000
47	1395.59910000	0.52780000	0.00000000
48	1414.16850000	4.96490000	0.00000000
49	1421.95730000	0.89080000	0.00000000
50	1475.27710000	2.13940000	0.00000000
51	1493.53660000	5.07120000	0.00000000
52	1493.64700000	4.55530000	0.00000000
53	1504.92490000	1.14820000	0.00000000
54	1506.58390000	1.00930000	0.00000000
55	1513.65680000	22.64830000	0.00000000
56	1514.65660000	27.31110000	0.00000000
57	1514.91980000	27.57610000	0.00000000
58	1538.42410000	4.15530000	0.00000000
59	1822.08200000	169.73160000	0.00000000
60	2897.56050000	66.07990000	0.00000000

61	3063.19070000	5.60720000	0.00000000
62	3065.01600000	7.70730000	0.00000000
63	3070.30420000	0.15150000	0.00000000
64	3079.84770000	2.89600000	0.00000000
65	3083.25310000	3.27670000	0.00000000
66	3083.93650000	2.40870000	0.00000000
67	3088.06300000	10.12790000	0.00000000
68	3103.14280000	2.07320000	0.00000000
69	3104.33010000	3.92010000	0.00000000
70	3120.07090000	1.07120000	0.00000000
71	3134.98930000	0.11400000	0.00000000
72	3139.46810000	3.90060000	0.00000000
73	3140.11610000	4.20250000	0.00000000
74	3161.08460000	1.04020000	0.00000000
75	3161.44710000	0.92270000	0.00000000

S49. CALCULATIONS ON 11 - H → 11 - H(CIS-ISOMER) (TS)



```

Route : # opt=qst2 freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd
       : 3bj int=ultrafine pop=regular
SMILES : C[N]12CCC(CC1)(CC2)[C]O
Formula : C9H16NO+
Charge : 1
Multiplicity : 1
Energy : -482.42052604 a.u.
Gibbs Energy : -482.21269900 a.u.
Number of imaginary frequencies : 1

```

S49.1. Cartesian Co-ordinates (XYZ format)

27

```

C -0.36112800 0.93564099 -1.24939799
C -1.02466905 0.17271200 -0.09368300
C 1.12769198 0.56843901 -1.30704296
H -0.83444500 0.67907602 -2.19527602
H -0.50090998 2.00475001 -1.10577404
H 1.35181499 -0.15297800 -2.08922100
H 1.76716495 1.43601298 -1.44759703
C -0.62717199 -1.30774295 -0.17116900
H -1.18191397 -1.88853502 0.56195700
H -0.86482900 -1.70511901 -1.15778804
C 0.87812001 -1.43973994 0.10268500
H 1.08929098 -1.80047596 1.10668695
H 1.37835205 -2.09183502 -0.60839301
C 1.06971705 0.78716701 1.14128196

```

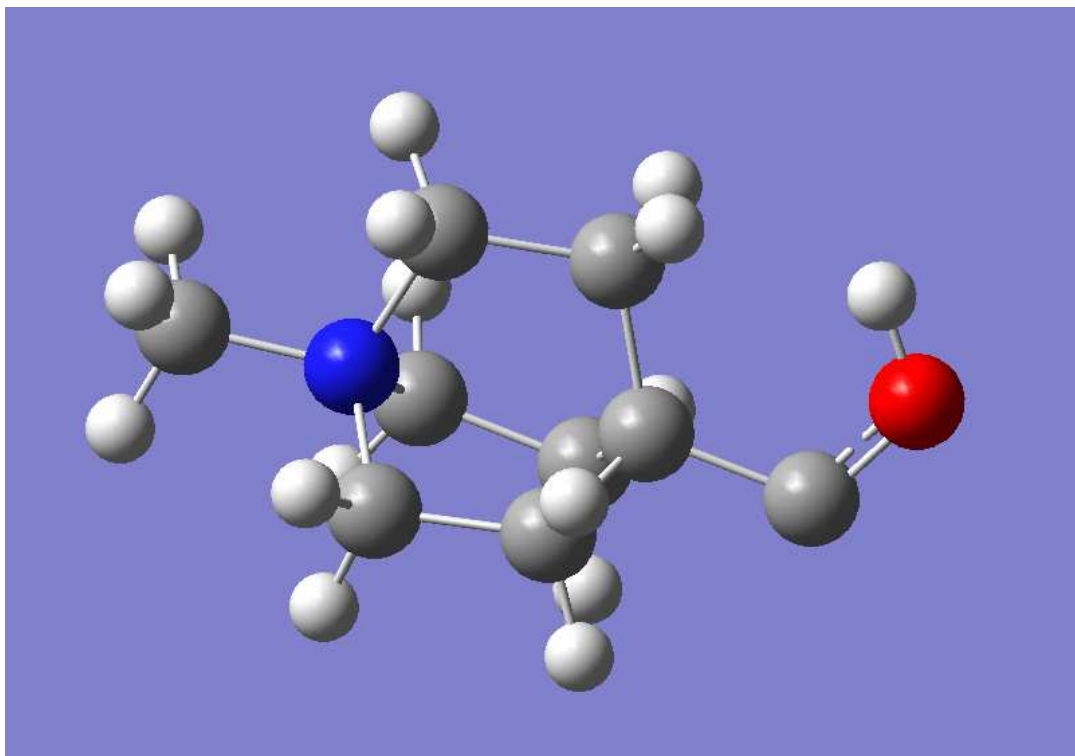
H	1.54517901	0.41442600	2.04487610
H	1.44635797	1.78691995	0.93967402
C	-0.46057299	0.74444199	1.23672700
H	-0.78214800	0.11537700	2.06426096
H	-0.84792900	1.74582696	1.41587496
N	1.54819000	-0.08212600	-0.00316000
C	3.03032899	-0.23177800	0.04690600
H	3.48517299	0.75463301	0.05437700
H	3.30165696	-0.77173901	0.94964302
H	3.35937691	-0.78441697	-0.82852101
C	-2.49656796	0.54115099	-0.02861500
O	-3.20219588	-0.42496699	0.56694800
H	-3.60983801	-1.13422704	0.05612500

S49.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-1111.42510000	177.14160000	0.00000000
2	70.40440000	7.16320000	0.00000000
3	124.42790000	0.15020000	0.00000000
4	184.48910000	2.63340000	0.00000000
5	249.23100000	17.03980000	0.00000000
6	260.86900000	0.02510000	0.00000000
7	270.21750000	1.06340000	0.00000000
8	277.32630000	8.27570000	0.00000000
9	334.22970000	1.10060000	0.00000000
10	375.44850000	10.12100000	0.00000000
11	414.82810000	3.18680000	0.00000000
12	420.96330000	0.04680000	0.00000000
13	423.44800000	0.57240000	0.00000000
14	530.61980000	0.09560000	0.00000000
15	535.01680000	2.44260000	0.00000000
16	568.71200000	2.41550000	0.00000000
17	671.89800000	9.55120000	0.00000000
18	718.51110000	220.77060000	0.00000000
19	724.45940000	45.90070000	0.00000000
20	797.99080000	0.65630000	0.00000000
21	829.09400000	9.31610000	0.00000000
22	836.96470000	8.59870000	0.00000000
23	849.83440000	24.00440000	0.00000000
24	922.25590000	1.55010000	0.00000000
25	926.56530000	3.58330000	0.00000000
26	953.48040000	4.33910000	0.00000000
27	982.59870000	0.41560000	0.00000000
28	1004.86580000	3.16640000	0.00000000
29	1019.15730000	9.99650000	0.00000000
30	1038.61930000	2.72830000	0.00000000
31	1051.12450000	1.07220000	0.00000000
32	1077.54900000	4.64880000	0.00000000
33	1137.97020000	17.76650000	0.00000000
34	1151.48360000	3.52310000	0.00000000
35	1155.85040000	23.60330000	0.00000000
36	1196.67130000	9.53810000	0.00000000
37	1201.52350000	0.64710000	0.00000000
38	1215.69170000	38.21320000	0.00000000
39	1236.04610000	153.44570000	0.00000000
40	1281.58590000	0.63490000	0.00000000
41	1287.16400000	9.19690000	0.00000000
42	1291.71980000	9.14130000	0.00000000
43	1325.50390000	3.35010000	0.00000000
44	1330.29560000	1.58660000	0.00000000
45	1350.83320000	3.80470000	0.00000000
46	1356.14570000	5.07350000	0.00000000
47	1377.10390000	1.70950000	0.00000000
48	1389.04950000	2.44660000	0.00000000
49	1392.20170000	2.32310000	0.00000000
50	1414.16180000	1.78260000	0.00000000
51	1474.38860000	2.08280000	0.00000000
52	1493.37720000	3.31020000	0.00000000
53	1493.79400000	4.44000000	0.00000000
54	1505.63760000	2.06950000	0.00000000
55	1508.40790000	2.47110000	0.00000000
56	1512.98580000	22.72060000	0.00000000
57	1514.44430000	24.89930000	0.00000000
58	1515.05340000	23.45690000	0.00000000
59	1537.78210000	4.96540000	0.00000000
60	3059.22590000	8.95020000	0.00000000

61	3069.60840000	0.42230000	0.00000000
62	3070.64730000	2.36550000	0.00000000
63	3074.42260000	2.98070000	0.00000000
64	3080.83260000	4.29590000	0.00000000
65	3082.35810000	3.87380000	0.00000000
66	3086.30850000	12.14500000	0.00000000
67	3109.55390000	3.27620000	0.00000000
68	3110.64410000	1.86530000	0.00000000
69	3112.22690000	1.54510000	0.00000000
70	3133.03430000	0.29490000	0.00000000
71	3137.15380000	5.38670000	0.00000000
72	3138.87490000	3.91990000	0.00000000
73	3160.42890000	1.17840000	0.00000000
74	3160.80840000	1.06690000	0.00000000
75	3807.15080000	261.32470000	0.00000000

S50. CALCULATIONS ON 11 – H(CIS-ISOMER)



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N]12CCC(CC1)(CC2)[C]O
Formula              : C9H16NO+
Charge               : 1
Multiplicity         : 1
Energy               : -482.45253033
Gibbs Energy         : -482.24219500
Number of imaginary frequencies : 0

```

a.u.
a.u.

S50.1. Cartesian Co-ordinates (XYZ format)

27

```

C -1.97534204 -0.30912301 0.24459000
C -0.43622899 -0.24566600 0.15944199
C -2.55928397 1.07247400 -0.08003200
H -2.36808991 -1.04226005 -0.45757201
H -2.26335311 -0.63724899 1.24030101
H -2.95984101 1.13133204 -1.08934295
H -3.34038997 1.36627102 0.61624700
C -0.05668900 0.43109900 -1.17086995
H 1.02115095 0.40328899 -1.34291506
H -0.53704202 -0.07564900 -2.00812411
C -0.49251699 1.90364802 -1.12846005
H 0.34007600 2.57770109 -0.94289702
H -0.98949701 2.21635890 -2.04285312
C -0.74263000 1.95992899 1.32151306

```

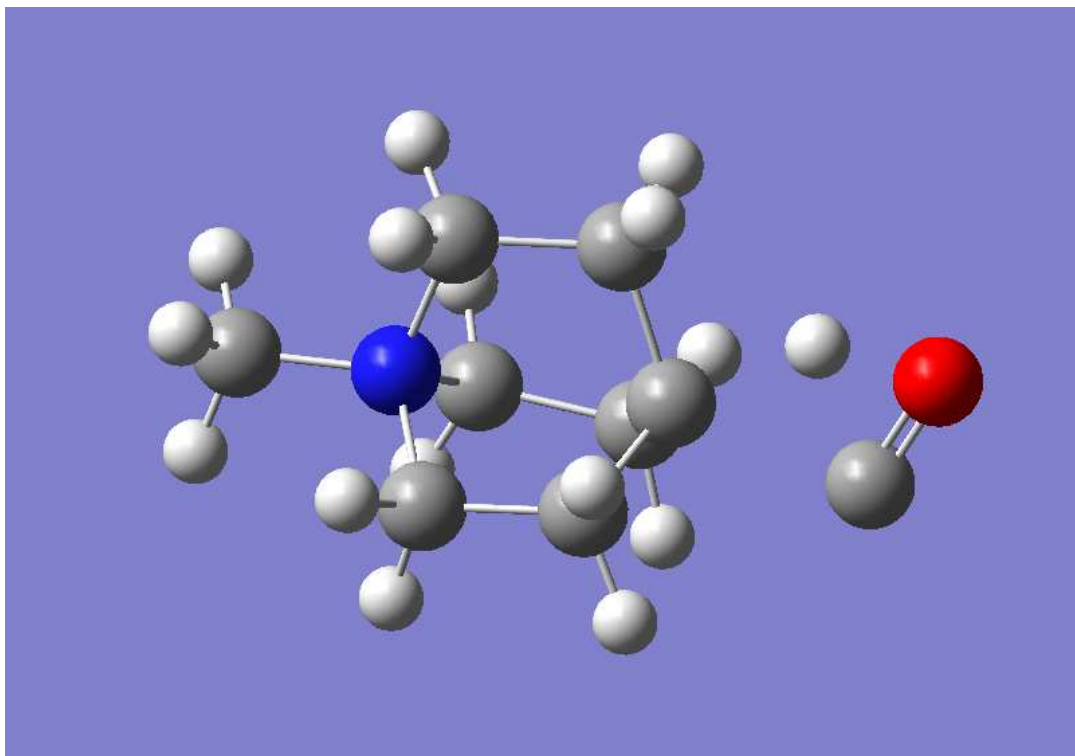
H	-0.10892800	2.83409905	1.44523597
H	-1.50698805	1.97680795	2.09467506
C	0.05768600	0.65135598	1.31414199
H	1.12115896	0.85462397	1.19552505
H	-0.06733600	0.13013101	2.26031399
N	-1.47415602	2.12645507	0.00450300
C	-2.06847596	3.49074602	-0.08892700
H	-2.70223808	3.65895700	0.77698600
H	-1.26806903	4.22494602	-0.11013400
H	-2.65853596	3.55843592	-0.99853301
C	0.06301400	-1.65359998	0.45642701
O	0.85753602	-2.15454006	-0.42970899
H	1.07094800	-1.59278703	-1.20829296

S50.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	54.29670000	5.73420000	0.00000000
2	118.52690000	0.09340000	0.00000000
3	192.23970000	5.39020000	0.00000000
4	256.11070000	8.34960000	0.00000000
5	260.13300000	0.07950000	0.00000000
6	267.92870000	0.45440000	0.00000000
7	285.53680000	17.50290000	0.00000000
8	341.62010000	1.87280000	0.00000000
9	389.62850000	26.58740000	0.00000000
10	406.20450000	2.96350000	0.00000000
11	421.66320000	0.46990000	0.00000000
12	423.70480000	0.03110000	0.00000000
13	529.91700000	0.19780000	0.00000000
14	537.96550000	0.30380000	0.00000000
15	568.07770000	6.57540000	0.00000000
16	661.26810000	1.92710000	0.00000000
17	711.16250000	0.90590000	0.00000000
18	797.92670000	19.57810000	0.00000000
19	800.28470000	20.57140000	0.00000000
20	835.50880000	6.75730000	0.00000000
21	839.13710000	22.27890000	0.00000000
22	848.35490000	19.16140000	0.00000000
23	928.41370000	4.02990000	0.00000000
24	932.39590000	7.61150000	0.00000000
25	978.96620000	0.20720000	0.00000000
26	988.03600000	0.14790000	0.00000000
27	999.93890000	1.52980000	0.00000000
28	1018.10920000	1.41720000	0.00000000
29	1043.21630000	2.97410000	0.00000000
30	1045.08860000	3.72020000	0.00000000
31	1077.69860000	0.22100000	0.00000000
32	1144.22920000	22.07290000	0.00000000
33	1148.74340000	2.64810000	0.00000000
34	1152.22480000	2.18310000	0.00000000
35	1201.21240000	0.38190000	0.00000000
36	1208.62530000	0.18160000	0.00000000
37	1212.53090000	1.76840000	0.00000000
38	1282.35180000	13.94270000	0.00000000
39	1293.02290000	17.36280000	0.00000000
40	1294.06600000	38.44370000	0.00000000
41	1315.57780000	166.69520000	0.00000000
42	1324.86550000	4.15520000	0.00000000
43	1333.12670000	2.16150000	0.00000000
44	1353.66420000	4.39810000	0.00000000
45	1358.71380000	7.22060000	0.00000000
46	1380.27480000	30.85690000	0.00000000
47	1385.83160000	59.58570000	0.00000000
48	1390.57510000	2.91180000	0.00000000
49	1394.36990000	7.37520000	0.00000000
50	1416.42760000	0.46050000	0.00000000
51	1474.72880000	1.70480000	0.00000000
52	1493.05970000	2.72660000	0.00000000
53	1494.25560000	5.23270000	0.00000000
54	1505.92760000	1.99090000	0.00000000
55	1508.36130000	2.63430000	0.00000000
56	1512.97620000	25.52390000	0.00000000
57	1514.95900000	24.56660000	0.00000000
58	1515.86010000	17.32170000	0.00000000
59	1538.62600000	6.18070000	0.00000000
60	3036.16580000	9.10160000	0.00000000

61	3067.06260000	5.35380000	0.00000000
62	3070.05280000	0.06540000	0.00000000
63	3075.51180000	2.10340000	0.00000000
64	3078.03120000	4.13120000	0.00000000
65	3082.75960000	4.18180000	0.00000000
66	3083.53030000	4.63850000	0.00000000
67	3087.41490000	11.67010000	0.00000000
68	3113.66050000	1.33820000	0.00000000
69	3115.38960000	0.77620000	0.00000000
70	3133.90080000	0.21020000	0.00000000
71	3138.01350000	4.15480000	0.00000000
72	3139.31360000	3.56250000	0.00000000
73	3160.41610000	1.07720000	0.00000000
74	3161.72960000	0.84930000	0.00000000
75	3414.19630000	36.82780000	0.00000000

S51. CALCULATIONS ON 11 – H(CIS-ISOMER) → 1 – methyl – 1λ⁴ – azabicyclo[2.2.2]octane (TS)



```

Route : # opt=(calcfc,qst3) freq b3lyp/cc-pvtz geom=connectivity empiricaldisp
       : ersion=gd3bj int=ultrafine pop=regular
SMILES : C[N]12CC[C](CC1)CC2.[C]O
Formula : C9H16NO+
Charge : 1
Multiplicity : 1
Energy : -482.36364287 a.u.
Gibbs Energy : -482.16111100 a.u.
Number of imaginary frequencies : 1

```

S51.1. Cartesian Co-ordinates (XYZ format)

27

```

C -0.43548399 0.86473298 -1.20560098
C -1.02800906 0.14510299 -0.00073400
C 1.07524204 0.57286298 -1.28365898
H -0.91065001 0.54029799 -2.13056493
H -0.61186802 1.93497896 -1.11443305
H 1.32855797 -0.11576200 -2.08635712
H 1.67194796 1.47355604 -1.40268195
C -0.62802202 -1.35135603 -0.09069200
H -1.11732900 -1.95728004 0.67356402
H -0.90521002 -1.76432598 -1.06008506
C 0.89943701 -1.45719600 0.10760600
H 1.16137505 -1.83836496 1.09141397
H 1.36906803 -2.08636189 -0.64420098
C 1.08913004 0.75657398 1.17634404

```

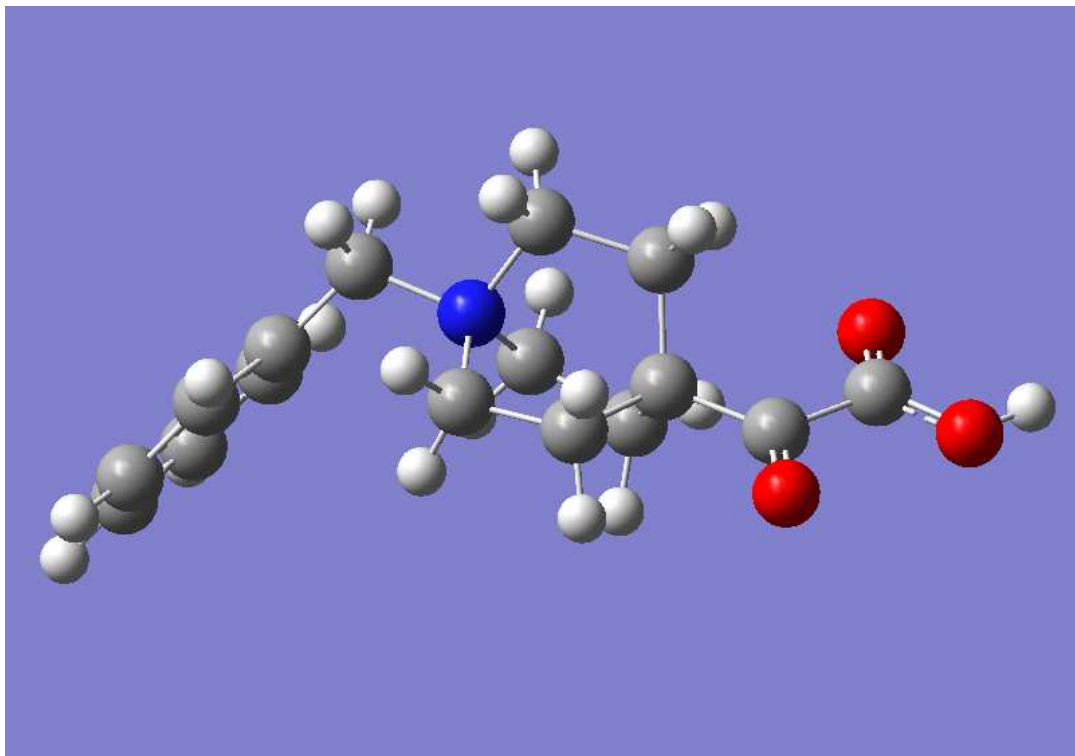
H	1.58310997	0.35681501	2.05825710
H	1.47222900	1.75704205	0.99020398
C	-0.44610199	0.72098601	1.28425801
H	-0.74755502	0.12095900	2.14252400
H	-0.82029599	1.73033094	1.44976902
N	1.54006195	-0.08951000	-0.00004800
C	3.02522612	-0.22001199	0.00091600
H	3.46579504	0.77281201	-0.00208800
H	3.33320498	-0.75869203	0.89256501
H	3.33400607	-0.76468402	-0.88678998
C	-2.85918093	0.88120103	0.01987700
O	-3.55251002	-0.15682600	0.02202700
H	-2.43435407	-0.46283901	0.00281300

S51.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2257.58760000	343.18610000	0.00000000
2	86.99150000	0.15020000	0.00000000
3	91.90580000	0.30350000	0.00000000
4	130.28850000	4.78600000	0.00000000
5	170.84770000	4.38710000	0.00000000
6	252.11340000	49.08060000	0.00000000
7	258.27470000	0.28650000	0.00000000
8	264.98000000	0.16980000	0.00000000
9	267.81350000	1.64340000	0.00000000
10	344.18740000	0.64350000	0.00000000
11	348.81690000	0.79670000	0.00000000
12	421.11240000	0.01520000	0.00000000
13	422.10750000	0.24290000	0.00000000
14	530.92380000	8.20810000	0.00000000
15	538.04090000	3.54620000	0.00000000
16	540.72170000	94.22050000	0.00000000
17	583.16380000	44.48180000	0.00000000
18	694.03280000	3.87660000	0.00000000
19	787.57510000	70.53740000	0.00000000
20	800.46160000	0.02410000	0.00000000
21	832.12860000	5.57030000	0.00000000
22	834.46710000	8.69100000	0.00000000
23	864.06410000	10.48120000	0.00000000
24	925.05640000	6.11000000	0.00000000
25	929.25110000	8.06770000	0.00000000
26	935.02630000	1.90610000	0.00000000
27	980.36330000	27.16440000	0.00000000
28	984.05720000	2.27930000	0.00000000
29	1011.28600000	1.15600000	0.00000000
30	1012.68730000	0.45420000	0.00000000
31	1035.10220000	1.84240000	0.00000000
32	1050.23450000	3.61960000	0.00000000
33	1129.81860000	26.83850000	0.00000000
34	1147.77540000	4.11930000	0.00000000
35	1154.49140000	0.10090000	0.00000000
36	1199.66180000	12.41100000	0.00000000
37	1207.24620000	0.18960000	0.00000000
38	1215.82910000	0.62590000	0.00000000
39	1282.09860000	1.39670000	0.00000000
40	1299.01070000	7.45500000	0.00000000
41	1307.73700000	7.67710000	0.00000000
42	1330.54150000	2.93180000	0.00000000
43	1332.91370000	1.35230000	0.00000000
44	1354.42740000	5.93790000	0.00000000
45	1355.18800000	5.74990000	0.00000000
46	1372.84670000	0.12540000	0.00000000
47	1385.94060000	7.79140000	0.00000000
48	1388.85770000	2.10900000	0.00000000
49	1410.61170000	15.57160000	0.00000000
50	1473.49670000	12.06010000	0.00000000
51	1491.04130000	2.71440000	0.00000000
52	1492.14240000	3.90480000	0.00000000
53	1499.02410000	162.91560000	0.00000000
54	1503.79470000	15.34430000	0.00000000
55	1505.87800000	162.81130000	0.00000000
56	1511.49610000	8.59350000	0.00000000
57	1512.63400000	59.02280000	0.00000000
58	1513.35990000	27.46210000	0.00000000
59	1533.67120000	5.00820000	0.00000000
60	2189.61430000	101.50570000	0.00000000

61	3044.46890000	7.30000000	0.00000000
62	3056.06760000	7.50710000	0.00000000
63	3062.46170000	4.70950000	0.00000000
64	3069.96480000	0.00850000	0.00000000
65	3079.80230000	3.78570000	0.00000000
66	3080.52260000	3.23690000	0.00000000
67	3084.87130000	14.93070000	0.00000000
68	3086.44010000	5.23090000	0.00000000
69	3095.74450000	3.75330000	0.00000000
70	3101.61470000	2.64060000	0.00000000
71	3131.76650000	0.65580000	0.00000000
72	3136.26090000	4.83370000	0.00000000
73	3137.37040000	4.25010000	0.00000000
74	3160.37320000	1.25120000	0.00000000
75	3161.35310000	0.95760000	0.00000000

S52. CALCULATIONS ON 13 – H



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : c1ccc(cc1)C[N+]23CCC(CC2)(CC3)C(=O)C(=O)O
Formula              : C16H20NO3+
Charge               : 1
Multiplicity         : 1
Energy                : -902.35097539 a.u.
Gibbs Energy         : -902.05386700 a.u.
Number of imaginary frequencies : 0

```

S52.1. Cartesian Co-ordinates (XYZ format)

40

```

C -1.94673896 -0.38259301 0.06057700
C -0.41795000 -0.25566599 0.03409100
C -2.57587695 0.98585802 -0.23272599
H -2.27923703 -1.10623300 -0.67871302
H -2.26935601 -0.75782502 1.03003800
H -2.93337202 1.07296598 -1.25354195
H -3.40288711 1.20770895 0.43552101
C -0.03149100 0.50314498 -1.25246704
H 1.04358602 0.49376199 -1.39967501
H -0.49388200 0.01926100 -2.11177707
C -0.51043499 1.95714498 -1.13537705
H 0.29614100 2.63429999 -0.86350399
H -0.96671498 2.31128597 -2.05288911
C -0.86910999 1.86277902 1.28884697

```

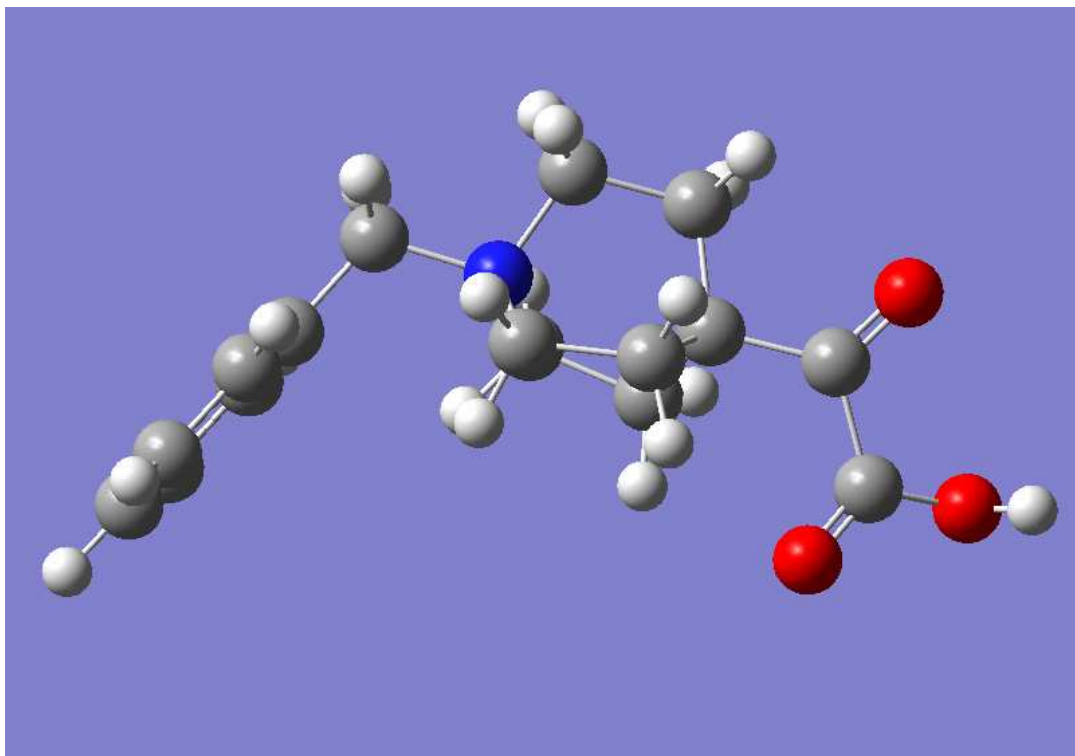
H	-0.28726700	2.75569201	1.50072706
H	-1.66474998	1.78884399	2.02620196
C	0.00985400	0.60436702	1.24315405
H	1.05932105	0.86696899	1.15714002
H	-0.11664400	0.04950400	2.17154789
N	-1.54850101	2.07935309	-0.04460100
C	-2.19394398	3.46775889	-0.04297900
H	-2.81764102	3.48913908	0.84811503
H	-1.36998796	4.16390991	0.09682700
C	0.21037900	-1.64570296	0.08351100
O	-0.44614801	-2.64929199	0.09460900
C	1.75693095	-1.72072601	0.12111700
O	2.46388006	-0.74461699	0.07157800
O	2.17857790	-2.97404599	0.20981300
H	3.14905000	-2.97263193	0.22635899
C	-2.98376799	3.80323100	-1.26986003
C	-4.34520483	3.50516605	-1.34115303
C	-2.37539697	4.45728683	-2.34241700
C	-5.07679081	3.82500196	-2.47591901
H	-4.84275198	3.03835797	-0.50127500
C	-3.10632896	4.77828407	-3.47779608
H	-1.33153903	4.73734617	-2.28345490
C	-4.45619011	4.45561314	-3.54810309
H	-6.13166380	3.59464192	-2.51863408
H	-2.62683010	5.29041290	-4.29963923
H	-5.02750301	4.71034098	-4.42932796

S52.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	24.34090000	1.85710000	0.00000000
2	32.35800000	1.05090000	0.00000000
3	55.83960000	1.25620000	0.00000000
4	69.17250000	0.46510000	0.00000000
5	75.07410000	0.36240000	0.00000000
6	119.48650000	0.79400000	0.00000000
7	130.72590000	1.94710000	0.00000000
8	141.85650000	1.87890000	0.00000000
9	205.85350000	2.97330000	0.00000000
10	225.57770000	3.13940000	0.00000000
11	241.89170000	0.88550000	0.00000000
12	264.18640000	7.68760000	0.00000000
13	314.02980000	0.18590000	0.00000000
14	326.96490000	5.58490000	0.00000000
15	339.74370000	2.32780000	0.00000000
16	367.60860000	2.00780000	0.00000000
17	399.49190000	0.03610000	0.00000000
18	412.41730000	0.28010000	0.00000000
19	418.56980000	0.01680000	0.00000000
20	424.63570000	0.00540000	0.00000000
21	467.15770000	3.73110000	0.00000000
22	472.70070000	4.50470000	0.00000000
23	539.99100000	0.24590000	0.00000000
24	544.21450000	0.24160000	0.00000000
25	572.20540000	7.89940000	0.00000000
26	599.48480000	2.25570000	0.00000000
27	633.84800000	7.26500000	0.00000000
28	639.08160000	0.09710000	0.00000000
29	665.45030000	111.99950000	0.00000000
30	678.34890000	123.74290000	0.00000000
31	708.64740000	17.03740000	0.00000000
32	724.21240000	44.24520000	0.00000000
33	786.38900000	35.92310000	0.00000000
34	800.06180000	0.80220000	0.00000000
35	814.54940000	10.18850000	0.00000000
36	836.17430000	7.91370000	0.00000000
37	841.68330000	2.58990000	0.00000000
38	845.51330000	21.35320000	0.00000000
39	855.15080000	2.34020000	0.00000000
40	869.32580000	0.09160000	0.00000000
41	901.03350000	48.97740000	0.00000000
42	910.80870000	40.18440000	0.00000000
43	954.81880000	1.21160000	0.00000000
44	984.98050000	2.41040000	0.00000000
45	994.41300000	1.29390000	0.00000000
46	999.79800000	2.11560000	0.00000000
47	1005.98860000	0.07230000	0.00000000
48	1012.55770000	4.57350000	0.00000000
49	1018.92510000	2.74090000	0.00000000
50	1028.35680000	3.45870000	0.00000000
51	1035.87080000	3.31410000	0.00000000
52	1037.07090000	13.26000000	0.00000000
53	1053.01450000	3.11280000	0.00000000
54	1056.74360000	2.22420000	0.00000000
55	1060.91410000	5.72580000	0.00000000
56	1073.14220000	4.63230000	0.00000000
57	1122.19360000	5.10710000	0.00000000
58	1151.62210000	301.51370000	0.00000000
59	1188.25660000	3.59150000	0.00000000
60	1195.52180000	16.18450000	0.00000000

61	1197.19240000	20.35600000	0.00000000
62	1207.85840000	0.14380000	0.00000000
63	1214.72360000	0.53010000	0.00000000
64	1223.07460000	2.16040000	0.00000000
65	1240.75130000	16.02950000	0.00000000
66	1257.94600000	2.32190000	0.00000000
67	1285.85800000	0.07100000	0.00000000
68	1297.91890000	5.40630000	0.00000000
69	1302.93970000	4.86770000	0.00000000
70	1328.92080000	4.60410000	0.00000000
71	1336.93270000	3.51440000	0.00000000
72	1347.61800000	1.28770000	0.00000000
73	1352.47530000	6.35650000	0.00000000
74	1362.69610000	6.23920000	0.00000000
75	1371.04200000	9.03090000	0.00000000
76	1377.10170000	0.61450000	0.00000000
77	1394.47260000	3.47950000	0.00000000
78	1396.40760000	34.92770000	0.00000000
79	1404.44580000	9.32420000	0.00000000
80	1405.89230000	9.04300000	0.00000000
81	1438.20200000	10.87670000	0.00000000
82	1493.77250000	4.04810000	0.00000000
83	1497.02150000	7.10170000	0.00000000
84	1503.24010000	7.21290000	0.00000000
85	1507.06350000	5.61750000	0.00000000
86	1514.02020000	4.71990000	0.00000000
87	1516.14600000	16.27720000	0.00000000
88	1519.30950000	16.71200000	0.00000000
89	1538.32110000	3.37510000	0.00000000
90	1542.32140000	5.38680000	0.00000000
91	1630.74690000	2.42270000	0.00000000
92	1647.95630000	2.85740000	0.00000000
93	1791.48640000	240.94030000	0.00000000
94	1808.70280000	147.42320000	0.00000000
95	3069.13780000	7.69960000	0.00000000
96	3073.13440000	7.26230000	0.00000000
97	3075.53490000	2.11030000	0.00000000
98	3077.52540000	4.51650000	0.00000000
99	3084.41780000	5.72360000	0.00000000
100	3086.99480000	7.23110000	0.00000000
101	3097.38960000	7.12460000	0.00000000
102	3121.58270000	1.87240000	0.00000000
103	3124.52030000	0.01670000	0.00000000
104	3129.35430000	1.69760000	0.00000000
105	3137.73280000	0.64770000	0.00000000
106	3144.20070000	2.34130000	0.00000000
107	3151.64900000	2.15010000	0.00000000
108	3155.59830000	3.51140000	0.00000000
109	3166.82570000	5.94850000	0.00000000
110	3169.62110000	6.23020000	0.00000000
111	3188.09690000	0.95780000	0.00000000
112	3197.66770000	4.44200000	0.00000000
113	3206.80620000	1.70860000	0.00000000
114	3723.76830000	142.07190000	0.00000000

S53. CALCULATIONS ON 11 - H → 11 - H (CIS-ISOMER) (TS)



Route : # opt=(calcf,ts,noeigen) freq b3lyp/cc-pvtz geom=connectivity empiric
 : aldispersion=gd3bj int=ultrafine pop=regular
 SMILES : c1ccc(cc1)C[N+]23CCC(CC2)(CC3)C(=O)C(=O)O
 Formula : C₁₆H₂₀NO₃⁺
 Charge : 1
 Multiplicity : 1
 Energy : -902.33246356 a.u.
 Gibbs Energy : -902.03714100 a.u.
 Number of imaginary frequencies : 1

S53.1. Cartesian Co-ordinates (XYZ format)

40

```

C -0.54934001 1.60637498 -0.25320899
C 0.31784600 0.37133700 0.02462300
C -2.02273703 1.24323905 -0.03445100
H -0.26436499 2.42157698 0.40588200
H -0.38492700 1.95159698 -1.27291095
H -2.39882493 1.59363306 0.92378998
H -2.66493702 1.63700902 -0.81738299
C -0.13093600 -0.22801000 1.37598097
H 0.54773498 -1.01558495 1.68831301
H -0.11640000 0.55005097 2.13768101
C -1.54478097 -0.80812901 1.21864700
H -1.54098797 -1.88837099 1.11698794
H -2.18680811 -0.54681098 2.05486488
C -1.48210394 -0.82677400 -1.23508096

```

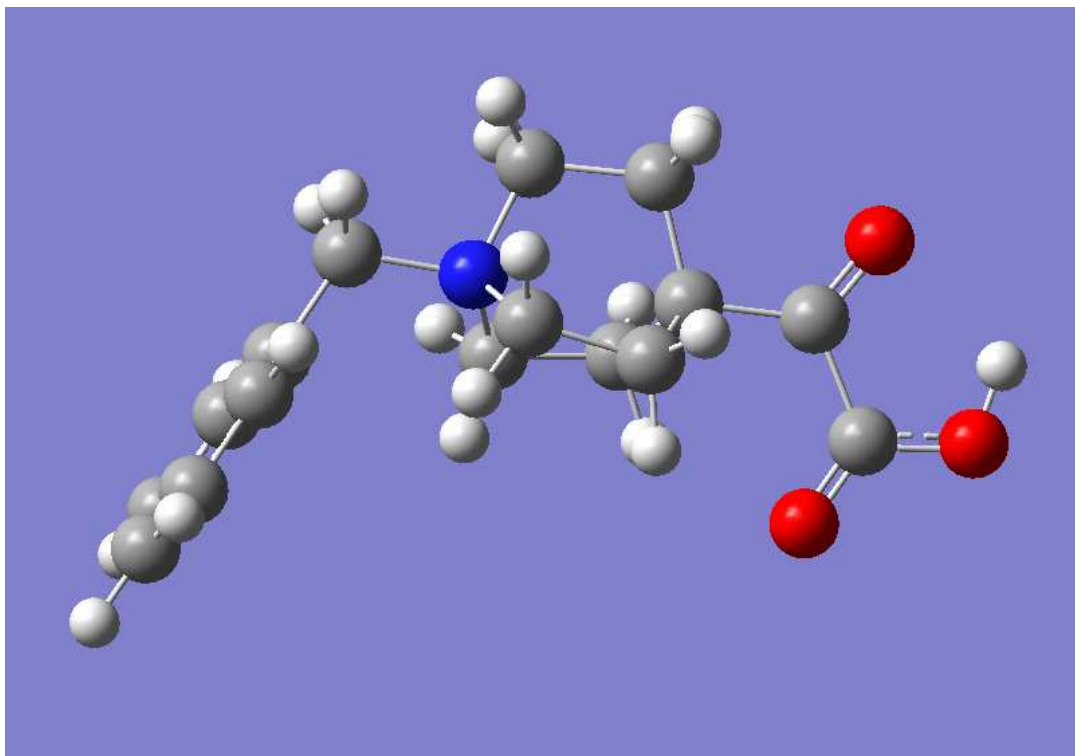
H -1.77817500 -1.86605501 -1.32327199
H -1.86362898 -0.28269300 -2.09600997
C 0.03745000 -0.67474198 -1.07013798
H 0.48855001 -1.62599599 -0.80180800
H 0.46791399 -0.36457399 -2.02142596
N -2.19648290 -0.26071301 -0.03019700
C -3.69360590 -0.58034199 -0.07083300
H -4.05053377 -0.14595900 -1.00203395
H -4.12468910 -0.02158300 0.75704497
C 1.78784096 0.77047199 0.08342200
O 2.14873290 1.90513504 0.25092301
C 2.84686089 -0.35097200 0.01644300
O 2.63337302 -1.43338501 0.48236299
O 3.97490811 0.00132300 -0.63098699
H 4.66766500 0.36030200 -0.06237500
C -4.03633022 -2.03519511 0.01537800
C -4.18238211 -2.79506898 -1.14629400
C -4.25451422 -2.64043593 1.25373101
C -4.50802517 -4.14210701 -1.07035100
H -4.06311703 -2.32930303 -2.11603189
C -4.57961607 -3.98710203 1.33091795
H -4.18943405 -2.05587292 2.16201901
C -4.69962788 -4.74075794 0.16903800
H -4.62459803 -4.71958017 -1.97618699
H -4.75160408 -4.44473124 2.29456997
H -4.95863008 -5.78820801 0.22893000

S53.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-640.23900000	118.40880000	0.00000000
2	31.14130000	0.09560000	0.00000000
3	43.75620000	4.72820000	0.00000000
4	49.77470000	0.14840000	0.00000000
5	57.64980000	0.08850000	0.00000000
6	82.46360000	3.14320000	0.00000000
7	115.53520000	0.49180000	0.00000000
8	130.57940000	1.52770000	0.00000000
9	141.08050000	2.49560000	0.00000000
10	198.01540000	13.51150000	0.00000000
11	225.69000000	0.20340000	0.00000000
12	232.90970000	0.12230000	0.00000000
13	260.09050000	7.69130000	0.00000000
14	297.55320000	0.86790000	0.00000000
15	321.65660000	0.13360000	0.00000000
16	348.24460000	9.83520000	0.00000000
17	366.23240000	1.02680000	0.00000000
18	375.63240000	2.04100000	0.00000000
19	405.84350000	1.17780000	0.00000000
20	418.56260000	0.03650000	0.00000000
21	423.07030000	0.05050000	0.00000000
22	441.86180000	3.75290000	0.00000000
23	479.55620000	1.05530000	0.00000000
24	539.39160000	0.66300000	0.00000000
25	542.91370000	0.12530000	0.00000000
26	586.92770000	7.24350000	0.00000000
27	633.13930000	38.61630000	0.00000000
28	639.08500000	0.14230000	0.00000000
29	645.39500000	14.68490000	0.00000000
30	697.22090000	12.29770000	0.00000000
31	724.49740000	42.45430000	0.00000000
32	737.35880000	32.39010000	0.00000000
33	778.32620000	37.10950000	0.00000000
34	786.47670000	30.15740000	0.00000000
35	801.31160000	1.98710000	0.00000000
36	833.91800000	7.19620000	0.00000000
37	841.16720000	20.98870000	0.00000000
38	845.35730000	13.71720000	0.00000000
39	855.83820000	2.21060000	0.00000000
40	869.29170000	0.11710000	0.00000000
41	903.06170000	85.02810000	0.00000000
42	905.97580000	2.67810000	0.00000000
43	954.75470000	1.69360000	0.00000000
44	988.06660000	25.96000000	0.00000000
45	991.92700000	12.26730000	0.00000000
46	999.35350000	0.13560000	0.00000000
47	1004.07550000	10.59710000	0.00000000
48	1006.07640000	0.05060000	0.00000000
49	1017.45190000	3.12100000	0.00000000
50	1028.39210000	5.35900000	0.00000000
51	1033.49020000	38.05260000	0.00000000
52	1036.48030000	3.27510000	0.00000000
53	1052.61770000	19.43010000	0.00000000
54	1056.29910000	2.24970000	0.00000000
55	1061.93300000	3.48060000	0.00000000
56	1067.51800000	109.68290000	0.00000000
57	1072.43390000	125.08920000	0.00000000
58	1122.10820000	5.98600000	0.00000000
59	1158.17870000	123.57270000	0.00000000
60	1185.40020000	3.71790000	0.00000000

61	1196.47120000	0.04380000	0.00000000
62	1207.70120000	0.84730000	0.00000000
63	1208.86770000	23.94570000	0.00000000
64	1214.69590000	1.98080000	0.00000000
65	1240.47630000	17.72460000	0.00000000
66	1255.27080000	0.74180000	0.00000000
67	1284.43280000	2.68420000	0.00000000
68	1290.53340000	17.72690000	0.00000000
69	1305.19200000	9.40840000	0.00000000
70	1306.45300000	19.02210000	0.00000000
71	1331.03640000	1.74260000	0.00000000
72	1337.47110000	1.76000000	0.00000000
73	1348.63210000	1.84330000	0.00000000
74	1351.04610000	9.45660000	0.00000000
75	1364.80420000	5.60100000	0.00000000
76	1368.19460000	8.40090000	0.00000000
77	1377.53950000	0.39630000	0.00000000
78	1396.36720000	0.87330000	0.00000000
79	1402.76670000	11.89930000	0.00000000
80	1406.82020000	10.65350000	0.00000000
81	1438.06530000	10.33570000	0.00000000
82	1493.24880000	4.73170000	0.00000000
83	1497.10870000	8.01570000	0.00000000
84	1504.63330000	1.96320000	0.00000000
85	1508.91790000	1.72370000	0.00000000
86	1513.03460000	18.52480000	0.00000000
87	1517.79280000	15.96400000	0.00000000
88	1518.55170000	13.27910000	0.00000000
89	1538.28810000	3.29360000	0.00000000
90	1542.51130000	4.40040000	0.00000000
91	1630.80170000	2.43800000	0.00000000
92	1647.86000000	2.87830000	0.00000000
93	1792.99660000	49.66210000	0.00000000
94	1812.51240000	290.73620000	0.00000000
95	3069.61320000	3.95240000	0.00000000
96	3071.93420000	7.22510000	0.00000000
97	3072.31640000	8.46850000	0.00000000
98	3074.99650000	2.53710000	0.00000000
99	3084.08050000	6.42230000	0.00000000
100	3087.59280000	5.90030000	0.00000000
101	3097.03890000	6.43340000	0.00000000
102	3121.92250000	1.77150000	0.00000000
103	3122.13220000	1.29270000	0.00000000
104	3127.76590000	0.62130000	0.00000000
105	3133.22480000	1.66680000	0.00000000
106	3139.09390000	4.31720000	0.00000000
107	3152.83370000	1.39250000	0.00000000
108	3155.65920000	1.76260000	0.00000000
109	3166.76100000	5.94470000	0.00000000
110	3169.65830000	6.37340000	0.00000000
111	3188.28950000	0.93540000	0.00000000
112	3197.81330000	4.38280000	0.00000000
113	3206.96880000	1.60220000	0.00000000
114	3795.61700000	230.14930000	0.00000000

S54. CALCULATIONS ON 13 – H(CIS-ISOMER)



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : c1ccc(cc1)C[N+]23CCC(CC2)(CC3)C(=O)C(=O)O
Formula              : C16H20NO3+
Charge               : 1
Multiplicity         : 1
Energy               : -902.35265575 a.u.
Gibbs Energy        : -902.05435900 a.u.
Number of imaginary frequencies : 0

```

S54.1. Cartesian Co-ordinates (XYZ format)

40

```

C -2.09077692 -0.28396299 -0.14576800
C -0.56623900 -0.38856900 -0.01039200
C -2.51582694 1.16616702 0.11748000
H -2.39774203 -0.60311103 -1.13999999
H -2.58339906 -0.94649202 0.56125098
H -3.25601292 1.51372504 -0.59785700
H -2.91768909 1.30502605 1.11826801
C 0.07578500 0.39503399 -1.17695999
H 1.14425600 0.48891500 -1.01119399
H -0.06651700 -0.13331200 -2.11834192
C -0.59092301 1.77552104 -1.27269995
H 0.13720401 2.56375289 -1.42786598
H -1.33315206 1.82627404 -2.06603694
C -0.39900199 1.81343102 1.17257404

```

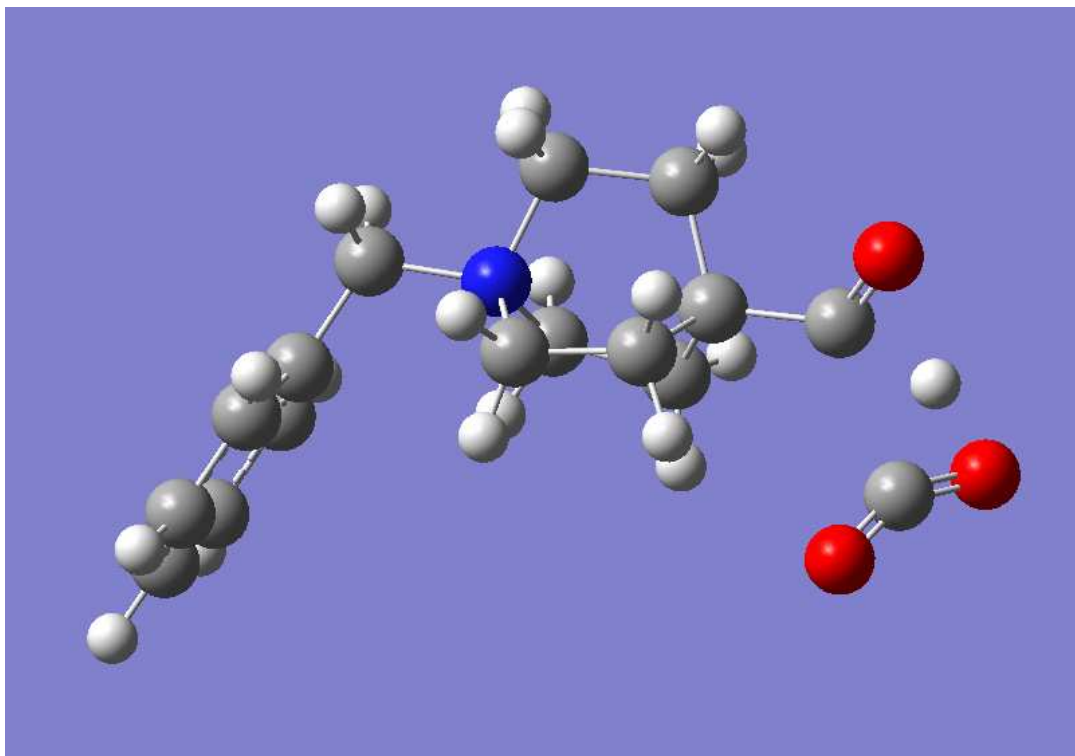
H	0.51534402	2.36442089	0.97868699
H	-0.86657703	2.22993398	2.05987501
C	-0.15490800	0.30301499	1.30743504
H	0.89470398	0.12909400	1.52088499
H	-0.73976099	-0.10616800	2.13019991
N	-1.32337403	2.09123492	0.00948000
C	-1.82436204	3.53923392	0.02160900
H	-2.44235206	3.61689711	0.91353798
H	-2.46761799	3.62300205	-0.85155499
C	-0.13428700	-1.84148395	-0.02991100
O	-0.91359001	-2.75885296	-0.11898300
C	1.37841702	-2.16953301	0.05957100
O	2.22295499	-1.31996703	0.15309800
O	1.62858605	-3.46835804	0.02243600
H	0.78344500	-3.94667697	-0.05525600
C	-0.75166398	4.58314323	0.00765300
C	-0.22973400	5.07971478	1.20283794
C	-0.28856200	5.10197496	-1.20260501
C	0.75974703	6.05223322	1.18780994
H	-0.60886800	4.72100401	2.15075397
C	0.70073497	6.07524776	-1.21878600
H	-0.71650898	4.76135015	-2.13662601
C	1.23079598	6.54566813	-0.02339200
H	1.15362000	6.43357515	2.11895609
H	1.04778504	6.47437000	-2.16102791
H	1.99737501	7.30725193	-0.03488800

S54.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	32.31620000	0.02260000	0.00000000
2	50.96320000	0.42110000	0.00000000
3	63.10240000	0.17560000	0.00000000
4	69.03940000	0.17400000	0.00000000
5	90.04110000	3.24560000	0.00000000
6	114.53620000	1.37990000	0.00000000
7	130.48740000	0.50140000	0.00000000
8	152.21850000	5.46370000	0.00000000
9	204.01270000	14.21400000	0.00000000
10	227.18730000	0.43770000	0.00000000
11	235.27870000	0.01100000	0.00000000
12	264.40140000	16.97650000	0.00000000
13	312.67130000	1.10000000	0.00000000
14	321.90800000	5.85320000	0.00000000
15	352.21320000	7.34980000	0.00000000
16	370.79040000	2.71320000	0.00000000
17	385.27390000	8.05030000	0.00000000
18	418.50420000	0.01860000	0.00000000
19	423.16780000	0.13370000	0.00000000
20	424.69850000	4.36620000	0.00000000
21	472.68630000	3.72850000	0.00000000
22	492.31590000	18.05480000	0.00000000
23	539.75230000	1.35080000	0.00000000
24	542.85470000	0.24040000	0.00000000
25	580.32680000	13.89580000	0.00000000
26	595.31030000	5.69850000	0.00000000
27	639.06020000	0.16010000	0.00000000
28	642.09380000	1.17410000	0.00000000
29	693.70530000	13.56670000	0.00000000
30	695.67400000	83.84460000	0.00000000
31	723.87040000	2.72310000	0.00000000
32	724.54730000	47.45500000	0.00000000
33	786.31430000	37.19090000	0.00000000
34	800.27130000	1.75720000	0.00000000
35	818.36930000	0.22400000	0.00000000
36	834.46750000	4.93660000	0.00000000
37	843.76980000	12.16080000	0.00000000
38	844.58000000	15.22990000	0.00000000
39	855.72710000	2.61720000	0.00000000
40	869.37580000	0.15560000	0.00000000
41	906.83240000	16.61160000	0.00000000
42	908.90040000	73.52530000	0.00000000
43	955.05620000	1.54800000	0.00000000
44	991.17040000	1.83660000	0.00000000
45	995.83100000	3.77160000	0.00000000
46	1000.24160000	1.63020000	0.00000000
47	1006.25700000	0.02600000	0.00000000
48	1006.59520000	8.91370000	0.00000000
49	1017.40860000	1.78380000	0.00000000
50	1028.39730000	4.15130000	0.00000000
51	1036.44500000	0.16600000	0.00000000
52	1041.43320000	9.94380000	0.00000000
53	1054.56850000	3.83810000	0.00000000
54	1056.33700000	1.41350000	0.00000000
55	1061.79550000	1.77130000	0.00000000
56	1071.64530000	14.73490000	0.00000000
57	1122.20990000	5.13740000	0.00000000
58	1168.14330000	80.61760000	0.00000000
59	1183.65460000	0.68270000	0.00000000
60	1196.60970000	0.08730000	0.00000000

61	1205.3280000	0.65890000	0.00000000
62	1208.54680000	0.40640000	0.00000000
63	1214.74930000	0.61210000	0.00000000
64	1239.67820000	189.64420000	0.00000000
65	1240.70510000	12.51390000	0.00000000
66	1256.24440000	2.81870000	0.00000000
67	1286.64650000	7.82470000	0.00000000
68	1294.51340000	8.83250000	0.00000000
69	1308.09810000	5.10700000	0.00000000
70	1331.22000000	5.51110000	0.00000000
71	1336.98750000	2.05470000	0.00000000
72	1348.86060000	0.57310000	0.00000000
73	1350.97350000	14.69230000	0.00000000
74	1363.80720000	7.47030000	0.00000000
75	1369.96110000	38.44490000	0.00000000
76	1376.74760000	31.69230000	0.00000000
77	1377.73640000	303.80040000	0.00000000
78	1398.51140000	4.39240000	0.00000000
79	1403.22020000	11.30870000	0.00000000
80	1406.27780000	11.74350000	0.00000000
81	1438.80450000	10.82800000	0.00000000
82	1493.52110000	4.85550000	0.00000000
83	1497.09460000	7.85040000	0.00000000
84	1502.79640000	1.74070000	0.00000000
85	1508.97910000	2.27500000	0.00000000
86	1511.29380000	18.38390000	0.00000000
87	1517.57870000	7.52660000	0.00000000
88	1519.06820000	20.14000000	0.00000000
89	1538.30170000	3.23990000	0.00000000
90	1542.26470000	4.62710000	0.00000000
91	1630.75340000	2.46310000	0.00000000
92	1647.74700000	3.02470000	0.00000000
93	1782.19410000	111.47100000	0.00000000
94	1831.34780000	218.72060000	0.00000000
95	3068.35070000	8.61110000	0.00000000
96	3074.48120000	7.05610000	0.00000000
97	3074.95560000	2.33680000	0.00000000
98	3077.74160000	3.08670000	0.00000000
99	3084.66850000	5.69100000	0.00000000
100	3087.94030000	7.21540000	0.00000000
101	3098.79280000	5.94320000	0.00000000
102	3118.14340000	1.58890000	0.00000000
103	3127.61640000	0.36230000	0.00000000
104	3134.06220000	1.82470000	0.00000000
105	3136.96940000	2.87340000	0.00000000
106	3138.77610000	4.56120000	0.00000000
107	3154.22360000	1.25950000	0.00000000
108	3157.51710000	0.85040000	0.00000000
109	3166.83370000	5.98710000	0.00000000
110	3169.35570000	6.52320000	0.00000000
111	3188.56530000	0.88010000	0.00000000
112	3198.06740000	4.20370000	0.00000000
113	3207.21490000	1.50080000	0.00000000
114	3649.15050000	104.19080000	0.00000000

S55. CALCULATIONS ON 13 – H → 15 – H (TS)



```

Route : # opt=(calcfc,ts,noeigen) freq b3lyp/cc-pvtz geom=connectivity empiric
       : aldispersion=gd3bj int=ultrafine pop=regular
SMILES : c1ccc(cc1)C[N+]23CCC(CC2)(CC3)[C]=O.[C](=O)O
Formula : C16H20NO3+
Charge : 1
Multiplicity : 1
Energy : -902.23325950 a.u.
Gibbs Energy : -901.94593500 a.u.
Number of imaginary frequencies : 1

```

S55.1. Cartesian Co-ordinates (XYZ format)

40

```

C -0.07893700 -0.65481597 1.03875697
C -0.26553100 0.49860999 0.04828300
C 1.41954994 -0.97489297 1.16013706
H -0.46693000 -0.38758200 2.02095389
H -0.62337500 -1.53531897 0.70184201
H 1.85736895 -0.56732303 2.06837893
H 1.61556995 -2.04081202 1.13109004
C 0.70883298 1.62583995 0.42339200
H 0.49327999 2.51030493 -0.17041300
H 0.57621998 1.89705896 1.47014201
C 2.14547396 1.15342200 0.16825400
H 2.55969095 1.56198800 -0.75039798
H 2.81517696 1.40437400 0.98631001
C 1.48475695 -0.71015400 -1.28128505

```

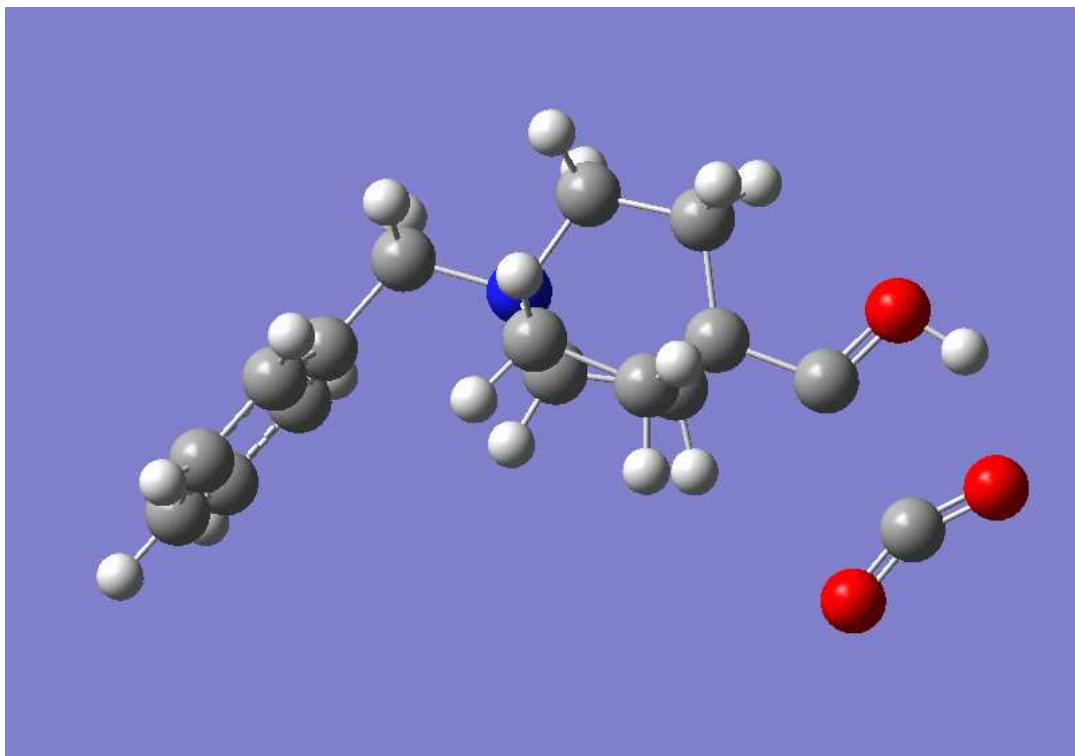
H 2.14333296 -0.40893701 -2.09100699
H 1.39951503 -1.79172397 -1.29711497
C 0.11974100 -0.00871600 -1.35663700
H 0.15148000 0.83409101 -2.04439998
H -0.62226701 -0.70902997 -1.73171306
N 2.18123507 -0.35293701 0.01172200
C 3.64383292 -0.80770200 0.00633900
H 4.12325191 -0.20906100 -0.76507097
H 4.03866720 -0.50298101 0.97299600
C -1.70531595 1.02605295 0.00507500
O -1.95486200 2.11050606 -0.45285299
C -3.18824601 -0.53009999 0.01062700
O -2.96129298 -1.34854198 -0.78258097
O -3.90157604 -0.06329000 0.92092198
H -2.92853594 0.66264802 0.87849700
C 3.85544610 -2.27107191 -0.22897200
C 3.93360305 -3.15474200 0.84866899
C 4.01998901 -2.76447701 -1.52398705
C 4.13961220 -4.51045704 0.63420600
H 3.85581708 -2.78109407 1.86154604
C 4.22547293 -4.11963987 -1.73964298
H 4.00703192 -2.08729291 -2.36789989
C 4.27839279 -4.99482584 -0.66092497
H 4.20517492 -5.18472910 1.47603798
H 4.35724783 -4.49038696 -2.74603105
H 4.44479895 -6.04935980 -0.82853299

S55.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2211.10150000	393.34860000	0.00000000
2	26.53950000	0.54970000	0.00000000
3	42.22170000	0.18700000	0.00000000
4	48.18410000	0.52200000	0.00000000
5	51.24400000	1.05820000	0.00000000
6	76.82630000	2.25740000	0.00000000
7	88.48360000	1.08640000	0.00000000
8	118.16780000	3.12870000	0.00000000
9	128.82010000	1.68050000	0.00000000
10	136.54990000	3.43220000	0.00000000
11	184.90360000	16.28300000	0.00000000
12	220.74440000	0.11880000	0.00000000
13	232.83560000	2.67720000	0.00000000
14	259.96790000	7.65340000	0.00000000
15	301.47660000	24.98670000	0.00000000
16	320.29850000	0.37720000	0.00000000
17	336.50690000	1.18380000	0.00000000
18	363.54610000	3.78130000	0.00000000
19	394.98250000	0.20220000	0.00000000
20	418.33640000	0.03400000	0.00000000
21	422.27840000	0.06460000	0.00000000
22	437.99090000	1.87350000	0.00000000
23	480.22770000	8.94110000	0.00000000
24	536.18700000	5.09500000	0.00000000
25	538.20660000	24.08860000	0.00000000
26	551.34890000	42.78300000	0.00000000
27	579.66730000	59.58450000	0.00000000
28	585.64040000	10.77690000	0.00000000
29	638.24900000	23.75760000	0.00000000
30	639.11440000	0.19570000	0.00000000
31	654.52380000	495.26130000	0.00000000
32	701.66160000	23.83650000	0.00000000
33	724.38230000	43.60230000	0.00000000
34	784.80060000	16.95490000	0.00000000
35	787.77890000	27.15650000	0.00000000
36	804.41820000	0.91600000	0.00000000
37	832.15760000	8.37020000	0.00000000
38	842.92130000	5.51680000	0.00000000
39	855.38680000	8.07840000	0.00000000
40	856.58090000	55.48660000	0.00000000
41	869.26700000	0.08850000	0.00000000
42	904.53080000	1.39450000	0.00000000
43	948.85860000	6.25760000	0.00000000
44	955.11040000	2.61000000	0.00000000
45	977.11470000	14.17840000	0.00000000
46	992.38680000	2.18230000	0.00000000
47	997.72880000	8.91140000	0.00000000
48	1003.96190000	12.48580000	0.00000000
49	1006.15890000	0.01970000	0.00000000
50	1017.86400000	3.09410000	0.00000000
51	1022.56720000	2.80510000	0.00000000
52	1028.36780000	3.91450000	0.00000000
53	1036.44640000	0.08200000	0.00000000
54	1050.91310000	2.51690000	0.00000000
55	1056.36270000	1.62290000	0.00000000
56	1059.71760000	5.17900000	0.00000000
57	1066.97630000	12.68630000	0.00000000
58	1122.11800000	5.31690000	0.00000000
59	1132.81620000	147.77470000	0.00000000
60	1186.03170000	1.38970000	0.00000000

61	1196.46770000	0.03430000	0.00000000
62	1201.38160000	41.08830000	0.00000000
63	1205.89850000	0.60280000	0.00000000
64	1214.58990000	2.33910000	0.00000000
65	1239.37900000	263.36790000	0.00000000
66	1241.09500000	159.04660000	0.00000000
67	1254.60500000	2.65970000	0.00000000
68	1284.95680000	0.86990000	0.00000000
69	1293.05560000	0.34150000	0.00000000
70	1309.07070000	15.04810000	0.00000000
71	1328.83220000	1.02880000	0.00000000
72	1337.18190000	1.83970000	0.00000000
73	1346.90920000	4.19370000	0.00000000
74	1350.18310000	7.18980000	0.00000000
75	1365.31650000	10.60000000	0.00000000
76	1366.21740000	7.37610000	0.00000000
77	1378.05500000	0.71810000	0.00000000
78	1389.76330000	0.49800000	0.00000000
79	1402.33280000	11.54280000	0.00000000
80	1407.02180000	9.45480000	0.00000000
81	1437.58390000	9.91840000	0.00000000
82	1492.97440000	4.31600000	0.00000000
83	1496.98750000	7.80790000	0.00000000
84	1504.47160000	2.67280000	0.00000000
85	1506.73460000	1.86610000	0.00000000
86	1513.49130000	19.80250000	0.00000000
87	1515.84720000	11.06350000	0.00000000
88	1517.16330000	14.15270000	0.00000000
89	1538.25840000	3.36980000	0.00000000
90	1541.27850000	6.11540000	0.00000000
91	1630.73340000	2.44580000	0.00000000
92	1647.82030000	2.87080000	0.00000000
93	1712.61210000	37.79780000	0.00000000
94	1795.06320000	157.66540000	0.00000000
95	2155.67470000	361.35820000	0.00000000
96	3061.35650000	6.72400000	0.00000000
97	3065.86090000	8.57980000	0.00000000
98	3074.87390000	5.48580000	0.00000000
99	3076.74520000	3.21610000	0.00000000
100	3083.33730000	6.95470000	0.00000000
101	3087.09510000	3.79400000	0.00000000
102	3095.89720000	6.96040000	0.00000000
103	3102.89850000	5.47470000	0.00000000
104	3117.95330000	2.58780000	0.00000000
105	3120.94570000	0.79300000	0.00000000
106	3127.73530000	0.42410000	0.00000000
107	3137.61550000	4.38820000	0.00000000
108	3151.53980000	1.13160000	0.00000000
109	3154.36460000	2.60010000	0.00000000
110	3166.59190000	5.92040000	0.00000000
111	3169.71170000	6.07920000	0.00000000
112	3188.27140000	0.89950000	0.00000000
113	3197.78140000	4.31570000	0.00000000
114	3206.94270000	1.56710000	0.00000000

S56. CALCULATIONS ON 13 – H → 14 – H (TS)



```

Route : # opt=(calcall,ts,noeigen) freq b3lyp/cc-pvtz geom=connectivity empiri
       : caldispersion=gd3bj int=ultrafine pop=regular
SMILES : c1ccc(cc1)C[N+]23CCC(CC2)(CC3)[C]O.C(=O)=O
Formula : C16H20NO3+
Charge : 1
Multiplicity : 1
Energy : -902.29174065 a.u.
Gibbs Energy : -901.99852100 a.u.
Number of imaginary frequencies : 1

```

S56.1. Cartesian Co-ordinates (XYZ format)

40

```

C -0.71700400 1.63863695 0.02055200
C 0.19248100 0.40327999 -0.01068400
C -2.16927505 1.19011998 -0.20029800
H -0.61430401 2.15340090 0.97419602
H -0.43071699 2.34566903 -0.75478101
H -2.85839891 1.66417599 0.49321899
H -2.51399207 1.38825297 -1.21230400
C -0.12224700 -0.47828600 1.21995902
H 0.39437500 -1.43071496 1.12554801
H 0.23425999 -0.00510100 2.13293099
C -1.64254403 -0.67337000 1.31181502
H -1.90709400 -1.70335400 1.52375102
H -2.09557700 -0.03579900 2.06737804
C -1.56448102 -1.00736904 -1.11733794

```

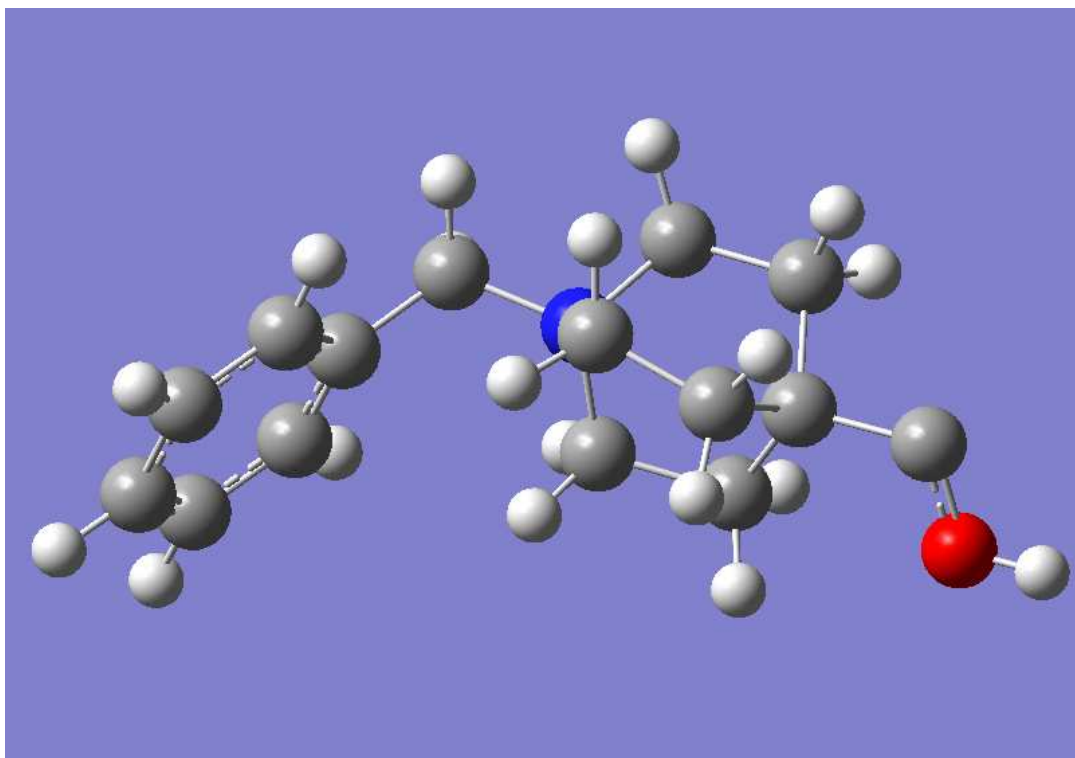
H -1.56230402 -2.06373191 -0.86997700
H -2.15376496 -0.87019998 -2.01928401
C -0.14704500 -0.43419001 -1.26379800
H 0.57079399 -1.24336302 -1.37589896
H -0.07753200 0.19223601 -2.15168405
N -2.29865193 -0.30574000 0.00209700
C -3.78859997 -0.66764897 0.00807400
H -4.18433094 -0.24943700 -0.91489202
H -4.21000195 -0.11531900 0.84501398
C 1.66524601 0.63449597 -0.00805800
O 2.02575302 1.85630095 0.02243500
C 3.54678702 -0.46024001 -0.03531800
O 3.32771897 -1.61270404 -0.07073600
O 4.22107601 0.52356899 -0.00493900
H 3.02651000 1.82343602 0.02481000
C -4.08775616 -2.13016891 0.11711400
C -4.22041321 -2.91417909 -1.02979696
C -4.27837801 -2.71954203 1.36801302
C -4.50511408 -4.26823997 -0.92693502
H -4.12014818 -2.46435499 -2.00889206
C -4.56368923 -4.07380390 1.47199595
H -4.22581816 -2.11548495 2.26463008
C -4.66989088 -4.85056114 0.32453999
H -4.61081219 -4.86535597 -1.82129002
H -4.71536684 -4.51878500 2.44490290
H -4.89732504 -5.90397882 0.40436599

S56.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-169.17330000	108.22720000	0.00000000
2	21.62070000	0.57370000	0.00000000
3	38.88780000	0.23220000	0.00000000
4	43.88610000	1.93410000	0.00000000
5	49.65980000	0.79840000	0.00000000
6	85.39140000	4.62750000	0.00000000
7	93.29660000	0.26800000	0.00000000
8	115.94310000	0.03860000	0.00000000
9	116.91460000	0.29340000	0.00000000
10	180.61960000	10.77740000	0.00000000
11	220.32620000	0.86490000	0.00000000
12	228.24980000	1.21600000	0.00000000
13	252.50940000	1.37640000	0.00000000
14	284.72280000	0.29650000	0.00000000
15	323.53790000	4.83500000	0.00000000
16	335.94850000	3.98100000	0.00000000
17	360.63700000	0.22230000	0.00000000
18	393.94180000	0.25100000	0.00000000
19	417.15560000	0.03690000	0.00000000
20	421.46810000	0.00770000	0.00000000
21	448.99690000	12.43510000	0.00000000
22	454.63200000	0.65680000	0.00000000
23	487.07960000	34.38020000	0.00000000
24	534.19820000	8.59260000	0.00000000
25	542.02000000	0.80660000	0.00000000
26	581.97560000	3.97280000	0.00000000
27	604.19770000	397.12030000	0.00000000
28	637.76770000	17.44950000	0.00000000
29	639.01010000	0.16190000	0.00000000
30	688.13580000	15.27260000	0.00000000
31	689.72420000	9.57100000	0.00000000
32	724.56970000	44.34260000	0.00000000
33	755.08950000	20.14600000	0.00000000
34	786.25180000	35.44440000	0.00000000
35	802.22950000	1.41140000	0.00000000
36	832.15550000	8.94690000	0.00000000
37	835.82220000	6.41190000	0.00000000
38	852.28220000	30.04760000	0.00000000
39	854.32310000	30.98710000	0.00000000
40	869.41370000	0.08450000	0.00000000
41	903.74770000	2.14150000	0.00000000
42	952.80610000	3.96480000	0.00000000
43	956.73100000	3.70580000	0.00000000
44	979.95420000	5.41270000	0.00000000
45	993.86460000	1.00510000	0.00000000
46	996.03150000	0.78390000	0.00000000
47	1006.44730000	0.03820000	0.00000000
48	1015.88230000	1.64890000	0.00000000
49	1022.70910000	13.47110000	0.00000000
50	1028.34060000	3.54770000	0.00000000
51	1036.90090000	0.02830000	0.00000000
52	1046.92800000	28.88310000	0.00000000
53	1054.84500000	2.48690000	0.00000000
54	1056.55330000	3.02110000	0.00000000
55	1060.66720000	21.41960000	0.00000000
56	1068.22820000	14.51290000	0.00000000
57	1122.17290000	6.80360000	0.00000000
58	1154.13750000	34.05280000	0.00000000
59	1181.67030000	4.39140000	0.00000000
60	1196.66770000	0.37150000	0.00000000

61	1200.66710000	27.18780000	0.00000000
62	1205.41340000	1.85410000	0.00000000
63	1214.68830000	1.27000000	0.00000000
64	1240.55230000	19.23380000	0.00000000
65	1255.11230000	2.73010000	0.00000000
66	1267.79590000	78.13830000	0.00000000
67	1283.77290000	1.99310000	0.00000000
68	1293.30070000	2.20200000	0.00000000
69	1303.36650000	20.82430000	0.00000000
70	1325.82730000	3.30030000	0.00000000
71	1335.04480000	2.75260000	0.00000000
72	1347.14950000	13.22760000	0.00000000
73	1348.04650000	2.68810000	0.00000000
74	1362.35000000	5.24300000	0.00000000
75	1368.13160000	20.14020000	0.00000000
76	1376.17730000	1.28970000	0.00000000
77	1392.41870000	12.34160000	0.00000000
78	1402.19610000	7.22040000	0.00000000
79	1404.27550000	11.86930000	0.00000000
80	1433.27800000	197.17600000	0.00000000
81	1437.91760000	25.26950000	0.00000000
82	1492.58170000	5.11500000	0.00000000
83	1496.16810000	157.11590000	0.00000000
84	1497.06130000	7.82610000	0.00000000
85	1502.22440000	1.27290000	0.00000000
86	1505.92830000	2.25080000	0.00000000
87	1511.09630000	26.01650000	0.00000000
88	1514.92150000	10.05100000	0.00000000
89	1516.86590000	15.29340000	0.00000000
90	1538.23930000	2.90930000	0.00000000
91	1540.29500000	5.35160000	0.00000000
92	1630.66800000	2.48770000	0.00000000
93	1647.56890000	3.13510000	0.00000000
94	2198.43370000	432.99660000	0.00000000
95	3068.95380000	6.38080000	0.00000000
96	3072.55430000	7.69940000	0.00000000
97	3074.12000000	3.91930000	0.00000000
98	3075.71940000	2.13830000	0.00000000
99	3084.18900000	6.25110000	0.00000000
100	3087.94760000	5.24250000	0.00000000
101	3098.39700000	5.80780000	0.00000000
102	3112.33910000	2.01670000	0.00000000
103	3115.15510000	1.28360000	0.00000000
104	3116.45330000	2.71320000	0.00000000
105	3127.88870000	0.27400000	0.00000000
106	3137.77740000	4.61060000	0.00000000
107	3152.46410000	1.47700000	0.00000000
108	3155.35780000	2.27240000	0.00000000
109	3166.76250000	6.11700000	0.00000000
110	3169.12460000	6.46670000	0.00000000
111	3188.63600000	0.88330000	0.00000000
112	3190.58840000	366.58910000	0.00000000
113	3198.13010000	4.03160000	0.00000000
114	3207.25320000	1.37010000	0.00000000

S57. CALCULATIONS ON 14 – H



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : c1ccc(cc1)C[N+]23CCC(CC2)(CC3)[C]O
Formula              : C15H20NO+
Charge               : 1
Multiplicity         : 1
Energy               : -713.62452289 a.u.
Gibbs Energy        : -713.33916900 a.u.
Number of imaginary frequencies : 0
  
```

S57.1. Cartesian Co-ordinates (XYZ format)

37

```

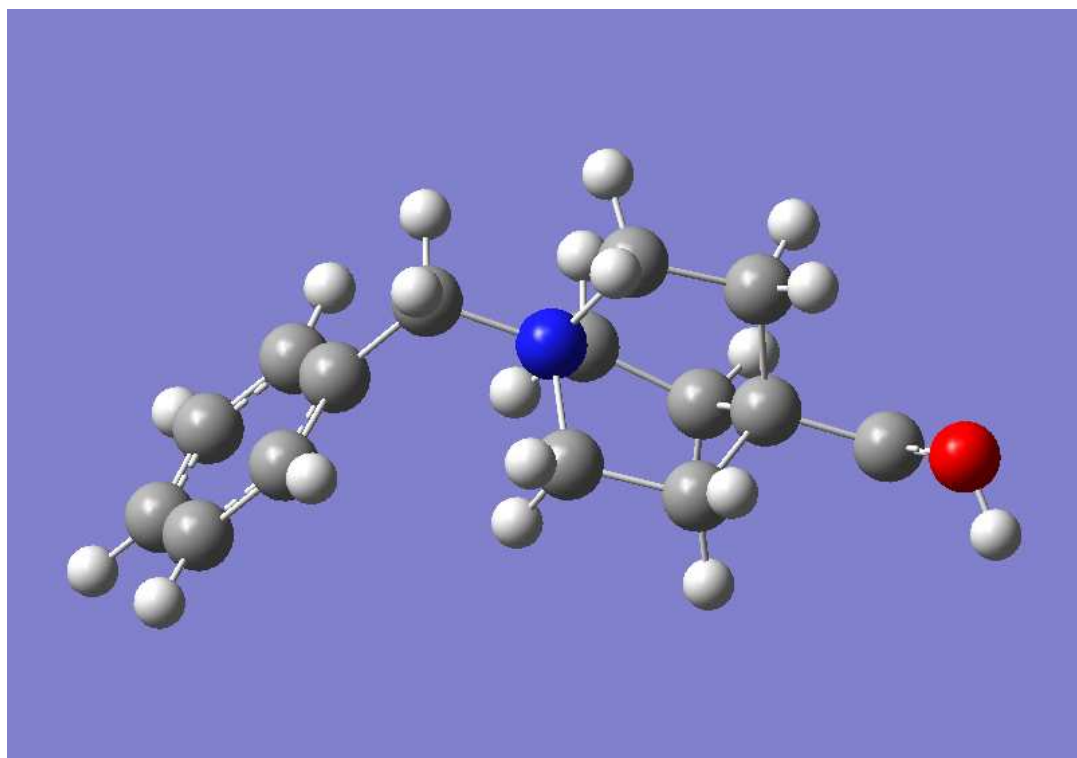
C -2.07805204 -0.39553300 -0.18976100
C -0.54569697 -0.39012200 -0.08329800
C -2.61588097 1.00752997 0.13025600
H -2.38022900 -0.70178002 -1.19003904
H -2.50752497 -1.11407399 0.50398803
H -3.36959910 1.33376002 -0.58097702
H -3.03924203 1.07630396 1.12705195
C 0.01900500 0.49856001 -1.21035004
H 1.08375597 0.65348899 -1.05141997
H -0.09277400 0.00940700 -2.17625308
C -0.74301898 1.83047605 -1.22467506
H -0.07819500 2.68276310 -1.33768499
H -1.48942697 1.87184596 -2.01424694
C -0.54218602 1.75717700 1.21815503
  
```

H	0.31790900	2.40171099	1.05078602
H	-1.04035902	2.07470989	2.12733006
C	-0.15985100	0.27101299	1.25626695
H	0.90883601	0.16607600	1.42977798
H	-0.67334199	-0.23249000	2.07405591
N	-1.49379098	2.02264094	0.07473800
C	-2.02928591	3.45529795	0.11888600
H	-1.14751399	4.09022903	0.06945200
H	-2.59209108	3.57663989	-0.80415303
C	0.18543300	-1.71287894	-0.15495600
O	-0.69156802	-2.67897391	-0.19960099
H	-0.22568201	-3.52743912	-0.24157700
C	-2.86720896	3.78696299	1.31494200
C	-4.24996090	3.60115910	1.28662896
C	-2.27902007	4.32708693	2.45962811
C	-5.02543688	3.91870403	2.39255190
H	-4.72774220	3.22419596	0.39193800
C	-3.05363393	4.64551210	3.56645703
H	-1.21425200	4.52020884	2.48070788
C	-4.42685890	4.43473911	3.53613091
H	-6.09602499	3.77610612	2.35781908
H	-2.58851099	5.06907415	4.44504213
H	-5.03160715	4.68793201	4.39522314

S57.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	27.72660000	2.13240000	0.00000000
2	36.59700000	0.02770000	0.00000000
3	68.71720000	0.60080000	0.00000000
4	84.33890000	0.79340000	0.00000000
5	120.19840000	0.03410000	0.00000000
6	171.01330000	1.06050000	0.00000000
7	200.97840000	4.47070000	0.00000000
8	238.67280000	1.34040000	0.00000000
9	252.69440000	0.60940000	0.00000000
10	271.71120000	0.82510000	0.00000000
11	324.03380000	1.36320000	0.00000000
12	354.58130000	0.36130000	0.00000000
13	390.70220000	0.20440000	0.00000000
14	407.46670000	0.30840000	0.00000000
15	418.38950000	0.07880000	0.00000000
16	419.18960000	0.81160000	0.00000000
17	424.37980000	0.73770000	0.00000000
18	478.42720000	4.70980000	0.00000000
19	538.02220000	0.02480000	0.00000000
20	538.80280000	0.32340000	0.00000000
21	585.12320000	8.86070000	0.00000000
22	623.83730000	2.31810000	0.00000000
23	639.17980000	0.11040000	0.00000000
24	678.10230000	23.41850000	0.00000000
25	720.80110000	2.74490000	0.00000000
26	724.42780000	49.67200000	0.00000000
27	786.00250000	36.03160000	0.00000000
28	800.07060000	3.48440000	0.00000000
29	818.48920000	57.88730000	0.00000000
30	835.03200000	3.74020000	0.00000000
31	842.43450000	14.07790000	0.00000000
32	846.90030000	48.88480000	0.00000000
33	852.98600000	4.82720000	0.00000000
34	869.19260000	0.03220000	0.00000000
35	903.53530000	0.96090000	0.00000000
36	954.06600000	2.80100000	0.00000000
37	968.43100000	7.41390000	0.00000000
38	986.07420000	13.27880000	0.00000000
39	990.08300000	0.87830000	0.00000000
40	1005.54900000	1.16330000	0.00000000
41	1007.07880000	9.13510000	0.00000000
42	1010.52530000	6.85240000	0.00000000
43	1017.17740000	5.67360000	0.00000000
44	1028.42530000	3.67370000	0.00000000
45	1035.65790000	0.03590000	0.00000000
46	1047.98170000	3.06950000	0.00000000
47	1053.12260000	0.63120000	0.00000000
48	1056.70320000	1.67230000	0.00000000
49	1065.79090000	13.82220000	0.00000000
50	1121.69120000	5.86300000	0.00000000
51	1130.22390000	51.82530000	0.00000000
52	1182.56240000	4.22350000	0.00000000
53	1191.29410000	18.07650000	0.00000000
54	1196.27160000	0.54650000	0.00000000
55	1201.96970000	0.22230000	0.00000000
56	1214.47180000	0.71920000	0.00000000
57	1240.35420000	16.60260000	0.00000000
58	1253.27460000	5.48620000	0.00000000
59	1280.58950000	1.53580000	0.00000000
60	1285.45110000	16.32190000	0.00000000

61	1293.64960000	5.04500000	0.00000000
62	1318.48800000	45.43960000	0.00000000
63	1325.09160000	37.41400000	0.00000000
64	1332.70050000	112.19370000	0.00000000
65	1345.59700000	1.94770000	0.00000000
66	1347.42600000	0.86870000	0.00000000
67	1359.71380000	6.84910000	0.00000000
68	1363.16140000	36.97950000	0.00000000
69	1374.72680000	3.89890000	0.00000000
70	1382.09730000	7.52280000	0.00000000
71	1383.67520000	2.22390000	0.00000000
72	1403.52100000	14.98250000	0.00000000
73	1404.76700000	9.05540000	0.00000000
74	1437.96750000	12.02960000	0.00000000
75	1493.09130000	4.24720000	0.00000000
76	1496.78950000	6.33090000	0.00000000
77	1501.65920000	5.75400000	0.00000000
78	1503.64260000	1.67040000	0.00000000
79	1511.25960000	17.51120000	0.00000000
80	1513.77150000	6.35750000	0.00000000
81	1514.63360000	16.86350000	0.00000000
82	1538.34650000	3.14540000	0.00000000
83	1539.34110000	6.81000000	0.00000000
84	1630.81280000	2.38360000	0.00000000
85	1648.19740000	2.59450000	0.00000000
86	3066.53380000	7.14150000	0.00000000
87	3070.03300000	7.26220000	0.00000000
88	3072.14660000	10.12910000	0.00000000
89	3075.25180000	0.93640000	0.00000000
90	3082.79670000	4.70700000	0.00000000
91	3085.32850000	7.49680000	0.00000000
92	3093.82570000	9.00810000	0.00000000
93	3110.53790000	1.64650000	0.00000000
94	3112.04520000	3.15040000	0.00000000
95	3113.36300000	3.66710000	0.00000000
96	3126.80860000	0.28940000	0.00000000
97	3136.37260000	5.37720000	0.00000000
98	3149.08290000	2.51810000	0.00000000
99	3153.16540000	3.58500000	0.00000000
100	3167.17190000	5.78960000	0.00000000
101	3169.69870000	6.20840000	0.00000000
102	3187.82430000	1.02650000	0.00000000
103	3197.34440000	4.82420000	0.00000000
104	3206.57060000	1.86440000	0.00000000
105	3715.35460000	201.26190000	0.00000000

S58. CALCULATIONS ON 14 – H (³A)

```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES              : c1ccc(cc1)C[N+]23CCC(CC2)(CC3)[C]O
Formula             : C15H20NO+,3
Charge              : 1
Multiplicity        : 3
Energy              : -713.58128558
Gibbs Energy        : -713.29852500
Number of imaginary frequencies : 0

```

a.u.
a.u.

S58.1. Cartesian Co-ordinates (XYZ format)

37

```

C -1.68401802  0.90308499  1.28863800
C -2.59223008  0.01107600  0.43156201
C -0.40860301  1.24337196  0.50360602
H -2.20425200  1.82064700  1.55451906
H -1.43735301  0.39063701  2.21693110
H -0.42902499  2.25259495  0.09837200
H  0.48615199  1.13271999  1.10586596
C -2.71938896  0.66743302 -0.96556598
H -3.45991611  0.13667700 -1.55919003
H -3.06688094  1.69206703 -0.84976900
C -1.35986698  0.62810701 -1.67624795
H -1.30904102 -0.14966100 -2.43452811
H -1.11068404  1.57712495 -2.14363408
C -0.42607099 -1.10729098 -0.21775401

```

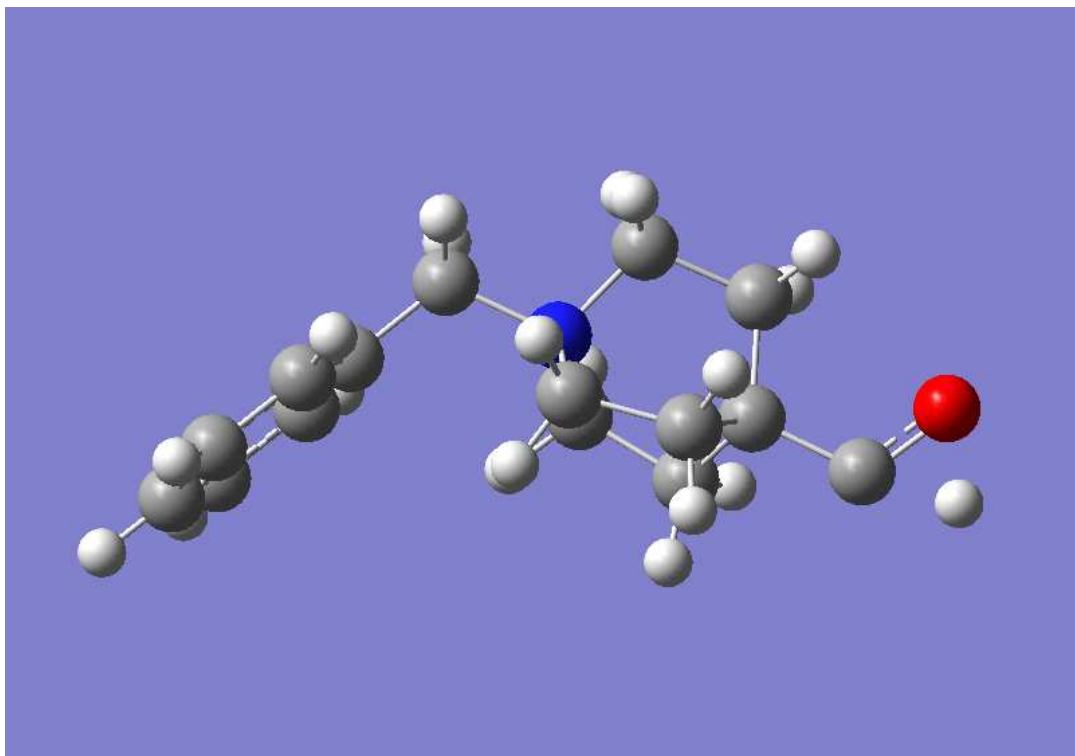
H	-0.14627799	-1.74612105	-1.05099595
H	0.29457101	-1.25577700	0.57969701
C	-1.87277699	-1.34590197	0.24225800
H	-2.41621399	-1.94542205	-0.48587099
H	-1.86573899	-1.89543903	1.18101895
N	-0.25827500	0.32078400	-0.68456203
C	1.08959794	0.52816898	-1.37957597
H	1.03998804	-0.07804700	-2.28149390
H	1.10028505	1.57623100	-1.67033994
C	-3.92787600	-0.13835400	1.06343198
O	-4.92952585	-0.83380800	0.52334797
H	-5.22635412	-1.56478298	1.08491099
C	2.29256606	0.18246301	-0.55772299
C	2.91972899	1.15692997	0.22020300
C	2.82805109	-1.10575104	-0.59193099
C	4.04133511	0.84177899	0.97459602
H	2.54439712	2.17208290	0.22146800
C	3.94902802	-1.42224205	0.16206300
H	2.38052392	-1.86179698	-1.22365105
C	4.55253983	-0.45024699	0.95155603
H	4.52251816	1.60563195	1.56842804
H	4.35881615	-2.42138791	0.12372100
H	5.42935181	-0.69496602	1.53394306

S58.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	34.44390000	0.53150000	0.00000000
2	58.15610000	0.72950000	0.00000000
3	74.86310000	1.67680000	0.00000000
4	92.41830000	0.90940000	0.00000000
5	113.85670000	0.05310000	0.00000000
6	139.91190000	0.37180000	0.00000000
7	203.13140000	8.00740000	0.00000000
8	222.86740000	4.73880000	0.00000000
9	254.46070000	55.48950000	0.00000000
10	257.99830000	23.01670000	0.00000000
11	291.76680000	47.85290000	0.00000000
12	304.82870000	2.27740000	0.00000000
13	358.57580000	0.60940000	0.00000000
14	386.84450000	3.80980000	0.00000000
15	418.37200000	0.14660000	0.00000000
16	421.37770000	0.52450000	0.00000000
17	428.30090000	3.06750000	0.00000000
18	445.80610000	7.35020000	0.00000000
19	478.58850000	6.51460000	0.00000000
20	531.50080000	0.23300000	0.00000000
21	539.92360000	0.08300000	0.00000000
22	571.09640000	4.27300000	0.00000000
23	623.62320000	3.87300000	0.00000000
24	639.19670000	0.09220000	0.00000000
25	673.27130000	14.23400000	0.00000000
26	716.73210000	1.95260000	0.00000000
27	724.26170000	44.36290000	0.00000000
28	786.00660000	34.61940000	0.00000000
29	802.38900000	1.14600000	0.00000000
30	828.97480000	5.39180000	0.00000000
31	837.86110000	5.67930000	0.00000000
32	850.97720000	11.87430000	0.00000000
33	853.19470000	22.23240000	0.00000000
34	869.07400000	0.03450000	0.00000000
35	902.74900000	0.69760000	0.00000000
36	953.77850000	4.40440000	0.00000000
37	970.27170000	16.10990000	0.00000000
38	980.15120000	7.87360000	0.00000000
39	989.90410000	11.65660000	0.00000000
40	994.97140000	4.21840000	0.00000000
41	1005.70780000	0.01850000	0.00000000
42	1012.38850000	6.81790000	0.00000000
43	1017.29310000	1.94690000	0.00000000
44	1028.37380000	4.12100000	0.00000000
45	1035.64550000	0.05530000	0.00000000
46	1039.89250000	2.83340000	0.00000000
47	1046.87570000	8.72410000	0.00000000
48	1056.60920000	1.86750000	0.00000000
49	1067.27570000	16.76510000	0.00000000
50	1112.04190000	0.56810000	0.00000000
51	1121.78990000	8.18140000	0.00000000
52	1143.06410000	171.54790000	0.00000000
53	1179.77720000	3.17630000	0.00000000
54	1195.67430000	1.63870000	0.00000000
55	1196.80450000	3.33380000	0.00000000
56	1201.94390000	0.21490000	0.00000000
57	1214.65130000	0.70730000	0.00000000
58	1240.79310000	17.18820000	0.00000000
59	1254.66410000	0.52340000	0.00000000
60	1279.15620000	3.97300000	0.00000000

61	1288.33830000	6.92560000	0.00000000
62	1296.72330000	4.81040000	0.00000000
63	1321.87580000	4.62790000	0.00000000
64	1327.06780000	2.51500000	0.00000000
65	1343.27290000	6.15660000	0.00000000
66	1346.81820000	2.58680000	0.00000000
67	1361.45180000	4.74940000	0.00000000
68	1363.74470000	32.41010000	0.00000000
69	1369.41120000	24.44650000	0.00000000
70	1376.74360000	1.01810000	0.00000000
71	1390.94940000	14.06650000	0.00000000
72	1403.24260000	11.31560000	0.00000000
73	1406.87260000	9.81490000	0.00000000
74	1437.13770000	12.02320000	0.00000000
75	1492.88520000	3.89960000	0.00000000
76	1496.88080000	7.11820000	0.00000000
77	1502.33610000	1.90640000	0.00000000
78	1504.05080000	3.50000000	0.00000000
79	1510.89910000	19.48740000	0.00000000
80	1514.13620000	12.62860000	0.00000000
81	1515.23340000	8.19830000	0.00000000
82	1538.36480000	3.14490000	0.00000000
83	1539.83980000	8.35000000	0.00000000
84	1630.75320000	2.37030000	0.00000000
85	1648.20260000	2.73470000	0.00000000
86	3068.51160000	9.51420000	0.00000000
87	3069.87670000	7.69070000	0.00000000
88	3073.10830000	10.07040000	0.00000000
89	3075.68070000	0.59690000	0.00000000
90	3081.80050000	6.80640000	0.00000000
91	3085.39490000	5.61370000	0.00000000
92	3093.15000000	7.80850000	0.00000000
93	3109.50380000	2.72020000	0.00000000
94	3111.78280000	5.20110000	0.00000000
95	3114.69550000	1.65340000	0.00000000
96	3127.21050000	0.22380000	0.00000000
97	3136.23670000	5.87260000	0.00000000
98	3149.33640000	2.10720000	0.00000000
99	3153.15800000	3.39120000	0.00000000
100	3167.55330000	5.60800000	0.00000000
101	3168.96280000	6.36410000	0.00000000
102	3187.77800000	1.00960000	0.00000000
103	3197.34480000	4.78500000	0.00000000
104	3206.55180000	1.85640000	0.00000000
105	3695.74360000	100.34580000	0.00000000

S59. CALCULATIONS ON 14 – H → 15 – H (TS)



```

Route                : # opt=(calcfc,ts,noeigen) freq b3lyp/cc-pvtz geom=connectivity empiric
                    : aldispersion=gd3bj int=ultrafine pop=regular
SMILES               : c1ccc(cc1)C[N]23CCC(CC2)(CC3)[C]O
Formula              : C15H20NO+
Charge               : 1
Multiplicity         : 1
Energy               : -713.57011548                                     a.u.
Gibbs Energy        : -713.29031500                                     a.u.
Number of imaginary frequencies : 1

```

S59.1. Cartesian Co-ordinates (XYZ format)

37

```

C  0.51098502 -1.11493099 -1.05414701
C  1.12456095 -0.14724000 -0.02984300
C -0.99566197 -0.83290398 -1.15860295
H  0.97084498 -0.98230201 -2.03162289
H  0.69621801 -2.14266396 -0.74811202
H -1.24678504 -0.25108999 -2.04244900
H -1.58404005 -1.74370301 -1.16564405
C  0.65450901  1.27661896 -0.35253099
H  1.19280195  2.00377607  0.25132200
H  0.86855298  1.51091599 -1.39393604
C -0.85032099  1.37087405 -0.07444700
H -1.06905103  1.86365497  0.86994100
H -1.38477397  1.89292204 -0.86343801
C -0.94180501 -0.66838998  1.28907001

```

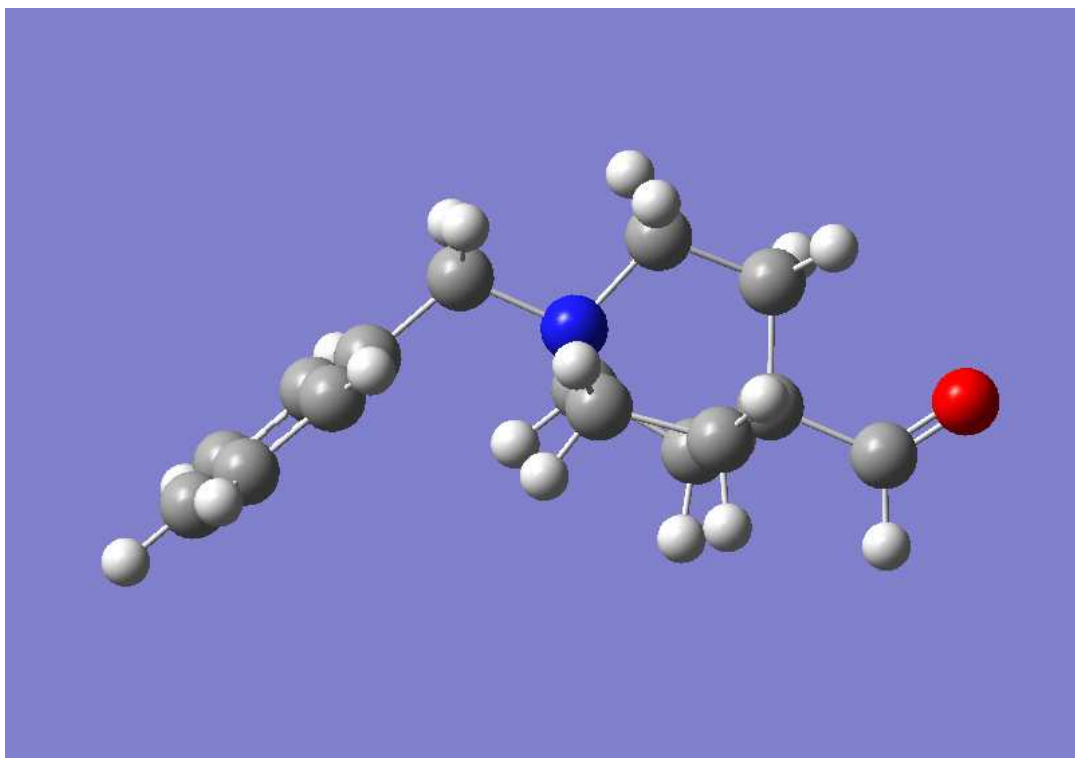
H	-1.43178499	-0.17757000	2.12500596
H	-1.27297902	-1.70120502	1.25969994
C	0.58721203	-0.53858602	1.36195004
H	0.87487102	0.21709099	2.09113503
H	1.02170300	-1.48308504	1.68266797
N	-1.45725095	-0.01586400	0.02702000
C	-2.98215294	0.12151800	0.04742400
H	-3.19240999	0.82590097	0.84935200
H	-3.23664403	0.59278297	-0.89928198
C	2.62470293	-0.29451299	-0.01252100
O	3.33114409	0.79022002	-0.04967700
H	3.88464689	-0.25070399	0.01565200
C	-3.73570609	-1.15863299	0.23527300
C	-4.06959105	-1.60368896	1.51510096
C	-4.15109205	-1.90139198	-0.87104797
C	-4.77630377	-2.78533411	1.68694401
H	-3.79449391	-1.01723194	2.38192606
C	-4.85859585	-3.08322597	-0.70043898
H	-3.94108391	-1.54550099	-1.87141895
C	-5.16534424	-3.52974105	0.57930100
H	-5.03463078	-3.11796904	2.68206811
H	-5.18100214	-3.64695406	-1.56407797
H	-5.72137022	-4.44669914	0.71288800

S59.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2044.59140000	591.06430000	0.00000000
2	34.32570000	0.63930000	0.00000000
3	44.18910000	0.28340000	0.00000000
4	64.09330000	0.33850000	0.00000000
5	91.08980000	0.36720000	0.00000000
6	125.93200000	0.14510000	0.00000000
7	153.48040000	2.31820000	0.00000000
8	214.82260000	0.85740000	0.00000000
9	221.69940000	0.80470000	0.00000000
10	256.48640000	0.39300000	0.00000000
11	267.15640000	0.22420000	0.00000000
12	328.82900000	1.42200000	0.00000000
13	347.30050000	1.59790000	0.00000000
14	375.83040000	1.10360000	0.00000000
15	395.30710000	1.36280000	0.00000000
16	417.79090000	0.08450000	0.00000000
17	421.40670000	0.05220000	0.00000000
18	424.86890000	0.44640000	0.00000000
19	480.80410000	4.20020000	0.00000000
20	532.44340000	0.32650000	0.00000000
21	541.21600000	0.30340000	0.00000000
22	583.10520000	4.92320000	0.00000000
23	606.63320000	35.90880000	0.00000000
24	638.04540000	3.58210000	0.00000000
25	639.13630000	0.01900000	0.00000000
26	683.38850000	17.73330000	0.00000000
27	724.13280000	44.55170000	0.00000000
28	735.98440000	13.03210000	0.00000000
29	786.18660000	35.41430000	0.00000000
30	798.77400000	2.33970000	0.00000000
31	830.24100000	13.49450000	0.00000000
32	838.51870000	5.04760000	0.00000000
33	849.72610000	52.10950000	0.00000000
34	853.23930000	7.38600000	0.00000000
35	869.01810000	0.05540000	0.00000000
36	903.34000000	0.43870000	0.00000000
37	953.54520000	3.26880000	0.00000000
38	971.37550000	5.03100000	0.00000000
39	979.21020000	2.74430000	0.00000000
40	993.28270000	0.75790000	0.00000000
41	995.99760000	3.31100000	0.00000000
42	1005.93690000	0.00880000	0.00000000
43	1015.62940000	1.66080000	0.00000000
44	1023.87030000	5.02340000	0.00000000
45	1028.34820000	3.47130000	0.00000000
46	1036.27020000	0.02740000	0.00000000
47	1047.92020000	3.63520000	0.00000000
48	1054.86750000	3.09820000	0.00000000
49	1056.68330000	3.31690000	0.00000000
50	1066.01210000	7.71650000	0.00000000
51	1122.07090000	5.47390000	0.00000000
52	1136.09690000	56.16700000	0.00000000
53	1180.02530000	1.86710000	0.00000000
54	1196.32270000	0.08420000	0.00000000
55	1201.20240000	0.51630000	0.00000000
56	1205.27100000	11.52100000	0.00000000
57	1214.84150000	1.20380000	0.00000000
58	1240.69670000	18.21500000	0.00000000
59	1253.83160000	0.48700000	0.00000000
60	1281.62390000	4.35220000	0.00000000

61	1286.66620000	6.24600000	0.00000000
62	1298.61920000	3.25020000	0.00000000
63	1323.97010000	7.11610000	0.00000000
64	1334.39350000	1.30590000	0.00000000
65	1346.18940000	10.14620000	0.00000000
66	1347.81470000	0.24430000	0.00000000
67	1362.60340000	4.86190000	0.00000000
68	1367.37750000	15.09320000	0.00000000
69	1376.48400000	1.61970000	0.00000000
70	1385.85700000	12.54030000	0.00000000
71	1401.09740000	21.57640000	0.00000000
72	1405.74980000	12.18120000	0.00000000
73	1428.01720000	151.79930000	0.00000000
74	1440.71710000	105.75140000	0.00000000
75	1493.08630000	4.42460000	0.00000000
76	1496.90420000	7.34600000	0.00000000
77	1502.38330000	0.78990000	0.00000000
78	1504.27430000	3.65240000	0.00000000
79	1511.41660000	21.09450000	0.00000000
80	1513.84280000	11.10250000	0.00000000
81	1515.14620000	11.71700000	0.00000000
82	1538.34760000	3.17800000	0.00000000
83	1539.67070000	6.00430000	0.00000000
84	1630.73200000	2.44080000	0.00000000
85	1647.92460000	2.73960000	0.00000000
86	2583.57800000	156.29790000	0.00000000
87	3067.82810000	6.97450000	0.00000000
88	3071.01490000	4.75020000	0.00000000
89	3072.05920000	6.65950000	0.00000000
90	3075.03400000	3.07140000	0.00000000
91	3083.06090000	6.91950000	0.00000000
92	3087.06400000	4.33000000	0.00000000
93	3097.35490000	6.15260000	0.00000000
94	3109.56840000	1.80450000	0.00000000
95	3111.16090000	5.17530000	0.00000000
96	3112.48730000	2.42090000	0.00000000
97	3127.23840000	0.25890000	0.00000000
98	3136.77710000	4.87300000	0.00000000
99	3151.48980000	1.23430000	0.00000000
100	3154.12580000	2.98010000	0.00000000
101	3166.94990000	5.81730000	0.00000000
102	3169.04020000	6.45210000	0.00000000
103	3188.14810000	0.91180000	0.00000000
104	3197.66640000	4.42110000	0.00000000
105	3206.84860000	1.65360000	0.00000000

S60. CALCULATIONS ON 15 – H



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : c1ccc(cc1)C[N+]23CCC(CC2)(CC3)C=O
Formula              : C15H20NO+
Charge               : 1
Multiplicity         : 1
Energy               : -713.70148962 a.u.
Gibbs Energy         : -713.41556600 a.u.
Number of imaginary frequencies : 0

```

S60.1. Cartesian Co-ordinates (XYZ format)

37

```

C -2.02687407 -0.39250699 0.05189400
C -0.49577299 -0.35033399 -0.10143100
C -2.57934594 1.03730094 -0.06229800
H -2.47275209 -1.01144600 -0.72481900
H -2.29761791 -0.83080798 1.01177204
H -3.02845812 1.22707105 -1.03424597
H -3.31202006 1.25794995 0.70598000
C -0.15285300 0.46351001 -1.34979904
H 0.90911299 0.38776100 -1.56944895
H -0.67928702 0.05770100 -2.21160698
C -0.54183197 1.92845798 -1.11128104
H 0.31830499 2.55614710 -0.89061701
H -1.07012498 2.35995007 -1.95698297
C -0.67219001 1.70197594 1.33089805

```

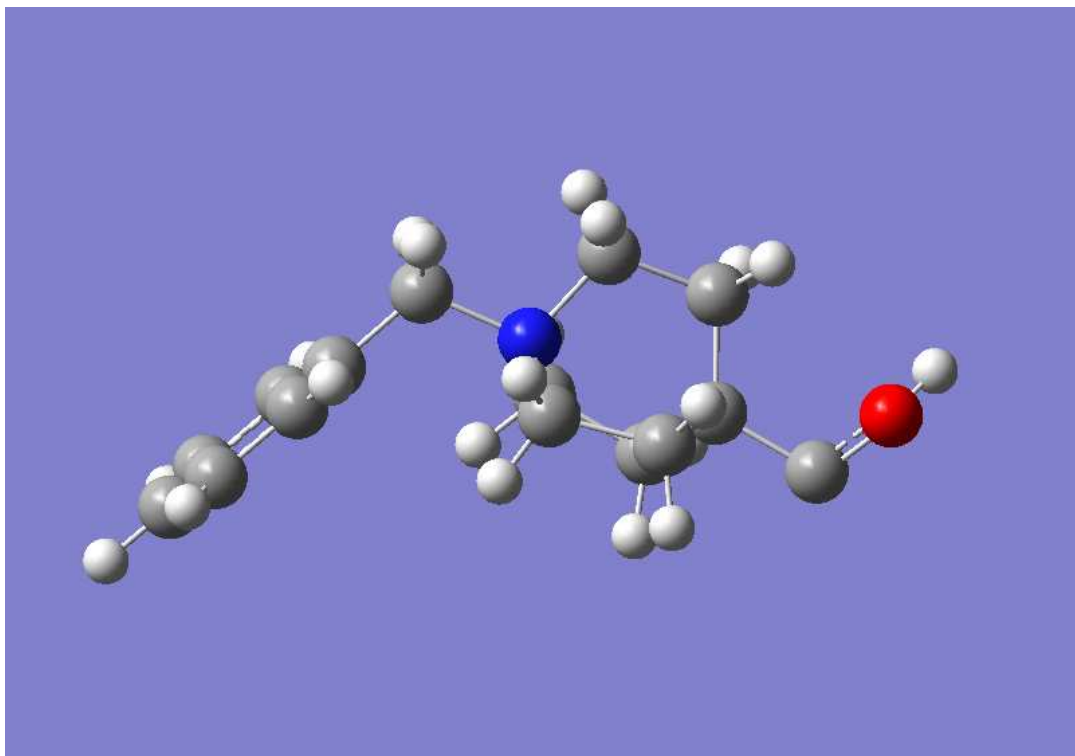
H	0.00764000	2.52923107	1.51293504
H	-1.38503695	1.66267705	2.14795709
C	0.07636600	0.37445399	1.13087904
H	1.14099598	0.55281699	0.98801303
H	-0.03231500	-0.23851401	2.02463102
N	-1.46207201	2.04287791	0.08853300
C	-2.00806499	3.47328806	0.14699100
H	-1.12808394	4.11243296	0.12650201
H	-2.55158496	3.60670805	-0.78564602
C	0.06335200	-1.75974405	-0.17296700
O	0.75520998	-2.15711689	-1.06761503
H	-0.21332800	-2.41267705	0.67893398
C	-2.87553501	3.77748489	1.32872295
C	-4.25877094	3.60746002	1.25064600
C	-2.31871104	4.27505112	2.50771999
C	-5.06665802	3.89850211	2.34105492
H	-4.71091223	3.26770496	0.32778201
C	-3.12532711	4.56583691	3.59865308
H	-1.25358605	4.45572186	2.57017112
C	-4.49939585	4.37110710	3.51842809
H	-6.13700199	3.76981211	2.26748800
H	-2.68475199	4.95647001	4.50471401
H	-5.12836313	4.60396004	4.36577988

S60.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	36.03960000	1.96610000	0.00000000
2	54.90740000	6.44960000	0.00000000
3	64.13060000	0.90560000	0.00000000
4	92.46910000	0.14570000	0.00000000
5	112.80080000	0.15690000	0.00000000
6	154.65360000	8.25630000	0.00000000
7	209.66820000	0.05070000	0.00000000
8	222.10610000	0.10270000	0.00000000
9	253.58590000	1.21350000	0.00000000
10	261.95040000	0.85780000	0.00000000
11	331.43260000	4.66260000	0.00000000
12	342.14890000	1.68420000	0.00000000
13	377.96350000	1.21350000	0.00000000
14	394.71610000	0.13470000	0.00000000
15	418.00950000	0.06320000	0.00000000
16	421.56450000	0.44800000	0.00000000
17	423.02700000	0.25710000	0.00000000
18	481.22280000	3.43430000	0.00000000
19	536.80660000	0.56080000	0.00000000
20	541.53080000	0.18070000	0.00000000
21	584.38060000	4.90910000	0.00000000
22	639.04370000	0.11210000	0.00000000
23	639.87430000	2.98540000	0.00000000
24	686.63140000	24.55090000	0.00000000
25	724.76030000	45.46880000	0.00000000
26	738.44180000	23.17290000	0.00000000
27	786.55780000	32.56210000	0.00000000
28	802.69710000	1.14030000	0.00000000
29	831.64140000	9.98890000	0.00000000
30	836.65450000	5.68690000	0.00000000
31	852.53060000	50.17540000	0.00000000
32	854.43520000	4.06010000	0.00000000
33	869.68750000	0.07190000	0.00000000
34	899.74710000	0.73960000	0.00000000
35	936.18310000	0.88050000	0.00000000
36	954.49540000	3.27320000	0.00000000
37	974.96570000	6.98090000	0.00000000
38	991.83780000	0.99160000	0.00000000
39	997.22810000	4.24220000	0.00000000
40	1006.50800000	0.00980000	0.00000000
41	1016.33230000	1.07940000	0.00000000
42	1025.06470000	2.32330000	0.00000000
43	1028.32210000	3.39020000	0.00000000
44	1036.75930000	0.02640000	0.00000000
45	1045.08280000	4.05860000	0.00000000
46	1055.22880000	0.39350000	0.00000000
47	1056.84300000	1.03040000	0.00000000
48	1062.96180000	2.23770000	0.00000000
49	1067.23680000	18.64420000	0.00000000
50	1122.29820000	5.33910000	0.00000000
51	1145.95800000	43.17330000	0.00000000
52	1189.70190000	1.59940000	0.00000000
53	1196.57740000	0.04180000	0.00000000
54	1204.12960000	0.12060000	0.00000000
55	1214.55420000	0.41030000	0.00000000
56	1216.67570000	12.91560000	0.00000000
57	1240.69550000	18.42690000	0.00000000
58	1256.46290000	0.88290000	0.00000000
59	1283.47860000	1.57160000	0.00000000
60	1295.64190000	5.03500000	0.00000000

61	1305.36030000	2.45280000	0.00000000
62	1327.29450000	8.49350000	0.00000000
63	1336.68970000	1.74180000	0.00000000
64	1347.98800000	1.47580000	0.00000000
65	1348.49760000	5.37000000	0.00000000
66	1364.10770000	5.02840000	0.00000000
67	1368.23580000	11.39010000	0.00000000
68	1376.97170000	0.53560000	0.00000000
69	1395.70890000	2.35290000	0.00000000
70	1403.07050000	11.64060000	0.00000000
71	1405.91520000	12.02570000	0.00000000
72	1419.27260000	3.50110000	0.00000000
73	1439.40570000	8.21100000	0.00000000
74	1493.04070000	4.47500000	0.00000000
75	1496.90800000	6.93160000	0.00000000
76	1501.85390000	1.95300000	0.00000000
77	1504.00310000	3.25290000	0.00000000
78	1511.12090000	20.72000000	0.00000000
79	1514.27390000	6.86660000	0.00000000
80	1515.10820000	19.87730000	0.00000000
81	1538.28870000	3.04860000	0.00000000
82	1539.62300000	5.07700000	0.00000000
83	1630.66750000	2.45450000	0.00000000
84	1647.74080000	2.89640000	0.00000000
85	1820.41740000	188.80690000	0.00000000
86	2893.74610000	67.19610000	0.00000000
87	3060.98850000	7.02520000	0.00000000
88	3062.71750000	9.94180000	0.00000000
89	3075.10640000	7.35880000	0.00000000
90	3078.48430000	1.91510000	0.00000000
91	3083.99220000	5.86720000	0.00000000
92	3087.79510000	2.90280000	0.00000000
93	3097.65760000	5.97170000	0.00000000
94	3100.66490000	3.54930000	0.00000000
95	3103.56320000	5.92360000	0.00000000
96	3118.11130000	1.40640000	0.00000000
97	3128.29920000	0.26940000	0.00000000
98	3138.35950000	4.51050000	0.00000000
99	3151.33190000	1.18140000	0.00000000
100	3154.11570000	3.13270000	0.00000000
101	3166.87220000	5.79580000	0.00000000
102	3169.08040000	6.29330000	0.00000000
103	3188.29700000	0.86650000	0.00000000
104	3197.79500000	4.22130000	0.00000000
105	3206.95280000	1.53010000	0.00000000

S61. CALCULATIONS ON 14 - H → 14 - H (CIS-ISOMER) (TS)



```

Route : # opt=(calcf,ts,noeigen) freq b3lyp/cc-pvtz geom=connectivity empiric
       : aldispersion=gd3bj int=ultrafine pop=regular
SMILES : c1ccc(cc1)C[N+]23CCC(CC2)(CC3)[C]O
Formula : C15H20NO+
Charge : 1
Multiplicity : 1
Energy : -713.57950977 a.u.
Gibbs Energy : -713.29717000 a.u.
Number of imaginary frequencies : 1

```

S61.1. Cartesian Co-ordinates (XYZ format)

37

```

C 0.44125101 -1.40015399 -0.76454401
C 1.13437498 -0.19047700 -0.12399700
C -1.06815195 -1.13402605 -0.85001302
H 0.83451903 -1.57849705 -1.76376700
H 0.65247500 -2.29174399 -0.17818800
H -1.38337398 -0.83603698 -1.84751797
H -1.65606701 -1.99250996 -0.54470998
C 0.64002198 1.09127796 -0.80729097
H 1.20423400 1.95188498 -0.45569000
H 0.78495699 1.01700199 -1.88503504
C -0.84854698 1.28799999 -0.48607901
H -1.01057303 2.04823089 0.27449501
H -1.43179595 1.55341804 -1.36367202
C -0.83903599 -0.25170299 1.42701995

```

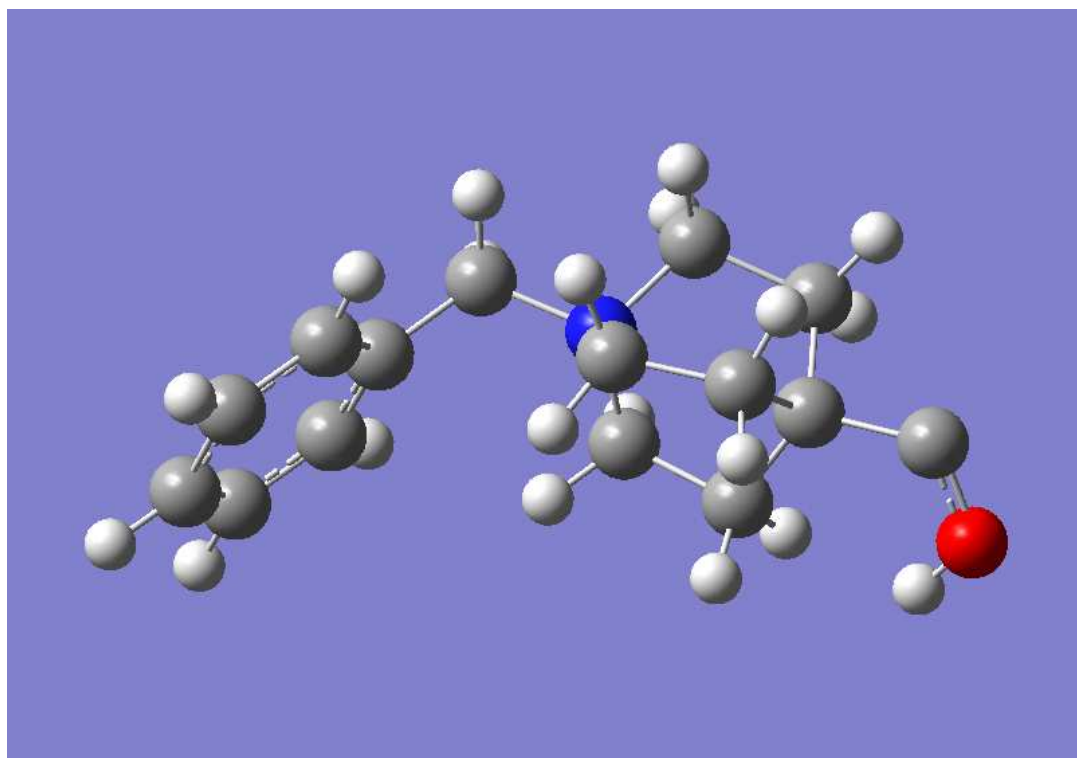
H	-1.27080297	0.47183299	2.11287403
H	-1.16649902	-1.24201202	1.72524798
C	0.68990701	-0.12958500	1.36364400
H	1.02528703	0.80913299	1.80015695
H	1.14735198	-0.93757802	1.93170202
N	-1.44430900	0.00866300	0.06692200
C	-2.96380401	0.17790000	0.15163000
H	-3.11662292	1.09449196	0.71729898
H	-3.28720999	0.34825400	-0.87286103
C	2.62406611	-0.45030299	-0.02712800
O	3.30481410	0.70160502	0.03027000
H	3.63266802	1.11796498	-0.77549601
C	-3.70010209	-0.97083801	0.76826400
C	-4.19130993	-2.00471711	-0.03039800
C	-3.94196606	-1.00187802	2.14230609
C	-4.88255119	-3.06578708	0.53767598
H	-4.05278206	-1.97208703	-1.10333204
C	-4.63235092	-2.06235409	2.71145511
H	-3.60722494	-0.18661900	2.77026200
C	-5.09710598	-3.09891510	1.91028905
H	-5.26362610	-3.85791993	-0.09074700
H	-4.81868219	-2.07384992	3.77578402
H	-5.63997221	-3.92195010	2.35270000

S61.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-1107.53850000	180.35000000	0.00000000
2	34.29100000	0.32460000	0.00000000
3	59.78020000	1.20610000	0.00000000
4	66.19180000	0.40060000	0.00000000
5	96.05340000	4.29080000	0.00000000
6	124.18780000	0.29780000	0.00000000
7	157.78490000	2.82520000	0.00000000
8	216.04910000	12.97100000	0.00000000
9	220.88670000	4.22360000	0.00000000
10	255.10620000	2.20180000	0.00000000
11	265.90320000	9.17190000	0.00000000
12	323.73270000	3.15530000	0.00000000
13	347.28640000	6.55430000	0.00000000
14	365.36840000	2.63990000	0.00000000
15	394.61950000	3.65190000	0.00000000
16	417.32110000	0.06000000	0.00000000
17	421.11130000	0.09770000	0.00000000
18	428.91300000	2.26250000	0.00000000
19	480.76660000	2.66430000	0.00000000
20	530.07150000	0.59650000	0.00000000
21	538.68740000	2.41710000	0.00000000
22	582.10600000	9.64950000	0.00000000
23	634.44060000	3.89370000	0.00000000
24	639.07870000	0.08610000	0.00000000
25	675.26450000	26.65080000	0.00000000
26	724.10300000	64.99530000	0.00000000
27	725.66010000	52.14130000	0.00000000
28	729.47300000	224.32480000	0.00000000
29	786.05060000	34.65080000	0.00000000
30	798.66420000	1.75530000	0.00000000
31	824.28770000	15.48380000	0.00000000
32	837.58950000	8.01270000	0.00000000
33	845.82200000	29.13300000	0.00000000
34	851.09170000	1.85610000	0.00000000
35	868.93530000	0.04900000	0.00000000
36	901.56840000	0.96830000	0.00000000
37	938.44700000	6.30350000	0.00000000
38	953.77520000	2.71770000	0.00000000
39	974.47620000	2.96550000	0.00000000
40	990.81110000	2.67410000	0.00000000
41	995.56420000	0.45870000	0.00000000
42	1005.82340000	0.00820000	0.00000000
43	1015.31200000	1.99630000	0.00000000
44	1020.97650000	7.47280000	0.00000000
45	1028.36580000	3.73270000	0.00000000
46	1036.06630000	0.04060000	0.00000000
47	1042.65710000	4.92550000	0.00000000
48	1051.75940000	6.05440000	0.00000000
49	1056.45830000	1.51420000	0.00000000
50	1066.17710000	3.80280000	0.00000000
51	1117.83620000	51.14300000	0.00000000
52	1122.71490000	11.49020000	0.00000000
53	1176.00300000	6.20750000	0.00000000
54	1196.37700000	0.24280000	0.00000000
55	1200.05130000	21.82490000	0.00000000
56	1202.46250000	20.10610000	0.00000000
57	1214.81670000	2.63910000	0.00000000
58	1226.57240000	180.24250000	0.00000000
59	1240.53760000	12.91610000	0.00000000
60	1251.69800000	4.65810000	0.00000000

61	1281.41280000	1.00050000	0.00000000
62	1285.33920000	10.85000000	0.00000000
63	1293.49080000	5.28840000	0.00000000
64	1320.50810000	4.17070000	0.00000000
65	1331.63660000	2.30680000	0.00000000
66	1343.46210000	5.02090000	0.00000000
67	1347.04410000	0.69570000	0.00000000
68	1361.35980000	4.27580000	0.00000000
69	1364.87070000	11.26630000	0.00000000
70	1375.99730000	2.09710000	0.00000000
71	1378.20710000	0.21050000	0.00000000
72	1400.90410000	11.66570000	0.00000000
73	1405.57410000	8.94980000	0.00000000
74	1436.71870000	11.08300000	0.00000000
75	1492.67180000	3.47780000	0.00000000
76	1496.96230000	7.46040000	0.00000000
77	1502.48340000	2.47160000	0.00000000
78	1504.02800000	5.48810000	0.00000000
79	1511.49040000	21.70530000	0.00000000
80	1513.05660000	6.87500000	0.00000000
81	1516.09450000	11.00130000	0.00000000
82	1538.31660000	3.55950000	0.00000000
83	1539.00260000	5.84420000	0.00000000
84	1630.78020000	2.44380000	0.00000000
85	1647.91820000	2.66540000	0.00000000
86	3057.19750000	11.28110000	0.00000000
87	3069.11550000	4.11040000	0.00000000
88	3072.26860000	4.36010000	0.00000000
89	3074.16350000	4.58940000	0.00000000
90	3081.53940000	7.36770000	0.00000000
91	3085.58410000	5.62790000	0.00000000
92	3095.80790000	6.27890000	0.00000000
93	3108.21160000	3.90710000	0.00000000
94	3110.05810000	2.49190000	0.00000000
95	3112.26850000	3.99980000	0.00000000
96	3126.48350000	0.18570000	0.00000000
97	3135.23120000	5.44510000	0.00000000
98	3151.05390000	1.50250000	0.00000000
99	3154.23550000	2.25200000	0.00000000
100	3167.36930000	5.70980000	0.00000000
101	3168.64630000	6.76550000	0.00000000
102	3188.20820000	0.91670000	0.00000000
103	3197.71510000	4.47390000	0.00000000
104	3206.92340000	1.68660000	0.00000000
105	3807.37960000	270.69690000	0.00000000

S62. CALCULATIONS ON 14 – H (CIS-ISOMER) (TS)



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES              : c1ccc(cc1)C[N+]23CCC(CC2)(CC3)[C]O
Formula             : C15H20NO+
Charge              : 1
Multiplicity        : 1
Energy              : -713.61192313 a.u.
Gibbs Energy        : -713.32711300 a.u.
Number of imaginary frequencies : 0

```

S62.1. Cartesian Co-ordinates (XYZ format)

37

```

C -1.95612299 -0.36100900 0.25375301
C -0.41692600 -0.29270899 0.19303100
C -2.54383206 1.01302099 -0.10057300
H -2.33369708 -1.10555100 -0.44484901
H -2.25868797 -0.67746502 1.24908304
H -2.93601108 1.05400300 -1.11150301
H -3.33594704 1.30643499 0.58253902
C -0.02426000 0.37092799 -1.13831496
H 1.05605197 0.34804600 -1.29673600
H -0.49075300 -0.14810200 -1.97612405
C -0.46939799 1.84186995 -1.12160301
H 0.35770801 2.52095604 -0.92841899
H -0.94805300 2.13656402 -2.04875207
C -0.76339197 1.92466998 1.31569004

```

H	-0.13886601	2.80430889	1.44602203
H	-1.54093504	1.94111097	2.07554007
C	0.05045500	0.62484002	1.34139800
H	1.11366498	0.83699298	1.23575199
H	-0.08400200	0.11669500	2.29342389
N	-1.47104001	2.07482791	-0.01385800
C	-2.06603909	3.48435903	-0.09312300
H	-2.66308689	3.58982992	0.80996799
H	-1.21365595	4.15641022	-0.02198100
C	0.08638400	-1.69207394	0.51359600
O	0.89139199	-2.19913507	-0.36107901
H	1.10547996	-1.64180505	-1.14266396
C	-2.87773395	3.76563597	-1.31938303
C	-2.27709103	4.31934118	-2.45126104
C	-4.25133181	3.51930690	-1.33241200
C	-3.02900696	4.59165096	-3.58564901
H	-1.22202897	4.56099319	-2.44044304
C	-5.00391912	3.79050899	-2.46615505
H	-4.74119902	3.13229394	-0.44858599
C	-4.39198780	4.32047892	-3.59620690
H	-2.55529308	5.02709818	-4.45375776
H	-6.06782913	3.60149598	-2.46354008
H	-4.97942877	4.53804588	-4.47677898

S62.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	34.92920000	1.19460000	0.00000000
2	44.65560000	0.67630000	0.00000000
3	70.81560000	1.59800000	0.00000000
4	85.01920000	3.17110000	0.00000000
5	120.19670000	0.17040000	0.00000000
6	168.97550000	8.05400000	0.00000000
7	207.21470000	10.88280000	0.00000000
8	237.47340000	1.01600000	0.00000000
9	250.41790000	1.10810000	0.00000000
10	269.30940000	13.49630000	0.00000000
11	325.32820000	1.72390000	0.00000000
12	360.35070000	7.41210000	0.00000000
13	378.88760000	18.50490000	0.00000000
14	400.43090000	6.25070000	0.00000000
15	416.33510000	1.18820000	0.00000000
16	418.49130000	0.08110000	0.00000000
17	422.97430000	0.09900000	0.00000000
18	477.73530000	1.69550000	0.00000000
19	534.99720000	0.16550000	0.00000000
20	540.56880000	0.20760000	0.00000000
21	582.81910000	19.37800000	0.00000000
22	624.70540000	10.14670000	0.00000000
23	639.05530000	0.10470000	0.00000000
24	671.31090000	2.36960000	0.00000000
25	714.15980000	3.83920000	0.00000000
26	724.39080000	43.74950000	0.00000000
27	785.98130000	36.20180000	0.00000000
28	799.26320000	24.36410000	0.00000000
29	801.41170000	14.99710000	0.00000000
30	833.49620000	25.73000000	0.00000000
31	837.30060000	13.35860000	0.00000000
32	842.34030000	21.60460000	0.00000000
33	854.18710000	3.39830000	0.00000000
34	869.31730000	0.26360000	0.00000000
35	904.63110000	2.26840000	0.00000000
36	954.11810000	6.64130000	0.00000000
37	961.29910000	13.19380000	0.00000000
38	982.01070000	1.90680000	0.00000000
39	991.39370000	0.07810000	0.00000000
40	1002.37880000	1.88010000	0.00000000
41	1006.28370000	0.02160000	0.00000000
42	1014.43660000	3.66960000	0.00000000
43	1016.40240000	1.15260000	0.00000000
44	1028.30630000	3.88580000	0.00000000
45	1036.61660000	0.06410000	0.00000000
46	1048.01370000	6.64480000	0.00000000
47	1050.41550000	7.29110000	0.00000000
48	1056.58990000	0.98940000	0.00000000
49	1064.63180000	11.43460000	0.00000000
50	1115.37700000	27.70560000	0.00000000
51	1122.15040000	5.09880000	0.00000000
52	1184.52900000	0.61920000	0.00000000
53	1193.59840000	2.32680000	0.00000000
54	1196.63670000	0.19990000	0.00000000
55	1205.48990000	0.26500000	0.00000000
56	1214.58390000	1.06810000	0.00000000
57	1240.16810000	18.18670000	0.00000000
58	1253.97790000	0.73920000	0.00000000
59	1281.92610000	12.61060000	0.00000000
60	1290.75230000	7.30470000	0.00000000

61	1295.97960000	40.32340000	0.00000000
62	1317.72270000	198.35040000	0.00000000
63	1321.90530000	1.98880000	0.00000000
64	1333.75420000	2.48800000	0.00000000
65	1344.36300000	3.63620000	0.00000000
66	1348.96010000	2.07090000	0.00000000
67	1364.11290000	8.82650000	0.00000000
68	1365.63890000	6.10200000	0.00000000
69	1376.26080000	26.11250000	0.00000000
70	1379.65410000	28.94070000	0.00000000
71	1383.86930000	34.91740000	0.00000000
72	1403.09600000	11.26500000	0.00000000
73	1406.57380000	10.01490000	0.00000000
74	1438.38530000	11.70600000	0.00000000
75	1493.44370000	4.39960000	0.00000000
76	1496.88470000	7.38890000	0.00000000
77	1503.27940000	3.98880000	0.00000000
78	1504.79710000	2.65800000	0.00000000
79	1512.78280000	14.86000000	0.00000000
80	1513.93060000	9.62150000	0.00000000
81	1515.74160000	12.01250000	0.00000000
82	1538.20220000	3.29430000	0.00000000
83	1540.11230000	7.28940000	0.00000000
84	1630.55940000	2.47770000	0.00000000
85	1647.72390000	2.88510000	0.00000000
86	3032.57160000	11.14630000	0.00000000
87	3065.23860000	7.08790000	0.00000000
88	3073.25240000	4.02120000	0.00000000
89	3074.62030000	7.50290000	0.00000000
90	3075.59440000	2.77660000	0.00000000
91	3084.23890000	5.17060000	0.00000000
92	3089.15870000	8.14010000	0.00000000
93	3095.72320000	6.35600000	0.00000000
94	3112.17160000	1.32550000	0.00000000
95	3114.43620000	1.96370000	0.00000000
96	3127.84420000	0.33100000	0.00000000
97	3137.52650000	4.09220000	0.00000000
98	3150.40750000	1.23470000	0.00000000
99	3153.17790000	2.87530000	0.00000000
100	3166.21500000	6.14160000	0.00000000
101	3169.63360000	5.90030000	0.00000000
102	3188.30560000	0.85940000	0.00000000
103	3197.77590000	4.22060000	0.00000000
104	3206.96340000	1.53980000	0.00000000
105	3413.35390000	40.38150000	0.00000000

S63. CALCULATIONS ON 14 – H (CIS-ISOMER) \rightarrow 1 – benzyl – 1 λ^4 – azabicyclo[2.2.2]octane

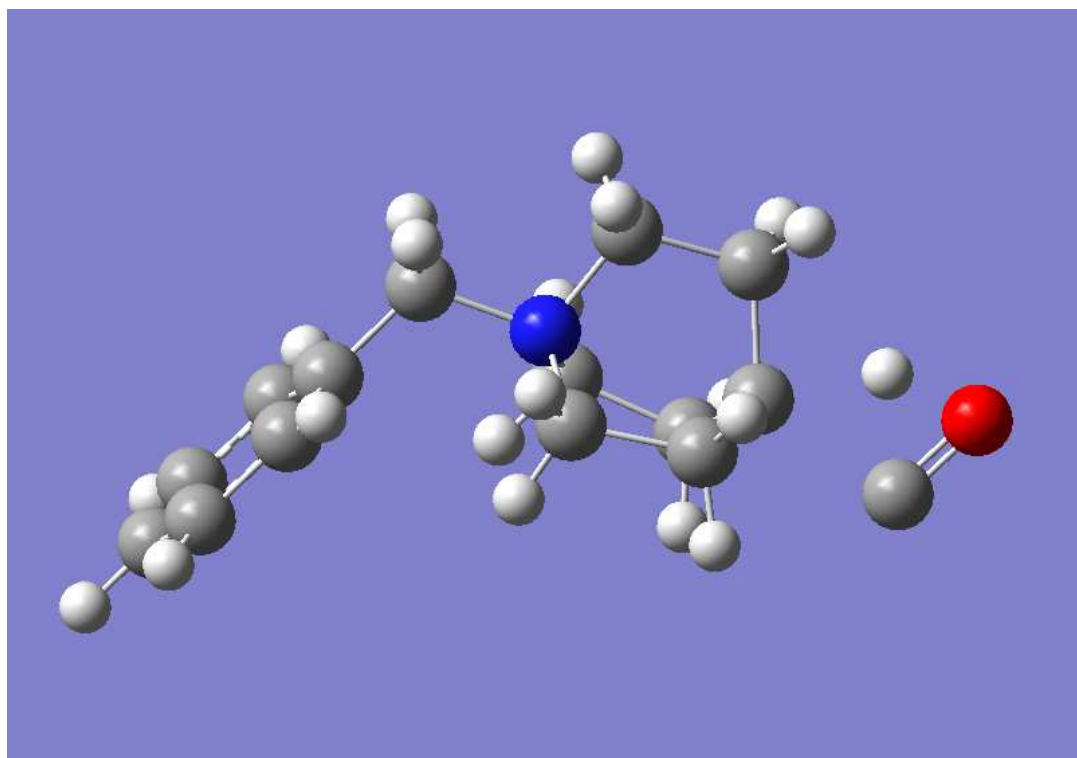


FIG. S1. Molecule

```

Route                : # opt=(calcf,ts,noeigen) freq b3lyp/cc-pvtz geom=connectivity empiric
                    : aldispersion=gd3bj int=ultrafine pop=regular
SMILES               : [C]O.c1ccc(cc1)C[N]23CC[C](CC2)CC3
Formula              : C15H20NO+
Charge               : 1
Multiplicity         : 1
Energy               : -713.52243117
Gibbs Energy         : -713.24525300
Number of imaginary frequencies : 1

```

a.u.
a.u.

S63.1. Cartesian Co-ordinates (XYZ format)

37

```

C -0.59399003 -0.77084899 1.19800496
C -1.09626901 0.02947100 0.00438500
C 0.94192201 -0.67245698 1.27284801
H -1.02208805 -0.40059599 2.12892294
H -0.90341997 -1.80942595 1.09554899
H 1.27905500 -0.01799300 2.07371306
H 1.41420805 -1.64060700 1.39707804
C -0.49716699 1.45845306 0.10474400
H -0.90927702 2.13525295 -0.64569402
H -0.70452702 1.89200306 1.08256304
C 1.02669597 1.35607898 -0.11492800
H 1.32036698 1.69787800 -1.10415196

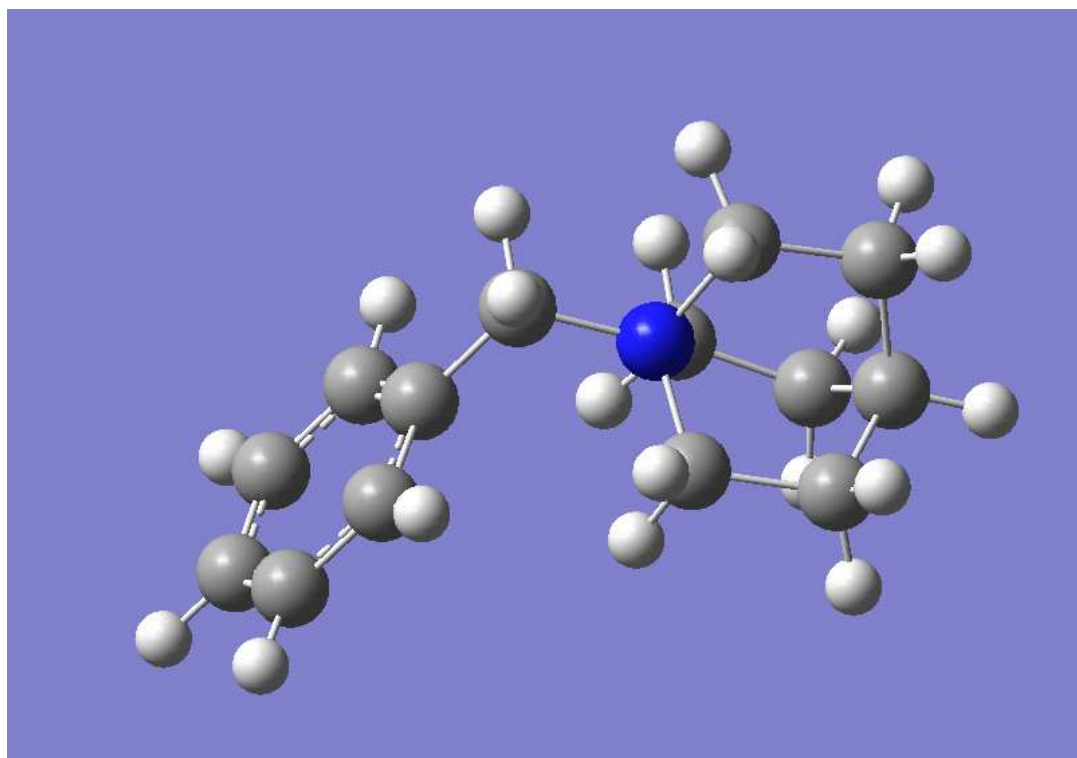
```

H	1.58348596	1.92413902	0.62571698
C	0.91986501	-0.85374701	-1.18119395
H	1.45681202	-0.52326697	-2.06610394
H	1.16265202	-1.89641595	-1.00500202
C	-0.59650898	-0.60568500	-1.28629398
H	-0.81409800	0.03929100	-2.13755298
H	-1.10511804	-1.55260897	-1.46199906
N	1.48663294	-0.08076900	-0.00906300
C	3.01858592	-0.09593600	-0.01787000
H	3.30299211	0.45467401	-0.91193199
H	3.31346107	0.48565799	0.85274702
C	-2.99412799	-0.44307500	-0.01072500
O	-3.54489803	0.67984998	-0.00412300
H	-2.38927388	0.82369500	0.01143100
C	3.64350295	-1.45652902	0.00388100
C	3.97382689	-2.06154990	1.21751499
C	3.94462109	-2.11749601	-1.18768501
C	4.56437206	-3.31728411	1.24055398
H	3.78848696	-1.54245603	2.14894891
C	4.53468895	-3.37312293	-1.16589904
H	3.73513889	-1.64426804	-2.13799596
C	4.83871412	-3.97708201	0.04861000
H	4.82137012	-3.77391410	2.18556499
H	4.76853323	-3.87390590	-2.09442997
H	5.30375290	-4.95241499	0.06550000

S63.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2260.59740000	371.58390000	0.00000000
2	35.09900000	0.00010000	0.00000000
3	60.61660000	0.42840000	0.00000000
4	69.89840000	0.59940000	0.00000000
5	96.52380000	0.34090000	0.00000000
6	101.02800000	0.43570000	0.00000000
7	124.40430000	4.90180000	0.00000000
8	169.78880000	5.67030000	0.00000000
9	211.72470000	13.15360000	0.00000000
10	232.44170000	0.09470000	0.00000000
11	236.05800000	13.93740000	0.00000000
12	295.62900000	32.82930000	0.00000000
13	309.52470000	0.34820000	0.00000000
14	319.97720000	0.29160000	0.00000000
15	370.53290000	0.56560000	0.00000000
16	398.52040000	5.03180000	0.00000000
17	417.39110000	0.03560000	0.00000000
18	421.32990000	0.00640000	0.00000000
19	466.92490000	4.82140000	0.00000000
20	530.66030000	0.28390000	0.00000000
21	541.40580000	0.42590000	0.00000000
22	570.43600000	172.29590000	0.00000000
23	586.18190000	11.56280000	0.00000000
24	637.62610000	5.46530000	0.00000000
25	639.08430000	0.09170000	0.00000000
26	696.76440000	1.58980000	0.00000000
27	724.31270000	43.09840000	0.00000000
28	783.18420000	95.98350000	0.00000000
29	790.44870000	26.08790000	0.00000000
30	800.69210000	0.39760000	0.00000000
31	831.29530000	5.71510000	0.00000000
32	834.84820000	3.17900000	0.00000000
33	850.52590000	3.27000000	0.00000000
34	862.43620000	9.71550000	0.00000000
35	869.41930000	0.12610000	0.00000000
36	898.64450000	7.34160000	0.00000000
37	906.52010000	4.66710000	0.00000000
38	954.45540000	5.85500000	0.00000000
39	978.04300000	23.21790000	0.00000000
40	984.65980000	0.49030000	0.00000000
41	997.54320000	8.64900000	0.00000000
42	1006.15590000	0.17230000	0.00000000
43	1012.08900000	1.16410000	0.00000000
44	1016.73410000	1.81590000	0.00000000
45	1020.50960000	3.21280000	0.00000000
46	1028.46430000	3.70210000	0.00000000
47	1036.16710000	0.23770000	0.00000000
48	1038.11500000	5.57730000	0.00000000
49	1056.45580000	2.90560000	0.00000000
50	1057.47460000	4.44540000	0.00000000
51	1071.28600000	54.00830000	0.00000000
52	1122.32620000	4.36770000	0.00000000
53	1180.71130000	19.32350000	0.00000000
54	1195.73780000	0.20730000	0.00000000
55	1197.84280000	0.47670000	0.00000000
56	1208.59210000	0.16880000	0.00000000
57	1214.78930000	1.20470000	0.00000000
58	1240.33410000	18.98200000	0.00000000
59	1254.95560000	1.30720000	0.00000000
60	1281.92200000	0.92690000	0.00000000

61	1298.62100000	3.15850000	0.00000000
62	1303.74360000	13.32780000	0.00000000
63	1325.94790000	9.37420000	0.00000000
64	1334.11910000	1.38810000	0.00000000
65	1344.21760000	7.61480000	0.00000000
66	1347.04590000	1.04420000	0.00000000
67	1361.47700000	11.82500000	0.00000000
68	1365.36070000	17.38730000	0.00000000
69	1372.94940000	0.39000000	0.00000000
70	1376.28250000	0.71800000	0.00000000
71	1400.80390000	14.65700000	0.00000000
72	1403.35890000	15.35880000	0.00000000
73	1433.37350000	8.87330000	0.00000000
74	1491.05420000	5.23070000	0.00000000
75	1494.67660000	280.23410000	0.00000000
76	1496.81760000	7.59450000	0.00000000
77	1500.58310000	51.27470000	0.00000000
78	1501.48450000	31.47170000	0.00000000
79	1508.75470000	58.02100000	0.00000000
80	1511.68160000	12.60030000	0.00000000
81	1512.33580000	4.64630000	0.00000000
82	1535.52670000	6.89890000	0.00000000
83	1538.33320000	3.55190000	0.00000000
84	1630.82770000	2.41800000	0.00000000
85	1647.90910000	2.86970000	0.00000000
86	2187.14290000	112.98840000	0.00000000
87	3042.90570000	8.90930000	0.00000000
88	3053.74900000	9.71210000	0.00000000
89	3060.78620000	5.74460000	0.00000000
90	3074.15070000	5.51670000	0.00000000
91	3081.41290000	3.37500000	0.00000000
92	3084.42500000	8.89740000	0.00000000
93	3085.53960000	4.63610000	0.00000000
94	3093.48400000	9.56340000	0.00000000
95	3094.15150000	3.40620000	0.00000000
96	3102.03880000	5.22600000	0.00000000
97	3126.53010000	0.40900000	0.00000000
98	3136.58020000	4.23440000	0.00000000
99	3149.99910000	1.48980000	0.00000000
100	3152.85770000	2.78270000	0.00000000
101	3167.61480000	5.78270000	0.00000000
102	3169.63790000	6.27140000	0.00000000
103	3188.22760000	0.96050000	0.00000000
104	3197.77130000	4.50800000	0.00000000
105	3206.90190000	1.66680000	0.00000000

S64. CALCULATIONS ON 1 – benzyl – 1 λ^4 – azabicyclo[2.2.2]octane

```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : c1ccc(cc1)C[N+]23CCC(CC2)CC3
Formula              : C14H20N+
Charge               : 1
Multiplicity         : 1
Energy               : -600.34413322 a.u.
Gibbs Energy         : -600.06361900 a.u.
Number of imaginary frequencies : 0

```

S64.1. Cartesian Co-ordinates (XYZ format)

35

```

C -0.38517401  0.97383100 -1.25735998
C -1.10891700  0.25440001 -0.11496300
C  1.09984195  0.57552397 -1.23443604
H -0.81613702  0.70278800 -2.21907306
H -0.49008900  2.05234909 -1.14925396
H  1.35260403 -0.12918299 -2.02306795
H  1.76223600  1.43279803 -1.31908405
C -0.78008801 -1.23949397 -0.19110399
H -1.37203801 -1.80078197  0.52901000
H -1.02224600 -1.62749100 -1.17950499
C  0.71489501 -1.44349504  0.11248900
H  0.88924497 -1.85440195  1.10145605
H  1.20045602 -2.09001994 -0.61313403
C  0.95166999  0.74382502  1.21461999

```

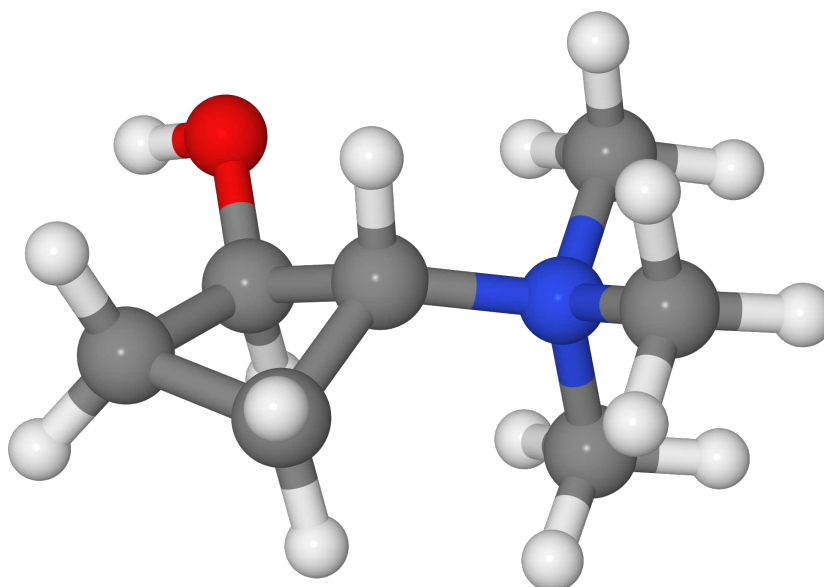
H	1.35189104	0.31296101	2.12555289
H	1.40369105	1.72240603	1.06877697
C	-0.58580500	0.80116302	1.21615195
H	-0.98390502	0.21723200	2.04471993
H	-0.90714002	1.83031499	1.36377597
N	1.43991804	-0.11580200	0.06967900
C	2.95775294	-0.30671600	0.13073400
H	3.37186098	0.69820899	0.08896100
H	3.21604395	-0.82327098	-0.79109299
H	-2.18220997	0.40914199	-0.19201100
C	3.46224189	-1.04992902	1.32885695
C	3.60808301	-2.43730307	1.29247606
C	3.83546996	-0.35893899	2.48265290
C	4.08720779	-3.12386703	2.39899302
H	3.36458802	-2.98410201	0.39099899
C	4.31510019	-1.04444206	3.59007692
H	3.77168489	0.72111797	2.51068997
C	4.43464088	-2.42844105	3.55133891
H	4.20163107	-4.19760323	2.35800505
H	4.60703897	-0.49882999	4.47592497
H	4.81379700	-2.96240091	4.41098309

S64.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	37.09030000	0.03240000	0.00000000
2	74.51180000	0.09670000	0.00000000
3	90.32240000	0.26930000	0.00000000
4	96.03460000	0.06860000	0.00000000
5	206.45250000	2.51890000	0.00000000
6	227.12820000	0.91020000	0.00000000
7	261.98190000	0.76430000	0.00000000
8	304.18340000	0.15430000	0.00000000
9	308.71330000	0.05850000	0.00000000
10	372.58710000	0.16060000	0.00000000
11	399.94180000	0.19630000	0.00000000
12	417.81830000	0.04970000	0.00000000
13	421.88330000	0.00070000	0.00000000
14	463.02000000	1.49790000	0.00000000
15	532.34870000	1.32650000	0.00000000
16	536.30400000	0.05460000	0.00000000
17	568.32080000	15.04600000	0.00000000
18	628.29420000	6.20740000	0.00000000
19	639.20030000	0.09190000	0.00000000
20	693.78750000	1.60870000	0.00000000
21	724.22150000	43.19000000	0.00000000
22	785.59890000	33.22740000	0.00000000
23	803.42820000	0.57580000	0.00000000
24	817.05400000	4.06370000	0.00000000
25	830.61740000	4.40450000	0.00000000
26	836.95330000	5.01200000	0.00000000
27	853.29170000	1.93110000	0.00000000
28	869.25730000	0.06540000	0.00000000
29	890.04250000	36.08620000	0.00000000
30	898.28130000	0.27980000	0.00000000
31	936.96730000	0.97800000	0.00000000
32	943.31880000	4.78350000	0.00000000
33	955.88410000	2.68960000	0.00000000
34	981.17630000	0.35880000	0.00000000
35	1001.83330000	9.65660000	0.00000000
36	1005.75970000	0.02100000	0.00000000
37	1016.67620000	1.82620000	0.00000000
38	1028.43770000	3.65360000	0.00000000
39	1035.62340000	0.08000000	0.00000000
40	1043.51220000	1.39130000	0.00000000
41	1051.48470000	2.96820000	0.00000000
42	1052.92440000	2.59050000	0.00000000
43	1056.88450000	2.20210000	0.00000000
44	1074.75370000	42.81540000	0.00000000
45	1121.82910000	5.08030000	0.00000000
46	1146.27970000	0.38520000	0.00000000
47	1146.87690000	0.80680000	0.00000000
48	1196.09000000	0.10170000	0.00000000
49	1201.94010000	0.00840000	0.00000000
50	1214.86430000	0.66000000	0.00000000
51	1227.46120000	0.64880000	0.00000000
52	1239.39380000	9.36650000	0.00000000
53	1244.65860000	9.87740000	0.00000000
54	1271.20350000	0.66720000	0.00000000
55	1281.20980000	0.37950000	0.00000000
56	1318.59230000	3.77280000	0.00000000
57	1321.90830000	3.15180000	0.00000000
58	1340.82200000	6.77600000	0.00000000
59	1345.99950000	0.29840000	0.00000000
60	1360.87030000	5.95930000	0.00000000

61	1364.07300000	8.46000000	0.00000000
62	1369.95940000	1.55410000	0.00000000
63	1379.79990000	4.74770000	0.00000000
64	1382.21650000	0.48650000	0.00000000
65	1384.85010000	2.50590000	0.00000000
66	1409.14260000	7.09790000	0.00000000
67	1411.54910000	8.48540000	0.00000000
68	1438.81690000	12.19720000	0.00000000
69	1492.86320000	4.02540000	0.00000000
70	1496.98020000	6.99090000	0.00000000
71	1503.10160000	2.96100000	0.00000000
72	1504.56770000	3.46230000	0.00000000
73	1512.94740000	20.29070000	0.00000000
74	1514.71840000	9.24480000	0.00000000
75	1516.28300000	13.13230000	0.00000000
76	1538.50500000	3.20740000	0.00000000
77	1540.18070000	7.20430000	0.00000000
78	1630.88970000	2.36650000	0.00000000
79	1648.27290000	2.76440000	0.00000000
80	3064.74410000	11.94290000	0.00000000
81	3065.26360000	10.46290000	0.00000000
82	3065.74030000	12.53270000	0.00000000
83	3074.77430000	3.80310000	0.00000000
84	3082.23250000	4.76480000	0.00000000
85	3085.08910000	6.69730000	0.00000000
86	3094.74090000	9.14700000	0.00000000
87	3099.96700000	5.46940000	0.00000000
88	3104.43630000	8.35680000	0.00000000
89	3105.15710000	6.89540000	0.00000000
90	3106.45770000	7.61150000	0.00000000
91	3126.86430000	0.11540000	0.00000000
92	3135.47630000	6.40390000	0.00000000
93	3149.50690000	2.15660000	0.00000000
94	3152.86370000	3.79280000	0.00000000
95	3167.61860000	5.64140000	0.00000000
96	3169.47340000	6.16090000	0.00000000
97	3187.88180000	0.99590000	0.00000000
98	3197.37420000	4.82790000	0.00000000
99	3206.60520000	1.78200000	0.00000000

S65. CALCULATIONS ON E-2-N,N,N TRIMETHYLAMMONIUM CYCLOBUTANOL



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N](C)(C)C1CCC1O
Formula              : C7H16NO+
Charge               : 1
Multiplicity         : 1
Energy               : -406.27786592
Gibbs Energy        : -406.08109400
Number of imaginary frequencies : 0

```

a.u.
a.u.

S65.1. Cartesian Co-ordinates (XYZ format)

25

```

C -0.10848200  0.41996700 -0.20535800
H -0.26445699  0.73943102 -1.23401105
C -0.54326898  1.52960396  0.76455599
H -0.39922401  2.55398202  0.43752500
H -0.13894200  1.40964496  1.76709497
C -1.96980000  0.92148298  0.65784001
H -2.53474689  1.35826099 -0.16240101
H -2.57401109  0.90691900  1.55889201
N  1.29426801 -0.16509300 -0.18618301
C  1.36698496 -1.24329805 -1.23223197
H  2.35784888 -1.68722999 -1.20703101
H  0.60359699 -1.98498297 -1.02270496
H  1.17986298 -0.79742402 -2.20413995
C  2.26688409  0.92650300 -0.51998103
H  1.99705005  1.35344696 -1.48115802
H  2.21992207  1.68781602  0.25217000
H  3.26650190  0.50443703 -0.56801200
C  1.65306604 -0.74962598  1.14503503
H  0.99010497 -1.57901800  1.36319196

```

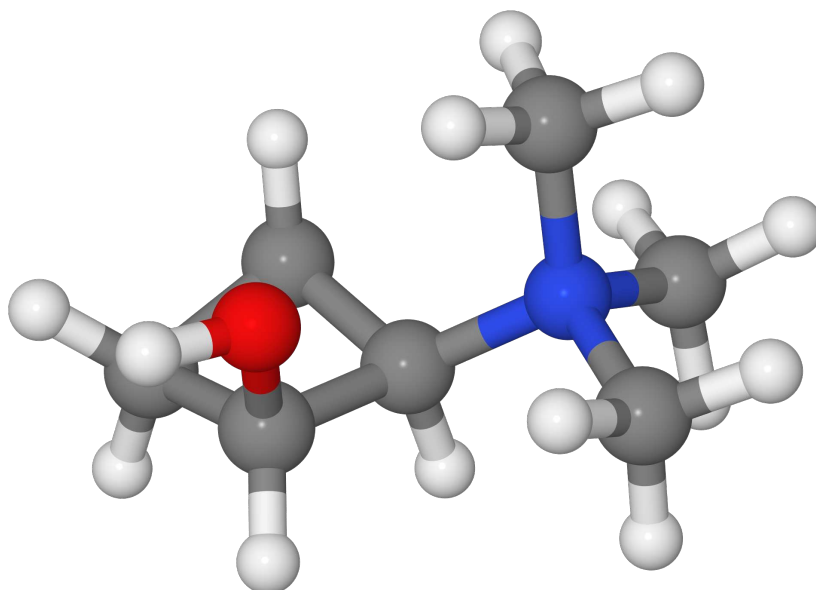
H 2.67804694 -1.10470605 1.09634495
H 1.56613398 0.01466800 1.90929699
C -1.31268299 -0.41553399 0.22101700
O -1.83879197 -1.18608403 -0.82273000
H -2.62978292 -1.65208602 -0.53111100
H -1.09757996 -1.02012706 1.10694695

S65.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	51.06660000	0.15480000	0.00000000
2	141.98830000	2.49980000	0.00000000
3	190.43960000	0.70560000	0.00000000
4	220.96020000	0.05970000	0.00000000
5	255.18400000	1.97940000	0.00000000
6	271.41210000	0.43730000	0.00000000
7	288.92200000	6.91640000	0.00000000
8	298.73680000	43.71350000	0.00000000
9	303.06010000	67.03490000	0.00000000
10	346.39320000	1.54380000	0.00000000
11	383.89610000	1.52580000	0.00000000
12	424.71390000	2.55520000	0.00000000
13	455.62000000	4.38220000	0.00000000
14	482.68270000	2.66960000	0.00000000
15	552.61040000	3.55020000	0.00000000
16	601.55020000	3.26160000	0.00000000
17	754.54780000	0.11780000	0.00000000
18	814.94910000	4.11340000	0.00000000
19	837.40480000	17.57700000	0.00000000
20	903.08010000	20.34780000	0.00000000
21	943.18890000	6.50520000	0.00000000
22	954.75500000	20.07120000	0.00000000
23	967.65040000	16.53790000	0.00000000
24	1002.98710000	11.88580000	0.00000000
25	1020.84500000	27.31570000	0.00000000
26	1078.51060000	0.08420000	0.00000000
27	1091.51340000	2.44300000	0.00000000
28	1101.10680000	3.84750000	0.00000000
29	1141.46090000	53.25750000	0.00000000
30	1158.35580000	17.49570000	0.00000000
31	1164.22250000	22.80420000	0.00000000
32	1200.54370000	16.96960000	0.00000000
33	1232.79260000	5.37990000	0.00000000
34	1245.01470000	1.13100000	0.00000000
35	1265.32050000	6.23120000	0.00000000
36	1270.80890000	6.59340000	0.00000000
37	1280.70270000	15.13440000	0.00000000
38	1294.86640000	3.58660000	0.00000000
39	1298.44750000	2.46730000	0.00000000
40	1322.50100000	43.83150000	0.00000000
41	1409.29350000	5.88560000	0.00000000
42	1442.83080000	7.40940000	0.00000000
43	1451.85000000	3.28620000	0.00000000
44	1456.26830000	3.44670000	0.00000000
45	1480.59240000	0.33920000	0.00000000
46	1488.71970000	3.98180000	0.00000000
47	1490.77590000	0.57540000	0.00000000
48	1493.51060000	0.37640000	0.00000000
49	1499.39580000	7.79950000	0.00000000
50	1508.64200000	8.00310000	0.00000000
51	1513.02990000	26.94570000	0.00000000
52	1517.90580000	35.34250000	0.00000000
53	1527.55140000	48.30420000	0.00000000
54	3018.53810000	24.24940000	0.00000000
55	3074.35220000	0.49270000	0.00000000
56	3077.67130000	2.06550000	0.00000000
57	3082.41440000	3.35730000	0.00000000
58	3088.71140000	2.49350000	0.00000000
59	3089.46640000	9.25060000	0.00000000
60	3097.32000000	4.47930000	0.00000000

61	3144.1630000	4.3526000	0.0000000
62	3155.2586000	7.3343000	0.0000000
63	3162.8481000	0.2739000	0.0000000
64	3166.4017000	1.1166000	0.0000000
65	3169.9007000	1.0173000	0.0000000
66	3170.7531000	2.3270000	0.0000000
67	3178.1453000	0.4464000	0.0000000
68	3185.2093000	0.6309000	0.0000000
69	3807.8779000	86.6370000	0.0000000

S66. CALCULATIONS ON Z-2-N,N,N TRIMETHYLAMMONIUM CYCLOBUTANOL



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N](C)(C)C1CCC1O
Formula              : C7H16NO+
Charge               : 1
Multiplicity         : 1
Energy               : -406.27607578
Gibbs Energy        : -406.07825800
Number of imaginary frequencies : 0

```

a.u.
a.u.

S66.1. Cartesian Co-ordinates (XYZ format)

25

```

C -0.04263000  0.47230899 -0.23582700
H -0.10049400  0.98695999 -1.19242501
C -0.55191499  1.38455701  0.89048201
H -0.40591300  2.45311403  0.76459098
H -0.20350300  1.08249998  1.87337399
C -1.96121299  0.79650098  0.60402399
H -2.54073906  1.40359795 -0.08726000
H -2.56889796  0.55526400  1.47138095
N  1.35619700 -0.12340600 -0.20341000
C  1.41291702 -1.26110697 -1.18235302
H  2.43698001 -1.61775398 -1.24150598
H  0.75621402 -2.04869604 -0.83013302
H  1.09021902 -0.90118003 -2.15514112
C  2.32658505  0.94350702 -0.61856598
H  2.10742211  1.24582303 -1.63810003
H  2.22366500  1.79032099  0.05305300
H  3.33415103  0.54272902 -0.55787498
C  1.75427794 -0.62292999  1.15929198
H  1.00892794 -1.32700706  1.50432503

```

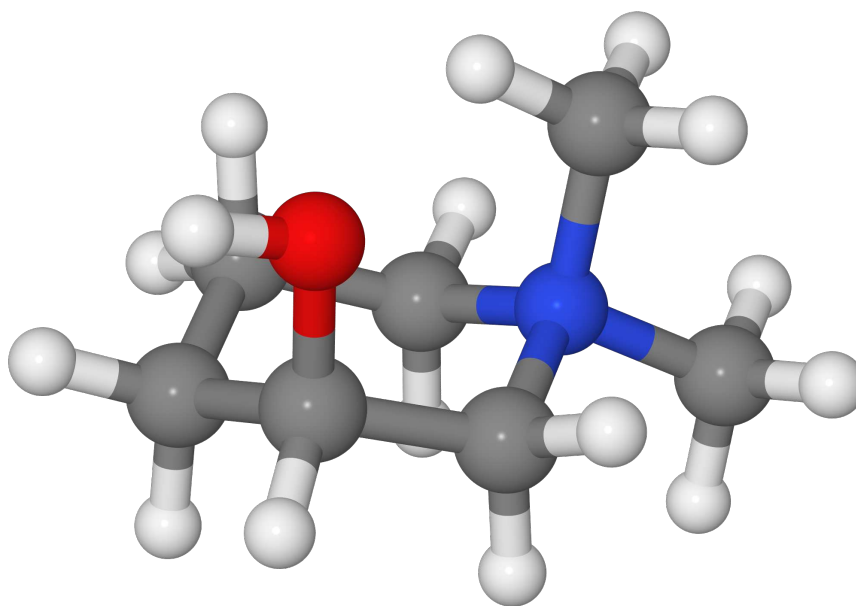
H 2.72640896 -1.09799802 1.06603205
H 1.82562006 0.22161600 1.83533800
C -1.29908299 -0.41878900 -0.09464000
O -1.04374599 -1.50836897 0.77160501
H -1.87223899 -1.95520103 0.97588903
H -1.74252200 -0.76010102 -1.03036702

S66.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	91.97680000	0.70960000	0.00000000
2	124.23270000	0.45930000	0.00000000
3	201.64920000	2.00210000	0.00000000
4	235.30020000	0.39090000	0.00000000
5	272.68610000	5.84650000	0.00000000
6	275.51330000	0.54530000	0.00000000
7	302.14650000	18.66800000	0.00000000
8	311.93960000	81.80570000	0.00000000
9	317.12240000	7.22180000	0.00000000
10	348.09970000	4.25820000	0.00000000
11	387.80620000	3.99480000	0.00000000
12	408.07400000	3.60110000	0.00000000
13	438.44250000	5.05970000	0.00000000
14	479.37860000	1.76060000	0.00000000
15	579.64550000	3.14090000	0.00000000
16	682.43770000	1.61060000	0.00000000
17	749.51060000	0.63490000	0.00000000
18	807.89520000	1.57360000	0.00000000
19	855.02210000	31.82170000	0.00000000
20	897.49870000	14.33990000	0.00000000
21	930.77390000	5.11660000	0.00000000
22	950.04780000	17.69170000	0.00000000
23	963.16500000	17.71050000	0.00000000
24	971.89120000	22.48300000	0.00000000
25	1025.78420000	2.06650000	0.00000000
26	1063.75120000	32.95860000	0.00000000
27	1082.39480000	0.16120000	0.00000000
28	1101.23850000	2.12890000	0.00000000
29	1122.63690000	32.66500000	0.00000000
30	1156.76180000	6.69440000	0.00000000
31	1164.43370000	12.92770000	0.00000000
32	1215.65220000	20.90380000	0.00000000
33	1230.59180000	26.86630000	0.00000000
34	1258.49340000	4.84130000	0.00000000
35	1270.77500000	2.79910000	0.00000000
36	1272.32380000	2.54850000	0.00000000
37	1281.73810000	1.88230000	0.00000000
38	1298.06960000	1.21080000	0.00000000
39	1310.84130000	7.57140000	0.00000000
40	1330.57790000	12.93530000	0.00000000
41	1412.39330000	4.57290000	0.00000000
42	1426.91180000	1.04910000	0.00000000
43	1449.50590000	7.06960000	0.00000000
44	1454.32530000	4.63680000	0.00000000
45	1478.03030000	3.67980000	0.00000000
46	1481.93950000	0.37490000	0.00000000
47	1494.39090000	5.83780000	0.00000000
48	1495.79210000	4.16730000	0.00000000
49	1498.03240000	1.67890000	0.00000000
50	1506.08500000	11.23040000	0.00000000
51	1512.02780000	17.79480000	0.00000000
52	1517.81020000	25.68630000	0.00000000
53	1535.56380000	43.56860000	0.00000000
54	3055.88920000	24.12020000	0.00000000
55	3073.05800000	0.84990000	0.00000000
56	3076.23630000	2.21420000	0.00000000
57	3086.24120000	3.68820000	0.00000000
58	3088.02770000	11.15960000	0.00000000
59	3096.30650000	3.40510000	0.00000000
60	3097.76370000	11.05890000	0.00000000

61	3139.2770000	1.29870000	0.00000000
62	3153.97770000	8.59910000	0.00000000
63	3159.57690000	0.72740000	0.00000000
64	3164.46190000	2.45140000	0.00000000
65	3166.96400000	1.01730000	0.00000000
66	3171.86670000	2.28640000	0.00000000
67	3180.52380000	0.31390000	0.00000000
68	3207.38770000	6.56230000	0.00000000
69	3805.54100000	86.12780000	0.00000000

S67. CALCULATIONS ON 3-HYDROXY-N,N-DIMETHYL-PIPERIDINIUM (AXIAL GEOMETRY)



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N+]1(CCCC(C1)O)C
Formula              : C7H16NO+
Charge               : 1
Multiplicity         : 1
Energy               : -406.31613803
Gibbs Energy        : -406.11486800
Number of imaginary frequencies : 0

```

a.u.
a.u.

S67.1. Cartesian Co-ordinates (XYZ format)

25

```

C  0.90509802  1.29832196  0.03341300
H  1.02401495  1.61144495 -1.00314200
H  1.65681601  1.80525100  0.63392198
C -0.50675899  1.57637596  0.51582098
H -0.67294502  2.64963198  0.42895001
H -0.60859001  1.33265805  1.57244205
C -1.52870405  0.80434602 -0.31413099
H -1.51582003  1.15805197 -1.34824598
H -2.53685594  0.97482902  0.06197600
N  1.25716901 -0.18068200  0.06192700
C  2.58051491 -0.36987600 -0.61634701
H  2.82794595 -1.42744505 -0.61523002
H  2.51453805 -0.00374100 -1.63626397
H  3.33588290  0.18734901 -0.06982700
C  1.38873005 -0.66877699  1.48002303
H  2.15283799 -0.07370600  1.97139704
H  0.43567300 -0.58446598  1.98234105
H  1.68795705 -1.71211004  1.45339894

```

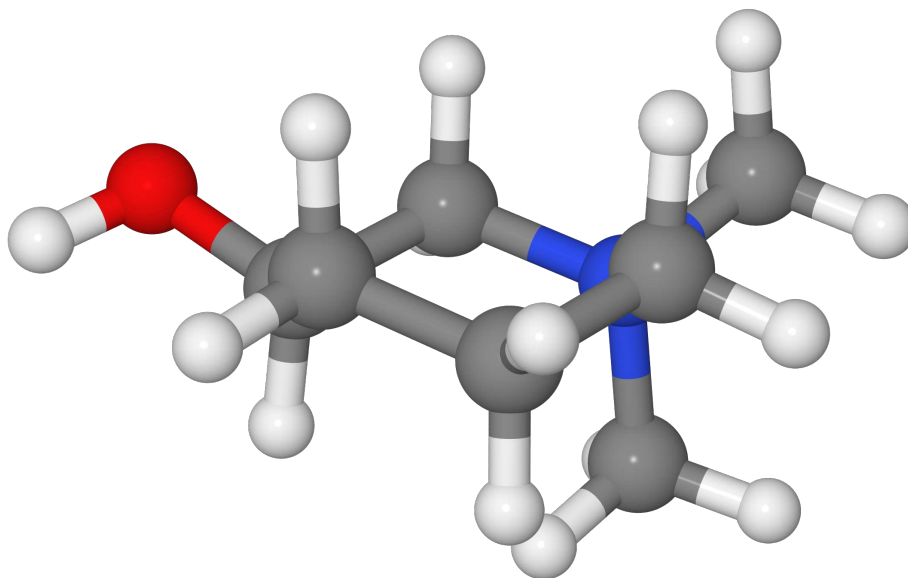
C 0.21241900 -0.97609597 -0.70399898
H 0.34625700 -0.71748197 -1.75203598
H 0.45073000 -2.02716589 -0.56311899
C -1.22739196 -0.69339198 -0.29745701
O -1.43091297 -1.27363801 0.98616701
H -2.37338901 -1.31273496 1.17783594
H -1.84548998 -1.20256698 -1.04272604

S67.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	133.34410000	0.90920000	0.00000000
2	177.02340000	3.93420000	0.00000000
3	240.94910000	4.38280000	0.00000000
4	275.23870000	1.17240000	0.00000000
5	282.95400000	3.61530000	0.00000000
6	294.33030000	103.56560000	0.00000000
7	312.90470000	2.64190000	0.00000000
8	334.83530000	5.20570000	0.00000000
9	368.93290000	9.78010000	0.00000000
10	425.91480000	1.14000000	0.00000000
11	435.85040000	0.24750000	0.00000000
12	450.16150000	0.52540000	0.00000000
13	517.90900000	3.98200000	0.00000000
14	519.69700000	1.85060000	0.00000000
15	681.34490000	4.87520000	0.00000000
16	711.97170000	1.62290000	0.00000000
17	816.60480000	3.77600000	0.00000000
18	856.39060000	1.30930000	0.00000000
19	882.36000000	3.53790000	0.00000000
20	913.81700000	11.40110000	0.00000000
21	917.29480000	22.70890000	0.00000000
22	956.15670000	26.62540000	0.00000000
23	978.17880000	20.09290000	0.00000000
24	1020.31070000	41.62770000	0.00000000
25	1031.12870000	9.13650000	0.00000000
26	1053.74860000	1.20950000	0.00000000
27	1096.27700000	2.55890000	0.00000000
28	1122.16440000	19.13710000	0.00000000
29	1133.04810000	4.01980000	0.00000000
30	1170.50670000	1.84100000	0.00000000
31	1192.98720000	1.14280000	0.00000000
32	1229.59820000	43.36850000	0.00000000
33	1251.41870000	1.00460000	0.00000000
34	1264.67140000	22.63720000	0.00000000
35	1281.83520000	1.53770000	0.00000000
36	1328.78190000	4.97700000	0.00000000
37	1349.33310000	5.49950000	0.00000000
38	1371.05300000	6.88090000	0.00000000
39	1378.76540000	3.95120000	0.00000000
40	1406.11120000	3.54070000	0.00000000
41	1407.12510000	0.70550000	0.00000000
42	1419.61700000	0.19120000	0.00000000
43	1436.34330000	4.65650000	0.00000000
44	1457.23070000	5.81320000	0.00000000
45	1472.35450000	1.73260000	0.00000000
46	1483.66840000	2.47890000	0.00000000
47	1485.27830000	3.08200000	0.00000000
48	1490.63540000	7.28950000	0.00000000
49	1493.39610000	8.52920000	0.00000000
50	1502.35560000	26.86800000	0.00000000
51	1510.82070000	27.16430000	0.00000000
52	1518.63450000	16.07640000	0.00000000
53	1526.10010000	34.82320000	0.00000000
54	3020.58920000	9.91880000	0.00000000
55	3038.42490000	15.84320000	0.00000000
56	3066.08570000	3.79790000	0.00000000
57	3068.71950000	3.20720000	0.00000000
58	3072.99540000	1.56850000	0.00000000
59	3082.73350000	5.30030000	0.00000000
60	3087.59320000	4.06710000	0.00000000

61	3090.61530000	8.68240000	0.00000000
62	3104.16770000	7.95650000	0.00000000
63	3124.98190000	5.22430000	0.00000000
64	3140.37560000	1.69650000	0.00000000
65	3160.45720000	0.03080000	0.00000000
66	3165.43640000	2.37610000	0.00000000
67	3166.20520000	2.06460000	0.00000000
68	3212.16740000	4.19460000	0.00000000
69	3816.40440000	77.11700000	0.00000000

S68. CALCULATIONS ON 3-HYDROXY-N,N-DIMETHYL-PIPERIDINIUM (EQUATORIAL GEOMETRY)



```

Route                : # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i
                    : nt=ultrafine pop=regular
SMILES               : C[N]1(CCCC(C1)O)C
Formula              : C7H16NO+
Charge               : 1
Multiplicity         : 1
Energy               : -406.31122553
Gibbs Energy         : -406.11061900
Number of imaginary frequencies : 0

```

a.u.
a.u.

S68.1. Cartesian Co-ordinates (XYZ format)

25

```

C  0.87289500  1.35127699 -0.01202800
H  0.98916698  1.59799302 -1.06596601
H  1.62746894  1.89146304  0.55513698
C -0.53751498  1.66173196  0.45599401
H -0.70946300  2.72233295  0.27462801
H -0.62544101  1.52429795  1.53450894
C -1.57082105  0.81761098 -0.29054400
H -1.57569802  1.07562804 -1.35196102
H -2.57032704  1.01847899  0.09438100
N  1.22132301 -0.12628800  0.10353400
C  2.54881191 -0.36050999 -0.55394602
H  2.79704690 -1.41514397 -0.47793600
H  2.48077512 -0.06979700 -1.59754002
H  3.30163407  0.23705199 -0.04805100
C  1.33300805 -0.53534198  1.54320395
H  2.11529493  0.05541900  2.01046300
H  0.39218101 -0.36735600  2.05092311
H  1.58899200 -1.58978105  1.58316100

```

C 0.17896500 -0.95583302 -0.61258698
H 0.26359999 -0.72646099 -1.67316198
H 0.42983899 -2.00267100 -0.46231100
C -1.25182104 -0.66801500 -0.16434599
O -2.01750708 -1.47917604 -1.03090000
H -2.93885899 -1.48420894 -0.75194401
H -1.38510704 -0.98839402 0.87518901

S68.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	140.94550000	4.79030000	0.00000000
2	157.90120000	0.10800000	0.00000000
3	221.39770000	0.37030000	0.00000000
4	242.48880000	112.70840000	0.00000000
5	265.53410000	1.44900000	0.00000000
6	300.59120000	0.95000000	0.00000000
7	302.07660000	1.18810000	0.00000000
8	338.13170000	1.96720000	0.00000000
9	346.25970000	2.94630000	0.00000000
10	428.08390000	1.21670000	0.00000000
11	441.61680000	1.17300000	0.00000000
12	455.25410000	0.32190000	0.00000000
13	483.92960000	1.42950000	0.00000000
14	506.12530000	6.08480000	0.00000000
15	572.92760000	2.37300000	0.00000000
16	729.92640000	1.16870000	0.00000000
17	830.33260000	0.89730000	0.00000000
18	876.53470000	5.36630000	0.00000000
19	894.90260000	5.14260000	0.00000000
20	906.60470000	46.83060000	0.00000000
21	925.46250000	31.32650000	0.00000000
22	977.09010000	7.90380000	0.00000000
23	992.64720000	3.95600000	0.00000000
24	1006.04990000	14.11450000	0.00000000
25	1055.22680000	19.24070000	0.00000000
26	1083.09600000	37.49890000	0.00000000
27	1103.99570000	19.01430000	0.00000000
28	1121.93680000	8.25500000	0.00000000
29	1138.42810000	11.34970000	0.00000000
30	1167.46420000	2.30390000	0.00000000
31	1195.17910000	1.83410000	0.00000000
32	1230.80920000	15.20720000	0.00000000
33	1250.78160000	2.70030000	0.00000000
34	1260.25340000	15.38130000	0.00000000
35	1287.80490000	12.62350000	0.00000000
36	1329.70660000	2.37110000	0.00000000
37	1352.27200000	1.39330000	0.00000000
38	1355.98050000	2.48840000	0.00000000
39	1375.04590000	3.95230000	0.00000000
40	1389.03630000	2.79460000	0.00000000
41	1403.53050000	14.50900000	0.00000000
42	1416.91920000	0.18050000	0.00000000
43	1445.70770000	6.30270000	0.00000000
44	1456.65770000	3.71920000	0.00000000
45	1477.65060000	0.17290000	0.00000000
46	1485.33500000	3.41630000	0.00000000
47	1488.06850000	0.98490000	0.00000000
48	1494.97780000	8.46980000	0.00000000
49	1501.15950000	12.29930000	0.00000000
50	1504.29710000	18.45000000	0.00000000
51	1511.97110000	24.03950000	0.00000000
52	1521.67030000	24.70380000	0.00000000
53	1525.09480000	24.16460000	0.00000000
54	2991.58140000	27.56530000	0.00000000
55	3041.24340000	6.63590000	0.00000000
56	3055.44840000	11.56690000	0.00000000
57	3071.40500000	0.65680000	0.00000000
58	3074.59720000	2.11890000	0.00000000
59	3081.61460000	2.54660000	0.00000000
60	3086.55950000	1.62960000	0.00000000

61	3091.23720000	4.51350000	0.00000000
62	3097.30000000	12.77820000	0.00000000
63	3127.88940000	3.94200000	0.00000000
64	3139.05750000	2.59970000	0.00000000
65	3161.47410000	0.03630000	0.00000000
66	3166.73360000	1.32570000	0.00000000
67	3168.18290000	1.17880000	0.00000000
68	3194.30740000	1.18860000	0.00000000
69	3817.31230000	82.94880000	0.00000000