Supporting Information

Part I: Mass Spectrometry, IR Spectroscopy, Synthesis, Crystallographic Data

Hydrogen Tunneling Avoided: Enol-Formation From a Charge-tagged Phenyl Pyruvic Acid Derivative Evidenced by Tandem-MS, IR Ion Spectroscopy and Theory

Mathias Paul,[1] Katrin Peckelsen,[1] Thomas Thomulka,[1] Jörg-M. Neudörfl,[1] Jonathan Martens,[2] Giel Berden,[2] Jos Oomens,[2,3] Albrecht Berkessel,[1] Anthony J. H. M. Meijer*,[4] and Mathias Schäfer*,[1]

[1] University of Cologne, Department of Chemistry, Greinstrasse 4, 50939 Köln, Germany.
[2] Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7c, 6525 ED Nijmegen, The Netherlands.
[3] Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands.
[4] University of Sheffield, Department of Chemistry, Sheffield S3 7HF, U.K.

Mathias Paul	https://orcid.org/0000-0003-4635-3605
Katrin Peckelsen	
Thomas Thomulka	
Jörg-M. Neudörfl	http://orcid.org/0000-0002-2918-0565
Jonathan Martens	https://orcid.org/0000-0001-9537-4117
Giel Berden	https://orcid.org/0000-0003-1500-922X
Jos Oomens	https://orcid.org/0000-0002-2717-1278
Anthony J. H. M. Meijer	https://orcid.org/0000-0003-4803-3488
Albrecht Berkessel	https://orcid.org/0000-0003-0470-7428
Mathias Schäfer	https://orcid.org/0000-0002-5943-4335

Contents

S1. Mass Spectrometry

S1.1 (+)ESI-MS and (+)ESI-MS^2 of 4

Iodine salt **4•I** of precursor compound **4** was dissolved in methanol (c ≈ 10^{-4} mol/L) and subjected to (+)ESI-MS. The (+)ESI-mass spectrum shows an abundant molecular ion at *m*/*z* 222 as **Figure S1** illustrates. The CO_2 loss was found to be a prominent fragmentation pathway of the molecular ion of **4** at *m*/*z* 222 as the (+)ESI-MS^2 product ion experiment documents (**Figure S1**).

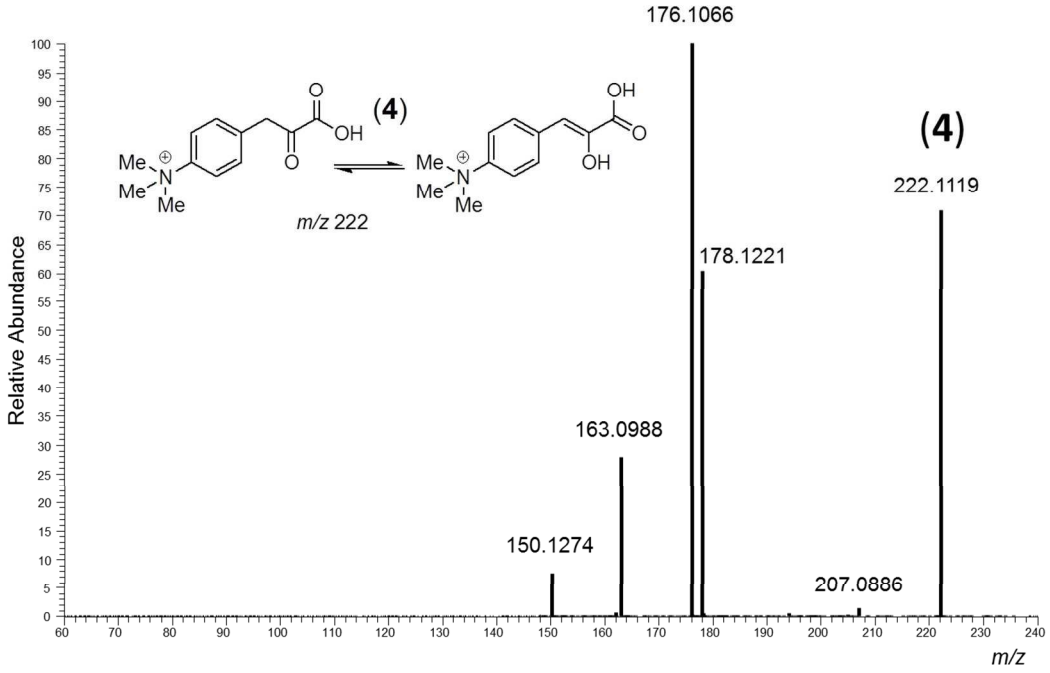
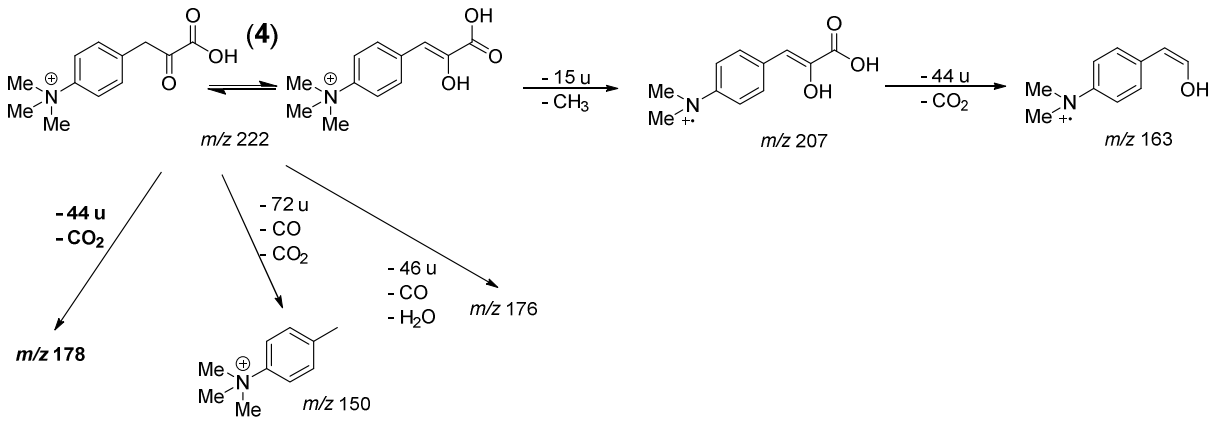


Figure S1. (+)ESI-MS^2 product ion spectrum of precursor **4** at *m*/*z* 222 acquired on an LTQ-orbitrap XL. The precursor ion at *m*/*z* 222 was selected monoisotopically and the accurate ion masses determined match the theoretical ion masses; see also **Scheme S1** below.

Table S1. Theoretical and measured ion masses of the molecular ion of **4** and the MS^2 product ions determined in the Orbitrap part of an LTQ-Orbitrap XL instrument.

Composition	Ion mass measured [u]	Theoretical ion mass [u]
(4) $[C_{12}H_{16}NO_3]^+$	222.1119	222.1125
$[\mathbf{4} - CO_2]^+$ $[C_{11}H_{16}NO]^+$	178.1221	178.1232
$[\mathbf{4} - \bullet CH_3]^+$ $[C_{11}H_{13}NO_3]^+$	207.0886	207.0895
$[\mathbf{4} - \bullet CH_3 - CO_2]^+$ $[C_{10}H_{13}NO]^+$	163.0988	163.0997
$[\mathbf{4} - CO - H_2O]^+$ $[C_{11}H_{14}NO]^+$	176.1066	176.1075
$[\mathbf{4} - CO - CO_2]^+$ $[C_{10}H_{16}N]^+$	150.1274	150.1283

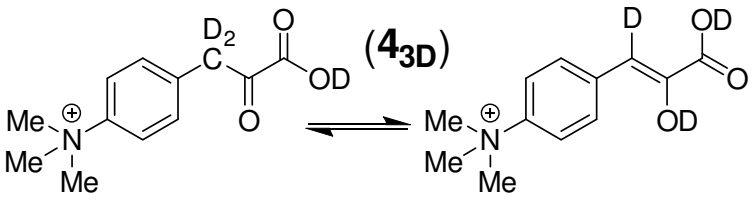


Scheme S1. (+)ESI-MS^2 CID product ions of the molecular ion of precursor **4** at *m/z* 222 formed in the linear QIT part of an LTQ-Orbitrap XL instrument.

Table S2. (+)ESI-MS^2 product ion experiments in the linear ion trap of the LTQ-Orbitrap XL and in the spherical Amazon Ion trap of precursor **4**.

	Precursor ion *m/z*	Fragment ions *m/z*
LTQ-Orbitrap XL	222	CID: 207; 178; 176; 163; 150
Amazon Ion trap	222	IRMPD: 178; 176; 163

S1.2 (+)ESI-MS and (+)ESI-MS^2 of $\mathbf{4_{3D}}$



Iodine salt **4•I** of precursor compound **4** was dissolved in CD_3OD / D_2O (80/20%) and diluted with CD_3OD ($c \approx 10^{-4}$ mol/L) to completely exchange the three enol protons to yield the triply deuterated $\mathbf{4_{3D}}$ precursor ion at *m*/*z* 225 in (+)ESI-MS (see **Figure S2**).

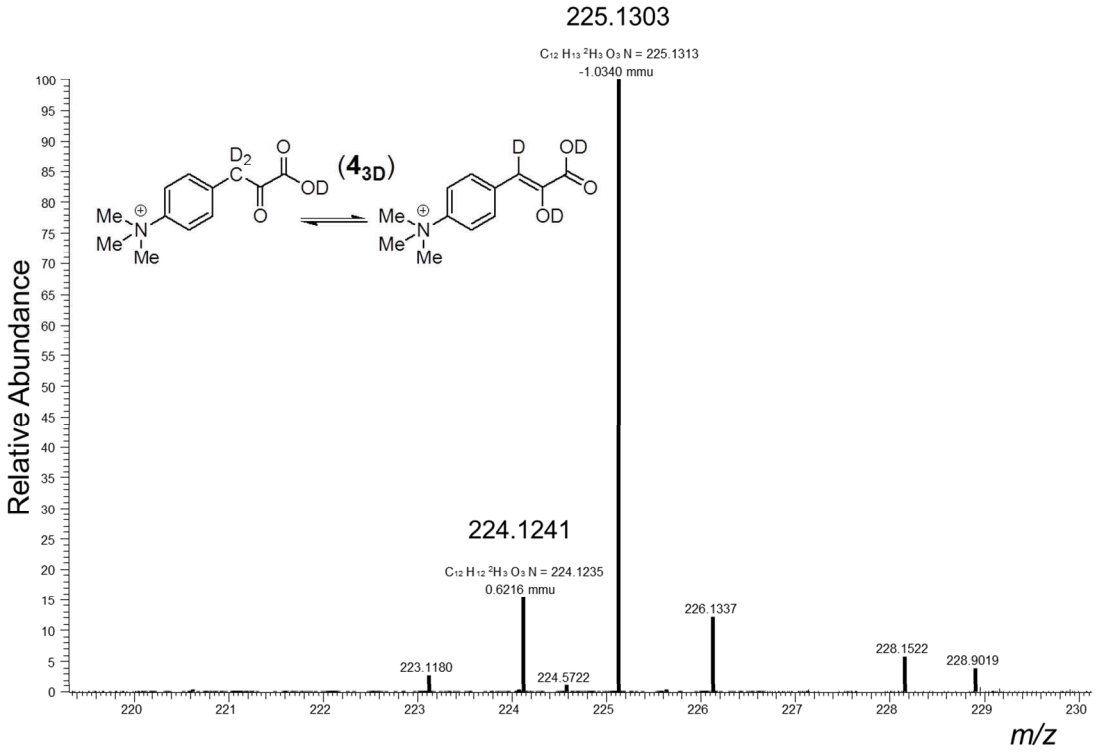


Figure S2. Isotopic distribution of precursor $\mathbf{4_{3D}}$ at *m*/*z* 225 in the (+)ESI-mass spectrum acquired on a LTQ-orbitrap XL. The accurate ion masses determined match the theoretical ion masses.

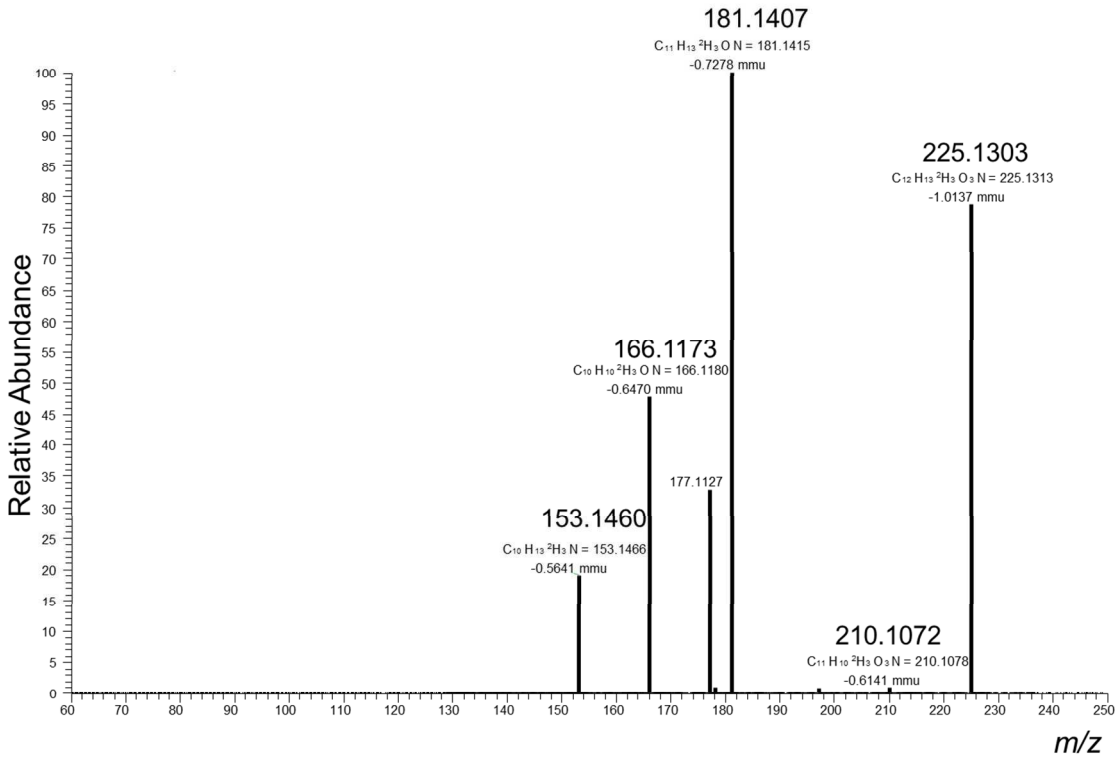
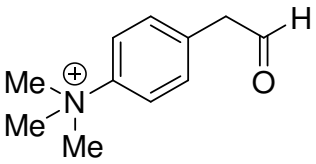


Figure S3. (+)ESI-MS^2 product ion spectrum of precursor $\mathbf{4_{3D}}$ at *m*/*z* 225 acquired in a LTQ-orbitrap XL. The precursor ion at *m*/*z* 225 was selected monoisotopically and the accurate ion masses determined match the theoretical ion masses.

Table S3. IRMPD-product ions of the CO_2 loss fragment ion at *m*/*z* 181 measured in the spherical Amazon Ion trap.

	Precursor ion *m*/*z*	**IRMPD: Fragment ions** *m*/*z*
Amazon Ion trap	181	166; 165; 153; 136; 93

S1.3 (+)ESI-MS and (+)ESI-MS^2 of 6



Iodine salt **6•I** of reference aldehyde **6** was dissolved in MeOH (c ≈ 10^{-4} mol/L) for (+)ESI-MS and the (+)ESI-MS^2 product experiments.

Table S4. Theoretical and measured ion masses of the reference aldehyde **6** and the MS^2 product ions determined in the Orbitrap part of an LTQ-Orbitrap XL instrument. *The ion mass of the molecular ion of **6** was measured in an independent (+)ESI-MS experiment.

Composition	Ion mass measured [u]	Theoretical ion mass [u]
(6) $[C_{11}H_{16}NO]^+$	178.1225*	178.1226
[**6** – •CH_3]$^+$ $[C_{10}H_{13}NO]^+$	163.0988	163.0992
[**6** – CH_3CHO]$^+$ $[C_9H_{12}N]^+$	134.0963	134.0964

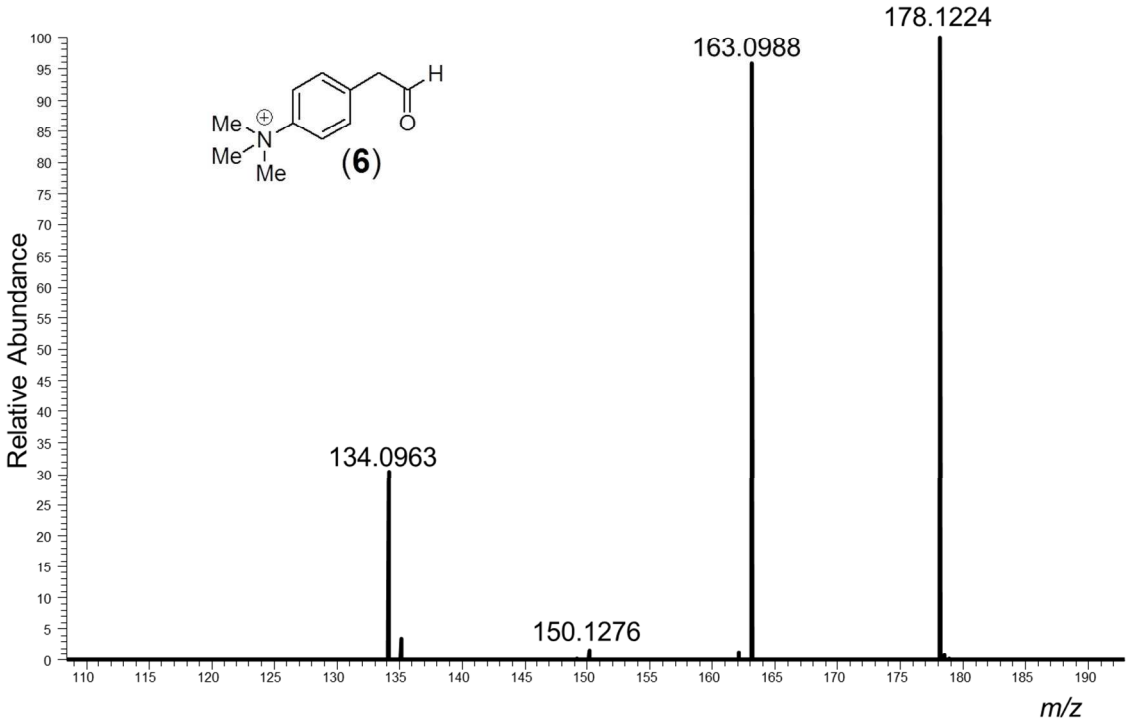


Figure S4. (+)ESI-MS^2 CID product ion spectrum of reference aldehyde **6** at *m*/*z* 178 acquired on a LTQ-orbitrap XL. The precursor ion at *m*/*z* 178 was selected monoisotopically and the accurate ion masses determined match the theoretical ion masses.

S2. IR Ion Spectroscopy

S2.1 (+)ESI-IR Ion spectroscopy of 4

Precursor compound **4** was dissolved as a iodine salt **4•I** in methanol (c ≈ 10^{-4} mol/L) for (+)ESI-MS and IR ion spectroscopy.

Table S5. Band origins of the enol-acid-tautomer ion structures **4A**–**4C** compared to the IR ion spectrum of the molecular ion of precursor ion **4** at *m*/*z* 222 as presented in **Figure 1**. Scaling factors: 0.97 in the range 600–1900 cm^{-1} and 0.95 in the range 3400–3800 cm^{-1}.

	IR Ion Spectrum **Figure 1**	**4A**	**4B**	**4C**
COO-H stretch	3577	3554	3563	3580
$O\text{-}H_{enol}$ stretch		3425	3557	3565
C=OOH stretch	1780		1772	
C=OOH stretch	1741	1729		1749
HC=C(OH) stretch		1667		1635
$HC_{ar}=C_{ar}H$ stretch		1592		1589
$HC_{ar}=C_{ar}R=C_{ar}H$ stretching		1499	1499	1499
$C\text{-}H_3$ bending	1483	1484–1464		1484–1461
$H_{enol}\text{-}C\text{-}C_{ar}$ bending				1423
H-C=C bending, C_{enol}-OH stretching, and $C_{enol}\text{-}C_{acid}$ stretching	1400	1403/1109	1385	1397
C_{acid}-O-H bending		1370		
$H\text{-}C_{ar}\text{-}C_{ar}\text{-}H$ rocking			1327	1327
$HC_{ar}\text{-}C_{ar}$ stretching			1315	1312
$C\text{-}O\text{-}H_{enol}$ bending	1301	1312	1307	
$HC\text{-}C_{ar}\text{-}C_{ar}H$ stretch and $O\text{-}H_{enol}$ bending			1292	
$O\text{-}H_{enol}$ rocking and $C\text{-}H_{enol}$ rocking				1219
$C\text{-}O\text{-}H_{enol}$ bending/C_{ar}-H bending				1161
$O\text{-}H_{acid}$ rocking	1142	1147		
C_{acid}O-H bending and $C_{enol}\text{-}C_{acid}$ stretch			1117	1134
C_{acid}-OH stretch/C_{ar}-N stretch				1106
C_{acid}-OH stretch and C_{enol}-OH stretch			1073	
	1028			
$H_3C\text{-}N\text{-}CH_3$ stretching				917
$HC\text{=}C\text{-}OH$ bending/$HC_{ar}=C_{ar}N\text{-}=C_{ar}H$ bending				882
N-C stretching		815		821
$O\text{-}H_{enol}$ rocking		631		
$O\text{-}H_{acid}$ rocking		602		

Table S6. All band origins of the computed keto-tautomer ion structures **4D**–**4G** compared to the IR ion spectrum of the molecular ion of precursor ion **4** at *m*/*z* 222 as presented in **Figure 2**. All bands are scaled by 0.97 in the range 600–1900 cm^{-1} and by 0.95 in the range 3400–3800 cm^{-1}.

	IR Ion Spectrum **Figure 2**	**4D**	**4E**	**4F**	**4G**
COO-H stretch	3577	3466	3543	3540	3482
C_{acid}=O stretch	1780	1781	1752	1740	1793
C_{keto}=O stretch	1741	1737	1761	1761	1734
HC_{ar}=C_{ar}R=C_{ar}H stretching		1502	1504	1502	1504/1315
C-H_3 bending	1483	1484–1464	1484	1484/1467	1484/1464
C_{keto}-C_{acid}-OH stretch	1400	1344		1356	1347
C_{ar}-H rocking					1324
C-H_2 wagging	1301	1269	1295	1266	1295
C-H_2 wagging/C-O-H_{acid} bending					1176
C-H_2 twisting/C-O-H_{acid} bending		1213	1158	1159	
	1142				
H-Car=Car-H bending			1132		
C_{keto}-CH_2 stretch	1028	1056	1013	1039	1030
C-H_2 rocking			922	922	920
C_{ar}-CH_2-C_{keto} bending		608	856		
C_{ar}-N stretch			826	826	826
O=C-OH stretch			701	713	
$C_{ar,\,q}$=C_{ar}H=C_{ar}H bending			637–631	637	
O-H_{acid} rocking		681	602	661	649/640

S2.2 (+)ESI-IR Ion spectroscopy of 4_{3D}

Precursor compound **4** was dissolved as an iodine salt **4•I** in methanol-d_4 ($c \approx 10^{-4}$ mol/L) and stirred for 48 h. The solution was used for (+)ESI-MS and IR ion spectroscopy.

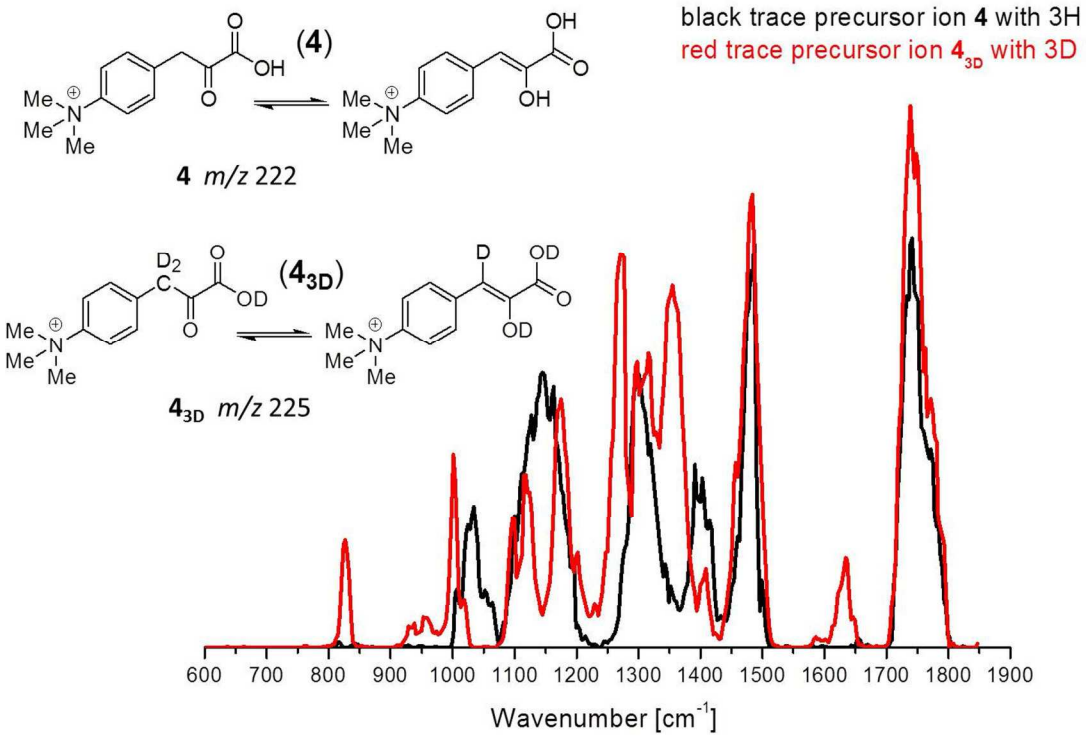


Figure S5. IR ion spectra of the precursor ions **4** at *m*/*z* 222 (black trace) and of the triply deuterated $\mathbf{4_{3D}}$ precursor ion at *m*/*z* 225 (red trace).

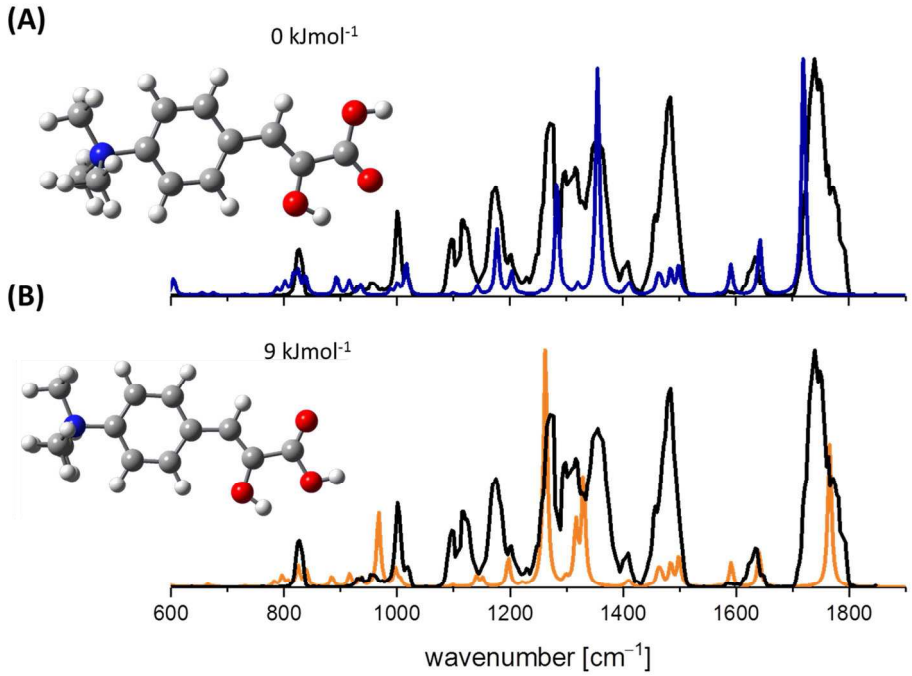


Figure S6. IR ion spectrum of the triply deuterated $\mathbf{4_{3D}}$ precursor ion at *m*/*z* 225 (black trace) compared to **(A)** the computed IR ion spectrum of the enol-acid-tautomer ion structures $\mathbf{4A_{3D}}$ (blue trace) and **(B)** $\mathbf{4B_{3D}}$ (orange trace).

S2.3 (+)ESI-IR Ion spectroscopy of aldehyde 6

Reference aldehyde **6** was dissolved in acetonitrile (c ≈ 10^{-4} mol/L) for (+)ESI-MS and IR ion spectroscopy.

Table S7. (+)ESI-MS^2 CID product ions of reference aldehyde **6** at *m*/*z* 178 acquired on a LTQ-orbitrap XL and a Bruker Amazon QIT.

	Precursor ion	**Product ions**
Orbitrap	*m*/*z* 178.1	CID: 163.1; 134.1
Amazon Ion trap	*m*/*z* 177.7	IRMPD: 162.7; 133.8

Table S8. All band origins of the computed aldehyde ion structure **6** compared to the IR ion spectrum of the CID product ion formed by CO_2 loss from precursor **4** at *m*/*z* 178 as presented in **Figure 4**. All bands are scaled by 0.97 in the range 600–1900 cm^{-1} and by 0.95 in the range 3400–3800 cm^{-1}.

	IR Ion Spectrum **Figure 4**	**6**
$C_{keto/aldehyde}$=O stretch		1761
	1646	
	1592	
HC_{ar}=C_{ar}R=C_{ar}H stretch		1504
C-H_3 bending	1477	1484–1467
H-C-H bending	1408	1420
CH_3 bending out of plane		1408
O=C_{ald}-H bending		1371
	1310	
C_{ald}-CH_2 stretch	1268	1277/902
	1223	
	1172	
	1105	
	1043	
CH_3-N stretch		934
CH_3-N-CH_3 stretch	920	917
H-C_{ar}=C_{ar} bending out of plane		844
C_{ar}-N stretch	820	824

S2.4 (+)ESI-IR Ion spectroscopy of the CID product ion formed by CO_2 loss from precursor 4

Table S9. All band origins of the computed hydroxycarbene ion structures **5A**–**5E** compared to the IR ion spectrum of the CID product ion formed by CO_2 loss from precursor **4** at *m*/*z* 178 as presented in **Figure 3**. All bands are scaled by 0.97 in the range 600–1900 cm^{-1} and by 0.95 in the range 3400–3800 cm^{-1}.

	IR Ion Spectrum **Figure 3**	**5A**	**5B**	**5C**	**5D**	**5E**
	1646					
	1592					
$HC_{ar}=C_{ar}R=C_{ar}H$ stretch		1499	1498	1502	1499/1324	1499
C-H_3 bending	1477	1484–1464	1482–1467	1484–1464	1484–1464	1484–1464
	1408					
$C_{carbene}$-OH stretch/CH_2 wagging		1342	1358	1289	1350	1277
C-H_2 bending			1342	1312		
H-C_{ar} rocking					1318	
$C_{carbene}$-O-H bending/HC_{ar}-$C_{ar}H$ stretch	1310	1304	1304		1301	
	1268					
CH_2-C_{ar} stretch/C-H_2 wagging	1223	1234	1234	1208/1187	1240	1234
H-C_{ar}=C_{ar}-H bending			1187			
C_{ar}-CH_2 stretch	1172		1172			
C-H_2 twisting	1106	1115				
	1043					
$C_{carbene}$-CH_2 stretch		940	939	876		
CH_3-N-CH_3 stretch	920				917	920
O-H rocking		879	877	888	882	888
C_{ar}-N stretch	820	821	830	821		824
H-C_{ar}=C_{ar}-H bending out of plane		806	807			
C-H_2 rocking				669	646	

Table S10. All band origins of the computed enol ion structures **7A**–**7C** compared to the IR ion spectrum of the CID product ion formed by CO_2 loss from precursor **4** at *m*/*z* 178 as presented in **Figure 5**. All bands are scaled by 0.97 in the range 600–1900 cm^{-1} and by 0.95 in the range 3400–3800 cm^{-1}.

	IR Ion Spectrum **Figure 5**	**7A**	**7B**	**7C**
HC=CH(OH) stretch	1646	1667	1644	1668
$HC_{ar}=C_{ar}H$ stretch	1592	1592	1592	1591
$HC_{ar}=C_{ar}R=C_{ar}H$ stretch		1502	1502	1505
C-H_3 bending	1477	1484–1461	1484–1461	1482–1467
	1408			
H-C=C-H bending	1310		1312	1358
$HC_{ar}=C_{ar}=C_{ar}H$ stretch				1304
C-O stretch/H-C=CH bending	1268	1051/1275		
C-O stretch/C_{ar}-CH stretch				1242
H-O-C-H bending	1223	1231		1180
C_{ar}-CH stretch		1211		
H-C_{ar} bending	1172	1190		1133
C-O-H bending	1106		1117	
H_3C wagging			1097	
	1043			
H-C=C-H bending out of plane				931
H_3C-N-CH_3 stretch	920	917		
H-C=C-H bending o. o. p./C_{ar}-H bending o. o. p.			850	854
H-C_{ar}-C_{ar} bending out of plane		841		
C_{ar}-N stretch	820	812		815

S2.5 (+)ESI-IR Ion spectroscopy of the CID product ion formed by CO_2 loss from precursor $\mathbf{4_{3D}}$

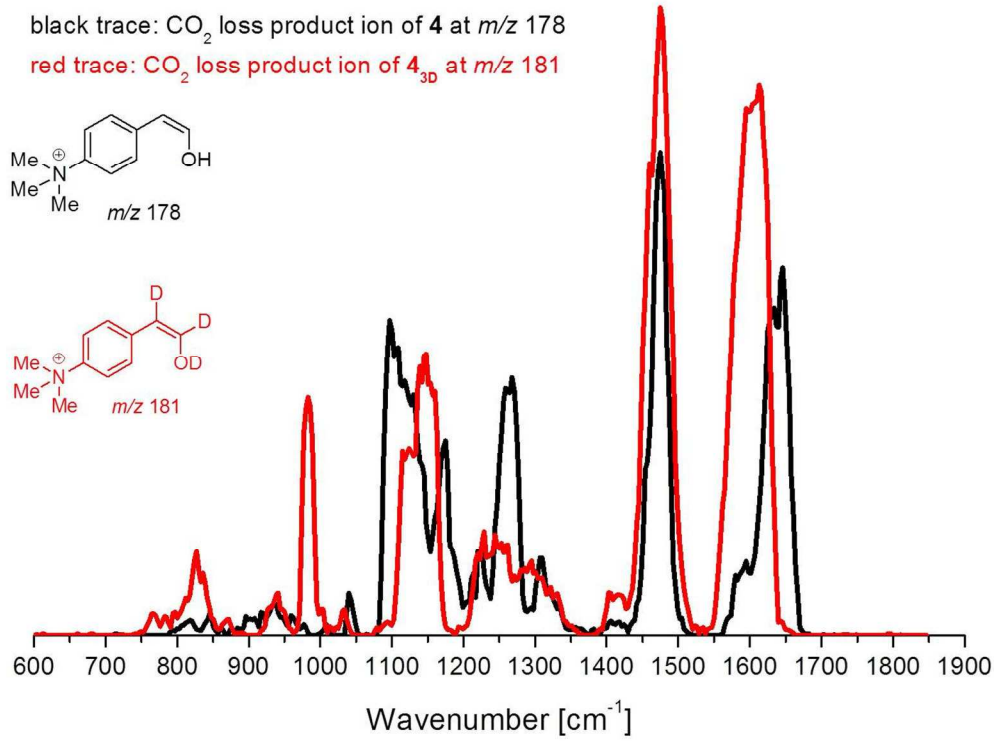


Figure S7. IR ion spectrum of the CID product ion at *m*/*z* 178 formed by CO_2 loss from precursor **4** (black trace) and of the product ion at *m*/*z* 181 formed by CO_2 loss from the triply deuterated precursor $\mathbf{4_{3D}}$ (red trace).

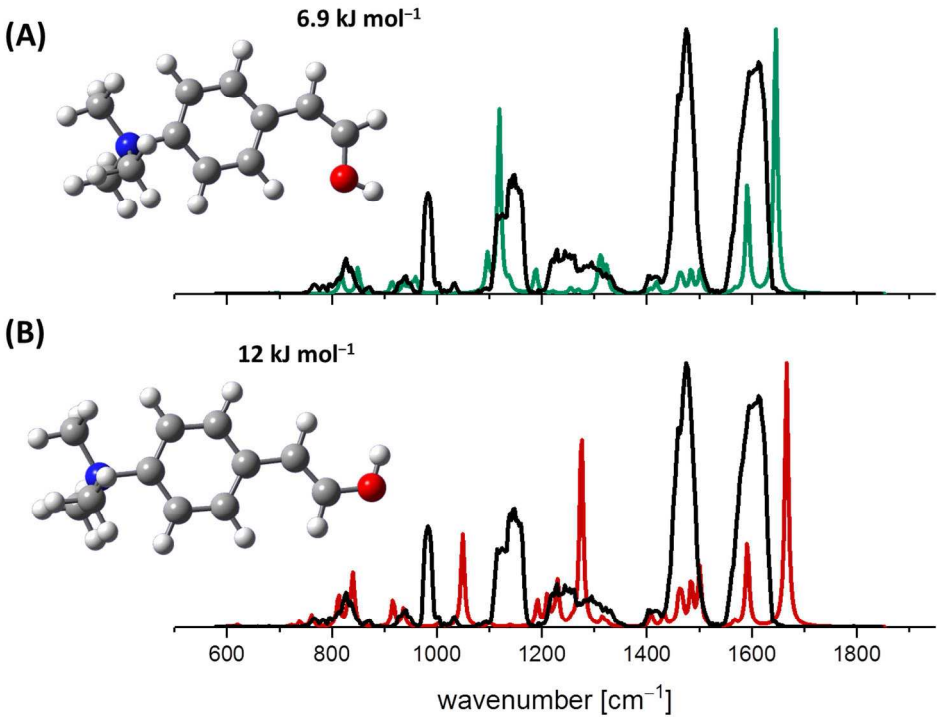


Figure S8. IR ion spectrum of the triply deuterated product ion at *m*/*z* 181 formed by CO_2 loss from precursor $\mathbf{4_{3D}}$ (black trace) compared to the IR spectra of the triply deuterated cis-enol $\mathbf{7A_{3D}}$ **(A)** and the trans enol $\mathbf{7B_{3D}}$ **(B)**.

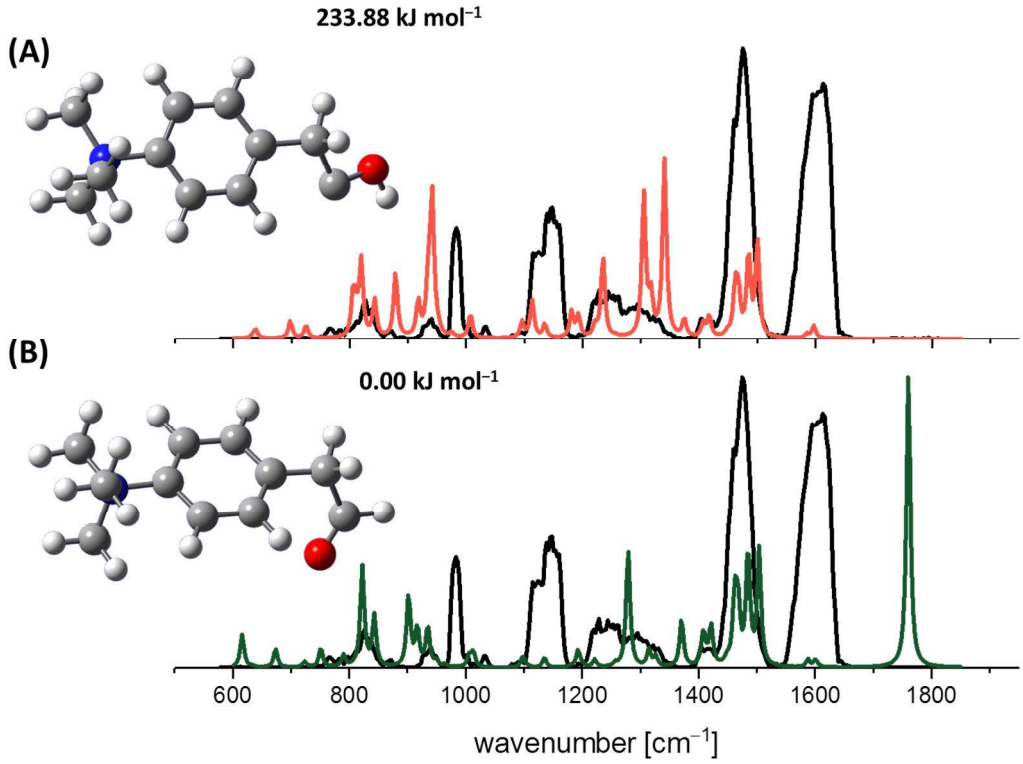


Figure S9. IR ion spectrum of the triply deuterated product ion at *m*/*z* 181 formed by CO_2 loss from precursor $\mathbf{4_{3D}}$ (black trace) compared to the IR spectra of the triply deuterated hydroxycarbene $\mathbf{5A_{3D}}$ **(A)** and the aldehyde $\mathbf{6_{3D}}$ **(B)**.

S3. General Synthesis and Analytical Procedures

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance II 600 instrument (^{1}H: 600.20 MHz, ^{13}C: 150.92 MHz). Spectra were recorded at room temperature unless otherwise stated. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS) or solvent residual signals.[1] The following abbreviations were used for chemical shift multiplicities in ^{1}H NMR spectra:

brs = broad singlet, brd = broad doublet, brm = broad multiplet, s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, ps = pseudo.

NMR signals were assigned by evaluation of 1D and 2D NMR data (^{1}H,^{1}H COSY, ^{1}H,^{1}H NOESY, ^{1}H,^{13}C HMQC, ^{1}H,^{13}C HMBC).

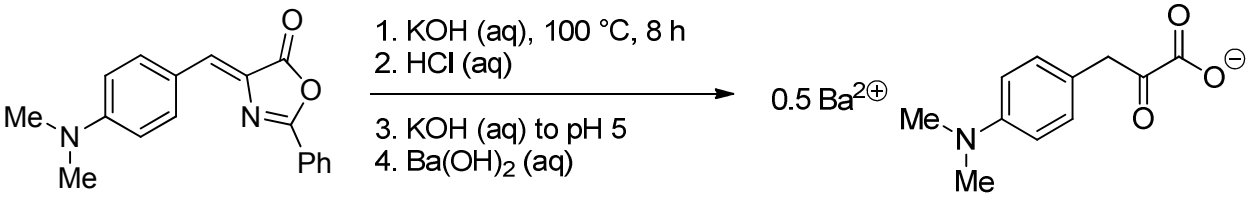
For GC-MS analyses, a Hewlett Packard HP 6890 chromatograph with a HP-5 MS crosslinked silicon gum capillary column (30 m × 0.25 mm, 0.25 µm film thickness) and a HP 5973 series mass sensitive detector was used. Hydrogen was used as the carrier gas at a flow of 2 mL min^{-1}. The following method was used: STAND50 (50 °C (5 min), 20 °C min^{-1}, 280 °C (10 min)).

S3.1 Synthesis of 4-(2-Carboxy-2-oxoethyl)-*N*,*N*,*N*-trimethylbenzene aminium iodide 4

This section describes the synthesis of the charge tagged α-ketoacid **4**. The azlactone **8** was synthesized according to Saravanan by an Erlenmeyer synthesis in one step.[2]

The subsequent hydrolysis leading to the barium salt **9** and acidification leading to the α-ketoacid **10** was done according to a procedure by Hellerman.[3]

S3.1.1 Barium 4-(dimethylamino)-α-oxobenzenepropanoate 9



8 **9**, 99%

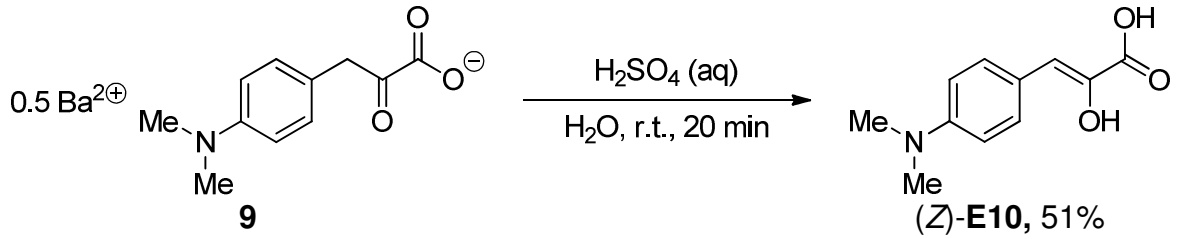
A 1000-mL-round bottom flask equipped with a reflux condenser and magnetic stir bar was charged with azlactone **8** (15.79 g, 54.0 mmol, 1.0 eq) and potassium hydroxide (128 g, 85%, 1934 mmol, 35.8 eq). It was evacuated and flushed with argon before water (630 mL) was added. The mixture was heated to reflux for 8 h. The suspension of the red crystalline azlactone **8** had become a pale yellow solution. The solution was cooled to 0 °C and hydrochloric acid solution (202 mL, 12 M, 2425 mmol, 44.9 eq) was added carefully. After the addition of half of the acid, a colorless to yellow solid started to precipitate. The color of the mixture changed from yellow to orange and the solid dissolved again. After that, benzoic acid started to precipitate and was filtered off by means of a Büchner funnel (quantitative by weight). The pale yellow solution (almost 1 L) was cooled on an ice bath and carefully brought to pH 5 with a freshly prepared concentrated solution of potassium hydroxide. The solution turned to a pale red and a colloidal precipitate formed. This could only be removed by addition of Celite (~3 g) to the mixture and passing the suspension through a sintered glass funnel covered with a small Celite pad. To the clear solution a freshly prepared saturated barium hydroxide solution (23 mL, 0.228 M, 256 mmol, 281 eq) was added and precipitation of the product started immediately. The mixture was cooled in an ice bath for 2 h. The product was filtered off by means of a sintered glass funnel, washed with water and dried under reduced pressure. The mother liquor was concentrated under reduced pressure (to 1 L) and cooled again for a second precipitation. This gave the desired barium salt **9** in excellent yield. However, NMR spectroscopy of this compound was not possible due to the insolubility of the salt in water and DMSO. The product was used without further analysis in the next step.

9: $C_{22}H_{24}BaN_2O_6$, M = 549.76 g mol^{-1}.

Yield: 14.7 g (99%).

Appearance: pale yellow powder.

S3.1.2 (2*Z*)-3-[4-(Dimethylamino)phenyl]-2-hydroxy-2-propenoic acid ((*Z*)-E9)



A 250-mL-round bottom flask equipped with a magnetic stir bar barium salt **9** (8.00 g, 14.6 mmol, 1.00 eq) was suspended in water (84 mL). Sulfuric acid (~14.5 mL, 25%) was added to adjust the pH to 3.6 by means of short range pH paper. The pale yellow suspension became more colorless. The protonated product could be observed by ESI MS. The formed barium sulfate was filtered off and the yellow aqueous solution was freeze-dried to leave a crispy orange residue which could be used in the next step. This material could not be purified well as it decomposed easily. However, the main side product was 4-dimethylaminobenzaldehyde (~7% by NMR). Many attempts of crystallization from the purest samples had failed and ended in decomposition (mainly gas phase diffusion of diethyl ether into an acetone solution). Sometimes small colorless microcrystalline clusters had formed which turned out the pure compound according to NMR spectroscopy. A few milligrams could be collected and were for example used for the melting point determination. A sample that contained more aldehyde gave crystals suitable for X-ray analysis. In these crystals the aldehyde cocrystallized with the desired product in its enol form (*Z*)-**E10**.

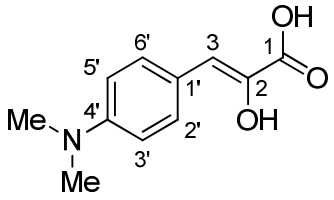
(*Z*)-**E10**: $C_{11}H_{13}NO_3$, M = 207.23 g mol^{-1}.

Yield: 3.080 g (51%).

Appearance: colorless microcrystalline solid.

m.p.: 136 °C turns pink, 174 °C decomposition (acetone/diethyl ether), lit.:[3] 120 °C turns pink, 141 °C melts with decomposition (acetone/ petroleum ether).

FT-IR: (ATR): $\tilde{\nu}$ [cm^{-1}] = 2525 (brw), 2160 (m), 2029 (m), 1977 (m), 1690 (s), 1655 (m), 1508 (w), 1171 (s), 1086 (s), 1038 (s), 993 (s), 866 (s), 779 (s), 692 (m).



^{1}H NMR (600 MHz, DMSO-d_6, 298 K) δ [ppm] = 12.80 (brs, 1H, OH-1), 8.63 (brs, 1H, OH-2), 7.62 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H-2',6'), 6.71 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H-3',5'), 6.35 (s, 1H, H-3), 2.92 (s, 6H, NMe_2).

^{13}C NMR (151 MHz, DMSO-d_6, 298 K) δ [ppm] = 166.6 (1C, C-1), 149.2 (1C, C-4'), 138.3 (1C, C-2), 130.5 (2C, C-2',6'), 122.9 (1C, C-1'), 111.9 (2C, C-3',5'), 111.0 (1C, C-3), 39.8 (2C, NMe_2).

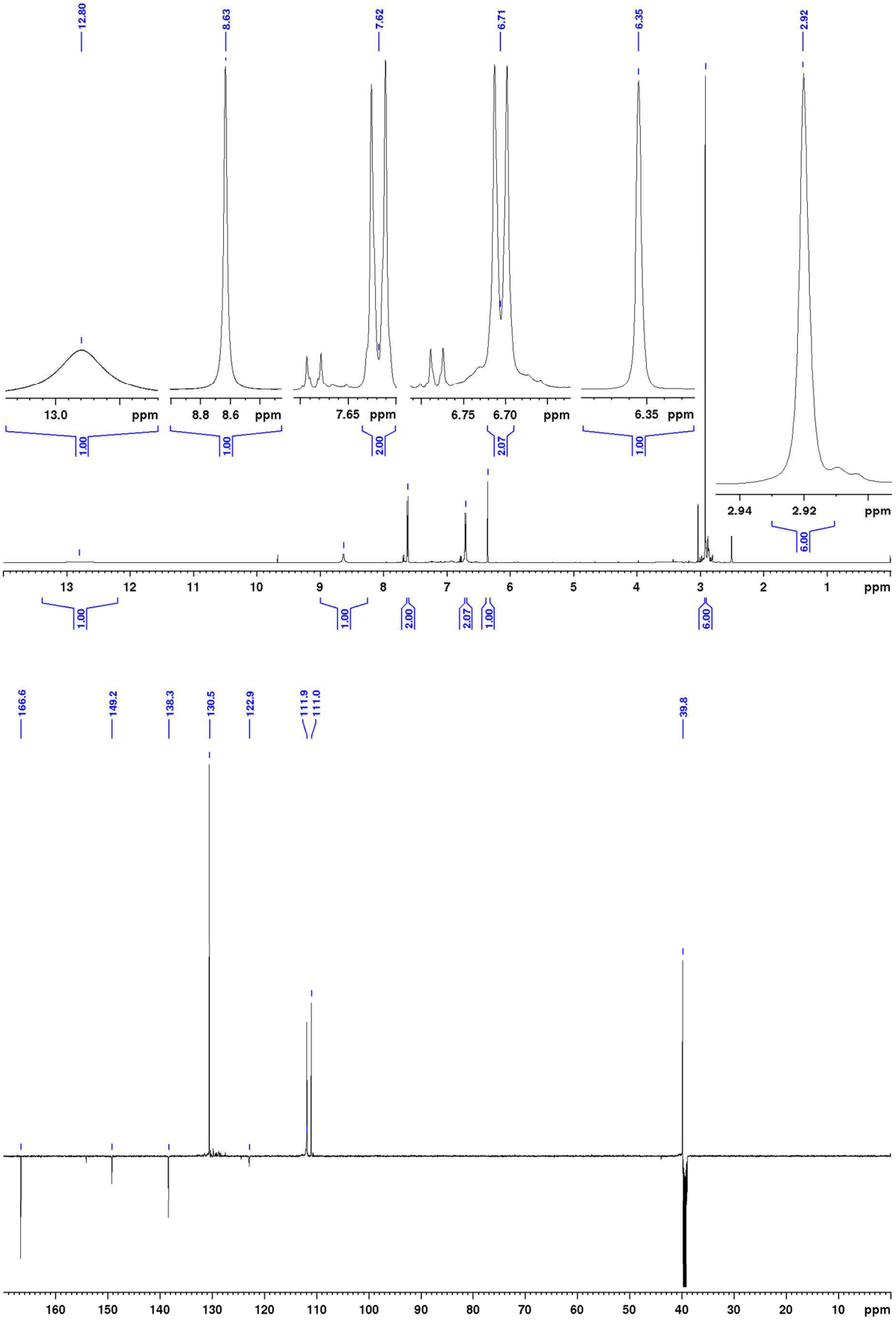


Figure S10. ^{1}H NMR spectrum (top, 600 MHz, THF-d_8, 298 K) and multiplicity-edited ^{13}C DEPTQ NMR spectrum (bottom, 151 MHz) of (*Z*)-**E10**.

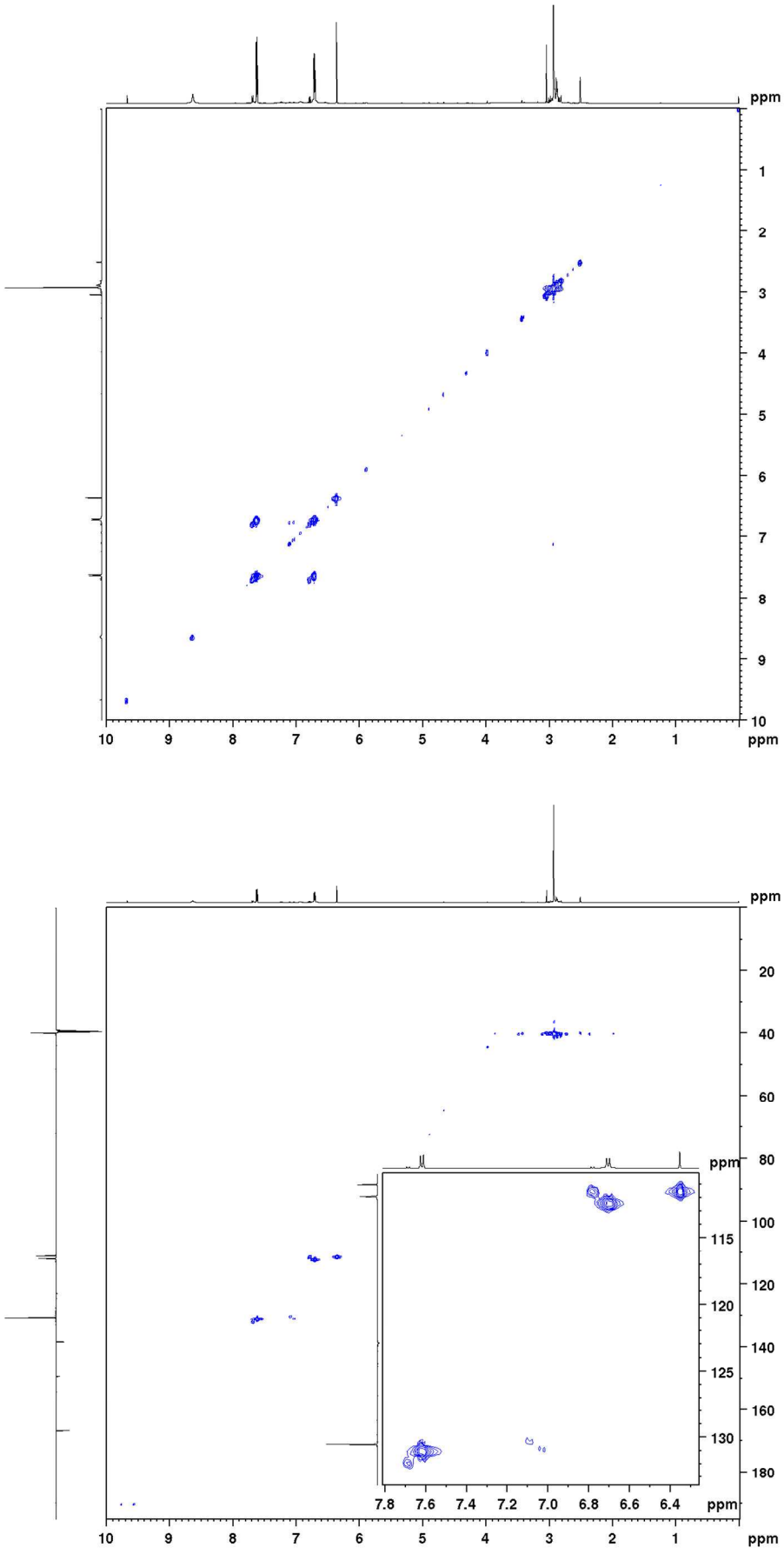


Figure S11. ^{1}H,^{1}H COSY spectrum (top, 600 MHz, THF-d_8, 298 K) and ^{1}H,^{13}C HMQC spectrum (bottom, 600 MHz/151 MHz, THF-d_8, 298 K) of (*Z*)-**E10**.

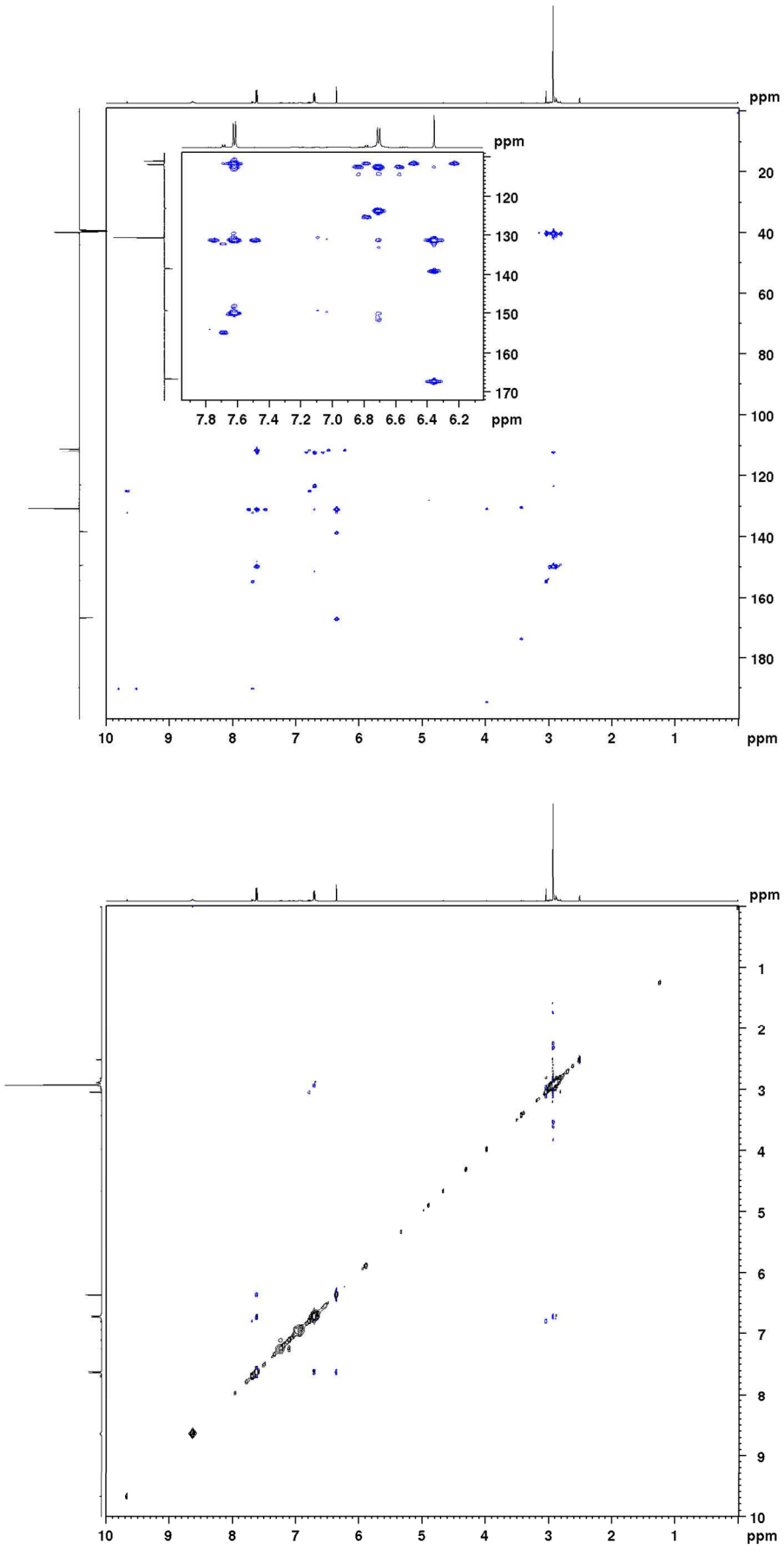


Figure S12. ^{1}H,^{13}C HMBC spectrum (top, 600 MHz/151 MHz, THF-d_8, 298 K) and ^{1}H,^{1}H NOESY spectrum (bottom, 600 MHz, THF-d_8, 298 K, mixing time = 600 ms) of (*Z*)-**E10**.

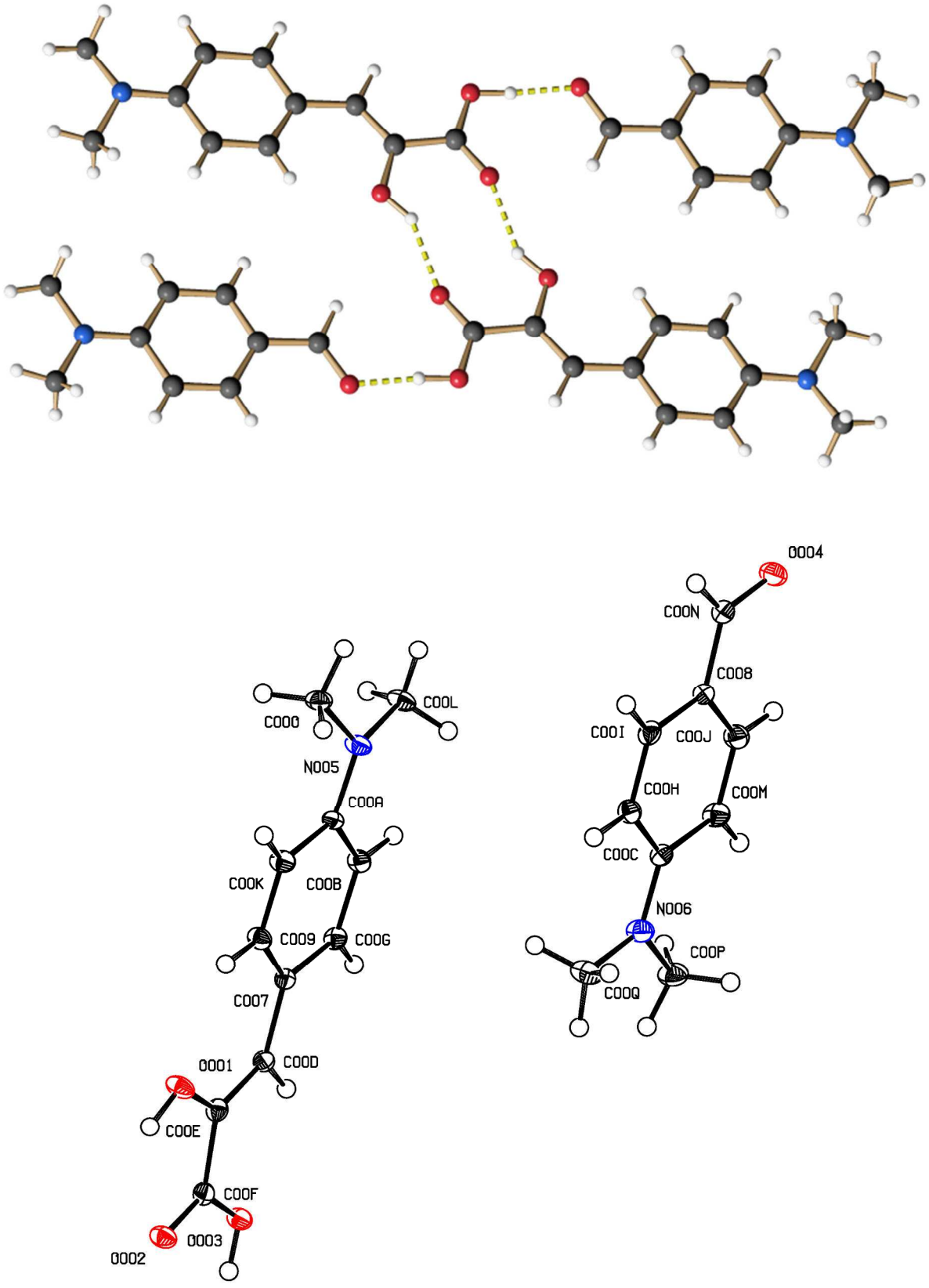
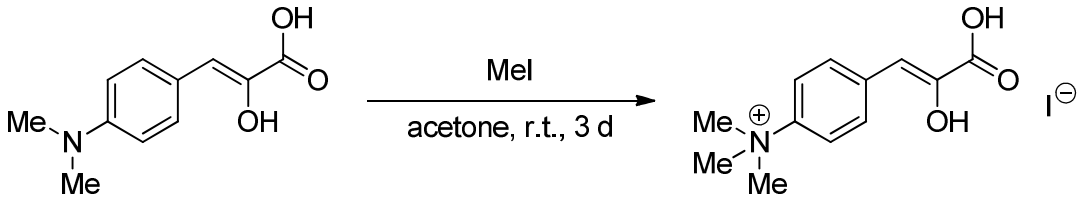


Figure S13. X-ray crystal structure (top) and ORTEP (bottom) of the (*Z*)-**E10** cocrystallized with 4-dimethylaminobenzaldehyde. Thermal ellipsoids are drawn at 50% probability level. Hydrogen bond interactions between acid and aldehyde are shown (top).
CCDC 1825830.

S3.1.3 4-(2-Carboxy-2-oxoethyl)-*N*,*N*,*N*-trimethylbenzenaminium iodide (E4·I)



Compound	*m* [mg] or *V* [mL]	*n* [mmol]	eq
E10	495 mg	2.389	1.00
acetone	50 mL	681	285
MeI	0.15 mL	2.389	1.00

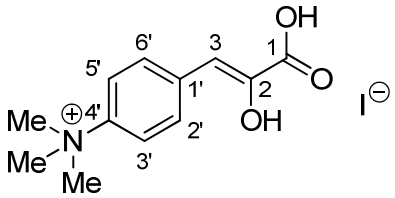
A 100-mL-round bottom flask was charged with a saturated solution of (*Z*)-**E10** in acetone (495 mg in 50 mL, 2.39 mmol, 1.00 eq). To this solution methyl iodide (0.15 mL, 2.39 mmol, 1.00 eq) was added and the mixture was allowed to sit at room temperature for 3 d. Some product had precipitated by that time. However, the ESI MS spectrum clearly showed that still a lot of starting material was present. Further methyl iodide (0.05 mL, 0.78 mmol, 0.33 eq) was added. After another 3 d the ratio of starting material and product did not change. To complete the precipitation of the product, the mixture was kept at –25 °C for 1 d. The mixture was sonicated and the solid was filtered off by means of a sintered glass funnel. The solid was dissolved in methanol and evaporation of most of the solvent gave some precipitation. This solid was dried under reduced pressure. The NMR spectrum shows that this solid was the desired product **E4·I** contaminated with some starting material (~20%) and acetone (~70%) and some other minor impurities. This material could be used in IRMPD measurements. The poor yield of 6% could not be increased since the material in the mother liquor could not be separated from impurities.

E4·I: $C_{12}H_{16}INO_3$, M = 349.16 g mol^{-1}.

Yield: 50.0 mg (6%).

Appearance: Light yellow solid.

FT-IR: (ATR): $\tilde{\nu}$ [cm^{-1}] = 3011 (w), 2361 (m), 2342 (m), 1701 (s), 1605 (m), 1508 (s), 1223 (s), 1179 (s), 1123 (s), 954 (s), 939 (s), 835 (s).



^{1}H NMR (600 MHz, DMSO-d_6, 298 K) δ [ppm] = 13.31 (brs, 1H, OH-1), 9.77 (brs, 1H, OH-2), 7.96 (m, 2H, H-2',6'), 7.93 (m, 2H, H-3',5'), 6.47 (s, 1H, H-3), 3.61 (s, 9H, NMe_3).

^{13}C NMR (151 MHz, DMSO-d_6, 298 K) δ [ppm] = 165.8 (1C, C-1), 145.1 (1C, C-4'), 143.7 (1C, C-2), 136.6 (1C, C-1'), 130.0 (2C, C-2',6'), 120.3 (2C, C-3',5'), 106.9 (1C, C-3), 56.2 (3C, NMe_3).

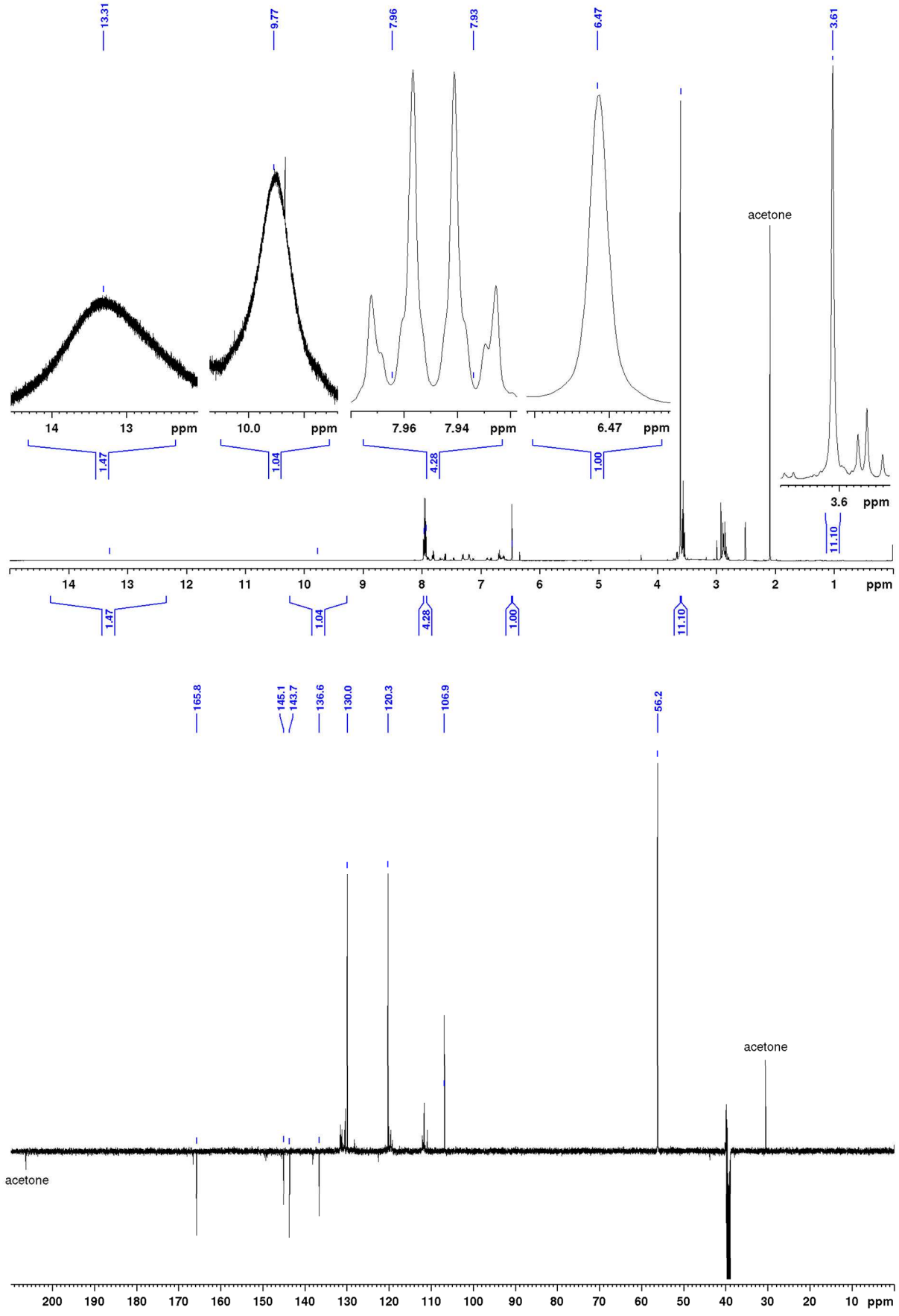


Figure S14. ^{1}H NMR spectrum (top, 600 MHz, THF-d_8, 298 K) and multiplicity-edited ^{13}C DEPTQ NMR spectrum (bottom, 151 MHz) of **E4·I**.

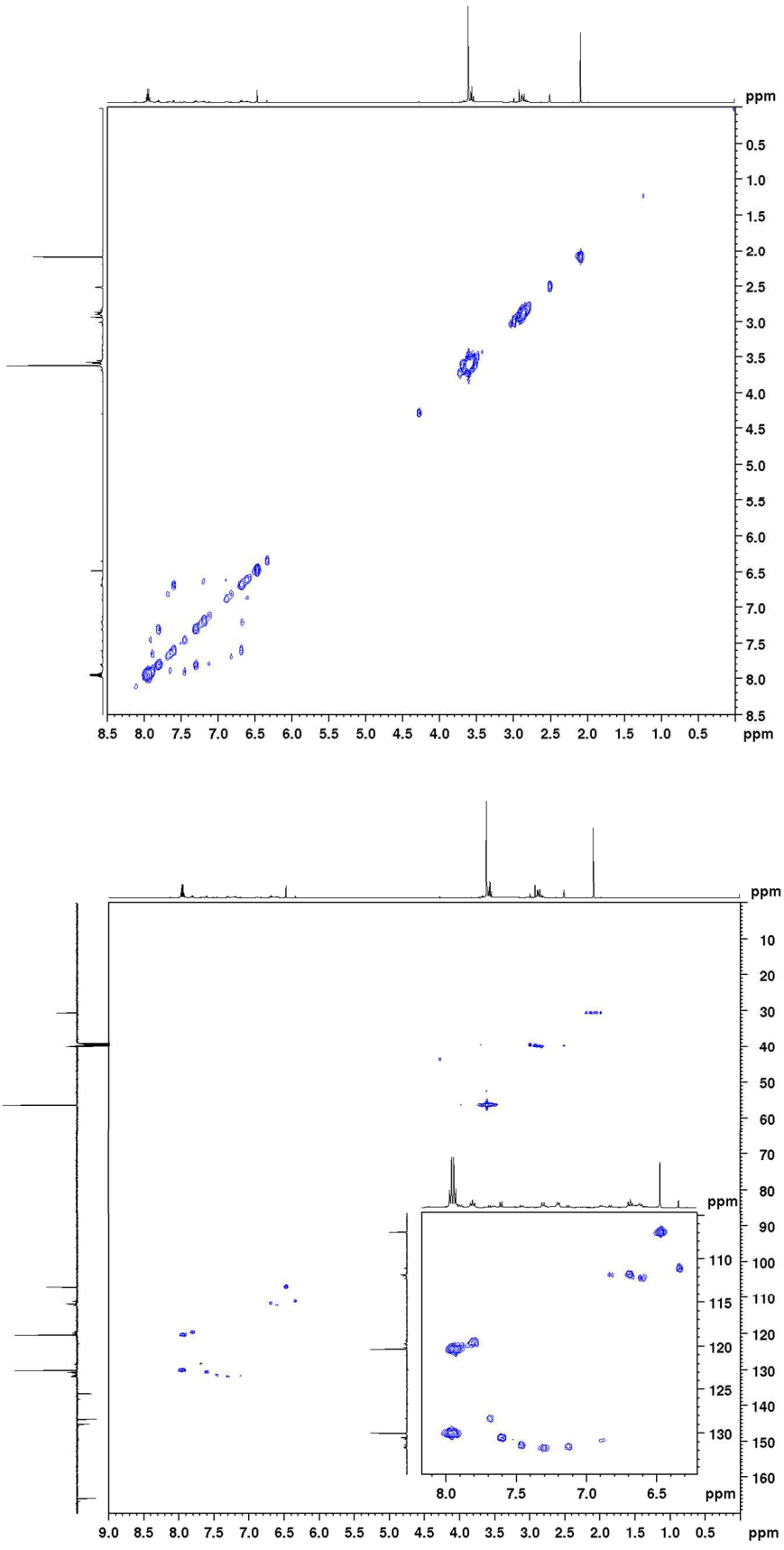


Figure S15. ^{1}H,^{1}H COSY spectrum (top, 600 MHz, THF-d_8, 298 K) and ^{1}H,^{13}C HMQC spectrum (bottom, 600 MHz/151 MHz, THF-d_8, 298 K) of **E4·I**.

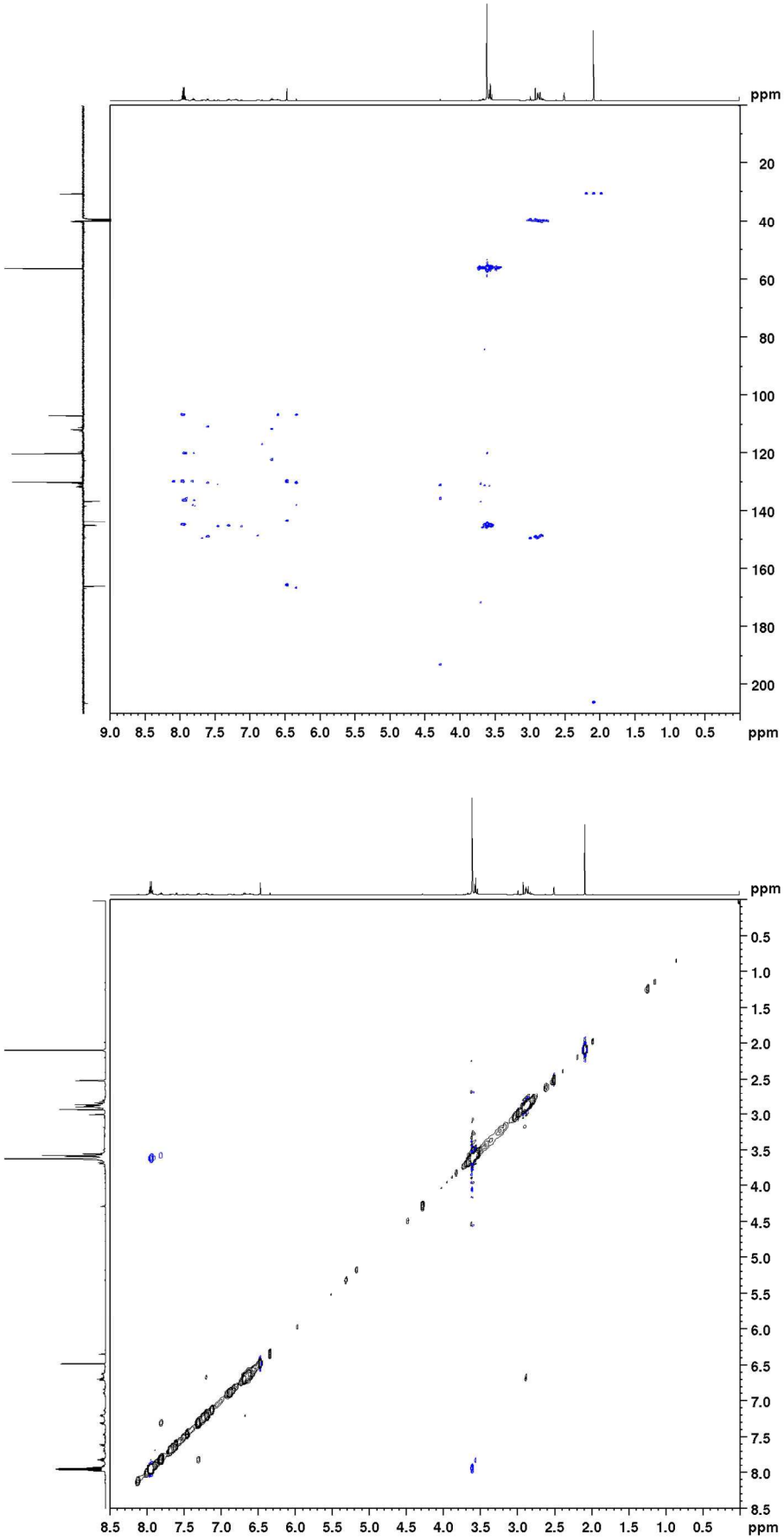


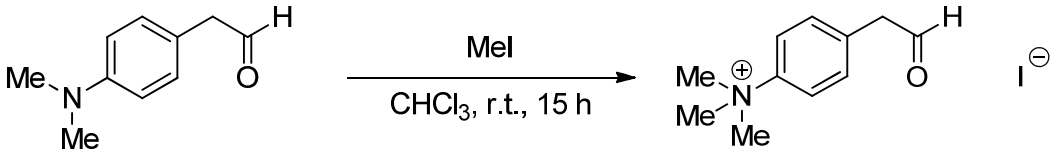
Figure S16. ^{1}H,^{13}C HMBC spectrum (top, 600 MHz/151 MHz, THF-d_8, 298 K) and ^{1}H,^{1}H NOESY spectrum (bottom, 600 MHz, THF-d_8, 298 K, mixing time = 600 ms) of **E4·I**.

S3.2 Synthesis of *N,N,N*-Trimethyl-4-(2-oxoethyl)benzenaminium iodide (6·I) as a Reference Compound

This section describes how the charge tagged carbaldehyde **6·I** was synthesized. 4-(Dimethylamino)benzeneacetaldehyde (**11**) was prepared by a modified procedure according to Gagosz and coworkers.[4]

The respective enol ether was prepared in an *E*/*Z* mixture. Instead of employing 5 N hydrochloric acid–which does lead to excessive aldol condensation of the desired aldehyde **6·I** –acetic acid with a catalytic amount of hydrochloric acid was used for the demethylation of the enol ether. 4-(Dimethylamino)benzeneacetaldehyde (**11**) is very air sensitive and was therefore worked up quickly. A flash column on silica gel (ethyl acetate/cyclohexane 50/50) was performed and care taken that not too much air got into contact with the purified fraction. After removal of the solvent the product was brought into a glovebox where the methylation described below followed.

S3.2.1 *N,N,N*-Trimethyl-4-(2-oxoethyl)benzenaminium iodide (6·I)



11 **6·I**, quant.

Compound	*m* [mg] or *V* [mL]	*n* [mmol]	eq
11	400 mg	2.45	1.00
$CHCl_3$	5.0 mL	62.4	25.5
MeI	0.15 mL	2.70	1.10

In a glovebox a small vial was charged with a stir bar and freshly prepared carbaldehyde **11**. It was dissolved in chloroform and methyl iodide was added with a syringe. The vial was capped and the reaction stirred for 15 h. Subsequently, the volatiles were evaporated under reduced pressure while also excluding air.

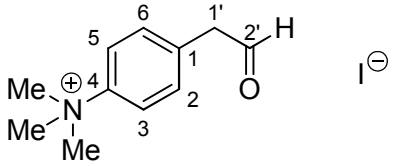
According to the NMR, the compound is not completely pure. This is due to oxidation of the very reactive starting material. These impurities could not be removed.

6·I: $C_{11}H_{16}INO$, M = 305.16 g mol^{-1}.

Yield: 748.0 mg (quant. according to NMR).

Appearance: Light yellow solid.

FT-IR: (ATR): $\tilde{\nu}$ [cm^{-1}] = **6·I** is very air and moisture sensitive – no IR possible



^{1}H NMR (600 MHz, DMSO-d_6, 298 K) δ [ppm] = 9.74 (t, $^3J_{HH}$ = 1.4 Hz, 1H, H-2'), 7.96 (dm, $^3J_{HH}$ = 9.1 Hz, 2H, H-3,5), 7.50 (dm, $^3J_{HH}$ = 9.1 Hz, 2H, H-2,6), 3.96 (brm, 2H, H-1'), 3.64 (s, 9H, NMe_3).

^{13}C NMR (151 MHz, DMSO-d_6, 298 K) δ [ppm] = 199.9 (1C, C-2'), 145.9 (1C, C-4), 135.3 (1C, C-1), 131.2 (2C, C-2,6), 120.4 (2C, C-3,5), 56.4 (1C, C-1'), 48.4 (3C, NMe_3).

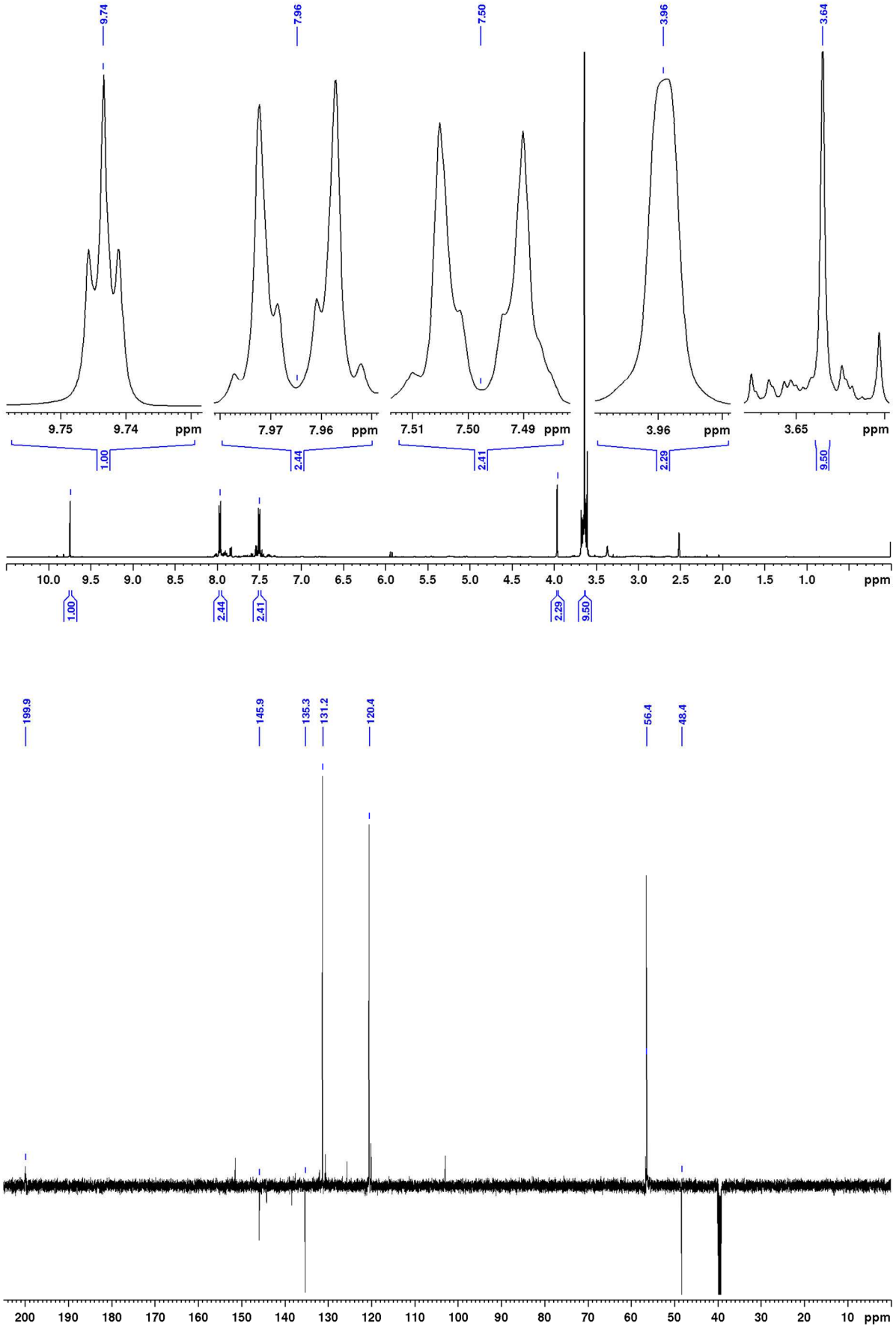


Figure S17. ^{1}H NMR spectrum (top, 600 MHz, THF-d_8, 298 K) and multiplicity-edited ^{13}C DEPTQ NMR spectrum (bottom, 151 MHz) of **6·I**.

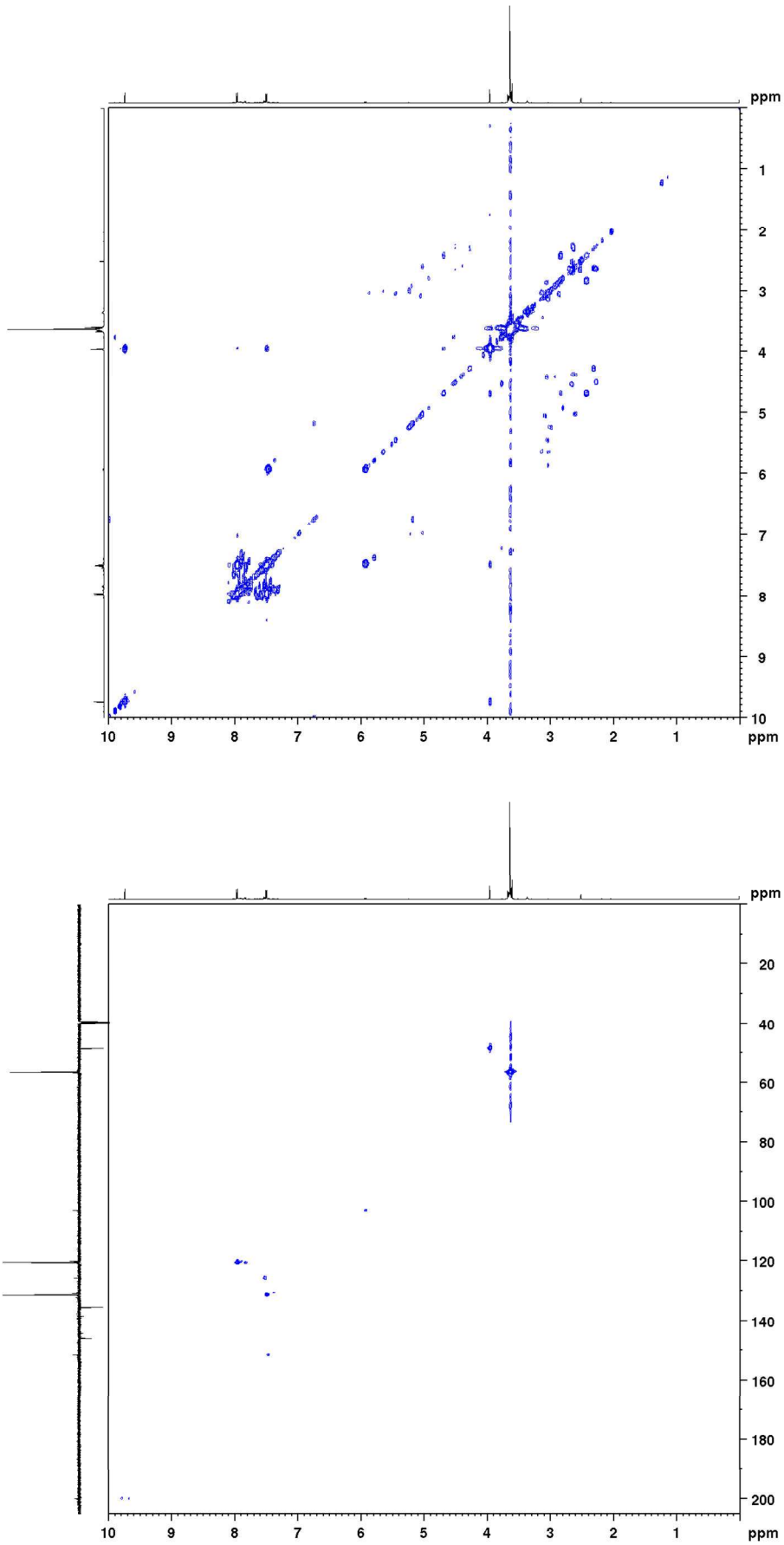


Figure S18. ^{1}H,^{1}H COSY spectrum (top, 600 MHz, THF-d_8, 298 K) and ^{1}H,^{13}C HMQC spectrum (bottom, 600 MHz/151 MHz, THF-d_8, 298 K) of **6·I**.

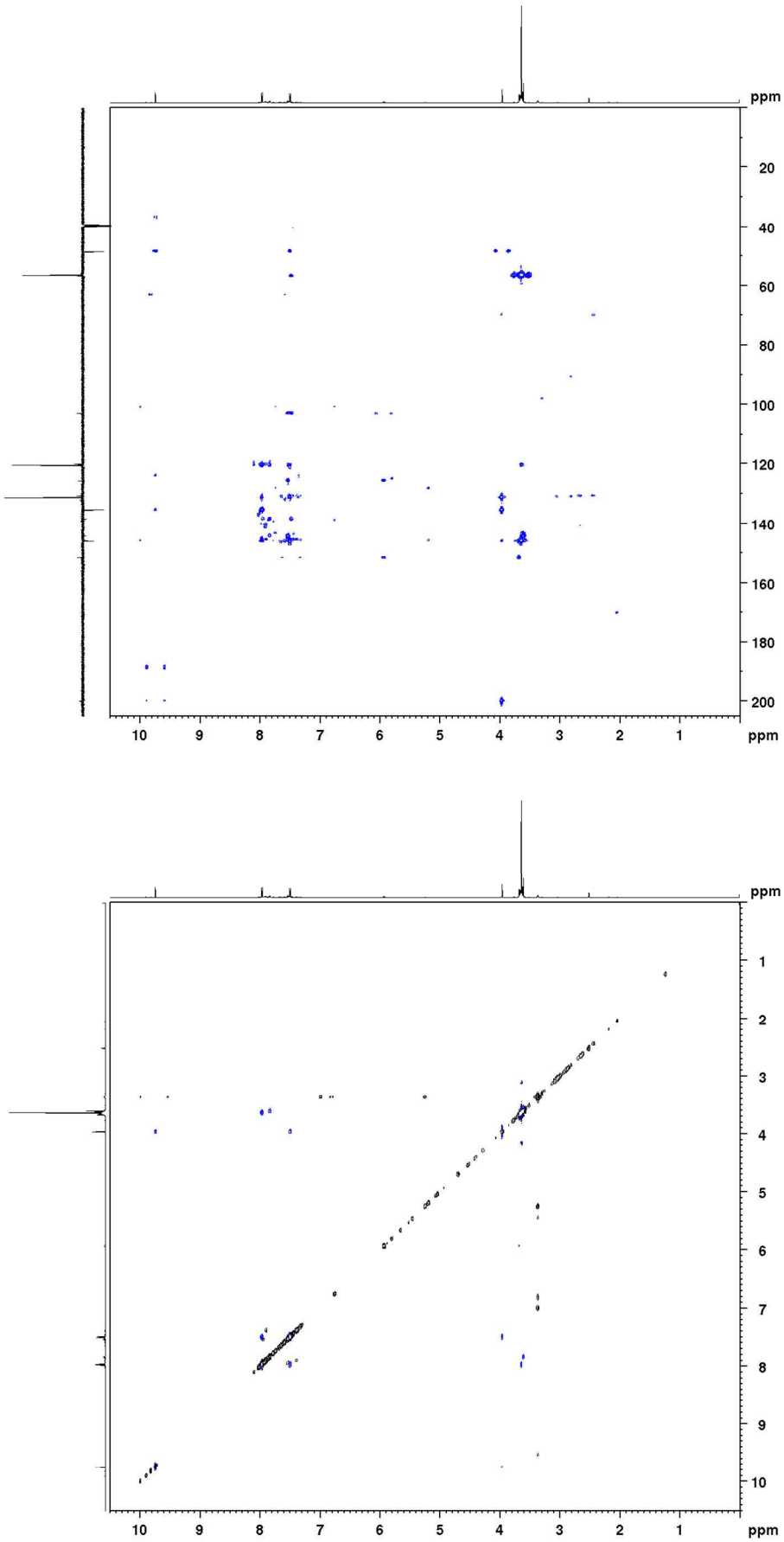


Figure S19. $^{1}H,^{13}C$ HMBC spectrum (top, 600 MHz/151 MHz, THF-d_8, 298 K) and $^{1}H,^{1}H$ NOESY spectrum (bottom, 600 MHz, THF-d_8, 298 K, mixing time = 600 ms) of **6**·**I**.

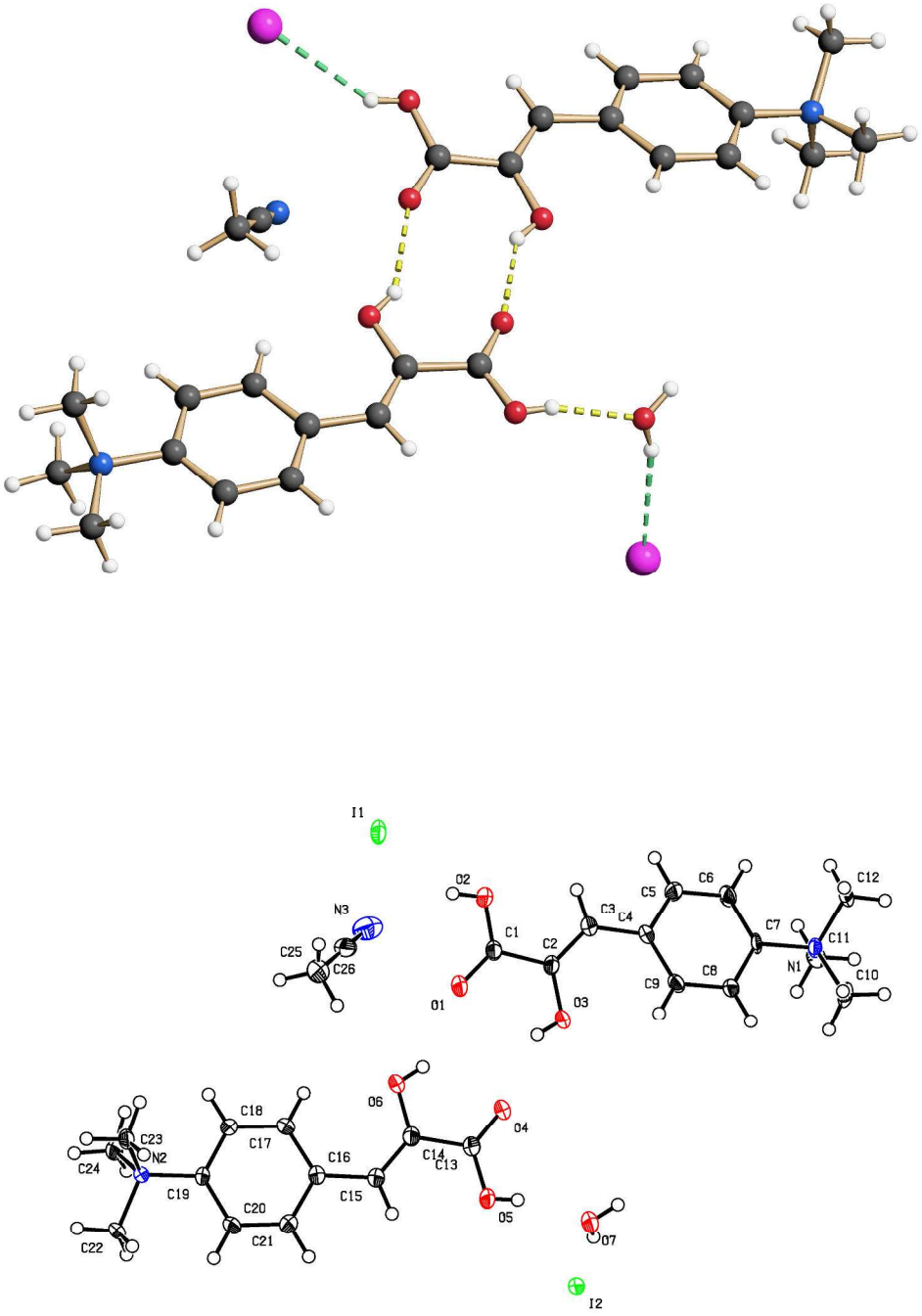
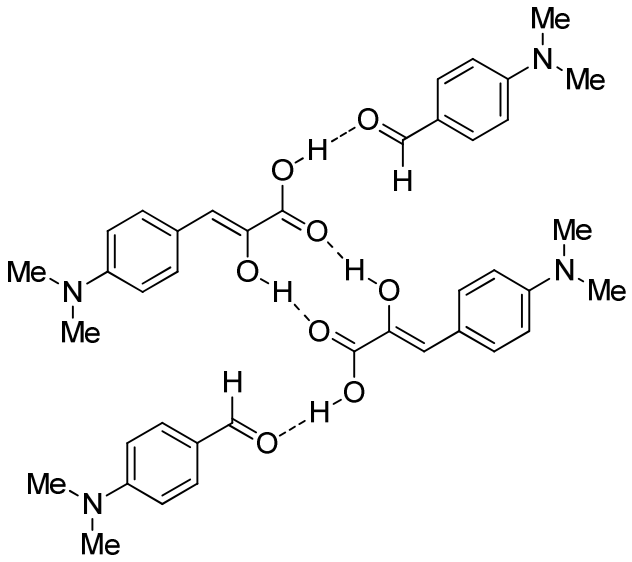


Figure S20. X-ray crystal structure (top; CCDC 1911879) and ORTEP (bottom) of the E4·I co-crystallized with acetonitrile and water. Thermal ellipsoids are drawn at 50% probability level. Hydrogen bond interactions between acid and water are shown (top).

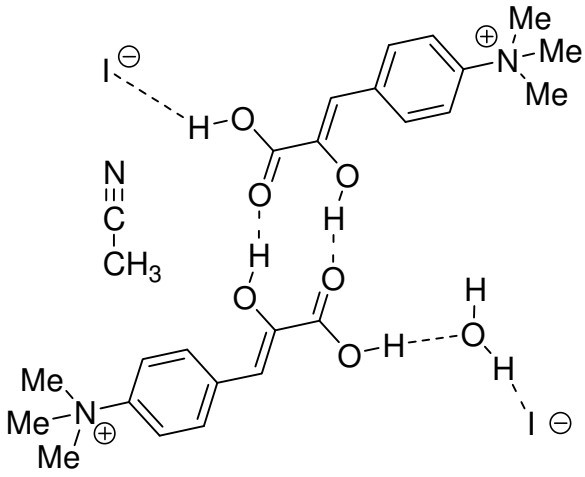
S4. Crystallographic Data

S4.1 (2*Z*)-3-[4-(Dimethylamino)phenyl]-2-hydroxy-2-propenoic acid ((*Z*)-E10) Cocrystallized with 4-Dimethylaminobenzaldehyde



CCDC	1825830
Empirical formula	$C_{20}H_{24}N_2O_4$
Moiety formula	$C_{11}H_{13}NO_3$, $C_9H_{11}NO$
Formula weight	356.41
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.6578(3) Å, α = 78.7640(10)°. b = 10.0035(4) Å, β = 75.9780(10)°. c = 11.6371(4) Å, γ = 67.1630(10)°.
Volume	895.44(6) $Å^3$
Z	2
Density (calculated)	1.322 g cm^{-3}
Absorption coefficient	0.754 mm^{-1}
F(000)	380
Crystal size	0.200 × 0.070 × 0.030 mm^3
Θ range for data collection	3.940 to 72.152°.
Index ranges	−10 ≤ h ≤ 10, −12 ≤ k ≤ 12, −13 ≤ l ≤ 14
Reflections collected	13387
Independent reflections	3476 [R(int) = 0.0290]
Completeness to Θ = 67.679°	98.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7536 and 0.6285
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3476 / 0 / 253
Goodness-of-fit on F^2	1.106
Final R indices [I > 2σ(I)]	R1 = 0.0440, wR2 = 0.1248
R indices (all data)	R1 = 0.0476, wR2 = 0.1273
Extinction coefficient	n/a
Largest diff. peak and hole	0.292 and −0.240 e $Å^{-3}$

S4.2 4-(2-Carboxy-2-oxoethyl)-*N,N,N*-trimethylbenzenaminium iodide (E4·I) with Acetonitrile and Water Inclusion



CCDC	1911879	
Empirical formula	C26 H37 I2 N3 O7	
Moiety formula	2(C12 H16 N O3), C2 H3 N, 2(I), H2 O	
Formula weight	757.38	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.2439(3) Å	a= 72.9180(10)°.
	b = 11.9323(3) Å	b= 83.3110(10)°.
	c = 14.7966(4) Å	g = 65.7470(10)°.
Volume	1576.24(8) $Å^3$	
Z	2	
Density (calculated)	1.596 Mg/m^3	
Absorption coefficient	16.039 mm^{-1}	
F(000)	752	
Crystal size	0.265 x 0.242 x 0.096 mm^3	
Theta range for data collection	3.124 to 72.171°.	
Index ranges	-12<=h<=12, -14<=k<=14, -18<=l<=18	
Reflections collected	40714	
Independent reflections	6163 [R(int) = 0.0555]	
Completeness to theta = 67.679°	99.6 %	
Absorption correction	Numerical	
Max. and min. transmission	0.1726 and 0.0170	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6163 / 1 / 374	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.0966	
R indices (all data)	R1 = 0.0384, wR2 = 0.0994	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.693 and -1.797 $e.Å^{-3}$	

S5. References

[1] G.R. Fulmer, A.J.M. Miller, N.H. Sherden, H.E. Gottlieb, A. Nudelman, B.M. Stoltz, J.E. Bercaw, K.I. Goldberg, *Organometallics*, **2010**, *29*, 2176–2179. http://dx.doi.org/10.1021/om100106e.

[2] S. Saravanana, P.S. Selvana, N. Gopala, J.K. Guptab, B. De, *Arch. Pharm. Chem. Life Sci.*, **2005**, *338*, 488–492. http://dx.doi.org/10.1002/ardp.200400944.

[3] L. Hellerman, C.C. Porter, H.J. Lowe, H.F. Koster, *J. Am. Chem. Soc.*, **1946**, *68*, 1890–1893. http://dx.doi.org/10.1021/ja01214a007.

[4] G. Henrion, T.E.J. Chavas, X. Le Goff, F. Gagosz, *Angew. Chem. Int. Ed.*, **2013**, *52*, 6277–6282. http://dx.doi.org/10.1002/anie.201301015.

Supporting Information

Part II: Computations

Hydrogen Tunneling Avoided: Enol-Formation From a Charge-tagged Phenyl Pyruvic Acid Derivative Evidenced by Tandem-MS, IR Ion Spectroscopy and Theory

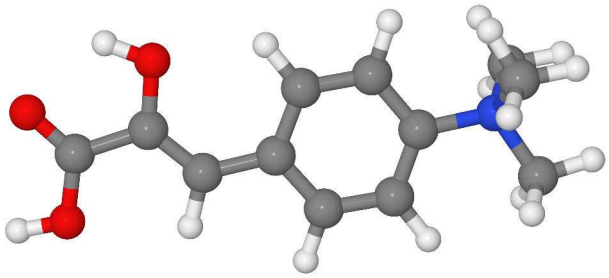
Mathias Paul,[1] Katrin Peckelsen,[1] Thomas Thomulka,[1] Jörg-M. Neudörfl,[1] Jonathan Martens,[2] Giel Berden,[2] Jos Oomens,[2,3] Albrecht Berkessel,[1] Anthony J. H. M. Meijer*,[4] and Mathias Schäfer*,[1]

[1] University of Cologne, Department of Chemistry, Greinstrasse 4, 50939 Köln, Germany.
[2] Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7c, 6525 ED Nijmegen, The Netherlands.
[3] Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands.
[4] University of Sheffield, Department of Chemistry, Sheffield S3 7HF, U.K.

Mathias Paul	https://orcid.org/0000-0003-4635-3605
Katrin Peckelsen	
Thomas Thomulka	
Jörg-M. Neudörfl	http://orcid.org/0000-0002-2918-0565
Jonathan Martens	https://orcid.org/0000-0001-9537-4117
Giel Berden	https://orcid.org/0000-0003-1500-922X
Jos Oomens	https://orcid.org/0000-0002-2717-1278
Anthony J. H. M. Meijer	https://orcid.org/0000-0003-4803-3488
Albrecht Berkessel	https://orcid.org/0000-0003-0470-7428
Mathias Schäfer	https://orcid.org/0000-0002-5943-4335

CONTENTS

S1. CALCULATIONS ON 4A



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=C(C(=O)O)O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.43896863	a.u.
Gibbs Energy	: -747.21256700	a.u.
Number of imaginary frequencies	: 0	

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

32

C	-3.26934099	-2.20802808	3.88297701
C	-3.53535891	-1.53192699	2.70748496
C	-4.85774708	-1.25555205	2.31561899
C	-5.88588905	-1.69178700	3.16197705
C	-5.62717676	-2.37040806	4.34248495
C	-4.31275082	-2.62754893	4.70072222
H	-2.23803091	-2.39722300	4.14189291
H	-2.71536112	-1.21429300	2.08628297
H	-6.91375685	-1.49591196	2.89103389
H	-6.46194601	-2.67888999	4.94893885
N	-3.97275305	-3.35985804	5.97002077
C	-5.18981314	-3.75374293	6.75547218
H	-4.85381603	-4.27247810	7.64742279
H	-5.74164581	-2.86269593	7.03357506
H	-5.80616188	-4.41411114	6.15559483
C	-3.21394897	-4.62185812	5.64007282
H	-2.29841208	-4.36318207	5.12268782
H	-2.98607302	-5.14106178	6.56668997
H	-3.83889890	-5.23600483	4.99998283
C	-3.12488508	-2.47769094	6.85329199
H	-3.68684292	-1.57539403	7.07127190
H	-2.89788508	-3.01892900	7.76743317
H	-2.20960593	-2.22498202	6.33250618
C	-4.38949394	-0.05559300	0.15997800
O	-3.04947805	-0.13398901	0.20046300
C	-5.21405077	-0.55289900	1.09954095
H	-6.26755285	-0.40641499	0.91800600
C	-4.87332201	0.65421999	-1.05977702
O	-4.07977915	1.07819104	-1.86820400
O	-6.19904900	0.76789999	-1.16323102
H	-6.39497805	1.24126196	-1.98598194

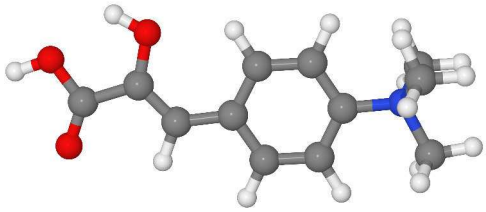
H	-2.72362995	0.30812600	-0.60589403

S1.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	29.32430000	0.02250000	0.00000000
2	37.76110000	2.71390000	0.00000000
3	63.19060000	0.28670000	0.00000000
4	91.52110000	2.67330000	0.00000000
5	93.04140000	0.07890000	0.00000000
6	141.57710000	0.04700000	0.00000000
7	188.28040000	0.05460000	0.00000000
8	220.76860000	0.07940000	0.00000000
9	229.77160000	1.60510000	0.00000000
10	270.79800000	0.00040000	0.00000000
11	282.26990000	0.53410000	0.00000000
12	301.54460000	1.07070000	0.00000000
13	350.98960000	0.08150000	0.00000000
14	360.46090000	10.56400000	0.00000000
15	371.21560000	1.66040000	0.00000000
16	389.01130000	1.11220000	0.00000000
17	414.16590000	5.89040000	0.00000000
18	422.81500000	0.00200000	0.00000000
19	438.99950000	0.13520000	0.00000000
20	481.36780000	3.09390000	0.00000000
21	509.18330000	33.56350000	0.00000000
22	514.26980000	2.21340000	0.00000000
23	567.03050000	1.26110000	0.00000000
24	569.20420000	69.85390000	0.00000000
25	621.91200000	76.05930000	0.00000000
26	649.78040000	3.50820000	0.00000000
27	649.95320000	66.91800000	0.00000000
28	675.09750000	17.91180000	0.00000000
29	717.56540000	14.83670000	0.00000000
30	748.00090000	0.61480000	0.00000000
31	787.51300000	31.09880000	0.00000000
32	829.44390000	3.85100000	0.00000000
33	840.08620000	45.58850000	0.00000000
34	852.83040000	18.92500000	0.00000000
35	867.22150000	1.61050000	0.00000000
36	892.21510000	26.77490000	0.00000000
37	899.80280000	22.74660000	0.00000000
38	944.50230000	28.20110000	0.00000000
39	964.61210000	18.26940000	0.00000000
40	981.51220000	0.51390000	0.00000000
41	1002.15500000	0.00000000	0.00000000
42	1033.72920000	6.00090000	0.00000000
43	1077.02260000	0.01890000	0.00000000
44	1131.35450000	8.76340000	0.00000000
45	1133.18400000	1.85180000	0.00000000
46	1140.00180000	0.51200000	0.00000000
47	1141.71550000	63.65190000	0.00000000
48	1174.92570000	0.61530000	0.00000000
49	1183.01170000	418.25860000	0.00000000
50	1228.30150000	11.78260000	0.00000000
51	1256.90880000	10.17240000	0.00000000
52	1259.02890000	1.32400000	0.00000000
53	1259.61560000	0.38020000	0.00000000
54	1295.45160000	6.38220000	0.00000000
55	1339.74950000	42.99510000	0.00000000
56	1351.97110000	150.86760000	0.00000000
57	1362.96420000	7.14210000	0.00000000
58	1411.96910000	72.19620000	0.00000000
59	1444.52730000	285.15790000	0.00000000
60	1449.18840000	7.23710000	0.00000000

61	1450.71810000	4.61130000	0.00000000
62	1462.80470000	17.01180000	0.00000000
63	1479.29980000	0.00950000	0.00000000
64	1489.44140000	0.31310000	0.00000000
65	1492.90770000	1.57200000	0.00000000
66	1495.76530000	0.21040000	0.00000000
67	1506.86290000	26.66380000	0.00000000
68	1512.44500000	23.67630000	0.00000000
69	1530.28840000	44.58940000	0.00000000
70	1546.36750000	59.35230000	0.00000000
71	1616.79600000	1.45980000	0.00000000
72	1640.90830000	41.29450000	0.00000000
73	1719.53960000	59.68370000	0.00000000
74	1780.59400000	430.26650000	0.00000000
75	3078.92810000	0.62220000	0.00000000
76	3080.44550000	2.11470000	0.00000000
77	3087.56190000	2.19880000	0.00000000
78	3166.56940000	0.00170000	0.00000000
79	3167.39830000	1.53000000	0.00000000
80	3174.53770000	8.94090000	0.00000000
81	3182.59840000	0.23450000	0.00000000
82	3185.94400000	5.60380000	0.00000000
83	3187.94350000	0.05640000	0.00000000
84	3189.70610000	1.41800000	0.00000000
85	3197.49850000	2.26770000	0.00000000
86	3212.45210000	1.07550000	0.00000000
87	3232.36100000	1.06080000	0.00000000
88	3245.66720000	5.92000000	0.00000000
89	3605.63790000	348.84650000	0.00000000
90	3741.29850000	181.50010000	0.00000000

S2. CALCULATIONS ON 4B



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=C(C(=O)O)O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.43503369	a.u.
Gibbs Energy	: -747.20912300	a.u.
Number of imaginary frequencies	: 0	

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

32

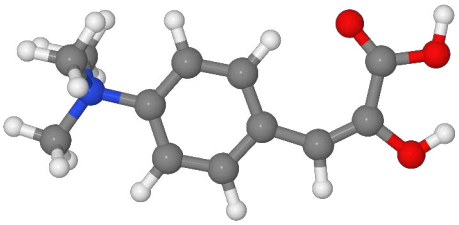
C	-2.46723890	-1.33187306	3.97201896
C	-3.01358294	-0.99823499	2.74719310
C	-3.32385492	0.33739001	2.43344998
C	-3.05731010	1.30794001	3.40882993
C	-2.50962400	0.98135698	4.63926888
C	-2.21493101	-0.34439400	4.91801119
H	-2.24576211	-2.37066293	4.16777182
H	-3.20238805	-1.77556396	2.02656794
H	-3.28412008	2.34374094	3.19961500
H	-2.32888508	1.77411604	5.34539890
N	-1.61941504	-0.75628698	6.23666811
C	-1.39933598	0.40574801	7.16127396
H	-0.97081399	0.01986100	8.08052540
H	-0.71205503	1.10638297	6.70023203
H	-2.35006905	0.88349700	7.37023878
C	-2.54563498	-1.72374105	6.93177891
H	-2.67631412	-2.60158110	6.31118298
H	-2.10428095	-2.00166798	7.88471794
H	-3.50101209	-1.23126698	7.08070087
C	-0.28188199	-1.41558802	6.00564623
H	0.36367100	-0.70516503	5.49966478
H	0.13640600	-1.69670200	6.96800709
H	-0.41884199	-2.29423189	5.38754511
C	-4.23151493	0.02192700	0.10796500
O	-4.07449102	-1.31699395	0.04593700
C	-3.89670396	0.76735401	1.17552996
H	-4.08808422	1.82400596	1.05988503
C	-4.81452084	0.70108497	-1.09054601
O	-5.01925087	1.87739801	-1.19833302
O	-5.08540916	-0.21001101	-2.05699992
H	-5.46073294	0.25388199	-2.81968808
H	-4.38419294	-1.62830698	-0.81586200

S2.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	29.34060000	2.08960000	0.00000000
2	37.95830000	1.81430000	0.00000000
3	62.89270000	0.11310000	0.00000000
4	83.85190000	1.02330000	0.00000000
5	90.58070000	1.29710000	0.00000000
6	136.78380000	0.01110000	0.00000000
7	191.78200000	2.92660000	0.00000000
8	220.90000000	0.19920000	0.00000000
9	228.57230000	1.41650000	0.00000000
10	270.78220000	0.16890000	0.00000000
11	282.15770000	0.33800000	0.00000000
12	301.88410000	0.60210000	0.00000000
13	351.07440000	0.05440000	0.00000000
14	359.51880000	1.79760000	0.00000000
15	370.95830000	1.54790000	0.00000000
16	388.63250000	1.97030000	0.00000000
17	408.64780000	1.11710000	0.00000000
18	422.75830000	0.15210000	0.00000000
19	437.78220000	0.48480000	0.00000000
20	481.01340000	3.29240000	0.00000000
21	493.29360000	107.43900000	0.00000000
22	514.41700000	10.34650000	0.00000000
23	532.82470000	20.44800000	0.00000000
24	561.48150000	5.18410000	0.00000000
25	572.96910000	98.62320000	0.00000000
26	618.13850000	8.66230000	0.00000000
27	645.40590000	35.17370000	0.00000000
28	658.20250000	26.04530000	0.00000000
29	716.14150000	10.16940000	0.00000000
30	748.06620000	0.31010000	0.00000000
31	780.82130000	28.73960000	0.00000000
32	829.94360000	2.12460000	0.00000000
33	839.92250000	37.50430000	0.00000000
34	853.75250000	18.99570000	0.00000000
35	865.76130000	5.97200000	0.00000000
36	878.95060000	29.34630000	0.00000000
37	917.47490000	18.32370000	0.00000000
38	945.03840000	30.66940000	0.00000000
39	964.47760000	18.69750000	0.00000000
40	983.91460000	0.97700000	0.00000000
41	1001.16240000	0.01280000	0.00000000
42	1033.86970000	4.78430000	0.00000000
43	1077.04720000	0.01900000	0.00000000
44	1107.21520000	56.45240000	0.00000000
45	1132.99170000	1.41490000	0.00000000
46	1134.47550000	2.13000000	0.00000000
47	1140.03090000	0.51110000	0.00000000
48	1152.39940000	546.68090000	0.00000000
49	1174.24870000	1.96020000	0.00000000
50	1227.48840000	15.94550000	0.00000000
51	1252.02240000	17.52910000	0.00000000
52	1259.04680000	1.32240000	0.00000000
53	1259.54160000	0.67910000	0.00000000
54	1295.28400000	4.48560000	0.00000000
55	1333.30110000	132.63740000	0.00000000
56	1346.52680000	144.61770000	0.00000000
57	1355.64440000	111.04910000	0.00000000
58	1368.25850000	86.01410000	0.00000000
59	1429.22380000	145.63210000	0.00000000
60	1448.88880000	1.33870000	0.00000000

61	1450.70980000	4.60410000	0.00000000
62	1459.07770000	11.96130000	0.00000000
63	1479.34020000	0.00850000	0.00000000
64	1489.48660000	0.30820000	0.00000000
65	1492.89610000	1.47250000	0.00000000
66	1495.74930000	0.22460000	0.00000000
67	1506.88620000	26.46820000	0.00000000
68	1512.41990000	23.68290000	0.00000000
69	1530.29440000	45.12400000	0.00000000
70	1546.32860000	63.98410000	0.00000000
71	1616.29120000	1.64390000	0.00000000
72	1640.96140000	41.65180000	0.00000000
73	1716.99080000	49.65820000	0.00000000
74	1826.45260000	271.15970000	0.00000000
75	3078.90150000	0.62410000	0.00000000
76	3080.44040000	2.15010000	0.00000000
77	3087.57830000	2.22330000	0.00000000
78	3166.52270000	0.00210000	0.00000000
79	3167.38050000	1.60840000	0.00000000
80	3174.54850000	8.90570000	0.00000000
81	3182.71510000	0.21910000	0.00000000
82	3185.81150000	5.64510000	0.00000000
83	3187.90850000	0.05170000	0.00000000
84	3191.10360000	1.47140000	0.00000000
85	3197.31480000	2.23770000	0.00000000
86	3202.58850000	1.15090000	0.00000000
87	3232.64670000	1.05540000	0.00000000
88	3245.53950000	4.89050000	0.00000000
89	3746.10750000	353.83400000	0.00000000
90	3753.13690000	165.85420000	0.00000000

S3. CALCULATIONS ON 4C



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=C(C(=O)O)O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.42604870	a.u.
Gibbs Energy	: -747.19847400	a.u.
Number of imaginary frequencies	: 1	

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

32

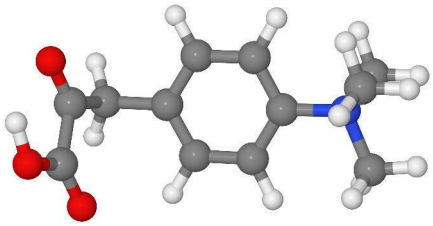
C	-1.50804901	-1.05090404	-0.27795601
C	-0.12729500	-0.99590999	-0.24694200
C	0.54472703	0.19160700	0.09109400
C	-0.25357300	1.30813098	0.39265299
C	-1.63786602	1.26171505	0.36398101
C	-2.26572895	0.07350100	0.02624400
H	-1.97209895	-1.98926198	-0.54429603
H	0.44002599	-1.87739003	-0.48573801
H	0.22245200	2.24143291	0.65774101
H	-2.18417811	2.15740108	0.60696203
N	-3.76465988	-0.03948000	-0.02223000
C	-4.45384216	1.24715197	0.32785800
H	-5.52381516	1.07614100	0.26813400
H	-4.18290615	1.53654003	1.33715904
H	-4.16338587	2.01452398	-0.38109601
C	-4.19915295	-0.42689899	-1.41430700
H	-3.76091409	-1.38315904	-1.67175496
H	-5.28322983	-0.49473500	-1.43233001
H	-3.85106397	0.33601099	-2.10296512
C	-4.22613811	-1.08749700	0.96034497
H	-3.89713192	-0.79180300	1.95118701
H	-5.30993795	-1.14853406	0.91788501
H	-3.78781891	-2.04190111	0.69622600
C	3.09177589	-0.34219801	-0.02849100
O	4.27217007	0.29397199	0.16201200
C	1.97947502	0.40154001	0.16585299
H	2.24054909	1.41432297	0.45071900
C	3.19599199	-1.77681398	-0.42665201
O	2.29583907	-2.54445195	-0.65058899
O	4.49578285	-2.14017701	-0.51301700
H	4.53577995	-3.07249093	-0.77207500
H	5.00295305	-0.31627101	0.00050000

S3.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-17.71250000	0.72630000	0.00000000
2	39.49010000	3.72250000	0.00000000
3	54.51250000	0.31930000	0.00000000
4	63.96380000	0.14560000	0.00000000
5	110.17430000	2.94160000	0.00000000
6	151.63090000	0.34310000	0.00000000
7	209.55080000	1.00810000	0.00000000
8	222.46910000	0.02750000	0.00000000
9	253.18720000	3.43040000	0.00000000
10	272.48650000	0.66710000	0.00000000
11	284.31090000	2.24010000	0.00000000
12	287.38620000	0.55720000	0.00000000
13	351.72560000	0.03740000	0.00000000
14	357.57670000	1.26150000	0.00000000
15	391.21950000	0.89540000	0.00000000
16	395.85930000	4.45530000	0.00000000
17	401.08890000	12.34680000	0.00000000
18	425.65470000	5.44770000	0.00000000
19	425.98520000	3.11970000	0.00000000
20	441.19790000	77.16370000	0.00000000
21	477.94840000	44.28480000	0.00000000
22	479.03990000	3.20740000	0.00000000
23	532.48910000	9.33360000	0.00000000
24	568.21670000	11.30490000	0.00000000
25	582.51420000	28.15410000	0.00000000
26	599.41890000	75.72710000	0.00000000
27	624.14680000	0.42820000	0.00000000
28	665.47710000	14.29530000	0.00000000
29	718.54370000	33.42680000	0.00000000
30	745.67810000	0.86700000	0.00000000
31	777.61200000	25.29510000	0.00000000
32	799.08890000	23.20190000	0.00000000
33	828.27840000	3.84970000	0.00000000
34	845.42950000	40.99290000	0.00000000
35	860.51020000	13.69680000	0.00000000
36	907.52180000	43.22670000	0.00000000
37	923.00190000	15.07690000	0.00000000
38	945.99730000	32.82690000	0.00000000
39	964.40410000	17.49630000	0.00000000
40	983.72460000	1.55010000	0.00000000
41	1021.26110000	0.18680000	0.00000000
42	1034.60510000	5.14120000	0.00000000
43	1076.64760000	0.01620000	0.00000000
44	1129.21680000	103.64770000	0.00000000
45	1134.30150000	63.82750000	0.00000000
46	1139.72500000	0.52860000	0.00000000
47	1140.50330000	285.85460000	0.00000000
48	1168.63220000	166.08150000	0.00000000
49	1197.84890000	71.10970000	0.00000000
50	1237.69040000	23.00820000	0.00000000
51	1256.33080000	259.92030000	0.00000000
52	1259.02270000	1.33270000	0.00000000
53	1260.86220000	114.59220000	0.00000000
54	1284.95370000	3.01030000	0.00000000
55	1297.11060000	3.63580000	0.00000000
56	1353.56910000	69.99460000	0.00000000
57	1365.75250000	70.43490000	0.00000000
58	1368.67930000	67.19770000	0.00000000
59	1440.16190000	127.76120000	0.00000000
60	1450.14150000	21.60000000	0.00000000

61	1450.65550000	4.55880000	0.00000000
62	1467.97730000	76.42680000	0.00000000
63	1478.74580000	0.00160000	0.00000000
64	1489.54950000	0.33000000	0.00000000
65	1493.07170000	1.74490000	0.00000000
66	1496.17940000	0.36980000	0.00000000
67	1506.13810000	26.72150000	0.00000000
68	1512.40200000	23.59080000	0.00000000
69	1530.56130000	44.98990000	0.00000000
70	1546.14090000	67.15110000	0.00000000
71	1614.00510000	1.98070000	0.00000000
72	1638.85860000	51.65320000	0.00000000
73	1686.49130000	76.08760000	0.00000000
74	1802.79380000	104.98630000	0.00000000
75	3079.07530000	0.67180000	0.00000000
76	3080.49470000	2.14410000	0.00000000
77	3087.55590000	2.59990000	0.00000000
78	3150.71400000	3.51920000	0.00000000
79	3166.48850000	0.00090000	0.00000000
80	3167.23540000	1.45250000	0.00000000
81	3174.26440000	9.23170000	0.00000000
82	3182.51140000	0.25790000	0.00000000
83	3185.72930000	6.31820000	0.00000000
84	3188.96470000	0.04810000	0.00000000
85	3190.25640000	1.67830000	0.00000000
86	3197.01260000	1.61700000	0.00000000
87	3233.38150000	0.87520000	0.00000000
88	3253.14960000	50.49460000	0.00000000
89	3751.99950000	211.78450000	0.00000000
90	3769.26280000	311.79900000	0.00000000

S4. CALCULATIONS ON 4D



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)CC(=O)C(=O)O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.43040473	a.u.
Gibbs Energy	: -747.20897400	a.u.
Number of imaginary frequencies	: 0	

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

32

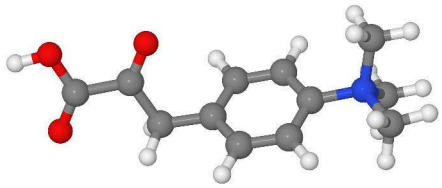
C	-3.36814499	3.74864507	4.95134497
C	-4.27629709	3.34081197	3.98837590
C	-3.84974790	2.96451402	2.71486211
C	-2.48897004	2.99539709	2.43143606
C	-1.56719005	3.40485907	3.38757205
C	-2.01325798	3.77942610	4.64453077
H	-3.73774290	4.03482103	5.92449188
H	-5.32883692	3.31473494	4.23340702
H	-2.13819408	2.67737103	1.46134198
H	-0.52453601	3.41342402	3.11901593
N	-1.05236495	4.22573280	5.71395922
C	0.37720701	4.21223879	5.25253677
H	0.99347001	4.54592991	6.08098507
H	0.65483499	3.20258307	4.97083807
H	0.49065799	4.88958120	4.41338015
C	-1.38246405	5.63675785	6.13593483
H	-2.38915300	5.66533089	6.53429604
H	-0.67105502	5.94446611	6.89684820
H	-1.31111896	6.27807617	5.26346016
C	-1.15594697	3.30392790	6.90468311
H	-0.92329001	2.29632497	6.57575083
H	-0.44747999	3.63397694	7.65895319
H	-2.16381788	3.34050393	7.29931307
C	-5.13718700	1.02209401	1.88338304
O	-6.09238577	0.58829600	2.47821689
C	-4.85418415	2.49631691	1.68631101
H	-5.79542589	3.02873993	1.80095100
H	-4.46103001	2.65214705	0.68410403
C	-4.09005022	0.03475500	1.32097805
O	-3.08992410	0.40830299	0.77096301
O	-4.40310192	-1.23721194	1.52846396
H	-5.25880003	-1.26585102	1.99340296

S4.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	0.60220000	0.59660000	0.00000000
2	39.20720000	2.09100000	0.00000000
3	45.26070000	0.64640000	0.00000000
4	64.44740000	0.33620000	0.00000000
5	81.23070000	3.58620000	0.00000000
6	123.92100000	8.80060000	0.00000000
7	180.57650000	5.08250000	0.00000000
8	215.03950000	0.58170000	0.00000000
9	246.70890000	7.67570000	0.00000000
10	261.10550000	8.93730000	0.00000000
11	279.31460000	0.66430000	0.00000000
12	311.46340000	10.53540000	0.00000000
13	341.54400000	5.36830000	0.00000000
14	353.93170000	0.05580000	0.00000000
15	367.38030000	6.74690000	0.00000000
16	384.28490000	0.99630000	0.00000000
17	406.42070000	5.44440000	0.00000000
18	421.37660000	0.33210000	0.00000000
19	427.70300000	13.41680000	0.00000000
20	454.52730000	4.56510000	0.00000000
21	481.38440000	1.69410000	0.00000000
22	528.98590000	4.41280000	0.00000000
23	546.51220000	15.92630000	0.00000000
24	569.45160000	7.74280000	0.00000000
25	627.38500000	45.14430000	0.00000000
26	653.83570000	0.27710000	0.00000000
27	667.99330000	7.75450000	0.00000000
28	700.32430000	82.28270000	0.00000000
29	749.47070000	0.59200000	0.00000000
30	763.05720000	7.70530000	0.00000000
31	805.68050000	5.61250000	0.00000000
32	837.95260000	0.61930000	0.00000000
33	839.06070000	21.93280000	0.00000000
34	851.81910000	27.16560000	0.00000000
35	891.23620000	0.02110000	0.00000000
36	944.72000000	13.53890000	0.00000000
37	952.03430000	13.30000000	0.00000000
38	962.72600000	15.68430000	0.00000000
39	989.94840000	0.40720000	0.00000000
40	1001.68200000	0.43940000	0.00000000
41	1039.76360000	14.27730000	0.00000000
42	1076.93690000	0.02290000	0.00000000
43	1089.94050000	80.89900000	0.00000000
44	1131.84190000	3.45490000	0.00000000
45	1134.79670000	2.79020000	0.00000000
46	1140.14860000	0.43260000	0.00000000
47	1170.60230000	14.54790000	0.00000000
48	1199.60500000	12.25880000	0.00000000
49	1219.37210000	34.78670000	0.00000000
50	1234.35270000	6.82780000	0.00000000
51	1251.18950000	112.11830000	0.00000000
52	1258.65280000	1.92170000	0.00000000
53	1259.24580000	9.41580000	0.00000000
54	1295.39250000	1.41640000	0.00000000
55	1307.77230000	63.88010000	0.00000000
56	1350.99350000	17.80220000	0.00000000
57	1365.77490000	8.59310000	0.00000000
58	1385.28720000	296.11730000	0.00000000
59	1449.70230000	2.84280000	0.00000000
60	1451.36280000	4.69990000	0.00000000

61	1460.63650000	11.16980000	0.00000000
62	1475.70060000	9.83230000	0.00000000
63	1479.80930000	0.00280000	0.00000000
64	1489.32310000	0.29860000	0.00000000
65	1493.33480000	1.96100000	0.00000000
66	1495.68310000	0.46170000	0.00000000
67	1507.28750000	27.10080000	0.00000000
68	1513.02410000	24.11550000	0.00000000
69	1530.56810000	49.04970000	0.00000000
70	1547.38980000	53.01640000	0.00000000
71	1634.11530000	2.16580000	0.00000000
72	1644.50190000	6.43660000	0.00000000
73	1791.30910000	111.03260000	0.00000000
74	1836.75780000	221.17120000	0.00000000
75	3079.91890000	0.43250000	0.00000000
76	3080.21110000	1.00120000	0.00000000
77	3081.07800000	1.22630000	0.00000000
78	3087.98830000	1.20000000	0.00000000
79	3137.24820000	0.21080000	0.00000000
80	3167.58430000	0.02330000	0.00000000
81	3168.21860000	0.68540000	0.00000000
82	3175.32030000	5.45330000	0.00000000
83	3183.17730000	0.13340000	0.00000000
84	3186.02680000	3.26850000	0.00000000
85	3188.24320000	0.05250000	0.00000000
86	3192.22620000	0.30000000	0.00000000
87	3204.95830000	1.55790000	0.00000000
88	3211.96660000	1.99770000	0.00000000
89	3236.75640000	1.23600000	0.00000000
90	3646.66220000	97.89600000	0.00000000

S5. CALCULATIONS ON 4E



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)CC(=O)C(=O)O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.42802970	a.u.
Gibbs Energy	: -747.20582000	a.u.
Number of imaginary frequencies	: 0	

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

32

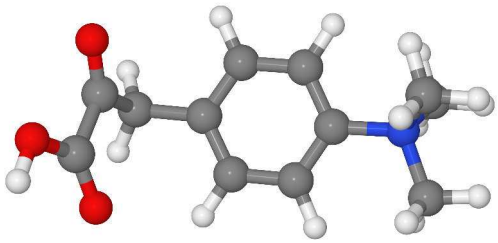
C	0.13170099	-0.92769200	0.48419100
C	-1.21699798	-0.68556303	0.67089301
C	-1.74676704	0.59640002	0.51408398
C	-0.88352603	1.62670100	0.16580400
C	0.47617099	1.40120304	-0.02597300
C	0.97489101	0.12013600	0.13180700
H	0.49988499	-1.93468106	0.61051100
H	-1.86547399	-1.50871694	0.93182600
H	-1.26705205	2.62883711	0.03483700
H	1.10099196	2.23532891	-0.29651701
N	2.43379903	-0.18433900	-0.07957400
C	3.23268890	1.03135002	-0.45155400
H	4.26413393	0.72073799	-0.58248597
H	2.85162711	1.44156206	-1.38015902
H	3.16696191	1.76271105	0.34639600
C	3.02486801	-0.74835402	1.18904996
H	2.50723505	-1.66324401	1.44937694
H	4.07829094	-0.95108300	1.01863897
H	2.89880896	-0.01446700	1.97840595
C	2.58223891	-1.18815696	-1.19726896
H	2.14120007	-0.76549703	-2.09412909
H	3.64002109	-1.38562405	-1.34549999
H	2.06619596	-2.10158110	-0.92859697
C	-4.04944515	0.14417800	-0.38815999
O	-3.62635708	-0.67786002	-1.15243995
C	-3.21496105	0.84372598	0.67568201
H	-3.57681394	0.48294401	1.64374697
H	-3.45572710	1.90576100	0.66358501
C	-5.53259516	0.57344103	-0.38905099
O	-5.95423794	1.40560806	0.37007001
O	-6.24206495	-0.08117900	-1.30421698
H	-7.15966177	0.22979200	-1.25351095

S5.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	14.63600000	0.03740000	0.00000000
2	23.12020000	0.48360000	0.00000000
3	38.58930000	5.64190000	0.00000000
4	40.45360000	2.02770000	0.00000000
5	64.75500000	0.63180000	0.00000000
6	118.76430000	0.97540000	0.00000000
7	179.78690000	11.06920000	0.00000000
8	216.86100000	0.56670000	0.00000000
9	220.46410000	1.95220000	0.00000000
10	261.91900000	0.45340000	0.00000000
11	280.62260000	0.61810000	0.00000000
12	307.94430000	2.52620000	0.00000000
13	339.01030000	2.69190000	0.00000000
14	353.57650000	0.16410000	0.00000000
15	370.45530000	0.21840000	0.00000000
16	376.33690000	0.59730000	0.00000000
17	383.90570000	0.25740000	0.00000000
18	395.79040000	2.63400000	0.00000000
19	420.56030000	0.28110000	0.00000000
20	448.61660000	0.73520000	0.00000000
21	481.25260000	2.28970000	0.00000000
22	508.37520000	4.26670000	0.00000000
23	552.73410000	11.37280000	0.00000000
24	563.20410000	12.86760000	0.00000000
25	620.13400000	84.86510000	0.00000000
26	650.18810000	50.21260000	0.00000000
27	657.03580000	52.52850000	0.00000000
28	697.49330000	19.99680000	0.00000000
29	722.58970000	38.17800000	0.00000000
30	743.14840000	13.24020000	0.00000000
31	804.95920000	8.86410000	0.00000000
32	831.50570000	5.15190000	0.00000000
33	833.58490000	0.96550000	0.00000000
34	852.79230000	31.96710000	0.00000000
35	882.65230000	21.84180000	0.00000000
36	941.00710000	8.45800000	0.00000000
37	949.70600000	18.29690000	0.00000000
38	964.00930000	15.02350000	0.00000000
39	983.61560000	0.27430000	0.00000000
40	994.59090000	0.40650000	0.00000000
41	1039.17770000	63.94550000	0.00000000
42	1043.36590000	132.70530000	0.00000000
43	1076.98270000	0.02000000	0.00000000
44	1131.82650000	2.00800000	0.00000000
45	1132.99710000	1.78670000	0.00000000
46	1140.77110000	0.46650000	0.00000000
47	1164.38250000	8.07560000	0.00000000
48	1188.68730000	42.47900000	0.00000000
49	1194.88220000	90.05840000	0.00000000
50	1230.60710000	4.34770000	0.00000000
51	1242.26390000	2.18670000	0.00000000
52	1259.12130000	1.45790000	0.00000000
53	1259.35620000	1.36740000	0.00000000
54	1295.66080000	1.17080000	0.00000000
55	1334.16570000	51.97950000	0.00000000
56	1355.59040000	11.98220000	0.00000000
57	1367.43880000	13.92130000	0.00000000
58	1396.65770000	13.30410000	0.00000000
59	1446.80040000	10.08260000	0.00000000
60	1450.29530000	4.91110000	0.00000000

61	1451.71680000	4.62260000	0.00000000
62	1462.04070000	14.30340000	0.00000000
63	1479.56140000	0.00550000	0.00000000
64	1489.53370000	0.25160000	0.00000000
65	1493.50300000	1.96900000	0.00000000
66	1495.92880000	0.39240000	0.00000000
67	1507.10900000	26.59350000	0.00000000
68	1512.86480000	23.79060000	0.00000000
69	1530.84400000	48.16360000	0.00000000
70	1550.46690000	49.40850000	0.00000000
71	1636.58110000	2.33970000	0.00000000
72	1650.65810000	4.14360000	0.00000000
73	1807.11080000	175.77400000	0.00000000
74	1816.27040000	162.72870000	0.00000000
75	3033.73630000	3.80570000	0.00000000
76	3080.00220000	0.46190000	0.00000000
77	3081.02790000	1.44620000	0.00000000
78	3087.94150000	1.51000000	0.00000000
79	3100.53740000	0.34950000	0.00000000
80	3167.52890000	0.14200000	0.00000000
81	3168.17460000	0.55780000	0.00000000
82	3175.10710000	6.14710000	0.00000000
83	3182.78460000	0.20020000	0.00000000
84	3187.43060000	5.05960000	0.00000000
85	3188.66980000	0.04270000	0.00000000
86	3189.37440000	0.83510000	0.00000000
87	3197.08450000	1.54430000	0.00000000
88	3208.67140000	0.38270000	0.00000000
89	3235.34540000	0.46040000	0.00000000
90	3727.96620000	123.06410000	0.00000000

S6. CALCULATIONS ON 4F



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)CC(=O)C(=O)O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.42812378	a.u.
Gibbs Energy	: -747.20556400	a.u.
Number of imaginary frequencies	: 0	

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

32

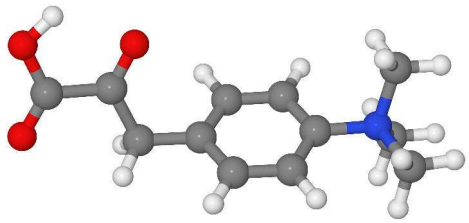
C	0.37202400	-0.92135203	1.08697295
C	-0.99287701	-0.79833502	1.28270495
C	-1.72564805	0.18943800	0.62348598
C	-1.05871499	1.04269302	-0.24821800
C	0.31206200	0.93245602	-0.45186999
C	1.02055800	-0.05097000	0.21903200
H	0.90385598	-1.69698906	1.61727202
H	-1.49539900	-1.48291504	1.95115805
H	-1.61470902	1.79313695	-0.79007399
H	0.78362799	1.61928797	-1.13405704
N	2.50556803	-0.21210501	0.03106600
C	3.08090401	0.78780597	-0.93042201
H	4.14694118	0.59883600	-1.00361502
H	2.61701894	0.66025102	-1.90219998
H	2.90972900	1.78965795	-0.55249703
C	3.20712805	-0.02851300	1.35457695
H	2.85702991	-0.77902699	2.05243301
H	4.27641296	-0.13548400	1.19629395
H	2.97259498	0.96267301	1.72887003
C	2.80109596	-1.58914995	-0.51137203
H	2.28038692	-1.70080304	-1.45684600
H	3.87425900	-1.68206501	-0.65124601
H	2.45130205	-2.33398199	0.19267400
C	-3.91246510	-0.74637097	-0.05730700
O	-4.10997677	-1.87874496	0.28254801
C	-3.21793509	0.28494900	0.82453299
H	-3.47637701	0.04461000	1.85354102
H	-3.56873488	1.28386199	0.58042902
C	-4.26311922	-0.25227901	-1.47621202
O	-3.80873489	0.77125800	-1.92274106
O	-5.07313490	-1.08618999	-2.11736798
H	-5.25002623	-0.72361702	-2.99975705

S6.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	6.18640000	0.29130000	0.00000000
2	30.31990000	1.96970000	0.00000000
3	44.50160000	1.76270000	0.00000000
4	53.68750000	5.02330000	0.00000000
5	60.79680000	0.24490000	0.00000000
6	114.91960000	4.28280000	0.00000000
7	179.30880000	1.00740000	0.00000000
8	214.43250000	0.37030000	0.00000000
9	246.47040000	3.21760000	0.00000000
10	263.08290000	2.65480000	0.00000000
11	278.43150000	0.43780000	0.00000000
12	309.24640000	3.02970000	0.00000000
13	330.73820000	0.44610000	0.00000000
14	353.25440000	0.06740000	0.00000000
15	367.65710000	0.26450000	0.00000000
16	383.58800000	0.35080000	0.00000000
17	397.47830000	1.33440000	0.00000000
18	413.17580000	0.81620000	0.00000000
19	421.17760000	0.28280000	0.00000000
20	448.76390000	0.04480000	0.00000000
21	481.46820000	1.69940000	0.00000000
22	529.43080000	2.45050000	0.00000000
23	546.96970000	22.55210000	0.00000000
24	563.55290000	6.71650000	0.00000000
25	612.60510000	114.72950000	0.00000000
26	653.30340000	6.75910000	0.00000000
27	656.61640000	45.53350000	0.00000000
28	682.44940000	64.11910000	0.00000000
29	735.24210000	20.39470000	0.00000000
30	753.03270000	7.51940000	0.00000000
31	804.39430000	9.21060000	0.00000000
32	835.79740000	2.01390000	0.00000000
33	838.59150000	20.07560000	0.00000000
34	851.69420000	31.24950000	0.00000000
35	894.73170000	0.32940000	0.00000000
36	944.58300000	9.38430000	0.00000000
37	949.80640000	27.80120000	0.00000000
38	963.33920000	16.13800000	0.00000000
39	987.92310000	0.58030000	0.00000000
40	999.85460000	0.62970000	0.00000000
41	1039.50920000	16.23450000	0.00000000
42	1070.08600000	146.70500000	0.00000000
43	1076.77250000	0.02210000	0.00000000
44	1131.27480000	2.73560000	0.00000000
45	1133.88990000	4.66190000	0.00000000
46	1140.29060000	0.48280000	0.00000000
47	1168.07250000	51.63820000	0.00000000
48	1184.91760000	146.87760000	0.00000000
49	1219.83010000	9.30010000	0.00000000
50	1231.46360000	1.66500000	0.00000000
51	1238.01710000	2.22290000	0.00000000
52	1258.95950000	1.53040000	0.00000000
53	1259.31340000	1.85670000	0.00000000
54	1295.26940000	2.28350000	0.00000000
55	1306.43230000	43.07130000	0.00000000
56	1352.44240000	6.10280000	0.00000000
57	1365.61700000	1.22070000	0.00000000
58	1399.49370000	25.02470000	0.00000000
59	1449.54880000	3.00240000	0.00000000
60	1451.29140000	4.69860000	0.00000000

61	1460.87190000	10.51230000	0.00000000
62	1479.49400000	0.10380000	0.00000000
63	1479.64940000	10.44800000	0.00000000
64	1489.31060000	0.27760000	0.00000000
65	1493.32230000	1.96070000	0.00000000
66	1495.65170000	0.45540000	0.00000000
67	1507.01430000	26.90420000	0.00000000
68	1512.88340000	23.83870000	0.00000000
69	1530.65040000	48.47800000	0.00000000
70	1546.73240000	55.72850000	0.00000000
71	1633.92130000	1.74380000	0.00000000
72	1643.98500000	8.11480000	0.00000000
73	1794.17710000	211.06460000	0.00000000
74	1816.49070000	181.43170000	0.00000000
75	3079.69450000	0.48770000	0.00000000
76	3080.93890000	1.44790000	0.00000000
77	3082.56190000	1.73880000	0.00000000
78	3087.93080000	1.42870000	0.00000000
79	3141.43670000	0.35090000	0.00000000
80	3167.33300000	0.00550000	0.00000000
81	3167.99220000	0.80770000	0.00000000
82	3175.08800000	5.98550000	0.00000000
83	3183.01310000	0.17790000	0.00000000
84	3186.26250000	3.63090000	0.00000000
85	3188.19260000	0.04340000	0.00000000
86	3193.94670000	0.48390000	0.00000000
87	3204.78060000	1.27110000	0.00000000
88	3207.61950000	0.90330000	0.00000000
89	3235.04200000	0.96950000	0.00000000
90	3726.71500000	113.83720000	0.00000000

S7. CALCULATIONS ON 4G



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)CC(=O)C(=O)O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.42854499	a.u.
Gibbs Energy	: -747.20548800	a.u.
Number of imaginary frequencies	: 0	

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

32

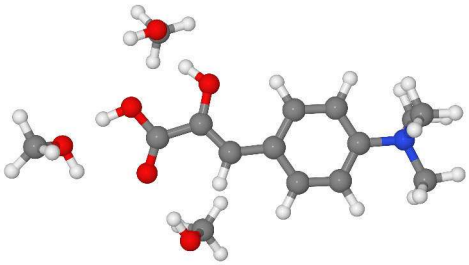
C	-3.15655804	3.27290893	4.83126402
C	-3.99691010	2.85786891	3.81396604
C	-3.59863091	2.92891312	2.47820091
C	-2.33385491	3.42662907	2.19343591
C	-1.47608602	3.84876990	3.20438790
C	-1.89437699	3.76659894	4.52095318
H	-3.50223207	3.19955111	5.85136509
H	-4.97201920	2.46824002	4.06665182
H	-1.99901402	3.49112606	1.16764200
H	-0.50646400	4.22716284	2.92876792
N	-1.00408697	4.20092297	5.65412378
C	0.32611299	4.71531677	5.18338919
H	0.89698398	5.00325012	6.06011486
H	0.84662098	3.92913294	4.64781809
H	0.17251600	5.57819700	4.54481316
C	-1.67322600	5.30904198	6.43017721
H	-2.60948610	4.94699383	6.83656311
H	-1.01083696	5.61520481	7.23470592
H	-1.85896206	6.13529015	5.75164795
C	-0.74268299	3.02867794	6.56880283
H	-0.27134401	2.24273300	5.98771095
H	-0.08905700	3.35695696	7.37178612
H	-1.68235397	2.67452788	6.97434092
C	-4.74475193	0.95925498	1.40763497
O	-4.46640682	0.22697400	2.32617307
C	-4.49939585	2.45128703	1.37999105
H	-5.48607016	2.92344499	1.43782306
H	-4.12379217	2.71570992	0.39229301
C	-5.42797279	0.37747601	0.14989799
O	-5.71379805	1.06416595	-0.78927201
O	-5.65378380	-0.92945701	0.23181100
H	-5.32664299	-1.24244201	1.09312403

S7.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	14.31780000	0.54530000	0.00000000
2	21.73790000	0.42010000	0.00000000
3	40.42280000	0.65420000	0.00000000
4	62.72560000	0.12900000	0.00000000
5	86.34520000	3.72260000	0.00000000
6	119.03570000	1.84500000	0.00000000
7	178.32170000	19.59960000	0.00000000
8	216.87830000	1.02360000	0.00000000
9	220.42800000	2.54330000	0.00000000
10	260.93810000	1.47680000	0.00000000
11	280.58600000	0.54460000	0.00000000
12	307.71920000	8.04270000	0.00000000
13	342.41380000	21.10110000	0.00000000
14	353.89400000	0.33960000	0.00000000
15	371.14140000	1.96220000	0.00000000
16	384.07520000	6.81570000	0.00000000
17	385.77930000	11.46710000	0.00000000
18	396.09790000	3.70300000	0.00000000
19	420.82750000	0.21790000	0.00000000
20	448.67870000	0.52930000	0.00000000
21	481.24660000	1.22130000	0.00000000
22	515.73520000	3.50970000	0.00000000
23	555.88240000	5.25340000	0.00000000
24	565.04710000	20.65800000	0.00000000
25	652.44210000	3.17020000	0.00000000
26	659.21080000	56.64700000	0.00000000
27	669.34440000	30.32410000	0.00000000
28	698.93740000	20.70530000	0.00000000
29	728.48460000	4.94860000	0.00000000
30	748.21620000	3.76570000	0.00000000
31	813.06060000	20.57910000	0.00000000
32	831.77310000	5.08400000	0.00000000
33	834.98070000	0.32350000	0.00000000
34	853.21520000	31.23260000	0.00000000
35	884.79130000	10.23670000	0.00000000
36	938.91820000	3.69130000	0.00000000
37	948.39460000	22.56570000	0.00000000
38	963.23040000	15.38360000	0.00000000
39	985.05810000	0.13210000	0.00000000
40	995.61020000	0.41200000	0.00000000
41	1039.87530000	13.94860000	0.00000000
42	1063.34920000	127.96660000	0.00000000
43	1076.97550000	0.02000000	0.00000000
44	1132.00320000	1.74430000	0.00000000
45	1133.26660000	2.06860000	0.00000000
46	1140.72680000	0.45840000	0.00000000
47	1164.91980000	5.32840000	0.00000000
48	1189.65780000	1.32420000	0.00000000
49	1211.16940000	22.11010000	0.00000000
50	1231.12070000	1.84500000	0.00000000
51	1243.65810000	4.21640000	0.00000000
52	1258.86770000	1.41710000	0.00000000
53	1259.09540000	1.89400000	0.00000000
54	1295.68980000	1.11400000	0.00000000
55	1335.86700000	234.44880000	0.00000000
56	1354.56930000	71.48380000	0.00000000
57	1365.42990000	95.46960000	0.00000000
58	1387.68840000	92.88820000	0.00000000
59	1443.73590000	16.00390000	0.00000000
60	1450.02410000	3.34570000	0.00000000

61	1451.80190000	4.78110000	0.00000000
62	1461.73500000	14.81960000	0.00000000
63	1479.72410000	0.00410000	0.00000000
64	1489.42890000	0.25460000	0.00000000
65	1493.60320000	1.91210000	0.00000000
66	1495.83730000	0.42900000	0.00000000
67	1507.27500000	26.81790000	0.00000000
68	1513.04090000	24.00460000	0.00000000
69	1530.80390000	48.06280000	0.00000000
70	1550.76570000	49.01510000	0.00000000
71	1636.39630000	2.30450000	0.00000000
72	1651.02260000	4.19320000	0.00000000
73	1787.95360000	66.22010000	0.00000000
74	1847.68010000	231.11800000	0.00000000
75	3028.88560000	4.76000000	0.00000000
76	3080.20310000	0.41230000	0.00000000
77	3081.17420000	1.28370000	0.00000000
78	3088.03460000	1.20500000	0.00000000
79	3099.44900000	0.23920000	0.00000000
80	3167.85170000	0.07910000	0.00000000
81	3168.41670000	0.57510000	0.00000000
82	3175.41910000	5.58730000	0.00000000
83	3182.82240000	0.17390000	0.00000000
84	3187.49370000	4.65360000	0.00000000
85	3188.52590000	0.04540000	0.00000000
86	3189.83910000	0.66180000	0.00000000
87	3196.69530000	1.35770000	0.00000000
88	3208.10430000	0.46560000	0.00000000
89	3236.06440000	0.41300000	0.00000000
90	3665.21550000	95.38730000	0.00000000

S8. CALCULATIONS ON 4B'



Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=C(C(=O)O)O.CO.CO.CO	
Formula	: $C_{15}H_{28}NO_6^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1094.89235605	a.u.
Gibbs Energy	: -1094.52922600	a.u.
Number of imaginary frequencies	: 1	

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

50

C	2.26272202	-1.17932999	-0.02932500
C	0.91714603	-0.92035103	-0.21508400
C	0.45655701	0.39206201	-0.41600299
C	1.41036606	1.41884696	-0.42535499
C	2.76032901	1.16612196	-0.24033099
C	3.18375111	-0.13828699	-0.04105900
H	2.57328010	-2.20138788	0.12323400
H	0.21749100	-1.73792696	-0.20280001
H	1.08685005	2.43915009	-0.57593697
H	3.44636202	1.99509203	-0.25557700
N	4.63088179	-0.46569300	0.17176200
C	5.51531410	0.74716598	0.12139400
H	6.53360319	0.41226301	0.28229499
H	5.42922688	1.21259403	-0.85340399
H	5.22536612	1.43445098	0.90741998
C	4.80858898	-1.10497105	1.52720201
H	4.23020411	-2.01894808	1.56823802
H	5.86274099	-1.32281303	1.66259801
H	4.46103001	-0.40490201	2.27880096
C	5.10119820	-1.41923404	-0.89947701
H	4.95860100	-0.94267499	-1.86303306
H	6.15147686	-1.62980294	-0.72682500
H	4.52439213	-2.33342004	-0.84234703
C	-2.02846003	-0.02532100	-0.59045601
O	-1.96696496	-1.35816002	-0.44242400
C	-0.93293399	0.76107502	-0.60263097
H	-1.11467695	1.81227696	-0.75869602
C	-3.36188197	0.61878997	-0.78784001
O	-3.54367900	1.82925606	-0.81810200
O	-4.35001993	-0.25126001	-0.92923403
H	-5.21031809	0.26384500	-1.04547000

H	-2.83983111	-1.79931104	-0.28476599
H	-2.52188993	3.26383400	-0.25712100
O	-1.91939294	3.94389391	0.08526700
C	-1.71990502	3.68181896	1.46850502
H	-2.65541291	3.73223209	2.03362203
H	-1.26710701	2.69948196	1.63608098
H	-1.04291296	4.44193888	1.85549605
H	-4.82274294	-2.47168803	-0.19001700
O	-4.05139685	-2.87128901	0.22619300
C	-4.20057583	-2.76973605	1.65008497
H	-4.30362797	-1.72966003	1.96401703
H	-5.06449413	-3.34027195	1.99129498
H	-3.30010796	-3.18802905	2.09205604
H	-5.83080912	2.10527802	-1.09754896
O	-6.39974880	1.33057296	-1.20406401
C	-7.02435923	1.38473201	-2.49776912
H	-6.28041315	1.40329897	-3.29510689
H	-7.63152885	0.48881599	-2.59252810
H	-7.66545677	2.26220393	-2.57488799

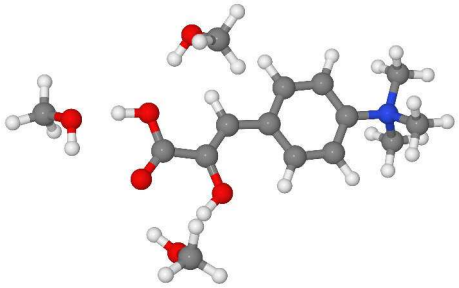
S8.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-7.35390000	0.98230000	0.00000000
2	6.35580000	1.31770000	0.00000000
3	20.15010000	3.30180000	0.00000000
4	30.56310000	10.55040000	0.00000000
5	33.59510000	4.05490000	0.00000000
6	35.83160000	2.97450000	0.00000000
7	39.34910000	0.19830000	0.00000000
8	50.03350000	3.22300000	0.00000000
9	58.30840000	8.91600000	0.00000000
10	63.16740000	4.29380000	0.00000000
11	65.59400000	6.82890000	0.00000000
12	74.51420000	7.26250000	0.00000000
13	83.71120000	9.16740000	0.00000000
14	94.83240000	1.48440000	0.00000000
15	99.21120000	3.61840000	0.00000000
16	109.48320000	5.43990000	0.00000000
17	115.54230000	1.56810000	0.00000000
18	122.43230000	5.17250000	0.00000000
19	137.83320000	4.27690000	0.00000000
20	146.94030000	4.90260000	0.00000000
21	151.90150000	1.23880000	0.00000000
22	163.51210000	5.17210000	0.00000000
23	167.15860000	20.27840000	0.00000000
24	195.65710000	1.27090000	0.00000000
25	225.68120000	25.31190000	0.00000000
26	232.23670000	4.95820000	0.00000000
27	272.61970000	60.23340000	0.00000000
28	282.65440000	3.97850000	0.00000000
29	299.79290000	9.18980000	0.00000000
30	315.66490000	58.46540000	0.00000000
31	368.57800000	53.00030000	0.00000000
32	369.31930000	76.51030000	0.00000000
33	376.10280000	18.79320000	0.00000000
34	396.43050000	2.35580000	0.00000000
35	419.83790000	26.42130000	0.00000000
36	426.50340000	0.01570000	0.00000000
37	444.61240000	47.97290000	0.00000000
38	464.44030000	185.33410000	0.00000000
39	484.35980000	10.45590000	0.00000000
40	526.43510000	208.69670000	0.00000000
41	537.91980000	84.51380000	0.00000000
42	546.48640000	3.86410000	0.00000000
43	574.00370000	4.97310000	0.00000000
44	589.24950000	31.99280000	0.00000000
45	652.40320000	2.79720000	0.00000000
46	669.37320000	248.50400000	0.00000000
47	695.99210000	22.75730000	0.00000000
48	753.54870000	3.19510000	0.00000000
49	758.79200000	37.78370000	0.00000000
50	778.74910000	0.77620000	0.00000000
51	839.55350000	3.81600000	0.00000000
52	845.53810000	66.06780000	0.00000000
53	855.97460000	85.50190000	0.00000000
54	865.89620000	29.69280000	0.00000000
55	876.39490000	14.24200000	0.00000000
56	909.55240000	33.48820000	0.00000000
57	929.21060000	42.82500000	0.00000000
58	947.57300000	57.30910000	0.00000000
59	965.38880000	31.78880000	0.00000000
60	991.77320000	0.19860000	0.00000000

61	1002.64040000	0.67770000	0.00000000
62	1006.89420000	110.83010000	0.00000000
63	1015.31430000	196.82100000	0.00000000
64	1023.06020000	202.96080000	0.00000000
65	1036.01550000	14.01460000	0.00000000
66	1043.57220000	122.12990000	0.00000000
67	1083.25010000	0.02950000	0.00000000
68	1086.87750000	32.11860000	0.00000000
69	1094.24870000	62.59690000	0.00000000
70	1114.62260000	17.74980000	0.00000000
71	1136.54040000	6.20530000	0.00000000
72	1140.76750000	0.30250000	0.00000000
73	1150.20730000	2.65050000	0.00000000
74	1151.51200000	18.08050000	0.00000000
75	1173.54810000	8.91370000	0.00000000
76	1178.51050000	0.94280000	0.00000000
77	1181.95520000	5.26930000	0.00000000
78	1182.17420000	0.57860000	0.00000000
79	1226.13300000	4.28600000	0.00000000
80	1254.43960000	239.56270000	0.00000000
81	1261.90310000	1.77300000	0.00000000
82	1262.66240000	1.74650000	0.00000000
83	1283.86120000	794.56240000	0.00000000
84	1303.17380000	10.77510000	0.00000000
85	1334.08010000	785.71040000	0.00000000
86	1345.83490000	242.80330000	0.00000000
87	1363.33870000	48.16780000	0.00000000
88	1374.62540000	163.51640000	0.00000000
89	1377.63820000	154.30460000	0.00000000
90	1426.11010000	127.92430000	0.00000000
91	1432.79810000	46.50680000	0.00000000
92	1453.54080000	0.82570000	0.00000000
93	1457.57680000	3.23760000	0.00000000
94	1460.06450000	18.81340000	0.00000000
95	1474.30480000	23.16610000	0.00000000
96	1477.47170000	2.14290000	0.00000000
97	1478.44120000	2.86030000	0.00000000
98	1481.08700000	0.16720000	0.00000000
99	1485.63610000	0.15920000	0.00000000
100	1487.72080000	2.15490000	0.00000000
101	1489.69650000	6.75590000	0.00000000
102	1490.27470000	4.25070000	0.00000000
103	1493.29190000	2.11100000	0.00000000
104	1497.27440000	13.88410000	0.00000000
105	1503.40730000	22.47090000	0.00000000
106	1505.37970000	31.80470000	0.00000000
107	1507.62420000	35.1.000000	0.00000000
108	1508.82280000	19.78480000	0.00000000
109	1509.99210000	3.38420000	0.00000000
110	1513.71650000	33.90570000	0.00000000
111	1532.73450000	63.91570000	0.00000000
112	1548.14860000	101.90490000	0.00000000
113	1617.23570000	4.48620000	0.00000000
114	1643.92880000	8.04170000	0.00000000
115	1681.65930000	338.15070000	0.00000000
116	1716.85280000	216.73230000	0.00000000
117	2924.25130000	3234.58340000	0.00000000
118	2989.61760000	75.04610000	0.00000000
119	3025.37900000	86.87110000	0.00000000
120	3032.94050000	88.95100000	0.00000000
121	3034.54780000	54.68000000	0.00000000
122	3088.00050000	62.22870000	0.00000000
123	3089.19260000	4.52930000	0.00000000
124	3091.63100000	5.44730000	0.00000000

125	3094.03620000	59.75420000	0.00000000
126	3095.07890000	6.54760000	0.00000000
127	3096.80640000	33.84190000	0.00000000
128	3129.22170000	25.66380000	0.00000000
129	3135.02580000	26.35850000	0.00000000
130	3179.74210000	0.41190000	0.00000000
131	3181.92870000	7.00380000	0.00000000
132	3185.60820000	10.74180000	0.00000000
133	3188.60690000	6.06000000	0.00000000
134	3190.06600000	1.64240000	0.00000000
135	3192.75970000	2.55790000	0.00000000
136	3195.58350000	6.28240000	0.00000000
137	3210.41700000	6.71400000	0.00000000
138	3217.46290000	54.32280000	0.00000000
139	3242.67960000	29.91920000	0.00000000
140	3247.19680000	1979.84200000	0.00000000
141	3248.34140000	706.90710000	0.00000000
142	3626.71200000	583.76230000	0.00000000
143	3746.16730000	171.64530000	0.00000000
144	3807.89910000	92.93630000	0.00000000

S9. CALCULATIONS ON 4A'



Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=C(C(=O)O)O.CO.CO.CO	
Formula	: $C_{15}H_{28}NO_6^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1094.89306189	a.u.
Gibbs Energy	: -1094.52812800	a.u.
Number of imaginary frequencies	: 2	

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

50

C	2.27501512	-1.31035197	-0.00457900
C	0.92148900	-1.09313297	-0.18568601
C	0.42737499	0.19554199	-0.44896099
C	1.35533595	1.24318397	-0.52245599
C	2.71309996	1.03230703	-0.34174800
C	3.17026806	-0.24991700	-0.08208100
H	2.61098695	-2.31568003	0.19675900
H	0.24234000	-1.92528701	-0.12102700
H	1.00485003	2.24689007	-0.71785700
H	3.37899399	1.87522101	-0.40753701
N	4.62704802	-0.53129297	0.13003799
C	5.48251104	0.69626802	-0.00308800
H	6.51035118	0.39407399	0.16292700
H	5.37347698	1.10258698	-1.00179803
H	5.18707895	1.42145097	0.74598700
C	4.83570385	-1.08527994	1.51831102
H	4.27592516	-2.00582504	1.62201905
H	5.89562082	-1.27469206	1.65052104
H	4.48493719	-0.34828699	2.23223996
C	5.10622883	-1.53574395	-0.88971698
H	4.92640495	-1.12701404	-1.87781203
H	6.16640377	-1.70066798	-0.72875899
H	4.56274891	-2.46302104	-0.76130301
C	-2.04991603	-0.28577301	-0.55308199
O	-1.95146000	-1.59925306	-0.29666501
C	-0.97276402	0.52187598	-0.64035398
H	-1.17258096	1.55664098	-0.86128199
C	-3.42288399	0.26085800	-0.75522602
O	-4.41844988	-0.44885299	-0.76205897
O	-3.49428606	1.57634997	-0.92571002

H	-4.46316290	1.82307303	-1.07970595
H	-2.82183099	-2.06545496	-0.21582200
H	-2.45753789	3.07363296	-0.12764600
O	-1.81193304	3.68412590	0.25089699
C	-1.59041703	3.29795909	1.60386205
H	-2.50811696	3.34486389	2.19656992
H	-1.17971206	2.28672099	1.67530894
H	-0.86894798	3.99427009	2.02750611
H	-4.69439316	-2.28128695	-0.24549100
O	-4.18736601	-3.04210997	0.07648000
C	-4.41819811	-3.17838693	1.48354697
H	-4.18563986	-2.25422192	2.01666188
H	-5.45355082	-3.45777392	1.68368101
H	-3.76323700	-3.96836901	1.84279096
H	-6.30963802	1.10804498	-1.181.0000
O	-6.02224493	2.01953793	-1.31909204
C	-6.39247608	2.43019104	-2.64711308
H	-5.92618513	1.79490602	-3.40079594
H	-7.47507000	2.40564990	-2.76441002
H	-6.04202223	3.45120907	-2.76869392

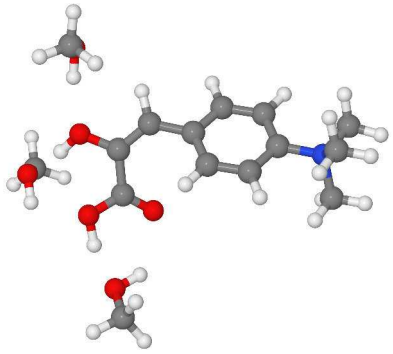
S9.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-14.50790000	0.82720000	0.00000000
2	-9.19230000	0.26600000	0.00000000
3	16.46910000	6.88330000	0.00000000
4	22.95050000	10.58410000	0.00000000
5	25.08880000	1.03690000	0.00000000
6	36.01430000	2.11150000	0.00000000
7	38.08100000	4.32870000	0.00000000
8	51.14010000	1.47860000	0.00000000
9	55.60630000	3.46390000	0.00000000
10	59.29610000	1.88300000	0.00000000
11	66.79580000	0.53290000	0.00000000
12	77.34430000	15.75690000	0.00000000
13	79.91500000	16.69410000	0.00000000
14	86.28710000	11.61600000	0.00000000
15	100.60540000	2.44430000	0.00000000
16	105.05200000	6.57090000	0.00000000
17	107.91370000	0.83500000	0.00000000
18	122.66130000	5.91010000	0.00000000
19	133.50250000	2.76120000	0.00000000
20	135.88260000	0.40230000	0.00000000
21	150.02140000	9.93480000	0.00000000
22	151.43160000	11.16740000	0.00000000
23	166.03590000	1.97110000	0.00000000
24	183.87950000	19.61430000	0.00000000
25	229.82050000	0.49790000	0.00000000
26	247.87100000	33.70100000	0.00000000
27	270.05640000	52.68870000	0.00000000
28	279.43610000	4.07460000	0.00000000
29	290.52160000	7.12610000	0.00000000
30	319.34010000	66.12070000	0.00000000
31	359.98210000	0.20810000	0.00000000
32	372.46410000	35.23940000	0.00000000
33	382.41310000	104.34090000	0.00000000
34	392.13070000	2.48120000	0.00000000
35	418.57180000	1.50570000	0.00000000
36	425.26350000	0.07810000	0.00000000
37	443.54190000	7.23160000	0.00000000
38	484.58890000	25.22190000	0.00000000
39	493.33220000	159.09020000	0.00000000
40	537.26750000	32.17460000	0.00000000
41	539.92040000	81.99500000	0.00000000
42	556.31460000	176.60690000	0.00000000
43	569.87110000	67.15270000	0.00000000
44	593.70910000	75.73450000	0.00000000
45	597.71180000	376.38780000	0.00000000
46	652.48640000	0.43100000	0.00000000
47	696.74490000	19.92750000	0.00000000
48	751.62800000	2.90190000	0.00000000
49	758.47440000	28.66170000	0.00000000
50	775.91880000	0.58410000	0.00000000
51	837.76720000	10.94830000	0.00000000
52	844.74950000	62.98910000	0.00000000
53	849.34410000	86.95700000	0.00000000
54	858.87900000	1.20100000	0.00000000
55	875.64030000	3.43460000	0.00000000
56	910.69660000	33.93460000	0.00000000
57	917.77650000	61.15730000	0.00000000
58	945.93320000	52.67120000	0.00000000
59	964.45880000	30.64770000	0.00000000
60	990.76120000	0.72810000	0.00000000

61	1002.78900000	6.87570000	0.00000000
62	1003.56230000	94.13710000	0.00000000
63	1020.16120000	244.83400000	0.00000000
64	1023.58190000	163.82570000	0.00000000
65	1036.18190000	14.28410000	0.00000000
66	1036.72630000	134.81080000	0.00000000
67	1083.47660000	0.06910000	0.00000000
68	1089.67630000	57.25230000	0.00000000
69	1100.85980000	17.60840000	0.00000000
70	1107.04510000	40.21430000	0.00000000
71	1136.58590000	7.53010000	0.00000000
72	1140.37990000	6.36760000	0.00000000
73	1146.89100000	0.45630000	0.00000000
74	1154.19110000	120.35310000	0.00000000
75	1172.93740000	6.72430000	0.00000000
76	1177.29460000	0.78980000	0.00000000
77	1178.93740000	1.14010000	0.00000000
78	1180.83720000	6.01060000	0.00000000
79	1225.23530000	15.56470000	0.00000000
80	1258.06120000	230.74480000	0.00000000
81	1259.95250000	72.37600000	0.00000000
82	1261.75610000	29.66280000	0.00000000
83	1267.64510000	617.62730000	0.00000000
84	1301.75580000	5.25890000	0.00000000
85	1338.00160000	177.62610000	0.00000000
86	1351.31890000	255.64050000	0.00000000
87	1364.33090000	43.15720000	0.00000000
88	1372.30200000	238.72980000	0.00000000
89	1403.28690000	188.26010000	0.00000000
90	1404.09780000	33.52080000	0.00000000
91	1434.40620000	210.60850000	0.00000000
92	1452.78940000	2.92580000	0.00000000
93	1455.68860000	2.52100000	0.00000000
94	1460.54610000	32.34720000	0.00000000
95	1474.47610000	10.54110000	0.00000000
96	1476.24050000	1.85130000	0.00000000
97	1477.99340000	3.51730000	0.00000000
98	1480.40450000	0.08200000	0.00000000
99	1484.47220000	0.60030000	0.00000000
100	1488.15660000	1.39530000	0.00000000
101	1489.24430000	6.99410000	0.00000000
102	1489.70600000	3.37510000	0.00000000
103	1492.32330000	1.32140000	0.00000000
104	1494.25570000	11.84500000	0.00000000
105	1502.83870000	11.84550000	0.00000000
106	1504.13960000	6.41980000	0.00000000
107	1507.08630000	8.78620000	0.00000000
108	1507.64380000	30.33030000	0.00000000
109	1512.29250000	36.61640000	0.00000000
110	1513.25830000	7.12330000	0.00000000
111	1528.53260000	60.19740000	0.00000000
112	1547.64770000	74.26910000	0.00000000
113	1617.58870000	5.84150000	0.00000000
114	1643.66070000	8.19350000	0.00000000
115	1693.32890000	369.22810000	0.00000000
116	1708.14690000	701.44050000	0.00000000
117	2882.36050000	3572.16950000	0.00000000
118	2996.88860000	66.01580000	0.00000000
119	3017.31250000	101.68990000	0.00000000
120	3035.87220000	37.88120000	0.00000000
121	3043.29490000	82.98170000	0.00000000
122	3076.33260000	69.81700000	0.00000000
123	3087.35270000	4.15840000	0.00000000
124	3091.00740000	5.49300000	0.00000000

125	3094.73890000	6.56380000	0.00000000
126	3100.14880000	33.44350000	0.00000000
127	3101.16670000	51.12530000	0.00000000
128	3121.24170000	34.47940000	0.00000000
129	3137.20140000	24.92460000	0.00000000
130	3177.14550000	0.62540000	0.00000000
131	3181.01390000	2.94080000	0.00000000
132	3184.32380000	14.26660000	0.00000000
133	3188.38220000	4.59240000	0.00000000
134	3190.33090000	1.28440000	0.00000000
135	3193.27340000	2.39230000	0.00000000
136	3196.14270000	6.46730000	0.00000000
137	3210.73440000	7.09780000	0.00000000
138	3234.13140000	163.43810000	0.00000000
139	3243.20970000	28.10180000	0.00000000
140	3246.82540000	2401.37500000	0.00000000
141	3249.49870000	55.82660000	0.00000000
142	3689.99440000	459.14840000	0.00000000
143	3734.53900000	301.22060000	0.00000000
144	3770.30390000	114.19600000	0.00000000

S10. CALCULATIONS ON 4C'



Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=C(C(=O)O)O.CO.CO.CO	
Formula	: $C_{15}H_{28}NO_6^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1094.88048560	a.u.
Gibbs Energy	: -1094.51757500	a.u.
Number of imaginary frequencies	: 1	

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

50

C	-1.02350998	-0.61041701	-0.86281103
C	0.29677999	-0.20652799	-0.90539002
C	0.73221397	0.92115903	-0.20005301
C	-0.22193401	1.65077198	0.51073098
C	-1.55118203	1.25154495	0.56721503
C	-1.94607306	0.11408900	-0.11521200
H	-1.31492198	-1.48470795	-1.42375898
H	0.99248803	-0.76892298	-1.50795102
H	0.07636700	2.54243898	1.04371297
H	-2.24116898	1.84382403	1.14278901
N	-3.36733508	-0.36219800	-0.08690800
C	-4.24775124	0.49102899	0.78052098
H	-5.24314690	0.06289100	0.75416601
H	-3.86746311	0.47876301	1.79528105
H	-4.27071714	1.49967802	0.38547099
C	-3.93705010	-0.33978900	-1.48469806
H	-3.35999703	-1.00414205	-2.11519694
H	-4.96911716	-0.67186397	-1.43796504
H	-3.87847710	0.67714298	-1.85665596
C	-3.41675210	-1.76891005	0.45814499
H	-2.99633288	-1.75798297	1.45758700
H	-4.45325613	-2.08836508	0.48151499
H	-2.84056711	-2.42176104	-0.18468501
C	3.26159596	0.71806097	-0.21190900
O	4.42824602	1.38163400	-0.41615701
C	2.11055589	1.40917504	-0.23698100
H	2.22176695	2.48501897	-0.30926600
C	3.35706210	-0.75684500	0.03446400

O	2.52192402	-1.39516306	0.64621502
O	4.47155714	-1.29114699	-0.46082401
H	4.45854521	-2.27316308	-0.24782901
H	5.22441006	0.92326099	-0.03402600
H	3.24451494	-3.43286991	0.66863698
O	4.05792618	-3.77677989	0.26979700
C	3.71107197	-4.72463417	-0.75148302
H	3.07830811	-4.27009392	-1.51547205
H	4.64049196	-5.05564785	-1.20676196
H	3.19883895	-5.58407497	-0.31917301
H	6.57449293	-0.57580101	0.51088101
O	6.60867500	0.37450400	0.66656202
C	6.67783213	0.61552799	2.08078504
H	5.81308317	0.19683300	2.59737802
H	7.59216309	0.19453999	2.49818611
H	6.68708897	1.69371605	2.21533489
H	4.33564281	3.22462893	-0.74563199
O	4.10502911	4.11762381	-1.04426396
C	3.93343592	4.05837584	-2.45502996
H	4.86034393	3.78779697	-2.96954894
H	3.15684605	3.34199595	-2.74125290
H	3.62848806	5.04751587	-2.79340410

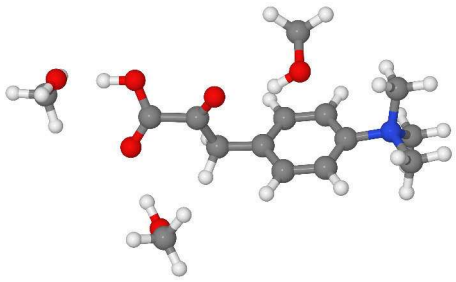
S10.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-6.18850000	0.12920000	0.00000000
2	15.84180000	3.19960000	0.00000000
3	18.39820000	0.31780000	0.00000000
4	22.52220000	3.47040000	0.00000000
5	29.43860000	0.30150000	0.00000000
6	33.40700000	8.51040000	0.00000000
7	41.46770000	1.12260000	0.00000000
8	50.59500000	2.10240000	0.00000000
9	58.78500000	9.00900000	0.00000000
10	60.67380000	7.60650000	0.00000000
11	67.12150000	2.02830000	0.00000000
12	75.93660000	2.45300000	0.00000000
13	81.71990000	11.46370000	0.00000000
14	91.95560000	4.22690000	0.00000000
15	100.23450000	3.85090000	0.00000000
16	107.82530000	7.16210000	0.00000000
17	116.74640000	1.39730000	0.00000000
18	122.67580000	4.90040000	0.00000000
19	127.61630000	4.09970000	0.00000000
20	145.10470000	2.69340000	0.00000000
21	154.46990000	3.81900000	0.00000000
22	160.46780000	3.75540000	0.00000000
23	186.33740000	21.48100000	0.00000000
24	213.11170000	2.55460000	0.00000000
25	217.39240000	12.35270000	0.00000000
26	228.97220000	4.42520000	0.00000000
27	262.40700000	16.52300000	0.00000000
28	290.16900000	32.73640000	0.00000000
29	301.90830000	48.28450000	0.00000000
30	324.96900000	26.49880000	0.00000000
31	363.26100000	11.90290000	0.00000000
32	367.14700000	46.72350000	0.00000000
33	376.52200000	28.53180000	0.00000000
34	401.83960000	139.81530000	0.00000000
35	413.10240000	87.76410000	0.00000000
36	424.56100000	1.08000000	0.00000000
37	439.49580000	2.37000000	0.00000000
38	461.74500000	28.79750000	0.00000000
39	475.20200000	94.32380000	0.00000000
40	486.17920000	1.37320000	0.00000000
41	545.14490000	8.16300000	0.00000000
42	563.65260000	250.64860000	0.00000000
43	572.71120000	7.74400000	0.00000000
44	599.26970000	30.80440000	0.00000000
45	639.40340000	37.84070000	0.00000000
46	661.82720000	71.35260000	0.00000000
47	669.82700000	132.24360000	0.00000000
48	720.71460000	22.03610000	0.00000000
49	755.11740000	1.18100000	0.00000000
50	805.66880000	7.36770000	0.00000000
51	813.37670000	20.17400000	0.00000000
52	836.22150000	1.91850000	0.00000000
53	847.29060000	41.83180000	0.00000000
54	854.36790000	34.60610000	0.00000000
55	873.61480000	100.14960000	0.00000000
56	911.93270000	18.23830000	0.00000000
57	922.53280000	63.73490000	0.00000000
58	947.08920000	53.30830000	0.00000000
59	963.95930000	25.93240000	0.00000000
60	986.97710000	2.97330000	0.00000000

61	995.75720000	40.83310000	0.00000000
62	998.34540000	6.15090000	0.00000000
63	1016.80510000	343.11190000	0.00000000
64	1018.54280000	96.11500000	0.00000000
65	1039.01320000	11.95960000	0.00000000
66	1041.53690000	135.21190000	0.00000000
67	1081.13610000	0.10500000	0.00000000
68	1086.62820000	42.62960000	0.00000000
69	1100.57630000	56.53610000	0.00000000
70	1110.18950000	13.50850000	0.00000000
71	1138.21410000	2.50510000	0.00000000
72	1139.46550000	20.34130000	0.00000000
73	1143.59990000	0.77460000	0.00000000
74	1170.76520000	9.00700000	0.00000000
75	1176.21900000	1.80620000	0.00000000
76	1181.03430000	6.20200000	0.00000000
77	1182.78370000	3.52460000	0.00000000
78	1192.32580000	121.00180000	0.00000000
79	1229.35000000	9.01590000	0.00000000
80	1246.00130000	800.74070000	0.00000000
81	1260.98960000	11.97440000	0.00000000
82	1262.95690000	9.18350000	0.00000000
83	1278.64200000	300.72390000	0.00000000
84	1299.72130000	4.82510000	0.00000000
85	1329.79310000	105.97380000	0.00000000
86	1350.16940000	35.26550000	0.00000000
87	1361.37920000	31.73060000	0.00000000
88	1373.68320000	22.35670000	0.00000000
89	1384.41790000	135.78410000	0.00000000
90	1426.30370000	58.48780000	0.00000000
91	1443.01270000	224.38230000	0.00000000
92	1453.35380000	8.94960000	0.00000000
93	1455.61320000	54.25150000	0.00000000
94	1459.72620000	104.37470000	0.00000000
95	1473.1.000000	15.63320000	0.00000000
96	1477.01790000	4.43460000	0.00000000
97	1478.50110000	7.59420000	0.00000000
98	1479.32560000	0.71590000	0.00000000
99	1482.73690000	0.71880000	0.00000000
100	1487.96680000	2.02910000	0.00000000
101	1489.70690000	7.00150000	0.00000000
102	1490.06430000	5.89640000	0.00000000
103	1493.40200000	5.48040000	0.00000000
104	1496.81310000	1.59350000	0.00000000
105	1498.33870000	36.93790000	0.00000000
106	1503.82740000	4.51800000	0.00000000
107	1506.22160000	11.31410000	0.00000000
108	1506.54810000	39.47620000	0.00000000
109	1507.72460000	1.86710000	0.00000000
110	1509.79220000	33.98990000	0.00000000
111	1529.42070000	69.08240000	0.00000000
112	1550.64230000	78.94630000	0.00000000
113	1622.60410000	1.77860000	0.00000000
114	1647.17390000	7.58280000	0.00000000
115	1695.04120000	139.86420000	0.00000000
116	1739.74350000	222.58870000	0.00000000
117	2988.60010000	85.25690000	0.00000000
118	3004.21500000	1639.20240000	0.00000000
119	3027.96750000	133.19930000	0.00000000
120	3032.09840000	88.55420000	0.00000000
121	3037.51560000	569.95100000	0.00000000
122	3087.23710000	4.79440000	0.00000000
123	3089.42410000	30.89650000	0.00000000
124	3092.64430000	5.10200000	0.00000000

125	3093.33660000	81.35880000	0.00000000
126	3094.19220000	63.98400000	0.00000000
127	3095.43550000	6.43000000	0.00000000
128	3131.62690000	27.78990000	0.00000000
129	3132.50660000	25.46070000	0.00000000
130	3150.68440000	1186.91350000	0.00000000
131	3153.13040000	1904.58690000	0.00000000
132	3176.83520000	1.02520000	0.00000000
133	3182.39000000	2.75390000	0.00000000
134	3184.89970000	9.42730000	0.00000000
135	3189.97500000	7.81300000	0.00000000
136	3191.28600000	0.88880000	0.00000000
137	3192.19930000	2.17370000	0.00000000
138	3196.59790000	6.38870000	0.00000000
139	3205.02140000	3.50520000	0.00000000
140	3218.01290000	5.24150000	0.00000000
141	3243.85180000	0.53620000	0.00000000
142	3656.25180000	580.50450000	0.00000000
143	3707.32940000	266.70410000	0.00000000
144	3805.40310000	100.60490000	0.00000000

S11. CALCULATIONS ON 4E'



Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)CC(=O)C(=O)O.CO.CO.CO	
Formula	: $C_{15}H_{28}NO_6^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1094.88940987	a.u.
Gibbs Energy	: -1094.52776900	a.u.
Number of imaginary frequencies	: 0	

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

50

C	-2.63393807	0.49352700	1.34389997
C	-1.26630795	0.39651200	1.53109705
C	-0.51175702	-0.53028399	0.81659299
C	-1.16533196	-1.38619697	-0.06111000
C	-2.53745794	-1.29981303	-0.25939700
C	-3.26069188	-0.34469101	0.43274301
H	-3.18266702	1.24121904	1.89413297
H	-0.78141499	1.06685102	2.22657204
H	-0.60196501	-2.12203097	-0.61728197
H	-2.99964809	-1.96871197	-0.96412098
N	-4.71971178	-0.13215999	0.16704801
C	-5.28770494	-1.13258398	-0.79849499
H	-6.34371805	-0.91367000	-0.90901101
H	-4.78901720	-1.03000700	-1.75490403
H	-5.15758419	-2.13106608	-0.39752200
C	-5.50735521	-0.23608100	1.44812799
H	-5.16490793	0.51831698	2.14425898
H	-6.55435991	-0.07557100	1.21417201
H	-5.35402107	-1.22699201	1.86132896
C	-4.89662409	1.24284697	-0.43581101
H	-4.25168324	1.30947006	-1.30514002
H	-5.94082212	1.36569095	-0.70293999
H	-4.60736895	1.98657405	0.29617801
C	1.63660300	0.36839300	-0.07982600
O	1.05080199	1.00865304	-0.92040497
C	0.98182201	-0.54674399	0.92522800
H	1.32321501	-0.23581700	1.91623497
H	1.39152896	-1.54903495	0.77451998
C	3.17661190	0.42675000	-0.01984100
O	3.83640194	-0.55531800	0.26615500
O	3.65015888	1.60648203	-0.31874800

H	4.66507912	1.60699105	-0.27647501
H	-0.88923901	1.29382098	-1.40315604
O	-1.69886899	1.74426305	-1.68147504
C	-1.66828895	3.05200291	-1.12433803
H	-1.68923497	3.02844906	-0.03087900
H	-0.78430599	3.61067891	-1.44408703
H	-2.55447793	3.57941198	-1.47419596
H	6.64040613	1.13588703	-0.85448802
O	6.23443604	1.67949104	-0.17001399
C	6.71498823	1.24461401	1.11682200
H	6.40563917	0.22027400	1.32177496
H	7.79976320	1.32528996	1.16116202
H	6.27442598	1.91041994	1.85367799
H	3.31681204	-2.35586905	0.23776101
O	2.88969493	-3.22392797	0.16872300
C	2.70719099	-3.51229310	-1.21306896
H	2.05837393	-2.77950501	-1.70311296
H	3.65871000	-3.54654598	-1.75105405
H	2.23416495	-4.49010897	-1.28550899

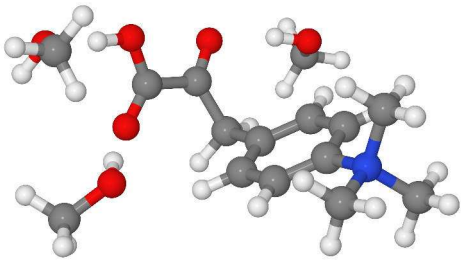
S11.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	13.47020000	6.70710000	0.00000000
2	20.09950000	0.94970000	0.00000000
3	23.83450000	1.08940000	0.00000000
4	31.30870000	5.79470000	0.00000000
5	39.56830000	1.12530000	0.00000000
6	50.97400000	0.10240000	0.00000000
7	54.01290000	0.22090000	0.00000000
8	58.48290000	0.05600000	0.00000000
9	68.51980000	7.87170000	0.00000000
10	72.83790000	5.61250000	0.00000000
11	73.94340000	2.34630000	0.00000000
12	79.33610000	15.36710000	0.00000000
13	90.25080000	4.83240000	0.00000000
14	92.98180000	5.92930000	0.00000000
15	99.40830000	5.75770000	0.00000000
16	100.58190000	7.07950000	0.00000000
17	108.76930000	1.01210000	0.00000000
18	117.68380000	1.75220000	0.00000000
19	123.59710000	0.48150000	0.00000000
20	126.90230000	2.97300000	0.00000000
21	133.59970000	4.94050000	0.00000000
22	146.34310000	2.92150000	0.00000000
23	158.83290000	5.82590000	0.00000000
24	206.98640000	32.21950000	0.00000000
25	218.41520000	3.45210000	0.00000000
26	228.31590000	3.31840000	0.00000000
27	239.29490000	4.64040000	0.00000000
28	274.72820000	1.96850000	0.00000000
29	295.67490000	0.74530000	0.00000000
30	322.64130000	25.56160000	0.00000000
31	352.03200000	63.17490000	0.00000000
32	360.32940000	10.40580000	0.00000000
33	367.37580000	3.95760000	0.00000000
34	387.77580000	1.26020000	0.00000000
35	397.25090000	4.59870000	0.00000000
36	414.62580000	33.28620000	0.00000000
37	425.89940000	0.36490000	0.00000000
38	449.65430000	119.56110000	0.00000000
39	455.09550000	2.73470000	0.00000000
40	485.19040000	1.93140000	0.00000000
41	533.73530000	1.95310000	0.00000000
42	548.52120000	217.95900000	0.00000000
43	567.87320000	4.76260000	0.00000000
44	570.92820000	16.25140000	0.00000000
45	655.50770000	10.16530000	0.00000000
46	659.85360000	236.73340000	0.00000000
47	670.88510000	102.45920000	0.00000000
48	719.82590000	62.31770000	0.00000000
49	733.71570000	6.17400000	0.00000000
50	765.84510000	29.07400000	0.00000000
51	821.76920000	29.87900000	0.00000000
52	836.47330000	18.59640000	0.00000000
53	844.32140000	0.64720000	0.00000000
54	860.14330000	25.72020000	0.00000000
55	897.16340000	22.46320000	0.00000000
56	946.34930000	47.42540000	0.00000000
57	950.75010000	2.28990000	0.00000000
58	966.16990000	25.73470000	0.00000000
59	987.51630000	0.45630000	0.00000000
60	995.90080000	121.05220000	0.00000000

61	1002.18900000	0.11110000	0.00000000
62	1040.06350000	125.15990000	0.00000000
63	1042.94780000	57.86670000	0.00000000
64	1043.04560000	100.10980000	0.00000000
65	1057.08310000	34.69440000	0.00000000
66	1072.55060000	160.37750000	0.00000000
67	1083.95540000	0.02980000	0.00000000
68	1105.01610000	10.07250000	0.00000000
69	1115.22880000	13.74540000	0.00000000
70	1137.68940000	1.73920000	0.00000000
71	1142.92920000	11.71870000	0.00000000
72	1146.97050000	116.56170000	0.00000000
73	1147.37540000	10.74150000	0.00000000
74	1171.31820000	11.50000000	0.00000000
75	1175.82620000	1.00200000	0.00000000
76	1180.66220000	0.78830000	0.00000000
77	1181.78650000	14.35240000	0.00000000
78	1205.84860000	3.83820000	0.00000000
79	1229.41940000	2.85250000	0.00000000
80	1249.52980000	1.23670000	0.00000000
81	1258.28060000	2.86150000	0.00000000
82	1264.27340000	1.64730000	0.00000000
83	1301.28520000	1.74070000	0.00000000
84	1311.14580000	308.60070000	0.00000000
85	1350.68200000	8.76830000	0.00000000
86	1362.35540000	8.26430000	0.00000000
87	1370.16730000	0.58210000	0.00000000
88	1372.28160000	64.30910000	0.00000000
89	1416.59280000	26.90780000	0.00000000
90	1424.70600000	27.51270000	0.00000000
91	1451.73660000	40.99090000	0.00000000
92	1453.09980000	9.04500000	0.00000000
93	1456.16520000	2.82060000	0.00000000
94	1463.09130000	12.09150000	0.00000000
95	1473.27310000	11.24750000	0.00000000
96	1476.54740000	1.65870000	0.00000000
97	1477.99830000	19.61780000	0.00000000
98	1479.00830000	0.32430000	0.00000000
99	1479.69940000	2.42600000	0.00000000
100	1487.05050000	3.62130000	0.00000000
101	1488.76840000	2.97290000	0.00000000
102	1489.79740000	9.67670000	0.00000000
103	1492.90120000	4.84850000	0.00000000
104	1495.85000000	3.90670000	0.00000000
105	1497.31070000	4.75990000	0.00000000
106	1502.74170000	11.86700000	0.00000000
107	1504.25850000	35.38720000	0.00000000
108	1507.69160000	8.25740000	0.00000000
109	1510.04290000	12.69340000	0.00000000
110	1513.91920000	31.56300000	0.00000000
111	1528.50870000	83.24890000	0.00000000
112	1557.61600000	60.62420000	0.00000000
113	1640.29290000	2.58060000	0.00000000
114	1657.30270000	3.21500000	0.00000000
115	1723.98360000	676.80530000	0.00000000
116	1775.04110000	198.52310000	0.00000000
117	2824.13090000	3027.48910000	0.00000000
118	2991.82230000	78.09820000	0.00000000
119	2995.84070000	76.72070000	0.00000000
120	3031.18800000	39.1.000000	0.00000000
121	3036.73460000	84.12250000	0.00000000
122	3041.47790000	81.73610000	0.00000000
123	3042.27140000	34.55600000	0.00000000
124	3064.04150000	28.19430000	0.00000000

125	3088.23730000	6.06430000	0.00000000
126	3092.88900000	4.26530000	0.00000000
127	3094.71700000	3.82250000	0.00000000
128	3095.13580000	58.85210000	0.00000000
129	3098.90890000	54.21710000	0.00000000
130	3111.23550000	29.87100000	0.00000000
131	3138.48670000	23.87000000	0.00000000
132	3180.38850000	1.93280000	0.00000000
133	3181.11630000	0.77780000	0.00000000
134	3184.53640000	8.48550000	0.00000000
135	3188.11480000	9.38900000	0.00000000
136	3188.67210000	6.36340000	0.00000000
137	3191.18400000	2.03120000	0.00000000
138	3194.61330000	3.83770000	0.00000000
139	3200.22240000	1.56720000	0.00000000
140	3219.26970000	2.83880000	0.00000000
141	3247.95900000	0.26500000	0.00000000
142	3651.73750000	591.10510000	0.00000000
143	3710.10710000	413.64000000	0.00000000
144	3803.41420000	94.51380000	0.00000000

S12. CALCULATIONS ON 4F'



Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)CC(=O)C(=O)O.CO.CO.CO	
Formula	: $C_{15}H_{28}NO_6^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1094.88779146	a.u.
Gibbs Energy	: -1094.52692100	a.u.
Number of imaginary frequencies	: 0	

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

50

C	1.14788198	-1.25017703	-0.22848099
C	-0.03992100	-1.62615001	0.37539700
C	-0.75135100	-0.72336400	1.16577196
C	-0.25450599	0.56393099	1.32752800
C	0.93272501	0.95378101	0.71830797
C	1.62901998	0.04225900	-0.05643400
H	1.67817700	-1.97537899	-0.82550400
H	-0.41905099	-2.62890601	0.23149499
H	-0.79017502	1.28621495	1.92416000
H	1.27599502	1.96274900	0.86650699
N	2.91971898	0.41356701	-0.72456998
C	3.30910897	1.84447896	-0.48351201
H	4.24227715	2.01838398	-1.00684595
H	2.53877497	2.49711609	-0.87730402
H	3.44787097	2.00397706	0.57925498
C	4.03074694	-0.45937201	-0.19262800
H	3.80526590	-1.49571300	-0.41005901
H	4.95393896	-0.16694801	-0.68170100
H	4.09885311	-0.30517599	0.87861598
C	2.79748106	0.21853800	-2.21660590
H	1.99085200	0.84710997	-2.57745409
H	3.73992300	0.50432903	-2.67165494
H	2.58514500	-0.82189000	-2.42578793
C	-3.17659807	-0.89879203	0.80276799
O	-3.67353201	-1.75212002	0.10631500
C	-2.06508493	-1.14524400	1.79359400
H	-2.04958701	-2.20448208	2.03257704
H	-2.25478005	-0.56540900	2.69314194
C	-3.65411091	0.56747699	0.68665498
O	-3.42376900	1.36228395	1.57910204
O	-4.29619122	0.81402802	-0.42180899

H	-4.56943321	1.79192197	-0.46398199
H	-2.43500400	2.94756794	1.47179699
O	-1.80544806	3.68343091	1.45029199
C	-2.23431802	4.65515900	2.39824009
H	-3.20678210	5.08100080	2.13370705
H	-2.29816389	4.23795080	3.40699697
H	-1.49775600	5.45674896	2.40253592
H	-5.19413185	3.68225598	0.24298100
O	-4.96985722	3.30343699	-0.61408597
C	-3.97962999	4.13658094	-1.25208795
H	-4.38563681	5.13157511	-1.42850900
H	-3.07728195	4.19941282	-0.64505500
H	-3.75056505	3.66900396	-2.20561504
H	-2.80061507	-3.45024109	0.02520700
O	-2.21849108	-4.22397184	0.07288700
C	-2.72991705	-5.10197878	1.06964004
H	-2.76844811	-4.62623978	2.05447793
H	-3.73133397	-5.46289396	0.81896698
H	-2.05935407	-5.95738411	1.12879300

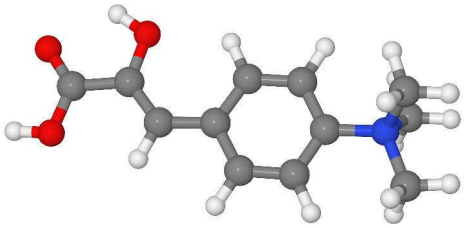
S12.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	8.15920000	2.38630000	0.00000000
2	15.81980000	0.39750000	0.00000000
3	22.99890000	5.66390000	0.00000000
4	28.07380000	2.52070000	0.00000000
5	39.16510000	2.06470000	0.00000000
6	44.42570000	2.32720000	0.00000000
7	51.88540000	6.89680000	0.00000000
8	55.07130000	0.78890000	0.00000000
9	56.79350000	7.10390000	0.00000000
10	64.29960000	8.53050000	0.00000000
11	66.63800000	3.23290000	0.00000000
12	76.04320000	3.50460000	0.00000000
13	85.68490000	7.61350000	0.00000000
14	93.70520000	3.14510000	0.00000000
15	97.19330000	2.55720000	0.00000000
16	106.82830000	4.08200000	0.00000000
17	113.00880000	6.27040000	0.00000000
18	115.78110000	1.72470000	0.00000000
19	127.04490000	4.80630000	0.00000000
20	138.42390000	2.12710000	0.00000000
21	153.94380000	8.66030000	0.00000000
22	158.25240000	2.48880000	0.00000000
23	169.29890000	3.28250000	0.00000000
24	191.75600000	0.94310000	0.00000000
25	214.13590000	3.38720000	0.00000000
26	231.22120000	13.26920000	0.00000000
27	254.40520000	4.1.000000	0.00000000
28	273.00720000	6.59580000	0.00000000
29	280.39140000	16.46490000	0.00000000
30	323.39440000	47.38240000	0.00000000
31	347.33400000	10.99200000	0.00000000
32	348.92860000	9.40610000	0.00000000
33	374.99560000	37.56030000	0.00000000
34	383.78170000	12.59160000	0.00000000
35	423.03490000	28.46610000	0.00000000
36	430.36390000	12.49680000	0.00000000
37	438.88560000	16.06420000	0.00000000
38	469.23920000	85.96600000	0.00000000
39	474.41850000	101.10260000	0.00000000
40	481.60150000	3.34110000	0.00000000
41	528.37910000	4.41290000	0.00000000
42	551.79300000	20.32920000	0.00000000
43	580.90650000	40.58320000	0.00000000
44	612.84150000	134.18000000	0.00000000
45	641.89970000	254.52100000	0.00000000
46	643.04600000	49.70360000	0.00000000
47	658.40460000	23.08840000	0.00000000
48	680.31860000	21.36030000	0.00000000
49	753.89870000	4.18640000	0.00000000
50	785.83710000	28.37350000	0.00000000
51	812.60560000	14.56660000	0.00000000
52	845.11230000	21.64030000	0.00000000
53	850.19410000	25.16180000	0.00000000
54	860.35360000	13.21440000	0.00000000
55	896.76960000	1.91870000	0.00000000
56	944.80060000	24.40580000	0.00000000
57	953.13340000	19.60780000	0.00000000
58	962.20360000	23.62610000	0.00000000
59	996.89030000	122.70890000	0.00000000
60	997.84700000	3.34430000	0.00000000

61	1029.18450000	19.03460000	0.00000000
62	1039.34860000	63.32500000	0.00000000
63	1041.22180000	116.01580000	0.00000000
64	1041.69950000	148.60040000	0.00000000
65	1067.76720000	16.79550000	0.00000000
66	1079.82050000	0.10850000	0.00000000
67	1088.04260000	91.74870000	0.00000000
68	1112.64400000	17.65780000	0.00000000
69	1113.34380000	11.89910000	0.00000000
70	1128.23110000	140.54940000	0.00000000
71	1137.29340000	10.82700000	0.00000000
72	1138.34810000	5.96160000	0.00000000
73	1144.78880000	0.20070000	0.00000000
74	1171.92070000	25.07070000	0.00000000
75	1175.87000000	1.91910000	0.00000000
76	1178.60320000	1.71590000	0.00000000
77	1191.26790000	4.96910000	0.00000000
78	1211.80040000	98.76530000	0.00000000
79	1225.55380000	64.94490000	0.00000000
80	1235.87690000	35.52200000	0.00000000
81	1257.22330000	2.29520000	0.00000000
82	1259.12730000	4.09040000	0.00000000
83	1297.21900000	1.37830000	0.00000000
84	1300.48820000	40.31070000	0.00000000
85	1329.22700000	158.68800000	0.00000000
86	1349.76760000	7.59830000	0.00000000
87	1368.97470000	0.29810000	0.00000000
88	1377.19860000	80.21300000	0.00000000
89	1420.39720000	72.22420000	0.00000000
90	1424.74690000	45.73510000	0.00000000
91	1450.41100000	1.78270000	0.00000000
92	1452.92190000	3.10240000	0.00000000
93	1460.47180000	13.67160000	0.00000000
94	1468.88150000	13.80850000	0.00000000
95	1477.54650000	10.89030000	0.00000000
96	1478.48600000	6.39610000	0.00000000
97	1479.46990000	0.24160000	0.00000000
98	1479.61700000	0.15330000	0.00000000
99	1484.56960000	0.15440000	0.00000000
100	1489.04660000	4.79800000	0.00000000
101	1490.42200000	2.65240000	0.00000000
102	1491.86160000	1.97320000	0.00000000
103	1492.84030000	5.16870000	0.00000000
104	1494.10650000	2.15810000	0.00000000
105	1494.86120000	13.23570000	0.00000000
106	1502.11170000	41.02450000	0.00000000
107	1506.11510000	6.90210000	0.00000000
108	1506.81630000	6.45420000	0.00000000
109	1508.18340000	38.32850000	0.00000000
110	1514.66080000	10.28030000	0.00000000
111	1523.11250000	68.58410000	0.00000000
112	1550.71360000	80.39150000	0.00000000
113	1635.13560000	2.83880000	0.00000000
114	1647.80630000	3.70260000	0.00000000
115	1727.73690000	645.40250000	0.00000000
116	1775.75690000	305.62910000	0.00000000
117	2816.05030000	2807.36310000	0.00000000
118	2992.37960000	88.47050000	0.00000000
119	2995.20320000	100.40620000	0.00000000
120	3037.86130000	86.27960000	0.00000000
121	3039.11560000	27.77030000	0.00000000
122	3040.92330000	75.14460000	0.00000000
123	3089.19790000	4.05770000	0.00000000
124	3089.64750000	4.01560000	0.00000000

125	3091.46920000	5.04090000	0.00000000
126	3094.41390000	4.59590000	0.00000000
127	3099.47380000	52.73560000	0.00000000
128	3100.35020000	52.11460000	0.00000000
129	3111.19650000	13.76890000	0.00000000
130	3138.21070000	20.72080000	0.00000000
131	3149.14720000	2.03310000	0.00000000
132	3178.40590000	0.76880000	0.00000000
133	3179.36630000	3.37000000	0.00000000
134	3179.91310000	11.80430000	0.00000000
135	3184.25040000	10.68470000	0.00000000
136	3189.02150000	1.73800000	0.00000000
137	3193.35250000	4.70080000	0.00000000
138	3198.42050000	3.34460000	0.00000000
139	3212.34100000	2.23110000	0.00000000
140	3213.92650000	4.80930000	0.00000000
141	3243.92030000	0.51960000	0.00000000
142	3656.80990000	698.75880000	0.00000000
143	3675.39230000	510.03040000	0.00000000
144	3806.36390000	89.90700000	0.00000000

S13. CALCULATIONS ON $4A_{3D}$



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=C(C(=O)O)O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.43896863	a.u.
Gibbs Energy	: -747.22318800	a.u.
Number of imaginary frequencies	: 0	

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

32

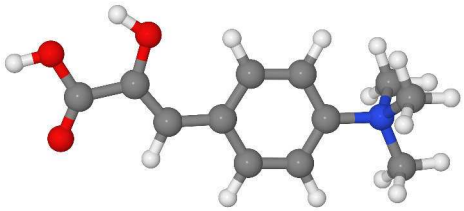
C	-1.36033595	-1.01119006	0.00022300
C	0.01419500	-0.86862499	0.00030500
C	0.60897398	0.40608701	0.00018100
C	-0.24560900	1.51666498	0.00010500
C	-1.62506294	1.38188803	0.00003500
C	-2.18054104	0.11160700	0.00005400
H	-1.77080095	-2.01016593	0.00025800
H	0.63427299	-1.74878597	0.00050200
H	0.17824601	2.51096702	0.00008500
H	-2.22653294	2.27520800	0.00000900
N	-3.67063808	-0.09480700	-0.00009200
C	-4.43457603	1.19736695	-0.00011600
H	-5.49248886	0.95575601	-0.00031300
H	-4.18589783	1.76159096	0.89186698
H	-4.18558216	1.76173604	-0.89191997
C	-4.07610321	-0.86510903	-1.23278296
H	-3.58355403	-1.82957399	-1.22933900
H	-5.15447712	-0.99576497	-1.22022998
H	-3.76874304	-0.29666501	-2.10448003
C	-4.07634592	-0.86522901	1.23243201
H	-3.76918602	-0.29686800	2.10425305
H	-5.15471411	-0.99592400	1.21964896
H	-3.58377504	-1.82968497	1.22900200
C	3.02360106	-0.28349900	0.00012400
O	2.82889390	-1.61222601	0.00019100
C	2.03986907	0.63424802	0.00013200
H	2.36432195	1.66332901	0.00022100
C	4.47272587	0.07113400	-0.00010600
O	5.30962896	-0.80214101	-0.00049500
O	4.73802710	1.37910604	0.00004900
H	5.70103979	1.48857999	-0.00011800
H	3.71518993	-2.02006412	-0.00026800

S13.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	28.65530000	0.03170000	0.00000000
2	37.30690000	2.67070000	0.00000000
3	62.81040000	0.24510000	0.00000000
4	90.15750000	2.59940000	0.00000000
5	92.85280000	0.09260000	0.00000000
6	137.54410000	0.08050000	0.00000000
7	184.75470000	0.07000000	0.00000000
8	219.25640000	0.12790000	0.00000000
9	228.05750000	1.51120000	0.00000000
10	264.71340000	0.05970000	0.00000000
11	282.01540000	0.46890000	0.00000000
12	298.71990000	1.20090000	0.00000000
13	346.18100000	12.14400000	0.00000000
14	350.97730000	0.07790000	0.00000000
15	369.85260000	1.38220000	0.00000000
16	379.99630000	12.12370000	0.00000000
17	407.53820000	13.90050000	0.00000000
18	411.56980000	6.64500000	0.00000000
19	422.57810000	0.27240000	0.00000000
20	451.85160000	4.30800000	0.00000000
21	476.45760000	47.79940000	0.00000000
22	480.38150000	8.73090000	0.00000000
23	489.30550000	33.63210000	0.00000000
24	539.93450000	50.44880000	0.00000000
25	562.26690000	0.68650000	0.00000000
26	568.99850000	12.76840000	0.00000000
27	623.88470000	30.33630000	0.00000000
28	653.88660000	1.26810000	0.00000000
29	675.59700000	4.37840000	0.00000000
30	696.44560000	4.55330000	0.00000000
31	753.64890000	1.79150000	0.00000000
32	812.16880000	10.50700000	0.00000000
33	826.92470000	21.70730000	0.00000000
34	832.21430000	0.48410000	0.00000000
35	842.97640000	32.98940000	0.00000000
36	851.28340000	35.86700000	0.00000000
37	864.49650000	32.19710000	0.00000000
38	921.21970000	33.44420000	0.00000000
39	944.28160000	25.20140000	0.00000000
40	964.51510000	18.47700000	0.00000000
41	980.52920000	0.04530000	0.00000000
42	1002.13020000	0.00020000	0.00000000
43	1019.37670000	8.66130000	0.00000000
44	1032.10080000	19.47090000	0.00000000
45	1047.91540000	57.01790000	0.00000000
46	1077.02270000	0.01890000	0.00000000
47	1132.84810000	2.61960000	0.00000000
48	1134.58740000	1.52440000	0.00000000
49	1140.00210000	0.51570000	0.00000000
50	1177.73080000	16.65480000	0.00000000
51	1213.84890000	109.75400000	0.00000000
52	1240.35460000	39.68240000	0.00000000
53	1259.02860000	1.33060000	0.00000000
54	1259.33910000	0.82870000	0.00000000
55	1294.69320000	4.53250000	0.00000000
56	1323.12750000	196.72690000	0.00000000
57	1340.15580000	4.04510000	0.00000000
58	1361.27630000	16.81380000	0.00000000
59	1397.17070000	375.87040000	0.00000000
60	1448.15340000	4.31750000	0.00000000

61	1450.71830000	4.61190000	0.00000000
62	1455.87910000	19.11210000	0.00000000
63	1479.29950000	0.00940000	0.00000000
64	1489.44130000	0.31140000	0.00000000
65	1492.87220000	1.82350000	0.00000000
66	1495.64210000	0.22320000	0.00000000
67	1506.81400000	27.76980000	0.00000000
68	1512.44450000	23.67530000	0.00000000
69	1530.28710000	44.81410000	0.00000000
70	1545.52840000	52.50000000	0.00000000
71	1615.35390000	2.30560000	0.00000000
72	1640.20280000	52.08820000	0.00000000
73	1693.04800000	96.75030000	0.00000000
74	1772.92360000	412.14460000	0.00000000
75	2370.78440000	1.84870000	0.00000000
76	2623.25230000	200.18560000	0.00000000
77	2721.98770000	112.38630000	0.00000000
78	3078.92640000	0.62230000	0.00000000
79	3080.44510000	2.10310000	0.00000000
80	3087.56270000	2.18510000	0.00000000
81	3166.56720000	0.00170000	0.00000000
82	3167.39810000	1.50840000	0.00000000
83	3174.53910000	8.82190000	0.00000000
84	3182.59990000	0.23450000	0.00000000
85	3185.94570000	5.51260000	0.00000000
86	3187.94320000	0.05630000	0.00000000
87	3189.90720000	1.39570000	0.00000000
88	3197.49960000	2.23290000	0.00000000
89	3232.36020000	1.06740000	0.00000000
90	3245.66880000	5.67550000	0.00000000

S14. CALCULATIONS ON $4B_{3D}$



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=C(C(=O)O)O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.43503369	a.u.
Gibbs Energy	: -747.21974400	a.u.
Number of imaginary frequencies	: 0	

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

32

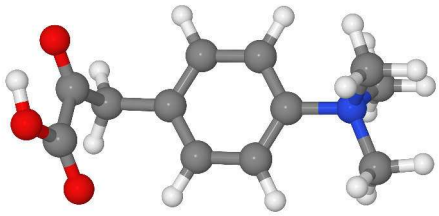
C	-1.36186194	-1.01134706	-0.00020100
C	0.01190200	-0.86042798	-0.00017800
C	0.59897202	0.41783100	-0.00001800
C	-0.26241601	1.52344894	0.00001900
C	-1.64086401	1.38034904	0.00000300
C	-2.18864489	0.10673400	-0.00008200
H	-1.76676297	-2.01260304	-0.00042000
H	0.63700402	-1.73703206	-0.00029500
H	0.15642200	2.51977801	0.00002100
H	-2.24753404	2.27012610	0.00009000
N	-3.67761588	-0.10800700	0.00001300
C	-4.44878721	1.17999601	0.00042800
H	-5.50531387	0.93238503	0.00041500
H	-4.20303488	1.74543202	0.89244401
H	-4.20312309	1.74595296	-0.89128202
C	-4.07912588	-0.88011301	-1.23273695
H	-3.58137488	-1.84191000	-1.22962797
H	-5.15678120	-1.01659906	-1.22009695
H	-3.77498889	-0.30976301	-2.10432005
C	-4.07882595	-0.88074201	1.23247194
H	-3.77452803	-0.31080499	2.10426998
H	-5.15647697	-1.01727104	1.21999300
H	-3.58100200	-1.84249997	1.22877598
C	3.02858710	-0.23655000	0.00024100
O	2.84311604	-1.57326806	0.00005200
C	2.02621889	0.65939301	0.00015700
H	2.34882402	1.69014001	0.00016800
C	4.43931913	0.26085800	-0.00001300
O	4.77612495	1.41142499	-0.00022600
O	5.30229616	-0.78450298	0.00005500
H	6.20599699	-0.43653801	-0.00010400
H	3.70686293	-2.00854897	0.00028900

S14.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	28.63510000	2.02320000	0.00000000
2	37.63300000	1.78260000	0.00000000
3	62.82320000	0.10520000	0.00000000
4	82.03750000	0.96370000	0.00000000
5	89.07180000	1.32050000	0.00000000
6	133.30640000	0.01940000	0.00000000
7	190.11130000	2.66190000	0.00000000
8	219.44050000	0.34940000	0.00000000
9	226.49290000	1.48430000	0.00000000
10	264.45950000	0.82670000	0.00000000
11	281.83270000	0.33180000	0.00000000
12	299.06120000	0.58260000	0.00000000
13	342.92790000	2.78720000	0.00000000
14	351.00770000	0.03820000	0.00000000
15	365.63480000	67.92190000	0.00000000
16	369.58860000	1.35620000	0.00000000
17	380.38090000	0.19890000	0.00000000
18	405.04840000	1.94560000	0.00000000
19	407.73260000	7.81090000	0.00000000
20	423.30040000	0.21680000	0.00000000
21	457.00030000	14.85140000	0.00000000
22	480.61940000	3.87190000	0.00000000
23	523.06440000	24.55240000	0.00000000
24	532.80660000	26.74460000	0.00000000
25	548.24380000	19.73570000	0.00000000
26	567.04080000	24.87830000	0.00000000
27	601.39530000	56.86070000	0.00000000
28	652.59190000	0.36800000	0.00000000
29	686.09210000	5.42880000	0.00000000
30	696.21790000	1.60090000	0.00000000
31	753.72200000	2.31910000	0.00000000
32	806.91780000	10.62350000	0.00000000
33	821.49250000	21.38780000	0.00000000
34	832.46810000	0.21340000	0.00000000
35	832.73440000	9.28230000	0.00000000
36	850.29930000	40.02920000	0.00000000
37	865.73450000	30.83140000	0.00000000
38	912.24220000	20.61460000	0.00000000
39	944.57850000	25.09830000	0.00000000
40	964.37400000	17.36390000	0.00000000
41	982.40150000	0.07540000	0.00000000
42	997.39590000	141.56150000	0.00000000
43	1001.12720000	0.00250000	0.00000000
44	1028.03270000	34.14370000	0.00000000
45	1036.86860000	12.63050000	0.00000000
46	1077.04690000	0.01900000	0.00000000
47	1132.55240000	4.36990000	0.00000000
48	1134.21460000	0.39510000	0.00000000
49	1140.03060000	0.51460000	0.00000000
50	1175.81040000	20.98530000	0.00000000
51	1187.16710000	16.93850000	0.00000000
52	1234.04540000	55.23290000	0.00000000
53	1259.04630000	1.32880000	0.00000000
54	1259.30390000	3.76850000	0.00000000
55	1294.09650000	13.83280000	0.00000000
56	1301.57630000	448.41360000	0.00000000
57	1338.73800000	13.58100000	0.00000000
58	1357.30590000	113.58650000	0.00000000
59	1371.00630000	207.38070000	0.00000000
60	1447.91330000	2.43840000	0.00000000

61	1450.70980000	4.60430000	0.00000000
62	1455.15410000	9.33070000	0.00000000
63	1479.33980000	0.00840000	0.00000000
64	1489.48630000	0.30660000	0.00000000
65	1492.86480000	1.78650000	0.00000000
66	1495.66330000	0.14150000	0.00000000
67	1506.83790000	27.63580000	0.00000000
68	1512.41950000	23.68170000	0.00000000
69	1530.29360000	45.20330000	0.00000000
70	1545.42290000	60.33220000	0.00000000
71	1615.08000000	1.72190000	0.00000000
72	1640.42050000	47.18880000	0.00000000
73	1691.42770000	66.59820000	0.00000000
74	1820.03460000	267.34060000	0.00000000
75	2362.91960000	1.44170000	0.00000000
76	2726.54130000	194.08060000	0.00000000
77	2731.14300000	119.77590000	0.00000000
78	3078.90200000	0.62410000	0.00000000
79	3080.44100000	2.13960000	0.00000000
80	3087.57920000	2.21110000	0.00000000
81	3166.52260000	0.00210000	0.00000000
82	3167.38080000	1.58850000	0.00000000
83	3174.54930000	8.80000000	0.00000000
84	3182.71670000	0.21910000	0.00000000
85	3185.81160000	5.53540000	0.00000000
86	3187.90880000	0.05170000	0.00000000
87	3191.52670000	1.17150000	0.00000000
88	3197.31950000	2.26560000	0.00000000
89	3232.64580000	1.03910000	0.00000000
90	3245.54030000	4.76810000	0.00000000

S15. CALCULATIONS ON $4D_{3D}$



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)CC(=O)C(=O)O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.43040474	a.u.
Gibbs Energy	: -747.21400400	a.u.
Number of imaginary frequencies	: 1	

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

32

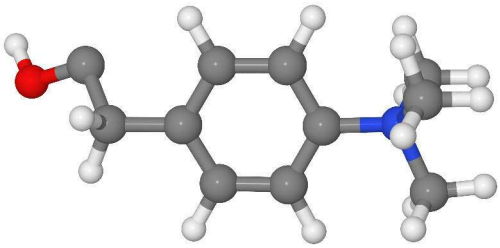
C	1.31027102	1.30388796	0.15809400
C	-0.00205700	1.56685805	-0.19830200
C	-0.77621502	0.60279298	-0.84377599
C	-0.20788801	-0.63690299	-1.11426401
C	1.10846198	-0.91317302	-0.76436597
C	1.86105800	0.06082800	-0.12864500
H	1.87777901	2.07694507	0.65391803
H	-0.42707500	2.53406191	0.03068200
H	-0.80211103	-1.40559900	-1.58464599
H	1.50358295	-1.88736403	-0.99709100
N	3.28918004	-0.19361401	0.27367201
C	3.75888205	-1.57263196	-0.09301800
H	4.78994799	-1.66624200	0.23194200
H	3.14500690	-2.30857491	0.41432101
H	3.69910407	-1.69882298	-1.16835403
C	4.19514418	0.79599398	-0.41764501
H	3.92052889	1.80083096	-0.12131500
H	5.22027397	0.58764499	-0.12528400
H	4.07145691	0.67913300	-1.48938799
C	3.42758989	-0.04740500	1.76958501
H	2.76205492	-0.76131803	2.24390602
H	4.46010113	-0.24681200	2.04149795
H	3.15472603	0.96028101	2.05769300
C	-3.10433197	0.62413698	-0.00623300
O	-3.50118899	1.47179306	0.75428998
C	-2.21520400	0.89998102	-1.20020497
H	-2.33547497	1.94833803	-1.46292198
H	-2.53034306	0.27224100	-2.03081894
C	-3.46720099	-0.85404903	0.26002401
O	-3.05443907	-1.74755394	-0.42814699
O	-4.24792719	-1.02047002	1.31916296
H	-4.43480587	-0.14243400	1.69778204

S15.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2.27470000	0.57600000	0.00000000
2	38.63810000	2.05400000	0.00000000
3	45.08110000	0.68210000	0.00000000
4	64.09780000	0.35640000	0.00000000
5	80.19600000	3.53530000	0.00000000
6	123.57030000	8.68530000	0.00000000
7	178.66110000	4.87830000	0.00000000
8	214.24700000	0.85760000	0.00000000
9	237.02840000	13.01800000	0.00000000
10	256.66200000	4.94840000	0.00000000
11	278.63560000	0.41280000	0.00000000
12	299.85550000	4.35720000	0.00000000
13	335.35790000	1.87940000	0.00000000
14	353.90390000	0.55690000	0.00000000
15	354.80230000	14.79580000	0.00000000
16	369.23680000	0.80310000	0.00000000
17	384.55540000	3.01700000	0.00000000
18	420.92300000	0.65140000	0.00000000
19	425.88180000	13.53500000	0.00000000
20	452.30910000	5.27710000	0.00000000
21	479.14150000	2.30950000	0.00000000
22	508.93670000	44.44590000	0.00000000
23	514.13030000	7.87940000	0.00000000
24	537.89300000	8.11180000	0.00000000
25	557.19700000	6.70790000	0.00000000
26	602.46380000	35.06850000	0.00000000
27	651.14980000	1.09220000	0.00000000
28	657.56550000	1.35390000	0.00000000
29	727.63460000	6.77600000	0.00000000
30	743.80790000	2.86360000	0.00000000
31	788.39150000	2.00320000	0.00000000
32	809.80330000	11.84430000	0.00000000
33	833.10860000	5.91410000	0.00000000
34	839.42480000	0.90650000	0.00000000
35	847.21810000	33.05040000	0.00000000
36	856.85940000	5.93610000	0.00000000
37	901.40900000	0.36180000	0.00000000
38	945.86450000	22.06850000	0.00000000
39	962.22520000	15.89900000	0.00000000
40	980.12910000	60.89450000	0.00000000
41	987.66470000	0.18280000	0.00000000
42	1001.70830000	0.93810000	0.00000000
43	1027.93450000	25.83530000	0.00000000
44	1044.44240000	6.16560000	0.00000000
45	1076.93650000	0.02070000	0.00000000
46	1077.64220000	7.06240000	0.00000000
47	1131.29890000	11.23150000	0.00000000
48	1133.80090000	0.01020000	0.00000000
49	1140.14660000	0.46410000	0.00000000
50	1159.03900000	259.53150000	0.00000000
51	1170.95590000	4.16680000	0.00000000
52	1229.34180000	10.87250000	0.00000000
53	1238.90110000	14.74710000	0.00000000
54	1258.56790000	1.74950000	0.00000000
55	1258.66710000	1.30280000	0.00000000
56	1295.32540000	2.33270000	0.00000000
57	1335.35890000	119.56000000	0.00000000
58	1341.26430000	2.24130000	0.00000000
59	1361.00180000	1.29690000	0.00000000
60	1448.40970000	0.15520000	0.00000000

61	1451.36130000	4.68770000	0.00000000
62	1454.28110000	14.17670000	0.00000000
63	1479.80960000	0.00150000	0.00000000
64	1489.32250000	0.29400000	0.00000000
65	1493.27880000	1.87410000	0.00000000
66	1495.50810000	0.42640000	0.00000000
67	1507.22260000	27.38330000	0.00000000
68	1513.02450000	24.08000000	0.00000000
69	1530.56470000	49.57360000	0.00000000
70	1546.80230000	56.24240000	0.00000000
71	1631.38610000	1.98360000	0.00000000
72	1644.31380000	7.20110000	0.00000000
73	1788.54550000	121.04500000	0.00000000
74	1829.37700000	251.89710000	0.00000000
75	2237.73260000	0.58600000	0.00000000
76	2330.35260000	0.19960000	0.00000000
77	2653.24630000	53.68460000	0.00000000
78	3079.92280000	0.42920000	0.00000000
79	3081.07540000	1.23260000	0.00000000
80	3087.98470000	1.19990000	0.00000000
81	3167.58970000	0.02260000	0.00000000
82	3168.21980000	0.68340000	0.00000000
83	3175.31830000	5.45970000	0.00000000
84	3183.16920000	0.13330000	0.00000000
85	3186.00530000	3.25200000	0.00000000
86	3188.23320000	0.04660000	0.00000000
87	3192.20520000	0.30620000	0.00000000
88	3204.93430000	1.56370000	0.00000000
89	3211.99670000	2.00570000	0.00000000
90	3236.73370000	1.23930000	0.00000000

S16. CALCULATIONS ON 5A



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C[C]O	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.70085008	a.u.
Gibbs Energy	: -558.48824000	a.u.
Number of imaginary frequencies	: 0	

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

29

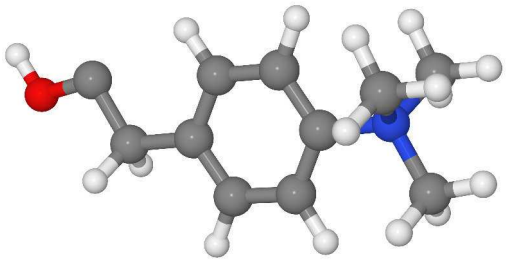
C	-0.34232500	-1.05754602	0.24214400
C	1.03033698	-0.91380203	0.33389300
C	1.62819302	0.34582499	0.24658599
C	0.80949700	1.45136297	0.05567300
C	-0.57327402	1.32369602	-0.03844100
C	-1.14156199	0.06540500	0.05658000
H	-0.76517802	-2.04864812	0.31396601
H	1.65503895	-1.78616500	0.45394301
H	1.24692297	2.43670201	-0.02533700
H	-1.16119599	2.21354699	-0.18714900
N	-2.63112593	-0.13185801	-0.04254800
C	-3.37529707	1.15685904	-0.23923901
H	-4.43315601	0.92192698	-0.29693699
H	-3.18895507	1.81162095	0.60479599
H	-3.05066705	1.62177002	-1.16348600
C	-2.94659996	-1.02537501	-1.21683002
H	-2.47015691	-1.98708904	-1.07238901
H	-4.02423811	-1.14726996	-1.27894497
H	-2.56159210	-0.55396998	-2.11517191
C	-3.14406204	-0.76590502	1.22680700
H	-2.89999390	-0.11041400	2.05642509
H	-4.21962404	-0.89138901	1.14060402
H	-2.66640496	-1.72804701	1.36425996
C	3.87667489	-0.57408202	-0.38979200
O	5.05172014	-0.08449400	-0.68368399
C	3.12071395	0.49635401	0.35415399
H	3.42033505	0.32694599	1.39954698
H	3.44870210	1.50916696	0.10223600
H	5.57568407	-0.76481003	-1.13053203

S16.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	31.69150000	0.80220000	0.00000000
2	48.93070000	1.36620000	0.00000000
3	78.06000000	1.90430000	0.00000000
4	107.34610000	1.57510000	0.00000000
5	147.13610000	4.44740000	0.00000000
6	213.40950000	0.09140000	0.00000000
7	236.72380000	0.55190000	0.00000000
8	266.06610000	1.28350000	0.00000000
9	284.19990000	0.50540000	0.00000000
10	290.62610000	2.66330000	0.00000000
11	351.81600000	0.09410000	0.00000000
12	353.71550000	0.53140000	0.00000000
13	382.54500000	0.09950000	0.00000000
14	413.57520000	0.88790000	0.00000000
15	421.45740000	0.06370000	0.00000000
16	441.32650000	2.93580000	0.00000000
17	456.78860000	0.45180000	0.00000000
18	486.00970000	1.85790000	0.00000000
19	552.36080000	21.53620000	0.00000000
20	580.42270000	9.97220000	0.00000000
21	652.62930000	1.30440000	0.00000000
22	658.14740000	5.00720000	0.00000000
23	719.71510000	10.00940000	0.00000000
24	747.55070000	7.26530000	0.00000000
25	831.15410000	25.90910000	0.00000000
26	837.21240000	8.86050000	0.00000000
27	845.05110000	42.03380000	0.00000000
28	868.71670000	20.91640000	0.00000000
29	905.79640000	36.67140000	0.00000000
30	946.05420000	19.70070000	0.00000000
31	963.76690000	29.36220000	0.00000000
32	970.67960000	78.87510000	0.00000000
33	981.53580000	2.86000000	0.00000000
34	1005.07710000	2.41740000	0.00000000
35	1038.53990000	13.64810000	0.00000000
36	1077.02110000	0.01980000	0.00000000
37	1129.40460000	8.18700000	0.00000000
38	1131.47750000	1.33330000	0.00000000
39	1140.50890000	0.47000000	0.00000000
40	1147.84720000	20.86330000	0.00000000
41	1170.03170000	7.89980000	0.00000000
42	1217.46260000	14.94210000	0.00000000
43	1229.42380000	12.14410000	0.00000000
44	1258.79550000	4.78800000	0.00000000
45	1259.48820000	1.45860000	0.00000000
46	1273.00140000	46.58580000	0.00000000
47	1295.23850000	0.70800000	0.00000000
48	1345.30020000	82.78160000	0.00000000
49	1357.56890000	17.77500000	0.00000000
50	1359.58740000	4.29540000	0.00000000
51	1381.95130000	100.74840000	0.00000000
52	1416.76640000	10.10520000	0.00000000
53	1449.53240000	3.46390000	0.00000000
54	1451.04410000	4.63710000	0.00000000
55	1461.24500000	11.99580000	0.00000000
56	1479.45310000	0.00810000	0.00000000
57	1489.65110000	0.27690000	0.00000000
58	1492.99670000	1.85650000	0.00000000
59	1495.93550000	0.30180000	0.00000000
60	1506.98950000	26.19740000	0.00000000

61	1512.58060000	23.66340000	0.00000000
62	1530.60120000	46.83210000	0.00000000
63	1546.39550000	54.39870000	0.00000000
64	1634.34730000	2.50080000	0.00000000
65	1646.07450000	6.98860000	0.00000000
66	2971.80470000	6.59640000	0.00000000
67	3036.88040000	14.27370000	0.00000000
68	3079.38890000	0.60840000	0.00000000
69	3080.73620000	1.67680000	0.00000000
70	3087.76110000	1.82010000	0.00000000
71	3166.86410000	0.03600000	0.00000000
72	3167.57370000	0.83890000	0.00000000
73	3174.60360000	6.67990000	0.00000000
74	3182.80590000	0.23470000	0.00000000
75	3186.11590000	4.88350000	0.00000000
76	3187.76370000	0.76350000	0.00000000
77	3188.28980000	0.05860000	0.00000000
78	3197.01280000	1.41400000	0.00000000
79	3211.02380000	1.89920000	0.00000000
80	3233.87990000	0.62150000	0.00000000
81	3724.62400000	166.93400000	0.00000000

S17. CALCULATIONS ON 5B



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C[C]O	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.69974973	a.u.
Gibbs Energy	: -558.48689100	a.u.
Number of imaginary frequencies	: 1	

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

29

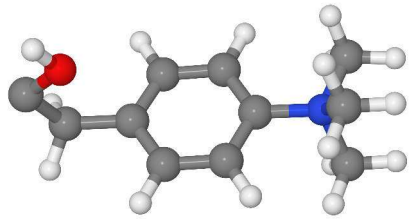
C	-0.35486299	-1.02487504	-0.00050300
C	1.02217805	-0.87038499	-0.00071200
C	1.60148203	0.39833900	-0.00051800
C	0.75761497	1.50548697	-0.00009600
C	-0.62478298	1.36742306	0.00011400
C	-1.17497098	0.09539600	-0.00009700
H	-0.76186597	-2.02535605	-0.00065100
H	1.66711700	-1.73602605	-0.00100100
H	1.17835295	2.50201201	0.00008600
H	-1.22974706	2.25831890	0.00044300
N	-2.66648197	-0.11393300	0.00013900
C	-3.43374705	1.17621005	0.00064200
H	-4.49103308	0.93178701	0.00074400
H	-3.18642998	1.74098396	0.89265001
H	-3.18671894	1.74150503	-0.89111698
C	-3.06981301	-0.88483101	-1.23252201
H	-2.57555199	-1.84840298	-1.22895896
H	-4.14794207	-1.01727295	-1.22039604
H	-2.76327801	-0.31589800	-2.10420799
C	-3.06931496	-0.88550502	1.23254097
H	-2.76245904	-0.31703201	2.10441399
H	-4.14744520	-1.01797402	1.22076404
H	-2.57502198	-1.84905899	1.22826600
C	3.90503907	-0.67552400	-0.00014100
O	5.16404676	-0.32486200	0.00060000
C	3.09809709	0.59212297	-0.00080700
H	3.39919090	1.18992400	-0.87064999
H	5.71447992	-1.12032902	0.00102700
H	3.39944911	1.19155800	0.86780202

S17.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-61.45690000	0.00380000	0.00000000
2	39.69870000	2.44240000	0.00000000
3	51.57720000	0.06080000	0.00000000
4	72.43680000	3.44940000	0.00000000
5	122.42630000	4.21980000	0.00000000
6	201.76240000	0.72480000	0.00000000
7	240.55100000	0.99170000	0.00000000
8	251.10420000	0.96230000	0.00000000
9	273.18350000	1.51430000	0.00000000
10	288.76100000	1.48430000	0.00000000
11	351.12670000	0.05780000	0.00000000
12	353.21350000	0.46510000	0.00000000
13	372.43240000	0.23040000	0.00000000
14	420.34610000	0.08630000	0.00000000
15	429.43330000	2.51190000	0.00000000
16	432.43490000	0.22430000	0.00000000
17	441.82970000	1.93060000	0.00000000
18	487.31570000	2.03950000	0.00000000
19	541.46580000	28.19560000	0.00000000
20	577.04950000	0.94650000	0.00000000
21	616.75100000	0.39890000	0.00000000
22	653.53550000	0.85820000	0.00000000
23	707.05600000	2.38970000	0.00000000
24	748.40630000	8.66620000	0.00000000
25	834.51890000	29.84000000	0.00000000
26	837.78750000	8.07040000	0.00000000
27	851.68640000	43.87610000	0.00000000
28	860.36800000	42.31890000	0.00000000
29	904.41920000	26.66530000	0.00000000
30	946.87750000	16.86560000	0.00000000
31	963.53710000	60.50480000	0.00000000
32	965.97720000	27.13480000	0.00000000
33	986.01020000	0.94490000	0.00000000
34	1027.04990000	0.18620000	0.00000000
35	1038.45010000	14.24180000	0.00000000
36	1077.13600000	0.01900000	0.00000000
37	1130.60950000	1.21440000	0.00000000
38	1131.50050000	0.08250000	0.00000000
39	1140.51200000	0.46520000	0.00000000
40	1162.54140000	4.10780000	0.00000000
41	1187.09820000	7.90290000	0.00000000
42	1204.83920000	25.11510000	0.00000000
43	1224.86340000	22.55560000	0.00000000
44	1258.88540000	3.93870000	0.00000000
45	1259.52420000	1.41470000	0.00000000
46	1274.44220000	88.84830000	0.00000000
47	1295.46150000	0.13500000	0.00000000
48	1342.62920000	73.09750000	0.00000000
49	1354.09530000	11.56810000	0.00000000
50	1357.82620000	7.48050000	0.00000000
51	1384.61680000	41.96930000	0.00000000
52	1398.66940000	39.28940000	0.00000000
53	1449.18930000	3.32040000	0.00000000
54	1451.03740000	4.63150000	0.00000000
55	1459.23040000	8.57650000	0.00000000
56	1479.43860000	0.00820000	0.00000000
57	1489.63100000	0.29280000	0.00000000
58	1492.96190000	1.73660000	0.00000000
59	1495.76180000	0.32480000	0.00000000
60	1507.08610000	26.49250000	0.00000000

61	1512.52440000	23.69890000	0.00000000
62	1530.37230000	46.34310000	0.00000000
63	1545.65310000	59.65850000	0.00000000
64	1631.77320000	2.60690000	0.00000000
65	1646.20170000	9.24250000	0.00000000
66	2986.23100000	4.42020000	0.00000000
67	3015.39770000	0.35100000	0.00000000
68	3079.21790000	0.62600000	0.00000000
69	3080.57560000	1.71450000	0.00000000
70	3087.62970000	1.85660000	0.00000000
71	3166.75930000	0.00040000	0.00000000
72	3167.41310000	0.84710000	0.00000000
73	3174.47360000	6.99640000	0.00000000
74	3181.01230000	2.03510000	0.00000000
75	3182.63500000	0.24300000	0.00000000
76	3185.28510000	2.86320000	0.00000000
77	3188.08490000	0.05760000	0.00000000
78	3196.29050000	1.36050000	0.00000000
79	3210.05030000	11.79010000	0.00000000
80	3232.71190000	0.83900000	0.00000000
81	3733.53870000	168.70400000	0.00000000

S18. CALCULATIONS ON 5C



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C[C]O	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.69836538	a.u.
Gibbs Energy	: -558.48407300	a.u.
Number of imaginary frequencies	: 1	

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

29

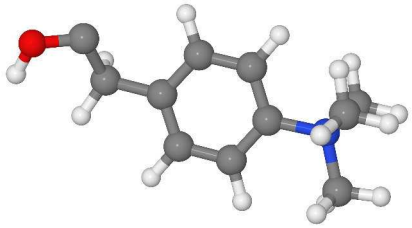
C	-0.44019499	-1.24246001	0.18130299
C	0.94301999	-1.24072599	0.13353400
C	1.66107798	-0.05797100	-0.05215600
C	0.94193000	1.12430704	-0.19883500
C	-0.44692600	1.14247203	-0.15384001
C	-1.13267696	-0.04595000	0.03723800
H	-0.95333803	-2.18045902	0.33303899
H	1.47168303	-2.17692900	0.24671400
H	1.46790195	2.05702710	-0.34792799
H	-0.95115000	2.08725595	-0.26744601
N	-2.63634992	-0.08251900	0.10001800
C	-3.25724411	1.27344704	-0.07354200
H	-4.33424282	1.15299904	-0.01727700
H	-2.91828799	1.92834401	0.72142100
H	-2.98165989	1.67341304	-1.04303706
C	-3.16844893	-0.97144598	-0.99694902
H	-2.78452492	-1.97500300	-0.86194301
H	-4.25332880	-0.97621101	-0.94266099
H	-2.83392191	-0.57287300	-1.94914901
C	-3.07536411	-0.61719501	1.44102705
H	-2.67475796	0.03165700	2.21302795
H	-4.16117477	-0.62508899	1.47180498
H	-2.69159698	-1.62187195	1.56817102
C	3.78271890	-0.30041701	-1.52898300
O	2.83456993	-0.46755999	-2.42108011
C	3.15615511	-0.07369100	-0.16685100
H	3.60437608	-0.84344202	0.46918499
H	3.60032892	0.86129498	0.18740299
H	3.25512290	-0.61115003	-3.28061795

S18.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-3.21740000	1.29380000	0.00000000
2	48.75200000	0.53480000	0.00000000
3	58.27500000	0.66600000	0.00000000
4	121.21730000	5.27470000	0.00000000
5	131.55740000	0.58580000	0.00000000
6	218.76760000	0.22860000	0.00000000
7	221.62920000	1.08290000	0.00000000
8	267.03660000	0.46290000	0.00000000
9	279.35150000	0.13510000	0.00000000
10	307.18850000	1.57620000	0.00000000
11	344.62060000	1.99010000	0.00000000
12	351.90210000	0.07800000	0.00000000
13	375.02130000	0.35270000	0.00000000
14	389.25810000	1.26260000	0.00000000
15	420.28540000	0.04810000	0.00000000
16	444.18860000	3.04040000	0.00000000
17	479.49280000	1.34990000	0.00000000
18	507.25480000	1.37740000	0.00000000
19	555.38290000	23.21790000	0.00000000
20	621.97680000	14.93430000	0.00000000
21	650.61320000	1.36520000	0.00000000
22	690.04820000	22.54760000	0.00000000
23	701.47170000	19.17190000	0.00000000
24	765.83200000	6.70190000	0.00000000
25	813.56620000	4.71720000	0.00000000
26	834.69370000	0.08810000	0.00000000
27	846.85900000	33.46620000	0.00000000
28	883.21410000	12.51030000	0.00000000
29	902.40870000	31.15130000	0.00000000
30	915.37910000	45.16500000	0.00000000
31	945.50940000	18.11930000	0.00000000
32	963.83570000	18.99450000	0.00000000
33	982.58480000	1.86260000	0.00000000
34	994.55890000	0.28200000	0.00000000
35	1038.36190000	7.48800000	0.00000000
36	1076.72600000	0.01720000	0.00000000
37	1129.74910000	1.28060000	0.00000000
38	1131.53630000	3.07080000	0.00000000
39	1140.01890000	0.45900000	0.00000000
40	1156.90450000	0.56510000	0.00000000
41	1185.54740000	7.84040000	0.00000000
42	1223.82120000	30.03960000	0.00000000
43	1234.40410000	0.1.000000	0.00000000
44	1244.79630000	144.40810000	0.00000000
45	1259.11440000	1.45900000	0.00000000
46	1259.36700000	1.69450000	0.00000000
47	1294.86120000	2.01600000	0.00000000
48	1330.06370000	45.29420000	0.00000000
49	1352.09530000	17.48200000	0.00000000
50	1352.51530000	30.01590000	0.00000000
51	1362.95050000	0.01940000	0.00000000
52	1439.47170000	9.56310000	0.00000000
53	1449.11640000	2.28510000	0.00000000
54	1450.86970000	4.63850000	0.00000000
55	1458.42570000	9.21560000	0.00000000
56	1479.24260000	0.00710000	0.00000000
57	1489.48340000	0.29340000	0.00000000
58	1493.07510000	2.15270000	0.00000000
59	1495.85860000	0.21890000	0.00000000
60	1506.87240000	27.04960000	0.00000000

61	1512.58080000	23.79990000	0.00000000
62	1530.44690000	46.73000000	0.00000000
63	1546.63460000	44.20130000	0.00000000
64	1631.48830000	1.82280000	0.00000000
65	1644.29980000	11.09500000	0.00000000
66	3031.41860000	10.08880000	0.00000000
67	3057.22740000	0.04980000	0.00000000
68	3079.54100000	0.58120000	0.00000000
69	3080.83370000	1.63230000	0.00000000
70	3087.83280000	1.74880000	0.00000000
71	3167.04020000	0.01100000	0.00000000
72	3167.64710000	0.82030000	0.00000000
73	3174.69520000	6.76700000	0.00000000
74	3182.20640000	5.05040000	0.00000000
75	3182.88380000	0.21930000	0.00000000
76	3186.60740000	1.17250000	0.00000000
77	3188.46910000	0.04410000	0.00000000
78	3190.84360000	0.32860000	0.00000000
79	3201.46760000	2.18270000	0.00000000
80	3232.67150000	0.75200000	0.00000000
81	3729.44930000	165.25450000	0.00000000

S19. CALCULATIONS ON 5D



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C[C]O	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.69330531	a.u.
Gibbs Energy	: -558.48151800	a.u.
Number of imaginary frequencies	: 0	

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

29

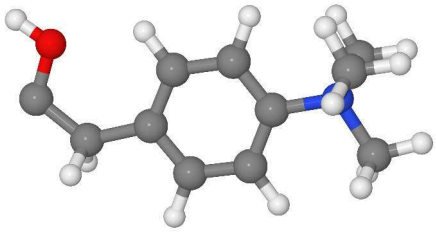
C	0.68153602	0.20341200	-4.16073322
C	1.72259104	-0.25410801	-3.37370610
C	2.81861496	0.56431597	-3.08951306
C	2.83570695	1.85122001	-3.60990500
C	1.79539096	2.32533789	-4.40419817
C	0.72178501	1.49510098	-4.67467308
H	-0.14913800	-0.45861199	-4.35496807
H	1.68220198	-1.24745500	-2.95279789
H	3.66736197	2.50859308	-3.39770389
H	1.85693300	3.33183908	-4.78191423
N	-0.43480700	1.95849800	-5.51968813
C	-0.26536199	3.36573100	-6.01426411
H	-1.13645601	3.61262107	-6.61239719
H	-0.19857000	4.03895378	-5.16685104
H	0.62926799	3.42696500	-6.62401676
C	-0.57170302	1.06370103	-6.72708702
H	-0.75537598	0.04762900	-6.40057182
H	-1.40397501	1.41920400	-7.32778788
H	0.35454801	1.10934198	-7.29056787
C	-1.70600796	1.90922594	-4.70749283
H	-1.58099306	2.55121398	-3.84162903
H	-2.52634907	2.25763202	-5.32846308
H	-1.88690603	0.89047003	-4.38775587
C	3.44204903	-0.68988901	-1.00902402
O	4.24142885	-0.58659399	0.00253900
C	3.93895006	0.05634500	-2.22285795
H	4.65750790	0.85692400	-1.98840499
H	4.49574900	-0.71468401	-2.77520490
H	5.03471613	-0.01803600	-0.13718501

S19.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	32.35560000	0.61500000	0.00000000
2	48.16660000	3.94300000	0.00000000
3	77.22480000	6.76850000	0.00000000
4	103.09800000	10.49320000	0.00000000
5	151.73730000	26.73630000	0.00000000
6	213.80870000	0.62830000	0.00000000
7	236.78410000	3.62120000	0.00000000
8	266.72630000	4.00340000	0.00000000
9	285.11340000	4.49190000	0.00000000
10	293.68790000	0.88420000	0.00000000
11	351.63140000	0.14580000	0.00000000
12	354.85220000	2.47620000	0.00000000
13	384.17990000	0.31490000	0.00000000
14	413.15680000	3.90090000	0.00000000
15	421.01660000	0.20660000	0.00000000
16	445.61580000	5.03740000	0.00000000
17	457.46380000	3.16510000	0.00000000
18	485.95680000	3.18720000	0.00000000
19	554.06390000	7.02780000	0.00000000
20	579.84370000	21.19750000	0.00000000
21	653.04500000	0.22870000	0.00000000
22	667.24990000	41.01740000	0.00000000
23	726.80660000	14.64410000	0.00000000
24	746.24550000	4.30070000	0.00000000
25	830.41760000	6.63680000	0.00000000
26	837.73930000	14.47980000	0.00000000
27	844.31080000	17.36270000	0.00000000
28	868.11320000	3.35780000	0.00000000
29	908.86160000	38.81880000	0.00000000
30	945.59220000	31.03050000	0.00000000
31	963.20890000	20.84020000	0.00000000
32	970.60950000	14.29010000	0.00000000
33	980.07590000	1.22870000	0.00000000
34	1004.63810000	0.61750000	0.00000000
35	1038.45320000	14.11070000	0.00000000
36	1077.02110000	0.02080000	0.00000000
37	1129.89340000	4.94150000	0.00000000
38	1132.14120000	0.26770000	0.00000000
39	1140.48690000	0.50040000	0.00000000
40	1152.05980000	6.60420000	0.00000000
41	1171.30730000	5.68980000	0.00000000
42	1220.95700000	23.11190000	0.00000000
43	1233.23560000	9.94790000	0.00000000
44	1258.68720000	2.53630000	0.00000000
45	1259.20180000	1.50150000	0.00000000
46	1277.57530000	29.16130000	0.00000000
47	1295.21590000	6.20870000	0.00000000
48	1340.81900000	198.13660000	0.00000000
49	1357.56480000	41.52700000	0.00000000
50	1366.57790000	52.04220000	0.00000000
51	1391.69500000	25.91050000	0.00000000
52	1418.31530000	7.55420000	0.00000000
53	1449.59300000	3.27170000	0.00000000
54	1451.22460000	4.67550000	0.00000000
55	1460.57360000	9.13630000	0.00000000
56	1479.50770000	0.00980000	0.00000000
57	1489.48890000	0.29090000	0.00000000
58	1493.06550000	1.85970000	0.00000000
59	1495.76640000	0.28980000	0.00000000
60	1507.05680000	26.64110000	0.00000000

61	1512.75970000	23.77250000	0.00000000
62	1530.54850000	46.98170000	0.00000000
63	1546.28780000	54.58280000	0.00000000
64	1634.62730000	2.08490000	0.00000000
65	1646.59760000	4.44120000	0.00000000
66	2937.64450000	44.26210000	0.00000000
67	2994.83220000	10.88920000	0.00000000
68	3079.59480000	0.52990000	0.00000000
69	3080.84930000	1.52850000	0.00000000
70	3087.80210000	1.55320000	0.00000000
71	3167.18280000	0.03770000	0.00000000
72	3167.84560000	0.72940000	0.00000000
73	3174.85380000	6.35680000	0.00000000
74	3182.65230000	0.22960000	0.00000000
75	3186.62060000	4.50160000	0.00000000
76	3187.43750000	0.80290000	0.00000000
77	3188.30000000	0.07560000	0.00000000
78	3198.09650000	1.54190000	0.00000000
79	3212.76150000	2.31540000	0.00000000
80	3234.30360000	0.48220000	0.00000000
81	3375.78360000	60.94940000	0.00000000

S20. CALCULATIONS ON 5E



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C[C]O	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.69189178	a.u.
Gibbs Energy	: -558.47705300	a.u.
Number of imaginary frequencies	: 2	

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

29

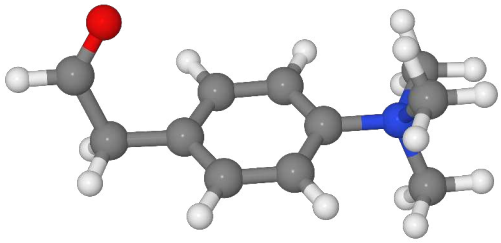
C	0.19726200	-0.96455002	0.00063000
C	-1.17181695	-0.73728400	0.00076800
C	-1.68656301	0.56083697	0.00054500
C	-0.77142298	1.61494994	0.00019200
C	0.60014403	1.40474296	0.00005400
C	1.08010197	0.10462900	0.00027900
H	0.54613602	-1.98661494	0.00079400
H	-1.83649194	-1.58230698	0.00103100
H	-1.13470900	2.63389802	0.00002500
H	1.25156605	2.26236510	-0.00023100
N	2.55706501	-0.18737601	0.00009800
C	3.39428997	1.05899405	-0.00054400
H	4.43644094	0.75653899	-0.00053100
H	3.17859793	1.63633204	-0.89272398
H	3.17881393	1.63710999	0.89118201
C	2.91742492	-0.97905397	1.23301804
H	2.37141395	-1.91430902	1.22944701
H	3.98667598	-1.17018902	1.22085094
H	2.64265490	-0.39407301	2.10468698
C	2.91689801	-0.97998101	-1.23238206
H	2.64179897	-0.39563599	-2.10437107
H	3.98614192	-1.17116594	-1.22050500
H	2.37085009	-1.91521597	-1.22788703
C	-4.35037184	0.01886000	-0.00050400
O	-3.99831009	-1.24737000	-0.00295000
C	-3.16001010	0.92916602	0.00090100
H	-3.35961199	1.59344101	0.85198897
H	-4.80522203	-1.78112805	-0.00374300
H	-3.35951304	1.59546697	-0.84863698

S20.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-82.49470000	3.62540000	0.00000000
2	-11.48880000	8.71250000	0.00000000
3	48.49580000	0.40670000	0.00000000
4	75.26120000	1.36300000	0.00000000
5	144.48460000	0.91440000	0.00000000
6	202.29620000	0.37250000	0.00000000
7	235.34860000	0.04640000	0.00000000
8	241.43810000	0.63240000	0.00000000
9	281.46780000	0.07570000	0.00000000
10	288.92760000	0.29360000	0.00000000
11	347.72810000	2.98350000	0.00000000
12	350.52580000	0.06280000	0.00000000
13	368.20010000	0.38580000	0.00000000
14	373.50220000	0.01710000	0.00000000
15	415.46860000	0.00750000	0.00000000
16	431.00440000	1.68250000	0.00000000
17	478.88280000	2.70780000	0.00000000
18	502.81100000	0.98040000	0.00000000
19	547.93600000	28.12600000	0.00000000
20	620.95220000	3.85430000	0.00000000
21	646.41780000	0.14940000	0.00000000
22	651.34420000	0.39540000	0.00000000
23	743.43090000	10.86500000	0.00000000
24	752.22030000	11.05450000	0.00000000
25	809.87800000	1.78280000	0.00000000
26	834.99320000	22.18550000	0.00000000
27	847.00250000	56.53420000	0.00000000
28	848.67670000	38.36960000	0.00000000
29	915.29290000	21.03760000	0.00000000
30	945.57890000	17.94690000	0.00000000
31	947.46010000	16.47460000	0.00000000
32	964.37150000	15.88230000	0.00000000
33	989.38250000	0.52700000	0.00000000
34	1012.07580000	0.09930000	0.00000000
35	1038.77160000	13.11360000	0.00000000
36	1077.05710000	0.01860000	0.00000000
37	1132.84110000	0.43990000	0.00000000
38	1134.39080000	2.57260000	0.00000000
39	1140.46260000	0.49150000	0.00000000
40	1171.04330000	1.00350000	0.00000000
41	1196.83570000	10.90870000	0.00000000
42	1231.81370000	4.00070000	0.00000000
43	1236.42550000	0.20770000	0.00000000
44	1259.07900000	10.45870000	0.00000000
45	1259.30860000	1.48360000	0.00000000
46	1270.73240000	129.09130000	0.00000000
47	1295.24580000	1.82830000	0.00000000
48	1317.08420000	77.30500000	0.00000000
49	1348.46590000	12.23800000	0.00000000
50	1357.82340000	3.49730000	0.00000000
51	1380.43480000	3.59240000	0.00000000
52	1408.27000000	5.58500000	0.00000000
53	1449.68230000	3.40130000	0.00000000
54	1451.17390000	4.63060000	0.00000000
55	1461.25010000	9.63800000	0.00000000
56	1479.48450000	0.00300000	0.00000000
57	1489.63290000	0.29580000	0.00000000
58	1493.13360000	1.68450000	0.00000000
59	1495.78330000	0.33660000	0.00000000
60	1507.03070000	26.79200000	0.00000000

61	1512.51390000	23.87650000	0.00000000
62	1530.31490000	46.98420000	0.00000000
63	1546.52230000	54.84390000	0.00000000
64	1628.86270000	3.82580000	0.00000000
65	1641.75200000	3.08220000	0.00000000
66	3002.98710000	3.33000000	0.00000000
67	3011.80710000	0.42060000	0.00000000
68	3079.59540000	0.55870000	0.00000000
69	3080.81860000	1.55940000	0.00000000
70	3087.76800000	1.62200000	0.00000000
71	3167.07510000	0.00120000	0.00000000
72	3167.71850000	0.76140000	0.00000000
73	3174.75920000	6.48940000	0.00000000
74	3180.06420000	1.27980000	0.00000000
75	3182.71410000	0.21410000	0.00000000
76	3186.91400000	3.55460000	0.00000000
77	3188.48230000	0.04280000	0.00000000
78	3198.03690000	1.77150000	0.00000000
79	3232.21060000	0.79690000	0.00000000
80	3260.16410000	7.50960000	0.00000000
81	3728.57050000	162.42550000	0.00000000

S21. CALCULATIONS ON 6



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)CC=O	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.78006058	a.u.
Gibbs Energy	: -558.56742500	a.u.
Number of imaginary frequencies	: 0	

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

29

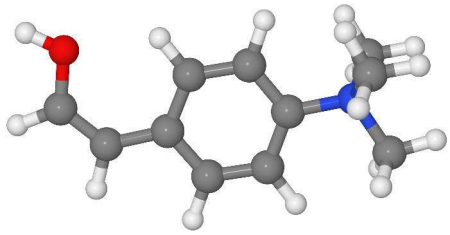
C	0.48585999	-1.18056500	-0.52929300
C	-0.88489598	-1.18180895	-0.73516297
C	-1.64521503	-0.03247700	-0.53429401
C	-0.99288797	1.12483597	-0.11920500
C	0.37902799	1.14391303	0.09271100
C	1.11209297	-0.01444100	-0.11101900
H	1.03637898	-2.09447193	-0.69437498
H	-1.36515296	-2.09717894	-1.05150402
H	-1.55780494	2.02789593	0.05757600
H	0.83330101	2.06364703	0.41975901
N	2.59852600	-0.05079000	0.12562101
C	3.14798093	1.27410495	0.57081300
H	4.21704292	1.15586102	0.71449500
H	2.95948696	2.01731491	-0.19598299
H	2.68064404	1.56116295	1.50620198
C	2.91233301	-1.05995798	1.20338297
H	2.58425689	-2.04054809	0.88128799
H	3.98522711	-1.06158805	1.37315094
H	2.38158202	-0.77036101	2.10449910
C	3.30851412	-0.43408099	-1.14915705
H	3.06226206	0.30000600	-1.90944695
H	4.37789917	-0.44492900	-0.95901000
H	2.97651100	-1.41600204	-1.46279395
C	-3.89288497	0.17843100	0.60161901
O	-3.38020802	0.50883001	1.63519394
C	-3.13416791	-0.05089900	-0.69948399
H	-3.46823311	0.73128903	-1.39028597
H	-3.48048091	-0.99151599	-1.13222206
H	-4.98524809	0.02824400	0.52161199

S21.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	17.99580000	1.80330000	0.00000000
2	52.46870000	0.41840000	0.00000000
3	61.68220000	6.72130000	0.00000000
4	131.52890000	7.50680000	0.00000000
5	138.46950000	4.96190000	0.00000000
6	219.81960000	1.02900000	0.00000000
7	220.60640000	0.56270000	0.00000000
8	267.46990000	1.55150000	0.00000000
9	278.69080000	0.41110000	0.00000000
10	311.31950000	1.33860000	0.00000000
11	345.71520000	0.97490000	0.00000000
12	353.54220000	0.07150000	0.00000000
13	376.96490000	0.45550000	0.00000000
14	388.68280000	1.55610000	0.00000000
15	420.58500000	0.02580000	0.00000000
16	443.62090000	0.69930000	0.00000000
17	480.39500000	1.56530000	0.00000000
18	514.01050000	3.44550000	0.00000000
19	557.01230000	20.72470000	0.00000000
20	634.75240000	12.57570000	0.00000000
21	652.89000000	0.84280000	0.00000000
22	694.37080000	7.35280000	0.00000000
23	744.57030000	2.39560000	0.00000000
24	773.68150000	7.28410000	0.00000000
25	814.78920000	4.35590000	0.00000000
26	832.63980000	0.19840000	0.00000000
27	847.85000000	41.19270000	0.00000000
28	869.12460000	20.53000000	0.00000000
29	930.01840000	28.17110000	0.00000000
30	946.07500000	15.21180000	0.00000000
31	963.24870000	15.84170000	0.00000000
32	979.80370000	3.04240000	0.00000000
33	992.45970000	0.09550000	0.00000000
34	1038.18390000	5.01030000	0.00000000
35	1042.70540000	5.36160000	0.00000000
36	1077.12040000	0.02040000	0.00000000
37	1132.51000000	4.10960000	0.00000000
38	1134.05840000	0.16190000	0.00000000
39	1140.64410000	0.47890000	0.00000000
40	1169.41710000	3.69060000	0.00000000
41	1214.85460000	1.02510000	0.00000000
42	1230.10560000	6.49340000	0.00000000
43	1237.28530000	1.00000000	0.00000000
44	1259.1.000000	1.39760000	0.00000000
45	1259.40600000	1.52700000	0.00000000
46	1295.29960000	1.09880000	0.00000000
47	1318.72750000	51.15700000	0.00000000
48	1353.07420000	5.46490000	0.00000000
49	1366.30800000	3.51960000	0.00000000
50	1412.70530000	19.1.000000	0.00000000
51	1448.93430000	3.96220000	0.00000000
52	1451.60880000	3.42430000	0.00000000
53	1453.03620000	8.23340000	0.00000000
54	1466.17590000	15.76490000	0.00000000
55	1479.57780000	0.00400000	0.00000000
56	1489.49750000	0.29090000	0.00000000
57	1493.37000000	2.26450000	0.00000000
58	1495.99840000	0.40970000	0.00000000
59	1507.34090000	26.70460000	0.00000000
60	1512.93500000	23.85780000	0.00000000

61	1530.70170000	47.98450000	0.00000000
62	1550.64410000	44.15580000	0.00000000
63	1635.81780000	3.45780000	0.00000000
64	1649.22060000	3.51760000	0.00000000
65	1814.83490000	118.74470000	0.00000000
66	2923.98590000	109.83330000	0.00000000
67	3020.36040000	10.42500000	0.00000000
68	3070.88820000	5.1.000000	0.00000000
69	3079.53300000	0.48860000	0.00000000
70	3080.91040000	1.48600000	0.00000000
71	3087.89850000	1.47050000	0.00000000
72	3167.17270000	0.02060000	0.00000000
73	3167.92710000	0.80760000	0.00000000
74	3175.08220000	5.76160000	0.00000000
75	3183.01790000	0.16600000	0.00000000
76	3184.06520000	4.82300000	0.00000000
77	3188.11280000	0.02970000	0.00000000
78	3191.01780000	0.08570000	0.00000000
79	3202.61670000	2.13640000	0.00000000
80	3204.10640000	0.64930000	0.00000000
81	3236.23320000	0.39310000	0.00000000

S22. CALCULATIONS ON 7A



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=CO	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.77967827	a.u.
Gibbs Energy	: -558.56426900	a.u.
Number of imaginary frequencies	: 0	

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

29

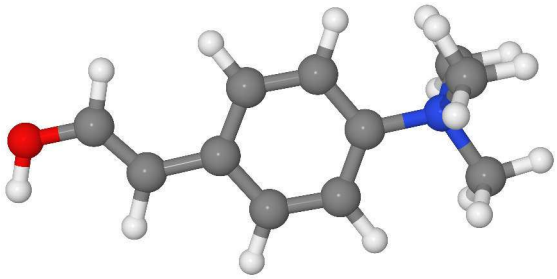
C	1.62153995	-2.15460491	-4.03779411
C	2.41061211	-1.52573895	-3.09357309
C	1.98899102	-0.33734599	-2.46895409
C	0.74001402	0.17483599	-2.84650803
C	-0.05777700	-0.44919300	-3.79235792
C	0.38742200	-1.61878002	-4.38900518
H	1.99023199	-3.06455112	-4.48826313
H	3.36265206	-1.95749700	-2.83610702
H	0.38197100	1.08609200	-2.38845205
H	-1.00676203	-0.00176000	-4.03592682
N	-0.43570900	-2.33907700	-5.42185688
C	-1.73973203	-1.65193999	-5.70399523
H	-2.26522899	-2.23429108	-6.45393705
H	-2.32675791	-1.60828495	-4.79335499
H	-1.54530501	-0.65420997	-6.08150816
C	0.33020699	-2.41481090	-6.71938276
H	1.25287604	-2.95829797	-6.55768824
H	-0.28269601	-2.92833710	-7.45490313
H	0.55028498	-1.40263796	-7.04255915
C	-0.74963802	-3.73354506	-4.93984079
H	-1.29477704	-3.65434694	-4.00498915
H	-1.35049796	-4.23448277	-5.69373989
H	0.17595001	-4.27305317	-4.78149223
C	3.96483493	0.07757900	-0.96371502
O	4.68828678	-1.00540197	-1.32589400
C	2.76125097	0.37819800	-1.47102106
H	2.31174207	1.27872300	-1.07707596
H	5.51898289	-1.03083003	-0.84154397
H	4.41274118	0.72043502	-0.21622300

S22.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	35.76270000	1.00530000	0.00000000
2	55.31220000	2.18610000	0.00000000
3	92.88000000	1.83830000	0.00000000
4	139.18360000	3.49300000	0.00000000
5	194.89110000	6.47480000	0.00000000
6	233.92930000	0.84360000	0.00000000
7	236.47860000	4.91870000	0.00000000
8	282.45740000	0.16530000	0.00000000
9	295.35860000	1.49620000	0.00000000
10	338.97640000	45.86860000	0.00000000
11	350.97260000	1.06920000	0.00000000
12	355.72300000	0.95800000	0.00000000
13	373.21720000	0.95450000	0.00000000
14	394.44100000	47.26360000	0.00000000
15	424.15080000	1.47270000	0.00000000
16	429.25720000	11.13110000	0.00000000
17	479.94150000	3.05020000	0.00000000
18	512.93400000	1.18500000	0.00000000
19	513.62750000	2.89370000	0.00000000
20	589.39830000	30.36590000	0.00000000
21	639.00030000	2.22960000	0.00000000
22	652.65200000	0.03020000	0.00000000
23	744.70080000	1.53570000	0.00000000
24	761.37620000	4.94510000	0.00000000
25	784.95470000	11.44530000	0.00000000
26	832.13860000	1.68290000	0.00000000
27	838.07790000	29.66350000	0.00000000
28	856.22760000	17.25290000	0.00000000
29	865.87730000	49.23280000	0.00000000
30	944.74200000	25.68820000	0.00000000
31	961.79410000	0.00020000	0.00000000
32	965.49210000	17.82110000	0.00000000
33	979.32430000	0.17480000	0.00000000
34	998.91040000	0.00000000	0.00000000
35	1032.96890000	3.06820000	0.00000000
36	1076.87250000	0.01810000	0.00000000
37	1081.59640000	89.12240000	0.00000000
38	1133.05250000	1.42700000	0.00000000
39	1134.36890000	3.24540000	0.00000000
40	1139.93860000	0.51880000	0.00000000
41	1174.52830000	1.71480000	0.00000000
42	1228.08600000	25.28150000	0.00000000
43	1247.98920000	30.02940000	0.00000000
44	1259.47750000	1.78590000	0.00000000
45	1259.53660000	4.48210000	0.00000000
46	1267.87200000	42.09450000	0.00000000
47	1295.06010000	4.38370000	0.00000000
48	1314.74970000	195.34850000	0.00000000
49	1355.98110000	8.47400000	0.00000000
50	1364.70820000	3.97990000	0.00000000
51	1447.33200000	0.71390000	0.00000000
52	1450.39070000	4.53480000	0.00000000
53	1453.18260000	7.81420000	0.00000000
54	1476.73010000	14.08300000	0.00000000
55	1479.04020000	0.00470000	0.00000000
56	1489.74150000	0.29860000	0.00000000
57	1492.74020000	1.29980000	0.00000000
58	1496.11050000	0.53530000	0.00000000
59	1506.44240000	26.86190000	0.00000000
60	1512.13570000	23.47770000	0.00000000

61	1530.34630000	43.44020000	0.00000000
62	1547.12820000	55.74720000	0.00000000
63	1615.73610000	5.16440000	0.00000000
64	1640.71390000	80.65810000	0.00000000
65	1717.88730000	252.88990000	0.00000000
66	3078.48220000	0.77640000	0.00000000
67	3080.14490000	2.42070000	0.00000000
68	3087.33850000	2.75500000	0.00000000
69	3165.90100000	0.00190000	0.00000000
70	3166.80970000	1.53770000	0.00000000
71	3167.31900000	1.85590000	0.00000000
72	3173.91340000	8.85740000	0.00000000
73	3182.48600000	0.27680000	0.00000000
74	3184.83050000	5.87530000	0.00000000
75	3187.32270000	0.22170000	0.00000000
76	3188.27710000	0.06150000	0.00000000
77	3192.46920000	8.20260000	0.00000000
78	3196.17650000	1.50460000	0.00000000
79	3231.21140000	1.05220000	0.00000000
80	3244.79490000	3.39230000	0.00000000
81	3830.59530000	225.31380000	0.00000000

S23. CALCULATIONS ON 7B



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=CO	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.77653344	a.u.
Gibbs Energy	: -558.56237300	a.u.
Number of imaginary frequencies	: 0	

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

29

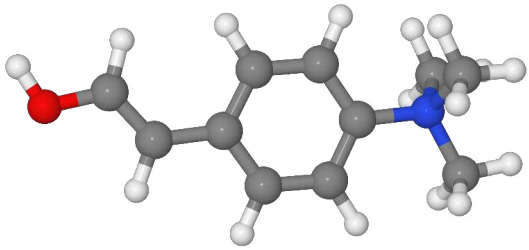
C	0.65882701	0.32373700	-3.99910212
C	1.66138303	-0.02985100	-3.12033010
C	2.70704198	0.85614800	-2.80227494
C	2.68076110	2.11285090	-3.42074394
C	1.67807806	2.47950602	-4.30596209
C	0.66356099	1.58198202	-4.59618616
H	-0.11889700	-0.39654601	-4.20631218
H	1.62423897	-1.01363504	-2.67770791
H	3.46482801	2.82492590	-3.20511293
H	1.72098005	3.46235609	-4.74461079
N	-0.44823599	1.92574406	-5.54761696
C	-0.31554499	3.30910707	-6.11450005
H	-1.15244102	3.47348189	-6.78545713
H	-0.34335199	4.03205490	-5.30681086
H	0.61680597	3.38413596	-6.66305685
C	-0.44695199	0.95671600	-6.70414400
H	-0.59928697	-0.04752800	-6.32835197
H	-1.24975300	1.22674704	-7.38447523
H	0.51548898	1.02281904	-7.20079899
C	-1.77363896	1.85164201	-4.83049107
H	-1.75047803	2.55186796	-4.00193977
H	-2.56254005	2.11116505	-5.53088808
H	-1.92214203	0.84548098	-4.45832586
C	3.93215704	-0.61916500	-1.22587800
O	4.91906786	-0.93173403	-0.37677401
C	3.78611207	0.53936899	-1.88630903
H	4.52719879	1.31663299	-1.73488200
H	5.54434490	-0.20110400	-0.28631300
H	3.23967195	-1.44439900	-1.31920803

S23.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	24.64540000	0.06440000	0.00000000
2	50.31950000	0.72270000	0.00000000
3	88.72770000	7.19310000	0.00000000
4	119.57860000	2.27650000	0.00000000
5	164.88510000	2.89690000	0.00000000
6	224.11250000	0.41660000	0.00000000
7	248.04800000	1.42960000	0.00000000
8	273.05770000	0.30670000	0.00000000
9	283.61180000	0.29210000	0.00000000
10	289.79880000	2.16270000	0.00000000
11	350.57710000	0.27880000	0.00000000
12	350.70670000	1.67970000	0.00000000
13	396.81750000	1.77660000	0.00000000
14	418.79840000	0.17200000	0.00000000
15	426.48100000	5.90840000	0.00000000
16	446.60050000	0.53540000	0.00000000
17	466.72280000	2.25460000	0.00000000
18	488.18600000	2.92980000	0.00000000
19	526.51530000	57.21510000	0.00000000
20	563.64560000	53.93710000	0.00000000
21	582.63550000	1.27900000	0.00000000
22	654.78920000	0.06560000	0.00000000
23	715.98700000	2.08830000	0.00000000
24	739.97700000	0.00040000	0.00000000
25	821.61510000	0.02190000	0.00000000
26	833.42330000	1.48760000	0.00000000
27	843.21020000	36.98130000	0.00000000
28	875.64390000	46.05600000	0.00000000
29	883.41240000	3.26650000	0.00000000
30	942.64930000	21.84470000	0.00000000
31	964.61180000	16.97280000	0.00000000
32	973.23470000	7.23030000	0.00000000
33	982.48010000	13.35150000	0.00000000
34	989.77740000	25.97500000	0.00000000
35	1029.62560000	1.75430000	0.00000000
36	1076.80730000	0.02120000	0.00000000
37	1130.24370000	61.23290000	0.00000000
38	1132.63090000	4.81590000	0.00000000
39	1139.78600000	0.47860000	0.00000000
40	1153.34880000	335.30890000	0.00000000
41	1173.19930000	19.30840000	0.00000000
42	1224.80830000	45.31430000	0.00000000
43	1241.45460000	2.75520000	0.00000000
44	1259.19550000	1.21650000	0.00000000
45	1259.37880000	2.35550000	0.00000000
46	1293.52440000	10.11410000	0.00000000
47	1308.97110000	6.69820000	0.00000000
48	1349.16960000	33.48500000	0.00000000
49	1353.80760000	50.08280000	0.00000000
50	1364.64370000	43.73630000	0.00000000
51	1419.55470000	1.87970000	0.00000000
52	1448.73600000	3.33570000	0.00000000
53	1450.25840000	4.56200000	0.00000000
54	1462.07710000	21.13200000	0.00000000
55	1479.14720000	0.01590000	0.00000000
56	1489.25970000	0.31890000	0.00000000
57	1492.74160000	1.74280000	0.00000000
58	1495.85980000	0.61910000	0.00000000
59	1506.81730000	26.72670000	0.00000000
60	1512.29650000	23.59790000	0.00000000

61	1530.27890000	42.00350000	0.00000000
62	1548.61490000	45.96580000	0.00000000
63	1615.96980000	5.81200000	0.00000000
64	1640.81790000	198.62060000	0.00000000
65	1696.28240000	487.38390000	0.00000000
66	3078.39540000	0.71550000	0.00000000
67	3080.19870000	2.42100000	0.00000000
68	3087.44640000	2.32600000	0.00000000
69	3143.72290000	15.21430000	0.00000000
70	3166.10640000	0.00340000	0.00000000
71	3167.13800000	1.76400000	0.00000000
72	3174.31870000	8.88440000	0.00000000
73	3182.50380000	0.24460000	0.00000000
74	3183.71860000	8.64390000	0.00000000
75	3187.25590000	0.07700000	0.00000000
76	3188.23940000	2.58310000	0.00000000
77	3191.92240000	3.50480000	0.00000000
78	3196.36430000	0.01850000	0.00000000
79	3209.36750000	2.79120000	0.00000000
80	3230.26320000	1.07210000	0.00000000
81	3769.84690000	127.01540000	0.00000000

S24. CALCULATIONS ON 7C



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=CO	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.77557862	a.u.
Gibbs Energy	: -558.56177800	a.u.
Number of imaginary frequencies	: 0	

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

29

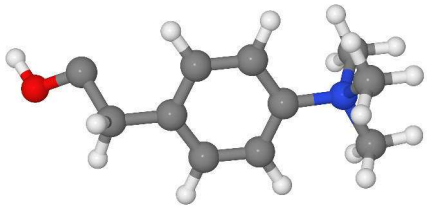
C	-0.39747599	-0.97728902	-0.10622800
C	0.97254002	-0.82273501	-0.15226600
C	1.74248004	-0.72558701	1.02145100
C	1.05022395	-0.79339898	2.23812199
C	-0.32628700	-0.94857901	2.29720306
C	-1.05285895	-1.04086494	1.12111294
H	-0.93803000	-1.04643500	-1.03882301
H	1.44555497	-0.77753401	-1.12172699
H	1.60352194	-0.72286397	3.16380596
H	-0.79205698	-0.99291998	3.26744199
N	-2.54661703	-1.20982397	1.12631500
C	-3.11629701	-1.26256895	2.51393199
H	-4.19098282	-1.38482106	2.42600107
H	-2.69133902	-2.10747194	3.04432797
H	-2.89169407	-0.33542800	3.02942705
C	-3.19328809	-0.04914400	0.41170099
H	-2.84229112	-0.02054200	-0.61245698
H	-4.27105379	-0.18425600	0.43370301
H	-2.91053391	0.86448401	0.92422098
C	-2.91625690	-2.49738908	0.43235499
H	-2.43755507	-3.31608200	0.95954299
H	-3.99701190	-2.60611391	0.45404500
H	-2.56571889	-2.46392608	-0.59181499
C	3.97786593	-0.48247701	-0.03267800
O	5.30719280	-0.33157501	0.10673600
C	3.18169403	-0.56260598	1.04106605
H	3.65475988	-0.50033998	2.01280189
H	5.74212313	-0.28789800	-0.75012201
H	3.60575795	-0.53376102	-1.04933703

S24.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	25.48190000	11.04700000	0.00000000
2	50.01950000	0.00000000	0.00000000
3	86.26780000	4.91640000	0.00000000
4	118.51300000	1.23320000	0.00000000
5	163.44750000	3.56450000	0.00000000
6	224.05090000	0.06260000	0.00000000
7	247.70950000	0.33790000	0.00000000
8	272.68990000	2.62070000	0.00000000
9	281.81740000	1.75260000	0.00000000
10	290.00440000	2.16460000	0.00000000
11	350.17850000	4.16480000	0.00000000
12	350.83960000	0.05740000	0.00000000
13	388.19650000	52.56430000	0.00000000
14	402.65650000	52.18960000	0.00000000
15	419.26250000	1.92940000	0.00000000
16	425.02280000	3.49310000	0.00000000
17	447.56790000	2.86450000	0.00000000
18	470.01910000	4.59010000	0.00000000
19	488.26990000	1.38880000	0.00000000
20	561.96340000	23.39100000	0.00000000
21	583.33790000	7.29730000	0.00000000
22	654.65180000	0.12560000	0.00000000
23	715.79410000	13.05180000	0.00000000
24	739.46700000	0.22480000	0.00000000
25	822.68320000	0.00540000	0.00000000
26	838.88170000	13.67590000	0.00000000
27	843.20550000	23.75580000	0.00000000
28	881.22240000	35.15390000	0.00000000
29	884.80630000	23.07180000	0.00000000
30	942.57700000	15.66990000	0.00000000
31	957.72780000	37.84950000	0.00000000
32	964.56950000	16.78870000	0.00000000
33	978.06120000	3.96620000	0.00000000
34	983.73790000	0.48360000	0.00000000
35	1029.44820000	1.02510000	0.00000000
36	1076.81870000	0.02190000	0.00000000
37	1130.97360000	10.81120000	0.00000000
38	1132.86440000	0.94240000	0.00000000
39	1139.77080000	0.47850000	0.00000000
40	1166.96500000	53.77970000	0.00000000
41	1181.14710000	18.44150000	0.00000000
42	1212.18630000	319.95390000	0.00000000
43	1232.70940000	6.67710000	0.00000000
44	1259.27550000	1.19500000	0.00000000
45	1259.47910000	3.01790000	0.00000000
46	1279.45530000	158.37220000	0.00000000
47	1296.62920000	6.02660000	0.00000000
48	1341.71400000	51.13010000	0.00000000
49	1359.46400000	6.54380000	0.00000000
50	1364.58660000	9.81880000	0.00000000
51	1401.34610000	66.82440000	0.00000000
52	1448.59500000	2.51260000	0.00000000
53	1450.15380000	4.54010000	0.00000000
54	1461.70290000	11.57900000	0.00000000
55	1479.12110000	0.01540000	0.00000000
56	1489.30010000	0.31510000	0.00000000
57	1492.67690000	1.80080000	0.00000000
58	1495.90080000	0.47210000	0.00000000
59	1506.76940000	26.52910000	0.00000000
60	1512.22750000	23.54640000	0.00000000

61	1530.29710000	41.72930000	0.00000000
62	1548.67600000	59.29620000	0.00000000
63	1615.46500000	1.20790000	0.00000000
64	1641.47030000	148.33380000	0.00000000
65	1723.93070000	379.82680000	0.00000000
66	3078.20440000	0.74780000	0.00000000
67	3080.08760000	2.56360000	0.00000000
68	3087.41460000	2.46710000	0.00000000
69	3155.37510000	7.60690000	0.00000000
70	3165.87900000	0.00180000	0.00000000
71	3166.97440000	2.05490000	0.00000000
72	3171.98720000	6.54610000	0.00000000
73	3174.20700000	9.07500000	0.00000000
74	3182.64200000	0.23250000	0.00000000
75	3183.23390000	6.99090000	0.00000000
76	3187.16740000	0.07510000	0.00000000
77	3190.65450000	3.03490000	0.00000000
78	3193.76510000	0.42800000	0.00000000
79	3205.30120000	3.19900000	0.00000000
80	3230.17400000	1.11800000	0.00000000
81	3831.93830000	257.71540000	0.00000000

S25. CALCULATIONS ON $5A_{3D}$



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C[C]O	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.70085008	a.u.
Gibbs Energy	: -558.49860100	a.u.
Number of imaginary frequencies	: 0	

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

29

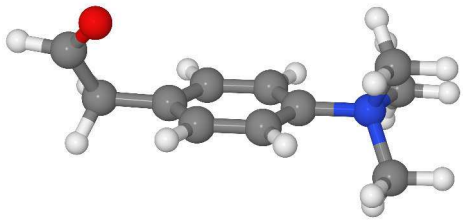
C	-0.36365601	-1.06184804	0.26071799
C	1.00816703	-0.94092101	0.39017299
C	1.63020205	0.30733100	0.30859500
C	0.83670098	1.42495704	0.08455600
C	-0.54487801	1.32025599	-0.04769400
C	-1.13755500	0.07290300	0.04242300
H	-0.80564803	-2.04478908	0.32938400
H	1.61386502	-1.82274497	0.53577000
H	1.29341698	2.40179896	0.00717300
H	-1.11269999	2.21866012	-0.22104700
N	-2.62694407	-0.09958700	-0.09725000
C	-3.34259200	1.19984305	-0.32659101
H	-4.40234518	0.98264301	-0.41223699
H	-3.16876507	1.85926199	0.51648903
H	-2.98387098	1.65031397	-1.24537003
C	-2.92466998	-0.99861801	-1.27195799
H	-2.46940303	-1.96698999	-1.10539603
H	-4.00208902	-1.10250401	-1.36359704
H	-2.50622296	-0.54245001	-2.16318488
C	-3.18658590	-0.71264601	1.16264606
H	-2.95464301	-0.05363000	1.99294996
H	-4.26131010	-0.82038498	1.04702103
H	-2.72991395	-1.68153298	1.32226300
C	3.87933993	-0.65718001	-0.25529501
O	5.07061195	-0.19072300	-0.52003598
C	3.12148905	0.43312600	0.45720899
H	3.38841796	0.26848900	1.51217902
H	3.47414088	1.43770301	0.20563500
H	5.59501886	-0.88417202	-0.94567502

S25.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	29.96970000	0.70830000	0.00000000
2	48.44330000	1.48040000	0.00000000
3	75.33360000	1.70800000	0.00000000
4	105.96070000	1.47960000	0.00000000
5	140.55150000	4.30850000	0.00000000
6	207.75070000	0.06130000	0.00000000
7	233.59090000	0.52590000	0.00000000
8	262.38060000	0.99540000	0.00000000
9	277.41960000	1.51030000	0.00000000
10	287.35350000	1.74480000	0.00000000
11	349.22590000	0.78820000	0.00000000
12	351.85500000	0.10530000	0.00000000
13	368.32100000	0.10250000	0.00000000
14	404.98530000	1.30760000	0.00000000
15	420.63670000	0.38580000	0.00000000
16	426.67990000	3.35110000	0.00000000
17	451.22650000	0.19850000	0.00000000
18	482.22770000	1.60040000	0.00000000
19	508.55120000	17.41360000	0.00000000
20	557.77250000	7.47020000	0.00000000
21	579.79310000	12.13020000	0.00000000
22	652.21040000	1.45310000	0.00000000
23	675.61840000	15.87780000	0.00000000
24	714.31610000	23.01900000	0.00000000
25	746.52190000	11.44020000	0.00000000
26	798.69630000	18.76260000	0.00000000
27	819.27560000	3.41940000	0.00000000
28	833.35870000	41.59270000	0.00000000
29	836.16820000	14.99750000	0.00000000
30	848.64160000	60.49010000	0.00000000
31	896.51960000	14.24240000	0.00000000
32	946.83240000	25.64790000	0.00000000
33	964.64370000	16.26180000	0.00000000
34	982.83520000	0.13680000	0.00000000
35	1005.35680000	1.33720000	0.00000000
36	1027.64020000	9.50670000	0.00000000
37	1034.96680000	12.50630000	0.00000000
38	1062.17800000	2.44620000	0.00000000
39	1077.02160000	0.02080000	0.00000000
40	1118.79590000	10.80080000	0.00000000
41	1130.65210000	3.56270000	0.00000000
42	1136.33470000	2.82240000	0.00000000
43	1140.51100000	0.53100000	0.00000000
44	1169.81470000	7.97840000	0.00000000
45	1225.73370000	1.41270000	0.00000000
46	1258.02050000	1.69870000	0.00000000
47	1259.48740000	1.43190000	0.00000000
48	1264.56360000	1.84860000	0.00000000
49	1295.27210000	2.98890000	0.00000000
50	1346.00640000	32.64730000	0.00000000
51	1354.79700000	188.80210000	0.00000000
52	1358.11970000	0.62040000	0.00000000
53	1447.87780000	0.30470000	0.00000000
54	1451.04350000	4.65390000	0.00000000
55	1453.59800000	12.62220000	0.00000000
56	1479.45360000	0.00780000	0.00000000
57	1489.65170000	0.27880000	0.00000000
58	1492.95460000	1.88010000	0.00000000
59	1495.76440000	0.23650000	0.00000000
60	1506.93600000	26.60790000	0.00000000

61	1512.58140000	23.67690000	0.00000000
62	1530.60120000	47.04330000	0.00000000
63	1545.93650000	54.90900000	0.00000000
64	1632.37090000	2.21070000	0.00000000
65	1645.80830000	6.63680000	0.00000000
66	2163.36380000	4.99310000	0.00000000
67	2245.14970000	7.57250000	0.00000000
68	2712.28760000	94.07010000	0.00000000
69	3079.38890000	0.60820000	0.00000000
70	3080.73570000	1.67710000	0.00000000
71	3087.76050000	1.81870000	0.00000000
72	3166.86470000	0.03490000	0.00000000
73	3167.57280000	0.83870000	0.00000000
74	3174.60320000	6.66170000	0.00000000
75	3182.80400000	0.23480000	0.00000000
76	3186.11420000	4.82050000	0.00000000
77	3187.73590000	0.67970000	0.00000000
78	3188.28850000	0.05880000	0.00000000
79	3197.01360000	1.41420000	0.00000000
80	3211.01520000	1.95890000	0.00000000
81	3233.87110000	0.62180000	0.00000000

S26. CALCULATIONS ON 6_{3D}



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)CC=O	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.78020946	a.u.
Gibbs Energy	: -558.57732000	a.u.
Number of imaginary frequencies	: 0	

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

29

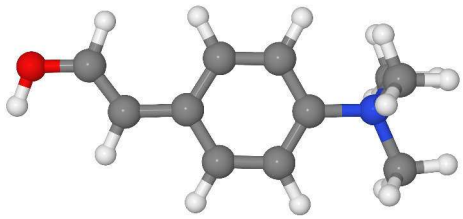
C	-0.21695600	-0.90264797	0.60871798
C	1.14403605	-0.71615100	0.76733798
C	1.75105798	0.49079600	0.41469899
C	0.95191002	1.50305498	-0.09953500
C	-0.41933700	1.33285701	-0.26513299
C	-0.99499398	0.12501299	0.08759100
H	-0.64541900	-1.85370898	0.88704401
H	1.74157703	-1.52607203	1.15797806
H	1.39521205	2.44629192	-0.38660800
H	-0.99213201	2.14977193	-1.00000997
N	-2.46888089	-0.12283500	-0.09113600
C	-3.19321704	1.06515396	-0.65522701
H	-4.24120998	0.79922402	-0.74739599
H	-3.08487201	1.90634894	0.02050200
H	-2.78718710	1.30306399	-1.63210905
C	-2.67320204	-1.27688897	-1.04280996
H	-2.21353197	-2.16638994	-0.63009000
H	-3.74037600	-1.43254602	-1.17241895
H	-2.20429707	-1.02443397	-1.98827696
C	-3.09596491	-0.44905999	1.24188399
H	-2.92951608	0.38950700	1.91022098
H	-4.15895987	-0.61466300	1.09200895
H	-2.63398409	-1.34105003	1.64643598
C	4.03126717	-0.28350499	-0.35367101
O	3.55381107	-1.19298303	-0.97467500
H	5.11662483	-0.07481800	-0.37923101
C	3.23461008	0.65978402	0.53810698
H	3.57299495	0.47027999	1.56309605
H	3.54369903	1.68217301	0.31209400

S26.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	22.74640000	1.75970000	0.00000000
2	48.03500000	2.51100000	0.00000000
3	69.55710000	4.38310000	0.00000000
4	116.21170000	5.83750000	0.00000000
5	132.17270000	4.67320000	0.00000000
6	206.28050000	0.49750000	0.00000000
7	218.77990000	1.07810000	0.00000000
8	263.91790000	1.96680000	0.00000000
9	278.28570000	0.61160000	0.00000000
10	293.60620000	0.84050000	0.00000000
11	336.70610000	0.78130000	0.00000000
12	351.46140000	0.15980000	0.00000000
13	367.65250000	0.25700000	0.00000000
14	387.75310000	1.60230000	0.00000000
15	419.90430000	0.23520000	0.00000000
16	440.17410000	0.60750000	0.00000000
17	478.50510000	2.18360000	0.00000000
18	503.50180000	2.89990000	0.00000000
19	546.13030000	10.42770000	0.00000000
20	578.25520000	10.98900000	0.00000000
21	627.53030000	7.69840000	0.00000000
22	653.00060000	0.38420000	0.00000000
23	705.71250000	16.09490000	0.00000000
24	743.55030000	6.03660000	0.00000000
25	766.58070000	5.50320000	0.00000000
26	806.71450000	14.92140000	0.00000000
27	827.30280000	1.78430000	0.00000000
28	833.04260000	0.16600000	0.00000000
29	848.42530000	32.41050000	0.00000000
30	889.47960000	3.12350000	0.00000000
31	945.50780000	20.02250000	0.00000000
32	963.85630000	16.47010000	0.00000000
33	974.09010000	0.36420000	0.00000000
34	980.27490000	2.07810000	0.00000000
35	993.61540000	1.06050000	0.00000000
36	1036.96680000	13.26540000	0.00000000
37	1045.83750000	9.83320000	0.00000000
38	1076.24240000	14.57180000	0.00000000
39	1076.82430000	0.03230000	0.00000000
40	1123.04460000	38.97470000	0.00000000
41	1132.76730000	1.50430000	0.00000000
42	1137.43630000	7.67940000	0.00000000
43	1140.28810000	0.46820000	0.00000000
44	1172.19280000	4.52560000	0.00000000
45	1231.83680000	2.54420000	0.00000000
46	1258.75540000	1.95310000	0.00000000
47	1258.99480000	1.33670000	0.00000000
48	1279.22940000	16.63430000	0.00000000
49	1296.10190000	3.38000000	0.00000000
50	1346.36880000	2.02900000	0.00000000
51	1360.91010000	0.94240000	0.00000000
52	1448.14840000	0.15240000	0.00000000
53	1451.31120000	4.70520000	0.00000000
54	1454.06250000	14.05720000	0.00000000
55	1479.37830000	0.00430000	0.00000000
56	1489.24150000	0.29820000	0.00000000
57	1493.25880000	1.97250000	0.00000000
58	1495.50370000	0.34910000	0.00000000
59	1506.97040000	26.70730000	0.00000000
60	1512.80190000	23.78840000	0.00000000

61	1530.47660000	47.27780000	0.00000000
62	1549.73330000	48.52180000	0.00000000
63	1634.16830000	2.95560000	0.00000000
64	1649.53780000	3.94320000	0.00000000
65	1790.83170000	126.90800000	0.00000000
66	2163.94700000	75.97080000	0.00000000
67	2201.66440000	11.91490000	0.00000000
68	2269.69050000	2.27140000	0.00000000
69	3079.76770000	0.46980000	0.00000000
70	3080.95210000	1.45350000	0.00000000
71	3087.87540000	1.50020000	0.00000000
72	3167.30920000	0.14440000	0.00000000
73	3168.10530000	0.53090000	0.00000000
74	3175.00120000	5.90920000	0.00000000
75	3182.71010000	0.20890000	0.00000000
76	3187.52800000	4.84230000	0.00000000
77	3188.38640000	0.57630000	0.00000000
78	3188.50340000	0.25380000	0.00000000
79	3197.88900000	1.63680000	0.00000000
80	3210.51260000	0.27100000	0.00000000
81	3235.44820000	0.42060000	0.00000000

S27. CALCULATIONS ON $7B_{3D}$



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=CO	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.77653346	a.u.
Gibbs Energy	: -558.57275200	a.u.
Number of imaginary frequencies	: 0	

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

29

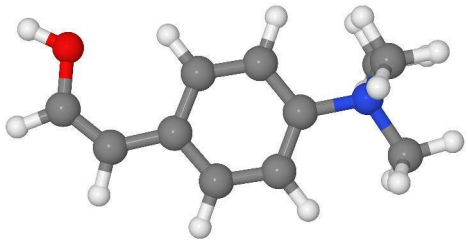
C	-0.37332600	-1.06570005	-0.00071000
C	1.00075495	-0.94619000	-0.00115000
C	1.62963796	0.31239799	-0.00081900
C	0.79375499	1.43659604	-0.00039100
C	-0.58892399	1.32884896	-0.00003000
C	-1.17460501	0.07344800	-0.00012000
H	-0.80170900	-2.05722189	-0.00096100
H	1.58863699	-1.85147500	-0.00196800
H	1.23465204	2.42347288	-0.00027400
H	-1.16990304	2.23587704	0.00032000
N	-2.66739893	-0.10299500	0.00032300
C	-3.40331292	1.20510399	0.00085400
H	-4.46629620	0.98677099	0.00111800
H	-3.14168096	1.76363301	0.89270002
H	-3.14217091	1.76406705	-0.89086902
C	-3.09076595	-0.86412400	-1.23175001
H	-2.61734700	-1.83818805	-1.22959495
H	-4.17150879	-0.97399700	-1.21788597
H	-2.77336693	-0.30150399	-2.10356402
C	-3.08993101	-0.86470401	1.23229897
H	-2.77207088	-0.30243501	2.10417604
H	-4.17067385	-0.97469300	1.21907198
H	-2.61636209	-1.83869302	1.22942805
C	3.98057890	-0.48474801	0.00113800
O	5.31106520	-0.33520299	0.00104400
C	3.06804705	0.49860400	-0.00107800
H	3.41634202	1.52574694	-0.00286500
H	5.55597496	0.59914100	-0.00137600
H	3.71916509	-1.53400898	0.00347100

S27.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	23.00830000	0.07590000	0.00000000
2	49.87640000	0.87520000	0.00000000
3	78.50670000	5.44700000	0.00000000
4	116.44100000	2.22110000	0.00000000
5	155.26050000	1.48030000	0.00000000
6	222.83310000	0.41030000	0.00000000
7	244.40240000	1.49270000	0.00000000
8	269.40090000	0.46950000	0.00000000
9	276.27180000	0.74590000	0.00000000
10	288.17320000	1.82110000	0.00000000
11	345.15790000	2.22190000	0.00000000
12	350.40020000	0.16290000	0.00000000
13	387.81040000	18.62000000	0.00000000
14	405.34280000	4.91090000	0.00000000
15	407.00460000	15.00380000	0.00000000
16	418.93790000	0.10620000	0.00000000
17	441.08380000	0.45180000	0.00000000
18	468.36830000	2.82030000	0.00000000
19	485.84400000	2.36170000	0.00000000
20	560.74770000	42.29960000	0.00000000
21	574.74420000	0.48880000	0.00000000
22	654.09090000	0.05090000	0.00000000
23	683.85060000	17.69060000	0.00000000
24	697.90410000	0.52690000	0.00000000
25	740.10900000	1.48260000	0.00000000
26	792.76360000	5.60140000	0.00000000
27	823.99210000	23.44770000	0.00000000
28	824.48390000	0.00850000	0.00000000
29	849.59390000	25.75030000	0.00000000
30	857.98120000	34.26980000	0.00000000
31	892.63770000	75.25360000	0.00000000
32	942.55740000	22.24030000	0.00000000
33	964.57160000	17.14560000	0.00000000
34	974.67790000	0.09420000	0.00000000
35	984.23760000	0.39310000	0.00000000
36	1013.65260000	60.87850000	0.00000000
37	1029.52410000	1.48020000	0.00000000
38	1072.90660000	107.39610000	0.00000000
39	1076.81910000	0.02250000	0.00000000
40	1133.19600000	1.94180000	0.00000000
41	1135.25100000	1.20600000	0.00000000
42	1139.81210000	0.49140000	0.00000000
43	1177.97240000	7.85730000	0.00000000
44	1204.70220000	98.93630000	0.00000000
45	1233.18500000	33.70870000	0.00000000
46	1259.17780000	1.23020000	0.00000000
47	1259.30610000	2.79840000	0.00000000
48	1293.84550000	7.76630000	0.00000000
49	1316.68410000	9.93650000	0.00000000
50	1345.29410000	11.42480000	0.00000000
51	1362.28400000	5.12040000	0.00000000
52	1447.92910000	2.40450000	0.00000000
53	1450.26480000	4.56140000	0.00000000
54	1456.93630000	25.60460000	0.00000000
55	1479.14410000	0.01660000	0.00000000
56	1489.26880000	0.31750000	0.00000000
57	1492.71040000	1.81930000	0.00000000
58	1495.71620000	0.54180000	0.00000000
59	1506.76700000	27.19550000	0.00000000
60	1512.28070000	23.59410000	0.00000000

61	1530.26640000	42.12220000	0.00000000
62	1547.57900000	29.22140000	0.00000000
63	1613.77350000	28.85210000	0.00000000
64	1633.33450000	581.10970000	0.00000000
65	1656.22150000	193.53340000	0.00000000
66	2319.42370000	20.17000000	0.00000000
67	2365.23590000	2.99080000	0.00000000
68	2743.64610000	82.12900000	0.00000000
69	3078.35790000	0.71650000	0.00000000
70	3080.17740000	2.42240000	0.00000000
71	3087.44080000	2.31050000	0.00000000
72	3166.07220000	0.00200000	0.00000000
73	3167.11640000	1.78160000	0.00000000
74	3174.30340000	8.83720000	0.00000000
75	3182.52680000	0.24440000	0.00000000
76	3183.91960000	7.00300000	0.00000000
77	3187.24120000	0.07750000	0.00000000
78	3188.13720000	2.41780000	0.00000000
79	3194.48110000	1.15630000	0.00000000
80	3207.53070000	1.63650000	0.00000000
81	3230.29250000	1.08380000	0.00000000

S28. CALCULATIONS ON $7A_{3D}$



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=CO	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.77967831	a.u.
Gibbs Energy	: -558.57469500	a.u.
Number of imaginary frequencies	: 0	

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

29

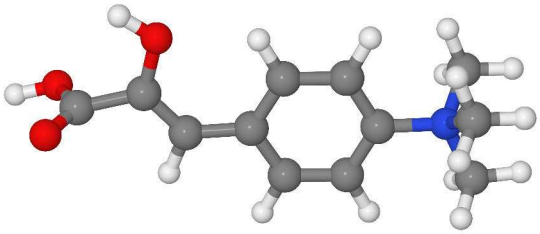
C	0.18453400	-0.95854598	-0.00018300
C	-1.17911100	-0.73464203	-0.00018100
C	-1.70113099	0.57215399	0.00004000
C	-0.77975601	1.62849700	0.00019600
C	0.58924299	1.41315603	0.00017400
C	1.07067204	0.11303400	0.00002500
H	0.53493297	-1.98032904	-0.00036600
H	-1.84771705	-1.57846606	-0.00036800
H	-1.14281404	2.64662409	0.00032700
H	1.24138904	2.27035093	0.00025400
N	2.54612303	-0.18060701	0.00008300
C	3.38349891	1.06479704	-0.00011800
H	4.42582417	0.76275003	-0.00010700
H	3.16724300	1.64251399	-0.89187700
H	3.16723394	1.64280105	0.89145100
C	2.90666294	-0.97264099	1.23236299
H	2.35725999	-1.90589797	1.22992301
H	3.97538996	-1.16747904	1.21949303
H	2.63390708	-0.38649499	2.10380006
C	2.90672302	-0.97313201	-1.23175895
H	2.63422799	-0.38731599	-2.10350800
H	3.97541809	-1.16815197	-1.21867001
H	2.35717106	-1.90630305	-1.22909498
C	-4.16413212	0.04738600	-0.00017100
O	-4.05359697	-1.29991996	-0.00063200
C	-3.11764312	0.88480002	0.00016200
H	-3.37329602	1.93495703	0.00062300
H	-4.92483521	-1.70764995	-0.00032600
H	-5.17259216	0.44185901	0.00007900

S28.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	34.66160000	0.95830000	0.00000000
2	54.80200000	2.21630000	0.00000000
3	88.77930000	1.73290000	0.00000000
4	134.58020000	3.45690000	0.00000000
5	187.74460000	8.41290000	0.00000000
6	230.43290000	0.80380000	0.00000000
7	232.79290000	6.73880000	0.00000000
8	281.88550000	0.13640000	0.00000000
9	283.24280000	47.95170000	0.00000000
10	291.77000000	1.54930000	0.00000000
11	350.74200000	0.30680000	0.00000000
12	350.96690000	1.01980000	0.00000000
13	354.50440000	1.68640000	0.00000000
14	371.47710000	0.95250000	0.00000000
15	412.08690000	1.11980000	0.00000000
16	423.79800000	0.35310000	0.00000000
17	479.40540000	3.30250000	0.00000000
18	490.36990000	1.80830000	0.00000000
19	504.56640000	1.21820000	0.00000000
20	565.93040000	34.13340000	0.00000000
21	623.51240000	1.11390000	0.00000000
22	628.07660000	3.14890000	0.00000000
23	651.57510000	0.1.000000	0.00000000
24	730.57400000	8.06120000	0.00000000
25	747.35000000	0.54040000	0.00000000
26	779.91520000	0.84320000	0.00000000
27	814.10620000	7.64680000	0.00000000
28	830.58870000	0.81000000	0.00000000
29	848.29760000	35.98030000	0.00000000
30	862.24700000	35.93890000	0.00000000
31	890.77880000	8.01000000	0.00000000
32	931.30570000	6.73490000	0.00000000
33	944.65500000	24.27070000	0.00000000
34	965.55680000	17.22900000	0.00000000
35	978.38520000	0.01770000	0.00000000
36	998.47240000	0.00040000	0.00000000
37	1032.22940000	3.76690000	0.00000000
38	1060.99450000	46.55390000	0.00000000
39	1076.83570000	0.01810000	0.00000000
40	1132.07790000	11.44390000	0.00000000
41	1133.57620000	2.68520000	0.00000000
42	1139.90610000	0.52300000	0.00000000
43	1161.68050000	143.89390000	0.00000000
44	1180.79260000	20.77310000	0.00000000
45	1235.89150000	7.95890000	0.00000000
46	1259.45700000	1.24970000	0.00000000
47	1259.85760000	1.77070000	0.00000000
48	1294.25240000	5.36140000	0.00000000
49	1334.84870000	32.80940000	0.00000000
50	1343.68690000	12.69840000	0.00000000
51	1363.26240000	0.25930000	0.00000000
52	1447.57250000	0.29220000	0.00000000
53	1450.36760000	4.53030000	0.00000000
54	1454.70330000	19.38090000	0.00000000
55	1479.02740000	0.00470000	0.00000000
56	1489.73520000	0.30120000	0.00000000
57	1492.69390000	1.71380000	0.00000000
58	1496.00290000	0.36060000	0.00000000
59	1506.35520000	28.06840000	0.00000000
60	1512.12480000	23.47650000	0.00000000

61	1530.33630000	43.52210000	0.00000000
62	1545.02640000	39.68920000	0.00000000
63	1614.00570000	8.31790000	0.00000000
64	1639.35500000	134.64330000	0.00000000
65	1671.61860000	269.05040000	0.00000000
66	2336.45140000	1.41490000	0.00000000
67	2364.35320000	8.56770000	0.00000000
68	2789.95420000	138.13510000	0.00000000
69	3078.58680000	0.77690000	0.00000000
70	3080.24260000	2.40630000	0.00000000
71	3087.42800000	2.75240000	0.00000000
72	3165.98870000	0.00220000	0.00000000
73	3166.90050000	1.56630000	0.00000000
74	3173.99510000	8.83340000	0.00000000
75	3182.58260000	0.27700000	0.00000000
76	3184.98350000	6.33280000	0.00000000
77	3188.30330000	1.77380000	0.00000000
78	3188.38910000	0.06150000	0.00000000
79	3196.29690000	1.77100000	0.00000000
80	3231.28260000	1.06500000	0.00000000
81	3244.84780000	3.33120000	0.00000000

S29. CALCULATIONS ON TRANSITION FROM 4B TO 4A



Route	: # opt=qst3 freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd	
	: 3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=C(C(=O)O)O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.41864646	a.u.
Gibbs Energy	: -747.19329600	a.u.
Number of imaginary frequencies	: 1	

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

32

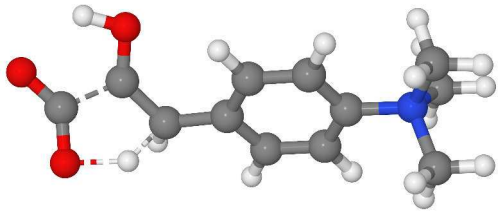
C	-1.37353301	-1.01467800	0.15125100
C	0.00156000	-0.88452500	0.19818300
C	0.61478001	0.37646899	0.08851900
C	-0.22562400	1.48616898	-0.07239700
C	-1.60528696	1.36449504	-0.12077500
C	-2.17876196	0.10756000	-0.00745000
H	-1.79633105	-2.00449991	0.24139500
H	0.60538000	-1.76685297	0.32246700
H	0.20973600	2.47157001	-0.16016699
H	-2.19291806	2.25848103	-0.24483299
N	-3.67012405	-0.08411500	-0.05013800
C	-4.41473007	1.20750999	-0.22356300
H	-5.47510815	0.97773099	-0.24383999
H	-4.19570208	1.86304605	0.61195803
H	-4.11983681	1.66904795	-1.15941000
C	-4.03446579	-0.98010802	-1.20796895
H	-3.55299711	-1.94171703	-1.08024895
H	-5.11388206	-1.10159898	-1.22617805
H	-3.68568993	-0.51141298	-2.12235808
C	-4.13850212	-0.71139097	1.23975205
H	-3.85917807	-0.05476100	2.05720091
H	-5.21726084	-0.83178902	1.19514203
H	-3.66040206	-1.67538905	1.36202896
C	3.03114796	-0.29815799	0.28807199
O	2.81678796	-1.62940896	0.41756800
C	2.04813409	0.59837401	0.13493700
H	2.36976600	1.62618804	0.04233800
C	4.47122288	0.14343300	0.37540001
O	5.00945616	0.44648701	1.40354300
O	5.07153177	0.10860300	-0.82531399
H	5.99804211	0.37514600	-0.70616502
H	3.64165092	-2.10494399	0.56536001

S29.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-109.12060000	3.52580000	0.00000000
2	26.44880000	1.18100000	0.00000000
3	35.00230000	2.42420000	0.00000000
4	60.15760000	0.13110000	0.00000000
5	90.96000000	1.05400000	0.00000000
6	111.02590000	0.70620000	0.00000000
7	177.47670000	2.77870000	0.00000000
8	209.67870000	0.63900000	0.00000000
9	231.47990000	1.76630000	0.00000000
10	241.68230000	3.01640000	0.00000000
11	282.64550000	1.18690000	0.00000000
12	287.05480000	66.45610000	0.00000000
13	303.15010000	2.18130000	0.00000000
14	326.88030000	9.37070000	0.00000000
15	342.23890000	10.80690000	0.00000000
16	350.95590000	0.32260000	0.00000000
17	373.58180000	0.85270000	0.00000000
18	403.71180000	1.24030000	0.00000000
19	408.01120000	3.93550000	0.00000000
20	422.79200000	0.38690000	0.00000000
21	476.74700000	0.22290000	0.00000000
22	482.34900000	3.38570000	0.00000000
23	543.26250000	15.84220000	0.00000000
24	567.11210000	36.89810000	0.00000000
25	626.88680000	46.78110000	0.00000000
26	646.97460000	45.31500000	0.00000000
27	657.35100000	49.92890000	0.00000000
28	700.87360000	3.23050000	0.00000000
29	717.65860000	19.68460000	0.00000000
30	744.94510000	0.28550000	0.00000000
31	799.38510000	17.05070000	0.00000000
32	821.73970000	0.18900000	0.00000000
33	840.55750000	0.22290000	0.00000000
34	843.31850000	45.07310000	0.00000000
35	874.06920000	25.24490000	0.00000000
36	877.00240000	49.20900000	0.00000000
37	879.06410000	13.81790000	0.00000000
38	944.33170000	25.68800000	0.00000000
39	964.89850000	19.12740000	0.00000000
40	978.63520000	0.17940000	0.00000000
41	997.24170000	0.07950000	0.00000000
42	1033.40090000	3.56910000	0.00000000
43	1076.99200000	0.01930000	0.00000000
44	1119.41770000	76.13350000	0.00000000
45	1132.98620000	0.80620000	0.00000000
46	1135.32110000	7.87280000	0.00000000
47	1140.02460000	0.51030000	0.00000000
48	1174.93720000	1.90650000	0.00000000
49	1189.51470000	321.04560000	0.00000000
50	1229.82270000	20.00000000	0.00000000
51	1252.00410000	32.03360000	0.00000000
52	1259.28130000	1.28680000	0.00000000
53	1259.80440000	0.65100000	0.00000000
54	1295.18000000	7.75960000	0.00000000
55	1305.25380000	140.90090000	0.00000000
56	1339.10960000	26.61250000	0.00000000
57	1360.74310000	29.75780000	0.00000000
58	1379.56360000	152.53020000	0.00000000
59	1420.41770000	127.71290000	0.00000000
60	1448.84120000	2.05360000	0.00000000

61	1450.51810000	4.57870000	0.00000000
62	1460.70350000	12.35710000	0.00000000
63	1479.18120000	0.01130000	0.00000000
64	1489.45800000	0.30350000	0.00000000
65	1492.81950000	1.46750000	0.00000000
66	1495.81820000	0.36230000	0.00000000
67	1506.77530000	26.40760000	0.00000000
68	1512.32510000	23.53240000	0.00000000
69	1530.31630000	44.25640000	0.00000000
70	1546.64510000	66.11260000	0.00000000
71	1617.06090000	3.01190000	0.00000000
72	1641.60310000	75.46770000	0.00000000
73	1725.12710000	244.07330000	0.00000000
74	1825.26080000	289.35800000	0.00000000
75	3078.58950000	0.69280000	0.00000000
76	3080.26170000	2.34680000	0.00000000
77	3087.47370000	2.40690000	0.00000000
78	3166.21170000	0.01060000	0.00000000
79	3167.13980000	1.64560000	0.00000000
80	3174.29220000	8.99610000	0.00000000
81	3182.62660000	0.24260000	0.00000000
82	3183.89410000	1.40970000	0.00000000
83	3185.19470000	6.64060000	0.00000000
84	3187.68880000	0.06290000	0.00000000
85	3190.17740000	3.54180000	0.00000000
86	3196.62300000	2.00780000	0.00000000
87	3231.60590000	1.02910000	0.00000000
88	3248.01390000	3.63260000	0.00000000
89	3706.66420000	117.30490000	0.00000000
90	3806.28570000	206.00530000	0.00000000

S30. CALCULATIONS ON TRANSITION FROM 4A TO 5A



Route	: # opt=(calcfc,qst3) freq b3lyp/cc-pvtz geom=connectivity empiricaldisp	
	: ersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C[C](C(=O)[O])O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.35103561	a.u.
Gibbs Energy	: -747.13153300	a.u.
Number of imaginary frequencies	: 1	

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

32

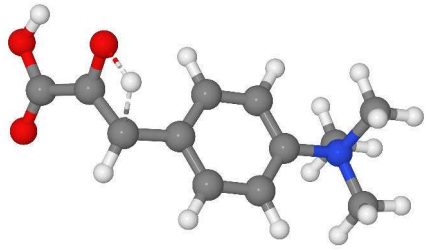
C	-1.59242702	-0.97613901	0.97402000
C	-0.21426301	-1.00894904	1.07759905
C	0.59511697	-0.18124400	0.29094100
C	-0.03435600	0.68456697	-0.60500997
C	-1.41739798	0.72624701	-0.71776098
C	-2.19412899	-0.10572600	0.07261700
H	-2.17335200	-1.63465405	1.60212398
H	0.24124700	-1.69420695	1.77874804
H	0.55017501	1.34298599	-1.22918904
H	-1.84837401	1.41310894	-1.42631197
N	-3.69527507	-0.09851400	-0.01782700
C	-4.21087599	0.88664198	-1.02780700
H	-5.29417419	0.82439202	-1.02544296
H	-3.89950991	1.88651097	-0.74627101
H	-3.83013010	0.62782598	-2.00962806
C	-4.18559790	-1.46752000	-0.42422000
H	-3.88128495	-2.19243693	0.32069600
H	-5.26901913	-1.43861401	-0.49605599
H	-3.74445200	-1.71558905	-1.38411403
C	-4.28381109	0.27152899	1.32219505
H	-3.91314006	1.25370800	1.59691298
H	-5.36623001	0.28151801	1.23262298
H	-3.97867298	-0.45888299	2.06134105
C	2.97387099	0.71005797	0.00407200
O	2.80725789	1.95136595	-0.25168401
C	2.05902410	-0.28754699	0.39472401
H	2.41349697	-0.77895200	1.30502403
C	4.35555077	0.15056799	-0.37712899
O	5.20368910	1.00298703	-0.61357701
O	4.29651785	-1.11003101	-0.46298701
H	2.86797404	-1.12047899	-0.22577700
H	3.71941710	2.24271894	-0.55506998

S30.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-1499.19120000	1904.61890000	0.00000000
2	10.06340000	0.42970000	0.00000000
3	43.24830000	1.31620000	0.00000000
4	52.39960000	0.01620000	0.00000000
5	77.77140000	1.92270000	0.00000000
6	120.88120000	3.74490000	0.00000000
7	164.86530000	1.20030000	0.00000000
8	207.15310000	0.81670000	0.00000000
9	219.71360000	0.78200000	0.00000000
10	251.01360000	3.15880000	0.00000000
11	275.66920000	3.23740000	0.00000000
12	286.26870000	13.74260000	0.00000000
13	293.19220000	37.24180000	0.00000000
14	329.81770000	8.63970000	0.00000000
15	352.87710000	0.05800000	0.00000000
16	368.27090000	2.08150000	0.00000000
17	393.00290000	0.16700000	0.00000000
18	411.67260000	2.21230000	0.00000000
19	420.12140000	0.00050000	0.00000000
20	449.92340000	2.58730000	0.00000000
21	478.13040000	2.51730000	0.00000000
22	513.69000000	21.16790000	0.00000000
23	563.55910000	35.67140000	0.00000000
24	579.56700000	4.94400000	0.00000000
25	613.54240000	14.78640000	0.00000000
26	652.68560000	2.23770000	0.00000000
27	701.94360000	7.28470000	0.00000000
28	711.74600000	15.30120000	0.00000000
29	751.49300000	79.86750000	0.00000000
30	756.02460000	5.46310000	0.00000000
31	825.40530000	15.90920000	0.00000000
32	834.69290000	0.17560000	0.00000000
33	843.74470000	53.78650000	0.00000000
34	868.01120000	25.11260000	0.00000000
35	889.30270000	30.78440000	0.00000000
36	902.84450000	22.99380000	0.00000000
37	943.70330000	29.61160000	0.00000000
38	962.10010000	16.06310000	0.00000000
39	962.45010000	68.68350000	0.00000000
40	984.38920000	0.41740000	0.00000000
41	995.27800000	0.11790000	0.00000000
42	1036.52450000	7.37620000	0.00000000
43	1076.55650000	0.02330000	0.00000000
44	1095.48170000	22.91200000	0.00000000
45	1132.42340000	2.15480000	0.00000000
46	1137.05300000	2.49340000	0.00000000
47	1139.86620000	0.48290000	0.00000000
48	1173.57810000	4.55870000	0.00000000
49	1213.21140000	25.61200000	0.00000000
50	1239.65040000	9.91790000	0.00000000
51	1258.20230000	1.38310000	0.00000000
52	1258.59910000	0.76180000	0.00000000
53	1295.29190000	4.34160000	0.00000000
54	1311.73570000	190.78270000	0.00000000
55	1322.99730000	190.43200000	0.00000000
56	1335.38090000	30.28220000	0.00000000
57	1359.01980000	2.14360000	0.00000000
58	1373.10640000	2.70420000	0.00000000
59	1449.46760000	2.57020000	0.00000000
60	1451.18410000	4.83020000	0.00000000

61	1461.05970000	16.91260000	0.00000000
62	1476.73880000	212.01460000	0.00000000
63	1479.59950000	0.02120000	0.00000000
64	1489.06370000	0.42190000	0.00000000
65	1493.39990000	1.65000000	0.00000000
66	1495.63430000	1.55390000	0.00000000
67	1507.19650000	24.53960000	0.00000000
68	1513.04520000	24.26230000	0.00000000
69	1530.46820000	47.35640000	0.00000000
70	1551.24800000	45.67490000	0.00000000
71	1623.40100000	111.69690000	0.00000000
72	1637.65570000	288.23070000	0.00000000
73	1651.08050000	20.90710000	0.00000000
74	1787.38410000	185.57960000	0.00000000
75	1834.37070000	293.72480000	0.00000000
76	3060.66920000	16.81270000	0.00000000
77	3080.00530000	0.39980000	0.00000000
78	3081.09410000	1.41440000	0.00000000
79	3087.93870000	1.15790000	0.00000000
80	3167.78990000	0.00460000	0.00000000
81	3168.37930000	1.04350000	0.00000000
82	3175.45150000	10.97680000	0.00000000
83	3181.79360000	423.95700000	0.00000000
84	3182.64260000	0.17890000	0.00000000
85	3184.71900000	1.30050000	0.00000000
86	3188.29050000	0.03100000	0.00000000
87	3191.18930000	0.22390000	0.00000000
88	3204.39280000	1.82590000	0.00000000
89	3210.00300000	0.07320000	0.00000000
90	3235.92330000	0.67590000	0.00000000

S31. CALCULATIONS ON TRANSITION FROM 4B TO 4F (SINGLE HYDROGEN SHIFT)



Route	: # opt=qst2 freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd	
	: 3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)[CH][C](C(=O)O)O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.31732791	a.u.
Gibbs Energy	: -747.09944000	a.u.
Number of imaginary frequencies	: 1	

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

32

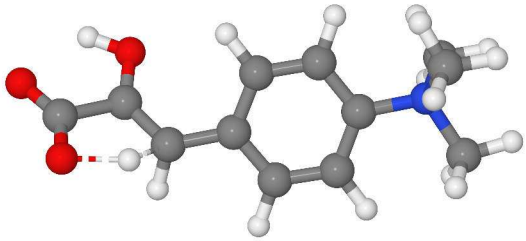
C	8.47461033	1.36861098	0.91315901
C	7.28849602	1.18814600	0.23059100
C	6.15790796	1.97292602	0.51380998
C	6.28830194	2.94798493	1.50986302
C	7.47768402	3.13814807	2.19603395
C	8.57507706	2.34596705	1.89854300
H	9.30966473	0.73137498	0.66199601
H	7.24803591	0.42545801	-0.53291798
H	5.43973494	3.56771111	1.76133394
H	7.50780916	3.90402389	2.95283389
N	9.88387489	2.50455403	2.61973906
C	9.84619236	3.59593391	3.65004897
H	10.82445812	3.64343190	4.11727524
H	9.62340260	4.53988504	3.16504693
H	9.09377575	3.36096907	4.39468002
C	10.23355770	1.21933496	3.32931709
H	10.32470226	0.42293400	2.60096002
H	11.17587185	1.35685396	3.85209203
H	9.43646908	0.99040699	4.02904081
C	10.97262764	2.84683204	1.63272500
H	10.69959927	3.77050996	1.13307095
H	11.90713406	2.96485591	2.17394495
H	11.06129360	2.04748392	0.90732598
C	4.57880878	0.74110198	-1.02413201
O	5.25537586	0.81361997	-2.10838509
C	4.85246706	1.83095706	-0.15682600
H	4.01893997	2.22826004	0.40867901
C	3.56608796	-0.36636201	-0.83397502
O	2.79138207	-0.34149599	0.07711200
O	3.62543988	-1.33855295	-1.74641299
H	4.26528311	-1.11388099	-2.44008803
H	5.40983295	1.99293804	-1.56617105

S31.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2179.29220000	438.64520000	0.00000000
2	22.48450000	0.74100000	0.00000000
3	34.78880000	3.21800000	0.00000000
4	53.54060000	2.15370000	0.00000000
5	58.09040000	1.60600000	0.00000000
6	95.52790000	7.30960000	0.00000000
7	120.33570000	0.77500000	0.00000000
8	194.69150000	9.56250000	0.00000000
9	211.18700000	5.15040000	0.00000000
10	224.75080000	1.79860000	0.00000000
11	258.27490000	2.79210000	0.00000000
12	281.46680000	0.82810000	0.00000000
13	288.13020000	5.38970000	0.00000000
14	351.19080000	0.21630000	0.00000000
15	355.44560000	1.23630000	0.00000000
16	367.94880000	4.48910000	0.00000000
17	389.45020000	0.23950000	0.00000000
18	399.22100000	14.31750000	0.00000000
19	420.63020000	0.08380000	0.00000000
20	443.63270000	10.37010000	0.00000000
21	468.56090000	23.45450000	0.00000000
22	485.03470000	16.28280000	0.00000000
23	522.63560000	5.54880000	0.00000000
24	554.35710000	30.29040000	0.00000000
25	568.30120000	20.42490000	0.00000000
26	593.12320000	84.21930000	0.00000000
27	651.72680000	1.60890000	0.00000000
28	678.06440000	1.60430000	0.00000000
29	712.72480000	39.70830000	0.00000000
30	737.87990000	2.43910000	0.00000000
31	784.28630000	29.69260000	0.00000000
32	810.79340000	1.24200000	0.00000000
33	830.40590000	0.83040000	0.00000000
34	844.88700000	19.43580000	0.00000000
35	856.89540000	37.09170000	0.00000000
36	881.96290000	30.60630000	0.00000000
37	941.35730000	8.61120000	0.00000000
38	944.74190000	40.80890000	0.00000000
39	964.01610000	21.54480000	0.00000000
40	978.28240000	1.19390000	0.00000000
41	992.41260000	0.44610000	0.00000000
42	1031.07400000	5.31220000	0.00000000
43	1076.40480000	0.02310000	0.00000000
44	1098.40280000	32.61870000	0.00000000
45	1133.06120000	1.09520000	0.00000000
46	1135.51580000	1.43930000	0.00000000
47	1139.64600000	0.45770000	0.00000000
48	1163.26550000	24.22530000	0.00000000
49	1179.17970000	3.55970000	0.00000000
50	1220.29720000	85.03760000	0.00000000
51	1224.17680000	44.82190000	0.00000000
52	1245.95040000	2.01750000	0.00000000
53	1258.79690000	1.60790000	0.00000000
54	1259.16490000	6.29170000	0.00000000
55	1295.35740000	11.38610000	0.00000000
56	1317.04640000	618.11800000	0.00000000
57	1347.78960000	203.84400000	0.00000000
58	1365.21810000	17.95080000	0.00000000
59	1435.14700000	21.35950000	0.00000000
60	1449.75570000	3.79310000	0.00000000

61	1450.28200000	3.67950000	0.00000000
62	1468.84280000	91.48510000	0.00000000
63	1479.11110000	0.00650000	0.00000000
64	1489.24550000	0.28960000	0.00000000
65	1492.82610000	0.96940000	0.00000000
66	1495.37920000	13.25070000	0.00000000
67	1506.55340000	26.85780000	0.00000000
68	1511.77090000	327.17070000	0.00000000
69	1512.58210000	22.71780000	0.00000000
70	1530.24500000	39.62870000	0.00000000
71	1545.59970000	90.77180000	0.00000000
72	1616.09460000	2.70820000	0.00000000
73	1643.40570000	53.28630000	0.00000000
74	1753.24100000	10.45340000	0.00000000
75	1839.56700000	174.04120000	0.00000000
76	3078.90620000	0.62830000	0.00000000
77	3080.47010000	2.06060000	0.00000000
78	3087.56580000	2.01120000	0.00000000
79	3159.69180000	1.40240000	0.00000000
80	3166.48720000	0.00860000	0.00000000
81	3167.43100000	1.51210000	0.00000000
82	3174.57820000	8.11090000	0.00000000
83	3182.49090000	0.21850000	0.00000000
84	3184.85280000	6.05240000	0.00000000
85	3187.91860000	0.05610000	0.00000000
86	3193.26260000	1.67860000	0.00000000
87	3194.37160000	0.05260000	0.00000000
88	3204.29420000	1.08880000	0.00000000
89	3232.13690000	0.76870000	0.00000000
90	3714.58680000	86.62380000	0.00000000

S32. CALCULATIONS ON TRANSITION FROM 4H TO 4F (DOUBLE HYDROGEN SHIFT)



Route	: # opt=qst2 freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd	
	: 3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C[C](C(=O)[O])O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.35105235	a.u.
Gibbs Energy	: -747.13137900	a.u.
Number of imaginary frequencies	: 1	

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

32

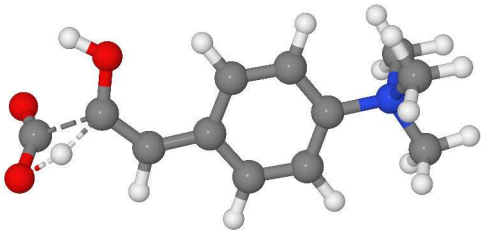
C	-1.31110001	-0.97480899	0.10474600
C	0.05968500	-0.79409999	0.08600200
C	0.61790401	0.48219201	-0.05490200
C	-0.25403500	1.56479394	-0.17671400
C	-1.63148201	1.39570296	-0.15876800
C	-2.15711308	0.12158400	-0.01719200
H	-1.69598198	-1.97736299	0.21646699
H	2.83555603	1.00100696	1.00759900
H	0.14404300	2.56426692	-0.28281400
H	-2.25406909	2.26889896	-0.25628901
N	-3.64163303	-0.11704400	0.01183200
C	-4.43551588	1.15032995	-0.12902901
H	-5.48729897	0.88549203	-0.09730300
H	-4.19916296	1.81594896	0.69378000
H	-4.20250702	1.61692595	-1.07979906
C	-4.03217697	-1.02922702	-1.12589896
H	-3.52052903	-1.97748101	-1.01631498
H	-5.10740709	-1.17967105	-1.09397495
H	-3.73915410	-0.55572802	-2.05728412
C	-4.02778721	-0.75371802	1.32531095
H	-3.73153400	-0.08537300	2.12724900
H	-5.10308409	-0.90701503	1.33141696
H	-3.51609612	-1.70281303	1.42719996
C	3.05042505	-0.24848101	-0.33645701
O	4.26567221	0.92188197	1.22337198
C	2.07053590	0.71442401	-0.02459600
H	2.38016391	1.69363105	-0.40010101
C	4.40063381	0.01407500	0.35296899
O	2.96334004	-1.37320995	-0.93795902
O	5.30268717	-0.74288201	0.01348700
H	0.69642001	-1.66035497	0.18120700
H	3.89572811	-1.73952997	-0.86546600

S32.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-1498.53430000	1901.69090000	0.00000000
2	11.98460000	0.40810000	0.00000000
3	40.81910000	0.86900000	0.00000000
4	55.56280000	0.81730000	0.00000000
5	78.11840000	1.73650000	0.00000000
6	120.19630000	3.62330000	0.00000000
7	163.91140000	1.03680000	0.00000000
8	217.14780000	0.48560000	0.00000000
9	220.24910000	1.45720000	0.00000000
10	242.17160000	2.80770000	0.00000000
11	275.19710000	3.13210000	0.00000000
12	281.78040000	2.24990000	0.00000000
13	295.26570000	52.94870000	0.00000000
14	328.15350000	5.16510000	0.00000000
15	352.56870000	0.09630000	0.00000000
16	374.31990000	0.56590000	0.00000000
17	393.46070000	0.16710000	0.00000000
18	409.39890000	2.24100000	0.00000000
19	420.16440000	0.02470000	0.00000000
20	450.09120000	2.64570000	0.00000000
21	480.67290000	1.08730000	0.00000000
22	512.66300000	23.03490000	0.00000000
23	563.54110000	35.82450000	0.00000000
24	579.61840000	4.83020000	0.00000000
25	613.61710000	14.85970000	0.00000000
26	652.88280000	2.15780000	0.00000000
27	701.74810000	7.74860000	0.00000000
28	711.99780000	15.55920000	0.00000000
29	751.68570000	78.36040000	0.00000000
30	756.42250000	6.72780000	0.00000000
31	824.82110000	16.54480000	0.00000000
32	835.03250000	0.18980000	0.00000000
33	843.92210000	52.38880000	0.00000000
34	867.91140000	23.64350000	0.00000000
35	889.12080000	29.90190000	0.00000000
36	902.47690000	26.11090000	0.00000000
37	943.77400000	29.25190000	0.00000000
38	961.76490000	46.98460000	0.00000000
39	962.58630000	38.02420000	0.00000000
40	984.06280000	0.40560000	0.00000000
41	995.68070000	0.20590000	0.00000000
42	1036.37610000	7.58560000	0.00000000
43	1076.93230000	0.02540000	0.00000000
44	1094.46490000	22.38270000	0.00000000
45	1133.33620000	1.29670000	0.00000000
46	1136.08290000	4.92120000	0.00000000
47	1140.32340000	0.46800000	0.00000000
48	1174.52260000	2.42930000	0.00000000
49	1216.03620000	27.12250000	0.00000000
50	1238.69910000	9.15260000	0.00000000
51	1258.15270000	1.70740000	0.00000000
52	1258.30860000	1.58390000	0.00000000
53	1295.48970000	4.48460000	0.00000000
54	1312.06600000	193.04980000	0.00000000
55	1322.10480000	165.56590000	0.00000000
56	1330.14400000	49.14140000	0.00000000
57	1360.21600000	2.56600000	0.00000000
58	1374.99640000	5.12780000	0.00000000
59	1449.73590000	1.89510000	0.00000000
60	1451.52990000	4.79130000	0.00000000

61	1460.58840000	20.98430000	0.00000000
62	1476.46950000	208.66540000	0.00000000
63	1479.86500000	0.09120000	0.00000000
64	1489.15550000	0.55800000	0.00000000
65	1493.45910000	1.84820000	0.00000000
66	1495.61320000	0.68860000	0.00000000
67	1507.47030000	28.86750000	0.00000000
68	1513.20410000	24.20070000	0.00000000
69	1530.44080000	47.91080000	0.00000000
70	1551.48020000	49.07060000	0.00000000
71	1623.21340000	81.35040000	0.00000000
72	1638.32930000	309.93050000	0.00000000
73	1650.22010000	15.43500000	0.00000000
74	1787.35510000	186.71900000	0.00000000
75	1834.34370000	292.53410000	0.00000000
76	3060.97790000	16.78860000	0.00000000
77	3079.80090000	0.39190000	0.00000000
78	3081.02360000	1.37920000	0.00000000
79	3087.88970000	1.10380000	0.00000000
80	3167.67850000	0.01020000	0.00000000
81	3168.41870000	1.20270000	0.00000000
82	3175.53000000	9.72040000	0.00000000
83	3182.55980000	0.20150000	0.00000000
84	3182.91050000	424.91430000	0.00000000
85	3187.26220000	0.42640000	0.00000000
86	3187.92310000	0.17170000	0.00000000
87	3188.69460000	0.47020000	0.00000000
88	3198.86990000	1.20910000	0.00000000
89	3214.30390000	0.49020000	0.00000000
90	3235.24280000	0.55710000	0.00000000

S33. CALCULATIONS ON TRANSITION FROM 4B/4A TO 7A



Route	: # opt=(calcfc,qst3) freq b3lyp/cc-pvtz geom=connectivity empiricaldisp	
	: ersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=[C]O.[C](=O)O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.31758152	a.u.
Gibbs Energy	: -747.10084200	a.u.
Number of imaginary frequencies	: 1	

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

32

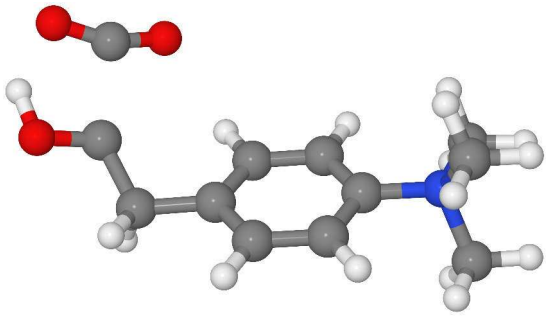
C	-1.60360503	-1.09232402	0.04807400
C	-0.22797599	-0.97820598	0.11882700
C	0.38724601	0.28454700	0.18181200
C	-0.44210601	1.41345096	0.17555800
C	-1.82231700	1.30668497	0.10432200
C	-2.39961910	0.04787200	0.03974000
H	-2.03375411	-2.08154607	-0.00104900
H	0.37706000	-1.86870003	0.12285600
H	0.00099400	2.39815092	0.22458100
H	-2.40676689	2.21103311	0.10073700
N	-3.89141297	-0.12675899	-0.04208900
C	-4.63001013	1.18092501	-0.04345300
H	-5.69070101	0.96036798	-0.10472200
H	-4.41793203	1.71463203	0.87637299
H	-4.32552814	1.76492202	-0.90491802
C	-4.24726391	-0.85337698	-1.31670105
H	-3.77650189	-1.82867002	-1.31597400
H	-5.32726812	-0.95969898	-1.36309695
H	-3.88345408	-0.26767501	-2.15464592
C	-4.37503386	-0.92308801	1.14564502
H	-4.10159779	-0.38676101	2.04849792
H	-5.45373583	-1.02862799	1.07405996
H	-3.90403104	-1.89823699	1.13840902
C	2.82437611	-0.43669301	0.27607501
O	2.57386303	-1.76707196	0.22100000
C	1.82338905	0.48008800	0.24152599
H	2.15307212	1.51078498	0.27715701
C	4.49018478	0.14206500	-0.38827601
O	4.80174923	-0.30737901	-1.42575502
O	4.86187220	0.85556102	0.57396102
H	3.79611897	0.22819300	1.01957095
H	3.39937401	-2.26225090	0.18261001

S33.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2004.75240000	1270.78470000	0.00000000
2	25.00000000	0.43730000	0.00000000
3	31.34510000	1.19510000	0.00000000
4	61.09850000	0.15870000	0.00000000
5	63.75600000	7.44410000	0.00000000
6	82.15970000	0.60250000	0.00000000
7	112.61720000	7.36070000	0.00000000
8	154.94400000	5.72290000	0.00000000
9	190.70930000	21.34220000	0.00000000
10	225.26000000	9.87370000	0.00000000
11	238.95310000	6.62600000	0.00000000
12	275.84650000	60.90410000	0.00000000
13	282.17460000	6.86260000	0.00000000
14	299.52460000	13.40520000	0.00000000
15	346.29980000	36.35580000	0.00000000
16	353.13770000	0.68430000	0.00000000
17	370.72330000	20.88040000	0.00000000
18	373.47590000	53.08200000	0.00000000
19	397.17670000	30.63730000	0.00000000
20	422.25930000	2.26830000	0.00000000
21	434.73520000	63.01640000	0.00000000
22	472.44000000	11.15640000	0.00000000
23	485.44200000	17.87950000	0.00000000
24	534.83540000	111.74710000	0.00000000
25	554.52120000	10.79440000	0.00000000
26	618.85850000	35.40710000	0.00000000
27	647.58990000	255.20850000	0.00000000
28	651.07060000	32.01680000	0.00000000
29	659.58540000	326.67420000	0.00000000
30	688.04900000	358.96930000	0.00000000
31	750.88840000	1.44990000	0.00000000
32	774.42670000	33.30790000	0.00000000
33	830.41230000	4.49720000	0.00000000
34	839.17020000	10.39260000	0.00000000
35	851.49150000	24.69570000	0.00000000
36	860.62740000	25.99340000	0.00000000
37	902.93360000	26.93460000	0.00000000
38	944.66930000	29.61830000	0.00000000
39	962.66530000	16.87170000	0.00000000
40	986.18840000	0.46850000	0.00000000
41	1005.77240000	0.09720000	0.00000000
42	1034.43610000	13.66200000	0.00000000
43	1076.51590000	312.00560000	0.00000000
44	1076.61180000	0.49590000	0.00000000
45	1130.73540000	53.42290000	0.00000000
46	1133.61810000	9.91770000	0.00000000
47	1138.81550000	34.53670000	0.00000000
48	1139.85070000	0.61570000	0.00000000
49	1174.18010000	4.51280000	0.00000000
50	1226.86660000	22.79920000	0.00000000
51	1247.18940000	118.96580000	0.00000000
52	1258.19580000	1.40820000	0.00000000
53	1258.52450000	2.51010000	0.00000000
54	1260.36540000	1010.16930000	0.00000000
55	1292.14160000	160.35000000	0.00000000
56	1296.25960000	19.08030000	0.00000000
57	1340.04060000	15.66840000	0.00000000
58	1361.64910000	0.20290000	0.00000000
59	1409.78210000	11.47520000	0.00000000
60	1449.01170000	0.26100000	0.00000000

61	1451.17250000	4.70860000	0.00000000
62	1456.62530000	23.74300000	0.00000000
63	1479.50030000	0.00260000	0.00000000
64	1489.34520000	0.31390000	0.00000000
65	1493.41150000	1.41810000	0.00000000
66	1495.76740000	0.45860000	0.00000000
67	1506.86950000	26.44970000	0.00000000
68	1512.87860000	23.92320000	0.00000000
69	1530.55630000	46.99040000	0.00000000
70	1543.52990000	45.10920000	0.00000000
71	1577.16480000	36.22190000	0.00000000
72	1620.89950000	4.17300000	0.00000000
73	1640.47350000	12.50960000	0.00000000
74	1702.61830000	85.62540000	0.00000000
75	2063.03960000	373.97800000	0.00000000
76	3079.91940000	0.44820000	0.00000000
77	3081.00410000	1.57600000	0.00000000
78	3087.92410000	1.58380000	0.00000000
79	3167.43790000	0.01410000	0.00000000
80	3168.06720000	1.13890000	0.00000000
81	3169.78900000	0.17870000	0.00000000
82	3175.17900000	7.75440000	0.00000000
83	3182.71480000	0.18460000	0.00000000
84	3187.96560000	4.98710000	0.00000000
85	3189.06740000	0.02890000	0.00000000
86	3191.1.000000	0.66610000	0.00000000
87	3199.49150000	2.34200000	0.00000000
88	3235.56220000	0.89180000	0.00000000
89	3246.80400000	6.57470000	0.00000000
90	3803.25760000	180.23830000	0.00000000

S34. CALCULATIONS ON TRANSITION FROM 4F TO 5A



Route	: # opt=(calcfc,ts,noeigentest,maxstep=3) freq b3lyp/cc-pvtz geom=connec	
	: tivity empiricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C[C]O.C(=O)=O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.37117705	a.u.
Gibbs Energy	: -747.14805800	a.u.
Number of imaginary frequencies	: 2	

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

32

C	-1.72112095	-1.46735895	0.04612600
C	-0.41542101	-1.90946603	0.19319500
C	0.62559301	-1.01232898	0.42129999
C	0.32896101	0.34524700	0.49379799
C	-0.97430998	0.80227602	0.34564799
C	-1.99465406	-0.10822600	0.12281500
H	-2.49828196	-2.19549298	-0.13129801
H	-0.21077900	-2.96880388	0.12498300
H	1.11898100	1.06623006	0.63926202
H	-1.14876199	1.86331296	0.40298700
N	-3.42047095	0.34272099	-0.05240000
C	-3.57458496	1.83303499	0.05660300
H	-4.62581301	2.06596398	-0.07830500
H	-3.24840212	2.15724111	1.03858602
H	-2.98858595	2.31303811	-0.71925598
C	-3.91796088	-0.06883700	-1.41636598
H	-3.87811995	-1.14780998	-1.50114298
H	-4.94129515	0.27731001	-1.52964199
H	-3.27519011	0.38507700	-2.16360211
C	-4.28599119	-0.28458399	1.01242697
H	-3.90527296	0.01881500	1.98224795
H	-5.30651522	0.06152100	0.87608802
H	-4.24313021	-1.36274898	0.91960800
C	3.06351495	-0.66341001	-0.08753800
O	4.09208202	-1.33343804	-0.43782499
C	2.03812504	-1.51336396	0.59053600
H	2.31473303	-1.44636202	1.65374804
H	2.13370109	-2.56655693	0.31544900
C	3.65682507	1.40962899	-0.68480301
O	2.81236100	2.17096090	-0.39014801

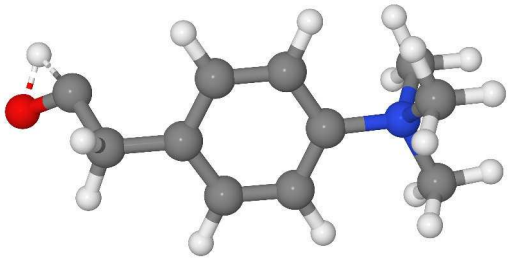
O	4.70148706	1.06265497	-1.13417196
H	4.71888494	-0.67212099	-0.84007001

S34.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-158.64140000	101.52250000	0.00000000
2	-8.61120000	0.45760000	0.00000000
3	31.85480000	1.69870000	0.00000000
4	45.54370000	1.48190000	0.00000000
5	65.14280000	2.71660000	0.00000000
6	96.25600000	2.46070000	0.00000000
7	123.89430000	1.37610000	0.00000000
8	184.77190000	10.00730000	0.00000000
9	213.43880000	0.19480000	0.00000000
10	218.90740000	0.09010000	0.00000000
11	248.24540000	0.37950000	0.00000000
12	260.04570000	0.98160000	0.00000000
13	278.67220000	0.20020000	0.00000000
14	323.86130000	2.39970000	0.00000000
15	328.18330000	0.31990000	0.00000000
16	353.20450000	0.07500000	0.00000000
17	365.52830000	0.69820000	0.00000000
18	382.28880000	0.10510000	0.00000000
19	421.95240000	0.44020000	0.00000000
20	428.31910000	6.65840000	0.00000000
21	446.12290000	1.28390000	0.00000000
22	473.31770000	4.39960000	0.00000000
23	500.85900000	43.23710000	0.00000000
24	557.06010000	20.51860000	0.00000000
25	572.90370000	64.00140000	0.00000000
26	608.59350000	254.52600000	0.00000000
27	654.70660000	7.41840000	0.00000000
28	668.13350000	10.74130000	0.00000000
29	696.63690000	15.26310000	0.00000000
30	741.41810000	1.89050000	0.00000000
31	789.20960000	0.50100000	0.00000000
32	839.88450000	1.64840000	0.00000000
33	841.96620000	20.63750000	0.00000000
34	861.31510000	34.20270000	0.00000000
35	866.99510000	23.28660000	0.00000000
36	945.99520000	27.58050000	0.00000000
37	962.30560000	15.14860000	0.00000000
38	985.55110000	0.72650000	0.00000000
39	1010.17120000	3.40670000	0.00000000
40	1027.16800000	68.55450000	0.00000000
41	1037.85710000	34.38300000	0.00000000
42	1039.79850000	17.37810000	0.00000000
43	1076.78860000	0.02370000	0.00000000
44	1132.46020000	2.15650000	0.00000000
45	1134.49900000	1.70760000	0.00000000
46	1140.23240000	0.42970000	0.00000000
47	1166.19260000	21.89560000	0.00000000
48	1177.94900000	12.47820000	0.00000000
49	1220.88960000	11.87920000	0.00000000
50	1238.53740000	0.92380000	0.00000000
51	1258.83890000	1.43590000	0.00000000
52	1258.86050000	1.41460000	0.00000000
53	1275.18430000	70.33600000	0.00000000
54	1294.92070000	3.89530000	0.00000000
55	1304.07960000	14.28260000	0.00000000
56	1354.08500000	9.24970000	0.00000000
57	1369.46530000	0.50680000	0.00000000
58	1418.49270000	10.02770000	0.00000000
59	1434.64730000	186.12990000	0.00000000
60	1449.90500000	5.25260000	0.00000000

61	1451.15560000	4.53010000	0.00000000
62	1461.64690000	27.14150000	0.00000000
63	1479.64510000	0.00450000	0.00000000
64	1489.39430000	0.24240000	0.00000000
65	1492.08940000	148.40460000	0.00000000
66	1493.33500000	3.92540000	0.00000000
67	1496.06260000	5.03570000	0.00000000
68	1507.34140000	27.11350000	0.00000000
69	1512.73280000	24.09510000	0.00000000
70	1530.64360000	48.48690000	0.00000000
71	1551.29910000	43.92610000	0.00000000
72	1635.33220000	3.34580000	0.00000000
73	1648.84450000	3.56680000	0.00000000
74	2208.60220000	506.70940000	0.00000000
75	2973.87000000	7.43610000	0.00000000
76	3052.05510000	11.12970000	0.00000000
77	3079.71600000	0.48790000	0.00000000
78	3080.98280000	1.42770000	0.00000000
79	3087.98860000	1.42320000	0.00000000
80	3167.33810000	0.01170000	0.00000000
81	3168.05100000	0.84930000	0.00000000
82	3175.20690000	5.92950000	0.00000000
83	3183.29940000	0.13690000	0.00000000
84	3184.08230000	4.10590000	0.00000000
85	3187.92930000	0.03540000	0.00000000
86	3190.72530000	0.19420000	0.00000000
87	3203.83000000	1.55690000	0.00000000
88	3212.36310000	18.17970000	0.00000000
89	3235.72980000	3.69150000	0.00000000
90	3262.36940000	268.37510000	0.00000000

S35. CALCULATIONS ON TRANSITION FROM 5A TO 6



Route	: # opt=(calcfc,ts) freq b3lyp/cc-pvtz geom=connectivity empiricaldisper	
	: sion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C[C]O	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.64482188	a.u.
Gibbs Energy	: -558.43858000	a.u.
Number of imaginary frequencies	: 1	

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

29

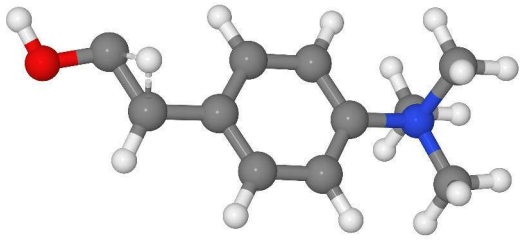
C	3.14183402	-0.99320501	4.06907606
C	3.62606692	-0.54001701	2.85505700
C	2.80828094	0.17531900	1.97697306
C	1.49099100	0.41260999	2.34799504
C	0.98993200	-0.03441700	3.56680703
C	1.82143497	-0.73646802	4.42213678
H	3.80630493	-1.54239500	4.71929121
H	4.64838886	-0.75284499	2.57899809
H	0.83406401	0.95464897	1.68253005
H	-0.03798700	0.17873199	3.80645299
N	1.32961297	-1.24545503	5.75073099
C	-0.10886700	-0.90001500	6.00824499
H	-0.37547100	-1.30146694	6.98048687
H	-0.22469400	0.17815000	6.01098680
H	-0.72954601	-1.35051703	5.24167109
C	1.45287299	-2.74906301	5.79447889
H	2.49257302	-3.02657104	5.67260122
H	1.08309305	-3.09801006	6.75436592
H	0.86240602	-3.16212106	4.98315382
C	2.15069699	-0.63845998	6.86201096
H	2.05350590	0.44086400	6.80581522
H	1.77410698	-1.00846398	7.81129885
H	3.18815398	-0.92271101	6.73675299
C	3.96467996	-0.44974801	-0.16080500
O	3.75252604	-0.41838500	-1.43619704
C	3.33789802	0.65156901	0.65447098
H	2.57275105	1.14918196	0.05190600
H	4.14880800	1.37204695	0.81911302
H	4.45057583	-1.26145005	-0.98665899

S35.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-2049.63170000	766.03540000	0.00000000
2	22.75440000	0.31740000	0.00000000
3	44.60160000	0.48830000	0.00000000
4	67.76880000	0.46120000	0.00000000
5	90.32790000	1.30080000	0.00000000
6	156.60880000	0.85310000	0.00000000
7	212.53570000	0.24560000	0.00000000
8	232.64370000	0.41110000	0.00000000
9	267.19710000	0.29410000	0.00000000
10	284.72070000	0.13890000	0.00000000
11	296.99610000	1.33450000	0.00000000
12	352.25900000	0.68190000	0.00000000
13	352.94170000	1.55800000	0.00000000
14	382.71410000	0.11830000	0.00000000
15	405.98340000	1.53150000	0.00000000
16	421.07200000	0.01350000	0.00000000
17	441.28890000	1.69900000	0.00000000
18	456.01930000	2.22050000	0.00000000
19	483.74110000	0.86610000	0.00000000
20	535.47290000	26.65790000	0.00000000
21	558.25470000	13.87780000	0.00000000
22	584.31700000	22.96500000	0.00000000
23	653.50840000	0.58840000	0.00000000
24	691.66100000	7.62490000	0.00000000
25	744.79210000	0.86130000	0.00000000
26	811.37500000	12.11490000	0.00000000
27	835.49750000	0.62270000	0.00000000
28	842.20310000	32.01050000	0.00000000
29	862.81150000	9.64260000	0.00000000
30	877.76160000	5.93960000	0.00000000
31	944.95870000	21.27610000	0.00000000
32	963.02700000	18.37130000	0.00000000
33	982.27070000	1.29810000	0.00000000
34	998.13670000	13.00200000	0.00000000
35	1009.32230000	65.36310000	0.00000000
36	1038.85550000	16.26280000	0.00000000
37	1076.97620000	0.02070000	0.00000000
38	1130.24720000	13.42650000	0.00000000
39	1131.88520000	3.61480000	0.00000000
40	1140.42650000	0.42740000	0.00000000
41	1148.45890000	43.02900000	0.00000000
42	1172.35430000	9.19270000	0.00000000
43	1222.35300000	12.99390000	0.00000000
44	1231.41340000	1.97060000	0.00000000
45	1258.60370000	1.77180000	0.00000000
46	1259.01430000	1.53300000	0.00000000
47	1286.09200000	0.61240000	0.00000000
48	1295.60280000	2.18200000	0.00000000
49	1353.72770000	2.37790000	0.00000000
50	1363.55440000	1.27480000	0.00000000
51	1436.44270000	7.09410000	0.00000000
52	1446.52420000	235.43710000	0.00000000
53	1450.16650000	39.51960000	0.00000000
54	1451.28140000	5.07350000	0.00000000
55	1462.50220000	49.97960000	0.00000000
56	1479.55970000	0.1.000000	0.00000000
57	1489.31810000	0.29360000	0.00000000
58	1493.24120000	2.27600000	0.00000000
59	1495.69650000	0.50790000	0.00000000
60	1507.16980000	26.33430000	0.00000000

61	1512.84740000	23.87290000	0.00000000
62	1530.62330000	46.03720000	0.00000000
63	1547.61560000	46.09130000	0.00000000
64	1633.76060000	2.24130000	0.00000000
65	1646.85200000	5.53090000	0.00000000
66	2598.83610000	122.34570000	0.00000000
67	2997.82720000	5.41160000	0.00000000
68	3052.41300000	7.12720000	0.00000000
69	3079.65950000	0.49260000	0.00000000
70	3080.91040000	1.45370000	0.00000000
71	3087.89110000	1.35770000	0.00000000
72	3167.33320000	0.01900000	0.00000000
73	3167.99930000	0.78870000	0.00000000
74	3175.08760000	5.95940000	0.00000000
75	3182.88340000	0.18750000	0.00000000
76	3186.63340000	4.17400000	0.00000000
77	3188.05250000	0.07170000	0.00000000
78	3191.48600000	0.84470000	0.00000000
79	3196.52790000	1.13780000	0.00000000
80	3207.61890000	0.70060000	0.00000000
81	3234.28330000	0.42080000	0.00000000

S36. CALCULATIONS ON TRANSITION FROM 5A TO 7C



Route	: # opt=(calcfc,qst3) freq b3lyp/cc-pvtz geom=connectivity empiricaldisp	
	: ersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)[CH][CH]O	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.66440567	a.u.
Gibbs Energy	: -558.45463900	a.u.
Number of imaginary frequencies	: 1	

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

29

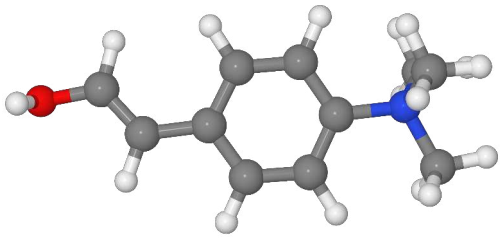
C	-0.45862299	-1.24052703	-0.13514200
C	0.91800803	-1.18318796	-0.23545501
C	1.58738804	0.04645900	-0.19946299
C	0.82964498	1.20978904	-0.09176000
C	-0.55696601	1.16452301	-0.00467300
C	-1.19457901	-0.06453400	-0.02177600
H	-0.93824297	-2.20755792	-0.16518100
H	1.49535406	-2.08840609	-0.34830800
H	1.32239497	2.17185092	-0.07462700
H	-1.09552801	2.09340906	0.07590300
N	-2.69351411	-0.17086200	0.06030100
C	-3.36472106	1.16637599	0.18691701
H	-4.43443823	0.99414802	0.24628000
H	-3.02013803	1.65715504	1.09044397
H	-3.13727307	1.76720905	-0.68661898
C	-3.22393894	-0.83213103	-1.18879402
H	-2.80379891	-1.82676196	-1.27277899
H	-4.30633307	-0.88825703	-1.11664701
H	-2.92736101	-0.23211800	-2.04294205
C	-3.07780600	-0.99044299	1.26805496
H	-2.68179798	-0.50016302	2.15142202
H	-4.16143322	-1.04859197	1.31497300
H	-2.65536809	-1.98337400	1.17628300
C	3.87259412	-1.00351202	-0.25321499
O	5.15731096	-0.70817500	-0.52045000
C	3.05905700	0.13323800	-0.29128000
H	3.41400695	-0.49356899	0.85101098
H	3.47119093	1.11532700	-0.53707302
H	5.68779278	-1.49689698	-0.36838099

S36.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-1417.07080000	57.29820000	0.00000000
2	45.05150000	0.32970000	0.00000000
3	52.50310000	0.84980000	0.00000000
4	108.37300000	1.80600000	0.00000000
5	126.72700000	4.03700000	0.00000000
6	182.31150000	1.36490000	0.00000000
7	226.16900000	0.32440000	0.00000000
8	250.22460000	1.53840000	0.00000000
9	270.00350000	1.33220000	0.00000000
10	287.18560000	2.39960000	0.00000000
11	305.27960000	0.12620000	0.00000000
12	349.76330000	0.08240000	0.00000000
13	352.12820000	0.08330000	0.00000000
14	399.59440000	0.74520000	0.00000000
15	419.95460000	0.55440000	0.00000000
16	430.58540000	1.39990000	0.00000000
17	445.05400000	1.56820000	0.00000000
18	471.12820000	1.26580000	0.00000000
19	489.12490000	3.67750000	0.00000000
20	572.13980000	29.29120000	0.00000000
21	585.55260000	7.86530000	0.00000000
22	651.37060000	31.67140000	0.00000000
23	656.22730000	73.85950000	0.00000000
24	715.94770000	8.80920000	0.00000000
25	748.88540000	0.68290000	0.00000000
26	835.24110000	5.00960000	0.00000000
27	841.21090000	21.10680000	0.00000000
28	855.15950000	22.51860000	0.00000000
29	879.33540000	24.83760000	0.00000000
30	941.53240000	9.98450000	0.00000000
31	953.98890000	26.79100000	0.00000000
32	963.31500000	16.07570000	0.00000000
33	988.24240000	2.93450000	0.00000000
34	1017.28890000	1.36080000	0.00000000
35	1035.55760000	9.66690000	0.00000000
36	1076.93500000	0.01940000	0.00000000
37	1128.54170000	1.85910000	0.00000000
38	1129.12270000	27.81700000	0.00000000
39	1140.18430000	0.51030000	0.00000000
40	1152.30210000	106.01020000	0.00000000
41	1169.91050000	7.18430000	0.00000000
42	1179.81900000	332.85890000	0.00000000
43	1194.40650000	24.96180000	0.00000000
44	1219.34750000	0.29820000	0.00000000
45	1257.51960000	9.48830000	0.00000000
46	1258.64600000	1.43020000	0.00000000
47	1262.29810000	35.82660000	0.00000000
48	1295.30770000	0.20920000	0.00000000
49	1337.61810000	27.58200000	0.00000000
50	1353.45700000	3.59200000	0.00000000
51	1375.32610000	24.61620000	0.00000000
52	1436.41660000	27.11180000	0.00000000
53	1450.30610000	10.93920000	0.00000000
54	1451.16400000	4.62650000	0.00000000
55	1479.51760000	0.00910000	0.00000000
56	1489.29310000	0.26710000	0.00000000
57	1490.59270000	19.54010000	0.00000000
58	1493.38010000	4.43770000	0.00000000
59	1496.95110000	6.38290000	0.00000000
60	1507.11830000	26.50710000	0.00000000

61	1512.82220000	23.92580000	0.00000000
62	1530.42370000	45.43190000	0.00000000
63	1544.39320000	61.88300000	0.00000000
64	1628.63060000	2.96790000	0.00000000
65	1644.76200000	11.67200000	0.00000000
66	2048.65680000	31.89320000	0.00000000
67	3047.71100000	19.92300000	0.00000000
68	3079.62550000	0.51200000	0.00000000
69	3080.87510000	1.44260000	0.00000000
70	3087.81940000	1.48250000	0.00000000
71	3167.33600000	0.01030000	0.00000000
72	3167.96390000	0.88790000	0.00000000
73	3175.07040000	6.53420000	0.00000000
74	3182.67540000	0.19880000	0.00000000
75	3186.75400000	3.64680000	0.00000000
76	3188.21860000	0.12560000	0.00000000
77	3189.66350000	0.67780000	0.00000000
78	3198.06250000	1.37740000	0.00000000
79	3212.54730000	4.83770000	0.00000000
80	3235.16700000	0.72120000	0.00000000
81	3806.54120000	213.33610000	0.00000000

S37. CALCULATIONS ON TRANSITION FROM 7C TO 7B



Route	: # opt=qst2 freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd	
	: 3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=CO	
Formula	: $C_{11}H_{16}NO^{+}$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -558.76550590	a.u.
Gibbs Energy	: -558.55295700	a.u.
Number of imaginary frequencies	: 1	

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

29

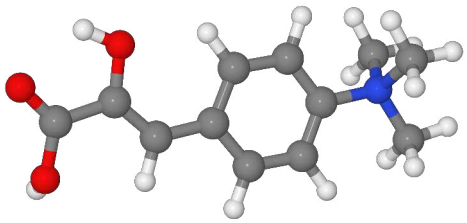
C	-0.38632199	-1.09381497	0.05902800
C	0.98995501	-0.99087697	0.04769800
C	1.62932801	0.25742999	-0.02960900
C	0.81246102	1.39130497	-0.07718700
C	-0.57266998	1.30177605	-0.06362200
C	-1.17118204	0.05489100	0.00137100
H	-0.82815301	-2.07753801	0.11720600
H	1.57142794	-1.89841497	0.10431400
H	1.26808405	2.36983991	-0.13232601
H	-1.14332795	2.21415710	-0.10657700
N	-2.66668892	-0.10191500	0.01413200
C	-3.38677597	1.21374202	-0.05272600
H	-4.45220709	1.00819802	-0.04024200
H	-3.11757302	1.81469297	0.80878800
H	-3.12061596	1.72234595	-0.97267801
C	-3.10121202	-0.92093098	-1.17661595
H	-2.64107203	-1.89992595	-1.12383497
H	-4.18325901	-1.01500702	-1.15611696
H	-2.77767491	-0.40885299	-2.07691193
C	-3.09567308	-0.79294002	1.28513598
H	-2.76761699	-0.19088000	2.12617111
H	-4.17785120	-0.88749802	1.27971804
H	-2.63662100	-1.77271998	1.33162904
C	3.97597003	-0.55552298	-0.15470199
O	5.31390476	-0.31688300	-0.26886800
C	3.07593989	0.42548299	-0.06364900
H	3.44599390	1.44323695	-0.04348200
H	5.73925400	-0.23343900	0.59159201
H	3.69921207	-1.60317099	-0.22854599

S37.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-511.26800000	97.63170000	0.00000000
2	20.69880000	3.70350000	0.00000000
3	50.12340000	0.46600000	0.00000000
4	85.81020000	5.16810000	0.00000000
5	118.71560000	0.72590000	0.00000000
6	164.72160000	4.32290000	0.00000000
7	224.45840000	0.64270000	0.00000000
8	249.12020000	0.22450000	0.00000000
9	271.74920000	1.00930000	0.00000000
10	289.57270000	1.64550000	0.00000000
11	291.14410000	2.58510000	0.00000000
12	350.43480000	1.53600000	0.00000000
13	351.35020000	0.13040000	0.00000000
14	398.97040000	1.59830000	0.00000000
15	418.86550000	0.06390000	0.00000000
16	428.02610000	1.07440000	0.00000000
17	446.29350000	0.98920000	0.00000000
18	469.58980000	1.94370000	0.00000000
19	488.46890000	1.74970000	0.00000000
20	565.72910000	28.96950000	0.00000000
21	583.43770000	2.91230000	0.00000000
22	654.52850000	0.01730000	0.00000000
23	716.78470000	5.26530000	0.00000000
24	743.20860000	4.01940000	0.00000000
25	827.46230000	4.10150000	0.00000000
26	838.90260000	33.82410000	0.00000000
27	843.42270000	19.22160000	0.00000000
28	884.61700000	21.44350000	0.00000000
29	887.94630000	17.37600000	0.00000000
30	943.46890000	15.13860000	0.00000000
31	962.41670000	53.11900000	0.00000000
32	963.80900000	16.63470000	0.00000000
33	984.81890000	10.70130000	0.00000000
34	991.11170000	0.52520000	0.00000000
35	1032.19910000	4.12640000	0.00000000
36	1076.79160000	0.02160000	0.00000000
37	1113.11650000	363.75480000	0.00000000
38	1132.34890000	0.14570000	0.00000000
39	1135.20730000	46.11720000	0.00000000
40	1139.92690000	0.48380000	0.00000000
41	1171.68110000	13.68020000	0.00000000
42	1219.10270000	1.39430000	0.00000000
43	1229.49090000	19.32020000	0.00000000
44	1258.88020000	1.64110000	0.00000000
45	1259.00470000	1.80620000	0.00000000
46	1273.08350000	2.10770000	0.00000000
47	1295.58660000	2.26210000	0.00000000
48	1313.98340000	0.14360000	0.00000000
49	1351.45470000	7.67270000	0.00000000
50	1363.14400000	7.94720000	0.00000000
51	1370.58420000	9.55580000	0.00000000
52	1448.50180000	1.58530000	0.00000000
53	1450.64090000	4.61560000	0.00000000
54	1457.61350000	13.97190000	0.00000000
55	1479.32340000	0.01200000	0.00000000
56	1489.27280000	0.32300000	0.00000000
57	1493.02150000	1.83300000	0.00000000
58	1495.78920000	0.32870000	0.00000000
59	1506.95620000	26.73280000	0.00000000
60	1512.51900000	23.76080000	0.00000000

61	1530.40820000	43.89730000	0.00000000
62	1548.42190000	44.63490000	0.00000000
63	1619.71520000	2.89100000	0.00000000
64	1643.09070000	70.19520000	0.00000000
65	1702.13950000	238.56150000	0.00000000
66	3078.98980000	0.59400000	0.00000000
67	3080.53620000	1.93900000	0.00000000
68	3087.65580000	1.89650000	0.00000000
69	3128.26730000	19.47670000	0.00000000
70	3166.56860000	7.42610000	0.00000000
71	3166.67540000	0.00300000	0.00000000
72	3167.55090000	1.03340000	0.00000000
73	3174.71400000	7.66500000	0.00000000
74	3182.69370000	0.21060000	0.00000000
75	3185.33910000	5.47410000	0.00000000
76	3187.66460000	0.05390000	0.00000000
77	3190.79380000	2.22710000	0.00000000
78	3195.88210000	0.93430000	0.00000000
79	3209.99780000	1.51520000	0.00000000
80	3232.31460000	0.93310000	0.00000000
81	3797.56080000	164.60360000	0.00000000

S38. CALCULATIONS ON TRANSTTION FROM 4A TO 4H



Route	: # opt=qst3 freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd	
	: 3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=C(C(=O)O)O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.41923652	a.u.
Gibbs Energy	: -747.19443000	a.u.
Number of imaginary frequencies	: 1	

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

32

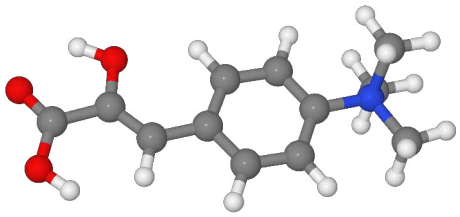
C	3.98891306	-2.09869599	5.50191307
C	4.09606218	-1.70156598	4.18258190
C	4.44787312	-0.38052601	3.85180306
C	4.67868423	0.51000702	4.90870714
C	4.57341290	0.11919300	6.23440123
C	4.22814608	-1.19109404	6.52776098
H	3.71811604	-3.12387204	5.70689011
H	3.90928602	-2.41768789	3.40064907
H	4.95141315	1.53283203	4.69005108
H	4.76624393	0.85095698	7.00057507
N	4.10502386	-1.67240202	7.94763517
C	4.38614082	-0.59281498	8.95228386
H	4.27449989	-1.02496004	9.94138527
H	5.40088892	-0.23424099	8.81985092
H	3.67425799	0.21451101	8.82072639
C	2.70280600	-2.17245102	8.19514370
H	2.49258399	-2.99478507	7.52259684
H	2.63152409	-2.50568509	9.22660255
H	2.01306796	-1.35603595	8.00751495
C	5.08969784	-2.79016495	8.19080734
H	6.08815289	-2.41037107	8.00022316
H	4.99376202	-3.11737108	9.22220993
H	4.87251711	-3.61022401	7.51760006
C	4.46092415	-0.58886099	1.34648395
O	4.16121578	-1.89627802	1.28231704
C	4.58978319	0.10511700	2.49368501
H	4.86279106	1.14263499	2.37893009
C	4.66597986	0.02466100	0.00022800
O	4.62821579	-0.67777699	-0.97505999
O	4.96673203	1.35002196	-0.04807600
H	4.17849779	1.90432799	-0.00873500
H	4.18331099	-2.13636208	0.33735600

S38.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-526.11320000	122.67240000	0.00000000
2	28.20450000	0.68250000	0.00000000
3	37.81950000	1.57100000	0.00000000
4	63.43890000	0.35610000	0.00000000
5	91.54240000	1.18410000	0.00000000
6	98.64210000	4.29720000	0.00000000
7	149.21990000	1.12030000	0.00000000
8	189.27240000	1.05650000	0.00000000
9	221.10450000	0.19560000	0.00000000
10	230.20190000	1.15280000	0.00000000
11	271.95200000	1.59010000	0.00000000
12	282.23490000	0.38380000	0.00000000
13	302.66280000	2.38660000	0.00000000
14	351.37010000	0.09150000	0.00000000
15	361.27520000	16.11440000	0.00000000
16	371.31900000	0.98100000	0.00000000
17	389.03710000	0.39090000	0.00000000
18	415.38450000	5.21600000	0.00000000
19	422.79910000	0.01390000	0.00000000
20	439.50250000	3.28720000	0.00000000
21	481.33730000	1.98190000	0.00000000
22	511.44720000	4.19440000	0.00000000
23	528.37310000	24.24420000	0.00000000
24	568.63680000	0.99150000	0.00000000
25	585.09380000	7.04400000	0.00000000
26	649.52580000	82.52660000	0.00000000
27	651.13890000	7.58690000	0.00000000
28	684.72310000	5.81370000	0.00000000
29	731.70560000	6.72980000	0.00000000
30	745.91890000	38.83180000	0.00000000
31	748.79870000	1.38430000	0.00000000
32	828.80720000	1.74720000	0.00000000
33	840.26690000	43.06500000	0.00000000
34	851.41400000	12.06960000	0.00000000
35	868.32200000	3.01030000	0.00000000
36	892.25100000	2.60120000	0.00000000
37	898.53330000	37.30910000	0.00000000
38	944.28570000	28.78120000	0.00000000
39	963.95810000	17.47690000	0.00000000
40	981.91820000	0.53900000	0.00000000
41	1002.69030000	0.01260000	0.00000000
42	1033.93090000	6.52420000	0.00000000
43	1076.84190000	0.01980000	0.00000000
44	1109.86130000	209.81590000	0.00000000
45	1132.28250000	17.41890000	0.00000000
46	1133.37320000	14.85930000	0.00000000
47	1139.77550000	98.72350000	0.00000000
48	1139.93800000	16.80060000	0.00000000
49	1174.94780000	1.80060000	0.00000000
50	1227.01570000	50.41590000	0.00000000
51	1250.19360000	308.81530000	0.00000000
52	1256.43940000	51.91870000	0.00000000
53	1258.76790000	1.36030000	0.00000000
54	1259.94710000	43.20270000	0.00000000
55	1295.49570000	3.39270000	0.00000000
56	1338.22930000	34.12790000	0.00000000
57	1360.29070000	38.61540000	0.00000000
58	1378.84930000	156.50740000	0.00000000
59	1428.39000000	168.06050000	0.00000000
60	1449.04660000	2.02040000	0.00000000

61	1450.81900000	4.64020000	0.00000000
62	1459.99120000	9.91380000	0.00000000
63	1479.33270000	0.00830000	0.00000000
64	1489.35710000	0.31710000	0.00000000
65	1493.11470000	1.57500000	0.00000000
66	1495.71910000	0.22150000	0.00000000
67	1506.86130000	26.75930000	0.00000000
68	1512.60810000	23.74240000	0.00000000
69	1530.36460000	45.49840000	0.00000000
70	1546.34490000	56.04780000	0.00000000
71	1616.70880000	1.50790000	0.00000000
72	1640.92620000	32.11500000	0.00000000
73	1711.28590000	18.72410000	0.00000000
74	1786.76270000	421.87050000	0.00000000
75	3079.21510000	0.57400000	0.00000000
76	3080.60280000	1.92950000	0.00000000
77	3087.67310000	1.98180000	0.00000000
78	3166.82020000	0.00190000	0.00000000
79	3167.58260000	1.38430000	0.00000000
80	3174.72500000	8.51050000	0.00000000
81	3182.61540000	0.22690000	0.00000000
82	3186.46600000	5.42170000	0.00000000
83	3188.27180000	0.11820000	0.00000000
84	3189.34020000	1.25550000	0.00000000
85	3198.02490000	2.25490000	0.00000000
86	3211.56160000	0.72870000	0.00000000
87	3233.17800000	0.96220000	0.00000000
88	3245.97460000	6.30000000	0.00000000
89	3612.77450000	311.42570000	0.00000000
90	3804.97270000	153.29540000	0.00000000

S39. CALCULATIONS ON 4H



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)c1ccc(cc1)C=C(C(=O)O)O	
Formula	: $C_{12}H_{16}NO_3^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -747.42692436	a.u.
Gibbs Energy	: -747.20006900	a.u.
Number of imaginary frequencies	: 1	

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

32

C	-1.36854899	-1.00591004	-0.00030000
C	0.00535900	-0.85703599	-0.00010100
C	0.59360999	0.42046300	0.00058100
C	-0.26686299	1.52615094	0.00100600
C	-1.64568305	1.38458204	0.00079400
C	-2.19511795	0.11186700	0.00017000
H	-1.77310097	-2.00722003	-0.00087100
H	0.62874597	-1.73438203	-0.00048200
H	0.14859600	2.52422690	0.00151400
H	-2.25126791	2.27507710	0.00114000
N	-3.68371391	-0.10239800	-0.00017000
C	-4.45479488	1.18578804	-0.00048800
H	-5.51130676	0.93825299	-0.00051200
H	-4.20947123	1.75153899	0.89149302
H	-4.20936489	1.75117195	-0.89266902
C	-4.08490086	-0.87531000	-1.23302698
H	-3.58765197	-1.83738601	-1.22917902
H	-5.16254616	-1.01143503	-1.22029996
H	-3.78066492	-0.30552199	-2.10495591
C	-4.08558512	-0.87505901	1.23262405
H	-3.78160691	-0.30521199	2.10460305
H	-5.16325617	-1.01093900	1.21944594
H	-3.58857298	-1.83725202	1.22914195
C	3.01509309	-0.26096001	0.00057300
O	2.80440688	-1.58178306	-0.00009000
C	2.02596593	0.65332198	0.00085000
H	2.30934811	1.69640398	0.00125600
C	4.49043798	0.05117800	0.00090900
O	5.26280689	-0.87431598	0.00030800
O	4.91555691	1.31420898	0.00186800
H	4.18563795	1.94318604	0.00253200
H	3.69524693	-1.98978496	-0.00027400

S39.2. Frequencies

Mode	IR frequency	IR intensity	Raman intensity
1	-17.71650000	8.03420000	0.00000000
2	37.34450000	1.27800000	0.00000000
3	42.91330000	2.12480000	0.00000000
4	67.91670000	1.66590000	0.00000000
5	94.48670000	3.26130000	0.00000000
6	126.56300000	0.00400000	0.00000000
7	196.04650000	3.33450000	0.00000000
8	219.01570000	0.00770000	0.00000000
9	229.60180000	1.78020000	0.00000000
10	266.02690000	0.21590000	0.00000000
11	282.29210000	0.65190000	0.00000000
12	305.64920000	5.54970000	0.00000000
13	350.79070000	0.09830000	0.00000000
14	372.18920000	0.79170000	0.00000000
15	374.24630000	24.16450000	0.00000000
16	376.46910000	79.88290000	0.00000000
17	389.56810000	1.46880000	0.00000000
18	417.10210000	10.40370000	0.00000000
19	422.12330000	0.02590000	0.00000000
20	443.15250000	0.43900000	0.00000000
21	481.25290000	1.29240000	0.00000000
22	504.31750000	1.97160000	0.00000000
23	535.75260000	13.04900000	0.00000000
24	566.46720000	0.00300000	0.00000000
25	590.06510000	13.53920000	0.00000000
26	651.36150000	0.83070000	0.00000000
27	687.01830000	6.74680000	0.00000000
28	700.72930000	53.19000000	0.00000000
29	727.65340000	10.41220000	0.00000000
30	745.74830000	14.19020000	0.00000000
31	763.43600000	39.92010000	0.00000000
32	821.85570000	0.38120000	0.00000000
33	838.08180000	0.64360000	0.00000000
34	840.42190000	43.21140000	0.00000000
35	866.06530000	48.03650000	0.00000000
36	869.01580000	2.44120000	0.00000000
37	891.33230000	2.52540000	0.00000000
38	943.49540000	26.29340000	0.00000000
39	964.16390000	17.65770000	0.00000000
40	976.91930000	0.02770000	0.00000000
41	1001.36970000	0.00000000	0.00000000
42	1033.60260000	6.17150000	0.00000000
43	1077.02160000	0.01910000	0.00000000
44	1131.85080000	11.86080000	0.00000000
45	1133.36360000	3.50740000	0.00000000
46	1140.04530000	0.50310000	0.00000000
47	1142.76780000	64.65370000	0.00000000
48	1176.01020000	3.88550000	0.00000000
49	1186.84640000	32.60820000	0.00000000
50	1231.94240000	14.73100000	0.00000000
51	1258.73870000	1.35880000	0.00000000
52	1258.83650000	3.72870000	0.00000000
53	1263.65630000	12.23050000	0.00000000
54	1295.76950000	13.36680000	0.00000000
55	1314.01780000	703.51580000	0.00000000
56	1340.27090000	8.17180000	0.00000000
57	1362.11760000	11.70960000	0.00000000
58	1394.34740000	143.58900000	0.00000000
59	1443.00570000	178.57600000	0.00000000
60	1449.77380000	7.53580000	0.00000000

61	1450.91820000	4.65170000	0.00000000
62	1464.53880000	16.84900000	0.00000000
63	1479.44790000	0.00840000	0.00000000
64	1489.35070000	0.31750000	0.00000000
65	1493.04520000	1.36020000	0.00000000
66	1495.67690000	0.29020000	0.00000000
67	1507.02760000	26.83930000	0.00000000
68	1512.59890000	23.85020000	0.00000000
69	1530.22960000	44.56910000	0.00000000
70	1546.74410000	62.44760000	0.00000000
71	1617.23340000	1.68800000	0.00000000
72	1641.50870000	39.80850000	0.00000000
73	1714.24000000	73.32550000	0.00000000
74	1805.57810000	356.63830000	0.00000000
75	3079.26990000	0.54250000	0.00000000
76	3080.63910000	1.83300000	0.00000000
77	3087.63260000	1.79980000	0.00000000
78	3166.99710000	0.00200000	0.00000000
79	3167.74930000	1.35080000	0.00000000
80	3174.85480000	7.78460000	0.00000000
81	3175.03650000	13.33560000	0.00000000
82	3182.44970000	0.22580000	0.00000000
83	3186.28310000	8.94910000	0.00000000
84	3187.06370000	1.09230000	0.00000000
85	3188.01910000	0.05180000	0.00000000
86	3198.28680000	2.12620000	0.00000000
87	3232.91430000	0.83070000	0.00000000
88	3249.80530000	7.13510000	0.00000000
89	3534.41840000	403.21620000	0.00000000
90	3810.63760000	35.16600000	0.00000000

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) map343n_0ma_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: map343n_0ma_a

```
Bond precision:  C-C = 0.0022 A          Wavelength=1.54178

Cell:          a=8.6578(3)       b=10.0035(4)     c=11.6371(4)
               alpha=78.764(1)   beta=75.978(1)   gamma=67.163(1)
Temperature:   100 K
```

	Calculated	Reported
Volume	895.44(6)	895.44(6)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C11 H13 N O3, C9 H11 N O	C11 H13 N O3, C9 H11 N O
Sum formula	C20 H24 N2 O4	C20 H24 N2 O4
Mr	356.41	356.41
Dx,g cm-3	1.322	1.322
Z	2	2
Mu (mm-1)	0.754	0.754
F000	380.0	380.0
F000'	381.18	
h,k,lmax	10,12,14	10,12,14
Nref	3536	3476
Tmin,Tmax	0.939,0.978	0.628,0.754
Tmin'	0.860	

```
Correction method= # Reported T Limits: Tmin=0.628 Tmax=0.754
AbsCorr = MULTI-SCAN

Data completeness= 0.983          Theta(max)= 72.152

R(reflections)= 0.0440( 3173)     wR2(reflections)= 0.1273( 3476)

S = 1.106                 Npar= 253
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT222_ALERT_3_C Non-Solv.  Resd 1  H   Uiso(max)/Uiso(min) Range        4.1 Ratio
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.679 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         40 Report
```

Alert level G

```
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.001 Degree
PLAT432_ALERT_2_G Short Inter X...Y Contact  N005     ..C00F            3.02 Ang.
                                                  1+x,y,z  =      1_655 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........        50 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        21 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....         2 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.        10 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   7 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

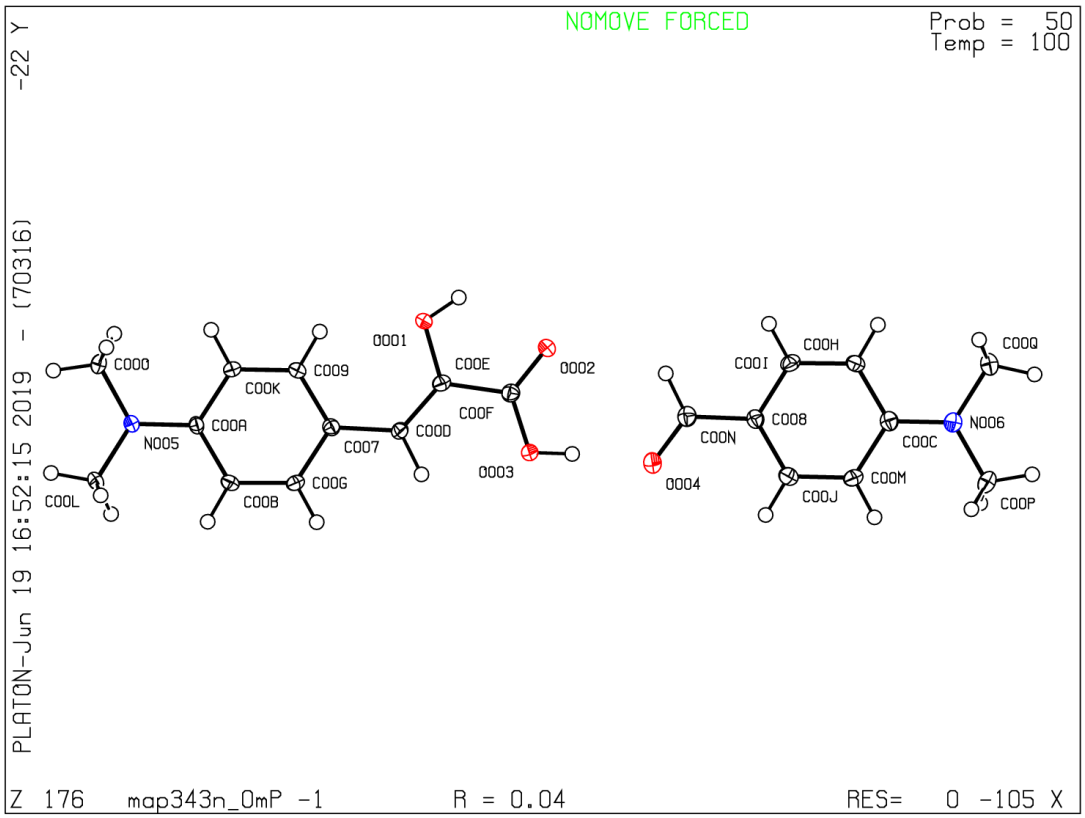
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 03/05/2019; check.def file version of 29/04/2019

Datablock map343n_0ma_a - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) tto_ma_acn1_0m_num1

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: tto_ma_acn1_0m_num1

```
Bond precision:  C-C = 0.0053 A          Wavelength=1.54178

Cell:          a=10.2439(3)      b=11.9323(3)     c=14.7966(4)
               alpha=72.918(1)   beta=83.311(1)   gamma=65.747(1)
Temperature:   100 K
```

	Calculated	Reported
Volume	1576.24(8)	1576.24(8)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	2(C12 H16 N O3), C2 H3 N, 2(I), H2 O	2(C12 H16 N O3), C2 H3 N, 2(I), H2 O
Sum formula	C26 H37 I2 N3 O7	C26 H37 I2 N3 O7
Mr	757.39	757.38
Dx,g cm-3	1.596	1.596
Z	2	2
Mu (mm-1)	16.039	16.039
F000	752.0	752.0
F000'	752.97	
h,k,lmax	12,14,18	12,14,18
Nref	6212	6163
Tmin,Tmax	0.036,0.214	0.017,0.173
Tmin'	0.006	

```
Correction method= # Reported T Limits: Tmin=0.017 Tmax=0.173
AbsCorr = NUMERICAL

Data completeness= 0.992          Theta(max)= 72.171

R(reflections)= 0.0365( 5858)     wR2(reflections)= 0.0994( 6163)

S = 1.048                 Npar= 374
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT250_ALERT_2_C	Large U3/U1 Ratio for Average U(i,j) Tensor	2.4	Note
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.600	24	Report
PLAT971_ALERT_2_C	Check Calcd Resid. Dens. 0.83A From I1	1.64	eA-3
PLAT972_ALERT_2_C	Check Calcd Resid. Dens. 0.88A From I2	-1.81	eA-3
PLAT972_ALERT_2_C	Check Calcd Resid. Dens. 0.76A From I2	-1.59	eA-3
PLAT972_ALERT_2_C	Check Calcd Resid. Dens. 0.89A From I1	-1.57	eA-3
PLAT972_ALERT_2_C	Check Calcd Resid. Dens. 0.79A From I1	-1.55	eA-3

Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	2	Note
PLAT154_ALERT_1_G	The s.u.'s on the Cell Angles are Equal ..(Note)	0.001	Degree
PLAT172_ALERT_4_G	The CIF-Embedded .res File Contains DFIX Records	1	Report
PLAT790_ALERT_4_G	Centre of Gravity not Within Unit Cell: Resd. # C12 H16 N O3	2	Note
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	1	Note
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please	Do !
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	26	Note
PLAT913_ALERT_3_G	Missing # of Very Strong Reflections in FCF	1	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	1	Info

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
7 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
9 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
8 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
3 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 03/05/2019; check.def file version of 29/04/2019

Datablock tto_ma_acn1_0m_num1 - ellipsoid plot