Unravelling the Configuration of Transient *ortho*-Quinone Methides by Combining Microfluidics with Gas Phase Vibrational Spectroscopy

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1. Microchip fabrication

The used microfluidic chips were tailor-made. Common methods¹ were used including photolithography, wet etching and high temperature bonding. A chromium-coated glass slide was coated with a positive photoresist. Then, it was developed after UV irradiation by using a photomask. The chromium and the glass were etched and structured in two successive steps. The structured glass slide was bonded to a cover plate which contained powder blasted holes for microfluidic contacting. The end of the chip was tailored accordingly and grinded for the integrated electrospray emitter.² To achieve an even better electrospray performance, the emitter was cleaned with sulfuric acid and was hydrophobized with the fluorinated silane Trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane.



Figure S-1. Fabrication of full glass microchips with chrome structuring, wet etching and high temperature bonding.

2. Tagging-effect demonstrated for [4a+H]⁺



Figure S-2. Simulated harmonic IR spectra of $[4a+H]^*$. Both, the *E*- and Z-isomer is shown, with a D₂-tagging molecule binding to various positions of the protonated *o*-QM. The corresponding minimum-energy structures and their ZPE-corrected relative electronic energies are also shown. The O-H stretching vibration exhibits a pronounced red-shift for one specific binding site, explaining the splitting of the O-H stretching region in the experimentally obtained spectrum.

3. Band assignment



Figure 8-3. Computed harmonic IR-spectra of $[4a+H]^*$ (a), $[4b+H]^*$ (b) and $[4c+H]^*$ in the spectral range from 1125 to 1440 cm⁻¹, which is diagnostic for the configuration of the protonated *o*-QMs. Isomer-specific IR bands are indicated by the shaded peaks and the ZPE-corrected relative electronic energies (in kJ mol⁻¹) are given in brackets.

Table S-1. Experimental	band positions,	computed	harmonic	vibrational	frequencies	(in cm ⁻¹) and b	band	assignments	; of
[4a+H]⁺.										

Band	B3LYP (scaled 0.975)	Experiment	Assignment
a_1^Z	1372	1382	C-H bend
a_2^Z	1317	1310	C-H bend
a_3^Z	1283	1278	C-H bend, O-H bend
a_4^Z	1238	1243	C-H bend
a_5^Z	1188	1188	C-H bend, O-H bend
a_6^Z	1148	1153	C-H bend, O-H bend
$\mathbf{a}_1^{\mathrm{E}}$	1371	1382	C-H bend, O-H bend
a_2^E	1342	1362/1330	C-H bend
$\mathbf{a}_3^{\mathrm{E}}$	1308	1310	C-H bend
a_4^E	1290	1310	C-H bend
$\mathbf{a}_5^{\mathrm{E}}$	1244	1243	C-H bend
\mathbf{a}_6^{E}	1226		C-H bend

$\mathbf{a}_7^{\mathrm{E}}$	1175	1188	C-H bend, O-H bend
a_8^E	1146	1153	C-H bend, O-H bend

Table S-2. Experi	mental band position	s, computed h	harmonic vi	brational fre	equencies (i1	n cm ⁻¹) and	band	assignments	of
[4 b+H]⁺.									

Band	B3LYP (scaled 0.975)	Experiment	Assignment
b_1^Z	1384	-	C-H bend
b_2^Z	1355	-	C=C stretch (ring), O-H bend
b_3^Z	1331	-	C-H bend, C-H bend (OMe)
b_4^Z	1294	-	C-H bend, C-O stretch
b_5^Z	1208	-	C-H bend
b_6^Z	1185	-	C-H bend
b_7^Z	1168	-	C-H bend
b_1^E	1356	1363	C-H bend, C=C stretch (ring), O-H bend
b_2^E	1326	1330	C-H bend, C-H bend (OMe)
b_3^E	1281	1275	C-H bend, C-O stretch
b_4^E	1252	1256	C-H bend, C=C stretch, O-H bend
b_5^E	1178	1176	C-H bend, O-H bend
b_6^E	1163	1162	C-H bend, O-H bend

Table S-3. Experimental band positions, computed harmonic vibrational frequencies (in cm^{-1}) and band assignments of $[4c+H]^*$.

B3LYP (scaled 0.975)	Experiment	Assignment
1380		C-H bend
1329		C-H bend, O-H bend
1297		C-H bend
1257		CH bend, C-C stretch
1217		C-H bend
1180		C-H bend, O-H bend
1354	1359	C=C stretch, O-H bend
1323	1324	C-H bend, C-O stretch,
	B3LYP (scaled 0.975) 1380 1329 1297 1257 1217 1180 1354 1323	B3LYP (scaled 0.975) Experiment 1380 - 1329 - 1297 - 1257 - 1217 - 1180 - 1354 1359 1323 1324

c_3^E	1284	1278	C-H bend, C-O stretch
c_4^E	1236	1240	C-H bend
c_5^E	1212	1213	C-H bend
c_6^E	1173	1173	C-H bend, O-H bend

4. Comparison of IRPD spectra to calculated sum spectra



Figure S-4. IRPD spectrum of the three protonated *o*-QMs, compared to calculated sum spectra of the Z- and *E*-isomer and the respective cosine similarity score.



Figure S-5. (a) Simulated IR spectrum of $[4d+H]^*$ (¹³C-labeled) and $[4a+H]^*$ (b), obtained from harmonic B3LYP/Def2-TZVP frequencies and intensities. Both calculated spectra are obtained by assuming the presence of the Z- and E-isomer with a ratio of 6/4. The corrsponding experimentally obtained IRPD spectra of D₂-tagged $[4d+H]^*$ (c) and $[4a+H]^*$ (d) are shown below. The IRPD spectra were measured at 13 K.

6. Activators

Precursor	Activator
la	HCO2H HCO2Na, HCO2Cs BINOL phosphric acid KI
1b	HCO₂H BINOL phosphoric acid KI
1c	HCO ₂ H
1d	HCO ₂ H

Table S-4. These different activators were used for the generation of the corresponding o-QMs.

7. IRPD spectra of $[4a+H]^+$ generated with different activators



Figure S-6. D_2 -tagged IRPD spectra of $[4a+H]^*$, measured at 13K. The particular o-QM $[4a+H]^*$ was generated on chip by the reaction with various activators. (a) potassium iodide, (b) caesium formate, (c) sodium formate, (d) chiral BINOL phosphric acid, (e) formic acid. The IRPD spectra show no significant differences.





Figure S-7. D₂-tagged IRPD spectra of $[4b+H]^+$, measured at 13K. The particular o-QM $[4b+H]^+$ was generated on chip by the reaction with various activators. (a) potassium iodide, (b) chiral BINOL phosphric acid, (e) formic acid. The IRPD spectra show no significant differences

9. General Information for synthesis and analysis of benzhydryl alcohols (1) and Tetrahydroxanthenone (2b):

¹H and ¹³C NMR spectra were recorded in CDCl₃ using a Varian MERCURYplus 300 spectrometer (300 MHz), Varian MERCURYplus 400 spectrometer (400 MHz) and Brucker Avance III HD 400 (400 MHz). The signals were referenced to residual chloroform (7.26 ppm, ¹H, 77.16 ppm, ¹³C). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), bs (broad singlet), d (doublet), t (triplet) and m (multiplet). IR spectra were obtained with a FTIR spectrometer (JASCO FT/IR-4100), bands are characterized as strong (s), medium (m), or weak (w). ESI-HR mass spectra were recorded on a Brucker ESI-TOF microTOF and Impact II Bruker DaltonicsMelting points were determined uncorrected on a Boetius heating table. THF for the synthesis of 1 was purified and dried by a Solvent Purification System MB SPS-800 (Braun). The solvents for coloumn chromatography were distilled from indicated drying reagents: hexane (KOH), ethyl acetate (KOH). Flash column chromatography was performed by using Merck silica gel 60 230-400 mesh (0.040-0.063 mm). Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel precoated TLC-sheets AlugramXtra SIL G/UV254. Spots were visualized by UV (Æ254 nm) and treated with a solution of vaniline in methanol (technical grade). Et₃N was destilled freshly prior to use over CaH₂. The ¹³C-labeled paraformaldehyde 6 was purchased from Sigma Aldrich (isotope purity: 99 atom% ¹³C), 3,5-dimethylphenol 5 is commercely available and was used as purchased. *o*-Formylation of phenol 5 proceded via a well established protocol.^{7,8} The non-¹³C-labeled benzhydryl alcohol **1a** was prepared according to the procedure of ¹³C-labeled benzhydryl alcohol **1d**, PMP-substituted benzhydryl alcohol 1b was prepared according to a literature known procedure and the analytic data matched the previously reported.⁹ The analytic data and X-Ray single crystal analysis of tetrahydroxanthenone 2a and 2b was reported earlier by Schneider (unpublished experiments).¹⁰

10. Synthesis of 2-Hydroxy-4,6-dimethylbenz-¹³C-aldehyde (7):



In a heat gun dried 50 mL two necked round bottom flask with reflux condenser were added 482 mg (3.95 mmol, 1.00 equiv) 3,5-dimethylphenol (5), 546 mg (5.92 mmol, 1.50 equiv) anhydrous MgCl₂ and 490 mg (15.8 mmol, 4.00 equiv) ¹³C-paraformaldehyde (6). 10 mL THF and 1.29 mL (939 mg, 9.28 mmol, 2.35 equiv) freshly distilled Et₃N were added, the apparatus flushed for 10 min with N₂ and the reaction heated to reflux for 2 h. After 2 h complete conversion of **5** was observed via TLC and the reaction subsequently cooled to rt. 25 mL 1N HCl were added, the biphasic system stirred for 5 min and the phases separated. The aqueos phase was extracted with ethyl acetate (3x25 mL), the combined organic phases dried with Na₂SO₄ and the solvent removed under reduced pressure. The crude product was purified via column chromatography (10% EE in hexan). 469 mg (79%) of an amorphos colorless solid was obtained.

R_{*t*} (hexan/EE 2/1): 0.69. IR (KBr): 3442 (m), 2979 (w), 2969 (w), 2927 (w), 2872 (m), 1632 (s), 1614 (s), 1580 (s), 1570 (s), 1503 (s), 1451 (s), 1377 (s), 1346 (s), 1307 (s), 1290 (s), 1235 (s), 1191 (s), 1151 (s), 1038 (m), 846 (s), 793 (s), 754 (s), 724 (s), 502 (s). HRMS (ESI): calculated for ¹³CC₈H₁₀NaO₂⁺ [M+Na]⁺: 174.0607, found 174.0607. ¹H-NMR (400 MHz; CDCl₃): 11.94 (d, ⁴J_{H,C} = 0.9 Hz, 1H), 10.23 (d, ¹J_{H,C} = 175.3 Hz, 1H), 6.62 (bs, 1H), 6.53 (bs, 1H), 2.55 (s, 3H), 2.30 (s,

3H). ¹³C-NMR (101 MHz; CDCl₃): 194.7, 163.6, 149.4, 142.0 (d, ${}^{2}J_{C,C}$ = 4.1 Hz), 123.3 (d, ${}^{3}J_{C,C}$ = 3.8 Hz), 116.7 (d, ${}^{1}J_{C,C}$ = 56.0 Hz), 116.3 (d, ${}^{3}J_{C,C}$ = 2.3 Hz), 22.3, 18.2 (d, ${}^{3}J_{C,C}$ = 4.1 Hz).

11. Synthesis of 2-(hydroxy(phenyl) -¹³C-methyl)-3,5-dimethylphenol (1d):



In a 25 mL two necked round bottom flask with reflux condenser were added 167 mg (6.88 mmol, 2.60 equiv) Mg turnings and the apparatus dried with a heat gun. 4 mL THF were added and additional 692 μ L (1.04 g, 6.62 mmol, 2.50 equiv) bromobenzene dropwise at rt. After initiation of the Grignard reagent formation the mixture was stirred for an additional 30 min at rt, plus 30 min at reflux. The Grignard reagent was cooled to 0°C and 400 mg (2.65 mmol, 1.00 equiv) 7 (dissolved in 5 mL THF) added at 0°C. After 2 h stirring at rt the complete conversion of 7 was observed via TLC and subsequently 15 mL NH₄Cl_(aq.) were added. The two phases were stirred for 10 min at rt, the phases separated and the aqueous phase extracted with ethyl acetate (3x 25 mL). The combined organic phases were washed with water and dried with Na₂SO₄. The solvent was removed under reduced pressure and the crude product purified via column chromatography (10% EE in hexan). 588 mg (97%) of an amorphous colorless solid was obtained.

R_ℓ(**Hexan/EE** 2/1): 0.61. **IR** (**KBr**): 3386 (s), 3246 (s), 3028 (w), 2921 (w), 1627 (s), 1577 (m), 1494 (m), 1460 (m), 1447 (m), 1400 (w), 1298 (s), 1217 (m), 1183 (w), 1132 (m), 991 (s), 852 (m), 830 (s), 723 (s), 695 (m), 639 (m), 527 (m). **HRMS (ESI)**: calculated for ¹³**C**C₁₄H₁₆NaO₂^{*} [M+Na]^{*}: 252.1076, found 252.1081. ¹**H**-**NMR (400 MHz; CDCl**₃): 8.47 (s, 1H), 7.47 –7.27 (m, 5H), 6.62 (bs, 1H), 6.53 (bs, 1H), 6.15 (dd, ¹*J*_{H,C} = 144.8 Hz, ³*J*_{H,H} = 2.7 Hz, 1H), 3.01 (dd, ³*J*_{H,C} = 2.7 Hz, ³*J*_{H,H} = 2.7 Hz, 1H), 2.27 (s, 3H), 2.14 (s, 3H). ¹³**C**NMR (101 MHz; **CDCl**₃): 156.3, 141.2 (d, ¹*J*_{C,C} = 47.5 Hz), 139.1, 135.8 (d, ²*J*_{C,C} = 3.8 Hz), 128.9 (d, ²*J*_{C,C} = 3.8 Hz), 128.4, 127.2 (d, ³*J*_{C,C} = 3.1 Hz), 123.2 (d, ³*J*_{C,C} = 3.4 Hz), 121.3 (d, ¹*J*_{C,C} = 49.3 Hz), 116.4 (d, ³*J*_{C,C} = 2.0 Hz), 74.8, 21.1, 19.7 (d, ³*J*_{C,C} = 3.5 Hz).

12. Synthesis of 2-(hydroxy(phenyl)methyl)-3,5-dimethylphenol (1a):



In a 25 mL two necked round bottom flask with reflux condenser were added 167 mg (6.88 mmol, 2.60 equiv) Mg turnings and the apparatus dried with a heat gun. 4 mL THF were added and additional 692 μ (1.04 g, 6.62 mmol, 2.50 equiv) bromobenzene at rt. After initiation of the Grignard reagent formation the mixture was stirred for an additional 30 min at rt, plus 30 min at reflux. The Grignard reagent was cooled to 0°C and 398 mg (2.65 mmol, 1.00 equiv) 2-hydroxy-4,6-dimethylbenzaldehyde (dissolved in 5 mL THF) added at 0°C. After 2 h stirring at rt the complete conversion of the benzaldehyde was observed via TLC and subsequently 15 mL NH₄Cl_(aq.) were added. The two phases were stirred for 10 min at rt, the phases separated and the aqueous phase extracted with ethyl acetate (3x 25 mL). The combined organic phases were washed with water and dried with Na₂SO₄. The solvent was removed under reduced

pressure and the crude product purified via column chromatography (10% EE in hexan). 573 mg (95%) of an amorphous colorless solid was obtained.

 R_{f} (Hexan/EE 2/1): 0.61. IR (KBr): 3387 (s), 3248 (s), 3029 (w), 2920 (w), 1626 (s), 1578 (m), 1494 (m), 1460 (m), 1447 (m), 1407 (m), 1298 (s), 1217 (m), 1184 (w), 1135 (s), 1011 (s), 851 (s), 811 (s), 726 (s), 695 (m), 642 (m), 528 (m). HRMS (ESI): calculated for $C_{15}H_{16}NaO_{2}^{+}$ [M+Na]⁺: 251.1043, found 251.1040. ¹H-NMR (400 MHz; CDCl₃): 8.41 (s, 1H), 7.41 – 7.25 (m, 5H), 6.63 (bs, 1H), 6.53 (bs, 1H), 6.17 (d, ³*J* = 2.8 Hz, 1H), 2.84 (d, ³*J* = 3.0 Hz, 1H), 2.27 (s, 3H), 2.14 (s, 3H). ¹³C-NMR (101 MHz; CDCl₃): 156.3, 141.2, 139.1, 135.8, 128.9, 128.4, 127.2, 123.2, 121.3, 116.3, 74.8, 21.1, 19.7.

13. Synthesis of 4-(*tert*-butyl)-2-(hydroxy(4-methoxyphenyl)methyl)phenol (1c):



In a 250 mL two necked round bottom flask with reflux condenser were added 1.42 g (58.5 mmol, 2.60 equiv) Mg turnings and the apparatus dried with a heat gun. 30 mL THF were added and additional 7.04 mL (10.5 g, 56.3 mmol, 2.50 equiv) 4-bromoanisole at rt. After initiation of the Grignard reagent formation the mixture was stirred for an additional 30 min at rt, plus 30 min at reflux. The Grignard reagent was cooled to 0°C and 4.01 g (22.5 mmol, 1.00 equiv) 5-(*tert*-butyl)-2-hydroxybenzaldehyde (dissolved in 10 mL THF) added at 0°C. After 2 h stirring at rt the complete conversion of the benzaldehyde was observed via TLC and subsequently 150 mL NH₄Cl_(aq.) were added. The two phases were stirred for 10 min at rt, the phases separated and the aqueous phase extracted with ethyl acetate (3x 100 mL). The combined organic phases were washed with water and dried with Na₂SO₄. The solvent was removed under reduced pressure and the crude product purified via column chromatography (10% EE in hexan). 6.26 g (97%) of an amorphous colorless solid was obtained.

R_{*t*} (Hexan/EE 2/1): 0.58. IR (KBr): 3374 (s), 3206 (s), 3031 (w), 2960 (s), 2905 (m), 2868 (m), 1606 (s), 1507 (s), 1466 (s), 1392 (m), 1367 (s), 1301 (m), 1245 (s), 1174 (s), 1027 (s), 1007 (s), 843 (s), 830 (s), 581 (m), 530 (m). HRMS (ESI): calculated for C₁₈H₂₂NaO₃⁺ [M+Na]⁺: 309.1461, found 309.1463. ¹H-NMR (400 MHz; CDCl₃): 7.70 (s, 1H), 7.35 − 7.26 (m, 2H), 7.22 (dd, J = 8.5, 2.5 Hz, 1H), 6.93 − 6.85 (m, 3H), 6.84 (d, J = 8.5 Hz, 1H), 5.95 (bs, 1H), 3.80 (s, 3H), 2.82 (d, J = 2.9 Hz, 1H), 1.23 (s, 9H). ¹³C-NMR (101 MHz; CDCl₃): 159.6, 153.2, 142.7, 134.3, 128.4, 126.2, 126.0, 125.2, 116.9, 114.2, 77.4, 55.4, 34.2, 31.6.

14. NMR spectras of new compounds:



Figure S-8: ¹H and ¹³C of benzaldehyde 7.



Figure S-9: ¹H and ¹³C of benzaldehyde 1d.





Figure S-10: ¹H and ¹³C of benzaldehyde 1a.





Overlay of ¹³C labeled (1d) and non-¹³C-labeled benzhydryl alcohol (1a):



7.3 7.2 7.1 7.0 6.9 6.2 3.0 2.7 2.5 2.3 2.2 2.1 3.6 8.5 8.4 . 7.4 6.8 6.7 6.6 6.5 6.4 6.3 6.1 6.0 3.1 2.9 2.8 2.6 2.4



^{56.5 141.5 141.0 139.0 135.5 129.0 128.5 128.0 127.5 127.0 123.0 121.5 121.0 116.26.0 75.5 75.0 74.5 74.0 73.521.5 21.0 20.5 20.0 19.5 19}

Figure S-12: Overlay of ¹H and ¹³C of benzhydryl alcohol 1d and 1a.

15. Coordinates of DFT geometries

Table S-6. \mathbb{Z} -[4b+H]⁺

Total energy: 691.831202 Hartree, zero-point energy: 0.236206 Hartree

Tag	Symbol	X	Y	Z
1	С	-3.8484600	1.1865980	0.1179030
2	С	-2.5046230	0.8489760	0.2332410
3	С	-2.0864610	-0.4992530	0.0394120
4	С	-3.1067070	-1.4606120	-0.2118860
5	С	-4.4265440	-1.1147840	-0.3456100
6	С	-4.7958480	0.2237990	-0.1816060
7	Н	-4.1499270	2.2157000	0.2728870
8	Н	-2.8093170	-2.4950390	-0.3233030
9	Н	-5.1723790	-1.8659190	-0.5613970
10	Н	-5.8343880	0.5135310	-0.2716200
11	С	-0.7702900	-1.0238180	0.1268410
12	Н	-0.7824810	-2.1006960	0.2661310
13	С	0.5279110	-0.5131830	0.0408020
14	С	1.5817300	-1.4259540	0.3458180
15	С	0.9026970	0.7923330	-0.3976230
16	С	2.9004320	-1.0689720	0.2829820
17	Н	1.3231410	-2.4320490	0.6503350
18	С	2.2134150	1.1473350	-0.4950140
19	Н	0.1423060	1.4995680	-0.6771840
20	С	3.2353420	0.2344200	-0.1389990
21	Н	3.6677240	-1.7827730	0.5391420
22	Н	2.5088330	2.1266770	-0.8446000
23	0	4.4674650	0.6878880	-0.2483780
24	С	5.5898530	-0.1500510	0.0826980
25	Н	6.4658300	0.4672960	-0.0846230
26	Н	5.5405860	-0.4536960	1.1283950
27	Н	5.6170830	-1.0219090	-0.5709430
28	0	-1.5894010	1.7691090	0.5852820
29	Н	-2.0162180	2.6123230	0.7877970

Table S-7. E-[4b+H]⁺

Total energy: -691.835454 Hartree, zero-point energy: 0.236430 Hartree

Tag	Symbol	X	Y	Z
1	С	4.401082	0.183029	-0.140073
2	С	3.176354	0.842751	-0.135237
3	С	1.966614	0.121779	0.100066
4	С	2.069685	-1.267959	0.371515

5	С	3.283325	-1.905581	0.376654
6	С	4.450137	-1.176108	0.106691
7	Н	5.310008	0.73789	-0.3377
8	Н	1.181722	-1.813431	0.650692
9	Н	3.346808	-2.958151	0.612384
10	Н	5.408426	-1.678558	0.107863
11	С	0.755692	0.847604	0.129731
12	0	3.068586	2.157154	-0.383855
13	Н	3.937124	2.562413	-0.505956
14	Н	0.874476	1.91724	0.264325
15	С	-0.568049	0.411977	0.014788
16	С	-1.594754	1.330697	0.370145
17	С	-0.96918	-0.868725	-0.469236
18	С	-2.920087	0.988165	0.33344
19	Н	-1.311394	2.320299	0.705016
20	С	-2.285822	-1.211791	-0.532832
21	Н	-0.228382	-1.555945	-0.847723
22	С	-3.283643	-0.299122	-0.112004
23	Н	-3.671721	1.702097	0.632264
24	Н	-2.604719	-2.168514	-0.922119
25	0	-4.524932	-0.734679	-0.199642
26	С	-5.626561	0.112062	0.174531
27	Н	-6.515454	-0.48821	0.013223
28	Н	-5.550108	0.391559	1.225408
29	Н	-5.654784	0.99884	-0.45879

Table S-8. $Z-[4a+H]^+$

Total energy: -655.919639 Hartree, zero-point energy: 0.258478 Hartree

Tag	Symbol	X	Y	Z
1	С	-2.381929	-1.401914	-0.2229
2	С	-1.057687	-1.00086	-0.26867
3	С	-0.694783	0.376272	-0.074535
4	С	-1.773823	1.323345	0.124026
5	С	-3.065827	0.873256	0.188557
6	С	-3.396039	-0.486255	0.020146
7	Н	-2.624484	-2.445203	-0.387366
8	Н	-3.864184	1.580122	0.371605
9	С	0.605424	0.880395	-0.160319

10	Н	0.636448	1.946964	-0.348705
11	С	1.908014	0.327137	-0.036202
12	С	2.97272	1.108281	-0.551785
13	С	2.221968	-0.870081	0.647126
14	С	4.278381	0.675074	-0.461731
15	Н	2.747417	2.048296	-1.039226
16	С	3.532942	-1.272583	0.773401
17	Н	1.438015	-1.450401	1.103615
18	С	4.559965	-0.516721	0.202886
19	Н	5.079196	1.265983	-0.883745
20	Н	3.769525	-2.175693	1.318897
21	0	-0.089474	-1.873188	-0.571574
22	Н	-0.462862	-2.737499	-0.791873
23	С	-4.822518	-0.917946	0.094779
24	Н	-5.427058	-0.357202	-0.622052
25	Н	-4.942001	-1.98108	-0.101434
26	Н	-5.228834	-0.698547	1.085713
27	С	-1.500819	2.788386	0.30952
28	Н	-0.850323	2.97673	1.165041
29	Н	-1.024039	3.223707	-0.572403
30	Н	-2.432159	3.324965	0.473004
31	Н	5.585199	-0.850363	0.295734

Table S-9. *E*-[4a+H]⁺

Total energy: -655.918782 Hartree, zero-point energy: 0.258457 Hartree

Tag	Symbol	X	Y	Z
1	С	-3.0558	0.912691	0.247716
2	С	-1.752069	1.344041	0.088019
3	С	-0.67725	0.415239	-0.168067
4	С	-1.028565	-0.969731	-0.379334
5	С	-2.341689	-1.341434	-0.234163
6	С	-3.364121	-0.433474	0.108307
7	Н	-3.833694	1.627949	0.486022
8	Н	-2.616574	-2.370316	-0.429144

9	С	0.597609	0.976079	-0.256981
10	0	-1.414379	2.63204	0.228088
11	Н	-2.193515	3.1837	0.379473
12	Н	0.608983	2.037948	-0.478951
13	С	1.883452	0.412007	-0.049382
14	С	2.999028	1.066244	-0.622506
15	С	2.104303	-0.703573	0.78782
16	С	4.272372	0.56828	-0.439405
17	Н	2.839882	1.94833	-1.22936
18	С	3.383234	-1.169507	1.000424
19	Н	1.269955	-1.151796	1.306008
20	С	4.465198	-0.549497	0.371363
21	Н	5.118905	1.054352	-0.903969
22	Н	3.552483	-2.00655	1.663656
23	С	-4.762112	-0.925664	0.284288
24	Н	-5.459386	-0.117406	0.492879
25	Н	-5.094489	-1.454291	-0.612228
26	Н	-4.806057	-1.645052	1.106294
27	С	-0.065957	-2.00031	-0.905844
28	Н	0.781198	-1.559378	-1.423653
29	Н	0.325007	-2.633503	-0.108825
30	Н	-0.589871	-2.653203	-1.602526
31	Н	5.466402	-0.925448	0.536082

Table S-10. Z-[4c+H]⁺

Total energy: -849.170099 Hartree, zero-point energy: 0.348291 Hartree

Tag	Symbol	X	Y	Z
1	С	2.154974	2.251756	-0.153382
2	С	0.895874	1.683678	-0.25943
3	С	0.764512	0.265935	-0.215204
4	С	1.964839	-0.492228	-0.117518
5	С	3.220642	0.061454	0.013133
6	С	3.284863	1.462787	-0.005535
7	Н	2.255025	3.330097	-0.193905
8	Н	4.240272	1.958875	0.079485

9	С	-0.423204	-0.501168	-0.316112
10	Н	-0.206321	-1.534379	-0.570323
11	С	-1.793044	-0.275888	-0.13646
12	С	-2.65729	-1.347466	-0.508123
13	С	-2.397703	0.874648	0.450856
14	С	-4.016668	-1.27426	-0.369151
15	Н	-2.21941	-2.244395	-0.92722
16	С	-3.747129	0.944274	0.623482
17	Н	-1.780417	1.690465	0.782208
18	С	-4.582974	-0.116029	0.200615
19	Н	-4.637786	-2.099988	-0.679392
20	Н	-4.21329	1.803643	1.084785
21	0	-5.875361	0.064189	0.393751
22	С	-6.820693	-0.947611	0.004916
23	Н	-6.640715	-1.868418	0.560017
24	Н	-7.793916	-0.543525	0.262153
25	Н	-6.763373	-1.128451	-1.068584
26	0	-0.198762	2.440878	-0.464217
27	Н	0.050008	3.36749	-0.579536
28	Н	1.859676	-1.568682	-0.122725
29	С	4.456187	-0.830487	0.157295
30	С	5.745608	-0.008351	0.259289
31	Н	5.74447	0.646123	1.132848
32	Н	6.596334	-0.682047	0.358911
33	Н	5.913697	0.599588	-0.631597
34	С	4.314932	-1.680956	1.4332
35	Н	3.435171	-2.32481	1.3959
36	Н	5.189165	-2.322076	1.552951
37	Н	4.233988	-1.048654	2.31879
38	С	4.560659	-1.753593	-1.070557
39	Н	4.653971	-1.173813	-1.990147
40	Н	5.439927	-2.392764	-0.981779
41	Н	3.690195	-2.403789	-1.167001

Table S-11. *E*-[4c+H]⁺

Total energy: -849.175804 Hartree, zero-point energy: 0.348392 Hartree

Tag	Symbol	X	Y	Z
1	С	2.719253	-0.301773	0.021722
2	С	1.378295	-0.017785	0.109336
3	С	0.863911	1.30641	0.030082

4	С	1.794629	2.376493	-0.111442
5	С	3.153285	2.098706	-0.213495
6	С	3.594586	0.793125	-0.155628
7	Н	0.683042	-0.812148	0.318557
8	Н	3.861293	2.908818	-0.339834
9	Н	4.658139	0.612804	-0.231546
10	С	-0.500946	1.630468	0.154791
11	Н	-0.696855	2.668102	0.40215
12	С	-1.647043	0.835226	0.014941
13	С	-2.875282	1.368728	0.490622
14	С	-1.684338	-0.448827	-0.602549
15	С	-4.045787	0.65729	0.439849
16	Н	-2.875219	2.358057	0.929948
17	С	-2.847396	-1.155526	-0.680362
18	Н	-0.796702	-0.846733	-1.068957
19	С	-4.043517	-0.625706	-0.141306
20	Н	-4.955347	1.085253	0.83164
21	Н	-2.893411	-2.118693	-1.168999
22	0	-5.109949	-1.396632	-0.254752
23	С	-6.386292	-0.950849	0.234047
24	Н	-6.701761	-0.050353	-0.29344
25	Н	-7.073189	-1.763653	0.023736
26	Н	-6.340232	-0.770034	1.308239
27	0	1.307067	3.625123	-0.178676
28	Н	2.019389	4.27347	-0.252966
29	С	3.289259	-1.71443	0.133785
30	С	4.071154	-2.041934	-1.15237
31	Н	4.488241	-3.047556	-1.0866
32	Н	3.421307	-1.99984	-2.027975
33	Н	4.901097	-1.353484	-1.314192
34	С	2.187462	-2.763476	0.314139
35	Н	1.616883	-2.603091	1.230909
36	Н	1.496244	-2.774984	-0.53128
37	Н	2.636898	-3.75396	0.380196
38	С	4.236086	-1.78236	1.346695
39	Н	5.06987	-1.085757	1.252786
40	Н	3.704865	-1.551282	2.271358
41	Н	4.654587	-2.785534	1.43657

Table S-12. TS-[4a+H]⁺

Tag	Symbol	Х	Y	Z
1	С	-2.594164	-1.24171	0.073984
2	С	-1.295907	-1.184839	-0.409517
3	С	-0.665572	0.048136	-0.595291
4	С	-1.345977	1.241159	-0.301167
5	С	-2.644261	1.154141	0.181715
6	С	-3.28528	-0.071305	0.37252
7	Н	-3.069251	-2.206206	0.213757
8	Н	-3.174677	2.070106	0.410232
9	С	0.690685	0.052627	-1.138558
10	Н	0.806585	0.086117	-2.222129
11	С	1.852656	0.012112	-0.393114
12	С	3.115481	0.017747	-1.058959
13	С	1.809384	-0.044407	1.032267
14	С	4.276907	-0.029966	-0.329324
15	Н	3.138478	0.058037	-2.140361
16	С	2.978512	-0.091774	1.747444
17	Н	0.845675	-0.051174	1.522455
18	С	4.205165	-0.084272	1.068065
19	Н	5.239315	-0.027143	-0.821211
20	Н	2.962762	-0.136149	2.827354
21	0	-0.553328	-2.28593	-0.720928
22	Н	-1.076796	-3.090237	-0.619763
23	С	-4.704281	-0.123707	0.860484
24	Н	-4.905971	0.674146	1.574832
25	Н	-5.397233	0.003069	0.024749
26	Н	-4.929945	-1.077993	1.334776
27	С	-0.670313	2.5701	-0.498391
28	Н	0.142297	2.716764	0.217929
29	Н	-0.240869	2.657902	-1.500352
30	Н	-1.37553	3.388115	-0.368507
31	Н	5.123573	-0.122171	1.640712

Total energy: -655.893703, zero-point energy: 0.255849

Table S-13. $TS-[4b+H]^+$

Total energy: -691.815405 Hartree, zero-point energy: 0.234811 Hartree

Tag	Symbol	Х	Y	Z
1	С	3.840882	0.452481	-0.953013
2	С	2.628583	0.851808	-0.403181
3	С	2.006973	0.059424	0.567474

4	С	2.616775	-1.125017	0.984698
5	С	3.825778	-1.521788	0.432685
6	С	4.434459	-0.729362	-0.533624
7	Н	4.316489	1.068488	-1.70701
8	Н	4.288841	-2.442723	0.757441
9	Н	5.378851	-1.031123	-0.965626
10	С	0.74233	0.512523	1.159121
11	Н	0.797725	1.120361	2.060305
12	С	-0.502418	0.233278	0.666361
13	С	-1.664962	0.738289	1.337227
14	С	-0.689198	-0.547813	-0.52505
15	С	-2.917967	0.493026	0.866968
16	Н	-1.529005	1.328314	2.234603
17	С	-1.93414	-0.795592	-0.999672
18	Н	0.183945	-0.931856	-1.033724
19	С	-3.070252	-0.280802	-0.314071
20	Н	-3.782328	0.881483	1.382668
21	Н	-2.104935	-1.378283	-1.893944
22	0	4.225373	-0.574244	-0.850247
23	С	-5.467141	-0.120865	-0.26531
24	Н	-5.49793	0.967806	-0.251752
25	Н	-6.24221	-0.510185	-0.915908
26	Н	-5.577761	-0.528481	0.738655
27	0	1.97895	1.995712	-0.759413
28	Н	2.502837	2.499361	-1.394033
29	Н	2.138664	-1.732445	1.741932

Table S-14. TS-[4c+H]⁺

Total energy: -849.153099 Hartree, zero-point energy: 0.346665Hartree

Tag	Symbol	Х	Y	Z
1	С	-2.92645	-0.045135	-0.062749
2	С	-1.692235	-0.121327	0.584885
3	С	-0.767294	0.918795	0.526979
4	С	-1.072089	2.08237	-0.185117
5	С	-2.293568	2.175709	-0.832363
6	С	-3.201674	1.126093	-0.767207
7	Н	-1.434013	-1.007649	1.148537
8	Н	-2.539133	3.071438	-1.390972
9	Н	-4.142716	1.237966	-1.283613
10	С	0.513555	0.828189	1.236092

11	Н	0.542553	1.161409	2.271934
12	С	1.67941	0.358303	0.695302
13	С	2.872229	0.322952	1.489156
14	С	1.753414	-0.09366	-0.665966
15	С	4.052085	-0.122433	0.977233
16	Н	2.821198	0.663707	2.515406
17	С	2.925054	-0.538503	-1.182683
18	Н	0.855326	-0.069909	-1.267198
19	С	4.094372	-0.560667	-0.372505
20	Н	4.941622	-0.140735	1.587417
21	Н	3.011094	-0.882808	-2.203689
22	0	5.173598	-1.005668	-0.962052
23	С	6.436213	-1.084849	-0.263862
24	Н	6.351966	-1.76119	0.585804
25	Н	7.135029	-1.482168	-0.9915
26	Н	6.749454	-0.09189	0.056095
27	0	-0.121543	3.062002	-0.1969
28	Н	-0.444833	3.838345	-0.669372
29	С	-3.902602	-1.221375	0.02349
30	С	-5.198205	-0.948353	-0.74832
31	Н	-5.861006	-1.809232	-0.65912
32	Н	-5.731128	-0.081962	-0.353416
33	Н	-5.012065	-0.786186	-1.811315
34	С	-4.260229	-1.477626	1.499155
35	Н	-3.380746	-1.73008	2.09294
36	Н	-4.727573	-0.598398	1.945104
37	Н	-4.960698	-2.310616	1.575727
38	С	-3.23871	-2.477458	-0.570399
39	Н	-2.973176	-2.319721	-1.617188
40	Н	-2.332914	-2.752605	-0.028152
41	Н	-3.924335	-3.324543	-0.518544

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